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# Catalytic selective oxidative coupling of secondary *N*-alkyl anilines: an approach to azoxyarene

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**Supporting information**

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## Supporting information

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## I. General Information

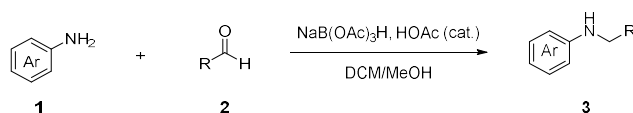
Glassware and stir bars were dried in an oven at 70 °C for at least 12h and then cooled in a desiccator cabinet over Drierite prior to use. Optimization and substrate screen were performed in 20 mL vials. All other reactions were performed in round-bottom flasks sealed with rubber septa. Plastic syringes or pipets were used to transfer liquid reagents. Reactions were stirred magnetically using Teflon-coated, magnetic stir bars. Analytical thin-layer chromatography (TLC) was performed using glass plates pre-coated with 0.25 mm of 230–400 mesh silica gel impregnated with a fluorescent indicator (254 nm and 320 nm). TLC plates were visualized by exposure to ultraviolet light and/or exposure to KMnO<sub>4</sub> stain as well as phosphomolydic acid (PMA) and cerium molybdate stain. Organic solutions were concentrated under reduced pressure using a rotary evaporator. Flash-column chromatography was performed on silica gel (60 Å, standard grade).

**Materials and Instrumentation.** Nuclear magnetic resonance spectra were recorded at ambient temperature (unless otherwise stated) on Bruke 400 MHz spectrometers. All values for proton chemical shifts are reported in parts per million ( $\delta$ ) and are referenced to the residual protium in CDCl<sub>3</sub> ( $\delta$  7.26), CD<sub>3</sub>OD ( $\delta$  3.31) and DMSO-D<sub>6</sub> ( $\delta$  2.50). All values for carbon chemical shifts are reported in parts per million ( $\delta$ ) and are referenced to the carbon resonances in CDCl<sub>3</sub> ( $\delta$  77.0), CD<sub>3</sub>OD (49.00) and DMSO-D<sub>6</sub> (39.52). NMR data are represented as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, quin = quintet, m = multiplet, br = broad), coupling constant (Hz), and integration. Infrared spectroscopic data is reported in wavenumbers (cm<sup>-1</sup>). High-resolution mass spectra was obtained using a liquid chromatography-electrospray ionization and Time-of-flight mass spectrometer.

## II. Starting Materials Preparation

### II-1. General procedure for the preparation of starting materials

**General procedure A** To the mixture of aniline **1** (5 mmol, 1.0 equiv) in DCM/MeOH (30/5mL) was added aldehyde (6.0 mmol, 1.2 equivalent) and HOAc (2 drops, catalytic amount). After stirring for around 2 min, NaB(OAc)<sub>3</sub>H (6.0 mmol, 1.2 equivalent)) was added. The mixture was stirred at room temperature until that aniline **1** was 100% consumed.<sup>1</sup> After completion, the reaction mixture was diluted with EtOAc (120 mL), washed by H<sub>2</sub>O (30 mL×2), NaHCO<sub>3</sub> (aq., 30 mL) and brine (30 mL), followed by being dried by Na<sub>2</sub>SO<sub>4</sub>. The desired product **3** was obtained though flash-chromatography (**Scheme S1**).



**Scheme S1.** General procedure A for *N*-alkyl aniline synthesis

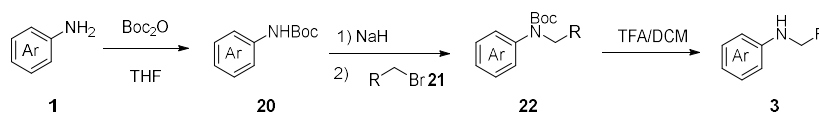
**General procedure B** To the mixture of compound **1** (10.0 mmol, 1.0 equivalent) in DCM (20mL) was added di-tert-butyl dicarbonate ((Boc)<sub>2</sub>O) (11mmol, 1.1 equivalent) compound **1** in THF. Next, the reaction mixture stirred at room temperature for overnight. Removing all the solvents, the crude product **20** was directly used in the following step without purification.

Compound **20** in THF was added into the mixture of NaH (14 mmol, 1.4 equivalent) in dried THF (25 mL). After stirring for around 2h at 0°C, alkylbromide **21** (11 mmol, 1.1 equivalent) was added dropwise, and the reaction solution then stirred from 0°C to room temperature for overnight. The reaction was quenched by adding around 2.0 mL H<sub>2</sub>O, diluted with 150 mL EtOAc, washed with H<sub>2</sub>O (30 mL × 2), brine (30 mL) and dried by Na<sub>2</sub>SO<sub>4</sub>. Compound **22** was obtained as crude mixture after filtration and concentration in *vacuum*, and directly used in the next step.

The compound **22** was slowly added into solvent of TFA (10 mL)/DCM (15 mL). After completion of

<sup>1</sup> Abdel-Magid, A. F.; Carson, K. G.; Harris, B. D.; Maryanoff, C. A.; Shah, R. D. Reductive amination of aldehydes and ketones with sodium triacetoxyborohydride: studies on direct and indirect reductive amination procedures. *J. Org. Chem.* **1996**, *61*, 3849.

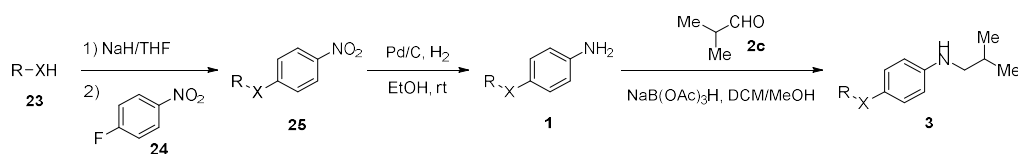
the reaction,  $\text{Na}_2\text{CO}_3$  added and reaction mixture continued stirring for around 2h. Next, EtOAc was added to dilute the reaction mixture, followed by washed with  $\text{H}_2\text{O}$ , brine and dried by  $\text{Na}_2\text{SO}_4$ . The desired product **3** was obtained though flash-chromatography after filtration and concertation in *vacuum* (PE/EA = 150: 1) (**Scheme S2**).



**Scheme S2.** General procedure B for *N*-alkyl aniline synthesis

**General procedure C** NaH (2.5 equivalent) was added into anhydrous THF (15 mL) under  $\text{N}_2$  balloon in one portion at  $0^\circ\text{C}$ . The mixture stirred in ice-water bath for about 15 min until no gas was generated, followed by adding compound **23** (1.0 equivalent) in anhydrous THF (6 mL) dropwise. The reaction mixture continued stirring for another 15 min, followed by adding compound **24** (1.0 equivalent) in THF (5 mL) was added at  $0^\circ\text{C}$ . The reaction then stirred form  $0^\circ\text{C}$  to room temperature for overnight. After compound **24** was all consumed, the reaction mixture was quenched by adding around 0.5 mL  $\text{H}_2\text{O}$  and diluted with 150 mL, washed with  $\text{H}_2\text{O}$  (30mL  $\times$  2), brine (30 mL) and dried by  $\text{Na}_2\text{SO}_4$ . Compound **25** was isolated through flash-chromatography, and directly used in nest step.

To the 250 mL flask was added compound **25**, EtOH (20 mL) and Pd/C (5% wt) in  $\text{H}_2$  gas balloon, and. the reaction mixture was stirred at room temperature for overnight. The crude product **1** was obtained after filtrating and concentration. Finally, compound **3** was obtained in the same procedure as described in **general procedure A** (**Scheme S3**).



**Scheme S3.** General procedure C for *N*-alkyl aniline synthesis

### III. Reaction Condition Optimization

**Table ST1.** Reaction Condition Optimization 1

3a-1  $\xrightarrow[\text{solvent, additive}]{\text{catalyst, oxidant}}$  6aa

Entry	Catalyst (mol %)	Oxidant (equiv)	Solvent (M)	T/°C	Conversion <sup>b</sup>	Yield (%) <sup>a</sup>
<i>Catalyst loading</i>						
1	Na <sub>2</sub> WO <sub>4</sub> ·2H <sub>2</sub> O (5.0)	H <sub>2</sub> O <sub>2</sub> (30%, 3.0)	EtOH	r.t.	>90	56
2	Na <sub>2</sub> WO <sub>4</sub> ·2H <sub>2</sub> O (2.5)	H <sub>2</sub> O <sub>2</sub> (30%, 3.0)	EtOH	r.t.	>90	56
3	Na <sub>2</sub> WO <sub>4</sub> ·2H <sub>2</sub> O (1.0)	H <sub>2</sub> O <sub>2</sub> (30%, 3.0)	EtOH	r.t.	>90	56
(1) 4	Na <sub>2</sub> WO <sub>4</sub> ·2H <sub>2</sub> O (0.5)	H <sub>2</sub> O <sub>2</sub> (30%, 3.0)	EtOH	r.t.	>90	55
<i>Oxidant loading</i>						
5	Na <sub>2</sub> WO <sub>4</sub> ·2H <sub>2</sub> O (2.5)	no oxidant	EtOH	r.t.	N.R	N.R <sup>c</sup>
6	Na <sub>2</sub> WO <sub>4</sub> ·2H <sub>2</sub> O (2.5)	H <sub>2</sub> O <sub>2</sub> (30%, 1.0)	EtOH	r.t.	<50	26
7	Na <sub>2</sub> WO <sub>4</sub> ·2H <sub>2</sub> O (2.5)	H <sub>2</sub> O <sub>2</sub> (30%, 2.0)	EtOH	r.t.	>80	51
8	Na <sub>2</sub> WO <sub>4</sub> ·2H <sub>2</sub> O (2.5)	H <sub>2</sub> O <sub>2</sub> (30%, 3.0)	EtOH	r.t.	>90	61
9	Na <sub>2</sub> WO <sub>4</sub> ·2H <sub>2</sub> O (2.5)	H <sub>2</sub> O <sub>2</sub> (30%, 4.0)	EtOH	r.t.	>90	69
10	Na <sub>2</sub> WO <sub>4</sub> ·2H <sub>2</sub> O (2.5)	H <sub>2</sub> O <sub>2</sub> (30%, 5.0)	EtOH	r.t.	>90	72
11	Na <sub>2</sub> WO <sub>4</sub> ·2H <sub>2</sub> O (2.5)	H <sub>2</sub> O <sub>2</sub> (30%, 6.0)	EtOH	r.t.	>90	71
<i>Catalyst</i>						
11	Na <sub>2</sub> WO <sub>4</sub> ·H <sub>2</sub> O (2.5)	H <sub>2</sub> O <sub>2</sub> (30%, 5.0)	EtOH	r.t.	>90	75
12	(NH <sub>4</sub> ) <sub>10</sub> [H <sub>2</sub> W <sub>12</sub> O <sub>42</sub> ]xH <sub>2</sub> O (2.5)	H <sub>2</sub> O <sub>2</sub> (30%, 5.0)	EtOH	r.t.	>90	78
13	CaWO <sub>4</sub> (2.5)	H <sub>2</sub> O <sub>2</sub> (30%, 5.0)	EtOH	r.t.	>90	66
14	K <sub>2</sub> WO <sub>4</sub> (2.5)	H <sub>2</sub> O <sub>2</sub> (30%, 5.0)	EtOH	r.t.	>90	77
15	H <sub>3</sub> PW <sub>12</sub> O <sub>40</sub> (2.5)	H <sub>2</sub> O <sub>2</sub> (30%, 5.0)	EtOH	r.t.	<50	N.D
16	TBAT (2.5)	H <sub>2</sub> O <sub>2</sub> (30%, 5.0)	EtOH	r.t.	<50	N.D
17	CuCl (2.5)	H <sub>2</sub> O <sub>2</sub> (30%, 5.0)	EtOH	r.t.	N.R	--
18	FeCl <sub>3</sub> (2.5)	H <sub>2</sub> O <sub>2</sub> (30%, 5.0)	EtOH	r.t.	N.R	--
<i>Oxidant</i>						
19	APT (2.5)	H <sub>2</sub> O <sub>2</sub> (30%, 5.0)	EtOH	r.t.	>90	73
20	APT (2.5)	2Na <sub>2</sub> CO <sub>3</sub> ·3H <sub>2</sub> O <sub>2</sub>	EtOH	r.t.	N.R	--
21	APT (2.5)	2Na <sub>2</sub> CO <sub>3</sub> ·3H <sub>2</sub> O <sub>2</sub>	EtOH/H <sub>2</sub> O	r.t.	<50	N.D
22	APT (2.5)	<sup>t</sup> BuOOH (5.0)	EtOH	r.t.	<10	N.D
23	APT (2.5)	CO(NH <sub>2</sub> ) <sub>2</sub> ·H <sub>2</sub> O <sub>2</sub> (5.0)	EtOH	r.t.	>90	73

a. all the reactions were set up the reaction in the open air with 2.0 mmol **1a**, rt for 24, isolated yield; b. based on TLC analysis; c. N.R = No Reaction; N.D = Not determined; APT = (NH<sub>4</sub>)<sub>10</sub>[H<sub>2</sub>W<sub>12</sub>O<sub>42</sub>]xH<sub>2</sub>O

**Table ST2. Reaction Condition Optimization 2**

3a-1  $\xrightarrow[\text{solvent additive}]{\text{catalyst, oxidant}}$  6aa

Entry	Catalyst (mol %)	Oxidant (equiv)	Solvent (M)	T/°C	Conversion(%) <sup>b</sup>	Yield (%) <sup>a</sup>
<i>Solvent</i>						
24	Na <sub>2</sub> WO <sub>4</sub> ·H <sub>2</sub> O (2.5)	H <sub>2</sub> O <sub>2</sub> (30%, 5.0)	MeOH	rt.	>90	71
25	Na <sub>2</sub> WO <sub>4</sub> ·H <sub>2</sub> O (2.5)	H <sub>2</sub> O <sub>2</sub> (30%, 5.0)	EtOH	rt.	>90	77
26	Na <sub>2</sub> WO <sub>4</sub> ·H <sub>2</sub> O (2.5)	H <sub>2</sub> O <sub>2</sub> (30%, 5.0)	EtOAc	rt.	>90	45
27	Na <sub>2</sub> WO <sub>4</sub> ·H <sub>2</sub> O (2.5)	H <sub>2</sub> O <sub>2</sub> (30%, 5.0)	DCM	rt.	<80	22
28	Na <sub>2</sub> WO <sub>4</sub> ·H <sub>2</sub> O (2.5)	H <sub>2</sub> O <sub>2</sub> (30%, 5.0)	MeCN	rt.	>90	65
29	Na <sub>2</sub> WO <sub>4</sub> ·H <sub>2</sub> O (2.5)	H <sub>2</sub> O <sub>2</sub> (30%, 5.0)	THF	rt.	>90	68
30	Na <sub>2</sub> WO <sub>4</sub> ·H <sub>2</sub> O (2.5)	H <sub>2</sub> O <sub>2</sub> (30%, 5.0)	Toluene	rt.	<50	N.D
31	Na <sub>2</sub> WO <sub>4</sub> ·H <sub>2</sub> O (2.5)	H <sub>2</sub> O <sub>2</sub> (30%, 5.0)	DMF	rt.	<50	N.D
<i>additive (rt in EtOH)</i>						
32	APT (2.5)	H <sub>2</sub> O <sub>2</sub> (30%, 5.0)	NaOH		<10	N.D
33	APT (2.5)	H <sub>2</sub> O <sub>2</sub> (30%, 5.0)	Na <sub>2</sub> CO <sub>3</sub>		<80	66
34	APT (2.5)	H <sub>2</sub> O <sub>2</sub> (30%, 5.0)	NaHCO <sub>3</sub>		>90	74
35	APT (2.5)	H <sub>2</sub> O <sub>2</sub> (30%, 5.0)	NH <sub>4</sub> HCO <sub>3</sub>		>90	75
36	APT (2.5)	H <sub>2</sub> O <sub>2</sub> (30%, 5.0)	PhCOOH		>90	69
37	APT (2.5)	H <sub>2</sub> O <sub>2</sub> (30%, 5.0)	Pyridine		>90	76

a. all the reactions were set up the reaction in the open air with 2.0 mmol **1a**, rt. 24h, isolated yield; b. based on TLC analysis; c. N.R = No Reaction; N.D = not determined; APT = (NH<sub>4</sub>)<sub>10</sub>[H<sub>2</sub>W<sub>12</sub>O<sub>42</sub>]·xH<sub>2</sub>O

**Table ST3. Condition optimization for cross coupling**

3j + 3d  $\xrightarrow[\text{H}_2\text{O}_2 (5.0 \text{ equiv}), \text{EtOH}, \text{rt}]{\text{APT (2.5 mol \%)}}$  6jd

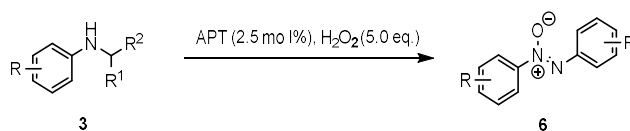
entry	3j (equiv)	3d (equiv)	yield (%) <sup>a</sup>		
			6jd (rr)	6jj	6dd
1	1.0	1.0	28(1.4:1)	11	24
2	R <sup>2</sup> =  (3j)	R <sup>3</sup> =  (3d)	51(1.4:1)	32	7
3	1.0	2.0	27(1.4:1)	N.D	N.D
4	2.0	R <sup>3</sup> = H (3d-2)	5(1.4:1)	N.D	N.D
5	R <sup>2</sup> =  (3j-2)	R <sup>3</sup> =  (3d)	34(1.4:1)	N.D	N.D

a. All the reactions were conducted in 1.0 mmol scale of limiting starting material, isolated yield; N.D = Not determined; rr = regioselectivity ratio

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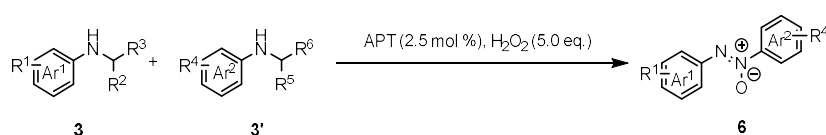
#### IV. General procedure for preparation of azoxyarene from oxidative coupling of secondary *N*-alkyl aniline

**IV-1. General procedure D: Oxidative Homocoupling of *N*-alkyl aniline** To the mixture of compound **3** (2.0 mmol) in 5.0 mL EtOH was added catalyst APT ((NH<sub>4</sub>)<sub>10</sub>[H<sub>2</sub>W<sub>12</sub>O<sub>42</sub>]xH<sub>2</sub>O, 153 mg, 2.5 mol %) and H<sub>2</sub>O<sub>2</sub> (30%, aq., 5.0 equivalent, 1.0 mL) at room temperature. Next, the mixture stirred at room temperature for 8-24h. After completion, the reaction mixture was then diluted with around 100 mL EtOAc and washed with H<sub>2</sub>O and brine, dried by Na<sub>2</sub>SO<sub>4</sub>. Compound **6** was isolated by flash chromatography (PE/EA = 100:1) after filtration and concentration (**Scheme S4**).



**Scheme S4.** General procedure for homo-coupling of secondary *N*-alkyl aniline

**IV-2. General procedure E: Oxidative Cross-coupling of *N*-alkyl aniline** The oxidative cross coupling of **3** and **3'** followed the same procedure as homocoupling. The ratio (**3**: **3'**) and reaction temperature adjusted subtly for certain substrates (**Scheme S5**).



**Scheme S5.** General procedure for homocoupling

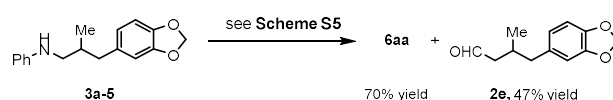
The structures of known azoxyarenes were determined by comparison of H-NMR with reported literatures. The structure of product **6ij** was determined by X-ray analysis, and the structures of other unknown azoxyarenes were assigned by comparison with product **6ij**.



## V. Mechanism study

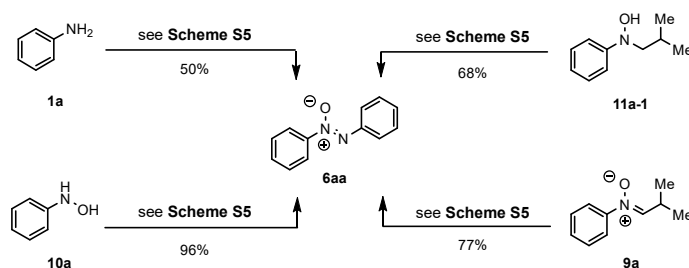
### V-I. Reaction pathway and intermediates confirmation experiments

The intermediates identification reactions were conducted as following. The reaction of substrate **3a-5** (538 mg, 2.0 mmol, 1.0 equivalent) was conducted according to **general procedure D**. After the reaction was finished, except the isolation of the desired product **6aa** (138 mg, 70% yield), aldehyde **2e** (180 mg, 47% yield) was also isolated (**Scheme S6**).



**Scheme S6.** Aldehyde identification experiment

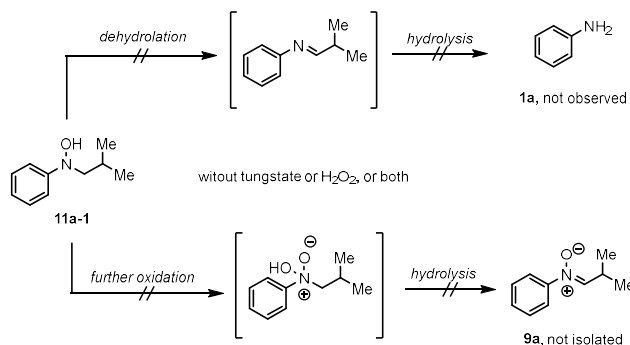
Reactions of anilines **1a**, **10a**, **11a-1** or **9a** (1.0 mmol) were carried out according to **general procedure D**. The desired product **6aa** was obtained by flash chromatography after filtration and concentration (99 mg, 50% yield for **1a**; 95 mg, 96% yield for **10a**; 66 mg, 66% yield for **11a-1**; 76 mg, 77% yield for **9a**) (**Scheme S7**).



**Scheme S7.** Reaction intermediate trapping experiments 2

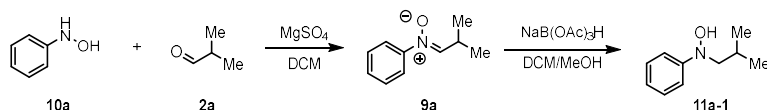
In order to explore the possibility that compound **11a-1** could transfer into nitrone **9a** or aniline **1a**, a control experiment was carried out as following. Compound **11a-1** (1.0 mmol, freshly prepared from **7a** and isobutyraldehyde) was dissolved in EtOH (5.0 mL), followed by adding H<sub>2</sub>O<sub>2</sub> without tungstate catalyst (or adding tungstate without H<sub>2</sub>O<sub>2</sub> or both were not added). To our surprise, the dehydration

procedure seemed not happen and no aniline **1a** was observed by TLC analysis after 24h. Instead, a new spot on TLC plate with the same  $R_f$  (Retardation factor) value as **9a** was observed, but we failed to isolate it (**Scheme S8**).



**Scheme S8.** Possible reaction pathway

Compound **11a-1** and **9a** were synthesized according to following procedure. Compound **10a** and **2a** were added into anhydrous DCM, followed by adding  $\text{MgSO}_4$ . Next, the reaction mixture stirred at room temperature until no **10a** was left. Crude product **9a** was obtained after filtration and concentration, and then was dissolved in anhydrous DCM/MeOH followed by adding  $\text{NaB}(\text{OAc})_3\text{H}$ . After completion, the reaction was quenched by adding  $\text{H}_2\text{O}$  and extracted with EtOAc, followed by being washed with  $\text{H}_2\text{O}$ ,  $\text{NaHCO}_3$  (aq.), brine and dried by  $\text{Na}_2\text{SO}_4$ . Compound **11a-1** was obtained as solid after filtration, concentration and purification by flash-chromatography. Of note, compound **9a** and **11a-1** were not stable in our hands and could not be purified by flash chromatography; therefore, it was used as crude products (**Scheme S9**).

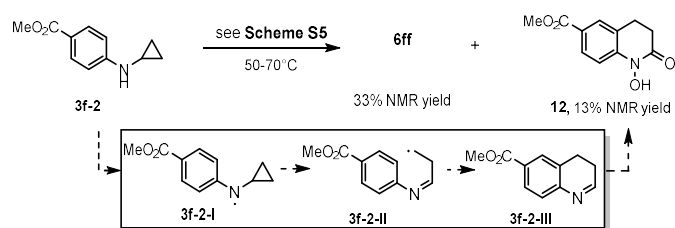


**Scheme S9.** Procedure for synthesis of compound **9a** and **11a-1**

## V-II. Kinetic Study of Reaction

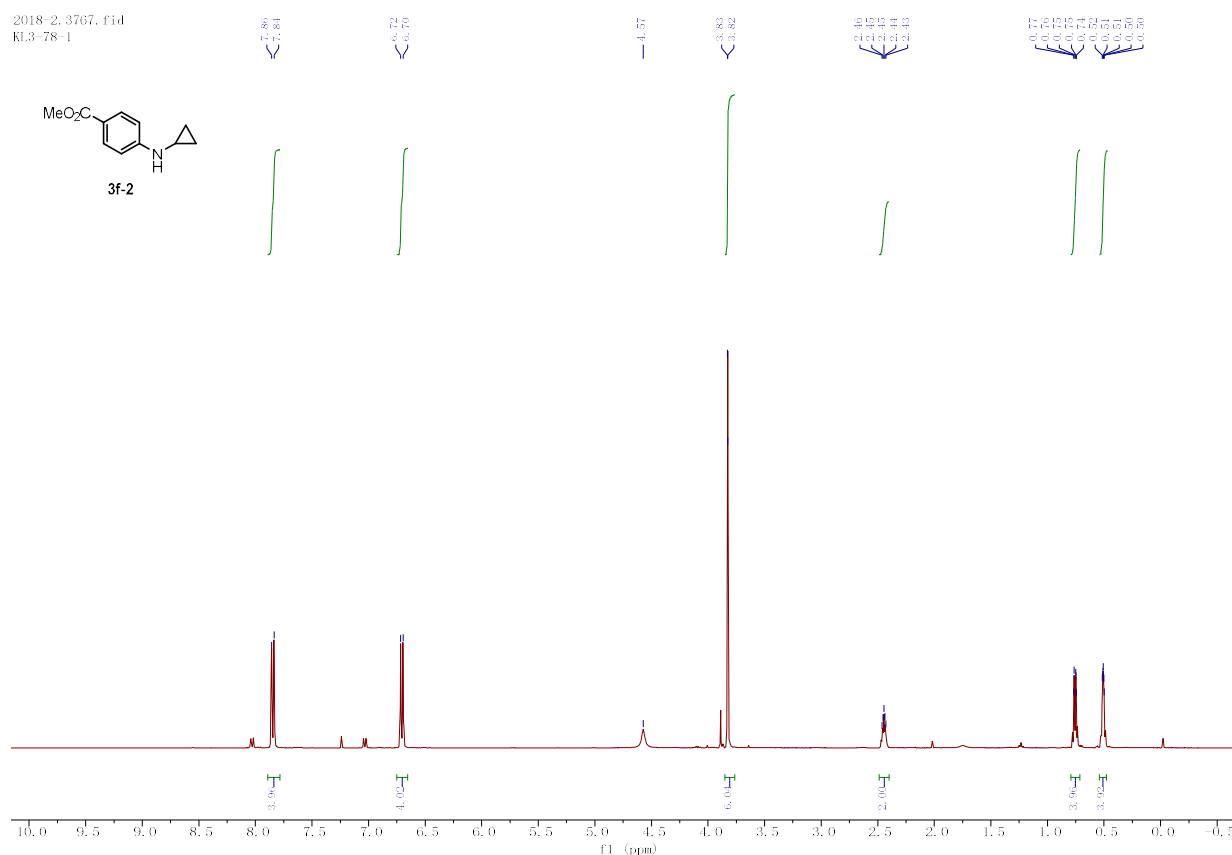
**V-II-1. Radical clock experiment** In order to figure out whether there existed any *N*-radical intermediate, like **3f-1-I** as shown as following, a radical clock experiment was conducted. To the solution

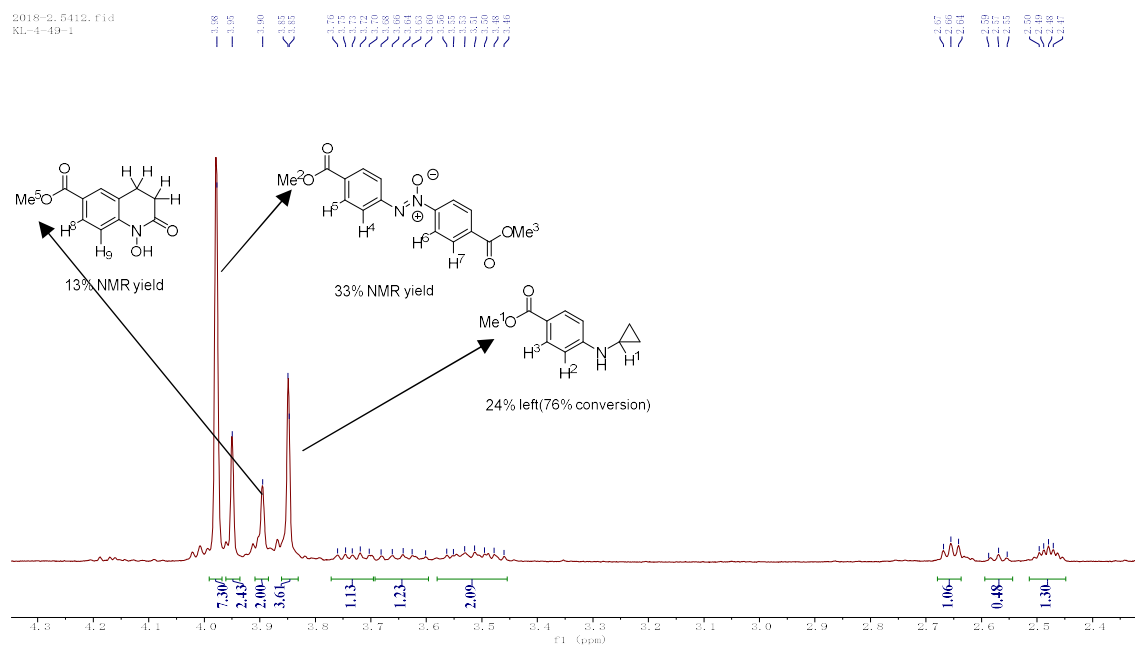
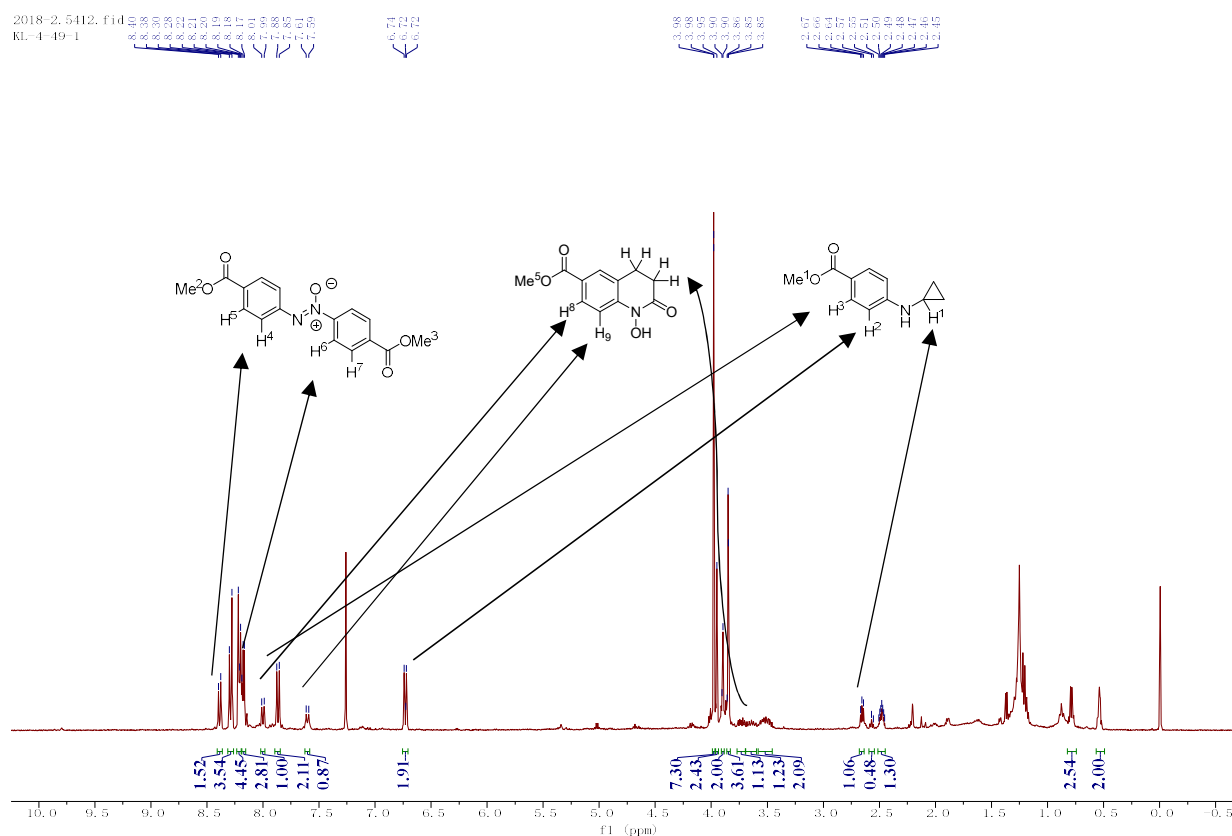
of compound **3f-2** (53 mg, 0.28 mmol, 1.0 equivalent) in EtOH (4 mL) was added APT (21.4 mg, 0.007 mmol, 2.5 mol%) and H<sub>2</sub>O<sub>2</sub> (30% aq., 0.14 mL, 5.0 equiv.) The mixture stirred at 50°C for 24h. Since the reaction proceeded slowly, the reaction was then heated to 70°C at around 50% conversion. Remove all the solvents, and residue was dissolved in EtOAc (30 mL). The mixtures was washed with H<sub>2</sub>O (5.0 mL), NaHCO<sub>3</sub> (5.0 mL), brine (5.0 mL) and dried by Na<sub>2</sub>SO<sub>4</sub>. The crude product was obtained as solid after filtration and concertation, which was directly used for NMR and LC-MS analysis without purification (**Scheme S10**).



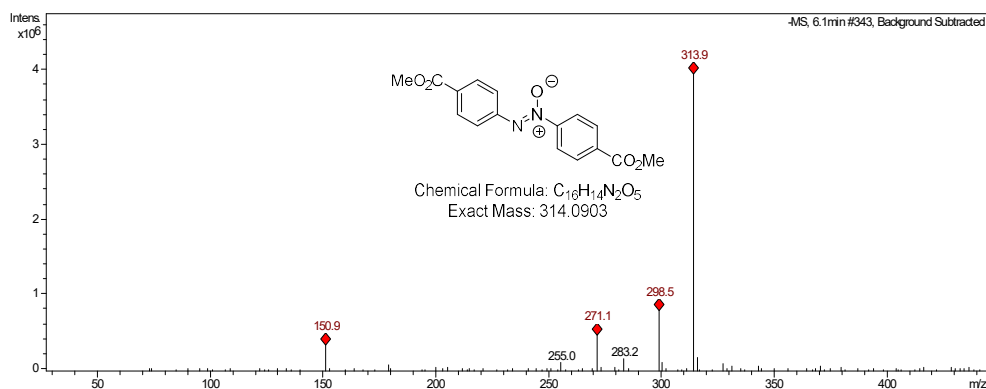
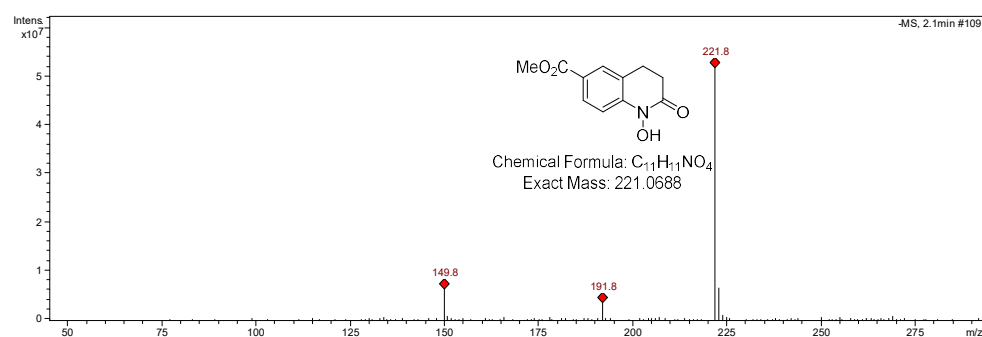
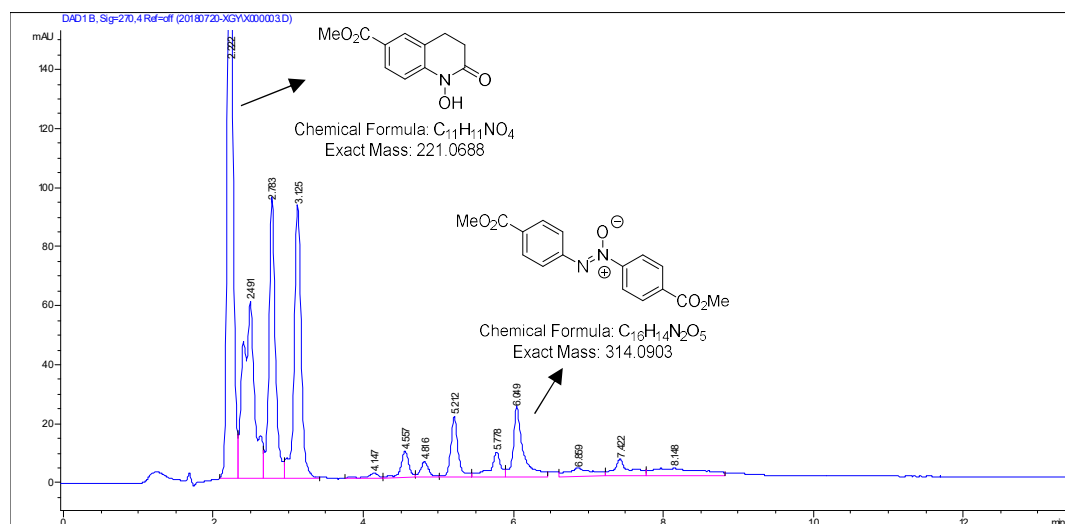
**Scheme S10.** Radical clock experiment

## Radical clock experiment



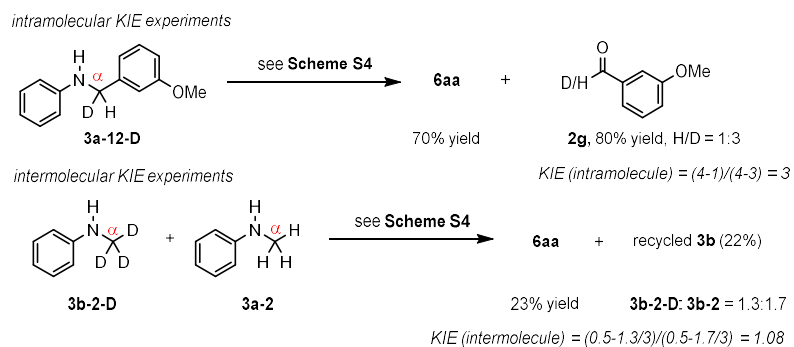


LC-MS of reaction mixture



**V-II-2. KIE (kinetic isotopic effect) Experiments** The intramolecular KIE experiment was conducted with substrate **3a-12-D** according to **general procedure D**. Aldehyde **2g** was isolated as colorless liquid (0.8 mmol scale, 110 mg, 80% yield). The intermolecular KIE experiment was conducted with substrate **3b-2-D** and **3a-2** (1:1 ration, 55 mg and 54 mg respectively, 0.5 mmol scale) with 5.0 equiv. of  $H_2O_2$  as **general procedure D**, and stopped when conversion < 100%. **3b-2-D** and **3a-2** were recycled in 22% yield (**Scheme S11**). By H-NMR analysis of isolated aldehyde **2g** and substrates (**3b-2-D** and **3b-2**), the

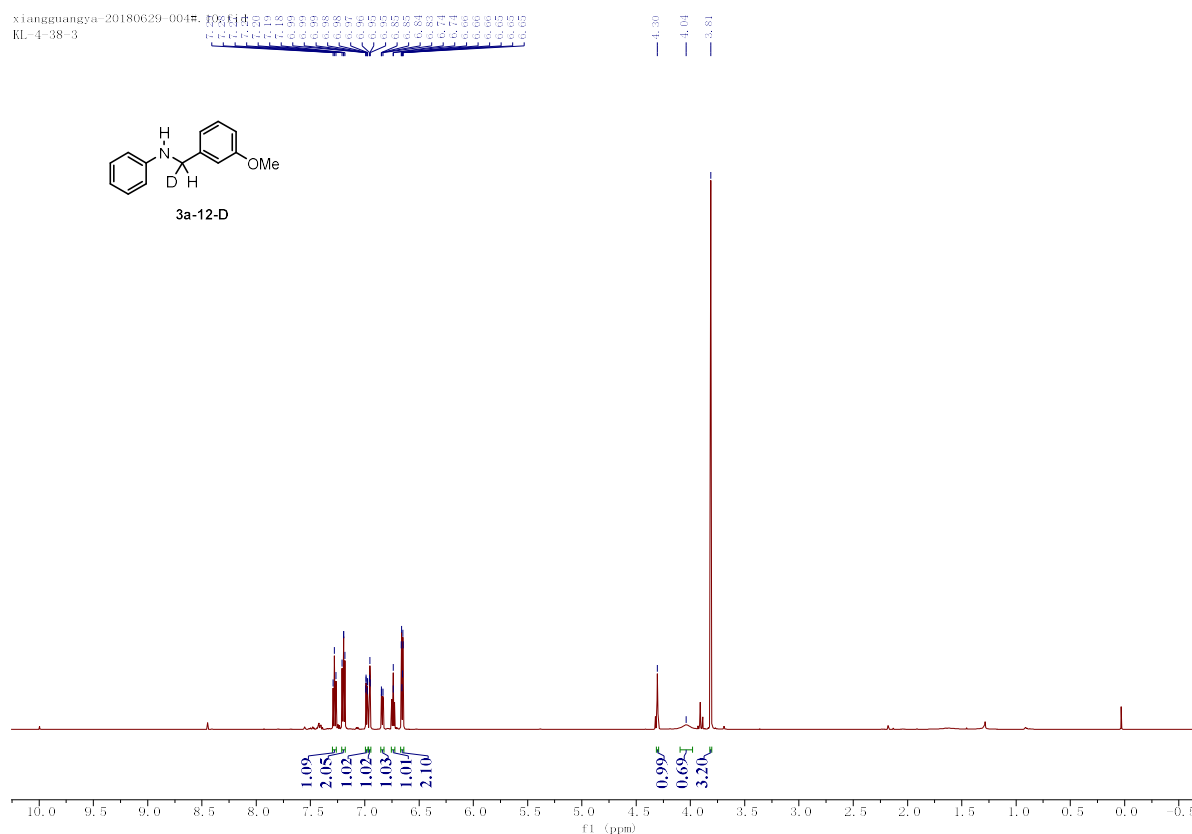
intramolecular thermodynamic KIE value was 3:1 while the intermolecular KIE value was 1.08. On the basis of these two KIE values, it could be concluded that C $\alpha$ -H of *N*-alkyl aniline in this transformation was not the RDS (rate-determining-step).

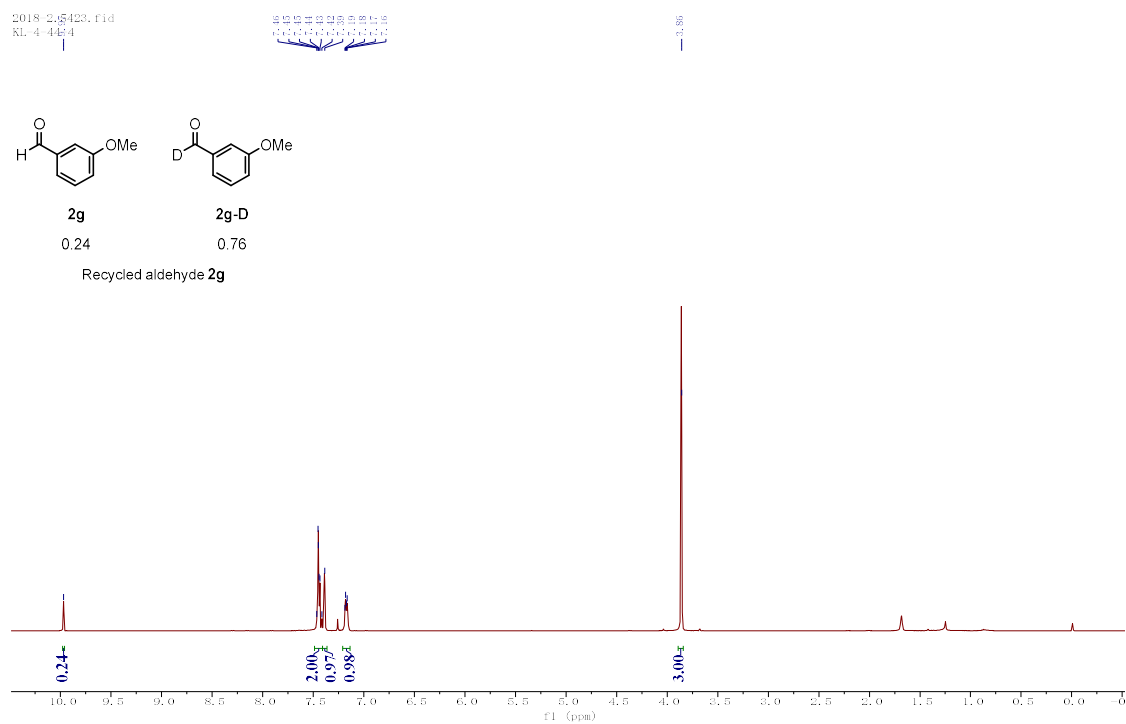
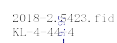


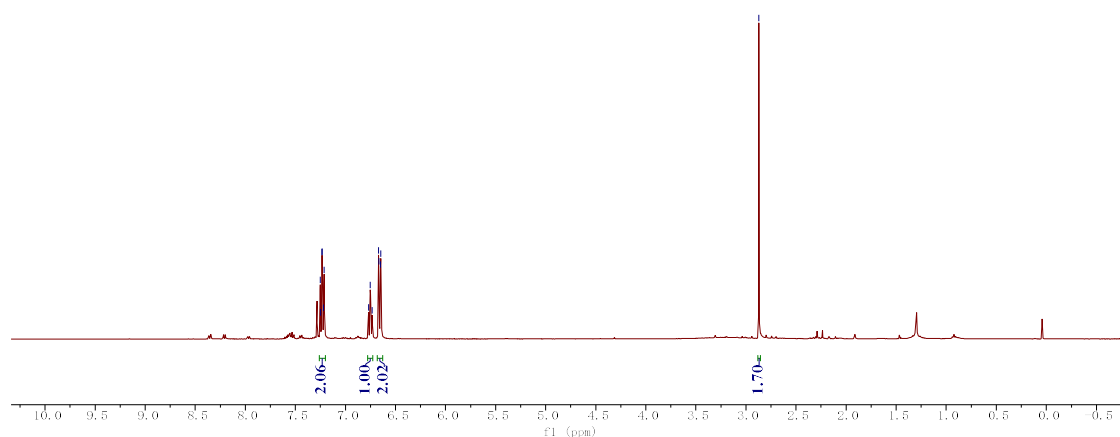
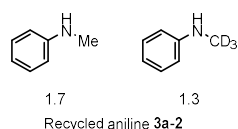
Scheme S11. KIE experiments

## H NMR of KIE studies

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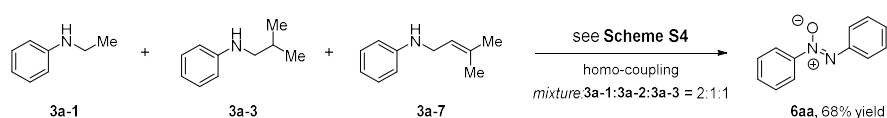


CN(C)Cc1ccccc1



### V-III. Reaction with mixture of starting materials

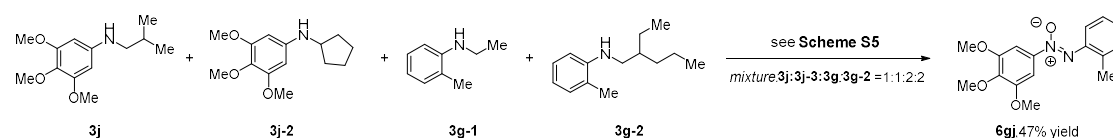
To the mixture of compound **3a-1** (121 mg, 1.0 mmol), **3a-3** (75 mg, 0.5 mmol) and **3a-7** (81 mg, 0.5 mmol) in 10 mL EtOH was added APT (0.05 mmol, 2.5 mol% for **3a-1** + **3a-3** + **3a-7**) and H<sub>2</sub>O<sub>2</sub> (30% aq., 10 mmol, 5.0 equiv. for (**3a-1** + **3a-3** + **3a-7**)). The reaction was conducted according to **general procedure D** for 24h at room temperature, and the desired product **6aa** was isolated in 135 mg (68% yield, **Scheme S12**).



**Scheme S12.** Homo-coupling with mixture of starting materials bearing different *N*-alkyl substitutes

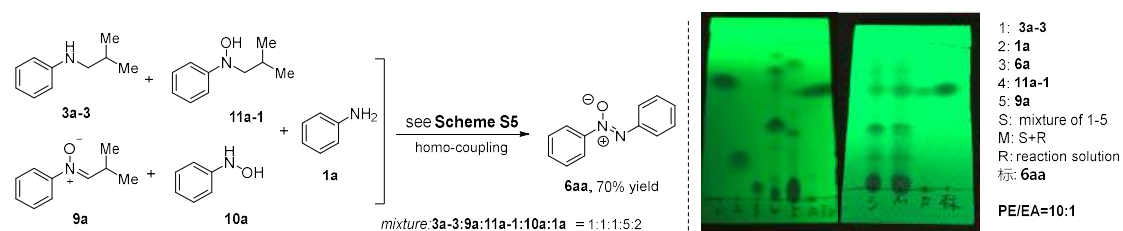
Compound **3g-1** (68mg, 0.5mmol) and **3g-2** (103 mg, 0.5 mmol) was mixed with compound **3j** (60 mg, 0.25 mmol) and **3j-2** (63 mg, 0.25 mmol), and the reaction was conducted according to **general procedure D** at room temperature for 24h, and the desired cross-coupling product **6gj** was isolated in 47% yield (71 mg, **Scheme S13**).





**Scheme S13.** Cross-coupling with mixture of starting materials bearing different *N*-alkyl substitutes

Compound **3a-3** (30 mg, 0.2 mmol), **11a-1** (33 mg, 0.2 mmol), **9a** (33 mg, 0.2 mmol), **10a** (109 mg, 1.0 mmol) and **1a** (37 mg, 0.4 mmol) were mixed. The reaction was carried out according to **general procedure D** and the desired product **6aa** was isolated in 70% yield (138 mg). As shown the on TLC plate, all the starting materials with different  $R_f$  value all transferred into the desired product **6aa** (**Scheme S14**).



**Scheme S14.** Homo-coupling with mixture of starting materials in different oxidation states

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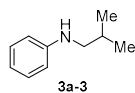
## VI. Cytotoxicity Study

Human lung cancer A549 cells and leukemia HL-60 cells were purchased from ATCC (Manassas, VA) and cultured in RPMI 1640 containing 10% FBS, 100 U/mL penicillin, and 100 µg/mL streptomycin at 37 °C with 5% CO<sub>2</sub>.

A549 proliferation rate was measured by using sulforhodamine B (SRB) assay. The cells were seeded in 96-well plates at a density of 2000 cells/well. After cultured overnight, the cells were treated with tested compounds at 100 µM (positive control – 25 nM Taxol; vehicle control - 1% DMSO) for 72 hr and SRB assay was used to measure the cell proliferation. Briefly, the cells were fixed with 10% trichloroacetic acid for 1 hr at 4°C. Then the cells were stained with 0.1% SRB for 30 minutes and washed thoroughly with 1% acetic acid to remove unbound dye. After the plates were air-dried, 100 µl 10 mM TRIS base was added to solubilize the protein-bound SRB. The absorbance at 540 nm was measured with a microplate reader (SpectraMax M2, Molecular Devices). The inhibitory rate of growth was determined by the following formula: inhibitory rate (%) = (A<sub>540</sub> of vehicle control – A<sub>540</sub> of treated cells) / (A<sub>540</sub> of vehicle control – A<sub>540</sub> of blank control) ×100.

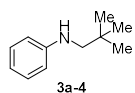
HL-60 proliferation rate was measured by using MTT colorimetric assay. Cells were seeded in 96-well plates at a density of 10000 cells/well and cultured overnight. The cells were treated with tested compounds at 100 µM (positive control – 25 nM Taxol; vehicle control - 1% DMSO) for 72 hr. Then 10 µl MTT reagent was added to each well and incubated for 3h at 37 °C. 100 µl dissolving solution containing 5% isobutanol, 10% SDS and 0.01M HCl was added. After incubated overnight at 37 °C, the absorbance at 570 nm was measured. The inhibitory rate of growth was determined by the following formula: inhibitory rate (%) = (A<sub>570</sub> of vehicle control – A<sub>570</sub> of treated cells) / (A<sub>570</sub> of vehicle control – A<sub>570</sub> of blank control) ×100.

## VII. Spectra of starting material and products



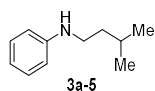
**N-isobutylaniline (3a-3)** was synthesized according to **general procedure A** and obtained as a brown liquid (6.0 mmol scale, 582 mg, 65% yield). The NMR spectrum was same as documented in literature.<sup>2</sup>

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz)  $\delta$  7.17 (dd,  $J_1 = 8.0$  Hz,  $J_2 = 8.0$  Hz, 2H), 6.68 (dd,  $J_1 = 8.0$  Hz,  $J_2 = 8.0$  Hz, 1H), 6.60 (d,  $J = 8.0$  Hz, 2H), 3.69 (br, 1H), 2.93 (d,  $J = 4.0$  Hz, 2H), 1.89 (q,  $J = 8.0$  Hz, 1H), 1.0 (d,  $J = 8.0$  Hz, 6H).



**N-neopentylaniline (3a-4)** was synthesized according to **general procedure A** and obtained as a brown liquid (2.6 mmol scale, 172 mg, 42% yield). The NMR spectrum was same as documented in literature.<sup>3</sup>

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz)  $\delta$  7.17 (dd,  $J_1 = 8.0$  Hz,  $J_2 = 8.0$  Hz, 2H), 6.68 (dd,  $J_1 = 8.0$  Hz,  $J_2 = 8.0$  Hz, 1H), 6.65 (d,  $J = 8.0$  Hz, 2H), 3.63 (s, 1H), 2.91 (s, 1H), 1.01 (s, 9H).

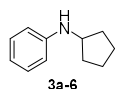


**N-neopentylaniline (3a-5)** was synthesized according to **general procedure A** and obtained as a colorless liquid (6.0 mmol scale, 694 mg, 71% yield). The NMR spectrum was same as documented in literature.<sup>3</sup>

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz)  $\delta$  7.18 (dd,  $J_1 = 8.0$  Hz,  $J_2 = 8.0$  Hz, 2H), 6.69 (dd,  $J_1 = 8.0$  Hz,  $J_2 = 8.0$  Hz, 1H), 6.61 (d,  $J = 8.0$  Hz, 2H), 3.55 (br, 1H), 3.13 (t,  $J = 8.0$  Hz, 2H), 1.75-1.68 (m, 1H), 1.51 (q,  $J = 8.0$  Hz, 2H), 0.96 (d,  $J = 8.0$  Hz, 6H).

2 Ogata, T.; Hartwig, J.F. Palladium-catalyzed amination of aryl and heteroaryl tosylates at room temperature. *J. Am. Chem. Soc.*, **2008**, *130*, 13848.

3 Byun, E.; Hong, B.; Castro, K. A. D.; Lim, M.; Rhee, H. One-pot reductive mono-N-alkylation of aniline and nitroarene derivatives using aldehydes. *J. Org. Chem.*, **2007**, *72*, 9815.



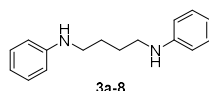
**N-cyclopentylaniline (3a-6)** was synthesized according to **general procedure A** and obtained as colorless liquid (6.0 mmol scale, 561 mg, 58% yield). The NMR spectrum was same as documented in literature.<sup>4</sup>

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) δ 7.24 (dd, *J*<sub>1</sub> = 8.0 Hz, *J*<sub>2</sub> = 8.0 Hz, 2H), 6.75 (dd, *J*<sub>1</sub> = 8.0 Hz, *J*<sub>2</sub> = 8.0 Hz, 1H), 6.67 (d, *J* = 8.0 Hz, 2H), 3.86 (dt, *J*<sub>1</sub> = 12.0 Hz, *J*<sub>2</sub> = 4.0 Hz, 1H), 3.54 (br, 1H), 2.13-2.05 (m, 2H), 1.86 -1.76 (m, 2H), 1.74-1.67 (m, 2H), 1.58-1.50 (m, 2H).



**N-(3-methylbut-2-en-1-yl) aniline (3a-7)** was synthesized according to **general procedure B** and obtained as a colorless liquid (6.0 mmol scale, 561 mg, 58% yield). The NMR spectrum was same as documented in literature.<sup>5</sup>

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) δ 7.24 (dd, *J*<sub>1</sub> = 8.0 Hz, *J*<sub>2</sub> = 8.0 Hz, 2H), 6.77 (dd, *J*<sub>1</sub> = 8.0 Hz, *J*<sub>2</sub> = 8.0 Hz, 1H), 6.67 (d, *J* = 8.0 Hz, 2H), 5.40 (d, *J* = 4.0 Hz, 1H), 3.75 (d, *J* = 4.0 Hz, 2H), 3.53 (br, 1H), 1.82 (s, 3H), 1.78 (s, 3H).



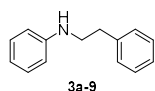
**N<sub>1</sub>,N<sub>4</sub>-diphenylbutane-1,4-diamine (3a-8)** was synthesized according to **general procedure B** and obtained as a yellow oil (6.0 mmol scale, 607 mg, 42% yield). The NMR spectrum was same as documented in literature.<sup>6</sup>

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) δ 7.24 (dd, *J* = 8.0 Hz, 4H), 6.77 (dd, *J*<sub>1</sub> = 8.0 Hz, *J*<sub>2</sub> = 8.0 Hz, 2H), 6.65 (d, *J* = 8.0 Hz, 4H), 3.62 (br, 2H), 3.21-3.18 (m, 4H), 1.77-1.74 (m, 4H)

4 Julien C, V.; Haralampos N, M.; Albert, I-L.; Stephen, S.; Allan J.B., W. Spectroscopic studies of the Chan–Lam Amination: a mechanism-inspired solution to boronic ester reactivity. *J. Am. Chem. Soc.* **2017**, *139*, 4769.

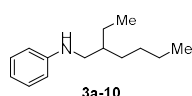
5 Sun, Z.; Wang, Q.; Xu, Y.; Wang, Z. A computationally designed titanium-mediated amination of allylic alcohols for the synthesis of secondary allylamines. *RSC Adv.*, **2015**, *5*, 84284.

6 Pamela G., A.; Mark, S. Addressing challenges in palladium-catalyzed Ccross-couplings of aryl mesylates: monoarylation of ketones and primary alkyl amines. *Angew. Chem. Int. Ed.* **2013**, *52*, 7242.



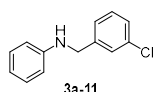
**N-phenethylamine (3a-9)** was synthesized according to **general procedure B** and obtained as a yellow liquid (15.6 mmol scale, 186 mg, 6% yield for two steps). The NMR spectrum was same as documented in literature.<sup>7</sup>

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz)  $\delta$  7.42-7.38 (m, 2H), 7.34-7.24 (m, 5H), 6.80 (dd,  $J_1 = 8.0$  Hz,  $J_2 = 8.0$  Hz, 1H), 6.69 (d,  $J = 8.0$  Hz, 2H), 3.48 (t,  $J = 8.0$ , 2H), 3.50-3.20 (br, 1H), 2.9 (t,  $J = 8.0$  Hz, 2H).



**N-(2-ethylhexyl)aniline (3a-10)** was synthesized according to **general procedure A** and obtained as a yellow liquid (6.0 mmol scale, 980 mg, 80% yield). The NMR spectrum was same as documented in literature.<sup>8</sup>

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.19 (dd,  $J_1 = 8.0$  Hz,  $J_2 = 8.0$  Hz, 2H), 6.70 (dd,  $J_1 = 8.0$  Hz,  $J_2 = 8.0$  Hz, 1H), 6.62 (d,  $J = 8.0$  Hz, 2H), 3.62 (br, 1H), 3.04 (d,  $J = 8.0$  Hz, 2H), 1.61-1.55 (m, 1H), 1.45-1.29 (m, 8H), 0.95-0.91 (m, 6H).



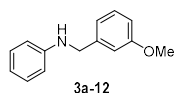
**N-(3-chlorobenzyl)aniline (3a-11)** was synthesized according to **general procedure A** and obtained as a colorless liquid (10 mmol scale, 1200 mg, 55% yield). The NMR spectrum was same as documented in literature.<sup>9</sup>

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.36 (s, 1H), 7.25 (m, 3H), 7.17 (dd,  $J_1 = 8.0$  Hz,  $J_2 = 8.0$  Hz, 2H), 6.73 (dd,  $J_1 = 8.0$  Hz,  $J_2 = 8.0$  Hz, 1H), 6.60 (d,  $J = 8.0$  Hz, 2H), 4.31 (s, 2H), 4.08 (s, 1H)

7 Yin, Z.; Zeng, H.; Wu, J.; Zheng, S.; Zhang, G. Cobalt-catalyzed synthesis of aromatic, aliphatic, and cyclic secondary amines via a "hydrogen-borrowing" strategy. *ACS Catal.* **2016**, *6*, 6546.

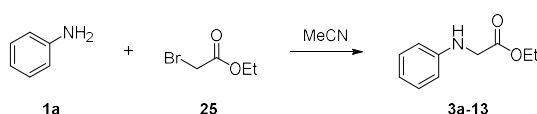
8 Chen, Z.; Zeng, H.; Girard, S. A.; Wang, F.; Chen, N.; Li, C.-J. Formal direct cross-coupling of phenols with amines. *Angew. Chem. Int. Ed.* **2015**, *54*, 14487.

9 Xu, Z.; Yu, X.; Sang, X.; Wang, D. BINAP-copper supported by hydrotalcite as an efficient catalyst for the borrowing hydrogen reaction and dehydrogenation cyclization under water or solvent-free conditions. *Green Chem.*, **2018**, *20*, 2571.



