Supporting Information

Stereospecific Cyanation of Olefinic C−H Bond Enabled by 1,4-Rhodium Migration

Xiaosa Lu,† and Yinhua Huang†*

†College of Materials, Chemistry and Chemical Engineering, Hangzhou Normal University, Hangzhou 311121, China

Email: yhhuang@hznu.edu.cn

Contents of Supporting Information:

1. General information

All air-sensitive manipulations were carried out with standard Schlenk techniques under nitrogen or argon. Solvents were degassed prior to use when necessary. NMR spectra were recorded on Bruker AMX 500 spectrophotometer (500 MHz for ^{1}H, 77 MHz for ^{2}H, 126 MHz for ^{13}C and 471 Hz for ^{19}F). Chemical shifts are reported in δ (ppm) referenced to an internal $SiMe_4$ standard (δ = 0 ppm) for ^{1}H NMR, chloroform-d (δ = 77.0 ppm) for ^{13}C NMR. The following abbreviations were used; s: singlet, d: doublet, t: triplet, q: quartet, m: multiplet, br: broad. HRMS (ESI-TOF) were recorded on a time-of-fligh (TOF) LC/MS instrument. Flash column chromatography was performed with Silica gel 60 (Merck) or Al_2O_3 (activated 200) (Merck).

All chemicals and solvents were purchased from commercial company and used as received. Solvents were degassed before use if necessary.

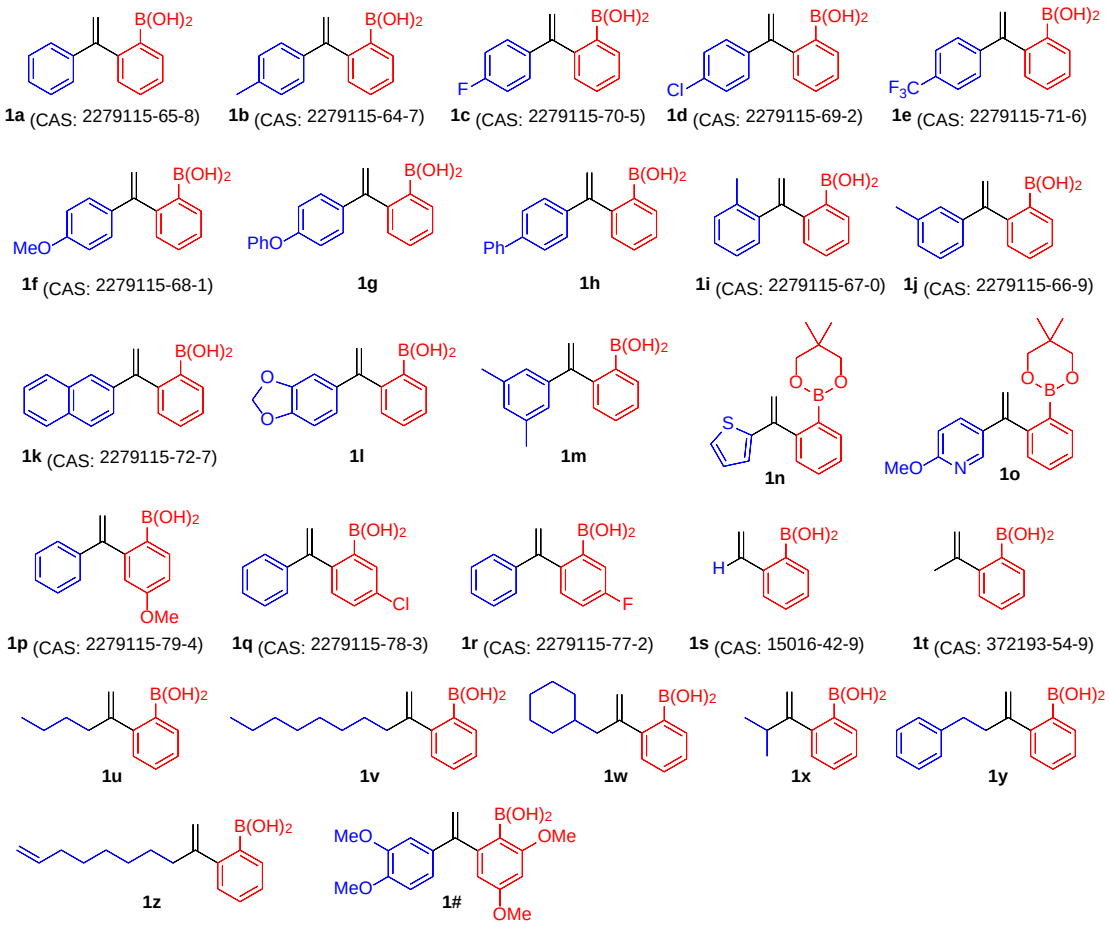
2. Experimental details

2.1 Preparation of substrates

Dess-Martin periodinane (CAS: 87413-09-0), methyltriphenylphosphonium bromide (CAS: 1779-49-3), triisopropyl borate (CAS: 5419-55-6), *n*-BuLi (2.5 M in hexane) (CAS: 109-72-8) and 2,2-dimethyl-1,3-propanediol (CAS: 126-30-7) were purchased from commercial company and used as received.

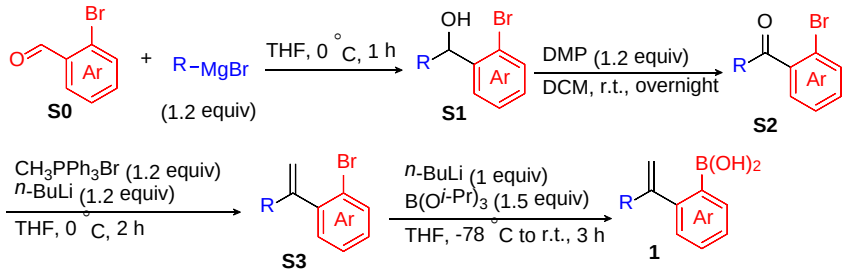
The known arylboronic acids (**1a**, **1b**, **1c**, **1d**, **1e**,**1f, 1i**, **1j**, **1k**, **1p**, **1q**, **1r**, **1s**, **1t**) were prepared according to the reported procedures.[1] The new arylboronic acids (**1g**, **1h**, **1l**, **1m**, **1n**, **1o**, **1u**, **1v, 1w, 1x, 1y, 1z, 1#**) were prepared by the same method.

N-cyano-*N*-phenyl-*p*-methylbenzenesulfonamide (NCTS) was prepared according to a reported procedure.[2]



Scheme S1. Arylboronic acids substrates

General method for the synthesis of arylboronic acid substrates[1]



A typical procedure for the synthesis of 1g:

To a solution of 2-bromobenzaldehyde (2.77 g, 10.0 mmol, 1.0 equiv) in THF (20 mL) was slowly added a solution of 4-$PhOC_6H_4MgBr$ (2.0 M in THF, 6 mL, 1.2 equiv) at 0 °C under predried argon. After stirring at 0 °C for 1 h, saturated aqueous NH_4Cl solution (10 mL) was added and the mixture was extracted with EtOAc (3 × 20 mL). The organic layers were combined, washed with brine and water, and dried

over anhydrous Na_2SO_4. After removal of solvent, the residue was purified by flash chromatography on silica gel (ethyl acetate/ petroleum ether = 1/20) to give **S1g** (3.37 g, 95%) as a white solid.

To a solution of above obtained **S1g** (3.37 g, 9.5 mmol, 1.0 equiv) in 20 mL DCM was added Dess-Martin Periodinane (DMP, CAS: 87413-09-0) (4.84 g, 11.4 mmol, 1.2 equiv) at 0 ℃ under air. After stirring at rt overnight, 20 mL of saturated aqueous Na_2CO_3 solution and saturated aqueous $Na_2S_2O_4$ solution (1:1) was added and the mixture was extracted with EtOAc (3 × 20 mL). The organic layers were combined, washed with brine and water, and dried over anhydrous Na_2SO_4. After removal of solvent, the residue was purified by flash chromatography on silica gel (ethyl acetate/ petroleum ether = 1/30) to give **S2g** (3.02 g, 90%) as a white solid.

To the solution of methyl triphenylphosphonium bromide (3.68 g, 10.3 mmol, 1.2 equiv) in THF (20 mL) was slowly added *n*-BuLi (4.1 mL, 2.5 M in hexane, 10.3 mmol, 1.2 equiv) at -40 ℃. After stirring at 0 ℃ for 30 min under argon, a solution of the above obtained **S2g** (3.02 g, 8.6 mmol, 1.0 equiv) in THF (10 mL) was slowly added and the resulting mixture was further stirred at 0 ℃ for 2 h. The reaction was quenched with saturated aqueous NH_4Cl solution (10 mL), and mixture was extracted with EtOAc (3 × 15 mL). The organic layers were combined, washed with brine and water, and dried over anhydrous Na_2SO_4. After removal of solvent, the residue was purified by flash chromatography on silica gel (ethyl acetate/ petroleum ether = 1/100) to give **S3g** (2.28 g, 76%) as a white solid.

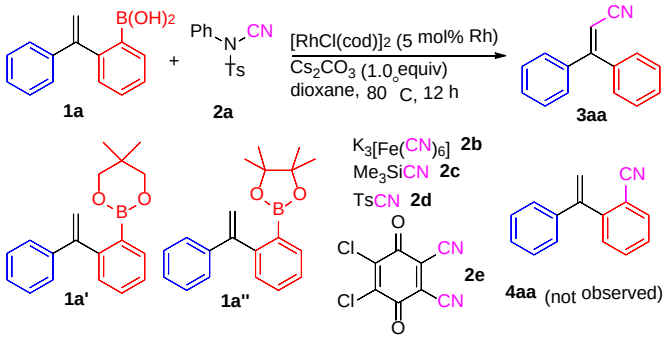
Under argon, to a solution of the above obtained **S3g** (2.28 g, 6.5 mmol, 1.0 equiv) in THF (15 mL) was slowly added *n*-BuLi (2.6 mL, 2.5 M in hexane, 6.5 mmol, 1.0 equiv) at -78 °C for 30 min. Then a solution of triisopropyl borate (1.84 g, 9.8 mmol, 1.5 equiv) in THF (10 mL) was added slowly. The reaction mixture was warmed to rt naturally and kept stirring for another 3 h. Saturated aqueous NH_4Cl solution (20 mL) was added and the mixture was extracted with EtOAc (3 × 15 mL). The organic layers were combined, washed with brine and water, and dried over anhydrous Na_2SO_4. After removal of solvent, the residue was purified by flash chromatography on silica gel (ethyl acetate/ petroleum ether = 1/5) to give **1g** (0.88 g,

43%) as a white solid.

In case of heteroaryl-containing substrates, the corresponding boronic acids were transformed into boronic esters by refluxing with neopentyl glycol in toluene and used as the substrates (**1n**, **1o**).

2.2 Optimization of Conditions

Table S1. Optimization of Conditions [a]



entry	variations from standard conditions (shown above)	yield (%)[c] **3aa**
1	**none**	**96(94)**
2	in the absence of $[RhCl(cod)]_2$	0
3	K_3PO_4, K_2CO_3, KOH instead of Cs_2CO_3	32, 45, 92
4	THF, Toluene, MTBE instead of dioxane	80, 84, 89
5	$[RhCl(binap)]_2$ instead of $[RhCl(cod)]_2$	32
6	$[RhCl(segphos)]_2$ instead of $[RhCl(cod)]_2$	24
7	$[RhCl(dppe)]_2$ instead of $[RhCl(cod)]_2$	7
8	$[RhCl(dppp)]_2$ instead of $[RhCl(cod)]_2$	11
9	$[RhCl(dppb)]_2$ instead of $[RhCl(cod)]_2$	31
10	$[RhCl(dppf)]_2$ instead of $[RhCl(cod)]_2$	49
11	$Pd(OAc)_2$, $Pd(PPh_3)_2Cl_2$ instead of $[RhCl(cod)]_2$	8, 3
12	**1a'**, **1a''** instead of **1a**	77, 18
13	**2b**, **2c**, **2d**, **2e** instead of **2a**	<1

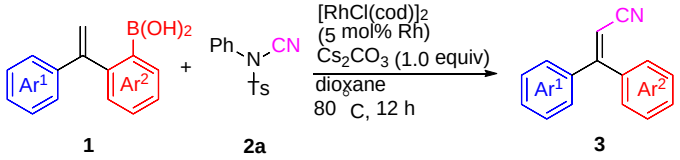
[a] Reaction conditions: **1a** (0.14 mmol), **2a** (0.12 mmol), base (1.0 equiv), solvent (1 mL), at 80 °C for 12 h. [b] Catalyst (5 mol% of M) was loaded if applicable. [c] The yields were obtained by ^1H NMR analysis of the crude reaction mixture with the aid of $Cl_2CHCHCl_2$ as an internal standard. Isolated yields in parentheses. THF = tetrahydrofuran; MTBE = methyl *tert*-butyl ether.

A typical procedure for entry 1:

Arylboronic acid **1a** (32.3 mg, 0.140 mmol, 1.2 equiv), NCTS (32.7 mg, 0.120

mmol, 1.0 equiv), Cs_2CO_3 (39.1 mg, 0.120 mmol, 1.0 equiv) and $[RhCl(cod)]_2$ (1.5 mg, 0.003 mmol, 5 mol% Rh) were placed in a Schlenk tube under nitrogen. Degassed dioxane (1.0 mL) was added, and the mixture was stirred at 80 °C for 12 h. The reaction mixture was passed through a short column of silica-gel with EtOAc as eluent. The solvent was removed on a rotary evaporator. After further removal of solvent by vacuum pump, the crude ^1H NMR was taken for analysis. The crude product was subjected to silica-gel chromatography (EtOAc/petroleum ether = 1/50) to give **3aa** (23.2 mg, 94% yield).

2.3 General procedure for synthesis of *β,β*-disubstituted acrylonitriles via rhodium-catalyzed cyanation of (1) with NCTS (2a)



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

A general procedure: Arylboronic acid **1** (0.140 mmol, 1.2 equiv), NCTS (32.7 mg, 0.120 mmol, 1.0 equiv), Cs_2CO_3 (39.1 mg, 0.120 mmol, 1.0 equiv) and $[RhCl(cod)]_2$ (1.50 mg, 0.003 mmol, 5 mol% Rh) were placed in a Schlenk tube under nitrogen. Degassed dioxane (1.0 mL) was added, and the mixture was stirred at 80 °C for 12 h. The reaction mixture was passed through a short column of silica-gel with EtOAc as eluent. The solvent was removed on a rotary evaporator. After further removal of solvent by vacuum pump, the crude ^1H NMR was taken for analysis. The crude product was subjected to silica-gel chromatography (EtOAc/petroleum ether = 1/50) to give the corresponding product **3**.

3. Mechanistic considerations

3.1 Isomerization experiments

Table S2. Optimization of Conditions [a]

entry	reactant	catalyst	base	ratio of *Z*/*E*[b]	
				reactant	product
1	(*Z*)-**3va**	$[RhCl(cod)]_2$	Cs_2CO_3 (1 equiv)	100/0	97/3
2	(*Z*)-**3va**	$[RhCl(cod)]_2$	none	100/0	100/0
3	(*Z*)-**3va**	none	Cs_2CO_3 (1 equiv)	100/0	97/3
4	(*Z*)-**3va**	none	none	100/0	100/0
5	(*Z*)-**3va**	none	KOH (1 equiv)	100/0	91/9
6	(*Z*)-**3va**	none	NaOMe (1 equiv)	100/0	34/66
7	(*Z*)-**3va**	none	NaOMe (3 equiv)	100/0	20/80
8	(*Z*)-**3va**	none	NaOMe (5 equiv)	100/0	19/81
9	(*Z*)-**3va**	none	NaOMe (10 equiv)	100/0	19/81
10[c]	(*E*)-**3va**	none	none	0/100	0/100
11[d]	(*E*)-**3va**	none	none	0/100	0/100
12	(*E*)-**3va**	none	NaOMe (10 equiv)	0/100	19/81
13	(*Z*)-**3ba**	none	NaOMe (10 equiv)	100/0	100/0

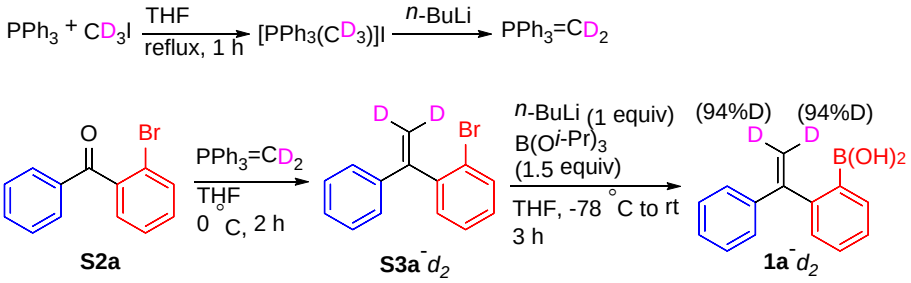
[a] Reaction conditions: **1a** (0.10 mmol), **2a** (0.12 mmol), $[RhCl(cod)]_2$ (5 mol% Rh), Cs_2CO_3 (1.0 equiv), dioxane (1 mL), at 80 °C for 12 h. [b] The ratio of the corresponding *Z*/*E* isomers determined by ^{1}H NMR analysis of the crude reaction mixture. [c] 12 h. [d] 24 h.

A typical procedure for entry 8:

(*Z*)-**3va** (24.1 mg, 0.100 mmol, 1.0 equiv) and NaOMe (27.0 mg, 0.500 mmol, 5.0 equiv) were placed in a Schlenk tube under nitrogen. Degassed dioxane (1.0 mL) was added, and the mixture was stirred at 80 °C for 12 h. The reaction mixture was passed through a short column of silica-gel with EtOAc as eluent. The solvent was removed on a rotary evaporator. After further removal of solvent by vacuum pump, the crude ^{1}H NMR was taken for analysis.

3.2 Control experiments

(a) Synthesis of 1a-*d*$_2$

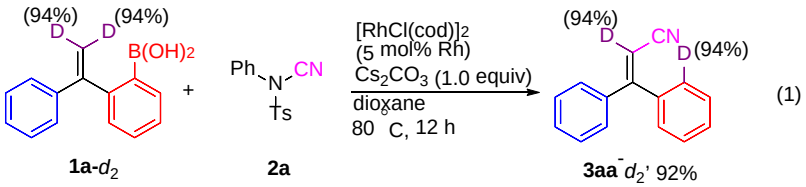


Triphenylphosphine (CAS: 603-35-0) and iodomethane-*d*$_3$ (CAS: 865-50-9) were purchased from commercial company and used as received. The known compounds [PPh$_3$(CD$_3$)]I (CAS: 1560-56-1) and **S3a**-*d*$_2$ (CAS: 2077165-36-5) were prepared according to the reported procedures.[3]

The arylboronic acids **1a**-*d*$_2$ was prepared according to following procedure:

Under argon, to a solution of **S3a**-*d*$_2$ (1.30 g, 4.98 mmol, 1 equiv) in THF (20 mL) was added *n*-BuLi (2.0 mL, 2.5 M in hexane, 4.98 mmol, 1 equiv) dropwise at -78 °C for 30 min. Then a solution of triisopropyl borate (1.41 g, 7.5 mmol, 1.5 equiv) in THF (10 mL) was added slowly. The reaction mixture was warmed to rt naturally and kept stirring for 3 h. Saturated aqueous NH$_4$Cl solution (10 mL) was added and the mixture was extracted with EtOAc (3 × 15 mL). The organic layers were combined, washed with brine and water, and dried over anhydrous Na$_2$SO$_4$. After removal of solvent, the residue was purified by flash chromatography on silica gel (ethyl acetate/ petroleum ether = 1/5) to give **1a**-*d*$_2$ (0.59 g, 53%) (94% D) as a white solid.

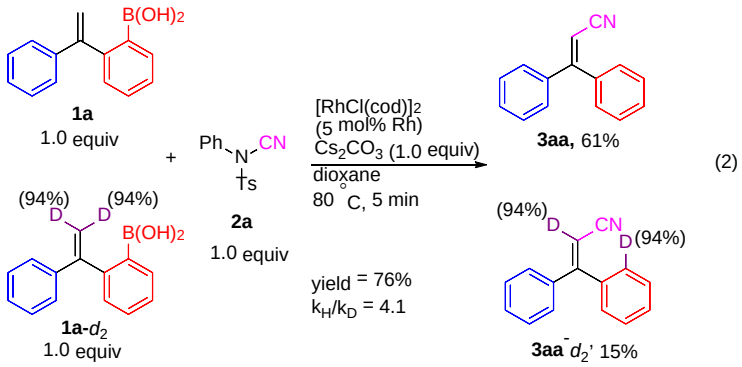
(b) Deuterium-labelling experiment



1a-*d*$_2$ (32.5 mg, 0.140 mmol, 1.2 equiv), NCTS (32.7 mg, 0.120 mmol, 1.0 equiv), Cs$_2$CO$_3$ (39.1 mg, 0.120 mmol, 1.0 equiv) and [RhCl(cod)]$_2$ (1.5 mg, 0.003 mmol, 5 mol% Rh) were placed in a Schlenk tube under nitrogen. Degassed dioxane

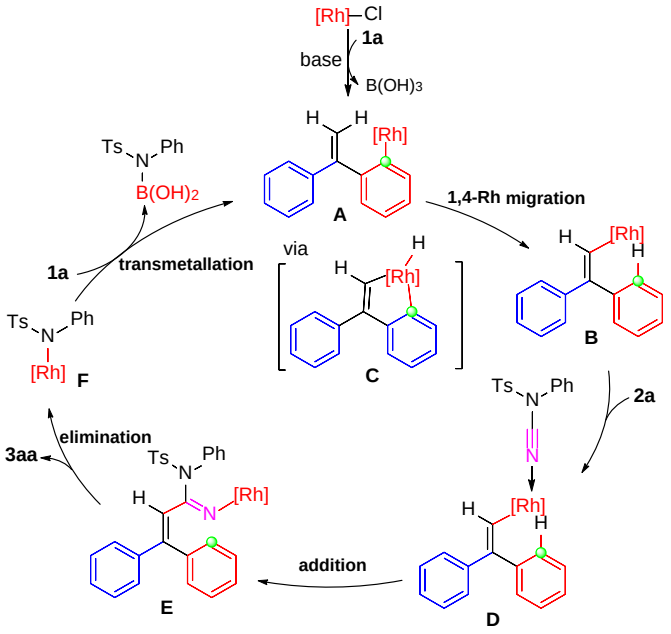
(1.0 mL) was added, and the mixture was stirred at 80 °C for 12 h. The reaction mixture was passed through a short column of silica-gel with EtOAc as eluent. The solvent was removed on a rotary evaporator. After further removal of solvent by vacuum pump, the crude ^{1}H NMR was taken for analysis. The crude product was subjected to silica-gel chromatography (EtOAc/petroleum ether = 1/50) to give **3aa**-d_2 (26.8 mg, 92% yield) (94% D).

(c) Intermolecular competition experiment



Arylboronic acid **1a** (32.3 mg, 0.140 mmol, 1.2 equiv), **1a**-d_2 (32.5 mg, 0.140 mmol, 1.2 equiv), NCTS (32.7 mg, 0.120 mmol, 1.0 equiv), Cs_2CO_3 (39.1 mg, 0.120 mmol, 1.0 equiv) and $[RhCl(cod)]_2$ (1.5 mg, 0.003 mmol, 5 mol% Rh) were placed in a Schlenk tube under nitrogen. Degassed dioxane (1.0 mL) was added, and the mixture was stirred at 80 °C for 5 min. The reaction mixture was passed through a short column of silica-gel with EtOAc as eluent. The solvent was removed on a rotary evaporator. After further removal of solvent by vacuum pump, the crude ^{1}H NMR was taken for analysis. The crude product was subjected to silica-gel chromatography (EtOAc/petroleum ether = 1/50) to give **3aa** (15.1 mg, 61%) and **3aa**-d_2 (4.4 mg, 15% yield) (94% D).

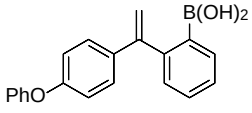
3.3 Proposed Catalytic Cycle



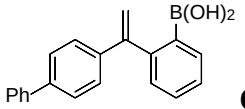
Scheme S2. Proposed mechanism for the cyanation of arylboronic acids by 1,4-rhodium migration

A catalytic cycle for the reaction of **1a** and **2a** producing **3aa** is illustrated in Scheme S2. Aryl-Rh species **A** which is generated by the transmetallation of **1a** with $[RhCl(cod)]_2$ in the presence of a base readily undergoes 1,4-Rh migration to give the alkenyl-Rh species **B**. The driving force of the migration may be attributed to the less congested vinyl position compared with the original aryl position. The coordination of **2a** with **B** facilitates the addition of alkenyl-Rh into the carbon-nitrogen triple bond to give the intermediate **E**, which followed by elimination to give the product **3aa**, leaving a [Rh]-N complex **F**. Finally, the [Rh]-N complex undergoes transmetalation with **1a** to regenerate aryl−Rh species **A** closing the catalytic cycle.

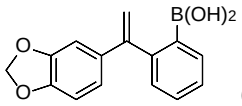
4. Characterization of the substrates



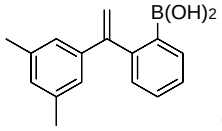
Compound 1g. Following the general procedure, the product **1g** was prepared (from **S1g**) and purified by flash column chromatography (eluent: EtOAc/petroleum ether = 1/5) as a yellow liquid (0.88 g, 43% yield) (It undergoes dehydrate partially to give a mixture of arylboronic acid and corresponding arylboroxine). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.95 (d, *J* = 7.4 Hz, 1H), 7.45 (dd, *J* = 7.4 Hz, 7.2 Hz, 1H), 7.38 (dd, *J* = 7.3 Hz, 7.2 Hz, 1H), 7.34 (dd, *J* = 7.9 Hz, 7.5 Hz, 2H), 7.27 (d, *J* = 7.9 Hz, 2H), 7.21 (d, *J* = 7.3 Hz, 1H), 7.12 (t, *J* = 7.5 Hz, 1H), 7.02 (d, *J* = 8.5 Hz, 2H), 6.92 (d, *J* = 8.5 Hz, 2H), 5.85 (s, 1H), 5.28 (s, 1H), 4.91 (s, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) (mixed with its corresponding arylboroxine) δ 157.7, 156.8, 156.7, 150.5, 150.2, 148.8, 146.8, 136.7, 135.9, 135.1, 134.5, 131.3, 130.6, 129.8, 129.7, 129.6, 128.6, 128.5, 126.7, 123.3, 119.3, 119.0, 118.4, 118.0, 114.1, 112.9. **HRMS** (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{20}H_{17}BO_3H^+$ 317.1344; Found 317.1348; deviation: -1.27 ppm.



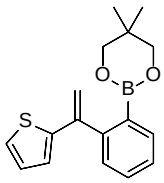
Compound 1h. Following the general procedure, the product **1h** was prepared (from **S1h**) and purified by flash column chromatography (eluent: EtOAc/petroleum ether = 1/5) as a yellow solid (0.83 g, 51% yield) (It undergoes dehydrate partially to give a mixture of arylboronic acid and corresponding arylboroxine). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.94 (dd, *J* = 7.4 Hz, 1.3 Hz, 1H), 7.59-7.53 (m, 3H), 7.49-7.41 (m, 3H), 7.40-7.33 (m, 3H), 7.26-7.24 (m, 3H), 5.98 (d, *J* = 0.9 Hz, 1H), 5.37 (d, *J* = 0.9 Hz, 1H), 4.81 (s, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) (mixed with its corresponding arylboroxine) δ 150.8, 150.5, 148.5, 146.7, 141.2, 140.6, 140.4, 140.3, 139.9, 138.5, 135.9, 135.2, 131.2, 130.6, 129.8, 129.6, 128.8, 128.7, 127.5, 127.4, 127.3, 127.2, 127.1, 127.0, 126.9, 126.6, 126.5, 115.1, 113.7. **HRMS** (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{20}H_{17}BO_2H^+$ 301.1394; Found 301.1399; deviation: -1.67 ppm.



Compound 1l. Following the general procedure, the product **1l** was prepared (from **S1l**) and purified by flash column chromatography (eluent: EtOAc/petroleum ether = 1/5) as a yellow liquid (1.27 g, 81% yield) (It undergoes dehydrate partially to give a mixture of arylboronic acid and corresponding arylboroxine). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.91 (d, *J* = 7.4 Hz, 1H), 7.46-7.44 (m, 1H), 7.40-7.37 (m, 1H), 7.20 (d, *J* = 7.6 Hz, 1H), 6.87 (s, 1H), 6.73-6.68 (m, 2H), 5.96 (s, 2H), 5.79 (s, 1H), 5.23 (s, 1H), 4.80 (s, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) (mixed with its corresponding arylboroxine) δ 161.94, 161.93, 147.6, 146.8, 137.8, 131.7,131.6, 131.3, 130.6, 127.4, 121.74, 121.73, 121.6, 118.71, 118.70, 118.6, 107.8, 107.7, 106.5, 106.4, 101.0, 86.9, 28.8. **HRMS** (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{15}H_{13}BO_4H^+$ 269.0980; Found 269.0981; deviation: -0.37 ppm.

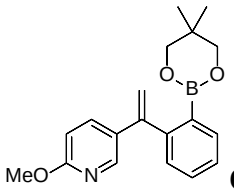


Compound 1m. Following the general procedure, the product **1m** was prepared (from **S1m**) and purified by flash column chromatography (eluent: EtOAc/petroleum ether = 1/5) as a yellow liquid (1.26 g, 72% yield) (It undergoes dehydrate partially to give a mixture of arylboronic acid and corresponding arylboroxine). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.93 (d, *J* = 7.4 Hz, 1H), 7.46-7.43 (m, 1H), 7.39 (ddd, *J* = 7.5 Hz, 7.4 Hz, 1.4 Hz, 1H), 7.19 (dd, *J* = 7.6 Hz, 1.0 Hz, 1H), 6.95 (s, 1H), 6.92 (s, 2H), 5.89 (d, *J* = 1.3 Hz, 1H), 5.29 (d, *J* = 1.3 Hz, 1H), 4.89 (s, 2H), 2.25 (s, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) (mixed with its corresponding arylboroxine) δ 151.2, 148.8, 141.7, 137.2, 135.7, 130.8, 129.7, 128.9, 126.4, 125.3, 124.9, 113.8, 21.1. **HRMS** (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{16}H_{17}BO_2H^+$ 253.1394; Found 253.1393; deviation: 0.40 ppm.

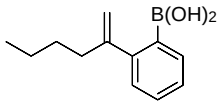


Compound 1n. Following the general procedure, the product **1n** was prepared (from **S1n**) and purified by flash column chromatography (eluent: EtOAc/petroleum ether = 1/5) as a red liquid (1.18 g, 60% yield). **^{1}H NMR** (500 MHz,

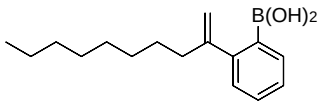
$CDCl_3$) δ 7.43 (d, *J* = 3.6 Hz, 2H), 7.42 (d, *J* = 1.8 Hz, 1H), 7.38-7.33 (m, 3H), 6.96 (d, *J* = 3.6 Hz, 1H), 5.65 (s, 1H), 5.27 (s, 1H), 3.76 (s, 4H), 1.03 (s, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 150.5, 145.7, 143.5, 141.0, 135.9, 133.6, 129.8, 128.3, 128.0, 127.1, 125.7, 114.3, 72.4, 32.0, 21.9. **HRMS** (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{17}H_{19}BO_2SH^+$ 298.1308; Found 298.1317; deviation: -3.07 ppm.



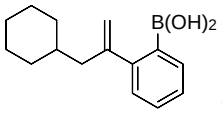
Compound 1o. Following the general procedure, the product **1o** was prepared (from **S1o**) and purified by flash column chromatography (eluent: EtOAc/petroleum ether = 1/5) as a red liquid (1.09 g, 65% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.13 (d, *J* = 2.1 Hz, 1H), 7.67 (d, *J* = 7.2 Hz, 1H), 7.42-7.38 (m, 2H), 7.33-7.31 (m, 2H), 6.64 (d, *J* = 8.7 Hz, 1H), 5.50 (s, 1H), 5.21 (s, 1H), 3.92 (s, 3H), 3.47 (s, 4H), 0.75 (s, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 163.3, 149.2, 145.5, 137.6, 134.0, 132.1, 129.9, 129.7, 128.3, 128.0, 127.0, 113.1, 109.8, 72.0, 53.4, 31.4, 21.6. **HRMS** (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{19}H_{22}BNO_3H^+$ 346.1585; Found 346.1580; deviation: 1.55 ppm.



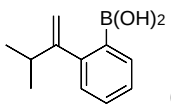
Compound 1u. Following the general procedure, the product **1u** was prepared (from **S1u**) and purified by flash column chromatography (eluent: EtOAc/petroleum ether = 1/5) as a yellow liquid (539 mg, 34% yield) (It undergoes dehydrate partially to give a mixture of arylboronic acid and corresponding arylboroxine). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.93 (d, *J* = 7.4 Hz, 1H), 7.42 (dd, *J* = 7.6, 7.5 Hz, 1H), 7.33 (dd, *J* = 7.5, 7.4 Hz, 1H), 7.14 (d, *J* = 7.6 Hz, 1H), 5.85 (s, 2H), 5.32 (s, 1H), 5.11 (s, 1H), 2.45-2.41 (m, 2H), 1.46-1.42 (m, 2H), 1.39-1.34 (m, 2H), 0.91 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) (mixed with its corresponding arylboroxine) δ 154.5, 152.9, 151.3, 148.9, 136.2, 135.1, 131.2, 130.4, 128.4, 127.8, 126.7, 126.1, 114.1, 112.2, 38.9, 38.5, 30.2, 30.0, 22.6, 22.5, 14.0, 13.9. **HRMS** (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{12}H_{17}BO_2H^+$ 227.1214; Found 227.1217; deviation: -1.47 ppm.



Compound 1v. Following the general procedure, the product **1v** was prepared (from **S1v**) and purified by flash column chromatography (eluent: EtOAc/petroleum ether = 1/5) as a white liquid (410 mg, 32% yield) (It undergoes dehydrate partially to give a mixture of arylboronic acid and corresponding arylboroxine). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.90 (d, *J* = 7.4 Hz, 1H), 7.40 (ddd, *J* = 7.6 Hz, 7.5 Hz, 1.5 Hz, 1H), 7.32 (dd, *J* = 7.5 Hz, 7.4 Hz, 1.5 Hz, 1H), 7.12 (d, *J* = 7.6 Hz, 1H), 5.49 (s, br, 2H), 5.31 (d, *J* = 1.7 Hz, 1H), 5.09 (d, *J* = 1.7 Hz, 1H), 2.40 (t, *J* = 7.8 Hz, 2H), 1.45-1.41 (m, 2H), 1.30-1.26 (m, 10H), 0.87 (t, *J* = 7.0 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) (mixed with its corresponding arylboroxine) δ 153.0, 151.3, 136.3, 131.2, 128.4, 128.2, 126.1, 112.2, 38.8, 31.9, 29.6, 29.5, 29.3, 28.0, 22.6, 14.1. **HRMS** (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{16}H_{25}BO_2H^+$ 261.2020; Found 261.2022; deviation: -0.77 ppm.

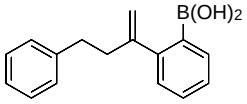


Compound 1w. Following the general procedure, the product **1w** was prepared (from **S1w**) and purified by flash column chromatography (eluent: EtOAc/petroleum ether = 1/5) as a yellow liquid (374 mg, 40% yield) (It undergoes dehydrate partially to give a mixture of arylboronic acid and corresponding arylboroxine). **^{1}H NMR** (500 MHz, $CDCl_3$) (mixed with its corresponding arylboroxine) δ 7.88 (d, *J* = 7.4 Hz, 1H), 7.41 (dd, *J* = 7.5, 7.4 Hz, 1H), 7.32 (m, 1H), 7.12 (d, *J* = 7.7 Hz, 1H), 5.29 (s, 1H), 5.28 (s, 2H), 5.14 (s, 1H), 2.32-2.30 (m, 2H), 1.69-1.65 (m, 5H), 1.31-1.27 (m, 1H), 1.10-1.07 (m, 3H), 0.88-0.84 (m, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) (mixed with its corresponding arylboroxine) δ 151.1, 150.9, 136.3, 131.2, 128.5, 126.1, 113.8, 47.2, 35.7, 33.4, 33.2, 26.6, 26.2. **HRMS** (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{15}H_{21}BO_2Na^+$ 267.1527; Found 267.1522; deviation: 0.15 ppm.

