SUPPORTING INFORMATION

In situ phosphonium-containing Lewis base-catalyzed 1,6-cyanation reaction: facile way to α-diaryl and α-triaryl acetonitriles

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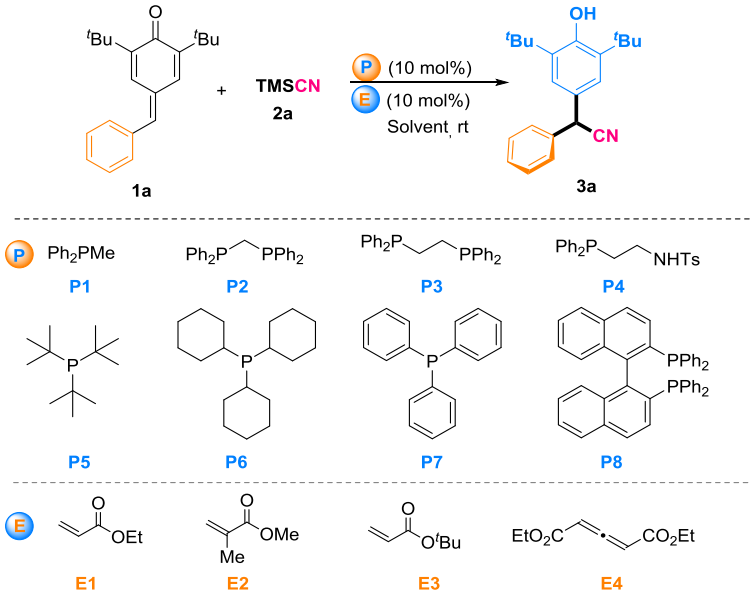
1. General Information

All the starting materials were obtained from commercial sources and used without further purification unless otherwise stated. ^{1}H and ^{13}C NMR spectra were recorded at ambient temperature in $CDCl_3$ on a Bruker Advance ((400 MHz) spectrometer. The chemical shifts are reported in parts permillion (ppm) relative to $CDCl_3$ (δ = 7.26) for ^{1}H-NMR and relative to the central resonances of $CDCl_3$ (δ = 77.16) for ^{13}C-NMR; Multiplicity was indicatedas follows: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), dd (doublet of doublet), dt (doublet of triplet), br s (broad singlet). Coupling constants (*J*) were reported in Hertz (Hz). All high resolution mass (ESI-MS) were obtained on Thermo LTQ mass spectrometer. For thin layer chromatography (TLC) was performed using commercially prepared and compounds were visualized with a UV light at 254 nm. Further visualization was achieved by staining with iodine, or ceric ammonium molybdate followed by heating on a hot plate. Flash chromatographic separations were performed on commercially prepared 200-300 mesh silicagel. Enantiomeric excess was determined by HPLC analysis using chiral column described below in detail.

All *para*-quinone methides **1** were synthesized following the known methods reported in the literature.[1] and the fuchsones were synthesized following the known methods reported in the literature.[2] All the achiral organophosphine catalysts **P1-P8** and electrophilic reagent **E1-E4** used in this study were commercially available and known compounds.

2. Optimization of Reaction Conditions

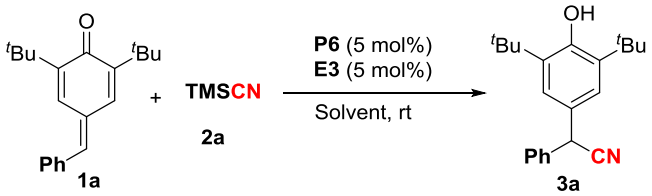
Table S1. The remote 1,6-cyanation of *para*-Quinone Methides with TMSCN by *in situ* phosphonium salts: screening of the catalyst[a]



Entry	**P**	**E**	Solvent	Time[h]	yield[b](%)
1	P1	E1	$CHCl_3$	12	65
2	P2	E1	$CHCl_3$	12	76
3	P3	E1	$CHCl_3$	12	74
4	P4	E1	$CHCl_3$	12	32
5	P5	E1	$CHCl_3$	12	86
6	P6	E1	$CHCl_3$	12	94
7	P7	E1	$CHCl_3$	12	trace
8	P8	E1	$CHCl_3$	12	trace
9	P6	E2	$CHCl_3$	12	55
10	**P6**	**E3**	**$CHCl_3$**	**12**	**98**
11	P6	E4	$CHCl_3$	24	NR

[a] Reaction conditions: **1a** (0.10 mmol), **2a** (0.2 mmol) and **P** (10 mol%), **E** (10 mol%) and in $CHCl_3$ (1.0 mL) at room temperature; [b] Yields of isolated products of **3a**.

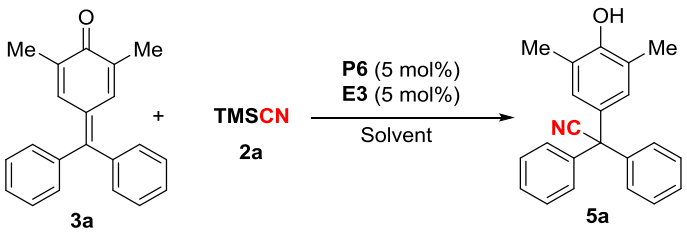
Table S2. The remote 1,6-cyanation of *para*-Quinone Methides with TMSCN by *in situ* phosphonium salts: screening of the solvent[a]



Entry	P	E	Solvent	Time[h]	yield[b](%)
1	**P6**	**E3**	**$CHCl_3$**	**12**	**98**
2	**P6**	**E3**	CH_2Cl_2	12	89
3	**P6**	**E3**	Et_2O	12	91
4	**P6**	**E3**	Hexane	12	88
5	**P6**	**E3**	PE	12	83
6	**P6**	**E3**	Toluene	12	75
7	**P6**	**E3**	EA	12	79
8	**P6**	**E3**	THF	12	82
9	**P6**	**E3**	CH_3CN	12	56
10	**P6**	**E3**	MeOH	12	NR
11[c]	**P6**	**E3**	**$CHCl_3$**	**24**	**98**

[a] Reaction conditions: **1a** (0.10 mmol), **2a** (0.2 mmol) and P (10 mol%), E 10 mol%) and in indicated solvent (1.0 mL) at rt for 24 h; [b] Yields of isolated products of **3a**. [c] Reaction at 5 mol % P_6 and 5 mol % E_3.

Table S3. The remote 1,6-cyanation of fuchsones with TMSCN by *in situ* phosphonium salts: Screening of the solvent and temperature[a]



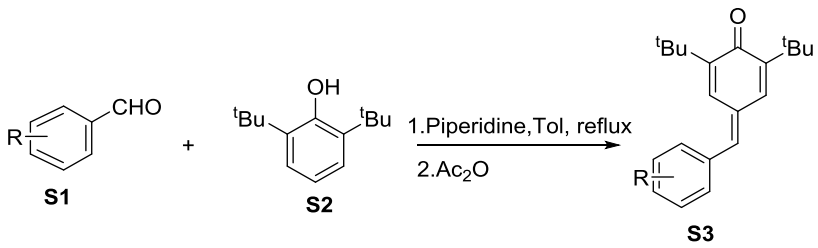
Entry	P	E	Solvent	Time[h]	yield[b](%)
1	P6	E3	$CHCl_3$	24	72
2	P6	E3	CH_2Cl_2	24	62

3	P6	E3	Et_2O	24	55
4	P6	E3	Hexane	24	23
5	P6	E3	PE	24	58
6	P6	E3	Toluene	24	61
7[c]	**P6**	**E3**	**$CHCl_3$**	**24**	**87**
8[d]	P6	E3	$CHCl_3$	24	82

[a] Reaction conditions: **1a** (0.10 mmol), **2a** (0.2 mmol) and P_6 (5 mol%), E_3 (5 mol%) and in indicated solvent (1.0 mL) at rt for 24 h; [b] Yields of isolated products of **3a**; [c] Reaction run at 45 °C for 24 h; [d] Reaction run at 60 °C for 24 h.

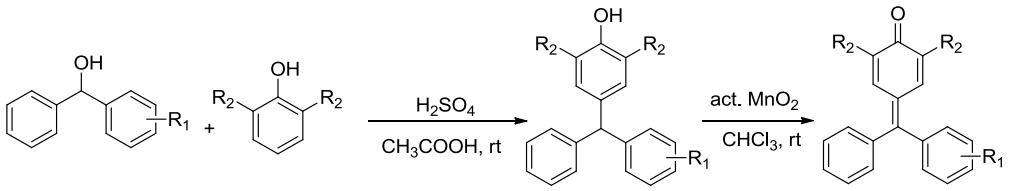
3. Preparation of *para*-Quinone Methides (*p*-QMs) and fuchsones.

All the *para*-quinonemethides (***p*-QMs**) were synthesized using the method as reported previously in the literature[1] from the corresponding aldehydes with 2,6-*tert*-butyl phenol as shown in ***Scheme S1.***



Scheme S1. The route for synthesis of *para*-quinonemethides

Fuchsones were synthesized using the method as reported previously in the literature[2] as shown in ***Scheme S2.*** and **4a, 4d, 4e, 4g** are known compounds. The unknown compounds **4b**, **4c**, **4f** were fully characterized.



Scheme S2. The route for synthesis of fuchsones.

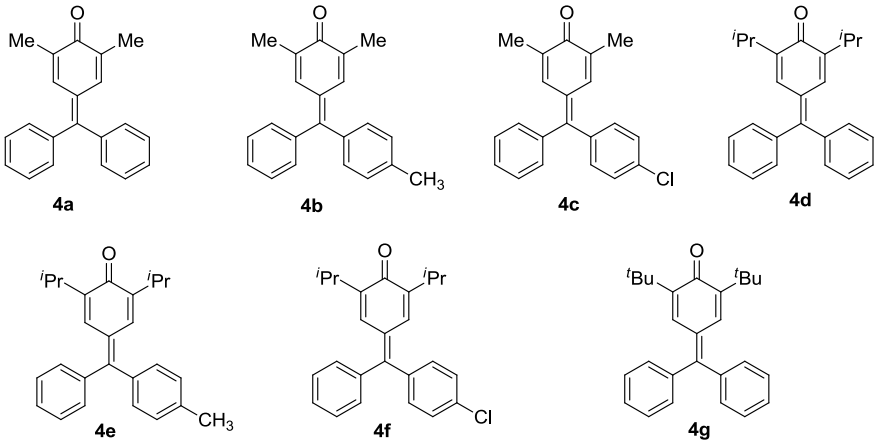
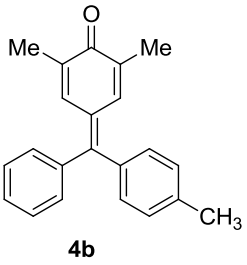


Figure S1. Substrates of fuchsones in this study

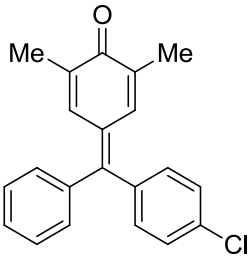
2,6-dimethyl-4-(phenyl(p-tolyl)methylene)cyclohexa-2,5-dienone (4b)



4b

A yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47-7.38 (m, 3H), 7.25-7.20 (m, 4H), 7.18 (dd, *J* = 2.6, 1.3 Hz, 1H), 7.14-7.11 (m, 2H), 7.10 (s, 1H), 2.42 (s, 3H), 2.02 (d, *J* = 1.2 Hz, 3H), 2.01 (d, *J* = 1.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 187.21, 157.04, 140.83, 139.82, 137.83, 135.75, 135.58, 132.17, 132.13, 129.62, 129.34, 128.87, 128.06, 21.44, 16.76; HRMS (ESI) *m/z* calcd for $C_{22}H_{20}O$ $[M+H]^+$ = 301.1592, found =301.1594.

4-((4-chlorophenyl)(phenyl)methylene)-2,6-dimethylcyclohexa-2,5-dienone (4c)

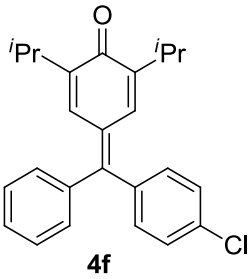


4c

A yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46-7.36 (m, 5H), 7.20 (dd, *J* = 7.6, 1.2 Hz, 2H), 7.16 (d, *J* = 8.4 Hz, 2H), 7.11 (d, *J* = 8.4 Hz, 2H), 2.02 (s, 3H), 2.00 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 187.27, 154.89, 140.37, 139.17, 136.18, 135.47, 135.13, 133.37 , 132.14 , 130.26, 129.67, 128.60, 128.37, 16.90; HRMS (ESI) *m/z*

calcd for $C_{21}H_{17}ClO$ $[M+H]^+$ = 321.1046, found = 321.1048.

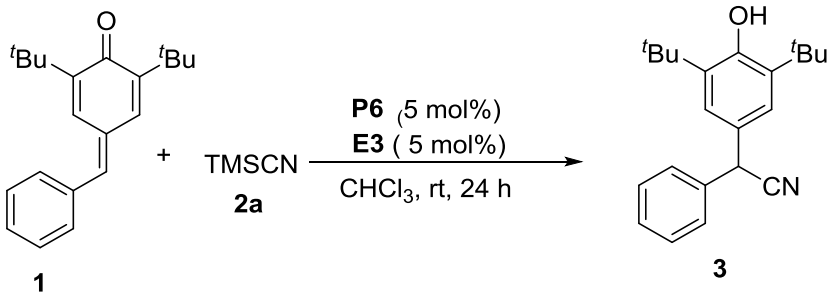
4-((4-chlorophenyl)(phenyl)methylene)-2,6-diisopropylcyclohexa-2,5-dienone (4f)



4f

A yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48-7.37 (m, 5H), 7.24-7.20 (m, 2H), 7.20-7.15 (m, 2H), 7.07 (dd, *J* = 8.4, 2.8 Hz, 2H), 3.25-3.09 (m, 2H), 1.07 (d, *J* = 7.0 Hz, 6H), 1.05 (d, *J* = 7.0 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 185.11, 154.86, 146.09, 140.46, 139.26, 135.72, 133.49, 132.24, 131.71, 131.32, 129.67, 128.52, 128.28, 26.97, 22.14; HRMS (ESI) *m/z* calcd for $C_{25}H_{25}ClO$ $[M+H]^+$ = 377.1672, found = 377.1673.

4. **Representative procedure for synthesis of α-diaryl acetonitriles**

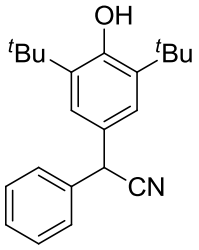


1 **3**

To a dried round bottle flask with a magnetic stirring bar were added **P6** (5 mol%), **E3** (5 mol%) in $CHCl_3$ (1.0 mL) and then *para*-Quinone Methide **1** (29.4 mg, 0.1 mmol) and TMSCN (20 mg, 0.2 mmol) were added, The reaction mixture was stirred at rt for 24 h, and TLC show that the reaction was completed. Then, 1M TFA was added to the mixture, and stirred for 5 mins, The resulting solution was quenched by Na_2CO_3 (aq.) and was extracted with CH_2Cl_2 (3×10 mL). Then the combined organic phases were washed with brine and dried over anhydrous Na_2SO_4. The solvent was removed to give the crude product which was purified by flash column chromatography (PE/ethyl acetate = 80/1 to 10/1) to afford the desired compounds **3a**

as yellow solid.

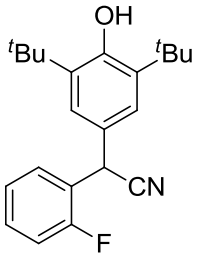
2-(3,5-di-tert-butyl-4-hydroxyphenyl)-2-phenylacetonitrile (3a)



3a

A yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34-7.27 (m, 4H), 7.21 (s, 1H), 7.05 (s, 2H), 5.20 (s, 1H), 5.02 (s, 1H), 1.36 (s, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.79, 136.67, 136.58, 129.19, 128.12, 127.81, 126.63, 124.63, 120.48, 42.67, 34.58 , 30.28. HRMS (ESI) *m/z* calcd for $C_{22}H_{27}NO$ $[M-H]^-$ = 320.2014, found = 320.2015.

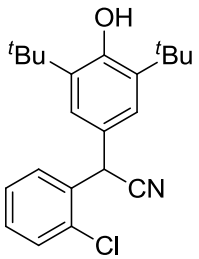
2-(3,5-di-tert-butyl-4-hydroxyphenyl)-2-(2-fluorophenyl)acetonitrile (3b)



3b

A pale yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (td, *J* = 7.6, 1.6 Hz, 1H), 7.36-7.28 (m, 1H), 7.19 (td, *J* = 7.6, 1.2 Hz, 1H), 7.16 (s, 2H), 7.13-7.05 (m, 1H), 5.36 (s, 1H), 5.26 (s, 1H), 1.41 (s, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.86, 136.78, 130.18 (d, *J* = 8.2 Hz), 129.29 (d, *J* = 3.0 Hz), 125.38, 124.99, 124.96, 124.42, 119.66, 116.17, 115.95, 36.12, 34.58, 30.26.; HRMS (ESI) *m/z* calcd for $C_{22}H_{26}$ FNO $[M-H]^-$ = 338.1920, found = 338.1928.

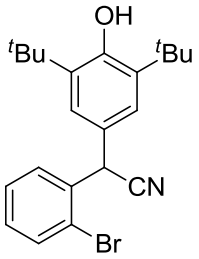
2-(3,5-di-tert-butyl-4-hydroxyphenyl)-2-(2-chlorophenyl)acetonitrile (3c)



3c

A yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.42 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.32 (td, *J* = 7.6, 1.6 Hz, 1H), 7.29 (dd, *J* = 7.6, 2.0 Hz, 1H), 7.16 (s, 2H), 5.55 (s, 1H), 5.26 (s, 1H), 1.41 (s, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.86, 136.71, 134.59, 133.22, 130.18, 129.69, 129.67, 127.81, 125.17, 124.65, 119.93, 39.48, 34.58, 30.27; HRMS (ESI) *m/z* calcd for $C_{22}H_{26}ClNO$ $[M-H]^-$ = 354.1625, found = 354.1631.

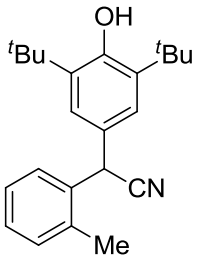
2-(3,5-di-tert-butyl-4-hydroxyphenyl)-2-(2-bromophenyl)acetonitrile (3d)



3d

A yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.52 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.36 (td, *J* = 7.6, 1.2 Hz, 1H), 7.20 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.17 (s, 2H), 5.56 (s, 1H), 5.26 (s, 1H), 1.41 (s, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.86, 136.71, 136.34, 133.51, 129.92, 129.88, 128.47, 125.25, 124.67, 123.68, 119.99, 41.95, 34.60, 30.28; HRMS (ESI) *m/z* calcd for $C_{22}H_{26}$ BrNO $[M-H]^-$ = 398.1120, found = 398.1120.

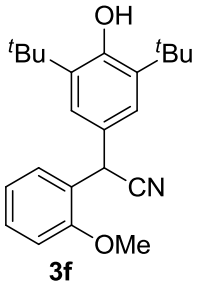
2-(3,5-di-tert-butyl-4-hydroxyphenyl)-2-o-tolylacetonitrile (3e)



3e

A orange gummy solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (dd, *J* = 6.0, 4.8 Hz, 1H), 7.29-7.27 (m, 2H), 7.25-7.18 (m, 1H), 7.06 (s, 2H), 5.25 (s, 1H), 5.21 (s, 1H), 2.34 (s, 3H), 1.41 (s, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.66, 136.65, 135.92, 134.43, 131.19, 128.53, 128.40, 126.89, 125.54, 124.68, 120.51, 39.80, 34.55, 30.28, 19.67; HRMS (ESI) *m/z* calcd for $C_{23}H_{29}$ NO $[M-H]^-$ = 334.2171, found = 334.2155.

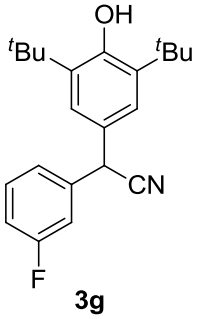
2-(3,5-di-tert-butyl-4-hydroxyphenyl)-2-(2-methoxyphenyl)acetonitrile (3f)



3f

A orange gummy solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37-7.27 (m, 2H), 7.19 (s, 2H), 6.97 (td, *J* = 7.6, 0.8 Hz, 1H), 6.91 (d, *J* = 8.0 Hz, 1H), 5.47 (s, 1H), 5.22 (s, 1H), 3.88 (s, 3H), 1.42 (s, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.21, 153.50, 136.42, 129.49, 128.78, 126.24, 125.45, 124.67, 121.16, 120.77, 111.01, 55.68, 36.31, 34.54, 30.32; HRMS (ESI) *m/z* calcd for $C_{23}H_{29}NO_2$ $[M-H]^-$ = 350.2120, found = 350.2108.

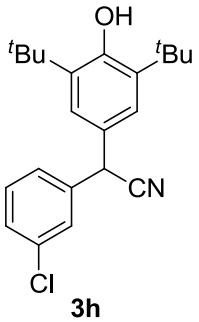
2-(3,5-di-tert-butyl-4-hydroxyphenyl)-2-(3-fluorophenyl)acetonitrile (3g)



3g

A orange gummy solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40-7.31 (m, 1H), 7.17 (d, *J* = 7.8 Hz, 1H), 7.08 (s, 2H), 7.07-6.98 (m, 2H), 5.29 (s, 1H), 5.05 (s, 1H), 1.41 (s, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.00, 138.94 (d, *J* = 7.6 Hz), 136.94, 130.77 (d, *J* = 8.4 Hz), 125.92, 124.61, 123.46 (d, *J* = 3.0 Hz), 119.92, 115.35, 115.14, 114.91, 42.34, 34.59, 30.26; HRMS (ESI) *m/z* calcd for $C_{22}H_{26}FNO$ $[M-H]^-$ = 338.1920, found = 338.1923.

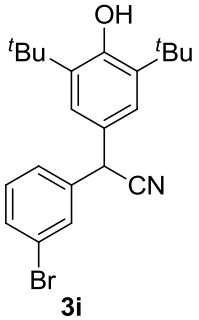
2-(3,5-di-tert-butyl-4-hydroxyphenyl)-2-(3-chlorophenyl)acetonitrile (3h)



3h

A yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (s, 1H), 7.33-7.29 (m, 2H), 7.28-7.27(m, 1H), 7.08 (s, 2H), 5.29 (s, 1H), 5.02 (s, 1H), 1.41 (s, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.03, 138.48, 136.96, 135.08, 130.44, 128.46, 128.00, 125.95, 125.85, 124.61, 119.85, 42.32, 34.60, 30.26; HRMS(ESI) *m/z* calcd for $C_{22}H_{26}ClNO$ $[M-H]^-$ = 354.1625, found = 354.1627.

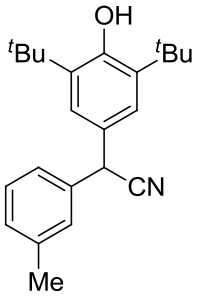
2-(3,5-di-tert-butyl-4-hydroxyphenyl)-2-(3-bromophenyl)acetonitrile (3i)



3i

A yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (dd, *J* = 2.0, 1.6 Hz, 1H), 7.46 (dt, *J* = 7.6,1.6 Hz, 1H), 7.31 (d, *J* = 7.6 Hz, 1H), 7.24 (d, *J* = 7.6 Hz, 1H), 7.08 (s, 2H), 5.29 (s, 1H), 5.02 (s, 1H), 1.41 (s, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.03, 138.71, 136.96, 131.39, 130.87, 130.71, 126.42, 125.83, 124.60, 123.19, 119.82, 42.26, 34.60, 30.26; HRMS (ESI) *m/z* calcd for $C_{22}H_{26}BrNO$ $[M-H]^-$ = 398.1120, found = 398.1121.

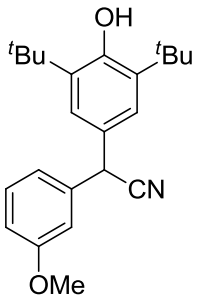
2-(3,5-di-tert-butyl-4-hydroxyphenyl)-2-m-tolylacetonitrile (3j)



3j

A orange gummy solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30-7.27 (m, 1H), 7.22 (s, 1H), 7.18-7.13 (m, 2H), 7.13 (s, 2H), 5.27 (s, 1H), 5.04 (s, 1H), 2.38 (s, 3H), 1.43 (s, 18H) ; ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.75, 139.01, 136.70, 136.44, 129.04, 128.88, 128.44, 126.74, 124.85, 124.59, 120.60, 42.63, 34.57, 30.28, 21.57; HRMS (ESI) *m/z* calcd for $C_{23}H_{29}NO$ $[M-H]^-$ = 334.2179, found = 334.2171.

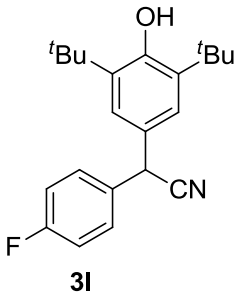
2-(3,5-di-tert-butyl-4-hydroxyphenyl)-2-(3-methoxyphenyl)acetonitrile (3k)



3k

A orange gummy solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (dd, *J* =8.0, 8.0 Hz ,1H), 7.11 (s, 2H), 6.95 (dd, *J* = 7.6, 0.8 Hz, 1H), 6.89 (dd, *J* = 2.4, 1.6 Hz, 1H), 6.85 (dd, *J* = 8.0, 2.0 Hz, 1H), 5.25 (s, 1H), 5.02 (s, 1H), 3.80 (s, 3H), 1.41 (s, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.15, 153.82, 138.03, 136.76, 130.21, 126.46, 124.61, 120.40, 120.12, 113.71, 113.43, 55.46, 42.65, 34.57, 30.29; HRMS (ESI) *m/z* calcd for $C_{23}H_{29}NO2$ $[M-H]^-$ = 350.2120, found = 350.2127.

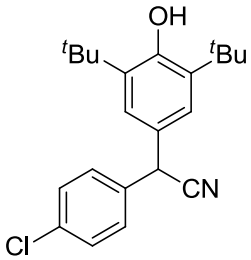
2-(3,5-di-tert-butyl-4-hydroxyphenyl)-2-(4-fluorophenyl)acetonitrile (3l)



3l

A orange solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (dd, *J* = 8.8, 5.2 Hz, 2H), 7.10-7.02 (m, 4H), 5.27 (s, 1H), 5.05 (s, 1H), 1.41 (s, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.49 (d, *J* = 245.4 Hz), 153.90, 136.89, 132.41, 129.54 (d, *J* = 8.4 Hz), 126.38, 124.55, 120.28, 116.15 (d, *J* = 21.8 Hz), 41.93, 34.59, 30.27; HRMS (ESI) *m/z* calcd for $C_{22}H_{26}FNO$ $[M-H]^-$ = 338.1920, found = 338.1926.

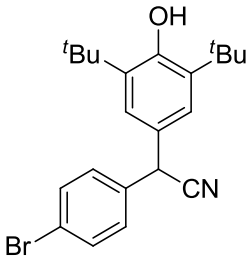
2-(3,5-di-tert-butyl-4-hydroxyphenyl)-2-(4-chlorophenyl)acetonitrile (3m)



3m

A orange solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38-7.32 (m, 2H), 7.31-7.27 (m, 2H), 7.07 (s, 2H), 5.28 (s, 1H), 5.03 (s, 1H), 1.41 (s, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.83, 136.82, 135.03, 134.05, 129.24, 129.02, 125.99, 124.42, 119.90, 41.97, 34.46, 30.13; HRMS (ESI) *m/z* calcd for $C_{22}H_{26}ClNO$ $[M-H]^-$ =354.1625, found = 354.1631.

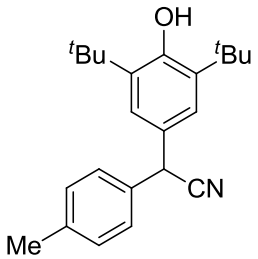
2-(3,5-di-tert-butyl-4-hydroxyphenyl)-2-(4-bromophenyl)acetonitrile (3n)



3n

A orange solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (d, *J* = 8.4 Hz, 2H), 7.23 (d, *J* = 8.4 Hz, 2H), 7.06 (s, 2H), 5.28 (s, 1H), 5.01 (s, 1H), 1.41 (s, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.97, 136.96, 135.71, 132.34, 129.46, 126.03, 124.55, 122.27, 119.94, 42.19, 34.59, 30.27; HRMS (ESI) *m/z* calcd for $C_{22}H_{26}BrNO$ $[M-H]^-$ = 398.1120, found = 398.1124.

2-(3,5-di-tert-butyl-4-hydroxyphenyl)-2-p-tolylacetonitrile (3o)

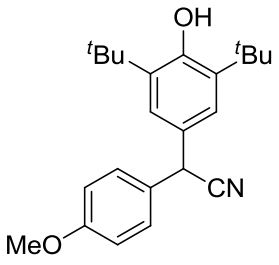


3o

A orange solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 (d, *J* = 8.0 Hz, 2H), 7.17 (d, *J* = 8.0 Hz, 2H), 7.09 (s, 2H), 5.23 (s, 1H), 5.02 (s, 1H), 2.34 (s, 3H), 1.40 (s, 18H); ^{13}C

NMR (100 MHz, $CDCl_3$) δ 153.73, 137.90, 136.71, 133.66, 129.84, 127.64, 126.85, 124.56, 120.64, 42.35, 34.57, 30.29, 21.21; HRMS (ESI) *m/z* calcd for $C_{23}H_{29}NO$ $[M-H]^-$ = 334.2171, found = 334.2169.

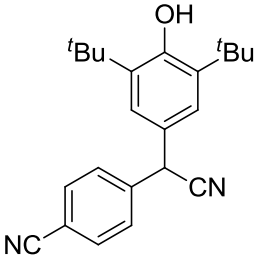
2-(3,5-di-tert-butyl-4-hydroxyphenyl)-2-(4-methoxyphenyl)acetonitrile (3p)



3p

A orange solid; ^1H NMR (400 MHz, $CDCl_3$) δ 7.24 (d, *J* =4.0 Hz, 2H), 7.08 (s, 2H), 6.91-6.88 (m, 1H), 6.88-6.86 (m, 1H), 5.23 (s, 1H), 5.00 (s, 1H), 3.80 (s, 3H), 1.40 (s, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.39, 153.71, 136.71, 128.95, 128.66, 126.93 , 124.53, 120.70, 114.51, 55.47, 41.89, 34.56, 30.29; HRMS (ESI) *m/z* calcd for $C_{23}H_{29}NO_2$ $[M-H]^-$ = 350.2120, found = 350.2123.

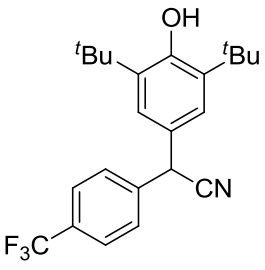
4-((3,5-di-tert-butyl-4-hydroxyphenyl)(cyano)methyl)benzonitrile(3q)



3q

A orange solid; ^1H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, *J* = 8.4 Hz, 2H), 7.48 (d, *J* = 8.0 Hz, 2H), 7.05 (s, 2H), 5.31 (s, 1H), 5.09 (s, 1H), 1.41 (s, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.40, 154.92, 139.58, 136.83, 127.16, 126.53, 126.26, 126.17, 124.46, 119.62, 38.03, 34.60, 30.28; HRMS (ESI) *m/z* calcd for $C_{23}H_{26}N_2O$ $[M-H]^-$ =345.1967, found =345.1969.

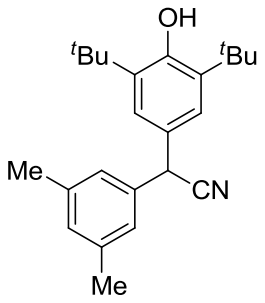
2-(3,5-di-tert-butyl-4-hydroxyphenyl)-2-(4-(trifluoromethyl)phenyl)acetonitrile(3r)



3r

A yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (d, *J* = 8.2 Hz, 2H), 7.49 (d, *J* = 8.4 Hz, 2H), 7.08 (s, 2H), 5.30 (s, 1H), 5.11 (s, 1H), 1.41 (s, 18H).; ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.11, 140.53 (d, *J* = 8.6 Hz), 137.11, 134.58, 134.38, 128.17, 126.24 (q, *J* = 3.8 Hz), 125.70, 124.61, 119.71, 42.53, 34.61, 30.25; HRMS (ESI) *m/z* calcd for $C_{23}H_{26}F_3NO$ $[M-H]^-$ = 388.1888, found = 388.1882.

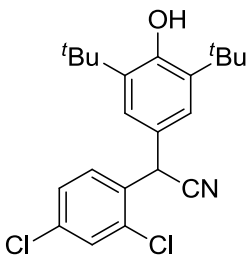
2-(3,5-di-tert-butyl-4-hydroxyphenyl)-2-(3,5-dimethylphenyl)acetonitrile (3s)



3s

A yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.11 (s, 2H), 6.97 (s, 2H), 6.94 (s, 1H), 5.24 (s, 1H), 4.97 (s, 1H), 2.31 (s, 6H), 1.41 (s, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.72, 138.84, 136.66, 136.35, 129.75, 126.87, 125.54, 124.56, 120.71, 42.60, 34.58, 30.30, 21.44; HRMS (ESI) *m/z* calcd for $C_{24}H_{31}NO$ $[M-H]^-$ = 348.2327, found = 348.2340.

2-(3,5-di-tert-butyl-4-hydroxyphenyl)-2-(2,4-dichlorophenyl)acetonitrile (3t)

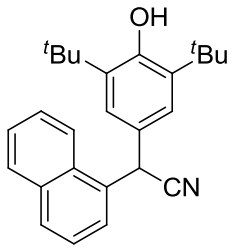


3t

A orange solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (s, 1H), 7.43 (d, *J* = 6.4 Hz, 1H),

7.30 (dd, *J* = 8.4, 2.0 Hz, 1H), 7.13 (s, 2H), 5.48 (s, 1H), 5.28 (s, 1H), 1.41 (s, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.01, 136.90, 134.98, 133.90, 133.34, 130.51, 130.00, 128.16, 124.67, 124.54, 119.45, 39.11, 34.59, 30.25; HRMS (ESI) *m/z* calcd for $C_{22}H_{25}Cl_2NO$ $[M-H]^-$ =388.1235, found = 388.1228.

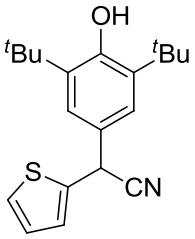
2-(3,5-di-tert-butyl-4-hydroxyphenyl)-2-(naphthalen-1-yl)acetonitrile (3u)



3u

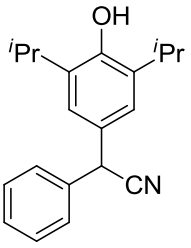
A orange solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02-7.96 (m, 1H), 7.91 (dd, *J* =7.2, 3.2 Hz, 1H), 7.87 (d, *J* = 8.2 Hz, 1H), 7.59 (d, *J* = 6.7 Hz, 1H), 7.57-7.46 (m, 3H), 7.14 (s, 2H), 5.77 (s, 1H), 5.24 (s, 1H), 1.37 (s, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.77, 136.70, 134.17, 131.79, 130.63, 129.32, 129.22, 126.99, 126.83, 126.23, 125.69, 125.60, 124.81, 123.20, 120.62, 39.63, 34.56, 30.26; HRMS (ESI) *m/z* calcd for $C_{26}H_{29}NO$ $[M-H]^-$ = 321.2171, found = 321.2179.

2-(3,5-di-tert-butyl-4-hydroxyphenyl)-2-(thiophen-2-yl)acetonitrile (3v)



3v

A pale yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 (d, *J* = 1.2 Hz, 1H), 7.17 (s, 2H), 7.07 (dd, *J* = 2.4, 1.0 Hz, 1H), 6.98 (dd, *J* = 4.8, 3.6 Hz, 1H), 5.29 (s, 1H), 5.27 (s, 1H), 1.43 (s, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.00, 139.45, 136.71, 127.04, 126.41, 126.12, 126.04, 124.34, 119. 49, 37.90, 34.47, 30.16; HRMS (ESI) *m/z* calcd for $C_{20}H_{25}NOS$ $[M-H]^-$ = 326.1579, found = 326.1569.



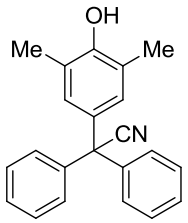
3w

A white solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39-7.30 (m, 5H), 6.99 (s, 2H), 5.07 (s, 1H), 4.85 (s, 1H), 3.17-3.06 (m, 2H), 1.23 (d, *J* =7.0 Hz, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.07, 136.62, 134.63, 129.20, 128.14, 127.76, 127.74, 123.21, 120.38, 42.51, 27.48, 22.71; HRMS (ESI) *m/z* calcd for $C_{20}H_{23}NO$ $[M-H]^-$ = 292.1701, found = 292.1712.

5. Representative procedure for synthesis of α-triary acetonitriles

To a dried round bottle flask with a magnetic stirring bar were added **P6** (5 mol%), **E3** (5 mol%) in $CHCl_3$(2.0 mL). then fuchsones (28.6 mg, 0.1 mmol) and TMSCN (20 mg, 0.2 mmol) were added, The reaction mixture was stirred at 45^{o}C for 24-48 h, and TLC show that the reaction was completed. Then, 1M TFA was added to the mixture, and stirred for 5 mins, The resulting solution was quenched by Na_2CO_3 (aq.) and was extracted with CH_2Cl_2 (3×10 mL). Then the combined organic phases were washed with brine and dried over anhydrous Na_2SO_4. The solvent was removed to give the crude product which was purified by flash column chromatography (PE/ethyl acetate = 80/1 to 10/1) to afford the desired compounds **5.**

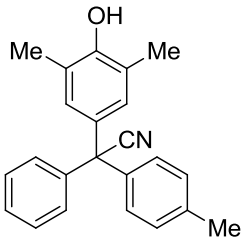
2-(4-hydroxy-3,5-dimethylphenyl)-2,2-diphenylacetonitrile（5a）



5a

A orange gummy solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37-3.31 (m, 6H), 7.25 – 7.20 (m, 4H), 6.80 (s, 2H), 4.82 (s, 1H), 2.19 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.16, 140.76, 131.63, 129.12, 128.91, 128.70, 128.12, 123.98, 123.36, 56.92, 16.23; HRMS (ESI) *m/z* calcd for $C_{20}H_{25}NO$ $[M-H]^-$ = 312.1388, found = 312.1374.

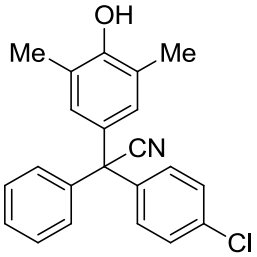
2-(4-hydroxy-3,5-dimethylphenyl)-2-phenyl-2-(p-tolyl)acetonitrile (5b)



5b

A orange gummy solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38-7.29 (m, 3H), 7.24-7.19 (m, 2H), 7.15 (d, *J* = 8.2 Hz, 2H), 7.09 (d, *J* = 8.4 Hz, 2H), 6.79 (s, 2H), 4.74 (s, 1H), 2.36 (s, 3H), 2.19 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.07, 140.94, 137.95, 137.80, 131.84, 129.39, 129.10, 128.88, 128.78, 128.66, 128.04, 124.07, 123.26, 56.60, 21.17, 16.22; HRMS (ESI) *m/z* calcd for $C_{23}H_{21}NO$ $[M-H]^-$ = 326.1545, found = 326.1547.

2-(4-chlorophenyl)-2-(4-hydroxy-3,5-dimethylphenyl)-2-phenylacetonitrile (5c)

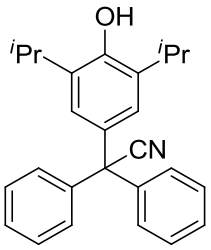


5c

A orange gummy solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41-7.28 (m, 5H), 7.23-7.12 (m, 4H), 6.77 (s, 2H), 4.78 (s, 1H), 2.19 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.28, 140.28, 139.42, 134.24, 131.18, 130.32, 129.01, 128.90, 128.86, 128.80,

128.35, 123.59, 123.48, 56.44, 16.23; HRMS (ESI) *m/z* calcd for $C_{22}H_{18}ClNO$ $[M-H]^-$ = 346.0999, found = 346.1002.

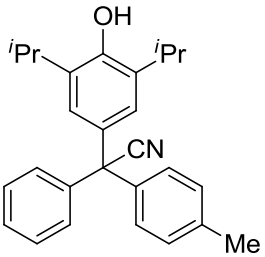
2-(4-hydroxy-3,5-diisopropylphenyl)-2,2-diphenylacetonitrile (5d)



5d

A orange solid; ^1H NMR (400 MHz, $CDCl_3$) δ 7.39-7.30 (m, 6H), 7.24-7.18 (m, 4H), 6.84 (s, 2H), 4.88 (s, 1H), 3.10 (dt, *J* = 13.6, 6.8 Hz, 2H), 1.16 (s, 6H), 1.14 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.85, 141.03, 133.85, 131.89, 128.91, 128.64, 128.08, 124.42, 123.97, 57.30, 27.49, 22.67; HRMS (ESI) *m/z* calcd for $C_{26}H_{27}NO$ $[M-H]^-$ = 368.2014, found = 368.2046.

