Supplementary Information for:

Direct activation of C(sp^3)−H bonds by carbon dots photoredox catalysts

Dingxi Li[1]†, Xianhao Chi[2]†, Keping Zhai[1], Mingwei Hui[1], Meifang Zhu[1], Di Chen[1], Yuyong Ma[2]*, Le Wang[1]*

Corresponding author: mayuyong@zjnu.edu.cn; le.wang@dhu.edu.cn

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Section S1 Catalyst Synthesis and Characterizations

Materials and reagents

All chemicals were used as received without further purification unless otherwise specified. Glassware was oven-dried for at least 1 hour and cooled in an evacuated antechamber before being transferred into the glovebox. Organic solutions were concentrated under reduced pressure using a rotary evaporator with a water bath maintained below 45 °C.

Methods

Characterization

The photoluminescence emission (PL) spectra were measured using a modular spectrofluorometer equipped with a 75 W xenon lamp as the excitation source (Photon Technology International Inc., QuantMaster 40). NMR spectra were recorded on a Bruker AVANCE III, HD 600 MHz spectrometers. The following abbreviations were used to describe signal multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. Liquid Chromatography-Mass Spectrometry (LC-MS) data were obtained using a Waters Xevo TQ-S Cronos system. XPS analysis was performed using X-ray Photoelectron Spectroscopy (XPS) with an Escalab 250Xi system (ThermoFisher Scientific, USA) equipped with a monochromatic Mg Kα X-ray excitation source (1200 eV). Cyclic voltammetry (CV) curves were obtained using a CHI 760e electrochemical workstation (Shanghai Chenhua Apparatus Inc., China).

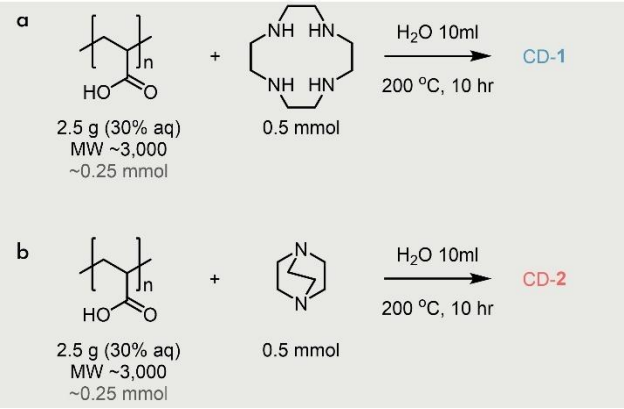


Figure S1. Synthesis of photoredox catalysts CD-**1** and CD-**2**.

Synthesis of CD-1

CD-**1** was synthesized via a hydrothermal method. 0.5 mmol of 1,4,7,10-tetraazacyclododecane was completely dissolved in 10 mL of deionized water. Subsequently, 2.5 g of poly(acrylic acid) (average molecular weight 3000, 30 wt% aqueous solution) was added to the mixture, followed by ultrasonication for 20 minutes to achieve homogeneity. The resulting solution was transferred into a 25 mL Teflon-lined stainless-steel autoclave and subjected to hydrothermal treatment at 200 °C for 10 hours. Upon cooling, the yellow solid product was collected by filtration and lyophilized for 72 hours.

Synthesis of CD-2

The CD-**2** was synthesized by the same procedure as CD-**1**. But instead of 1,4,7,10-Tetraazacyclododecane, 1.0 mol of 1,4-Diazabicyclo[2.2.2]octane was mixed with the same amount of poly(acrylic acid) in 10 ml of water, followed by a 10-hours hydrothermal treatment at 200 ℃. The yellow solid was collected by filtration and dried.

The as-synthesized CDs photocatalysts were bench stable and retained their photoluminescence (PL) properties after 1 month in air at room temperature. However, as a precaution to eliminate potential moisture interference, the CDs were stored in a glovebox prior to use.

Synthesis of CD-3

The CD-**3** was synthesized using the same method with the same amount of carbon source and solvents, however, without any nitrogen source. Reaction mixture was transferred into a 25 mL Teflon-lined stainless-steel autoclave followed by hydrothermal treatment at 200 ℃ for 10 h. After cooled down naturally, the CDs were obtained by the dialysis using a dialysis bag (1000, molecular weight cutoff) and freeze-drying. CD-**3** presented **no** strong PL signals under irradiation hence **only** used for control experiments.

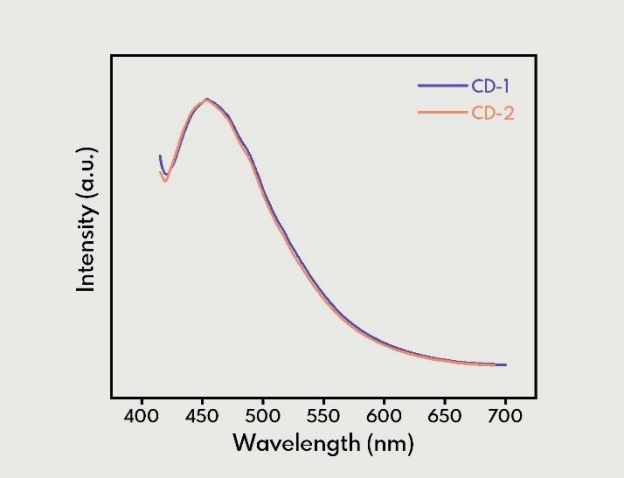


Figure S2. PL spectra of photoredox catalysts with 400nm excitation dispersed in MeCN. 50mg CDs photocatalyst were dispersed in 2.0mL MeCN and the suspension was vigorously stirred for 1 hour before test. The suspension was then transferred to a quartz cuvette. The cuvette was agitated gently to prevent possible precipitation prior to characterization.

Figure S3. Photograph of the WATTCAS Parallel-Light Reactor (WP-TEc-1020HSL) photoreactor. Reaction was conducted with room-temperature cooling and magnetic stirring in a sealed tube under N_2 atmosphere.

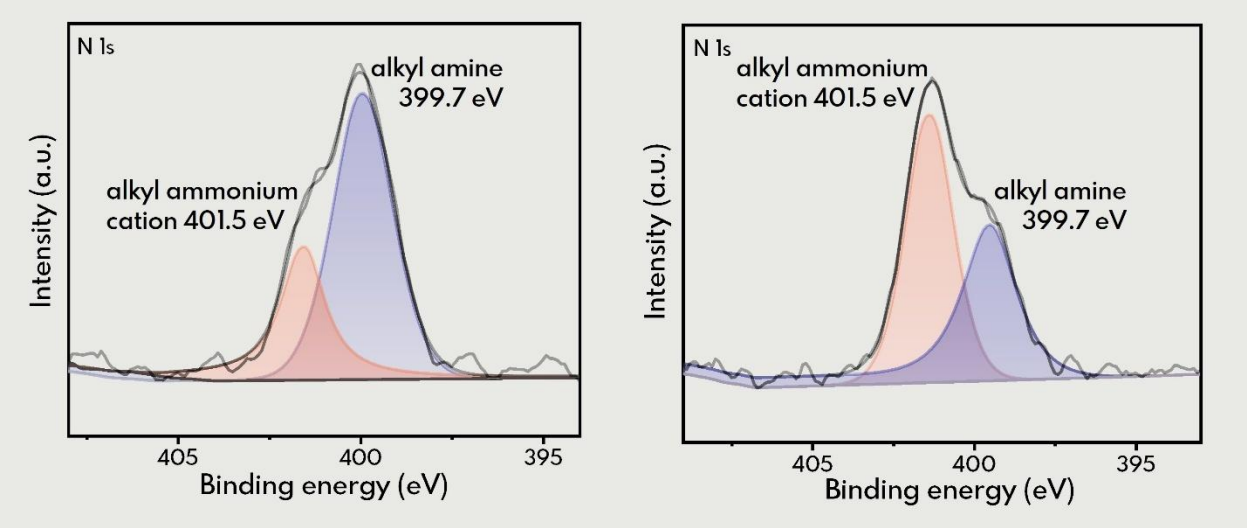


Figure S4. XPS spectra of N 1s in photoredox catalysts CD-**1** (left) and CD-**2** (right).

Figure S5. The vessel was under positive pressure, causing spontaneous volume expansion when purged with a needle attached to a 2.0-mL syringe.

The reaction vessel was loaded under N_2 protection and carefully balanced to atmospheric pressure prior to irradiation. This headspace gas expansion phenomenon was exclusively observed in dehydrogenative annulation reactions, whereas no such effect occurred during Giese radical addition reactions.

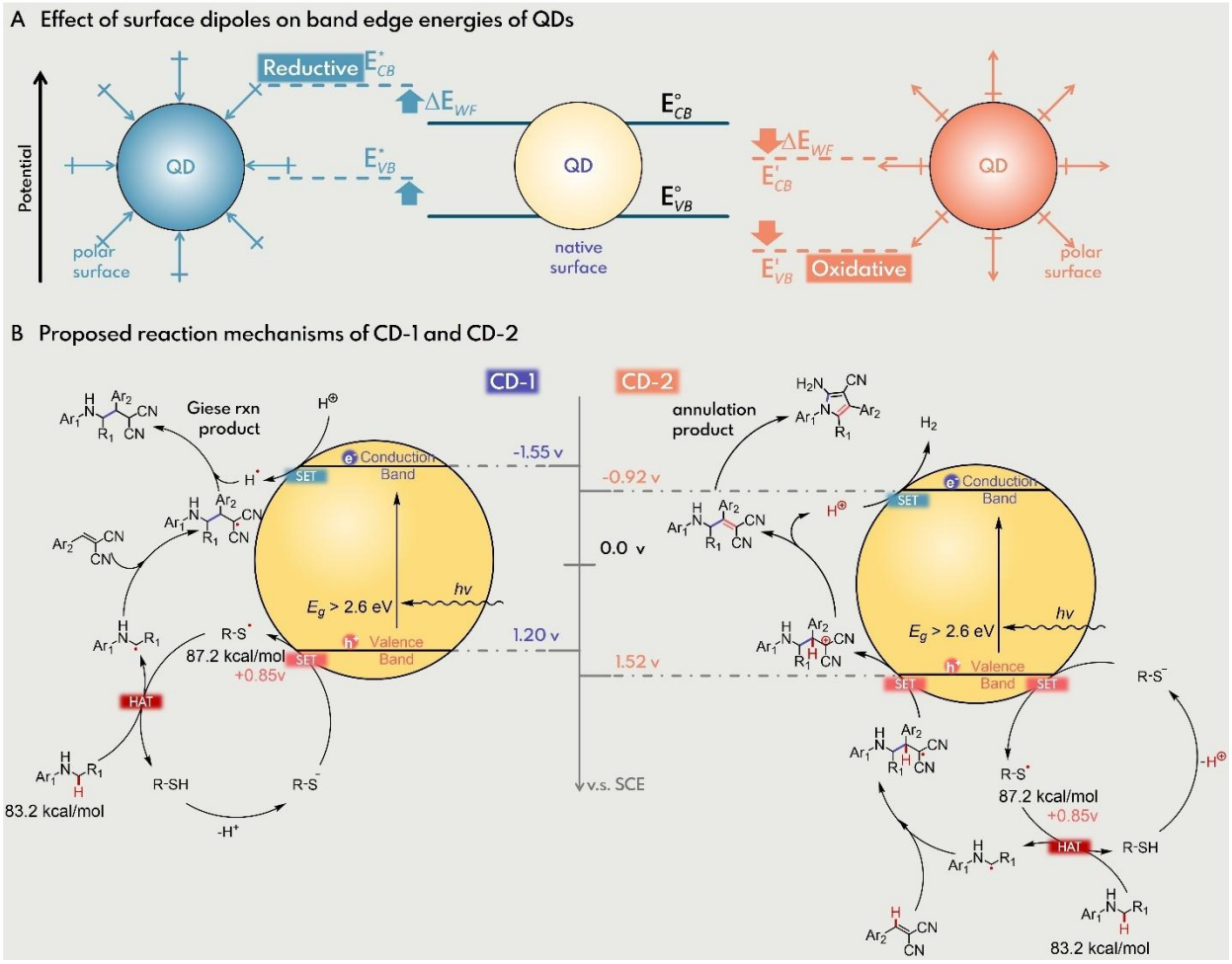


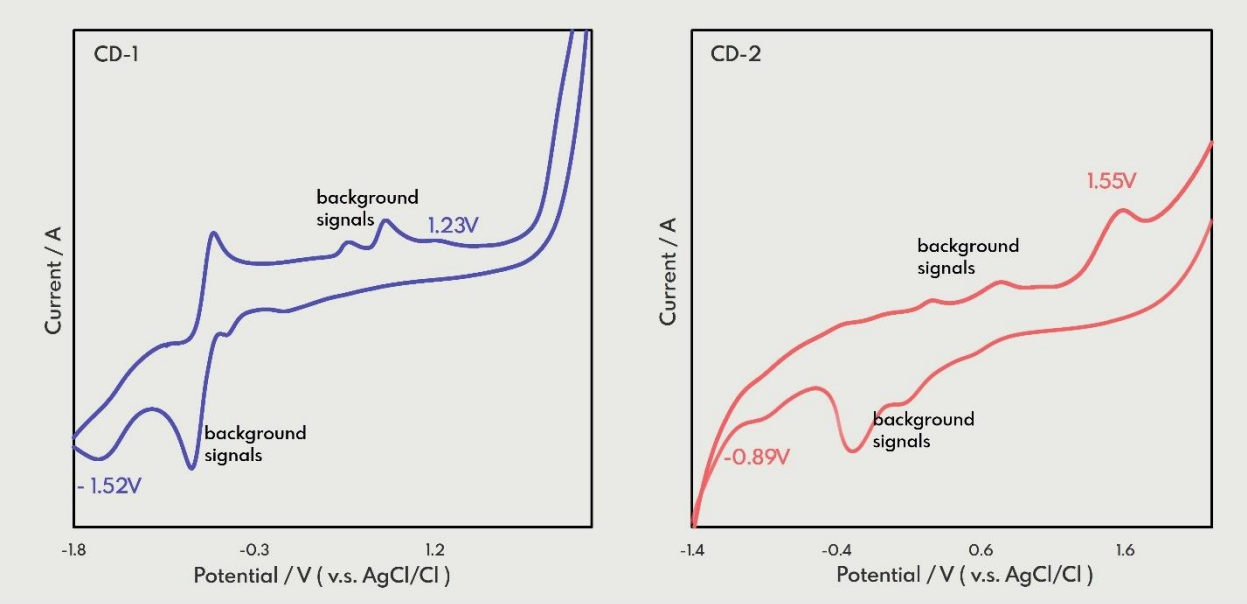
Figure S6. Proposed mechanism of CD-**1**, **2** photocatalysis.

A. Scheme of band shifting in QDs due to surface functionalization by polar groups. The band energy levels of the quantum dots (QDs) prior to the addition of the surface dipole layer are shown in black: the conduction band energy level E°_{CB} and valence band energy level E°_{VB}. Upon application of the surface dipole layer, these bands shift, with the new positions indicated as E'_{CB}, E^{*}_{CB} for the conduction band and E'_{VB}, E^{*}_{VB} for the valence band.

B. The photoredox CD catalyst is excited by visible light to produce a long-lived excited state. This excited state facilitates the oxidation of deprotonated hydrogen atom transfer (HAT) catalysts, yielding a thiyl- radical for both CD-**1** and CD-**2**. The thiyl- radical abstracts a hydrogen atom from alkyl aniline substrates, generating a highly nucleophilic α-amino radical.

This reactive carbon-centered radical then reacts with electron-deficient alkenes to form a Giese radical addition intermediate. In the catalytic cycle using the less oxidative photoredox CD-**1**, the catalyst is turned over by single electron transfer (SET) between the CDs and the radical addition intermediate, producing the Giese radical addition product. Conversely, in the catalytic cycle using the more oxidative CD-**2**, the Giese radical addition intermediate undergoes further oxidation to form a carbocation. This carbocation eliminates a proton, yielding an intermediate that undergoes acid-base catalyzed redox-neutral annulation. The CD-**2** catalyst is turned over by SET or proton-coupled electron transfer (PCET) between the CDs and protons or other species, producing unidentified gaseous products (represented as H_2 in the figure for clarity).

Cyclic voltammetry (CV) curves were obtained using a CHI 760e electrochemical workstation (Shanghai Chenhua Apparatus Inc., China), with ITO glass as the working electrodes and a platinum coil as counter. CDs materials were dispersed into an EtOH solution with 0.5mg CDs and 10µl Nafion per ml of EtOH. The suspension was ultra-sonicated for 20 minutes and then dip-coated onto an ITO glass electrode (1cm*1cm) with an aliquot of 50µl CDs paste. The ITO electrode was oven dried and the CV curves were taken in a MeCN solution with 0.1 M of TBA-PF_6. All potentials are quoted against an Ag/AgCl/KCl (saturated aq.) electrode. Scan rate was 100mV/s.

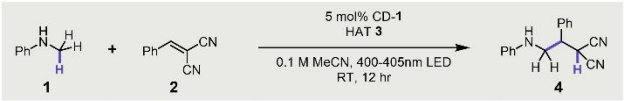


Section S2 General Procedure of Catalysis Experiments

In a glovebox, 10 mg of CDs photocatalyst was charged into a quartz reaction tube and sealed under a nitrogen atmosphere. Once the tube was transferred out of the glovebox, an anhydrous acetonitrile solution (2 mL, 0.1 M) containing thiol HAT catalyst (**3**) (0.05 equiv.), C–H bond substrates (1 mmol, 5.0 equiv.), and alkene substrates (0.2 mmol, 1.0 equiv.) was added via syringe. The resulting mixture was irradiated using 400-405 nm LED beads on a WATTCAS Parallel-Light Reactor with room-temperature water cooling under vigorous stirring for 12-16 hours.

Work-up procedure: After the reaction was completed, the solution inside the quartz tube was transferred, and the quartz tube was washed with excess acetonitrile. The combined solution was concentrated with rotor-evaporation, and the concentrated mixture was purified by column chromatography with hexane: ethylacetate from 0 : 100% to 30% : 70%.

Table S1. CD-**1** photocatalytic reaction condition optimization.

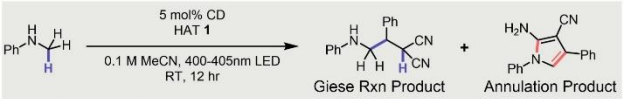


Entry	Solvent	Variation	Yield (%)
1	THF	No	ND
2	DCE	No	11
3	MeOH	No	29
4	HFIP	No	34
5	Acetone	No	36
6	MeCN	stoichiometric	48
7	MeCN	**2** 5-fold excess	63
8	MeCN	**1** 8-fold excess	67
9	MeCN	**1** 5-fold excess	71
10	MeCN	no light	ND
11	MeCN	no HAT	ND
12	MeCN	no CDs Cat.	9
13	MeCN	HAT **3'**	53
14	MeCN	Pyridine-N-oxide	ND
15	MeCN	K_2CO_3	ND
16	MeCN	TMA·HCl	ND

Table **S2**. Elemental analysis of the C, H, and N contents in CD-**1** and CD-**2**

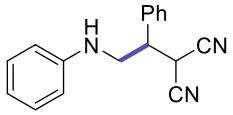
Entry	C content / %	N content / %	H content / %	O content / %
CD-**1**	55.21	1.93	5.88	36.98
CD-**2**	55.13	3.03	6.03	35.81

Table **S3**. CD-**2** photocatalytic reaction condition optimization.

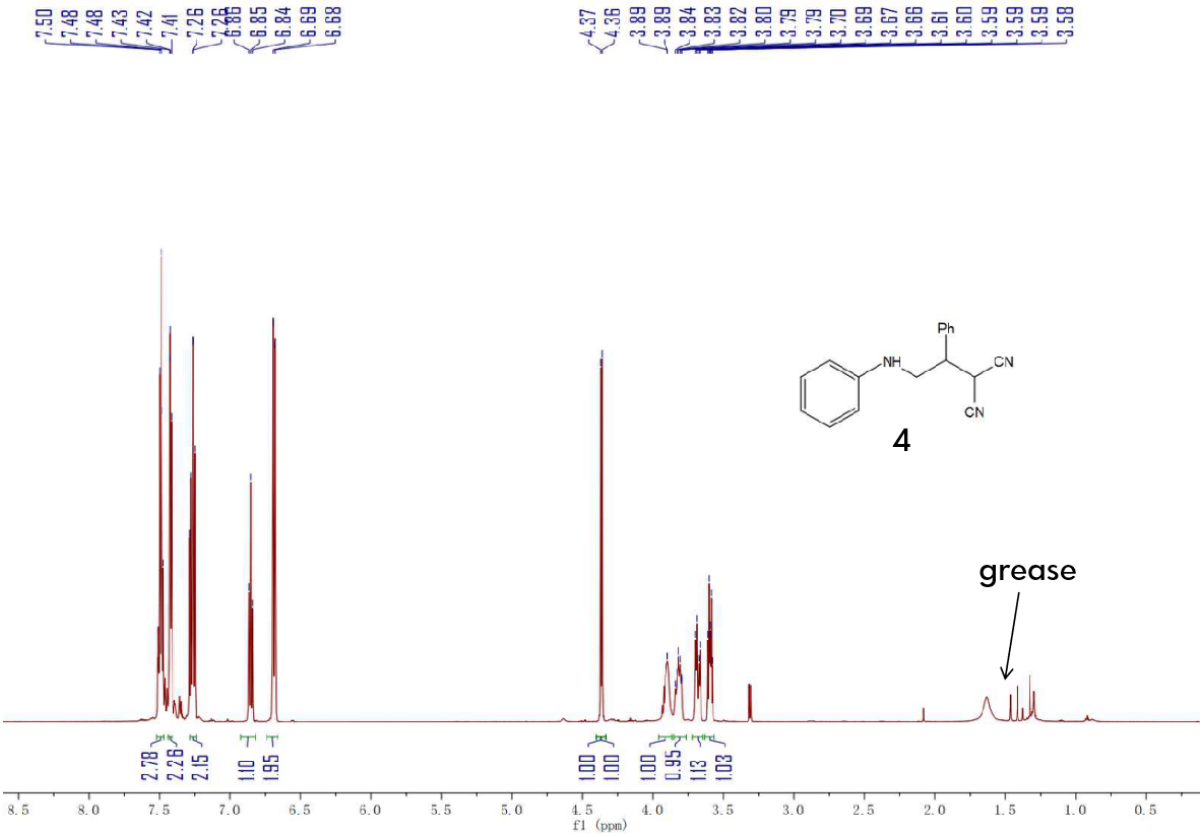


Entry	Solvent	Variation	Giese Rxn	Annulation
1	MeCN	No	24	71
2	THF	No	trace	29
3	MeOH	No	trace	53
4	DCE	No	27	70
5	MeCN	30%mol TsOH	18	44
6	MeCN	30%mol AcOH	trace	60
7	MeCN	30%mol K_3PO_4	trace	trace
8	MeCN	30%mol Lutidine	22	64
9	MeCN	5%mol TMA^+Cl^-	13	65
10	MeCN	5%mol TMA^+Cl^- CD-**1**	57	trace

Section S3 Characterizations of the Products



4 The reaction was set up following the general procedure using N-methylbenzenamine (107 mg, 1 mmol) and benzylidenemalononitrile (31 mg, 0.2 mmol). After 16 hours, the reaction was purified following general work-up to give 37 mg (71 % yield) of the title compound. **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 7.52 – 7.47 (m, 3H), 7.43 – 7.41 (m, 2H), 7.28 – 7.24 (m, 2H), 6.85 (t, *J* = 7.4, 1.1 Hz, 1H), 6.7 – 6.67 (d, 2H), 4.36 (d, *J* = 5.4 Hz, 1H), 3.91 (m, *J* = 14.1, 6.5 Hz, 1H), 3.82 (m, *J* = 15.1, 7.5 Hz, 1H), 3.68 (m, *J* = 13.9, 5.9 Hz, 1H), 3.59 (m, *J* = 8.8, 5.7 Hz, 1H); **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 146.44, 134.76, 129.67, 129.54, 129.45, 128.04, 119.15, 113.44, 112.08, 111.66, 45.84, 45.69, 27.12; MS2 (ES^+)exact mass calculated for $[M+H]^+$ ($C_{17}H_{16}N_3$) requires m/z 262.1, found m/z 262.1.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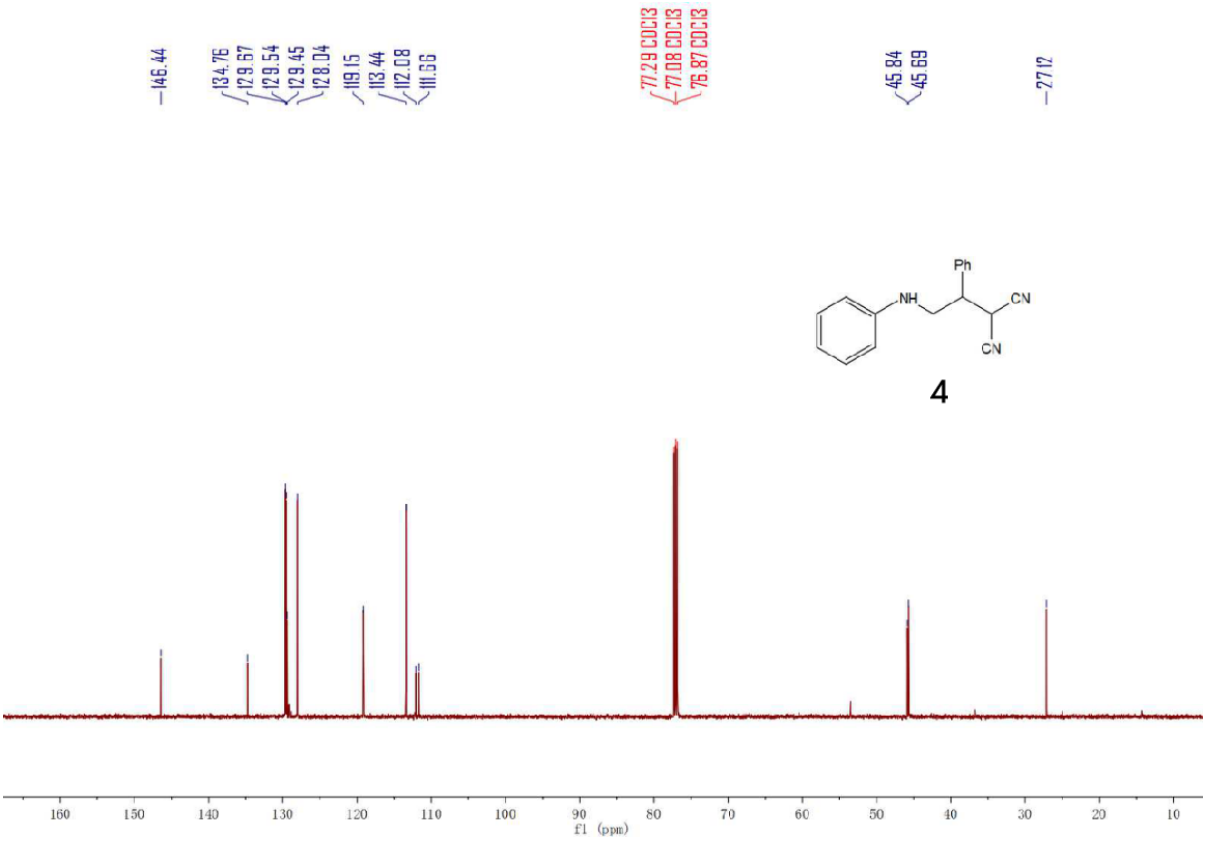
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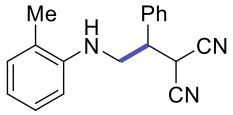
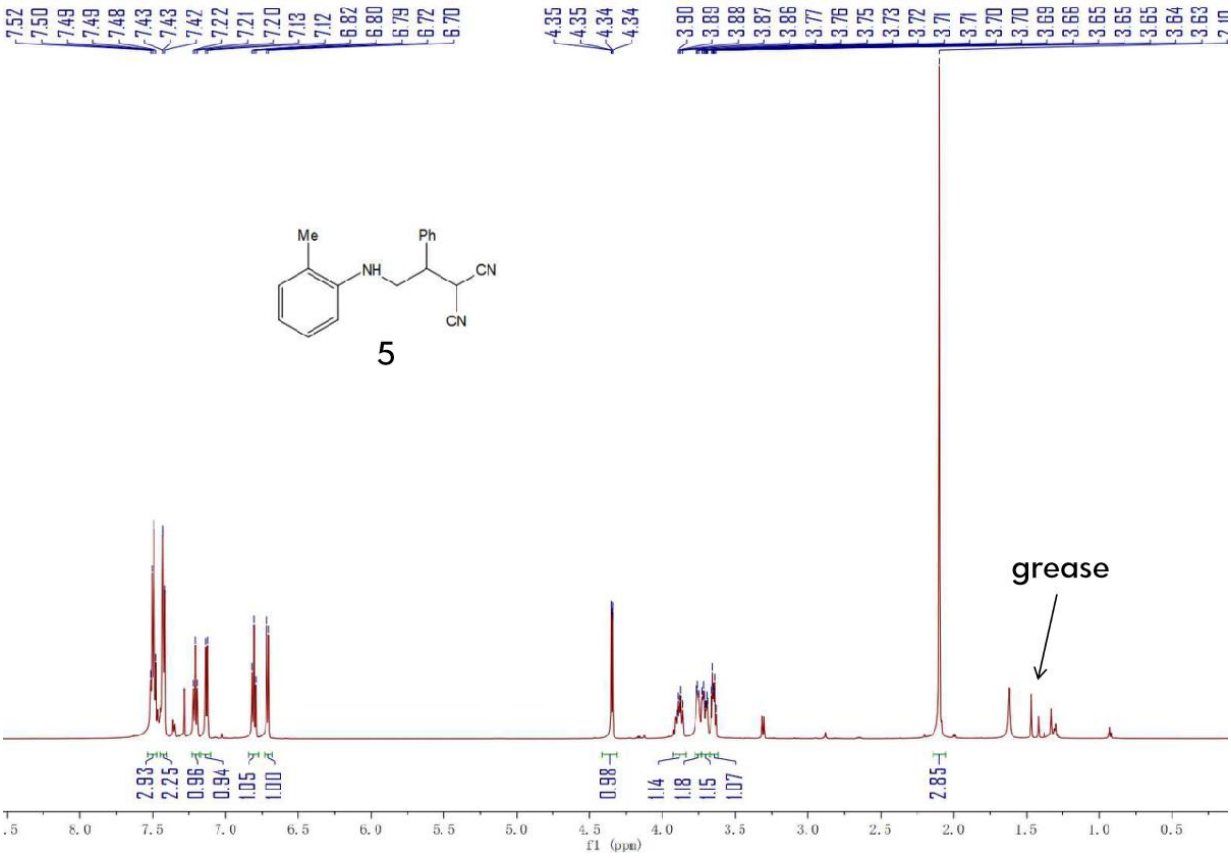


5 The reaction was set up following the general procedure using 2-methyl-N-methylbenzenamine (121 mg, 1 mmol) and benzylidenemalononitrile (31 mg, 0.2 mmol). After 16 hours, the reaction was purified following general work-up to give 39 mg (71 % yield) of the title compound. **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 7.54 – 7.43 (m, 3H), 7.45 – 7.40 (m, 2H), 7.21 (t, *J* = 7.7 Hz, 1H), 7.13 (d, *J* = 7.4 Hz, 1H), 6.80 (t, *J* = 7.4 Hz, 1H), 6.71 (d, *J* = 8.0 Hz, 1H), 4.35 (m, *J* = 5.4, 1.0 Hz, 1H), 3.93 – 3.84 (m, 1H), 3.78 – 3.67 (m, 2H), 3.65 (m, *J* = 8.8, 5.6 Hz, 1H), 2.10 (s, 3H); **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 144.31, 134.86, 130.73, 129.55, 129.46, 128.01, 127.39, 123.16, 118.75, 112.08, 111.71, 110.08, 45.65, 45.40, 27.17, 17.43; MS2 (ES^+) exact mass calculated for $[M+H]^+$ ($C_{18}H_{18}N_3$) requires m/z 276.1, found m/z 276.1.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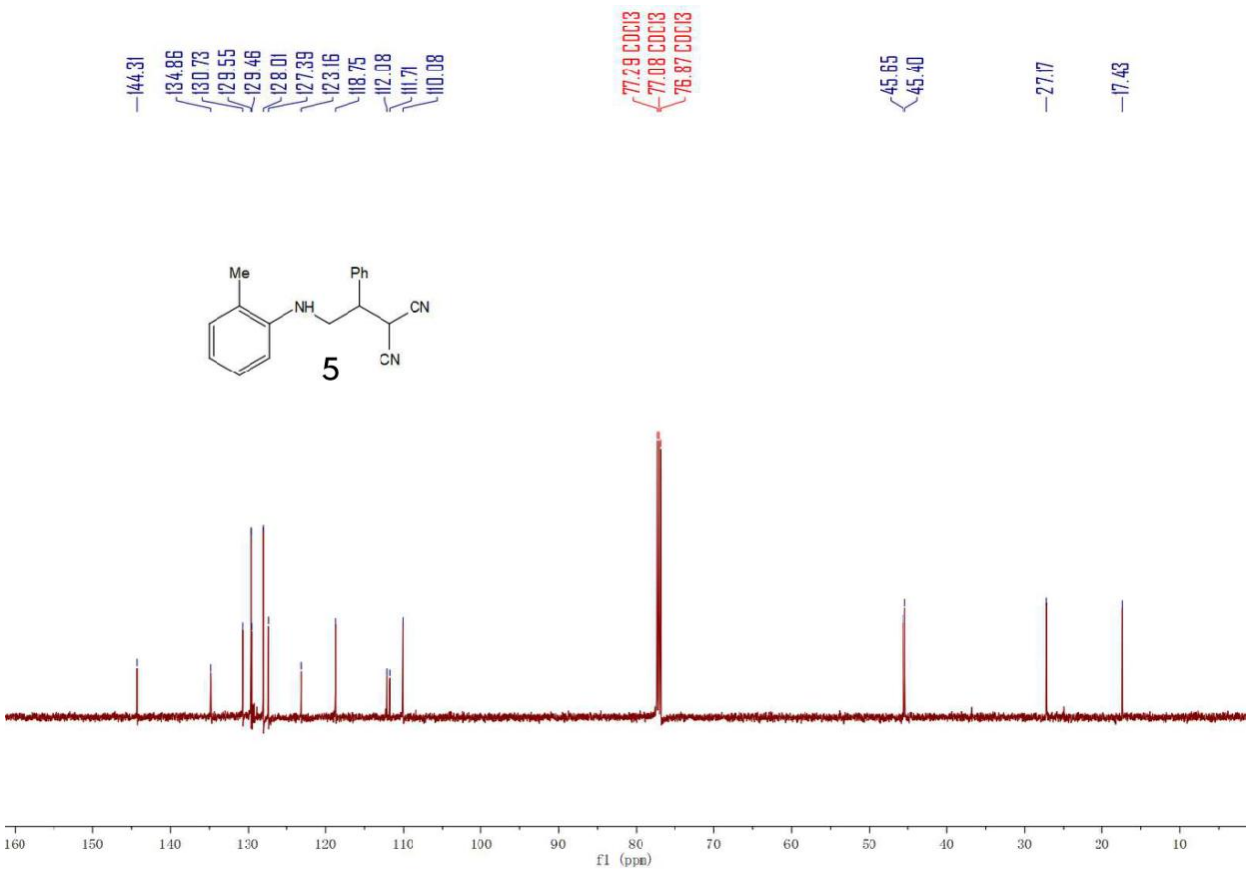
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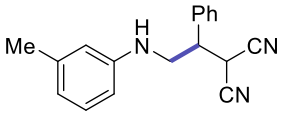
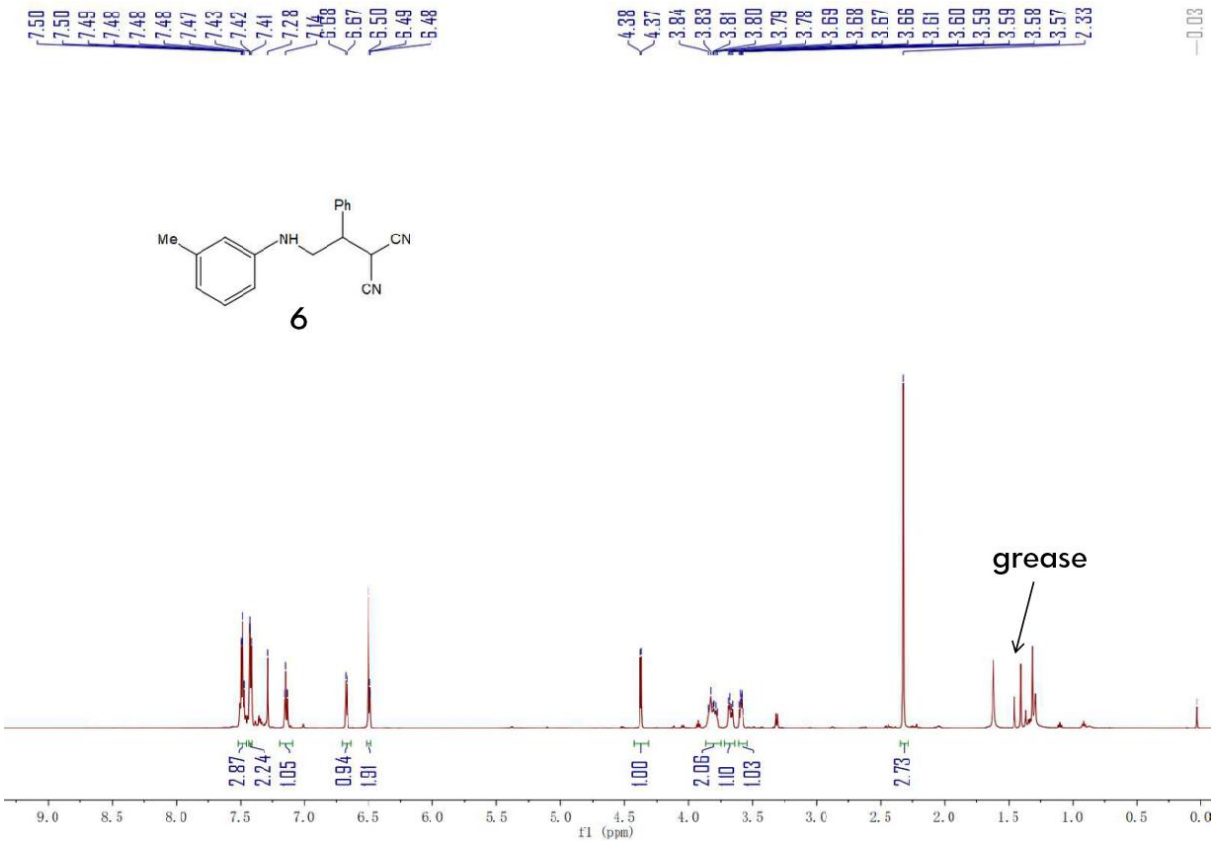


6 The reaction was set up following the general procedure using 3-methyl-N-methylbenzenamine (121 mg, 1 mmol) and benzylidenemalononitrile (31 mg, 0.2 mmol). After 16 hours, the reaction was purified following general work-up to give 34 mg (61 % yield) of the title compound. **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 7.49 (m, *J* = 7.7, 6.6, 3.5 Hz, 3H), 7.47 – 7.31 (m, 2H), 7.14 (t, *J* = 7.6 Hz, 1H), 6.67 (d, *J* = 7.5 Hz, 1H), 6.50 (s, 2H), 4.37 (d, *J* = 5.4 Hz, 1H), 3.86 – 3.76 (m, 2H), 3.67 (m, *J* = 12.9, 5.9 Hz, 1H), 3.59 (m, *J* = 8.2, 5.6 Hz, 1H), 2.33 (s, 3H); **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 146.45, 139.58, 134.78, 129.52, 129.42, 129.15, 128.05, 120.08, 114.27, 112.07, 111.64, 110.49, 45.83, 45.79, 27.10, 21.63; MS2 (ES^+) exact mass calculated for $[M+H]^+$ ($C_{18}H_{18}N_3$) requires m/z 276.1, found m/z 276.1.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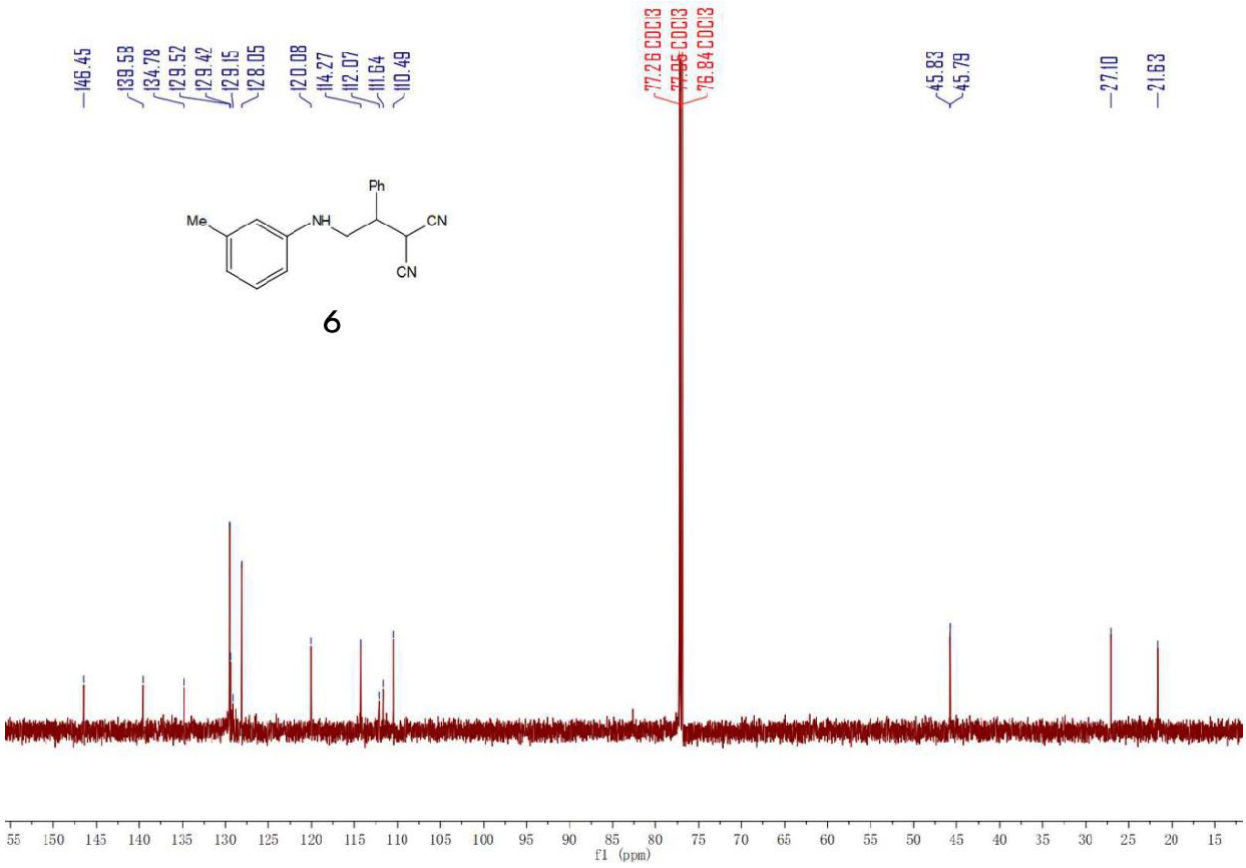
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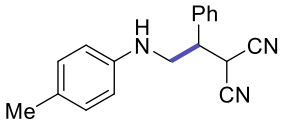
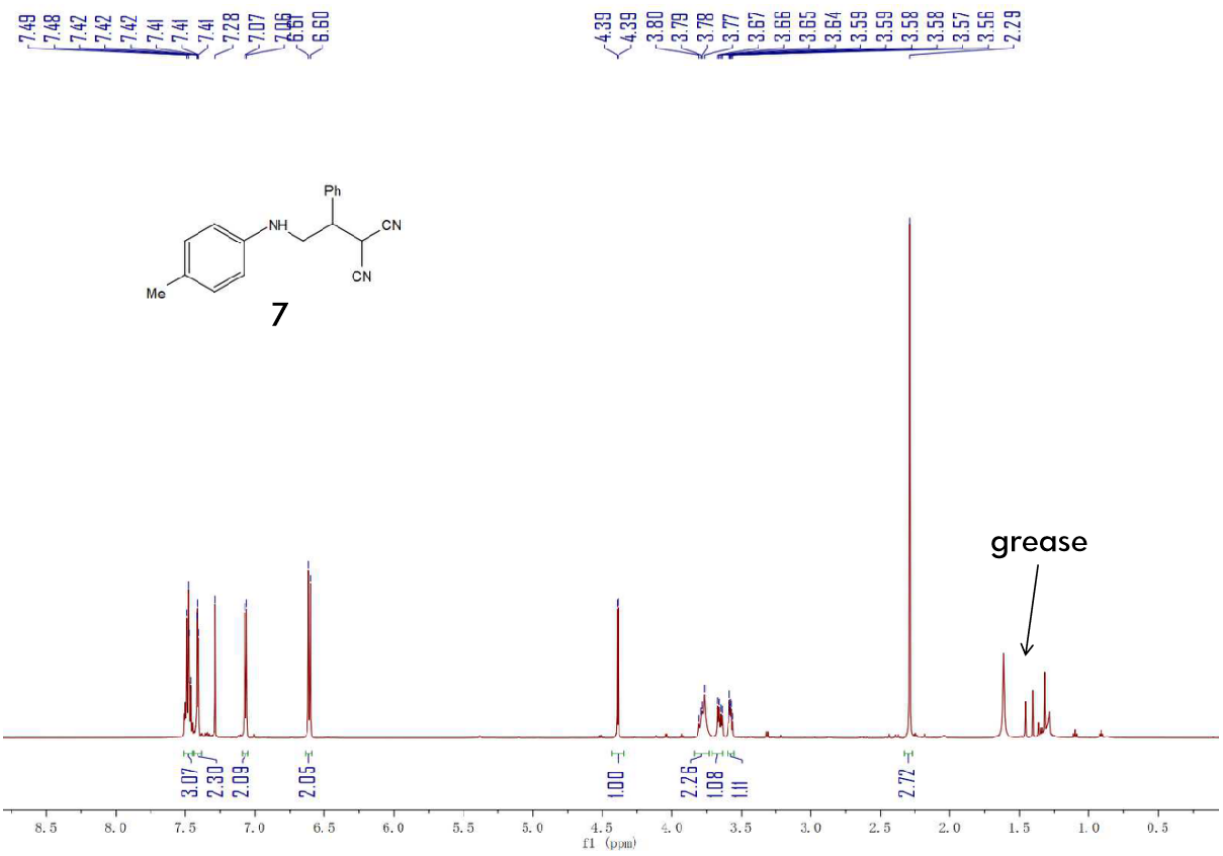


7 The reaction was set up following the general procedure using 4-methyl-N-methylbenzenamine (121 mg, 1 mmol) and benzylidenemalononitrile (31 mg, 0.2 mmol). After 16 hours, the reaction was purified following general work-up to give 30 mg (54 % yield) of the title compound. **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 7.52 – 7.42 (m, 3H), 7.45 – 7.38 (m, 2H), 7.07 (d, *J* = 8.1 Hz, 2H), 6.63 – 6.58 (m, 2H), 4.39 (d, *J* = 5.4 Hz, 1H), 3.81 – 3.73 (m, 2H), 3.65 (m, *J* = 13.1, 5.8 Hz, 1H), 3.58 (m, *J* = 8.8, 5.5 Hz, 1H), 2.29 (s, 3H); **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 144.04, 134.79, 130.13, 129.51, 129.40, 128.57, 128.04, 113.66, 112.09, 111.64, 46.19, 45.77, 27.06, 20.42; MS2 (ES^+) exact mass calculated for $[M+H]^+$ ($C_{18}H_{18}N_3$) requires m/z 276.1, found m/z 276.1.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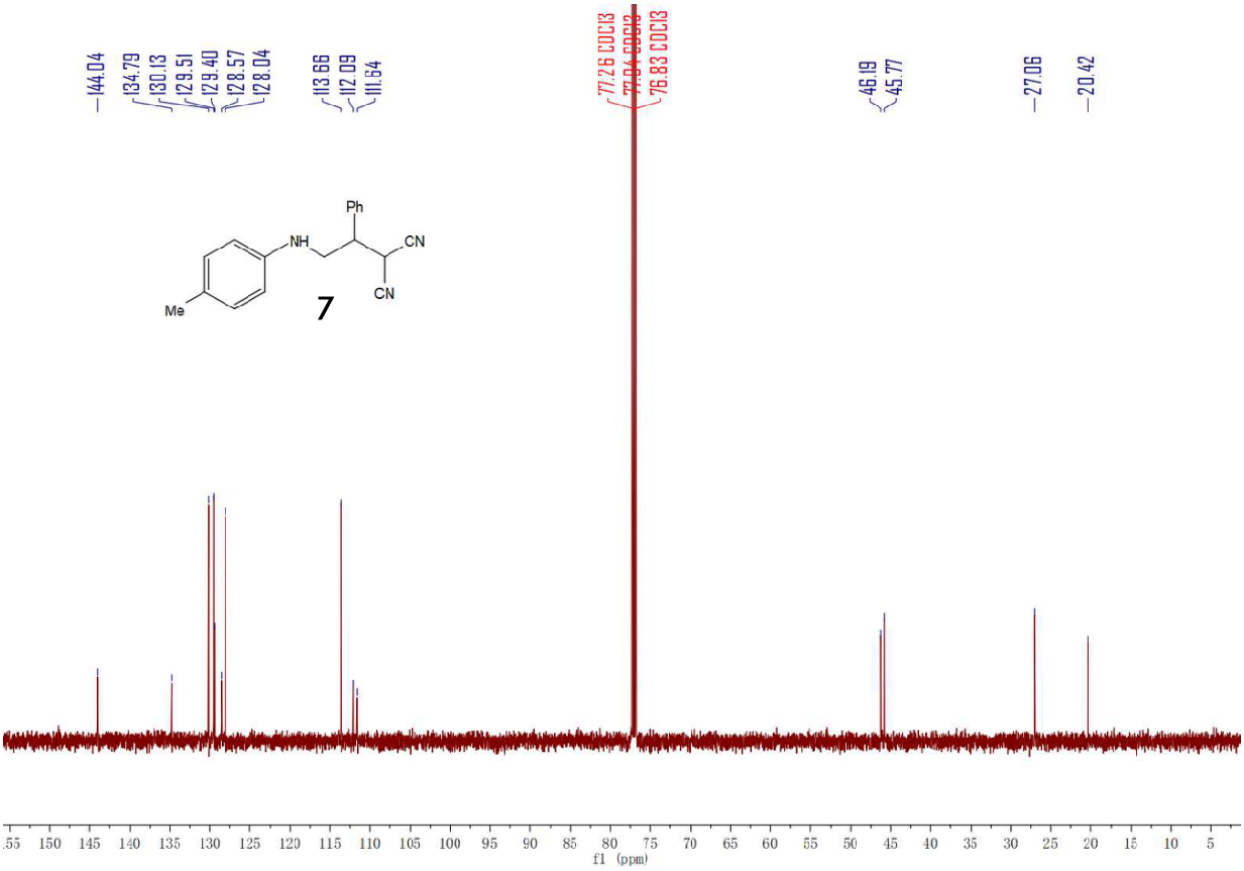
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128.04
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111.64
77.26 CDCl3
76.83 CDCl3
46.19
45.77
27.06
20.42
Ph
NH
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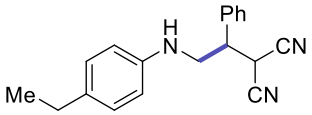
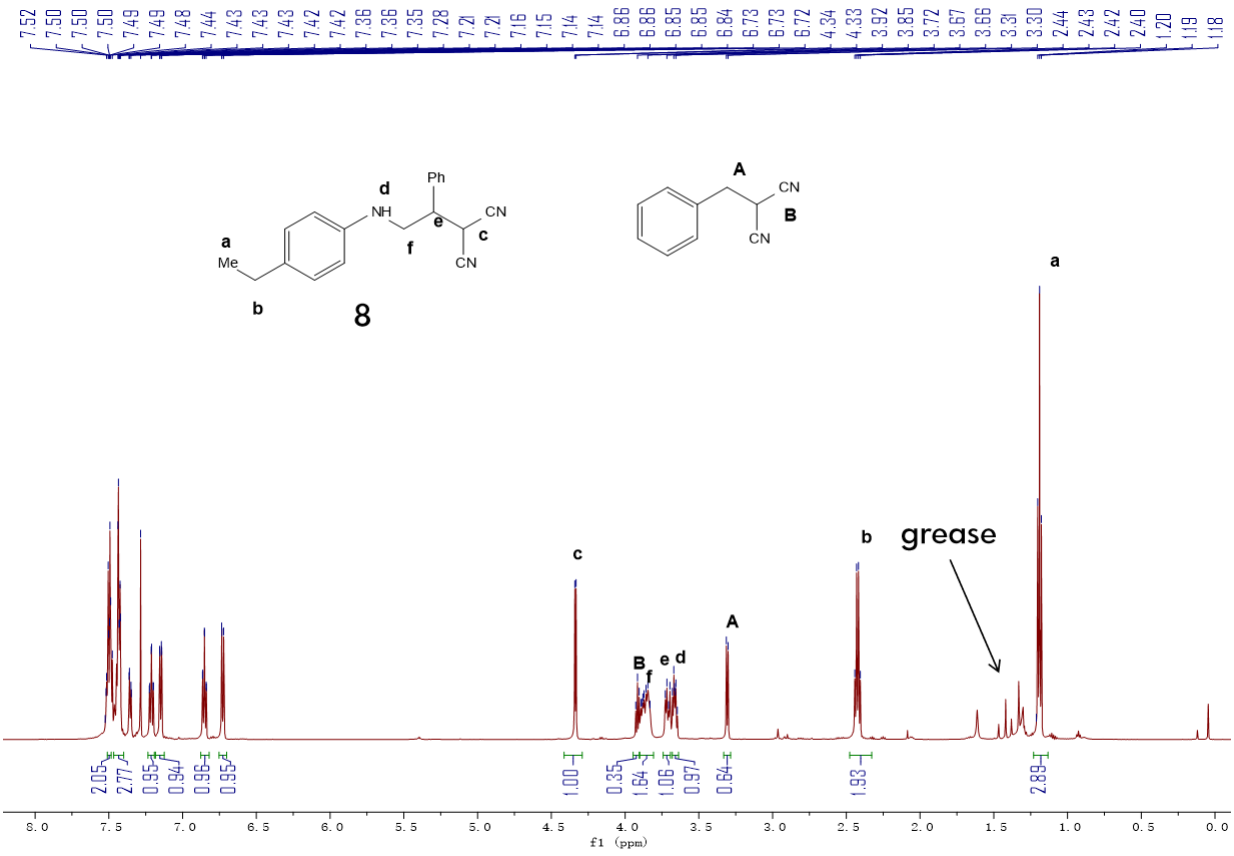
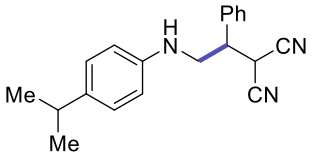
CN
Me
7
f1 (ppm)

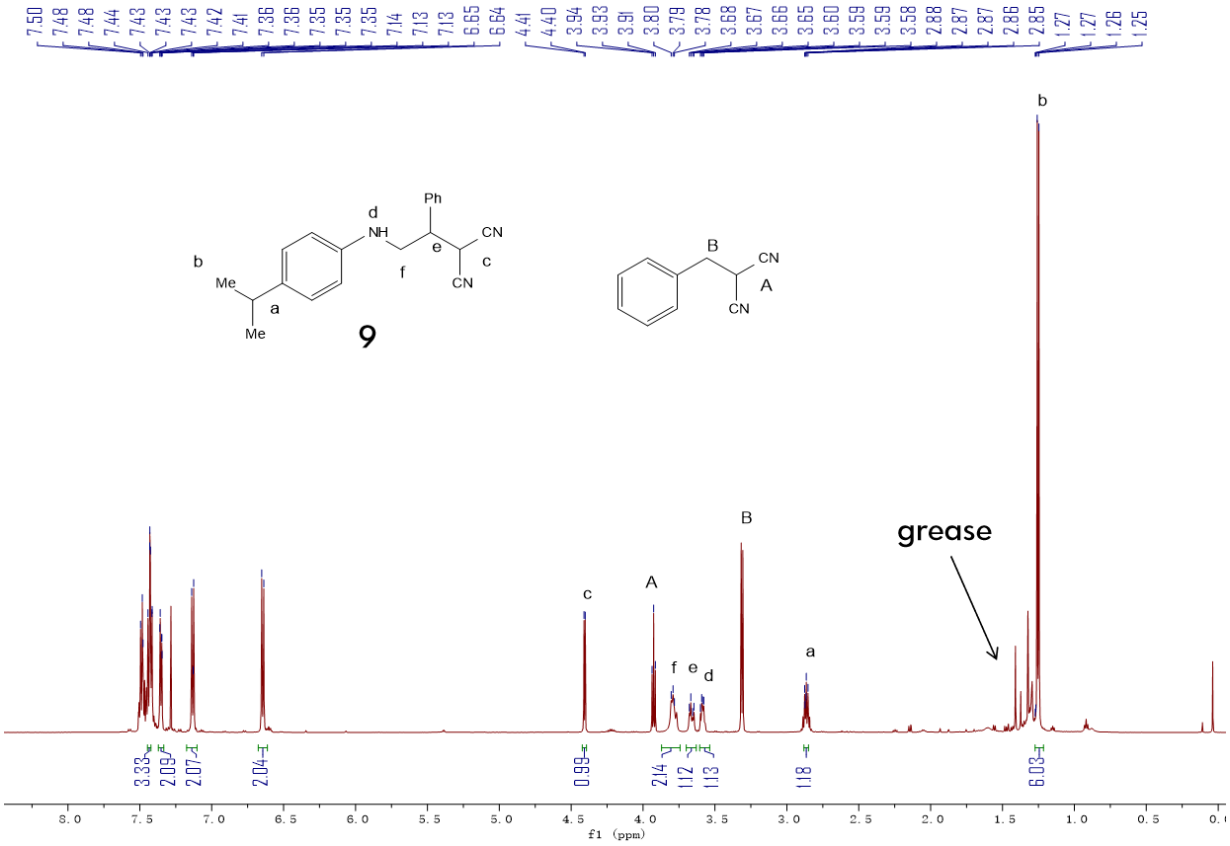


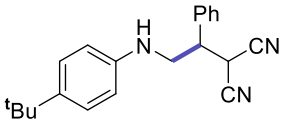
8 The reaction was set up following the general procedure using 4-ethyl-N-methylbenzenamine (135 mg, 1mmol) and benzylidenemalononitrile (31 mg, 0.2 mmol). After 16 hours, the reaction was purified following general work-up to give 33 mg (57 % yield) of the title compound. **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 7.50 (m, *J* = 7.7, 6.6, 3.6 Hz, 3H), 7.44 – 7.42 (m, 2H), 7.21 (m, *J* = 7.7, 1.6 Hz, 1H), 7.15 (m, *J* = 7.5, 1.5 Hz, 1H), 6.85 (m, *J* = 7.4, 1.1 Hz, 1H), 6.76 – 6.69 (m, 1H), 4.34 (d, *J* = 5.4 Hz, 1H), 3.88 (m, *J* = 29.4, 16.4, 7.8 Hz, 2H), 3.75 – 3.61 (m, 2H), 2.42 (m, *J* = 7.5 Hz, 2H), 1.19 (t, *J* = 7.5 Hz, 3H). MS2 (ES^+) exact mass calculated for $[M+H]^+$ ($C_{19}H_{20}N_3$) requires m/z 290.1, found m/z 290.1.


