Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Direct Acylcyanation of Aryl Alkenes by Dual Photoredox and Copper Catalysis

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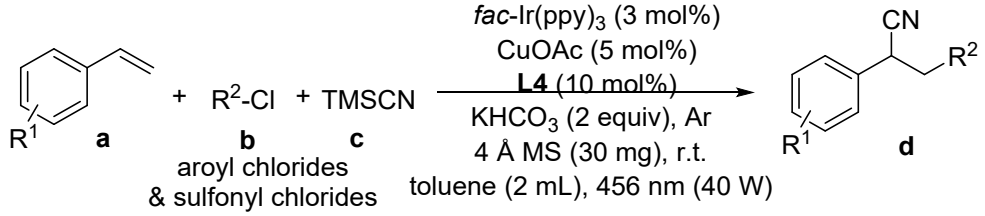
Contents

1. General methods

Unless otherwise noted, all reagents were purchased from commercial suppliers and used without further purification. All solvents were pre-dried with active molecular sieves. Reactions were monitored by thin-layer chromatography (TLC) with Haiyang GF 254 silica gel plates (Qingdao Haiyang chemical industry Co Ltd, Qingdao, China) using UV light and phosphomolybdic acid as visualizing agents. Flash column chromatography was performed using 200-300 mesh silica gel at increased pressure. ^{1}H NMR spectra, ^{13}C NMR spectra and ^{19}F spectra were respectively recorded on 600/400 MHz NMR Bruker spectrometers. Chemical shifts (δ) were expressed in ppm with TMS as the internal standard, and coupling constants (*J*) were reported in Hz. High-resolution mass spectra were obtained by using ESI ionization sources (quadrupole time-of-flight mass spectrometer, Bruker Impact II, Bremen, Germany).

2. General procedure for the synthesis of products d

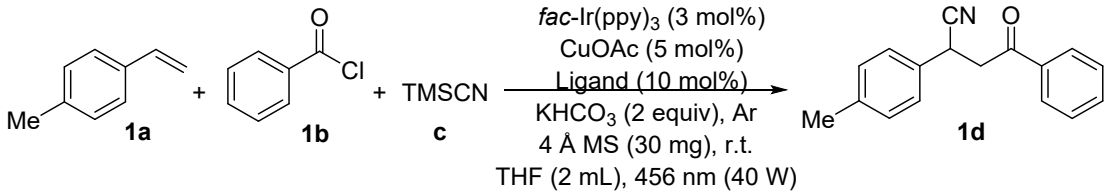


A 10 mL flame-dried Schlenk tube equipped with a stirring bar was charged with alkene **a** (0.2 mmol, 1.0 equiv) (if soild), aroyl chloride or sulfonyl chloride **b** (0.6 mmol, 3.0 equiv) (if soild), *fac*-Ir(ppy)$_3$ (0.006 mmol, 3 mol%), CuOAc (0.01 mmol, 5 mol%), **L4** (0.02 mmol, 10 mol%), $KHCO_3$ (0.4 mmol, 2.0 equiv) and 4 Å MS powder (30 mg). The resulting mixture was evacuated and backfilled with Ar three times, followed by the addition of toluene (2 mL). Then, the mixture was stirred at room temperature for 30 min. Subsequently, alkene **a** (0.2 mmol, 1.0 equiv) (if liquid), aroyl chloride or sulfonyl chloride **b** (0.6 mmol, 3.0 equiv) (if liquid) and TMSCN **c** (0.6 mmol, 3.0 equiv) were added into the mixture by microliter syringes. The mixture was stirred under irradiation of 40 W 456 nm Kessil Tuna blue lamp (the distance between lamp and the tube is about 3 cm). After completion of the reaction (detected by TLC), the reaction mixture was diluted with dichloromethane, filtered through a short pad of celite. The filtratewas evaporated in vacuo to remove the solvent and purified by flash chromatography on silica gel with petroleum ether/ethyl acetate as the eluent to give

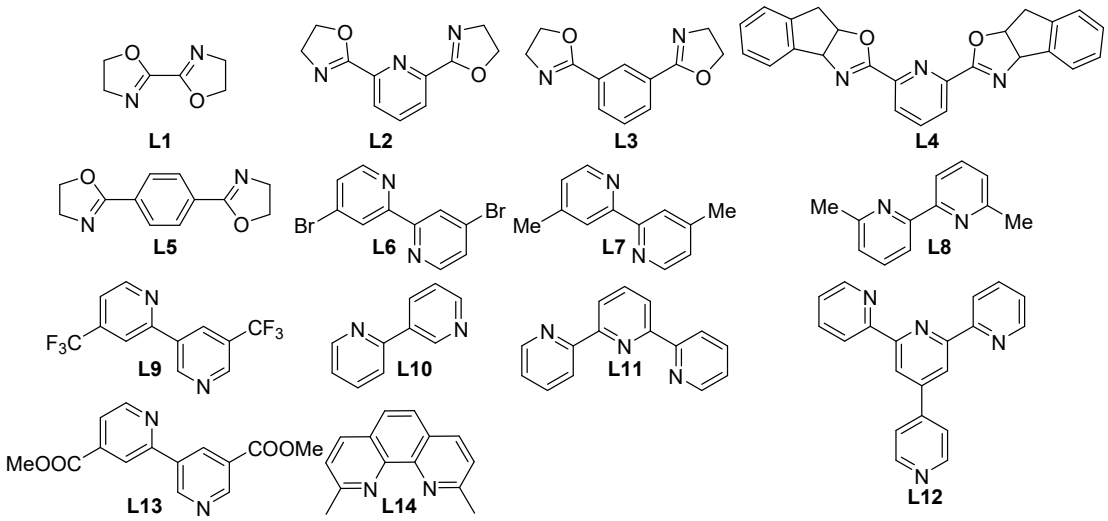
desired product **d**.

3. Optimization of reaction conditions

Table S1. Ligand screening [a]



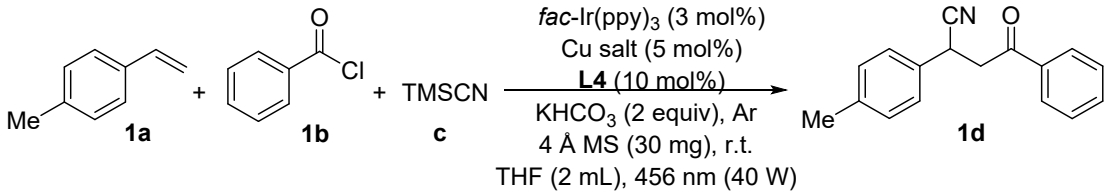
Entry	Ligand	Yield (%) [b]
1	--	35
2	**L1**	54
3	**L2**	66
4	**L3**	42
5	**L4**[c]	**72**
6	**L5**	37
7	**L6**	50
8	**L7**	Trace
9	**L8**	20
10	**L9**	42
11	**L10**	46
12	**L11**	N.D.[d]
13	**L12**	N.D.[d]
14	**L13**	59
15	**L14**	45



[a]Reaction conditions: **1a** (0.2 mmol, 1.0 equiv), **1b** (0.6 mmol, 3.0 equiv), **c** (0.6 mmol, 3.0 equiv), *fac*-Ir(ppy)$_3$ (0.006 mmol, 3 mol%), CuOAc (0.01 mmol, 5 mol%), ligand (0.02 mmol, 10 mol%), $KHCO_3$ (0.4 mmol, 2.0 equiv) and 4 Å MS powder (30 mg) in THF (2 mL)

irradiated with 40 W 456 nm Kessil Tuna blue lamp under Ar atmosphere (Ar balloon) at room temperature for 27 h. [b]Yield of the isolated product after chromatography on silica gel. [c]**L4** is a racemic mixture. [d]N.D. = Not Detected.

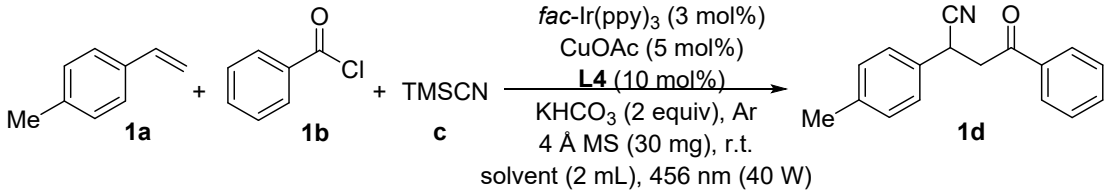
Table S2. Copper salt screening [a]



Entry	Cu salts	Yield (%) [b]
1	**CuOAc**	**72**
2	$Cu(MeCN)_4BF_4$	43
3	$Cu(MeCN)_4PF_6$	30
4	$Cu(OAc)_2$	60
5	CuCl	61
6	CuBr	70
7	CuI	48

[a]Reaction conditions: **1a** (0.2 mmol, 1.0 equiv), **1b** (0.6 mmol, 3.0 equiv), **c** (0.6 mmol, 3.0 equiv), *fac*-Ir(ppy)$_3$ (0.006 mmol, 3 mol%), Cu salt (0.01 mmol, 5 mol%), **L4** (0.02 mmol, 10 mol%), $KHCO_3$ (0.4 mmol, 2.0 equiv) and 4 Å MS powder (30 mg) in THF (2 mL) irradiated with 40 W 456 nm Kessil Tuna blue lamp under Ar atmosphere (Ar balloon) at room temperature for 27 h. [b]Yield of the isolated product after chromatography on silica gel.

Table S3. Effect of solvent on the reaction [a]

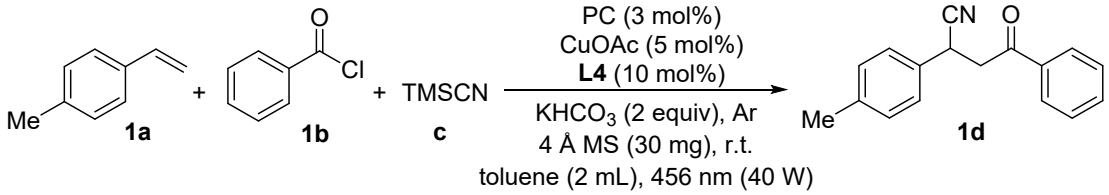


Entry	Solvent	Yield (%) [b]
1	MeCN	N.D.
2	1,4-Dioxane	Trace
3	DCM	Trace
4	DMF	N.D.
5	THF	72
6	DCE	45
7	MTBE	43
8	**Toluene**	**76**

[a]Reaction conditions: **1a** (0.2 mmol, 1.0 equiv), **1b** (0.6 mmol, 3.0 equiv), **c** (0.6 mmol, 3.0 equiv), *fac*-Ir(ppy)$_3$ (0.006 mmol, 3 mol%), CuOAc (0.01 mmol, 5 mol%), **L4** (0.02 mmol, 10 mol%), $KHCO_3$ (0.4 mmol, 2.0 equiv) and 4 Å MS powder (30 mg) in solvent (2 mL)

irradiated with 40 W 456 nm Kessil Tuna blue lamp under Ar atmosphere (Ar balloon) at room temperature for 27 h. [b]Yield of the isolated product after chromatography on silica gel.

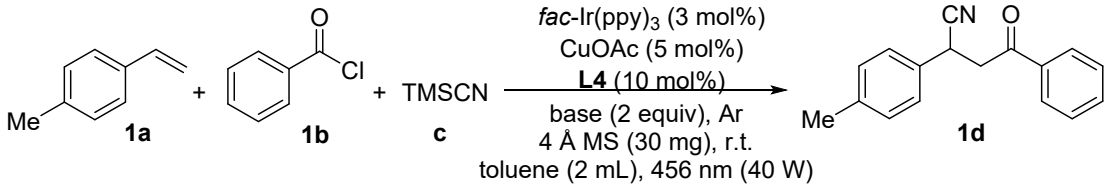
Table S4. Photocatalyst screening [a]



Entry	PC	Yield (%) [b]
1	$Ir[dF(CF_3)ppy]_2(5,5'\text{-}CF_3bpy))PF_6$	Trace
2	Perylene	Trace
3	Ph-PTZ	N.D.
4	***Fac*-Ir(ppy)$_3$**	**76**

[a]Reaction conditions: **1a** (0.2 mmol, 1.0 equiv), **1b** (0.6 mmol, 3.0 equiv), **c** (0.6 mmol, 3.0 equiv), PC (0.006 mmol, 3 mol%), CuOAc (0.01 mmol, 5 mol%), **L4** (0.02 mmol, 10 mol%), $KHCO_3$ (0.4 mmol, 2.0 equiv) and 4 Å MS powder (30 mg) in toluene (2 mL) irradiated with 40 W 456 nm Kessil Tuna blue lamp under Ar atmosphere (Ar balloon) at room temperature for 27 h. [b]Yield of the isolated product after chromatography on silica gel.

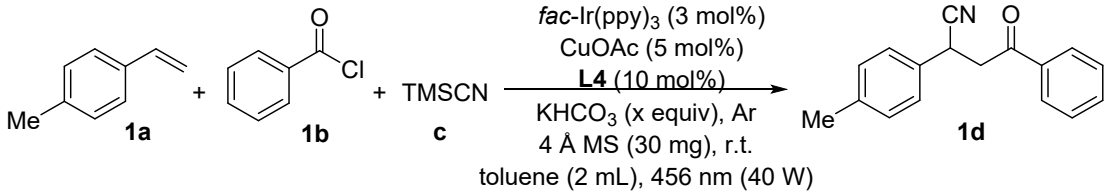
Table S5. Influence of base on the reaction [a]



Entry	Base	Yield
1	--	61
2	**$KHCO_3$**	**76**
3	$NaHCO_3$	61
4	K_2CO_3	64

[a]Reaction conditions: **1a** (0.2 mmol, 1.0 equiv), **1b** (0.6 mmol, 3.0 equiv), **c** (0.6 mmol, 3.0 equiv), *fac*-Ir(ppy)$_3$ (0.006 mmol, 3 mol%), CuOAc (0.01 mmol, 5 mol%), **L4** (0.02 mmol, 10 mol%), base (0.4 mmol, 2.0 equiv) and 4 Å MS powder (30 mg) in toluene (2 mL) irradiated with 40 W 456 nm Kessil Tuna blue lamp under Ar atmosphere (Ar balloon) at room temperature for 27 h. [b]Yield of the isolated product after chromatography on silica gel.

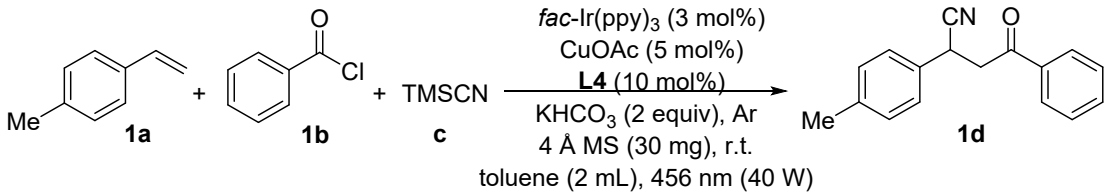
Table S6. Effect of $KHCO_3$ loading on the reaction [a]



Entry	$KHCO_3$ (x equiv)	Yield (%) [b]
1	0.0	61
2	1.0	74
3	**2.0**	**76**
4	3.0	61
5	4.0	65

[a]Reaction conditions: **1a** (0.2 mmol, 1.0 equiv), **1b** (0.6 mmol, 3.0 equiv), **c** (0.6 mmol, 3.0 equiv), *fac*-Ir(ppy)$_3$ (0.006 mmol, 3 mol%), CuOAc (0.01 mmol, 5 mol%), **L4** (0.02 mmol, 10 mol%), $KHCO_3$ (x equiv) and 4 Å MS powder (30 mg) in toluene (2 mL) irradiated with 40 W 456 nm Kessil Tuna blue lamp under Ar atmosphere (Ar balloon) at room temperature for 27 h. [b]Yield of the isolated product after chromatography on silica gel.

Table S7. Control experiments [a]



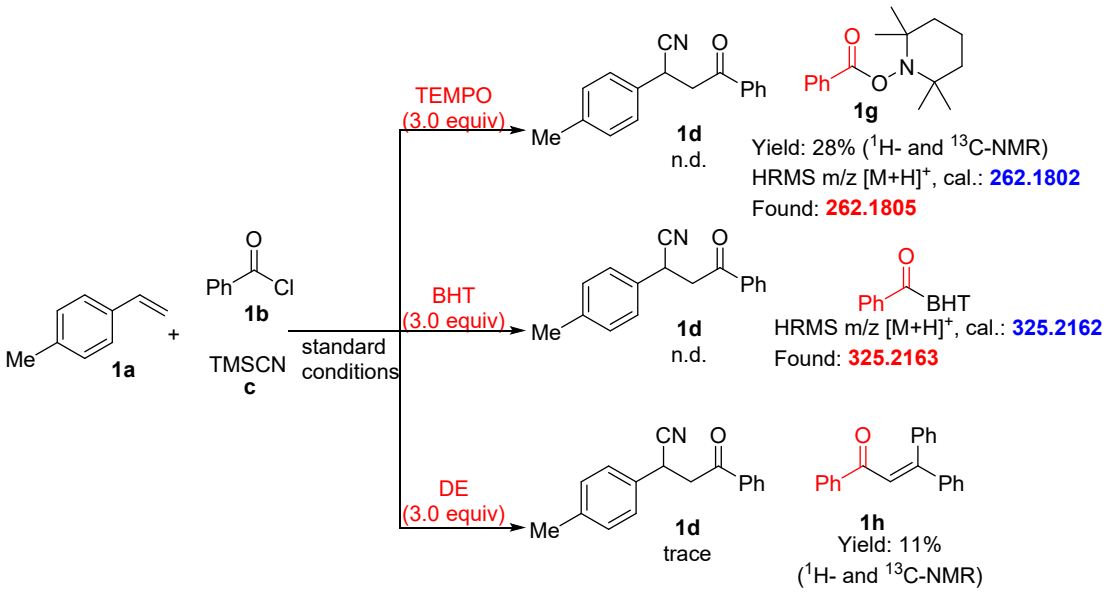
Entry	Variation from standard conditions	Yield (%) [b]
1	None	76
2	Dark	N.D.
3	No *fac*-Ir(ppy)$_3$	N.D.
4	No CuOAc	N.D.
5	No **L4**	31
6	No 4 Å MS	61

[a]Standard conditions: **1a** (0.2 mmol, 1.0 equiv), **1b** (0.6 mmol, 3.0 equiv), **c** (0.6 mmol, 3.0 equiv), *fac*-Ir(ppy)$_3$ (0.006 mmol, 3 mol%), CuOAc (0.01 mmol, 5 mol%), **L4** (0.02 mmol, 10 mol%), $KHCO_3$ (0.4 mmol, 2.0 equiv) and 4 Å MS powder (30 mg) in toluene (2 mL) irradiated with 40 W 456 nm Kessil Tuna blue lamp under Ar atmosphere (Ar balloon) at room temperature for 27 h. [b]Yield of the isolated product after chromatography on silica gel.

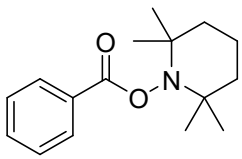
4. Mechanistic investigation

4.1 Radical trapping experiments

In order to confirm if the reaction undergoes a radical mechanism, common radical scavengers, 2,2,6,6-tetramethylpiperidinooxy (TEMPO), 2,6-di-*tert*-butyl-4-methylphenol (BHT) and 1,1-diphenylethylene (DE) were employed for the radical trapping and inhibition experiments (Scheme S1). When TEMPO (3.0 equiv to **1a**) and BHT (3.0 equiv to **1a**) were added separately into the model reaction system at the beginning of the reaction under the standard conditions, no product was detected even after 27 h. Only a trace amount of product was observed when DE (3.0 equiv to **1a**) was added at the beginning of the reaction. These results suggested that the reaction may involve a radical process. After 27 hours, a small amount of reaction mixture was taken out for high-resolution mass spectrometry (HRMS) measurement (Figures S5 and S6).



Scheme S1. Radical trapping experiments.



2,2,6,6-Tetramethylpiperidin-1-yl benzoate (1g)[1]: R_f = 0.25 (Petroleum ether/EtOAc, 100:1). 44.6 mg, 28% yield. White solid. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.09 – 8.07 (m, 2H), 7.59 – 7.55 (m, 1H), 7.48 – 7.44 (m, 2H), 1.83 – 1.64 (m, 3H), 1.61 – 1.57 (m, 2H), 1.48 – 1.43 (m, 1H), 1.28 (s, 6H), 1.12 (s, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 166.4, 132.8, 129.8, 129.6, 128.4, 60.4, 39.1, 32.0, 20.9, 17.0.

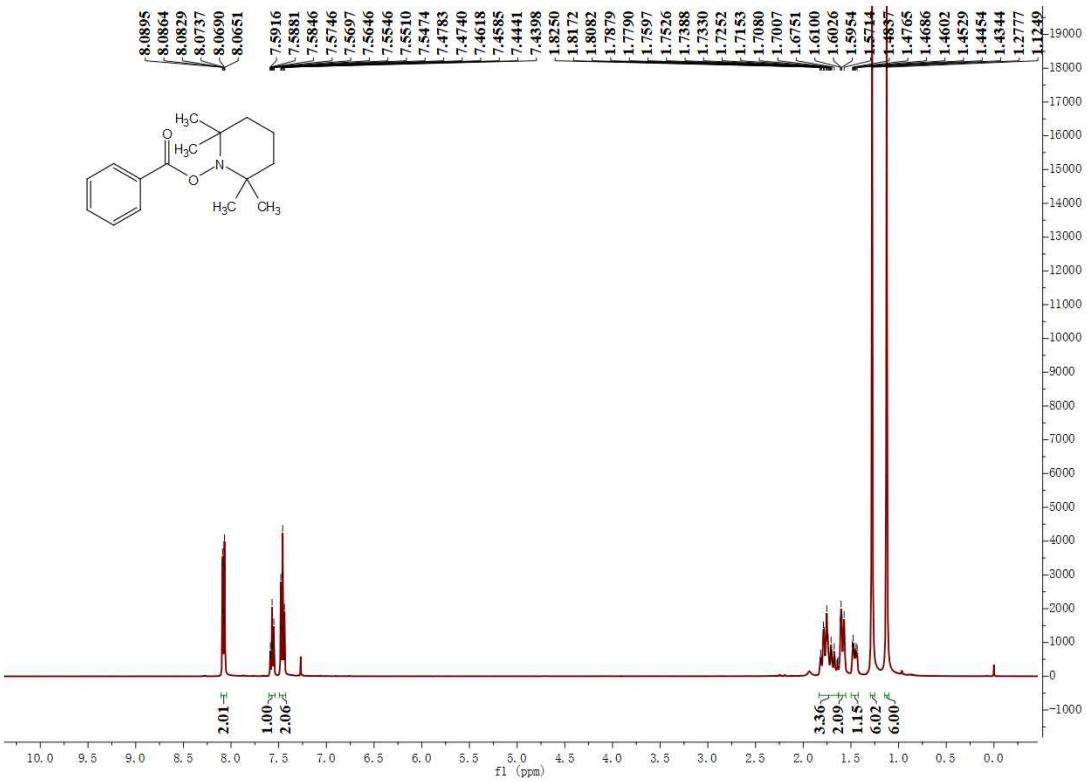


Figure S1. ^{1}H-NMR Spectrum (400 MHz, $CDCl_3$) of **1g**

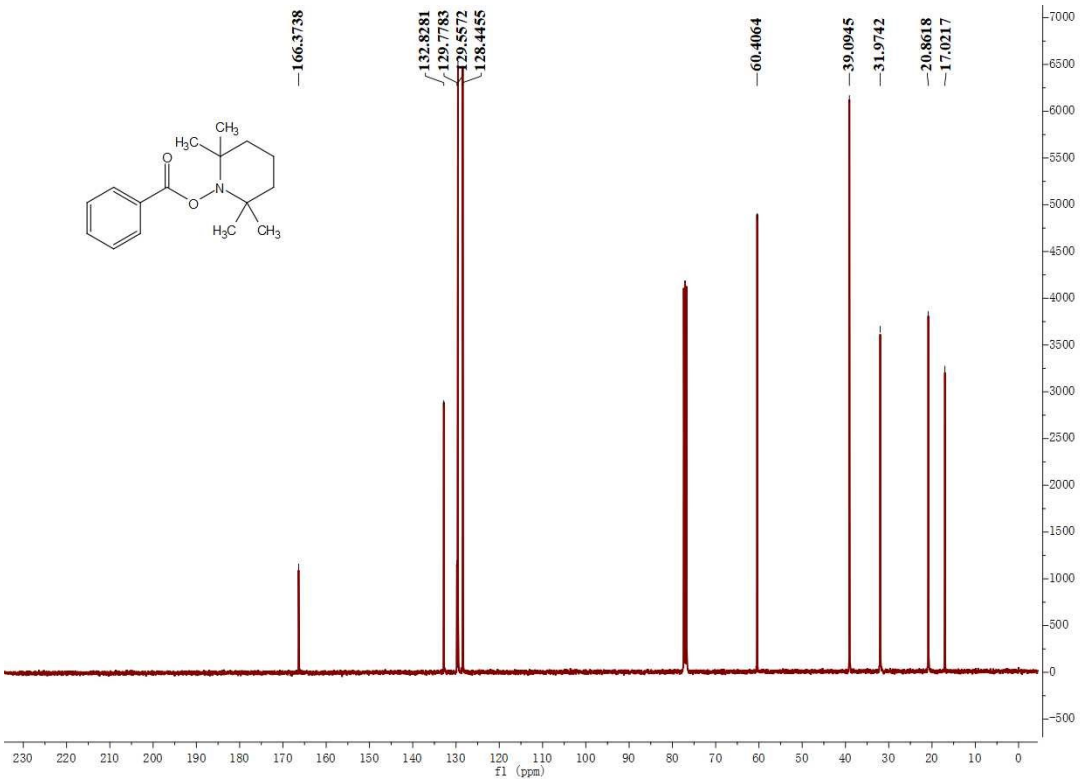
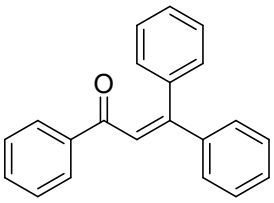


Figure S2. ^{13}C-NMR Spectrum (101 MHz, $CDCl_3$) of **1g**



1,3,3-Triphenylprop-2-en-1-one (**1h**)[2]: R_f = 0.25 (Petroleum ether/EtOAc, 50:1). 17.9 mg, 11% yield. Yellow liquid. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.72 – 7.70 (m, 2H), 7.30 – 7.25 (m, 1H), 7.21 – 7.15 (m, 7H), 7.08 – 7.05 (m, 3H), 7.00 – 6.97 (m, 2H), 6.92 (s, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 192.7, 154.7, 141.4, 139.0, 138.3, 132.6, 132.5, 129.8, 129.3, 128.8, 128.6, 128.5, 128.4, 128.1, 124.1.

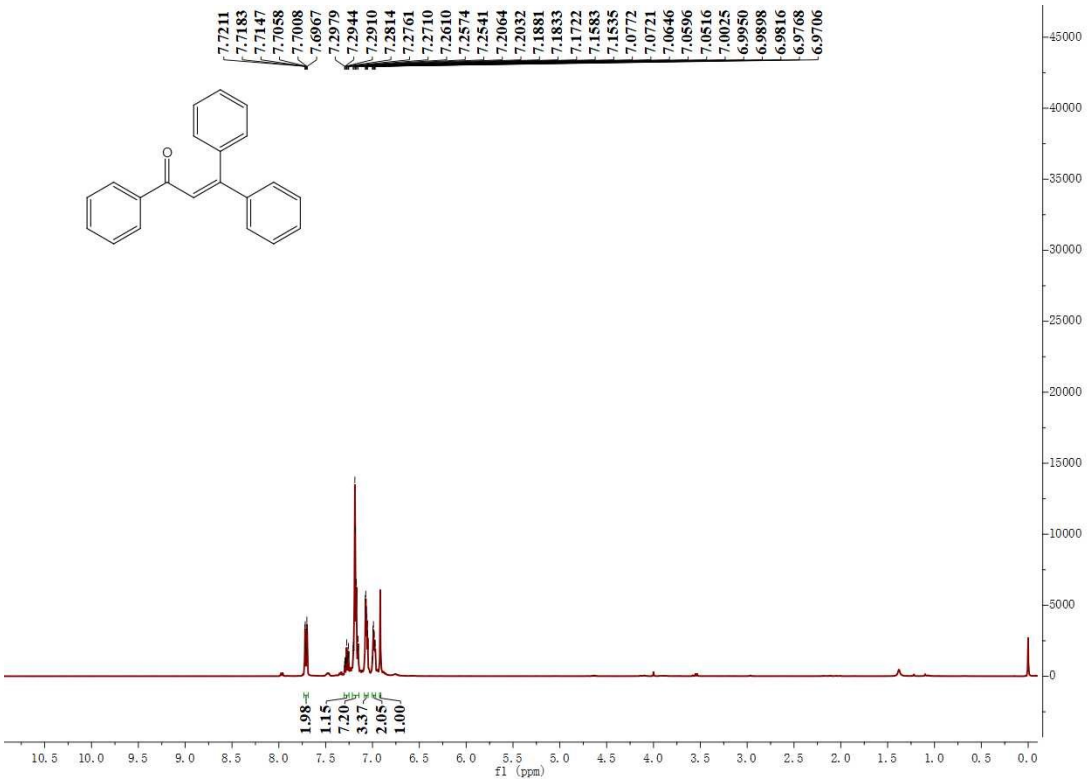


Figure S3. ^{1}H-NMR Spectrum (400 MHz, $CDCl_3$) of **1h**

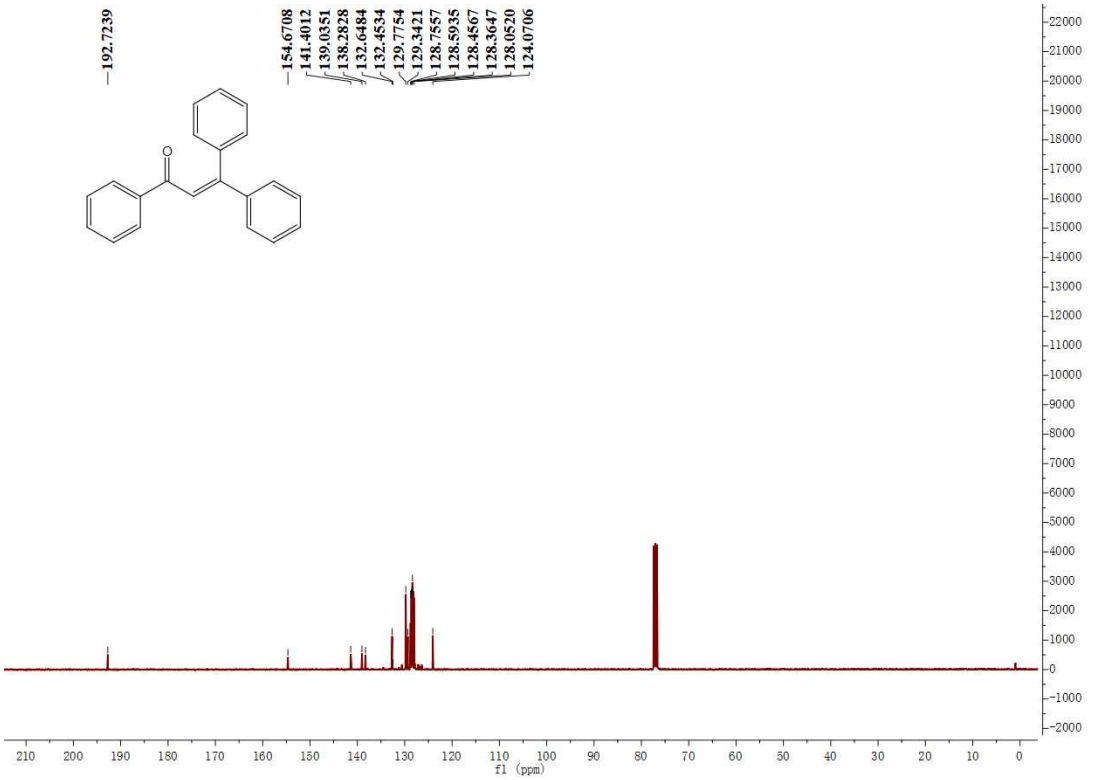


Figure S4. ^{13}C-NMR Spectrum (101 MHz, $CDCl_3$) of **1h**

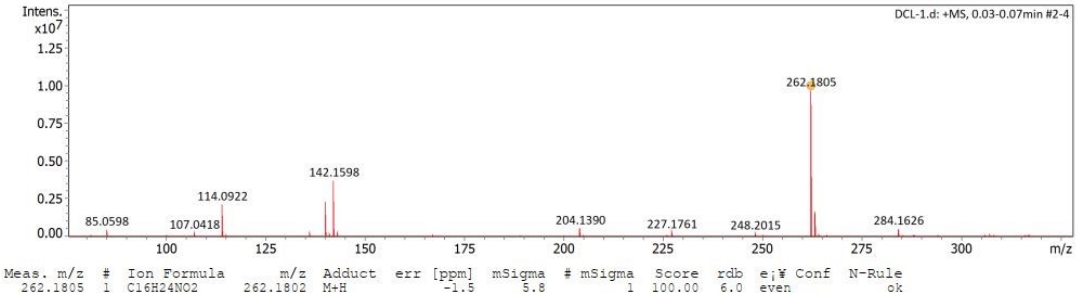


Figure S5. Mass spectrometry (HRMS) data of the radical trapping experiments (with TEMPO)

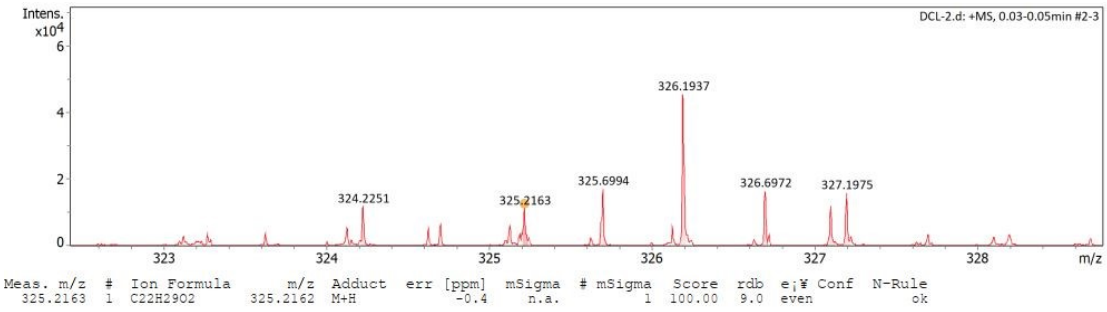


Figure S6. Mass spectrometry (HRMS) data of the radical trapping experiments (with BHT)

4.2 Emission spectrum of the LED light

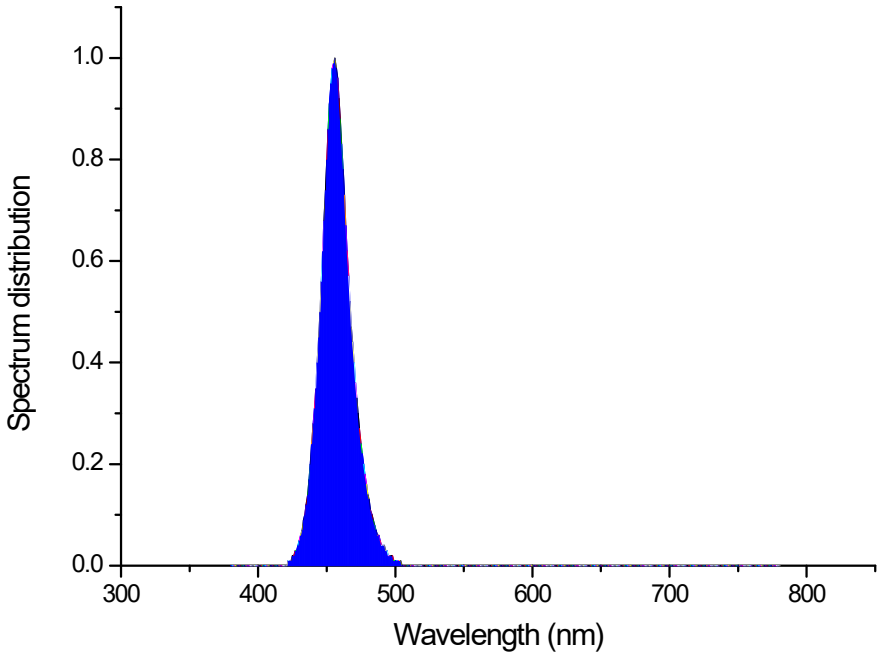


Figure S7. Spectrum distribution of light source.

Table S8. The detail information of light source.

Chromaticity Coordinates	x=0.1459 y=0.0367 u=0.1854 v=0.1050		
Correlated Color Temperature	>25000 K	Peak wavelength	457 nm
SDCM	0	Main wavelength	460 nm
Color Shift	0.000000 duv	Half-width of spectrum	0 nm
Red Ratio	0	Color purity	98.00%
Luminous Flux	2.680e^2 lux	Radiant flux	5.7560e^3 W/m^2
Color Rendering Index	Ra=50.0 R1=14.0 R2=49.0 R3=99.0 R4=89.0 R5=0.0 R6=61.0 R7=54.0 R8=40.0 R9=99.0 R10=99.0 R11=99.0 R12=99.0 R13=35.0 R14=34.0		

4.3 The UV-Vis absorption spectrum

UV-Vis absorption spectra were collected on UV-2600 (SHIMADZU). All samples were dissolved in toluene. The UV-Vis absorption of *fac*-Ir(ppy)$_3$ (0.003 M), **1a** (0.1 M), **1b** (0.3

M), **c** (0.3 M), CuOAc (0.005 M) were showed in the figure below.

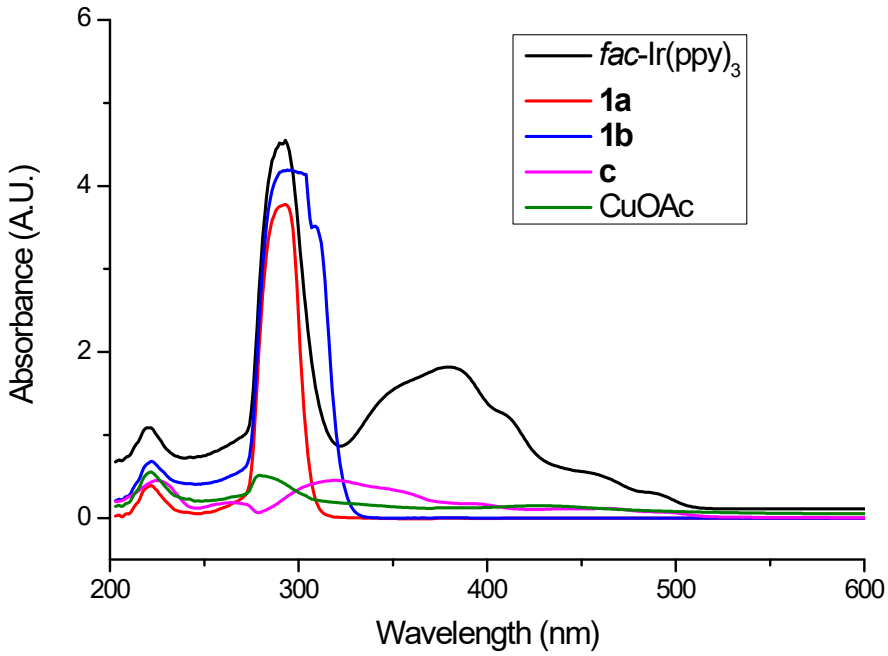


Figure S8. The UV-Vis absorption spectrum.

4.4 Fluorescence quenching experiments

The quenching of *fac*-Ir(ppy)$_3^*$ by 4-methylstyrene **1a**, benzoyl chloride **1b**, TMSCN **c** were carried out in THF separately (Figures S9-S14). The results revealed that **1b** could significantly quench *fac*-Ir(ppy)$_3^*$, and other components did not display obvious quenching ability to *fac*-Ir(ppy)$_3^*$ (excitation wavelength 452 nm; emission wavelength 513 nm).

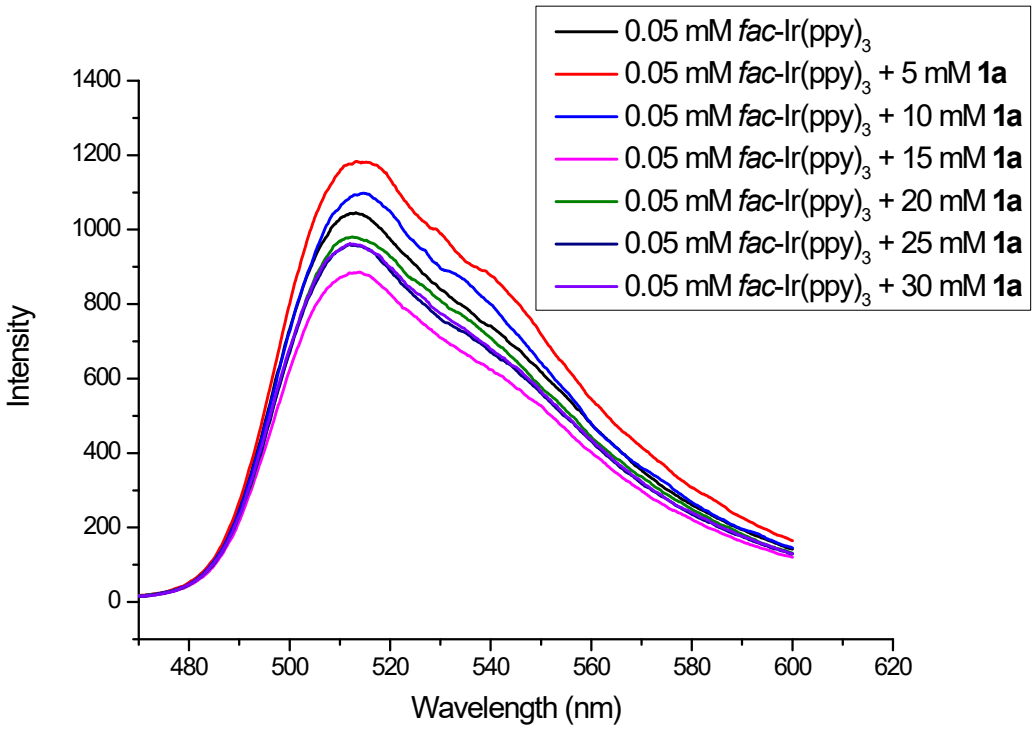


Figure S9. Fluorescence quenching of 0.05 mM *fac*-Ir(ppy)$_3$ (in THF) by increasing concentration of **1a**.

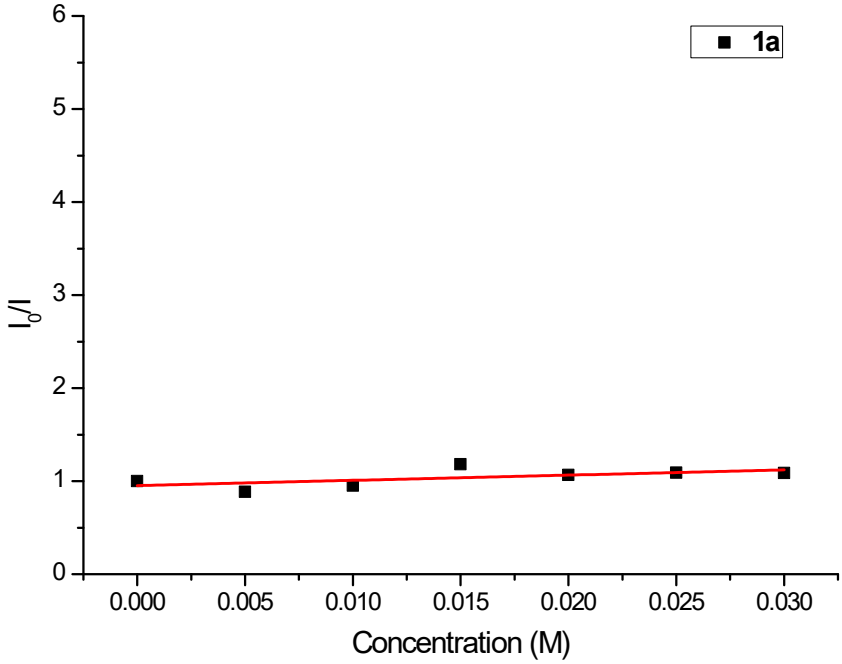


Figure S10. Stern–Volmer plots of fluorescence quenching of 0.05 mM *fac*-Ir(ppy)$_3$ (in THF) by **1a**.

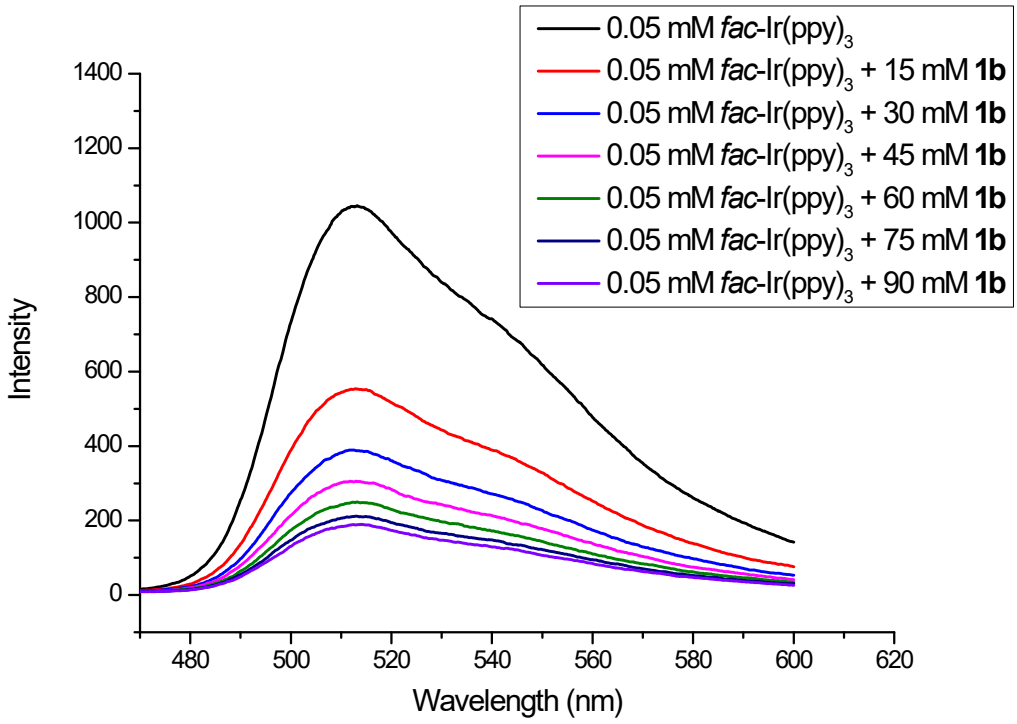


Figure S11. Fluorescence quenching of 0.05 mM *fac*-Ir(ppy)$_3$ (in THF) by increasing concentration of **1b**.

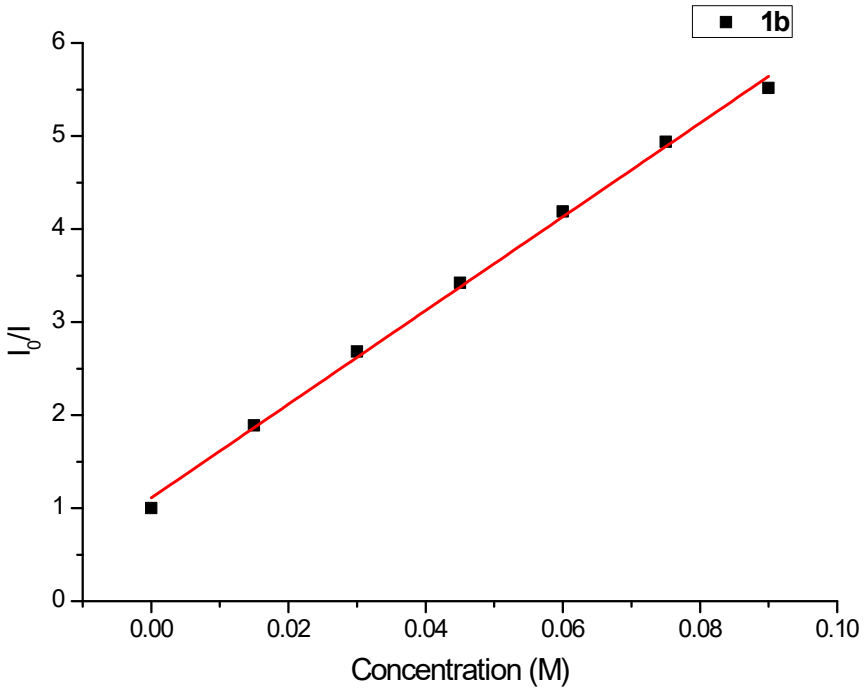


Figure S12. Stern–Volmer plots of fluorescence quenching of 0.05 mM *fac*-Ir(ppy)$_3$ (in THF) by **1b**.

