Electronic Supporting Information

for

Ru/UiO-66 Catalyst for the Reduction of Nitroarenes and Tandem reaction of Alcohol Oxidation/Knoevenagel Condensation

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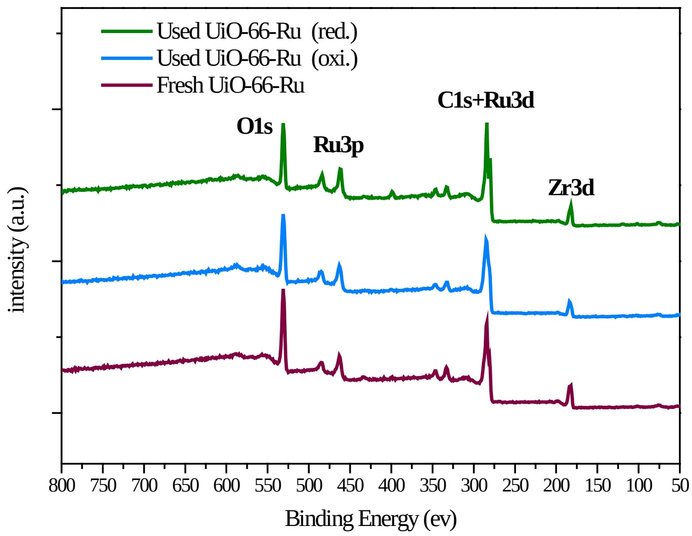
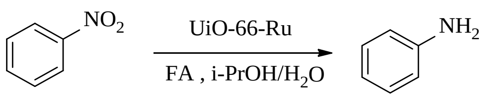


Figure S1. XPS wide scan spectra of the fresh and used samples of UiO-66-Ru

Table S1

Reduction of nitrobenzene to aniline with different dose of FA over UiO-66-Ru



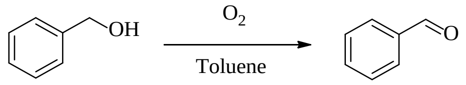
Entry	FA (mmol)	Conversion (%) [a]	Selectivity (%) [a]
1	1.5	60.3	91.3
2	2.0	84.9	89.6
3	2.5	100	>99

Reaction conditions: nitrobenzene (0.5 mmol), UiO-66-Ru (1 mol% Ru), i-PrOH/H_2O (9/1) (3 mL), reaction temperature 150 °C, reaction time 3h.

[a] Conversation and selectivity were determined by GC based on area%

Table S2

Aerobic oxidation of benzyl alcohol to benzaldehyde with different catalysts



Entry	Catalyst	Time (h)	Conversion (%) [a]	Selectivity (%) [a]
1	UiO-66-Ru	1	>99	>99
2	UiO-66	27	3.0	100.0
3	UiO-66-$RuCl_3$	27	5.8	99.2

Reaction conditions: Benzyl alcohol (0.25 mmol), catalyst (3.6 mol% Ru), toluene (1.5 ml), O_2 1atm, reaction temperature 100℃.

[a] Conversation and selectivity were determined by GC based on area%.

Table S3

The molar ratio of Ru to Zr determined by XPS

Sample	Ru/Zr (molar ratio)
Fresh UiO-66-Ru	2.62
Used UiO-66-Ru (red.)	2.88
Used UiO-66-Ru (oxi.)	2.46

Table S4

The content of Ru and Zr in the samples.

Catalysts	Ru (wt%)	Zr (wt%)
Fresh UiO-66-Ru	3.1	31.2
Used UiO-66-Ru (red.)	3.3	32.4
Used UiO-66-Ru (oxi.)	3.2	29.4

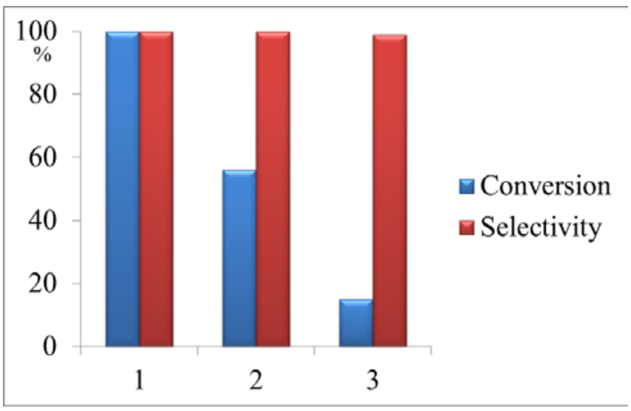


Figure S2. Recyclability of UiO-66-Ru in the aerobic oxidation of benzyl alcohol

[1]H NMR of reduced products of nitro compounds

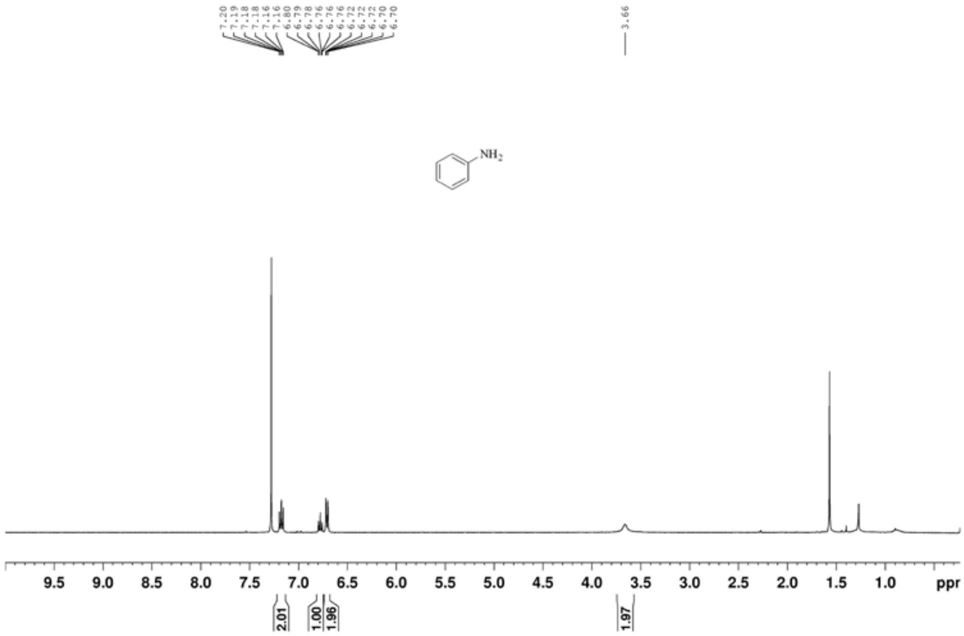


Figure S3. Aniline ^{1}H NMR ($CDCl_3$, 400 MHz) δ=3.66 (s, 2H), 6.70-7.20 (m, 5H).

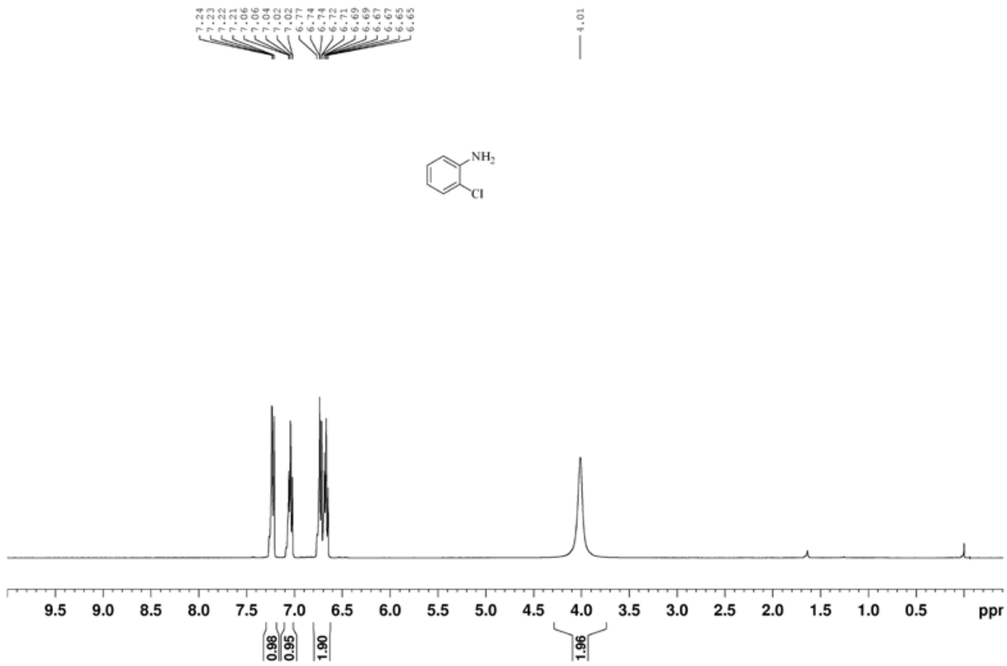


Figure S4. 2-chloroaniline ^{1}H NMR ($CDCl_3$, 400 MHz) δ=4.01 (s, 2H), 6.65-7.24 (m, 4H).