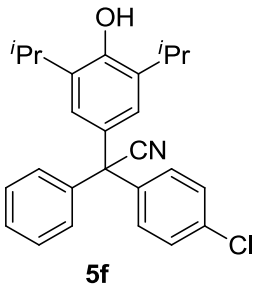
2-(4-hydroxy-3,5-diisopropylphenyl)-2-phenyl-2-(p-tolyl)acetonitrile (5e)



5e

A orange solid; ^1H NMR (400 MHz, $CDCl_3$) δ 7.38-7.28 (m, 3H), 7.22 (dd, *J* = 7.6, 1.8 Hz, 2H), 7.15 (d, *J* = 8.2 Hz, 2H), 7.10 (d, *J* = 8.2 Hz, 2H), 6.86 (s, 2H), 4.91 (s, 1H), 3.11 (dt, *J* = 13.6, 6.8Hz, 2H), 2.36 (s, 3H), 1.17 (d, *J* = 1.7 Hz, 6H), 1.15 (d, *J* = 1.7 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.81, 141.25, 138.07, 137.85, 133.83, 132.02, 129.30, 128.86, 128.78, 128.58, 127.98, 124.38, 124.05, 57.00, 27.50, 22.68, 21.16; HRMS (ESI) *m/z* calcd for $C_{27}H_{29}NO$ $[M-H]^-$ = 382.2171, found = 382.2169.

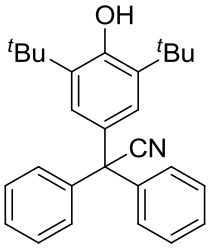
2-(4-chlorophenyl)-2-(4-hydroxy-3,5-diisopropylphenyl)-2-phenylacetonitrile (5f)



5f

A orange solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40-7.32 (m, 4H), 7.40-7.33 (m, 4H), 7.32-7.30 (m, 1H), 7.18-7.12 (m, 2H), 6.83 (s, 2H), 4.93 (s, 1H), 3.20-3.00 (m, 2H), 1.17 (d, *J* = 1.2 Hz, 6H), 1.15 (d, *J* = 1.2 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.04, 140.53, 139.72, 134.19, 134.08, 131.39, 130.31, 128.82, 128.78, 128.31, 124.27, 123.55, 56.84, 27.51, 22.66; HRMS (ESI) *m/z* calcd for $C_{26}H_{26}ClNO[M-H]^-$ = 402.1625, found = 402.1631.

2-(3,5-di-tert-butyl-4-hydroxyphenyl)-2,2-diphenylacetonitrile (5g)

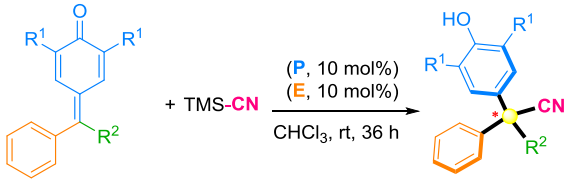


5g

A orange solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41-7.28 (m, 6H), 7.25-7.18 (m, 4H), 6.96 (s, 2H), 5.28 (s, 1H), 1.34 (s, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.55, 141.10, 135.91, 130.53, 128.90, 128.61, 128.03, 125.88, 124.02, 57.39, 34.59, 30.26; HRMS (ESI) *m/z* calcd for $C_{28}H_{31}NO[M-H]^-$ = 396.2327, found = 396.2332.

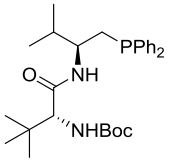
6. Attempted enantioselective synthesis of α-diaryl or α-triary nitriles[a]

All the chiral organophosphine catalysts **P9** and **P10** are known compound and the chiral acrylate **E5-E7** were synthetized using the method as follow and were fully characterized.

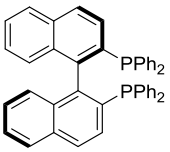


1 or 4 2a 3a or 5b

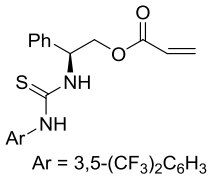
Entry	Cat.	product	Yield (%)	ee (%)
1	**P9 + E3**	**3a**	48	0
2	**P9 + E3**	**5b**	31	0
3	**P6 + E5**	**3a**	89	0
4	**P6 + E5**	**5b**	67	1
5	**P9 + E5**	**3a**	39	2
6	**P9 + E5**	**5b**	22	1
7	**P10 + E5**	**3a**	37	0
8	**P6 + E6**	**3a**	83	2
9	**P6 + E7**	**3a**	77	1



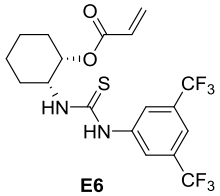
P9



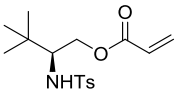
P10



E5



E6

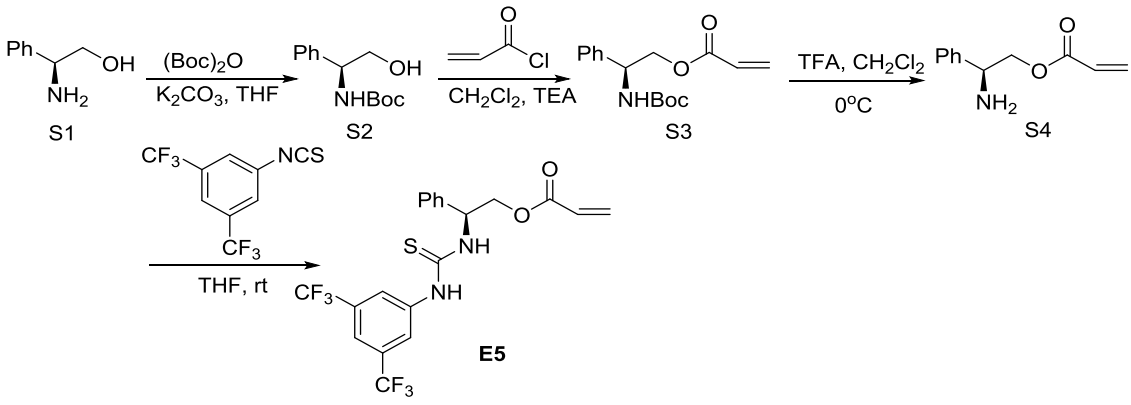


E7

[a]Reactions were performed with **1a** or **4b** (0.1 mmol), TMSCN (0.2 mmol) and **P** (10 mol%) and **E** (10 mol%) in $CHCl_3$ (1.0 mL) at rt. [b]Isolated yields. [c]Enantiomeric ratio (er) determined by chiral HPLC.

Scheme S3. Enantioselective synthesis of α-diaryl or α-triary nitriles

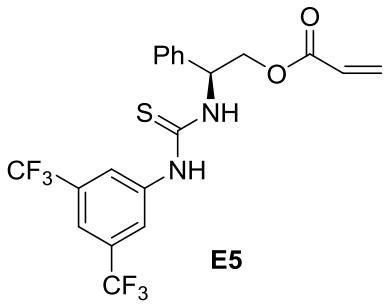
Preparation of chiral acrylates



To a (S)-2-amino-2-phenylethanol (5 mmol) and K_2CO_3 (10 mmol, 2.0 equiv.) in THF, $(Boc)_2O$ (7.5 mmol, 1.5 equiv.) was added at 0 °C. Then, the reaction mixture was stirred at room temperature for 6 h and TLC show that the rection was completed. After evaporation of solvent, the crude product S2 was obtained and used directly for next step. To product S2 in CH_2Cl_2 at 0°C. Then TEA (2.0 equiv.) and acryloyl

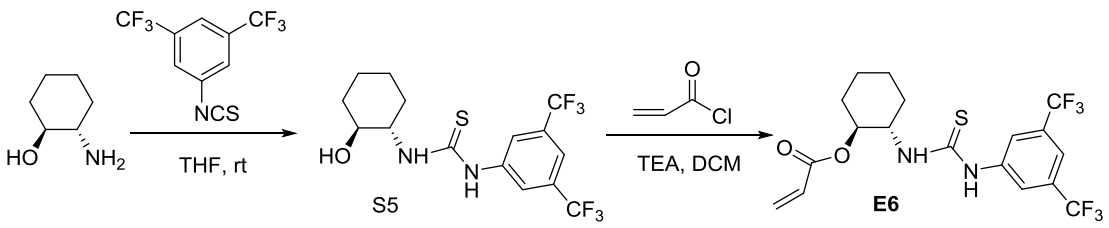
chloride (1.5 equiv.) were added slowly at 0°C. The mixture was stirred at rt for 4 h, TLC show that the rection was completed, then the reaction was quenched by Na_2CO_3 (aq.) and extracted with CH_2Cl_2 three times. The combined organic layers were dried over Na_2SO_4. After evaporation of solvent, the crude product S3 was obtained and used directly for next step without purified. The crude product S3 was deprotectived N-Boc giving the target product S4 by TFA in CH_2Cl_2 at rt. then to S4 in THF at rt, then 1-isothiocyanato-3,5-bis (trifluoromethyl)benzene (1.2 equiv.) was added, the mixture was stirred at rt for 8 h and TLC show that the reaction was completed. After evaporation of solvent, the final product **E5** was obtained by flash chromatography on silica gel.

(S)-2-(3-(3,5-bis(trifluoromethyl)phenyl)thioureido)-2-phenylethyl acrylate (E5)



E5

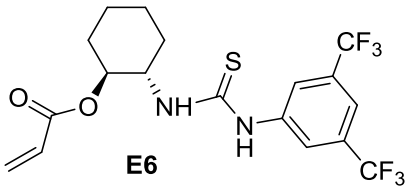
A colorless oil ; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.55 (s, 1H), 7.74 (s, 2H), 7.64 (s, 1H), 7.35-7.27 (m, 3H), 7.22 (dd, *J* = 9.4, 3.6 Hz, 2H), 6.31 (dd, *J* = 17.2, 0.6 Hz, 1H), 6.01 (dd, *J* = 17.2, 10.4 Hz, 1H), 5.81 (dd, *J* = 10.5, 1.0 Hz, 1H), 5.73 (s, 1H), 4.55 (dd, *J* = 11.8, 7.2 Hz, 1H), 4.35 (dd, *J* = 11.8, 4.2Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 180.75, 167.06, 139.06, 136.98, 132.69 (q, *J*= 27.3 Hz), 129.22, 128.66, 127.42, 127.00, 126.89, 124.24 (d, *J* = 2.8 Hz), 121.58, 119.54, 66.38, 58.41; HRMS (ESI) *m/z* calcd for $C_{20}H_{17}F_6N_2O_2S[M+H]^+$=463.0909, found = 463.0910.



To a (1S, 2S)-2-aminocyclohexanol (10 mmol) and 1-isothiocyanato-3,5-bis

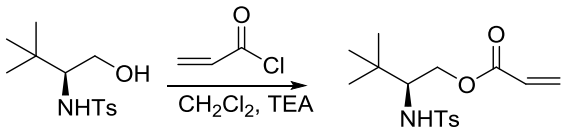
(trifluoromethyl)benzene (12 mmol, 1.2 equiv.) in THF, the reaction mixture was stirred at room temperature for 6 h and TLC show that the rection was completed. After evaporation of solvent, the crude product S5 was obtained and was used directly for next step. To the product S5 in CH_2Cl_2 at 0^oC, TEA (20 mmol, 2.0 equiv.) and acryloyl chloride (15 mmol, 1.5 equiv.) were added slowly at 0^oC. Then the mixture was stirred at rt for 3 h, TLC show that the reaction was completed, then quenched by Na_2CO_3 (aq.) and extracted with CH_2Cl_2 three times. The combined organic layer was dried over Na_2SO_4. After evaporation of solvent, the crude product was purified by flash chromatography on silica gel to afford the final product **E6**.

(1S,2R)-2-(3-(3,5-bis(trifluoromethyl)phenyl)thioureido)cyclohexyl acrylate (E6)



E6

A colorless oil ; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (s, 1H), 7.49 (s, 2H), 6.36 (dd, *J* = 17.2, 1.6 Hz, 1H), 6.05 (dd, *J* = 17.2, 10.4 Hz, 1H), 5.80 (dd, *J* = 10.4, 1.6 Hz, 1H), 4.64- 4.50 (m, 1H), 3.43 (td, *J* = 8.8, 4.4 Hz, 1H), 3.23-3.16 (m, 2H), 3.15- 3.08 (m, 2H), 1.89-1.79 (m, 1H), 1.55 (s, 1H), 1.39-1.19 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.62, 165.06, 148.48, 140.11, 132.13 (q, *J* = 33.8 Hz), 130.54, 129.98 (d, *J* = 3.0 Hz), 128.90, 124.49, 121.78, 119.07, 75.37, 62.46, 35.89, 29.81 (d, *J* = 80.2 Hz), 23.25 (d, *J* = 17.2 Hz), 22.34. HRMS (ESI) *m/z* calcd for $C_{18}H_{18}F_6N_2O_2S$ $[M+H]^+$ = 441.1071, found = 441.1073.

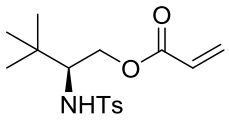


E7

To a (*S*)-N-(1-hydroxy-3,3-dimethylbutan-2-yl)-4-methylbenzenesulfonamide (10 mmol) in CH_2Cl_2 at 0^oC. then, TEA (20 mmol, 2.0 equiv.) was added and acryloyl chloride (15 mmol, 1.5 equiv.) was added slowly at 0^oC. Then the mixture was stirred at rt for 5 h, TLC show that the reaction was completed, then the reaction was quenched by Na_2CO_3(aq.) and extracted with CH_2Cl_2 three times. The combined

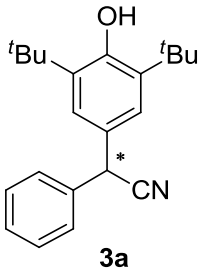
organic layers were dried over Na_2SO_4. After evaporation of solvent, the crude product was purified by flash chromatography on silica gel to afford the final product **E7**.

(S)-3,3-dimethyl-2-(4-methylphenylsulfonamido)butyl acrylate (E7)



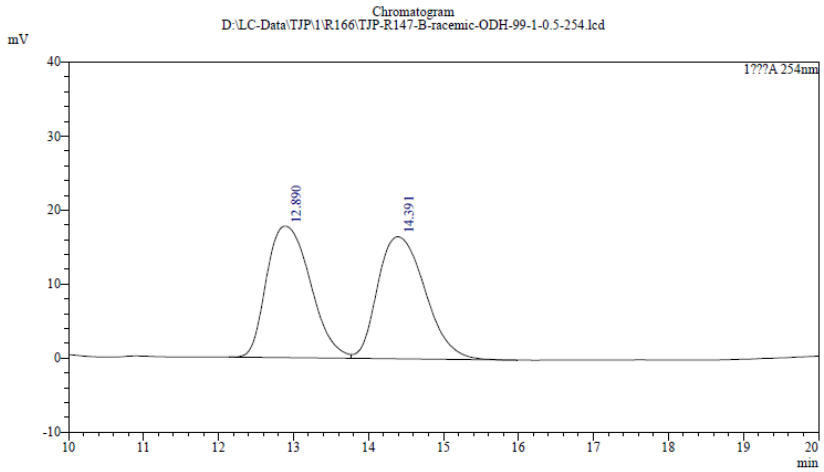
E7

A colorless oil ; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 8.3 Hz, 2H), 7.28-7.23 (m, 2H), 6.31 (dd, *J* = 16.8, 1.9 Hz, 1H), 5.79 (ddd, *J* = 13.6, 12.3, 6.2 Hz, 2H), 4.84 (d, *J* = 9.8 Hz, 1H), 4.06 (ddd, *J* = 15.9, 11.9, 5.0 Hz, 2H), 3.34 (ddd, *J* = 10.0, 6.1, 4.0 Hz, 1H), 2.40 (s, 3H), 0.92 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.07, 143.31, 138.79, 131.31, 129.76, 127.88, 127.07, 63.87, 61.09, 34.54, 27.07, 21.62; HRMS (ESI) *m/z* calcd for $C_{16}H_2NO_4S[M+H]^+$= 326.1426, found = 326.1424.



3a

HPLC: (Chiralcel ODH, λ = 254 nm, 1% *i*-PrOH/hexane, flow rate = 0.5 mL/min) , t_1 = 12.9 min, t_2 = 14.4 min, 2% ee.

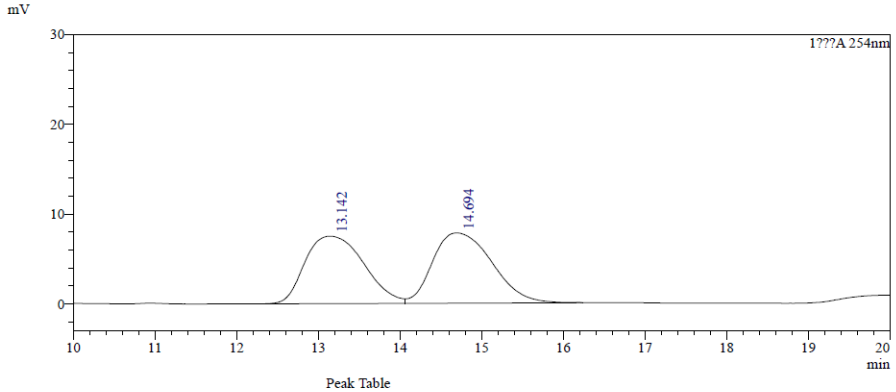


Peak Table

???A 254nm

Peak#	Ret. Time	Height	Area	Height%	Area%
1	12.890	17776	722253	51.891	49.906
2	14.391	16481	724980	48.109	50.094
Total		34257	1447233	100.000	100.000

Racemic **3a**

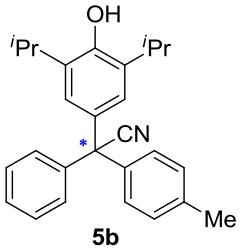


Peak Table

???A 254nm

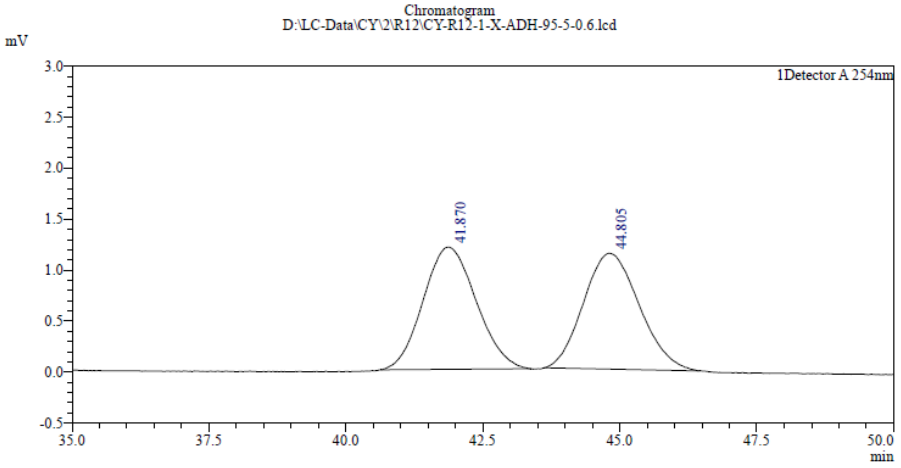
Peak#	Ret. Time	Height	Area	Height%	Area%
1	13.142	7505	376209	48.962	48.795
2	14.694	7823	394797	51.038	51.205
Total		15328	771006	100.000	100.000

Enantiomerically enriched **3a**



5b

HPLC: (Chiralcel ADH, λ = 254 nm, 5% *i*-PrOH/hexane, flow rate = 0.5 mL/min), t_1 = 41.9 min, t_2 = 44.8 min, 1% ee .

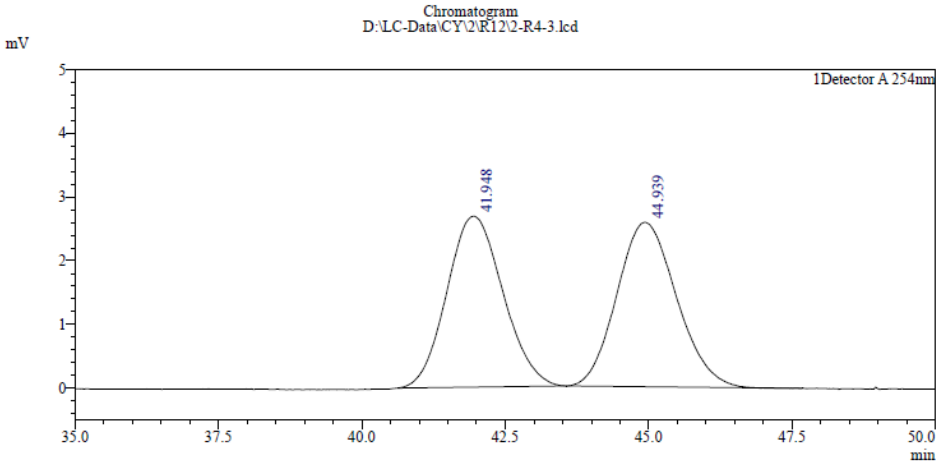


Peak Table

Detector A 254nm

Peak#	Ret. Time	Area	Height	Height%	Area%
1	41.870	80735	1198	51.335	50.067
2	44.805	80518	1136	48.665	49.933
Total		161252	2334	100.000	100.000

Racemic **5b**



Peak Table

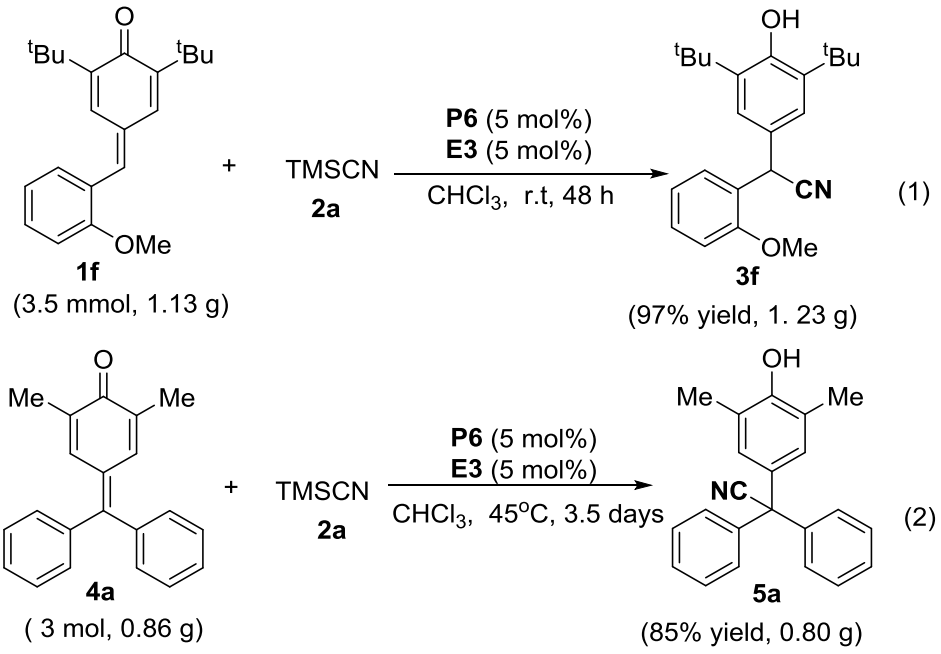
Detector A 254nm

Peak#	Ret. Time	Area	Height	Height%	Area%
1	41.948	182621	2684	50.964	49.428
2	44.939	186845	2583	49.036	50.572
Total		369466	5267	100.000	100.000

Enantiomerically enriched **5b**

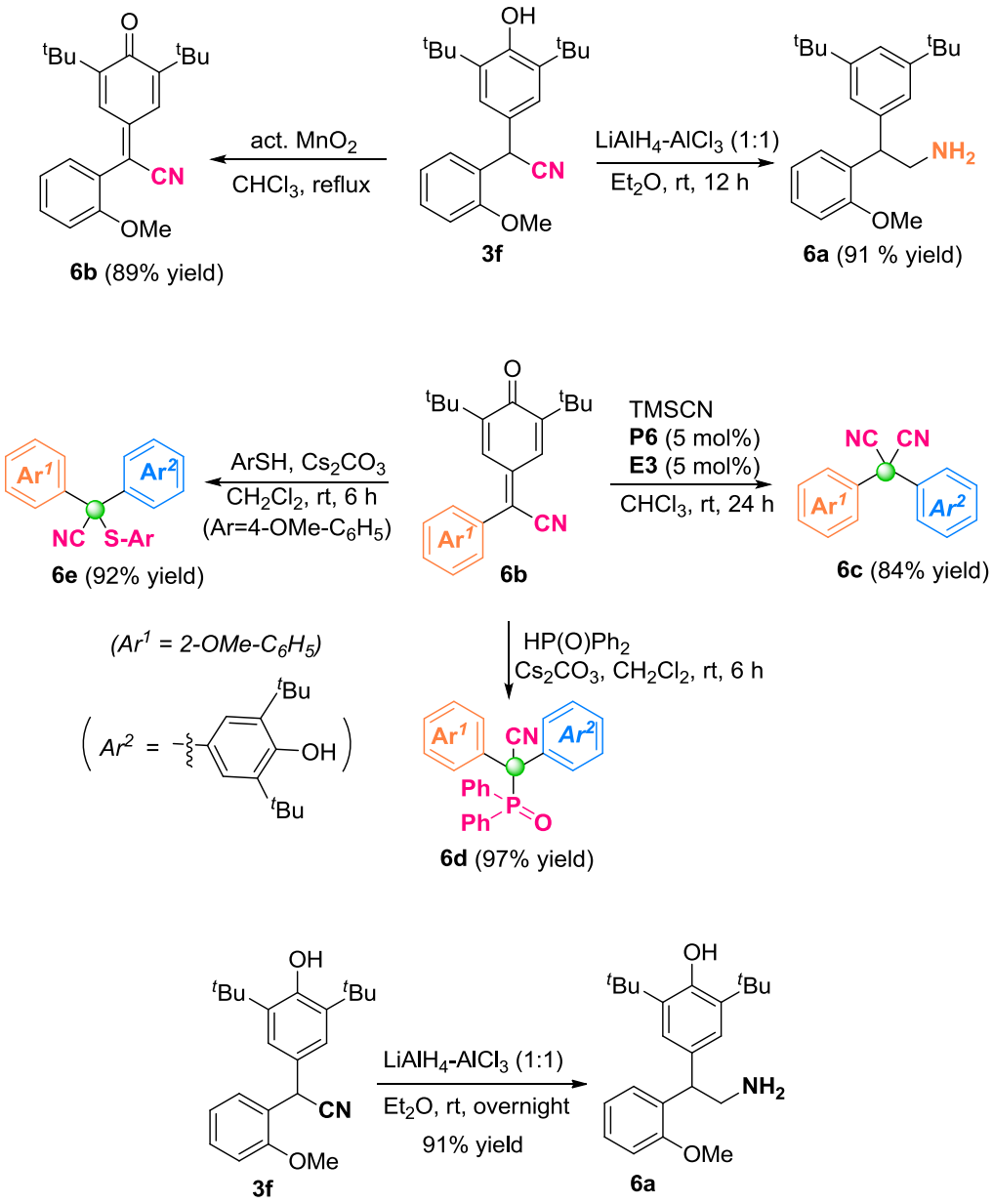
7. Gram-scale synthesis and elaboration of reaction product

(a) Gram-scale synthesis



To a dried round bottle flask with a magnetic stirring bar were added P_6 (5 mol%), E_3(5 mol%) in $CHCl_3$ (10.0 mL) and then *para*-Quinone Methide **1f** (3.5 mmol, 1.13 g) and TMSCN (7.0 mmol, 0.7g) were added. The reaction mixture was stirred at rt for 48 h, and TLC show that the reaction was completed. Then, 1M TFA (5 mL) was added to the mixture and stirred for 5mins, The resulting solution was quenched by Na_2CO_3 (aq.) and was extracted with CH_2Cl_2 (3×100 mL). Then the combined organic phases were washed with brine and dried over anhydrous Na_2SO_4. The solvent was removed to give the crude product which was purified by flash column chromatography (PE/ethyl acetate = 80/1 to 10/1) to afford the desired compounds **3f** (1.19 g, 97% yield).

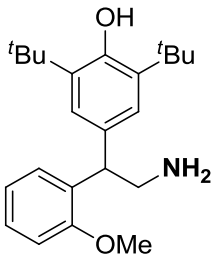
(b) Synthetic elaboration of product



To a dried round bottle flask with a magnetic stirring bar were added $LiAlH_4$ (0.6 mmol, 23 mg). $AlCl_3$ (0.6 mmol, 80 mg) were added together, then *para*-Quinone Methides **3f** (0.4 mmol, 128 mg) and Et_2O (5 mL) were added. The reaction mixture was stirred at rt overnight, and TLC show that the reaction was completed. Then, the reaction was quenched by water. The resulting solution was extracted with CH_2Cl_2 (3×100 mL). Then the combined organic phases were washed with brine and dried over anhydrous Na_2SO_4. The solvent was removed to give the crude product which

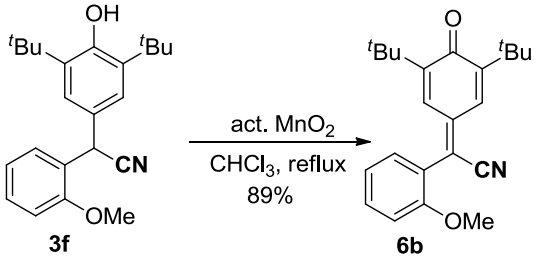
was purified by flash column chromatography to afford the desired compounds **6a** (194 mg, yield 91%).

4-(2-amino-1-(2-methoxyphenyl)ethyl)-2,6-di-tert-butylphenol (6a)



6a

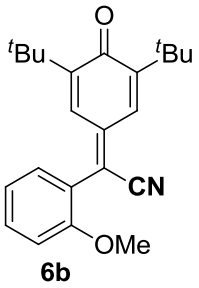
A white solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19 -7.10 (m, 2H), 7.07 (s, 2H), 6.85 (dd, *J* = 12.2, 7.8 Hz, 2H), 4.92 (s, 3H), 4.45 (t, *J* = 8.1 Hz, 1H), 3.81 (s, 3H), 3.52-3.38 (m, 1H), 3.37-3.32 (m, 1H), 1.40 (s, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.40, 152.62, 135.93, 131.53, 129.77, 128.71, 127.97, 124.92, 120.82, 111.11, 55.49, 45.96, 44.78, 34.48, 30.42; HRMS (ESI) *m/z* calcd for $C_{23}H_{33}NO_2$ $[M+H]^+$ = 356.2590, found = 356.2548.



3f **6b**

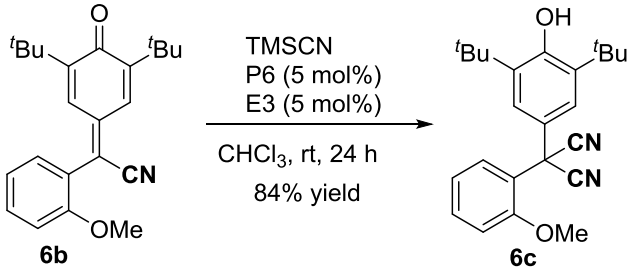
To a dried round bottle flask with a magnetic stirring bar were added act.MnO_2 (3 mmol, 261 mg) and *para*-Quinone Methide **3f** (1 mmol, 372 mg), then 5 mL $CHCl_3$ was added. The reaction mixture was stirred reflux overnight, and TLC show that the rection was completed. Then, the reaction was filtrated by celite. the solvent was removed under reduced press to give the crude product which was purified by flash column chromatography to afford the desired compounds **6b** (310 mg, yield 89%).

2-(3,5-di-tert-butyl-4-oxocyclohexa-2,5-dien-1-ylidene)-2-(2-methoxyphenyl)acetonitrile (6b)



6b

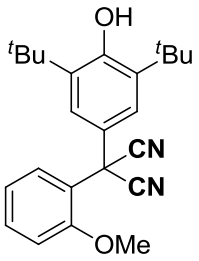
A orange solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, *J* = 2.6 Hz, 1H), 7.47 (td, *J* = 8.4, 1.7 Hz, 1H), 7.20 (dd, *J* = 7.6, 1.7 Hz, 1H), 7.09-7.00 (m, 2H), 6.98 (d, *J* = 2.6 Hz, 1H), 3.91 (s, 3H), 1.35 (s, 9H), 1.18 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 186.57, 157.58, 151.51, 150.82, 141.84, 132.30, 132.19, 129.53, 127.84, 121.18, 120.82, 117.42, 117.09, 111.83, 5.93, 35.83, 35.77, 29.63, 29.55; HRMS (ESI) *m/z* calcd for $C_{23}H_{27}NO_2$ $[M+H]^+$ =350.2120, found = 350.2122.



6b **6c**

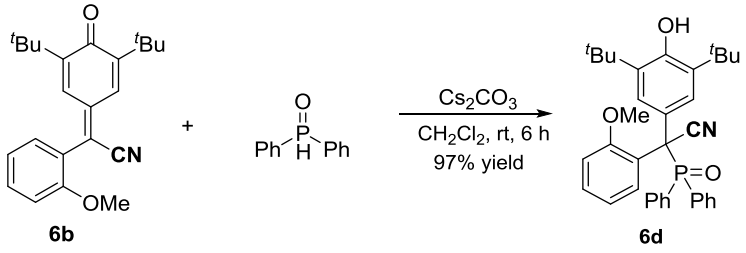
To a dried round bottle flask with a magnetic stirring bar were added P_6 (5 mol%), E_3(5mol%) in $CHCl_3$ (1.0 mL).and then **6b** (35 mg, 0.1 mmol) and TMSCN (20 mg, 0.2 mmol) were added. The reaction mixture was stirred at rt for 24 h, and TLC show that the rection was completed. Then, 1 M TFA (2 mL) was added to the mixture, and stirred for 5 mins, the resulting solution was extracted with CH_2Cl_2 (3×10 mL). Then the combined organic phases were washed with brine and dried over anhydrous Na_2SO_4. The solvent was removed to give the crude product which was purified by flash column chromatography (PE/ethyl acetate = 60/1 to 10/1) to afford the desired compounds **6c.**

2-(3,5-di-tert-butyl-4-hydroxyphenyl)-2-(2-methoxyphenyl)malononitrile (6c)



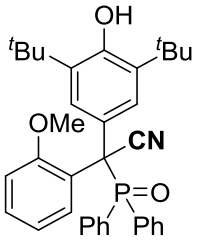
6c

A orange solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47-7.39 (m, 1H), 7.33 (s, 2H), 7.06 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.02-6.95 (m, 2H), 5.44 (s, 1H), 3.92 (s, 3H), 1.43 (s, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.81, 154.84, 136.96, 131.79, 128.17, 124.23, 122.30, 122.21, 121.14, 115.19, 112.48, 56.08, 43.23, 34.74, 30.21; HRMS (ESI) *m/z* calcd for $C_{24}H_{28}N_2O_2$ $[M-H]^-$ =375.2073, found = 375.2070.



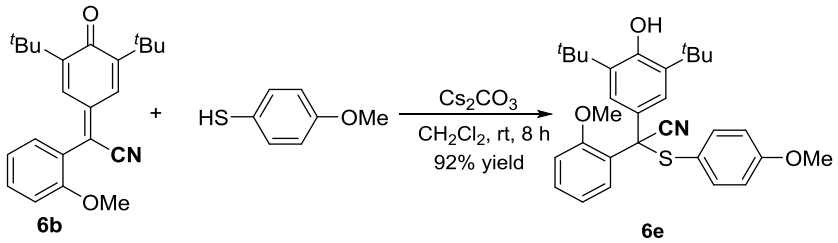
To a dried round bottle flask with a magnetic stirring bar were added **6b** (35 mg, 0.1 mmol) and diphenylphosphine oxide (0.12 mmol) and Cs_2CO_3 (0.2 mmol) in CH_2Cl_2, The reaction mixture was stirred at rt for 6 h, and TLC show that the reaction was completed. The crude mixture was purified by flash column chromatography (PE/ethyl acetate = 20/1 to 3/1) to afford the desired compounds **6d.**

2-(3,5-di-tert-butyl-4-hydroxyphenyl)-2-(diphenylphosphoryl)-2-(2-methoxyphenyl)acetonitrile (6d)



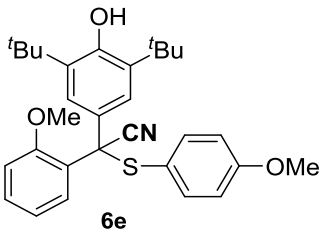
6d

A white foam; ^{1}H NMR (400 MHz, $CDCl_3$)δ 8.26 (dt, *J* = 8.1, 1.4 Hz, 1H), 8.17 – 8.10 (m, 2H), 7.57 – 7.52 (m, 1H), 7.50 – 7.40 (m, 3H), 7.36 – 7.26 (m, 4H), 7.25 – 7.23 (m, 1H), 6.95 (d, *J* = 2.0 Hz, 2H), 6.90 – 6.85 (m, 2H), 5.17 (s, 1H), 3.56 (s, 3H), 1.27 (s, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.58 (d, *J* = 7.4 Hz), 153.46 (d, *J* = 2.7 Hz), 134.84 (d, *J* = 2.2 Hz), 133.72, 133.63, 132.87, 132.79, 132.28 (d, *J* = 2.8 Hz), 132.12 (d, *J* = 2.8 Hz), 131.02 (d, *J* = 3.1 Hz), 130.90, 130.02, 129.29, 128.72 (d, *J* = 11.8 Hz), 127.52 (d, *J* = 12.4 Hz), 126.37 (d, *J* = 1.8 Hz), 124.75, 122.82 (d, *J* = 5.9 Hz), 120.52, 119.77, 113.33, 56.03, 49.74 (d, *J* = 58.8 Hz), 34.45, 30.27; ^{31}P NMR (162 MHz, $CDCl_3$) δ 32.76; HRMS (ESI) *m/z* calcd for $C_{35}H_{38}NO_3P$ $[M-H]^-$ = 550.2517, found = 550.2493.



To a dried round bottle flask with a magnetic stirring bar were added **6b** (35 mg, 0.1 mmol) and 4-methoxybenzenethiol (0.12 mmol) and Cs_2CO_3 (0.2 mmol) in CH_2Cl_2, The reaction mixture was stirred at rt for 8 h, and TLC show that the reaction was completed. The crude mixture was purified by flash column chromatography (PE/ethyl acetate = 20/1 to 3/1) to afford the desired compounds **6e.**

2-(3,5-di-tert-butyl-4-hydroxyphenyl)-2-(2-methoxyphenyl)-2-((4-methoxyphenyl)thio)acetonitrile (6e)

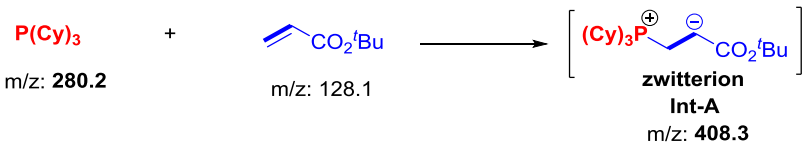


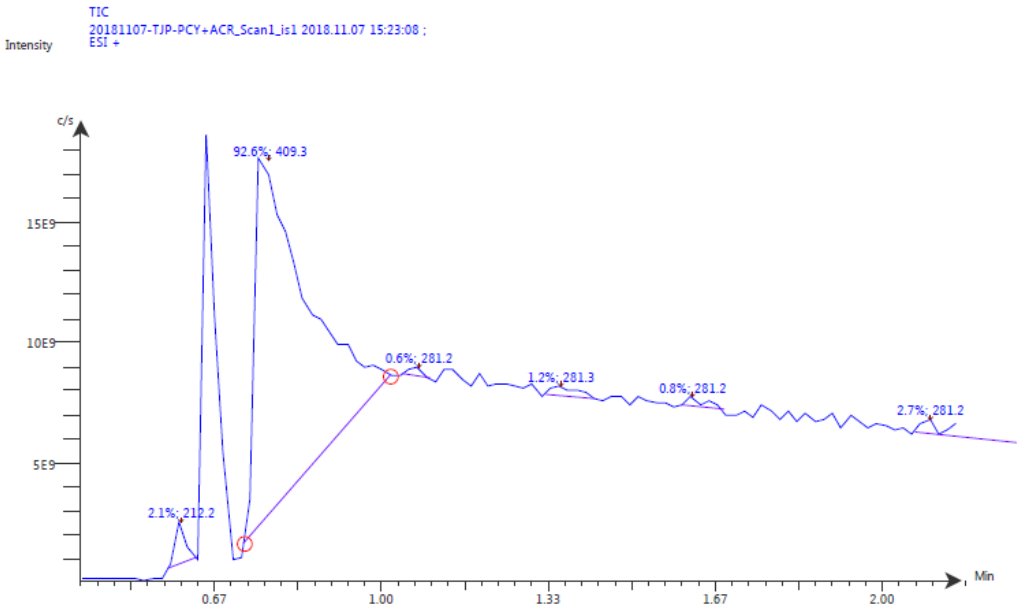
6e

A pale yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.37 (td, *J* = 8.2, 1.6 Hz, 1H), 7.16 (d, *J* = 8.2 Hz, 2H), 7.07-6.99 (m, 3H), 6.97 (s, 2H), 6.91 (dd, *J* = 8.2, 0.8 Hz, 1H), 5.15 (s, 1H), 3.64 (s, 3H), 2.30 (s, 3H), 1.30 (s, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.30, 153.29, 140.11, 137.01, 135.25, 131.69, 130.37, 129.54, 128.60, 128.50, 127.08, 126.07, 124.15, 120.59, 113.15, 56.10,55.39, 34.46, 30.25, 21.42. HRMS (ESI) *m/z* calcd for $C_{30}H_{35}NO_3S$ $[M-H]^-$ =488.2259, found = 488.2261.

