Visible-Light-Mediated Decarboxylative Allylation of Vinylcyclopropanes with α-Keto Acids toward β,γ-Alkenyl Ketones

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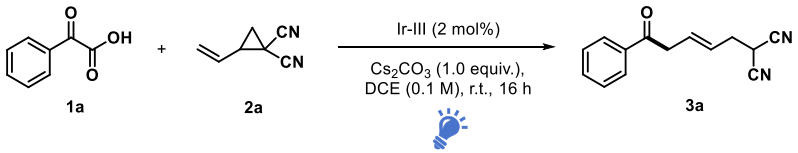
Contents

I. General Methods

Unless noted, all reactions were conducted under N_2 atmosphere employing standard Schlenk technique or using a N_2-filled glove box. All glassware was oven-dried prior to use. Analytical thin-layer chromatography was performed using glass plates pre-coated with silica (SiliaPlate G TLC - Glass-Backed, 250 μm, Silicycle). GC-MS analyses of compounds were performed on a Shimadzu GCMS-QP2010 SE. Flash column chromatography was performed over silica gel 200-300. NMR spectra (^1H, ^{13}C) were obtained on a Bruker AVANCE III 400 MHz spectrometer. HRMS analyses of compounds were performed on a Waters Xevo G2 Qtof instrument (ESI). The starting material and reagents were purchased from commercial vendors (Bidepharm, Energy chemical, Leyan, Innochem, Heowns, Aladdin, Macklin and TCI). α-keto acids **1** and VCPs **2** were prepared according to the literature procedure.

II. General Experimental Details

General procedure for the construction of **3a-3ae** (**3a** as example).

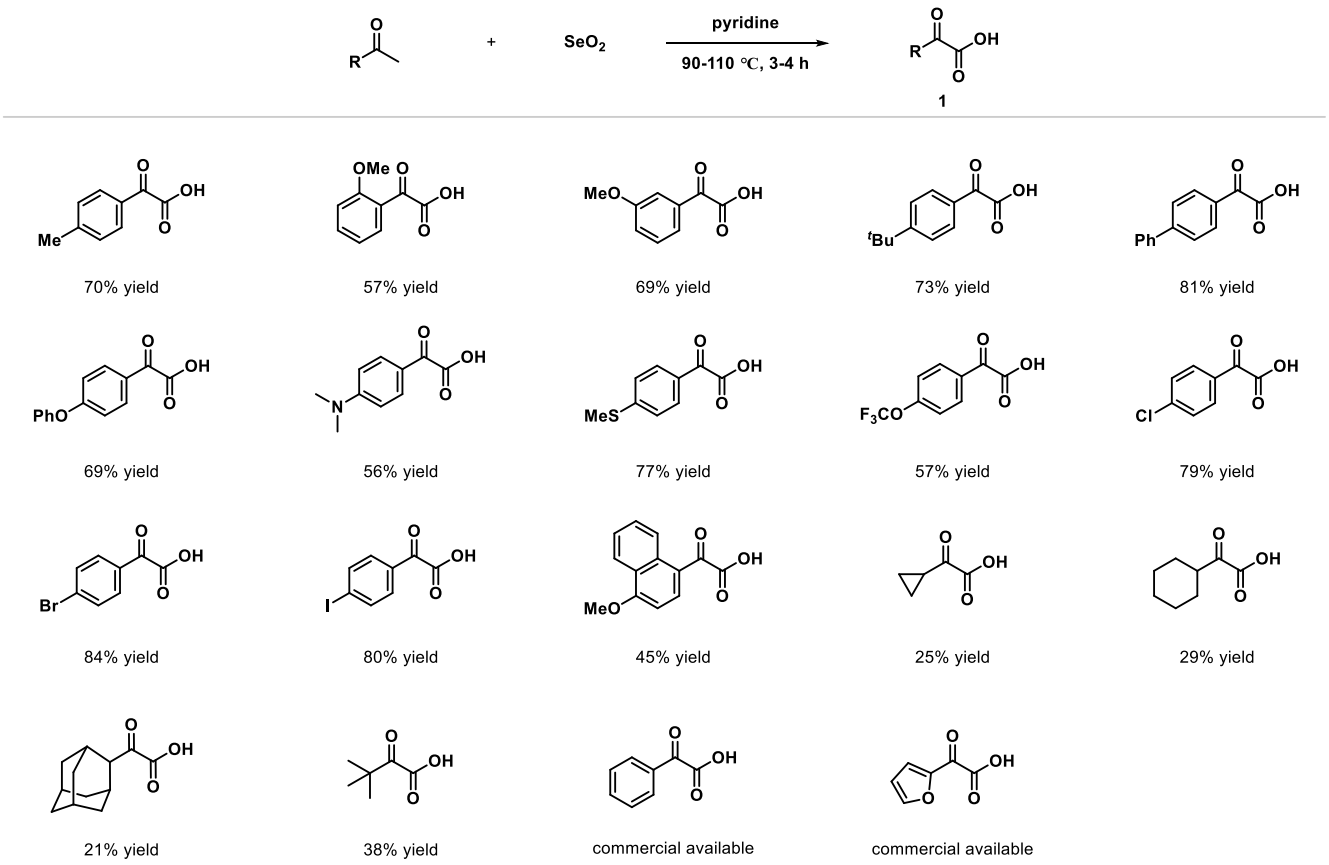


In a N_2-filled glovebox, an oven-dried vial (4 mL) equipped with a magnet stir bar was charged with α-keto acid **1a** (45.0 mg, 0.3 mmol), vinylcyclopropane **2a** (23.6 mg, 0.2 mmol), Cs_2CO_3 (65.2 mg, 0.3 mmol), $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (4.5 mg, 0.004 mmol), and dry DCE (0.1 M). The reaction mixture was stirred at room temperature under blue LEDs irradiation (The distance between the Kessil lamps and the reactor vessel is approximately 5 cm). After 16 h of reaction time, the mixture was quenched with water (10 mL) and extracted with ethyl acetate (EtOAc, 3 × 4 mL). The combined organic extracts were washed with brine, dried over anhydrous Na_2SO_4, and concentrated in vacuo. The crude residue was purified by flash column chromatography (silica gel, 200-300 mesh) using a gradient of hexane and EtOAc as the eluent to afford product **3a** (35.9 mg, 80% yield).

III. Syntheses of Substrates

1. Preparation of substituted α-keto acids: (**Scheme S1**)

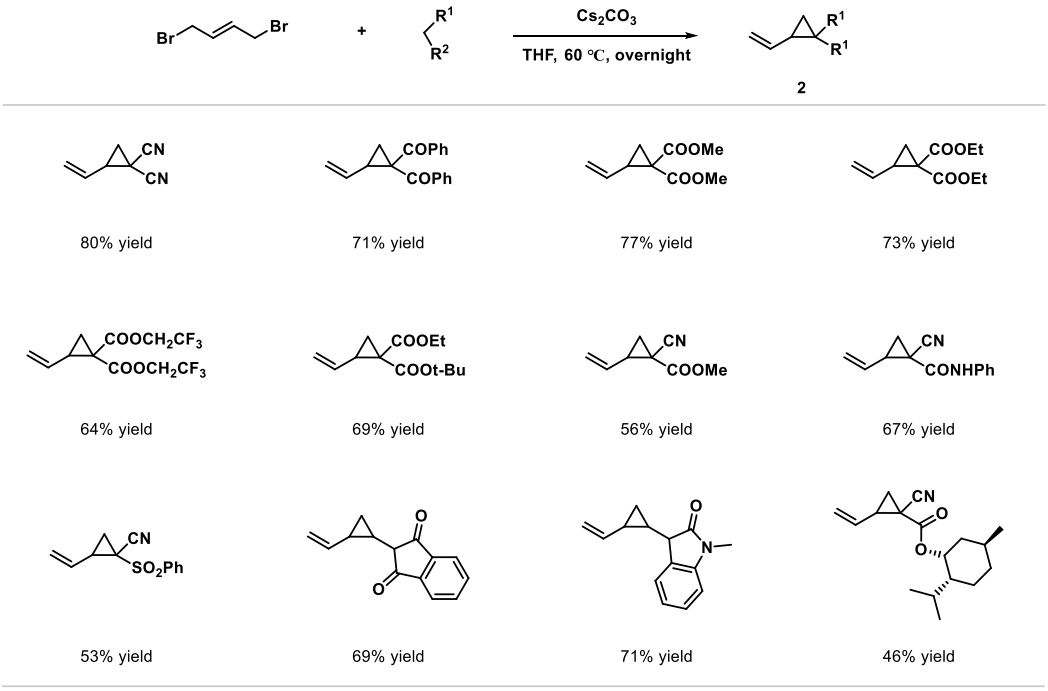
All kinds of substituted α-keto acids were prepared from oxidation of corresponding methyl ketones with SeO_2 according to the reported procedure.[1]



Scheme S1. Syntheses of substituted α-keto acids.

2. Preparation of substituted vinylcyclopropanes: (**Scheme S2**)

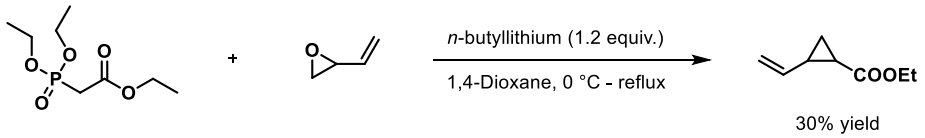
All kinds of substituted vinylcyclopropanes were prepared from (*E*)-1,4-dibromobut-2-ene with corresponding active methylene compound according to the reported procedure.[2]



Scheme S2. Syntheses of substituted vinylcyclopropanes.

3. Preparation of ethyl 2-vinylcyclopropane-1-carboxylate: (**Scheme S3**)

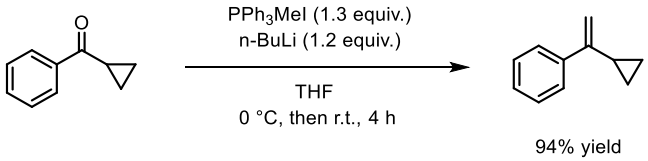
Ethyl 2-vinylcyclopropane-1-carboxylate was prepared from 2-vinyloxirane with ethyl 2-(diethoxyphosphoryl)acetate according to the reported procedure.[3]



Scheme S3. Preparation of ethyl 2-vinylcyclopropane-1-carboxylate.

4. Preparation of (1-cyclopropylvinyl)benzene: (**Scheme S4**)

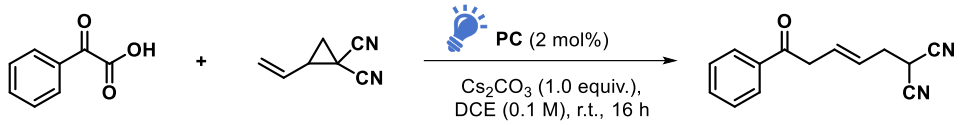
(1-Cyclopropylvinyl)benzene was prepared from cyclopropyl(phenyl)methanone according to the reported procedure.[4]



Scheme S4. Preparation of (1-cyclopropylvinyl)benzene.

IV. Optimization of Reaction Conditions

Table S1. Optimization of photocatalysts[a]

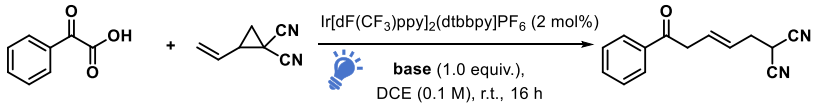


1a **2a** **3a**

entry	Photocatalyst	**3a** (% yield)[a]
1	**Ir[dF(CF$_3$)ppy]$_2$(dtbbpy]PF$_6$**	**85 (80)**[b]
2	4CzIPN	51
3	5CzBN	15
4	4OMeCzBN	6
5	4CzFBN	17
6	4OPhIPN	*n.d.*
7	Ir[(dtbbpy)(ppy)$_2$]PF$_6$	3
8	Ir[dF(Me)ppy)]$_2$(dtbbpy)]PF$_6$	65

[a] Reaction conditions: α-keto acid **1a** (0.3 mmol, 1.5 equiv.), vinylcyclopropane **2a** (0.2 mmol, 1.0 equiv.), PC (2.0 mol%), Cs_2CO_3 (1.0 equiv.), DCE (2.0 mL), blue LED, under nitrogen atmosphere at room temperature for 16 h. [b] GC yield. [c] Isolated yield.

Table S2. Optimization of base[a]

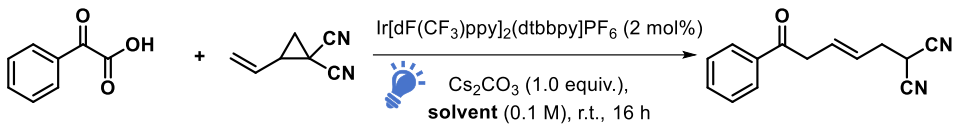


1a **2a** **3a**

entry	base	**3a** (% yield)[a]
1	**Cs_2CO_3**	**85 (80)**[b]
2	Na_2CO_3	31
3	K_3PO_4	36
4	Et_3N	16
5	DIPEA	8

[a] Reaction conditions: α-keto acid **1a** (0.3 mmol, 1.5 equiv.), vinylcyclopropane **2a** (0.2 mmol, 1.0 equiv.), Ir-III (2.0 mol%), base (1.0 equiv.), DCE (2.0 mL), blue LED, under nitrogen atmosphere at room temperature for 16 h. [b] GC yield. [c] Isolated yield.

Table S3. Optimization of solvent[a]

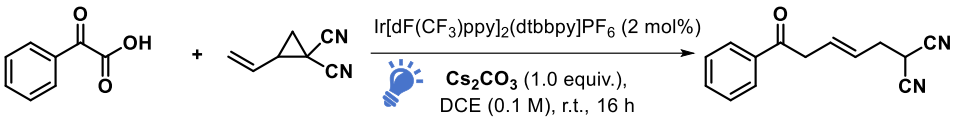


1a **2a** **3a**

entry	solvent	**3a** (% yield)[a]
1	**DCE**	**85 (80)**[b]
2	DCM	65
3	THF	24
4	DMA	*n.d.*
5	DMSO	*n.d.*
6	MeOH	10
7	DME	7
8	MeCN	15
9	Toluene	13
10	1,4-Dioxane	20

[a] Reaction conditions: α-keto acid **1a** (0.3 mmol, 1.5 equiv.), vinylcyclopropane **2a** (0.2 mmol, 1.0 equiv.), Ir-III (2.0 mol%), Cs_2CO_3 (1.0 equiv.), solvent (2.0 mL), blue LED, under nitrogen atmosphere at room temperature for 16 h. [b] GC yield. [c] Isolated yield.

Table S4. Optimization of equivalence ratio of **1a** and **2a**[a]

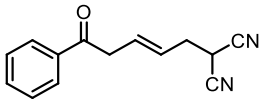


1a **2a** **3a**

entry	ratio (**1a:2a**)	**3a** (% yield)[a]
1	**1.5:1**	**85 (80)**[b]
2	3:1	79
3	2:1	78
4	1:1	34
5	1:1.5	*n.d.*
6	1:2	*n.d.*

[a] Reaction conditions: α-keto acid **1a**, vinylcyclopropane **2a**, Ir-III (2.0 mol%), base (1.0 equiv.), DCE (2.0 mL), blue LED, under nitrogen atmosphere at room temperature for 16 h. [b] GC yield. [c] Isolated yield.

V. Specific Experimental Details and Product Characterization Data

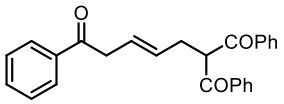


3a prepared according to General Procedure from vinylcyclopropane (23.6 mg, 0.20 mmol, 1.0 equiv.), α-keto acid (45.0 mg, 0.30 mmol, 1.5 equiv.) in DCE (2.0 mL). The reaction mixture was allowed to stir at room temperature under blue LEDs irradiation for 16 hours. After purification by silica gel column chromatography (PE/EA = 5/1), the desired product was obtained in 80% yield (35.9 mg) (*E*/*Z* >20:1) as a yellow solid.

^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm) 7.96 (d, J = 7.3 Hz, 2H), 7.59 (t, J = 7.4 Hz, 1H), 7.48 (t, J = 7.7 Hz, 2H), 6.17 – 6.10 (m, 1H), 5.71 – 5.64 (m, 1H), 3.83 (d, J = 6.7 Hz, 2H), 3.78 (t, J = 6.7 Hz, 1H), 2.80 (t, J = 6.9 Hz, 2H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm) 197.3, 136.4, 133.6, 131.3, 128.9, 128.3, 124.9, 112.3, 41.9, 34.0, 23.4.

HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{14}H_{13}N_2O$: 225.1030. Found 225.1022.

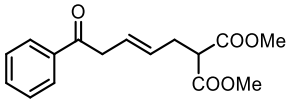


3b prepared according to General Procedure from vinylcyclopropane (55.2 mg, 0.20 mmol, 1.0 equiv.), α-keto acid (45.0 mg, 0.30 mmol, 1.5 equiv.) in DCE (2.0 mL). The reaction mixture was allowed to stir at room temperature under blue LEDs irradiation for 16 hours. After purification by silica gel column chromatography (PE/EA = 5/1), the desired product was obtained in 61% yield (46.7 mg) (*E*/*Z* >20:1) as a yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.96 – 7.88 (m, 6H), 7.57 – 7.52 (m, 3H), 7.43 (t, J = 7.6 Hz, 6H), 5.84 – 5.77 (m, 1H), 5.74 – 5.65 (m 1H), 5.29 (t, J = 6.7 Hz, 1H), 3.65 (d, J = 6.4 Hz, 2H), 2.88 (t, J = 6.7 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 198.2, 195.7, 136.1, 133.7, 133.3, 131.1, 129.0, 128.7, 128.4, 125.6, 57.2, 42.3, 32.6.

HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{26}H_{23}O_3$: 383.1642. Found: 383.1644;

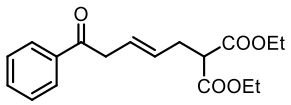


3c prepared according to General Procedure from vinylcyclopropane (36.8 mg, 0.20 mmol, 1.0 equiv.), α-keto acid (45.0 mg, 0.30 mmol, 1.5 equiv.) in DCE (2.0 mL). The reaction mixture was allowed to stir at room temperature under blue LEDs irradiation for 16 hours. After purification by silica gel column chromatography (PE/EA = 7/1), the desired product was obtained in 84% yield (48.8 mg) (*E*/*Z* >20:1) as a yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.93 (d, J = 8.0 Hz, 2H), 7.55 (t, J = 7.3 Hz, 1H), 7.45 (t, J = 7.6 Hz, 2H), 5.84 – 5.77 (m, 1H), 5.61 – 5.54 (m, 1H), 3.69 (d, J = 11.5 Hz, 8H), 3.44 (t, J = 7.5 Hz, 1H), 2.65 (t, J = 7.2 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 198.0, 169.4, 136.6, 133.3, 129.8, 128.7, 128.4, 126.2, 52.6, 51.7, 42.4, 32.0.

HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{16}H_{19}O_5$: 291.1227. Found: 291.1232.

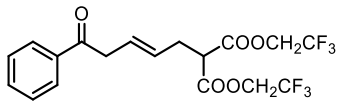


3d prepared according to General Procedure from vinylcyclopropane (42.4 mg, 0.20 mmol, 1.0 equiv.), α-keto acid (45.0 mg, 0.30 mmol, 1.5 equiv.) in DCE (2.0 mL). The reaction mixture was allowed to stir at room temperature under blue LEDs irradiation for 16 hours. After purification by silica gel column chromatography (PE/EA = 7/1), the desired product was obtained in 75% yield (47.8 mg) (*E*/*Z* >20:1) as a yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.93 (d, J = 8.5 Hz, 2H), 7.55 (t, J = 7.4 Hz, 1H), 7.45 (t, J = 7.6 Hz, 2H), 5.85 – 5.78 (m, 1H), 5.62 – 5.55 (m, 1H), 4.20 – 4.12 (m, 4H), 3.68 (d, J = 6.6 Hz, 2H), 3.40 (t, J = 7.5 Hz, 1H), 2.65 (t, J = 7.1 Hz, 2H), 1.24 (t, J = 7.1 Hz, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 198.0, 168.9, 136.5, 133.2, 129.9, 128.6, 128.3, 125.8, 61.4, 51.9, 42.3, 31.8, 14.1.

HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{18}H_{23}O_5$: 319.1540. Found: 319.1537.



3e prepared according to General Procedure from vinylcyclopropane (64.0 mg, 0.20 mmol, 1.0 equiv.), α-keto acid (45.0 mg, 0.30 mmol, 1.5 equiv.) in DCE (2.0 mL). The reaction mixture was allowed to stir at room temperature under blue LEDs irradiation for 16 hours. After

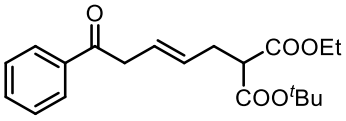
purification by silica gel column chromatography (PE/EA = 5/1), the desired product was obtained in 66% yield (56.2 mg) (*E*/*Z* >20:1) as a yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.93 (d, *J* = 7.9 Hz, 2H), 7.57 (t, *J* = 7.3 Hz, 1H), 7.46 (t, *J* = 7.6 Hz, 2H), 5.89 – 5.82 (m, 1H), 5.61 – 5.54 (m, 1H), 4.52 (q, *J* = 8.2 Hz, 4H), 3.71 – 3.65 (m, 3H), 2.74 (t, *J* = 7.2 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 197.8, 166.6, 136.6, 133.4, 128.8, 128.4, 128.3, 127.5, 124.1, 121.3, 61.2 (q, *J* = 37.1 Hz), 51.1, 42.1, 31.8.

^{19}F NMR (376 MHz, $CDCl_3$): δ (ppm) -73.84.

HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{18}H_{17}F_6O_5$: 427.0975. Found: 427.0972.

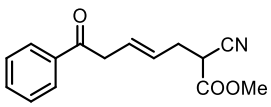


3f prepared according to General Procedure from vinylcyclopropane (48.0 mg, 0.20 mmol, 1.0 equiv.), α-keto acid (45.0 mg, 0.30 mmol, 1.5 equiv.) in DCE (2.0 mL). The reaction mixture was allowed to stir at room temperature under blue LEDs irradiation for 16 hours. After purification by silica gel column chromatography (PE/EA = 7/1), the desired product was obtained in 76% yield (52.7 mg) (*E*/*Z* >20:1) as a yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.94 (d, *J* = 7.4 Hz, 2H), 7.56 (t, *J* = 7.4 Hz, 1H), 7.45 (t, *J* = 7.6 Hz, 2H), 5.85 – 5.78 (m, 1H), 5.63 – 5.56 (m, 1H), 4.23 – 4.09 (m, 2H), 3.69 (d, *J* = 6.7 Hz, 2H), 3.30 (t, *J* = 7.5 Hz, 1H), 2.61 (t, *J* = 7.2 Hz, 2H), 1.43 (s, 9H), 1.25 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 198.1, 169.4, 168.1, 136.7, 133.3, 130.3, 128.8, 128.4, 125.6, 82.0, 61.3, 53.0, 42.5, 31.9, 28.0, 14.3.

HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{20}H_{27}O_5$: 347.1853. Found: 347.1862.

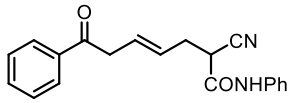


3g prepared according to General Procedure from vinylcyclopropane (30.2 mg, 0.20 mmol, 1.0 equiv.), α-keto acid (45.0 mg, 0.30 mmol, 1.5 equiv.) in DCE (2.0 mL). The reaction mixture was allowed to stir at room temperature under blue LEDs irradiation for 16 hours. After purification by silica gel column chromatography (PE/EA = 5/1), the desired product was obtained in 72% yield (37.0 mg) (*E*/*Z* >20:1) as a yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.95 (d, J = 7.7 Hz, 2H), 7.58 (t, J = 7.3 Hz, 1H), 7.47 (t, J = 7.7 Hz, 2H), 6.01 – 5.94 (m, 1H), 5.67 – 5.60 (m, 1H), 3.80 (s, 3H), 3.78 – 3.75 (m, 2H), 3.57 (t, J = 6.7 Hz, 1H), 2.72 (t, J = 7.3 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 197.5, 166.0, 136.4, 133.3, 128.7, 128.2, 127.0, 116.0, 53.5, 42.0, 37.6, 32.9.

HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{15}H_{16}NO_3$: 258.1125. Found: 258.1133.

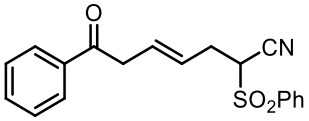


3h prepared according to General Procedure from vinylcyclopropane (42.4 mg, 0.20 mmol, 1.0 equiv.), α-keto acid (45.0 mg, 0.30 mmol, 1.5 equiv.) in DCE (2.0 mL). The reaction mixture was allowed to stir at room temperature under blue LEDs irradiation for 16 hours. After purification by silica gel column chromatography (PE/EA = 5/1), the desired product was obtained in 72% yield (45.8 mg) (E/Z >20:1) as a yellow solid;

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.99 (s, 1H), 7.94 (d, J = 7.2 Hz, 2H), 7.57 (t, J = 7.4 Hz, 1H), 7.34 (t, J = 7.9 Hz, 2H), 7.51 (d, J = 7.8 Hz, 2H), 7.46 (t, J = 7.7 Hz, 2H), 7.17 (t, J = 7.4 Hz, 1H), 6.01 – 5.97 (m, 1H), 5.63 – 5.56 (m, 1H), 3.77 (d, J = 6.7 Hz, 2H), 3.62 (t, J = 6.6 Hz, 1H), 2.81 (t, J = 6.9 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 197.8, 162.1, 136.7, 136.4, 133.4, 129.1, 128.7, 128.3, 127.7, 125.5, 120.5, 117.6, 41.9, 39.8, 33.0.

HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{20}H_{19}N_2O_2$: 319.1441. Found: 319.1450.



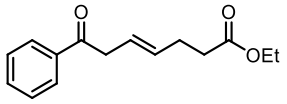
3i prepared according to General Procedure from vinylcyclopropane (46.4 mg, 0.20 mmol, 1.0 equiv.), α-keto acid (45.0 mg, 0.30 mmol, 1.5 equiv.) in DCE (2.0 mL). The reaction mixture was allowed to stir at room temperature under blue LEDs irradiation for 16 hours. After purification by silica gel column chromatography (PE/EA = 5/1), the desired product was obtained in 88% yield (59.7 mg) (E/Z >20:1) as a yellow solid;

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.01 (d, J = 9.0 Hz, 2H), 7.93 (d, J = 8.9 Hz, 2H), 7.77 (t, J = 7.5 Hz, 1H), 7.65 (t, J = 7.8 Hz, 2H), 7.57 (t, J = 7.4 Hz, 1H), 7.46 (t, J = 7.6 Hz, 2H), 6.04 – 5.97

(m, 1H), 5.63 – 5.56 (m, 1H), 3.98 (dd, *J* = 10.5, 4.6 Hz, 1H), 3.76 (d, *J* = 6.6 Hz, 2H), 3.00 – 2.97 (m, 1H), 2.75 – 2.60 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 197.4, 136.3, 135.5, 135.4, 133.4, 129.7, 128.7, 128.2, 125.4, 113.6, 57.3, 41.9, 30.2.

HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{19}H_{18}NO_3S$: 340.1002. Found:340.1004.

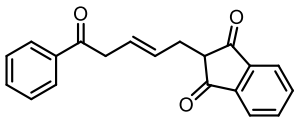


3j prepared according to General Procedure from vinylcyclopropane (28.0 mg, 0.20 mmol, 1.0 equiv.), α-keto acid (45.0 mg, 0.30 mmol, 1.5 equiv.) in DCE (2.0 mL). The reaction mixture was allowed to stir at room temperature under blue LEDs irradiation for 16 hours. After purification by silica gel column chromatography (PE/EA = 20/1), the desired product was obtained in 88% yield (28.6 mg) (*E*/*Z* >20:1) as a yellow oil;

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.94 (d, *J* = 8.2 Hz, 2H), 7.56 (t, *J* = 7.3 Hz, 1H), 7.47 (t, *J* = 7.5 Hz, 2H), 5.82 – 5.73 (m, 1H), 5.69 – 5.60 (m, 1H), 4.10 (q, *J* = 7.1 Hz, 2H), 3.68 (d, *J* = 6.5 Hz, 2H), 2.38 (d, *J* = 2.3 Hz, 4H), 1.22 (m, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 198.4, 173.2, 133.3, 132.8, 129.3, 128.8, 128.4, 123.8, 60.5, 42.5, 34.1, 28.1, 14.4.

HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{15}H_{19}O_3$: 247.1329. Found: 247.1325.

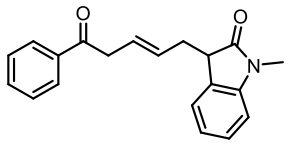


3k prepared according to General Procedure from vinylcyclopropane (42.4 mg, 0.20 mmol, 1.0 equiv.), α-keto acid (45.0 mg, 0.30 mmol, 1.5 equiv.) in DCE (2.0 mL). The reaction mixture was allowed to stir at room temperature under blue LEDs irradiation for 16 hours. After purification by silica gel column chromatography (PE/EA = 5/1), the desired product was obtained in 74% yield (45.0 mg) (*E*/*Z* >20:1) as a yellow oil;

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.94 (d, *J* = 8.1 Hz, 2H), 7.89 – 7.77 (m, 4H), 7.52 (t, *J* = 7.3 Hz, 1H), 7.40 (t, *J* = 7.5 Hz, 2H), 5.86 – 5.79 (m, 1H), 5.63 – 5.56 (m, 1H), 3.59 (d, *J* = 6.7 Hz, 2H), 3.09 (t, *J* = 5.9 Hz, 1H), 2.75 (t, *J* = 6.4 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 200.2, 197.9, 142.6, 136.6, 135.8, 133.2, 129.0, 128.7, 128.4, 126.8, 123.3, 53.6, 42.4, 29.9.

HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{20}H_{17}O_3$: 305.1172. Found: 305.1178.