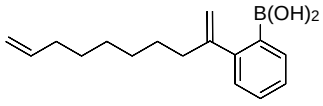


Compound 1x. Following the general procedure, the product **1x** was prepared (from **S1x**) and purified by flash column chromatography (eluent: EtOAc/petroleum ether = 1/5) as a yellow liquid (317 mg, 43% yield) (It undergoes

dehydrate partially to give a mixture of arylboronic acid and corresponding arylboroxine). **^{1}H NMR** (500 MHz, $CDCl_3$) (mixed with its corresponding arylboroxine) δ 7.96 (d, *J* = 7.4 Hz, 1H), 7.37 (dd *J* = 7.4, 7.0 Hz, 1H), 7.31 (dd, *J* = 7.7, 7.0 Hz, 1H), 7.01 (d, *J* = 7.7 Hz, 1H), 5.57 (s, 2H), 5.07 (s, 1H), 4.87 (s, 1H), 2.55-2.50 (m, 1H), 1.02 (d, *J* = 6.9 Hz, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) (mixed with its corresponding arylboroxine) δ 160.4, 158.1, 151.1, 148.8, 136.2, 135.1, 130.9, 130.2, 128.7, 128.2, 126.6, 126.0, 111.9, 110.3, 36.1, 35.3, 21.5, 21.4. **HRMS** (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{11}H_{15}BO_2H^+$ 191.1238; Found 191.1237; deviation: 0.53 ppm.

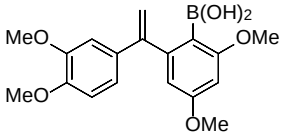


Compound 1y. Following the general procedure, the product **1y** was prepared (from **S1y**) and purified by flash column chromatography (eluent: EtOAc/petroleum ether = 1/5) as a yellow liquid (521 mg, 55% yield) (It undergoes dehydrate partially to give a mixture of arylboronic acid and corresponding arylboroxine). **^{1}H NMR** (500 MHz, $CDCl_3$) (mixed with its corresponding arylboroxine) δ 7.87 (d, *J* = 7.4 Hz, 1H), 7.50 (dd, *J* = 7.6, 7.4 Hz, 1H), 7.39-7.36 (m, 1H), 7.21-7.13 (m, 4H), 7.07 (d, *J* = 7.1 Hz, 2H), 5.34 (s, 1H), 5.13 (s, 1H), 4.91 (s, 2H), 2.83-2.80 (m, 4H). **^{13}C NMR** (126 MHz, $CDCl_3$) (mixed with its corresponding arylboroxine) δ 152.7, 152.1, 150.9, 147.9, 142.0, 141.0, 136.3, 135.2, 131.4, 130.3, 128.5, 128.4, 128.3, 128.24, 128.22, 127.6, 126.9, 126.4, 126.1, 125.7, 115.2, 112.8, 40.5, 40.0, 34.3, 33.9. **HRMS** (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{16}H_{17}BO_2H^+$ 253.1394; Found 253.1404; deviation: 3.97 ppm.



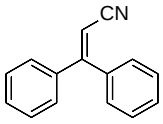
Compound 1z. Following the general procedure, the product **1z** was prepared (from **S1z**) and purified by flash column chromatography (eluent: EtOAc/petroleum ether = 1/5) as a yellow liquid (366 mg, 49% yield) (It undergoes dehydrate partially to give a mixture of arylboronic acid and corresponding arylboroxine). **^{1}H NMR** (500 MHz, $CDCl_3$) (mixed with its corresponding arylboroxine) δ 8.05 (d, *J* = 7.4 Hz, 1H), 7.48 (dd, *J* = 7.5, 7.4 Hz, 1H), 7.43-7.40 (m, 1H), 7.27-7.23 (m, 1H), 5.82-5.86 (m, 2H), 5.30 (s, 1H), 5.28 (s, 1H), 5.16 (s, 1H),

4.93 (s, 2H), 2.53-2.49 (m, 2H), 2.01-1.98 (m, 2H), 1.33-1.29 (m, 8H). **^{13}C NMR** (126 MHz, $CDCl_3$) (mixed with its corresponding arylboroxine) δ 154.4, 152.9, 151.2, 148.9, 139.1, 139.0, 136.2, 135.1, 131.2, 130.4, 128.4, 127.8, 126.7, 126.1, 114.2, 114.1, 112.3, 39.2, 38.8, 33.74, 33.70, 29.2, 29.0, 28.9, 28.8, 28.7, 27.9, 27.8. **HRMS** (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{16}H_{23}BO_2Na^+$ 281.1683; Found 261.1686; deviation: -1.16 ppm.

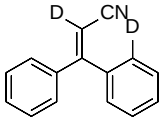


Compound 1#. Following the general procedure, the product **1#** was prepared (from **S1#**) and purified by flash column chromatography (eluent: EtOAc/petroleum ether = 1/5) as a yellow liquid (62 mg, 5% yield) (It undergoes dehydrate partially to give a mixture of arylboronic acid and corresponding arylboroxine). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 6.95 (s, 1H), 6.76 (s, 1H), 6.74 (s, 1H), 6.49 (d, *J* = 2.2 Hz, 1H), 6.40 (d, *J* = 2.2 Hz, 1H), 5.96 (s, 2H), 5.79 (s, 1H), 5.22 (s, 1H), 3.91 (s, 3H), 3.87 (s, 3H), 3.83 (s, 3H), 3.81 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 165.7, 162.1, 150.9, 150.7, 149.5, 148.9, 132.1, 120.3, 113.1, 110.8, 109.5, 108.0, 97.5, 55.90, 55.86, 55.8, 55.4. **HRMS** (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{15}H_{21}BO_2Na^+$ 267.1527; Found 267.1522; deviation: 0.15 ppm.

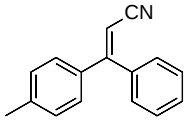
5. Characterization of the Products



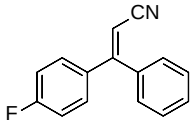
Compound 3aa (CAS: 3531-24-6).[5] Following the general procedure, the product **3aa** was prepared and purified by flash column chromatography (eluent: EtOAc/petroleum ether = 1/50) as a yellow liquid (23.2 mg, 94% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.49-7.40 (m, 6H), 7.39 (dd, *J* = 8.0 Hz, 7.3 Hz, 2H), 7.32-7.30 (m, 2H), 5.75 (s, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 163.2, 139.0, 137.1, 130.5, 130.1, 129.6, 128.7, 128.6, 128.5, 118.0, 95.0. **HRMS** (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{15}H_{11}NH^+$ 206.0964; Found 206.0963; deviation: 0.61 ppm.



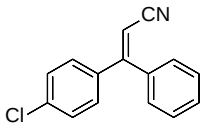
Compound 3aa-d_2. Following equation (1), the product **3aa-d_2** was prepared and purified by flash column chromatography (eluent: EtOAc/petroleum ether = 1/50) as a yellow liquid (22.9 mg, 92% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.49-7.40 (m, 5H), 7.38 (dd, *J* = 8.0 Hz, 7.3 Hz, 2H), 7.32-7.30 (m, 2H), 5.75 (s, 0.06H). **^{2}H NMR** (77 MHz, $CHCl_3$) δ 7.48 (s, 1D), 5.75 (s, 1D). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 163.0, 138.8, 136.9, 130.4, 130.0, 129.5, 128.6, 128.5, 128.41, 128.38, 117.8. **HRMS** (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{15}H_9D_2NH^+$ 208.1090; Found 208.1083; deviation: 3.28 ppm.



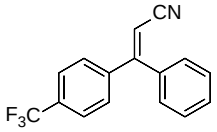
Compound 3ba (CAS: 176445-14-0).[6] Following the general procedure, the product **3ba** was prepared and purified by flash column chromatography (eluent: EtOAc/petroleum ether = 1/50) as a yellow liquid (26.1 mg, 99% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.49-7.41 (m, 5H), 7.21-7.17 (m, 4H), 5.72 (s, 1H), 2.39 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 163.1, 140.9, 137.3, 136.1, 130.0, 129.6, 129.4, 128.54, 128.45, 118.1, 94.0, 21.4. **HRMS** (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{16}H_{13}NH^+$ 220.1121; Found 220.1114; deviation: 3.08 ppm.



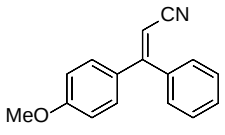
Compound 3ca (CAS: 854278-57-2).[7] Following the general procedure, the product **3ca** was prepared and purified by flash column chromatography (eluent: EtOAc/petroleum ether = 1/50) as a yellow liquid (22.5 mg, 84% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.49-7.41 (m, 5H), 7.30 (dd, *J* = 8.9 Hz, 5.3 Hz, 2H), 7.07 (dd, *J* = 8.9 Hz, 8.9 Hz, 2H), 5.70 (s, 1H). **^{19}F NMR** (471 MHz, $CDCl_3$) δ -109.67 (m). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 164.1 (d, *J* = 252.2 Hz), 162.0, 136.9, 135.1 (d, *J* = 3.3 Hz), 130.5 (d, *J* = 8.6 Hz), 130.2, 129.5, 128.7, 117.8, 115.9 (d, *J* = 21.9 Hz), 94.8 (d, *J* = 1.3 Hz). **HRMS** (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{15}H_{10}FNH^+$ 224.0870; Found 224.0865; deviation: 2.26 ppm.



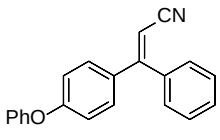
Compound 3da (CAS: 198996-03-1).[7] Following the general procedure, the product **3da** was prepared and purified by flash column chromatography (eluent: EtOAc/petroleum ether = 1/50) as a yellow liquid (25.3 mg, 88% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.49-7.44 (m, 3H), 7.43-7.41 (m, 2H), 7.36 (d, *J* = 8.5 Hz, 2H), 7.24 (d, *J* = 8.5, 2H), 5.73 (s, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 161.9, 137.4, 136.7, 136.6, 130.3, 129.8, 129.5, 129.0, 128.7, 117.6, 95.3. **HRMS** (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{15}H_{10}ClNH^+$ 240.0575; Found 240.0568; deviation: 2.73 ppm.



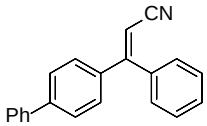
Compound 3ea (CAS: 198996-06-4).[7] Following the general procedure, the product **3ea** was prepared and purified by flash column chromatography (eluent: EtOAc/petroleum ether = 1/50) as a yellow liquid (23.6 mg, 72% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.65 (d, *J* = 8.2 Hz, 2H), 7.50-7.45 (m, 3H), 7.43-7.41 (m, 4H), 5.78 (s, 1H). **^{19}F NMR** (471 MHz, $CDCl_3$) δ -62.89 (s). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 161.6, 142.5, 136.3, 132.1 (q, *J* = 32.9 Hz), 130.5, 129.5, 128.9, 128.8, 125.7 (q, *J* = 3.7 Hz), 123.7 (q, *J* = 272.9 Hz), 117.3, 96.8. **HRMS** (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{16}H_{10}F_3NH^+$ 274.0838; Found 274.0829; deviation: 3.33 ppm.



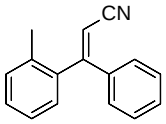
Compound 3fa (CAS: 170879-13-7).[7] Following the general procedure, the product **3fa** was prepared and purified by flash column chromatography (eluent: EtOAc/petroleum ether = 1/50) as a yellow liquid (26.5 mg, 94% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.44 (dd, *J* = 7.4, 7.2 Hz, 1H), 7.39-7.35 (m, 3H), 7.32-7.30 (m, 2H), 7.03-6.99 (m, 2H), 6.97-6.95 (m, 1H), 5.74 (s, 1H), 3.82 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 162.7, 161.6, 137.3, 131.2, 130.0, 129.9, 129.6, 128.5, 118.4, 114.1, 92.8, 55.5. **HRMS** (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{16}H_{13}NOH^+$ 236.1070; Found 236.1079; deviation: -3.87 ppm.



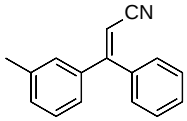
Compound 3ga. Following the general procedure, the product **3ga** was prepared and purified by flash column chromatography (eluent: EtOAc/petroleum ether = 1/50) as a yellow solid (35.0 mg, 98% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.49-7.43 (m, 5H), 7.39 (dd, *J* = 8.5, 7.5 Hz, 2H), 7.28-7.26 (m, 2H), 7.19 (t, *J* = 7.5 Hz, 1H), 7.07 (d, *J* = 8.8 Hz, 2H), 6.97 (d, *J* = 8.8 Hz, 2H), 5.71 (s, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 162.3, 159.8, 155.8, 137.0, 133.1, 130.1, 130.0, 129.9, 129.5, 128.5, 124.3, 119.8, 118.0, 117.9, 93.6. **HRMS** (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{21}H_{15}NOH^+$ 298.1126; Found 298.1122; deviation: 1.48 ppm.



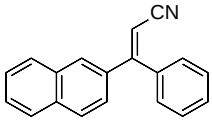
Compound 3ha. Following the general procedure, the product **3ha** was prepared and purified by flash column chromatography (eluent: EtOAc/petroleum ether = 1/50) as a yellow solid (33.4 mg, 99% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.63-7.61 (m, 4H), 7.50-7.46 (m, 7H), 7.42-7.38 (m, 3H), 5.81 (s, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 162.7, 143.2, 139.8, 137.6, 137.0, 130.0, 129.5, 128.90, 128.89, 128.5, 128.0, 127.2, 127.0, 117.9, 94.5. **HRMS** (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{21}H_{15}NH^+$ 282.1277; Found 282.1277; deviation: 0.09 ppm.



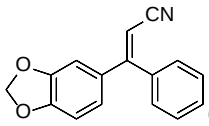
Compound 3ia (CAS: 1391868-32-8).[8] Following the general procedure, the product **3ia** was prepared and purified by flash column chromatography (eluent: EtOAc/petroleum ether = 1/50) as a yellow solid (25.6 mg, 82% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.50-7.48 (m, 2H), 7.42-7.38 (m, 3H), 7.33 (t, *J* = 7.4 Hz, 1H), 7.27-7.24 (m, 1H), 7.21 (dd, *J* = 8.5, 8.0 Hz, 2H), 5.49 (s, 1H), 1.99 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 163.6, 139.6, 137.1, 136.1, 130.9, 130.2, 129.5, 129.4, 128.7, 126.0, 117.7, 96.8, 20.2. **HRMS** (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{16}H_{13}NH^+$ 220.1121; Found 220.1121; deviation: -0.11 ppm.



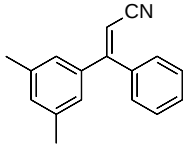
Compound 3ja. Following the general procedure, the product **3ja** was prepared and purified by flash column chromatography (eluent: EtOAc/petroleum ether = 1/50) as a yellow liquid (23.2 mg, 88% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.47-7.40 (m, 5H), 7.25-7.23 (m, 2H), 7.09 (s, 1H), 7.08-7.05 (m, 1H), 5.71 (s, 1H), 2.33 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 163.3, 138.9, 138.4, 137.1, 131.2, 129.9, 129.5, 129.0, 128.5, 128.4, 125.7, 117.9, 94.6, 21.3. **HRMS** (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{16}H_{13}NH^+$ 220.1121; Found 220.1128; deviation: -3.30 ppm.



Compound 3ka (CAS: 1201634-42-5).[7] Following the general procedure, the product **3ka** was prepared and purified by flash column chromatography (eluent: EtOAc/petroleum ether = 1/50) as a yellow liquid (25.4 mg, 83% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.85 (t, *J* = 8.9 Hz, 2H), 7.81 (d, *J* = 8.0 Hz, 1H), 7.75 (s, 1H), 7.57-7.49 (m, 7H), 7.42 (dd, *J* = 8.6 Hz, 1.9 Hz, 1H), 5.88 (s, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 163.1, 137.1, 136.2, 134.1, 132.9, 130.1, 129.7, 129.1, 128.8, 128.7, 128.5, 127.7, 127.6, 126.9, 125.0, 118.0, 95.2. **HRMS** (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{19}H_{13}NH^+$ 256.1121; Found 256.1115; deviation: 2.26 ppm.

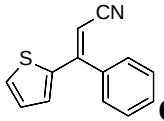


Compound 3la. Following the general procedure, the product **3la** was prepared and purified by flash column chromatography (eluent: EtOAc/petroleum ether = 1/50) as a yellow liquid (22.1 mg, 74% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.47-7.43 (m, 3H), 7.42-7.40 (m, 2H), 6.80-6.79 (m, 2H), 6.78 (s, 1H), 6.01 (s, H), 5.65 (s, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 162.6, 149.7, 148.1, 137.1, 132.9, 130.0, 129.5, 128.5, 123.5, 118.1, 108.3, 101.7, 93.4. **HRMS** (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{16}H_{11}NO_2H^+$ 250.0863; Found 250.0863; deviation: 0.62 ppm.

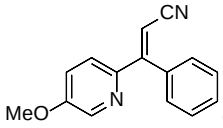


Compound 3ma. Following the general procedure, the product **3ma**

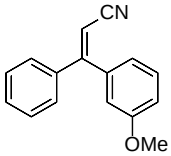
was prepared and purified by flash column chromatography (eluent: EtOAc/petroleum ether = 1/50) as a yellow liquid (21.6 mg, 77% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.48-7.42 (m, 5H), 7.08 (s, 1H), 6.90 (s, 2H), 5.71 (s, 1H), 2.31 (s, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 163.5, 139.0, 138.2, 137.2, 132.1, 129.9, 129.5, 128.4, 126.3, 118.0, 94.5, 21.2. **HRMS** (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{17}H_{15}NH^+$ 234.1277; Found 234.1274; deviation: 1.40 ppm.



Compound 3na. Following the general procedure, the product **3na** was prepared and purified by flash column chromatography (eluent: EtOAc/petroleum ether = 1/50) as a red liquid (17.2 mg, 68% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.50-7.48 (m, 5H), 7.46-7.43 (m, 1H), 7.07-7.04 (m, 1H), 7.03-7.00 (m, 1H), 5.78 (s, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 155.8, 142.0, 136.3, 130.8, 130.1, 129.3, 129.1, 128.5, 128.3, 117.6, 92.8. **HRMS** (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{13}H_9NSH^+$ 212.0528; Found 212.0525; deviation: 1.64 ppm.

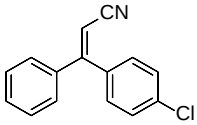


Compound 3oa. Following the general procedure, the product **3oa** was prepared and purified by flash column chromatography (eluent: EtOAc/petroleum ether = 1/50) as a red liquid (27.8 mg, 98% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.12 (d, *J* = 2.3 Hz, 1H), 7.49-7.41 (m, 6H), 6.73 (d, *J* = 8.7 Hz, 1H), 5.68 (s, 1H), 3.96 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 165.4, 159.9, 147.1, 138.1, 136.3, 130.2, 129.3, 128.7, 127.9, 117.7, 110.9, 93.6, 53.8. **HRMS** (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{15}H_{12}N_2OH^+$ 237.1022; Found 237.1015; deviation: 3.13 ppm.

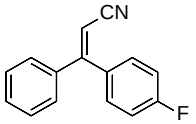


Compound 3pa (CAS: 920317-68-6).[9] Following the general procedure, the product **3pa** was prepared and purified by flash column chromatography (eluent: EtOAc/petroleum ether = 1/50) as a yellow liquid (18.6 mg, 66% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.46-7.40 (m, 5H), 7.26-7.24 (m, 2H), 6.88 (d, *J* = 8.8 Hz, 2H), 5.67 (s, 1H), 3.83 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 163.0, 159.5, 138.8, 138.3,

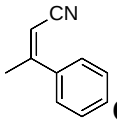
130.5, 129.7, 128.7, 128.5, 122.0, 117.8, 115.9, 114.9, 95.0, 55.4. **HRMS** (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{16}H_{13}NOH^+$ 236.1070; Found 236.1073; deviation: -1.32 ppm.



Compound 3qa (CAS: 198996-08-6).[10] Following the general procedure, the product **3qa** was prepared and purified by flash column chromatography (eluent: EtOAc/petroleum ether = 1/50) as a yellow liquid (21.6 mg, 75% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.45-7.41 (m, 3H), 7.40-7.38 (m, 4H), 7.29-7.26 (m, 2H), 5.75 (s, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 162.0, 138.5, 136.3, 135.5, 131.0, 130.7, 129.0, 128.8, 128.4, 117.7, 95.3. **HRMS** (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{15}H_{10}ClNH^+$ 240.0575; Found 240.0571; deviation: 1.48 ppm.

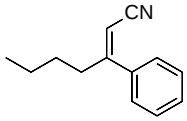


Compound 3ra (CAS: 1201634-38-9).[7] Following the general procedure, the product **3ra** was prepared and purified by flash column chromatography (eluent: EtOAc/petroleum ether = 1/50) as a yellow liquid (20.1 mg, 75% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.47-7.43 (m, 3H), 7.39 (dd, *J* = 7.8, 7.4 Hz, 2H), 7.29 (d, *J* = 7.4 Hz, 2H), 7.15 (t, *J* = 8.7 Hz, 2H), 5.72 (s, 1H). **^{19}F NMR** (471 MHz, $CDCl_3$) δ -110.03 (m). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 163.7 (d, *J* = 251.3 Hz), 162.11, 138.8, 133.1 (d, *J* = 3.4 Hz), 131.7 (d, *J* = 8.6 Hz), 130.6, 128.8, 128.5, 117.8, 115.8 (d, *J* = 21.9 Hz), 95.0. **HRMS** (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{15}H_{10}FNH^+$ 224.0870; Found 224.0872; deviation: -0.88 ppm.

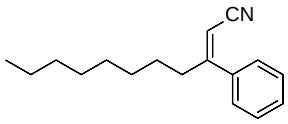


Compound 3ta (CAS: 14799-79-2).[11] Following the general procedure, the product **3ta** was prepared (*Z*/*E* = 96/4 from ^{1}H NMR analysis of crude reaction mixture) and purified by flash column chromatography (eluent: EtOAc/petroleum ether = 1/50) as a yellow liquid (12.7 mg, 74% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.55-7.53 (m, 2H), 7.45-7.42 (m, 3H), 5.40 (s, 1H), 2.28 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 161.1, 137.9, 129.9, 128.7, 127.1, 117.6, 95.5, 24.7. **HRMS** (ESI-TOF) m/z:

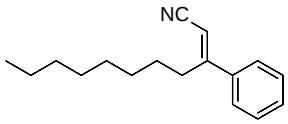
$[M+H]^+$ Calcd for $C_{10}H_9NH^+$ 144.0808; Found 144.0812; deviation: -2.97 ppm.



Compound 3ua (CAS: 67231-21-4).[12] Following the general procedure, the product **3ua** was prepared (*Z*/*E* = 96/4 from ^{1}H NMR analysis of crude reaction mixture) and purified by flash column chromatography (eluent: EtOAc/petroleum ether = 1/50) as a yellow liquid (17.8 mg, 80% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.45-7.40 (m, 5H), 5.37 (s, 1H), 2.57 (t, *J* = 6.8 Hz, 2H), 1.41-1.30 (m, 4H), 0.88 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 166.2, 137.6, 129.6, 128.7, 127.3, 117.6, 95.2, 37.9, 29.8, 22.1, 13.7. **HRMS** (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{13}H_{15}NH^+$ 186.1277; Found 186.1279; deviation: -0.94 ppm.

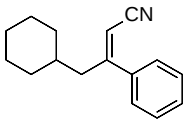


Compound (*Z*)-**3va**. Following the general procedure, the product (*Z*)-**3va** was prepared (*Z*/*E* = 97/3 from ^{1}H NMR analysis of crude reaction mixture) and purified by flash column chromatography (eluent: EtOAc/petroleum ether = 1/50) as a yellow liquid (27.5 mg, 95% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.45-7.40 (m, 5H), 5.37 (s, 1H), 2.56 (t, *J* = 7.5 Hz, 2H), 1.42-1.36 (m, 2H), 1.30-1.24 (m, 10H), 0.87 (t, *J* = 7.0 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 166.2, 137.6, 129.6, 128.7, 127.3, 117.6, 95.2, 38.2, 31.8, 29.2, 29.1, 29.0, 27.7, 22.6, 14.1. **HRMS** (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{17}H_{23}NH^+$ 242.1903; Found 242.1902; deviation: 0.52 ppm.

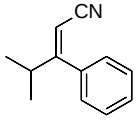


Compound (*E*)-**3va**. Following the general procedure, the product (*E*)-**3va** was prepared (*Z*/*E* = 97/3 from ^{1}H NMR analysis of crude reaction mixture) and purified by flash column chromatography (eluent: EtOAc/petroleum ether = 1/50) as a yellow liquid (0.8 mg, 3% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.42-7.39 (m, 5H), 5.49 (s, 1H), 2.88 (t, *J* = 7.7 Hz, 2H), 1.50-1.44 (m, 2H), 1.38-1.22 (m, 10H), 0.87 (t, *J* = 7.0 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 165.2, 137.7, 129.9, 128.8, 126.2, 117.4, 95.6, 33.9, 31.7, 29.2, 29.13, 29.05, 28.4, 22.6, 14.0.

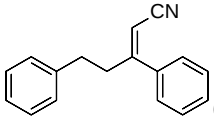
HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{17}H_{23}NH^+$ 242.1903; Found 242.1898; deviation: 2.18 ppm.



Compound 3wa. Following the general procedure, the product **3wa** was prepared (*Z*/*E* = 97/3 from ^{1}H NMR analysis of crude reaction mixture) and purified by flash column chromatography (eluent: EtOAc/petroleum ether = 1/50) as a white solid (25.7 mg, 95% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.45-7.40 (m, 5H), 5.34 (s, 1H), 2.45 (d, *J* = 7.2 Hz, 2H), 1.65-1.58 (m, 5H), 1.29-1.25 (m, 1H), 1.15-1.07 (m, 3H), 0.93-0.85 (m, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 164.8, 137.4, 129.5, 128.6, 127.3, 117.5, 96.1, 46.1, 35.8, 32.9, 26.1, 25.9. **HRMS** (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{16}H_{19}NH^+$ 226.1590; Found 226.1591; deviation: -0.33 ppm.

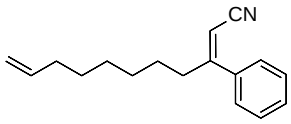


Compound 3xa (CAS: 106359-45-9).[12] Following the general procedure, the product **3xa** was prepared (*Z* only from ^{1}H NMR analysis of crude reaction mixture) and purified by flash column chromatography (eluent: EtOAc/petroleum ether = 1/50) as a yellow solid (17.3 mg, 84% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.44-7.40 (m, 3H), 7.35-7.33 (m, 2H), 5.35 (s, 1H), 2.86 (m, 1H), 2.31 (d, *J* = 6.8 Hz, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 172.4, 138.2, 129.2, 128.6, 127.3, 117.7, 94.3, 35.8, 21.2. **HRMS** (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{12}H_{13}NH^+$ 172.1121; Found 172.1116; deviation: 2.78 ppm.

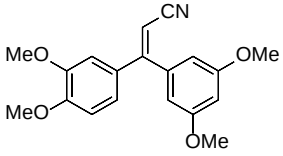


Compound 3ya. Following the general procedure, the product **3ya** was prepared (*Z* only from ^{1}H NMR analysis of crude reaction mixture) and purified by flash column chromatography (eluent: EtOAc/petroleum ether = 1/50) as a yellow liquid (26.0 mg, 93% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.49-7.43 (m, 5H), 7.30 (t, *J* = 7.5 Hz, 2H), 7.22 (t, *J* = 7.3 Hz, 1H), 7.11 (d, *J* = 7.4 Hz, 2H), 5.32 (s, 1H), 2.90 (t, *J* = 7.7 Hz, 2H), 2.72 (t, *J* = 7.7 Hz, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 164.7, 140.0, 137.1, 129.8, 128.8, 128.6, 128.3, 127.4, 126.5, 117.4, 96.0, 39.8, 33.9. **HRMS**

(ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{17}H_{15}NH^+$ 234.1277; Found 234.1275; deviation: 0.97 ppm.



Compound 3za. Following the general procedure, the product **3za** was prepared (*Z* only from ^{1}H NMR analysis of crude reaction mixture) and purified by flash column chromatography (eluent: EtOAc/petroleum ether = 1/50) as a yellow liquid (22.7 mg, 79% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.44-7.40 (m, 5H), 5.82-5.74 (m, 1H), 5.37 (s, 1H), 5.00-4.95 (m, 1H), 4.94-4.91 (m, 1H), 2.56 (t, *J* = 7.5 Hz, 2H), 2.04-1.99 (m, 2H), 1.42-1.24 (m, 8H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 166.1, 138.8, 137.5, 129.5, 128.6, 127.2, 117.5, 114.3, 95.2, 38.1, 33.6, 28.8, 28.6, 27.5. **HRMS** (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{17}H_{21}NH^+$ 240.1747; Found 240.1737; deviation: 4.08 ppm.



Compound CC-5079 (CAS: 1198105-56-4).[13] Following the general procedure, the product **CC-5079** was prepared and purified by flash column chromatography (eluent: EtOAc/petroleum ether = 1/50) as a yellow liquid (4.7 mg, 12% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 6.90 (dd, *J* = 8.4 Hz, 2.0 Hz, 1H), 6.84-6.82 (m, 2H), 6.56 (s, 3H), 5.66 (s, 1H), 3.91 (s, 3H), 3.84 (s, 3H), 3.80 (s, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 164.7, 161.1, 151.4, 149.4, 138.8, 129.5, 122.3, 117.5, 111.3, 106.2, 102.4, 95.2, 56.3, 56.23, 56.19. **HRMS** (ESI-TOF) m/z: $[M+K]^+$ Calcd for $C_{19}H_{19}NO_4K^+$ 364.0946; Found 364.0951; deviation: -1.64 ppm.

6. References

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7. X-Ray Crystallographic Data of 3ia

Colorless crystals of product **3ia** (CCDC-2057676) suitable for X-ray crystallographic analysis were obtained by recrystallization from dichloromethane/pentane. The ORTEP drawing of compound **3ia** is shown in Figure S1.

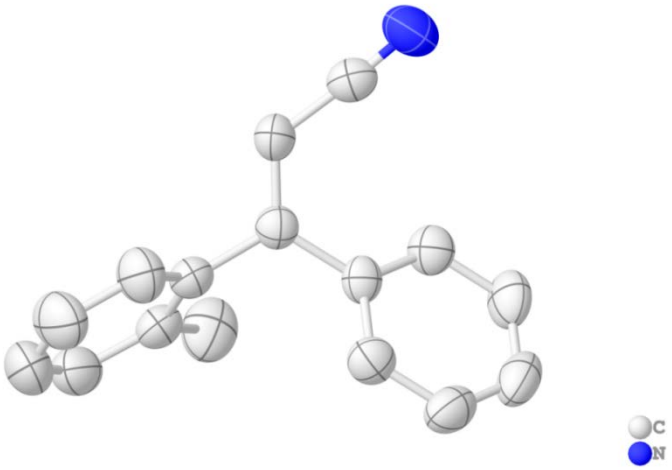


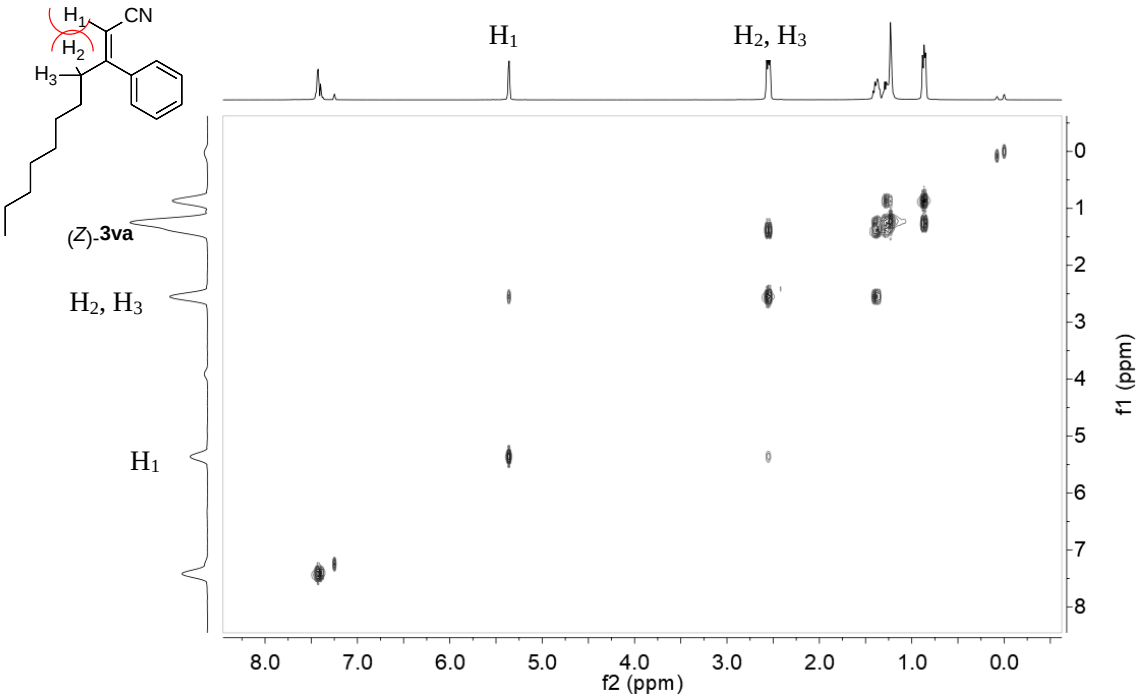
Figure S1. ORTEP illustration of compound 3ia with thermal ellipsoids drawn at 50% probability level

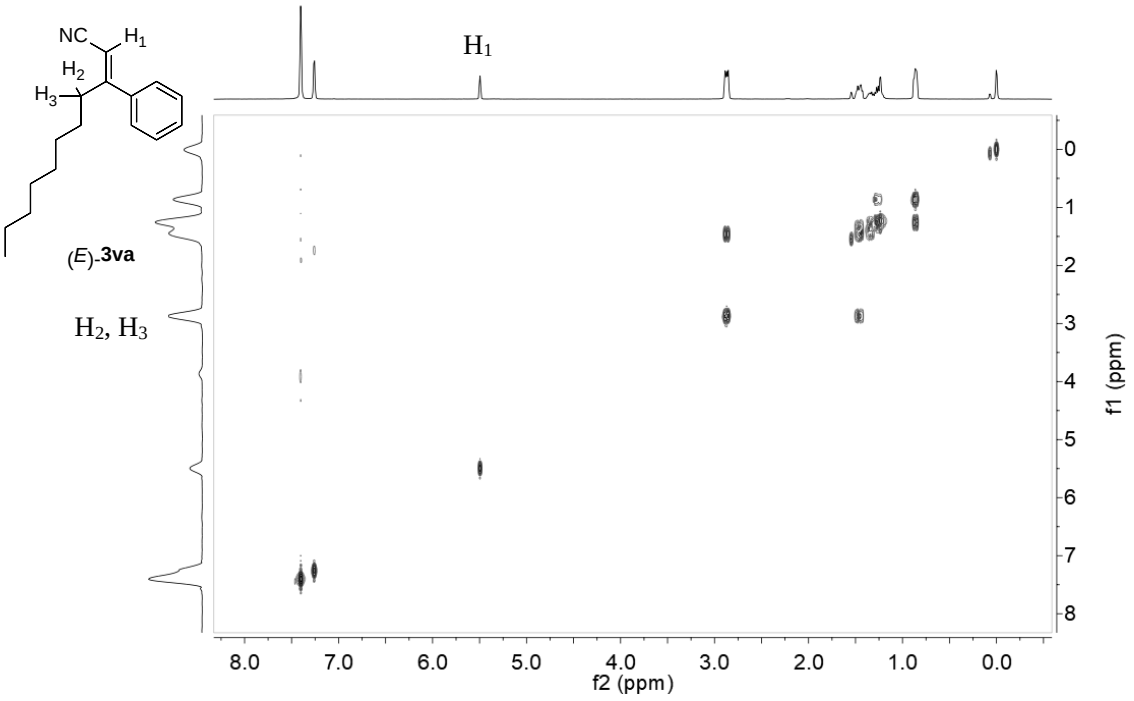
Table S3. Crystal data and structure refinement for compound 3ia

Identification code	mo210113b
Empirical formula	$C_{16}H_{13}N$
Formula weight	219.27
Temperature/K	296.15
Crystal system	orthorhombic
Space group	Fdd2
a/Å	19.031(16)
b/Å	36.93(4)
c/Å	7.092(6)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	4984(8)
Z	16

ρ_{calc}g/cm^3	1.169
μ/mm^{-1}	0.068
F(000)	1856.0
Crystal size/mm^3	0.15 × 0.15 × 0.08
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.412 to 61.2
Index ranges	$-26 \leq h \leq 26$, $-49 \leq k \leq 48$, $-9 \leq l \leq 9$
Reflections collected	10435
Independent reflections	3176 [R_{int} = 0.1031, R_{sigma} = 0.1231]
Data/restraints/parameters	3176/1/155
Goodness-of-fit on F^2	0.946
Final R indexes [I>=2σ (I)]	R_1 = 0.0567, wR_2 = 0.0912
Final R indexes [all data]	R_1 = 0.1898, wR_2 = 0.1235
Largest diff. peak/hole / e Å^{-3}	0.12/-0.12
Flack parameter	0.0(10)

