

Supplementary Information for:

Direct activation of C(sp³)-H bonds by carbon dots photoredox catalysts

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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 K α X-ray excitation source (1200 eV). Cyclic voltammetry (CV) curves were obtained using a CHI 760e electrochemical workstation (Shanghai Chenhua Apparatus Inc., China).

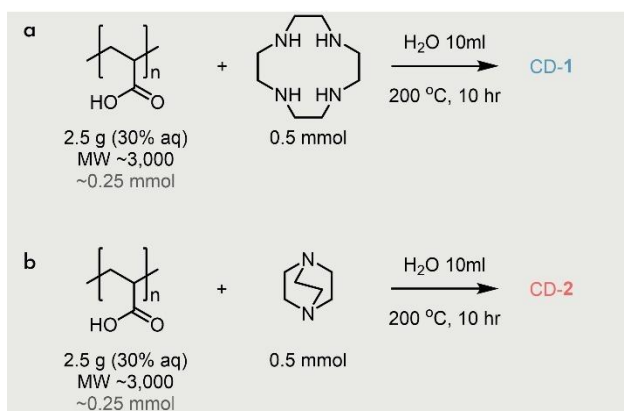


Figure S1. Synthesis of photoredox catalysts CD-1 and CD-2.

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 $200\text{ }^\circ\text{C}$ 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 $200\text{ }^\circ\text{C}$. 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 °C 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.

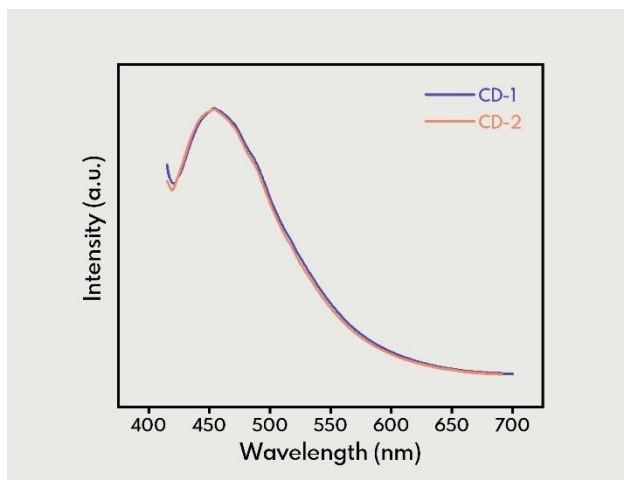


Figure S2. PL spectra of photoredox catalysts with 400nm excitation dispersed in MeCN. 50mg CDs photocatalyst were dispersed in 2.0mL MeCN and the suspension was vigorously stirred for 1 hour before test. The suspension was then transferred to a quartz cuvette. The cuvette was agitated gently to prevent 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 N₂ atmosphere.

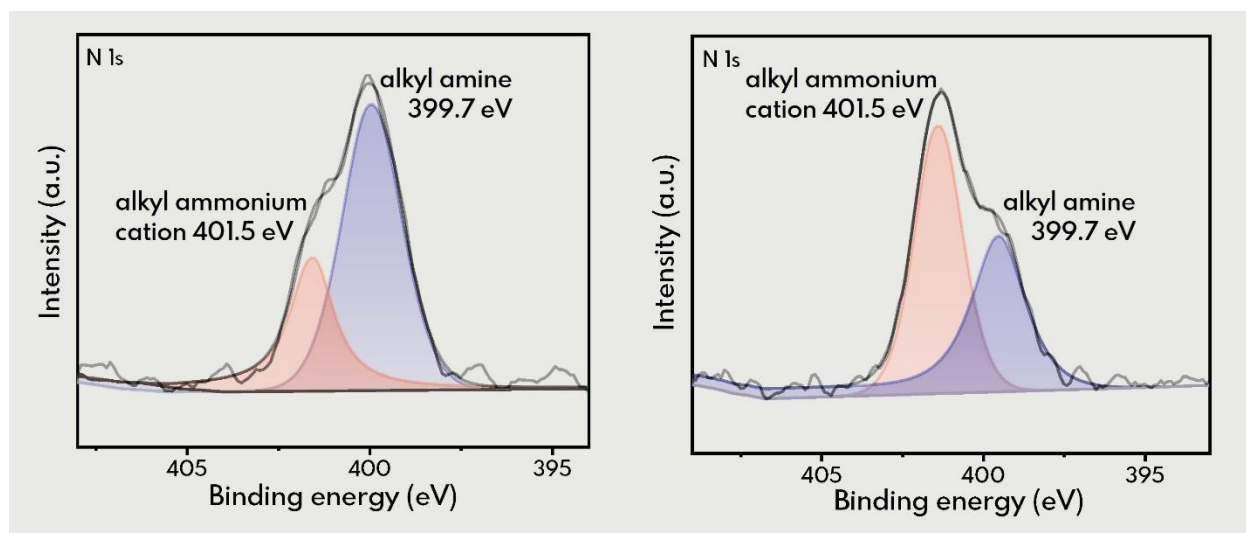


Figure S4. XPS spectra of N 1s in photoredox catalysts CD-1 (left) and CD-2 (right).



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 N₂ 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.

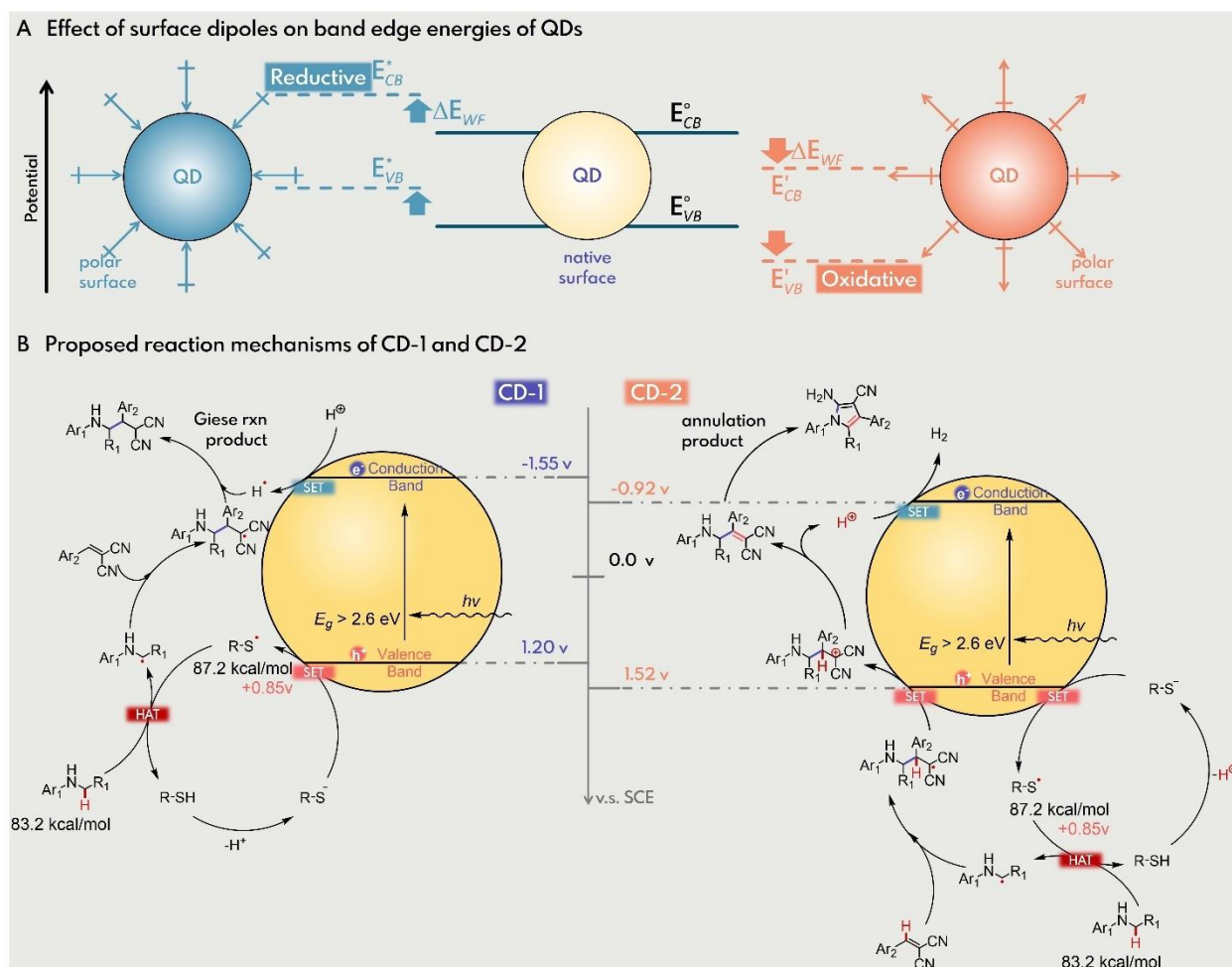


Figure S6. Proposed mechanism of CD-1, 2 photocatalysis.

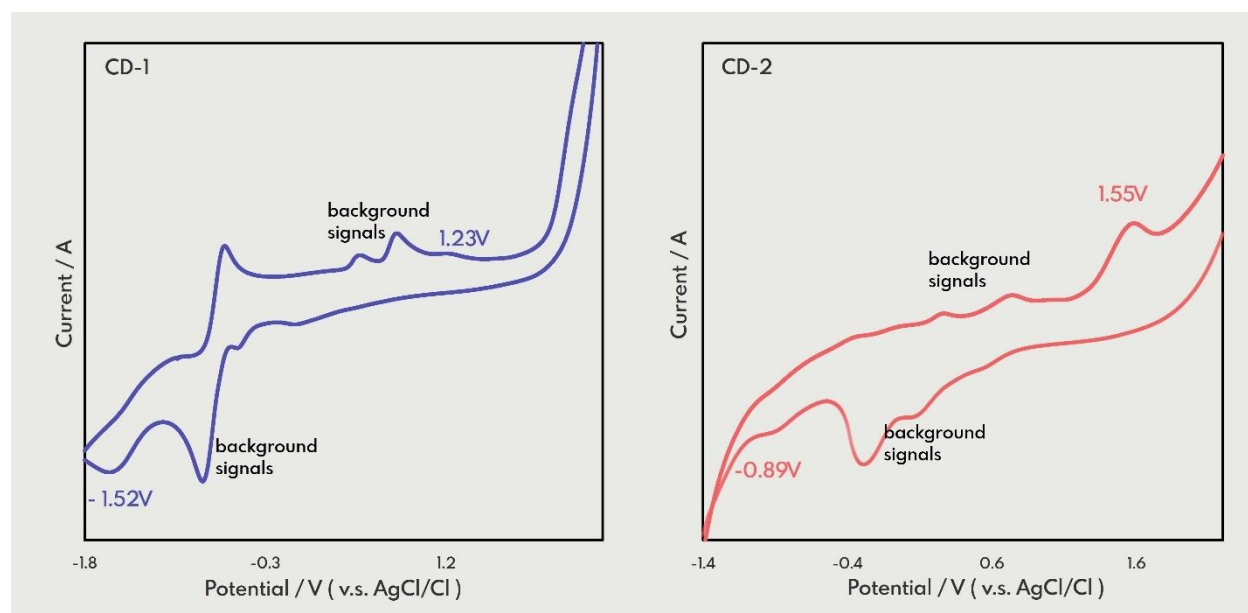
A. Scheme of band shifting in QDs due to surface functionalization by polar groups. The band energy levels of the quantum dots (QDs) prior to the addition of the surface dipole layer are shown in black: the conduction band energy level E_{CB}° and valence band energy level E_{VB}° .

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 H₂ 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 10 μ l 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 50 μ l CDs paste. The ITO electrode was oven dried and the CV curves were taken in a MeCN solution with 0.1 M of TBA-PF₆. 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 ₂ CO ₃	ND
16	MeCN	TMA·HCl	ND

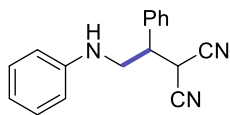
Table S2. Elemental analysis of the C, H, and N contents in CD-1 and CD-2

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

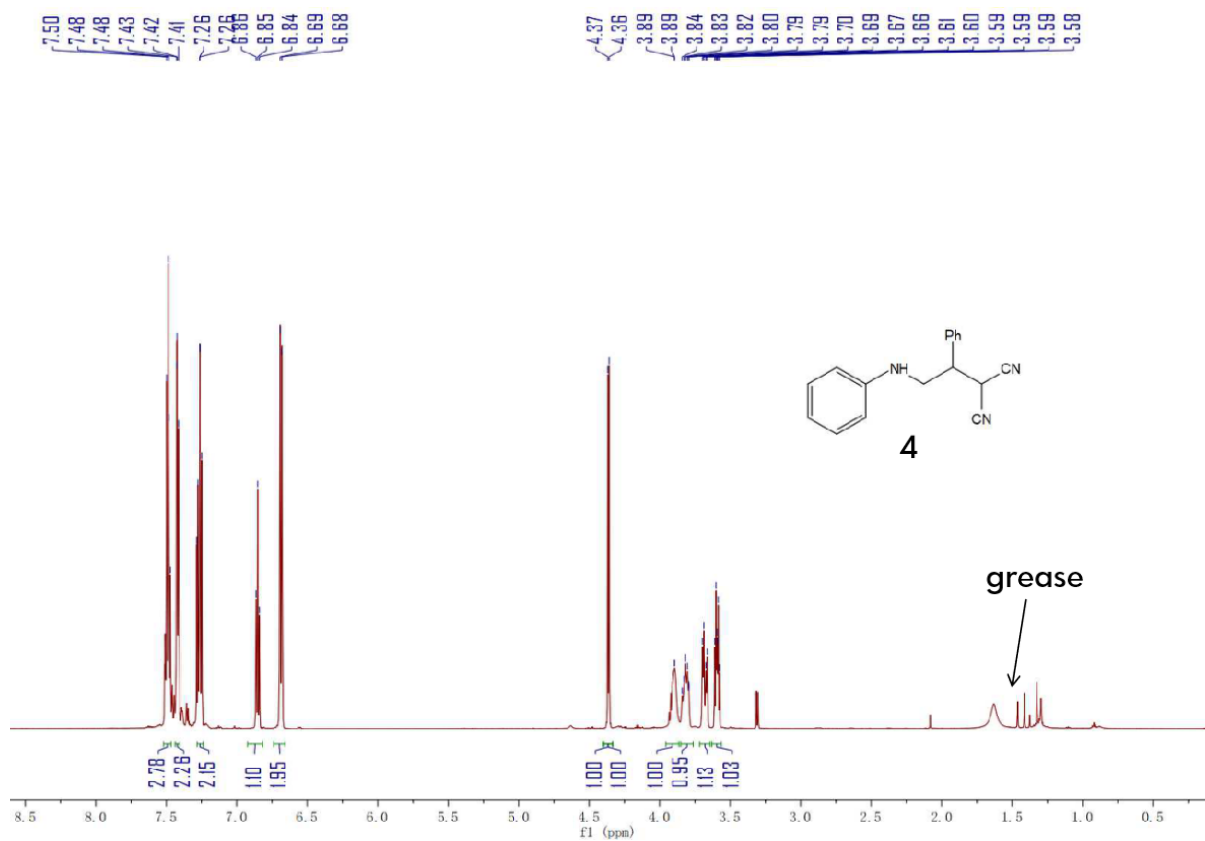
Table S3. CD-2 photocatalytic reaction condition optimization.

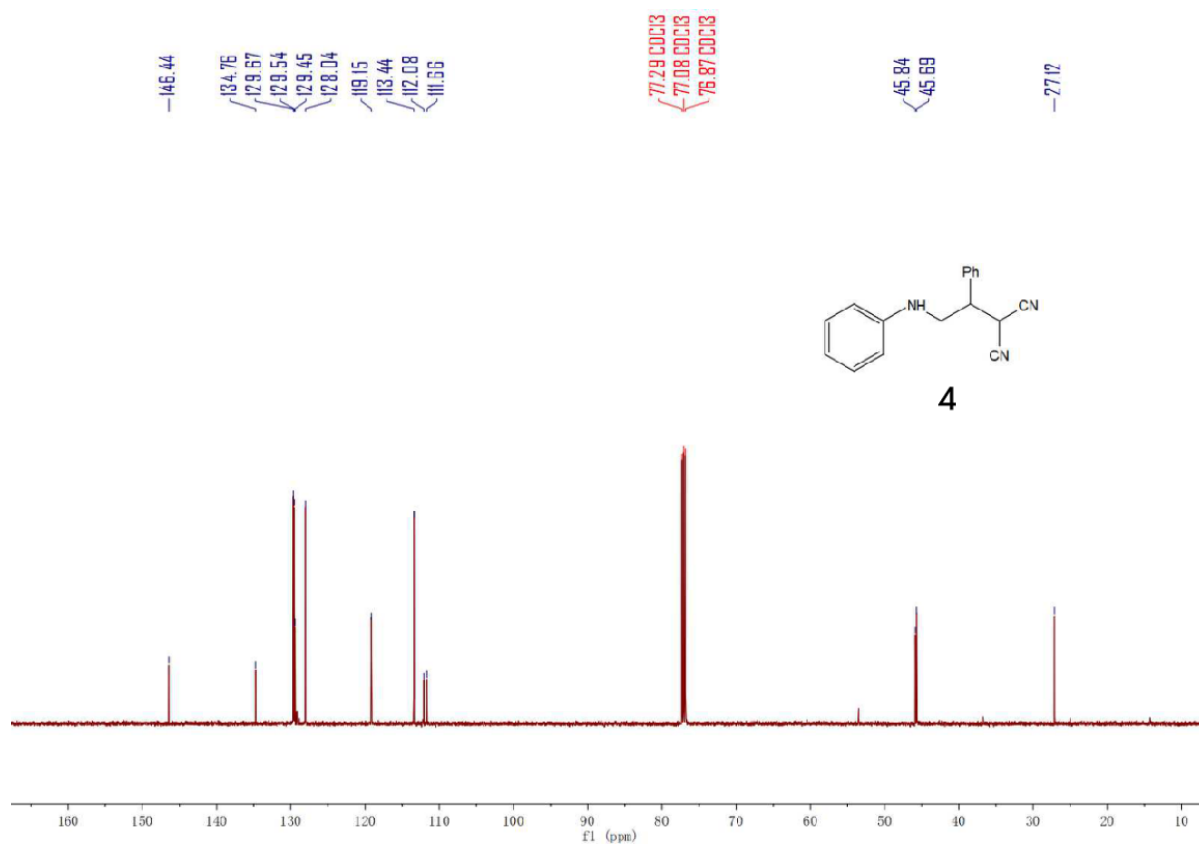
Entry	Solvent	Variation	Giese Rxn	Annulation
1	MeCN	No	24	71
2	THF	No	trace	29
3	MeOH	No	trace	53
4	DCE	No	27	70
5	MeCN	30%mol TsOH	18	44
6	MeCN	30%mol AcOH	trace	60
7	MeCN	30%mol K ₃ PO ₄	trace	trace
8	MeCN	30%mol Lutidine	22	64
9	MeCN	5%mol TMA ⁺ Cl ⁻	13	65
10	MeCN	5%mol TMA ⁺ Cl ⁻ CD-1	57	trace

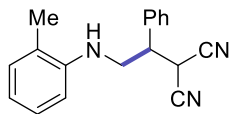
Section S3 Characterizations of the Products



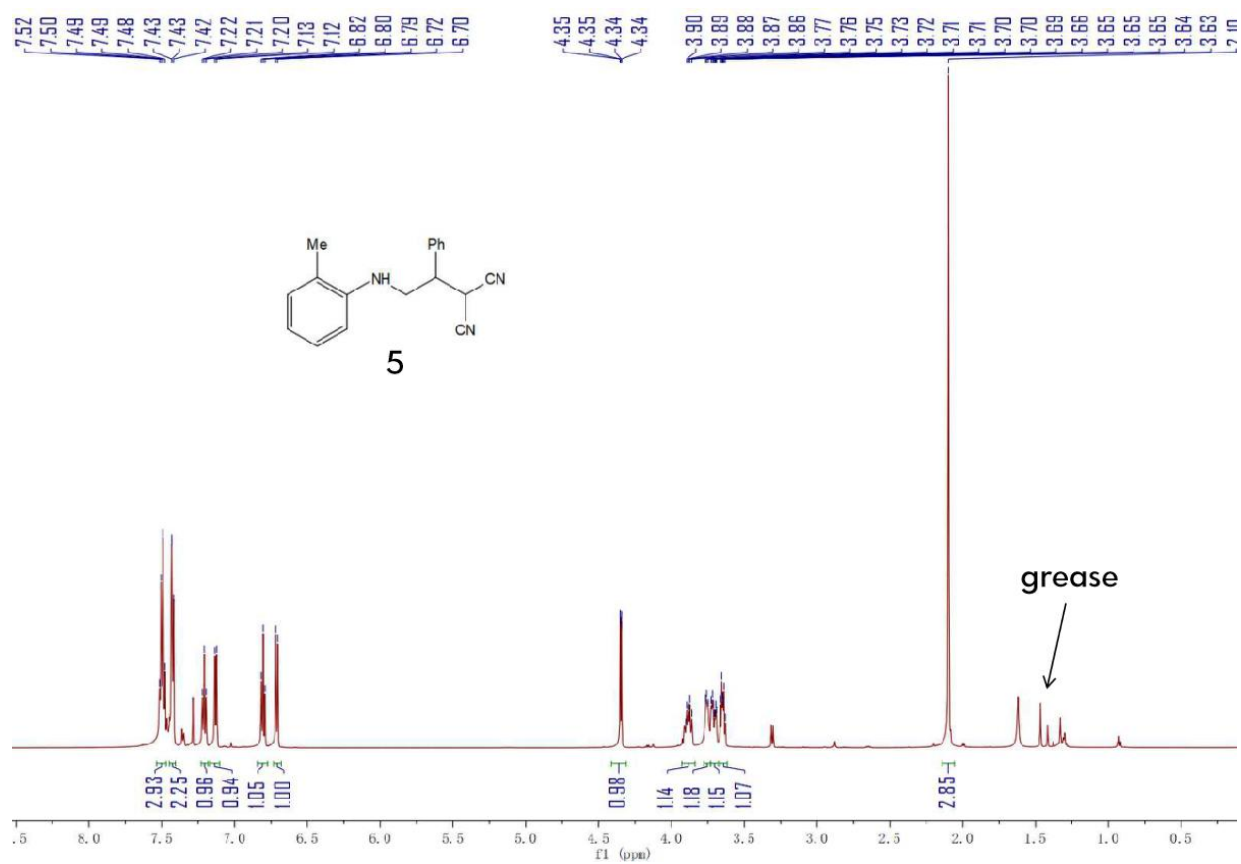
4 The reaction was set up following the general procedure using N-methylbenzenamine (107 mg, 1 mmol) and benzylidenemalononitrile (31 mg, 0.2 mmol). After 16 hours, the reaction was purified following general work-up to give 37 mg (71 % yield) of the title compound. **¹H NMR** (600 MHz, Chloroform-*d*) 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); **¹³C 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]⁺ (C₁₇H₁₆N₃) requires m/z 262.1, found m/z 262.1.

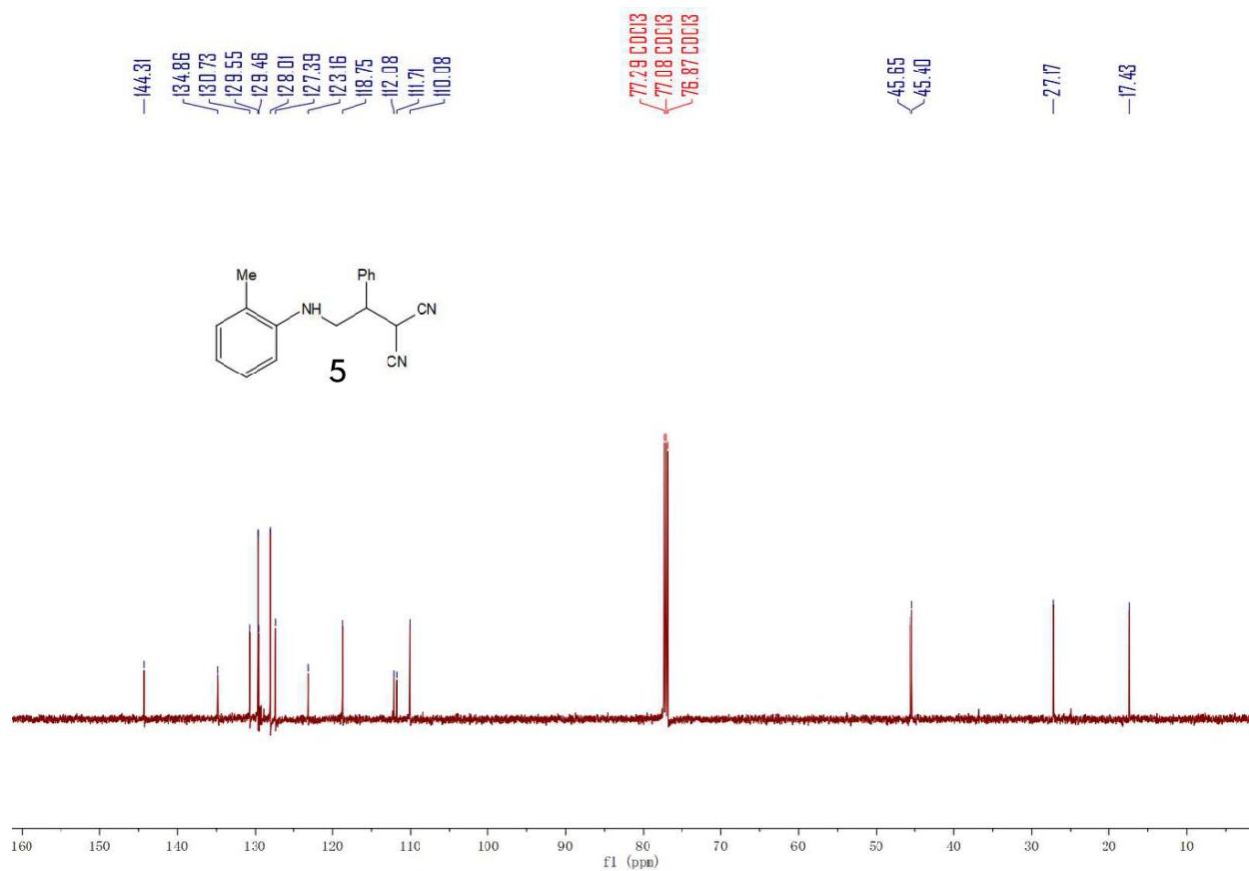


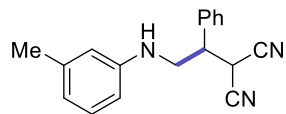




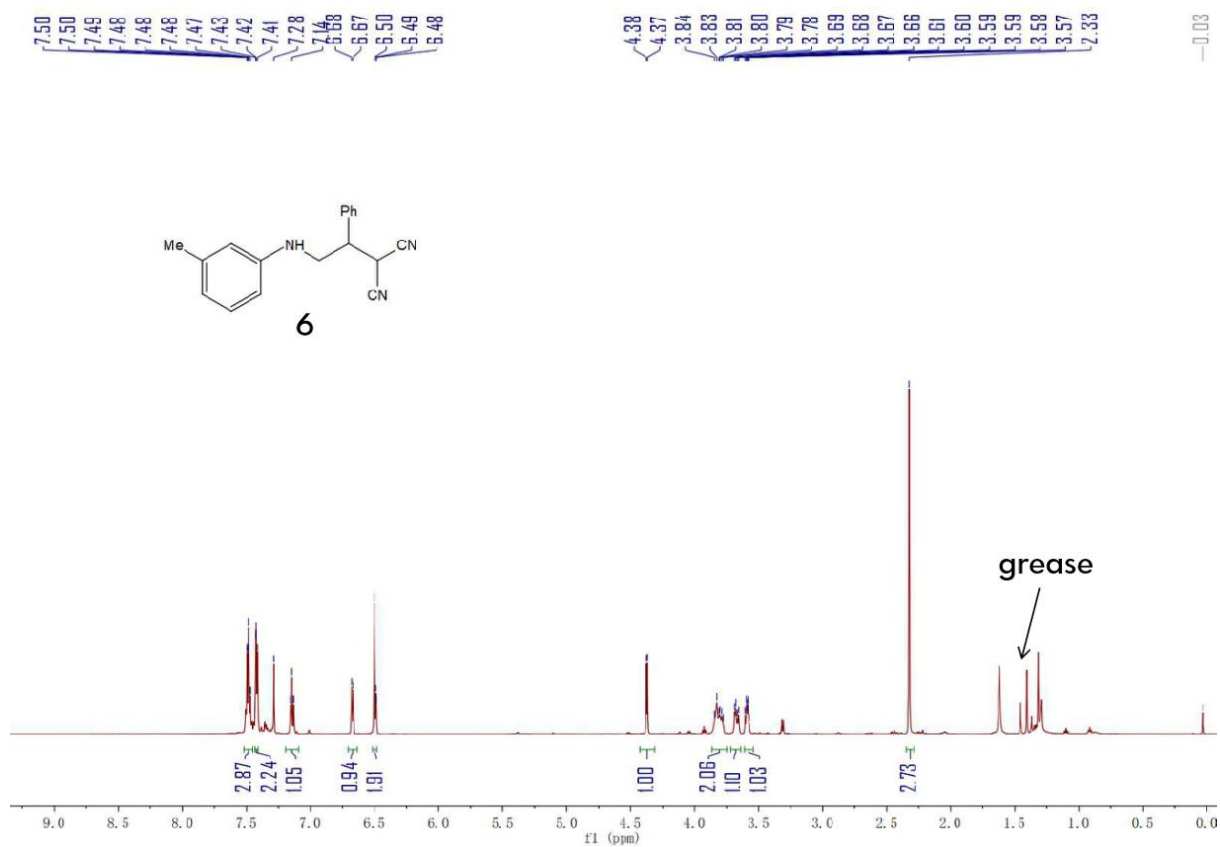
5 The reaction was set up following the general procedure using 2-methyl-N-methylbenzenamine (121 mg, 1 mmol) and benzylidenemalononitrile (31 mg, 0.2 mmol). After 16 hours, the reaction was purified following general work-up to give 39 mg (71 % yield) of the title compound. **¹H NMR** (600 MHz, Chloroform-*d*) 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); **¹³C 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]⁺ (C₁₈H₁₈N₃) requires *m/z* 276.1, found *m/z* 276.1.

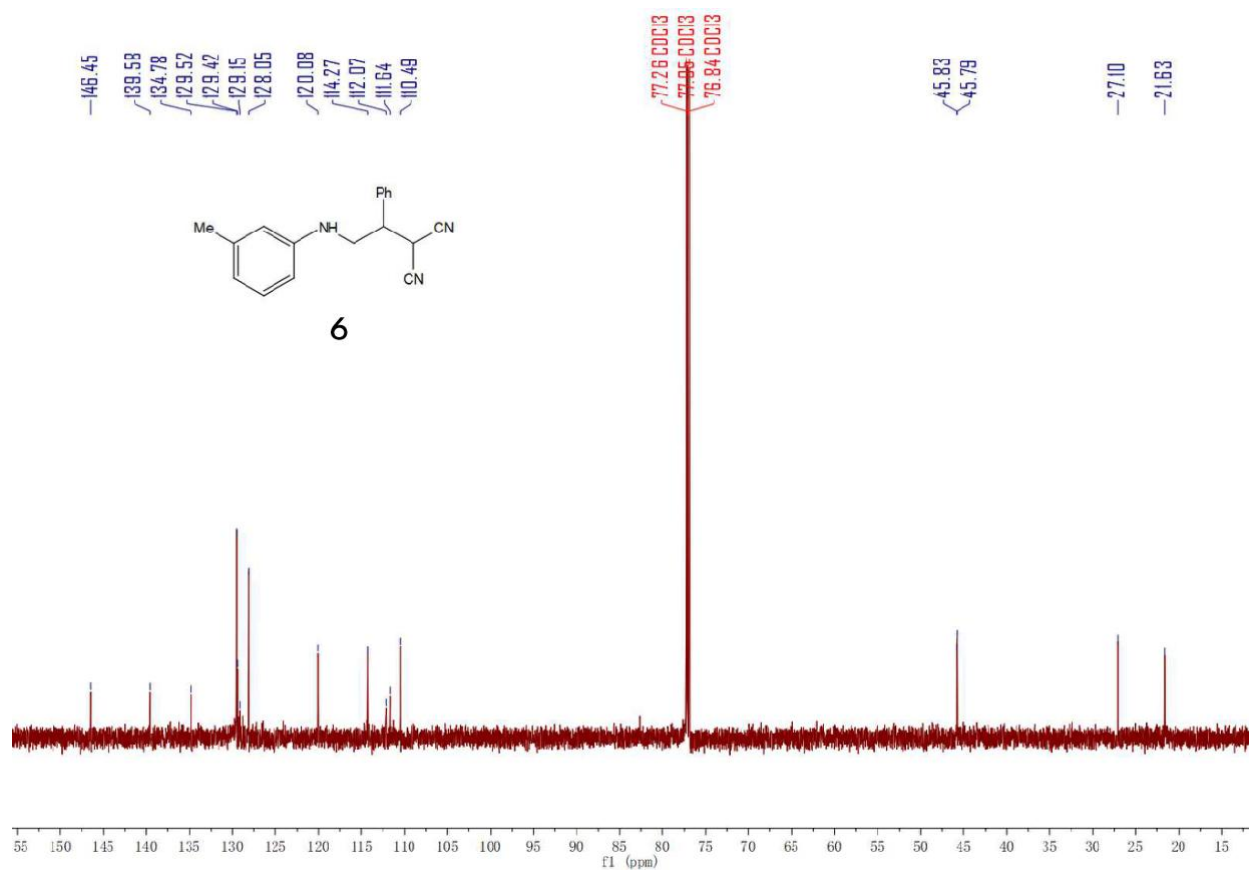


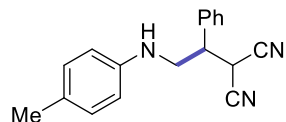




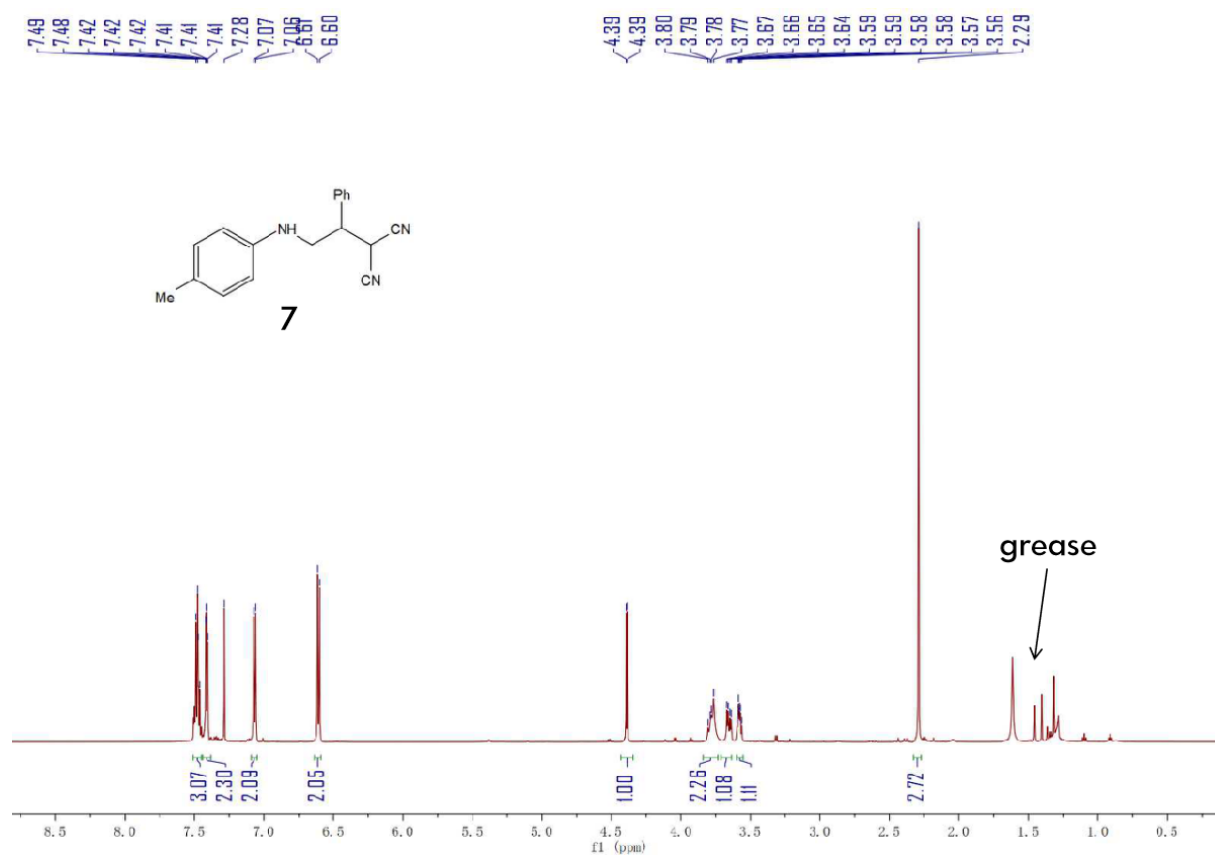
6 The reaction was set up following the general procedure using 3-methyl-N-methylbenzenamine (121 mg, 1 mmol) and benzylidenemalononitrile (31 mg, 0.2 mmol). After 16 hours, the reaction was purified following general work-up to give 34 mg (61 % yield) of the title compound. **¹H NMR** (600 MHz, Chloroform-*d*) 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); **¹³C 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]⁺ (C₁₈H₁₈N₃) requires m/z 276.1, found m/z 276.1.

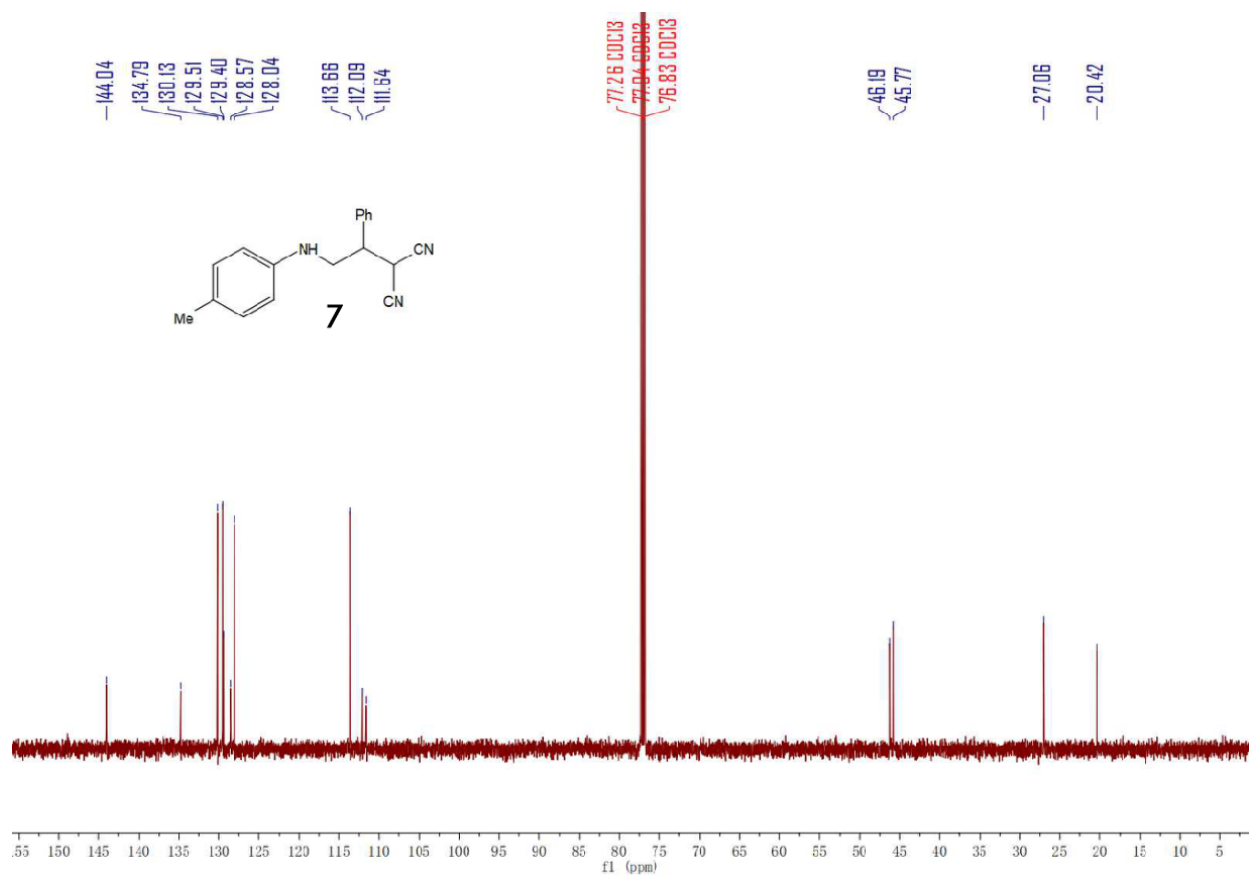


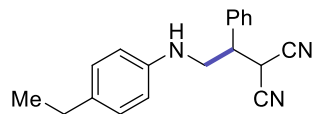




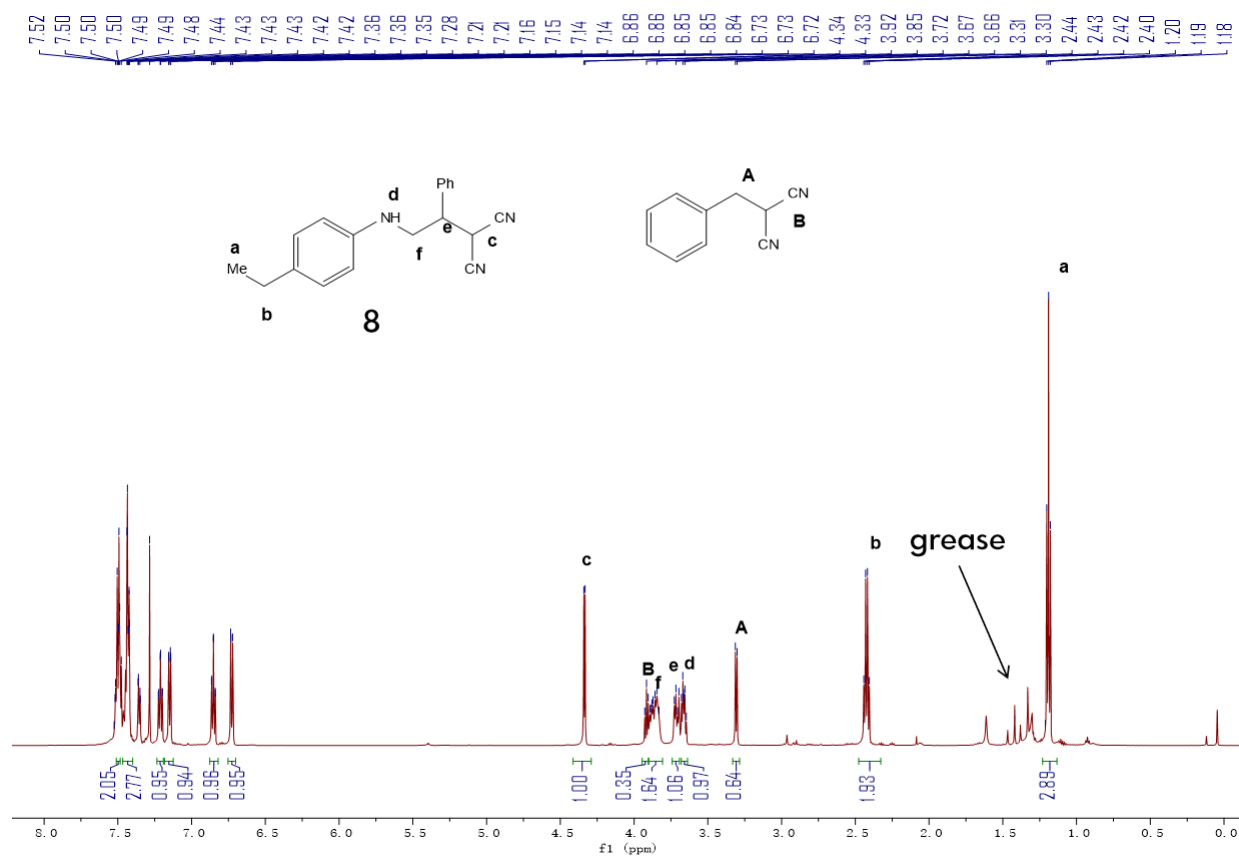
7 The reaction was set up following the general procedure using 4-methyl-N-methylbenzenamine (121 mg, 1 mmol) and benzylidenemalononitrile (31 mg, 0.2 mmol). After 16 hours, the reaction was purified following general work-up to give 30 mg (54 % yield) of the title compound. **¹H NMR** (600 MHz, Chloroform-*d*) 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); **¹³C 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]⁺ (C₁₈H₁₈N₃) requires m/z 276.1, found m/z 276.1.