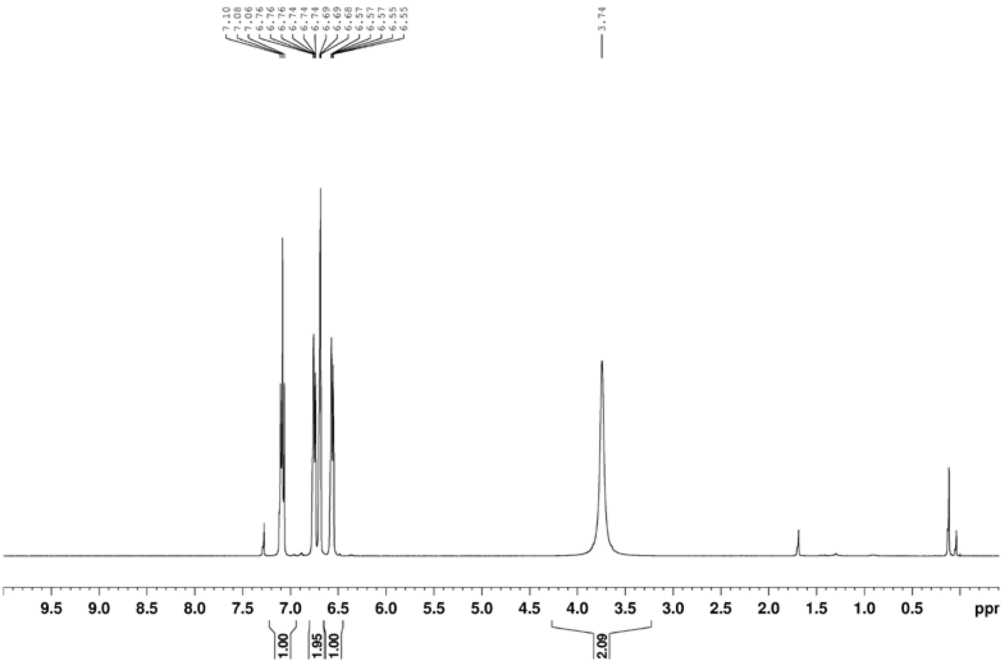


Figure S5. 3-chloroaniline ^{1}H NMR ($CDCl_3$, 400 MHz) δ=3.74 (s, 2H), 6.55-7.10 (m, 4H).

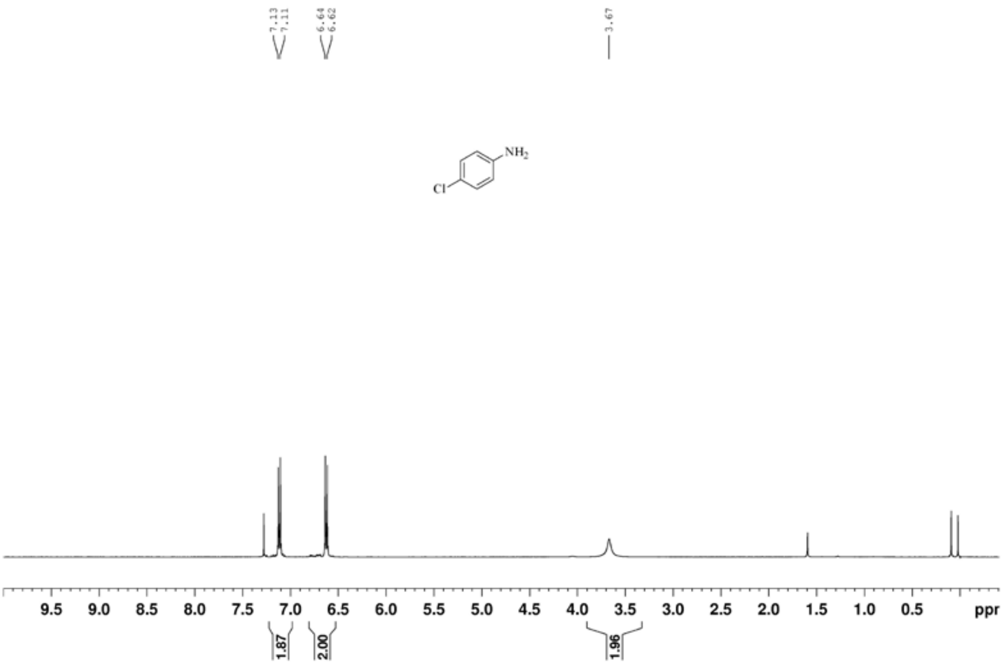


Figure S6. 4-chloroaniline ^{1}H NMR ($CDCl_3$, 400 MHz) δ=3.67 (s, 2H), 6.63 (d, J =8.0 Hz, 2H), 7.12 (d, J =8.0 Hz, 2H).

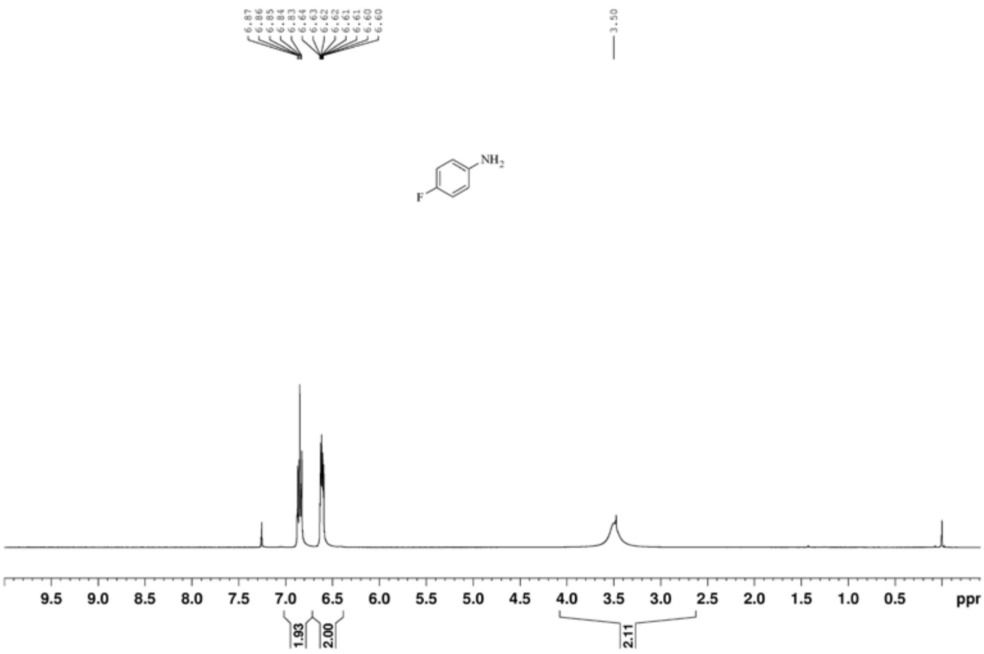


Figure S7. 4-fluoroaniline ^{1}H NMR ($CDCl_3$, 400 MHz) δ=3.50 (s, 2H), 6.60-6.87 (m, 4H).