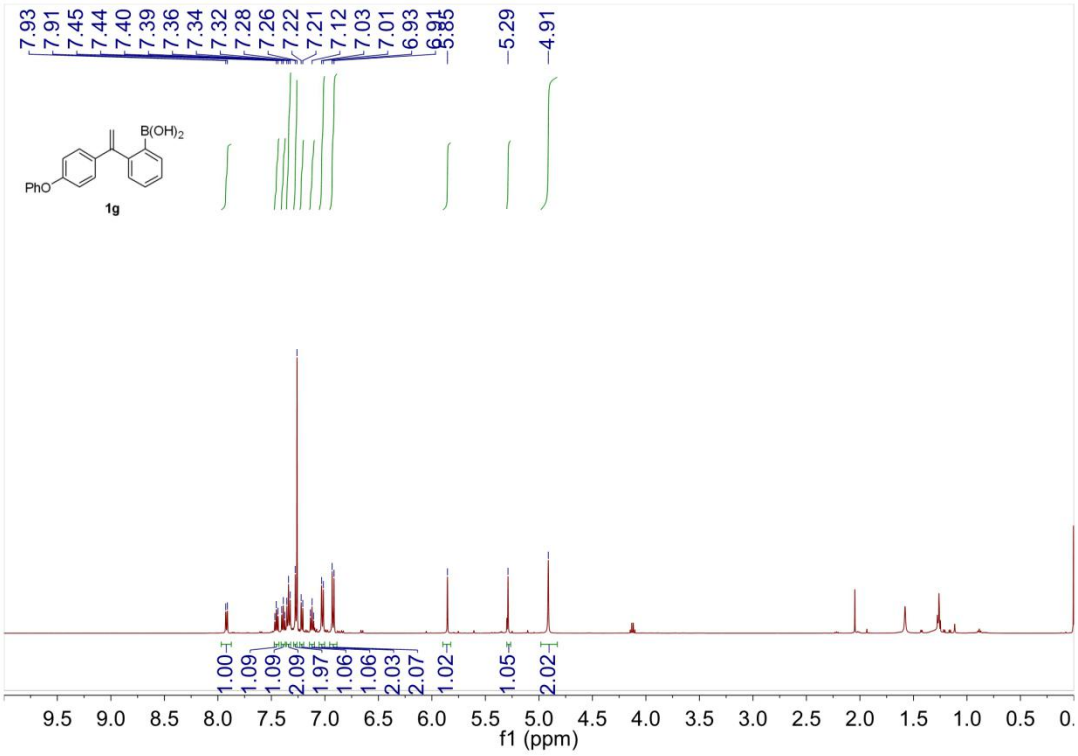
8. COSY Spectra of (*Z*)-3va and (*E*)-3va



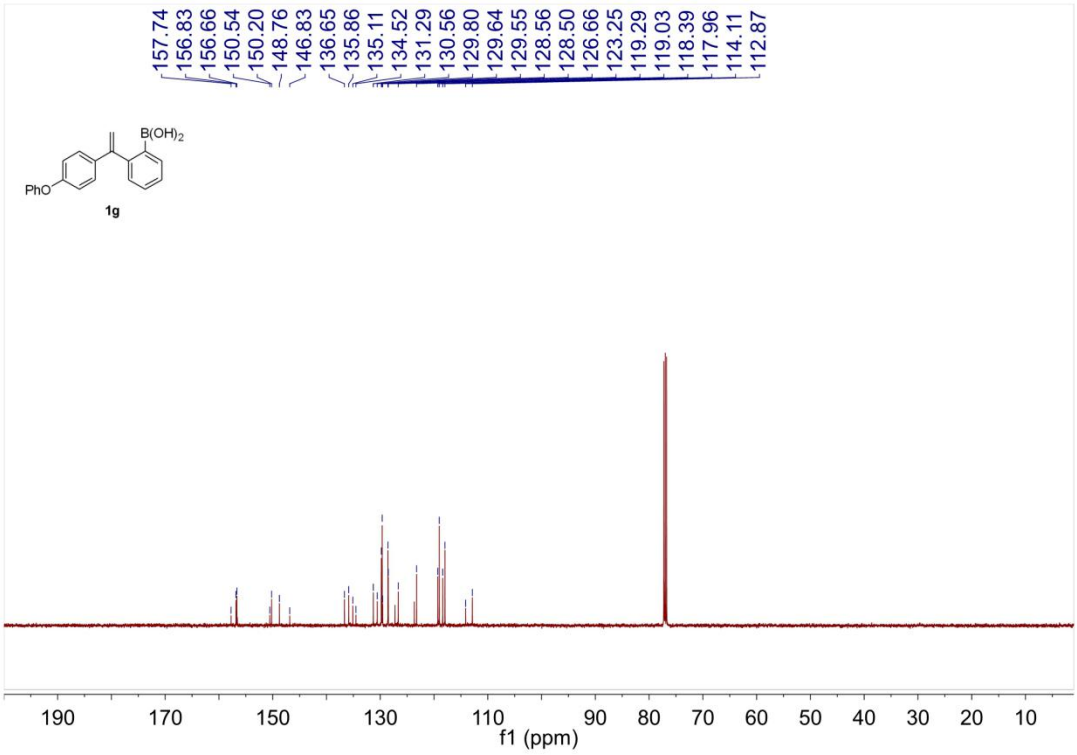


9. NMR Spectra

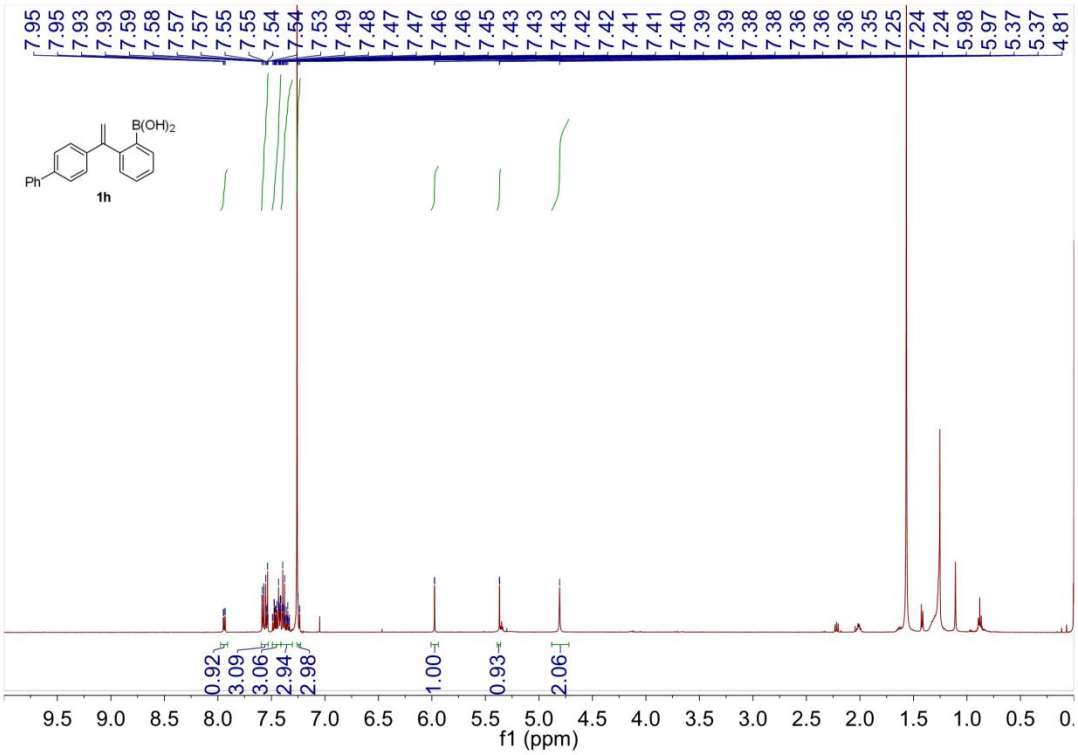
^{1}H NMR spectrum of **1g** (500 MHz, $CDCl_3$)



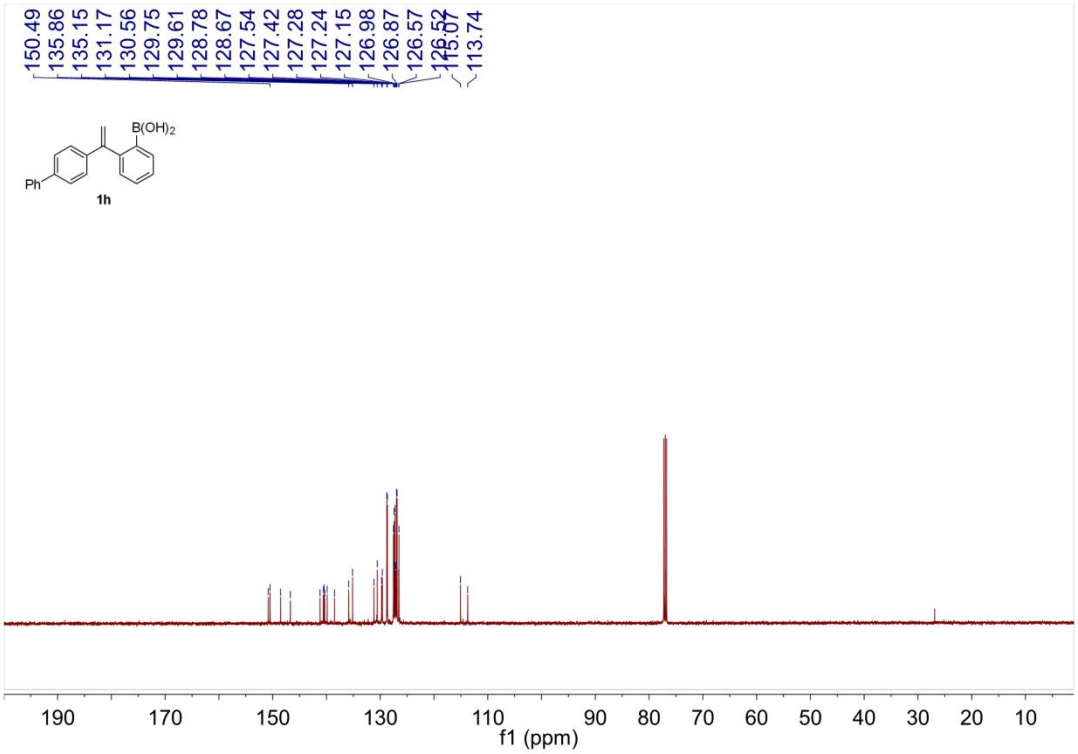
^{13}C NMR spectrum of **1g** (126 MHz, $CDCl_3$)



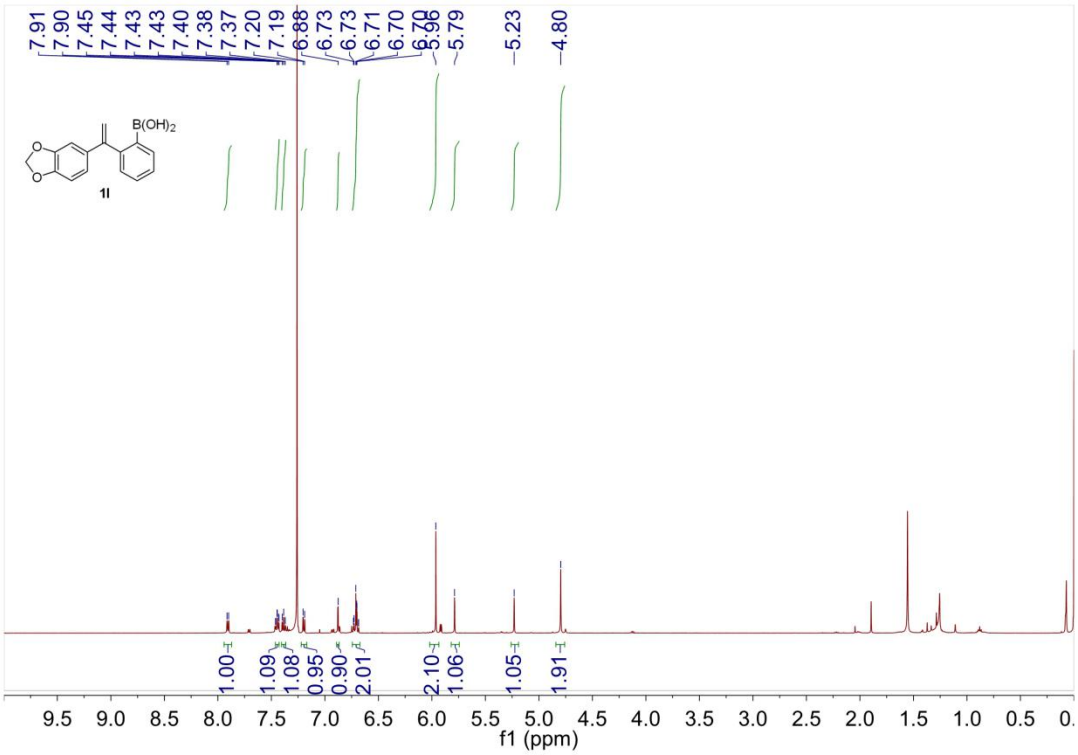
^{1}H NMR spectrum of **1h** (500 MHz, $CDCl_3$)



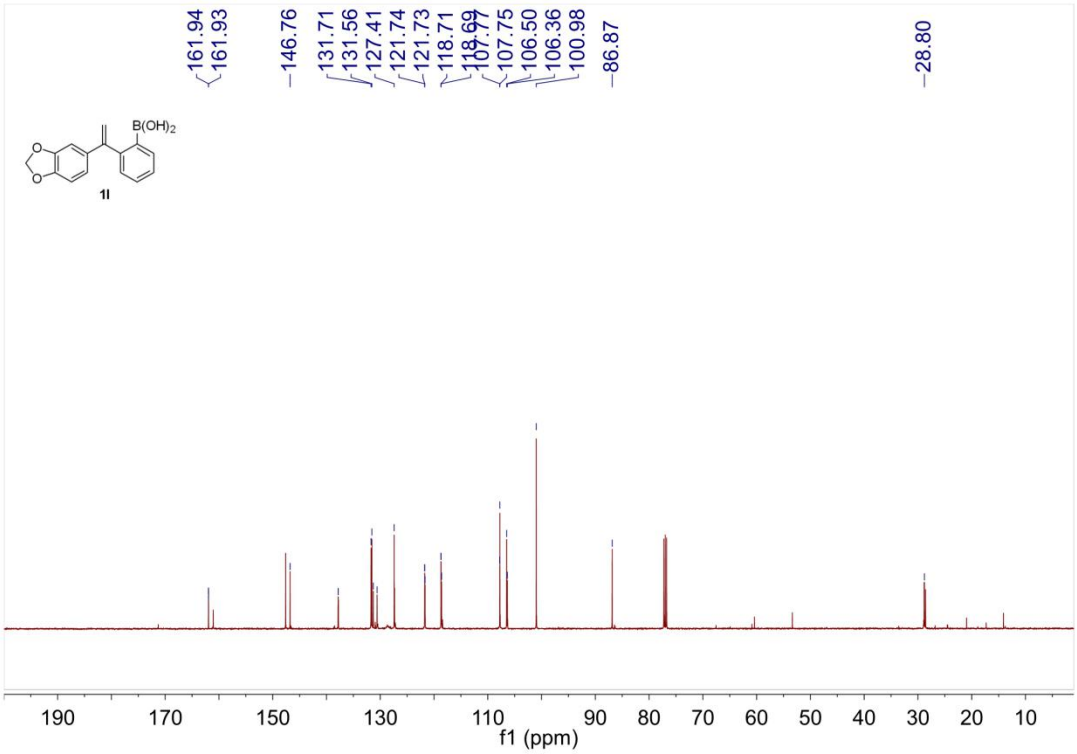
^{13}C NMR spectrum of **1h** (126 MHz, $CDCl_3$)



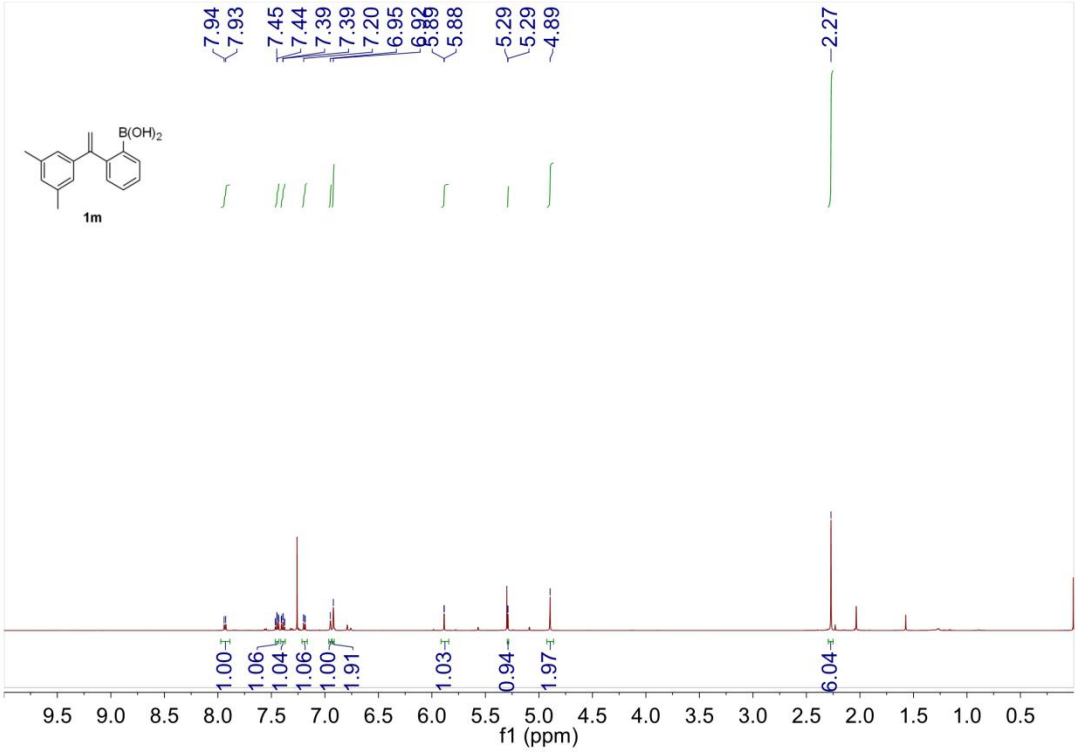
^{1}H NMR spectrum of **1l** (500 MHz, $CDCl_3$)



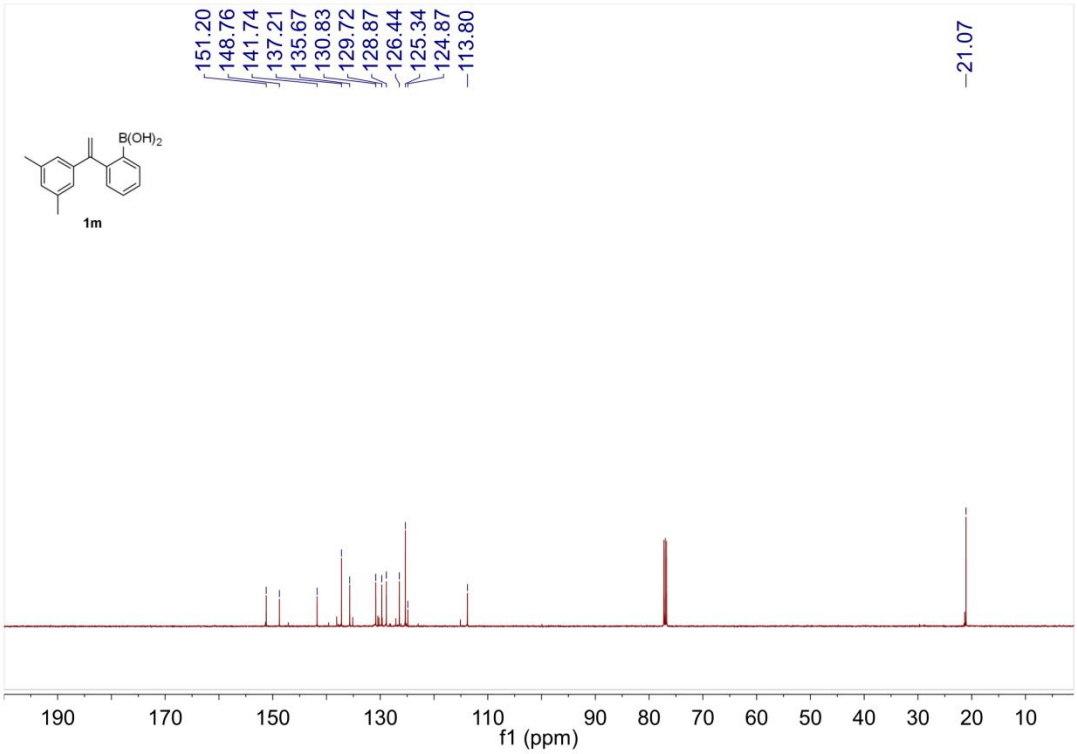
^{13}C NMR spectrum of **1l** (126 MHz, $CDCl_3$)



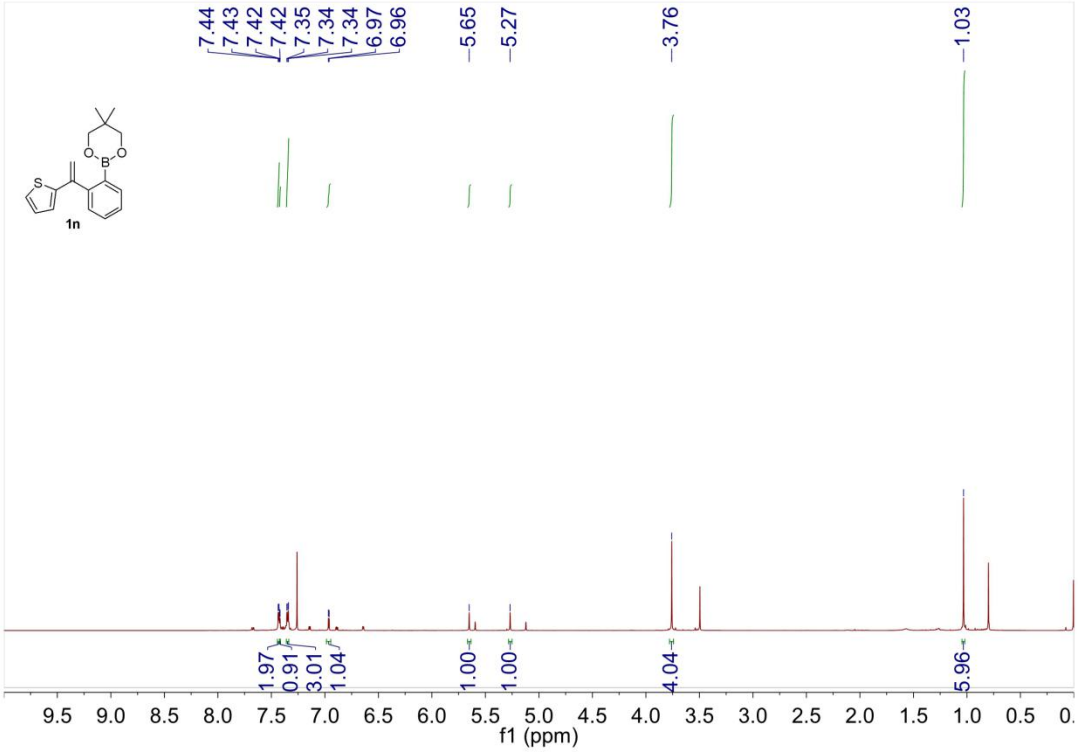
^{1}H NMR spectrum of **1m** (500 MHz, $CDCl_3$)



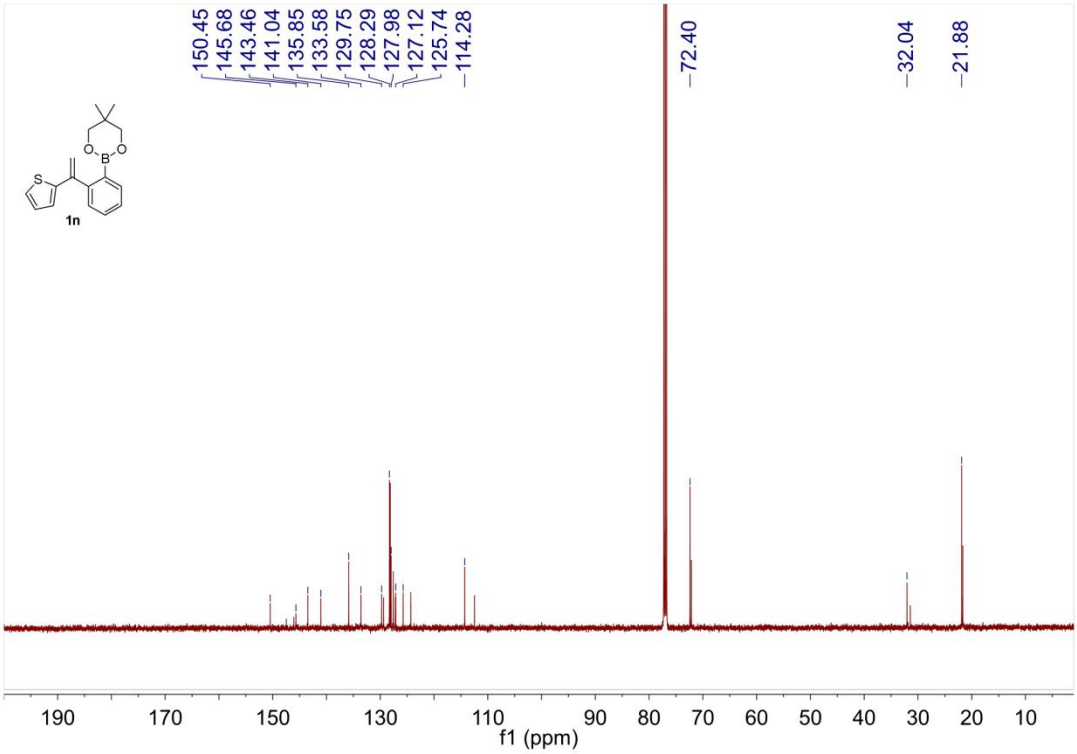
^{13}C NMR spectrum of **1m** (126 MHz, $CDCl_3$)



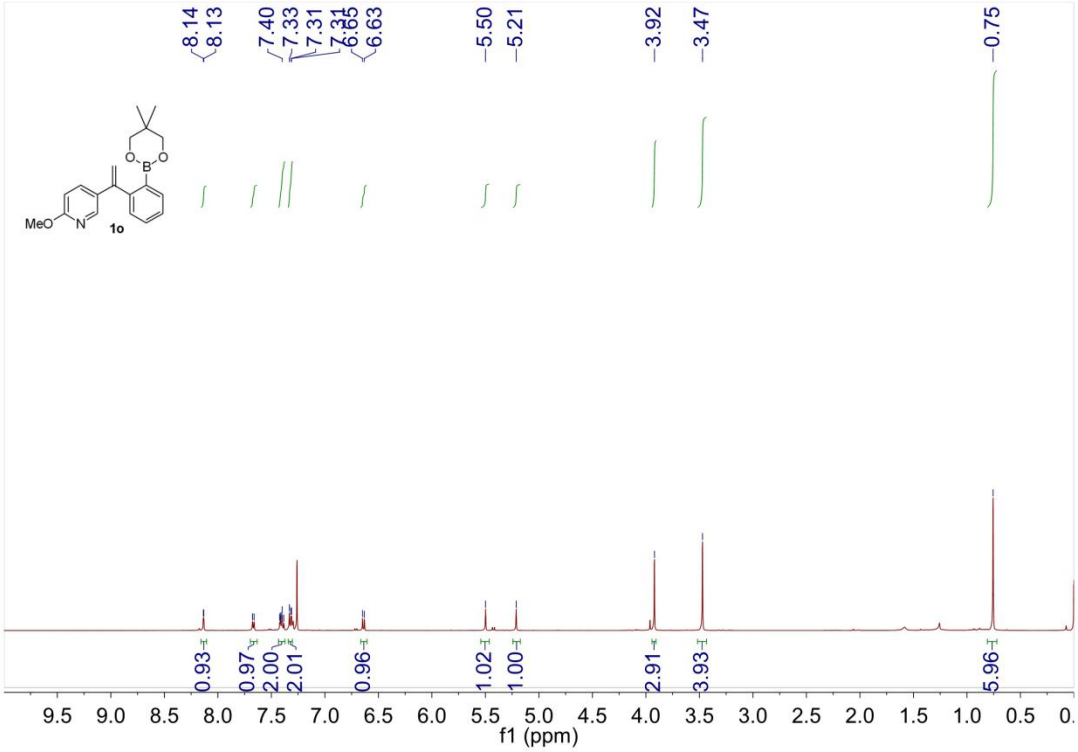
^{1}H NMR spectrum of **1n** (500 MHz, $CDCl_3$)



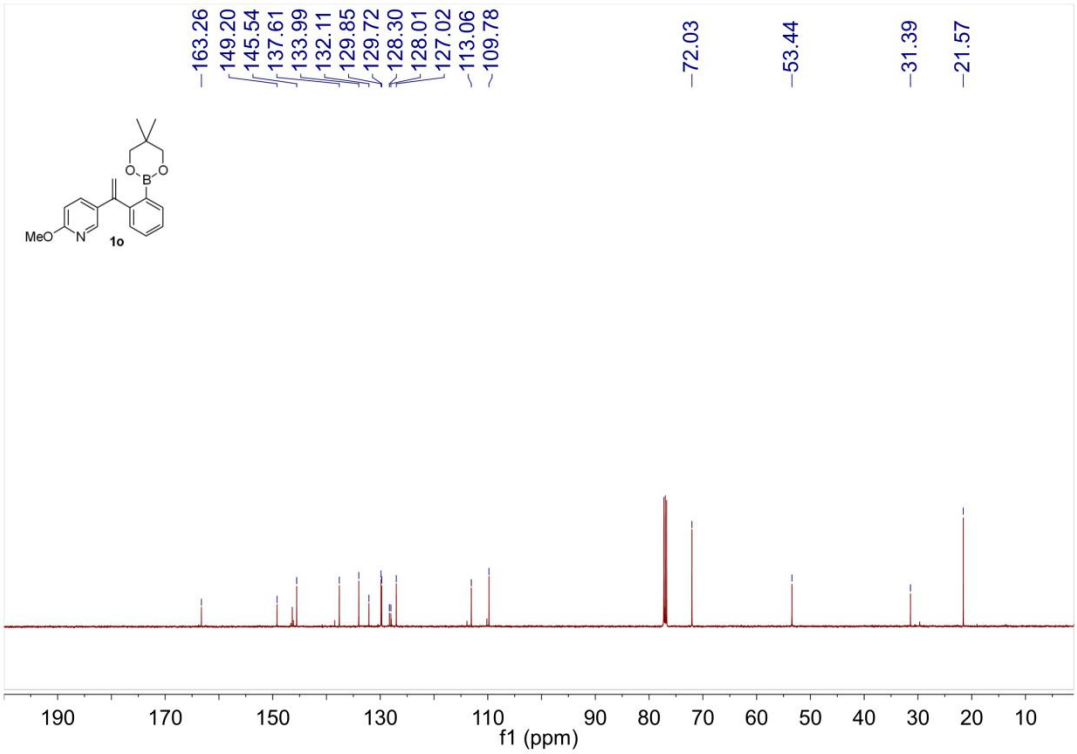
^{13}C NMR spectrum of **1n** (126 MHz, $CDCl_3$)



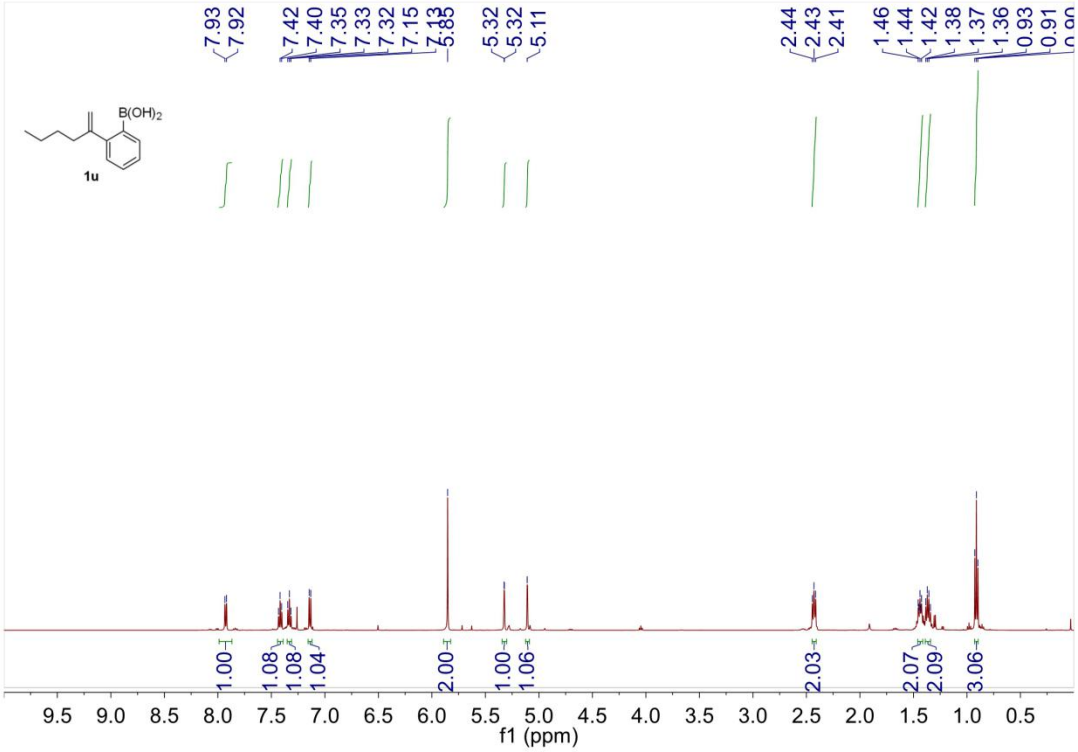
^{1}H NMR spectrum of **1o** (500 MHz, $CDCl_3$)



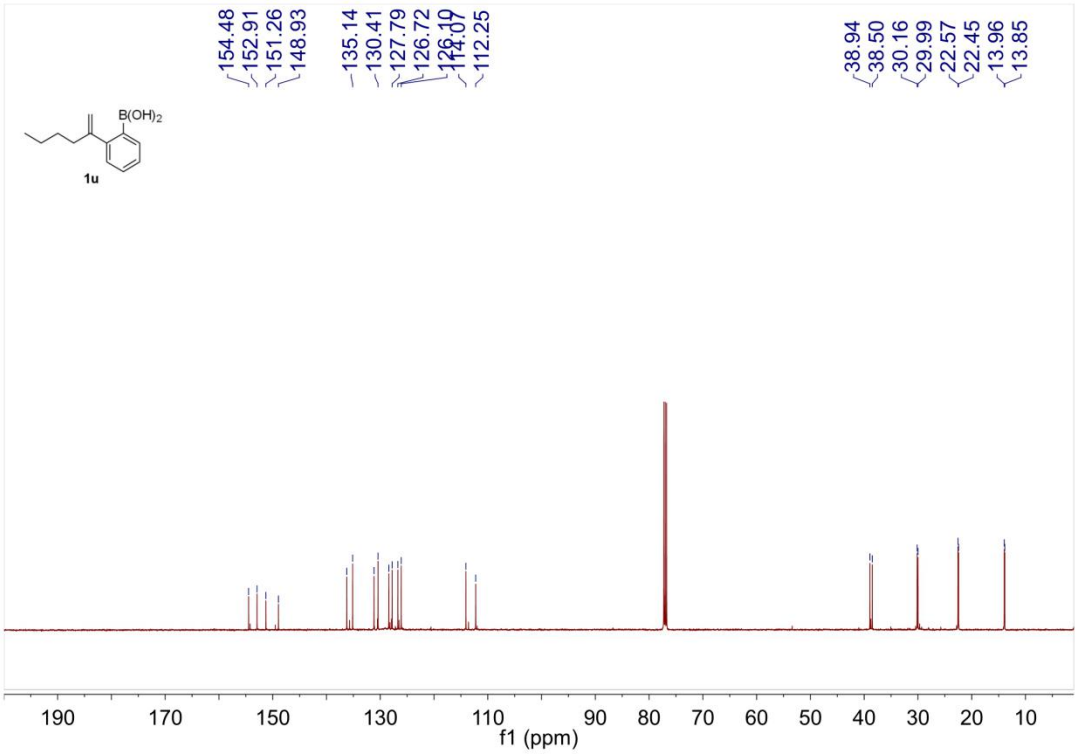
^{13}C NMR spectrum of **1o** (126 MHz, $CDCl_3$)



