Electronic Supplementary Information (ESI)

A porphyrin-linked conjugated microporous polymer with selective carbon dioxide adsorption and heterogeneous organocatalytic performances

Xiaoming Liu,*[a] Sigen A,[a] Yuwei Zhang,[a] Xiaolong Luo,[b] Hong Xia,[c] He Li,[a] and Ying Mu*[a]

[a] *State Key Laboratory for Supramolecular Structure and Materials, College of Chemistry, Jilin University, Changchun 130012, P. R.China*
[b] *State Key Laboratory of Inorganic Synthesis and Preparative Chemistry, College of Chemistry, Jilin University, Changchun, 130012, P.R.China.*
[c] *State Key Laboratory on Integrated Optoelectronics, College of Electronic Science and Technology, Jilin University, Changchun 130012, P. R.China*

Email: xm_liu@jlu.edu.cn

Section A. Synthesis of monomer

5,10,15,20-tetrakis[4-(trimethylsilylethynyl)phenyl]porphyrin.[1]

Pyrrole (0.75 mL, 10 mmol) was added through a dropping funnel to a solution of 4-(trimethylsilylethynyl)benzaldehyde (2.0 g, 10 mmol) in refluxing propionic acid (75 mL). The mixture was heated at reflux for 4 h, stirred overnight at room temperature, followed by vacuum distillation to remove the solvents from the reaction vessel. The mixture was cooled, washed with methanol and filtered through a silica funnel with CH_2Cl_2 as eluent and the purple product (0.9 g, 18.3%) was obtained. ^{1}H NMR (300 MHz, $CDCl_3$): δ –2.85 (s, 2H), 0.38 (s, 36H), 7.87 (d, J = 6.0 Hz, 8H), 8.14 (d, J = 6.0 Hz, 8H), 8.82 (s, 8H) ppm. Anal. Calcd for $C_{64}H_{62}N_4Si_4$ (999.5): C, 76.90; H, 6.25; N, 5.61. Found: C, 76.98; H, 6.26; N, 5.48. MALDI-TOF MS: m/z 998.41, calcd. for $C_{64}H_{62}N_4Si_4$; found, $[M]^+$ 999.02. FT-IR (KBr):ν 562, 662, 731, 758, 801, 859, 967, 990, 1025, 1098, 1179, 1221, 1248, 1349, 1399, 1474, 1497, 1560, 1602, 1710, 1823, 1911, 2151, 2895, 2959, 3034, 3314 cm^{-1}

Synthesis of 5,10,15,20-tetrakis(4-ethynylphenyl)porphyrin.

Tetrabutylammonium fluoride (2.1 mL, C = 1.0 mol L^{-1} in THF) was added to a solution of 5,10,15,20-tetra[4-(trimethylsilylethynyl)phenyl]porphyrin (270 mg, 0.27 mmol) in THF (20 mL) with vigorous stirring. After 2 h, glacial acetic acid (1 mL) was added and the reaction mixture was filtered through a silica funnel using CH_2Cl_2 as eluent to afford target product as a purple crystalline solid (190 mg, 99%).^{1}H NMR (300 MHz, $CDCl_3$): δ –2.83 (s, 2H), 3.32 (s, 4H), 7.90 (d, J = 9.0 Hz, 8H), 8.17 (d, J = 9.0 Hz, 8H), 8.84 (s, 8H) ppm. Anal. Calcd for $C_{52}H_{30}N_4$ (710.8): C, 87.86; H, 4.25; N, 7.88. Found: C, 87.93; H, 5.23; N, 7.79. MALDI-TOF MS: m/z 710.25, calcd. for $C_{52}H_{30}N_4$; found, $[M]^+$ 710.42. FT-IR (KBr):ν 651, 727, 802, 854, 964, 999, 1218, 1259, 1351, 1397, 1472, 1520, 1559, 1600, 1693, 1814, 2014, 3034, 3271 cm^{-1}.

Section B. The electronic adsorption properties of HP_E-CMP

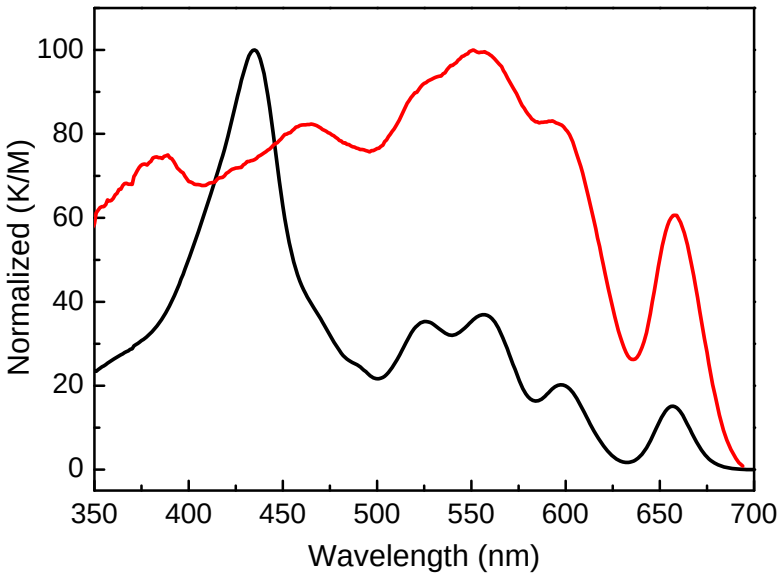


Fig. S1 The absorption spectra of HP_E-CMP (red line) and its monomer (black line).

Section C. The stability of HP_E-CMP

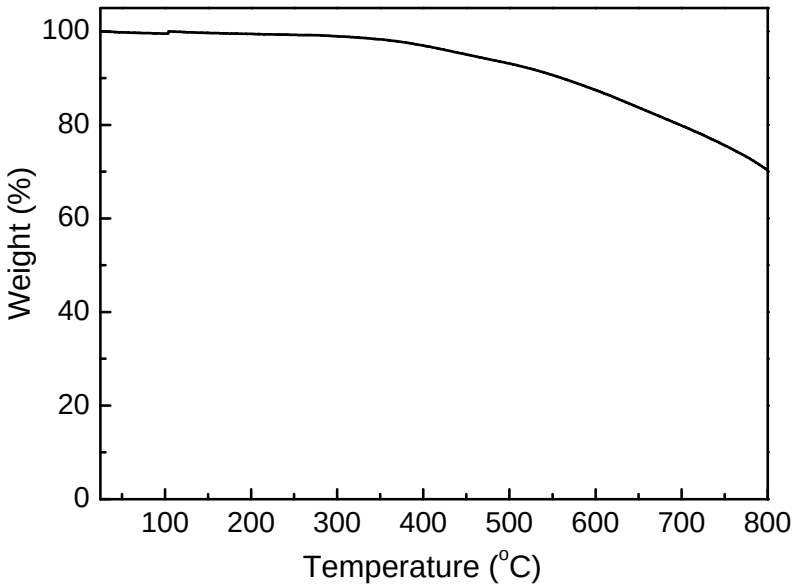


Fig. S2 TGA curve of HP_E-CMP under nitrogen.