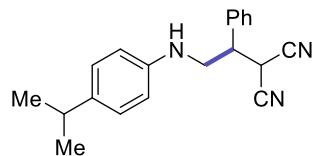




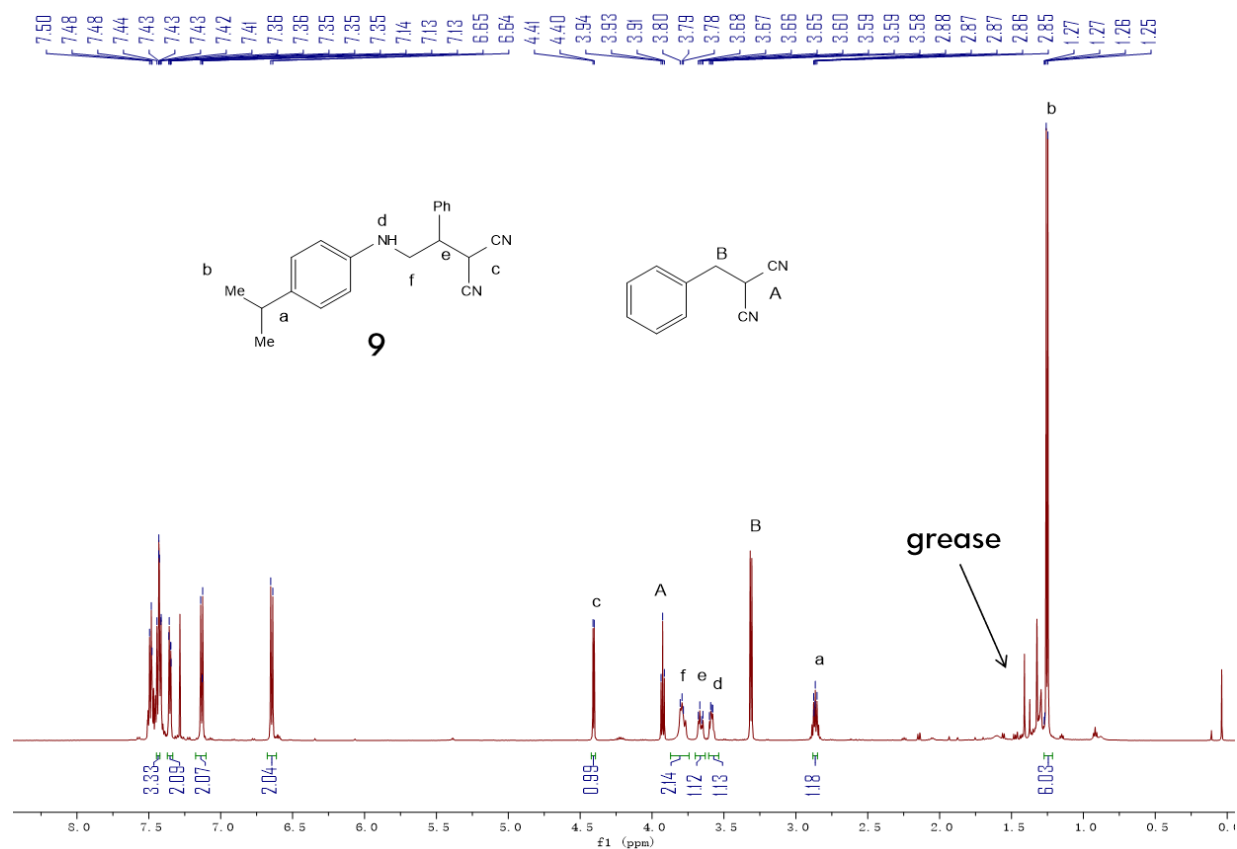


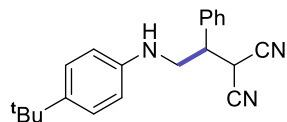
8 The reaction was set up following the general procedure using 4-ethyl-N-methylbenzenamine (135 mg, 1mmol) and benzylidenemalononitrile (31 mg, 0.2 mmol). After 16 hours, the reaction was purified following general work-up to give 33 mg (57 % yield) of the title compound. ¹H NMR (600 MHz, Chloroform-*d*) 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]⁺ (C₁₉H₂₀N₃) requires m/z 290.1, found m/z 290.1.



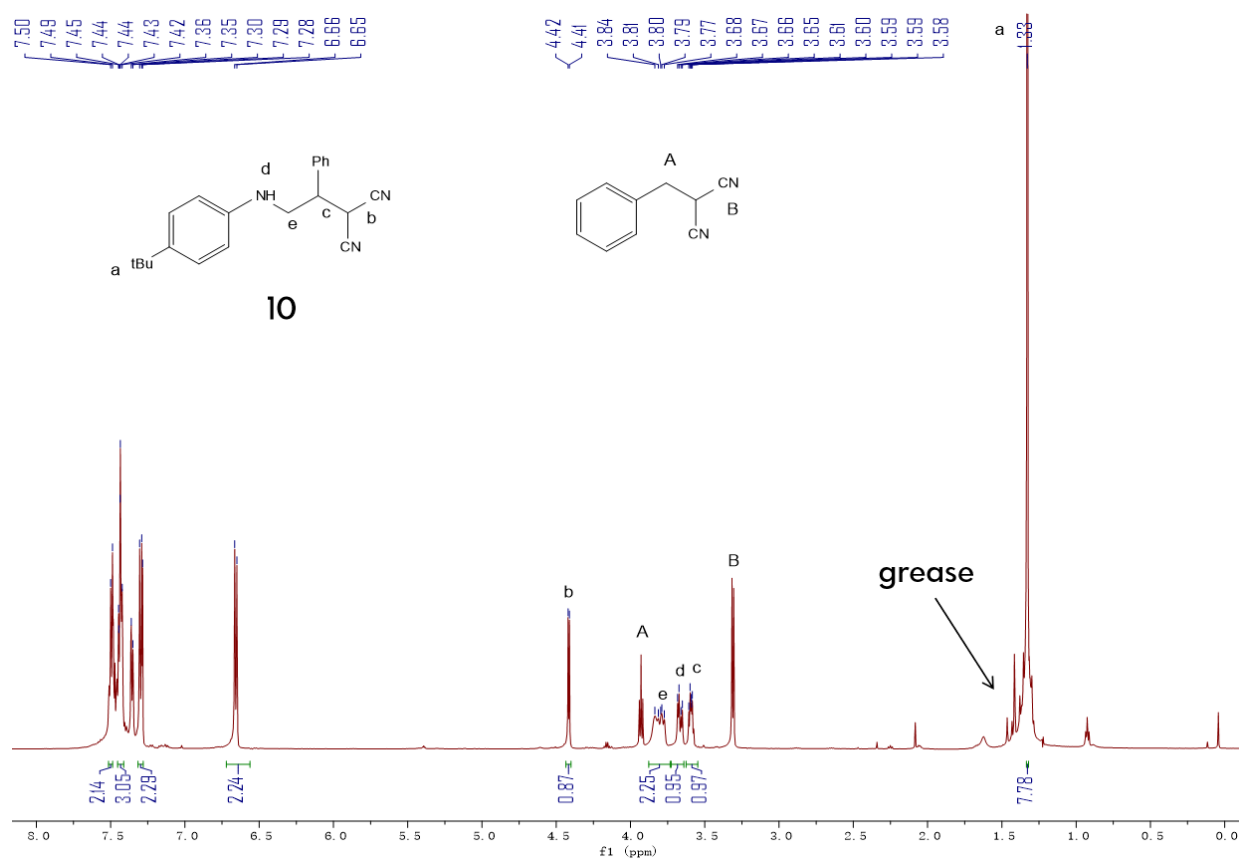


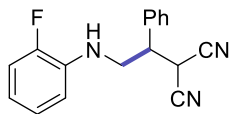
9 The reaction was set up following the general procedure using N-methyl-4-(1-methylethyl)benzenamine (149 mg, 1 mmol) and benzylidenemalononitrile (31 mg, 0.2 mmol). After 16 hours, the reaction was purified following general work-up to give 38 mg (63 % yield) of the title compound. **¹H NMR** (600 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]⁺ (C₂₀H₂₂N₃) requires m/z 304.1, found m/z 304.1.



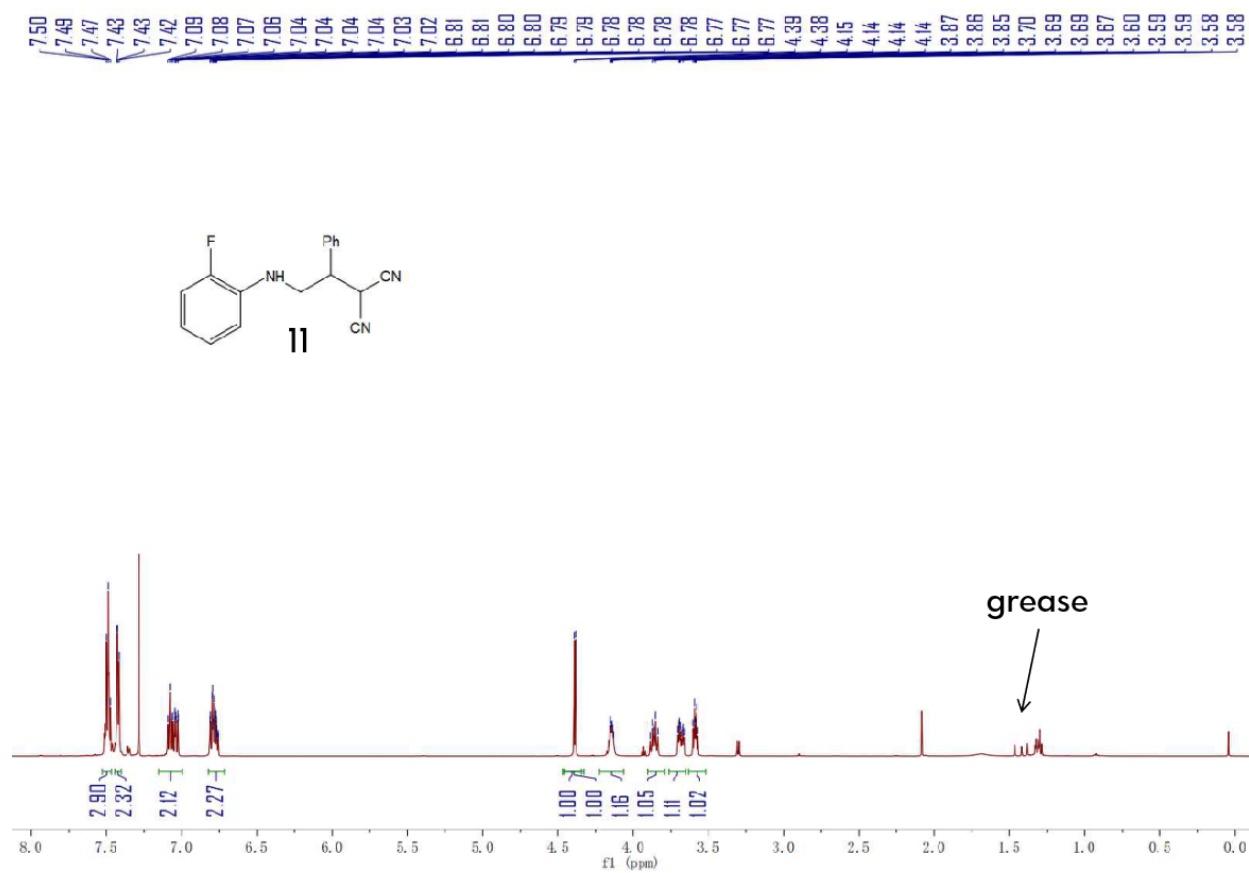


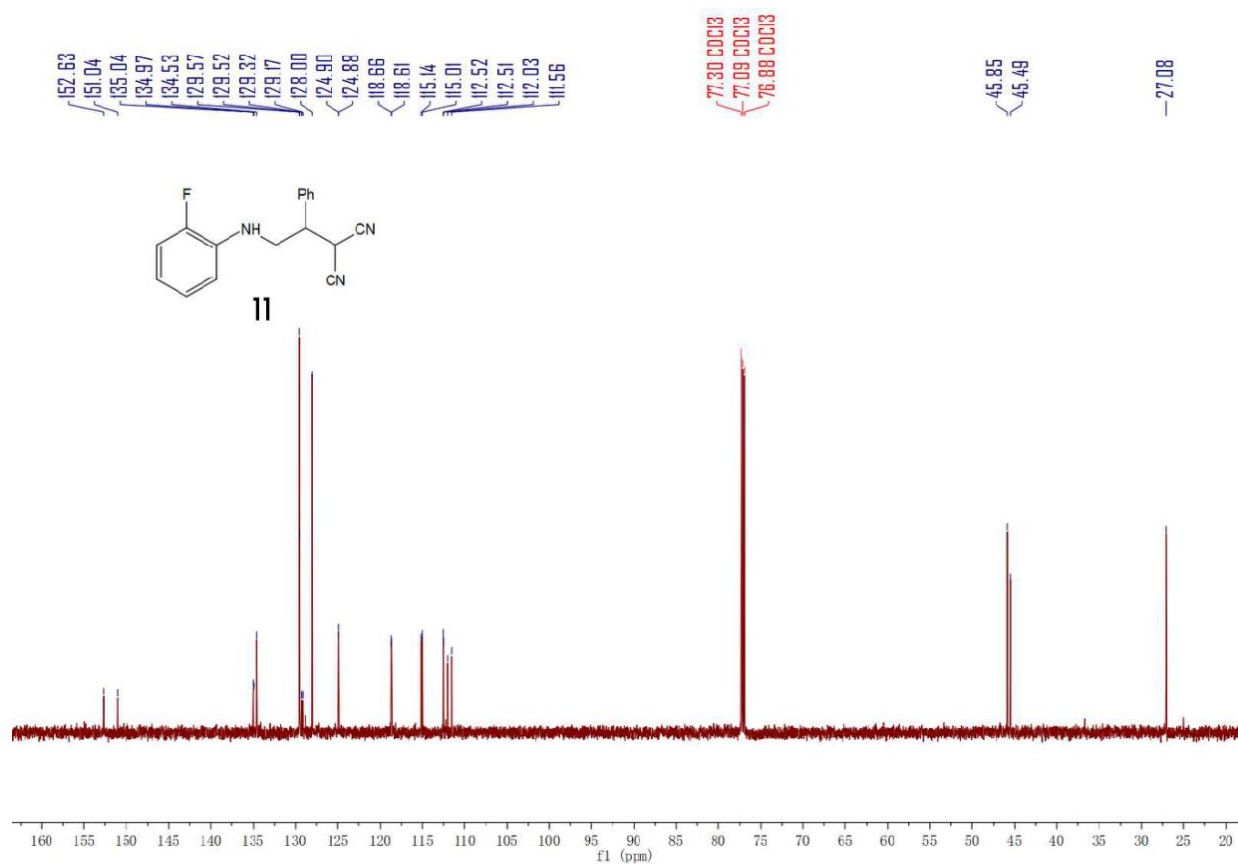
10 The reaction was set up following the general procedure using 4-(1,1-dimethylethyl)-N-methylbenzenamine (163 mg, 1 mmol) and benzylidenemalononitrile (31 mg, 0.2 mmol). After 16 hours, the reaction was purified following general work-up to give 40 mg (62 % yield) of the title compound. **¹H NMR** (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]⁺ (C₂₁H₂₄N₃) requires m/z 318.1, found m/z 318.1.

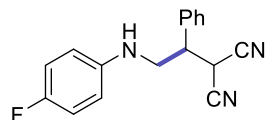




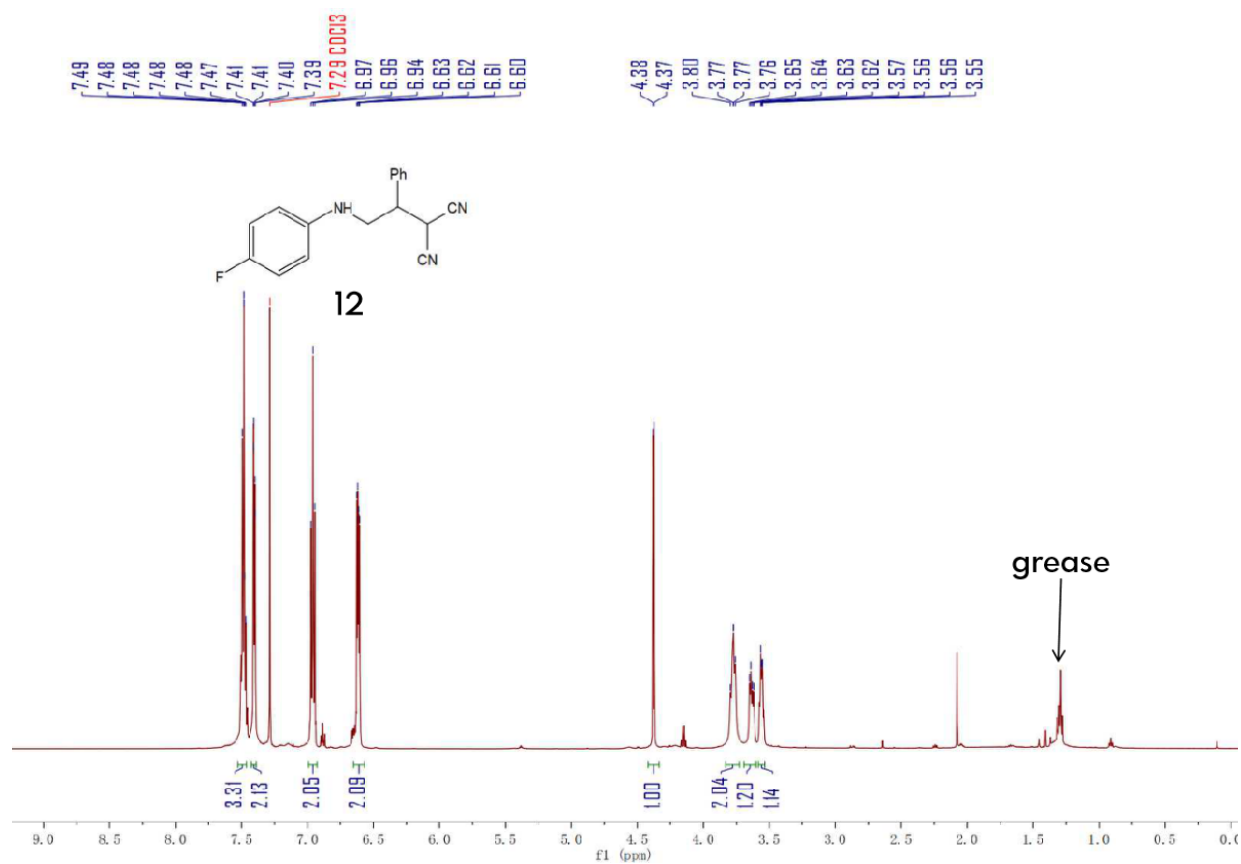
11 The reaction was set up following the general procedure using 2-fluoro-N-methylbenzenamine (125 mg, 1 mmol) and benzyldenemalononitrile (31 mg, 0.2 mmol). After 16 hours, the reaction was purified following general work-up to give 46 mg (82 % yield) of the title compound. **¹H NMR** (600 MHz, Chloroform-*d*) 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); **¹³C 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]⁺ (C₁₇H₁₅FN₃) requires m/z 280.1, found m/z 280.1.

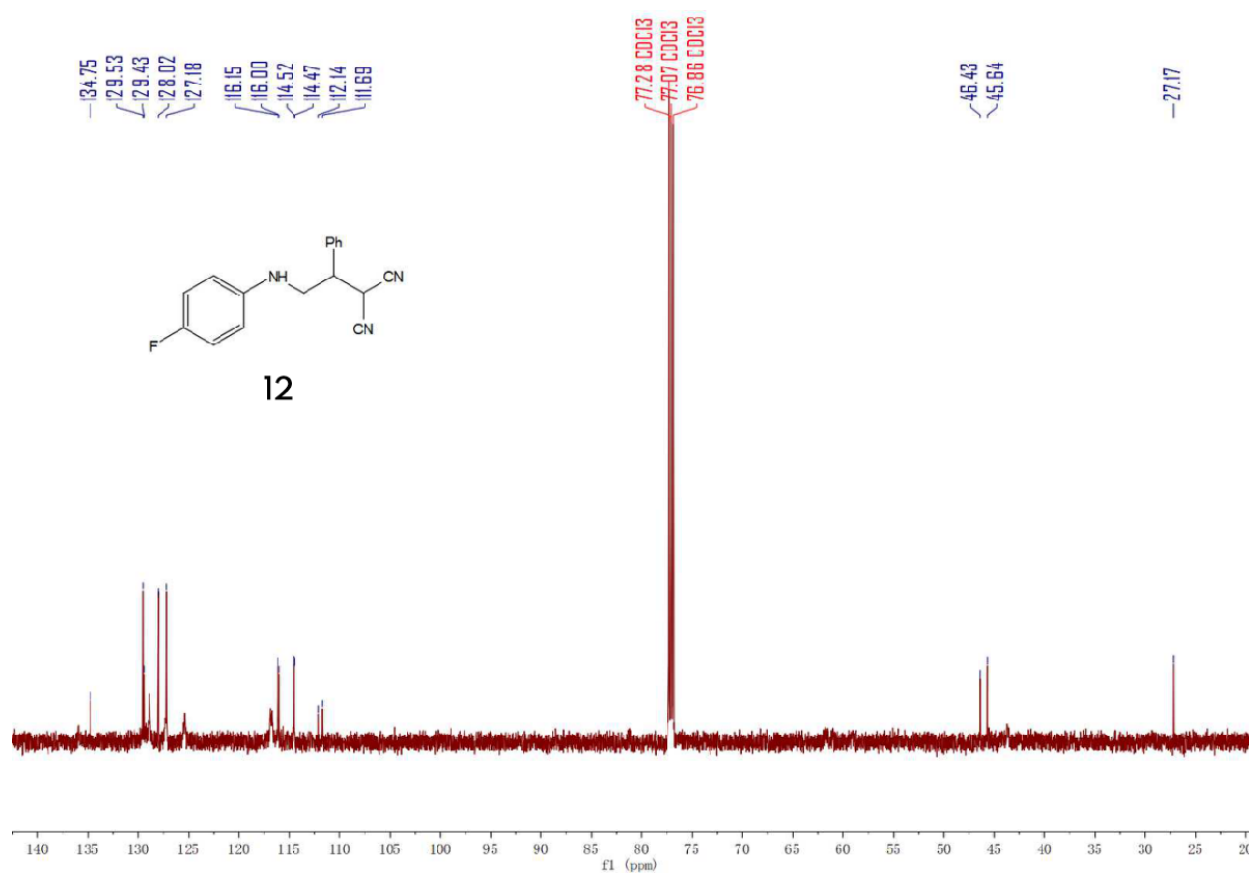


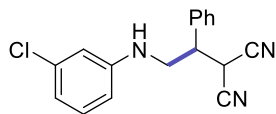




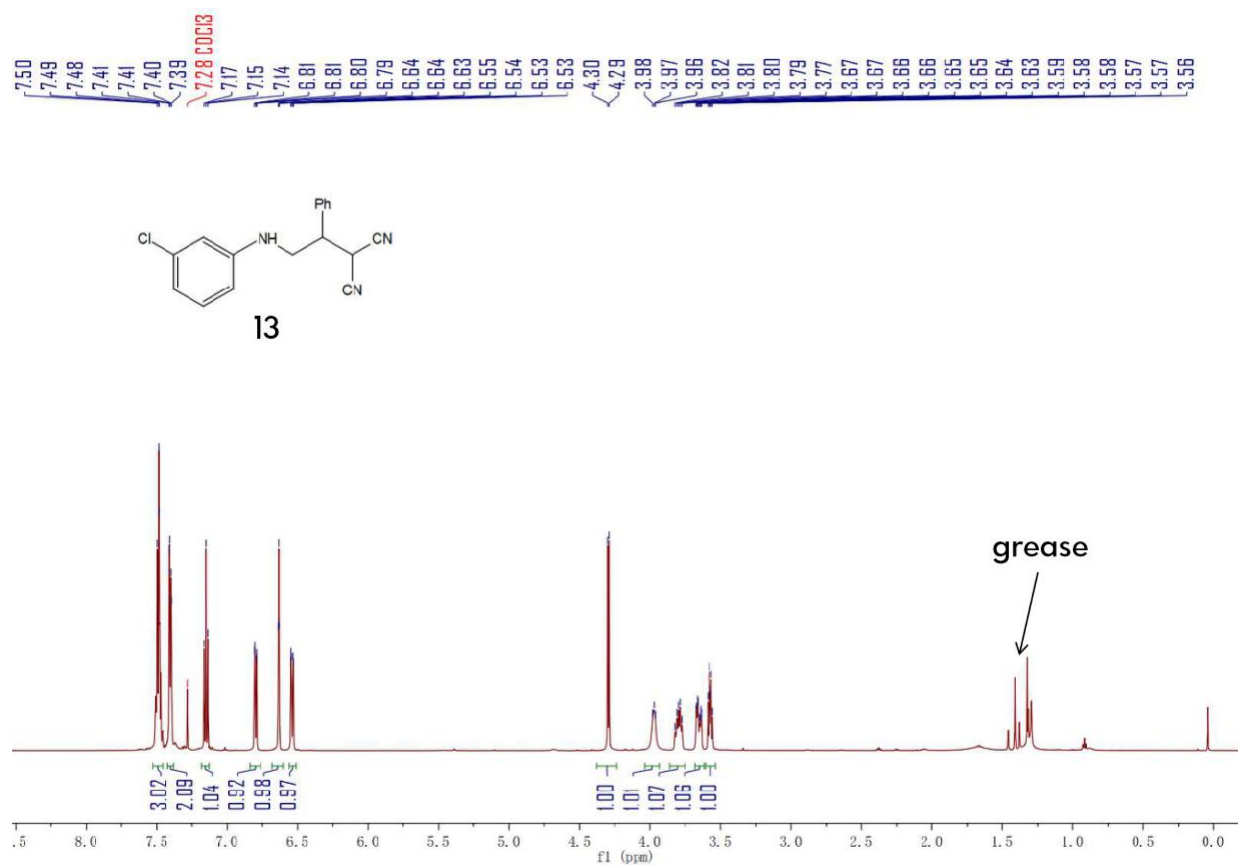
12 The reaction was set up following the general procedure using 4-fluoro-N-methylbenzenamine (125 mg, 1 mmol) and benzylidenemalononitrile (31 mg, 0.2 mmol). After 16 hours, the reaction was purified following general work-up to give 41 mg (73 % yield) of the title compound. **¹H NMR** (600 MHz, Chloroform-*d*) 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); **¹³C 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]⁺ (C₁₇H₁₅FN₃) requires m/z 280.1, found m/z 280.1.

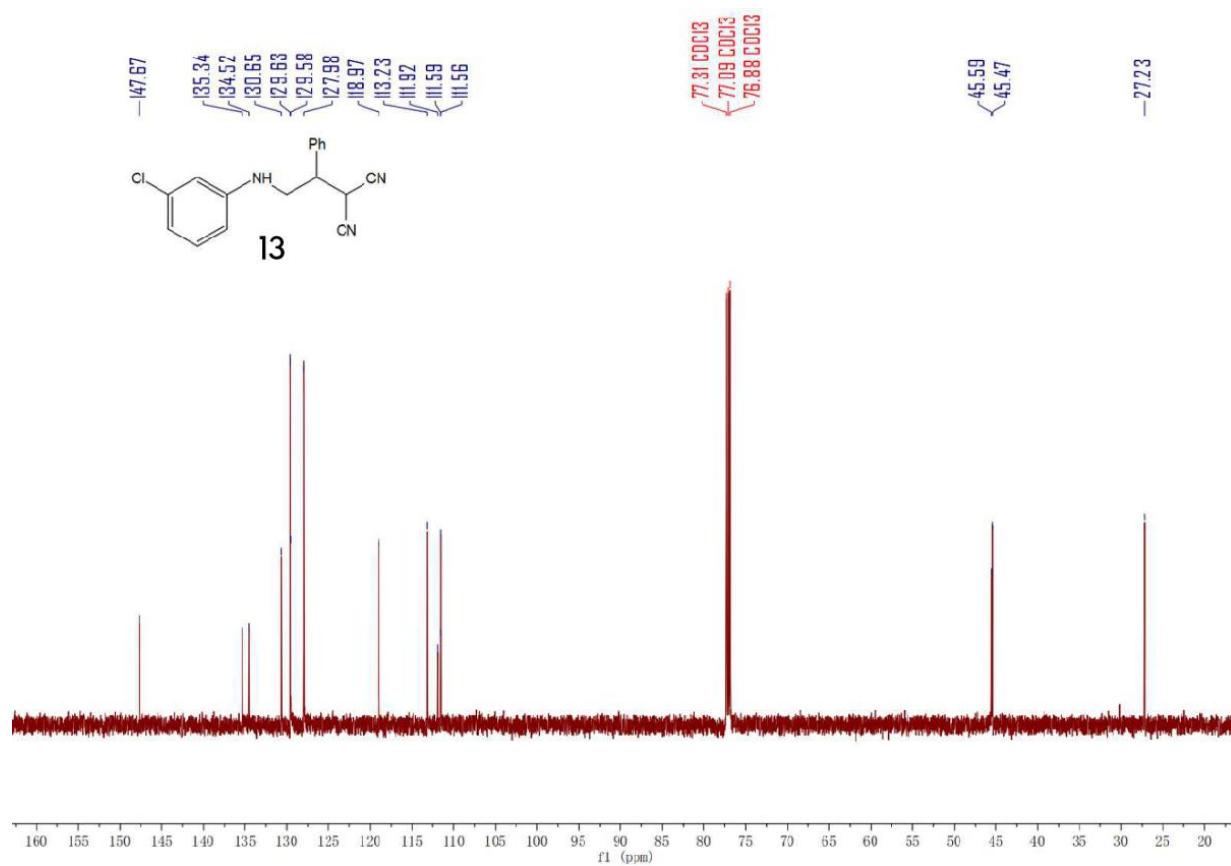


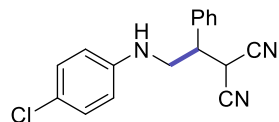




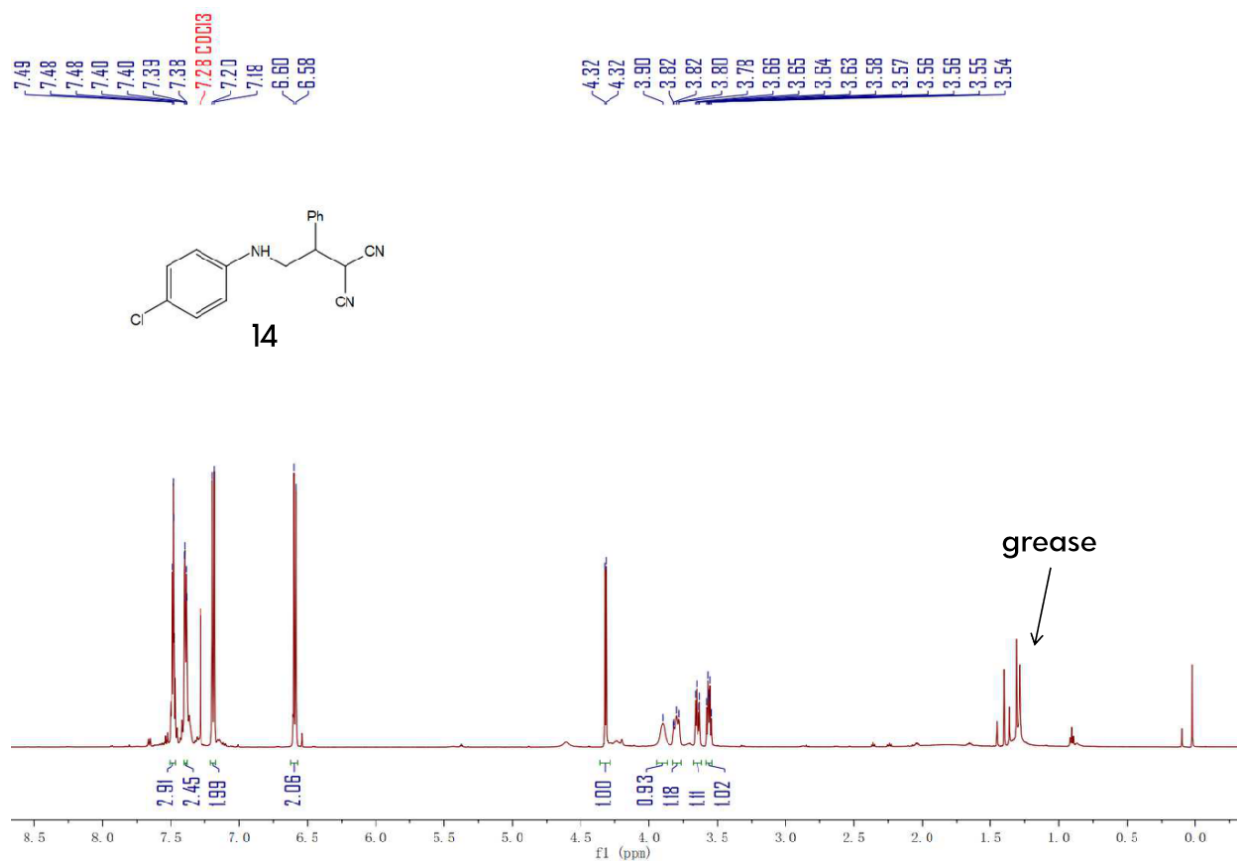
13 The reaction was set up following the general procedure using 3-chloro-N-methylbenzenamine (141 mg, 1 mmol) and benzyldenemalononitrile (31 mg, 0.2 mmol). After 16 hours, the reaction was purified following general work-up to give 46 mg (78 % yield) of the title compound. **¹H NMR** (600 MHz, Chloroform-*d*) 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); **¹³C 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]⁺ (C₁₇H₁₅ClN₃) requires *m/z* 296.1, found *m/z* 296.1.

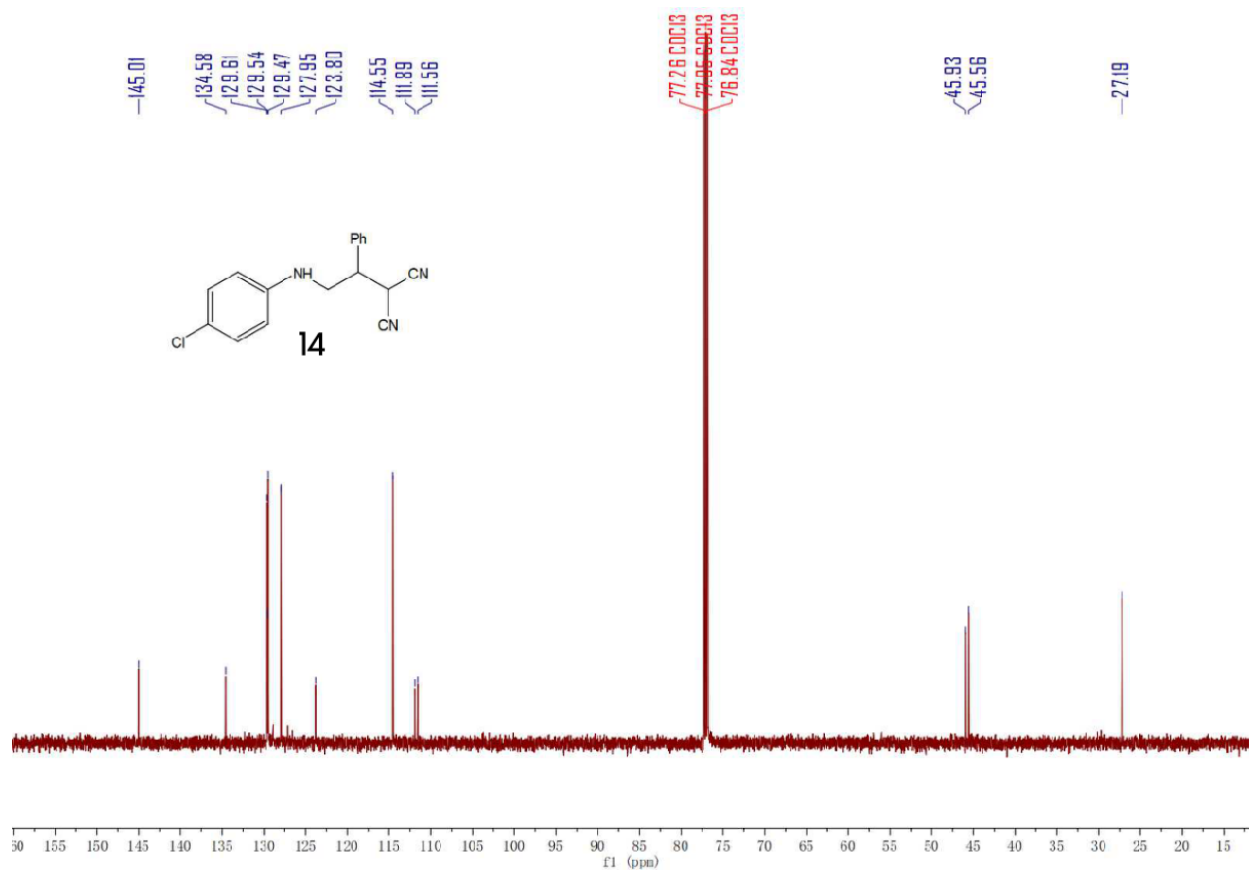


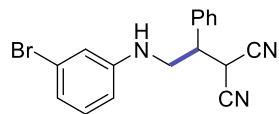




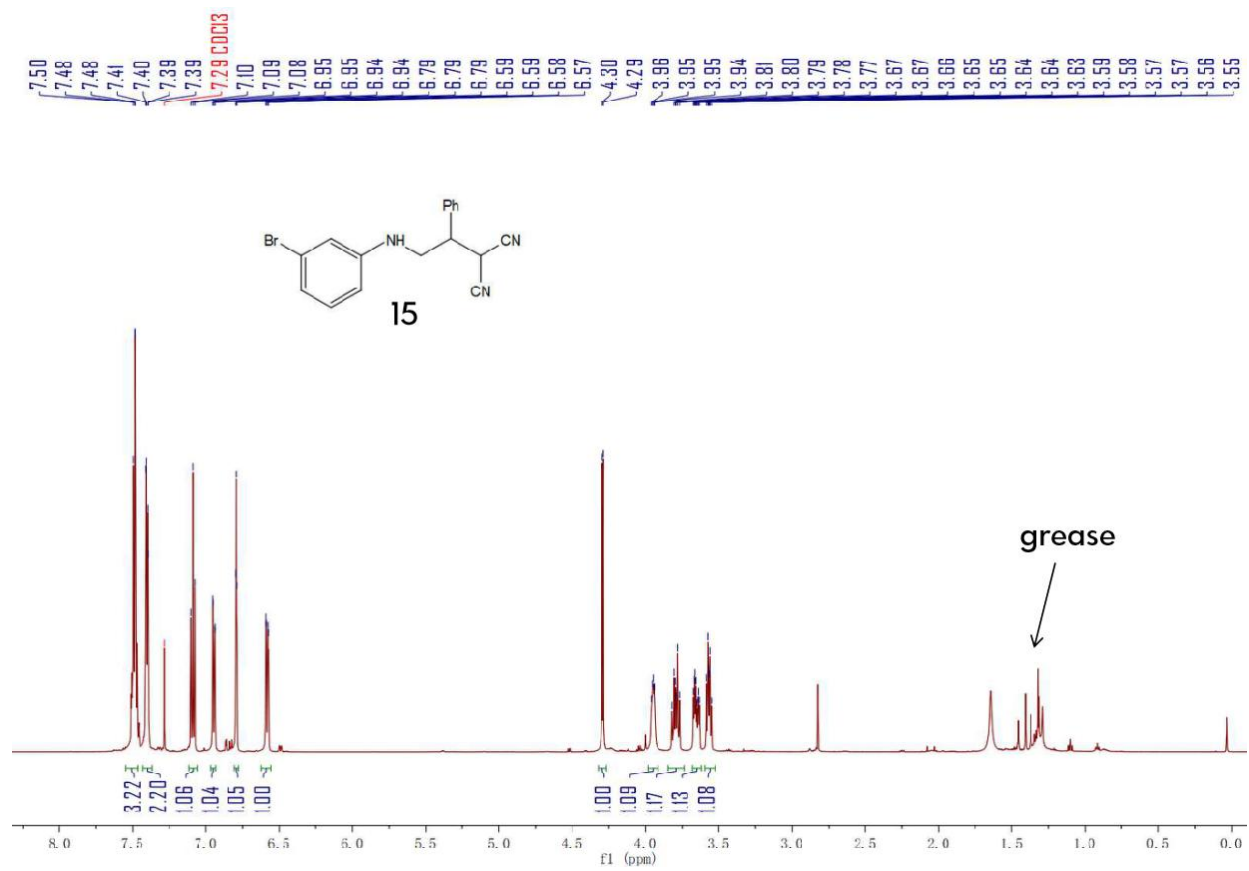
13 The reaction was set up following the general procedure using 4-chloro-N-methylbenzenamine (141 mg, 1 mmol) and benzyldenemalononitrile (31 mg, 0.2 mmol). After 16 hours, the reaction was purified following general work-up to give 40 mg (69 % yield) of the title compound. **¹H NMR** (600 MHz, Chloroform-*d*) 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); **¹³C 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]⁺ (C₁₇H₁₅ClN₃) requires *m/z* 296.1, found *m/z* 296.1.

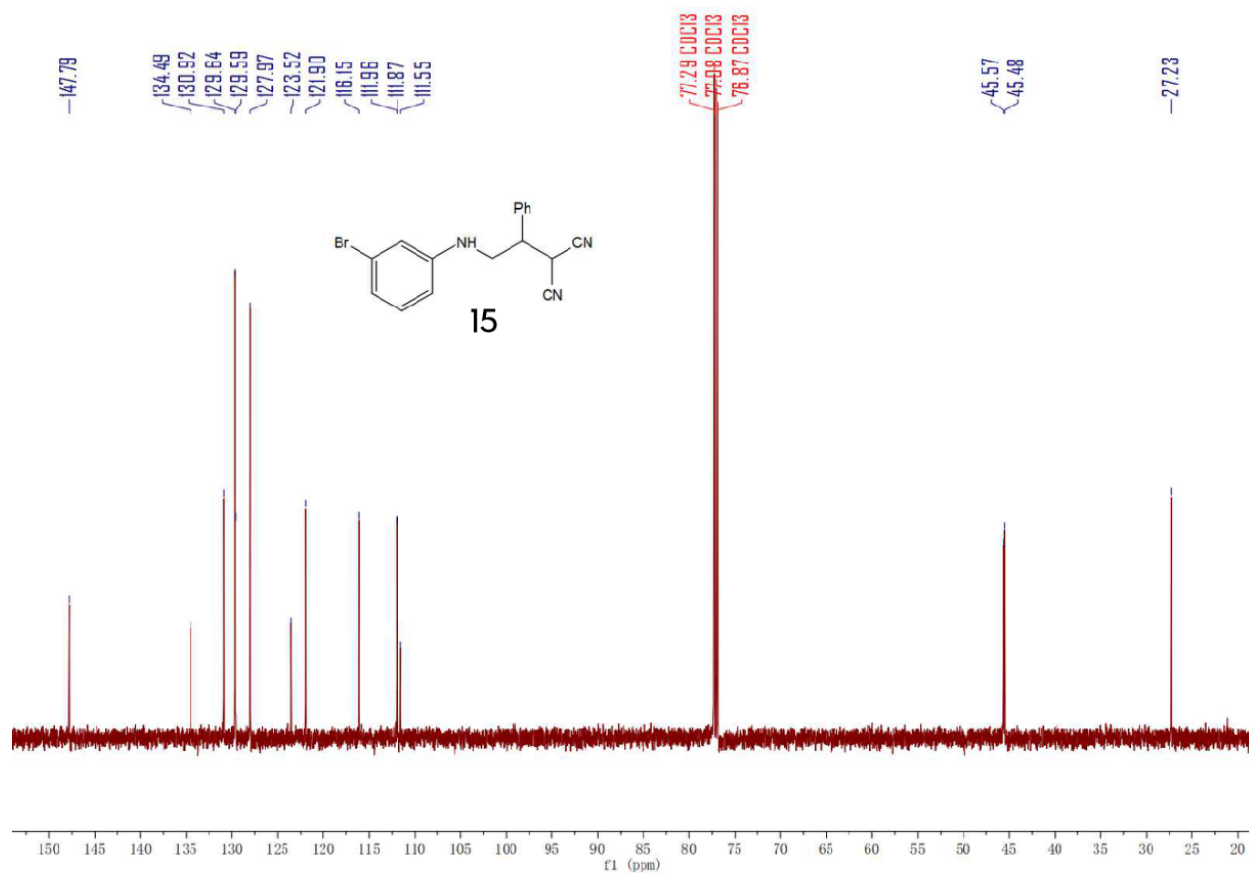


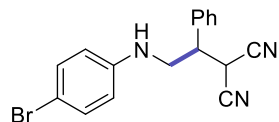




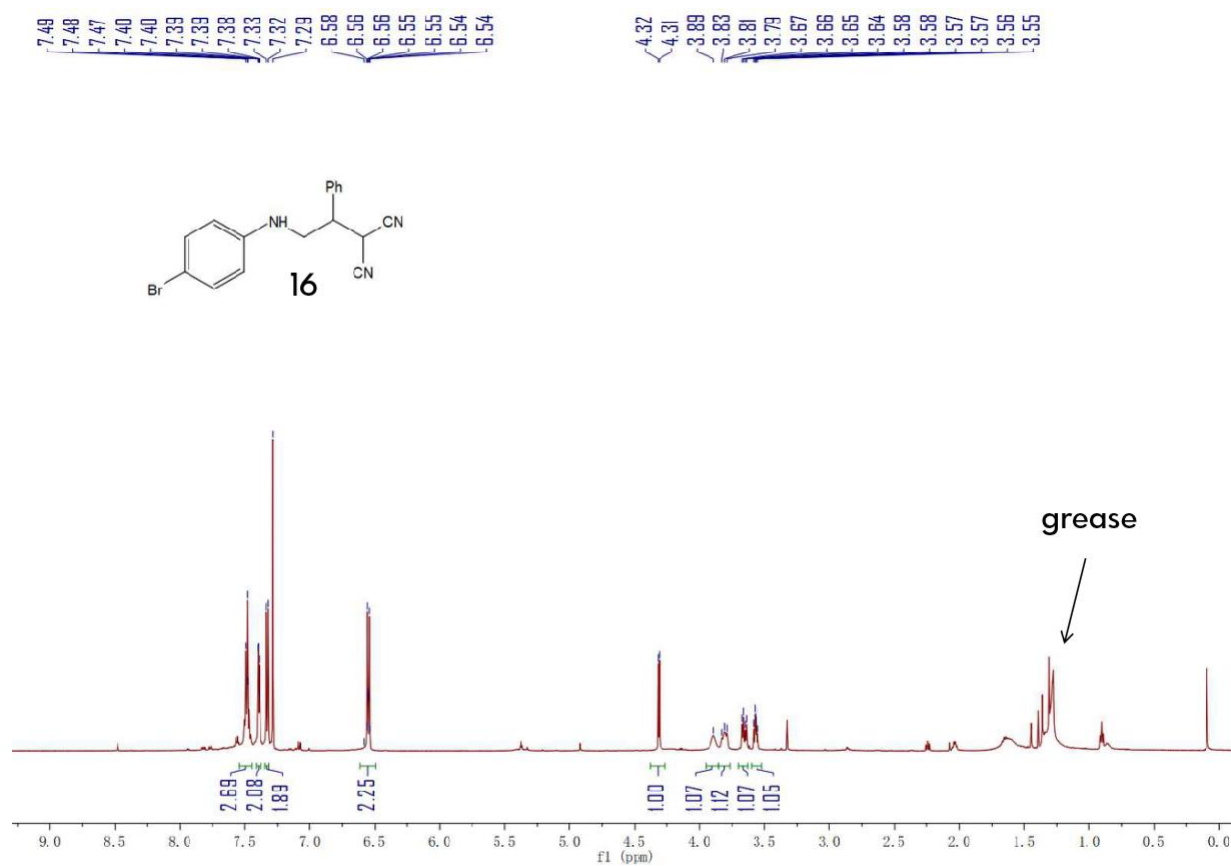
15 The reaction was set up following the general procedure using 3-bromo-N-methylbenzenamine (186 mg, 1 mmol) and benzyldenemalononitrile (31 mg, 0.2 mmol). After 16 hours, the reaction was purified following general work-up to give 42 mg (61 % yield) of the title compound. **¹H NMR** (600 MHz, Chloroform-*d*) 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); **¹³C 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]⁺ (C₁₇H₁₅BrN₃) requires *m/z* 340.0, found *m/z* 340.0.