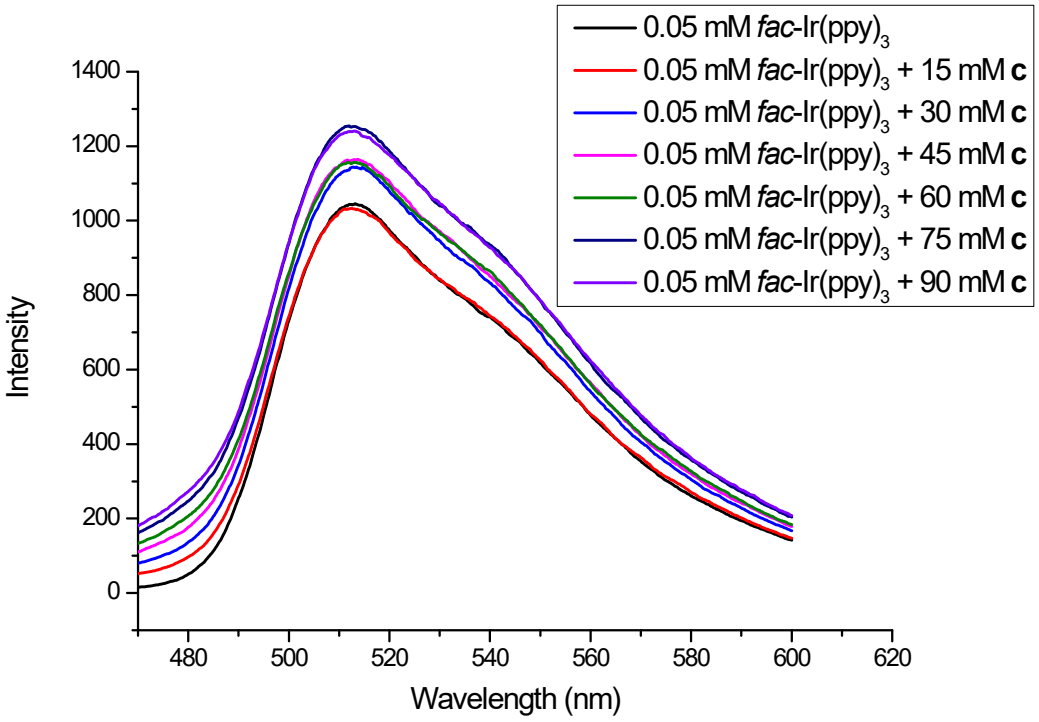


Figure S13. Fluorescence quenching of 0.05 mM *fac*-Ir(ppy)$_3$ (in THF) by increasing concentration of **c**.

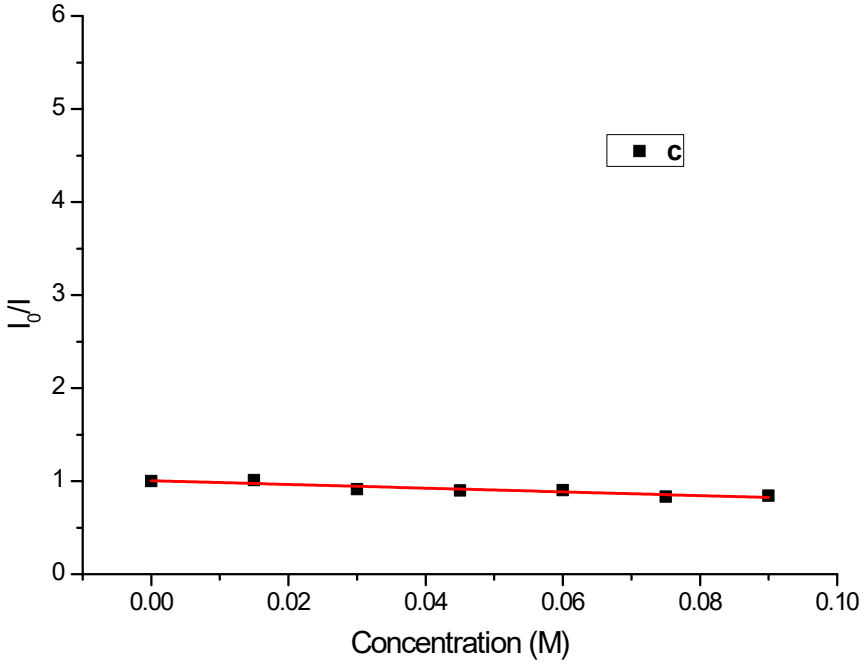


Figure S14. Stern–Volmer plots of fluorescence quenching of 0.05 mM *fac*-Ir(ppy)$_3$ (in THF) by **c**.

4.5 Cyclic voltammetry experiments

The cyclic voltammetry experiments were performed separately. The reduction potential of **1a**, **1b**, **c** and CuOAc/**L4** were determined as: **1a** (E_{red} = -2.42 V *vs* SCE in MeCN), **1b** (E_{red} = -1.15 V *vs* SCE in MeCN), **c** (E_{red} = -2.07 V *vs* SCE in MeCN) (Figure S15), **L4** (E_{red} = -1.91 V *vs* SCE in MeCN), CuOAc/**L4** (E_{red} = -1.91 V *vs* SCE in MeCN) (Figure S16), while the reduction peak of CuOAc were not detected obviously. The data indicated that **1b** can be reduced by the excited *fac*-Ir(ppy)$_3^*$ (E^*_{ox} = -1.73 V *vs* SCE in MeCN).[3] The electrochemical measurements were carried out by a computer-controlled electrochemical analyzer. Cyclic voltammetry was performed in a three-electrode cell (volume 10 mL; MeCN as solvent, nBu$_4$N$^+$ClO$_4^-$ 0.05 M as the supporting electrolyte, 10 mM concentration of **1a**, **1b** and **c**, 1.0 mM concentration of CuOAc and 2.0 mM concentration of **L4**) with glassy carbon (diameter 3 mm) as the working electrode, Pt wire as the auxiliary electrode, and saturated calomel electrode (SCE) (3 M KCl) as the reference electrode. The scan speed was 100 mV·s^{-1}. The potential ranges investigated for reductions of reaction components and blank were 0.0 to -3.0 V *vs* SCE (3 M KCl). As shown below, E_{red} of **1b** was determined to be -1.15 V *vs* SCE (in MeCN), which suggest that single electron reduction of **1b** by the excited *fac*-Ir(ppy)$_3^*$ is feasible (E^*_{ox} = -1.73 V *vs* SCE in MeCN).[3]

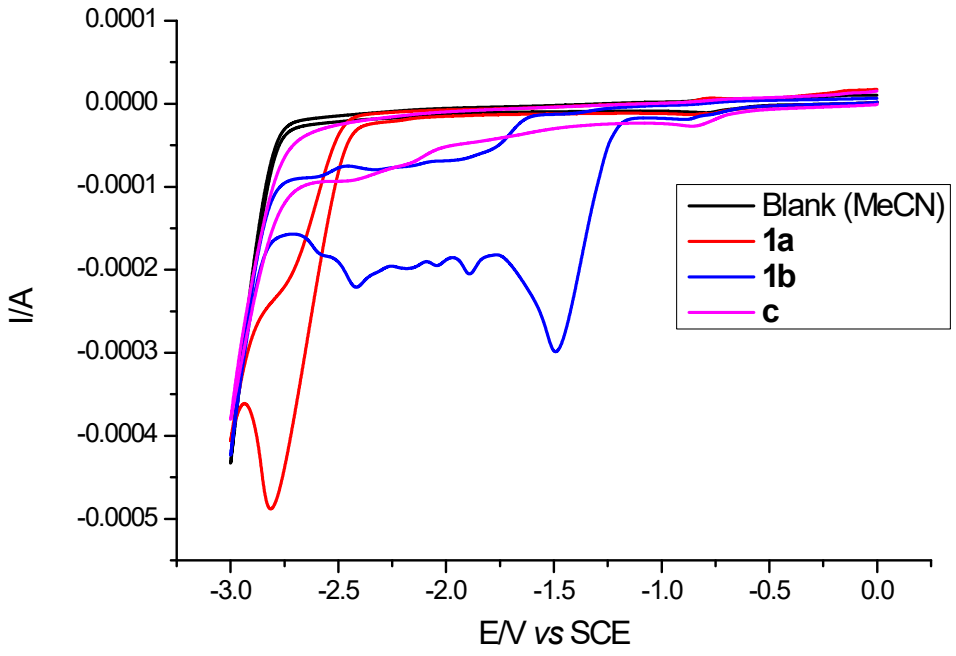


Figure S15. Cyclic voltammetry (CV) of 4-methylstyrene **1a,** benzoyl chloride **1b**, TMSCN **c** and MeCN.

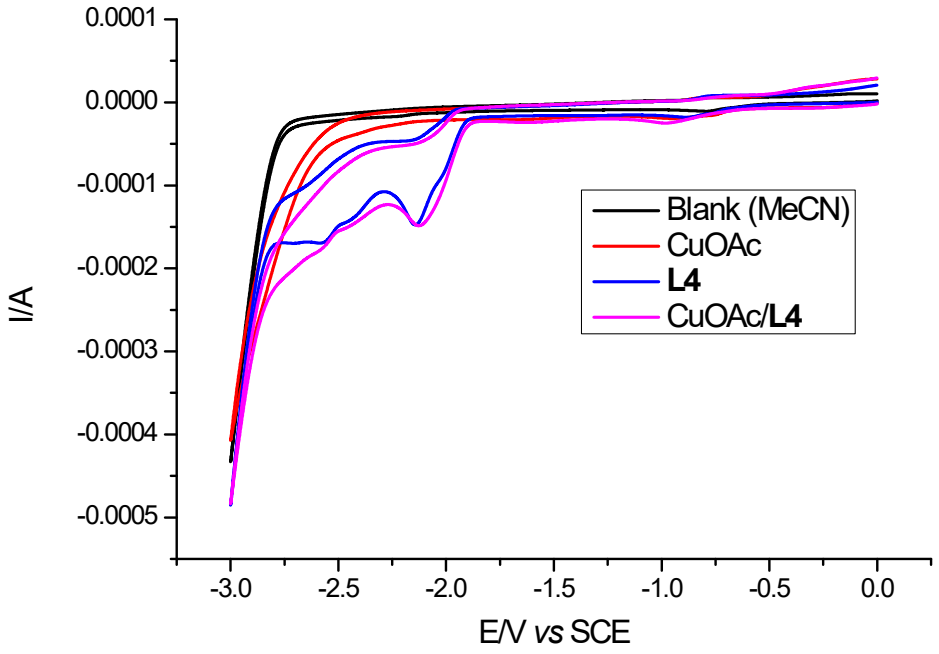


Figure S16. Cyclic voltammetry (CV) of CuOAc**, L4**, CuOAc/**L4** and MeCN.

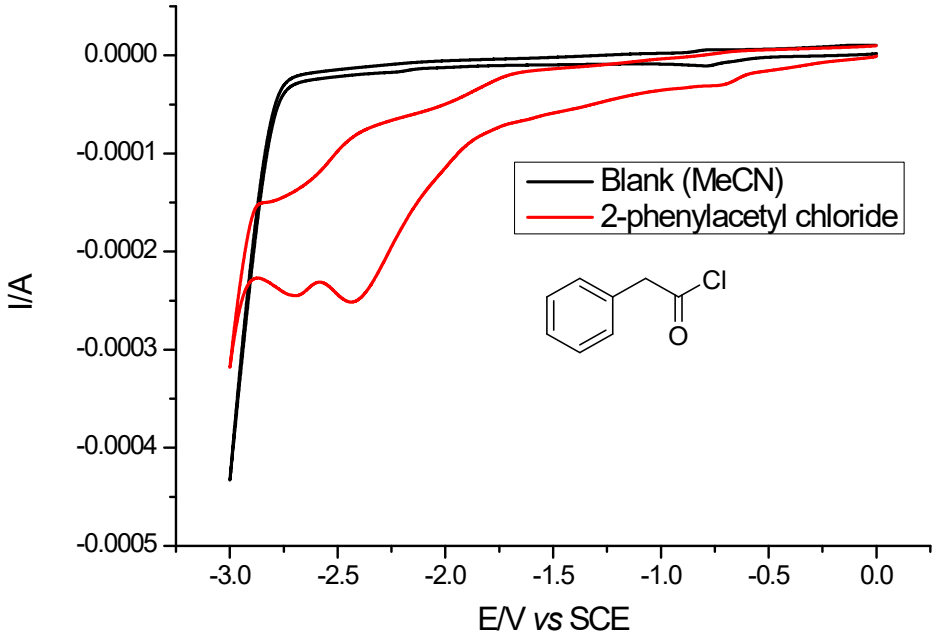


Figure S17. Cyclic voltammetry (CV) of 2-phenylacetyl chloride.

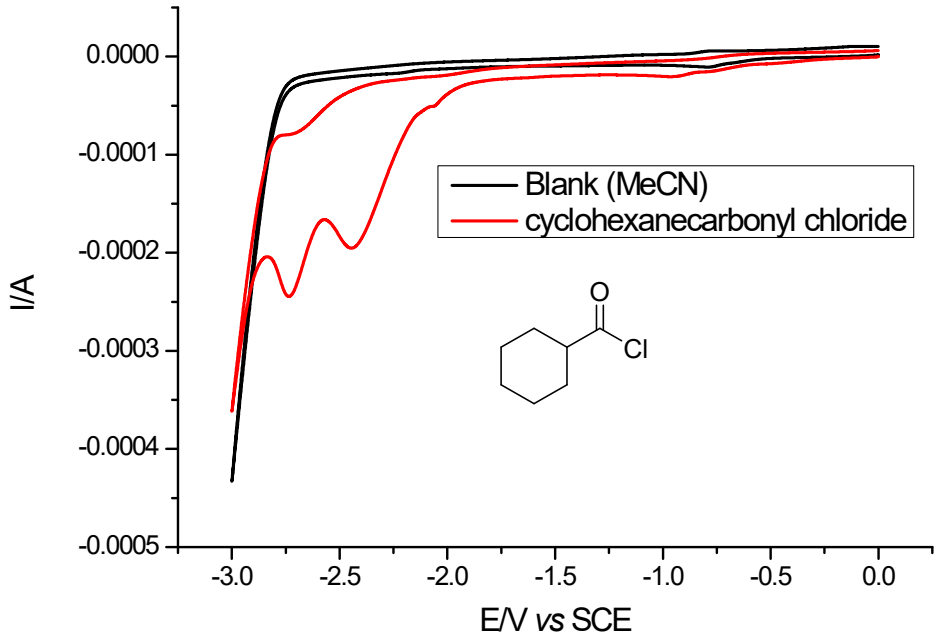
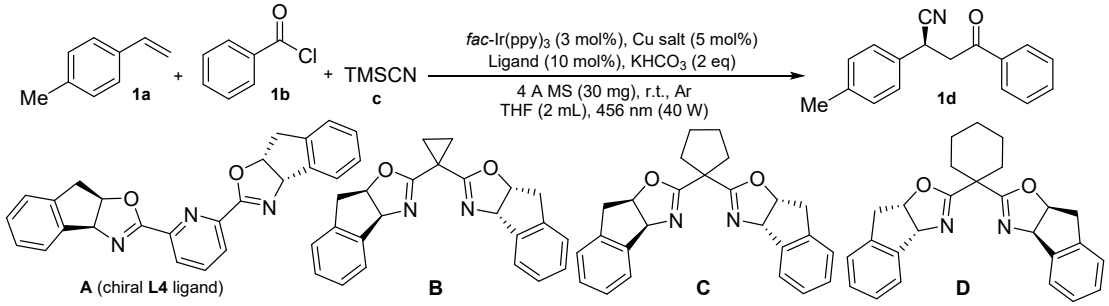


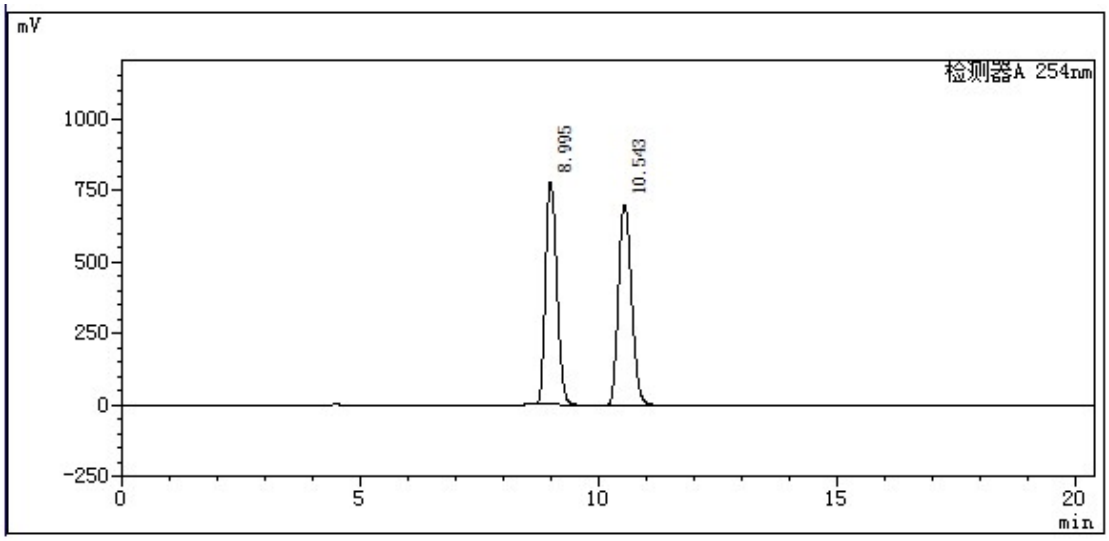
Figure S18. Cyclic voltammetry (CV) of cyclohexanecarbonyl chloride.

5. The enantioselective acylcyanation of 4-methylstyrene 1a[a]



Entry	Cu salts	Ligand	Yield (%)[b]	Ee (%)[c]
1	CuOAc	**A**	80	4
2	$Cu(MeCN)_4BF_4$	**A**	55	3
3[d]	CuOAc	**A**	79	1
4	CuOAc	**B**	16	86
5	$Cu(MeCN)_4BF_4$	**B**	27	83
6	CuCl	**B**	11	87
7[d]	CuCl	**B**	18	81
8	CuOAc	**C**	13	83
9	$Cu(MeCN)_4BF_4$	**C**	15	80
10	$Cu(MeCN)_4BF_4$	**D**	5	-45

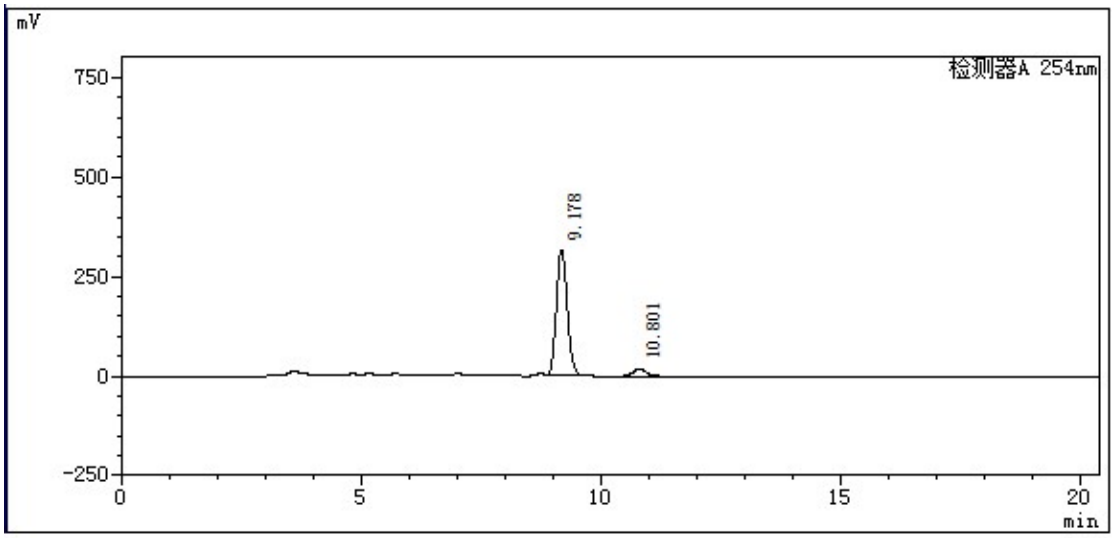
[a]Unless otherwise noted, conditions: **1a** (0.2 mmol, 1.0 equiv), **1b** (0.6 mmol, 3 equiv), **c** (0.6 mmol, 3.0 equiv), *fac*-Ir(ppy)$_3$ (0.006 mmol, 3 mol%), Cu salt (0.01 mmol, 5 mol%), ligand (0.02 mmol, 10 mol%), $KHCO_3$ (0.4 mmol, 2 equiv) and 4Å MS powder (30 mg) in THF (2 mL) irradiated with 40 W 456 nm Kessil Tuna blue lamp under Ar atmosphere (Ar balloon) at room temperature. [b]Isolated yield. [c]Determined by HPLC analysis with a chiral column (Daicel Chiralpak OD-H, hexane/isopropanol = 70:30, flow rate 1.0 mL/min, λ = 254 nm) and the absolute configuration of products **1d** was assigned by comparison with reported chiral HPLC analysis. [d]Toluene instead of THF.



检测器A 254nm

No.	Retention Time	Area	Height	Concentration
1	8.995	12737850	773837	48.601
2	10.543	13471384	698104	51.399
总计		26209234	1471941	

Figure S19. HPLC of **1d** (racemate)

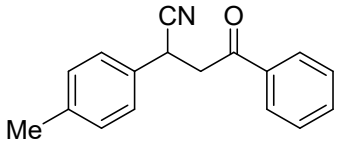


检测器A 254nm

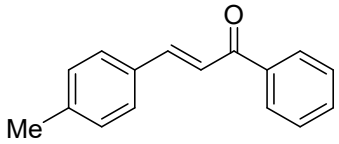
No.	Retention Time	Area	Height	Concentration
1	9.178	4898346	313899	93.251
2	10.801	354538	19550	6.749
总计		5252884	333448	

Figure S20. HPLC of **1d** (chiral)

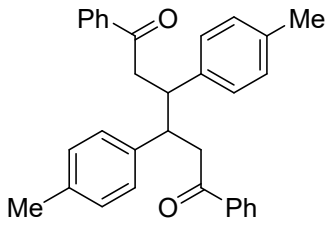
6. Characterization data of the products



4-Oxo-4-phenyl-2-(p-tolyl)butanenitrile (1d)[4]: R_f = 0.25 (Petroleum ether/EtOAc, 15:1). 37.4 mg, 76% yield. White solid. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.91 (d, *J* = 7.4 Hz, 2H), 7.58 (t, *J* = 7.4 Hz, 1H), 7.46 (t, *J* = 7.6 Hz, 2H), 7.31 (d, *J* = 7.7 Hz, 2H), 7.18 (d, *J* = 7.8 Hz, 2H), 4.53 (t, *J* = 6.9 Hz, 1H), 3.69 (dd, *J* = 17.8, 7.8 Hz, 1H), 3.48 (dd, *J* = 17.8, 6.1 Hz, 1H), 2.34 (s, 3H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 194.7, 138.2, 135.9, 133.8, 132.3, 129.9, 128.8, 128.1, 127.3, 120.7, 44.5, 31.6, 21.0.

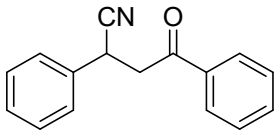


(*E*)-1-Phenyl-3-(p-tolyl)prop-2-en-1-one (1e)[5]: R_f = 0.25 (Petroleum ether/EtOAc, 75:1). Light yellow solid. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.01 – 8.00 (m, 2H), 7.79 (d, *J* = 15.7 Hz, 1H), 7.59 – 7.53 (m, 3H), 7.51 – 7.47 (m, 3H), 7.22 (d, *J* = 7.8 Hz, 2H), 2.39 (s, 3H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 190.7, 144.9, 141.0, 138.5, 132.6, 132.3, 129.7, 128.6, 128.5, 121.3, 21.5.

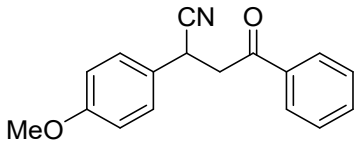


1,6-Diphenyl-3,4-di-p-tolylhexane-1,6-dione (1f): R_f = 0.25 (Petroleum ether/EtOAc, 16:1). White solid. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.65 – 7.63 (m, 4H), 7.46 – 7.43 (m, 2H), 7.32 (t, *J* = 7.8 Hz, 4H), 7.24 (d, *J* = 7.8 Hz, 4H), 7.07 (d, *J* = 7.7 Hz, 4H), 3.64 – 3.63 (m, 2H), 3.26 – 3.22 (m, 2H), 2.92 (dd, *J* = 16.6, 2.3 Hz, 2H), 2.26 (s, 6H). ^{13}C NMR (151 MHz,

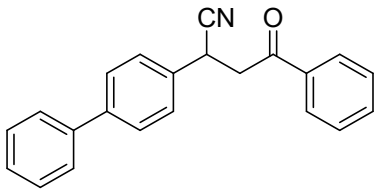
$CDCl_3$) δ 199.0, 139.8, 137.2, 136.3, 132.6, 129.4, 128.3, 128.2, 127.9, 46.7, 44.1, 21.0. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{32}H_{31}O_2$ 447.2319; Found 447.2322.



4-Oxo-2,4-diphenylbutanenitrile (**2d**)[4]: R_f = 0.25 (Petroleum ether/EtOAc, 15:1). 37.0 mg, 79% yield. Yellow solid. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.93 – 7.91 (m, 2H), 7.61 – 7.57 (m, 1H), 7.48 – 7.42 (m, 4H), 7.41 – 7.37 (m, 2H), 7.35 – 7.31 (m, 1H), 4.56 (dd, *J* = 8.0, 5.9 Hz, 1H), 3.73 (dd, *J* = 18.0, 8.0 Hz, 1H), 3.51 (dd, *J* = 17.9, 6.0 Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 194.6, 135.7, 135.3, 133.9, 129.3, 128.8, 128.4, 128.1, 127.5, 120.6, 44.5, 31.9.

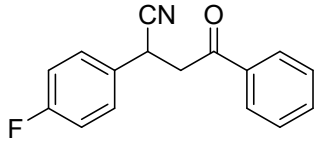


2-(4-Methoxyphenyl)-4-oxo-4-phenylbutanenitrile (**3d**)[4]: R_f = 0.25 (Petroleum ether/EtOAc, 9:1). 26.5 mg, 50% yield. Yellow solid. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.93 – 7.91 (m, 2H), 7.61 – 7.59 (m, 1H), 7.48 – 7.45 (m, 2H), 7.36 – 7.33 (m, 2H), 6.92 – 6.88 (m, 2H), 4.52 (dd, *J* = 7.7, 6.3 Hz, 1H), 3.80 (s, 3H), 3.69 (dd, *J* = 17.9, 7.7 Hz, 1H), 3.49 (dd, *J* = 17.9, 6.3 Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 194. 8, 159.6, 135.8, 133.9, 128.8, 128.7, 128.1, 127.2, 120.9, 114.6, 55.4, 44.6, 31.2.

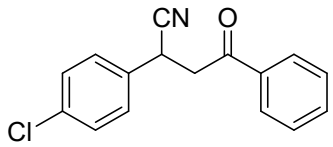


2-([1,1'-Biphenyl]-4-yl)-4-oxo-4-phenylbutanenitrile (**4d**)[6]: R_f = 0.25 (Petroleum ether/EtOAc, 15:1). 39.2 mg, 63% yield. Light yellow solid. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.95 – 7.92 (m, 2H), 7.61 – 7.55 (m, 5H), 7.52 – 7.42 (m, 6H), 7.38 – 7.33 (m, 1H), 4.61 (dd, *J* = 7.8, 6.1 Hz, 1H), 3.75 (dd, *J* = 17.9, 7.8 Hz, 1H), 3.55 (dd, *J* = 17.9, 6.1

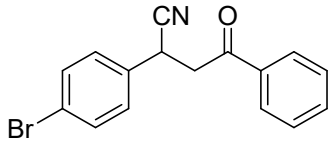
Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 194.6, 141.4, 140.2, 135.7, 134.2, 133.9, 128.9, 128.9, 128.1, 128.0, 127.7, 127.1, 120.6, 44.5, 31.6.



2-(4-Fluorophenyl)-4-oxo-4-phenylbutanenitrile (5d)[4]: R_f = 0.25 (Petroleum ether/EtOAc, 13:1). 37.5 mg, 74% yield. White solid. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.92 (d, *J* = 7.7 Hz, 2H), 7.60 (t, *J* = 7.4 Hz, 1H), 7.47 (t, *J* = 7.7 Hz, 2H), 7.44 – 7.40 (m, 2H), 7.07 (t, *J* = 8.5 Hz, 2H), 4.57 (t, *J* = 6.9 Hz, 1H), 3.71 (dd, *J* = 17.9, 7.4 Hz, 1H), 3.51 (dd, *J* = 17.9, 6.4 Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 194.4, 162.5 (d, *J* = 247.9 Hz), 135.6, 133.9, 131.1 (d, *J* = 3.4 Hz), 129.3 (d, *J* = 8.3 Hz), 128.8, 128.1, 120.5, 116.2 (d, *J* = 21.9 Hz), 44.4, 31.2. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -113.22.

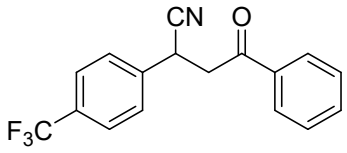


2-(4-Chlorophenyl)-4-oxo-4-phenylbutanenitrile (6d)[4]: R_f = 0.25 (Petroleum ether/EtOAc, 13:1). 36.8 mg, 68% yield. Light yellow solid. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.91 (d, *J* = 7.8 Hz, 2H), 7.60 (t, *J* = 7.4 Hz, 1H), 7.47 (t, *J* = 7.6 Hz, 2H), 7.40 – 7.35 (m, 4H), 4.56 (t, *J* = 6.9 Hz, 1H), 3.71 (dd, *J* = 18.0, 7.4 Hz, 1H), 3.51 (dd, *J* = 17.9, 6.4 Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 194.6, 135.8, 134.7, 134.3, 134.1, 129.7, 129.2, 129.1, 128.3, 120.5, 44.5, 31.6.

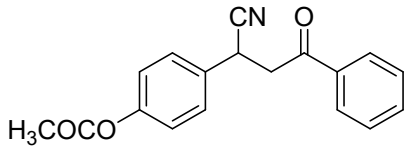


2-(4-Bromophenyl)-4-oxo-4-phenylbutanenitrile (7d)[4]: R_f = 0.25 (Petroleum ether/EtOAc, 11:1). 38.4 mg, 61% yield. Light yellow solid. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.91 (d, *J* = 7.7 Hz, 2H), 7.60 (t, *J* = 7.4 Hz, 1H), 7.52 – 7.45 (m, 4H), 7.32 (d, *J* = 8.1 Hz, 2H), 4.54 (t, *J* = 6.9 Hz, 1H), 3.71 (dd, *J* = 18.0, 7.4 Hz, 1H), 3.50 (dd, *J* = 18.0, 6.4 Hz, 1H). ^{13}C NMR

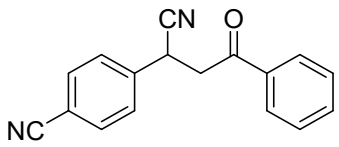
(101 MHz, Chloroform-*d*) δ 194.3, 135.5, 134.3, 134.0, 132.4, 129.3, 128.9, 128.1, 122.5, 120.2, 44.2, 31.4.



4-Oxo-4-phenyl-2-(4-(trifluoromethyl)phenyl)butanenitrile (**8d**)[7]: R_f = 0.25 (Petroleum ether/EtOAc, 10:1). 46.8 mg, 77% yield. Light yellow solid. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.93 – 7.91 (m, 2H), 7.66 (d, *J* = 8.2 Hz, 2H), 7.63 – 7.58 (m, 3H), 7.48 (t, *J* = 7.8 Hz, 2H), 4.66 (t, *J* = 6.8 Hz, 1H), 3.76 (dd, *J* = 18.0, 7.3 Hz, 1H), 3.55 (dd, *J* = 18.0, 6.5 Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 194.1, 139.3, 135.5, 134.1, 130.8 (q, *J* = 32.7 Hz), 128.9, 128.1, 128.1, 126.3 (q, *J* = 3.8 Hz), 123.7 (q, *J* = 272.2 Hz), 119.9, 44.2, 31.7. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -62.77.

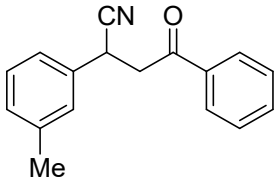


4-(1-Cyano-3-oxo-3-phenylpropyl)phenyl acetate (**9d**)[6]: R_f = 0.25 (Petroleum ether/EtOAc, 2:1). 46.9 mg, 80% yield. Light yellow solid. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.91 (d, *J* = 7.7 Hz, 2H), 7.59 (t, *J* = 7.4 Hz, 1H), 7.49 – 7.44 (m, 4H), 7.12 (d, *J* = 8.3 Hz, 2H), 4.59 – 4.56 (m, 1H), 3.72 (dd, *J* = 18.0, 7.8 Hz, 1H), 3.50 (dd, *J* = 18.0, 6.0 Hz, 1H), 2.30 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 194.5, 169.2, 150.6, 135.6, 134.0, 132.8, 128.9, 128.7, 128.1, 122.5, 120.4, 44.5, 31.4, 21.1.

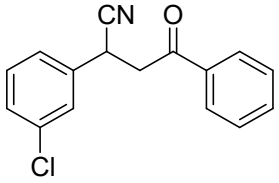


4-(1-Cyano-3-oxo-3-phenylpropyl)benzonitrile (**10d**): R_f = 0.25 (Petroleum ether/EtOAc, 5:1). 25.4 mg, 49% yield. White solid. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.93 – 7.90 (m, 2H), 7.71 – 7.68 (m, 2H), 7.64 – 7.58 (m, 3H), 7.51 – 7.46 (m, 2H), 4.68 – 4.64 (m, 1H), 3.80 – 3.73 (m, 1H), 3.59 – 3.52 (m, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 193.9, 140.4,

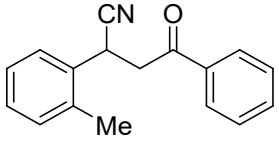
135.3, 134.2, 133.0, 129.0, 128.6, 128.1, 119.5, 118.0, 112.6, 43.9, 31.9. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{17}H_{12}N_2ONa$ 283.0842; Found 283.0847.



4-Oxo-4-phenyl-2-(m-tolyl)butanenitrile (11d)[6]: R_f = 0.25 (Petroleum ether/EtOAc, 16:1). 31.4 mg, 63% yield. Light yellow solid. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.94 – 7.91 (m, 2H), 7.61 – 7.57 (m, 1H), 7.48 – 7.44 (m, 2H), 7.29 – 7.20 (m, 3H), 7.14 (d, *J* = 7.4 Hz, 1H), 4.52 (dd, *J* = 8.1, 5.8 Hz, 1H), 3.71 (dd, *J* = 17.9, 8.2 Hz, 1H), 3.48 (dd, *J* = 17.9, 5.8 Hz, 1H), 2.36 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 194.7, 139.2, 135.8, 135.2, 133.9, 129.2, 129.1, 128.8, 128.1, 128.1, 124.5, 120.7, 44.6, 31.8, 21.4.

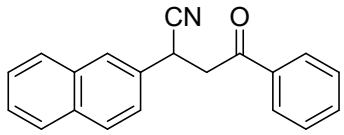


2-(3-Chlorophenyl)-4-oxo-4-phenylbutanenitrile (12d)[8]: R_f = 0.25 (Petroleum ether/EtOAc, 15:1). 36.4 mg, 68% yield. Light yellow solid. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.94 – 7.91 (m, 2H), 7.62 – 7.58 (m, 1H), 7.50 – 7.44 (m, 3H), 7.35 – 7.31 (m, 3H), 4.56 (dd, *J* = 7.6, 6.1 Hz, 1H), 3.73 (dd, *J* = 18.0, 7.6 Hz, 1H), 3.51 (dd, *J* = 18.0, 6.2 Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 194.2, 137.2, 135.5, 135.1, 134.0, 130.5, 128.9, 128.7, 128.1, 127.8, 125.8, 120.1, 44.3, 31.5.

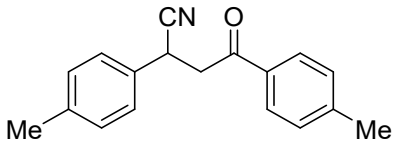


4-Oxo-4-phenyl-2-(o-tolyl)butanenitrile (13d)[6]: R_f = 0.25 (Petroleum ether/EtOAc, 16:1). 18.4 mg, 37% yield. Light yellow liquid. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.96 – 7.93 (m, 2H), 7.63 – 7.58 (m, 1H), 7.51 – 7.46 (m, 3H), 7.27 – 7.25 (m, 2H), 7.23 – 7.20 (m, 1H),

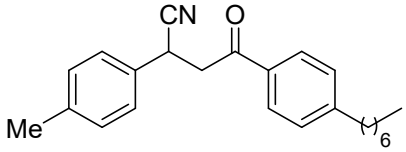
4.71 (dd, *J* = 9.0, 5.0 Hz, 1H), 3.74 (dd, *J* = 18.0, 9.1 Hz, 1H), 3.42 (dd, *J* = 18.0, 5.0 Hz, 1H), 2.42 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 194.8, 135.7, 135.3, 133.9, 133.4, 131.3, 128.9, 128.5, 128.1, 127.5, 127.0, 120.7, 43.1, 28.8, 19.3.



2-(Naphthalen-2-yl)-4-oxo-4-phenylbutanenitrile (**14d**)[4]: R_f = 0.25 (Petroleum ether/EtOAc, 12:1). 35.2 mg, 62% yield. Light yellow solid. m. p. 122-123 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.93 – 7.91 (m, 3H), 7.88 – 7.82 (m, 3H), 7.60 – 7.56 (m, 1H), 7.52 – 7.43 (m, 5H), 4.74 (dd, *J* = 7.9, 5.9 Hz, 1H), 3.80 (dd, *J* = 17.9, 7.9 Hz, 1H), 3.59 (dd, *J* = 17.9, 6.0 Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 194.6, 135.7, 133.9, 133.3, 132.9, 132.6, 129.3, 128.9, 128.1, 127.9, 127.7, 126.8, 126.8, 126.7, 124.8, 120.7, 44.5, 32.1.

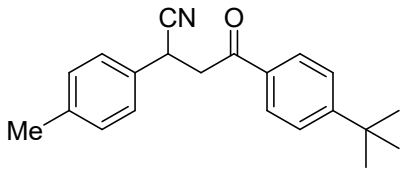


4-Oxo-2,4-di-p-tolylbutanenitrile (**15d**)[9]: R_f = 0.25 (Petroleum ether/EtOAc, 20:1). 39.7 mg, 75% yield. Yellow solid. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.82 – 7.81 (m, 2H), 7.31 (d, *J* = 8.0 Hz, 2H), 7.26 – 7.25 (m, 3H), 7.18 (d, *J* = 7.7 Hz, 2H), 4.52 (dd, *J* = 7.9, 6.1 Hz, 1H), 3.67 (dd, *J* = 17.8, 7.9 Hz, 1H), 3.45 (dd, *J* = 17.8, 6.1 Hz, 1H), 2.41 (s, 3H), 2.34 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 194.3, 144.8, 138.2, 133.3, 132.4, 129.9, 129.5, 128.2, 127.4, 120.9, 44.4, 31.6, 21.7, 21.1.

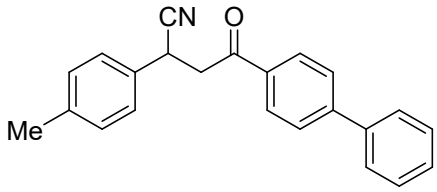


4-(4-Heptylphenyl)-2-(4-methoxyphenyl)-4-oxobutanenitrile (**16d**): R_f = 0.25 (Petroleum ether/EtOAc, 33:1). 45.8 mg, 69% yield. Yellow liquid. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.86 (d, *J* = 7.8 Hz, 2H), 7.34 (d, *J* = 7.6 Hz, 2H), 7.29 – 7.28 (m, 2H), 7.21 (d, *J* = 7.7 Hz, 2H), 4.56 (t, *J* = 7.0 Hz, 1H), 3.70 (dd, *J* = 17.8, 7.8 Hz, 1H), 3.49 (dd, *J* = 17.8, 6.1 Hz, 1H), 2.68 (t, *J* = 7.7 Hz, 2H), 2.37 (s, 3H), 1.66 – 1.63 (m, 2H), 1.35 – 1.28 (m, 8H), 0.91 (t, *J* =

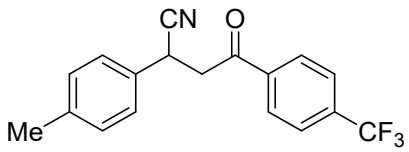
6.9 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 194.3, 149.8, 138.2, 133.5, 132.4, 129.9, 128.8, 128.2, 127.4, 120.9, 44.4, 36.0, 31.7, 31.6, 31.0, 29.2, 29.1, 22.6, 21.0, 14.0. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{24}H_{30}NO$ 348.2322; Found 348.2322.



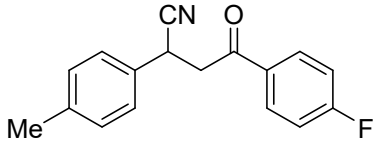
4-(4-(Tert-butyl)phenyl)-2-(4-methoxyphenyl)-4-oxobutanenitrile (**17d**): R_f = 0.25 (Petroleum ether/EtOAc, 25:1). 36.6 mg, 60% yield. Yellow liquid. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.87 – 7.84 (m, 2H), 7.49 – 7.46 (m, 2H), 7.32 – 7.30 (m, 2H), 7.18 (d, *J* = 7.9 Hz, 2H), 4.54 (dd, *J* = 7.7, 6.2 Hz, 1H), 3.67 (dd, *J* = 17.8, 7.7 Hz, 1H), 3.47 (dd, *J* = 17.8, 6.2 Hz, 1H), 2.34 (s, 3H), 1.33 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 194.3, 157.8, 138.2, 133.3, 132.4, 129.9, 128.1, 127.4, 125.8, 120.9, 44.4, 35.2, 31.5, 31.0, 21.0. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{21}H_{23}NONa$ 328.1672; Found 328.1670.



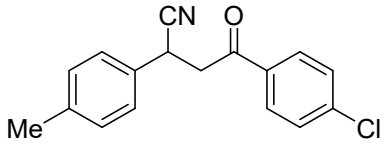
4-([1,1'-Biphenyl]-4-yl)-2-(4-methoxyphenyl)-4-oxobutanenitrile (**18d**): R_f = 0.25 (Petroleum ether/EtOAc, 15:1). 33.8 mg, 52% yield. Yellow solid. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.00 – 7.98 (m, 2H), 7.70 – 7.67 (m, 2H), 7.62 – 7.60 (m, 2H), 7.49 – 7.44 (m, 2H), 7.43 – 7.38 (m, 1H), 7.36 – 7.32 (m, 2H), 7.20 (d, *J* = 7.9 Hz, 2H), 4.55 (dd, *J* = 7.9, 6.1 Hz, 1H), 3.73 (dd, *J* = 17.8, 7.9 Hz, 1H), 3.51 (dd, *J* = 17.8, 6.1 Hz, 1H), 2.35 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 194.3, 146.6, 139.6, 138.3, 134.5, 132.3, 129.9, 129.0, 128.7, 128.5, 127.4, 127.4, 127.3, 120.8, 44.6, 31.6, 21.1. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{23}H_{20}NO$ 326.1539; Found 326.1538.



2-(4-Methoxyphenyl)-4-oxo-4-(4-(trifluoromethyl)phenyl)butanenitrile (**19d**): R_f = 0.25 (Petroleum ether/EtOAc, 22:1). 37.1 mg, 59% yield. Light yellow solid. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.02 (d, *J* = 8.1 Hz, 2H), 7.73 (d, *J* = 8.1 Hz, 2H), 7.31 (d, *J* = 7.8 Hz, 2H), 7.20 (d, *J* = 7.8 Hz, 2H), 4.51 (dd, *J* = 8.0, 5.9 Hz, 1H), 3.72 (dd, *J* = 17.9, 7.8 Hz, 1H), 3.50 (dd, *J* = 18.0, 5.8 Hz, 1H), 2.35 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 193.9, 138.5, 138.4, 135.1 (q, *J* = 32.9 Hz), 131.9, 130.0, 128.5, 127.3, 125.91 (q, *J* = 3.7 Hz), 123.4 (q, *J* = 272.8 Hz), 120.5, 44.8, 31.5, 21.0. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -63.26. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{18}H_{14}F_3NONa$ 340.0920; Found 340.0920.

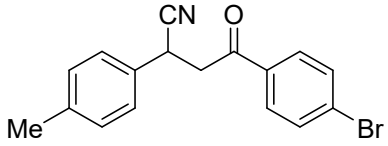


4-(4-Fluorophenyl)-2-(4-methoxyphenyl)-4-oxobutanenitrile (**20d**): R_f = 0.25 (Petroleum ether/EtOAc, 20:1). 33.1 mg, 62% yield. White liquid. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.96 - 7.94 (m, 2H), 7.30 (d, *J* = 7.7 Hz, 2H), 7.19 (d, *J* = 7.8 Hz, 2H), 7.13 (t, *J* = 8.5 Hz, 2H), 4.51 (t, *J* = 6.9 Hz, 1H), 3.67 (dd, *J* = 17.8, 8.0 Hz, 1H), 3.45 (dd, *J* = 17.8, 5.9 Hz, 1H), 2.34 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 193.2, 166.2 (d, *J* = 256.3 Hz), 138.3, 132.2 (d, *J* = 3.0 Hz), 132.1, 130.8 (d, *J* = 9.5 Hz), 129.9, 127.3, 120.7, 116.0 (d, *J* = 22.1 Hz), 44.5, 31.6, 21.1. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -103.54. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{17}H_{14}FNONa$ 290.0952; Found 290.0951.

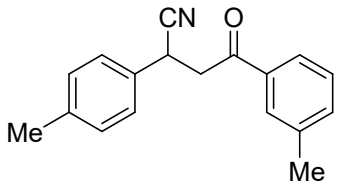


4-(4-Chlorophenyl)-2-(4-methoxyphenyl)-4-oxobutanenitrile (**21d**)[9]: R_f = 0.25 (Petroleum ether/EtOAc, 30:1). 39.8 mg, 70% yield. White solid. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.85 (d, *J* = 8.3 Hz, 2H), 7.43 (d, *J* = 8.8 Hz, 2H), 7.30 (d, *J* = 7.6 Hz, 2H), 7.19 (d, *J* = 7.8 Hz, 2H), 4.50 (dd, *J* = 8.0, 5.9 Hz, 1H), 3.66 (dd, *J* = 17.9, 7.9 Hz, 1H), 3.44 (dd, *J* = 17.9, 5.9 Hz,

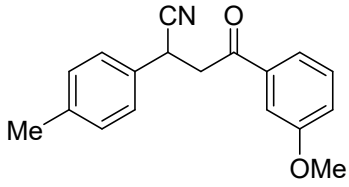
1H), 2.34 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 193.6, 140.4, 138.4, 134.1, 132.1, 130.0, 129.5, 129.2, 127.3, 120.6, 44.5, 31.5, 21.1.



4-(4-Bromophenyl)-2-(4-methoxyphenyl)-4-oxobutanenitrile (**22d**): R_f = 0.25 (Petroleum ether/EtOAc, 20:1). 40.7 mg, 62% yield. Light yellow solid. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.77 (d, *J* = 8.6 Hz, 2H), 7.60 (d, *J* = 8.6 Hz, 2H), 7.30 (d, *J* = 8.1 Hz, 2H), 7.19 (d, *J* = 7.9 Hz, 2H), 4.49 (dd, *J* = 8.0, 6.0 Hz, 1H), 3.66 (dd, *J* = 17.9, 8.0 Hz, 1H), 3.44 (dd, *J* = 17.9, 6.0 Hz, 1H), 2.34 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 193.8, 138.4, 134.5, 132.2, 132.1, 130.0, 129.6, 129.2, 127.3, 120.6, 44.5, 31.5, 21.1. HRMS (ESI) m/z: [M + Na]$^+$ Calcd for $C_{17}H_{14}BrNONa$ 350.0151; Found 350.0149.

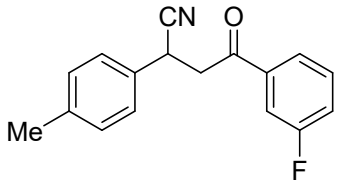


2-(4-Methoxyphenyl)-4-oxo-4-(m-tolyl)butanenitrile (**23d**): R_f = 0.25 (Petroleum ether/EtOAc, 13:1). 38.2 mg, 73% yield. Yellow solid. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.73 – 7.69 (m, 2H), 7.39 (d, *J* = 7.5 Hz, 1H), 7.35 (d, *J* = 7.5 Hz, 1H), 7.31 (d, *J* = 8.1 Hz, 2H), 7.18 (d, *J* = 7.9 Hz, 2H), 4.52 (dd, *J* = 7.9, 6.1 Hz, 1H), 3.68 (dd, *J* = 17.9, 7.9 Hz, 1H), 3.47 (dd, *J* = 17.9, 6.1 Hz, 1H), 2.39 (s, 3H), 2.34 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 194.9, 138.7, 138.2, 135.8, 134.6, 132.4, 129.9, 128.7, 128.6, 127.4, 125.3, 120.8, 44.6, 31.6, 21.3, 21.0. HRMS (ESI) m/z: [M + Na]$^+$ Calcd for $C_{18}H_{17}NONa$ 286.1202; Found 286.1199.

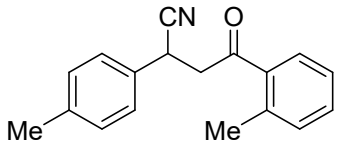


4-(3-Methoxyphenyl)-2-(4-methoxyphenyl)-4-oxobutanenitrile (**24d**): R_f = 0.25

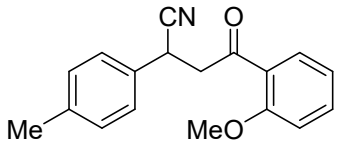
(Petroleum ether/EtOAc, 10:1). 42.5 mg, 76% yield. Light yellow liquid. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.48 – 7.44 (m, 2H), 7.37 – 7.30 (m, 3H), 7.20 – 7.18 (m, 2H), 7.14 – 7.11 (m, 1H), 4.51 (dd, *J* = 7.9, 6.0 Hz, 1H), 3.84 (s, 3H), 3.68 (dd, *J* = 17.9, 7.9 Hz, 1H), 3.47 (dd, *J* = 17.9, 6.1 Hz, 1H), 2.34 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 194.6, 160.0, 138.3, 137.1, 132.3, 129.9, 129.8, 127.4, 120.8, 120.6, 120.4, 112.3, 55.5, 44.6, 31.6, 21.1. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{18}H_{17}NO_2Na$ 302.1151; Found 302.1148.