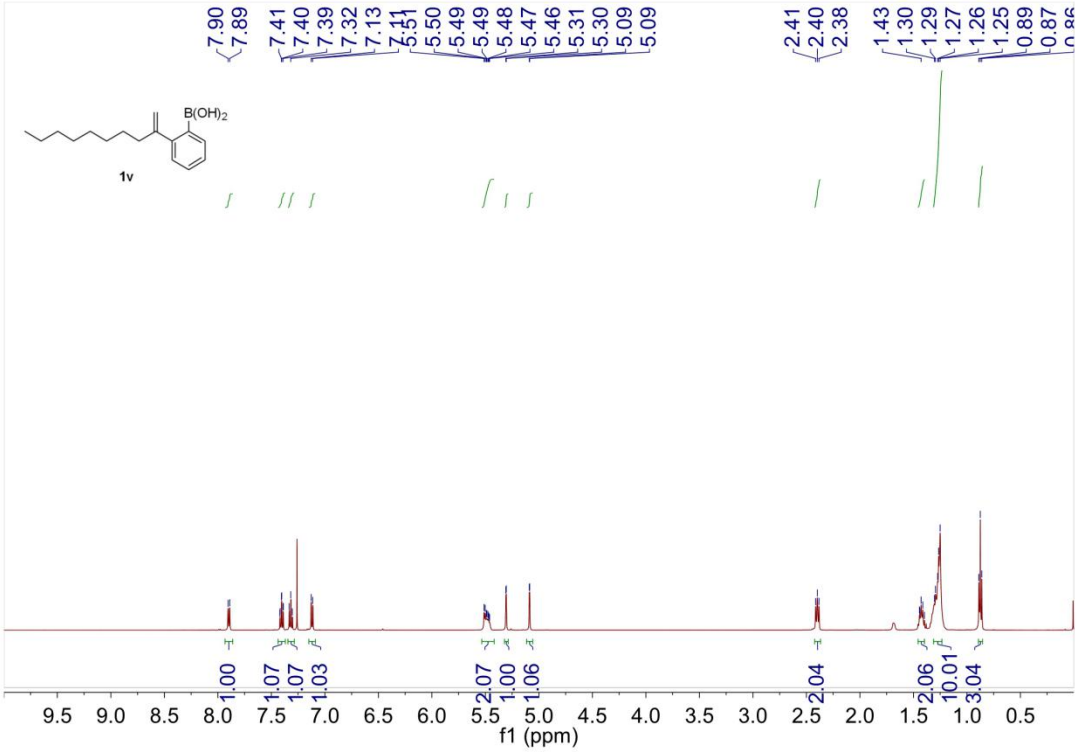
^{1}H NMR spectrum of **1u** (500 MHz, $CDCl_3$)



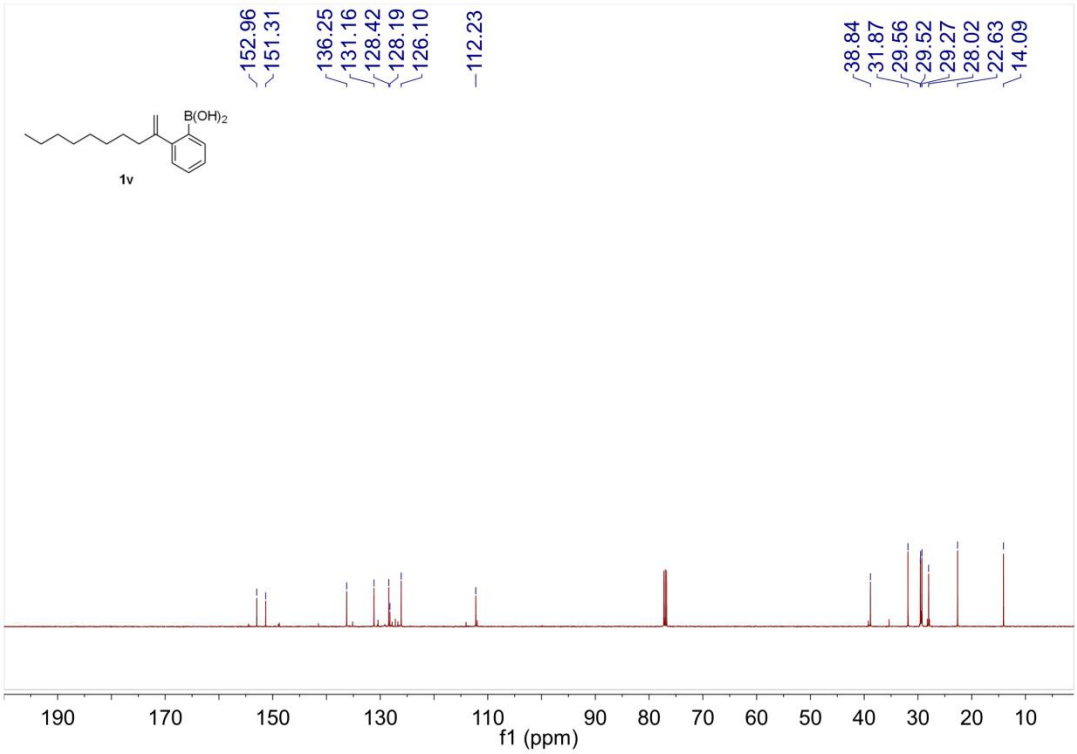
^{13}C NMR spectrum of **1u** (126 MHz, $CDCl_3$)



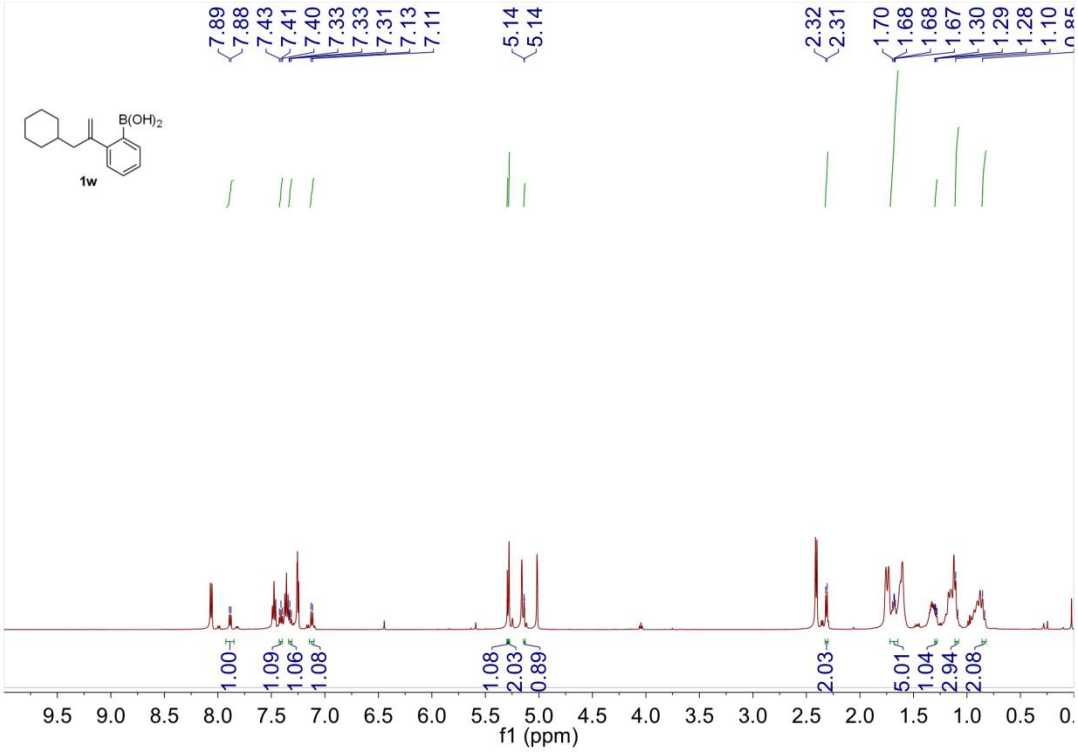
^{1}H NMR spectrum of **1v** (500 MHz, $CDCl_3$)



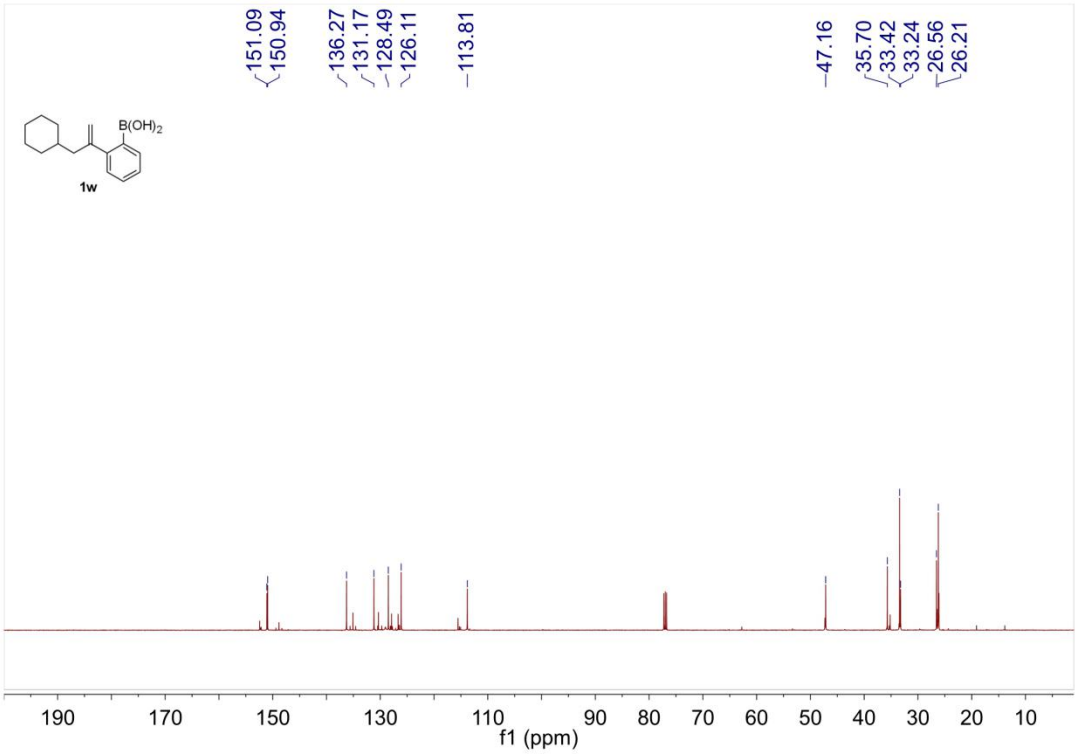
^{13}C NMR spectrum of **1v** (126 MHz, $CDCl_3$)



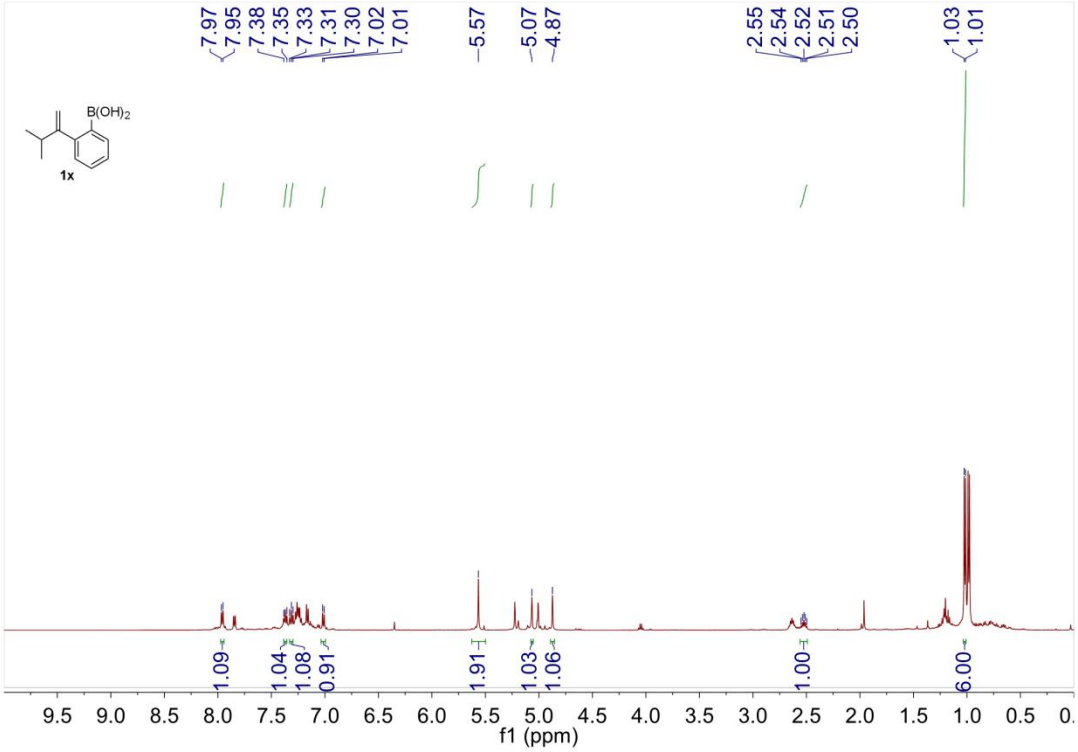
^{1}H NMR spectrum of **1w** (500 MHz, $CDCl_3$)



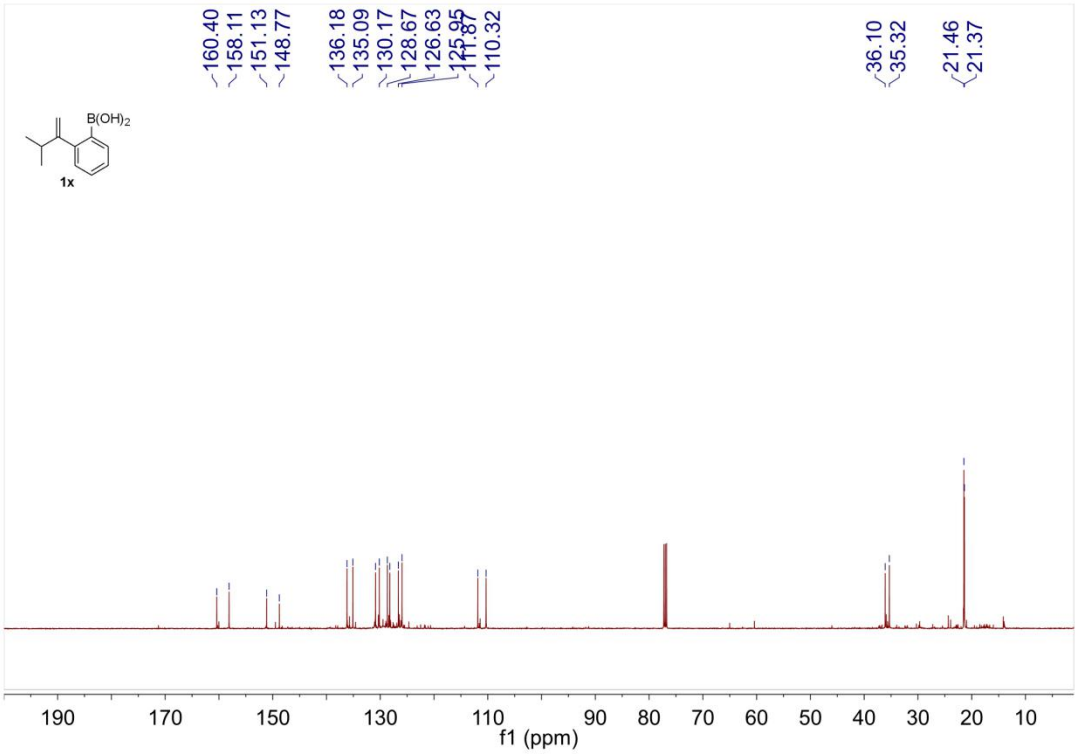
^{13}C NMR spectrum of **1w** (126 MHz, $CDCl_3$)



^{1}H NMR spectrum of **1x** (500 MHz, $CDCl_3$)



^{13}C NMR spectrum of **1x** (126 MHz, $CDCl_3$)



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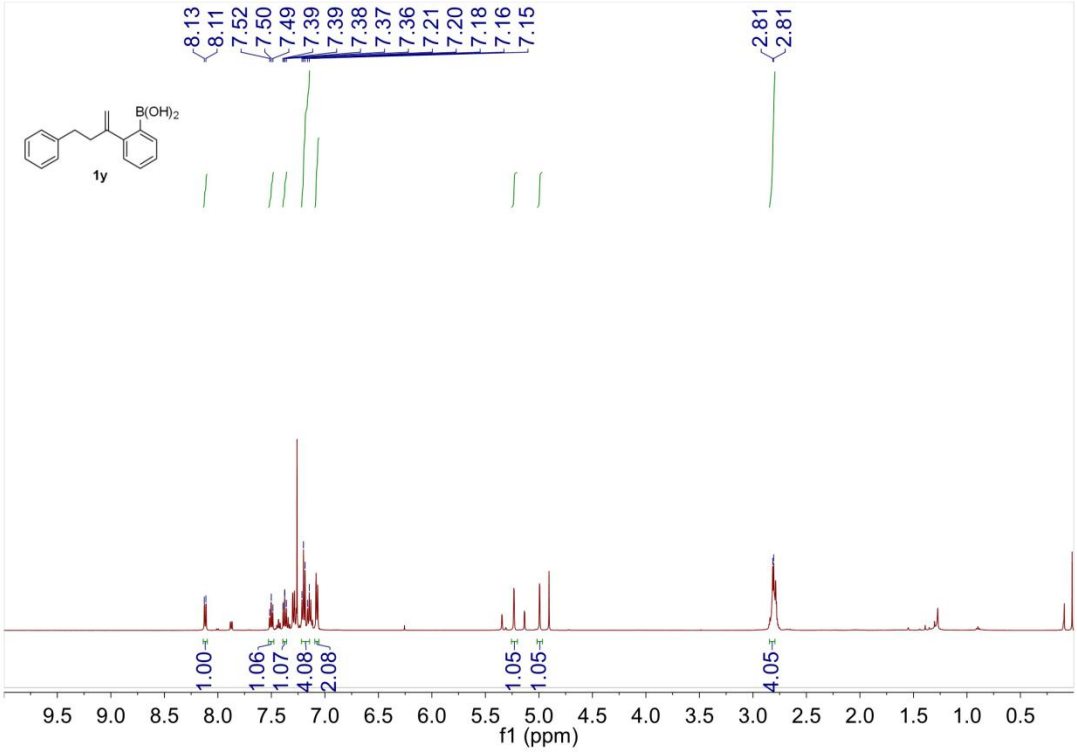
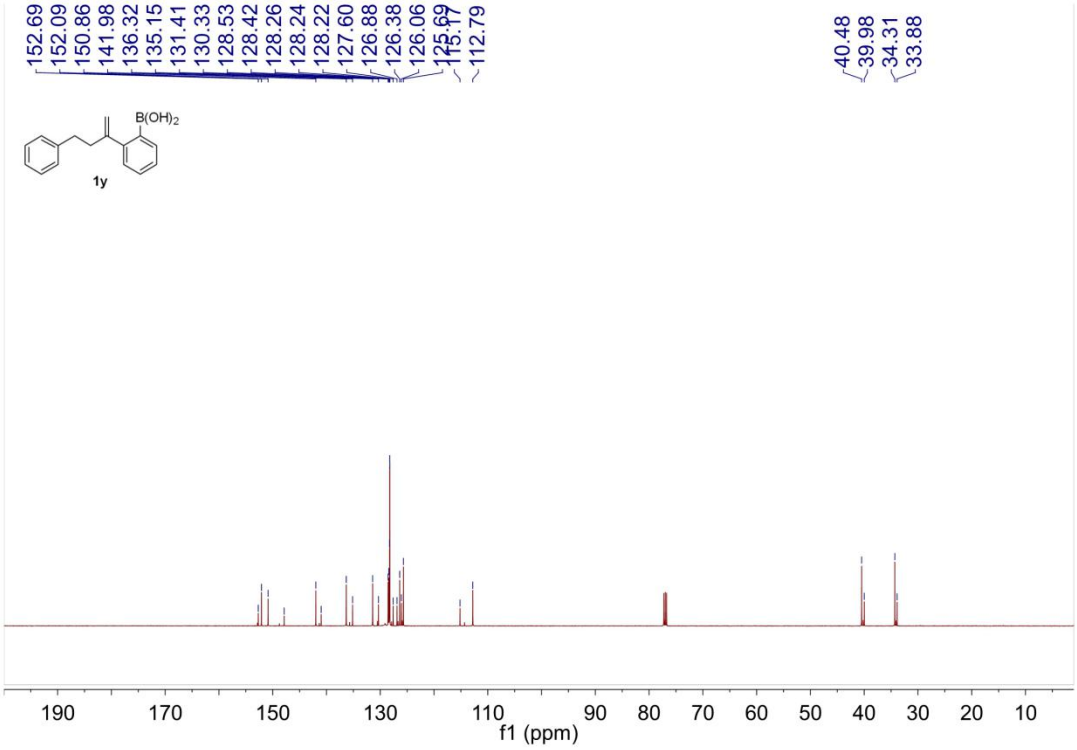
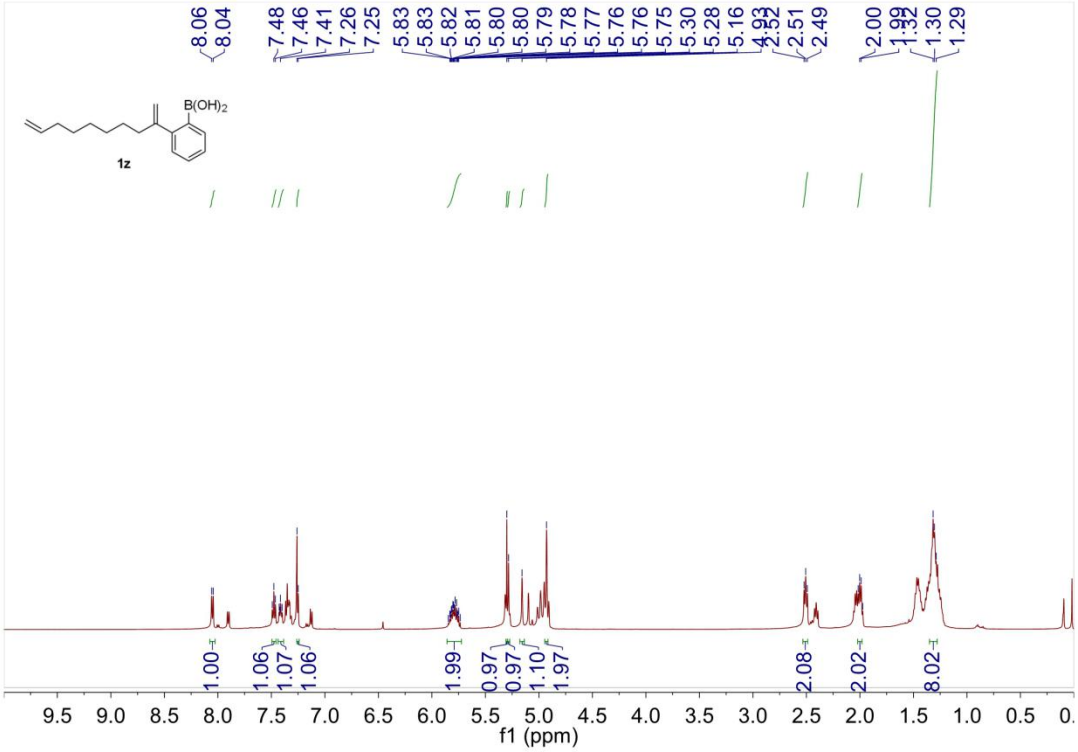


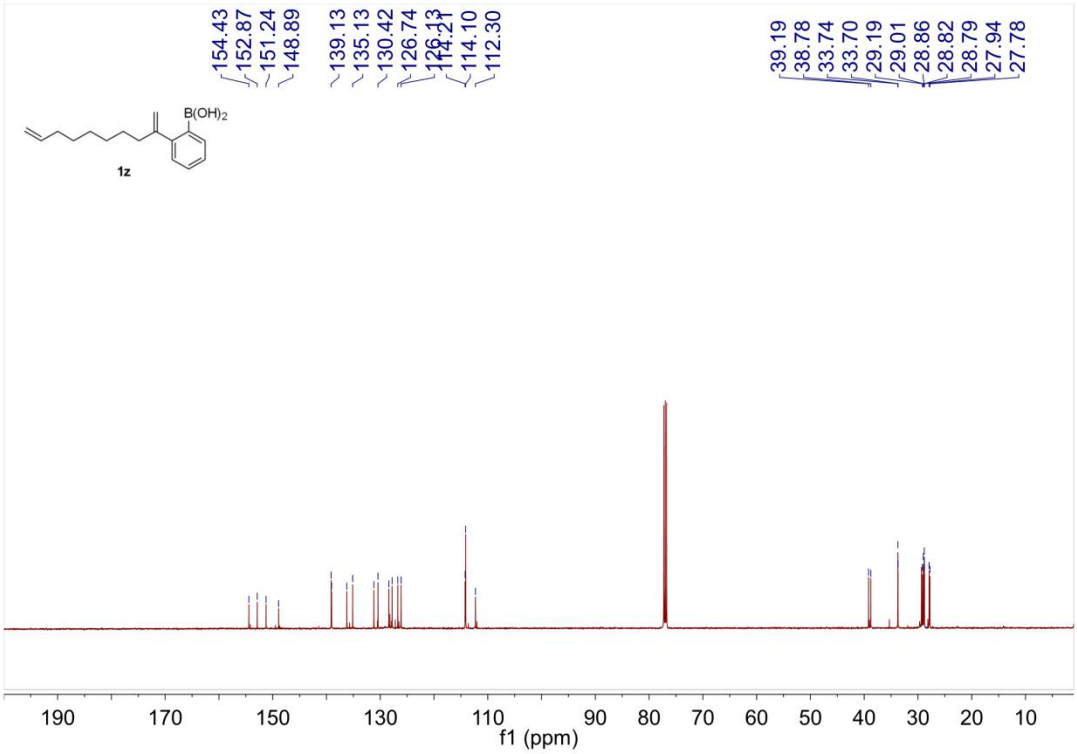
^{13}C NMR spectrum of **1y** (126 MHz, $CDCl_3$)



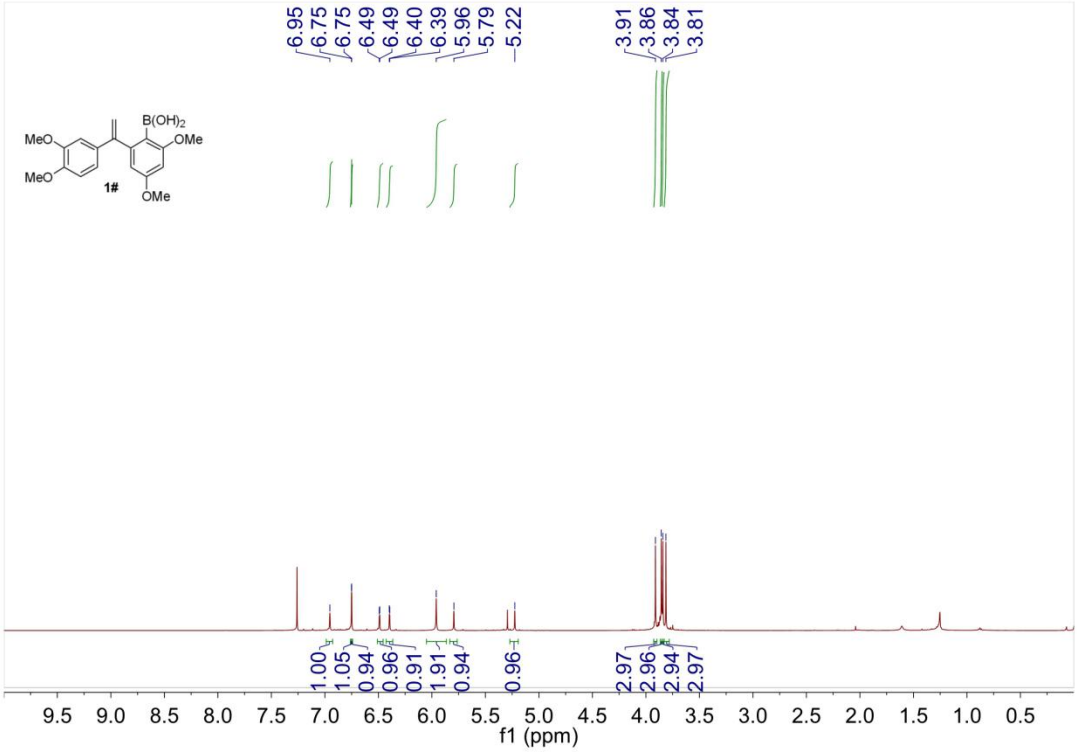
^{1}H NMR spectrum of **1z** (500 MHz, $CDCl_3$)



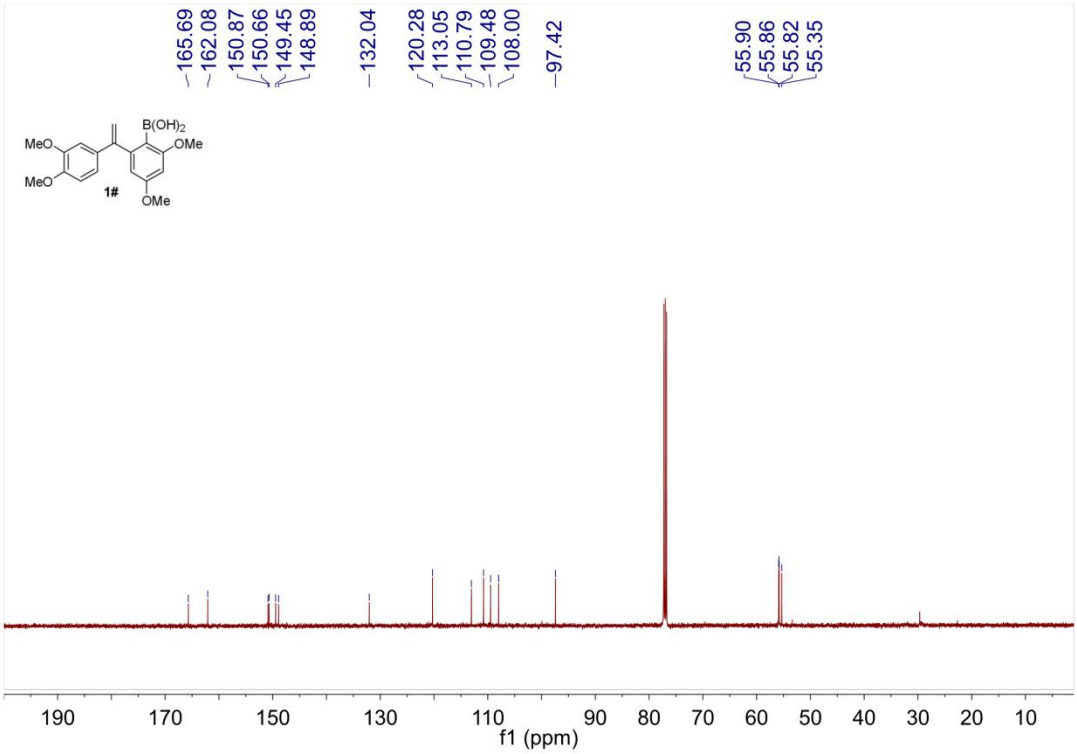
^{13}C NMR spectrum of **1z** (126 MHz, $CDCl_3$)



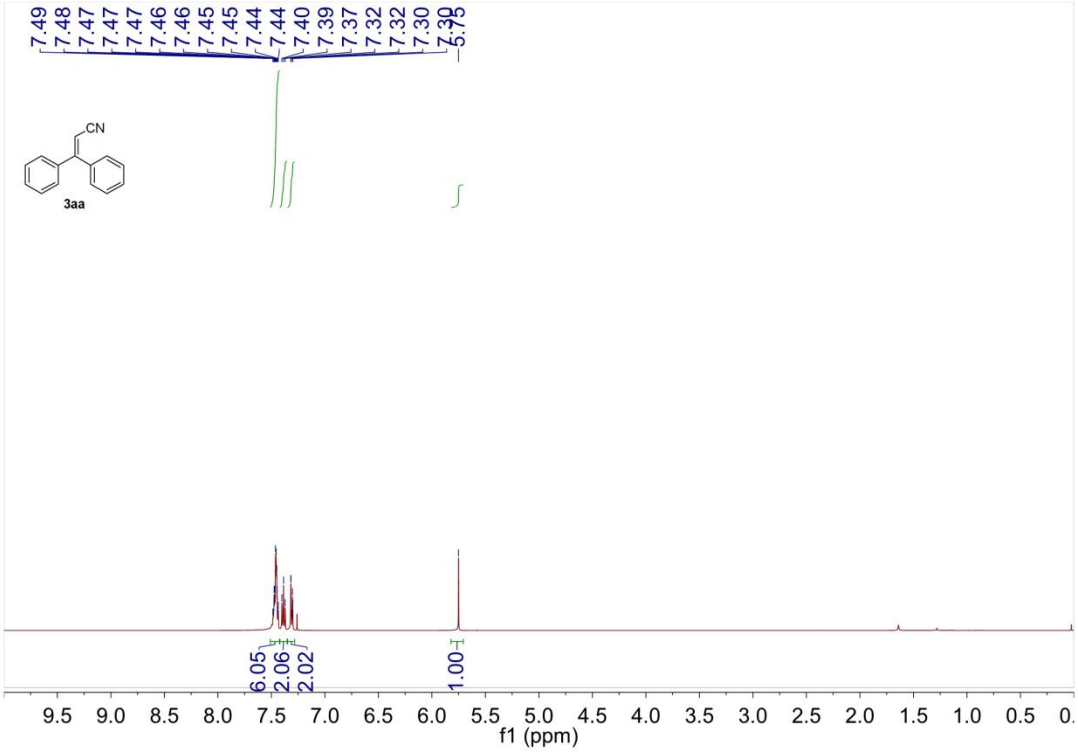
^{1}H NMR spectrum of **1#** (500 MHz, $CDCl_3$)



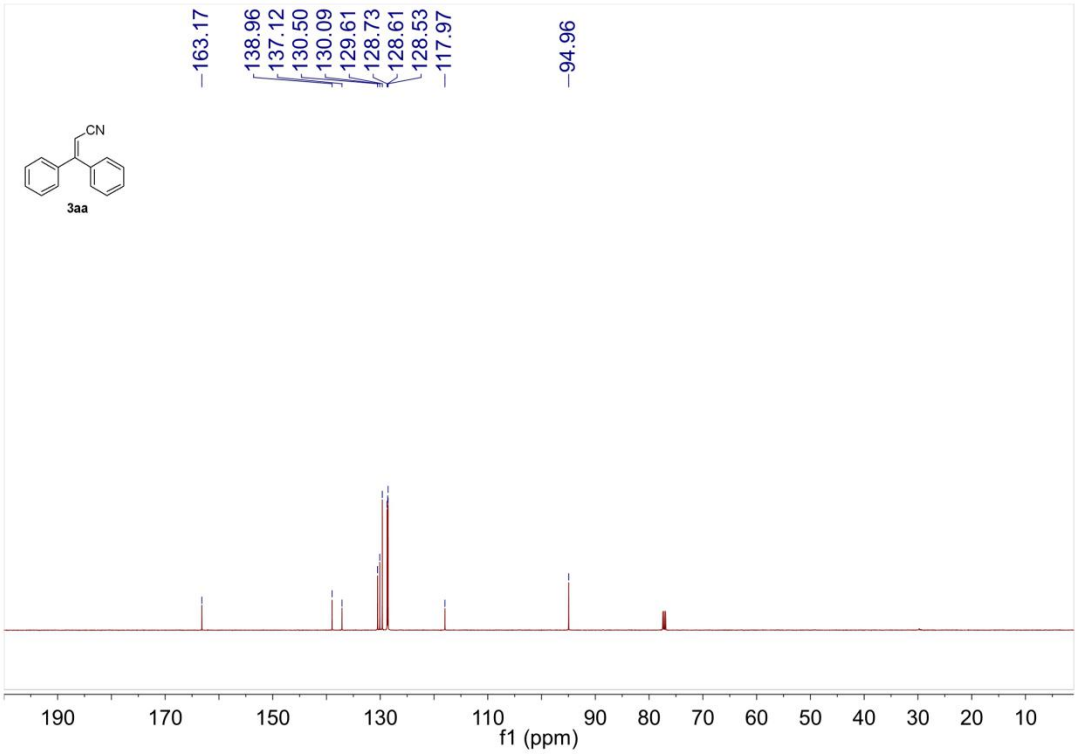
^{13}C NMR spectrum of **1#** (126 MHz, $CDCl_3$)



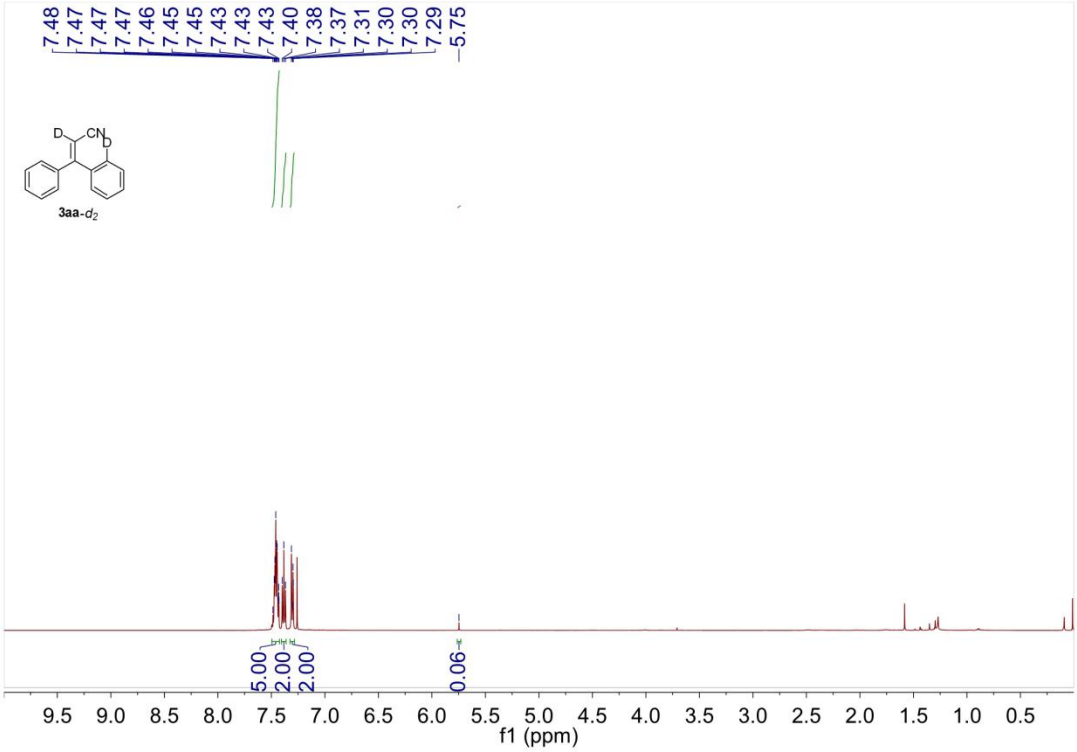
^{1}H NMR spectrum of **3aa** (500 MHz, $CDCl_3$)