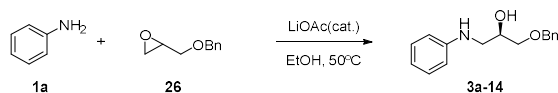
**N-(3-methoxybenzyl)aniline (3a-12)** was synthesized according to **general procedure A** and obtained as colorless liquid (6.4 mmol scale, 561 mg, 58% yield). The NMR spectrum was same as documented in literature.<sup>10</sup>

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.25 (t, *J* = 4.0 Hz, 1H), 7.19-7.14 (m, 2H), 6.97-6.91 (m, 2H), 6.81 (dd, *J* = 8.0, 4.0 Hz, 1H), 6.73-6.69 (m, 1H), 6.62 (dd, *J* = 8.0, 4.0 Hz, 2H), 4.29 (s, 2H), 4.00 (br, 1H), 3.78 (s, 3H)



**Ethyl phenylglycinate (3a-13)** was synthesized according to following procedure: To the mixture of **1a** (20 mmol, 1.86 g, 2.0 equiv.) in MeCN (20 mL) was added ethyl bromoacetate (10.0 mmol, 1.67 g, 1.0 equiv.). The mixture was stirred at room temperature until all aniline was consumed, and then EtOAc (150 mL) was added to dilute the reaction mixture. The reaction mixture was washed by H<sub>2</sub>O (20 mL), brine (20 mL) and dried by Na<sub>2</sub>SO<sub>4</sub>. The desired product **3a-13** was obtained though flash chromatography (PE/EA = 100:1) as a pale-yellow solid (1100 mg, 62% yield). The NMR spectrum was same as documented in literature.<sup>11</sup>

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) δ 7.20 (dd, *J*<sub>1</sub> = 8.0 Hz, *J*<sub>2</sub> = 8.0 Hz, 2H), 6.76 (dd, *J*<sub>1</sub> = 8.0 Hz, *J*<sub>2</sub> = 8.0 Hz, 1H), 6.62 (d, *J* = 8.0 Hz, 2H), 4.29-4.23 (m, 3H), 3.90 (s, 2H), 1.30 (t, *J* = 12.0 Hz, 3H).



**1-(benzyloxy)-3-(phenylamino) propan-2-ol (3a-14)** was synthesized according to following procedure.

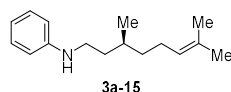
To the solution of compound **1a** (5.1 mmol, 474 mg, 1.02 equiv.) and **26** (5.0 mmol, 820 mg, 1.0 equiv.) in EtOH was added LiOAc (132 mg, 2.0 mmol, 0.4 equiv.). The reaction was then heated to 50°C. After

10 Choi, I.; Chun, S.; Chung, Y. K. Bimetallic cobalt-rhodium nanoparticle-catalyzed reductive amination of aldehydes with nitroarenes under atmospheric hydrogen. *J. Org. Chem.* **2017**, *82*, 12771.

11 Sullivan, S. O.; Doni, E.; Tuttle, T.; Murphy, J. A. Metal-free reductive cleavage of C-N and S-N bonds by photoactivated electron transfer from a neutral organic donor. *Angew. Chem. Int. Ed.* **2014**, *53*, 474.

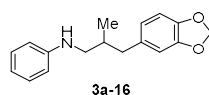
compound **1a** was consumed, the reaction mixture was cooled to room temperature and diluted with EtOAc (150 mL), followed by being washed with H<sub>2</sub>O (20 mL), brine (30 mL) and dried by Na<sub>2</sub>SO<sub>4</sub>. Compound **3a-14** was obtained as yellow oil (834 mg, 65% yield) after filtration, concentration and flash-chromatography (PE:EtOAc = 20:1).

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) δ 7.48-7.37 (m, 5H), 7.26 (dd, *J*<sub>1</sub> = 8.0 Hz, *J*<sub>2</sub> = 8.0 Hz, 2H), 6.81 (dd, *J*<sub>1</sub> = 8.0 Hz, *J*<sub>2</sub> = 8.0 Hz, 1H), 6.70 (d, *J* = 8.0 Hz, 2H), 4.62 (s, 2H), 4.13-4.05 (m, 1H), 3.64 (dd, *J*<sub>1</sub> = 12.0 Hz, *J*<sub>2</sub> = 4.0 Hz, 1H), 3.58 (dd, *J*<sub>1</sub> = 12.0 Hz, *J*<sub>2</sub> = 4.0 Hz, 1H), 3.35 (dd, *J*<sub>1</sub> = 12.0 Hz, *J*<sub>2</sub> = 8.0 Hz, 1H), 3.20 (dd, *J*<sub>1</sub> = 12.0 Hz, *J*<sub>2</sub> = 8.0 Hz, 1H)



(*S*)-*N*-(3,7-dimethyloct-6-en-1-yl)aniline (**3a-15**) was synthesized according to **general procedure A** and obtained as a yellow liquid (6.0 mmol scale, 980 mg, 80% yield). The NMR spectrum was same as documented in literature.<sup>12</sup>

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.21 (dd, *J*<sub>1</sub> = 8.0 Hz, *J*<sub>2</sub> = 8.0 Hz, 2H), 6.73 (dd, *J*<sub>1</sub> = 8.0 Hz, *J*<sub>2</sub> = 8.0 Hz, 1H), 6.64 (d, *J* = 8.0 Hz, 2H), 5.14 (dd, *J*<sub>1</sub> = 8.0 Hz, *J*<sub>2</sub> = 4.0 Hz, 1H), 3.56 (br, 1H), 3.21-3.10 (m, 2H), 2.10-1.97 (m, 2H), 1.73 (s, 3H), 1.68 (s, 3H), 1.73-1.60 (m, 2H), 1.52-1.37 (m, 2H), 1.29-1.20 (m, 1H), 0.98 (d, *J* = 8.0 Hz, 3H)



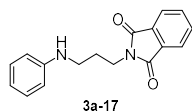
*N*-(3-(benzo[d][1,3]dioxol-5-yl)-2-methylpropyl)aniline (**3a-16**) was synthesized according to **general procedure A** and obtained as a pale yellow oil (6.0 mmol scale, 1202 mg, 75% yield). The NMR spectrum was same as documented in literature.<sup>13</sup>

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) δ 7.17 (dd, *J*<sub>1</sub> = 8.0 Hz, *J*<sub>2</sub> = 8.0 Hz, 2H), 6.73 (d, *J* = 8.0 Hz, 1H), 6.69 (dd, *J*<sub>1</sub> = 8.0 Hz, *J*<sub>2</sub> = 8.0 Hz, 1H), 6.67 (s, 1H), 6.63 (d, *J* = 8.0 Hz, 1H), 6.56 (d, *J* = 8.0 Hz, 2H), 5.93 (s, 2H), 3.69 (br, 1H), 3.09 (dd, *J*<sub>1</sub> = 12.0 Hz, *J*<sub>2</sub> = 8.0 Hz, 1H), 2.93 (dd, *J*<sub>1</sub> = 12.0 Hz, *J*<sub>2</sub> = 8.0 Hz, 1H), 2.69 (dd, *J*<sub>1</sub> = 12.0 Hz, *J*<sub>2</sub> = 8.0

12 Li, Q.-Q.; Xiao, Z.-F.; Yao, C.-Z.; Zheng, H.-X.; Kang, Y.-B. Direct alkylation of amines with alcohols catalyzed by base. *Org. Lett.*, **2015**, *17*, 5328.

13 Hoshimoto, Y.; Kinoshita, T.; Hazra, S.; Ohashi, M.; Ogoshi, S. Main-Group-catalyzed reductive alkylation of multiply substituted amines with aldehydes using H<sub>2</sub>. *J. Am. Chem. Soc.* **2018**, *140*, 7292.

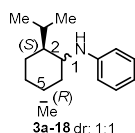
Hz, 1H), 2.43 (dd,  $J_1 = 12.0$  Hz,  $J_2 = 8.0$  Hz, 1H), 2.06-1.98 (m, 1H), 0.97 (d,  $J = 8.0$  Hz, 3H)



**2-(3-(phenylamino)propyl)isoindoline-1,3-dione (3a-17)** was synthesized according to **general procedure B** and obtained as a pale yellow solid (6.0 mmol scale, 382 mg, 23% yield). The NMR spectrum was same as documented in literature.<sup>14</sup>

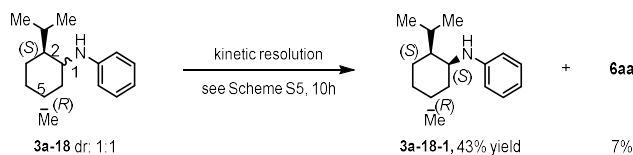
<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz)  $\delta$  7.85 (d,  $J = 8.0$  Hz, 2H), 7.72 (d,  $J = 8.0$  Hz, 2H), 7.17 (dd,  $J_1 = 8.0$  Hz,  $J_2 = 8.0$  Hz, 2H), 6.70-6.62 (m, 3H), 4.05 (br, 1H), 3.81 (t,  $J = 8.0$  Hz, 2H), 3.19 (t,  $J = 8.0$  Hz, 2H), 2.01-1.95 (m, 2H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  168.6, 147.9, 134.0, 132.0, 129.3, 123.3, 117.3, 112.9, 40.7, 35.4, 27.9



**N-((2S, 5R)-2-isopropyl-5-methylcyclohexyl)aniline (3a-18)** was synthesized according to **general procedure A** and obtained as a light brown oil (10.0 mmol scale, 429 mg, 19% yield), the product was isolated as a mixture of two diastereomers).

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz)  $\delta$  7.18-7.13 (m, 2H), 6.66-6.54 (m, 3H), 3.81-3.80 (m, 0.5 H, *syn*-isomer, **3a-18-1**), 3.63-3.61 (m, 0.5H, *anti*-isomer, **3a-18-2**), 2.03 (dd,  $J_1 = 8.0$  Hz,  $J_1 = 4.0$  Hz, 0.5H), 1.87-1.85 (m, 0.5H), 1.78-7.72 (m, 2H), 1.61-1.49 (m, 3H), 1.28-1.26 (m, 1H), 1.15-1.11 (m, 1H), 0.99-0.92 (m, 7H), 0.90-0.83 (m, 3H)



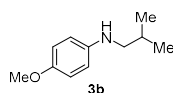
**N-((1S, 2S, 5R)-2-isopropyl-5-methylcyclohexyl)aniline (3a-18-1)** was prepared according to **general procedure D** as a brown oil (1.0 mmol scale, 100 mg, 87% yield). The NMR spectrum was same as

14 Kolarič, A.; Švajger, U.; Tomašič, T.; Brox, R.; Frank, T.; Minovski, N.; Tschammer, N.; Anderluh, M., *Eur. J. Med. Chem.* Insight into structural requirements for selective and/or dual CXCR3 and CXCR4 allosteric modulators. **2018**, *154*, 68.



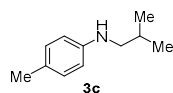
documented in literature.<sup>15</sup>

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz)  $\delta$  7.20-7.16 (m, 2H), 6.68-6.60 (m, 3H), 3.83 (t,  $J$  = 4.0 Hz, 1H), 3.69 (br, 1H), 2.06 (d,  $J$  = 12.0 Hz, 1H), 1.90-1.87 (m, 1H), 1.80-1.75 (m, 1H), 1.64-1.52 (m, 2H), 1.20-1.09 (m, 2H), 1.01-0.94 (m, 5H), 0.90-0.85 (m, 6H).



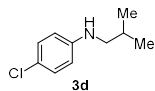
**N-isobutyl-4-methoxyaniline (3b)** was synthesized according to **general procedure A** and obtained as a brown liquid (6.0 mmol scale, 511 mg, 48% yield). The NMR spectrum was same as documented in literature.<sup>16</sup>

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  6.80 (d,  $J$  = 8.0 Hz, 2H), 6.60 (d,  $J$  = 8.0 Hz, 2H), 3.76 (s, 3H), 3.21 (br, 1H), 2.91 (d,  $J$  = 8.0 Hz, 2H), 1.94-1.83 (m, 1H), 1.00 (d,  $J$  = 8.0 Hz, 6H)



**N-isobutyl-4-methylaniline (3c)** was synthesized according to **general procedure A** and obtained as a yellow liquid (6.0 mmol scale, 695 mg, 71% yield). The NMR spectrum was same as documented in literature.<sup>17</sup>

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.04 (d,  $J$  = 8.0 Hz, 2H), 6.58 (d,  $J$  = 8.0 Hz, 2H), 3.44 (br, 1H), 2.96 (d,  $J$  = 8.0 Hz, 2H), 2.29 (s, 3H), 1.99-1.87 (m, 1H), 1.03 (d,  $J$  = 8.0 Hz, 6H).



**4-chloro-N-isobutylaniline (3d)** was synthesized according to **general procedure A** and obtained as a yellow liquid (6.0 mmol scale, 879 mg, 80% yield). The NMR spectrum was same as documented in

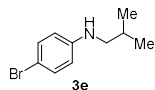
15 Heidena, Z. M.; Stephan, D. W. Metal-free diastereoselective catalytic hydrogenations of imines using B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>. *Chem. Commun.* **2011**, 47, 5729.

16 Chusov, D.; List, B. Reductive amination without an external hydrogen Source. *Angew. Chem., Int. Ed.* **2014**, 53, 5199.

17 Shen, Q.; Ogata, T.; Hartwig, J. F. Highly reactive, general and long-lived catalysts for palladium-catalyzed amination of heteroaryl and aryl Chlorides, bromides, and iodides: scope and structure–activity relationships. *J. Am. Chem. Soc.*, **2008**, 130, 6586.

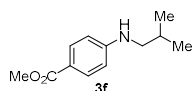
literature.<sup>18</sup>

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.13 (d, *J* = 8.0 Hz, 2H), 6.53 (d, *J* = 8.0 Hz, 2H), 3.72 (br, 1H), 2.91 (d, *J* = 4.0 Hz, 2H), 1.94-1.84 (m, 1H), 1.01 (d, *J* = 8.0 Hz, 6H).



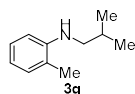
**4-bromo-N-isobutylaniline (3e)** was synthesized according to **general procedure A** and obtained as a yellow liquid (6.0 mmol scale, 802 mg, 59% yield). This compound is commercially available.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.25 (d, *J* = 8.0 Hz, 2H), 6.48 (d, *J* = 8.0 Hz, 2H), 3.74 (br, 1H), 2.90 (d, *J* = 8.0 Hz, 2H), 1.94-1.83 (m, 1H), 1.00 (d, *J* = 8.0 Hz, 6H).



**Methyl 4-(isobutylamino)benzoate (3f)** was synthesized according to **general procedure A** and obtained as a gray solid (6.0 mmol scale, 727 mg, 59% yield). The NMR spectrum was same as documented in literature.<sup>17</sup>

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.85 (d, *J* = 8.0 Hz, 2H), 6.54 (d, *J* = 8.0 Hz, 2H), 4.17 (br, 1H), 3.84 (s, 3H), 2.99 (t, *J* = 8.0 Hz, 2H), 1.92-1.88 (m, 1H), 0.99 (d, *J* = 8.0 Hz, 6H)



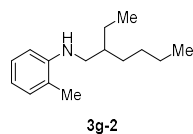
**N-isobutyl-2-methylaniline (3g)** was synthesized according to **general procedure A** and obtained as a pale yellow liquid (6.0 mmol scale, 699 mg, 72% yield). The NMR spectrum was same as documented in literature.<sup>19</sup>

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.22 (dd, *J*<sub>1</sub> = 8.0 Hz, *J*<sub>2</sub> = 8.0 Hz, 1H), 7.15 (d, *J* = 8.0 Hz, 1H), 6.74 (dd, *J*<sub>1</sub> = 8.0 Hz, *J*<sub>2</sub> = 8.0 Hz, 1H), 6.70 (d, *J* = 8.0 Hz, 1H), 3.57 (br, 1H), 3.08 (d, *J* = 8.0 Hz, 2H), 2.24 (s, 3H), 2.06-2.00 (m,

18 Larrosa, M.; Guerrero, C.; Rodríguez, R.; Cruces, J. Selective copper-promoted cross-coupling of aromatic amines with alkyl boronic acids. *Synlett*. **2010**, 14, 2101.

19 Shen, Q.; Hartwig, J. F. [(CyPF-tBu)PdCl<sub>2</sub>]: an air-stable, one-component, highly efficient catalyst for amination of heteroaryl and aryl halides. *Org. Lett.* **2008**, 10, 4109.

1H), 1.11 (d,  $J = 8.0$  Hz, 6H).



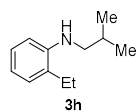
**N-(2-ethylpentyl)-2-methylaniline (3g-2)** was synthesized according to **general procedure A** and obtained as a yellow liquid (9.7mmol scale, 2133 mg, 65% yield).

**$^1\text{H}$  NMR** (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.16 (dd,  $J_1 = 8.0$  Hz,  $J_2 = 8.0$  Hz, 1H), 7.78 (d,  $J = 8.0$  Hz, 1H), 6.69-6.64 (m, 2H), 3.51 (br, 1H), 3.10 (d,  $J = 8.0$  Hz, 2H), 2.17 (s, 3H), 1.67-1.63 (m, 1H), 1.50-1.36 (m, 8H), 0.97-0.93 (m, 6H).

**$^{13}\text{C}$  NMR** (101 MHz,  $\text{CDCl}_3$ )  $\delta$  145.6, 129.9, 127.1, 121.5, 116.4, 109.4, 46.9, 40.0, 31.4, 29.0, 24.7, 23.1, 17.4, 14.1, 10.9

**HRMS-ESI** ( $m/z$ ): calcd for  $\text{C}_{15}\text{H}_{26}\text{N}^+$  ( $[\text{M} + \text{H}]^+$ ) 220.2060, found 220.2059

**FTIR** (film,  $\text{cm}^{-1}$ ): 3442, 2959, 2926, 2858, 1607, 1514, 1446, 744



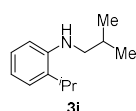
**2-ethyl-N-isobutylaniline (3h)** was synthesized according to **general procedure A** and obtained as a pale yellow transparent liquid (20.0 mmol scale, 1626 mg, 46% yield).

**$^1\text{H}$  NMR** (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.22 (dd,  $J_1 = 8.0$  Hz,  $J_2 = 8.0$  Hz, 1H), 7.17 (d,  $J = 8.0$  Hz, 1H), 6.78 (dd,  $J_1 = 8.0$  Hz,  $J_2 = 2.0$  Hz, 1H), 6.72 (d,  $J = 8.0$  Hz, 1H), 3.74 (br, 1H), 3.07 (d,  $J = 8.0$  Hz, 2H), 2.60 (q,  $J = 8.0$  Hz, 2H), 2.06-2.01 (m, 1H), 1.36 (t,  $J = 8.0$  Hz, 3H), 1.10 (d,  $J = 8.0$  Hz, 6H)

**$^{13}\text{C}$  NMR** (101 MHz,  $\text{CDCl}_3$ )  $\delta$  145.8, 127.9, 127.3, 127.0, 116.7, 109.9, 51.8, 28.0, 23.9, 20.6, 12.9

**HRMS-ESI** ( $m/z$ ): calcd for  $\text{C}_{12}\text{H}_{20}\text{N}^+$  ( $[\text{M} + \text{H}]^+$ ) 178.1590, found 178.1602

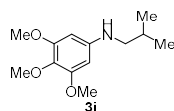
**FTIR** (film,  $\text{cm}^{-1}$ ): 3444, 2960, 1807, 1511, 1054, 745



**Isobutyl-2-isopropylaniline (3i)** was synthesized according to **general procedure A** and obtained as a

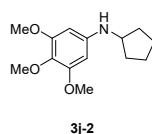
pale yellow liquid (10.0 mmol scale, 1895 mg, 99% yield). The NMR spectrum was same as documented in literature.<sup>17</sup>

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.26-7.10 (m, 2H), 6.83 (dd, *J*<sub>1</sub> = 8.0 Hz, *J*<sub>2</sub> = 8.0 Hz, 1H), 6.73 (d, *J* = 8.0 Hz, 1H), 3.83 (br, 1H), 3.08 (d, *J* = 8.0 Hz, 2H), 2.99-2.95 (m, 1H), 2.09-2.02 (m, 1H), 1.38 (d, *J* = 8.0 Hz, 6H), 1.12 (d, *J* = 8.0 Hz, 6H).



**N-isobutyl-3,4,5-trimethoxyaniline (3j)** was synthesized according to **general procedure A** and obtained as a brown oil (6.0 mmol scale, 827 mg, 58% yield). The NMR spectrum was same as documented in literature.<sup>20</sup>

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 5.8 (s, 2H), 3.78 (s, 6H), 3.72 (s, 3H), 2.86 (d, *J* = 8.0 Hz, 2H), 1.90-1.78 (m, 1H), 0.96 (d, *J* = 8.0 Hz, 6H).



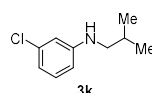
**N-cyclopentyl-3,4,5-trimethoxyaniline (3j-2)** was synthesized according to **general procedure A** and obtained as a brown oil (3.6 mmol scale, 913 mg, 60% yield).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 5.81 (s, 2H), 3.78 (s, 6H), 3.73 (s, 3H), 3.59 (br, 1H), 2.00-1.95 (m, 2H), 1.71-1.67 (m, 2H), 1.60-1.57 (m, 2H), 1.47-1.41 (m, 2H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 153.9, 144.8, 129.7, 90.6, 61.1, 55.9, 55.0, 33.6, 24.0

HRMS-ESI (*m/z*): calcd for C<sub>14</sub>H<sub>21</sub>NO<sub>3</sub> [*M* + *H*]<sup>+</sup> 252.1594, found 252.1594

FTIR (film, cm<sup>-1</sup>): 3386, 2955, 2868, 1611, 1509, 1236, 1129, 1013, 775



**3-chloro-N-isobutylaniline (3k)** was synthesized according to **general procedure A** and obtained as a

20 azzuk, A.; Biehl, E. A. The reaction of various methoxy-substituted haloarenes with amines and nitriles under aryne-forming conditions. *J. Org. Chem.* **1987**, 52, 2619.

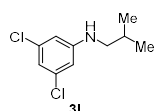
yellow liquid (6.0 mmol scale, 276 mg, 25% yield).

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.06 (dd, *J*<sub>1</sub> = 8.0 Hz, *J*<sub>2</sub> = 2.0 Hz, 1H), 6.64 (d, *J* = 8.0 Hz, 1H), 6.57 (s, 1H), 6.46 (dd, *J*<sub>1</sub> = 8.0 Hz, *J*<sub>2</sub> = 2.0 Hz, 1H), 3.78 (br, 1H), 2.91 (d, *J* = 8.0 Hz, 2H), 1.88 (qd, *J*<sub>1</sub> = 4.0 Hz, *J*<sub>2</sub> = 8.0 Hz, 1H), 0.99 (d, *J* = 4.0 Hz, 6H).

**<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) 149.7, 134.5, 130.1, 116.7, 112.1, 110.1, 51.6, 28.0, 20.4

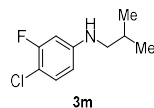
**HRMS-ESI** (*m/z*): calcd for C<sub>10</sub>H<sub>14</sub>NCl ([M + H]<sup>+</sup>) 184.0888, found 184.0893.8

**FTIR** (film, cm<sup>-1</sup>): 3425, 2968, 2870, 1600, 1504, 1471, 762



**3,5-dichloro-N-isobutylaniline (3l)** was synthesized according to **general procedure A** and obtained as a yellow oil (20 mmol scale, 3159 mg, 72% yield).

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 6.63 (d, *J* = 4.0 Hz, 1H), 6.43 (d, *J* = 4.0 Hz, 2H), 3.86 (br, 1H), 2.88 (d, *J* = 8.0 Hz, 2H), 1.85 (q, *J* = 8.0 Hz, 1H), 0.96 (d, *J* = 8.0 Hz, 6H).



**3-chloro-4-fluoro-N-isobutylaniline (3m)** was synthesized according to **general procedure A** and obtained as a yellow oil (6.0 mmol scale, 985 mg, 82% yield).

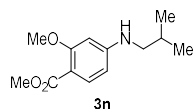
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 6.93 (dd, *J*<sub>1</sub> = 8.0 Hz, *J*<sub>2</sub> = 8.0 Hz, 1H), 6.55 (dd, *J*<sub>1</sub> = 8.0 Hz, *J*<sub>2</sub> = 4.0 Hz, 1H), 6.43-6.39 (m, 1H), 3.63 (br, 1H), 2.87 (d, *J* = 4.0 Hz, 2H), 1.88-1.85 (m, 1H), 0.98 (d, *J* = 8.0 Hz, 6H).

**<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 150.6 (d, *J*<sub>1(C-F)</sub> = 235 Hz, 1C), 149.5 (d, *J*<sub>3(C-F)</sub> = 2 Hz, 1C), 121.9 (d, *J*<sub>2(C-F)</sub> = 19 Hz, 1C), 116.8 (d, *J*<sub>1(C-F)</sub> = 21 Hz, 1C), 113.4, 111.9 (d, *J*<sub>3(C-F)</sub> = 7 Hz, 1C), 52.2, 28.0, 20.4

**<sup>19</sup>F NMR**: δ 132.0

**HRMS-ESI** calcd for C<sub>10</sub>H<sub>14</sub>NFCI ([M + H]<sup>+</sup>) 202.0793, found 202.0788

**FTIR** (film, cm<sup>-1</sup>): 3428, 2969, 1693, 1112, 1083, 797



**Methyl 4-(isobutylamino)-2-methoxybenzoate (3n)** was synthesized according to **general procedure A** and obtained as a white powder-like solid (10 mmol scale, 1008 mg, 43% yield).

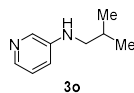
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.67 (d, *J* = 8.0 Hz, 1H), 6.06 (d, *J* = 8.0 Hz, 1H), 6.01 (s, 1H), 4.51 (br, 1H), 3.74 (s, 3H), 3.73 (s, 3H), 2.88 (d, *J* = 8.0 Hz, 2H), 1.82-1.77 (m, 1H), 0.90 (d, *J* = 8.0 Hz, 6H).

**<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 166.2, 161.9, 153.5, 134.1, 107.3, 104.1, 95.2, 55.7, 51.3, 51.2, 28.2, 20.4

**HRMS-ESI** (*m/z*): calcd for C<sub>13</sub>H<sub>20</sub>NO<sub>3</sub> ([M + H]<sup>+</sup>) 238.1438, found 238.1438

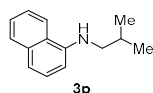
**FTIR** (film, cm<sup>-1</sup>): 3367, 2964, 1662, 1617, 1441, 1224, 803, 767

**M.p.**: 49.0-50.6 °C



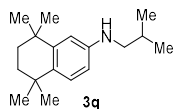
**N-isobutylpyridin-3-amine (3o)** was synthesized according to **general procedure A** and obtained as a dark brown liquid (6.0 mmol scale, 563 mg, 63% yield). The NMR spectrum was same as documented in literature.<sup>17</sup>

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.98 (s, 1H), 7.87 (d, *J* = 4.0 Hz, 1H), 7.04 (dd, *J*<sub>1</sub> = 8.0 Hz, *J*<sub>2</sub> = 4.0 Hz, 1H), 6.83 (d, *J* = 8.0 Hz, 1H), 2.99 (d, *J* = 8.0 Hz, 2H), 2.05-1.79 (m, 1H), 0.94 (d, *J* = 8.0 Hz, 6H).



**N-isobutyl-1-naphthylamine (3p)** was synthesized according to **general procedure A** and obtained as a pink liquid (6.0 mmol scale, 743 mg, 62% yield).

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.58 (d, *J* = 8.0 Hz, 2H), 7.24-7.18 (m, 2H), 7.14 (dd, *J*<sub>1</sub> = 8.0 Hz, *J*<sub>2</sub> = 8.0 Hz, 1H), 7.01 (d, *J* = 8.0 Hz, 1H), 6.38 (d, *J* = 8.0 Hz, 1H), 4.16 (br, 1H), 2.86 (d, *J* = 8.0 Hz, 2H), 1.85-1.76 (m, 1H), 0.85 (d, *J* = 8.0 Hz, 6H).



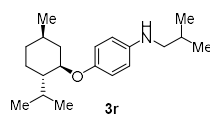
**N-isobutyl-5,5,8,8-tetramethyl-5,6,7,8-tetrahydronaphthalen-2-amine (3q)** was synthesized according to **general procedure A** and obtained as a yellow oil (10 mmol scale, 1436 mg, 55% yield).

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.22 (d, *J* = 8.0 Hz, 1H), 6.64 (d, *J* = 4.0 Hz, 1H), 6.55 (dd, *J*<sub>1</sub> = 8.0 Hz, *J*<sub>2</sub> = 4.0 Hz, 1H), 3.54 (br, 1H), 3.00 (d, *J* = 8.0 Hz, 2H), 1.98-1.95 (m, 1H), 1.78-1.73 (s, 4H), 1.37 (s, 6H), 1.34 (s, 6H), 1.09 (d, *J* = 8.0 Hz, 6H)

**<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 146.1, 145.5, 133.7, 127.2, 111.08, 110.3, 52.1, 35.4, 35.3, 34.2, 33.4, 32.0 (two carbons), 31.8 (two carbons), 28.1, 20.6

**HRMS-ESI** (*m/z*): calcd for C<sub>18</sub>H<sub>29</sub>N<sup>+</sup> ([*M* + *H*]<sup>+</sup>) 260.2373, found 260.2407.

**FTIR** (film, cm<sup>-1</sup>): 3417, 2957, 2867, 1614, 1507, 1458, 1250, 808



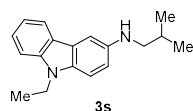
**N-isobutyl-4-(((2*S*,5*R*)-2-isopropyl-5-methylcyclohexyl)oxy)aniline (3r)** was synthesized according to **general procedure B** and obtained as a yellow oil (6.0 mmol scale, 691 mg, 38% yield).

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 6.80 (d, *J* = 8.0 Hz, 2H), 6.56 (d, *J* = 8.0 Hz, 2H), 3.83 (ddd, *J*<sub>1</sub> = 8.0 Hz, *J*<sub>2</sub> = 8.0 Hz, *J*<sub>3</sub> = 4.0 Hz, 1H), 3.29 (br, 1H), 2.89 (d, *J* = 8.0 Hz, 2H), 2.36-2.28 (m, 1H), 2.15-2.10 (m, 1H), 1.93-1.84 (m, 1H), 1.73-1.68 (m, 2H), 1.50-1.34 (m, 2H), 1.09-1.02 (m, 2H), 0.96 (d, *J* = 4.0 Hz, 6H), 0.93 (d, *J* = 8.0 Hz, 3H), 0.92-0.86 (m, 1H), 0.88 (d, *J* = 4.0 Hz, 3H), 0.80 (d, *J* = 8.0 Hz, 3H)

**<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 150.3, 143.1, 118.2, 113.8, 79.3, 52.8, 48.2, 40.7, 34.6, 31.5, 28.1, 25.9, 23.6, 22.2, 20.9, 20.5, 16.5

**HRMS-ESI** (*m/z*): calcd for C<sub>20</sub>H<sub>34</sub>NO<sup>+</sup> ([*M* + *H*]<sup>+</sup>): 304.2625; found 304.2635

**FTIR** (film, cm<sup>-1</sup>): 3412, 2966, 1511, 1228. 993, 819



**9-ethyl-N-isobutyl-9H-carbazol-3-amine (3s)** was synthesized according to **general procedure A** and obtained as a brown solid (10.0 mmol scale, 474 mg, 18% yield).

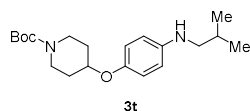
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 8.09 (d, *J* = 8.0 Hz, 1H), 7.48 (dd, *J*<sub>1</sub> = 8.0 Hz, *J*<sub>2</sub> = 8.0 Hz, 1H), 7.46 (d, *J* = 4.0 Hz, 1H), 7.39 (d, *J* = 8.0 Hz, 1H), 7.28 (d, *J* = 8.0 Hz, 1H), 7.23 (dd, *J*<sub>1</sub> = 8.0 Hz, *J*<sub>2</sub> = 8.0 Hz, 1H), 6.98 (dd, *J*<sub>1</sub> = 8.0 Hz, *J*<sub>2</sub> = 4.0 Hz, 1H), 4.31 (q, *J* = 8.0 Hz, 2H), 4.00 (br, 1H), 3.13 (d, *J* = 4.0 Hz, 2H), 2.07-2.04 (m, 1H), 1.43 (t, *J* = 8.0 Hz, 3H), 1.12 (d, *J* = 8.0 Hz, 6H)

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 140.3, 139.5, 134.8, 125.4, 123.5, 122.6, 120.4, 118.1, 115.6, 109.1, 108.3, 105.4, 55.0, 37.4, 27.7, 20.7, 13.8

HRMS-ESI (m/z): calcd for C<sub>18</sub>H<sub>23</sub>N<sub>2</sub><sup>+</sup> ([M + H]<sup>+</sup>): 267.1855; found 267.1856

FTIR(film, cm<sup>-1</sup>): 3402, 2952, 1472, 1320, 746

M.p.:49.9-50.6 °C.



**tert-butyl 4-(4-(isobutylamino)phenoxy)piperidine-1-carboxylate (3t)** was synthesized according to **general procedure B** and obtained as a white solid (14.8 mmol scale, 878 mg, 17% yield for three steps).

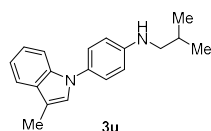
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 6.79 (d, *J* = 4.0 Hz, 2H), 6.54 (d, *J* = 8.0 Hz, 2H), 4.27-4.21 (m, 1H), 3.74-3.68 (m, 2H), 3.48 (br, 1H), 3.28-3.22 (m, 2H), 2.88 (d, *J* = 8.0 Hz, 2H), 1.88-1.83 (m, 2H), 1.73-1.66 (m, 2H), 1.61-1.57 (m, 1H), 1.48 (s, 9H), 0.97 (d, *J* = 4.0 Hz, 6H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 154.9, 148.9, 143.6, 118.5, 113.7, 79.5, 73.9, 52.7, 30.8, 28.44, 28.41, 28.1, 20.5

HRMS-ESI (m/z): calcd for C<sub>20</sub>H<sub>33</sub>N<sub>2</sub>O<sub>3</sub> ([M + H]<sup>+</sup>) 349.2486, found 349.2499

FTIR (film, cm<sup>-1</sup>): 3380, 2969, 1689, 1517, 1429, 1227, 815

M.p.: 58.7-60.4 °C.



**N-isobutyl-4-(2-methyl-1H-indol-1-yl) aniline (3u)** was synthesized according to **general procedure B** and obtained as a khaki liquid (6.0 mmol scale, 373 mg, 22% yield for three steps).

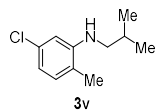
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.65 (dd, *J*<sub>1</sub> = 8.0 Hz, *J*<sub>2</sub> = 4.0 Hz, 1H), 7.46 (dd, *J*<sub>1</sub> = 8.0 Hz, *J*<sub>2</sub> = 2.0 Hz, 1H), 7.26-7.16 (m, 4H), 7.05 (dd, *J*<sub>1</sub> = 8.0 Hz, *J*<sub>2</sub> = 8.0 Hz, 1H), 6.64 (dd, dd, *J*<sub>1</sub> = 8.0 Hz, *J*<sub>2</sub> = 4.0 Hz, 2H), 3.71 (br, 1H), 2.94 (t, *J* = 8.0 Hz, 2H), 2.41 (s, 3H), 1.93-1.88 (m, 1H), 1.01 (d, *J* = 8.0 Hz, 6H)

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 147.2, 136.7, 129.7, 129.1, 126.2, 125.9, 121.8, 119.1, 118.9, 113.0, 111.4, 110.4, 52.1, 28.1, 20.3, 9.6

HRMS-ESI (m/z): calcd for C<sub>19</sub>H<sub>23</sub>N<sub>2</sub> ([M + H]<sup>+</sup>) 279.1856, found 279.1858



**FTIR** (film,  $\text{cm}^{-1}$ ): 2967, 1615, 1522, 1459, 1230, 825, 740



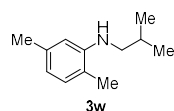
**N-isobutyl-2,4-dimethylaniline (3v)** was synthesized according to **general procedure A** and obtained as a brown liquid (20 mmol scale, 3435 mg, 87% yield).

**$^1\text{H}$  NMR** (400 MHz,  $\text{CDCl}_3$ )  $\delta$  6.97(d,  $J$  = 8.0 Hz, 1H), 6.63 (dd,  $J_1$  = 8.0 Hz,  $J_2$  = 4.0 Hz, 1H), 6.58 (s, 1H), 3.64 (br, 1H), 2.98 (d,  $J$  = 4.0 Hz, 2H), 2.12 (s, 3H), 1.98-1.93 (m, 1H), 1.05 (d,  $J$  = 4.0 Hz, 6H).

**$^{13}\text{C}$  NMR** (101 MHz,  $\text{CDCl}_3$ ) 147.4, 132.7, 130.7, 119.9, 116.0, 109.5, 51.6, 27.9, 20.5, 16.9

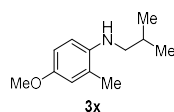
**HRMS-ESI** ( $m/z$ ): calcd for  $\text{C}_{11}\text{H}_{16}\text{NCl}^+$  ( $[\text{M} + \text{H}]^+$ ) 198.1044, found 198.1056.

**FTIR** (film,  $\text{cm}^{-1}$ ): 3446, 2968, 2896, 1603, 1511, 1468, 1416, 1278, 831, 788



**N-isobutyl-2,4-dimethylaniline (3w)** was synthesized according to **general procedure A** and obtained as a pale-yellow liquid (20 mmol scale, 1961 mg, 55% yield). The NMR spectrum was same as documented in literature.<sup>21</sup>

**$^1\text{H}$  NMR** (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.01 (d,  $J$  = 8.0 Hz, 1H), 6.54 (d,  $J$  = 8.0 Hz, 1H), 6.51 (s, 1H), 3.57 (br, 1H), 3.05 (d,  $J$  = 8.0 Hz, 2H), 2.38 (s, 3H), 2.18 (s, 3H), 2.07-1.97 (m, 1H), 1.10 (d,  $J$  = 4.0 Hz, 6H).



**N-isobutyl-4-methoxy-2-methylaniline (3x)** was synthesized according to **general procedure A** and obtained as a colorless liquid (20 mmol scale, 1408 mg, 37% yield).

**$^1\text{H}$  NMR** (400 MHz,  $\text{CDCl}_3$ )  $\delta$  6.75 (m, 2H), 6.58 (d,  $J$  = 4.0 Hz, 1H), 3.77 (s, 3H), 3.26 (br, 1H), 2.97 (d,  $J$  =

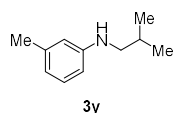
21 Ouvry, G.; Atrux-Tallau, N.; Bihl, F.; Bondu, A.; Bouix-Peter, C.; Carlavan, I.; Christin, O.; Cuadrado, M.; Defoin-Platel, C.; Deret, S.; Duvert, D.; Feret, C.; Forissier, M.; Fournier, J.; Froude, D.; Hacini-Rachinel, F.; Harris, C.; Steven H., C.; Huguet, H.; Lafitte, G.; Luzy, A.; Musicki, B.; Orfila, D.; Ozello, B.; Pascau, C.; Pascau, J.; Parnet, V.; Peluchon, G.; Pierre, R.; Piwnica, D.; Raffin, C.; Rossio, P.; Spiess, D.; Taquet, N.; Thoreau, E.; Vatinel, R.; Vial, E.; Hennequin, L. Discovery and characterization of CD12681, a potent ROR $\gamma$  inverse agonist, preclinical candidate for the topical treatment of psoriasis. *Chem. Med. Chem.* **2018**, *13*, 321.

8.0 Hz, 2H), 2.18 (s, 3H), 1.99-1.92 (m, 1H), 1.05 (d,  $J = 4.0$  Hz, 6H)

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  151.4, 140.8, 123.4, 117.0, 111.6, 110.7, 55.8, 52.6, 28.0, 20.6, 17.6

HRMS-ESI ( $m/z$ ): calcd for  $\text{C}_{12}\text{H}_{19}\text{NO}^+$  ( $[\text{M} + \text{H}]^+$ ) 194.1539, found 198.194.1556

FTIR (film,  $\text{cm}^{-1}$ ): 2965, 2839, 1512, 1287, 1225, 1049, 847, 796



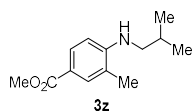
**N-isobutyl-3-methylaniline (3y)** was synthesized according to **general procedure A** and obtained a pale-yellow liquid (20 mmol scale, 1641 mg, 50% yield).<sup>21</sup>

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.11-7.07 (m, 1H), 6.54 (d,  $J = 8.0$  Hz, 1H), 6.46-6.43 (m, 2H), 3.62 (s, 1H), 2.95 (d,  $J = 8.0$  Hz, 2H), 2.31 (s, 3H), 1.96-1.86 (m, 1H), 1.01 (d,  $J = 8.0$  Hz, 6H)

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  148.6, 138.7, 129.0, 117.9, 113.4, 109.8, 51.2, 28.0, 21.6, 20.4

HRMS-ESI ( $m/z$ ): calcd for  $\text{C}_{11}\text{H}_{17}\text{N}^+$  ( $[\text{M} + \text{H}]^+$ ) 164.1434, found 164.1445

FTIR (film,  $\text{cm}^{-1}$ ): 3416, 2957, 2889, 1606, 1491, 769, 692



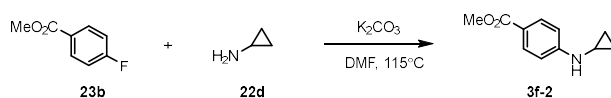
**Methyl 4-(isobutylamino)-3-methylbenzoate (3z)** was synthesized according to **general procedure A** and obtained as a pale yellow oil (20 mmol scale, 3363 mg, 76% yield). The NMR spectrum was same as documented in literature.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.80 (dd,  $J_1 = 8.0$  Hz,  $J_2 = 4.0$  Hz, 1H), 7.71 (s, 1H), 6.48 (d,  $J = 8.0$  Hz, 1H), 4.12 (br, 1H), 3.79 (s, 3H), 2.96 (d,  $J = 8.0$  Hz, 2H), 2.09 (s, 3H), 1.89-1.84 (m, 1H), 0.95 (d,  $J = 8.0$  Hz, 6H)

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  167.5, 150.2, 131.5, 129.7, 120.4, 117.3, 108.2, 51.4, 51.2, 27.9, 20.4, 17.2

HRMS-ESI  $m/z$ : calcd for  $\text{C}_{13}\text{H}_{20}\text{NO}_2$  ( $[\text{M} + \text{H}]^+$ ) 222.1489, found 222.1487

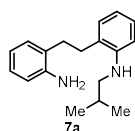
FTIR (film,  $\text{cm}^{-1}$ ): 3419, 2965, 1703, 1609, 1285, 769



**Scheme S15.** Preparation of starting material **3f-2**

**Methyl 4-(cyclopropylamino) benzoate (3f-2)** was prepared according to following procedure. To the solution of compound **23b** (1.54 g, 10.0 mmol, 1.0 equiv.) in anhydrous DMSO (20 mL) was added K<sub>2</sub>CO<sub>3</sub> (1.37 g, 10.0 mmol, 1.0 equiv.) and cyclopropanamine **22d** (576 mg, 10.1 mmol, 1.01 equiv.), and then heated to 115°C until all **23b** was consumed. The reaction mixture was then cooled to room temperature, diluted with EtOAc (150 mL), washed by H<sub>2</sub>O (30mL × 3) and brine (30 mL), and dried by Na<sub>2</sub>SO<sub>4</sub>. The desired product **3f-2** was isolated by flash chromatography (PE:EtOAc = 20:1, 226 mg, 14% yield). The HNMR spectrum was in accord with reported literature (**Scheme S15**).<sup>22</sup>

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.85 (d, *J* = 8.0Hz, 2H), 6.71(d, *J* = 8.0 Hz, 3H), 4.75 (br, 1H), 3.83 (s, 3H), 2.46-2.43 (m, 1H), 0.77-0.75 (m, 2H), 0.52-0.50 (m, 2H)



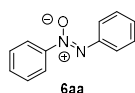
**2-(2-aminophenethyl)-N-isobutylaniline (7a)** was synthesized according to **general procedure A** and obtained as yellow oil (10 mmol scale, 1240 mg, 46% yield).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.12 (dd, *J*<sub>1</sub> = 8.0 Hz, *J*<sub>2</sub> = 8.0 Hz, 1H), 7.05 (d, *J* = 8.0 Hz, 2H), 7.03 (dd, *J*<sub>1</sub> = 8.0 Hz, *J*<sub>2</sub> = 8.0 Hz, 1H), 6.73 (dd, *J*<sub>1</sub> = 8.0 Hz, *J*<sub>2</sub> = 8.0 Hz, 1H), 6.66 (dd, *J*<sub>1</sub> = 8.0 Hz, *J*<sub>2</sub> = 8.0 Hz, 1H), 6.61 (dd, dd, *J*<sub>1</sub> = 8.0 Hz, *J*<sub>2</sub> = 8.0 Hz, 2H), 3.51 (br, 3H), 2.88 (d, *J* = 4.0 Hz, 2H), 2.81-2.70 (m, 4H), 1.87-1.78 (m, 1H), 0.96 (d, *J* = 8.0 Hz, 6H)

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 146.1, 144.3, 129.5, 129.0, 127.4, 127.2, 126.4, 125.4, 119.1, 116.9, 115.9, 110.3, 51.9, 30.9, 30.8, 28.0, 20.6

HRMS *m/z* (ESI) calcd for C<sub>18</sub>H<sub>25</sub>N<sub>2</sub> [M +H]<sup>+</sup> 269.2012, found 269.2039

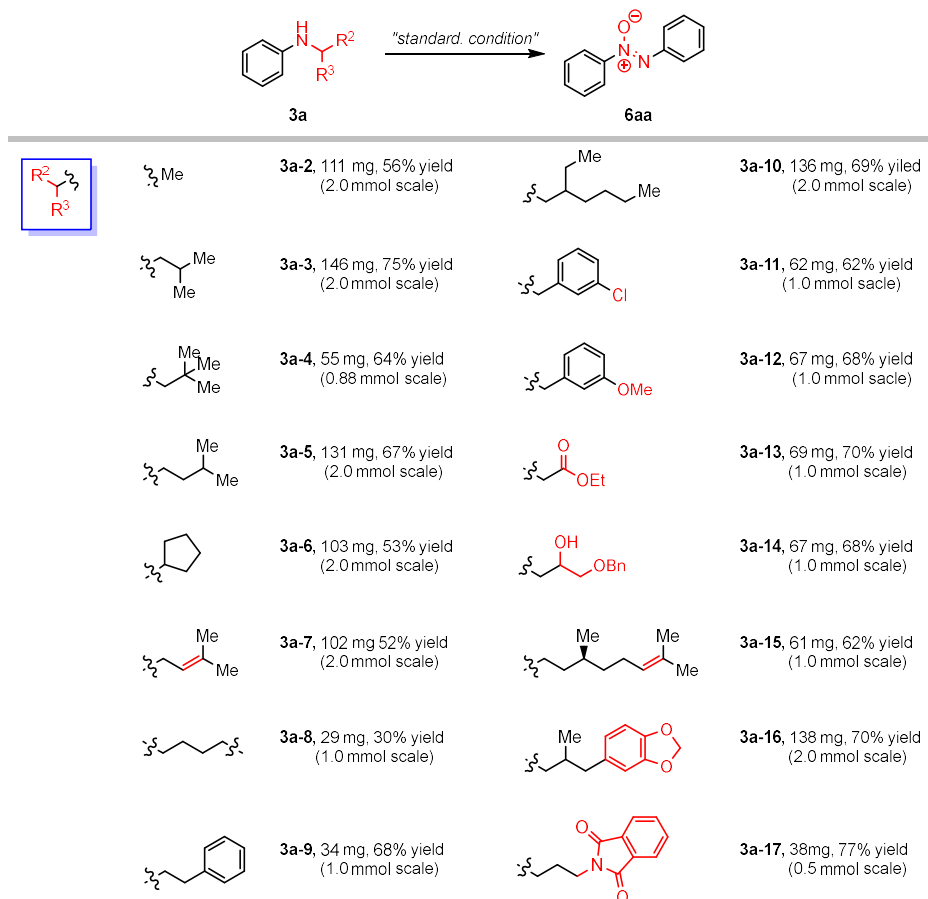
FTIR (film, cm<sup>-1</sup>): 3439, 2965, 1804, 1499, 748



**(Z)-1, 2-diphenyldiazene 1-oxide (6aa)** was synthesized according to **general procedure D**. The H NMR

22 Gildner, P. G.; DeAngelis, A.; Colacot, T. J. Palladium-catalyzed N-arylation of cyclopropylamines. *Org. Lett.* **2016**, *18*, 1442.

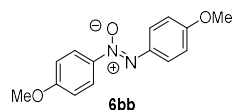
spectrum was same as documented in literature.<sup>23</sup> All the reactions with substrates secondary *N*-alkyl aniline (**3a-x**) in **Table 1** were conducted in 2.0 mmol scale, and the yield of **6aa** was recorded as following (**Scheme S16**).



**Scheme S16.** Yield of compound **6aa** with various *N*-alkyl substitutes

The gram scale reaction was conducted in 50 mmol scale with substrate **3a-1**, **6aa** was obtained as colorless solid (3.8 g, 78% yield)

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.34-8.32 (m, 2H), 8.21 -8.18 (m, 2H), 7.57-7.49 (m, 5H), 7.43-7.41 (m, 1H)

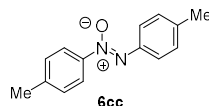


(*Z*)-1,2-bis(4-methoxyphenyl)diazene 1-oxide (**6bb**) was synthesized according to **general procedure D**

23 Voutyritsa, E.; Theodorou, A.; Kokotou, M. G.; Kokotos, C. G. Organocatalytic oxidation of substituted anilines to azoxybenzenes and nitro compounds: mechanistic studies excluding the involvement of a dioxirane intermediate. *Green Chem.* **2017**, *19*, 1291.

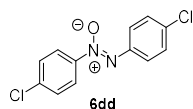
and obtained as a khaki solid (2.0 mmol scale, 192 mg, 74% yield ). The NMR spectrum was same as documented in literature.<sup>24</sup>

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.30-8.14 (m, 4H), 6.99-6.88 (m, 4H), 3.87 (s, 3H), 3.85 (s, 3H).



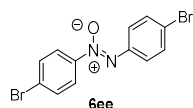
(Z)-1,2-di-p-tolyldiazene 1-oxide (**6cc**) was synthesized according to **general procedure D** and obtained a yellow solid (2.0 mmol scale, 179 mg, 74% yield). The NMR spectrum was same as documented in literature.<sup>23</sup>

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.18 (d, *J* = 8.0 Hz, 2H), 8.10 (d, *J* = 8.0 Hz, 2H), 7.28 (d, *J* = 8.0 Hz, 4H), 2.44 (s, 3H), 2.41 (s, 3H).



(Z)-1,2-bis(4-chlorophenyl)diazene 1-oxide (**6dd**) was synthesized according to **general procedure D** and obtained as a yellow solid (2.0 mmol scale, 219 mg, 82% yield). The NMR spectrum was same as documented in literature.<sup>23</sup>

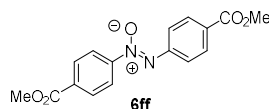
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.25 (d, *J* = 8.0 Hz, 2H), 8.16 (d, *J* = 8.0 Hz, 2H), 7.48 (d, *J* = 8.0 Hz, 2H), 7.45 (d, *J* = 8.0 Hz, 2H)



(Z)-1,2-bis(4-bromophenyl)diazene 1-oxide (**6ee**) was synthesized according to **general procedure D** and obtained as a yellow solid (2.0 mmol scale, 316 mg, 89% yield). The NMR spectrum was same as documented in literature.<sup>23</sup>

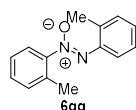
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.17 (d, *J* = 8.0 Hz, 2H), 8.07 (d, *J* = 8.0 Hz, 2H), 7.63 (d, *J* = 8.0 Hz, 2H), 7.60 (d, *J* = 8.0 Hz, 2H)

<sup>24</sup> Kashiwara, M.; Yadav, M. R.; Nakao, Y. Reductive denitration of nitroarenes. *Org. Lett.* **2018**, *20*, 1655.



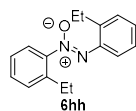
**(Z)-1,2-bis(4-(methoxycarbonyl)phenyl)diazene 1-oxide (6ff)** was synthesized according to **general procedure D** and obtained as pale yellow solid (1.0 mmol scale, 88 mg, 56% yield). The H-NMR spectrum was same as documented in literature.<sup>25</sup>

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.38 (d, *J* = 4.0 Hz, 2H), 8.22-8.11 (m, 6H), 3.9 (s, 3H), 3.9 (s, 3H).



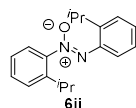
**(Z)-1,2-di-o-tolyldiazene 1-oxide (6gg)** was synthesized according to **general procedure D** and obtained as a brown solid (1.0 mmol scale, 72 mg, 64% yield). The NMR spectrum was same as documented in literature.<sup>25</sup>

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.98 (d, *J* = 8.0 Hz, 1H), 7.61(d, *J* = 8.0 Hz, 1H), 7.32 (dd, *J*<sub>1</sub> = 8.0 Hz, *J*<sub>2</sub> = 8.0 Hz, 1H), 7.27-7.17 (m, 5H), 2.46 (s, 3H), 2.31(s, 3H).



**(Z)-1,2-bis(2-ethylphenyl)diazene 1-oxide (6hh)** was synthesized according to **general procedure D** and obtained as a brown solid (1.0 mmol scale, 76 mg, 60% yield). The NMR spectrum was same as documented in literature.<sup>26</sup>

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.09 (d, *J* = 8.0 Hz, 1H), 7.62 (d, *J* = 8.0 Hz, 1H), 7.46-7.43 (m, 1H), 7.39-7.31 (m, 5H), 2.88 (q, *J*<sub>1</sub> = 8.0 Hz, *J*<sub>2</sub> = 8.0 Hz, 2H), 2.78 (q, *J*<sub>1</sub> = 8.0 Hz, *J*<sub>2</sub> = 8.0 Hz, 2H), 1.31 (t, *J* = 8.0 Hz, 3H), 1.23 (t, *J* = 8.0 Hz, 3H).

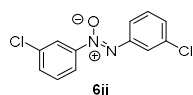


25 Sakai, N.; Fujii, K.; Nabeshima, S.; Ikeda, R.; Konakahara, T. Highly selective conversion of nitrobenzenes using a simple reducing system combined with a trivalent indium salt and a hydrosilane. *Chem. Commun.*, **2010**, 46, 3173.

26 Ghosh, S.; Acharyya, S. S.; Sasakib, T.; Bal, B. Room temperature selective oxidation of aniline to azoxybenzene over a silver supported tungsten oxide nanostructured catalyst. *Green. Chem.* **2015**, 17, 1867.

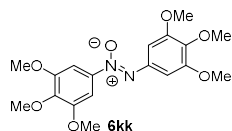
(Z)-1,2-bis(2-isopropylphenyl)diazene 1-oxide (6ii) was synthesized according to **general procedure D** and obtained as brown oil (1.0 mmol scale, 86 mg, 61% yield). The NMR spectrum was same as documented in literature.<sup>27</sup>

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.03 (d, *J* = 8.0 Hz, 1H), 7.54 (d, *J* = 8.0 Hz, 1H), 7.48 (d, *J* = 8.0 Hz, 2H), 7.44 (d, *J* = 8.0 Hz, 1H), 3.45-3.35 (m, 2H), 1.34 (d, *J* = 8.0 Hz, 6H), 1.33 (d, *J* = 8.0 Hz, 6H), 1.27 (d, *J* = 8.0 Hz, 6H), 1.25 (d, *J* = 8.0 Hz, 6H)



(Z)-1,2-bis(3-chlorophenyl)diazene 1-oxide (6jj) was synthesized according to **general procedure D** and obtained colorless liquid (1.0 mmol scale, 96 mg, 72% yield). The NMR spectrum was same as documented in literature.<sup>26</sup>

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.31 (s, 1H), 8.26 (s, 1H), 8.20 (d, *J* = 8.0 Hz, 1H), 8.00 (d, *J* = 8.0 Hz, 1H), 7.55 (d, *J* = 8.0 Hz, 1H), 7.48-7.37 (m, 3H).



(Z)-1,2-bis(3,4,5-trimethoxyphenyl)diazene 1-oxide (6kk) was synthesized according to **general procedure D** and obtained as a light brown solid (1.0 mmol scale, 119 mg, 63% yield).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.63 (s, 2H), 7.58 (s, 2H), 3.97 (s, 6H), 3.93 (s, 9H), 3.92 (s, 3H)

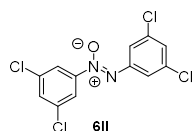
<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 152.8, 152.6, 143.9, 141.0, 139.7, 139.4, 103.6, 99.9, 61.01, 60.97, 56.4, 56.2

HRMS-ESI: calcd for C<sub>18</sub>H<sub>22</sub>N<sub>2</sub>O<sub>7</sub><sup>+</sup> ([M + H]<sup>+</sup>) 379.1500, found 379.1514

FTIR (film, cm<sup>-1</sup>): 2947, 1612, 1587, 1478, 1214, 1132, 995, 838.

M.p.: 145.4-147.1°C

27 Goon, D. J. W.; Murray, N. G.; Schoch, J-P.; Bunce, N-J. Evidence against a hydrogen abstraction mechanism in the photorearrangement of azoxybenzene to 2-Hydroxyazobenzen. *Can. J. Chem.* **1973**, *51*, 3827.

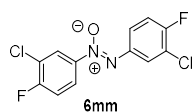


**(Z)-1,2-bis(3,5-dichlorophenyl)diazene 1-oxide (6ll)** was synthesized according to **general procedure D** and obtained as a pale yellow solid (1.0 mmol scale, 124 mg, 74% yield)

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 8.21 (s, 2H), 8.10 (s, 2H), 7.59 (s, 1H), 7.42 (s, 1H)

**<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 149.0, 144.6, 135.6, 135.1, 132.2, 13.0.0, 124.1, 121.3

**HRMS-APCI** (m/z): calcd for C<sub>12</sub>H<sub>6</sub>Cl<sub>4</sub>N<sub>2</sub>O [M+e]: 333.9240; found 333.9239



**(Z)-1,2-bis(3-chloro-4-fluorophenyl)diazene 1-oxide (6mm)** was synthesized according to **general procedure D** and obtained as a pale yellow solid (1.0 mmol scale, 86 mg, 57% yield).

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 8.50 (dd, *J*<sub>1</sub> = 8.0 Hz, *J*<sub>2</sub> = 4.0 Hz, 1H), 8.45 (dd, *J*<sub>1</sub> = 8.0 Hz, *J*<sub>2</sub> = 4.0 Hz, 1H), 8.27-8.23 (m, 1H), 8.13-8.09 (m, 1H), 7.34-7.28 (m, 2H).

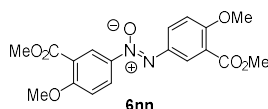
**<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 161.5, 159.3, 158.9, 156.8, 128.0, 126.5 (d, *J*<sub>C-F</sub> = 7 Hz, 1C), 125.2, 122.5 (d, *J*<sub>C-F</sub> = 8 Hz, 1C), 121.8 (d, *J*<sub>C-F</sub> = 19 Hz, 1C), 121.2 (d, *J*<sub>C-F</sub> = 18 Hz, 1C), 116.7 (d, *J*<sub>C-F</sub> = 5 Hz, 1C), 116.5 (d, *J*<sub>C-F</sub> = 4 Hz, 1C)

**<sup>19</sup>F NMR**: δ -109.3, 110.2

**HRMS-ESI** (m/z): calcd for C<sub>12</sub>H<sub>7</sub>Cl<sub>2</sub>F<sub>2</sub>N<sub>2</sub>O<sup>+</sup> ([M + H]<sup>+</sup>): 302.9898; found 302.9899

**FTIR** (film, cm<sup>-1</sup>): 3435, 3111, 1491, 1262, 1106, 824

**M.p.**: 119.2-120.1 °C



**(Z)-1,2-bis(4-methoxy-3-(methoxycarbonyl)phenyl)diazene 1-oxide (6nn)** was synthesized according to **general procedure D** and obtained as a khaki solid (1.0 mmol scale, 107 mg, 57% yield).

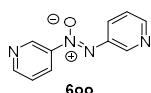
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.93-7.90 (m, 4H), 7.86 (s, 1H), 7.71 (dd, *J*<sub>1</sub> = 8.0 Hz, *J*<sub>2</sub> = 8.0 Hz, 1H), 4.02 (s, 3H), 3.97 (s, 3H), 3.93 (s, 3H), 3.91 (s, 3H).



<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 165.9, 165.6, 159.4, 159.3, 151.3, 147.5, 132.0, 131.9, 123.4, 120.9, 117.7, 114.0, 108.8, 106.3, 56.5, 56.2, 52.4, 52.2

HRMS-ESI (m/z): calcd for C<sub>18</sub>H<sub>19</sub>N<sub>2</sub>O<sub>7</sub> ([M + H]<sup>+</sup>) 375.1187, found 375.1189

FTIR (film, cm<sup>-1</sup>): 3430, 2961, 1738, 1433, 1243, 1085, 880, 772



(Z)-1,2-di(pyridin-3-yl)diazene 1-oxide (**6oo**) was synthesized according to **general procedure D** and obtained as a gray solid (1.0 mmol scale, 34 mg, 17% yield).

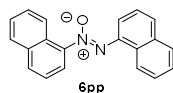
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 9.57(d, *J* = 4.0 Hz, 1H), 9.24(d, *J* = 4.0 Hz, 1H), 8.83(d, *J* = 4.0 Hz, 1H), 8.76(d, *J* = 8.0 Hz, 1H), 8.62-8.58(m, 2H), 7.51(dd, *J*<sub>1</sub> = 8.0 Hz, *J*<sub>2</sub> = 4.0 Hz, 1H), 7.45(dd, *J*<sub>1</sub> = 8.0 Hz, *J*<sub>2</sub> = 4.0 Hz, 1H)

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 152.6, 150.4, 148.3, 144.1, 144.0, 139.9, 131.4, 129.9, 123.5, 123.4

HRMS-ESI (m/z): calcd for C<sub>10</sub>H<sub>9</sub>N<sub>4</sub>O<sup>+</sup> ([M + H]<sup>+</sup>): 201.0771; found 201.0770

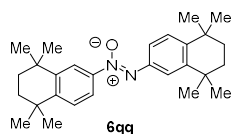
FTIR (film, cm<sup>-1</sup>): 3390, 2966, 1581, 1480, 1416, 1298, 816, 591

M.p.: 97.5-99.0°C



(Z)-1,2-di(naphthalen-2-yl)diazene 1-oxide (**6pp**) was synthesized according to **general procedure D** and obtained as a red solid (2.0 mmol scale, 98 mg, 33% yield). The NMR spectrum was same as documented in literature.<sup>23</sup>

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 9.16 (d, *J* = 8.0 Hz, 1H), 8.54 (dd, *J*<sub>1</sub> = 8.0 Hz, *J*<sub>2</sub> = 4.0 Hz, 1H), 8.37 (dd, *J*<sub>1</sub> = 8.0 Hz, *J*<sub>2</sub> = 4.0 Hz, 1H), 8.03 (dd, *J*<sub>1</sub> = 8.0 Hz, *J*<sub>2</sub> = 8.0 Hz, 2H), 7.97 (dd, *J*<sub>1</sub> = 8.0 Hz, *J*<sub>2</sub> = 8.0 Hz, 2H), 7.90 (d, *J* = 8.0 Hz, 1H), 7.66-7.59 (m, 4H), 7.58-7.53 (m, 2H).



(Z)-1,2-bis(5,5,8,8-tetramethyl-5,6,7,8-tetrahydronaphthalen-2-yl)diazene 1-oxide (**6qq**) was

synthesized according to **general procedure D** and obtained as a yellow solid (1.0 mmol scale, 182 mg, 87% yield).

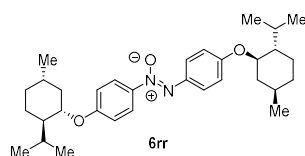
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 8.22 (d, *J* = 2.4 Hz, 1H), 8.11(d, *J* = 2.0 Hz, 1H), 8.03 (dd, *J*<sub>1</sub> = 8.0 Hz, *J*<sub>2</sub> = 8.0 Hz, 2H), 7.41 (dd, *J*<sub>1</sub> = 8.0 Hz, *J*<sub>2</sub> = 4.0 Hz, 2H), 1.73 (s, 8H), 1.36 (s, 6H), 1.35 (s, 6H), 1.32 (s, 12H)

**<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 148.8, 146.9, 146.3, 145.9, 145.4, 142.0, 127.1, 126.8, 124.2, 122.6, 120.4, 119.4, 35.1, 35.0, 34.9, 34.8, 34.7, 34.59, 34.57, 34.5, 31.84 (two carbons), 31.78 (two carbons), 31.74 (two carbons), 31.71 (two carbons)

**HRMS-ESI** (*m/z*): calcd for C<sub>28</sub>H<sub>39</sub>N<sub>2</sub>O ([*M* + *H*]<sup>+</sup>) 419.3057, found 419.3050

**FTIR** (flim, cm<sup>-1</sup>): 3440, 2968, 1487, 1458, 1381, 825

**M.p.**:142.1-143.8°C.



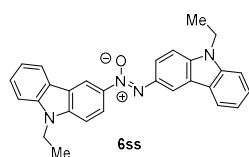
**(Z)-1,2-bis(4-(((2S,5R)-2-isopropyl-5-methylcyclohexyl)oxy)phenyl)diazene 1-oxide (6rr)** was synthesized according to **general procedure D** and obtained as a green oil (1.0 mmol scale, 180 mg, 71% yield).

