

Supporting Information

Qianqian Liang,^{‡a} Hua Cheng,^{‡a} Chengwen Li,^d Liangmin Ning^{*b} and Liming Shao^{*a,c}

^a School of Pharmacy, Fudan University, 826 Zhangheng Road, Zhangjiang Hi-tech Park, Pudong, Shanghai, 201203, China.

^b College of Chemical and Biological Engineering, Shandong University of Science and Technology, Qingdao, 266590, China.

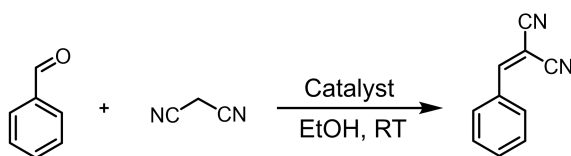
^c State Key Laboratory of Medical Neurobiology, Fudan University, 138 Yixueyuan Road, Shanghai, 200032, China.

^d DezhouDeyao Pharmaceutical Co, Ltd, No.6000 East Dongfanghong Road, Shandong, 253084, China.

[‡] These authors contributed equally to this study.

^{*} Corresponding author : Liming Shao Ph.D. at limingshao@fudan.edu.cn and Liangmin Ning Ph.D. at 791695627@qq.com

Table S1. Knoevenagel condensation reaction between benzaldehyde and malononitrile using mixing catalyst.



Entry	Catalyst	Time (min)	Conversion (%)
1 ^a	UiO-66-(alkyne) ₂ +Co(PPh ₃) ₂ Cl ₂	10	6.5
2 ^b	UiO-66+Co(PPh ₃) ₂ Cl ₂	10	16.7

^a The simple mixing of nearly equivalent UiO-66-(alkyne)₂ (7 mg) and Co(PPh₃)₂Cl₂ (3 mg) according to UiO-66-(alkyne-Co)₂.

^b The simple mixing of nearly equivalent UiO-66-(alkyne)₂ (7 mg) and Co(PPh₃)₂Cl₂ (3 mg) according to UiO-66-(alkyne-Co)₂.

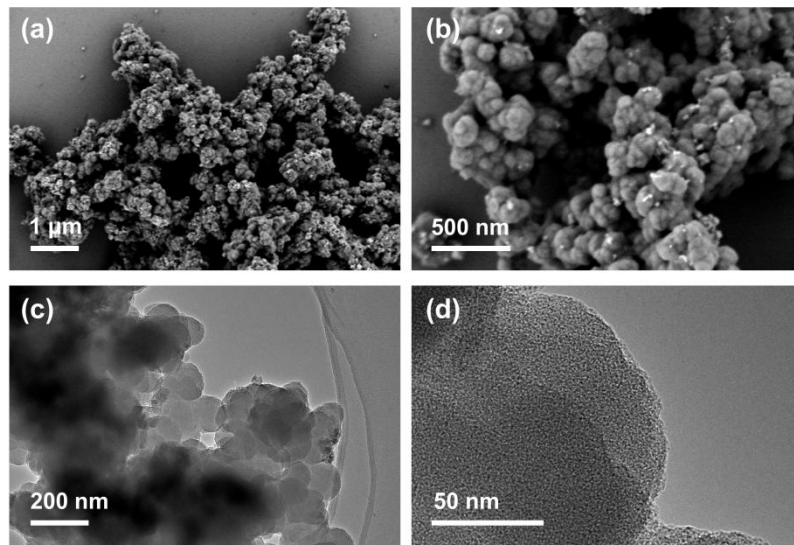


Fig. S1 SEM (a-b) and TEM (c-d) images of UiO-66-(alkyne-Co)₂-recycle.

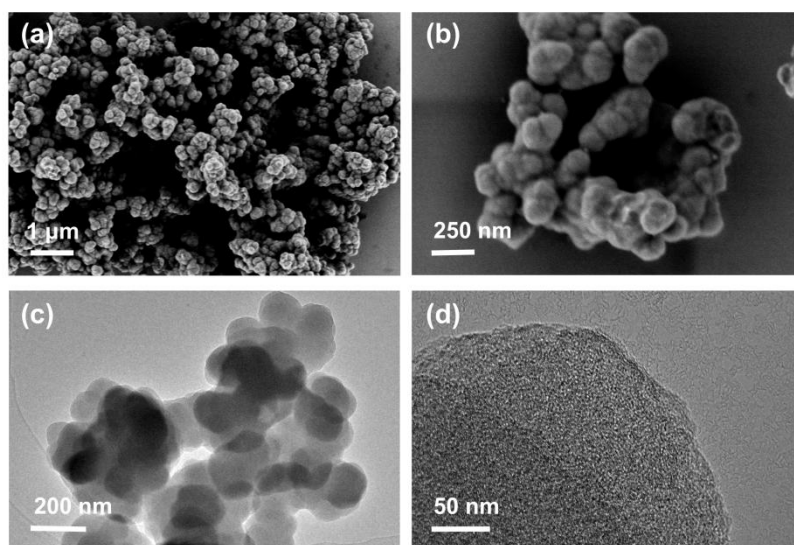


Fig. S2 SEM (a-b) and TEM (c-d) images of UiO-66.

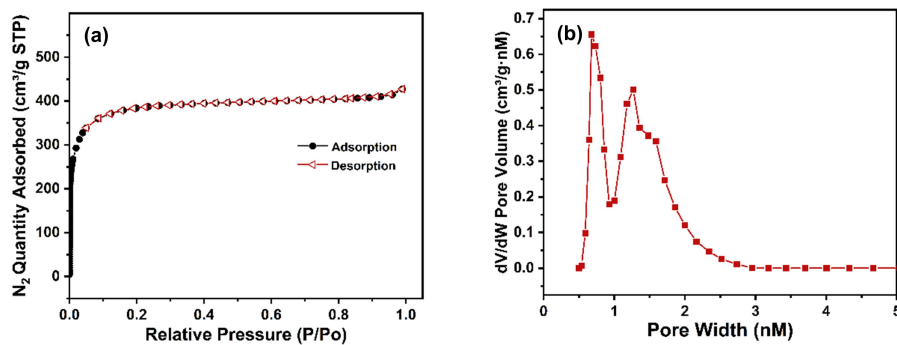


Fig. S3 Nitrogen adsorption measurements at 77 K for UiO-66.

