

A Convenient Synthesis towards 2-Bromo-2-(methoxy(phenyl)methyl)malononitrile and 2-Iodo-2-(methoxy(phenyl)methyl)malononitrile

1. Materials

N-bromosuccinimide, N-iodosuccinimide, malononitrile, benzaldehyde, MeOH, EtOAc, Petroleum and silica gel (300-400 mesh) were purchased from Shanghai Aladdin Bio-Chem Technology Co, LTD and used without further purification. The starting β , β -Dicyanostyrene was synthesized from malononitrile and benzaldehyde according to the literature [17].

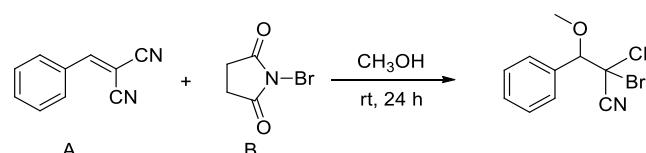
2. Instrument

NMR spectra were recorded on a Bruker Avance AV400 (400/100 MHz $^1\text{H}/^{13}\text{C}$) spectrometer (Bruker, Billerica, MA, USA) and chemical shifts (δ , ppm) were down field from TMS. The chemical shifts are reported relative to residue the solvent signal in part per million (δ) (CDCl_3 ^1H : δ 7.26, ^{13}C : δ 77.23) For the ^1H -NMR spectrum, data are assumed to be first order with apparent singlet, doublet, triplet, quartets and multiplet reported as s, d, t, q, and m, respectively. Doublet of doublet was reported as dd, triplet of doublet was reported as td, and the resonance that appears broad was designated as br.

3. Experiment for condition optimization

The optimizing condition was shown in table S1. Reactant concentration, temperature and time were examined, and found that higher or lower concentration of reactants has no obvious effect on the reaction rate, while increasing the temperature will significantly accelerating the reaction.

Table S1. condition optimization.

					
Entry	$c_A / \text{mol} \cdot \text{L}^{-1}$	$c_B / \text{mol} \cdot \text{L}^{-1}$	T / $^{\circ}\text{C}$	Time / h	Yield / %
1	0.5	0.5	rt	24	77.4%
2	2	2	rt	24	76.8%
3	5	5	rt	24	76.4%
4	2	2	rt	12	54.5%
5	2	2	50	8	75.7%
6	2	2	60	4	75.2%