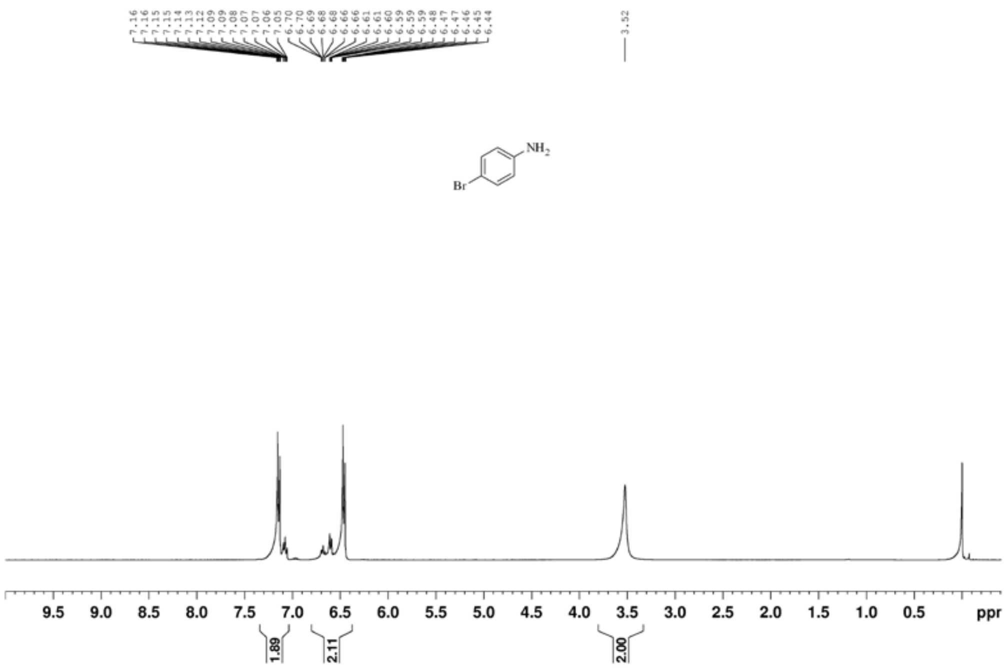


Figure S8. 4-bromoaniline ^{1}H NMR ($CDCl_3$, 400 MHz) δ=3.52 (s, 2H), 6.44-7.16 (m, 4H).

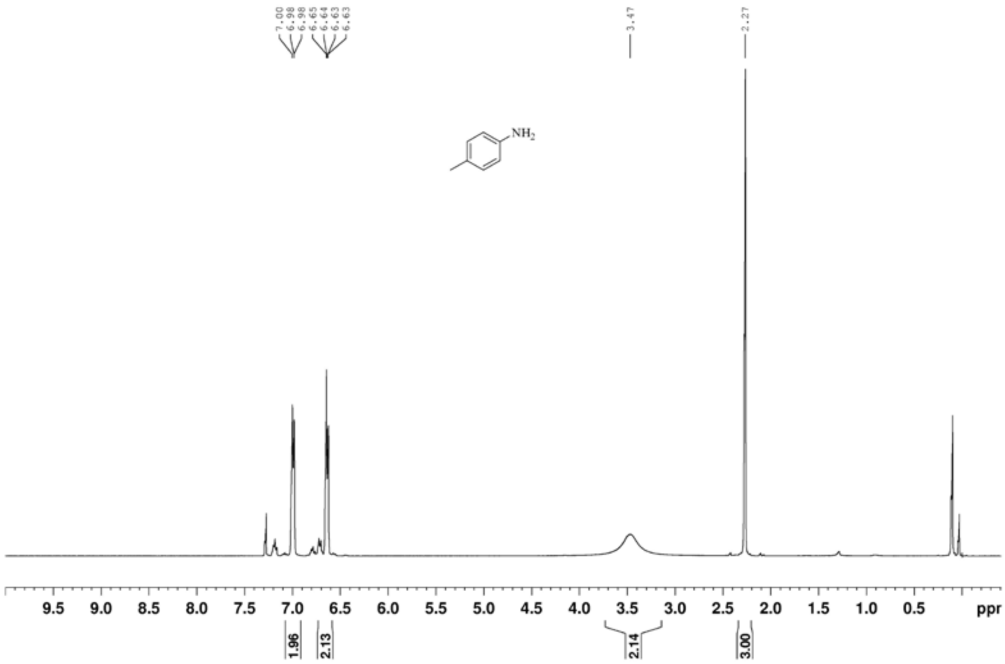


Figure S9. p-toluidine ^{1}H NMR ($CDCl_3$, 400 MHz) δ=3.47 (s, 2H), 6.63-7.00 (m, 4H).

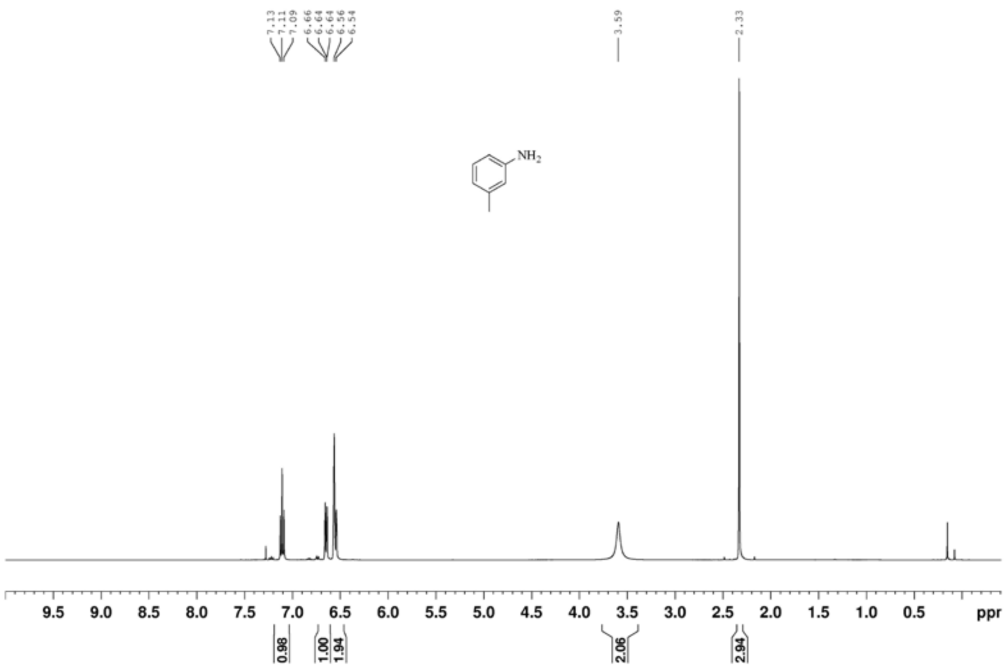


Figure S10. m-toluidine ^{1}H NMR ($CDCl_3$, 400 MHz) δ=3.59 (s, 2H), 6.54-7.13 (m, 4H).

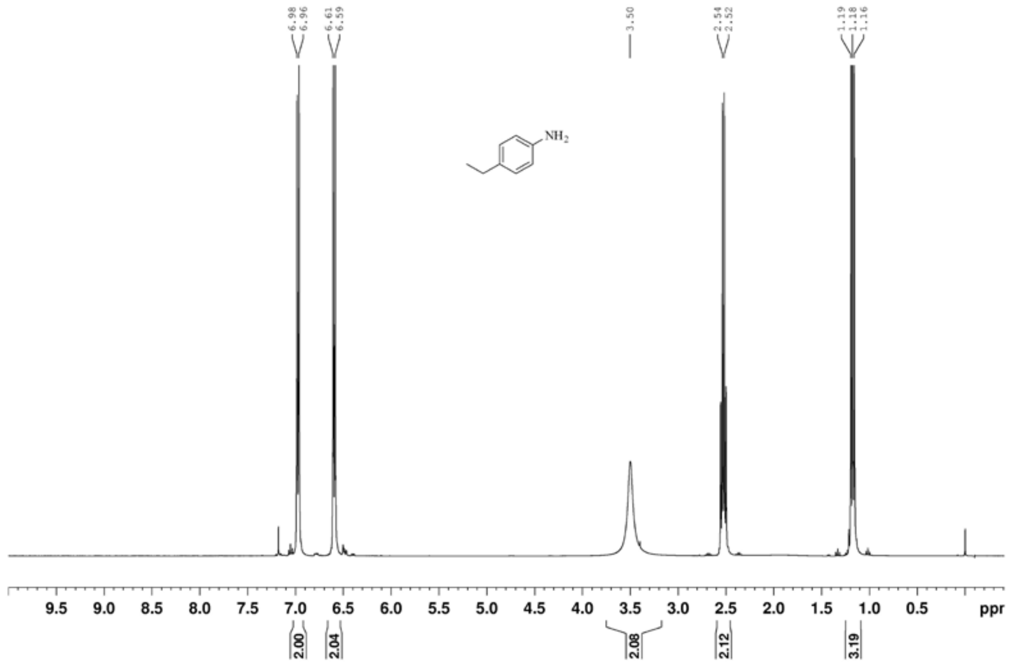


Figure S11. 4-ethylaniline ^{1}H NMR ($CDCl_3$, 400 MHz) δ=1.16-2.54 (m, 5H), 3.50 (s, 2H), 6.60(d, J =8.0 Hz, 2H), 6.97(d, J =8.0 Hz, 2H).