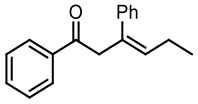


3l prepared according to General Procedure from vinylcyclopropane (42.6 mg, 0.20 mmol, 1.0 equiv.), α-keto acid (45.0 mg, 0.30 mmol, 1.5 equiv.) in DCE (2.0 mL). The reaction mixture was allowed to stir at room temperature under blue LEDs irradiation for 16 hours. After purification by silica gel column chromatography (PE/EA = 5/1), the desired product was obtained in 76% yield (46.4 mg) (*E*/*Z* >20:1) as a yellow solid;

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.91 (d, J = 7.4 Hz, 2H), 7.55 (t, J = 7.4 Hz, 1H), 7.46 (t, J = 7.5 Hz, 2H), 7.24 (dd, J = 12.6, 5.4 Hz, 2H), 7.00 (t, J = 7.5 Hz, 1H), 6.77 (d, J = 7.7 Hz, 1H), 5.79 – 5.72 (m, 1H), 5.62 – 5.55 (m, 1H), 3.65 (d, J = 5.6 Hz, 2H), 3.48 – 3.42 (m, 1H), 3.15 (s, 3H), 2.81 – 2.58 (m, 1H), 2.56 – 2.50 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 198.1, 177.2, 144.3, 136.6, 133.2, 130.2, 128.7, 128.4, 128.0, 126.1, 124.3, 122.4, 108.0, 45.4, 42.4, 34.0, 26.2.

HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{20}H_{20}NO_2$: 306.1489. Found: 306.1493.

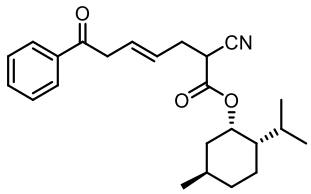


3m prepared according to General Procedure from vinylcyclopropane (28.8 mg, 0.20 mmol, 1.0 equiv.), α-keto acid (45.0 mg, 0.30 mmol, 1.5 equiv.) in DCE (2.0 mL). The reaction mixture was allowed to stir at room temperature under blue LEDs irradiation for 16 hours. After purification by silica gel column chromatography (PE/EA = 20/1), the desired product was obtained in 70% yield (35.0 mg) (*E*/*Z* >20:1) as a yellow solid;

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.99 (d, J = 7.4 Hz, 2H), 7.58 – 7.38 (m, 8H), 7.05 (s, 1H), 3.10 – 3.01 (m, 2H), 1.55 – 1.47 (m, 2H), 0.95 (t, J = 7.3 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 139.5, 132.7, 129.1, 128.8, 128.7, 128.5, 127.0, 122.8, 77.5, 76.8, 33.7, 22.5, 14.3.

HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{18}H_{19}O$: 251.1430. Found:251.1436.

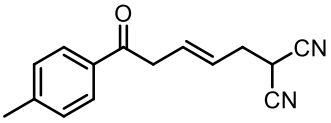


3n prepared according to General Procedure from vinylcyclopropane (55.0 mg, 0.20 mmol, 1.0 equiv.), α-keto acid (45.0 mg, 0.30 mmol, 1.5 equiv.) in DCE (2.0 mL). The reaction mixture was allowed to stir at room temperature under blue LEDs irradiation for 16 hours. After purification by silica gel column chromatography (PE/EA = 10/1), the desired product was obtained in 46% yield (35.1 mg) (*E*/*Z* >20:1) as a yellow oil; When the reaction mixture was stirred at at room temperature under blue LEDs irradiation for 16 hours in the presence of α-keto acid (60.0 mg, 0.40 mmol, 2.0 equiv.), the desired product was obtained in 59% yield (45.0 mg) (*E*/*Z* >20:1) as a yellow oil;

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.95 (d, *J* = 7.7 Hz, 2H), 7.58 (t, *J* = 7.2 Hz, 1H), 7.48 (t, *J* = 7.6 Hz, 2H), 6.02 – 5.95 (m, 1H), 5.67 – 5.60 (m, 1H), 4.83 – 4.69 (m, 1H), 3.76 (d, *J* = 6.6 Hz, 1H), 3.53 (t, *J* = 8.4 Hz, 1H), 2.79 – 2.53 (m, 2H), 2.05 – 1.82 (m, 2H), 1.70 (d, *J* = 12.4 Hz, 2H), 1.63 – 1.35 (m, 4H), 1.13 – 0.99 (m, 2H), 0.95 – 0.74 (m, 9H).

^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 197.7, 165.2, 136.5, 133.5, 129.3, 128.8, 128.6, 128.4, 127.3, 46.9, 42.1, 40.6, 38.2, 34.1, 33.1, 31.5, 26.3, 23.4, 22.1, 20.9, 16.3.

HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{24}H_{32}NO_3$: 382.2377. Found: 382.2377.

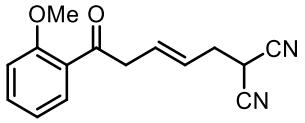


3o prepared according to General Procedure from vinylcyclopropane (23.6 mg, 0.20 mmol, 1.0 equiv.), α-keto acid (45.0 mg, 0.30 mmol, 1.5 equiv.) in DCE (2.0 mL). The reaction mixture was allowed to stir at room temperature under blue LEDs irradiation for 16 hours. After purification by silica gel column chromatography (PE/EA = 5/1), the desired product was obtained in 73% yield (34.8 mg) (*E*/*Z* >20:1) as a yellow oil;

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.85 (d, *J* = 8.4 Hz, 2H), 7.27 (d, *J* = 8.4 Hz, 2H), 6.19 – 6.07 (m, 1H), 5.73 – 5.61 (m, 1H), 3.79 (d, *J* = 6.6 Hz, 3H), 2.78 (t, *J* = 6.9 Hz, 2H), 2.42 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 197.0, 144.5, 133.9, 131.5, 129.6, 128.5, 124.7, 112.3, 41.8, 34.0, 23.3, 21.8.

HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{15}H_{15}N_2O$: 239.1179. Found: 239.1179.

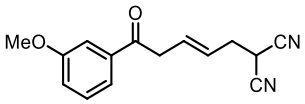


3p prepared according to General Procedure from vinylcyclopropane (23.6 mg, 0.20 mmol, 1.0 equiv.), *α*-keto acid (54.0 mg, 0.30 mmol, 1.5 equiv.) in DCE (2.0 mL). The reaction mixture was allowed to stir at room temperature under blue LEDs irradiation for 16 hours. After purification by silica gel column chromatography (PE/EA = 5/1), the desired product was obtained in 65% yield (33.1 mg) (*E*/*Z* >20:1) as a yellow solid;

^{1}H NMR (400 MHz, $CDCl_3$): *δ* (ppm) 7.73 (dd, *J* = 7.7, 1.7 Hz, 1H), 7.51 – 7.46 (m, 1H), 7.06 – 6.96 (m, 3H), 6.14 – 6.07 (m, 1H), 5.64 – 5.57 (m, 1H), 3.93 (s, 3H), 3.83 (d, *J* = 7.0 Hz, 2H), 3.75 (t, *J* = 6.7 Hz, 1H), 2.77 (t, *J* = 6.9 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): *δ* (ppm) 199.3, 159.9, 134.2, 132.2, 130.8, 127.5, 124.1, 120.9, 112.3, 111.7, 55.7, 47.1, 34.0, 23.4.

HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{15}H_{15}N_2O_2$: 255.1128. Found: 255.1131.

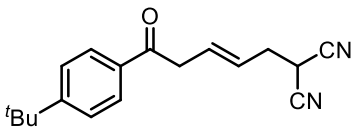


3q prepared according to General Procedure from vinylcyclopropane (23.6 mg, 0.20 mmol, 1.0 equiv.), *α*-keto acid (54.0 mg, 0.30 mmol, 1.5 equiv.) in DCE (2.0 mL). The reaction mixture was allowed to stir at room temperature under blue LEDs irradiation for 16 hours. After purification by silica gel column chromatography (PE/EA = 5/1), the desired product was obtained in 63% yield (32.0 mg) (*E*/*Z* >20:1) as a yellow solid;

^{1}H NMR (400 MHz, $CDCl_3$): *δ* (ppm) 7.53 (d, *J* = 7.5 Hz, 1H), 7.47 (s, 1H), 7.39 (t, *J* = 7.9 Hz, 1H), 7.13 (dd, *J* = 8.2, 2.5 Hz, 1H), 6.16 – 6.09 (m, 1H), 5.70 – 5.62 (m, 1H), 3.86 (s, 3H), 3.84 – 3.79 (m, 3H), 2.79 (t, *J* = 6.9 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): *δ* (ppm) 197.1, 160.1, 137.7, 131.3, 129.9, 124.9, 120.9, 120.1, 112.6, 112.3, 55.6, 42.0, 34.0, 23.4.

HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{15}H_{15}N_2O_2$: 255.1128. Found:255.1131.



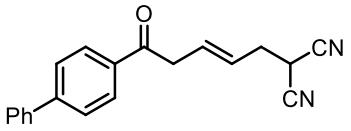
3r prepared according to General Procedure from vinylcyclopropane (23.6 mg, 0.20 mmol, 1.0 equiv.), *α*-keto acid (61.8 mg, 0.30 mmol, 1.5 equiv.) in DCE (2.0 mL). The reaction mixture

was allowed to stir at room temperature under blue LEDs irradiation for 16 hours. After purification by silica gel column chromatography (PE/EA = 5/1), the desired product was obtained in 89% yield (49.9 mg) (*E*/*Z* >20:1) as a yellow solid;

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.89 (d, *J* = 8.5 Hz, 2H), 7.49 (d, *J* = 8.5 Hz, 2H), 6.16 – 6.09 (m, 1H), 5.69 – 5.62 (m, 1H), 3.79 (t, *J* = 7.2 Hz, 3H), 2.79 (t, *J* = 6.9 Hz, 2H), 1.34 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 197.0, 157.5, 133.8, 131.5, 128.3, 125.8, 124.8, 112.3, 41.8, 35.3, 34.0, 31.2, 23.4.

HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{18}H_{21}N_2O$: 281.1648. Found: 281.1652.

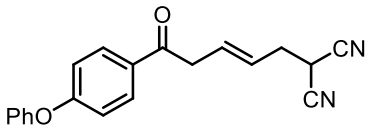


3s prepared according to General Procedure from vinylcyclopropane (23.6 mg, 0.20 mmol, 1.0 equiv.), α-keto acid (67.8 mg, 0.30 mmol, 1.5 equiv.) in DCE (2.0 mL). The reaction mixture was allowed to stir at room temperature under blue LEDs irradiation for 16 hours. After purification by silica gel column chromatography (PE/EA = 5/1), the desired product was obtained in 84% yield (50.5 mg) (*E*/*Z* >20:1) as a yellow solid;

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.03 (d, *J* = 8.3 Hz, 2H), 7.71 (d, *J* = 8.3 Hz, 2H), 7.63 (d, *J* = 7.2 Hz, 2H), 7.48 (t, *J* = 7.4 Hz, 2H), 7.42 (d, *J* = 7.2 Hz, 1H), 6.20-6.13 (m, 1H), 5.73 – 5.66 (m, 1H), 3.86 (d, *J* = 6.7 Hz, 2H), 3.78 (t, *J* = 6.7 Hz, 1H), 2.81 (t, *J* = 6.9 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 196.9, 146.3, 139.9, 131.4, 129.1, 129.0, 128.5, 127.5, 127.4, 124.9, 112.2, 42.0, 34.0, 23.4.

HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{20}H_{17}N_2O$: 301.1335. Found: 301.1338.

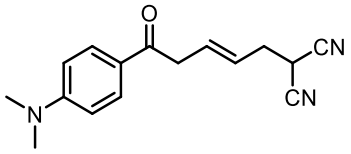


3t prepared according to General Procedure from vinylcyclopropane (23.6 mg, 0.20 mmol, 1.0 equiv.), α-keto acid (72.6 mg, 0.30 mmol, 1.5 equiv.) in DCE (2.0 mL). The reaction mixture was allowed to stir at room temperature under blue LEDs irradiation for 16 hours. After purification by silica gel column chromatography (PE/EA = 5/1), the desired product was obtained in 80% yield (50.6 mg) (*E*/*Z* >20:1) as a yellow solid;

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.93 (d, J = 8.8 Hz, 2H), 7.40 (t, J = 8.0 Hz, 2H), 7.21 (t, J = 7.4 Hz, 1H), 7.07 (d, J = 8.7 Hz, 2H), 7.01 (d, J = 8.8 Hz, 2H), 6.16 – 6.09 (m, 1H), 5.69 – 5.62 (m, 1H), 3.83 – 3.76 (m, 3H), 2.79 (t, J = 6.9 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 195.8, 162.4, 155.4, 131.4, 130.9, 130.6, 130.2, 124.8, 120.4, 117.5, 112.3, 41.7, 33.9, 23.3.

HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{20}H_{17}N_2O_2$: 317.1285. Found: 317.1295.

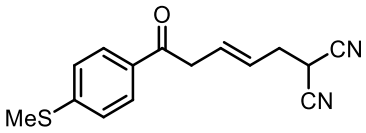


3u prepared according to General Procedure from vinylcyclopropane (23.6 mg, 0.20 mmol, 1.0 equiv.), α-keto acid (62.7 mg, 0.30 mmol, 1.5 equiv.) in DCE (2.0 mL). The reaction mixture was allowed to stir at room temperature under blue LEDs irradiation for 16 hours. After purification by silica gel column chromatography (PE/EA = 5/1), the desired product was obtained in 70% yield (37.2 mg) (E/Z >20:1) as a yellow solid;

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.86 (d, J = 9.1 Hz, 2H), 6.65 (d, J = 9.1 Hz, 2H), 6.16 – 6.09 (m, 1H), 5.67 – 5.59 (m, 1H), 3.76 (t, J = 6.8 Hz, 1H), 3.72 (d, J = 6.8 Hz, 2H), 3.07 (s, 6H), 2.77 (t, J = 6.9 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 195.2, 153.7, 132.5, 130.6, 124.1, 112.4, 110.8, 41.3, 40.2, 34.1, 23.4.

HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{16}H_{18}N_3O$: 268.1444. Found: 268.1451.

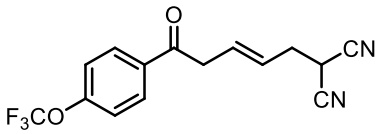


3v prepared according to General Procedure from vinylcyclopropane (23.6 mg, 0.20 mmol, 1.0 equiv.), α-keto acid (63.6 mg, 0.30 mmol, 1.5 equiv.) in DCE (2.0 mL). The reaction mixture was allowed to stir at room temperature under blue LEDs irradiation for 16 hours. After purification by silica gel column chromatography (PE/EA = 5/1), the desired product was obtained in 93% yield (50.3 mg) (E/Z >20:1) as a yellow solid;

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.86 (d, J = 8.5 Hz, 2H), 7.27 (d, J = 8.7 Hz, 2H), 6.16 – 6.09 (m, 1H), 5.69 – 5.62 (m, 1H), 3.81 – 3.74 (m, 3H), 2.79 (t, J = 6.9 Hz, 2H), 2.53 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 196.2, 146.7, 132.6, 131.5, 128.7, 125.2, 124.8, 112.3, 41.7, 34.0 23.4, 14.9.

HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{15}H_{15}N_2OS$: 271.0900. Found:271.0905.



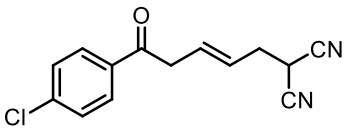
3w prepared according to General Procedure from vinylcyclopropane (23.6 mg, 0.20 mmol, 1.0 equiv.), α-keto acid (75.0 mg, 0.30 mmol, 1.5 equiv.) in DCE (2.0 mL). The reaction mixture was allowed to stir at room temperature under blue LEDs irradiation for 16 hours. After purification by silica gel column chromatography (PE/EA = 5/1), the desired product was obtained in 40% yield (24.7 mg) (*E*/*Z* >20:1) as a yellow solid; When the reaction mixture was stirred at at room temperature under blue LEDs irradiation for 16 hours in the presence of α-keto acid (93.6 mg, 0.40 mmol, 2.0 equiv.), the desired product was obtained in 65% yield (40.0 mg) (*E*/*Z* >20:1) as a yellow solid;

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.01 (d, *J* = 8.8 Hz, 2H), 7.31 (d, *J* = 8.1 Hz, 2H), 6.16 – 6.09 (m, 1H), 5.71 – 5.64 (m, 1H), 3.87 – 3.74 (m, 3H), 2.80 (t, *J* = 6.8 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 195.7, 153.0, 134.6, 130.9, 130.4, 125.2, 120.7, 112.2, 41.9, 33.9, 23.4.

^{19}F NMR (376 MHz, $CDCl_3$): δ (ppm) -57.60.

HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{15}H_{12}F_3N_2O_2$: 309.0845. Found: 309.0833.

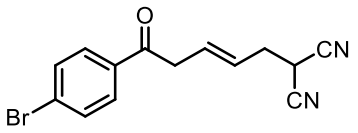


3x prepared according to General Procedure from vinylcyclopropane (23.6 mg, 0.20 mmol, 1.0 equiv.), α-keto acid (60.0 mg, 0.30 mmol, 1.5 equiv.) in DCE (2.0 mL). The reaction mixture was allowed to stir at room temperature under blue LEDs irradiation for 16 hours. After purification by silica gel column chromatography (PE/EA = 5/1), the desired product was obtained in 55% yield (28.5 mg) (*E*/*Z* >20:1) as a yellow solid;

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.89 (d, *J* = 8.6 Hz, 2H), 7.46 (d, *J* = 8.6 Hz, 2H), 6.20 – 6.07 (m, 1H), 5.73 – 5.61 (m, 1H), 3.82 – 3.73 (m, 3H), 2.80 (t, *J* = 6.9 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 196.0, 140.2, 134.7, 131.0, 129.8, 129.3, 125.13, 112.2, 41.8, 34.0 23.4.

HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{14}H_{12}ClN_2O$: 259.0633. Found: 259.0638.

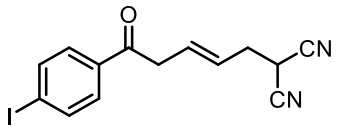


3y prepared according to General Procedure from vinylcyclopropane (23.6 mg, 0.20 mmol, 1.0 equiv.), α-keto acid (72.9 mg, 0.30 mmol, 1.5 equiv.) in DCE (2.0 mL). The reaction mixture was allowed to stir at room temperature under blue LEDs irradiation for 16 hours. After purification by silica gel column chromatography (PE/EA = 5/1), the desired product was obtained in 56% yield (34.0mg) (*E*/*Z* >20:1) as a yellow solid;

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.81 (d, J = 8.7 Hz, 2H), 7.63 (d, J = 8.6 Hz, 2H), 6.15 – 6.08 (m, 1H), 5.77 – 5.63 (m, 1H), 3.79 – 3.76 (m, 3H), 2.80 (t, J = 6.8 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 196.2, 135.1, 132.3, 130.9, 129.8, 128.9, 125.2, 112.2, 41.8, 34.0, 23.4.

HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{14}H_{12}BrN_2O$: 303.0128. Found: 303.0135.

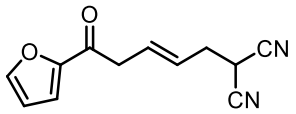


3z prepared according to General Procedure from vinylcyclopropane (23.6 mg, 0.20 mmol, 1.0 equiv.), α-keto acid (87.3 mg, 0.30 mmol, 1.5 equiv.) in DCE (2.0 mL). The reaction mixture was allowed to stir at room temperature under blue LEDs irradiation for 16 hours. After purification by silica gel column chromatography (PE/EA = 5/1), the desired product was obtained in 36% yield (25.2 mg) (*E*/*Z* >20:1) as a yellow solid; When the reaction mixture was stirred at at room temperature under blue LEDs irradiation for 16 hours in the presence of α-keto acid (110.4 mg, 0.40 mmol, 2.0 equiv.), the desired product was obtained in 57% yield (39.9 mg) (*E*/*Z* >20:1) as a yellow solid;

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.85 (d, J = 8.1 Hz, 2H), 7.65 (d, J = 8.5 Hz, 2H), 6.14 – 6.07 (m, 1H), 5.70 – 5.63 (m, 1H), 3.78 – 3.76 (m, 3H), 2.79 (t, J = 6.9 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 196.5, 138.2, 135.6, 130.9, 129.7, 125.2, 112.2, 101.7, 41.7, 33.9, 23.4.

HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{14}H_{12}IN_2O$: 350.9989. Found: 350.9988.

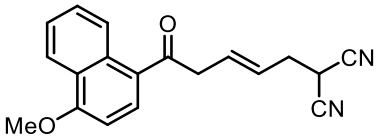


3aa prepared according to General Procedure from vinylcyclopropane (23.6 mg, 0.20 mmol, 1.0 equiv.), α-keto acid (42.0 mg, 0.30 mmol, 1.5 equiv.) in DCE (2.0 mL). The reaction mixture was allowed to stir at room temperature under blue LEDs irradiation for 16 hours. After purification by silica gel column chromatography (PE/EA = 5/1), the desired product was obtained in 70% yield (30.0 mg) (*E*/*Z* >20:1) as a yellow solid;

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.61 (s, 1H), 7.23 (d, *J* = 3.5 Hz, 1H), 6.56 (dd, *J* = 3.5, 1.6 Hz, 1H), 6.11 – 6.03 (m, 1H), 5.73 – 5.65 (m, 1H), 3.78 (t, *J* = 6.7 Hz, 1H), 3.68 (d, *J* = 6.9 Hz, 2H), 2.78 (t, *J* = 6.9 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 186.1, 146.9, 130.5, 125.3, 117.8, 112.6, 112.2, 41.8, 33.9, 23.3.

HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{12}H_{11}N_2O_2$: 215.0815. Found: 215.0806.

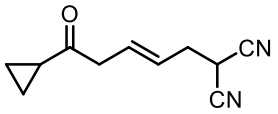


3ab prepared according to General Procedure from vinylcyclopropane (23.6 mg, 0.20 mmol, 1.0 equiv.), α-keto acid (78.6 mg, 0.30 mmol, 1.5 equiv.) in DCE (2.0 mL). The reaction mixture was allowed to stir at room temperature under blue LEDs irradiation for 16 hours. After purification by silica gel column chromatography (PE/EA = 5/1), the desired product was obtained in 60% yield (36.5 mg) (*E*/*Z* >20:1) as a yellow solid;

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.92 (d, *J* = 8.6 Hz, 1H), 8.33 (d, *J* = 8.3 Hz, 1H), 8.00 (d, *J* = 8.2 Hz, 1H), 7.63 (t, *J* = 8.4 Hz, 1H), 7.53 (t, *J* = 8.0 Hz, 1H), 6.81 (d, *J* = 8.2 Hz, 1H), 6.21 – 6.13 (m, 1H), 5.72 – 5.64 (m, 1H), 4.08 (s, 3H), 3.89 (d, *J* = 6.9 Hz, 2H), 3.76 (t, *J* = 6.7 Hz, 1H), 2.79 (t, *J* = 6.9 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 199.0, 159.7, 132.3, 131.5, 129.1, 126.6, 126.1, 124.5, 122.3, 112.3, 102.2, 56.0, 44.4, 34.0, 23.4.

HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{19}H_{17}N_2O_2$: 305.1285. Found: 305.1293.

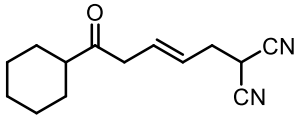


3ac prepared according to General Procedure from vinylcyclopropane (23.6 mg, 0.20 mmol, 1.0 equiv.), α-keto acid (34.2 mg, 0.30 mmol, 1.5 equiv.) in DCE (2.0 mL). The reaction mixture was allowed to stir at room temperature under blue LEDs irradiation for 16 hours. After purification by silica gel column chromatography (PE/EA = 5/1), the desired product was obtained in 77% yield (30.0mg) (*E*/*Z* >20:1) as a yellow solid;

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 6.06 – 5.94 (m, 1H), 5.68 – 5.56 (m, 1H), 3.77 (t, *J* = 6.6 Hz, 1H), 3.39 (d, *J* = 6.9 Hz, 2H), 2.77 (t, *J* = 6.8 Hz, 2H), 1.98 – 1.92 (m, 1H), 1.05 (t, *J* = 5.5 Hz, 2H), 0.94 – 0.89 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 207.9, 131.1, 124.8, 112.2, 46.6, 33.9, 23.4, 20.5, 11.4.

HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{11}H_{13}N_2O$: 189.1022. Found: 189.1021.

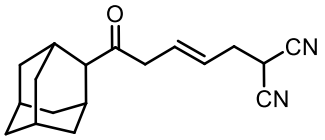


3ad prepared according to General Procedure from vinylcyclopropane (23.6 mg, 0.20 mmol, 1.0 equiv.), α-keto acid (46.8 mg, 0.30 mmol, 1.5 equiv.) in DCE (2.0 mL). The reaction mixture was allowed to stir at room temperature under blue LEDs irradiation for 16 hours. After purification by silica gel column chromatography (PE/EA = 5/1), the desired product was obtained in 47% yield (21.6 mg) (*E*/*Z* >20:1) as a yellow solid; When the reaction mixture was stirred at at room temperature under blue LEDs irradiation for 16 hours in the presence of α-keto acid (62.4 mg, 0.40 mmol, 2.0 equiv.), the desired product was obtained in 56% yield (25.8 mg) (*E*/*Z* >20:1) as a yellow solid;

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 5.99 – 5.92 (m, 1H), 5.60 – 5.53 (m, 1H), 3.76 (t, *J* = 6.6 Hz, 1H), 3.27 (d, *J* = 6.9 Hz, 2H), 2.76 (t, *J* = 6.9 Hz, 2H), 2.38 (t, *J* = 12.7 Hz, 1H), 1.87 – 1.76 (m, 4H), 1.38 – 1.17 (m, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 211.0, 131.3, 124.5, 112.3, 50.8, 43.8, 33.9, 28.5, 25.90, 25.7, 23.4.

HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{14}H_{19}N_2O$: 231.1492. Found: 231.1500.

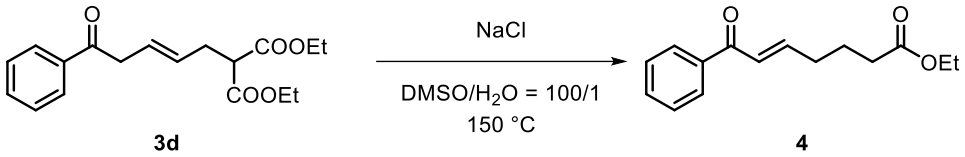


3ae prepared according to General Procedure from vinylcyclopropane (23.6 mg, 0.20 mmol, 1.0 equiv.), α-keto acid (62.4 mg, 0.30 mmol, 1.5 equiv.) in DCE (2.0 mL). The reaction mixture was allowed to stir at room temperature under blue LEDs irradiation for 16 hours. After purification by silica gel column chromatography (PE/EA = 5/1), the desired product was obtained in 50% yield (28.2 mg) (*E*//*Z* >20:1) as a yellow solid;

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 5.98 – 5.91 (m, 1H), 5.58 – 5.50 (m, 1H), 3.75 (t, *J* = 6.6 Hz, 1H), 3.30 (d, *J* = 6.7 Hz, 2H), 2.75 (t, *J* = 6.8 Hz, 2H), 2.06 (s, 4H), 1.91 (s, 1H), 1.72 (q, *J* = 12.4 Hz, 10H).

^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 212.8, 132.0, 124.2, 112.3, 46.7, 39.4, 38.8, 38.3, 36.6, 34.0, 28.0, 23.4.

HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{18}H_{23}N_2O$: 283.1805. Found: 283.1809.



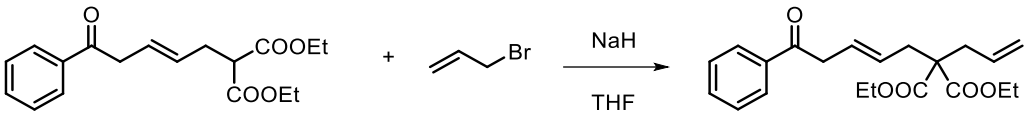
3d **4**

A mixture of **3d** (0.2 mmol, 1.0 equiv.), sodium chloride (0.4 mmol, 2.0 equiv.) , dimethylsulfoxide (2 mL) and water (20 μL) was stirred at 150 °C for about 3 hours. The reaction mixture was then quenched by the addition of water (20 mL).The resulting solution was extracted with ethyl acetate (3 x 10 mL) and the organic layers were combined, washed with water (2 x 10 mL), brine (2 x 10 mL), The organic layer was concentrated, After purification by silica gel column chromatography (PE/EA = 5/1), the desired product **4** was obtained in 70% yield (34.5 mg) (*E*/*Z* >20:1) as a yellow oil;

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.92 (d, *J* = 9.3 Hz, 2H), 7.55 (d, *J* = 7.4 Hz, 1H), 7.48 (d, *J* = 7.7 Hz, 2H), 7.09 – 6.99 (m, 1H), 6.90 (d, *J* = 15.4 Hz, 1H), 4.18 – 4.12 (m, 2H), 2.38 (d, *J* = 7.0 Hz, 4H), 1.88 (p, *J* = 7.4 Hz, 2H), 1.26 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 190.8, 173.3, 148.4, 138.0, 132.8, 128.7, 126.7, 123.8, 60.6, 33.7, 32.1, 23.5, 14.4.

HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{15}H_{19}O_3$: 247.1329. Found: 247.1335.



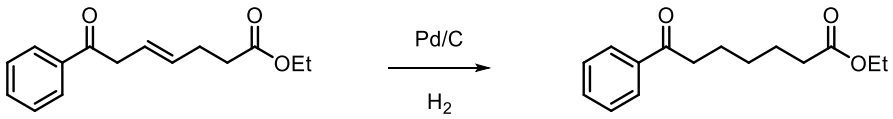
3d **5**

In a N_2-filled glovebox, an oven-dried vial (0.5 dram) equipped with a magnet stir bar was charged with NaH (0.22 mmol, 1.1 equiv.) in THF (2 mL) put under an argon atmosphere, and cooled to 0 °C using an ice water bath. **3d** (0.2 mmol, 1.0 equiv.) was added and the suspension was stirred at 0 °C for 1 hour. Allyl bromide (0.24 mmol, 1.2 equiv.) was then added dropwise by syringe, and the suspension was allowed to warm to 23 °C and stir for 15 hours. Upon completion (as determined by TLC analysis), the reaction mixture was diluted with ethyl acetate (20 mL) and extracted with water (1 x 30 mL). After purification by silica gel column chromatography (PE/EA = 10/1), the desired product **5** was obtained in 68% yield (48.7 mg) (*E*/*Z* >20:1) as a yellow oil;

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.93 (q, *J* = 8.1, 7.2 Hz, 2H), 7.56 (t, *J* = 7.4 Hz, 1H), 7.46 (t, *J* = 7.6 Hz, 2H), 5.83 – 5.76 (m, 1H), 5.69 – 5.58 (m, 1H), 5.50 – 5.43 (m, 1H), 5.13 – 5.05 (m, 2H), 4.16 (q, *J* = 7.1 Hz, 4H), 3.70 (d, *J* = 6.7 Hz, 2H), 2.63 (dd, *J* = 14.8, 7.4 Hz, 4H), 1.23 (t, *J* = 7.1 Hz, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 198.1, 170.9, 136.7, 133.3, 132.4, 129.3, 128.8, 128.4, 127.9, 127.4, 126.3, 119.4, 61.4, 57.5, 42.6, 37.0, 35.8, 14.3.

HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{21}H_{27}O_5$: 359.1853. Found: 359.1862.



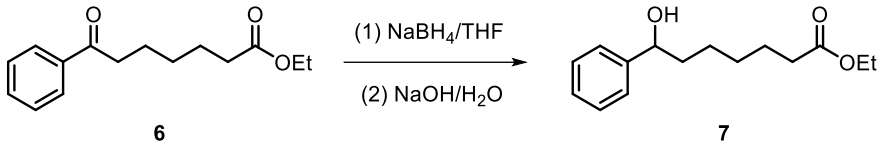
3j **6**

To a stirring solution of **3j** (49.2 mg, 0.20 mmol, 1.0 equiv.) in EA (2.0 mL) was slowly added palladium on-activated-charcoal (5%, 8.0 mg) at room temperature. The resulting mixture was stirred at room temperature in an atmosphere of hydrogen gas for 16 hours. The mixture was filtered and concentrated under reduced pressure. After purification by silica gel column chromatography (PE/EA = 10/1), the desired product **6** was obtained in 90% yield (44.7 mg) as a yellow oil;

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.94 (d, *J* = 8.5 Hz, 2H), 7.55 (t, *J* = 7.4 Hz, 1H), 7.45 (t, *J* = 7.6 Hz, 2H), 4.12 (q, *J* = 7.1 Hz, 2H), 2.97 (t, *J* = 7.3 Hz, 2H), 2.31 (t, *J* = 7.5 Hz, 2H), 1.83 – 1.72 (m, 2H), 1.67 (q, *J* = 7.6 Hz, 2H), 1.45 – 1.38 (m, 2H), 1.24 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 200.3, 173.8, 137.1, 133.1, 128.7, 128.1, 60.4, 38.4, 34.3, 28.9, 24.9, 24.0, 14.4.

HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{15}H_{21}O_3$: 249.1485. Found: 249.1490.



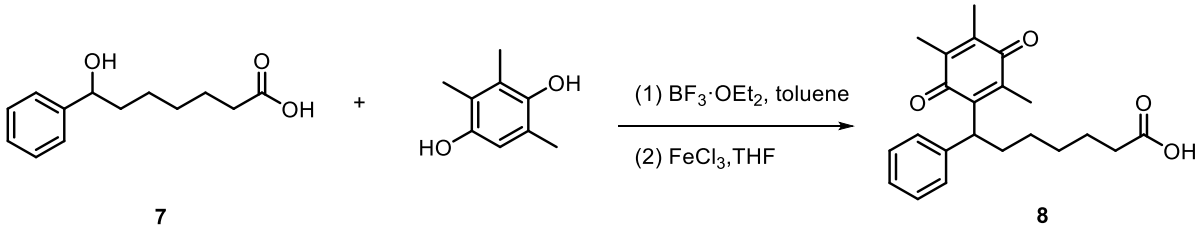
6 **7**

Dissolve **6** in 2 mL of tetrahydrofuran, cool to 0 °C, and add potassium borohydride (4.4 mg, 0.12 mmol, 0.6 equiv.) portionwise over approximately 10 minutes. Continue stirring for 40 minutes, then remove methanol by evaporation. Add 15 mL of water and extract with 10 mL of ethyl acetate. Wash the extract with hydrochloric acid, dry, and evaporate the solvent to obtain a yellow oily substance， then add 2 mL of tetrahydrofuran and 2 mL of 2.5 N sodium hydroxide, then stir the mixture at 70 °C for 3 hours. Cool to room temperature, add 2 mL of isopropyl ether, and extract the aqueous layer. Adjust the pH of the aqueous layer to 3-4 using 4 N HCl, then extract again with 10 mL of ethyl acetate. Wash the extract sequentially with water and brine, dry, and evaporate the solvent. After purification by silica gel column chromatography (PE/EA = 8/1), the desired product **7** was obtained in 88% yield (39.1 mg) as a yellow oil;

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.39 – 7.26 (m, 5H), 6.39 (s, 1H), 4.71 – 4.62 (m, 1H), 2.32 (t, J = 7.4 Hz, 2H), 1.85 – 1.68 (m, 2H), 1.67 – 1.57 (m, 2H), 1.35 (ddt, J = 18.7, 12.4, 6.5 Hz, 4H).

^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 179.6, 144.8, 128.6, 127.7, 126.0, 77.5, 76.8, 74.7, 38.9, 34.02, 29.0, 25.5, 24.7.

HRMS (ESI): m/z $[M+Na]^+$ calcd for $C_{13}H_{18}O_3Na$: 245.1148. Found: 245.1144.



7 **8**

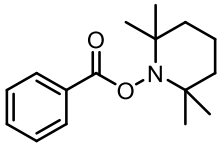
Boron trifluoride diethyl etherate (8.46 mg, 0.06 mmol, 0.3 equiv.) dropwise at 60 °C to a solution containing of **7** (44.4 mg, 0.2 mmol, 1.0 equiv.) and 2,3,5-trimethylhydroquinone (30.4 mg, 0.20 mmol, 1.0 equiv.), and 2 mL of toluene. Continue stirring the reaction at 60 °C for 2 hours. Remove the toluene under reduced pressure, and dissolve the residue in 2 mL of

tetrahydrofuran. Add 1 mL of 1.5 N ferric chloride solution at room temperature, stir for 30 minutes, then remove THF under reduced pressure. Extract the residual liquid with 10 mL of ethyl acetate. Wash the organic layer sequentially with saturated brine and water, dry, filter, and rinse with ethyl acetate. Remove the ethyl acetate by evaporation, after purification by silica gel column chromatography (PE/EA =2/1), the desired product **8** was obtained in 75% yield (52.2 mg) as a yellow solid;

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.32 – 7.25 (m, 4H), 7.23 – 7.16 (m, 1H), 4.31 (dd, J = 8.9, 6.7 Hz, 1H), 2.35 (t, J = 7.4 Hz, 2H), 2.28 – 2.11 (m, 2H), 2.08 (s, 3H), 2.02 (q, J = 1.2 Hz, 3H), 1.99 (q, J = 1.2 Hz, 3H), 1.65 (p, J = 7.5 Hz, 2H), 1.49 – 1.20 (m, 4H);

^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 188.1, 187.2, 179.0, 145.9, 142.4, 141.6, 141.0, 140.4, 128.7, 128.4, 128.0, 126.3, 125.8, 43.6, 33.9, 31.7, 29.3, 28.2, 24.7, 12.7.

HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{22}H_{27}O_4$: 355.1904. Found: 355.1905.



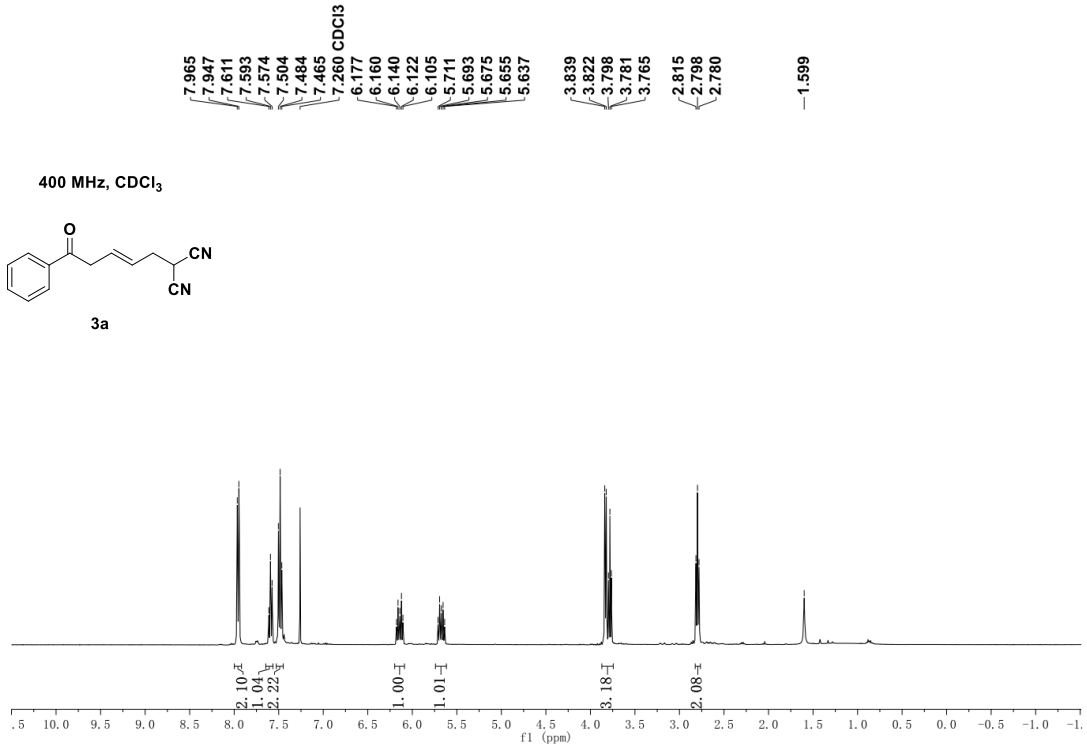
9 prepared according to General Procedure from vinylcyclopropane (23.6 mg, 0.20 mmol, 1.0 equiv.), α-keto acid (45.0 mg, 0.30 mmol, 1.5 equiv.) and TEMPO (46.9 mg, 0.30 mmol, 1.5 equiv.) in DCE (2.0 mL). The reaction mixture was allowed to stir at room temperature under blue LEDs irradiation for 16 hours. After purification by silica gel column chromatography (PE/EA = 5/1), the desired product was obtained in 73% yield (38.2 mg) as a white solid;

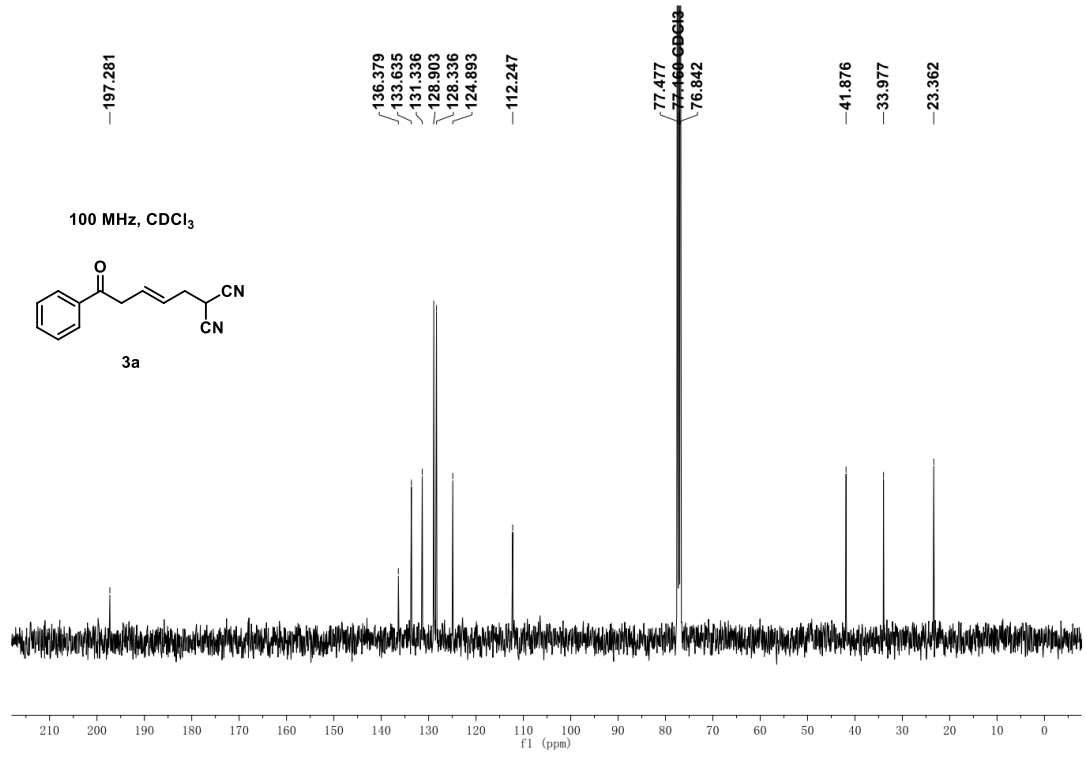
^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.08 (d, J = 7.6 Hz, 2H), 7.58 (t, J = 7.4 Hz, 1H), 7.46 (t, J = 7.7 Hz, 2H), 1.82 – 1.67 (m, 3H), 1.59 (d, J = 12.4 Hz, 3H), 1.28 (s, 6H), 1.12 (s, 6H).

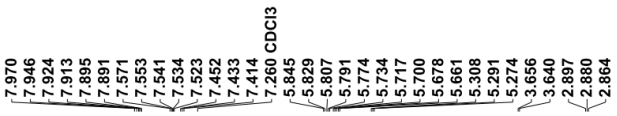
^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 133.0, 129.7, 128.6, 77.5, 76.8, 60.6, 39.2, 32.1, 21.0, 17.2.

HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{16}H_{24}NO_2$: 262.1802. Found: 262.1802.

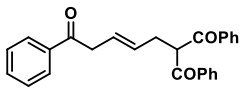
VI. NMR Spectra



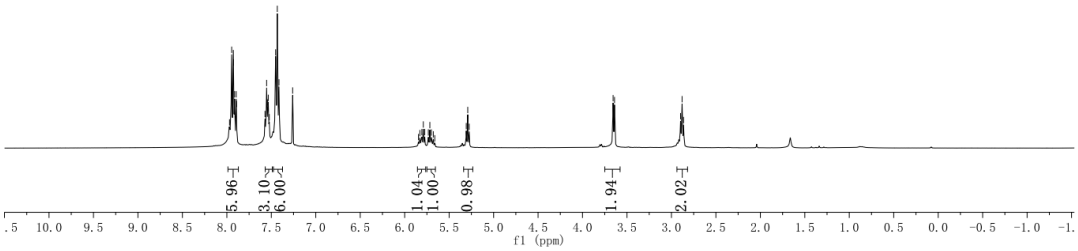


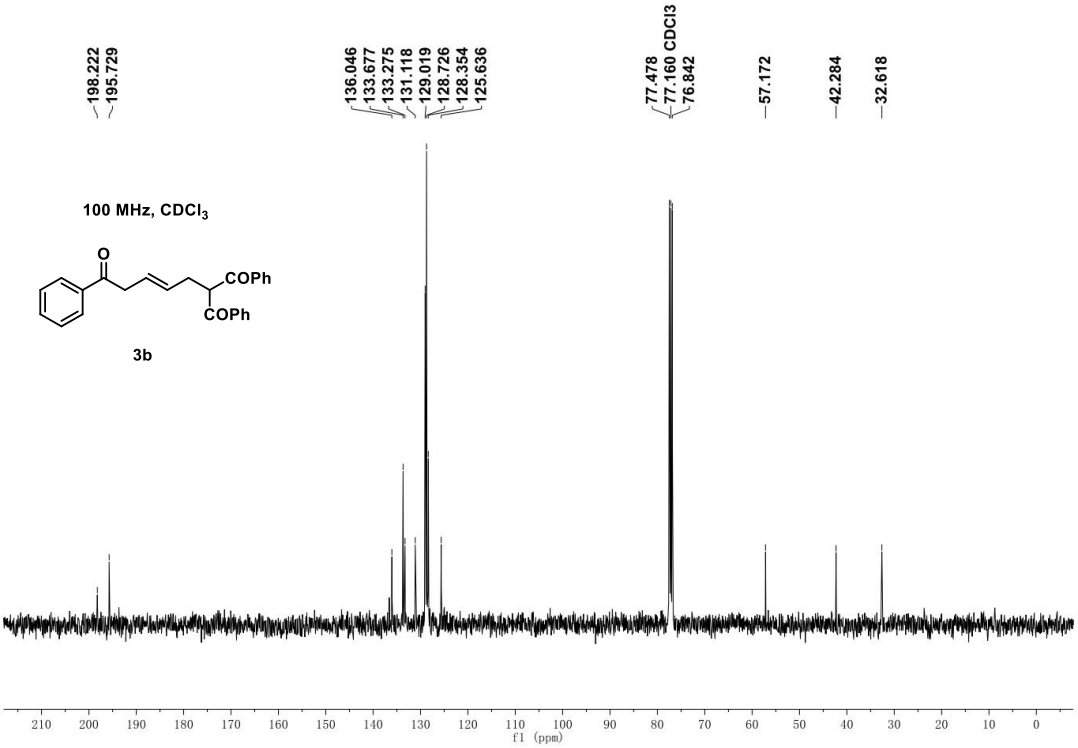


400 MHz, $CDCl_3$



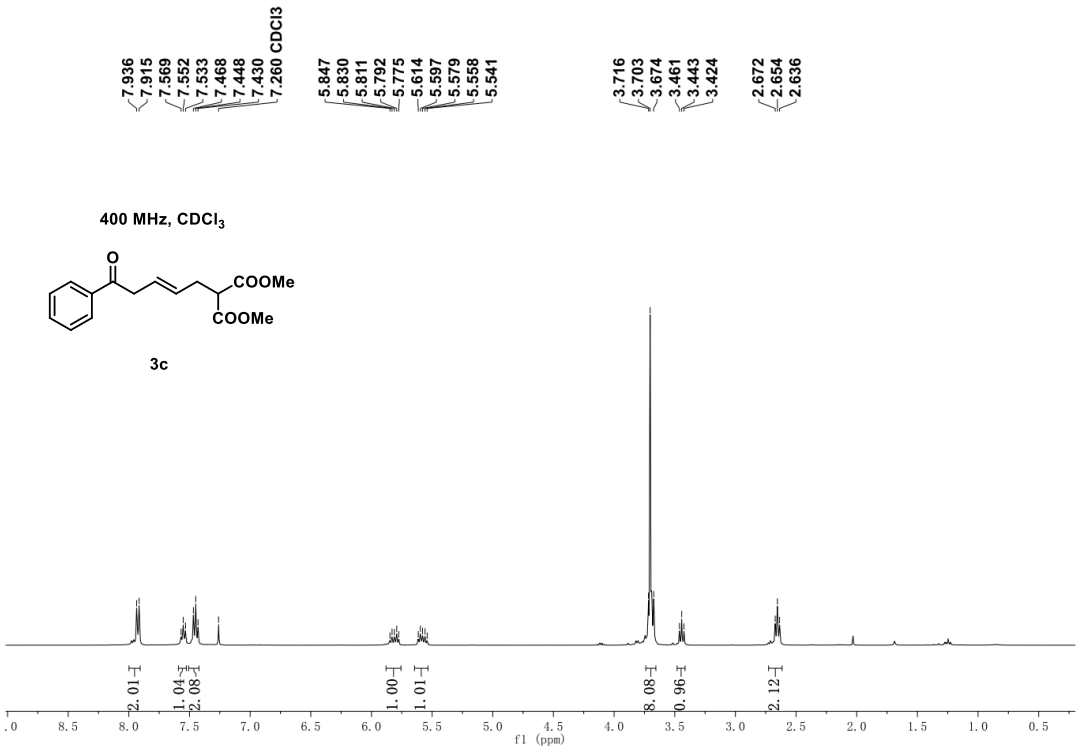
3b

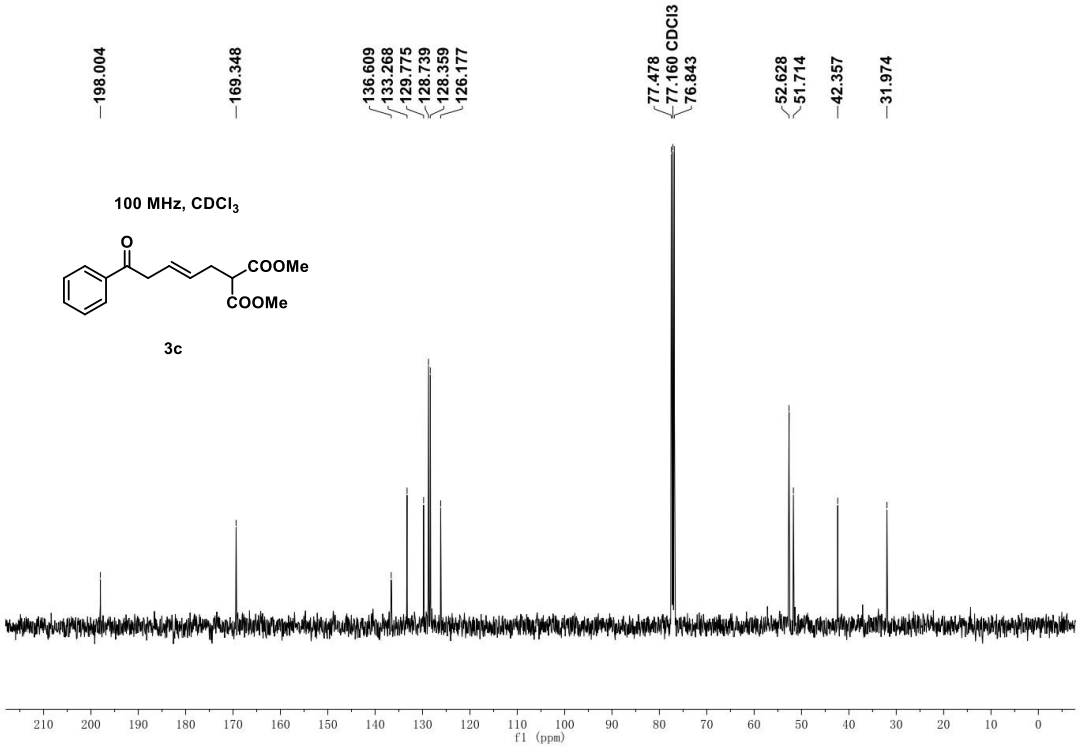




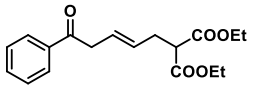
100 MHz, $CDCl_3$

3b

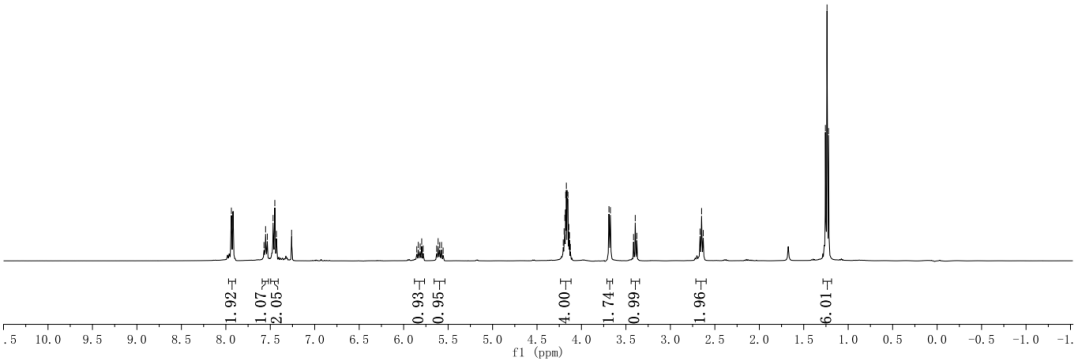

7.936
7.915
7.569
7.552
7.533
7.468
7.448
7.430
7.260 CDCl3
5.847
5.830
5.811
5.792
5.775
5.614
5.597
5.579
5.558
5.541
3.716
3.703
3.674
3.461
3.443
3.424
2.672
2.654
2.636
400 MHz, CDCl3
O
COOMe
COOMe
3c
2.01
1.04
2.08
1.00
1.01
8.08
0.96
2.12
f1 (ppm)

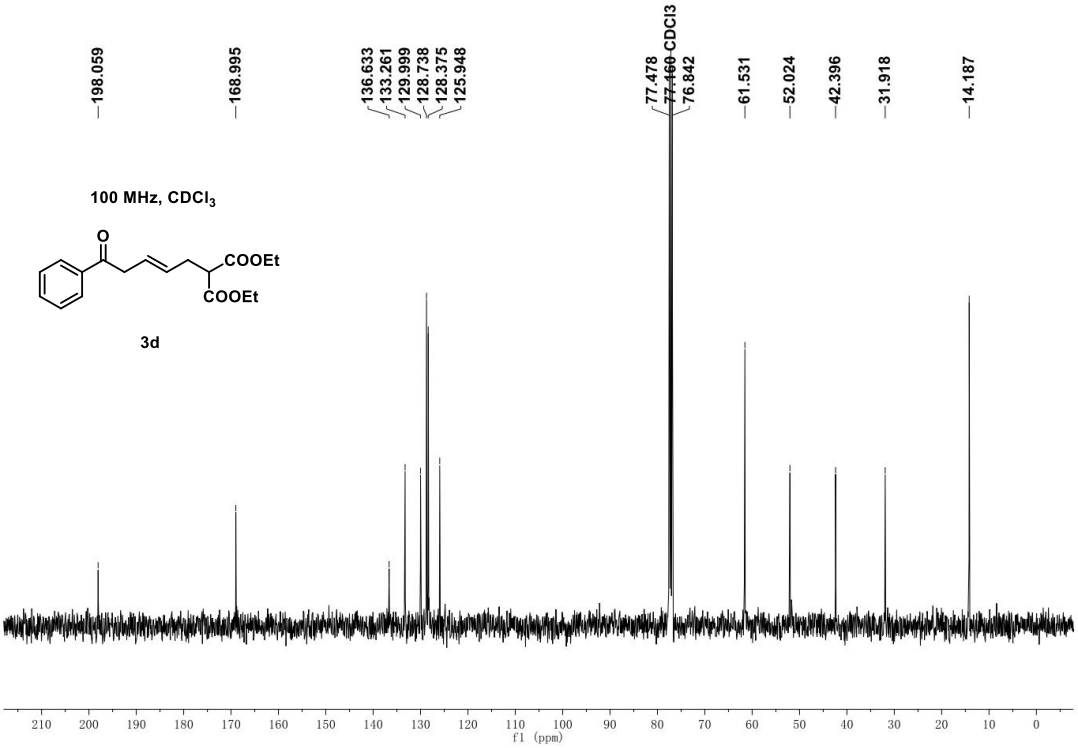

198.004
169.348
136.609
133.268
129.775
128.739
128.359
126.177
77.478
77.160 CDCl3
76.843
52.628
51.714
42.357
31.974
100 MHz, CDCl3
O
COOMe
COOMe
3c
f1 (ppm)