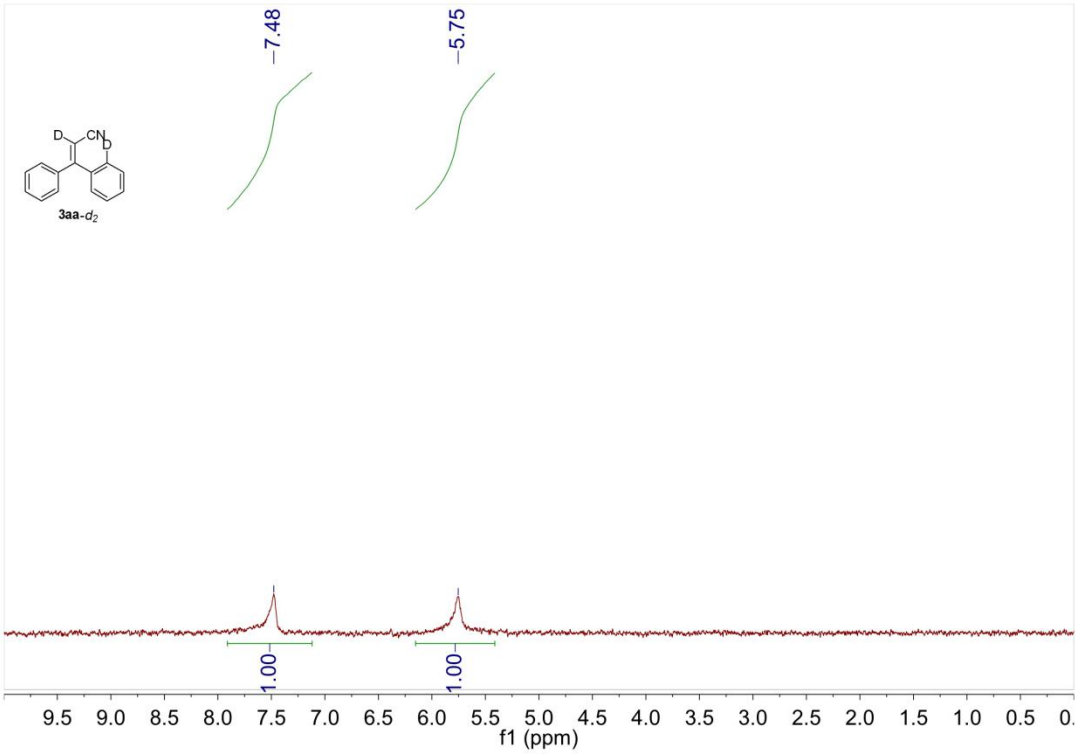
^{13}C NMR spectrum of **3aa** (126 MHz, $CDCl_3$)



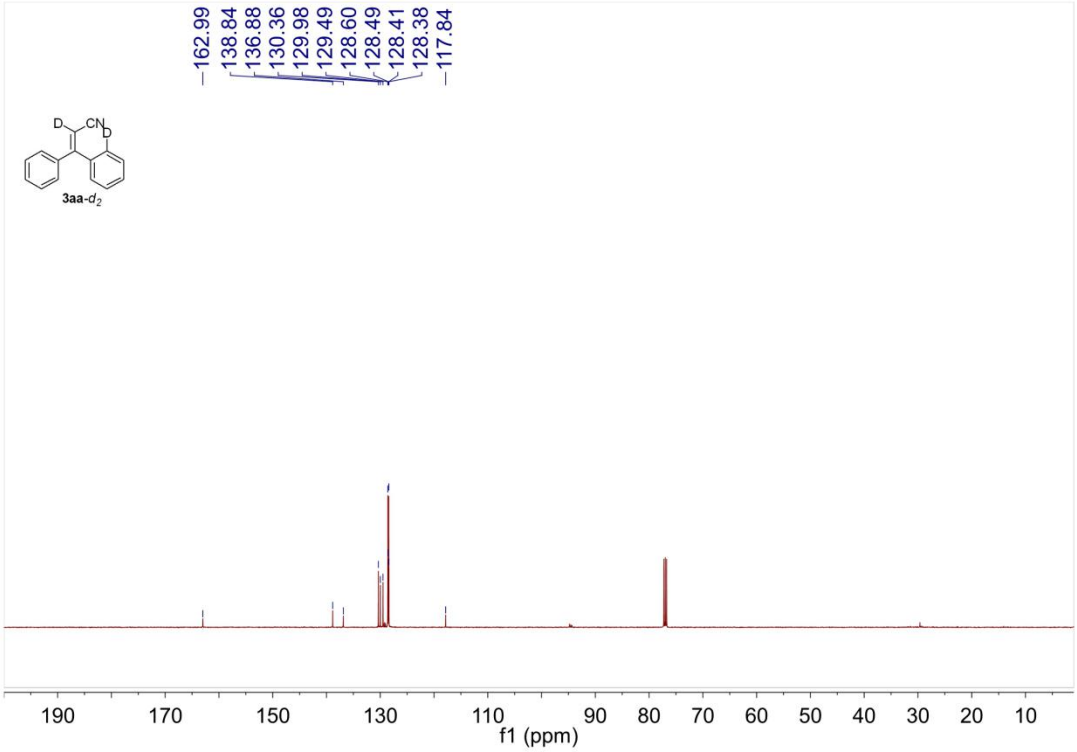
^{1}H NMR spectrum of **3aa**-d_2 (500 MHz, $CDCl_3$)



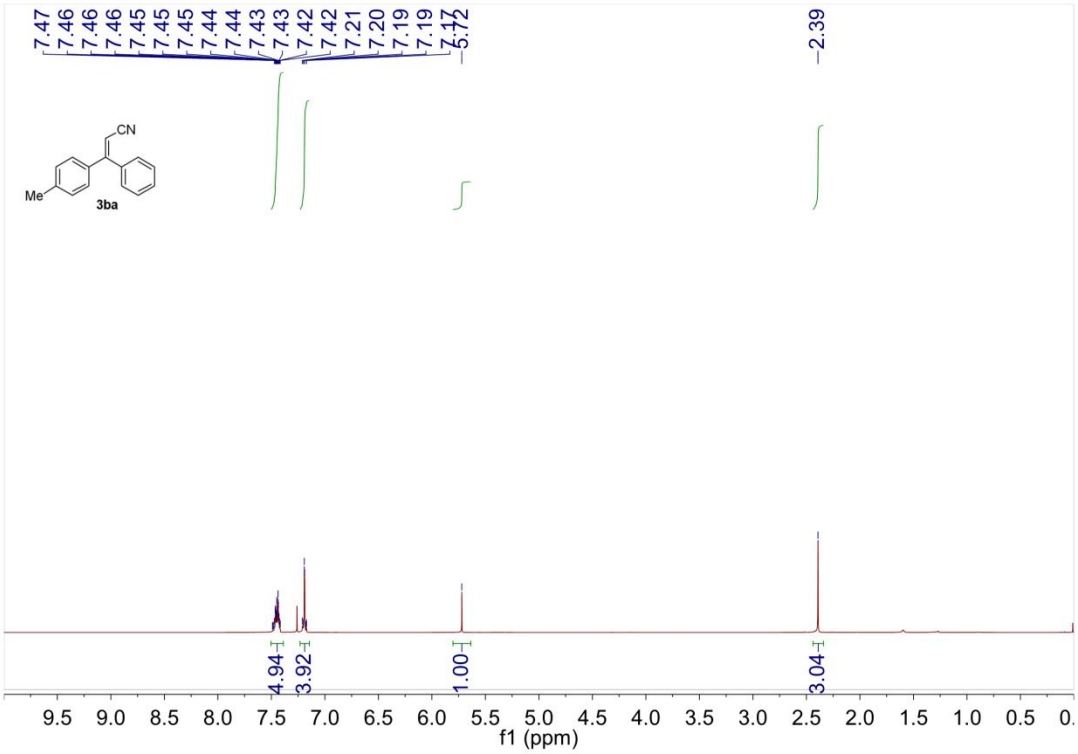
^{2}H NMR spectrum of **3aa**-d_2 (77 MHz, $CDCl_3$)



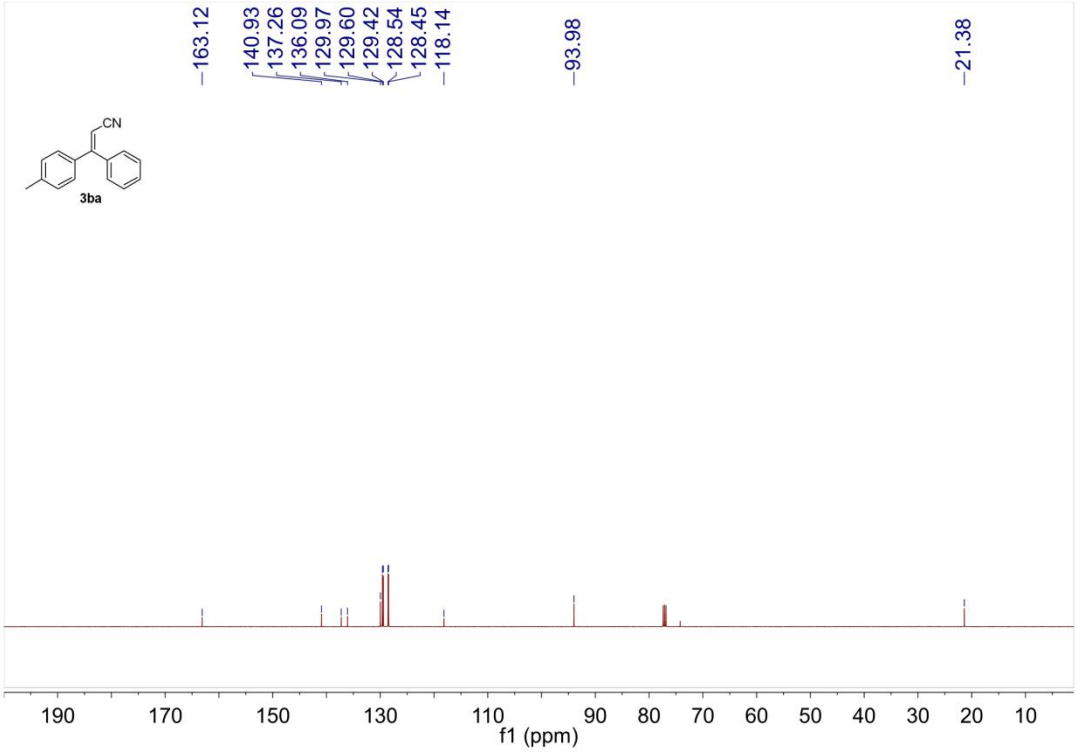
^{13}C NMR spectrum of **3aa**-d_2 (126 MHz, $CDCl_3$)



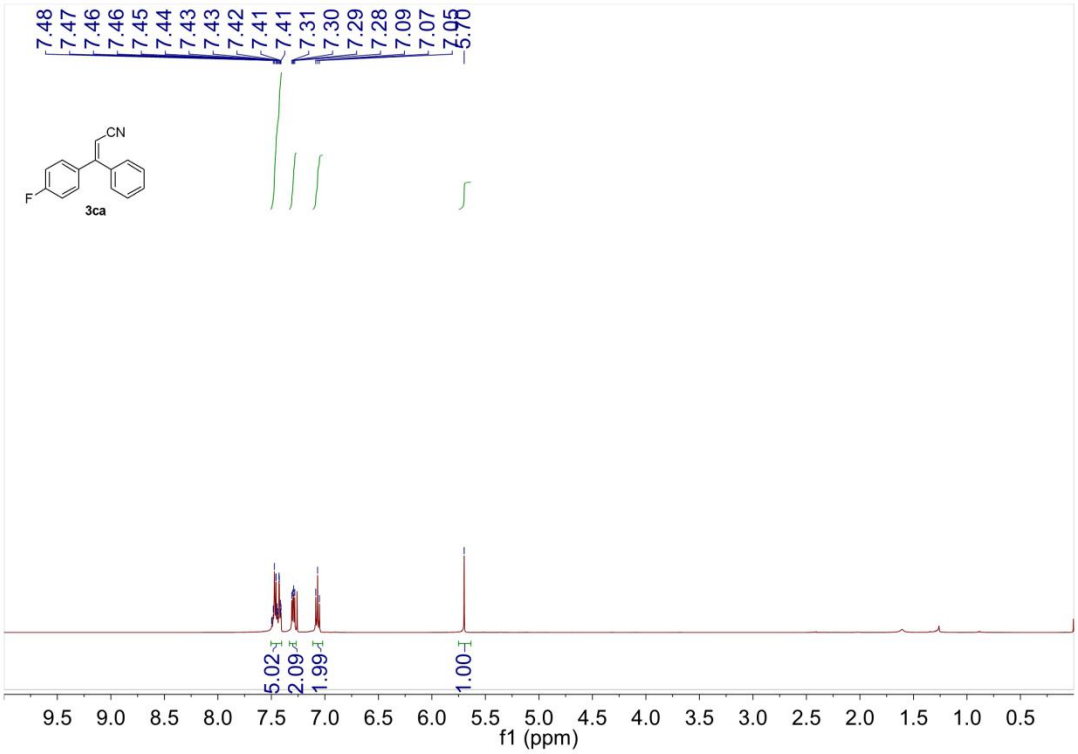
^{1}H NMR spectrum of **3ba** (500 MHz, $CDCl_3$)



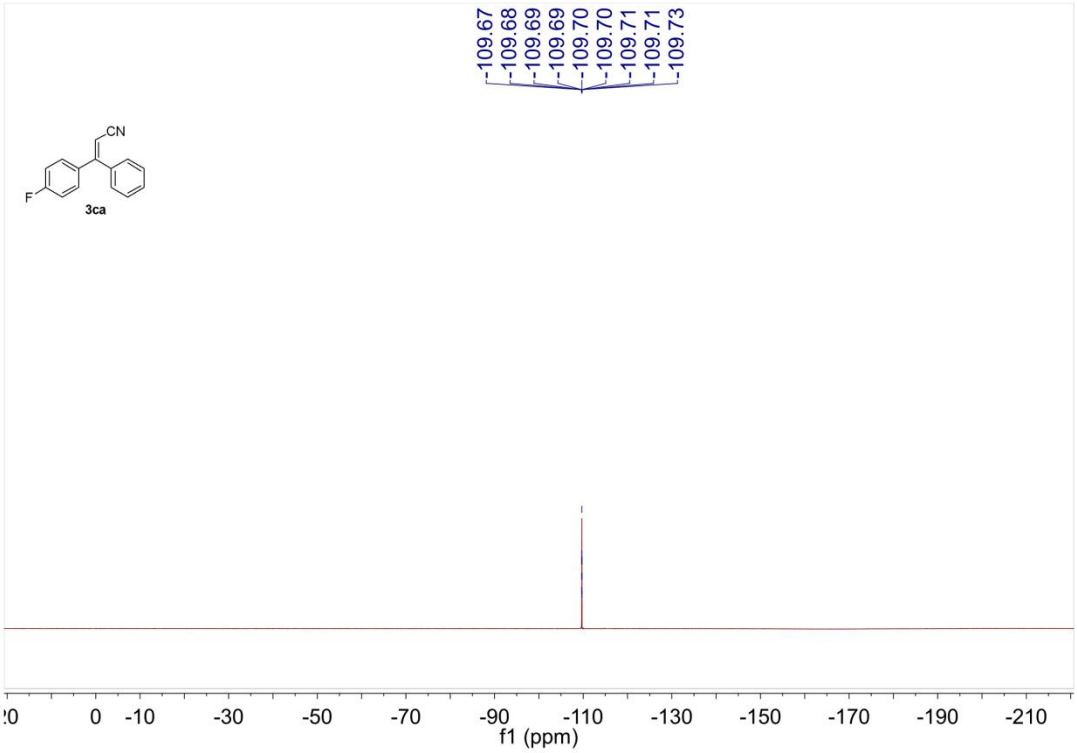
^{13}C NMR spectrum of **3ba** (126 MHz, $CDCl_3$)



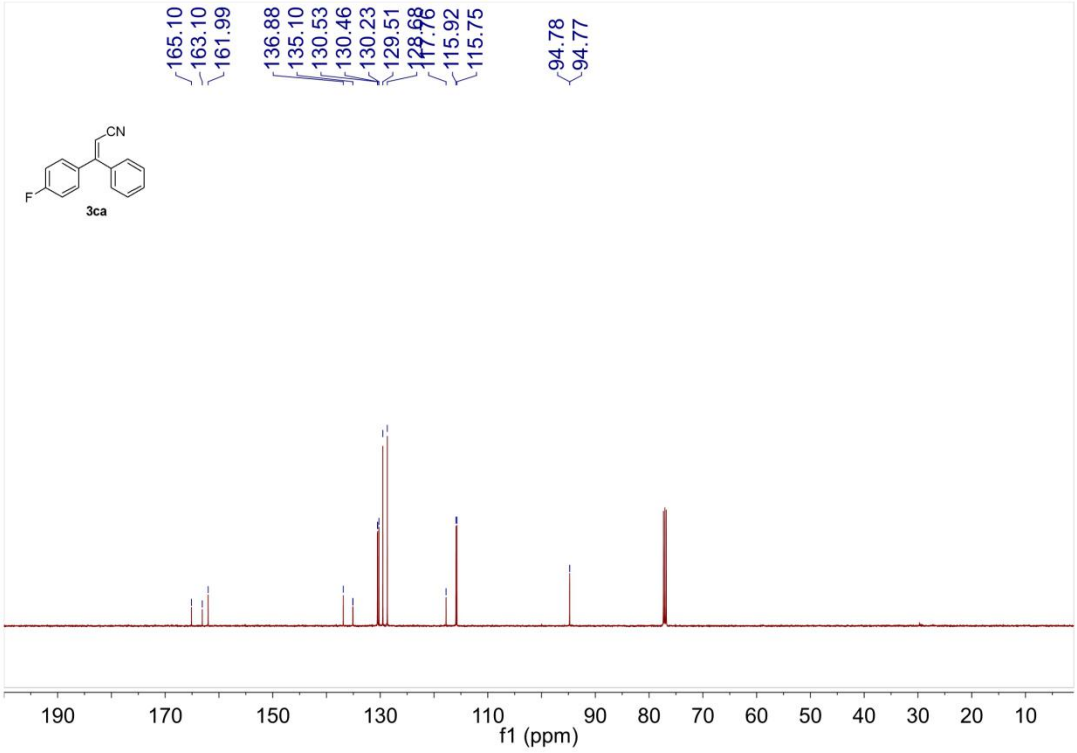
^{1}H NMR spectrum of **3ca** (500 MHz, $CDCl_3$)



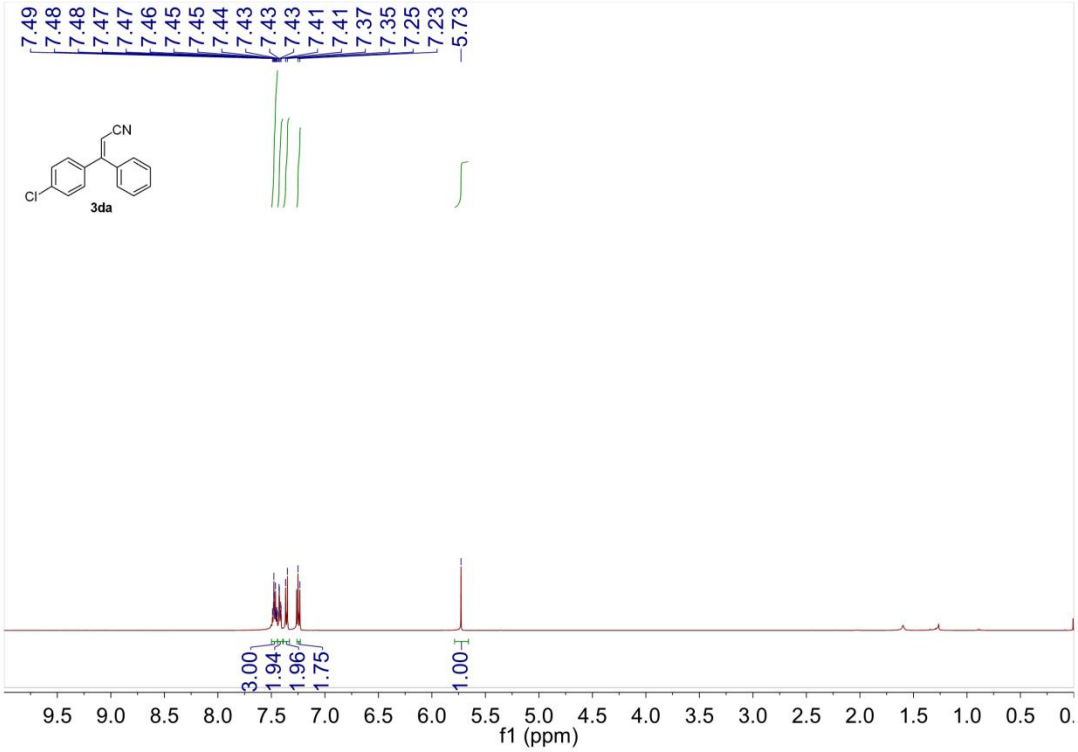
^{19}F NMR spectrum of **3ca** (471 MHz, $CDCl_3$)



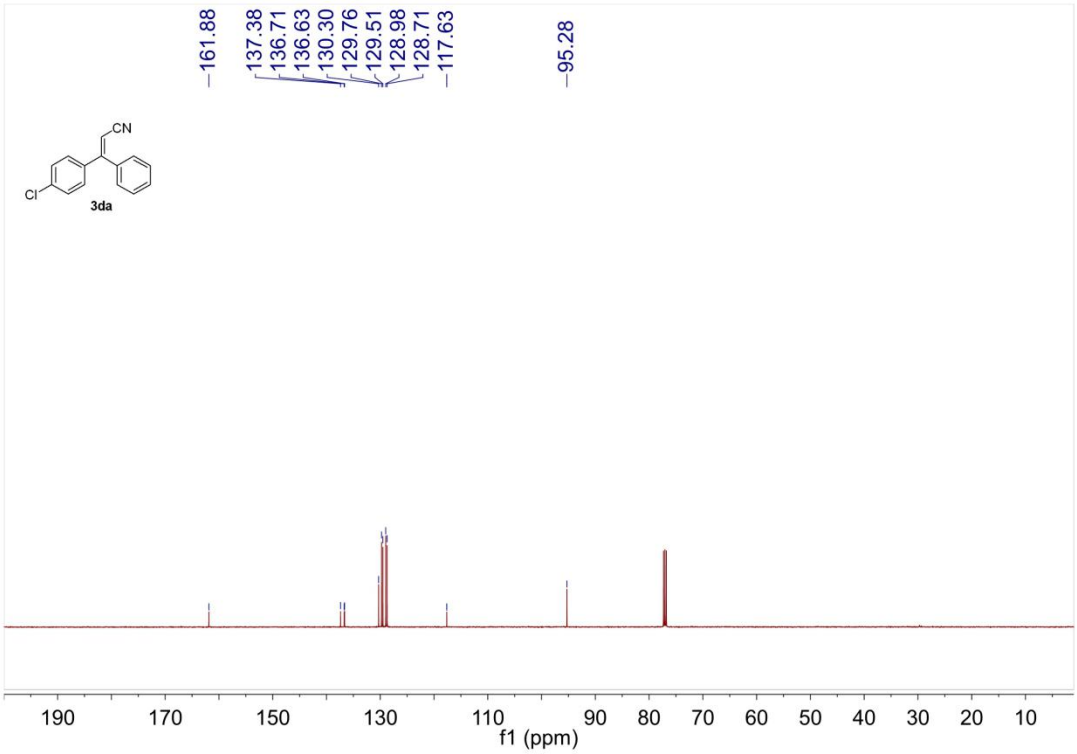
^{13}C NMR spectrum of **3ca** (126 MHz, $CDCl_3$)



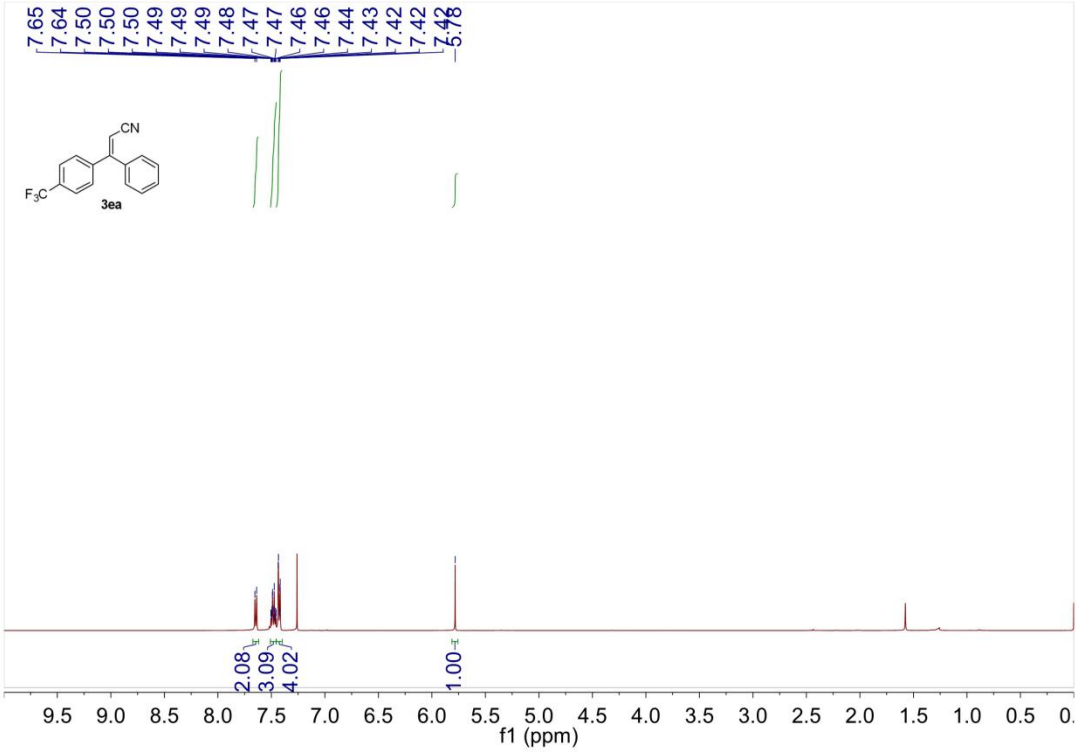
^{1}H NMR spectrum of **3da** (500 MHz, $CDCl_3$)



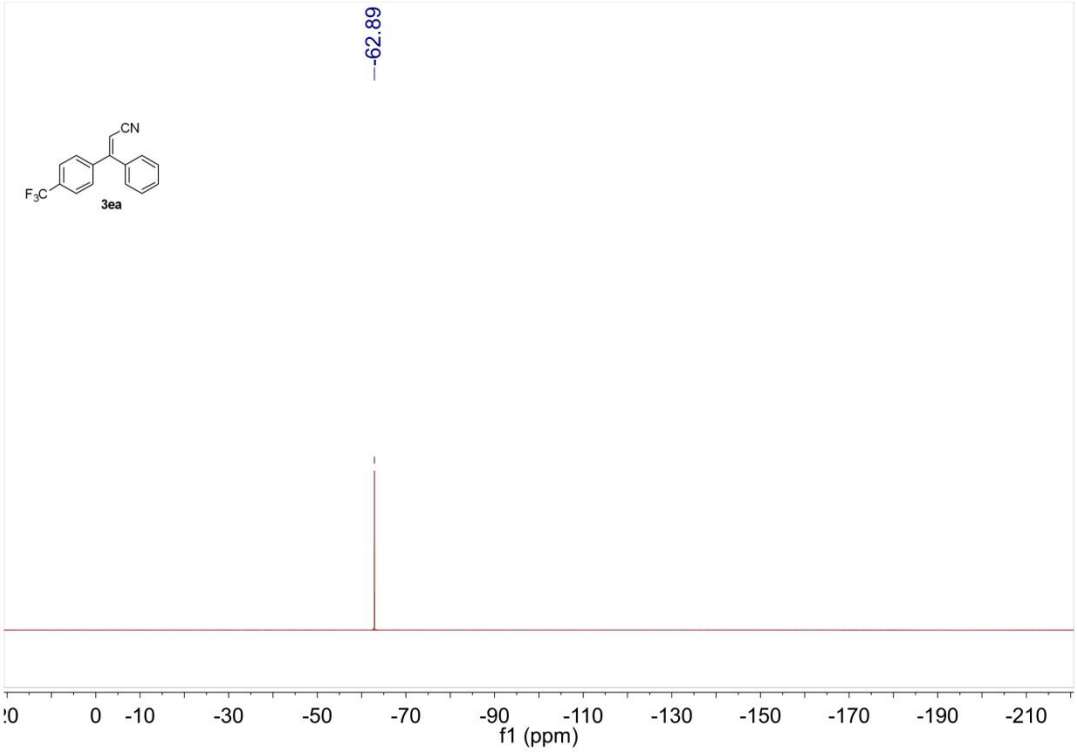
^{13}C NMR spectrum of **3da** (126 MHz, $CDCl_3$)



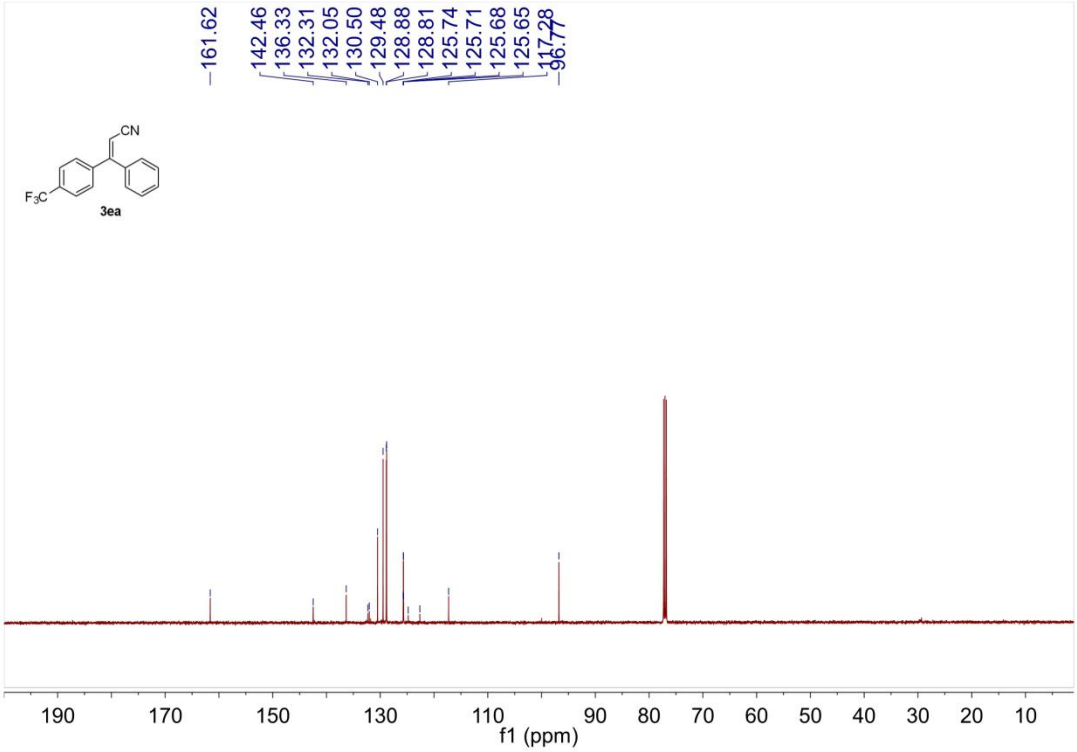
^{1}H NMR spectrum of **3ea** (500 MHz, $CDCl_3$)



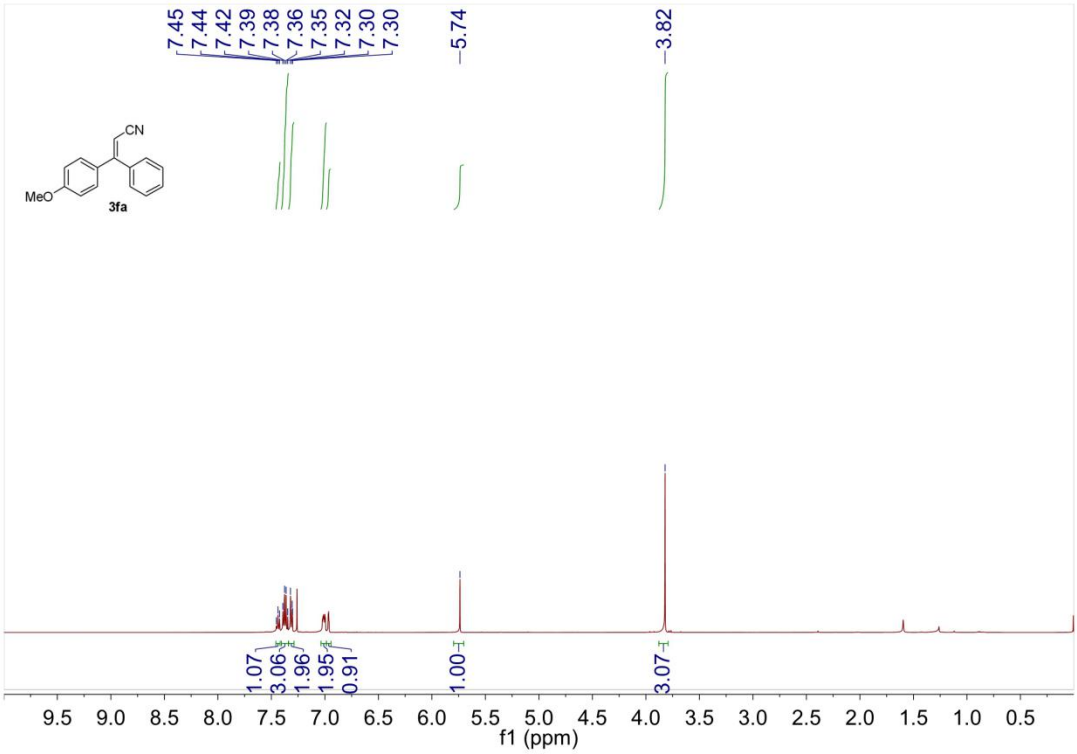
^{19}F NMR spectrum of **3ea** (471 MHz, $CDCl_3$)



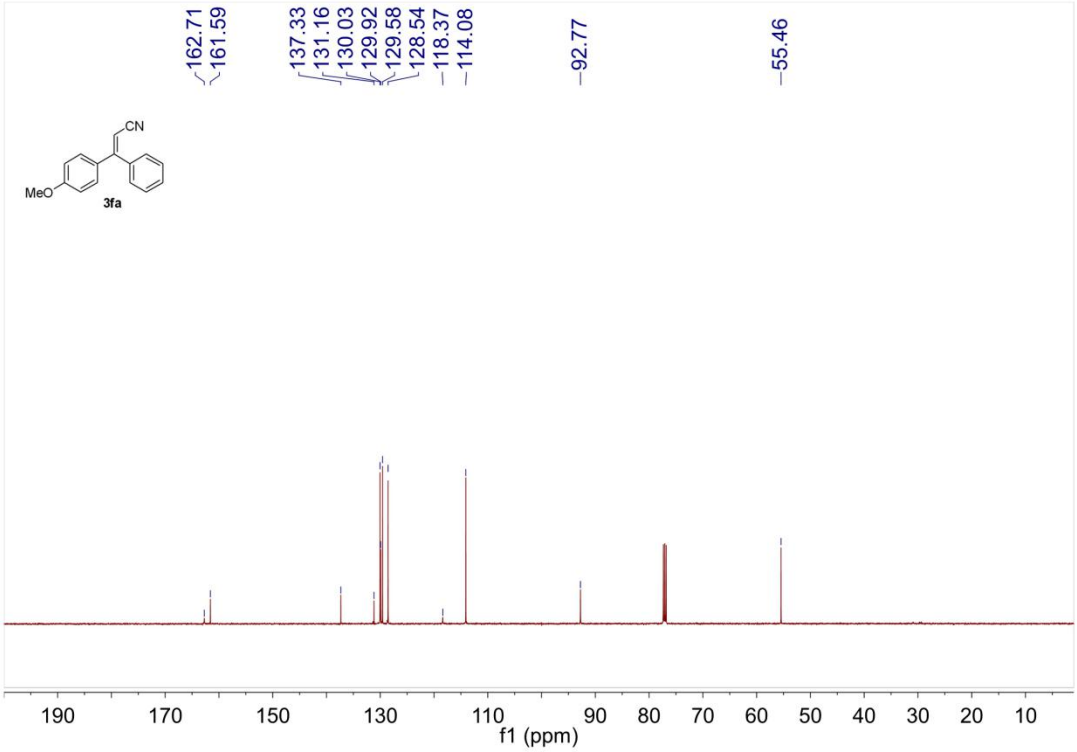
^{13}C NMR spectrum of **3ea** (126 MHz, $CDCl_3$)