8. Experimental studies on mechanism and proposed reaction pathway

a) Experimental studies on mechanism





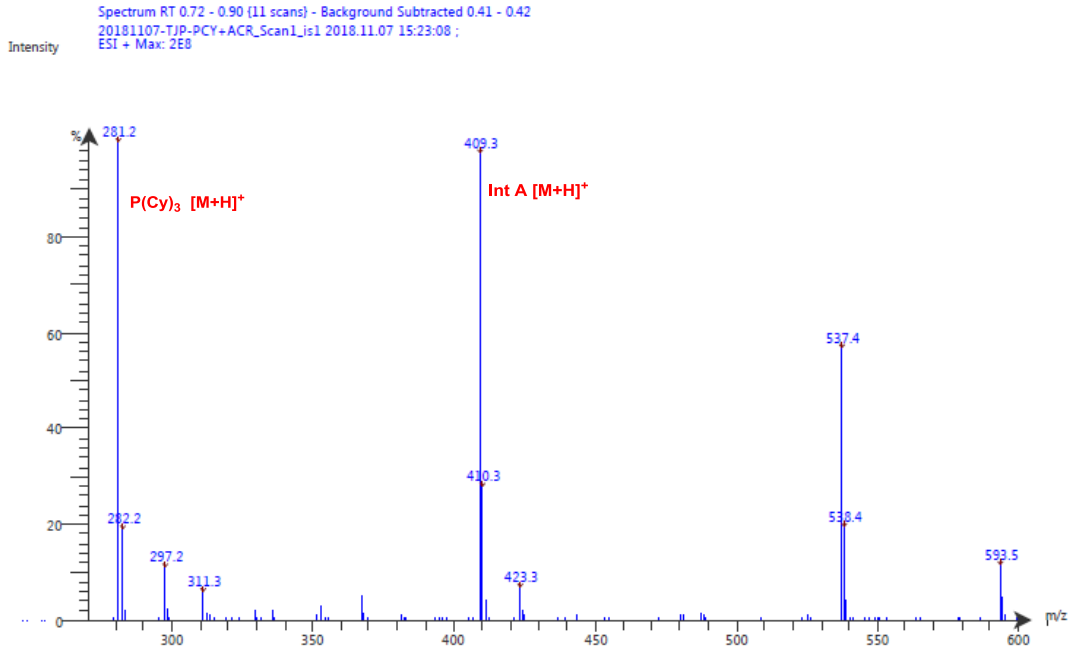
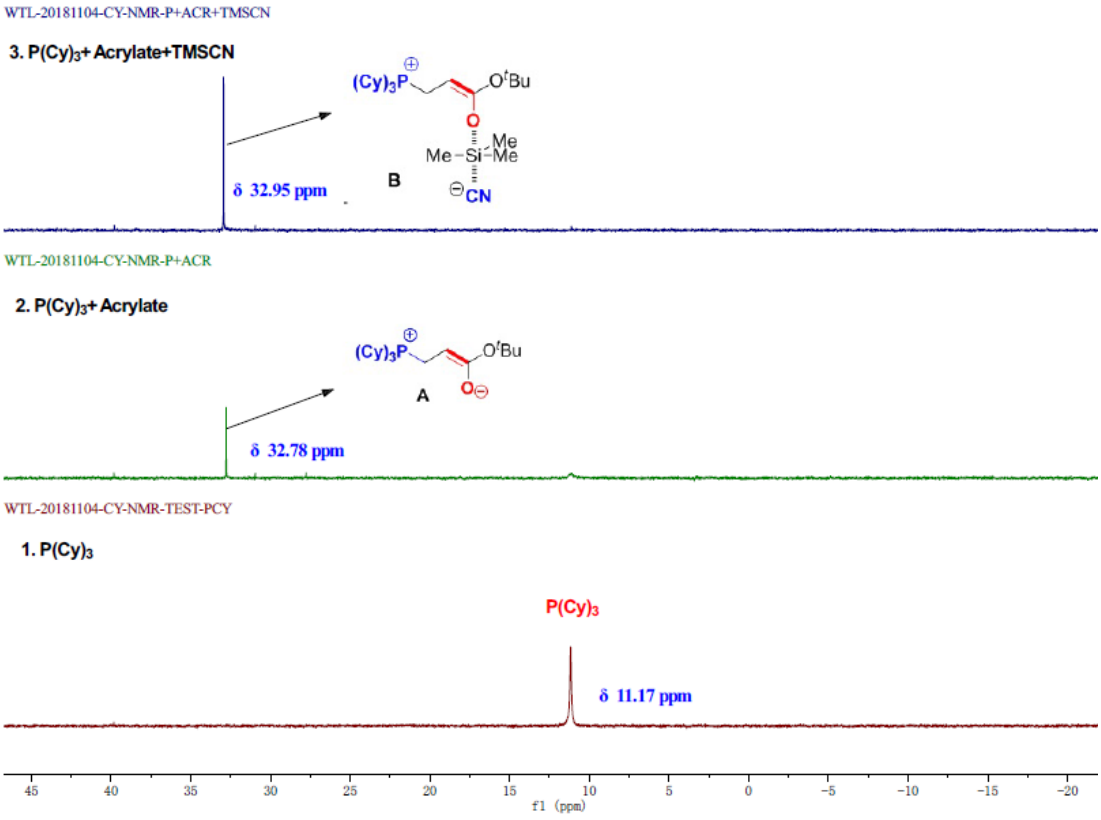


Figure S2. ESI-MS experimental studies on mechanism



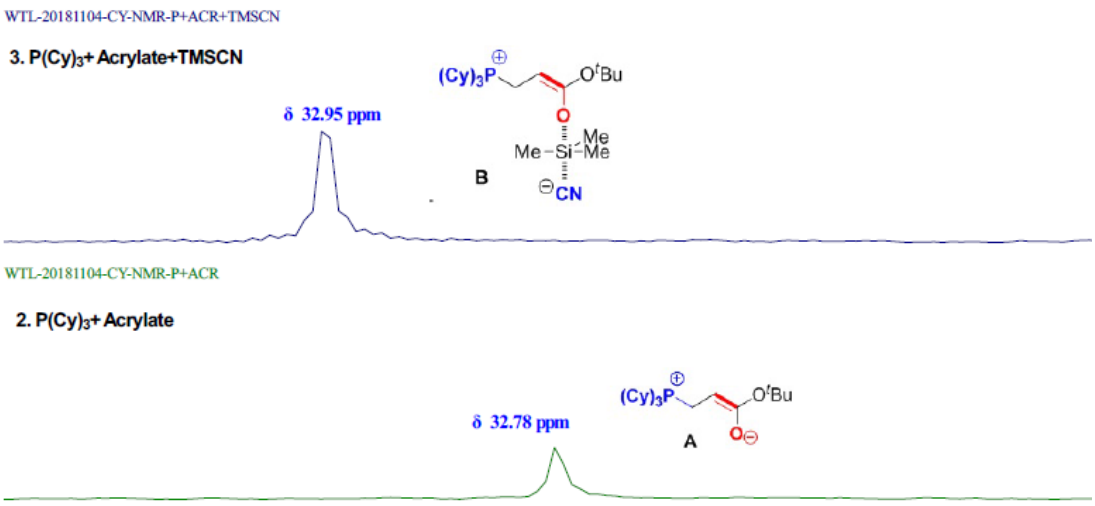


Figure S3. ^{31}P NMR experimental studies on mechanism

To gain further insight of the reaction mechanism, we then employed ESI-MS techniques and ^{31}P NMR for characterization of this catalytic system. $P(Cy)_3$ and *tert*-butyl acrylate was added together and The resulting mixture was shaken up and immediately applied to ESI-MS analysis, then generate a zwitterion in situ int-A which was confirmed by ESI-MS with a new single peak **int-A.H** (m/z 409.3) (Figure S2).

Furthermore, the ^{31}P NMR study to track the reaction intermediate was carried out (Figure S3). when $P(Cy)_3$ and *tert*-butyl acrylate were added into in an NMR tube and shaked 5 mins, the formation of the zwitterion intermediate A as a new ^{31}PNMR chemical shift was generated at δ = 32.78 ppm .Then TMSCN was added into the NMR tube and another new ^{31}PNMR chemical shift was generated at δ = 32.95 ppm, suggesting that efficient activation of TMSCN by the zwitterion intermediate A to form a new specie. We proposed that the zwitterion intermediate A may conduct as a Lewis base to active the Si of TMSCN to form a new intermediate ion-pair B (Figure S4).

b). Proposed reaction pathway

According to the studies on the above mechanism experimental results and several control experiments, we proposed a plausible reaction pathway for the dual-reagent

catalysis promoted direct 1,6-cyanation reaction (Figure S4). Fisrt, the Michael-type addition of $P(Cy)_3$ to *tert*-butyl acrylate generate a zwitterion **A**, which serves as a lewis base to active TMSCN to form a new species **B**. Then this zwitterion **B** release the active CN anion, which attack to C=C bond of *p*-QMs or fuchsone to accomplish 1,6 addition/aromatization affording the intermediate **C**, which was queenched by acid quickly to give the target product.

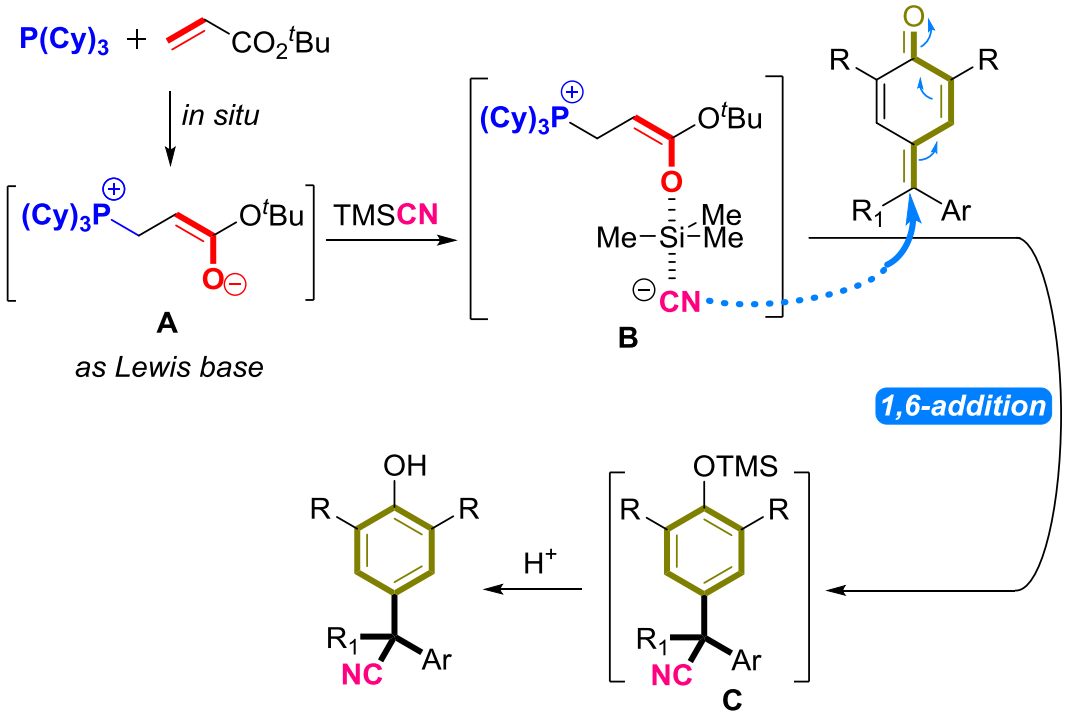


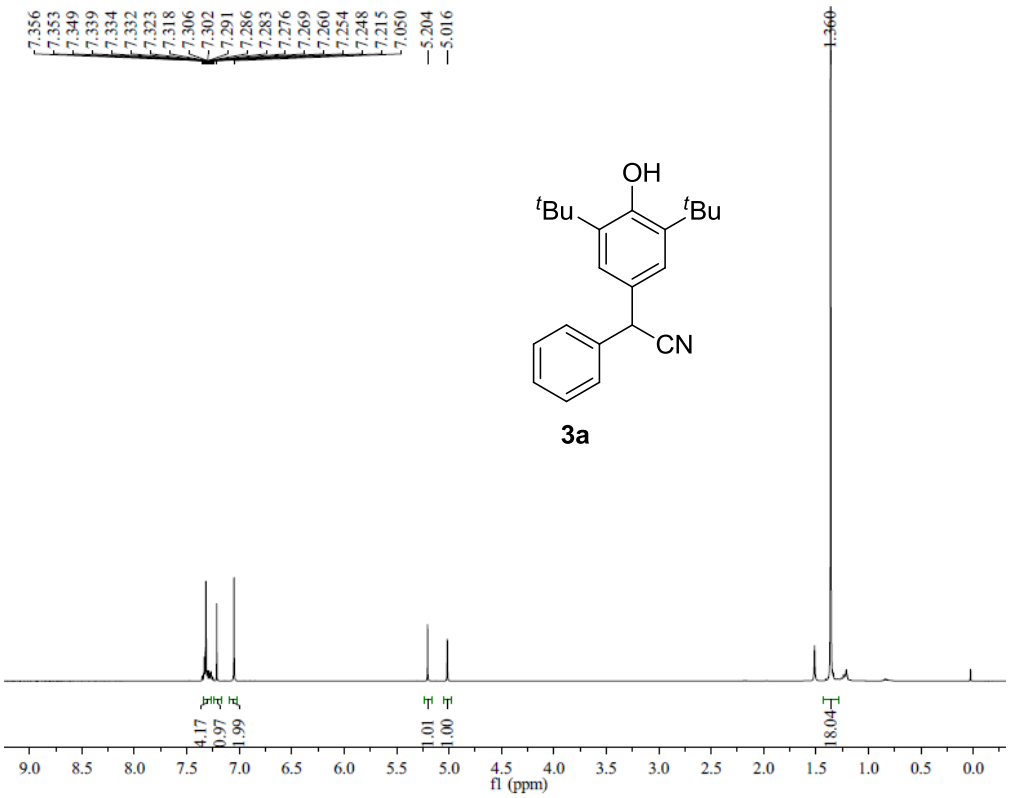
Figure S4. Proposed reaction pathway

9. References

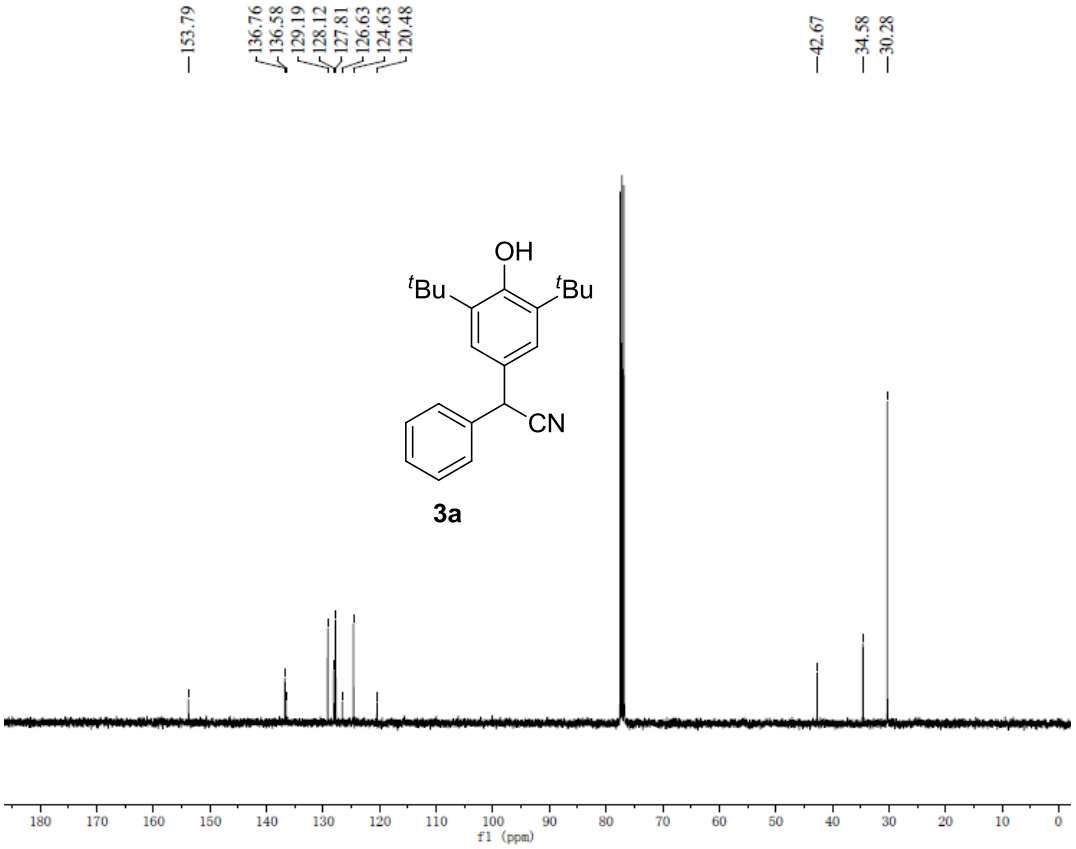
[1] W.-D. Chu, L.-F. Zhang, X. Bao, X.-H. Zhao, C. Zeng, J.-Y. Du, G.-B. Zhang, F.-X. Wang, X.-Y. Ma, C.-A. Fan, *Angew. Chem. Int. Ed*., **2013**, 52, 9229.

[2] H. D. Becker, *J. Org. Chem*., **1967**, 32, 2943.

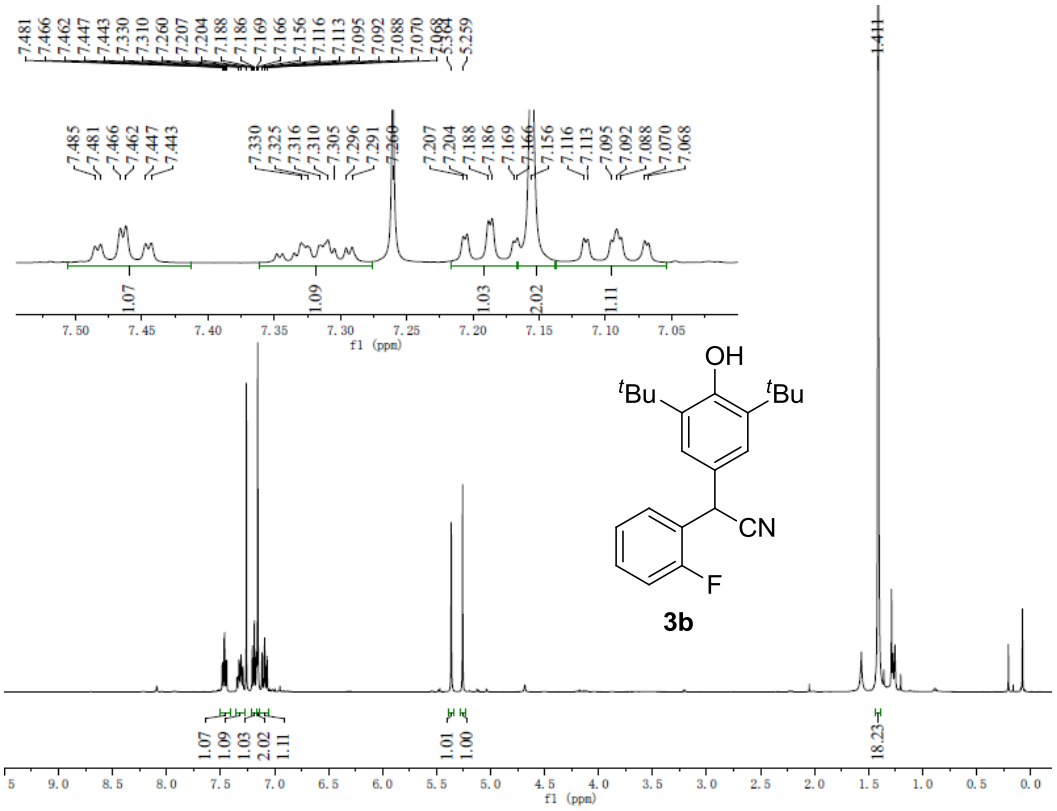
10. NMR Spectra



^{1}HNMR of 3a



^{13}CNMR of 3a



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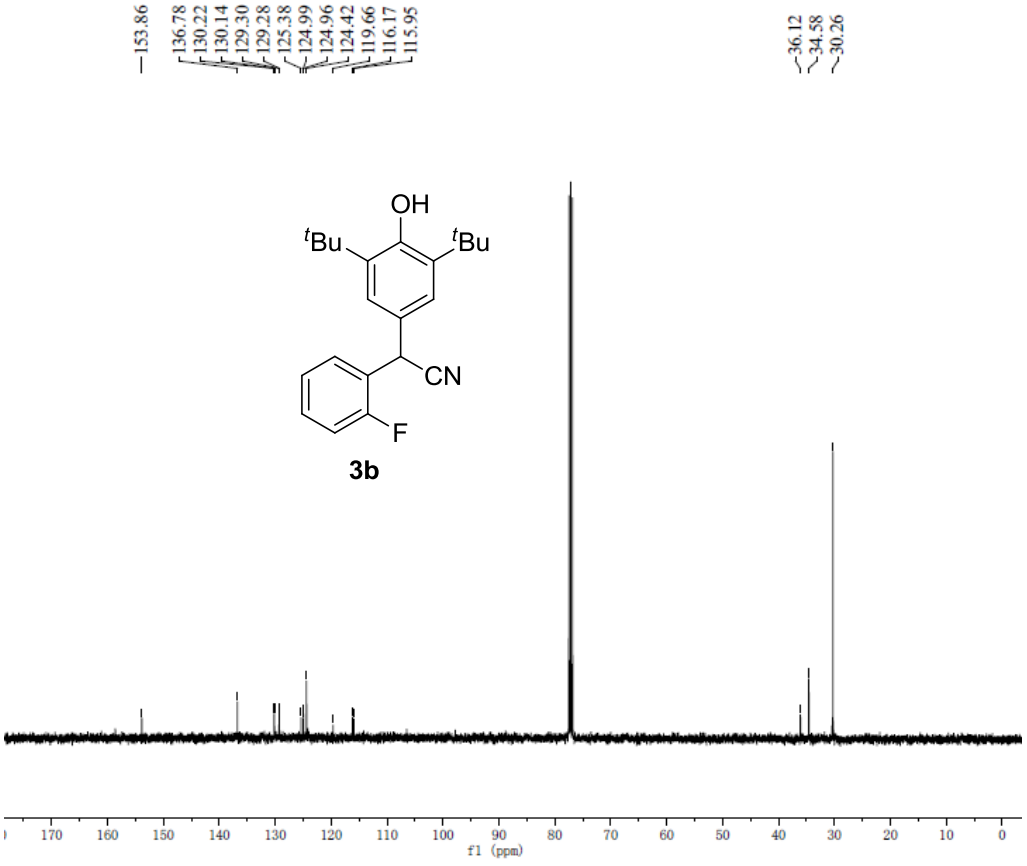

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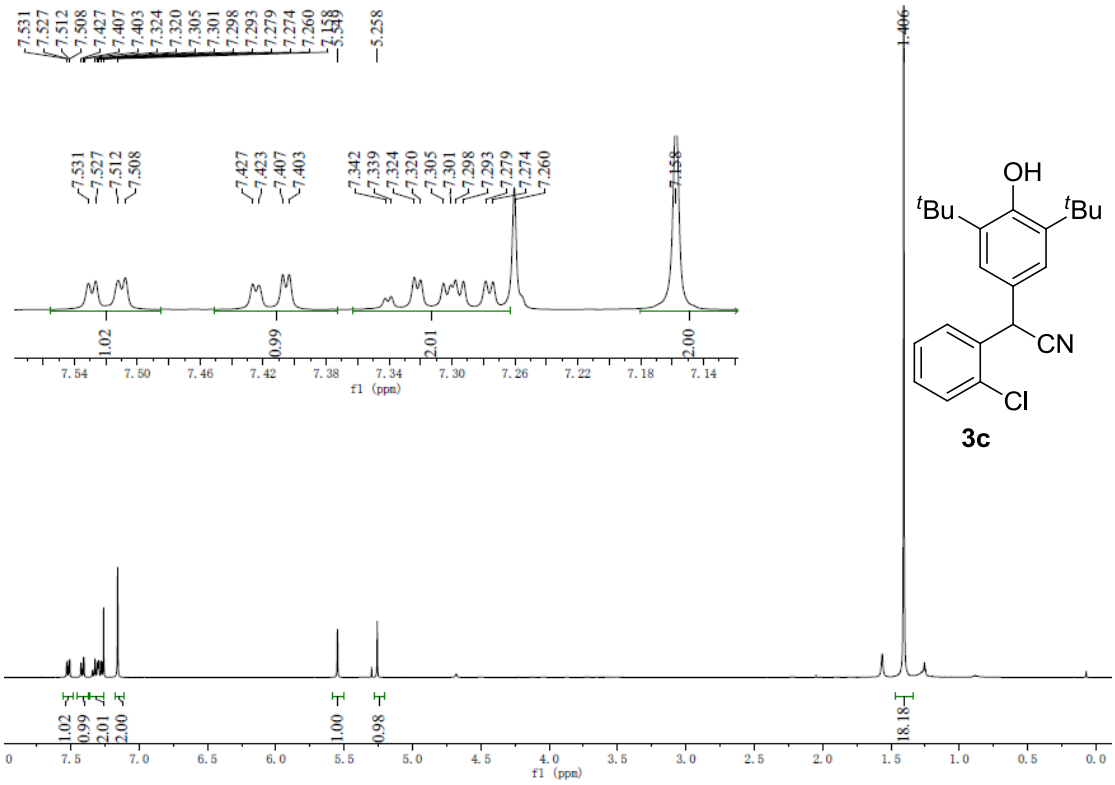

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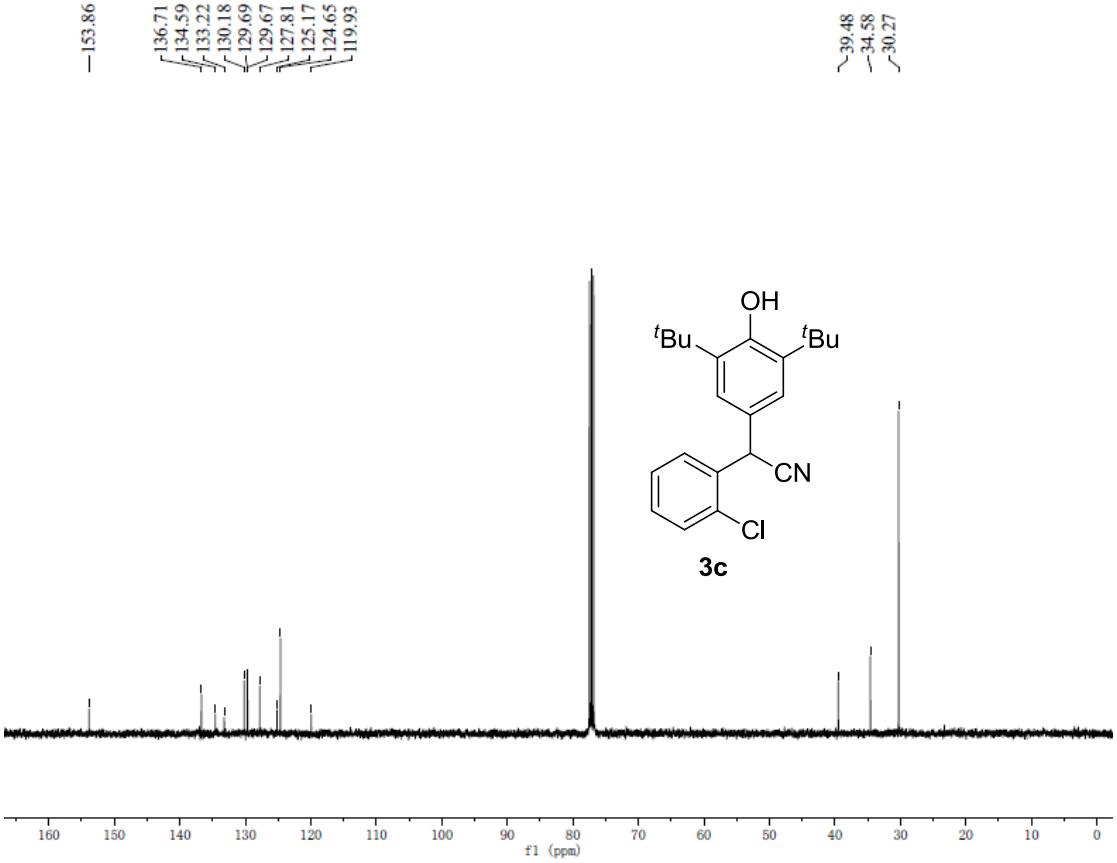

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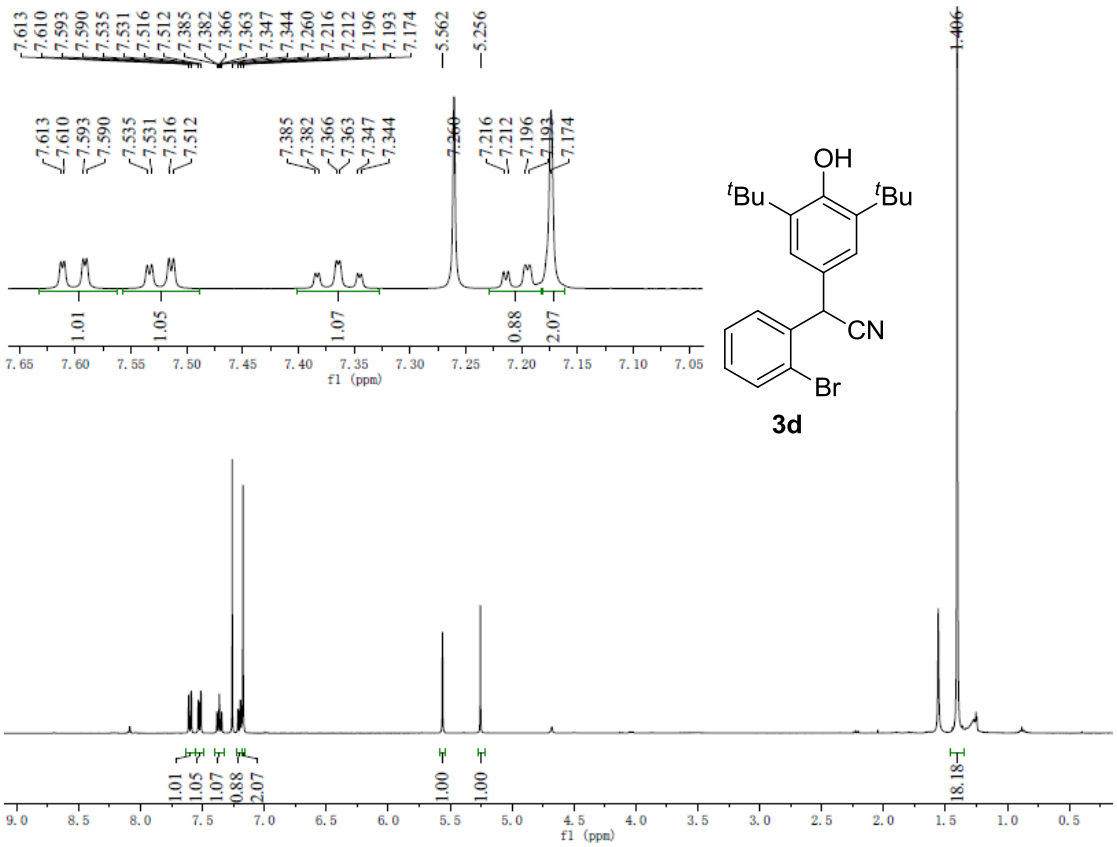

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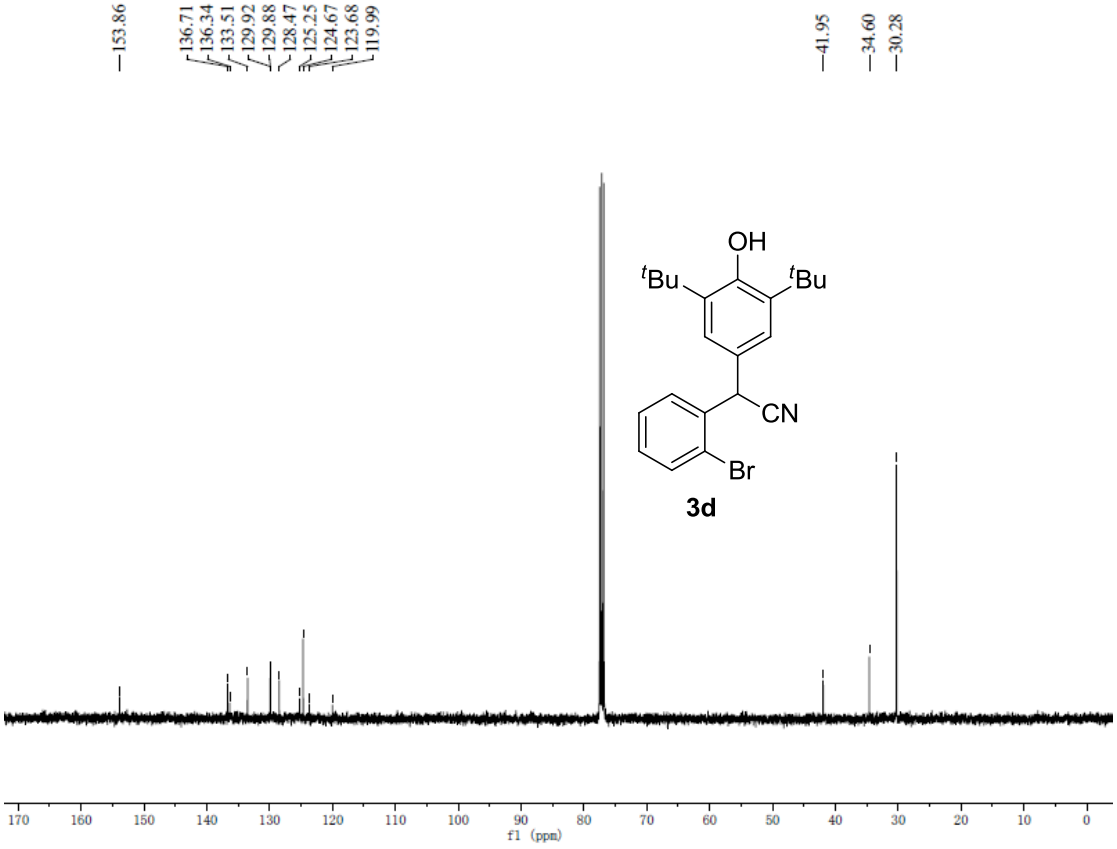

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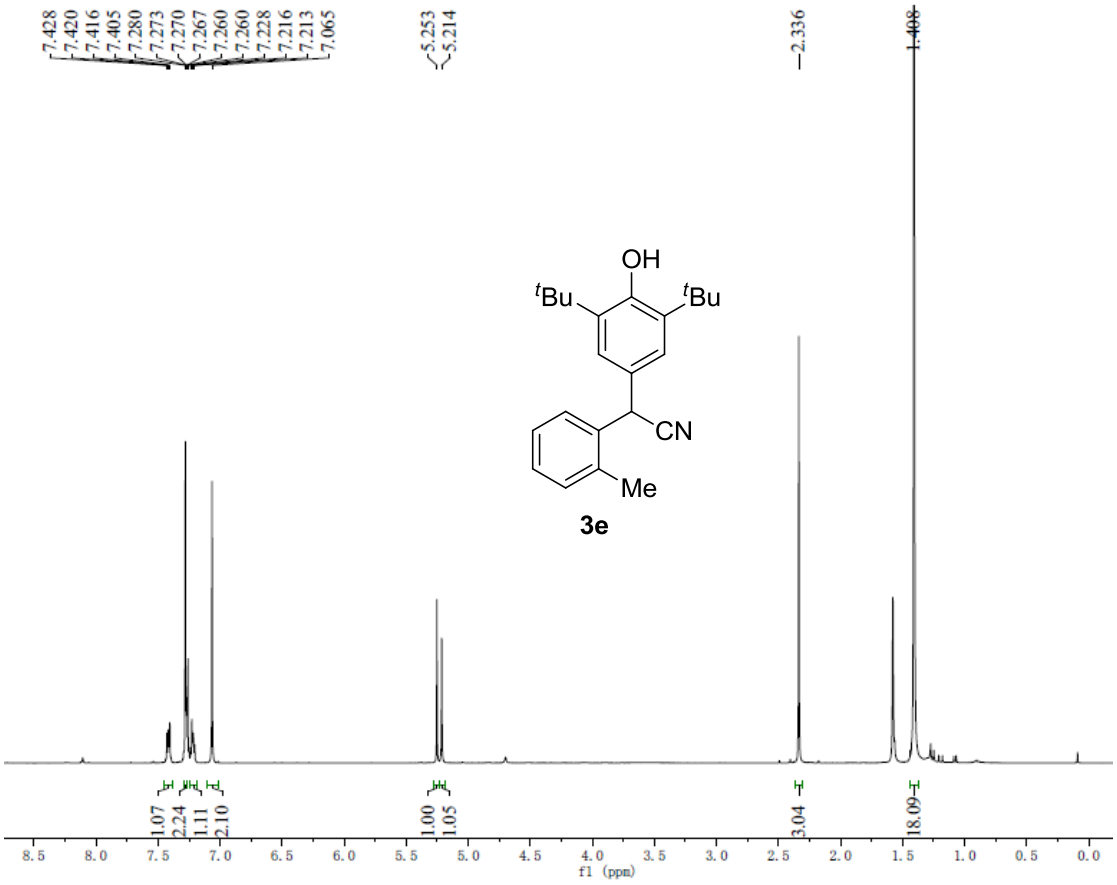

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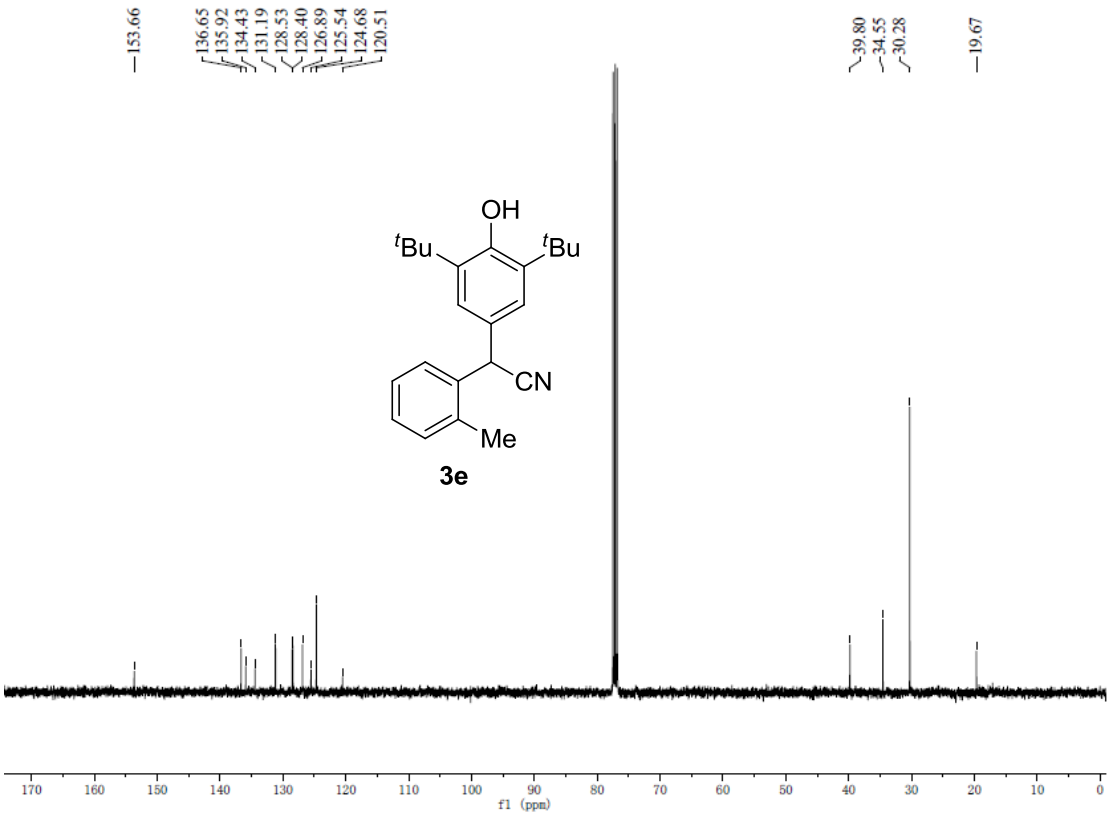

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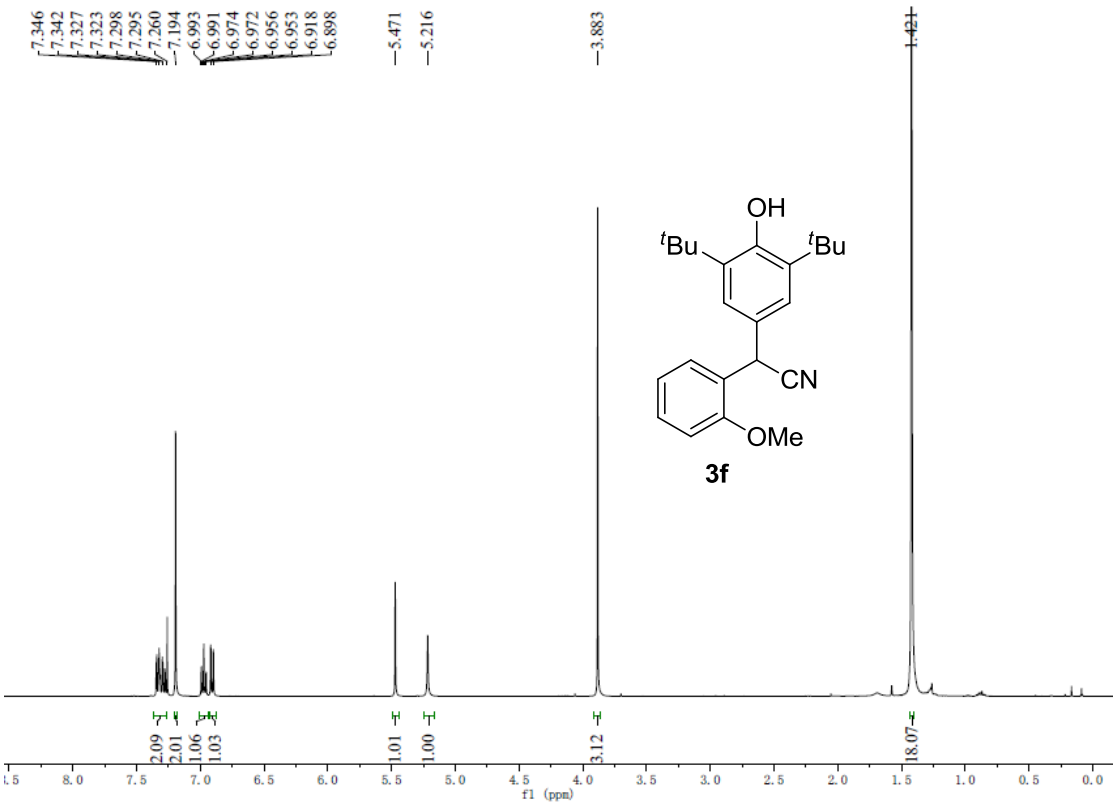