Section D. The crystallinity of HP_E-CMP

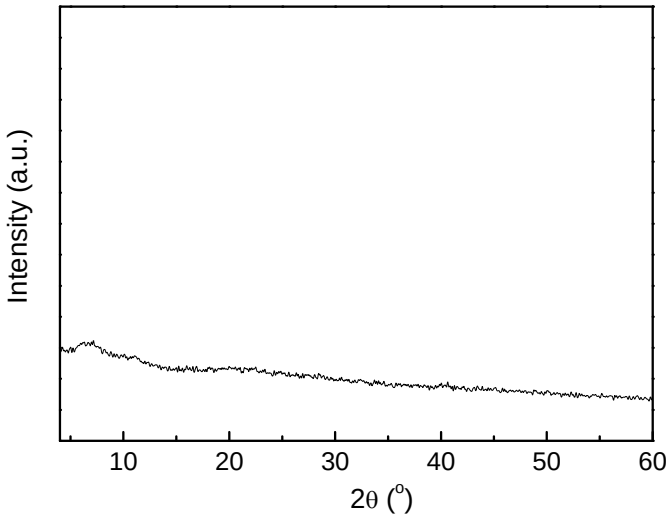


Fig. S3 P-XRD curve of HP_E-CMP.

Section E. EDS spectrum of HP_E-CMP

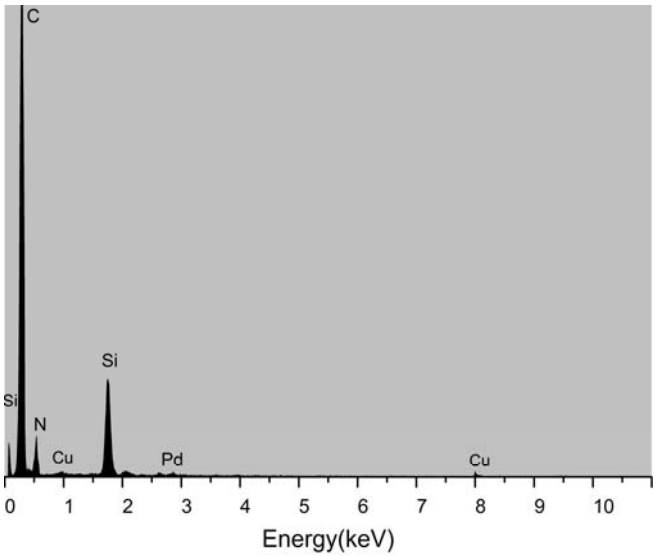


Fig. S4 EDS spectrum of conjugated microporous polymer HP_E-CMP. The low palladium and copper contents are due to the incomplete washing after cross-coupling reaction. The silicon element is from silicon substrate.

Section F. FT-IR spectra for HP_E-CMP

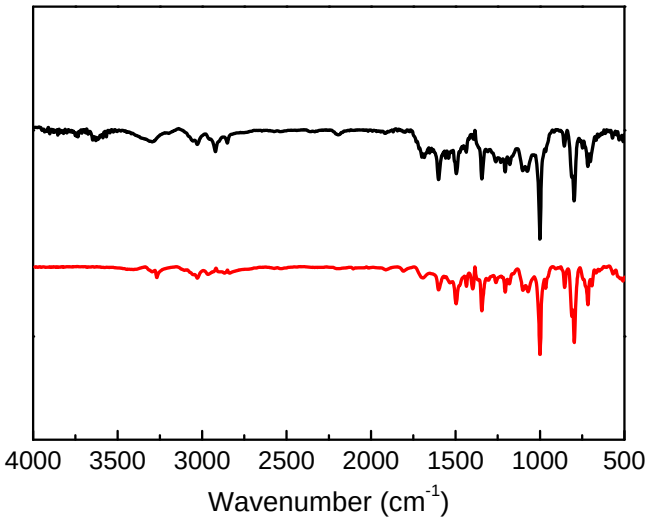
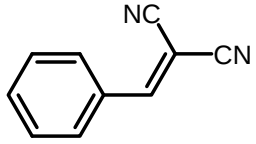


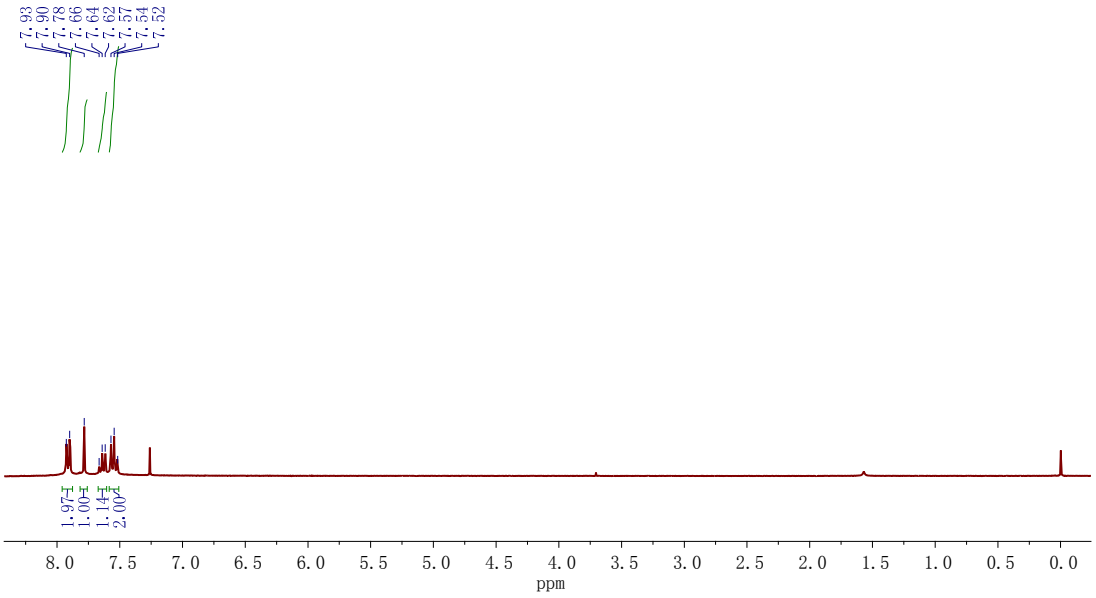
Fig. S5 IR spectra of HP_E-CMP samples fresh (red line) and after ten-time catalytic reaction (black line). It is evident that the structure of HP_E-CMP was maintained after catalytic reactions.

