

Supporting Information

**Visible-light-induced C(sp³)-C(sp³) bond formation via
radical/radical cross-coupling**

Haoyuan Li, Sen Li, Huimin Hu, Runbo Sun, Meixia Liu, Anjun Ding,
Xiaoyong Liu, Wenlin Luo, Zhengjiang Fu, Shengmei Guo,* and Hu Cai*

Department of Chemistry, Nanchang University, Nanchang, 330031, P. R. China.

Email: smguo@ncu.edu.cn

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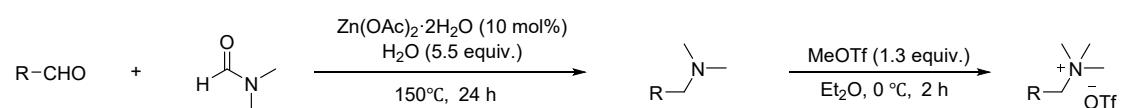
1. General Information.

All reactions were performed in oven-dried glassware using Schlenk techniques under a nitrogen atmosphere unless otherwise stated. Materials were purchased from the Sinopharm Chemical Reagent Co., Adams, Sigma-Aldrich, Energy Chemical, and TCI. Unless otherwise noted, commercial reagents were used without further purification. Column chromatography was performed on silica gel 300-400 mesh and petroleum ether (PE)/ethyl acetate (EA). Cyclic voltammograms were obtained on an IVIUMSTAT potentiostat. Fluorescence spectrum was carried out by a Hitachi F-4500 spectrophotometer. ^1H and ^{13}C NMR spectra were recorded on Bruker Ascend™ 400 (400 MHz) using tetramethylsilane as an internal reference. NMR multiplicities are abbreviated as follows: s = singlet, d = doublet, m = multiplet. Chemical shifts (δ) and coupling constants (J) were expressed in ppm and Hz, respectively. High-resolution mass spectra (HRMS) were obtained on an Agilent mass spectrometer using ESI-TOF (electrospray ionization-time of flight).

2. Experimental procedure

An oven-dried Schlenk tube (10 ml) was charged with ammonium salt (0.2 mmol), Hansester (0.4 mmol), DABCO (1equiv., 0.2 mmol), Flrpic (1 mmol%, 0.002 mmol,) and a stir bar. After the Schlenk tube was filled with nitrogen, methanol (1 ml) was added by syringe under nitrogen. The tube was sealed and the reaction mixture was stirred and illuminated by CFL LED (36 W) under the room temperature for 24 h. After completion of the reaction, the mixture was diluted with ethyl acetate and concentrated under reduced pressure. The residue was purified by silica gel column chromatography with petroleum ether/ethyl acetate (100 : 1) as the eluent to provide corresponding product.

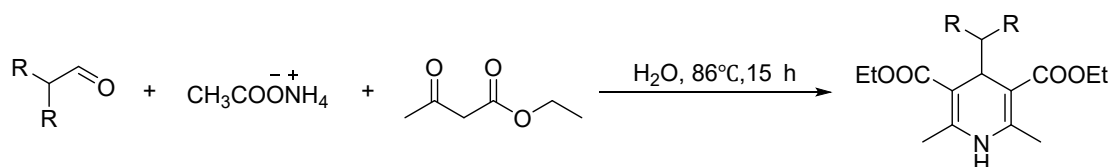
2.1 The synthesis of substituted Trimethylammonium triflates



An oven-dried reaction vessel was charged with Aldehyde (20 mmol, 1 equiv.), Zincacetate

dihydrate (0.02 mmol, 10 mol %), H₂O (5.5 equiv.), *N, N*-dimethylformamide (12.5 mL) under air. The vessel was sealed and heated at 150 °C (oil bath temperature) for 24 h. After cooling down, 30 mL brine was added in, followed by extractions with ether (3x30 mL). The organic layer was combined, washed with brine (2x30 mL), dried with anhydrous sodium sulfate, filtered and concentrated in vacuo to give substituted *N, N*-dimethyl-methanamine. *N, N*-dimethyl-methanamine was dissolved in Et₂O (20-30 mL). MeOTf (1.3 equiv.) was added dropwise at 0 °C under air. After complete addition, the mixture was allowed to stir for an additional 90 minutes at 0 °C. The white precipitate was filtered and washed with Et₂O (3 x 15 mL) to give the corresponding substituted Trimethylammonium triflates.

2.2 The synthesis of substituted Hantzsch esters.



An oven-dried reaction vessel was charged with Aldehyde (10 mmol, 1.0 equiv.), Ammonium acetate (2.0 equiv.), Ethyl Acetoacetate (4.0 equiv.) under air in H₂O (15 mL). The resulting suspension was stirred for 15 h at 86 °C and was then cool to rt. The combined organic layers were washed with water and brine, dried over anhydrous Na₂SO₄, and then evaporated in vacuo. The resulting residue was purified by flash column chromatography to give the corresponding substituted Hantzsch esters.

3. Optimization of the Reaction Conditions

Table S1: Screen of light source

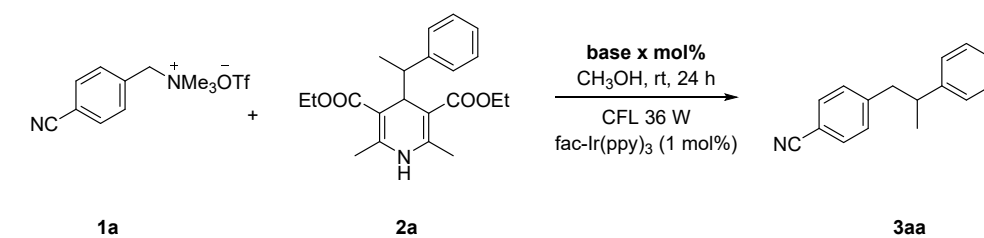
Entry	Light source	Yield of 3aa (%) ^a
1	UV, 365-367 nm	Trace
2	Blue light, 450-455 nm	40
3	Blue light, 480-485 nm	30
4	Green light, 505-510 nm	24
5	White light, 6000-6500 K	55
6	White bulb, 7 W	48
7	Blue bulb, 7 W	29
8	White light, 36 W CFL	60

^aReaction condition: **1a** (0.2 mmol), **2a** (2 equiv.), DIPEA (1 equiv.), CH₃OH (1 ml), rt, under nitrogen atmosphere with light irradiation for 24 h, and isolated yields were given.

Table S2: Screen of base

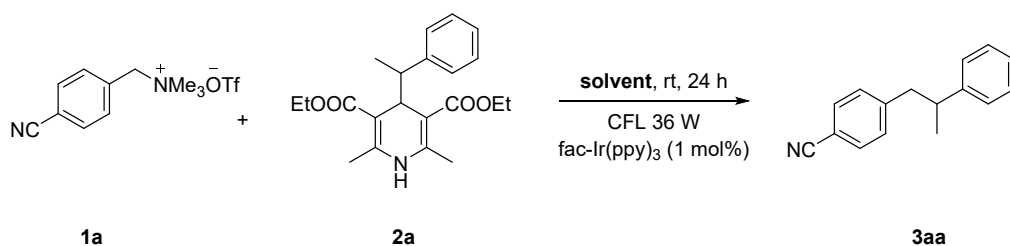
Entry	Base	Yield of 3aa (%) ^a
1	DIPEA	60
2	DABCO	64
3	DBU	49
4	DMAP	53
5	Et ₃ N	29
6	K ₂ CO ₃	28
7	Cs ₂ CO ₃	32
8	Dipropylamine	53

^aReaction condition: **1a** (0.2 mmol), **2a** (2 equiv), base (1 equiv), CH₃OH (1 ml), rt, under nitrogen atmosphere with light irradiation for 24 h, and isolated yields were given.

Table S3: Screen of amount of base

Entry	Base (X mol%)	Yield of 3aa (%) ^a
1	0	22
2	100	64
3	200	42

^aReaction condition: **1a** (0.2 mmol), **2a** (2 equiv), CH₃OH (1 ml), rt, under nitrogen atmosphere with light irradiation for 24 h, and isolated yields were given.

Table S4: Screen of solvent

Entry	solvent	Yield of 3aa (%) ^a
1	CH₃OH	64
2	CH ₃ CN	42
3	1,4-dioxane	36
4	NMP	47
5	Toluene	18
6	DMF	30
7	DMSO	25
8	MTBE	Trace
9	Hexane	Trace
10	EtOH	43
11	TFA	Trace
12	HFIP	Trace

^aReaction condition: **1a** (0.2 mmol), **2a** (2 equiv.), DABCO (1 equiv.), solvent (1 ml), rt, under nitrogen atmosphere with light irradiation for 24 h, and isolated yields were given.

Table S5: Screen of Photocatalyst

Entry	photocatalyst	Yield of 3aa (%) ^a
1	fac-Ir(ppy) ₃	64
2	Ir(dtbbpy) ₃ PF ₆	36
3	Ir[dF(CF ₃)ppy ₂ (dtbbpy)]PF ₆	12
4	Eosin Y	Trace
5	Base Blue	18
6	[Ru(bpy) ₃]Cl ₂	22
7	4CzIPN	27
8	4DPAIPN	24
9	FIrpic	82

^aReaction condition: **1a** (0.2 mmol), **2a** (2 equiv.), DABCO (1 equiv.), CH₃OH (1 ml), rt, under nitrogen atmosphere with light irradiation for 24 h, and isolated yields were given.

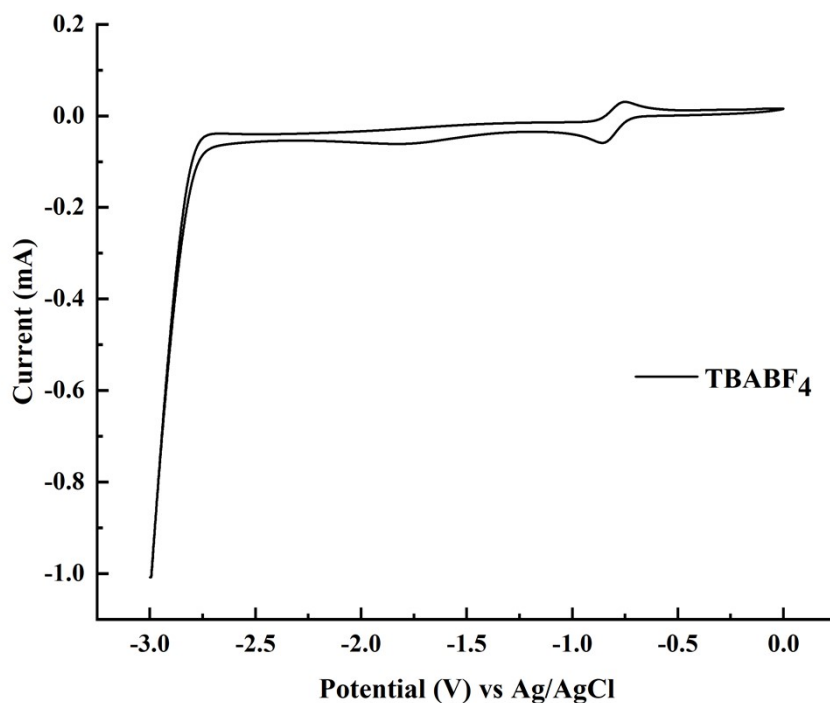
Table S6: Screen of amount of Photocatalyst

Entry	photocatalyst (x mol%)	Yield of 3aa (%) ^a
1	0	-
2	0.5	55
3	1	82
4	1.5	60

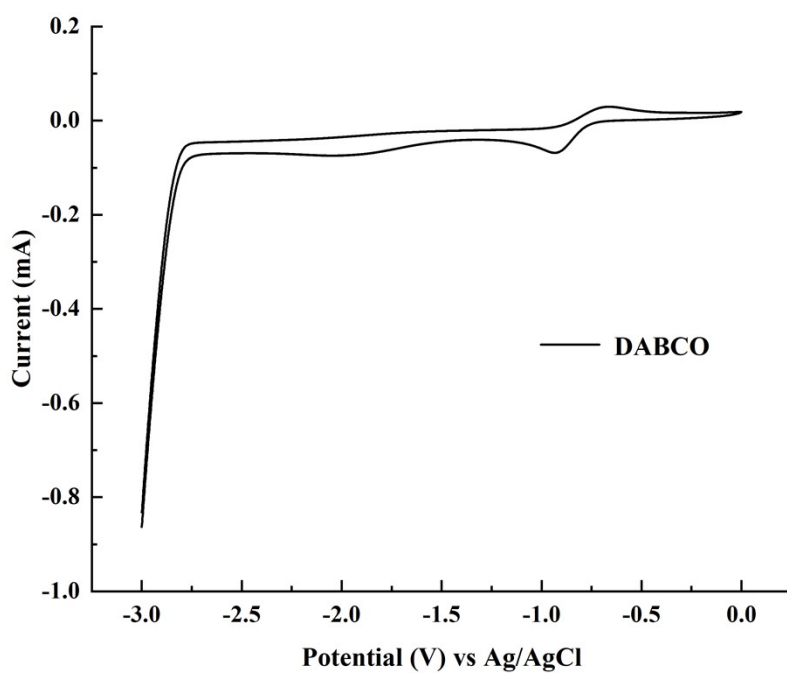
^aReaction condition: **1a** (0.2 mmol), **2a** (2 equiv.), DABCO (1 equiv.), CH₃OH (1 ml), rt, under nitrogen atmosphere with light irradiation for 24 h, and isolated yields were given.

4. General procedure for cyclic voltammetry (CV).

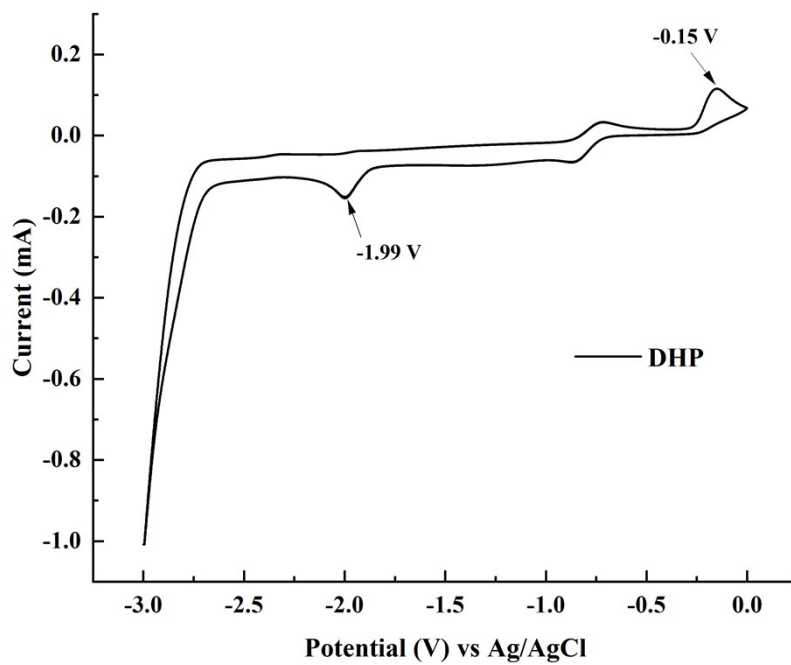
Cyclic voltammetry was performed in a three-electrode cell connected to a schlenk line under room temperature. Glassy carbon electrode was used as working electrode, and platinum wire was employed as counter electrode. Ag/AgCl reference electrode was submerged in saturated aqueous KCl solution and separated from reaction by a salt bridge. The mixture of acetonitrile (10 mL) containing 0.1 M TBABF₄ was poured into the electrochemical cell in all experiments. The scan rate was 100 mV/s ranging from -3.0 V to 0 V. Prior to each measurement, solutions were purged with nitrogen (N₂) for 10 min to ensure the oxygen-free conditions.



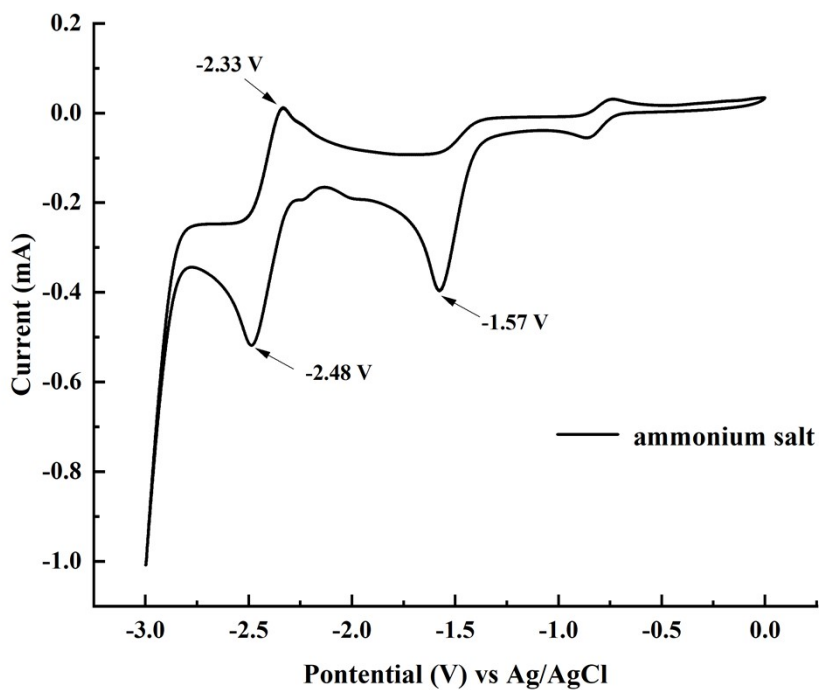
(a) TBABF₄ (0.1 M) in CH₃CN



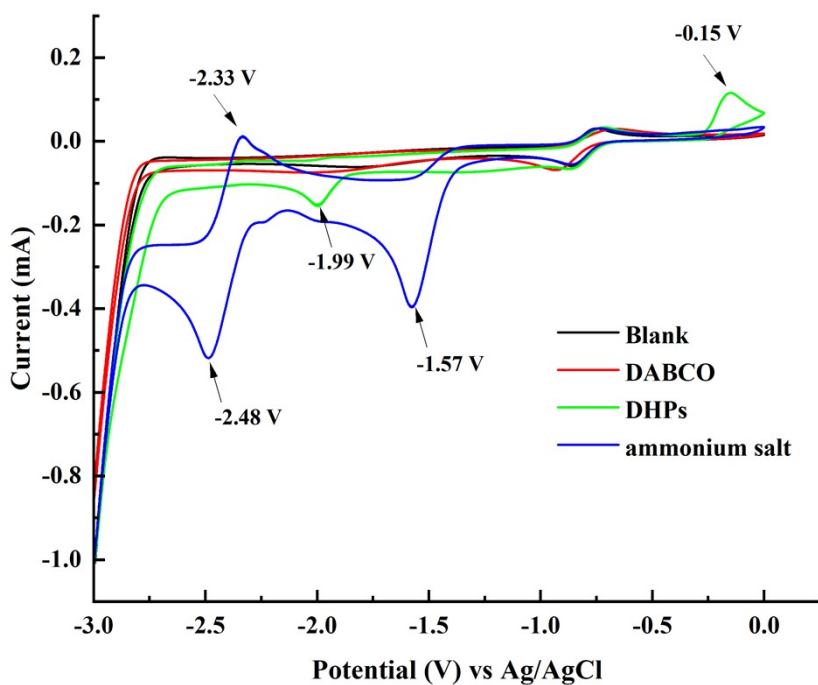
(b) DABCO (0.1 M)+ TBABF₄ (0.1 M) in CH₃CN



(c) DHPs (2a) (0.1 M) + TBABF₄ (0.1 M) in CH₃CN



(d) ammonium salt (1a) (0.1 M) + TBABF₄

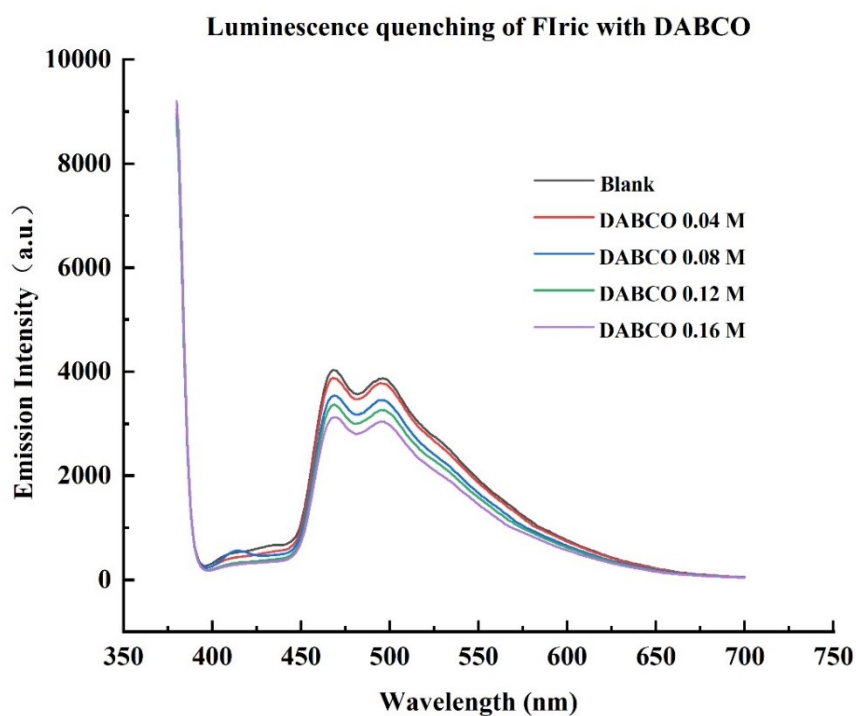


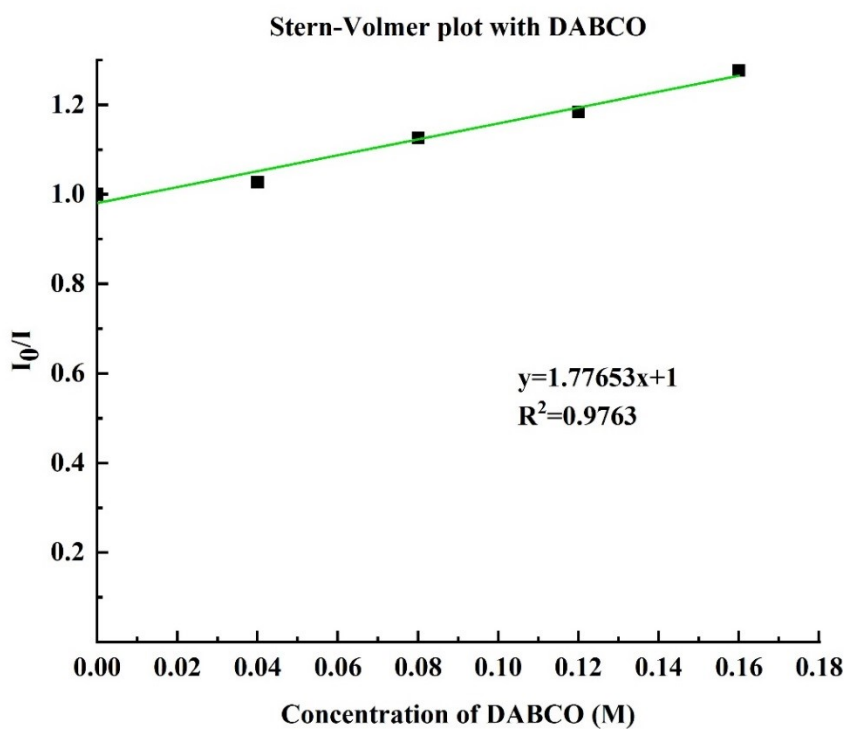
(0.1 M) in CH₃CN

5. Stern-Volmer Quenching Experiments

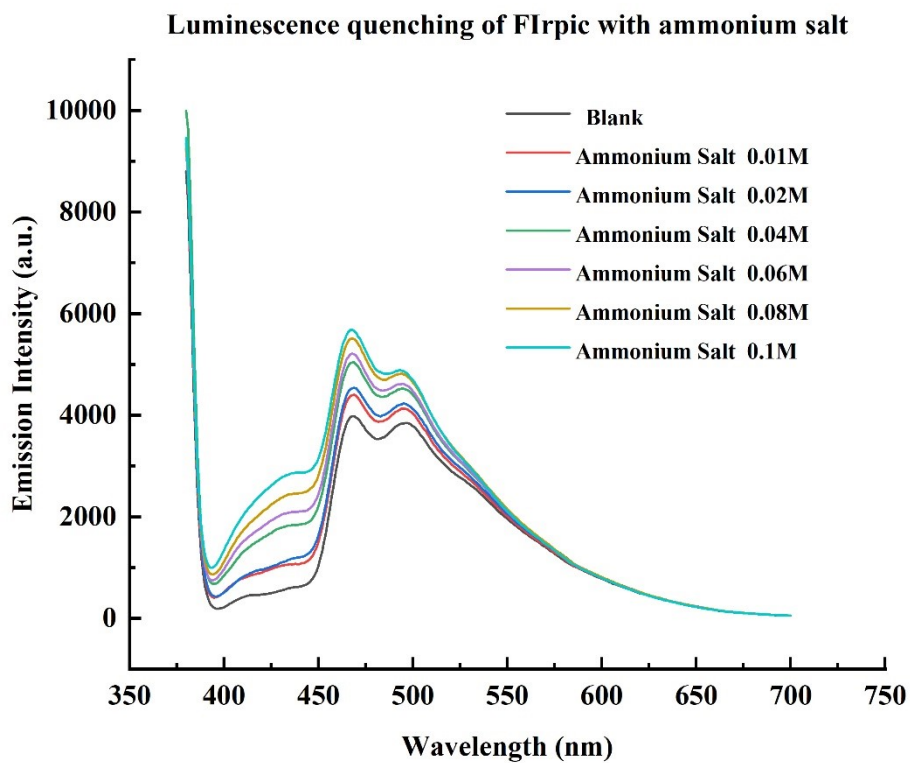
Stern-Volmer quenching experiments were conducted in a degassed cuvette using degassed solutions of FIrpic (50 μM) containing various amounts of quencher (namely DABCO, ammonium salt **1a** and DHP **2a**). All solutions were prepared in volumetric flasks using degassed methanol (prepared by bubbling nitrogen during 45 minutes), The solutions were irradiated at 370 nm and luminescence was measured between 380 and 700 nm.