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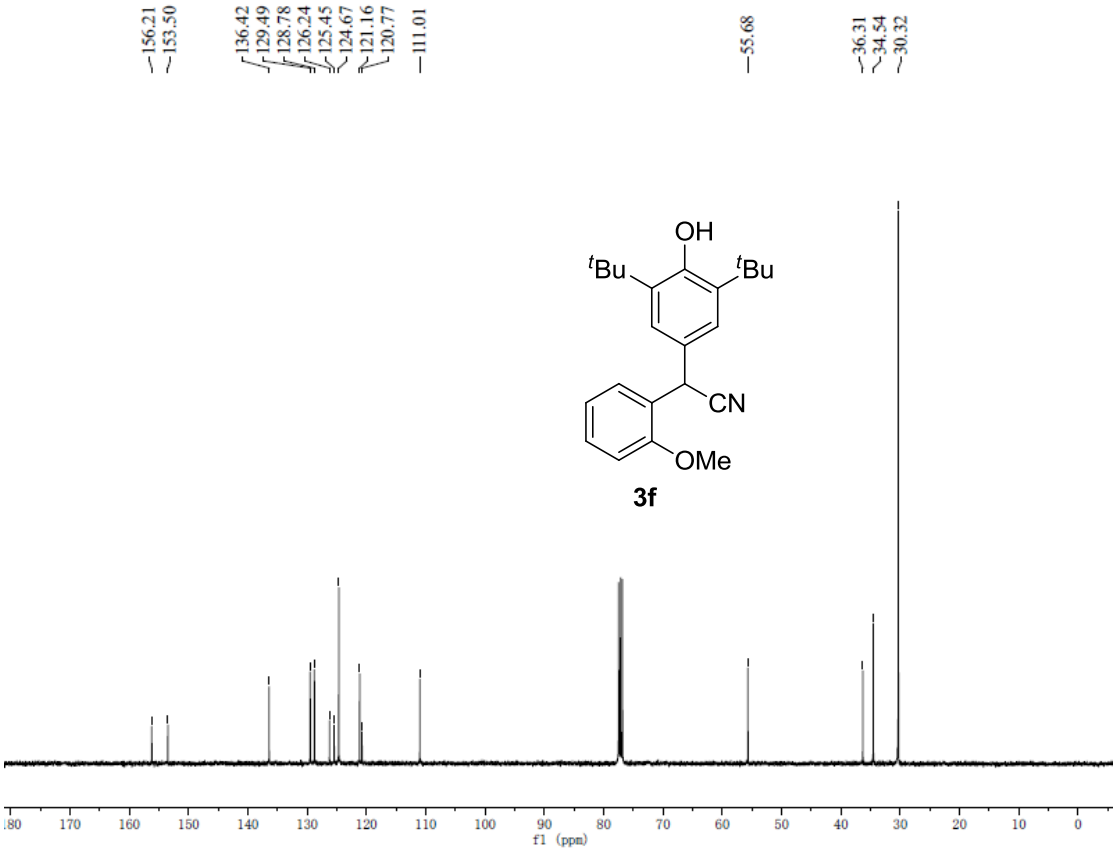

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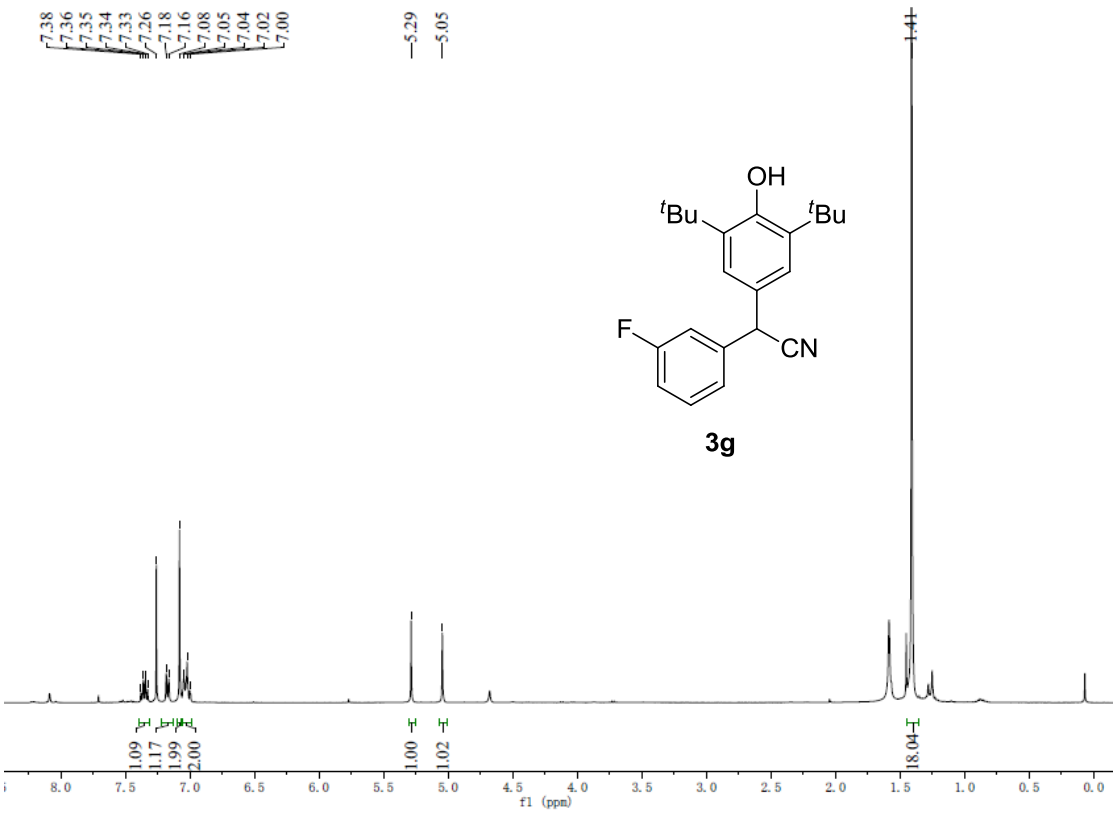

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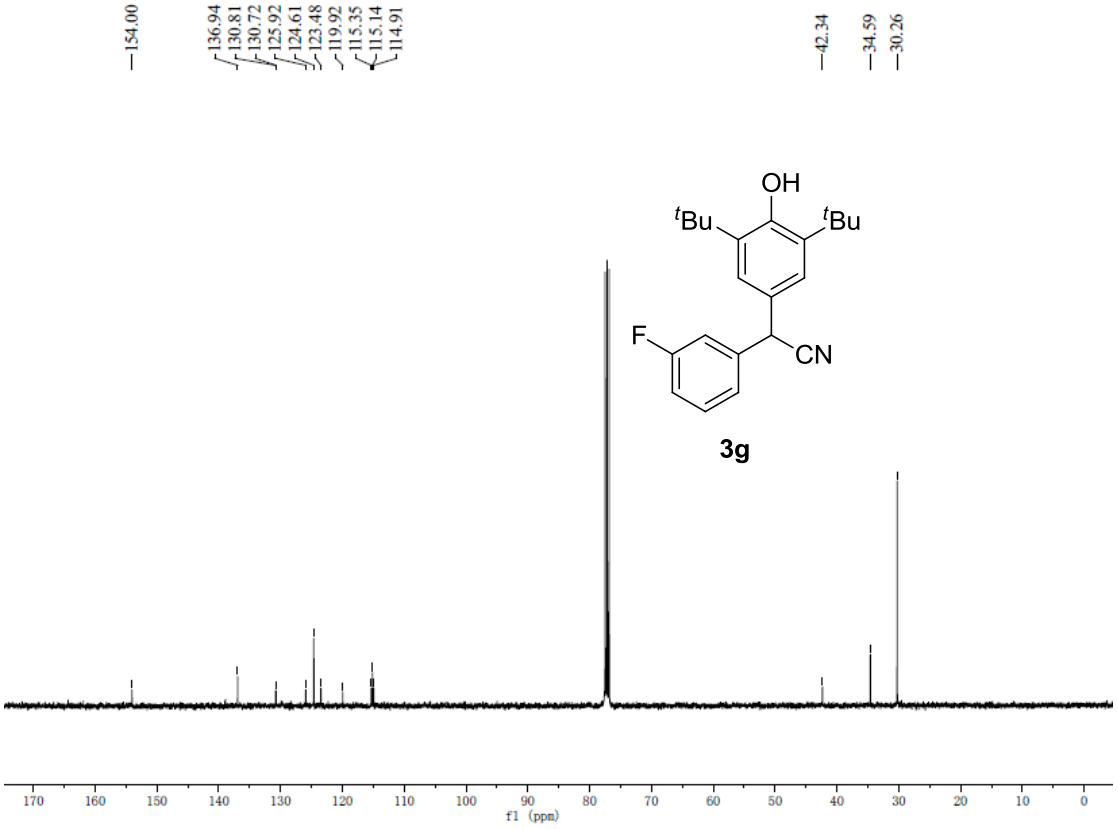

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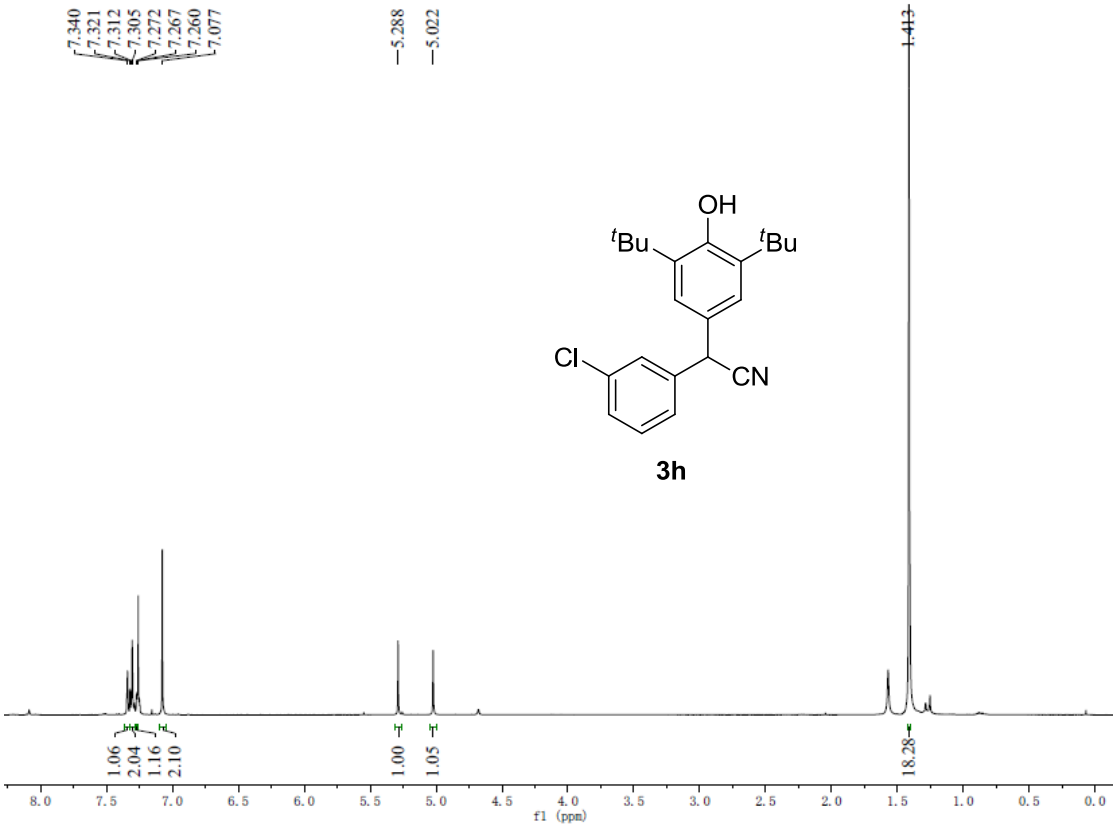

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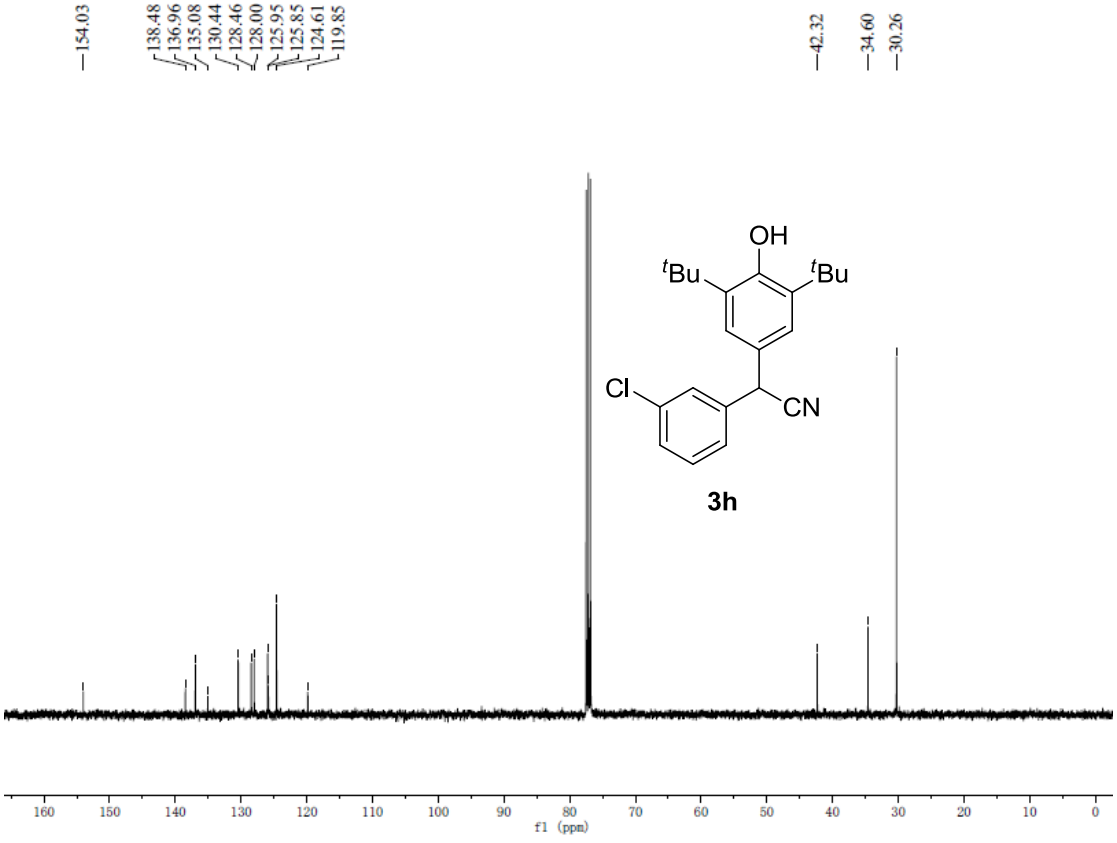

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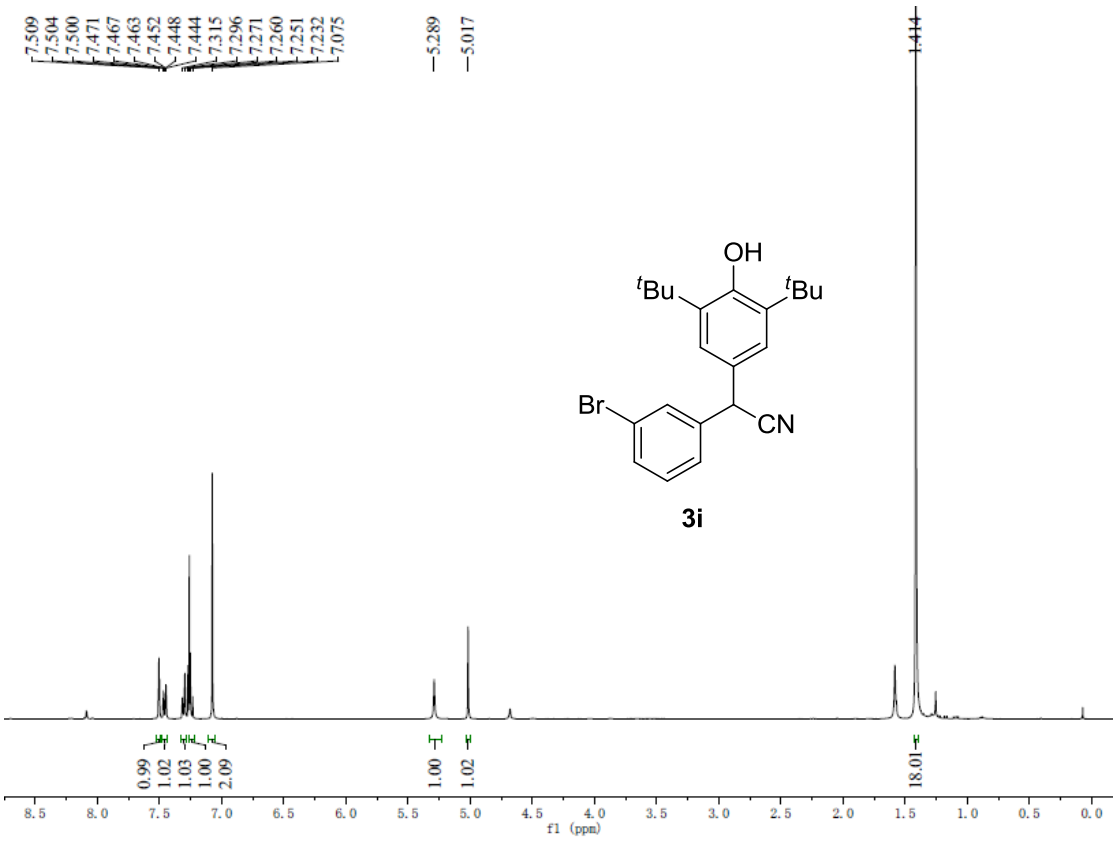

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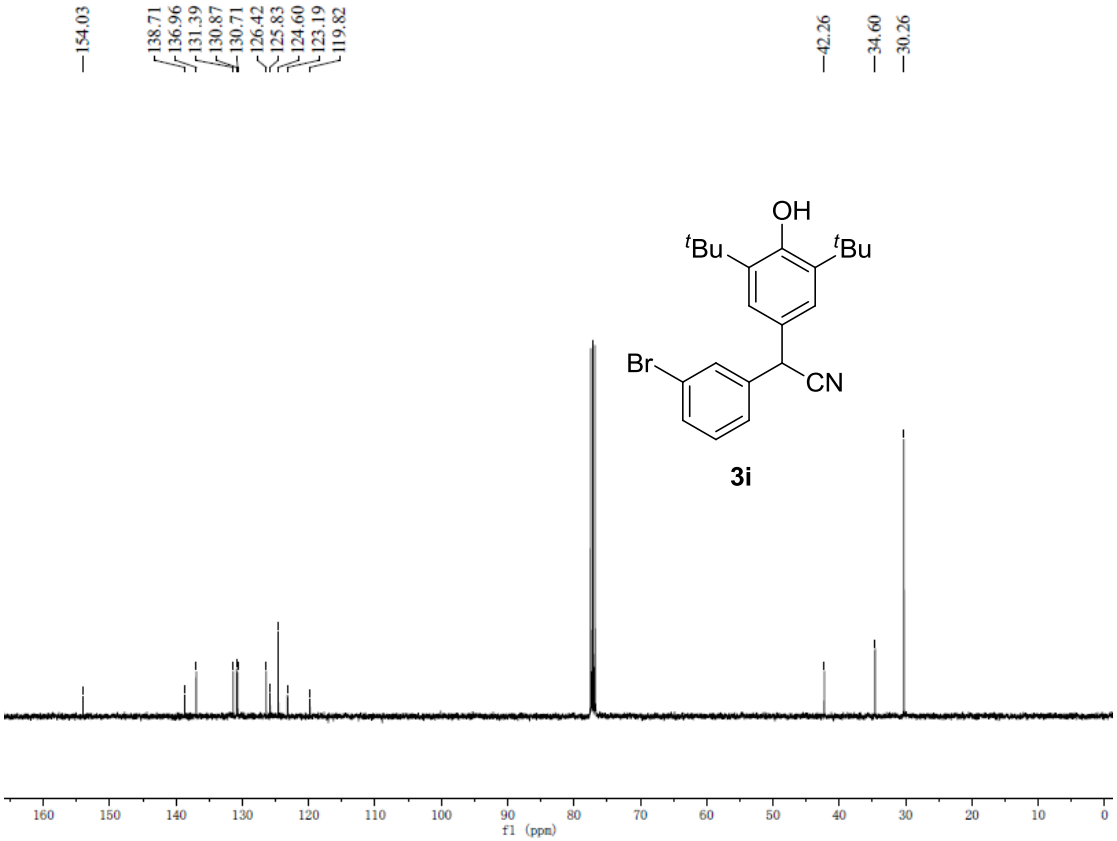

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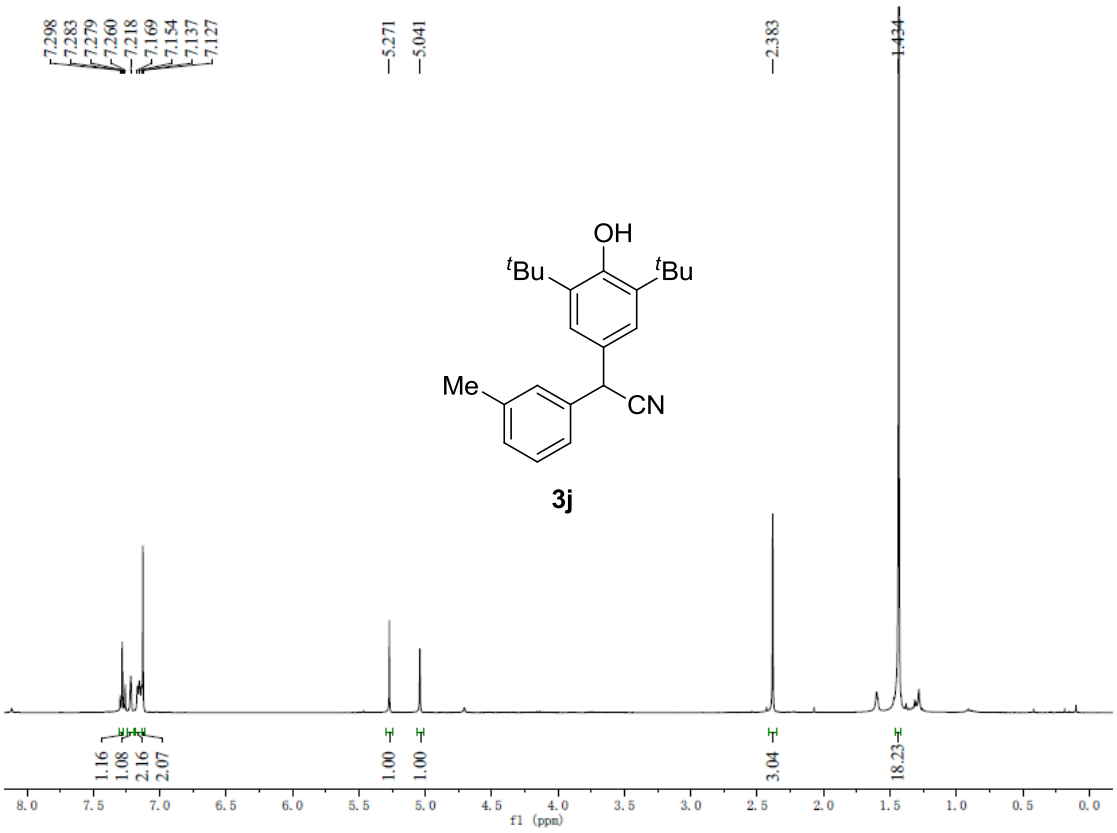

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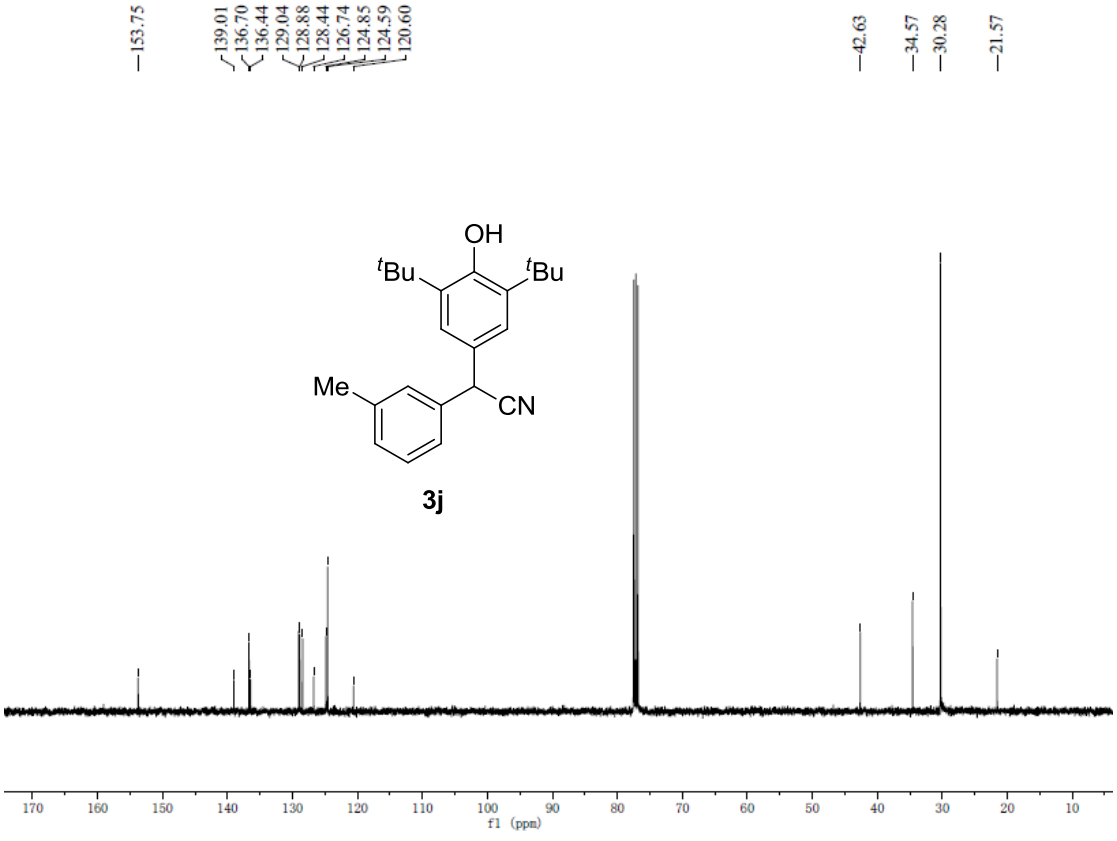

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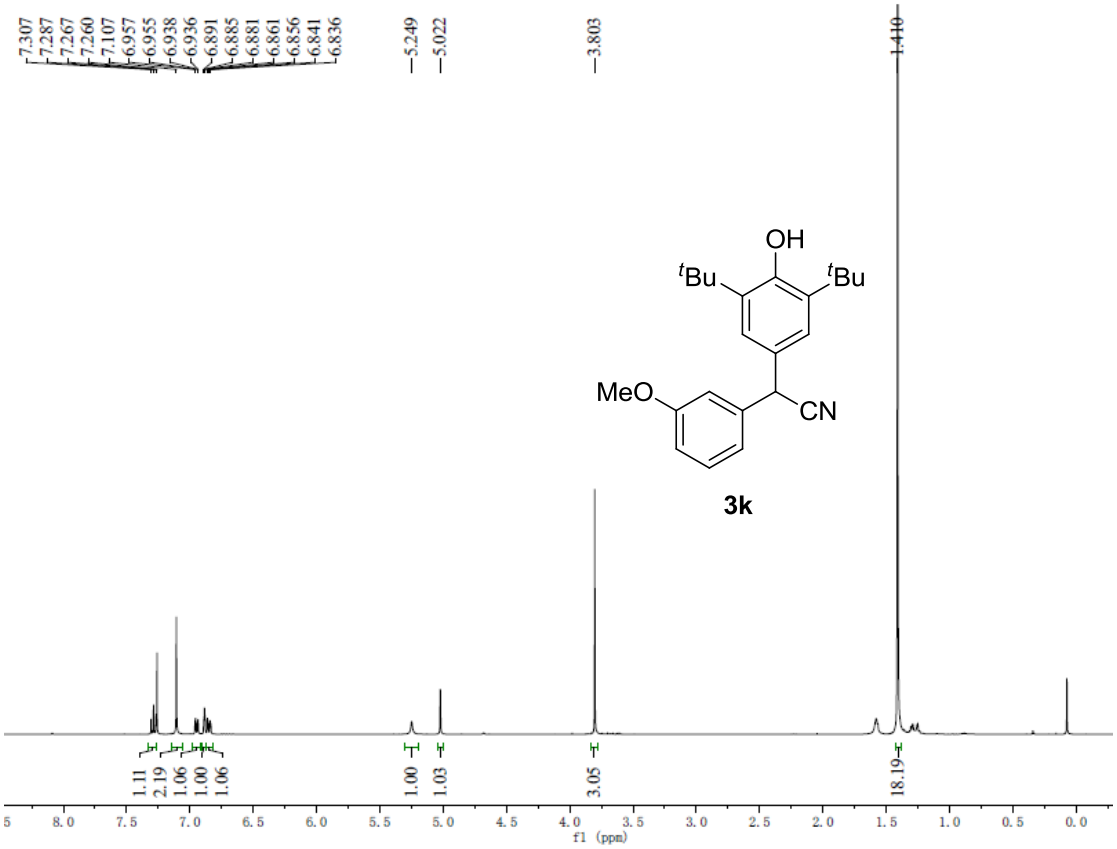

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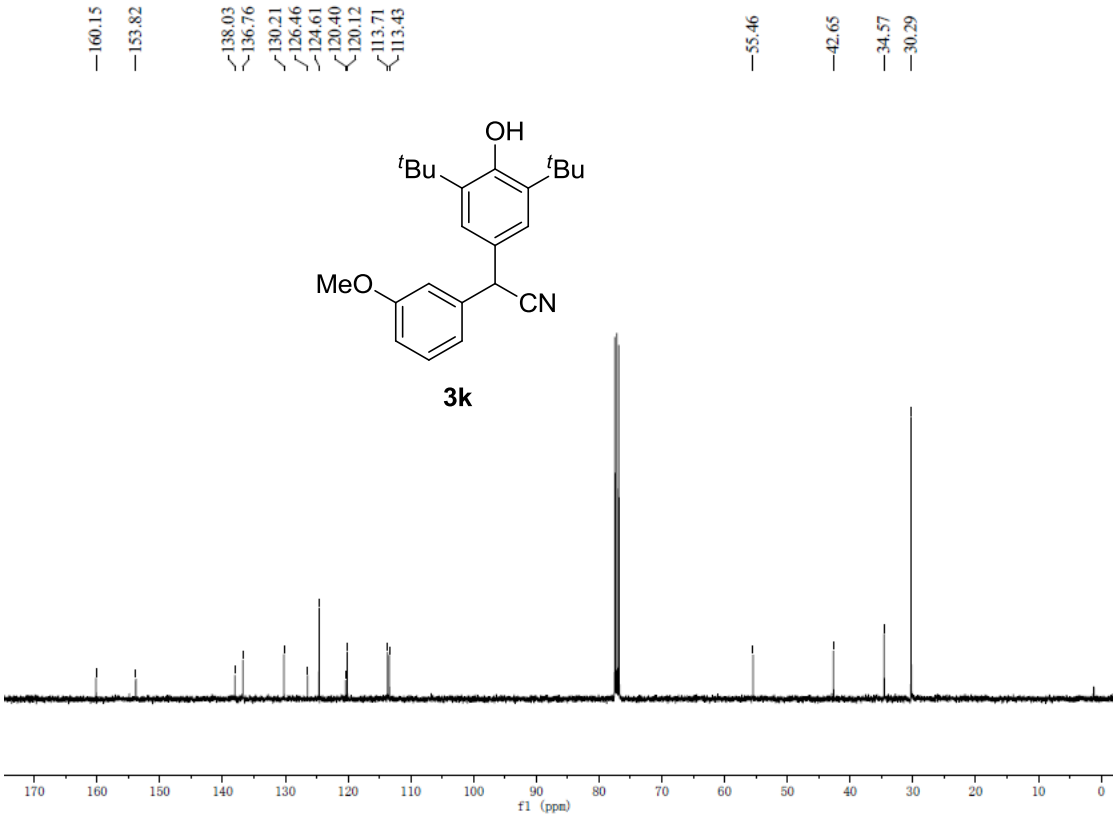

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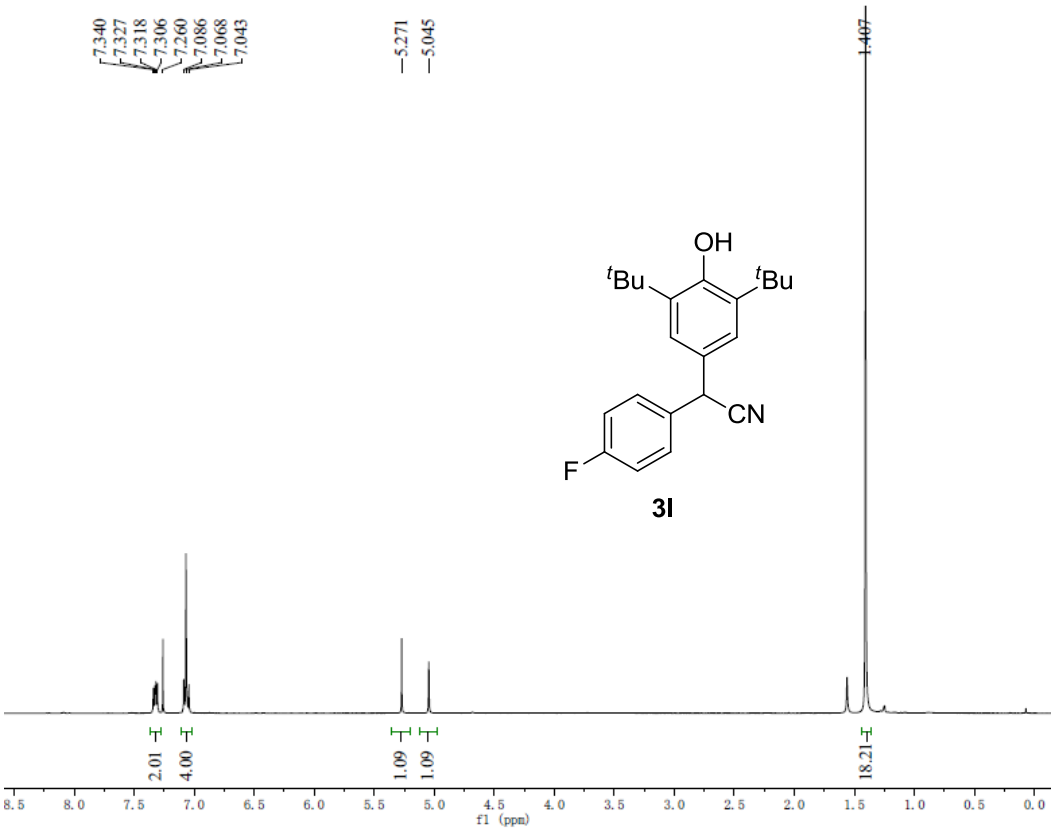

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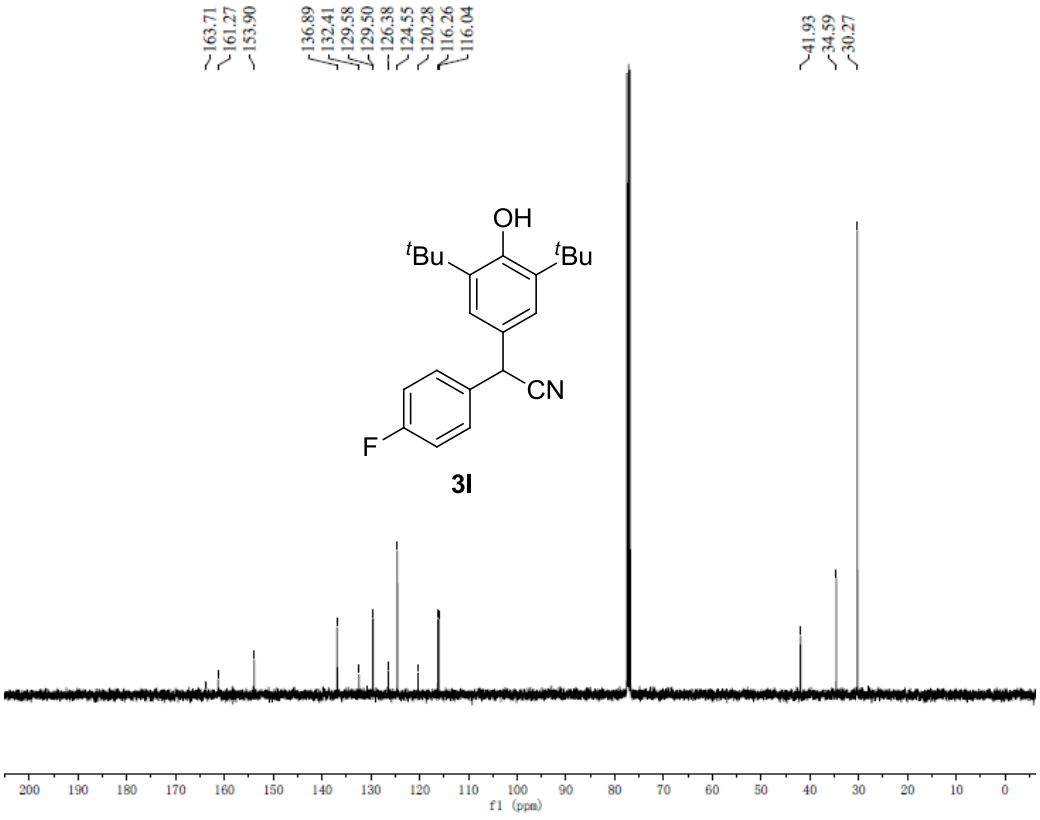

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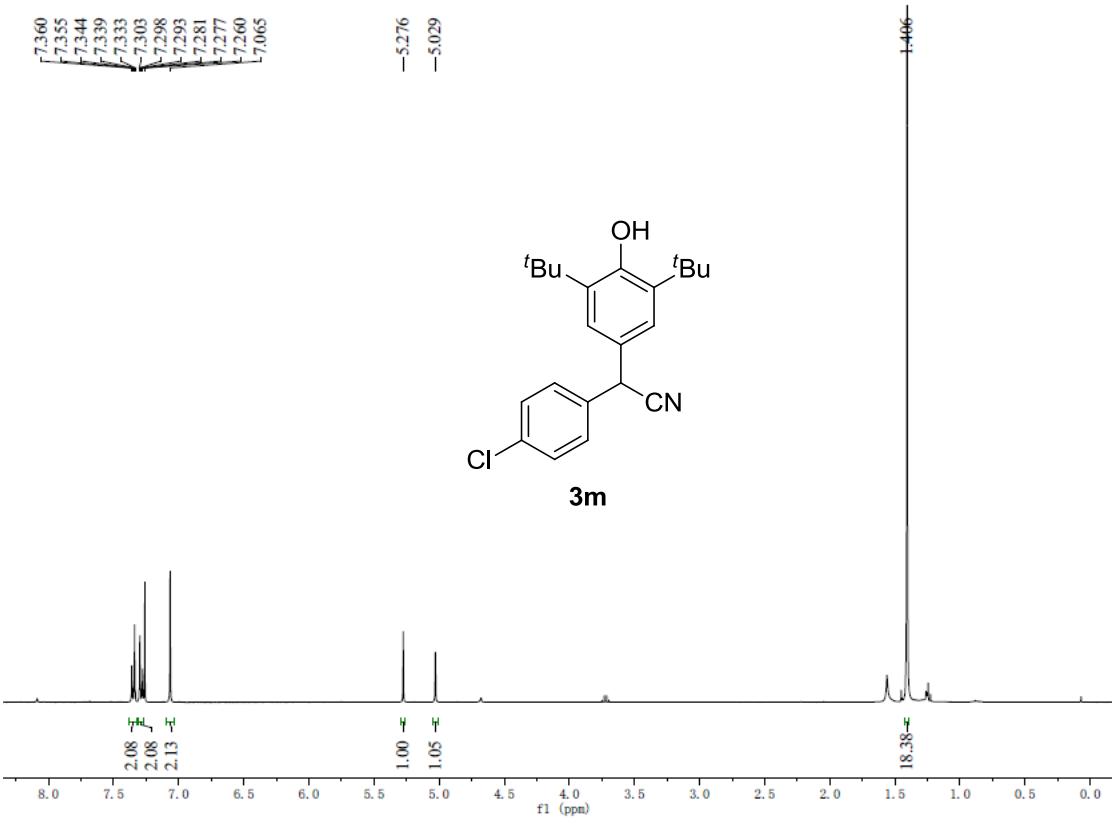