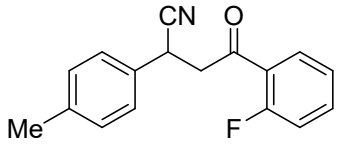
4-(3-Fluorophenyl)-2-(4-methoxyphenyl)-4-oxobutanenitrile (**25d**): R_f = 0.25 (Petroleum ether/EtOAc, 15:1). 37.7 mg, 71% yield. Yellow liquid. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.70 – 7.67 (m, 1H), 7.62 – 7.58 (m, 1H), 7.49 – 7.42 (m, 1H), 7.32 – 7.26 (m, 3H), 7.20 – 7.18 (m, 2H), 4.50 (dd, *J* = 8.0, 6.0 Hz, 1H), 3.67 (dd, *J* = 18.0, 8.0 Hz, 1H), 3.46 (dd, *J* = 18.0, 6.0 Hz, 1H), 2.34 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 193.6 (d, *J* = 2.3 Hz), 162.9 (d, *J* = 248.8 Hz), 138.4, 137.8 (d, *J* = 6.2 Hz), 132.0, 130.6 (d, *J* = 7.7 Hz), 130.0, 127.3, 123.8 (d, *J* = 3.1 Hz), 120.9 (d, *J* = 21.5 Hz), 120.6, 114.9 (d, *J* = 22.5 Hz), 44.7, 31.5, 21.0. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -111.10. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{17}H_{14}FNONa$ 290.0952; Found 290.0951.



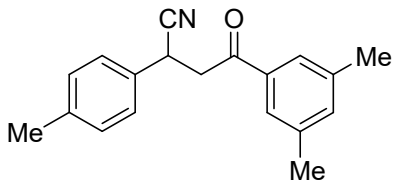
2-(4-Methoxyphenyl)-4-oxo-4-(o-tolyl)butanenitrile (**26d**): R_f = 0.25 (Petroleum ether/EtOAc, 20:1). 33.8 mg, 64% yield. Yellow liquid. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.58 – 7.55 (m, 1H), 7.42 – 7.36 (m, 1H), 7.30 – 7.26 (m, 3H), 7.24 – 7.22 (m, 1H), 7.19 – 7.17 (d, *J* = 7.9 Hz, 2H), 4.50 (dd, *J* = 7.9, 6.3 Hz, 1H), 3.61 (dd, *J* = 17.6, 7.9 Hz, 1H), 3.42 (dd, *J* = 17.6, 6.3 Hz, 1H), 2.49 (s, 3H), 2.34 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 198.1, 139.1, 138.2, 136.2, 132.3, 132.2, 132.2, 129.9, 128.6, 127.4, 125.9, 120.8, 46.9, 31.8, 21.4, 21.1. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{18}H_{17}NONa$ 286.1202; Found 286.1199.



4-(2-Methoxyphenyl)-2-(4-methoxyphenyl)-4-oxobutanenitrile (**27d**): R_f = 0.25 (Petroleum ether/EtOAc, 10:1). 21.6 mg, 39% yield. Yellow solid. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.80 - 7.78 (m, 1H), 7.51 – 7.48 (m, 1H), 7.29 (d, *J* = 7.9 Hz, 2H), 7.18 (d, *J* = 7.9 Hz, 2H), 7.01 (t, *J* = 7.7 Hz, 1H), 6.96 (d, *J* = 8.4 Hz, 1H), 4.52 (dd, *J* = 7.8, 6.3 Hz, 1H), 3.89 (s, 3H), 3.73 (dd, *J* = 18.3, 7.8 Hz, 1H), 3.52 (dd, *J* = 18.3, 6.3 Hz, 1H), 2.34 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 196.3, 159.1, 137.9, 134.5, 132.7, 130.9, 129.8, 127.4, 126.5, 120.9, 111.6, 55.6, 49.4, 31.8, 21.0. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{18}H_{18}NO_2$ 280.1332; Found 280.1332.

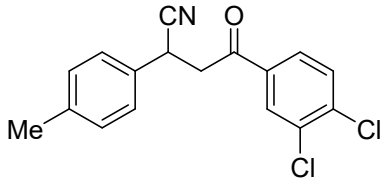


4-(2-Fluorophenyl)-2-(4-methoxyphenyl)-4-oxobutanenitrile (**28d**): R_f = 0.25 (Petroleum ether/EtOAc, 18:1). 36.3 mg, 68% yield. Light yellow solid. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.95 – 7.90 (m, 1H), 7.58 – 7.53 (m, 1H), 7.32 – 7.30 (m, 2H), 7.27 – 7.23 (m, 1H), 7.19 (d, *J* = 7.9 Hz, 2H), 7.16 – 7.11 (m, 1H), 4.50 (dd, *J* = 8.3, 5.8 Hz, 1H), 3.74 – 3.67 (m, 1H), 3.53 – 3.46 (m, 1H), 2.34 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 192.9 (d, *J* = 4.1 Hz), 162.3 (d, *J* = 254.9 Hz), 138.2, 135.5 (d, *J* = 9.2 Hz), 132.2, 130.9 (d, *J* = 2.3 Hz), 129.9, 127.4, 124.8 (d, *J* = 3.3 Hz), 124.2 (d, *J* = 12.5 Hz), 120.7, 116.8 (d, *J* = 23.8 Hz), 49.1 (d, *J* = 9.0 Hz), 31.5 (d, *J* = 2.8 Hz), 21.1. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -108.53. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{17}H_{14}FNONa$ 290.0952; Found 290.0948.

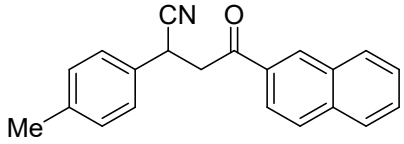


4-(3,5-Dimethylphenyl)-2-(4-methoxyphenyl)-4-oxobutanenitrile (**29d**): R_f = 0.25

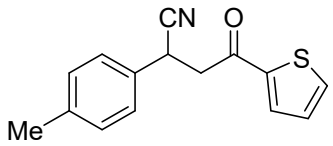
(Petroleum ether/EtOAc, 23:1). 38.2 mg, 69% yield. Yellow liquid. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.52 – 7.52 (m, 2H), 7.32 – 7.30 (m, 2H), 7.21 – 7.17 (m, 3H), 4.51 (dd, *J* = 7.9, 6.1 Hz, 1H), 3.67 (dd, *J* = 17.9, 7.9 Hz, 1H), 3.45 (dd, *J* = 17.9, 6.1 Hz, 1H), 2.35 (s, 6H), 2.34 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 195.0, 138.5, 138.2, 135.9, 135.5, 132.4, 129.9, 127.4, 125.9, 120.9, 44.7, 31.6, 21.2, 21.1. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{19}H_{19}NONa$ 300.1359; Found 300.1363.



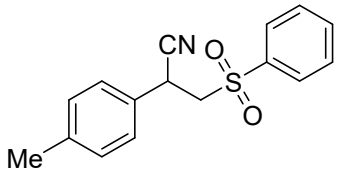
4-(3,4-Dichlorophenyl)-2-(4-methoxyphenyl)-4-oxobutanenitrile (**30d**): R_f = 0.25 (Petroleum ether/EtOAc, 19:1). 35.2 mg, 56% yield. Yellow solid. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.98 (d, *J* = 2.0 Hz, 1H), 7.74 – 7.72 (m, 1H), 7.54 (d, *J* = 8.4 Hz, 1H), 7.31 – 7.28 (m, 2H), 7.19 (d, *J* = 7.9 Hz, 2H), 4.48 (dd, *J* = 8.0, 5.9 Hz, 1H), 3.65 (dd, *J* = 18.0, 8.0 Hz, 1H), 3.43 (dd, *J* = 18.0, 5.9 Hz, 1H), 2.34 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 192.7, 138.6, 138.5, 135.3, 133.7, 131.8, 131.0, 130.1, 130.0, 127.3, 127.0, 120.4, 44.6, 31.5, 21.1. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{17}H_{13}Cl_2NONa$ 340.0266; Found 340.0266.



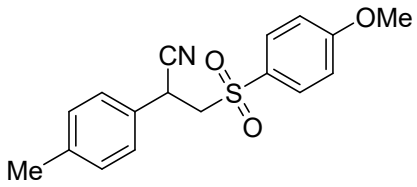
2-(4-Methoxyphenyl)-4-(naphthalen-2-yl)-4-oxobutanenitrile (**31d**): R_f = 0.25 (Petroleum ether/EtOAc, 12:1). 36.4 mg, 61% yield. Yellow solid. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.40 (s, 1H), 8.00 – 7.97 (m, 1H), 7.93 – 7.85 (m, 3H), 7.63 – 7.53 (m, 2H), 7.36 – 7.34 (m, 2H), 7.20 (d, *J* = 7.9 Hz, 2H), 4.58 (dd, *J* = 7.9, 6.1 Hz, 1H), 3.83 (dd, *J* = 17.8, 7.9 Hz, 1H), 3.62 (dd, *J* = 17.8, 6.1 Hz, 1H), 2.34 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 194.7, 138.3, 135.9, 133.1, 132.4, 132.4, 130.0, 129.9, 129.6, 128.9, 128.8, 127.9, 127.4, 127.1, 123.5, 120.8, 44.6, 31.7, 21.1. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{21}H_{18}NO$ 300.1383; Found 300.1385.



2-(4-Methoxyphenyl)-4-oxo-4-(thiophen-2-yl)butanenitrile (**32d**): R_f = 0.25 (Petroleum ether/EtOAc, 10:1). 22.4 mg, 44% yield. White solid. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.68 – 7.67 (m, 2H), 7.30 (d, *J* = 7.8 Hz, 2H), 7.18 (d, *J* = 7.8 Hz, 2H), 7.12 (t, *J* = 4.4 Hz, 1H), 4.51 (t, *J* = 7.0 Hz, 1H), 3.62 (dd, *J* = 17.2, 7.7 Hz, 1H), 3.41 (dd, *J* = 17.3, 6.4 Hz, 1H), 2.34 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 187.5, 142.8, 138.3, 134.7, 132.5, 132.0, 129.9, 128.3, 127.3, 120.5, 44.9, 31.6, 21.1. HRMS (ESI) m/z: [M + Na]$^+$ Calcd for $C_{15}H_{13}NOSNa$ 278.0610; Found 278.0612.

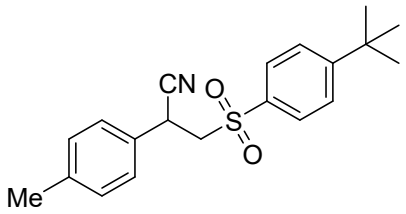


3-(Phenylsulfonyl)-2-(p-tolyl)propanenitrile (**33d**): R_f = 0.25 (Petroleum ether/EtOAc, 6:1). 35.3 mg, 62% yield. Colorless liquid. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.93 – 7.91 (m, 2H), 7.71 – 7.68 (m, 1H), 7.59 – 7.57 (m, 2H), 7.19 – 7.15 (m, 4H), 4.36 (dd, *J* = 9.4, 4.6 Hz, 1H), 3.74 (dd, *J* = 14.6, 9.3 Hz, 1H), 3.45 (dd, *J* = 14.6, 4.7 Hz, 1H), 2.33 (s, 3H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 139.2, 138.3, 134.5, 130.2, 129.9, 129.6, 128.3, 127.2, 118.1, 60.1, 31.7, 21.1. HRMS (ESI) m/z: [M + Na]$^+$ Calcd for $C_{16}H_{15}NO_2SNa$ 308.0716; Found 308.0714.

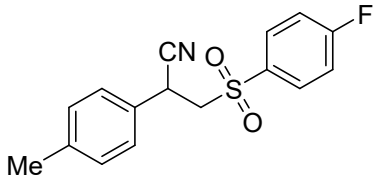


3-((4-Methoxyphenyl)sulfonyl)-2-(p-tolyl)propanenitrile (**34d**)[10]: R_f = 0.25 (Petroleum ether/EtOAc, 5:1). 46.0 mg, 73% yield. White solid. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.84 (d, *J* = 8.9 Hz, 2H), 7.19 - 7.14 (m, 4H), 7.03 - 7.01 (m, 2H), 4.33 (dd, *J* = 9.4, 4.5 Hz, 1H), 3.89 (s, 3H), 3.71 (dd, *J* = 14.5, 9.4 Hz, 1H), 3.41 (dd, *J* = 14.5, 4.6 Hz, 1H), 2.33 (s, 3H).

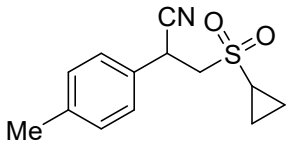
^{13}C NMR (101 MHz, Chloroform-*d*) δ 164.4, 139.1, 130.6, 130.2, 130.1, 129.7, 127.2, 118.2, 114.8, 60.3, 55.8, 31.9, 21.1.



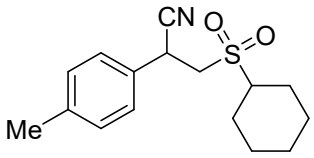
3-((4-(Tert-butyl)phenyl)sulfonyl)-2-(p-tolyl)propanenitrile (**35d**): R_f = 0.25 (Petroleum ether/EtOAc, 12:1). 51.8 mg, 76% yield. White solid. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.80 (d, *J* = 8.3 Hz, 2H), 7.55 (d, *J* = 8.4 Hz, 2H), 7.17 (d, *J* = 7.9 Hz, 2H), 7.13 (d, *J* = 8.0 Hz, 2H), 4.36 (dd, *J* = 8.9, 5.1 Hz, 1H), 3.72 (dd, *J* = 14.5, 8.9 Hz, 1H), 3.45 (dd, *J* = 14.5, 5.1 Hz, 1H), 2.32 (s, 3H), 1.34 (s, 9H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 158.6, 139.0, 135.3, 130.1, 130.0, 128.1, 127.3, 126.5, 118.2, 60.0, 35.4, 31.7, 31.0, 21.1. HRMS (ESI) m/z: [M + Na]$^+$ Calcd for $C_{20}H_{23}NO_2SNa$ 364.1342; Found 364.1341.



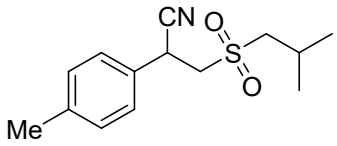
3-((4-Fluorophenyl)sulfonyl)-2-(p-tolyl)propanenitrile (**36d**): R_f = 0.25 (Petroleum ether/EtOAc, 8:1). 43.6 mg, 72% yield. White solid. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.95 – 7.90 (m, 2H), 7.26 – 7.21 (m, 2H), 7.19 – 7.15 (m, 4H), 4.36 (dd, *J* = 9.3, 4.8 Hz, 1H), 3.73 (dd, *J* = 14.5, 9.3 Hz, 1H), 3.46 (dd, *J* = 14.6, 4.8 Hz, 1H), 2.33 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 166.3 (d, *J* = 258.0 Hz), 139.3, 134.4 (d, *J* = 3.2 Hz), 131.3 (d, *J* = 9.8 Hz), 130.3, 129.7, 127.2, 118.0, 116.9 (d, *J* = 22.8 Hz), 60.2, 31.8, 21.1. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -101.74. HRMS (ESI) m/z: [M + Na]$^+$ Calcd for $C_{16}H_{14}FNO_2SNa$ 326.0621; Found 326.0621.



3-(Cyclopropylsulfonyl)-2-(p-tolyl)propanenitrile (**37d**): R_f = 0.25 (Petroleum ether/EtOAc, 5:1). 35.7 mg, 72% yield. White solid. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.30 (d, *J* = 7.9 Hz, 2H), 7.23 (d, *J* = 7.8 Hz, 2H), 4.44 (dd, *J* = 9.3, 5.0 Hz, 1H), 3.69 (dd, *J* = 14.6, 9.3 Hz, 1H), 3.36 (dd, *J* = 14.6, 5.0 Hz, 1H), 2.41 – 2.38 (m, 1H), 2.37 (s, 3H), 1.39 – 1.35 (m, 1H), 1.27 – 1.23 (m, 1H), 1.12 – 1.06 (m, 2H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 139.3, 130.3, 130.0, 127.3, 118.9, 58.3, 32.0, 30.6, 21.1, 5.9, 5.5. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{13}H_{15}NO_2SNa$ 272.0716; Found 272.0713.

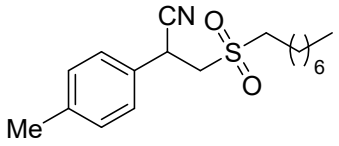


3-(Cyclohexylsulfonyl)-2-(p-tolyl)propanenitrile (**38d**): R_f = 0.25 (Petroleum ether/EtOAc, 8:1). 42.0 mg, 72% yield. White solid. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.30 (d, *J* = 7.8 Hz, 2H), 7.23 (d, *J* = 7.9 Hz, 2H), 4.43 (dd, *J* = 8.8, 5.3 Hz, 1H), 3.61 (dd, *J* = 14.5, 8.7 Hz, 1H), 3.23 (dd, *J* = 14.5, 5.3 Hz, 1H), 2.79 – 2.74 (m, 1H), 2.37 (s, 3H), 2.14 – 2.09 (m, 2H), 1.93 – 1.89 (m, 2H), 1.72 – 1.70 (m, 1H), 1.57 – 1.49 (m, 2H), 1.28 – 1.18 (m, 3H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 139.3, 130.3, 130.1, 127.4, 118.8, 62.0, 53.7, 31.3, 25.2, 24.9, 24.9, 24.4, 21.1. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{16}H_{21}NO_2SNa$ 314.1185; Found 314.1185.



3-(Isobutylsulfonyl)-2-(p-tolyl)propanenitrile (**39d**): R_f = 0.25 (Petroleum ether/EtOAc, 8:1). 38.1 mg, 72% yield. White solid. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.29 (d, *J* = 8.1 Hz, 2H), 7.24 (d, *J* = 7.9 Hz, 2H), 4.43 (dd, *J* = 8.8, 5.5 Hz, 1H), 3.60 (dd, *J* = 14.7, 8.7 Hz, 1H), 3.30 (dd, *J* = 14.7, 5.6 Hz, 1H), 2.87 (dd, *J* = 13.9, 6.8 Hz, 1H), 2.78 (dd, *J* = 13.9, 6.3 Hz, 1H), 2.37 (s, 3H), 2.35 – 2.32 (m, 1H), 1.09 – 1.08 (m, 6H). ^{13}C NMR (151 MHz,

Chloroform-*d*) δ 139.4, 130.4, 129.8, 127.4, 118.8, 61.8, 58.3, 31.9, 23.7, 22.7, 22.6, 21.1. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{14}H_{19}NO_2SNa$ 288.1029; Found 288.1033.



3-(Octylsulfonyl)-2-(p-tolyl)propanenitrile (**40d**): R_f = 0.25 (Petroleum ether/EtOAc, 10:1). 43.3 mg, 67% yield. Colorless liquid. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.29 (d, *J* = 7.9 Hz, 2H), 7.24 (d, *J* = 7.9 Hz, 2H), 4.42 (dd, *J* = 8.7, 5.6 Hz, 1H), 3.60 (dd, *J* = 14.7, 8.6 Hz, 1H), 3.30 (dd, *J* = 14.8, 5.6 Hz, 1H), 2.94 – 2.86 (m, 2H), 2.37 (s, 3H), 1.84 – 1.73 (m, 2H), 1.39 – 1.34 (m, 2H), 1.31 – 1.23 (m, 8H), 0.88 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 139.5, 130.4, 129.7, 127.4, 118.7, 56.9, 54.3, 31.9, 31.7, 28.9, 28.9, 28.3, 22.6, 21.9, 21.1, 14.0. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{18}H_{27}NO_2SNa$ 344.1655; Found 344.1657.

7. References

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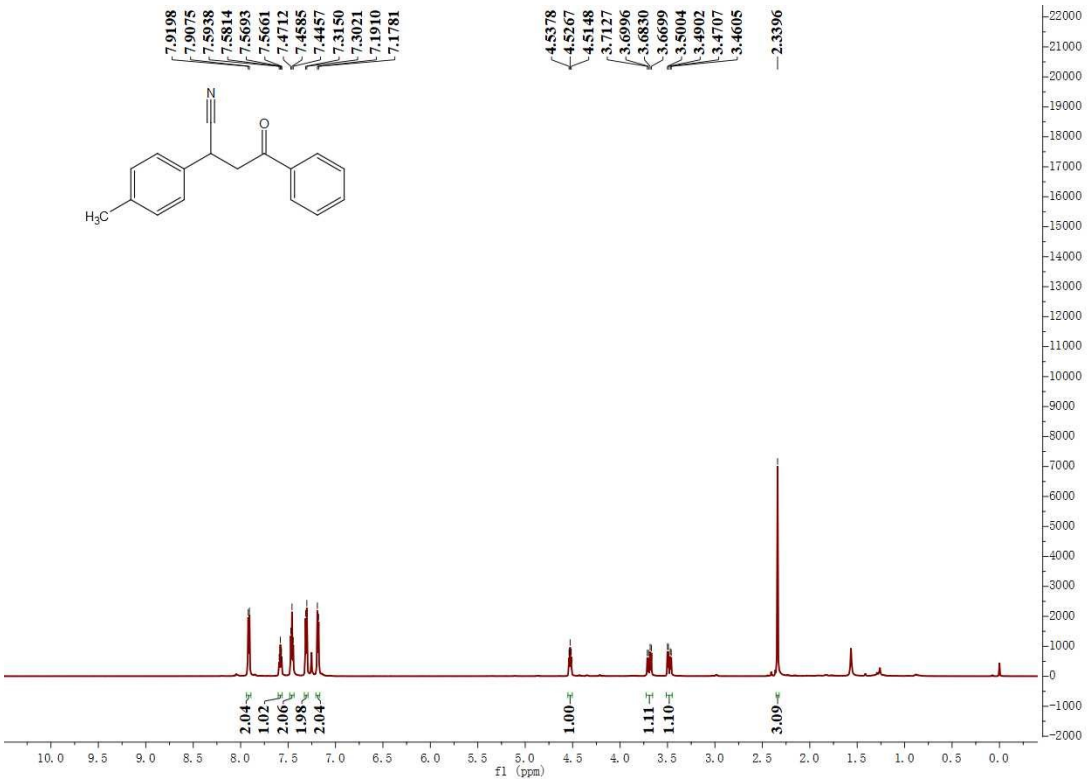
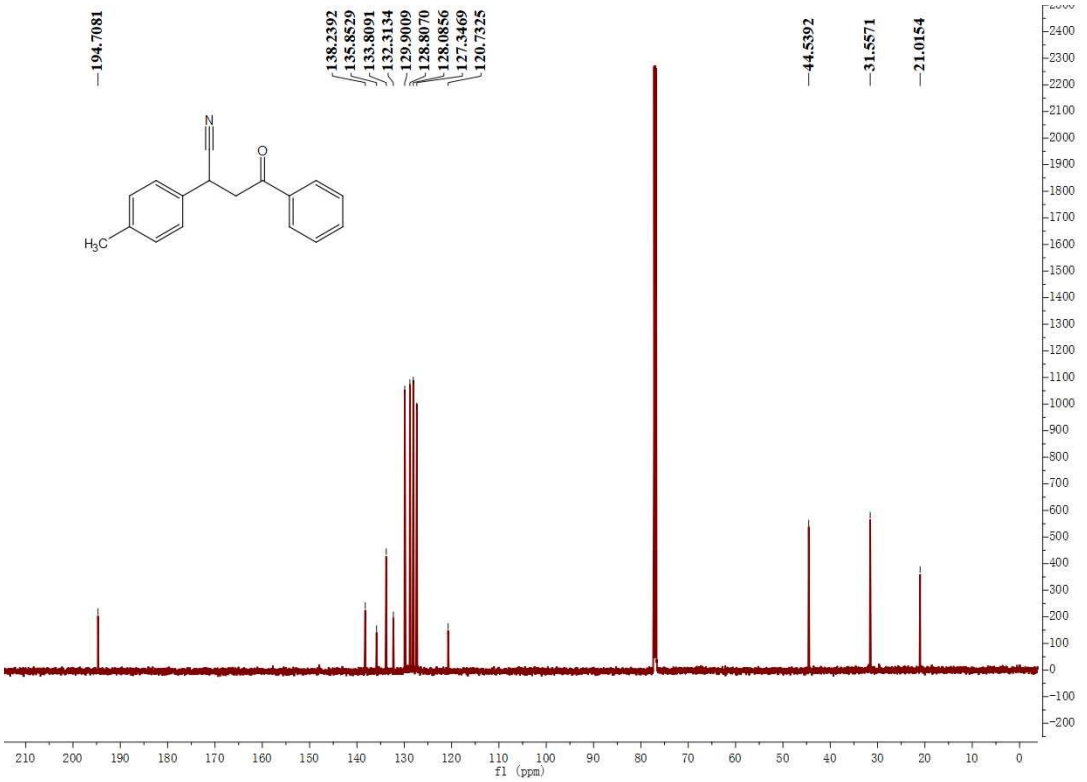
8. NMR of products

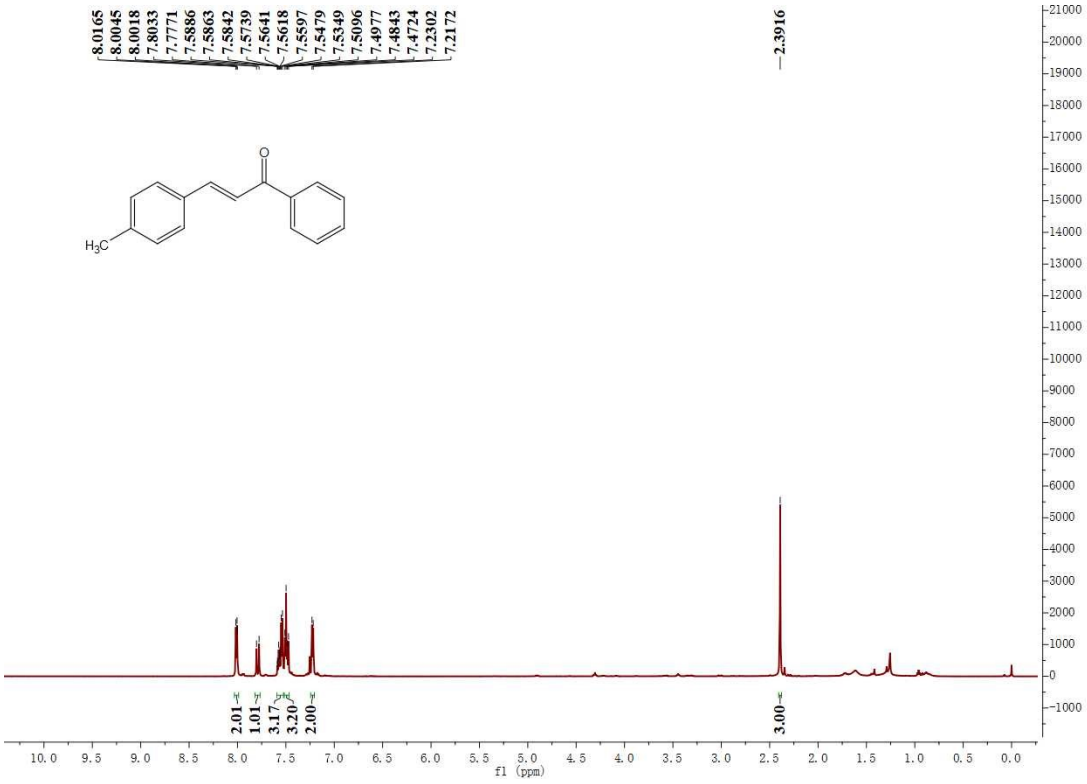
^{1}H-NMR Spectrum (600 MHz, $CDCl_3$) of **1d**



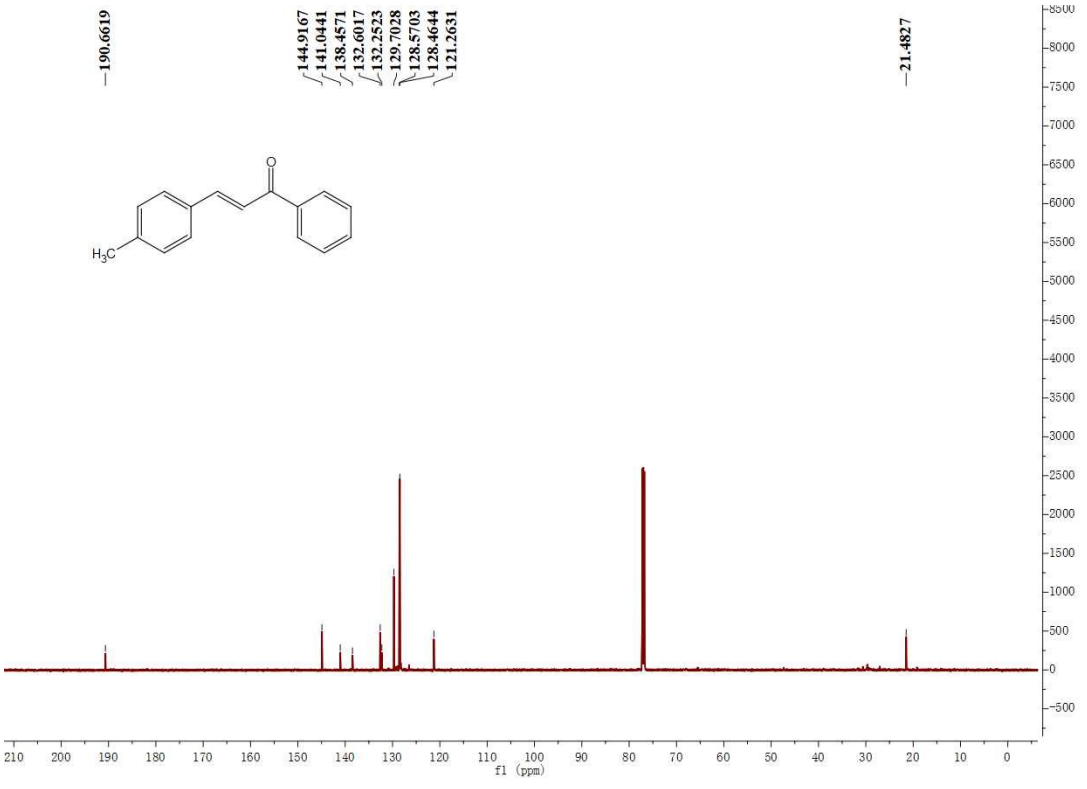
^{13}C-NMR Spectrum (151 MHz, $CDCl_3$) of **1d**



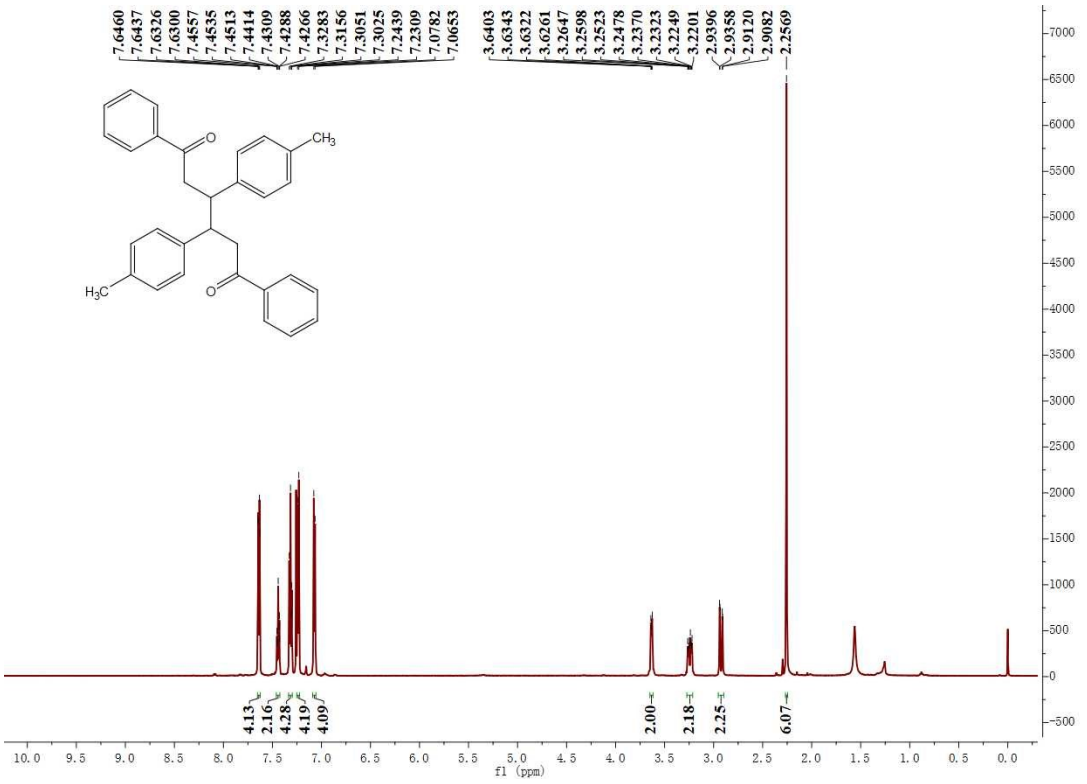
^{1}H-NMR Spectrum (600 MHz, $CDCl_3$) of **1e**



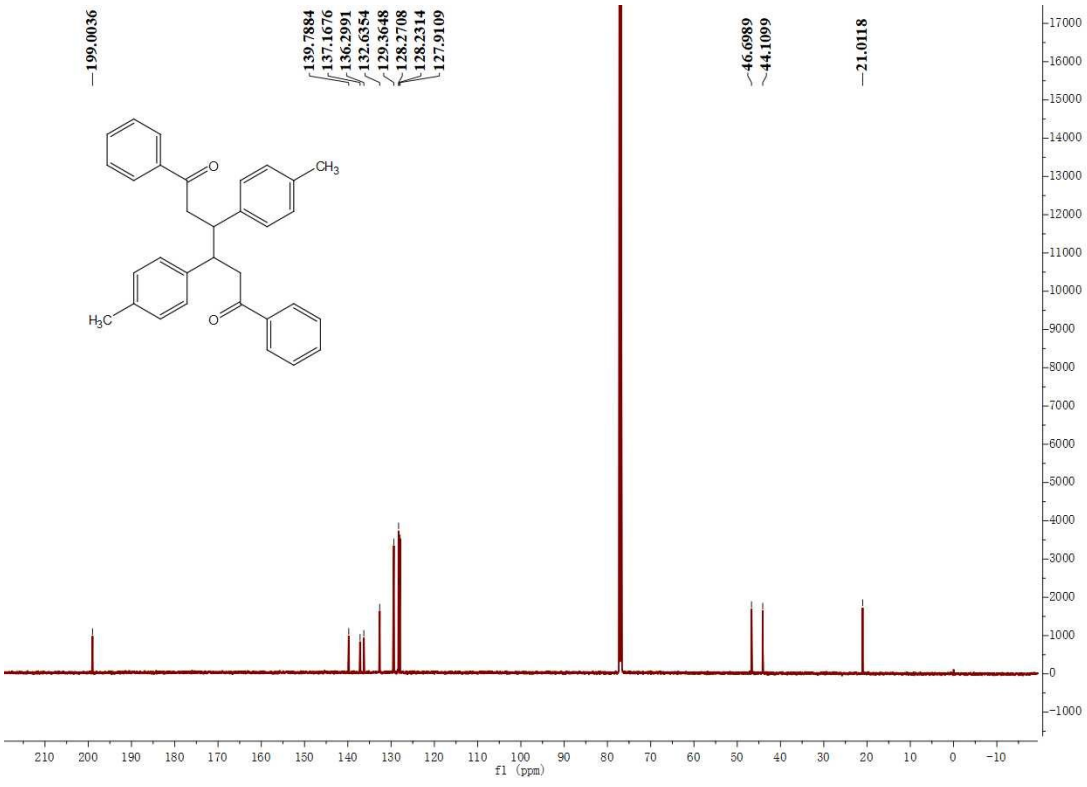
^{13}C-NMR Spectrum (151 MHz, $CDCl_3$) of **1e**



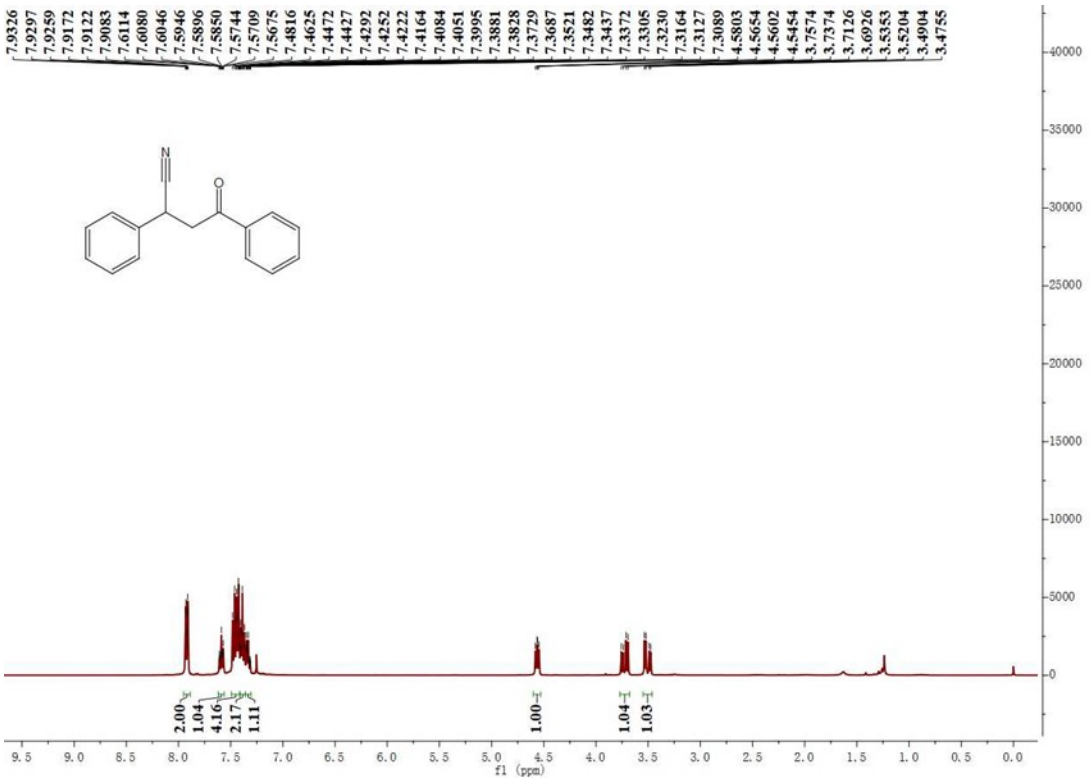
^{1}H-NMR Spectrum (600 MHz, $CDCl_3$) of **1f**



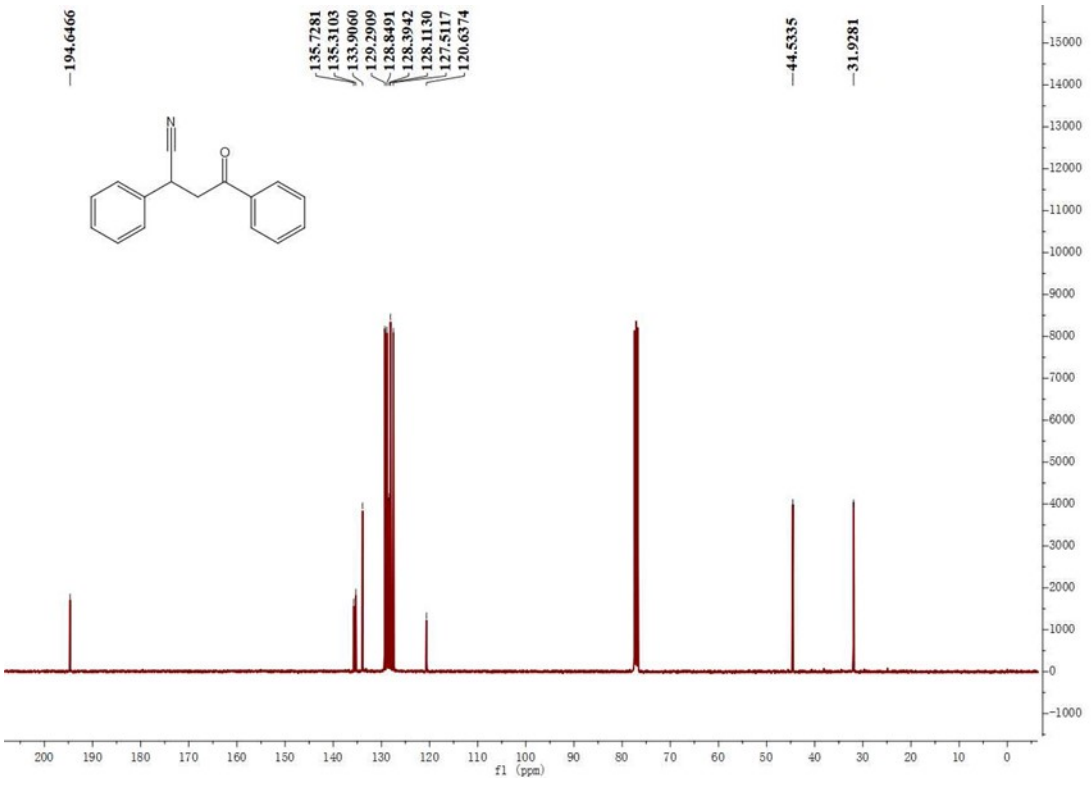
^{13}C-NMR Spectrum (151 MHz, $CDCl_3$) of **1f**



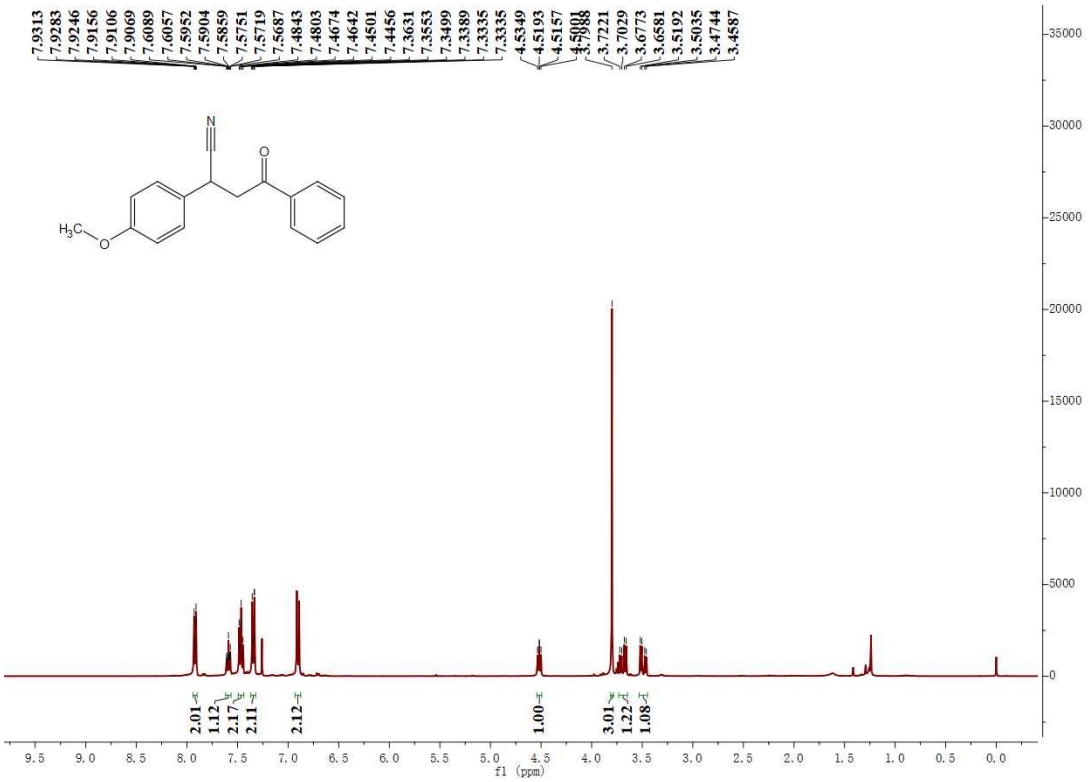
^{1}H-NMR Spectrum (400 MHz, $CDCl_3$) of **2d**



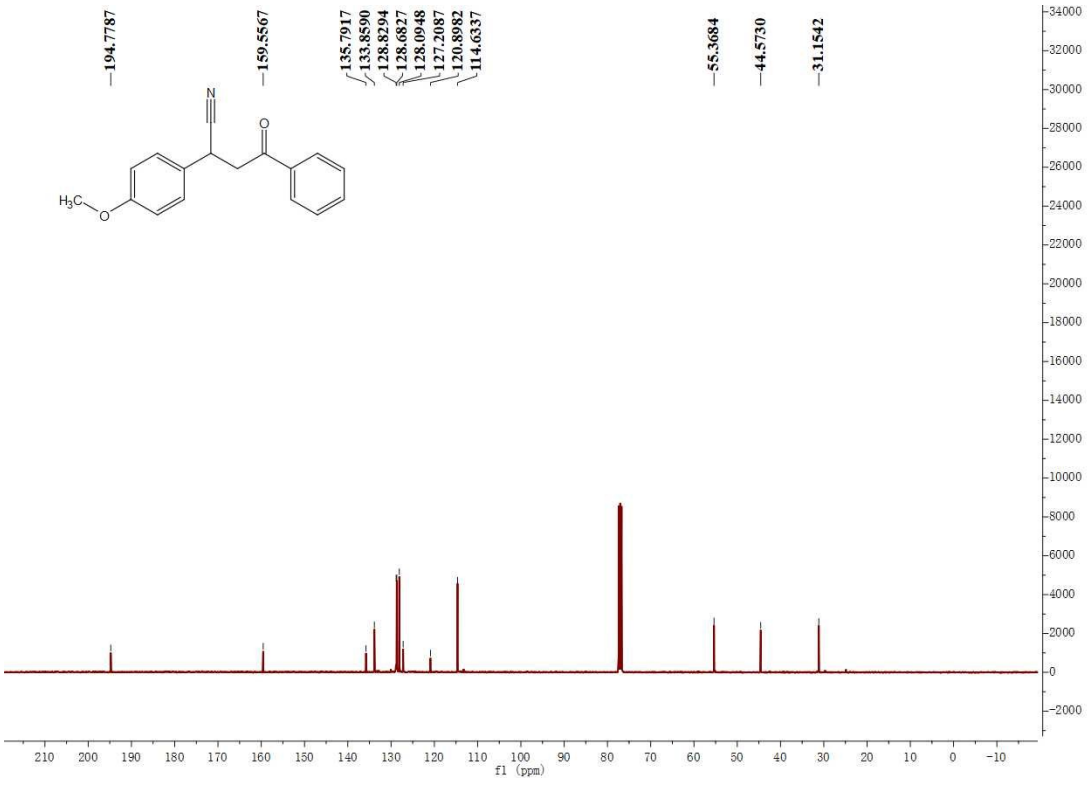
^{13}C-NMR Spectrum (101 MHz, $CDCl_3$) of **2d**



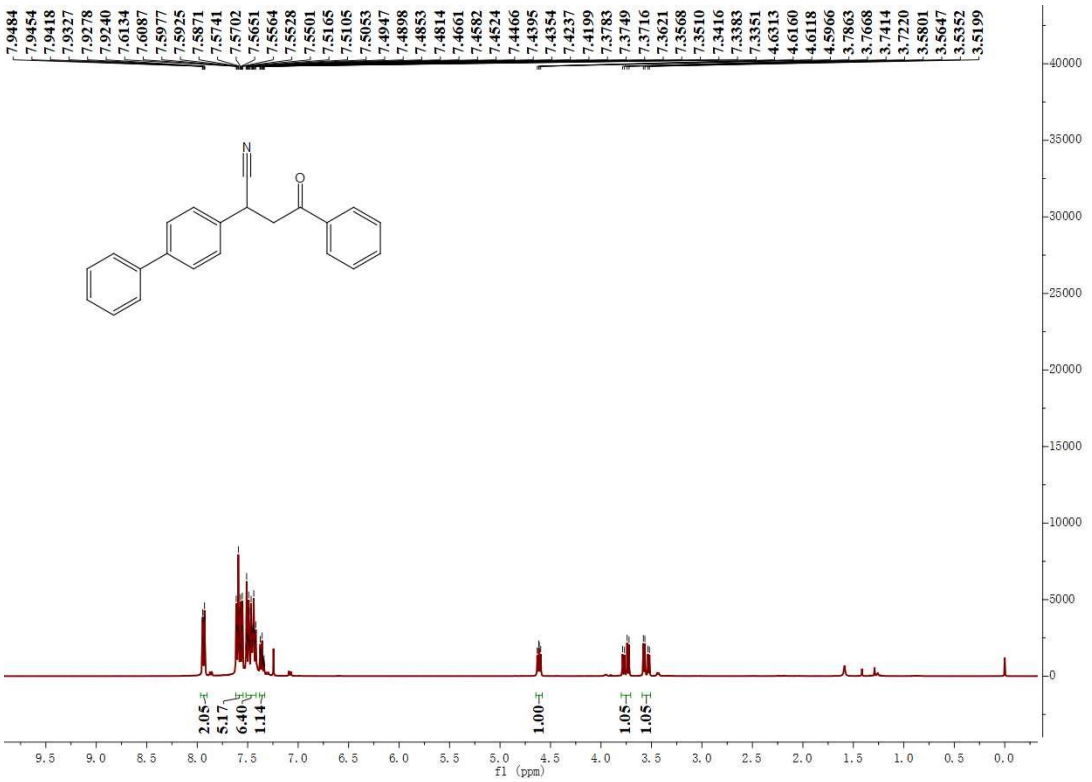
^{1}H-NMR Spectrum (400 MHz, $CDCl_3$) of **3d**