400 MHz, $CDCl_3$



3d

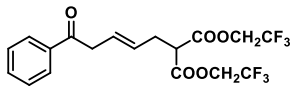




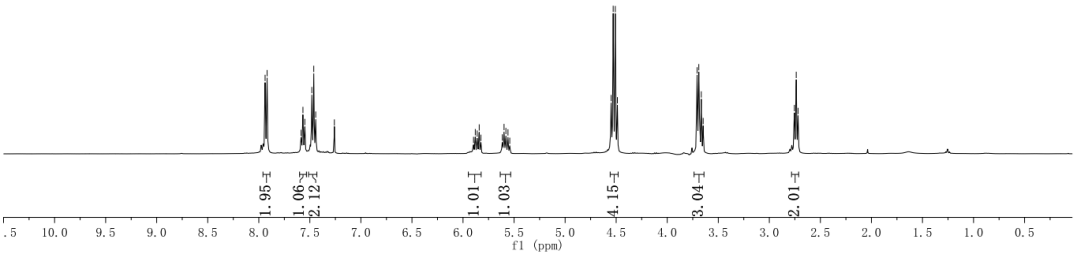
100 MHz, $CDCl_3$

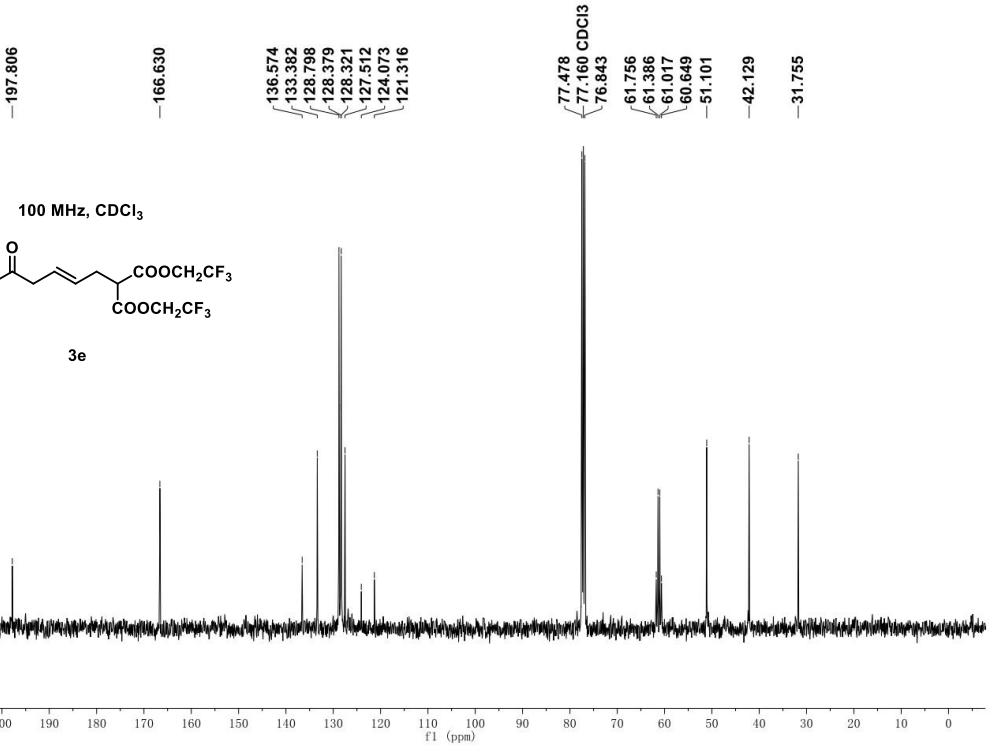
3d

400 MHz, $CDCl_3$



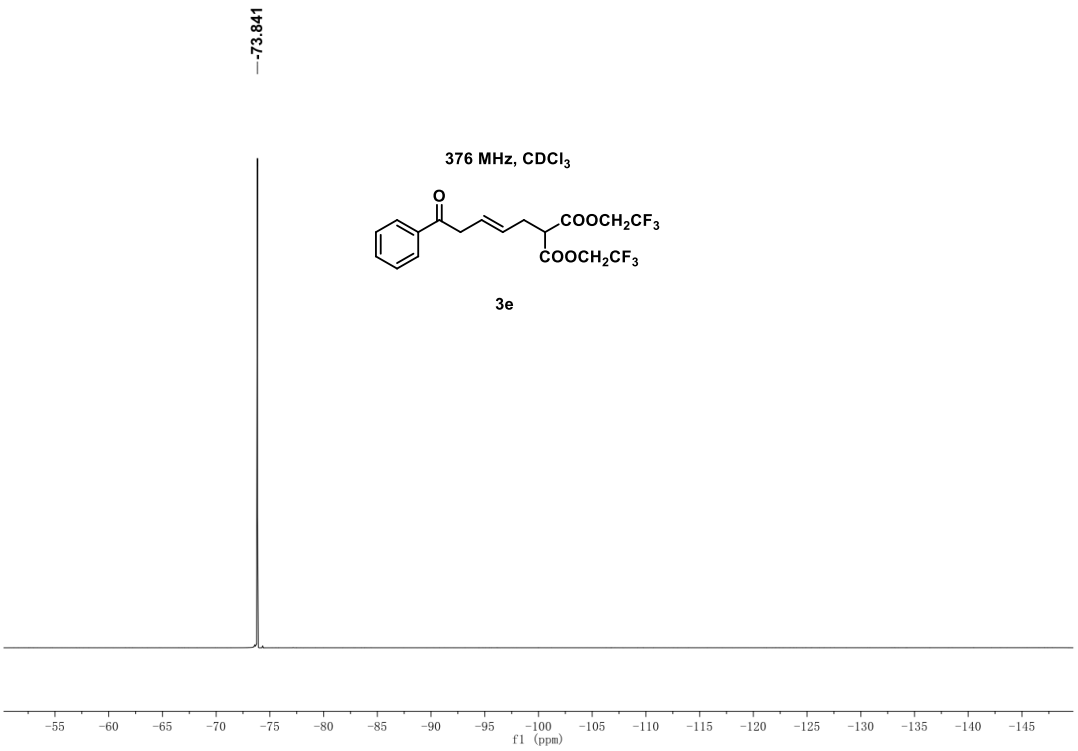
3e

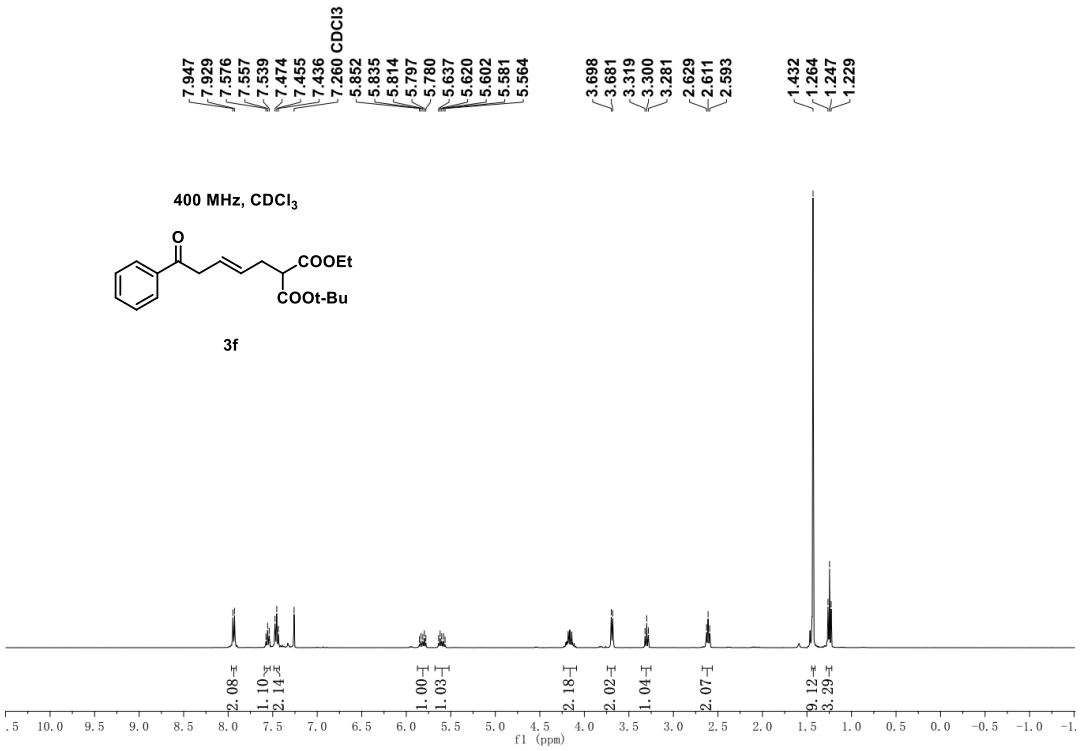


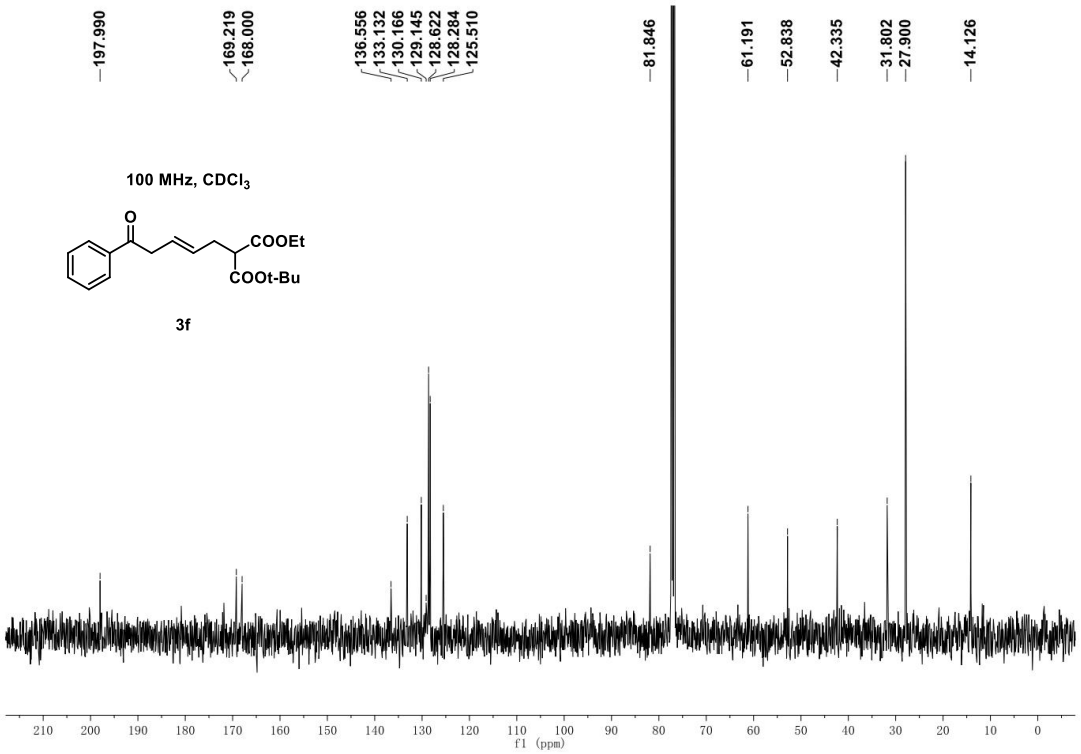


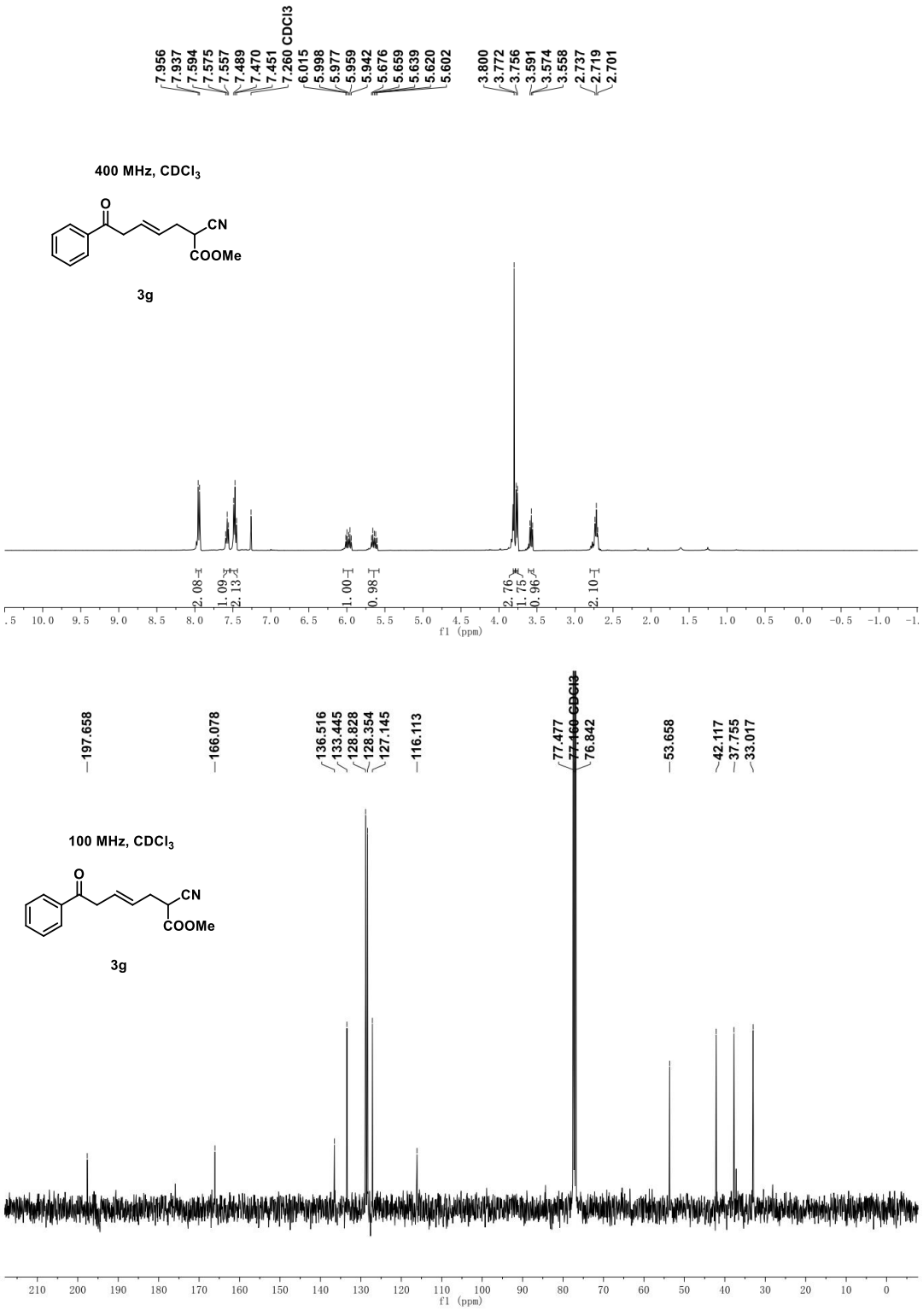
100 MHz, $CDCl_3$

3e

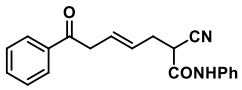

-73.841
376 MHz, CDCl3
O
COOCH2CF3
COOCH2CF3
3e
−55 −60 −65 −70 −75 −80 −85 −90 −95 −100 −105 −110 −115 −120 −125 −130 −135 −140 −145
f1 (ppm)


7.947
7.929
7.576
7.557
7.539
7.474
7.455
7.436
7.260 CDCl3
5.852
5.835
5.814
5.797
5.780
5.637
5.620
5.602
5.581
5.564
3.698
3.681
3.319
3.300
3.281
2.629
2.611
2.593
1.432
1.264
1.247
1.229
400 MHz, CDCl3
O
COOEt
COOt-Bu
3f
2.08
1.10
2.14
1.00
1.03
2.18
2.02
1.04
2.07
9.12
3.29
f1 (ppm)

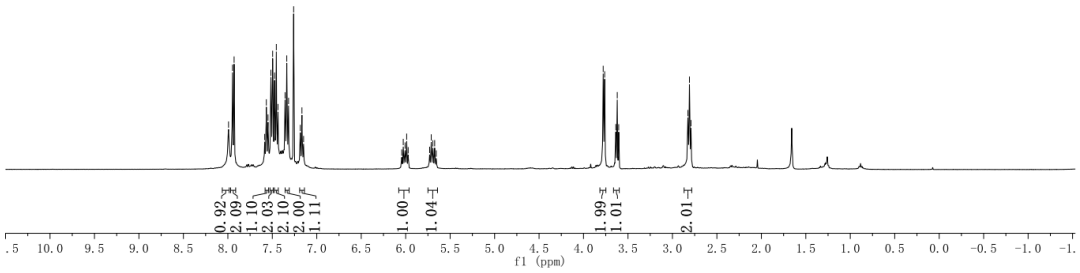

197.990
169.219
168.000
136.556
133.132
130.166
129.145
128.622
128.284
125.510
81.846
61.191
52.838
42.335
31.802
27.900
14.126
100 MHz, CDCl3
O
COOEt
COOt-Bu
3f
f1 (ppm)

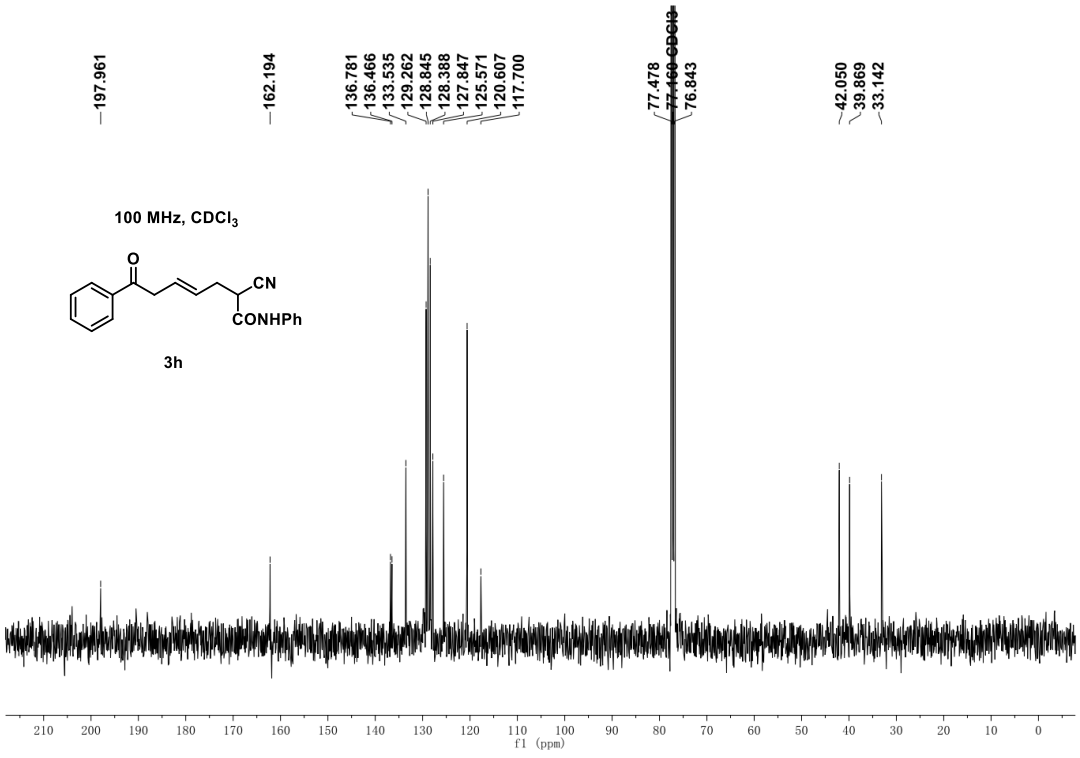

7.956
7.937
7.594
7.575
7.557
7.489
7.470
7.451
7.260 CDCl3
6.015
5.998
5.977
5.959
5.942
5.676
5.659
5.639
5.620
5.602
3.800
3.772
3.756
3.591
3.574
3.558
2.737
2.719
2.701
400 MHz, CDCl3
O
CN
COOMe
3g
2.08
1.09
2.13
1.00
0.98
2.76
1.75
0.96
2.10
f1 (ppm)
197.658
166.078
136.516
133.445
128.828
128.354
127.145
116.113
77.477
77.160 CDCl3
76.842
53.658
42.117
37.755
33.017
100 MHz, CDCl3
O
CN
COOMe
3g
f1 (ppm)