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 8.25 (d, *J* = 8.0 Hz, 2H), 8.20 (d, *J* = 8.0 Hz, 2H), 6.96 (d, *J* = 8.0 Hz, 2H), 6.94 (d, *J* = 8.0 Hz, 2H), 4.16-4.09 (m, 2H), 2.20-2.15 (m, 4H), 1.75-1.72 (m, 4H), 1.54-1.51 (m, 4H), 1.14-1.07 (m, 4H), 0.94-0.92 (m, 14H), 0.76 (d, *J* = 8.0 Hz, 6H)

**<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ. 150.8, 159.2, 141.3, 137.7, 127.8, 123.8, 115.2, 115.0, 48.00, 47.99, 40.3, 40.1, 34.46, 34.41, 34.4 (two carbons), 31.4, 26.19, 26.18, 23.8 (two carbons), 22.10, 22.08, 20.68, 20.65, 16.6(two carbons)

**HRMS-ESI** (*m/z*): calcd for C<sub>32</sub>H<sub>47</sub>N<sub>2</sub>O<sub>3</sub><sup>+</sup> ([*M* + *H*]<sup>+</sup>) 507.3581, found 507.3517

**FTIR** (flim, cm<sup>-1</sup>): 2966, 2926, 1595, 496, 1249, 991, 837



(Z)-2-(9-ethyl-9H-carbazol-2-yl)-1-(9-ethyl-9H-carbazol-3-yl)diazene 1-oxide (6ss) was synthesized according to **general procedure D** and obtained as a dark brown solid (1.0 mmol scale, 168 mg, 78% yield).

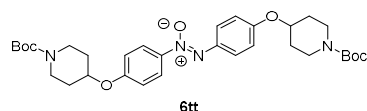
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 9.51(s, 1H), 9.15(s, 1H), 8.56 (d, *J* = 8.0 Hz, 1H), 8.36 (d, *J* = 8.0 Hz, 1H), 8.22 (dd, *J*<sub>1</sub> = 8.0 Hz, *J*<sub>2</sub> = 8 Hz, 2H), 7.57-7.44(m, 6H), 7.32 (dd, *J*<sub>1</sub> = 8.0 Hz, *J*<sub>2</sub> = 8 Hz, 2H), 4.45-4.36 (m, 4H), 1.49 (t, *J* = 8.0 Hz, 6H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 141.2, 140.9, 140.6, 140.2, 137.2, 126.5, 126.1, 126.0, 123.7, 123.2, 122.7, 122.6, 121.0, 120.9, 120.2, 119.8, 119.6, 117.9, 115.0, 109.0, 108.9, 108.2, 107.8, 38.0, 37.8, 13.90, 13.85 (one carbon was buried in other peaks)

HRMS-ESI (*m/z*): calcd for C<sub>28</sub>H<sub>25</sub>N<sub>4</sub>O ([*M* + *H*]<sup>+</sup>) 433.2023, found 433.2000

FTIR (flim, cm<sup>-1</sup>): 3435, 2968, 1594, 1481, 1233, 747

M.p.: 83.3-84.9°C.



(Z)-1,2-bis(4-((1-(tert-butoxycarbonyl)piperidin-4-yl)oxy)phenyl)diazene 1-oxide (6tt) was synthesized according to **general procedure D** and obtained as a colorless liquid (0.5 mmol scale, 87 mg, 78% yield).

The NMR spectrum was same as documented in literature.

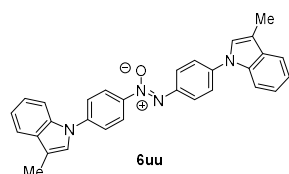
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.28 (d, *J* = 8.0 Hz, 2H), 8.25 (d, *J* = 8.0 Hz, 2H), 6.99 (d, *J* = 8.0 Hz, 2H), 6.98 (d, *J* = 8.0 Hz, 2H), 4.61-4.57 (m, 2H), 3.76-3.69 (m, 4H), 3.43-3.36 (m, 4H), 2.01-1.94 (m, 4H), 1.84-1.77 (m, 4H), 1.4 9(s, 18H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 159.6, 157.8, 154.81, 154.78, 141.7, 138.0, 127.9, 123.9, 115.5, 115.3, 79.72, 79.66, 72.6, 72.3, 40.5 (2 carbons), 30.5, 30.4, 28.5 (2 carbons)

HRMS-ESI (*m/z*): calcd for C<sub>32</sub>H<sub>45</sub>N<sub>4</sub>O<sub>7</sub> ([*M*+*H*]<sup>+</sup>) 597.3283, found 597.3350

FTIR (flim, cm<sup>-1</sup>): 3380, 2950, 1690, 1241, 1131, 838

M.p.:180.4-181.6°C.



(*Z*)-1,2-bis(4-(3-methyl-1*H*-indol-1-yl)phenyl)diazene 1-oxide (**6uu**) was synthesized according to **general procedure D** and obtained as a khaki solid (0.5 mmol scale, 83 mg, 73% yield).

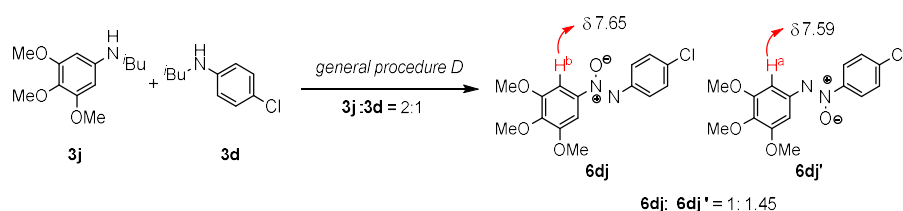
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.51 (d, *J* = 8.0 Hz, 2H), 8.47 (d, *J* = 8.0 Hz, 2H), 7.47-7.66 (m, 8H), 7.36-7.24 (m, 6H), 2.45 (s, 6H)

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 145.1, 142.8, 141.4, 140.7, 135.7, 135.7, 130.5, 130.3, 127.4, 125.0, 124.9, 123.9, 123.1, 123.1, 123.0, 122.9, 120.6, 120.4, 119.6, 119.4, 114.5, 114.0, 110.7, 110.5, 9.64, 9.63.

HRMS-ESI (*m/z*): calcd for C<sub>30</sub>H<sub>25</sub>N<sub>4</sub>O<sup>+</sup> ([M+H]<sup>+</sup>): 457.1993; found 457.2023

FTIR (flim, cm<sup>-1</sup>): 2968, 1596, 1504, 1454, 1356, 1223, 731

M.p.: 168.4-169.9°C



(*Z*)-2-(4-chlorophenyl)-1-(3,4,5-trimethoxyphenyl)diazene 1-oxide (**6dj**) and (*Z*)-1-(4-chlorophenyl)-2-(3,4,5-trimethoxyphenyl)diazene 1-oxide (**6dj'**) were synthesized according to **general procedure D**. To the mixture of compound **3j** (92 mg, 0.5 mmol, 2.0 equivalent) and **3d** (32 mg, 0.25 mmol, 1.0 equivalent) in 5.0 mL EtOH was added APT (60 mg, 0.018 mmol, 2.5 mol % based on **3j** + **3d**), H<sub>2</sub>O<sub>2</sub> (30% aq., 3.75 mmol, 5.0 equivalent based on **3j** + **3d**, 375 μL) at room temperature. Next, the mixture was stirred at room temperature for 24h until that **3j** was almost consumed. And then around 100 mL EtOAc was added to dilute the reaction solution, which was washed by H<sub>2</sub>O and brine. The organic layer was collected and dried by Na<sub>2</sub>SO<sub>4</sub>. After filtration and concentration, the crude product was purified by flash chromatography (PE/EtOAc = 100:1) to afford the desired products **6dj** and **6dj'** in an inseparable mixture as a brown solid (41 mg, 51% yield, **6dj**:**6dj'** = 1:1.45).

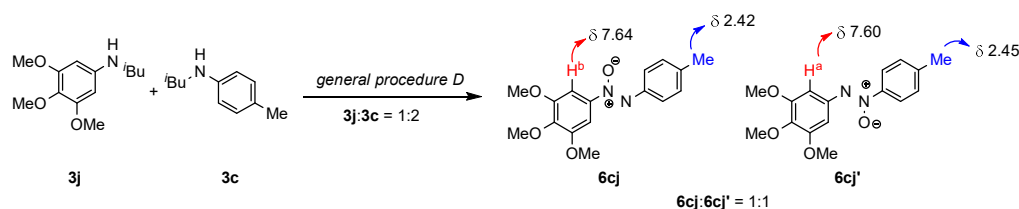
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ **6dj** (**minor**) 8.25 (d, *J* = 8.0 Hz, 2H), 7.65 (s, 2H), 7.48 (d, *J* = 8.0 Hz, 2H), 3.96 (s, 3H), 3.92 (s, 6H); **6dj'** (**major**) 8.13 (d, *J* = 8.0 Hz, 2H), 7.59 (s, 2H), 7.45 (d, *J* = 8.0 Hz, 2H), 3.96 (s, 3H), 3.93 (s, 6H)

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ **6dj** (**minor**) 152.6, 146.7, 143.6, 141.3, 139.7, 128.9, 123.5, 103.8, 60.1, 56.2; **6dj'** (**major**) 152.8, 142.4, 139.5, 137.7, 134.8, 128.9, 126.9, 100.1, 61.0, 56.4

**HRMS-ESI** (m/z) (as a mixture): calcd for C<sub>15</sub>H<sub>16</sub>N<sub>2</sub>O<sub>4</sub>Cl<sup>+</sup> ([M + H]<sup>+</sup>) 323.0793, found 323.0742

**FTIR** (flim, cm<sup>-1</sup>, as a mixture): 2967, 1499, 1476, 1326, 1131, 996, 830

**M.p.** (as a mixture): 101.6-103.1 °C



(Z)-2-(p-tolyl)-1-(3,4,5-trimethoxyphenyl)diazene 1-oxide (6cj) and (Z)-1-(p-tolyl)-2-(3,4,5-trimethoxyphenyl)diazene 1-oxide (6cj') were synthesized according to **general procedure D**. To the mixture of compound **3j** (92 mg, 0.5 mmol, 1.0 equivalent) and **3c** (121 mg, 1.0 mmol, 2.0 equivalent) in 5.0 mL EtOH was added APT (115 mg, 0.0375 mmol, 2.5 mol % based on **3j** + **3c**), H<sub>2</sub>O<sub>2</sub> (30% aq., 7.5 mmol, 5.0 equivalent based on **3j** + **3c**, 0.75 mL) at room temperature. Next, the mixture was stirred at room temperature for 24h until that **3j** was almost consumed. And then around 100 mL EtOAc was added to dilute the reaction solution, which was washed by H<sub>2</sub>O and brine. The organic layer was collected and dried by Na<sub>2</sub>SO<sub>4</sub>. After filtration and concentration, the crude product was purified by flash chromatography (PE/EtOAc = 100:1) to afford the desired products **6cj** and **6cj'** in an inseparable mixture as a colorless liquid (77 mg, 51% yield, **6cj**:**6cj'** = 1:1).

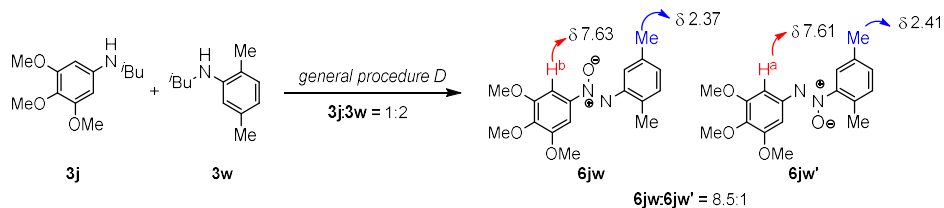
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ **6cj**: 8.17 (d, *J* = 8.0 Hz, 2H), 7.60 (s, 2H), 7.29 (d, *J* = 8.0 Hz, 2H), 3.96 (s, 3H), 3.93 (s, 6H), 2.45 (s, 3H); **6cj'**: 8.11 (d, *J* = 8.0 Hz, 2H), 7.60 (s, 2H), 7.59 (s, 1H), 7.29 (d, *J* = 8.0 Hz, 2H), 3.93 (s, 3H), 3.92 (s, 6H), 2.42 (s, 3H).

**<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ **6cj**: 152.6, 143.9, 141.8, 140.2, 139.9, 129.33, 122.0, 103.6, 55.1, 21.3; **6cj'**: 152.8, 146.2, 142.0, 140.8, 139.2, 129.29, 125.6, 100.0, 61.1, 56.3, 21.5

**HRMS-ESI** (m/z) (as a mixture): calcd for C<sub>16</sub>H<sub>19</sub>N<sub>2</sub>O<sub>4</sub><sup>+</sup> ([M + H]<sup>+</sup>) 303.1339, found 303.1371

**FTIR** (flim, cm<sup>-1</sup>, as a mixture): 2985, 1566, 1481, 1216, 1130, 1002, 825

**M.p.** (as a mixture): 58.0-59.9 °C



(*Z*)-2-(2,5-dimethylphenyl)-1-(3,4,5-trimethoxyphenyl)diazene 1-oxide (**6jw**) was synthesized according to **general procedure D**. To the mixture of compound **3j** (92 mg, 0.5 mmol, 1.0 equivalent) and **3w** (121 mg, 0.5 mmol, 1.0 equivalent) in 5.0 mL EtOH was added APT (115 mg, 0.0375 mmol, 2.5 mol % based on **3j** + **3w**), H<sub>2</sub>O<sub>2</sub> (30% aq., 7.5 mmol, 5.0 equivalent based on **3j** + **3w**, 0.75 mL) at room temperature. Next, the mixture was stirred at room temperature for 24h until that **3j** was almost consumed. And then around 100 mL EtOAc was added to dilute the reaction solution, which was washed by H<sub>2</sub>O and brine. The organic layer was collected and dried by Na<sub>2</sub>SO<sub>4</sub>. After filtration and concentration, the crude product was purified by flash chromatography (PE/EtOAc = 100:1) to afford the desired product **6jw** with its isomer **6jw'** in an inseparable mixture as a yellow solid (67 mg, 43% yield, **6jw**:**6jw'** = 8.5:1).

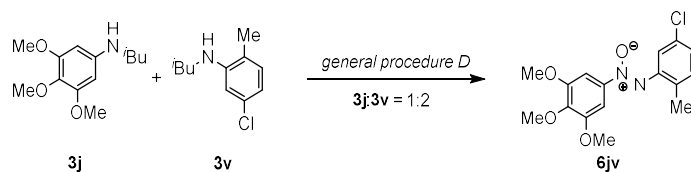
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ **6jw** (**major**) 7.88 (s, 1H), 7.63 (s, 2H), 7.19 (d, *J* = 4.0 Hz, 1H), 7.07 (d, *J* = 4.0 Hz, 1H), 3.96 (s, 6H), 3.93 (s, 3H), 2.37 (s, 3H), 2.34 (s, 3H)

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ **6jw** (**major**) 152.8, 143.7, 142.6, 141.1, 135.7, 131.3, 130.5, 129.5, 122.2, 100.1, 61.1, 56.4, 21.2, 17.9

HRMS-ESI (*m/z*) (as a mixture): calcd for C<sub>17</sub>H<sub>21</sub>N<sub>2</sub>O<sub>4</sub> ([*M*+*H*]<sup>+</sup>) 317.1496, found 317.1509

FTIR (flim, cm<sup>-1</sup>, as a mixture): 2967, 1499, 1475, 1129, 100, 845

M.p. (as a mixture): 110.0-113.0°C.



(*Z*)-2-(5-chloro-2-methylphenyl)-1-(3,4,5-trimethoxyphenyl)diazene 1-oxide (**6jv**) was synthesized according to **general procedure D**. To the mixture of compound **3j** (92 mg, 0.5 mmol, 1.0 equivalent) and **3v** (141 mg, 1.0 mmol, 2.0 equivalent) in 5.0 mL EtOH was added APT (115 mg, 0.0375 mmol, 2.5 mol % based on **3j** + **3v**), H<sub>2</sub>O<sub>2</sub> (30% aq., 7.5 mmol, 5.0 equivalent based on **3j** + **3v**, 0.75 mL) at room temperature.

Next, the mixture was stirred at room temperature for 24h until that **3j** was almost consumed. And then around 100 mL EtOAc was added to dilute the reaction solution, which was washed by H<sub>2</sub>O and brine. The organic layer was collected and dried by Na<sub>2</sub>SO<sub>4</sub>. After filtration and concentration, the crude product was purified by flash chromatography (PE/EtOAc = 100:1) to afford the desired product **6jv** as a yellow solid (37 mg, 22% yield, rr>20:1).

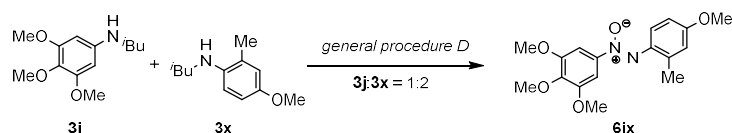
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.14 (s, 1H), 7.62 (s, 2H), 7.24 (s, 2H), 3.97 (s, 6H), 3.94 (s, 3H), 2.36 (s, 3H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 152.8, 143.4, 143.3, 141.4, 133.0, 131.5, 131.4, 128.3, 122.0, 100.1, 61.1, 56.4, 17.9

HRMS-ESI (m/z): calcd for C<sub>16</sub>H<sub>18</sub>N<sub>2</sub>O<sub>4</sub>Cl ([M+H])<sup>+</sup> 337.0950, found 337.0975

FTIR (flim, cm<sup>-1</sup>): 2969, 1617, 1499, 1323, 1132, 839

M.p.: 99.9-101.1 °C.



(*Z*)-2-(4-methoxy-2-methylphenyl)-1-(3,4,5-trimethoxyphenyl)diazene 1-oxide (**6jx**) was synthesized according to **general procedure D**. To the mixture of compound **3j** (92 mg, 0.5 mmol, 1.0 equivalent) and **3x** (138 mg, 1.0 mmol, 2.0 equivalent) in 5.0 mL EtOH was added APT (115 mg, 0.0375 mmol, 2.5 mol % based on **3j** + **3x**), H<sub>2</sub>O<sub>2</sub> (30% aq., 7.5 mmol, 5.0 equivalent based on **3j** + **3x**, 0.75 mL) at room temperature. Next, the mixture was stirred at room temperature for 24h until that **3j** was almost consumed. And then around 100 mL EtOAc was added to dilute the reaction solution, which was washed by H<sub>2</sub>O and brine. The organic layer was collected and dried by Na<sub>2</sub>SO<sub>4</sub>. After filtration and concentration, the crude product was purified by flash chromatography (PE/EtOAc = 100:1) to afford the desired product **6jx** as a brown solid (27 mg, 17% yield, rr> 15:1).

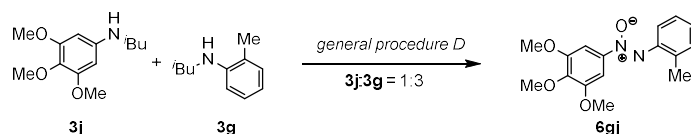
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.75 (d, *J* = 4.0 Hz, 1H), 7.60 (s, 2H), 6.86 (d, *J* = 4.0 Hz, 1H), 6.80 (dd, *J*<sub>1</sub> = 8.0 Hz, *J*<sub>2</sub> = 4.0 Hz, 1H), 3.95 (s, 6H), 3.92 (s, 3H), 3.85 (s, 3H), 2.51 (s, 3H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 160.0, 152.8, 144.2, 140.7, 139.1, 136.1, 124.1, 116.3, 110.6, 99.9, 61.0, 56.3, 55.4, 19.0

HRMS-ESI (m/z): calcd for C<sub>17</sub>H<sub>21</sub>N<sub>2</sub>O<sub>5</sub><sup>+</sup> ([M+H])<sup>+</sup> 333.1445, found 333.1465

FTIR (flim, cm<sup>-1</sup>): 2967, 1594, 1498, 1124, 1009, 833

M.p.: 89.0-89.0°C.



(Z)-2-(o-tolyl)-1-(3,4,5-trimethoxyphenyl)diazene 1-oxide (**6gj**) was synthesized according to **general procedure D**. To the mixture of compound **3j** (92 mg, 0.5 mmol, 1.0 equivalent) and **3g** (161 mg, 1.5 mmol, 3.0 equivalent) in 5.0 mL EtOH was added APT (153 mg, 0.05 mmol, 2.5 mol % based on **3j** + **3g**), H<sub>2</sub>O<sub>2</sub> (30% aq., 10.0 mmol, 5.0 equivalent based on **3j** + **3g**, 1.0 mL) at room temperature. Next, the mixture was stirred at room temperature for 24h until that **3j** was almost consumed. And then around 100 mL EtOAc was added to dilute the reaction solution, which was washed by H<sub>2</sub>O and brine. The organic layer was collected and dried by Na<sub>2</sub>SO<sub>4</sub>. After filtration and concentration, the crude product was purified by flash chromatography (PE/EtOAc = 100:1) to afford the desired product **6gj** as a yellow solid (1.0 mmol scale, 83 mg, 55% yield, rr>15:1).

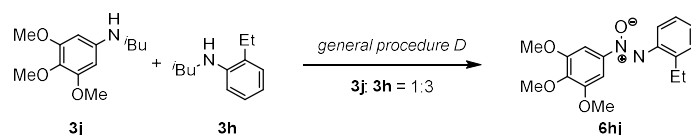
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.07 (d, *J* = 8.0 Hz, 1H), 7.63 (s, 2H), 7.32-7.25 (m, 3H), 3.97 (s, 6H), 3.93 (s, 3H), 2.40 (s, 3H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 152.8, 143.7, 142.7, 141.1, 134.5, 130.7, 128.6, 126.1, 121.8, 100.1, 61.1, 56.4, 18.4

HRMS-ESI (*m/z*): calcd for C<sub>16</sub>H<sub>19</sub>N<sub>2</sub>O<sub>4</sub> ([M+H]<sup>+</sup>) 303.1339, found 303.1361

FTIR (flim, cm<sup>-1</sup>): 2970, 1817, 1474, 1126, 1006, 749

M.p.: 56.5-58.0°C.



(Z)-2-(2-ethylphenyl)-1-(3,4,5-trimethoxyphenyl)diazene 1-oxide (**6hj**) was synthesized according to **general procedure D**. To the mixture of compound **3j** (92 mg, 0.5 mmol, 1.0 equivalent) and **3h** (182 mg, 1.5 mmol, 3.0 equivalent) in 5.0 mL EtOH was added APT (153 mg, 0.05 mmol, 2.5 mol % based on **3j** + **3h**), H<sub>2</sub>O<sub>2</sub> (30% aq., 10.0 mmol, 5.0 equivalent based on **3j** + **3h**, 1.0 mL) at room temperature. Next, the



mixture was stirred at room temperature for 24h until that **3j** was almost consumed. And then around 100 mL EtOAc was added to dilute the reaction solution, which was washed by H<sub>2</sub>O and brine. The organic layer was collected and dried by Na<sub>2</sub>SO<sub>4</sub>. After filtration and concentration, the crude product was purified by flash chromatography (PE/EtOAc = 100:1) to afford the desired product **6hj** and obtained as a yellow solid (71 mg, 45% yield, rr>15:1).

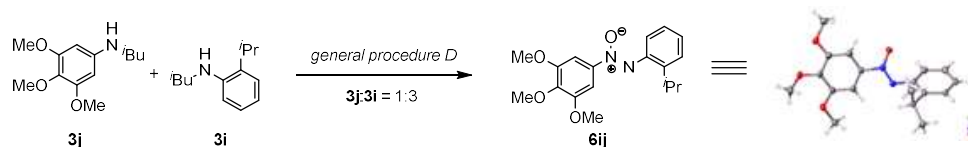
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.20-8.17 (m, 1H), 7.64 (s, 2H), 7.35-7.29 (m, 3H), 3.96 (s, 6H), 3.93 (s, 3H), 2.83 (q, *J* = 8.0 Hz, 2H), 1.26 (t, *J* = 8.0 Hz, 3H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 152.8, 143.8, 141.9, 141.0, 140.8, 129.2, 128.9, 126.1, 121.8, 100.0, 61.0, 56.3, 25.6, 15.4

HRMS-ESI (*m/z*): calcd for C<sub>17</sub>H<sub>21</sub>N<sub>2</sub>O<sub>4</sub><sup>+</sup> ([*M*+*H*]<sup>+</sup>) 317.1496, found 317.1523

FTIR (flim, cm<sup>-1</sup>): 2966, 1613, 1484, 1310, 1126, 744

M.p.: 48.2-49.1 °C



**(Z)-2-(2-isopropylphenyl)-1-(3,4,5-trimethoxyphenyl)diazene 1-oxide (6ij)** was synthesized according to **general procedure D**. To the mixture of compound **3j** (92 mg, 0.5 mmol, 1.0 equivalent) and **3i** (203 mg, 1.5 mmol, 3.0 equivalent) in 5.0 mL EtOH was added APT (153mg, 0.05 mmol, 2.5 mol % based on **3j** + **3i**), H<sub>2</sub>O<sub>2</sub> (30% aq., 10 mmol, 5.0 equivalent based on **3j** + **3i**, 1.0 mL) at room temperature. Next, the mixture was stirred at room temperature for 24h until that **3j** was almost consumed. And then around 100 mL EtOAc was added to dilute the reaction solution, which was washed by H<sub>2</sub>O and brine. The organic layer was collected and dried by Na<sub>2</sub>SO<sub>4</sub>. After filtration and concentration, the crude product was purified by flash chromatography (PE/EtOAc = 100:1) to afford the desired product **6ij** as a yellow solid (67 mg, 45% yield, rr>20: 1).

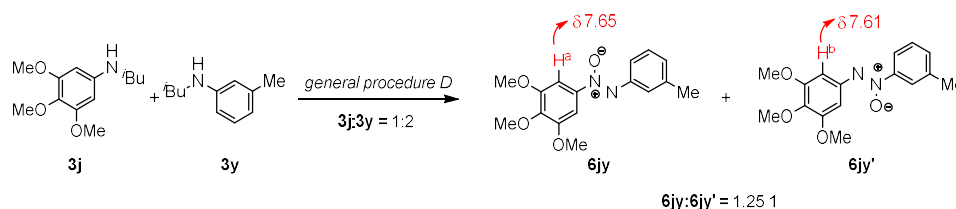
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.03-8.01 (m, 1H), 7.64 (s, 2H), 7.42 (d, *J* = 4.0 Hz, 1H), 7.34-7.29 (m, 2H), 3.96 (s, 6H), 3.93 (s, 3H), 3.45-3.35 (m, 1H), 1.28 (d, *J* = 4.0 Hz, 6H)

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 152.8, 144.5, 143.8, 141.5, 1414.2, 128.8, 126.0, 125.9, 121.6, 100.1, 61.0, 56.3, 29.1, 23.3

**HRMS-ESI** (m/z): calcd for C<sub>18</sub>H<sub>23</sub>N<sub>2</sub>O<sub>4</sub> ([M+H]<sup>+</sup>) 331.1652, found 331.1651

**FTIR** (flim, cm<sup>-1</sup>): 2969, 1615, 1498, 1323, 1127, 844, 781

**M.p.**: 68.2-70.2 °C



(Z)-2-(m-tolyl)-1-(3,4,5-trimethoxyphenyl)diazene 1-oxide (6jy) and (Z)-1-(m-tolyl)-2-(3,4,5-trimethoxyphenyl)diazene 1-oxide (6jy') were synthesized according to **general procedure D**. To the mixture of compound **3j** (92 mg, 0.5 mmol, 1.0 equivalent) and **3y** (108 mg, 0.5 mmol, 1.0 equivalent) in 5.0 mL was added APT (115 mg, 0.0375 mmol, 2.5 mol % based on **3j** + **3y**) and H<sub>2</sub>O<sub>2</sub> (30%, aq., 7.5 mmol, 0.75 mL) at room temperature in the open air. Next, the reaction mixture was stirred at room temperature for 36h until that **3j** was almost consumed. And then around 100 mL EtOAc was added to dilute the reaction solution, which was washed by H<sub>2</sub>O and brine. The organic layer was collected and dried by Na<sub>2</sub>SO<sub>4</sub>. After filtration and concentration, the crude product was purified by flash chromatography (PE/EtOAc = 100:1) to afford the desired products **6jy** and **6jy'** in an inseparable mixture as a yellow solid (73 mg, 48% yield, as a mixture with two isomers, **6jy**:**6jy'** = 1.25:1).

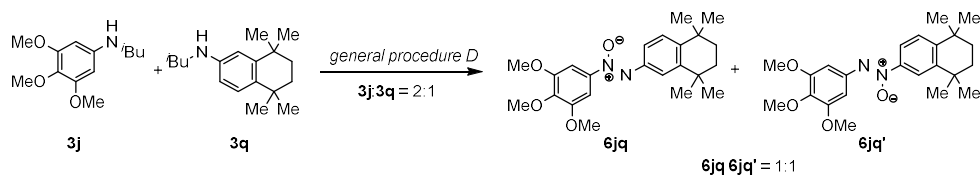
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ **6jy (major)** 8.09 (s, 1H), 8.07 (d, *J* = 8.0 Hz, 1H), 7.65 (s, 2H), 7.38-7.35 (m, 2H), 3.94 (s, 6H), 3.93 (s, 3H), 2.47 (s, 3H); **6jy' (minor)** 7.96 (d, *J* = 8.0 Hz, 1H), 7.95 (s, 1H), 7.61 (s, 2H), 7.41-7.38 (m, 1H), 7.32 (d, *J* = 8.0 Hz, 1H), 3.96 (s, 6H), 3.93 (s, 3H), 2.43 (s, 3H)

**<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ **6jy (major)** 152.3, 143.9, 139.8, 139.0, 138.4, 132.2, 128.6, 122.6, 119.3, 103.7, 60.9, 21.3; **6jy' (minor)** 152.8, 148.4, 143.8, 141.0, 139.4, 130.3, 128.5, 125.9, 122.4, 110.1, 61.0, 56.3, 21.4

**HRMS-ESI** (m/z, as a mixture): calcd for C<sub>16</sub>H<sub>19</sub>N<sub>2</sub>O<sub>4</sub><sup>+</sup> ([M + H]<sup>+</sup>) 303.1339, found 303.1330

**FTIR** (flim, cm<sup>-1</sup>): 2938, 1590, 1498, 1412, 1325, 1218, 1004, 887

**M.p.** (as a mixture): 51.3-52.1 °C.



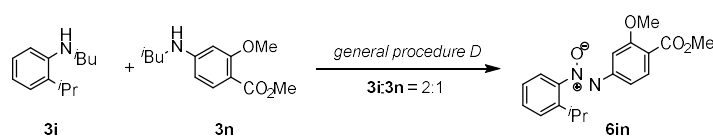
**(Z)-2-(5,5,8,8-tetramethyl-5,6,7,8-tetrahydronaphthalen-2-yl)-1-(3,4,5-trimethoxyphenyl)diazene 1-oxide (6jq)** and **(Z)-1-(5,5,8,8-tetramethyl-5,6,7,8-tetrahydronaphthalen-2-yl)-2-(3,4,5-trimethoxyphenyl)diazene 1-oxide (6jq')** were synthesized according to **general procedure D**. To the mixture of compound **3j** (183 mg, 1.0 mmol, 2.0 equivalent) and **3q** (102 mg, 0.5 mmol, 1.0 equivalent) in 5.0 mL was added APT (115 mg, 0.0375 mmol, 2.5 mol % based on **3j** + **3q**) and H<sub>2</sub>O<sub>2</sub> (30%, aq., 7.5 mmol, 0.75 mL) at room temperature in the open air. Next, the reaction mixture was stirred at room temperature for 36 h until that **3j** was almost consumed. And then around 100 mL EtOAc was added to dilute the reaction solution, which was washed by H<sub>2</sub>O and brine. The organic layer was collected and dried by Na<sub>2</sub>SO<sub>4</sub>. After filtration and concentration, the crude product was purified by flash chromatography (PE/EtOAc = 100:1) to afford the desired products **6jq** and **6jq'** in an inseparable mixture as a yellow oil (102 mg, 48% yield, **6jq**:**6jq'** = 1:1).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ **6jq** 8.09 (d, *J* = 4.0 Hz, 1H), 8.00 (dd, *J*<sub>1</sub> = 8.0 Hz, *J*<sub>2</sub> = 4.0 Hz, 1H), 7.64 (s, 2H), 7.41 (d, *J* = 8.0 Hz, 1H), 3.97 (s, 6H), 3.93 (s, 3H), 1.72 (s, 4H), 1.35 (s, 6H), 1.32 (s, 6H); **6jq'** 8.20 (d, *J* = 4.0 Hz, 1H), 8.03 (dd, *J*<sub>1</sub> = 8.0 Hz, *J*<sub>2</sub> = 4.0 Hz, 1H), 7.60 (s, 2H), 7.42 (d, *J* = 8.0 Hz, 1H), 3.94 (s, 6H), 3.92 (s, 3H), 1.73 (s, 4H), 1.36 (s, 6H), 1.32 (s, 6H)

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 152.7, 152.5, 148.9, 147.2, 146.1, 145.9, 145.4, 143.9, 141.7, 140.6, 140.8, 139.9, 139.1, 127.1, 126.7, 122.5, 120.2, 119.2, 103.6, 100.0, 60.92, 60.88, 56.3, 56.1, 34.9, 34.82, 34.75, 34.7, 34.6, 34.52, 34.49, 34.39, 31.74, 31.68, 31.62, 31.59 (hard to distinguish **6jq** and **6jq'**)

**HRMS-ESI** (*m/z*, as a mixture): calcd for C<sub>23</sub>H<sub>31</sub>N<sub>2</sub>O<sub>4</sub><sup>+</sup> ([M + H]<sup>+</sup>) 399.2278, found 399.2282

**FTIR** (flim, cm<sup>-1</sup>): 2968, 1589, 1497, 1127, 831



**(Z)-2-(2-isopropylphenyl)-1-(3-methoxy-4-(methoxycarbonyl)phenyl)diazene 1-oxide (6in)** was synthesized according to **general procedure D**. To the mixture of compound **3i** (135 mg, 1.0 mmol, 2.0

equivalent) and **3n** (91 mg, 0.5 mmol, 1.0 equivalent) in 5.0 mL EtOH was added catalyst APT (115 mg, 0.0375 mmol, 2.5 mol % based on **3i** + **3n**), H<sub>2</sub>O<sub>2</sub> (30%, aq., 10 mmol, 5.0 equivalent based on **3i** + **3n**) at room temperature in the open air. Next, the reaction mixture continued stirring at room temperature for 24h. It was found that all compound **3i** was consumed while considerable part of **3n** left, thus compound **3i** (68 mg, 0.5 mmol, 1.0 equivalent) and H<sub>2</sub>O<sub>2</sub> (30% aq., 2.5 mmol) were added into the reaction solution for another 12h. After the reaction was finished, around 100 mL EtOAc was added to dilute the reaction solution, which was then washed by H<sub>2</sub>O and brine. The organic layer was collected and dried by Na<sub>2</sub>SO<sub>4</sub>. After filtration and concentration, the crude product was purified by flash chromatography (PE/EtOAc = 100:1) to afford the desired product **6in** as a yellow solid (72 mg, 44% yield, rr>20:1).

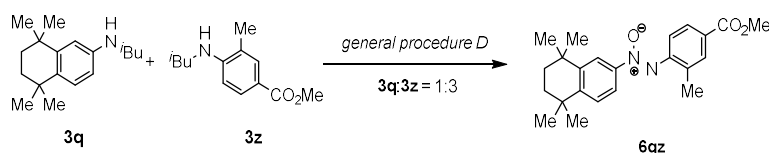
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.23 (d, *J* = 8.0 Hz, 1H), 7.97 (s, 1H), 7.93 (s, 2H), 7.43 (d, *J* = 8.0 Hz, 1H), 7.36 (dd, *J*<sub>1</sub> = 8.0 Hz, *J*<sub>2</sub> = 8.0 Hz, 1H), 7.30 (dd, *J*<sub>1</sub> = 8.0 Hz, *J*<sub>2</sub> = 8.0 Hz, 1H), 4.02 (s, 3H), 3.94 (s, 3H), 3.54-3.47 (m, 1H), 1.57 (s, 3H), 1.29 (d, *J* = 8.0 Hz, 6H)

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 165.7, 159.4, 145.4, 141.1, 132.0, 129.5, 126.1, 125.9, 121.8, 115.0, 113.9, 107.0, 106.4, 56.4, 52.4, 29.0, 23.4

HRMS-ESI (*m/z*): calcd for C<sub>18</sub>H<sub>21</sub>N<sub>2</sub>O<sub>4</sub><sup>+</sup> ([*M* + *H*]<sup>+</sup>) 329.1496; found 329.1496

FTIR (flim, cm<sup>-1</sup>): 2966, 1735, 1588, 1463, 1254, 867, 769

M.p.: 47-48°C



**(Z)-2-(4-(methoxycarbonyl)-2-methylphenyl)-1-(5,5,8,8-tetramethyl-5,6,7,8-tetrahydronaphthalen-2-yl)diazene 1-oxide (6qz)** was synthesized according to **general procedure D**. To the mixture of compound **3q** (130 mg, 0.5 mmol, 1.0 equivalent) and **3z** (332 mg, 1.5 mmol, 3.0 equivalent) in 5.0 mL EtOH was added catalyst APT (153 mg, 0.05 mmol, 2.5 mol% based on **3q** + **3z**), H<sub>2</sub>O<sub>2</sub> (30%, aq., 10.0 mmol, 5.0 equivalent based on **3q** + **3z**, 1.0 mL) at room temperature. Next, the mixture was stirred at room temperature for 24h. After the reaction was finished, around 100 mL EtOAc was added to dilute the reaction solution, and the reaction mixture was then washed by H<sub>2</sub>O and brine. The organic layer was collected and dried by Na<sub>2</sub>SO<sub>4</sub>. After filtration and concentration, the crude product was purified by flash

chromatography (PE/EtOAc = 100:1) to afford the desired product **6qz** as a yellow solid (1.0 mmol scale, 86 mg, 45% yield, only one isomer, rr>20: 1).

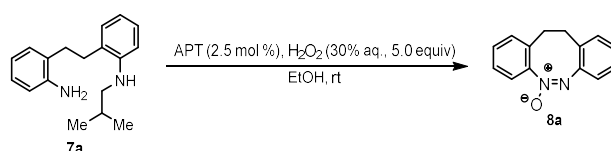
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 8.25 (d, *J* = 4.0 Hz, 1H), 8.04 (dd, *J*<sub>1</sub> = 8.0 Hz, *J*<sub>2</sub> = 4.0 Hz, 1H), 8.02-7.93 (m, 3H), 7.44 (d, *J* = 8.0 Hz, 1H), 3.93 (s, 3H), 2.40 (s, 3H), 1.74 (s, 4H), 1.36 (s, 6H), 1.32 (s, 6H).

**<sup>13</sup>C NMR** (CDCl<sub>3</sub>, 101 MHz) δ 149.8, 146.2, 134.1, 131.8, 129.1, 128.0, 127.6, 127.3, 124.6, 121.7, 120.6, 119.5, 52.1, 34.8 (two carbons), 34.7, 31.8, 31.7, 18.2 (four carbons)

**HRMS-ESI** (*m/z*): calcd for C<sub>23</sub>H<sub>29</sub>N<sub>2</sub>O<sub>3</sub><sup>+</sup> ([*M*+*H*]<sup>+</sup>) 381.2173, found 381.2166

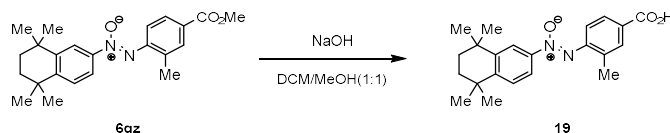
**FTIR** (flim, cm<sup>-1</sup>): 3419, 2961, 1727, 1432, 1287, 770

**M.p.:** 69.4-71.3°C



**(*E*)-11,12-dihydrodibenzo[*c,g*][1,2]diazocine 5-oxide (8a)** was synthesized according to **general procedure D**. To the solution of compound **7a** (268 mg, 1.0 mmol, 1.0 equivalent) in 50 mL EtOH was added ATT (77 mg, 0.025 mmol, 2.5 mol %) and H<sub>2</sub>O<sub>2</sub> (30% aq. 5.0 mmol, 5.0 equivalent, 5.0 mL) at room temperature in the open air. The reaction solution continued stirring until that all compound **7a** was consumed. Remove the solvent in rotate evaporation, the residue was diluted with EtOAc followed by being washed by brine and dried by Na<sub>2</sub>SO<sub>4</sub>. The desired product **8a** was obtained as brown solid (2.0 mmol scale, 11 mg, 5% yield) after filtration, concentration and flash chromatography (PE/EtOAc = 100:1). The H NMR spectrum was in accord with reported literature.<sup>28</sup>

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.21-7.08 (m, 4H), 7.06-6.98 (m, 3H), 6.92 (d, *J* = 4.0 Hz, 1H), 3.44-3.31 (m, 1H), 3.29-3.17 (m, 1H), 3.03-2.91 (m, 1H), 2.93-2.80 (m, 1H).



28 Joshi, D. K.; Mitchell, M. J.; Bruce, D.; Lough, A. J.; Yan, H. Synthesis of cyclic azobenzene analogues. *Tetrahedron*. **2012**, 68, 8670.

**(Z)-2-(4-carboxy-2-methylphenyl)-1-(5,5,8,8-tetramethyl-5,6,7,8-tetrahydronaphthalen-2-yl)diazene 1-**

**oxid (19)** was prepared according to following procedure. To the solution of compound **6qz** (21 mg, 0.055 mmol, 1.0 equiv.) in DCM/MeOH (1:1 v/v, 1.0 mL) was added NaOH (1N, 0.1 mL) at room temperature. The reaction mixture continued stirring at room temperature until that no **6qz** was detected by TLC analysis, followed by adding HCl (1N aq., 0.12 mL). The resulting reaction mixture was extracted by EtOAc. The organic layer was then washed by brine and dried by Na<sub>2</sub>SO<sub>4</sub>. The desired product **19** was obtained as a pale yellow solid (18.5 mg, 92% yield) after filtration, concentration and dried in *vacuum*.

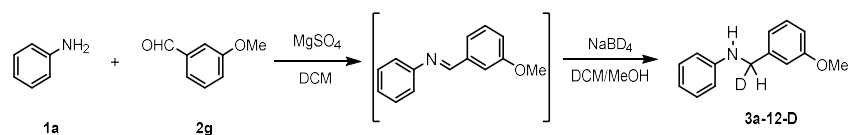
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.26 (d, *J* = 4.0 Hz, 1H), 8.06 (d, *J* = 4.0 Hz, 2H), 8.03 (t, *J* = 4.0 Hz, 1H), 7.95 (d, *J* = 8.0 Hz, 1H), 7.45 (d, *J* = 8.0 Hz, 1H), 2.41 (s, 3H), 1.74 (s, 4H), 1.36 (s, 6H), 1.33 (s, 6H)

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 171.4, 150.0, 147.6, 146.2, 145.6, 134.2, 132.5, 128.3, 128.0, 127.3, 121.8, 120.7, 119.6, 34.8 (two carbons), 34.7, 31.8 (two carbons), 31.7 (two carbons), 20.0, 18.2

HRMS-ESI (*m/z*): calcd for C<sub>22</sub>H<sub>27</sub>N<sub>2</sub>O<sub>3</sub><sup>+</sup> ([*M* + *H*]<sup>+</sup>) 367.2016, found 367.2006

FTIR (flim, cm<sup>-1</sup>): 2969, 1890, 1444, 1310, 1283, 906, 759

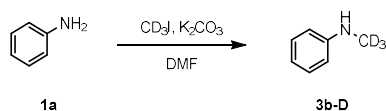
M.p.: 205.5-207.2 °C.



**N-((3-methoxyphenyl) methyl-*d*)aniline (3a-12-D)** was prepared according to general procedure A by utilizing NaBD<sub>4</sub> as reductant. Compound **1a** (485 mg, 5.2 mmol, 1.04 equiv.) and **2g** (680 mg, 5 mmol, 1.0 equiv.) were dissolved in anhydrous DCM (10 mL), followed by adding MgSO<sub>4</sub> (1.43 g, 10 mmol, 2.0 equiv.). The reaction mixture stirred for overnight. After filtration and concentration in *vacuum*, the imine intermediate was dissolved in anhydrous DCM/MeOH (20 mL/1 mL) at room temperature, and was cooled to 0°C in ice-water bath followed by adding NaBD<sub>4</sub> (63 mg, 1.5 mmol, 0.3 equiv.) and one drop of acetic acid. The reaction continued stirring from 0°C to room temperature until no **1a** was detected by TLC analysis and then quenched by adding H<sub>2</sub>O (1.0 mL). The reaction mixture was extracted by EtOA (around 150 mL), and then washed by H<sub>2</sub>O (20 mL), brine (20 mL) and dried by Na<sub>2</sub>SO<sub>4</sub>. The desired

product **3a-12-D** was obtained as colorless liquid after filtration, concentration and flash chromatography (304 mg, 28% yield).

$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.28 (dd,  $J_1 = 8.0$  Hz,  $J_2 = 8.0$  Hz, 1H), 7.20 (d,  $J = 8.0$  Hz, 1H), 7.19 (d,  $J = 8.0$  Hz, 1H), 6.98 (d,  $J = 8.0$  Hz, 1H), 6.95 (s, 1H), 6.85 (dd,  $J_1 = 8.0$  Hz,  $J_2 = 4.0$  Hz, 1H), 6.74 (dd,  $J_1 = 8.0$  Hz,  $J_2 = 8.0$  Hz, 1H), 6.65 (d,  $J = 4.0$  Hz, 2H), 4.30 (s, 1H), 4.04 (br, 1H), 3.81 (s, 3H)

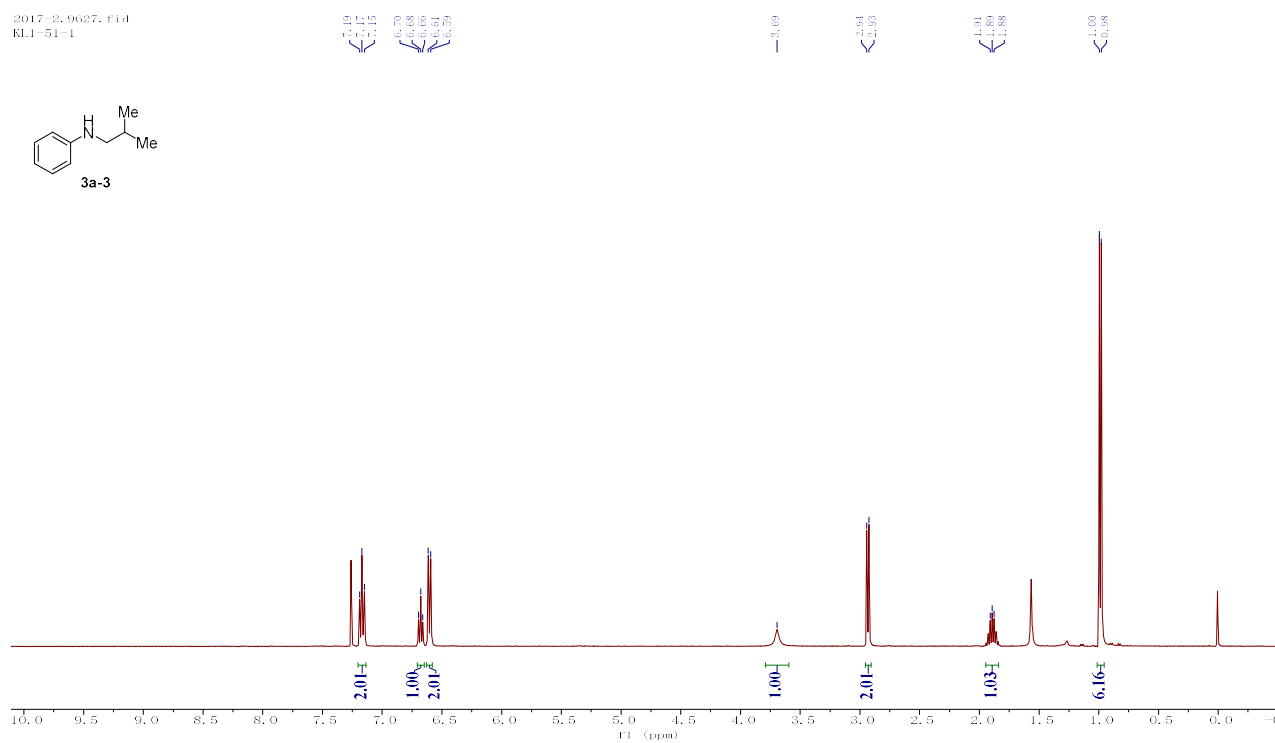


*N*-(methyl- $d_3$ )aniline (**3b-D**) was prepared according following procedure. To the mixture of compound **1a** (558 mg, 6.0 mmol, 1.0 equiv.) and  $\text{K}_2\text{CO}_3$  (828 mg, 6.0 mmol, 1.0 equiv.) in 10 mL DMF was added  $\text{CD}_3\text{I}$  (870 mg, 6.0 mmol, 1.0 equiv.), and then the mixture was heated to  $100^\circ\text{C}$  for 2h. When no compound **1a** was left, the reaction was cooled to room temperature and diluted with around 150 mL EtOAc. The resulting reaction mixture was washed by  $\text{H}_2\text{O}$  (30 mL  $\times$  3), brine (30 mL) and dried by  $\text{Na}_2\text{SO}_4$ .

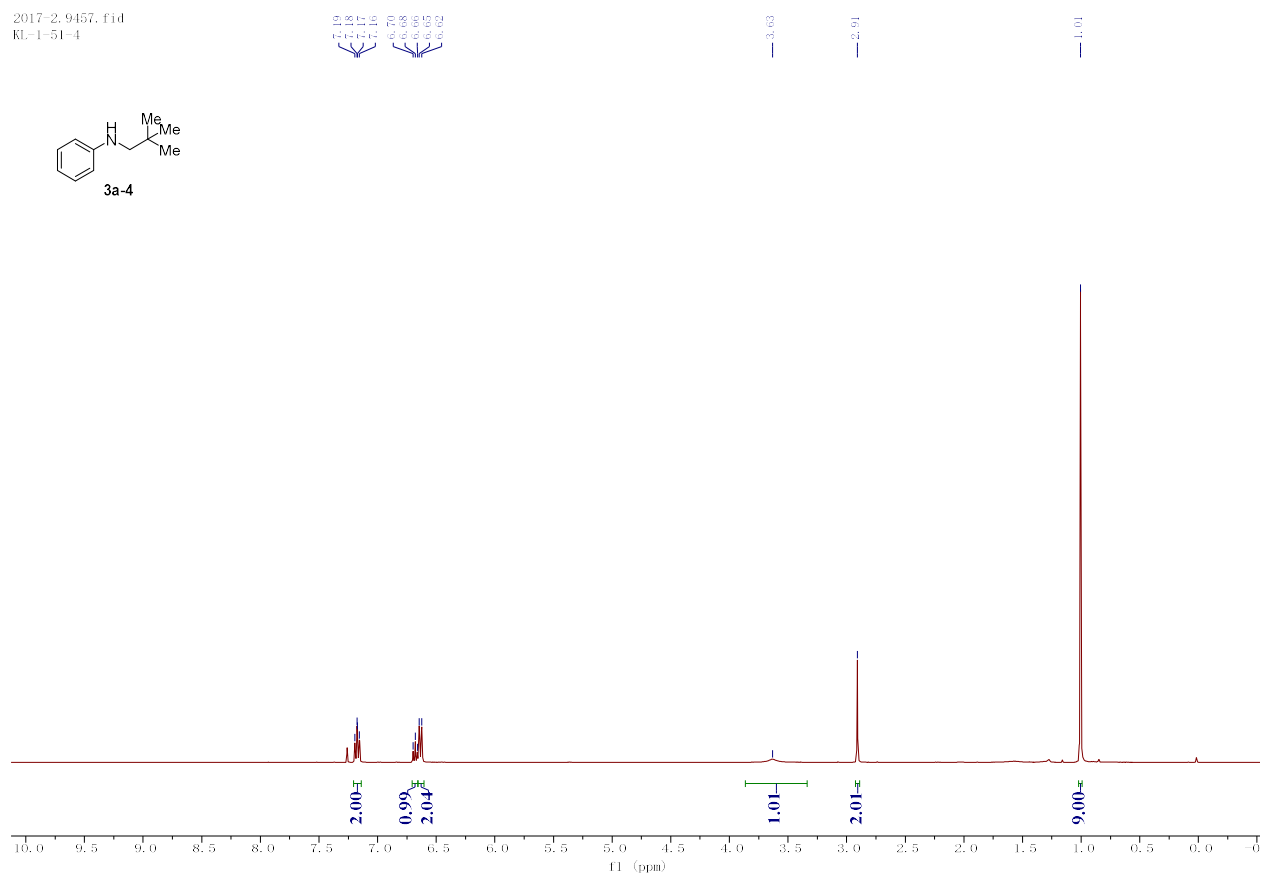
$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.20 (dd,  $J_1 = 8.0$  Hz,  $J_2 = 8.0$  Hz, 2H), 5.72 (dd, dd,  $J_1 = 8.0$  Hz,  $J_2 = 8.0$  Hz, 1H), 6.62 (d,  $J = 8.0$  Hz, 2H), 3.48 (br, 1H).

## Spectra

2017-2, 9627, f1d  
KL1-51-1

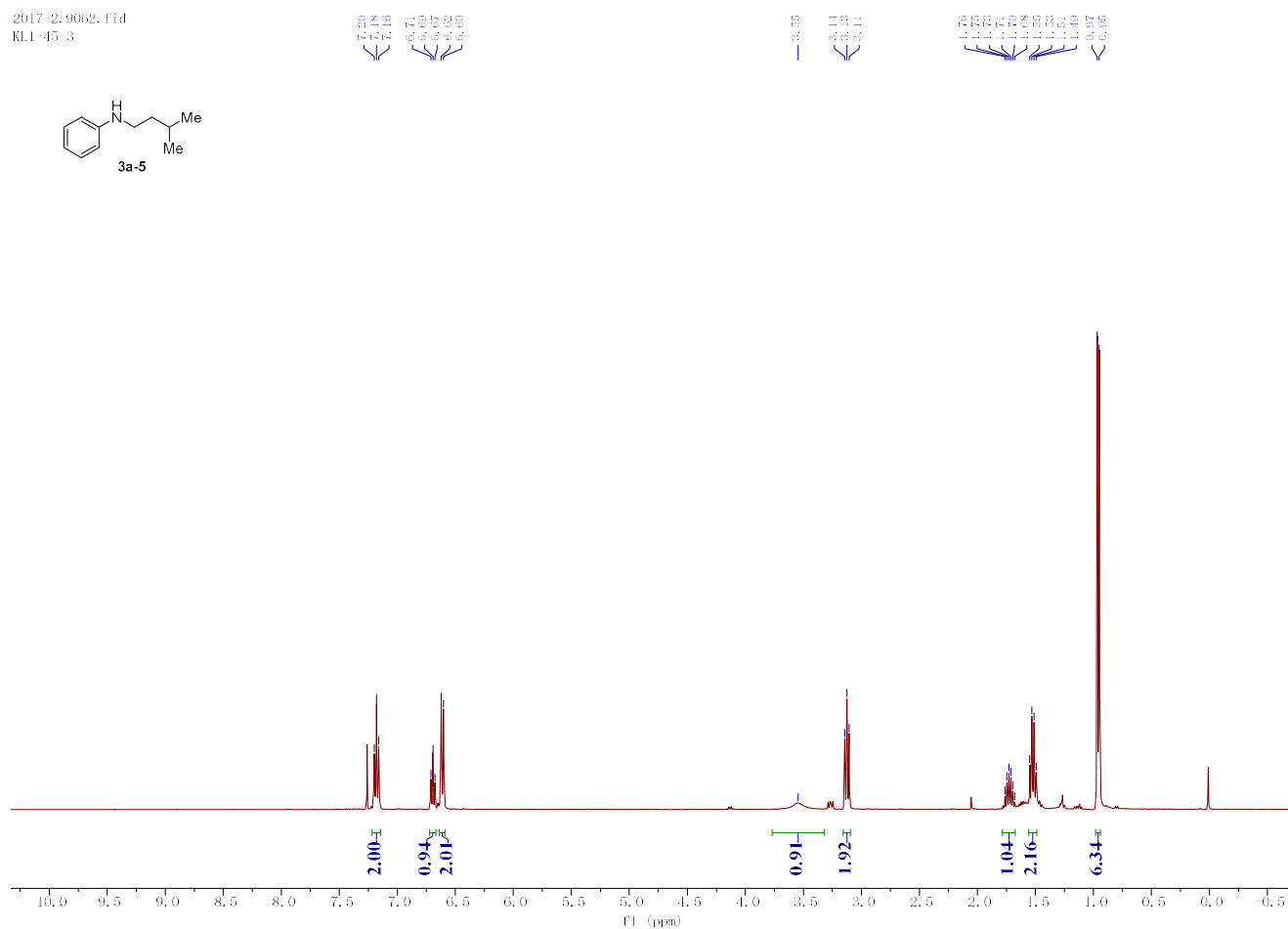
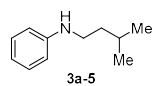


2017-2, 9457, f1d  
KL1-51-4

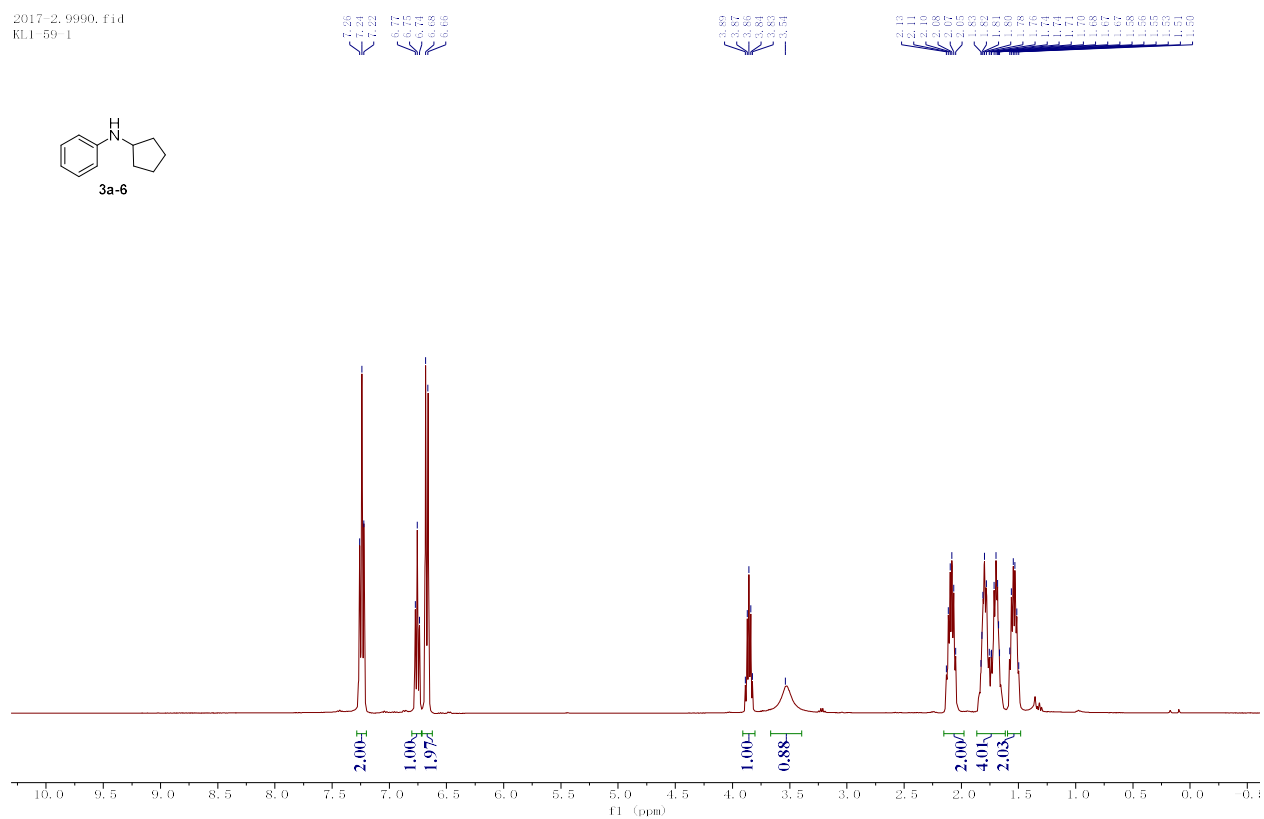
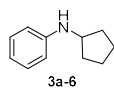




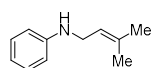
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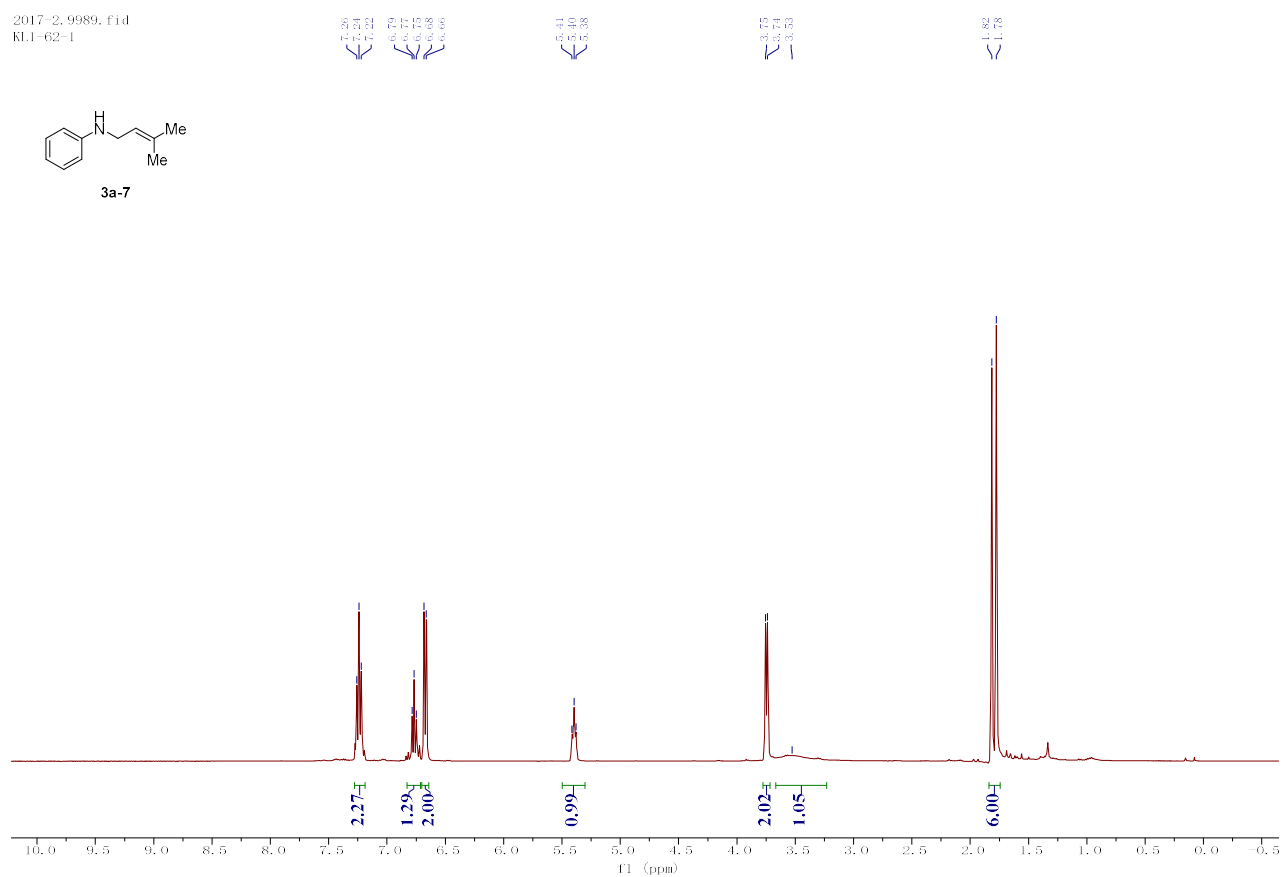
2017-2-9990.fid  
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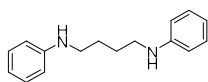
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KL1-62-1