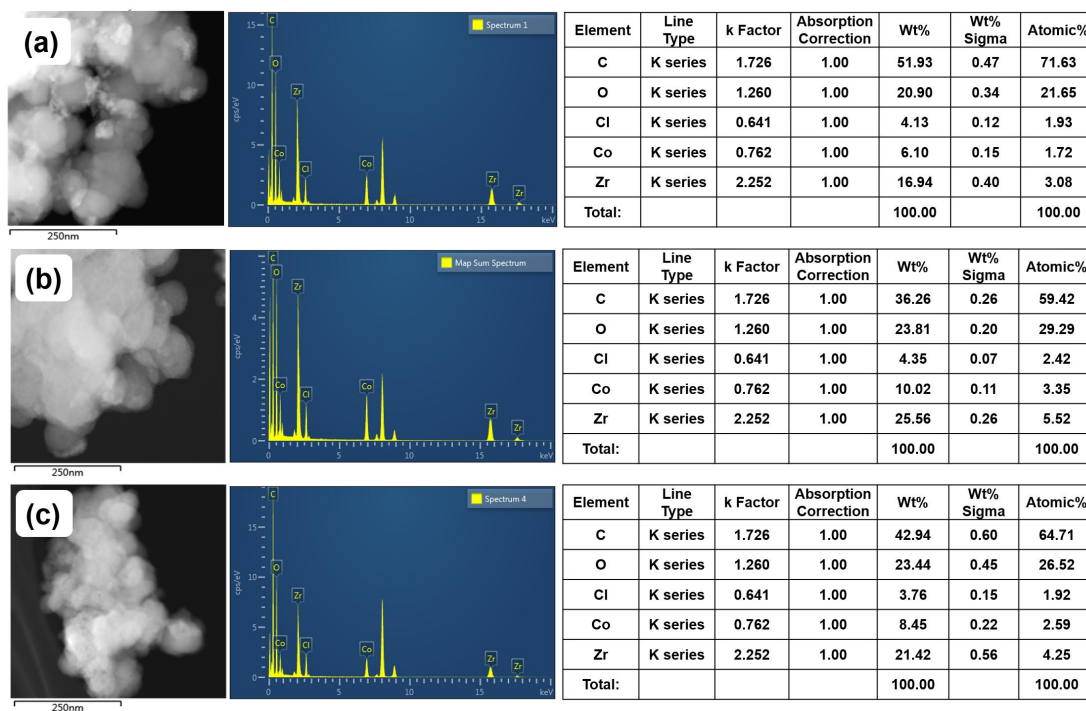
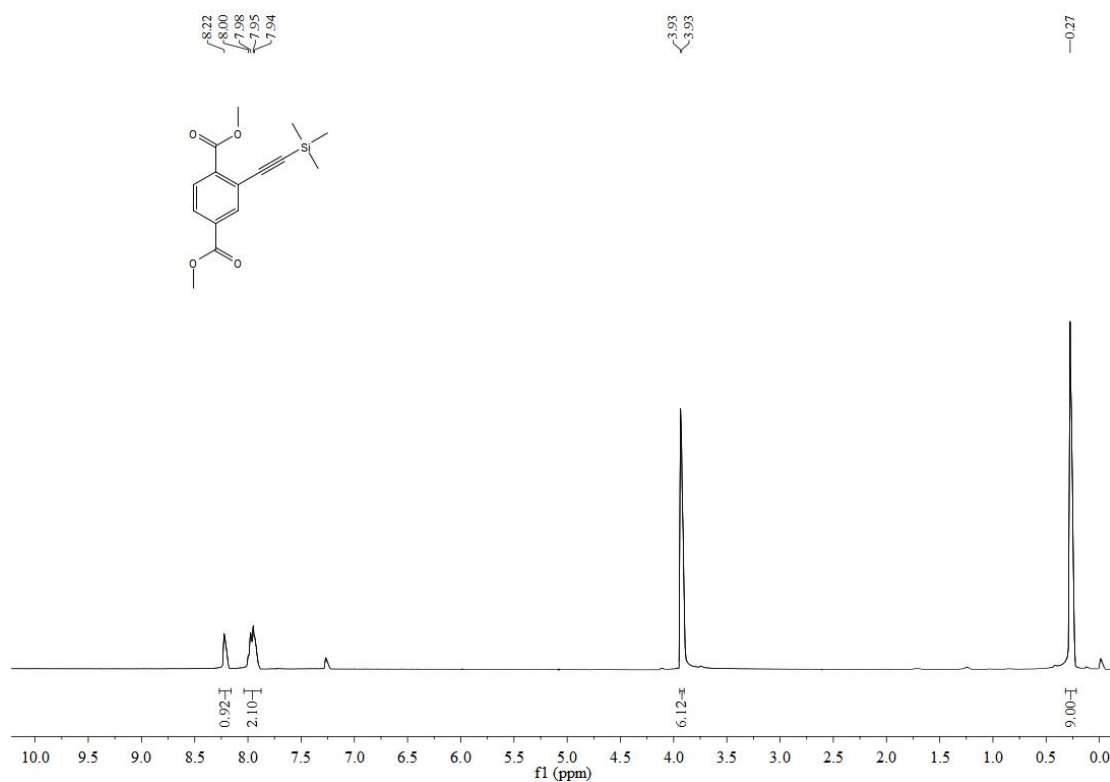
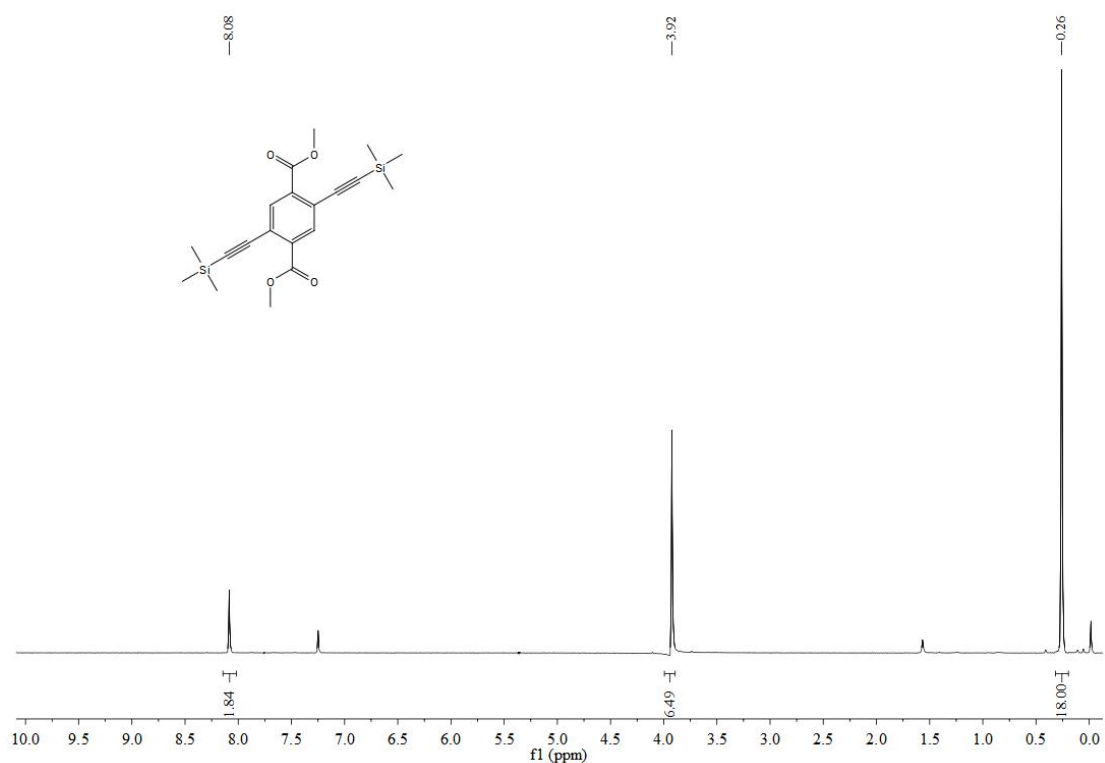