4. NMR spectrum of compound 1 and 2

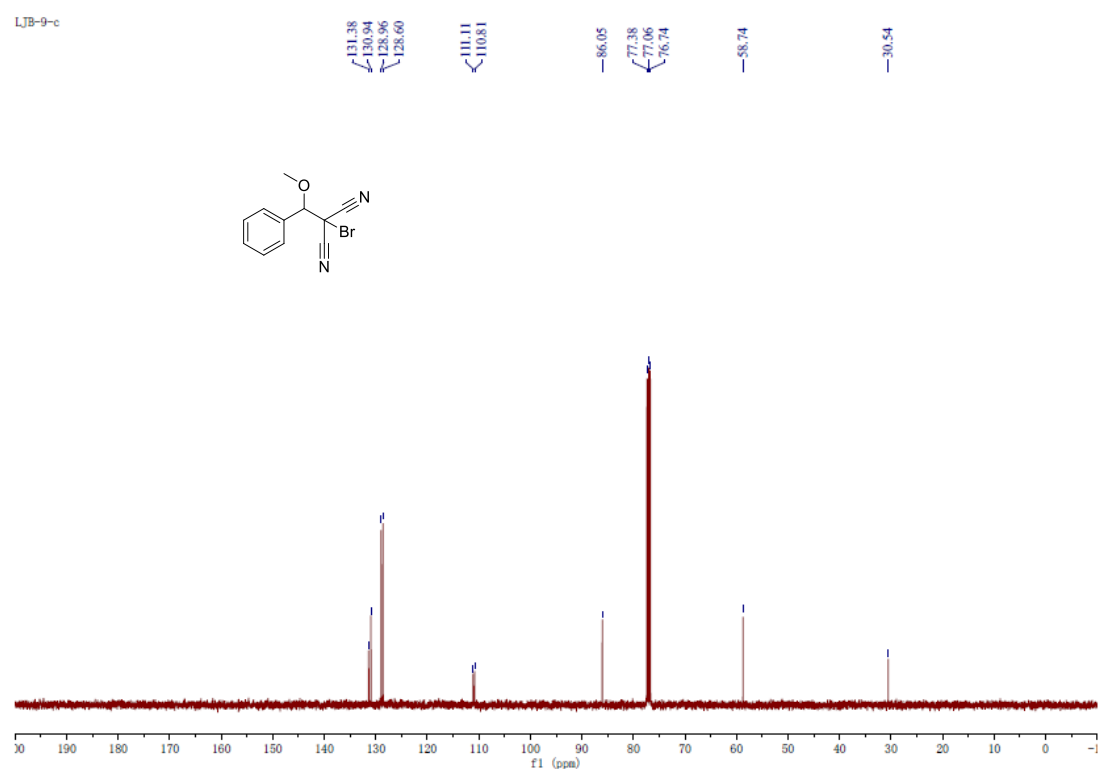
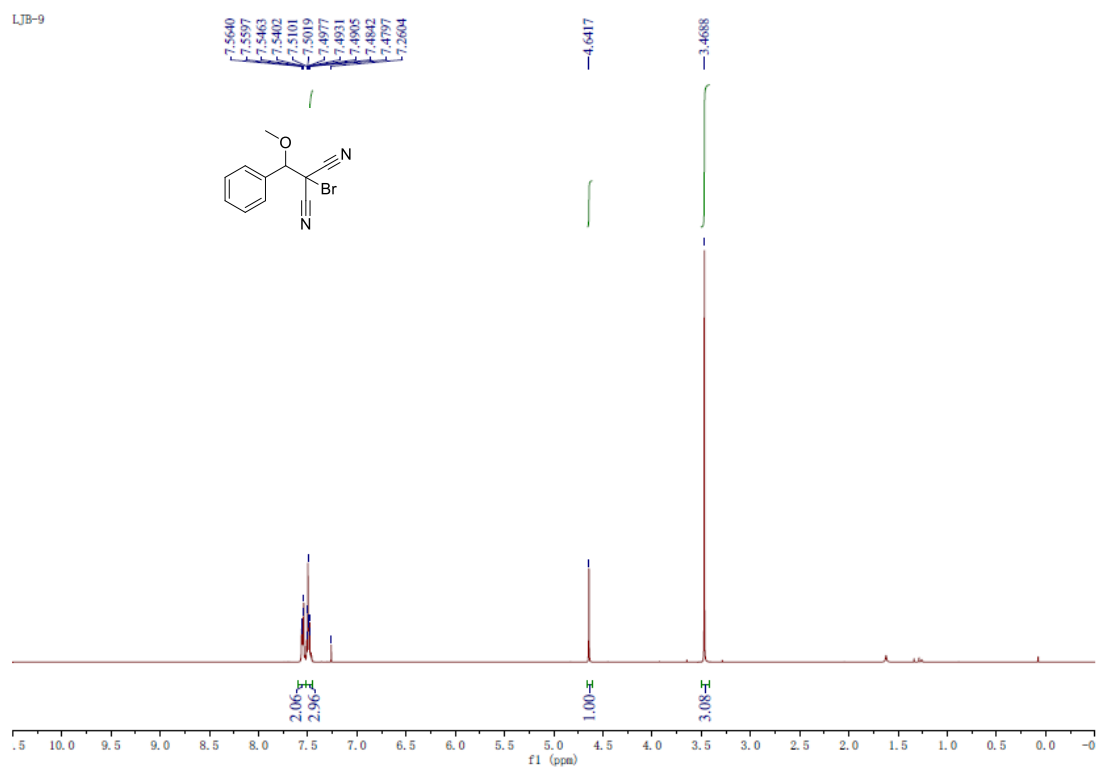


Figure S1. H-NMR and ¹³C-NMR spectra of compound 1.