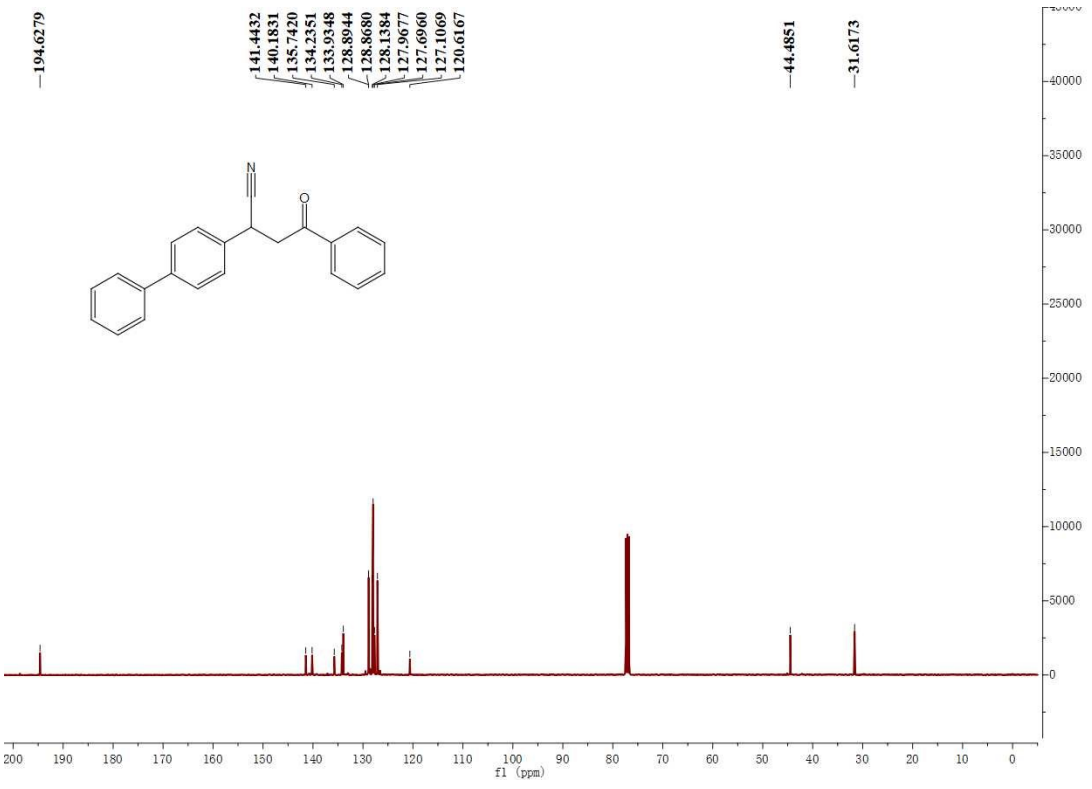
^{13}C-NMR Spectrum (101 MHz, $CDCl_3$) of **3d**



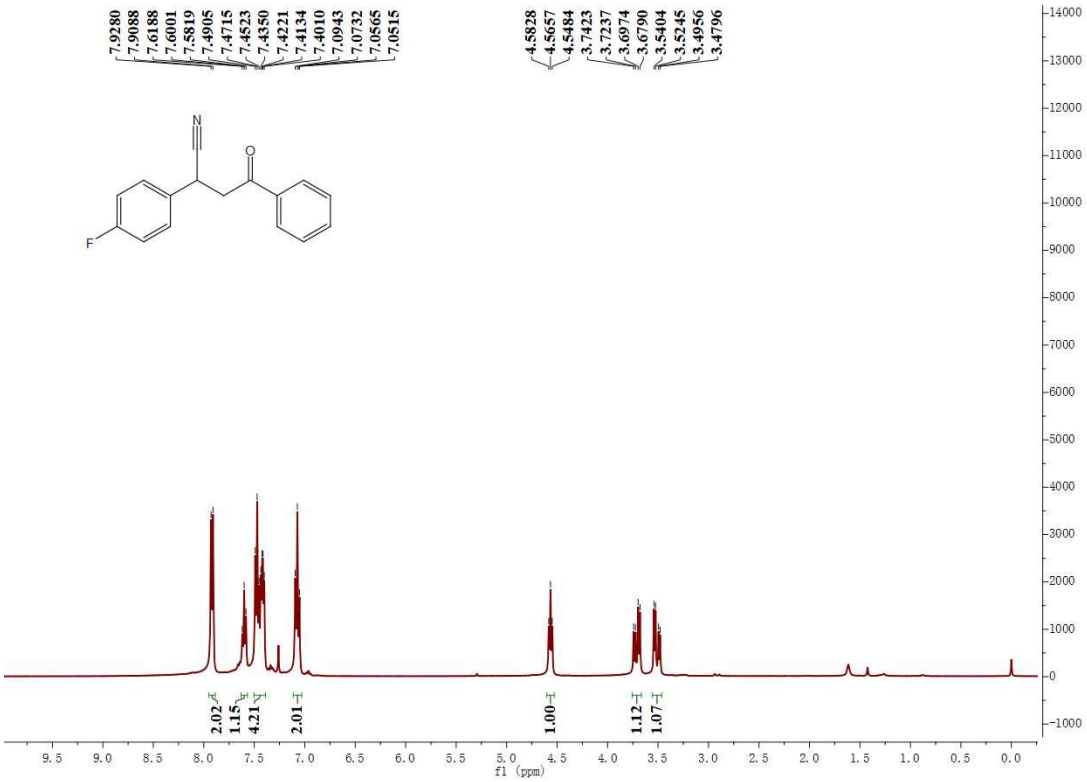
^{1}H-NMR Spectrum (400 MHz, $CDCl_3$) of **4d**



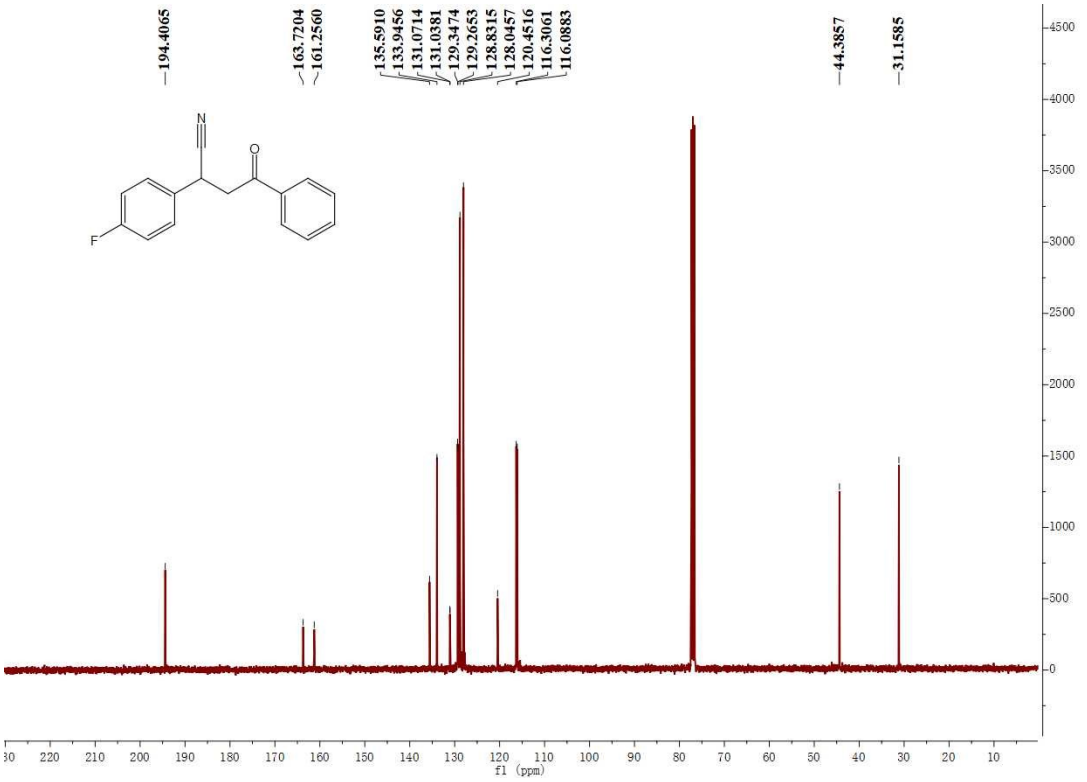
^{13}C-NMR Spectrum (101 MHz, $CDCl_3$) of **4d**



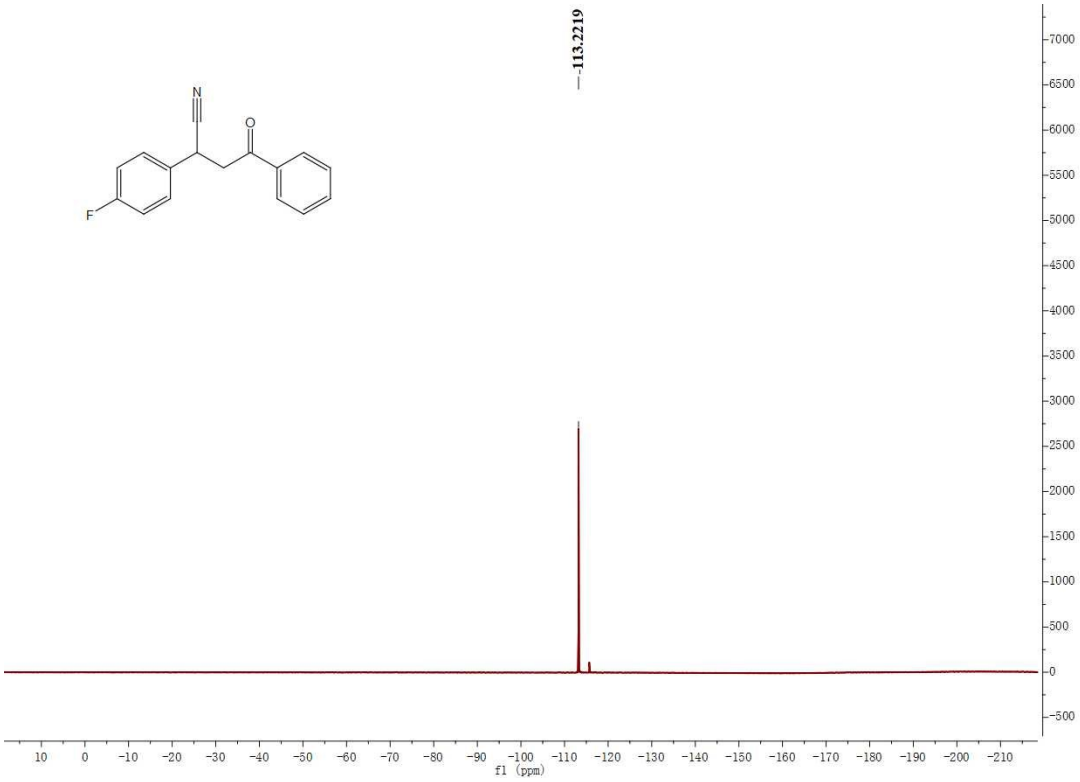
^{1}H-NMR Spectrum (400 MHz, $CDCl_3$) of **5d**



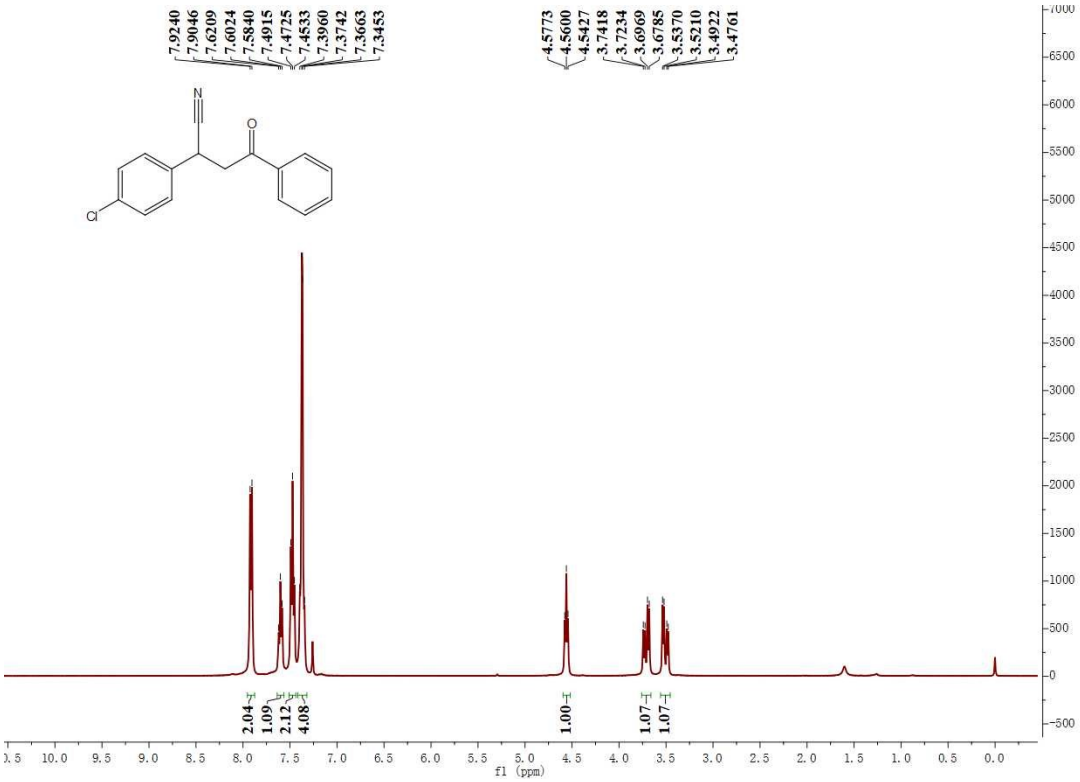
^{13}C-NMR Spectrum (101 MHz, $CDCl_3$) of **5d**



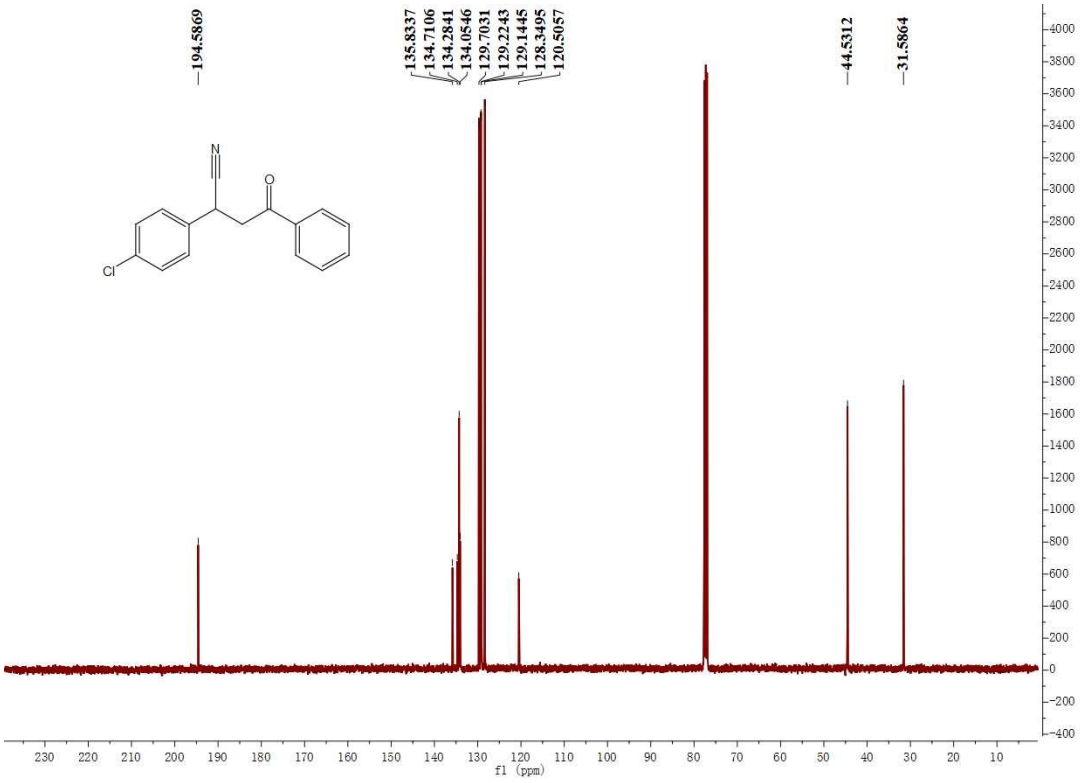
^{19}F-NMR Spectrum (376 MHz, $CDCl_3$) of **5d**



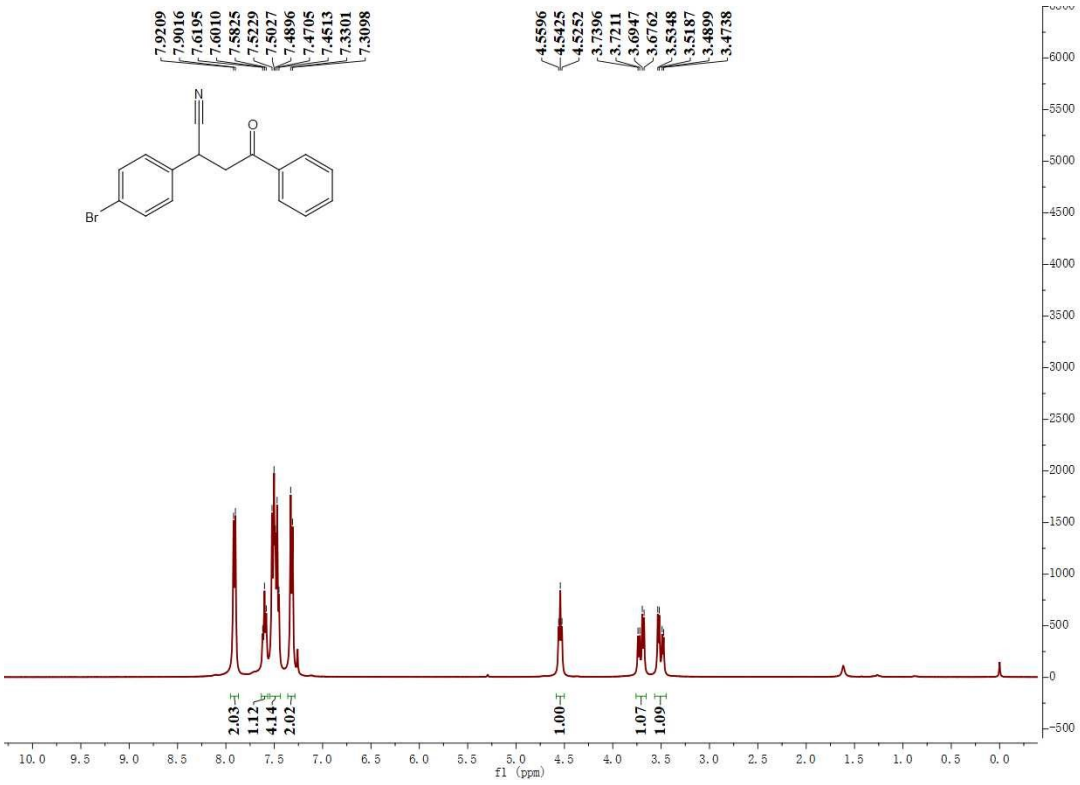
^{1}H-NMR Spectrum (400 MHz, $CDCl_3$) of **6d**



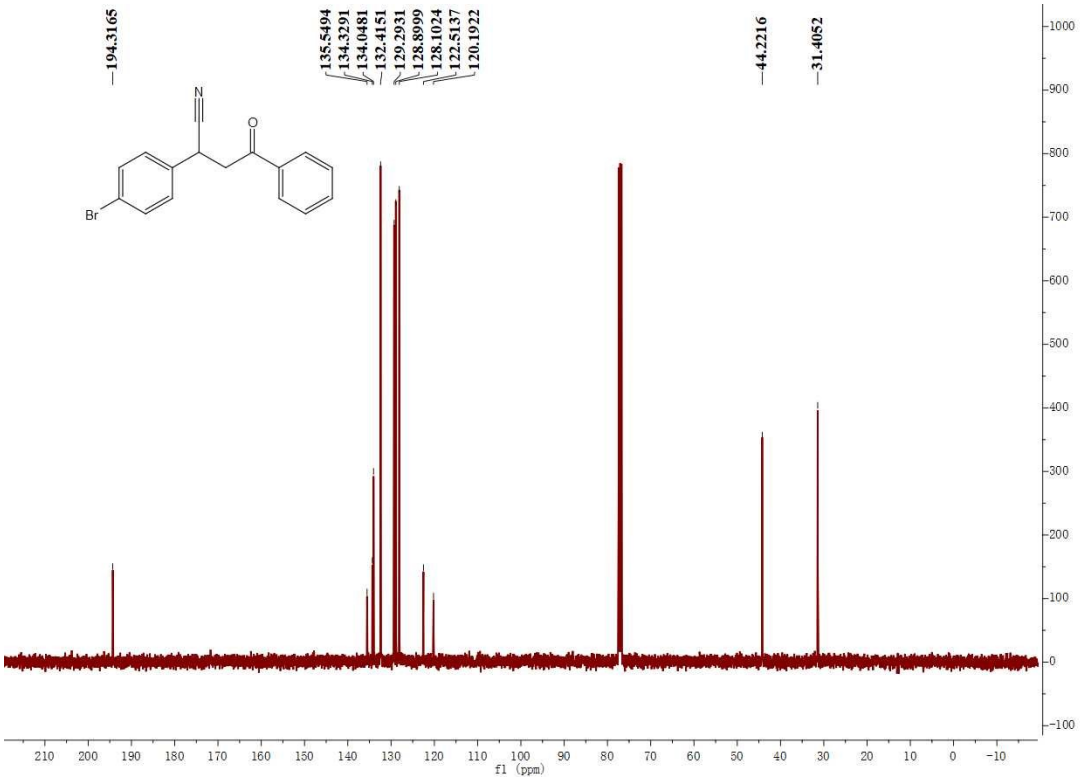
^{13}C-NMR Spectrum (101 MHz, $CDCl_3$) of **6d**



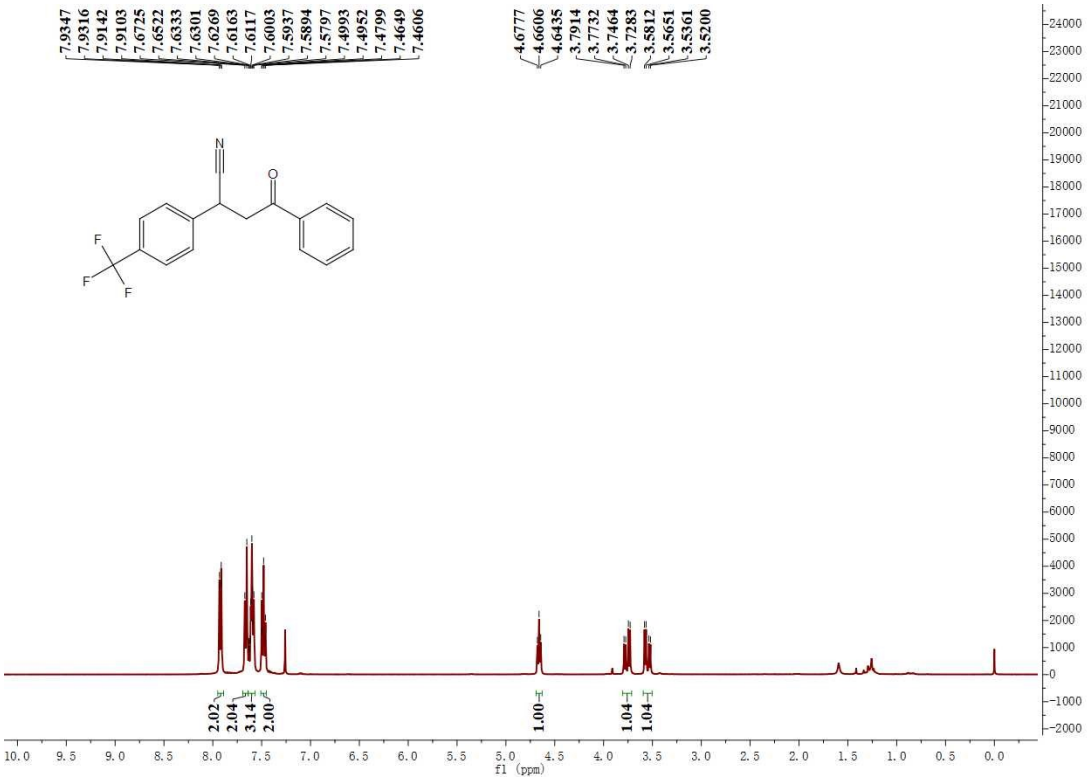
^{1}H-NMR Spectrum (400 MHz, $CDCl_3$) of **7d**



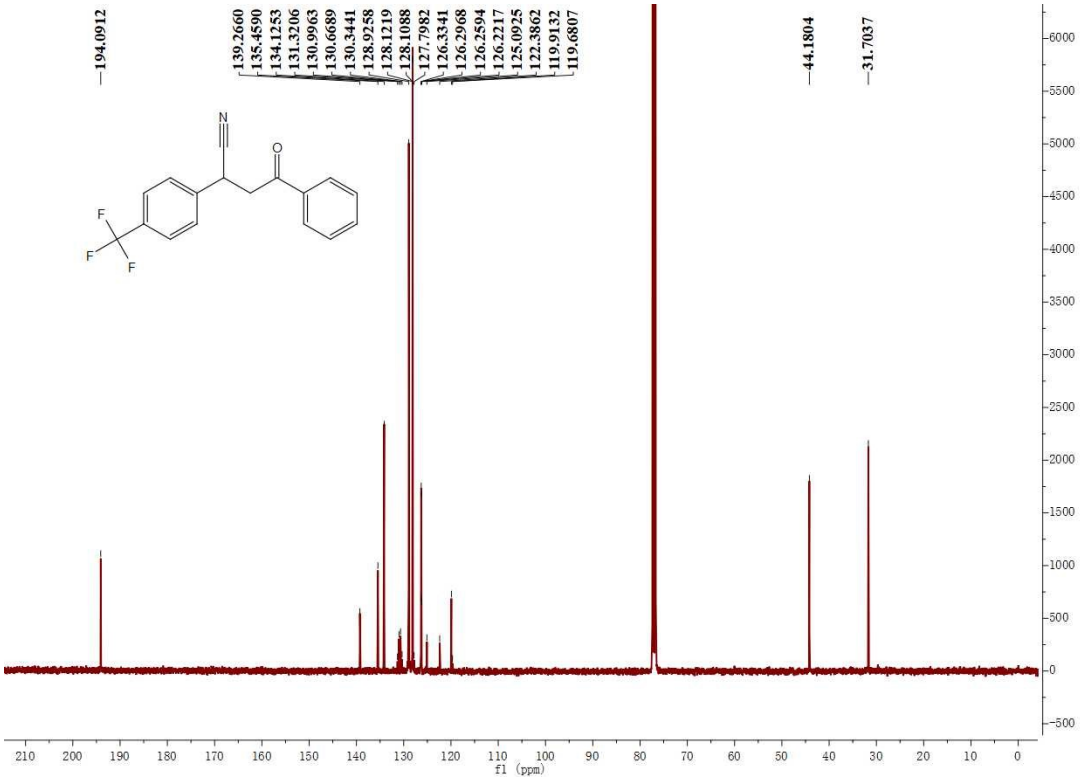
^{13}C-NMR Spectrum (101 MHz, $CDCl_3$) of **7d**



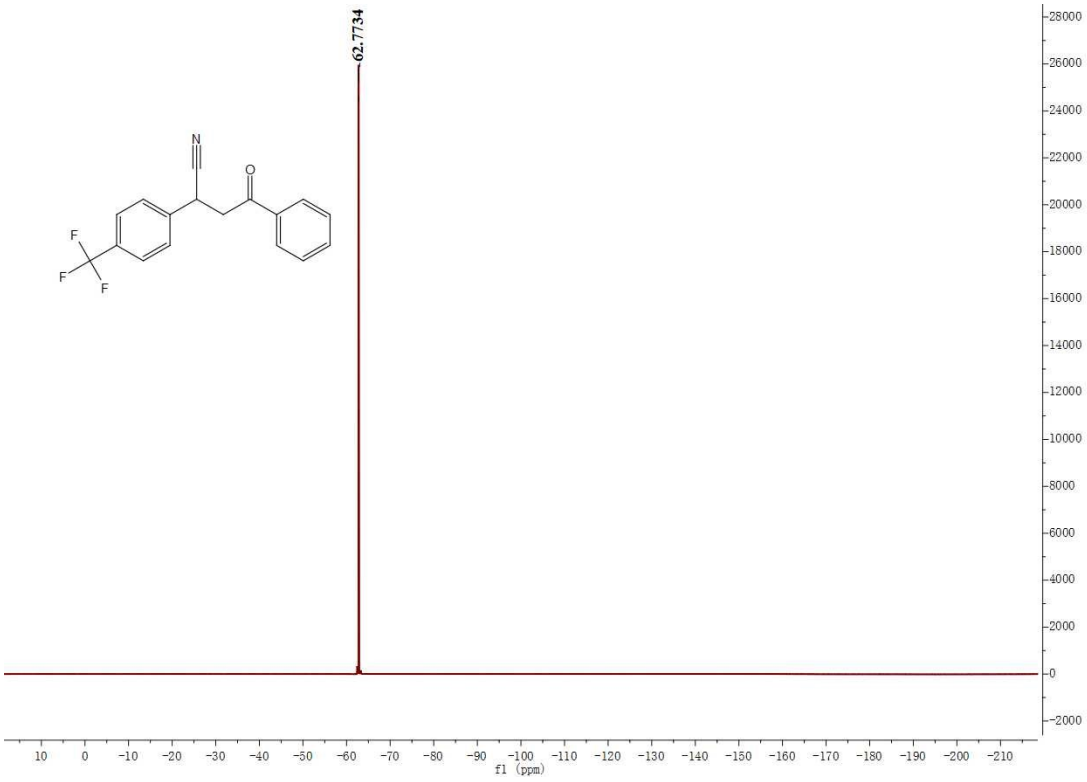
^{1}H-NMR Spectrum (400 MHz, $CDCl_3$) of **8d**



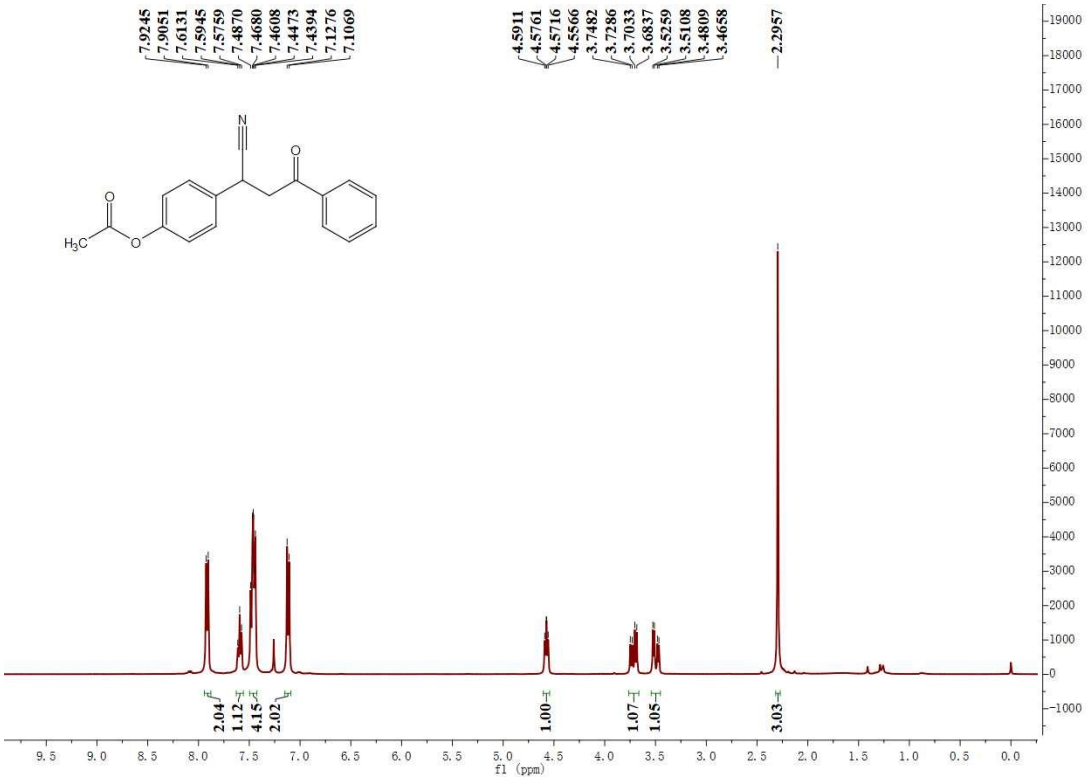
^{13}C-NMR Spectrum (101 MHz, $CDCl_3$) of **8d**



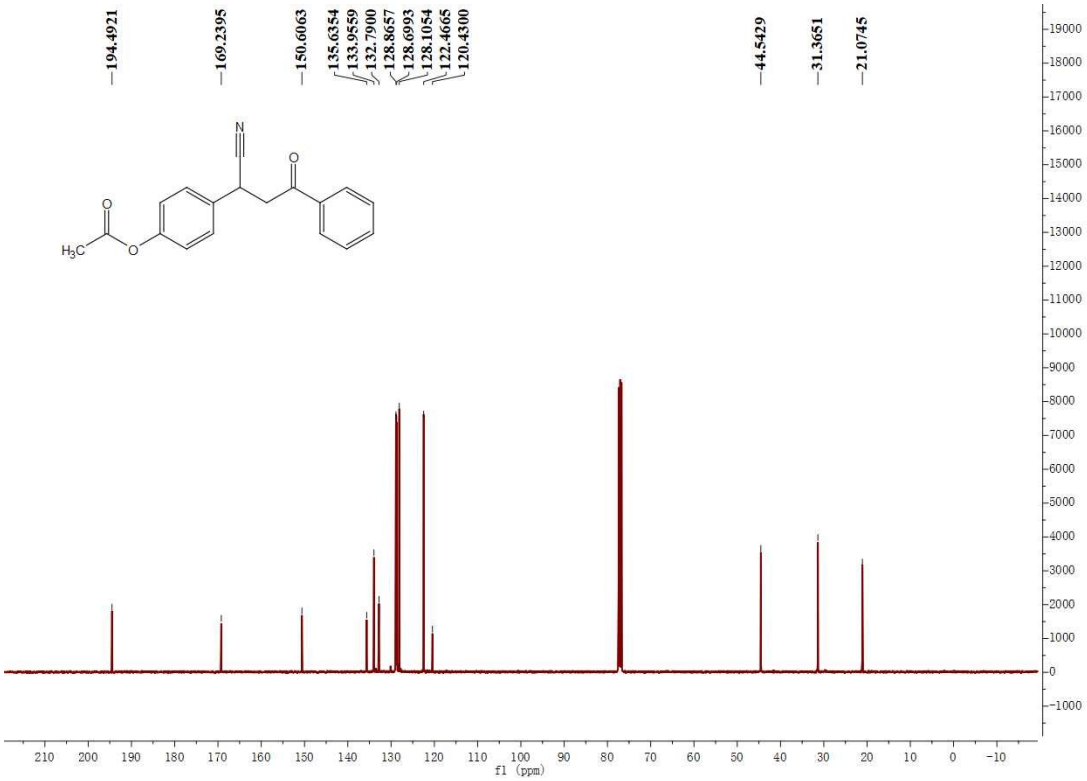
^{19}F-NMR Spectrum (376 MHz, $CDCl_3$) of **8d**



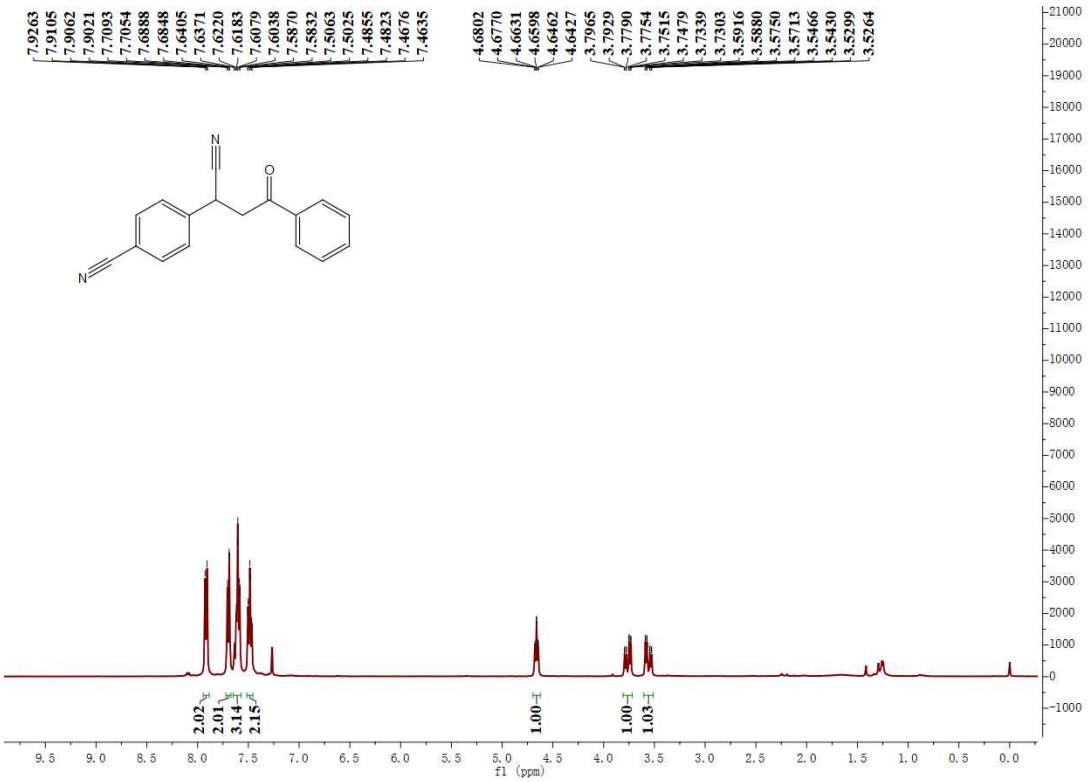
^{1}H-NMR Spectrum (400 MHz, $CDCl_3$) of **9d**



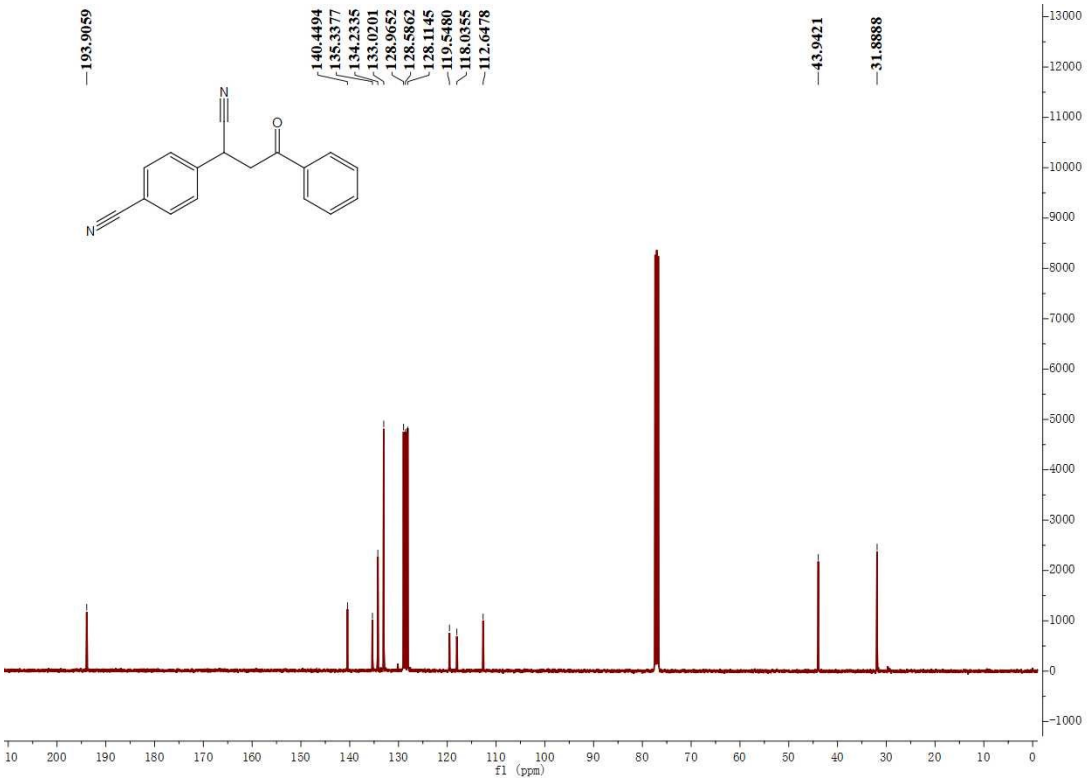
^{13}C-NMR Spectrum (101 MHz, $CDCl_3$) of **9d**



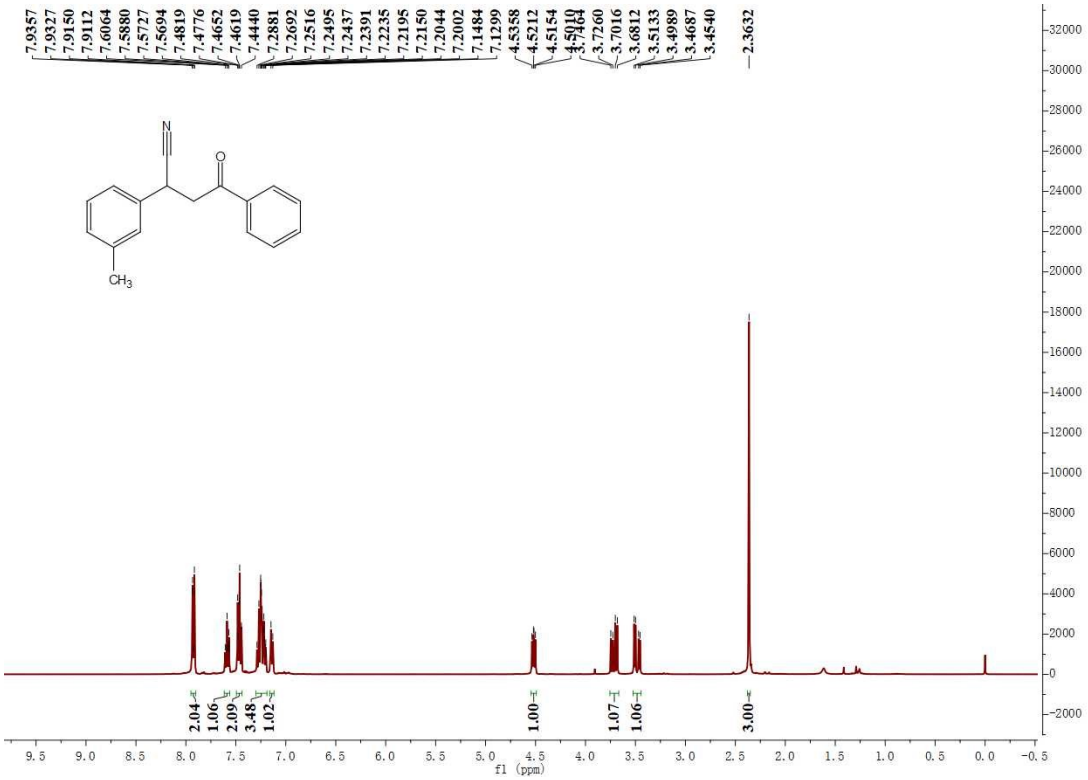
^{1}H-NMR Spectrum (400 MHz, $CDCl_3$) of **10d**



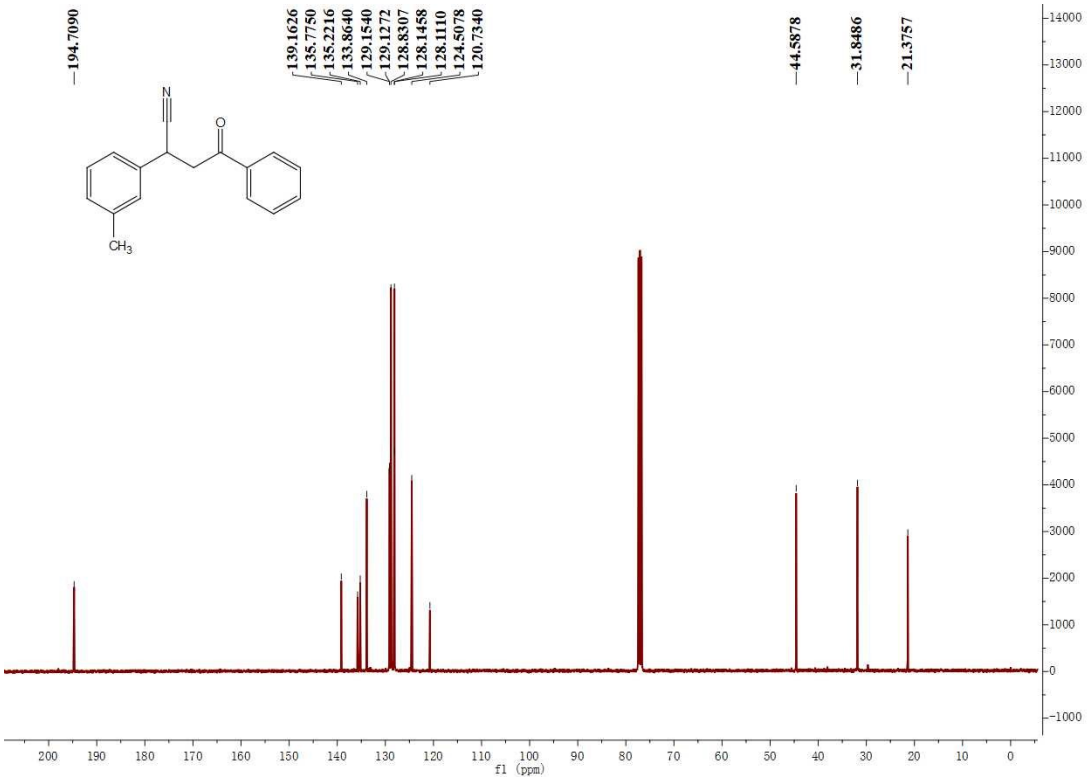
^{13}C-NMR Spectrum (101 MHz, $CDCl_3$) of **10d**



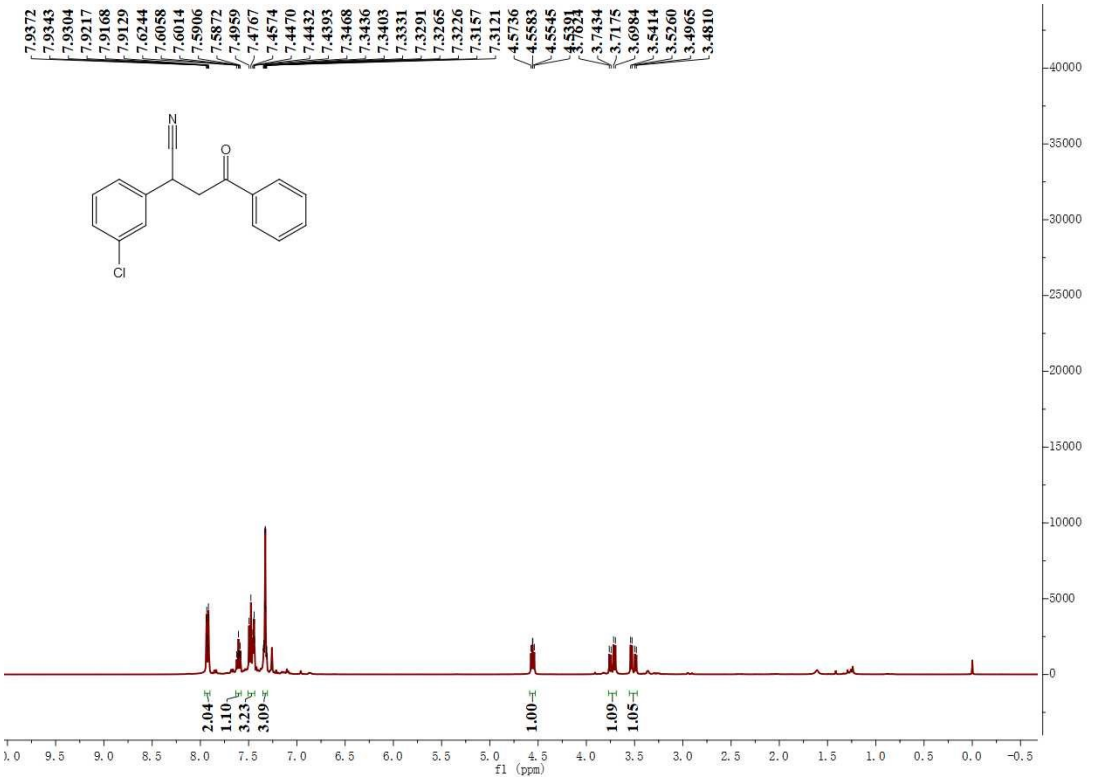
^{1}H-NMR Spectrum (400 MHz, $CDCl_3$) of **11d**