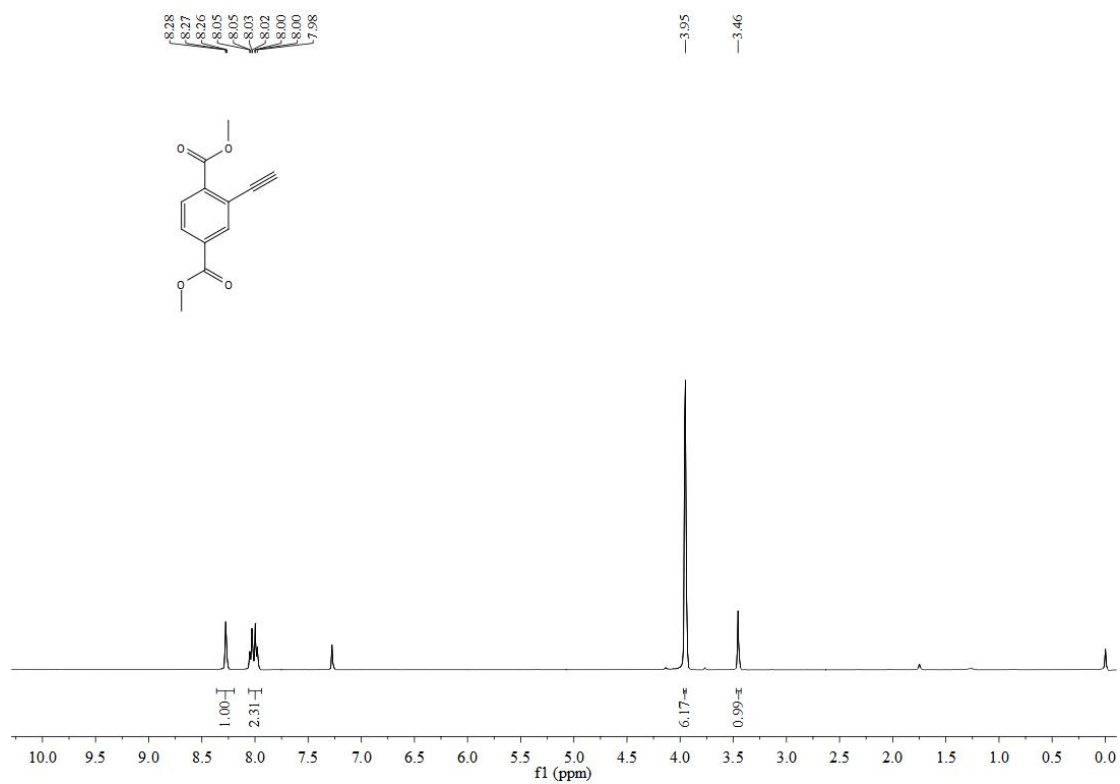
Fig. S4 Energy dispersive X-ray (EDX) analysis of functionalized UiO-66 materials: (a) UiO-66-alkyne-Co; (b) UiO-66-(alkyne-Co)₂; (c) UiO-66-(alkyne-Co)₂-recycle.



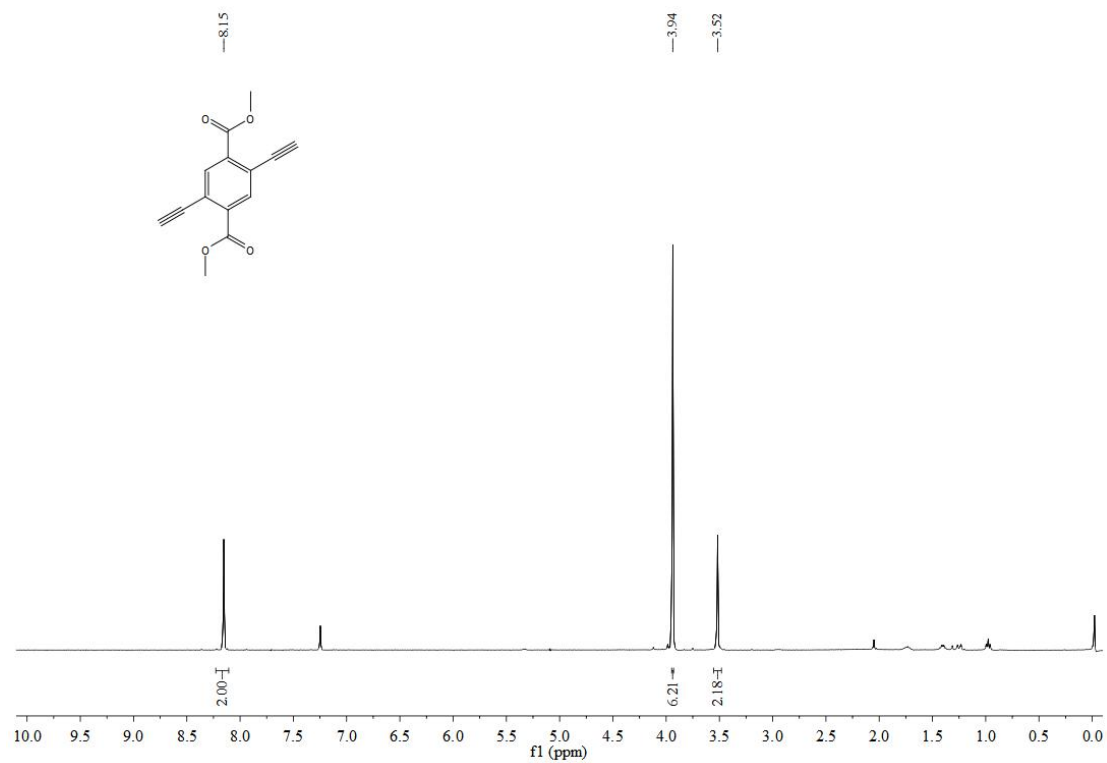
Compound 2a 2-((trimethylsilyl)ethynyl)terephthalic acid ^1H NMR (400 MHz, CDCl_3) δ 8.22 (d, J = 18.1 Hz, 1H), 7.94 (s, 2H), 3.92 (d, J = 14.4 Hz, 6H), 0.32 – 0.22 (m, 9H).