Section G. The characterization of products

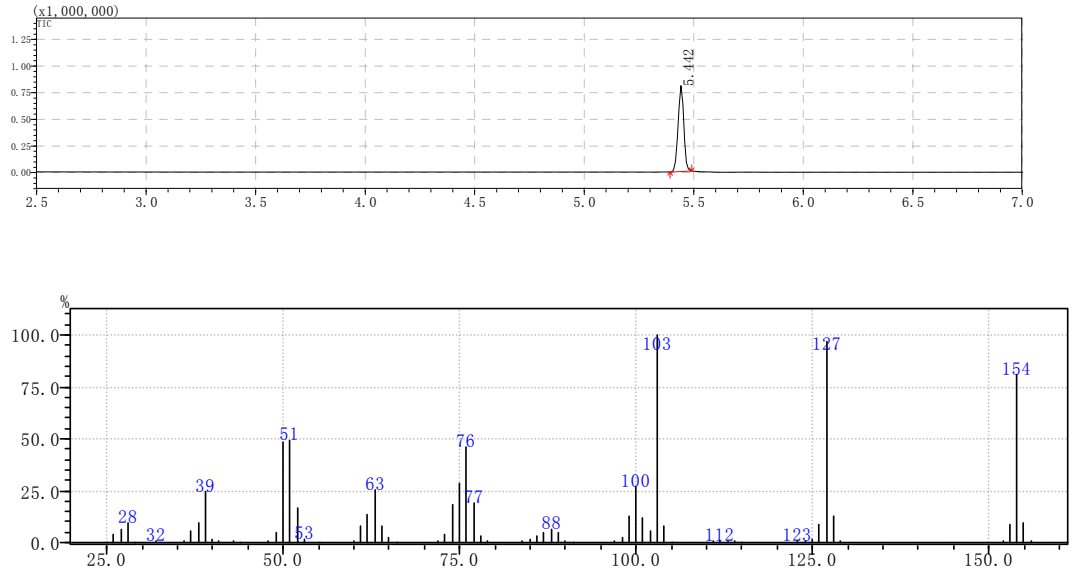


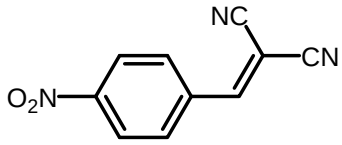
2a: White solid; m.p. 83-84 °C (lit.,[2] 84 °C); ^{1}H NMR (300MHz, $CDCl_3$) δ 7.54 (t, *J* = 9.0 Hz, *J* = 6.0 Hz, 2H), 7.64 (t, *J* = 6.0 Hz, 1H), 7.78 (s, 1H), 7.92 (d, J = 9.0 Hz, 2H) ppm. GC-MS retention time 5.442 min., m/z (EI) 154 (M+, 81), 127 (98), 103 (100).

^{1}H-NMR spectrum of 2a



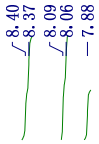
GC-MS spectra of 2a

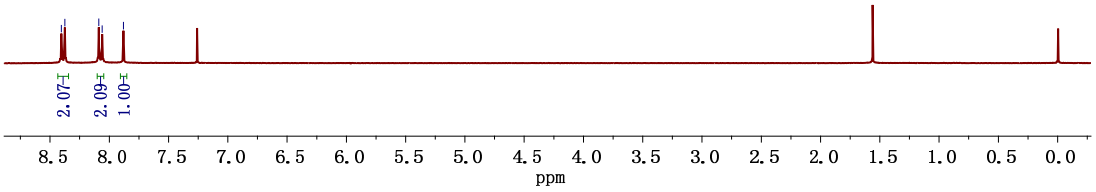




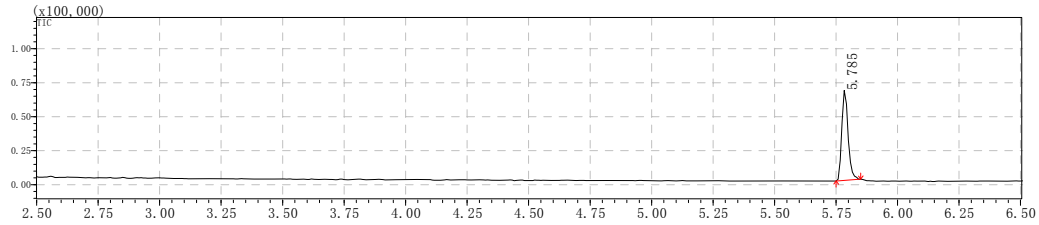
2b: Pale solid; m.p. 164-166 °C (lit.,[3] 167-168 °C); ^{1}H NMR (300MHz, $CDCl_3$) δ 7.88 (s, 1H), 8.08 (d, J = 9.0 Hz, 2H), 8.39 (d, J = 9.0 Hz, 2H) ppm. GC-MS retention time 5.785 min., m/z (EI) 199 (M+, 13), 153 (16), 141 (23), 126 (35), 114 (28), 100 (29), 75 (49), 63 (29).