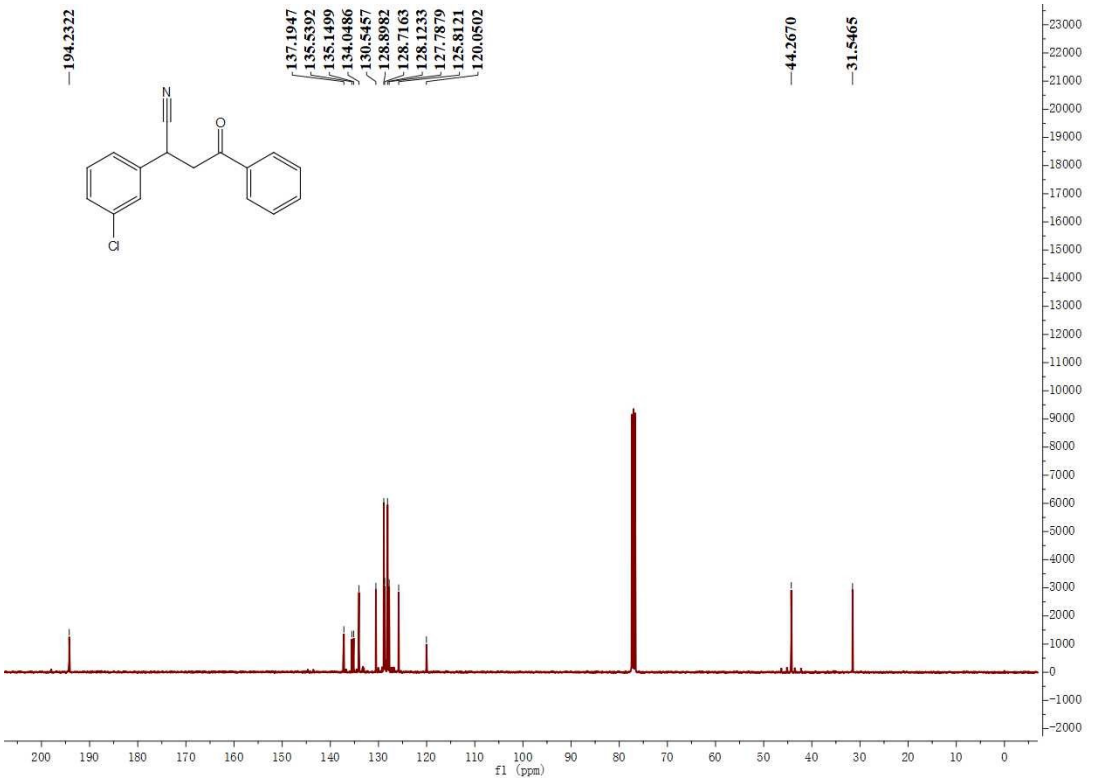
^{13}C-NMR Spectrum (101 MHz, $CDCl_3$) of **11d**



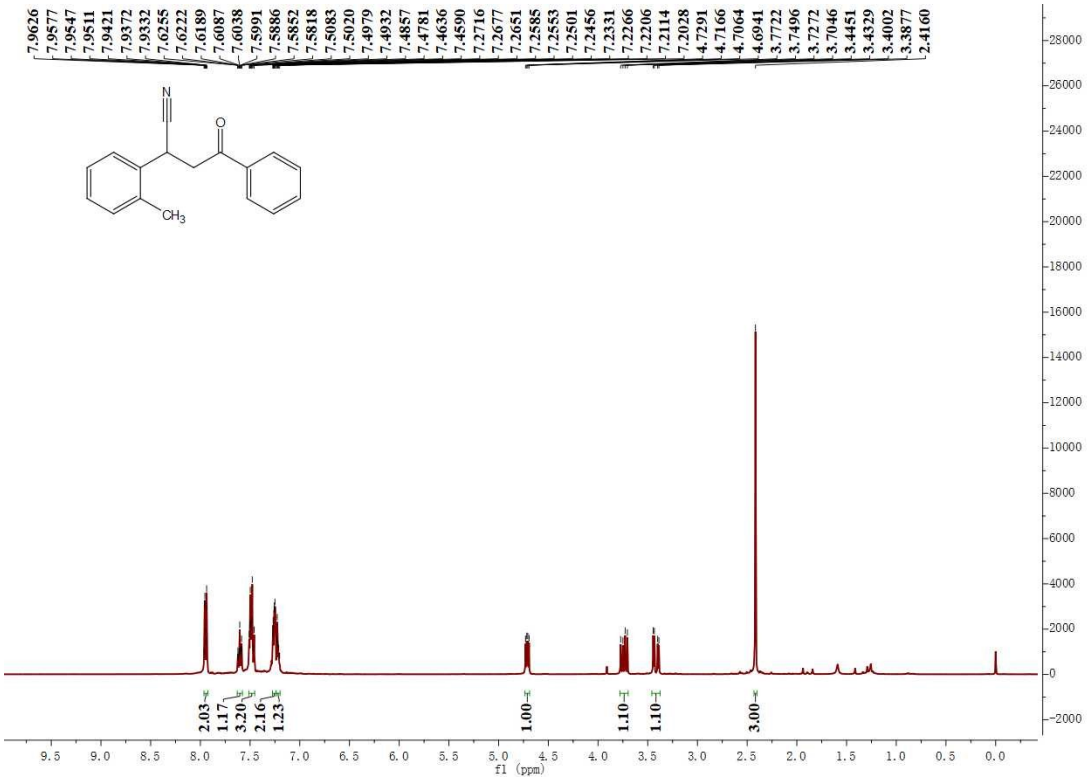
^{1}H-NMR Spectrum (400 MHz, $CDCl_3$) of **12d**



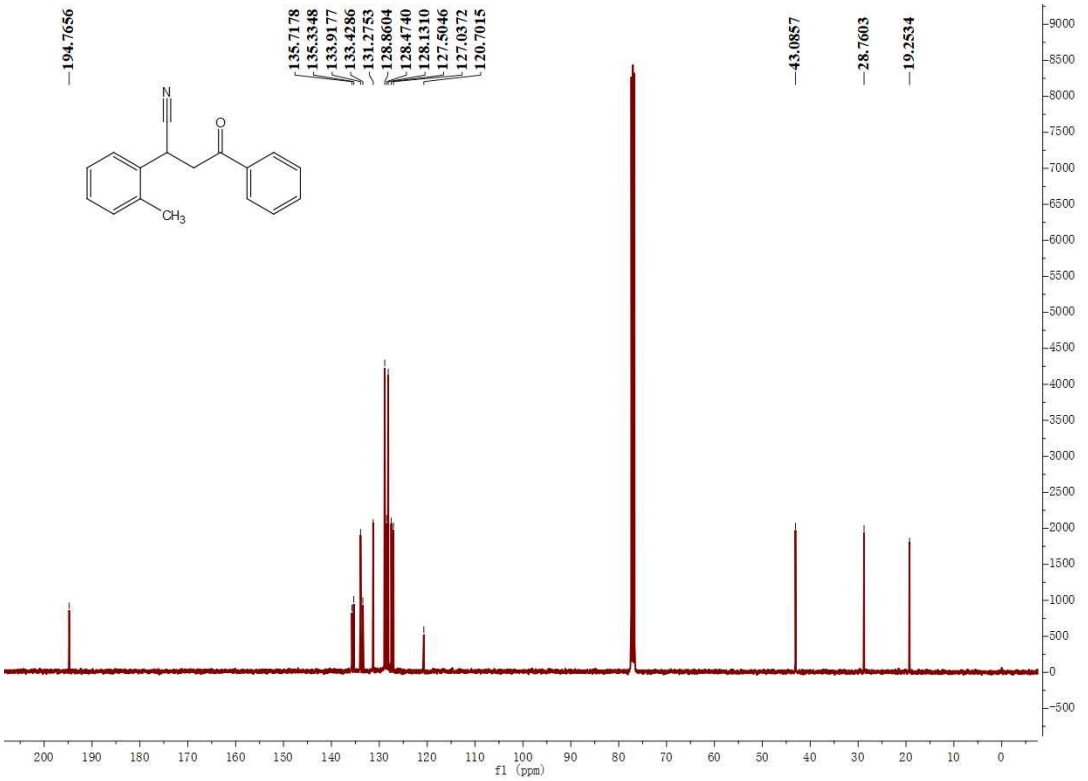
^{13}C-NMR Spectrum (101 MHz, $CDCl_3$) of **12d**



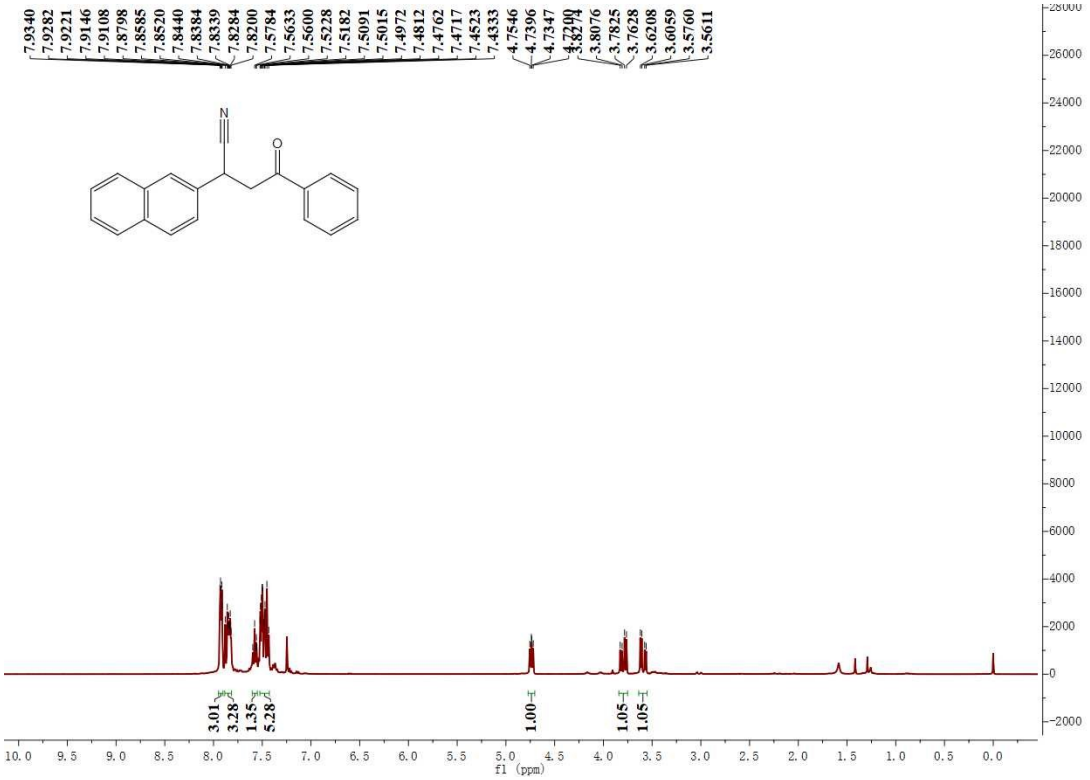
^{1}H-NMR Spectrum (400 MHz, $CDCl_3$) of **13d**



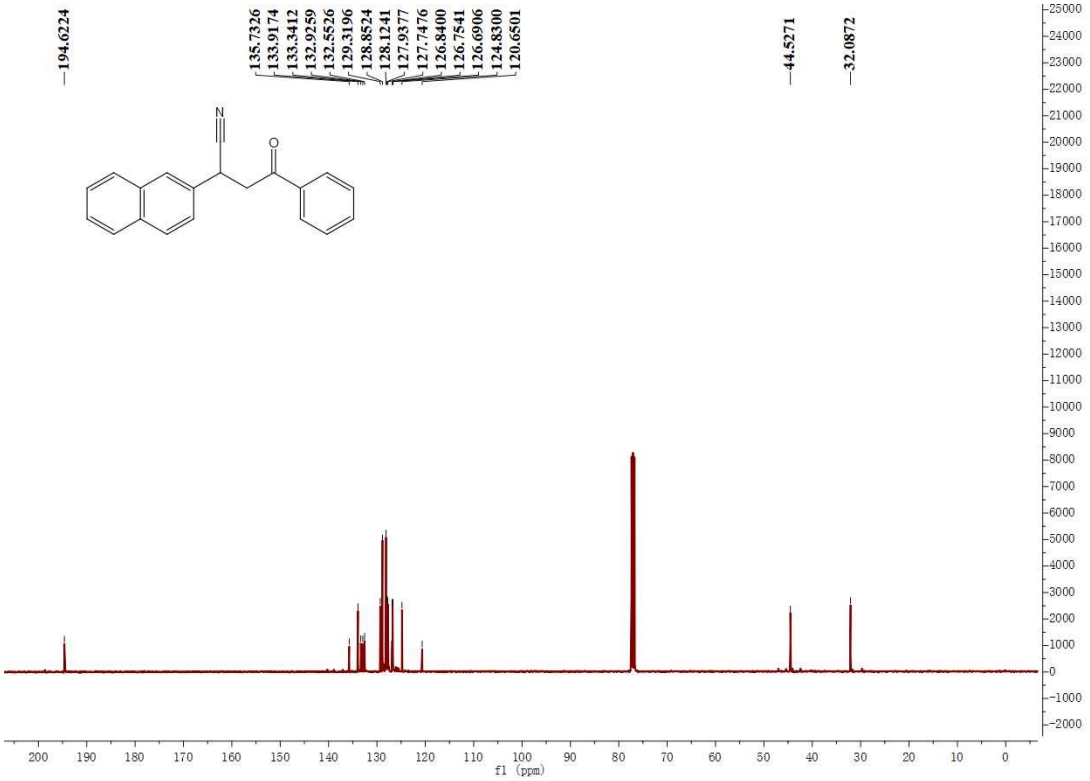
^{13}C-NMR Spectrum (101 MHz, $CDCl_3$) of **13d**



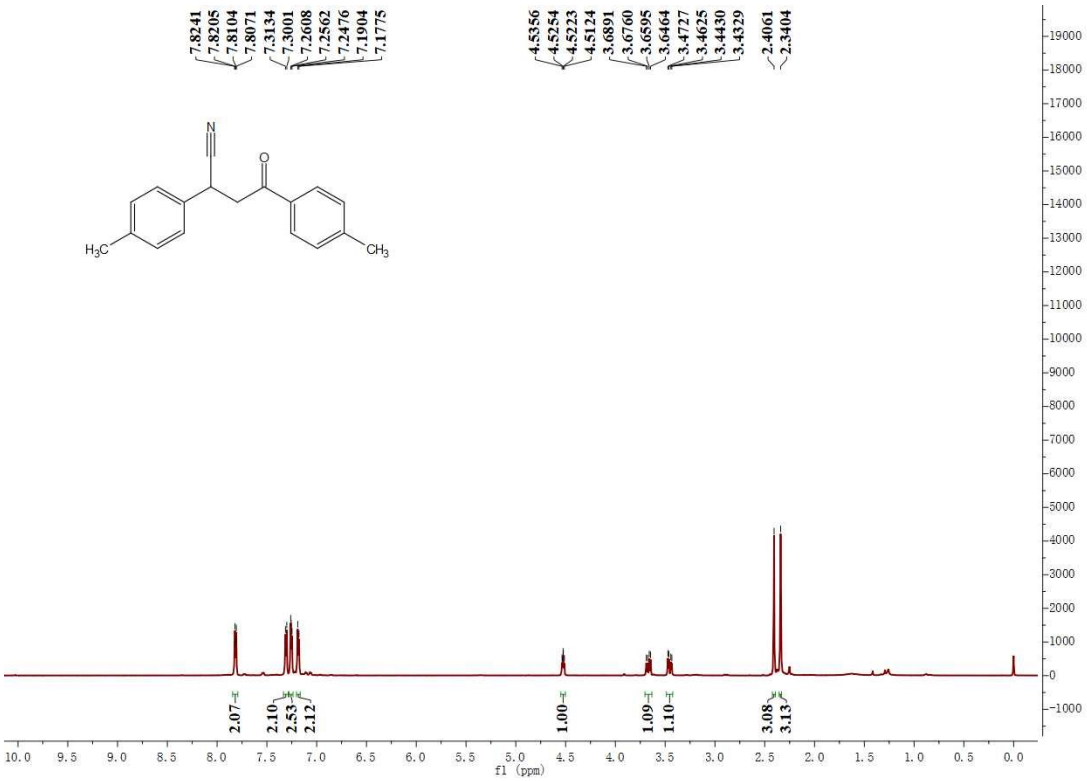
^{1}H-NMR Spectrum (400 MHz, $CDCl_3$) of **14d**



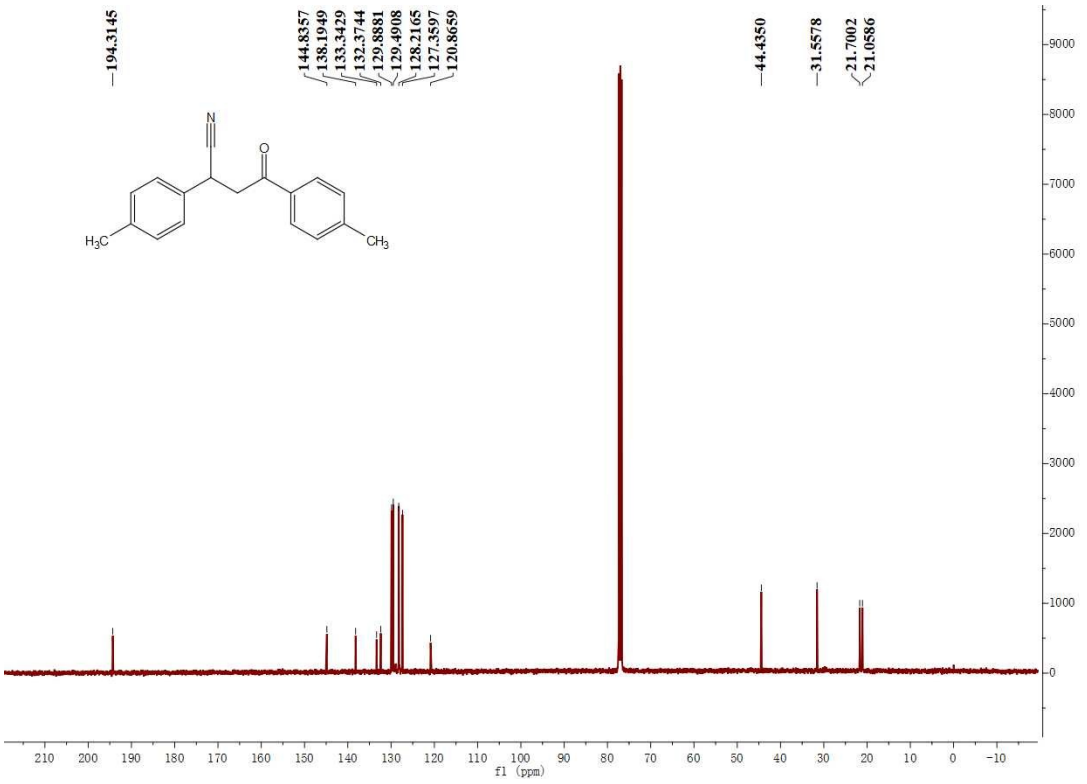
^{13}C-NMR Spectrum (101 MHz, $CDCl_3$) of **14d**



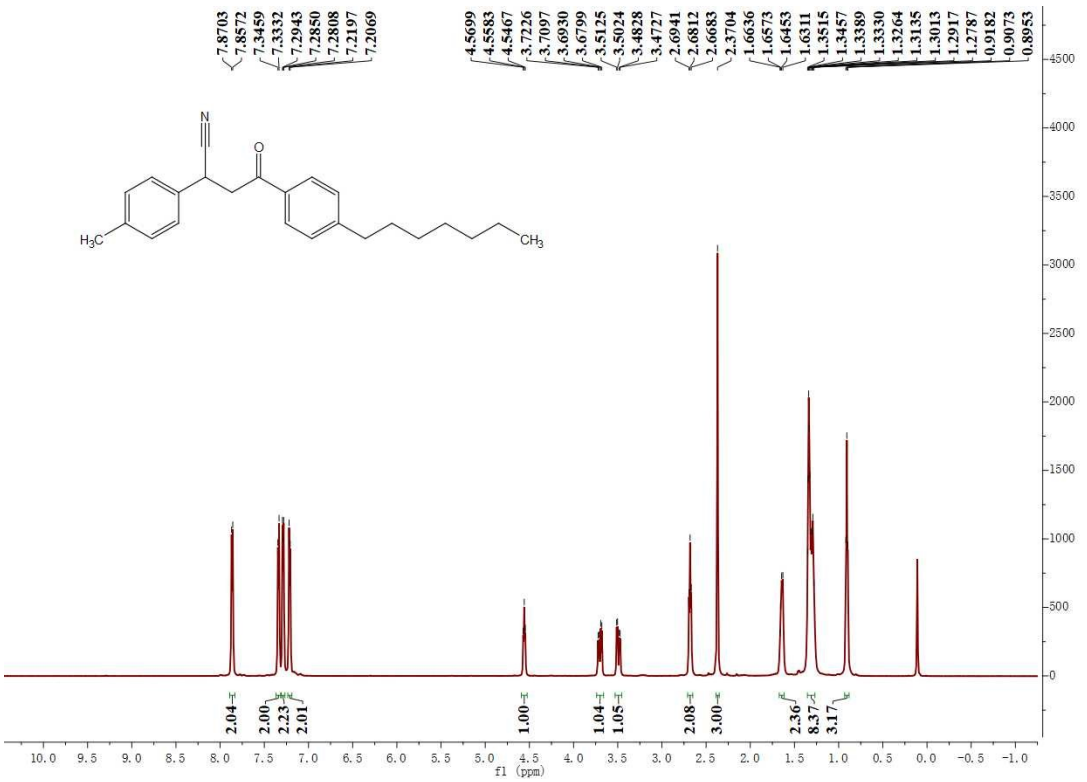
^{1}H-NMR Spectrum (600 MHz, $CDCl_3$) of **15d**



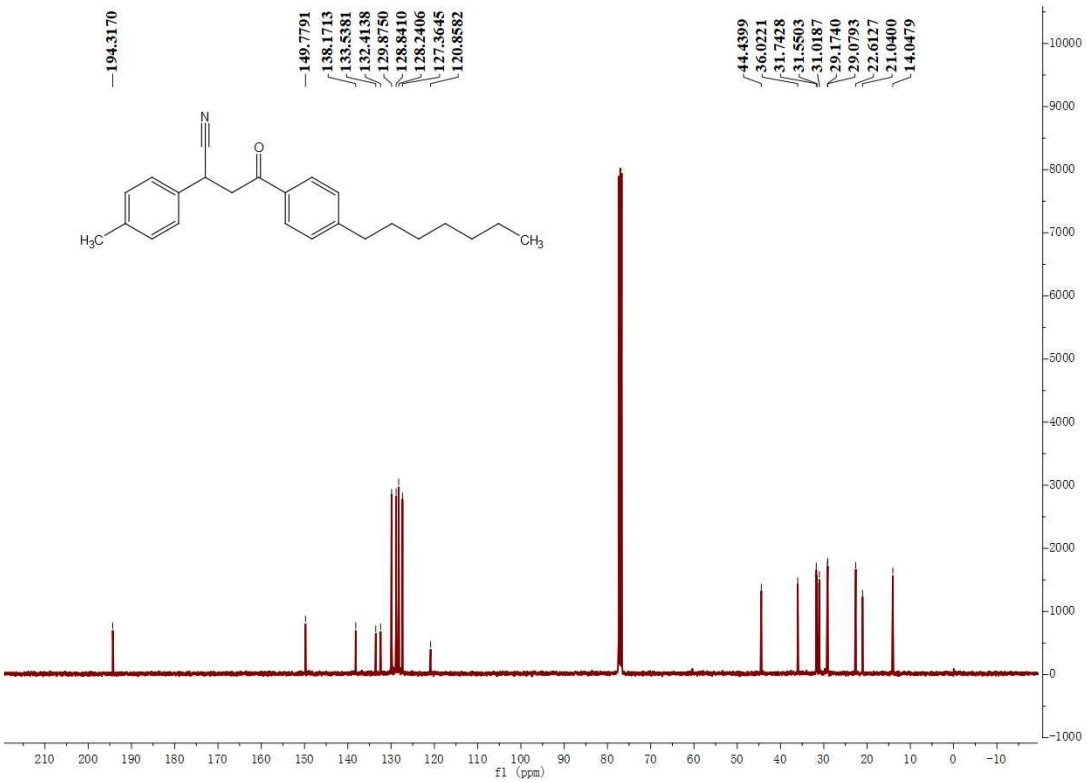
^{13}C-NMR Spectrum (101 MHz, $CDCl_3$) of **15d**



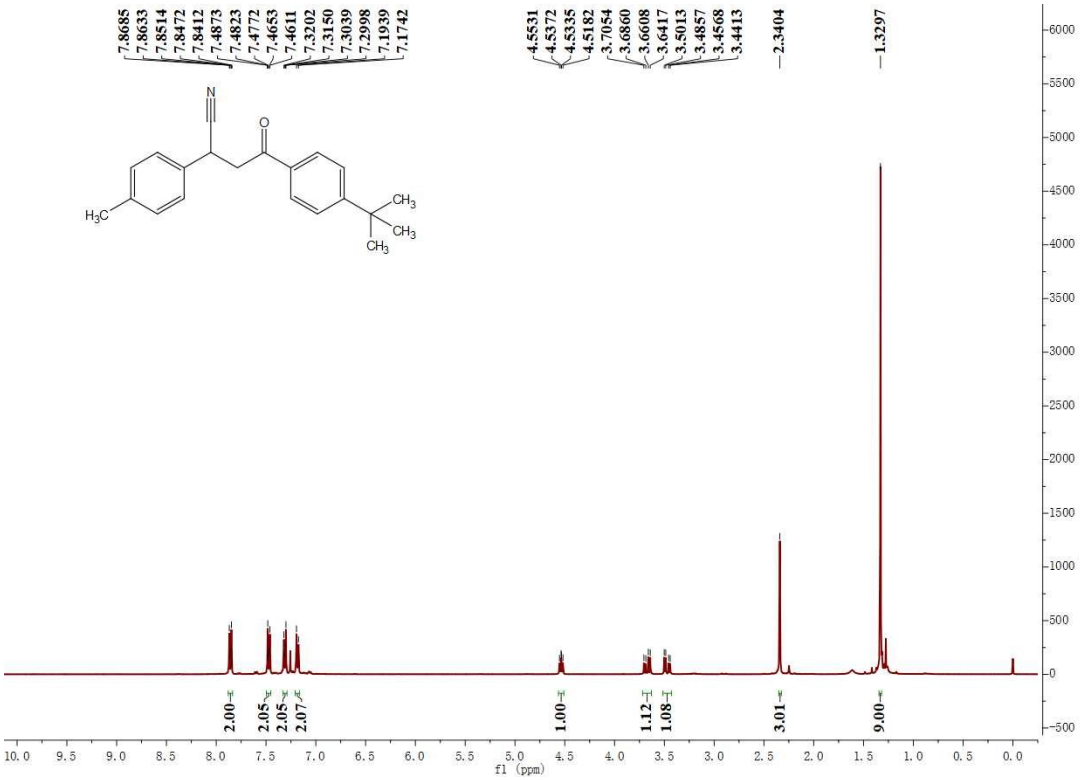
^{1}H-NMR Spectrum (600 MHz, $CDCl_3$) of **16d**



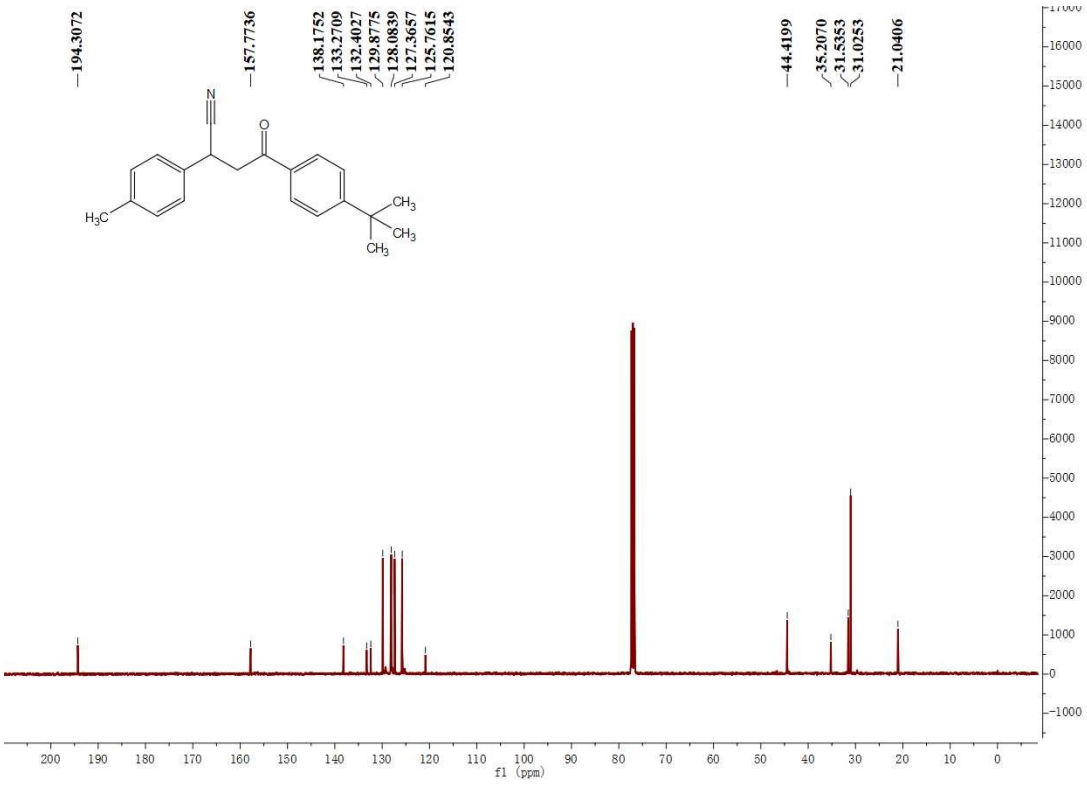
^{13}C-NMR Spectrum (101 MHz, $CDCl_3$) of **16d**



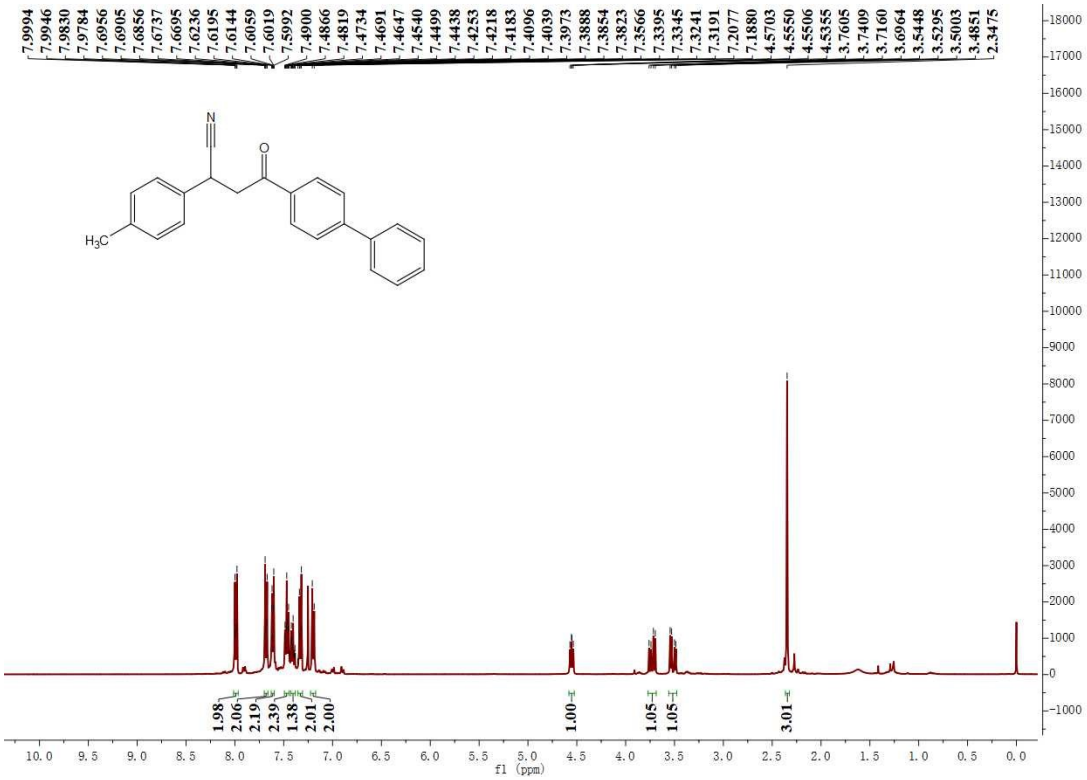
^{1}H-NMR Spectrum (400 MHz, $CDCl_3$) of **17d**



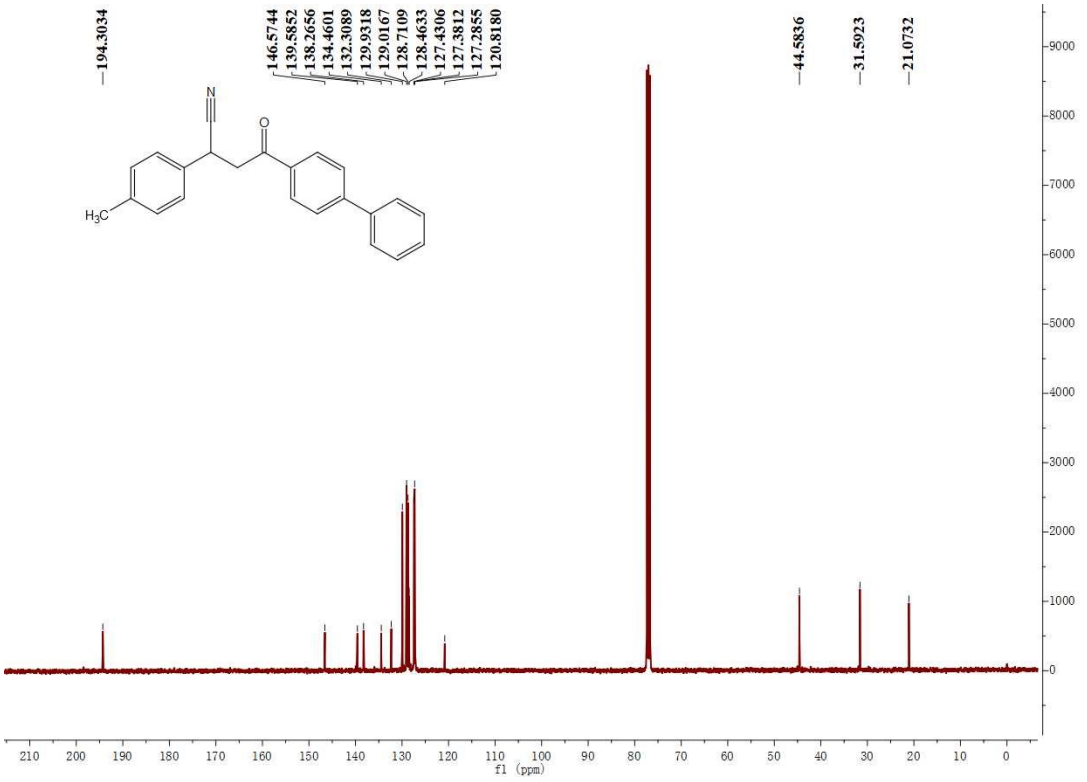
^{13}C-NMR Spectrum (101 MHz, $CDCl_3$) of **17d**



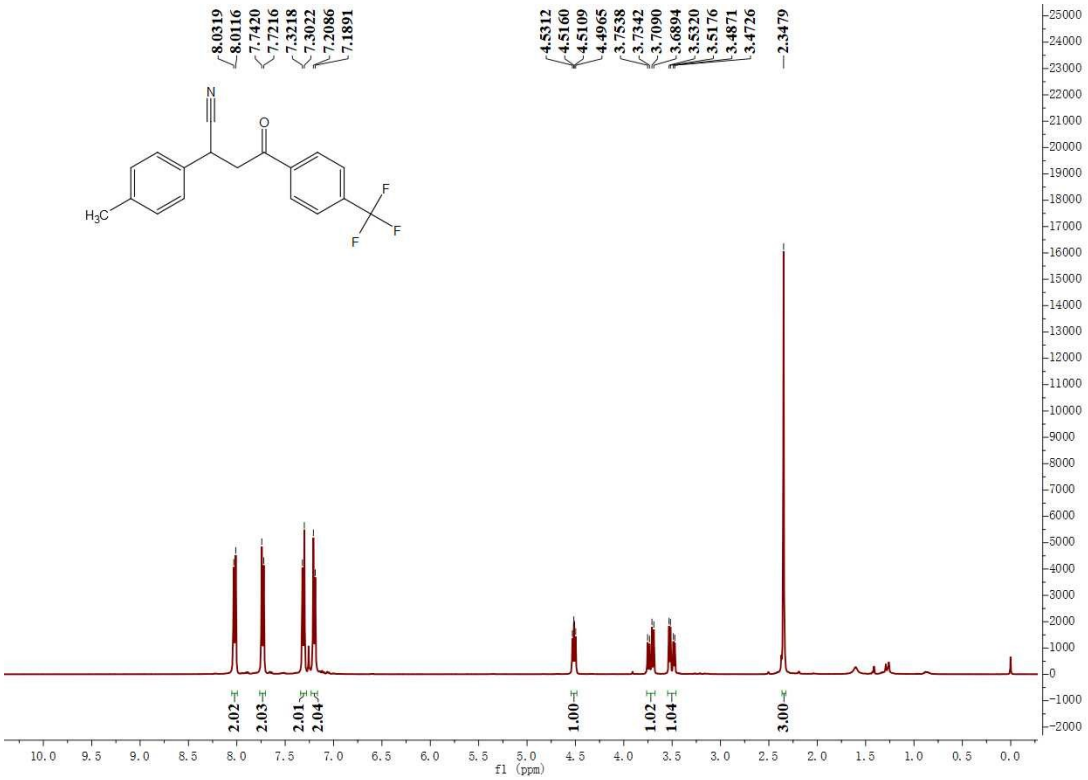
^{1}H-NMR Spectrum (400 MHz, $CDCl_3$) of **18d**



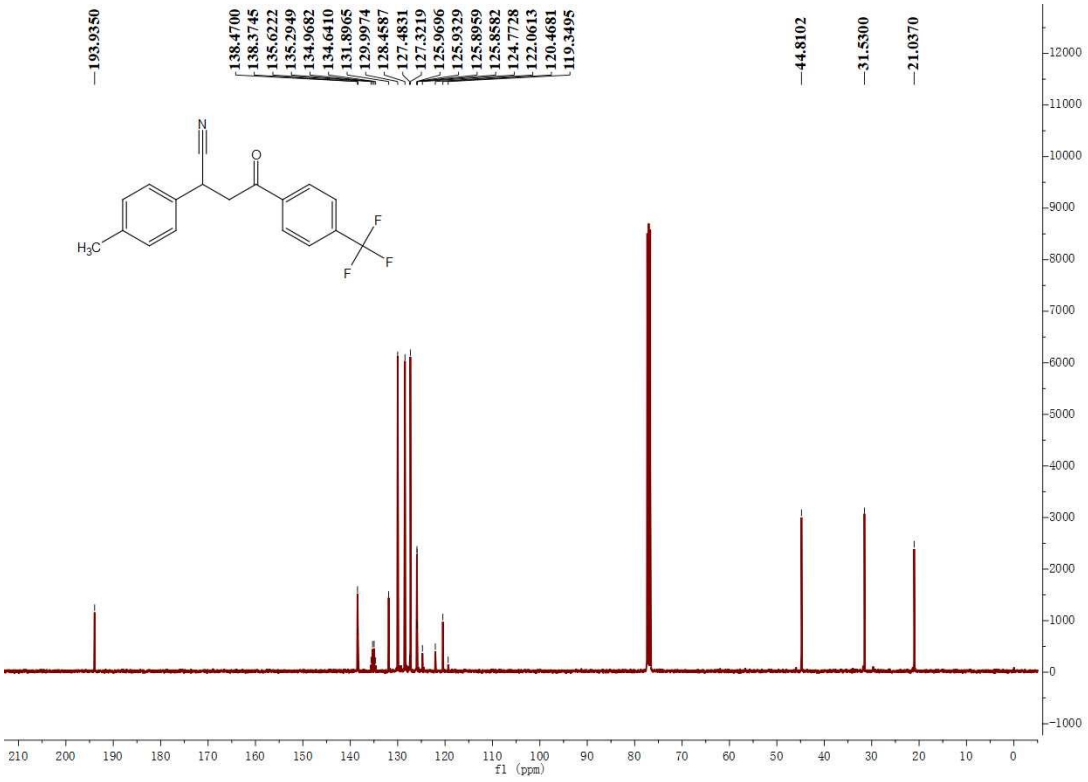
^{13}C-NMR Spectrum (101 MHz, $CDCl_3$) of **18d**



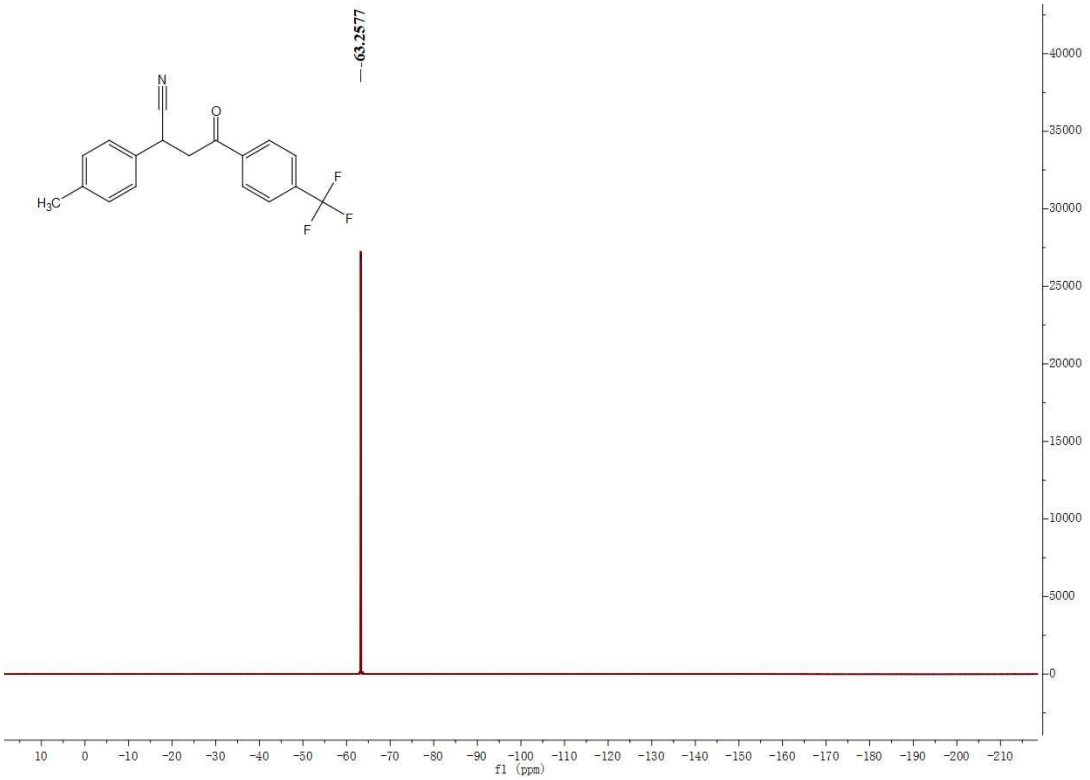
^{1}H-NMR Spectrum (400 MHz, $CDCl_3$) of **19d**



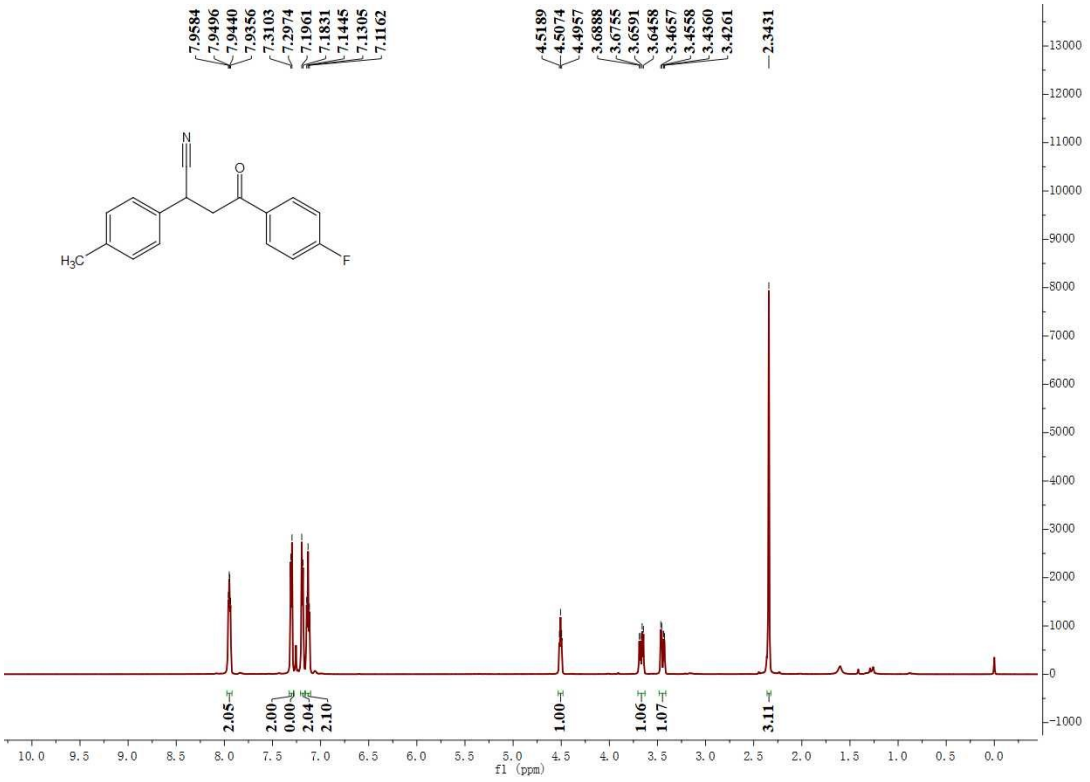
^{13}C-NMR Spectrum (101 MHz, $CDCl_3$) of **19d**



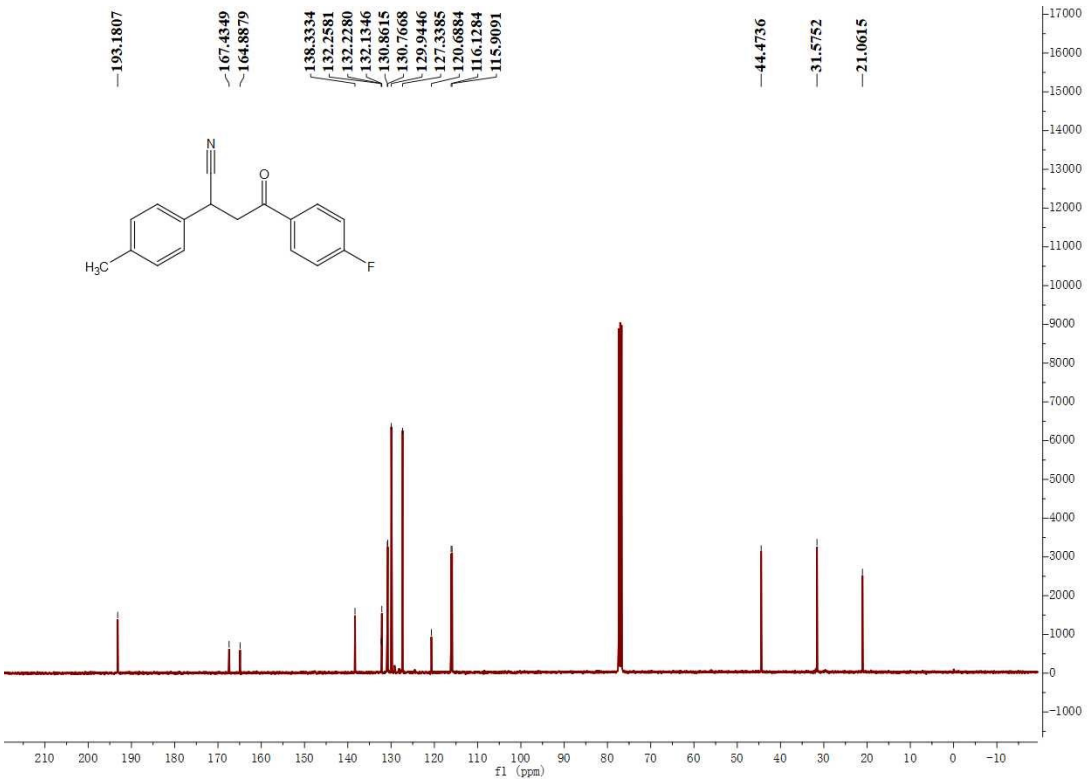
^{19}F-NMR Spectrum (376 MHz, $CDCl_3$) of **19d**



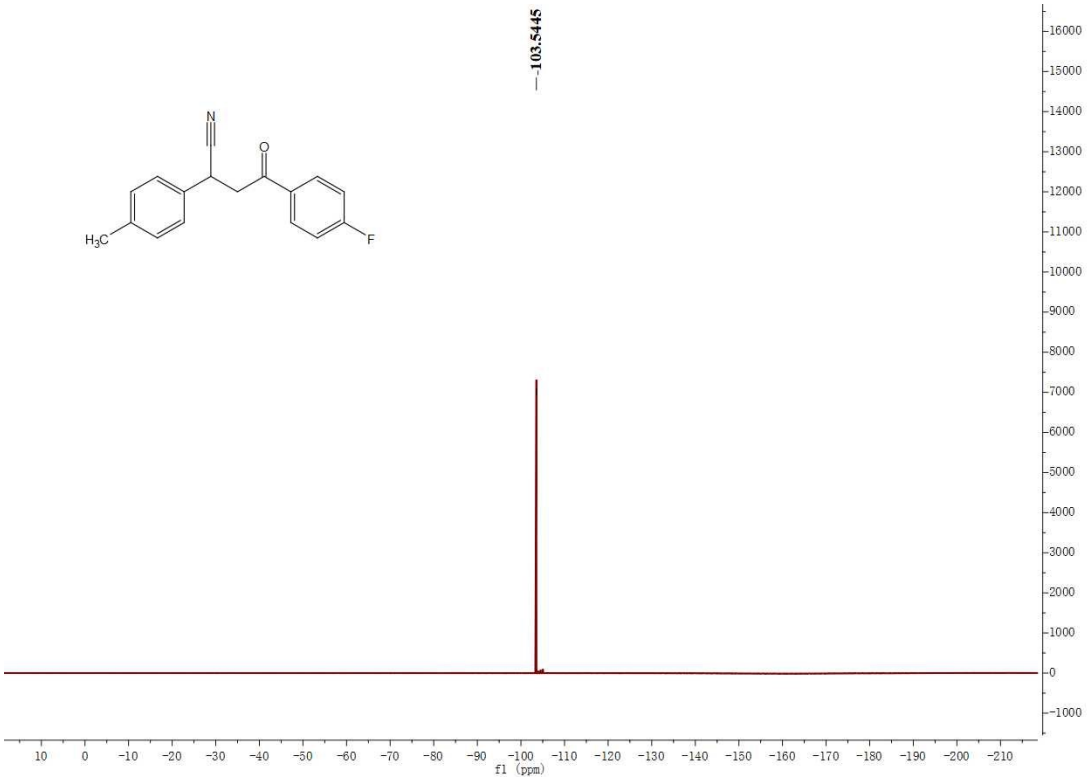
^{1}H-NMR Spectrum (600 MHz, $CDCl_3$) of **20d**