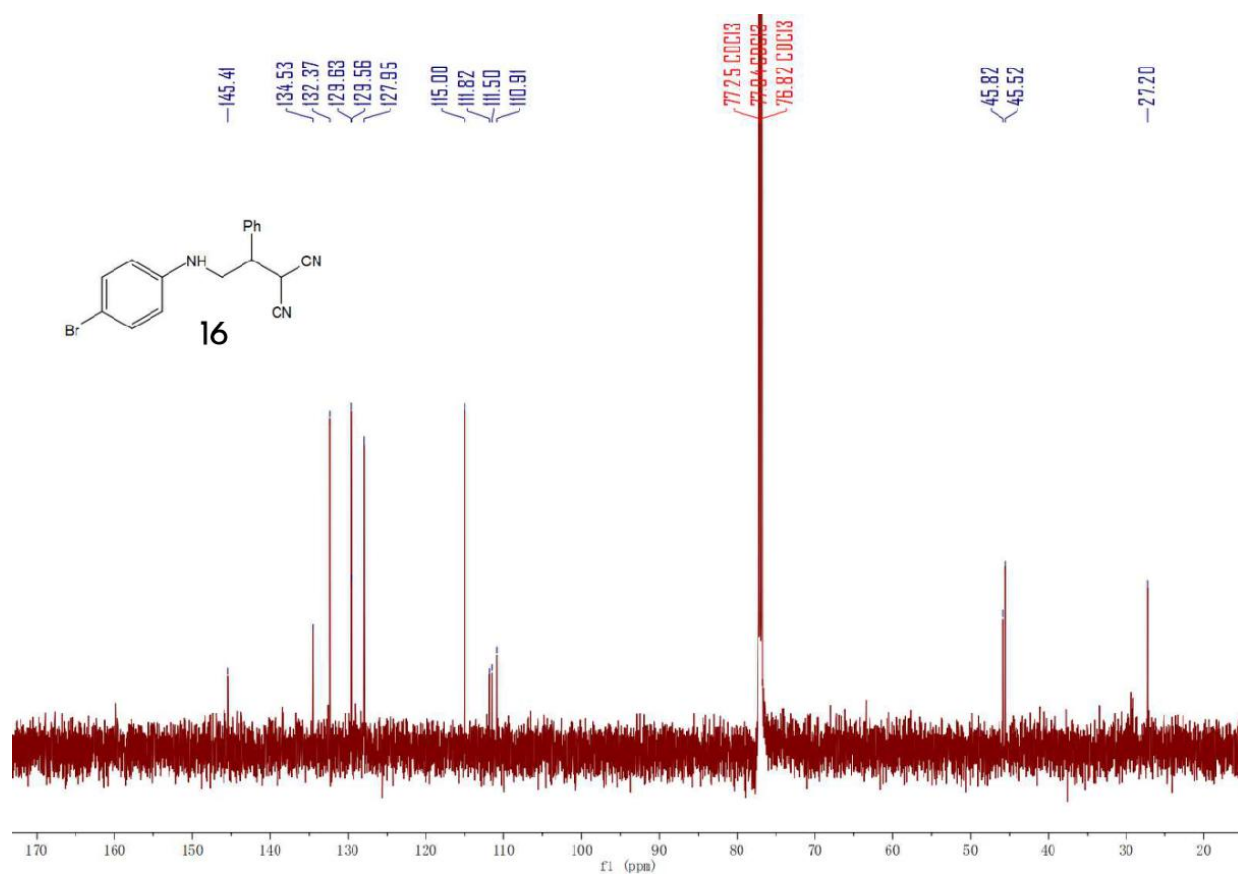


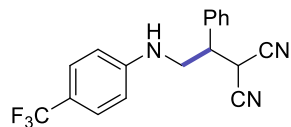




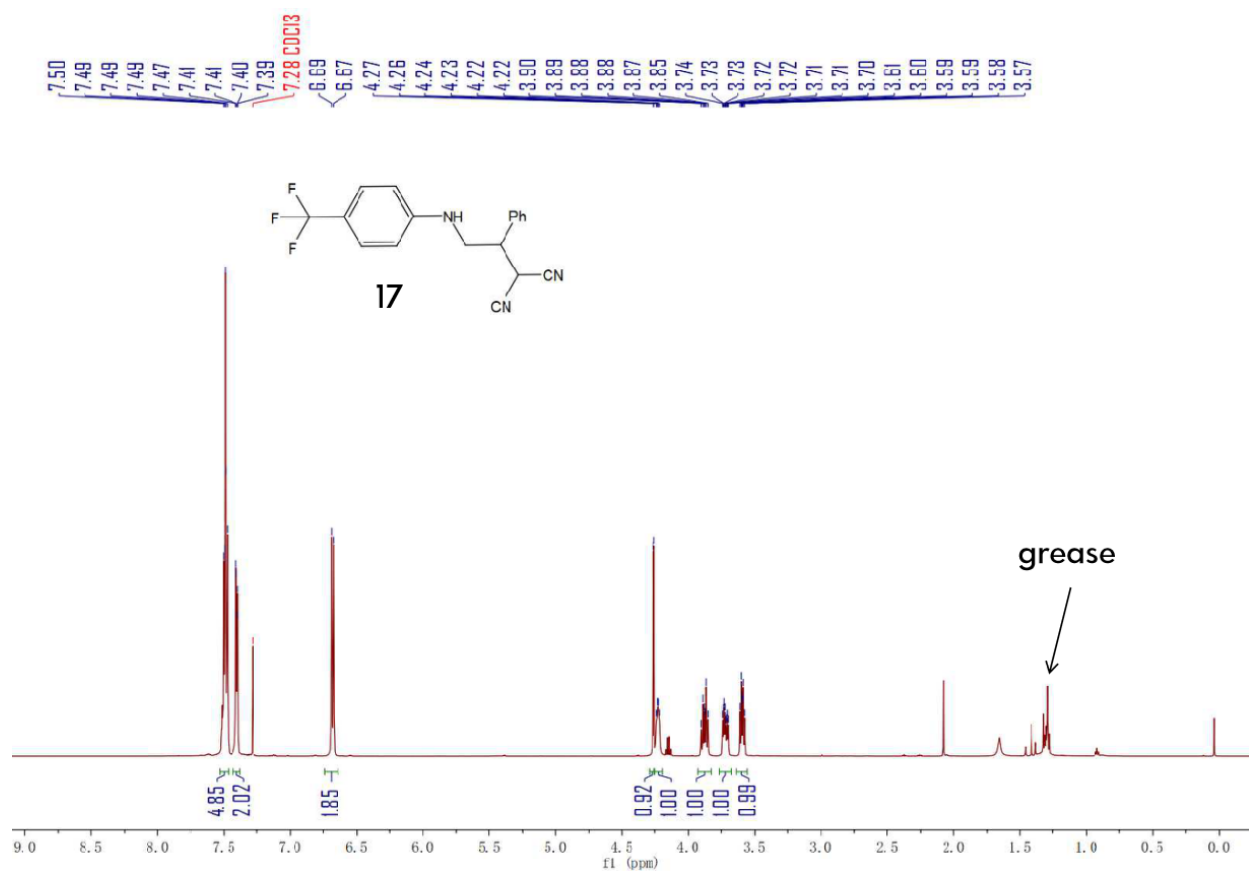
16 The reaction was set up following the general procedure using 4-bromo-N-methylbenzenamine (186 mg, 1 mmol) and benzyldenemalononitrile (31 mg, 0.2 mmol). After 16 hours, the reaction was purified following general work-up to give 22 mg (32 % yield) of the title compound. **¹H NMR** (600 MHz, Chloroform-*d*) 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); **¹³C 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]⁺ (C₁₇H₁₅BrN₃) requires *m/z* 340.0, found *m/z* 340.0.

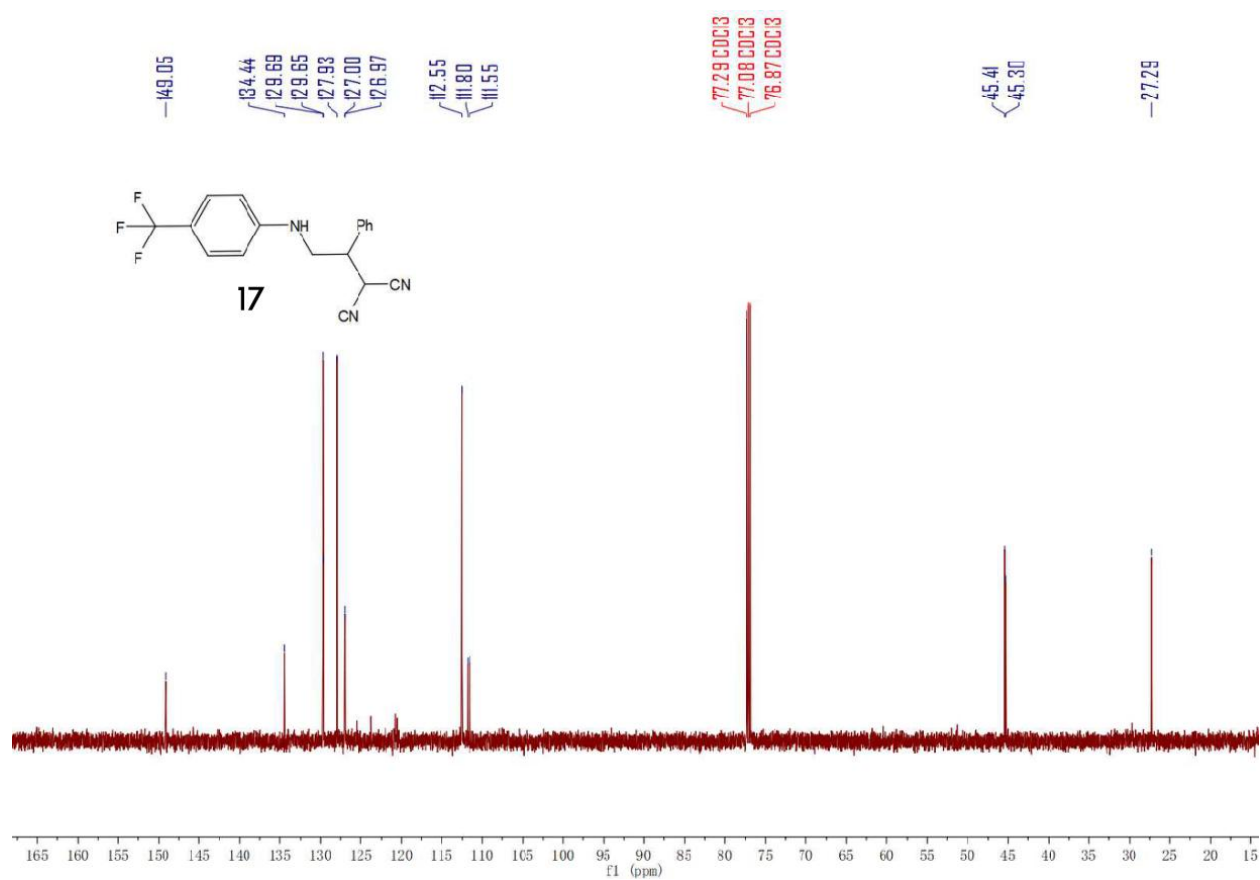


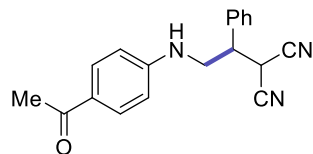




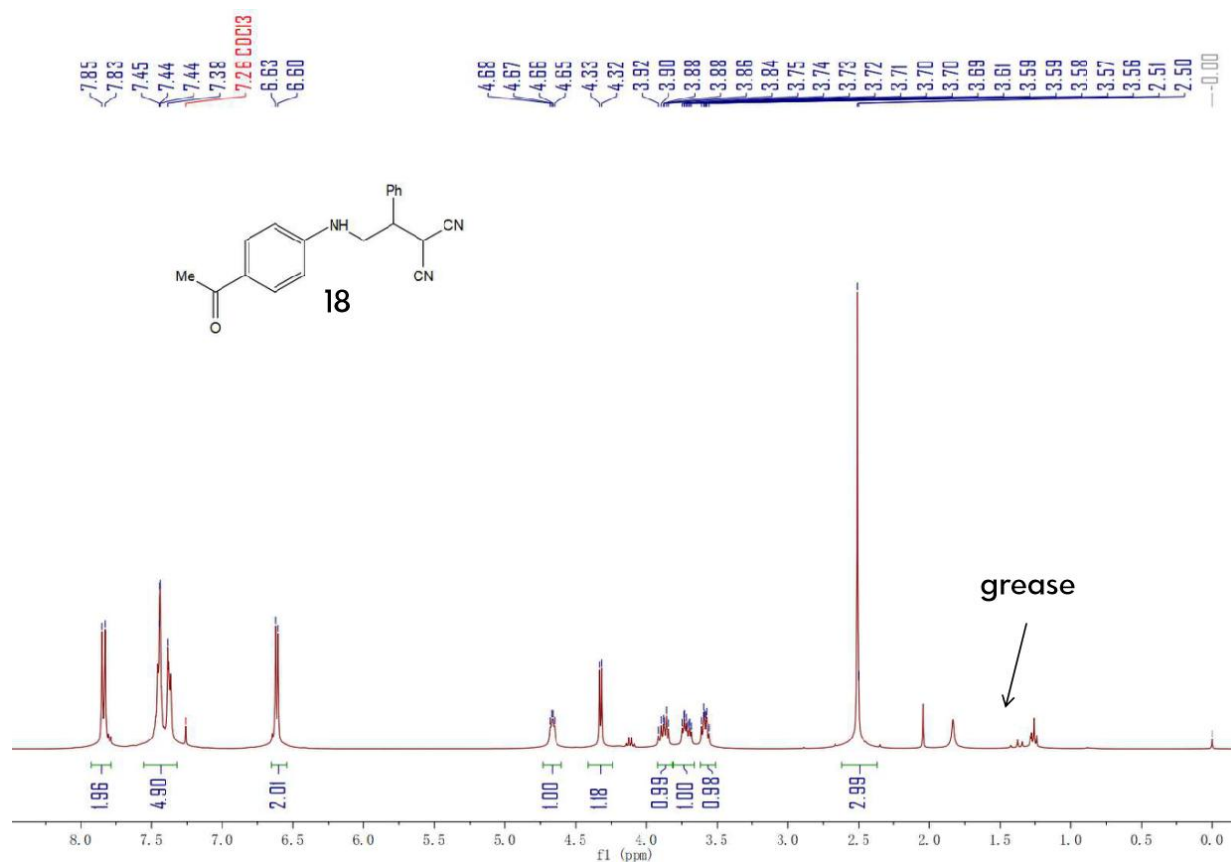
17 The reaction was set up following the general procedure using 4-trifluoromethyl-N-methylbenzenamine (175 mg, 1 mmol) and benzyldenemalononitrile (31 mg, 0.2 mmol). After 16 hours, the reaction was purified following general work-up to give 52.1 mg (79 % yield) of the title compound. **¹H NMR** (600 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); **¹³C 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]⁺ (C₁₈H₁₅F₃N₃) requires *m/z* 330.1, found *m/z* 330.1.

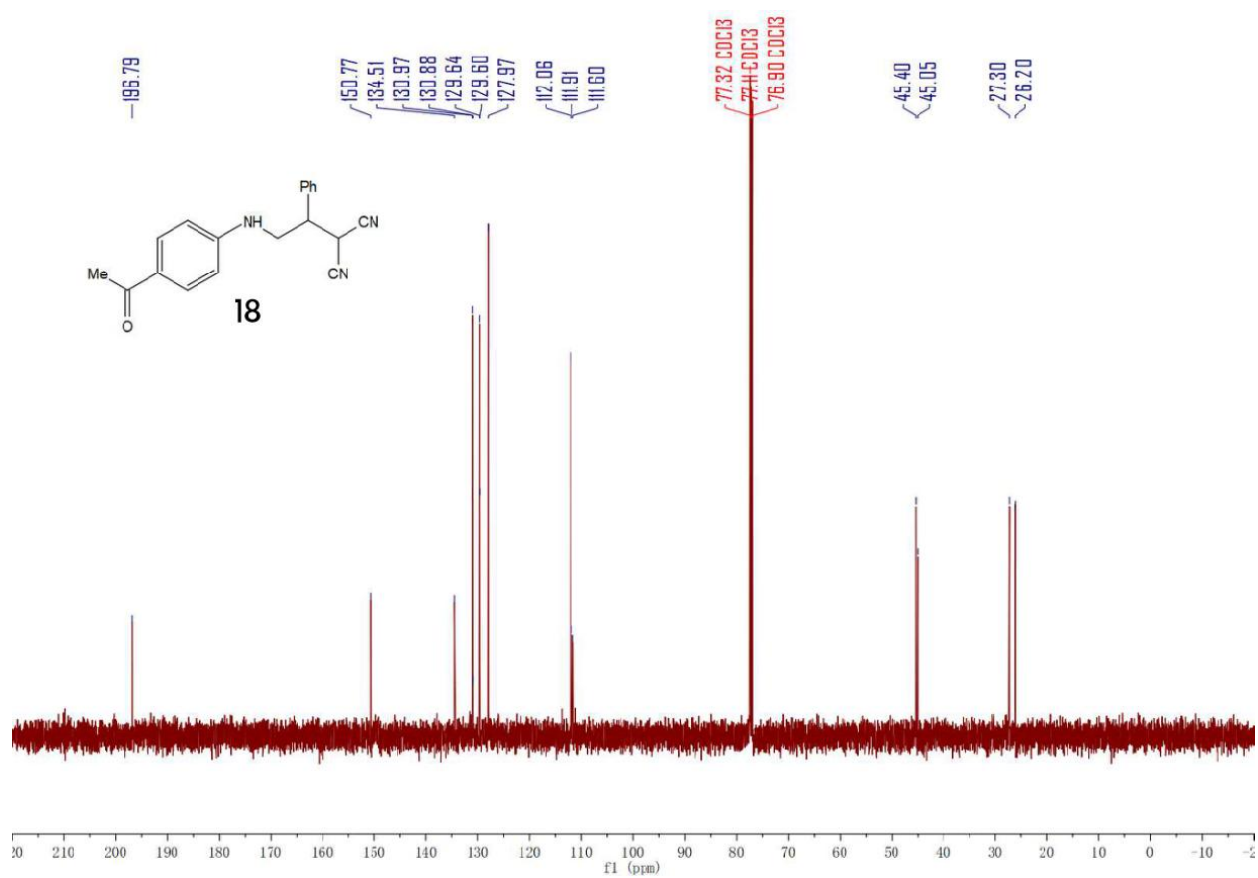


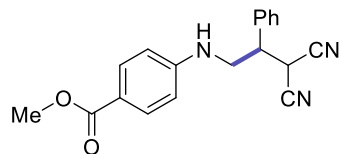




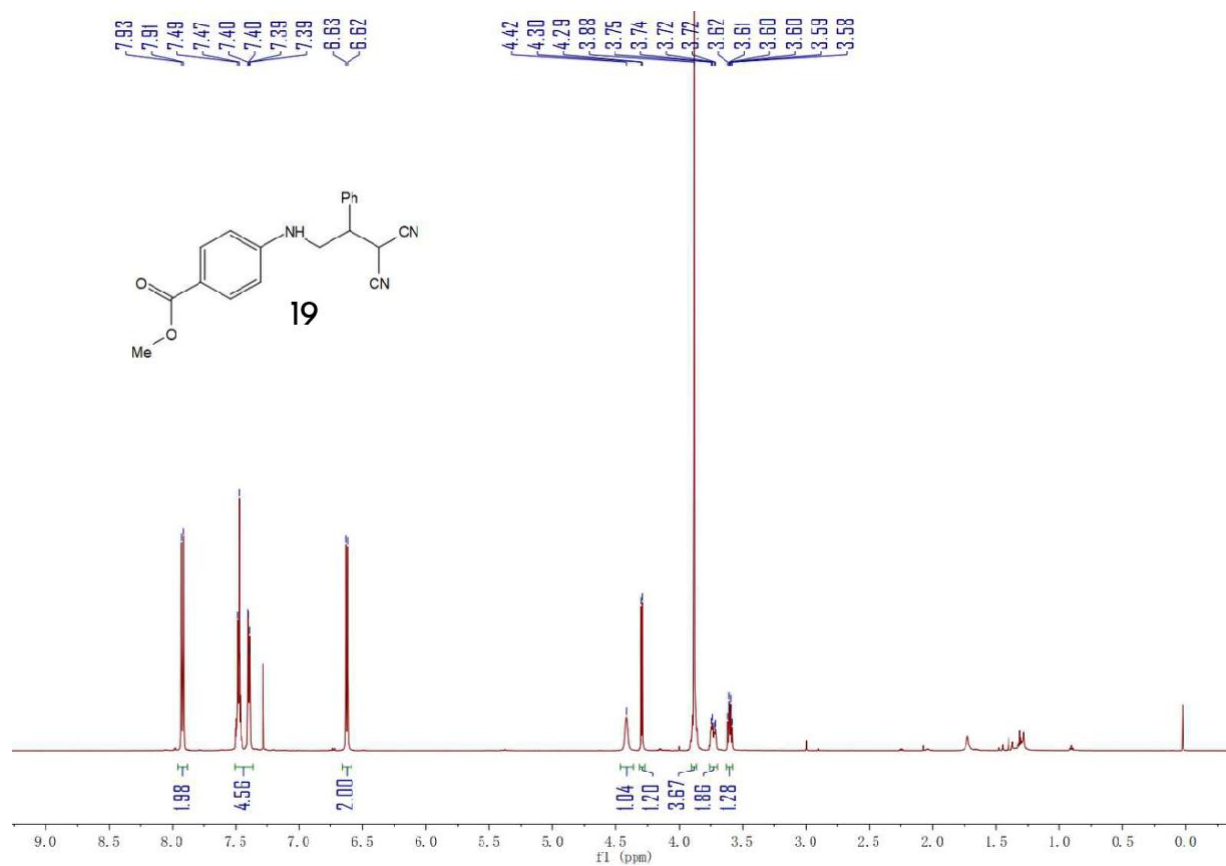
18 The reaction was set up following the general procedure using 4-N-methylaminoacetophenone (149 mg, 1 mmol) and benzylidenemalononitrile (31 mg, 0.2 mmol). After 16 hours, the reaction was purified following general work-up to give 38 mg (63 % yield) of the title compound. **¹H NMR** (400 MHz, Chloroform-*d*) 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); **¹³C 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]⁺ (C₁₉H₁₈N₃O) requires m/z 304.1, found m/z 304.1.

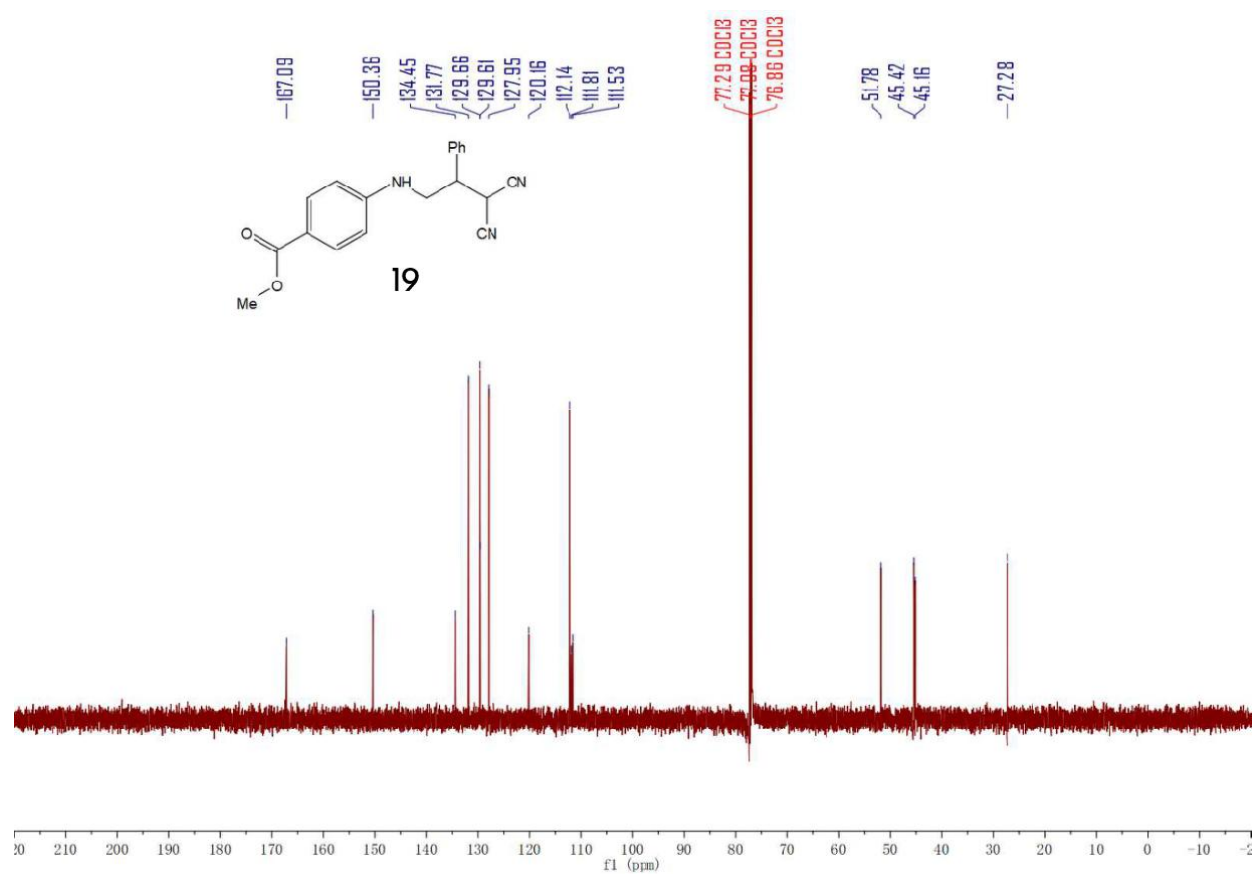


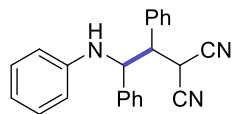




19 The reaction was set up following the general procedure using methyl 4-methylaminobenzoate (165 mg, 1 mmol) and benzylidenemalononitrile (31 mg, 0.2 mmol). After 16 hours, the reaction was purified following general work-up to give 52 mg (82 % yield) of the title compound. **¹H NMR** (600 MHz, Chloroform-*d*) 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); **¹³C 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]⁺ (C₁₉H₁₈N₃O₂) requires m/z 320.1, found m/z 320.1.

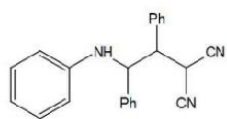




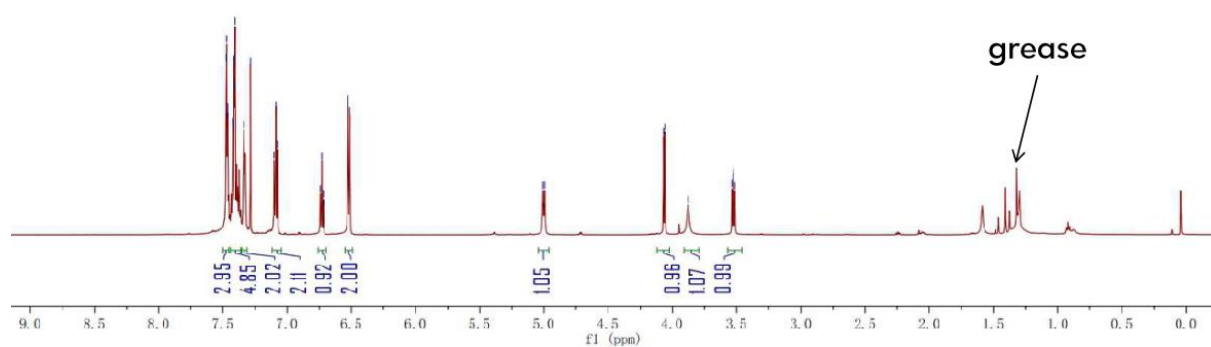


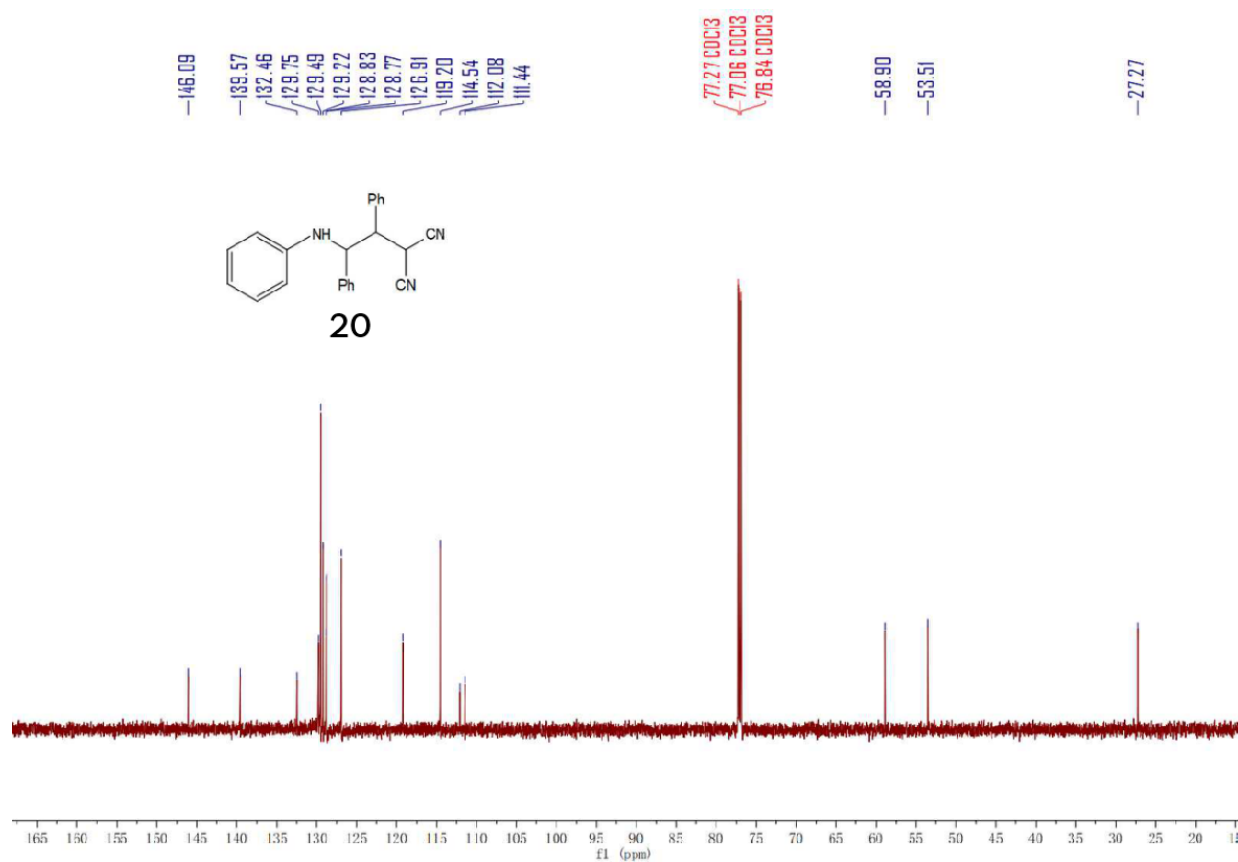
20 The reaction was set up following the general procedure using benzyllaniline (183 mg, 1 mmol) and benzylidenemalononitrile (31 mg, 0.2 mmol). After 16 hours, the reaction was purified following general work-up to give 49 mg (72 % yield) of the title compound. **¹H NMR** (600 MHz, Chloroform-*d*) δ 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); **¹³C 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]⁺ (C₂₃H₂₀N₃) requires m/z 338.1, found m/z 338.1.

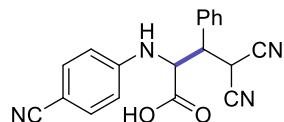
7.47 7.47 7.46 7.46 7.42 7.42 7.41 7.41 7.34 7.29 7.10 7.09 7.08 6.74 6.73 6.72 6.53 6.51 5.01 4.99 4.07 4.06 3.88 3.54 3.53 3.52 3.51



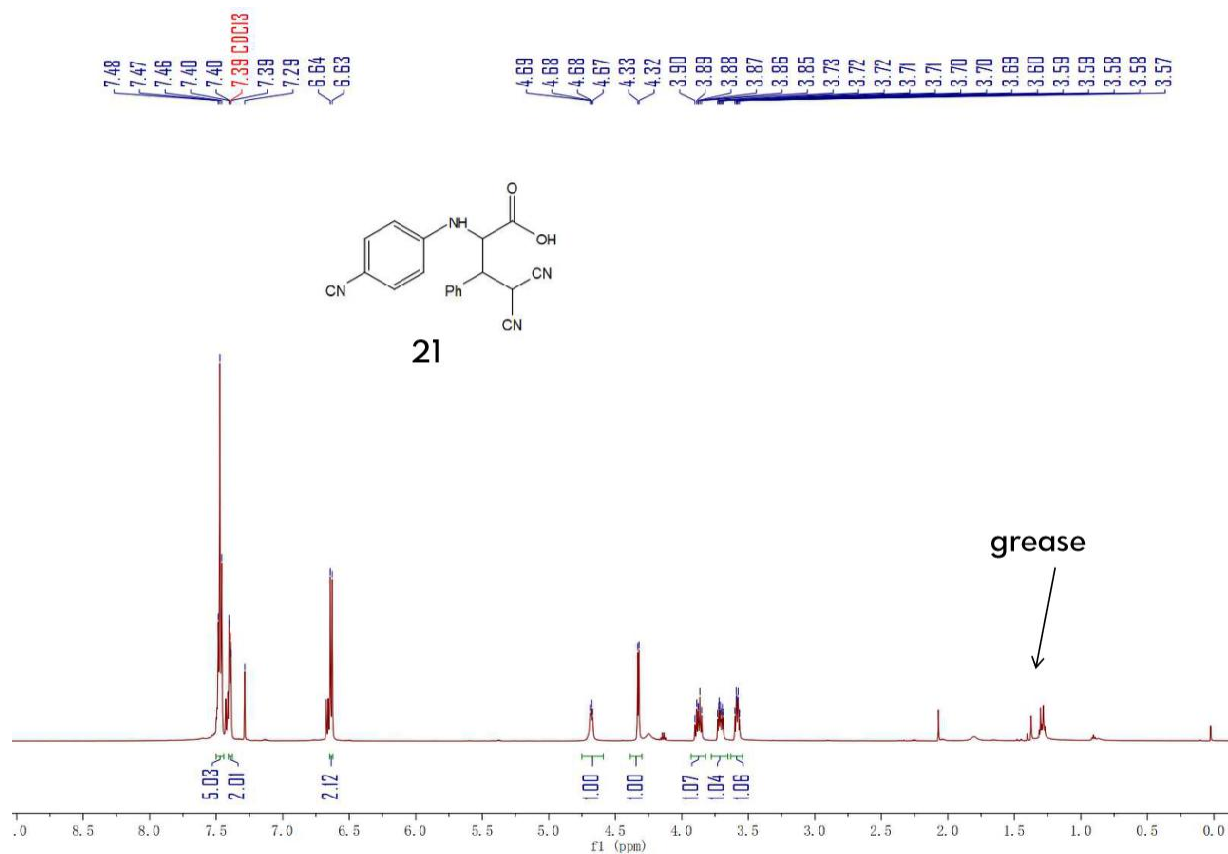
20

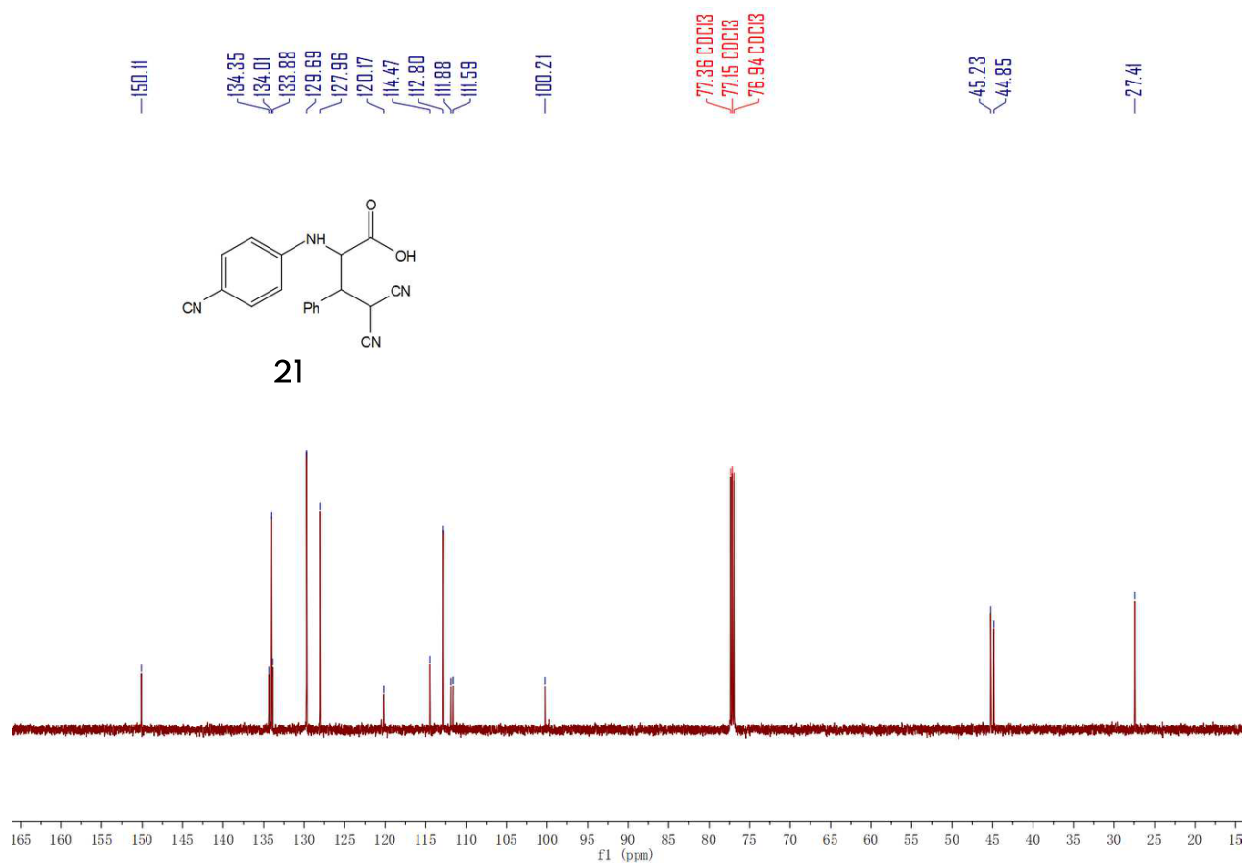


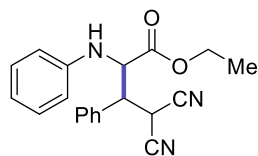




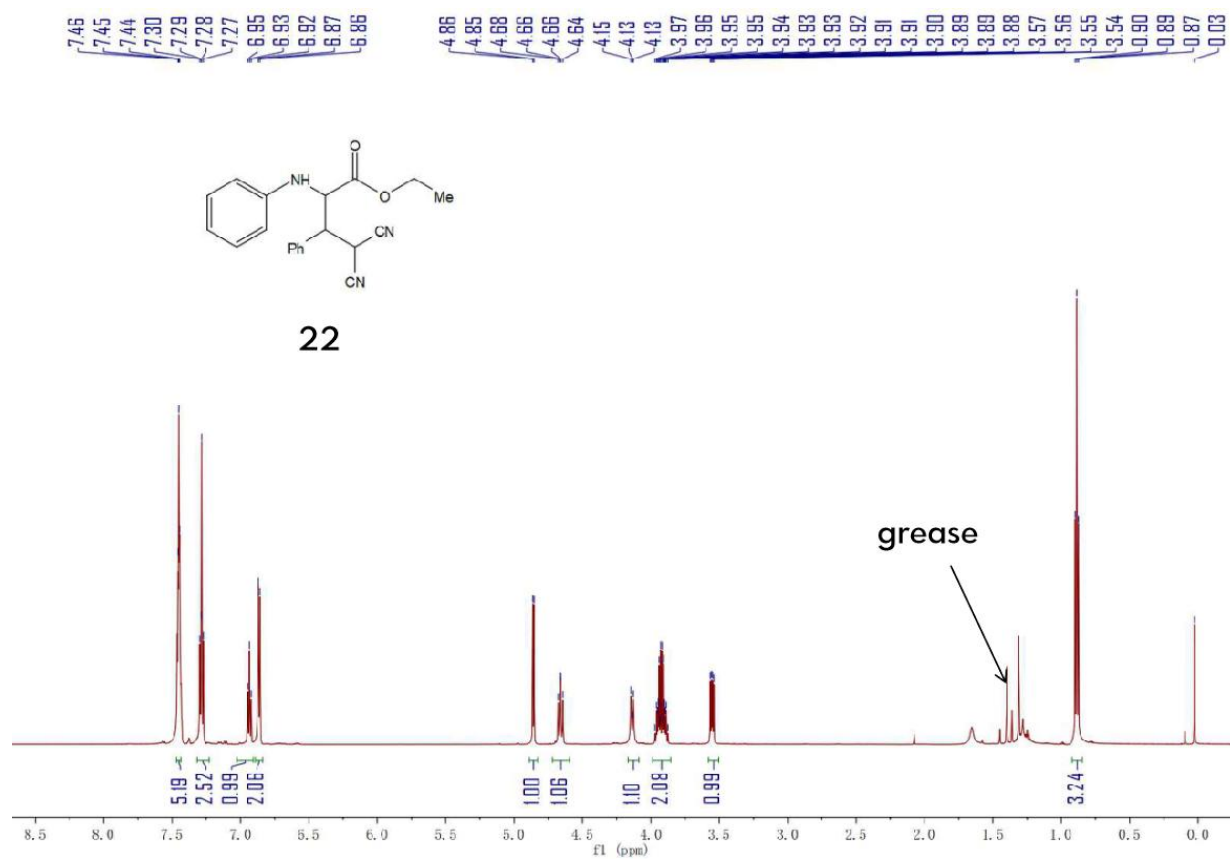
21 The reaction was set up following the general procedure using N-(4-cyanophenyl) glycine (176 mg, 1 mmol) and benzylidenemalononitrile (31 mg, 0.2 mmol). After 16 hours, the reaction was purified following general work-up to give 45 mg (68 % yield) of the title compound. **¹H NMR** (600 MHz, Chloroform-*d*) 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); **¹³C 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]⁺ (C₁₉H₁₅N₄O₂) requires m/z 331.1, found m/z 331.1.

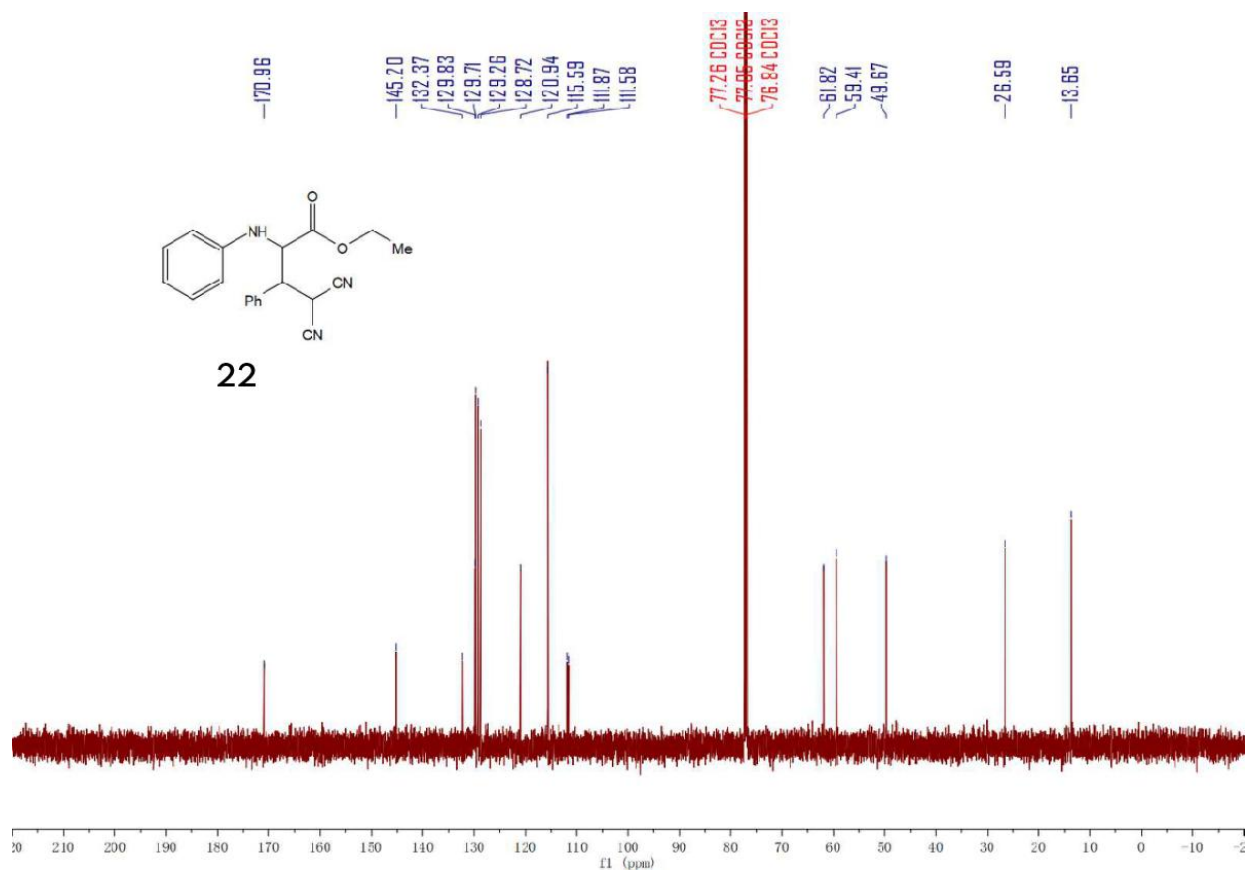


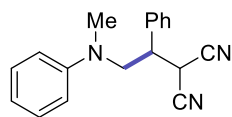




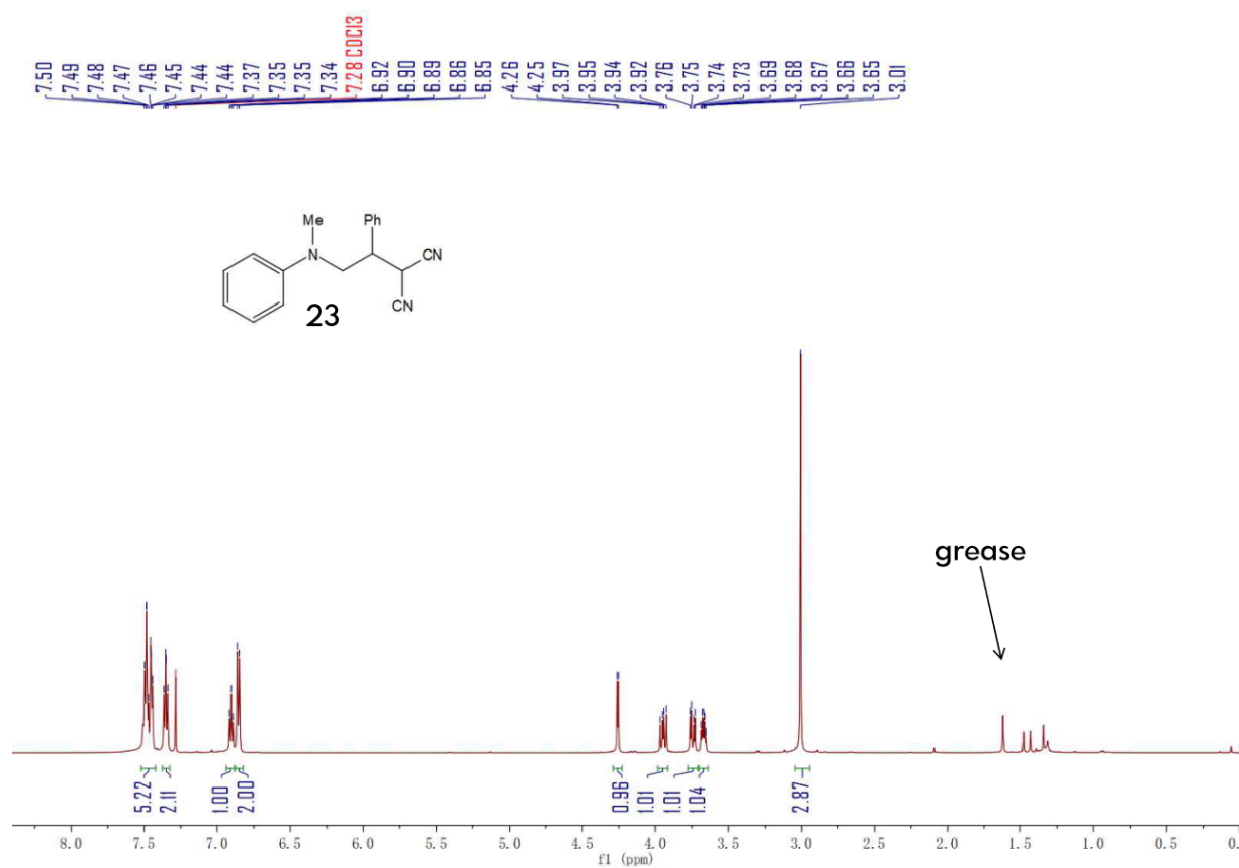
22 The reaction was set up following the general procedure using N-phenylglycine ethyl ester (179 mg, 1 mmol) and benzylidenemalononitrile (31 mg, 0.2 mmol). After 16 hours, the reaction was purified following general work-up to give 35 mg (53 % yield) of the title compound. **¹H NMR** (600 MHz, Chloroform-*d*) 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); **¹³C 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]⁺ (C₂₀H₂₀N₃O₂) requires *m/z* 334.1, found *m/z* 334.1.