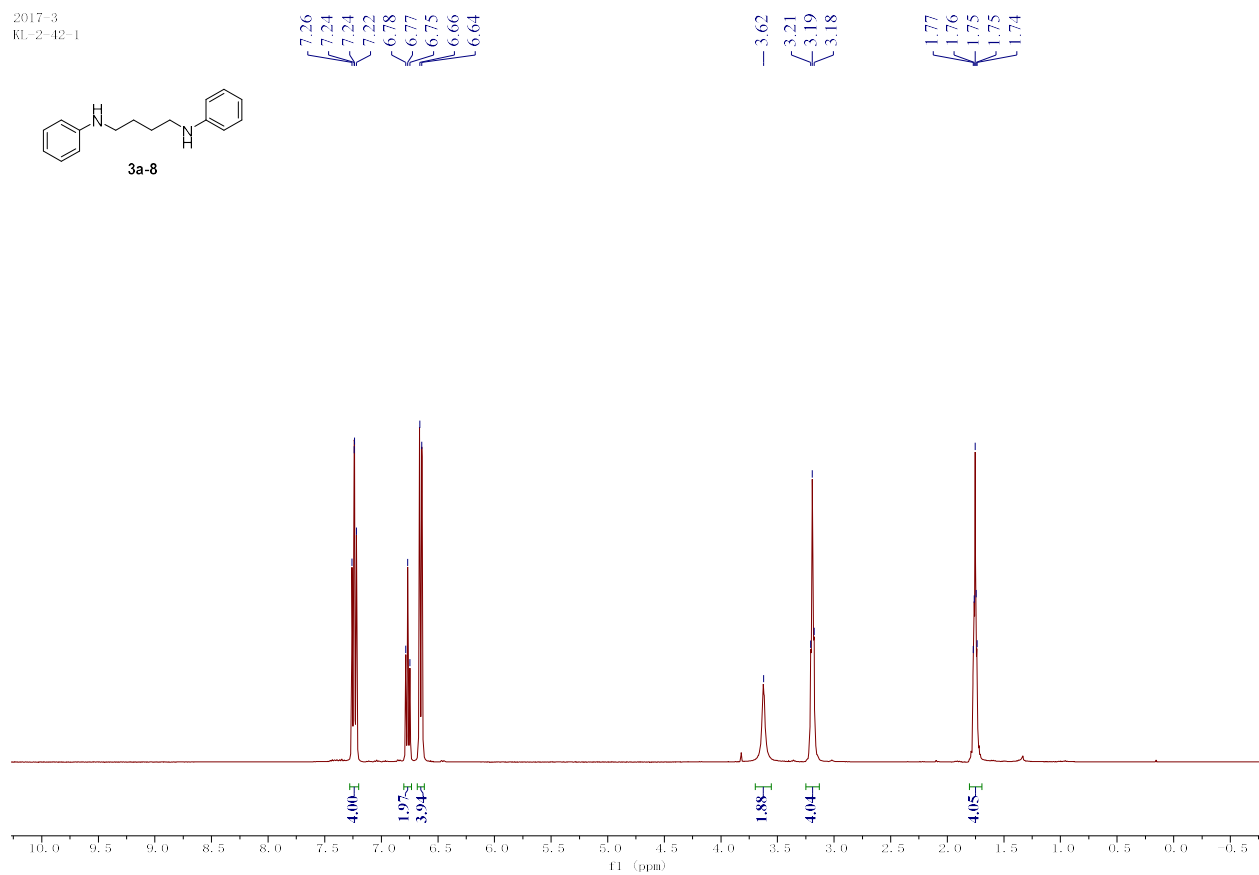
3a-7



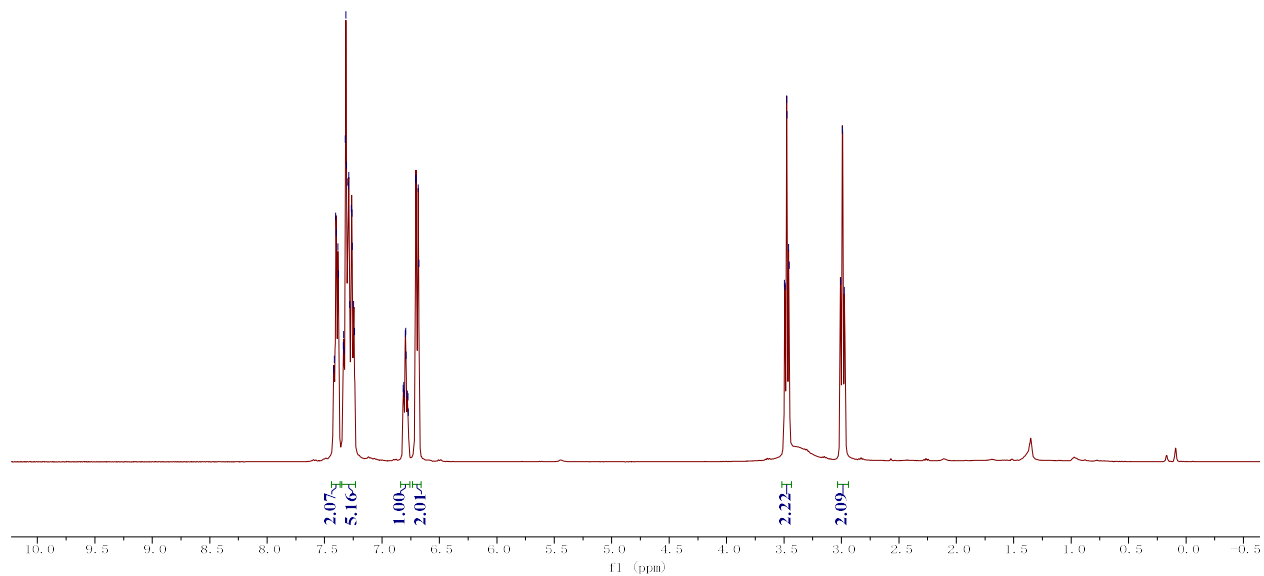
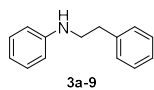
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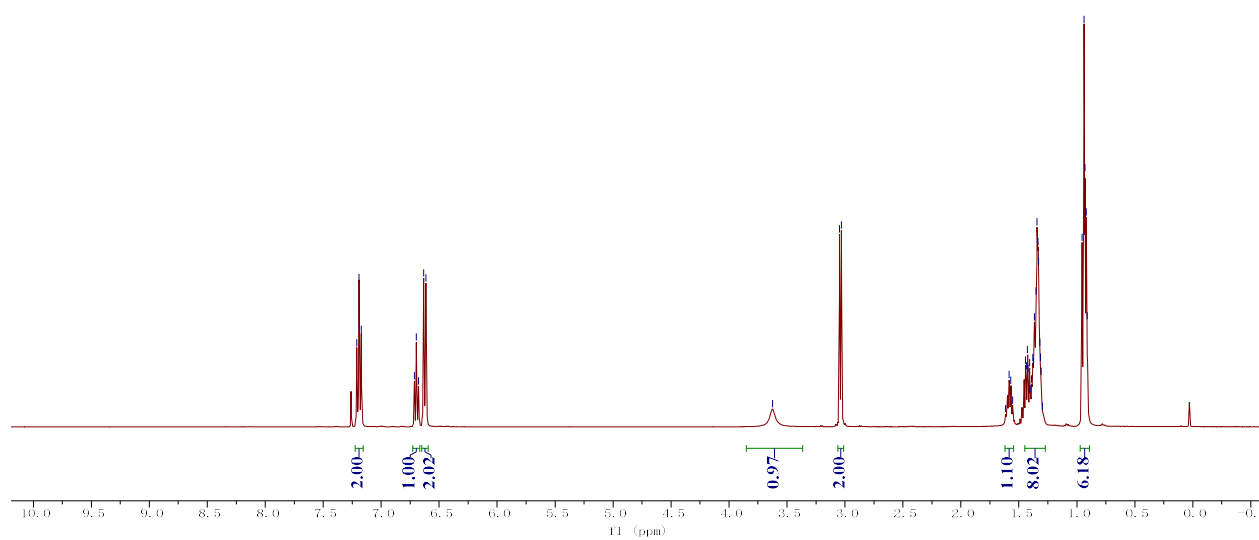
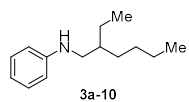
3a-8



xiangguangya-20180127-48#  
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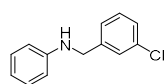
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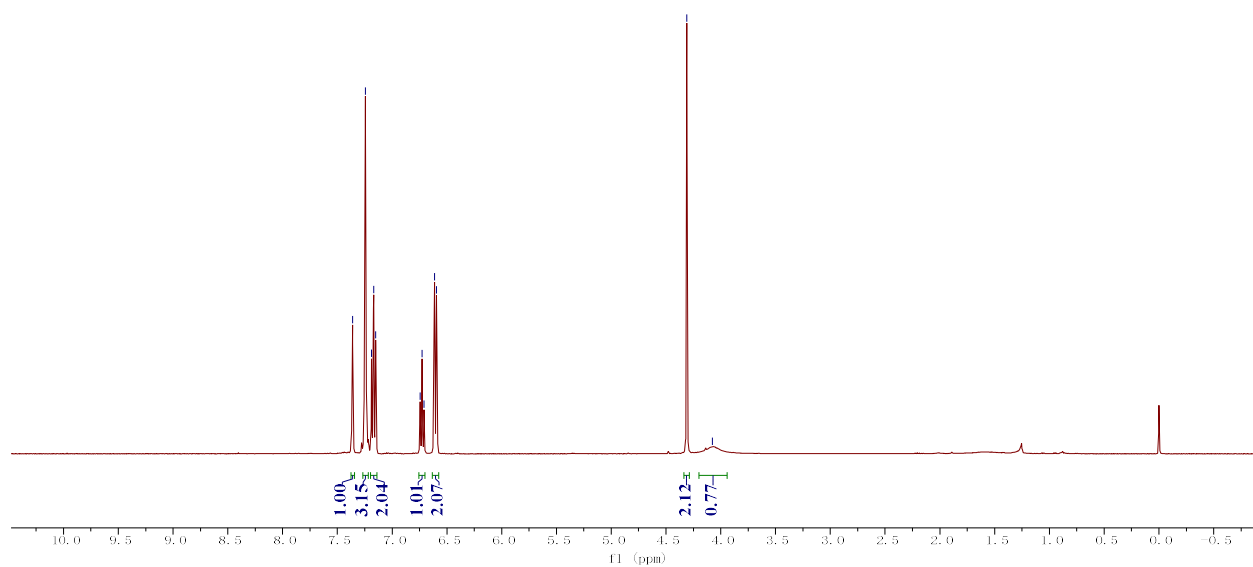
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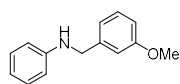
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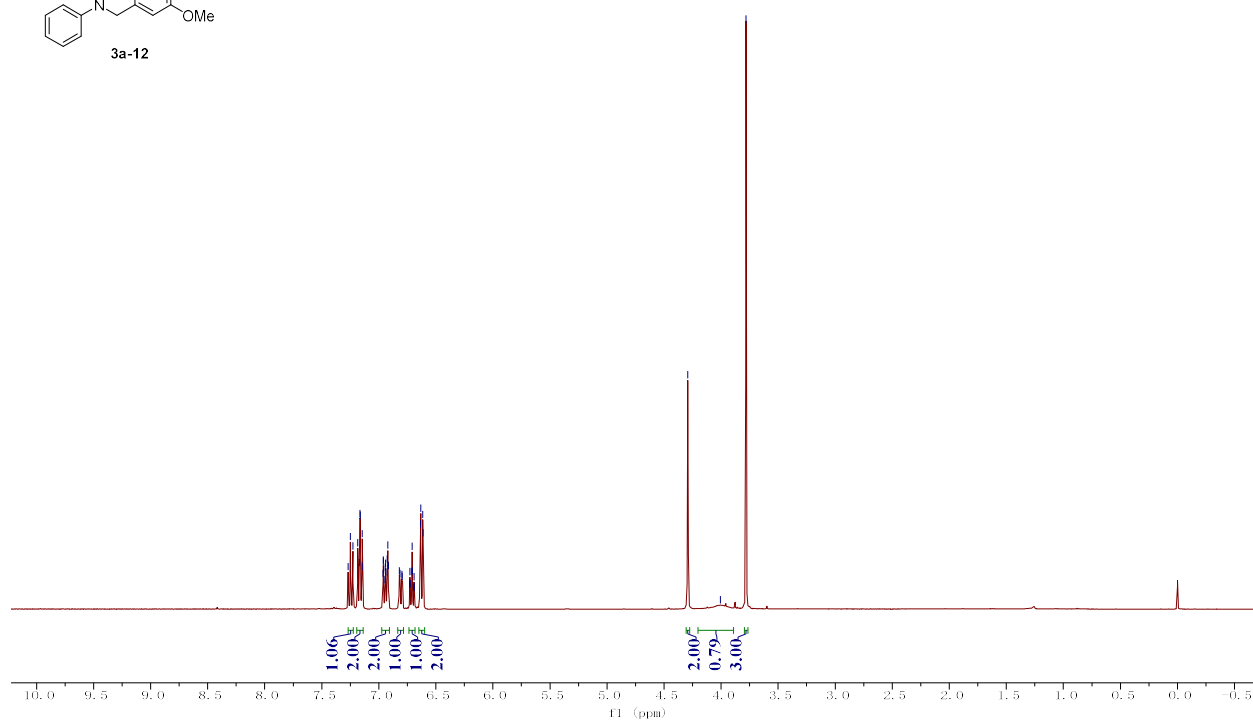
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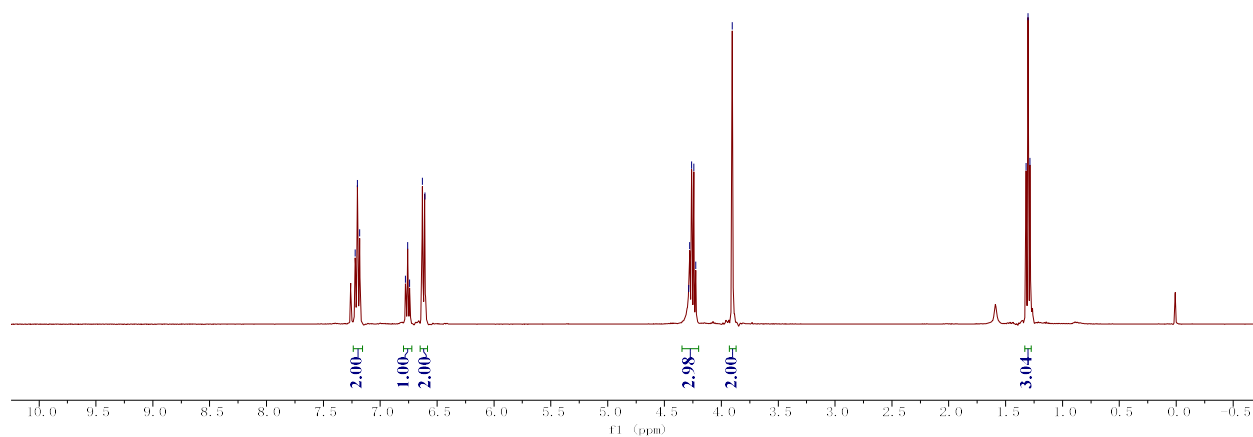


3a-12



$$\begin{array}{r} 32 \\ 30 \\ 29 \\ \hline \end{array}$$

  
3a-13




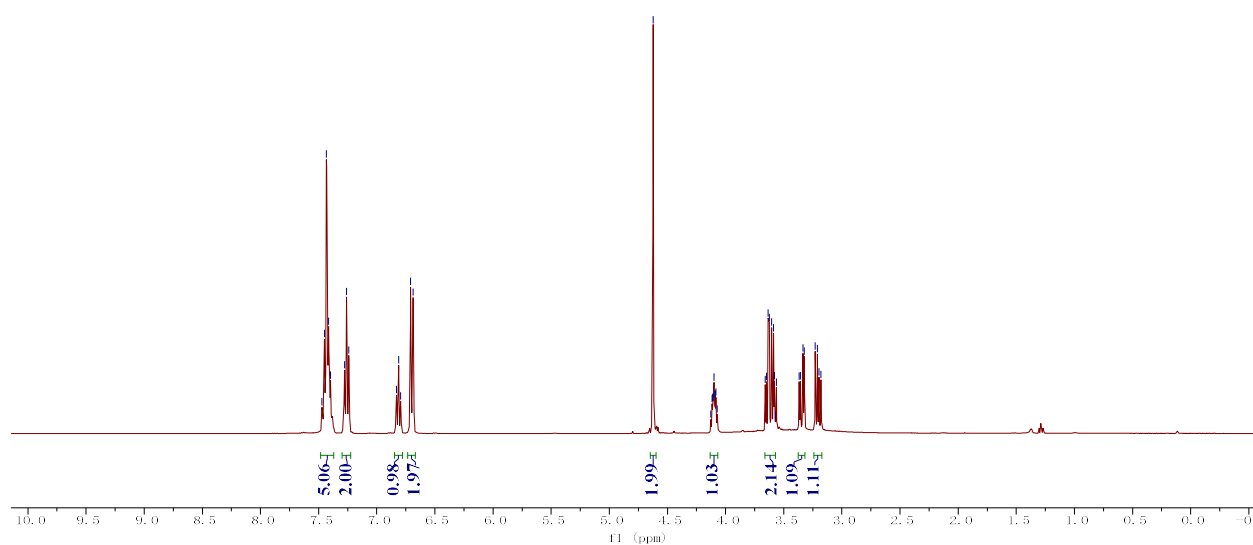
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4.11  
4.10  
4.09  
4.09  
4.08  
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3.66  
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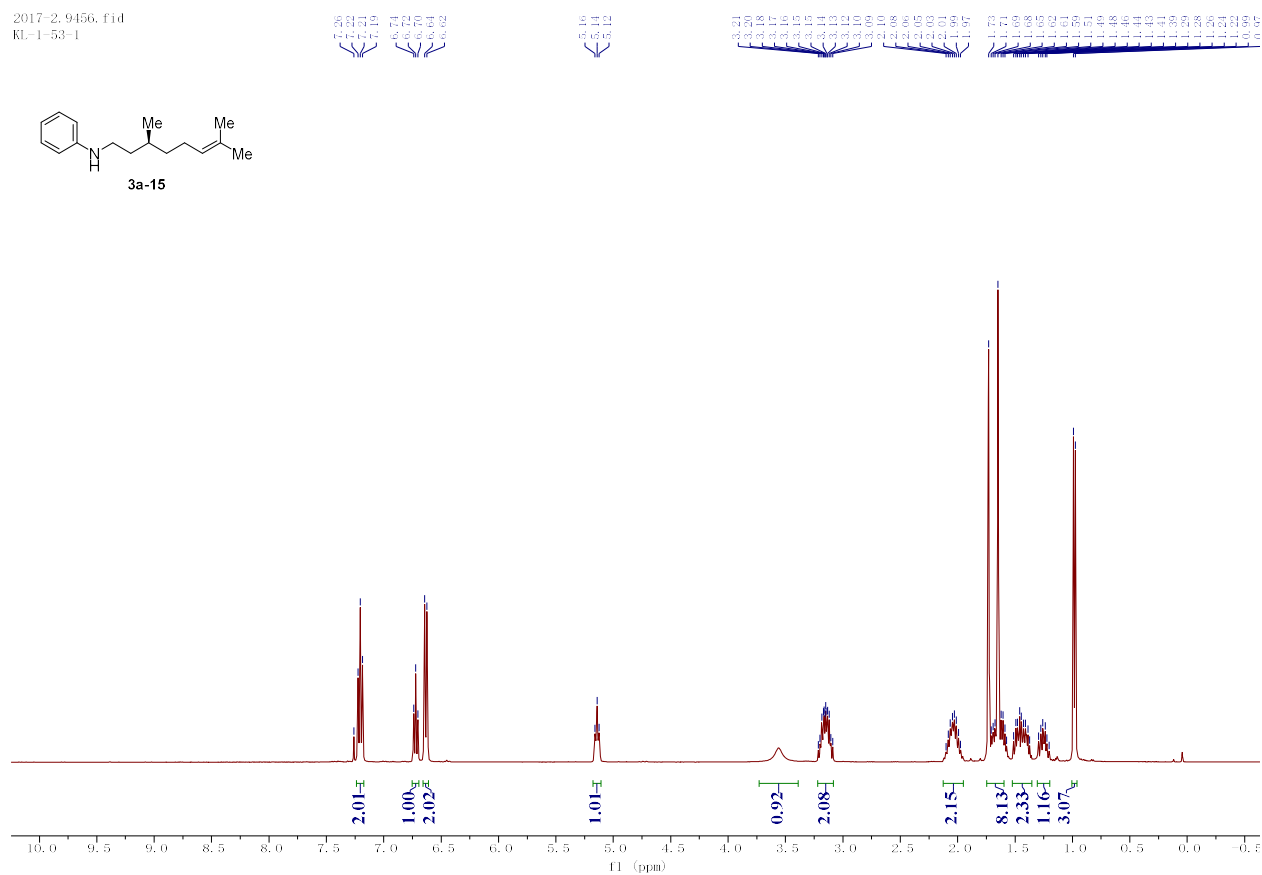
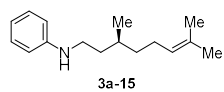
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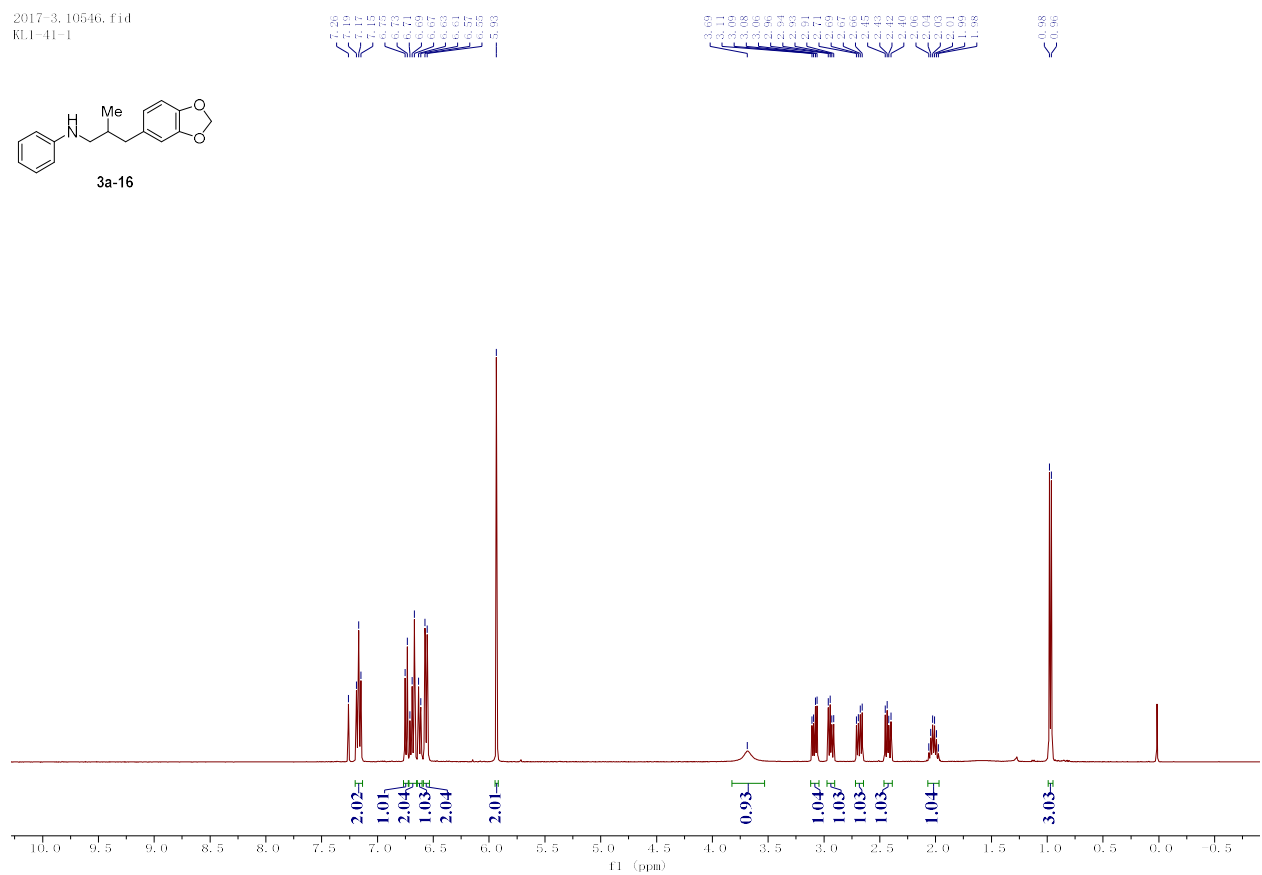
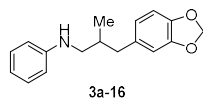
  
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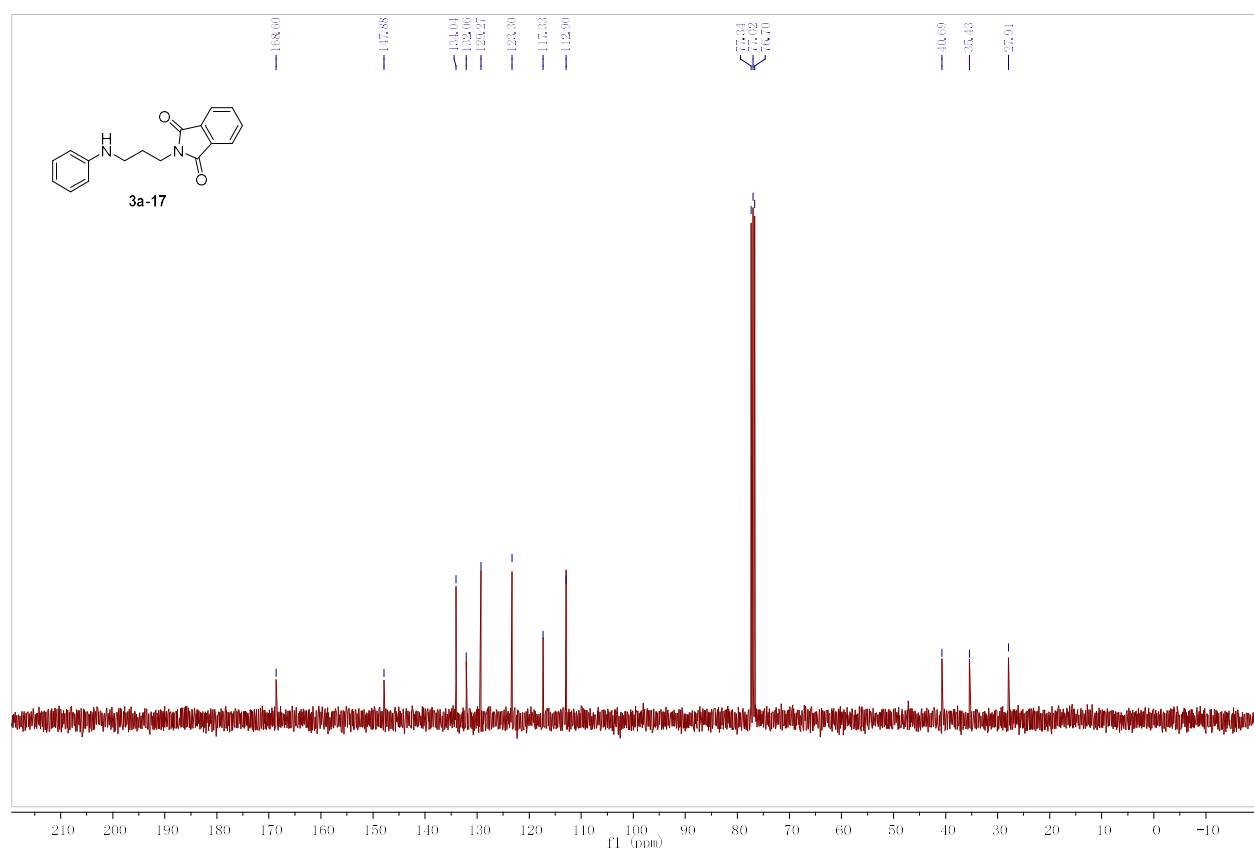
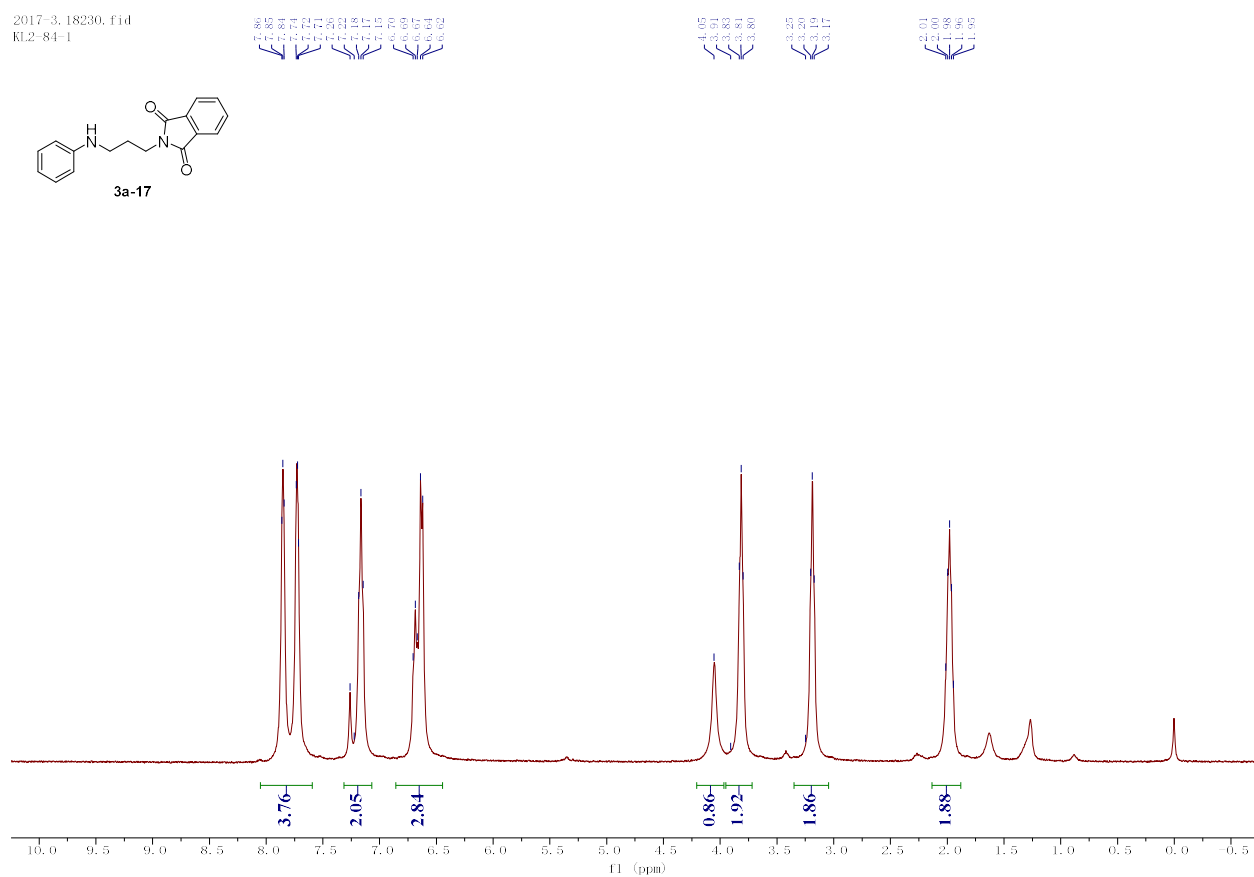
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KL1-53-1



2017-3-10546.fid  
KL1-41-1

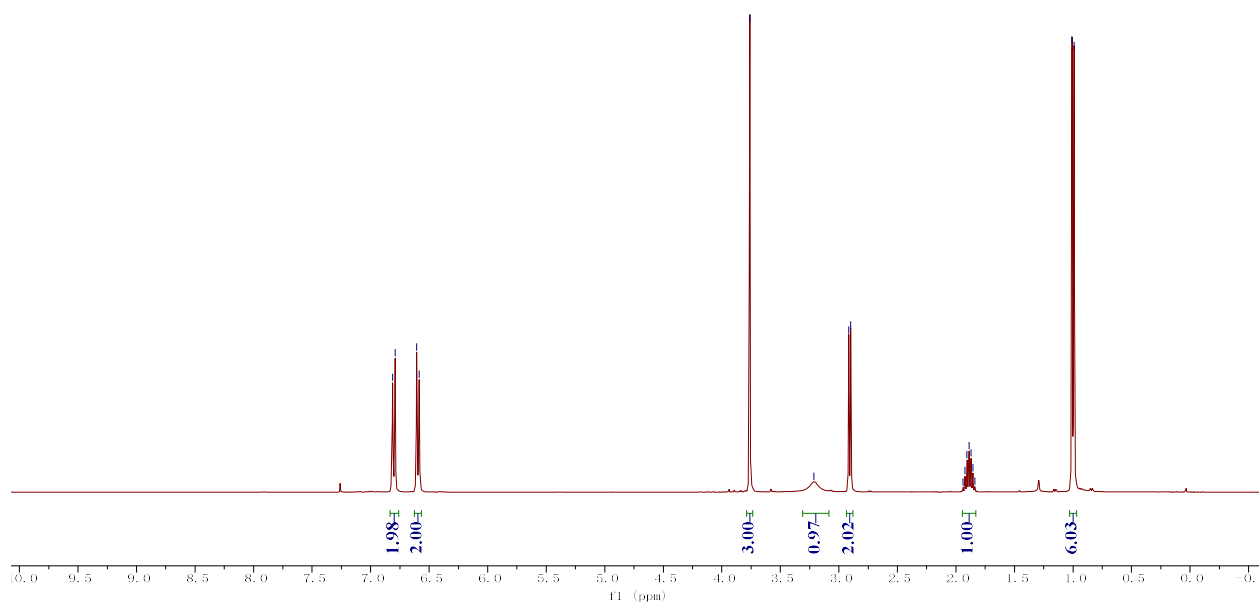
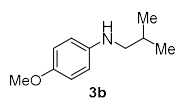
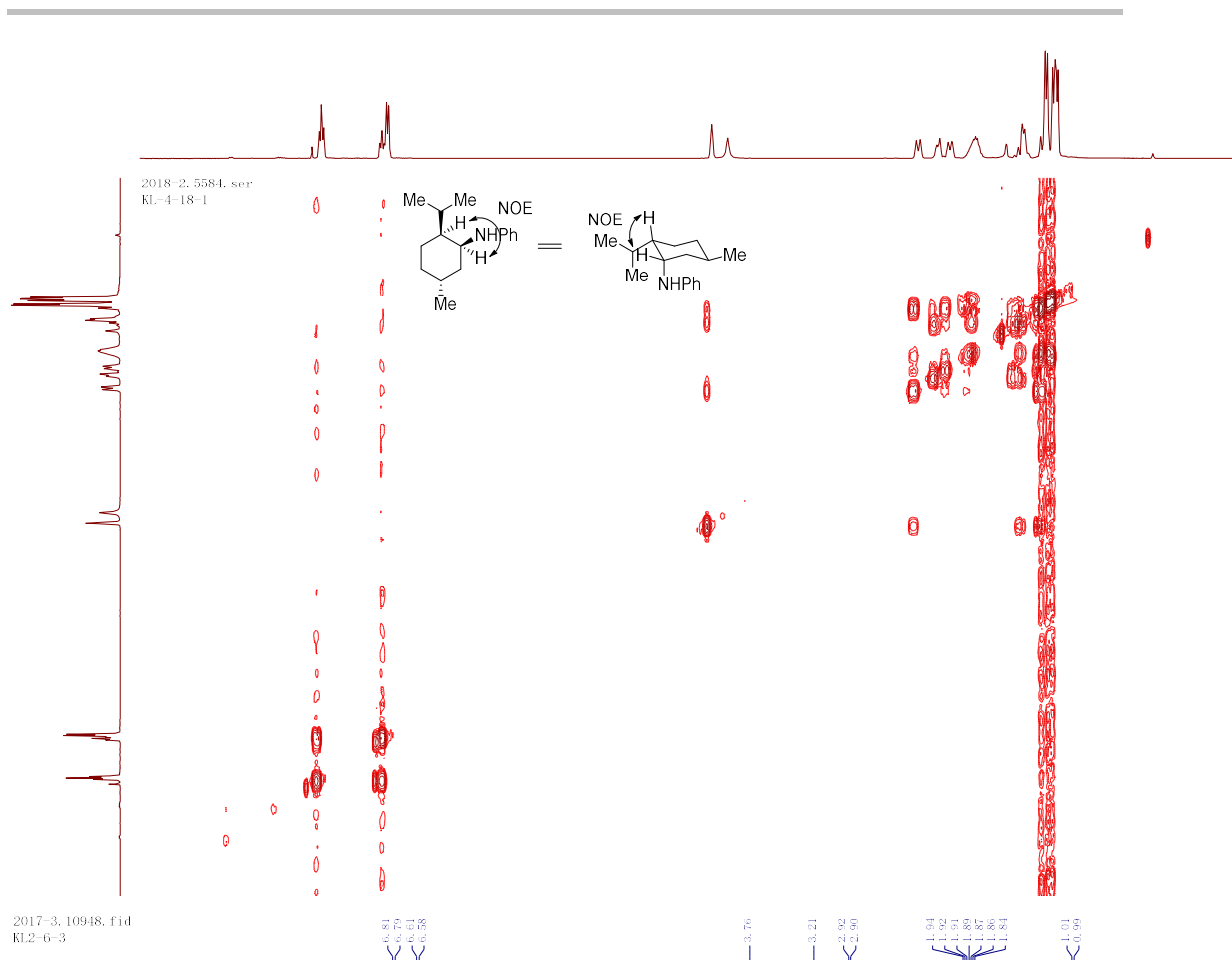


  
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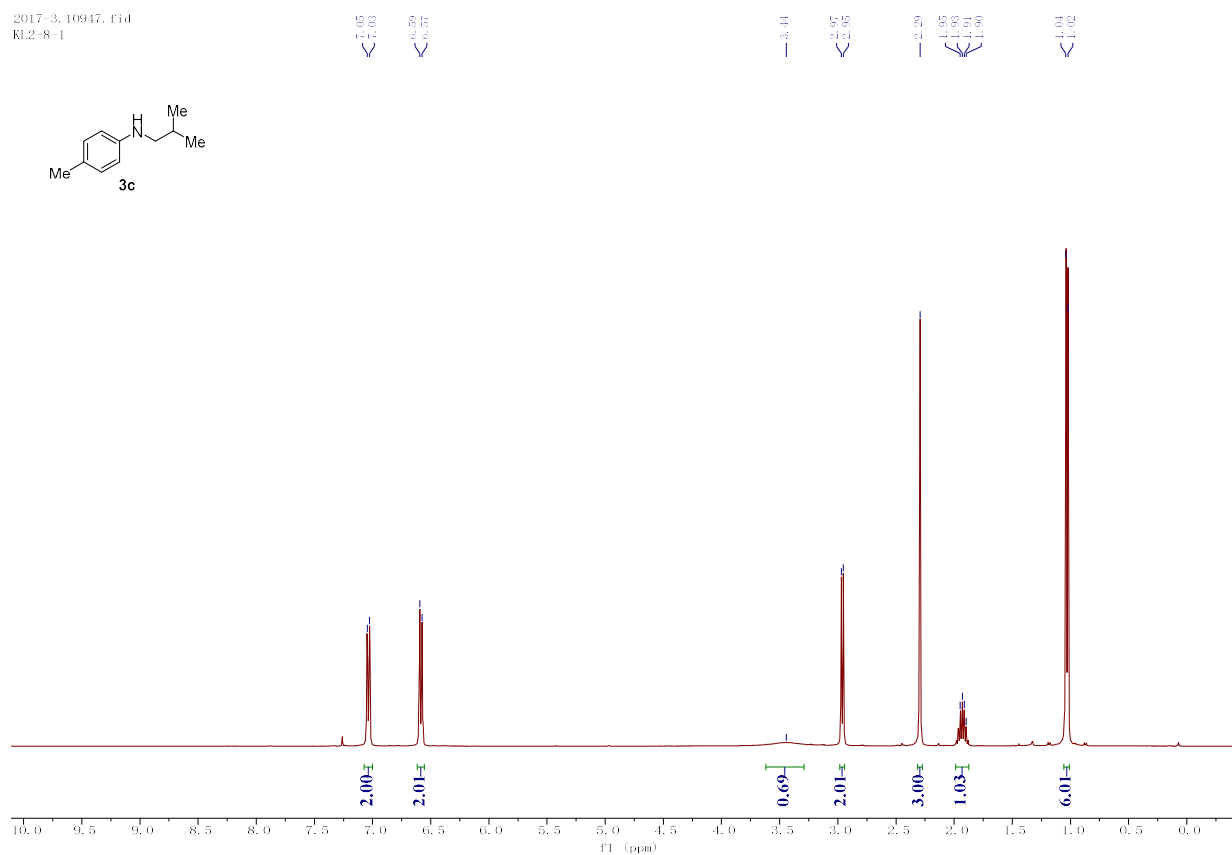
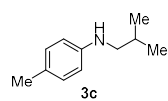




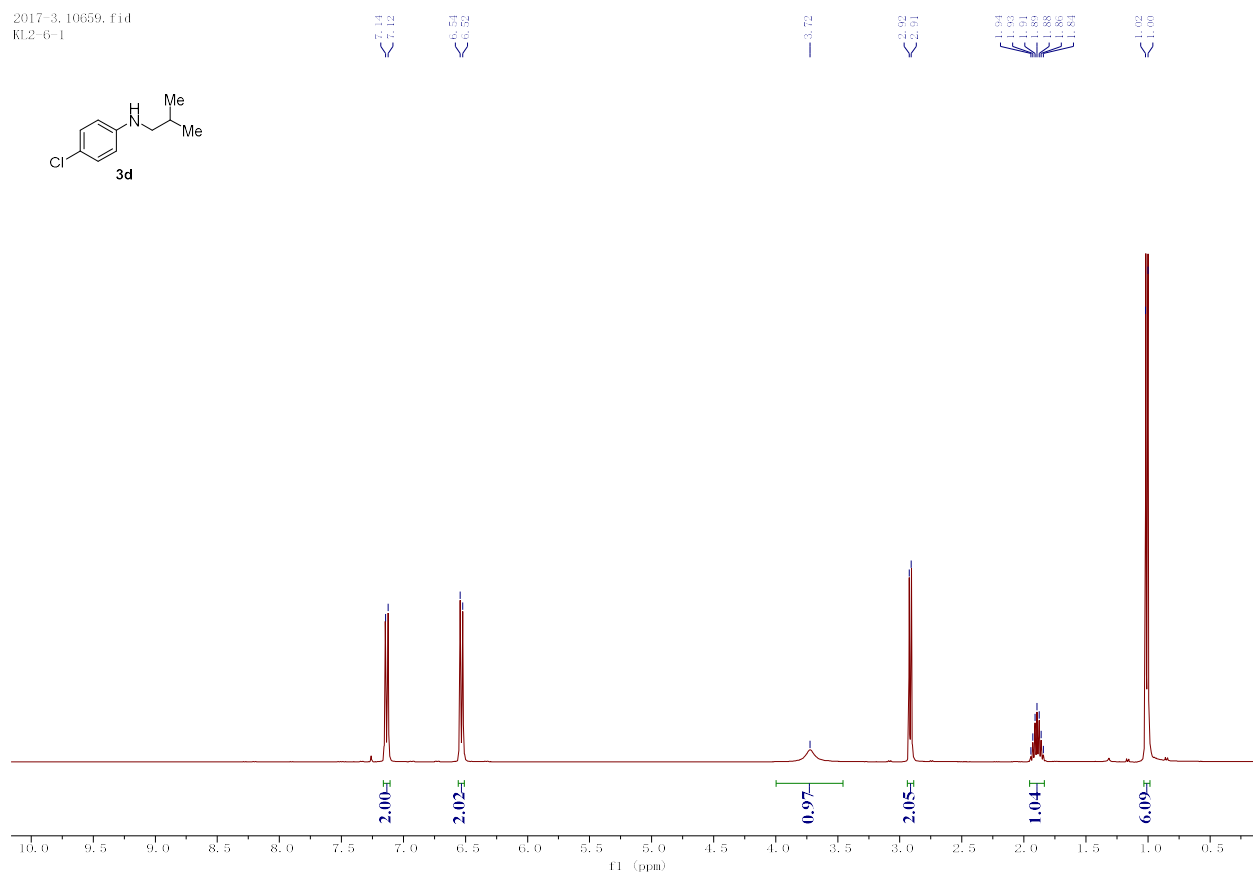
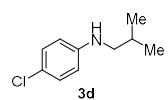




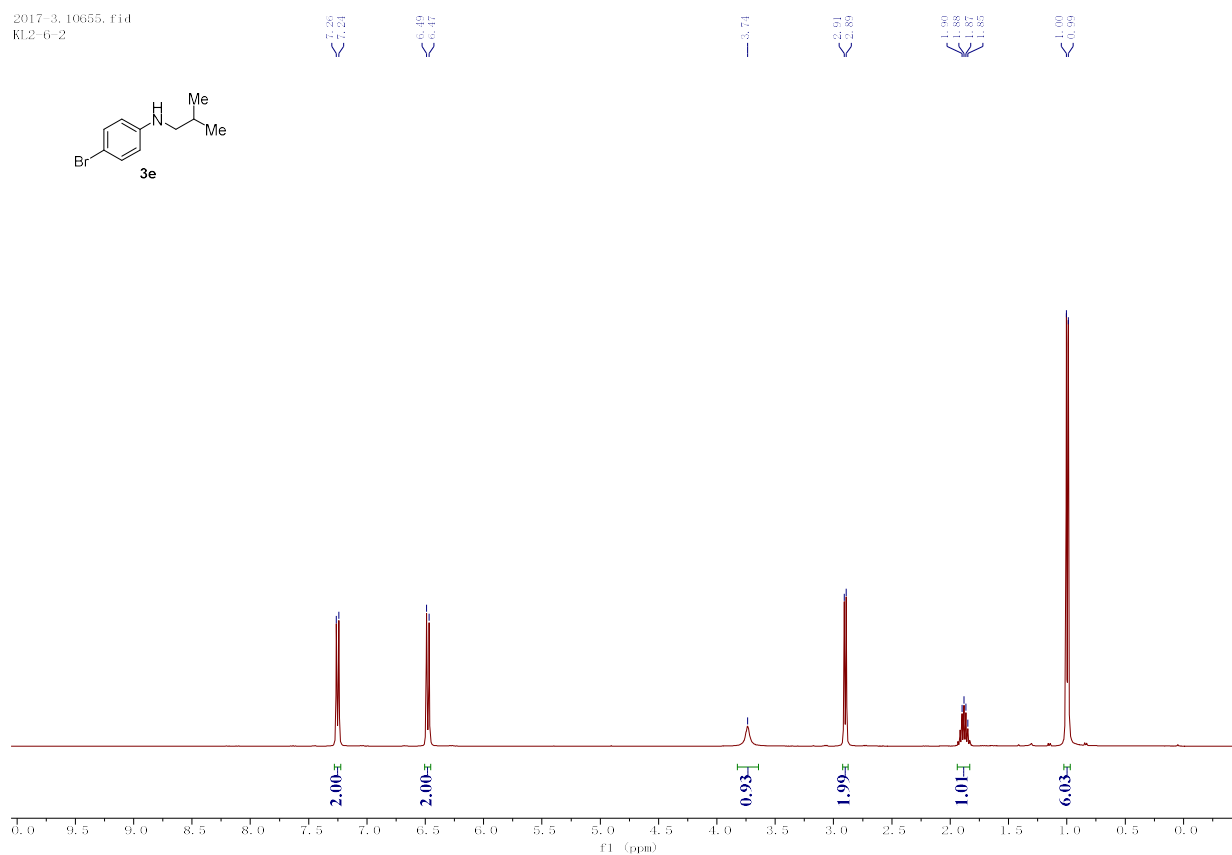
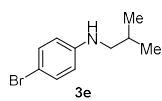
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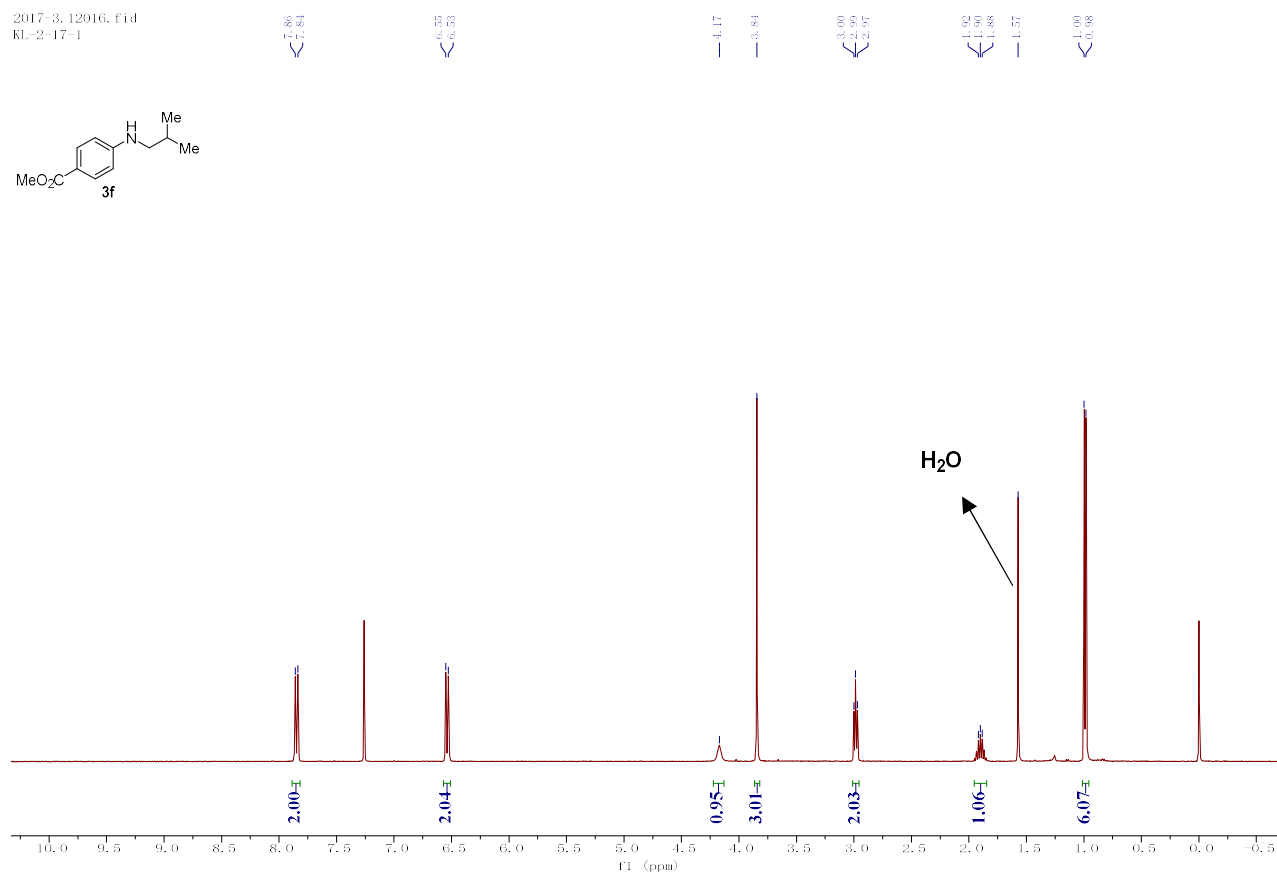
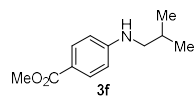
2017-3\_10659.f1d  
K1.2-6-1



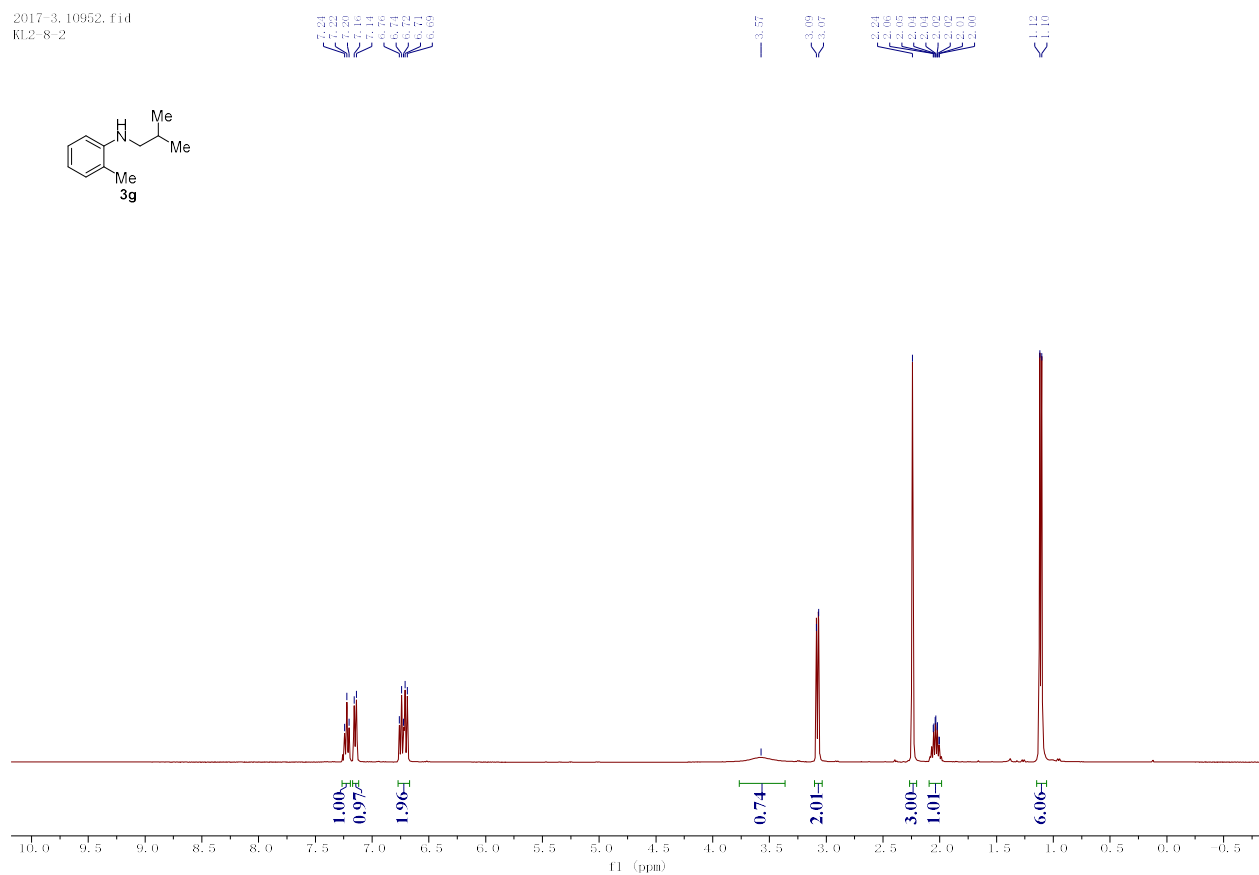
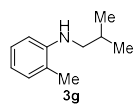
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KL2-6-2



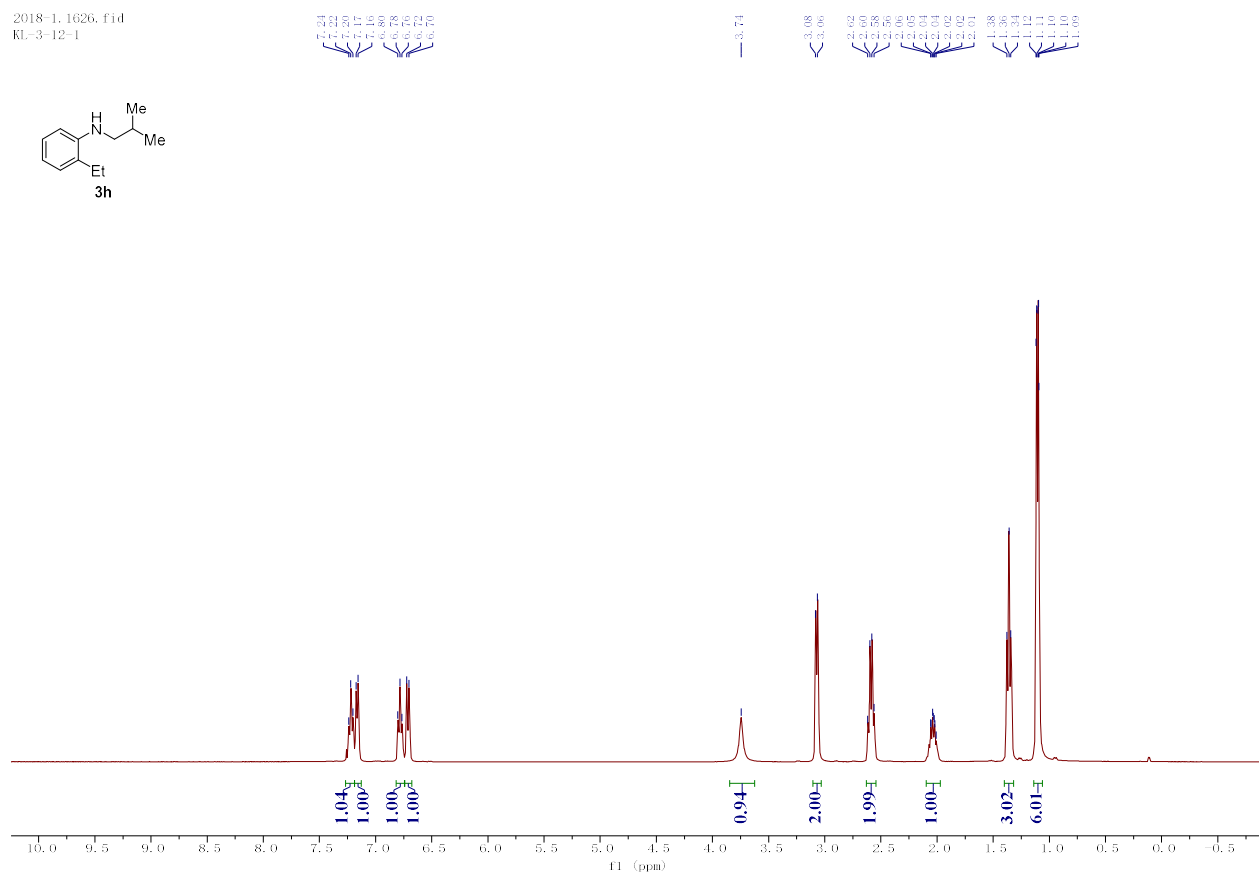
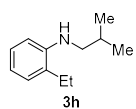
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KL-2-17-1



2017-3.10952.fid  
KL2-8-2



2018-1.1626.fid  
KL-3-12-1



[illegible]

2018-1-1634.fid  
KL-3+16-2

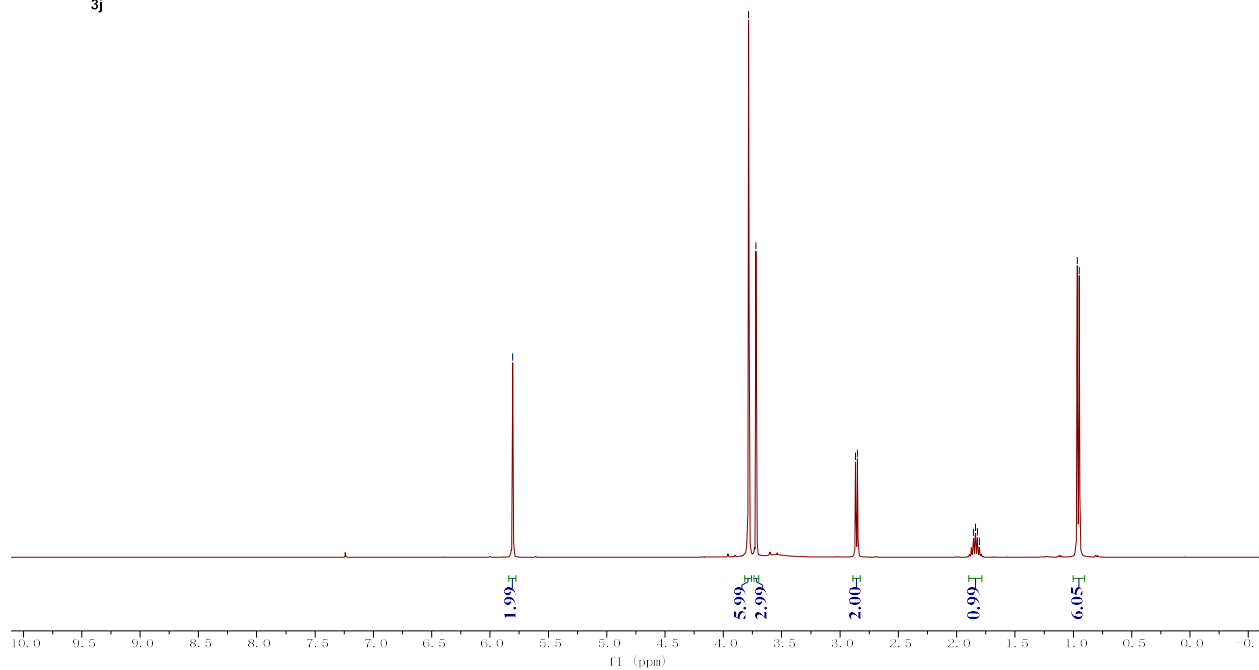
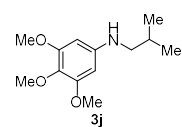
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**3i**

7.25 (m, 2H)  
7.05 (m, 1H)  
6.95 (m, 1H)  
3.85 (s, 1H)  
3.05 (m, 1H)  
2.95 (m, 1H)  
2.05 (s, 1H)  
1.35 (d, 3H)  
1.15 (d, 3H)