7.52 7.50 7.50 7.50 7.49 7.49 7.48 7.44 7.43 7.43 7.42 7.42 7.36 7.36 7.35 7.28 7.21 7.21 7.16 7.15 7.14 7.14 6.86 6.86 6.85 6.85 6.84 6.73 6.73 6.72 4.34 4.33 3.92 3.85 3.72 3.67 3.66 3.31 3.30 2.44 2.43 2.42 2.40 1.20 1.19 1.18
d
Ph
NH
e
CN
c
f
CN
a
Me
b
8
A
CN
B
CN
a
b
grease
c
A
B
f
e
d
2.05 2.77 0.95 0.94 0.96 0.95 1.00 0.35 1.64 1.06 0.97 0.64 1.93 2.89
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

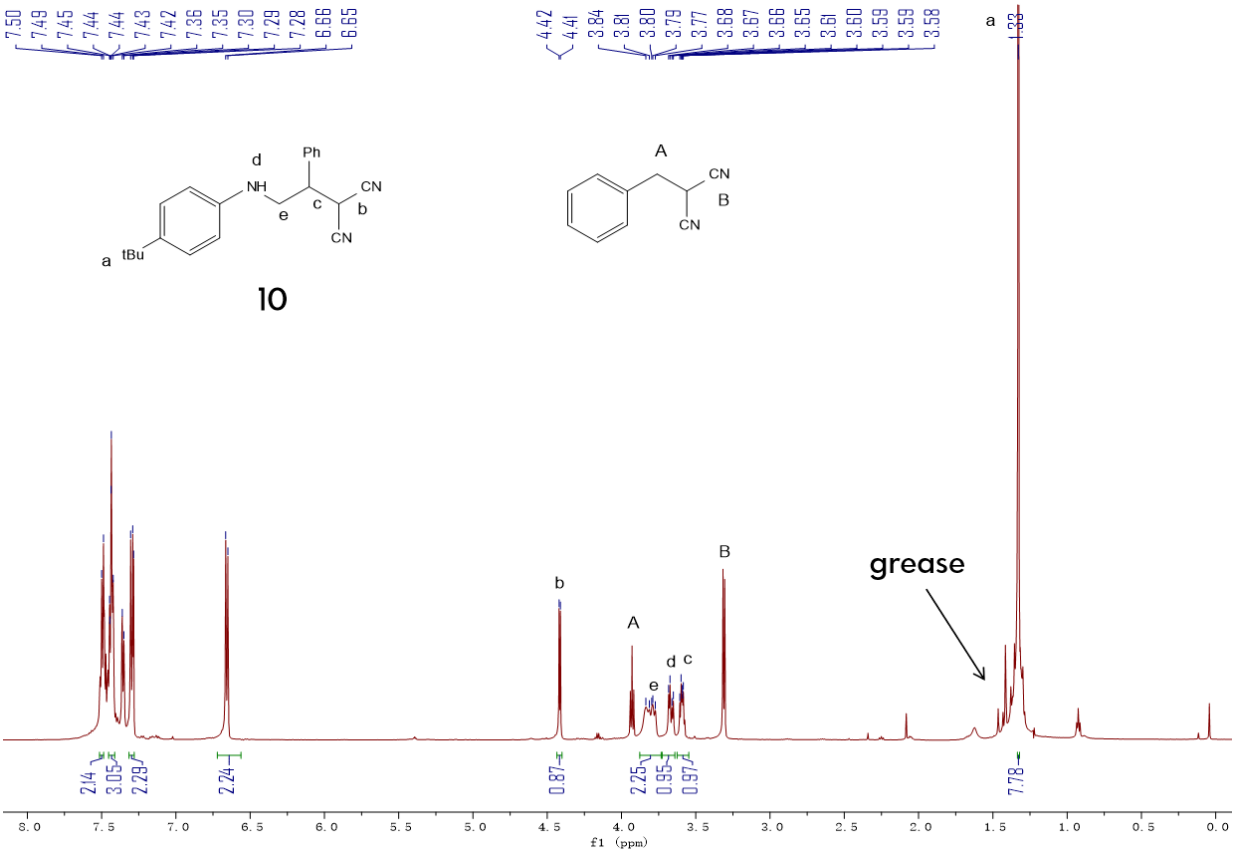


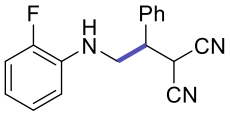
9 The reaction was set up following the general procedure using N-methyl-4-(1-methylethyl)benzenamine (149 mg, 1 mmol) and benzylidenemalononitrile (31 mg, 0.2 mmol). After 16 hours, the reaction was purified following general work-up to give 38 mg (63 % yield) of the title compound. **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 7.45 – 7.42 (m, 3H), 7.37 – 7.33 (m, 2H), 7.17 – 7.10 (m, 2H), 6.68 – 6.61 (m, 2H), 4.41 (d, *J* = 5.3 Hz, 1H), 3.79 (m, *J* = 14.2, 8.5 Hz, 2H), 3.66 (m, *J* = 13.4, 5.7 Hz, 1H), 3.58 (m, *J* = 10.9, 5.6 Hz, 1H), 2.94 – 2.79 (m, 1H), 1.25 (d, *J* = 6.9 Hz, 6H); MS2 (ES^+) exact mass calculated for $[M+H]^+$ ($C_{20}H_{22}N_3$) requires m/z 304.1, found m/z 304.1.


7.50 7.48 7.48 7.44 7.43 7.43 7.43 7.42 7.41 7.36 7.36 7.35 7.35 7.35 7.14 7.13 7.13 6.65 6.64
4.41 4.40 3.94 3.93 3.91 3.80 3.79 3.78 3.68 3.67 3.66 3.65 3.60 3.59 3.59 3.58 2.88 2.87 2.87 2.86 2.85 1.27 1.27 1.26 1.25
Ph
d
NH
CN
e
c
b
f
CN
Me
a
Me
9
B
CN
A
CN
b
grease
B
c
A
f e d
a
3.33 2.09 2.07 2.04 0.99 2.14 1.12 1.13 1.18 6.03
f1 (ppm)

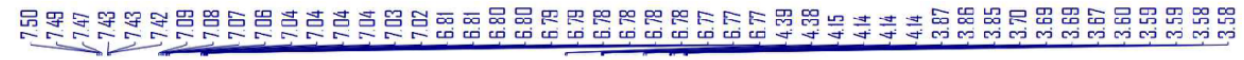


10 The reaction was set up following the general procedure using 4-(1,1-dimethylethyl)-N-methylbenzenamine (163 mg, 1 mmol) and benzylidenemalononitrile (31 mg, 0.2 mmol). After 16 hours, the reaction was purified following general work-up to give 40 mg (62 % yield) of the title compound. **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 7.50 (m, *J* = 8.0, 5.8 Hz, 2H), 7.45 – 7.41 (m, 3H), 7.32 – 7.28 (m, 2H), 6.72 – 6.56 (m, 2H), 4.42 (d, *J* = 5.3 Hz, 1H), 3.88 – 3.73 (m, 2H), 3.67 (m, *J* = 13.6, 5.6 Hz, 1H), 3.59 (m, *J* = 8.8, 5.5 Hz, 1H), 1.33 (s, 9H); MS2 (ES^+) exact mass calculated for $[M+H]^+$ ($C_{21}H_{24}N_3$) requires m/z 318.1, found m/z 318.1.


7.50
7.49
7.45
7.44
7.44
7.43
7.42
7.36
7.35
7.30
7.29
7.28
6.66
6.65
4.42
4.41
3.84
3.81
3.80
3.79
3.77
3.68
3.67
3.66
3.65
3.61
3.60
3.59
3.59
3.58
1.33
a
d
Ph
NH
e
c
CN
b
CN
a
tBu
10
A
CN
B
CN
b
A
e
d
c
B
grease
2.14
3.05
2.29
2.24
0.87
2.25
0.95
0.97
7.78
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)



11 The reaction was set up following the general procedure using 2-fluoro-N-methylbenzenamine (125 mg, 1 mmol) and benzylidenemalononitrile (31 mg, 0.2 mmol). After 16 hours, the reaction was purified following general work-up to give 46 mg (82 % yield) of the title compound. **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 7.53 – 7.47 (m, 3H), 7.44 – 7.40 (m, 2H), 7.15 – 7.00 (m, 2H), 6.82 – 6.72 (m, 2H), 4.39 (d, *J* = 5.5 Hz, 1H), 4.15 (m, *J* = 8.3, 7.8, 3.9 Hz, 1H), 3.86 (m, *J* = 14.0, 8.5 Hz, 1H), 3.68 (m, *J* = 14.0, 5.8, 4.1 Hz, 1H), 3.59 (m, *J* = 8.8, 5.7 Hz, 1H); **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 152.63, 151.04, 135.04, 134.97, 134.53, 129.57, 129.52, 129.32, 129.17, 128.00, 124.90, 124.88, 118.66, 118.61, 115.14, 115.01, 112.52, 112.51, 112.03, 111.56, 45.85, 45.49, 27.08; MS2 (ES^+) exact mass calculated for $[M+H]^+$ ($C_{17}H_{15}FN_3$) requires m/z 280.1, found m/z 280.1.


7.50
7.49
7.47
7.43
7.43
7.42
7.09
7.08
7.07
7.06
7.04
7.04
7.04
7.04
7.03
7.02
6.81
6.81
6.80
6.80
6.79
6.79
6.78
6.78
6.78
6.78
6.77
6.77
6.77
4.39
4.38
4.15
4.14
4.14
4.14
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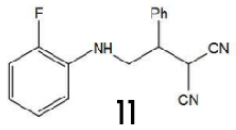
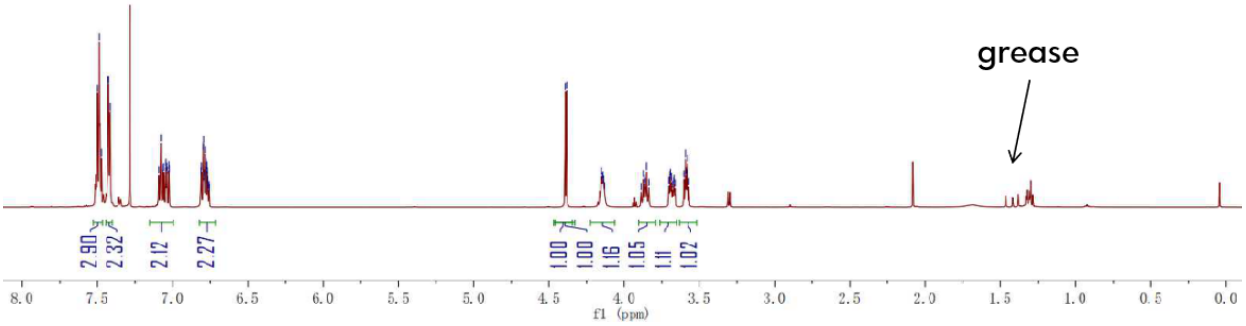
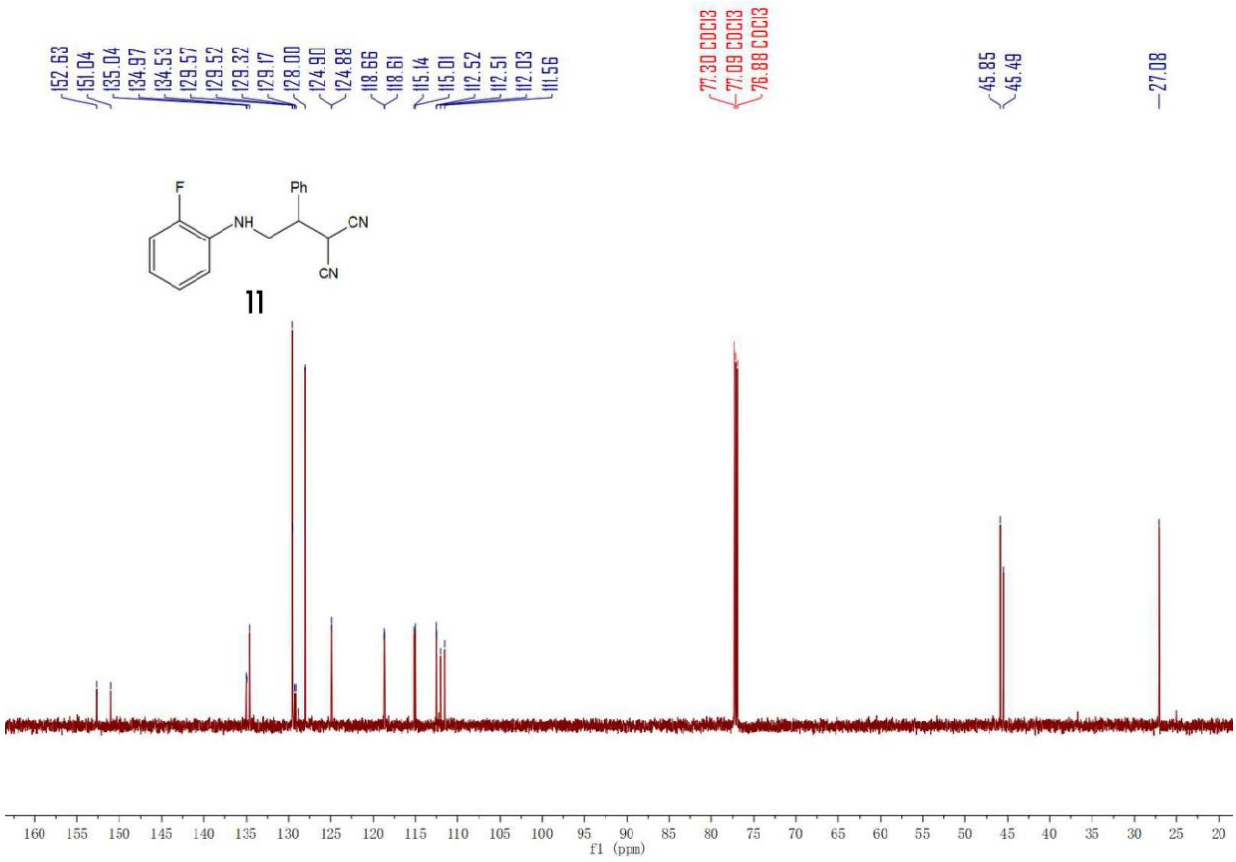
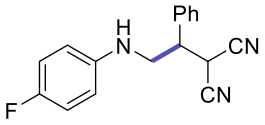
3.67
3.60
3.59
3.59
3.58
3.58


F
NH
Ph
CN
CN

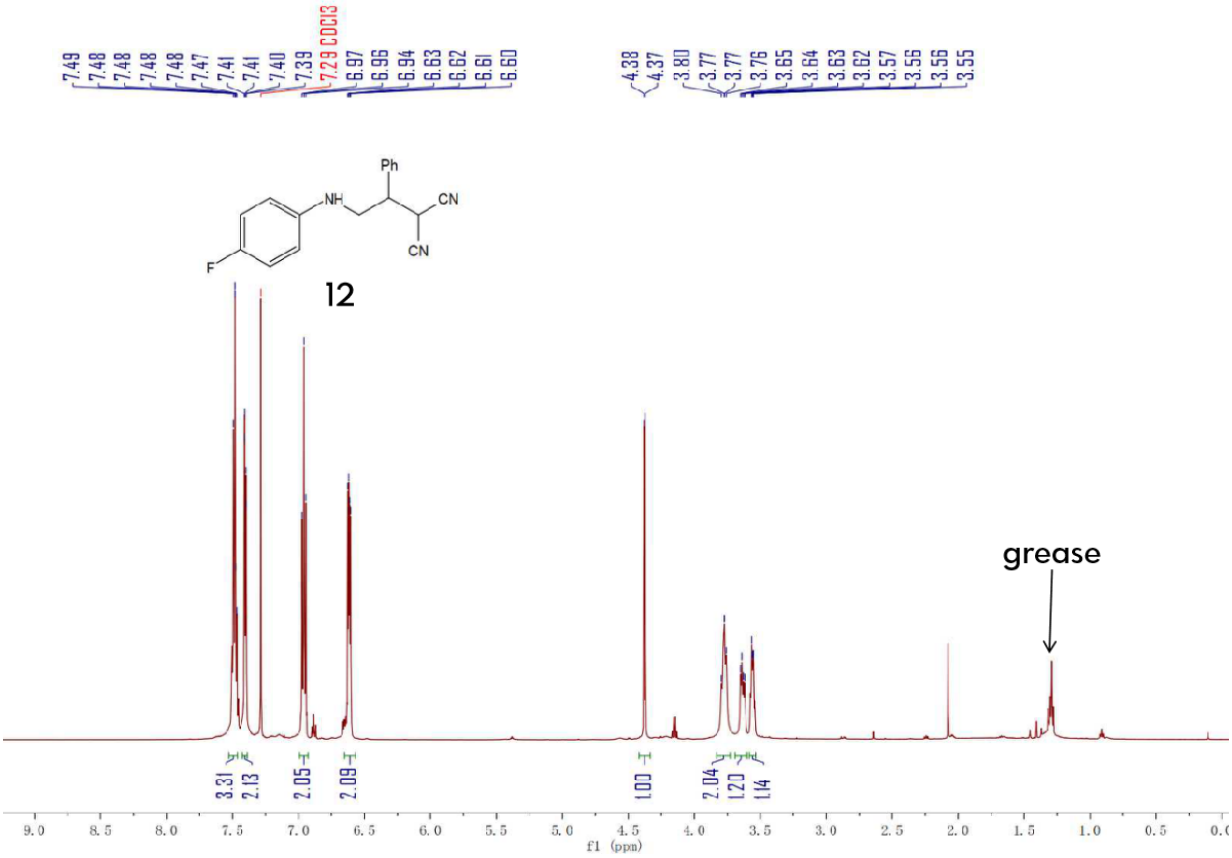
11


grease
2.90
2.32
2.12
2.27
1.00
1.00
1.16
1.05
1.11
1.02
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


152.63
151.04
135.04
134.97
134.53
129.57
129.52
129.32
129.17
128.00
124.90
124.88
118.66
118.61
115.14
115.01
112.52
112.51
112.03
111.56
77.30 CDCl3
77.09 CDCl3
76.88 CDCl3
45.85
45.49
27.08
F
NH
Ph
CN
CN
11
160 155 150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20
f1 (ppm)



12 The reaction was set up following the general procedure using 4-fluoro-N-methylbenzenamine (125 mg, 1 mmol) and benzylidenemalononitrile (31 mg, 0.2 mmol). After 16 hours, the reaction was purified following general work-up to give 41 mg (73 % yield) of the title compound. **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 7.54 – 7.44 (m, 3H), 7.44 – 7.36 (m, 2H), 7.00 – 6.92 (t, 2H), 6.68 – 6.58 (m, 2H), 4.38 (d, *J* = 5.5 Hz, 1H), 3.78 (m, *J* = 13.7, 8.8 Hz, 2H), 3.63 (m, *J* = 13.1, 6.1 Hz, 1H), 3.56 (m, *J* = 8.3, 5.7 Hz, 1H); **^{13}C NMR** (151 MHz, Chloroform-d) δ 134.75, 129.53, 129.43, 128.02, 127.18, 116.15, 116.00, 114.52, 114.47, 112.14, 111.69, 46.43, 45.64, 27.17; MS2 (ES^+) exact mass calculated for $[M+H]^+$ ($C_{17}H_{15}FN_3$) requires m/z 280.1, found m/z 280.1.


7.49
7.48
7.48
7.48
7.48
7.47
7.41
7.41
7.40
7.39
7.29 CDCl3
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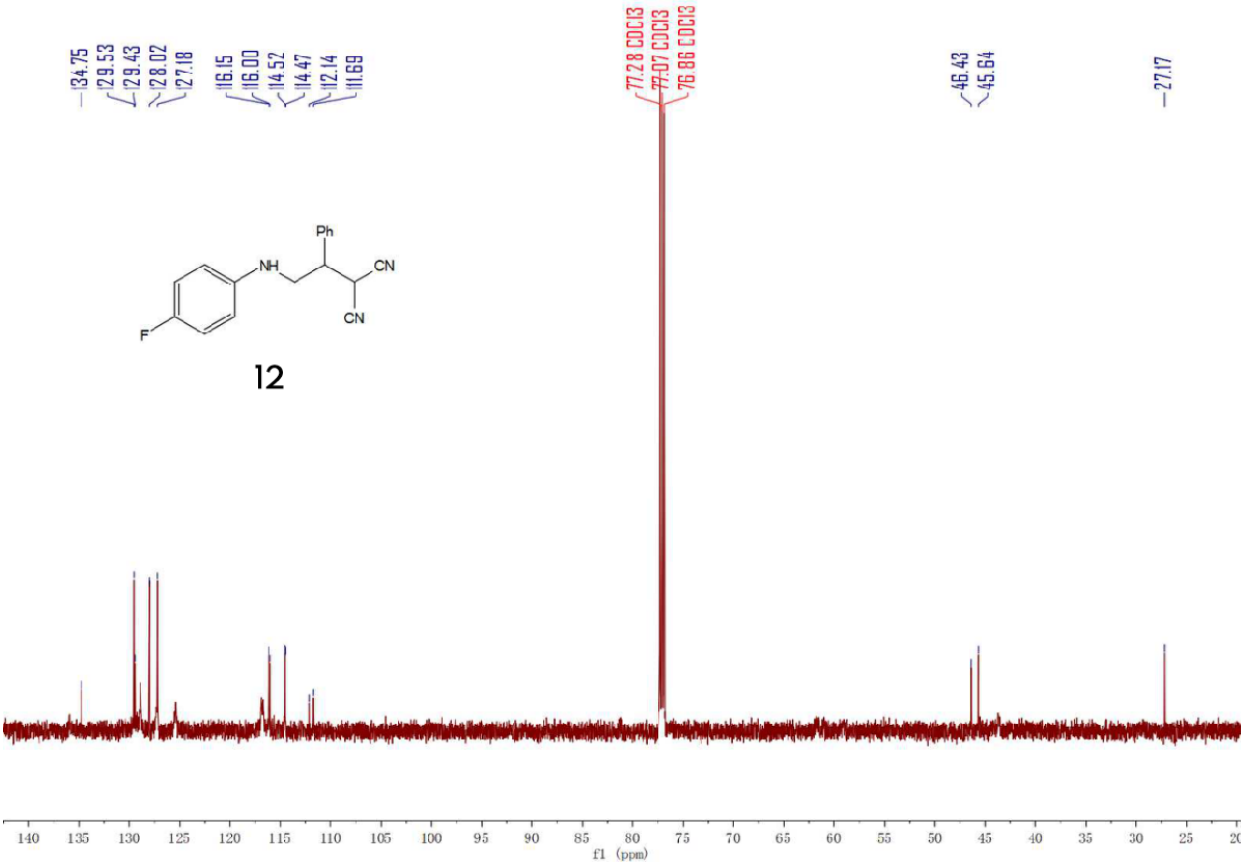
6.96
6.94
6.63
6.62
6.61
6.60
4.38
4.37
3.80
3.77
3.77
3.76
3.65
3.64
3.63
3.62
3.57
3.56
3.56
3.55
Ph
NH
CN
CN
F
12
grease
3.31
2.13
2.05
2.09
1.00
2.04
1.20
1.14
f1 (ppm)


134.75
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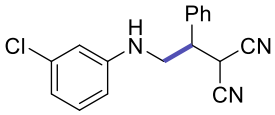
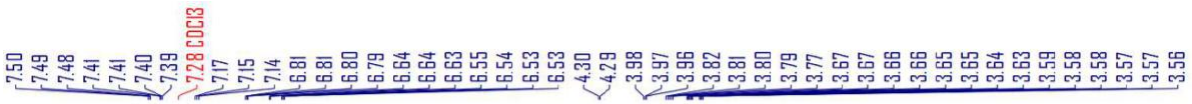
129.43
128.02
127.18
116.15
116.00
114.52
114.47
112.14
111.69
77.28 CDCl3
77.07 CDCl3
76.86 CDCl3
46.43
45.64
27.17
Ph
NH
CN
CN
F
12
140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25
f1 (ppm)



13 The reaction was set up following the general procedure using 3-chloro-N-methylbenzenamine (141 mg, 1 mmol) and benzylidenemalononitrile (31 mg, 0.2 mmol). After 16 hours, the reaction was purified following general work-up to give 46 mg (78 % yield) of the title compound. **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 7.53 – 7.43 (m, 3H), 7.44 – 7.33 (m, 2H), 7.15 (t, *J* = 8.0 Hz, 1H), 6.80 (m, *J* = 7.9, 1.8 Hz, 1H), 6.64 (t, *J* = 2.1 Hz, 1H), 6.54 (m, *J* = 8.2, 2.3 Hz, 1H), 4.30 (d, *J* = 5.5 Hz, 1H), 3.97 (t, *J* = 6.1 Hz, 1H), 3.80 (m, *J* = 14.9, 7.6 Hz, 1H), 3.65 (m, *J* = 14.2, 6.4, 2.4 Hz, 1H), 3.57 (m, *J* = 8.6, 5.9 Hz, 1H); **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 147.67, 135.34, 134.52, 130.65, 129.63, 129.58, 127.98, 118.97, 113.23, 111.92, 111.59, 111.56, 45.59, 45.47, 27.23; MS2 (ES^+) exact mass calculated for $[M+H]^+$ ($C_{17}H_{15}ClN_3$) requires m/z 296.1, found m/z 296.1.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7.49
7.48
7.41
7.41
7.40
7.39
7.28 CDCl3
7.17
7.15
7.14
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6.81
6.80
6.79
6.64
6.64
6.63
6.55
6.54
6.53
6.53
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4.29
3.98
3.97
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3.81
3.80
3.79
3.77
3.67
3.67
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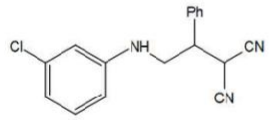
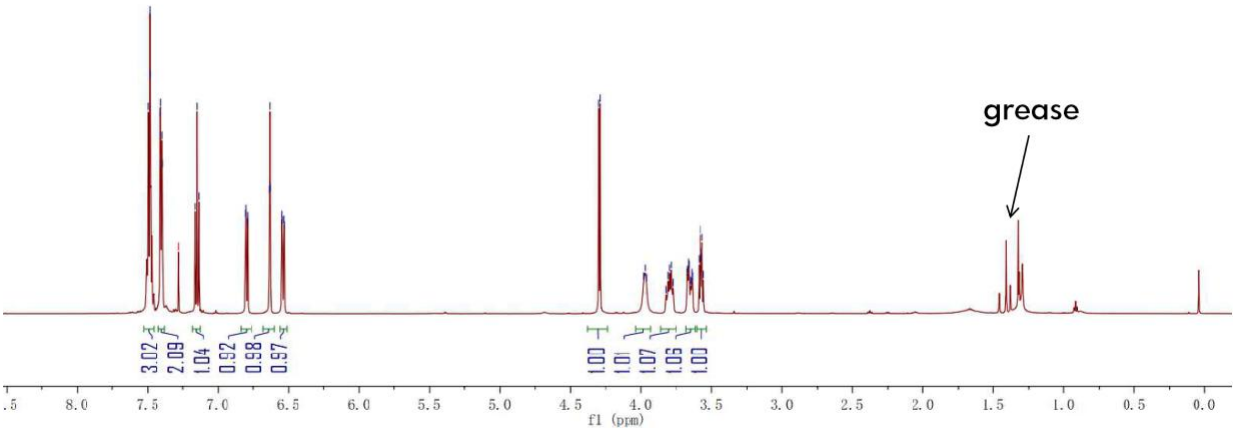
3.58
3.58
3.57
3.57
3.56


Ph
Cl
NH
CN
CN

13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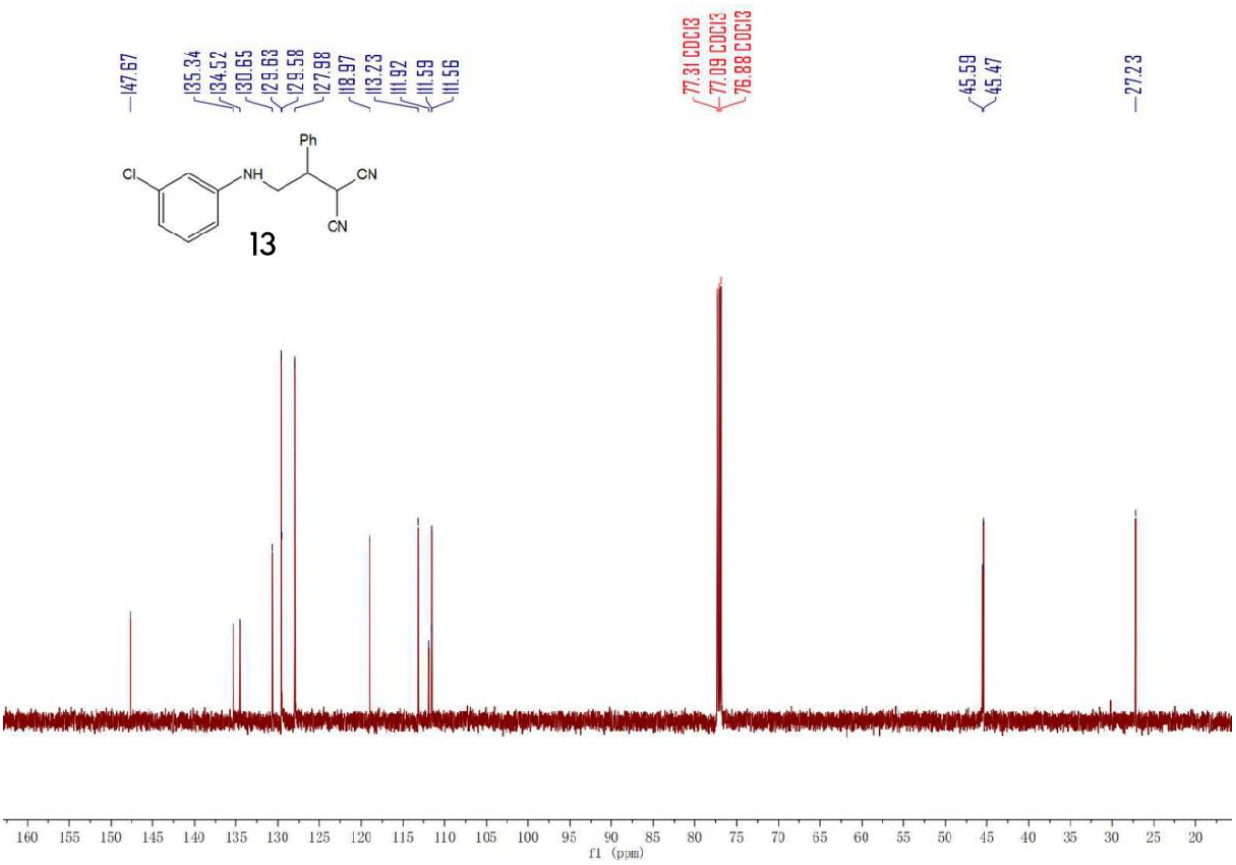
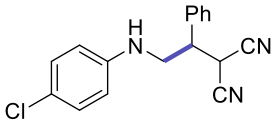
3.02
2.09
1.04
0.92
0.98
0.97
1.00
1.01
1.07
1.05
1.00
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


147.67
135.34
134.52
130.65
129.63
129.58
127.98
118.97
113.23
111.92
111.59
111.56
77.31 CDCl3
77.09 CDCl3
76.88 CDCl3
45.59
45.47
27.23
Ph
Cl
NH
CN
CN
13
160 155 150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20
f1 (ppm)



13 The reaction was set up following the general procedure using 4-chloro-N-methylbenzenamine (141 mg, 1 mmol) and benzylidenemalononitrile (31 mg, 0.2 mmol). After 16 hours, the reaction was purified following general work-up to give 40 mg (69 % yield) of the title compound. **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 7.51 – 7.47 (m, 3H), 7.41 – 7.38 (m, 2H), 7.21 – 7.17 (m, 2H), 6.62 – 6.56 (m, 2H), 4.32 (d, *J* = 5.5 Hz, 1H), 3.90 (s, 1H), 3.81 – 3.78 (m, *J* = 11.1 Hz, 1H), 3.65 – 3.62 (m, *J* = 14.0, 6.2 Hz, 1H), 3.56 – 3.54 (m, *J* = 8.5, 5.9 Hz, 1H); **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 145.01, 134.58, 129.61, 129.54, 129.47, 127.95, 123.80, 114.55, 111.89, 111.56, 45.93, 45.56, 27.19; MS2 (ES^+) exact mass calculated for $[M+H]^+$ ($C_{17}H_{15}ClN_3$) requires m/z 296.1, found m/z 296.1.


7.49
7.48
7.48
7.40
7.40
7.33
7.38
7.28 CDCl3
7.20
7.18
6.60
6.58
4.32
4.32
3.90
3.82
3.82
3.80
3.78
3.66
3.65
3.64
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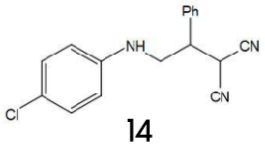
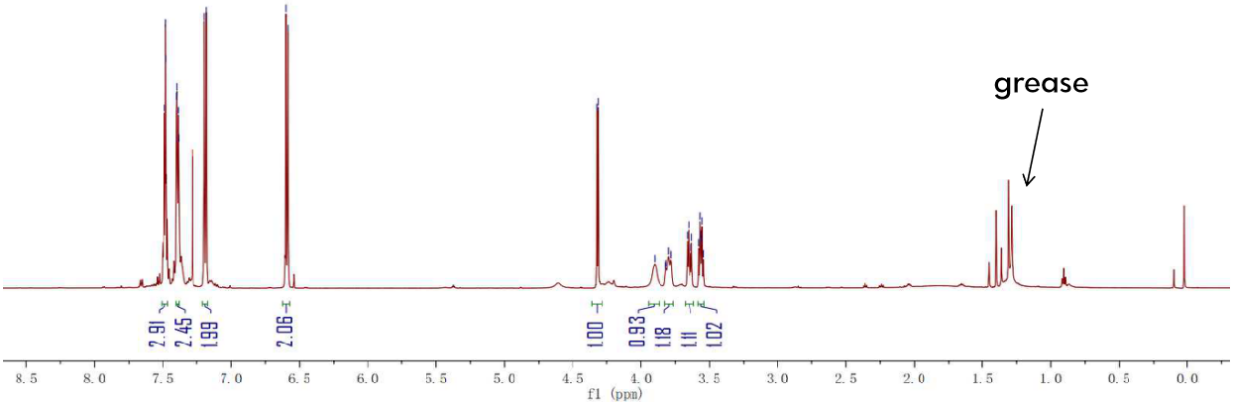
3.58
3.57
3.56
3.56
3.55
3.54


Ph
NH
CN
CN
Cl

14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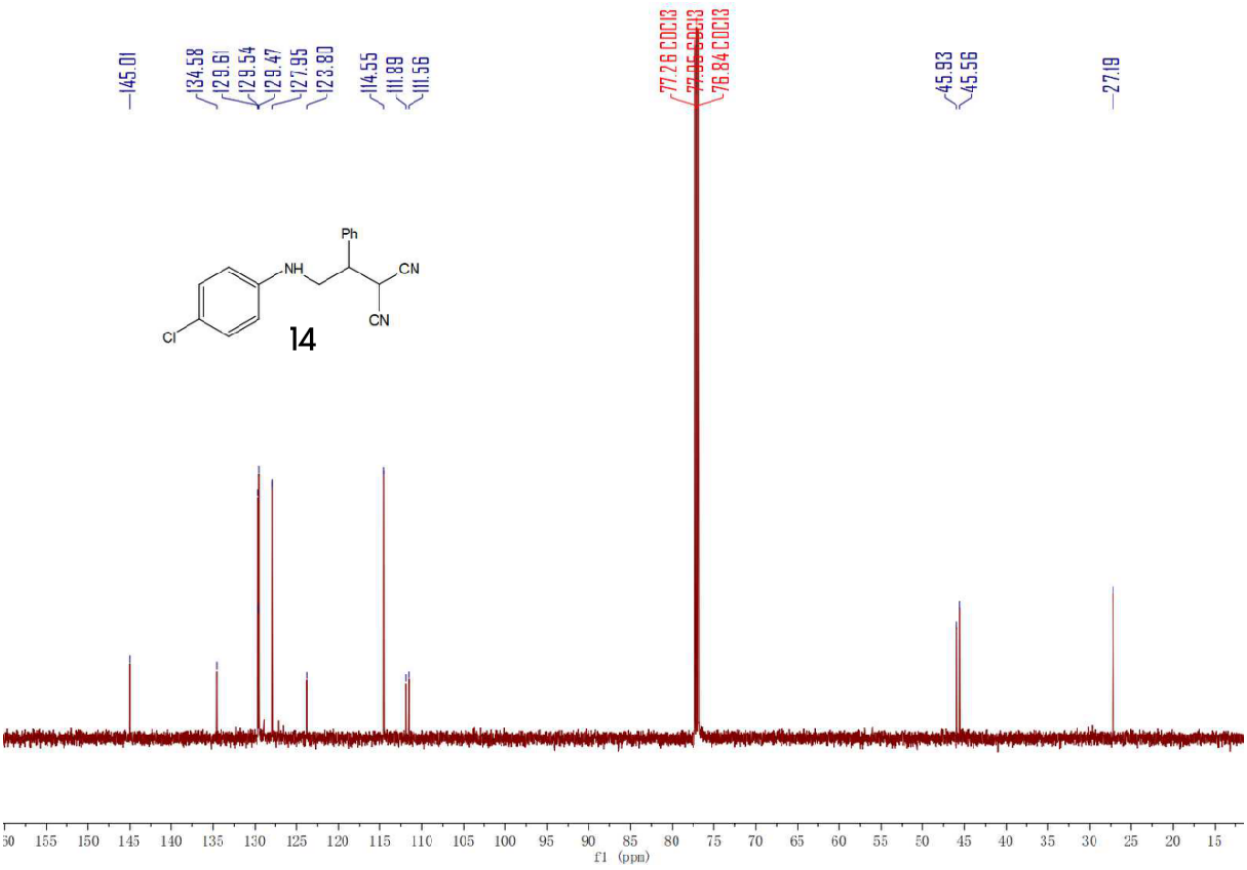
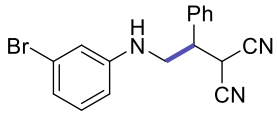
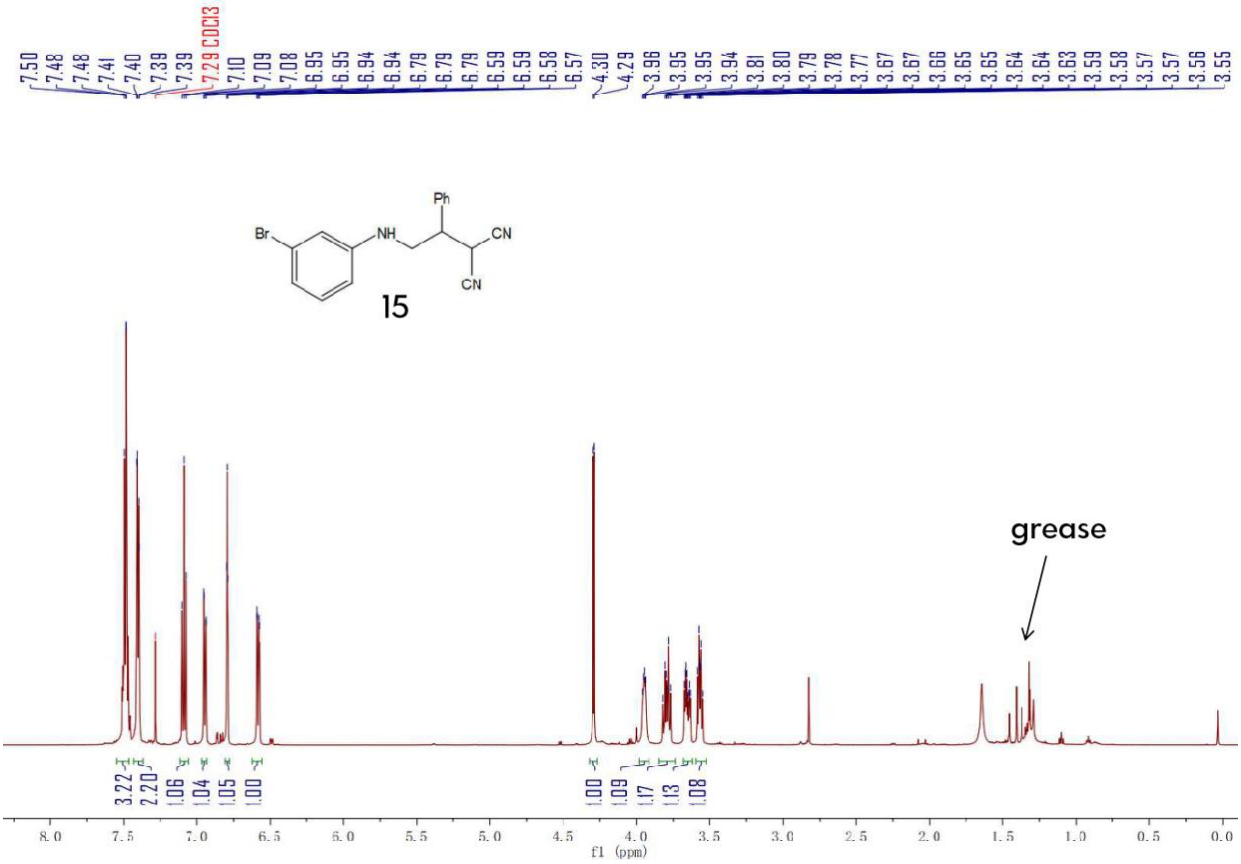
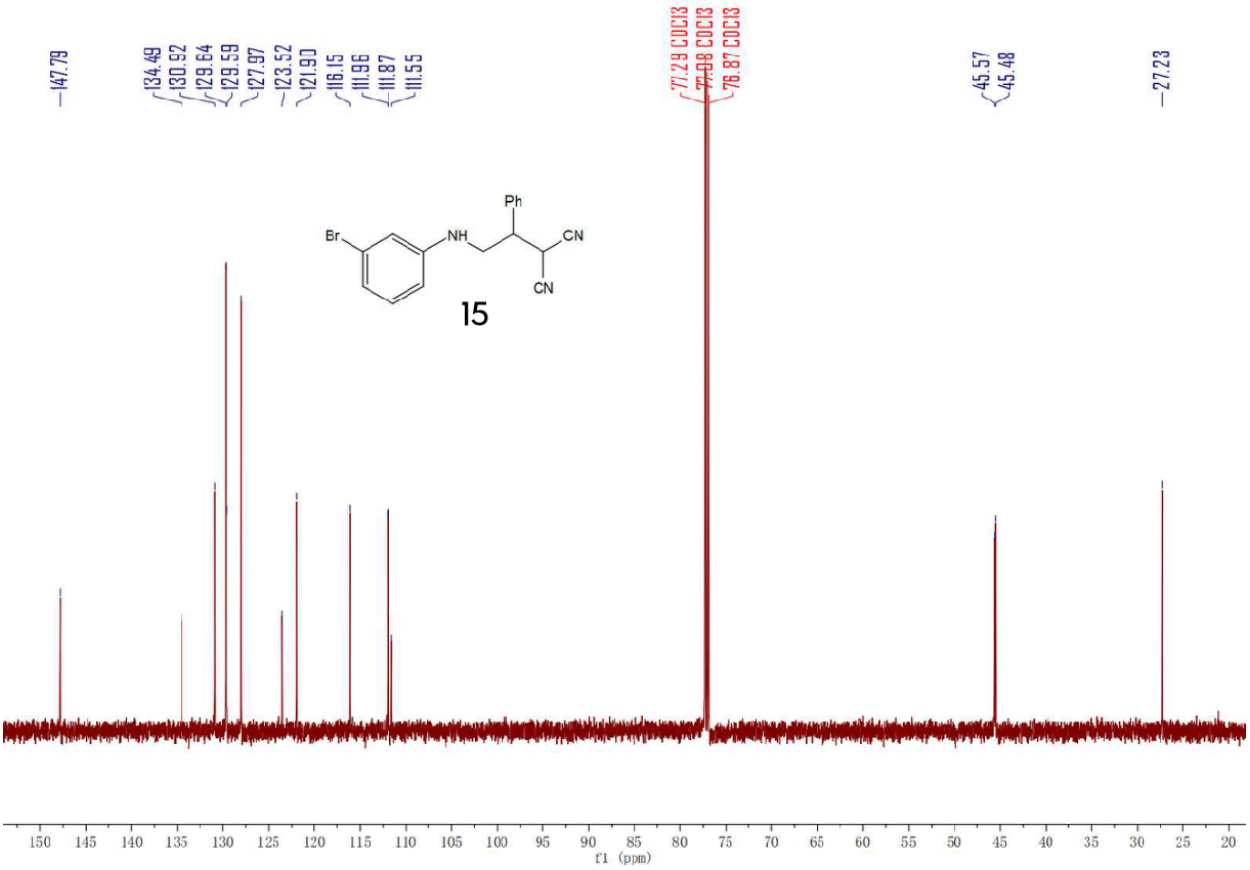
1.18
1.11
1.02
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

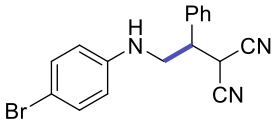

145.01
134.58
129.61
129.54
129.47
127.95
123.80
114.55
111.89
111.56
77.26 CDCl3
77.05 CDCl3
76.84 CDCl3
45.93
45.56
27.19
Ph
NH
CN
CN
Cl
14
f1 (ppm)



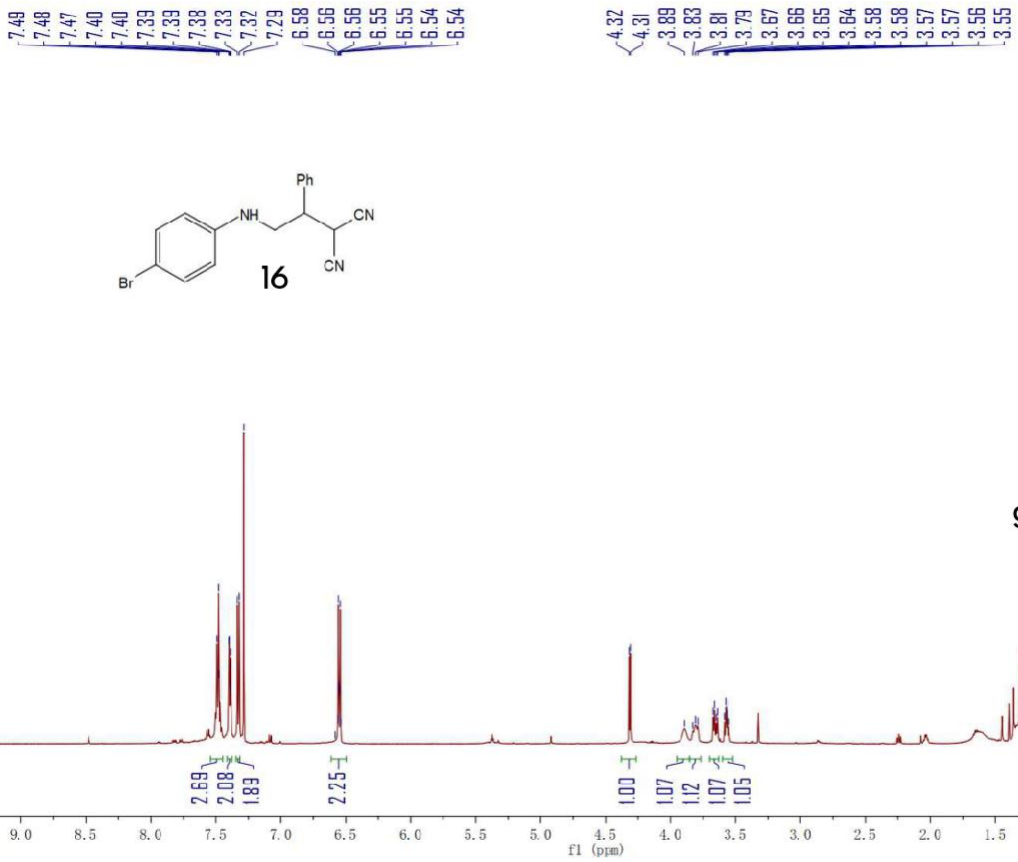
15 The reaction was set up following the general procedure using 3-bromo-N-methylbenzenamine (186 mg, 1 mmol) and benzylidenemalononitrile (31 mg, 0.2 mmol). After 16 hours, the reaction was purified following general work-up to give 42 mg (61 % yield) of the title compound. **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 7.54 – 7.44 (m, 3H), 7.44 – 7.37 (m, 2H), 7.09 (t, *J* = 8.0 Hz, 1H), 6.95 (m, *J* = 7.7, 1.6 Hz, 1H), 6.79 (t, *J* = 2.1 Hz, 1H), 6.58 (m, *J* = 8.1, 2.3 Hz, 1H), 4.29 (d, *J* = 5.6 Hz, 1H), 3.95 (m, *J* = 8.2, 4.4 Hz, 1H), 3.79 (m, *J* = 13.9, 8.2 Hz, 1H), 3.65 (m, *J* = 13.9, 6.3, 4.2 Hz, 1H), 3.57 (m, *J* = 8.5, 6.0 Hz, 1H); **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 147.79, 134.49, 130.92, 129.64, 129.59, 127.97, 123.52, 121.90, 116.15, 111.96, 111.87, 111.55, 45.57, 45.48, 27.23; MS2 (ES^+) exact mass calculated for $[M+H]^+$ ($C_{17}H_{15}BrN_3$) requires m/z 340.0, found m/z 340.0.