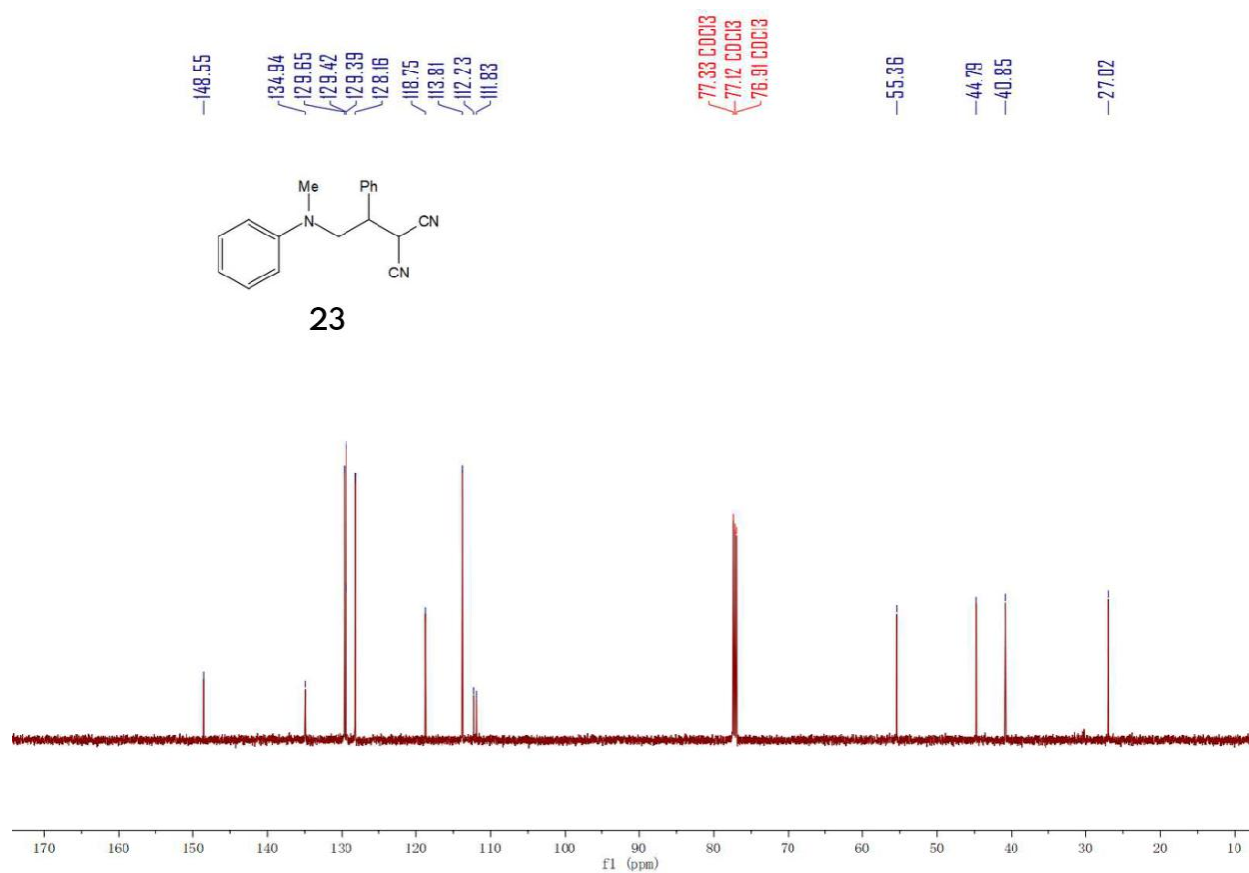


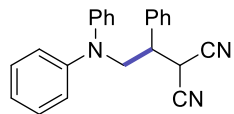




23 The reaction was set up following the general procedure using N,N-dimethylaniline (121 mg, 1 mmol) and benzylidenemalononitrile (31 mg, 0.2 mmol). After 16 hours, the reaction was purified following general work-up to give 34 mg (61 % yield) of the title compound. **¹H NMR** (600 MHz, Chloroform-*d*) 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); **¹³C 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]⁺ (C₁₈H₁₈N₃) requires m/z 276.1, found m/z 276.1.

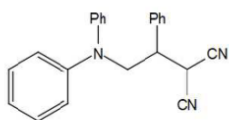




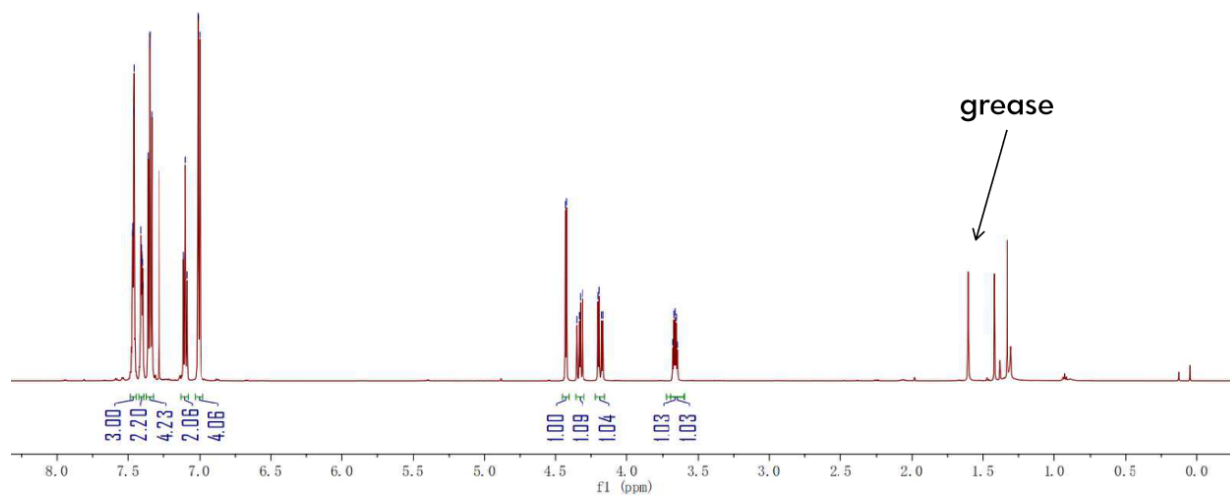


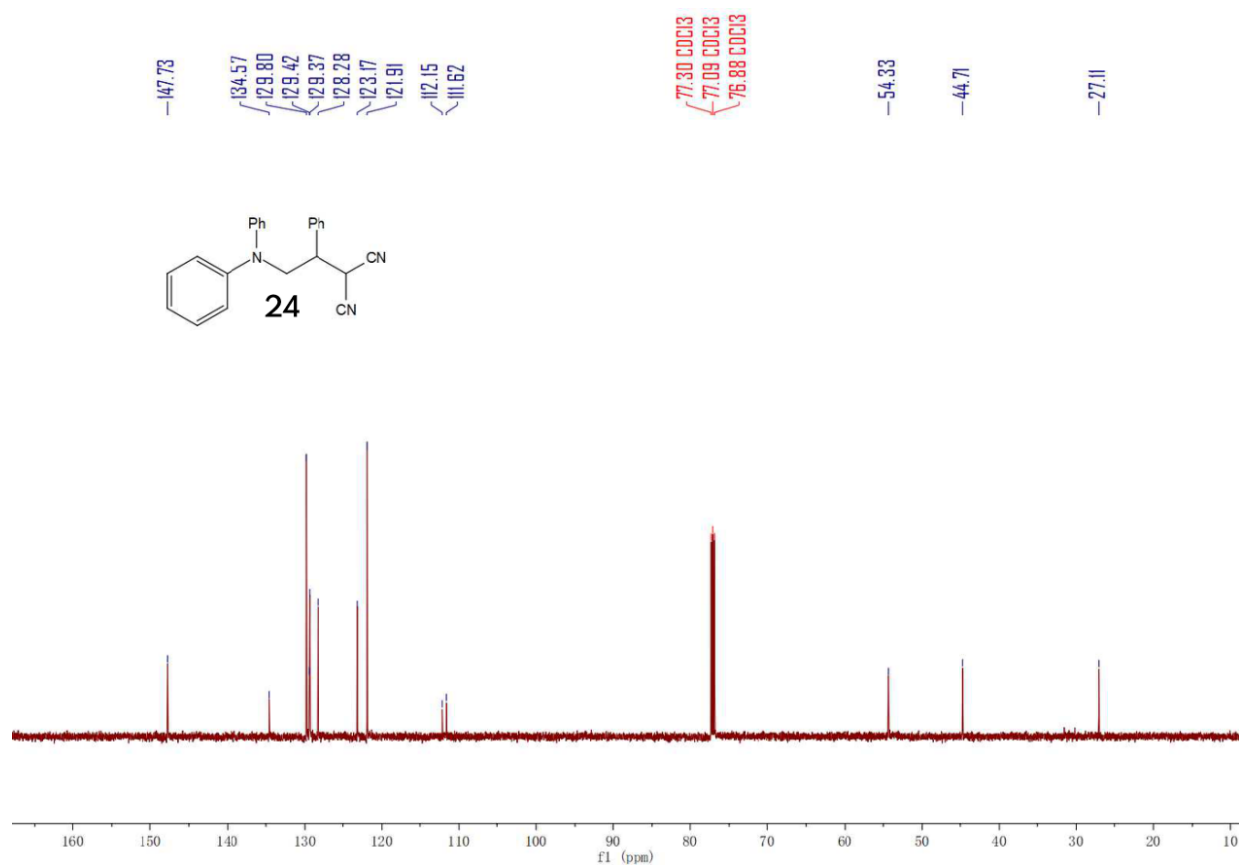
24 The reaction was set up following the general procedure using N-methyl-N-phenylbenzenamine (183 mg, 1 mmol) and benzyldenemalononitrile (31 mg, 0.2 mmol). After 16 hours, the reaction was purified following general work-up to give 47 mg (69 % yield) of the title compound. **¹H NMR** (600 MHz, Chloroform-*d*) 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); **¹³C 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]⁺ (C₂₃H₂₀N₃) requires m/z 338.1, found m/z 338.1.

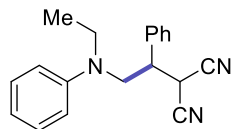
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4.17
3.68
3.67
3.66
3.65
3.64



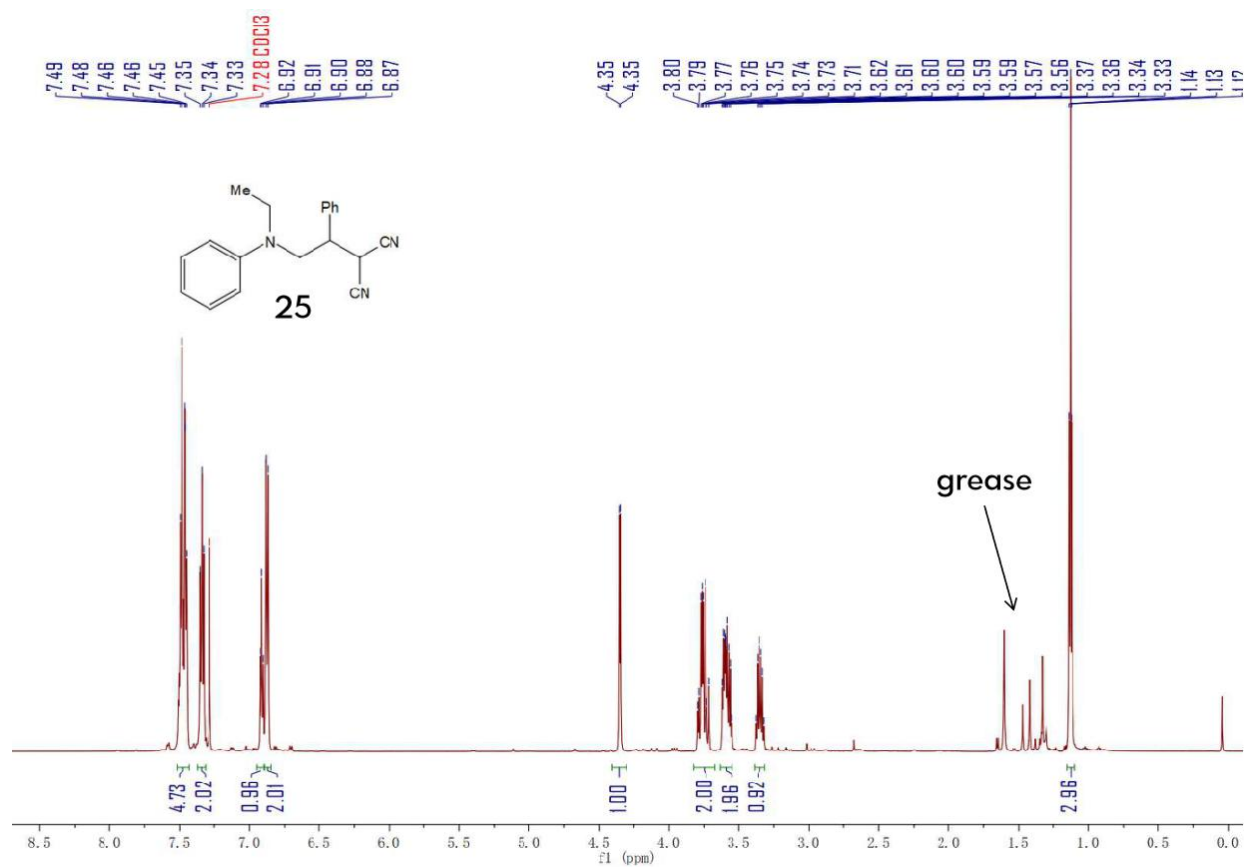
24

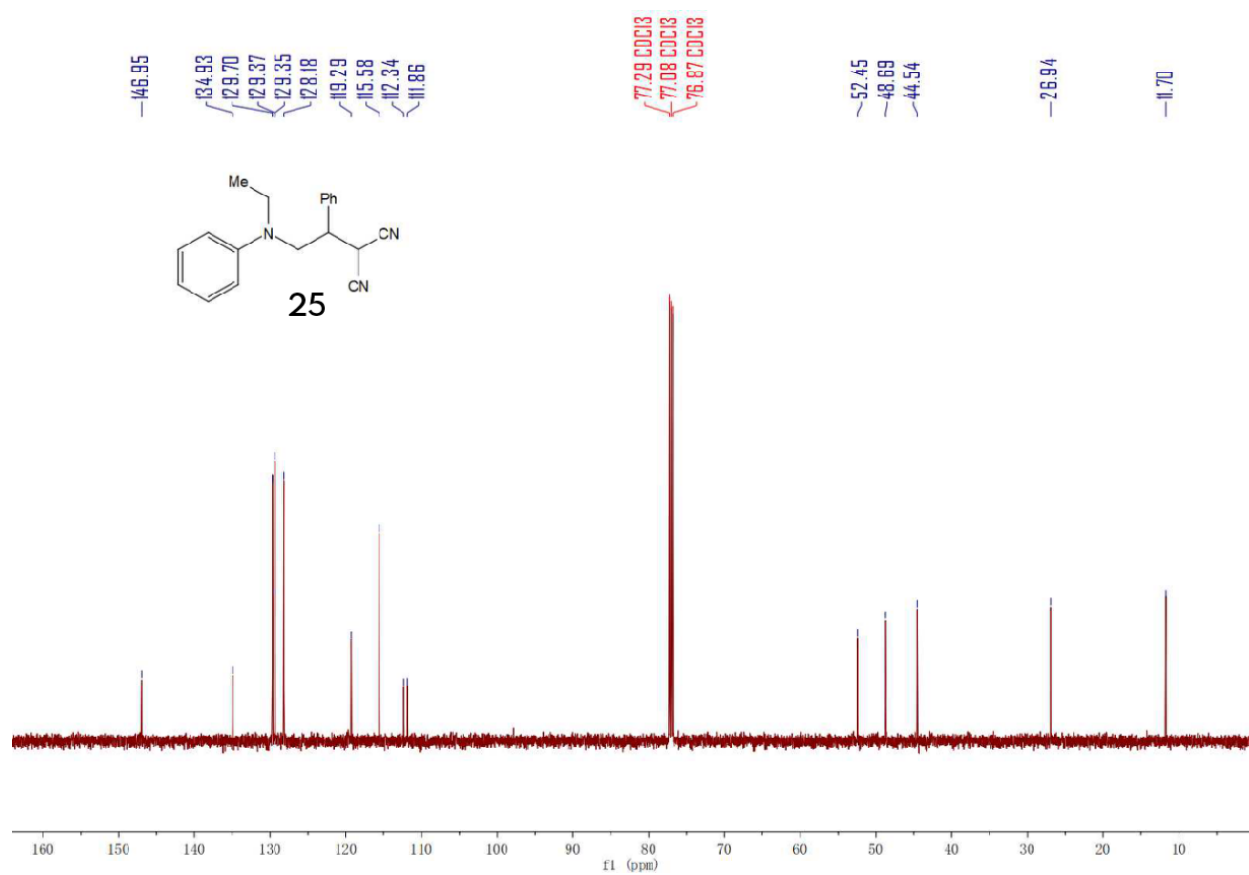


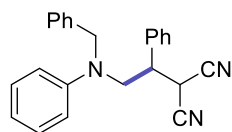




25 The reaction was set up following the general procedure using N-ethyl-N-methylaniline (135 mg, 1 mmol) and benzylidenemalononitrile (31 mg, 0.2 mmol). After 16 hours, the reaction was purified following general work-up to give 41 mg (69 % yield) of the title compound. **¹H NMR** (600 MHz, Chloroform-*d*) 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); **¹³C 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]⁺ (C₁₉H₂₀N₃) requires m/z 290.1, found m/z 290.1.

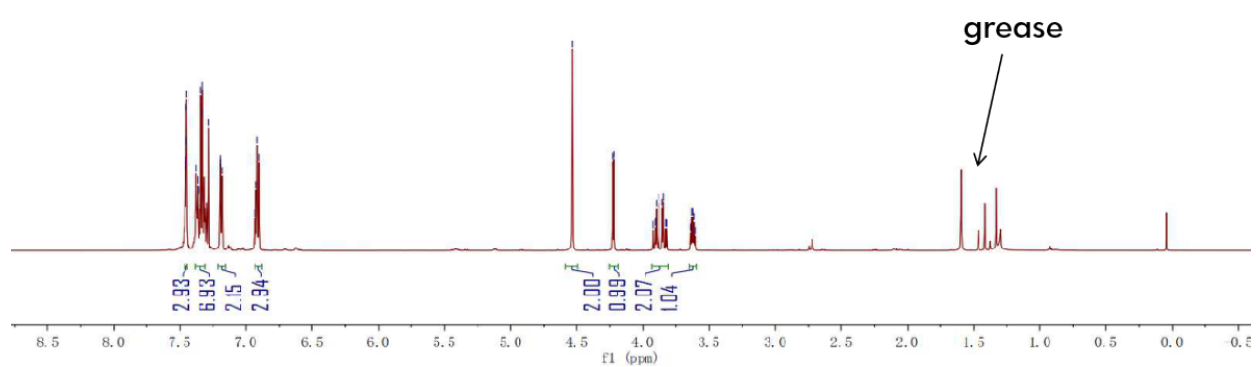
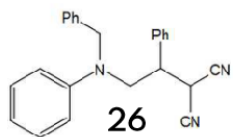


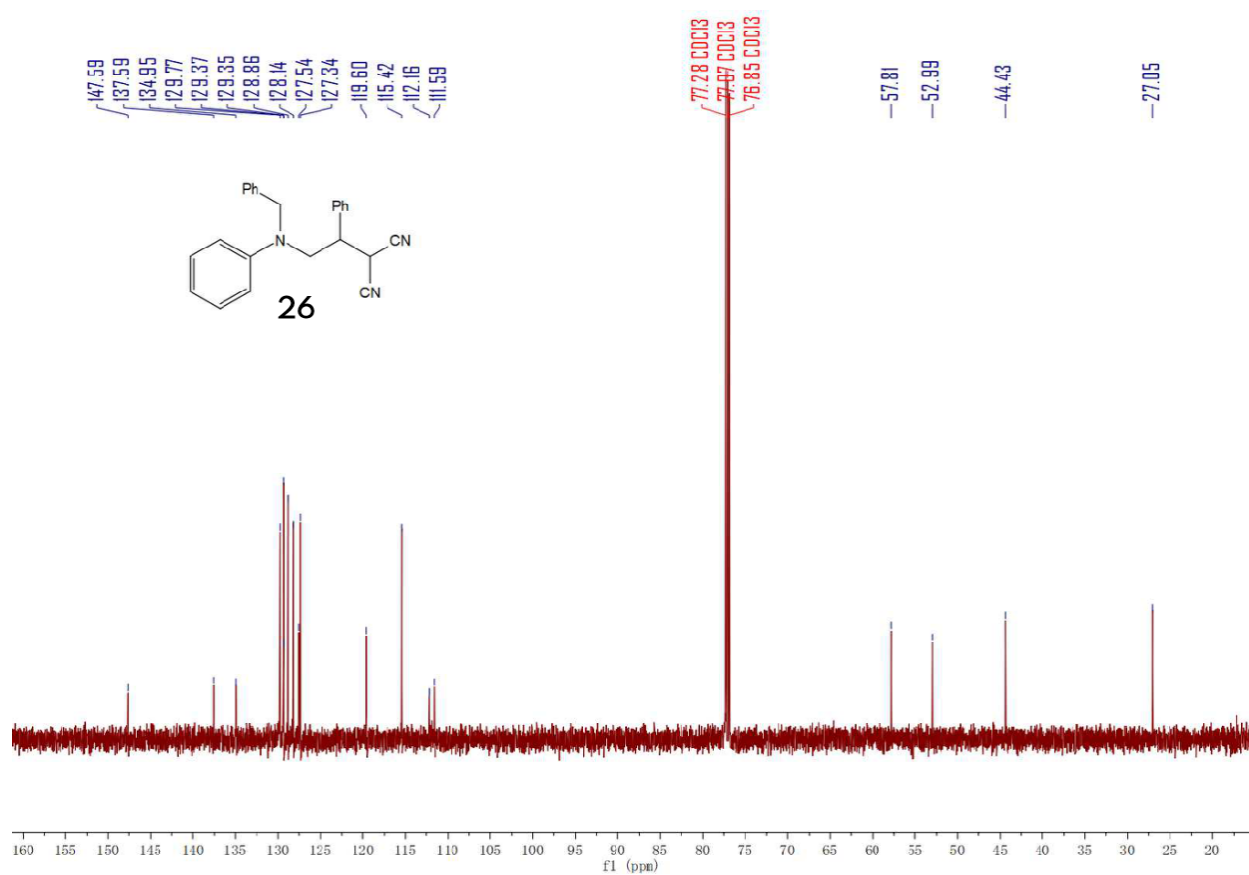


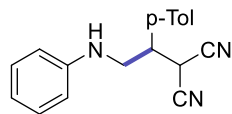


26 The reaction was set up following the general procedure using N-benzyl-N-methylaniline (197 mg, 1 mmol) and benzylidenemalononitrile (31 mg, 0.2 mmol). After 16 hours, the reaction was purified following general work-up to give 45 mg (63 % yield) of the title compound. **¹H NMR** (600 MHz, Chloroform-*d*) 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); **¹³C 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]⁺ (C₂₄H₂₂N₃) requires m/z 352.1, found m/z 352.1.

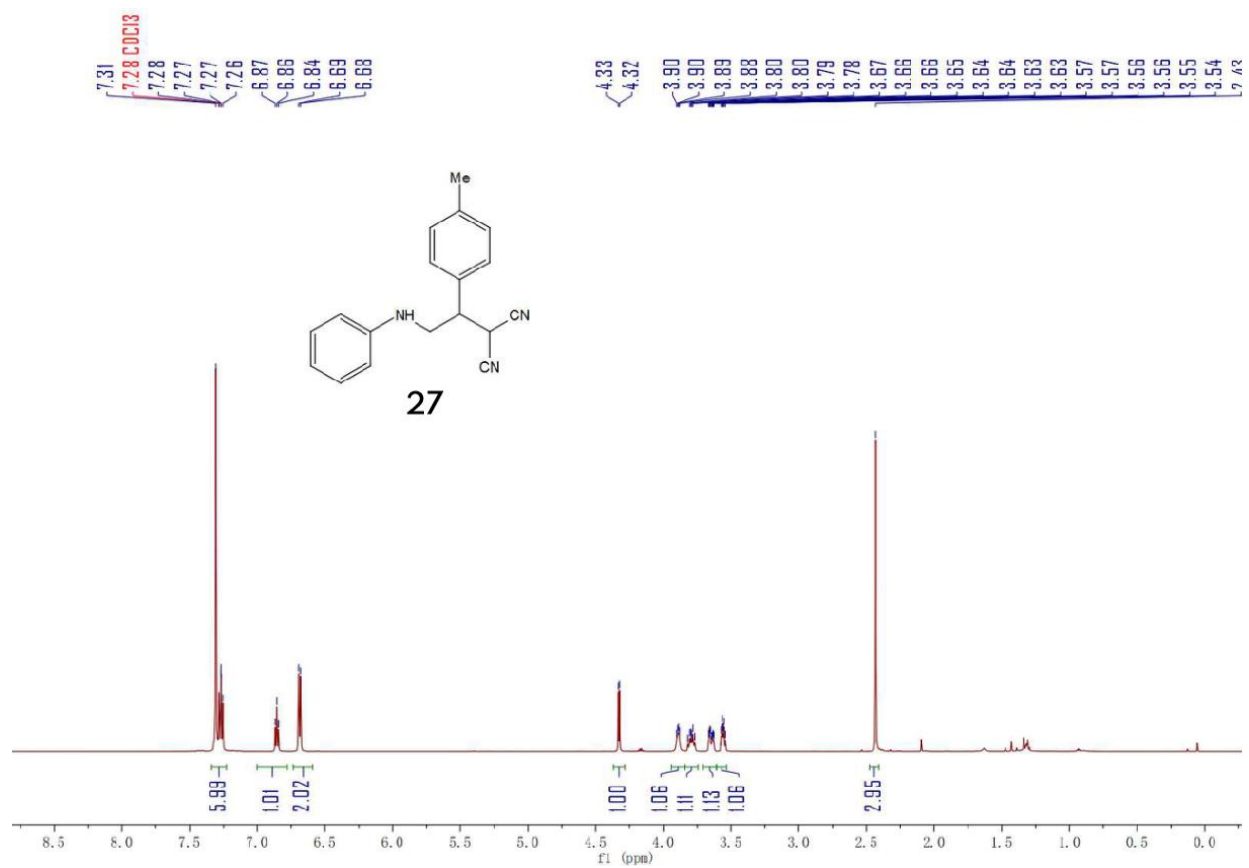
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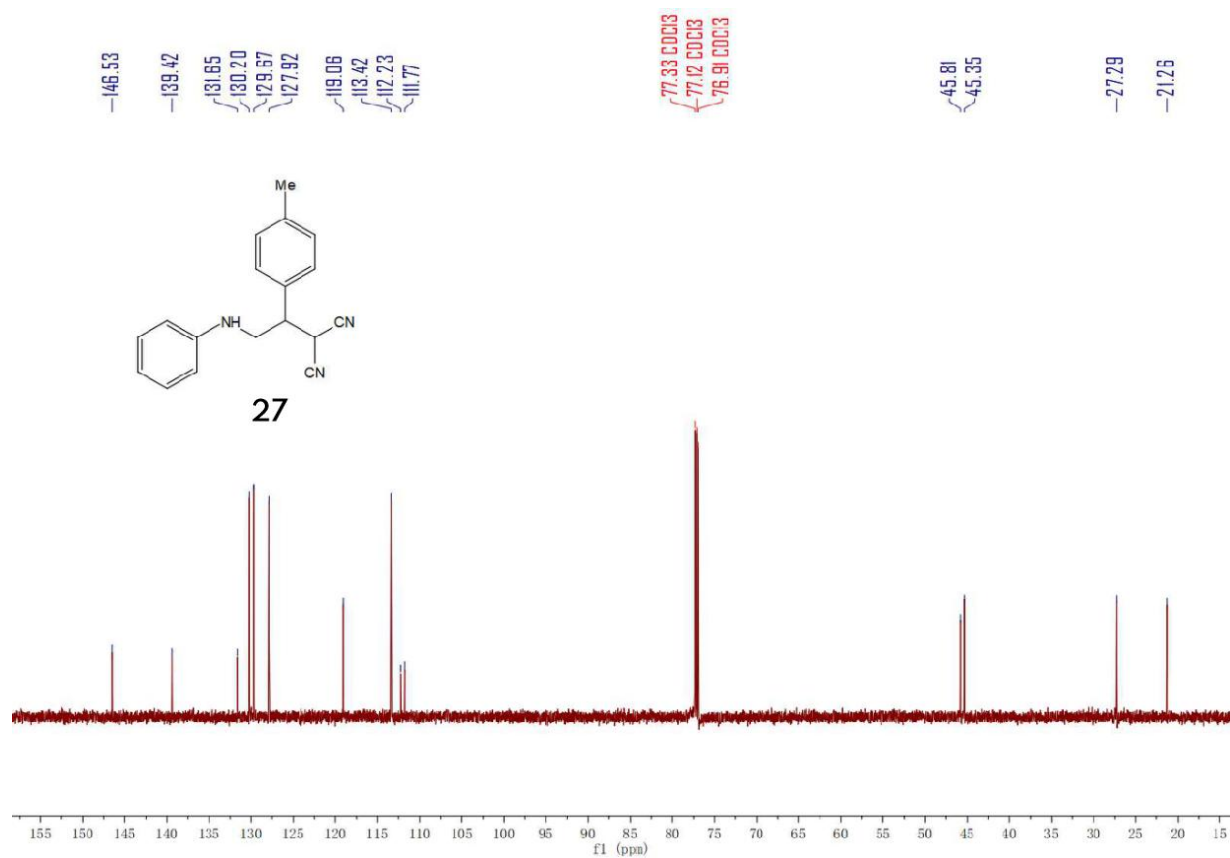


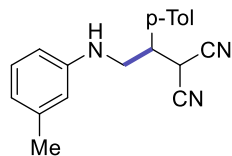




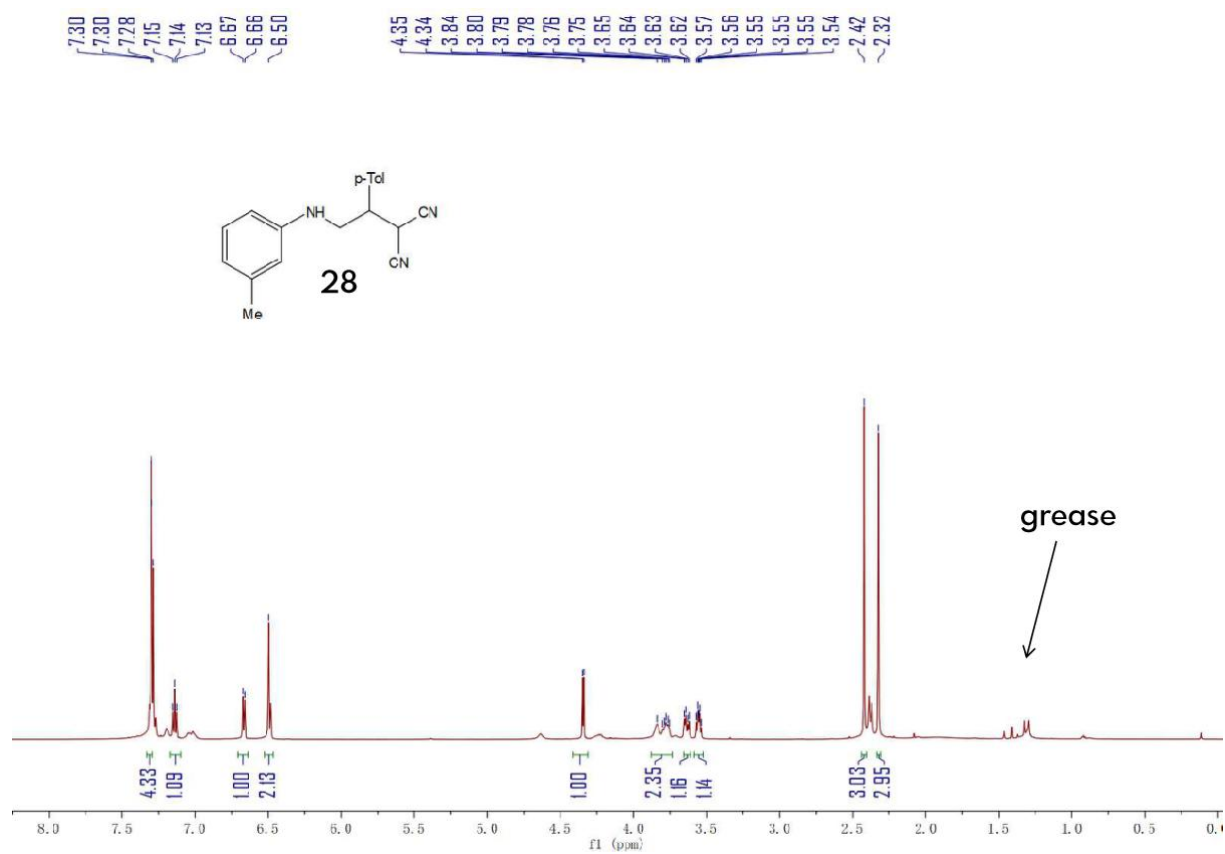
27 The reaction was set up following the general procedure using N-methylaniline (107 mg, 1 mmol) and 4-methylbenzylidenemalononitrile (34 mg, 0.2 mmol). After 16 hours, the reaction was purified following general work-up to give 42 mg (74 % yield) of the title compound. **¹H NMR** (600 MHz, Chloroform-*d*) 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); **¹³C 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]⁺ (C₁₈H₁₈N₃) requires m/z 276.1, found m/z 276.1.

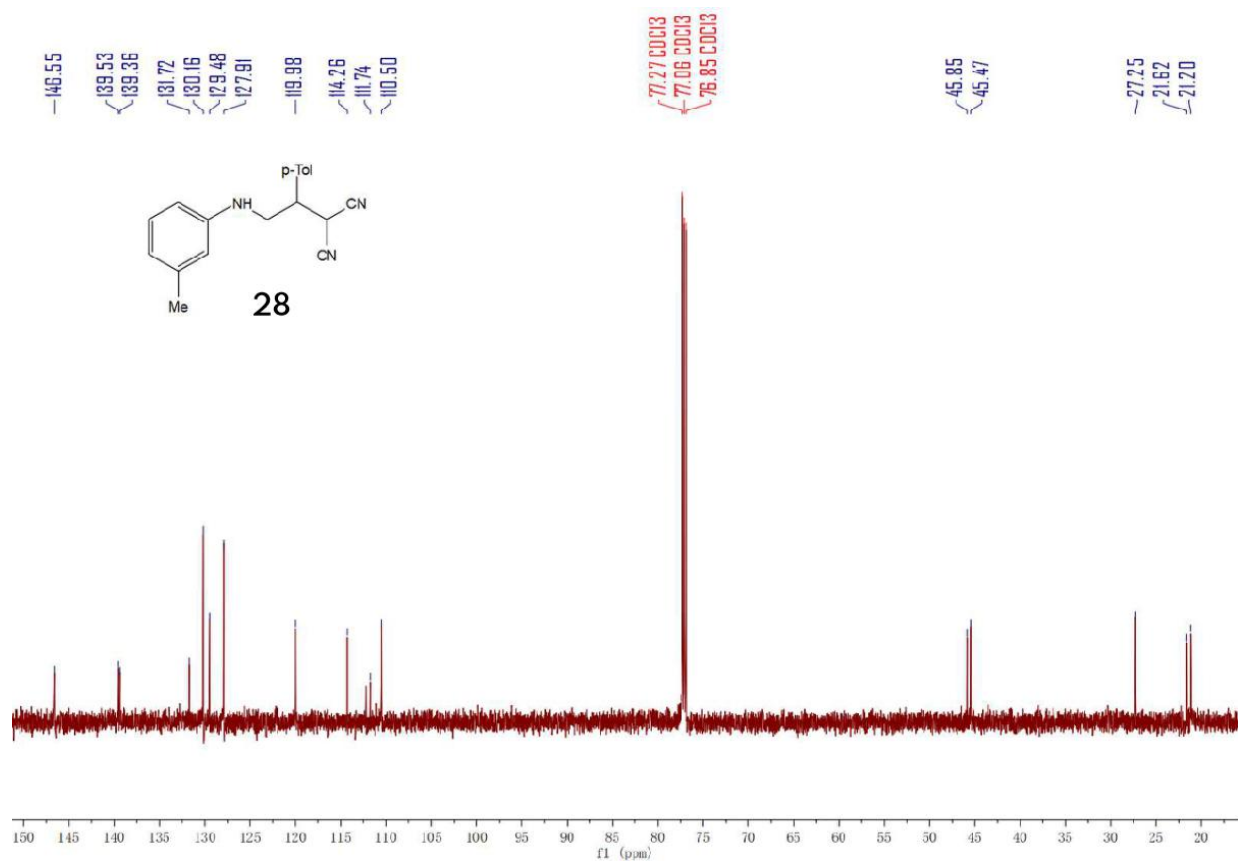


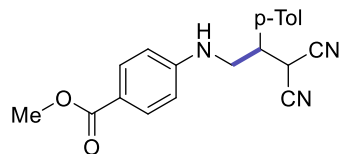




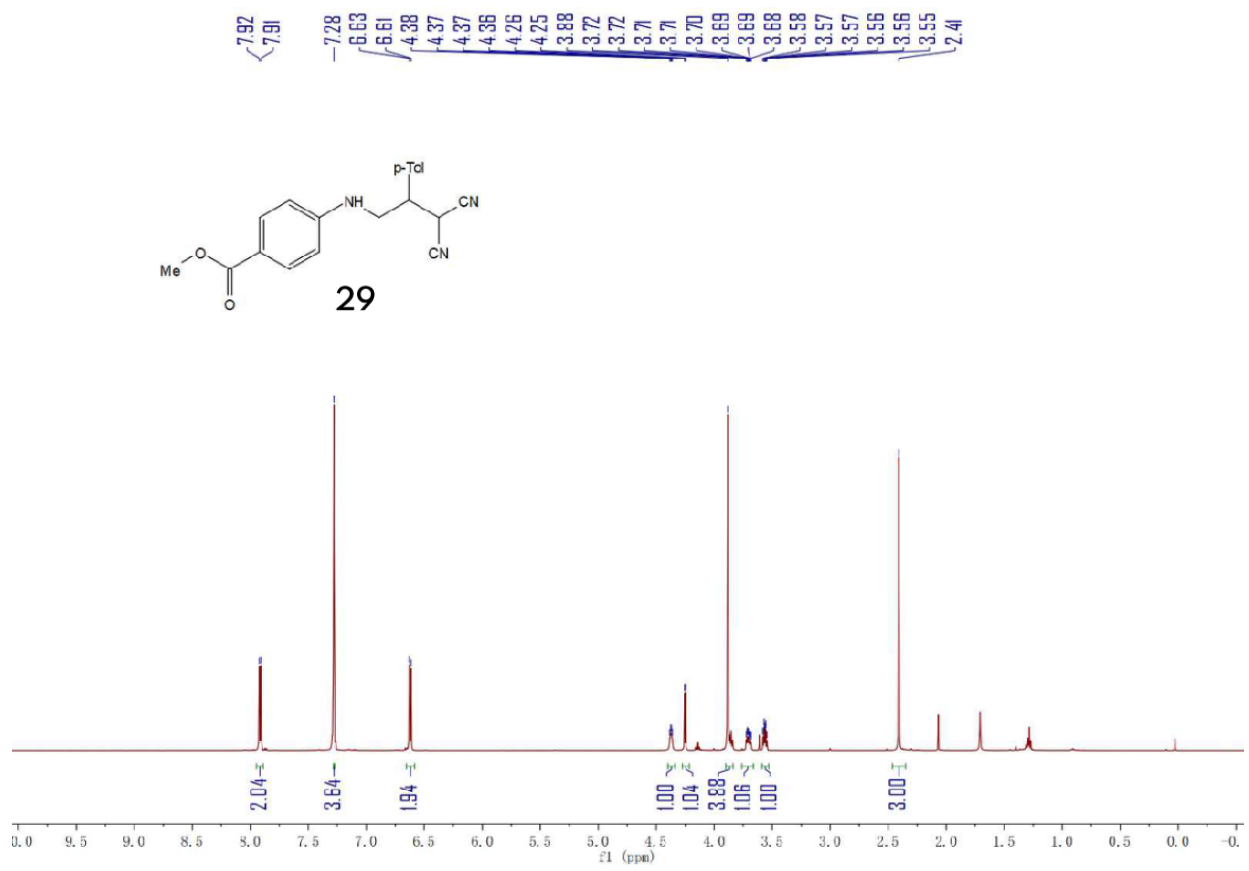
28 The reaction was set up following the general procedure using 3-methyl-N-methylbenzenamine (121 mg, 1 mmol) and 4-methylbenzylidenemalononitrile (34 mg, 0.2 mmol). After 16 hours, the reaction was purified following general work-up to give 31 mg (52 % yield) of the title compound. **¹H NMR** (600 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); **¹³C 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]⁺ (C₁₉H₂₀N₃) requires m/z 290.1, found m/z 290.1.