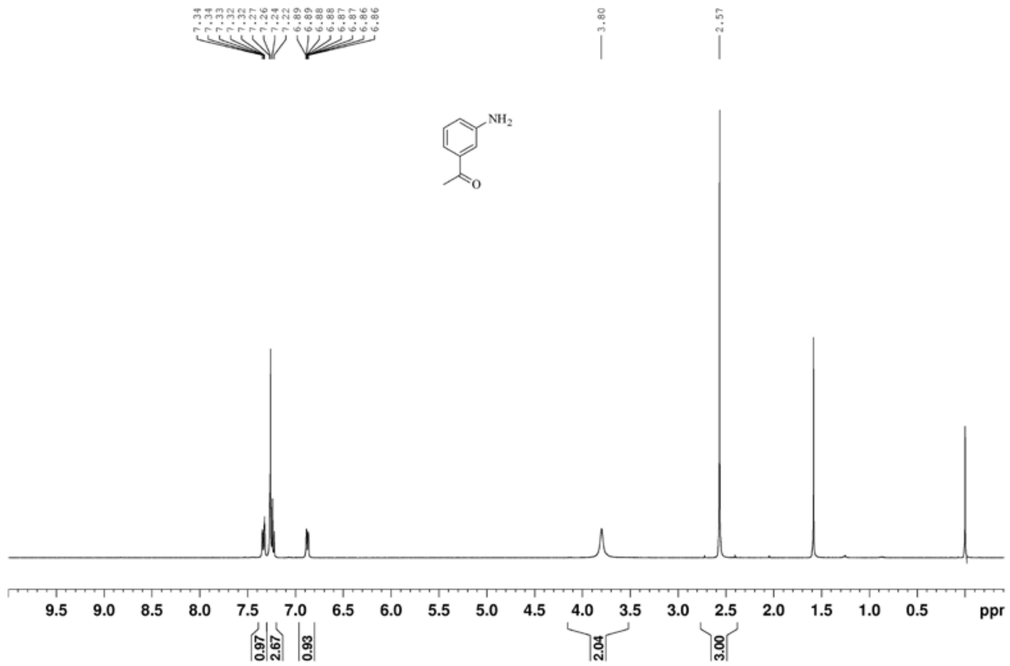


Figure S12. 1-(3-aminophenyl)ethanone ^{1}H NMR ($CDCl_3$, 400 MHz) δ=2.57 (s, 3H), 6.86-7.34(m, 4H).

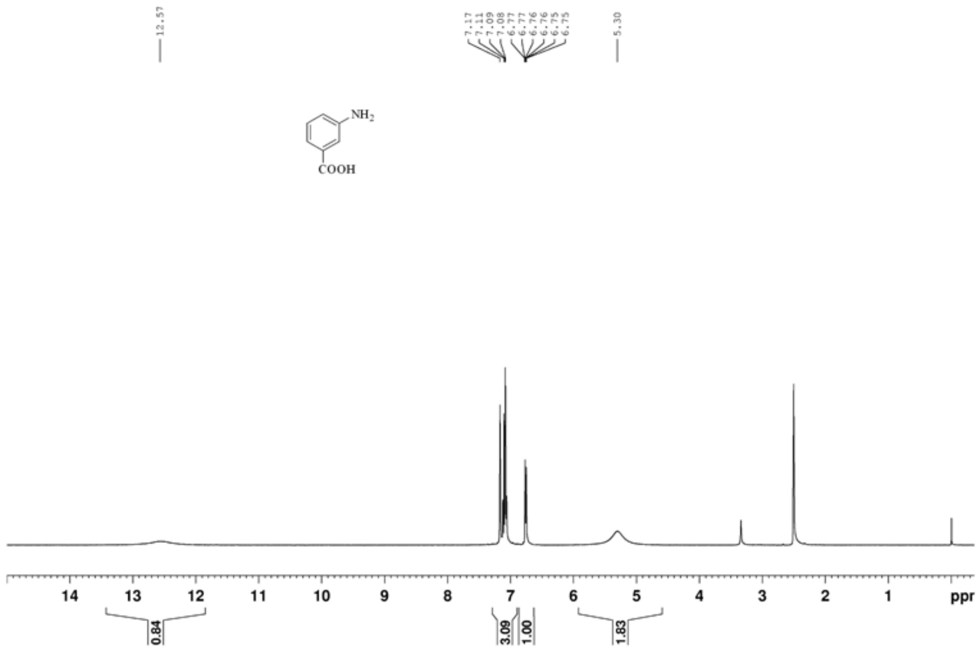


Figure S13. 3-aminobenzoic acid ^{1}H NMR (DMSO, 400 MHz) δ=5.30 (s, 2H), 6.75-7.17(m, 4H), δ=12.57 (s, 1H).

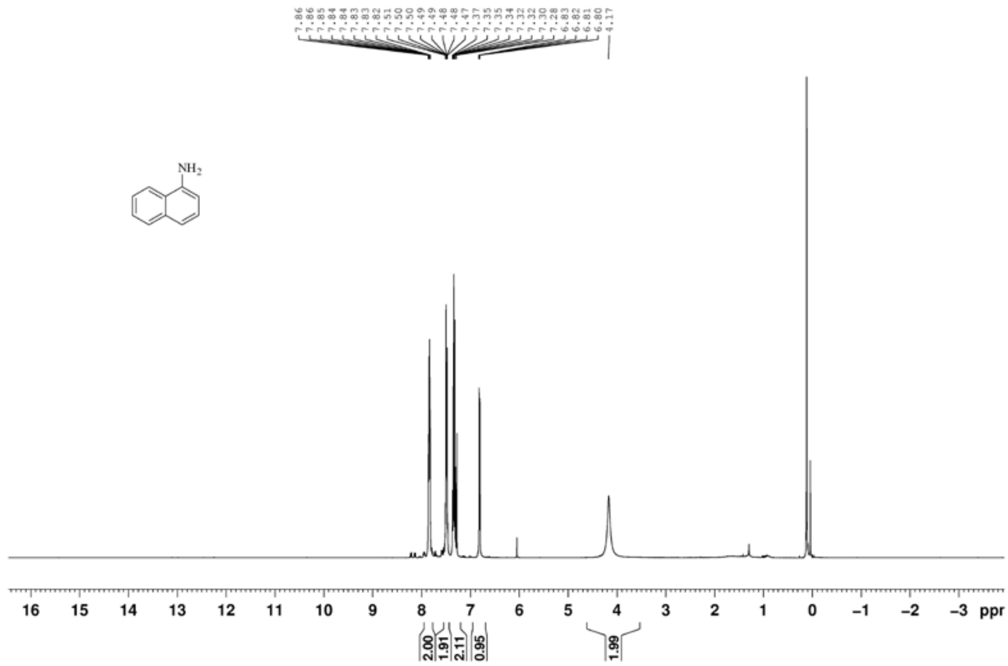


Figure S14. naphthalen-1-amine ^{1}H NMR ($CDCl_3$, 400 MHz) δ=4.17 (s, 2H), 6.80-7.86 (m, 7H).

^{1}H NMR of oxidation/Knoevenagel condensation products of alcohols

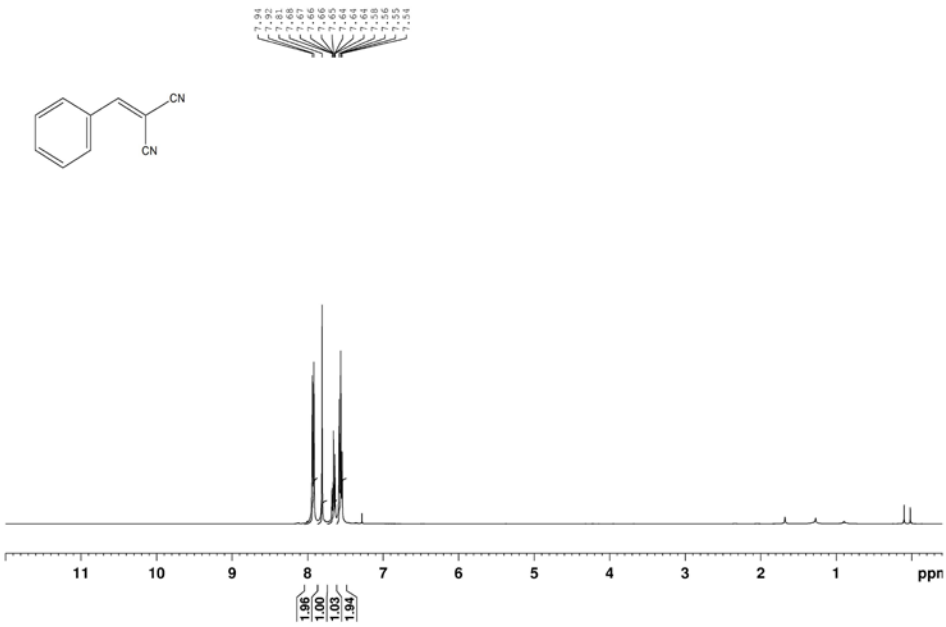


Figure S15. Benzalmalononitrile ^{1}H NMR ($CDCl_3$, 400 MHz) δ=7.54-7.68 (m, 3H), 7.81(s, 1H), 7.93 (d, J =8.0 Hz, 2H).