400 MHz, $CDCl_3$



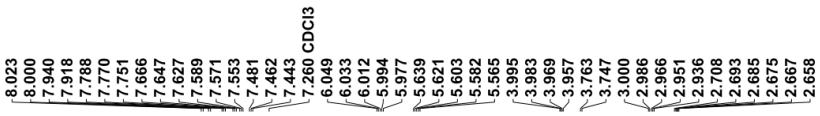
3h



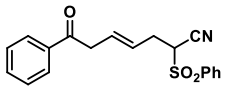


100 MHz, $CDCl_3$

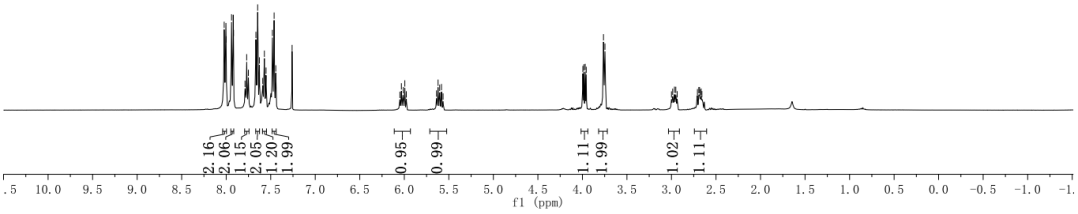
3h

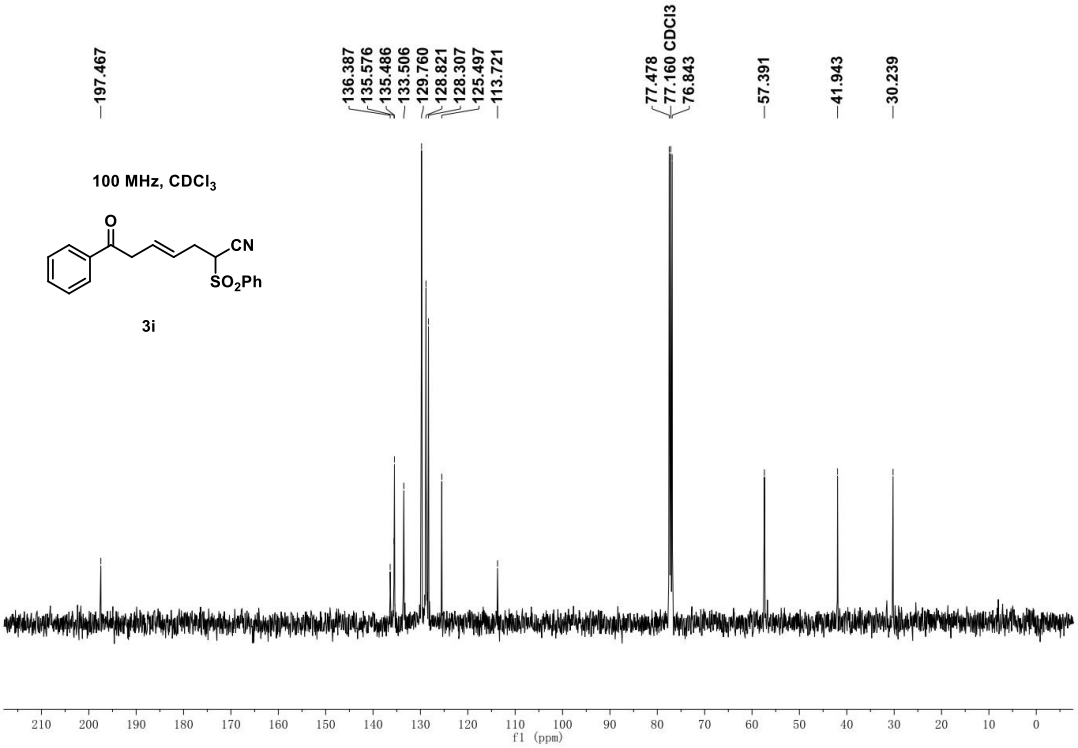


400 MHz, $CDCl_3$



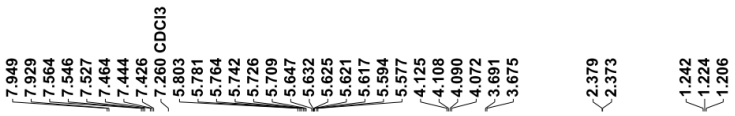
3i



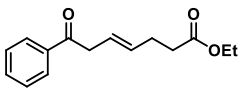


100 MHz, $CDCl_3$

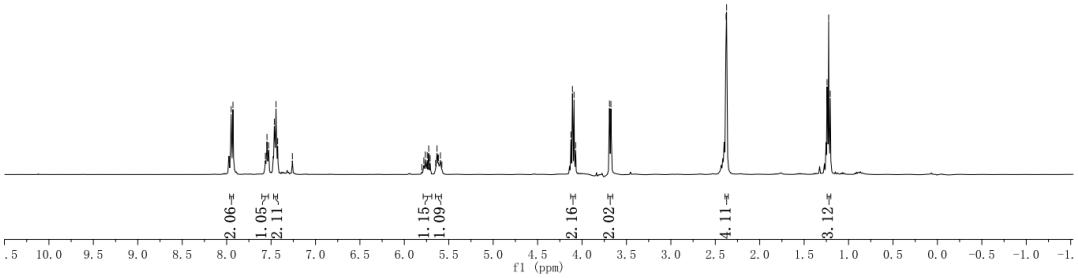
3i

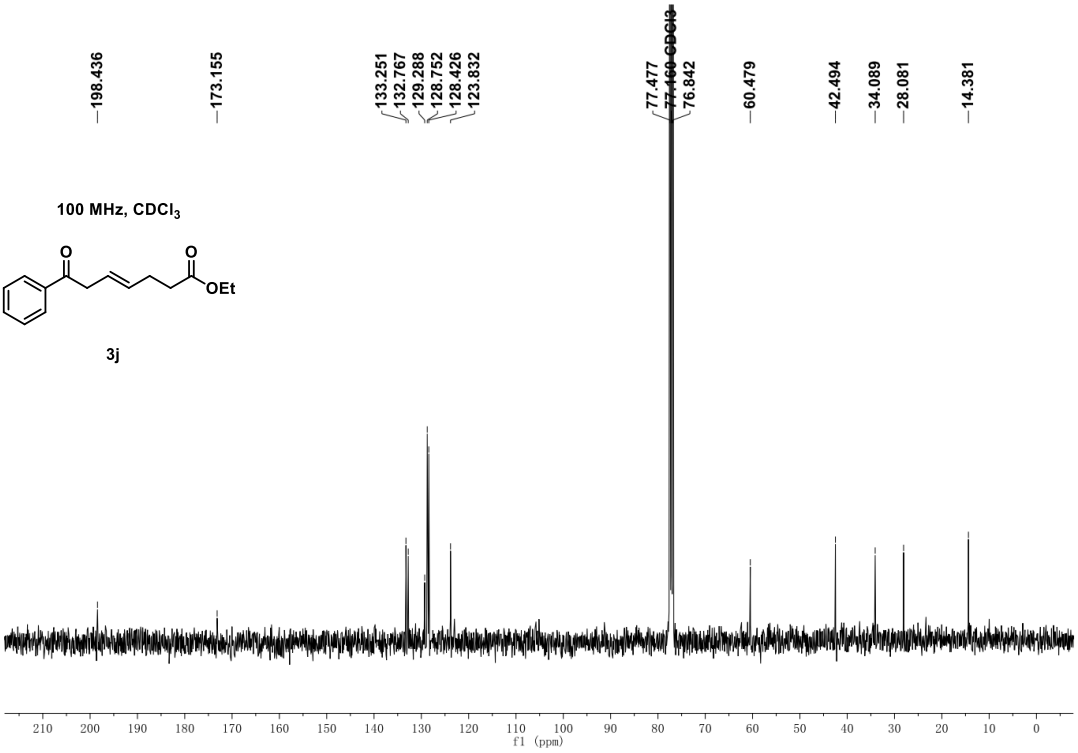


400 MHz, $CDCl_3$



3j

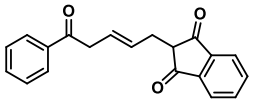




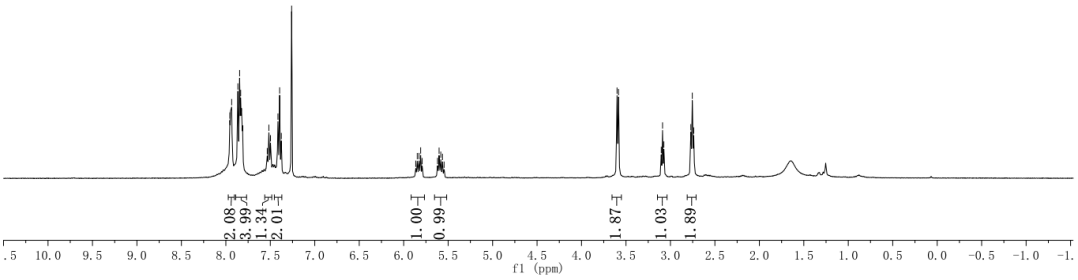
100 MHz, $CDCl_3$

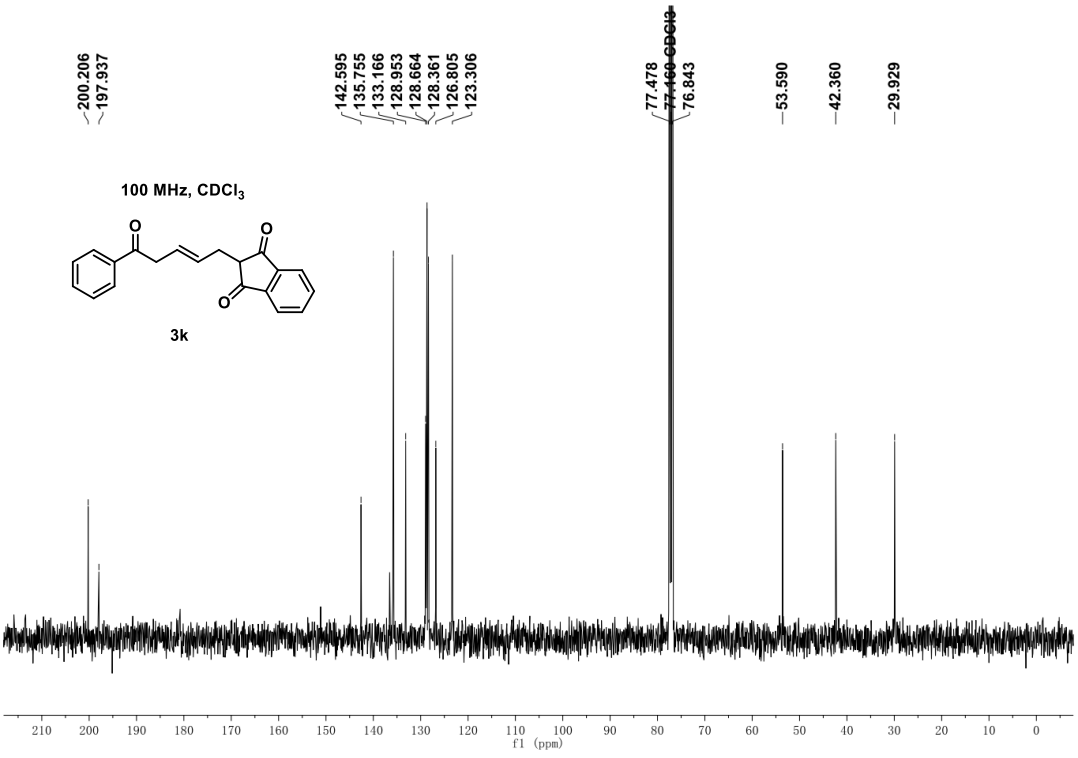
3j

400 MHz, $CDCl_3$



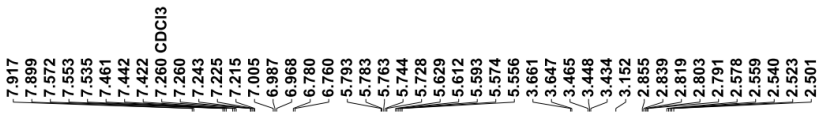
3k

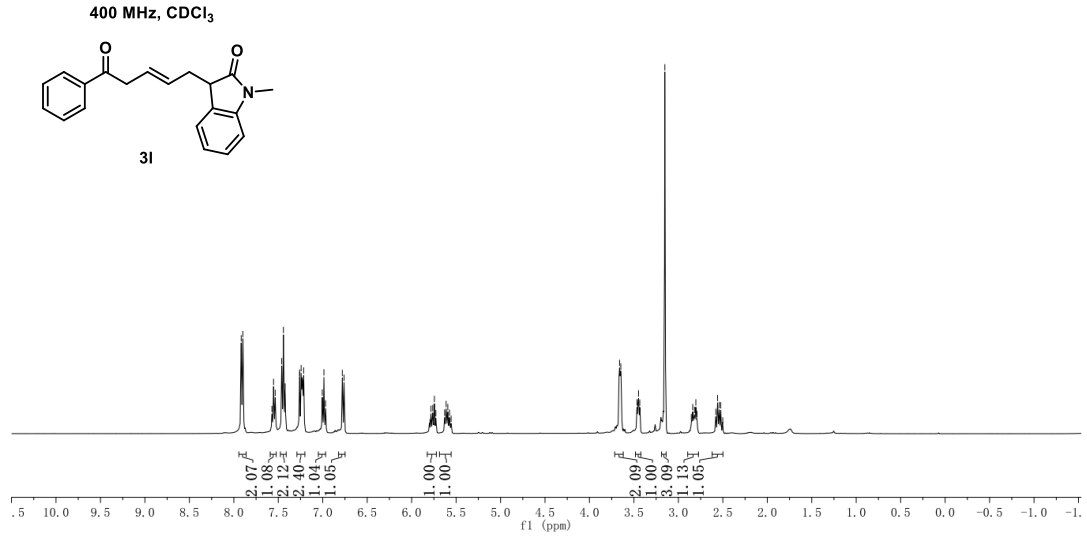


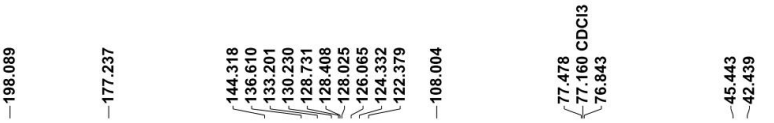


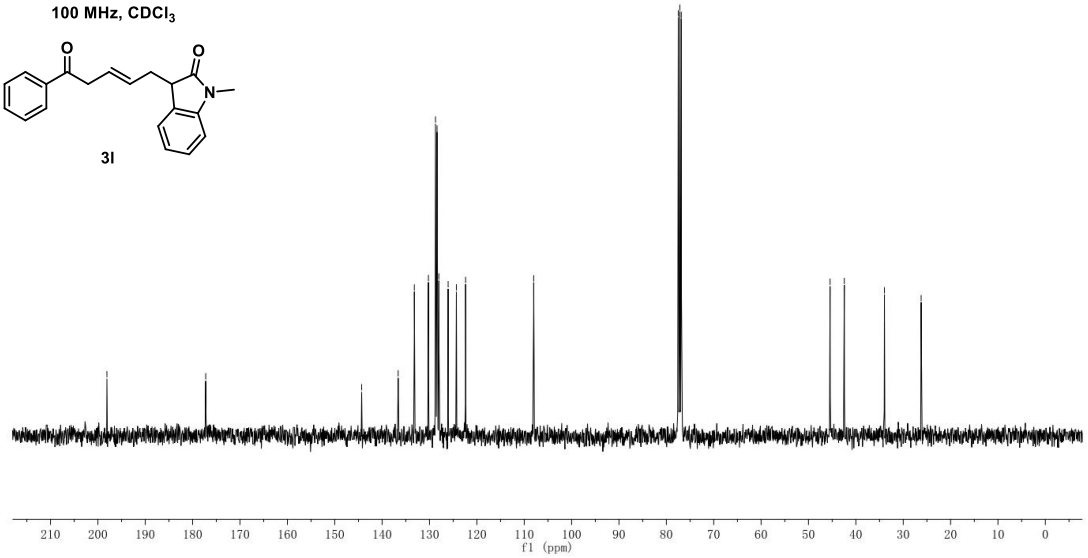
100 MHz, $CDCl_3$

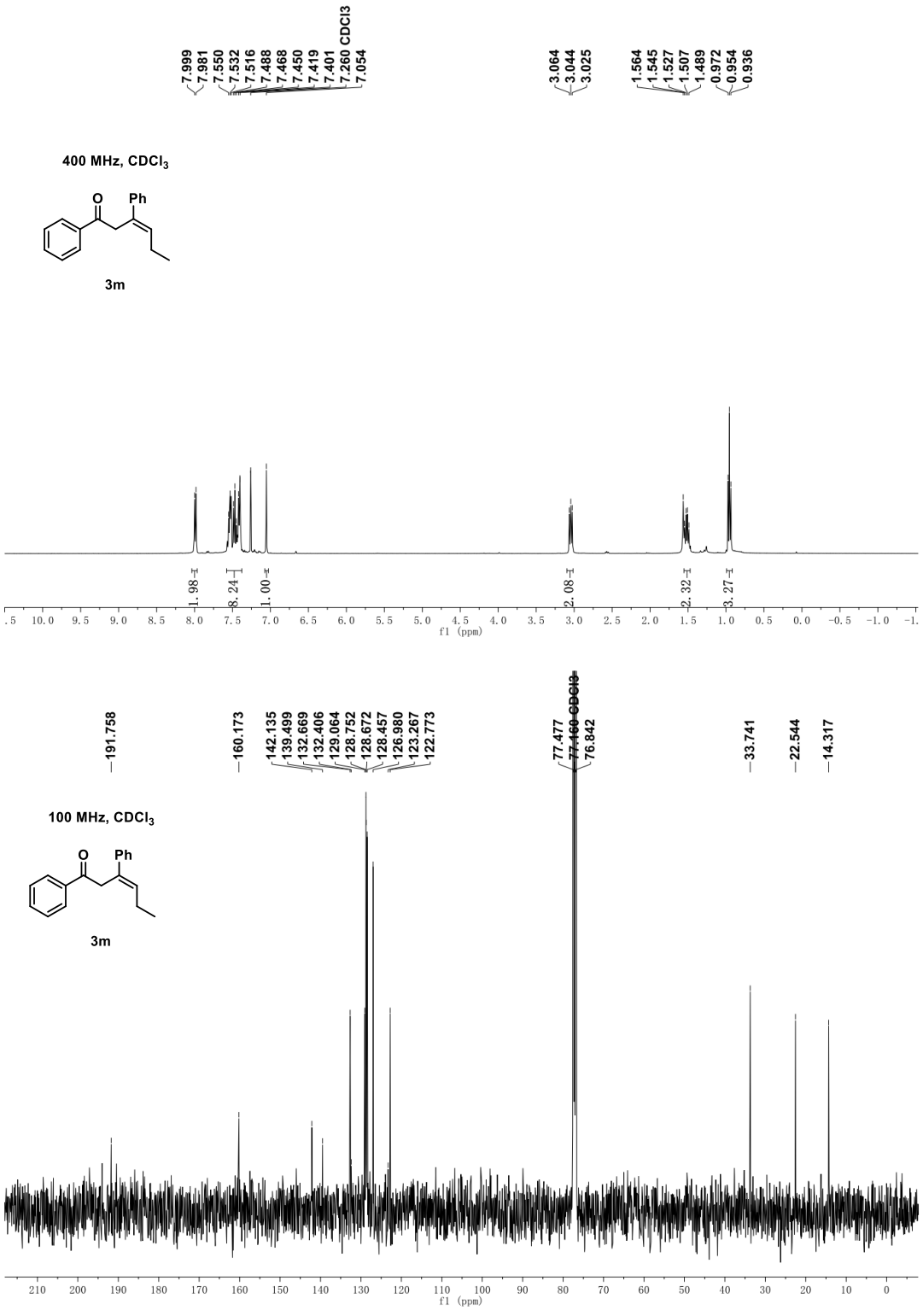
3k

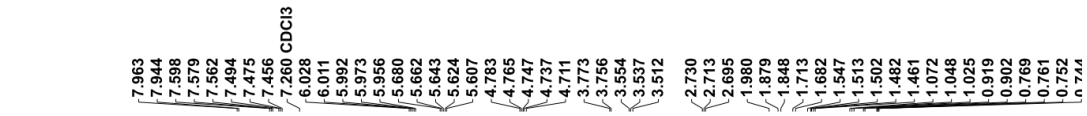

7.917
7.899
7.572
7.553
7.535
7.461
7.442
7.422
7.260 CDCl3
7.260
7.243
7.225
7.215
7.005
6.987
6.968
6.780
6.760
5.793
5.783
5.763
5.744
5.728
5.629
5.612
5.593
5.574
5.556
3.661
3.647
3.465
3.448
3.434
3.152
2.855
2.839
2.819
2.803
2.791
2.578
2.559
2.540
2.523
2.501


400 MHz, CDCl3
3l
2.07
1.08
2.12
2.40
1.04
1.05
1.00
1.00
2.09
1.00
3.09
1.13
1.05
f1 (ppm)

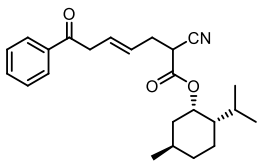

198.089
177.237
144.318
136.610
133.201
130.230
128.731
128.408
128.025
126.065
124.332
122.379
108.004
77.478
77.160 CDCl3
76.843
45.443
42.439
33.966
26.217


100 MHz, CDCl3
3l
f1 (ppm)

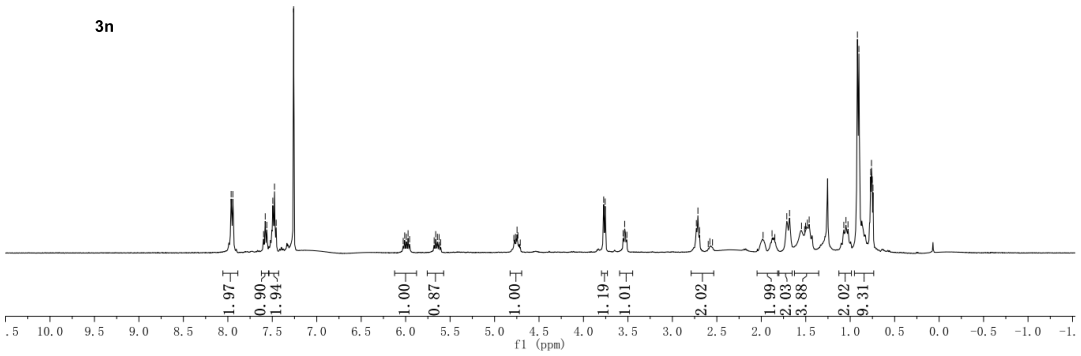

7.999
7.981
7.550
7.532
7.516
7.488
7.468
7.450
7.419
7.401
7.260 CDCl3
7.054
3.064
3.044
3.025
1.564
1.545
1.527
1.507
1.489
0.972
0.954
0.936
400 MHz, CDCl3
O
Ph
3m
1.98
8.24
1.00
2.08
2.32
3.27
f1 (ppm)
191.758
160.173
142.135
139.499
132.669
132.406
129.064
128.752
128.672
128.457
126.980
123.267
122.773
77.477
77.160 CDCl3
76.842
33.741
22.544
14.317
100 MHz, CDCl3
O
Ph
3m
f1 (ppm)