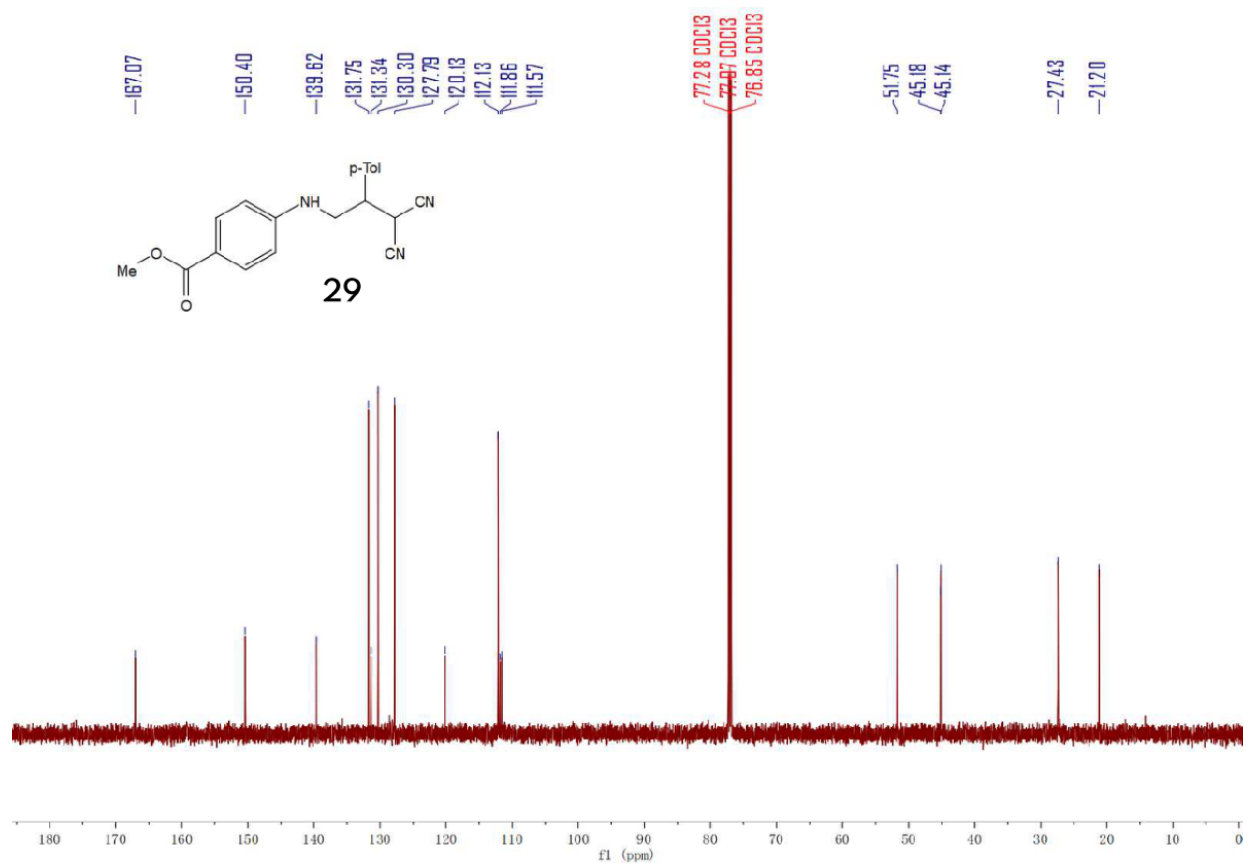


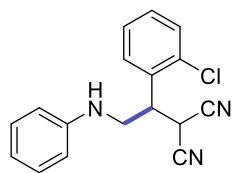




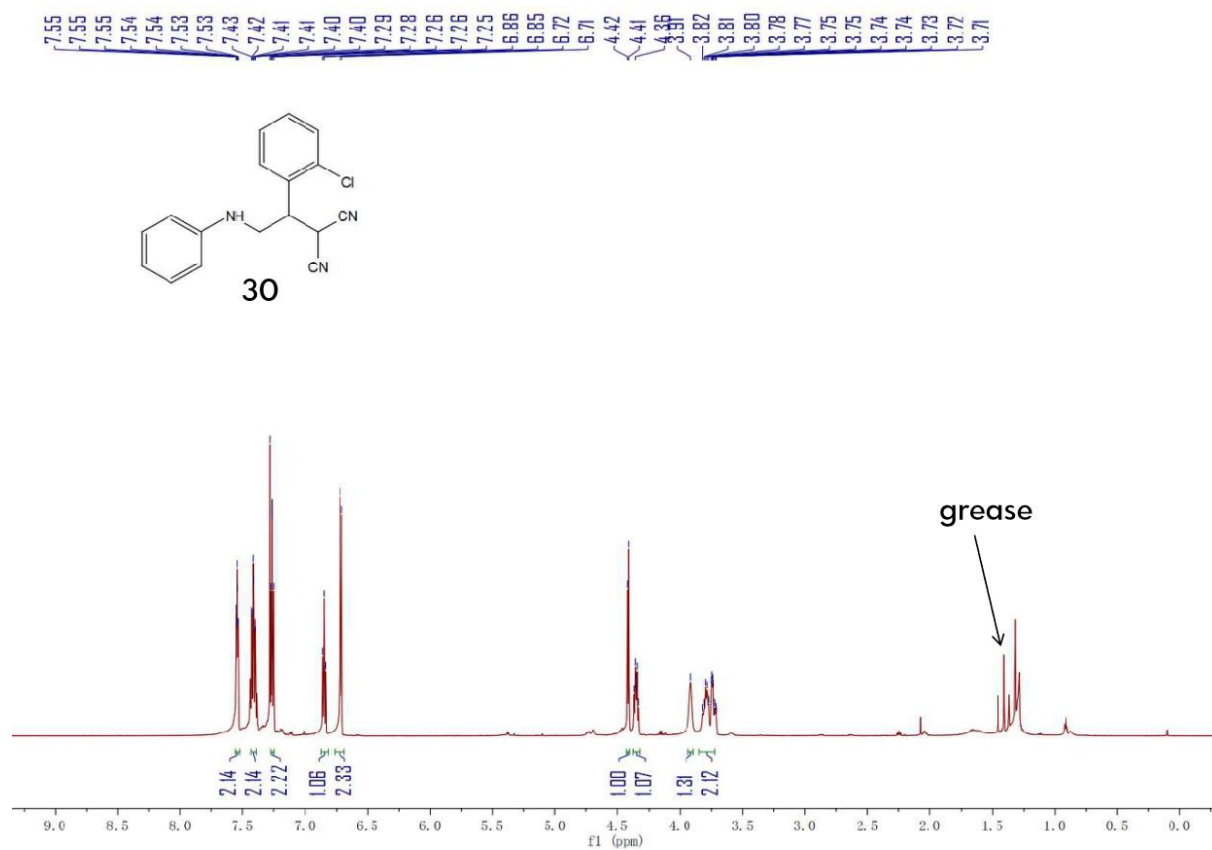
29 The reaction was set up following the general procedure using methyl 4-methylaminobenzoate (165 mg, 1 mmol) and 4-methylbenzylidenemalononitrile (34 mg, 0.2 mmol). After 16 hours, the reaction was purified following general work-up to give 30 mg (43 % yield) of the title compound. **¹H NMR** (600 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); **¹³C 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]⁺ (C₂₀H₂₀N₃O₂) requires m/z 334.1, found m/z 334.1.

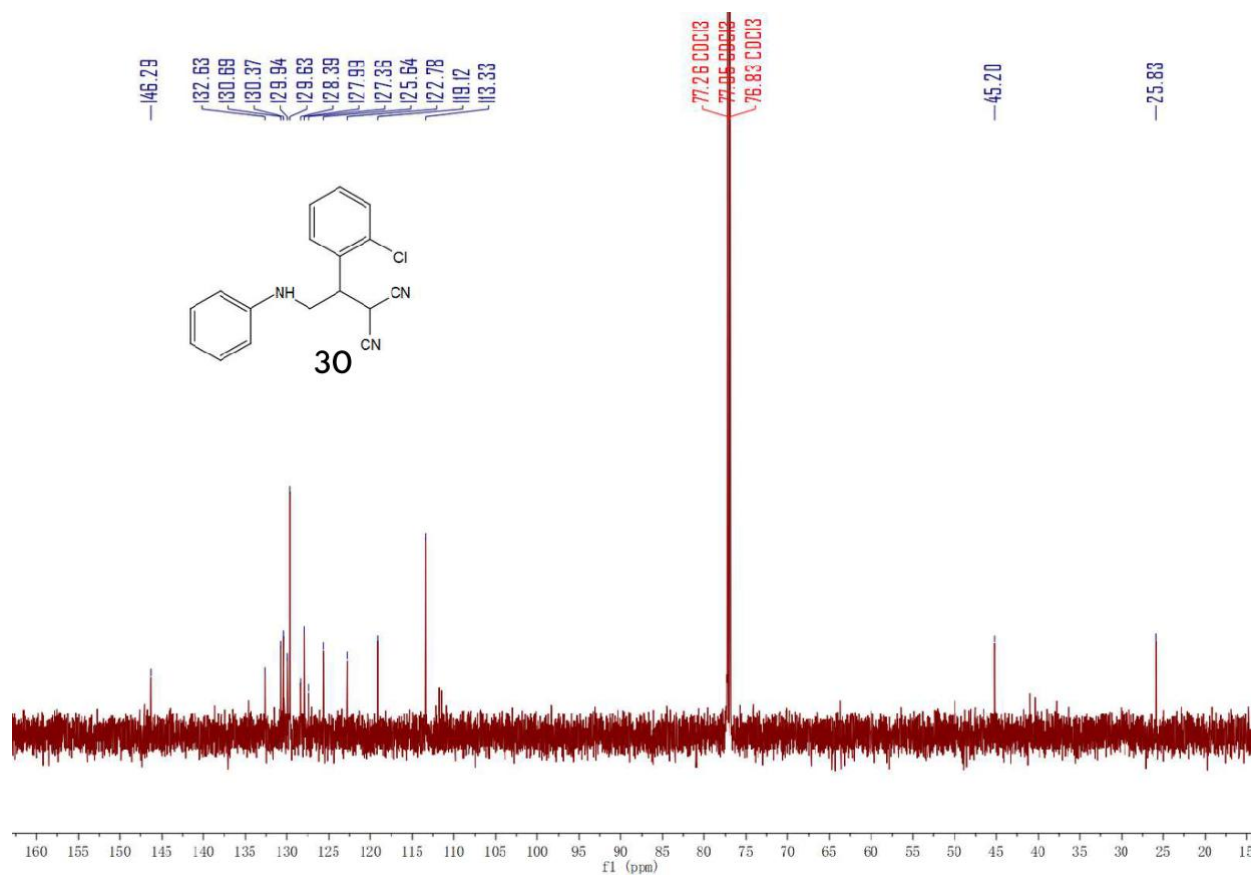


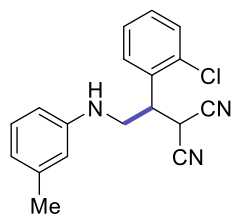




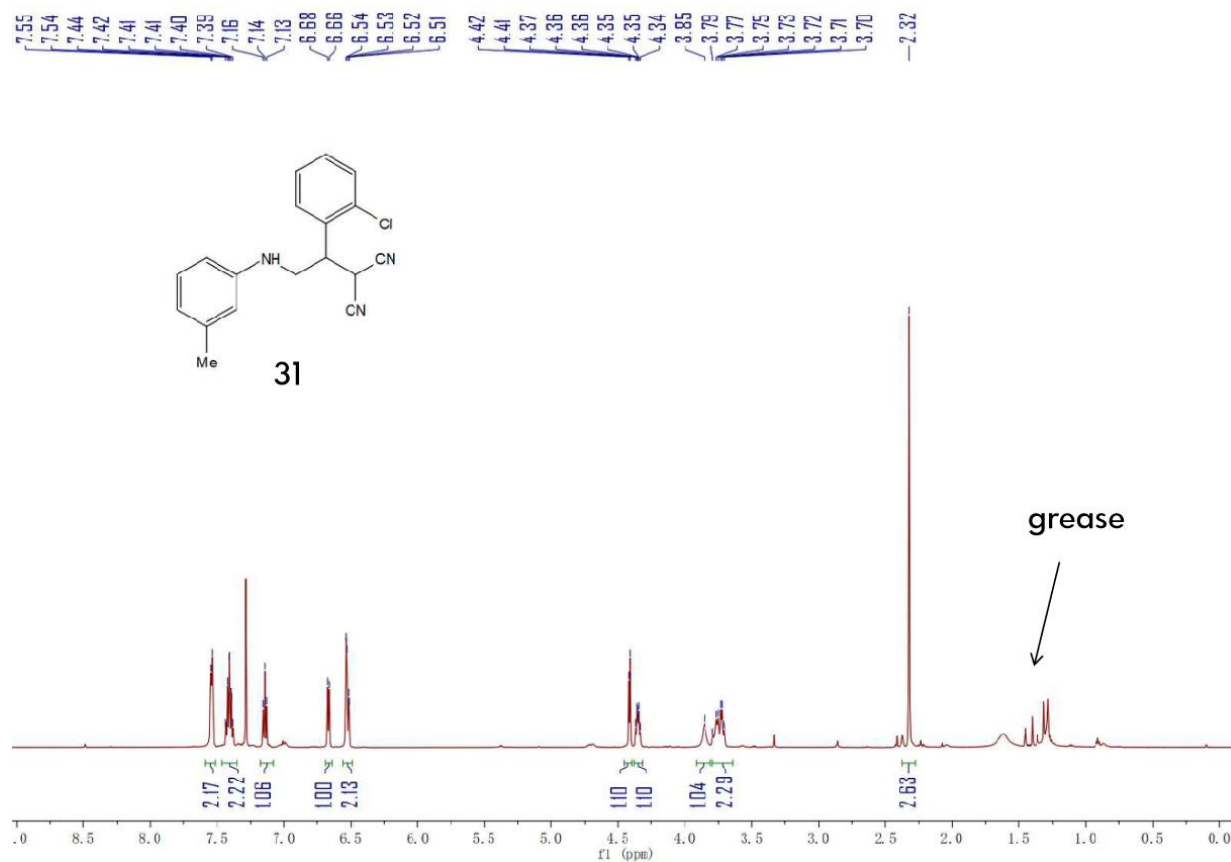
30 The reaction was set up following the general procedure using N-methylaniline (107 mg, 1 mmol) and 2-chlorobenzylidenemalononitrile (38 mg, 0.2 mmol). After 16 hours, the reaction was purified following general work-up to give 23 mg (37 % yield) of the title compound. **¹H NMR** (600 MHz, Chloroform-*d*) 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); **¹³C 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]⁺ (C₁₇H₁₅ClN₃) requires m/z 296.1, found m/z 296.1.

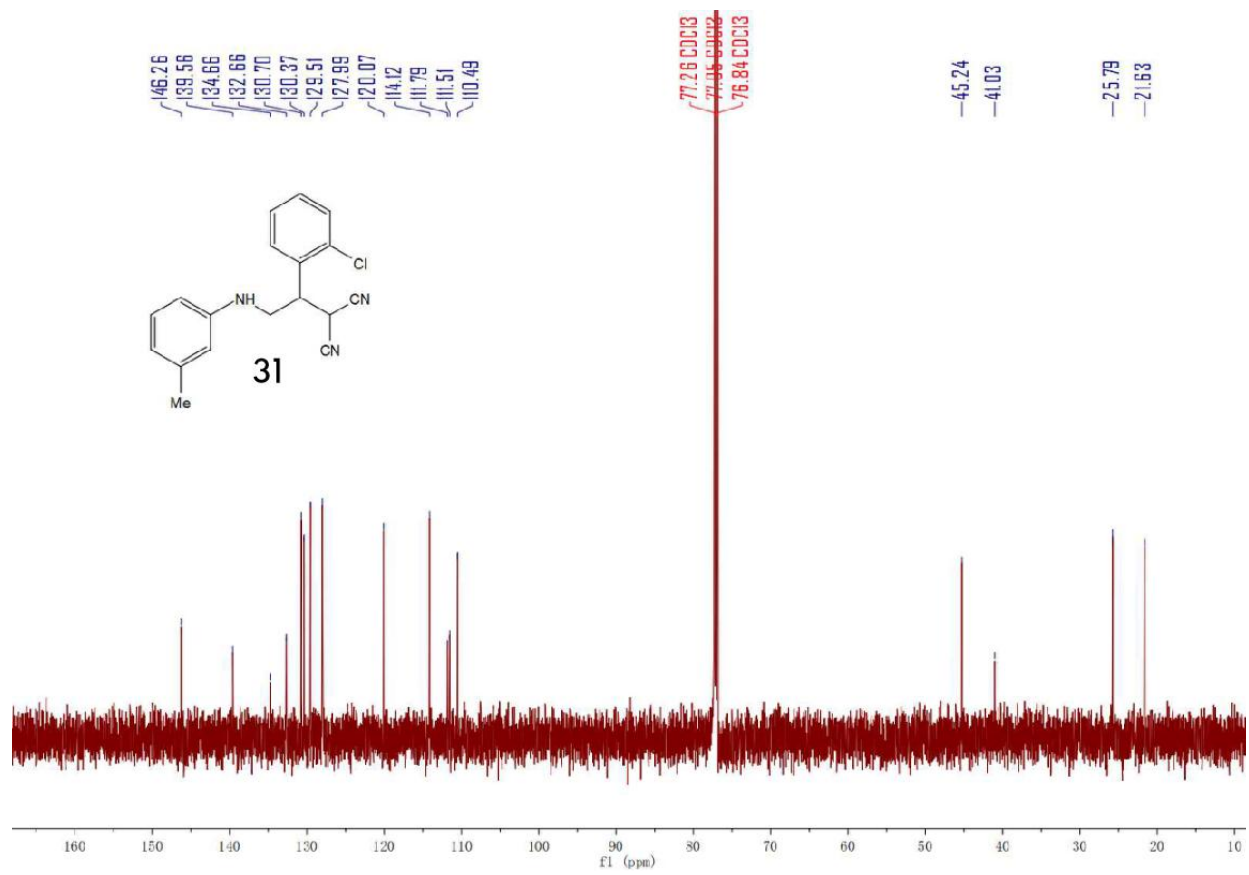


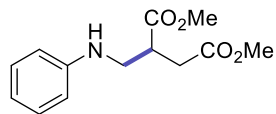




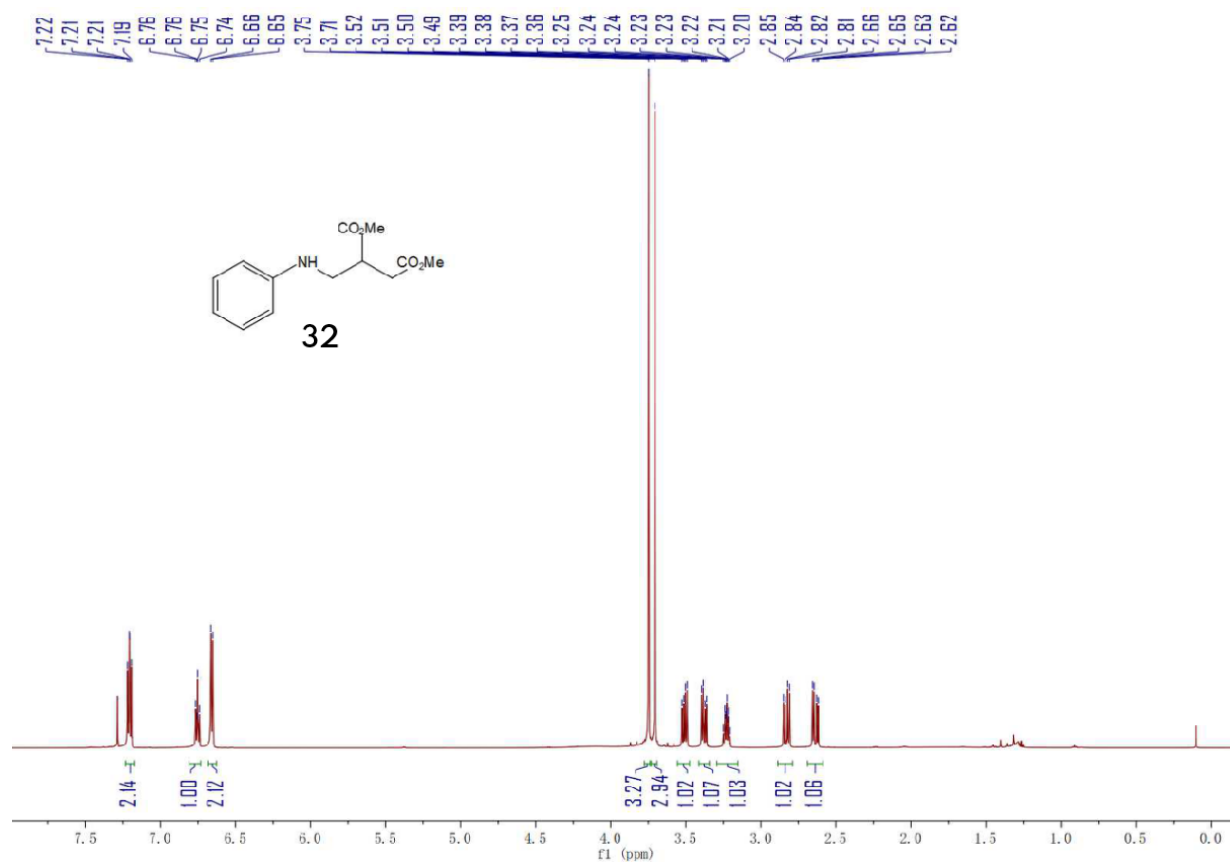
31 The reaction was set up following the general procedure using 3-methyl-N-methylbenzenamine (121 mg, 1 mmol) and 2-chlorobenzylidenemalononitrile (38 mg, 0.2 mmol). After 16 hours, the reaction was purified following general work-up to give 21 mg (33 % yield) of the title compound. **¹H NMR** (600 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); **¹³C 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]⁺ (C₁₈H₁₇ClN₃) requires m/z 310.1, found m/z 310.1.

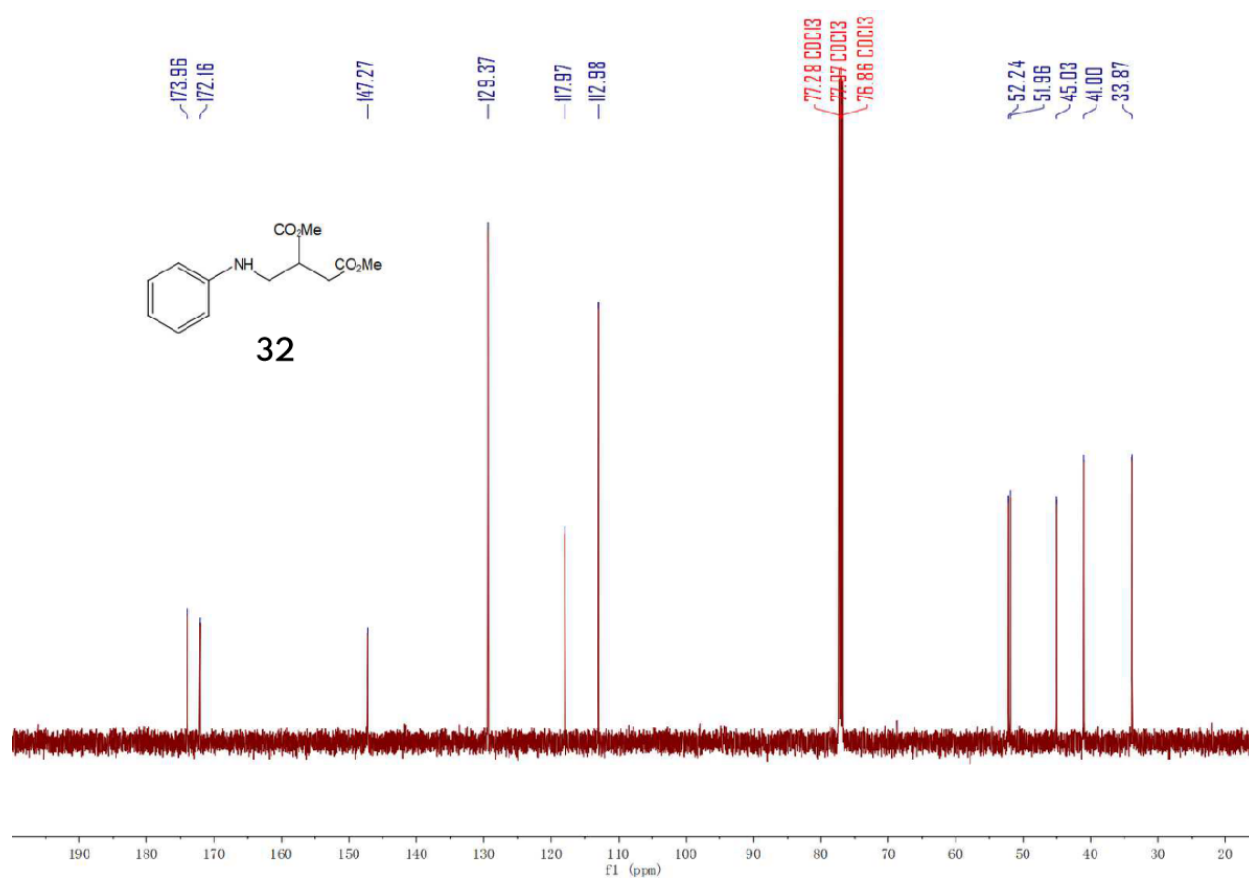


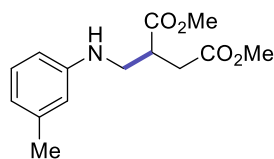




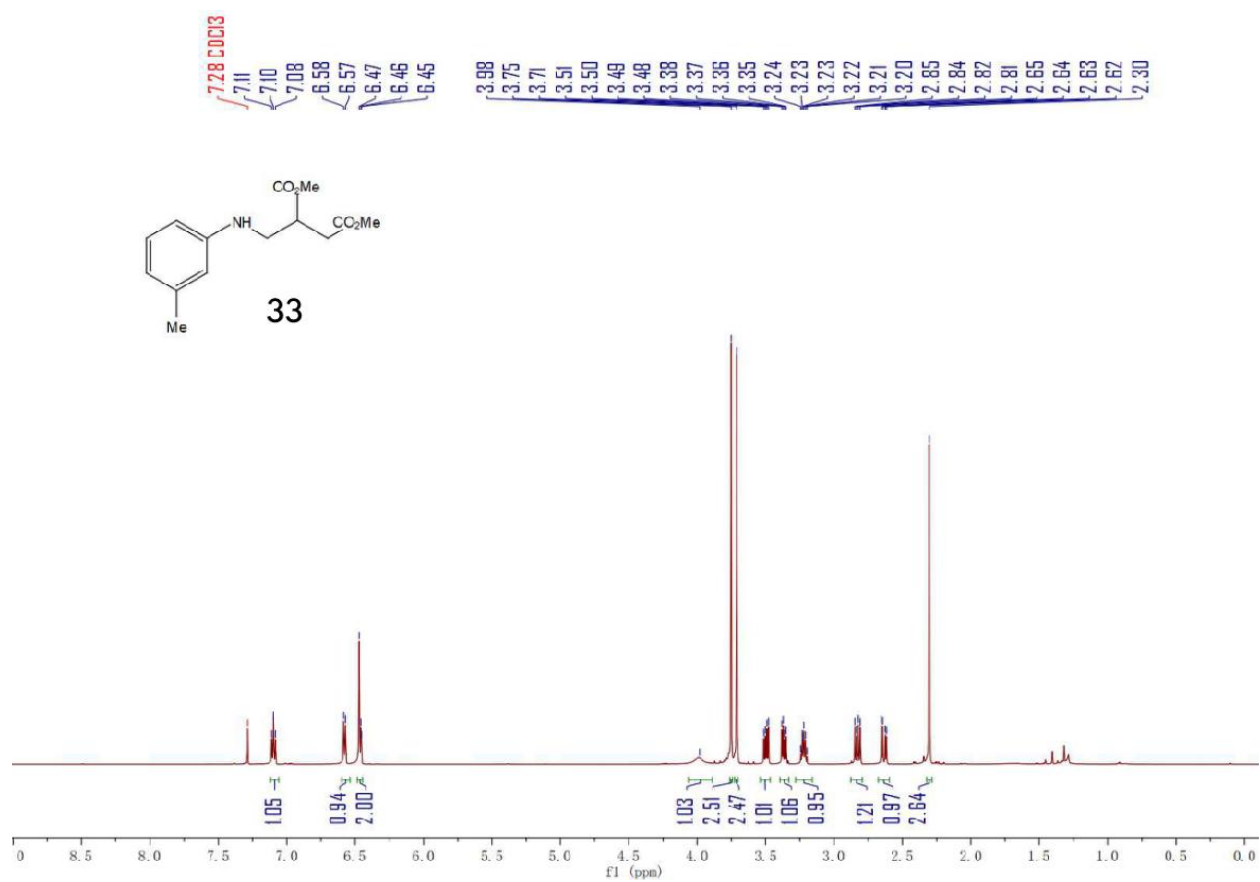
32 The reaction was set up following the general procedure using N-methylaniline (107 mg, 1 mmol) and dimethyl fumarate (29 mg, 0.2 mmol). After 16 hours, the reaction was purified following general work-up to give 33 mg (63 % yield) of the title compound. **¹H NMR** (600 MHz, Chloroform-*d*) δ 7.23 – 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); **¹³C 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]⁺ (C₁₃H₁₈NO₄) requires *m/z* 252.1, found *m/z* 252.1.

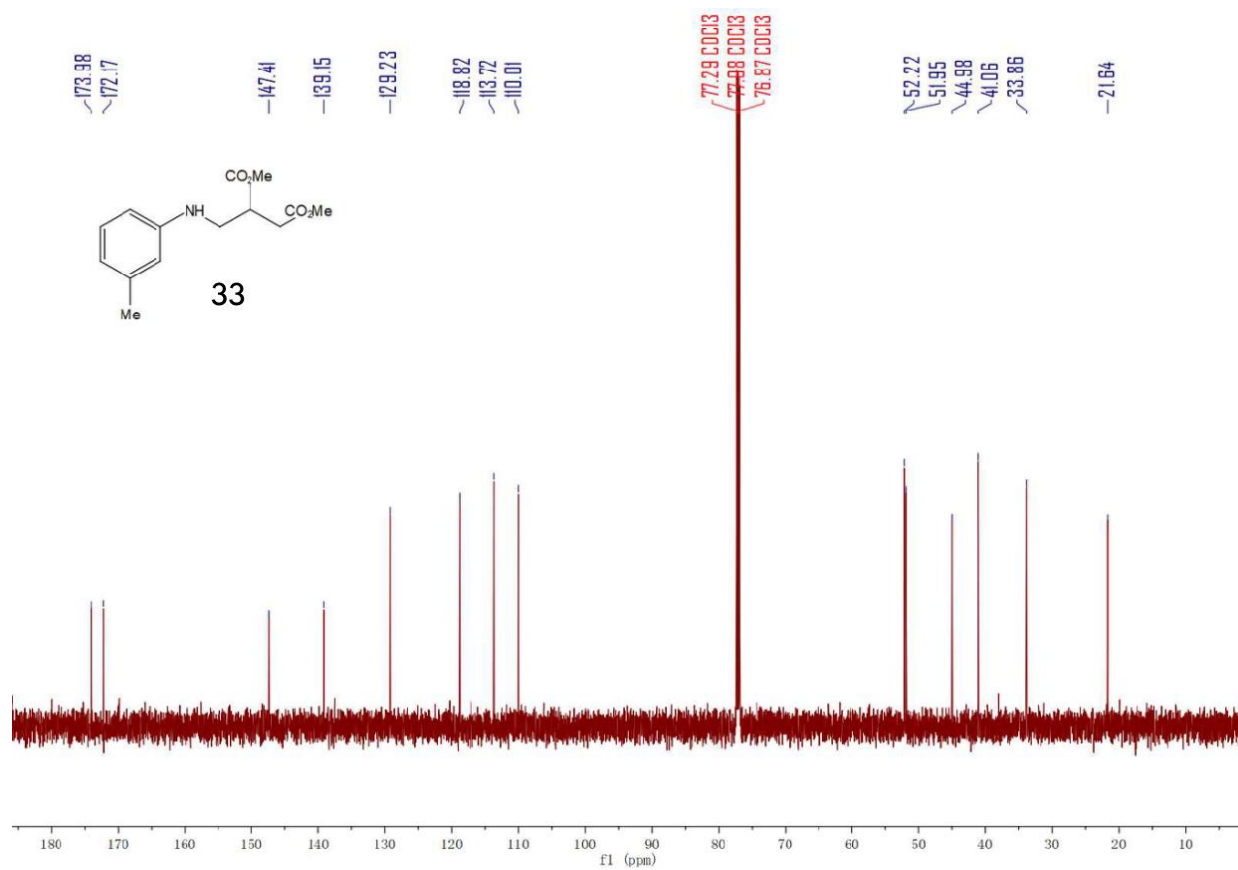


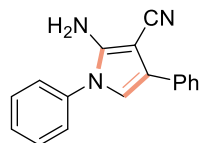




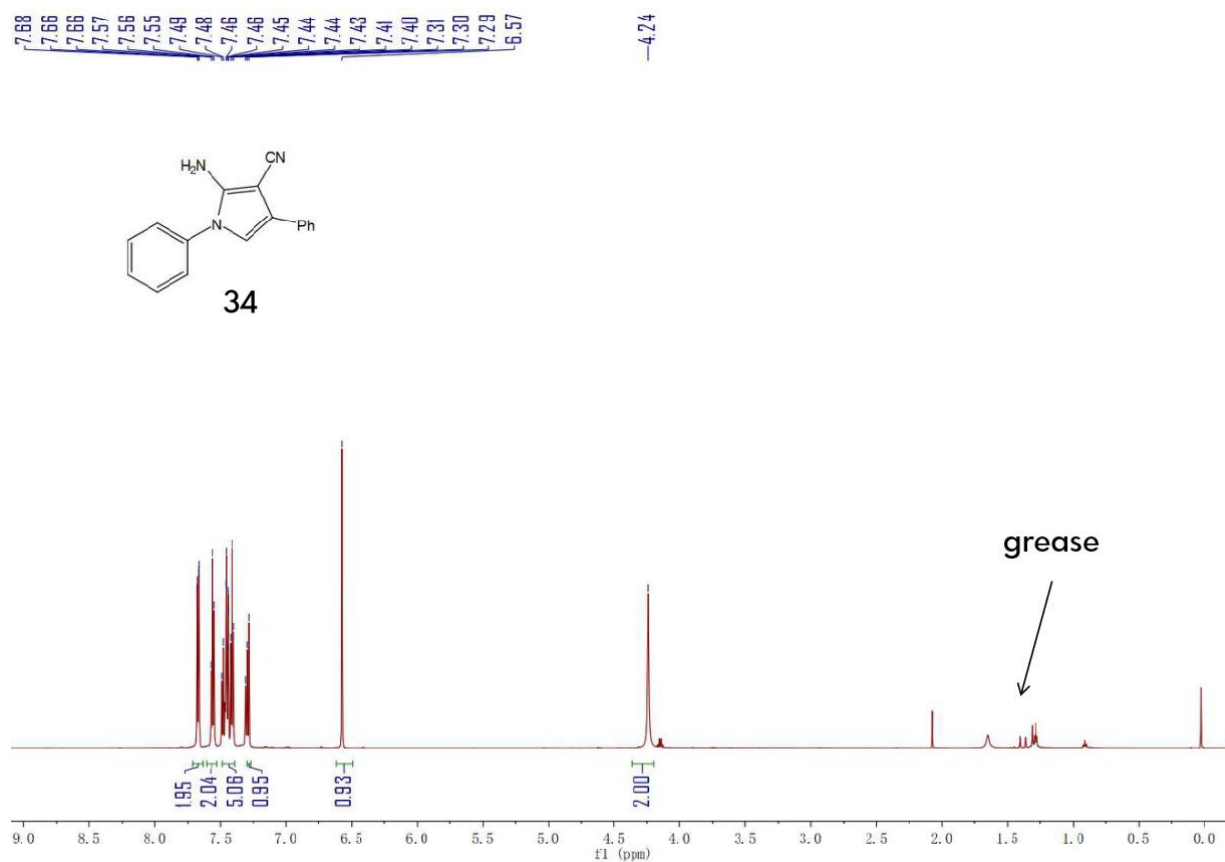
33 The reaction was set up following the general procedure using 3-Methyl-N-methylbenzenamine (121 mg, 1 mmol) and dimethyl fumarate (29 mg, 0.2 mmol). After 16 hours, the reaction was purified following general work-up to give 33 mg (60 % yield) of the title compound. **¹H NMR** (600 MHz, Chloroform-*d*) 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); **¹³C 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]⁺ (C₁₄H₂₀NO₄) requires m/z 266.1, found m/z 266.1.

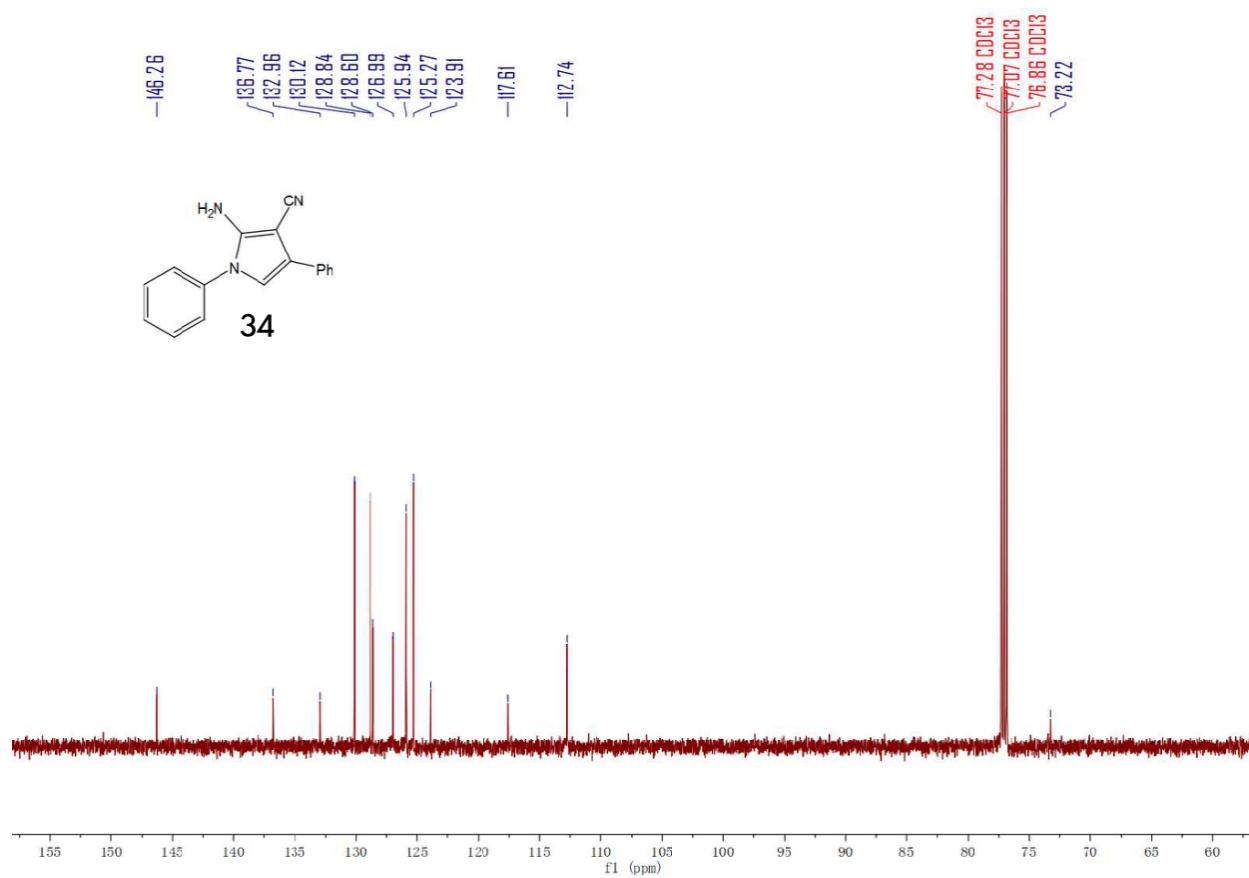


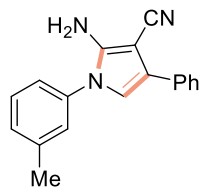




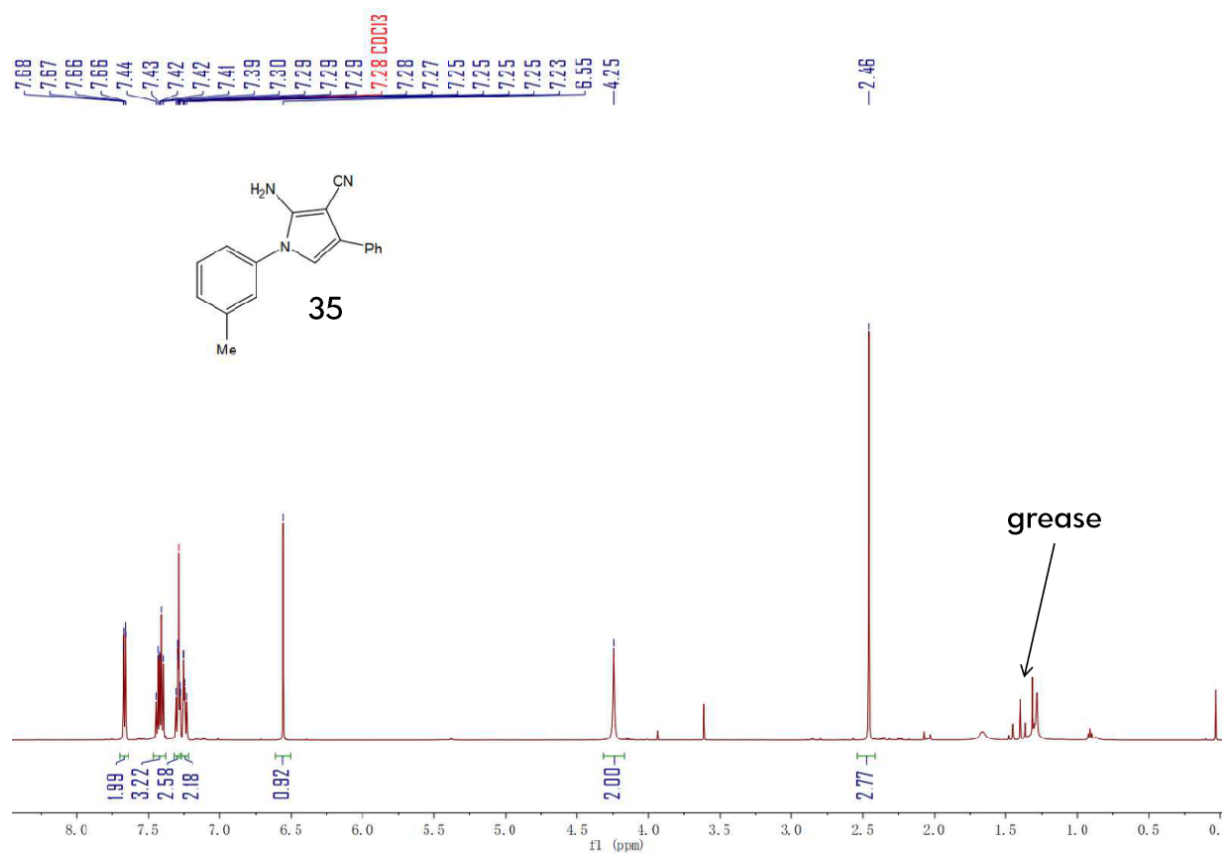
34 The reaction was set up following the general procedure using N-methylaniline (107 mg, 1 mmol) and benzylidenemalononitrile (31 mg, 0.2 mmol). After 16 hours, the reaction was purified following general work-up to give 38 mg (71 % yield) of the title compound. **¹H NMR** (600 MHz, Chloroform-*d*) 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); **¹³C 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]⁺ (C₁₇H₁₄N₃) requires *m/z* 260.1, found *m/z* 260.1.

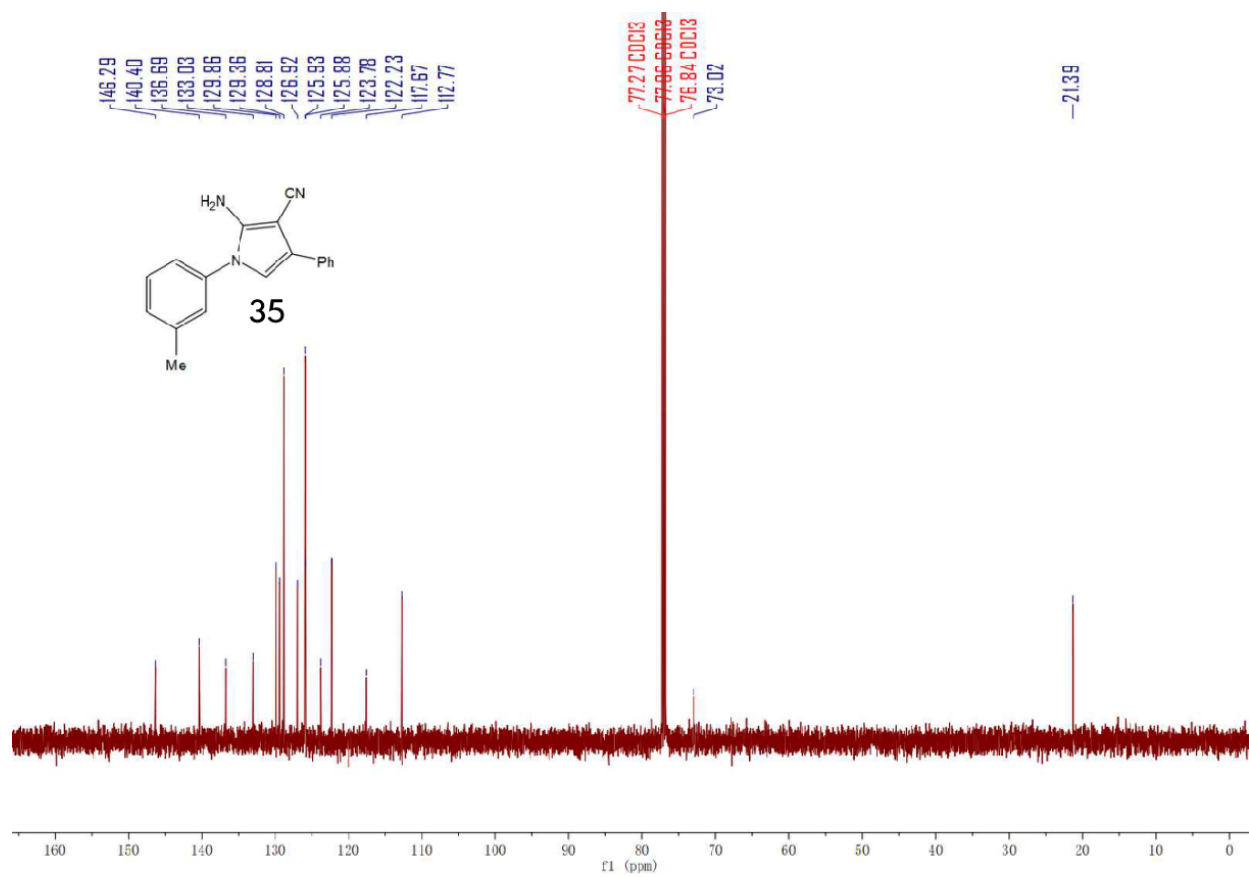


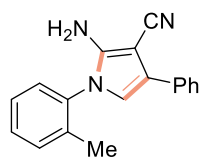




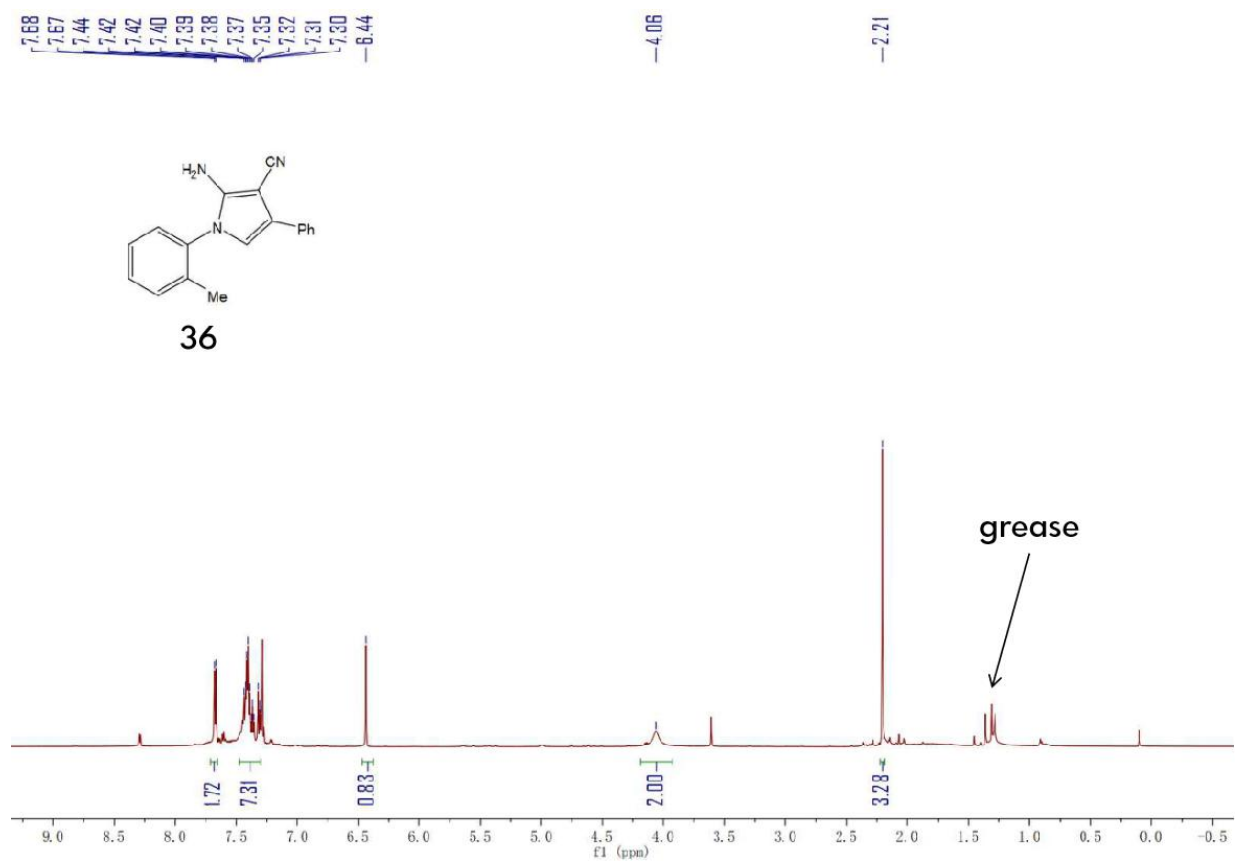
35 The reaction was set up following the general procedure using 3-methyl-N-methylbenzenamine (121 mg, 1 mmol) and benzylidenemalononitrile (31 mg, 0.2 mmol). After 16 hours, the reaction was purified following general work-up to give 37 mg (65 % yield) of the title compound. **¹H NMR** (600 MHz, Chloroform-*d*) 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); **¹³C 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]⁺ (C₁₈H₁₆N₃) requires *m/z* 274.1, found *m/z* 274.1.