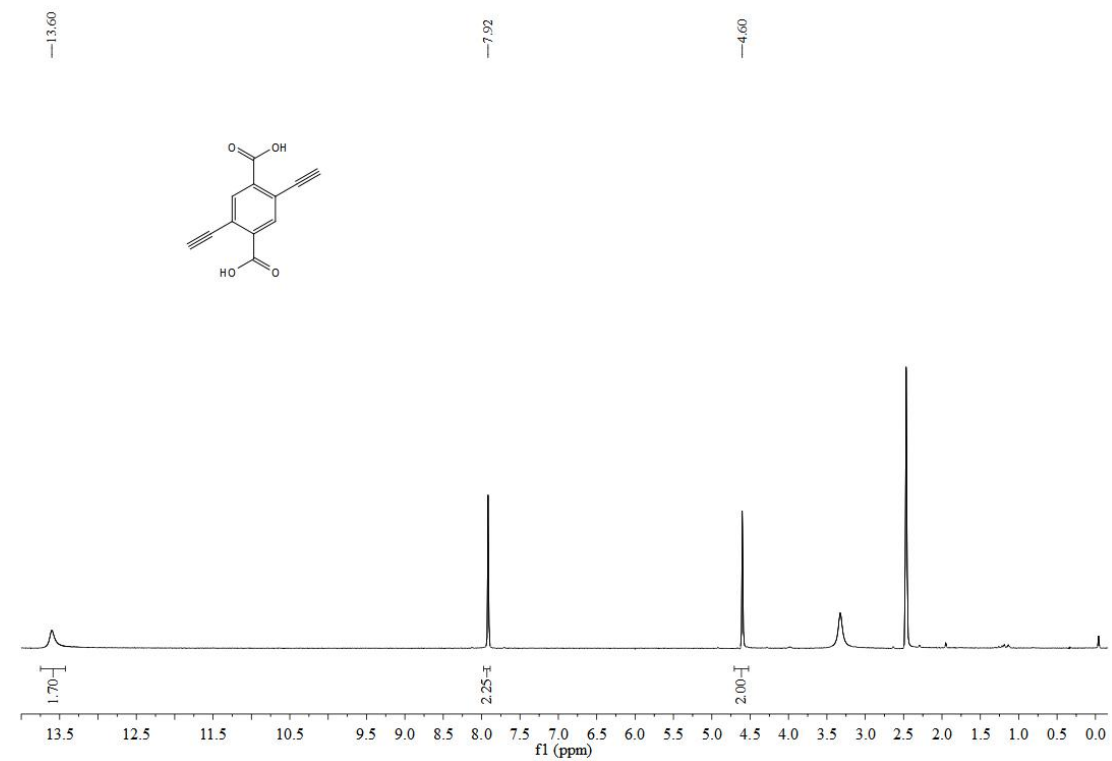
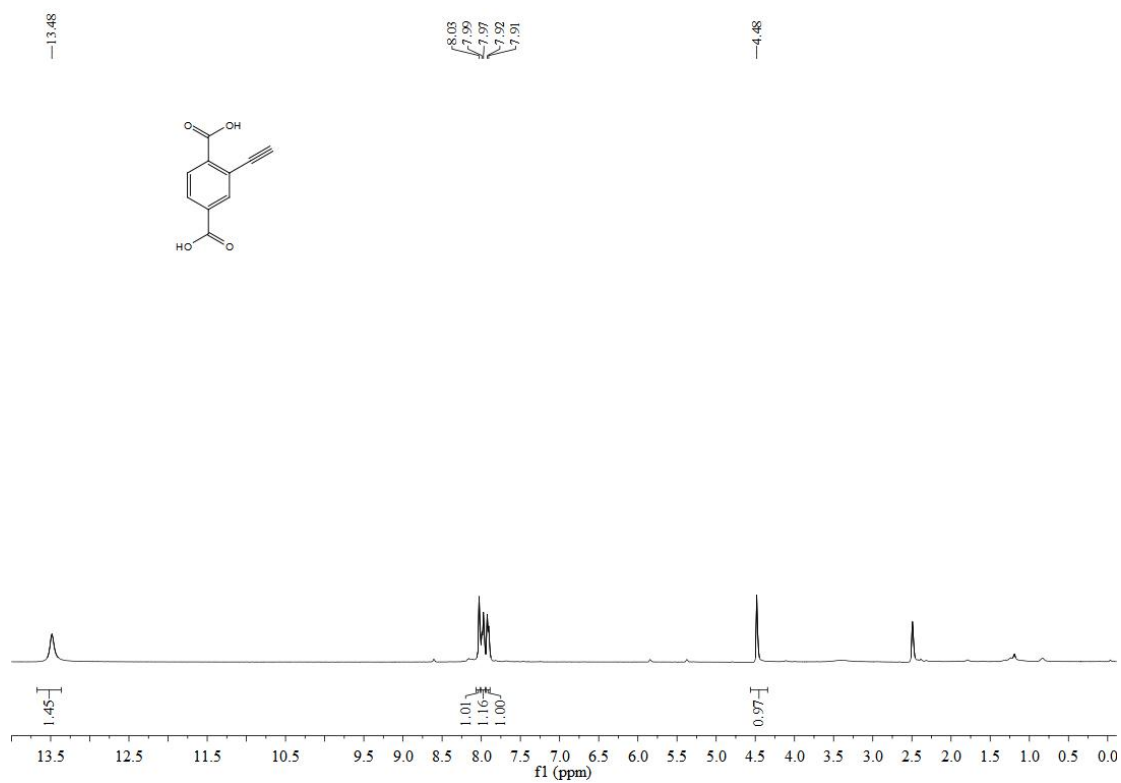
Compound 2b (dimethyl 2,5-bis((trimethylsilyl)ethynyl)terephthalate) ^1H NMR (400 MHz, CDCl_3) δ 8.08 (s, 2H), 3.92 (s, 6H), 0.26 (s, 18H).



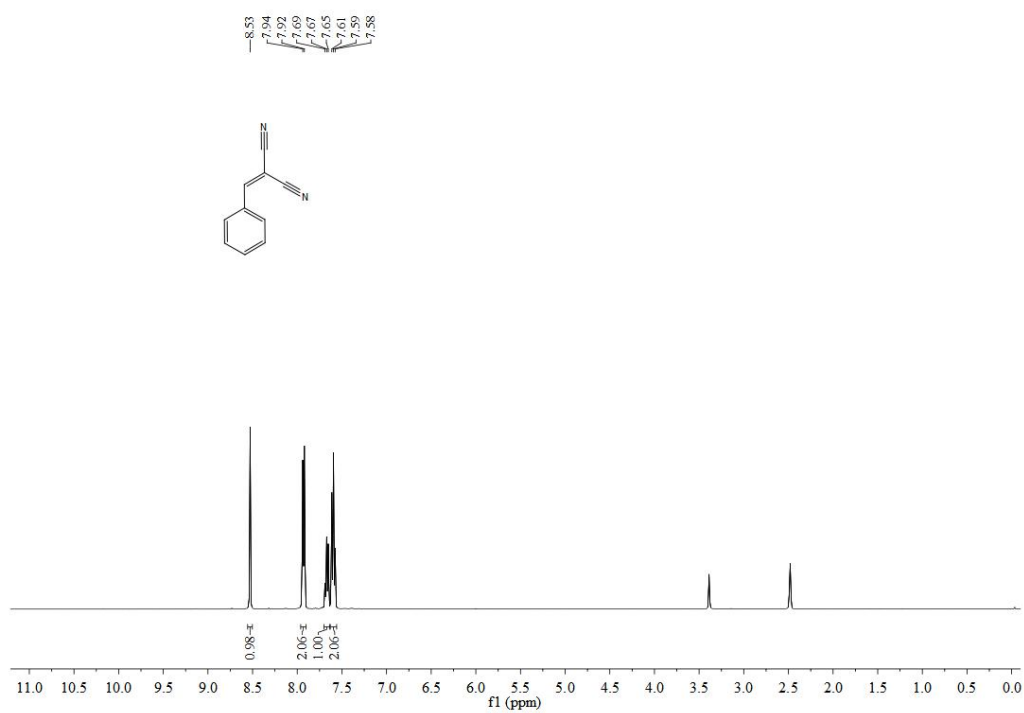
Compound 3a dimethyl 2-ethynylterephthalate $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.26 (d, $J = 9.5$ Hz, 1H), 7.98 (s, 2H), 3.95 (s, 6H), 3.46 (s, 1H).