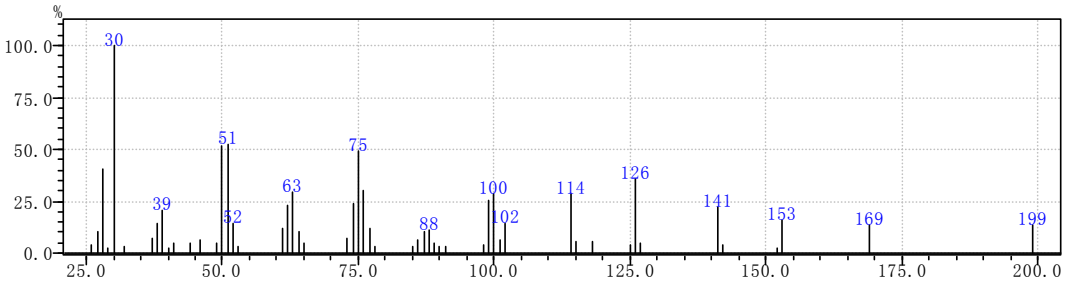
^{1}H-NMR spectrum of 2b

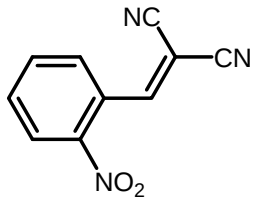




GC-MS spectra of 2b

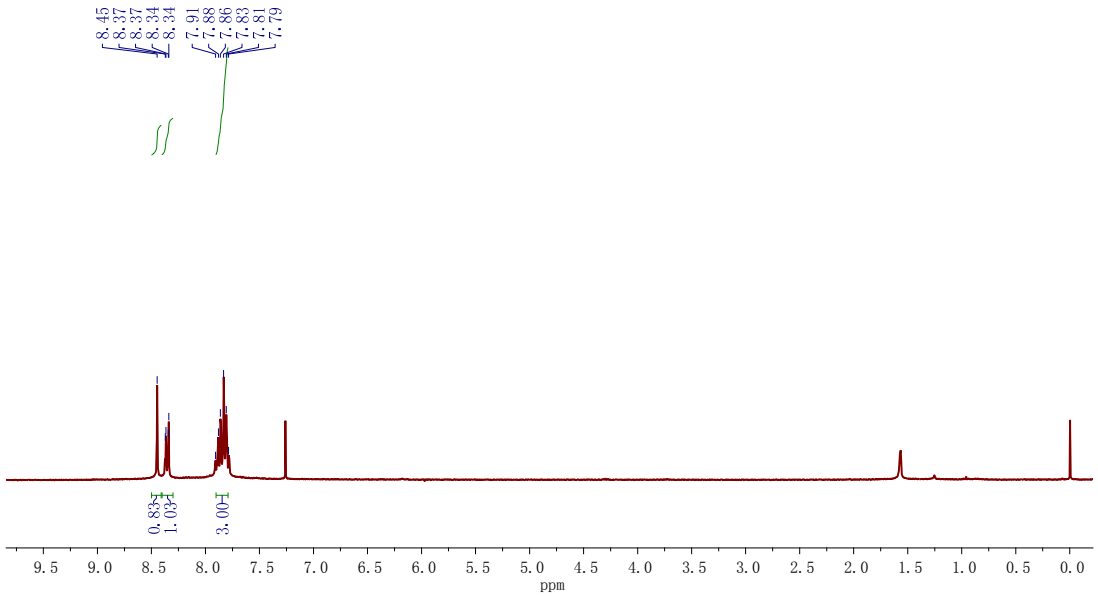




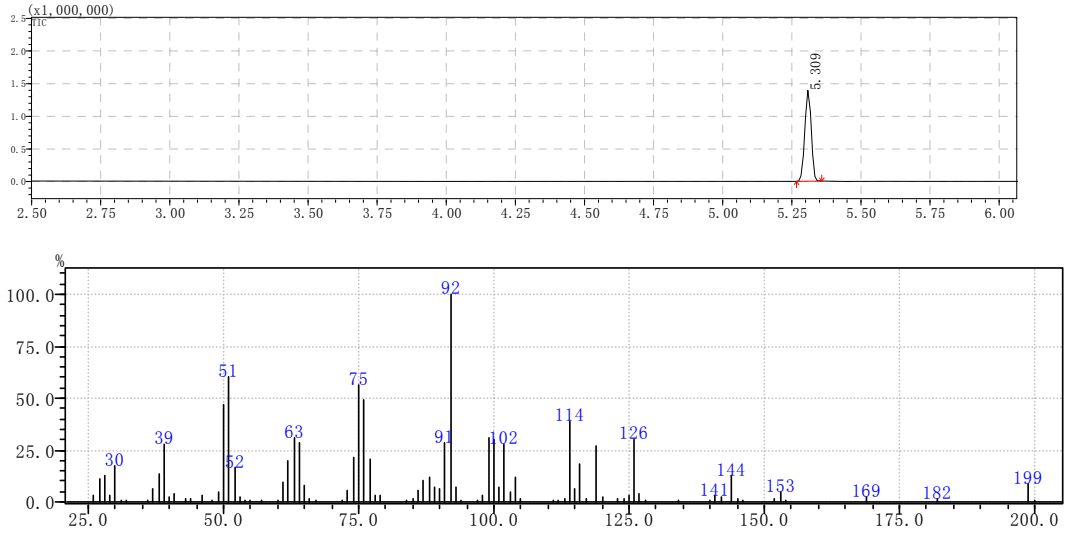


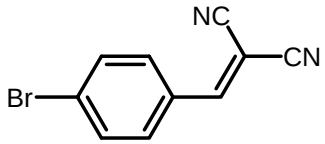
2c: White solid; m.p. 135-136 °C (lit.,[4] 136-138 °C); ^{1}H NMR (300MHz, $CDCl_3$) δ 7.81–7.88 (m, 5H), 8.35 (d, *J* = 9.0 Hz, 1H), 8.45 (s, 1H) ppm. GC-MS retention time 5.309 min., m/z (EI) 199 (M+, 16), 144 (18), 126 (39), 114 (47), 92 (100), 75 (53), 51 (50).