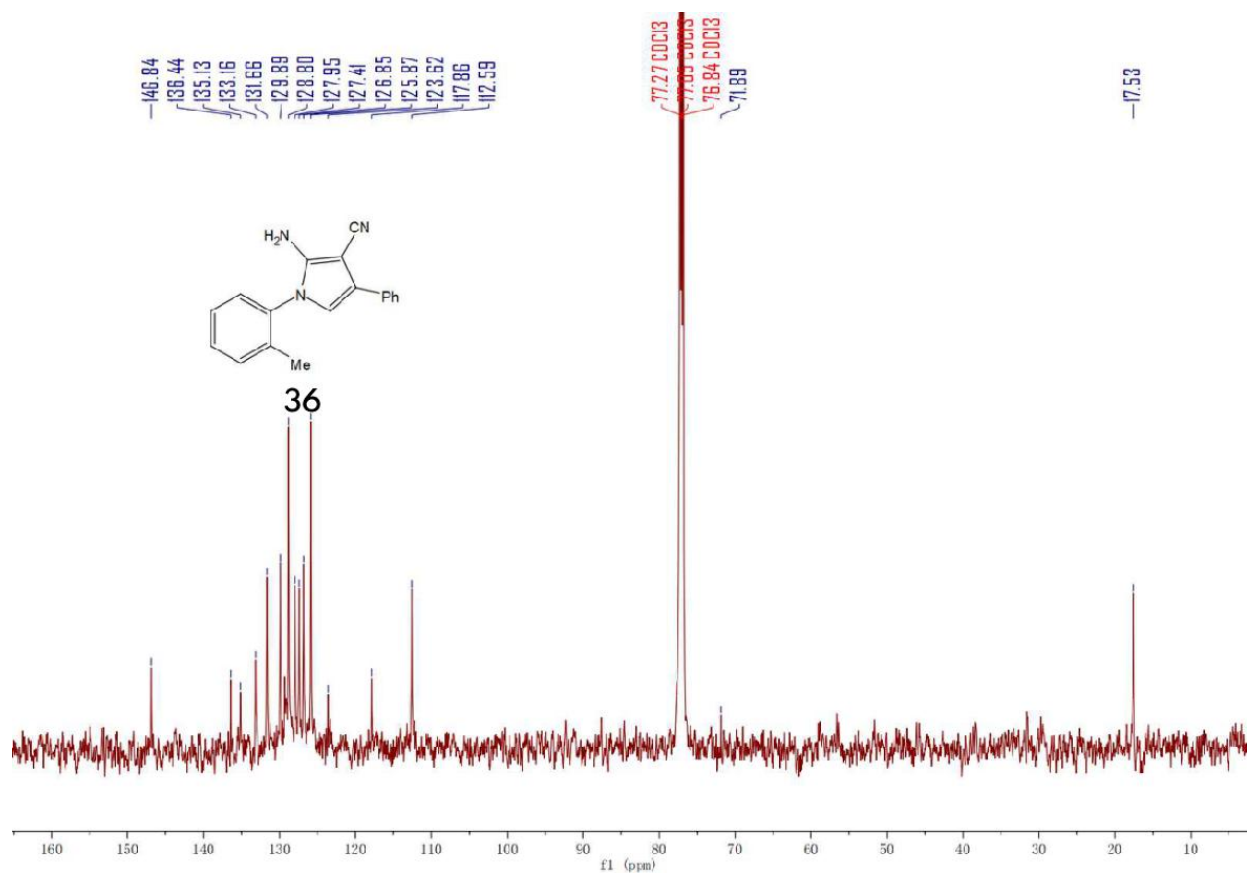


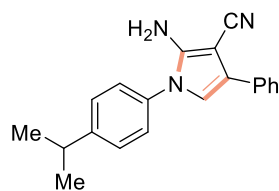




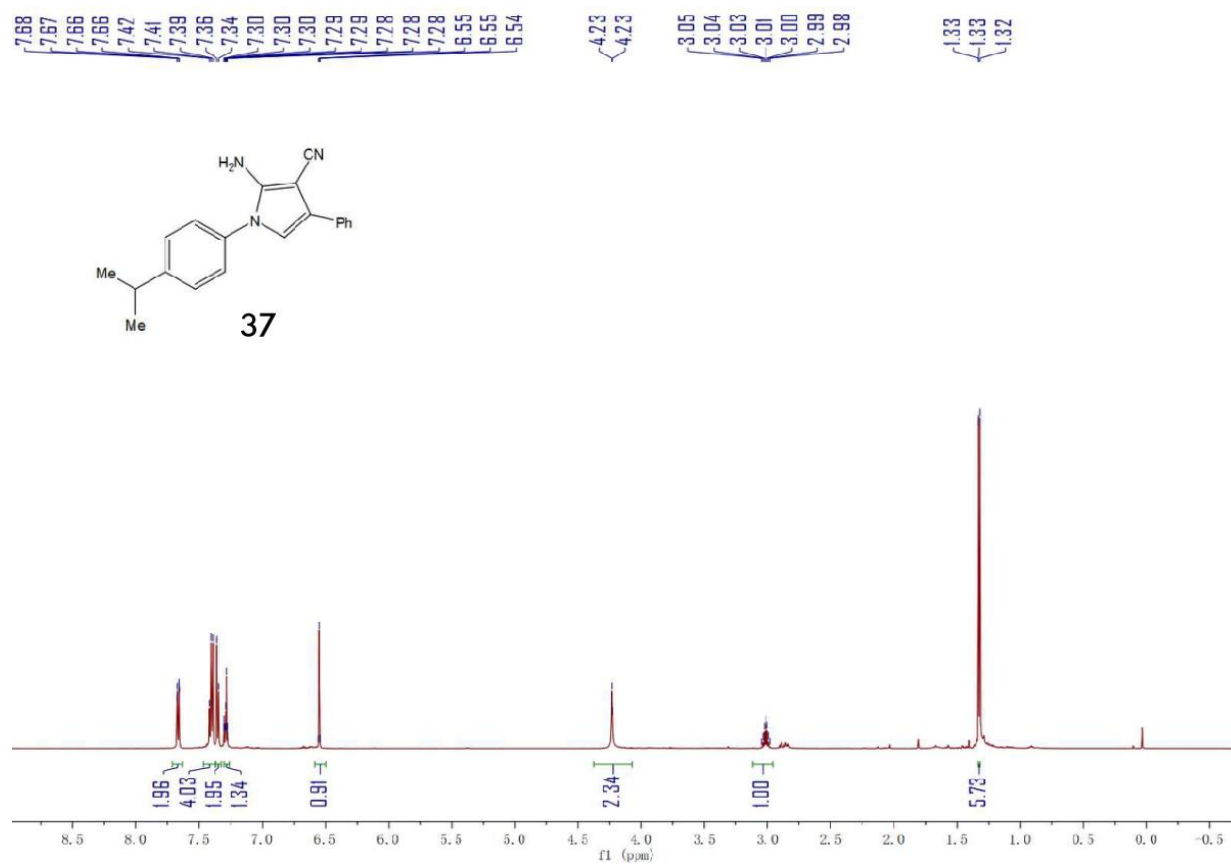
36 The reaction was set up following the general procedure using 2-methyl-N-methylbenzenamine (121 mg, 1 mmol) and benzylidenemalononitrile (31 mg, 0.2 mmol). After 16 hours, the reaction was purified following general work-up to give 25 mg (45 % yield) of the title compound. **¹H NMR** (600 MHz, Chloroform-*d*) 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); **¹³C 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]⁺ (C₁₈H₁₆N₃) requires m/z 274.1, found m/z 274.1.

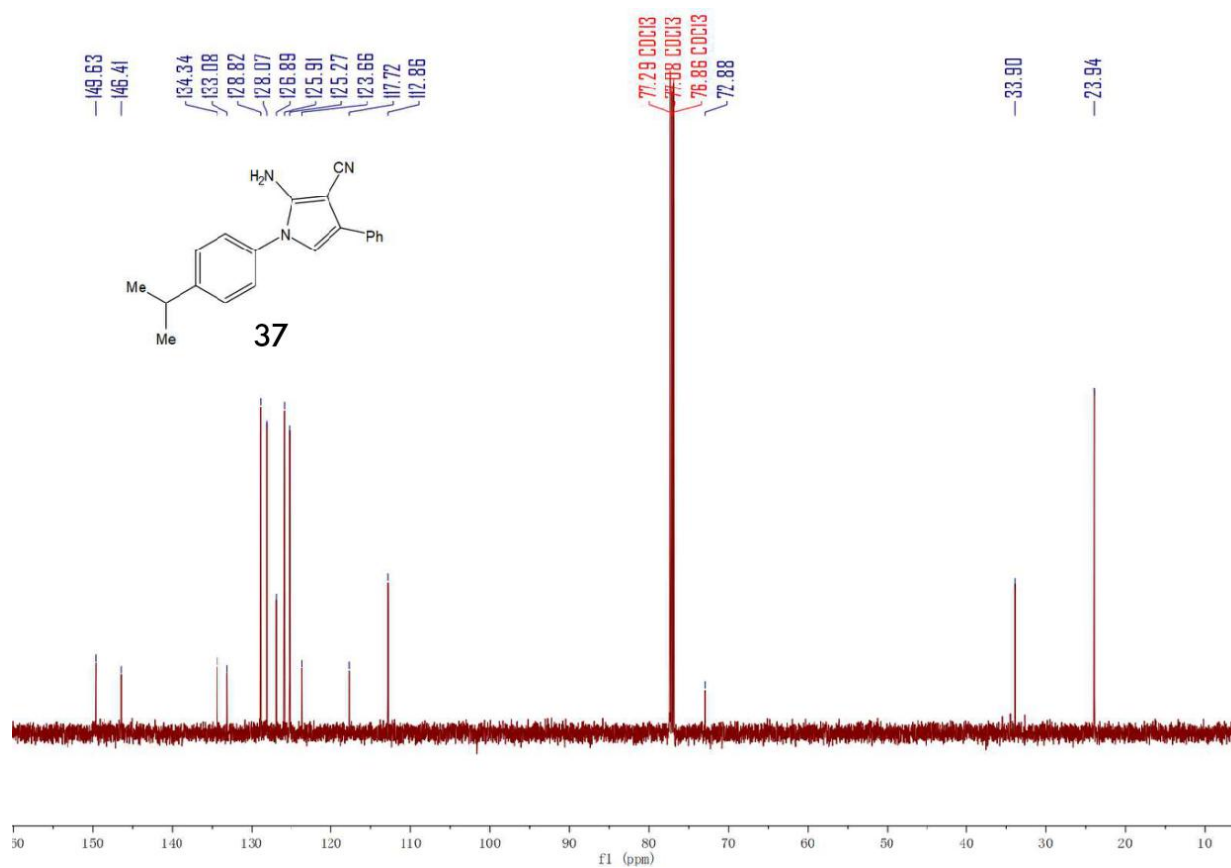


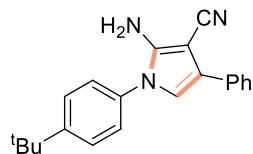




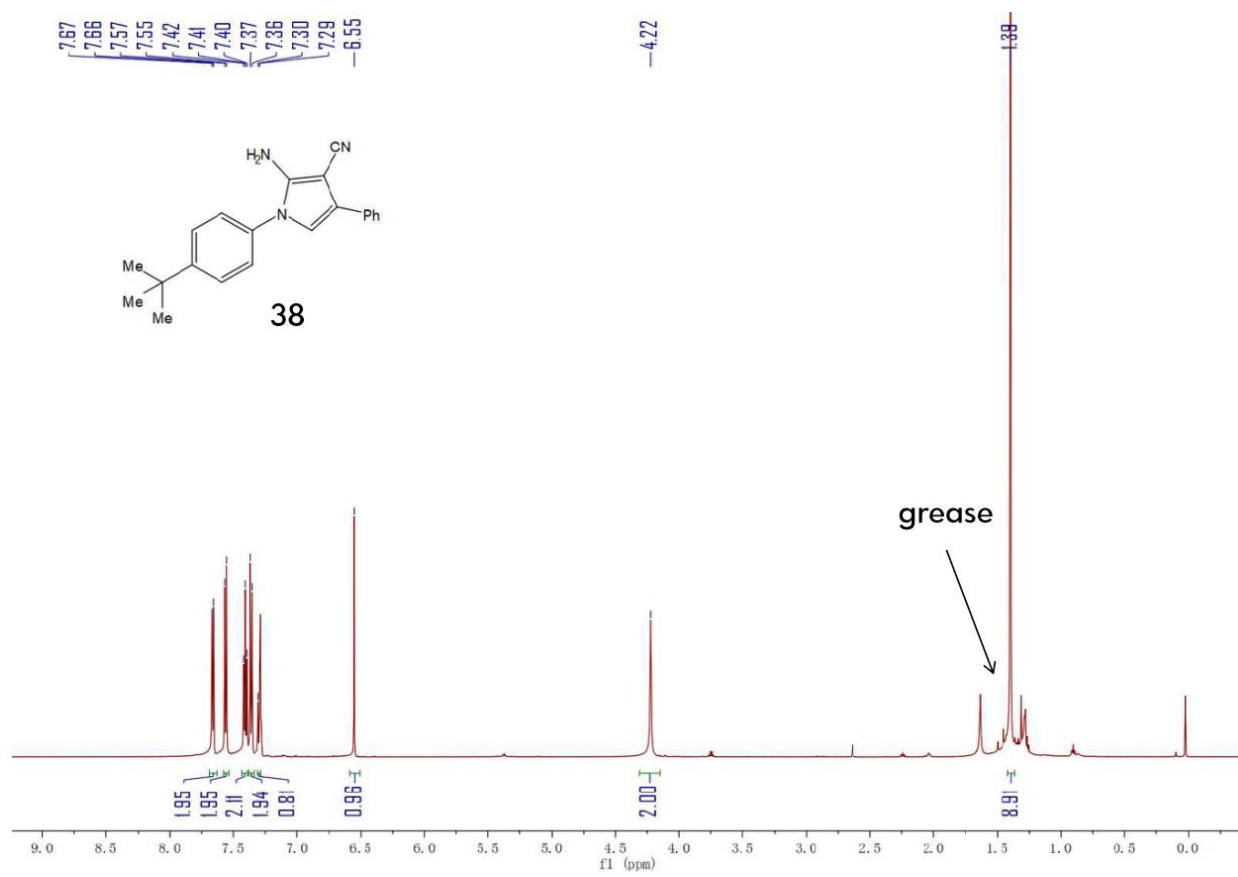
37 The reaction was set up following the general procedure using N-methyl-4-(1-methylethyl)benzenamine (149 mg, 1 mmol) and benzylidenemalononitrile (31 mg, 0.2 mmol). After 16 hours, the reaction was purified following general work-up to give 32 mg (52 % yield) of the title compound. **¹H NMR** (600 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); **¹³C 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]⁺ (C₂₀H₂₀N₃) requires m/z 302.1, found m/z 302.1.

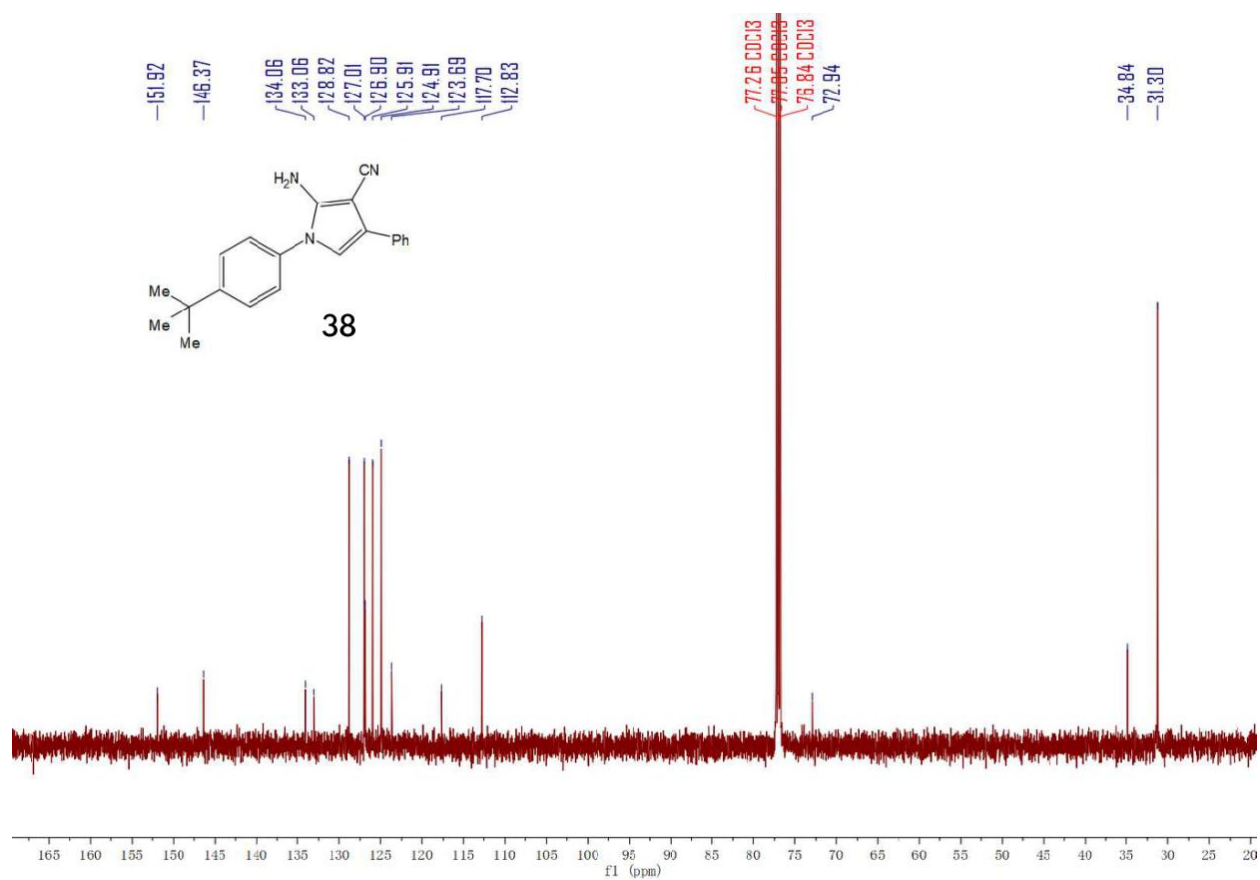


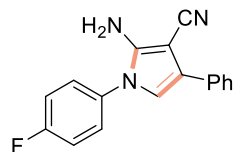




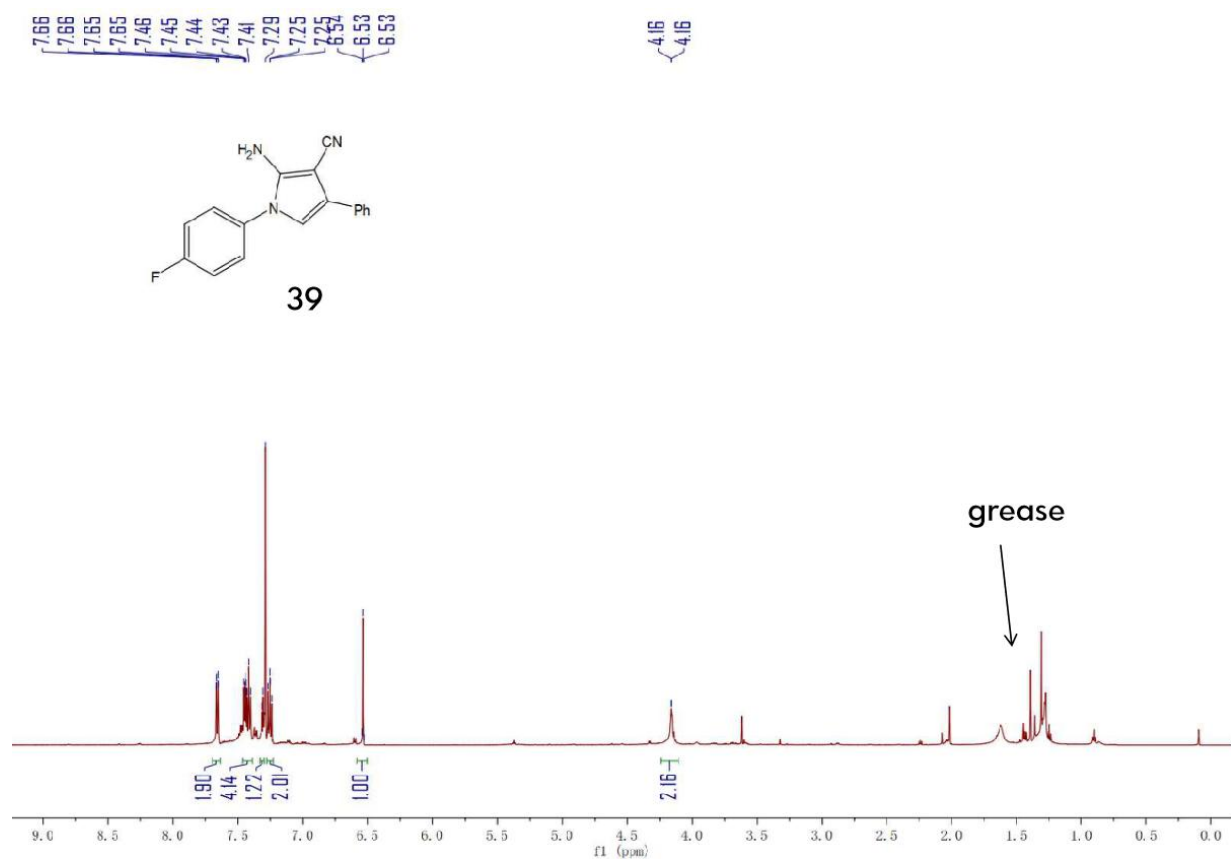
38 The reaction was set up following the general procedure using 4-(1,1-dimethylethyl)-N-methylbenzenamine (163 mg, 1 mmol) and benzylidenemalononitrile (31 mg, 0.2 mmol). After 16 hours, the reaction was purified following general work-up to give 43 mg (66 % yield) of the title compound. **¹H NMR** (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); **¹³C 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]⁺ (C₂₁H₂₂N₃) requires m/z 316.1, found m/z 316.1.

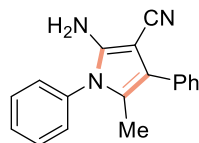




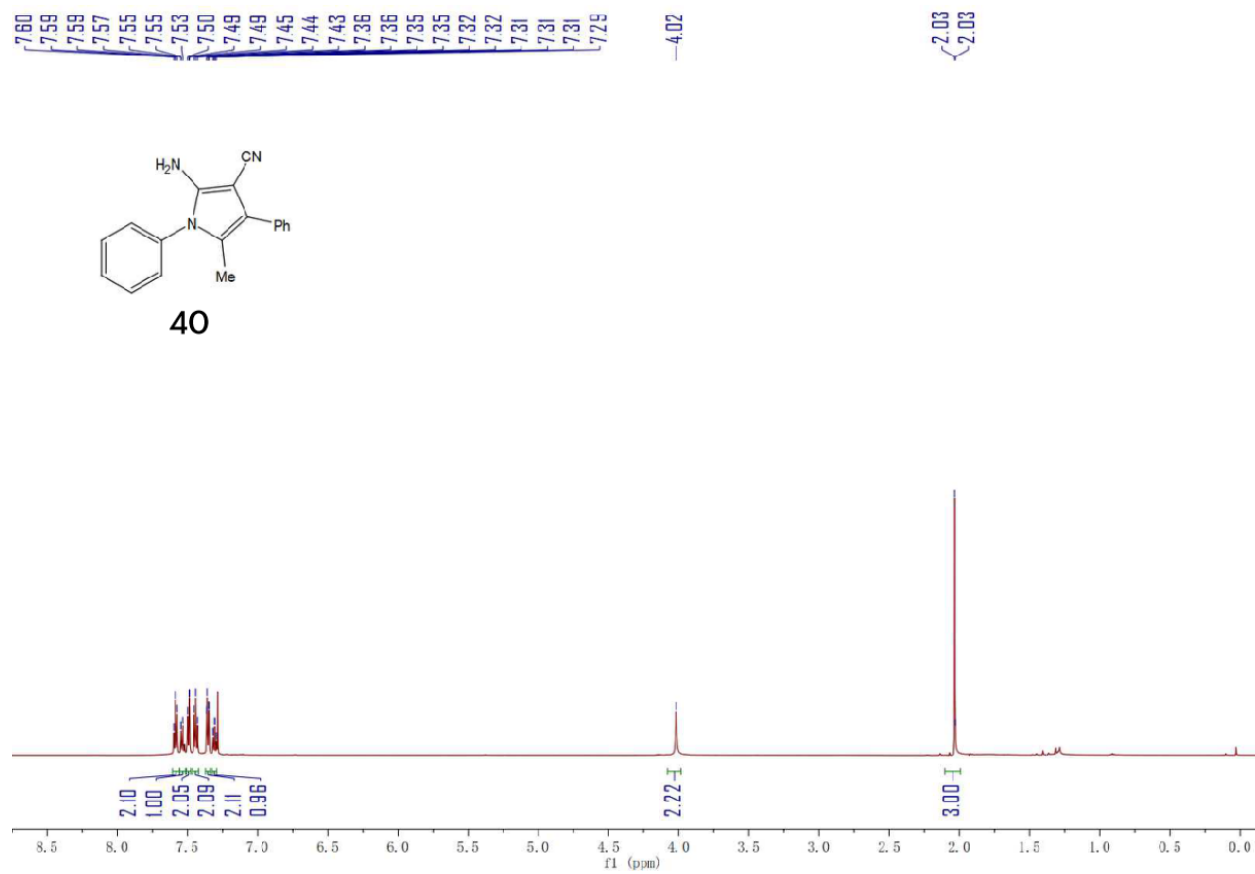


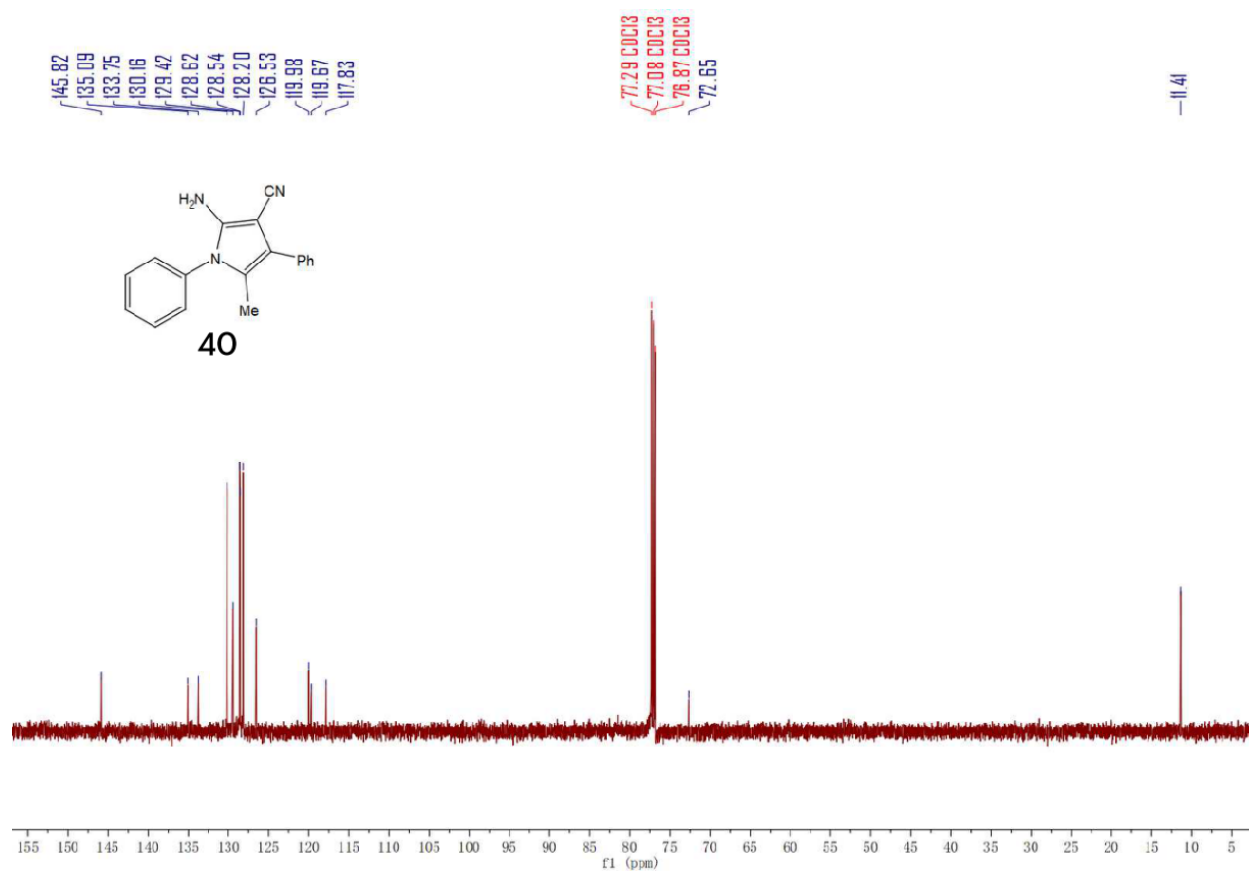
39 The reaction was set up following the general procedure using 4-fluoro-N-methylbenzenamine (125mg, 1 mmol) and benzylidenemalononitrile (31 mg, 0.2 mmol). After 16 hours, the reaction was purified following general work-up to give 6 mg (10 % yield) of the title compound. **¹H NMR** (600 MHz, Chloroform-*d*) 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]⁺ (C₁₇H₁₃FN₃) requires m/z 278.1, found m/z 278.1.

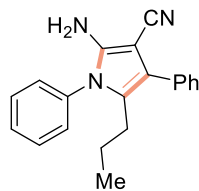




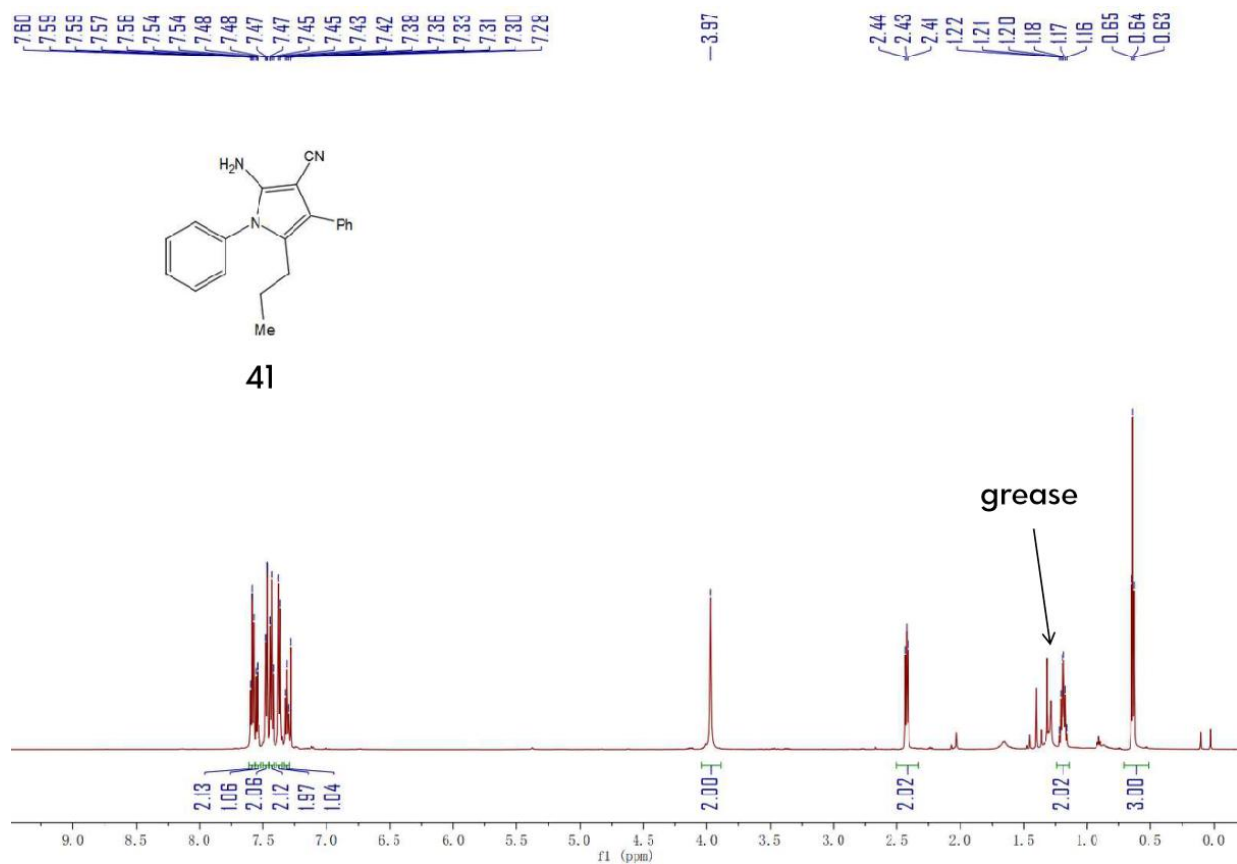
40 The reaction was set up following the general procedure using N-ethylaniline (121 mg, 1 mmol) and benzylidenemalononitrile (31 mg, 0.2 mmol). After 16 hours, the reaction was purified following general work-up to give 40 mg (71 % yield) of the title compound. **¹H NMR** (600 MHz, Chloroform-*d*) δ 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); **¹³C 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]⁺ (C₁₈H₁₆N₃) requires *m/z* 274.1, found *m/z* 274.1.

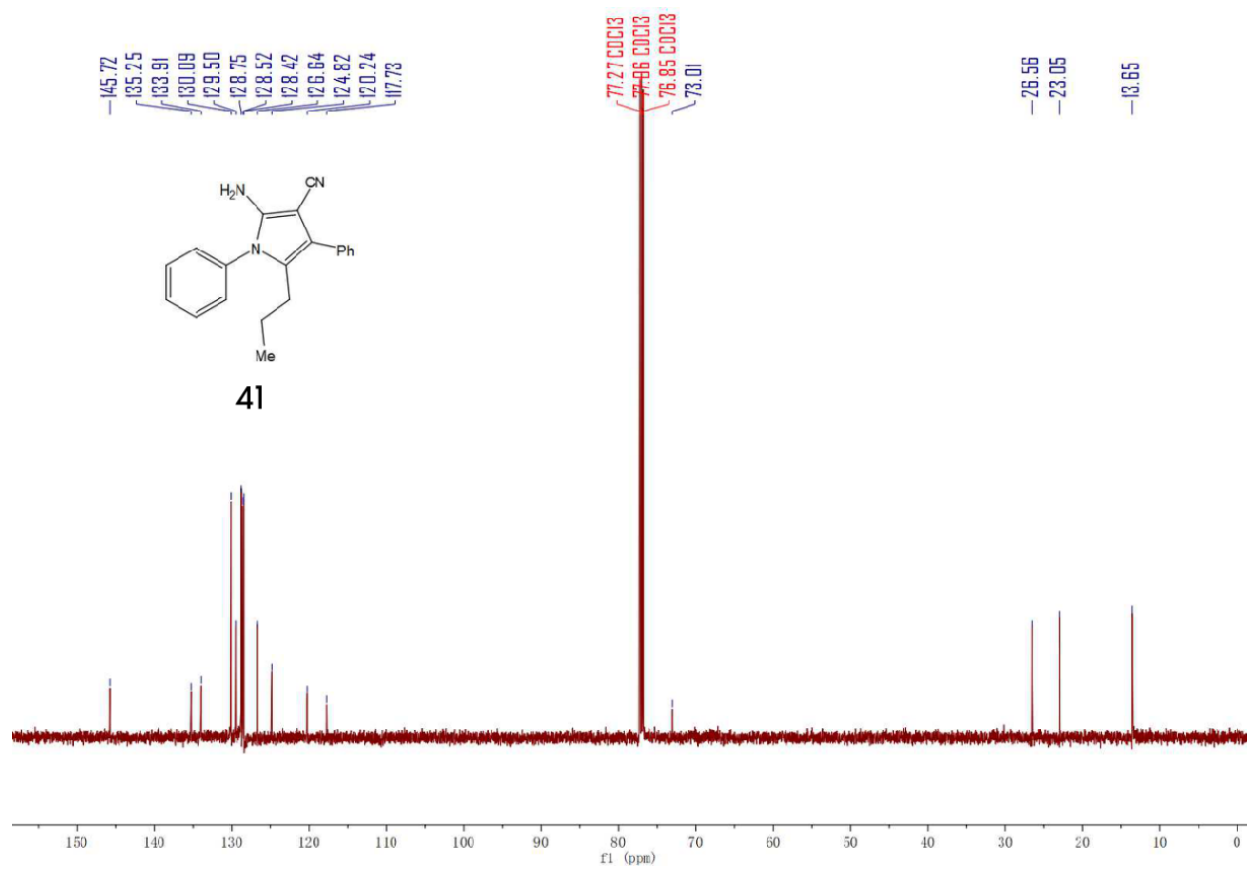


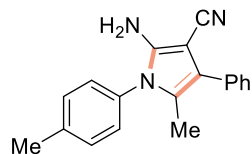




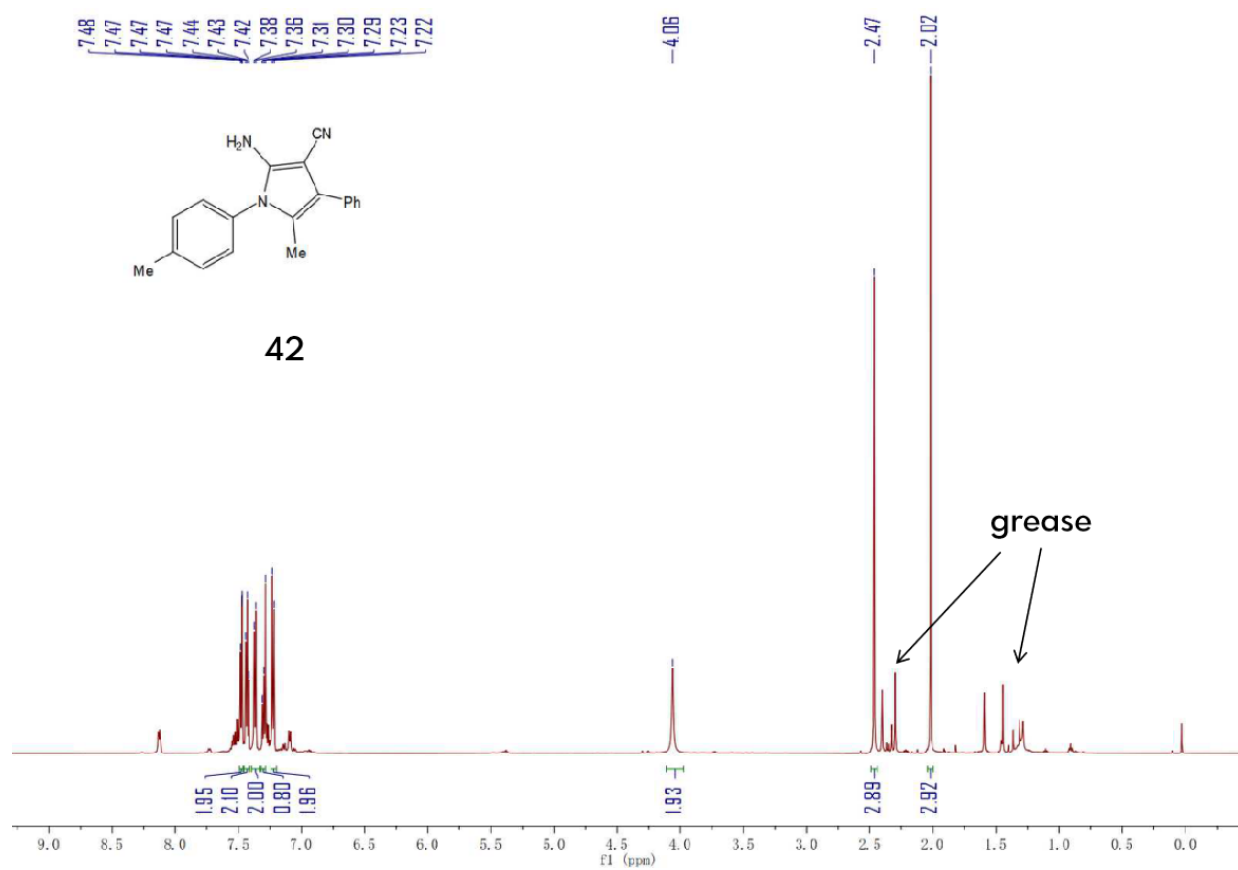
41 The reaction was set up following the general procedure using N-Butylaniline (149 mg, 1 mmol) and benzylidenemalononitrile (31 mg, 0.2 mmol). After 16 hours, the reaction was purified following general work-up to give 36 mg (58 % yield) of the title compound. **¹H NMR** (600 MHz, Chloroform-*d*) δ 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); **¹³C 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]⁺ (C₂₀H₂₀N₃) requires m/z 302.1, found m/z 302.1.

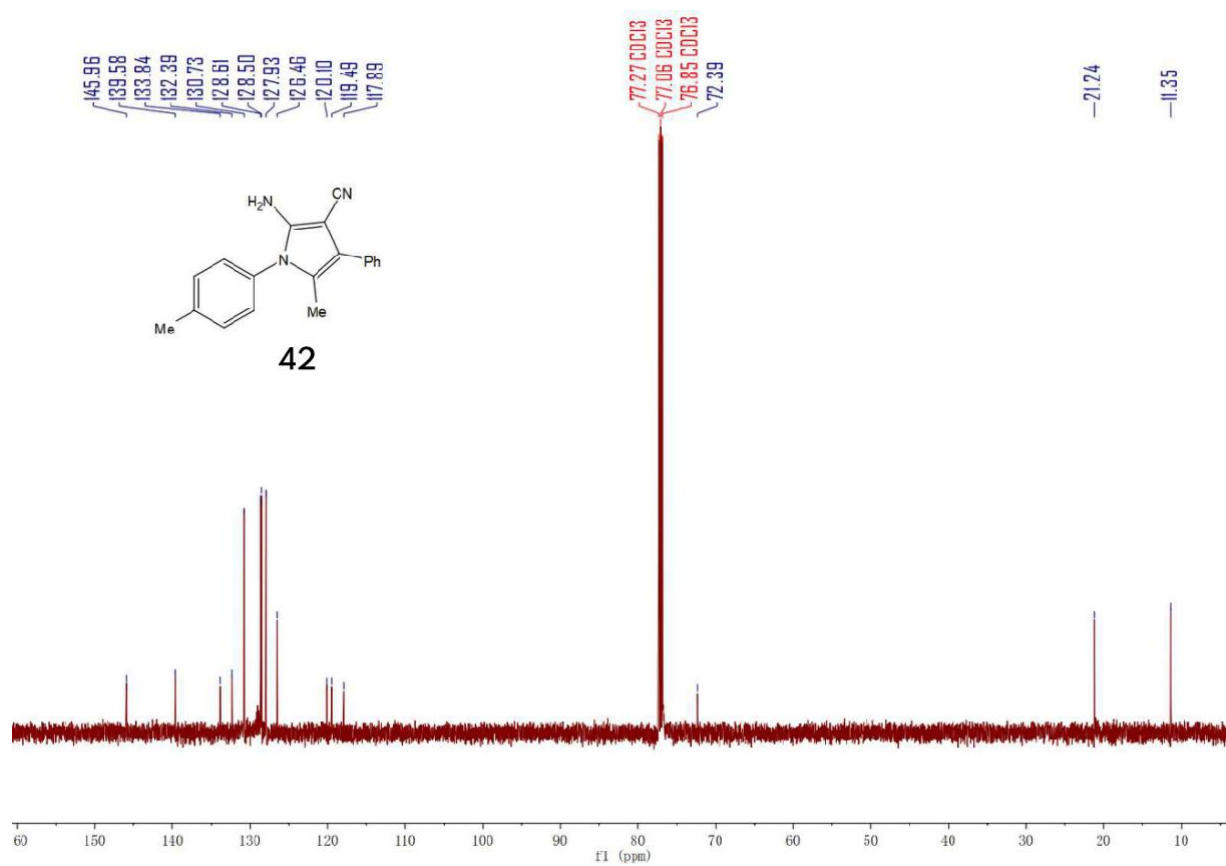


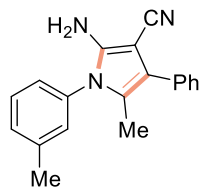




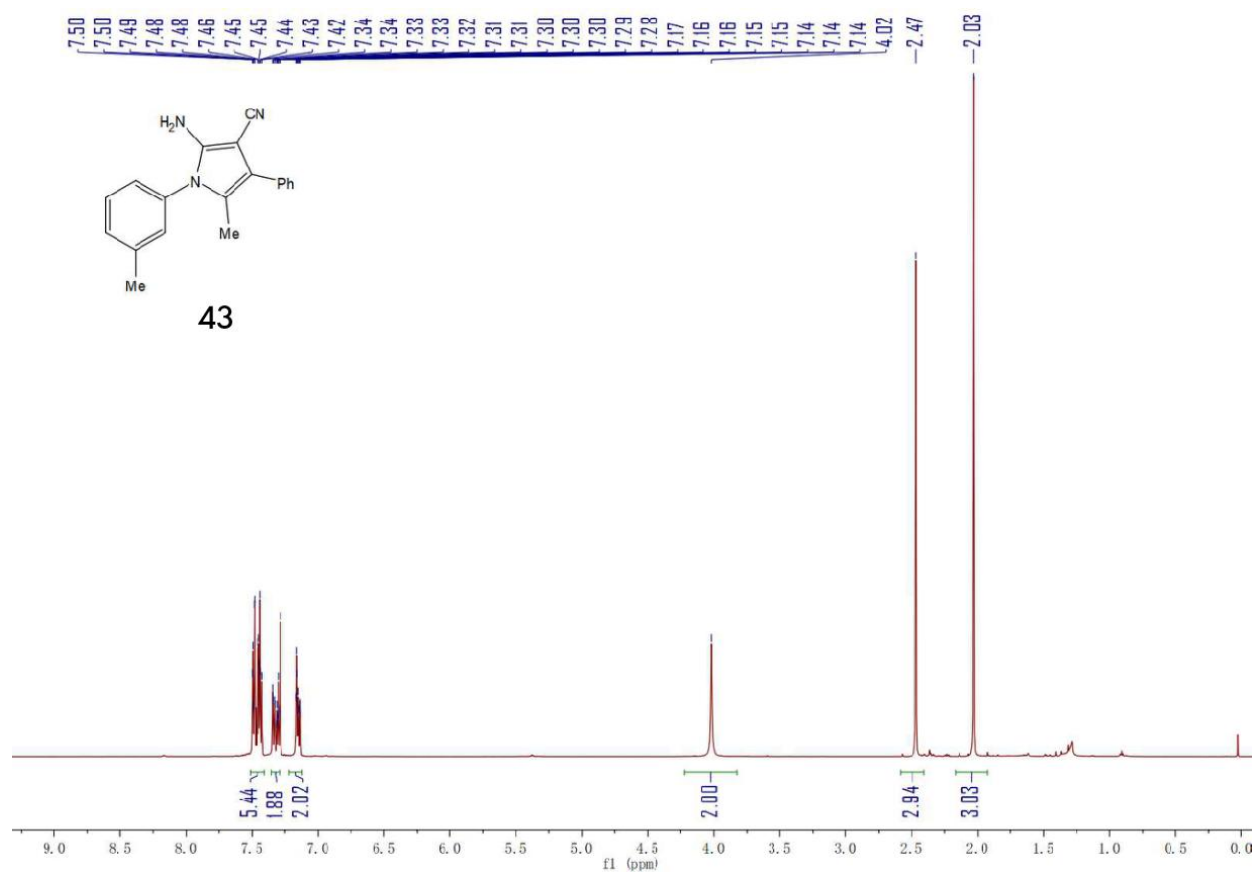
42 The reaction was set up following the general procedure using 4-methyl-N-ethylbenzenamine (135 mg, 1 mmol) and benzyldenemalononitrile (31 mg, 0.2 mmol). After 16 hours, the reaction was purified following general work-up to give 47 mg (81 % yield) of the title compound. **¹H NMR** (600 MHz, Chloroform-*d*) 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); **¹³C 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]⁺ (C₁₉H₁₈N₃) requires m/z 288.1, found m/z 288.1.