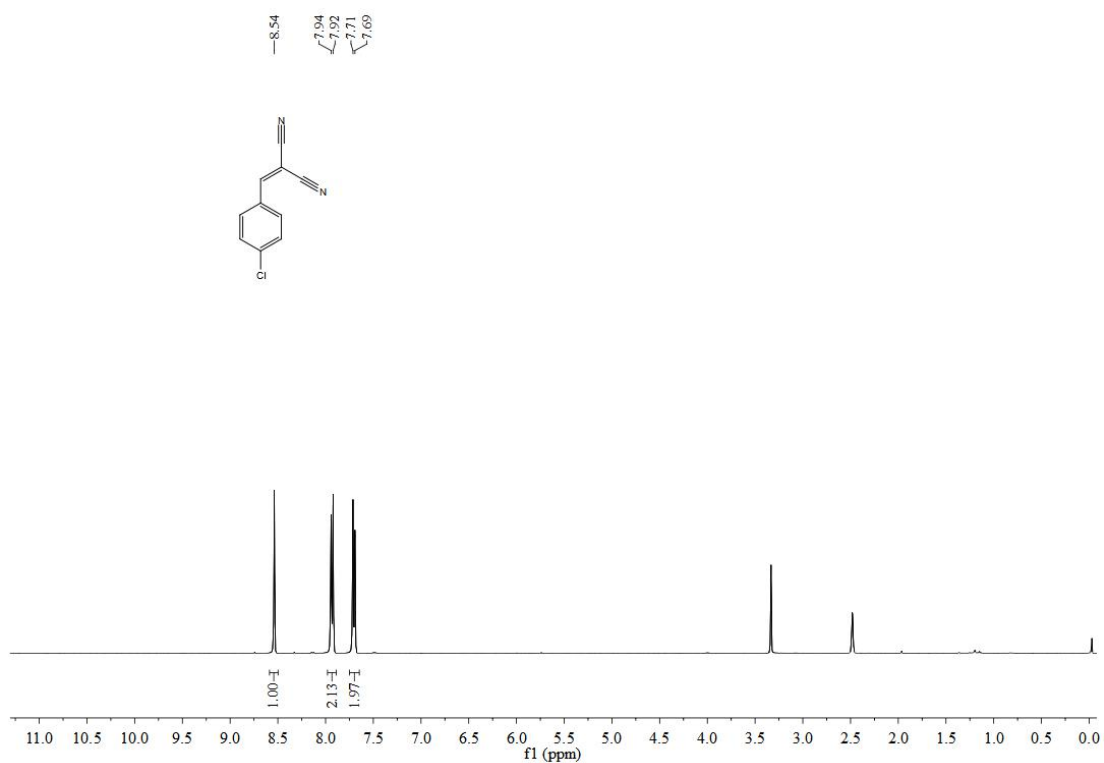
Compound 3b (dimethyl 2,5-diethynylterephthalate) $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.15 (s, 2H), 3.94 (s, 6H), 3.52 (s, 2H).



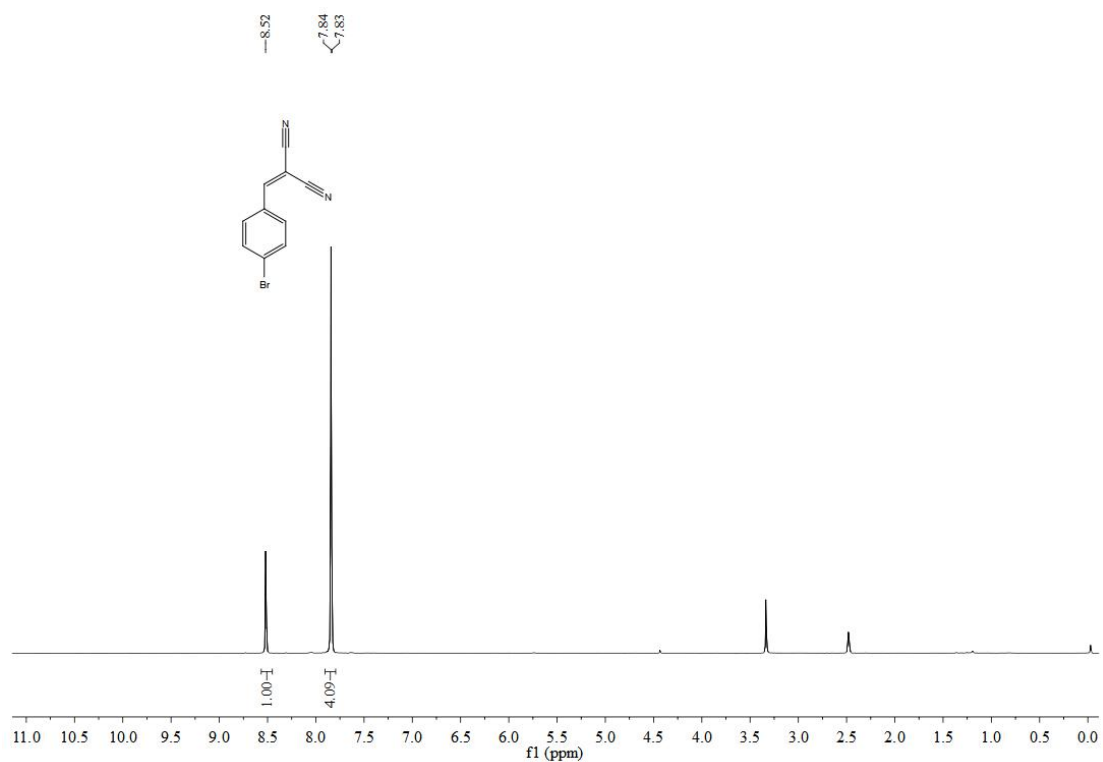
Compound 4b (2,5-diethynylterephthalic acid) $^1\text{H NMR}$ (400 MHz, $\text{DMSO-}d_6$) δ 13.60 (s, 2H), 7.92 (s, 2H), 4.60 (s, 2H).