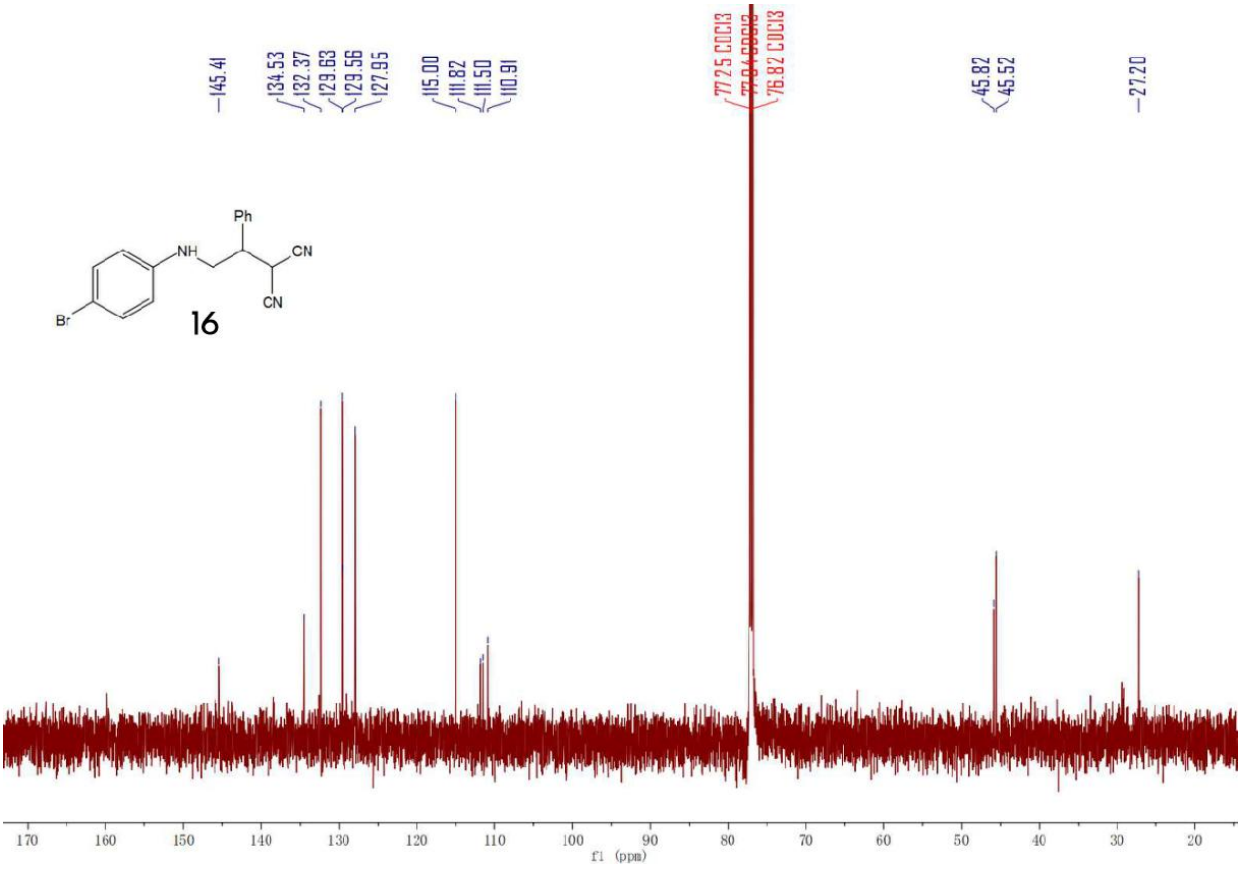

7.50
7.48
7.48
7.41
7.40
7.39
7.39
7.29 CDCl3
7.10
7.09
7.08
6.95
6.95
6.94
6.94
6.79
6.79
6.79
6.59
6.59
6.58
6.57
4.30
4.29
3.96
3.95
3.95
3.94
3.81
3.80
3.79
3.78
3.77
3.67
3.67
3.66
3.65
3.65
3.64
3.64
3.63
3.59
3.58
3.57
3.57
3.56
3.55
Ph
Br
NH
CN
CN
15
grease
3.22
2.20
1.06
1.04
1.05
1.00
1.00
1.09
1.17
1.13
1.08
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

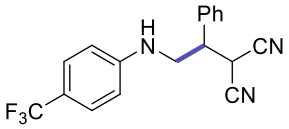

147.79
134.49
130.52
129.64
129.59
127.97
123.52
121.90
116.15
111.96
111.87
111.55
77.29 CDCl3
77.08 CDCl3
76.87 CDCl3
45.57
45.48
27.23
Br
NH
Ph
CN
CN
15
150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20
f1 (ppm)



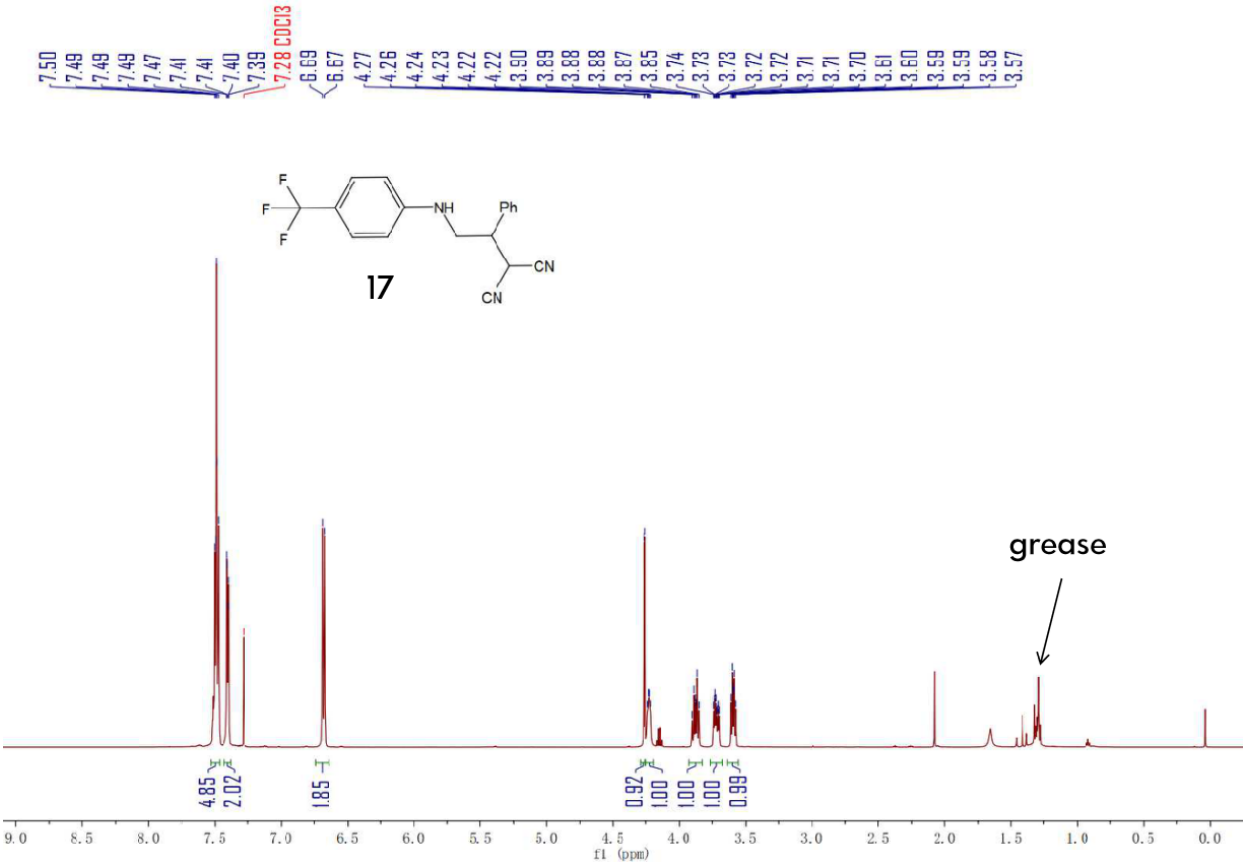
16 The reaction was set up following the general procedure using 4-bromo-N-methylbenzenamine (186 mg, 1 mmol) and benzylidenemalononitrile (31 mg, 0.2 mmol). After 16 hours, the reaction was purified following general work-up to give 22 mg (32 % yield) of the title compound. **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 7.52 – 7.43 (m, 3H), 7.39 (m, *J* = 7.7, 1.8 Hz, 2H), 7.36 – 7.30 (m, 2H), 6.60 – 6.52 (m, 2H), 4.31 (d, *J* = 5.5 Hz, 1H), 3.89 (s, 1H), 3.81 (t, *J* = 11.6 Hz, 1H), 3.65 (m, *J* = 13.9, 6.3 Hz, 1H), 3.57 (m, *J* = 8.5, 5.9 Hz, 1H); **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 145.41, 134.53, 132.37, 129.63, 129.56, 127.95, 115.00, 111.82, 111.50, 110.91, 45.82, 45.52, 27.20; MS2 (ES^+) exact mass calculated for $[M+H]^+$ ($C_{17}H_{15}BrN_3$) requires m/z 340.0, found m/z 340.0.

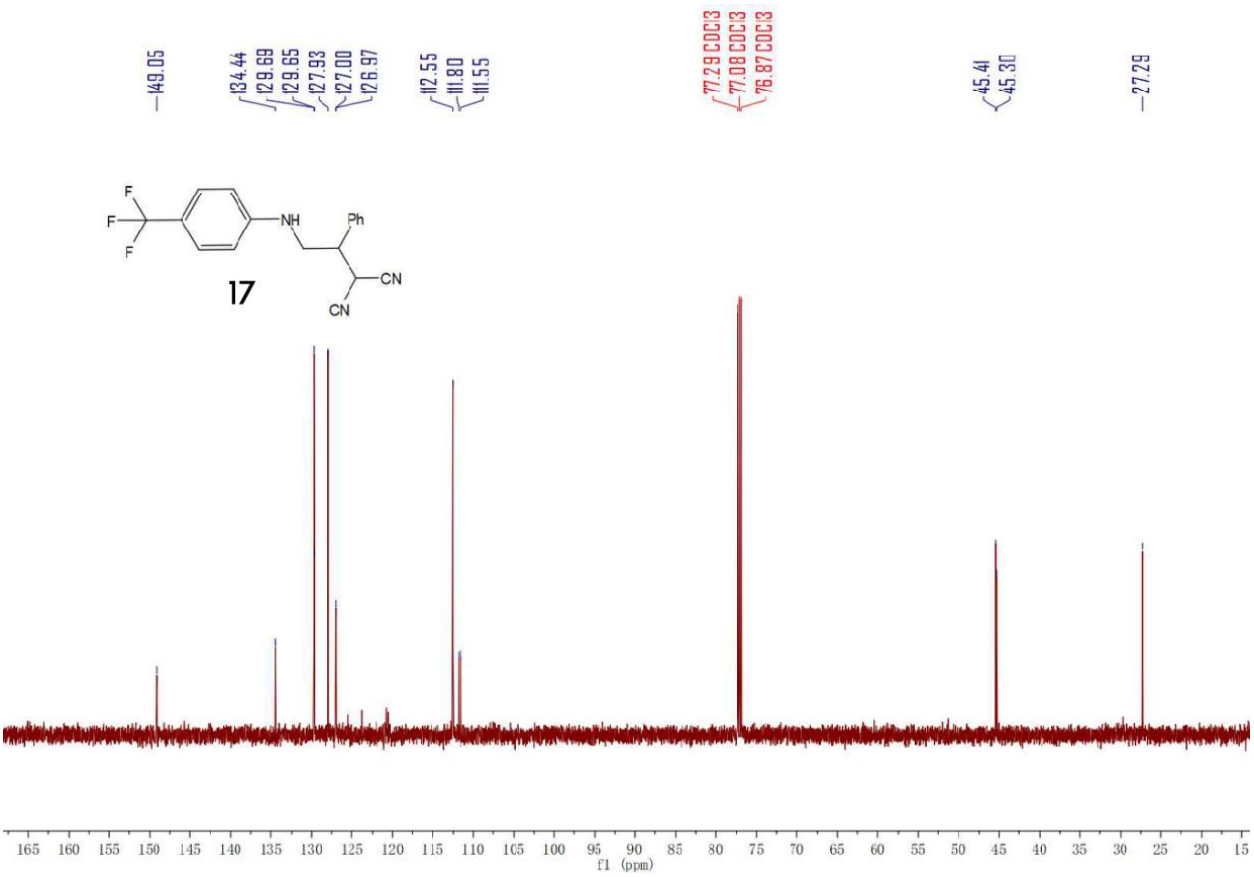

7.49
7.48
7.47
7.40
7.40
7.39
7.39
7.38
7.33
7.32
7.29
6.58
6.56
6.56
6.55
6.55
6.54
6.54
4.32
4.31
3.89
3.83
3.81
3.79
3.67
3.66
3.65
3.64
3.58
3.58
3.57
3.57
3.56
3.55
Ph
NH
CN
CN
Br
16
grease
2.69
2.08
1.83
2.25
1.00
1.07
1.12
1.07
1.05
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

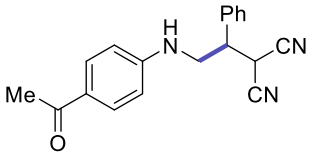

145.41
134.53
132.37
129.63
129.56
127.95
115.00
111.82
111.50
110.91
77.25 CDCl3
76.82 CDCl3
45.82
45.52
27.20
Ph
NH
CN
CN
Br
16
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
f1 (ppm)



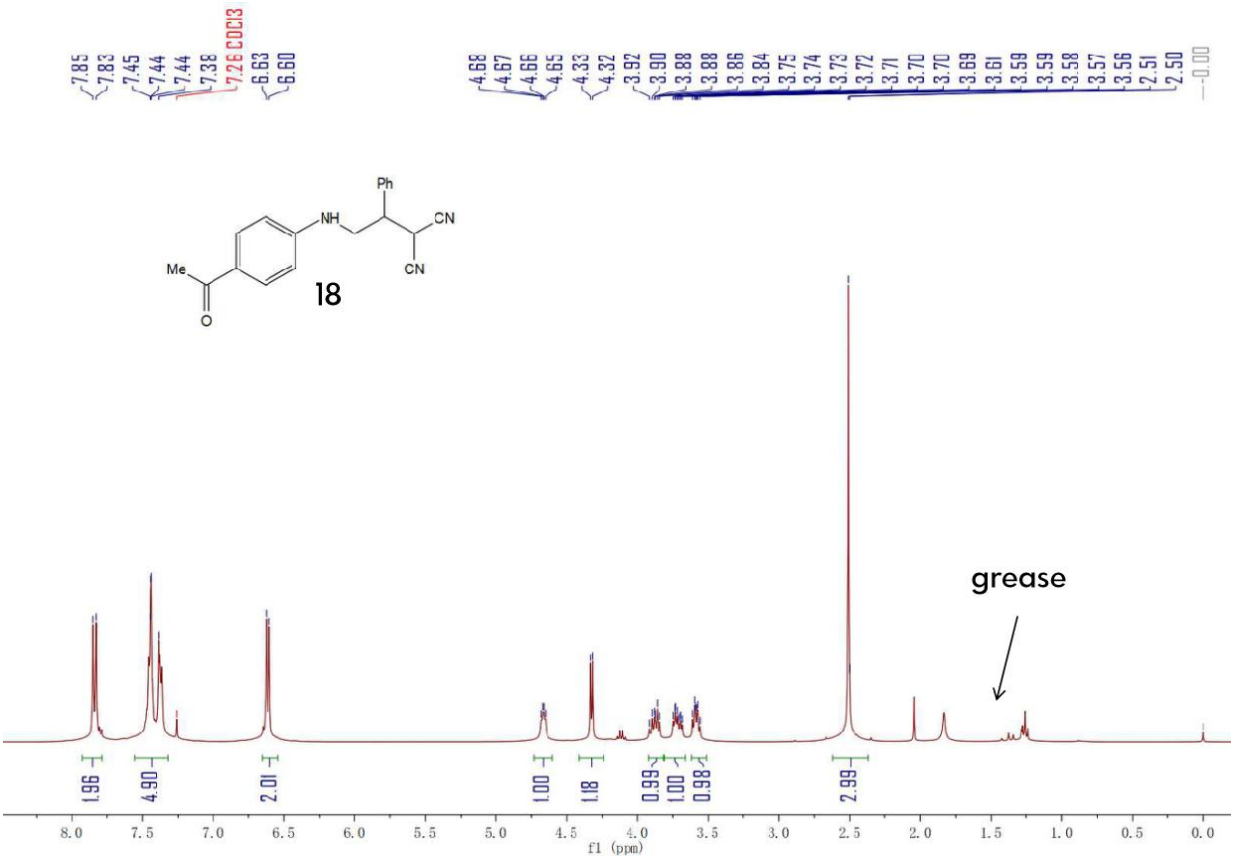
17 The reaction was set up following the general procedure using 4-trifluoromethyl-N-methylbenzenamine (175 mg, 1 mmol) and benzylidenemalononitrile (31 mg, 0.2 mmol). After 16 hours, the reaction was purified following general work-up to give 52.1 mg (79 % yield) of the title compound. **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 7.53 – 7.45 (m, 5H), 7.44 – 7.37 (m, 2H), 6.68 (d, *J* = 8.4 Hz, 2H), 4.24 (m, *J* = 21.1, 4.6 Hz, 2H), 3.88 (m, *J* = 14.2, 8.1 Hz, 1H), 3.72 (m, *J* = 14.2, 6.5, 4.4 Hz, 1H), 3.59 (m, *J* = 8.1, 6.0 Hz, 1H); **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 149.05, 134.44, 129.69, 129.65, 127.93, 127.02, 127.00, 126.97, 126.95, 112.55, 111.80, 111.55, 45.41, 45.30, 27.29; MS2 (ES^+) exact mass calculated for $[M+H]^+$ ($C_{18}H_{15}F_3N_3$) requires m/z 330.1, found m/z 330.1.

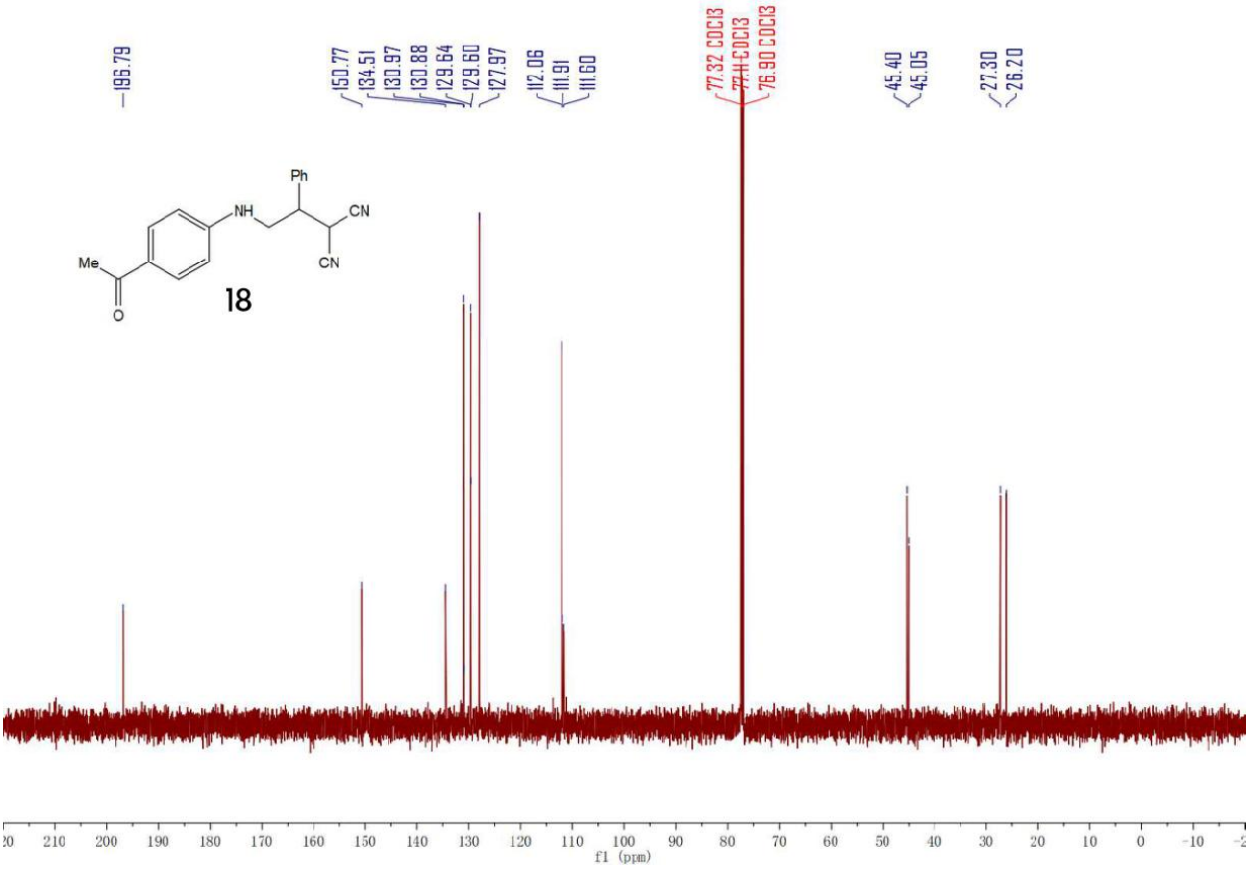

7.50
7.49
7.48
7.49
7.47
7.41
7.41
7.40
7.39
7.28 CDCl3
6.69
6.67
4.27
4.26
4.24
4.23
4.22
4.22
3.90
3.89
3.88
3.88
3.87
3.85
3.74
3.73
3.73
3.72
3.72
3.71
3.71
3.70
3.61
3.60
3.59
3.59
3.58
3.57
F
F
F
NH
Ph
CN
CN
17
grease
4.85
2.02
1.85
0.92
1.00
1.00
1.00
0.99
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

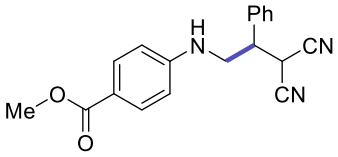

149.05
134.44
129.69
129.65
127.93
127.00
126.97
112.55
111.80
111.55
77.29 CDCl3
77.08 CDCl3
76.87 CDCl3
45.41
45.30
27.29
F
F
F
NH
Ph
CN
CN
17
165 160 155 150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15
f1 (ppm)



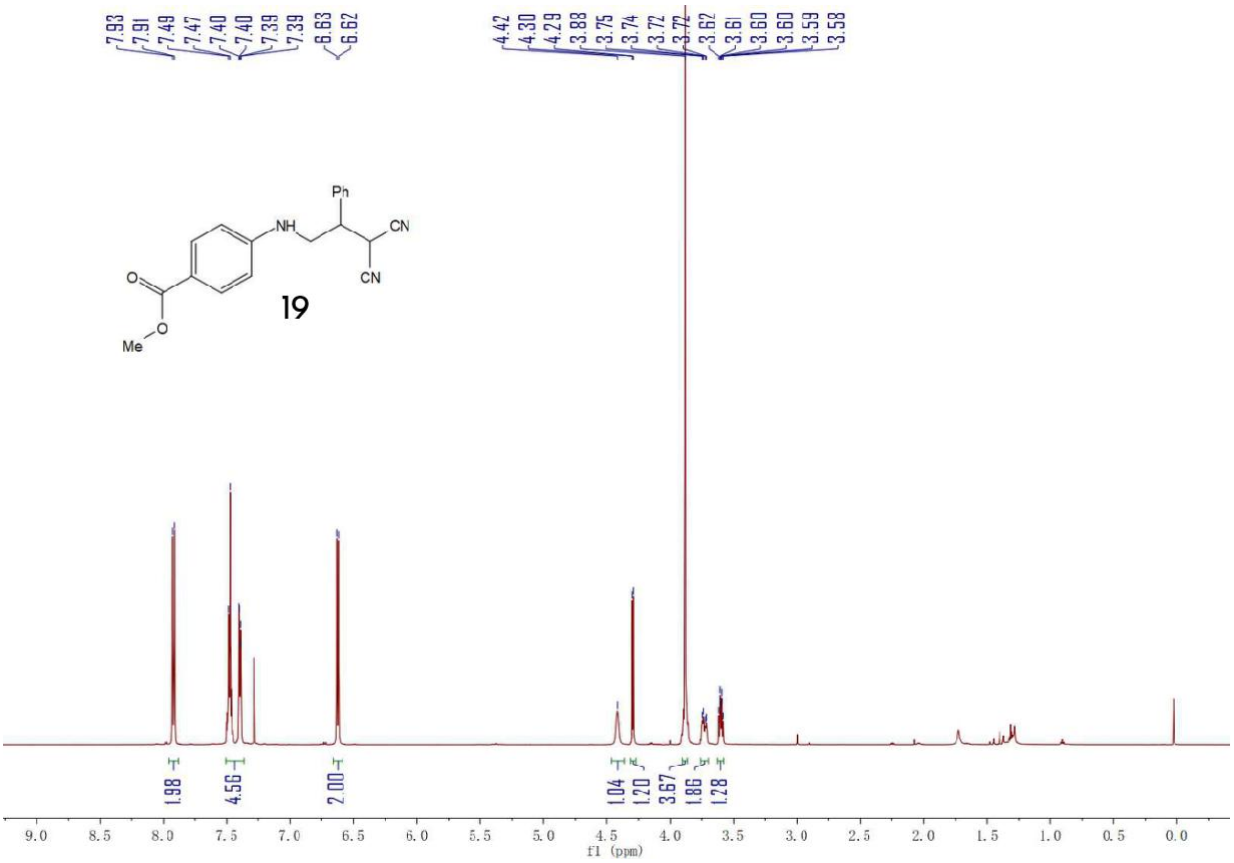
18 The reaction was set up following the general procedure using 4-N-methylaminoacetophenone (149 mg, 1 mmol) and benzylidenemalononitrile (31 mg, 0.2 mmol). After 16 hours, the reaction was purified following general work-up to give 38 mg (63 % yield) of the title compound. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.88 – 7.76 (m, 2H), 7.51 – 7.33 (m, 5H), 6.68 – 6.57 (m, 2H), 4.67 (m, *J* = 7.6, 4.8 Hz, 1H), 4.32 (d, *J* = 5.6 Hz, 1H), 3.88 (m, *J* = 14.0, 8.0 Hz, 1H), 3.72 (m, *J* = 14.0, 6.3, 4.6 Hz, 1H), 3.58 (m, *J* = 8.4, 6.0 Hz, 1H), 2.51 (s, 3H); **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 196.79, 150.77, 134.51, 130.97, 130.88, 129.64, 129.60, 127.97, 112.06, 111.91, 111.60, 45.40, 45.05, 27.30, 26.20; MS2 (ES^{+}) exact mass calculated for $[M+H]^{+}$ ($C_{19}H_{18}N_3O$) requires m/z 304.1, found m/z 304.1.


7.85
7.83
7.45
7.44
7.44
7.38
7.26 CDCl3
6.63
6.60
4.68
4.67
4.66
4.65
4.33
4.32
3.92
3.90
3.88
3.88
3.86
3.84
3.75
3.74
3.73
3.72
3.71
3.70
3.70
3.69
3.61
3.59
3.59
3.58
3.57
3.56
2.51
2.50
0.00
Ph
NH
CN
CN
Me
O
18
grease
1.96
4.90
2.01
1.00
1.18
0.99
1.00
0.98
2.99
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


196.79
150.77
134.51
130.97
130.88
129.64
129.60
127.97
112.06
111.91
111.60
77.32 CDCl3
77.11 CDCl3
76.90 CDCl3
45.40
45.05
27.30
26.20
Ph
NH
CN
CN
Me
O
18
f1 (ppm)



19 The reaction was set up following the general procedure using methyl 4-methylaminobenzoate (165 mg, 1 mmol) and benzylidenemalononitrile (31 mg, 0.2 mmol). After 16 hours, the reaction was purified following general work-up to give 52 mg (82 % yield) of the title compound. **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 7.92 (d, *J* = 8.8 Hz, 2H), 7.45-7.51 (m, *J* = 7.5 Hz, 3H), 7.39 (m, *J* = 7.7, 1.8 Hz, 2H), 6.63 (d, *J* = 8.8 Hz, 2H), 4.42 (s, 1H), 4.29 (d, *J* = 5.6 Hz, 1H), 3.88 (s, 3H), 3.69 – 3.78 (m, 2H), 3.60 (m, *J* = 8.4, 6.1 Hz, 1H); **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 167.09, 150.36, 134.45, 131.77, 129.63 (d, *J* = 6.2 Hz), 127.95, 120.16, 112.14, 111.81, 111.53, 51.78, 45.42, 45.16, 27.28; MS2 (ES^+) exact mass calculated for $[M+H]^+$ ($C_{19}H_{18}N_3O_2$) requires m/z 320.1, found m/z 320.1.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7.47
7.40
7.40
7.39
7.39
6.63
6.62
4.42
4.30
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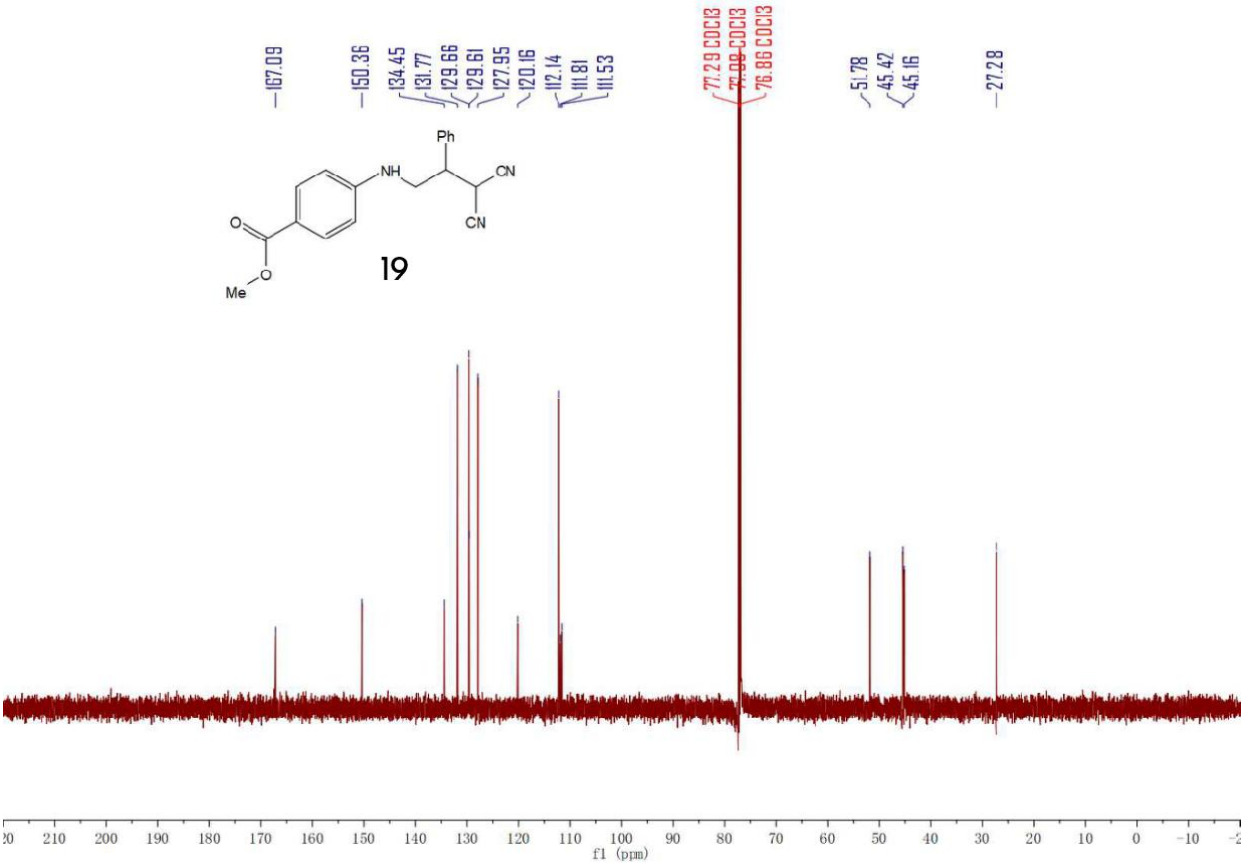
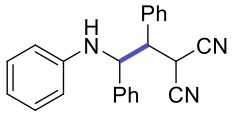
3.88
3.75
3.74
3.72
3.72
3.72
3.62
3.61
3.60
3.60
3.59
3.58
Ph
NH
CN
CN
O
O
Me
19
1.98
4.56
2.00
1.04
1.20
3.67
1.86
1.28
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


167.09
150.36
134.45
131.77
129.66
129.61
127.95
120.16
112.14
111.81
111.53
77.29 CDCl3
77.09 CDCl3
76.86 CDCl3
51.78
45.42
45.16
27.28
Ph
NH
CN
CN
O
O
Me
19
f1 (ppm)



20 The reaction was set up following the general procedure using benzylaniline (183 mg, 1 mmol) and benzylidenemalononitrile (31 mg, 0.2 mmol). After 16 hours, the reaction was purified following general work-up to give 49 mg (72 % yield) of the title compound. **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 7.61 – 7.56 (m, 3H), 7.46 – 7.5 (m, 5H), 7.36 – 7.44 (m, 2H), 7.13 – 7.05 (t, 2H), 6.73 (t, *J* = 7.2 Hz, 1H), 6.55 – 6.50 (d, 2H), 5.00 (d, *J* = 8.2 Hz, 1H), 4.06 (d, *J* = 6.5 Hz, 1H), 3.88 (s, 1H), 3.53 (m, *J* = 8.2, 6.5 Hz, 1H); **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 146.09, 139.57, 132.46, 129.75, 129.49, 129.22, 128.83, 128.77, 126.91, 119.20, 114.54, 112.08, 111.44, 58.90, 53.51, 27.27; MS2 (ES^+) exact mass calculated for $[M+H]^+$ ($C_{23}H_{20}N_3$) requires m/z 338.1, found m/z 338.1.


7.47
7.47
7.46
7.46
7.42
7.42
7.41
7.41
7.41
7.34
7.29
7.10
7.09
7.08
6.74
6.73
6.72
6.72
6.53
6.51
5.01
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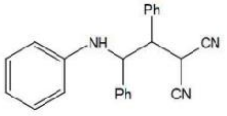
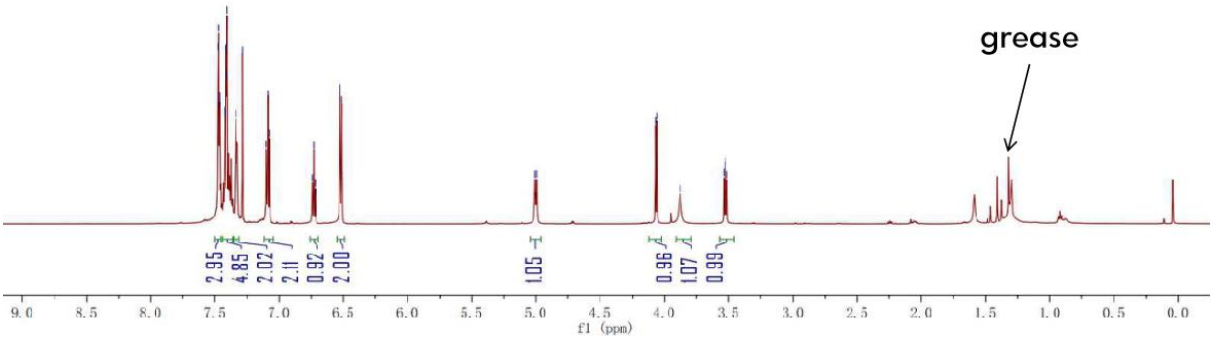
4.07
4.06
3.88
3.54
3.53
3.52
3.51


Ph
NH
CN
Ph
CN

20


grease
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2.11
0.92
2.00
1.05
0.96
1.07
0.99
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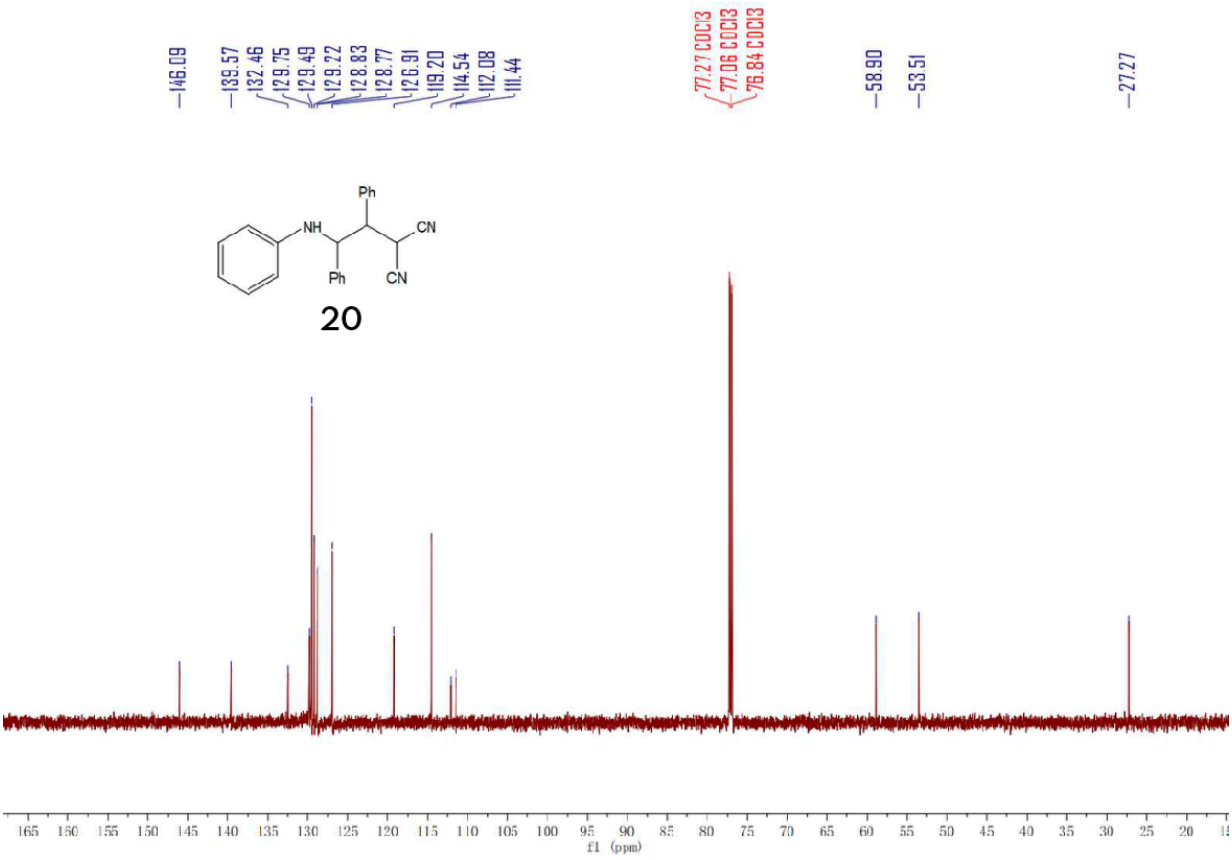
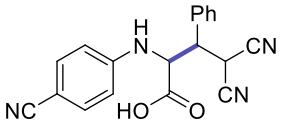
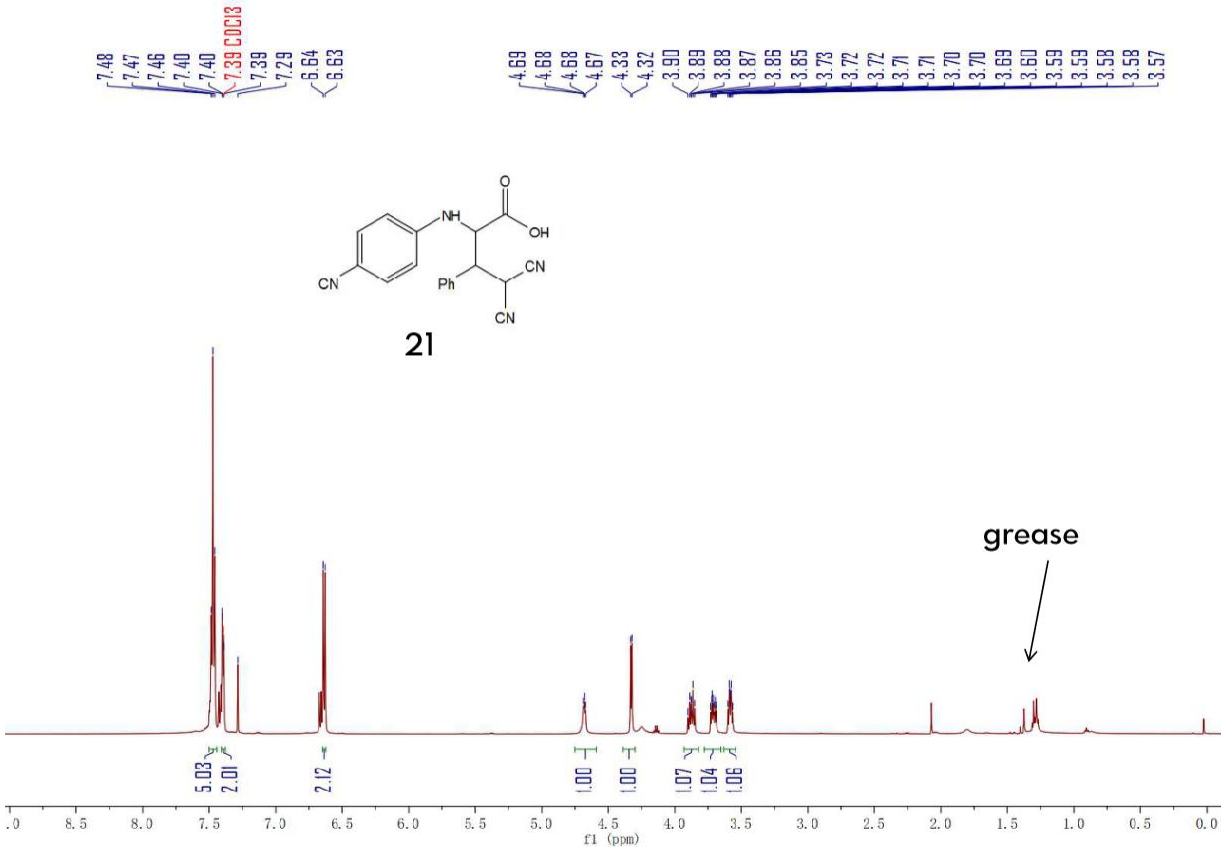
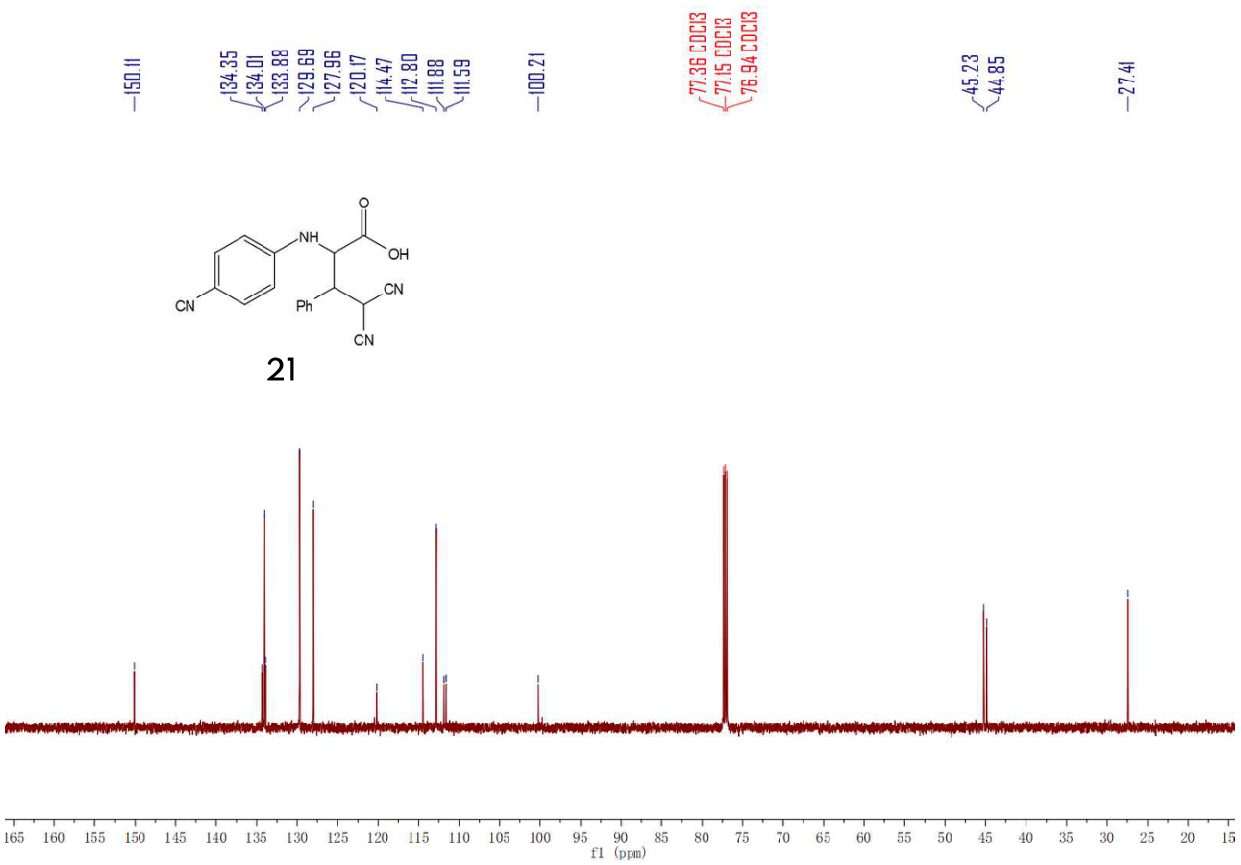
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

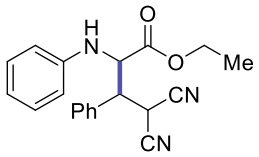

146.09
139.57
132.46
129.75
129.49
129.22
128.83
128.77
126.91
119.20
114.54
112.08
111.44
77.27 CDCl3
77.06 CDCl3
76.84 CDCl3
58.90
53.51
27.27
Ph
NH
CN
Ph
CN
20
f1 (ppm)



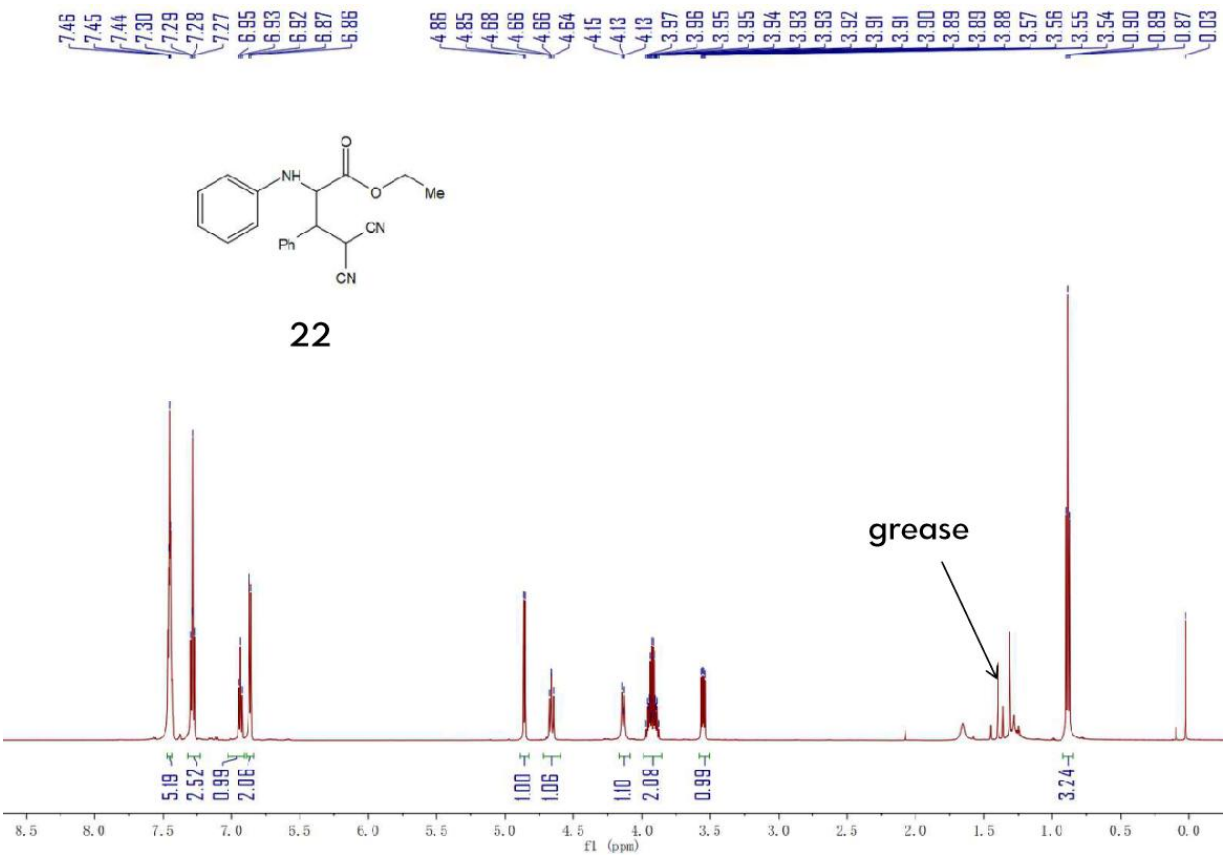
21 The reaction was set up following the general procedure using N-(4-cyanophenyl) glycine (176 mg, 1 mmol) and benzylidenemalononitrile (31 mg, 0.2 mmol). After 16 hours, the reaction was purified following general work-up to give 45 mg (68 % yield) of the title compound. **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 7.43 – 7.55(m, 5H), 7.37– 7.45 (m, 2H), 6.65 (d, *J* = 17.0, 8.7 Hz, 2H), 4.68 (m, *J* = 7.7, 4.8 Hz, 1H), 4.33 (d, *J* = 5.7, 2.1 Hz, 1H), 3.88 (m, *J* = 14.3, 8.0 Hz, 1H), 3.71 (m, *J* = 14.3, 6.5, 4.7 Hz, 1H), 3.58 (m, *J* = 8.4, 6.1 Hz, 1H); **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 150.11, 134.35, 134.01, 133.88, 129.69, 127.96, 120.17, 114.47, 112.80, 111.88, 111.59, 100.21, 45.23, 44.85, 27.41; MS2 (ES^+) exact mass calculated for $[M+H]^+$ ($C_{19}H_{15}N_4O_2$) requires m/z 331.1, found m/z 331.1.

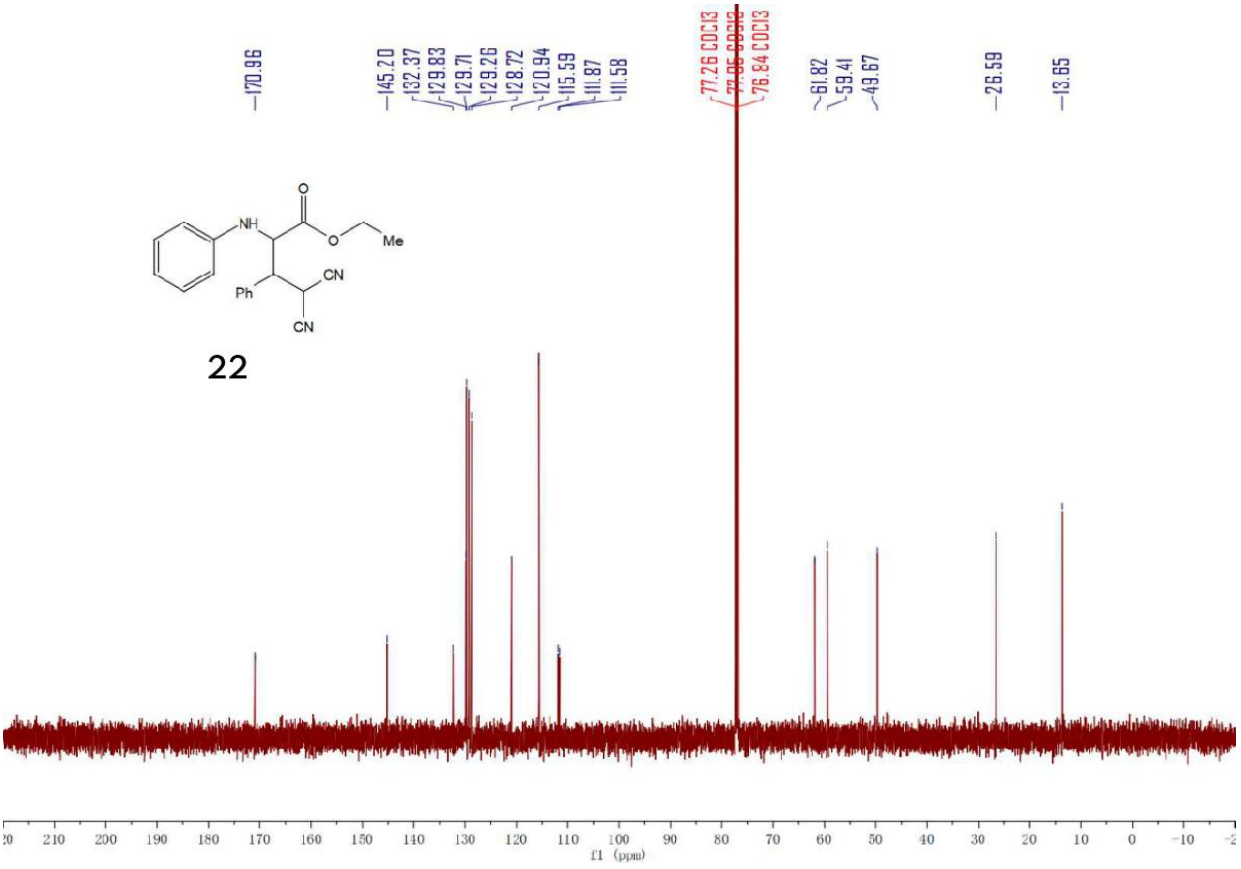

7.48
7.47
7.46
7.40
7.40
7.39 CDCl3
7.39
7.29
6.64
6.63
4.69
4.68
4.68
4.67
4.33
4.32
3.90
3.89
3.88
3.87
3.86
3.85
3.73
3.72
3.72
3.71
3.71
3.70
3.70
3.69
3.60
3.59
3.59
3.58
3.58
3.57
NH
O
OH
CN
Ph
CN
CN
21
grease
5.03
2.01
2.12
1.00
1.00
1.07
1.04
1.06
f1 (ppm)

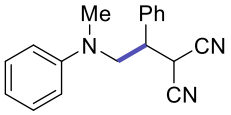

150.11
134.35
134.01
133.88
129.69
127.96
120.17
114.47
112.80
111.88
111.59
100.21
77.36 CDCl3
77.15 CDCl3
76.94 CDCl3
45.23
44.85
27.41
NH
O
OH
CN
Ph
CN
CN
21
165 160 155 150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15
f1 (ppm)



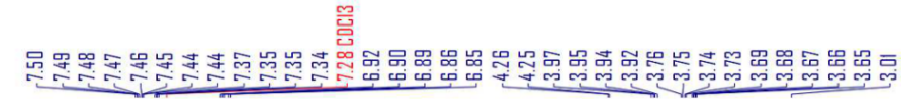
22 The reaction was set up following the general procedure using N-phenylglycine ethyl ester (179 mg, 1 mmol) and benzylidenemalononitrile (31 mg, 0.2 mmol). After 16 hours, the reaction was purified following general work-up to give 35 mg (53 % yield) of the title compound. **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 7.48 – 7.41 (m, 5H), 7.31 – 7.25 (m, 2H), 6.93 (m, *J* = 7.3, 1.1 Hz, 1H), 6.89 – 6.84 (m, 2H), 4.86 (d, *J* = 5.5 Hz, 1H), 4.66 (m, *J* = 11.3, 10.0 Hz, 1H), 4.14 (d, *J* = 11.3 Hz, 1H), 3.93 – 3.86 (m, 2H), 3.55 (m, *J* = 10.0, 5.5 Hz, 1H), 0.89 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 170.96, 145.20, 132.37, 129.83, 129.71, 129.26, 128.72, 120.94, 115.59, 111.87, 111.58, 61.82, 59.41, 49.67, 26.59, 13.65; MS2 (ES^+) exact mass calculated for $[M+H]^+$ ($C_{20}H_{20}N_3O_2$) requires m/z 334.1, found m/z 334.1.