^{1}H-NMR spectrum of 2c



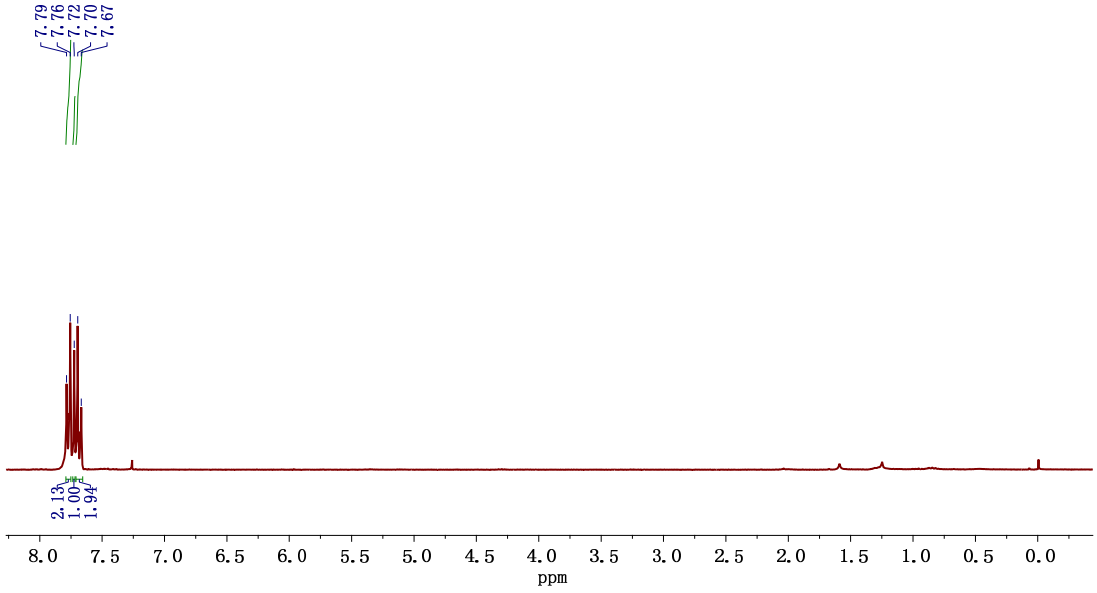
GC-MS spectra of 2c



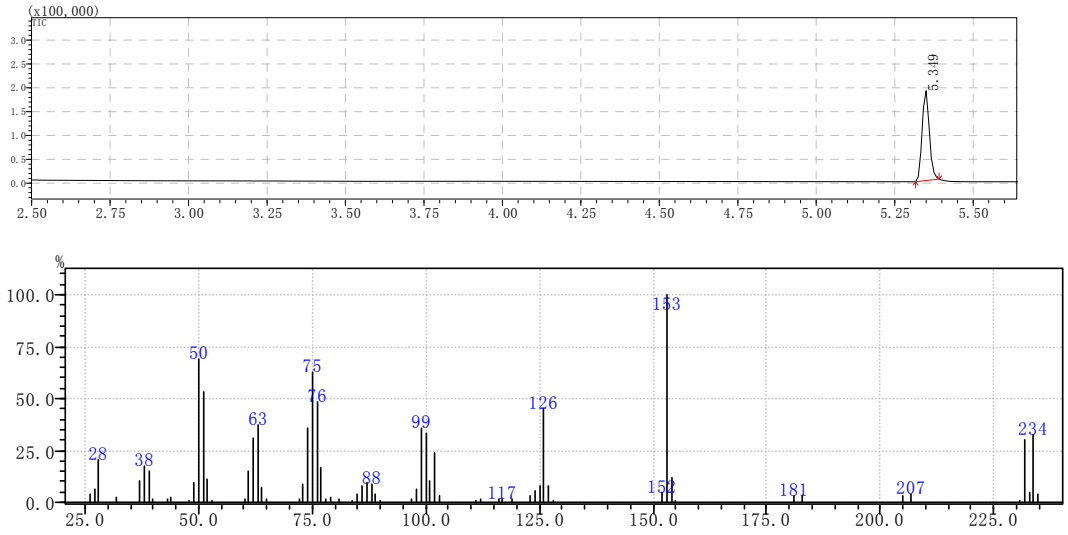


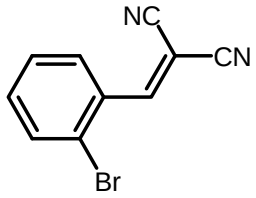
2d: White solid; m.p. 155-157 °C (lit.,[5] 159-161 °C); ^{1}H NMR (300MHz, $CDCl_3$) δ 7.69 (d, *J* = 9.0 Hz, 2H), 7.72 (s, 1H), 7.78 (d, *J* = 9.0 Hz, 2H) ppm. GC-MS retention time 5.349 min., m/z (EI) 234 (M+, 32), 153 (100), 126 (45), 99 (36), 75 (63), 63 (38), 50 (69).