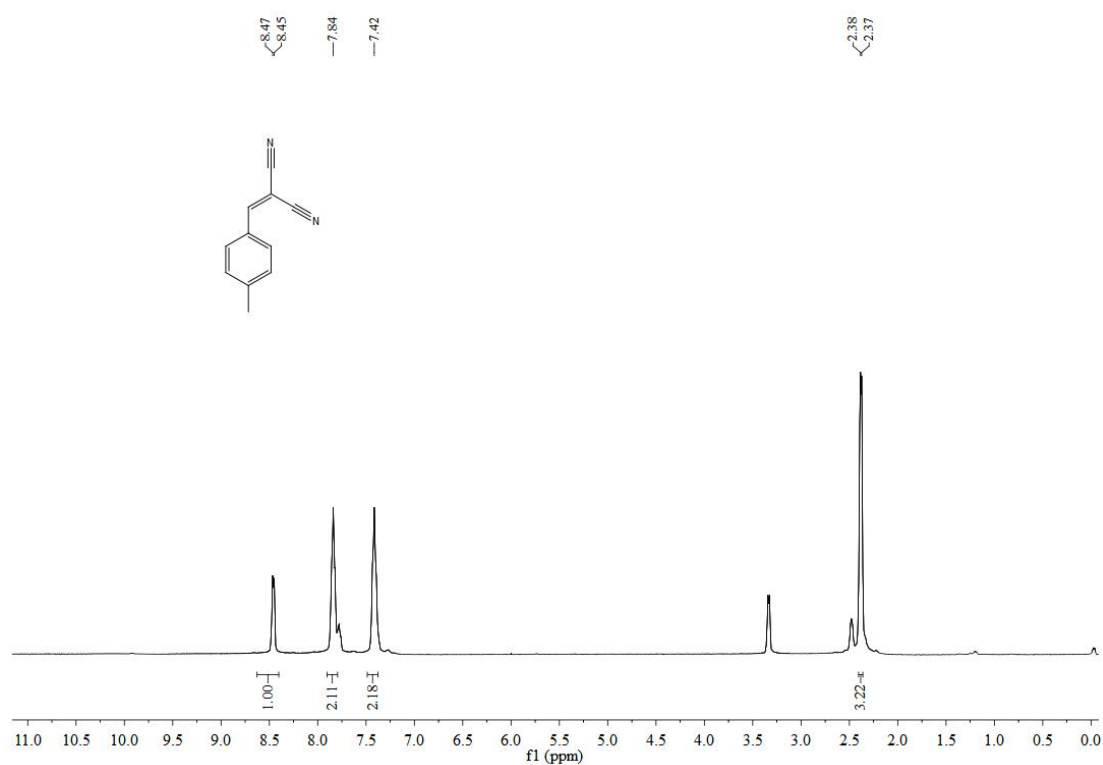
2-benzylidenemalononitrile ¹H NMR (400 MHz, DMSO-*d*₆) δ 8.53 (s, 1H), 7.93 (d, *J* = 7.4 Hz, 2H), 7.67 (t, *J* = 7.4 Hz, 1H), 7.59 (t, *J* = 7.5 Hz, 2H).



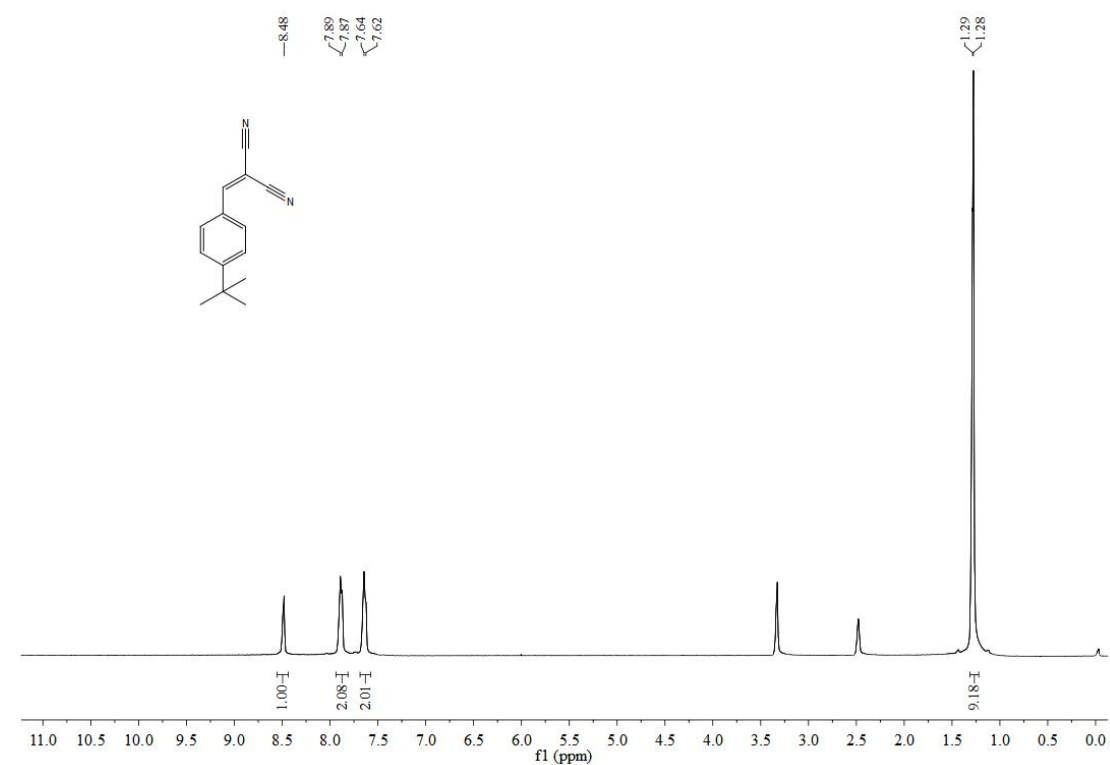
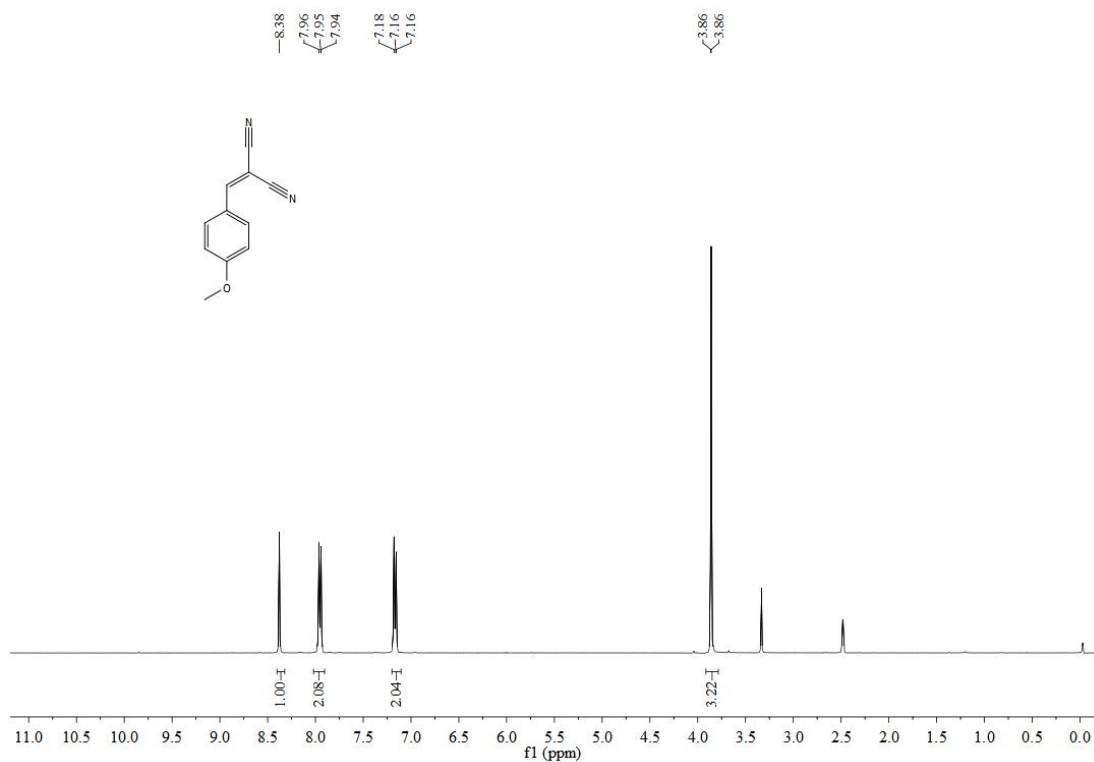
2-(4-chlorobenzylidene)malononitrile ¹H NMR (400 MHz, DMSO-*d*₆) δ 8.54 (s, 1H), 7.93 (d, *J* = 8.4 Hz, 2H), 7.70 (d, *J* = 8.1 Hz, 2H).