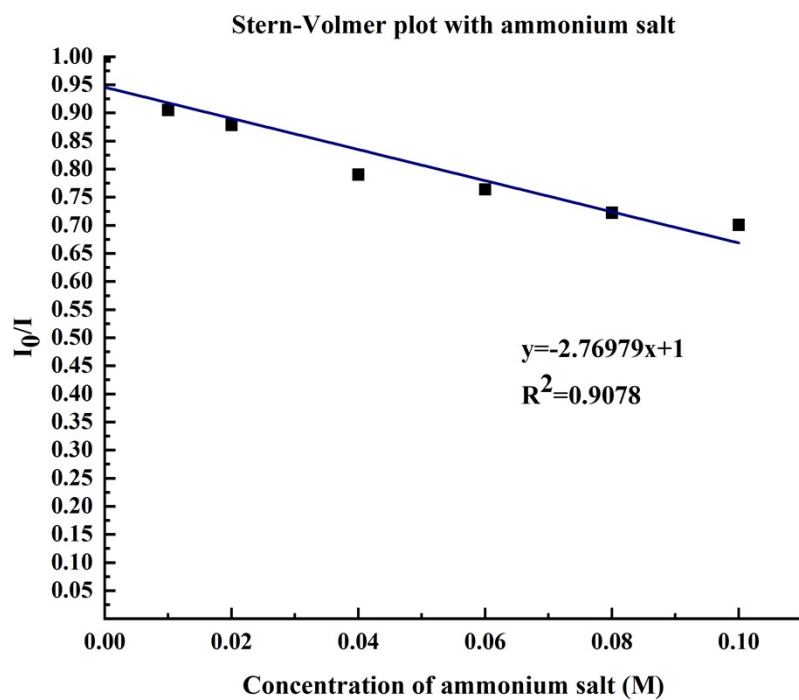
Stern-Volmer quenching experiment with FIrpic and DABCO as quencher



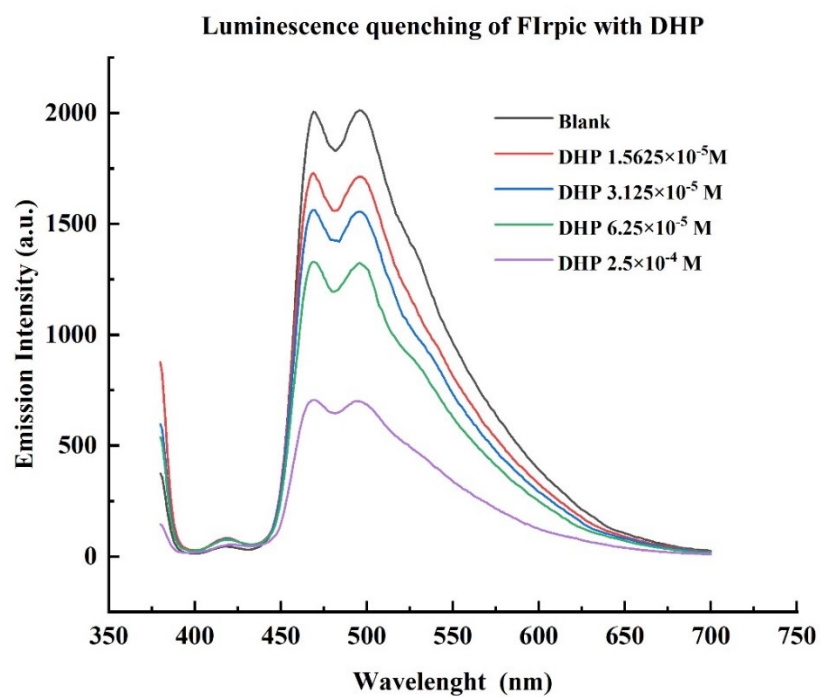


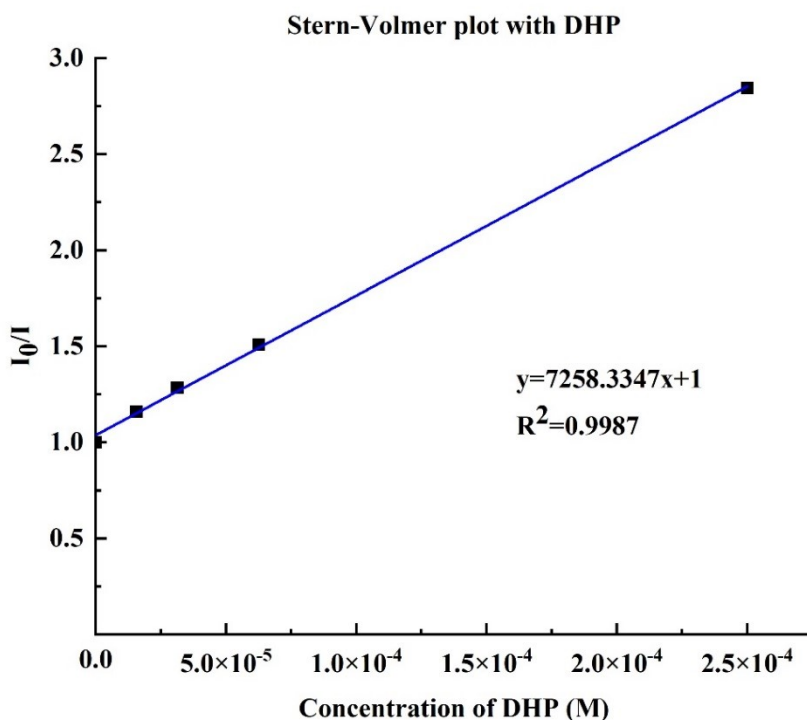
Stern-Volmer quenching experiment with Flrpic and ammonium salt as quencher





Stern-Volmer quenching experiment with Flrpic and DHP as quencher





6. Quantum yield measurement

In order to determine whether a radical-chain reaction is involved, the quantum yield measurement was conducted, which gives the quantum yield (Φ) of the photoreaction of 0.17, implying that the reaction is highly possible to proceed in a photoredox catalytic pathway rather than a radical-chain mechanism.

The actinometry measurements were done as follows based on previous literature:

(i) The actinometry measurements were determined by standard ferrioxalate actinometry. A solution of ferrioxalate was prepared by dissolving 73.7 mg of potassium ferrioxalate hydrate and 67 μL of concentrated sulfuric acid in a 25 mL volumetric flask and filled to the mark with water (HPLC grade). A buffered solution of phenanthroline was prepared by dissolving 25.0 mg of phenanthroline, 5.2 g of sodium acetate and 0.56 mL of concentrated sulfuric acid in a 50 mL volumetric flask and filled to the mark with water (HPLC grade). Both solutions were stored in the dark.

(ii) The actinometry solutions (V_1 , 1mL) were irradiated with 36W CFL for specified time intervals (30 s, 60 s, 90 s, 120 s, and 150 s). After irradiation, 20 μL (V_2) of the actionmeter solutions were removed and placed in 10 mL (V_3) volumetric flasks. 1.5 mL of buffered solutions were added to these flasks and filled to the mark with water (HPLC grade). The UV-Vis spectra of actinometry samples were recorded for each time interval. The absorbance of the actinometry solutions were monitored at 510 nm. A

non-irradiated sample was also prepared and the absorbance at 510 nm measured in cuvette ($l = 1$ cm). ϵ is the molar absorptivity at 510 nm ($11,100 \text{ Lmol}^{-1}\text{ml}^{-1}$). Based on the data, we got the graph (**Fig.1b**) between the number of moles of products (y axis) and time (x axis).

$$\text{mol Fe}^{2+} = \frac{V_1 \times V_3 \times \Delta A (510 \text{ nm})}{10^3 \times V_2 \times l \times \epsilon (510 \text{ nm})} = \frac{1 \text{ ml} \times 10 \text{ ml} \times \Delta A (510 \text{ nm})}{10^3 \times (20 \times 10^{-3} \text{ ml}) \times 1 \text{ cm} \times 11100} = \frac{\Delta A (510 \text{ nm})}{22200} = 2.45441 \times 10^{-8}$$

The quantum yield for Fe^{2+} ($\Phi_{\text{Fe}^{2+}} = 1.13$), $F = \text{mol Fe}^{2+} / \Phi_{\text{Fe}^{2+}}$. Then, the irradiated light intensity was estimated to $2.17 \times 10^{-8} \text{ einstein S}^{-1}$ by using $\text{K}_3[\text{Fe}(\text{C}_2\text{O}_4)_3]$ as an actinometer.

(iii) For five clean tubes, according to the general procedure, the 0.2 mmol scale model reaction solution was irradiated with 36W CFL for specified time intervals (30 min, 60 min, 90 min, 120 min and 150 min). The moles of products formed were determined by ^1H NMR yield with 1,3,5-Trimethoxybenzene as reference standard. The number of moles of products (y axis) per unit time is related to the number of photons (x axis, calculated from the light intensity) (**Fig.1c**). The slope gives the quantum yield (Φ) of the photoreaction, 0.17.

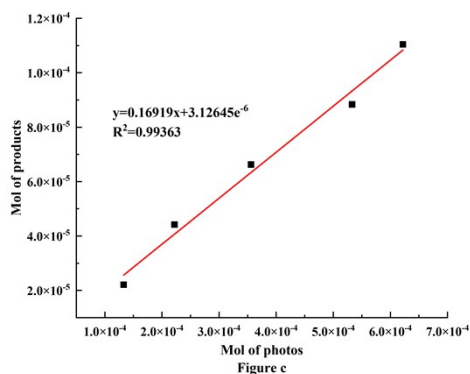
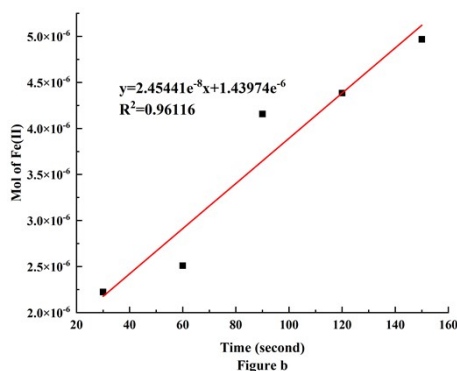
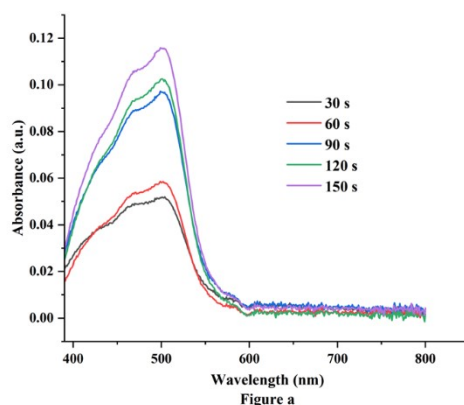
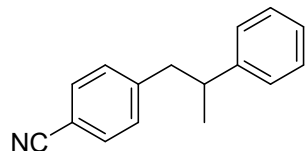


Figure 1. The UV-Vis spectra and data of quantum yield measurement.

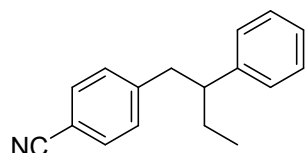
7. Products Characterization



4-(2-phenylpropyl) benzonitrile (3a)

Colorless liquid, isolated yield is 82%. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.40 (d, $J = 8.3$ Hz, 2H), 7.20 – 7.14 (m, 2H), 7.13 – 7.08 (m, 1H), 7.03 (d, $J = 7.7$ Hz, 4H), 2.98 – 2.74 (m, 3H), 1.19 (d, $J = 6.7$ Hz, 3H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 146.4, 145.7, 131.9, 129.9, 128.5, 127.0, 126.4, 119.1, 109.8, 45.1, 41.7, 21.4.

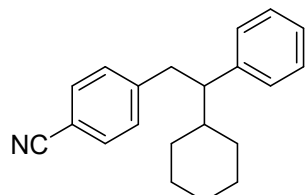
HRMS (ESI-TOF) m/z : $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{16}\text{H}_{15}\text{NNa}^+$: 244.1097; Found: 244.1094



4-(2-phenylbutyl) benzonitrile (3b)

Colorless liquid, isolated yield is 40 %. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.45 (d, $J = 8.22$ Hz, 2H), 7.27 – 7.21 (m, 2H), 7.20 – 7.10 (m, 1H), 7.09 – 7.00 (m, 4H), 2.99 (dd, $J = 13.38, 6.39$ Hz, 1H), 2.88 (dd, $J = 13.36, 8.48$ Hz, 1H), 2.69 (m, 1H), 1.80 – 1.58 (m, 2H), 0.79 (t, $J = 7.34$ Hz, 3H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 146.5, 143.7, 131.8, 129.9, 128.3, 127.7, 126.3, 119.1, 109.6, 49.6, 43.5, 28.7, 12.1.

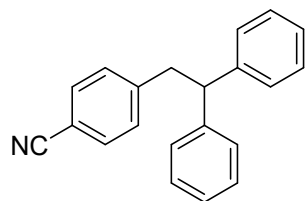
HRMS (ESI-TOF) m/z : $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{17}\text{H}_{17}\text{NNa}^+$: 258.1253; Found: 258.1258



4-(2-cyclohexyl-2-phenylethyl)benzonitrile (3c)

Colorless liquid, isolated yield is 40 %. Colorless liquid, isolated yield is 40 %. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.38 (m, $J = 8.17, 1.45$ Hz, 2H), 7.21 – 7.09 (m, 3H), 6.97 (m, $J = 10.99, 7.43, 1.43$ Hz, 4H), 3.23 (m, $J = 13.44, 4.58$ Hz, 1H), 2.81 (m, $J = 13.42, 10.54$ Hz, 1H), 2.57 (m, $J = 11.37, 7.76, 4.59$ Hz, 1H), 2.00 (m, $J = 12.45, 2.99$ Hz, 1H), 1.82 – 1.74 (m, 1H), 1.69 – 1.45 (m, 5H), 1.30 – 0.96 (m, 4H), 0.81 (m, $J = 12.79, 12.22, 3.54$ Hz, 1H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 147.2, 142.6, 131.7, 129.7, 128.6, 128.0, 126.2, 119.1, 109.3, 54.3, 42.6, 39.7, 31.6, 30.8, 26.5, 26.4, 26.4.

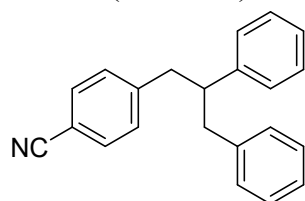
HRMS (ESI-TOF) m/z : $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{21}\text{H}_{23}\text{NNa}^+$: 312.1723; Found: 312.1724



4-(2,2-diphenylethyl)benzonitrile (3d)

White solid, isolated yield is 77%; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.44 (d, $J = 8.2$ Hz, 2H), 7.23 (s, 2H), 7.18 (dd, $J = 6.9, 3.8$ Hz, 7H), 7.08 (t, $J = 8.2$ Hz, 3H), 4.19 (t, $J = 7.9$ Hz, 1H), 3.40 (d, $J = 7.9$ Hz, 2H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 146.0, 143.6, 131.9, 129.9, 128.6, 127.9, 126.6, 119.1, 109.9, 52.8, 42.2.

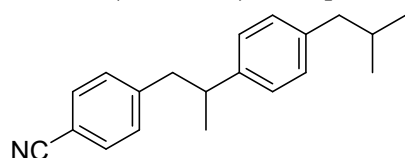
HRMS (ESI-TOF) m/z : $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{12}\text{H}_{17}\text{NNa}^+$: 306.1253; Found: 306.1254



4-(2,3-diphenylpropyl)benzonitrile (3e)

White solid, isolated yield is 56%; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.42 (d, $J = 7.94$ Hz, 2H), 7.27 – 7.13 (m, 6H), 7.09 – 6.98 (m, 6H), 3.18 – 2.86 (m, 5H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 146.2, 143.17, 139.9, 131.8, 129.8, 129.1, 128.4, 128.3, 127.8, 126.6, 126.2, 119.1, 109.7, 49.7, 42.9, 42.3.

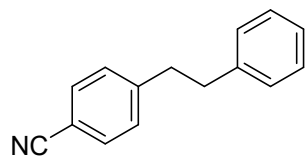
HRMS (ESI-TOF) m/z : $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{22}\text{H}_{19}\text{NNa}^+$: 320.1410; Found: 320.1413



4-(2-(4-isopropylphenyl)propyl)benzonitrile (3f)

Colorless liquid, isolated yield is 45%. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.41 (m, $J = 8.2, 1.5$ Hz, 2H), 7.06 – 7.00 (m, 2H), 7.00 – 6.90 (m, 4H), 2.94 – 2.73 (m, 3H), 2.36 (d, $J = 7.2$ Hz, 2H), 1.76 (m, $J = 13.6, 6.7$ Hz, 1H), 1.23 – 1.13 (m, 3H), 0.82 (m, $J = 6.6, 1.4$ Hz, 6H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 146.5, 142.8, 139.7, 131.8, 129.9, 129.1, 126.6, 119.1, 109.7, 45.2, 45.0, 41.3, 30.2, 22.3, 21.3.

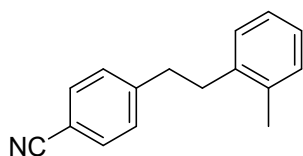
HRMS (ESI-TOF) m/z : $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{20}\text{H}_{23}\text{NNa}^+$: 300.1723; Found: 300.1725



4-phenethylbenzonitrile (3g)

Colorless liquid, isolated yield is 62%; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.55 (d, $J = 8.1$ Hz, 2H), 7.25 (m, 5H), 7.13 (d, $J = 7.4$ Hz, 2H), 3.02 – 2.96 (m, 2H), 2.96 – 2.89 (m, 2H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 147.26, 140.6, 132.2, 129.4, 128.5, 128.5, 126.3, 119.1, 109.9, 37.9, 37.2.

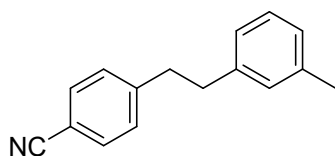
HRMS (ESI-TOF) m/z : $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{15}\text{H}_{13}\text{NNa}^+$: 230.0940; Found: 230.0943



4-(2-methylphenethyl)benzonitrile (3h)

Colorless liquid, isolated yield is 43%; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.49 (d, $J = 8.22$ Hz, 2H), 7.21 – 7.15 (m, 2H), 7.10 – 6.96 (m, 4H), 2.84 (m, 4H), 2.20 (s, 3H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 147.4, 140.6, 138.1, 132.2, 129.3, 129.3, 128.4, 127.0, 125.4, 119.2, 109.8, 38.0, 37.2, 21.4.

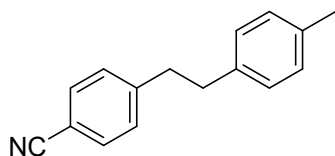
HRMS (ESI-TOF) m/z : $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{16}\text{H}_{15}\text{NNa}^+$: 244.1097; Found: 244.1099



4-(3-methylphenethyl)benzonitrile (3i)

Colorless liquid, isolated yield is 37%; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.55 (d, $J = 8.20$ Hz, 2H), 7.24 (d, $J = 7.96$ Hz, 2H), 7.17 (t, $J = 7.56$ Hz, 1H), 7.02 (d, $J = 7.68$ Hz, 1H), 6.98 – 6.88 (m, 2H), 2.99 – 2.94 (m, 2H), 2.92 – 2.84 (m, 2H), 2.32 (s, 3H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 147.5, 138.8, 135.9, 132.2, 130.4, 129.3, 128.9, 126.5, 126.1, 119.1, 109.9, 36.8, 34.7, 19.3.

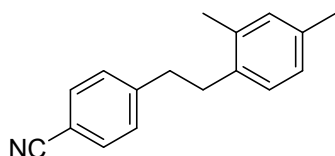
HRMS (ESI-TOF) m/z : $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{16}\text{H}_{15}\text{NNa}^+$: 244.1097; Found: 244.1096



4-(4-methylphenethyl)benzonitrile (3j)

Colorless liquid, isolated yield is 61%; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.55 (d, $J = 8.2$ Hz, 2H), 7.24 (d, $J = 8.1$ Hz, 2H), 7.09 (d, $J = 7.9$ Hz, 2H), 7.01 (d, $J = 7.9$ Hz, 2H), 2.96 (dd, $J = 8.7, 6.2$ Hz, 2H), 2.88 (dd, $J = 8.7, 6.2$ Hz, 2H), 2.32 (s, 3H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 147.4, 137.6, 135.8, 132.2, 129.2, 129.4, 128.3, 119.2, 109.8, 38.1, 36.8, 21.0.

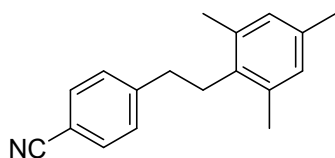
HRMS (ESI-TOF) m/z : $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{16}\text{H}_{15}\text{NNa}^+$: 244.1097; Found: 244.1093



4-(2,4-dimethylphenethyl)benzonitrile (3k)

Colorless liquid, isolated yield is 49%; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.57 (d, $J = 8.23$ Hz, 2H), 7.26 (d, $J = 8.24$ Hz, 2H), 7.01 – 6.94 (m, 3H), 2.96 – 2.90 (m, 2H), 2.90 – 2.84 (m, 2H), 2.31 (s, 3H), 2.25 (s, 3H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 147.6, 135.9, 135.8, 135.6, 132.2, 131.2, 129.3, 128.8, 126.7, 119.1, 109.8, 37.0, 34.3, 20.9, 19.2.