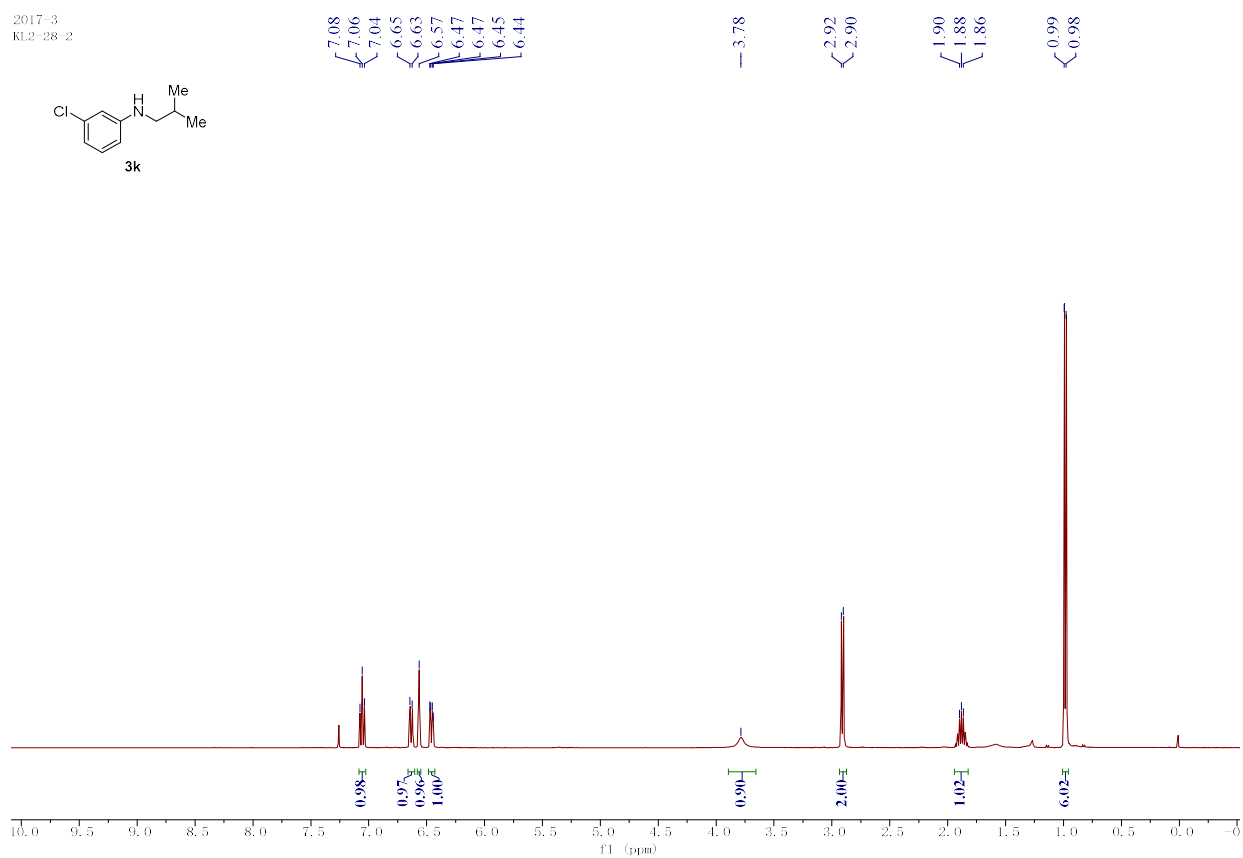
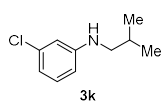
2.02  
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f1 (ppm)

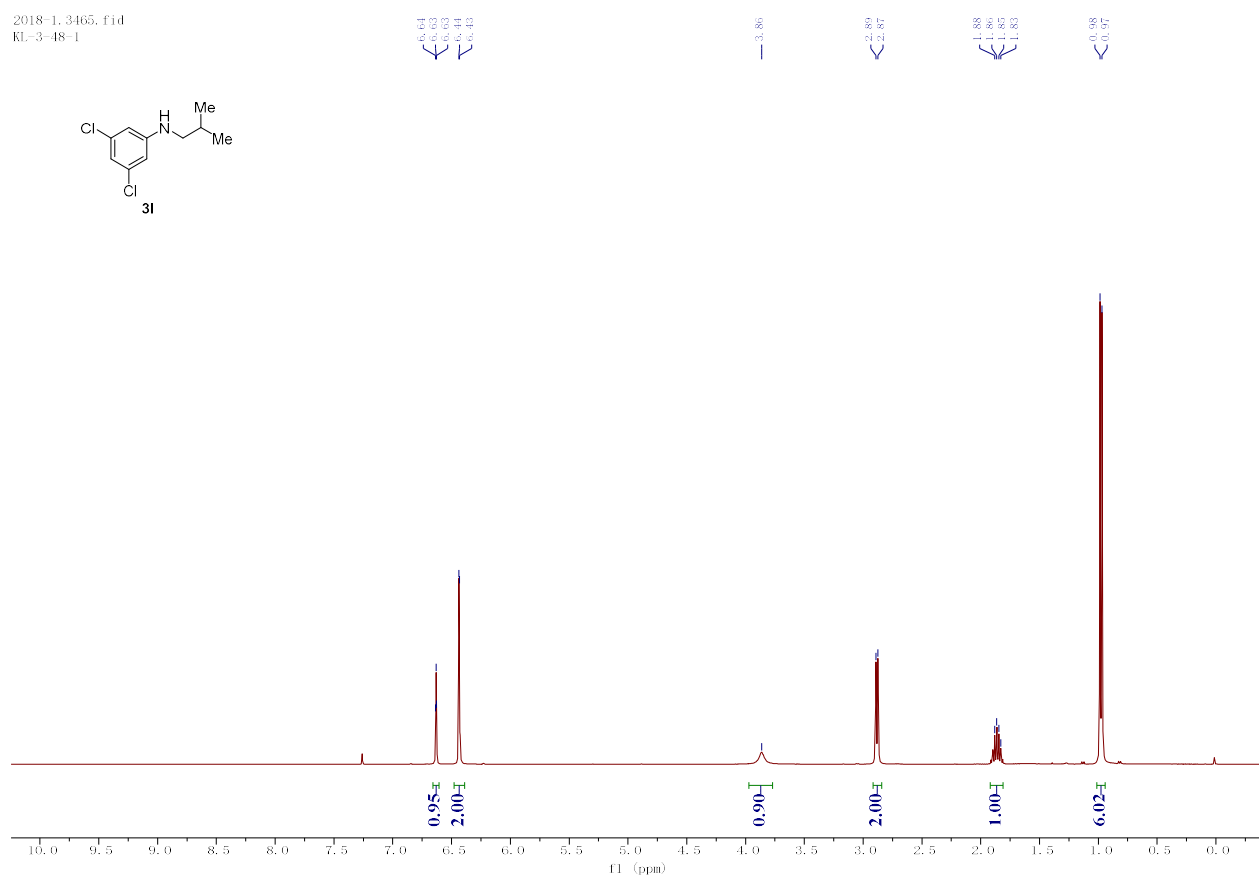
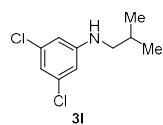
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KL-2-44-1



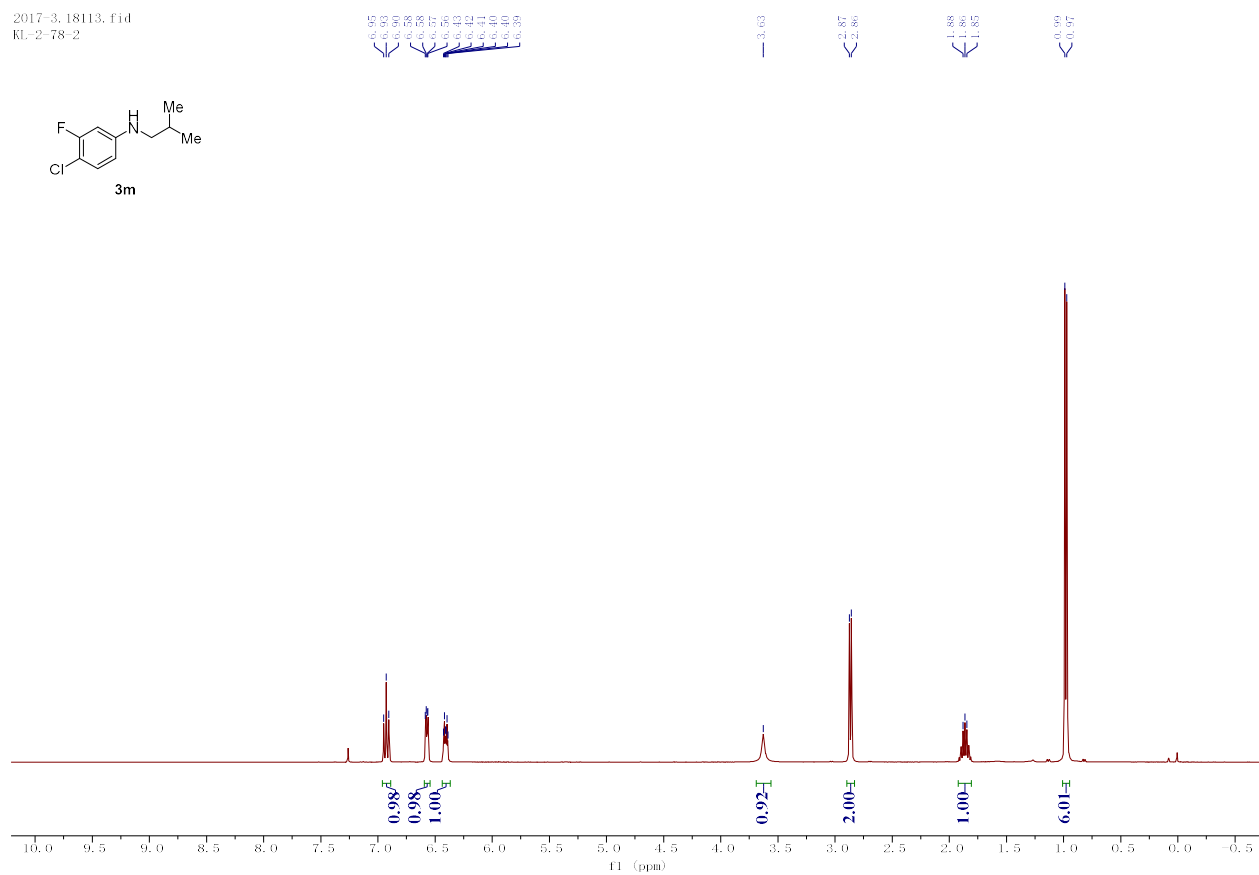
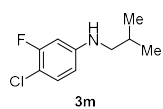
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KL-2-28-2



2018-1.3465.fid  
KL-3-48-1

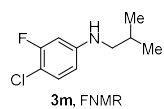
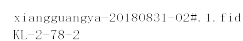


2017-3.18113.fid  
KL-2-78-2



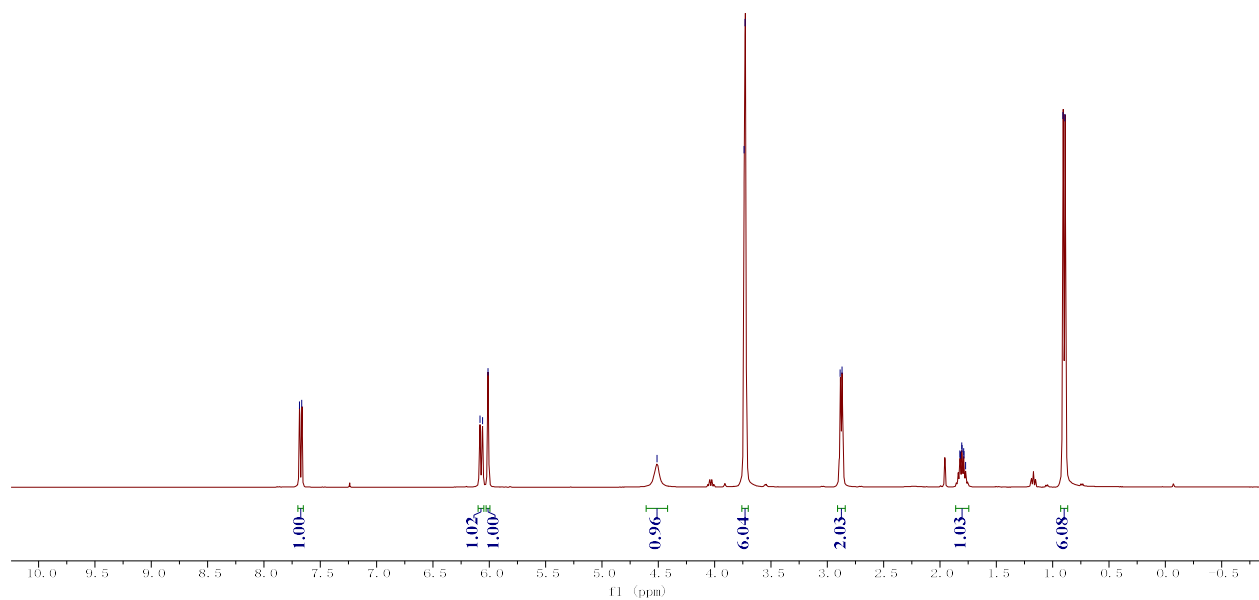
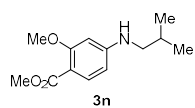
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**3m**

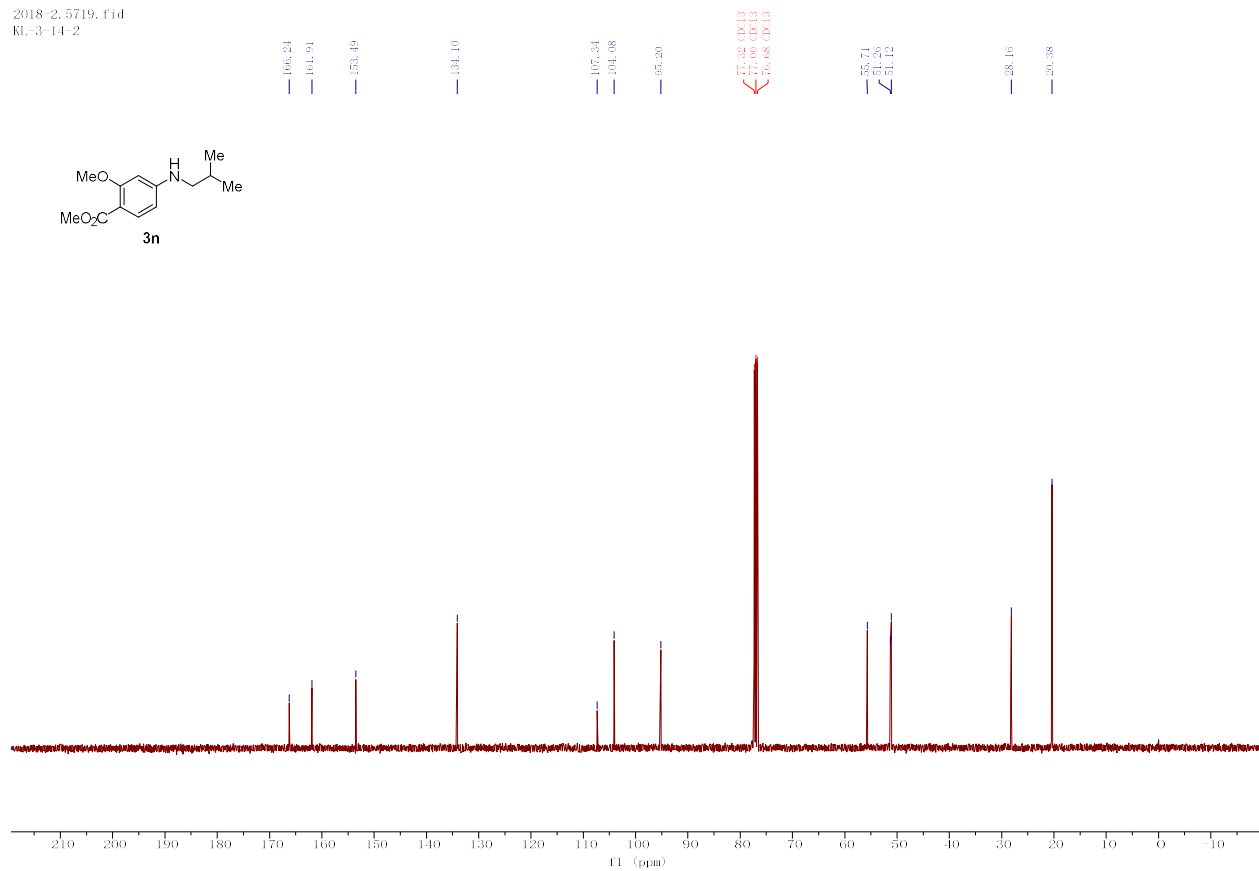
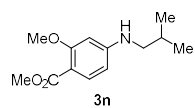




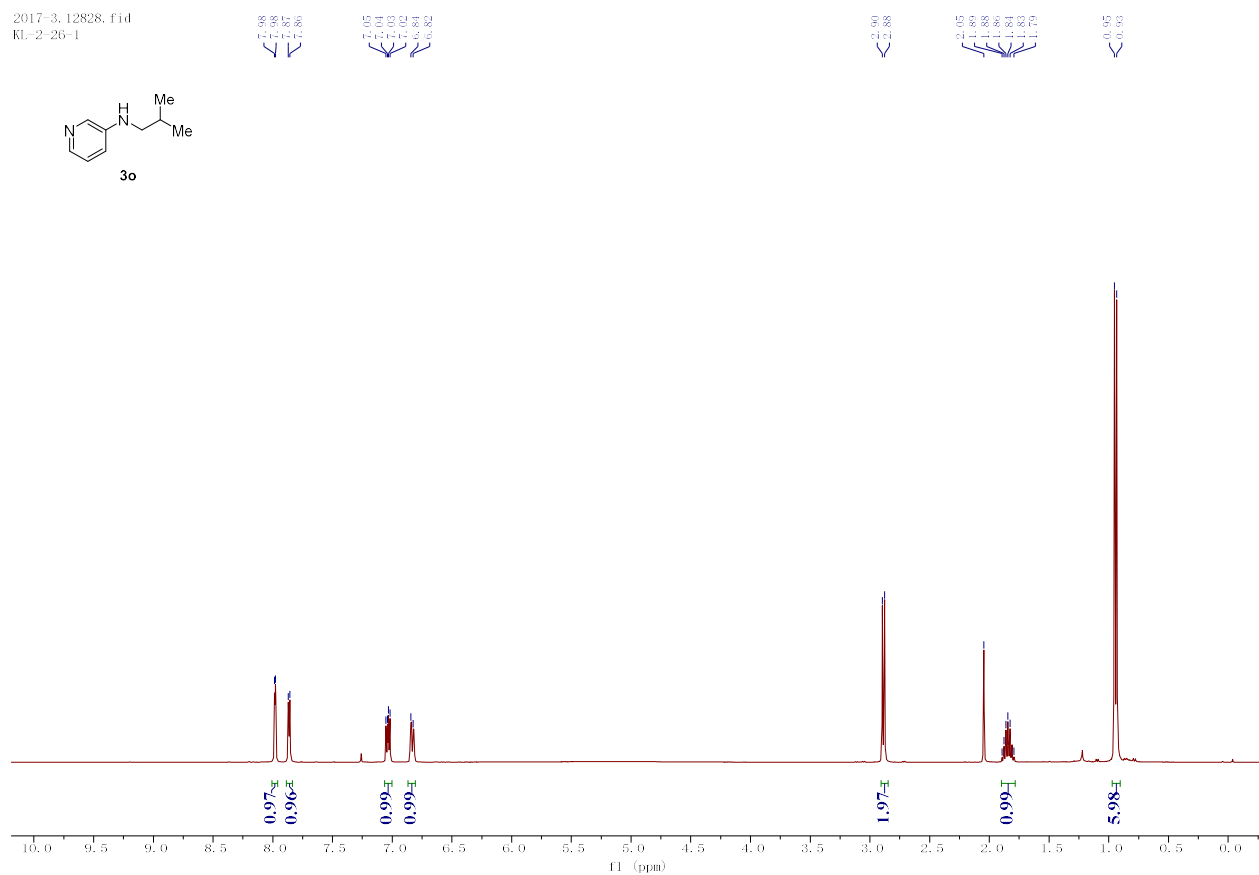
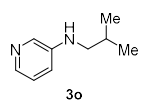
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KL-3-14-2



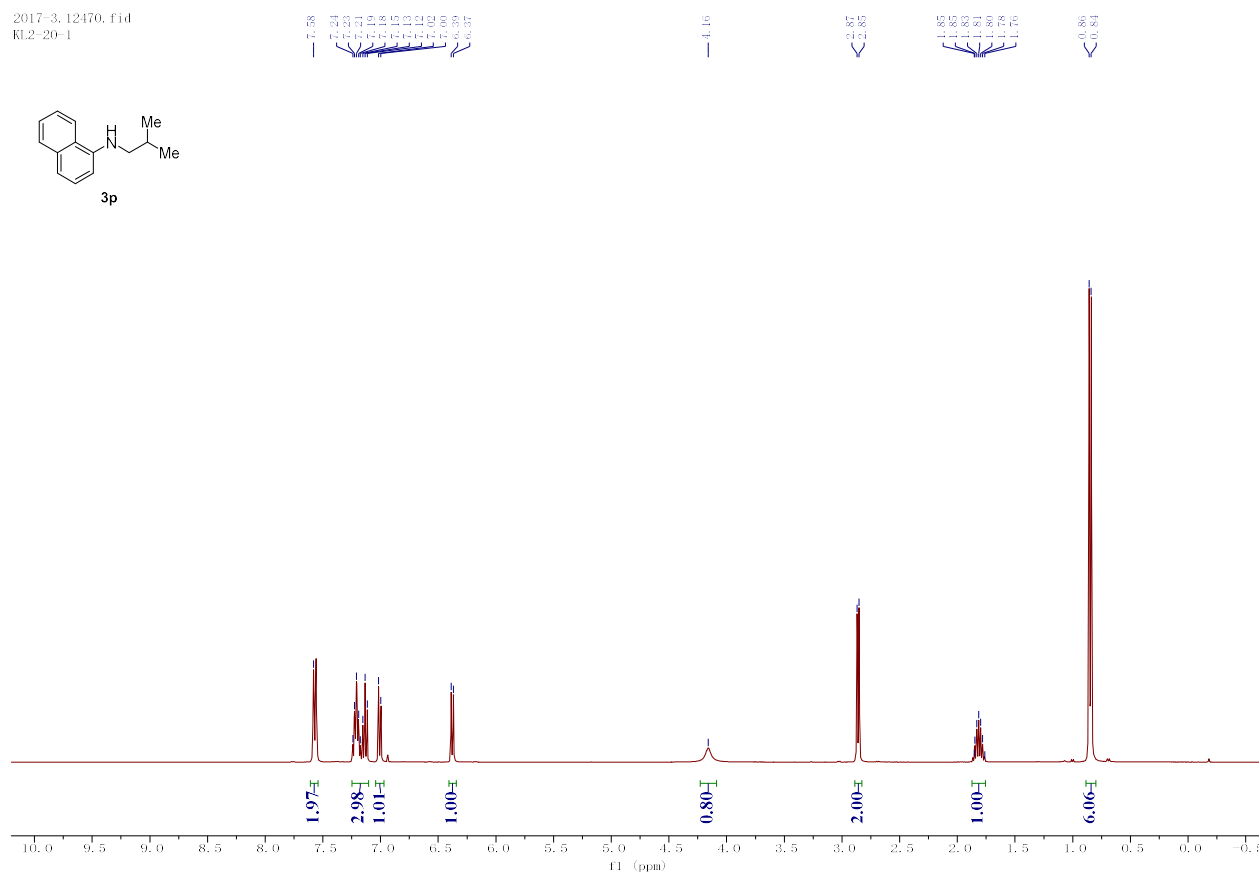
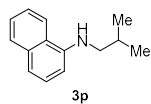
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KL-3-14-2

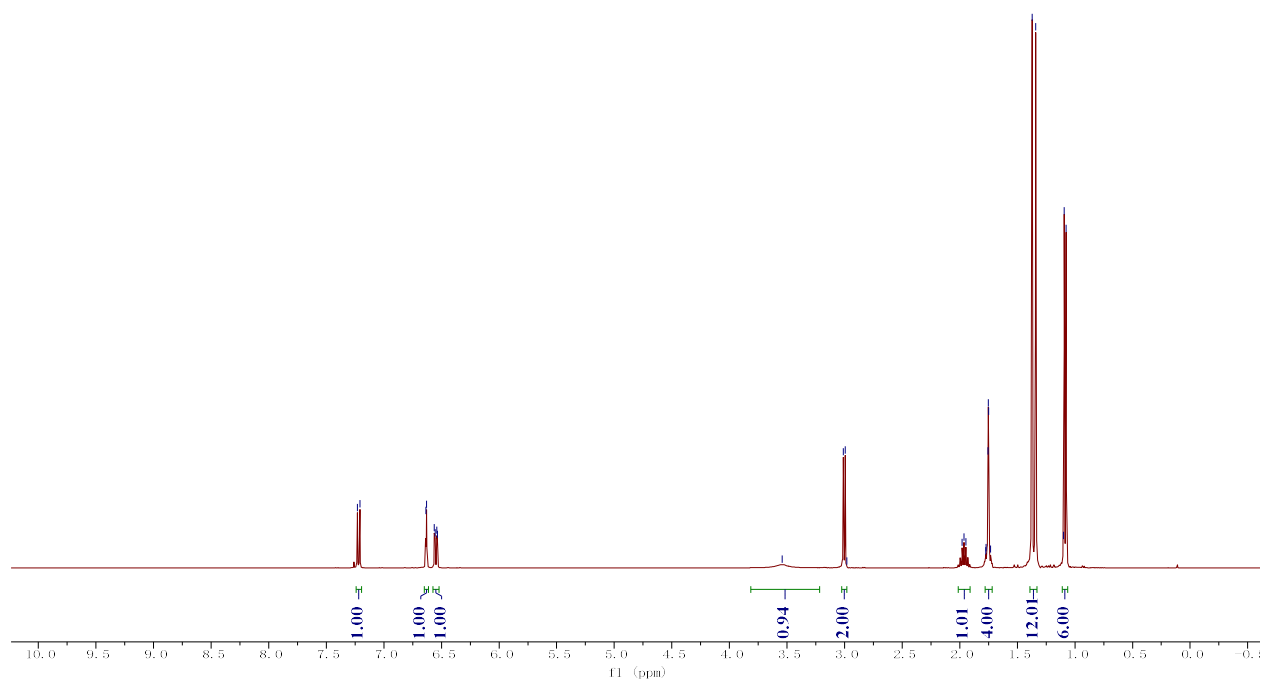
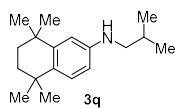


2017-3, 12828, f1d  
KL-2-26-1

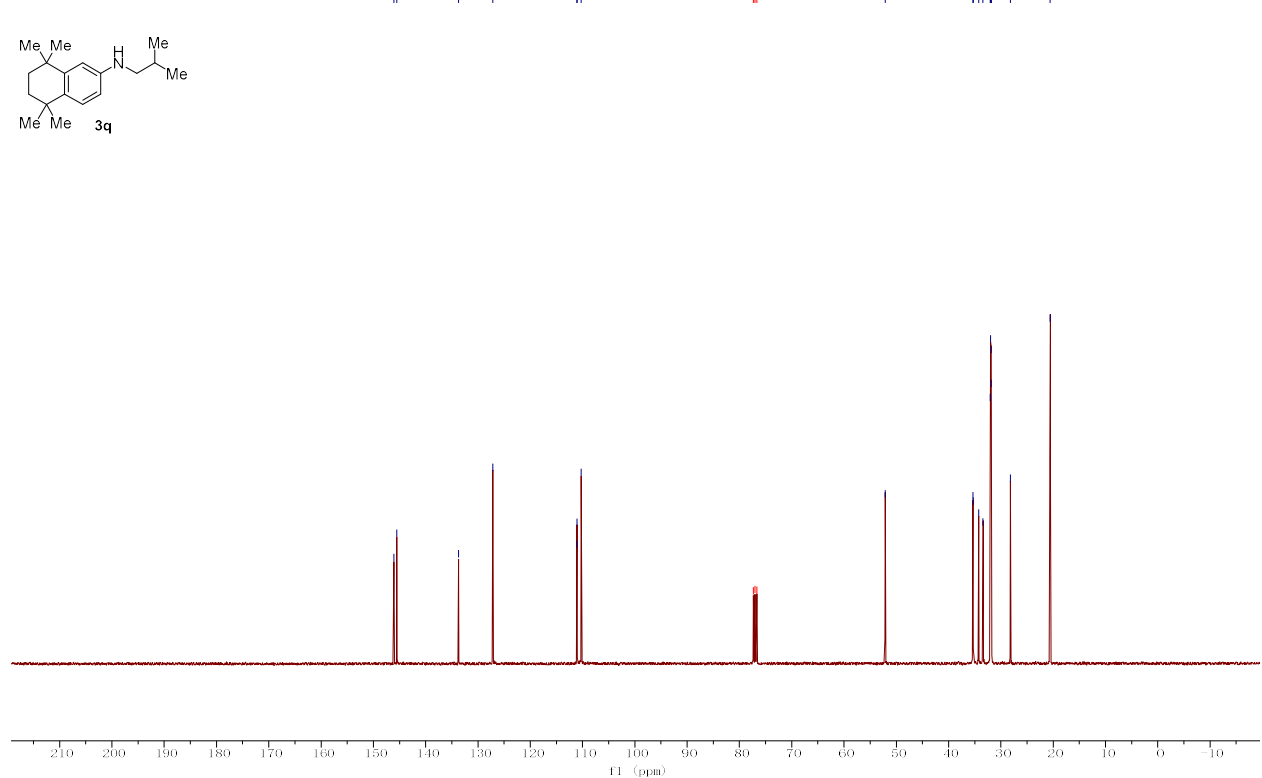
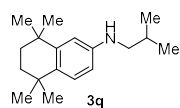


2017-3, 12470, f1d  
KL-2-20-1

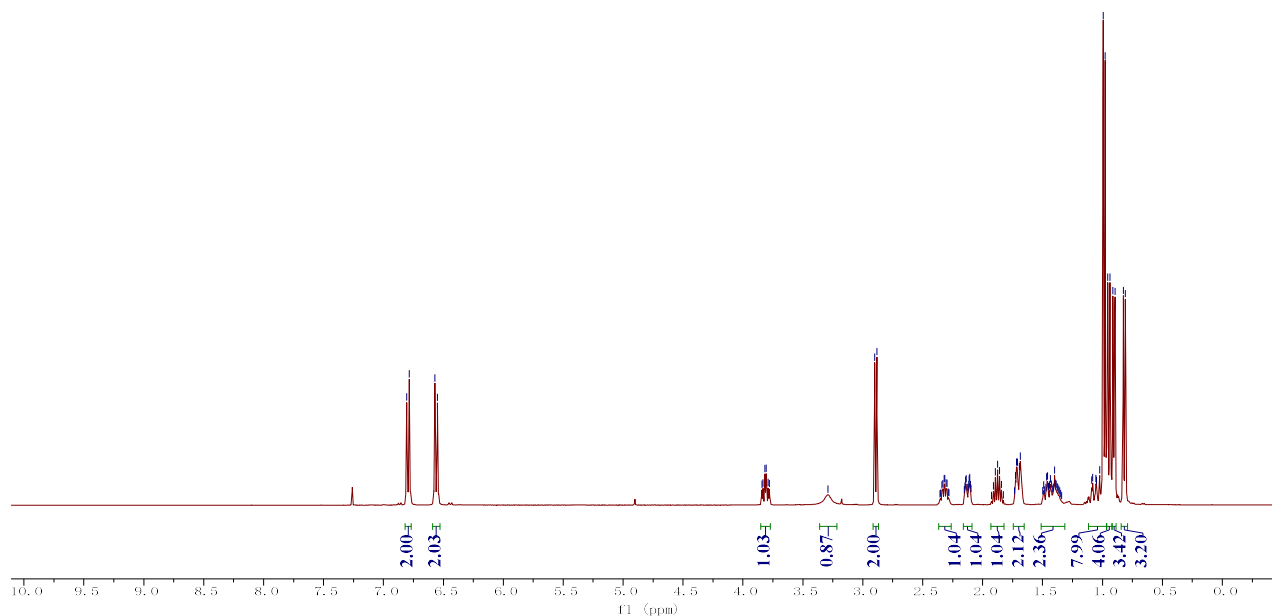
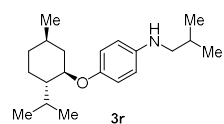


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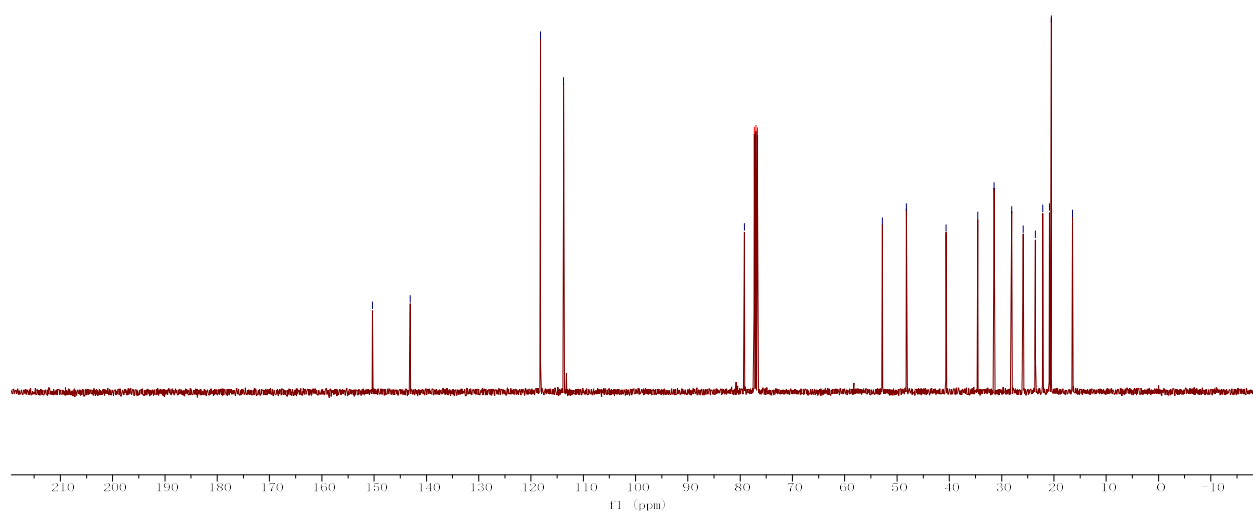
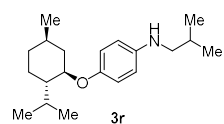
Age Group	Percentage
18-24	45.05%
25-34	45.52%
35-44	33.73%
45-54	27.19%
55-64	11.08%
65-74	11.06%
75-84	10.25%
85+	52.13%



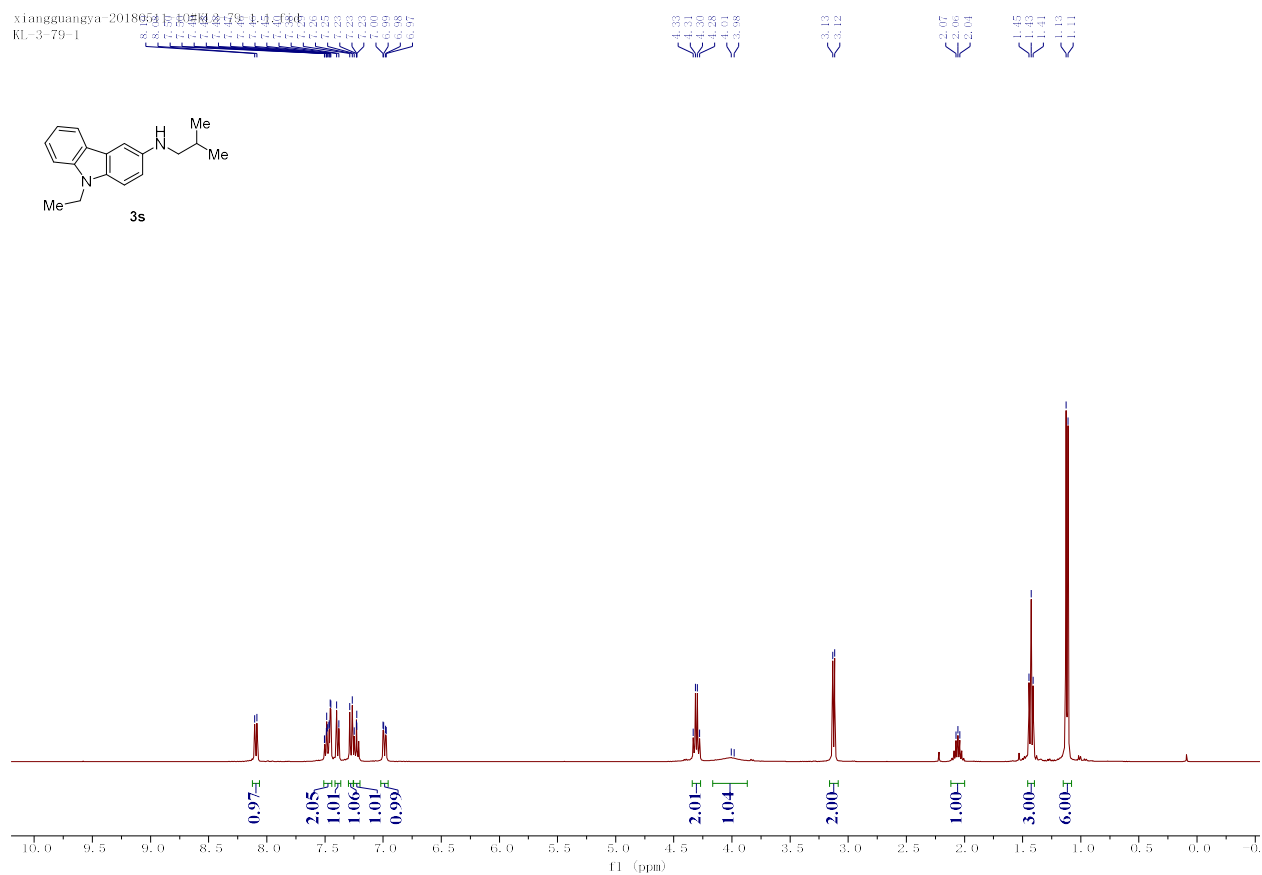
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KL-2-46-2



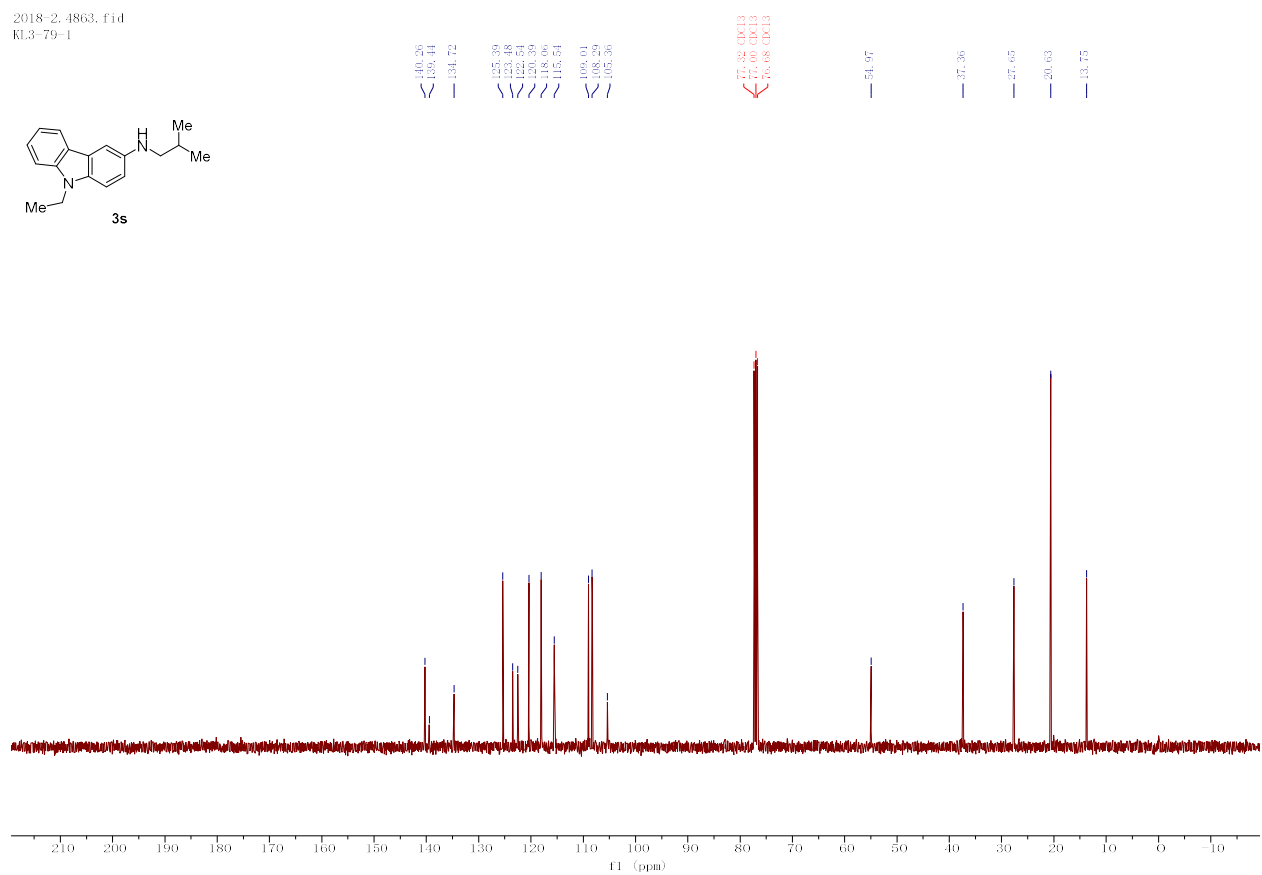
2018-2\_5727.fid  
KL-2-46-3



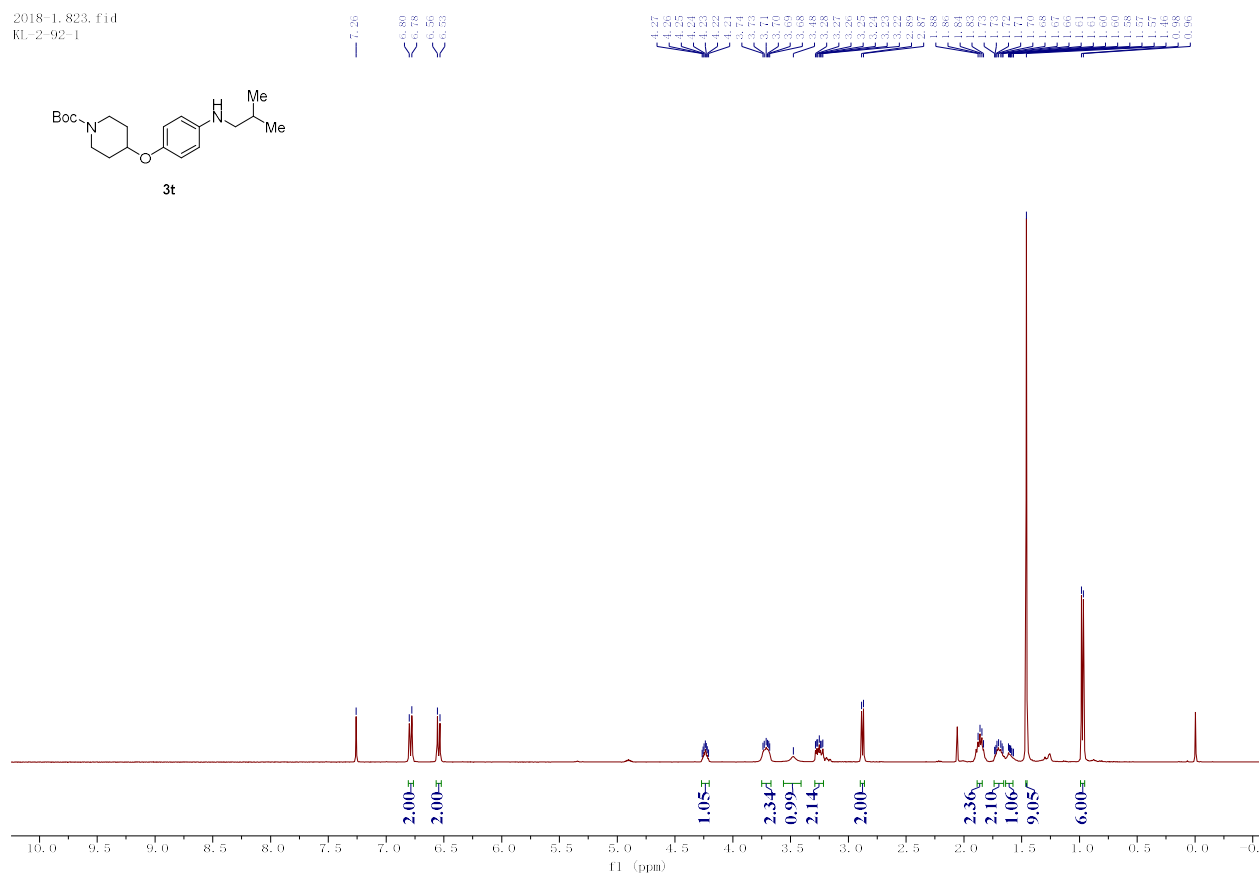
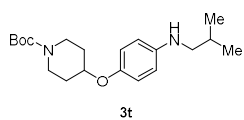
xiangguangya-20180528 样品谱图文件名称: KL-3-79-1



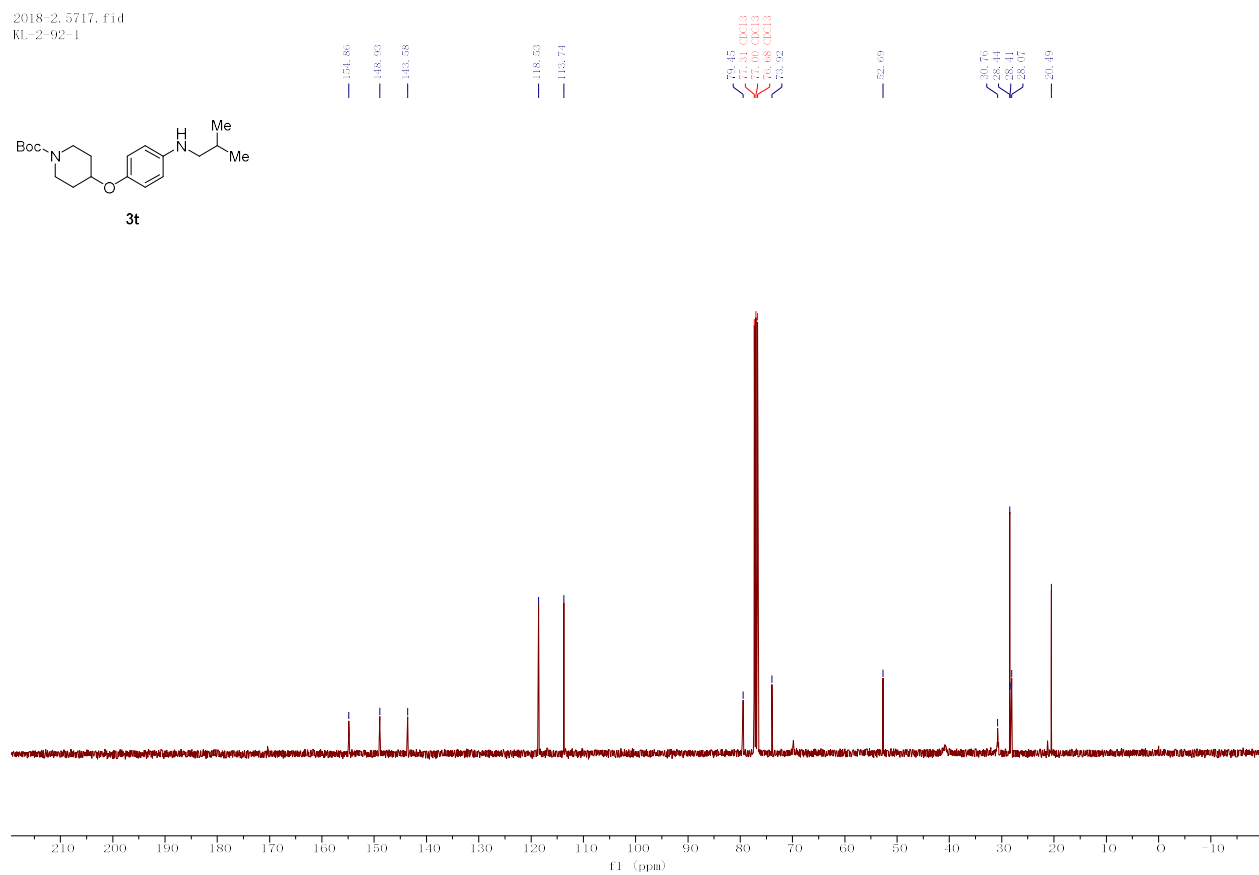
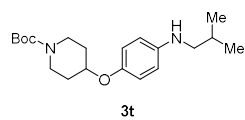
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KL3-79-1



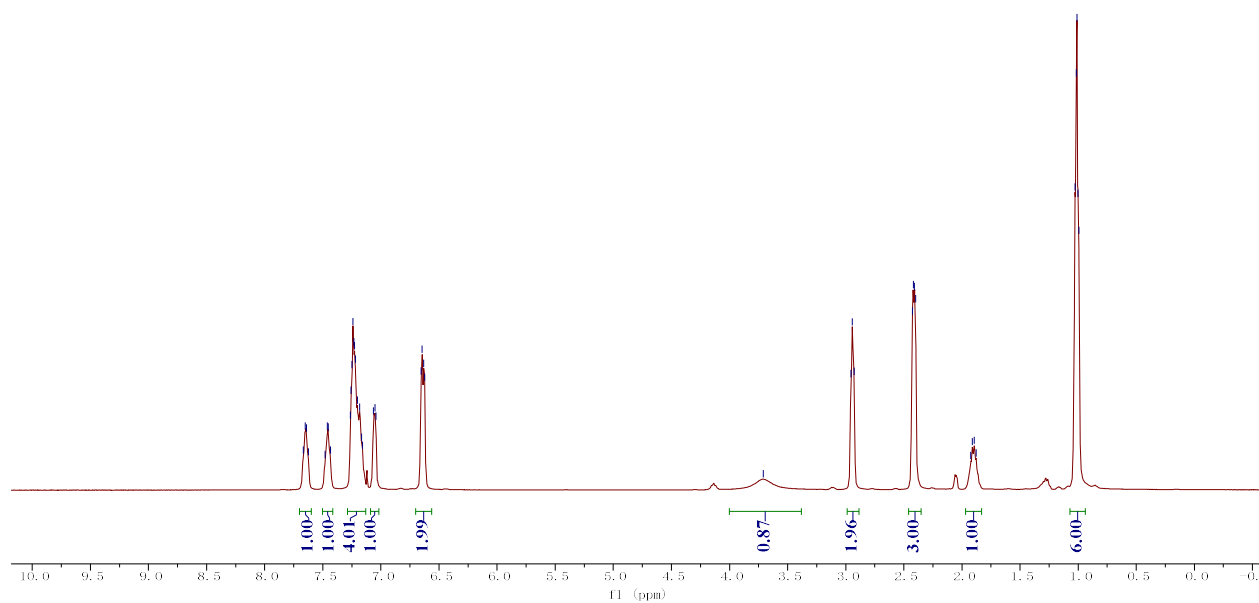
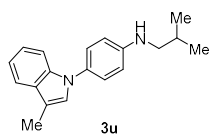
2018-1-823, f1d  
KL-2-92-1



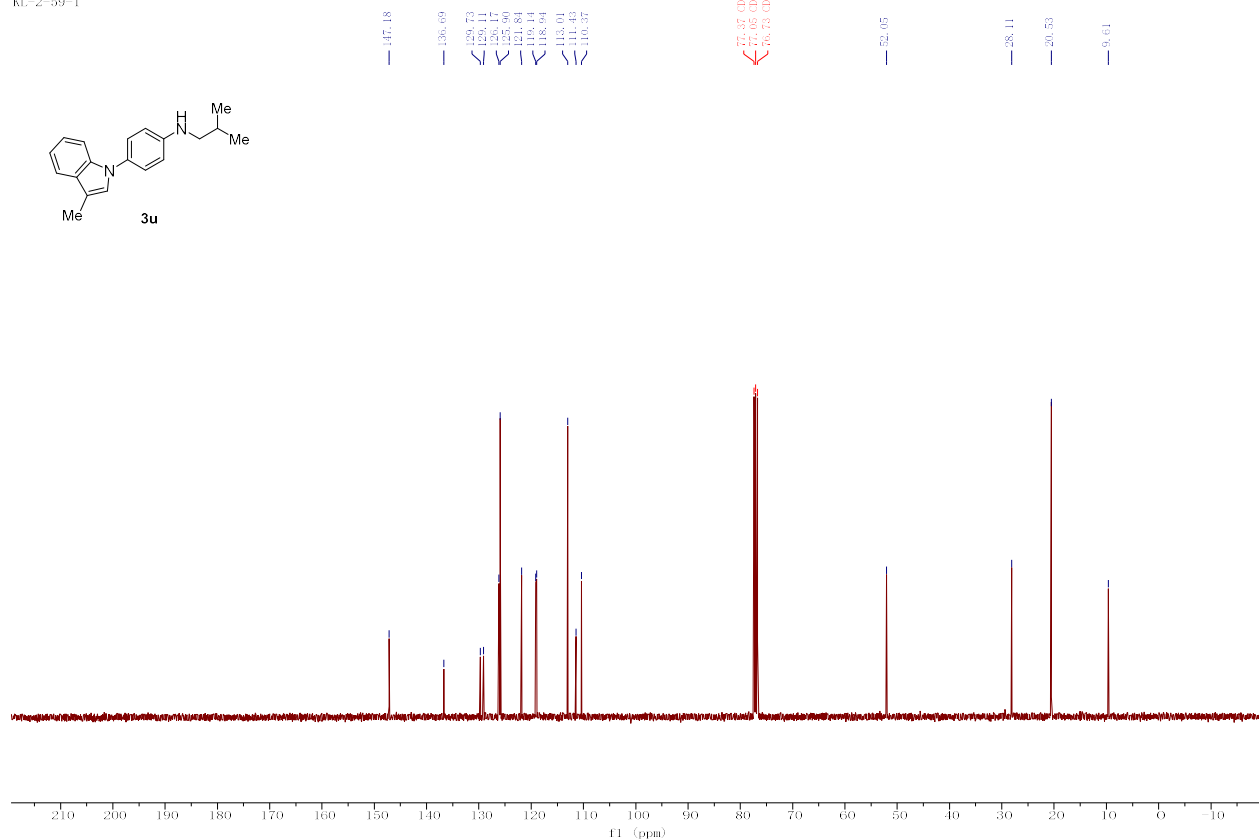
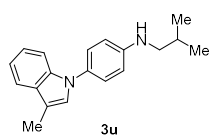
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KL-2-92-1



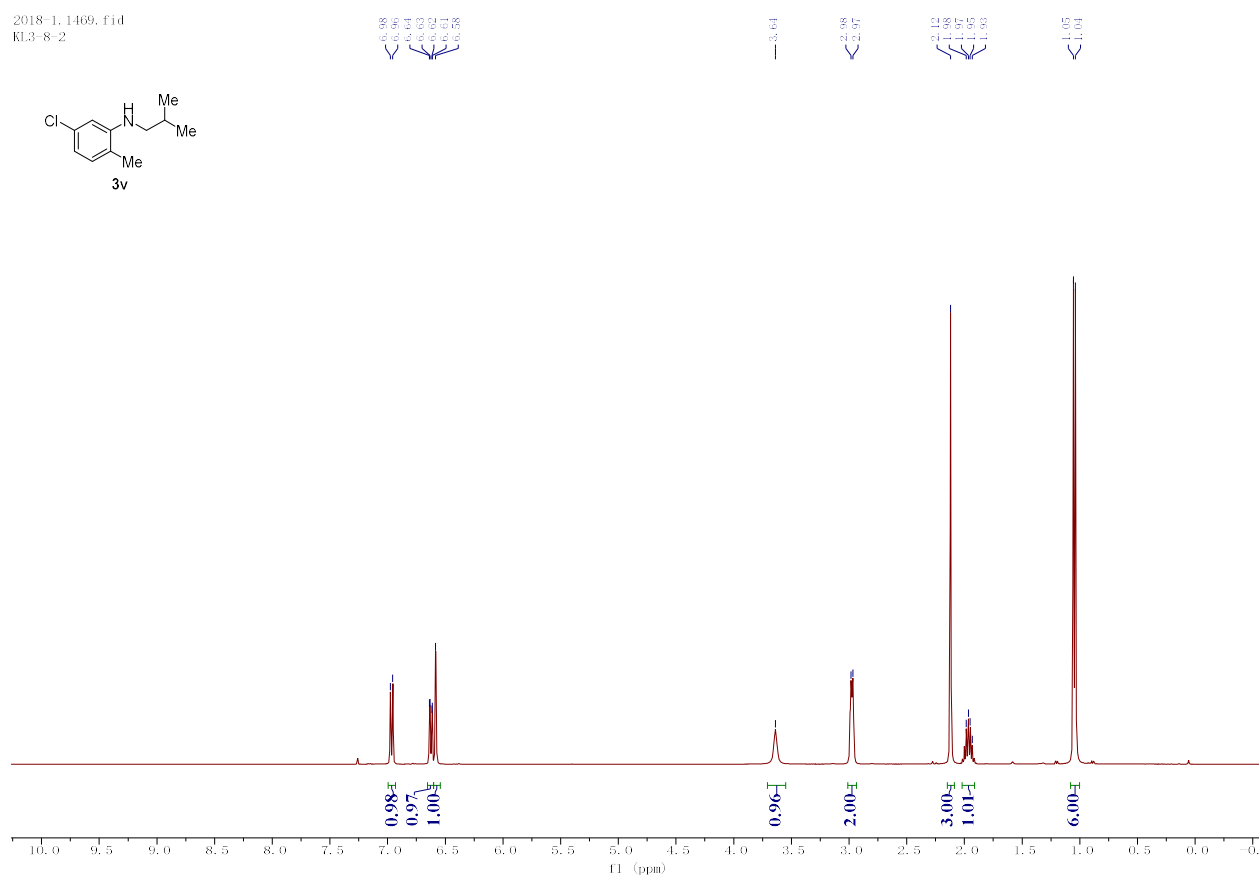
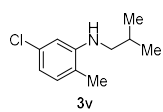
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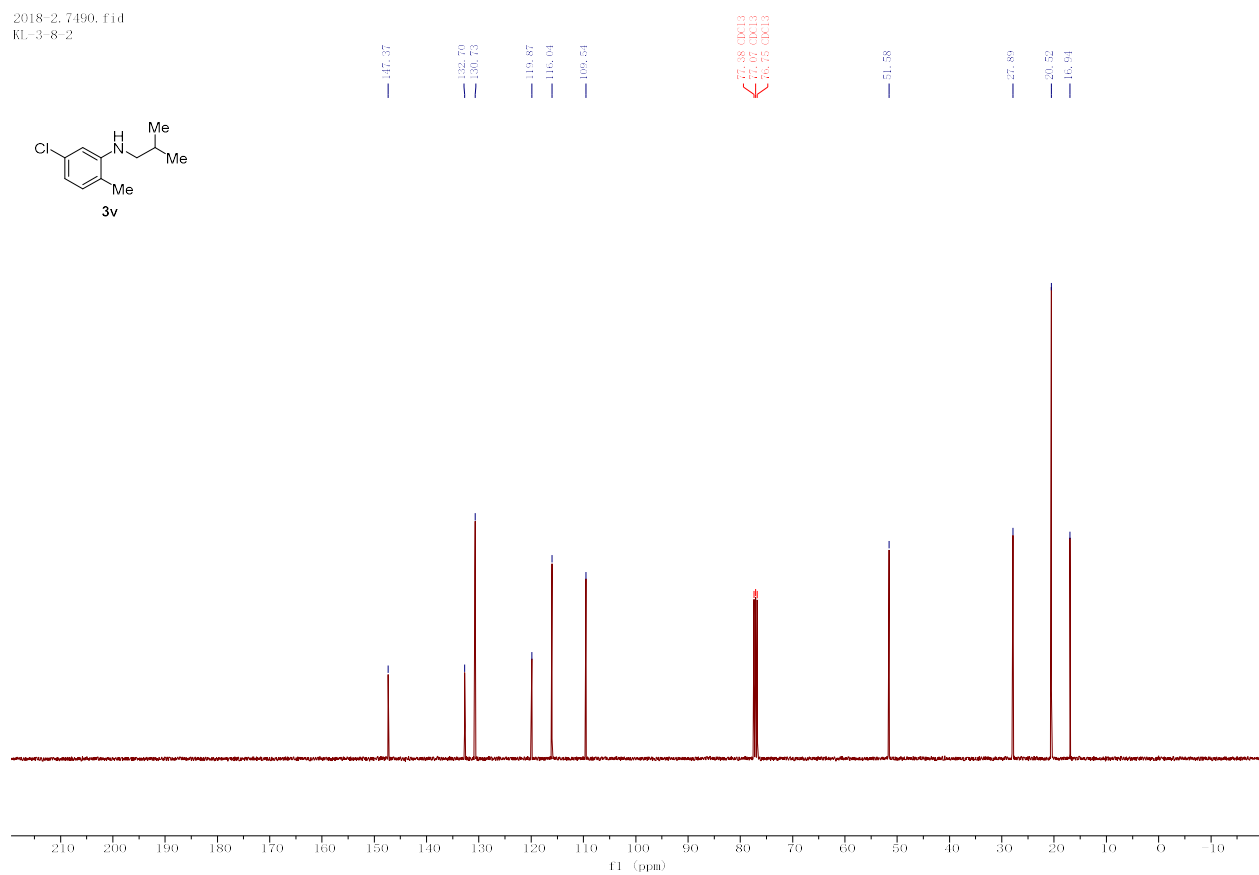
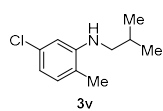
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2018-1.1469.fid  
KL3-8-2

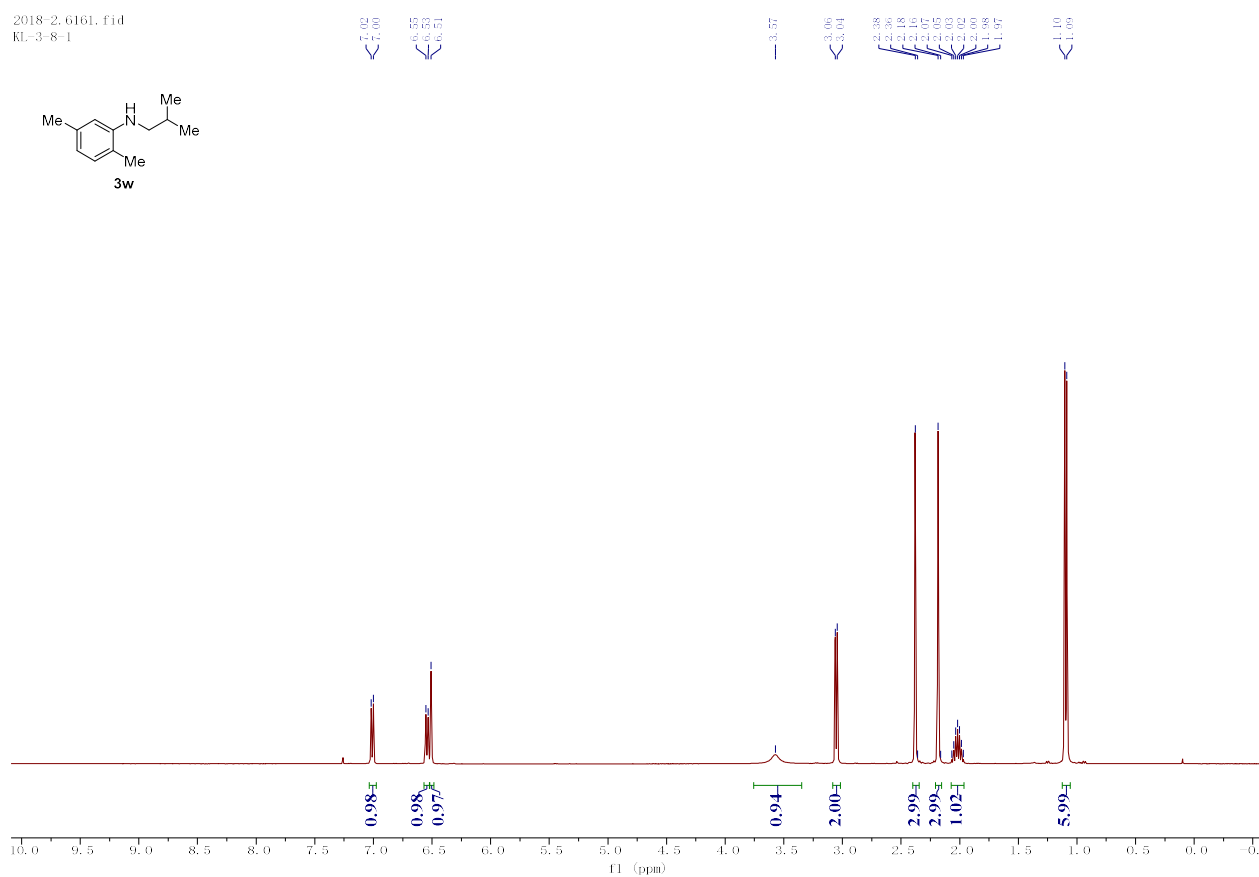
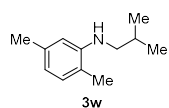