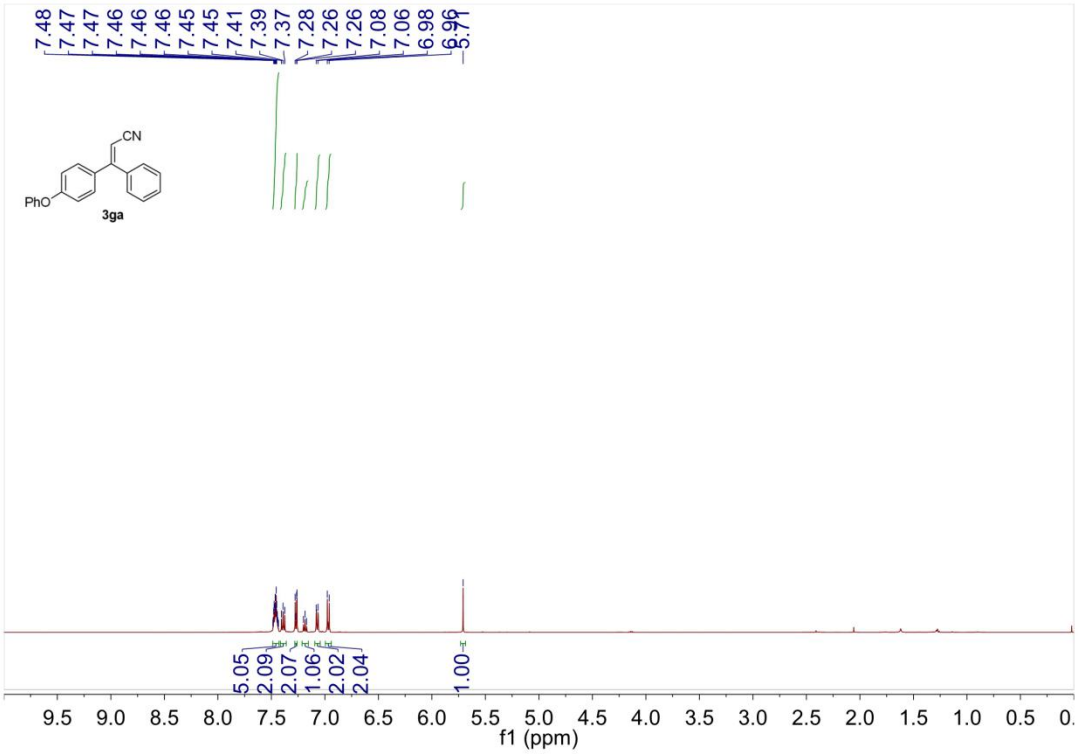
^{1}H NMR spectrum of **3fa** (500 MHz, $CDCl_3$)



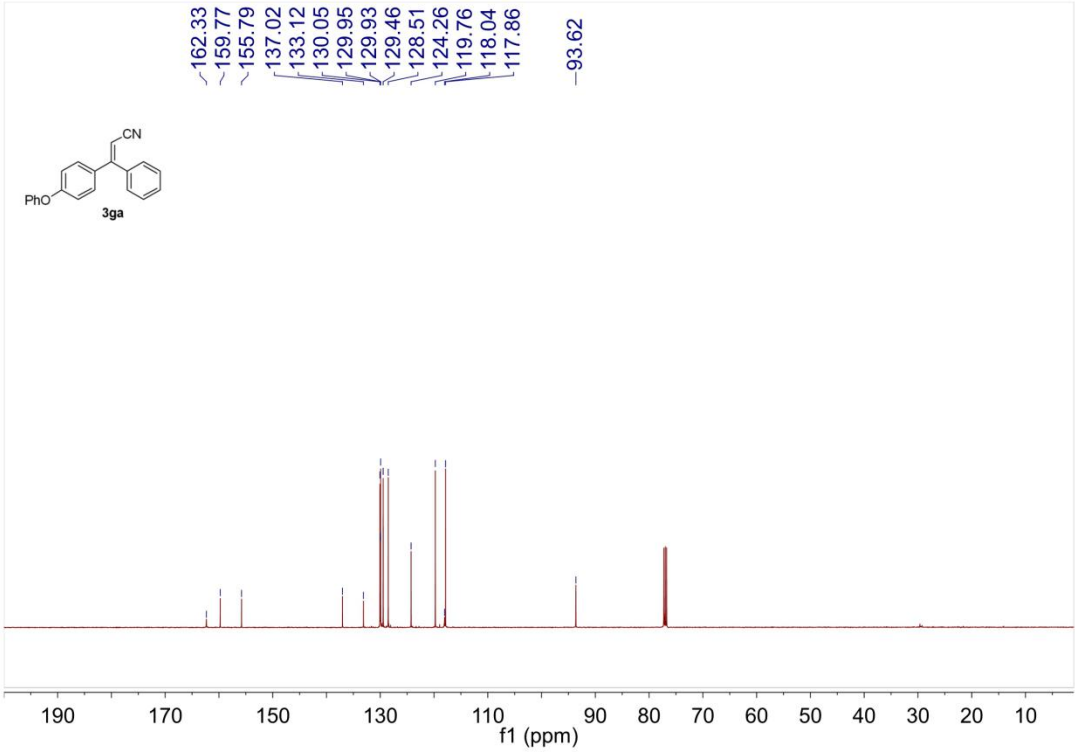
^{13}C NMR spectrum of **3fa** (126 MHz, $CDCl_3$)



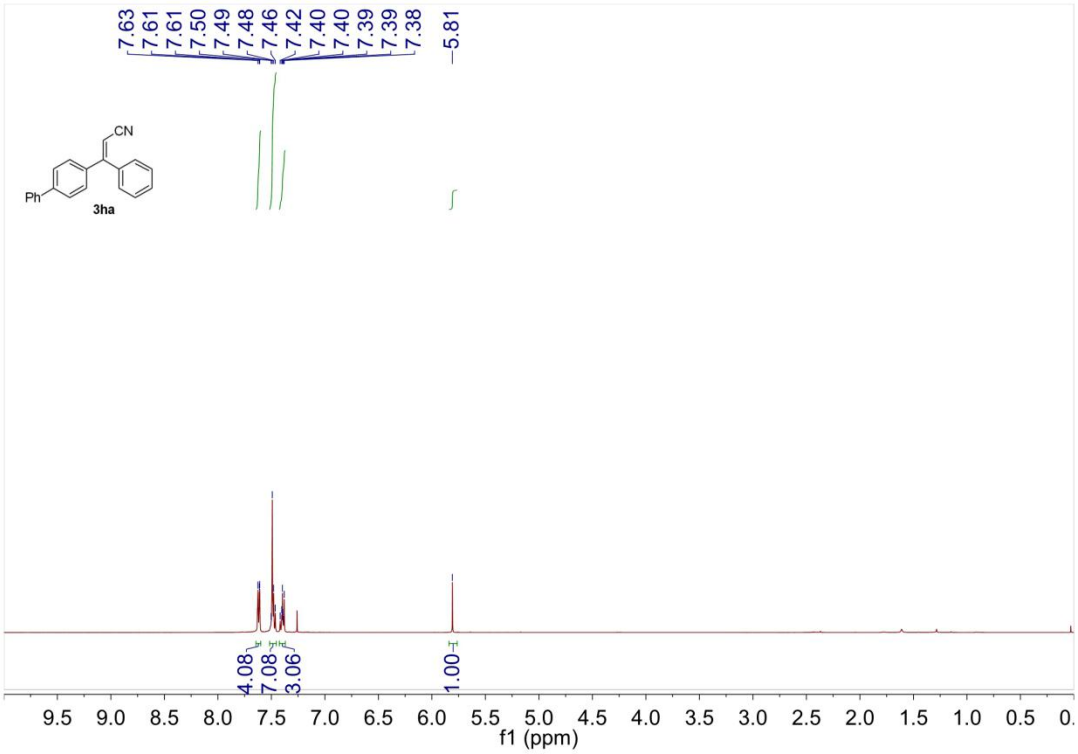
^{1}H NMR spectrum of **3ga** (500 MHz, $CDCl_3$)



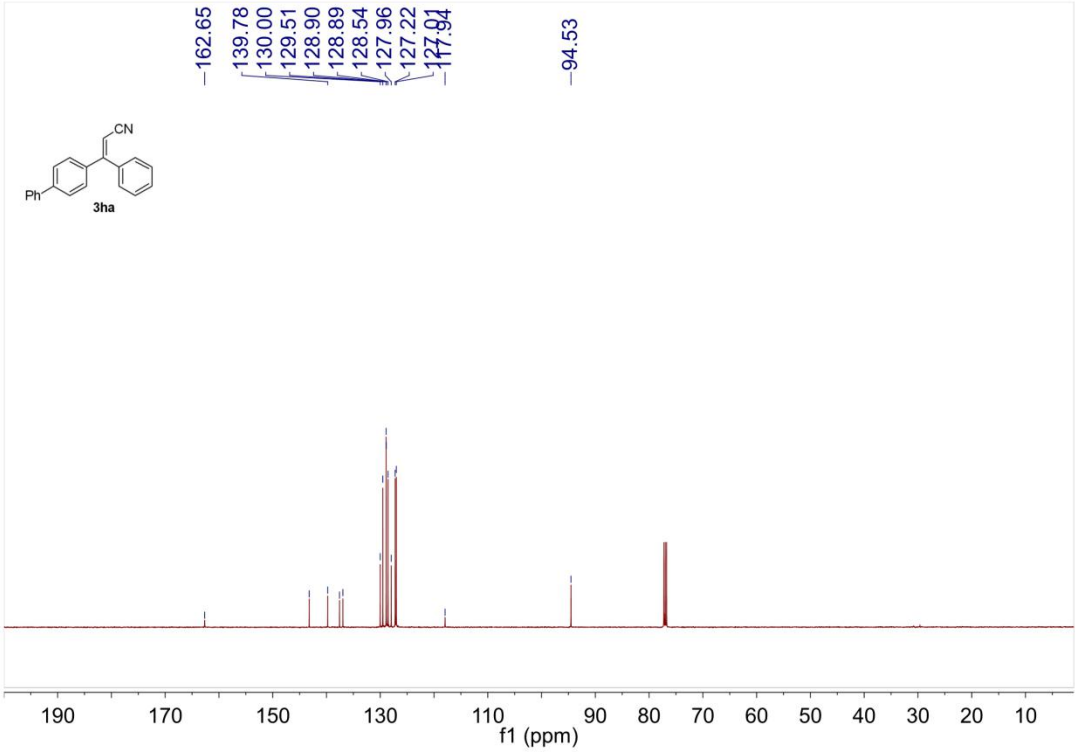
^{13}C NMR spectrum of **3ga** (126 MHz, $CDCl_3$)



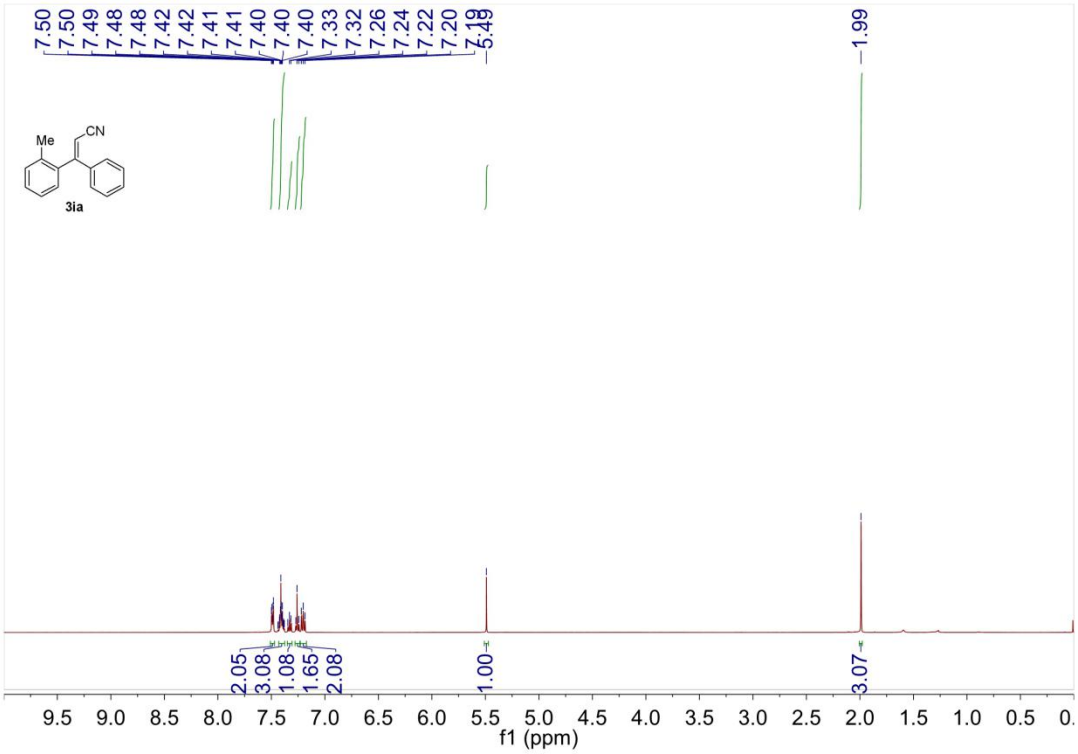
^{1}H NMR spectrum of **3ha** (500 MHz, $CDCl_3$)



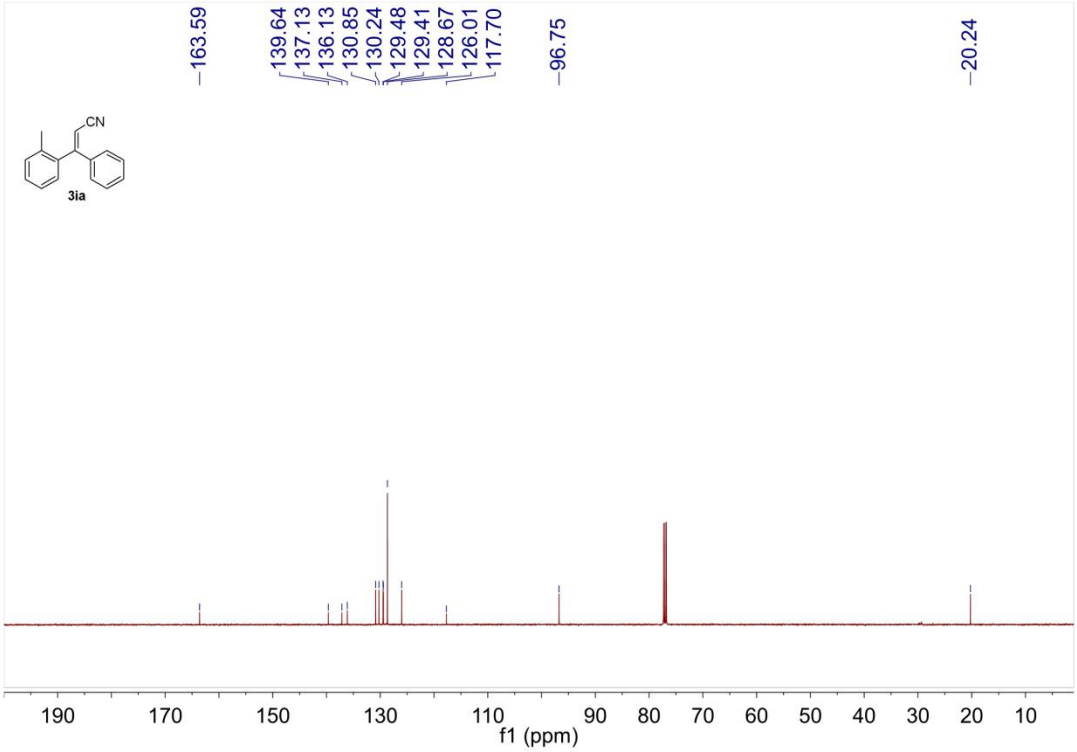
^{13}C NMR spectrum of **3ha** (126 MHz, $CDCl_3$)



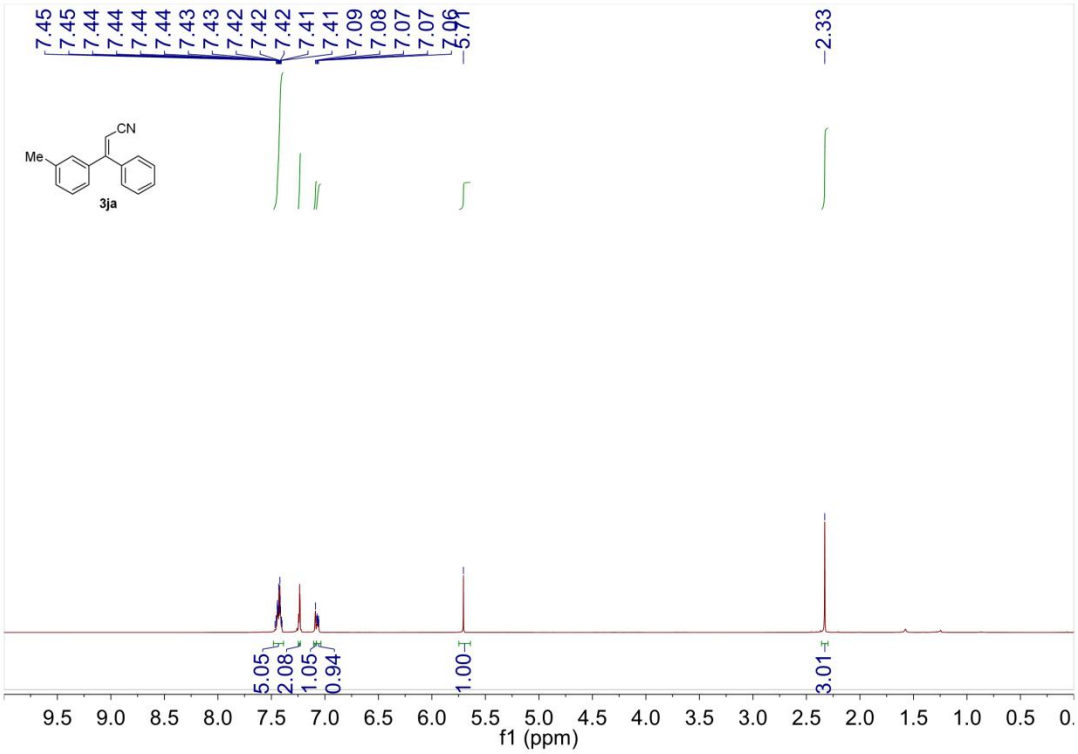
^{1}H NMR spectrum of **3ia** (500 MHz, $CDCl_3$)



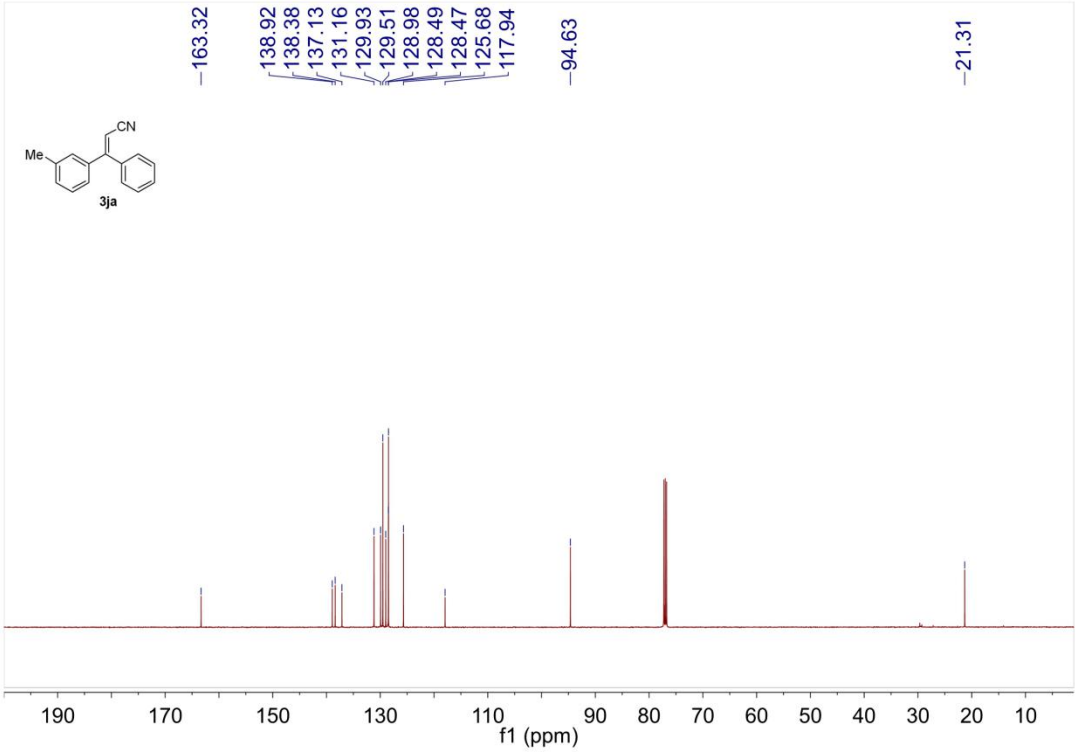
^{13}C NMR spectrum of **3ia** (126 MHz, $CDCl_3$)



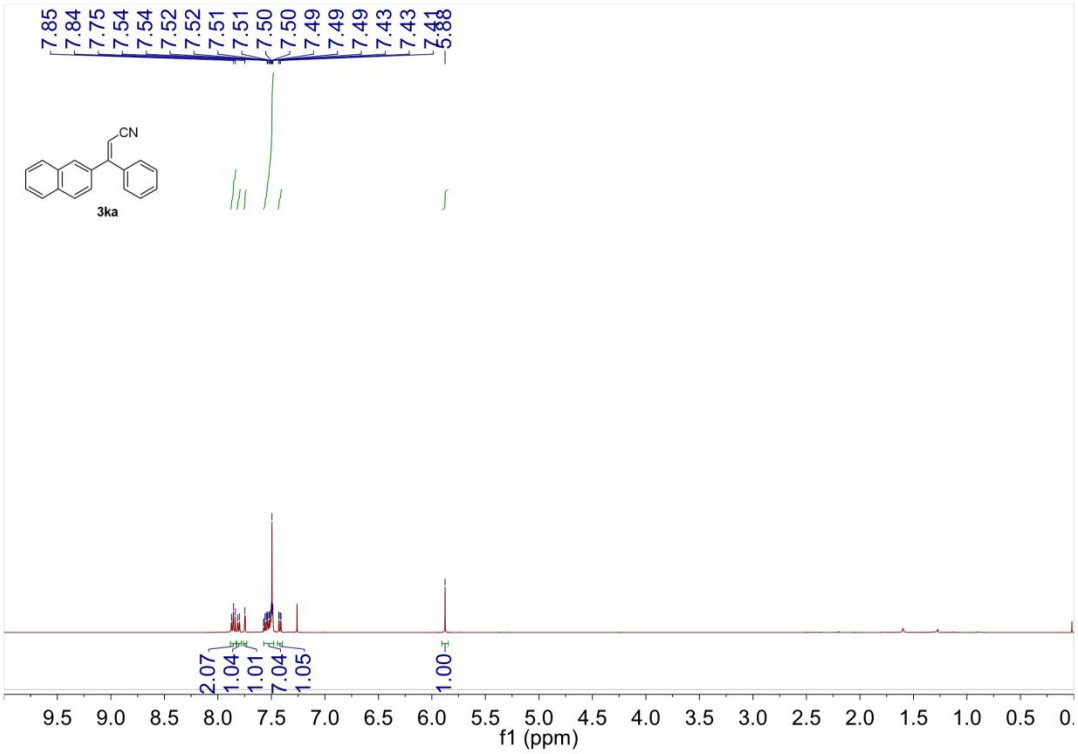
^{1}H NMR spectrum of **3ja** (500 MHz, $CDCl_3$)



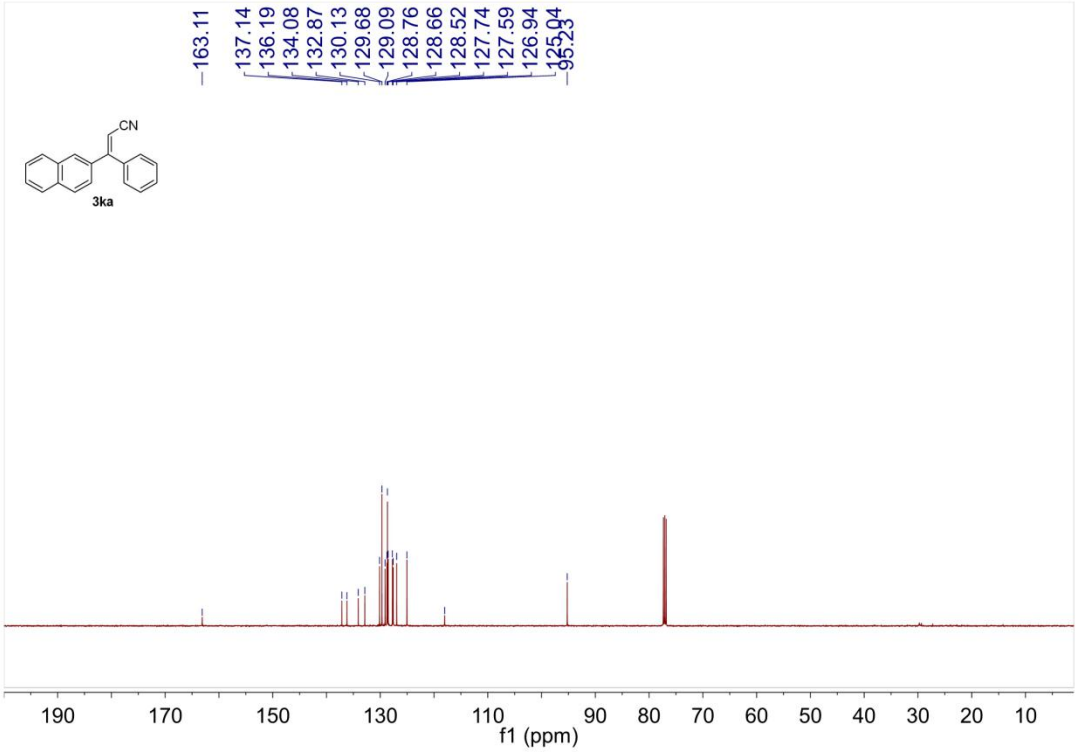
^{13}C NMR spectrum of **3ja** (126 MHz, $CDCl_3$)



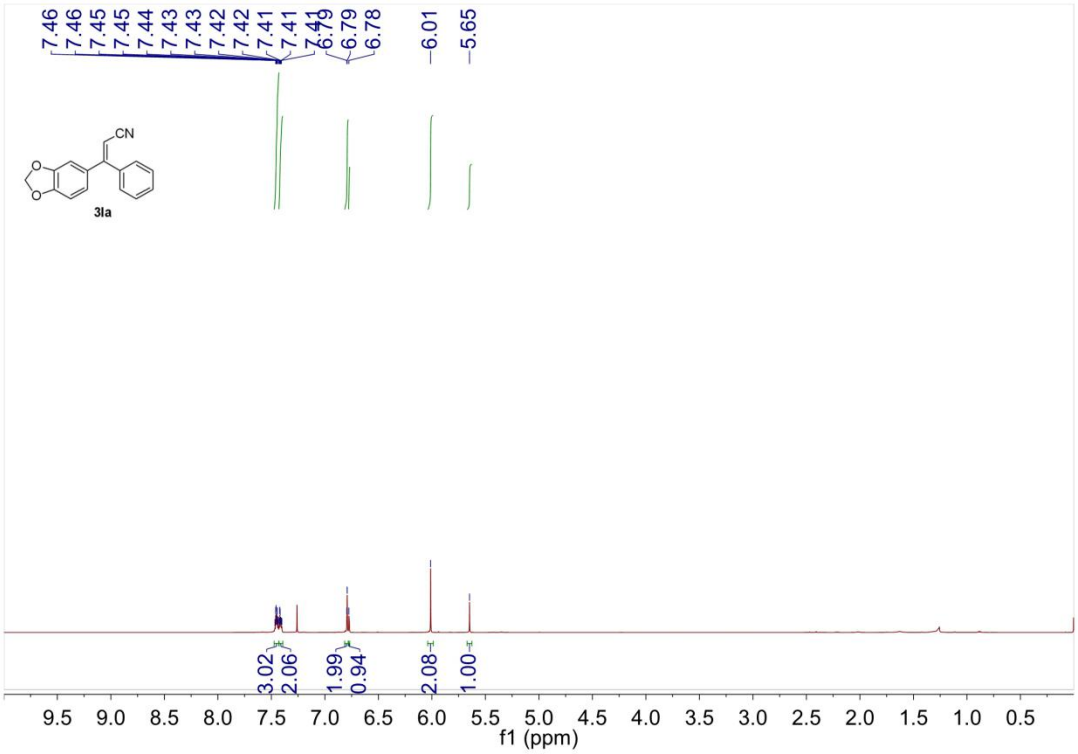
^{1}H NMR spectrum of **3ka** (500 MHz, $CDCl_3$)



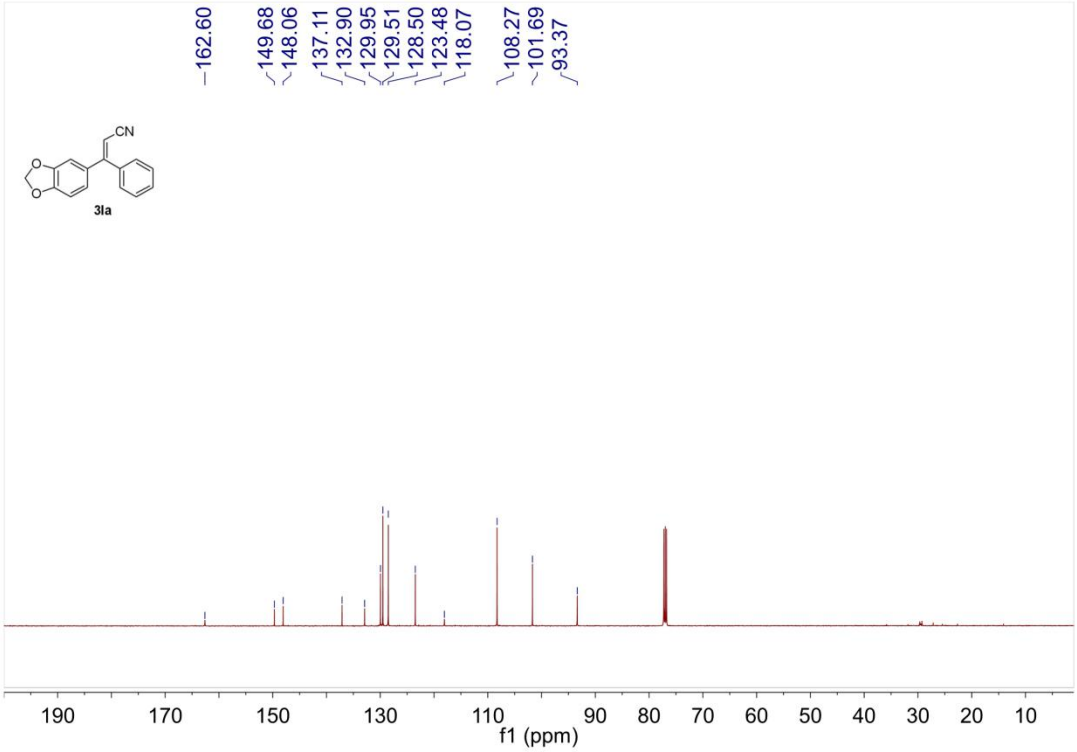
^{13}C NMR spectrum of **3ka** (126 MHz, $CDCl_3$)



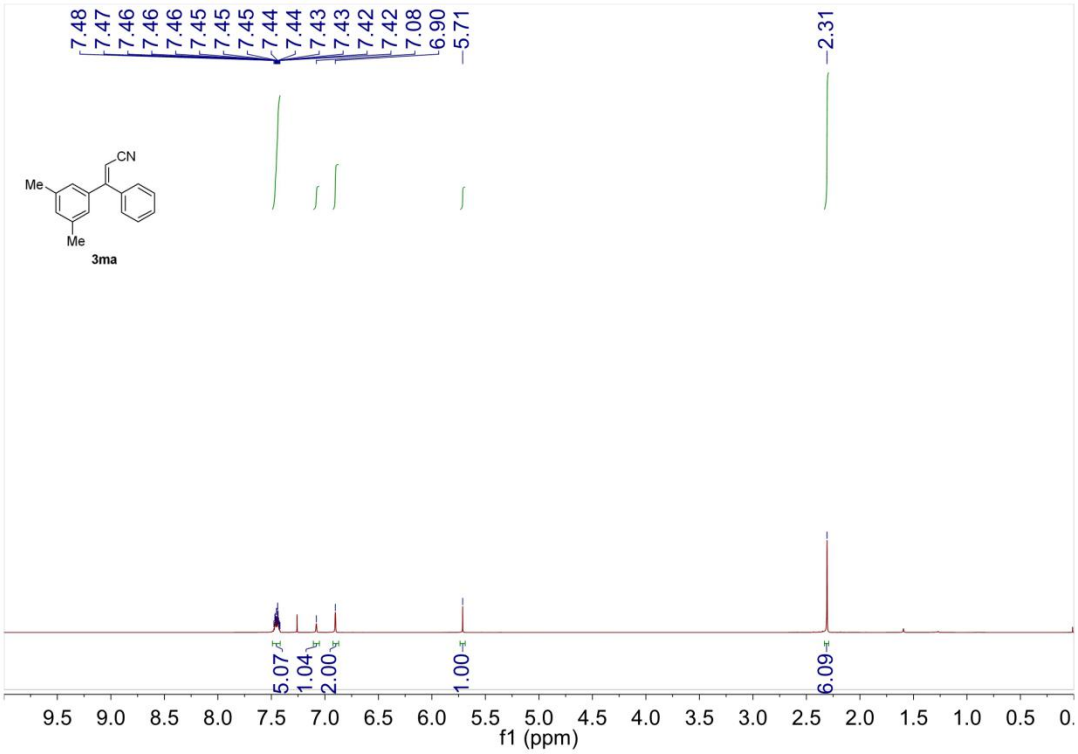
^{1}H NMR spectrum of **3la** (500 MHz, $CDCl_3$)



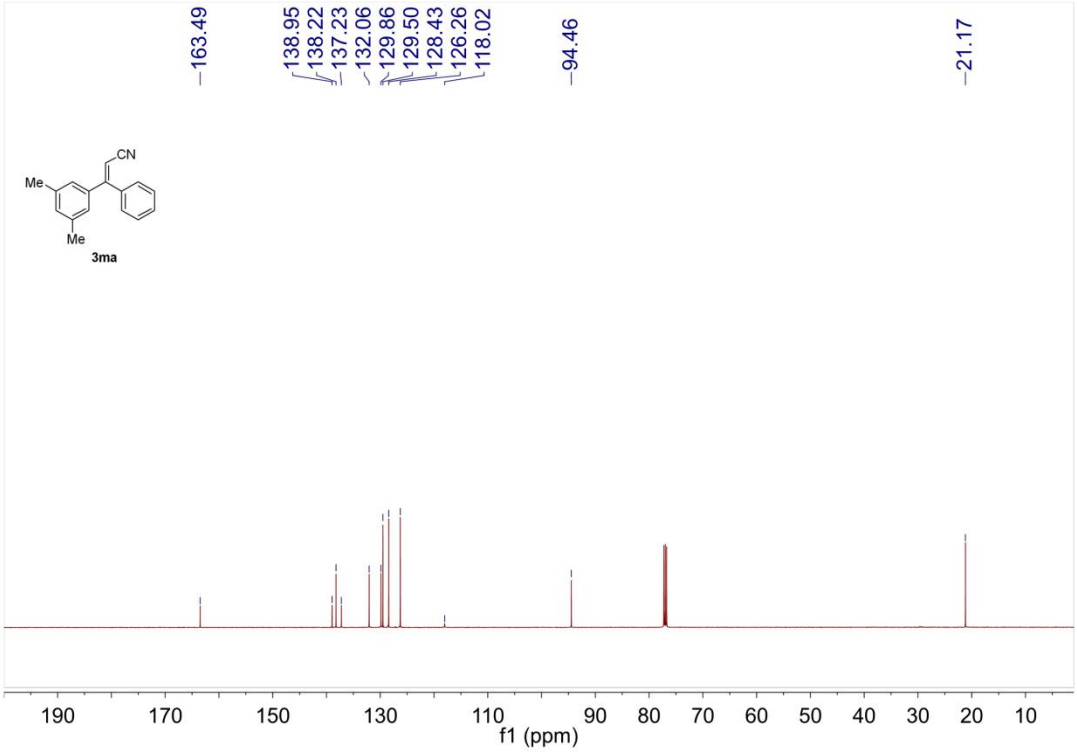
^{13}C NMR spectrum of **3la** (126 MHz, $CDCl_3$)