7.46
7.45
7.44
7.30
7.29
7.28
7.27
6.95
6.93
6.92
6.87
6.86
4.86
4.85
4.68
4.66
4.66
4.64
4.15
4.13
4.13
3.97
3.96
3.95
3.95
3.94
3.93
3.93
3.92
3.91
3.91
3.90
3.89
3.89
3.88
3.57
3.56
3.55
3.54
0.90
0.89
0.87
0.03
NH
O
O
Me
CN
Ph
CN
22
grease
5.19
2.52
0.99
2.06
1.00
1.06
1.10
2.08
0.99
3.24
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


170.96
145.20
132.37
129.83
129.71
129.26
128.72
120.94
115.59
111.87
111.58
77.26 CDCl3
78.84 CDCl3
61.82
59.41
49.67
26.59
13.65
NH
O
O
Me
CN
Ph
CN
22
f1 (ppm)



23 The reaction was set up following the general procedure using N,N-dimethylaniline (121 mg, 1 mmol) and benzylidenemalononitrile (31 mg, 0.2 mmol). After 16 hours, the reaction was purified following general work-up to give 34 mg (61 % yield) of the title compound. **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 7.54 – 7.42 (m, 5H), 7.40 – 7.32 (t, 2H), 6.90 (t, *J* = 7.3 Hz, 1H), 6.86 (d, *J* = 8.2 Hz, 2H), 4.26 (d, *J* = 4.7 Hz, 1H), 3.94 (m, *J* = 15.0, 10.1 Hz, 1H), 3.75 (m, *J* = 15.0, 5.2 Hz, 1H), 3.67 (m, *J* = 10.0, 5.0 Hz, 1H), 3.01 (s, 3H); **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 148.55, 134.94, 129.65, 129.41 (d, *J* = 5.0 Hz), 128.16, 118.75, 113.81, 112.23, 111.83, 55.36, 44.79, 40.85, 27.02; MS2 (ES^+) exact mass calculated for $[M+H]^+$ ($C_{18}H_{18}N_3$) requires m/z 276.1, found m/z 276.1.


7.50
7.49
7.48
7.47
7.46
7.45
7.44
7.44
7.37
7.35
7.35
7.34
7.28 CDCl3
6.92
6.90
6.89
6.86
6.85
4.26
4.25
3.97
3.95
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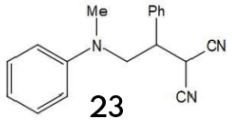
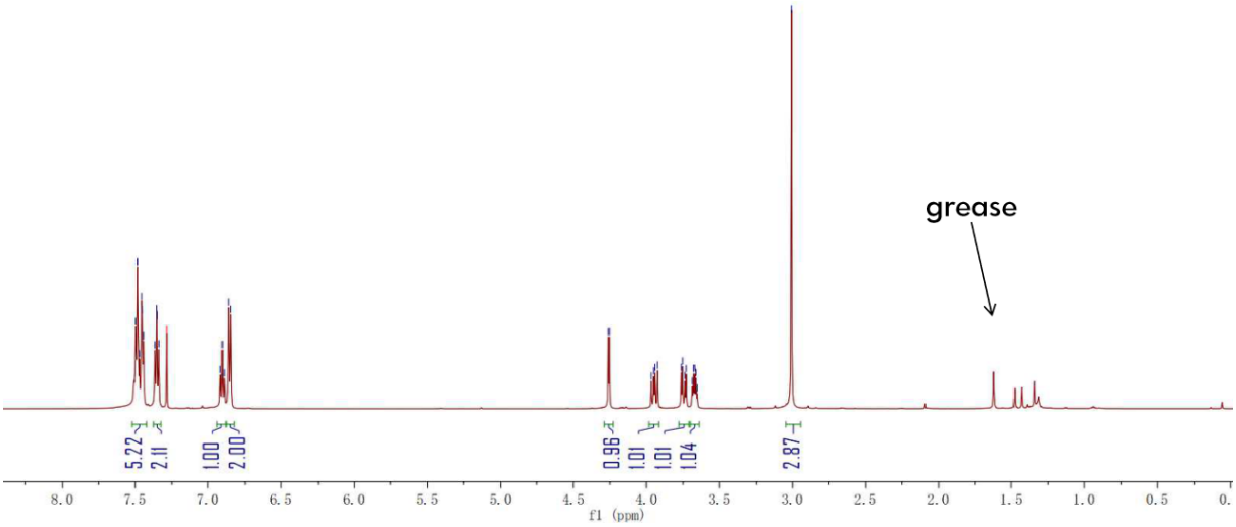
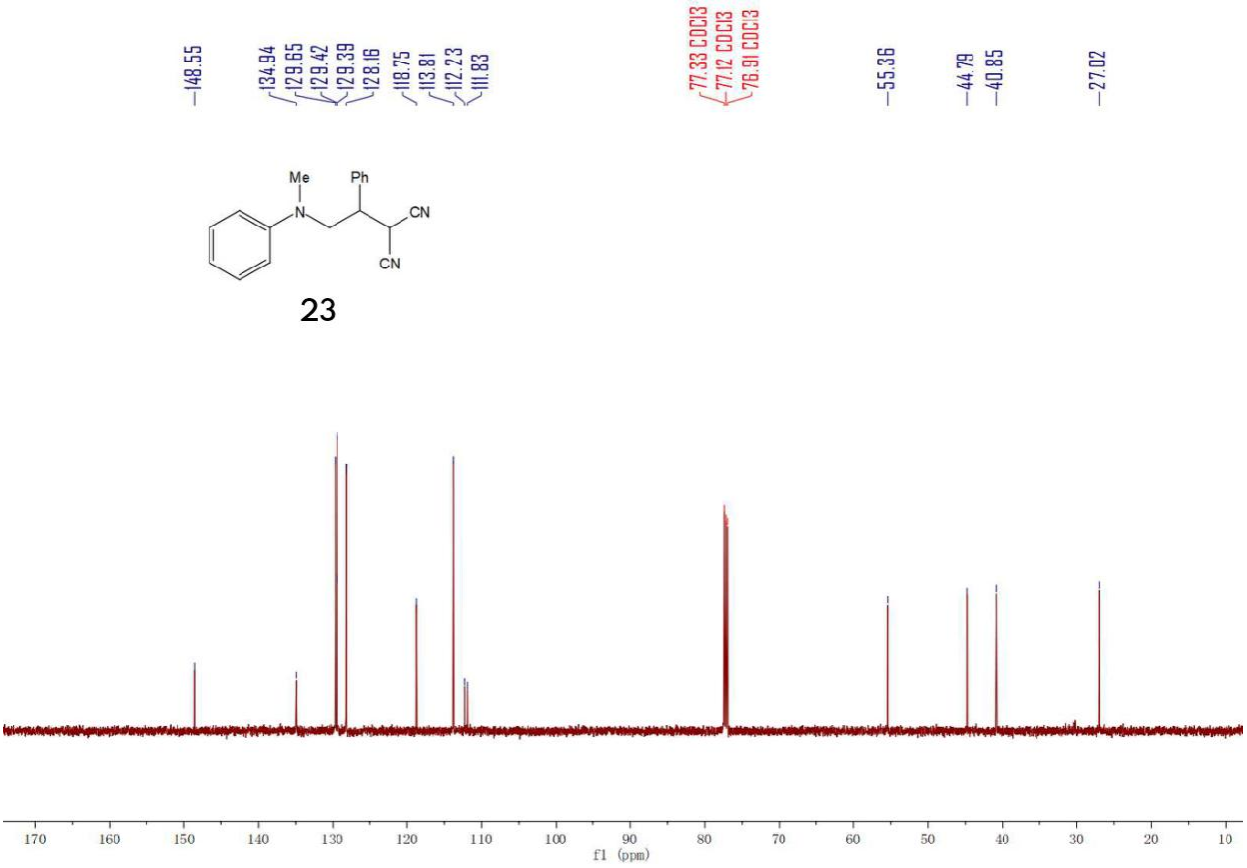
3.69
3.68
3.67
3.66
3.65
3.01

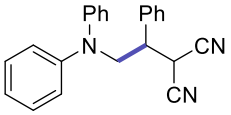

Me
Ph
N
CN
CN

23

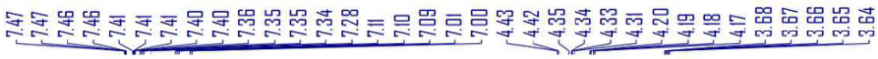

grease
5.22
2.11
1.00
2.00
0.96
1.01
1.01
1.04
2.87
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.
f1 (ppm)

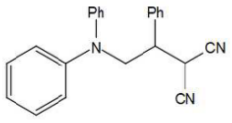

148.55
134.94
129.65
129.42
129.39
128.16
118.75
113.81
112.23
111.83
77.33 CDCl3
77.12 CDCl3
76.91 CDCl3
55.36
44.79
40.85
27.02
Me
Ph
N
CN
CN
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

23

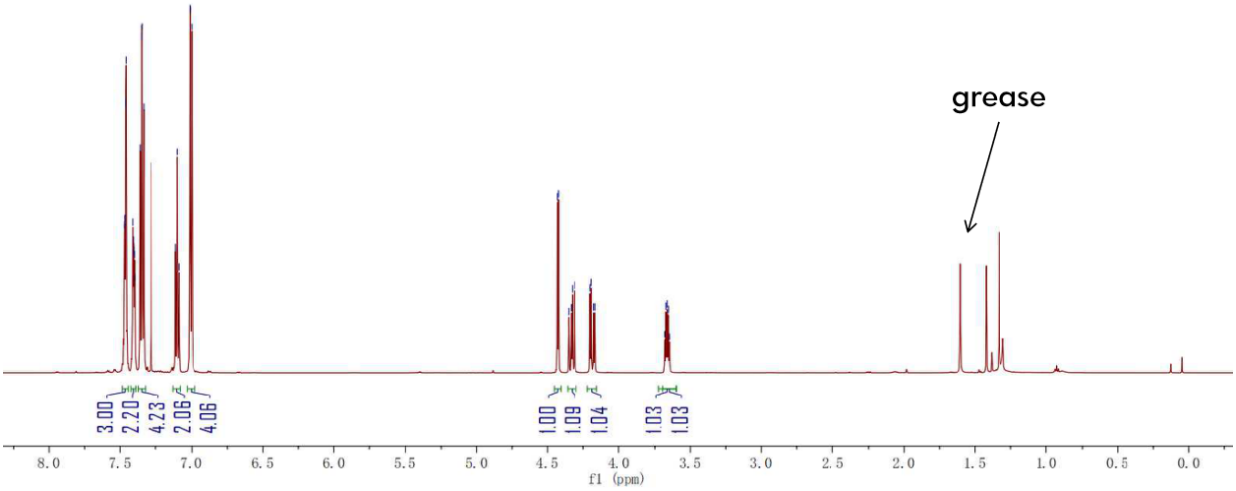


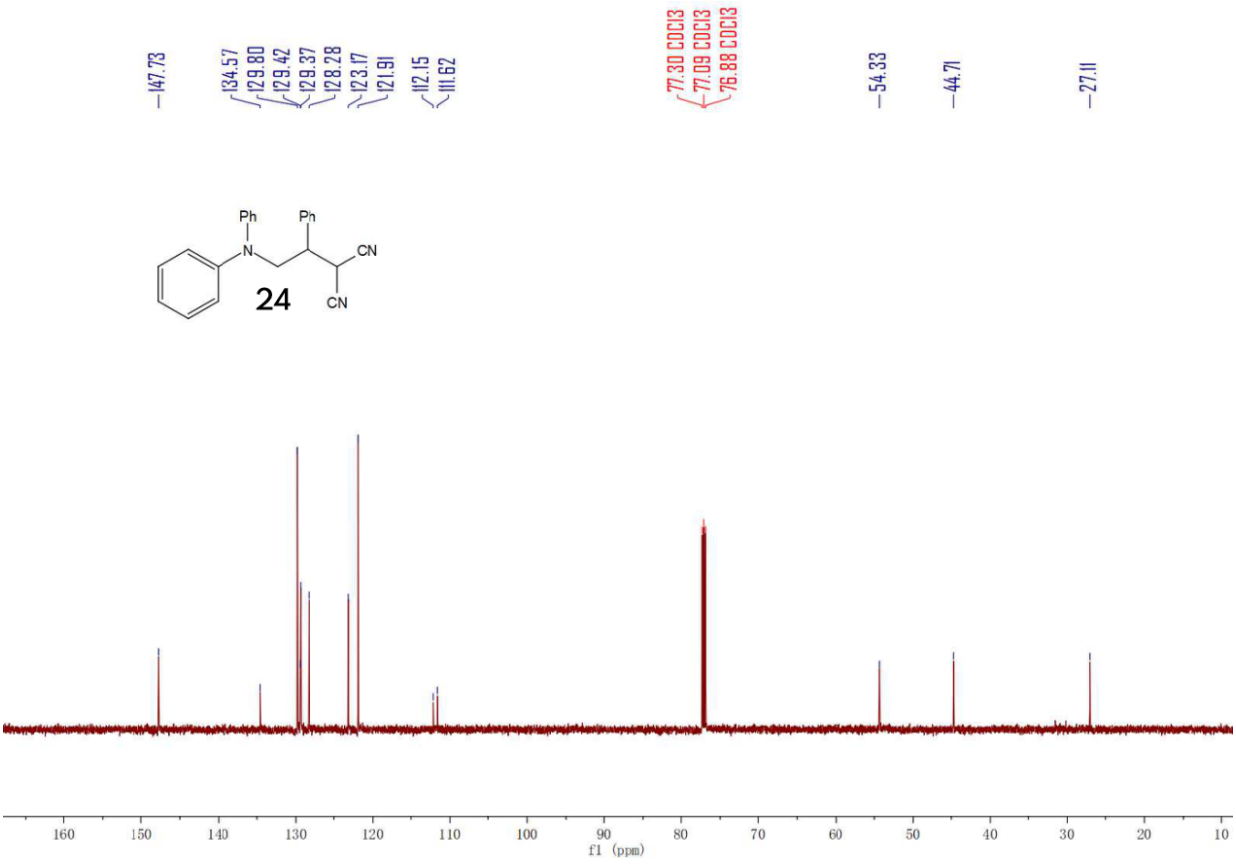
24 The reaction was set up following the general procedure using N-methyl-N-phenylbenzenamine (183 mg, 1 mmol) and benzylidenemalononitrile (31 mg, 0.2 mmol). After 16 hours, the reaction was purified following general work-up to give 47 mg (69 % yield) of the title compound. **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 7.48-7.46 (m, *J* = 5.0, 1.9 Hz, 3H), 7.43 – 7.39 (m, 2H), 7.38 – 7.32(m, 4H), 7.10-7.08 (m, *J* = 7.3, 1.2 Hz, 2H), 7.03 – 6.98 (m, 4H), 4.43 (d, *J* = 4.5 Hz, 1H), 4.33 (m, *J* = 15.0, 10.1 Hz, 1H), 4.19 (m, *J* = 15.0, 5.1 Hz, 1H), 3.66 (m, *J* = 9.8, 4.8 Hz, 1H); **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 147.73, 134.57, 129.80, 129.42, 129.37, 128.28, 123.17, 121.91, 112.15, 111.62, 54.33, 44.71, 27.11; MS2 (ES^+) exact mass calculated for $[M+H]^+$ ($C_{23}H_{20}N_3$) requires m/z 338.1, found m/z 338.1.

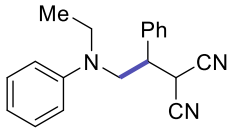

7.47
7.47
7.46
7.46
7.41
7.41
7.41
7.40
7.40
7.36
7.35
7.35
7.34
7.28
7.11
7.10
7.09
7.01
7.00
4.43
4.42
4.35
4.34
4.33
4.31
4.20
4.19
4.18
4.17
3.68
3.67
3.66
3.65
3.64


Ph
Ph
N
CN
CN

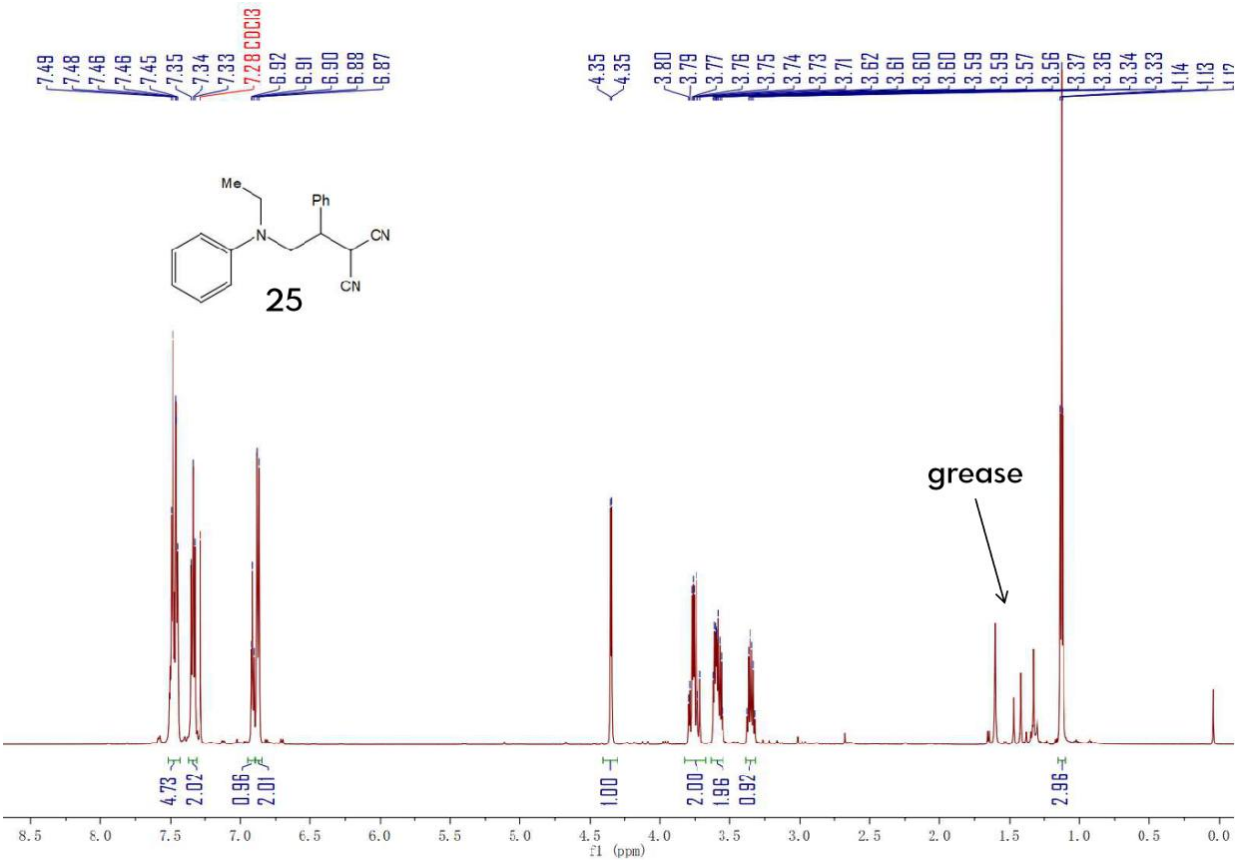
24

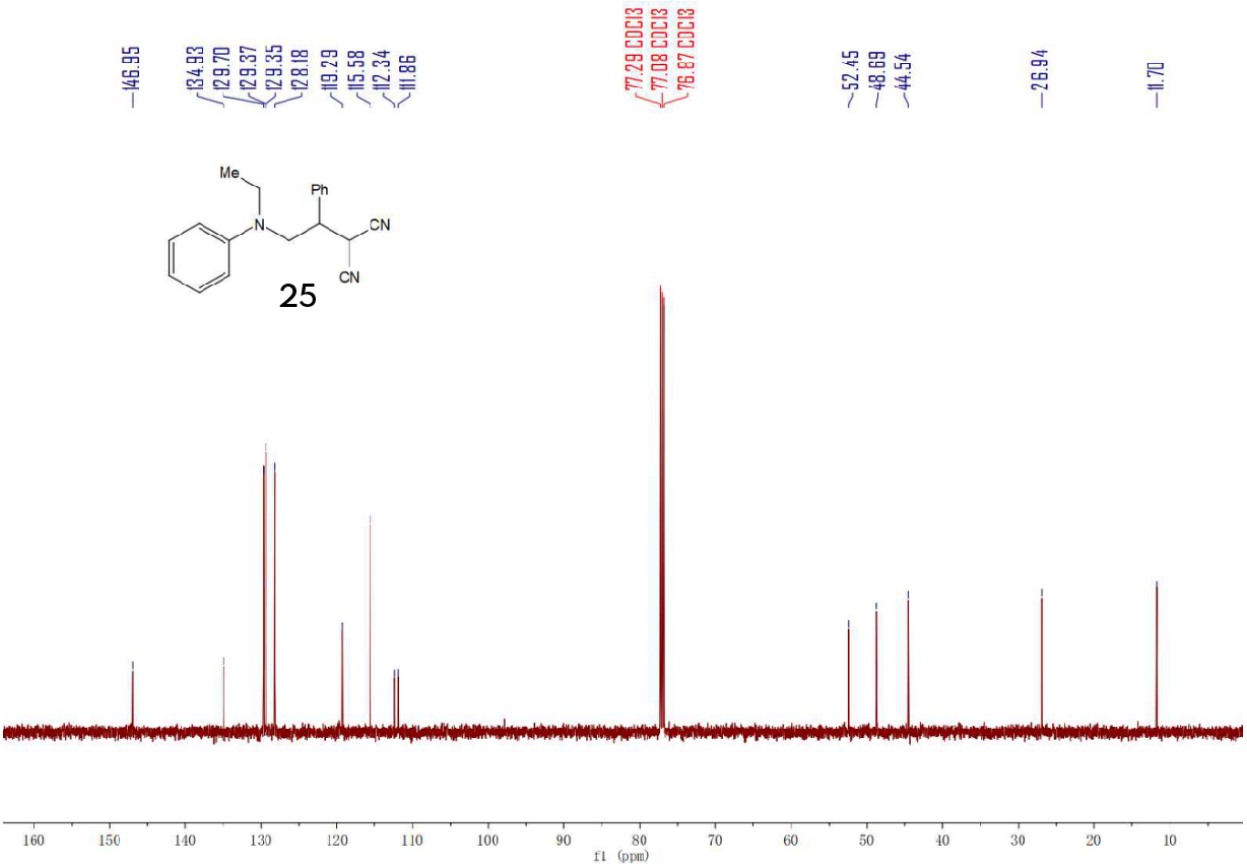

grease
3.00
2.20
4.23
2.06
4.06
1.00
1.09
1.04
1.03
1.03
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

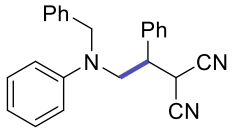

147.73
134.57
129.80
129.42
129.37
128.28
123.17
121.91
112.15
111.62
77.30 CDCl3
77.09 CDCl3
76.88 CDCl3
54.33
44.71
27.11
Ph
Ph
N
CN
CN
24
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)



25 The reaction was set up following the general procedure using N-ethyl-N-methylaniline (135 mg, 1 mmol) and benzylidenemalononitrile (31 mg, 0.2 mmol). After 16 hours, the reaction was purified following general work-up to give 41 mg (69 % yield) of the title compound. **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 7.53 – 7.43 (m, 5H), 7.34 (m, *J* = 7.3, 2.2 Hz, 2H), 6.93-6.91 (t, *J* = 7.9, 6.8 Hz, 1H), 6.9– 6.85 (d, 2H), 4.35 (d, *J* = 4.4 Hz, 1H), 3.8-3.78 (m, *J* = 14.9, 5.2 Hz, 2H), 3.64 – 3.53(m, 2H), 3.35 (m, *J* = 14.3, 7.0 Hz, 1H), 1.13 (t, *J* = 7.0 Hz, 3H); **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 146.95, 134.93, 129.70, 129.37, 129.35, 128.18, 119.29, 115.58, 112.34, 111.86, 52.45, 48.69, 44.54, 26.94, 11.70; MS2 (ES^+) exact mass calculated for $[M+H]^+$ ($C_{19}H_{20}N_3$) requires m/z 290.1, found m/z 290.1.


7.49
7.48
7.46
7.46
7.45
7.35
7.34
7.33
7.28 CDCl3
6.92
6.91
6.90
6.88
6.87
4.35
4.35
3.80
3.79
3.77
3.76
3.75
3.74
3.73
3.71
3.62
3.61
3.60
3.60
3.59
3.59
3.57
3.56
3.37
3.36
3.34
3.33
1.14
1.13
Me
Ph
N
CN
CN
25
grease
4.73
2.02
0.98
2.01
1.00
2.00
1.96
0.92
2.96
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


146.95
134.93
129.70
129.37
129.35
128.18
119.29
115.58
112.34
111.86
77.29 CDCl3
77.08 CDCl3
76.87 CDCl3
52.45
48.69
44.54
26.94
11.70
Me
Ph
N
CN
CN
25
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)



26 The reaction was set up following the general procedure using N-benzyl-N-methylaniline (197 mg, 1 mmol) and benzylidenemalononitrile (31 mg, 0.2 mmol). After 16 hours, the reaction was purified following general work-up to give 45 mg (63 % yield) of the title compound. **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 7.50 – 7.41 (m, 3H), 7.42 – 7.24 (m, 7H), 7.21 – 7.16 (m, 2H), 6.97 – 6.88 (m, 3H), 4.54 (s, 2H), 4.23 (d, *J* = 4.8 Hz, 1H), 3.90 (m, *J* = 15.0, 9.8 Hz, 1H), 3.84 (m, *J* = 15.0, 5.2 Hz, 1H), 3.62 (m, *J* = 9.8, 4.9 Hz, 1H); **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 147.59, 137.59, 134.95, 129.77, 129.37, 129.35, 128.86, 128.14, 127.54, 127.34, 119.60, 115.42, 112.16, 111.59, 57.81, 52.99, 44.43, 27.05; MS2 (ES^+) exact mass calculated for $[M+H]^+$ ($C_{24}H_{22}N_3$) requires m/z 352.1, found m/z 352.1.


7.46
7.46
7.45
7.45
7.45
7.38
7.37
7.36
7.34
7.33
7.33
7.28
7.19
7.19
7.18
6.94
6.93
6.91
6.90
4.54
4.23
4.22
3.92
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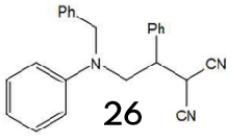
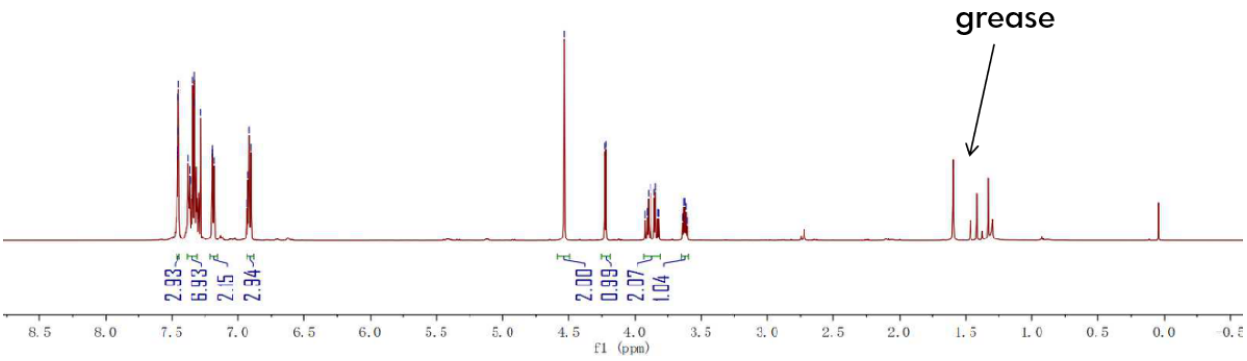
3.82
3.64
3.63
3.62
3.61
3.61


Ph
Ph
N
CN
CN

26


grease
2.93
6.93
2.15
2.34
2.00
0.99
2.07
1.04
8.5
8.0
7.5
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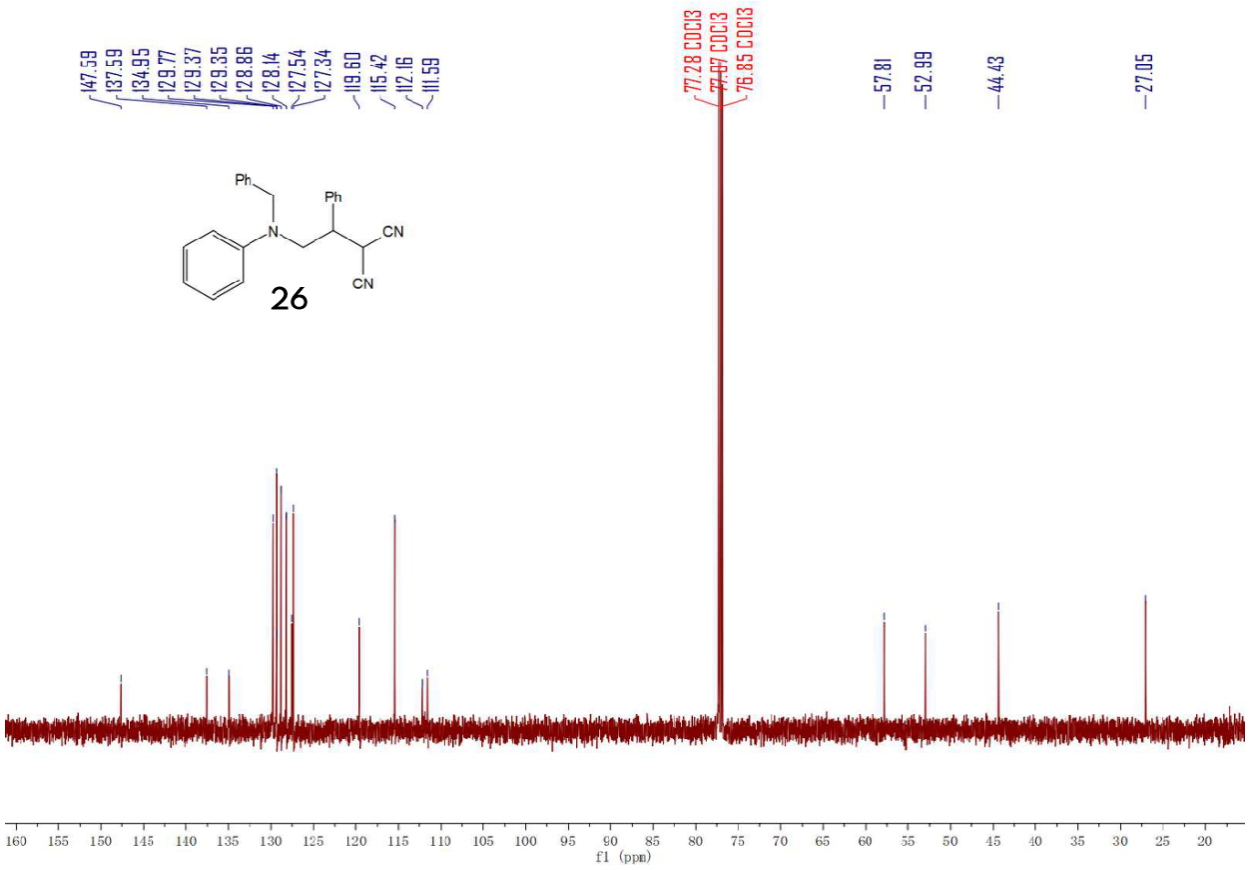
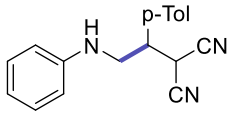
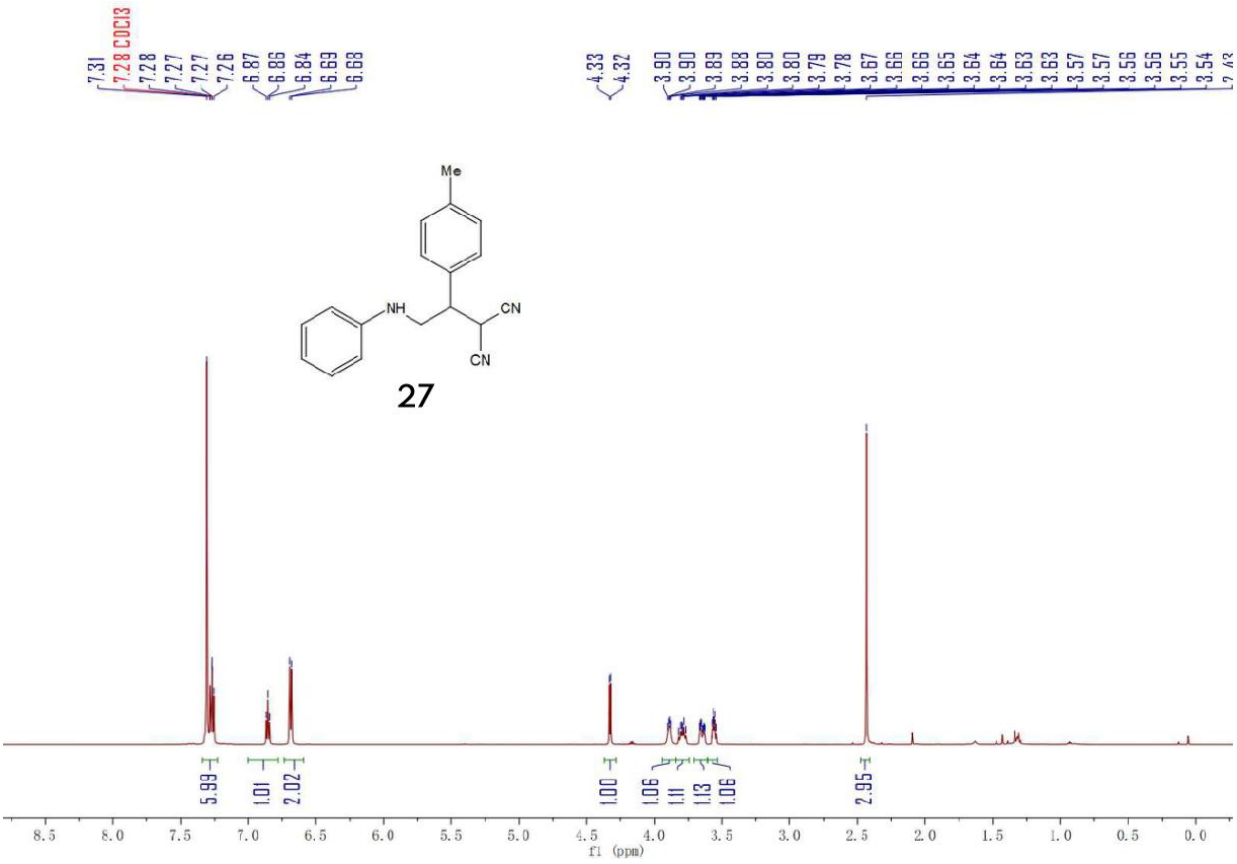
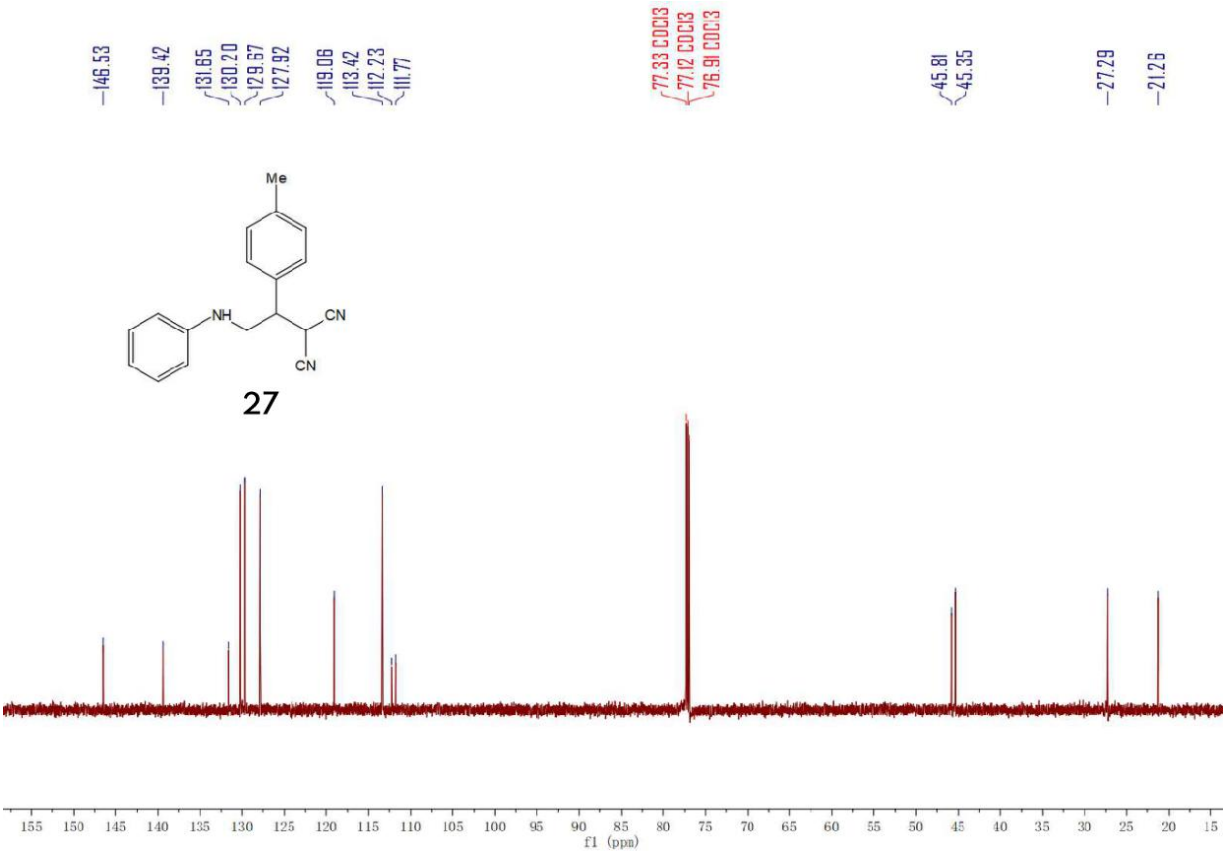
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

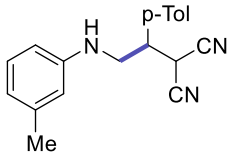

147.59
137.59
134.95
129.77
129.37
129.35
128.88
128.14
127.54
127.34
119.60
115.42
112.16
111.59
77.28 CDCl3
77.07 CDCl3
76.85 CDCl3
57.81
52.99
44.43
27.05
Ph
Ph
N
CN
CN
26
160 155 150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20
f1 (ppm)



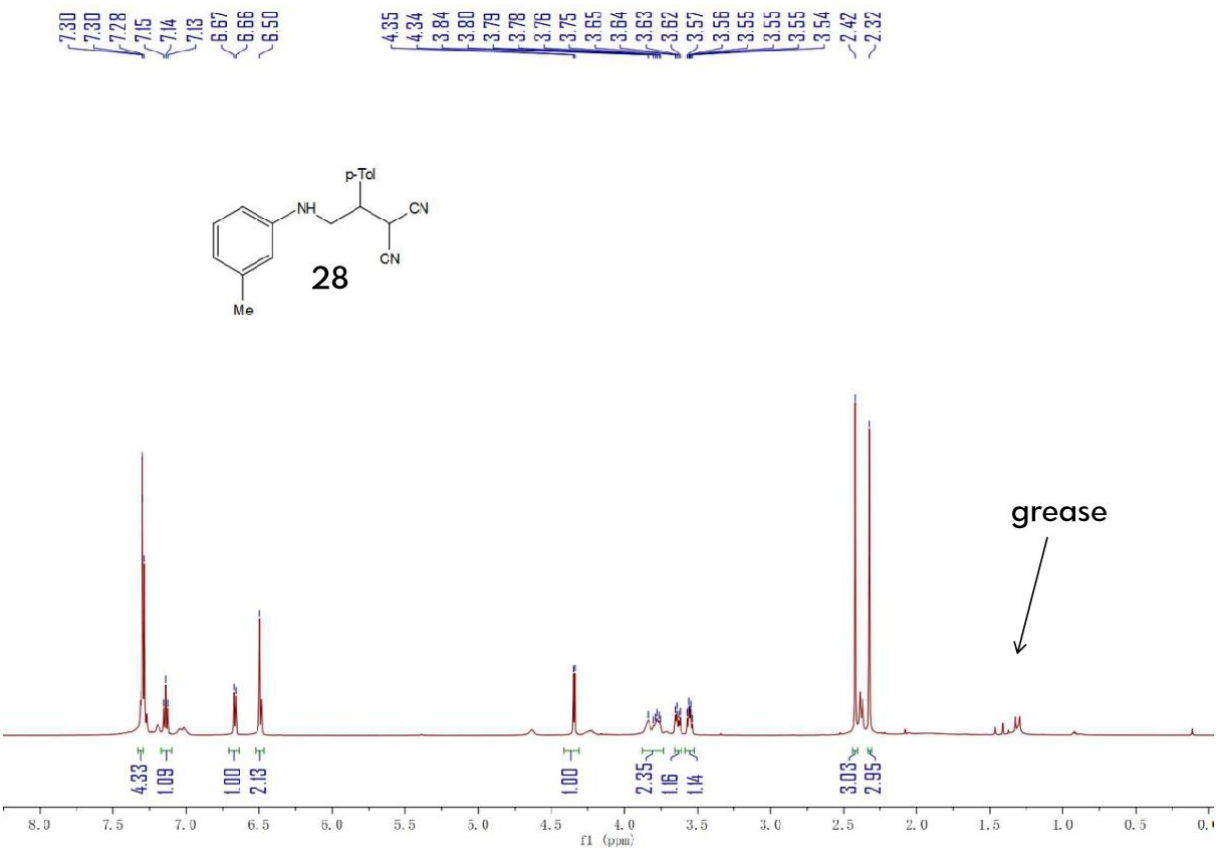
27 The reaction was set up following the general procedure using N-methylaniline (107 mg, 1 mmol) and 4-methylbenzylidenemalononitrile (34 mg, 0.2 mmol). After 16 hours, the reaction was purified following general work-up to give 42 mg (74 % yield) of the title compound. **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 7.34 – 7.24 (m, 6H), 6.86 (t, *J* = 7.3 Hz, 1H), 6.69 (d, *J* = 7.9 Hz, 2H), 4.33 (d, *J* = 5.4 Hz, 1H), 3.89 (m, *J* = 8.2, 4.0 Hz, 1H), 3.79 (m, *J* = 14.0, 8.3 Hz, 1H), 3.65 (m, *J* = 14.2, 5.8, 2.9 Hz, 1H), 3.56 (m, *J* = 8.9, 5.7 Hz, 1H), 2.43 (s, 3H); **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 146.53, 139.42, 131.65, 130.20, 129.67, 127.92, 119.06, 113.42, 112.23, 111.77, 45.81, 45.35, 27.29, 21.26; MS2 (ES^+) exact mass calculated for $[M+H]^+$ ($C_{18}H_{18}N_3$) requires m/z 276.1, found m/z 276.1.

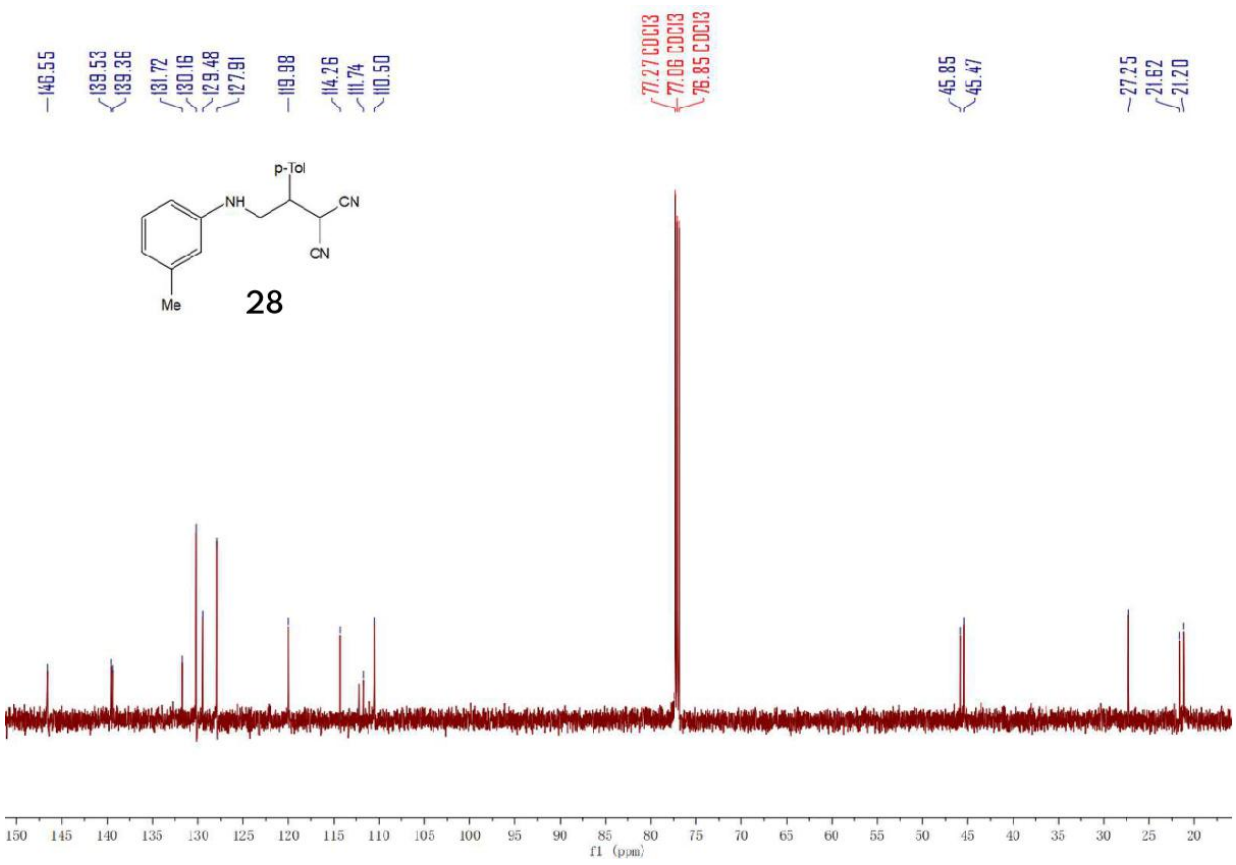

7.31
7.28 CDCl3
7.28
7.27
7.27
7.26
6.87
6.86
6.84
6.69
6.68
4.33
4.32
3.90
3.90
3.89
3.88
3.80
3.80
3.79
3.78
3.67
3.66
3.66
3.65
3.64
3.64
3.63
3.63
3.57
3.57
3.56
3.56
3.55
3.54
Me
NH
CN
CN
27
5.99
1.01
2.02
1.00
1.06
1.11
1.13
1.08
2.95
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

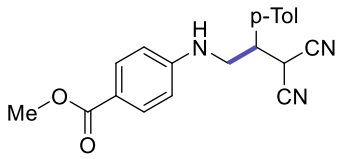

146.53
139.42
131.85
130.20
129.67
127.92
119.06
113.42
112.23
111.77
77.33 CDCl3
77.12 CDCl3
76.91 CDCl3
45.81
45.35
27.29
21.26
Me
NH
CN
CN
27
155 150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15
f1 (ppm)



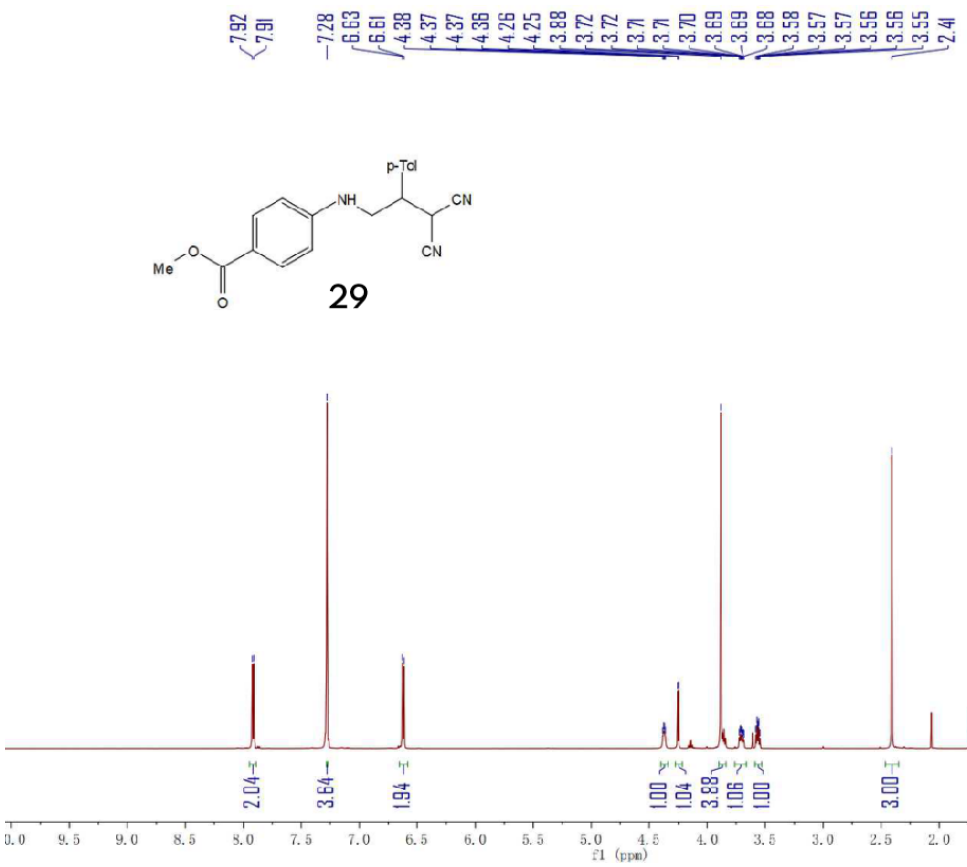
28 The reaction was set up following the general procedure using 3-methyl-N-methylbenzenamine (121 mg, 1 mmol) and 4-methylbenzylidenemalononitrile (34 mg, 0.2 mmol). After 16 hours, the reaction was purified following general work-up to give 31 mg (52 % yield) of the title compound. **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 7.30 (d, *J* = 1.7 Hz, 4H), 7.14 (t, *J* = 7.6 Hz, 1H), 6.67 (d, *J* = 7.5 Hz, 1H), 6.49 (d, *J* = 8.0 Hz, 2H), 4.34 (d, *J* = 5.5 Hz, 1H), 3.88 – 3.73 (m, 2H), 3.64 (m, *J* = 13.7, 6.0 Hz, 1H), 3.55 (m, *J* = 8.6, 5.7 Hz, 1H), 2.42 (s, 3H), 2.32 (s, 3H); **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 146.55, 139.53, 139.36, 131.72, 130.16, 129.48, 127.91, 119.98, 114.26, 112.19,111.74, 110.50, 45.85, 45.47, 27.25, 21.62, 21.20; MS2 (ES^+) exact mass calculated for $[M+H]^+$ ($C_{19}H_{20}N_3$) requires m/z 290.1, found m/z 290.1.