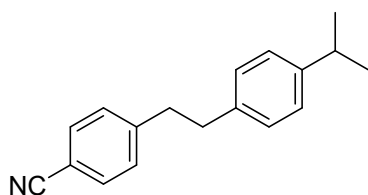
HRMS (ESI-TOF) m/z : $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{17}\text{H}_{17}\text{NNa}^+$: 258.1253; Found: 258.1259



4-(2,4,6-trimethylphenethyl)benzonitrile (3l)

Colorless solid, isolated yield is 60%; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.60 (d, $J = 8.06$ Hz, 2H), 7.31 (d, $J = 8.01$ Hz, 2H), 6.87 (s, 2H), 2.93 – 2.86 (m, 2H), 2.85 – 2.78 (m, 2H), 2.29 (s, 9H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 147.8, 135.9, 135.6, 134.4, 132.3, 129.2, 129.1, 119.1, 109.9, 35.7, 31.1, 20.9, 19.7.

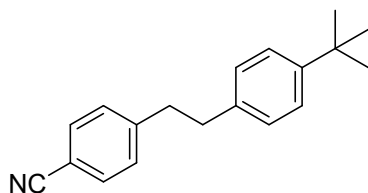
HRMS (ESI-TOF) m/z : $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{18}\text{H}_{19}\text{NNa}^+$: 272.1410; Found: 272.1413



4-(4-isopropylphenethyl)benzonitrile (3m)

Colorless liquid, isolated yield is 50%; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.57 (t, $J = 7.31$ Hz, 2H), 7.27 (t, $J = 7.00$ Hz, 2H), 7.17 (t, $J = 7.29$ Hz, 2H), 7.09 (t, $J = 7.29$ Hz, 2H), 3.04 – 2.83 (m, 4H), 1.38 – 1.20 (m, 7H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) 147.4, 146.8, 137.9, 132.1, 129.3, 128.3, 126.5, 119.1, 109.7, 37.9, 36.8, 33.7, 24.0.

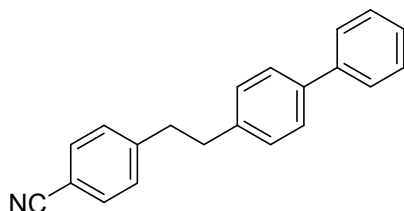
HRMS (ESI-TOF) m/z : $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{18}\text{H}_{19}\text{NNa}^+$: 272.1410; Found: 272.1414



4-(4-(tert-butyl)phenethyl)benzonitrile (3n)

Colorless liquid, isolated yield is 39%; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.48 (d, $J = 8.20$ Hz, 2H), 7.24 (d, $J = 8.21$ Hz, 2H), 7.19 (d, $J = 8.51$ Hz, 2H), 7.01 (d, $J = 8.28$ Hz, 2H), 2.94 – 2.86 (m, 2H), 2.85 – 2.78 (m, 2H), 1.24 (s, 9H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 149.2, 147.5, 137.6, 132.2, 129.3, 128.0, 125.4, 119.2, 109.8, 37.9, 36.7, 34.4, 31.4.

HRMS (ESI-TOF) m/z : $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{19}\text{H}_{21}\text{NNa}^+$: 286.1566; Found: 286.1571

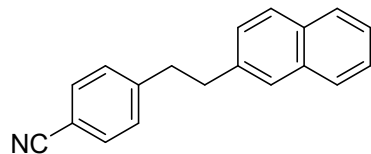


4-(2-([1,1'-biphenyl]-4-yl)ethyl)benzonitrile (3o)

Colorless solid, isolated yield is 52%; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.53 – 7.47 (m, 4H), 7.46 – 7.42 (m, 2H), 7.39 – 7.32 (m, 2H), 7.30 – 7.24 (m, 1H), 7.19 (d, $J = 8.5$ Hz, 2H), 7.13 (d, $J = 8.2$ Hz, 2H), 2.98 – 2.92 (m, 2H), 2.92 – 2.86 (m, 2H). $^{13}\text{C NMR}$

(101 MHz, CDCl₃) δ 147.2, 140.9, 139.7, 139.2, 132.2, 129.4, 128.9, 128.8, 127.2, 127.0, 119.1, 109.9, 37.9, 36.9.

HRMS (ESI-TOF) m/z : [M+Na]⁺ calcd for C₂₁H₁₇NNa⁺: 306.1253; Found: 306.1257

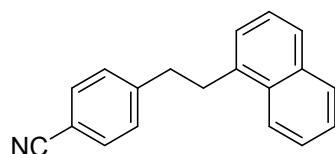


4-(2-(naphthalen-2-yl)ethyl)benzonitrile (3p)

White solid, isolated yield is 47%; **¹H NMR** (400 MHz, CDCl₃) δ 7.75 – 7.63 (m, 3H), 7.45 (d, J = 6.74 Hz, 3H), 7.41 – 7.32 (m, 2H), 7.17 (t, J = 8.79 Hz, 3H), 2.99 (s, 4H).

¹³C NMR (101 MHz, CDCl₃) δ 147.2, 138.1, 133.5, 132.2, 129.4, 128.1, 127.6, 127.4, 127.0, 126.6, 126.1, 125.4, 119.1, 109.9, 37.8, 37.4.

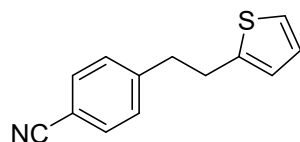
HRMS (ESI-TOF) m/z : [M+Na]⁺ calcd for C₁₉H₁₅NNa⁺: 280.1097; Found: 280.1100



4-(2-(naphthalen-1-yl)ethyl)benzonitrile (3q)

White solid, isolated yield is 39%; **¹H NMR** (400 MHz, CDCl₃) δ 8.02 (d, J = 8.1 Hz, 1H), 7.88 (d, J = 7.9 Hz, 1H), 7.73 (d, J = 8.3 Hz, 1H), 7.52 (dt, J = 22.2, 7.1 Hz, 4H), 7.35 (t, J = 7.7 Hz, 1H), 7.26 (d, J = 7.1 Hz, 2H), 7.19 (d, J = 7.1 Hz, 1H), 3.41 – 3.34 (m, 2H), 3.15 – 3.08 (m, 2H). **¹³C NMR** (101 MHz, CDCl₃) δ 147.43 (s), 136.57 (s), 133.9, 132.2, 131.6, 129.3, 129.0, 127.2, 126.3, 126.1, 125.7, 125.5, 123.3, 119.1, 109.9, 37.1, 34.5.

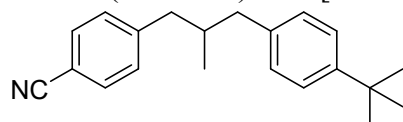
HRMS (ESI-TOF) m/z : [M+Na]⁺ calcd for C₁₉H₁₅NNa⁺: 280.1097; Found: 280.1099



4-(2-(thiophen-2-yl)ethyl)benzonitrile (3r)

Colorless liquid, isolated yield is 54%; **¹H NMR** (400 MHz, CDCl₃) δ 7.56 (d, J = 8.2 Hz, 2H), 7.27 – 7.22 (m, 3H), 6.91 – 6.87 (m, 2H), 2.97 (tt, J = 8.0, 4.0 Hz, 4H). **¹³C NMR** (101 MHz, CDCl₃) δ 147.2, 140.9, 132.2, 129.3, 127.9, 125.7, 120.7, 119.0, 109.9, 37.0, 31.5.

HRMS (ESI-TOF) m/z : [M+Na]⁺ calcd for C₁₃H₁₁NSNa⁺: 236.0504; Found: 236.0507



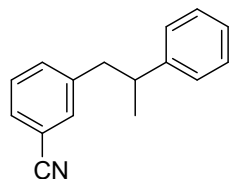
4-(3-(4-(tert-butyl)phenyl)-2-methylpropyl)benzonitrile (3s)

Colorless liquid, isolated yield is 61%; **¹H NMR** (400 MHz, CDCl₃) δ 7.55 (d, J = 8.2 Hz, 2H), 7.30 (d, J = 8.2 Hz, 2H), 7.23 (d, J = 8.1 Hz, 2H), 7.07 (d, J = 8.1 Hz, 2H), 2.76 (dd, J = 13.4, 5.5 Hz, 1H), 2.60 (dd, J = 13.5, 6.5 Hz, 1H), 2.43 (ddd, J = 17.8, 9.0, 5.0 Hz, 2H), 2.06 (dt, J = 14.0, 7.0 Hz, 1H), 1.31 (s, 9H), 0.83 (d, J = 6.6 Hz, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 148.8, 147.2, 137.4, 132.0, 129.9, 128.8, 125.2, 119.2,

109.7, 43.3, 42.9, 36.9, 34.4, 31.4, 19.3.

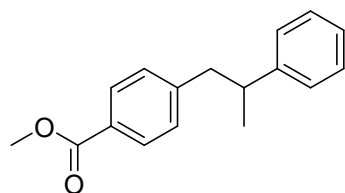
HRMS (ESI-TOF) m/z : $[M+Na]^+$ calcd for $C_{21}H_{25}NNa^+$: 314.1884; Found: 314.1888



3-(2-phenylpropyl)benzonitrile (3t)

Colorless liquid, isolated yield is 44%; **1H NMR** (400 MHz, $CDCl_3$) δ 7.50 – 7.34 (m, 2H), 7.33 – 7.26 (m, 3H), 7.23 – 7.08 (m, 4H), 3.03 – 2.78 (m, 3H), 1.27 (d, $J = 6.7$ Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 145.6, 142.1, 133.7, 132.6, 129.7, 128.8, 128.5, 127.0, 126.4, 119.0, 112.1, 44.5, 41.7, 21.3.

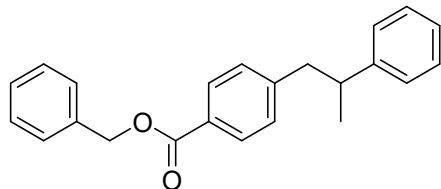
HRMS (ESI-TOF) m/z : $[M+Na]^+$ calcd for $C_{16}H_{15}NNa^+$: 244.1097; Found: 244.1096



methyl 4-(2-phenylpropyl)benzoate (3u)

Colorless liquid, isolated yield is 79%; **1H NMR** (400 MHz, $CDCl_3$) δ 7.90 (d, $J = 8.1$ Hz, 2H), 7.28 (d, $J = 7.3$ Hz, 2H), 7.20 – 7.09 (m, 5H), 3.89 (s, 3H), 3.07 – 2.94 (m, 2H), 2.85 (dd, $J = 12.8, 7.5$ Hz, 1H), 1.26 (d, $J = 6.7$ Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 167.2, 146.3, 146.3, 129.5, 129.2, 128.4, 127.9, 127.0, 126.2, 52.0, 45.1, 41.7, 21.3.

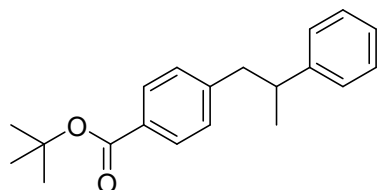
HRMS (ESI-TOF) m/z : $[M+Na]^+$ calcd for $C_{18}H_{17}O_2Na^+$: 277.1199; Found: 277.1195



benzyl 4-(2-phenylpropyl)benzoate (3v)

Colorless liquid, isolated yield is 82%. **1H NMR** (400 MHz, $CDCl_3$) δ 7.93 (d, $J = 8.24$ Hz, 2H), 7.49 – 7.30 (m, 5H), 7.29 – 7.22 (m, 2H), 7.21 – 7.08 (m, 5H), 5.33 (s, 2H), 3.07 – 2.92 (m, 2H), 2.91 – 2.80 (m, 1H), 1.25 (d, $J = 6.72$ Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 166.5, 146.4, 146.2, 136.2, 129.6, 129.2, 128.6, 128.4, 128.2, 128.2, 127.0, 126.2, 66.5, 45.0, 41.7, 21.3.

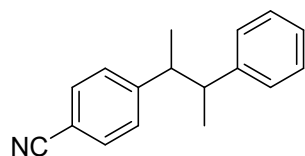
HRMS (ESI-TOF) m/z : $[M+Na]^+$ calcd for $C_{23}H_{22}O_2Na^+$: 353.1512; Found: 353.1521



tert-butyl 4-(2-phenylpropyl)benzoate (3w)

Colorless liquid, isolated yield is 77%. **¹H NMR** (400 MHz, CDCl₃) δ 7.86 (d, *J* = 7.63 Hz, 2H), 7.31 – 7.23 (m, 2H), 7.22 – 7.14 (m, 3H), 7.10 (d, *J* = 7.90 Hz, 2H), 3.08 – 2.93 (m, 2H), 2.85 (dd, *J* = 12.79, 7.41 Hz, 1H), 1.59 (s, 9H), 1.26 (d, *J* = 6.75 Hz, 3H). **¹³C NMR** (101 MHz, CDCl₃) δ 165.9, 146.4, 145.7, 129.3, 129.0, 128.4, 127.0, 126.2, 45.0, 41.7, 28.2, 21.3.

HRMS (ESI-TOF) *m/z*: [M+Na]⁺ calcd for C₂₀H₂₄O₂Na⁺: 319.1669; Found: 319.1669



4-(3-phenylbutan-2-yl)benzonitrile (3x)

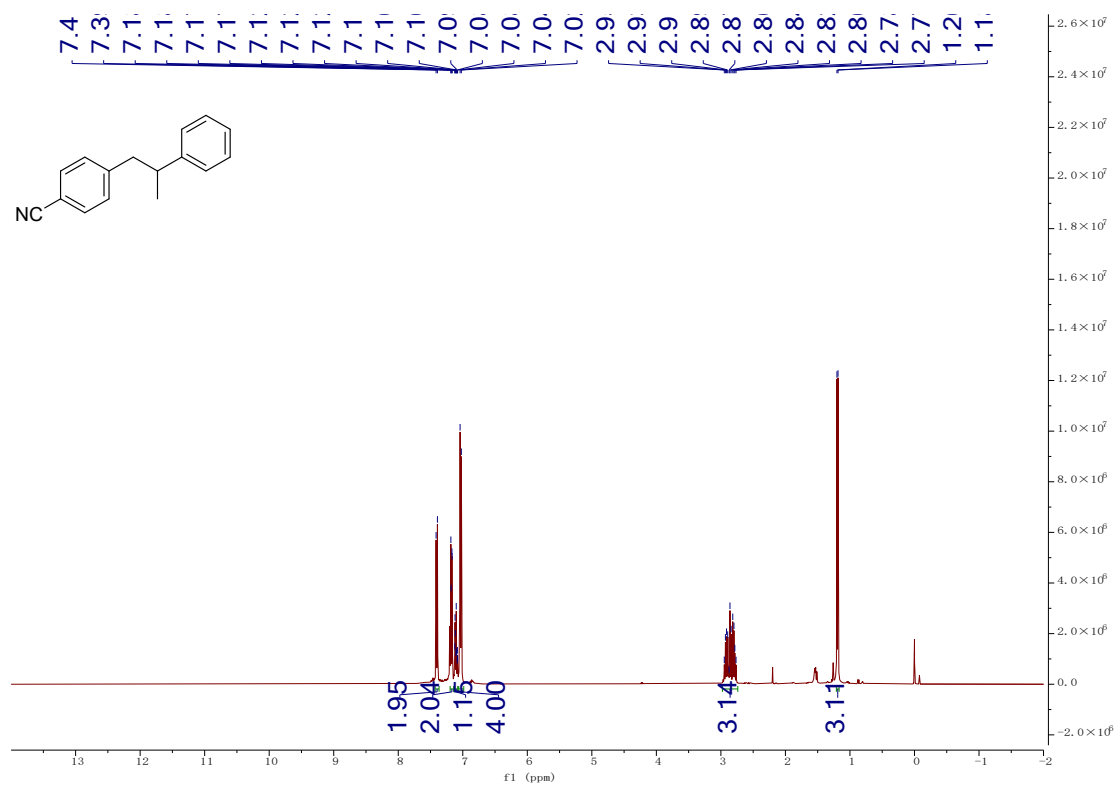
Colorless liquid, isolated yield is 43%. **¹H NMR** (400 MHz, CDCl₃) δ 7.60 (d, *J* = 8.0 Hz, 1H), 7.42 (d, *J* = 8.0 Hz, 1H), 7.34 – 7.27 (m, 2H), 7.26 – 7.03 (m, 4H), 6.93 (d, *J* = 7.1 Hz, 1H), 3.01 – 2.76 (m, 2H), 1.32 (d, *J* = 6.9 Hz, 3H), 1.03 (t, *J* = 6.1 Hz, 3H).

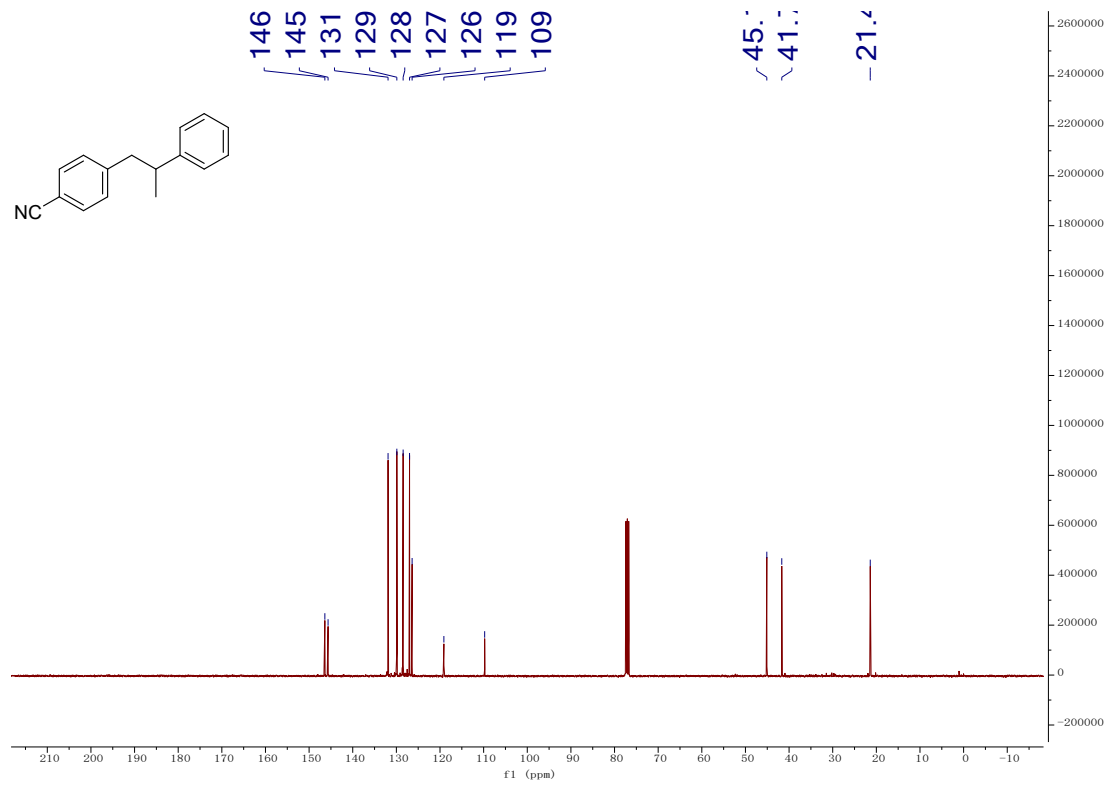
¹³C NMR (101 MHz, CDCl₃) δ 152.1, 151.7, 145.2, 144.9, 132.2, 131.7, 128.5, 128.5, 128.4, 128.0, 127.6, 127.5, 126.4, 126.1, 119.1, 119.1, 109.9, 109.5, 47.4, 47.0, 46.8, 46.6, 20.6, 20.4, 18.7, 18.5.

HRMS (ESI-TOF) *m/z*: [M+Na]⁺ calcd for C₁₇H₁₇NNa⁺: 258.1253; Found: 258.1255

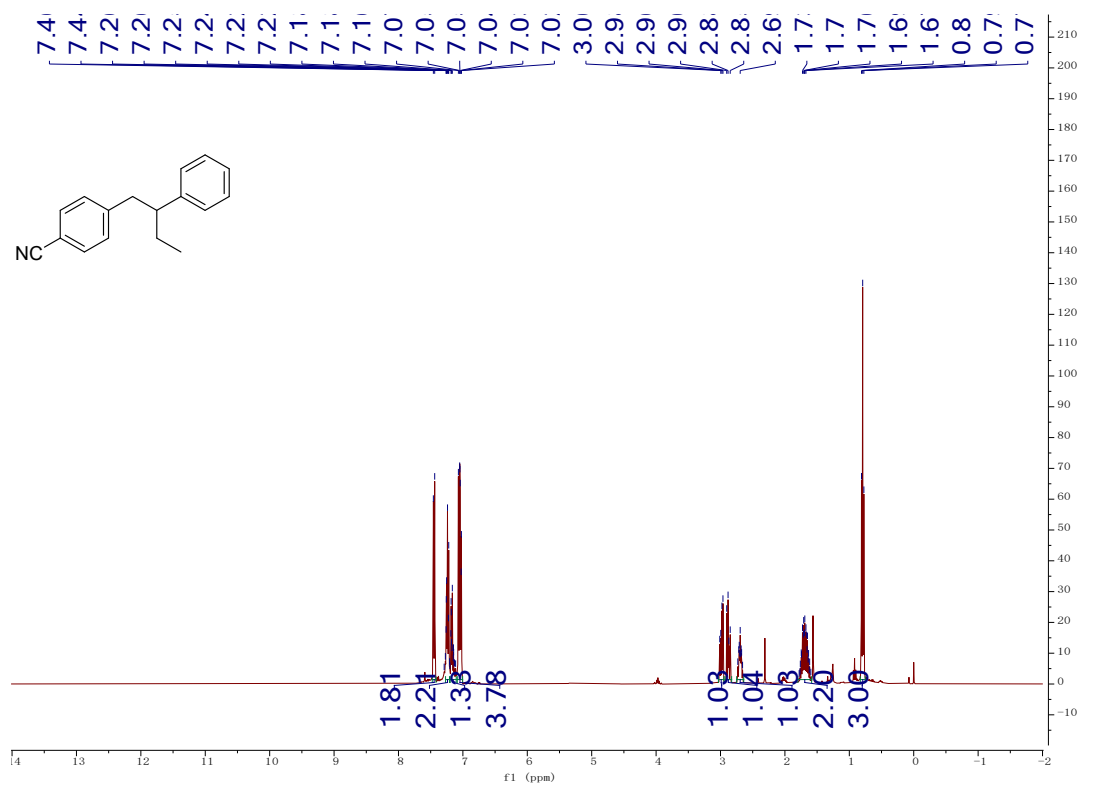
8. ^1H and ^{13}C NMR spectra

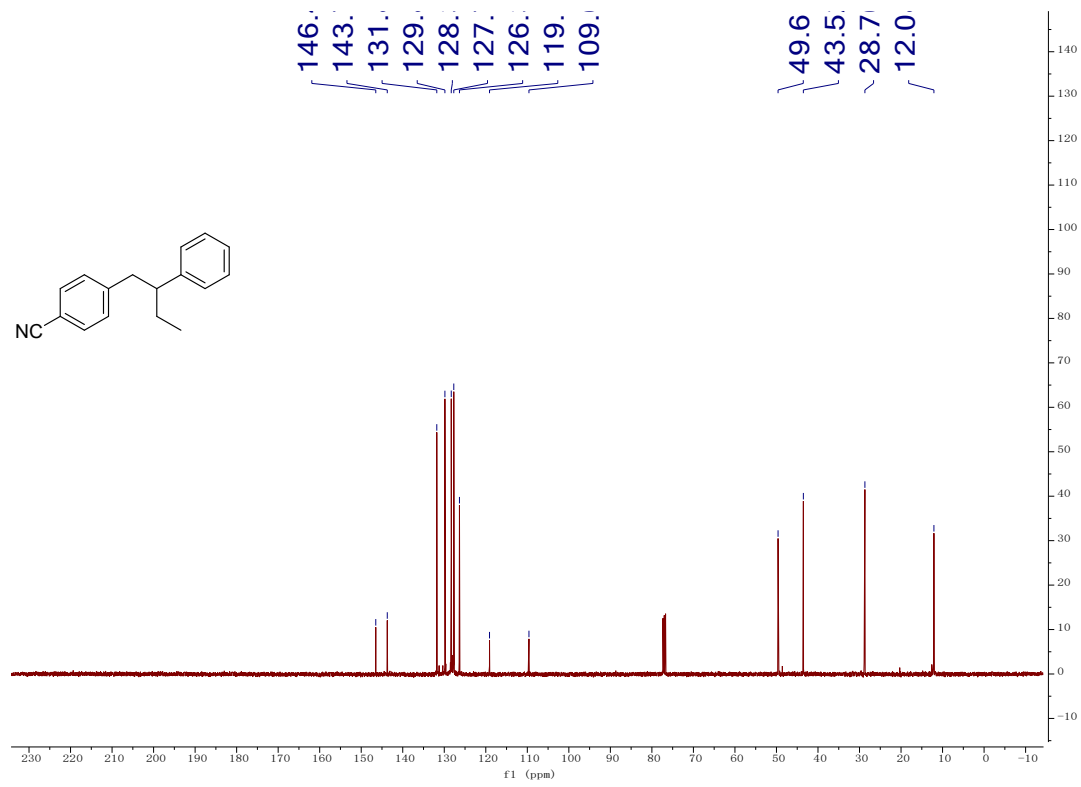
4-(2-phenylpropyl) benzonitrile (3a)