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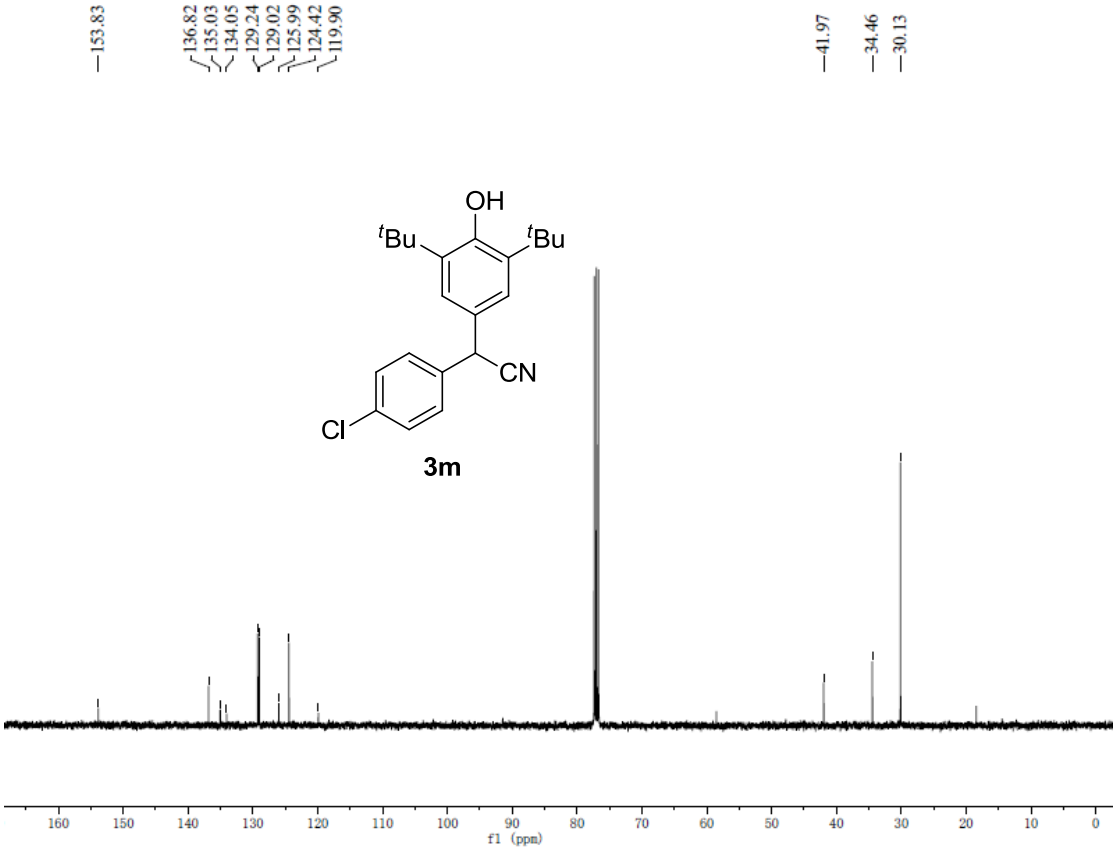

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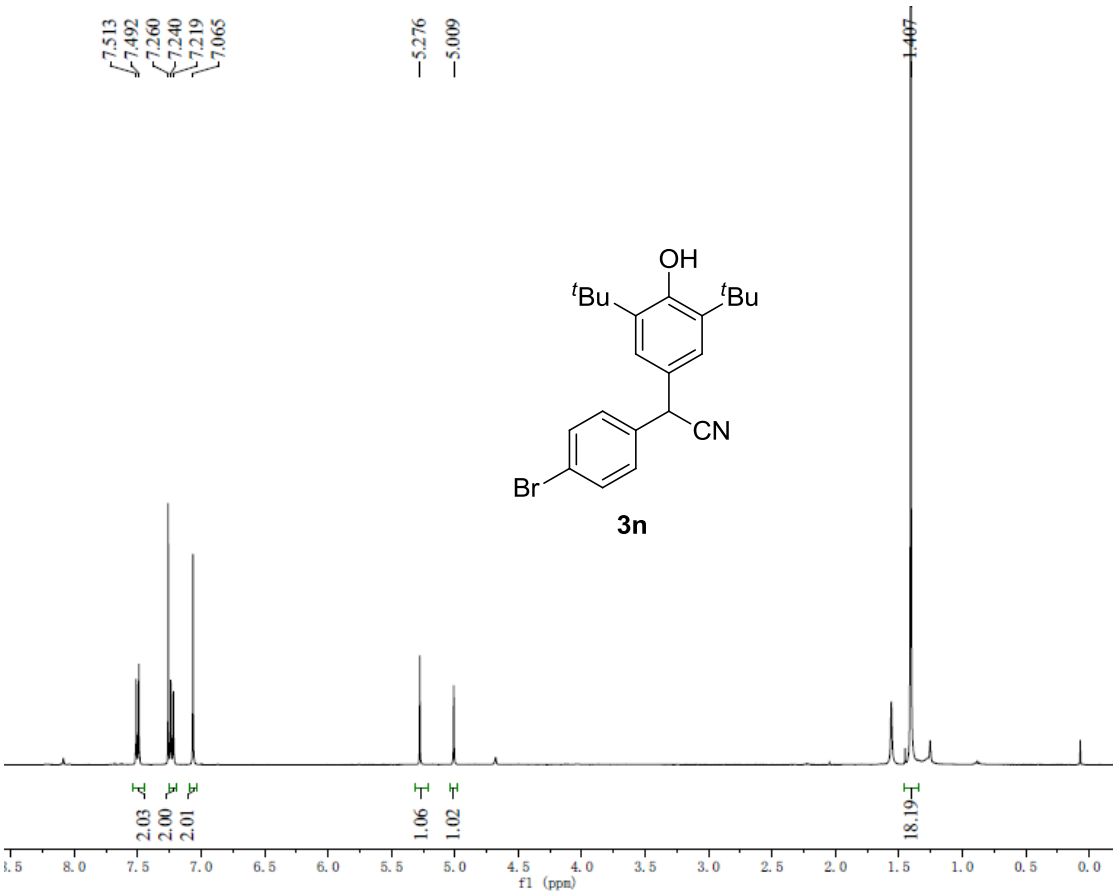

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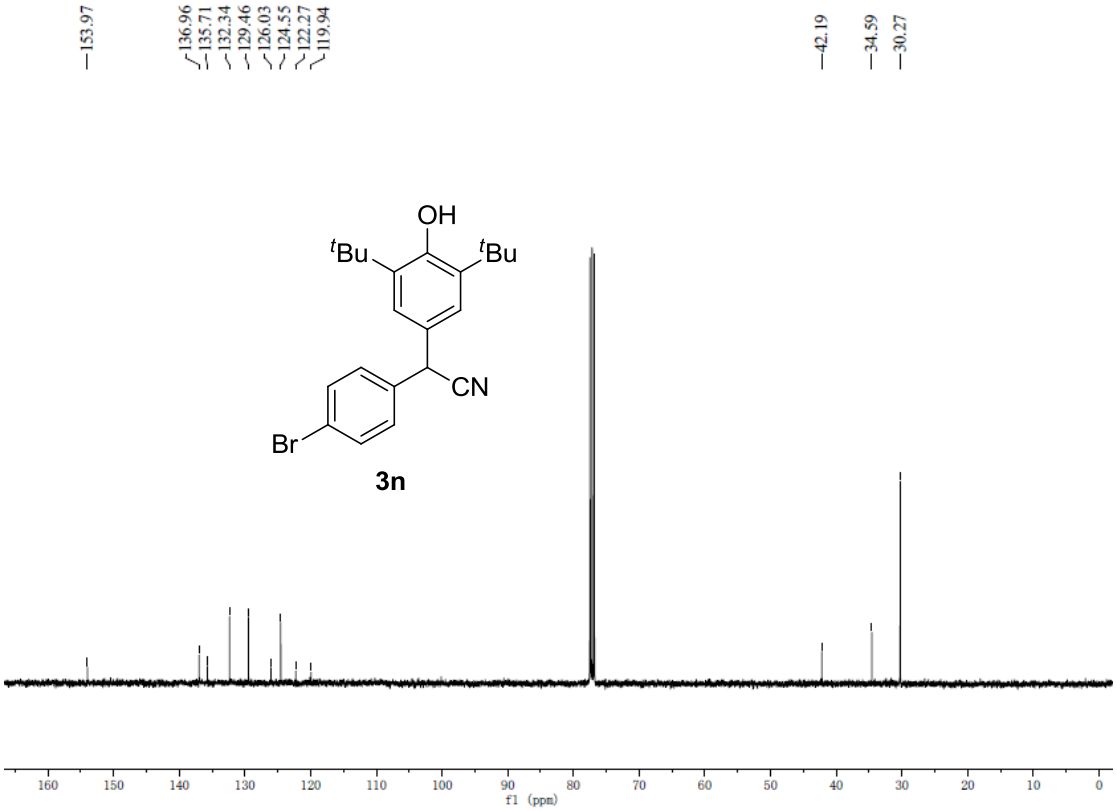

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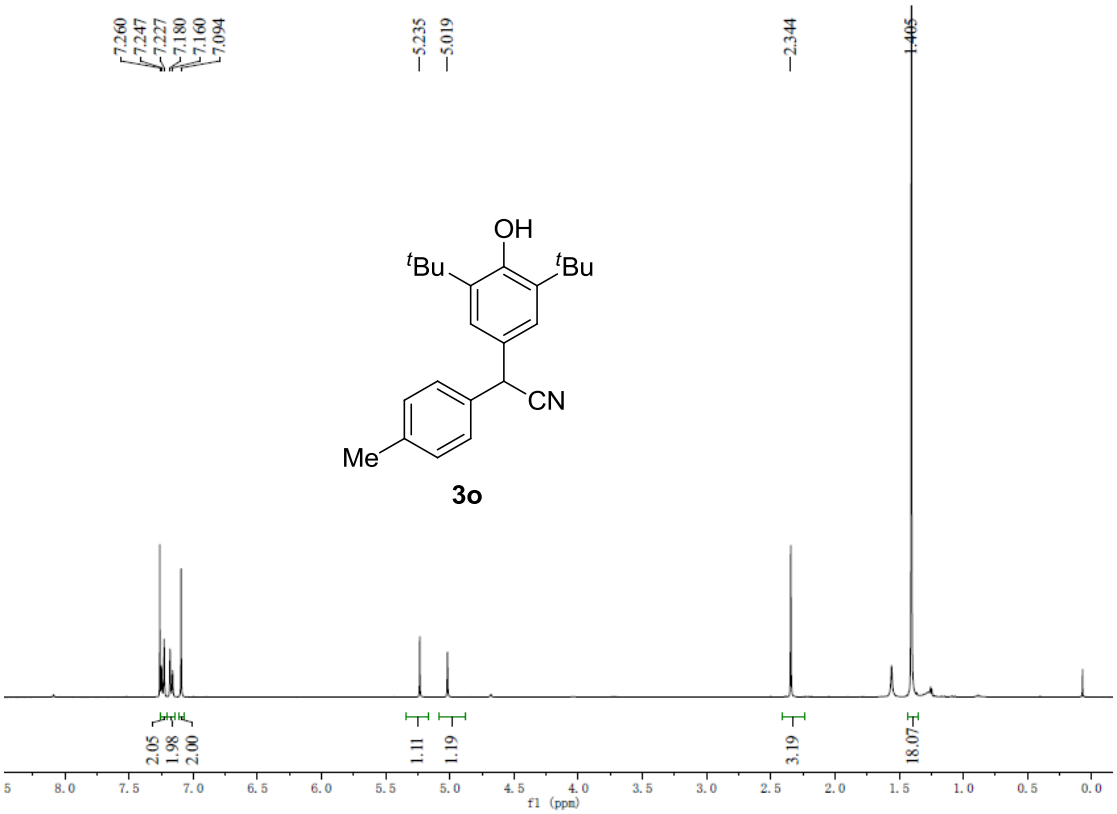
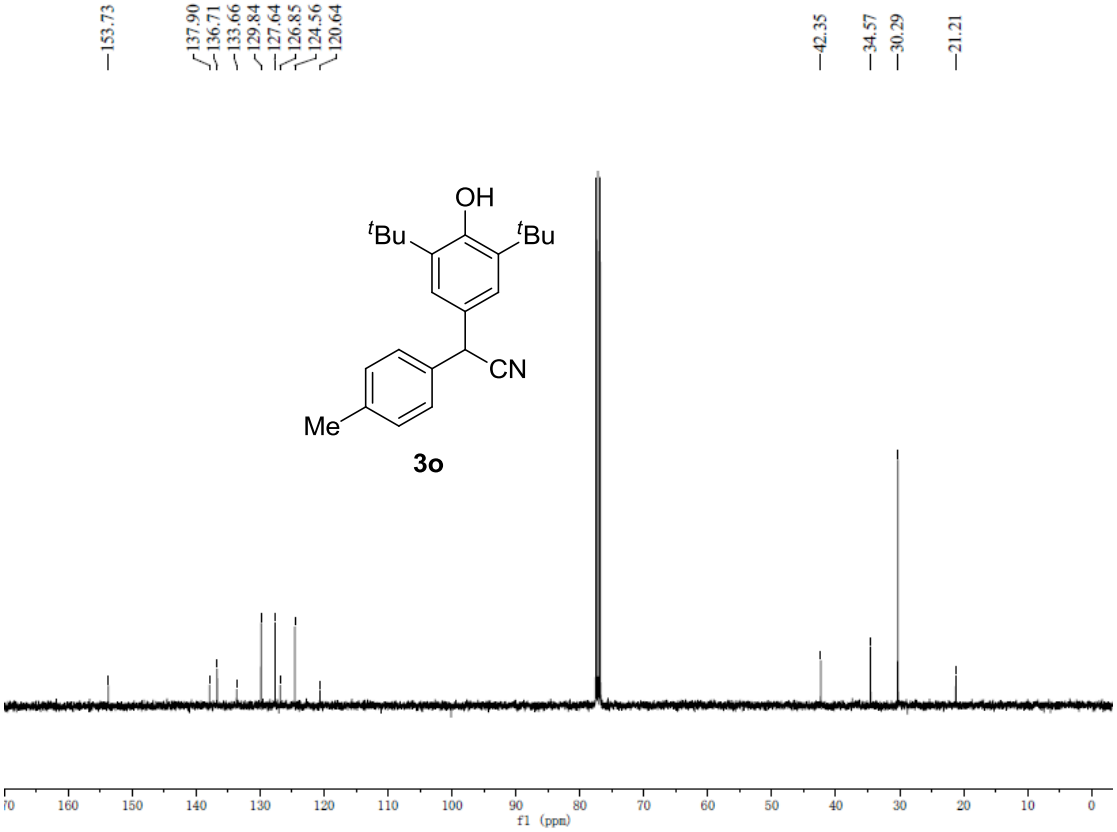


^{1}HNMR of 3o



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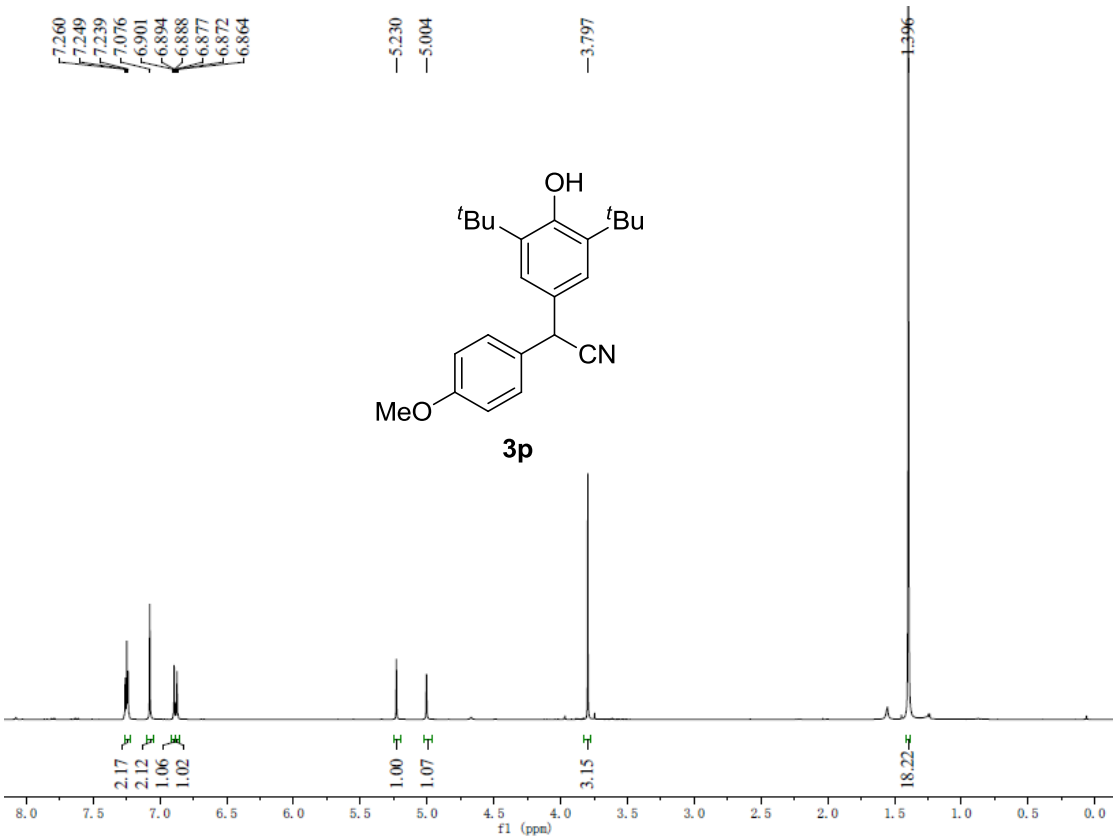
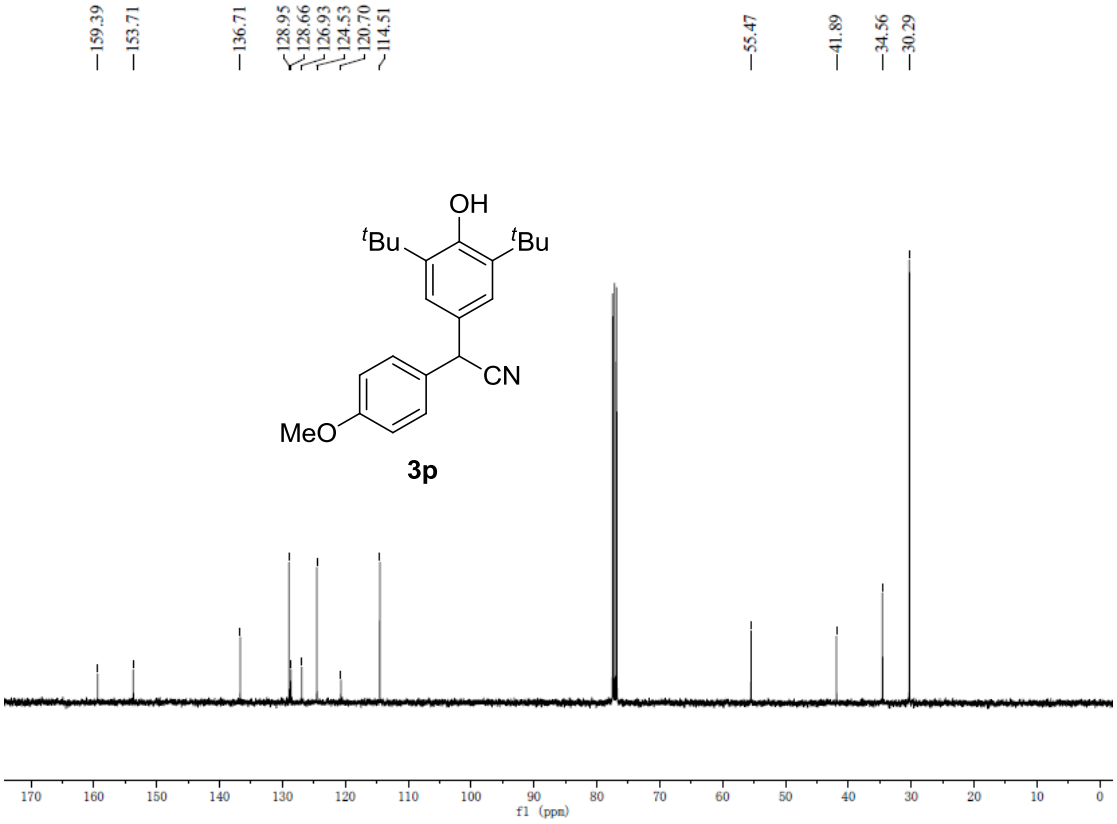
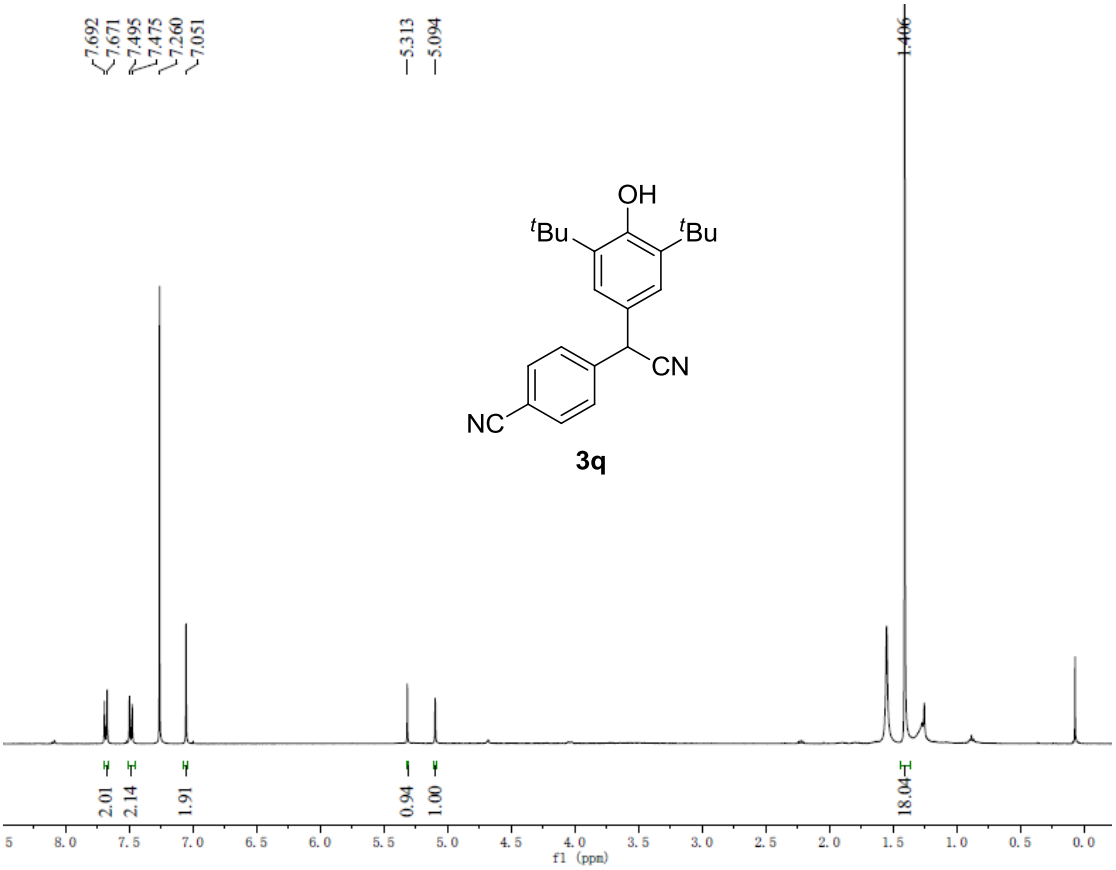