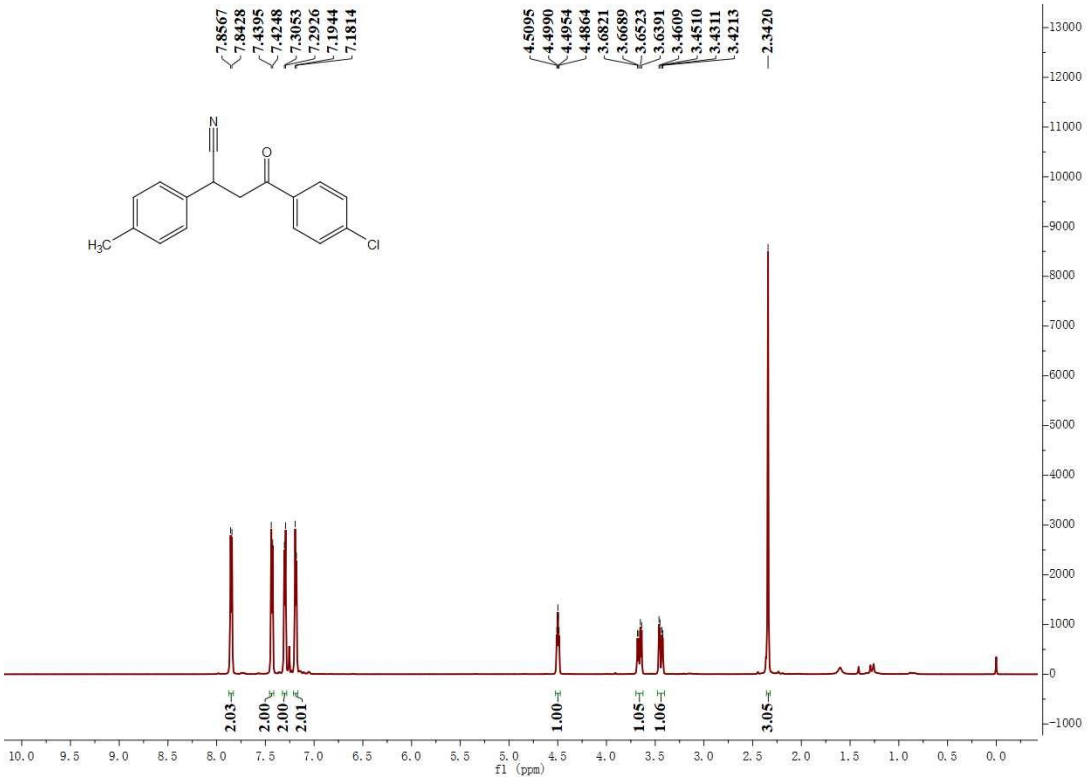
^{13}C-NMR Spectrum (101 MHz, $CDCl_3$) of **20d**



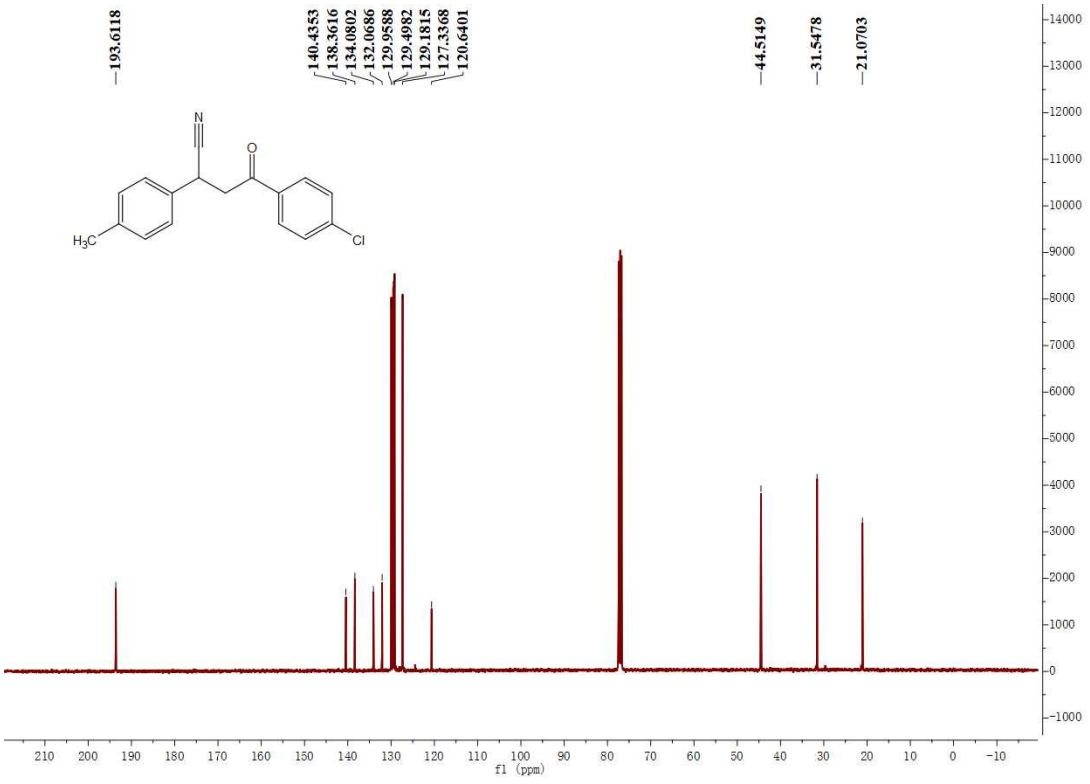
^{19}F-NMR Spectrum (376 MHz, $CDCl_3$) of **20d**



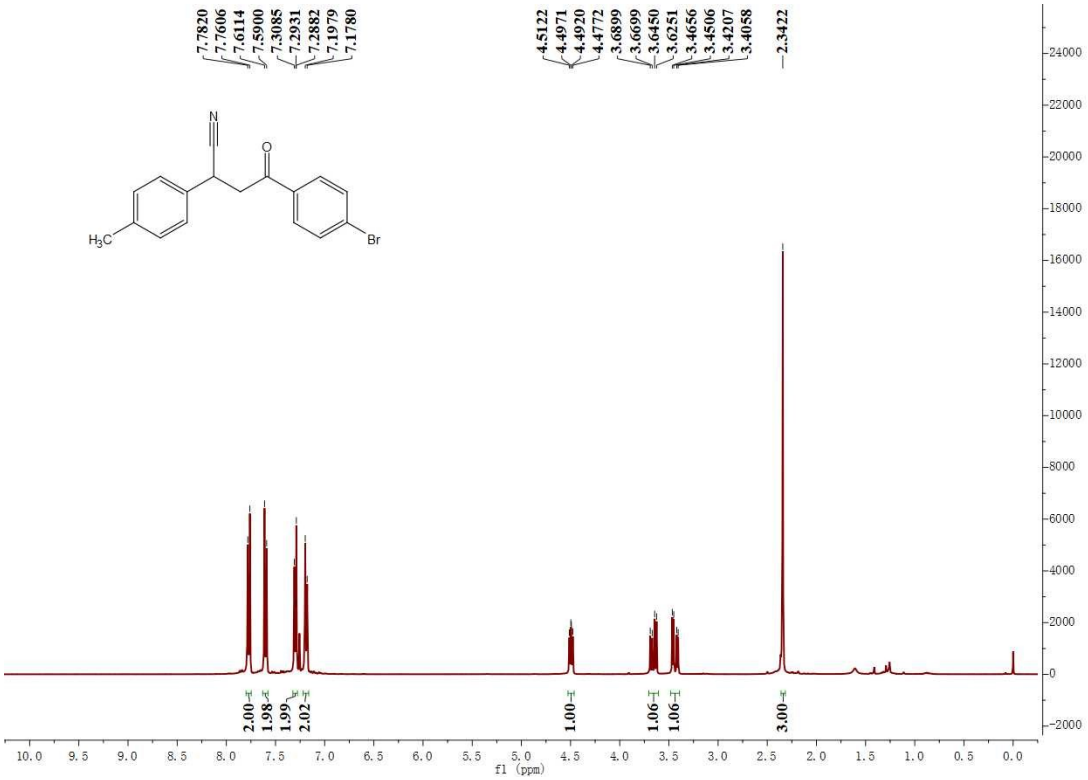
^{1}H-NMR Spectrum (600 MHz, $CDCl_3$) of **21d**



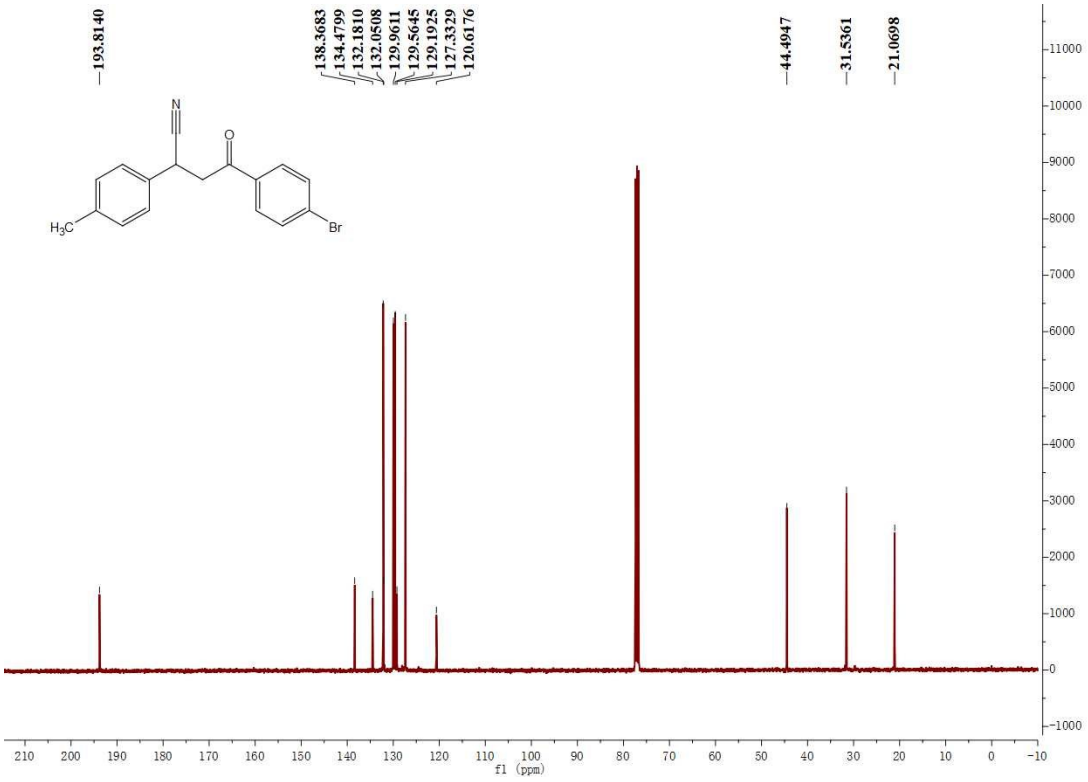
^{13}C-NMR Spectrum (101 MHz, $CDCl_3$) of **21d**



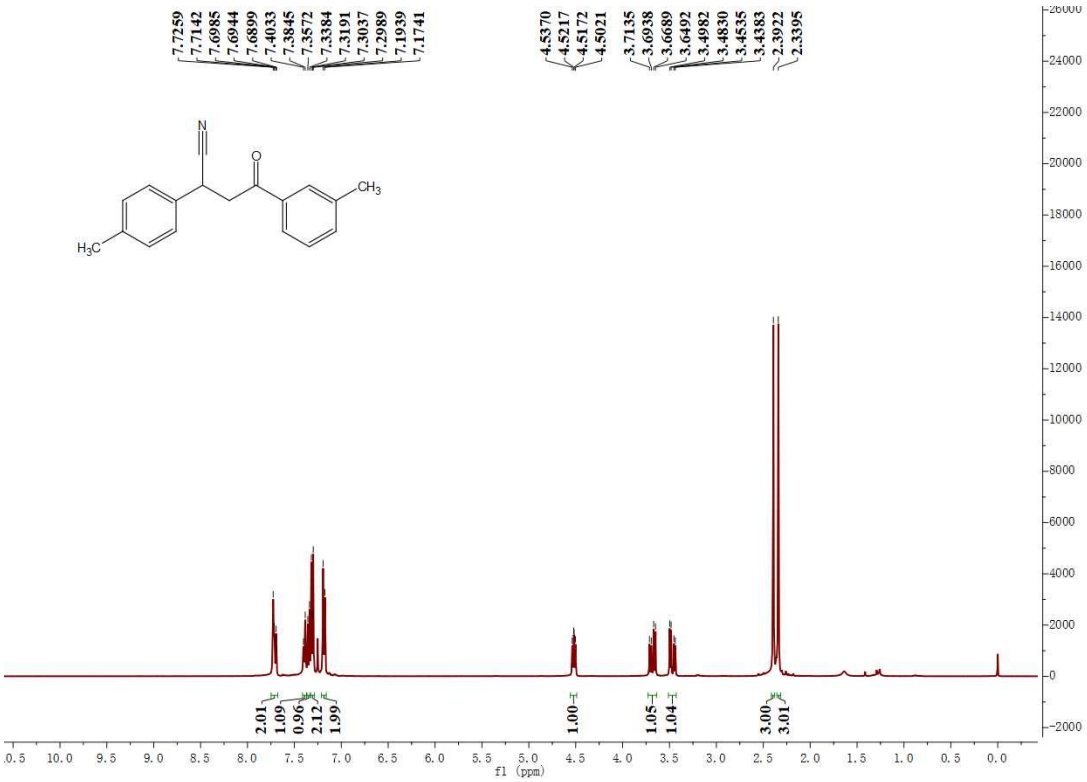
^{1}H-NMR Spectrum (400 MHz, $CDCl_3$) of **22d**



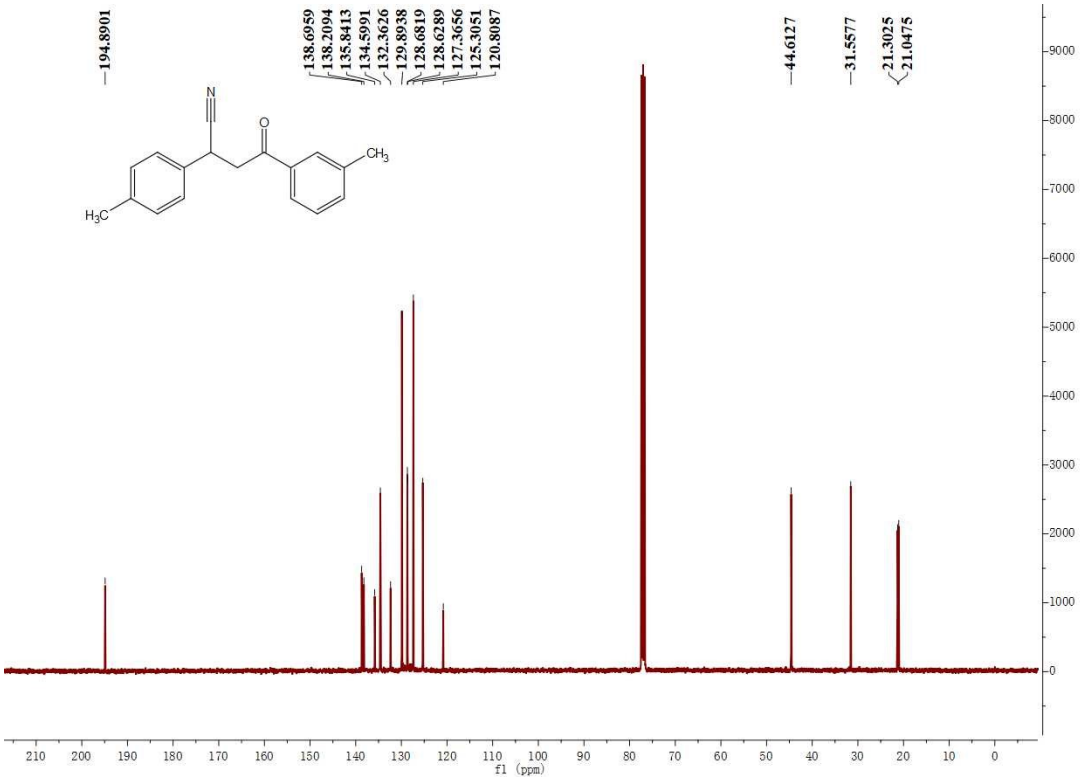
^{13}C-NMR Spectrum (101 MHz, $CDCl_3$) of **22d**



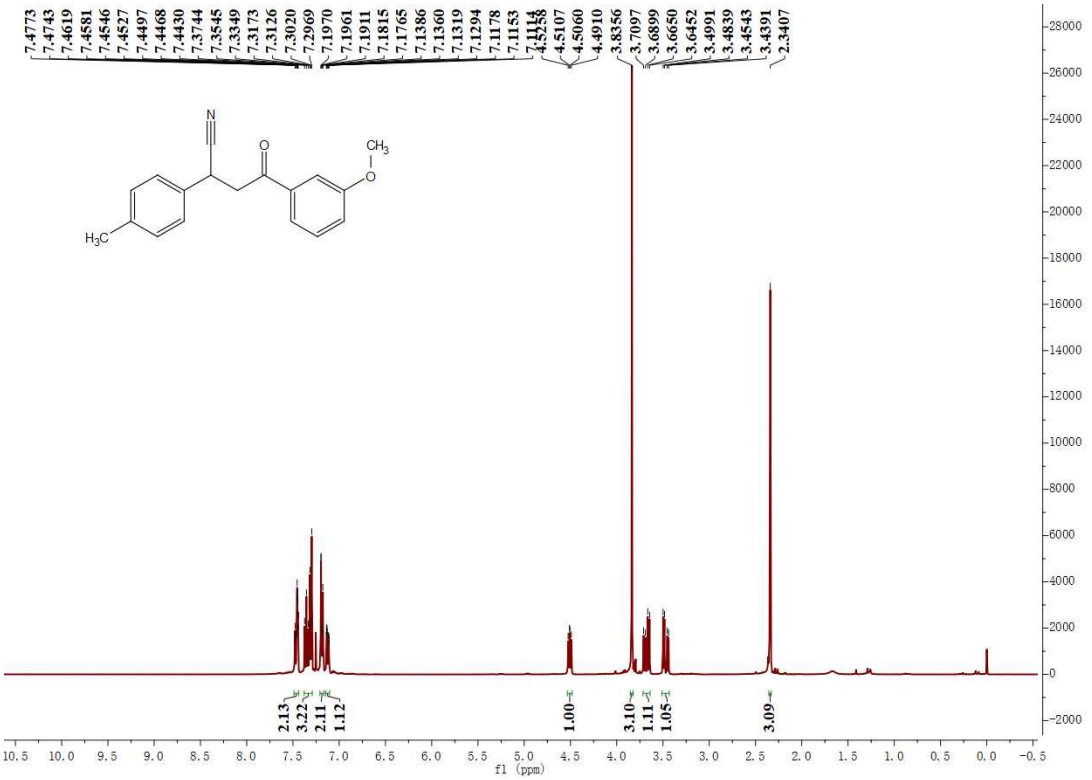
^{1}H-NMR Spectrum (400 MHz, $CDCl_3$) of **23d**



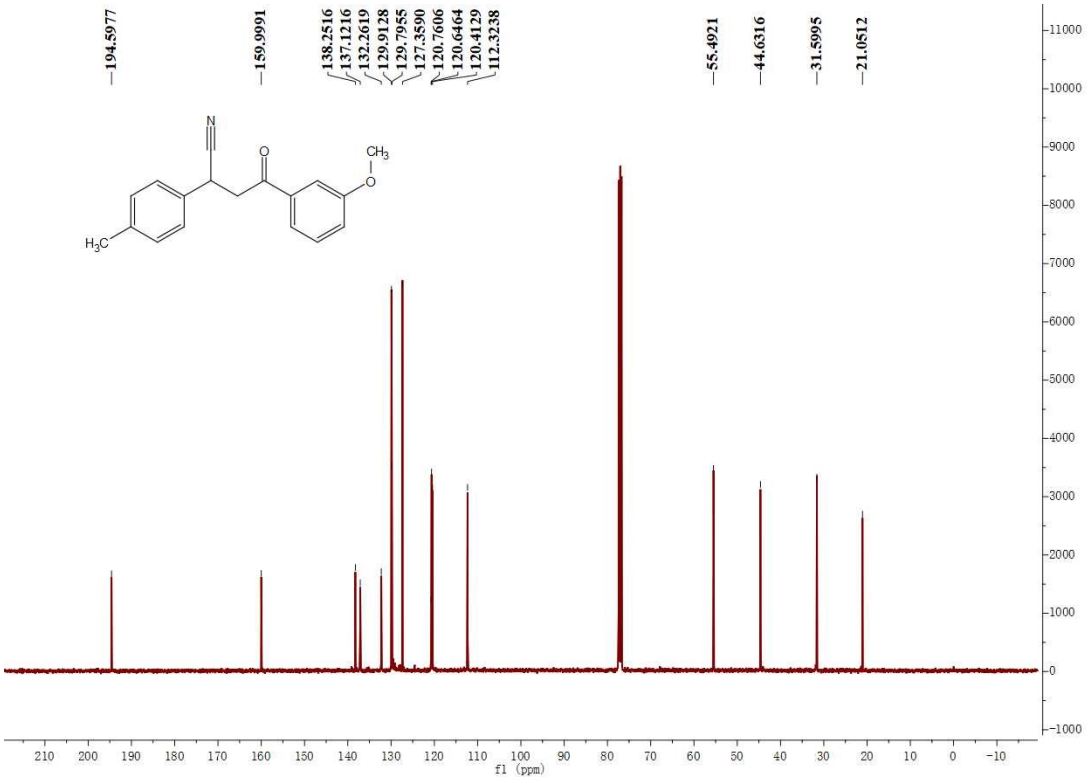
^{13}C-NMR Spectrum (101 MHz, $CDCl_3$) of **23d**



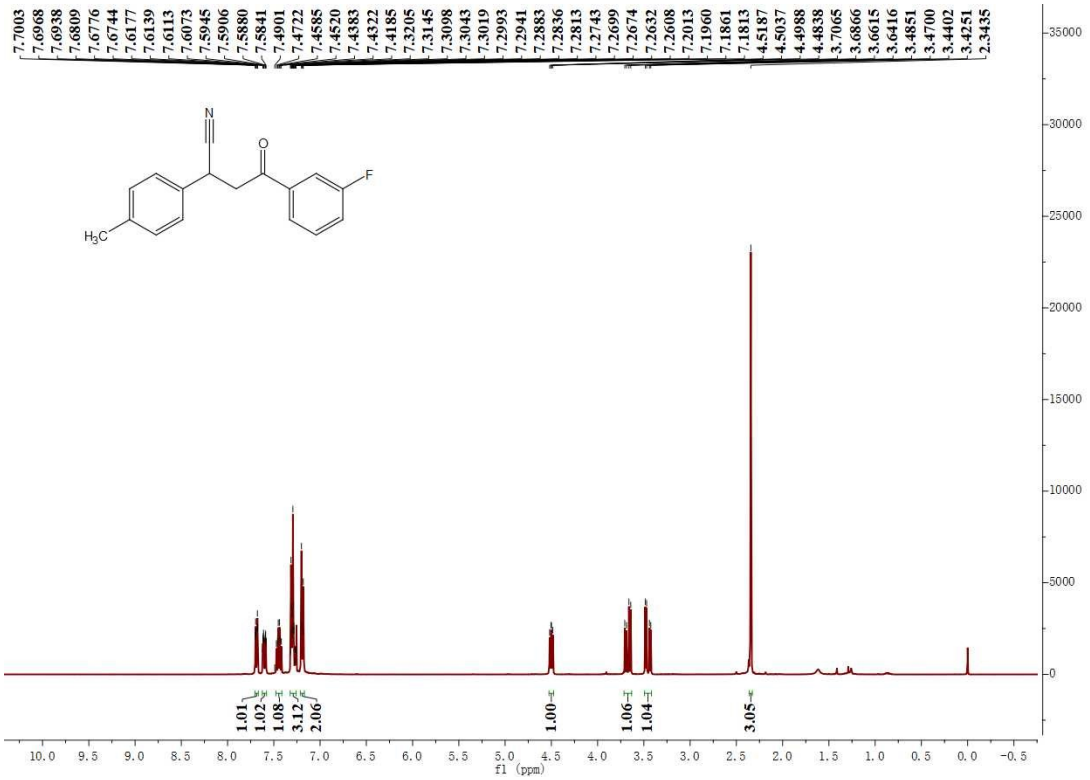
^{1}H-NMR Spectrum (400 MHz, $CDCl_3$) of **24d**



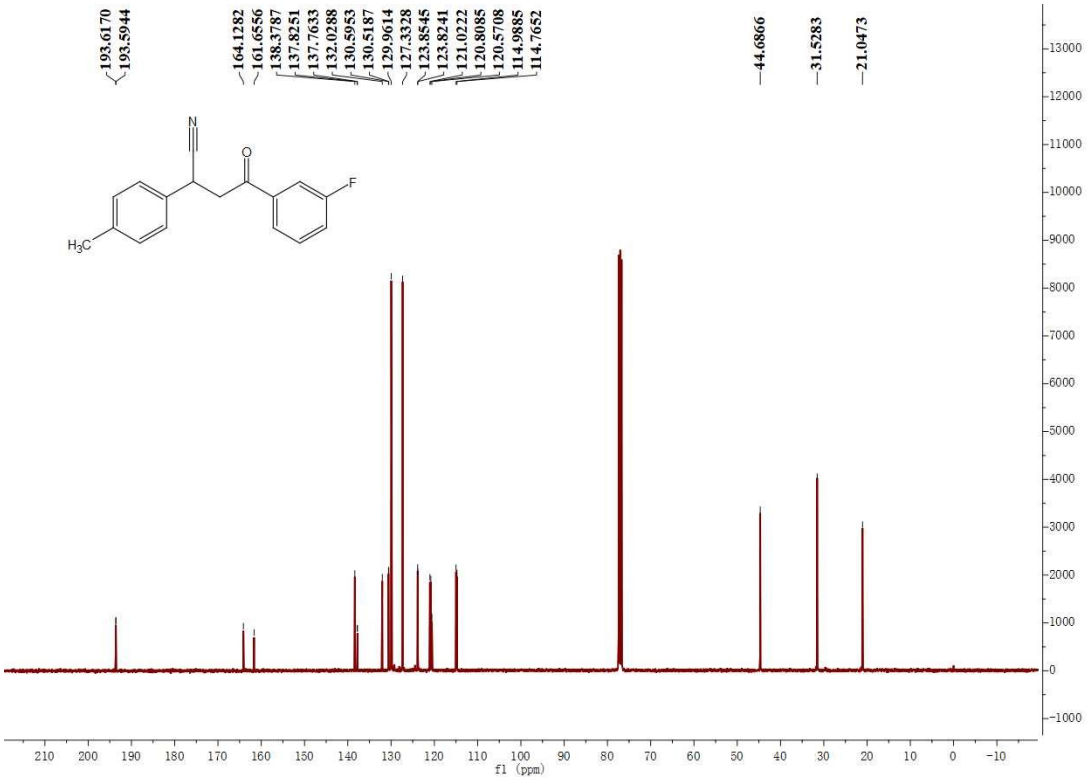
^{13}C-NMR Spectrum (101 MHz, $CDCl_3$) of **24d**



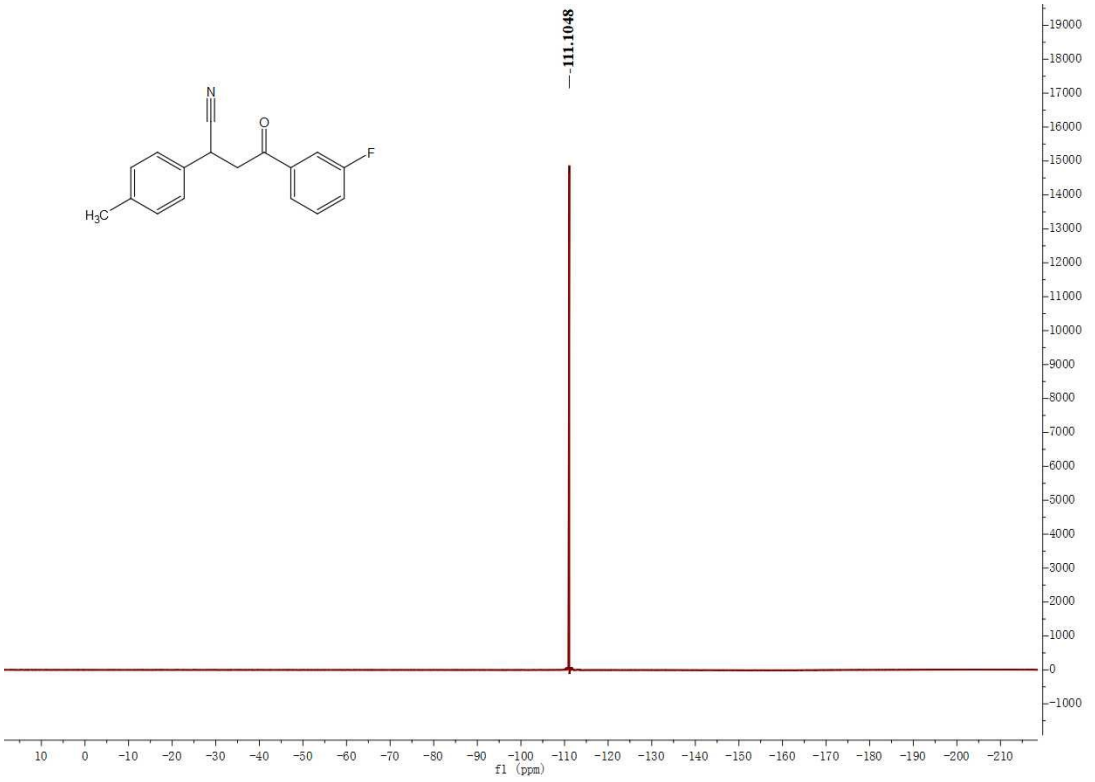
^{1}H-NMR Spectrum (400 MHz, $CDCl_3$) of **25d**



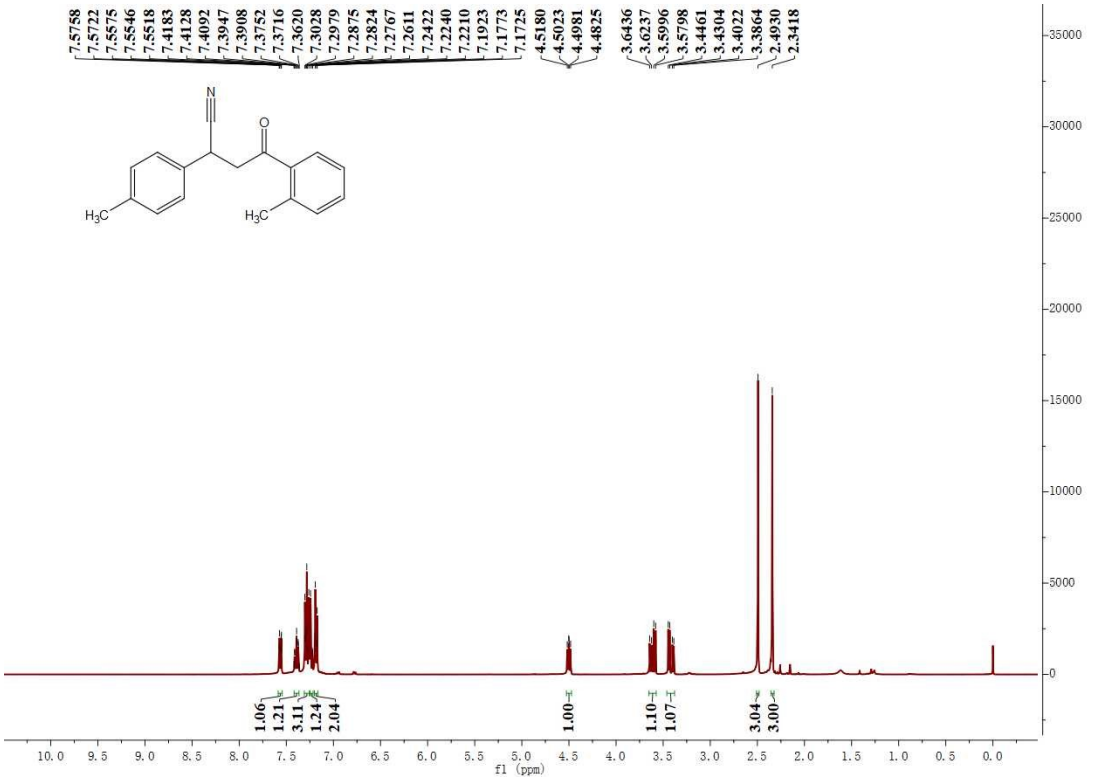
^{13}C-NMR Spectrum (101 MHz, $CDCl_3$) of **25d**



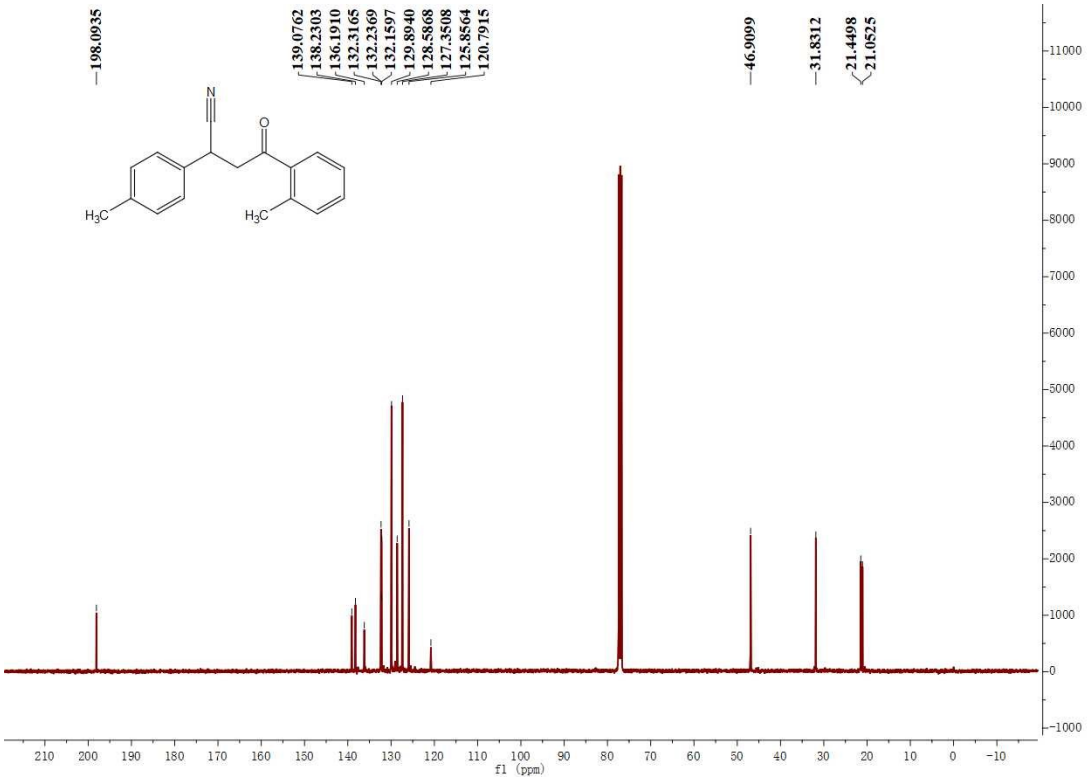
^{19}F-NMR Spectrum (376 MHz, $CDCl_3$) of **25d**



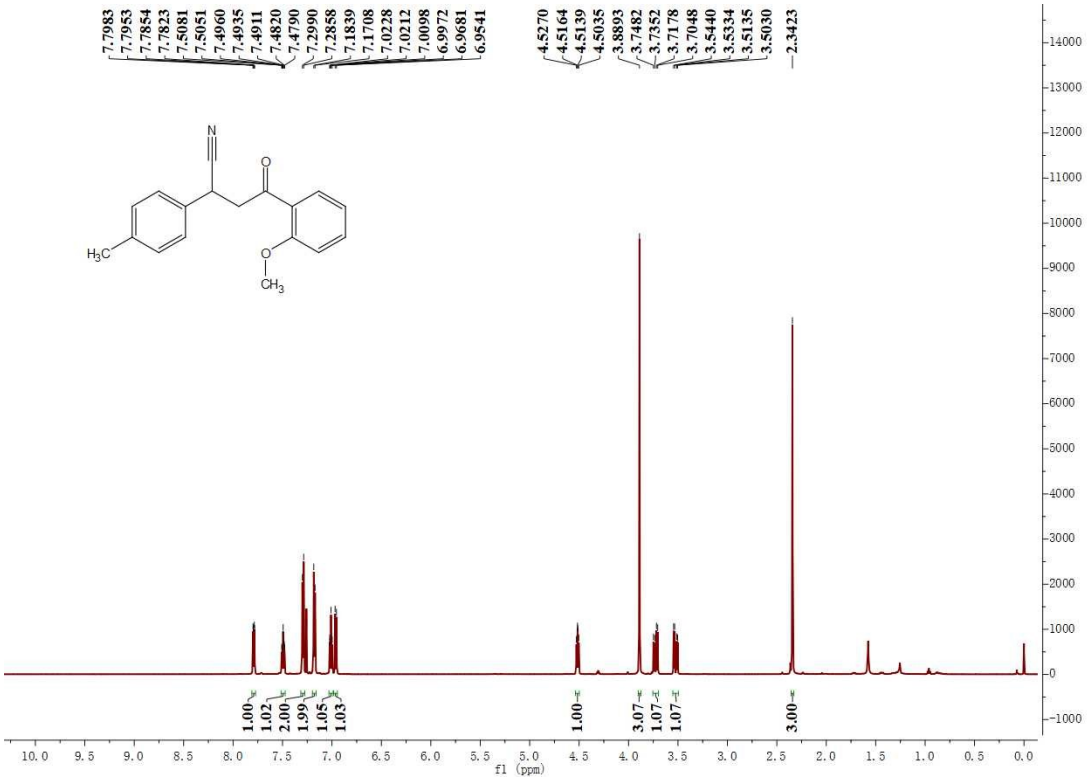
^{1}H-NMR Spectrum (400 MHz, $CDCl_3$) of **26d**



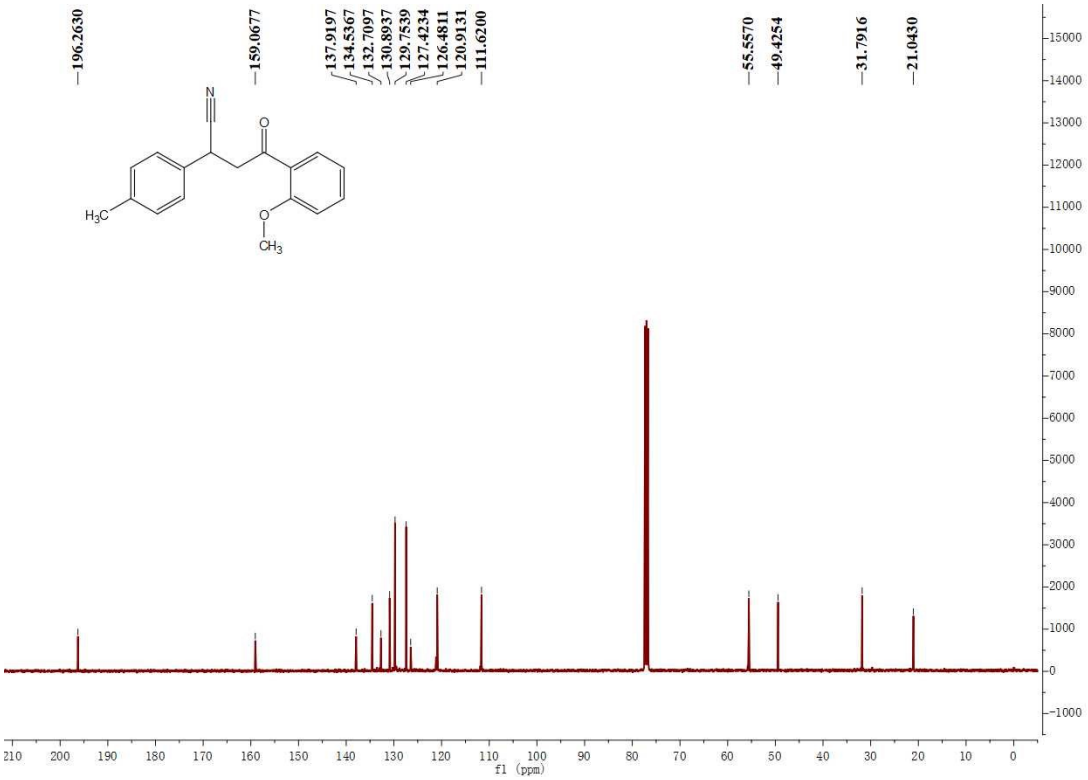
^{13}C-NMR Spectrum (101 MHz, $CDCl_3$) of **26d**



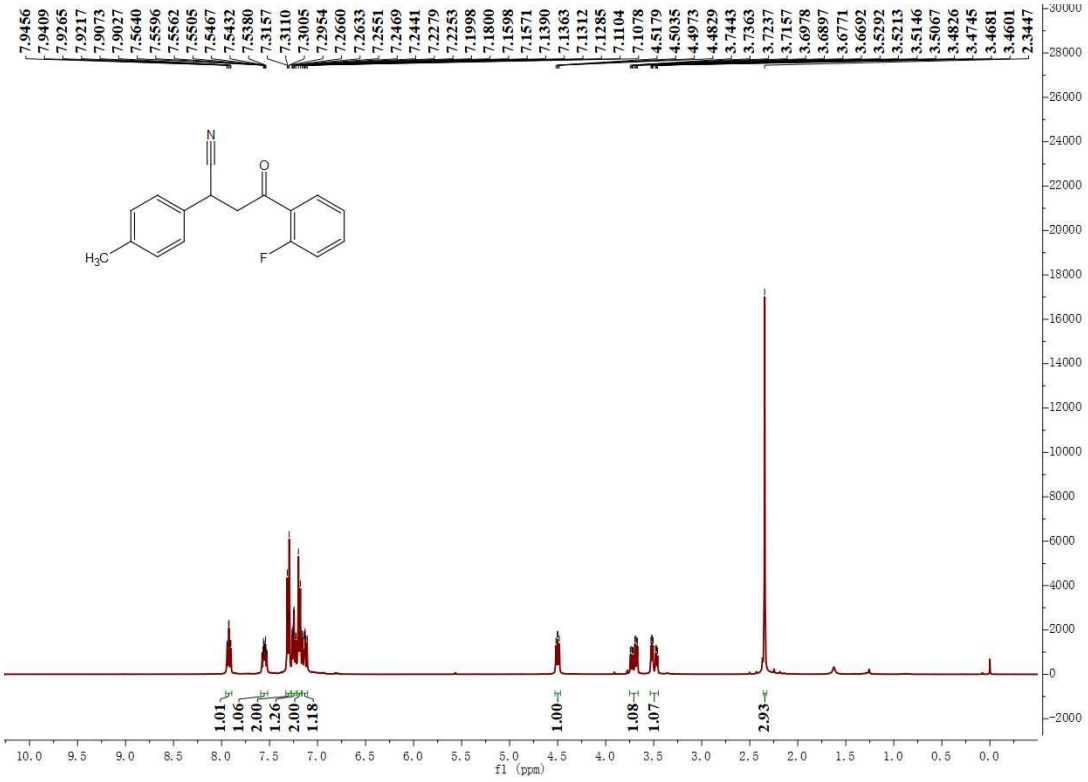
^{1}H-NMR Spectrum (600 MHz, $CDCl_3$) of **27d**



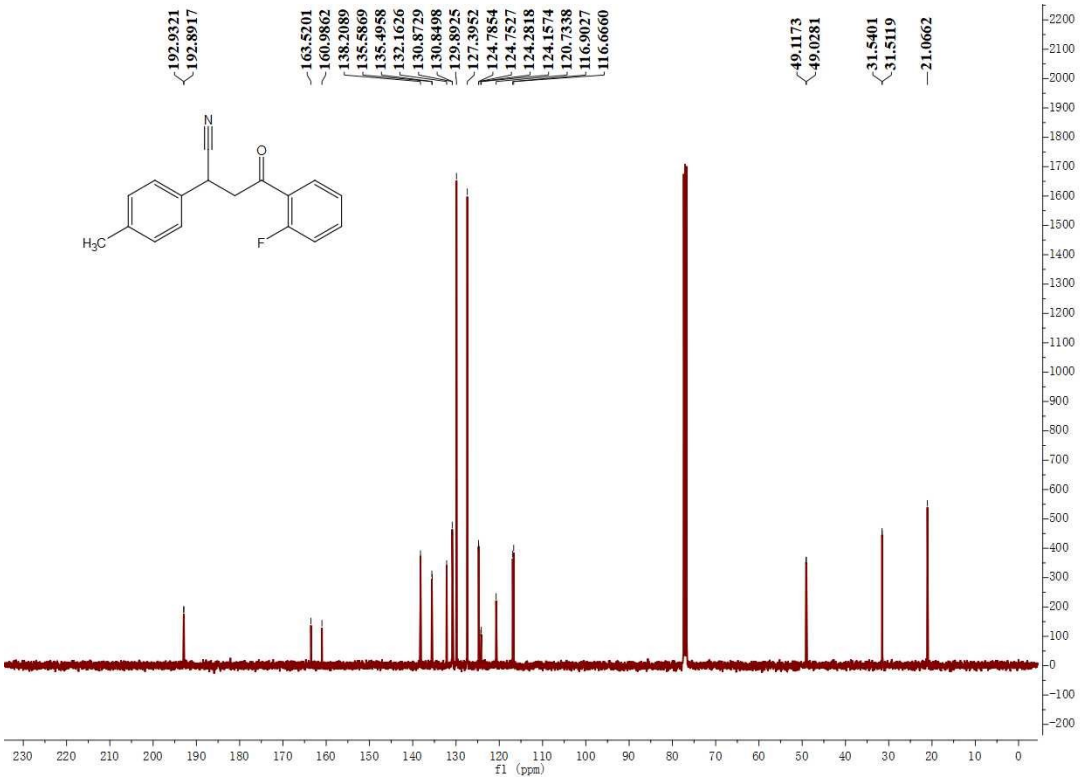
^{13}C-NMR Spectrum (101 MHz, $CDCl_3$) of **27d**



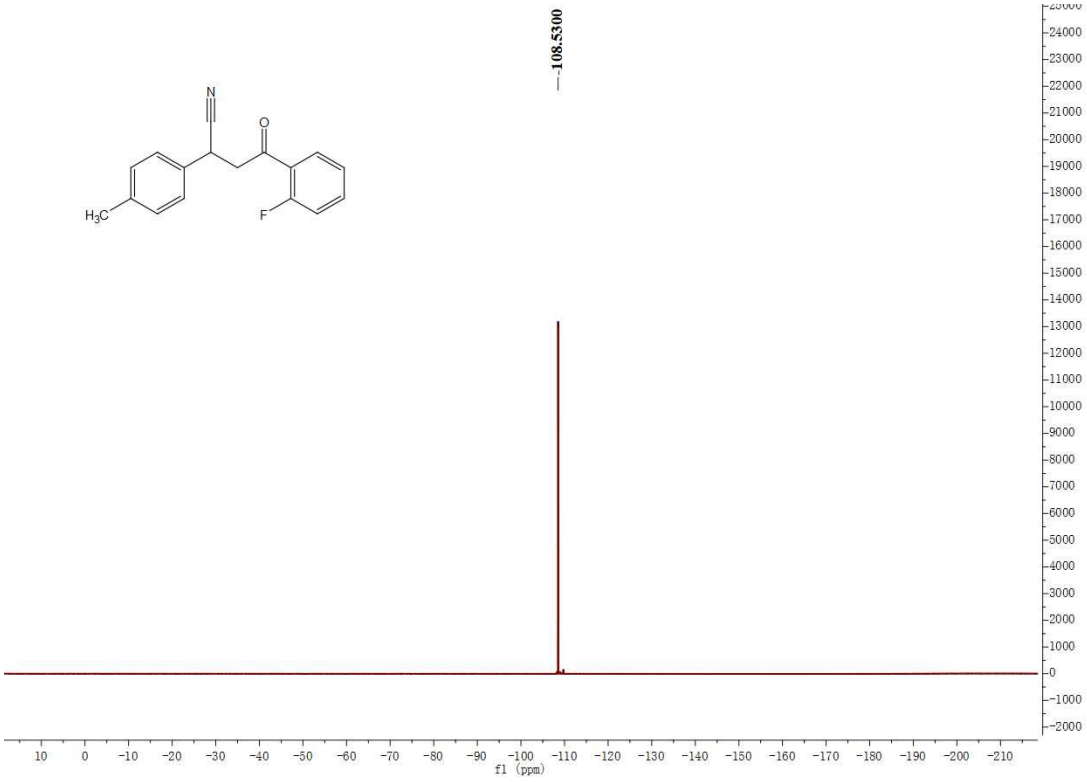
^{1}H-NMR Spectrum (400 MHz, $CDCl_3$) of **28d**