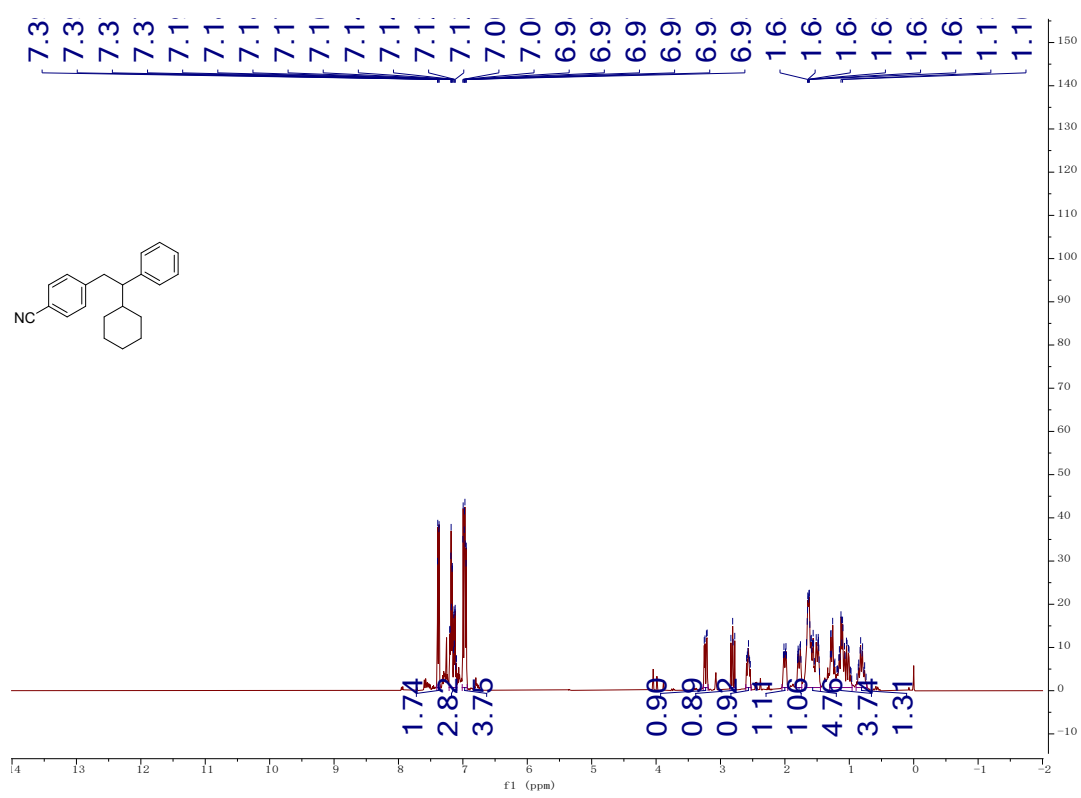


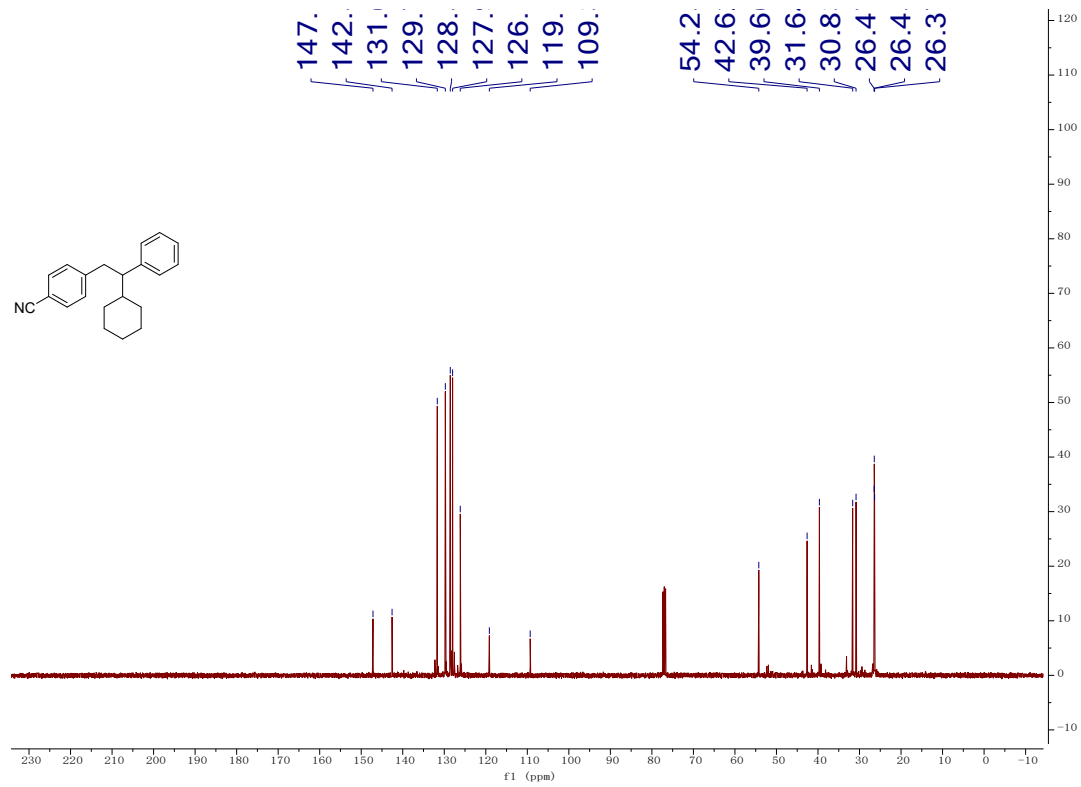
4-(2-phenylbutyl) benzonitrile (3b)



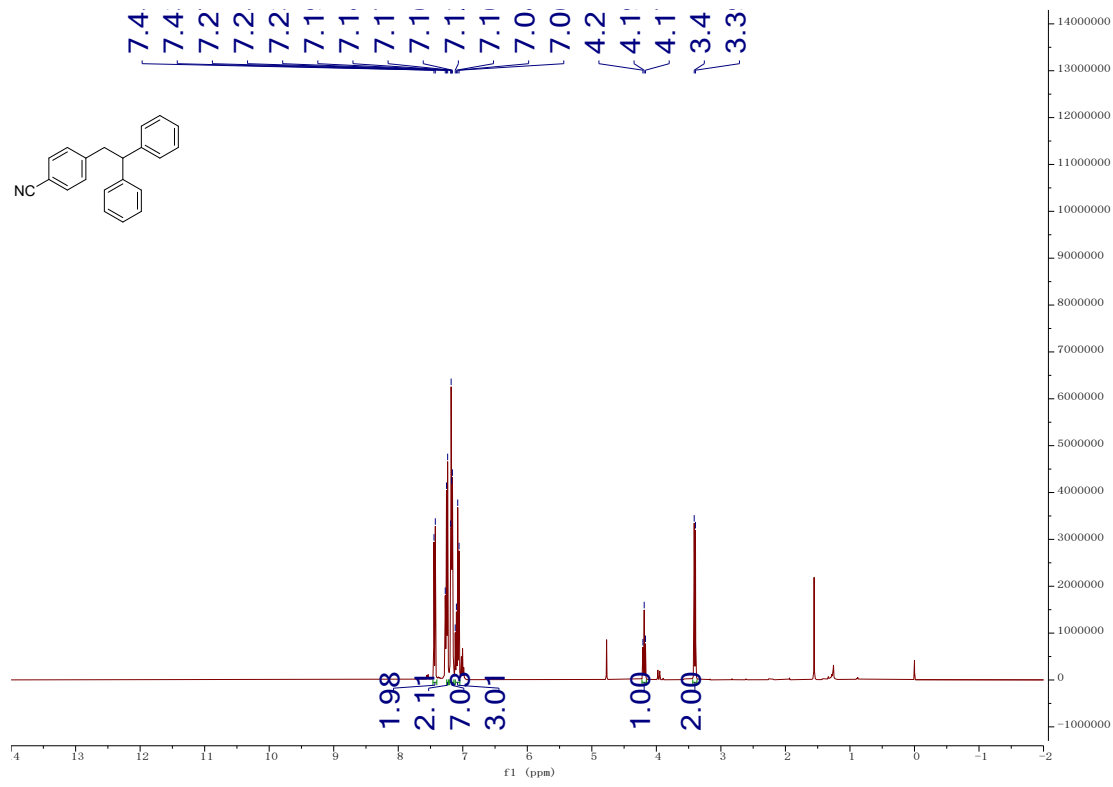


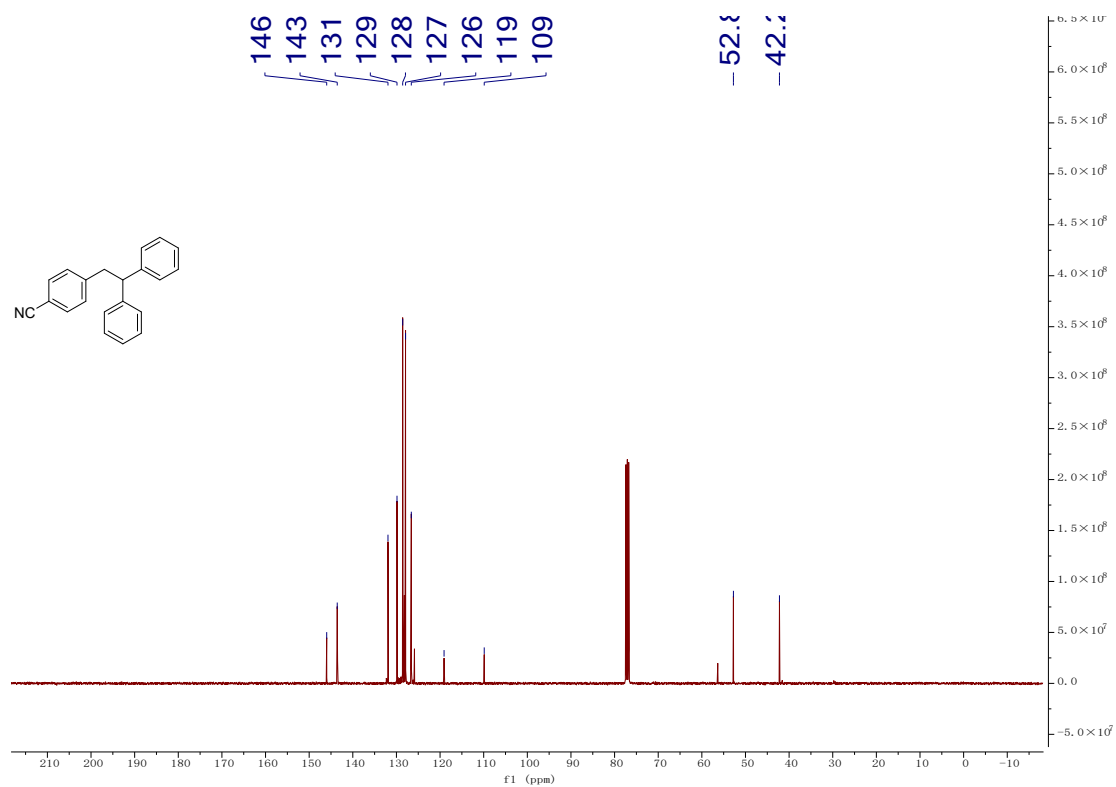
4-(2-cyclohexyl-2-phenylethyl)benzonitrile (3c)



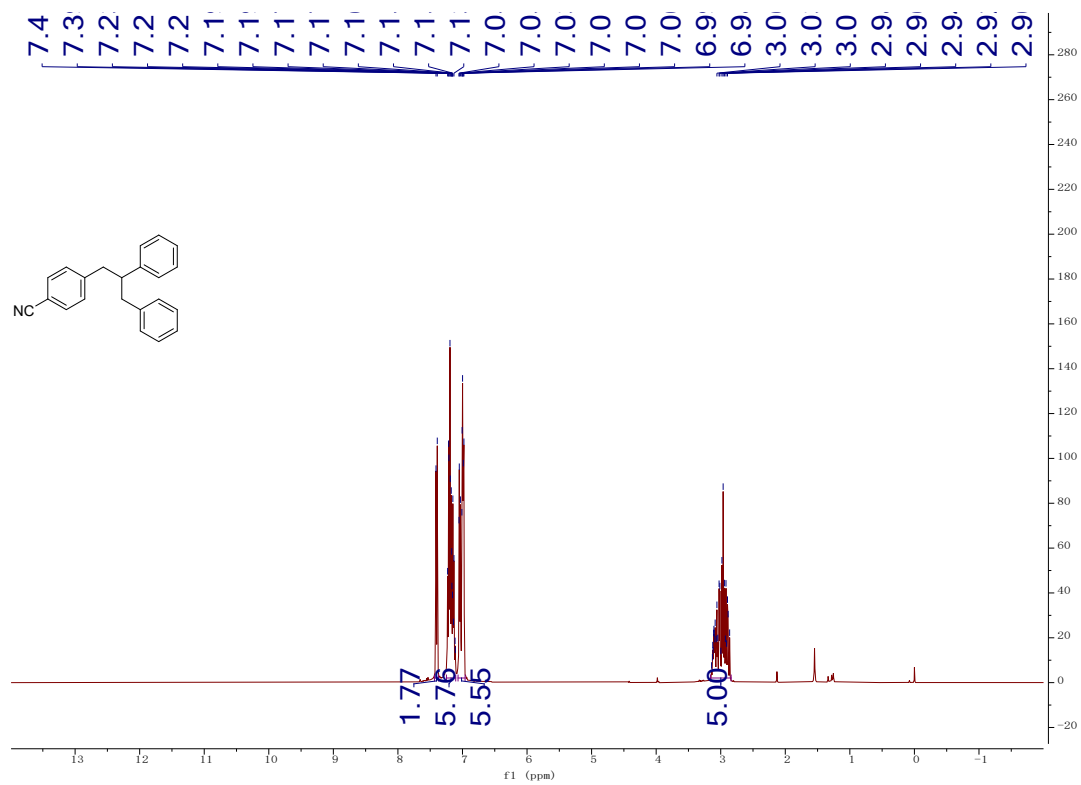


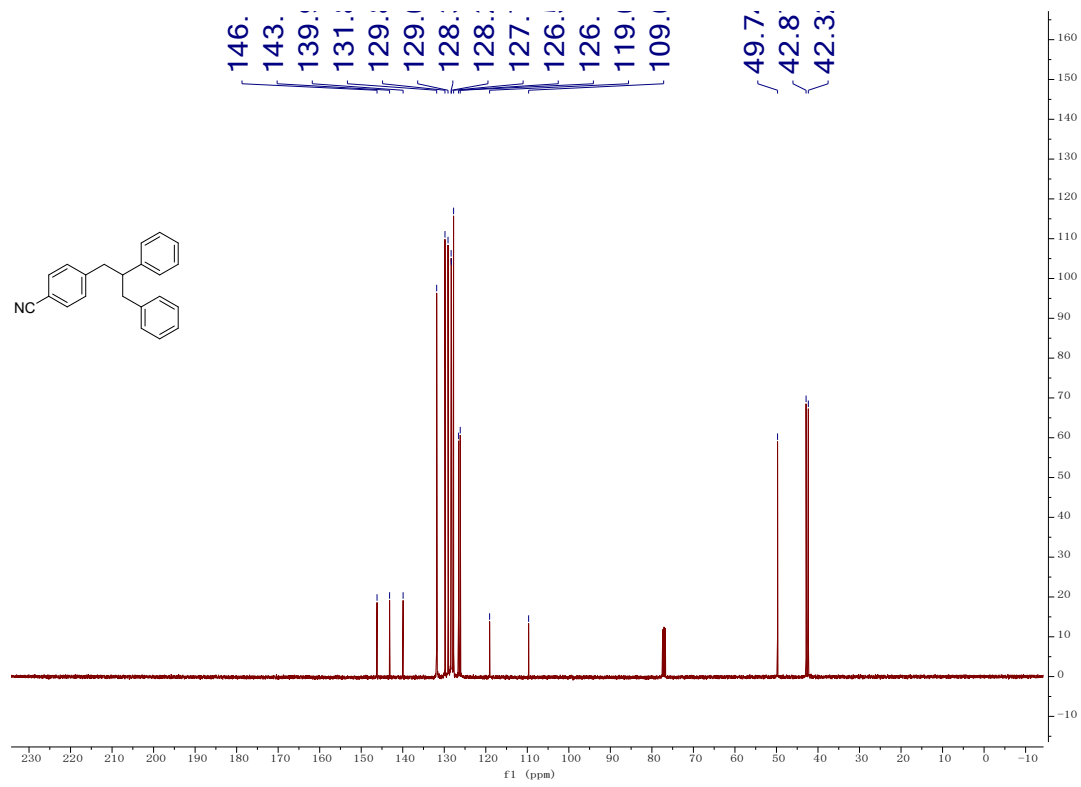
4-(2,2-diphenylethyl)benzonitrile (3d)



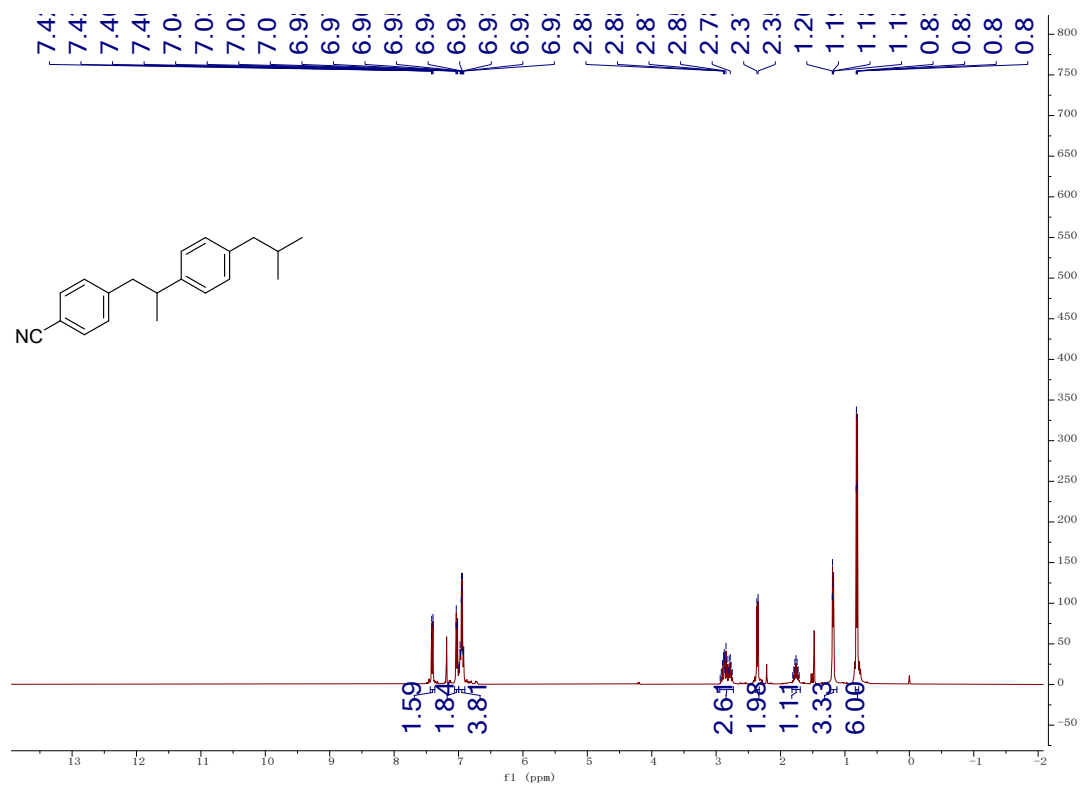


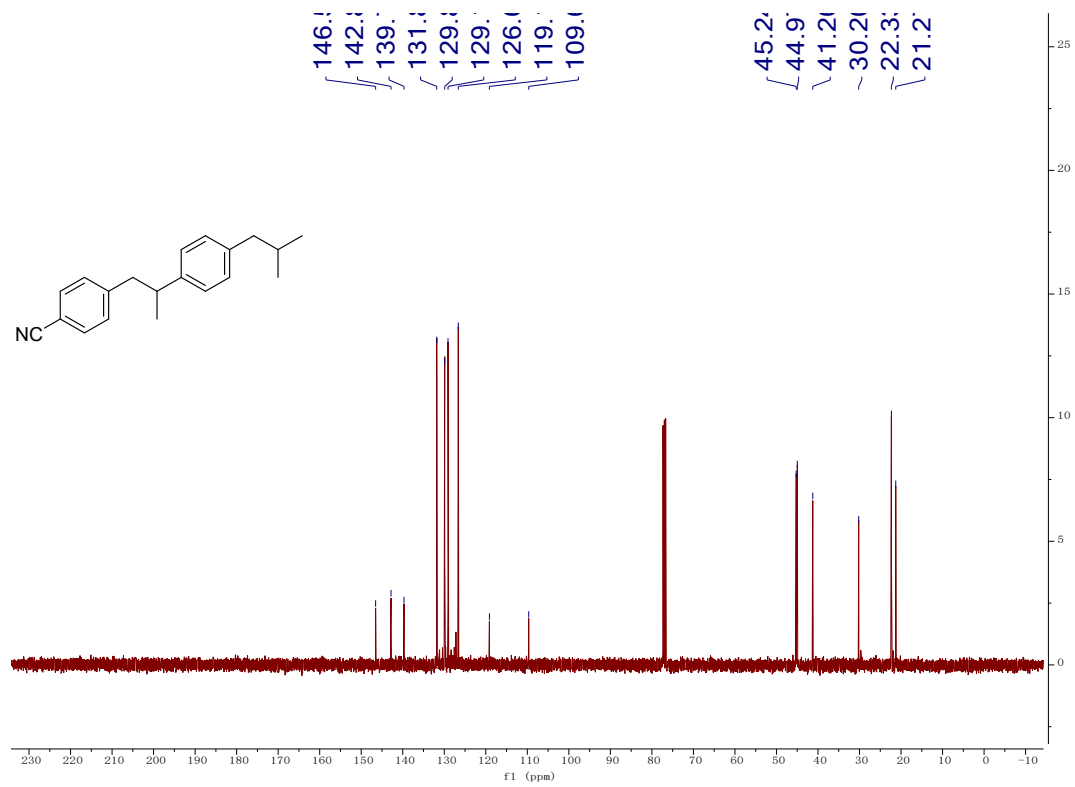
4-(2,3-diphenylpropyl)benzonitrile (3e)