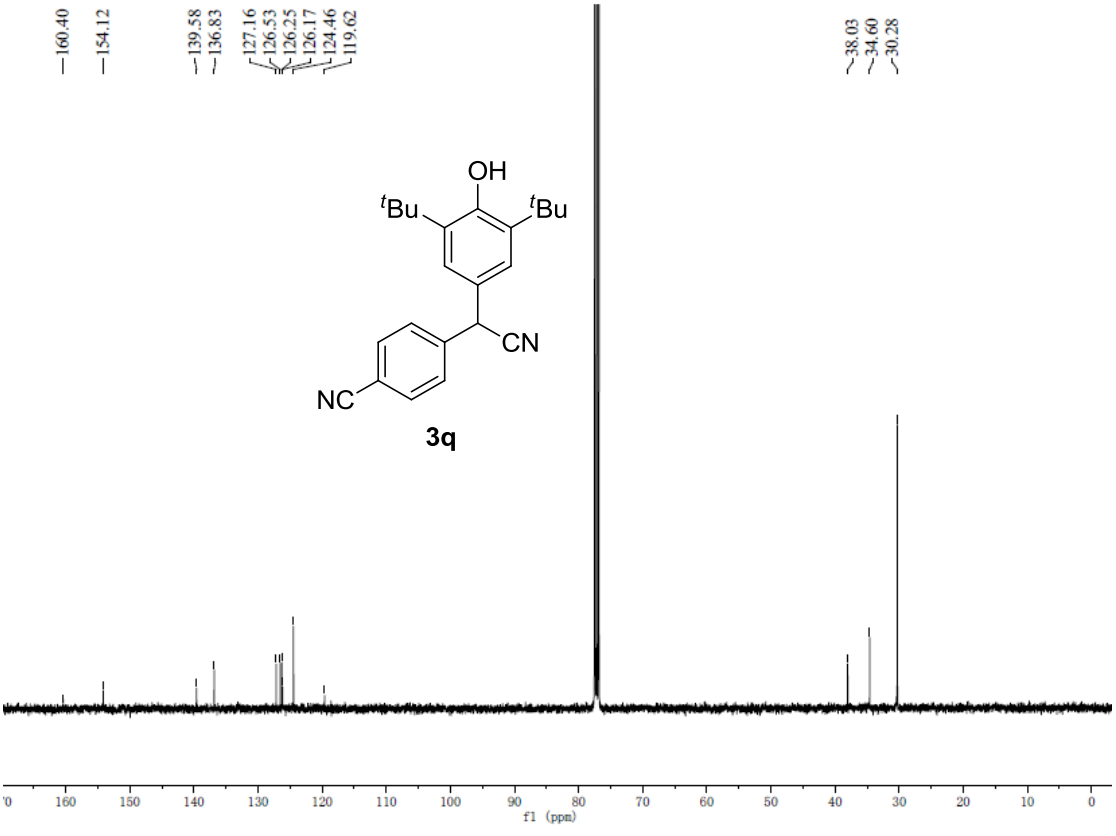
^{1}HNMR of 3p



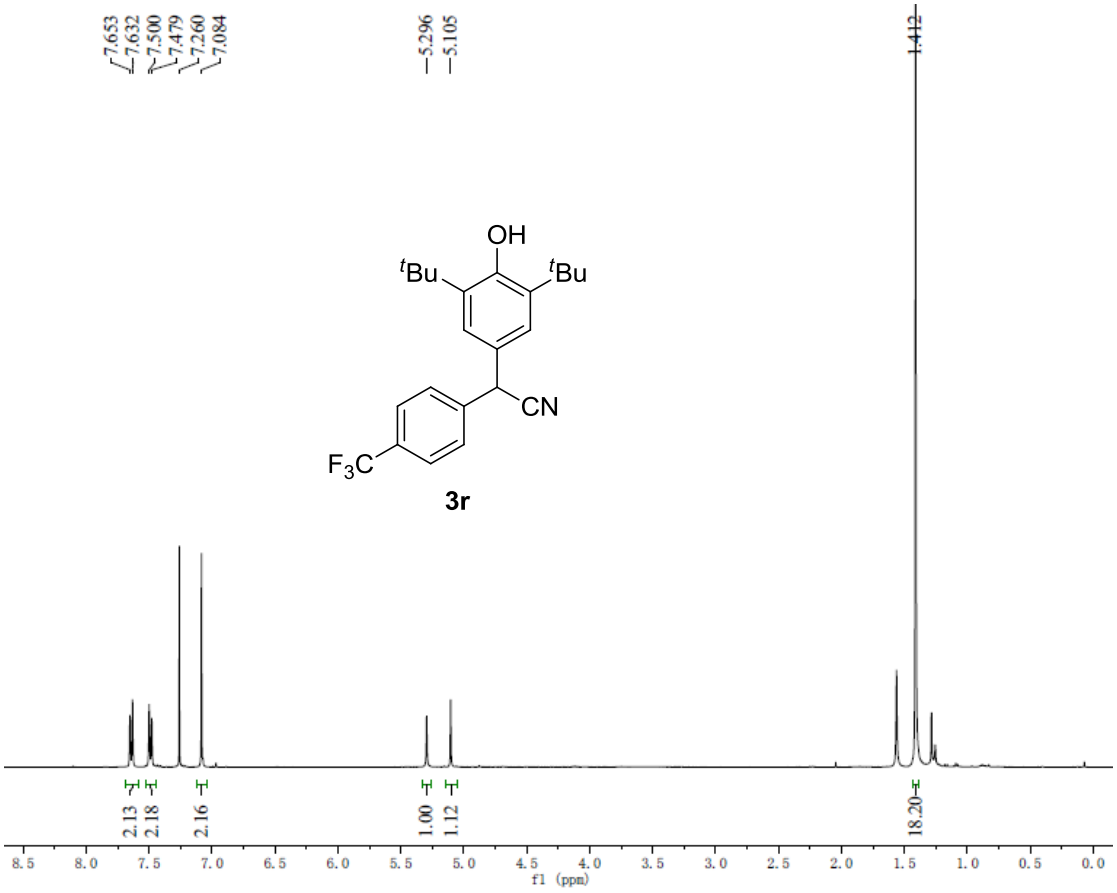
^{13}CNMR of 3p



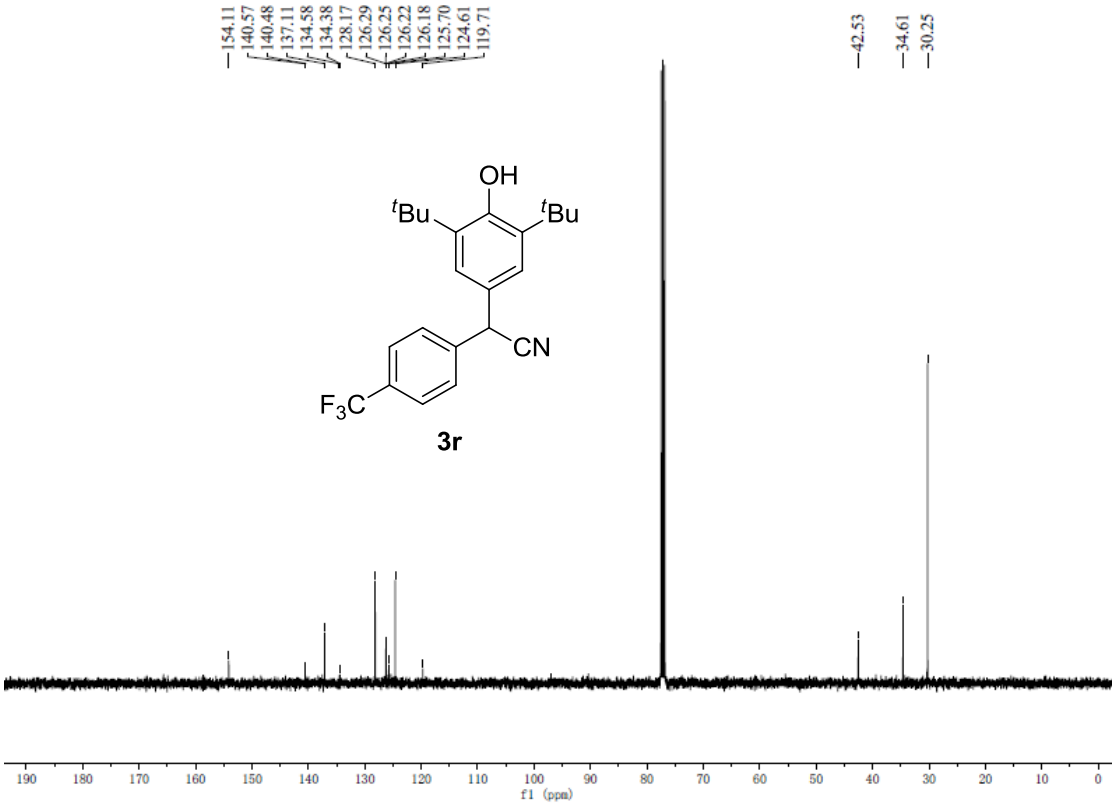
^{1}HNMR of 3q



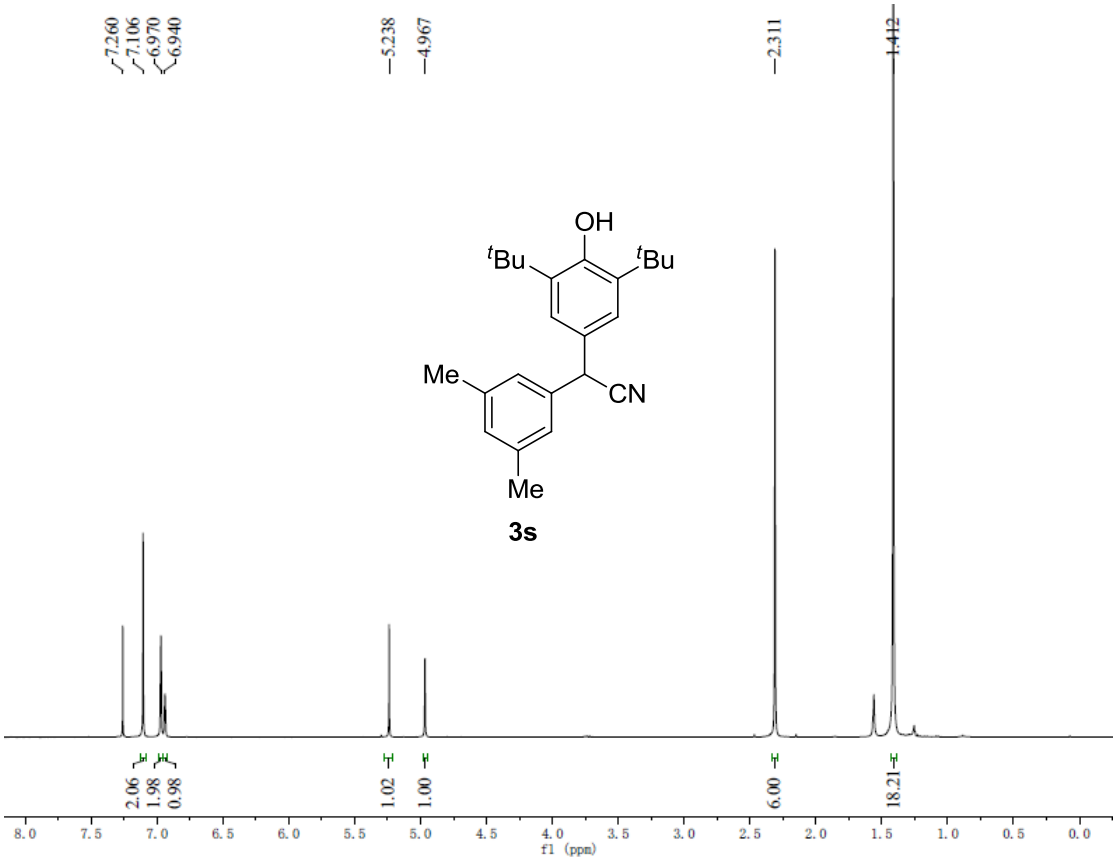
^{13}CNMR of 3q



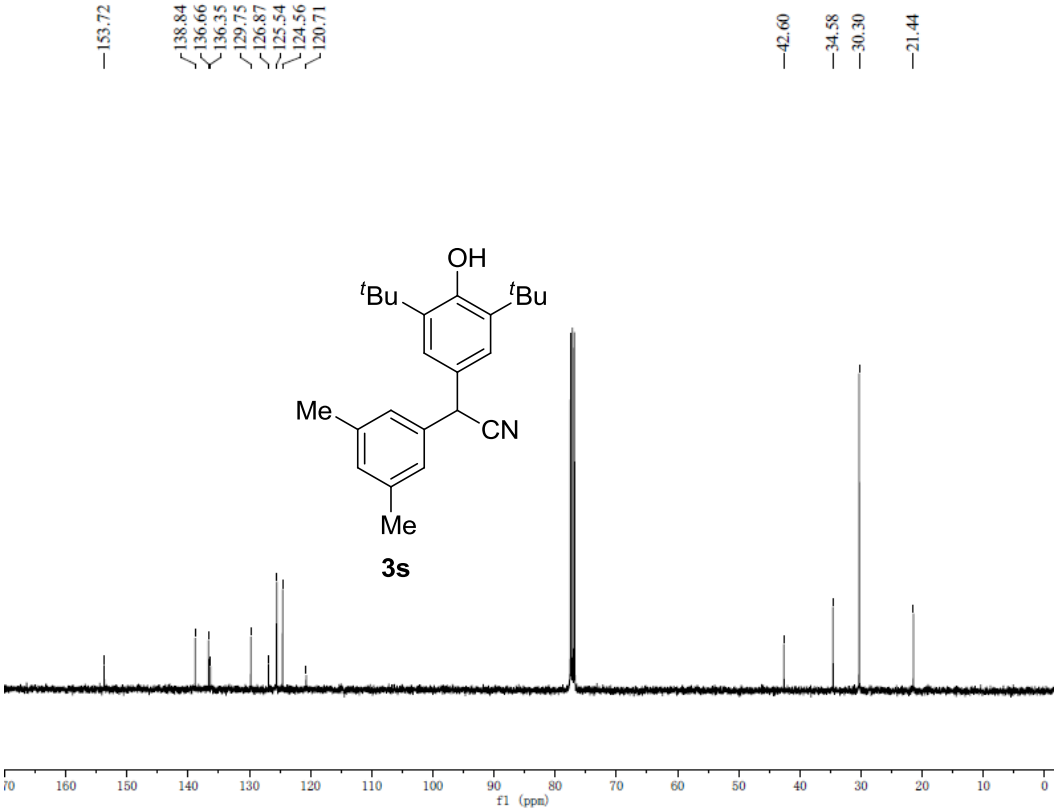
^{1}HNMR of 3r



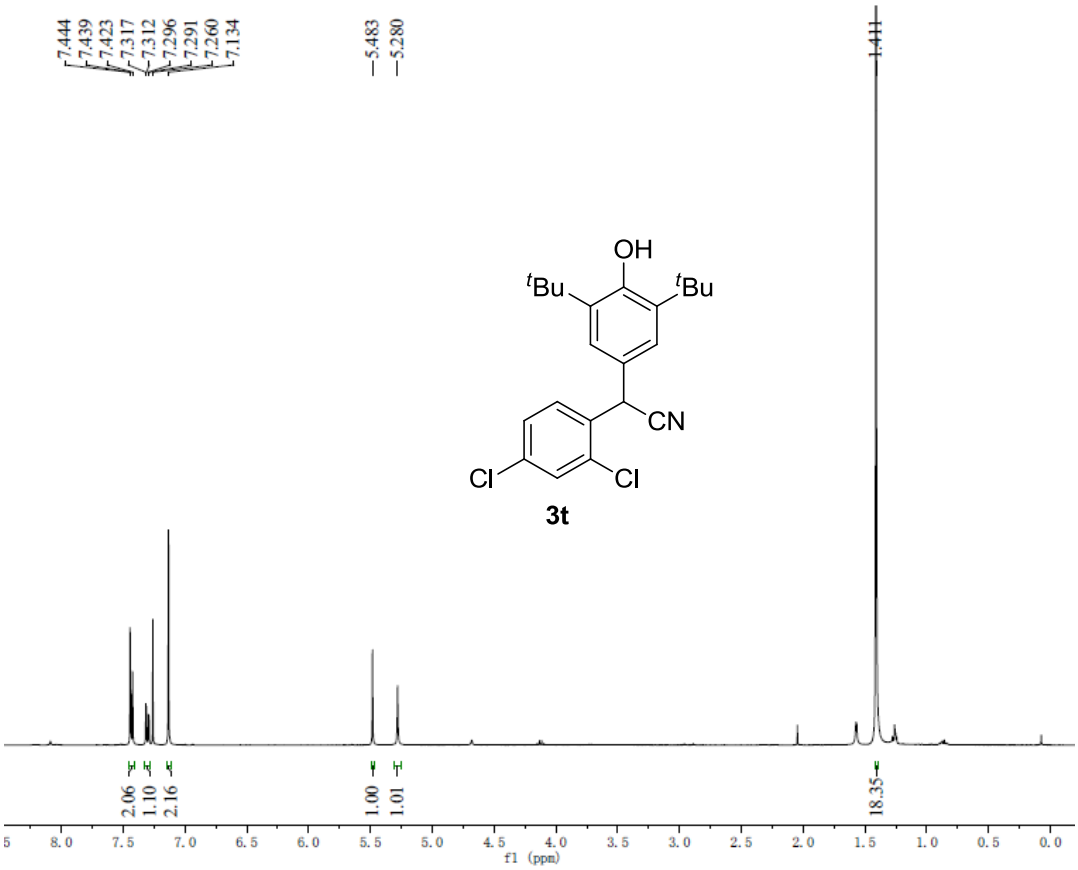
^{13}CNMR of 3r



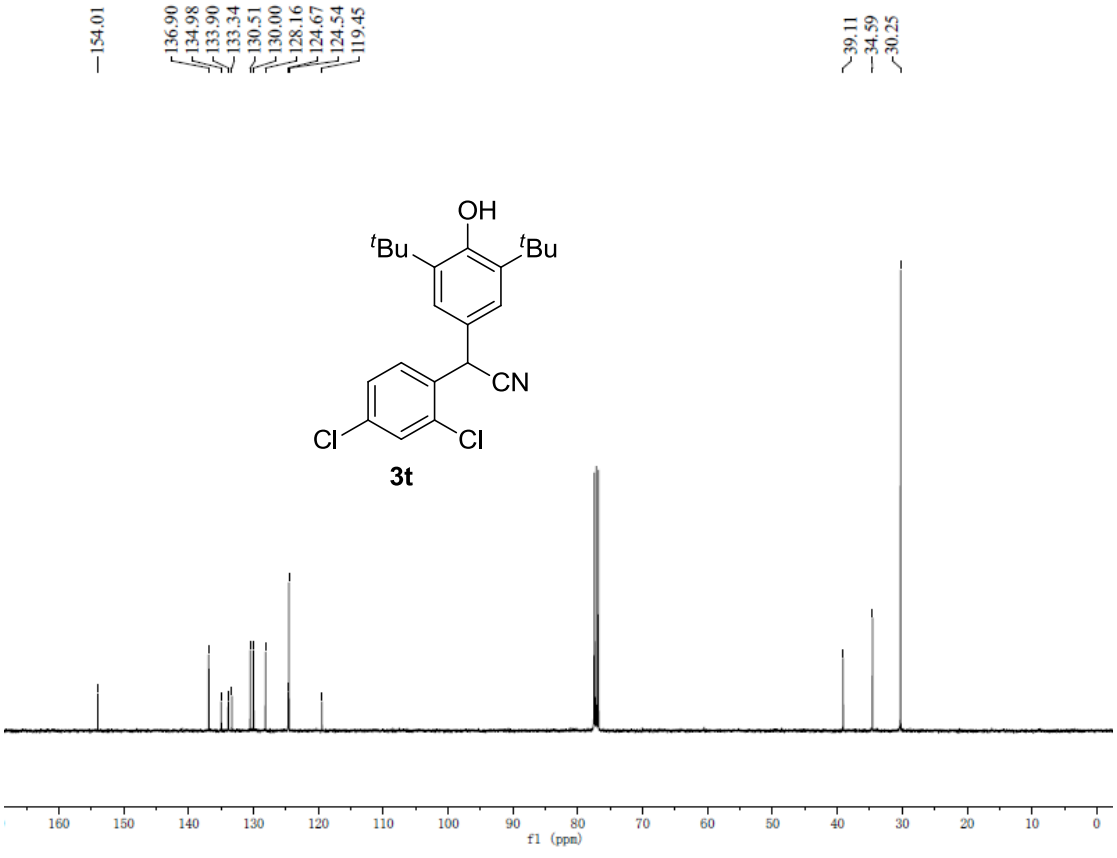
^{1}HNMR of 3s



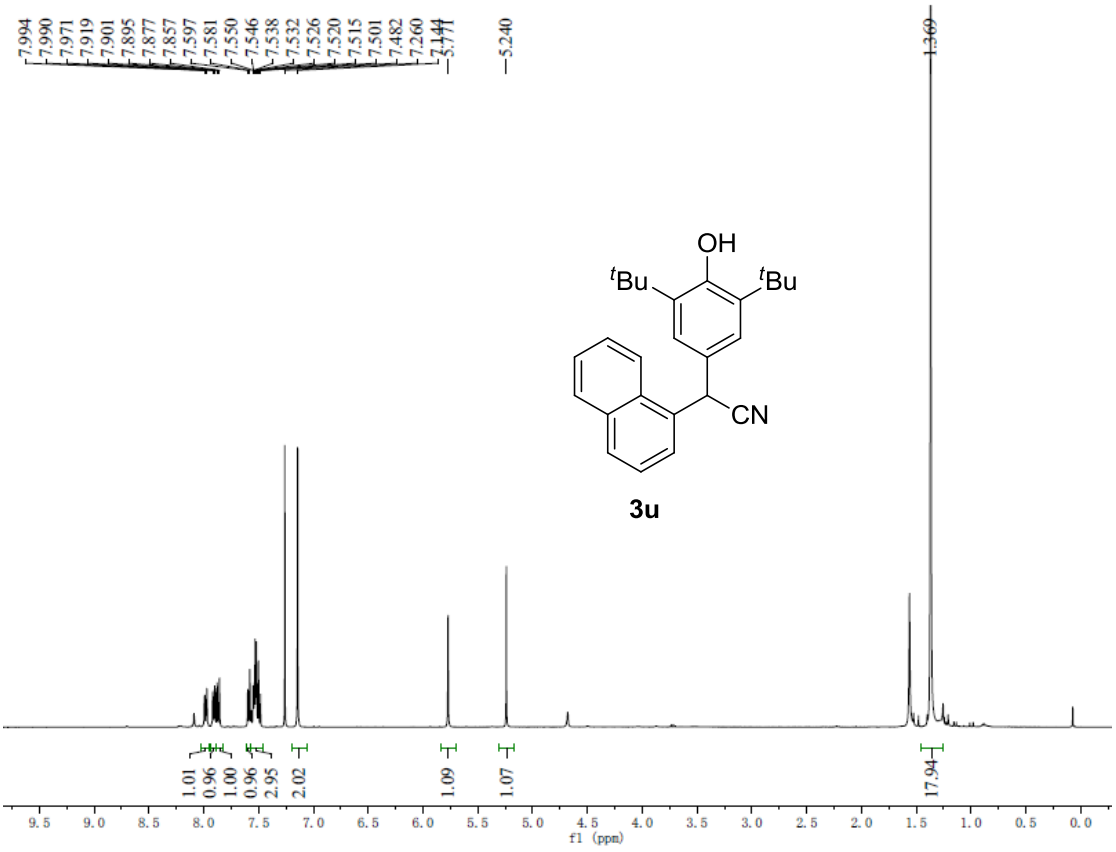
^{13}CNMR of 3s



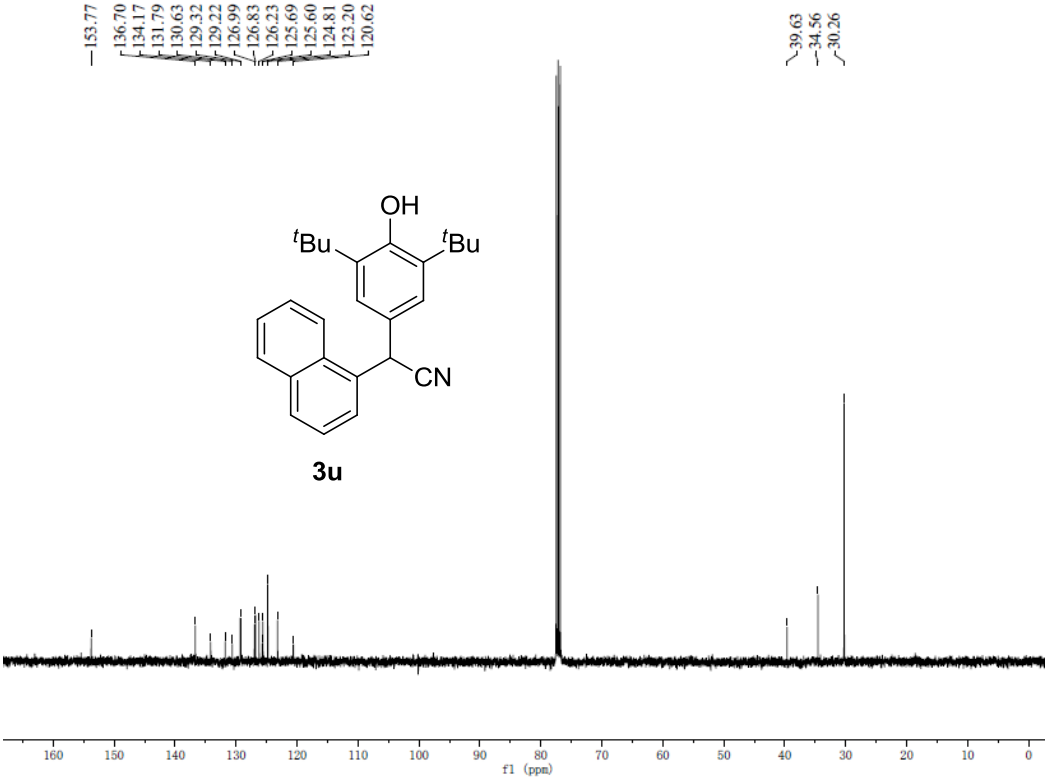
^{1}HNMR of 3t



^{13}CNMR of 3t



^{1}HNMR of 3u



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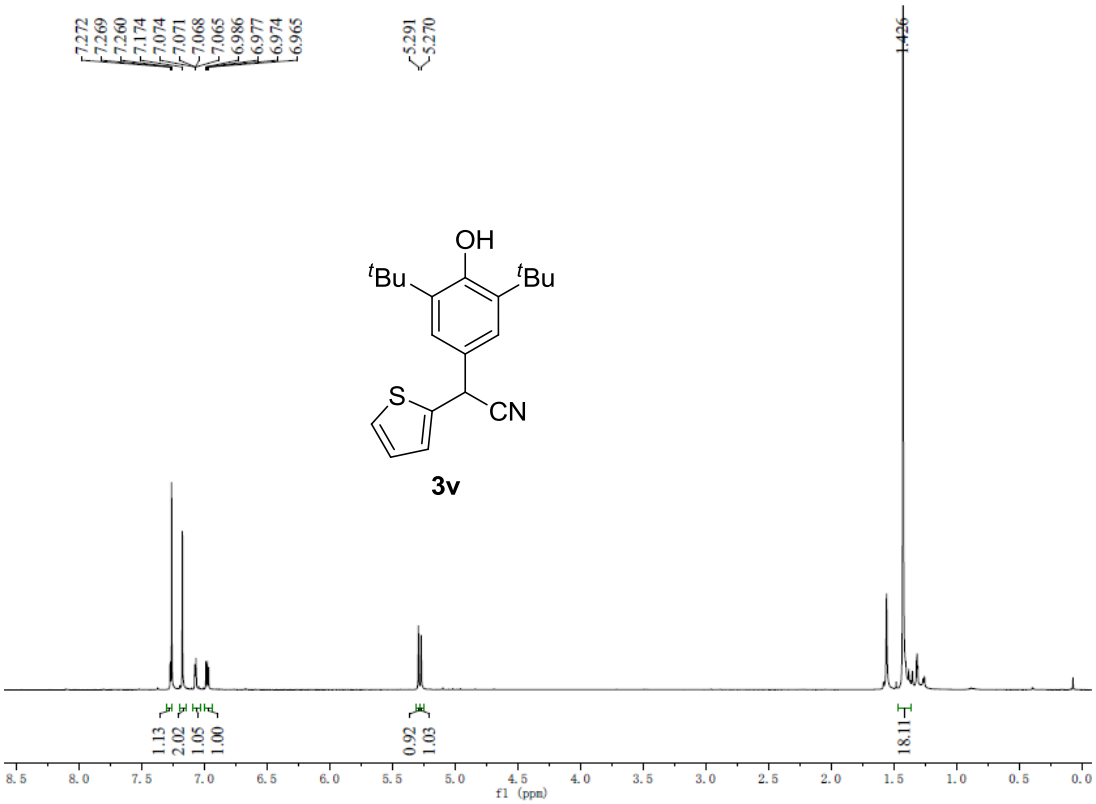
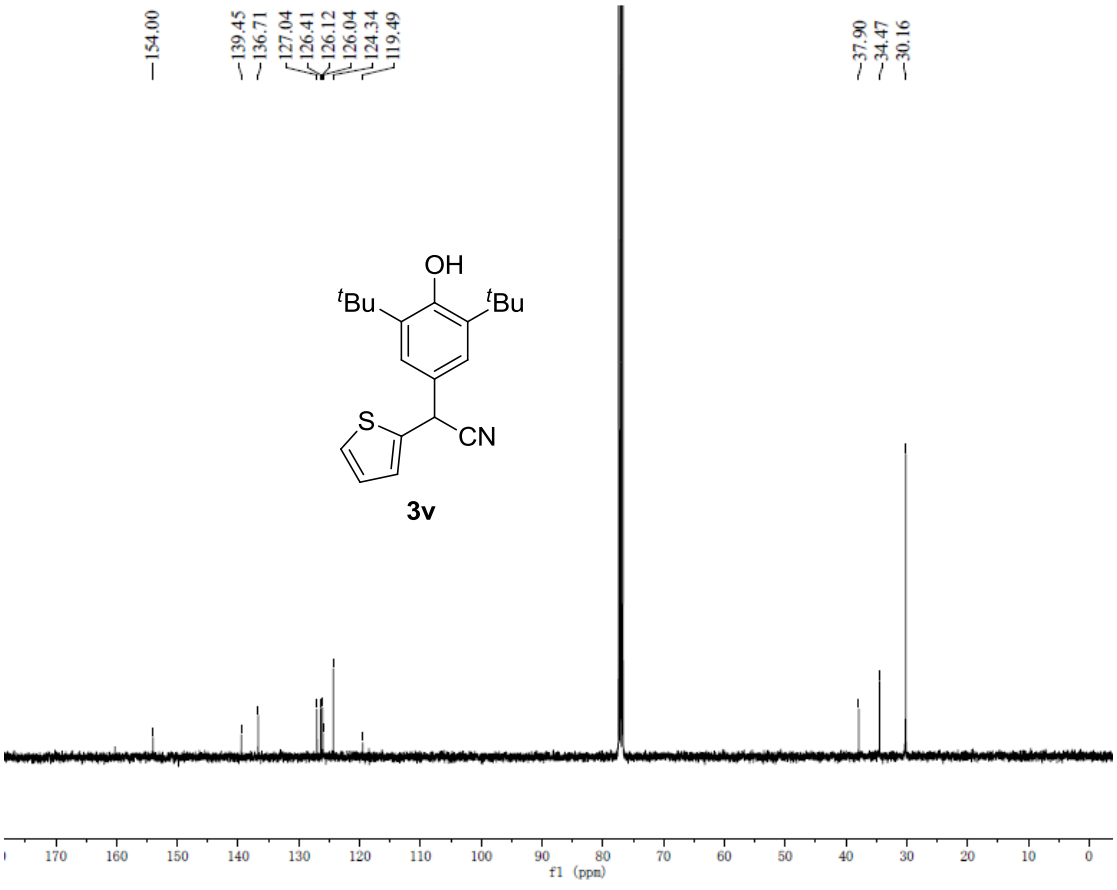
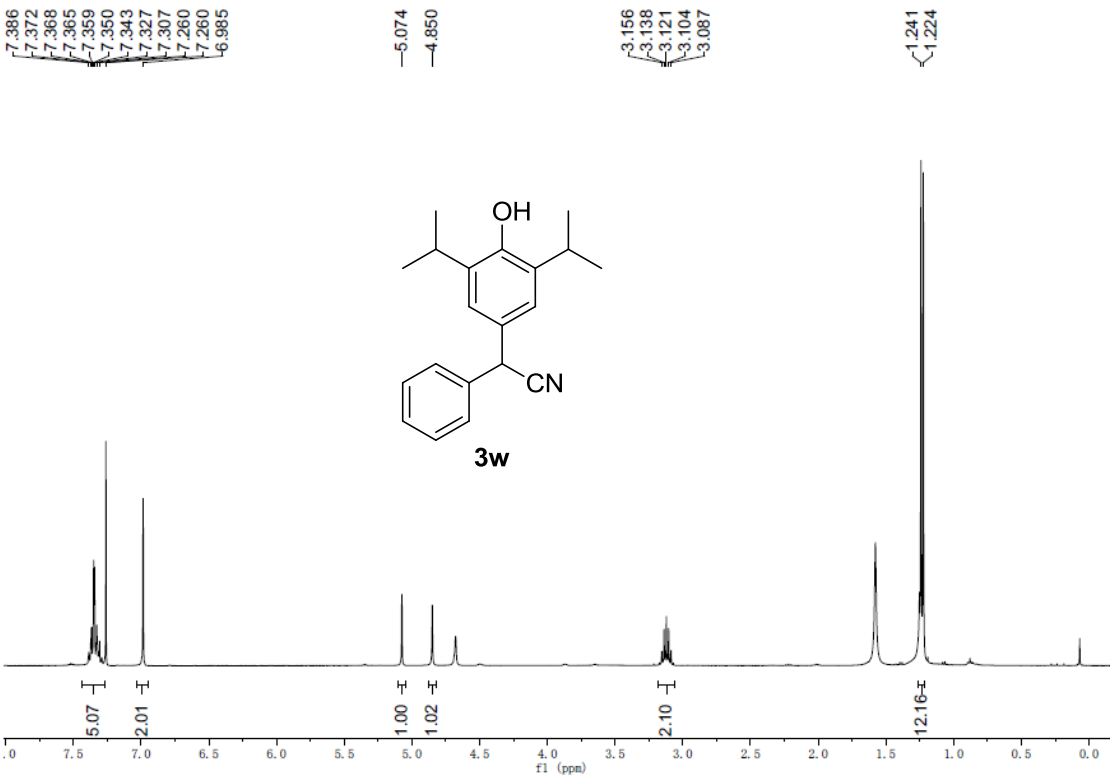