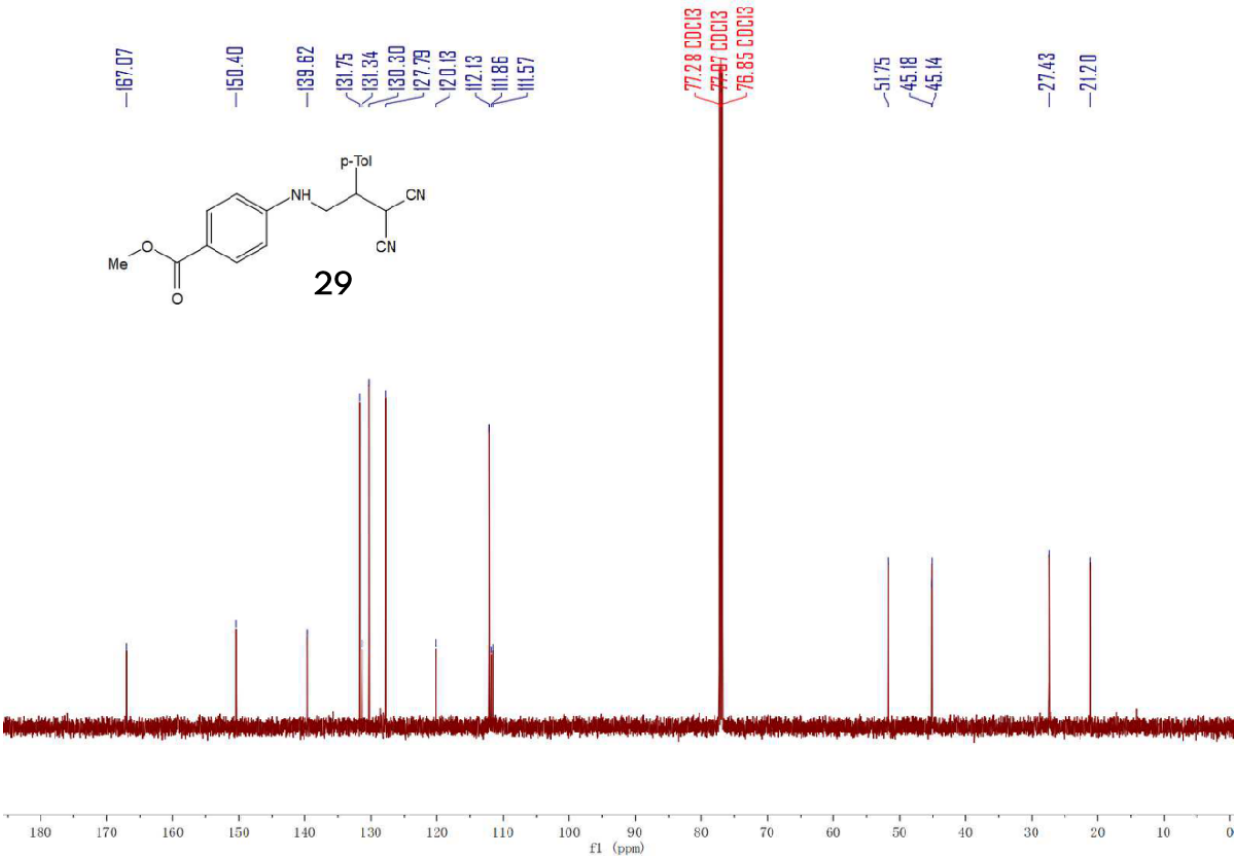

7.30
7.30
7.28
7.15
7.14
7.13
6.67
6.66
6.50
4.35
4.34
3.84
3.80
3.79
3.78
3.76
3.75
3.65
3.64
3.63
3.62
3.57
3.56
3.55
3.55
3.54
2.42
2.32
p-Tol
NH
CN
CN
Me
28
grease
4.33
1.09
1.00
2.13
1.00
2.35
1.16
1.14
3.03
2.95
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

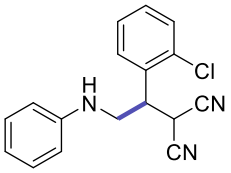

146.55
139.53
139.36
131.72
130.16
129.48
127.91
119.98
114.26
111.74
110.50
77.27 CDCl3
77.06 CDCl3
76.85 CDCl3
45.85
45.47
27.25
21.62
21.20
p-Tol
NH
CN
CN
Me
28
150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20
f1 (ppm)



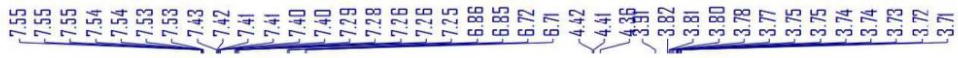
29 The reaction was set up following the general procedure using methyl 4-methylaminobenzoate (165 mg, 1 mmol) and 4-methylbenzylidenemalononitrile (34 mg, 0.2 mmol). After 16 hours, the reaction was purified following general work-up to give 30 mg (43 % yield) of the title compound. **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 7.95 – 7.89 (m, 2H), 7.28 (d, *J* = 2.7 Hz, 4H), 6.65 – 6.58 (m, 2H), 4.37 (m, *J* = 7.8, 4.5 Hz, 1H), 4.25 (d, *J* = 5.6 Hz, 1H), 3.90 – 3.84 (m, 4H), 3.70 (m, *J* = 14.0, 6.6, 4.3 Hz, 1H), 3.56 (m, *J* = 8.2, 6.2 Hz, 1H), 2.41 (s, 3H); **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 167.07, 150.40, 139.62, 131.75, 131.34, 130.30, 127.79, 120.13, 112.13, 111.86, 111.57, 51.75, 45.18, 45.14, 27.43, 21.20; MS2 (ES^+) exact mass calculated for $[M+H]^+$ ($C_{20}H_{20}N_3O_2$) requires m/z 334.1, found m/z 334.1.


7.92
7.91
7.28
6.63
6.61
4.38
4.37
4.37
4.36
4.26
4.25
3.88
3.72
3.72
3.71
3.71
3.70
3.69
3.69
3.68
3.58
3.57
3.57
3.56
3.56
3.55
2.41
p-Tol
NH
CN
CN
Me
O
O
29
2.04
3.64
1.94
1.00
1.04
3.88
1.06
1.00
3.00
f1 (ppm)


167.07
150.40
139.62
131.75
131.34
130.30
127.79
120.13
112.13
111.86
111.57
77.28 CDCl3
77.07 CDCl3
76.85 CDCl3
51.75
45.18
45.14
27.43
21.20
p-Tol
NH
CN
CN
Me
O
O
29
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



30 The reaction was set up following the general procedure using N-methylaniline (107 mg, 1 mmol) and 2-chlorobenzylidenemalononitrile (38 mg, 0.2 mmol). After 16 hours, the reaction was purified following general work-up to give 23 mg (37 % yield) of the title compound. **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 7.54 (m, *J* = 6.6, 4.5, 1.8 Hz, 2H), 7.41 (m, *J* = 7.7, 1.8 Hz, 2H), 7.28 – 7.25 (m, 2H), 6.85 (t, *J* = 7.3 Hz, 1H), 6.72 (d, *J* = 8.0 Hz, 2H), 4.41 (d, *J* = 5.7 Hz, 1H), 4.35 (m, *J* = 8.6, 5.9 Hz, 1H), 3.91 (s, 1H), 3.85 – 3.73 (m, 2H); **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 146.29, 132.63, 130.69, 130.37, 129.94, 129.63, 128.39,127.99, 127.36, 125.64, 122.78, 119.12, 113.33, 45.20, 25.83; MS2 (ES^+) exact mass calculated for $[M+H]^+$ ($C_{17}H_{15}ClN_3$) requires m/z 296.1, found m/z 296.1.


7.55
7.55
7.55
7.54
7.54
7.53
7.53
7.43
7.42
7.41
7.41
7.40
7.40
7.29
7.28
7.26
7.26
7.25
6.86
6.85
6.72
6.71
4.42
4.41
4.36
3.91
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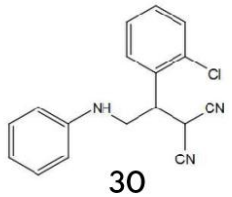
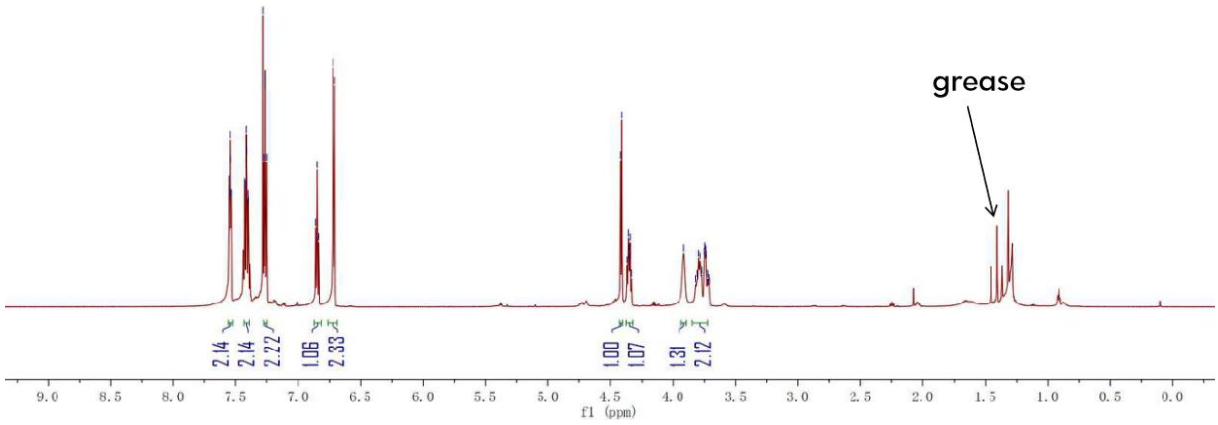
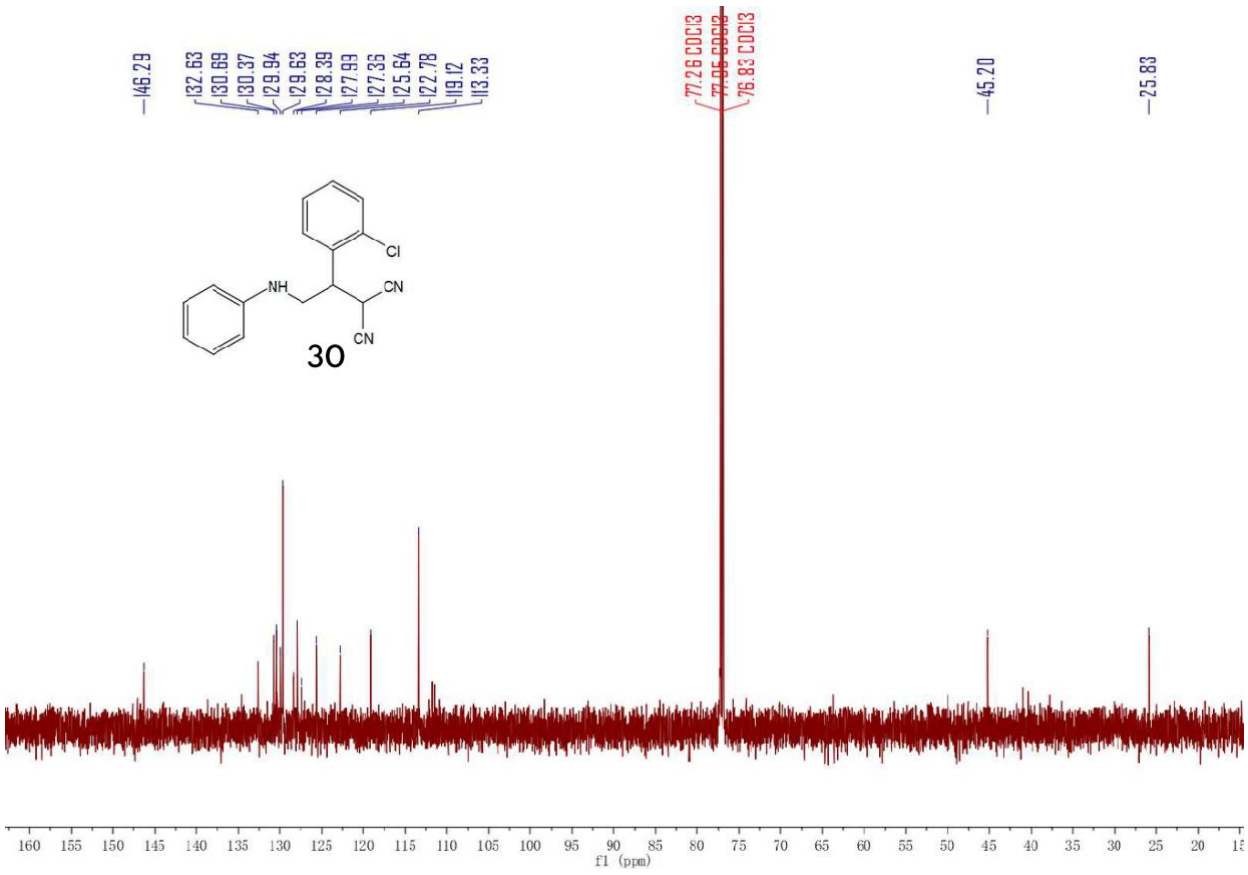
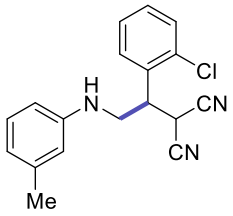
3.75
3.74
3.74
3.73
3.72
3.71


Cl
NH
CN
CN

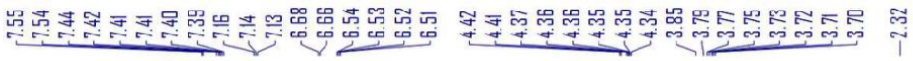
30

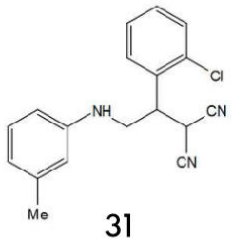

grease
2.14
2.14
2.22
1.06
2.33
1.00
1.07
1.31
2.12
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


146.29
132.63
130.69
130.37
129.94
129.63
128.39
127.93
127.35
125.64
122.78
119.12
113.33
77.26 CDCl3
76.83 CDCl3
45.20
25.83
Cl
NH
CN
CN
30
160 155 150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20
f1 (ppm)

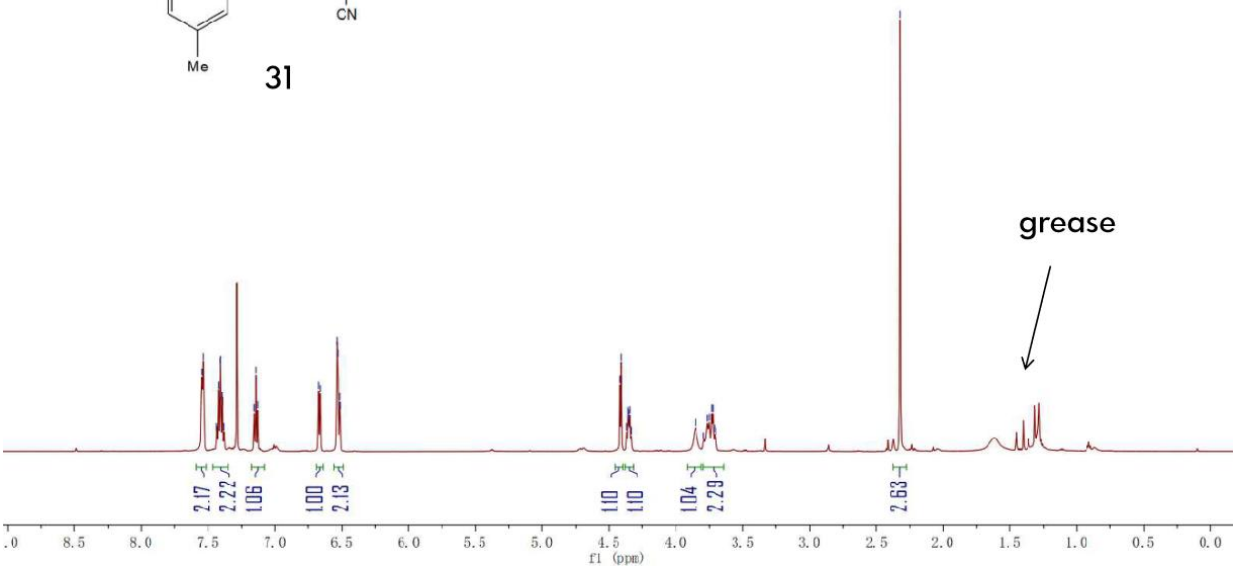


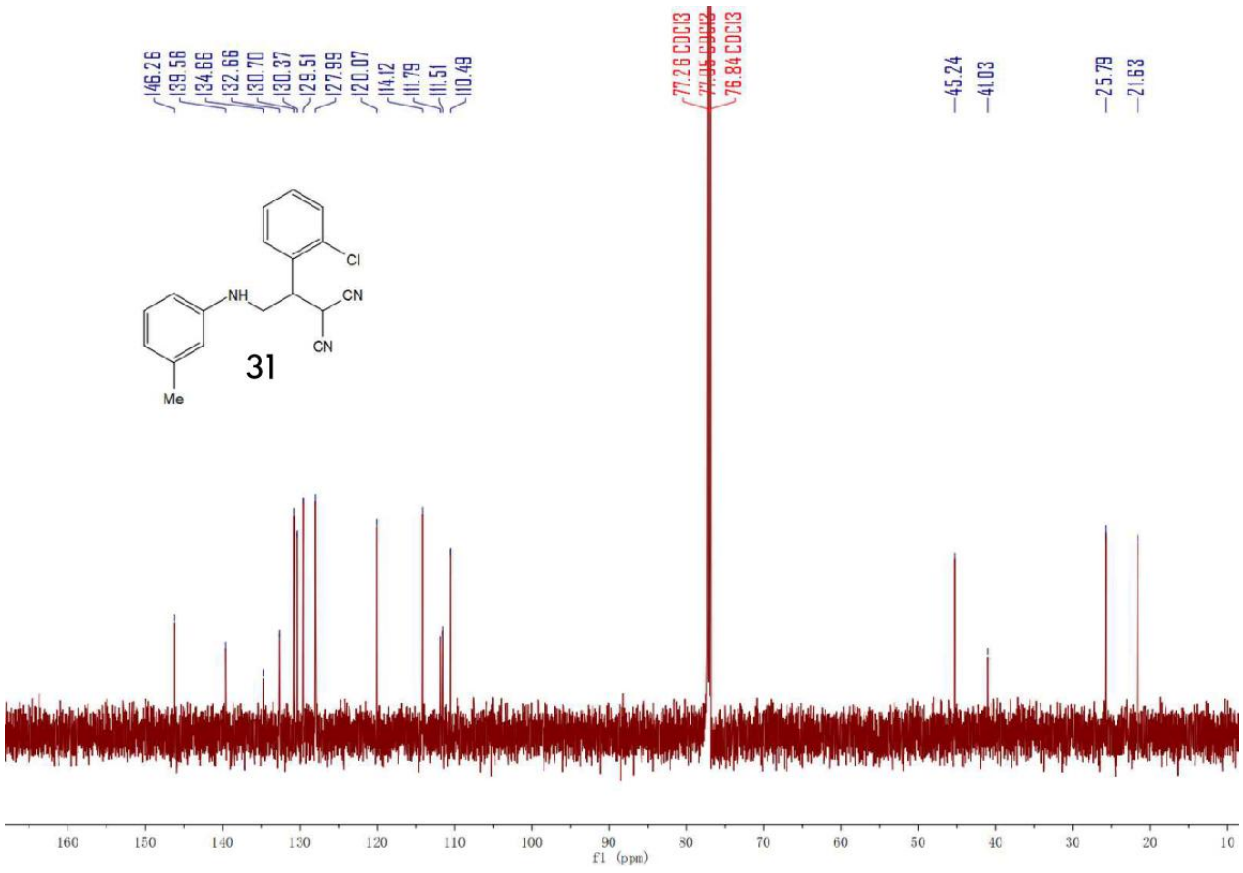
31 The reaction was set up following the general procedure using 3-methyl-N-methylbenzenamine (121 mg, 1 mmol) and 2-chlorobenzylidenemalononitrile (38 mg, 0.2 mmol). After 16 hours, the reaction was purified following general work-up to give 21 mg (33 % yield) of the title compound. **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 7.54 (m, *J* = 7.6, 3.4, 1.9 Hz, 2H), 7.41 (m, *J* = 7.4, 1.7 Hz, 2H), 7.14 (t, *J* = 7.7 Hz, 1H), 6.67 (d, *J* = 7.4 Hz, 1H), 6.52 (m, *J* = 10.8, 2.6 Hz, 2H), 4.41 (d, *J* = 5.8 Hz, 1H), 4.35 (m, *J* = 8.6, 6.0 Hz, 1H), 3.85 (s, 1H), 3.75 (m, *J* = 15.0, 14.0, 4.0 Hz, 2H), 2.32 (s, 3H); **^{13}C NMR** (151 MHz, Chloroform-d) δ 146.26, 139.56, 134.66, 132.66, 130.70, 130.37, 129.51, 127.99, 120.07, 114.12, 111.79, 111.51, 110.49, 45.24, 41.03, 25.79, 21.63; MS2 (ES^+) exact mass calculated for $[M+H]^+$ ($C_{18}H_{17}ClN_3$) requires m/z 310.1, found m/z 310.1.

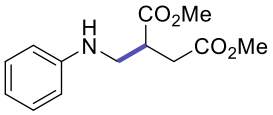

7.55
7.54
7.44
7.42
7.41
7.41
7.40
7.39
7.16
7.14
7.13
6.68
6.66
6.54
6.53
6.52
6.51
4.42
4.41
4.37
4.36
4.36
4.35
4.35
4.34
3.85
3.79
3.77
3.75
3.73
3.72
3.71
3.70
2.32


Cl
NH
CN
CN
Me

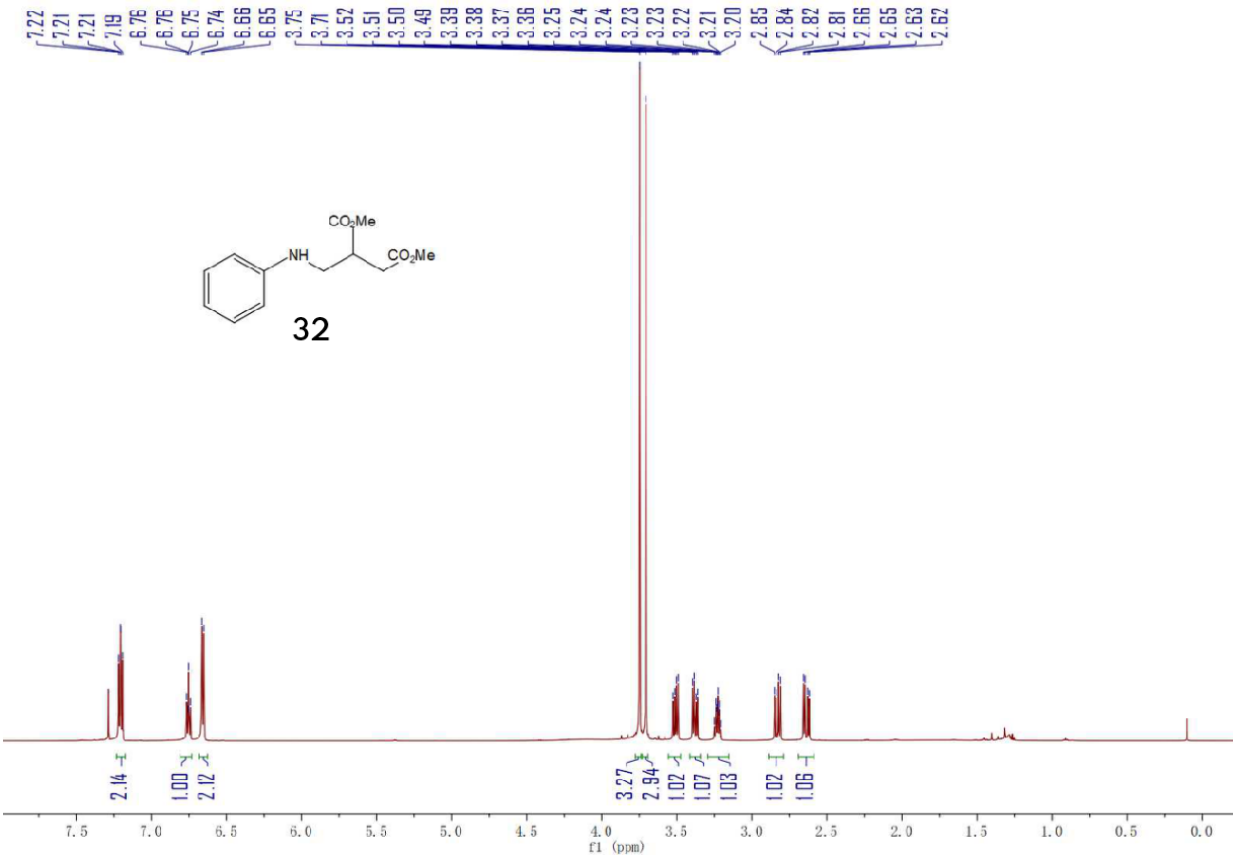
31

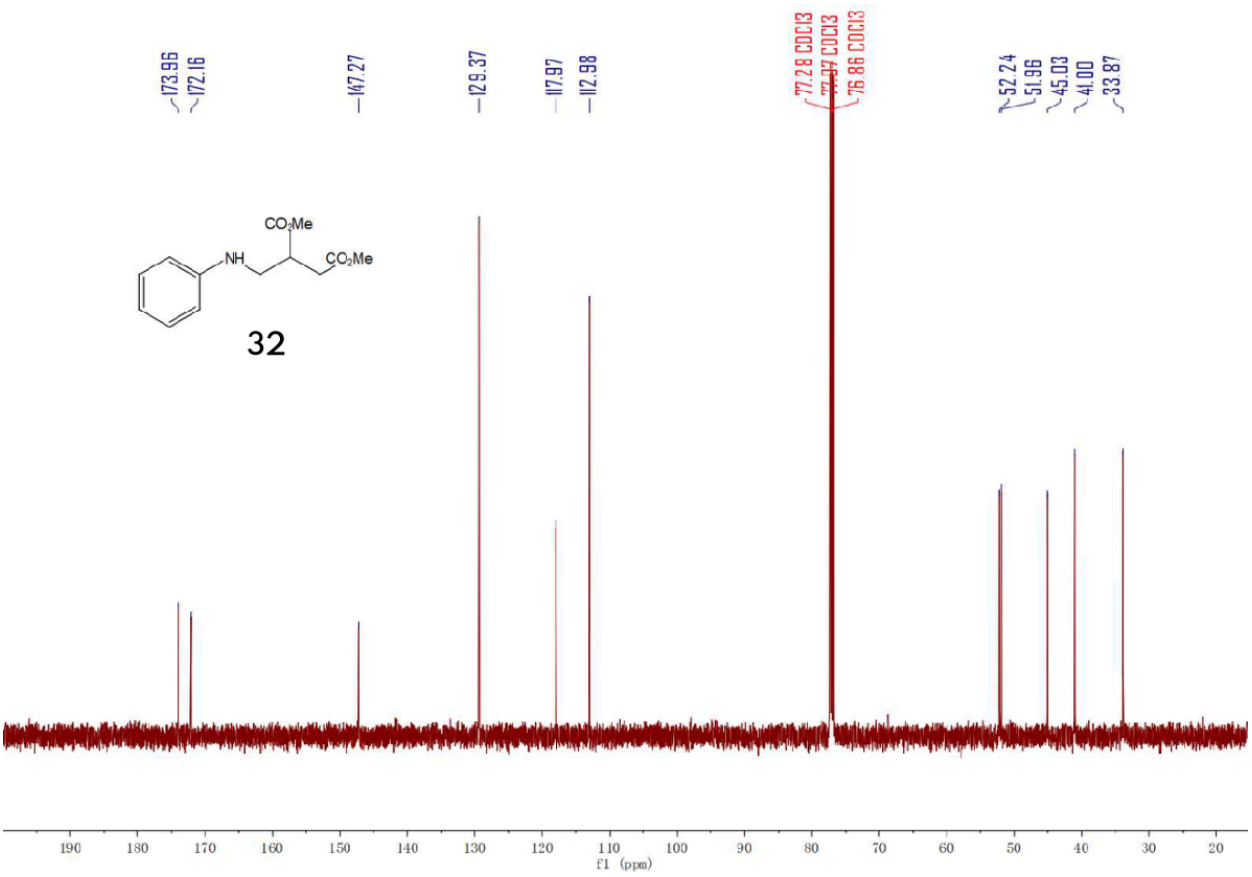

grease
2.17
2.22
1.06
1.00
2.13
1.10
1.10
1.04
2.29
2.63
f1 (ppm)

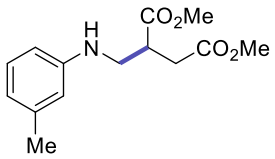

146.26
139.56
134.66
132.66
130.70
130.37
129.51
127.99
120.07
114.12
111.79
111.51
110.49
77.26 CDCl3
76.84 CDCl3
45.24
41.03
25.79
21.63
Cl
NH
CN
CN
Me
31
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)



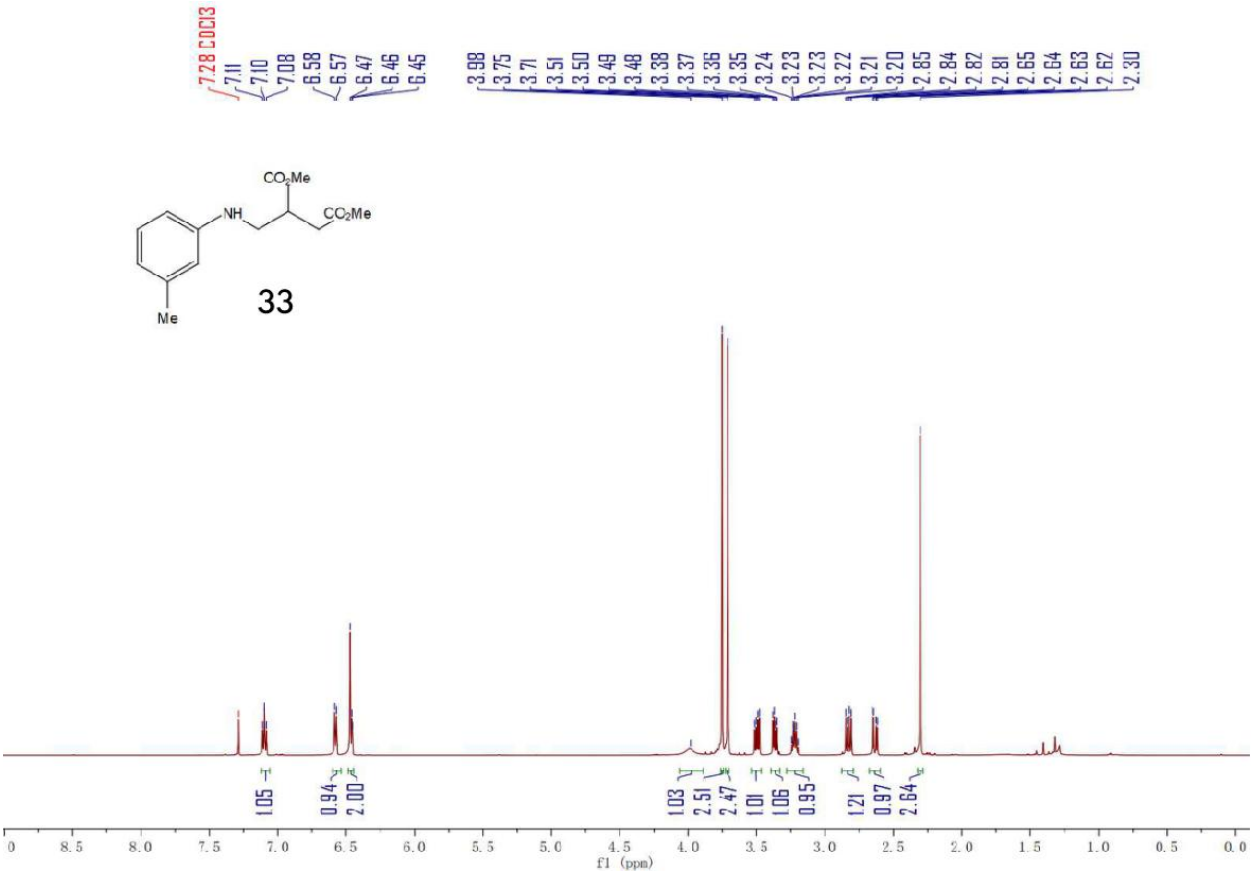
32 The reaction was set up following the general procedure using N-methylaniline (107 mg, 1 mmol) and dimethyl fumarate (29 mg, 0.2 mmol). After 16 hours, the reaction was purified following general work-up to give 33 mg (63 % yield) of the title compound. **^{1}H NMR** (600 MHz, Chloroform-d) δ 7.23 – 7.17 (m, 2H), 6.75 (m, J = 7.4, 1.1 Hz, 1H), 6.68 – 6.63 (m, 2H), 3.75 (s, 3H), 3.71 (s, 3H), 3.51 (m, J = 13.3, 6.9 Hz, 1H), 3.38 (m, J = 13.3, 6.1 Hz, 1H), 3.23 (m, J = 7.5, 6.2 Hz, 1H), 2.83 (m, J = 16.8, 7.6 Hz, 1H), 2.64 (m, J = 16.8, 6.2 Hz, 1H); **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 173.96, 172.16, 147.27, 129.37, 117.97, 112.98, 52.24, 51.96, 45.03, 41.00, 33.87; MS2 (ES^+) exact mass calculated for $[M+H]^+$ ($C_{13}H_{18}NO_4$) requires m/z 252.1, found m/z 252.1.

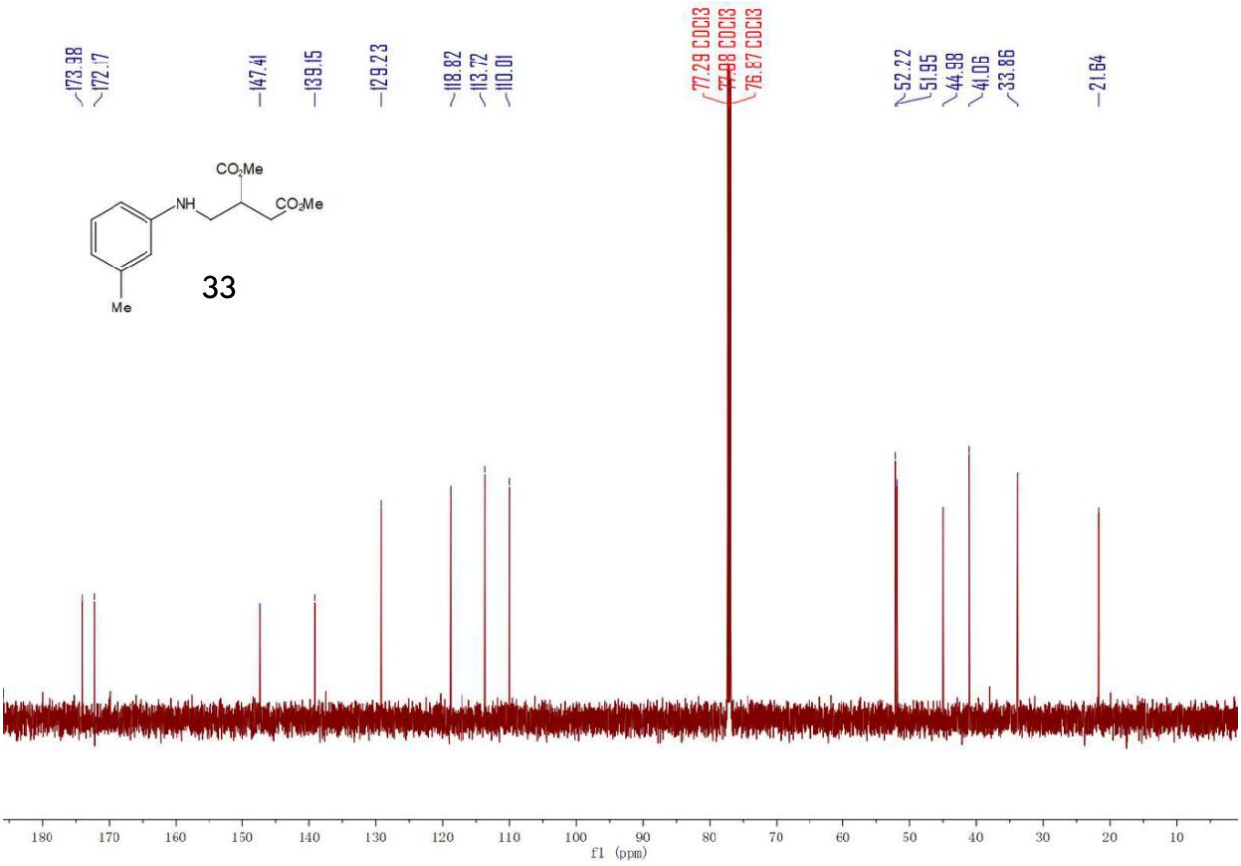

7.22
7.21
7.21
7.19
6.76
6.76
6.75
6.74
6.66
6.65
3.75
3.71
3.52
3.51
3.50
3.49
3.39
3.38
3.37
3.36
3.25
3.24
3.24
3.23
3.23
3.22
3.21
3.20
2.85
2.84
2.82
2.81
2.66
2.65
2.63
2.62
CO2Me
NH
CO2Me
32
2.14
1.00
2.12
3.27
2.94
1.02
1.07
1.03
1.02
1.06
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

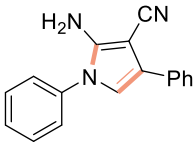

173.96
172.16
147.27
129.37
117.97
112.98
77.28 CDCl3
77.07 CDCl3
76.86 CDCl3
52.24
51.96
45.03
41.00
33.87
CO2Me
NH
CO2Me
32
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
f1 (ppm)



33 The reaction was set up following the general procedure using 3-Methyl-N-methylbenzenamine (121 mg, 1 mmol) and dimethyl fumarate (29 mg, 0.2 mmol). After 16 hours, the reaction was purified following general work-up to give 33 mg (60 % yield) of the title compound. **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 7.14 – 7.07 (m, 1H), 6.58 (d, *J* = 7.5 Hz, 1H), 6.46 (d, *J* = 2.3 Hz, 2H), 4.02 – 3.97 (m, 1H), 3.73 (d, *J* = 24.2 Hz, 6H), 3.50 (m, *J* = 13.3, 6.9 Hz, 1H), 3.37 (m, *J* = 13.2, 6.2 Hz, 1H), 3.26 – 3.18 (m, 1H), 2.83 (m, *J* = 16.8, 7.7 Hz, 1H), 2.64 (m, *J* = 16.8, 6.1 Hz, 1H), 2.30 (s, 3H); **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 173.98, 172.17, 147.41, 139.15, 129.23, 118.82, 113.72, 110.01, 52.22, 51.95, 44.98, 41.06, 33.86, 21.64; MS2 (ES^+) exact mass calculated for $[M+H]^+$ ($C_{14}H_{20}NO_4$) requires m/z 266.1, found m/z 266.1.

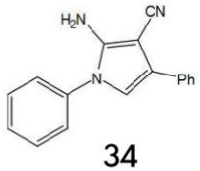

7.28 CDCl3
7.11
7.10
7.08
6.58
6.57
6.47
6.46
6.45
3.98
3.75
3.71
3.51
3.50
3.49
3.48
3.38
3.37
3.36
3.35
3.24
3.23
3.23
3.22
3.21
3.20
2.85
2.84
2.82
2.81
2.65
2.64
2.63
2.62
2.30
CO2Me
NH
CO2Me
Me
33
1.05
0.94
2.00
1.03
2.51
2.47
1.01
1.06
0.95
1.21
0.97
2.64
f1 (ppm)


173.38
172.17
147.41
139.15
129.23
118.82
113.72
110.01
77.29 CDCl3
77.08 CDCl3
76.87 CDCl3
52.22
51.95
44.98
41.06
33.86
21.64
CO2Me
NH
CO2Me
Me
33
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

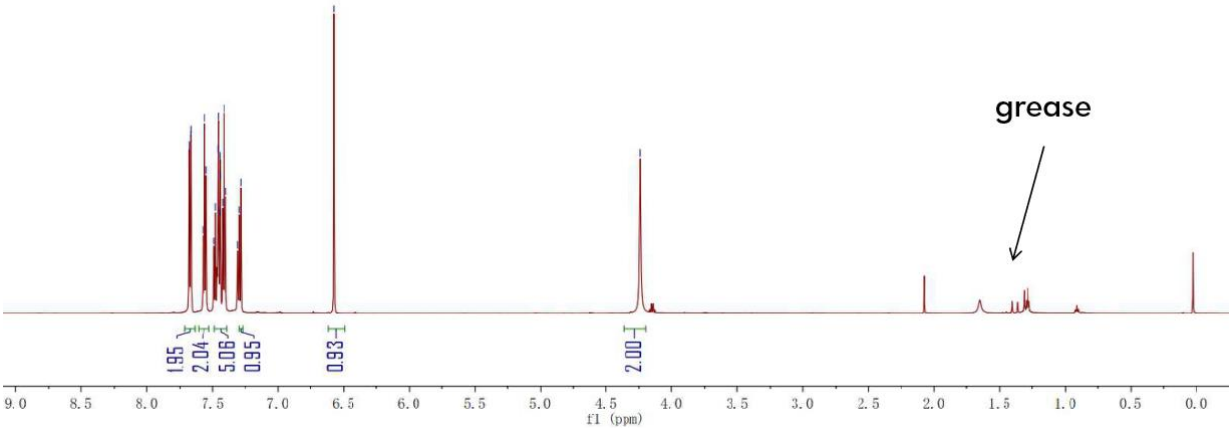


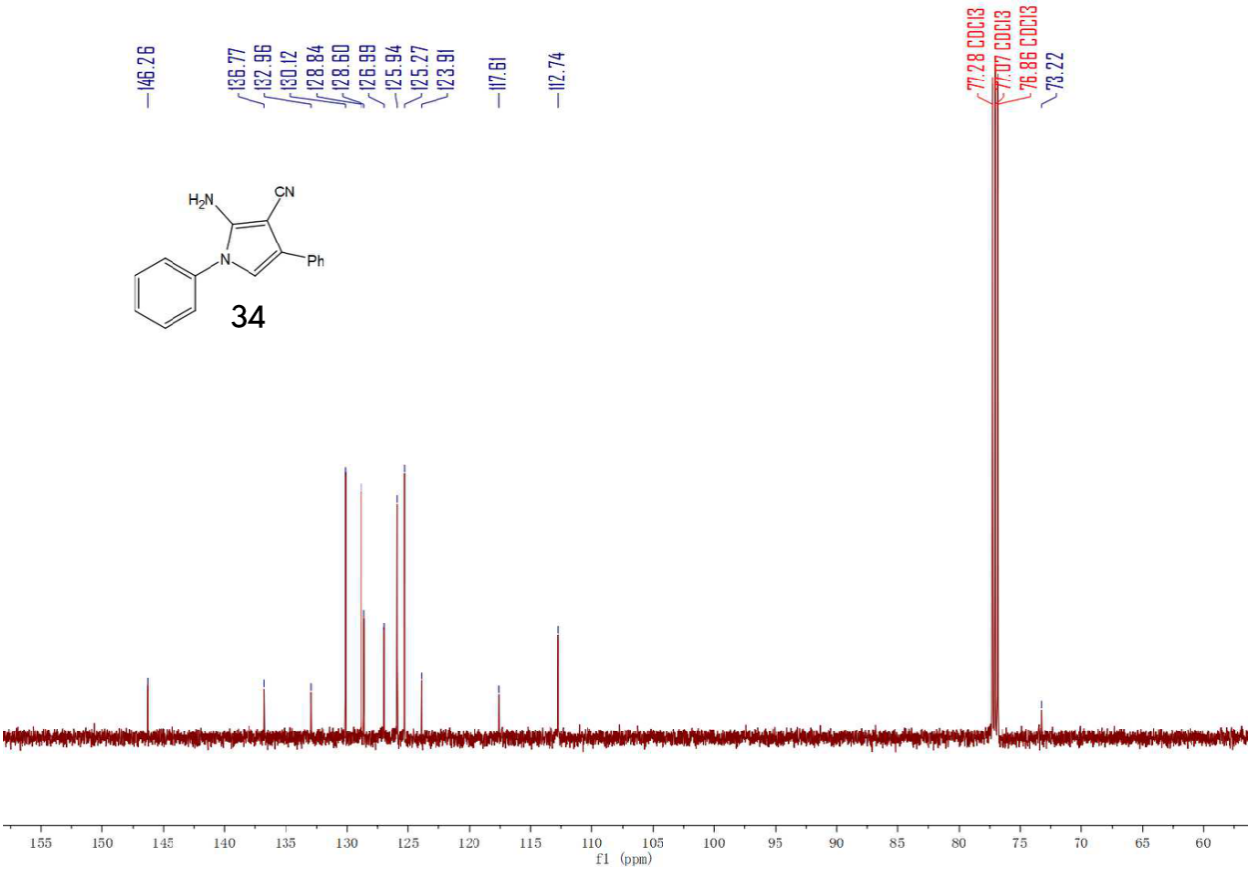
34 The reaction was set up following the general procedure using N-methylaniline (107 mg, 1 mmol) and benzylidenemalononitrile (31 mg, 0.2 mmol). After 16 hours, the reaction was purified following general work-up to give 38 mg (71 % yield) of the title compound. **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 7.69 – 7.65 (m, 2H), 7.56 (t, *J* = 7.8 Hz, 2H), 7.51 – 7.38 (m, 5H), 7.35 – 7.28 (m, 1H), 6.57 (s, 1H), 4.24 (s, 2H); **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 146.26, 136.77, 132.96, 130.12, 128.84, 128.60, 126.99, 125.94, 125.27, 123.91, 117.61, 112.74, 73.22; MS2 (ES^+) exact mass calculated for $[M+H]^+$ ($C_{17}H_{14}N_3$) requires m/z 260.1, found m/z 260.1.


7.68
7.66
7.66
7.57
7.56
7.55
7.49
7.48
7.46
7.46
7.45
7.44
7.44
7.43
7.41
7.40
7.31
7.30
7.29
6.57
4.24


H2N
CN
N
Ph

34


grease
1.95
2.04
5.08
0.95
0.93
2.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


146.26
136.77
132.96
130.12
128.84
128.60
126.99
125.94
125.27
123.91
117.61
112.74
77.28 CDCl3
77.07 CDCl3
76.86 CDCl3
73.22
H2N
CN
N
Ph
34
155
150
145
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135
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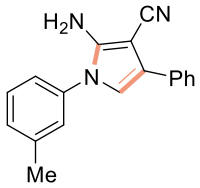
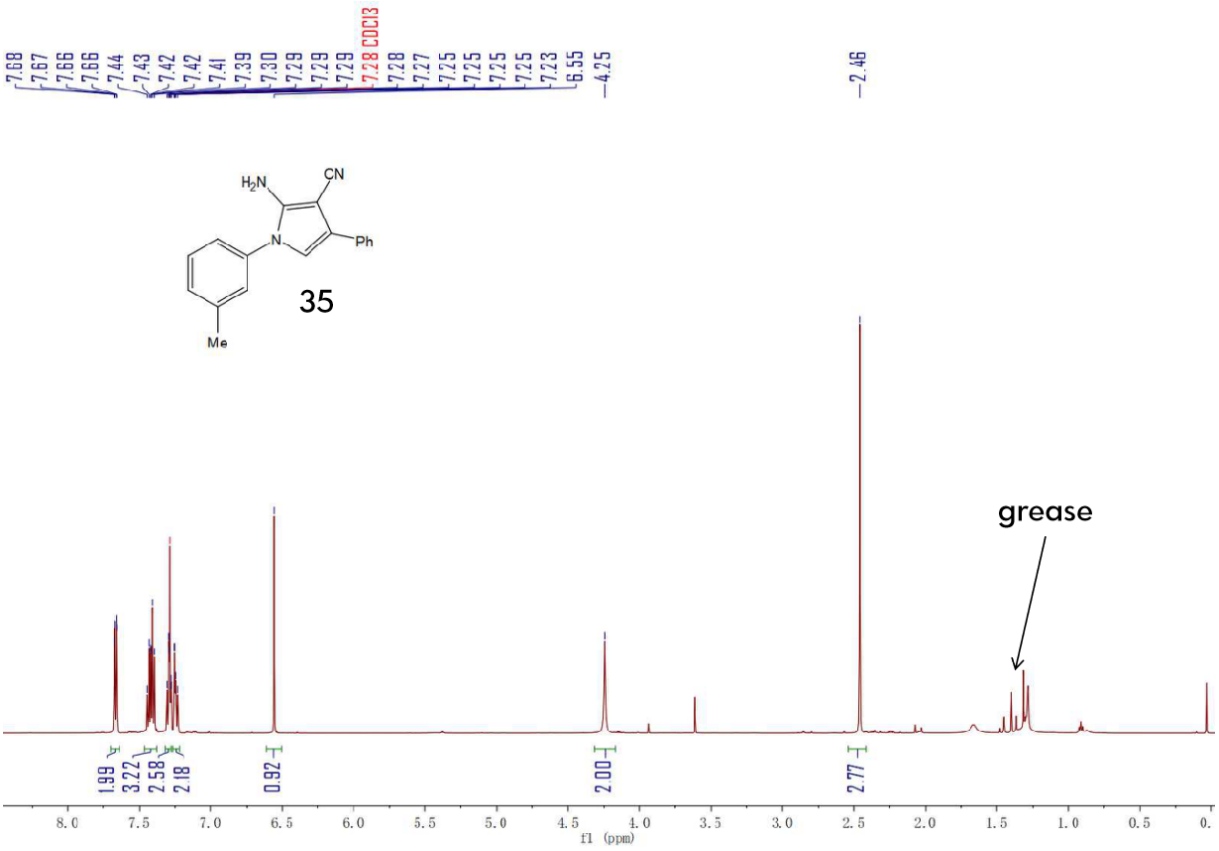
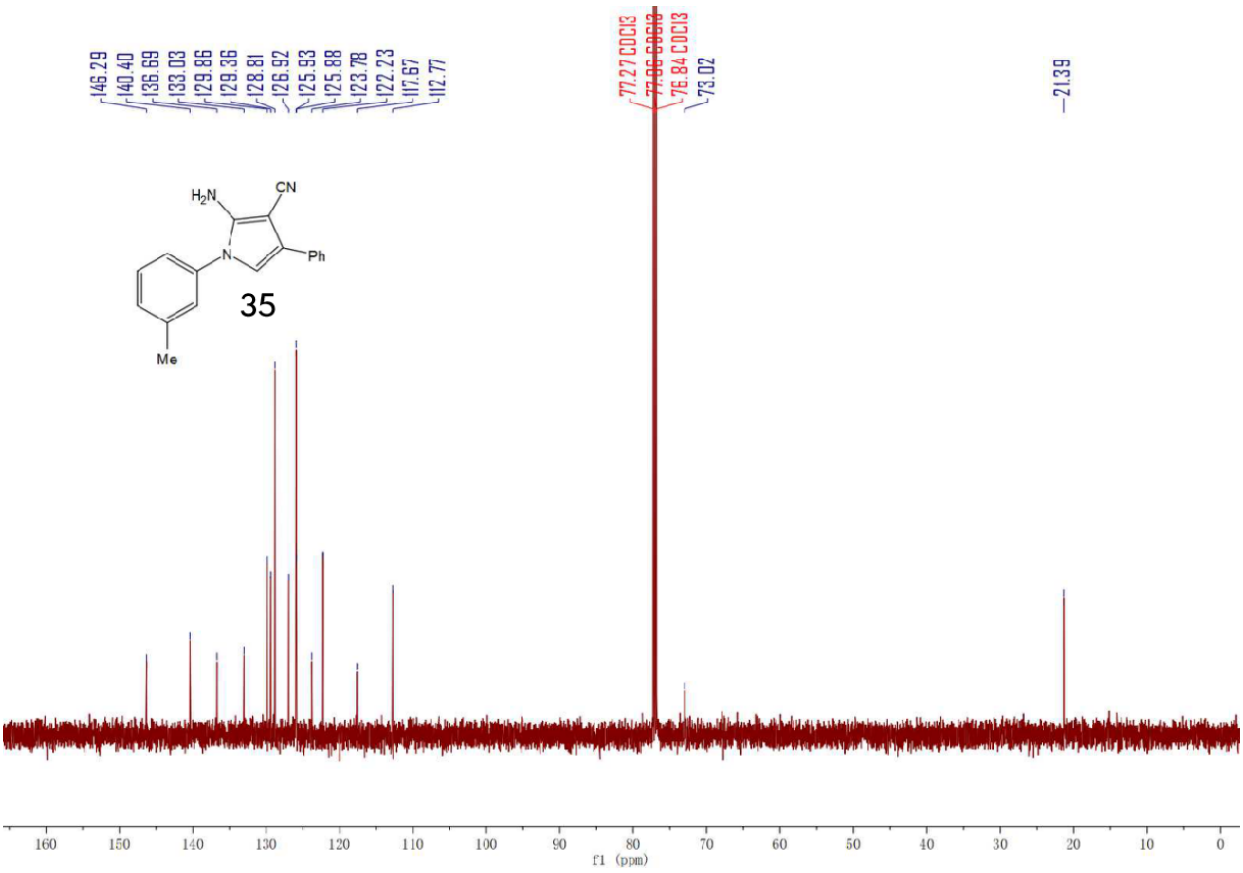
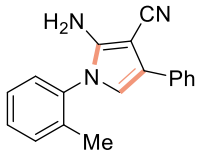
115
110
105
100
95
90
85
80
75
70
65
60
f1 (ppm)



35 The reaction was set up following the general procedure using 3-methyl-N-methylbenzenamine (121 mg, 1 mmol) and benzylidenemalononitrile (31 mg, 0.2 mmol). After 16 hours, the reaction was purified following general work-up to give 37 mg (65 % yield) of the title compound. **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 7.69 – 7.64 (m, 2H), 7.42 (m, *J* = 13.9, 7.8 Hz, 3H), 7.32 – 7.25 (m, 2H), 7.26 – 7.21 (m, 2H), 6.55 (s, 1H), 4.25 (s, 2H), 1.34 – 1.27 (m, 3H); **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 146.29, 140.40, 136.69, 133.03, 129.86, 129.36, 128.81, 126.92, 125.93, 125.88, 123.78, 122.23, 117.67, 112.77, 73.02, 21.39; MS2 (ES^+) exact mass calculated for $[M+H]^+$ ($C_{18}H_{16}N_3$) requires m/z 274.1, found m/z 274.1.