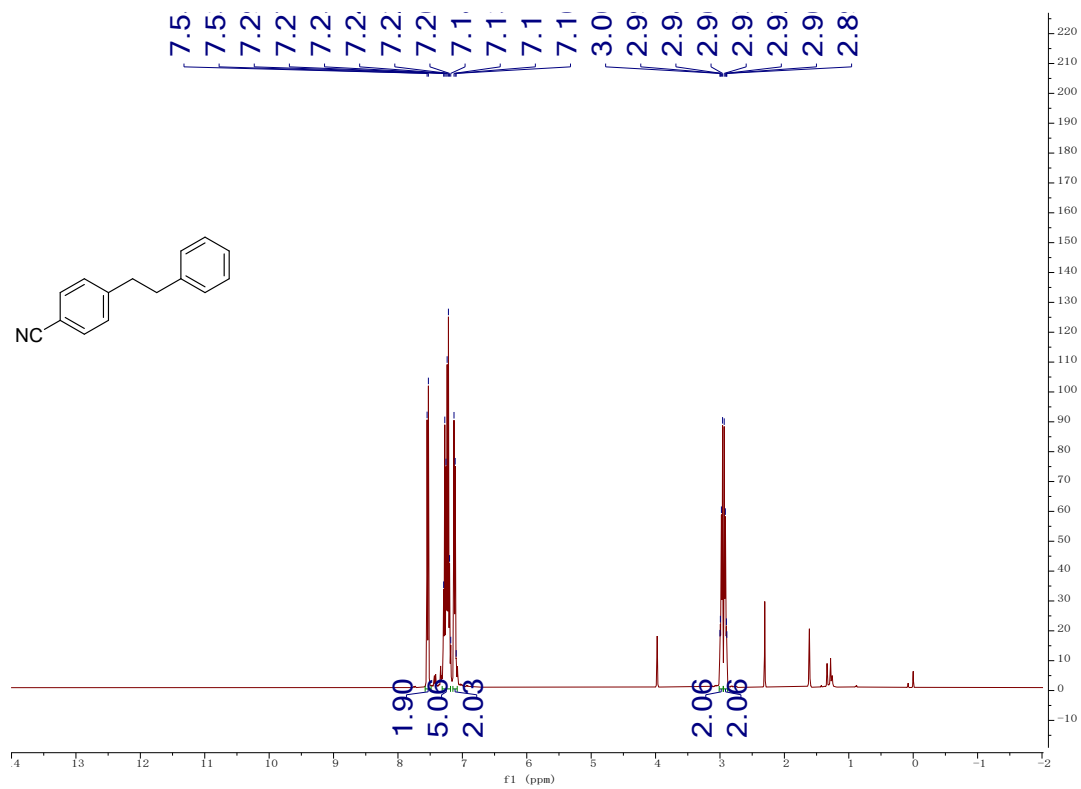


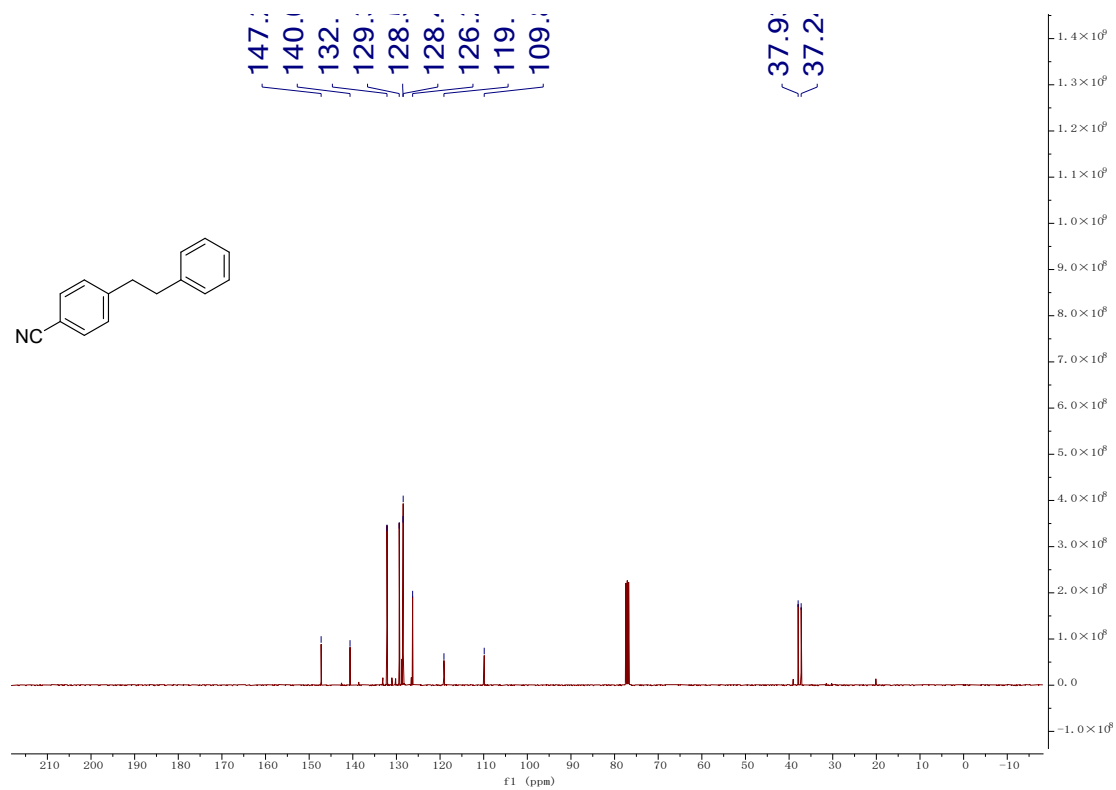
4-(2-(4-isopropylphenyl)propyl)benzonitrile (3f)



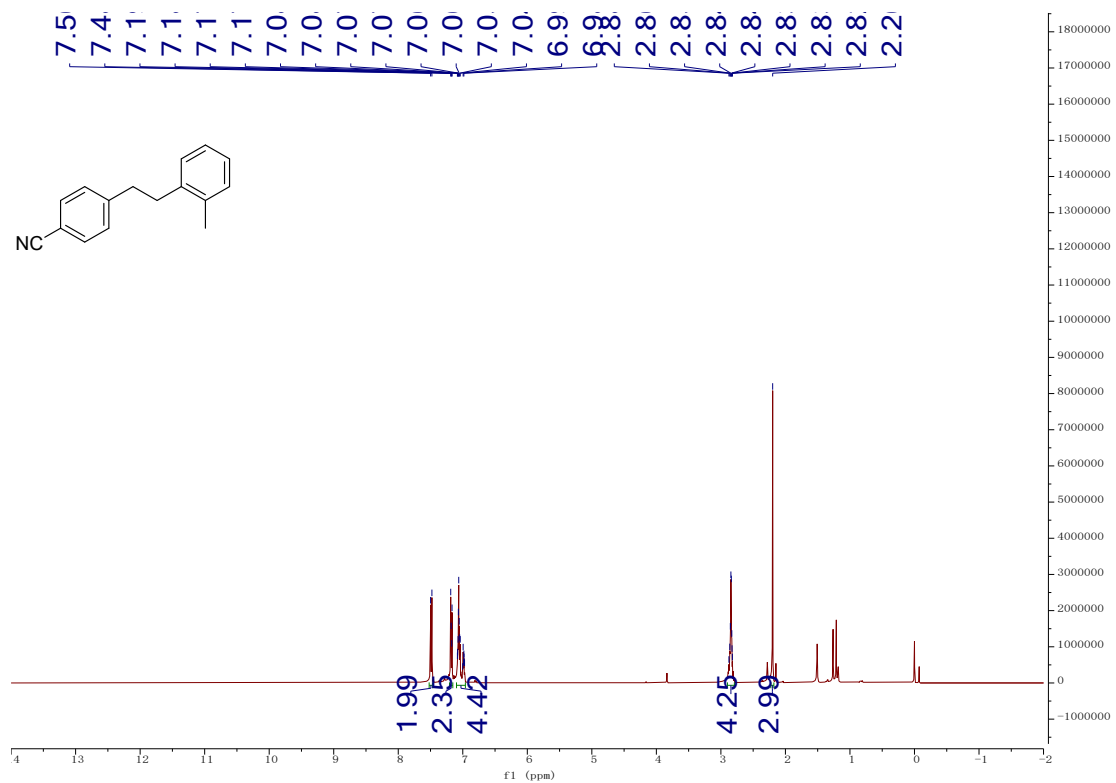


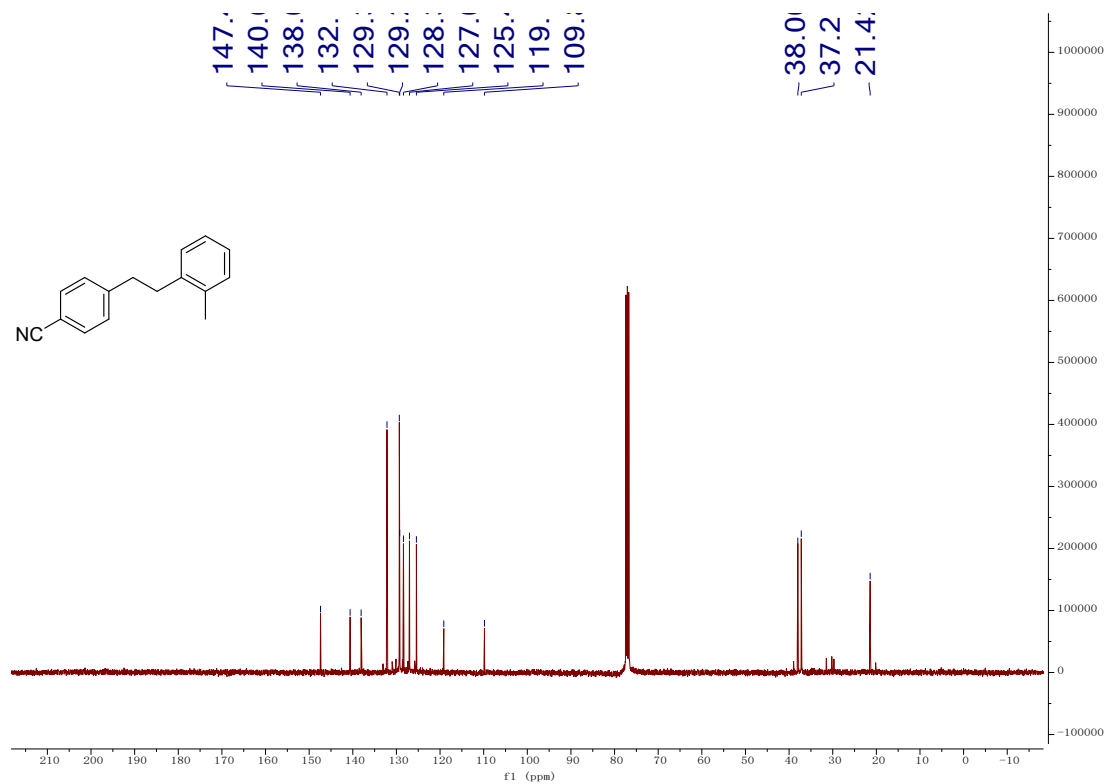
4-phenethylbenzonitrile (3g)



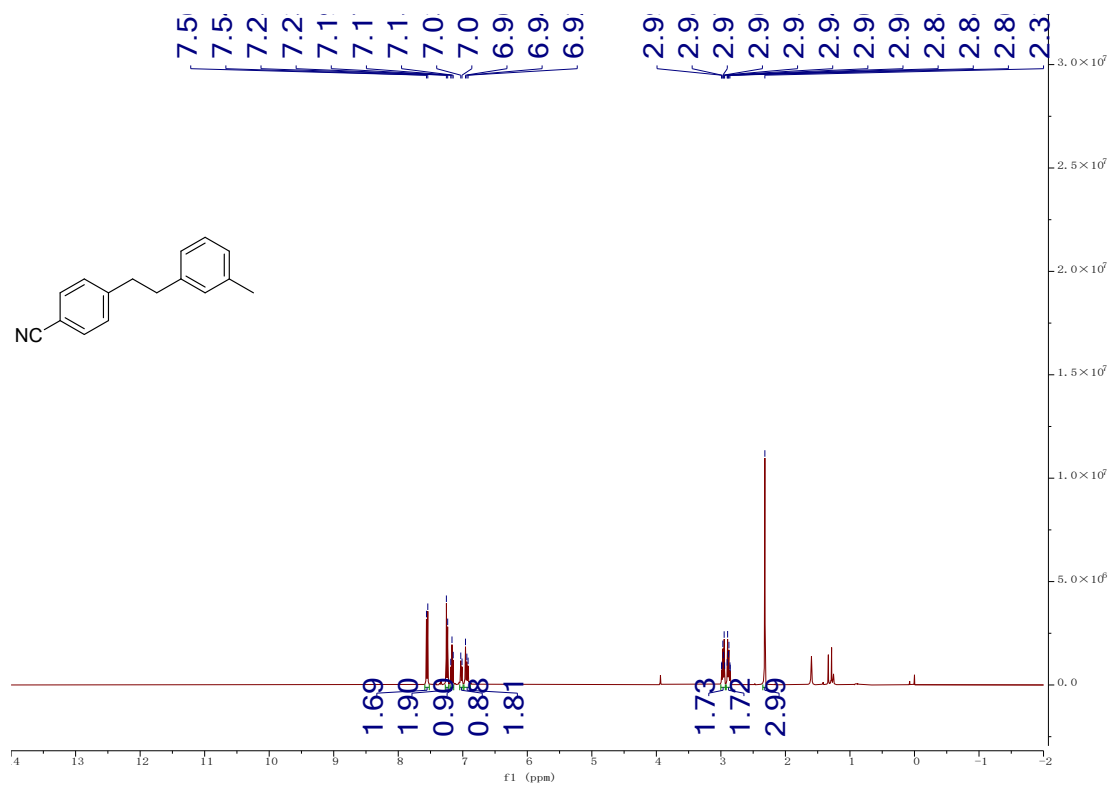


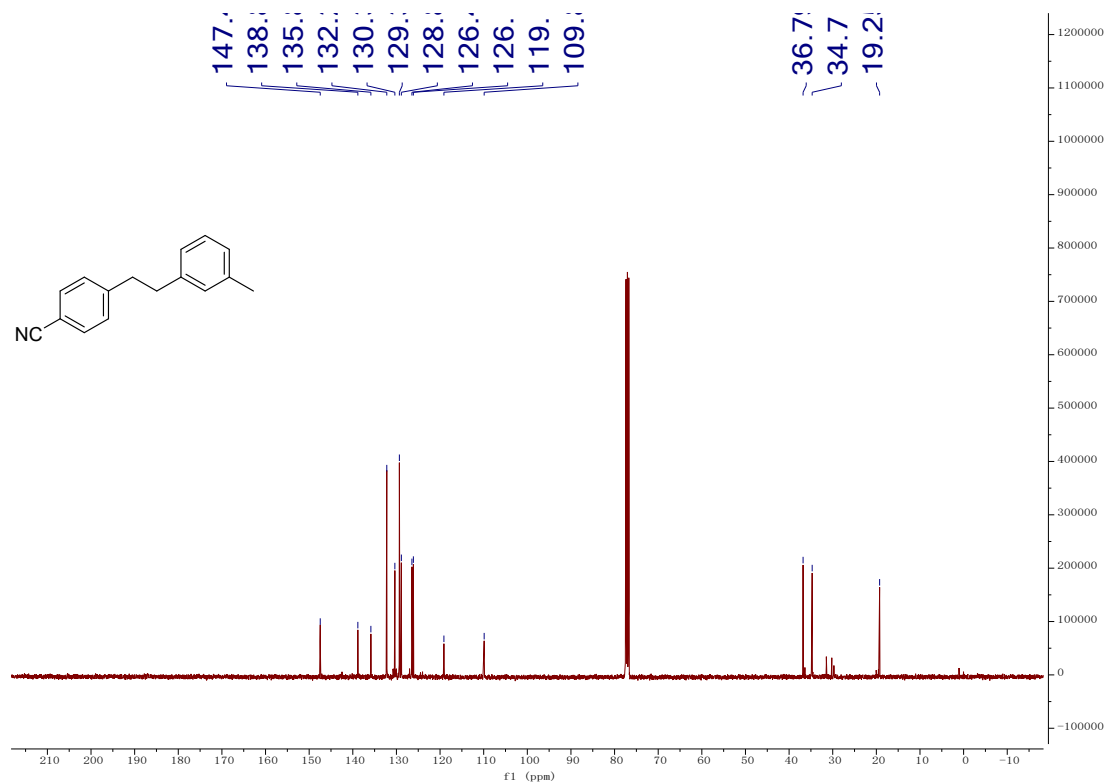
4-(2-methylphenethyl)benzonitrile (3h)



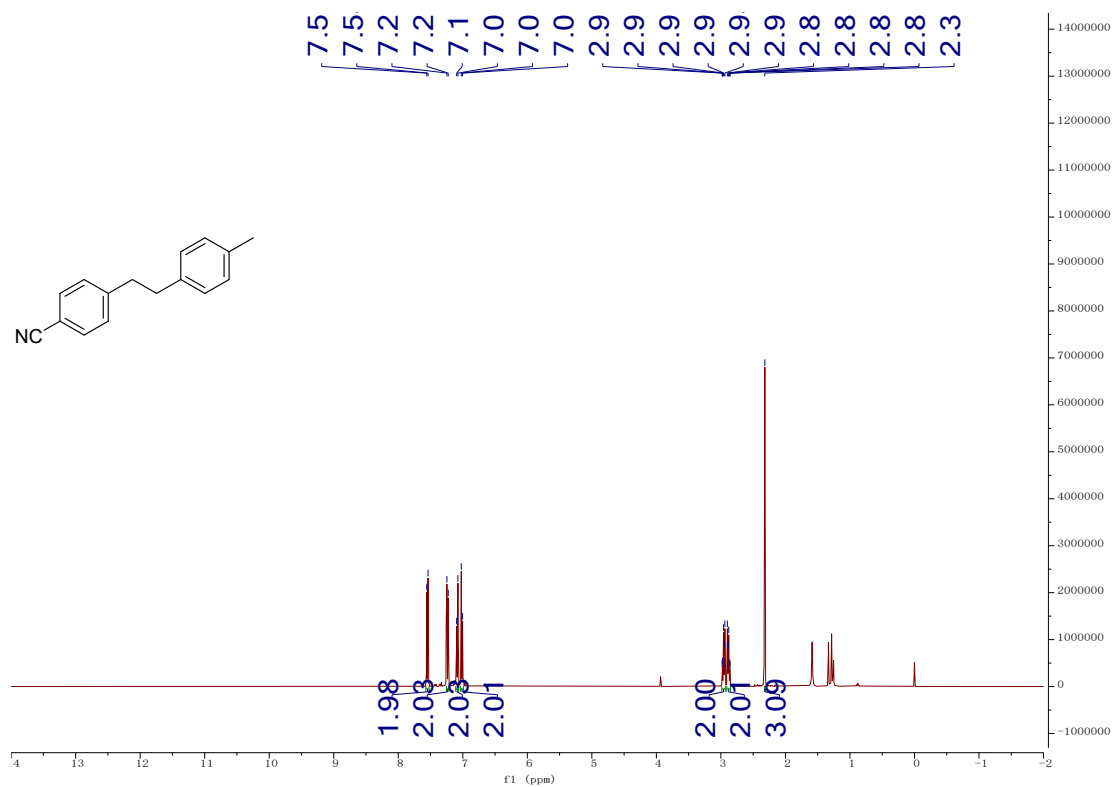


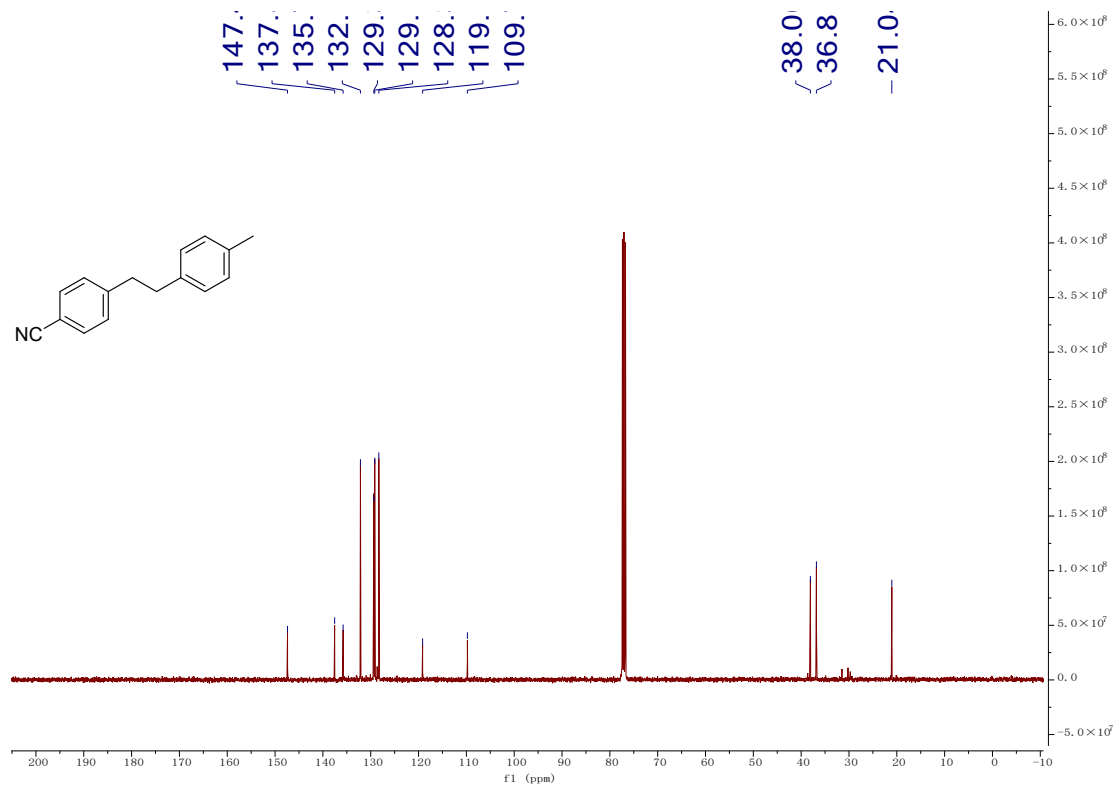
4-(3-methylphenethyl)benzonitrile (3i)