^{1}H-NMR spectrum of 2d



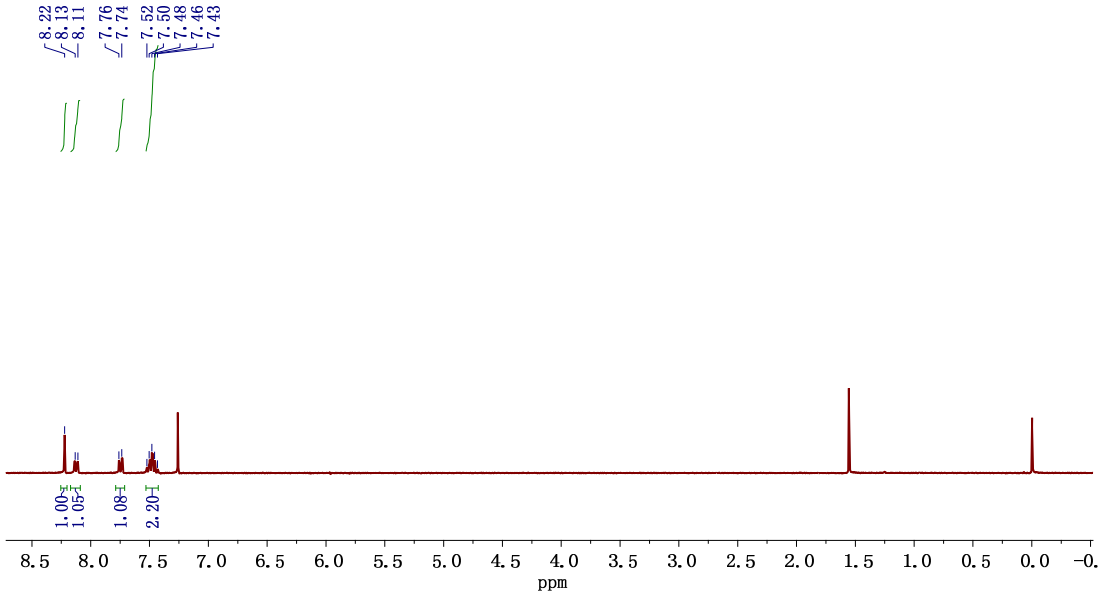
GC-MS spectra of 2d



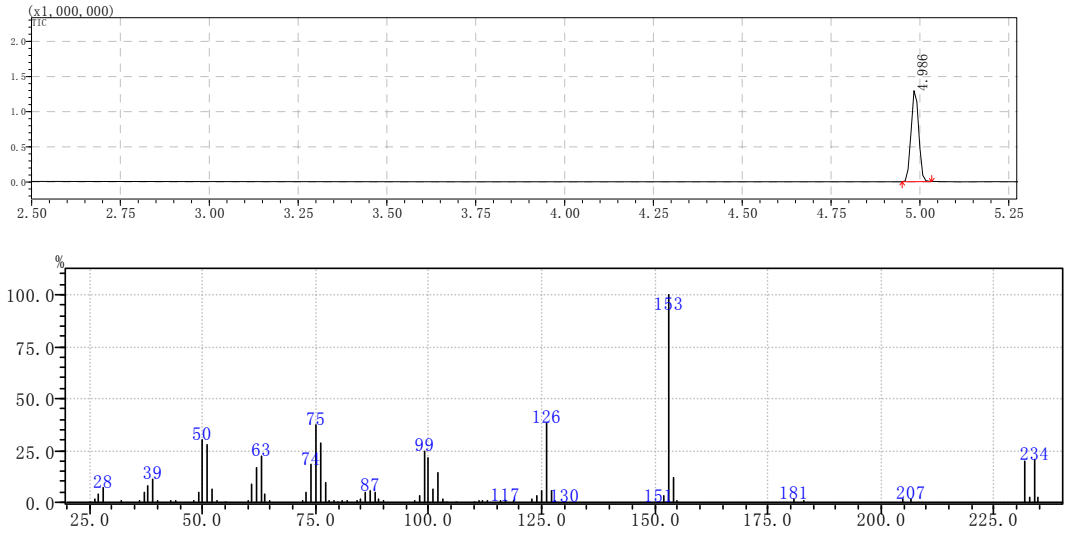


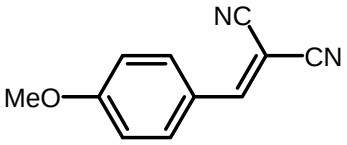
2e: White solid; m.p. 90-92 °C (lit.,[5] 92-93 °C); ^{1}H NMR (300MHz, $CDCl_3$) δ 7.48 (m, 2H), 7.75 (d, *J* = 6.0 Hz, 1H), 8.12 (d, *J* = 6.0 Hz, 1H), 8.22 (s, 1H) ppm. GC-MS retention time 4.986 min., m/z (EI) 234 (M+, 21), 153 (100), 126 (38), 99 (24), 75 (37), 63 (22), 50 (30).

^{1}H-NMR spectrum of 2e



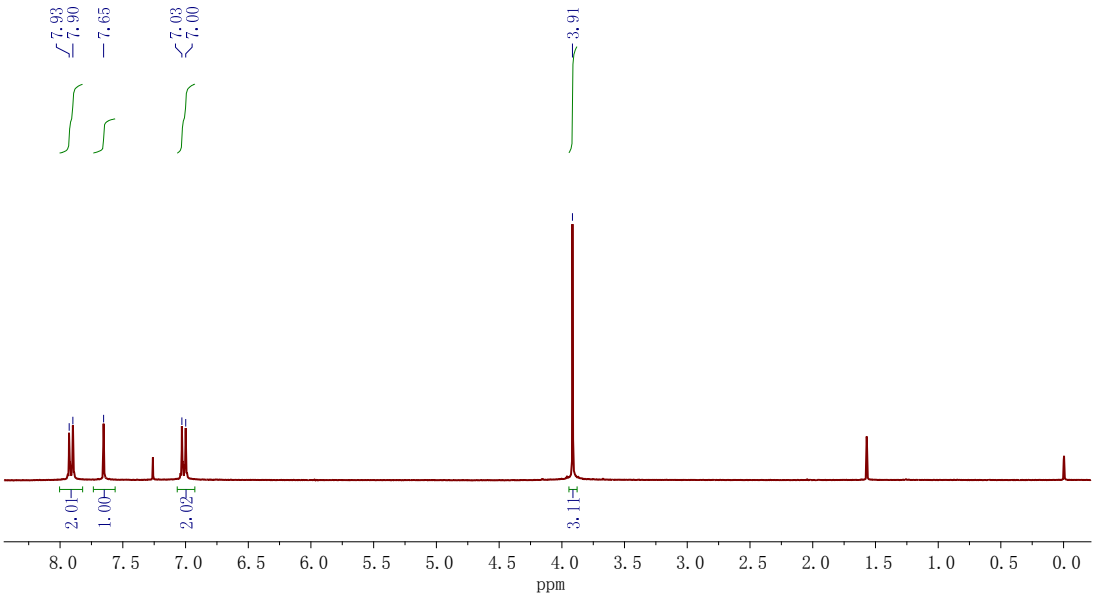
GC-MS spectra of 2e



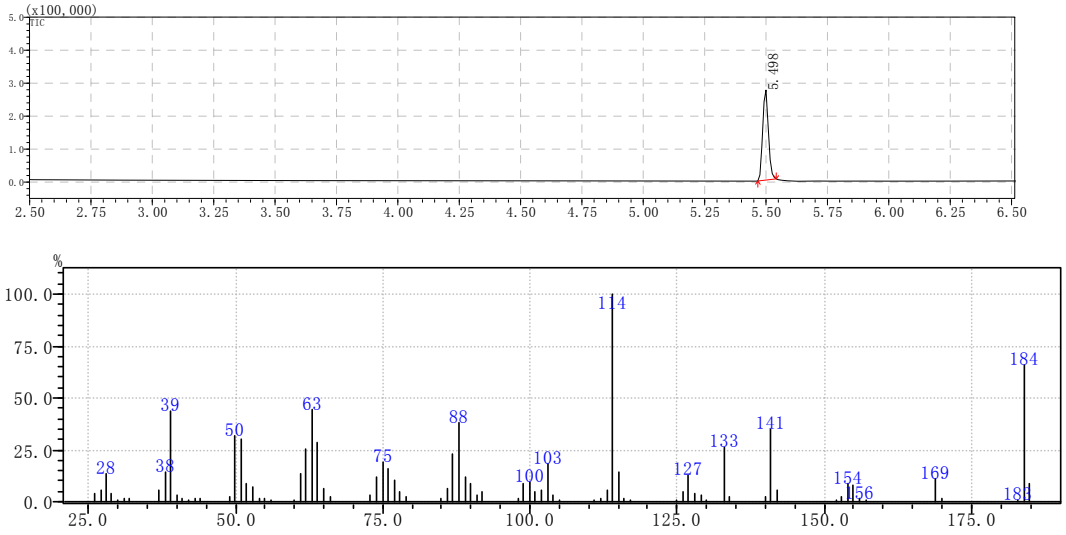


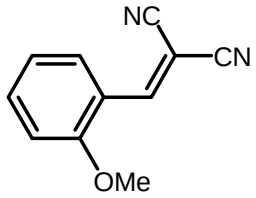
2f: Yellow solid; m.p. 114-115 °C (lit.,[2] 116 °C); ^{1}H NMR (300MHz, $CDCl_3$) δ 3.91 (s, 3H), 7.02 (d, *J* = 9.0 Hz, 2H), 7.65 (s, 1H), 7.92 (d, *J* = 9.0 Hz, 2H) ppm. GC-MS retention time 5.498 min., m/z (EI) 184 (M+, 66), 141 (35), 133 (26), 114 (100), 88 (38), 64 (28).