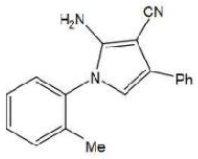

7.68
7.67
7.66
7.66
7.44
7.43
7.42
7.42
7.41
7.39
7.30
7.29
7.29
7.29
7.28 CDCl3
7.28
7.27
7.25
7.25
7.25
7.25
7.23
6.55
4.25
2.46
H2N
CN
N
Ph
Me
35
grease
1.99
3.22
2.58
2.18
0.92
2.00
2.77
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.
f1 (ppm)


146.29
140.40
136.69
133.03
129.86
129.36
128.81
126.92
125.93
125.88
123.78
122.23
117.67
112.77
77.27 CDCl3
76.84 CDCl3
73.02
21.39
H2N
CN
Ph
N
Me
35
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

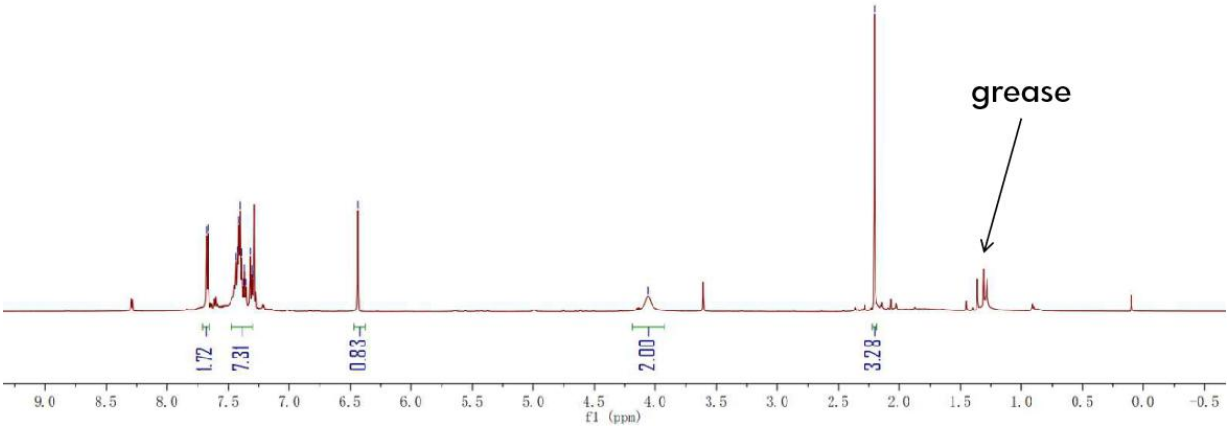


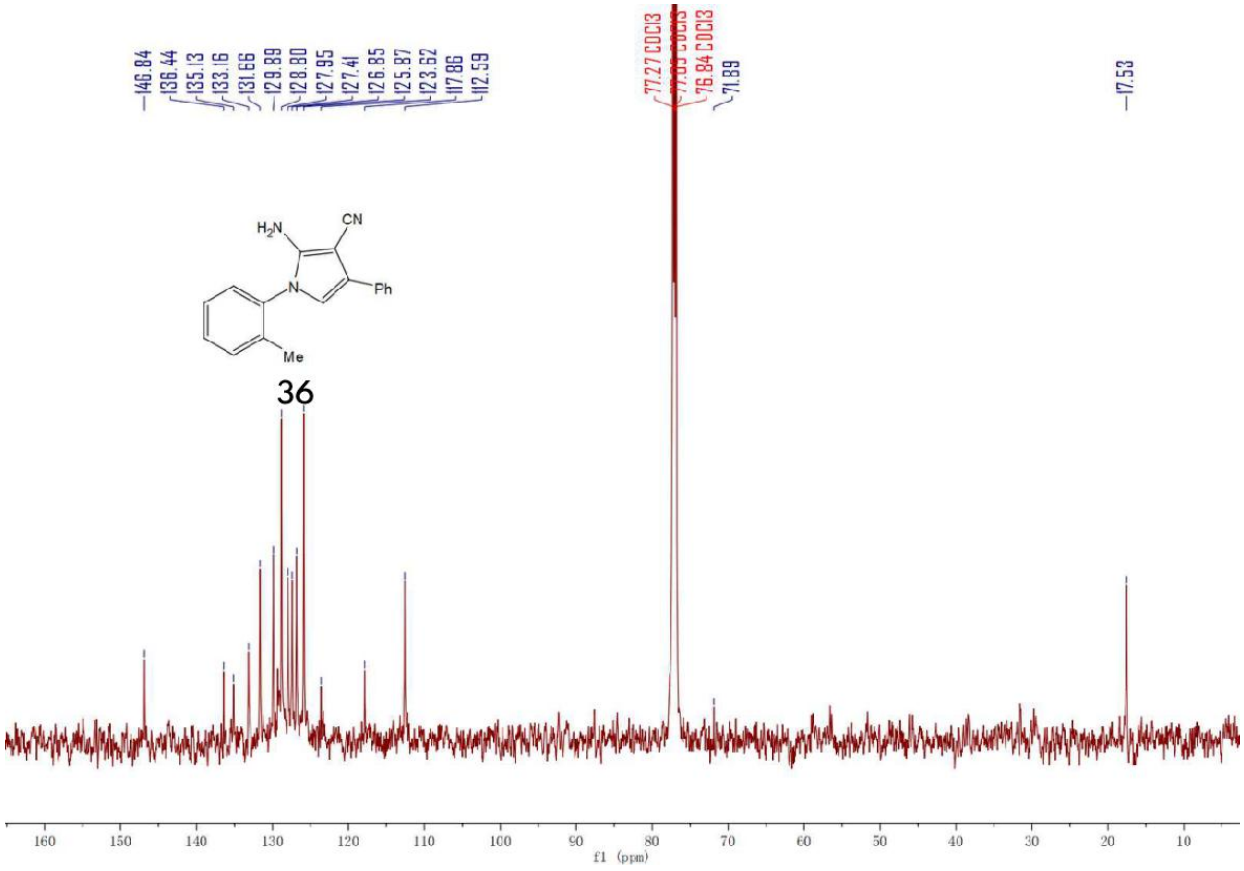
36 The reaction was set up following the general procedure using 2-methyl-N-methylbenzenamine(121 mg, 1 mmol) and benzylidenemalononitrile (31 mg, 0.2 mmol). After 16 hours, the reaction was purified following general work-up to give 25 mg (45 % yield) of the title compound. **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 7.67 (d, *J* = 8.1 Hz, 2H), 7.47 – 7.30 (m, 7H), 6.44 (s, 1H), 4.04 (s, 2H), 2.21 (s, 3H); **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 146.84, 136.44, 135.13, 133.16, 131.66, 129.89, 128.80, 127.95, 127.41, 126.85, 125.87, 123.62, 117.86, 112.59, 71.89, 17.53; MS2 (ES^+) exact mass calculated for $[M+H]^+$ ($C_{18}H_{16}N_3$) requires m/z 274.1, found m/z 274.1.

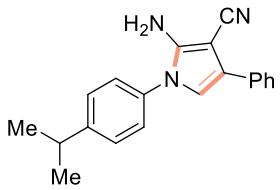

7.68
7.67
7.44
7.42
7.42
7.40
7.39
7.38
7.37
7.35
7.32
7.31
7.30
6.44
4.06
2.21


H2N
CN
N
Ph
Me

36


grease
1.72
7.31
0.83
2.00
3.28
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


146.84
136.44
135.13
133.16
131.66
129.89
128.80
127.95
127.41
126.85
125.87
123.62
117.86
112.59
77.27 CDCl3
76.84 CDCl3
71.89
17.53
H2N
CN
Ph
N
Me
36
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)



37 The reaction was set up following the general procedure using N-methyl-4-(1-methylethyl)benzenamine (149 mg, 1 mmol) and benzylidenemalononitrile (31 mg, 0.2 mmol). After 16 hours, the reaction was purified following general work-up to give 32 mg (52 % yield) of the title compound. **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 7.70 – 7.64 (m, 2H), 7.47 – 7.38 (m, 4H), 7.40 – 7.32 (m, 2H), 7.31 – 7.25 (m, 1H), 6.55 (s, 1H), 4.23 (s, 2H), 3.01 (m, *J* = 6.9 Hz, 1H), 1.32 (d, *J* = 6.9 Hz, 6H); **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 149.63, 146.41, 134.34, 133.08, 128.82, 128.07, 126.89, 125.91, 125.27, 123.66, 117.72, 112.86, 72.88, 33.90, 23.94; MS2 (ES^+) exact mass calculated for $[M+H]^+$ ($C_{20}H_{20}N_3$) requires m/z 302.1, found m/z 302.1.


7.68
7.67
7.66
7.66
7.42
7.41
7.39
7.36
7.34
7.30
7.30
7.30
7.29
7.29
7.28
7.28
7.28
6.55
6.55
6.54
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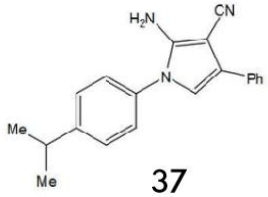
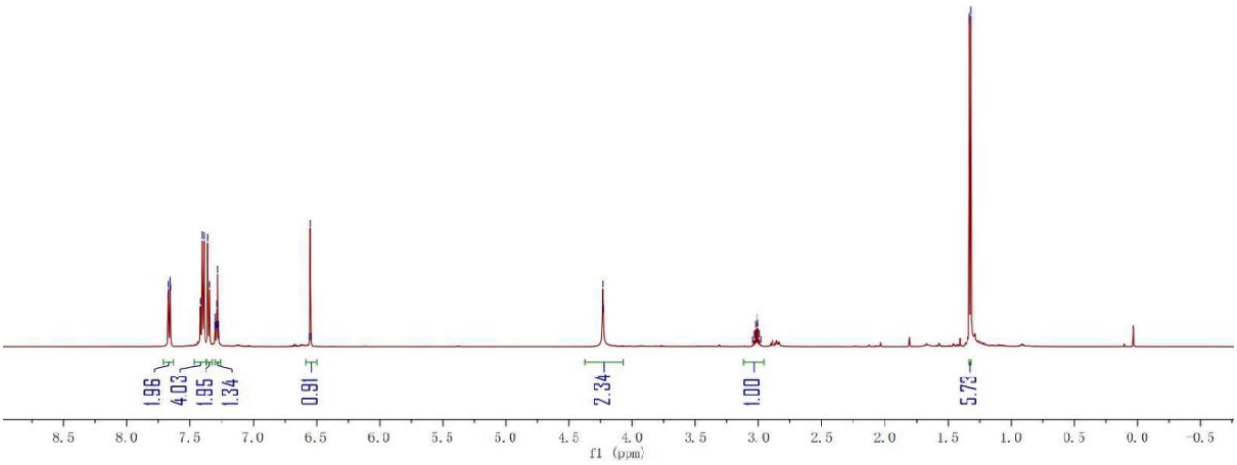
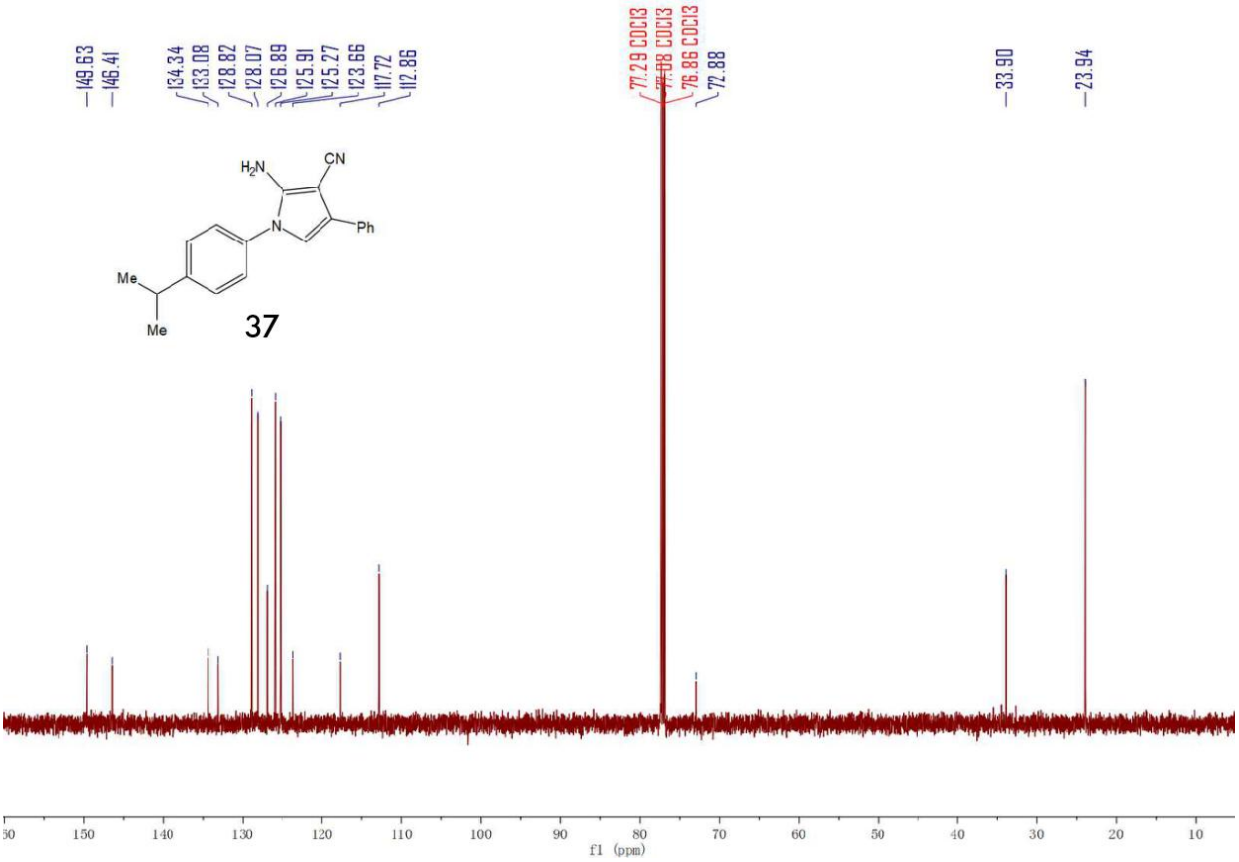
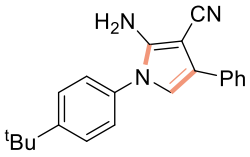
3.00
2.99
2.98
1.33
1.33
1.32


H2N
CN
N
Ph
Me
Me

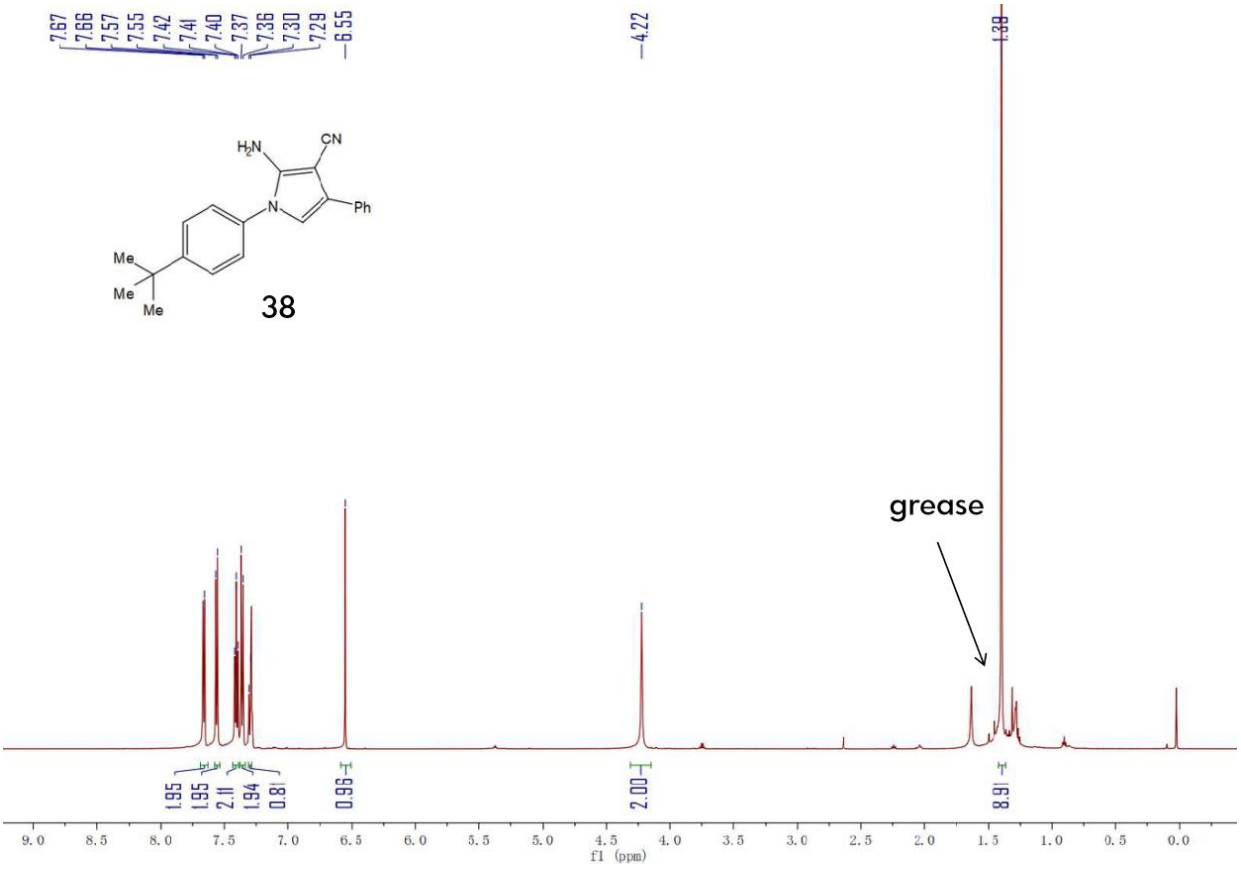
37

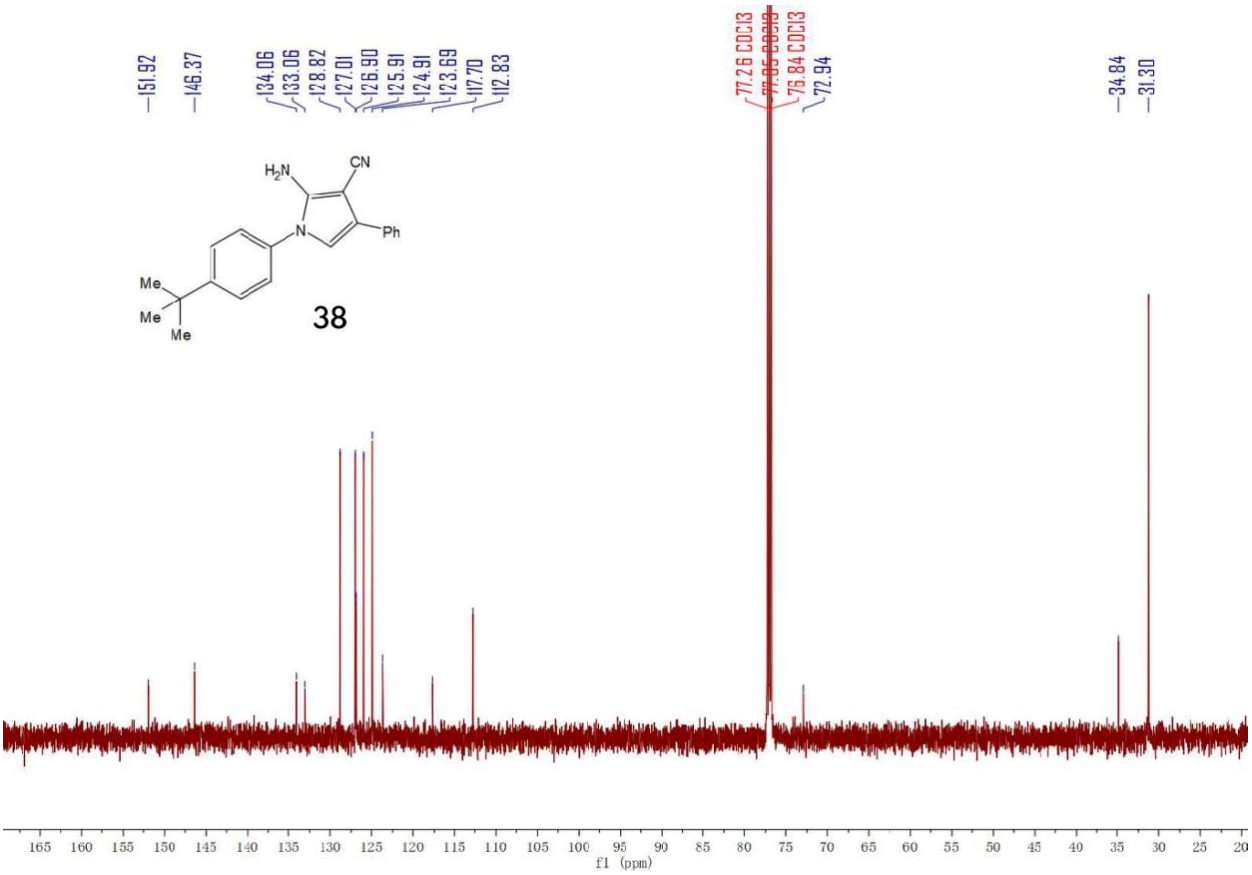

1.96
4.03
1.95
1.34
0.91
2.34
1.00
5.72
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

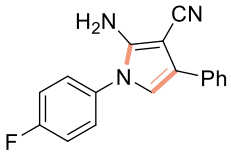

149.63
146.41
134.34
133.08
128.82
128.07
126.89
125.91
125.27
123.66
117.72
112.86
77.29 CDCl3
77.08 CDCl3
76.86 CDCl3
72.88
33.90
23.94
H2N
CN
N
Ph
Me
Me
37
f1 (ppm)



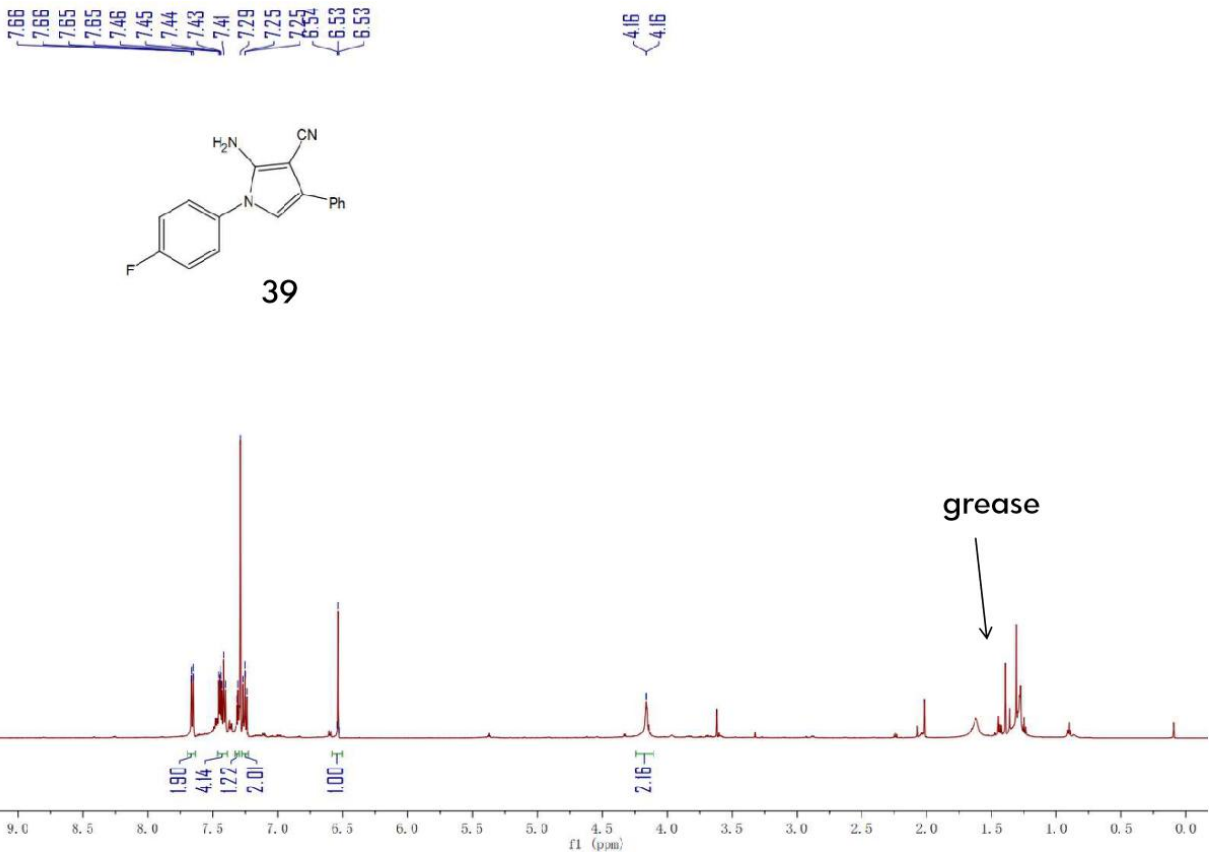
38 The reaction was set up following the general procedure using 4-(1,1-dimethylethyl)-N-methylbenzenamine (163 mg, 1 mmol) and benzylidenemalononitrile (31 mg, 0.2 mmol). After 16 hours, the reaction was purified following general work-up to give 43 mg (66 % yield) of the title compound. **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 7.69 – 7.63 (m, 2H), 7.58 – 7.54 (m, 2H), 7.41 (t, *J* = 7.8 Hz, 2H), 7.38 – 7.34 (m, 2H), 7.31 – 7.29 (m, 1H), 6.55 (s, 1H), 4.22 (s, 2H), 1.39 (s, 9H); **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 151.92, 146.37, 134.06, 133.06, 128.82, 127.01, 126.90, 125.91, 124.91, 123.69, 117.70, 112.83, 72.94, 34.84, 31.30; MS2 (ES^+) exact mass calculated for $[M+H]^+$ ($C_{21}H_{22}N_3$) requires m/z 316.1, found m/z 316.1.

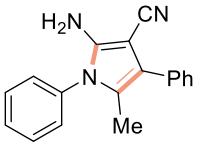

7.67
7.66
7.57
7.55
7.42
7.41
7.40
7.37
7.36
7.30
7.29
6.55
4.22
1.38
H2N
CN
Ph
N
Me
Me
Me
38
grease
1.95
1.95
2.11
1.94
0.81
0.96
2.00
8.91
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


151.92
146.37
134.06
133.06
128.82
127.01
126.90
125.91
124.91
123.69
117.70
112.83
77.26 CDCl3
77.85 CDCl3
76.84 CDCl3
72.94
34.84
31.30
H2N
CN
N
Ph
Me
Me
Me
38
f1 (ppm)

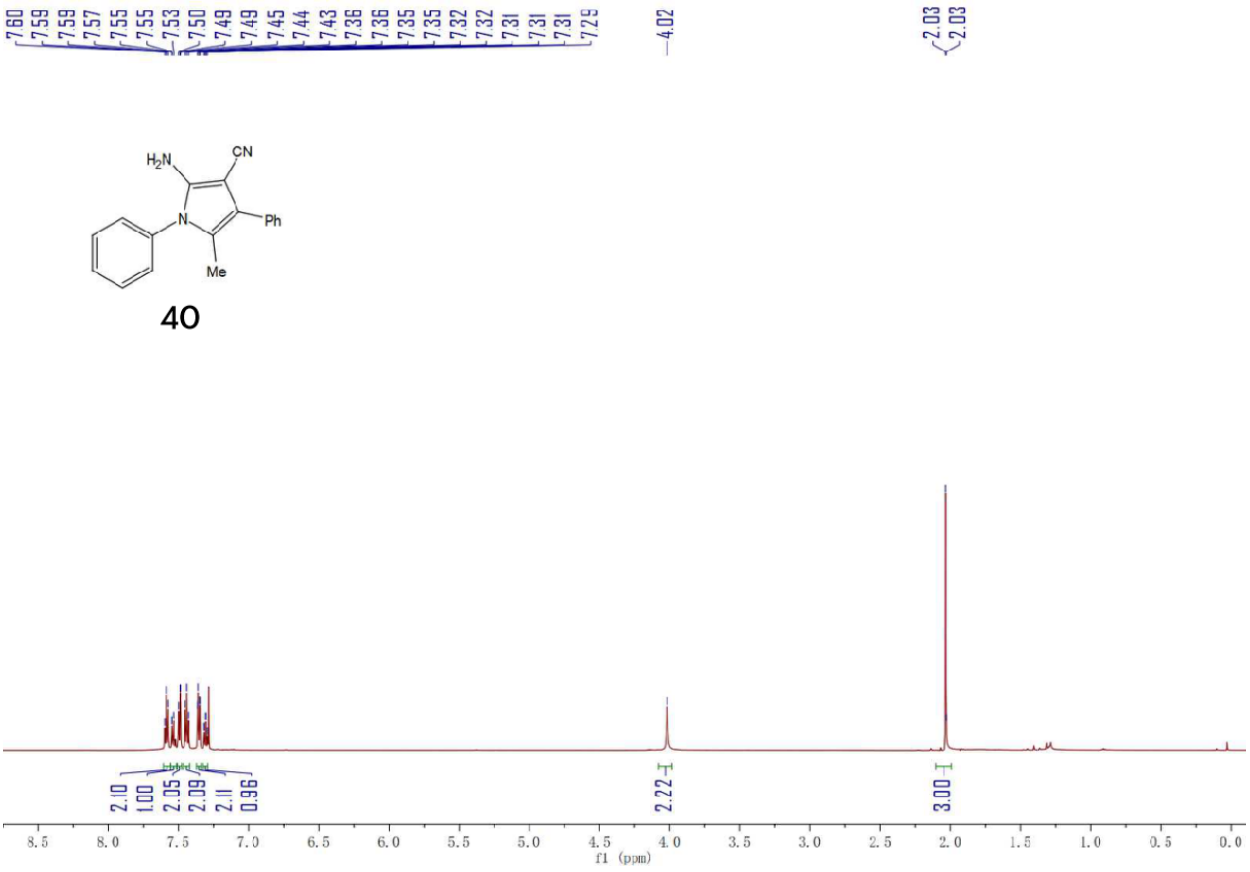


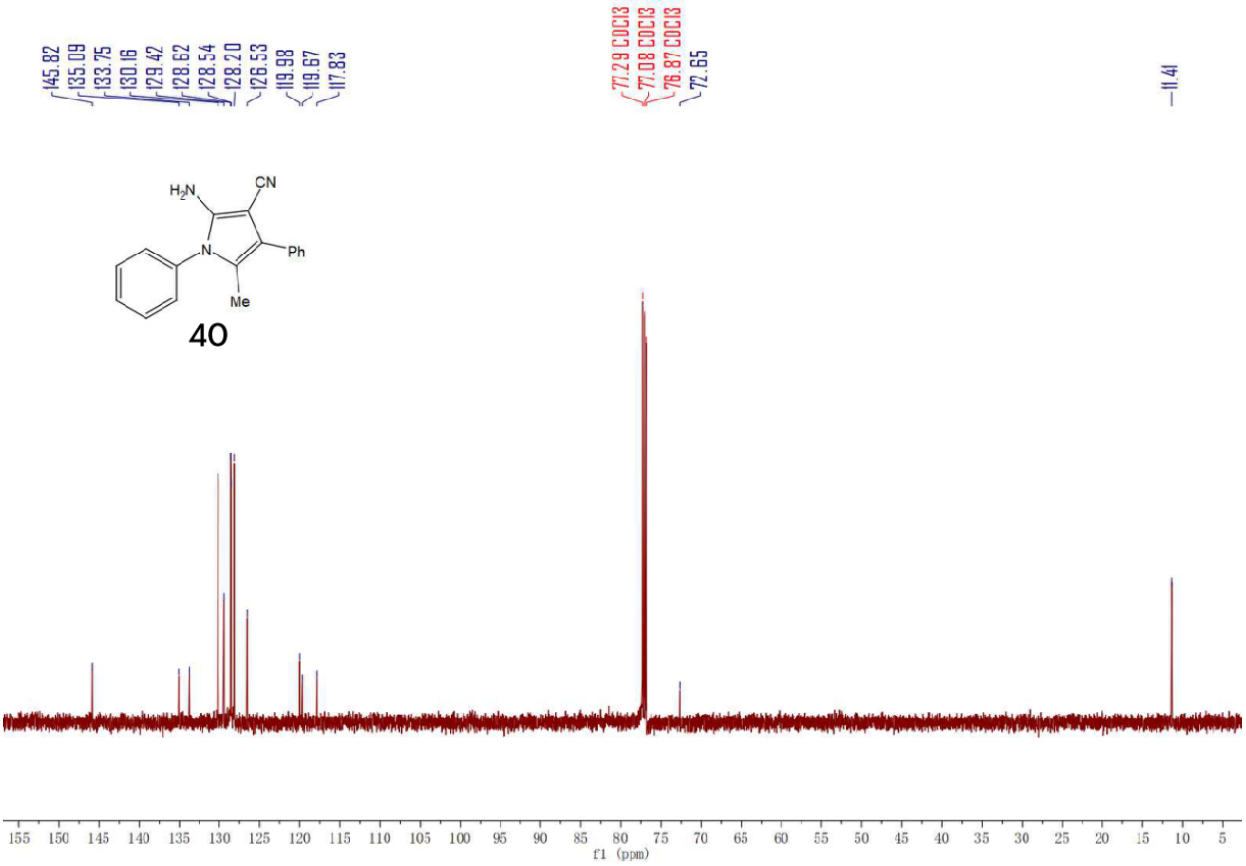
39 The reaction was set up following the general procedure using 4-fluoro-N-methylbenzenamine (125mg, 1 mmol) and benzylidenemalononitrile (31 mg, 0.2 mmol). After 16 hours, the reaction was purified following general work-up to give 6 mg (10 % yield) of the title compound. **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 7.69 – 7.62 (m, 2H), 7.52 – 7.23 (m, 7H), 6.53 (s, 1H), 4.21 – 4.12 (m, 2H); MS2 (ES^+) exact mass calculated for $[M+H]^+$ ($C_{17}H_{13}FN_3$) requires m/z 278.1, found m/z 278.1.

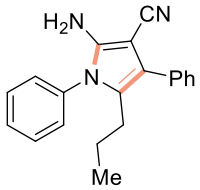

7.66
7.66
7.65
7.65
7.46
7.45
7.44
7.43
7.41
7.29
7.25
7.25
6.54
6.53
6.53
4.16
4.16
H2N
CN
N
Ph
F
39
grease
1.90
4.14
1.22
2.01
1.00
2.16
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)



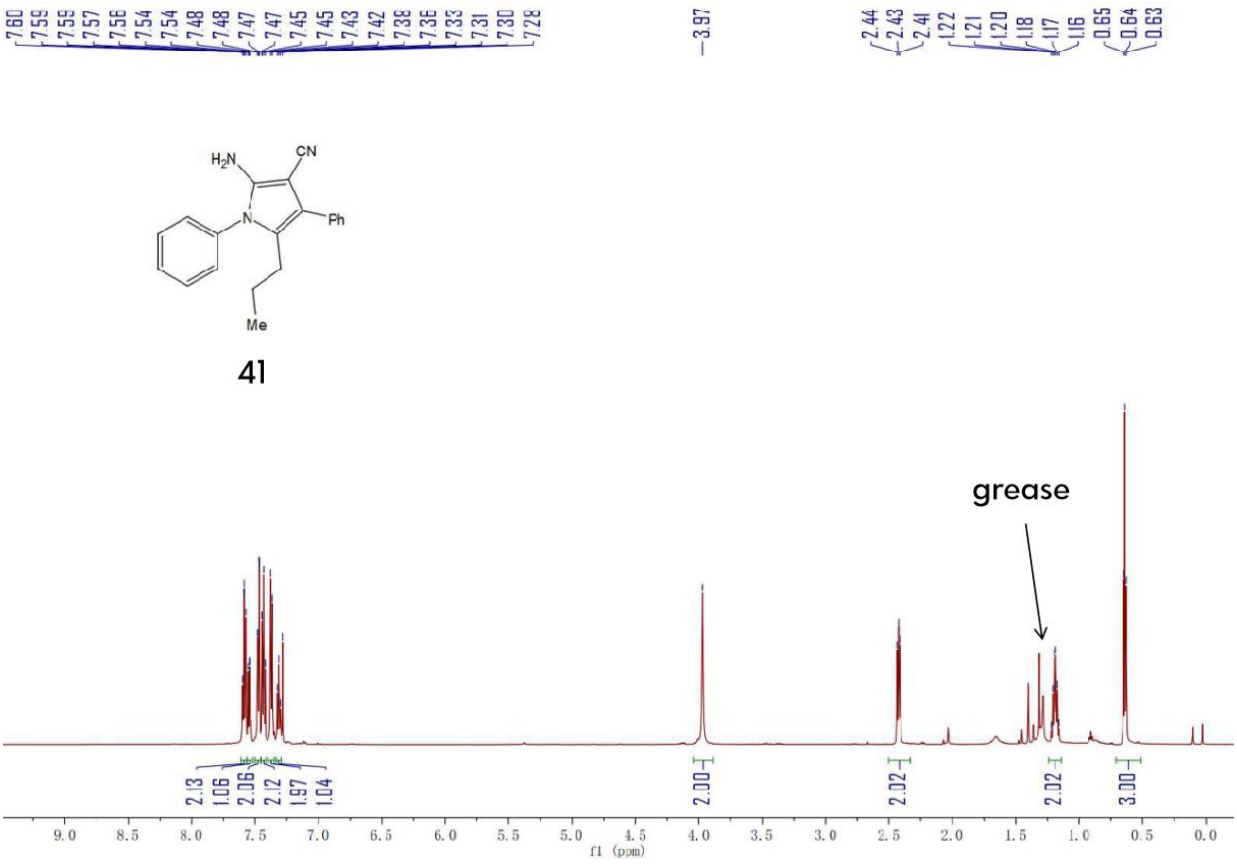
40 The reaction was set up following the general procedure using N-ethylaniline (121 mg, 1 mmol) and benzylidenemalononitrile (31 mg, 0.2 mmol). After 16 hours, the reaction was purified following general work-up to give 40 mg (71 % yield) of the title compound. **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 7.61 – 7.56 (m, 2H), 7.56 – 7.51 (m, 1H), 7.51 – 7.48 (m, 2H), 7.44 (m, *J* = 8.6, 7.0 Hz, 2H), 7.37 – 7.34 (m, 2H), 7.33 – 7.29 (m, 1H), 4.02 (s, 2H), 2.03 (s, 3H); **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 145.82, 135.09, 133.75, 130.16, 129.42, 128.62, 128.54, 128.20, 126.53, 119.98, 119.67, 117.83, 72.65, 11.41; MS2 (ES^+) exact mass calculated for $[M+H]^+$ ($C_{18}H_{16}N_3$) requires m/z 274.1, found m/z 274.1.


7.60
7.59
7.59
7.57
7.55
7.55
7.53
7.50
7.49
7.49
7.45
7.44
7.43
7.36
7.36
7.35
7.35
7.32
7.32
7.31
7.31
7.31
7.29
4.02
2.03
2.03
H2N
CN
N
Ph
Me
40
2.10
1.00
2.05
2.09
2.11
0.96
2.22
3.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


145.82
135.09
133.75
130.16
129.42
128.62
128.54
128.20
126.53
119.98
119.67
117.83
77.29 CDCl3
77.08 CDCl3
76.87 CDCl3
72.65
11.41
H2N
CN
N
Ph
Me
40
155 150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5
f1 (ppm)



41 The reaction was set up following the general procedure using N-Butylaniline (149 mg, 1 mmol) and benzylidenemalononitrile (31 mg, 0.2 mmol). After 16 hours, the reaction was purified following general work-up to give 36 mg (58 % yield) of the title compound. **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 7.59 (m, *J* = 8.3, 6.5 Hz, 2H), 7.58 – 7.52 (m, 1H), 7.47 (m, *J* = 8.1, 1.5 Hz, 2H), 7.43 (t, *J* = 7.7 Hz, 2H), 7.37 (m, *J* = 7.4, 1.9 Hz, 2H), 7.34 – 7.27 (m, 1H), 3.97 (s, 2H), 2.45 – 2.39 (m, 2H), 1.19 (m, *J* = 7.4 Hz, 2H), 0.64 (t, *J* = 7.4 Hz, 3H); **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 145.72, 135.25, 133.91, 130.09, 129.50, 128.75, 128.52, 128.42, 126.64, 124.82, 120.24, 117.73, 73.01, 26.56, 23.05, 13.65; MS2 (ES^+) exact mass calculated for $[M+H]^+$ ($C_{20}H_{20}N_3$) requires m/z 302.1, found m/z 302.1.


7.60
7.59
7.59
7.57
7.56
7.54
7.54
7.48
7.48
7.47
7.47
7.45
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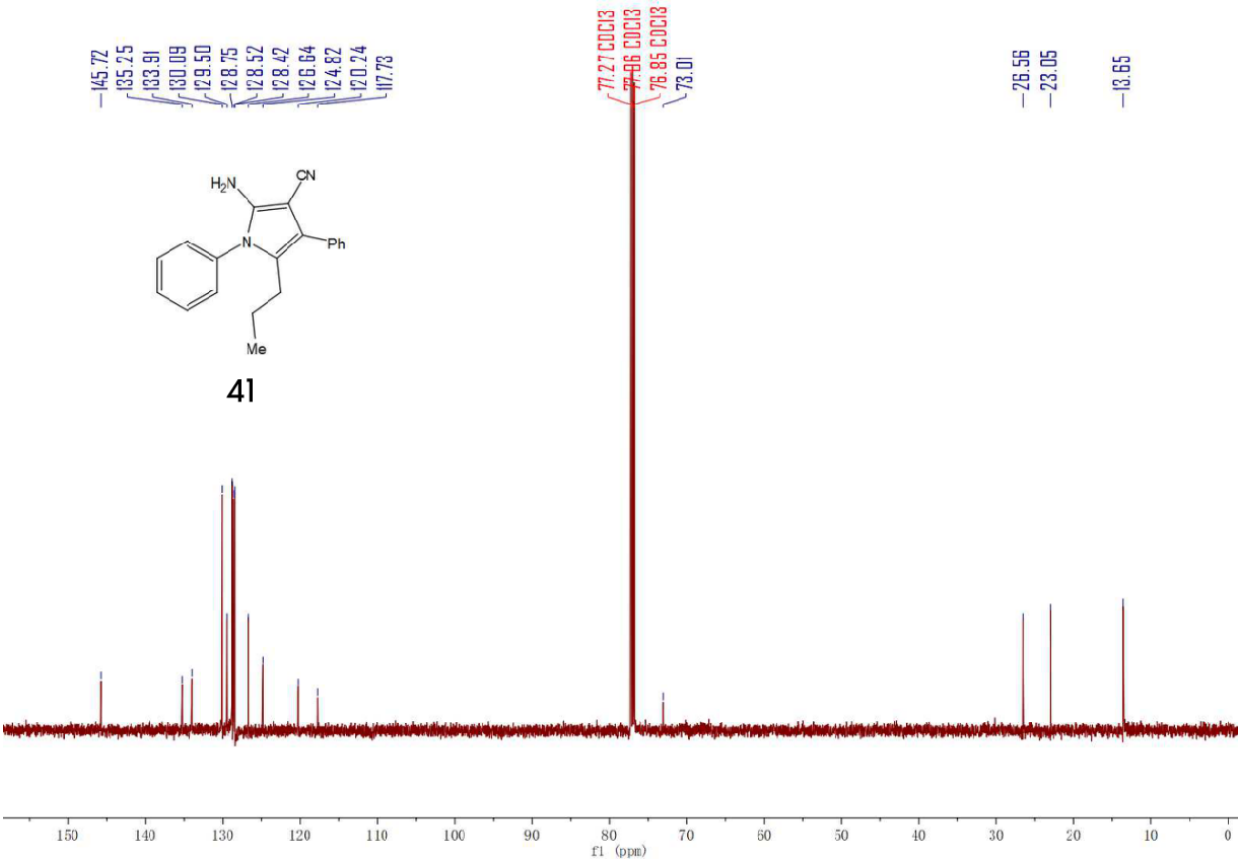
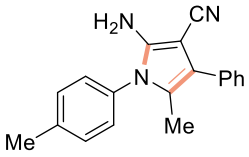
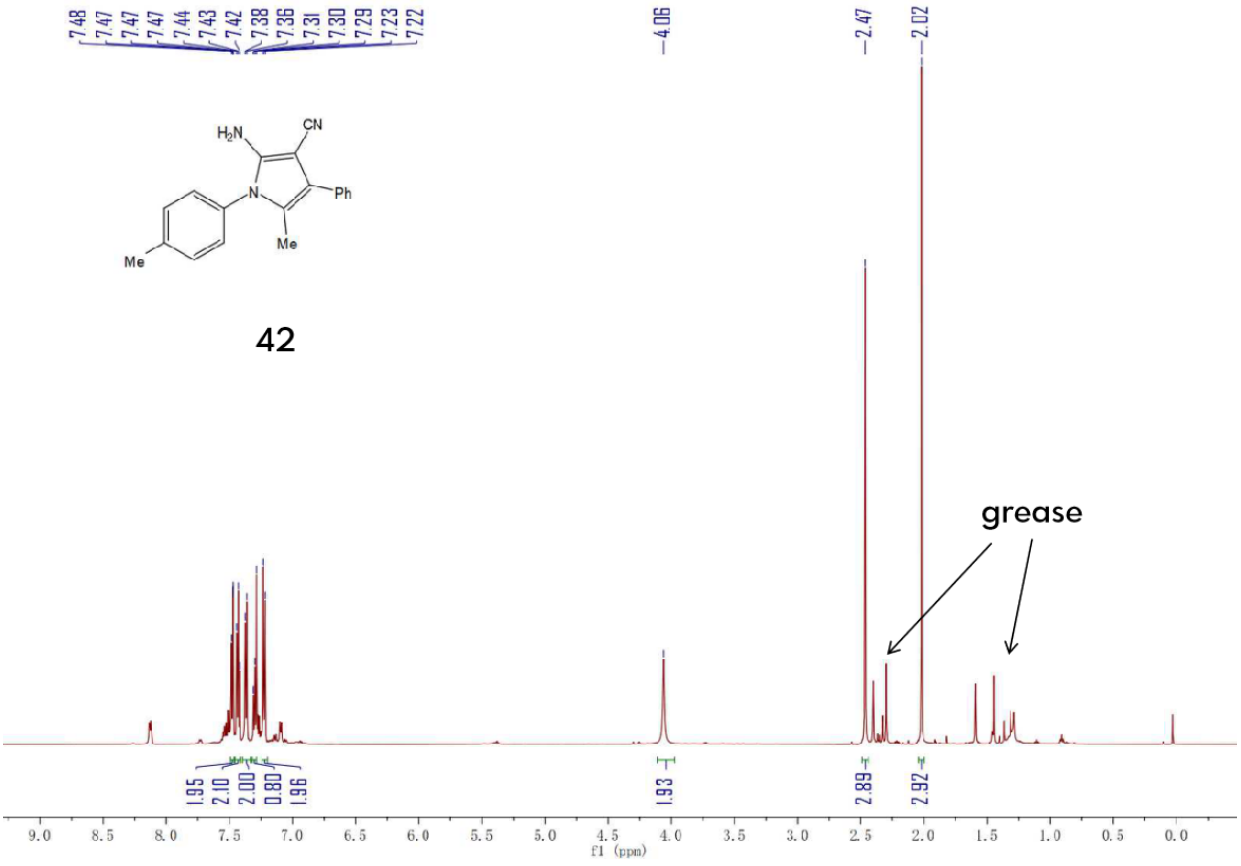
7.43
7.42
7.38
7.36
7.33
7.31
7.30
7.28
3.97
2.44
2.43
2.41
1.22
1.21
1.20
1.18
1.17
1.16
0.65
0.64
0.63
H2N
CN
N
Ph
Me
41
grease
2.13
1.06
2.06
2.12
1.97
1.04
2.00
2.02
2.02
3.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

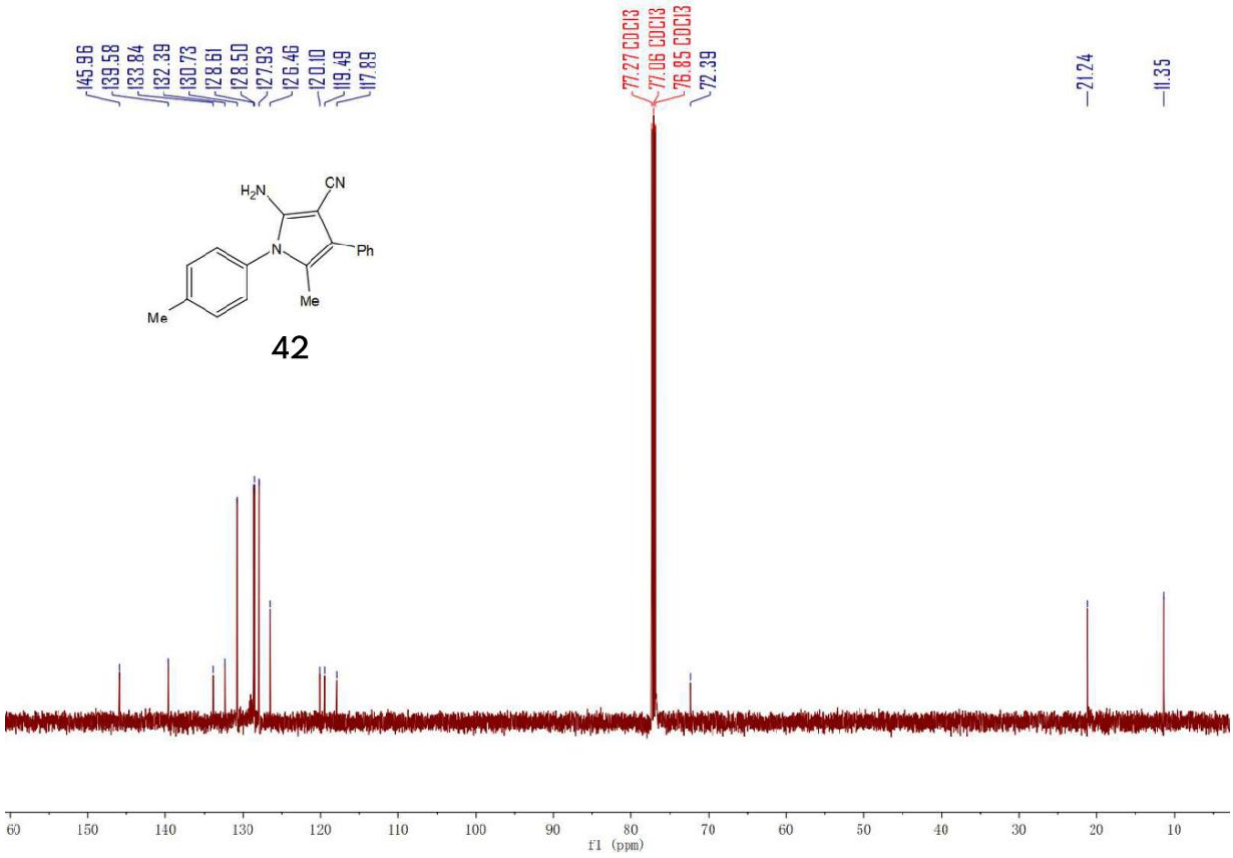

145.72
135.25
133.91
130.09
129.50
128.75
128.52
128.42
126.64
124.82
120.24
117.73
77.27 CDCl3
77.06 CDCl3
76.85 CDCl3
73.01
26.56
23.05
13.65
H2N
CN
N
Ph
Me
41
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



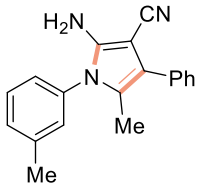
42 The reaction was set up following the general procedure using 4-methyl-N-ethylbenzenamine (135 mg, 1 mmol) and benzylidenemalononitrile (31 mg, 0.2 mmol). After 16 hours, the reaction was purified following general work-up to give 47 mg (81 % yield) of the title compound. **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 7.48 (m, 2H), 7.43 (t, *J* = 7.7 Hz, 2H), 7.37 (d, *J* = 7.9 Hz, 2H), 7.33 – 7.26 (m, 1H), 7.27 – 7.20 (m, 2H), 4.06 (s, 2H), 2.47 (s, 3H), 2.02 (s, 3H); **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 145.96, 139.58, 133.84, 132.39, 130.73, 128.61, 128.50, 127.93, 126.46, 120.10, 119.49, 117.89, 72.39, 21.24, 11.35; MS2 (ES^+) exact mass calculated for $[M+H]^+$ ($C_{19}H_{18}N_3$) requires m/z 288.1, found m/z 288.1.


7.48
7.47
7.47
7.47
7.44
7.43
7.42
7.38
7.36
7.31
7.30
7.29
7.23
7.22
4.06
2.47
2.02
H2N
CN
N
Ph
Me
Me
grease
1.95
2.10
2.00
0.80
1.96
1.93
2.89
2.92
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

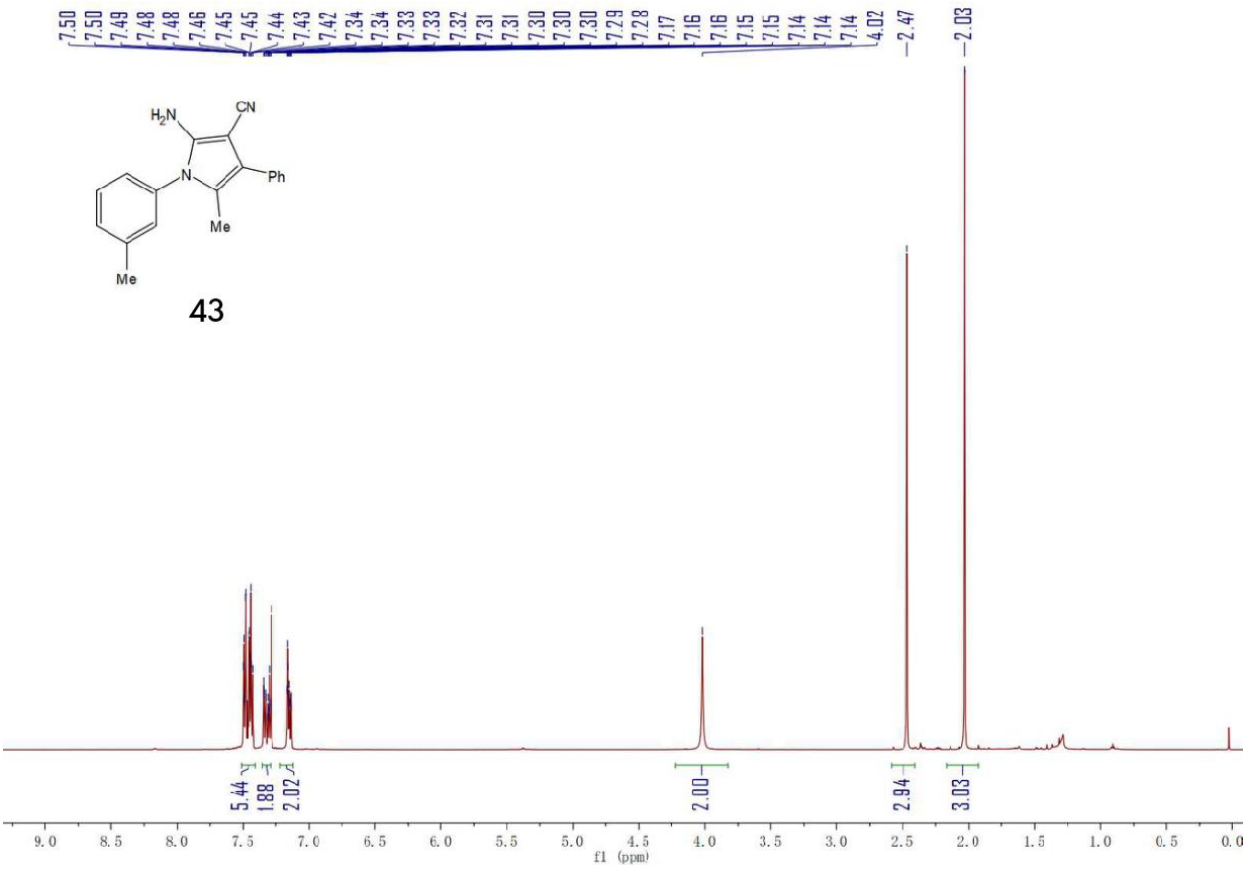
42


145.96
139.58
133.84
132.39
130.73
128.61
128.50
127.93
126.46
120.10
119.49
117.89
77.27 CDCl3
77.06 CDCl3
76.85 CDCl3
72.39
21.24
11.35
H2N
CN
N
Ph
Me
Me
60
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

42



43 The reaction was set up following the general procedure using 3-methyl-N-ethylbenzenamine (135 mg, 1 mmol) and benzylidenemalononitrile (31 mg, 0.2 mmol). After 16 hours, the reaction was purified following general work-up to give 42 mg (72 % yield) of the title compound. **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 7.52 – 7.42 (m, 5H), 7.32 (m, *J* = 17.7, 7.4, 1.4 Hz, 2H), 7.22 – 7.12 (m, 2H), 4.02 (s, 2H), 2.47 (s, 3H), 2.03 (s, 3H); **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 145.77, 140.41, 135.00, 133.82, 130.19, 129.90, 128.68, 128.61, 128.52, 126.48, 125.13, 120.01, 119.55, 117.85, 72.55, 21.35, 11.40; MS2 (ES^+) exact mass calculated for $[M+H]^+$ ($C_{19}H_{18}N_3$) requires m/z 288.1, found m/z 288.1.