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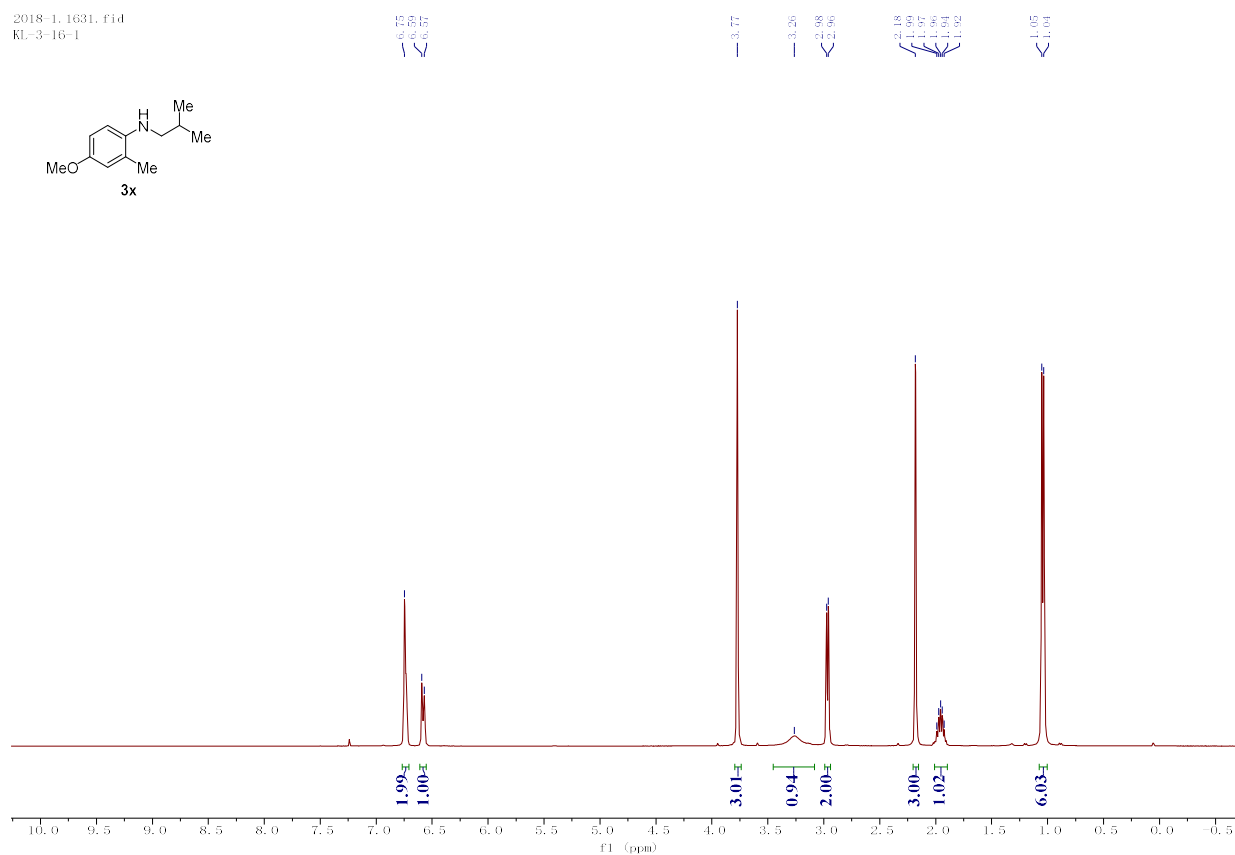
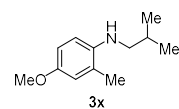




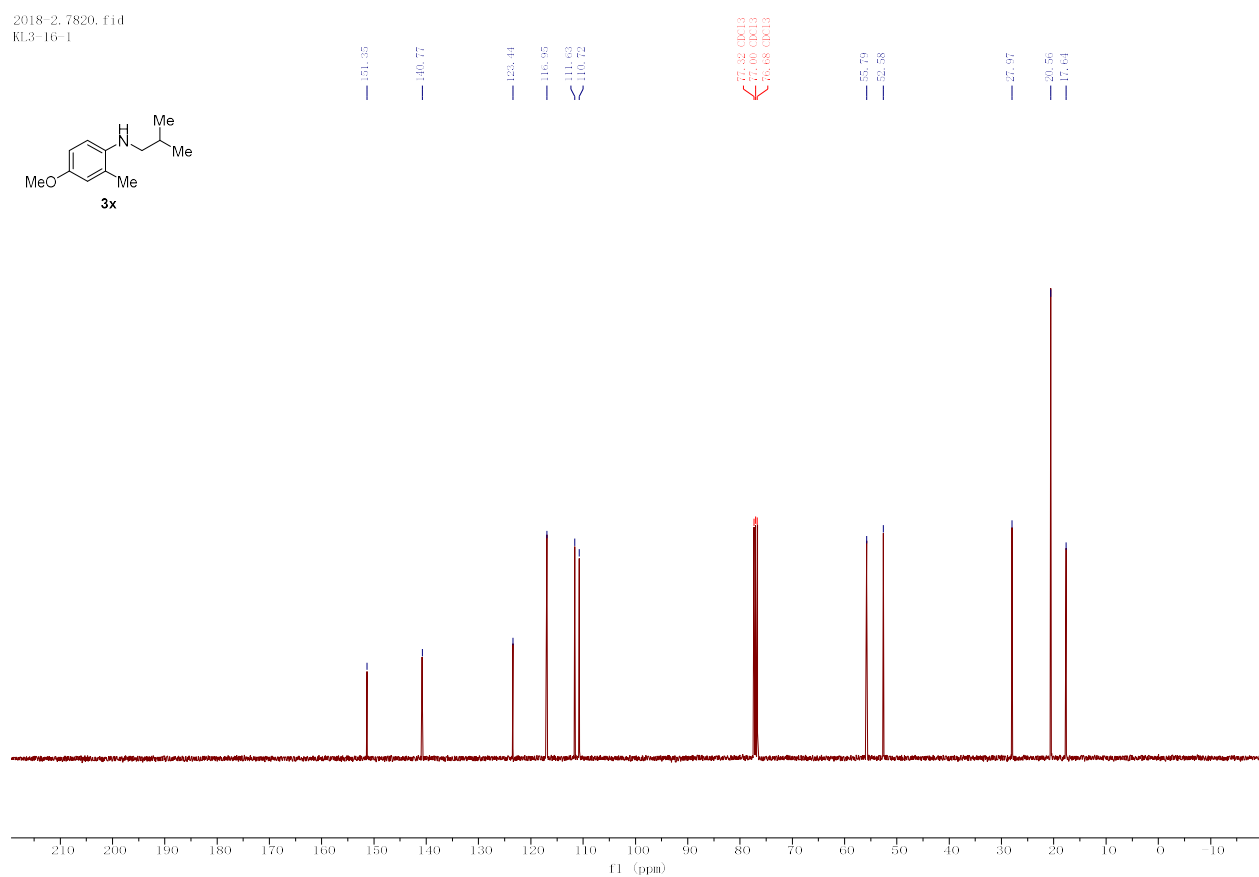
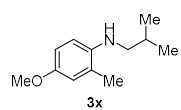
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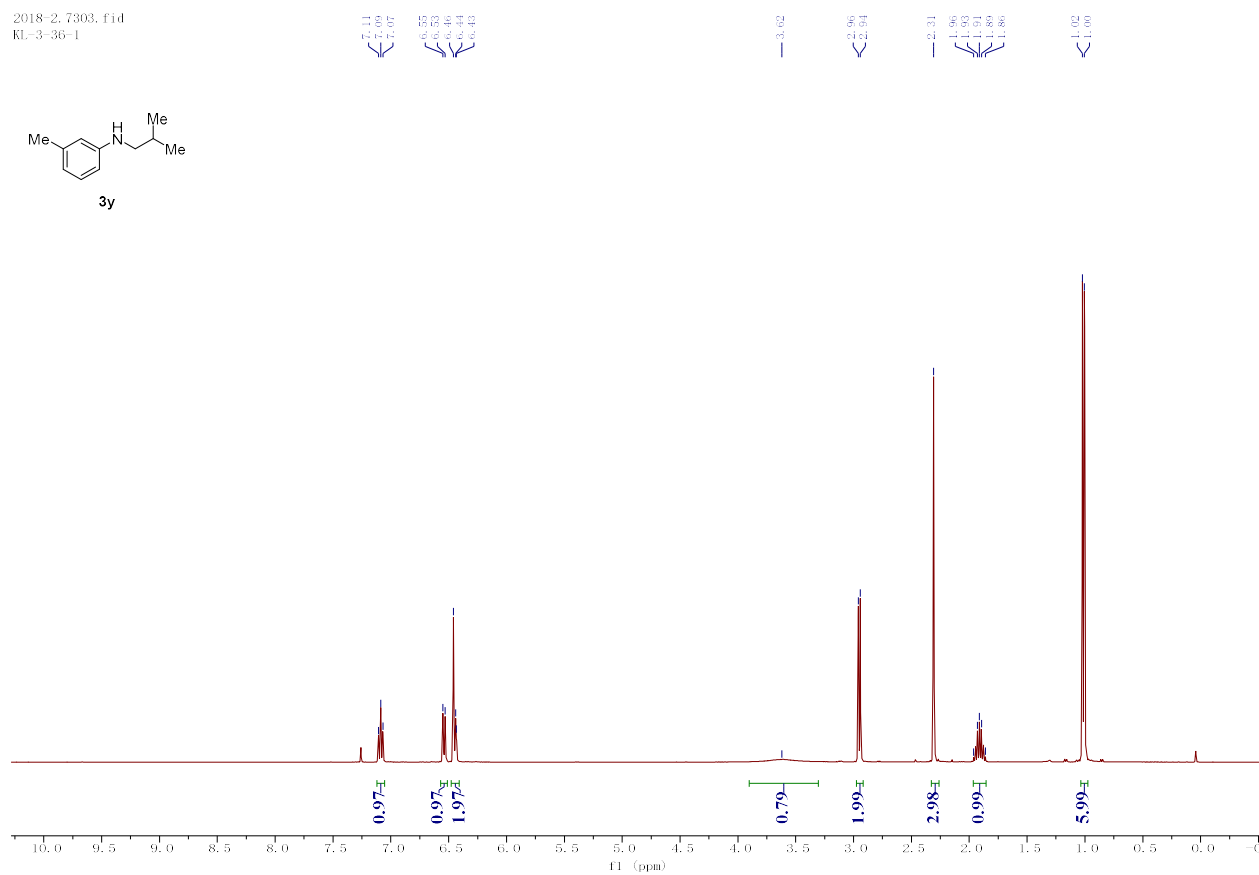
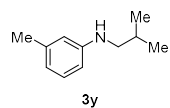
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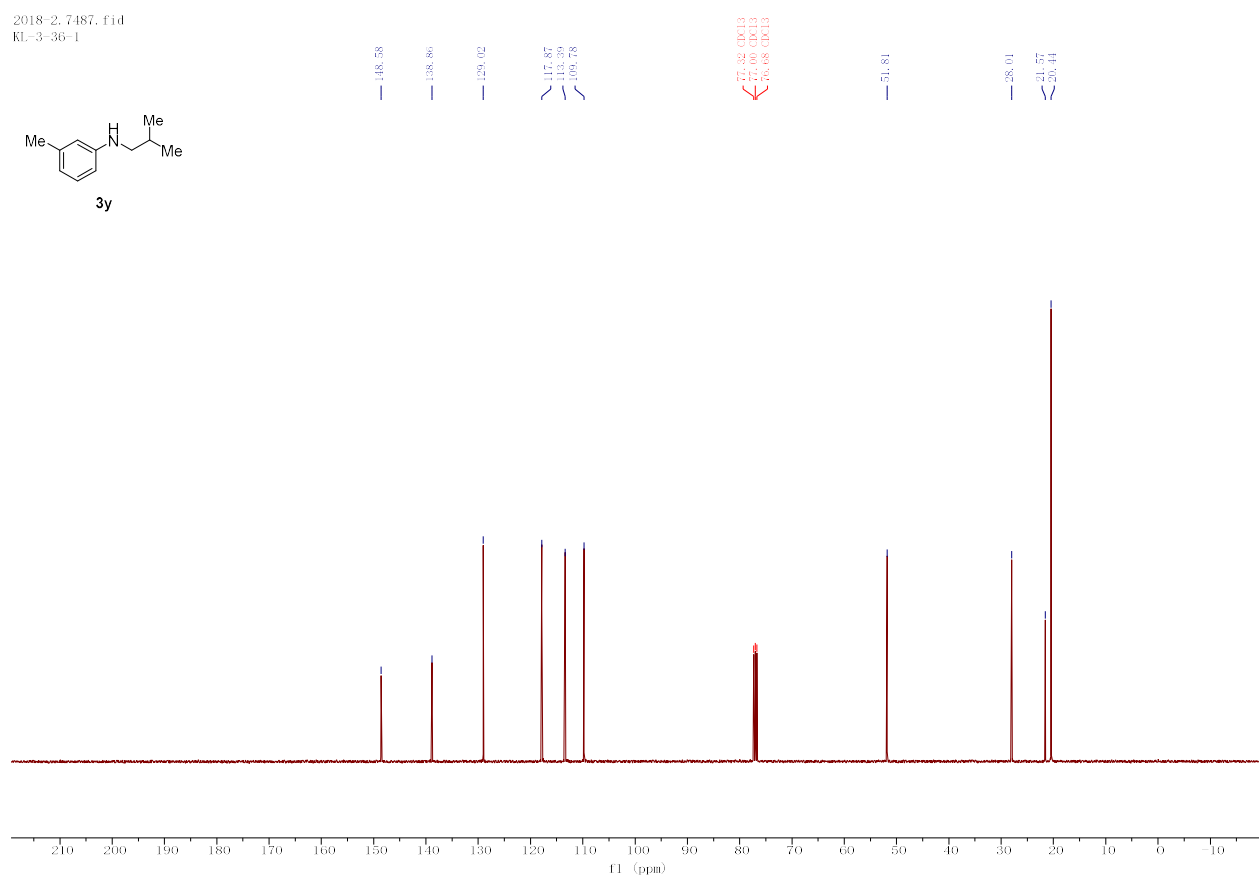
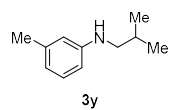
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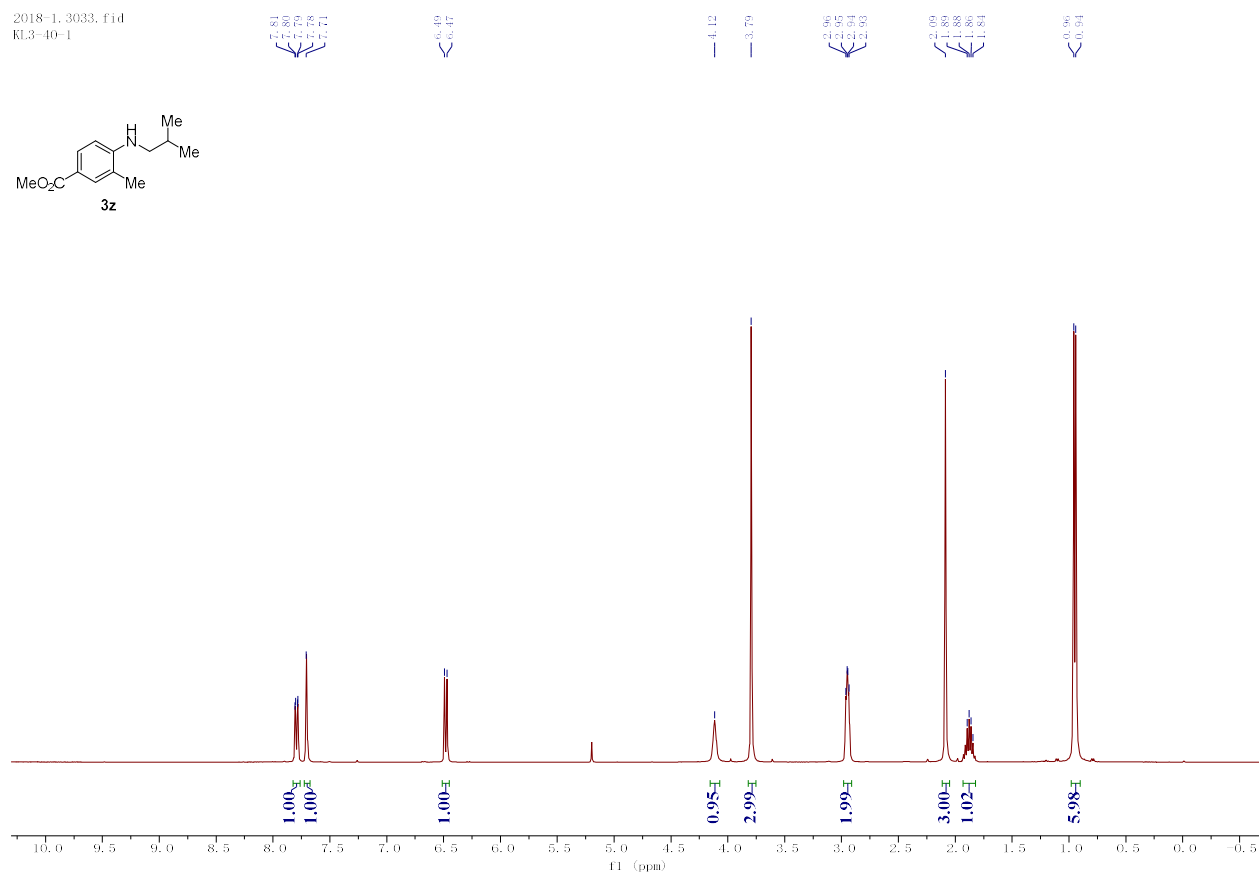
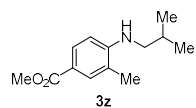
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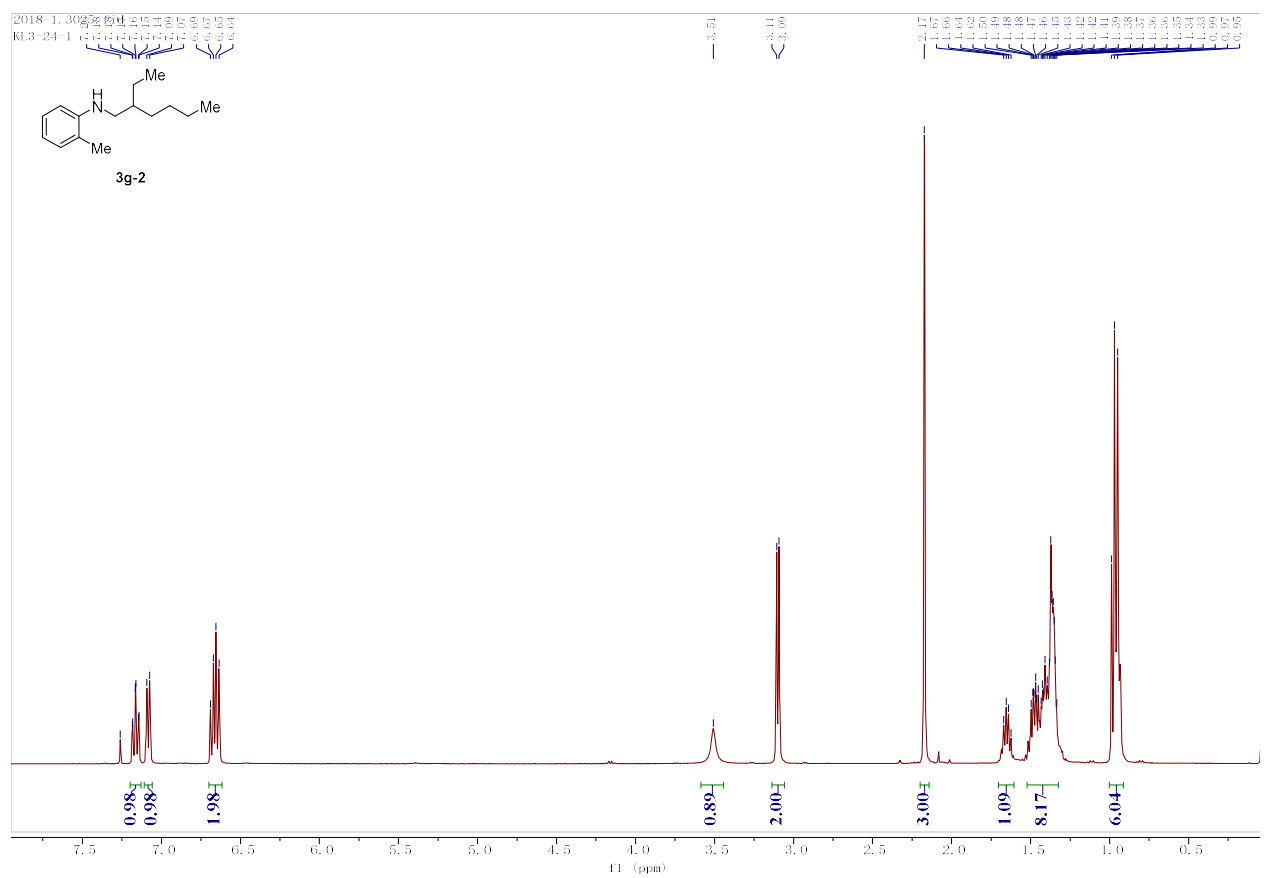
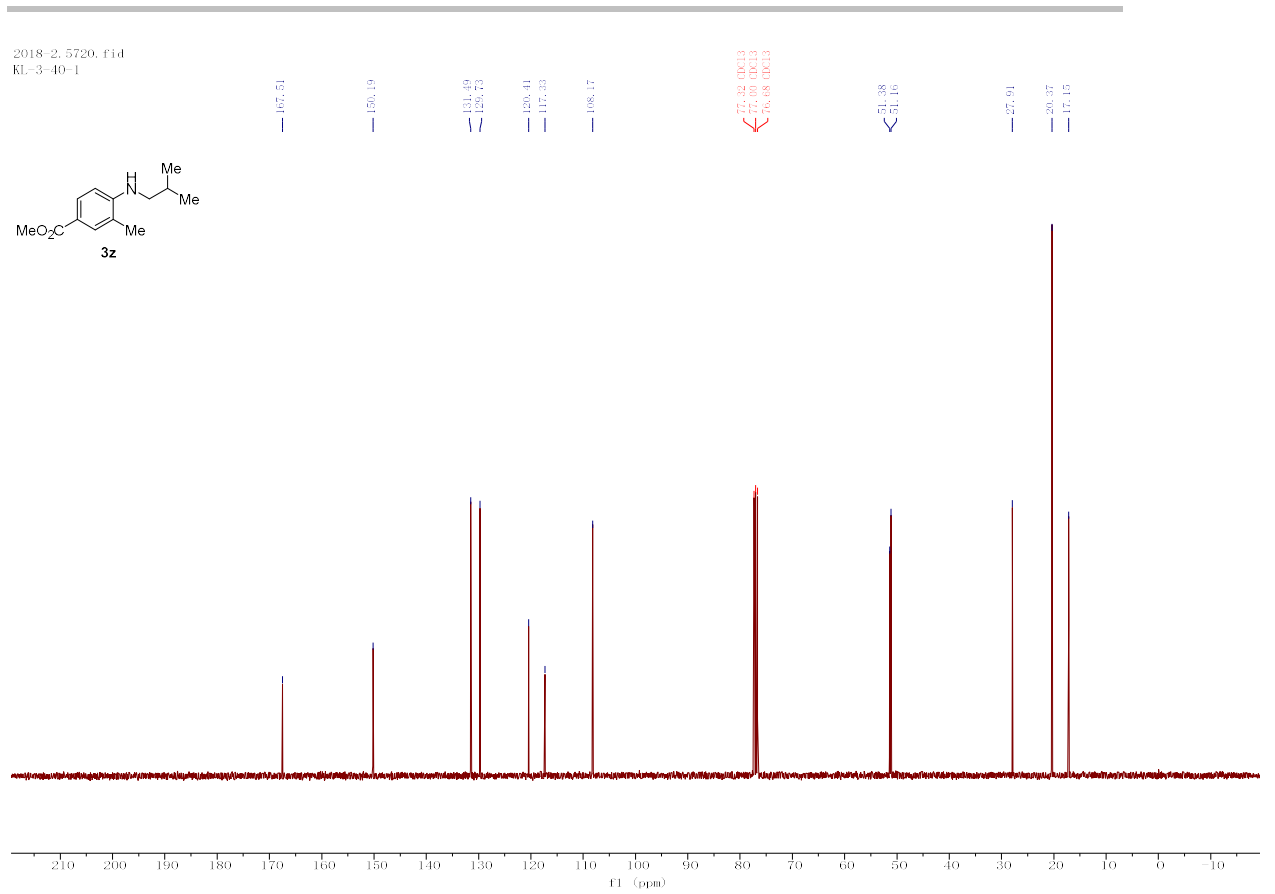


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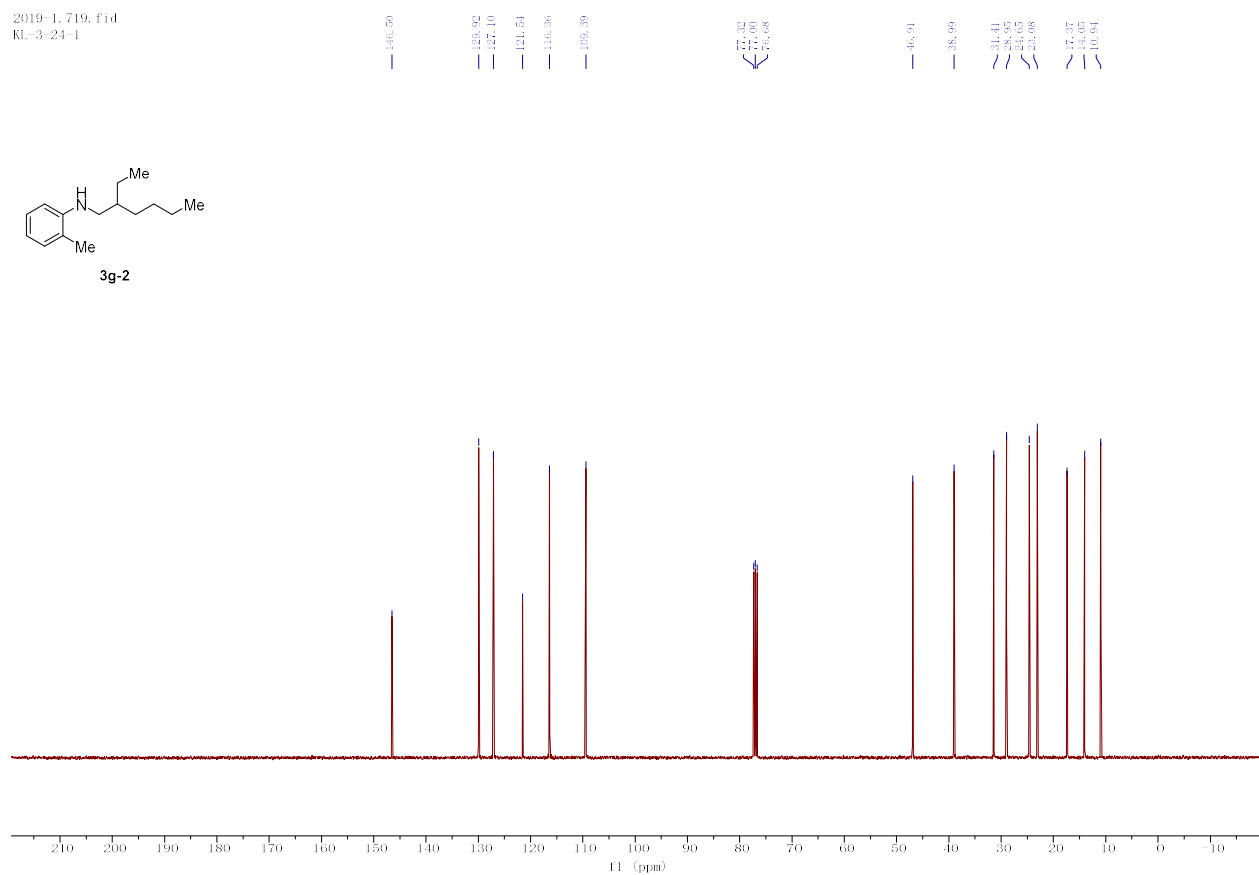
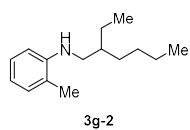


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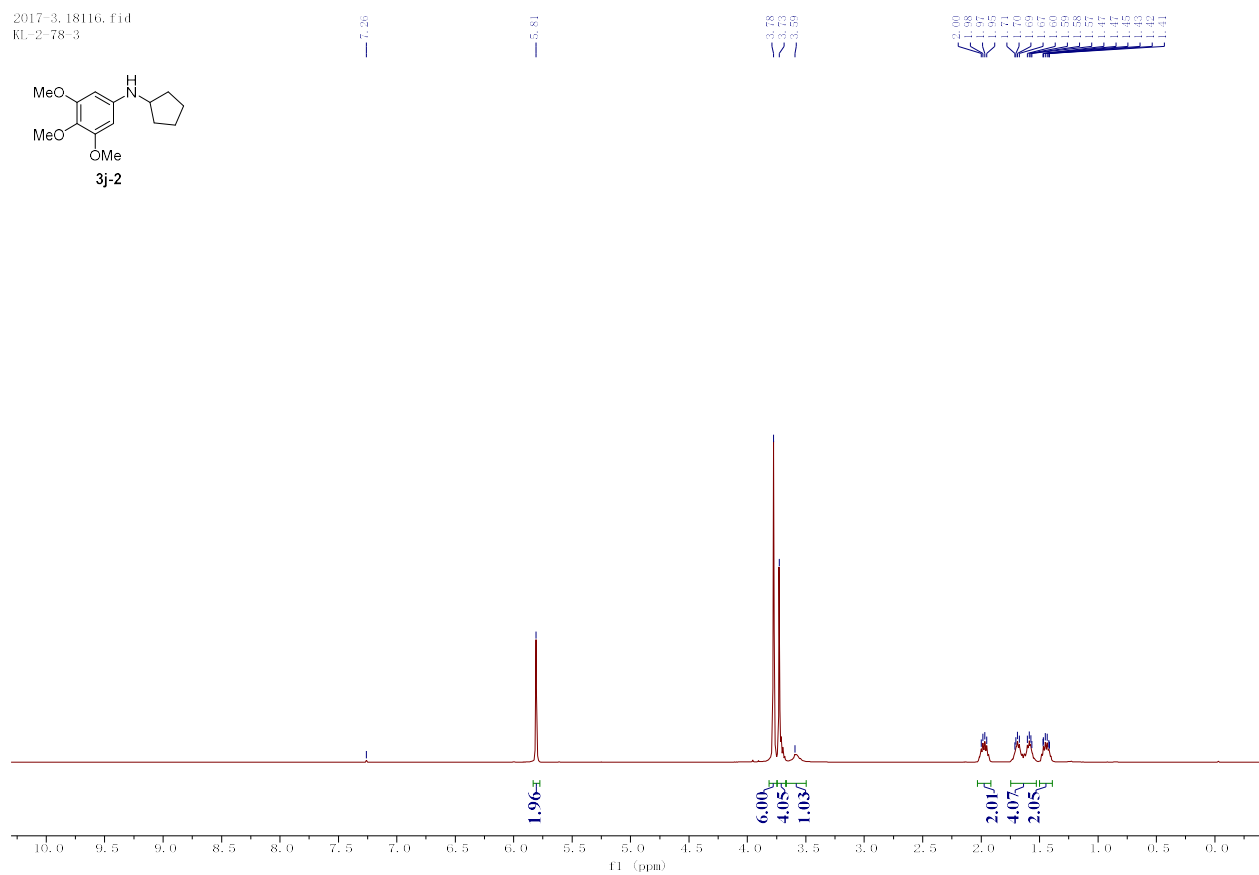
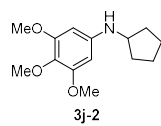




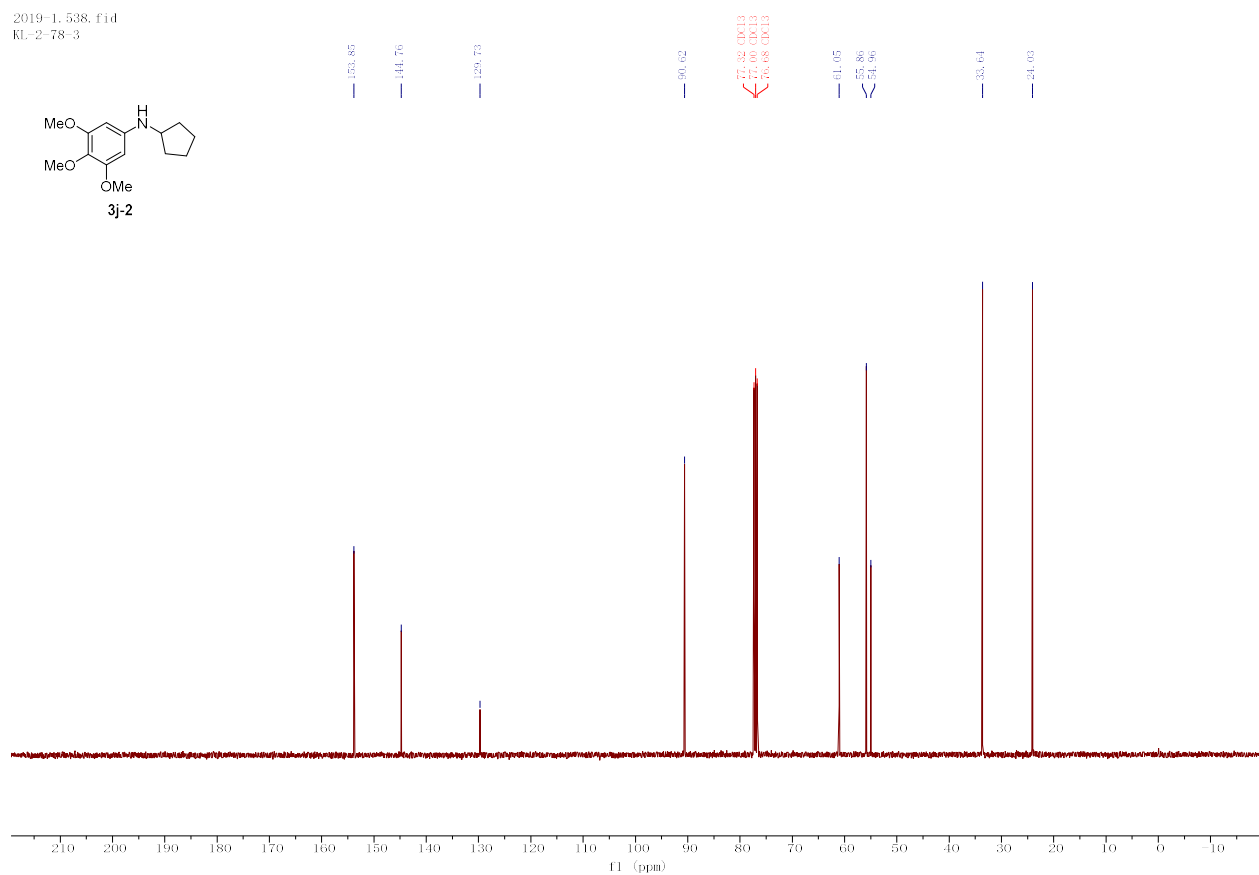
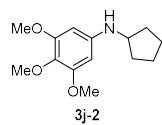
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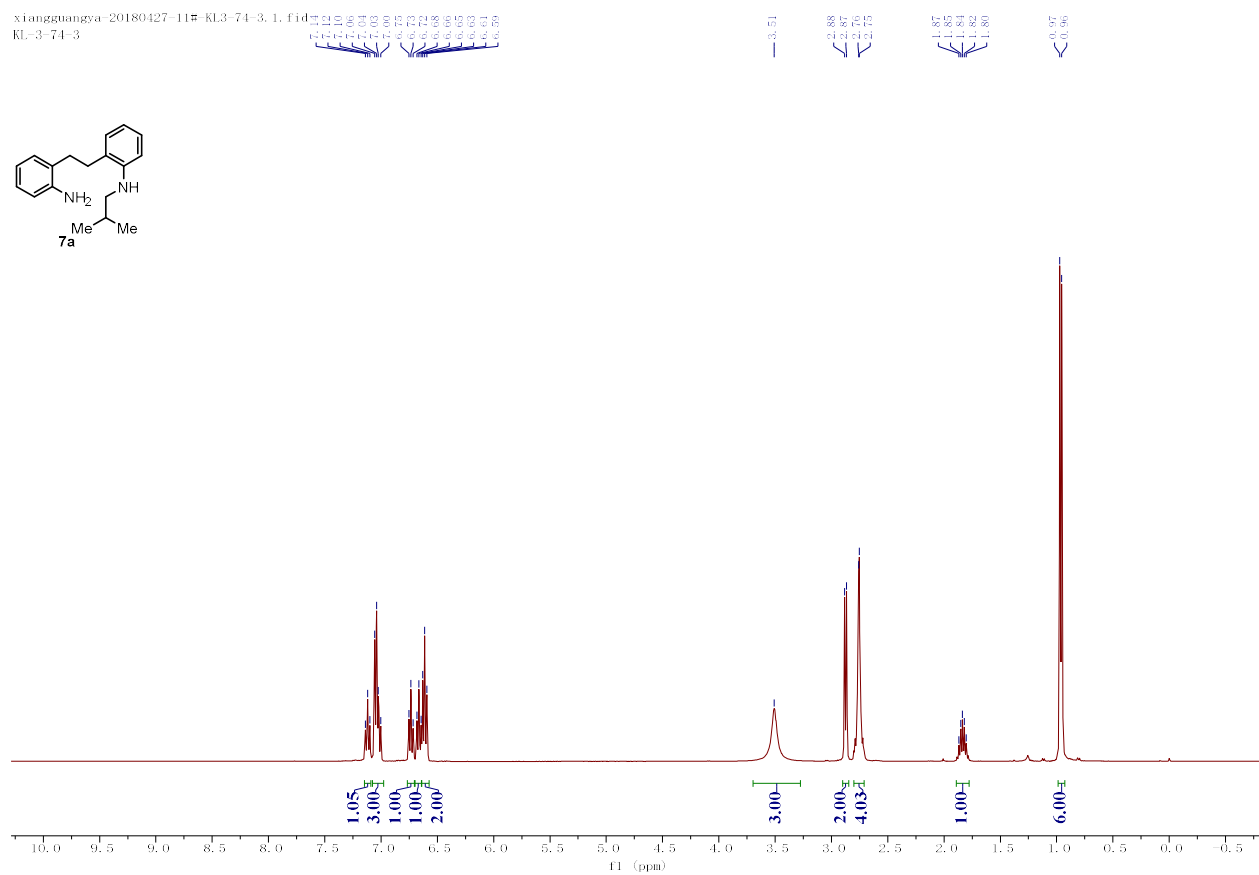
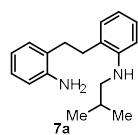
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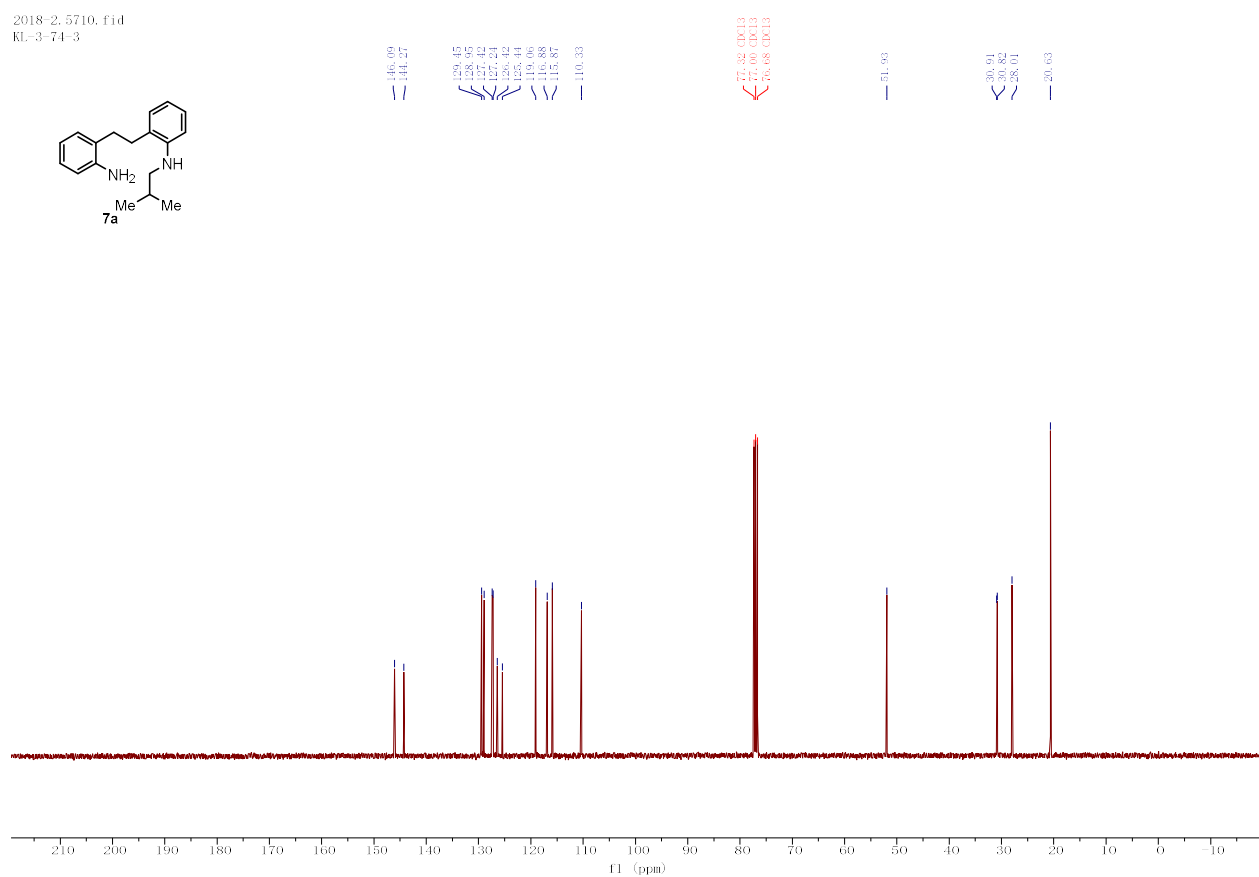
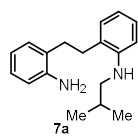
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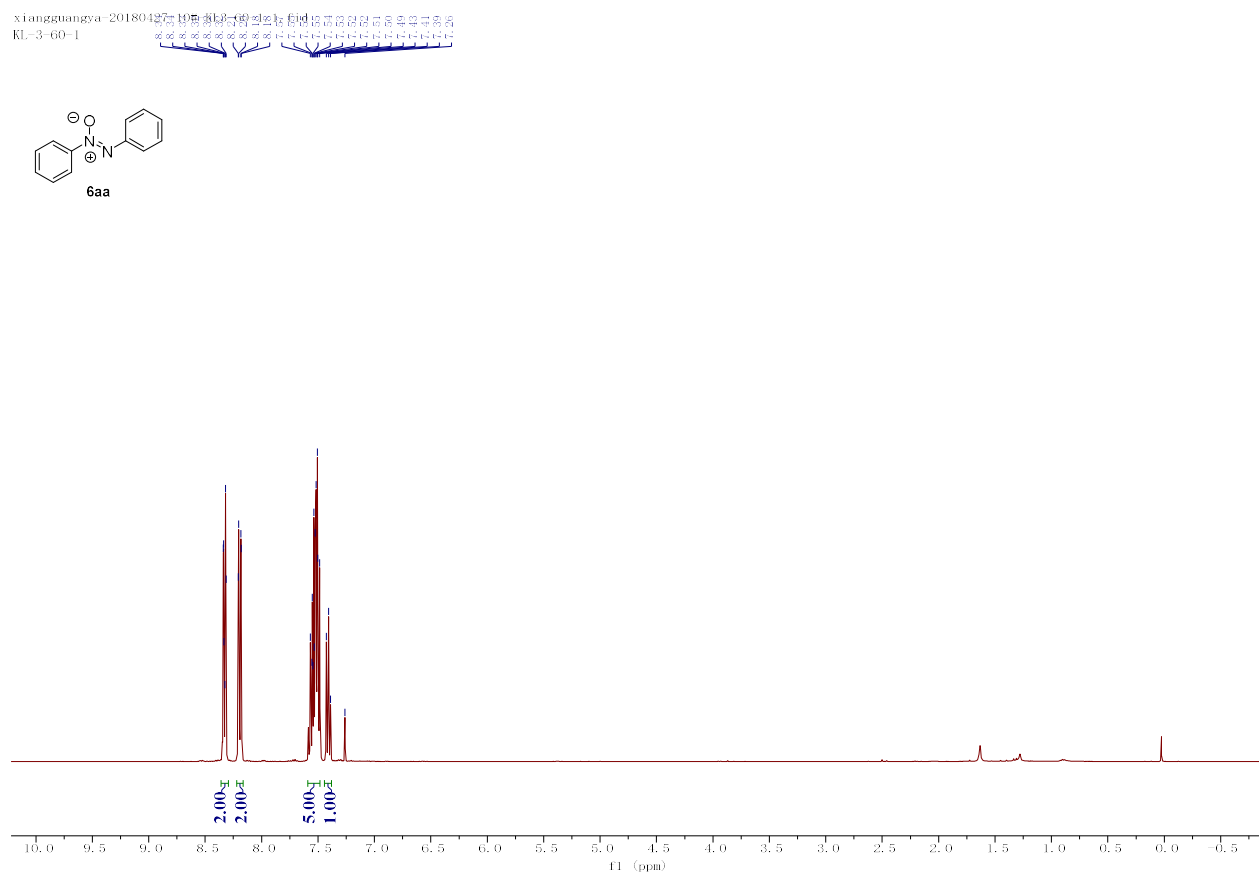
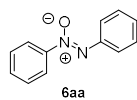
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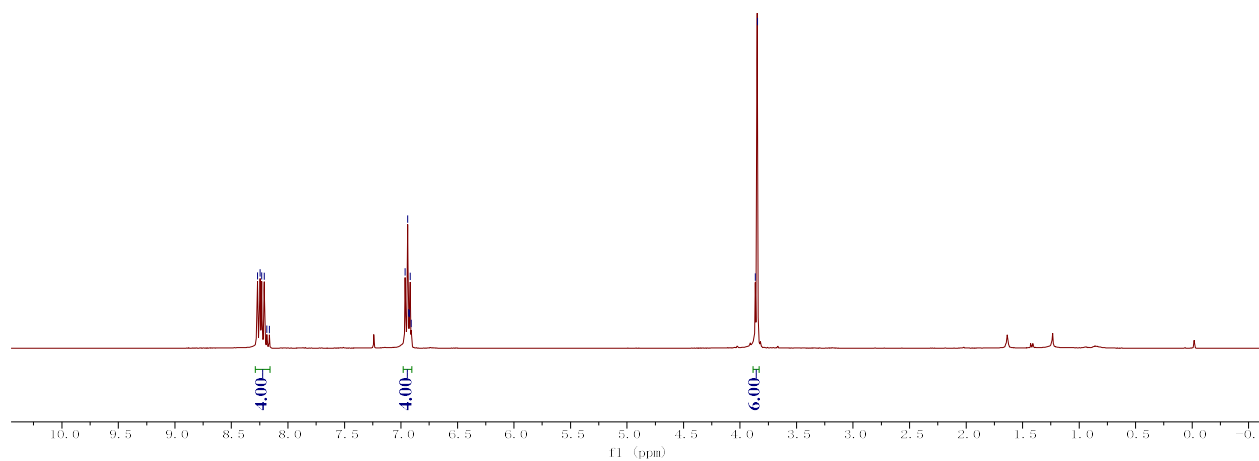
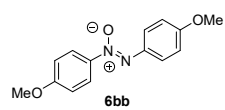
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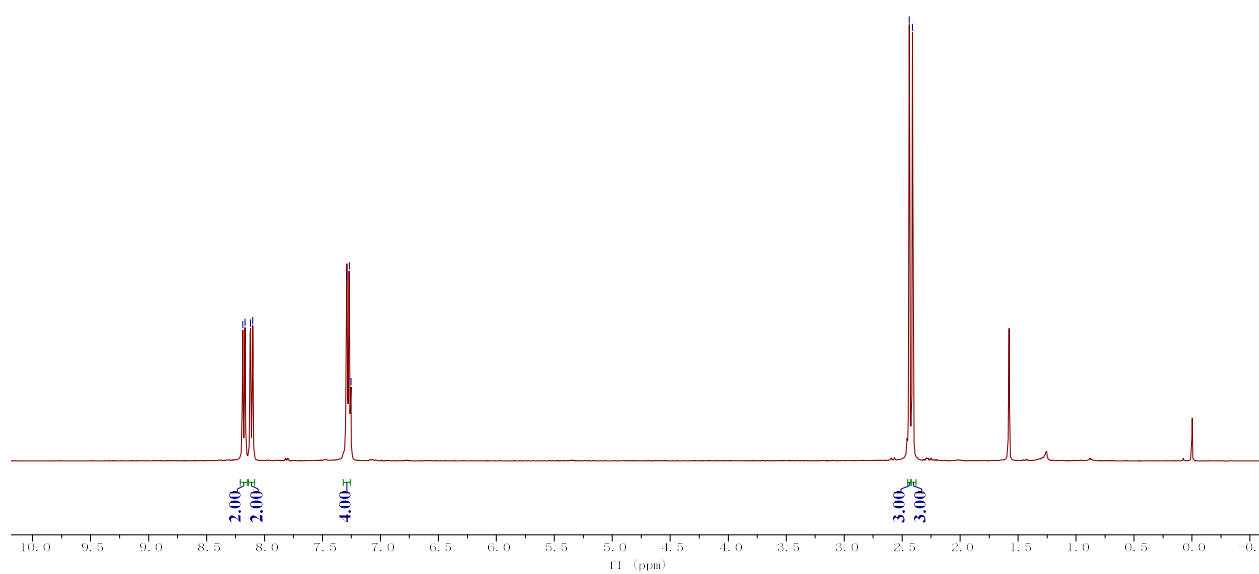
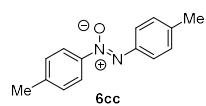
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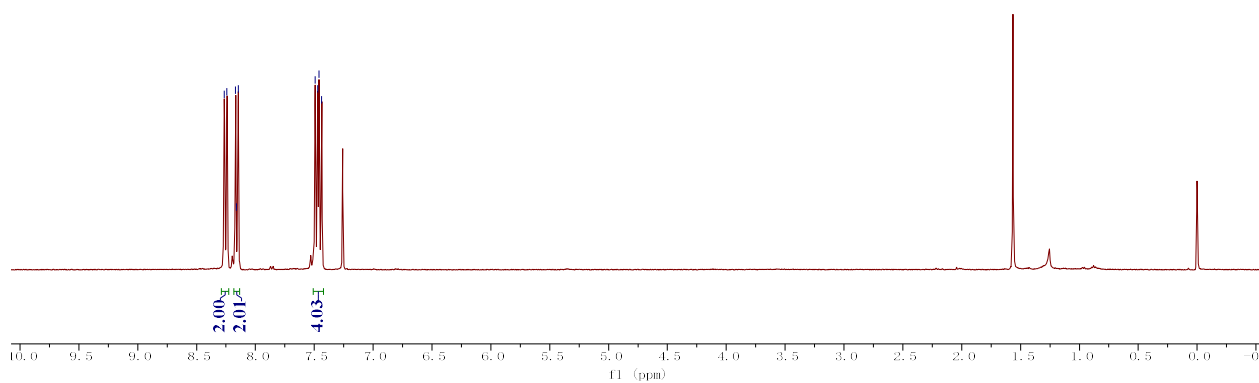
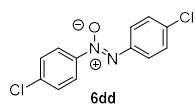
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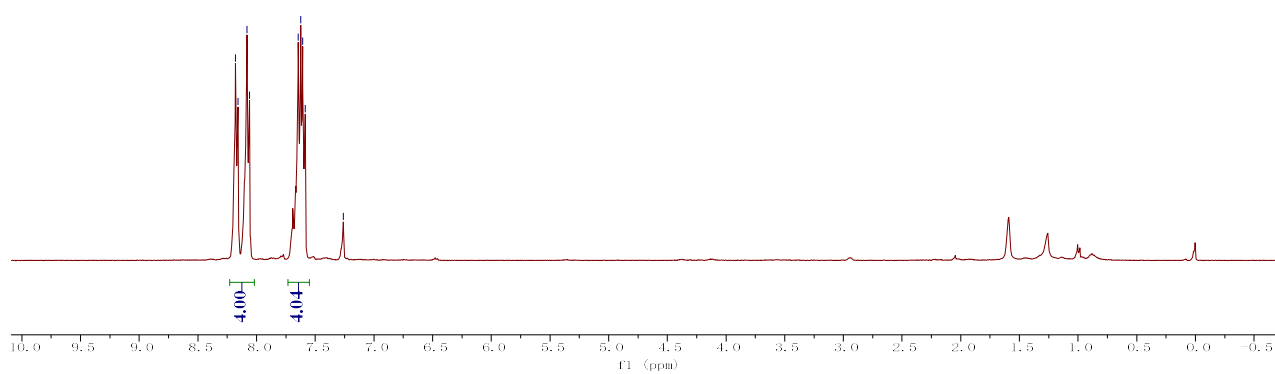
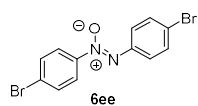
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KL2-10-2

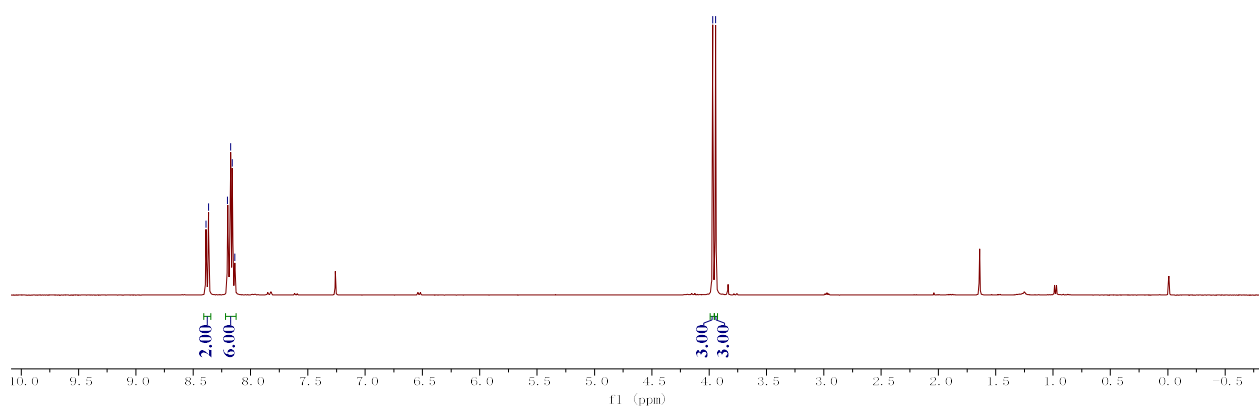
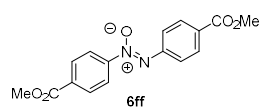
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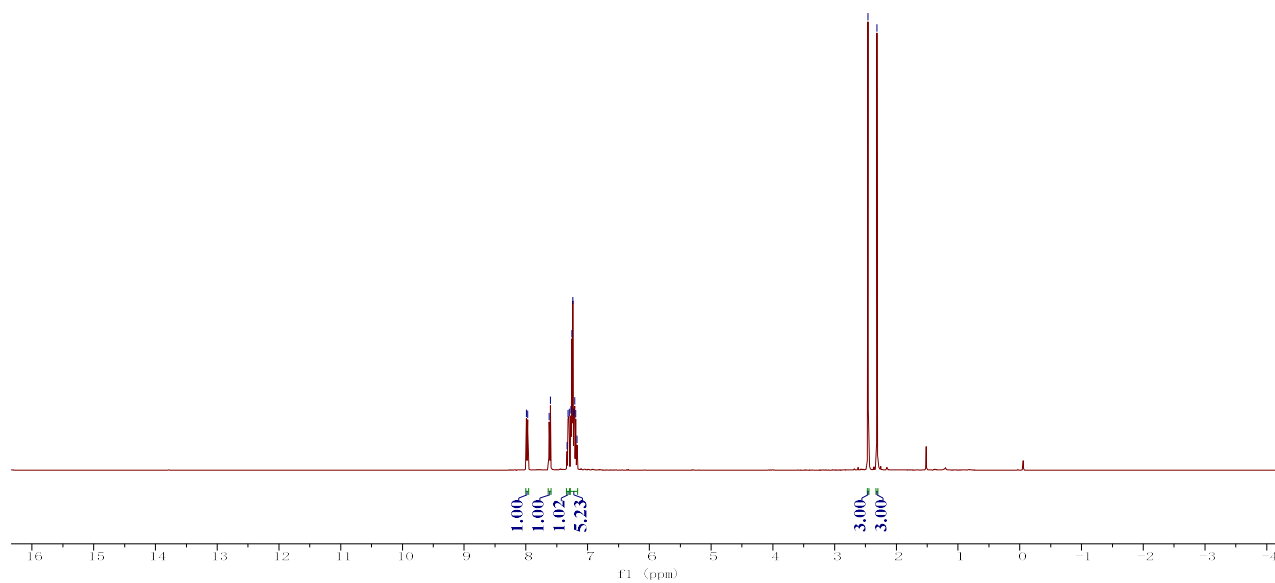
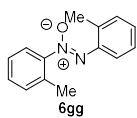
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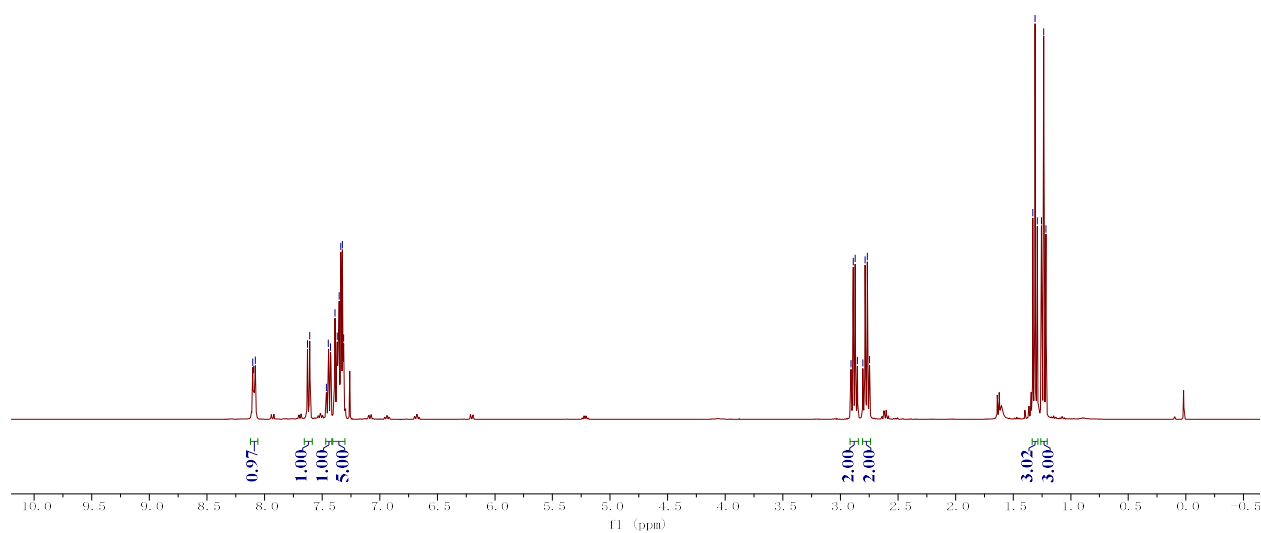
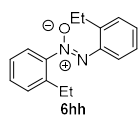
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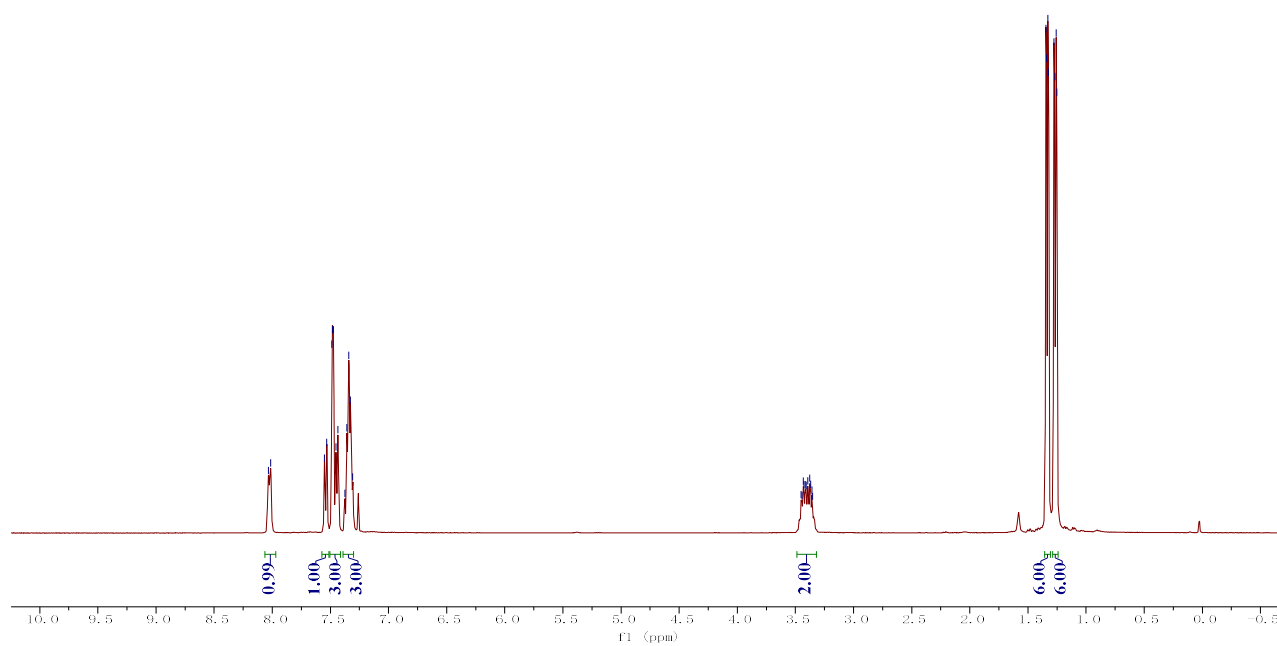
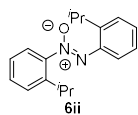
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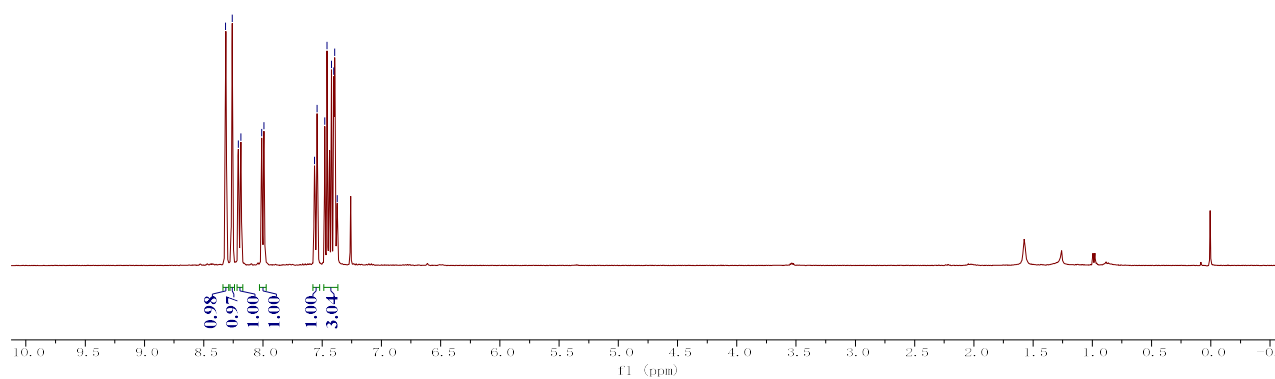
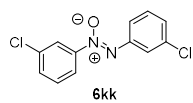