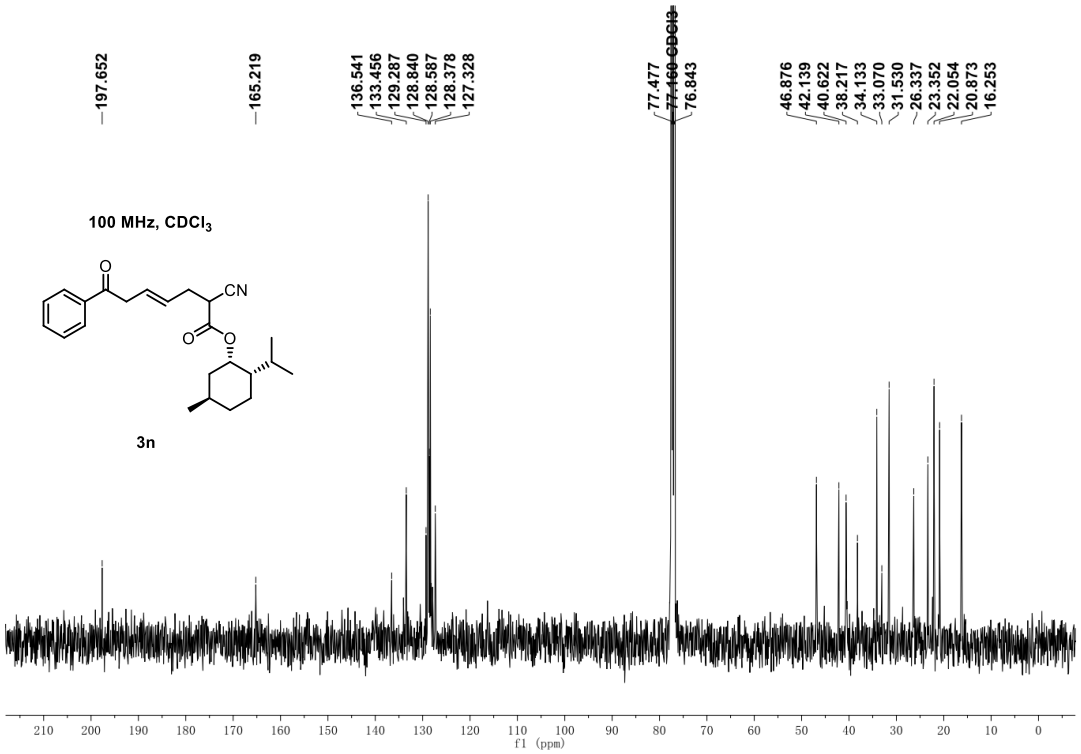


400 MHz, $CDCl_3$



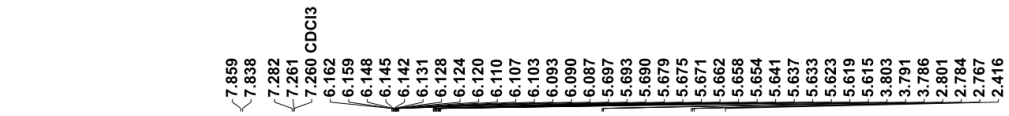
3n



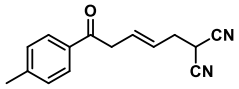


100 MHz, $CDCl_3$

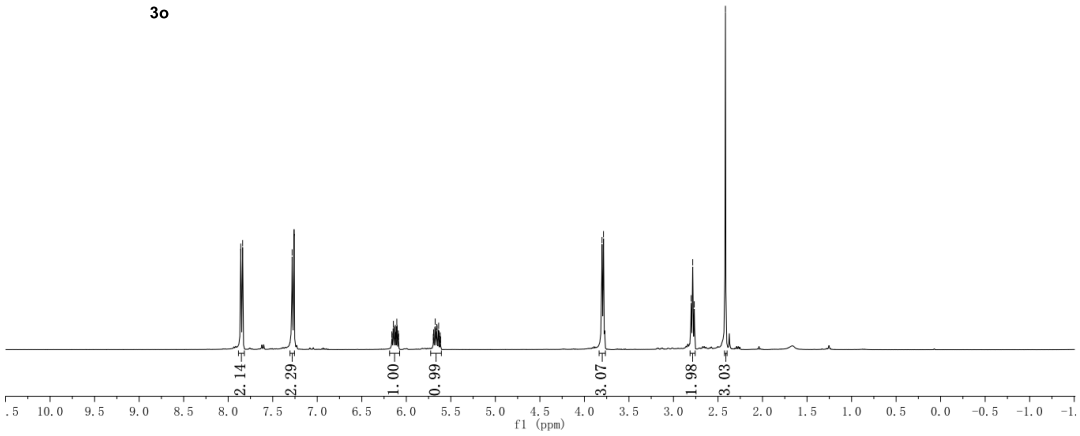
3n

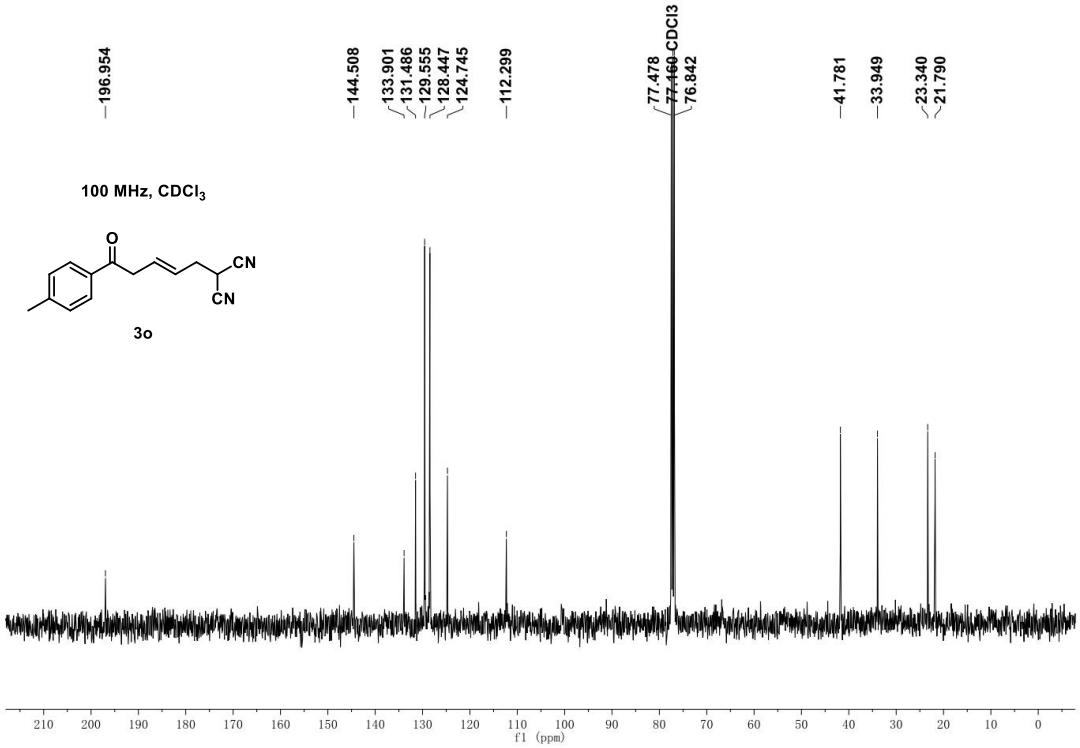


400 MHz, $CDCl_3$



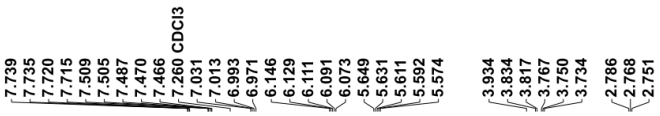
3o



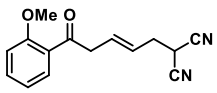


100 MHz, $CDCl_3$

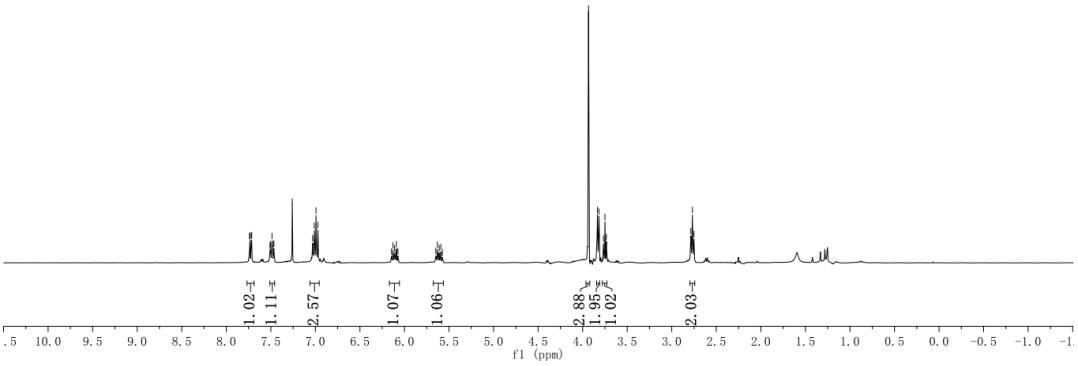
3o

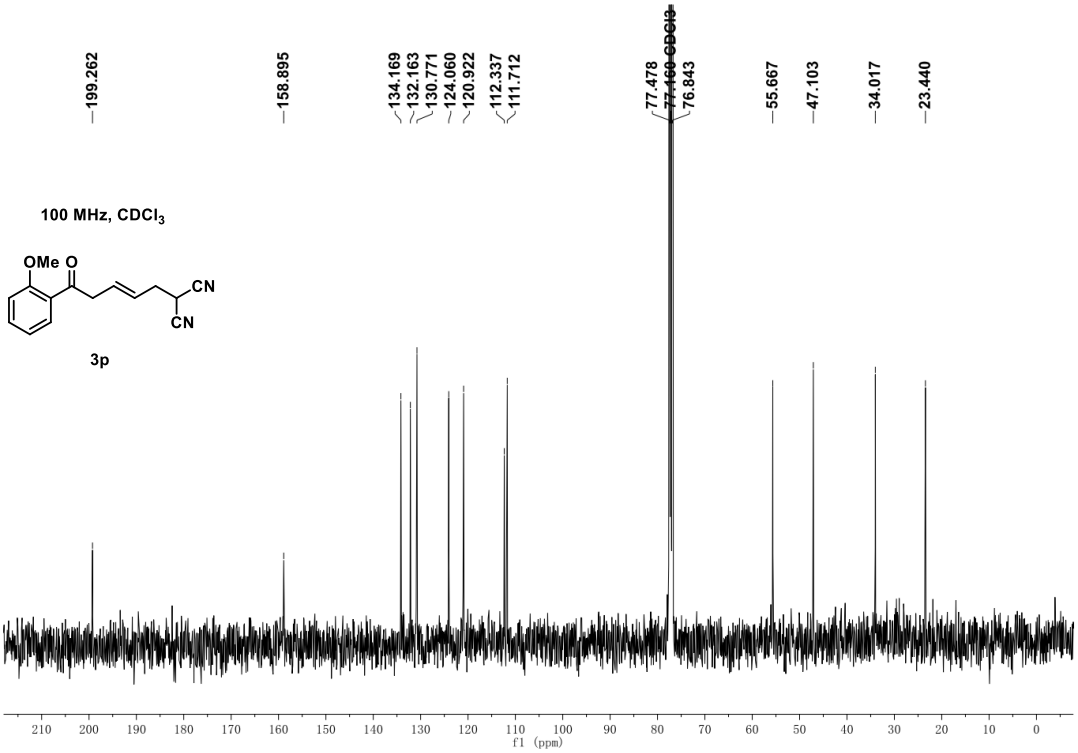


400 MHz, $CDCl_3$



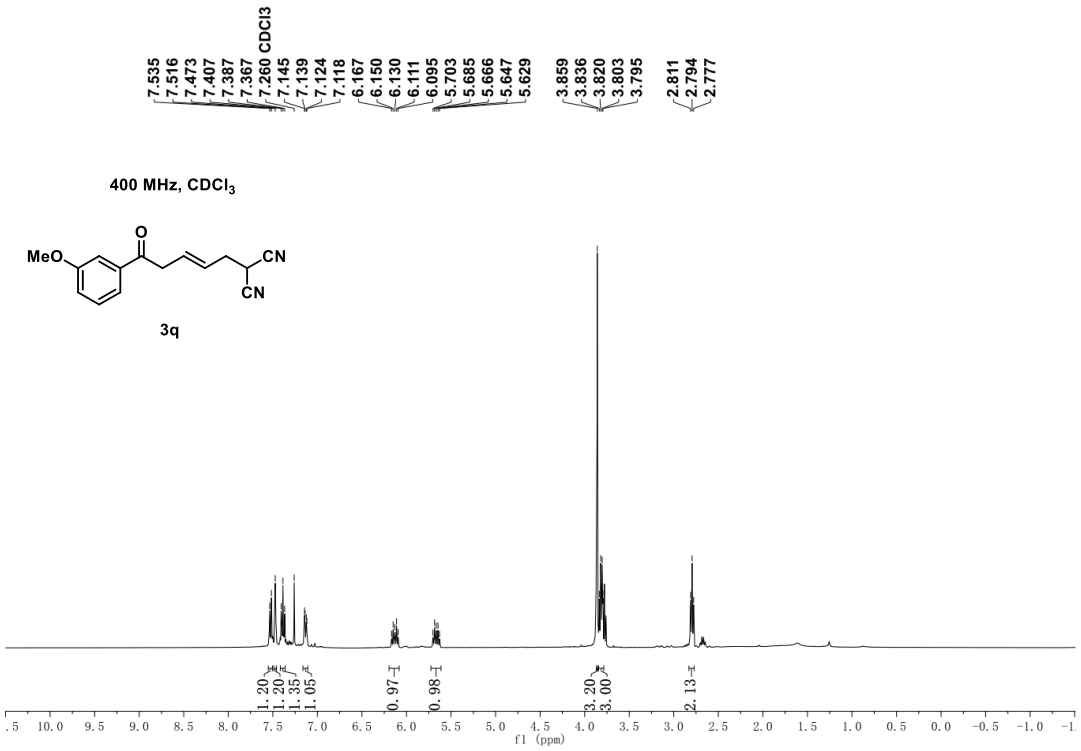
3p

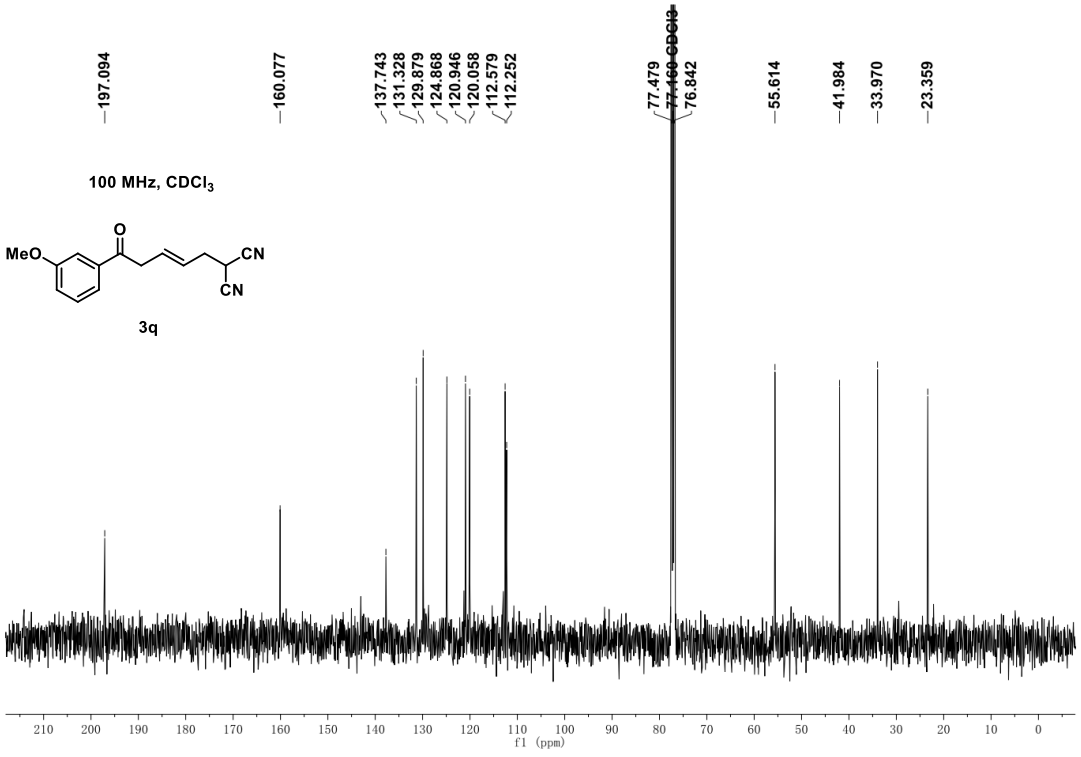


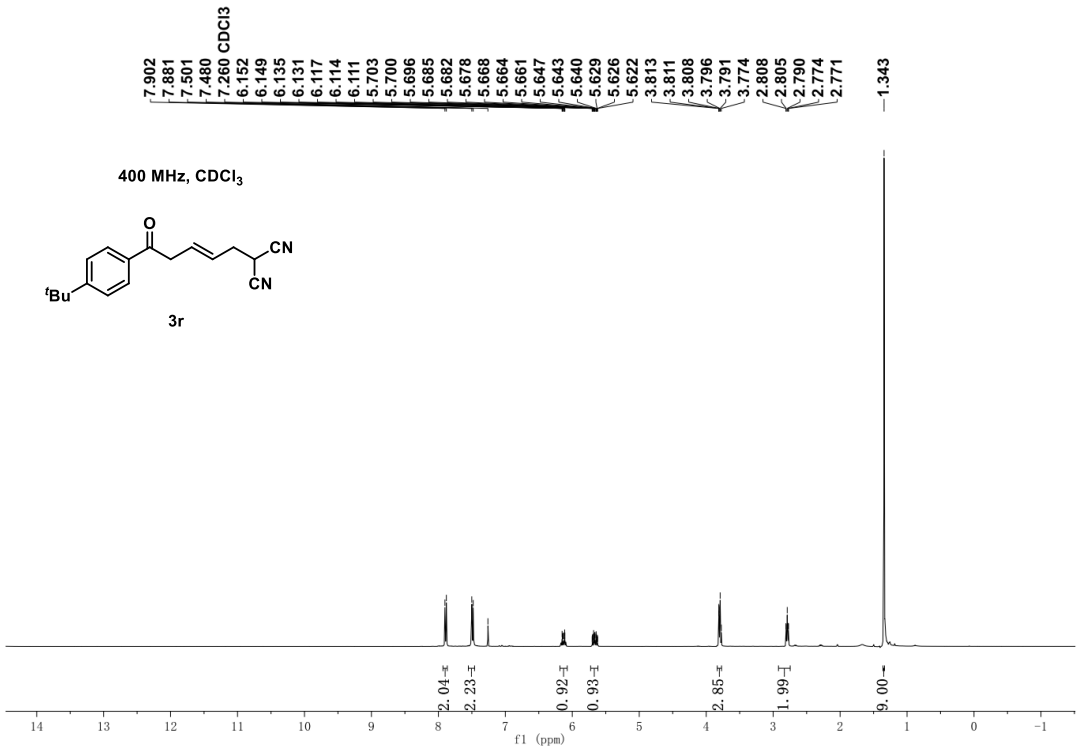


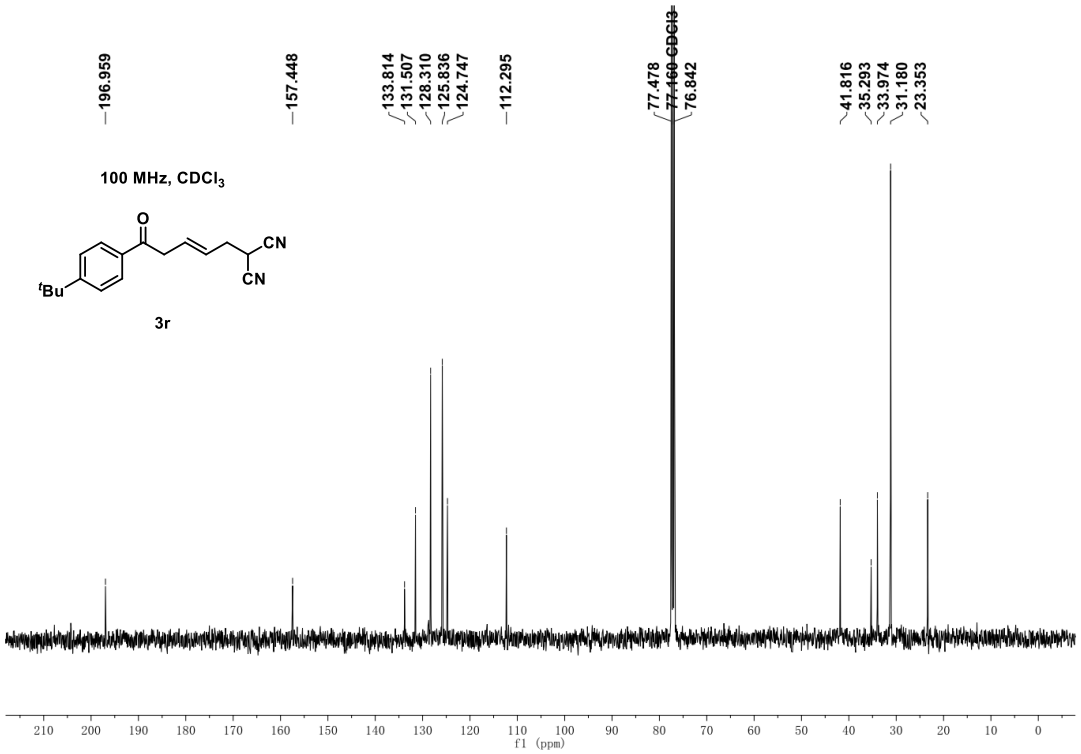
100 MHz, $CDCl_3$

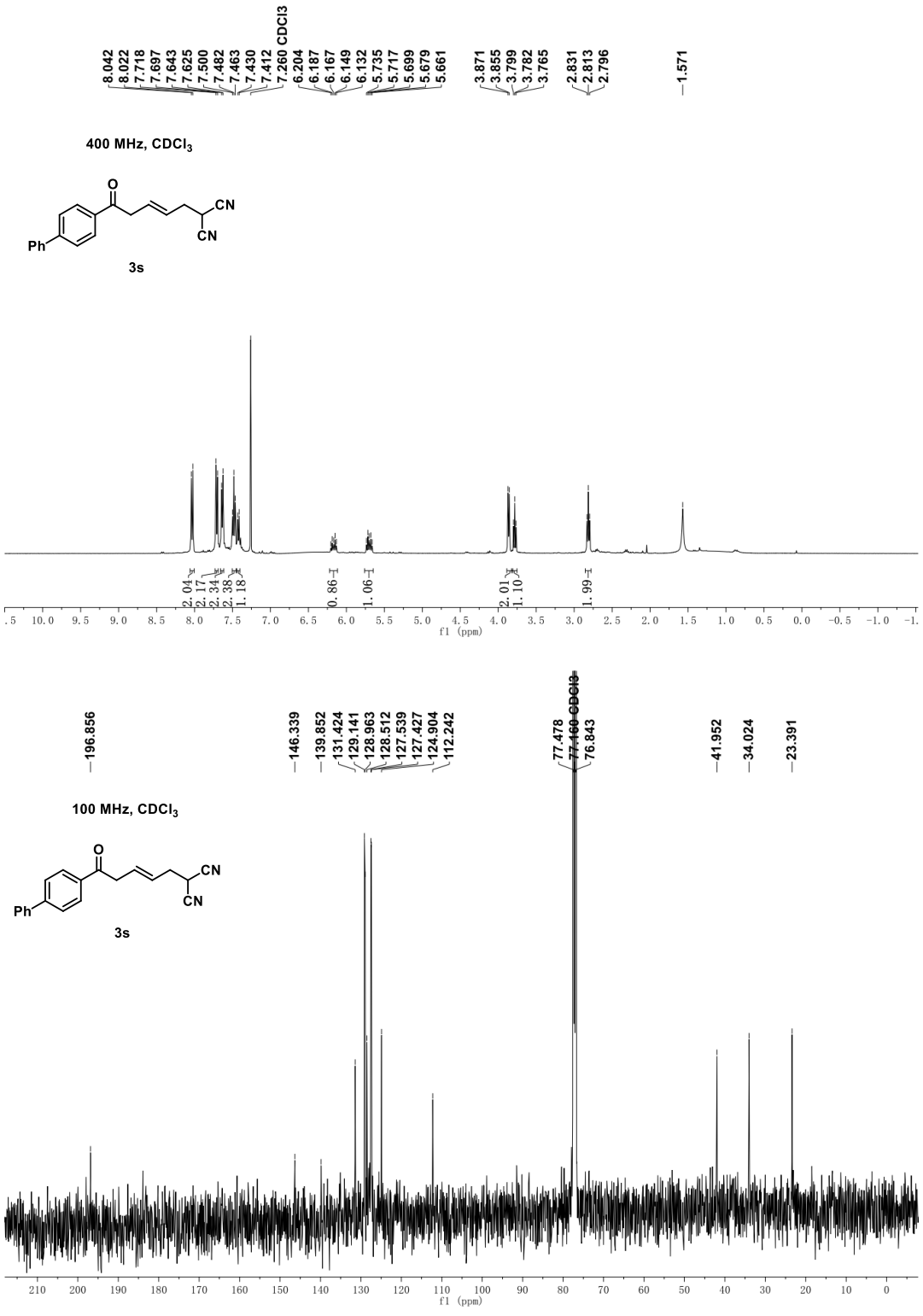
3p

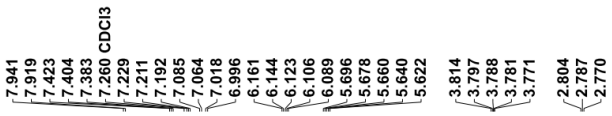

7.535
7.516
7.473
7.407
7.387
7.367
7.260 CDCl3
7.145
7.139
7.124
7.118
6.167
6.150
6.130
6.111
6.095
5.703
5.685
5.666
5.647
5.629
3.859
3.836
3.820
3.803
3.795
2.811
2.794
2.777
400 MHz, CDCl3
MeO
O
CN
CN
3q
1.20
1.20
1.35
1.05
0.97
0.98
3.20
3.00
2.13
f1 (ppm)


197.094
160.077
137.743
131.328
129.879
124.868
120.946
120.058
112.579
112.252
77.479
77.160 CDCl3
76.842
55.614
41.984
33.970
23.359
100 MHz, CDCl3
MeO
O
CN
CN
3q
f1 (ppm)

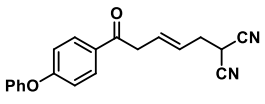

7.902
7.881
7.501
7.480
7.260 CDCl3
6.152
6.149
6.135
6.131
6.117
6.114
6.111
5.703
5.700
5.696
5.685
5.682
5.678
5.668
5.664
5.661
5.647
5.643
5.640
5.629
5.626
5.622
3.813
3.811
3.808
3.796
3.791
3.774
2.808
2.805
2.790
2.774
2.771
1.343
400 MHz, CDCl3
O
CN
CN
tBu
3r
2.04
2.23
0.92
0.93
2.85
1.99
9.00
14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 −1
f1 (ppm)


196.959
157.448
133.814
131.507
128.310
125.836
124.747
112.295
77.478
77.160 CDCl3
76.842
41.816
35.293
33.974
31.180
23.353
100 MHz, CDCl3
O
CN
CN
tBu
3r
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

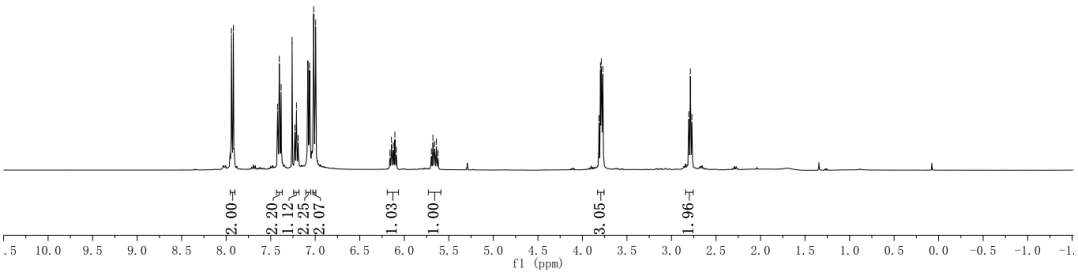

8.042
8.022
7.718
7.697
7.643
7.625
7.500
7.482
7.463
7.430
7.412
7.260 CDCl3
6.204
6.187
6.167
6.149
6.132
5.735
5.717
5.699
5.679
5.661
3.871
3.855
3.799
3.782
3.765
2.831
2.813
2.796
1.571
400 MHz, CDCl3
O
CN
CN
Ph
3s
2.04
2.17
2.34
2.38
1.18
0.86
1.06
2.01
1.10
1.99
f1 (ppm)
196.856
146.339
139.852
131.424
129.141
128.963
128.512
127.539
127.427
124.904
112.242
77.478
77.160 CDCl3
76.843
41.952
34.024
23.391
100 MHz, CDCl3
O
CN
CN
Ph
3s
f1 (ppm)

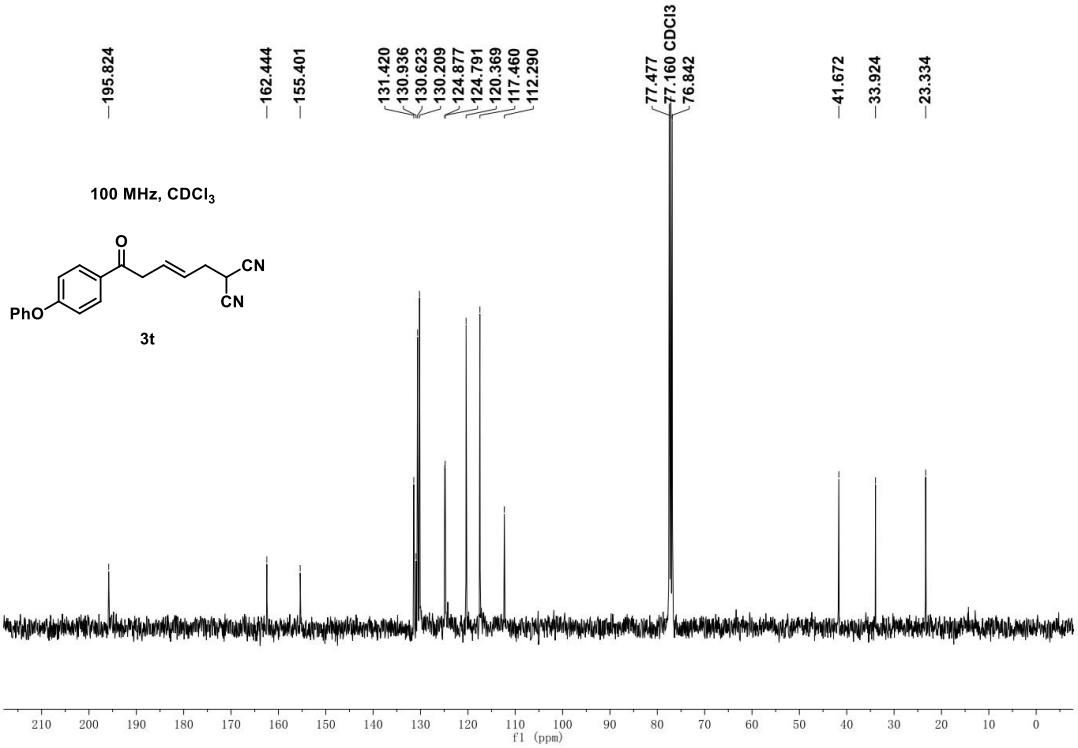


400 MHz, $CDCl_3$



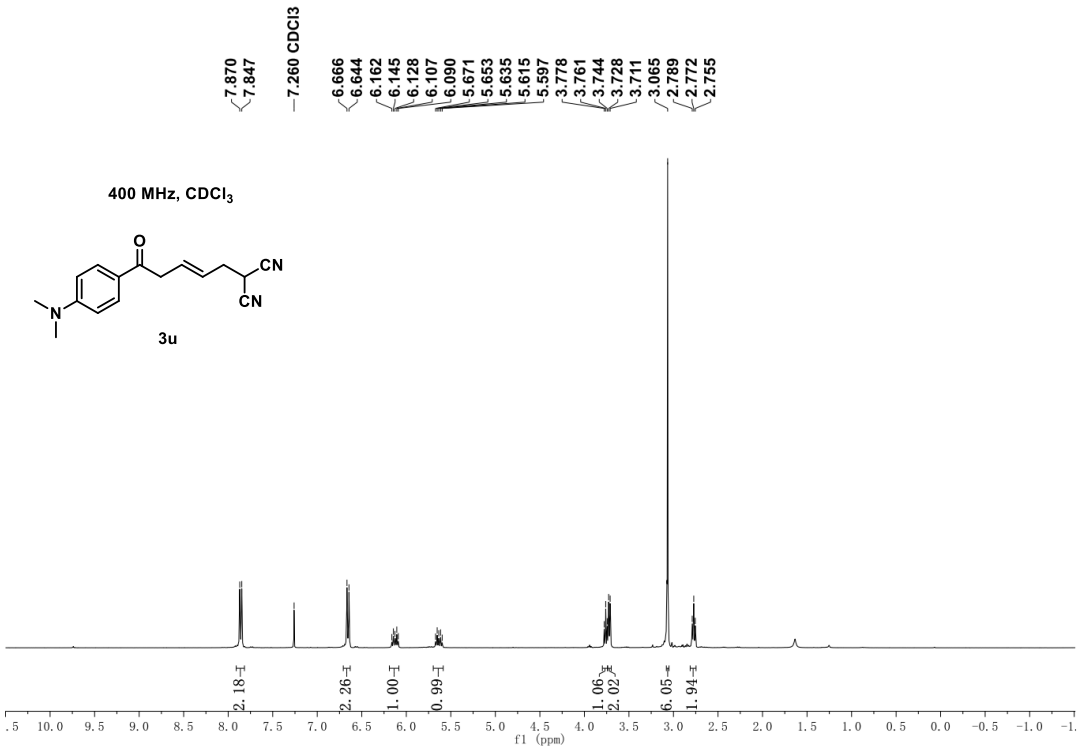
3t

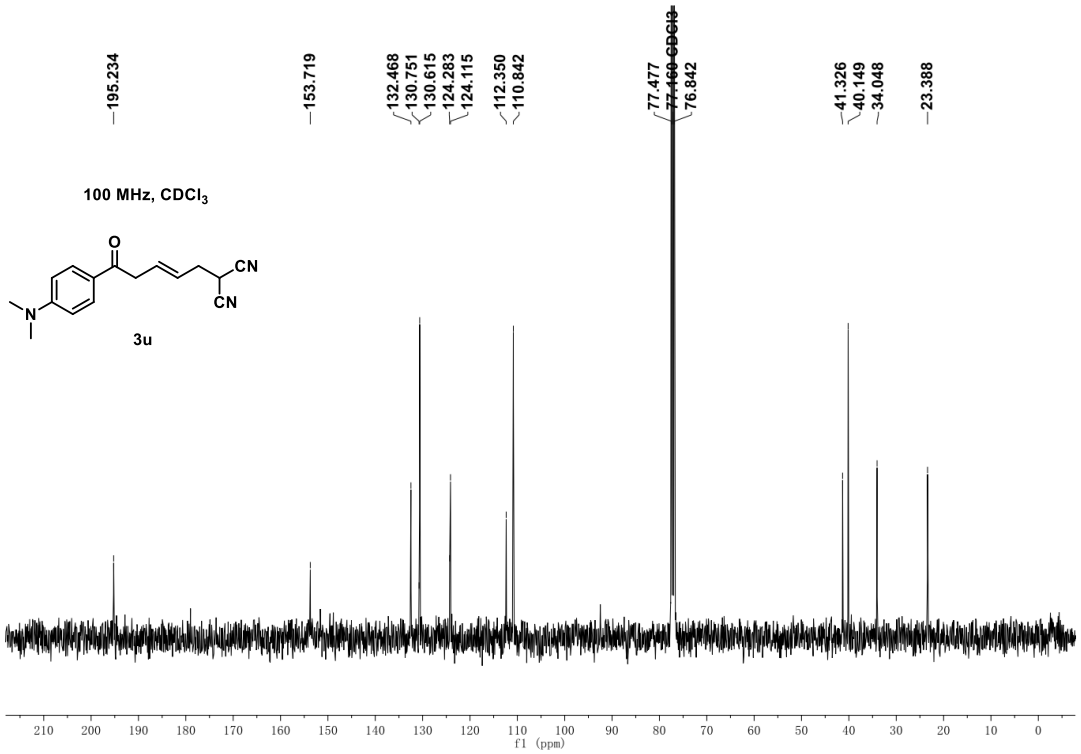


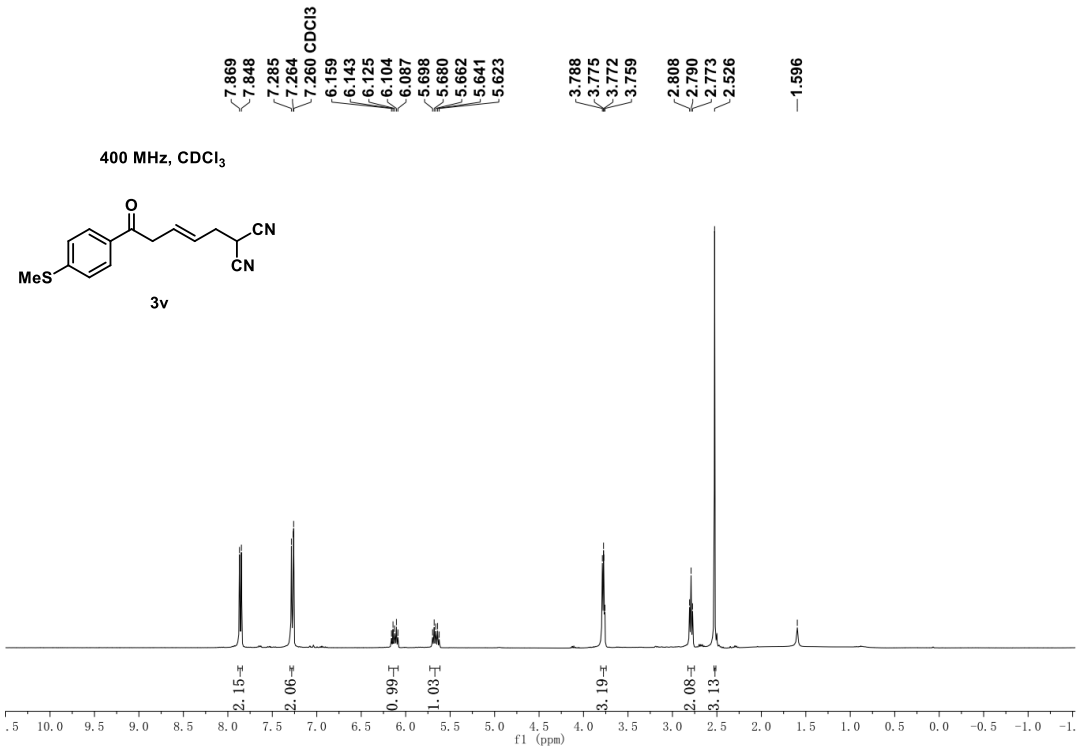


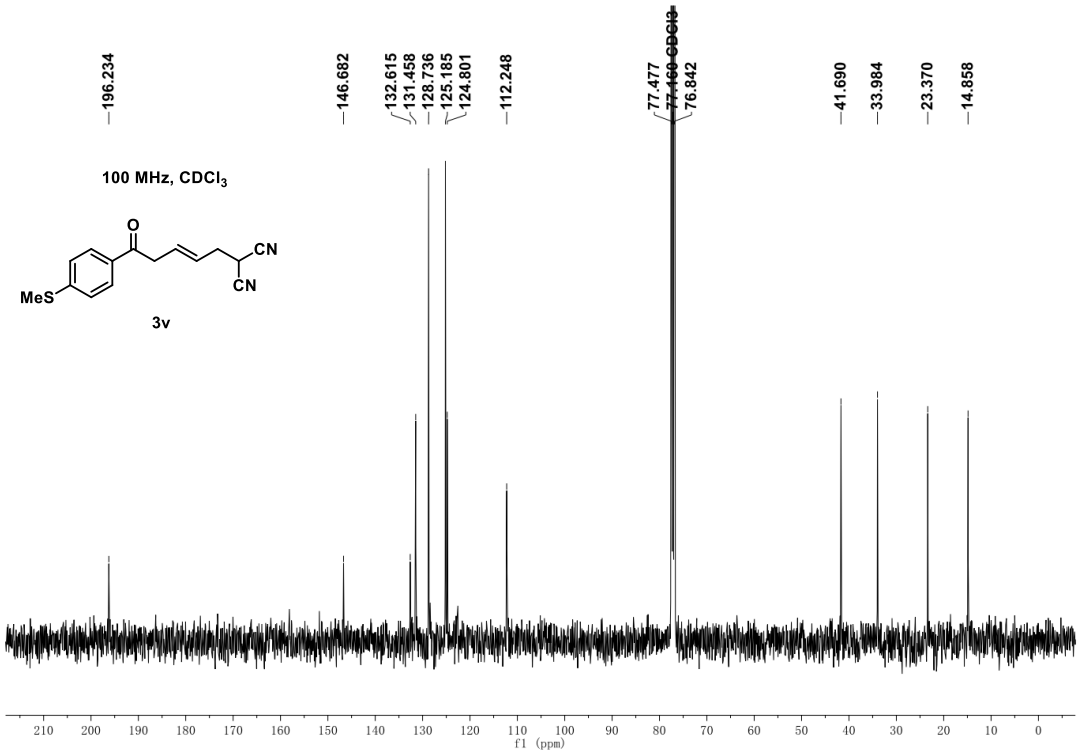
100 MHz, $CDCl_3$

3t

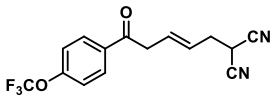

7.870
7.847
7.260 CDCl3
6.666
6.644
6.162
6.145
6.128
6.107
6.090
5.671
5.653
5.635
5.615
5.597
3.778
3.761
3.744
3.728
3.711
3.065
2.789
2.772
2.755
400 MHz, CDCl3
O
CN
CN
N
3u
2.18
2.26
1.00
0.99
1.06
2.02
6.05
1.94
f1 (ppm)


195.234
153.719
132.468
130.751
130.615
124.283
124.115
112.350
110.842
77.477
77.160 CDCl3
76.842
41.326
40.149
34.048
23.388
100 MHz, CDCl3
O
CN
CN
N
3u
f1 (ppm)

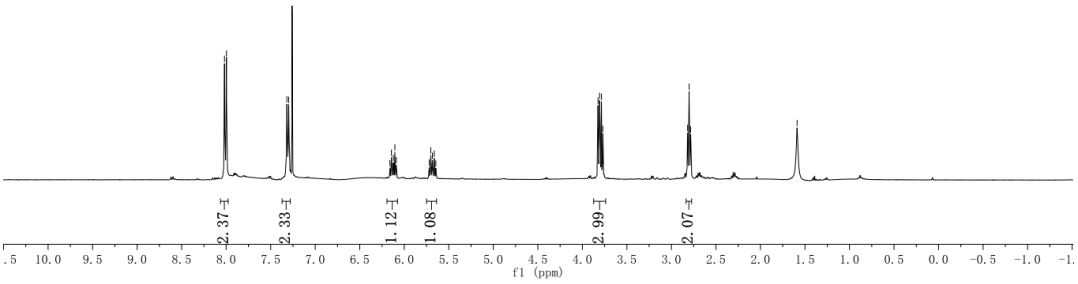

7.869
7.848
7.285
7.264
7.260 CDCl3
6.159
6.143
6.125
6.104
6.087
5.698
5.680
5.662
5.641
5.623
3.788
3.775
3.772
3.759
2.808
2.790
2.773
2.526
1.596
400 MHz, CDCl3
O
CN
CN
MeS
3v
2.15
2.06
0.99
1.03
3.19
2.08
3.13
f1 (ppm)

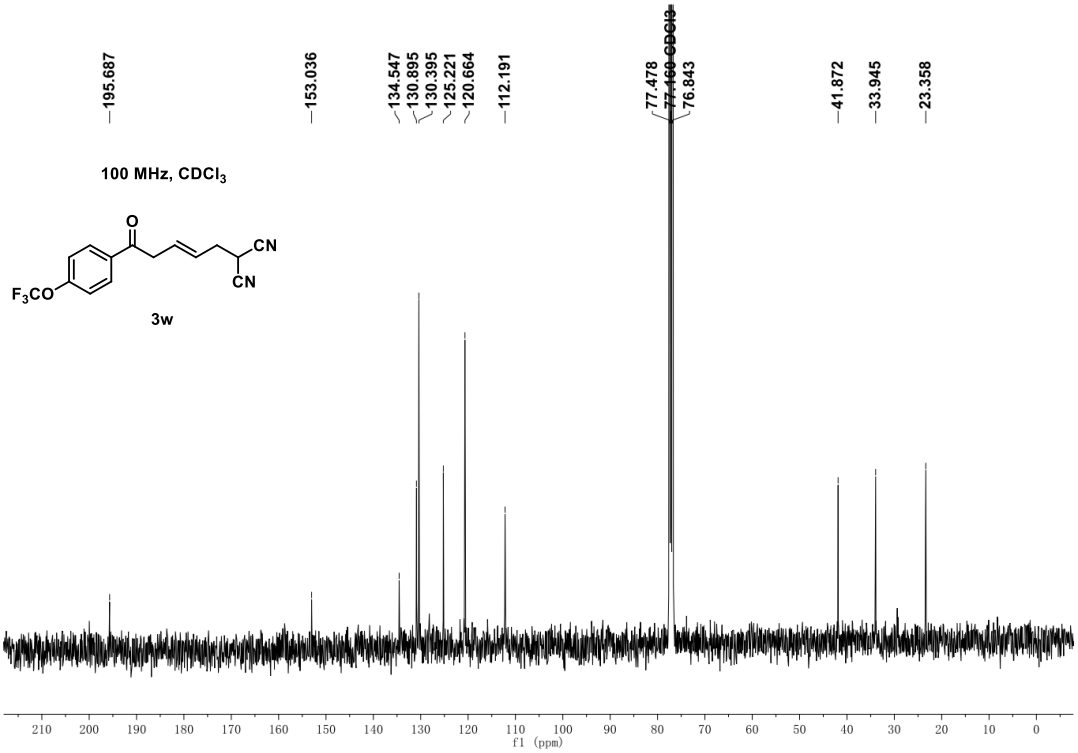

196.234
146.682
132.615
131.458
128.736
125.185
124.801
112.248
77.477
77.160 CDCl3
76.842
41.690
33.984
23.370
14.858
100 MHz, CDCl3
O
CN
CN
MeS
3v
f1 (ppm)