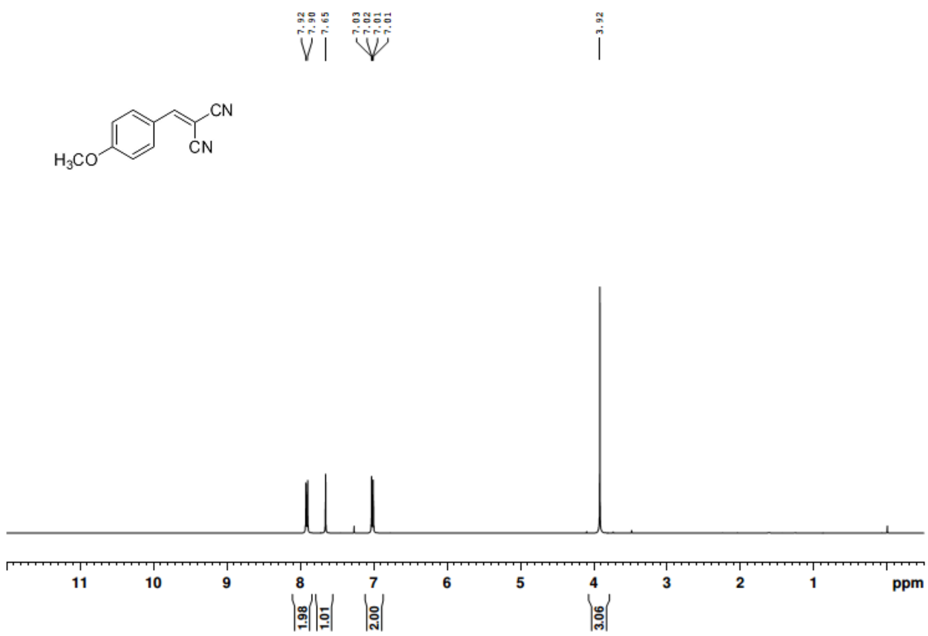


Figure S16. 2-(4-Methoxybenzylidene)malonitrile ^{1}H NMR ($CDCl_3$, 400 MHz) δ=3.92 (s, 3H), 7.01-7.03 (m, 2H), 7.65(s, 1H), 7.91 (d, J =8.0 Hz, 2H).

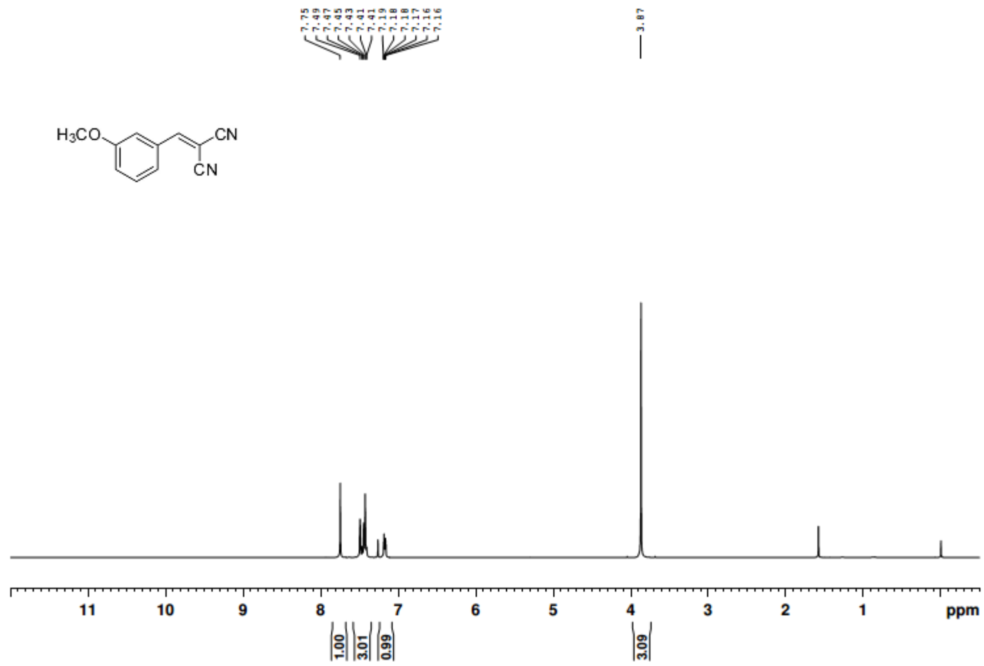


Figure S17. 2-(3-Methoxybenzylidene)malonitrile ^{1}H NMR ($CDCl_3$, 400 MHz) δ=3.87 (s, 3H), 7.16-7.49 (m, 4H), 7.75 (s, 1H).

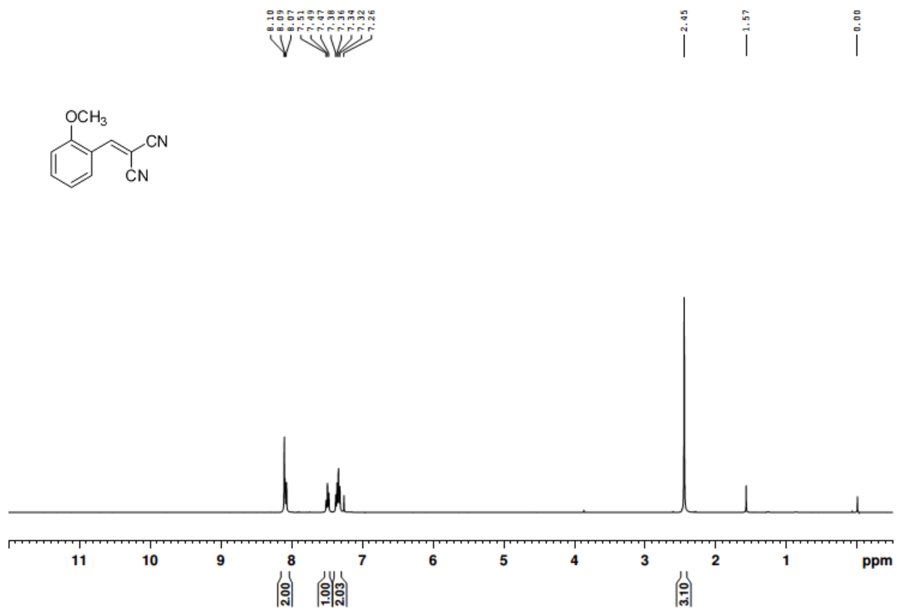


Figure S18. 2-(2-Methoxybenzylidene)malonitrile ^{1}H NMR ($CDCl_3$, 400 MHz) δ=2.45 (s, 3H), 7.32-7.51 (m, 3H), 8.07-8.10 (m, 2H).

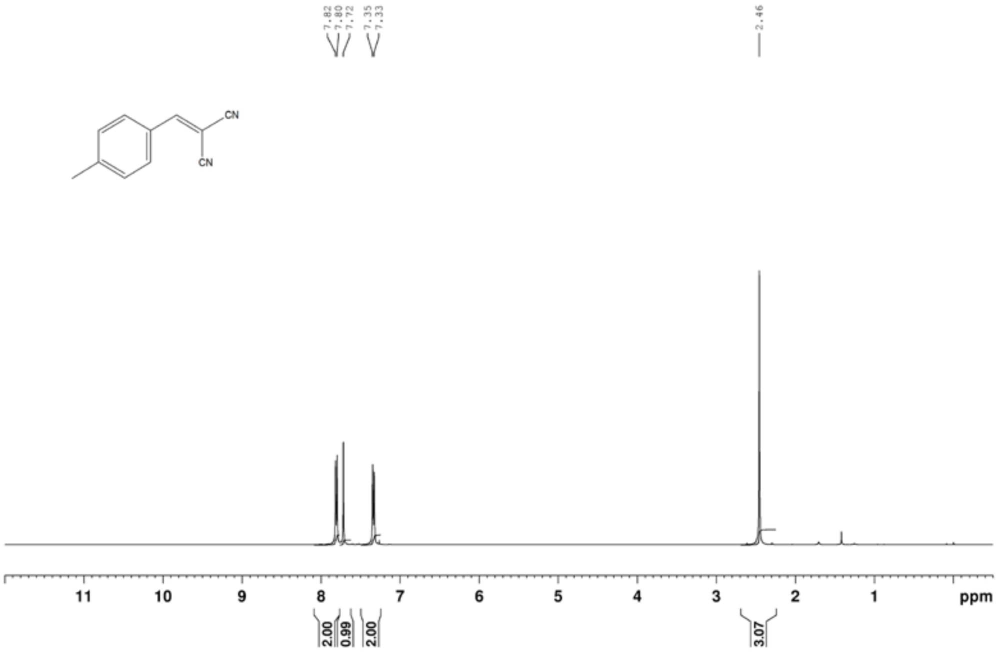


Figure S19. (4-Methylbenzylidene)malononitrile ^{1}H NMR ($CDCl_3$, 400 MHz) δ=2.46 (s, 3H), 7.34 (d, J =8.0 Hz, 2H), 7.72(s, 1H), 7.81 (d, J =8.0 Hz, 2H).