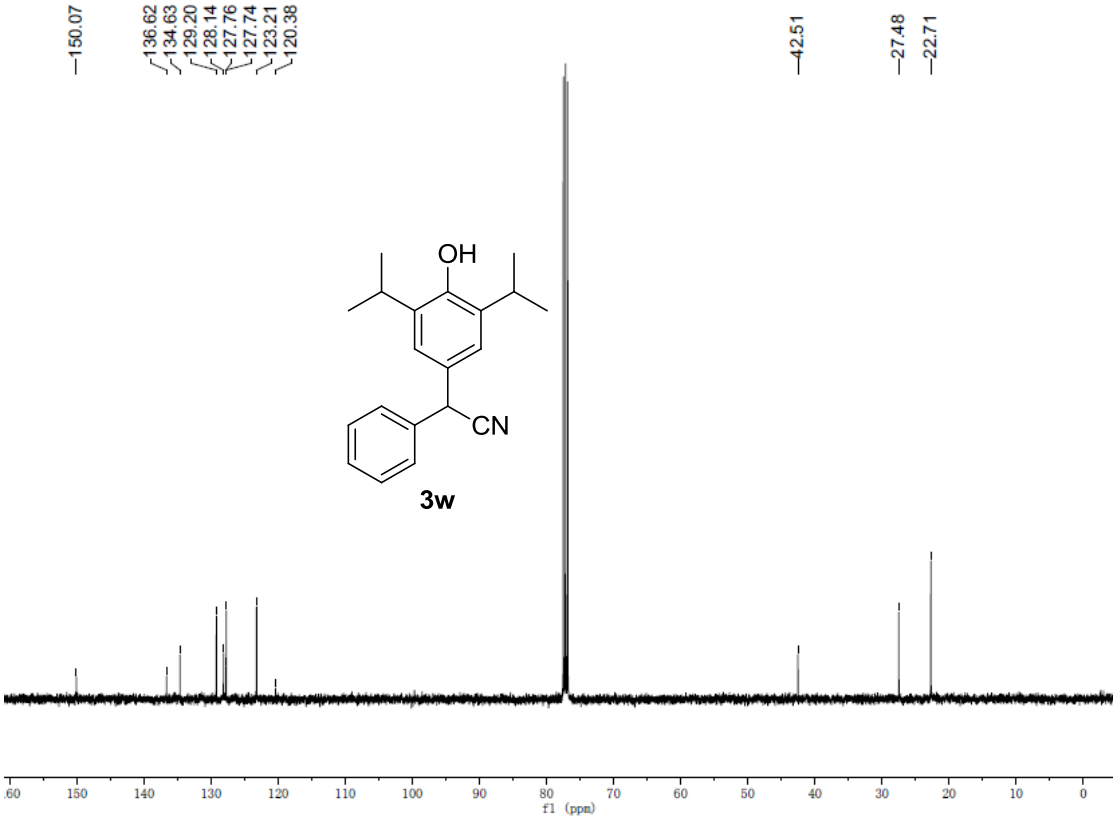
^{1}HNMR of 3v



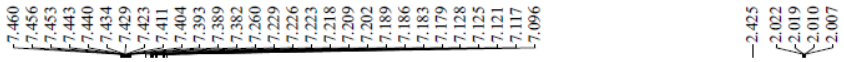
^{13}CNMR of 3v

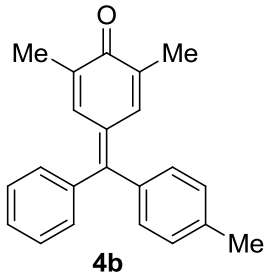


^{1}HNMR of 3w

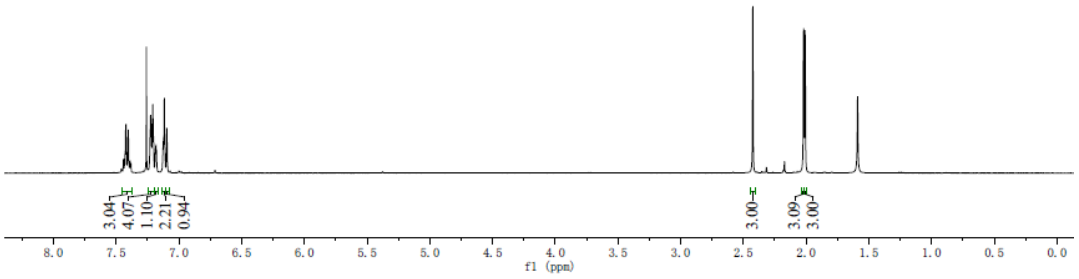


^{13}CNMR of 3w

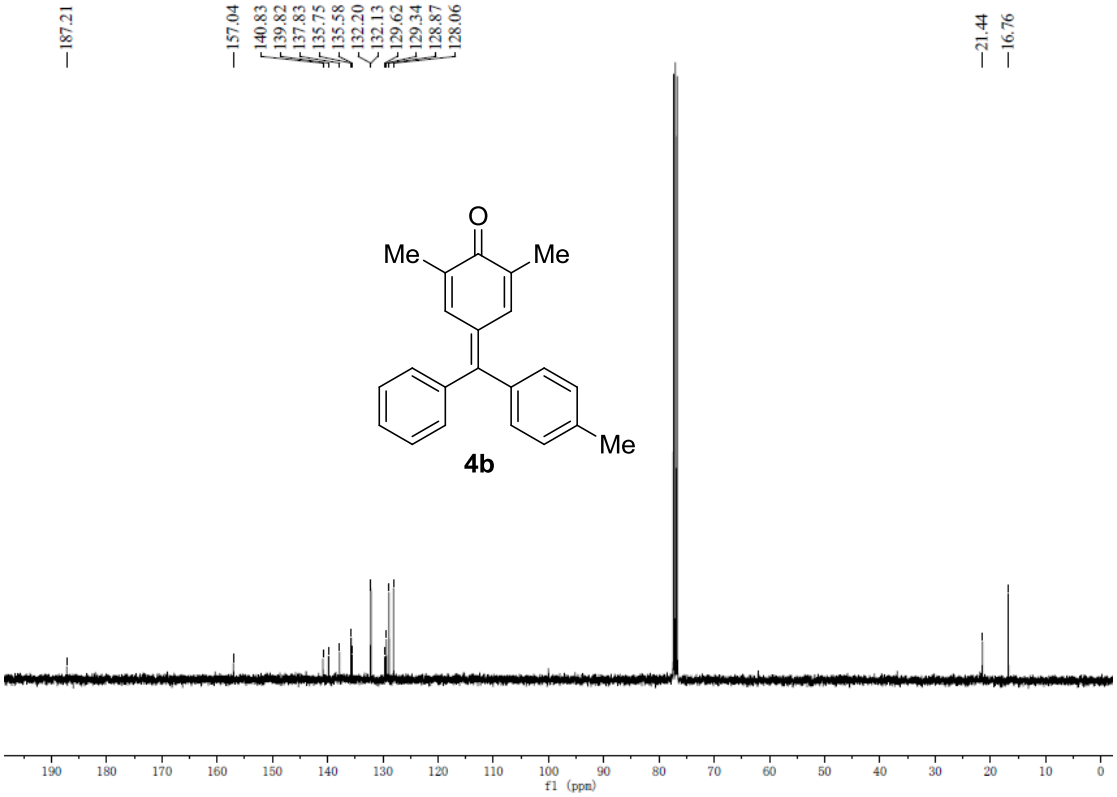




4b

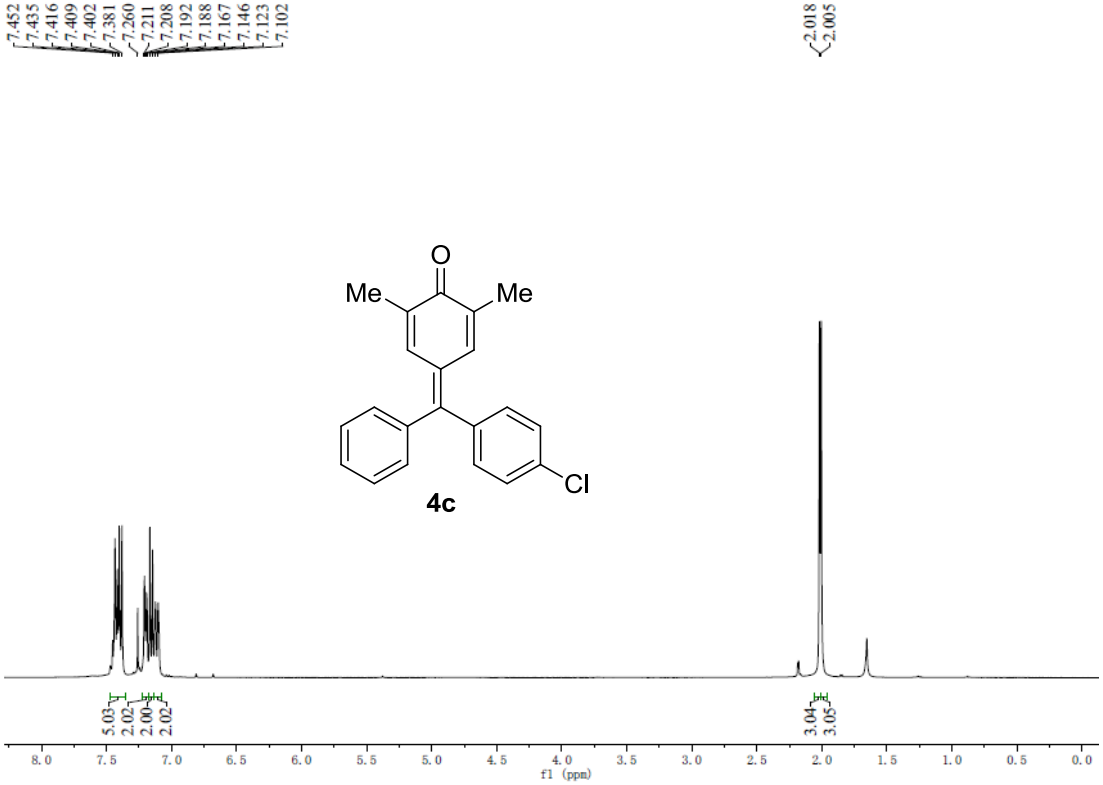


^{1}HNMR of 4b

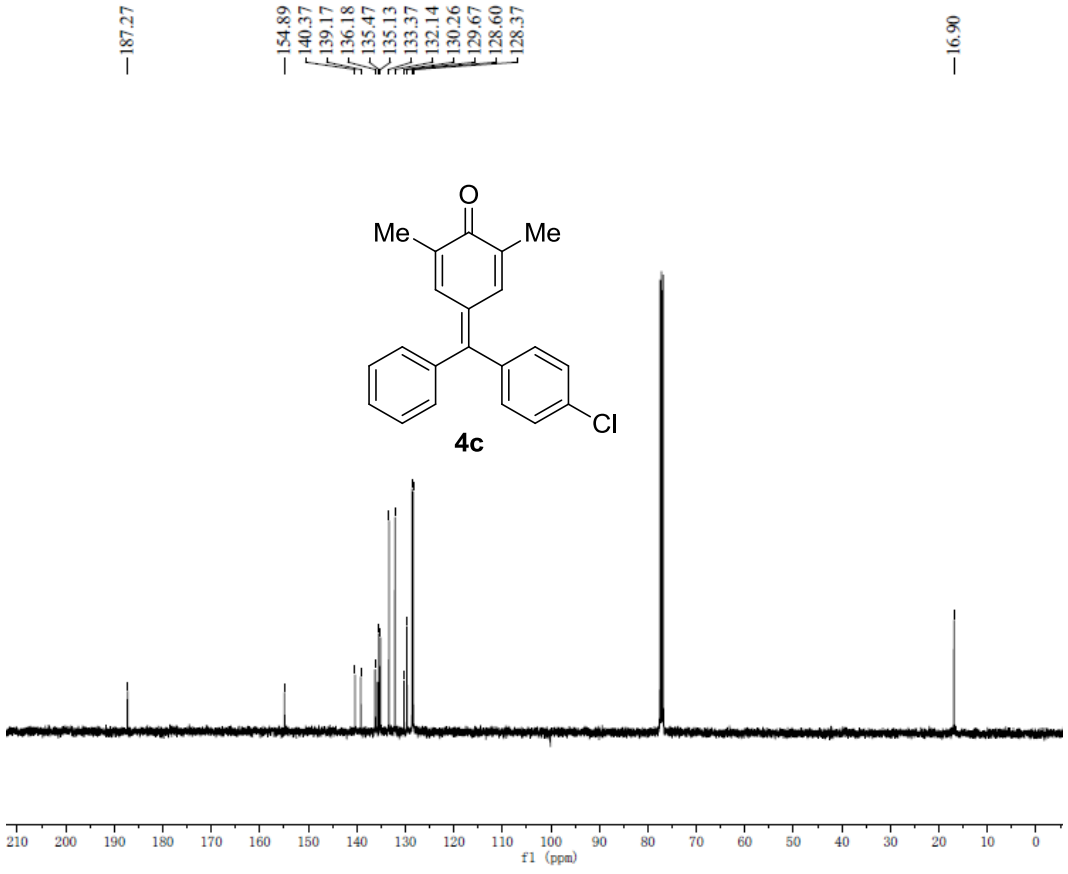


4b

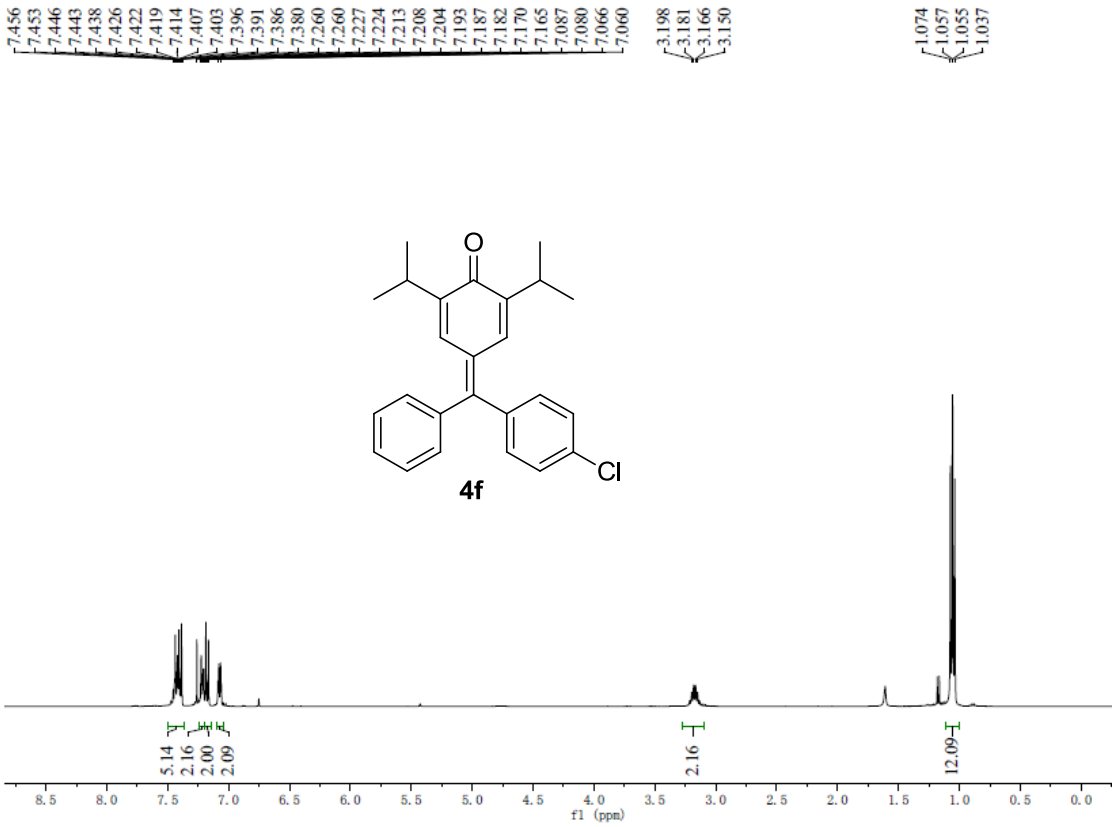
^{13}CNMR of 4b



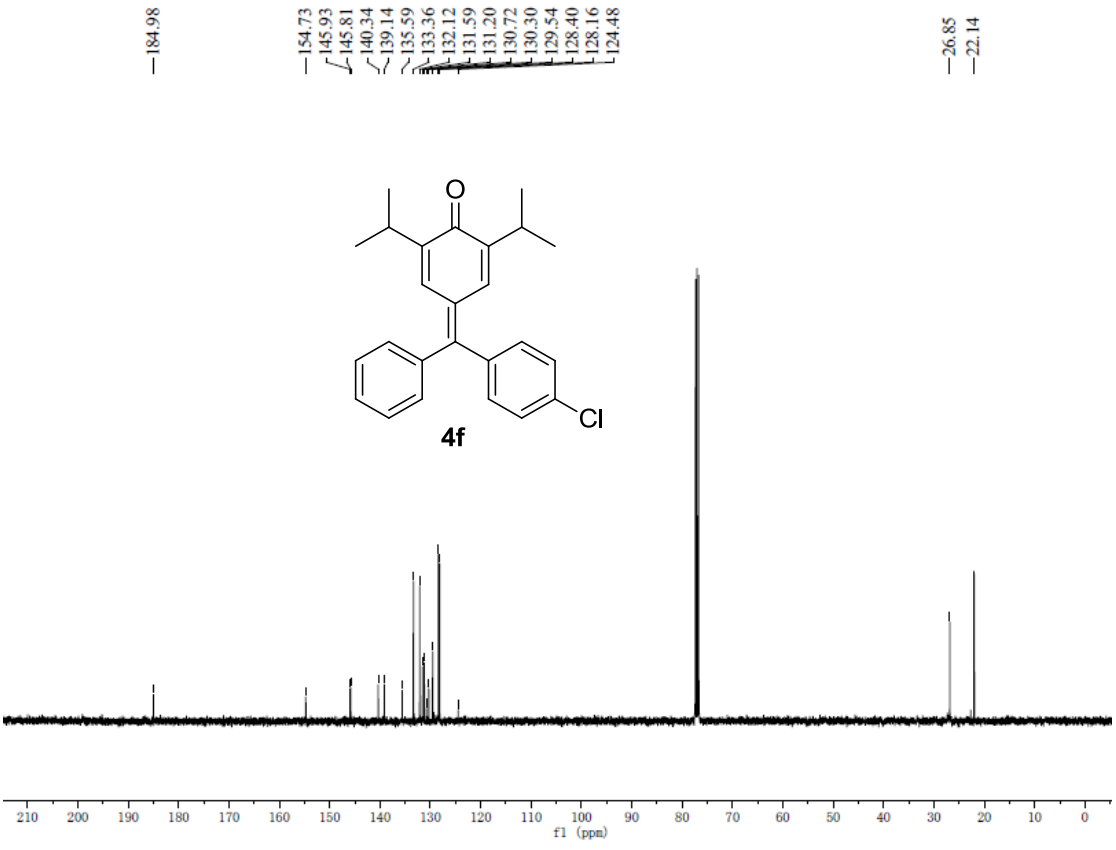
^{1}HNMR of 4c



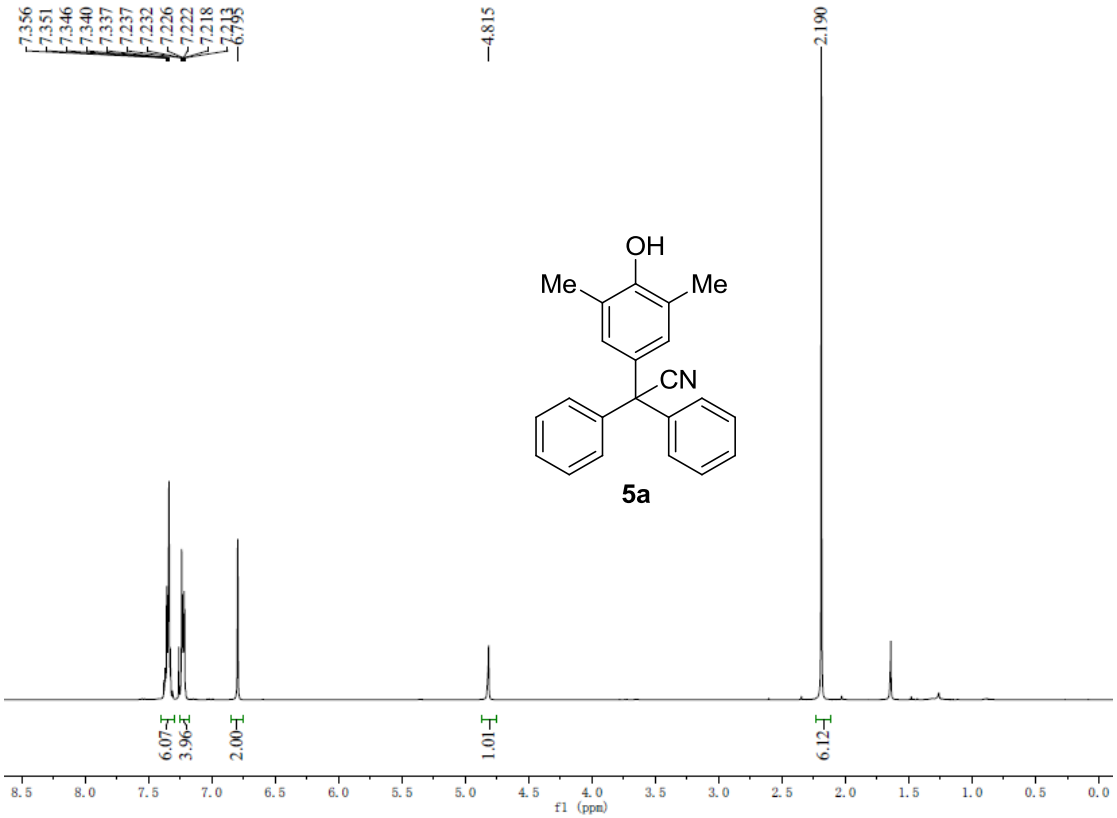
^{13}CNMR of 4c



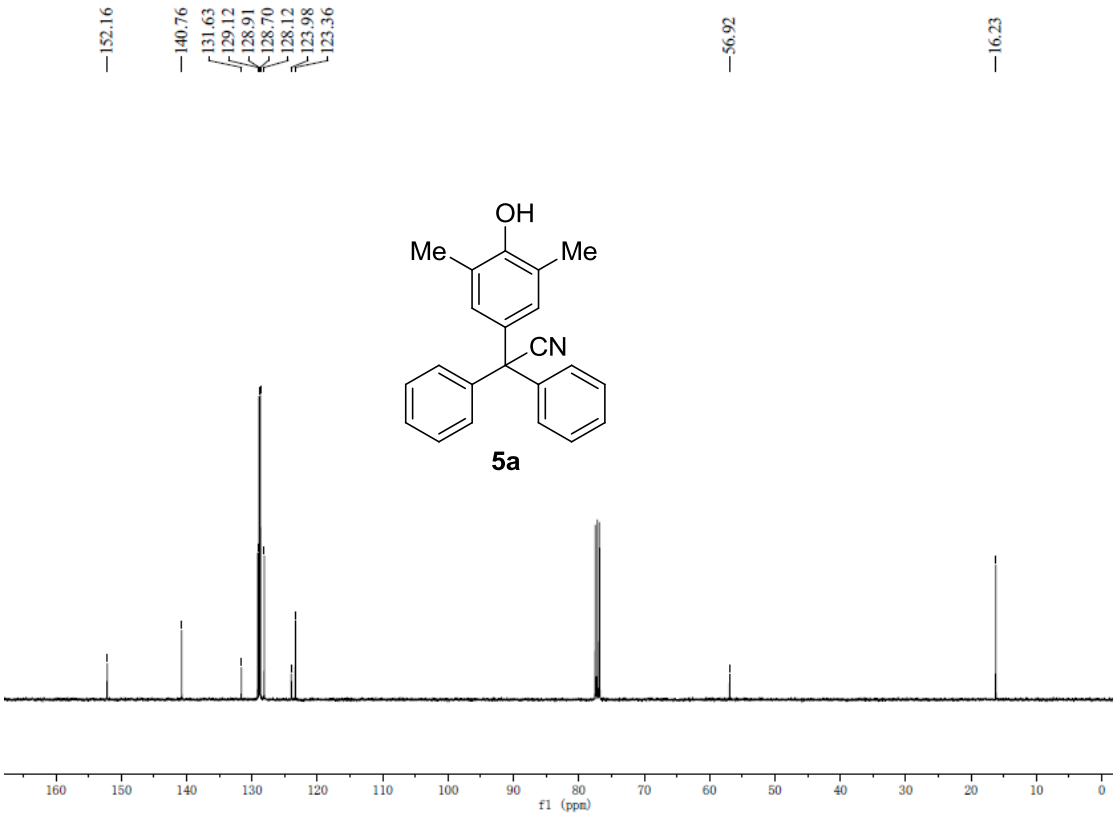
^{1}HNMR of 4f



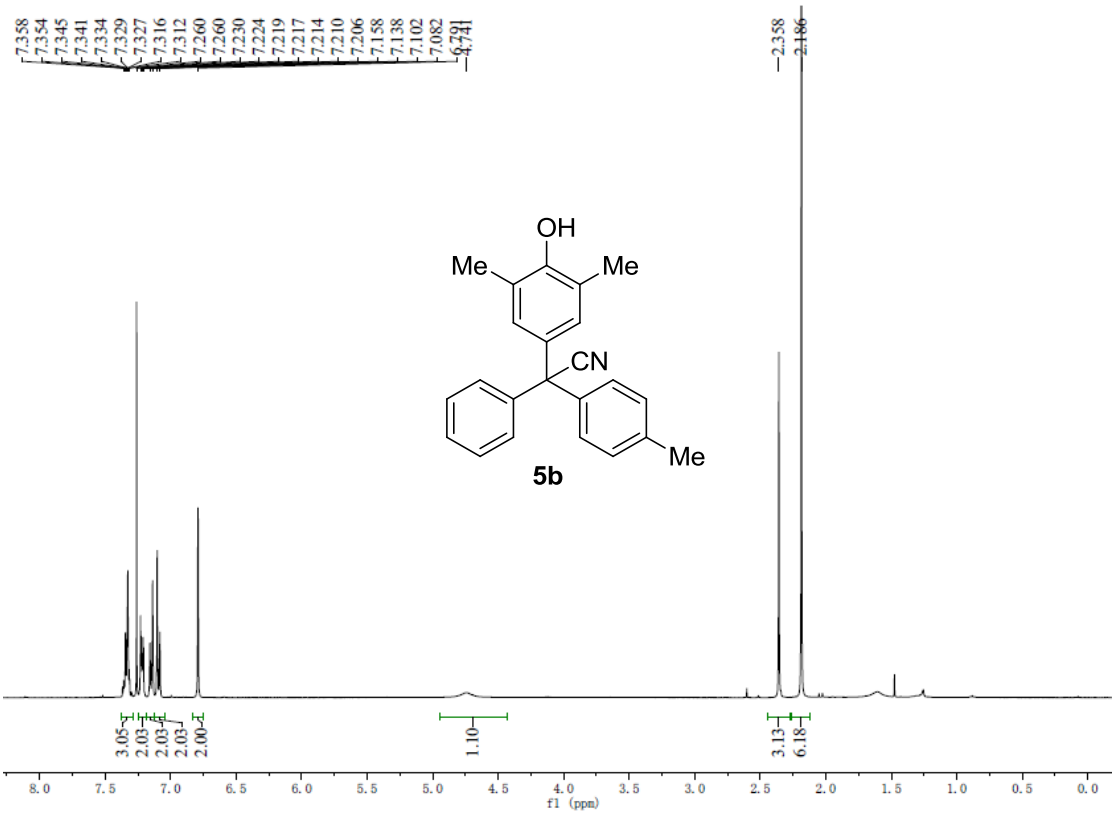
^{13}CNMR of 4f



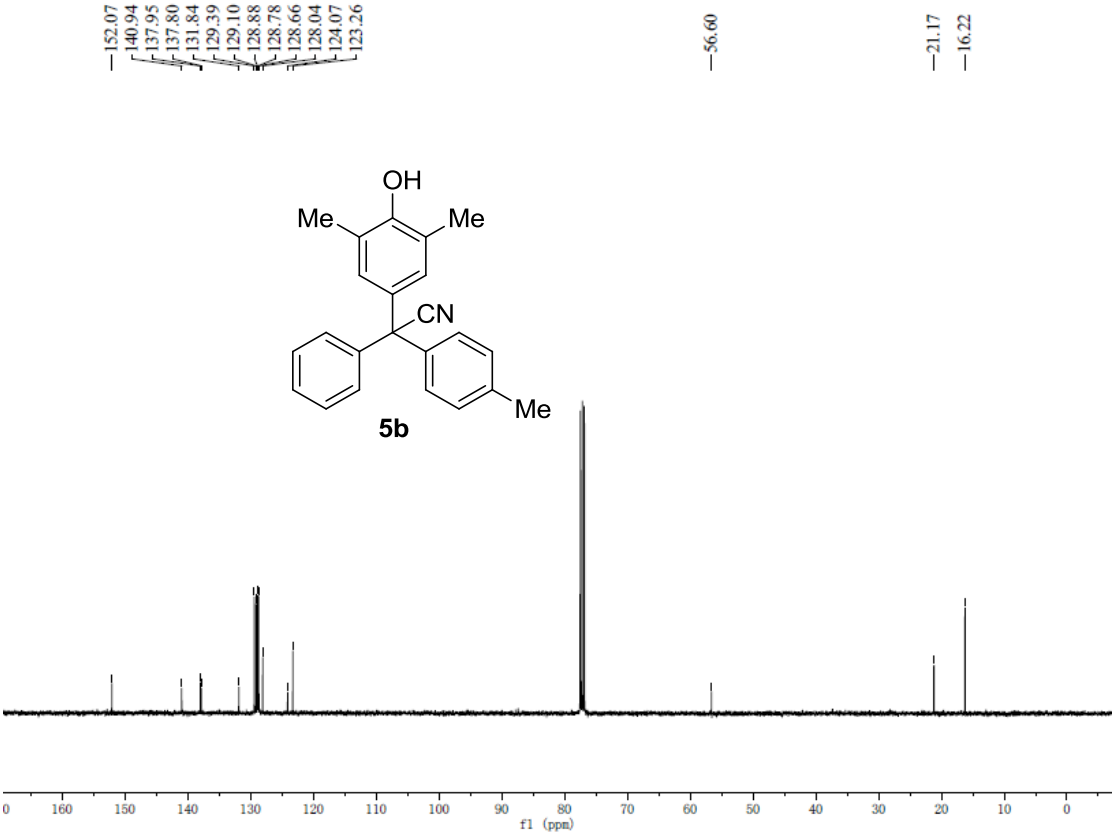
^{1}HNMR of 5a



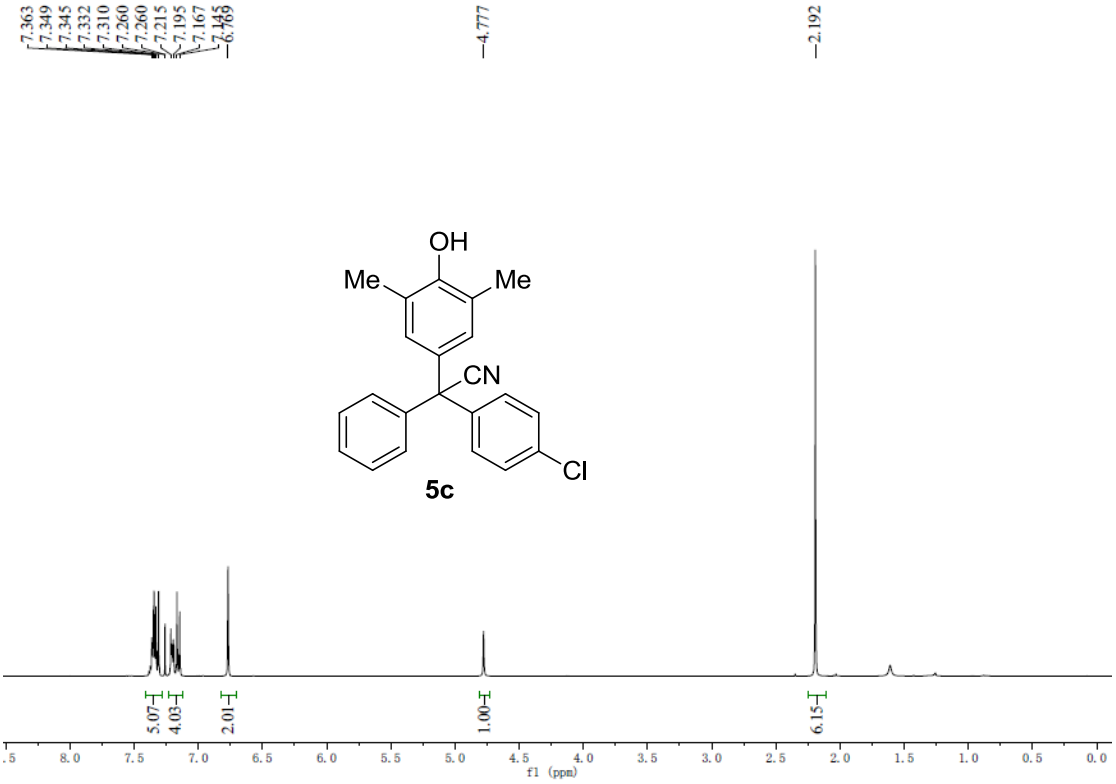
^{13}CNMR of 5a



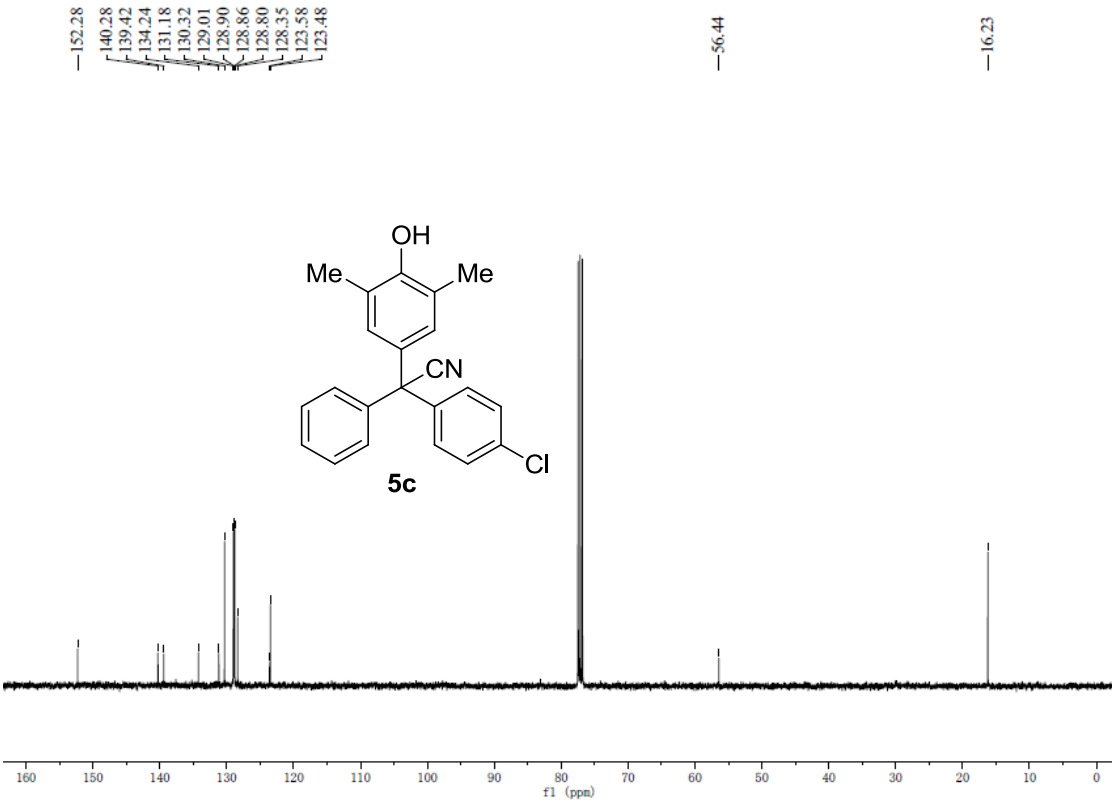
^{1}HNMR of 5b



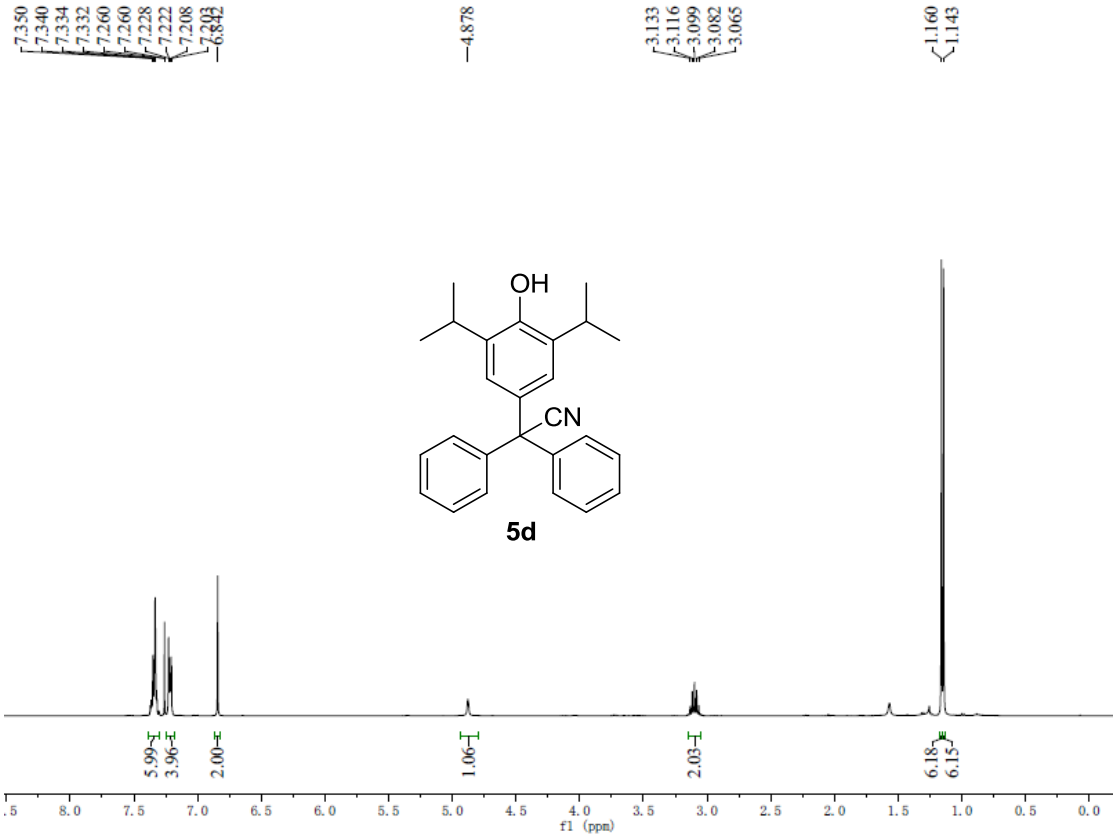
^{13}CNMR of 5b



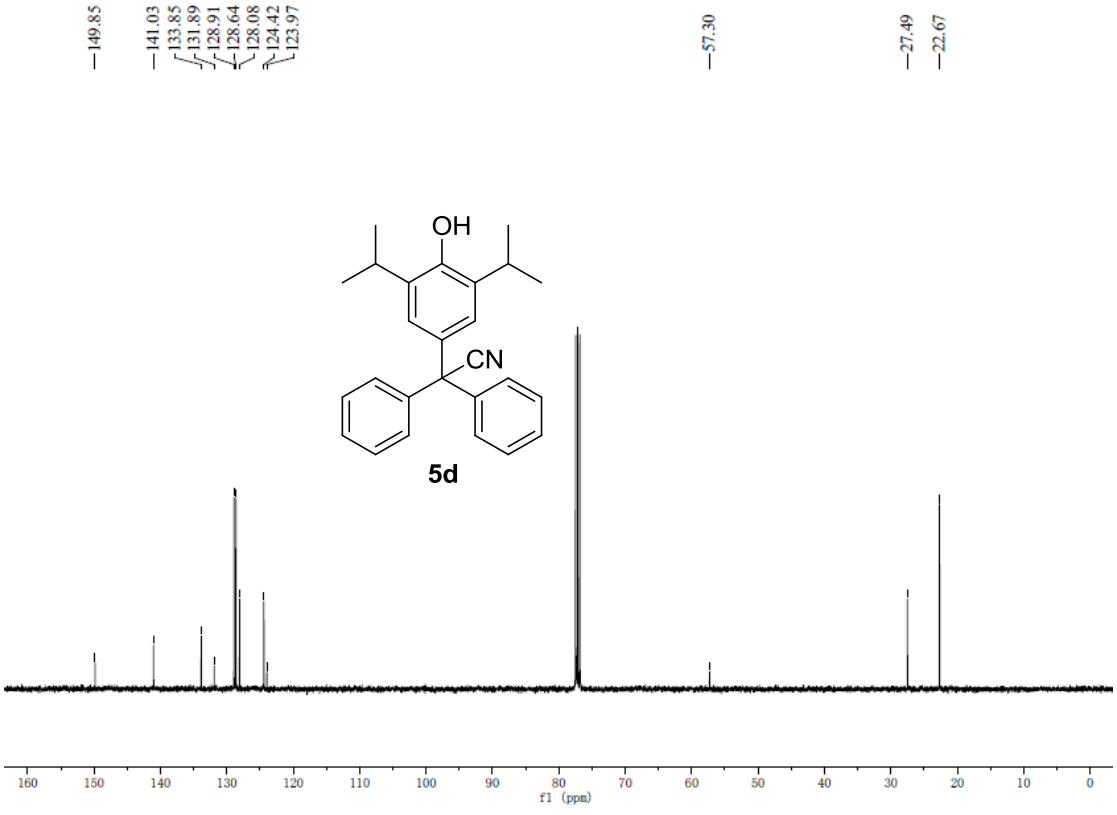
^{1}HNMR of 5c



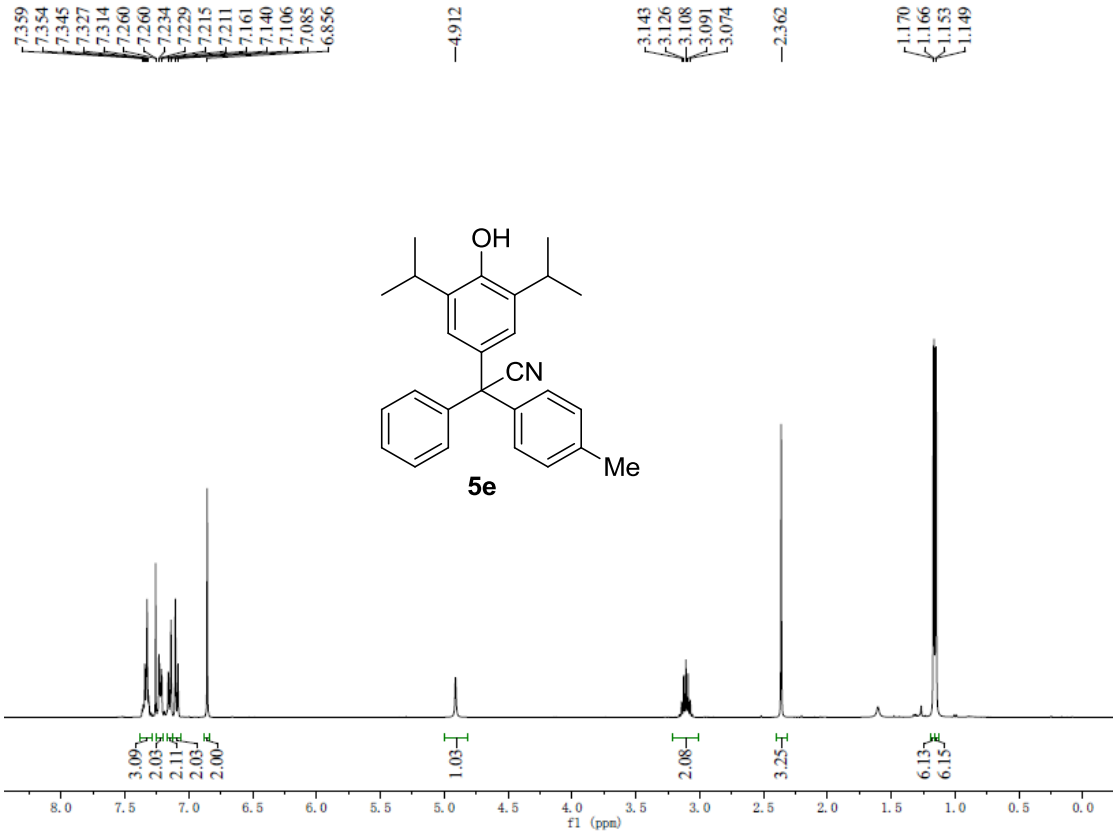
^{13}CNMR of 5c



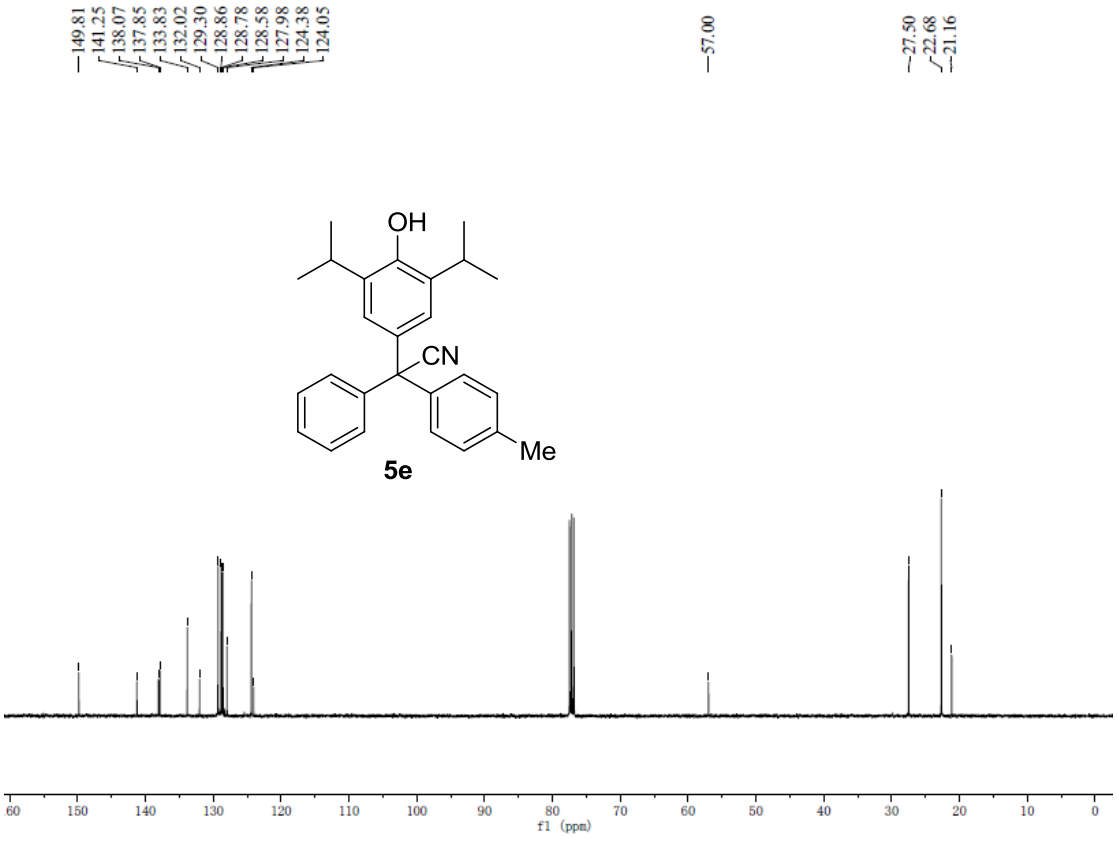
^{1}HNMR of 5d



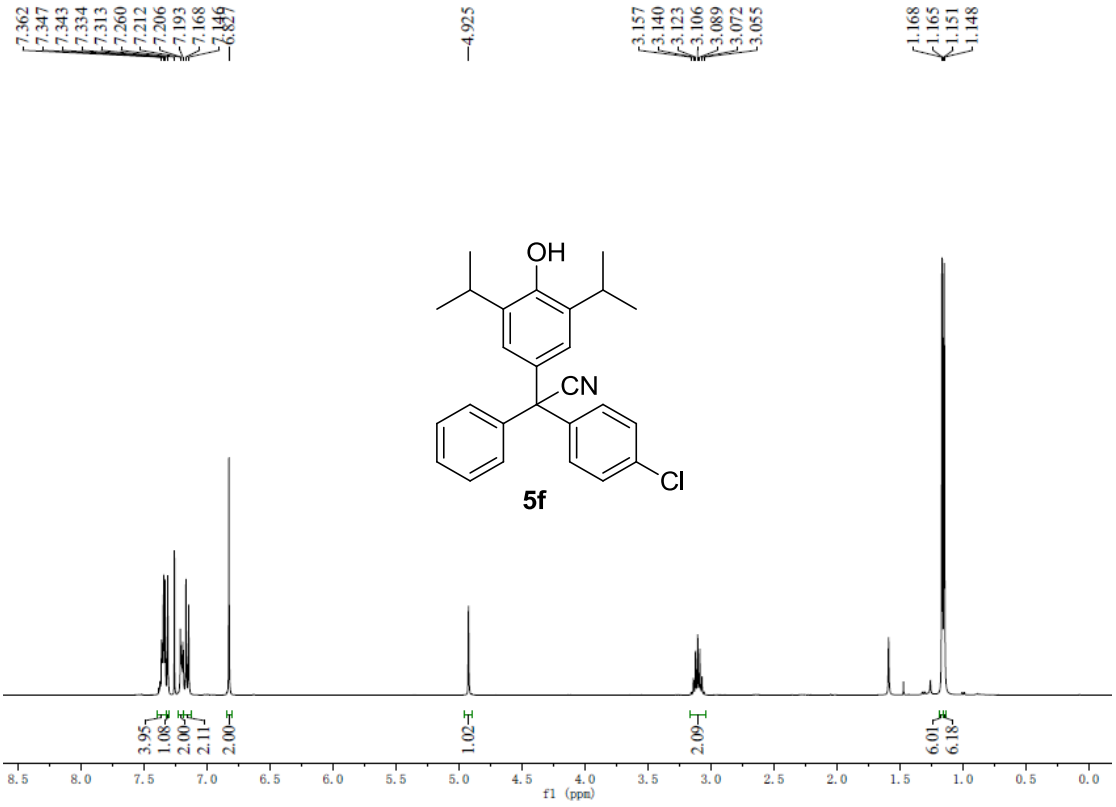
^{13}CNMR of 5d



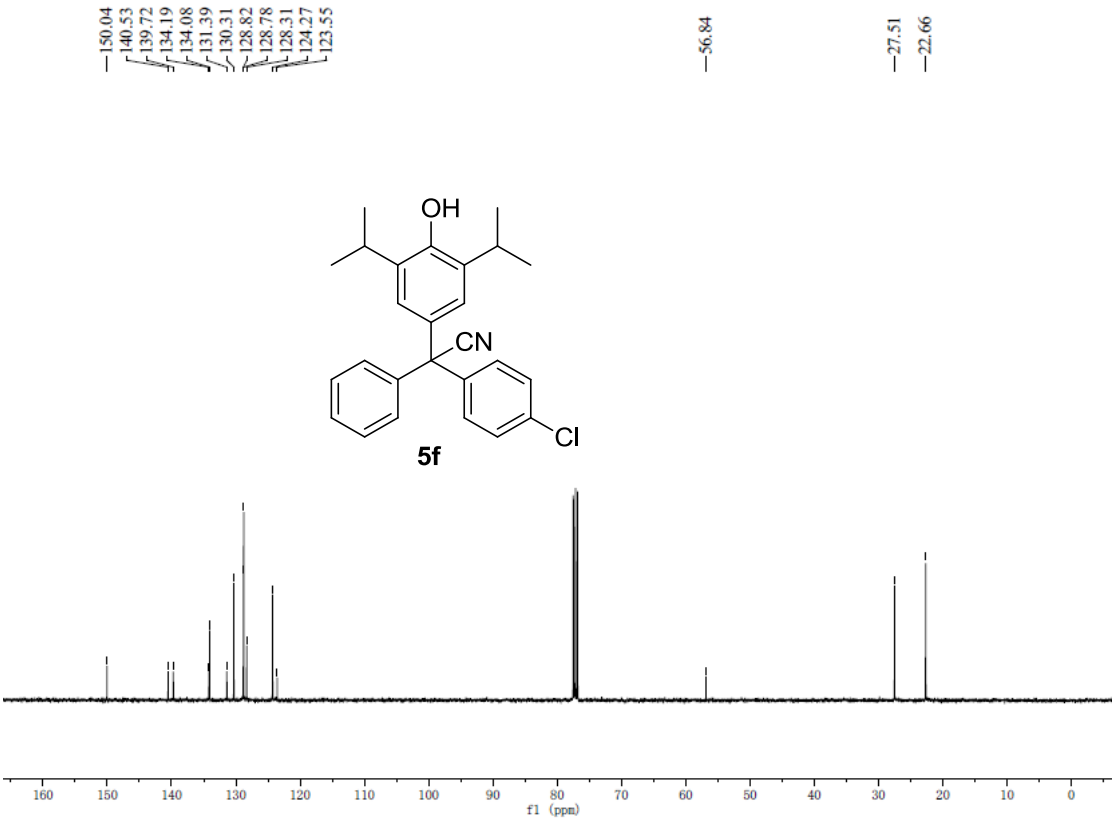
^{1}HNMR of 5e



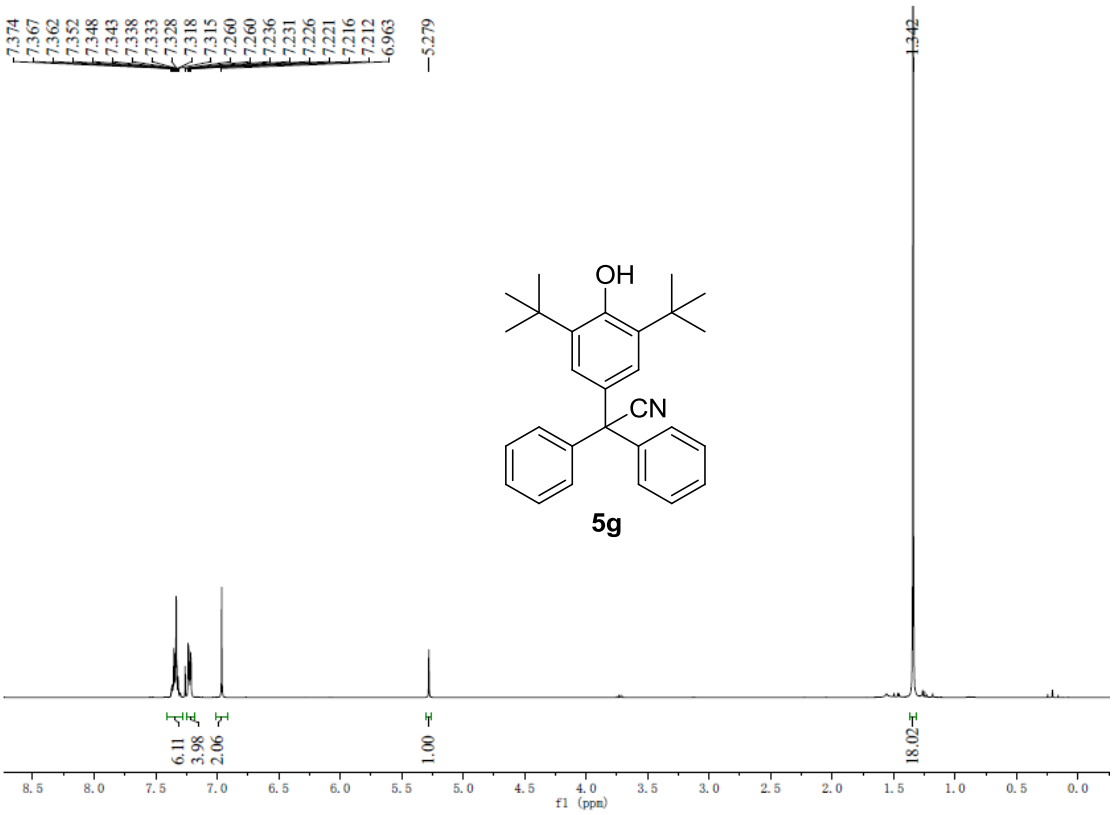