^{1}H-NMR spectrum of 2f



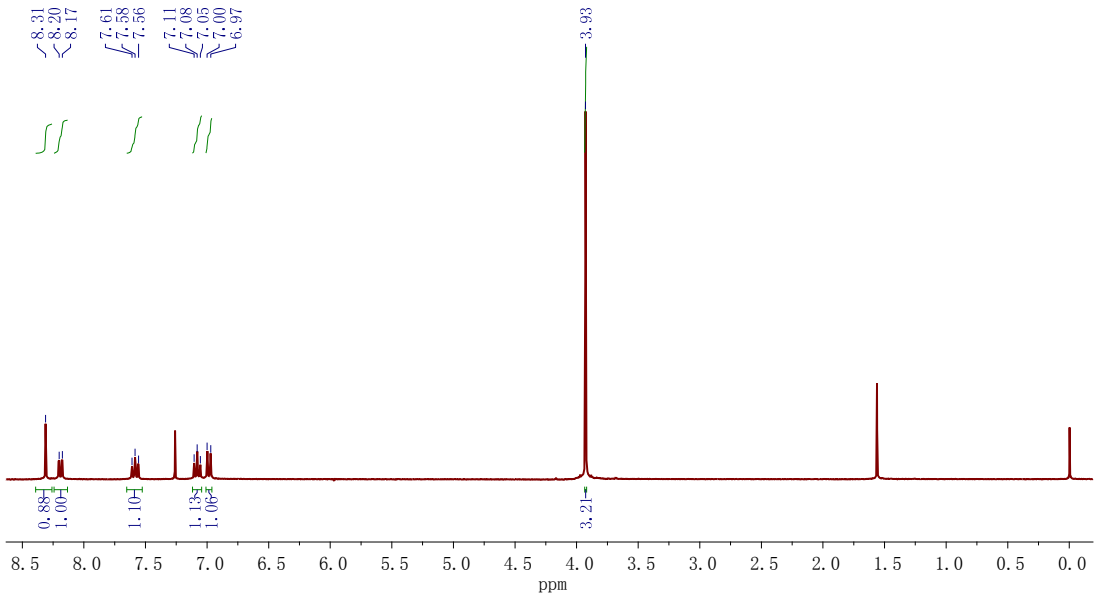
GC-MS spectra of 2f



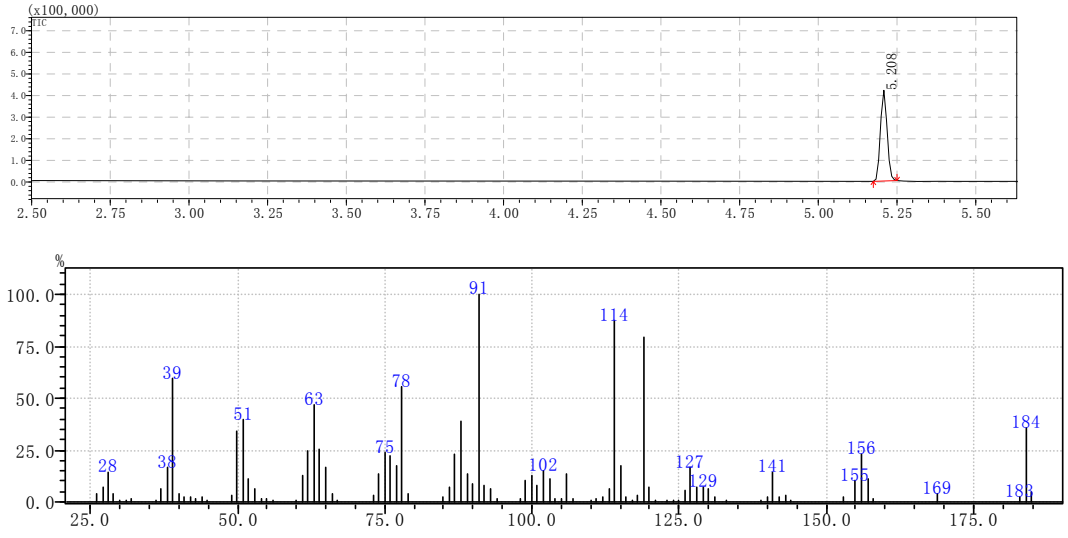


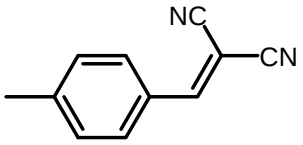
2g: Pale yellow solid; m.p. 79-80 °C (lit.,[6] 79-80 °C); ^{1}H NMR (300MHz, $CDCl_3$) δ 3.93 (s, 3H), 6.99 (d, *J* = 9.0 Hz, 1H), 7.08 (t, *J* = 9.0 Hz, 1H), 7.58 (t, J = 9.0 Hz, 1H), 8.19 (d, J = 9.0 Hz, 1H), 8.31 (s, 1H) ppm. GC-MS retention time 5.208 min., m/z (EI) 184 (M+, 36), 119 (79), 114 (87), 91 (100), 88 (39), 78 (56), 63 (47), 51 (40).