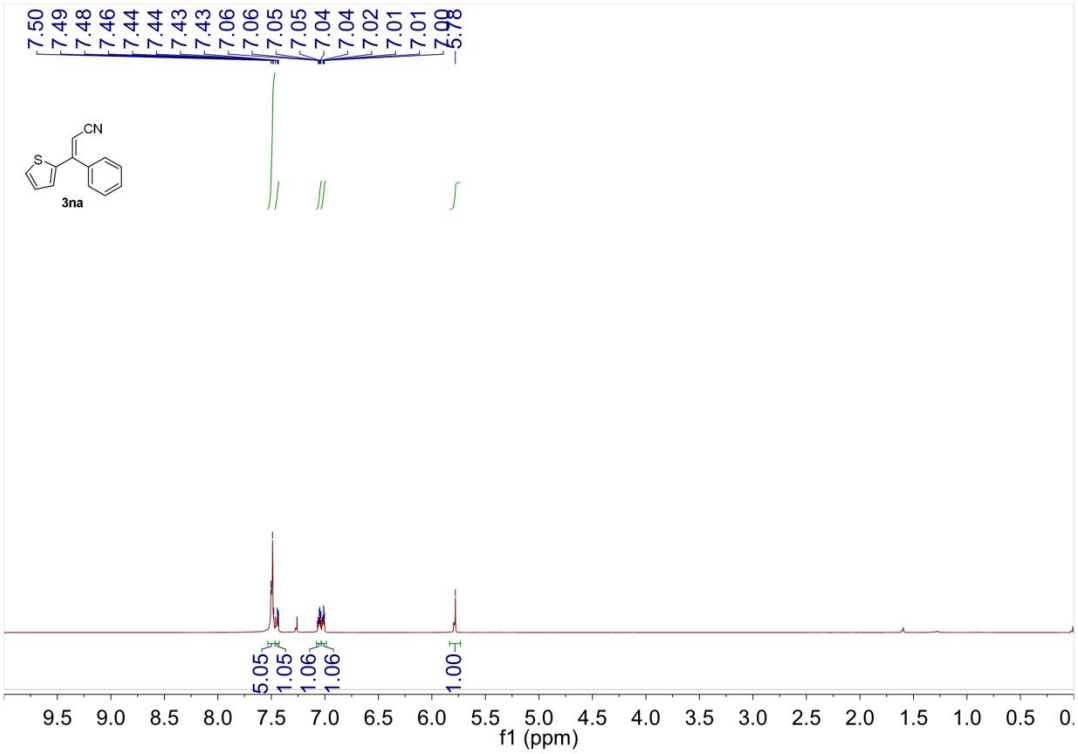
^{1}H NMR spectrum of **3ma** (500 MHz, $CDCl_3$)



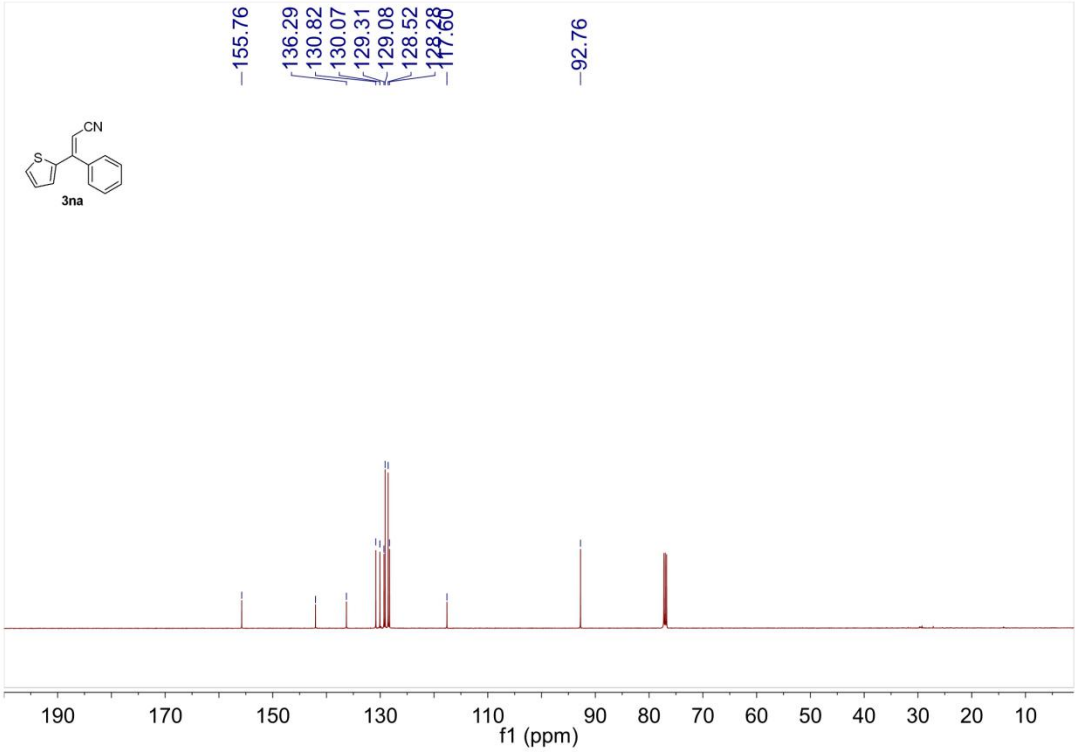
^{13}C NMR spectrum of **3ma** (126 MHz, $CDCl_3$)



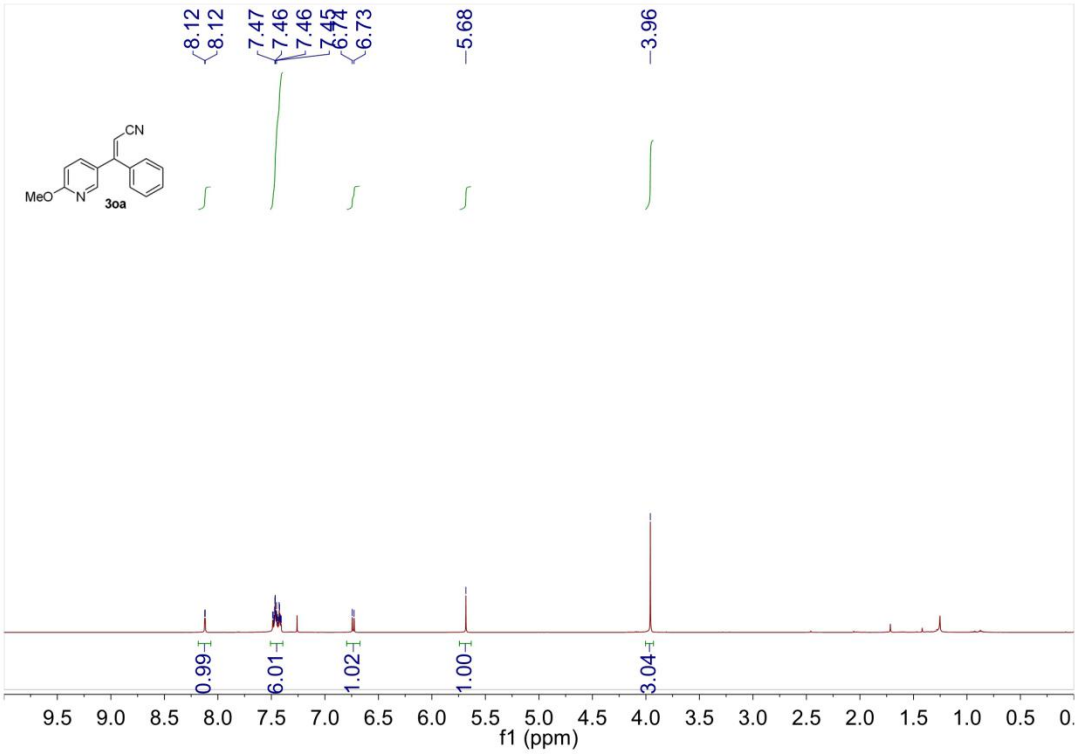
^{1}H NMR spectrum of **3na** (500 MHz, $CDCl_3$)



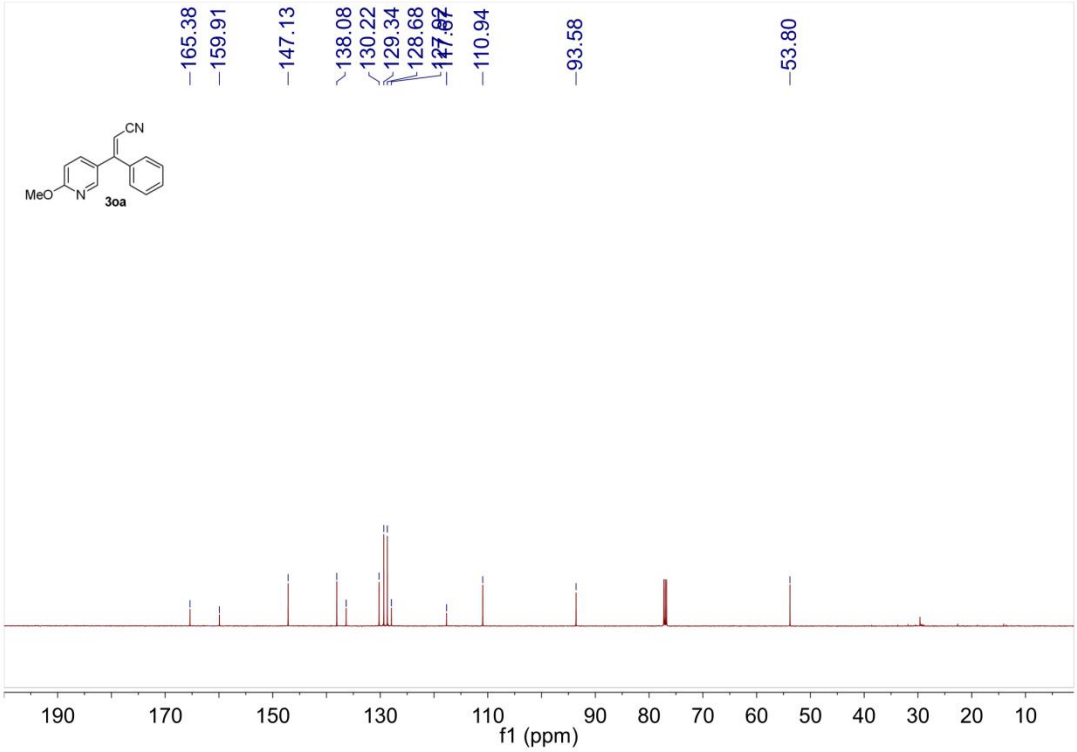
^{13}C NMR spectrum of **3na** (126 MHz, $CDCl_3$)



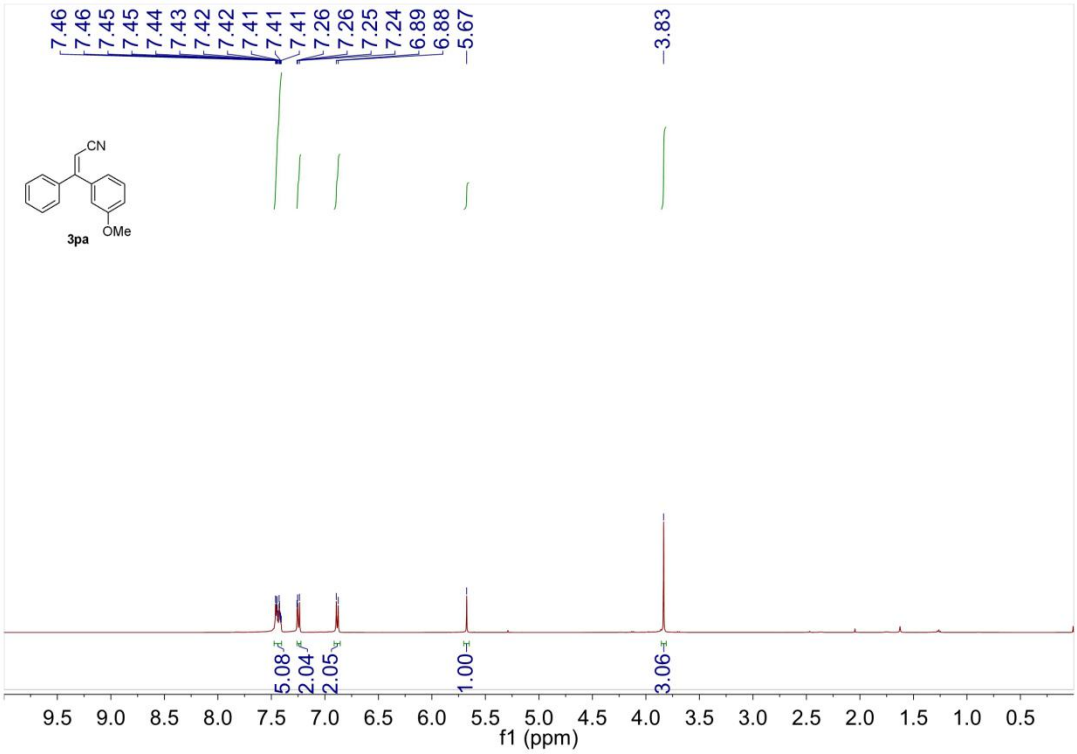
^{1}H NMR spectrum of **3oa** (500 MHz, $CDCl_3$)



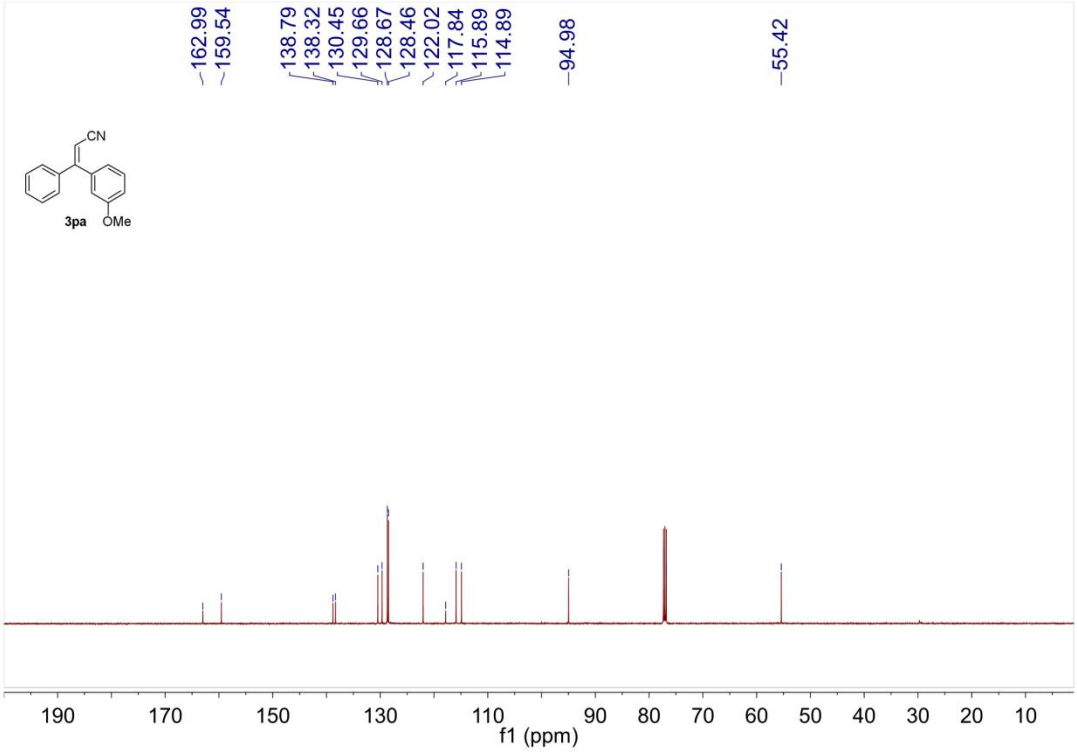
^{13}C NMR spectrum of **3oa** (126 MHz, $CDCl_3$)



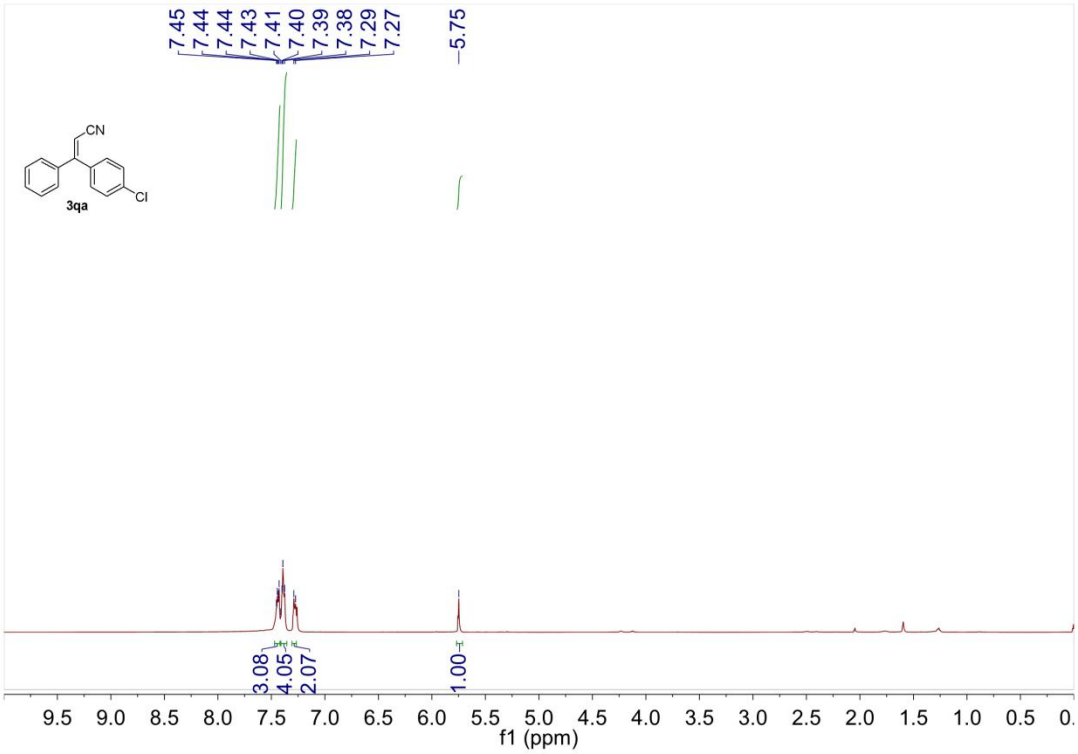
^{1}H NMR spectrum of **3pa** (500 MHz, $CDCl_3$)



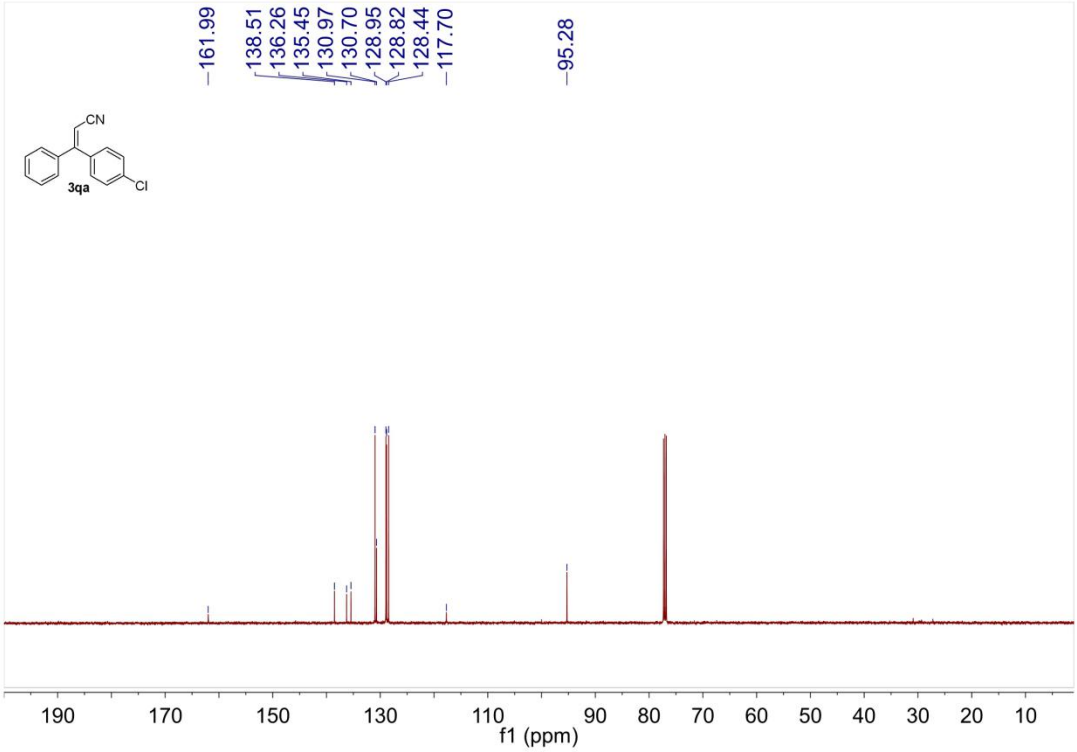
^{13}C NMR spectrum of **3pa** (126 MHz, $CDCl_3$)



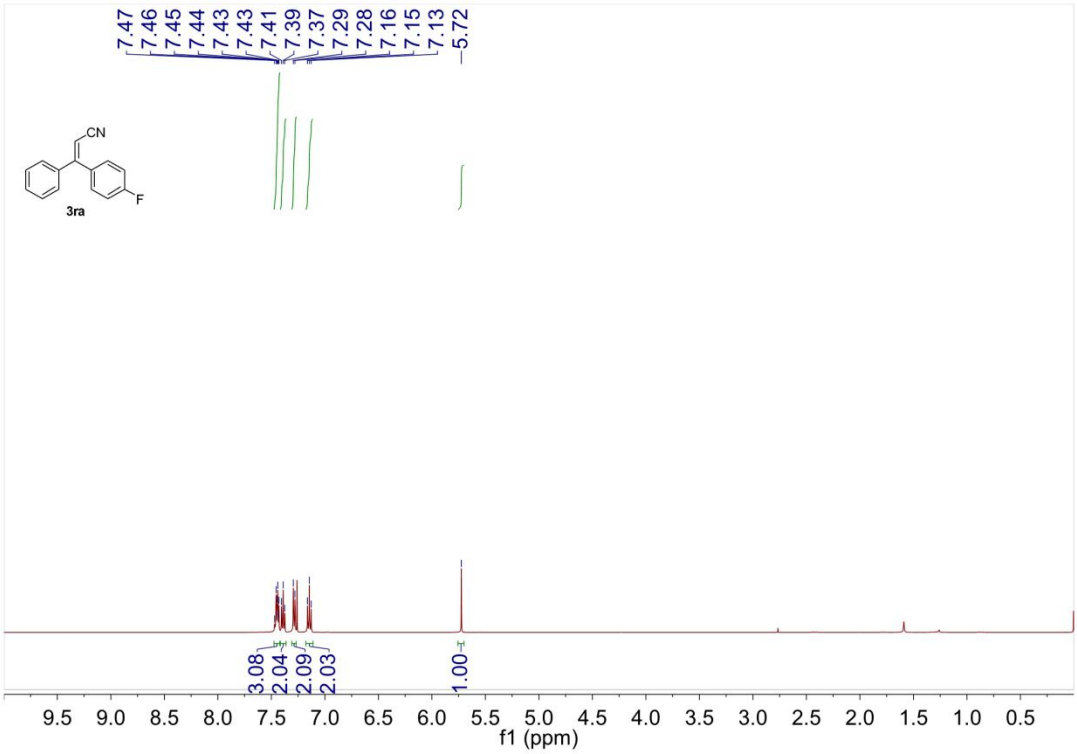
^{1}H NMR spectrum of **3qa** (500 MHz, $CDCl_3$)



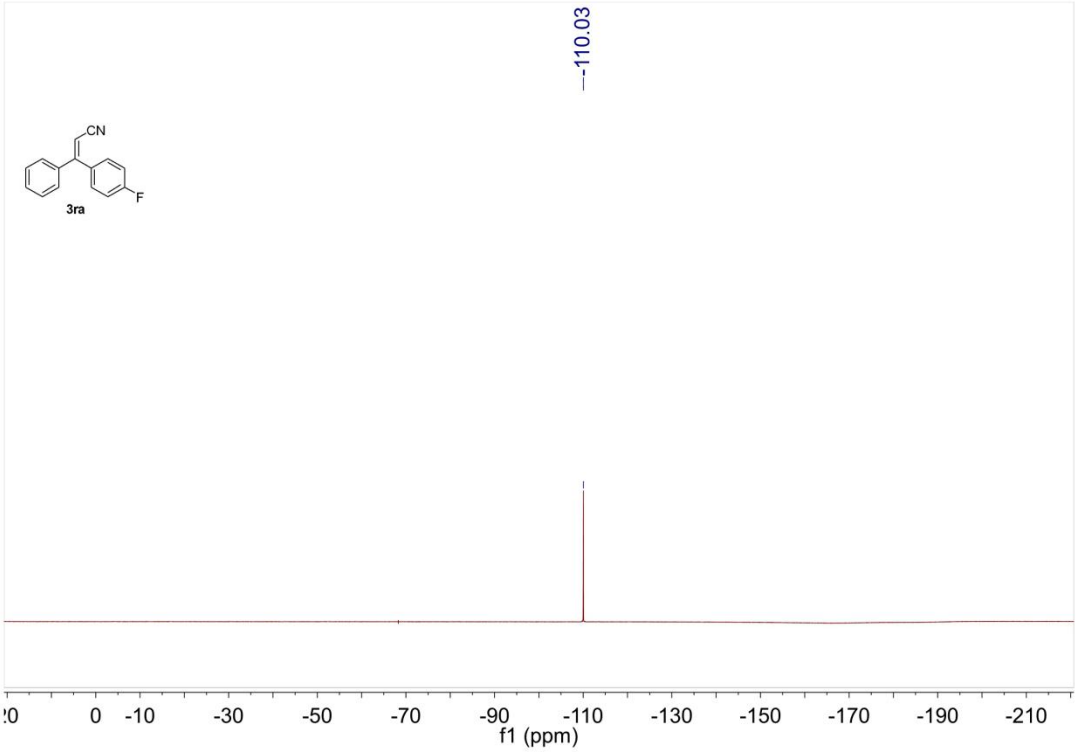
^{13}C NMR spectrum of **3qa** (126 MHz, $CDCl_3$)



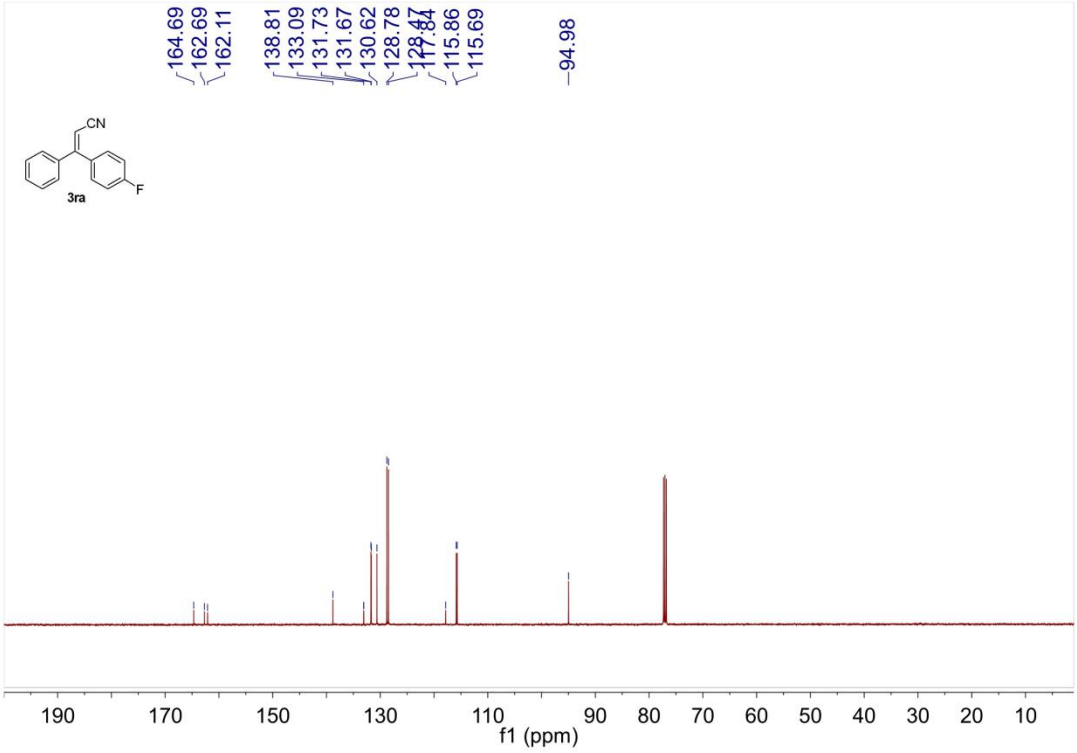
^{1}H NMR spectrum of **3ra** (500 MHz, $CDCl_3$)



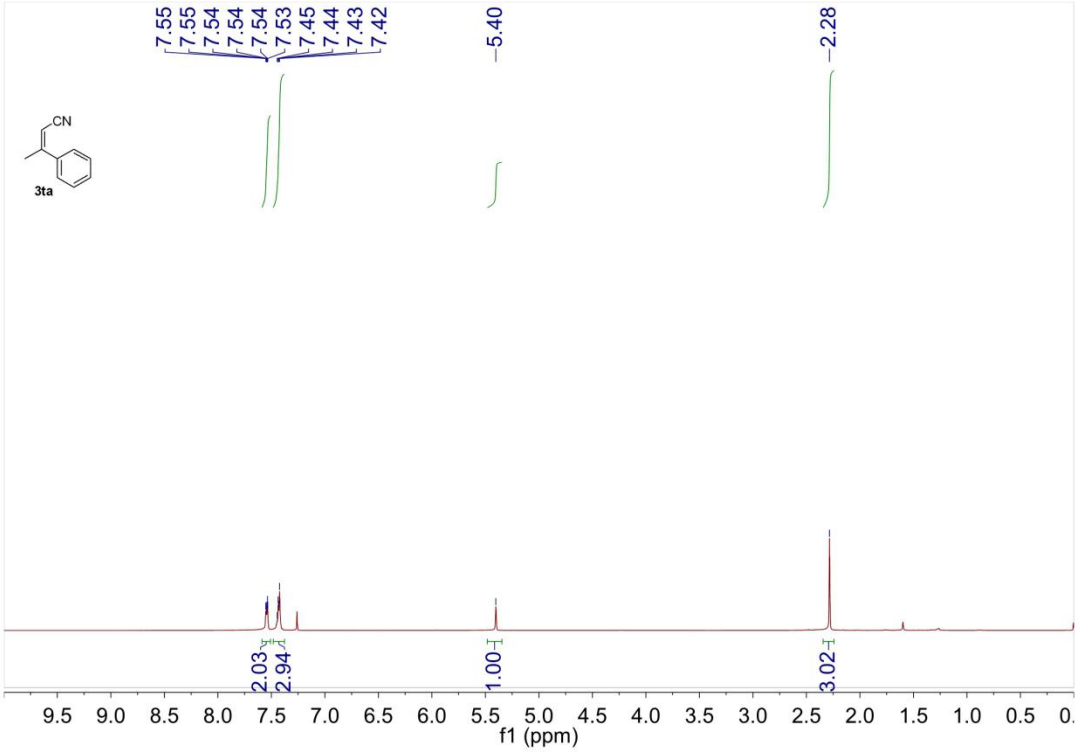
^{19}F NMR spectrum of **3ra** (471 MHz, $CDCl_3$)



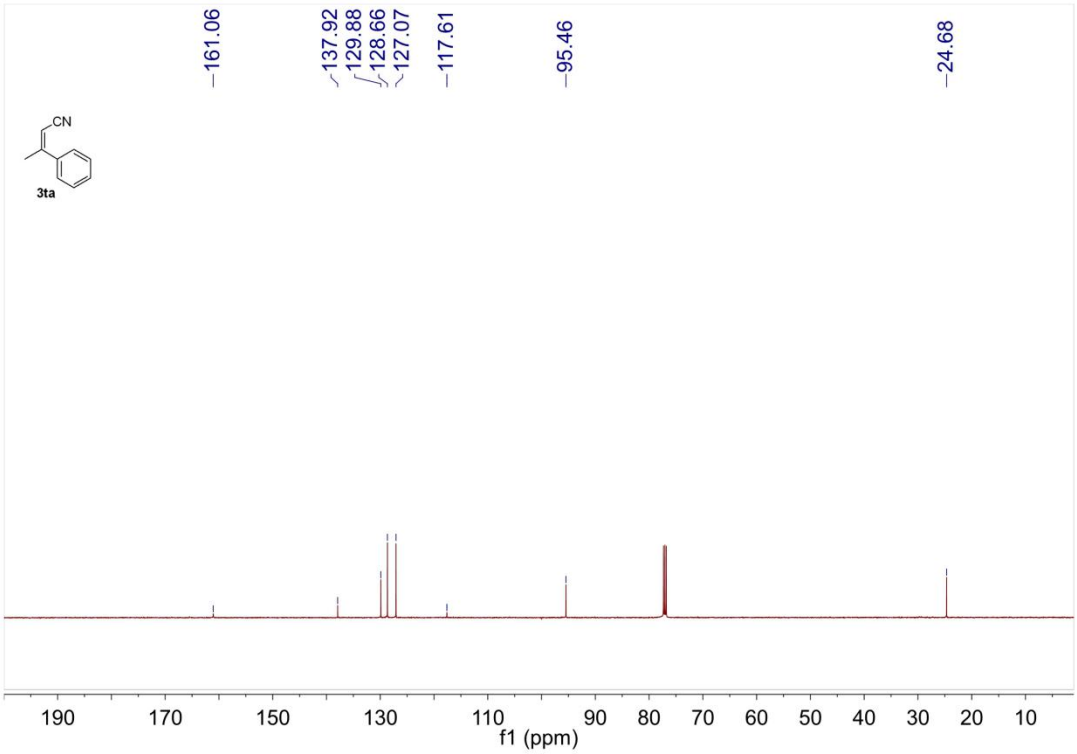
^{13}C NMR spectrum of **3ra** (126 MHz, $CDCl_3$)



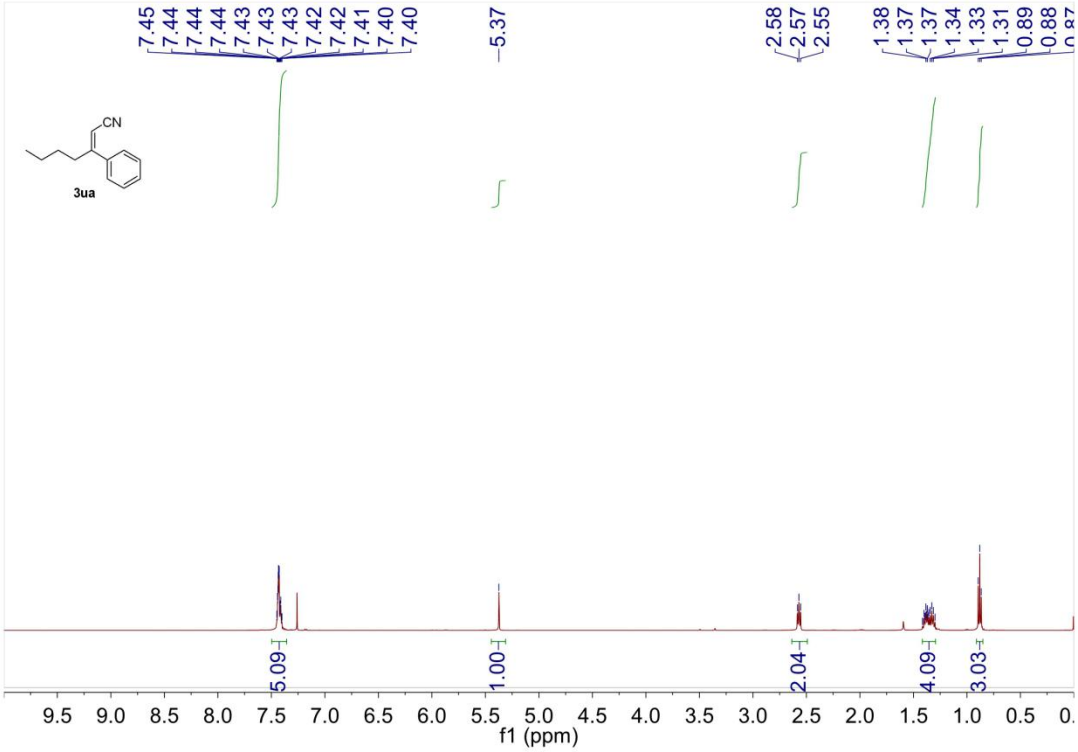
^{1}H NMR spectrum of **3ta** (500 MHz, $CDCl_3$)