400 MHz, $CDCl_3$



3w



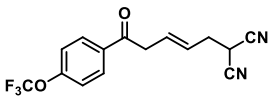


100 MHz, $CDCl_3$

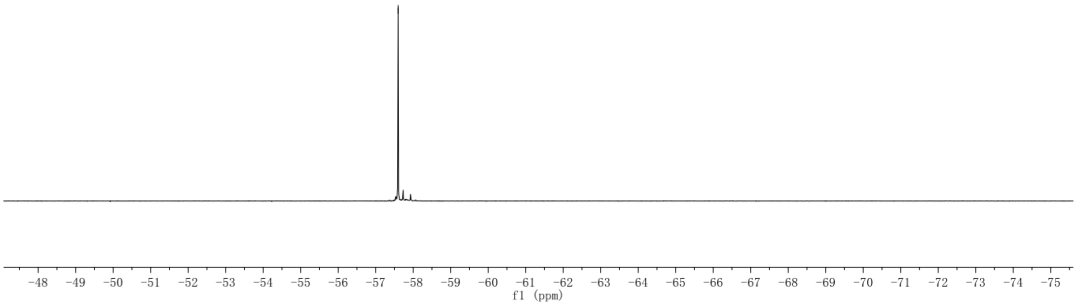
3w

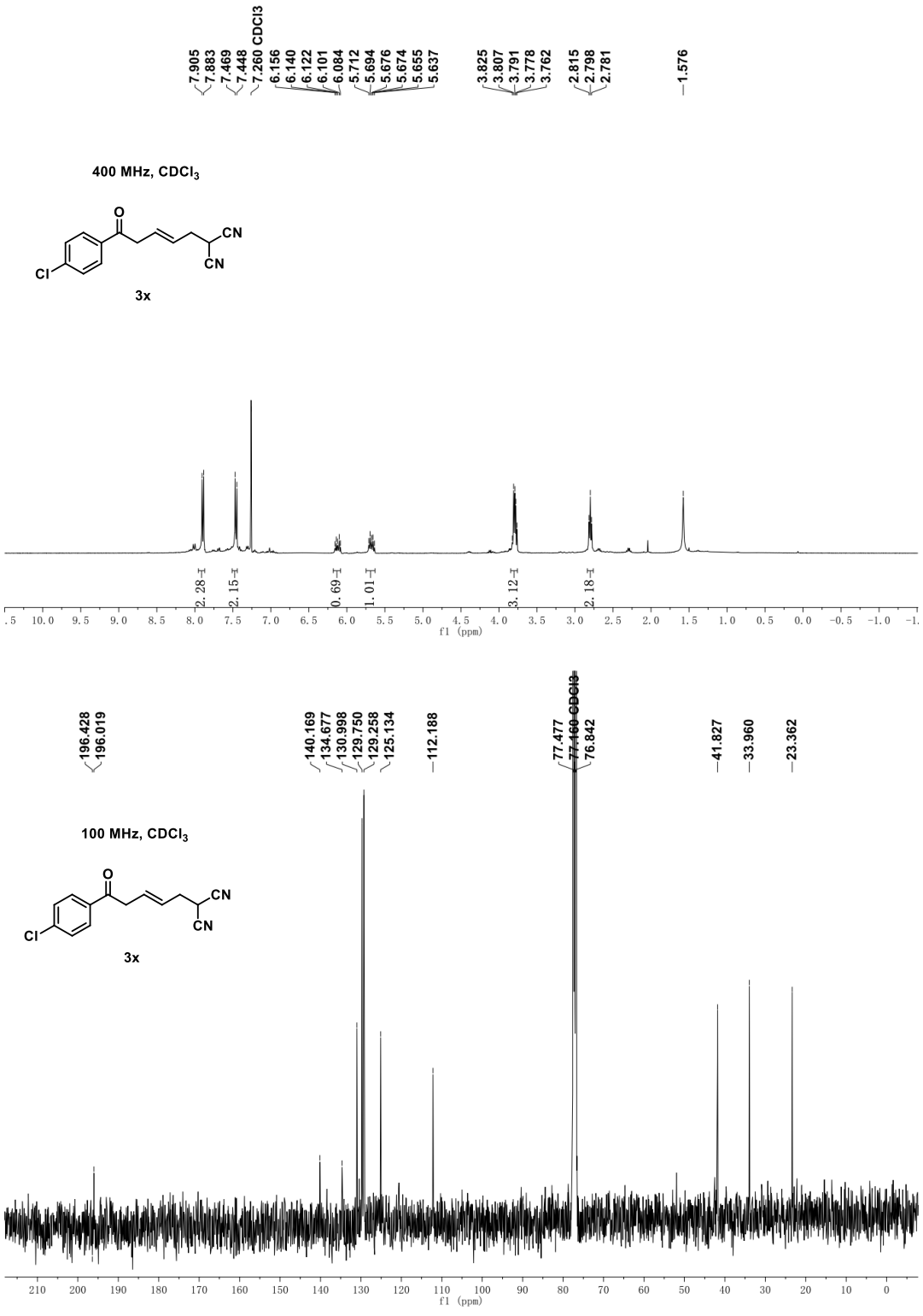
-57.599

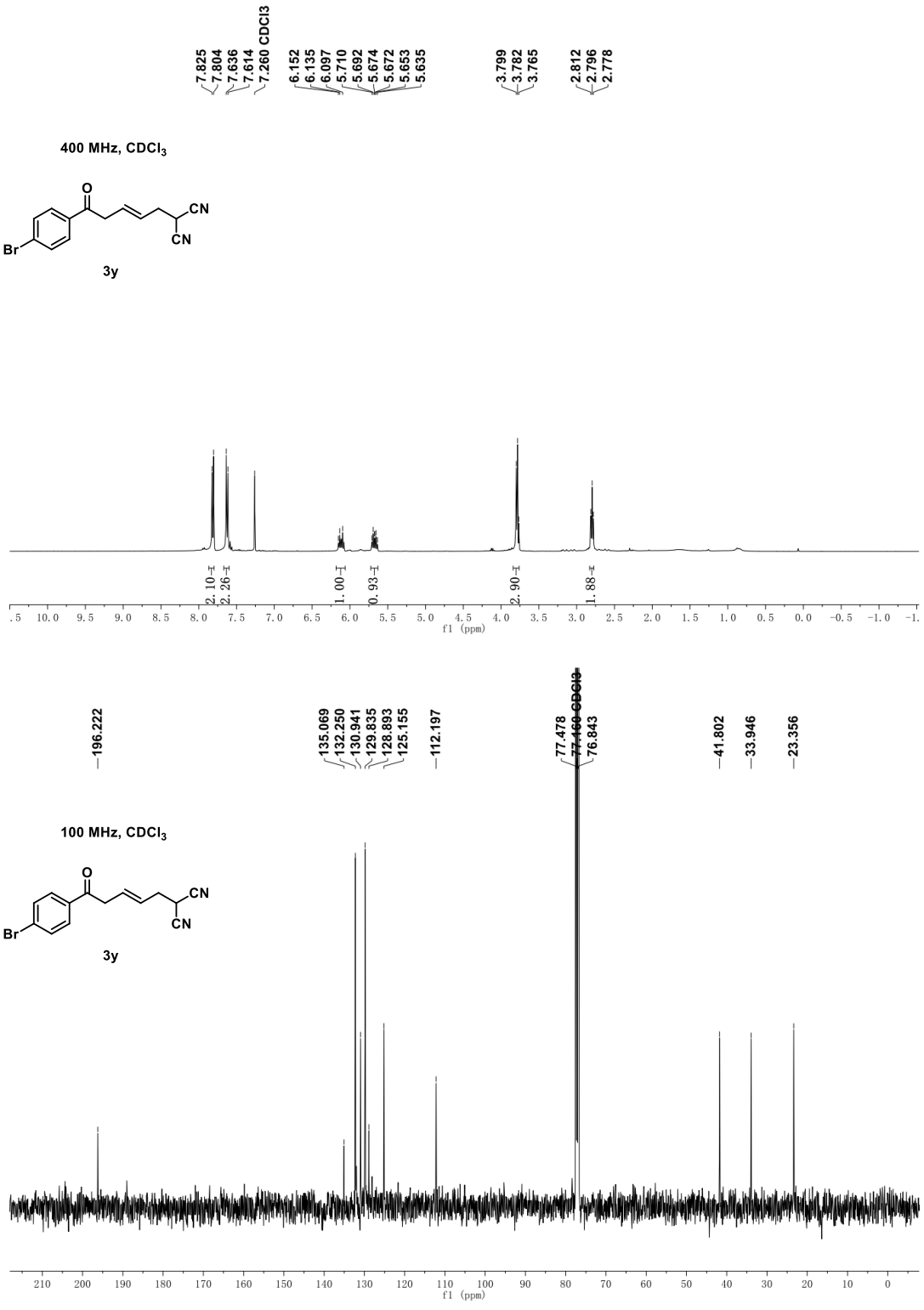
376 MHz, $CDCl_3$

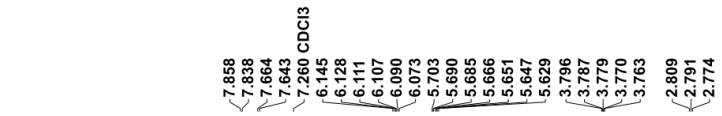


3w

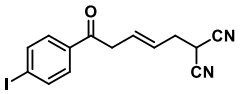



7.905
7.883
7.469
7.448
7.260 CDCl3
6.156
6.140
6.122
6.101
6.084
5.712
5.694
5.676
5.674
5.655
5.637
3.825
3.807
3.791
3.778
3.762
2.815
2.798
2.781
1.576
400 MHz, CDCl3
O
CN
CN
Cl
3x
2.28
2.15
0.69
1.01
3.12
2.18
f1 (ppm)
196.428
196.019
140.169
134.677
130.998
129.750
129.258
125.134
112.188
77.477
77.160 CDCl3
76.842
41.827
33.960
23.362
100 MHz, CDCl3
O
CN
CN
Cl
3x
f1 (ppm)

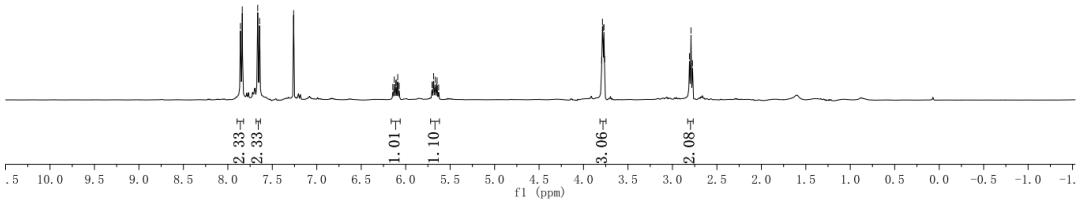

7.825
7.804
7.636
7.614
7.260 CDCl3
6.152
6.135
6.097
5.710
5.692
5.674
5.672
5.653
5.635
3.799
3.782
3.765
2.812
2.796
2.778
400 MHz, CDCl3
O
CN
CN
Br
3y
2.10
2.26
1.00
0.93
2.90
1.88
f1 (ppm)
196.222
135.069
132.250
130.941
129.835
128.893
125.155
112.197
77.478
77.160 CDCl3
76.843
41.802
33.946
23.356
100 MHz, CDCl3
O
CN
CN
Br
3y
f1 (ppm)

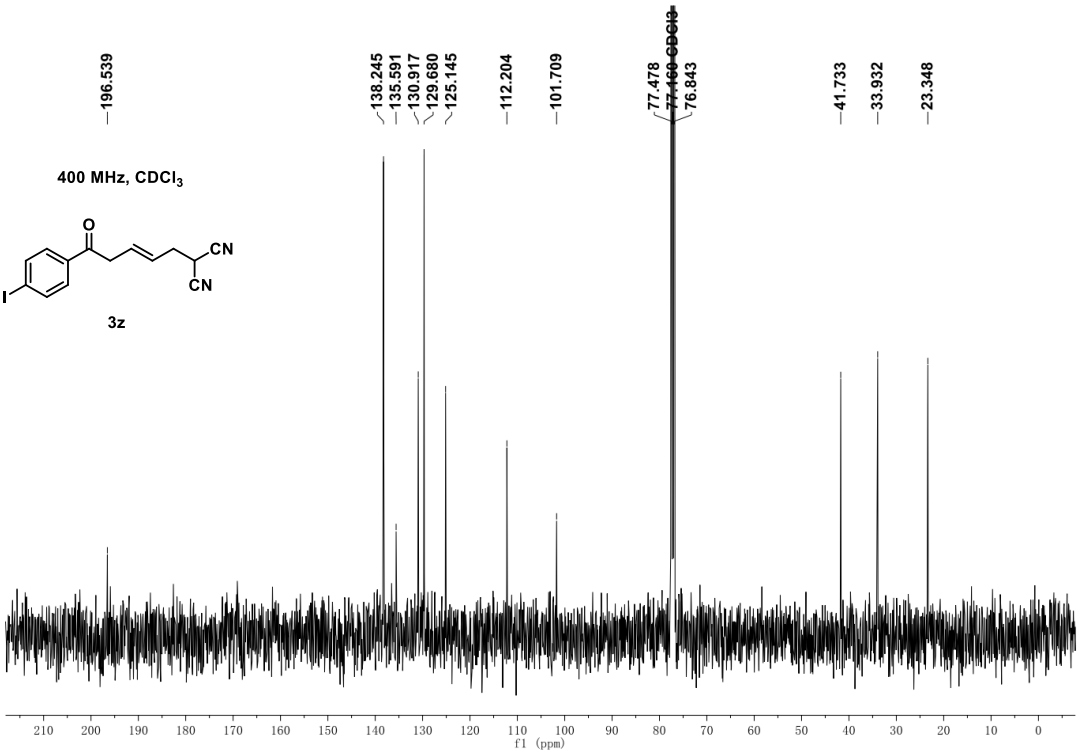


100 MHz, $CDCl_3$



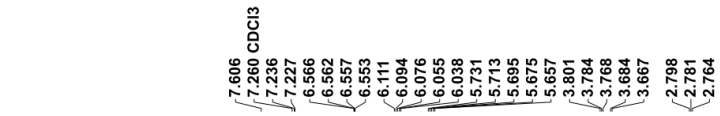
3z



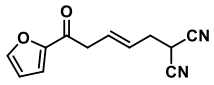


400 MHz, $CDCl_3$

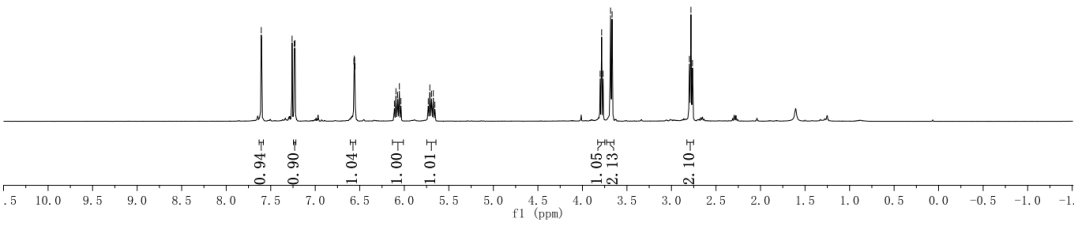
3z

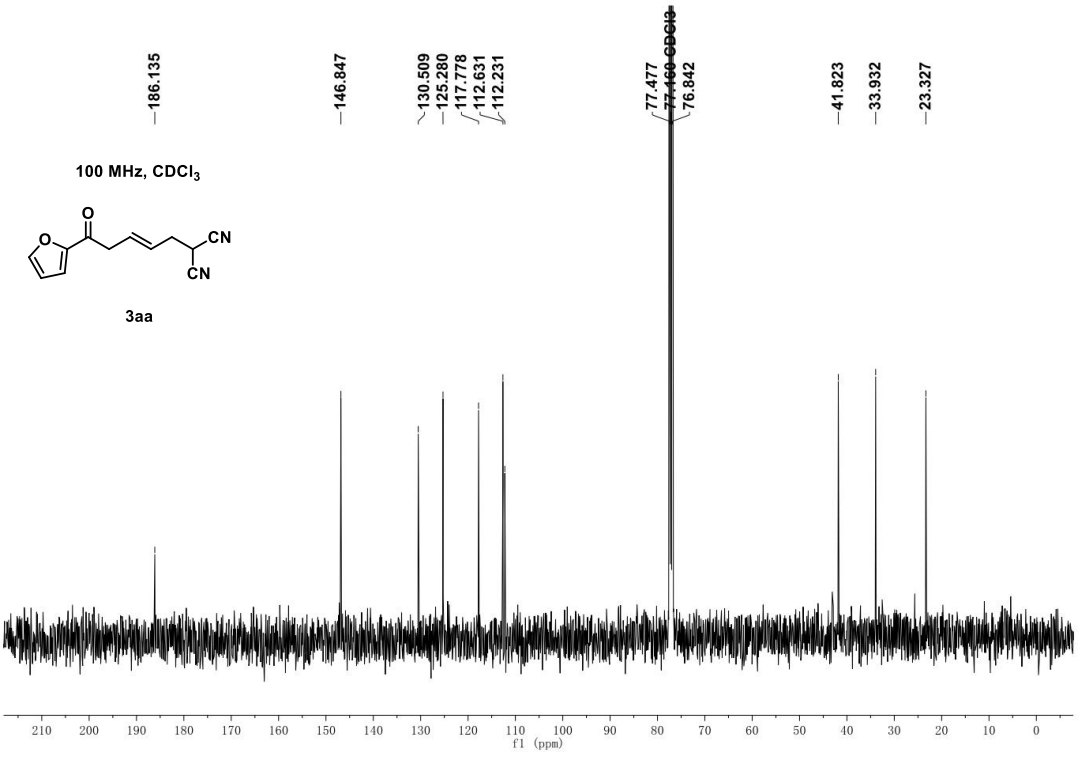


400 MHz, $CDCl_3$



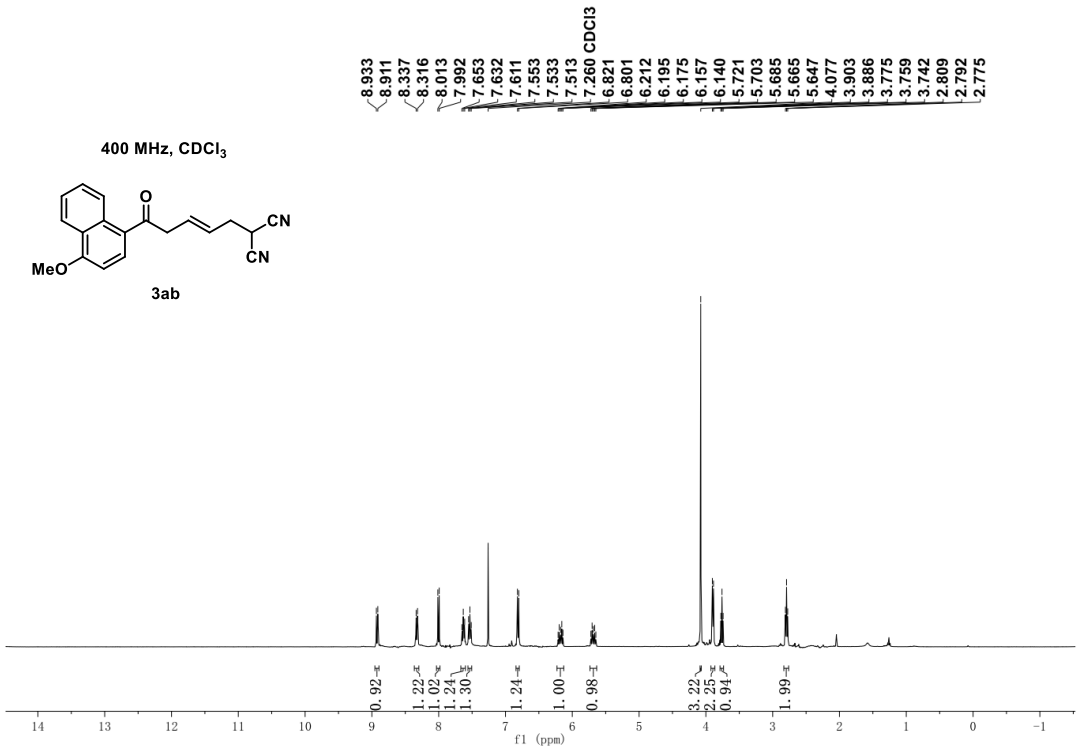
3aa

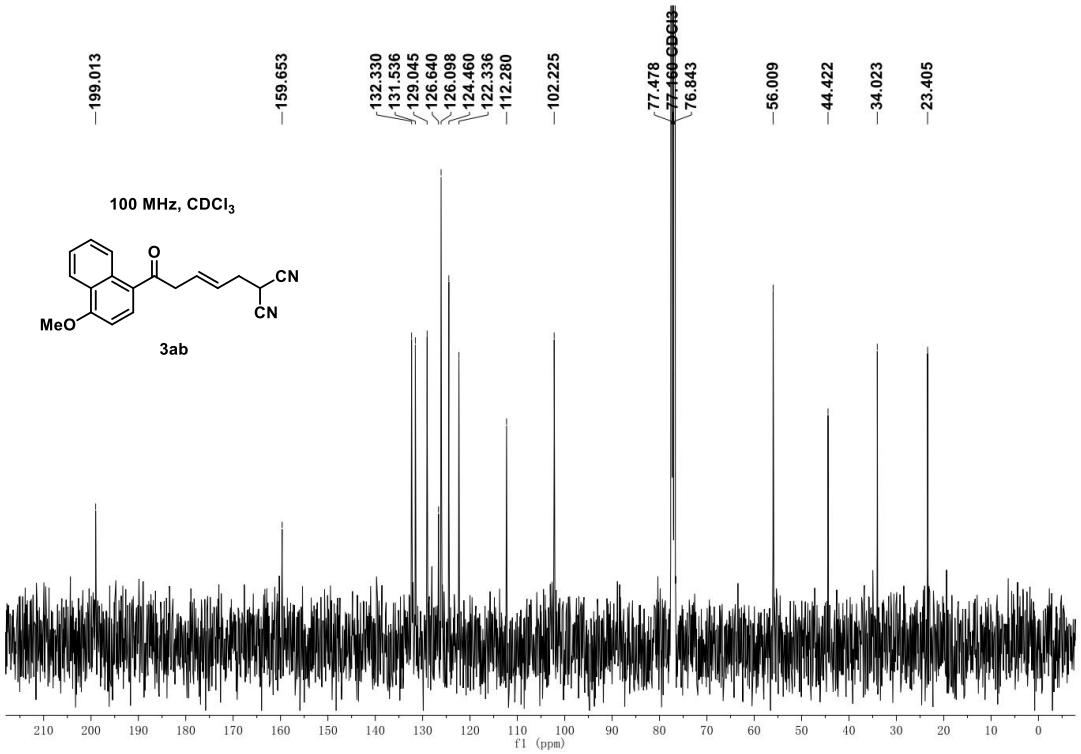


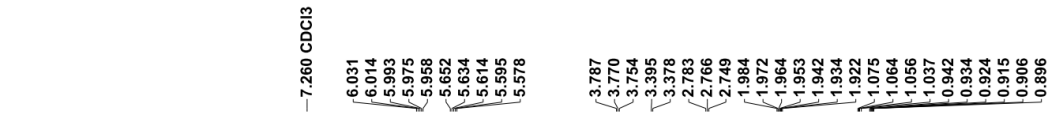


100 MHz, $CDCl_3$

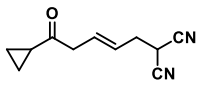
3aa


8.933
8.911
8.337
8.316
8.013
7.992
7.653
7.632
7.611
7.553
7.533
7.513
7.260 CDCl3
6.821
6.801
6.212
6.195
6.175
6.157
6.140
5.721
5.703
5.685
5.665
5.647
4.077
3.903
3.886
3.775
3.759
3.742
2.809
2.792
2.775
400 MHz, CDCl3
O
CN
CN
MeO
3ab
0.92
1.22
1.02
1.24
1.30
1.24
1.00
0.98
3.22
2.25
0.94
1.99
f1 (ppm)

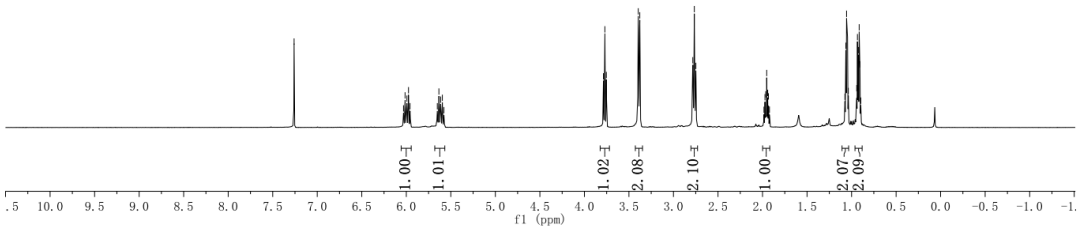

199.013
159.653
132.330
131.536
129.045
126.640
126.098
124.460
122.336
112.280
102.225
77.478
77.160 CDCl3
76.843
56.009
44.422
34.023
23.405
100 MHz, CDCl3
O
CN
CN
MeO
3ab
f1 (ppm)

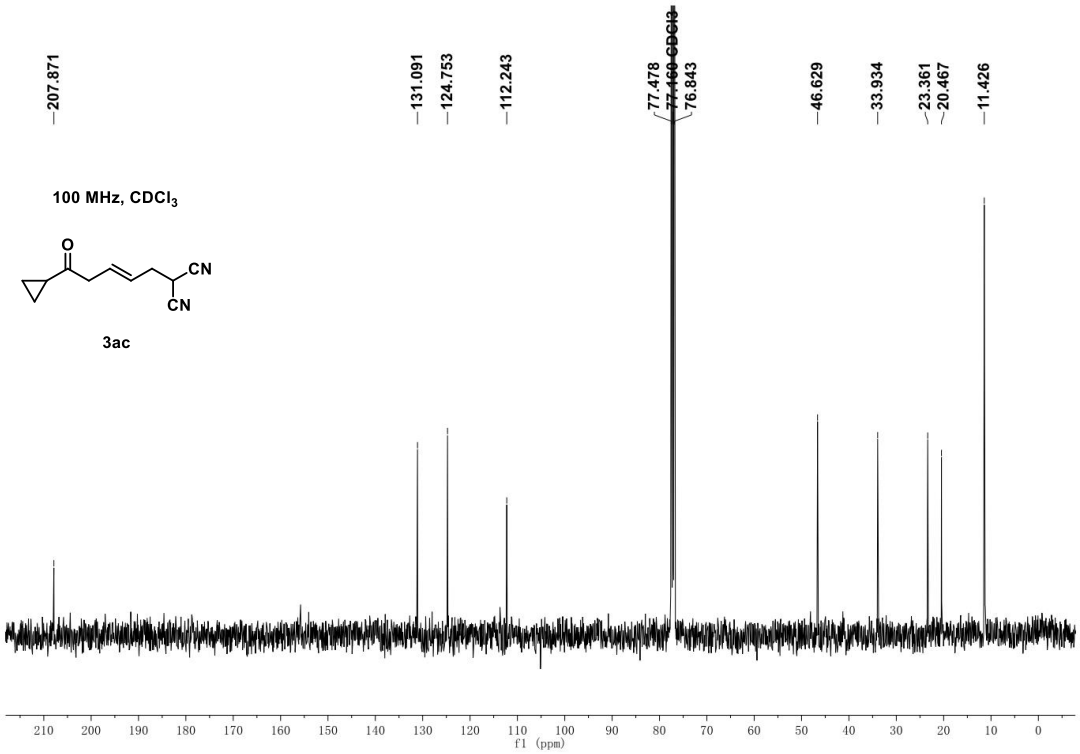


400 MHz, $CDCl_3$



3ac

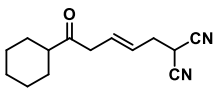




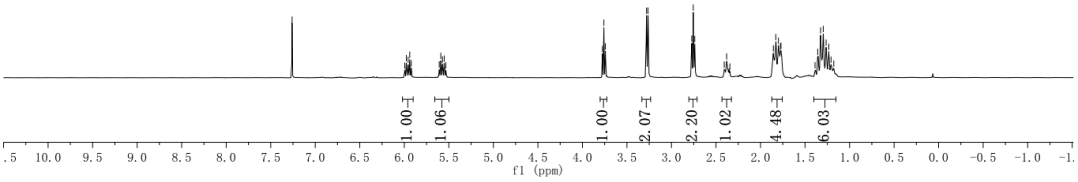
100 MHz, $CDCl_3$

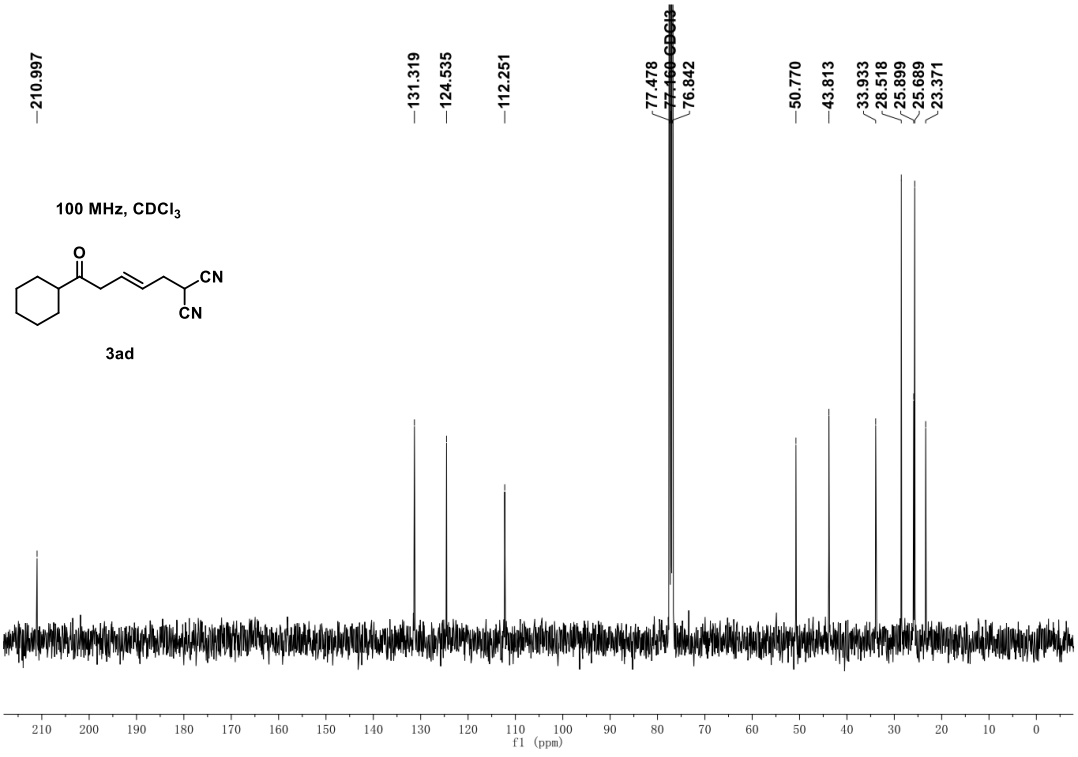
3ac

400 MHz, $CDCl_3$



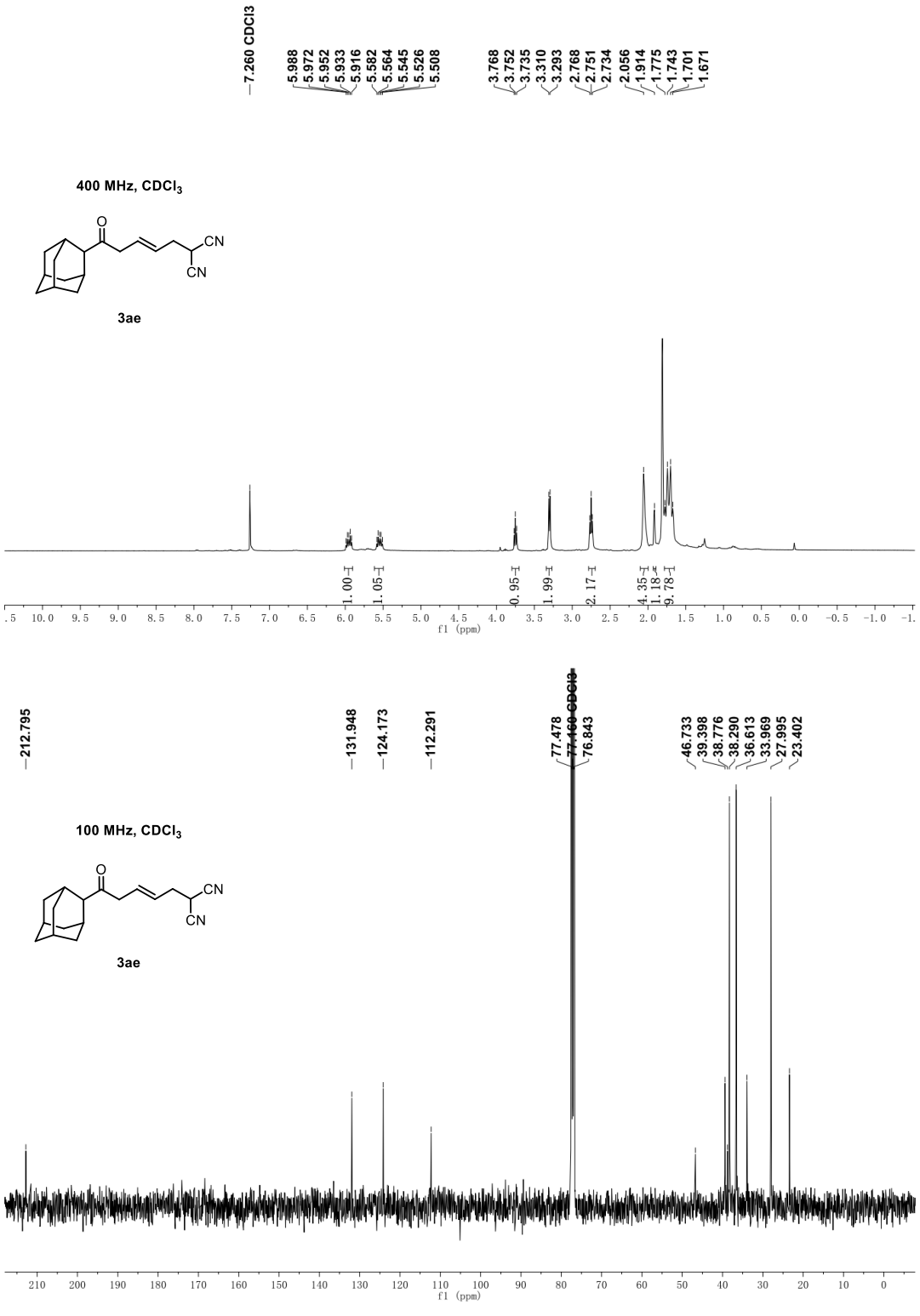
3ad

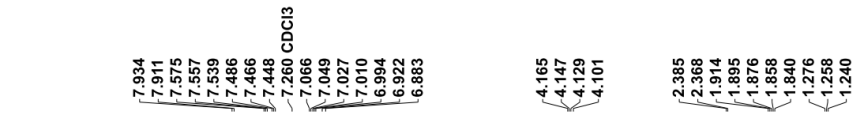




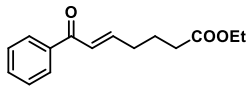
100 MHz, $CDCl_3$

3ad

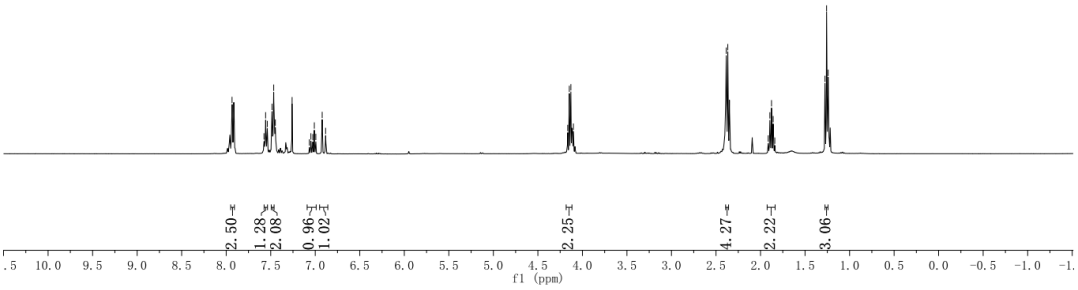

7.260 CDCl3
5.988
5.972
5.952
5.933
5.916
5.582
5.564
5.545
5.526
5.508
3.768
3.752
3.735
3.310
3.293
2.768
2.751
2.734
2.056
1.914
1.775
1.743
1.701
1.671
400 MHz, CDCl3
O
CN
CN
3ae
1.00
1.05
0.95
1.99
2.17
4.35
1.18
9.78
f1 (ppm)
212.795
131.948
124.173
112.291
77.478
77.160 CDCl3
76.843
46.733
39.398
38.776
38.290
36.613
33.969
27.995
23.402
100 MHz, CDCl3
O
CN
CN
3ae
f1 (ppm)