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KL-2-32-1

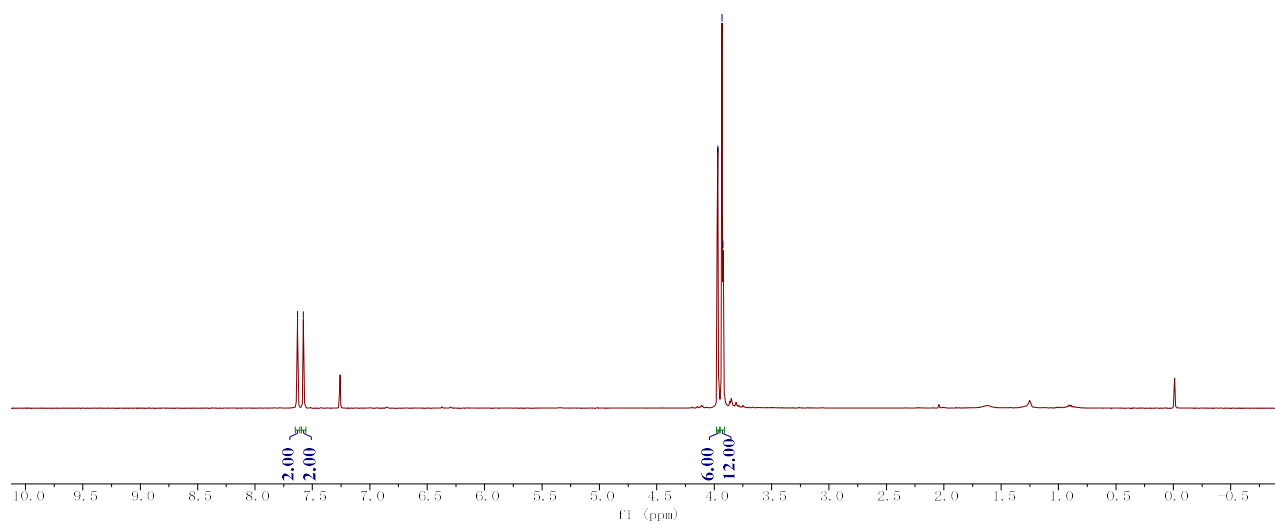
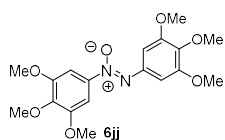
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2017-3, 16063, f1d  
KL2-64-1

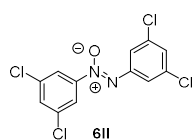
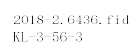
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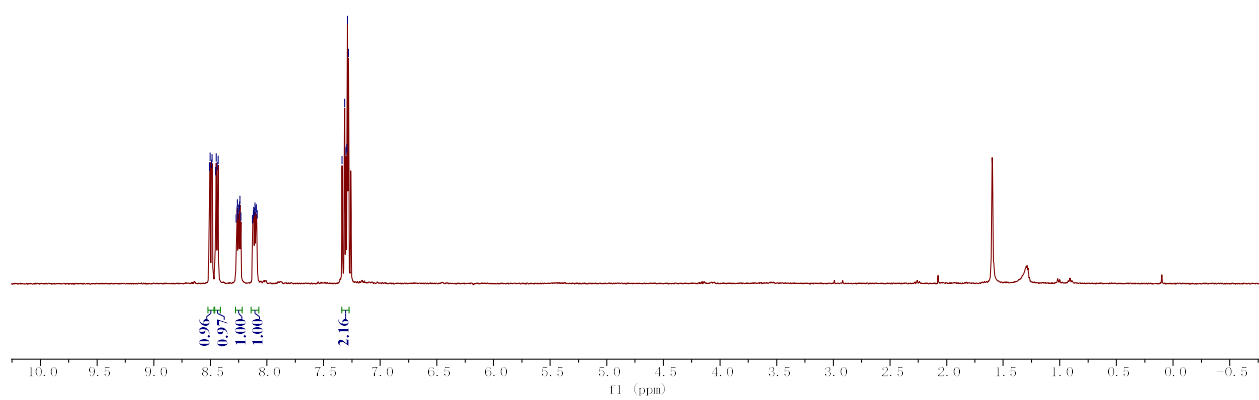
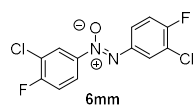
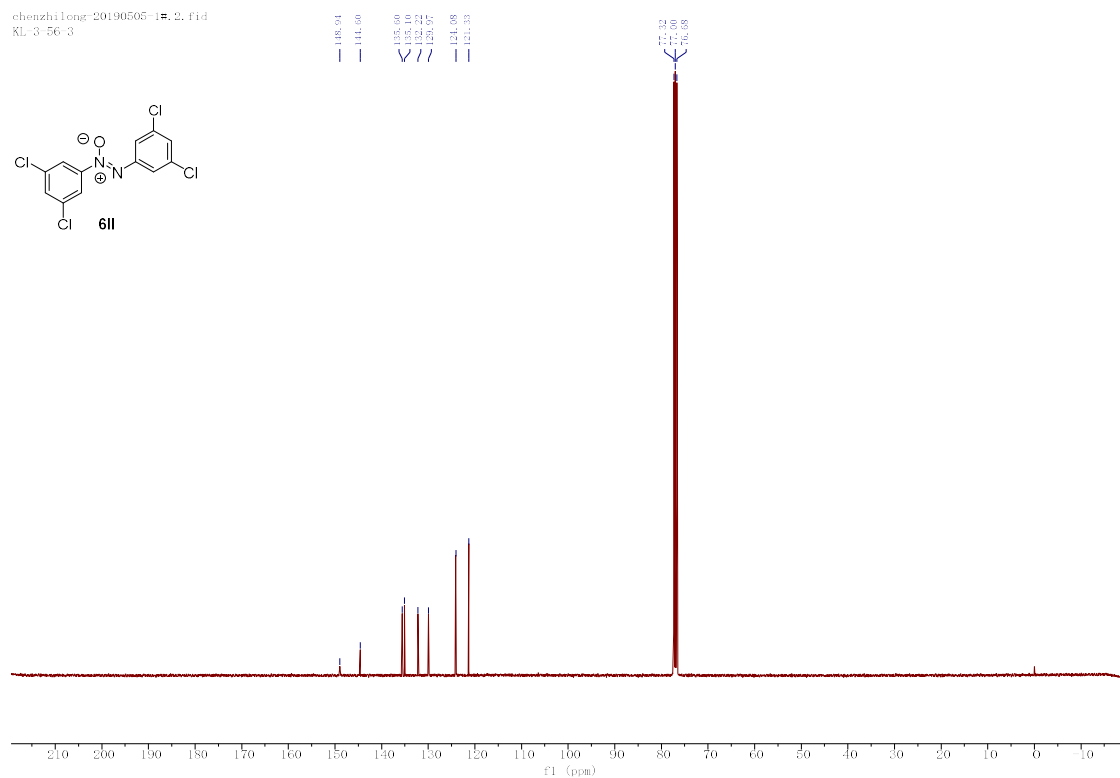
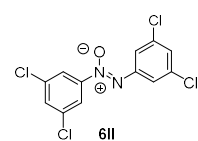


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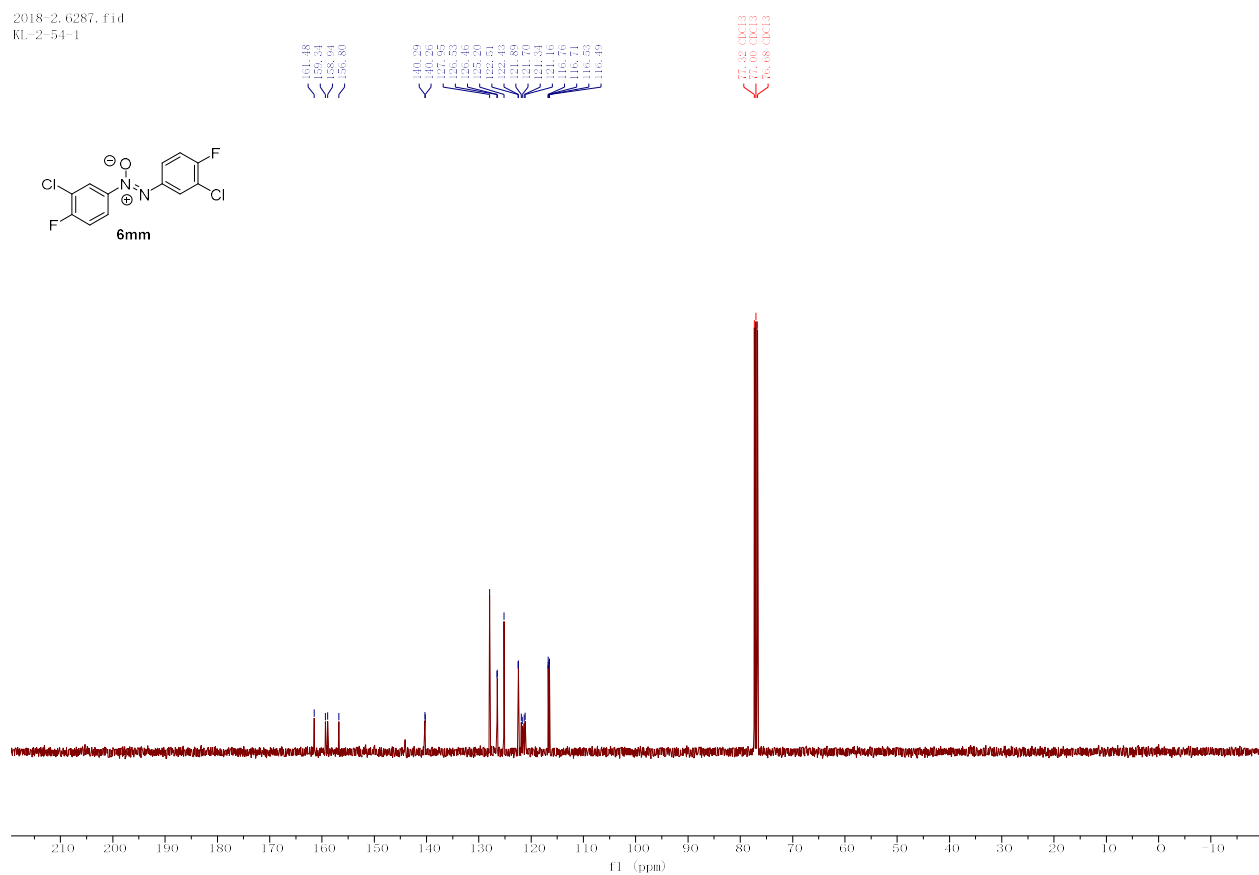
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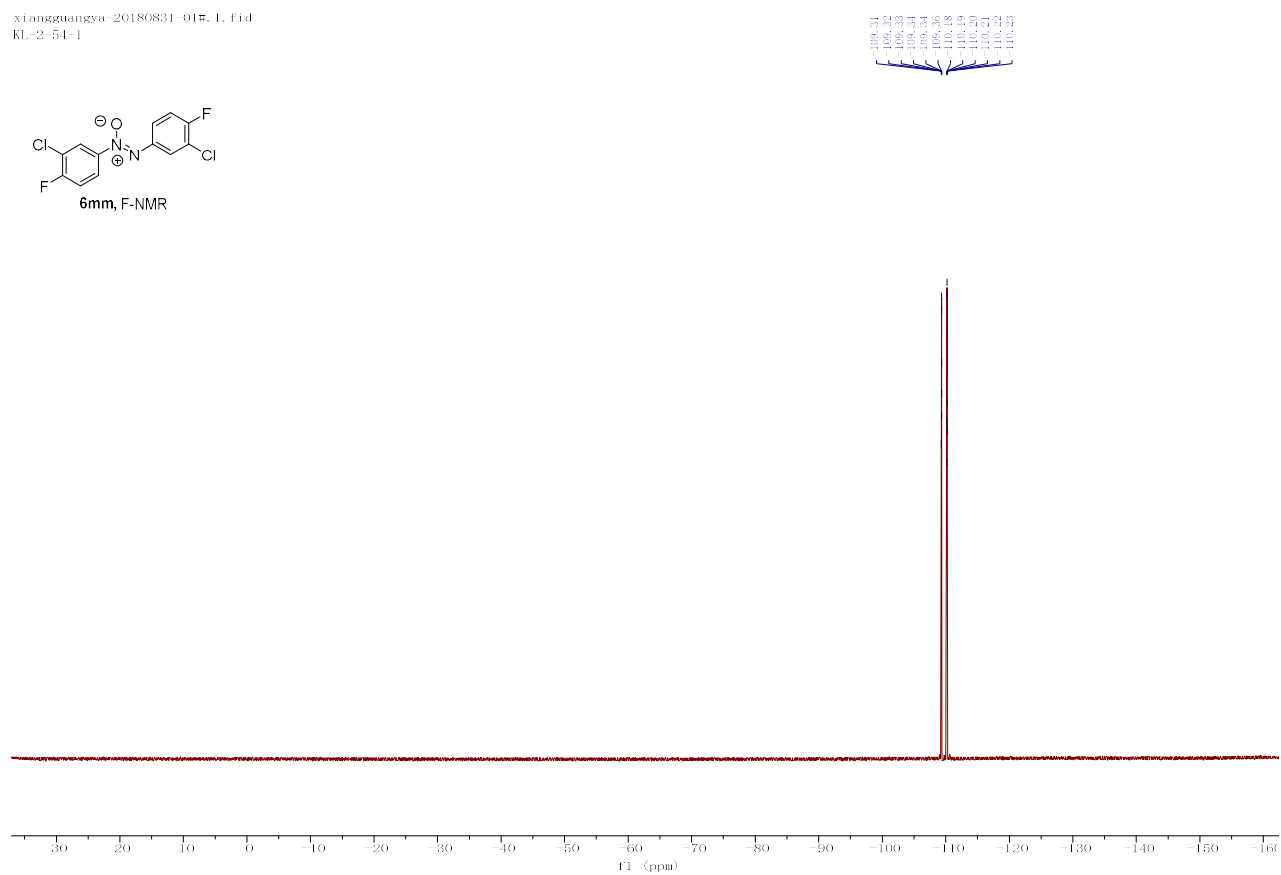
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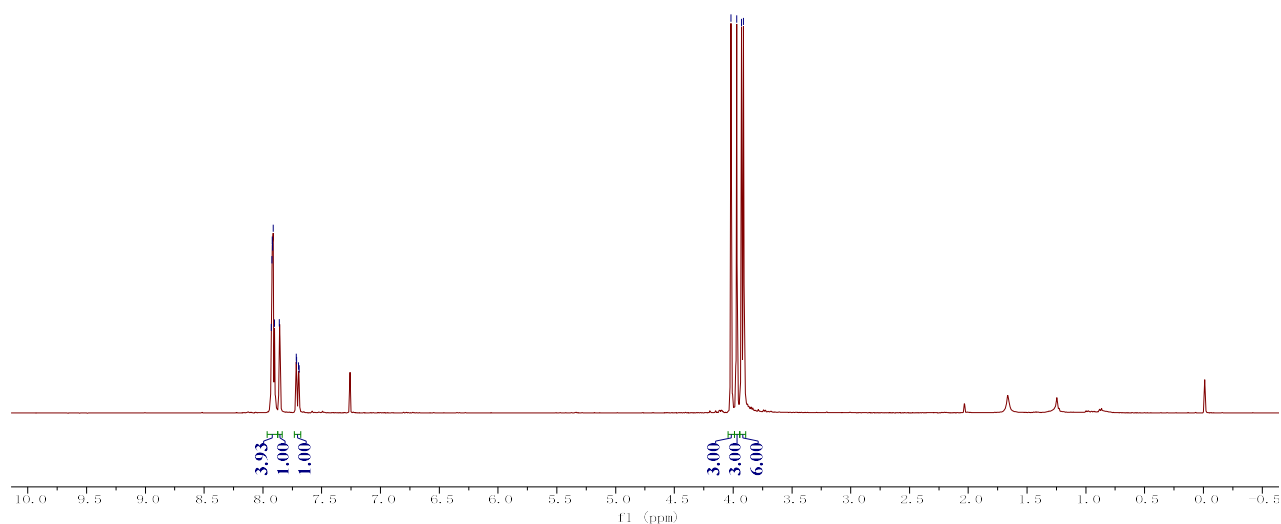
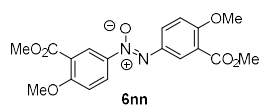
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4.02 3.97 3.93 3.89



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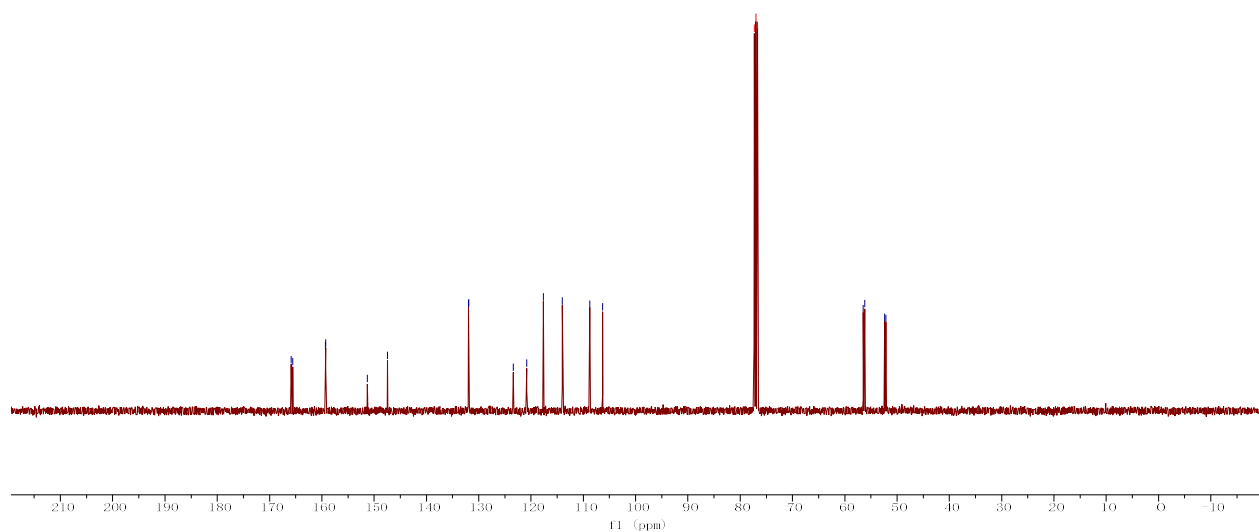
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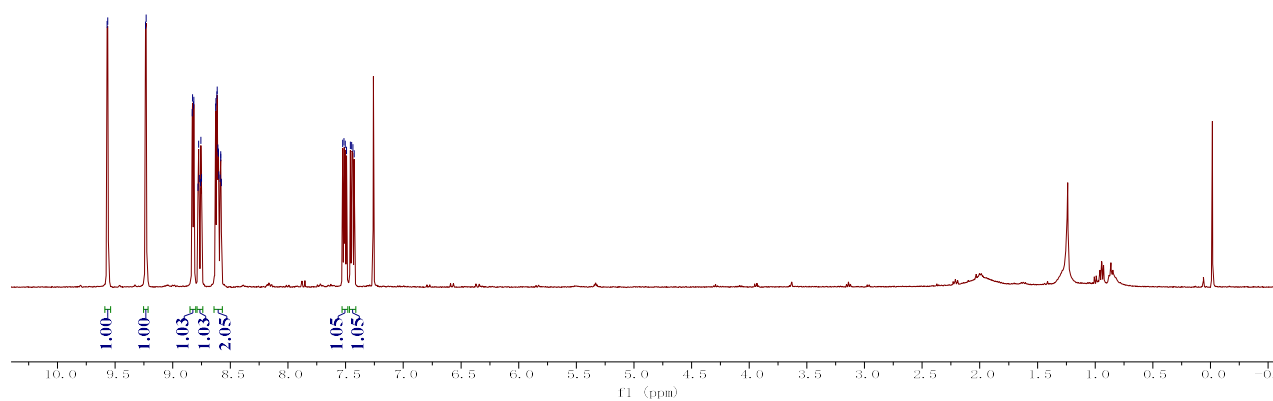
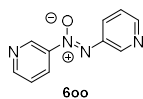
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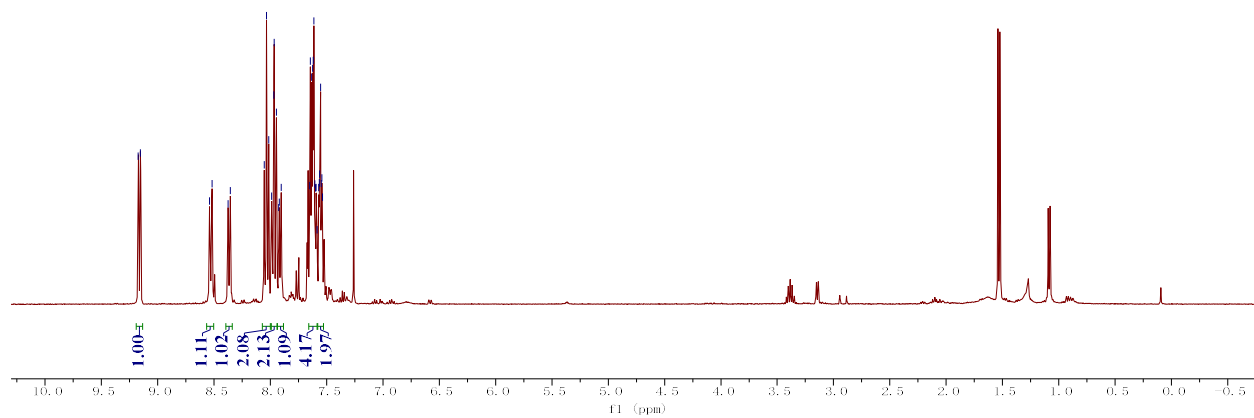
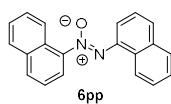




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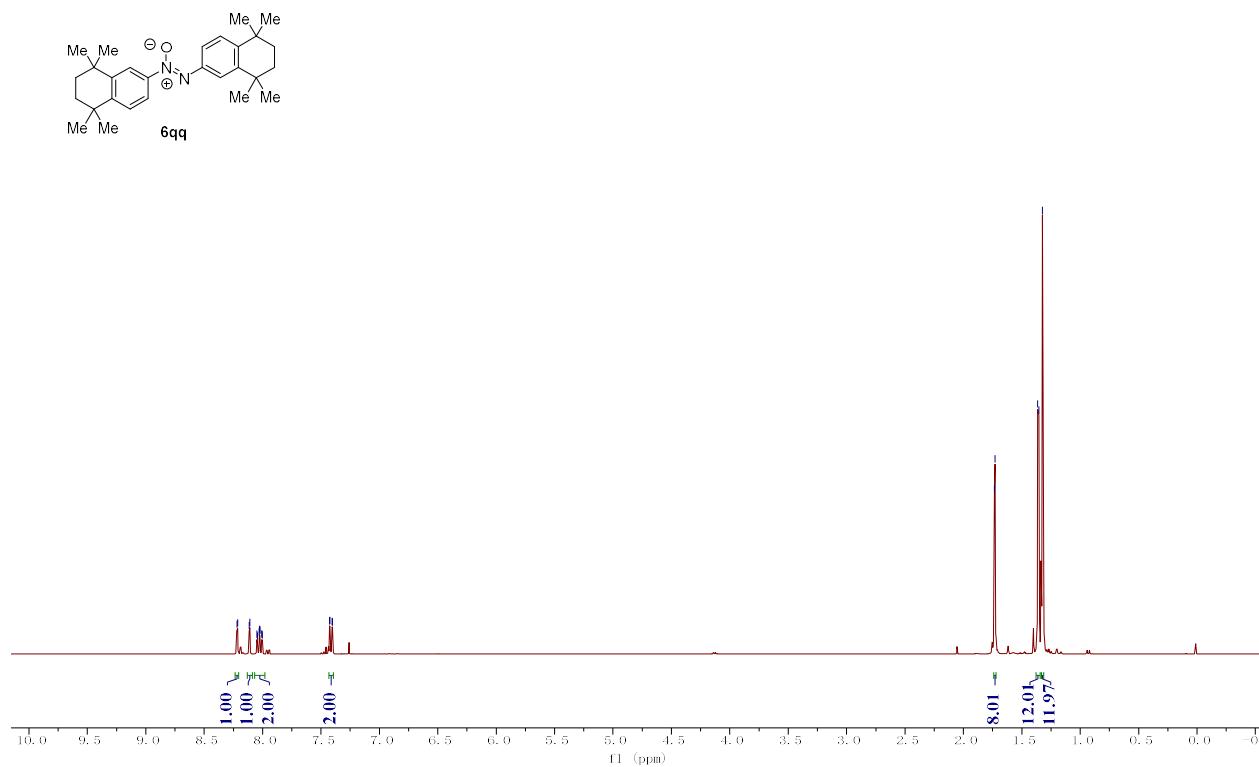
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xiangguangya-20180427  
KL-3-68-2



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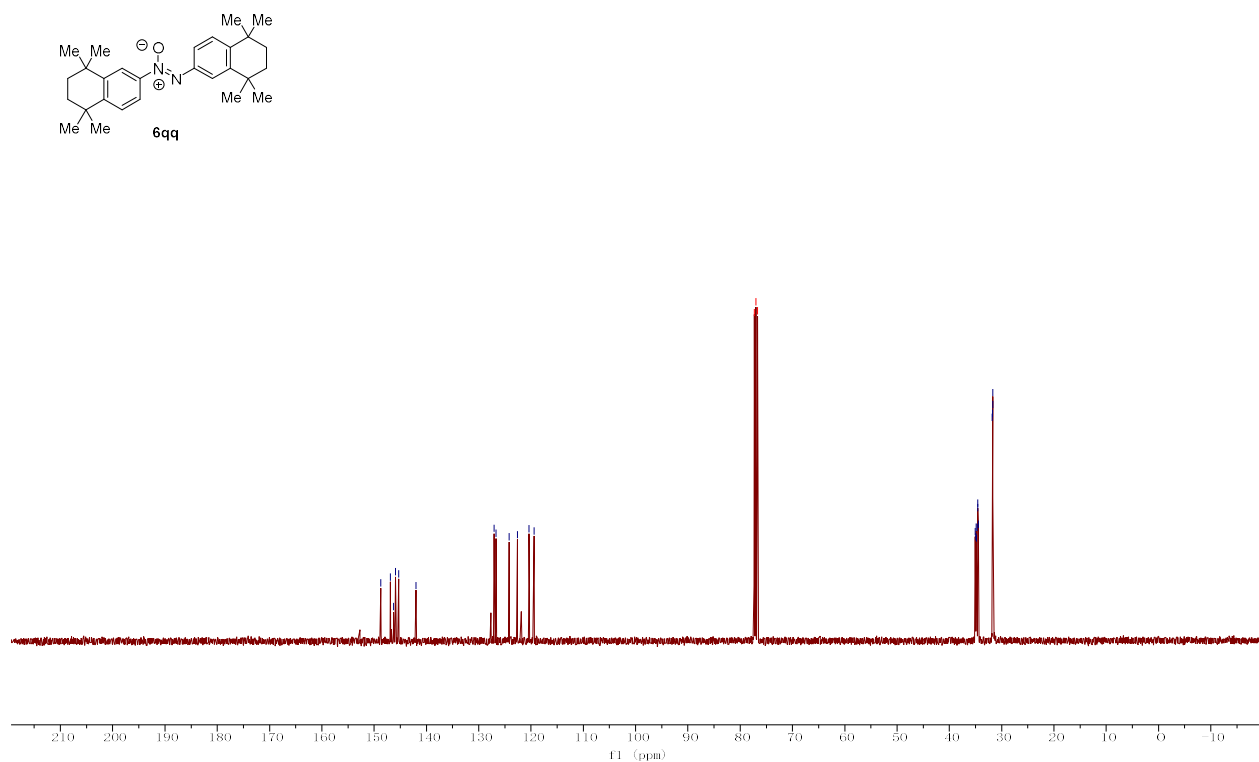
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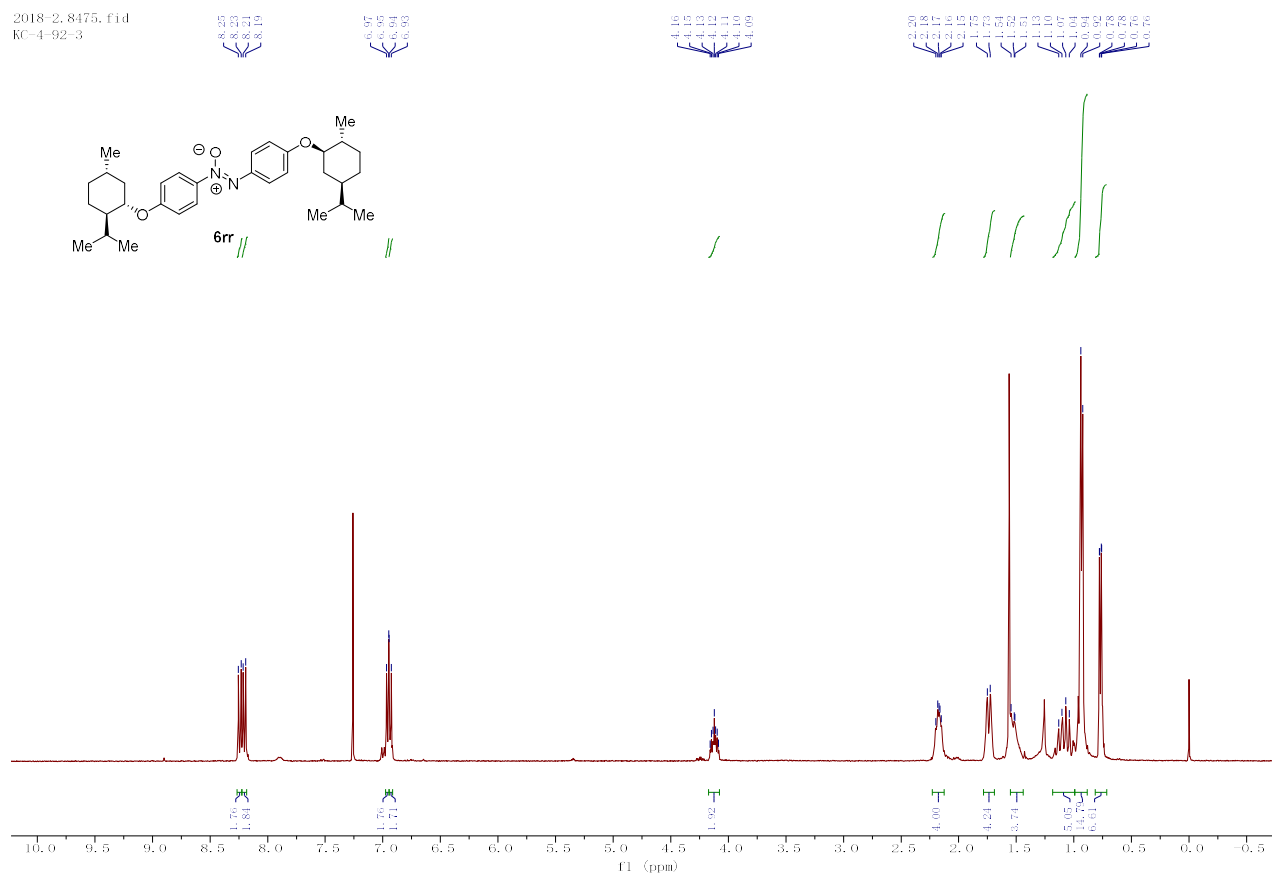
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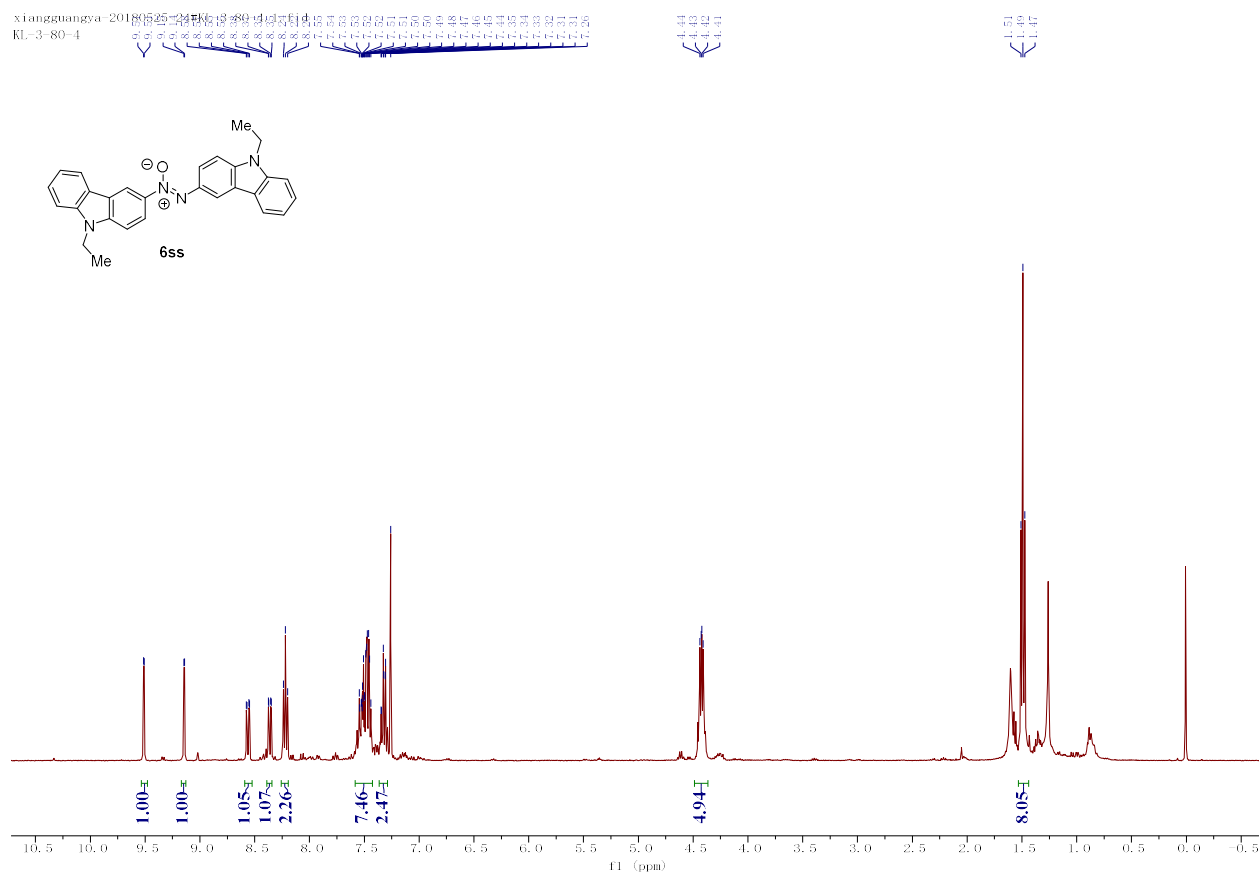
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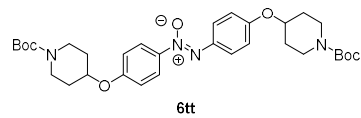


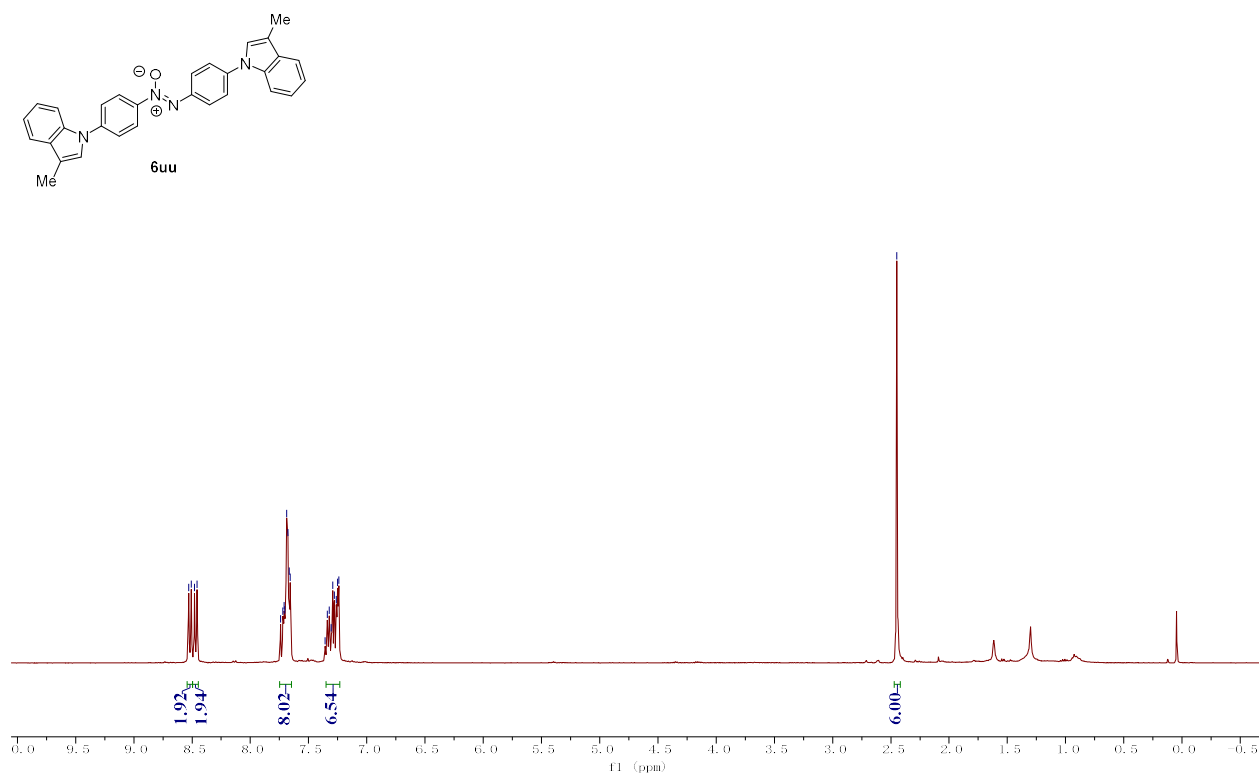
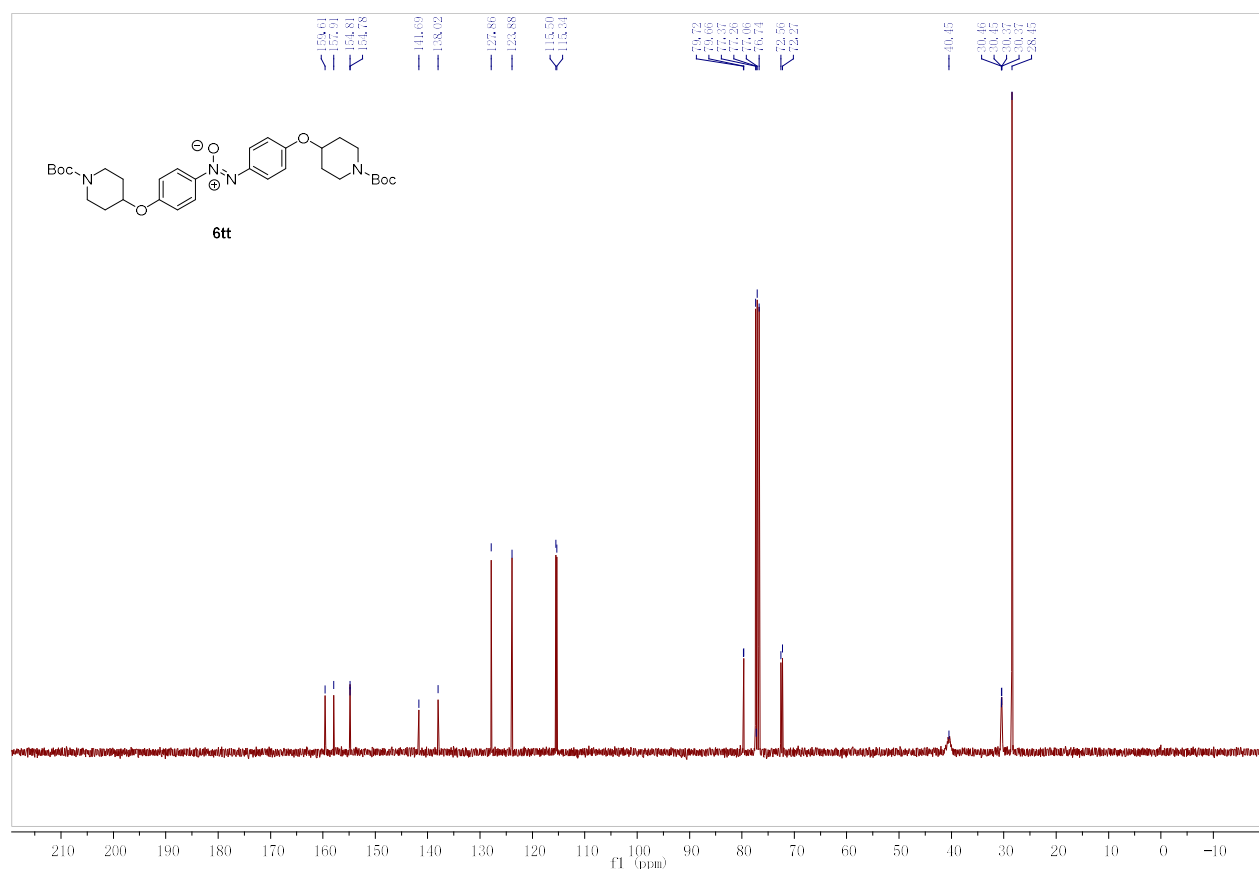
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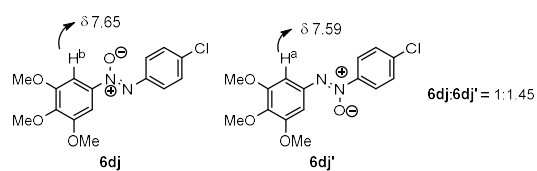
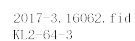




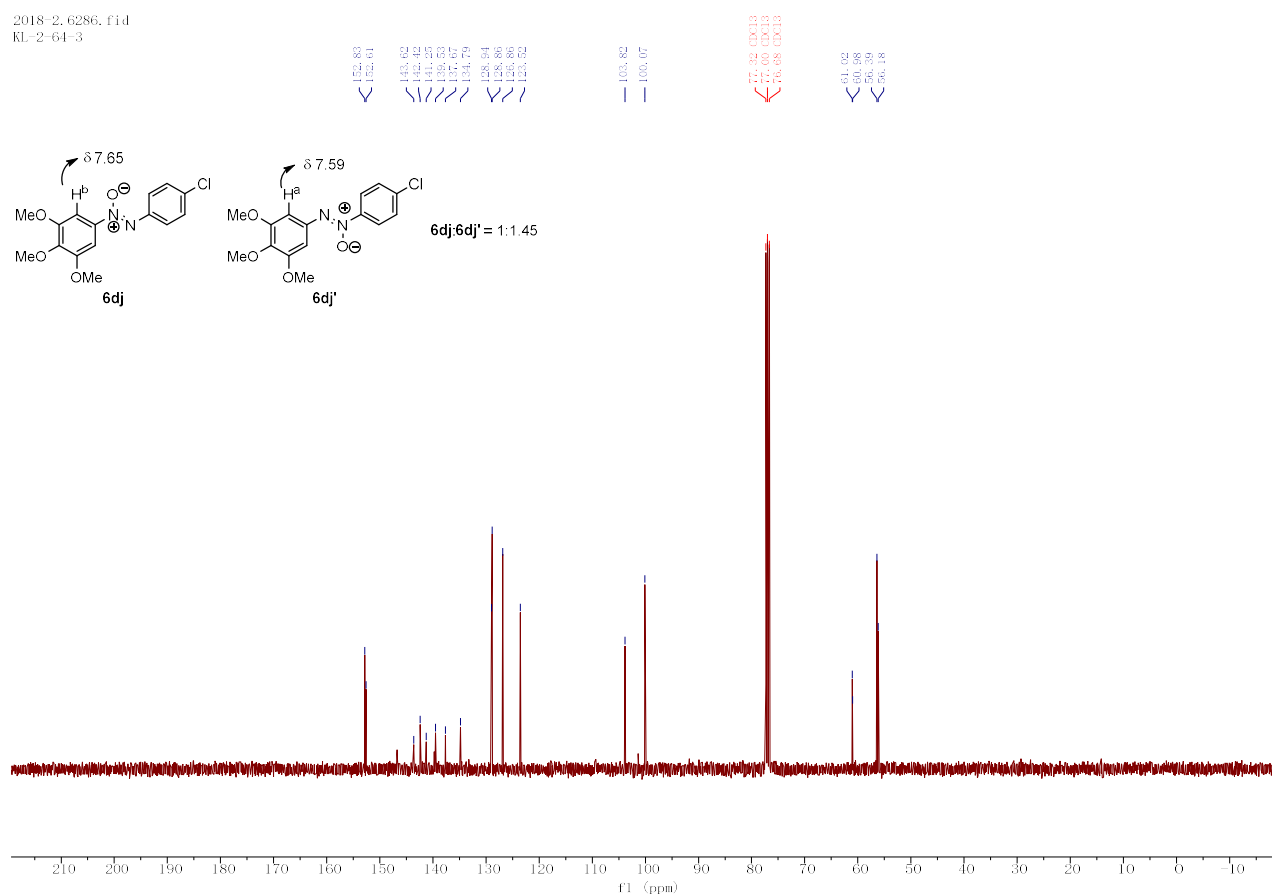
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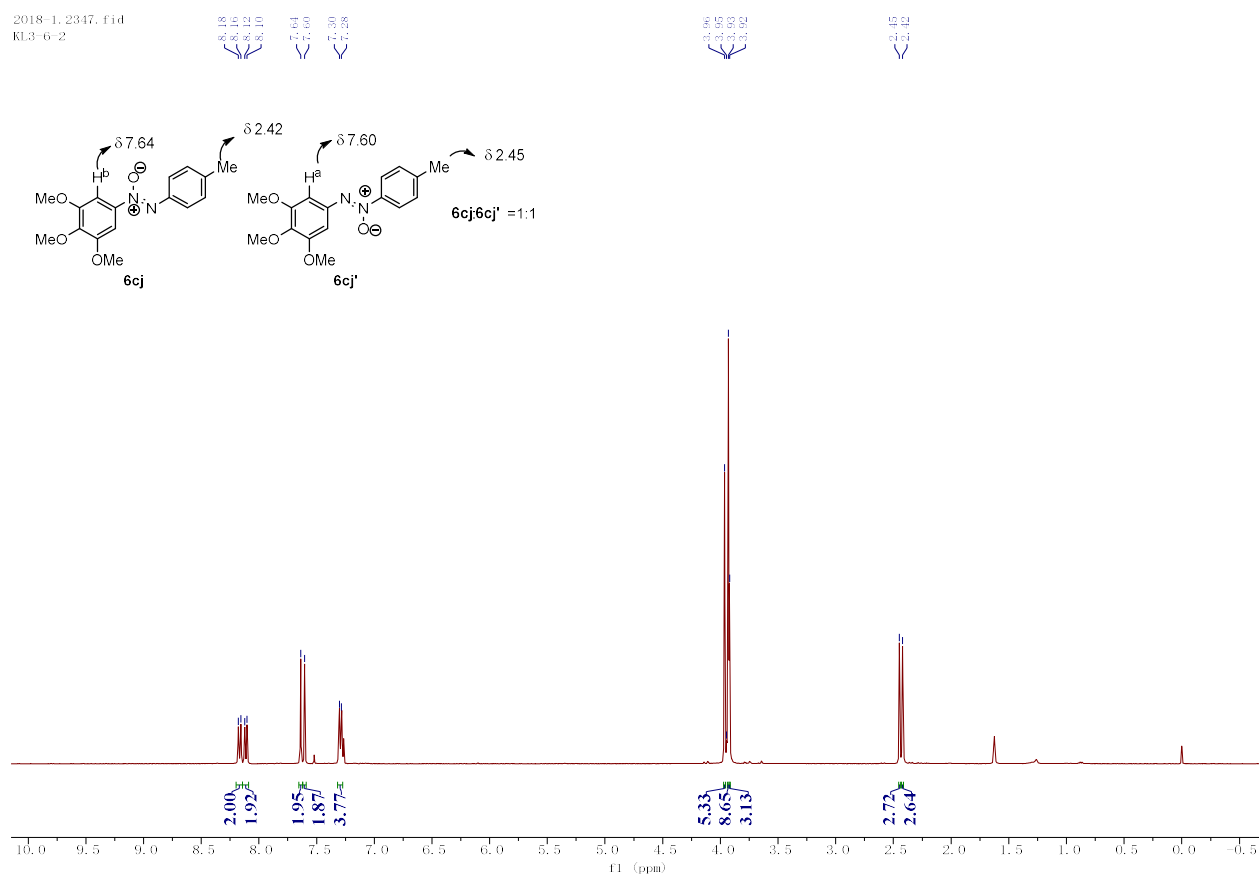




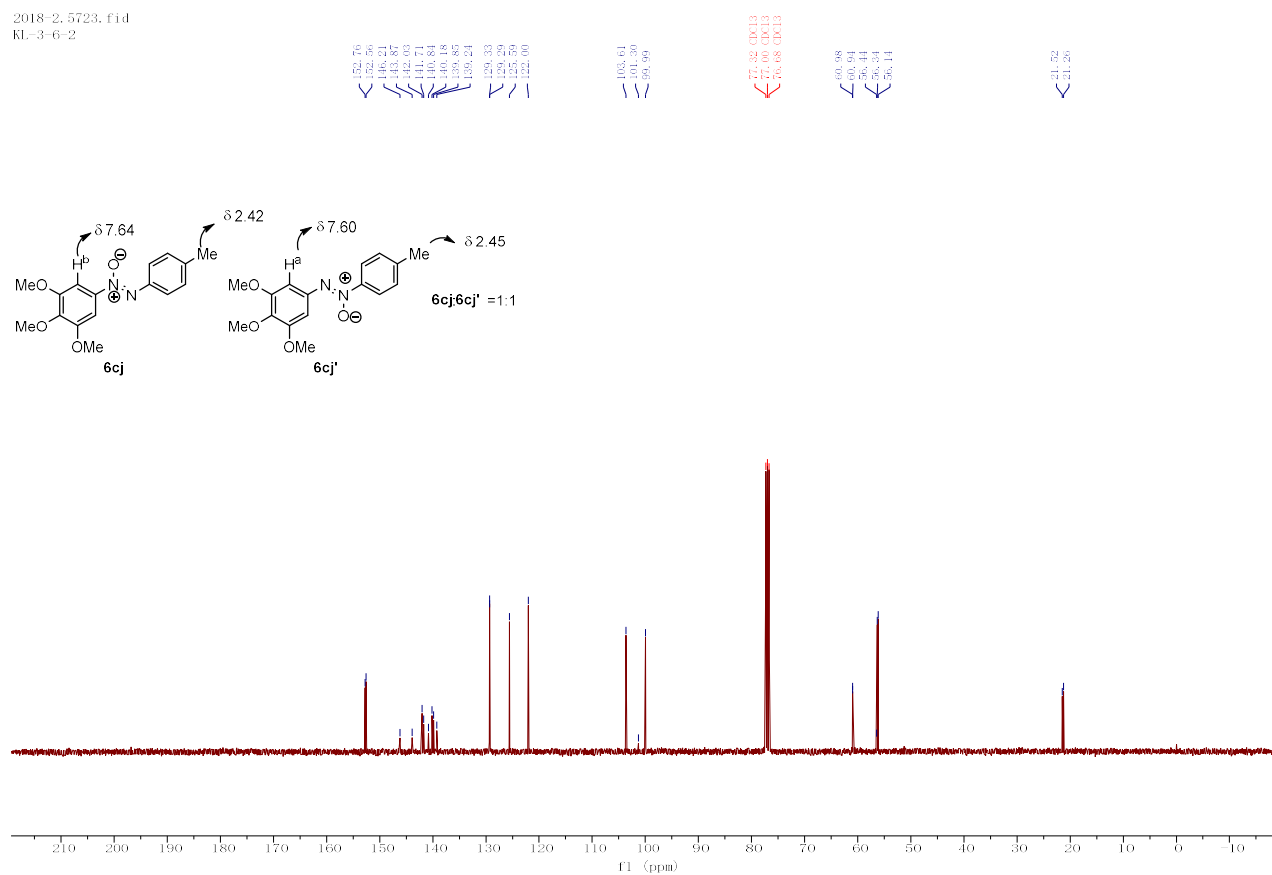
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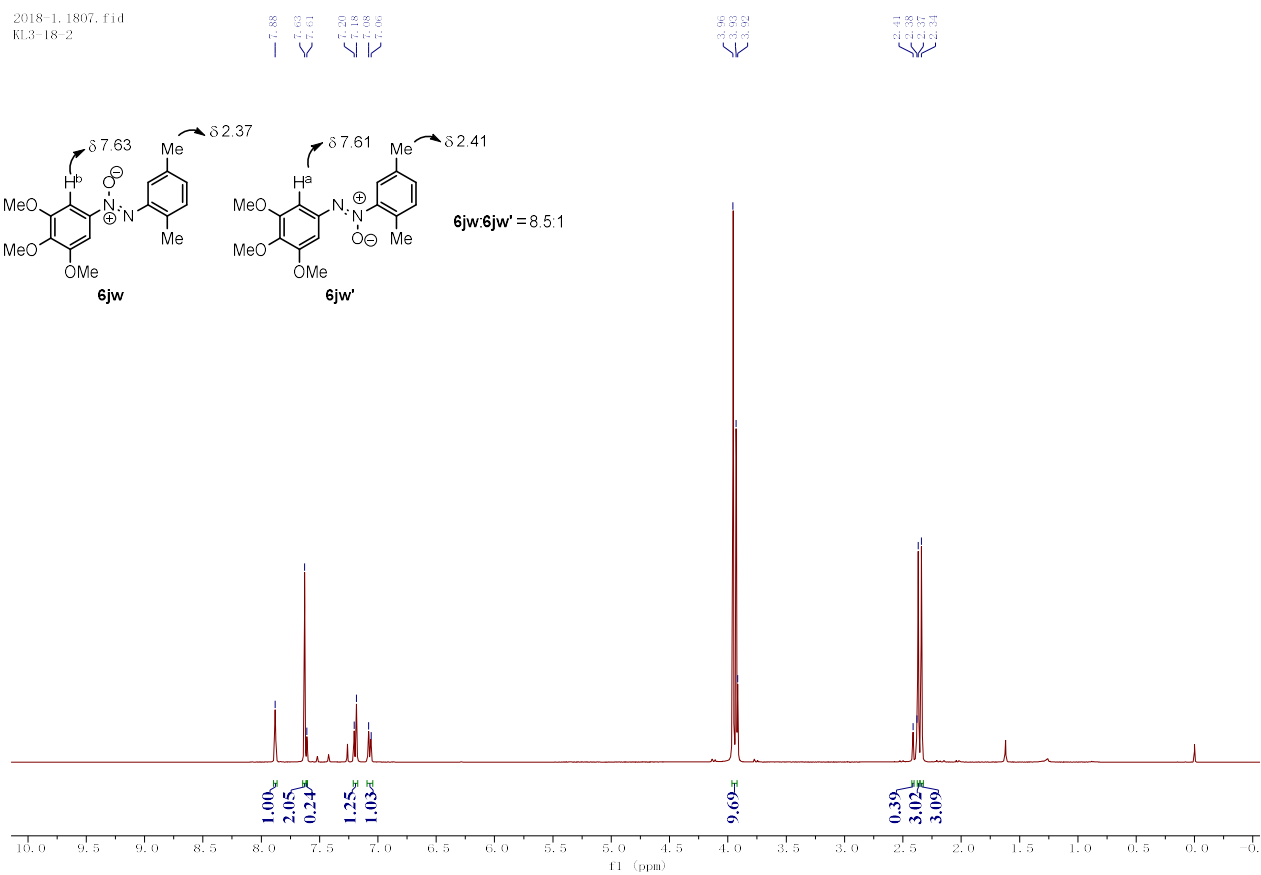
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KL3-6-2



2018-2-5723.fid  
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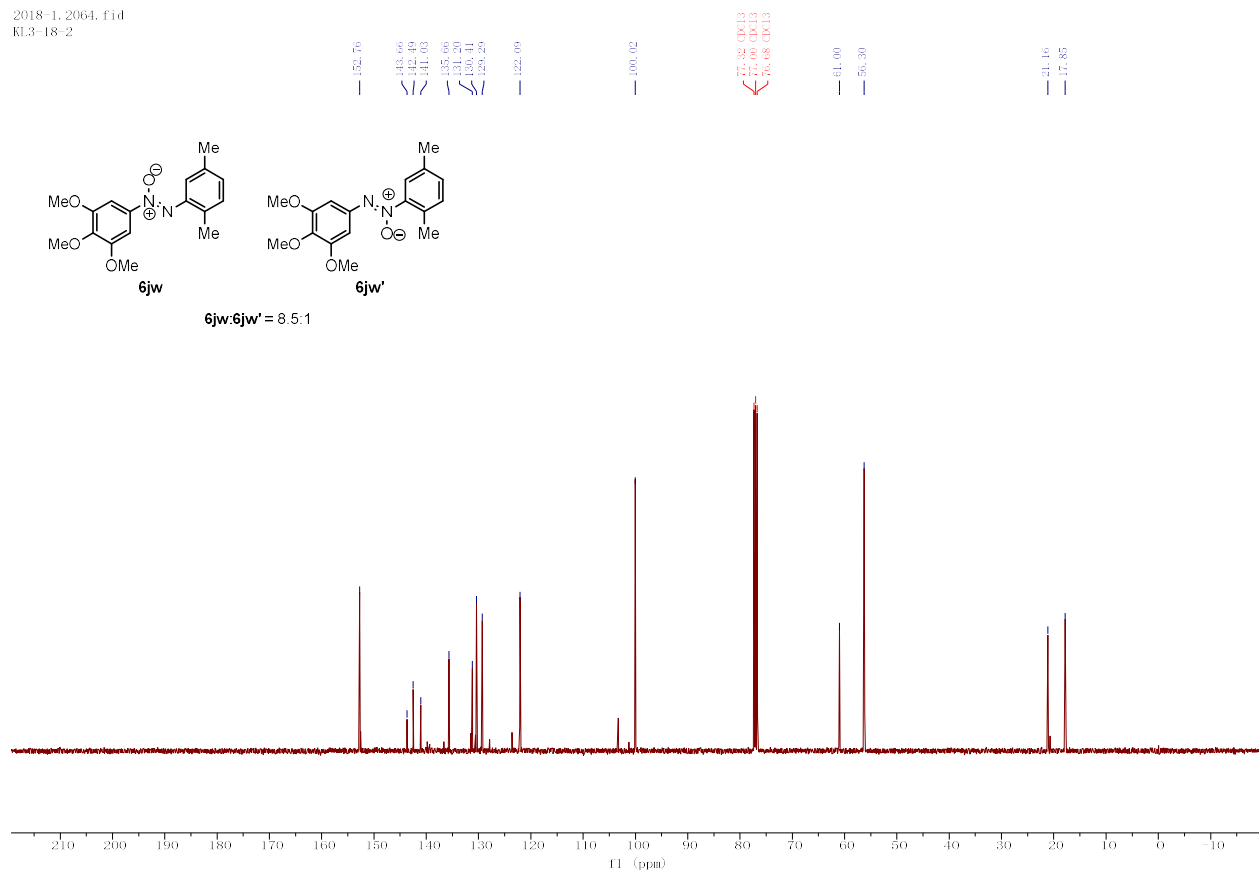


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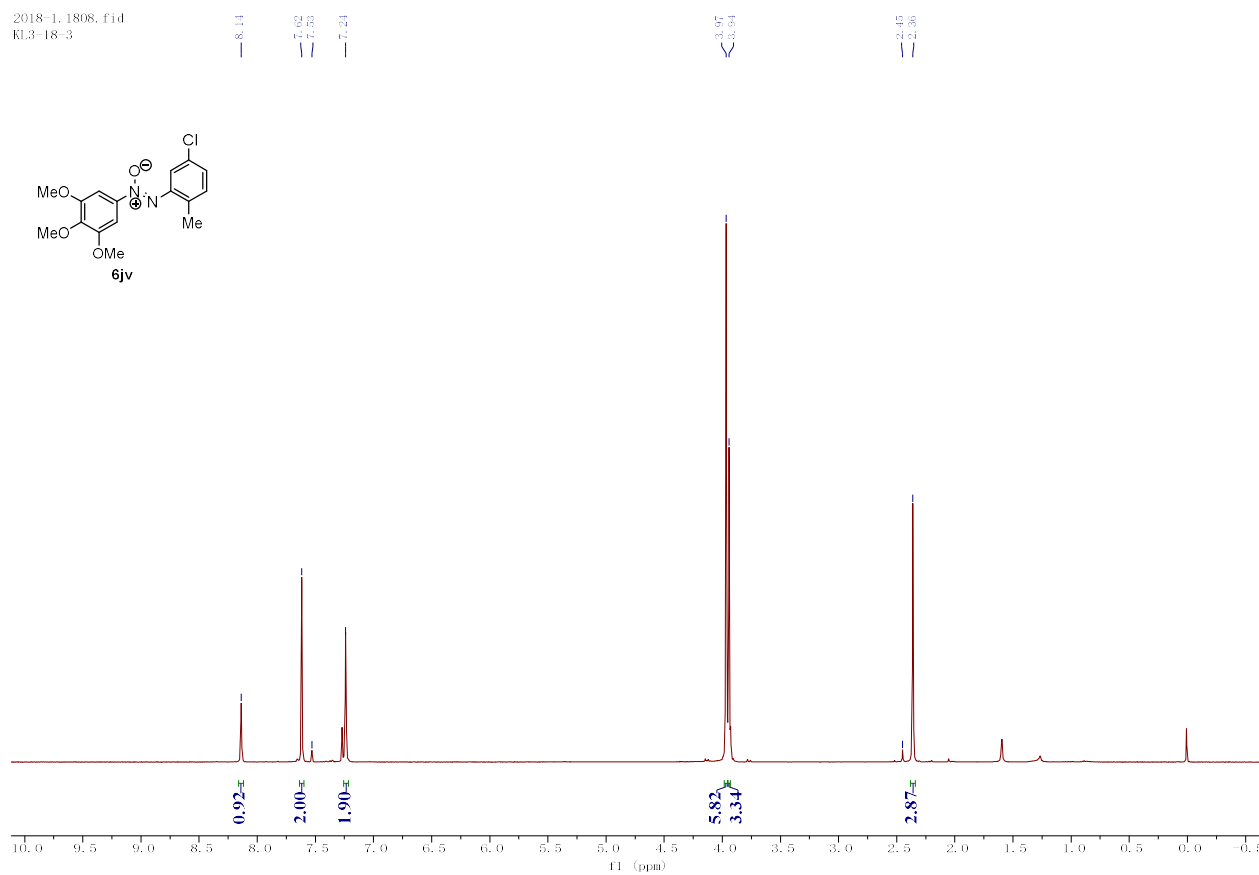