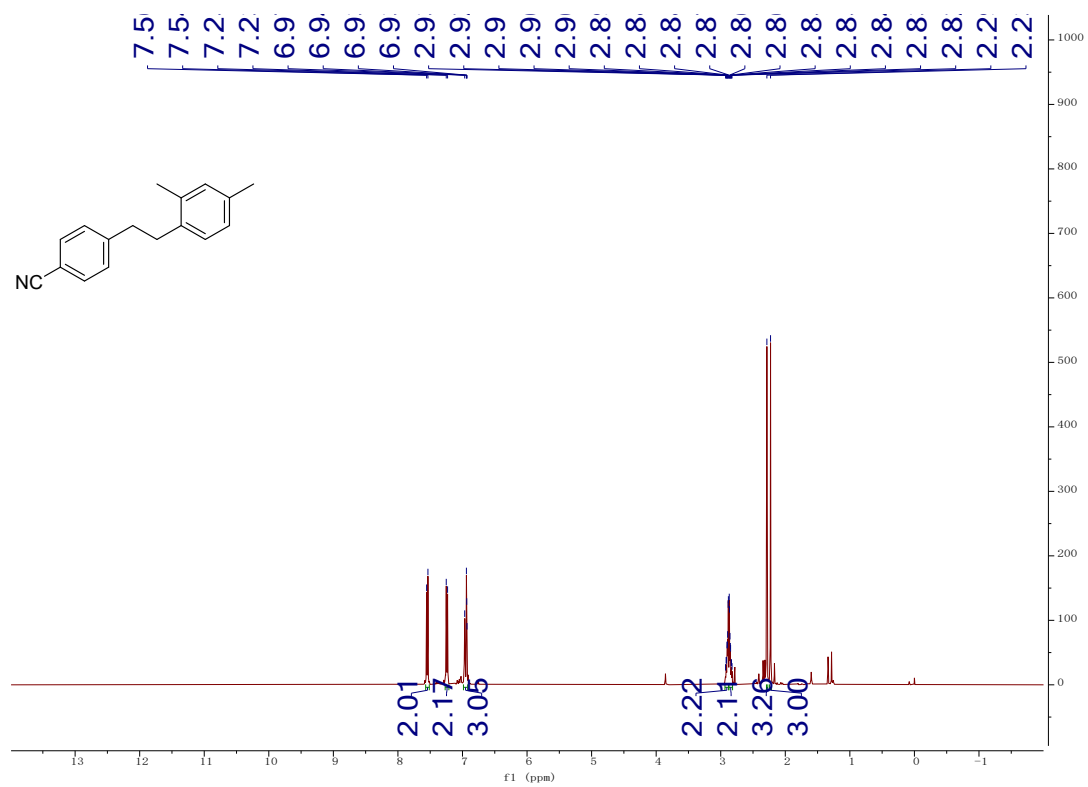


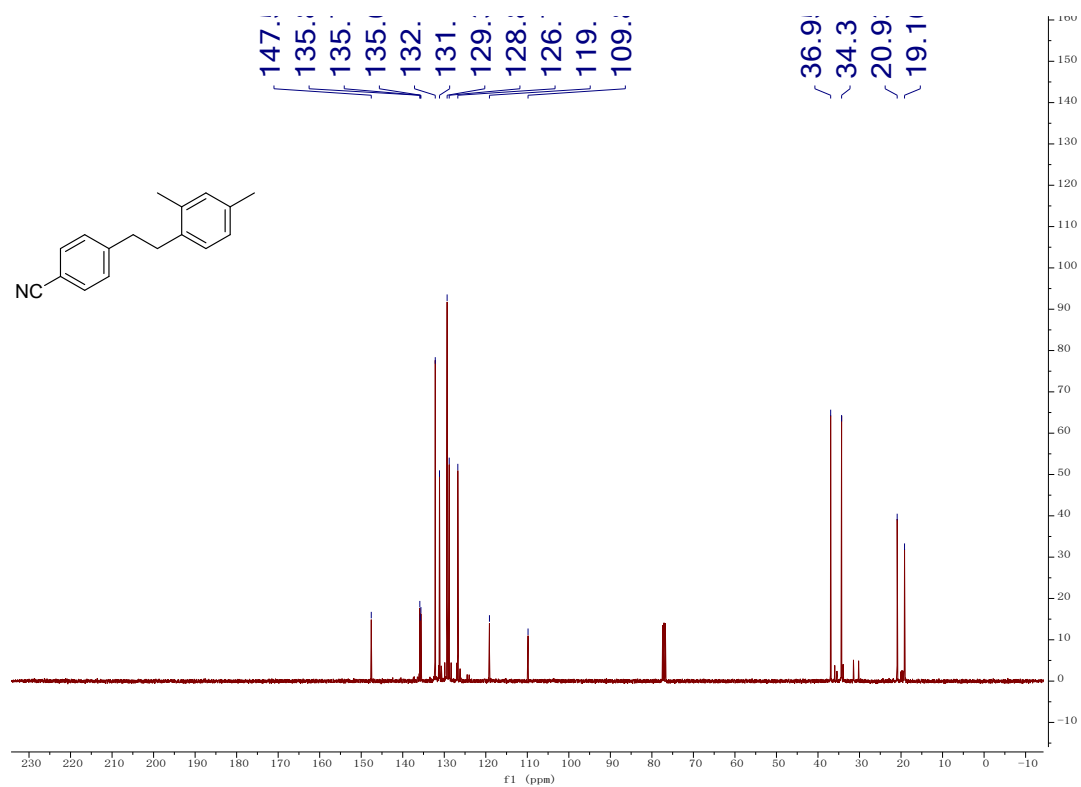
4-(4-methylphenethyl)benzonitrile (3j)



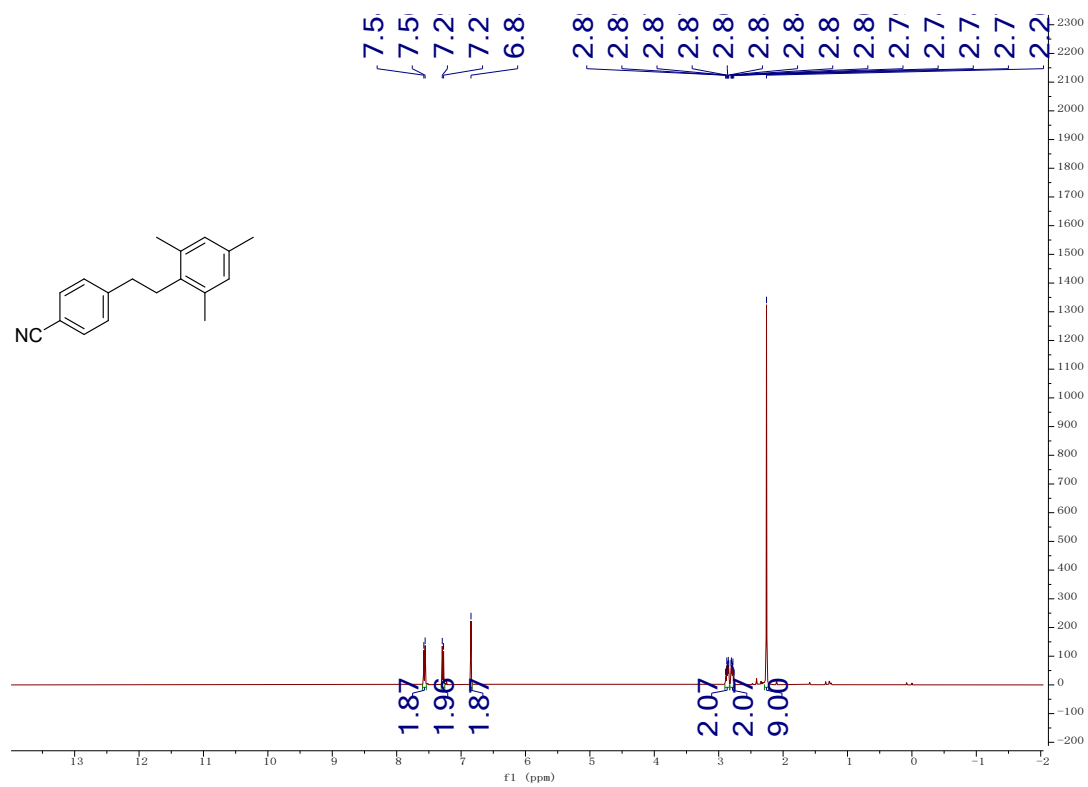


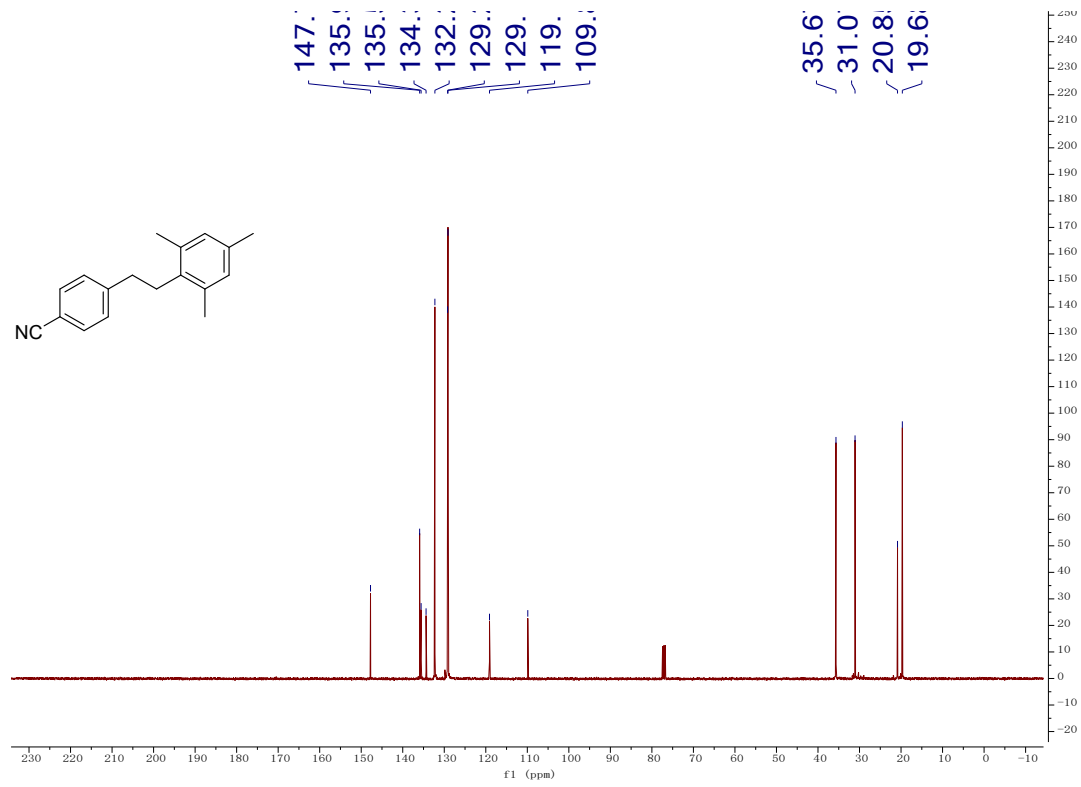
4-(2,4-dimethylphenethyl)benzonitrile (3k)



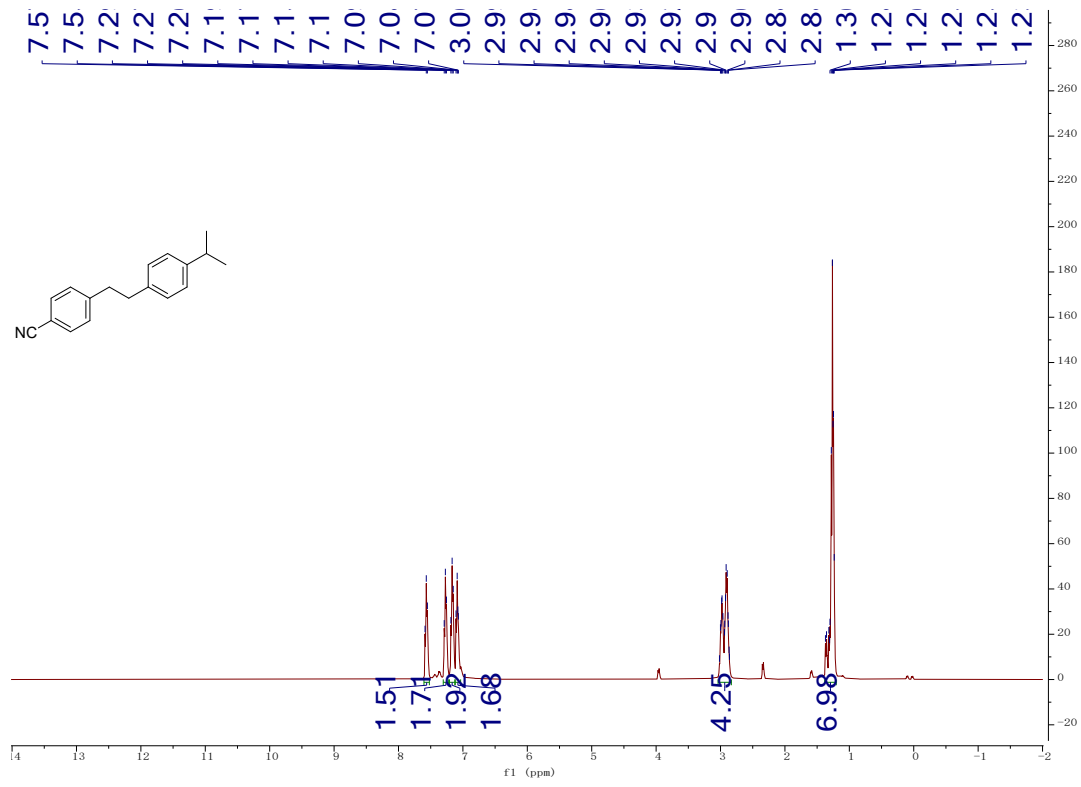


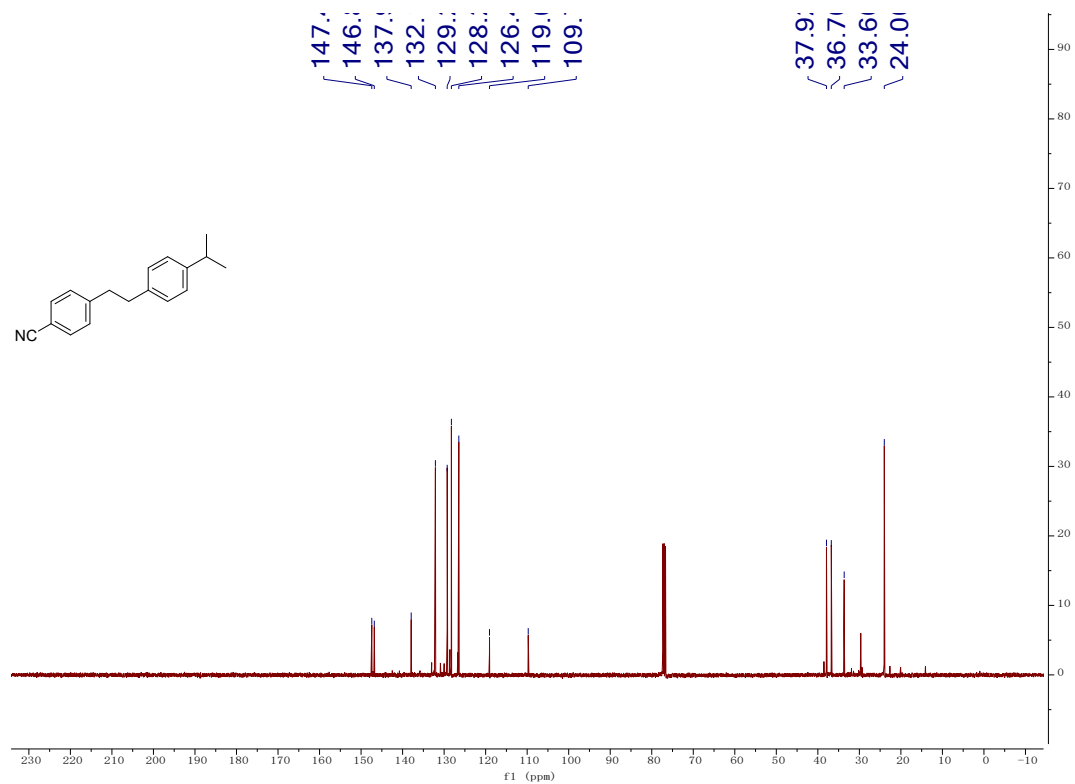
4-(2,4,6-trimethylphenethyl)benzonitrile (31)



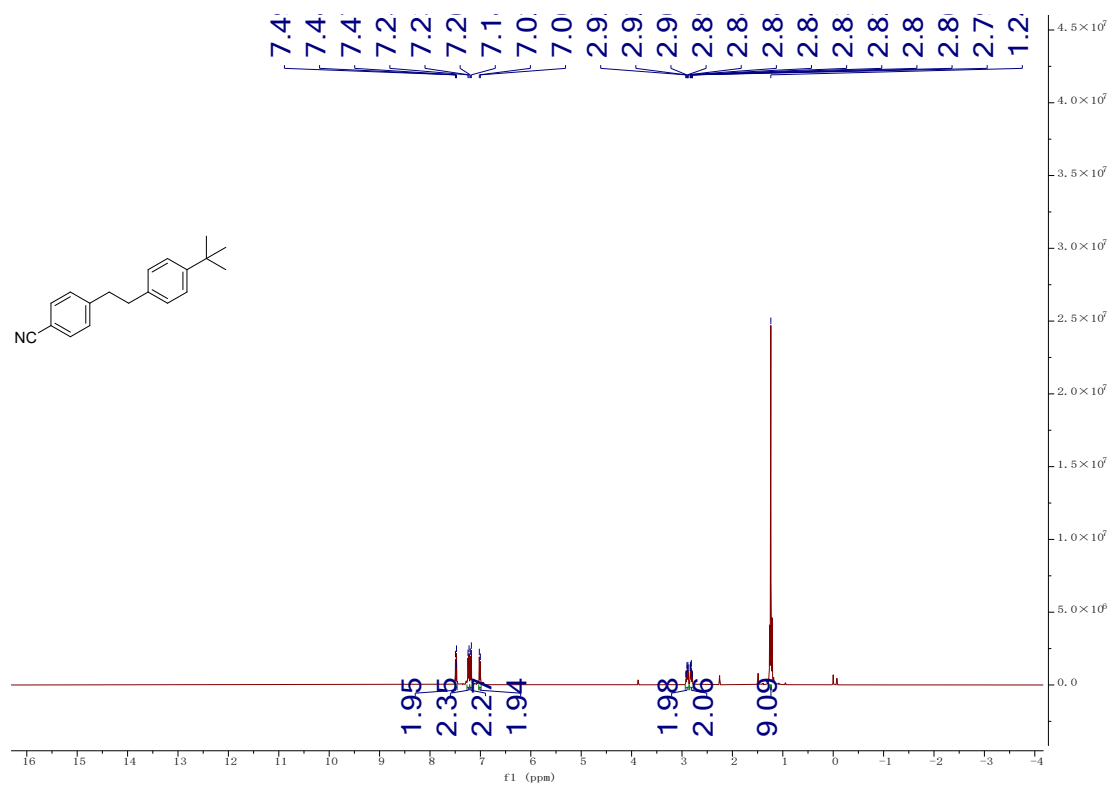


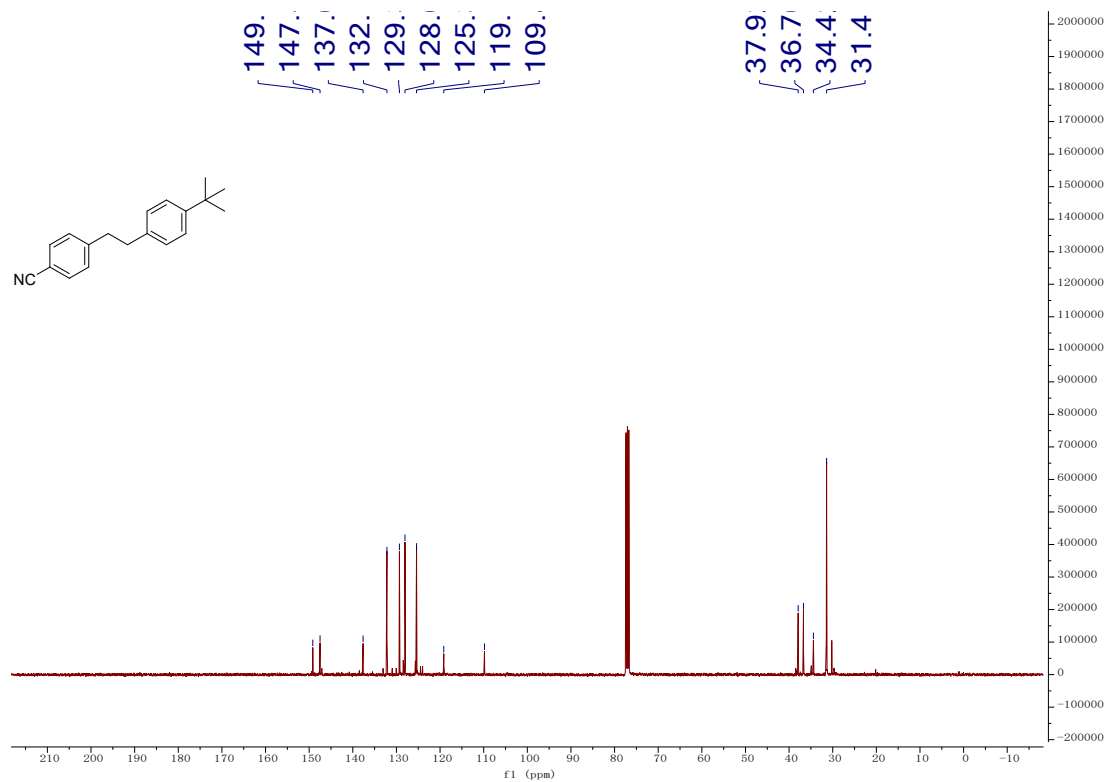
4-(4-isopropylphenethyl)benzonitrile (3m)



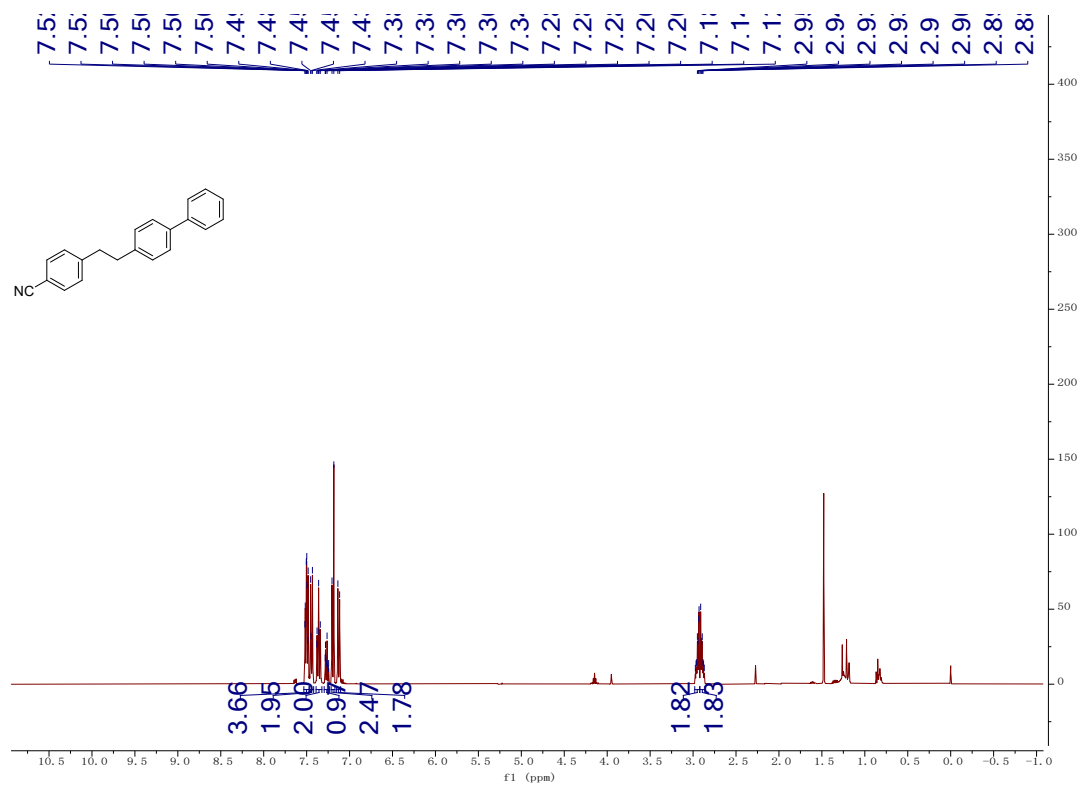


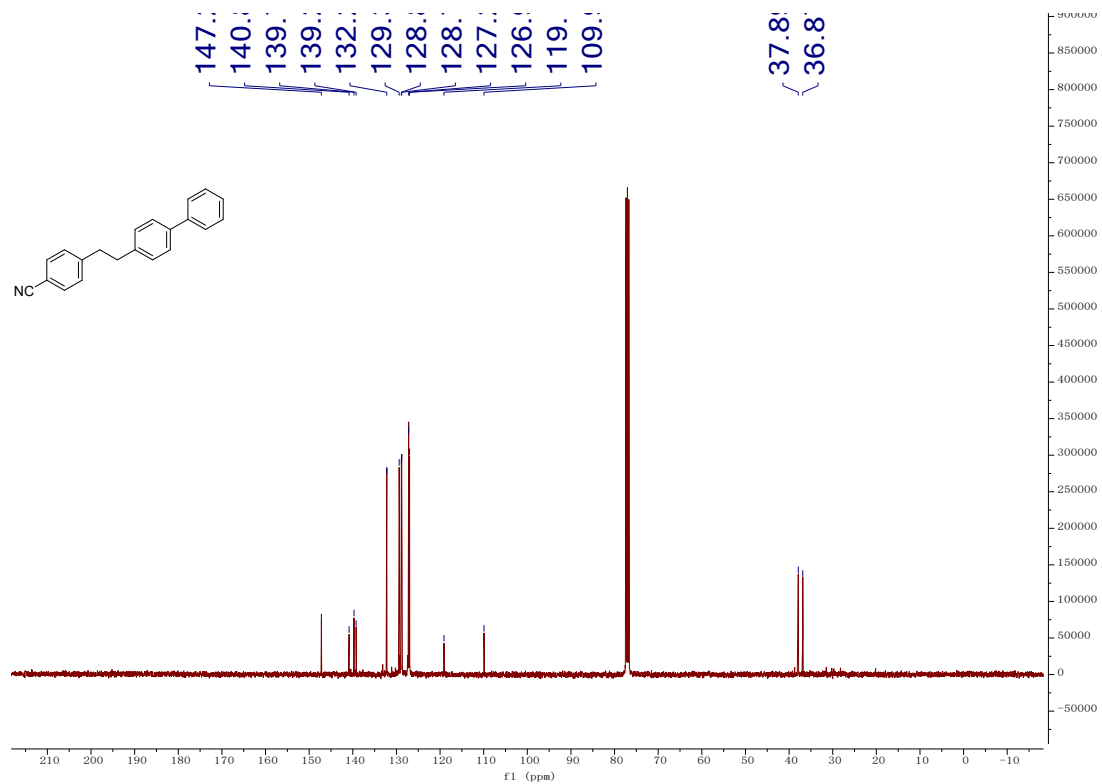
4-(4-(tert-butyl)phenyl)benzonitrile (3n)