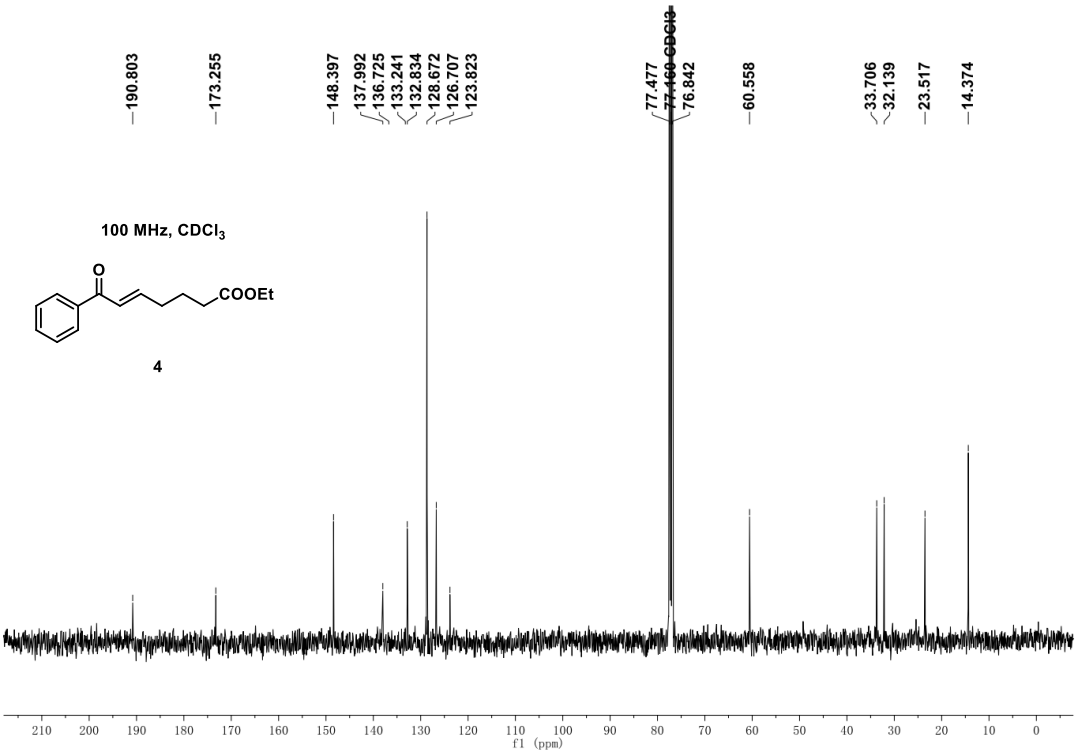


400 MHz, $CDCl_3$



4

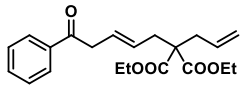




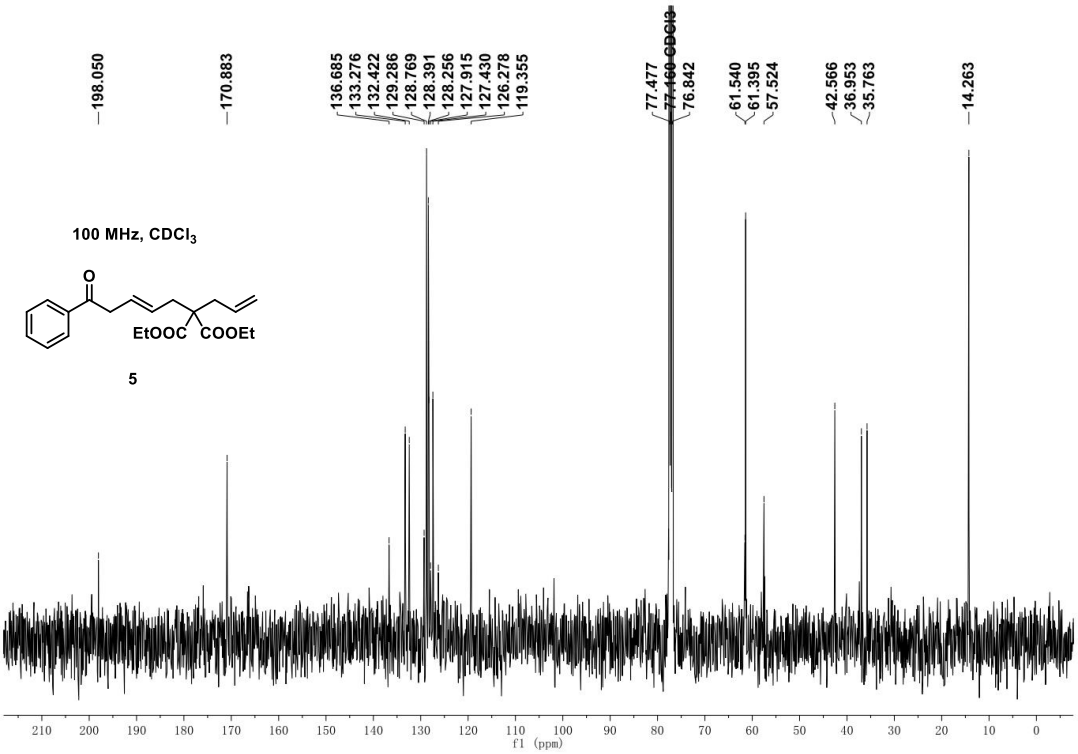
100 MHz, $CDCl_3$

4

400 MHz, $CDCl_3$

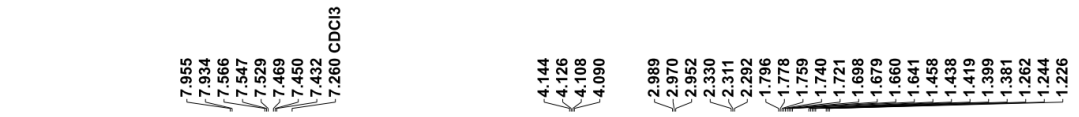


5

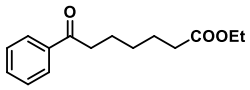


100 MHz, $CDCl_3$

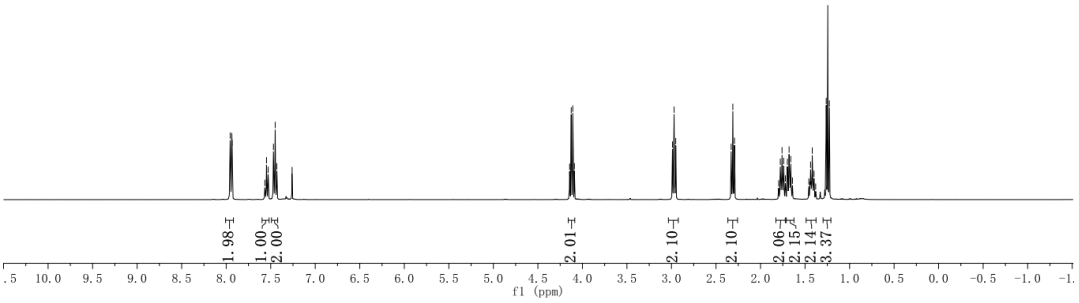
5

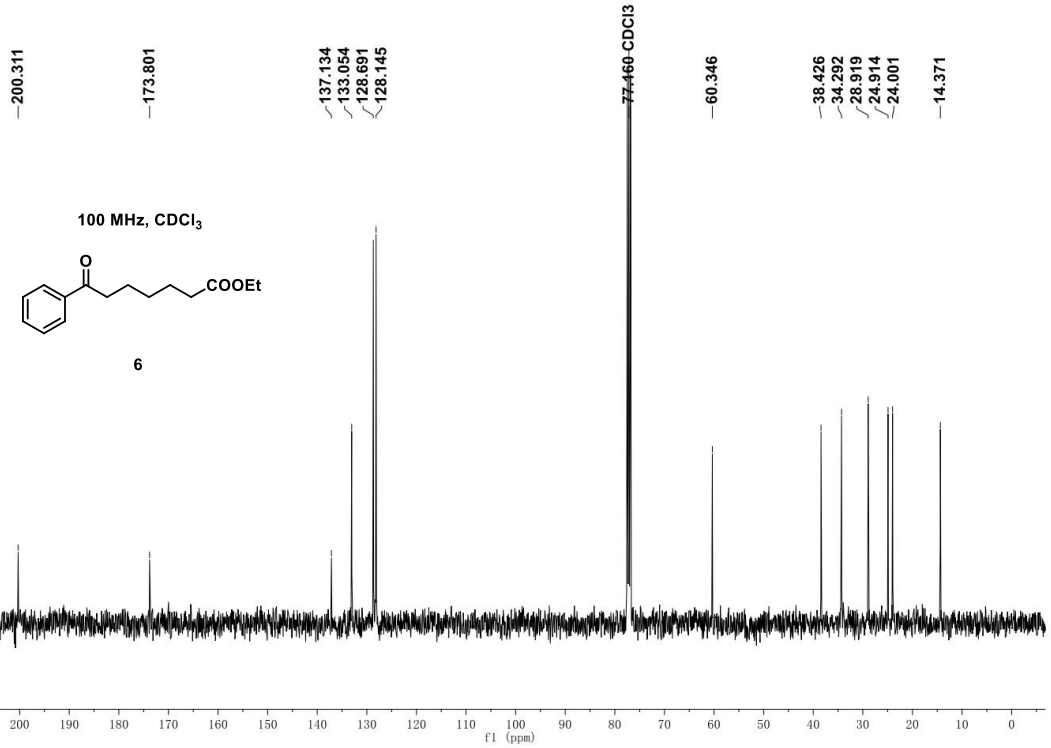


400 MHz, $CDCl_3$



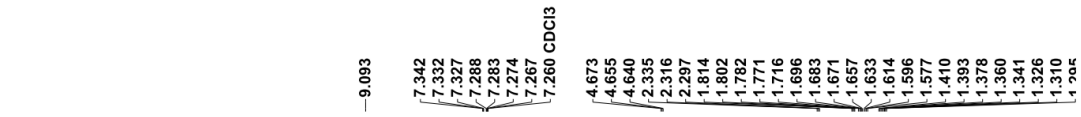
6



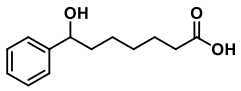


100 MHz, $CDCl_3$

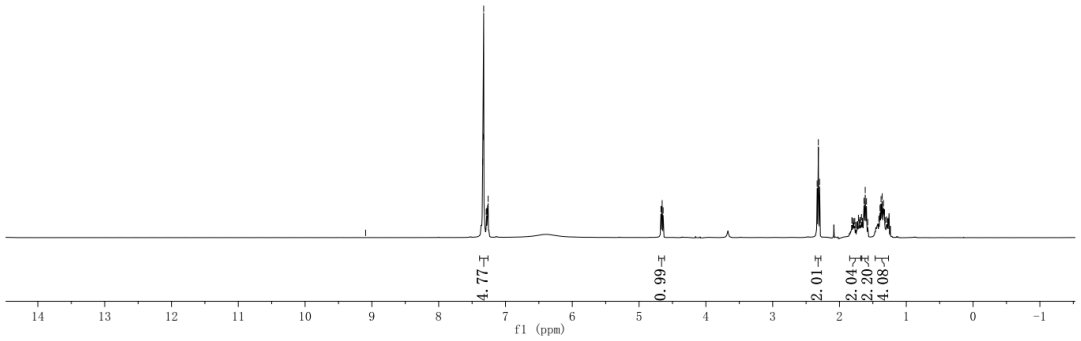
6

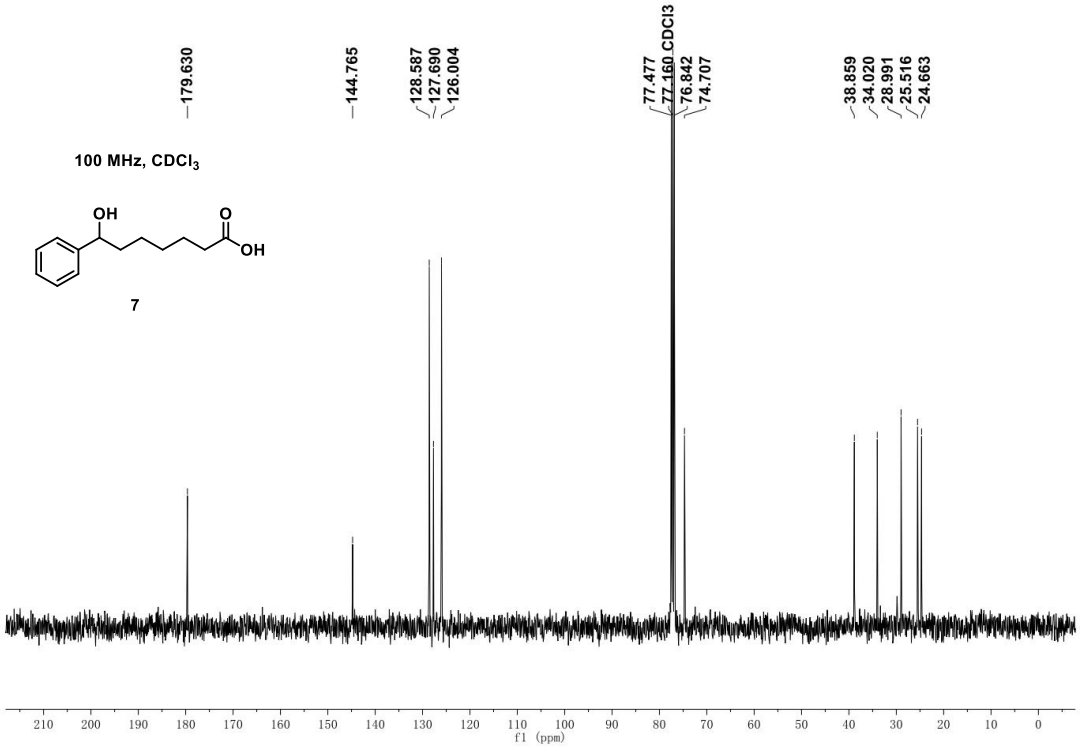


400 MHz, $CDCl_3$



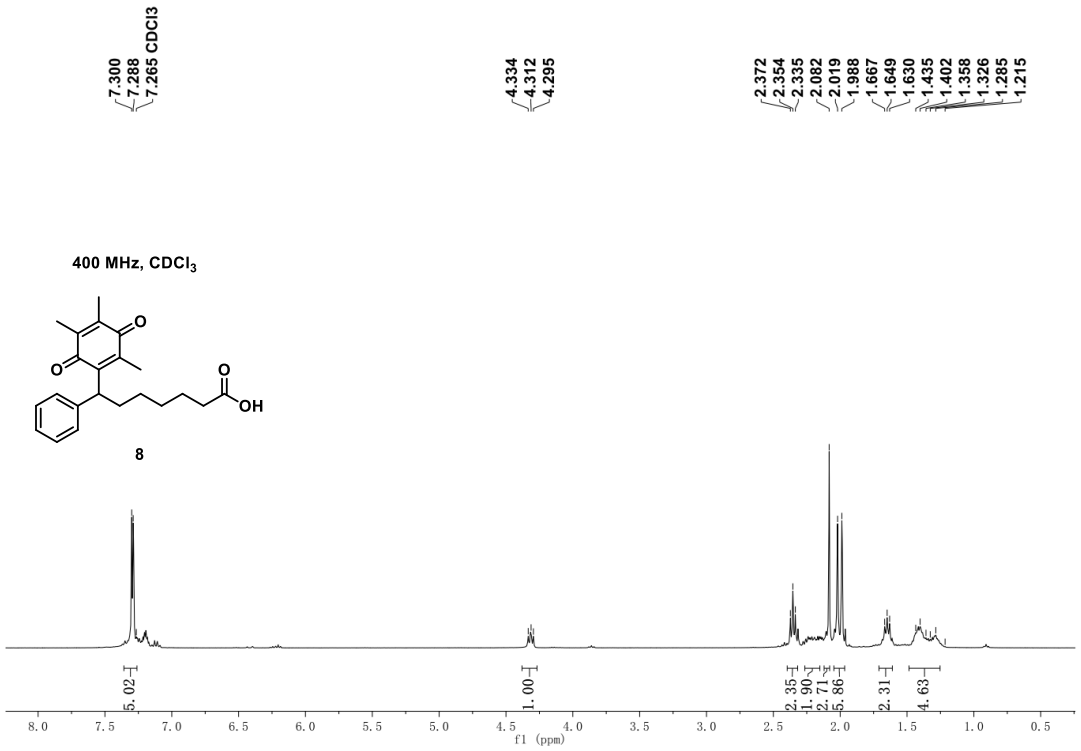
7

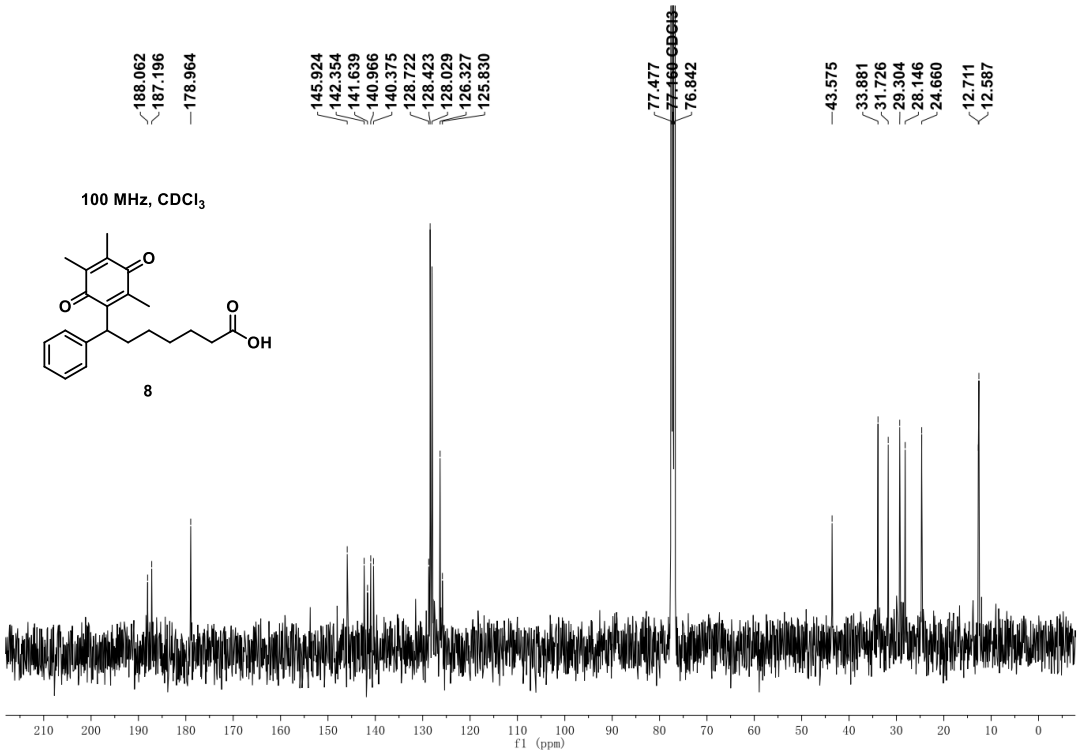


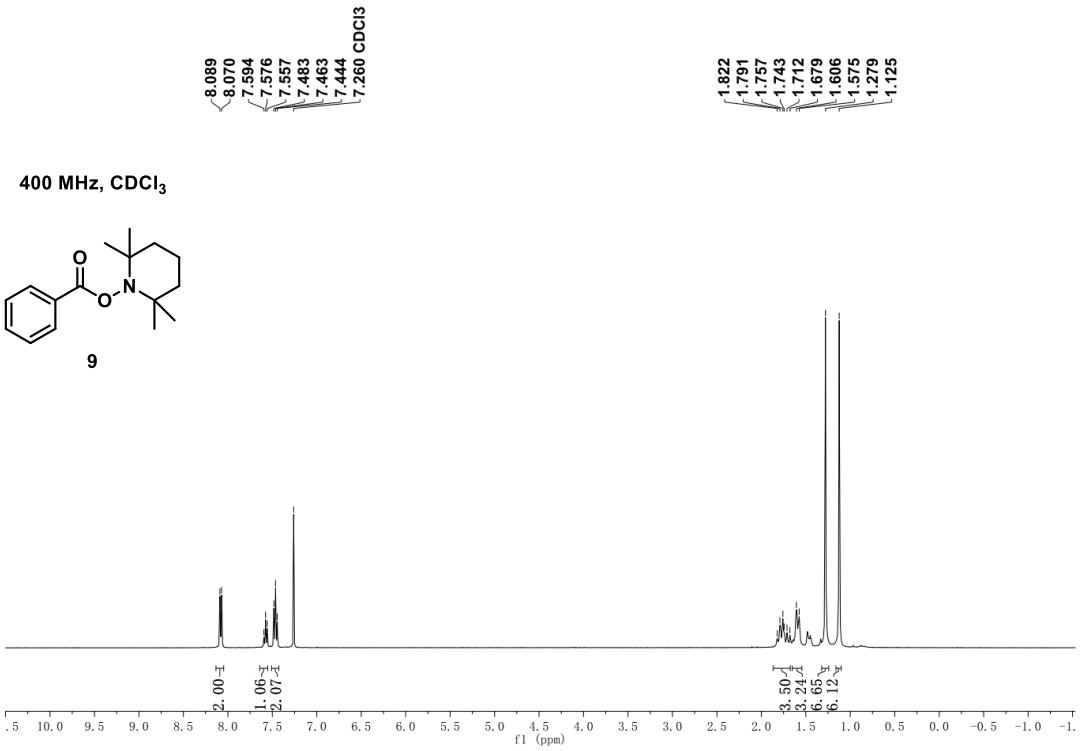


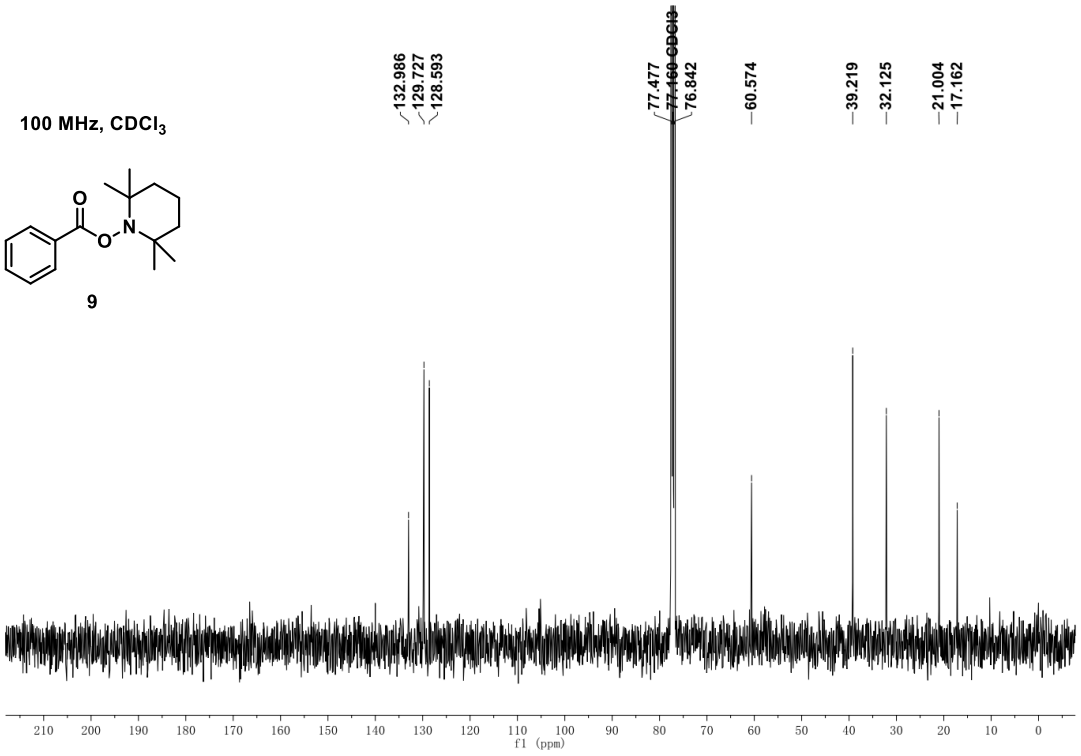
100 MHz, $CDCl_3$

7


7.300
7.288
7.265 CDCl3
4.334
4.312
4.295
2.372
2.354
2.335
2.082
2.019
1.988
1.667
1.649
1.630
1.435
1.402
1.358
1.326
1.285
1.215
400 MHz, CDCl3
O
O
O
OH
8
5.02
1.00
2.35
1.90
2.71
5.86
2.31
4.63
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


188.062
187.196
178.964
145.924
142.354
141.639
140.966
140.375
128.722
128.423
128.029
126.327
125.830
77.477
77.160 CDCl3
76.842
43.575
33.881
31.726
29.304
28.146
24.660
12.711
12.587
100 MHz, CDCl3
O
O
O
OH
8
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


8.089
8.070
7.594
7.576
7.557
7.483
7.463
7.444
7.260 CDCl3
1.822
1.791
1.757
1.743
1.712
1.679
1.606
1.575
1.279
1.125
400 MHz, CDCl3
9
2.00
1.06
2.07
3.50
3.24
6.65
6.12
f1 (ppm)


132.986
129.727
128.593
77.477
77.160 CDCl3
76.842
60.574
39.219
32.125
21.004
17.162
100 MHz, CDCl3
9
f1 (ppm)

VII. References

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3 Zhao, G.; Khosravi, A.; Sharma, S.; Musaev, D. G.; Ngai, M.-Y., Cobalt-Hydride-Catalyzed Alkene-Carboxylate Transposition (ACT) of Allyl Carboxylates. *J. Am. Chem. Soc.* **2024,** *146*, 31391-31399.

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