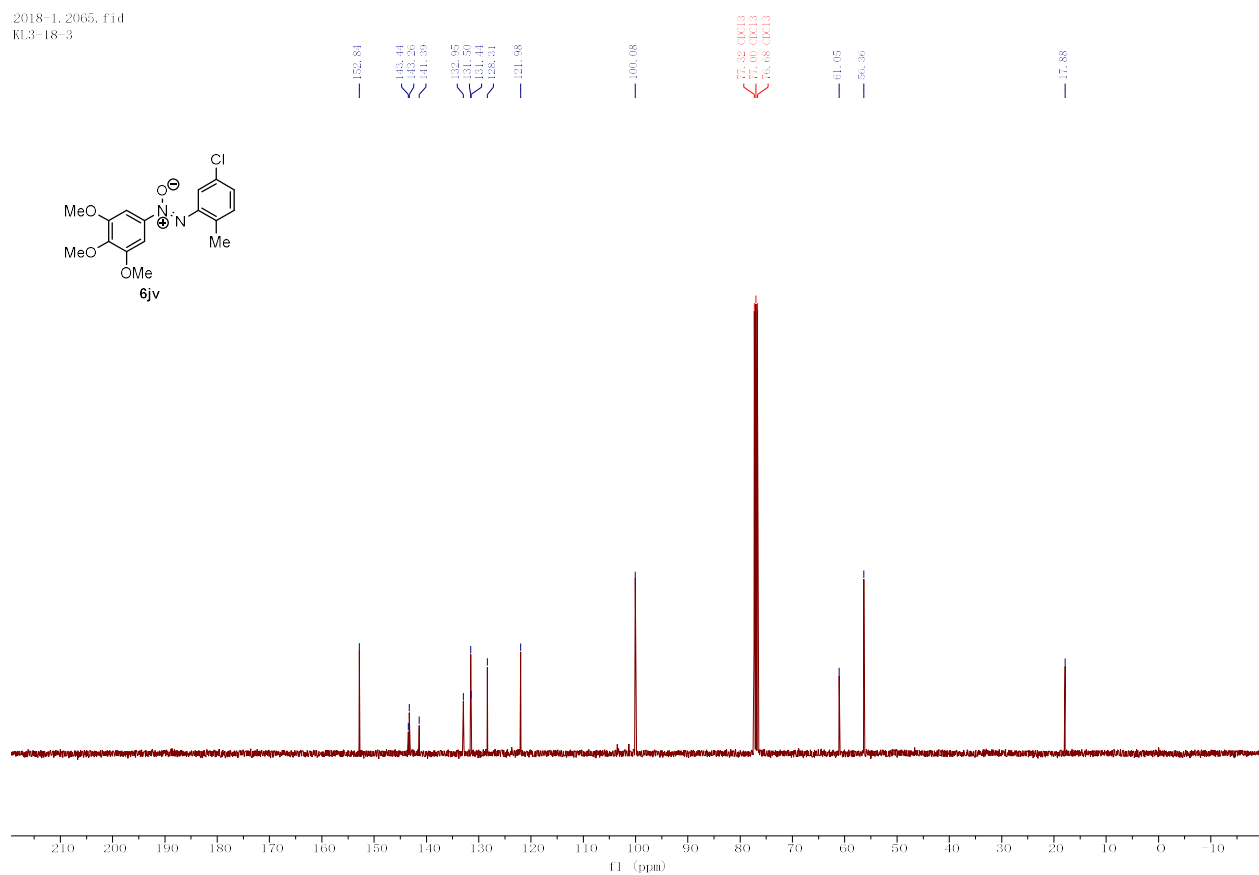
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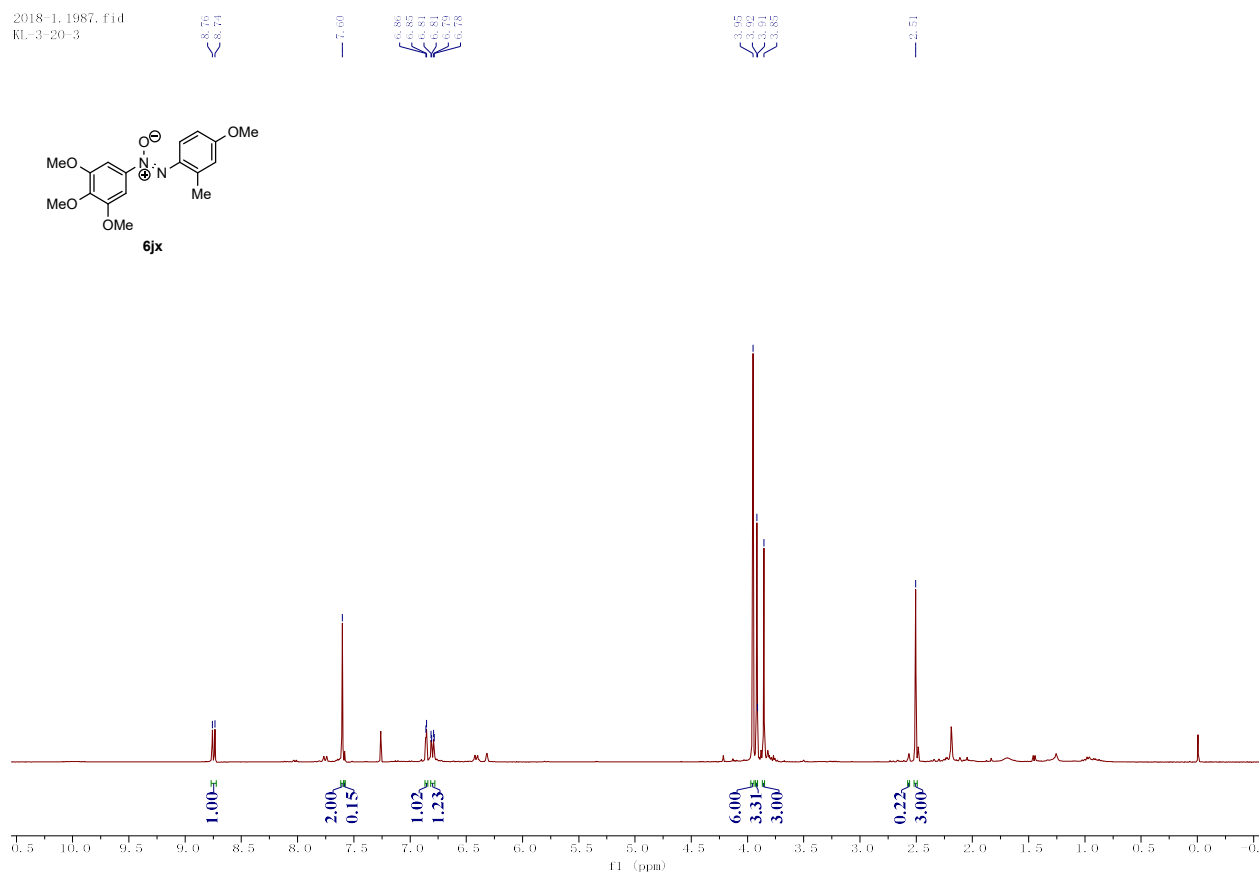
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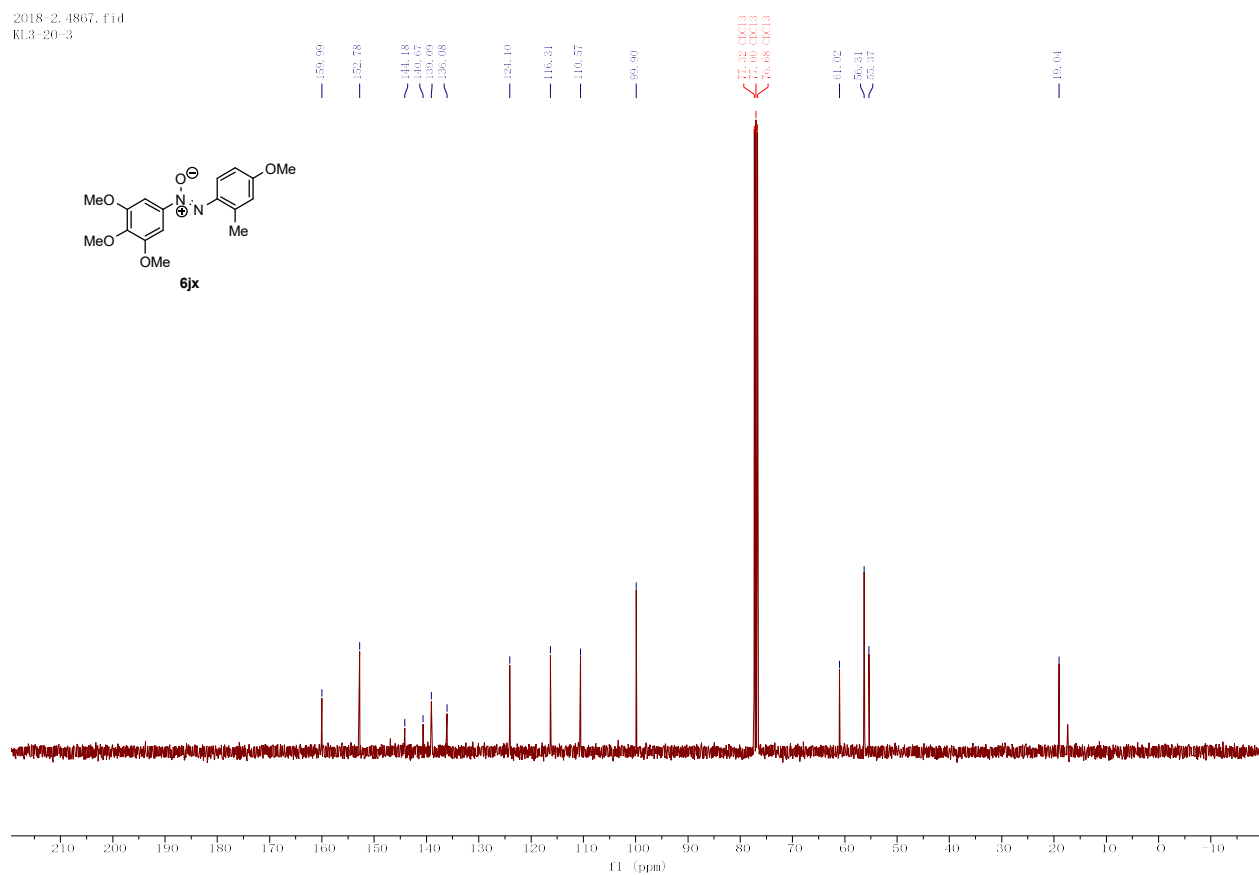
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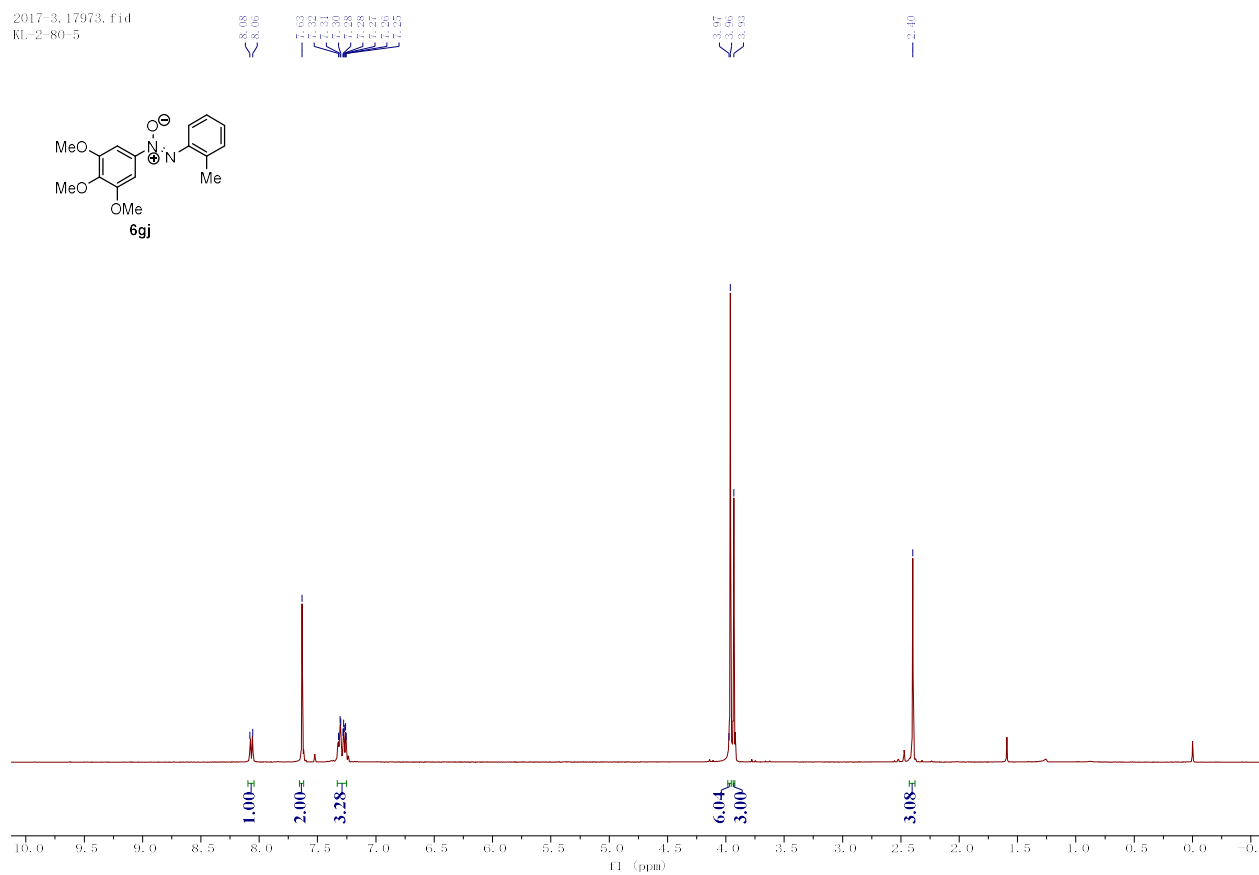
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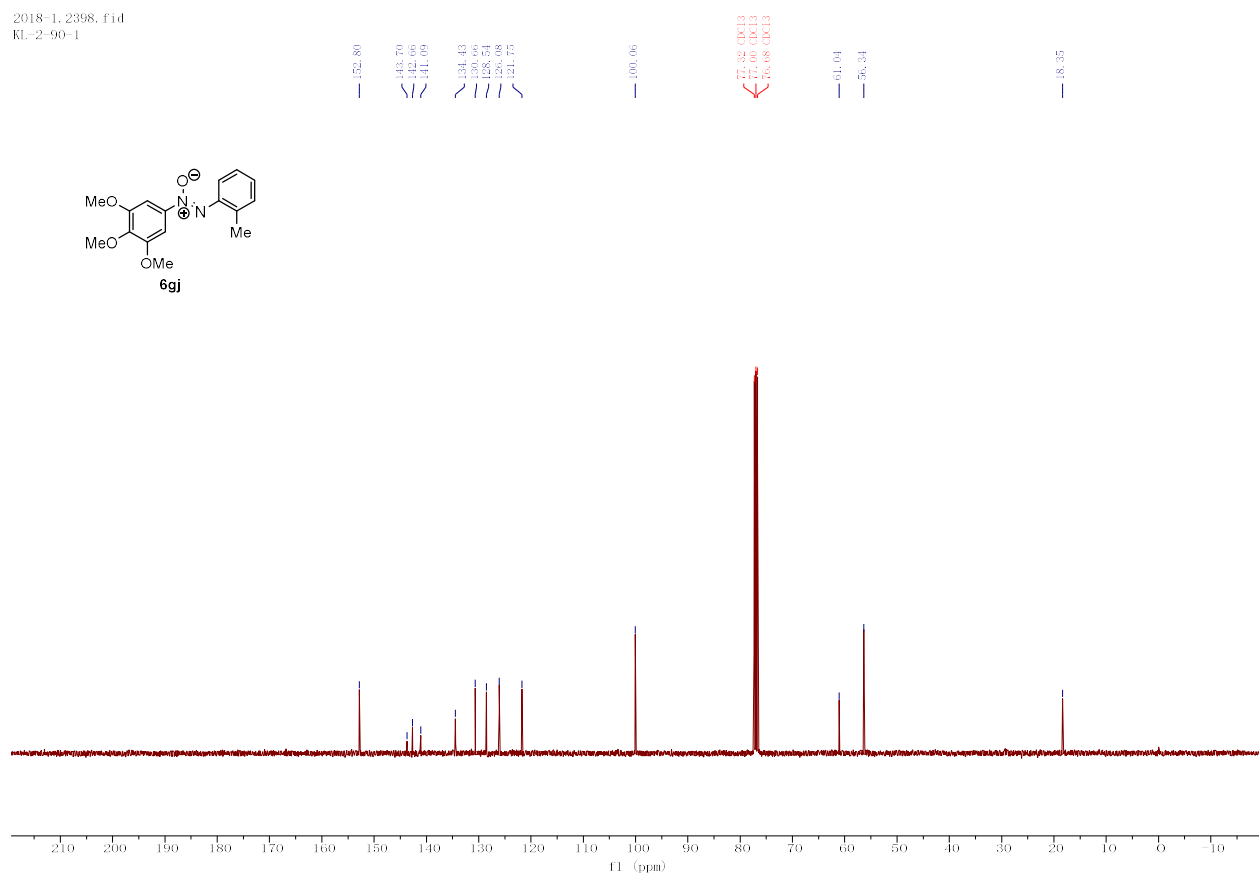
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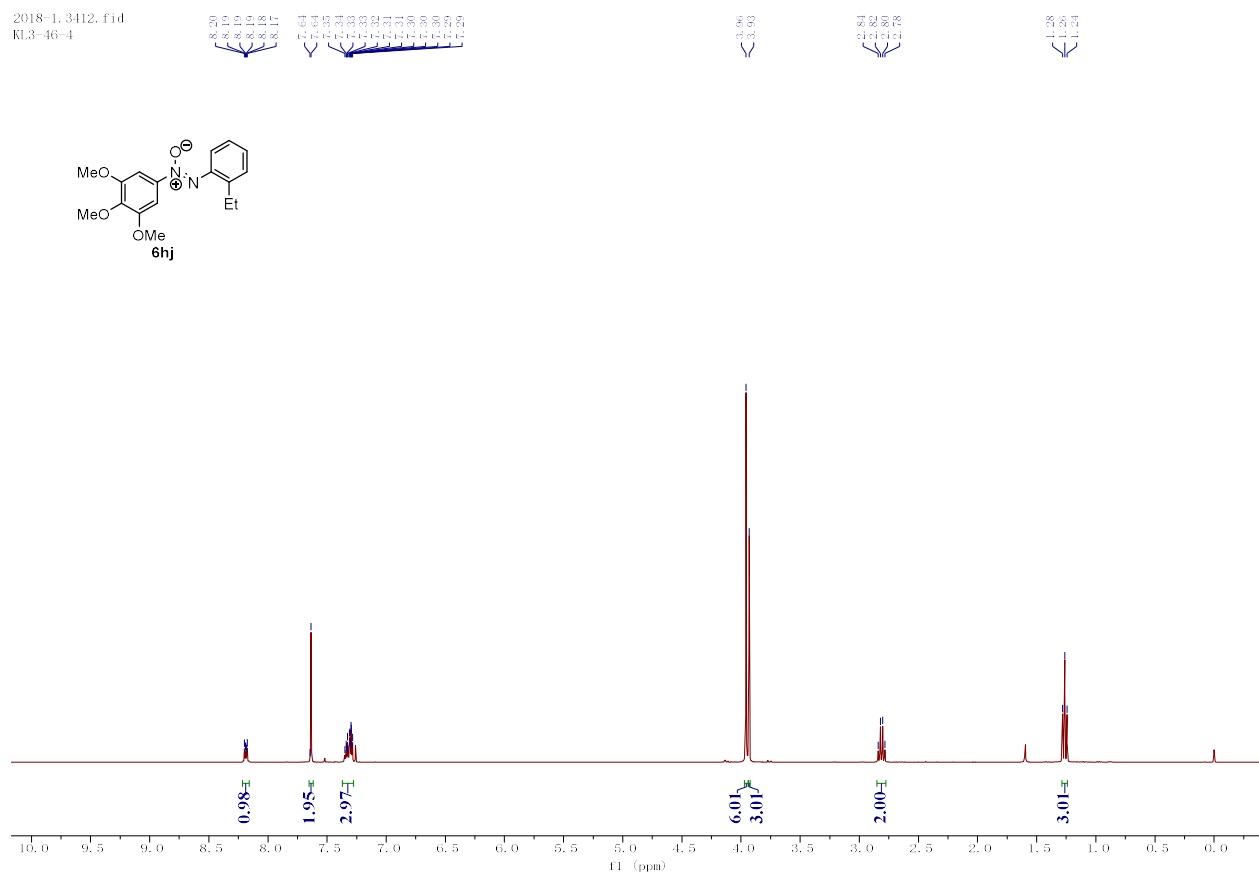
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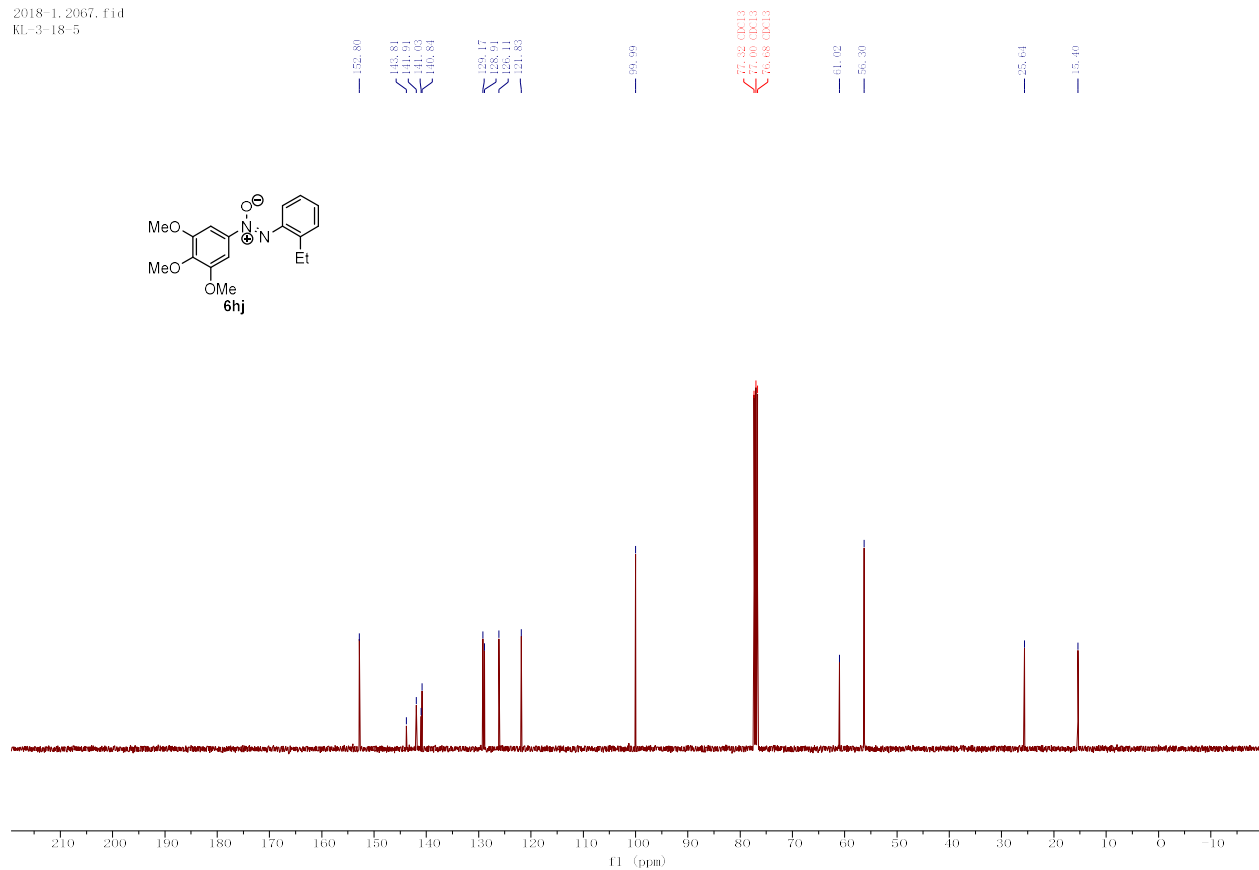
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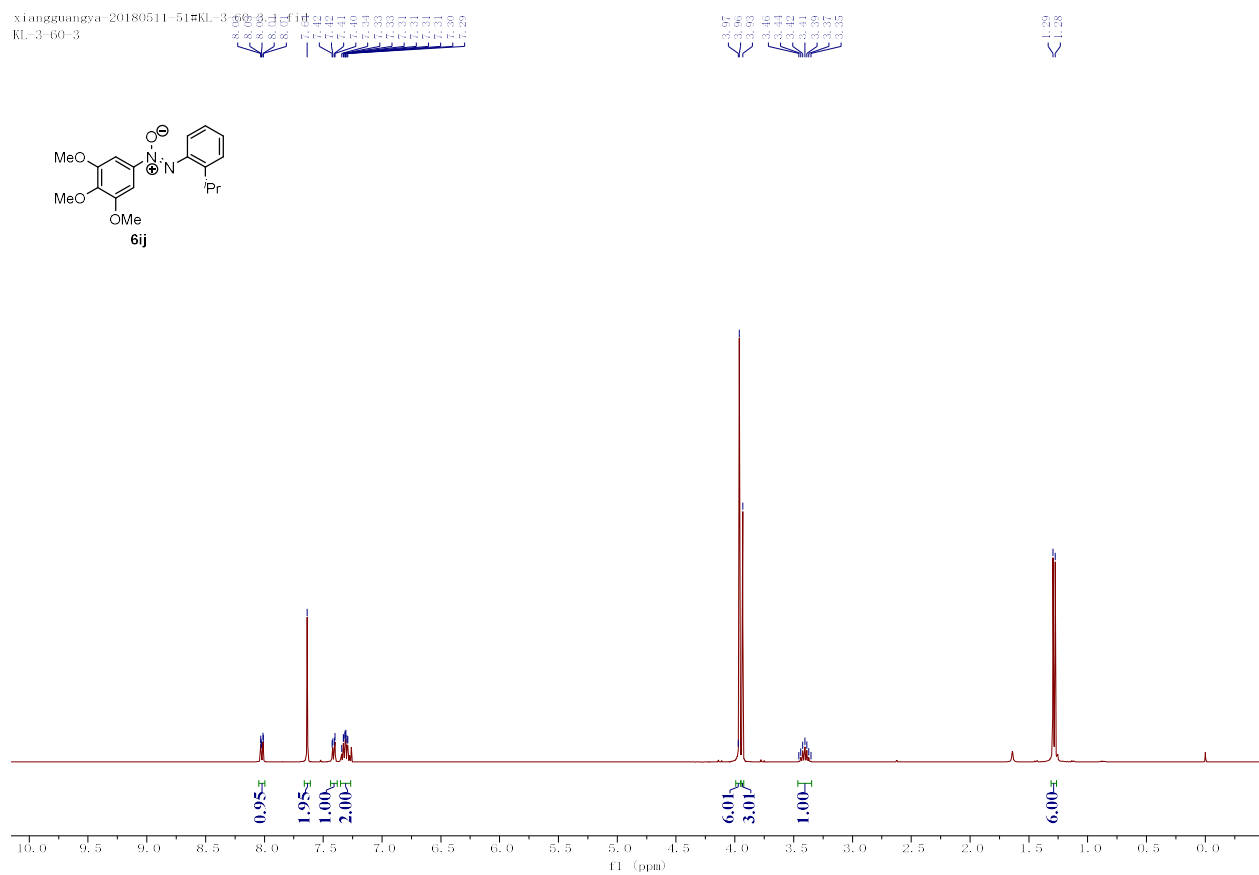
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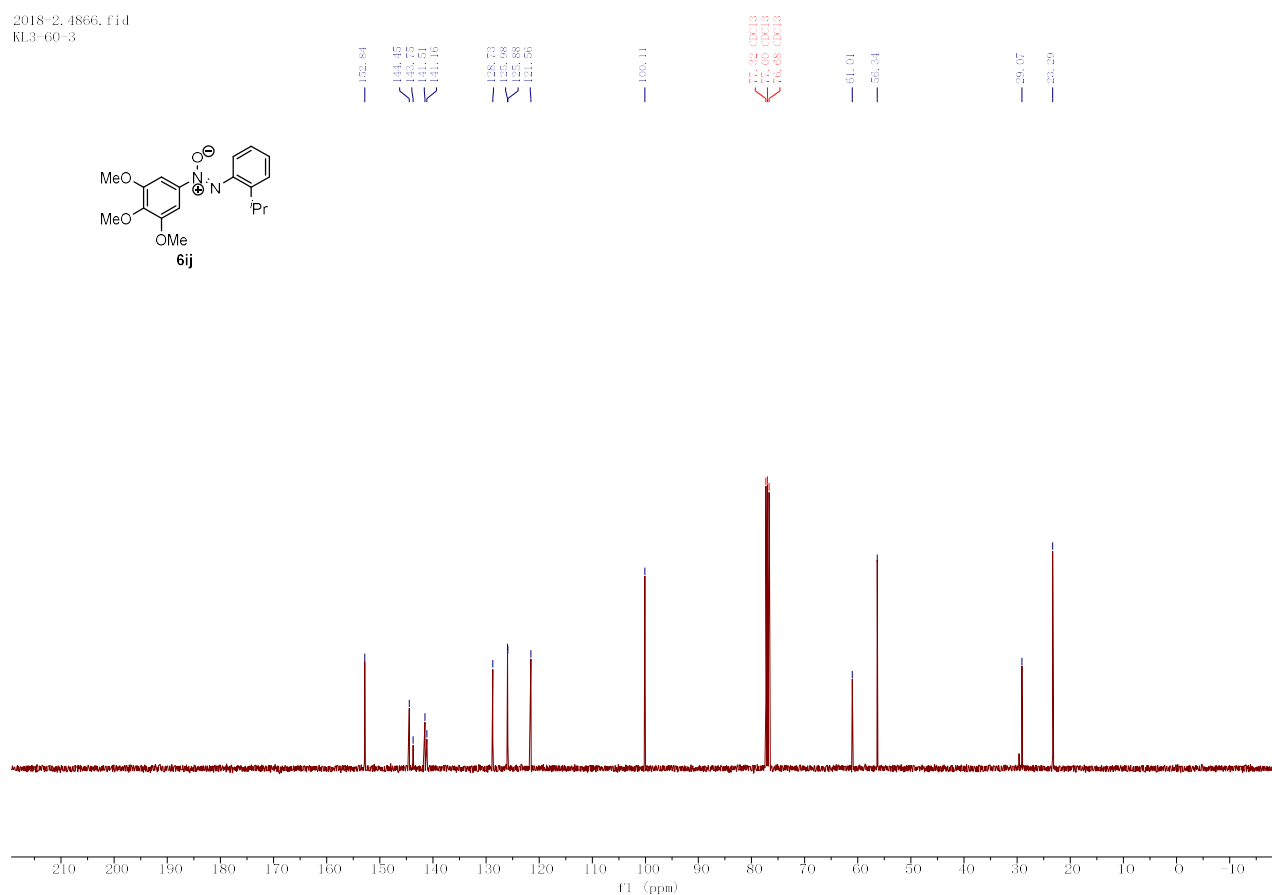
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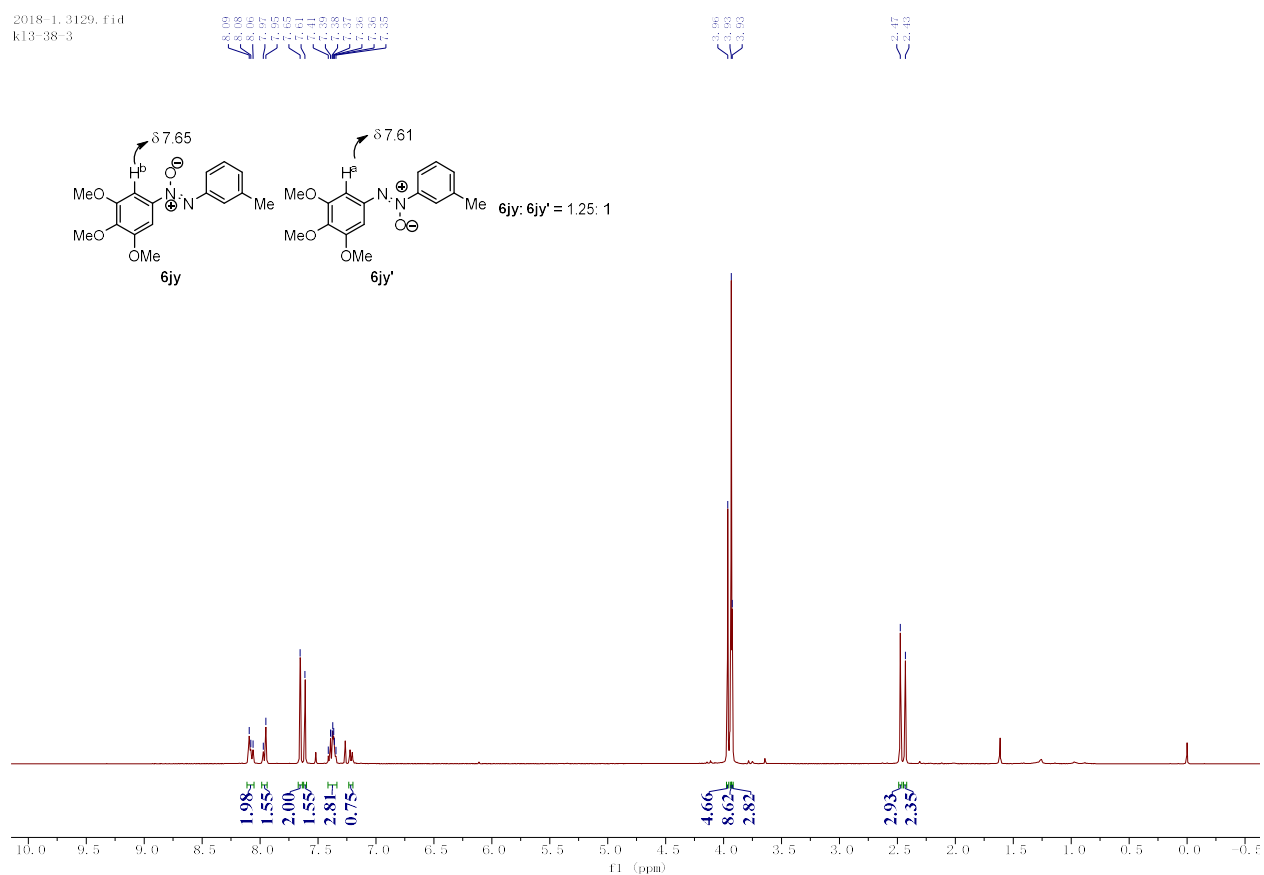
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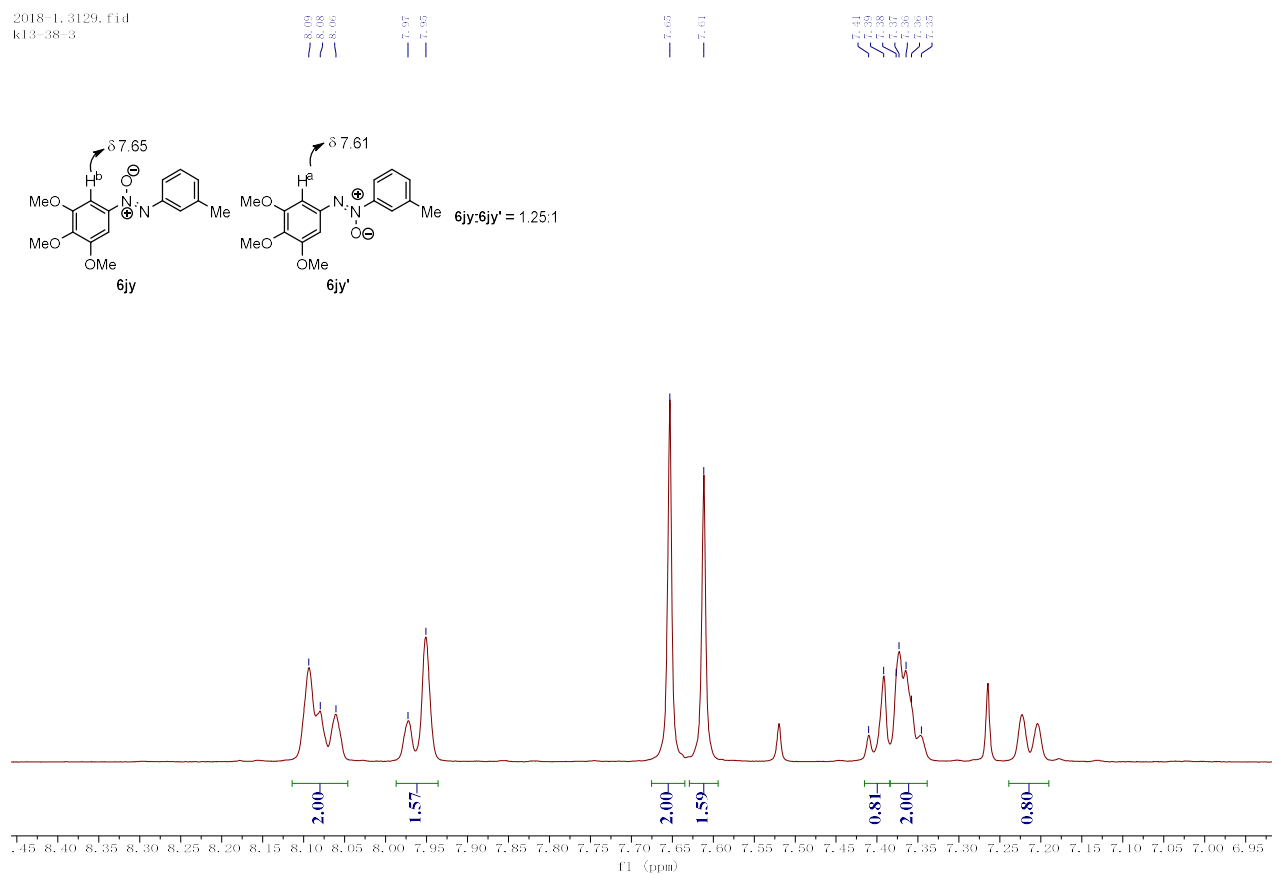
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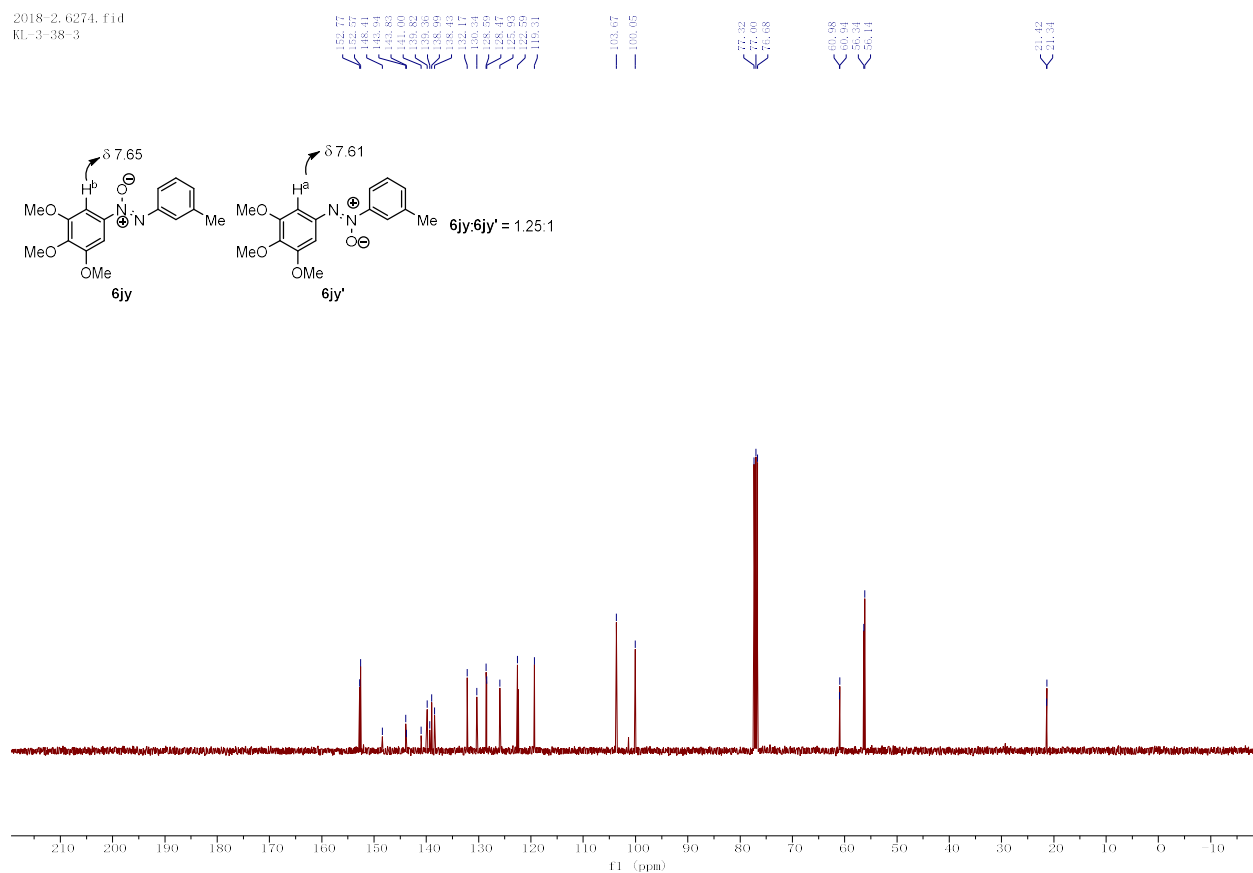
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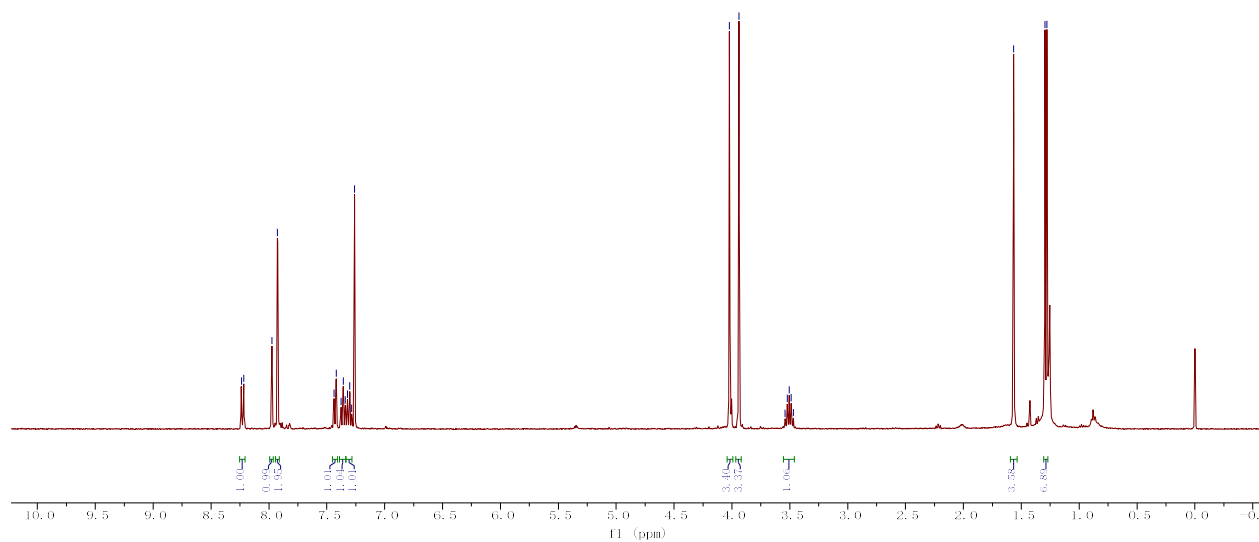
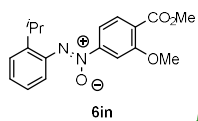


$$\begin{array}{r} 8.24 \\ < 8.22 \end{array} \quad \begin{array}{r} 7.97 \\ < 7.93 \end{array} \quad \begin{array}{r} 7.44 \\ 7.42 \\ 7.38 \\ 7.36 \\ 7.34 \\ 7.32 \\ 7.30 \\ 7.29 \\ 7.26 \end{array}$$

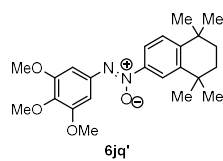
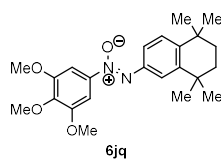
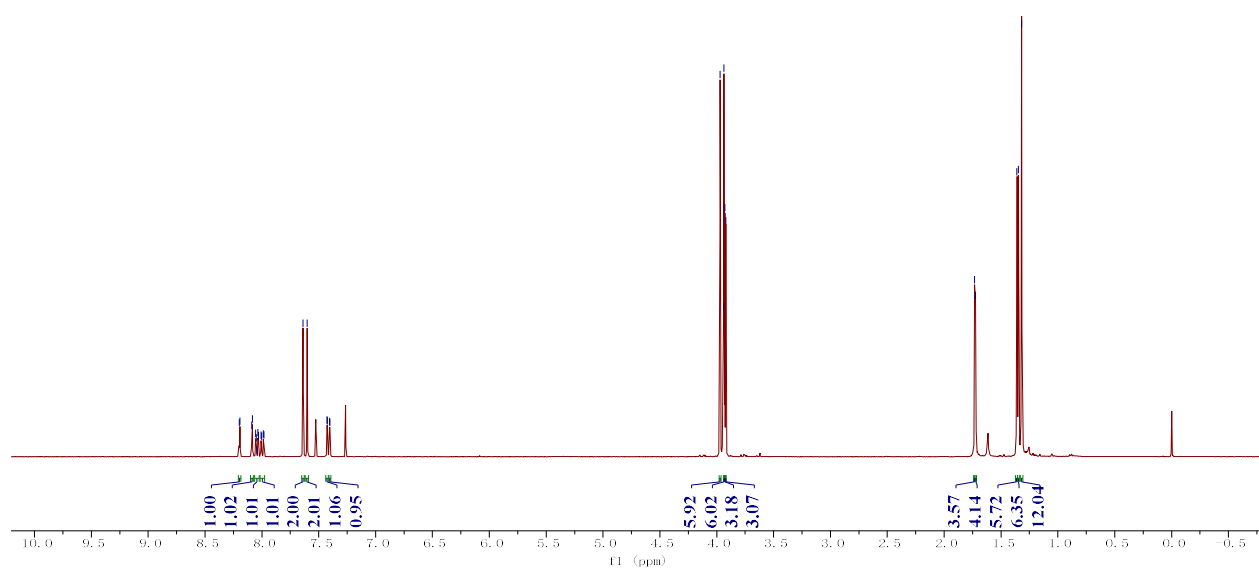
4.02  
3.94

3.54  
3.52  
3.50  
3.49  
3.47

— 1.57  
 < 1.30  
 < 1.28

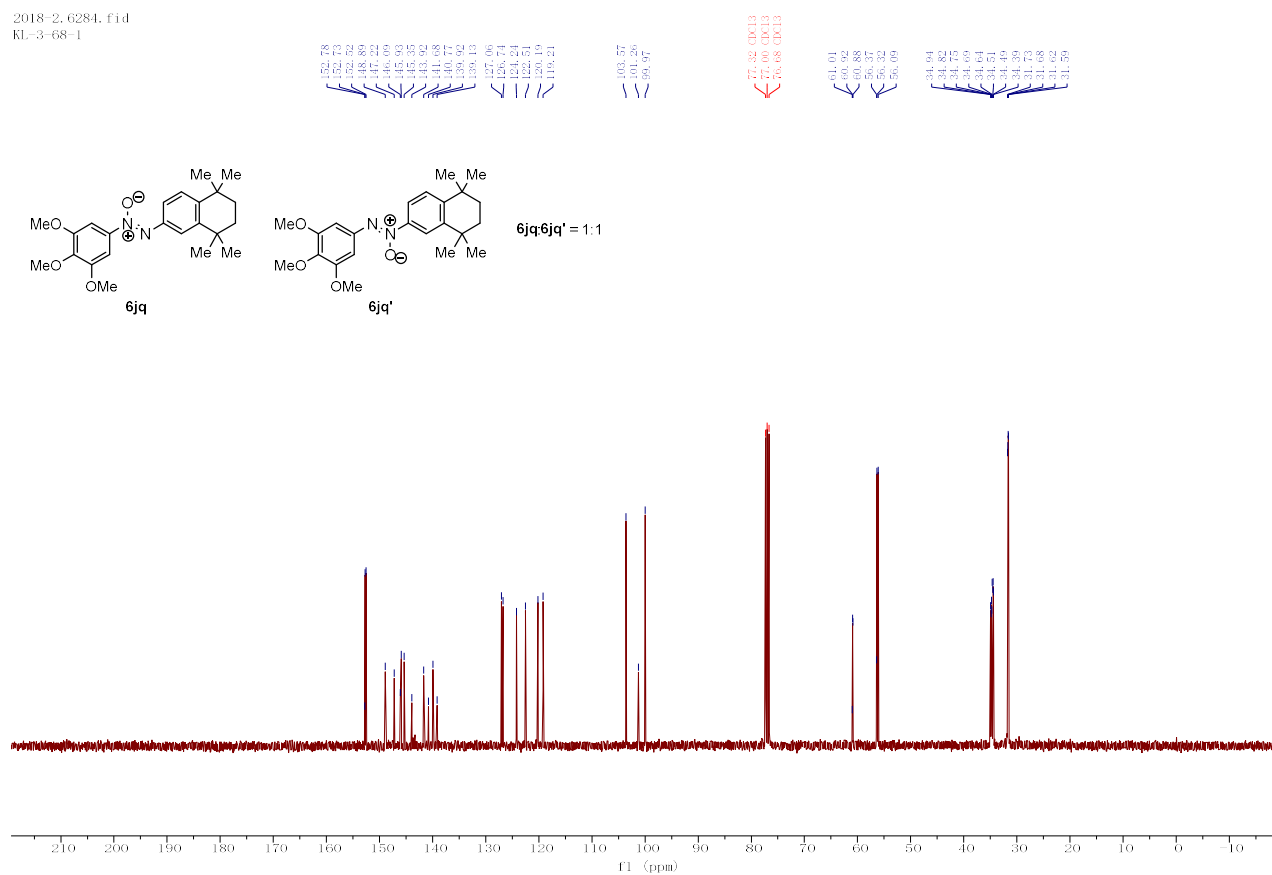


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KL-3-68-1

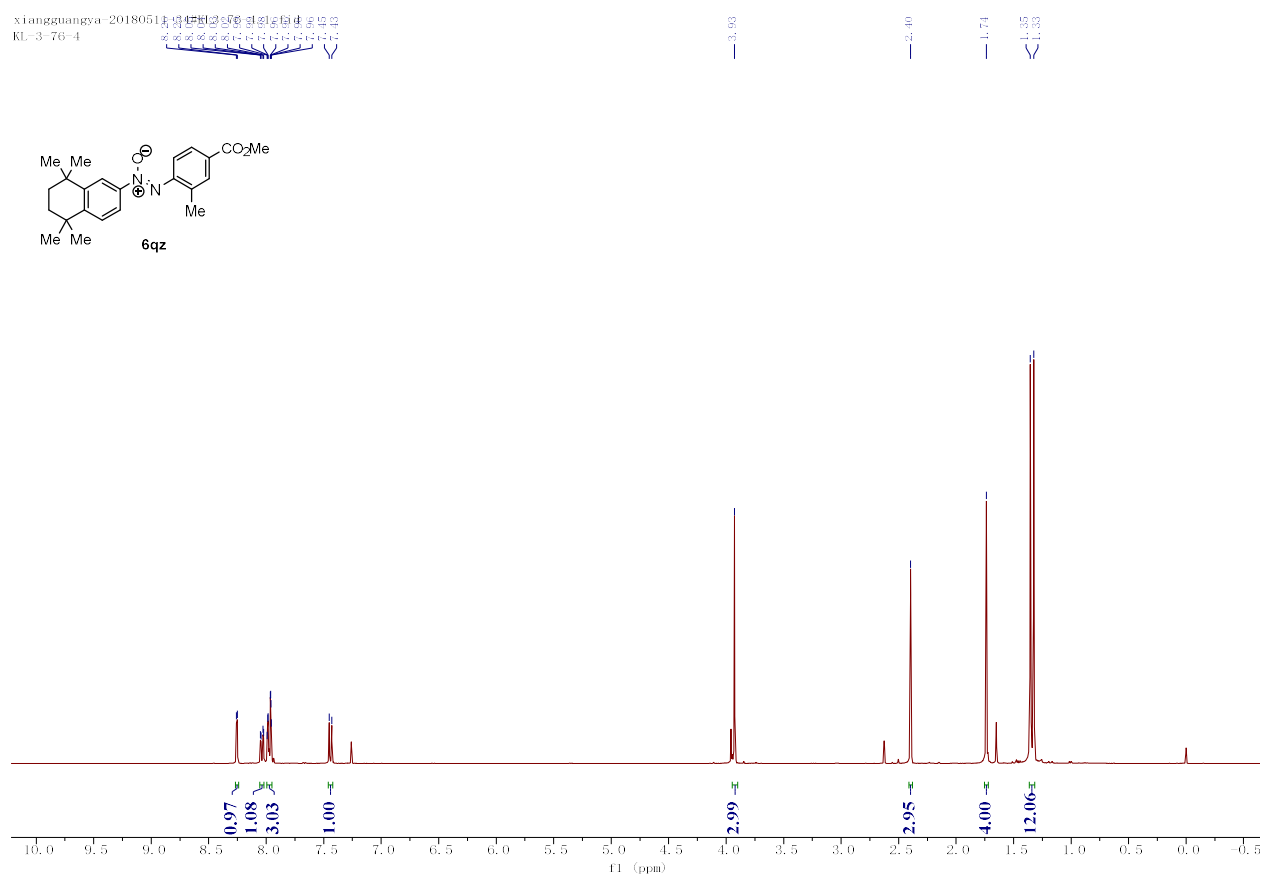

$$6jq:6jq' = 1:1$$




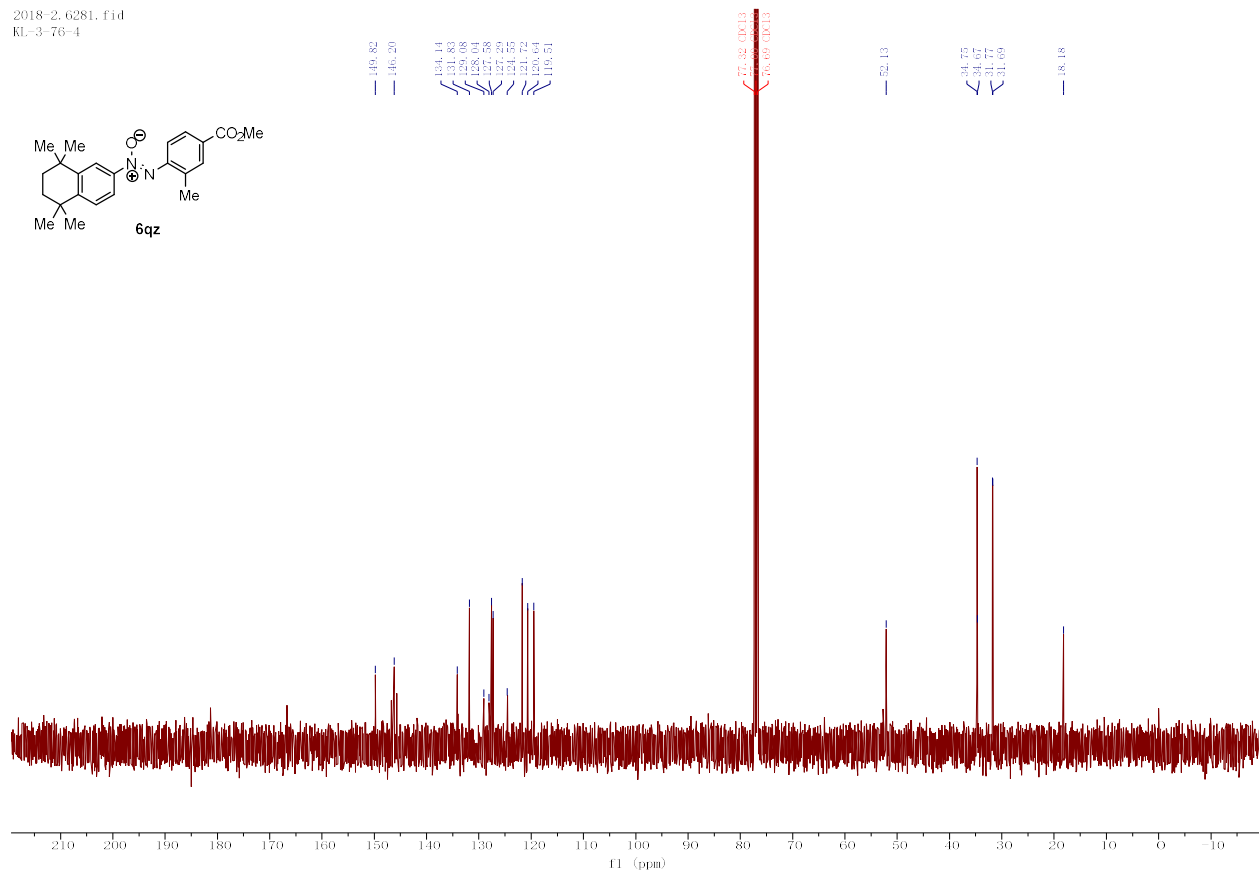
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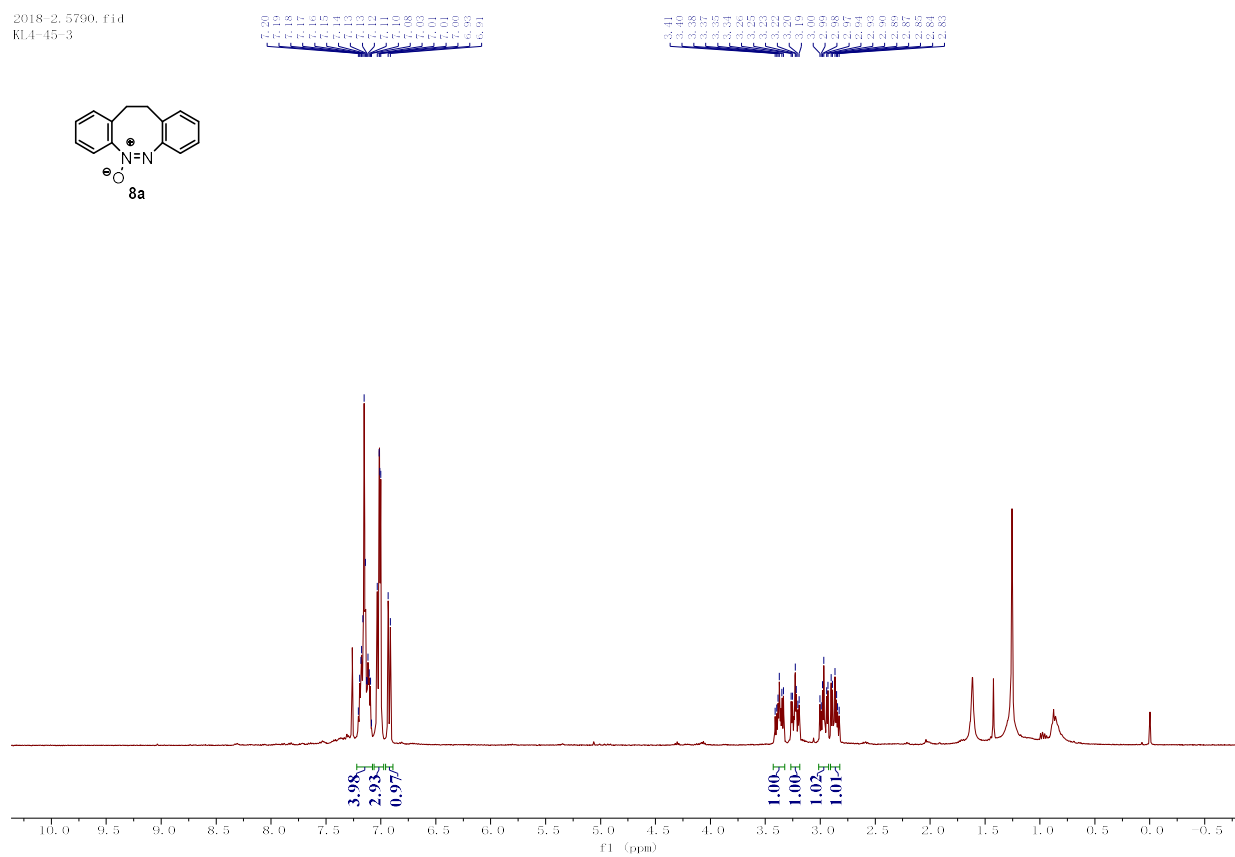
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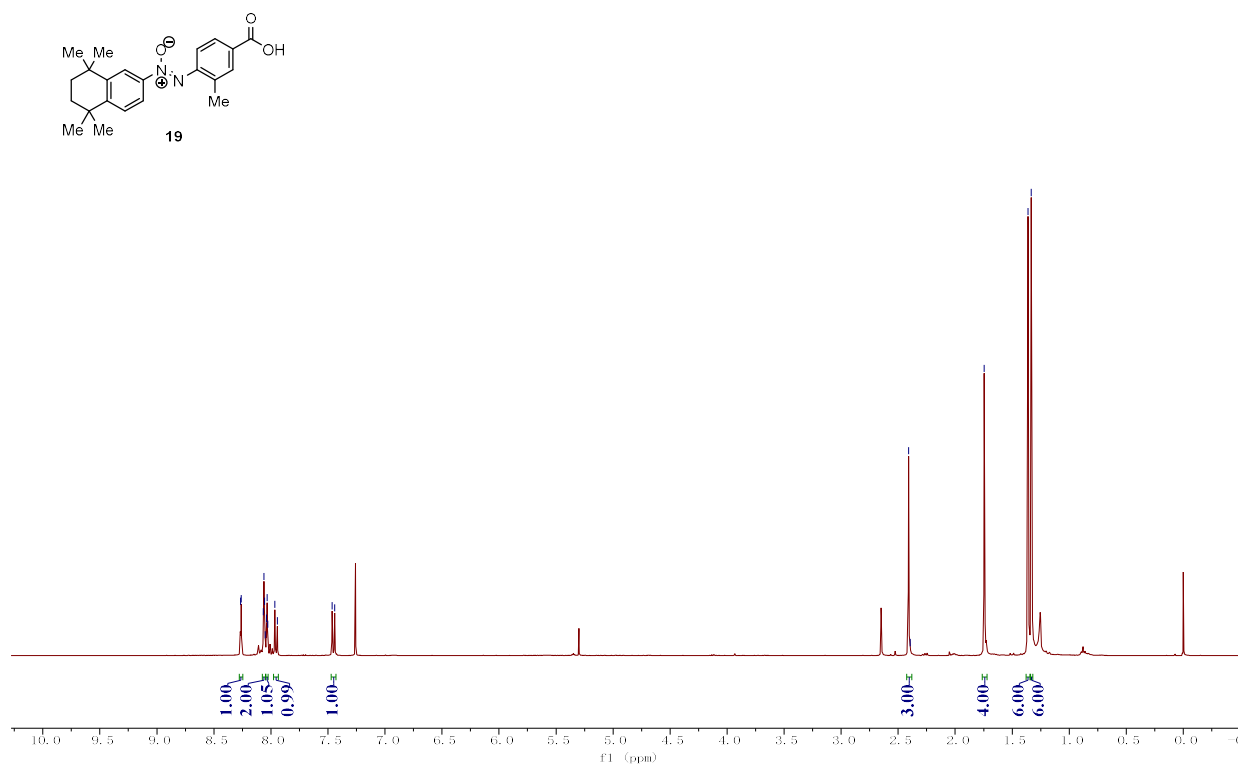
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2018-2-5790.fid  
KL4-45-3



xiangguangya-20180601-4峰  
KL-4-7-1



2018-2-6285.fid  
KL-4-7-1