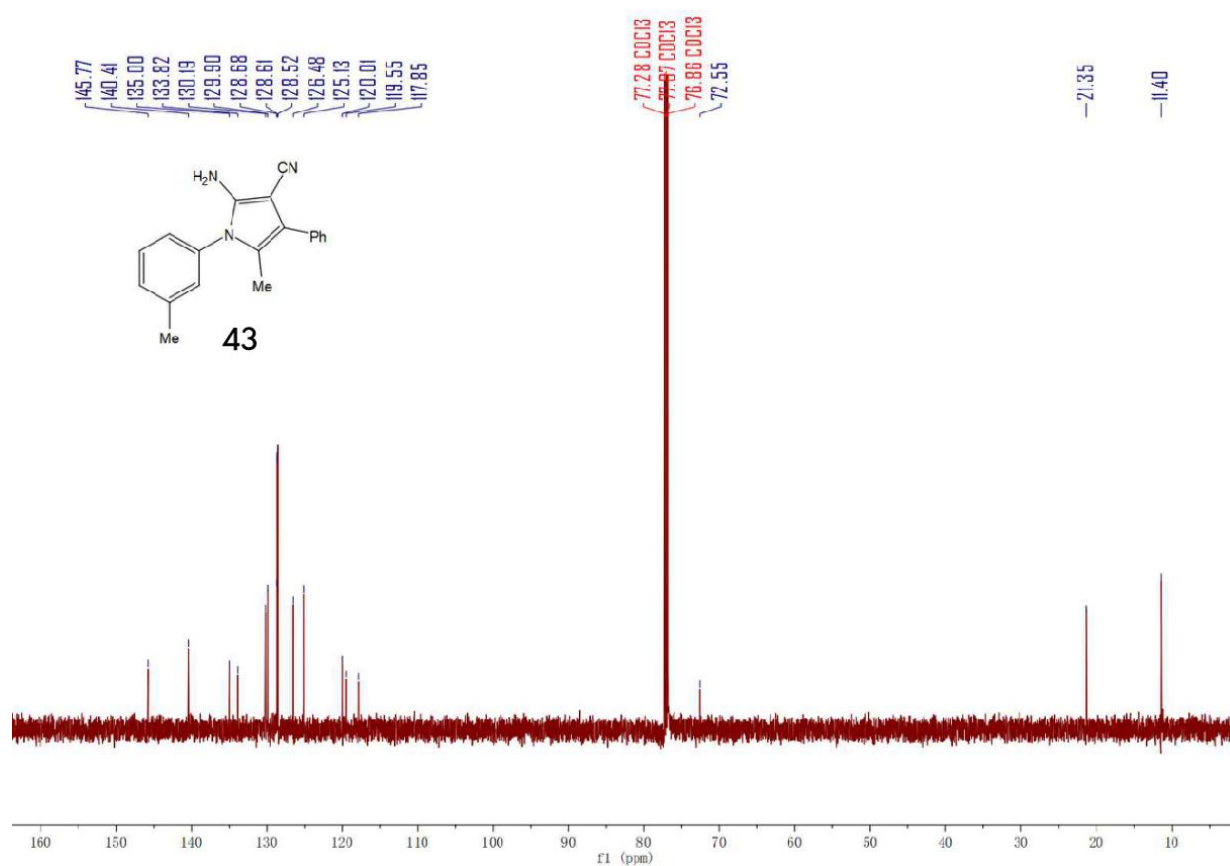


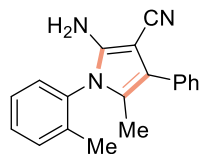




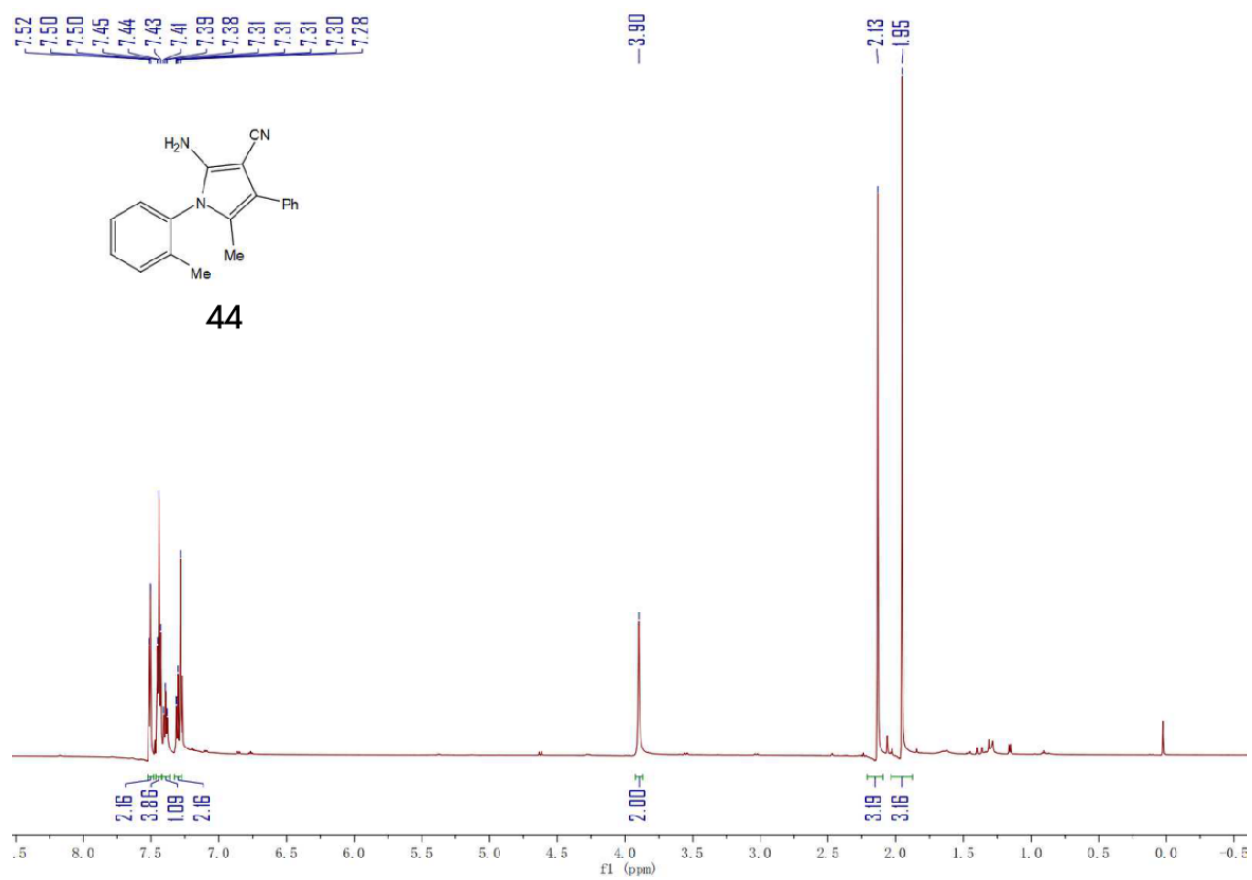
43 The reaction was set up following the general procedure using 3-methyl-N-ethylbenzenamine (135 mg, 1 mmol) and benzylidenemalononitrile (31 mg, 0.2 mmol). After 16 hours, the reaction was purified following general work-up to give 42 mg (72 % yield) of the title compound. **¹H NMR** (600 MHz, Chloroform-*d*) 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); **¹³C 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]⁺ (C₁₉H₁₈N₃) requires *m/z* 288.1, found *m/z* 288.1.

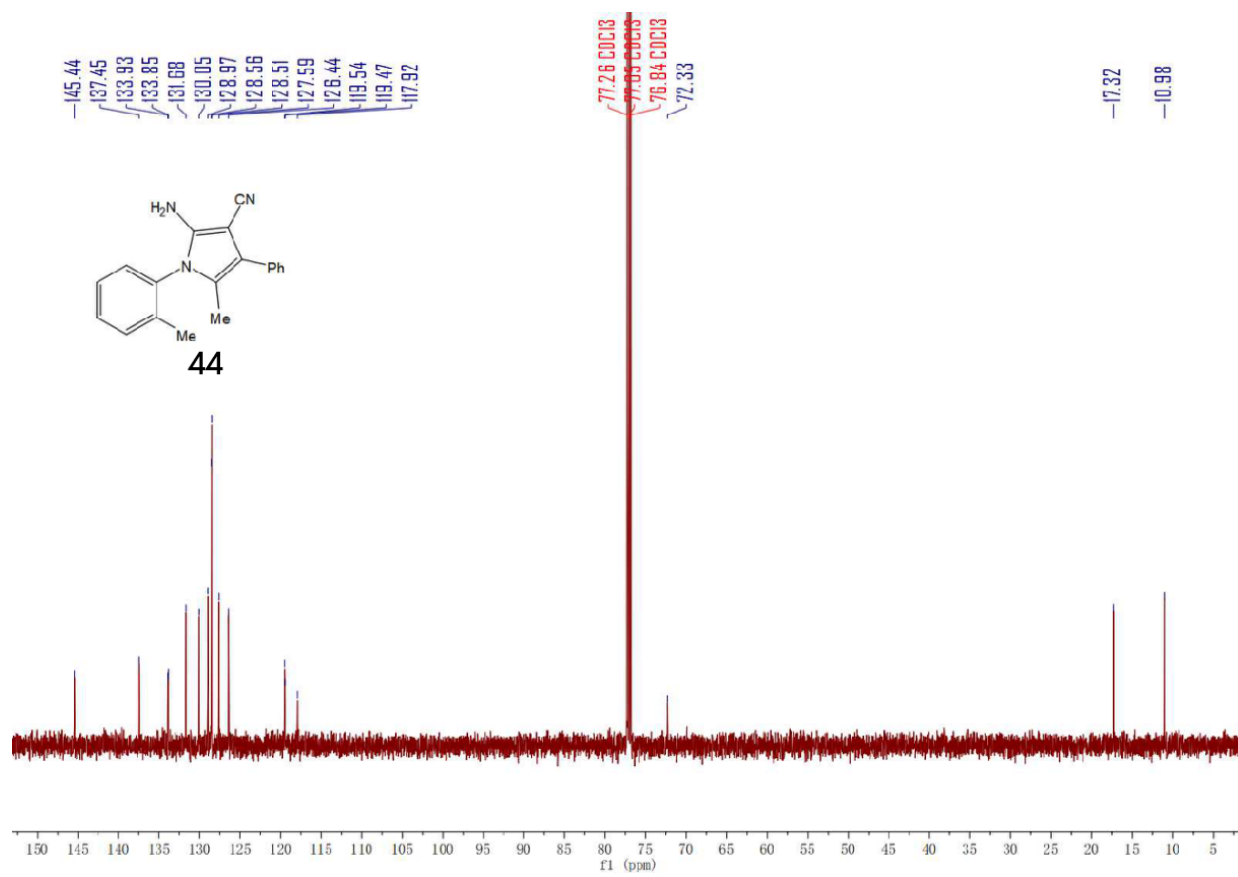


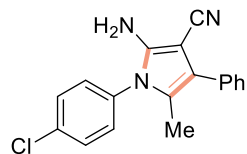




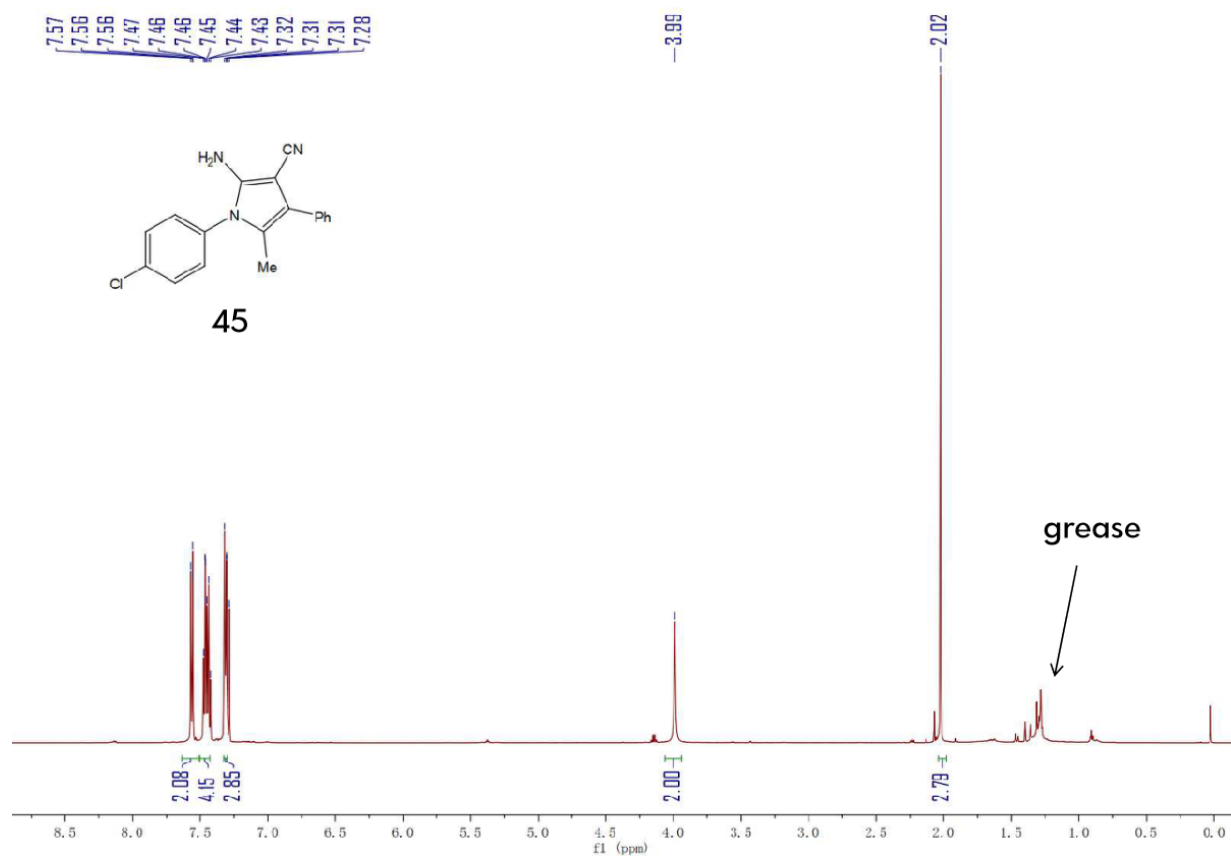
44 The reaction was set up following the general procedure using 2-methyl-N-ethylbenzenamine (135 mg, 1 mmol) and benzylidenemalononitrile (31 mg, 0.2 mmol). After 16 hours, the reaction was purified following general work-up to give 30 mg (51 % yield) of the title compound. **¹H NMR** (600 MHz, Chloroform-*d*) 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); **¹³C 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]⁺ (C₁₉H₁₈N₃) requires *m/z* 288.1, found *m/z* 288.1.

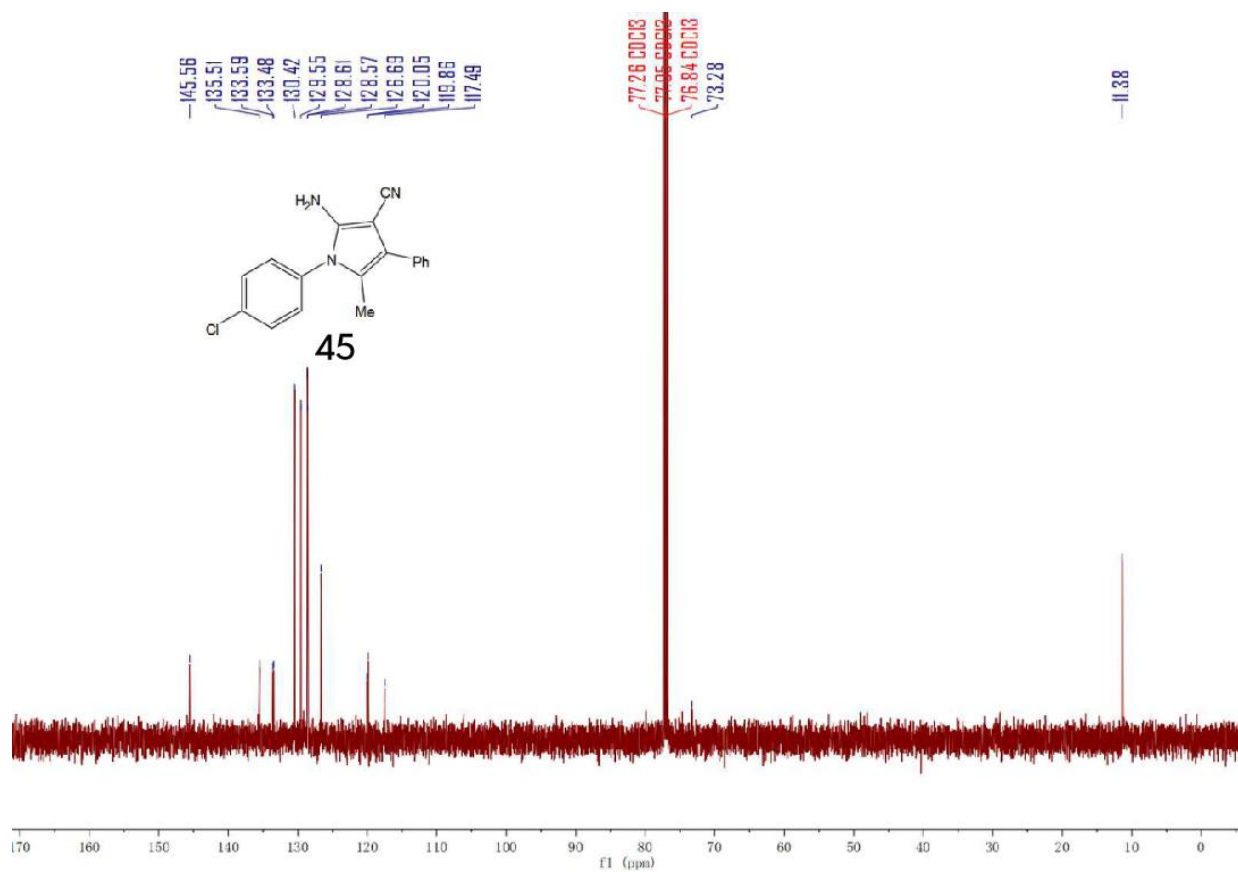


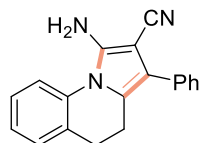




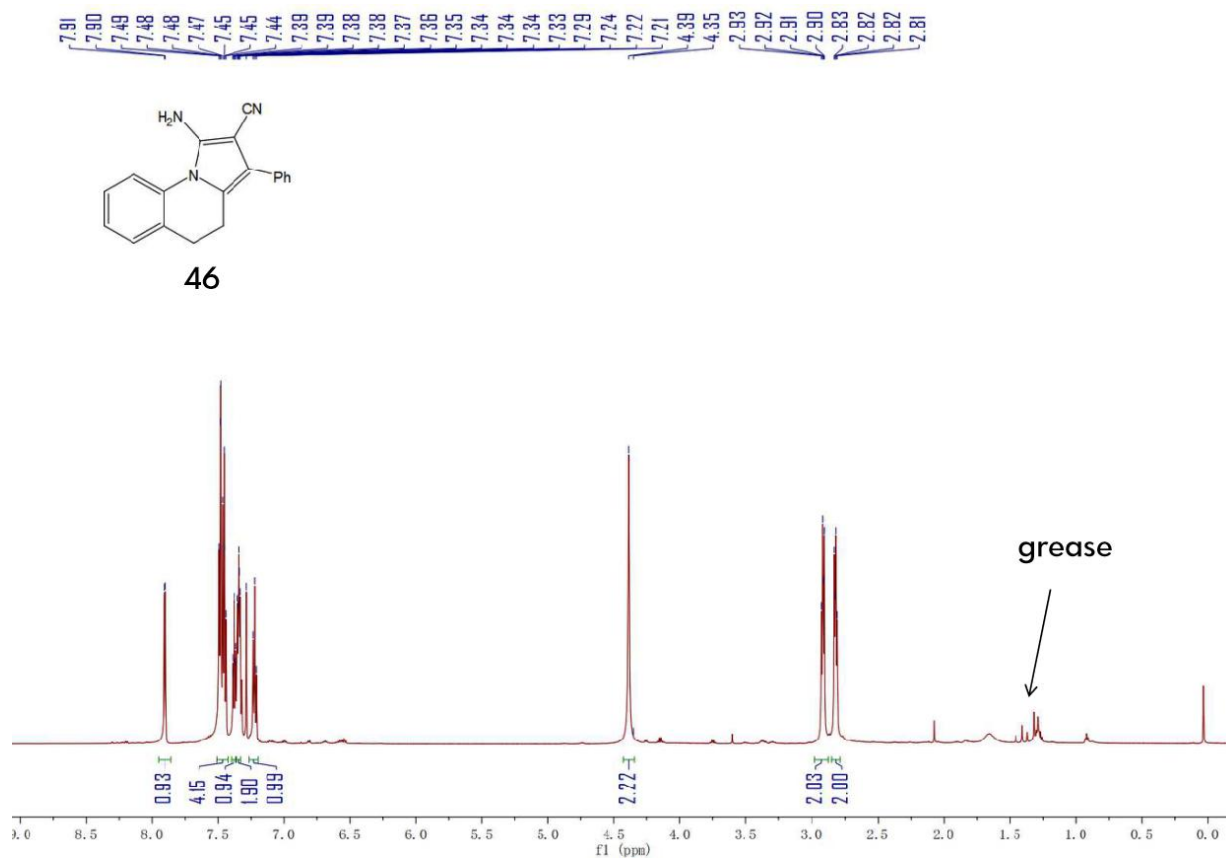
45 The reaction was set up following the general procedure using 4-chloro-N-ethylbenzenamine (155 mg, 1 mmol) and benzylidenemalononitrile (31 mg, 0.2 mmol). After 16 hours, the reaction was purified following general work-up to give 33 mg (54 % yield) of the title compound. **¹H NMR** (600 MHz, Chloroform-*d*) 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); **¹³C 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]⁺ (C₁₈H₁₅ClN₃) requires m/z 308.1, found m/z 308.1.

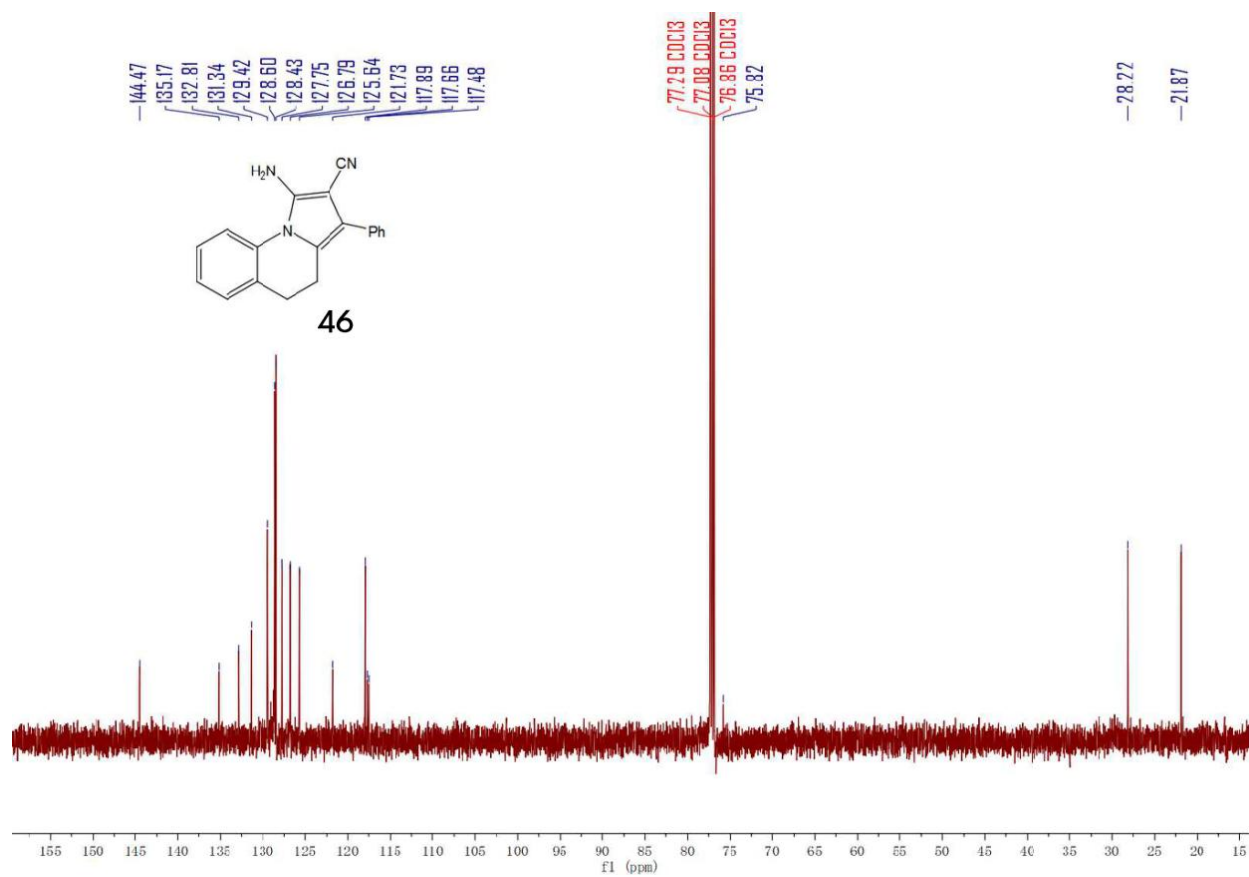


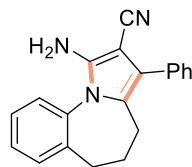




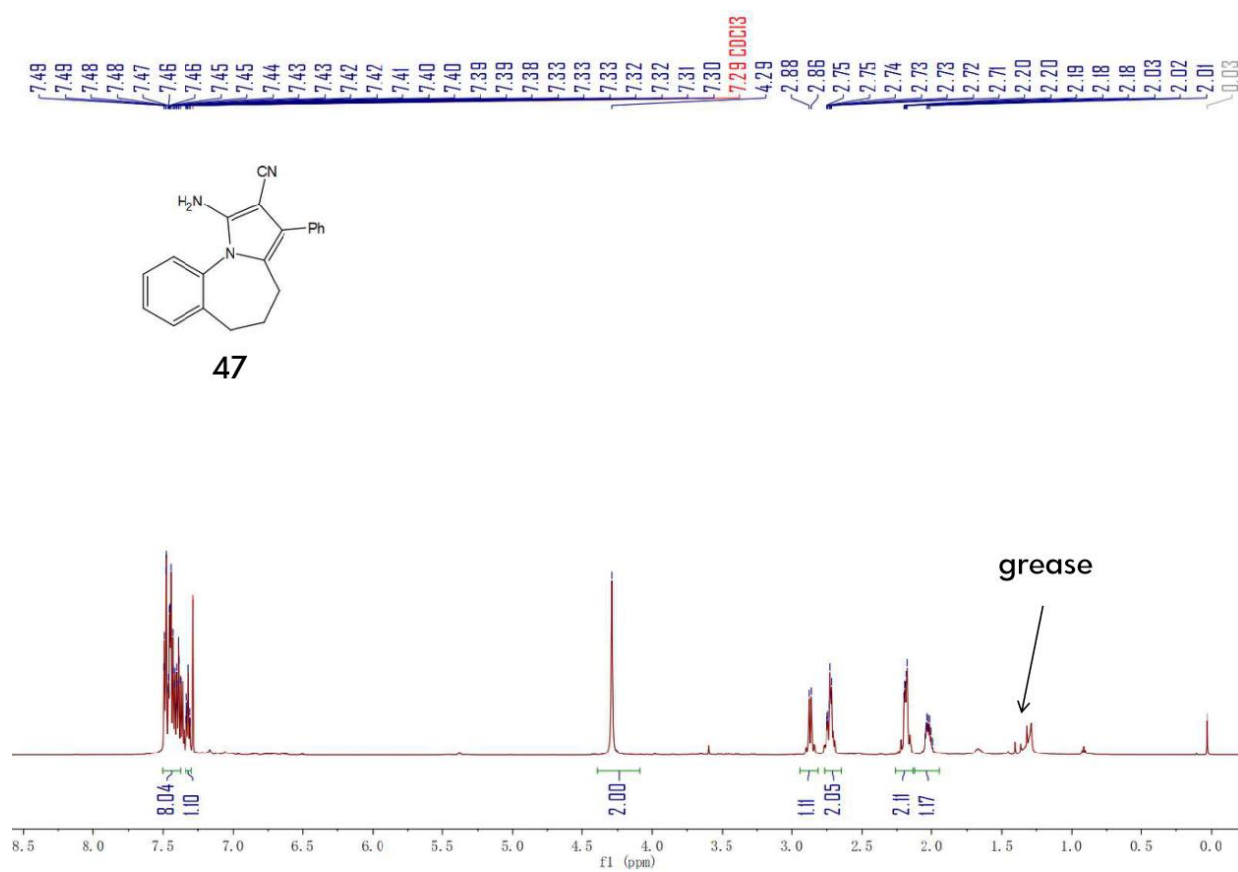
46 The reaction was set up following the general procedure using 1,2,3,4-tetrahydroquinoline (133 mg, 1 mmol) and benzylidenemalononitrile (31 mg, 0.2 mmol). After 16 hours, the reaction was purified following general work-up to give 33 mg (58 % yield) of the title compound. **¹H NMR** (600 MHz, Chloroform-*d*) 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); **¹³C 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]⁺ (C₁₉H₁₆N₃) requires m/z 286.1, found m/z 286.1.

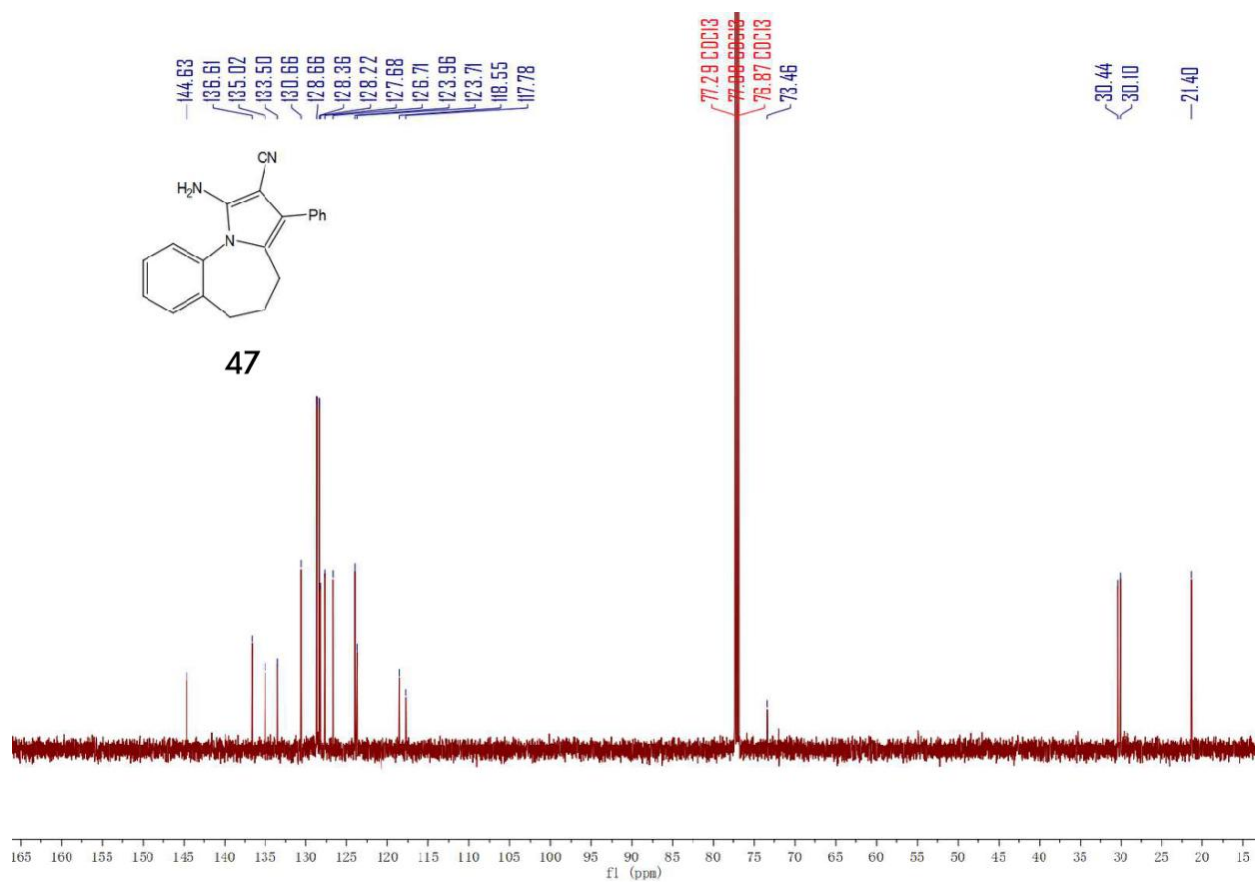


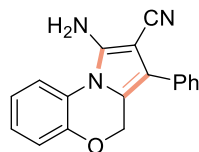




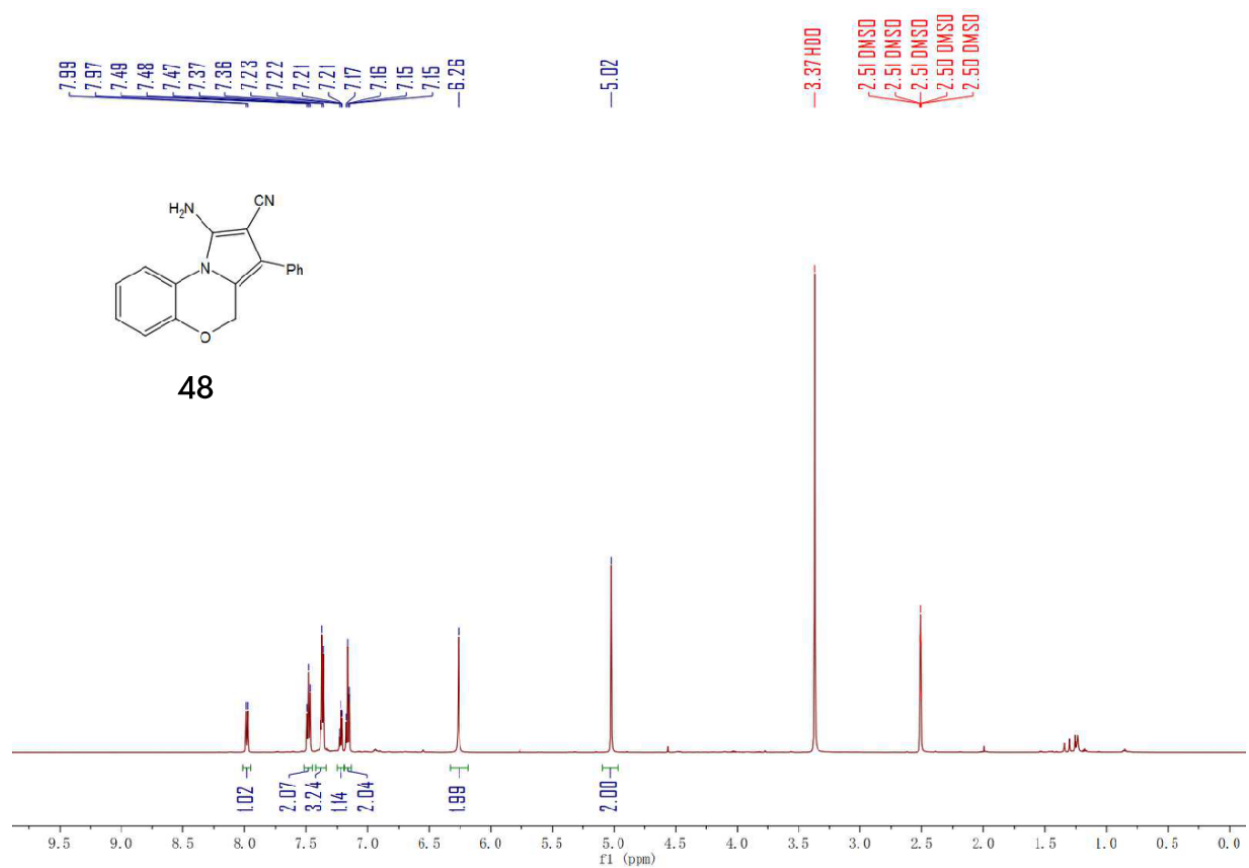
47 The reaction was set up following the general procedure using 2,3,4,5-tetrahydro-1H-1-benzazepine (147 mg, 1 mmol) and benzyldenemalononitrile (31 mg, 0.2 mmol). After 16 hours, the reaction was purified following general work-up to give 36 mg (61 % yield) of the title compound. **¹H NMR** (600 MHz, 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); **¹³C 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]⁺ (C₂₀H₁₈N₃) requires m/z 300.1, found m/z 300.1.

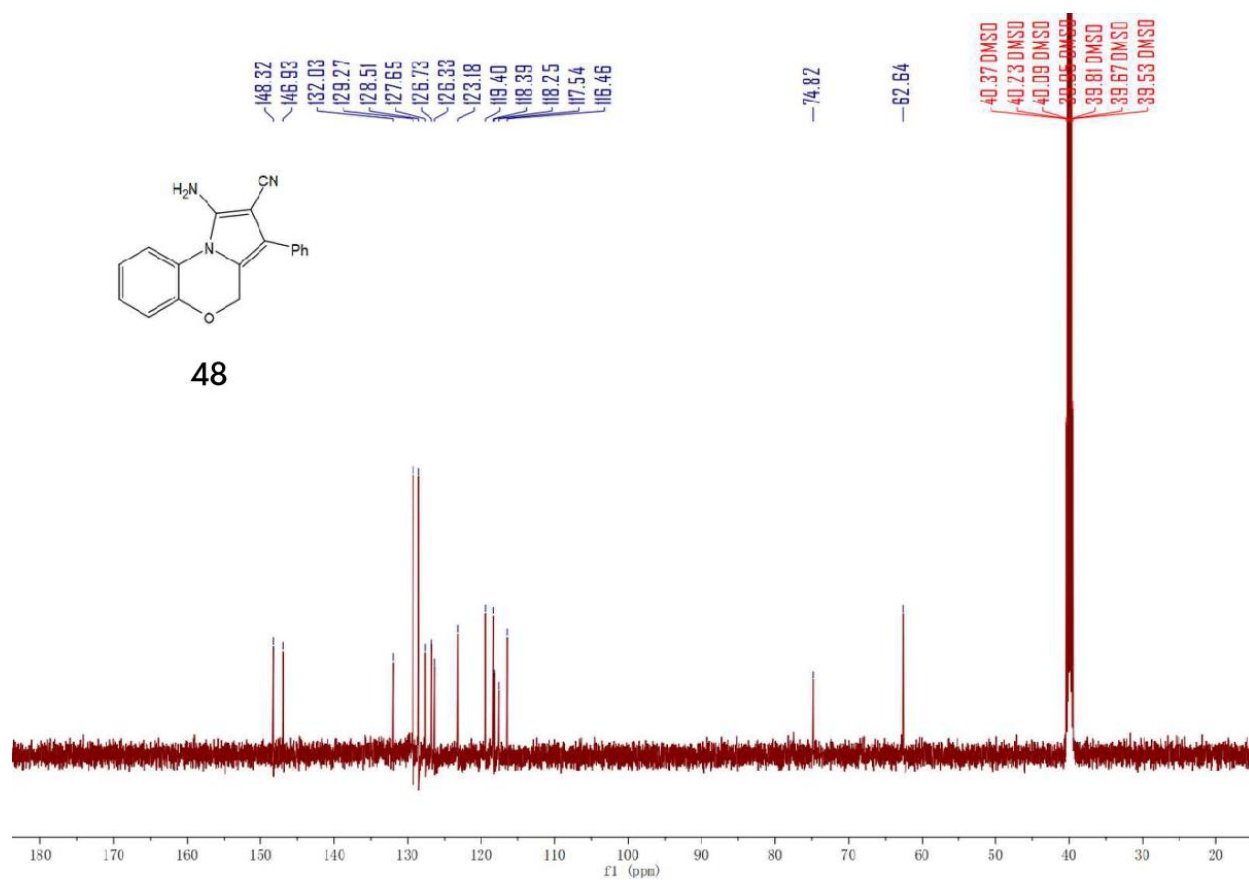


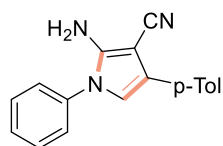




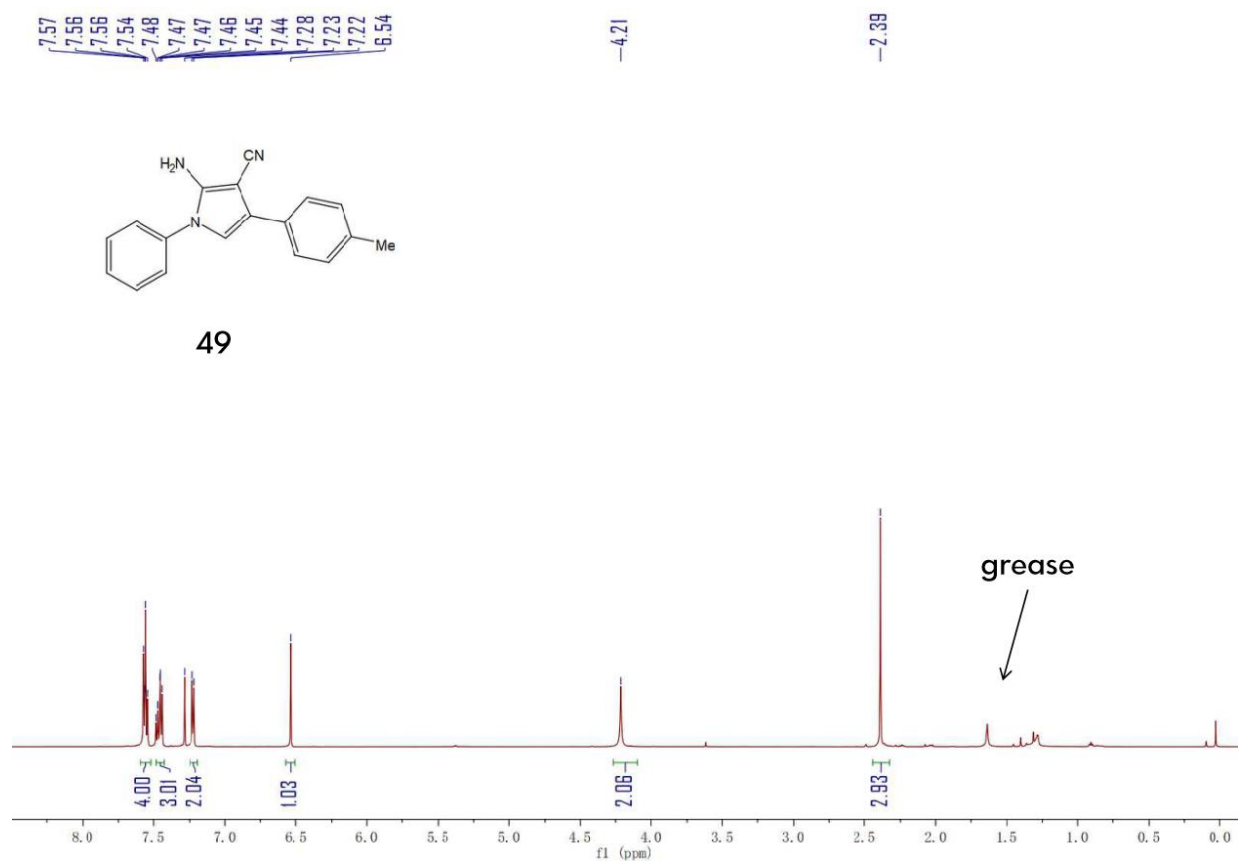
48 The reaction was set up following the general procedure using 3,4-dihydro-2H-1,4-benzoxazine (135 mg, 1 mmol) and benzylidenemalononitrile (31 mg, 0.2 mmol). After 16 hours, the reaction was purified following general work-up to give 29 mg (51 % yield) of the title compound. **¹H NMR** (600 MHz, DMSO-*d*₆) 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); **¹³C 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]⁺ (C₁₈H₁₄N₃O) requires *m/z* 288.1, found *m/z* 288.1.