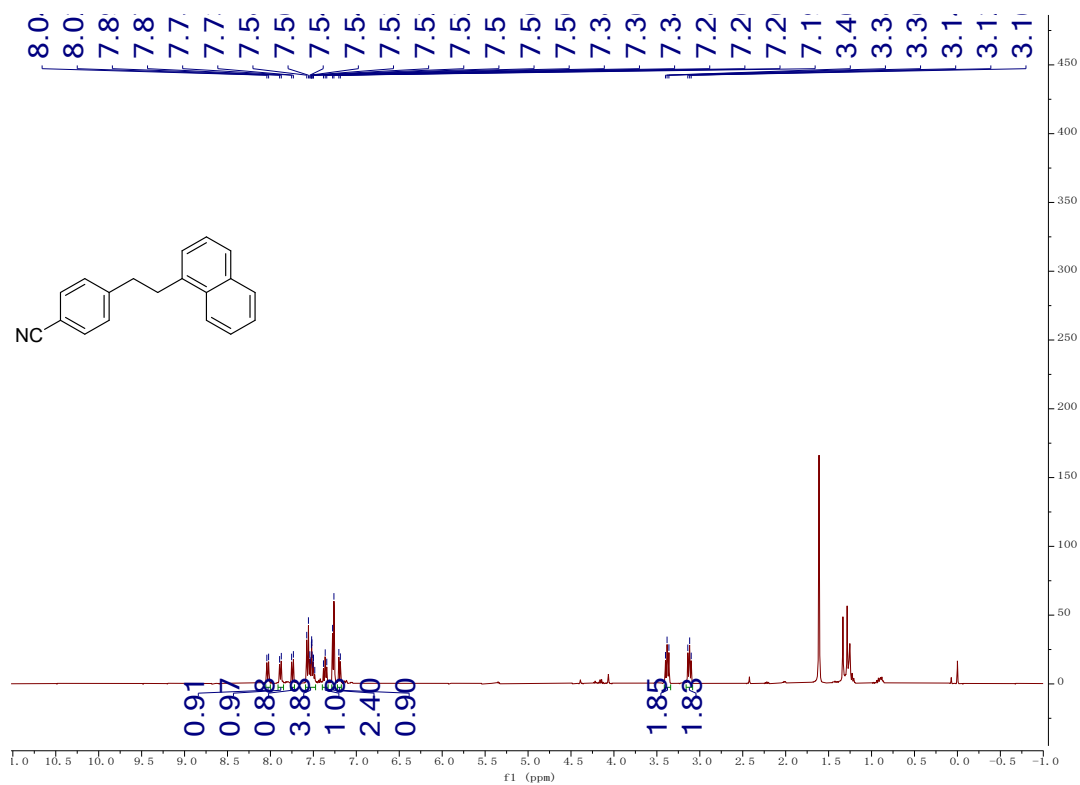


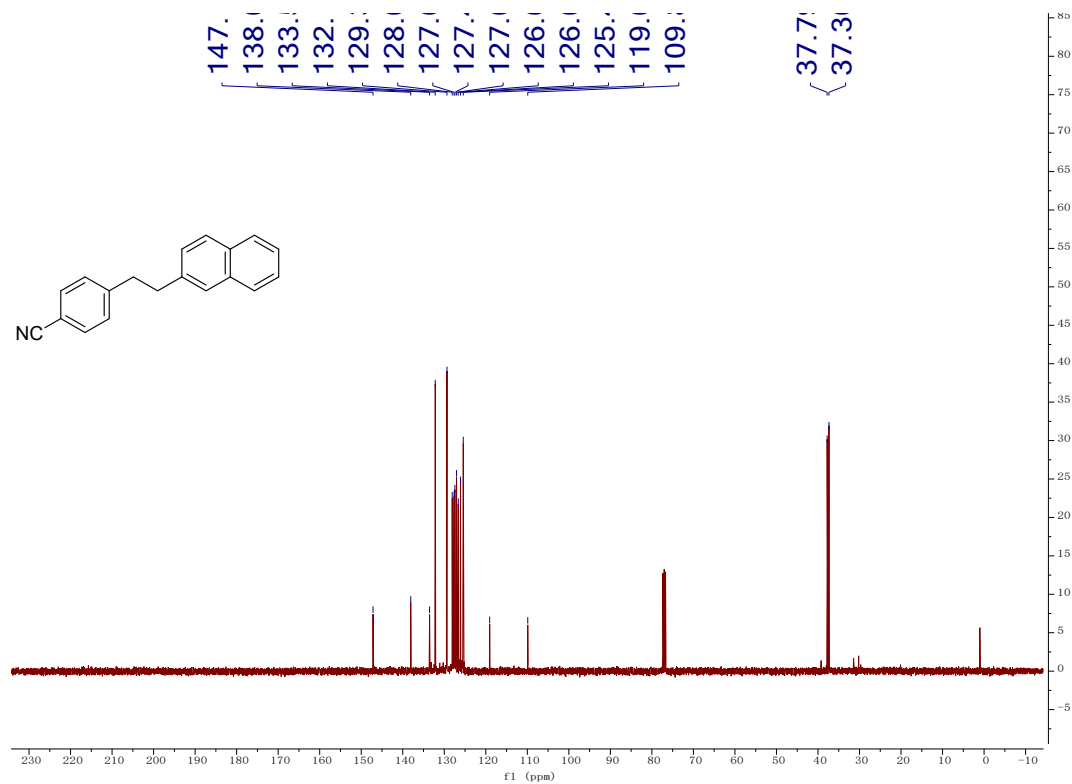
4-(2-([1,1'-biphenyl]-4-yl)ethyl)benzonitrile (3o)



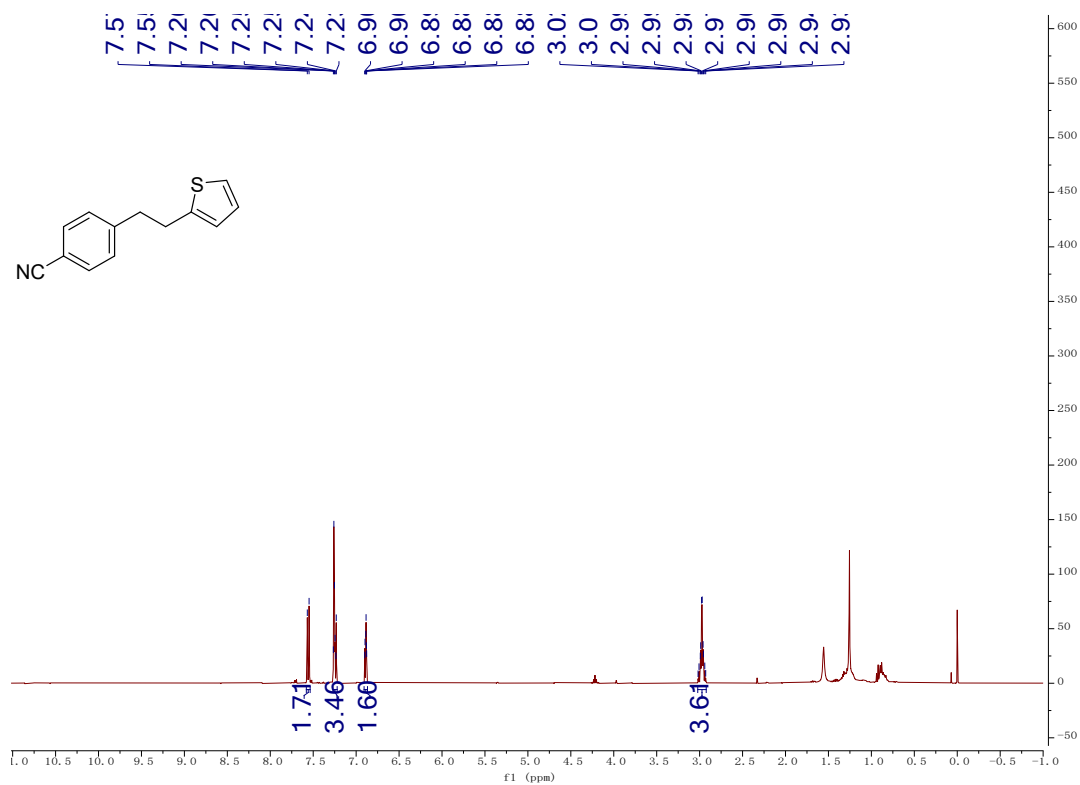


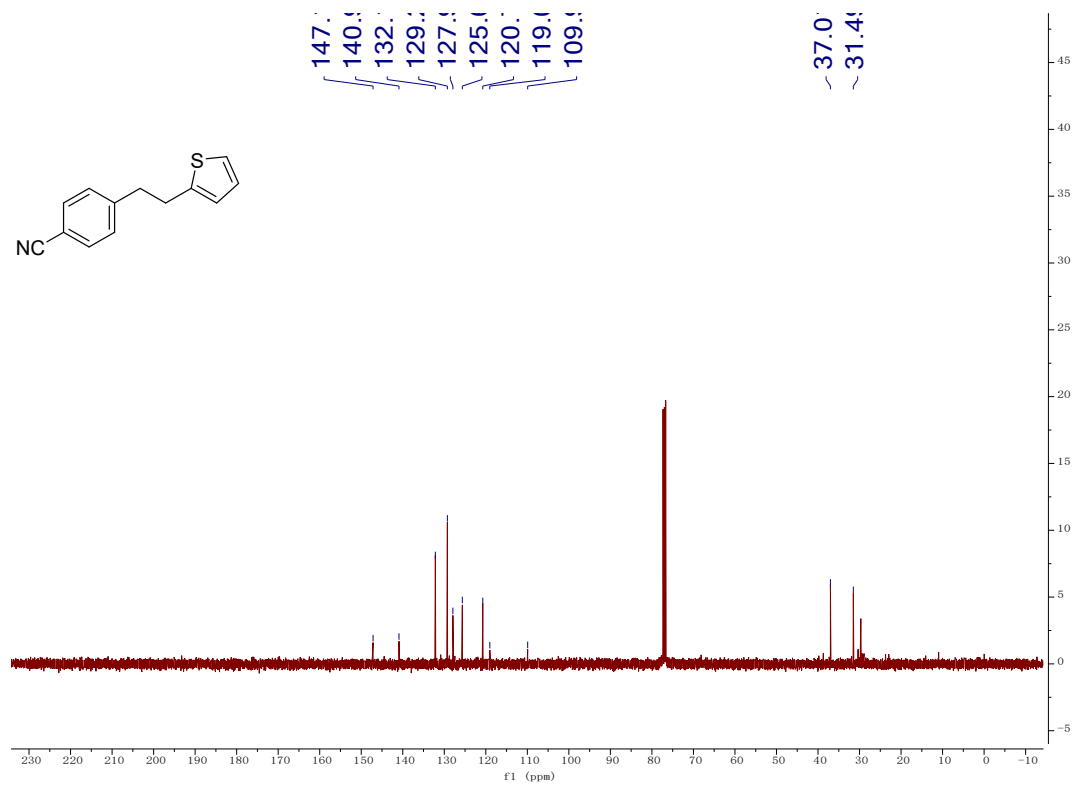
4-(2-(naphthalen-1-yl)ethyl)benzonitrile (3p)



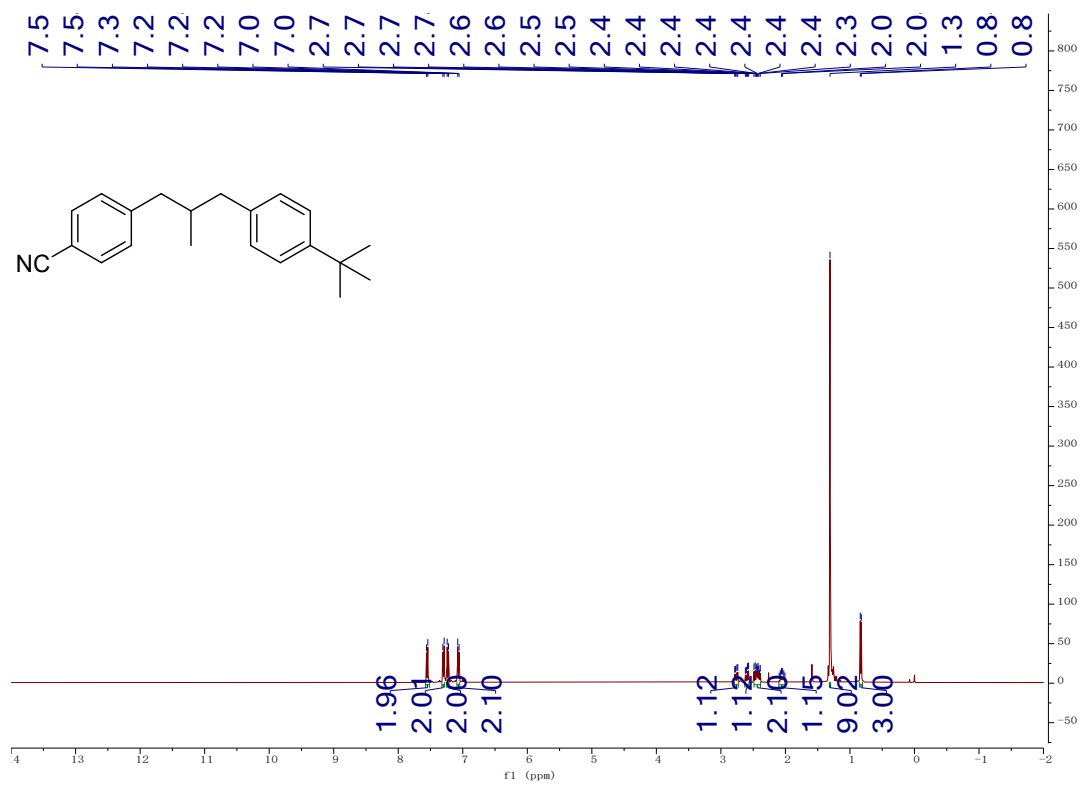


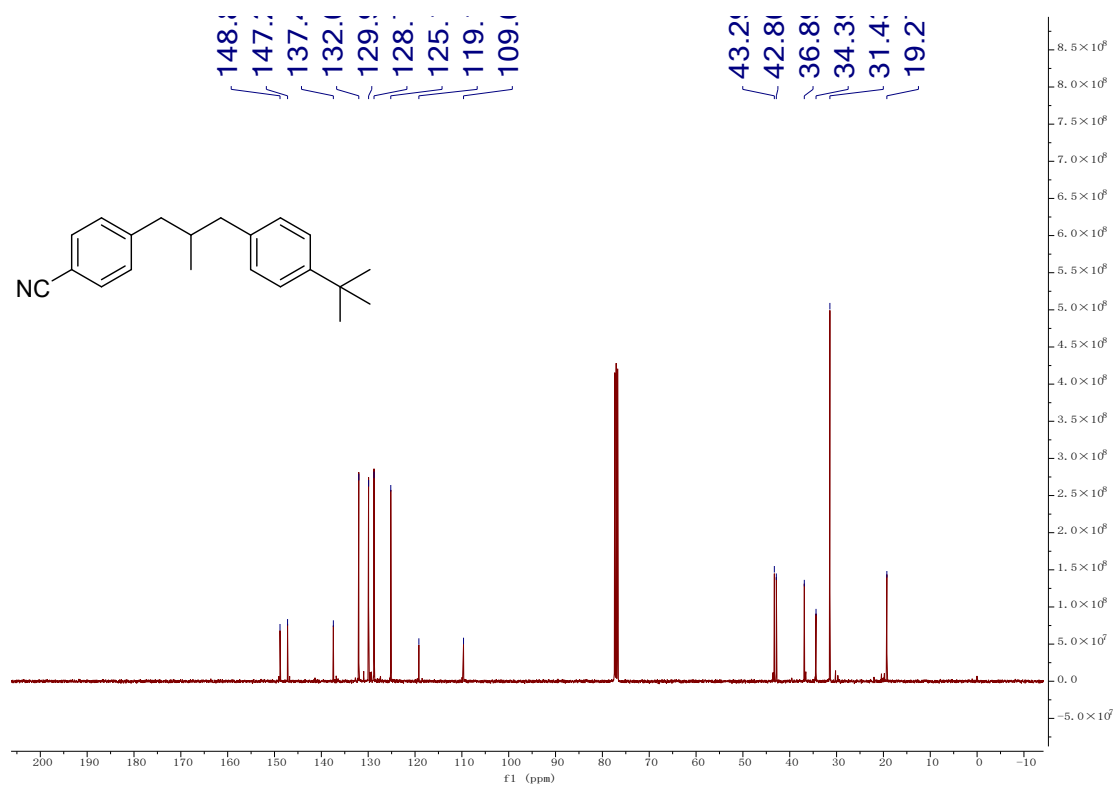
4-(2-(thiophen-2-yl)ethyl)benzonitrile (3r)



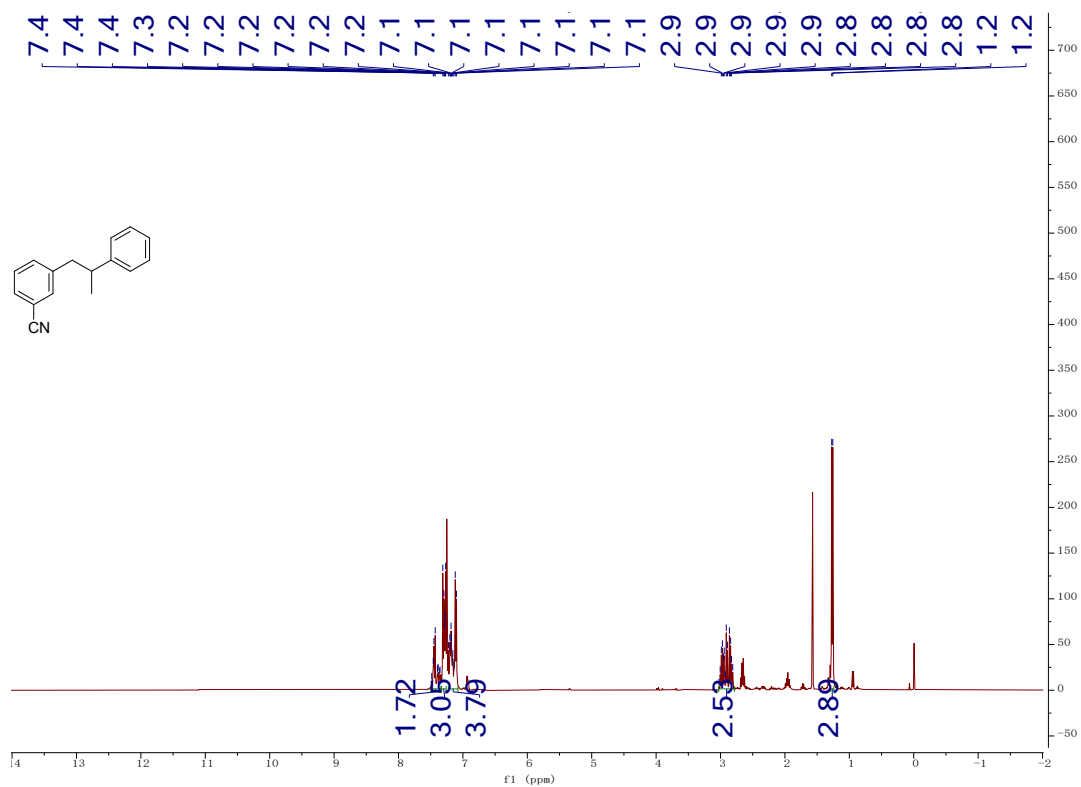


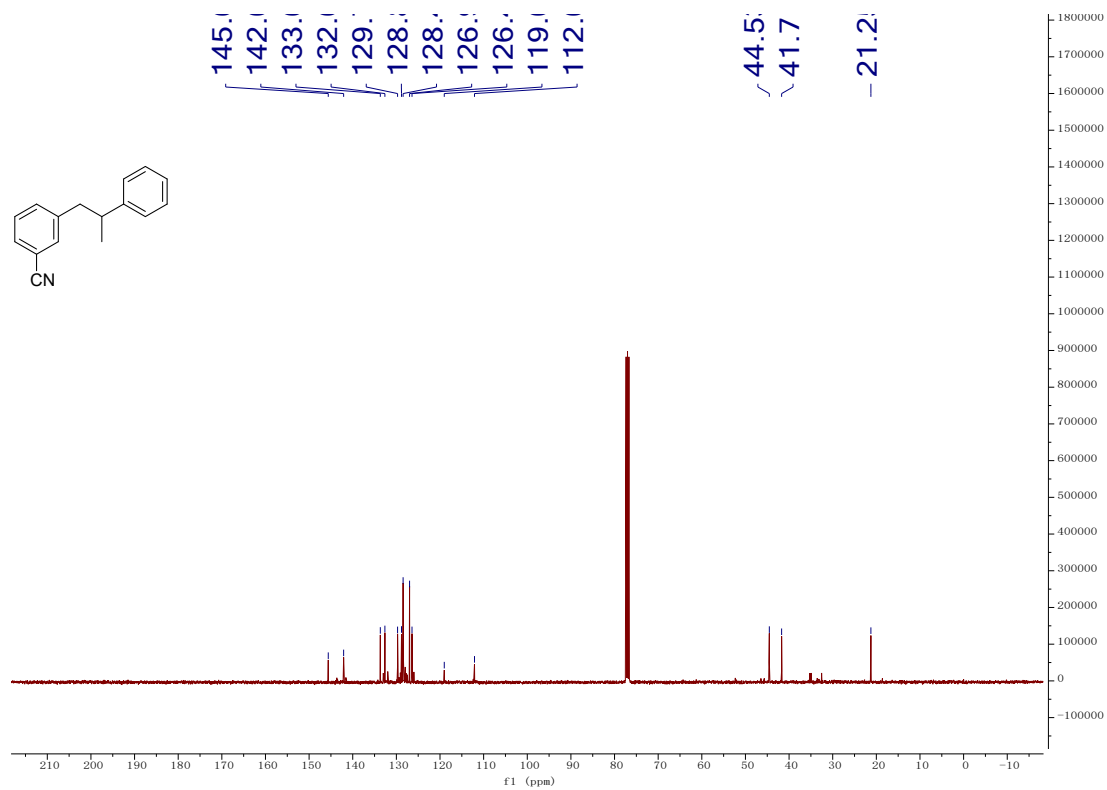
4-(3-(4-(tert-butyl)phenyl)-2-methylpropyl)benzonitrile (3s)