7.50
7.50
7.49
7.48
7.48
7.46
7.45
7.45
7.44
7.43
7.42
7.34
7.34
7.33
7.33
7.32
7.31
7.31
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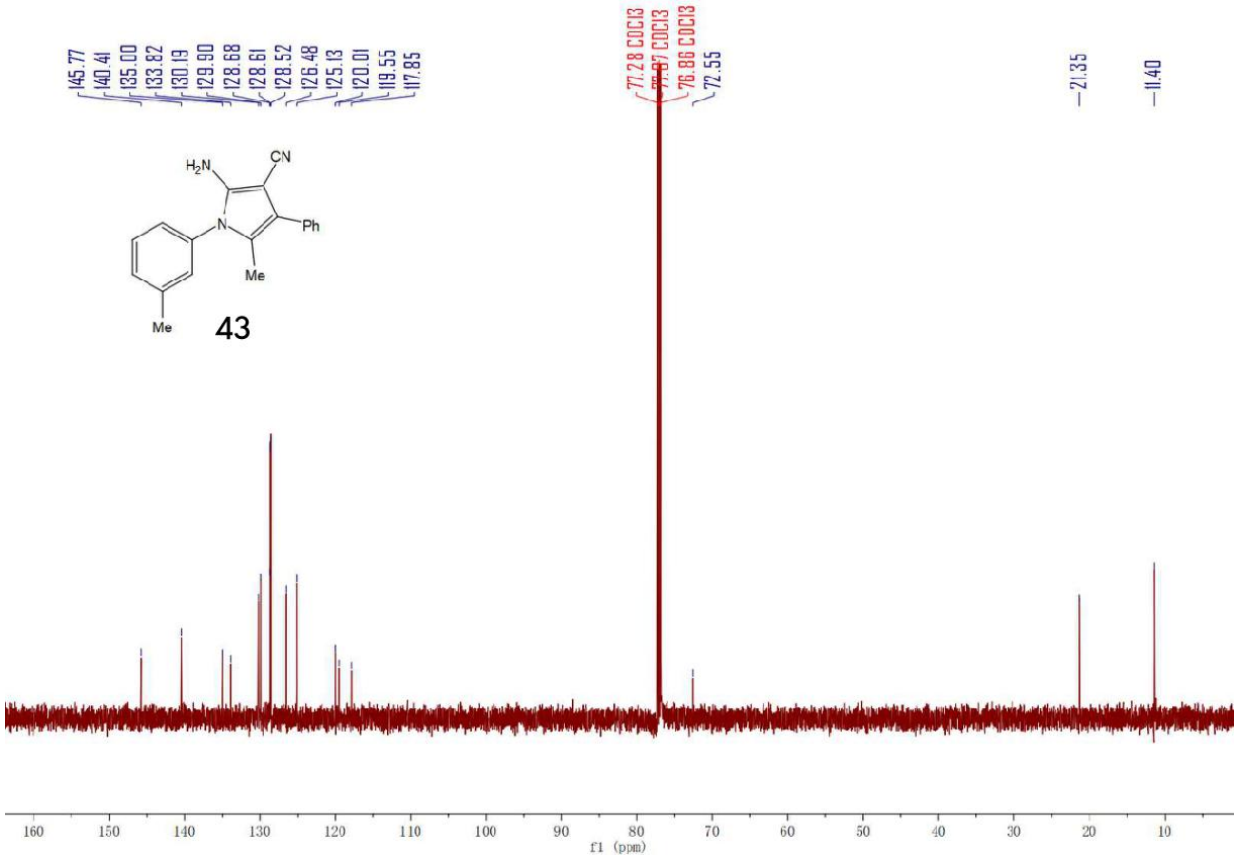
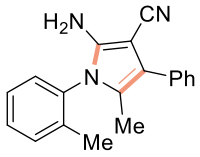
7.30
7.29
7.28
7.17
7.16
7.16
7.15
7.15
7.14
7.14
7.14
4.02
2.47
2.03
H2N
CN
N
Ph
Me
Me
5.44
1.88
2.02
2.00
2.94
3.03
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

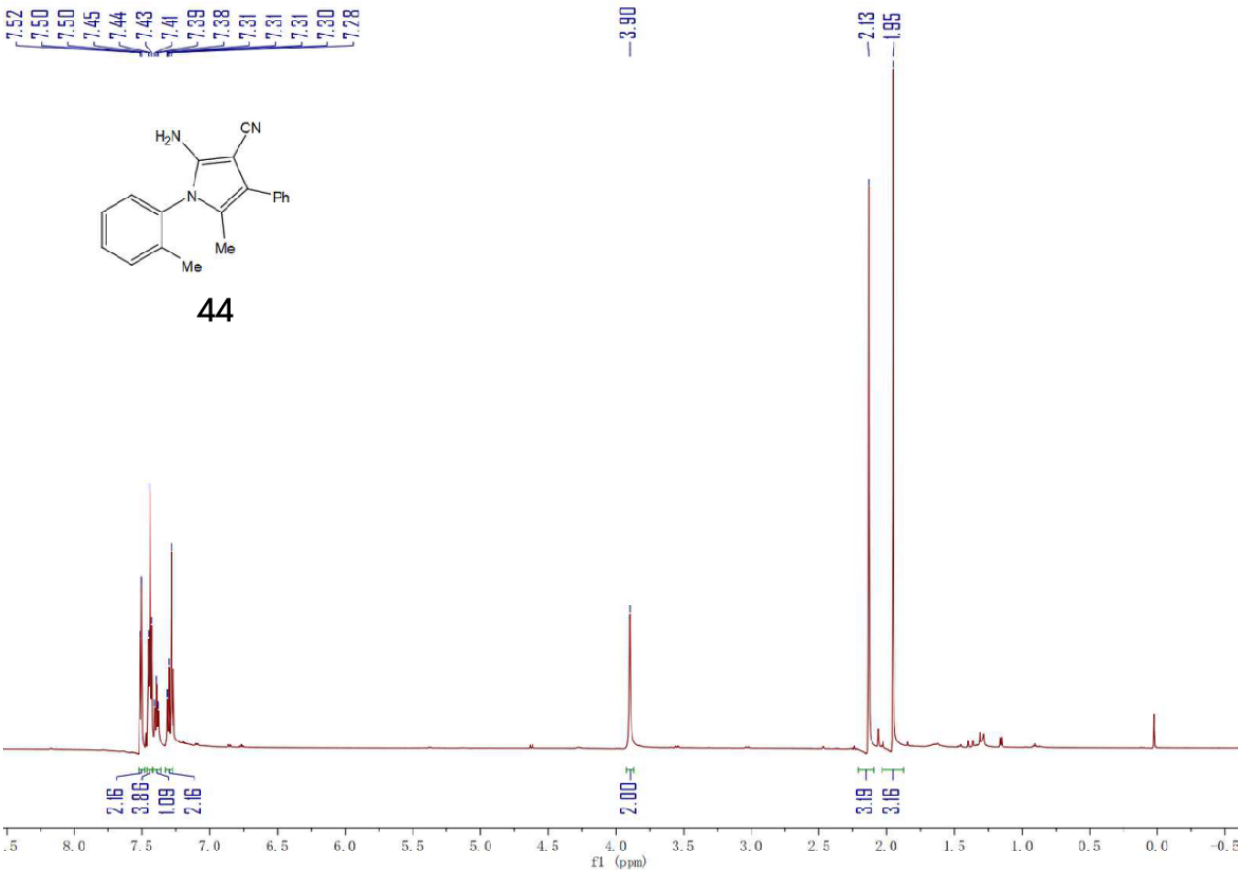
43


145.77
140.41
135.00
133.82
130.19
129.90
128.68
128.61
128.52
126.48
125.13
120.01
119.55
117.85
77.28 CDCl3
77.07 CDCl3
76.86 CDCl3
72.55
21.35
11.40
H2N
CN
N
Ph
Me
Me
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

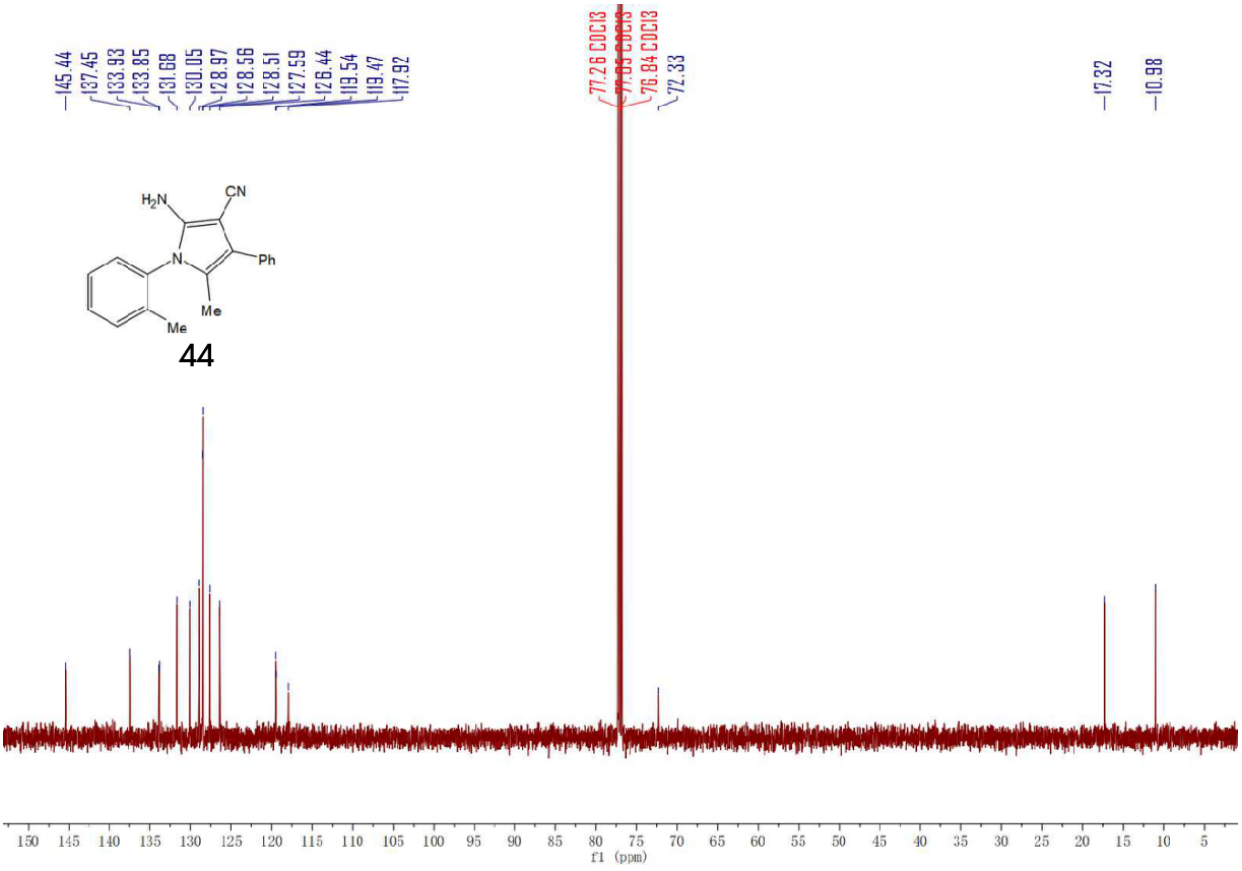
43



44 The reaction was set up following the general procedure using 2-methyl-N-ethylbenzenamine (135 mg, 1 mmol) and benzylidenemalononitrile (31 mg, 0.2 mmol). After 16 hours, the reaction was purified following general work-up to give 30 mg (51 % yield) of the title compound. **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 7.53 – 7.48 (m, 2H), 7.47 – 7.42 (m, 4H), 7.39 (m, *J* = 7.4, 2.0 Hz, 1H), 7.33 – 7.27 (m, 2H), 3.90 (s, 2H), 2.13 (s, 3H), 1.95 (s, 3H); **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 145.44, 137.45, 133.93, 133.85, 131.68, 130.05, 128.97, 128.56, 128.51, 127.59, 126.44, 119.54, 119.47, 117.92, 72.33, 17.32, 10.98; MS2 (ES^+) exact mass calculated for $[M+H]^+$ ($C_{19}H_{18}N_3$) requires m/z 288.1, found m/z 288.1.


7.52
7.50
7.50
7.45
7.44
7.43
7.41
7.39
7.38
7.31
7.31
7.31
7.30
7.28
3.90
2.13
1.95
H2N
CN
N
Ph
Me
Me
2.16
3.86
1.09
2.16
2.00
3.19
3.16
f1 (ppm)

44


145.44
137.45
133.93
133.85
131.68
130.05
128.97
128.56
128.51
127.59
126.44
119.54
119.47
117.92
77.26 CDCl3
77.05 CDCl3
76.84 CDCl3
72.33
17.32
10.98
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CN
Ph
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Me
Me
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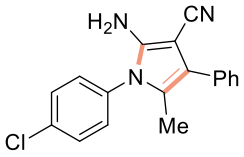
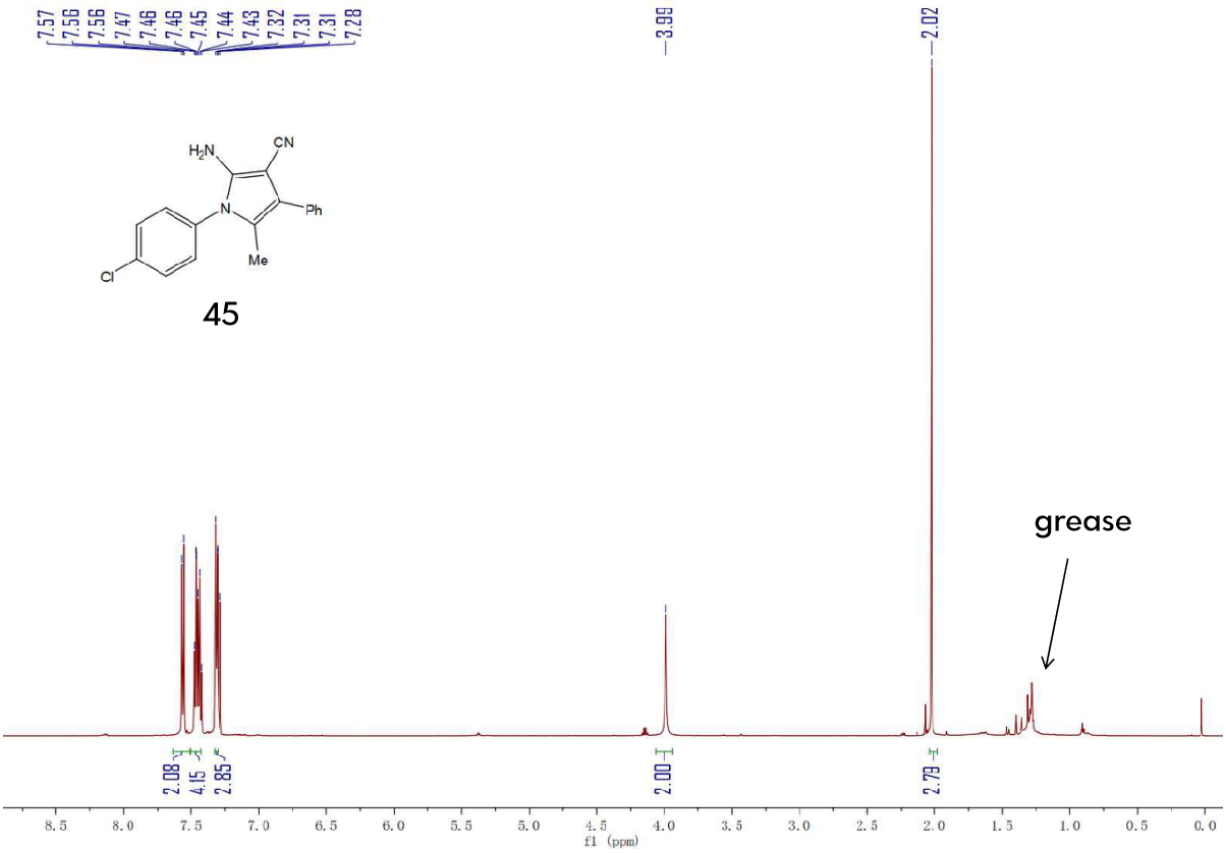
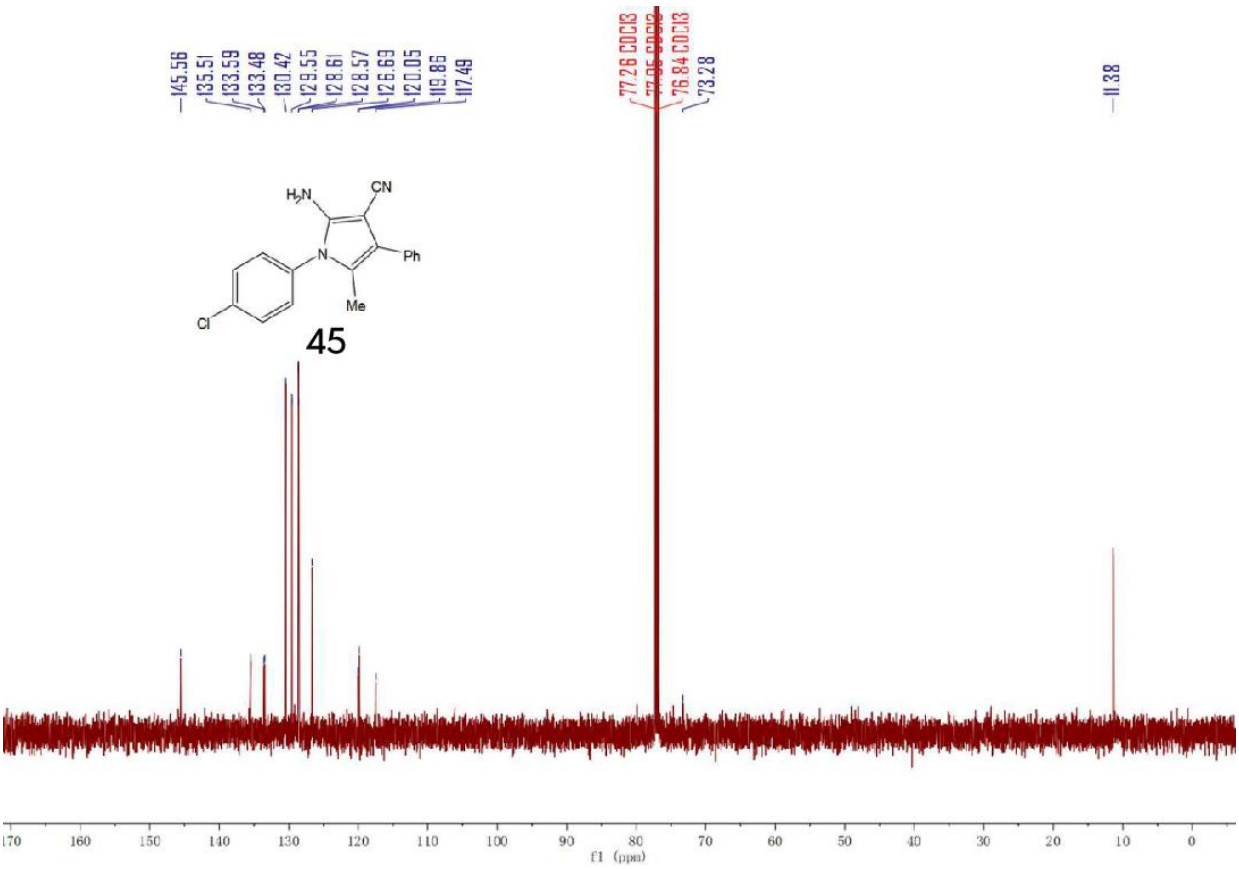
f1 (ppm)

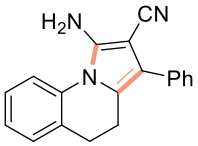
44



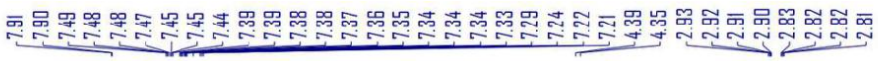
45 The reaction was set up following the general procedure using 4-chloro-N-ethylbenzenamine (155 mg, 1 mmol) and benzylidenemalononitrile (31 mg, 0.2 mmol). After 16 hours, the reaction was purified following general work-up to give 33 mg (54 % yield) of the title compound. **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 7.64 – 7.51 (m, 2H), 7.50 – 7.39 (m, 4H), 7.33 – 7.18 (m, 3H), 3.99 (s, 2H), 2.02 (s, 3H); **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 145.56, 135.51, 133.59, 133.48, 130.42, 129.55, 128.61, 128.57, 126.69, 120.05, 119.86, 117.49, 73.28, 11.38; MS2 (ES^+) exact mass calculated for $[M+H]^+$ ($C_{18}H_{15}ClN_3$) requires m/z 308.1, found m/z 308.1.


7.57
7.56
7.56
7.47
7.46
7.46
7.45
7.44
7.43
7.32
7.31
7.31
7.28
3.99
2.02
H2N
CN
N
Ph
Me
Cl
45
grease
2.08
4.15
2.85
2.00
2.79
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


145.56
135.51
133.59
133.48
130.42
129.55
128.61
128.57
126.63
120.05
116.86
117.49
77.26 CDCl3
76.84 CDCl3
73.28
11.38
H2N
CN
Ph
Me
Cl
45
f1 (ppm)



46 The reaction was set up following the general procedure using 1,2,3,4-tetrahydroquinoline (133 mg, 1 mmol) and benzylidenemalononitrile (31 mg, 0.2 mmol). After 16 hours, the reaction was purified following general work-up to give 33 mg (58 % yield) of the title compound. **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 7.90 (d, *J* = 8.0 Hz, 1H), 7.53 – 7.43 (m, 4H), 7.41 – 7.35 (m, 1H), 7.34 – 7.31 (m, 2H), 7.22 (t, *J* = 7.5 Hz, 1H), 4.39 (s, 2H), 2.92 (m, *J* = 7.9, 5.1 Hz, 2H), 2.82 (m, *J* = 8.0, 5.0 Hz, 2H); **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 144.47, 135.17, 132.81, 131.34, 129.42, 128.60, 128.43, 127.75, 126.79, 125.64, 121.73, 117.89, 117.66, 117.48, 75.82, 28.22, 21.87; MS2 (ES^+) exact mass calculated for $[M+H]^+$ ($C_{19}H_{16}N_3$) requires m/z 286.1, found m/z 286.1.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7.90
7.49
7.48
7.48
7.47
7.45
7.45
7.44
7.39
7.39
7.38
7.38
7.37
7.36
7.35
7.34
7.34
7.34
7.33
7.29
7.24
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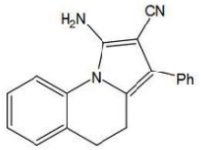
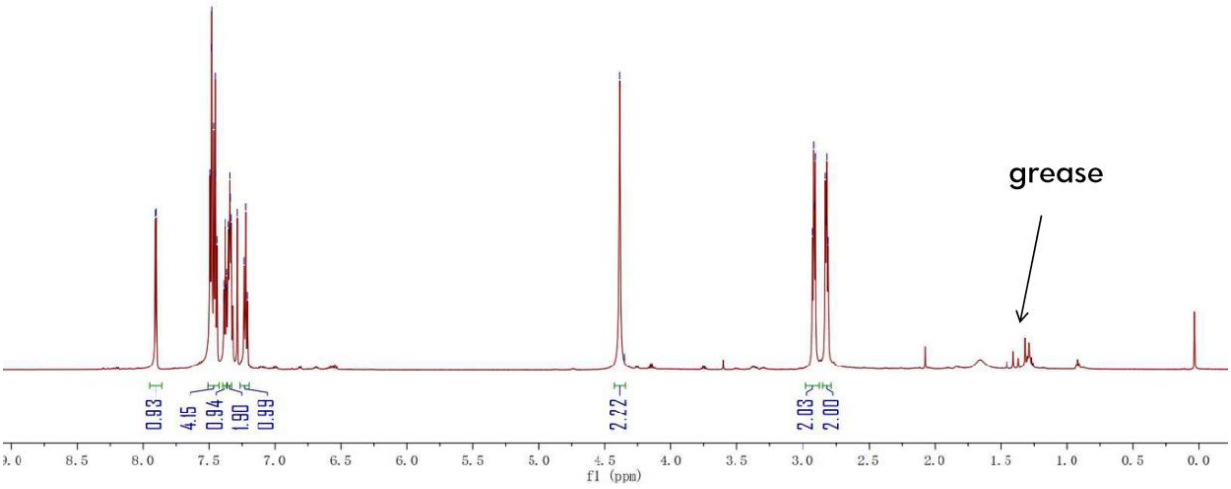
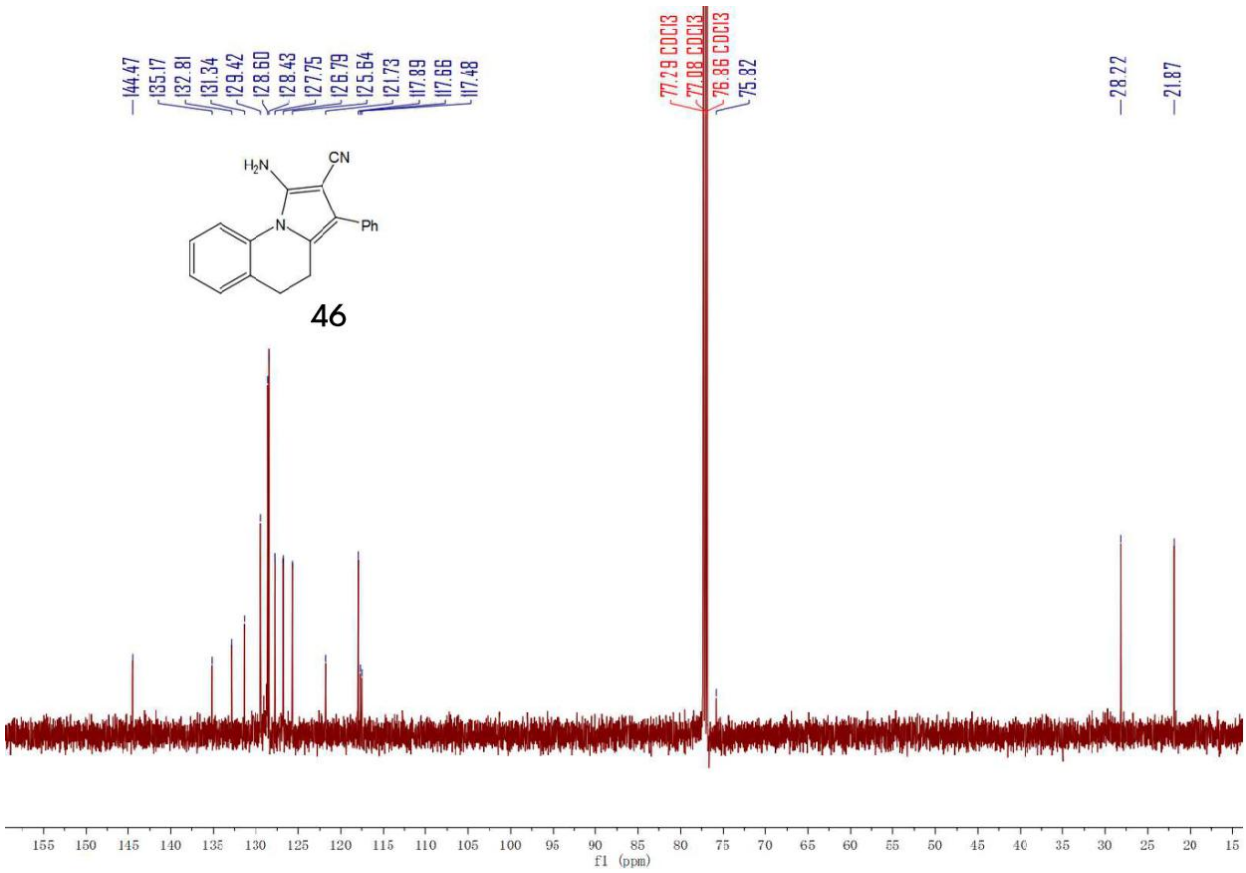
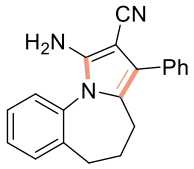
2.91
2.90
2.83
2.82
2.82
2.81


H2N
CN
N
Ph

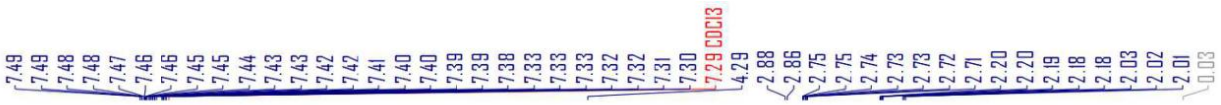
46

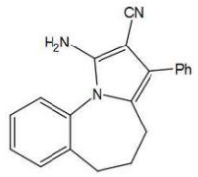

grease
0.93
4.15
0.94
1.90
0.99
2.22
2.03
2.00
f1 (ppm)


144.47
135.17
132.81
131.34
129.42
128.60
128.43
127.75
126.79
125.64
121.73
117.89
117.66
117.48
77.29 CDCl3
77.08 CDCl3
76.86 CDCl3
75.82
28.22
21.87
H2N
CN
N
Ph
46
f1 (ppm)

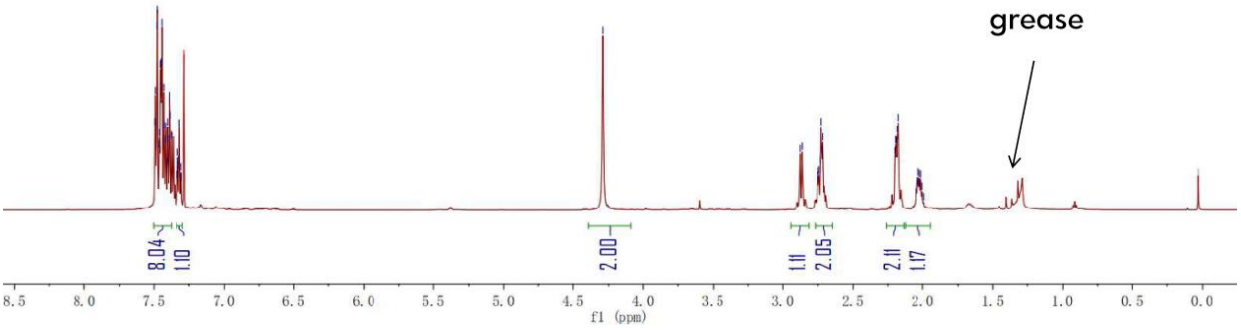


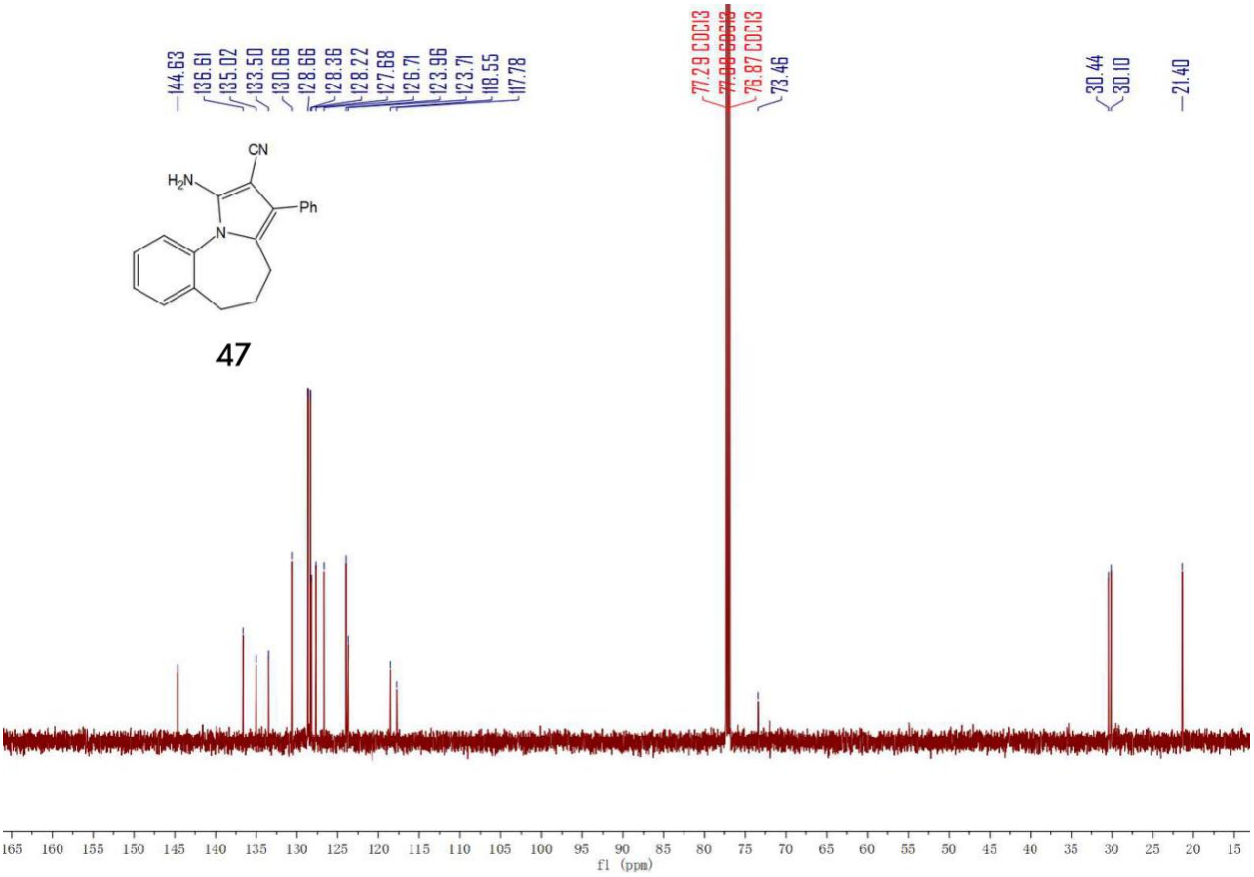
47 The reaction was set up following the general procedure using 2,3,4,5-tetrahydro-1H-1-benzazepine (147 mg, 1 mmol) and benzylidenemalononitrile (31 mg, 0.2 mmol). After 16 hours, the reaction was purified following general work-up to give 36 mg (61 % yield) of the title compound. **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 7.51 – 7.33 (m, 8H), 7.32 (t, *J* = 7.3 Hz, 1H), 4.29 (s, 2H), 2.86 (m, *J* = 12.1, 9.0 Hz, 1H), 2.73 (m, *J* = 13.4, 9.9, 4.9 Hz, 2H), 2.24 – 2.13 (m, 2H), 2.06 – 1.98 (m, 1H); ^{13}C **NMR** (151 MHz, Chloroform-*d*) δ 144.63, 136.61, 135.02, 133.50, 130.66, 128.66, 128.36, 128.22, 127.68, 126.71, 123.96, 123.71, 118.55, 117.78, 73.46, 30.44, 30.10, 21.40; MS2 (ES^+) exact mass calculated for $[M+H]^+$ ($C_{20}H_{18}N_3$) requires m/z 300.1, found m/z 300.1.

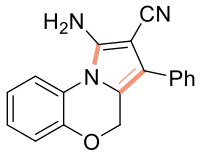

7.49
7.49
7.48
7.48
7.47
7.46
7.46
7.45
7.45
7.44
7.43
7.43
7.42
7.42
7.41
7.40
7.40
7.39
7.39
7.38
7.33
7.33
7.33
7.32
7.32
7.31
7.30
7.29 CDCl3
4.29
2.88
2.86
2.75
2.75
2.74
2.73
2.73
2.72
2.71
2.20
2.20
2.19
2.18
2.18
2.03
2.02
2.01
0.03


CN
H2N
Ph
N

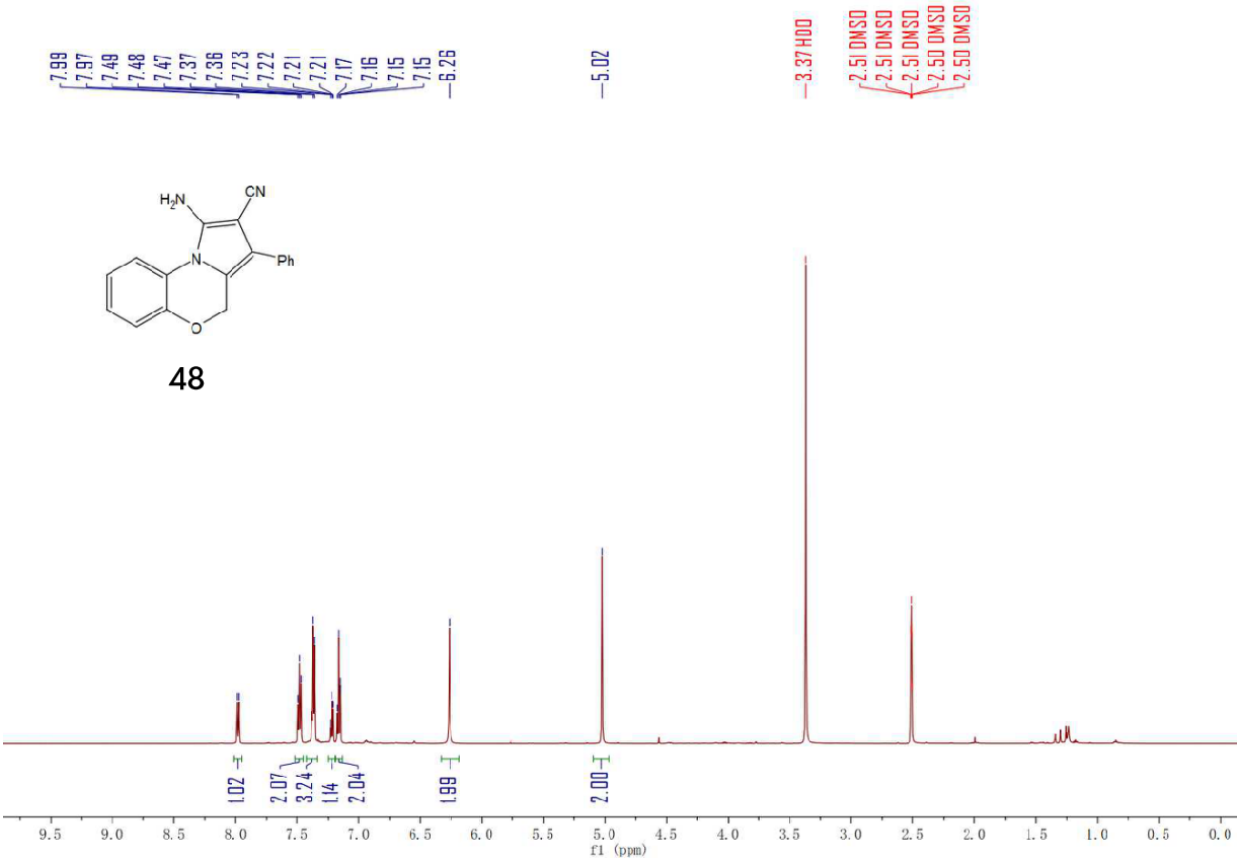
47

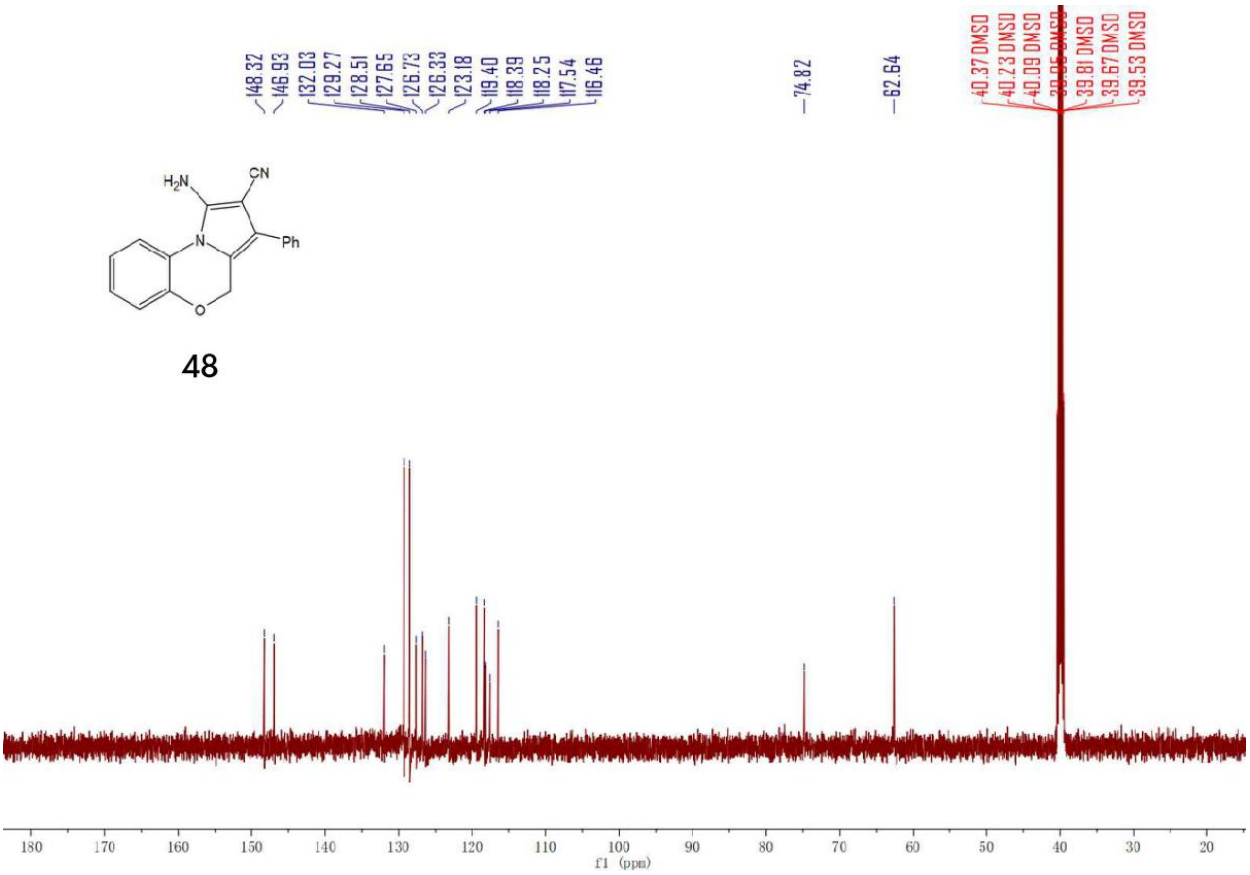

grease
8.04
1.10
2.00
1.11
2.05
2.11
1.17
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

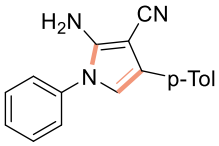

144.63
136.61
135.02
133.50
130.66
128.66
128.36
128.22
127.68
126.71
123.96
123.71
118.55
117.78
77.29 CDCl3
76.87 CDCl3
73.46
30.44
30.10
21.40
CN
H2N
Ph
N
47
f1 (ppm)



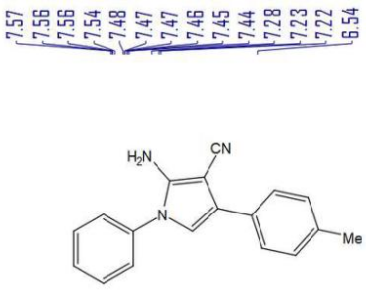
48 The reaction was set up following the general procedure using 3,4-dihydro-2H-1,4-benzoxazine (135 mg, 1 mmol) and benzylidenemalononitrile (31 mg, 0.2 mmol). After 16 hours, the reaction was purified following general work-up to give 29 mg (51 % yield) of the title compound. **^{1}H NMR** (600 MHz, DMSO-d_6) δ 7.98 (d, J = 7.7, 1.8 Hz, 1H), 7.48 (t, J = 7.6 Hz, 2H), 7.40 – 7.34 (m, 3H), 7.25 – 7.20 (m,1H), 7.22 – 7.13 (m, 2H), 6.26 (s, 2H), 5.02 (s, 2H); **^{13}C NMR** (151 MHz, DMSO-d_6) δ 148.32, 146.93, 132.03, 129.27, 128.51, 127.65, 126.73, 126.33, 123.18, 119.40, 118.39, 118.25, 117.54, 116.46, 74.82, 62.64; MS2 (ES^+) exact mass calculated for $[M+H]^+$ ($C_{18}H_{14}N_3O$) requires m/z 288.1, found m/z 288.1.


7.99
7.97
7.49
7.48
7.47
7.37
7.36
7.23
7.22
7.21
7.21
7.17
7.16
7.15
7.15
6.26
5.02
3.37 HDO
2.51 DMSO
2.51 DMSO
2.50 DMSO
2.50 DMSO
2.50 DMSO
H2N
CN
Ph
N
O
48
1.02
2.07
3.24
1.14
2.04
1.99
2.00
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

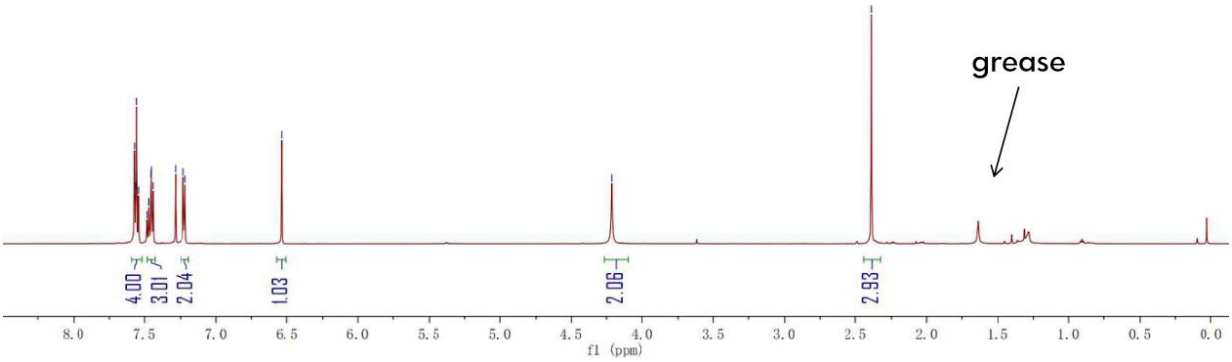

148.32
146.93
132.03
129.27
128.51
127.65
126.73
126.33
123.18
119.40
118.39
118.25
117.54
116.46
74.82
62.64
40.37 DMSO
40.23 DMSO
40.09 DMSO
39.81 DMSO
39.67 DMSO
39.53 DMSO
H2N
CN
Ph
N
O
48
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
f1 (ppm)

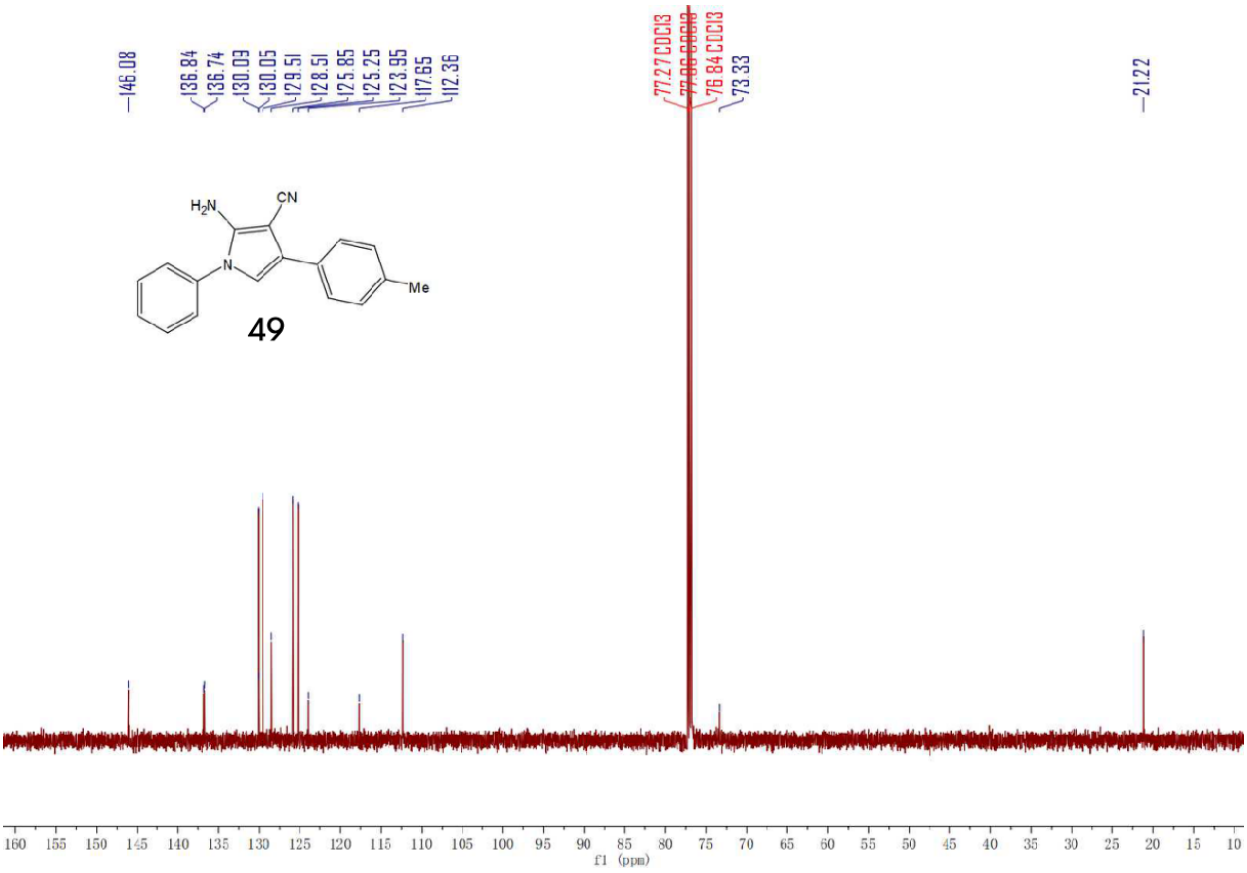


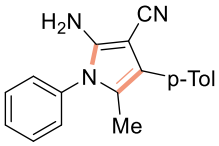
49 The reaction was set up following the general procedure using N-methylaniline (107 mg, 1 mmol) and 4-methylbenzylidenemalononitrile (34 mg, 0.2 mmol). After 16 hours, the reaction was purified following general work-up to give 39 mg (72 % yield) of the title compound. **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 7.56 (t, *J* = 8.1 Hz, 4H), 7.50 – 7.42 (m, 3H), 7.22 (d, *J* = 7.8 Hz, 2H), 6.54 (s, 1H), 4.21 (s, 2H), 2.39 (s, 3H); **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 146.08, 136.84, 136.74, 130.09, 130.05, 129.51, 128.51, 125.85, 125.25, 123.95, 117.65, 112.36, 73.33, 21.22; MS2 (ES^+) exact mass calculated for $[M+H]^+$ ($C_{18}H_{16}N_3$) requires m/z 274.1, found m/z 274.1.