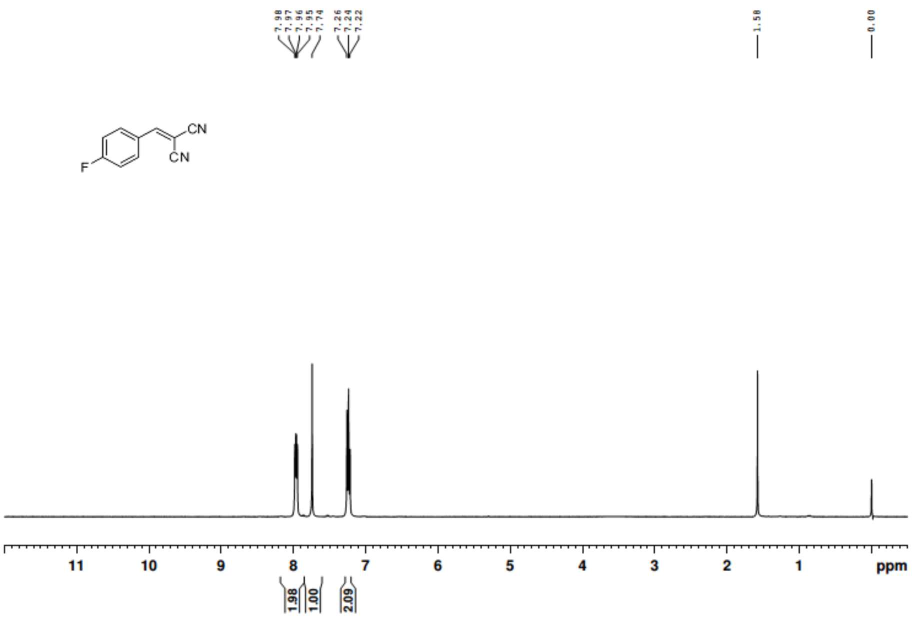


Figure S20. (4-Fluorobenzylidene)malononitrile ^{1}H NMR ($CDCl_3$, 400 MHz) δ=7.22-7.26 (m, 2H), 7.74 (s, 1H), 7.95-7.98(m, 2H).

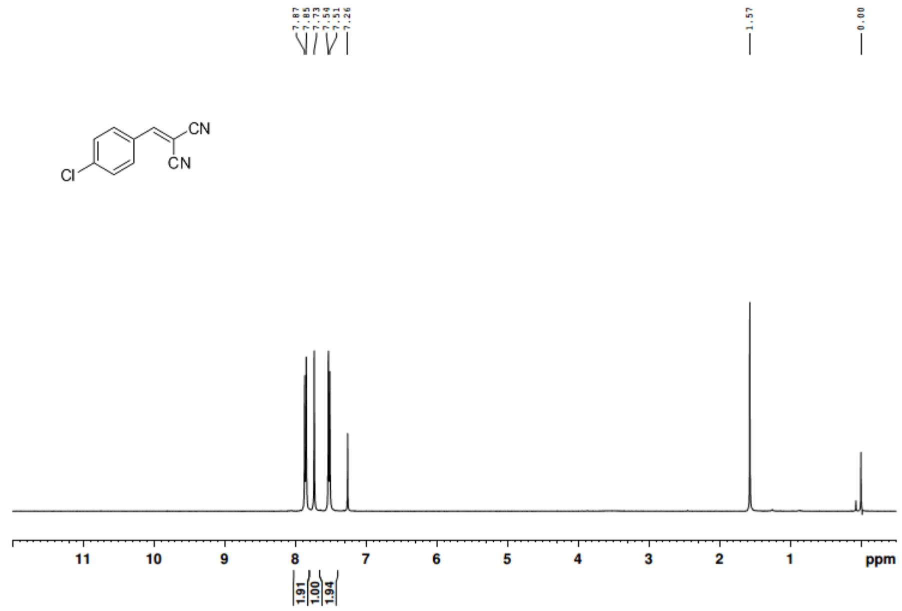


Figure S21. 2-(4-Chlorobenzylidene)malononitrile ^{1}H NMR ($CDCl_3$, 400 MHz) δ=7.53 (d, J =8.0 Hz, 2H), 7.73 (s, 1H), 7.86(d, J =8.0 Hz, 2H).

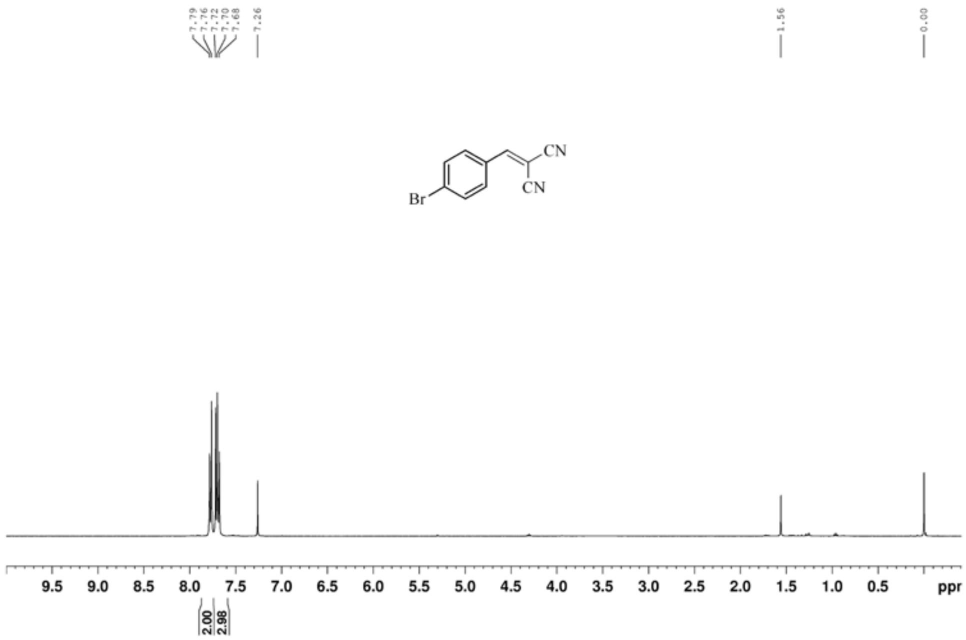


Figure S22. 2-[(4-BroMophenyl)Methylene]Malononitrile ^{1}H NMR ($CDCl_3$, 400 MHz) δ=7.68-7.72 (m, 3H), 7.76-7.79 (m, 2H).