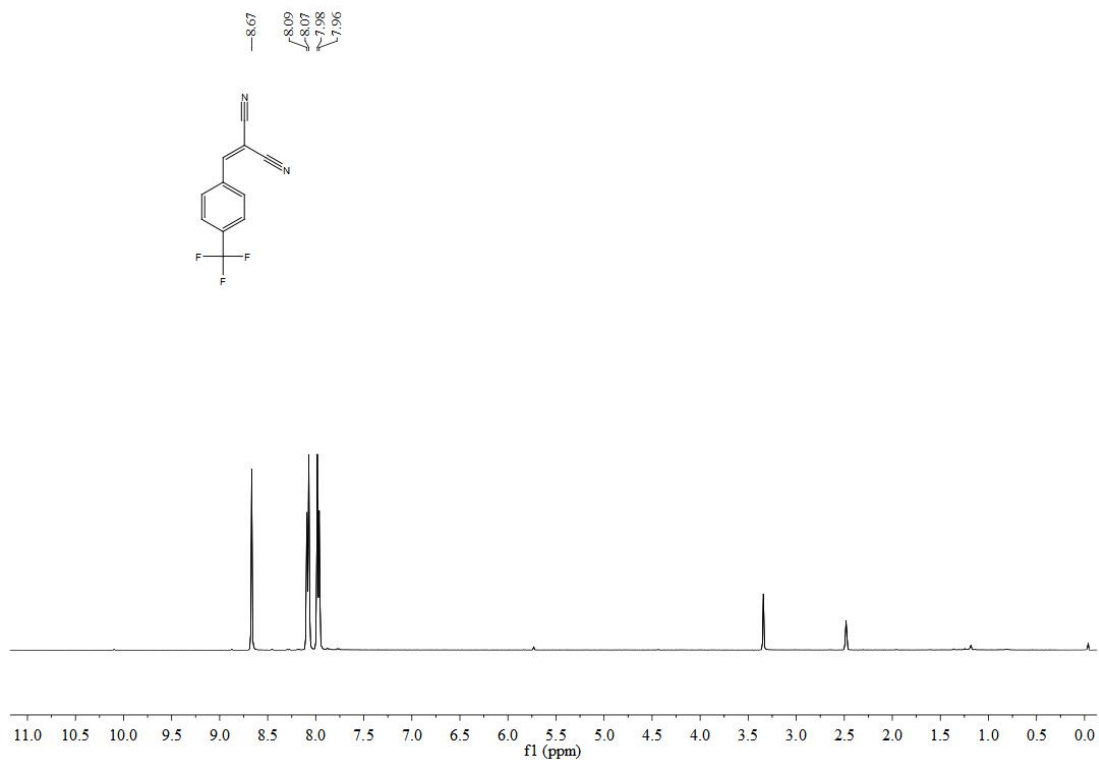
2-(4-bromobenzylidene)malononitrile $^1\text{H NMR}$ (400 MHz, $\text{DMSO-}d_6$) δ 8.54 (s, 1H), 7.93 (d, $J = 8.4$ Hz, 2H), 7.70 (d, $J = 8.1$ Hz, 2H).



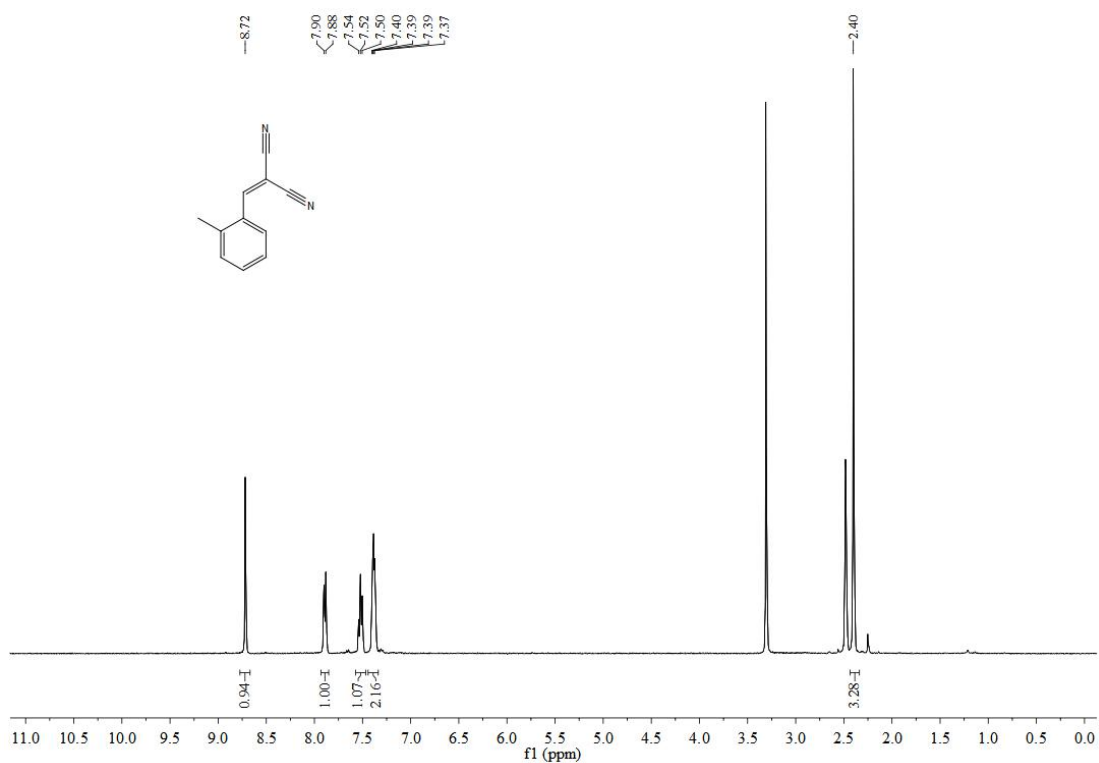
2-(4-methylbenzylidene)malononitrile $^1\text{H NMR}$ (400 MHz, $\text{DMSO-}d_6$) δ 8.46 (d, $J = 6.4$ Hz, 1H), 7.84 (s, 2H), 7.42 (s, 2H), 2.38 (d, $J = 4.5$ Hz, 3H), 2.37 (d, $J = 4.5$ Hz, 3H).



2-(4-(tert-butyl)benzylidene)malononitrile $^1\text{H NMR}$ (400 MHz, $\text{DMSO-}d_6$) δ 8.48 (s, 1H), 7.88 (d, $J = 7.9$ Hz, 2H), 7.63 (d, $J = 8.1$ Hz, 2H), 1.28 (d, $J = 3.7$ Hz, 9H).