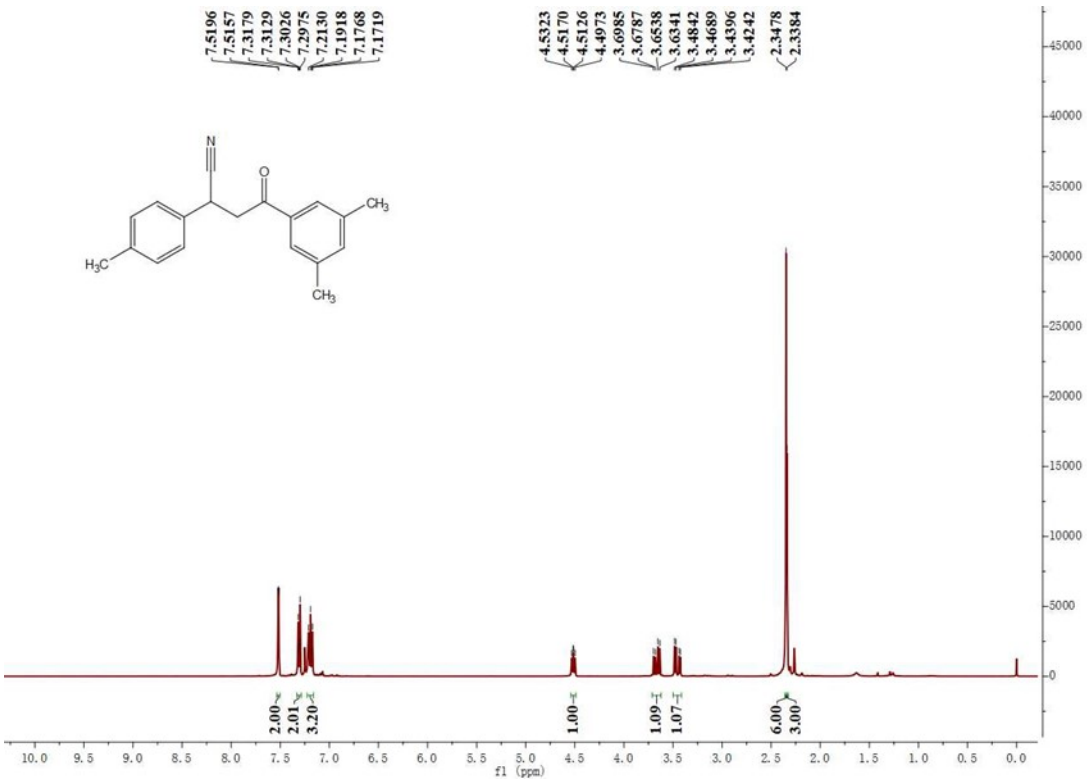
^{13}C-NMR Spectrum (101 MHz, $CDCl_3$) of **28d**



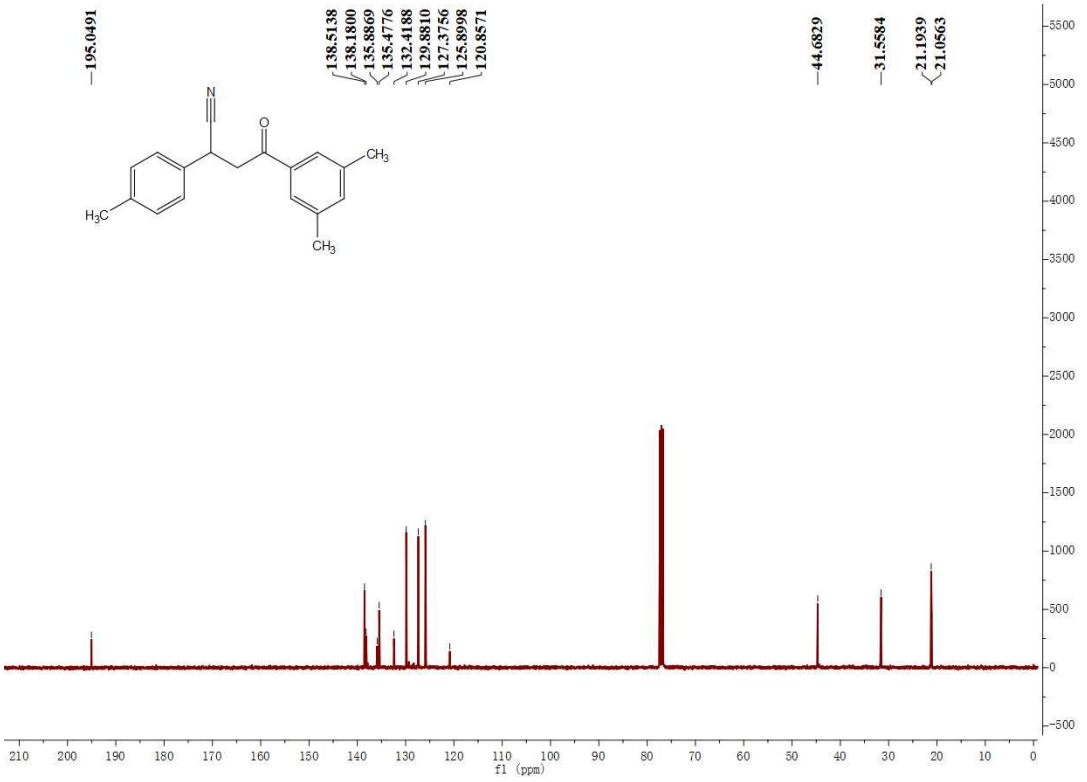
^{19}F-NMR Spectrum (376 MHz, $CDCl_3$) of **28d**



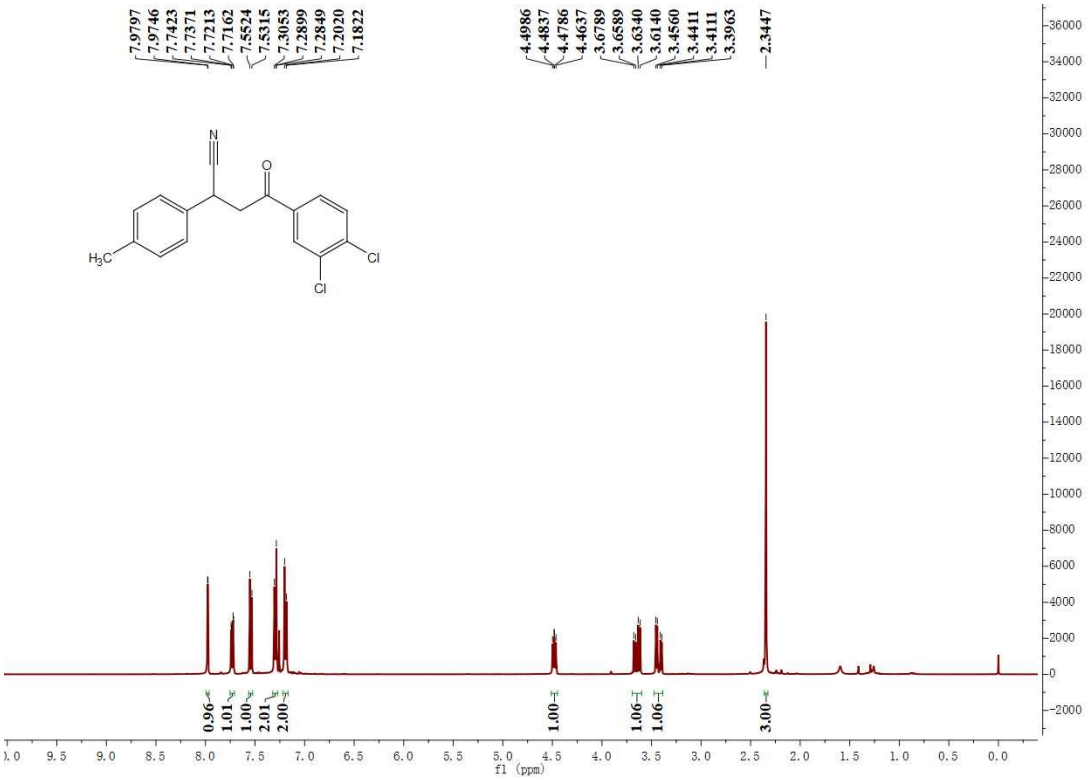
^{1}H-NMR Spectrum (400 MHz, $CDCl_3$) of **29d**



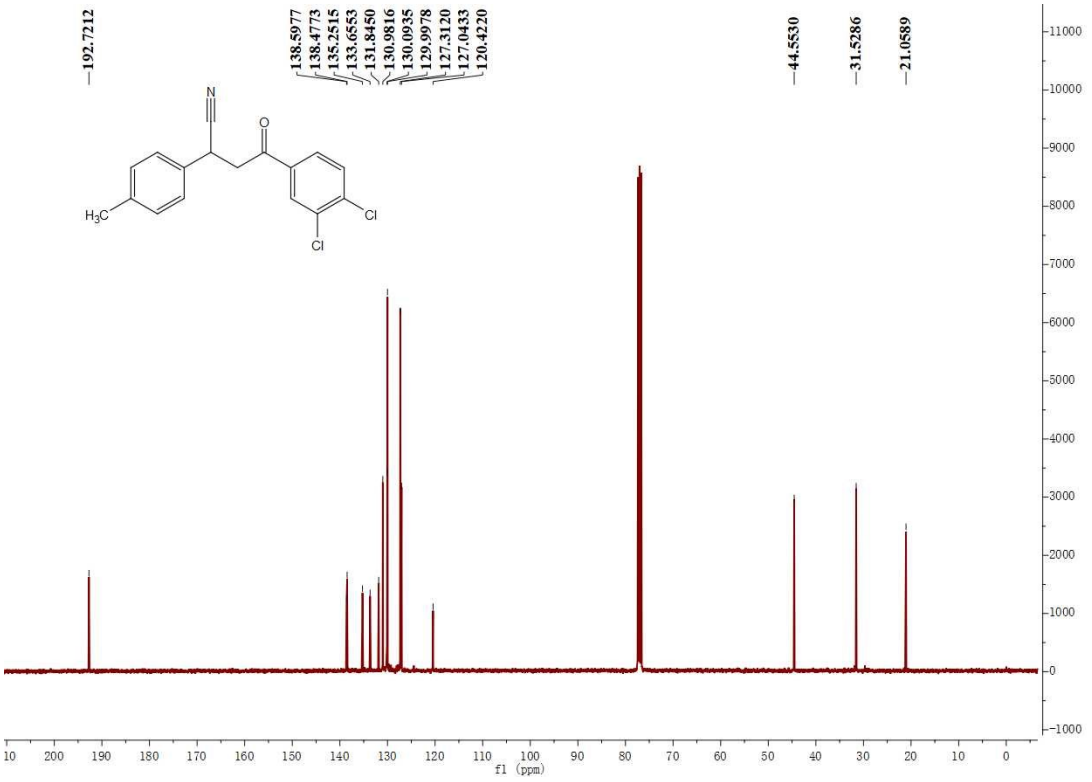
^{13}C-NMR Spectrum (101 MHz, $CDCl_3$) of **29d**



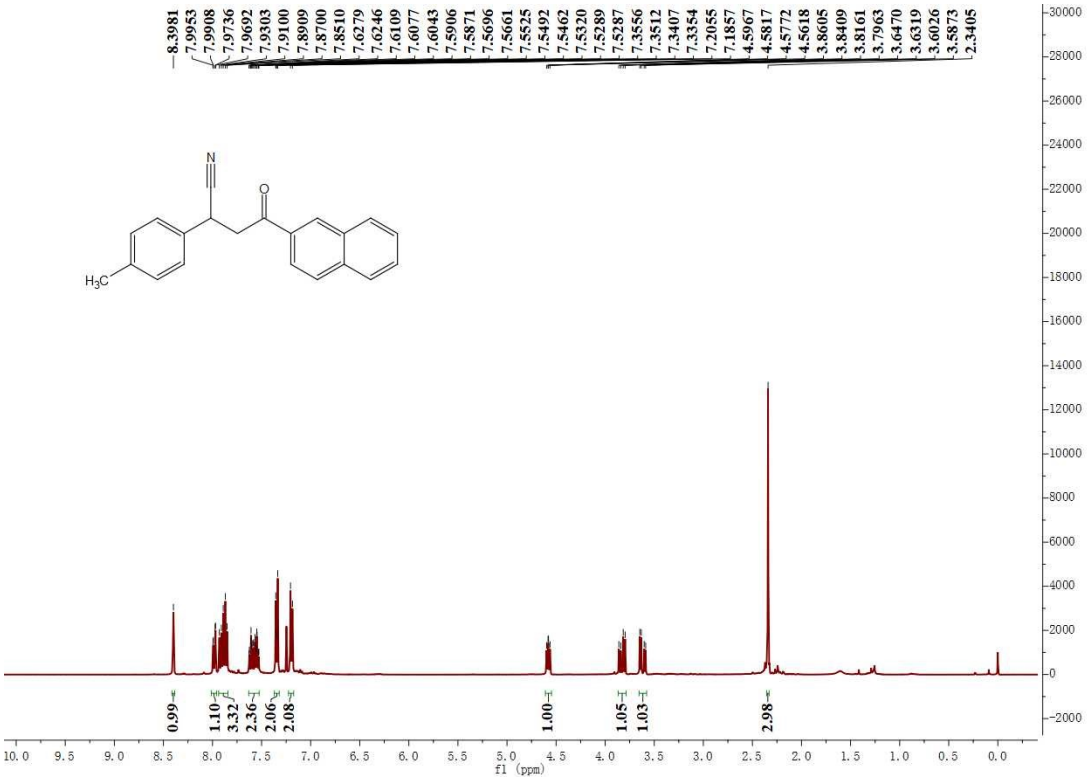
^{1}H-NMR Spectrum (400 MHz, $CDCl_3$) of **30d**



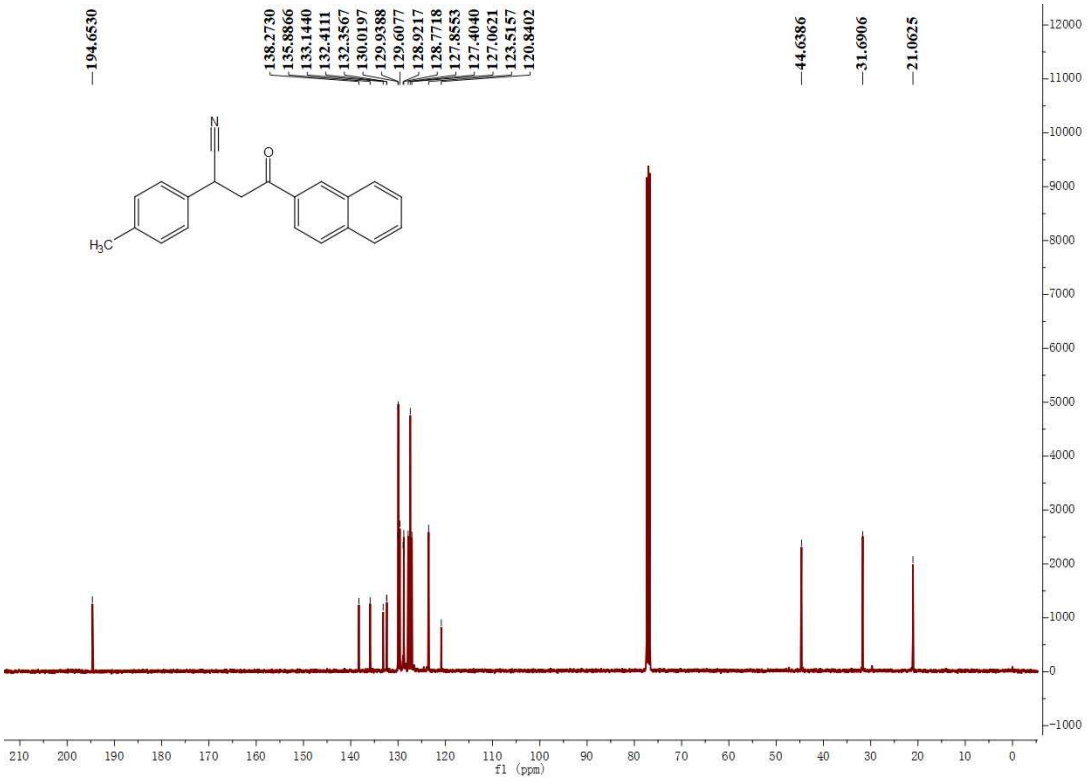
^{13}C-NMR Spectrum (101 MHz, $CDCl_3$) of **30d**



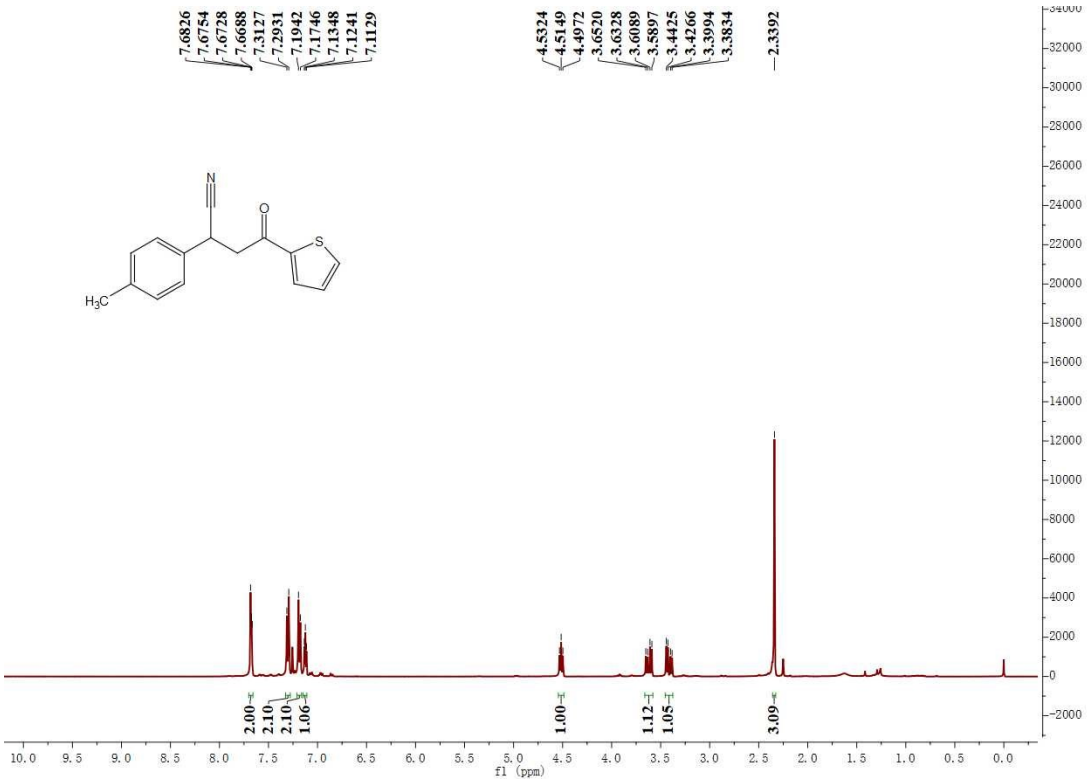
^{1}H-NMR Spectrum (400 MHz, $CDCl_3$) of **31d**



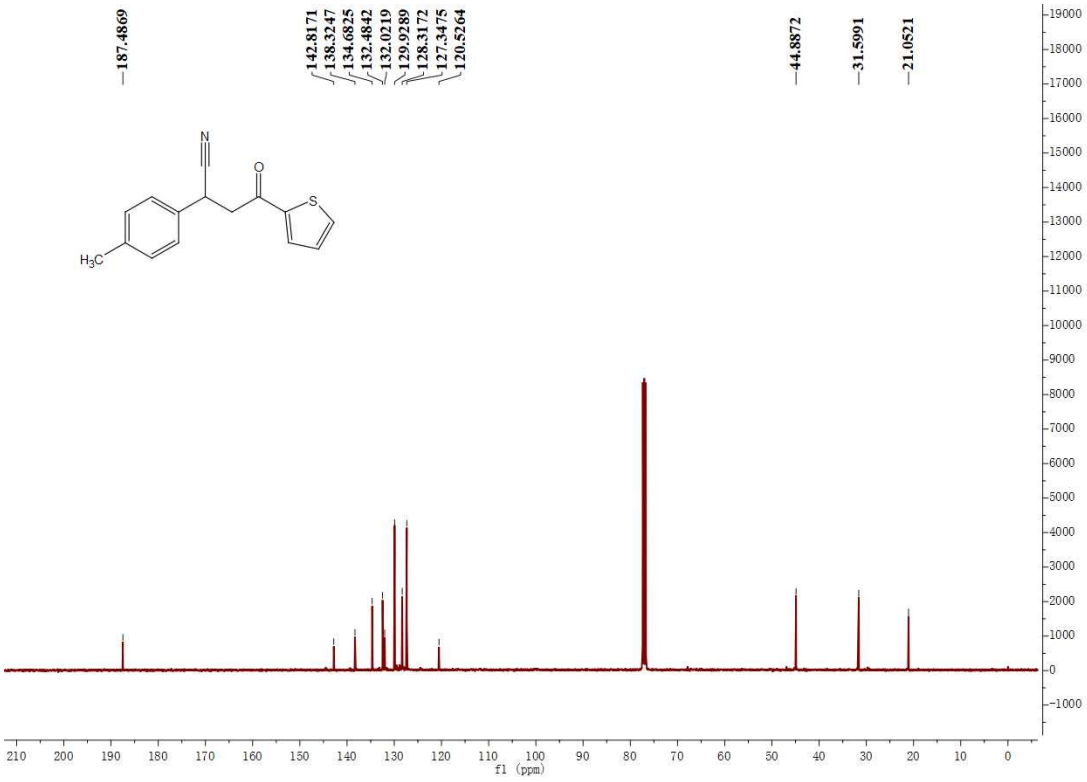
^{13}C-NMR Spectrum (101 MHz, $CDCl_3$) of **31d**



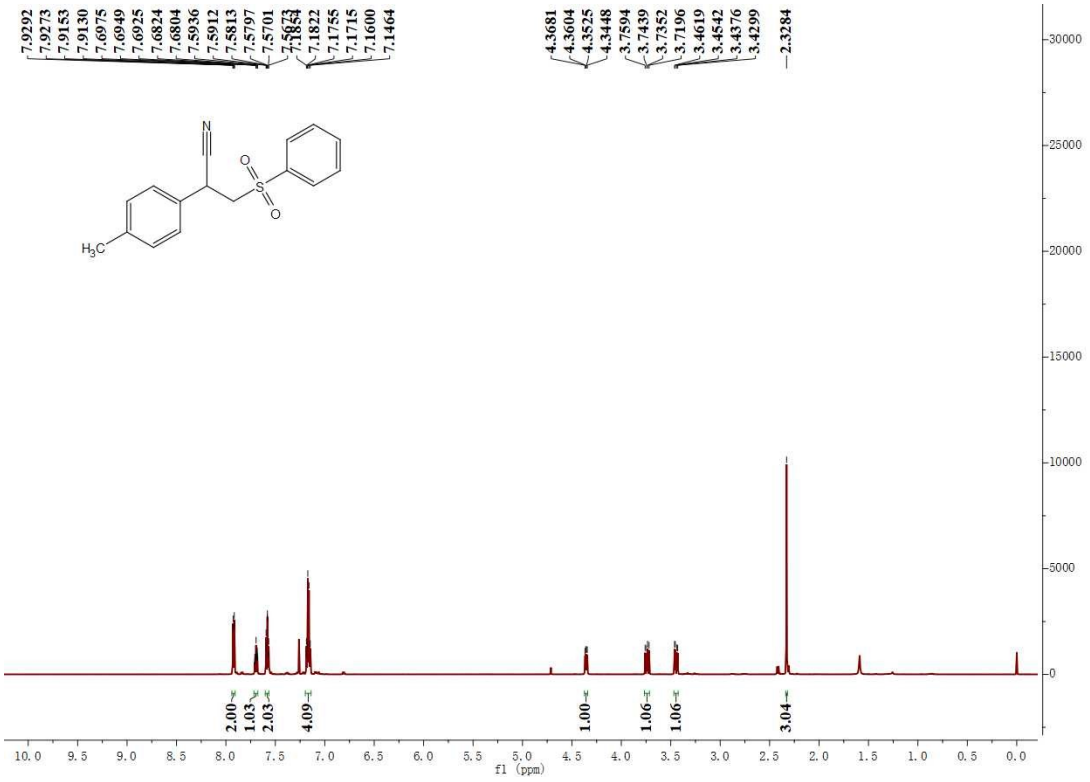
^{1}H-NMR Spectrum (400 MHz, $CDCl_3$) of **32d**



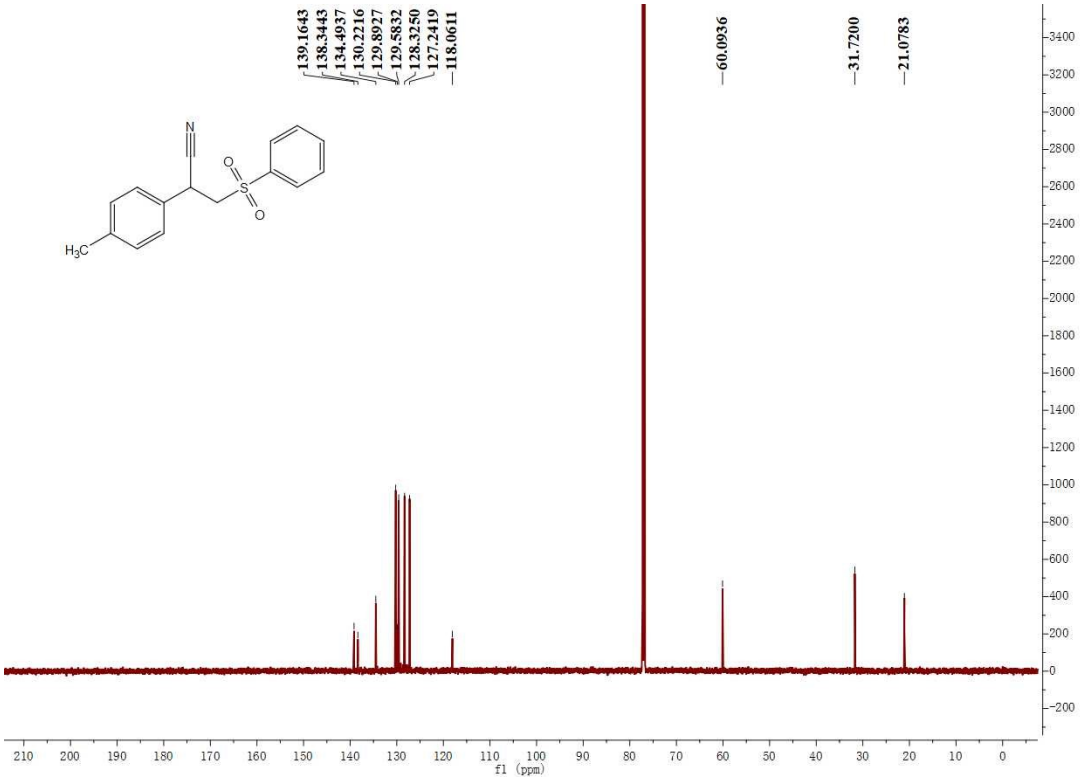
^{13}C-NMR Spectrum (101 MHz, $CDCl_3$) of **32d**



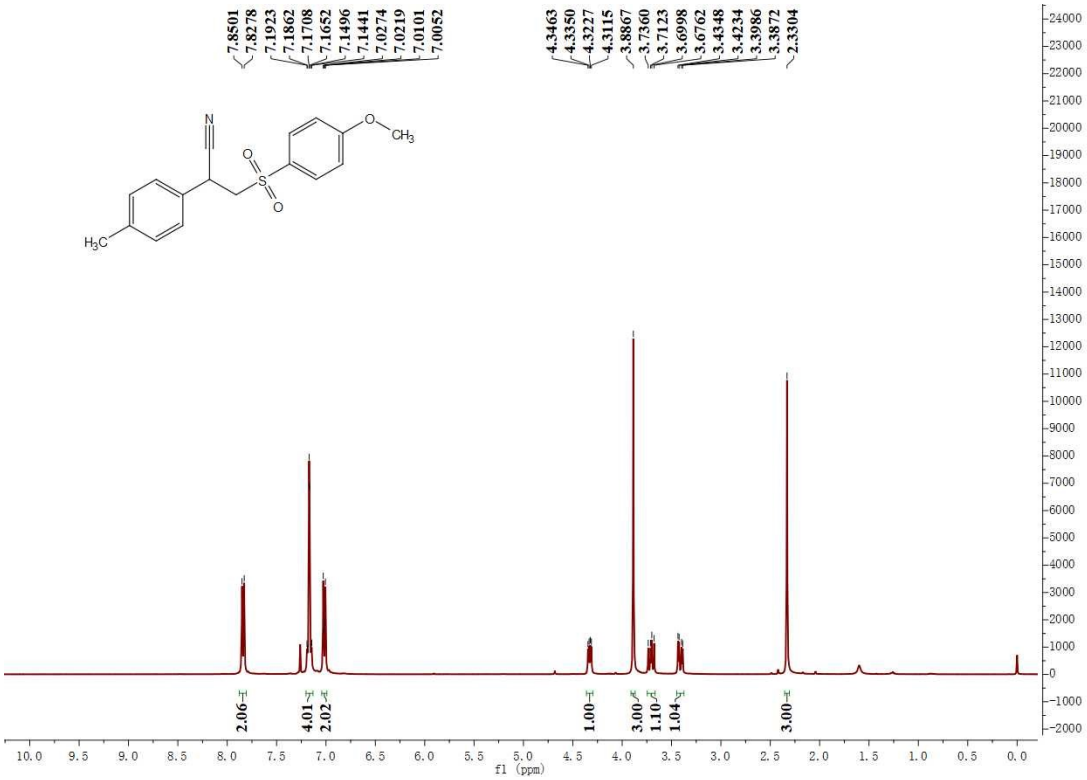
^{1}H-NMR Spectrum (600 MHz, $CDCl_3$) of **33d**



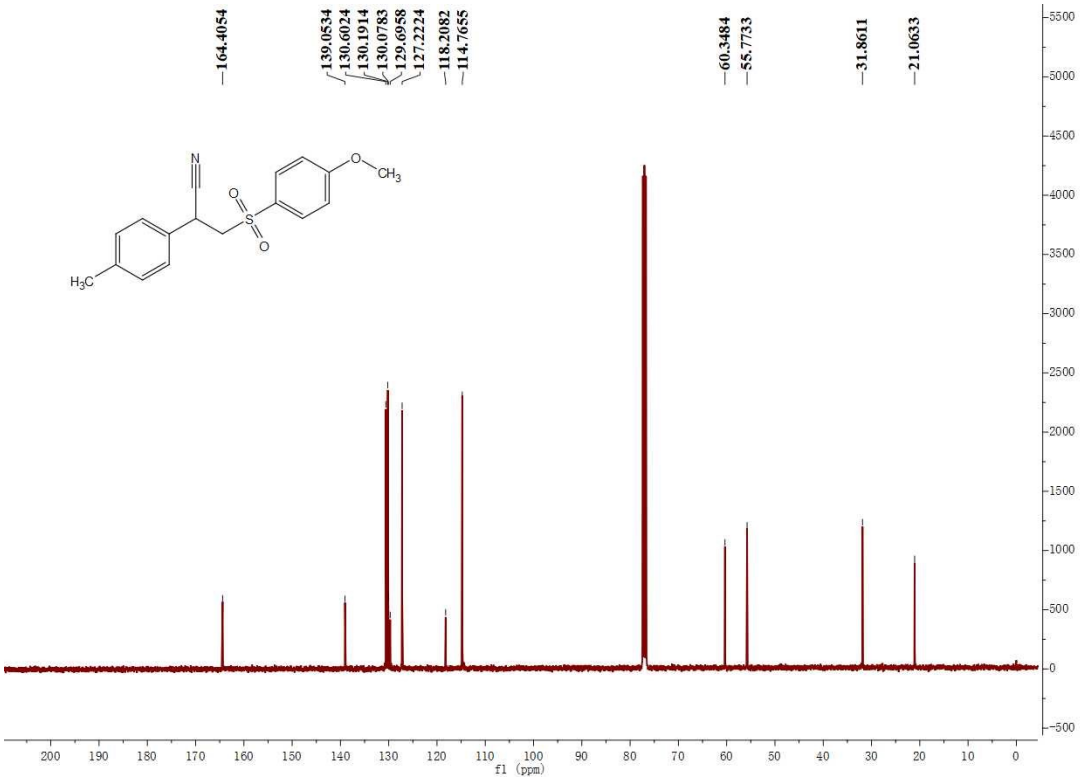
^{13}C-NMR Spectrum (151 MHz, $CDCl_3$) of **33d**



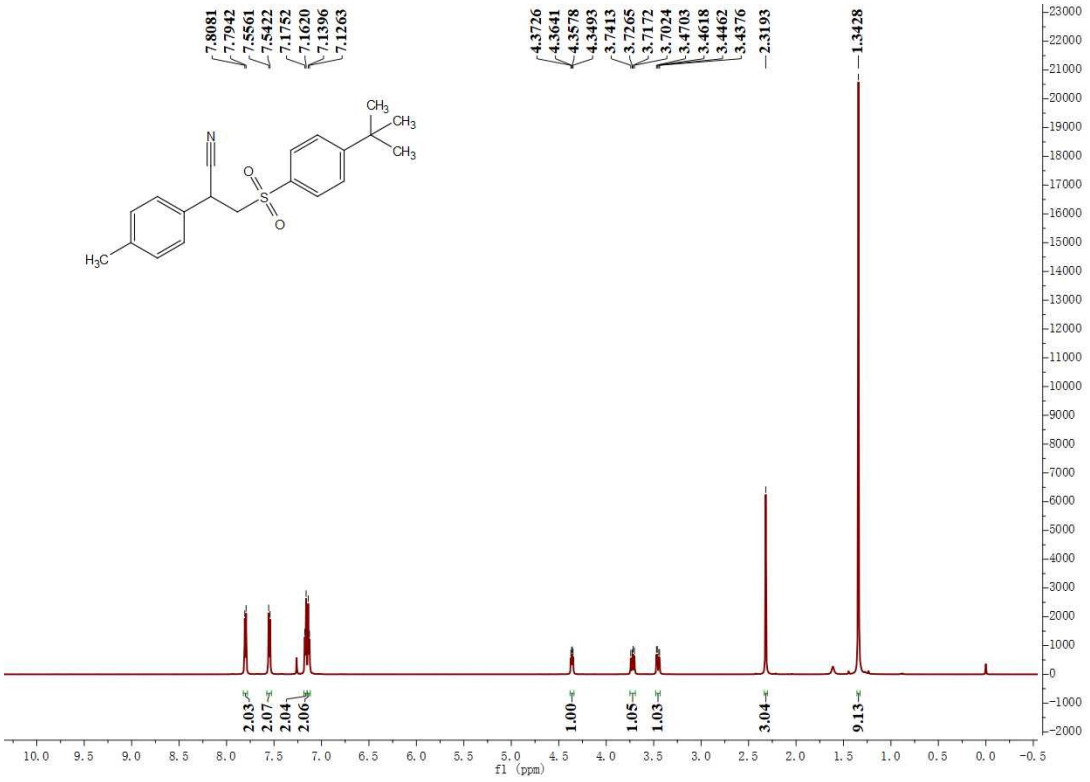
^{1}H-NMR Spectrum (400 MHz, $CDCl_3$) of **34d**



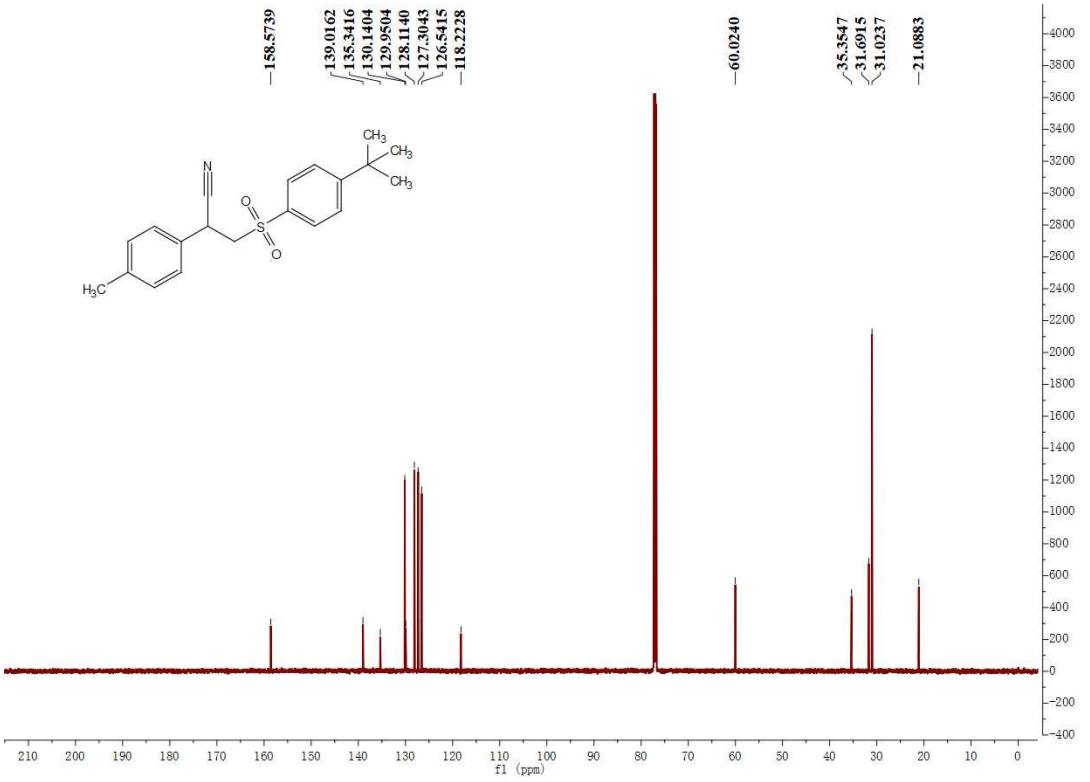
^{13}C-NMR Spectrum (101 MHz, $CDCl_3$) of **34d**



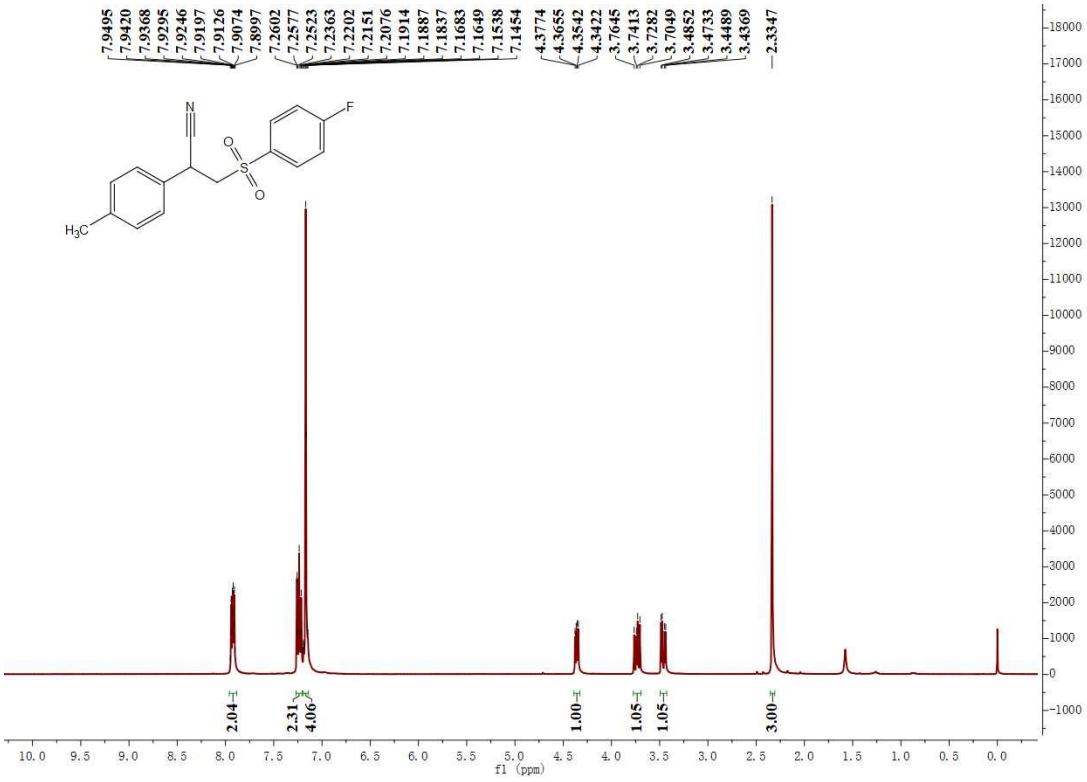
^{1}H-NMR Spectrum (600 MHz, $CDCl_3$) of **35d**



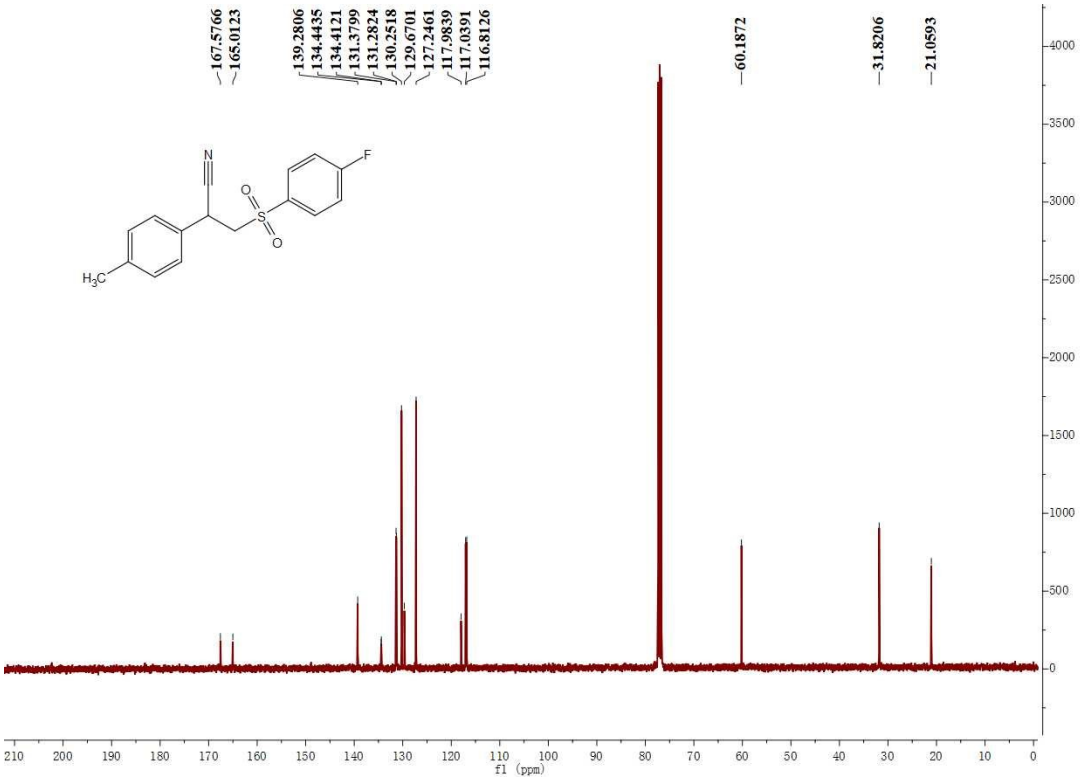
^{13}C-NMR Spectrum (151 MHz, $CDCl_3$) of **35d**



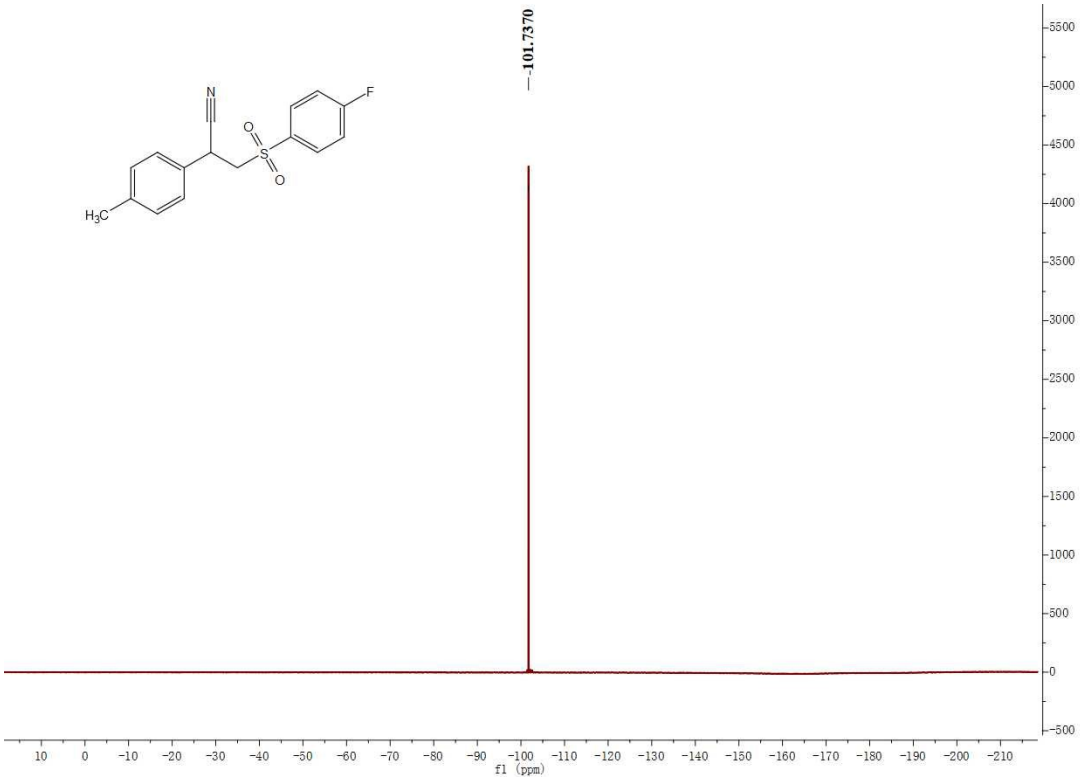
^{1}H-NMR Spectrum (400 MHz, $CDCl_3$) of **36d**



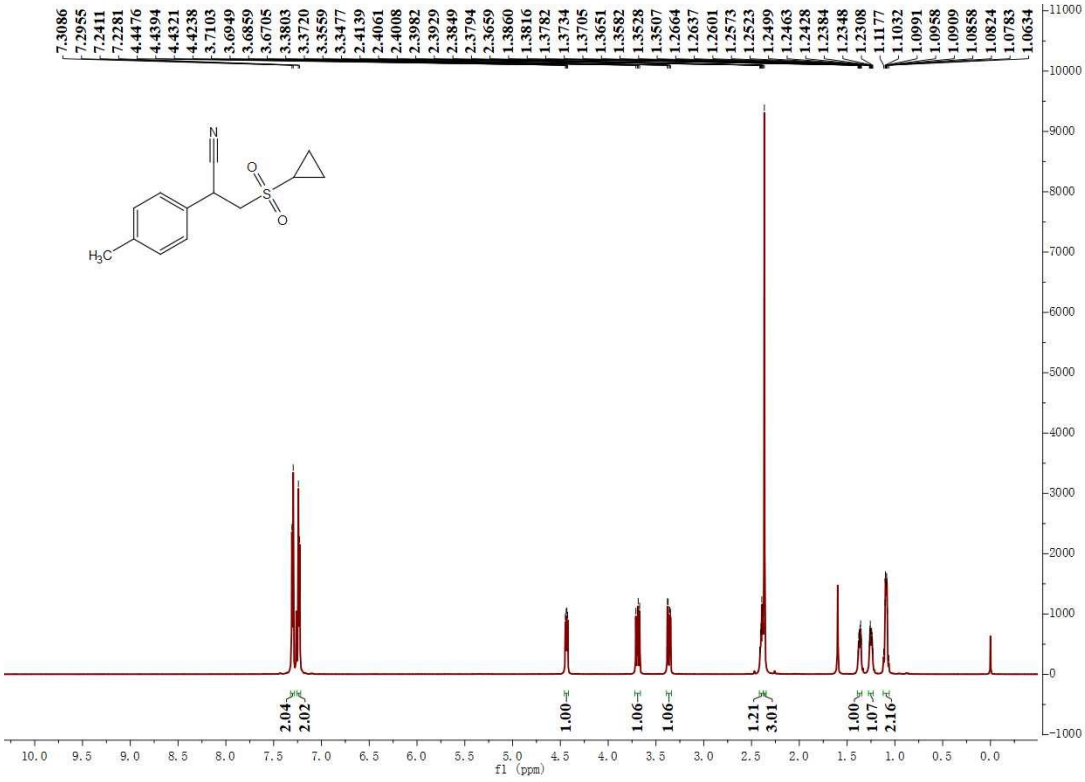
^{13}C-NMR Spectrum (101 MHz, $CDCl_3$) of **36d**