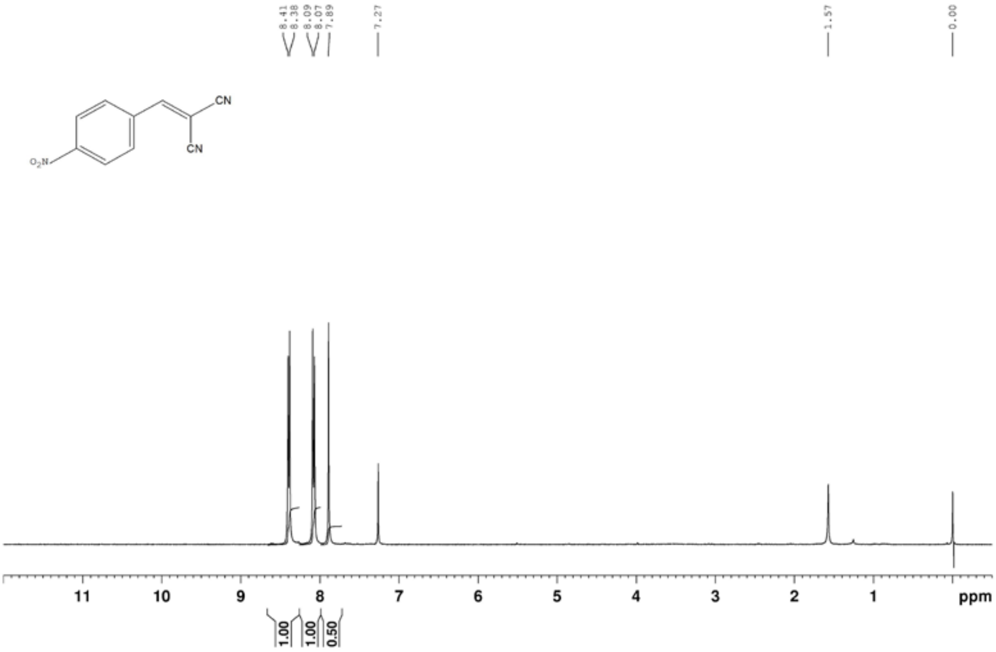


Figure S23. 2-(4-Nitrobenzylidene)malononitrile ^{1}H NMR ($CDCl_3$, 400 MHz) δ=7.89 (s, 1H), 8.08 (d, J =8.0 Hz, 2H), 8.39(d, J =8.0 Hz, 2H).

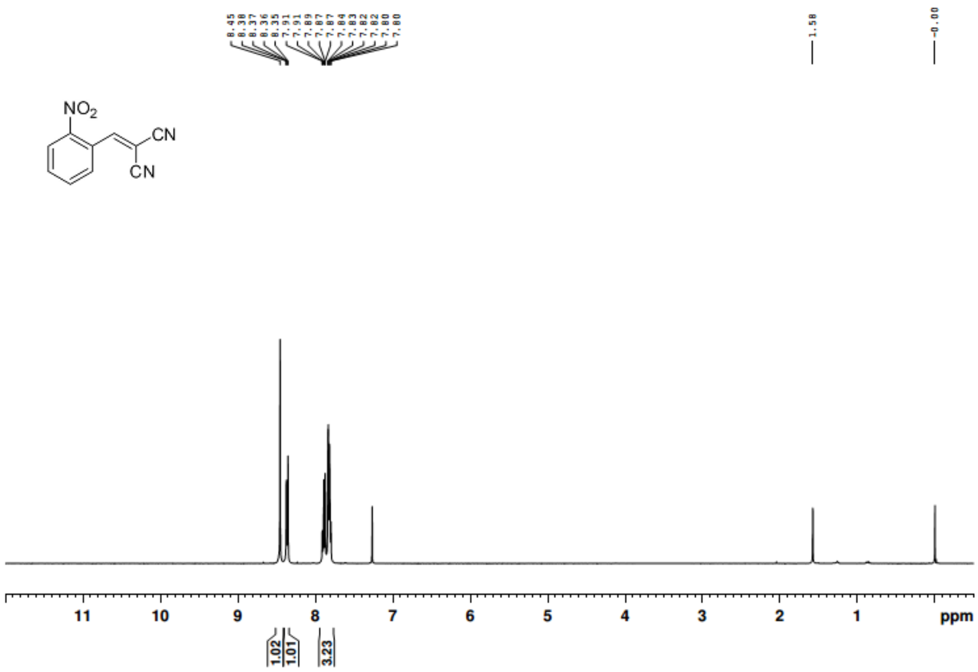


Figure S24. 2-(2-nitrobenzylidene)malononitrile ^{1}H NMR ($CDCl_3$, 400 MHz) δ=7.80-7.91 (m, 3H), 8.35-8.38 (m, 1H), 8.45 (s, 1H).

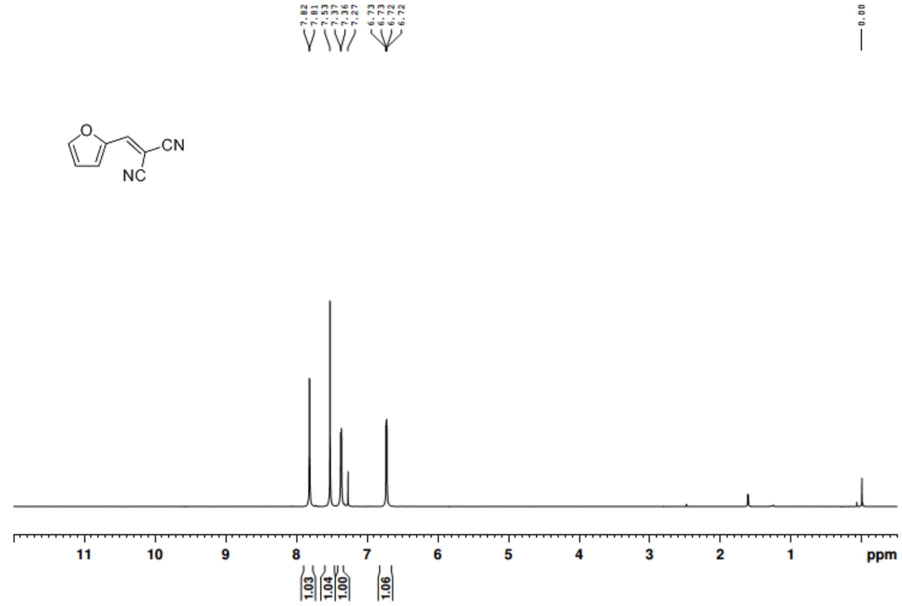


Figure S25. (2-Furanylmethylene)malononitrile ^{1}H NMR ($CDCl_3$, 400 MHz) δ=6.72-6.73 (m, 1H), 7.37 (d, J =4.0 Hz, 1H), 7.53 (s, 1H), 7.82 (d, J =4.0 Hz, 1H).

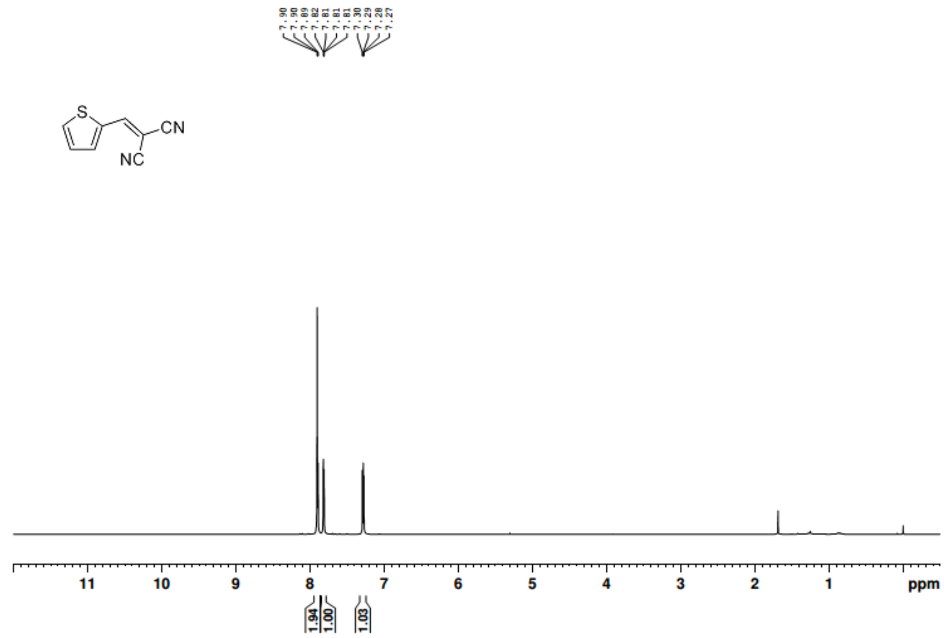


Figure S26. 2-(2-ThienylMethylene)Malononitrile ^{1}H NMR ($CDCl_3$, 400 MHz) δ=7.27-7.30 (m, 1H), 7.81-7.82 (m, 1H), 7.89-7.89 (m, 2H).