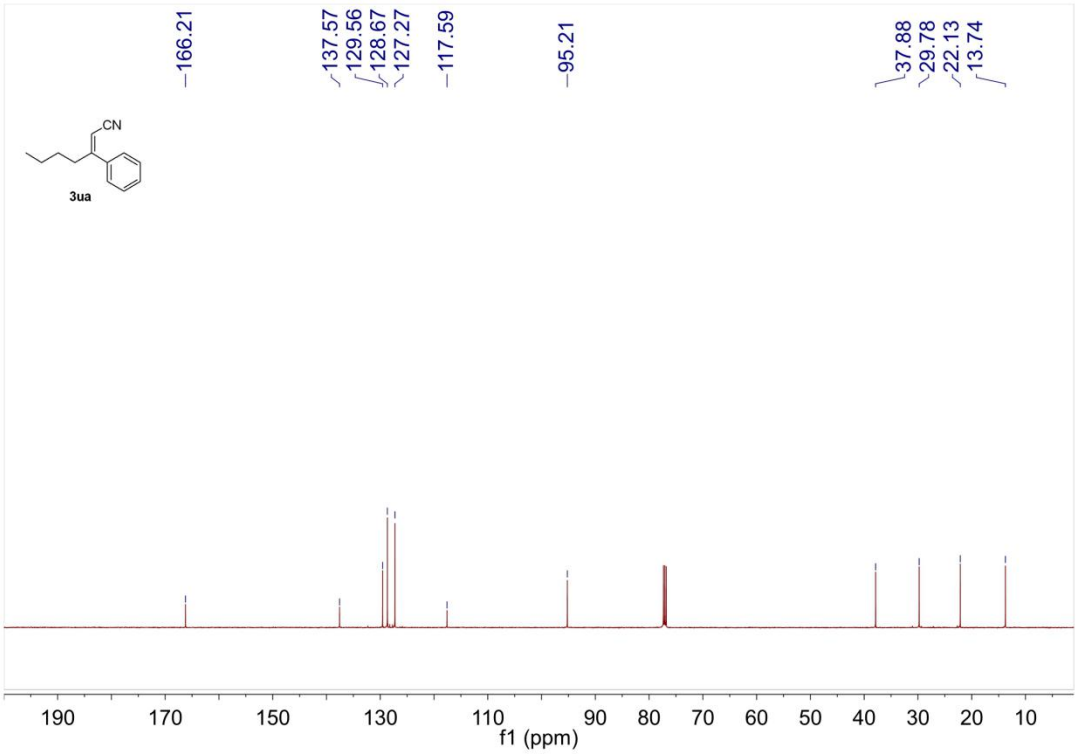
^{13}C NMR spectrum of **3ta** (126 MHz, $CDCl_3$)



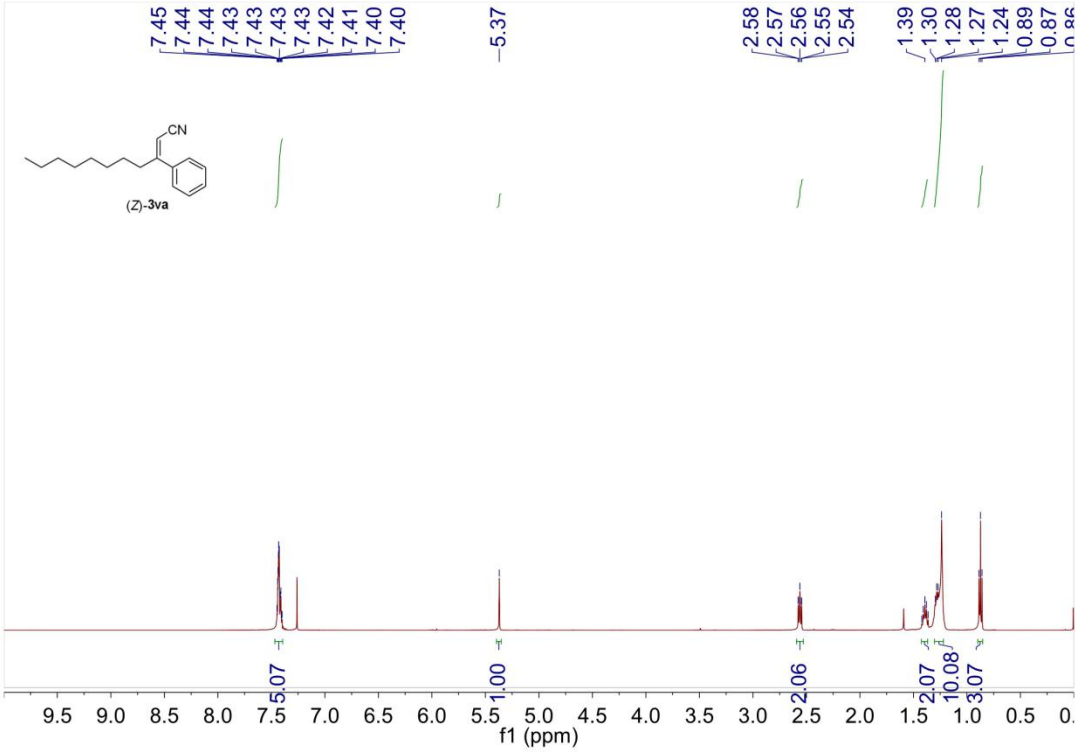
^{1}H NMR spectrum of **3ua** (500 MHz, $CDCl_3$)



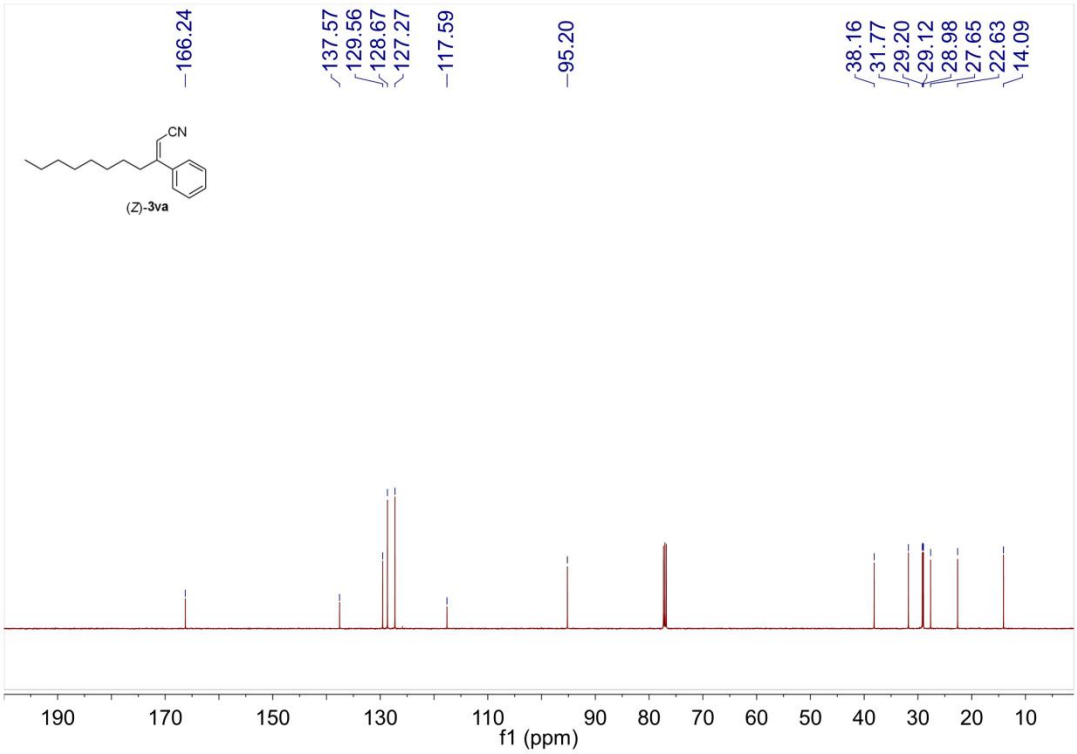
^{13}C NMR spectrum of **3ua** (126 MHz, $CDCl_3$)



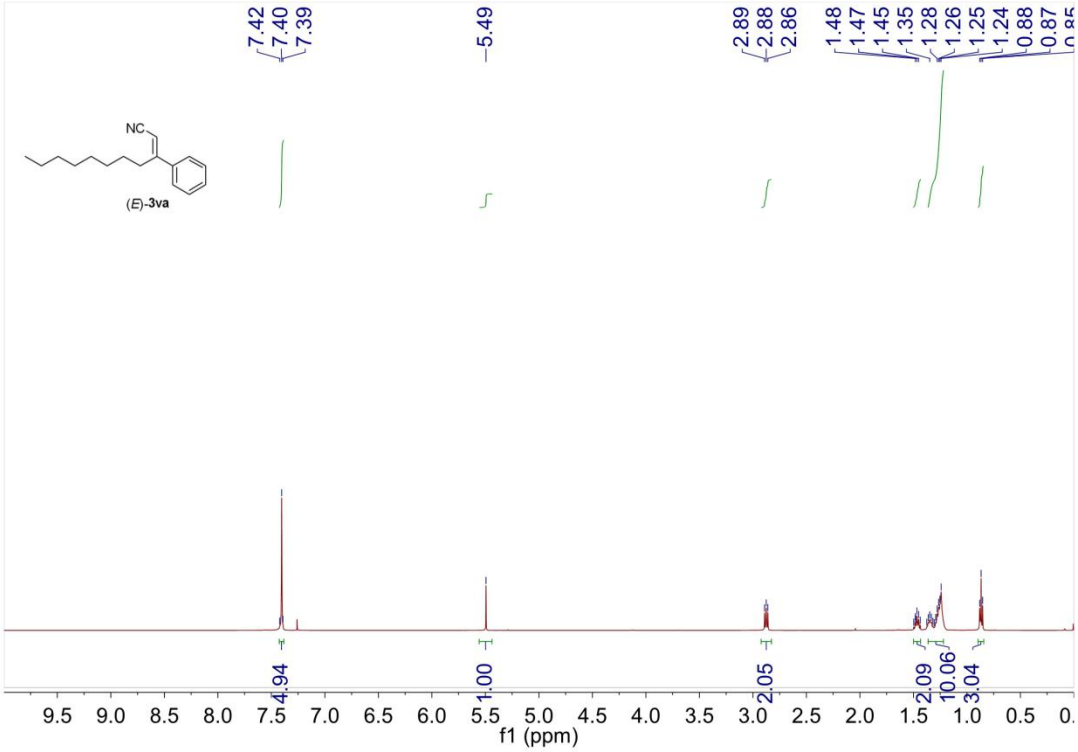
^{1}H NMR spectrum of (*Z*)-**3va** (500 MHz, $CDCl_3$)



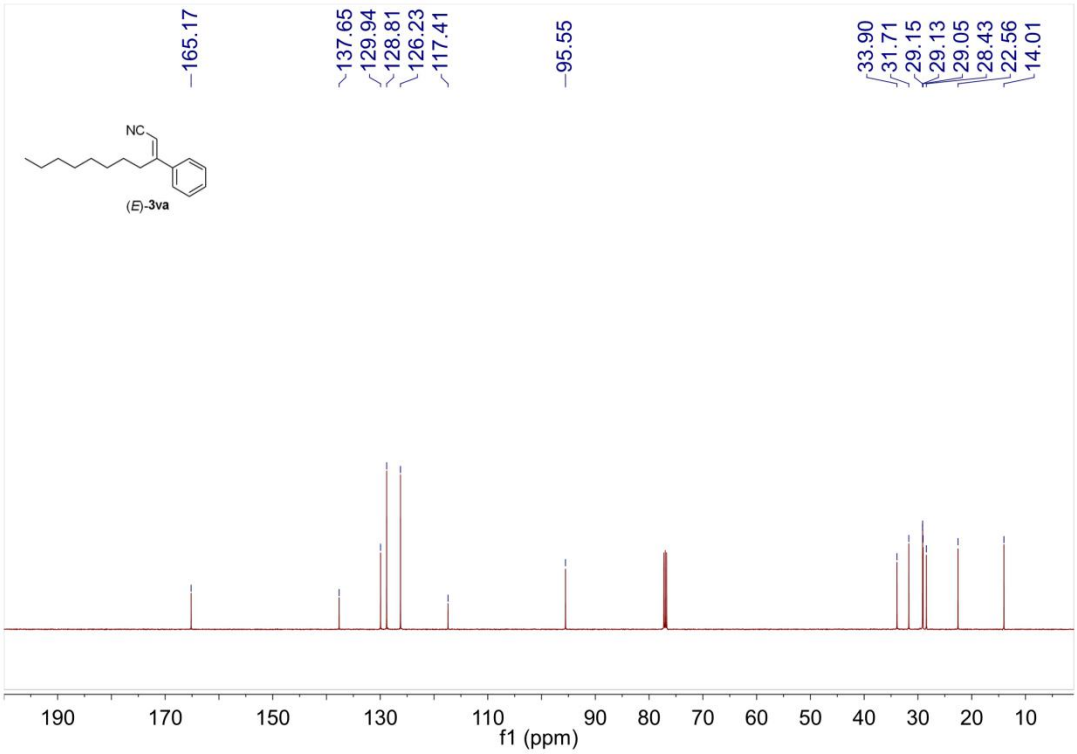
^{13}C NMR spectrum of (*Z*)-**3va** (126 MHz, $CDCl_3$)



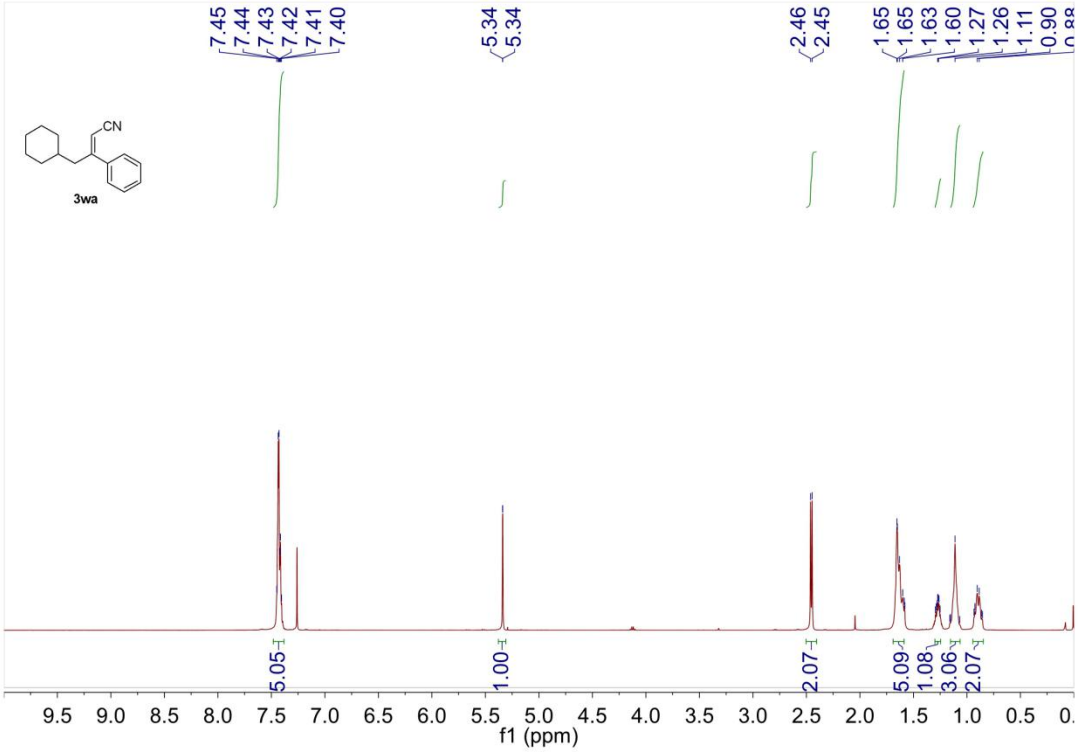
^{1}H NMR spectrum of (*E*)-**3va** (500 MHz, $CDCl_3$)



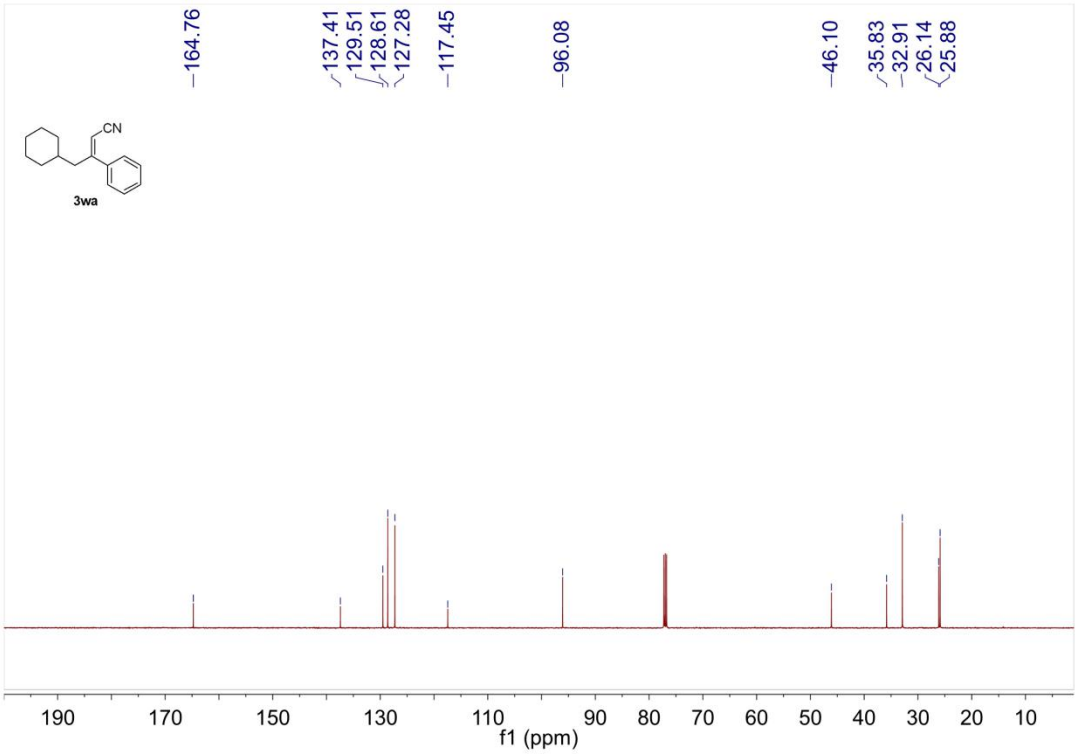
^{13}C NMR spectrum of (*E*)-**3va** (126 MHz, $CDCl_3$)



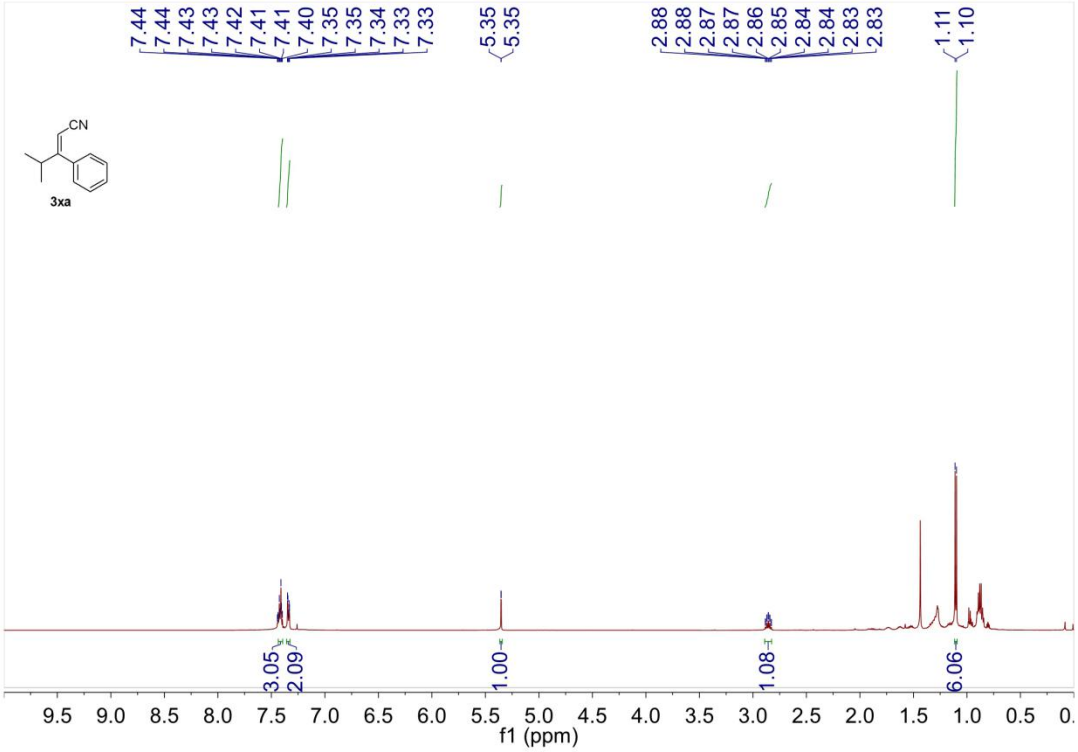
^{1}H NMR spectrum of **3wa** (500 MHz, $CDCl_3$)



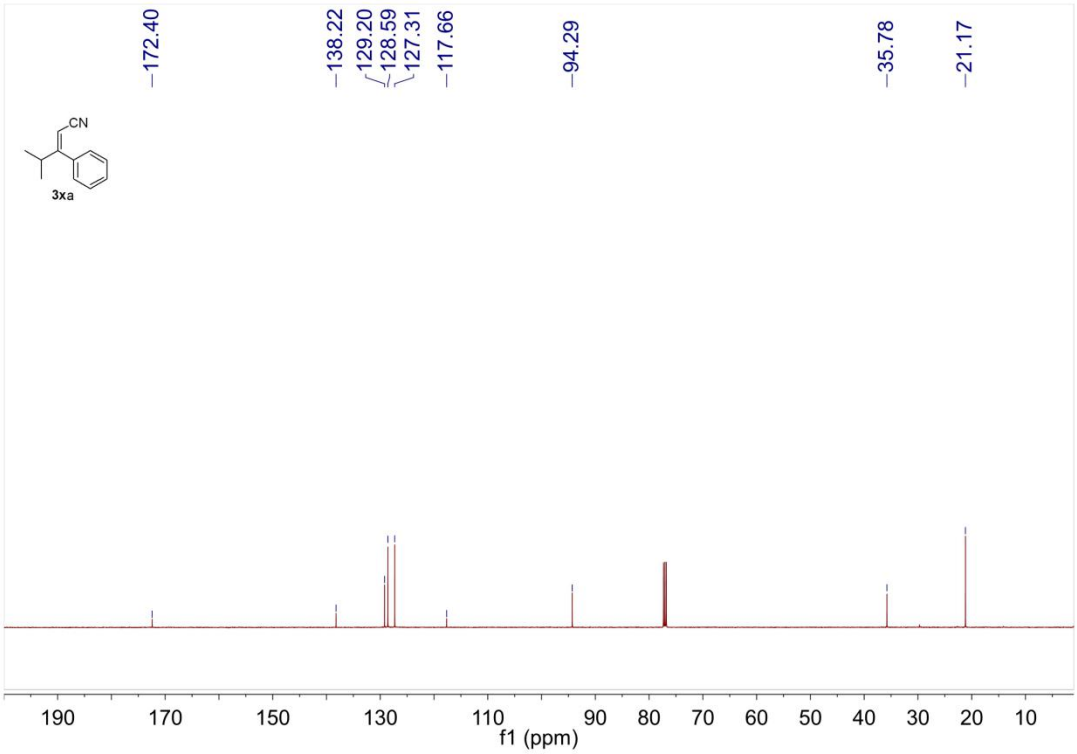
^{13}C NMR spectrum of **3wa** (126 MHz, $CDCl_3$)



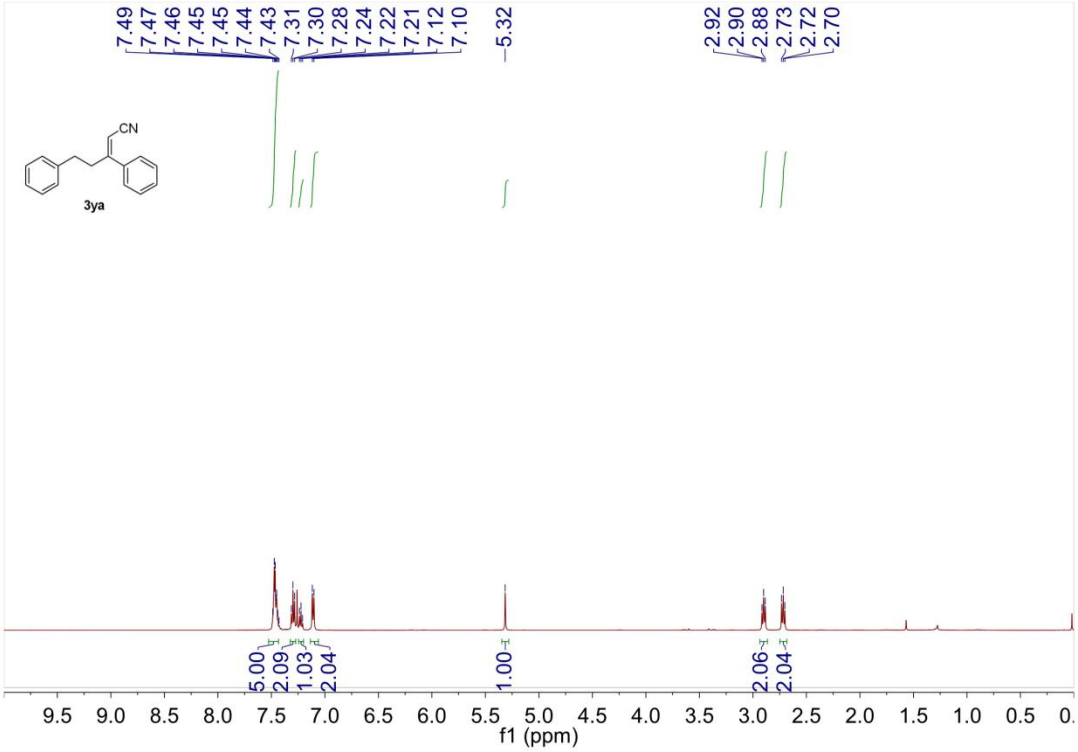
^{1}H NMR spectrum of **3xa** (500 MHz, $CDCl_3$)



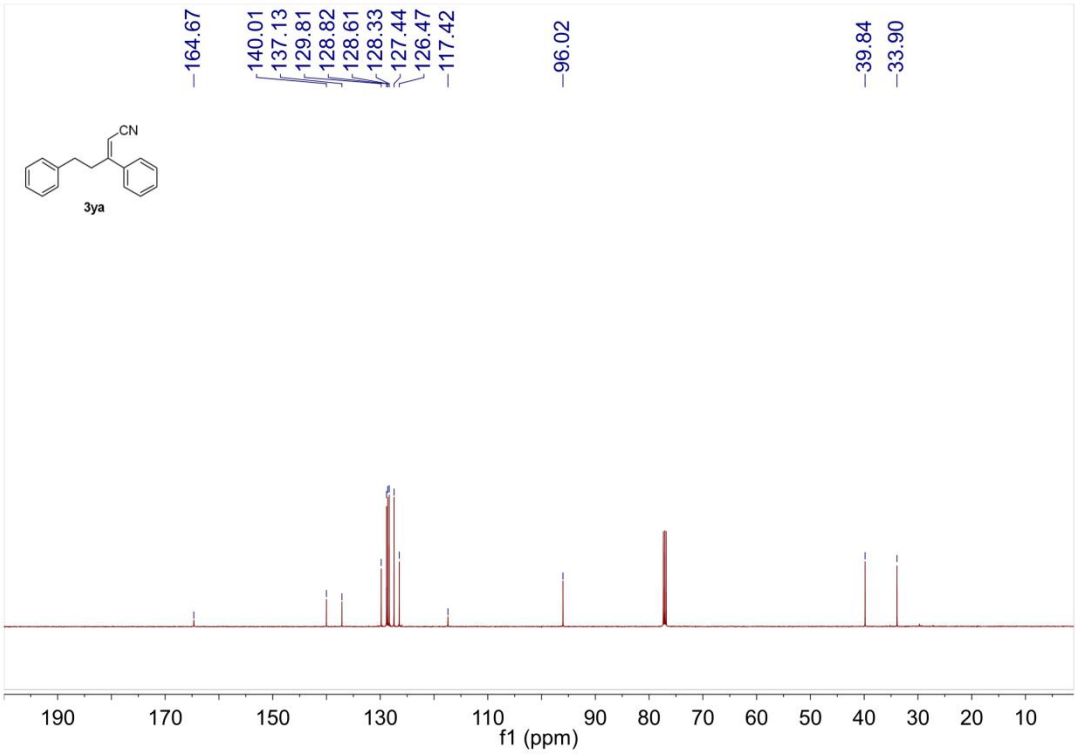
^{13}C NMR spectrum of **3xa** (126 MHz, $CDCl_3$)



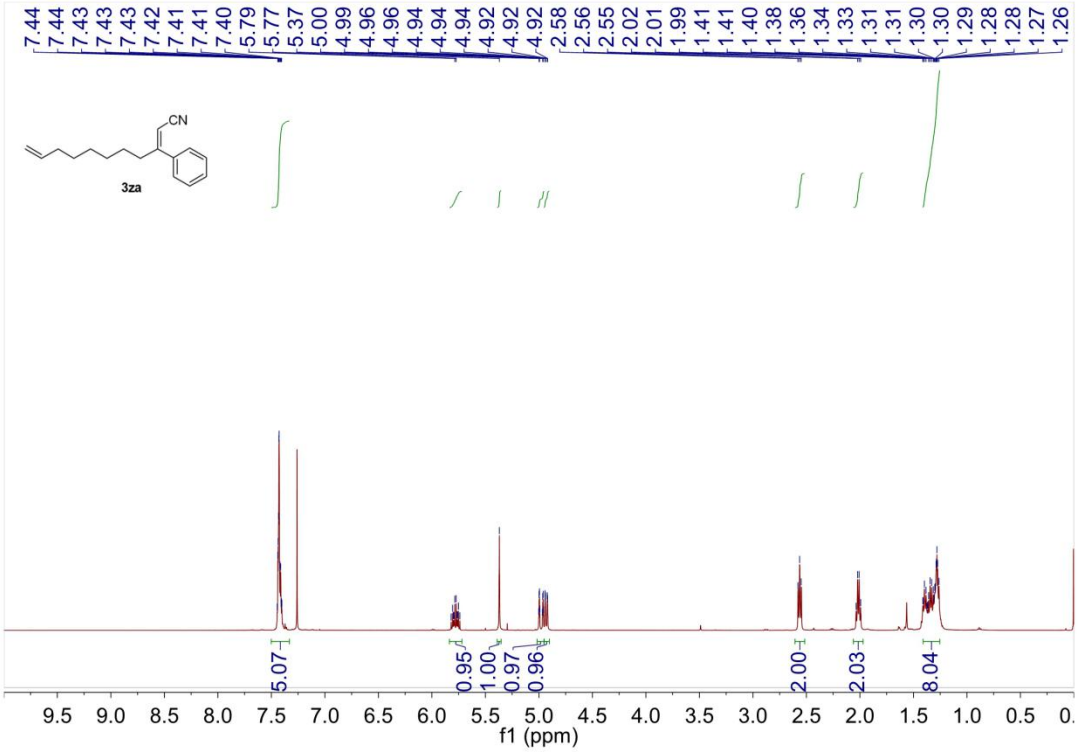
^{1}H NMR spectrum of **3ya** (500 MHz, $CDCl_3$)



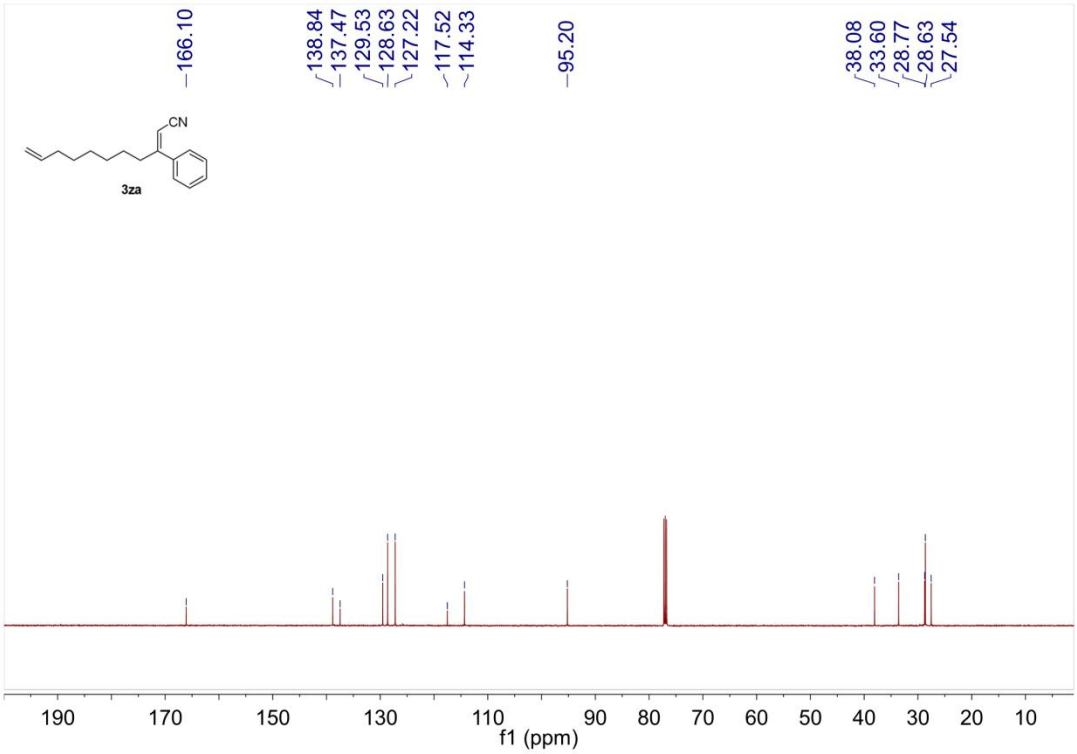
^{13}C NMR spectrum of **3ya** (126 MHz, $CDCl_3$)



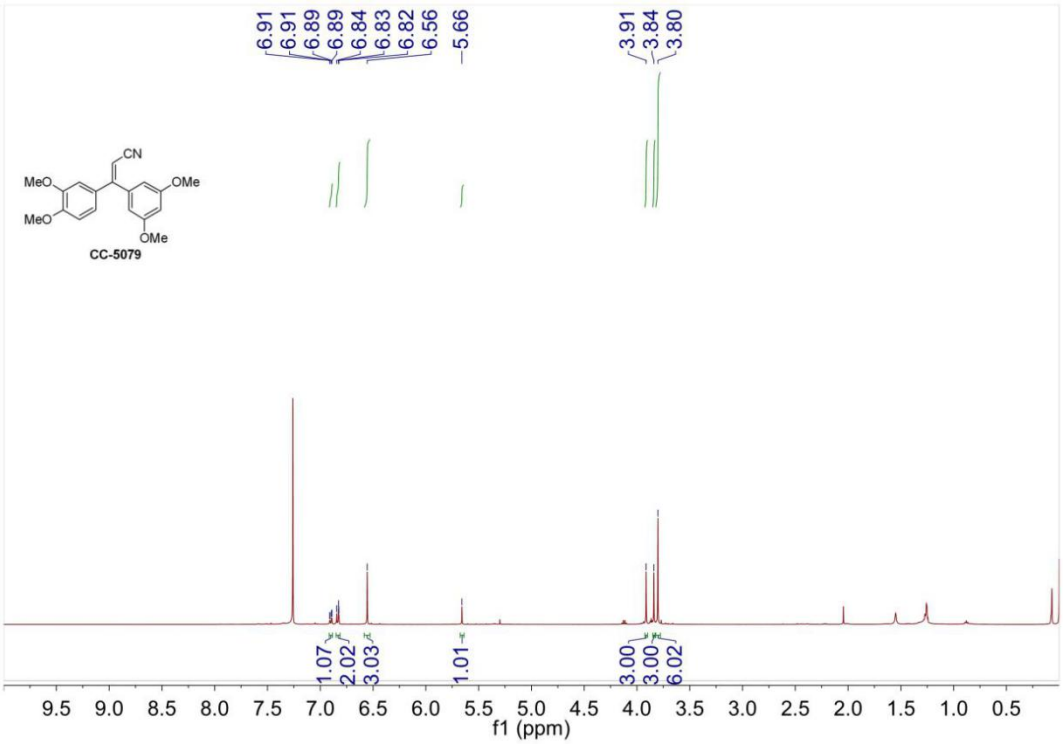
^{1}H NMR spectrum of **3za** (500 MHz, $CDCl_3$)



^{13}C NMR spectrum of **3za** (126 MHz, $CDCl_3$)



^{1}H NMR spectrum of **CC-5079** (500 MHz, $CDCl_3$)



^{13}C NMR spectrum of **CC-5079** (126 MHz, $CDCl_3$)