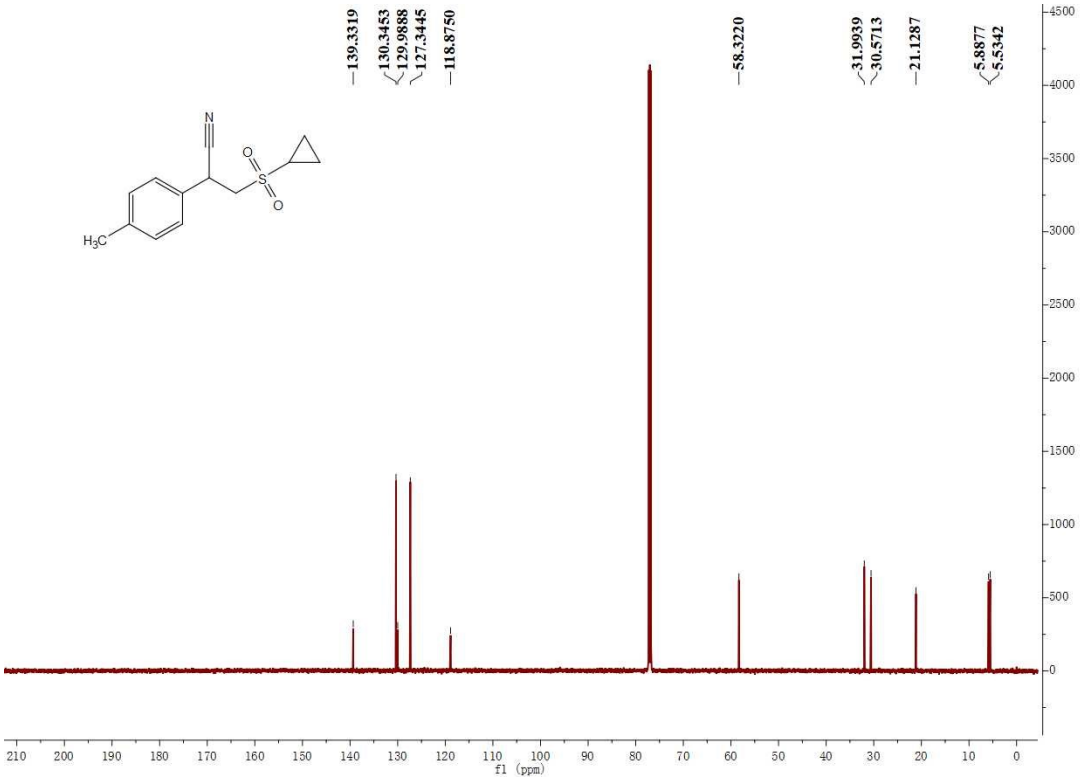
^{19}F-NMR Spectrum (376 MHz, $CDCl_3$) of **36d**



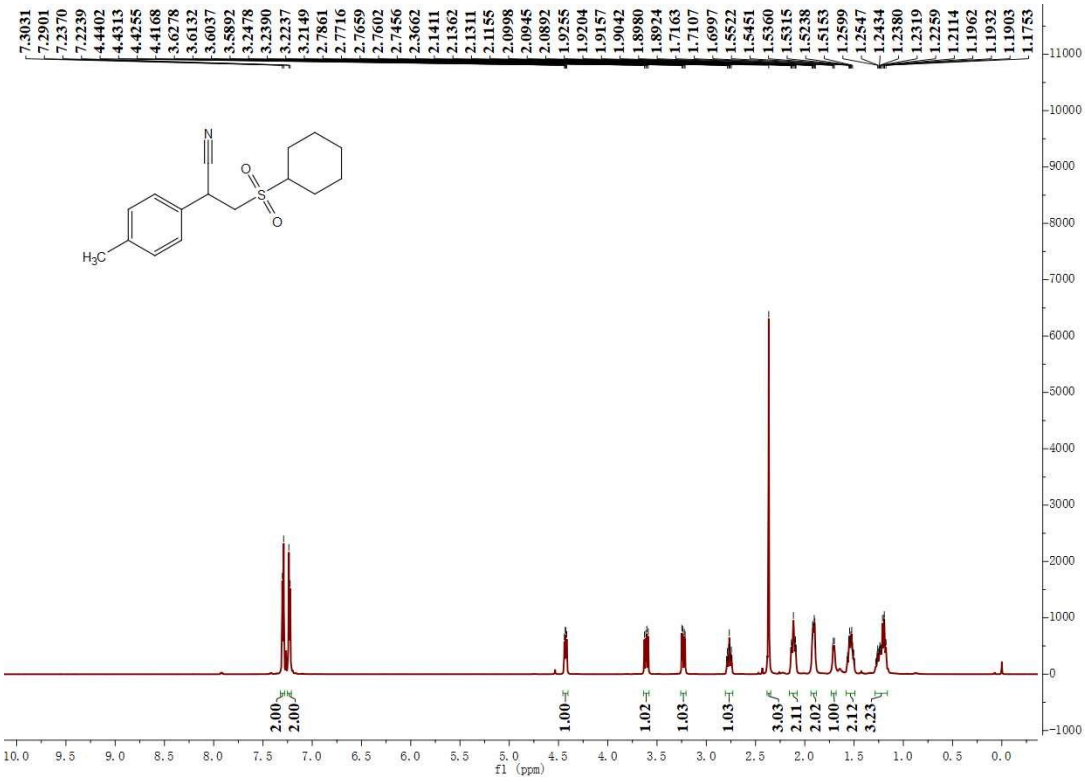
^{1}H-NMR Spectrum (600 MHz, $CDCl_3$) of **37d**



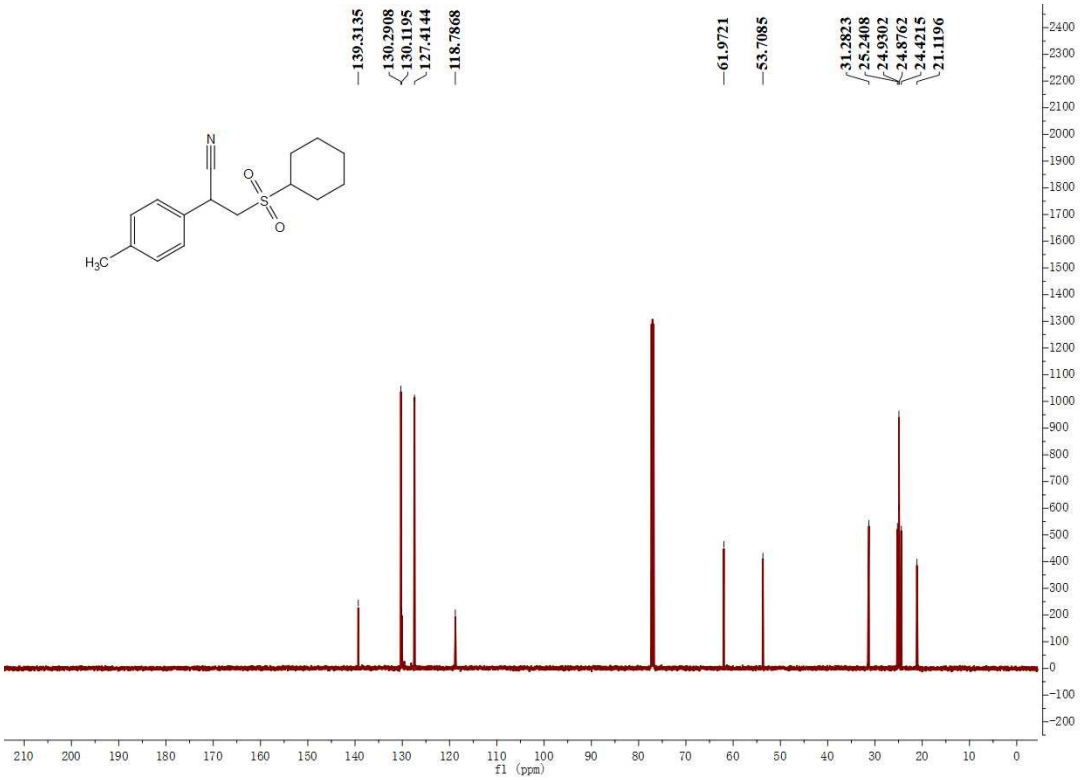
^{13}C-NMR Spectrum (151 MHz, $CDCl_3$) of **37d**



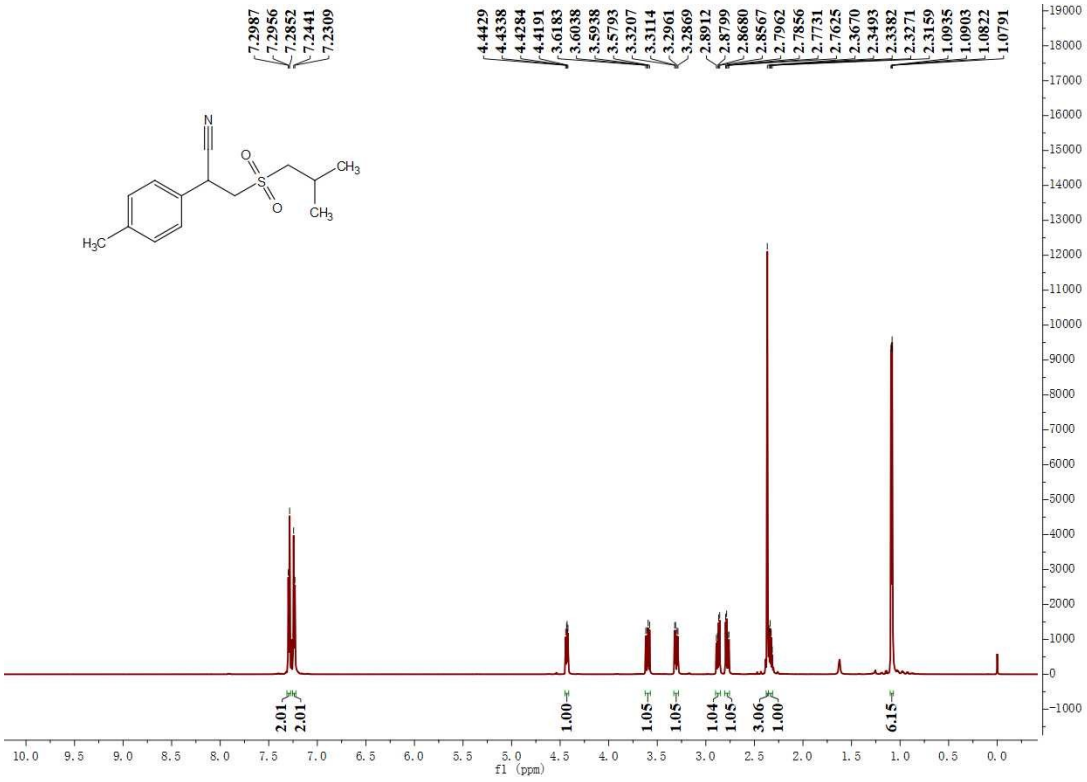
^{1}H-NMR Spectrum (600 MHz, $CDCl_3$) of **38d**



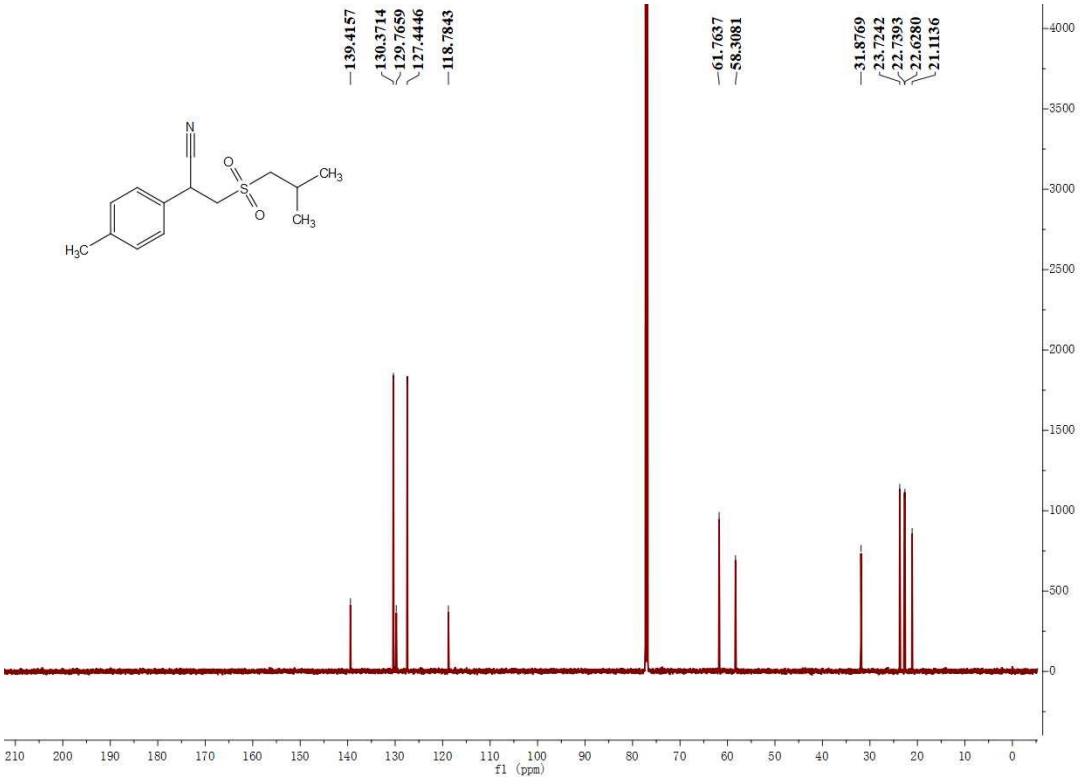
^{13}C-NMR Spectrum (151 MHz, $CDCl_3$) of **38d**



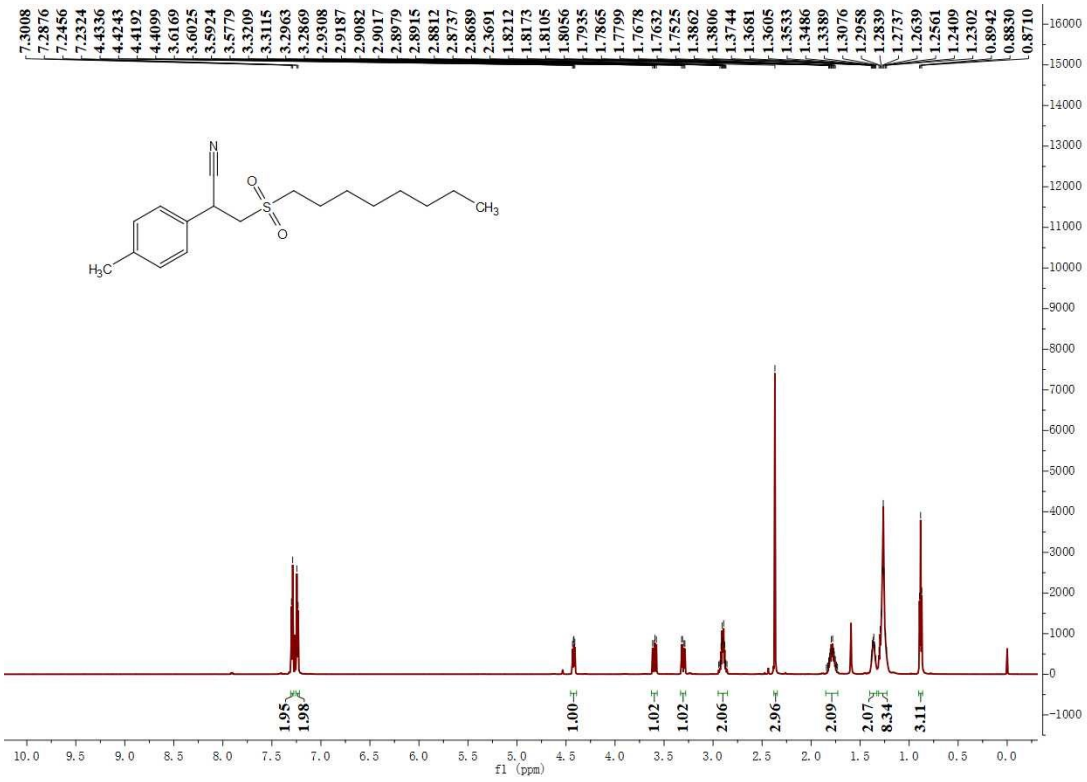
^{1}H-NMR Spectrum (600 MHz, $CDCl_3$) of **39d**



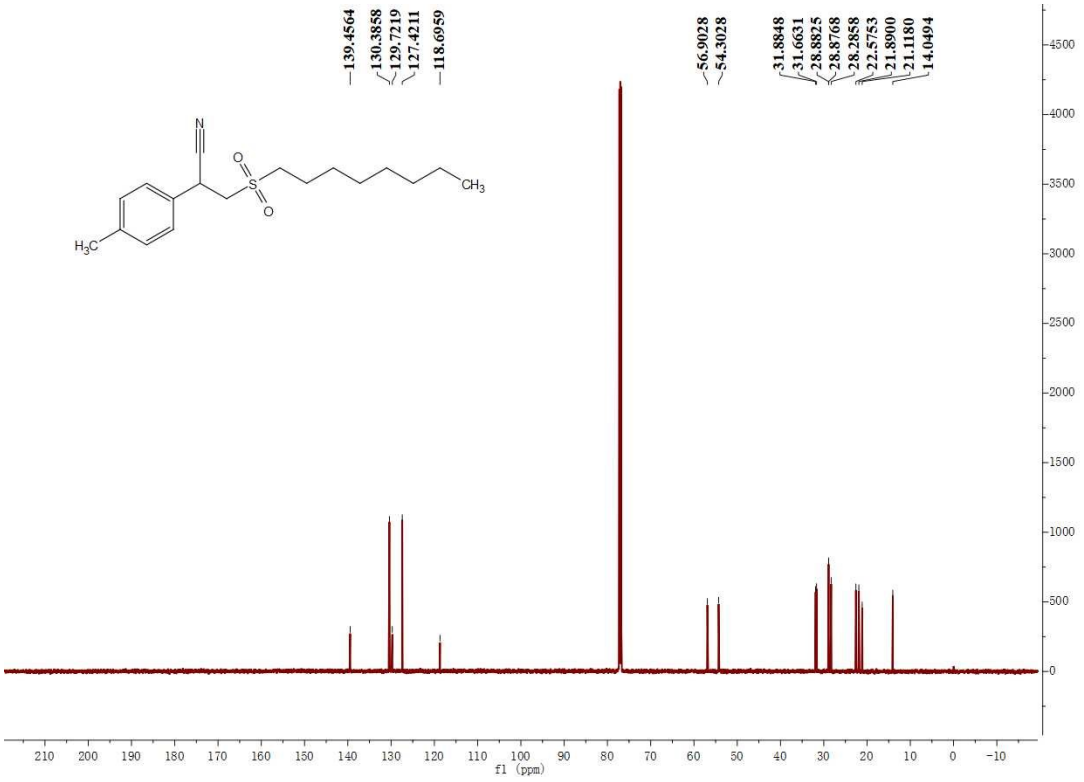
^{13}C-NMR Spectrum (151 MHz, $CDCl_3$) of **39d**



^{1}H-NMR Spectrum (600 MHz, $CDCl_3$) of **40d**

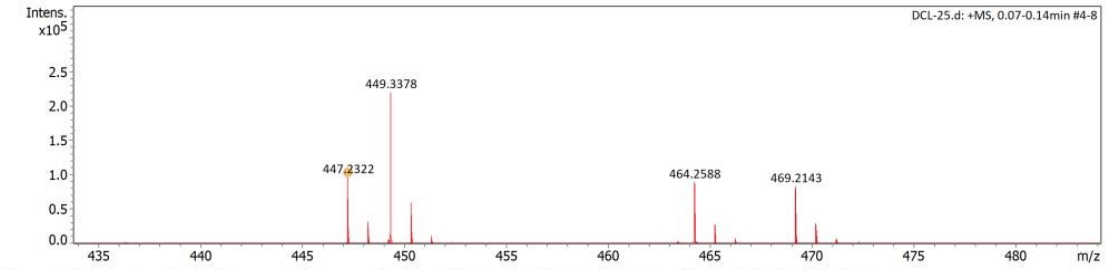


^{13}C-NMR Spectrum (151 MHz, $CDCl_3$) of **40d**


139.4564
130.3858
129.7219
127.4211
118.6959
56.9028
54.3028
31.8848
31.6631
28.8825
28.8768
28.2858
22.5753
21.8900
21.1180
14.0494
N
O
S
O
CH3
H3C
4500
4000
3500
3000
2500
2000
1500
1000
500
0
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

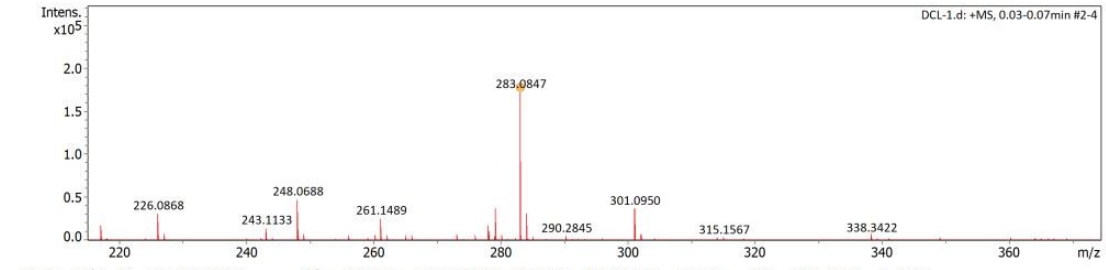
9. HRMS of products

HRMS of **1f**



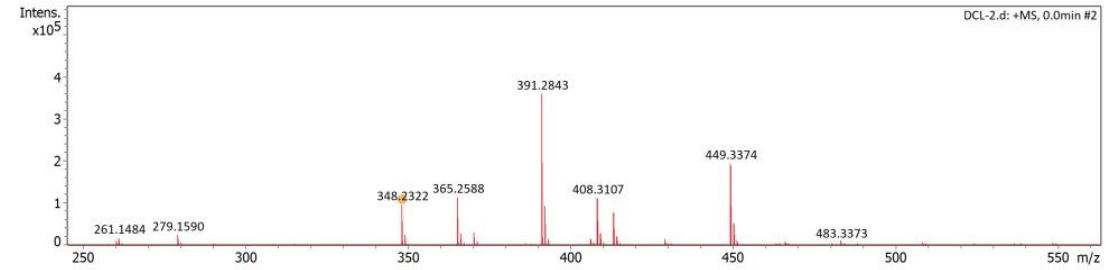
Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	# mSigma	Score	rdb	e¡¥ Conf	N-Rule
447.2322	1	C32H31O2	447.2319	-0.7	14.6	1	100.00	18.0	even	ok

HRMS of **10d**



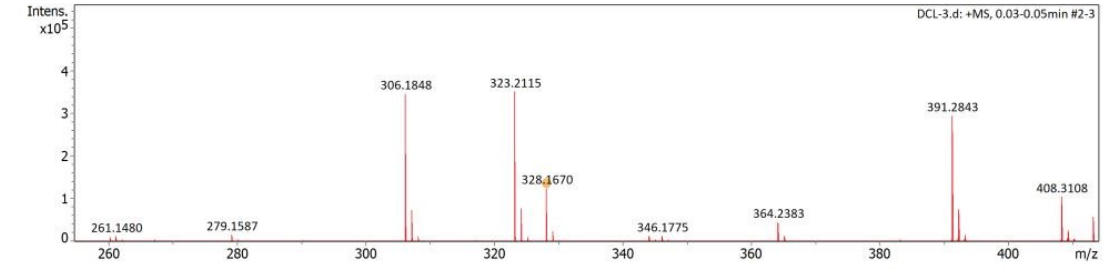
Meas. m/z	#	Ion Formula	m/z	Adduct	err [ppm]	mSigma	# mSigma	Score	rdb	e¡¥ Conf	N-Rule
283.0847	1	C17H12N2NaO	283.0842	M+Na	-1.8	5.9	1	100.00	13.0	even	ok

HRMS of **16d**



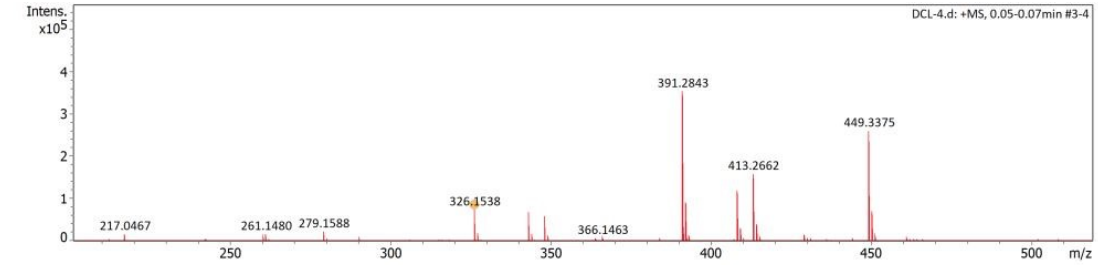
Meas. m/z	#	Ion Formula	m/z	Adduct	err [ppm]	mSigma	# mSigma	Score	rdb	e¡¥ Conf	N-Rule
348.2322	1	C24H30NO	348.2322	M+H	0.0	10.1	1	100.00	11.0	even	ok

HRMS of **17d**



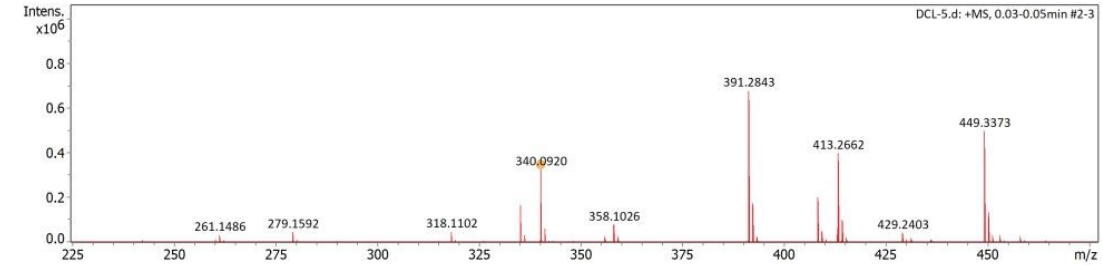
Meas. m/z	#	Ion Formula	m/z	Adduct	err [ppm]	mSigma	# mSigma	Score	rdb	e¡¥ Conf	N-Rule
328.1670	1	C21H23NNaO	328.1672	M+Na	0.6	21.8	1	100.00	11.0	even	ok

HRMS of **18d**



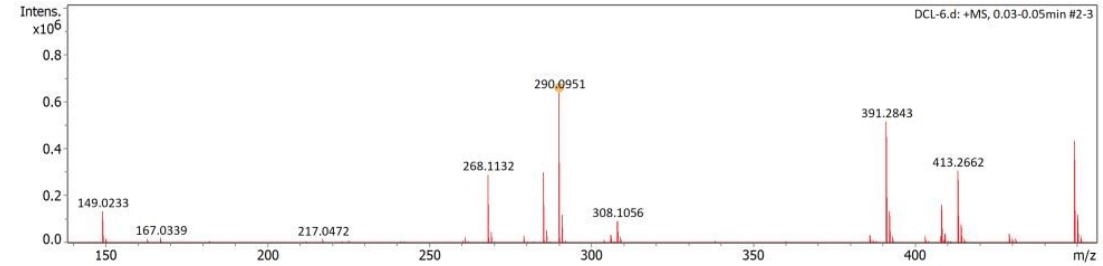
Meas. m/z	#	Ion Formula	m/z	Adduct	err [ppm]	mSigma	# mSigma	Score	rdb	e¡¥ Conf	N-Rule
326.1538	1	C23H20NO	326.1539	M+H	0.4	9.9	1	100.00	15.0	even	ok

HRMS of **19d**



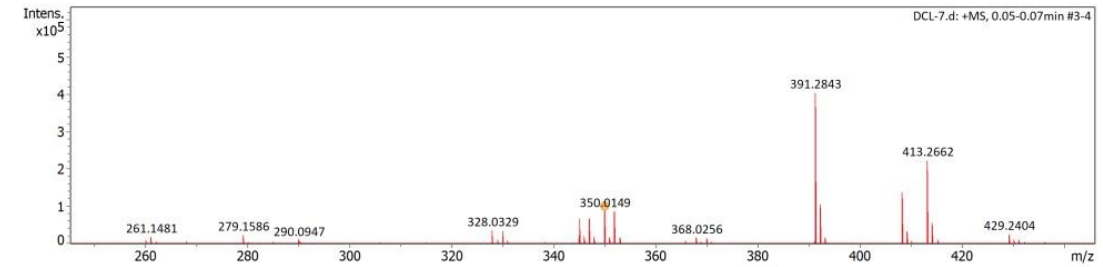
Meas. m/z	#	Ion Formula	m/z	Adduct	err [ppm]	mSigma	# mSigma	Score	rdb	e¡¥ Conf	N-Rule
340.0920	1	C18H14F3NNaO	340.0920	M+Na	-0.2	10.5	1	100.00	11.0	even	ok

HRMS of **20d**



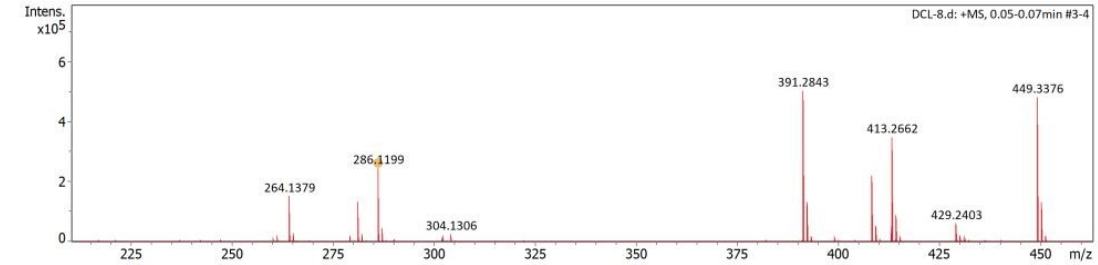
Meas. m/z	#	Ion Formula	m/z	Adduct	err [ppm]	mSigma	# mSigma	Score	rdb	e¡¥ Conf	N-Rule
290.0951	1	C17H14FNNaO	290.0952	M+Na	0.2	2.8	1	100.00	11.0	even	ok

HRMS of **22d**



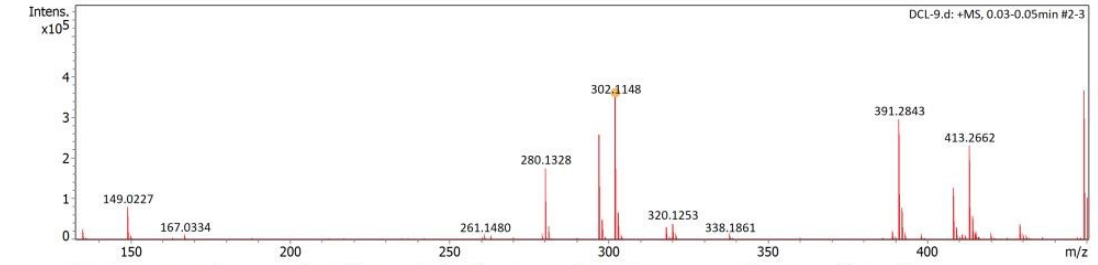
Meas. m/z	#	Ion Formula	m/z	Adduct	err [ppm]	mSigma	# mSigma	Score	rdb	e¡¥ Conf	N-Rule
350.0149	1	C17H14BrNNaO	350.0151	M+Na	0.7	6.5	1	100.00	13.0	even	ok

HRMS of **23d**



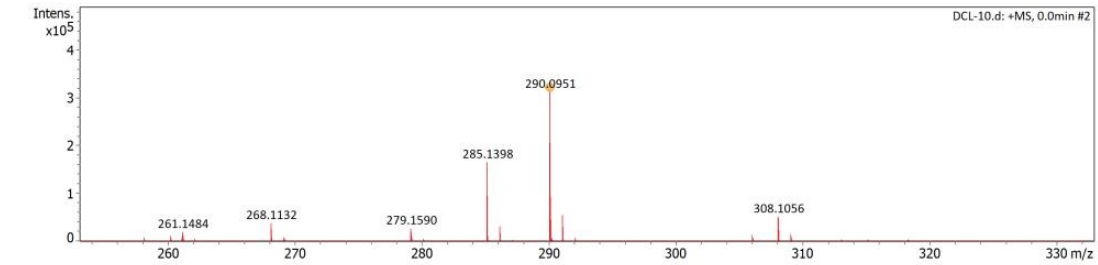
Meas. m/z	#	Ion Formula	m/z	Adduct	err [ppm]	mSigma	# mSigma	Score	rdb	e¡¥ Conf	N-Rule
286.1199	1	C18H17NNaO	286.1202	M+Na	1.0	10.0	1	100.00	11.0	even	ok

HRMS of **24d**



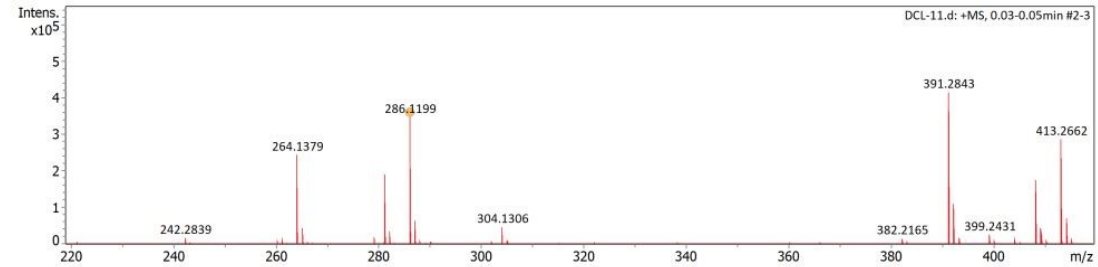
Meas. m/z	#	Ion Formula	m/z	Adduct	err [ppm]	mSigma	# mSigma	Score	rdb	e¡¥ Conf	N-Rule
302.1148	1	C18H17NNaO2	302.1151	M+Na	1.0	7.1	1	100.00	11.0	even	ok

HRMS of **25d**



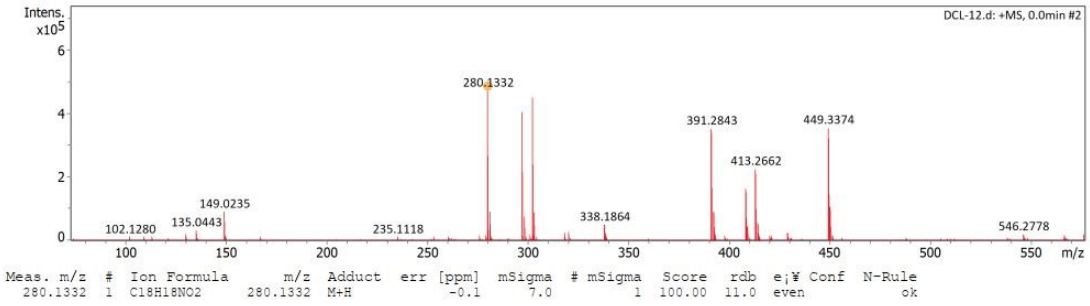
Meas. m/z	#	Ion Formula	m/z	Adduct	err [ppm]	mSigma	# mSigma	Score	rdb	e¡¥ Conf	N-Rule
290.0951	1	C17H14FNNaO	290.0952	M+Na	0.4	9.1	1	100.00	11.0	even	ok

HRMS of **26d**



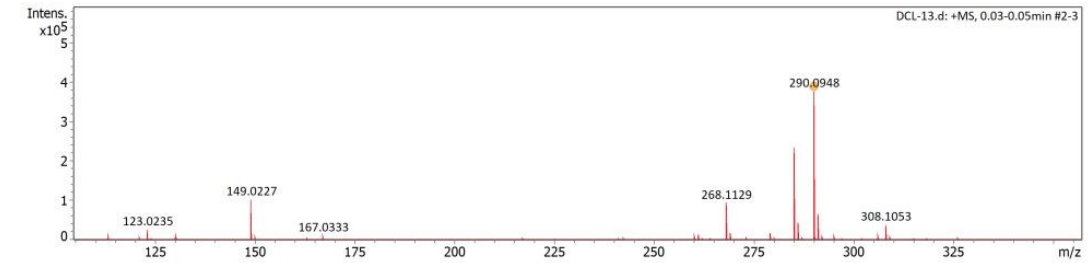
Meas. m/z	#	Ion Formula	m/z	Adduct	err [ppm]	mSigma	# mSigma	Score	rdb	e¡¥ Conf	N-Rule
286.1199	1	C18H17NNaO	286.1202	M+Na	1.1	9.0	1	100.00	11.0	even	ok

HRMS of **27d**



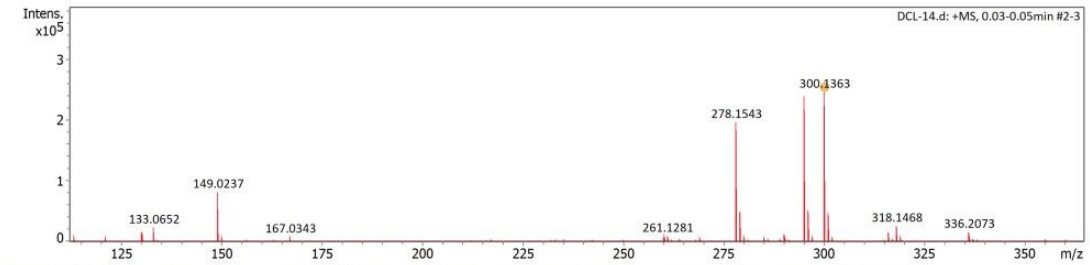
Meas. m/z	#	Ion Formula	m/z	Adduct	err [ppm]	mSigma	# mSigma	Score	rdb	e¡¥ Conf	N-Rule
280.1332	1	C18H18NO2	280.1332	M+H	-0.1	7.0	1	100.00	11.0	even	ok

HRMS of **28d**



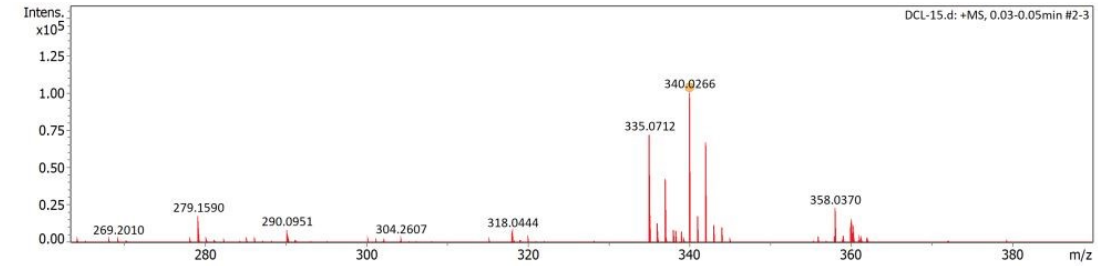
Meas. m/z	#	Ion Formula	m/z	Adduct	err [ppm]	mSigma	# mSigma	Score	rdb	e¡¥ Conf	N-Rule
290.0948	1	C17H14FNNaO	290.0952	M+Na	1.3	9.7	1	100.00	11.0	even	ok

HRMS of **29d**



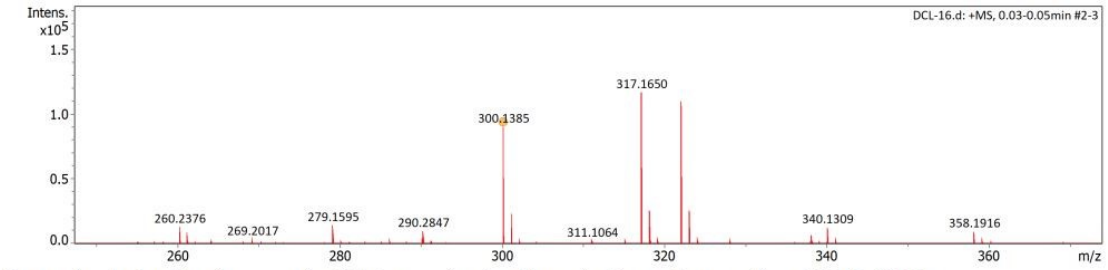
Meas. m/z	#	Ion Formula	m/z	Adduct	err [ppm]	mSigma	# mSigma	Score	rdb	e¡¥ Conf	N-Rule
300.1363	1	C19H19NNaO	300.1359	M+Na	-1.5	13.2	1	100.00	11.0	even	ok

HRMS of **30d**



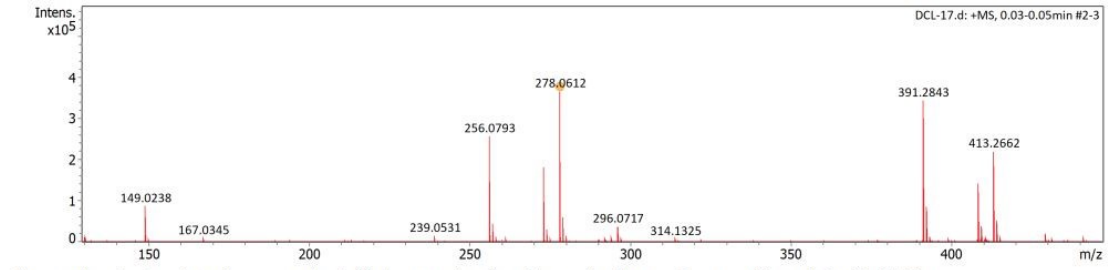
Meas. m/z	#	Ion Formula	m/z	Adduct	err [ppm]	mSigma	# mSigma	Score	rdb	e¡¥ Conf	N-Rule
340.0266	1	C17H13Cl2NNaO	340.0266	M+Na	0.2	9.3	1	100.00	17.0	even	ok

HRMS of **31d**



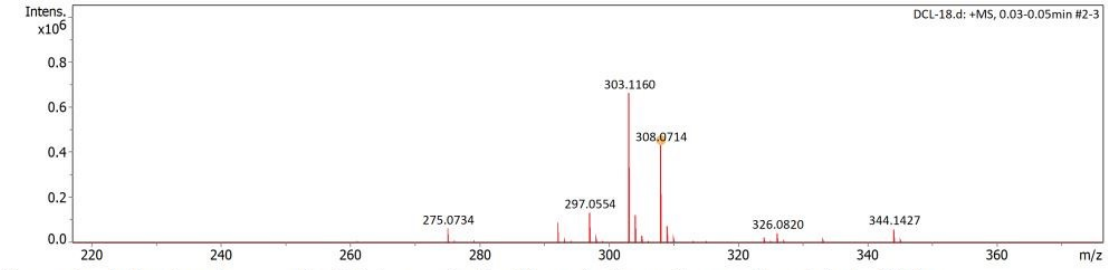
Meas. m/z	#	Ion Formula	m/z	Adduct	err [ppm]	mSigma	# mSigma	Score	rdb	e¡¥ Conf	N-Rule
300.1385	1	C21H18NO	300.1383	M+H	-0.8	11.7	1	100.00	14.0	even	ok

HRMS of **32d**



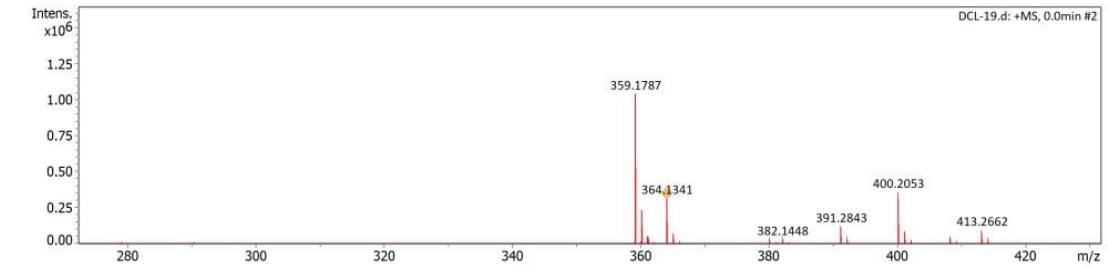
Meas. m/z	#	Ion Formula	m/z	Adduct	err [ppm]	mSigma	# mSigma	Score	rdb	e¡¥ Conf	N-Rule
278.0612	1	C15H13NNaOS	278.0610	M+Na	-0.5	10.9	1	100.00	12.0	even	ok

HRMS of **33d**



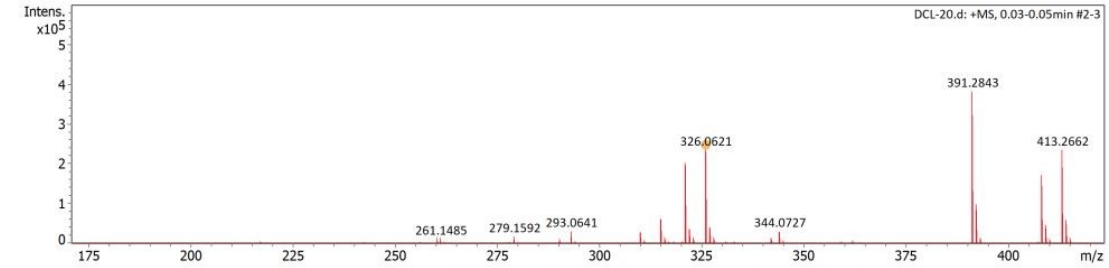
Meas. m/z	#	Ion Formula	m/z	Adduct	err [ppm]	mSigma	# mSigma	Score	rdb	e¡¥ Conf	N-Rule
308.0714	1	C16H15NNaO2S	308.0716	M+Na	0.6	14.8	1	100.00	12.0	even	ok

HRMS of **35d**



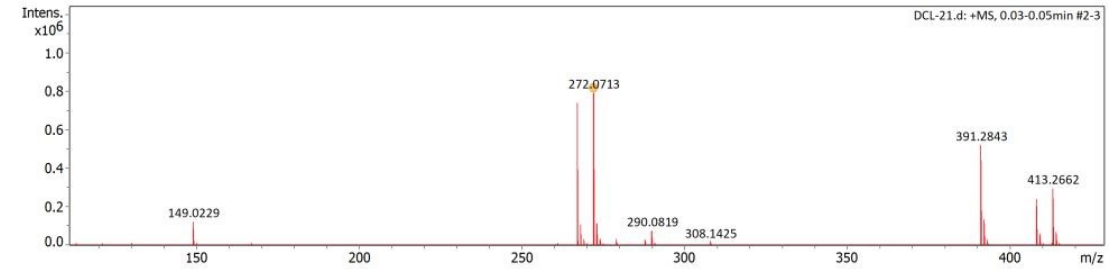
Meas. m/z	#	Ion Formula	m/z	Adduct	err [ppm]	mSigma	# mSigma	Score	rdb	e¡¥ Conf	N-Rule
364.1341	1	C20H23NNaO2S	364.1342	M+Na	0.1	14.5	1	100.00	12.0	even	ok

HRMS of **36d**



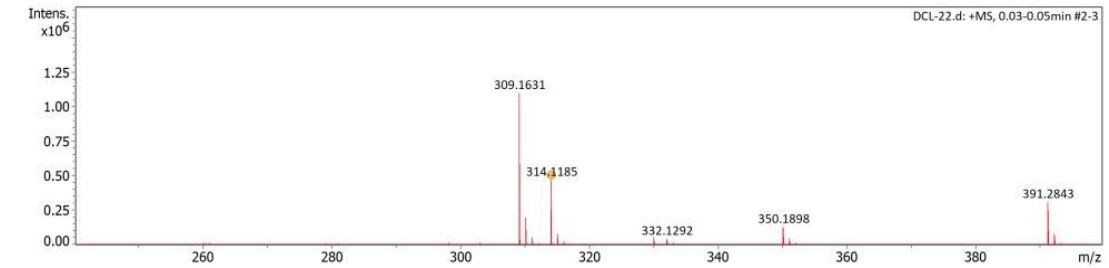
Meas. m/z	#	Ion Formula	m/z	Adduct	err [ppm]	mSigma	# mSigma	Score	rdb	e¡¥ Conf	N-Rule
326.0621	1	C16H14FNNaO2S	326.0621	M+Na	0.0	12.6	1	100.00	12.0	even	ok

HRMS of **37d**



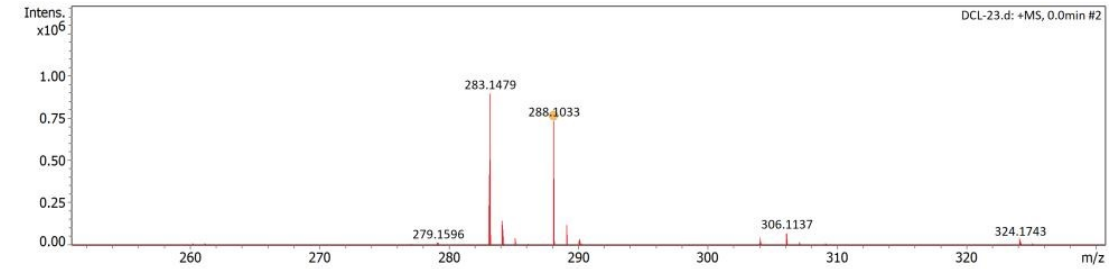
Meas. m/z	#	Ion Formula	m/z	Adduct	err [ppm]	mSigma	# mSigma	Score	rdb	e¡¥ Conf	N-Rule
272.0713	1	C13H15NNaO2S	272.0716	M+Na	1.1	10.8	1	100.00	9.0	even	ok

HRMS of **38d**



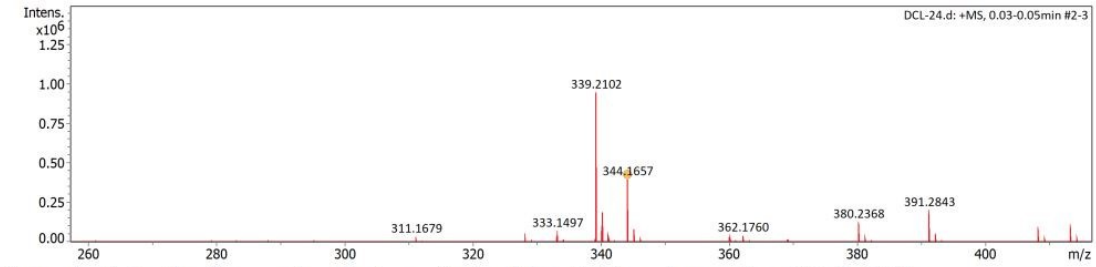
Meas. m/z	#	Ion Formula	m/z	Adduct	err [ppm]	mSigma	# mSigma	Score	rdb	e¡¥ Conf	N-Rule
314.1185	1	C16H21NNaO2S	314.1185	M+Na	-0.1	13.9	1	100.00	9.0	even	ok

HRMS of **39d**



Meas. m/z	#	Ion Formula	m/z	Adduct	err [ppm]	mSigma	# mSigma	Score	rdb	e¡¥ Conf	N-Rule
288.1033	1	C14H19NNaO2S	288.1029	M+Na	-1.6	11.3	1	100.00	8.0	even	ok

HRMS of **40d**



Meas. m/z	#	Ion Formula	m/z	Adduct	err [ppm]	mSigma	# mSigma	Score	rdb	e¡¥ Conf	N-Rule
344.1657	1	C18H27NNaO2S	344.1655	M+Na	-0.6	14.3	1	100.00	8.0	even	ok