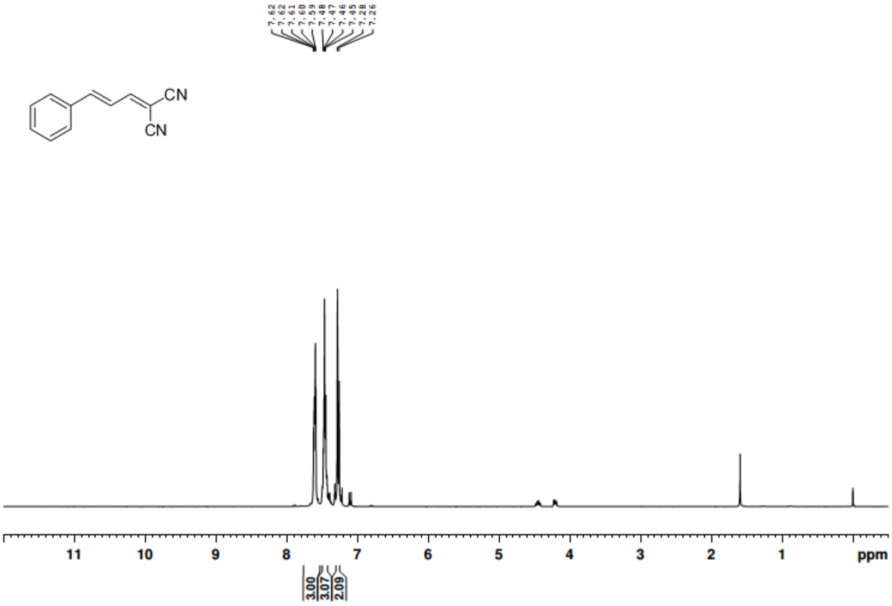


Figure S27. 2-(3-phenylallylidene)malononitrile [1]H NMR ($CDCl_3$, 400 MHz) δ=7.27 (d, J =8.0 Hz, 2H), 7.45-7.48 (m, 3H) , 7.59-7.62 (m, 3H).

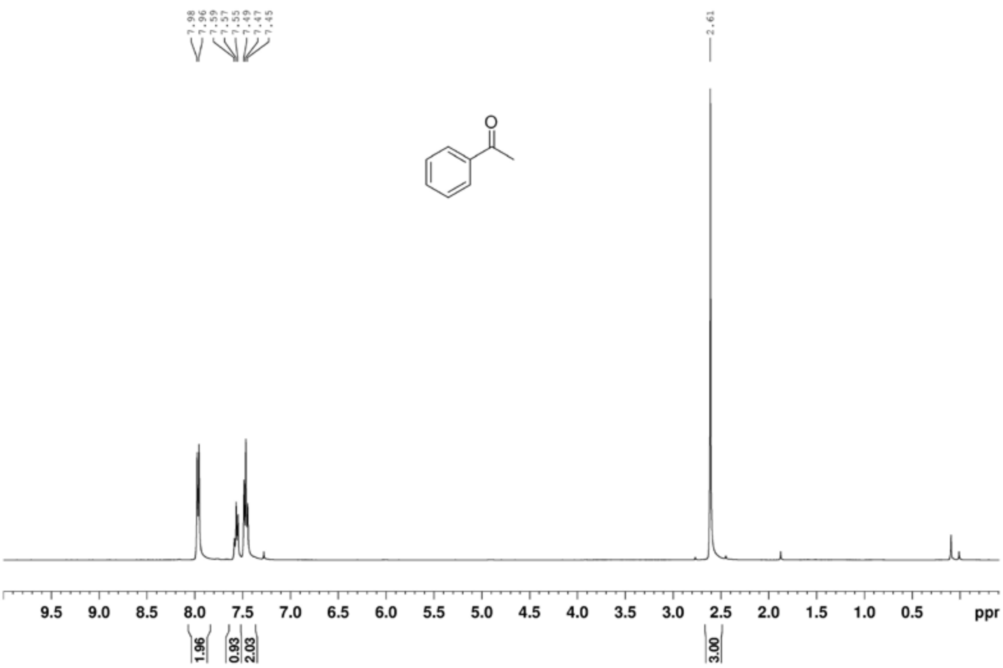


Figure S28. Acetophenone [1]H NMR ($CDCl_3$, 400 MHz) 7.45-7.59 (m, 3H) , δ=7.97 (d, J =8.0 Hz, 2H).

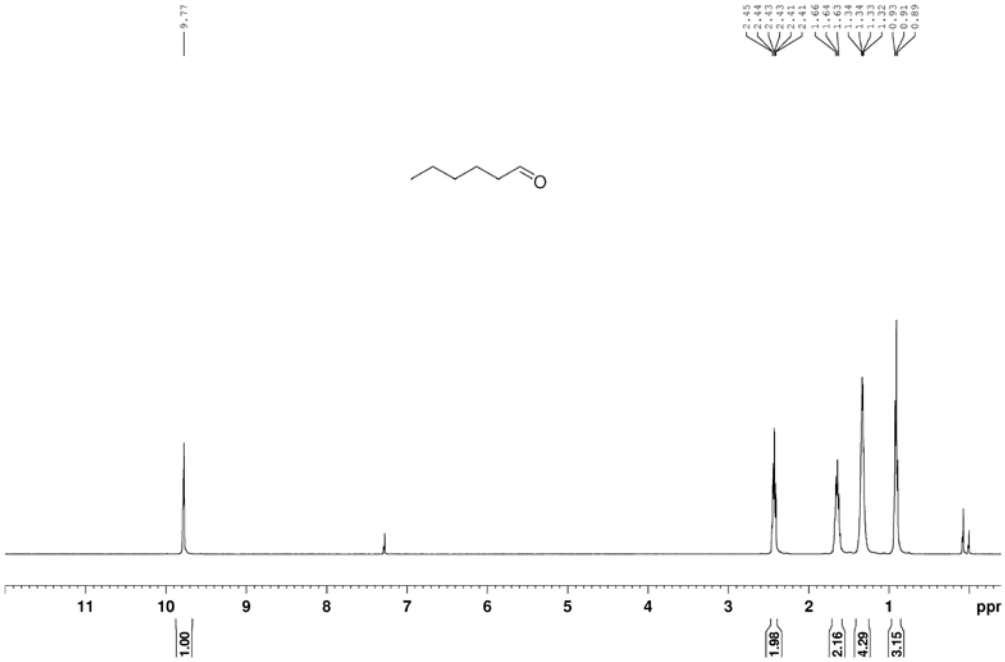


Figure S29. Hexan-1-ol ^{1}H NMR ($CDCl_3$, 400 MHz) 0.89-2.45 (m, 11H) , δ=9.77 (s, 1H).

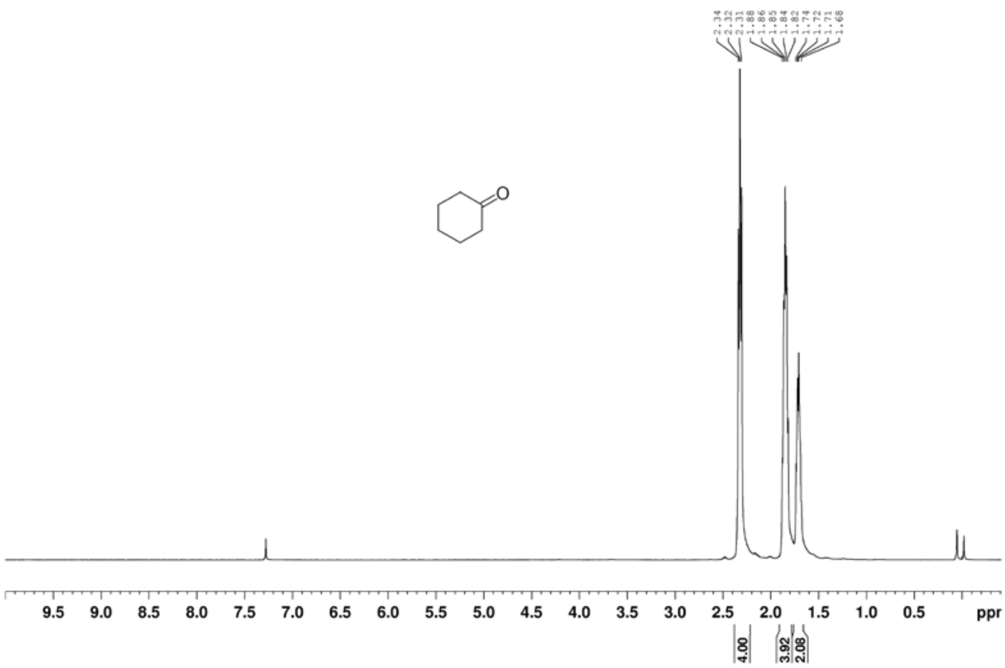


Figure S30. Cyclohexanol ^{1}H NMR ($CDCl_3$, 400 MHz) 1.68-2.34 (m, 10H).