^{13}CNMR of 5e



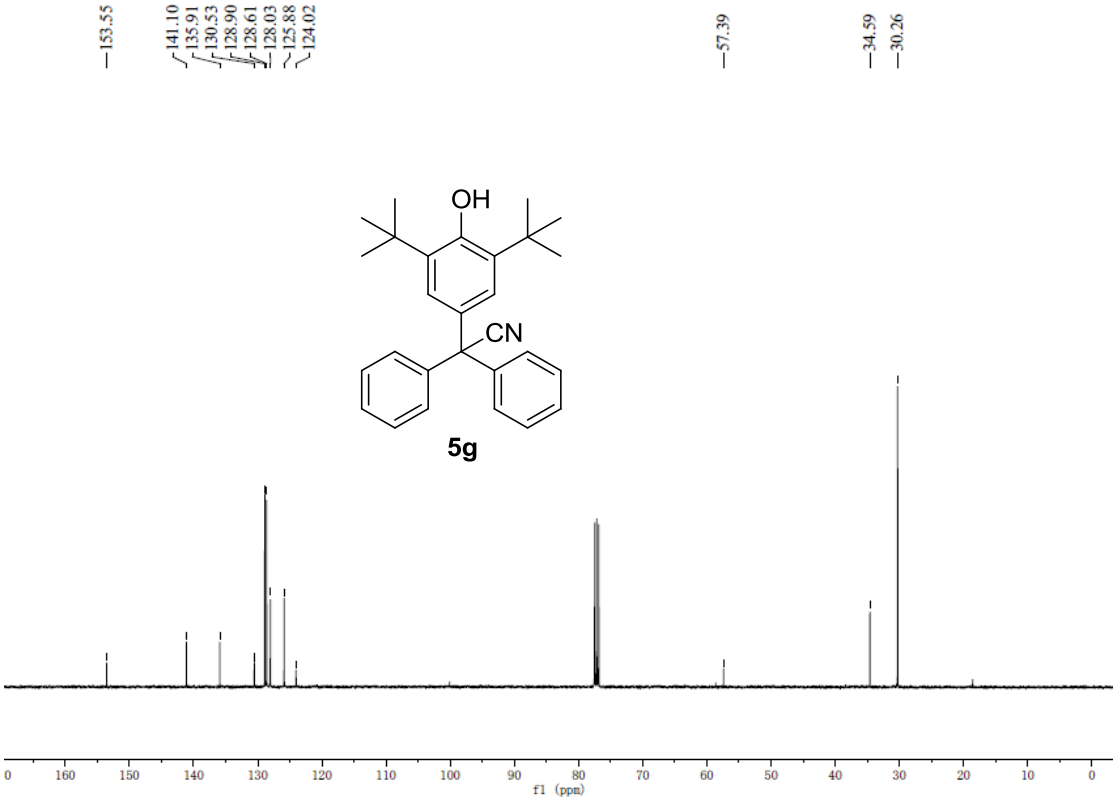
^{1}HNMR of 5f



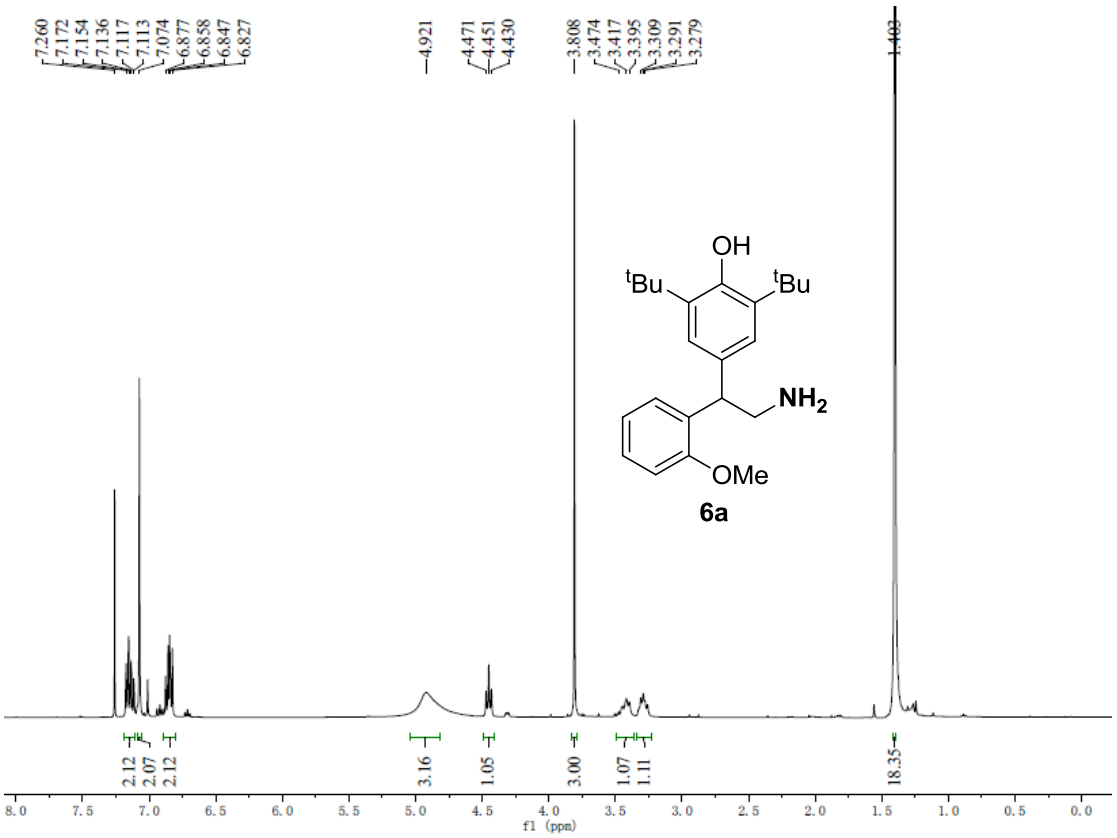
^{13}CNMR of 5f



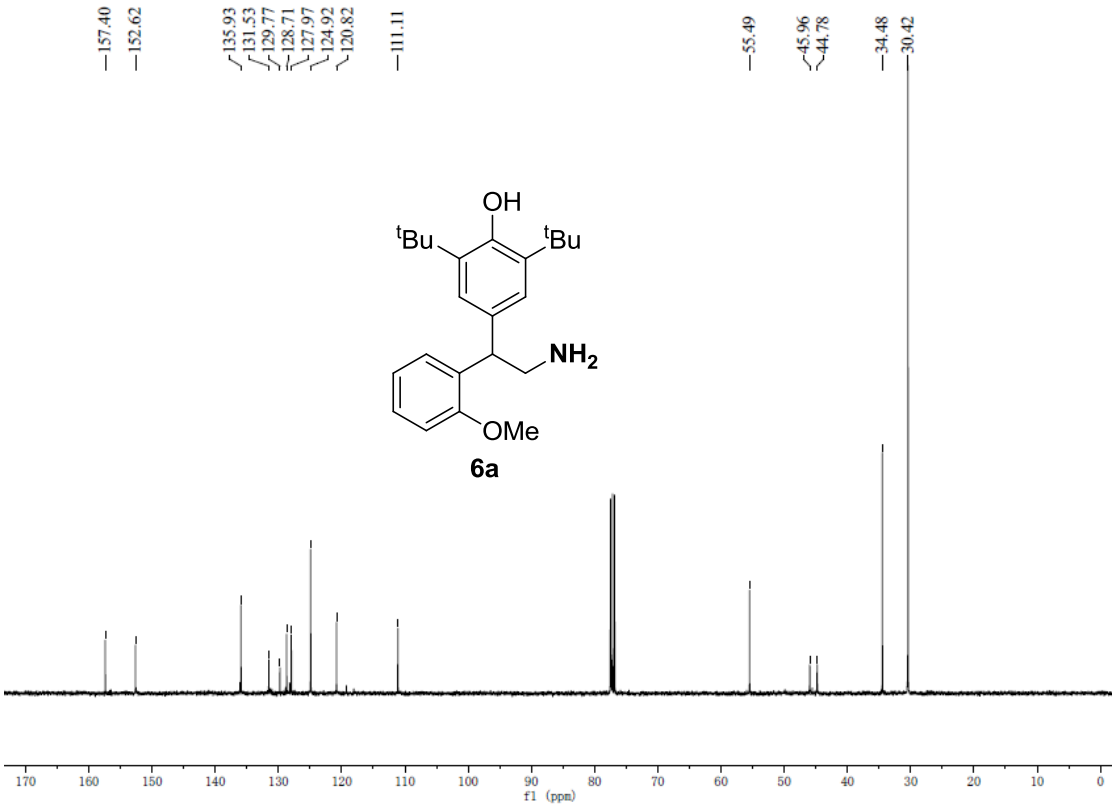
^{1}HNMR of 5g



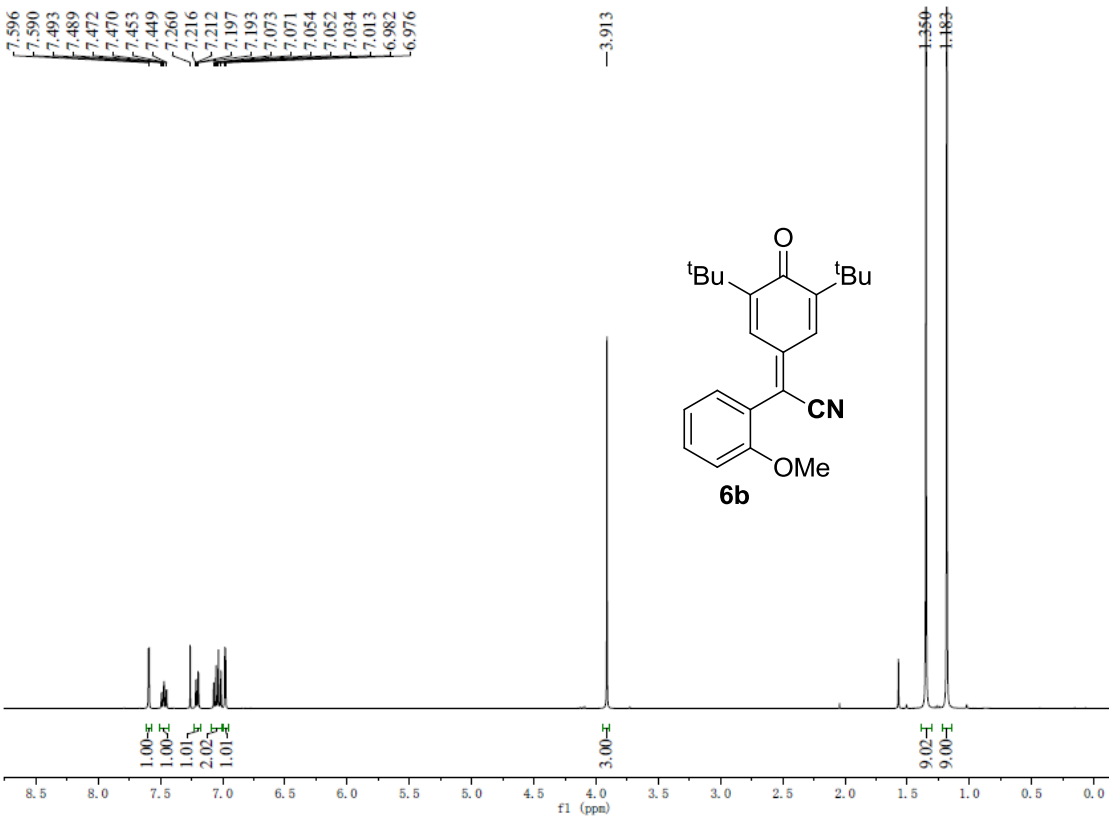
^{13}CNMR of 5g



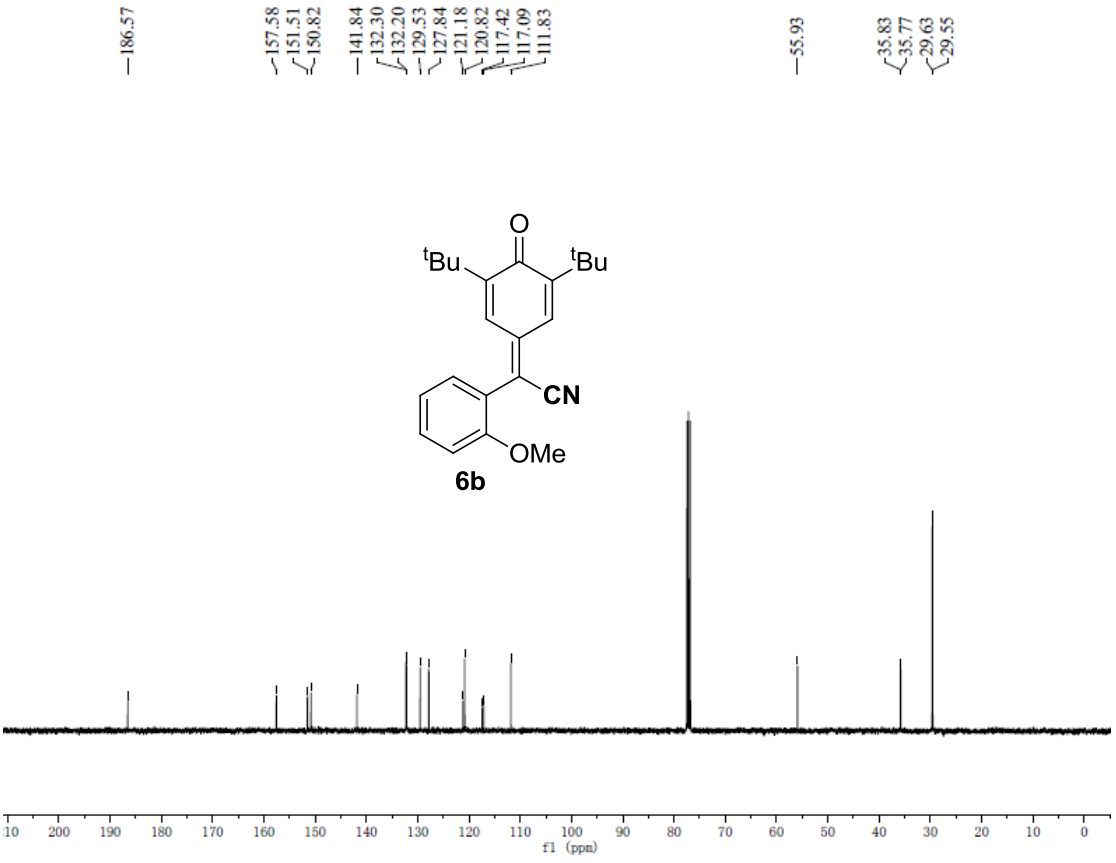
^{1}HNMR of 6a



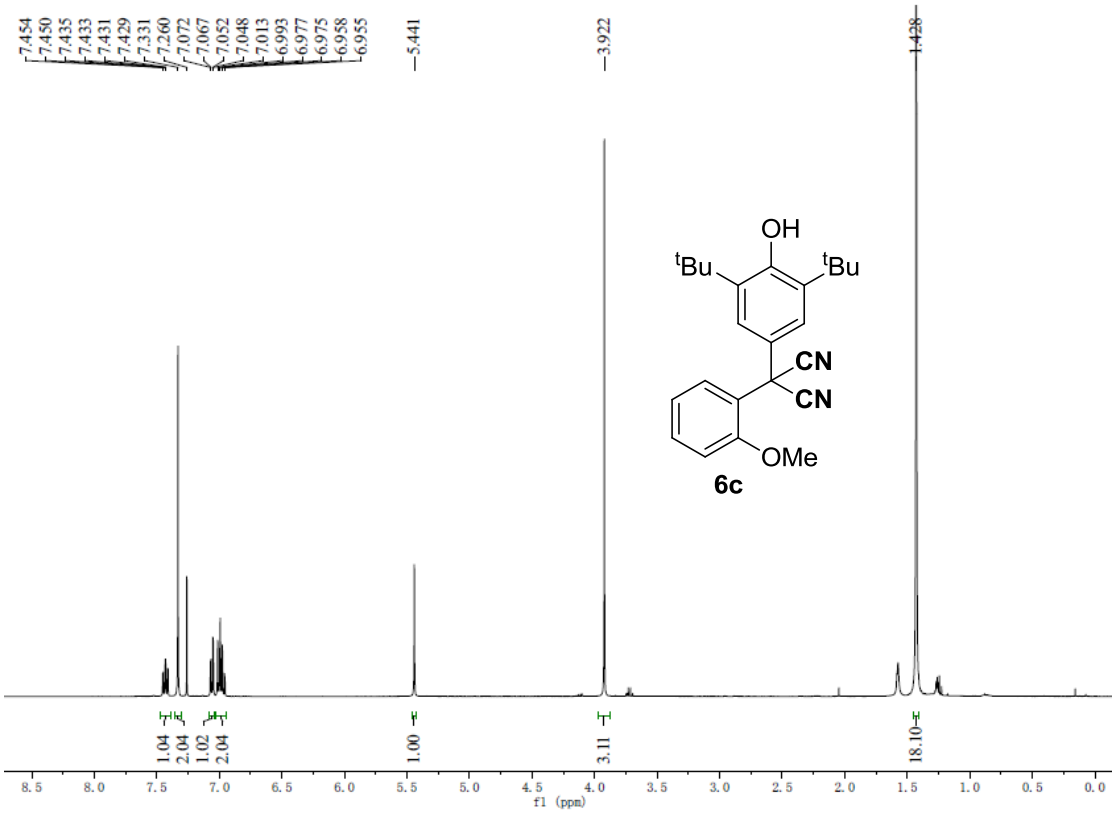
^{13}CNMR of 6a



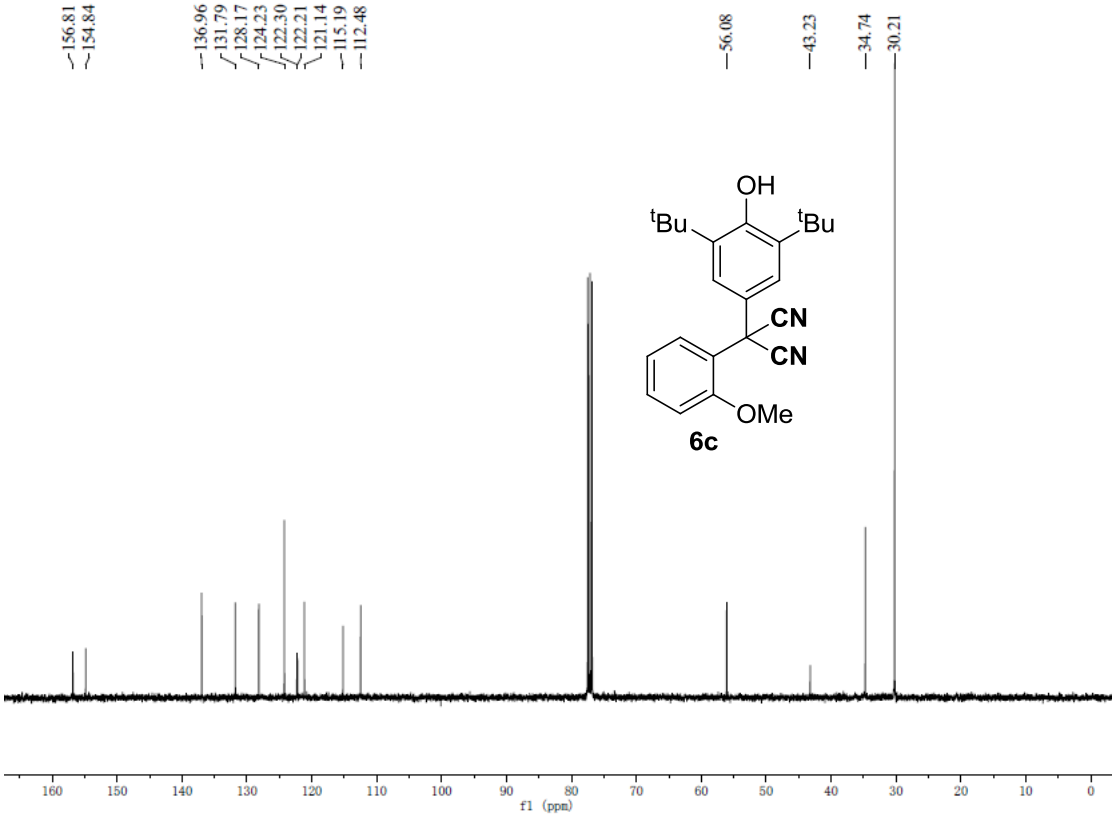
^{1}HNMR of 6b



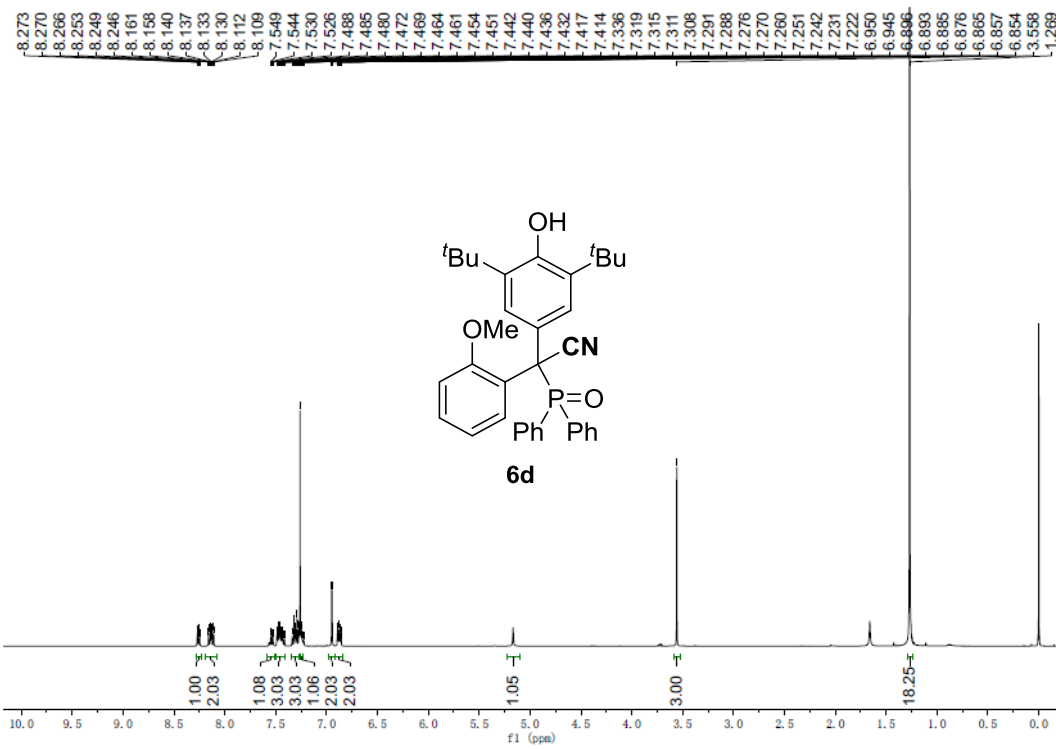
^{13}CNMR of 6b



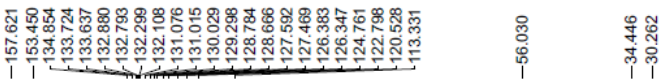
^{1}HNMR of 6c

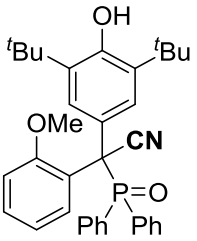


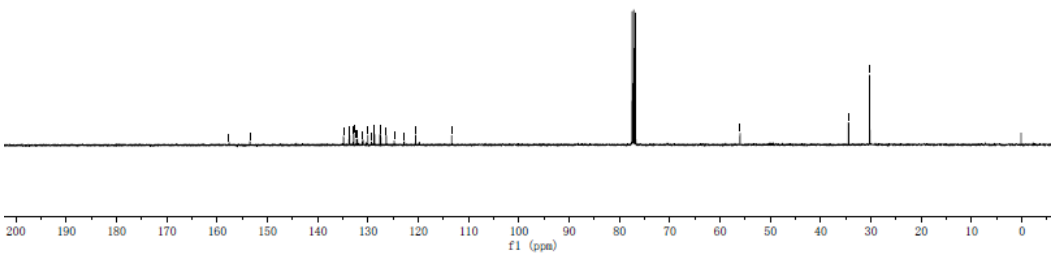
^{13}CNMR of 6c



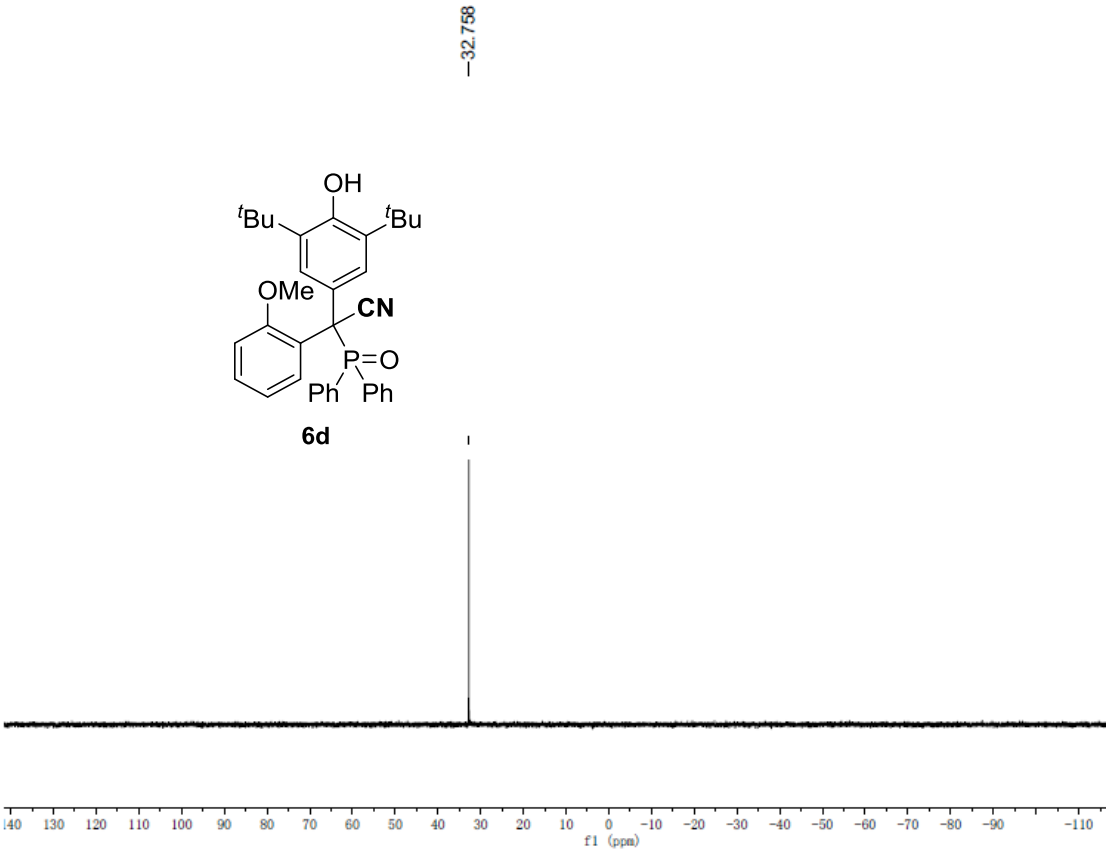
^{1}H-NMR of 6d



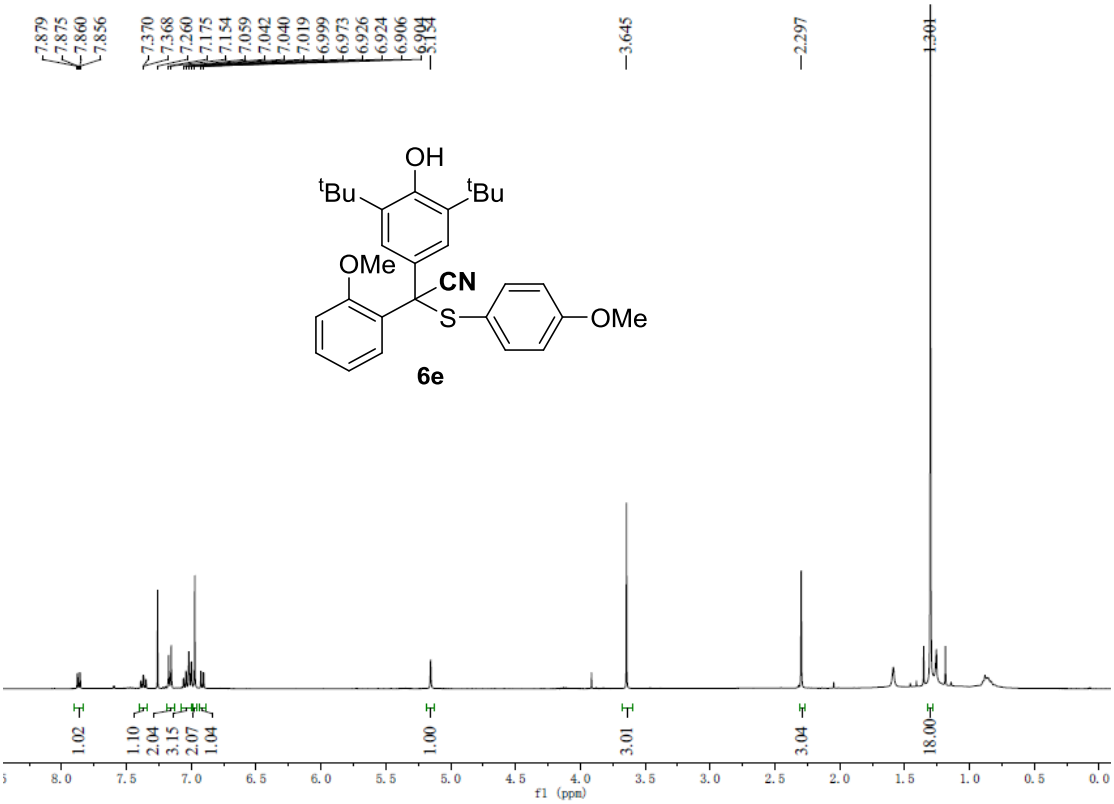




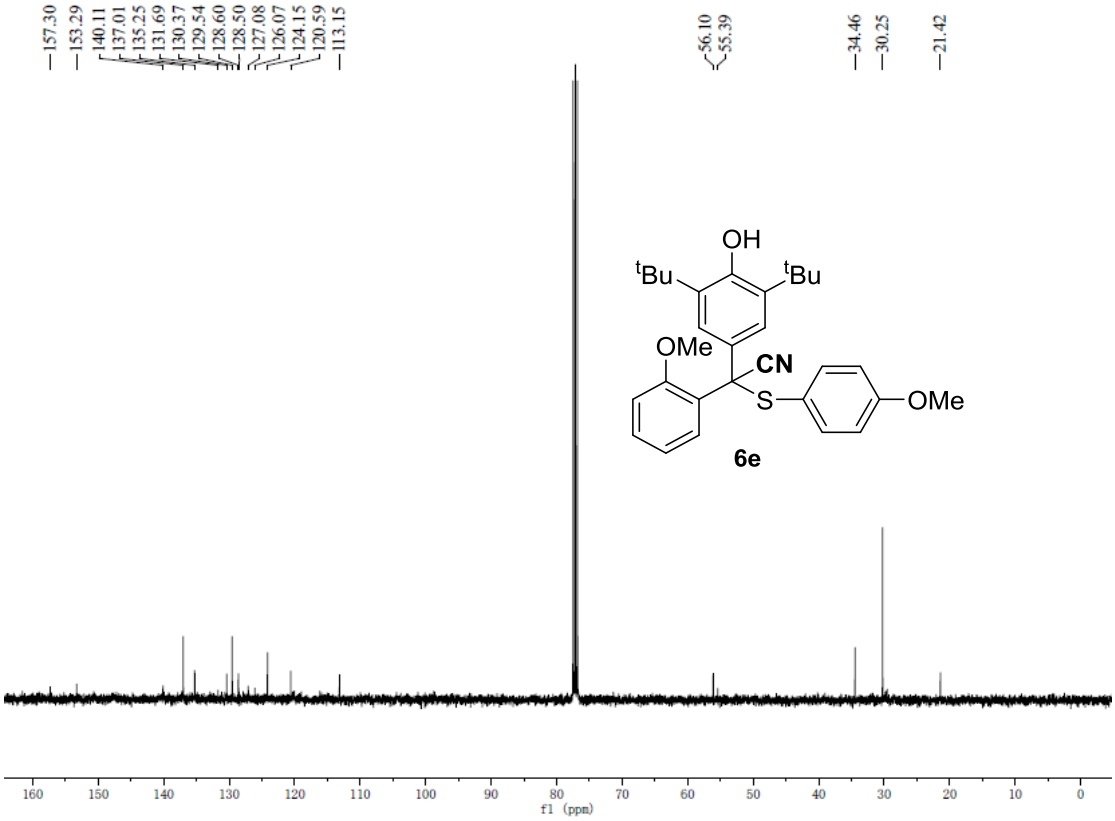
^{13}C-NMR of 6d



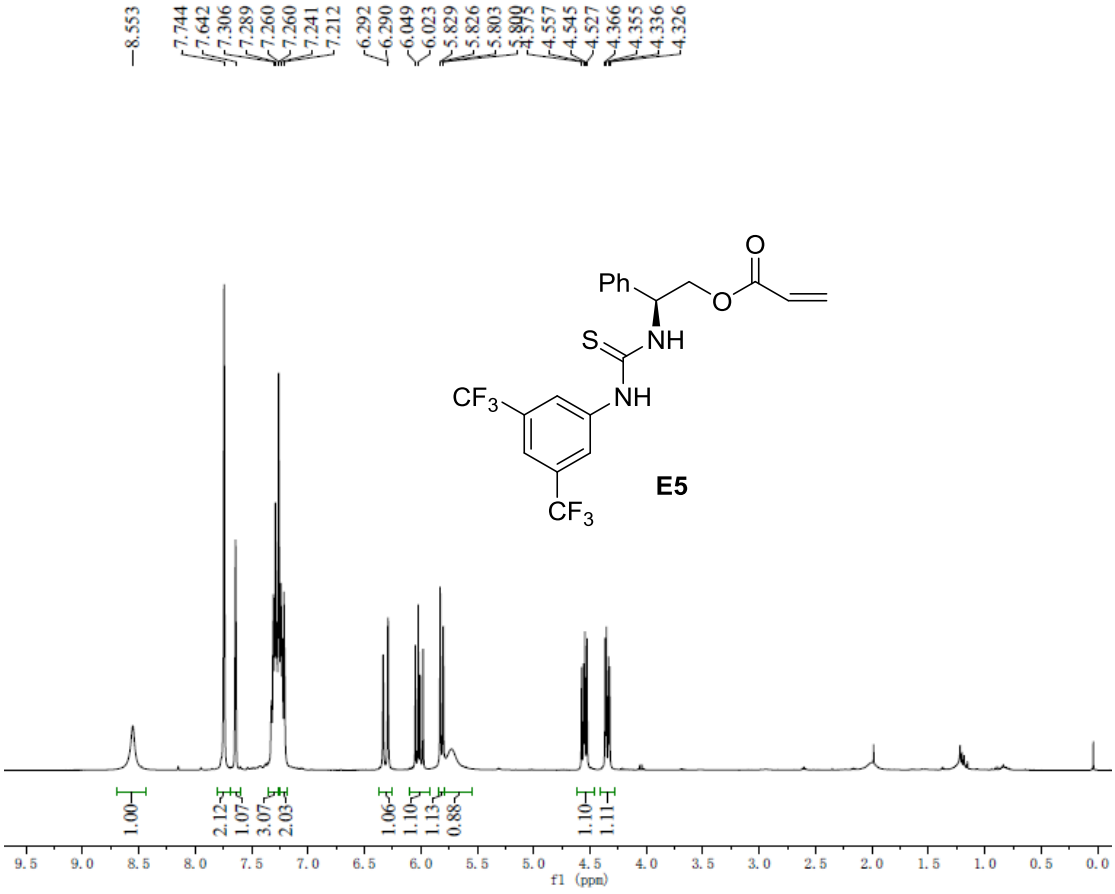
^{31}PNMR of 6d



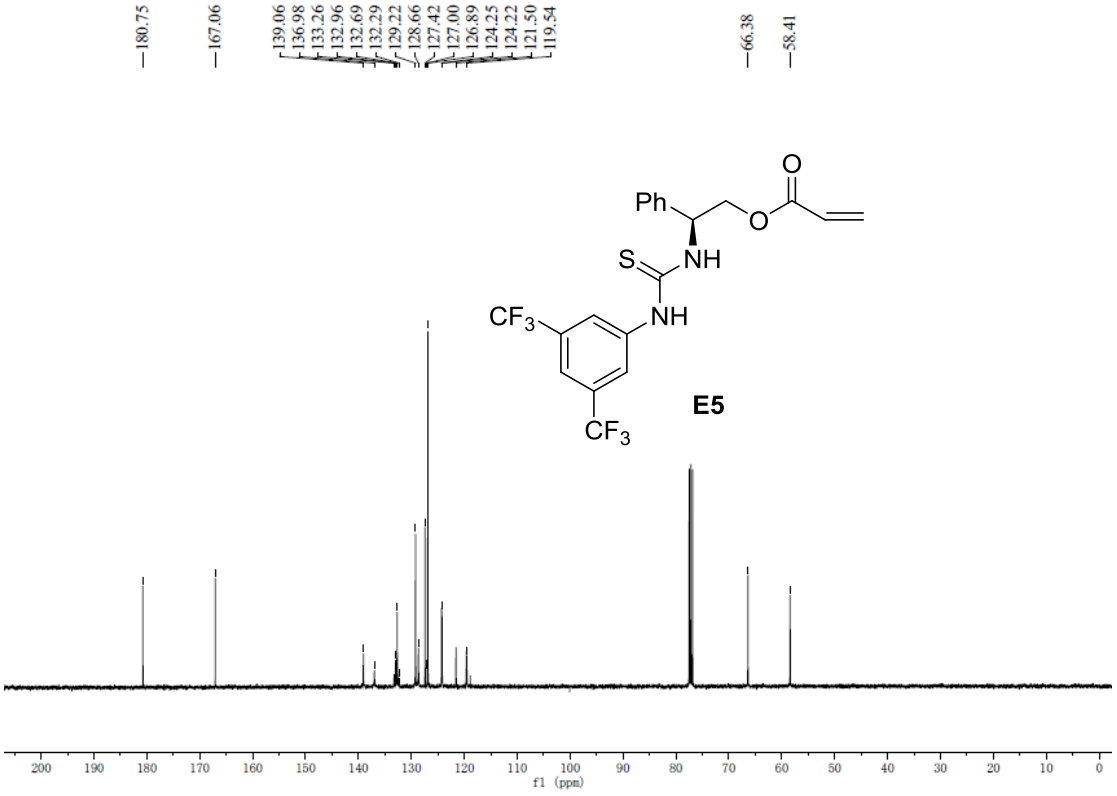
^{1}HNMR of 6e



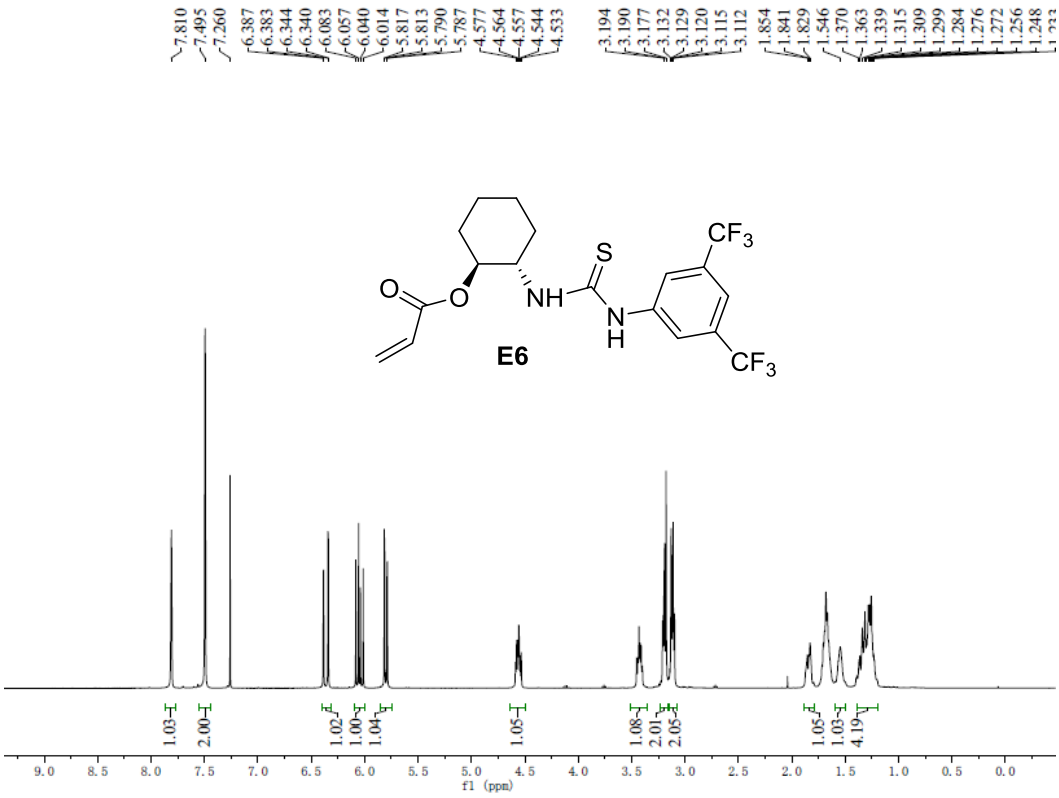
^{13}CNMR of 6e



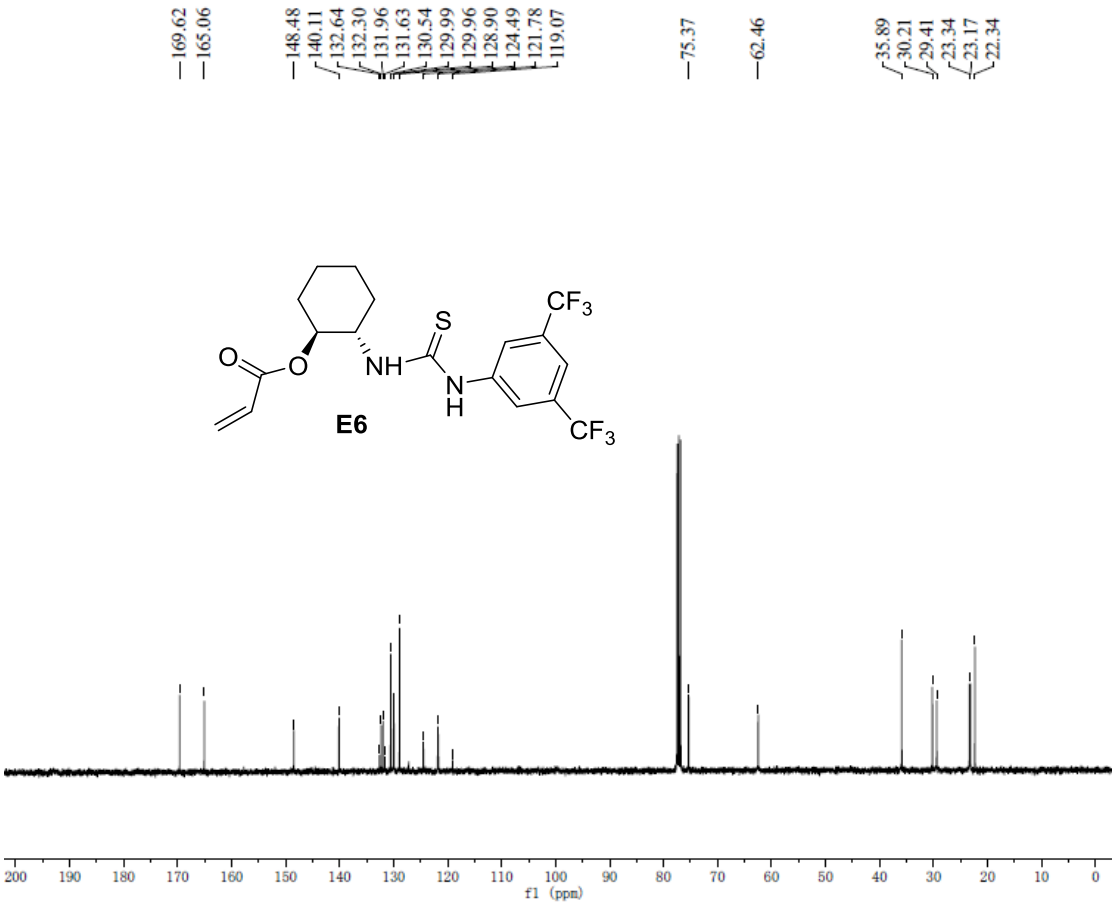
^{1}HNMR of E5



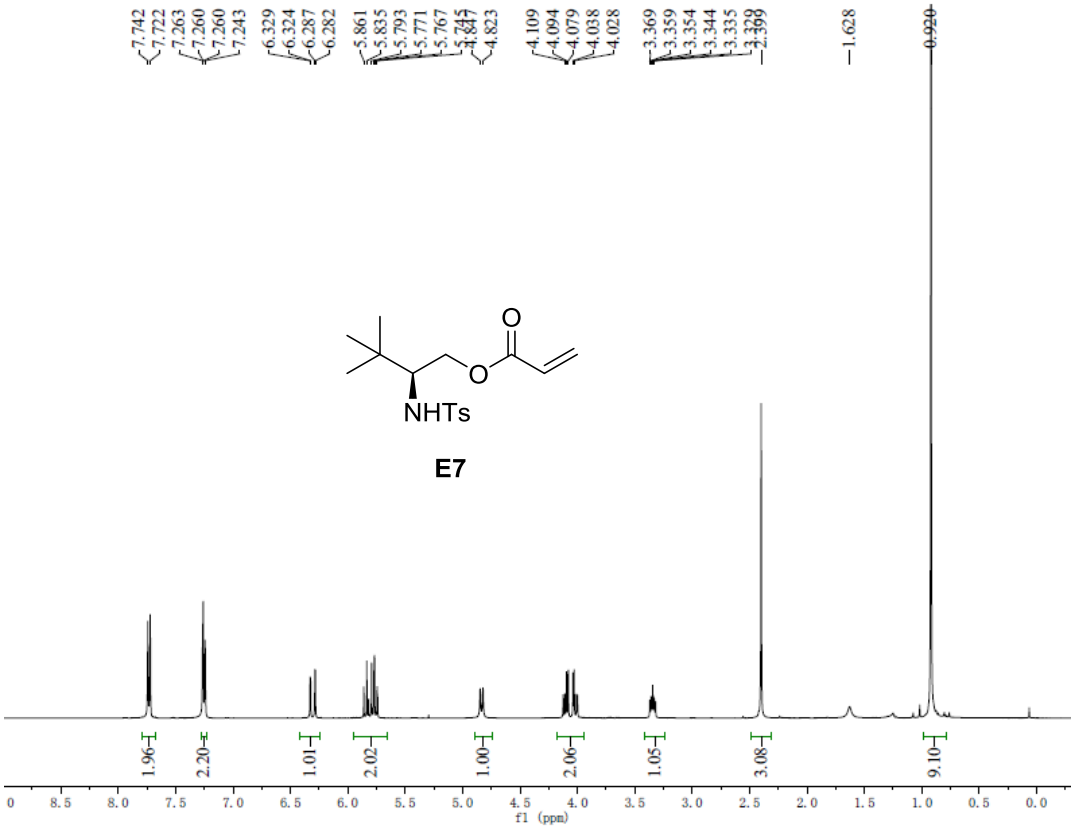
^{13}CNMR of **E5**



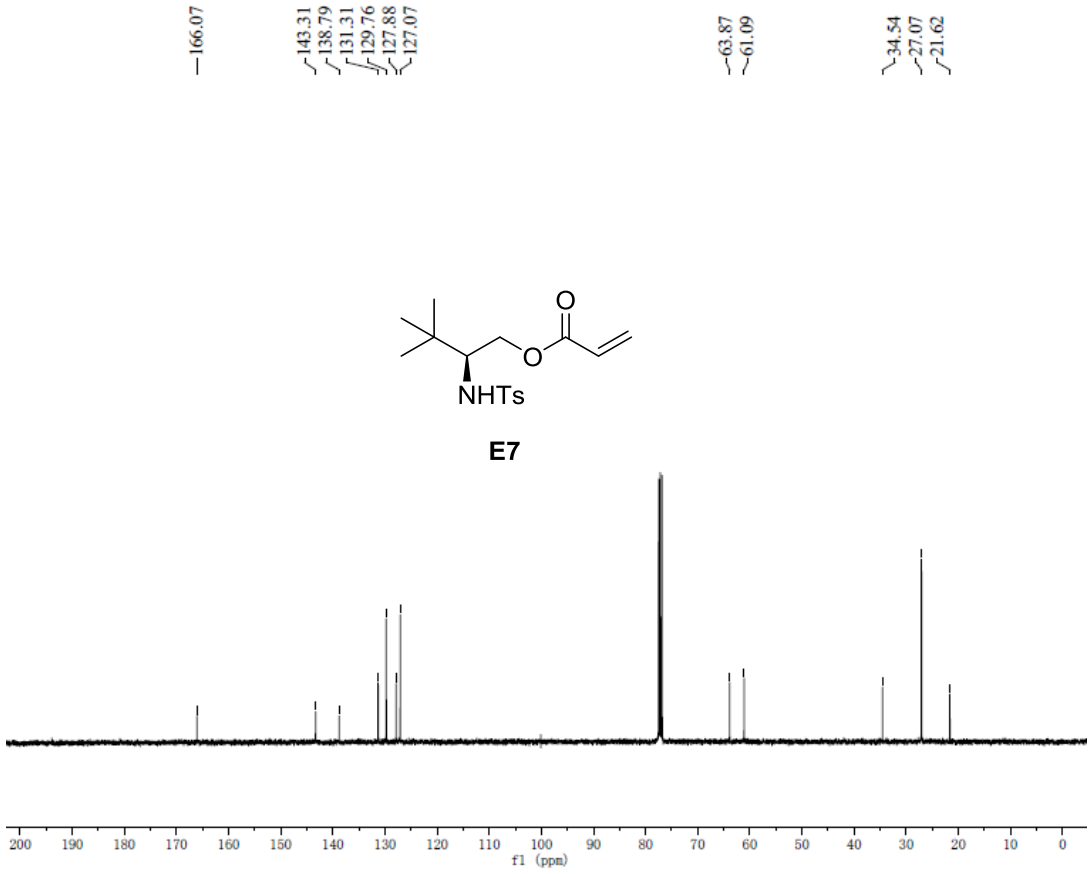
^{1}HNMR of E6



^{13}CNMR of E6



^{1}HNMR of **E7**



E7

^{13}CNMR of **E7**