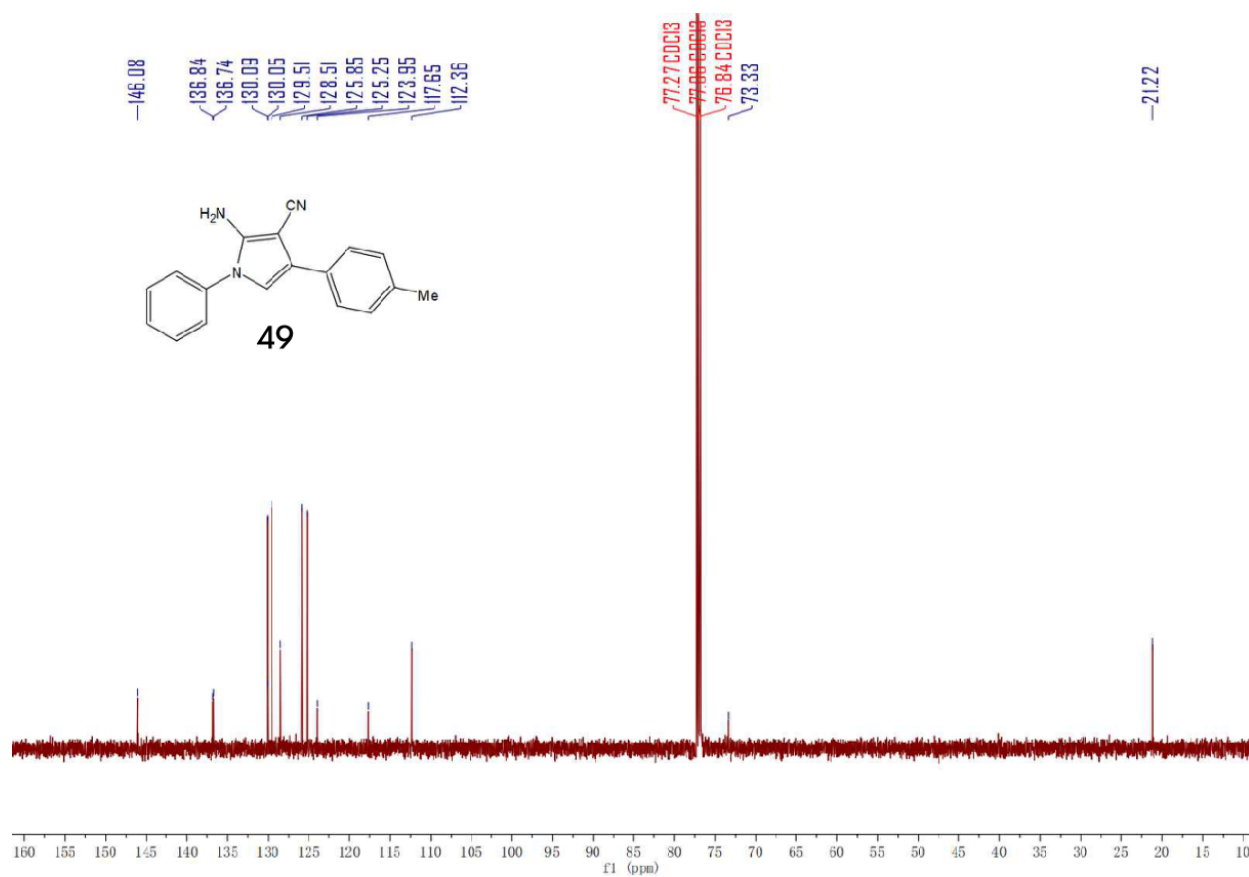


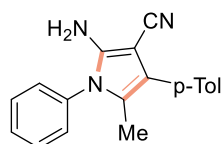




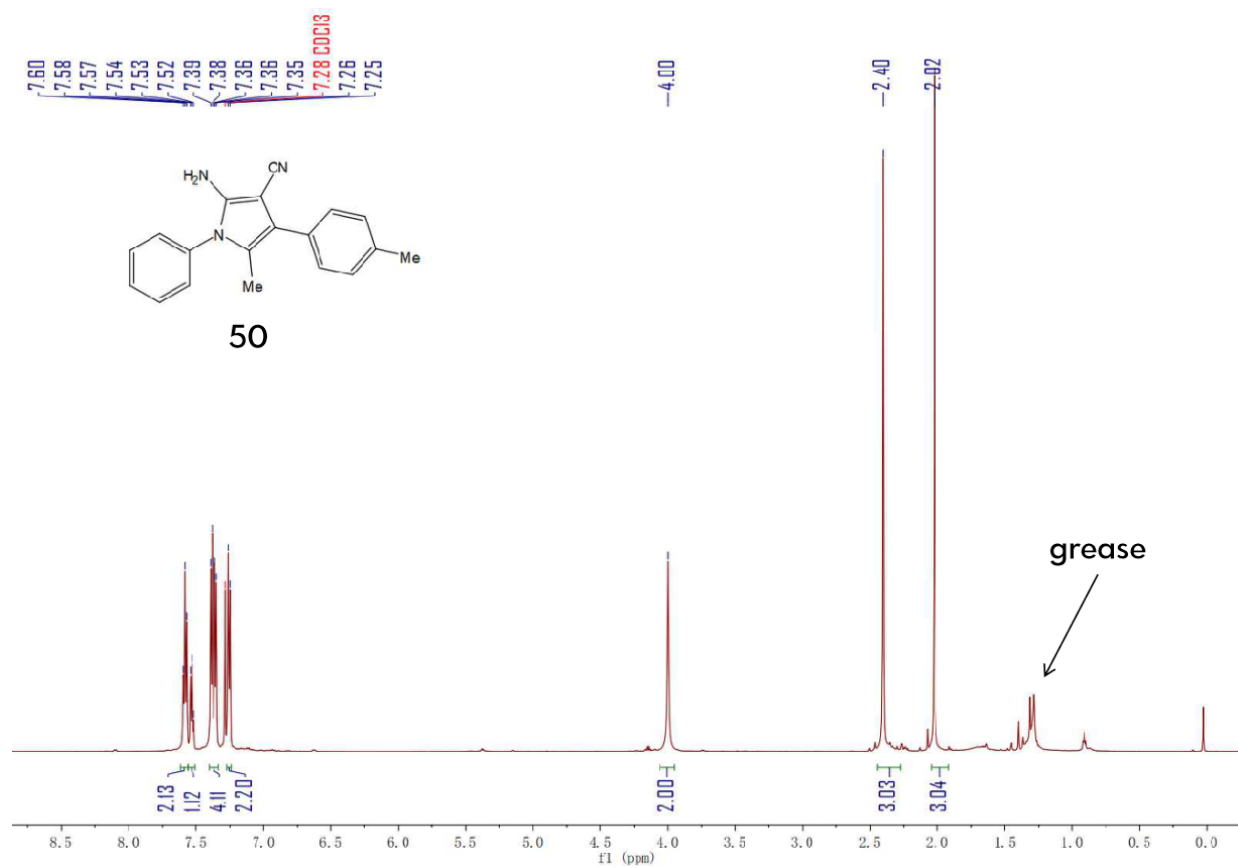
49 The reaction was set up following the general procedure using N-methylaniline (107 mg, 1 mmol) and 4-methylbenzylidenemalononitrile (34 mg, 0.2 mmol). After 16 hours, the reaction was purified following general work-up to give 39 mg (72 % yield) of the title compound. **¹H NMR** (600 MHz, Chloroform-*d*) 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); **¹³C 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]⁺ (C₁₈H₁₆N₃) requires m/z 274.1, found m/z 274.1.

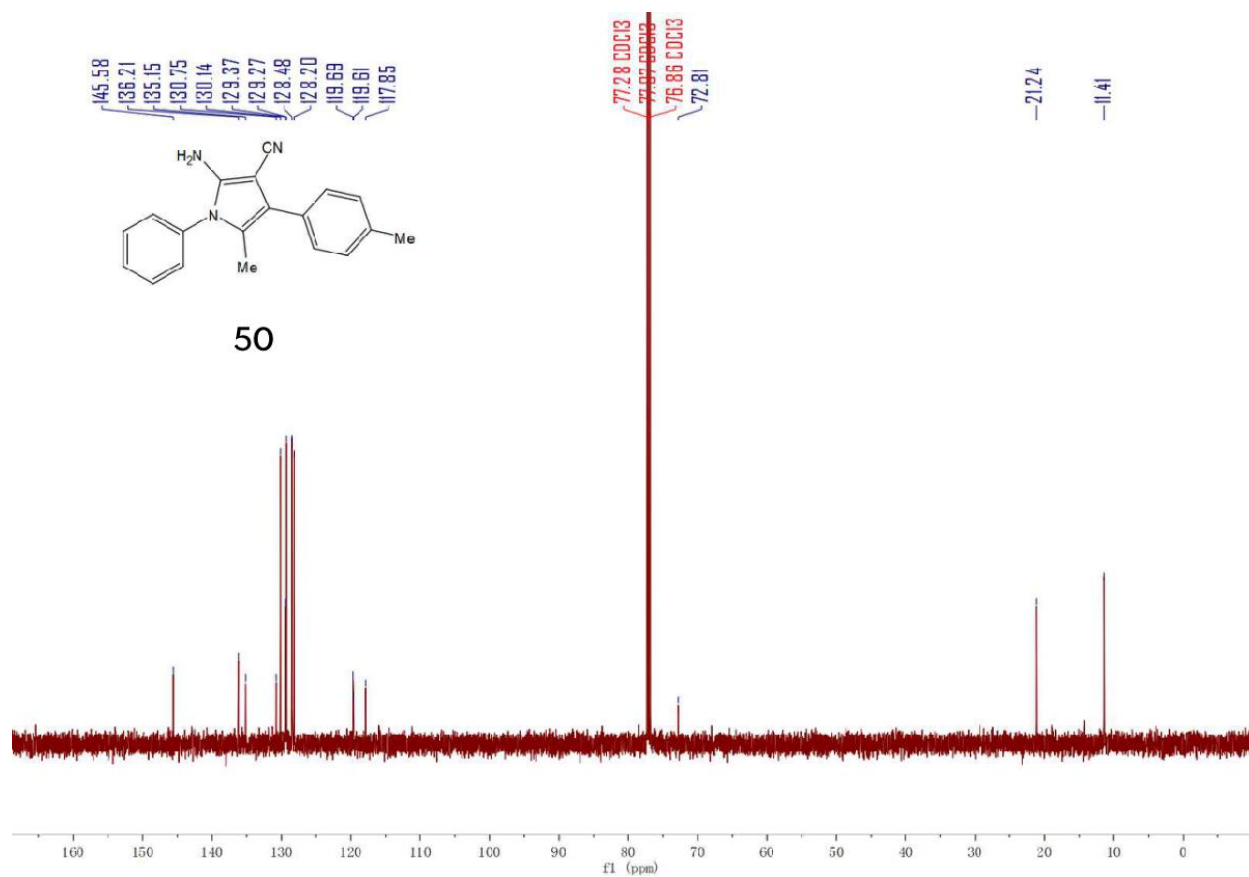


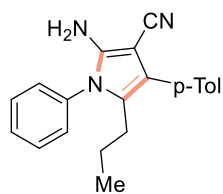




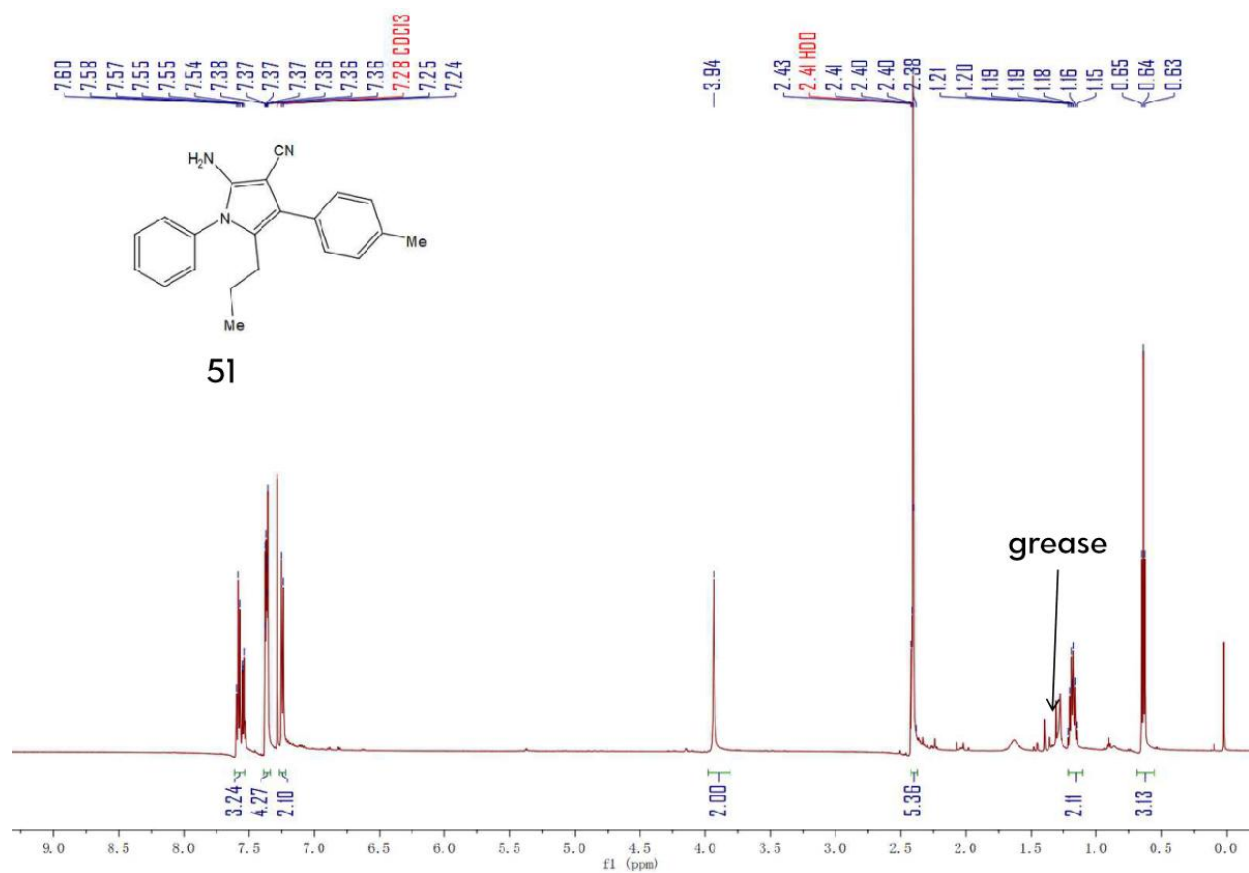
50 The reaction was set up following the general procedure using N-ethylaniline (121 mg, 1 mmol) and 4-methylbenzylidenemalononitrile (34 mg, 0.2 mmol). After 16 hours, the reaction was purified following general work-up to give 45 mg (79 % yield) of the title compound. **¹H NMR** (600 MHz, Chloroform-*d*) 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); **¹³C 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]⁺ (C₁₉H₁₈N₃) requires m/z 288.1, found m/z 288.1.

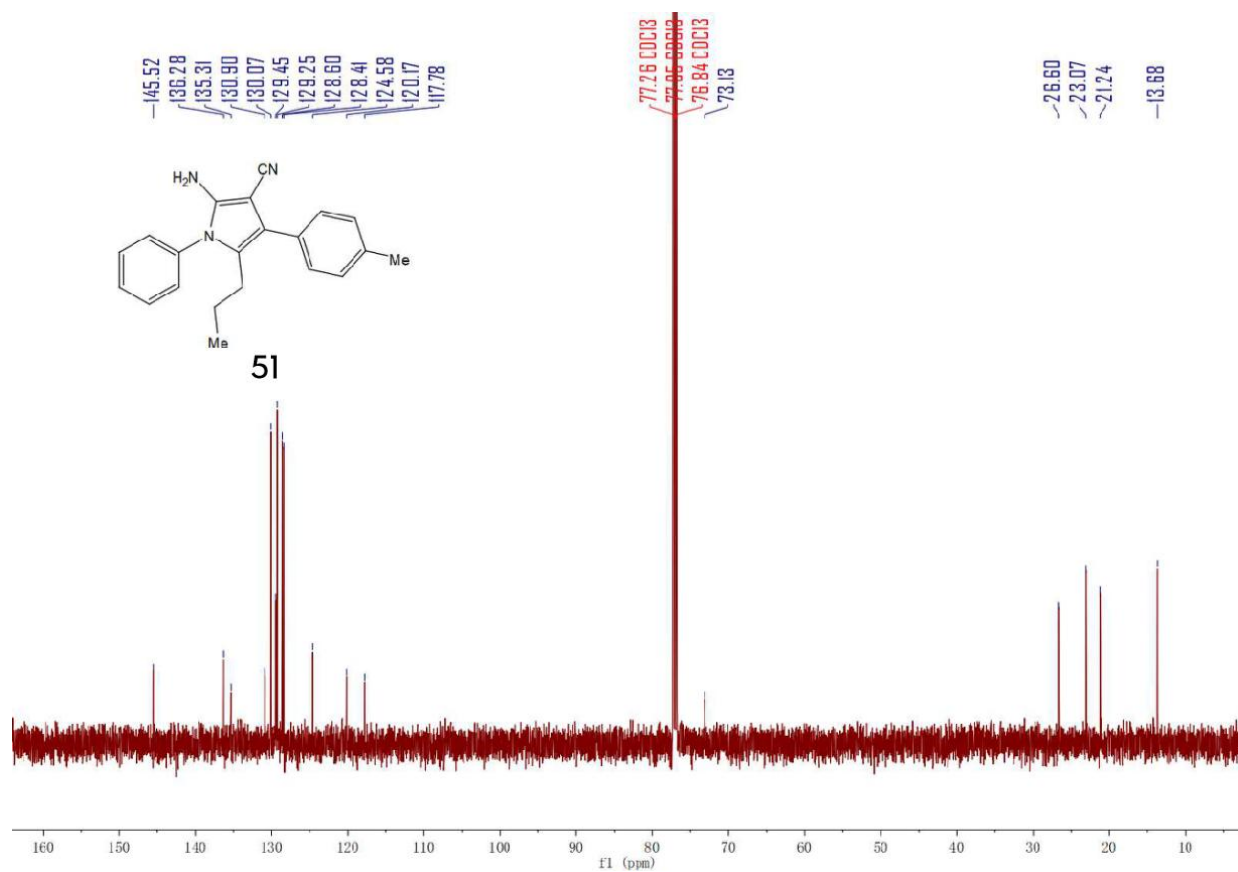


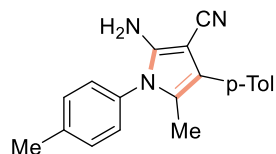




51 The reaction was set up following the general procedure using N-butylaniline (149 mg, 1 mmol) and 4-methylbenzylidenemalononitrile (34 mg, 0.2 mmol). After 16 hours, the reaction was purified following general work-up to give 28 mg (44 % yield) of the title compound. **¹H NMR** (600 MHz, Chloroform-*d*) 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); **¹³C 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]⁺ (C₂₁H₂₂N₃) requires m/z 316.1, found m/z 316.1.

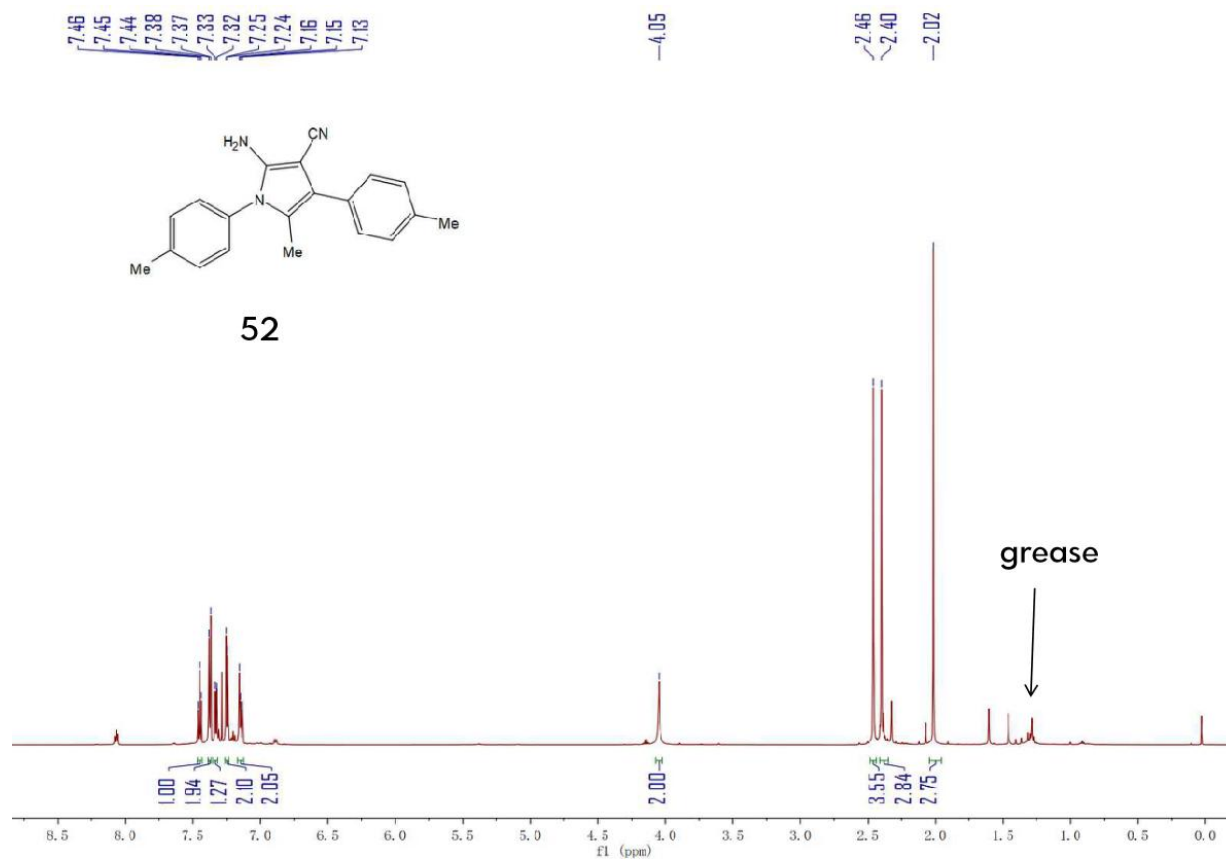


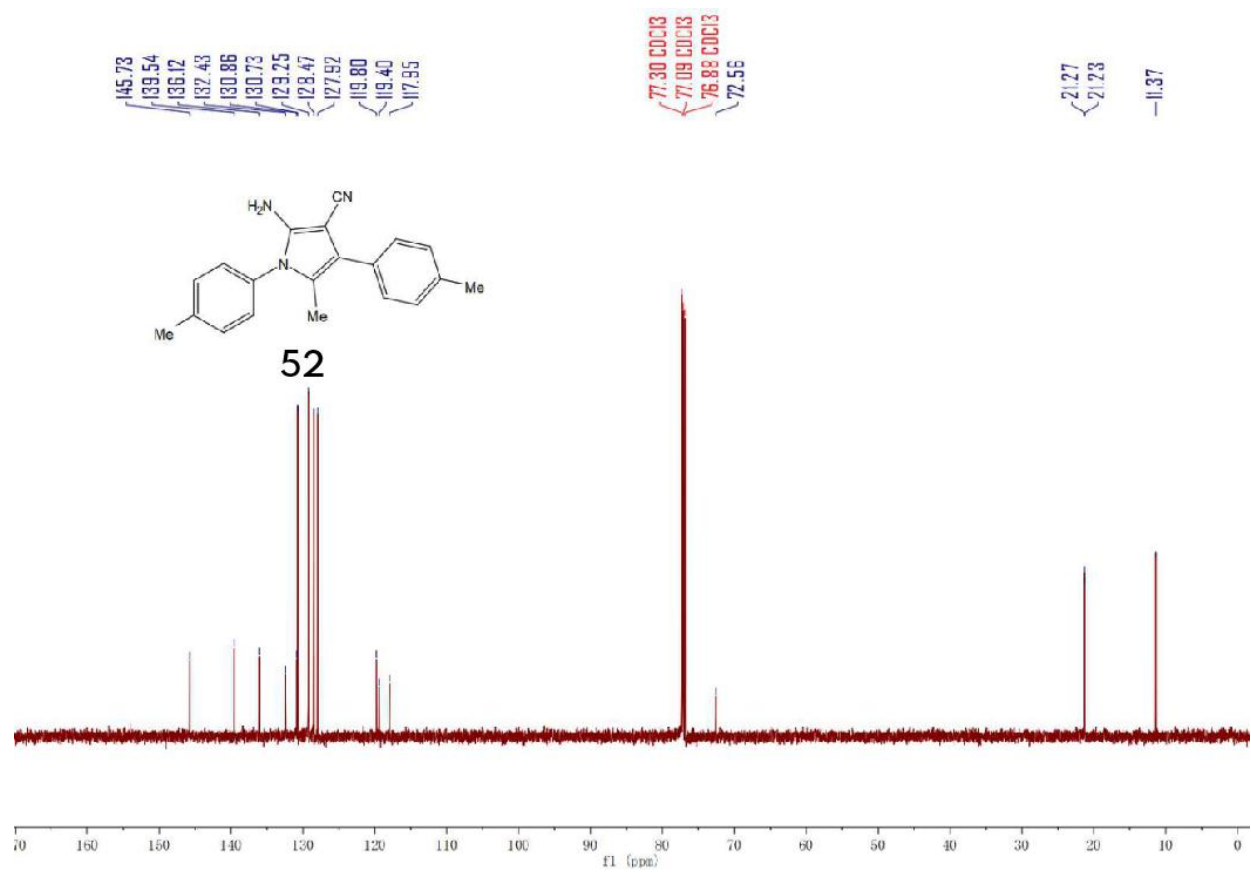


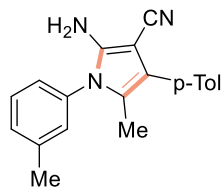


52

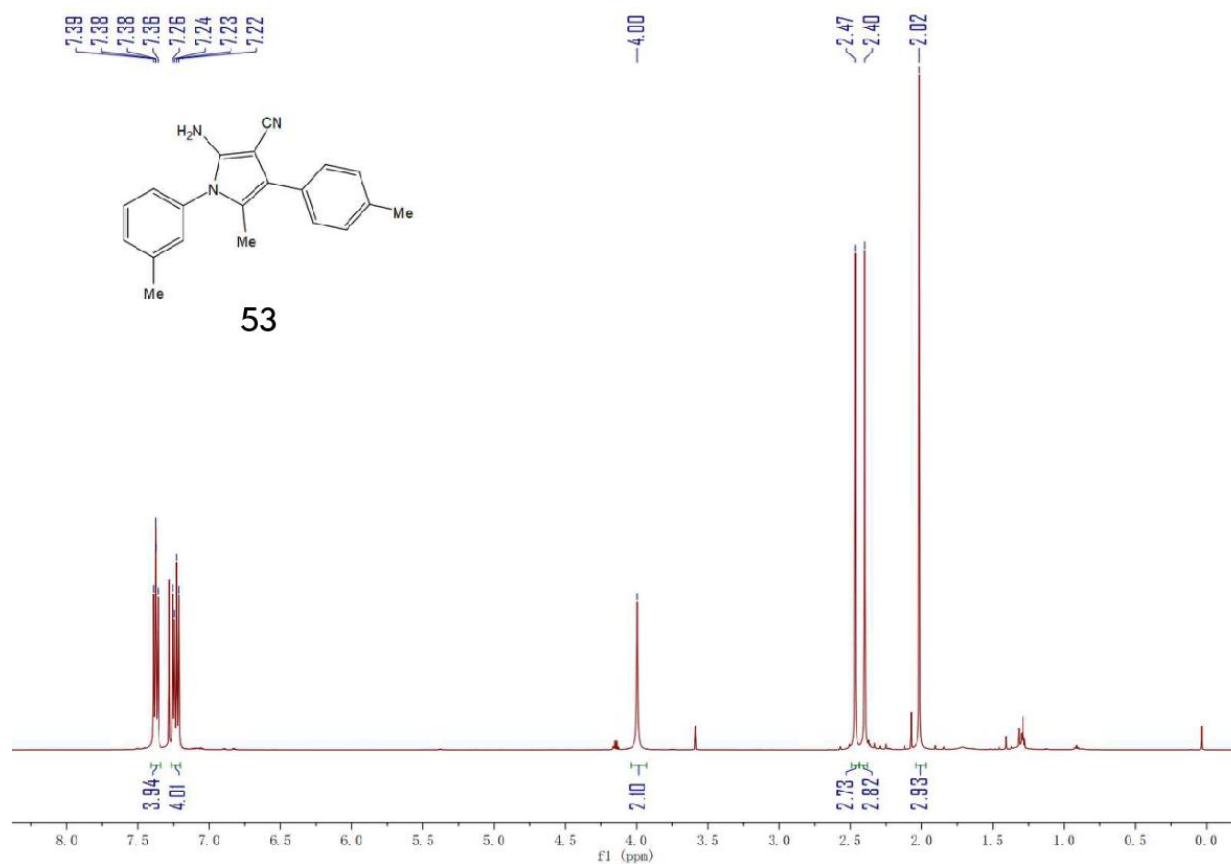
The reaction was set up following the general procedure using 3-methyl-N-ethylbenzenamine (135 mg, 1 mmol) and 4-methylbenzylidenemalononitrile (34 mg, 0.2 mmol). After 16 hours, the reaction was purified following general work-up to give 40 mg (66 % yield) of the title compound. **¹H NMR** (600 MHz, 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); **¹³C 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]⁺ (C₂₀H₂₀N₃) requires m/z 302.1, found m/z 302.1.

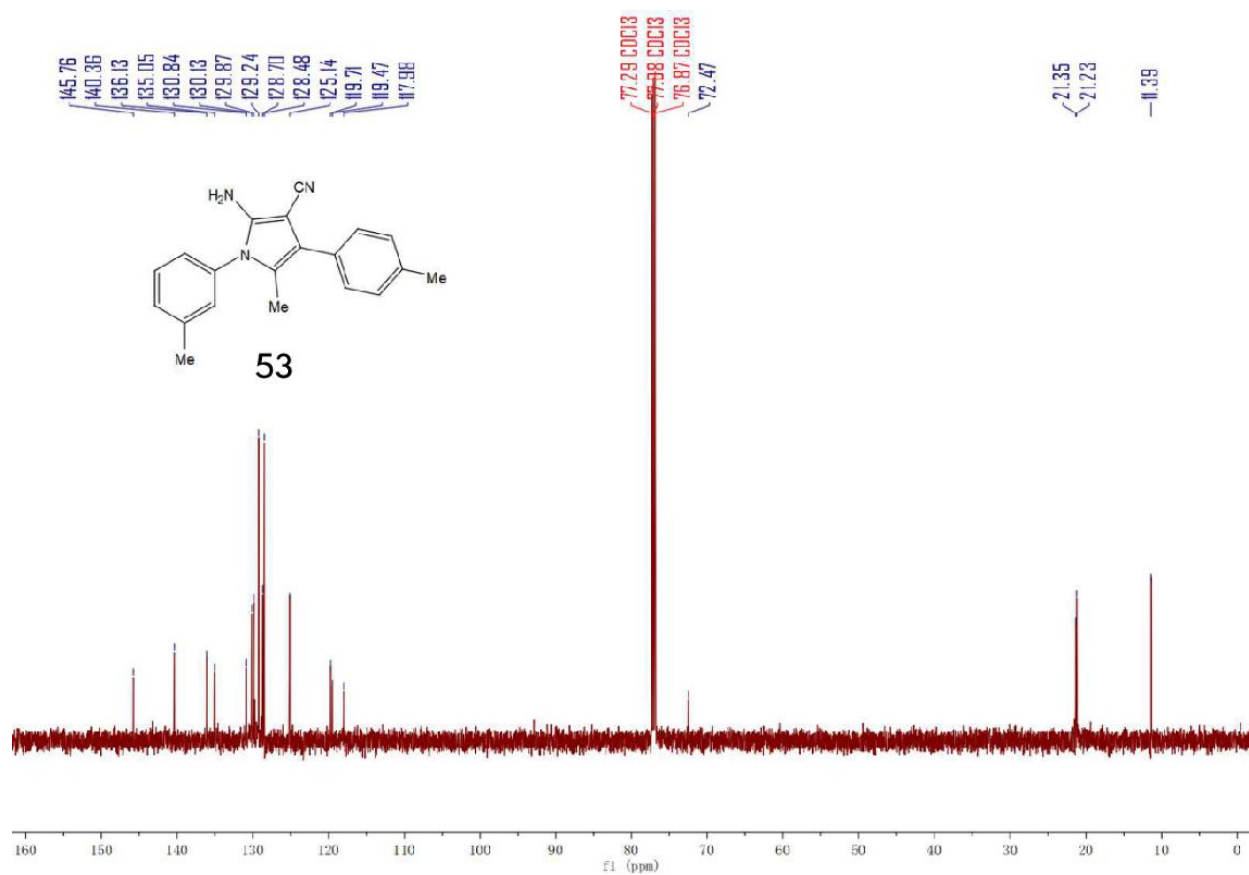


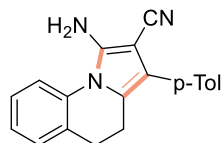




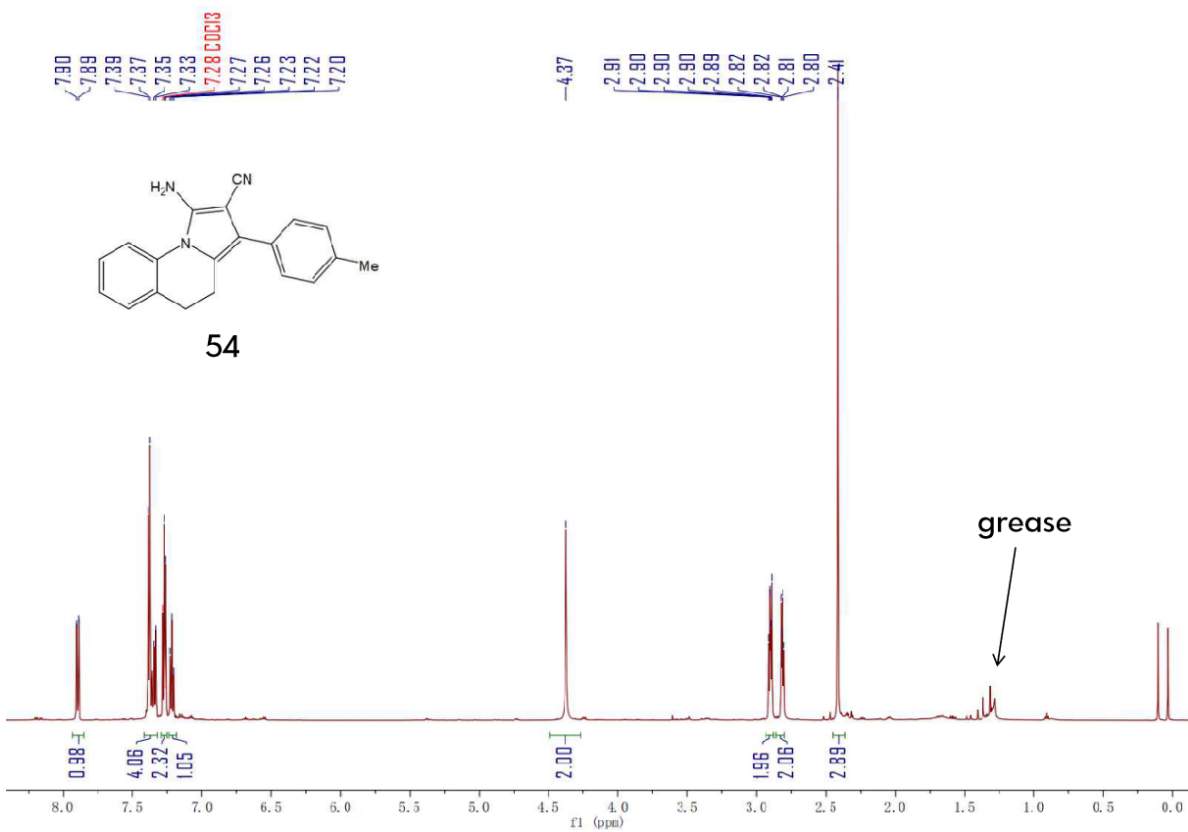
53 The reaction was set up following the general procedure using 4-methyl-N-ethylbenzenamine (135 mg, 1 mmol) and 4-methylbenzylidenemalononitrile (34 mg, 0.2 mmol). After 16 hours, the reaction was purified following general work-up to give 36 mg (58 % yield) of the title compound. **¹H NMR** (600 MHz, 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); **¹³C 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.

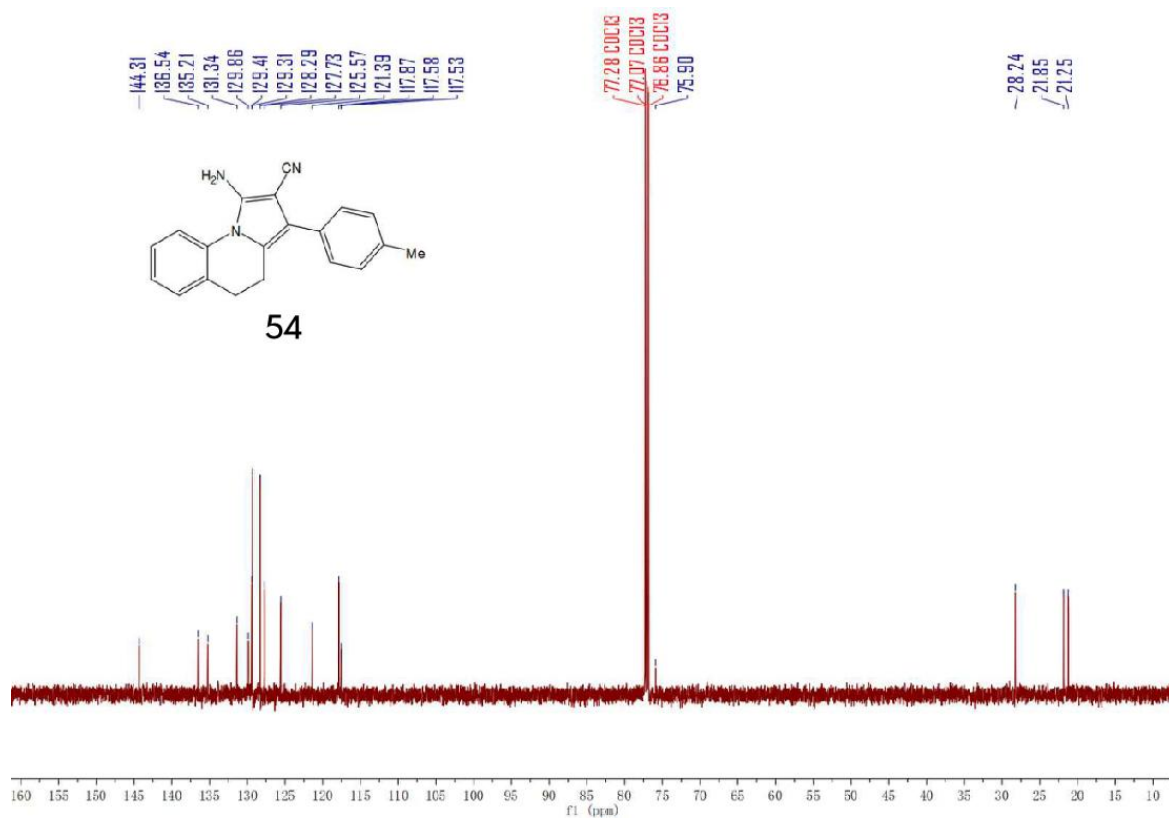


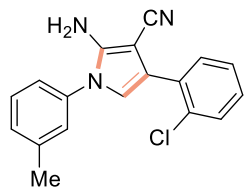




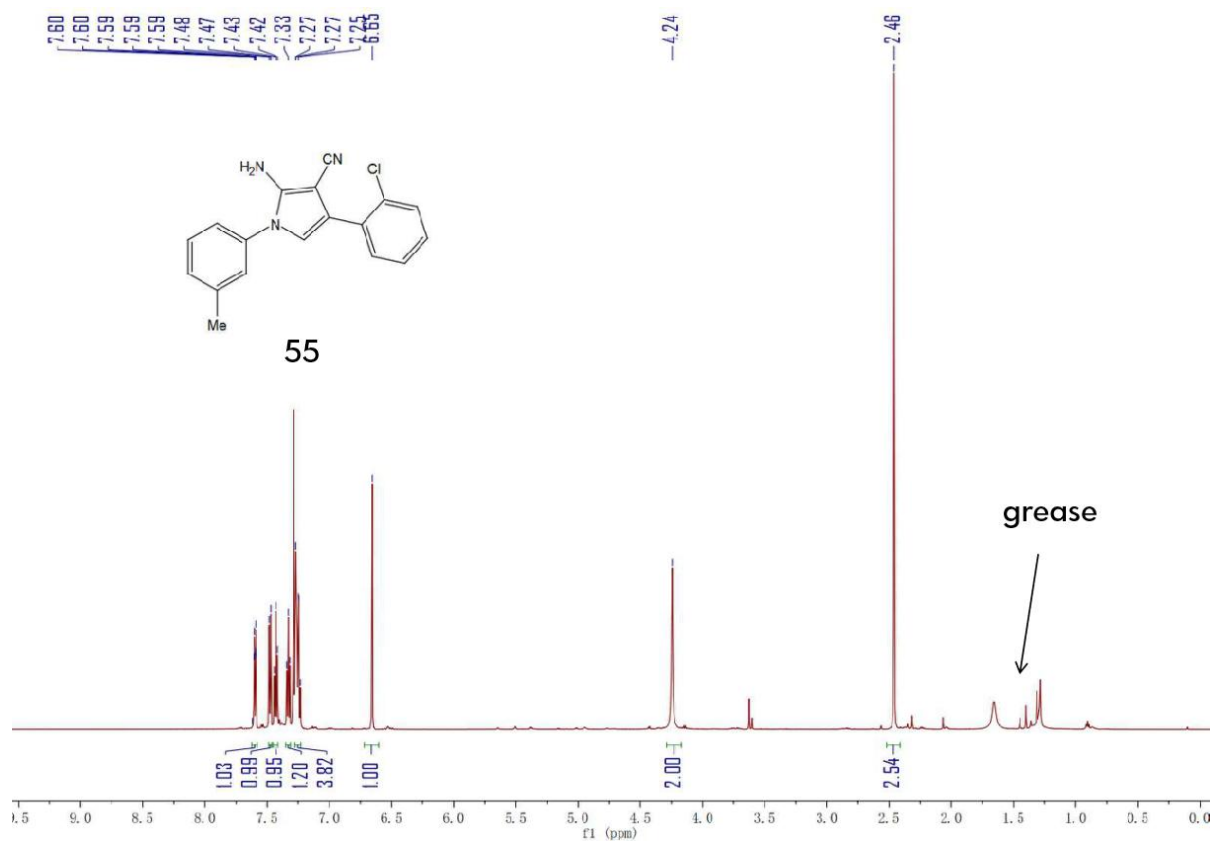
54 The reaction was set up following the general procedure using 1,2,3,4-tetrahydroquinoline (133 mg, 1 mmol) and 4-methylbenzylidenemalononitrile (34 mg, 0.2 mmol). After 16 hours, the reaction was purified following general work-up to give 39 mg (64 % yield) of the title compound. **¹H NMR** (600 MHz, 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); **¹³C 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]⁺ (C₂₀H₁₈N₃) requires m/z 300.1, found m/z 300.1.

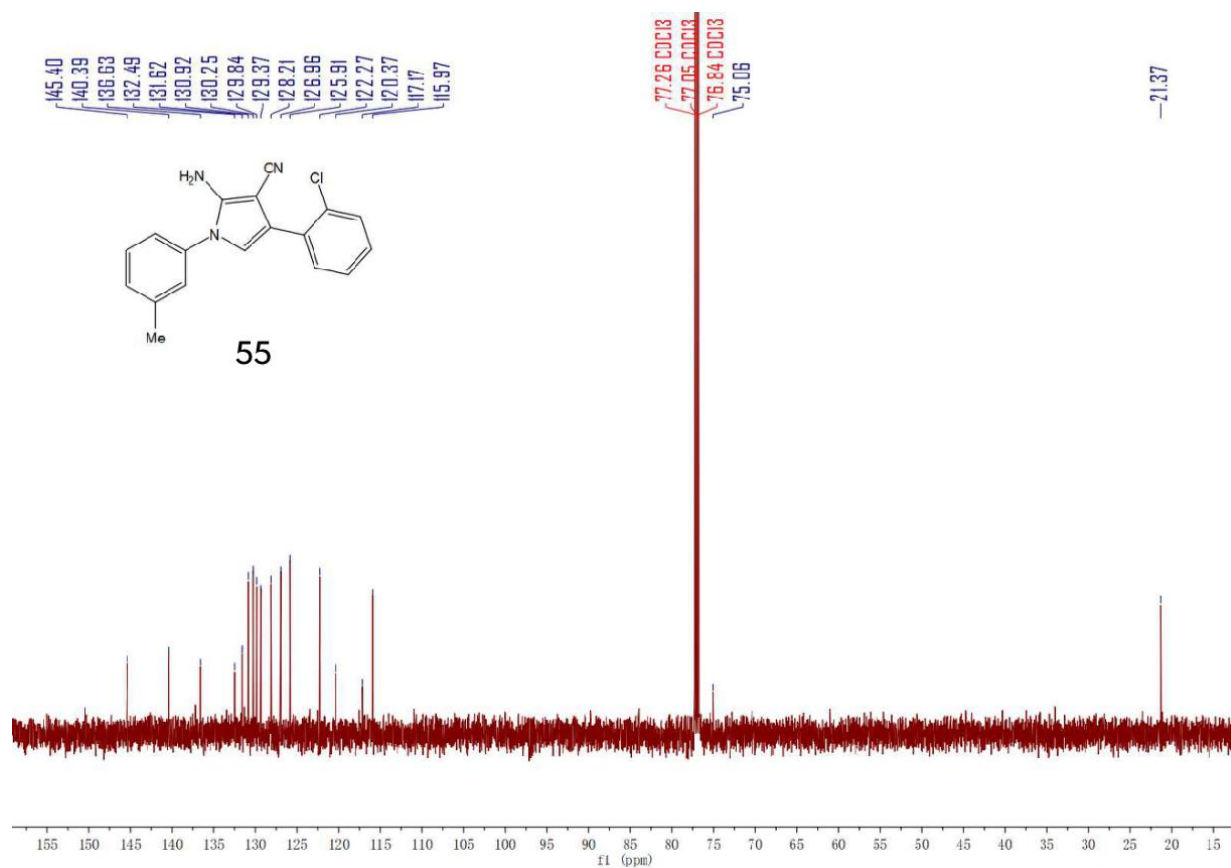


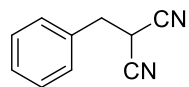




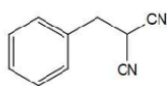
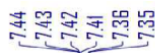
55 The reaction was set up following the general procedure using 3-methyl-N-methylbenzenamine (121 mg, 1 mmol) and 2-chlorobenzylidenemalononitrile (38 mg, 0.2 mmol). After 16 hours, the reaction was purified following general work-up to give 29 mg (46 % yield) of the title compound. **¹H NMR** (600 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); **¹³C 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]⁺ (C₁₈H₁₅ClN₃) requires m/z 308.1, found m/z 308.1.







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).



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