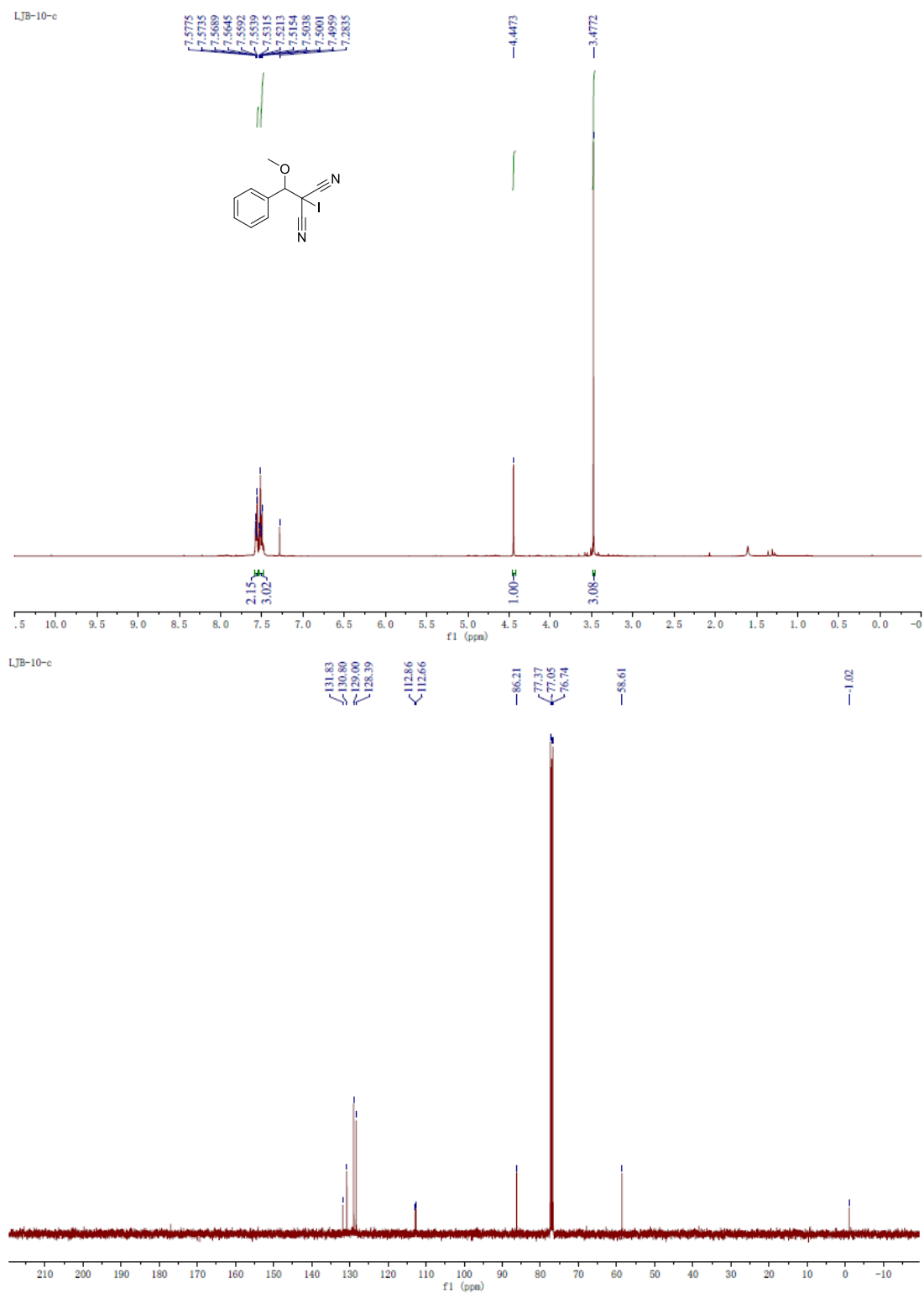


Figure S2. ¹H NMR and ¹³C NMR spectra of compound 2.

Reference

17. Chen, Z. G.; Li, Y. N.; Zhou, J. M.; Wang, D.; Miao, G. K₃PO₄-catalyzed regiospecific bromoamidation of β, β-dicyanostyrene derivatives with N-bromoacetamide (NBA). *Chem. Res. Chin. Univ.* **2014**, *30*, 266–271.