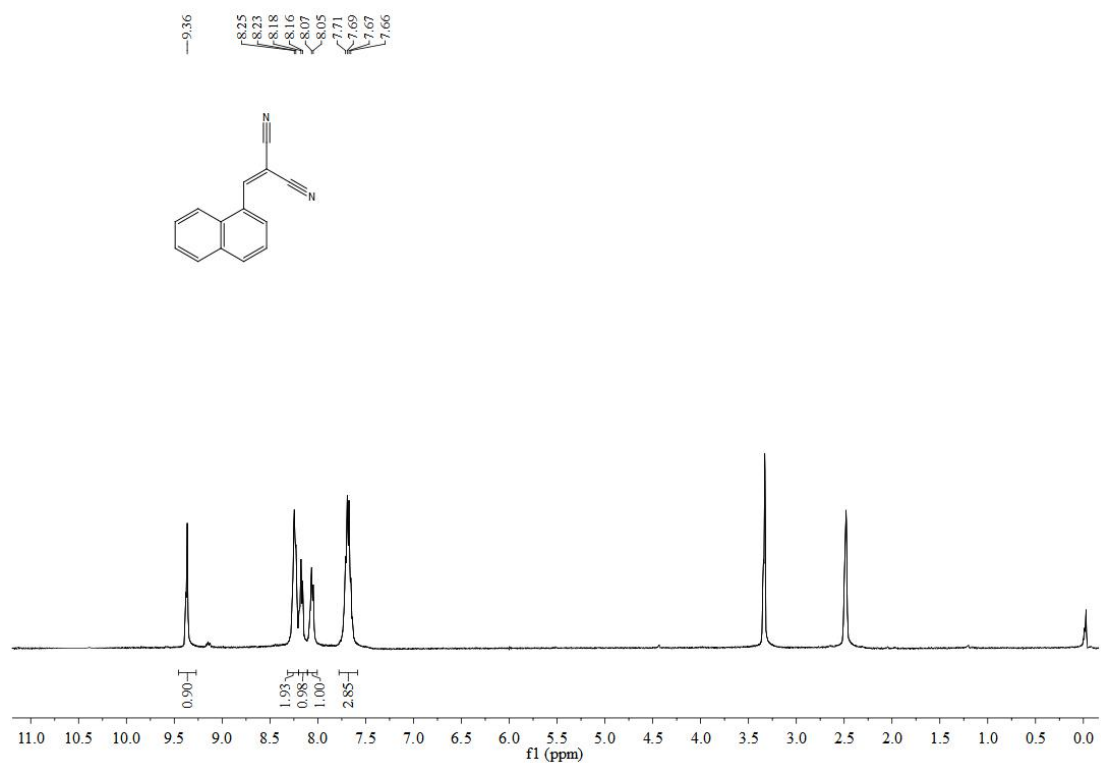
2-(4-(trifluoromethyl)benzylidene)malononitrile $^1\text{H NMR}$ (400 MHz, $\text{DMSO-}d_6$) δ 8.67 (s, 1H), 8.08 (d, $J = 8.0$ Hz, 2H), 7.97 (d, $J = 8.0$ Hz, 2H).



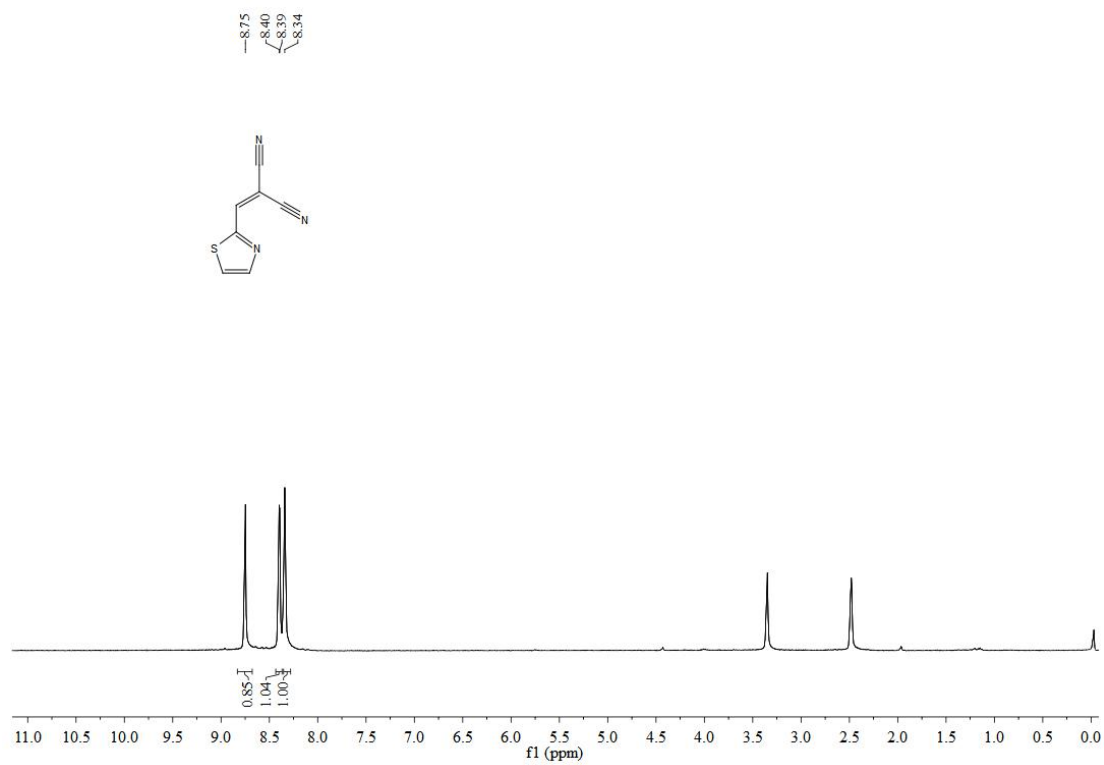
2-(2-methylbenzylidene)malononitrile $^1\text{H NMR}$ (400 MHz, $\text{DMSO-}d_6$) δ 8.72 (s, 1H), 7.89 (d, $J = 7.7$ Hz, 1H), 7.52 (t, $J = 7.5$ Hz, 1H), 7.39 (dd, $J = 7.1, 4.3$ Hz, 2H), 2.40 (s, 3H).



2-(3-methylbenzylidene)malononitrile ¹H NMR (400 MHz, DMSO-*d*₆) δ 8.48 (s, 1H), 7.76 (s, 1H), 7.72 (s, 1H), 7.51 (s, 2H), 2.35 (s, 3H).



2-(naphthalen-1-ylmethylene)malononitrile ¹H NMR (400 MHz, DMSO-*d*₆) δ 9.36 (s, 1H), 8.24 (d, *J* = 6.6 Hz, 2H), 8.17 (d, *J* = 7.3 Hz, 1H), 8.06 (d, *J* = 7.0 Hz, 1H), 7.68 (dd, *J* = 14.7, 7.4 Hz, 3H).



2-(thiazol-2-ylmethylene)malononitrile ^1H NMR (400 MHz, $\text{DMSO-}d_6$) δ 8.75 (s, 1H), 8.40 (d, $J=2.6$ Hz, 1H), 8.34 (s, 1H).