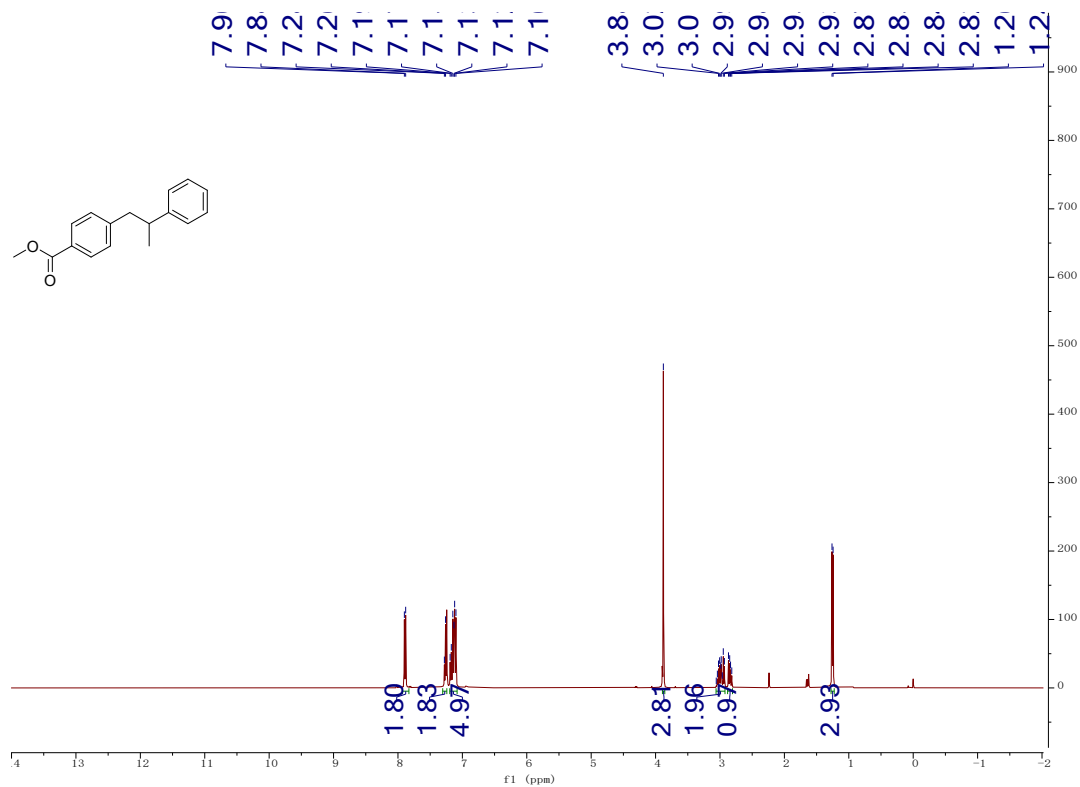


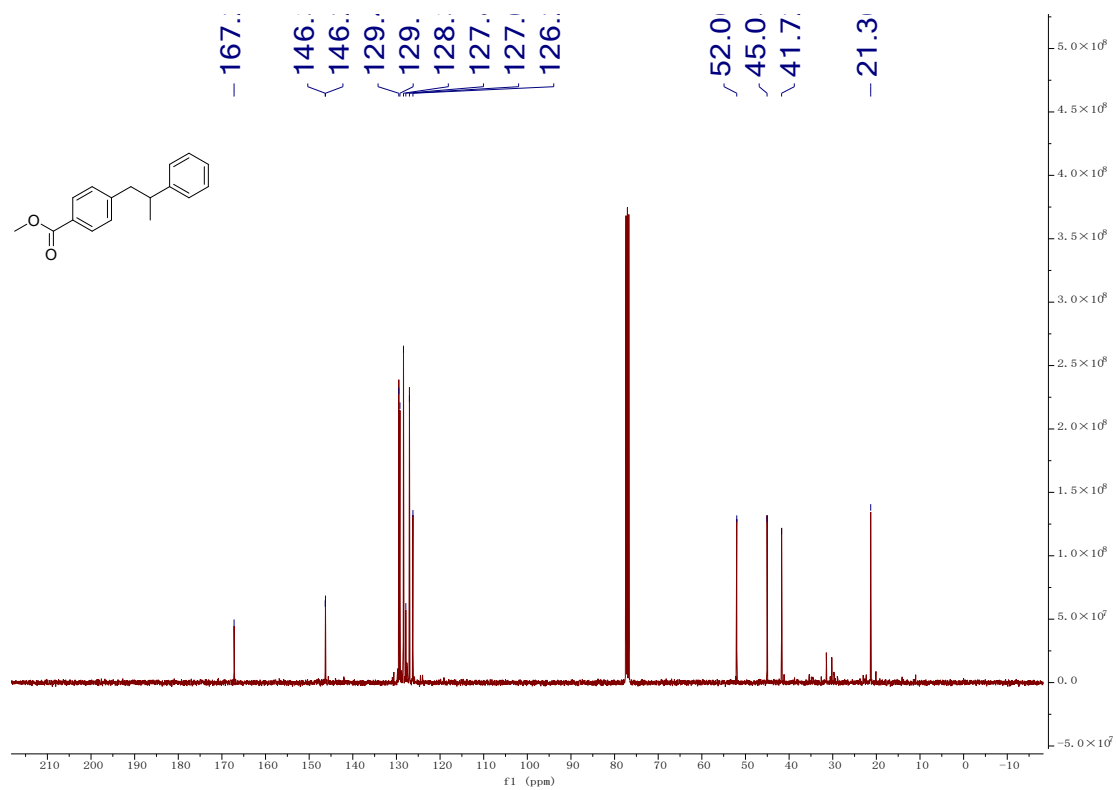
3-(2-phenylpropyl)benzonitrile (3t)



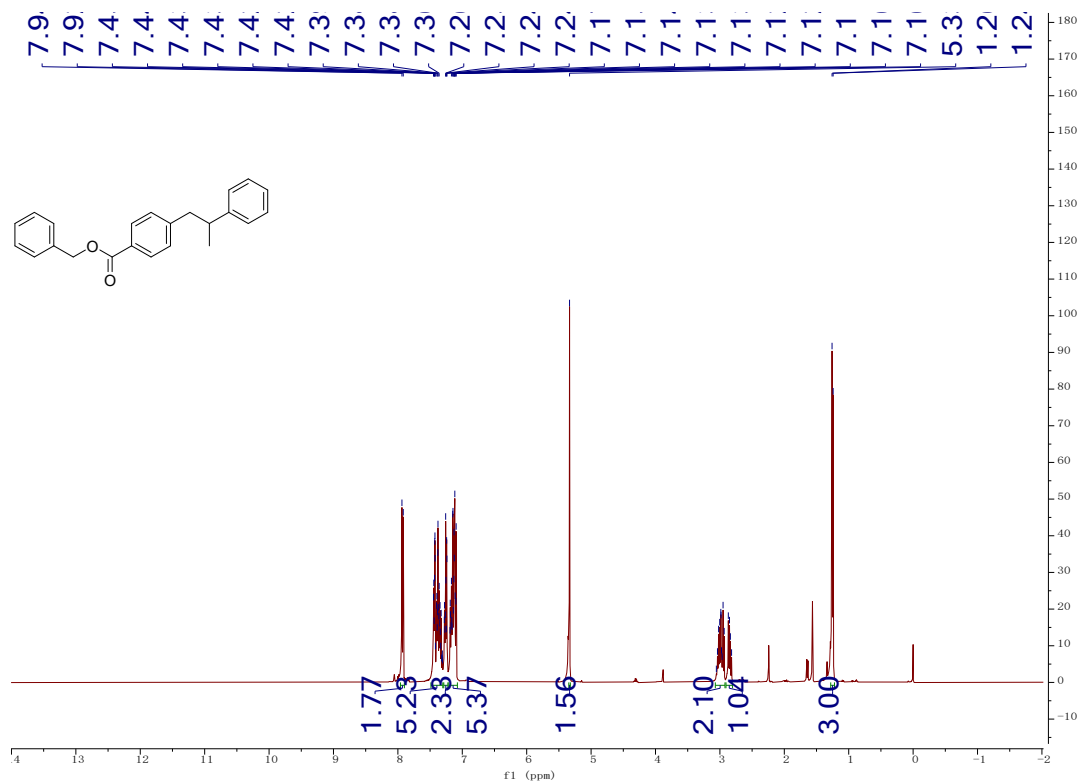


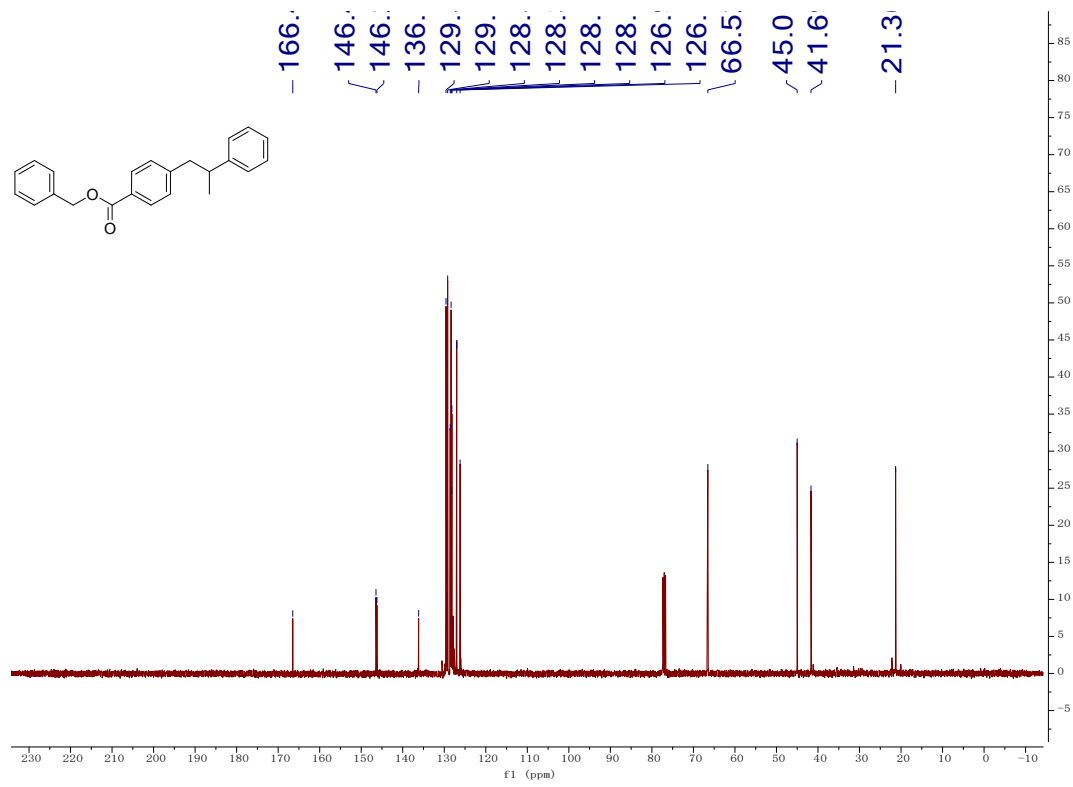
methyl 4-(2-phenylpropyl)benzoate (3u)



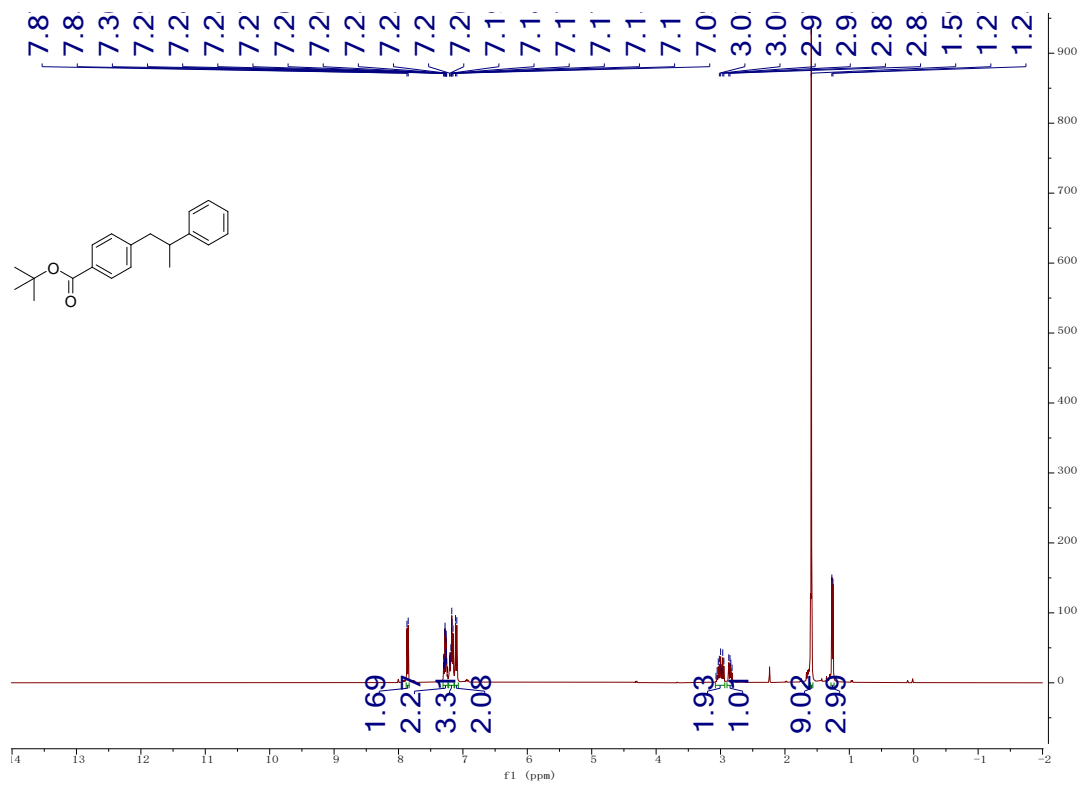


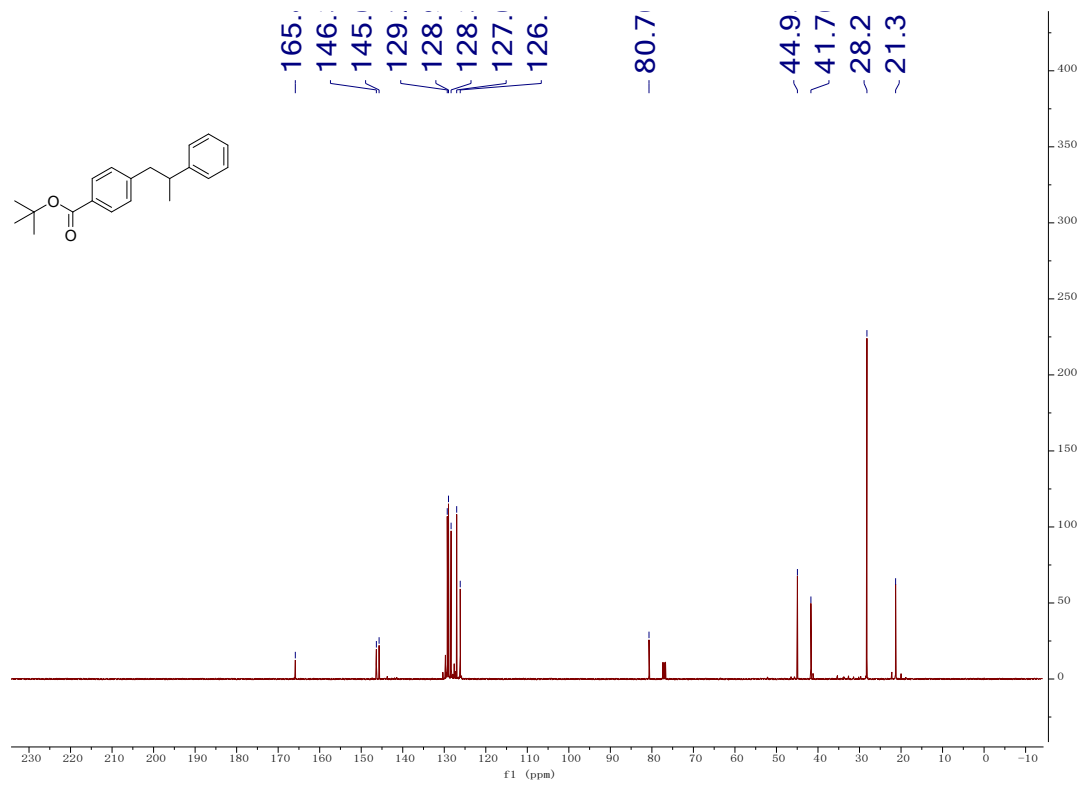
benzyl 4-(2-phenylpropyl)benzoate (3v)



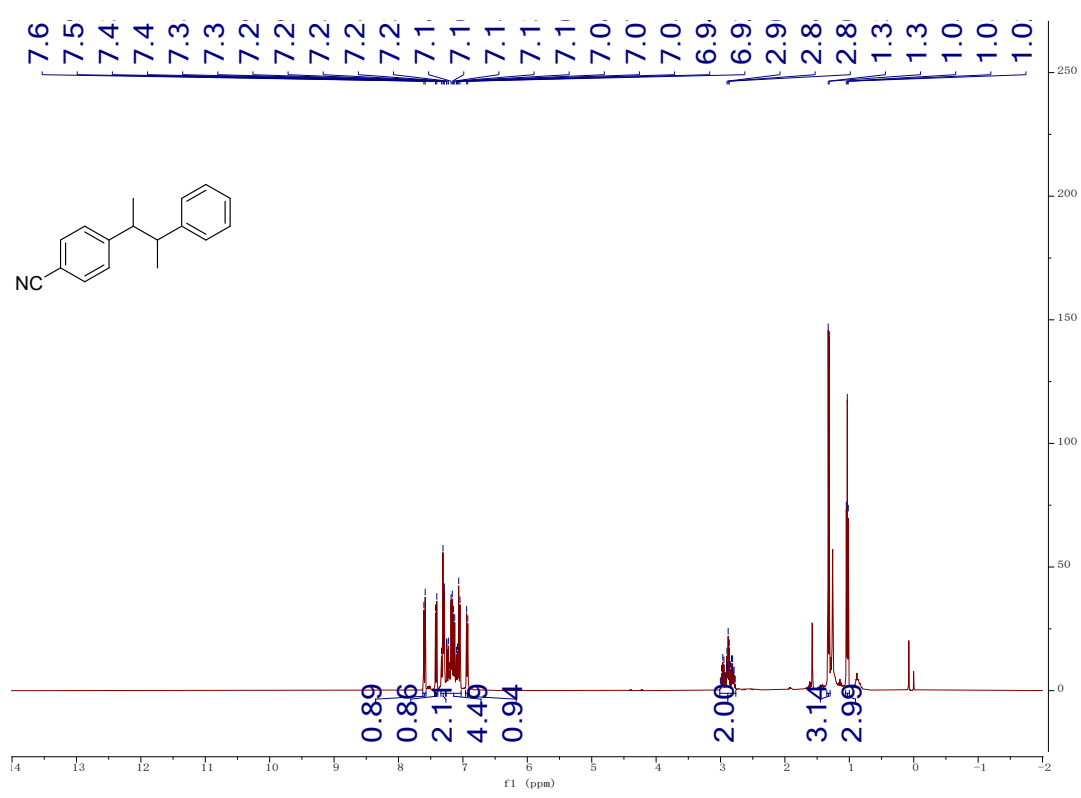


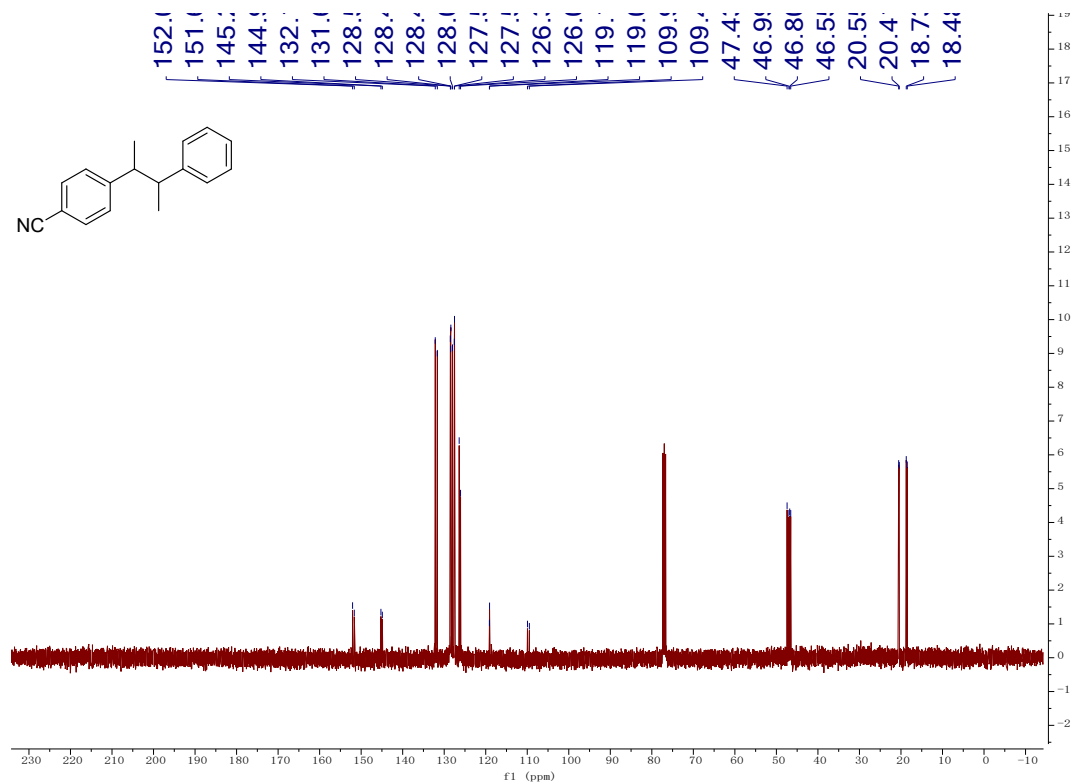
tert-butyl 4-(2-phenylpropyl)benzoate (3w)



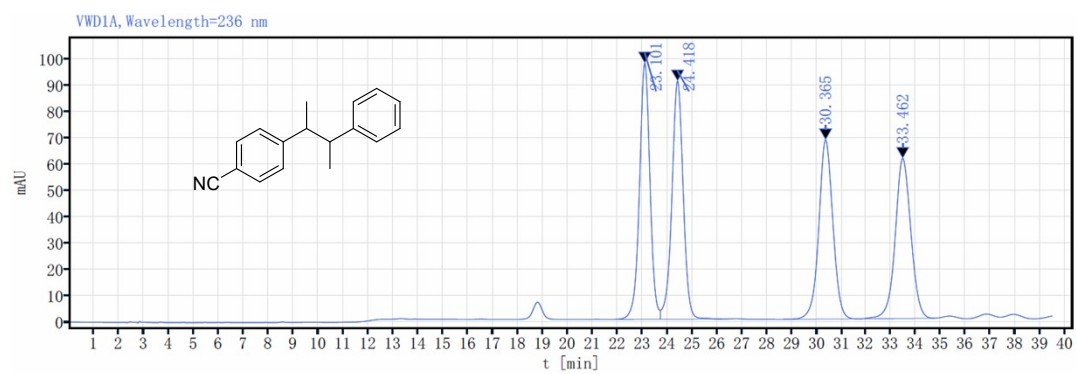


4-(3-phenylbutan-2-yl)benzonitrile (3x)





9. Diastereomeric ratio of 3x



VWD1A, Wavelength=236 nm

RT(min)	Integration Type	Area(mV*min)	Height (mV)	%Height	%Area
1	BV	2870.793	97.897	30.73	25.82
1	VB	2872.684	91.017	28.57	25.84
1	BB	2695.477	68.502	21.50	24.25
1	BB	2677.993	61.191	19.21	24.09

10. HRMS Data for Compound 8

HRMS (ESI-TOF) m/z : $[M+H]^+$ calcd for $C_{17}H_{25}N_2O^+$: 273.1961; Found: 273.1962