7.57
7.56
7.56
7.54
7.48
7.47
7.47
7.46
7.45
7.44
7.28
7.23
7.22
6.54
4.21
2.39
H2N
CN
N
Me

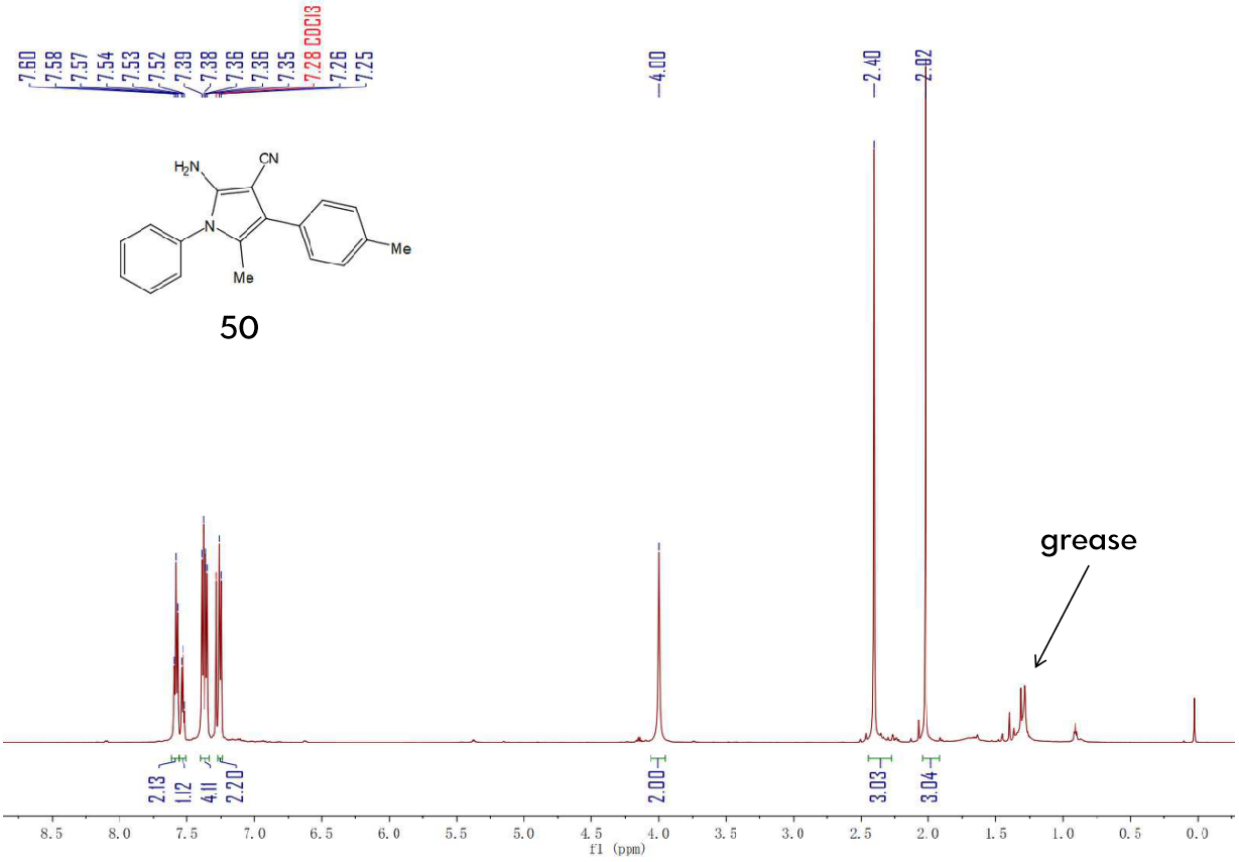
49

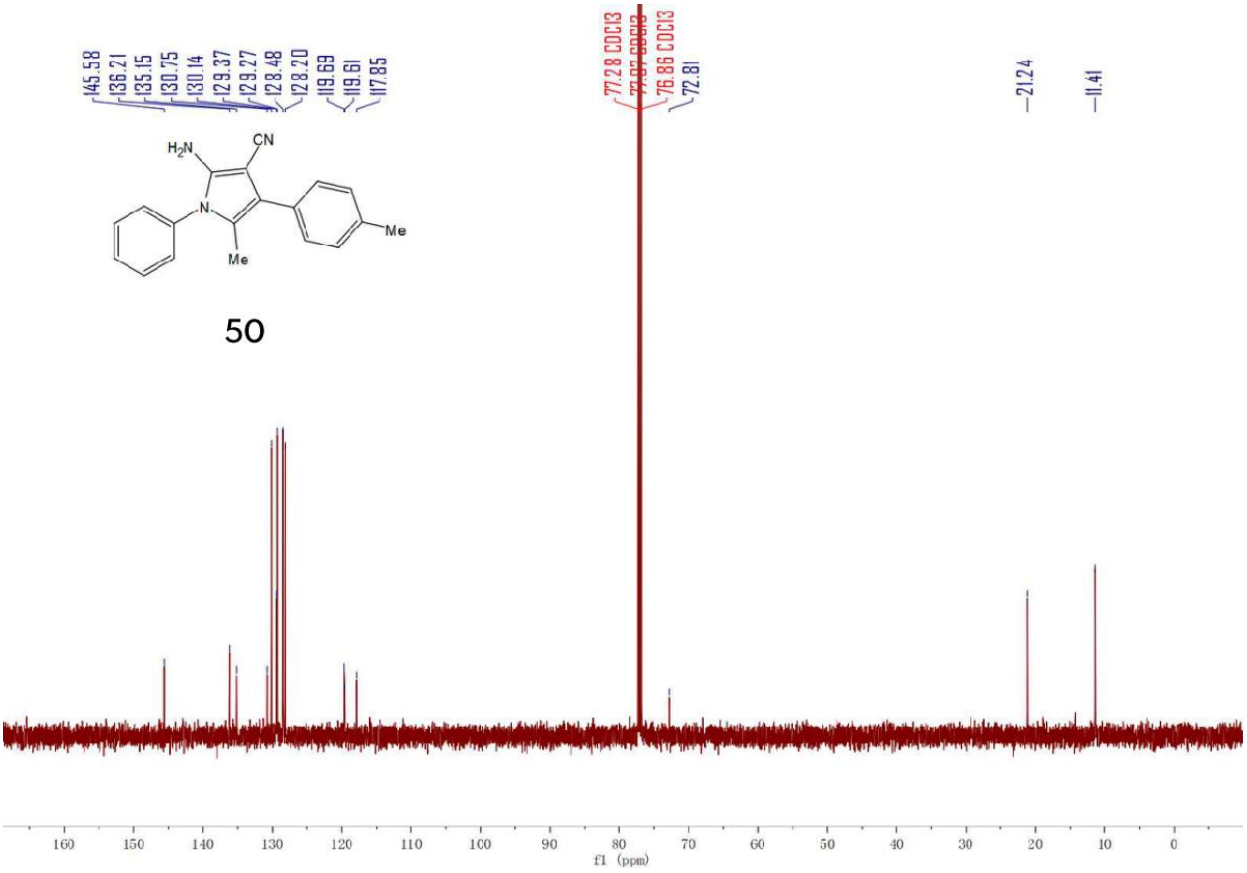

grease
4.00
3.01
2.04
1.03
2.06
2.93
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

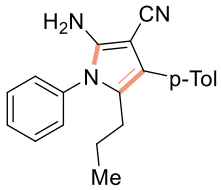

146.08
136.84
136.74
130.09
130.05
129.51
128.51
125.85
125.25
123.95
117.65
112.36
77.27 CDCl3
76.84 CDCl3
73.33
21.22
H2N
CN
N
Me
49
160 155 150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10
f1 (ppm)



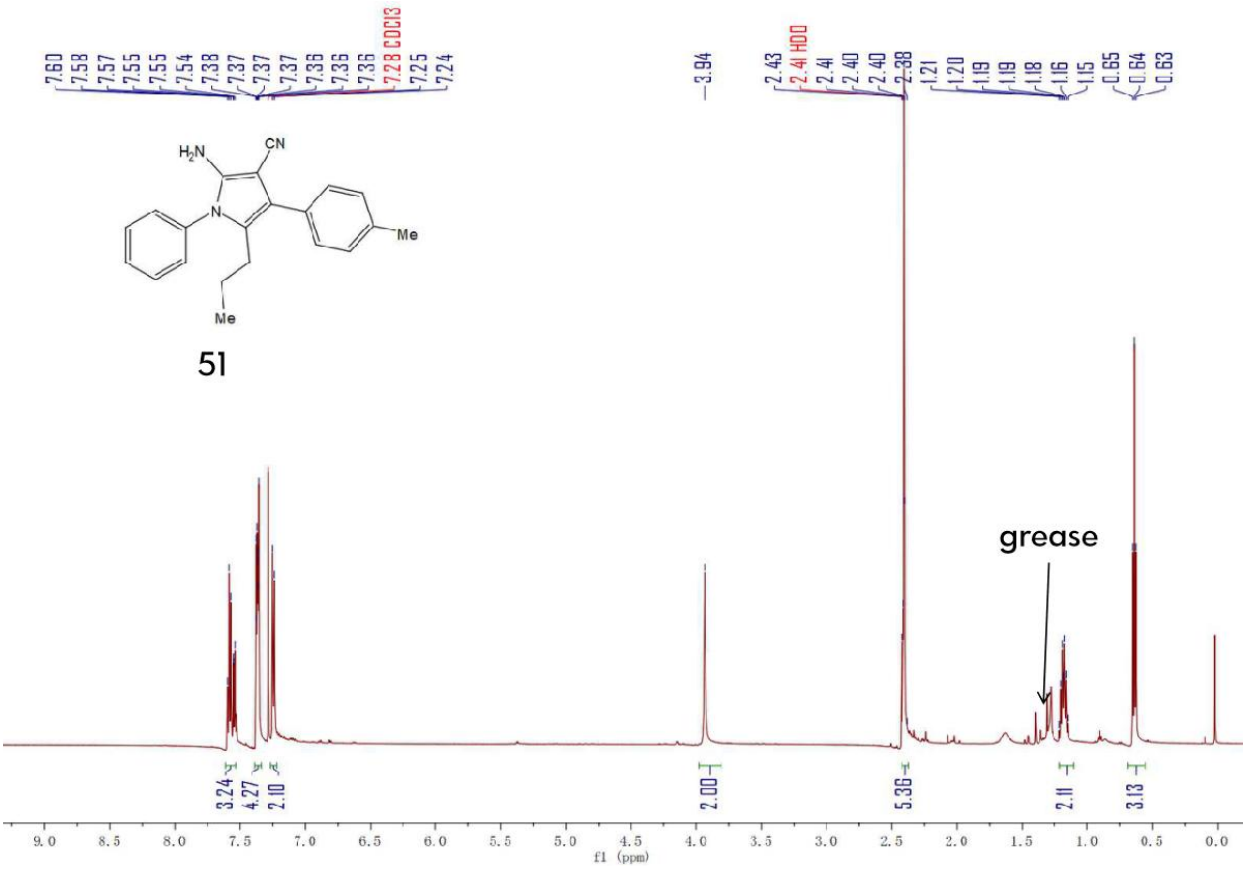
50 The reaction was set up following the general procedure using N-ethylaniline (121 mg, 1 mmol) and 4-methylbenzylidenemalononitrile (34 mg, 0.2 mmol). After 16 hours, the reaction was purified following general work-up to give 45 mg (79 % yield) of the title compound. **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 7.58 (t, *J* = 7.5 Hz, 2H), 7.53 (t, *J* = 7.3 Hz, 1H), 7.41 – 7.33 (m, 4H), 7.26 (d, *J* = 7.9 Hz, 2H), 4.00 (s, 2H), 2.40 (s, 3H), 2.02 (s, 3H); **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 145.58, 136.21, 135.15, 130.75, 130.14, 129.37, 129.27, 128.48, 128.20, 119.69, 119.61, 117.85, 72.81, 21.24, 11.41; MS2 (ES^+) exact mass calculated for $[M+H]^+$ ($C_{19}H_{18}N_3$) requires m/z 288.1, found m/z 288.1.


7.60
7.58
7.57
7.54
7.53
7.52
7.39
7.38
7.36
7.36
7.35
7.28 CDCl3
7.26
7.25
4.00
2.40
2.02
H2N
CN
N
Me
Me
50
grease
2.13
1.12
4.11
2.20
2.00
3.03
3.04
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


145.58
136.21
135.15
130.75
130.14
129.37
129.27
128.48
128.20
119.69
119.61
117.85
77.28 CDCl3
76.86 CDCl3
72.81
21.24
11.41
H2N
CN
N
Me
Me
50
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



51 The reaction was set up following the general procedure using N-butylaniline (149 mg, 1 mmol) and 4-methylbenzylidenemalononitrile (34 mg, 0.2 mmol). After 16 hours, the reaction was purified following general work-up to give 28 mg (44 % yield) of the title compound. **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 7.61 – 7.48 (m, 3H), 7.39 – 7.34 (m, 4H), 7.25 (d, *J* = 7.8 Hz, 2H), 3.94 (s, 2H), 2.44 – 2.36 (m, 5H), 1.33 – 1.25 (m, 2H), 0.64 (t, *J* = 7.3 Hz, 3H); **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 145.52, 136.28, 135.31, 130.90, 130.07, 129.45, 129.25, 128.60, 128.41, 124.58, 120.17, 117.78, 73.13, 26.60, 23.07, 21.24, 13.68; MS2 (ES^+) exact mass calculated for $[M+H]^+$ ($C_{21}H_{22}N_3$) requires m/z 316.1, found m/z 316.1.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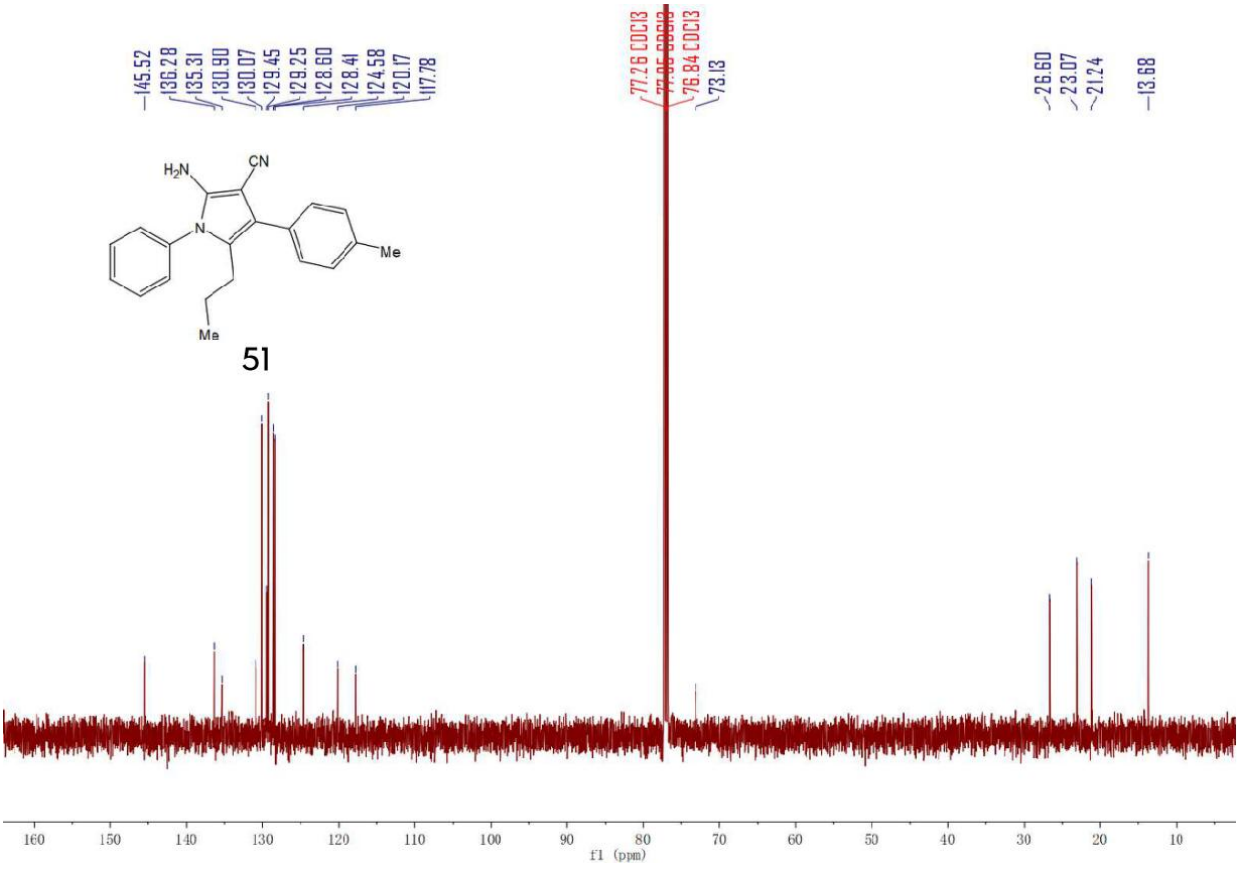
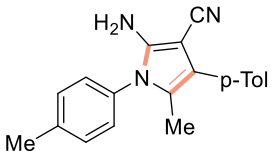
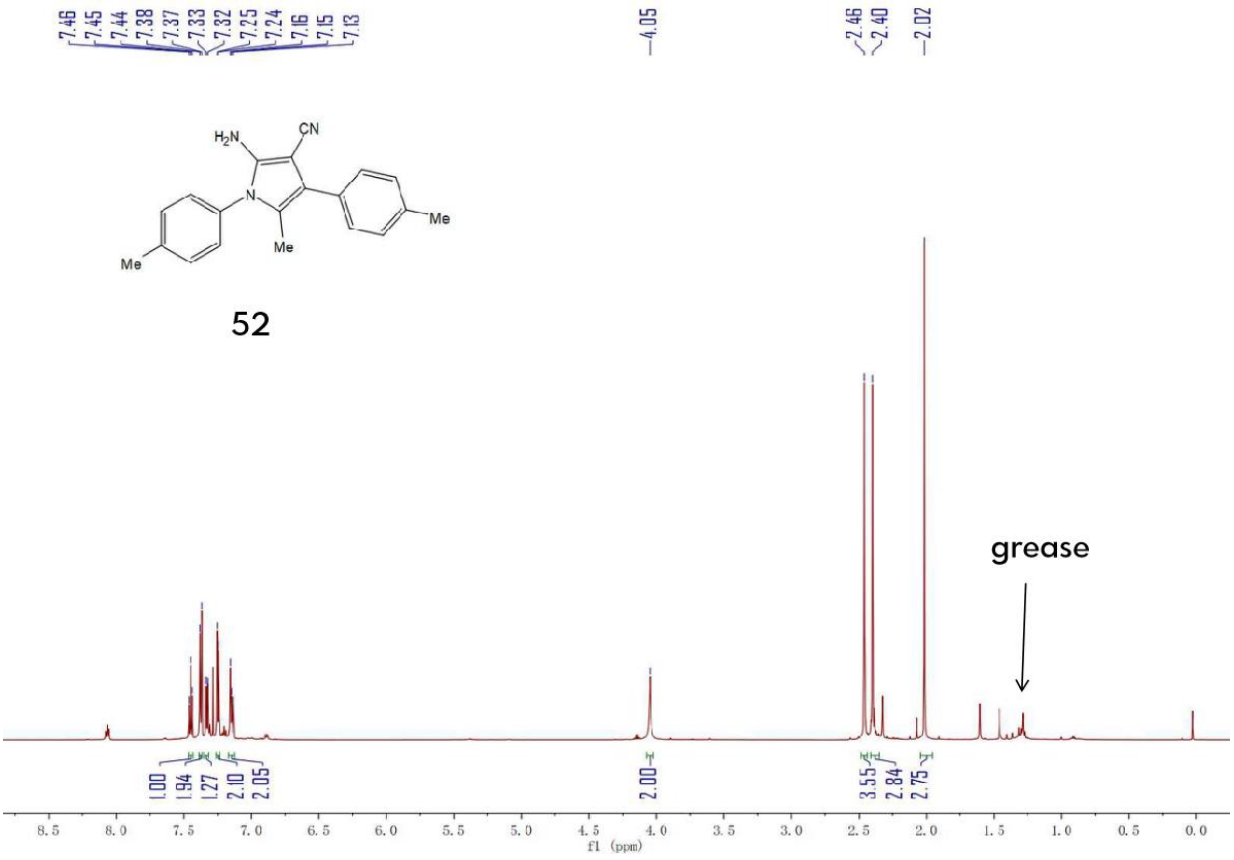
7.58
7.57
7.55
7.55
7.54
7.38
7.37
7.37
7.37
7.36
7.36
7.36
7.28 CDCl3
7.25
7.24
3.94
2.43
2.41 HDO
2.41
2.40
2.40
2.38
1.21
1.20
1.19
1.19
1.18
1.16
1.15
0.65
0.64
0.63
H2N
CN
N
Me
Me
51
grease
3.24
4.27
2.10
2.00
5.36
2.11
3.13
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

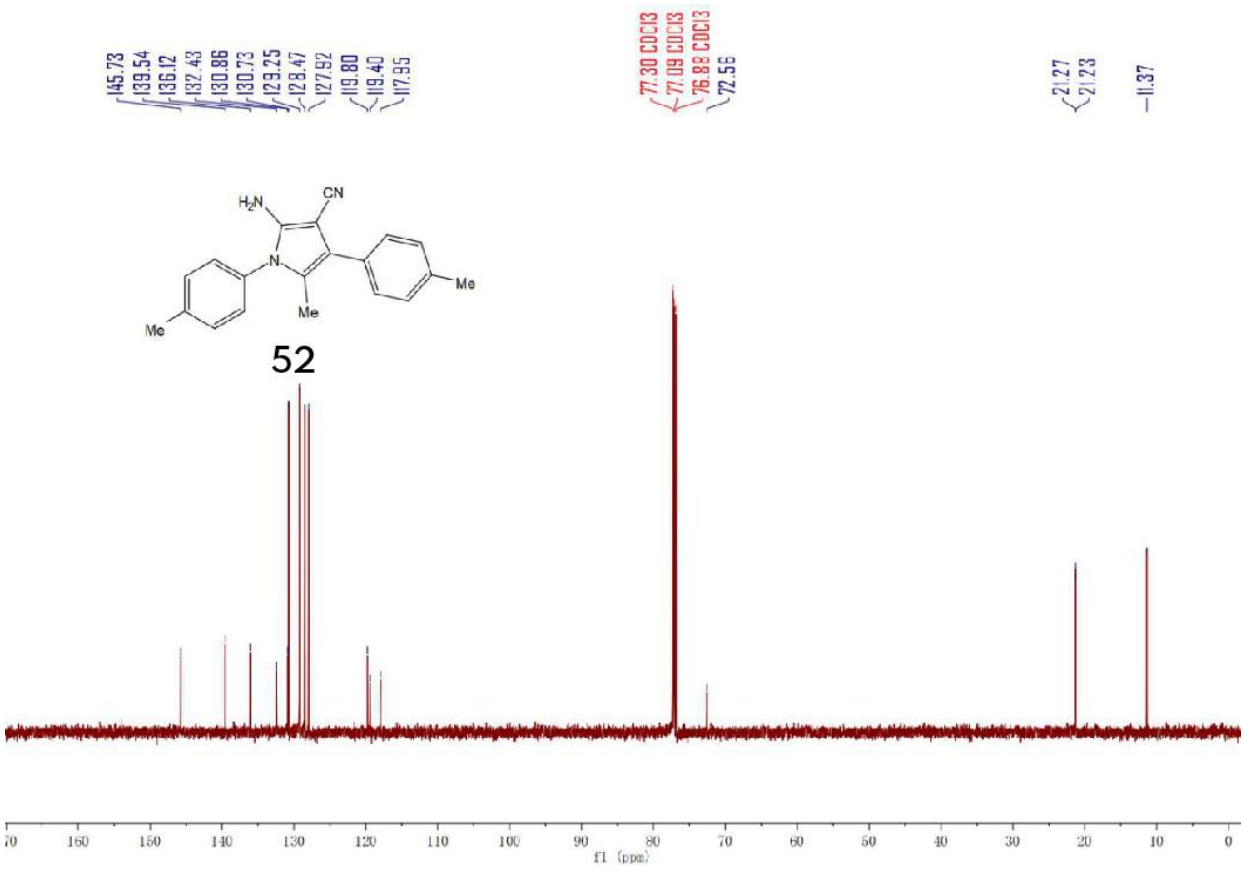

145.52
136.28
135.31
130.90
130.07
129.45
129.25
128.60
128.41
124.58
120.17
117.78
77.26 CDCl3
76.84 CDCl3
73.13
26.60
23.07
21.24
13.68
H2N
CN
N
Me
Me
51
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

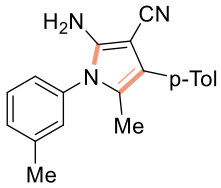


52 The reaction was set up following the general procedure using 3-methyl-N-ethylbenzenamine (135 mg, 1 mmol) and 4-methylbenzylidenemalononitrile (34 mg, 0.2 mmol). After 16 hours, the reaction was purified following general work-up to give 40 mg (66 % yield) of the title compound. **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 7.41 – 7.34 (m, 4H), 7.27 – 7.21 (m, 4H), 4.00 (s, 2H), 2.47 (s, 3H), 2.40 (s, 3H), 2.02 (s, 3H); **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 145.73, 139.54, 136.12, 132.43, 130.86, 130.73, 129.25, 128.47, 127.92, 119.80, 119.40, 117.95, 72.56, 21.27, 21.23, 11.37; MS2 (ES^+) exact mass calculated for $[M+H]^+$ ($C_{20}H_{20}N_3$) requires m/z 302.1, found m/z 302.1.

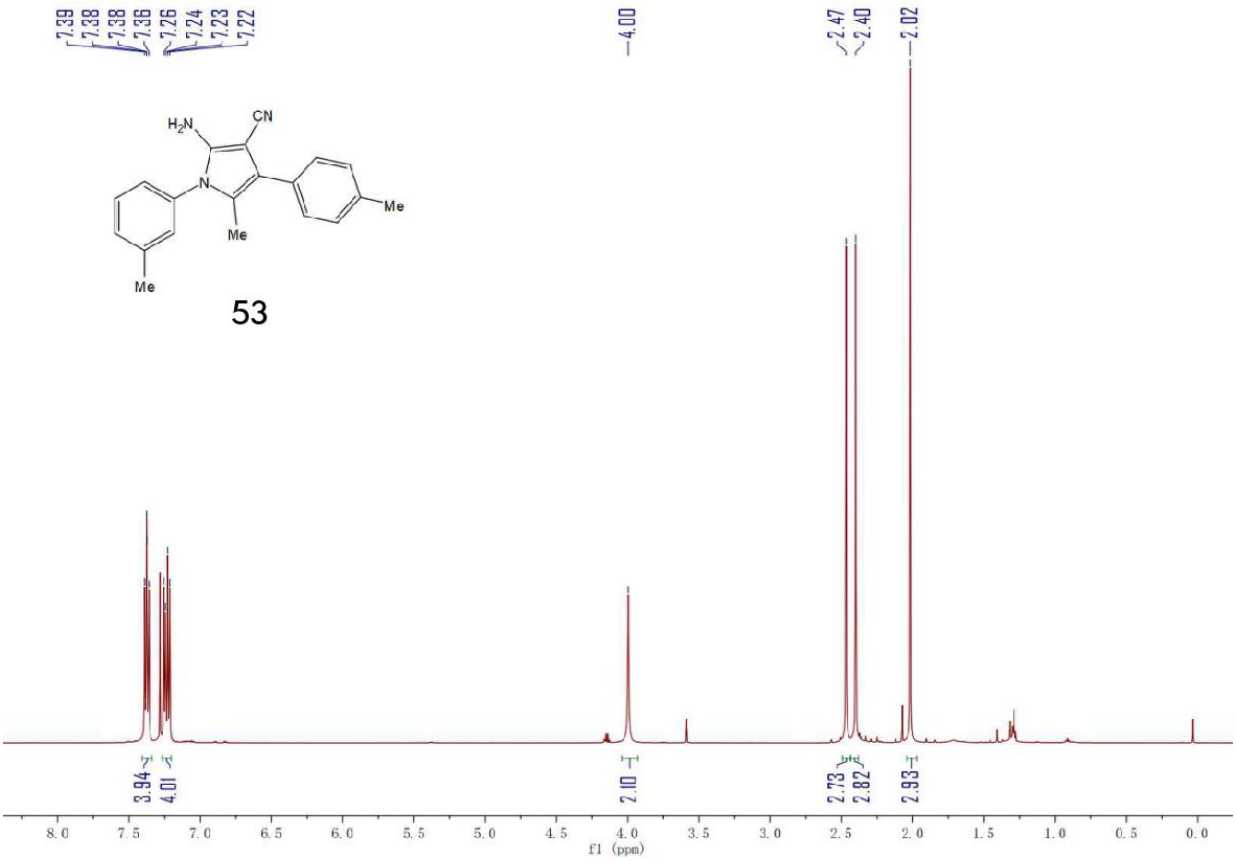

7.46
7.45
7.44
7.38
7.37
7.33
7.32
7.25
7.24
7.16
7.15
7.13
4.05
2.46
2.40
2.02
H2N
CN
N
Me
Me
Me
grease
1.00
1.94
1.27
2.10
2.05
2.00
3.55
2.84
2.75
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

52

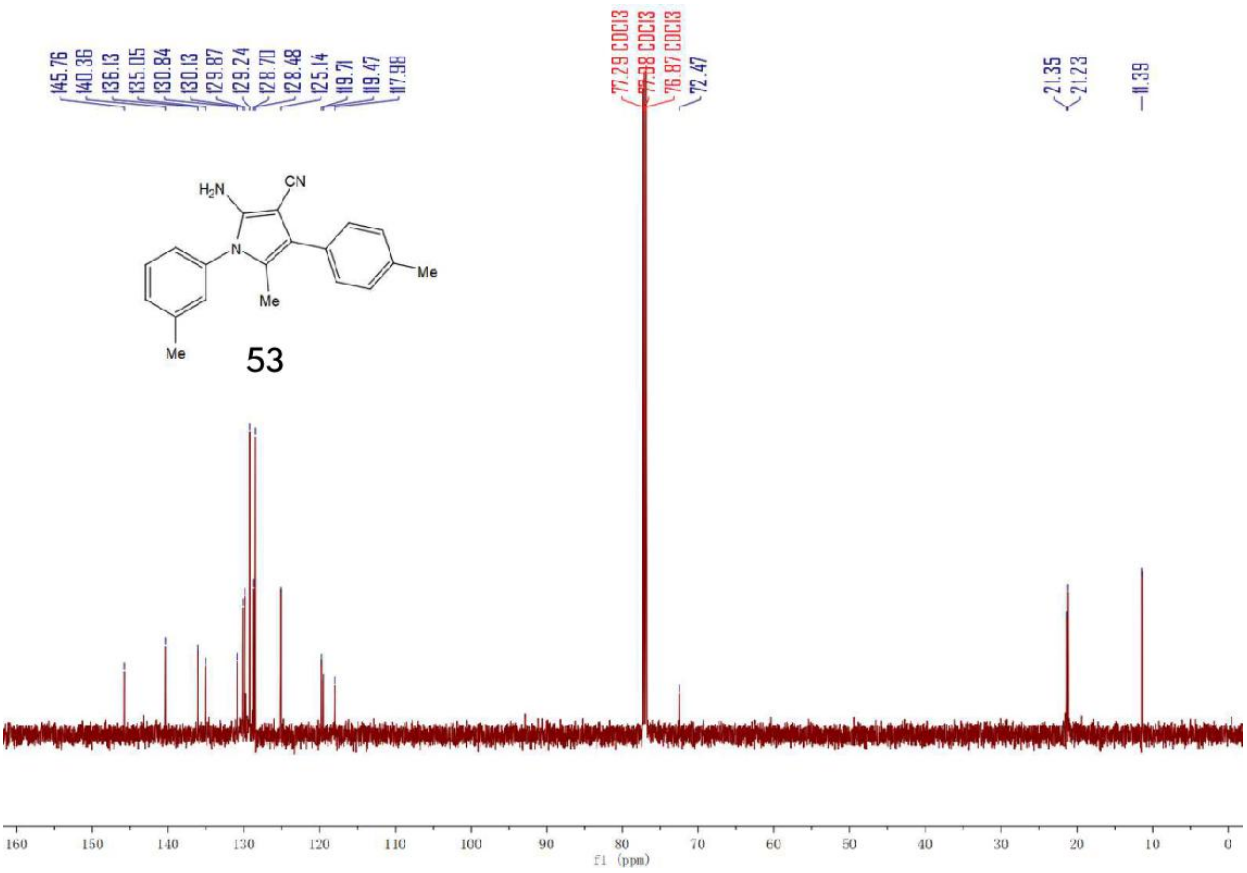

145.73
139.54
136.12
132.43
130.86
130.73
129.25
128.47
127.92
119.80
119.40
117.95
77.30 CDCl3
77.09 CDCl3
76.88 CDCl3
72.56
21.27
21.23
11.37
H2N
CN
N
Me
Me
Me
52
f1 (ppm)

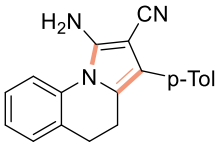


53 The reaction was set up following the general procedure using 4-methyl-N-ethylbenzenamine (135 mg, 1 mmol) and 4-methylbenzylidenemalononitrile (34 mg, 0.2 mmol). After 16 hours, the reaction was purified following general work-up to give 36 mg (58 % yield) of the title compound. **^{1}H NMR** (600 MHz, Chloroform-d) δ 7.45 (t, J = 7.7 Hz,1H), 7.39 – 7.36 (m, 2H), 7.35 – 7.32 (m, 1H), 7.25 (d, J = 7.9 Hz, 2H), 7.17 – 7.12 (m, 2H), 4.05 (s, 2H), 2.46 (s, J = 3.2 Hz, 3H), 2.40 (s, 3H), 2.02 (s, 3H); **^{13}C NMR** (151 MHz, Chloroform-d) δ 145.76, 140.36, 136.13, 135.05, 130.84, 130.13, 129.87, 129.24, 128.70, 128.48, 125.14, 119.71, 119.47, 117.98, 72.47, 21.35, 21.23, 11.39; MS2 (ES+) exact mass calculated for $[M+H]^+$ ($C_{20}H_{20}N_3$) requires m/z 302.1, found m/z 302.1.

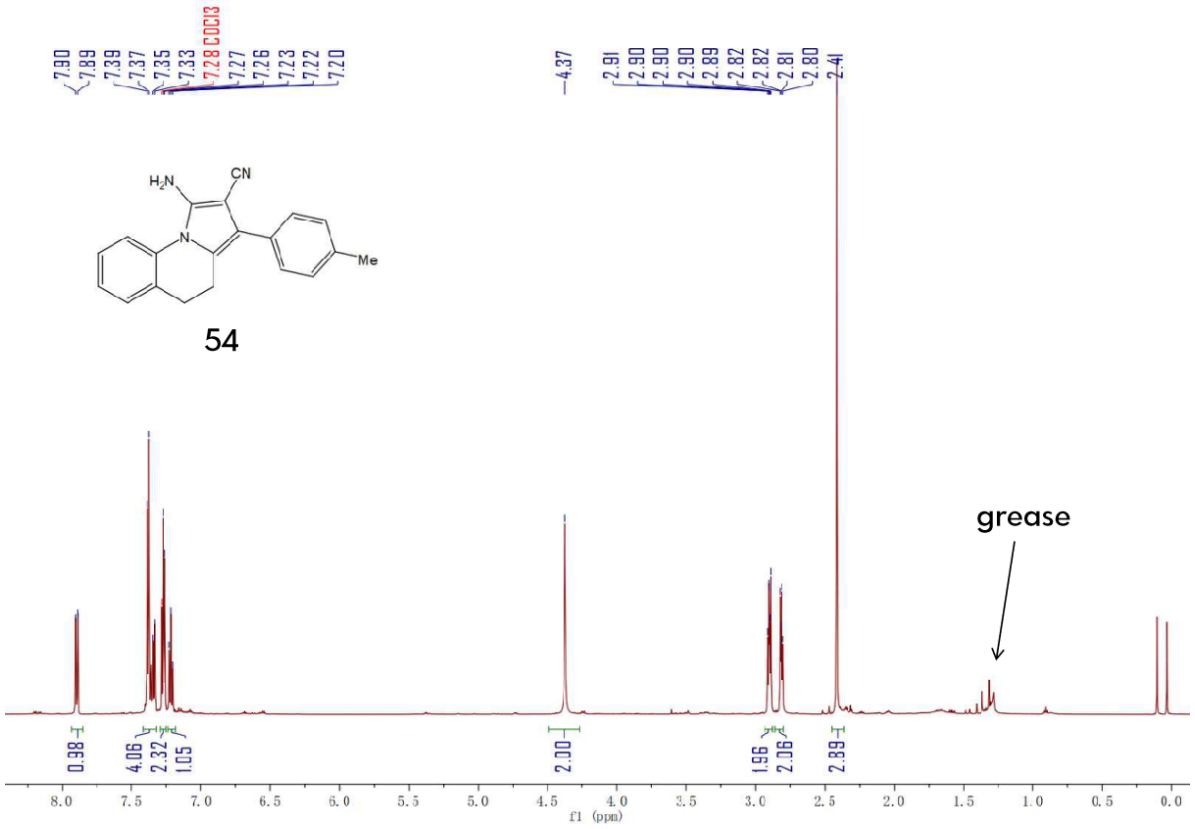

7.39
7.38
7.38
7.36
7.26
7.24
7.23
7.22
4.00
2.47
2.40
2.02
H2N
CN
N
Me
Me
Me
3.94
4.01
2.10
2.73
2.82
2.93
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

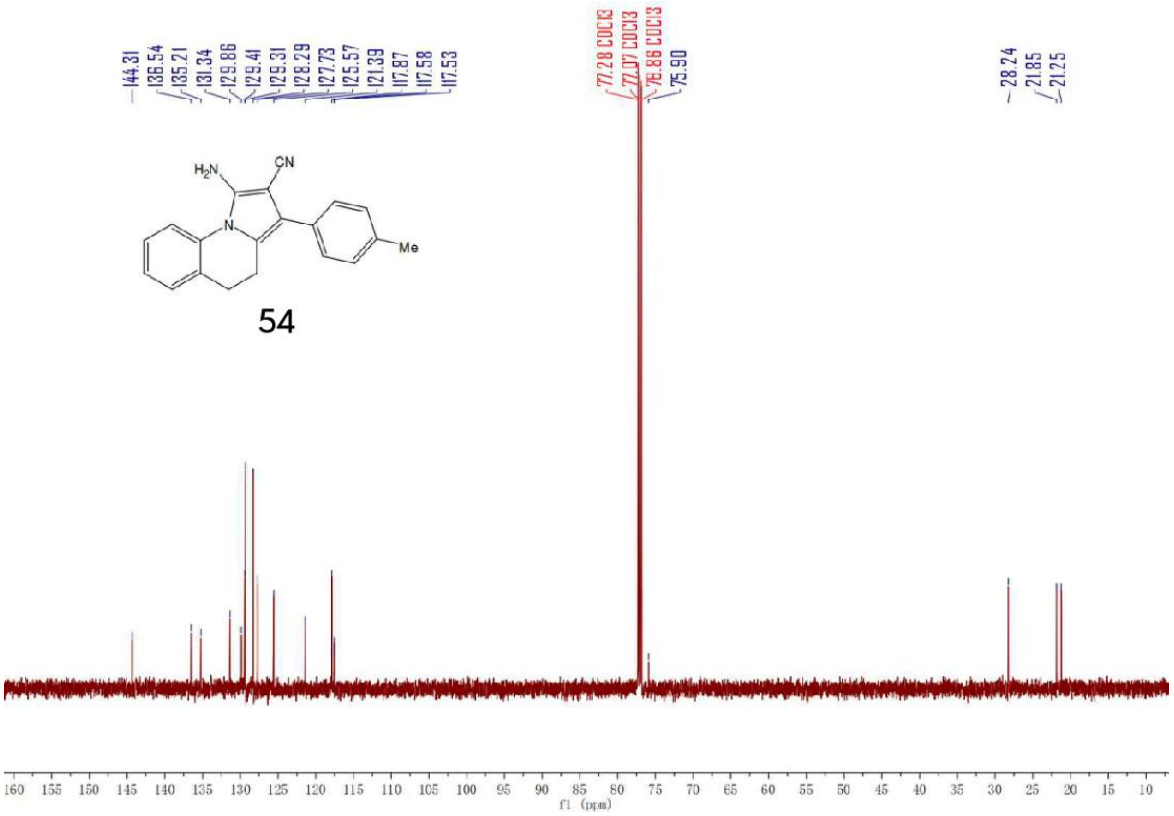
53


145.76
140.36
136.13
135.05
130.84
130.13
129.87
129.24
128.70
128.48
125.14
119.71
119.47
117.96
77.29 CDCl3
77.08 CDCl3
76.87 CDCl3
72.47
21.35
21.23
11.59
H2N
CN
N
Me
Me
Me
53
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



54 The reaction was set up following the general procedure using 1,2,3,4-tetrahydroquinoline (133 mg, 1 mmol) and 4-methylbenzylidenemalononitrile (34 mg, 0.2 mmol). After 16 hours, the reaction was purified following general work-up to give 39 mg (64 % yield) of the title compound. **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 7.90 (m, *J* = 8.1, 1.1 Hz, 1H), 7.42 – 7.29 (m, 4H), 7.27 (d, *J* = 7.8 Hz, 2H), 7.22 (m, *J* = 7.5, 1.1 Hz, 1H), 4.37 (s, 2H), 2.93 – 2.87 (m, 2H), 2.81 (m, *J* = 8.0, 4.9 Hz, 2H), 2.41 (s, 3H); **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 144.31, 136.54, 135.21, 131.34, 129.86, 129.41, 129.31, 128.29, 127.73, 125.57, 121.39, 117.87, 117.58, 117.53, 75.90, 28.24, 21.85, 21.25; MS2 (ES^+) exact mass calculated for $[M+H]^+$ ($C_{20}H_{18}N_3$) requires m/z 300.1, found m/z 300.1.


7.90
7.89
7.39
7.37
7.35
7.33
7.28 CDCl3
7.27
7.26
7.23
7.22
7.20
4.37
2.91
2.90
2.90
2.90
2.89
2.82
2.82
2.81
2.80
2.41
H2N
CN
N
Me
54
grease
0.98
4.06
2.32
1.05
2.00
1.96
2.06
2.89
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


144.31
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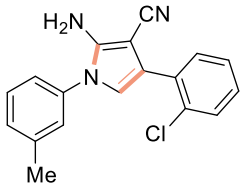
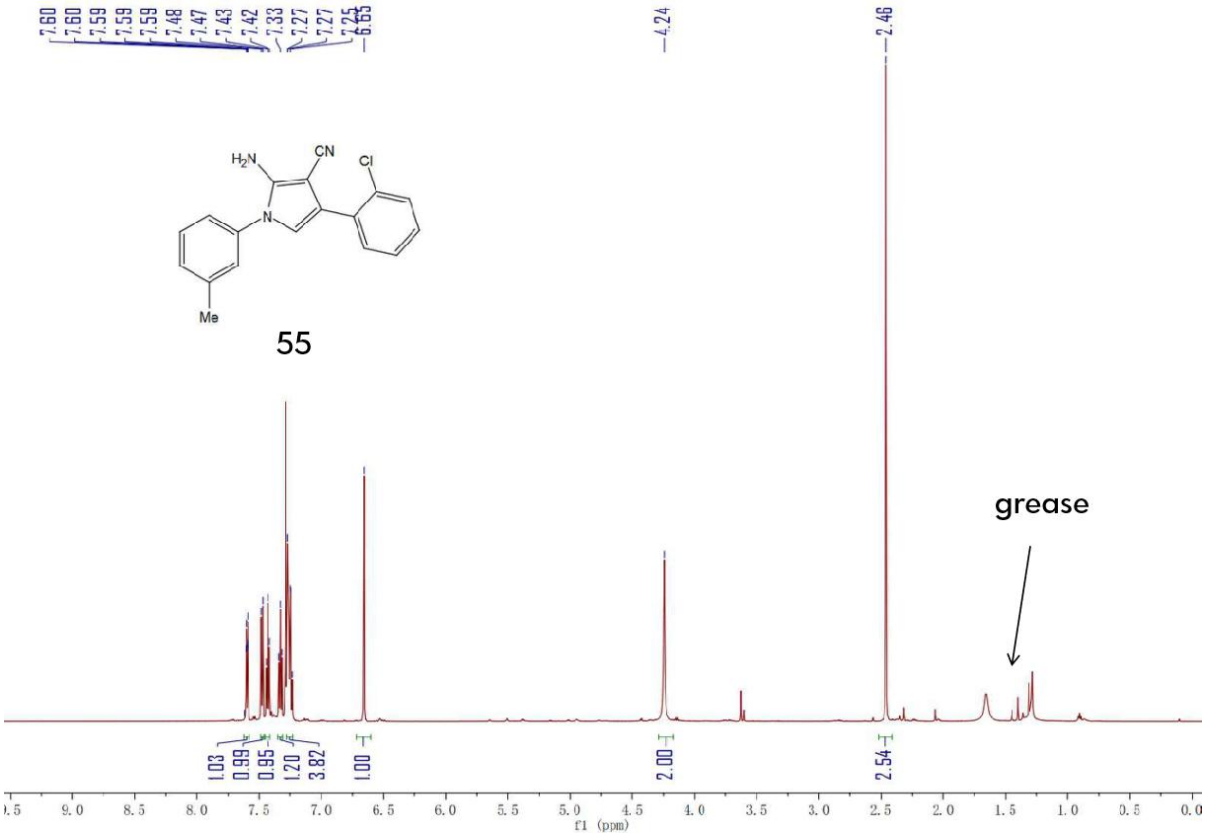
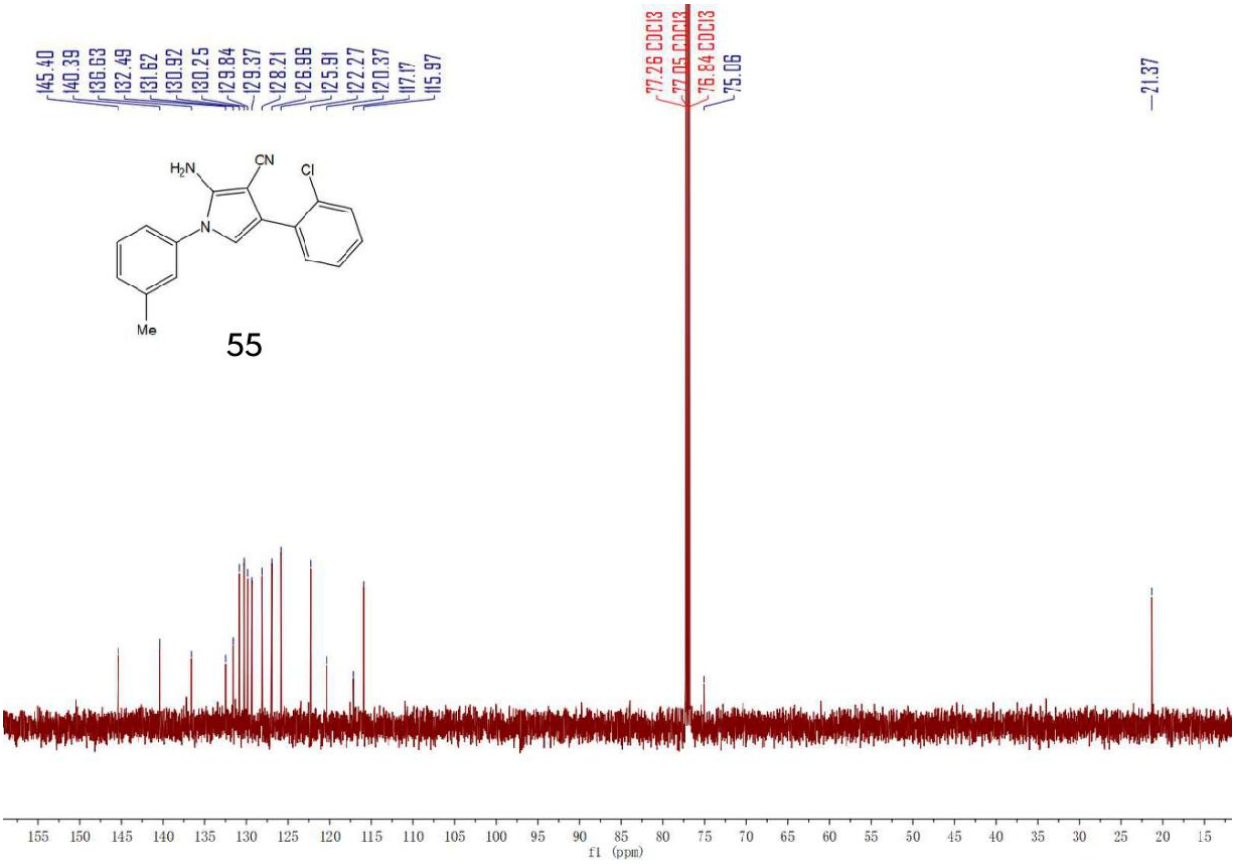
135.21
131.34
129.86
129.41
129.31
128.29
127.73
125.57
121.39
117.87
117.58
117.53
77.28 CDCl3
77.07 CDCl3
76.86 CDCl3
75.90
28.24
21.85
21.25
H2N
CN
N
Me
160 155 150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10
f1 (ppm)

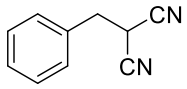
54



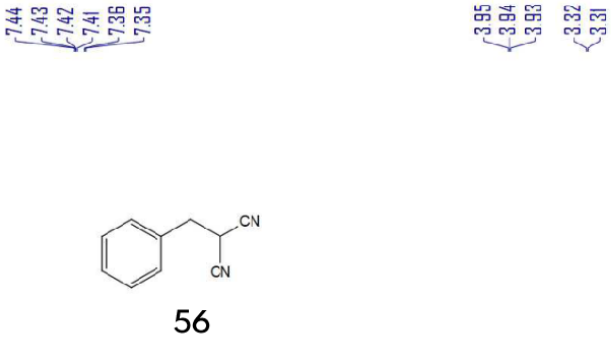
55 The reaction was set up following the general procedure using 3-methyl-N-methylbenzenamine (121 mg, 1 mmol) and 2-chlorobenzylidenemalononitrile (38 mg, 0.2 mmol). After 16 hours, the reaction was purified following general work-up to give 29 mg (46 % yield) of the title compound. **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 7.60 (m, *J* = 7.7, 1.3 Hz, 1H), 7.48 (d, *J* = 8.0 Hz, 1H), 7.43 (t, *J* = 7.7 Hz, 1H), 7.35 – 7.31 (m, 1H), 7.25 (m, *J* = 15.5, 8.8, 1.8 Hz, 4H), 6.65 (d, *J* = 1.0 Hz, 1H), 4.24 (s, 2H), 2.46 (s, 3H); **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 145.40, 140.39, 136.63, 132.49, 131.62, 130.92, 130.25, 129.84, 129.37, 128.21, 126.96, 125.91, 122.27, 120.37, 117.17, 115.97, 75.06, 21.37; MS2 (ES^+) exact mass calculated for $[M+H]^+$ ($C_{18}H_{15}ClN_3$) requires m/z 308.1, found m/z 308.1.


7.60
7.60
7.59
7.59
7.59
7.48
7.47
7.43
7.42
7.33
7.27
7.27
7.25
6.65
4.24
2.46
H2N
CN
Cl
N
Me
55
grease
1.03
0.99
0.95
1.20
3.82
1.00
2.00
2.54
f1 (ppm)


145.40
140.39
136.63
132.49
131.62
130.92
130.25
129.84
129.37
128.21
126.96
125.91
122.27
120.37
117.17
115.97
77.26 CDCl3
77.05 CDCl3
76.84 CDCl3
75.06
21.37
H2N
CN
Cl
N
Me
55
155 150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15
f1 (ppm)



56 The reaction was set up following the general procedure using amine (1 mmol) and benzylidenemalononitrile (31 mg, 0.2 mmol). After 16 hours, the reaction was purified following general work-up to give the title compound. 1H NMR (600 MHz, Chloroform-d) δ 7.46 – 7.39 (m, 3H), 7.37 – 7.33 (m, 2H), 3.94 (t, J = 7.0 Hz, 1H), 3.32 (d, J = 7.0 Hz, 2H).



Section S4 Crystal Data of Products

General procedure of single-crystal x-ray diffraction data collection, structure solution and refinement

Data was collected on a Bruker D8 diffractometer equipped with a CCD area detector and operated at 50 kV, 35 mA to generate Cu Kα radiation (1.54184 Å). The incident X-ray beam was focused and monochromated. All crystals were mounted on glass fiber with N grease under room temperature. Neither crack nor crystal decay was ever encountered under this condition. Initial scans of each crystal were taken to gain preliminary unit cell parameters and to assess the mosaicity of the crystal to select the required frame width for data collection. Frame widths were set as 0.5°. Following data collection, reflections were sampled from all regions to re-determine unit cell parameters for data integration. The highest possible space group was chosen.

All structures were solved by direct methods and refined using the *OLEX 2* software suite.

Atoms were located from iterative examination of difference F-maps following least squares refinements of the earlier models. Final models were refined anisotropically until full convergence was achieved.

Table S4. Crystal Data of Product **54**

Empirical formula	$C_{80}H_{64}N_{12}$
Temperature	300 K
Crystal system	monoclinic
Space group	$P2_1/c$
Unit cell dimensions	a/Å 8.7434(3) α/90°
	b/Å 11.3513(4) β/ 98.474(2)°
	c/Å 16.3377(6) γ/ 90°
Cell Volume	1603.8(1)
Z	1
Density (Calculated)	1.236
μ/mm^{-1}	0.581
F(000)	629.9
2 theta range for data collection	9.52° ⩽ theta ⩽ 136.92°
Index ranges	-10 ⩽ h ⩽ 10, -13 ⩽ k ⩽ 13, -19 ⩽ l ⩽ 19
Reflections collected	18547
Independent reflections	2927 [R_{int} = 0.1038, R_{sigma} = 0.0770]
Data/restraints/parameters	2927/0/210
Goodness-of-fit on F2	1.031
Final R indexes [I>=2 σ (I)]	R_1 = 0.0758, wR_2 = 0.2120
Final R indexes [all data]	R_1 = 0.0884, wR_2 = 0.2256

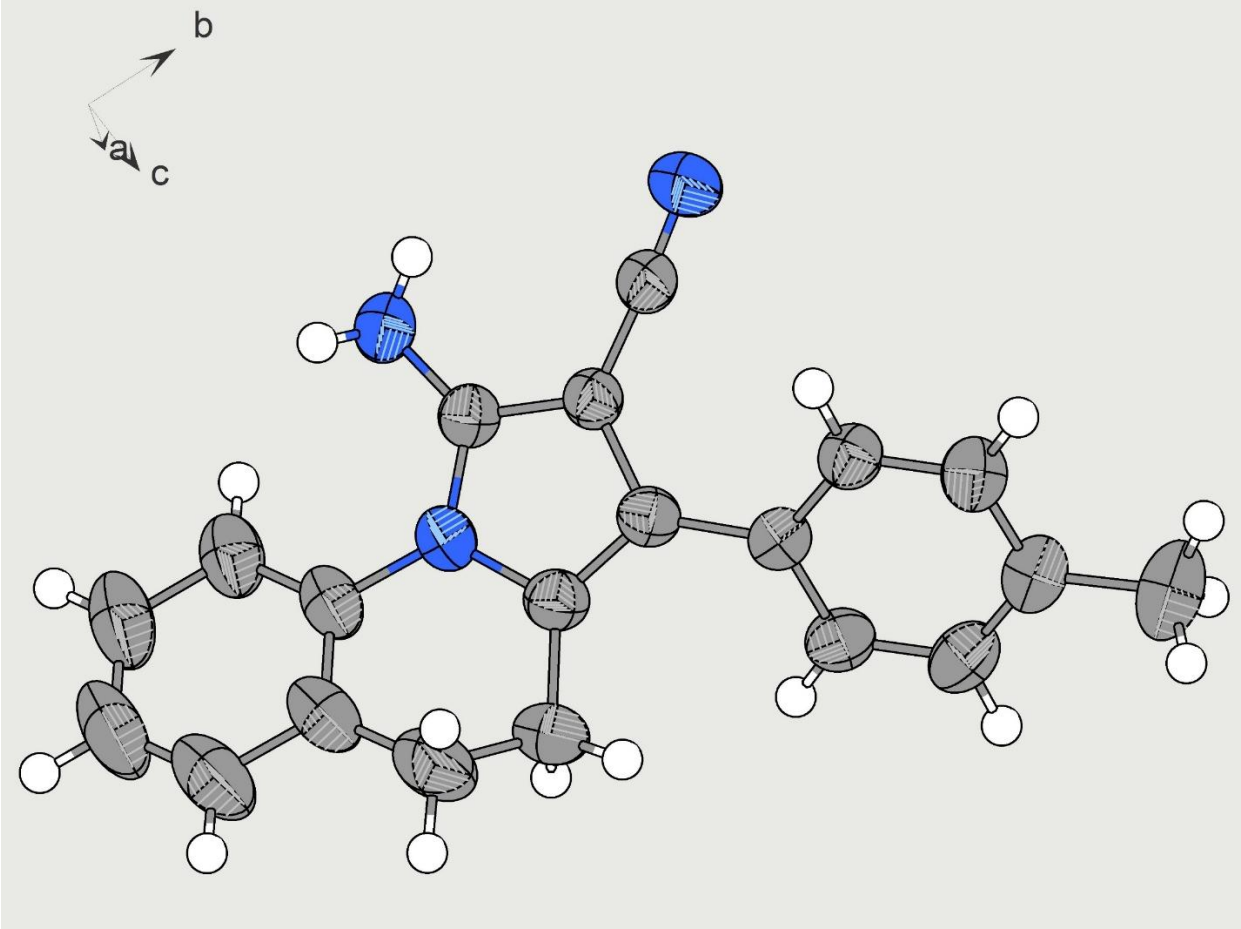


Figure S7. ORTEP drawing of product **54**. (Grey: carbon; blue: nitrogen; white: hydrogen.)

Ellipsoids are displayed at the 50% probability level.