^{1}H-NMR spectrum of 2g



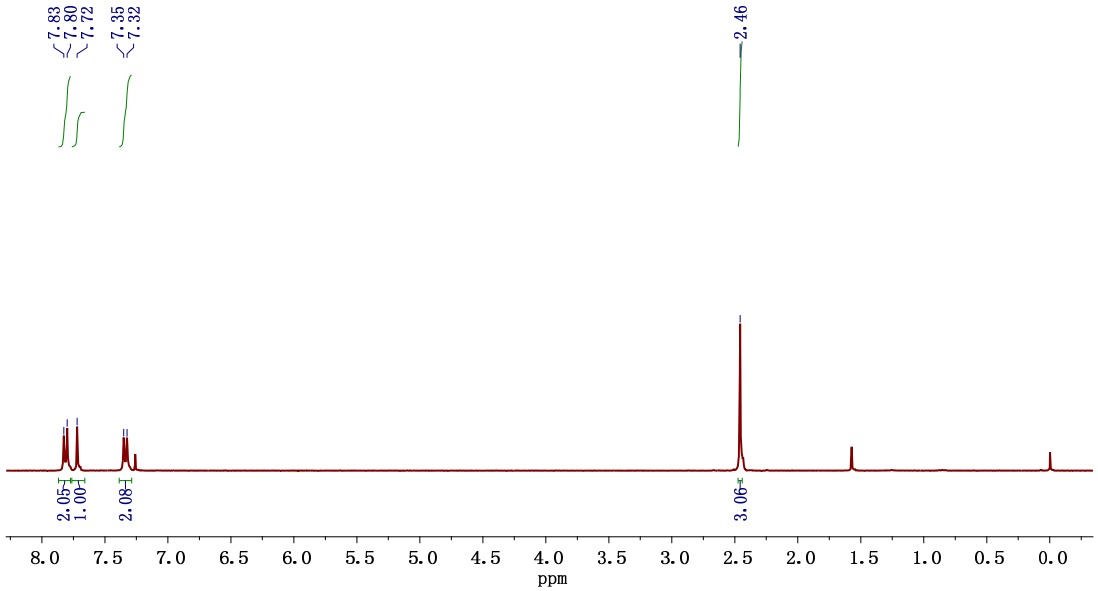
GC-MS spectra of 2g



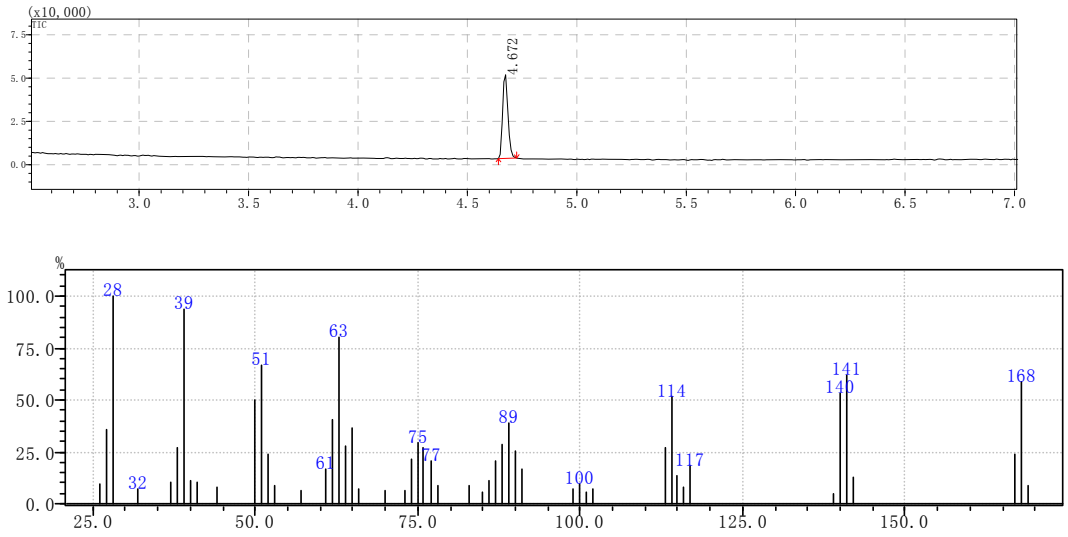


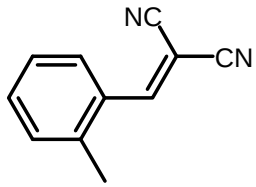
2h: White solid; m.p. 130-131 °C (lit.,[3] 132-134 °C); ^{1}H NMR (300MHz, $CDCl_3$) δ 2.46 (s, 3H), 7.34 (d, *J* = 9.0 Hz, 2H), 7.72 (s, 1H), 7.82 (d, *J* = 9.0 Hz, 2H) ppm. GC-MS retention time 4.672 min., m/z (EI) 168 (M+, 59), 141 (63), 114 (51), 63 (75), 51 (63).

^{1}H-NMR spectrum of 2h



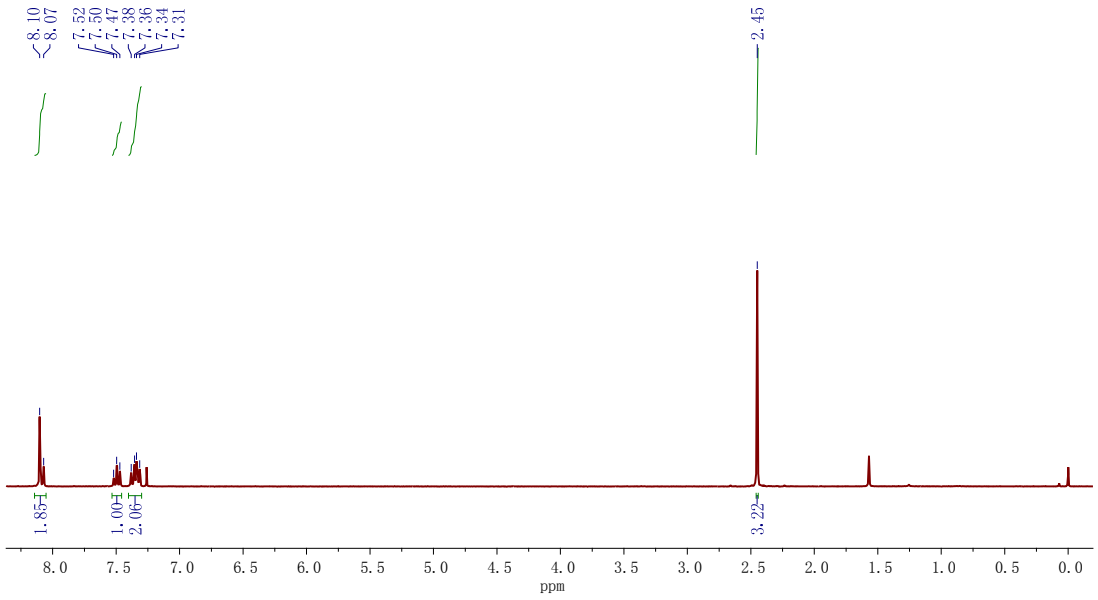
GC-MS spectra of 2h



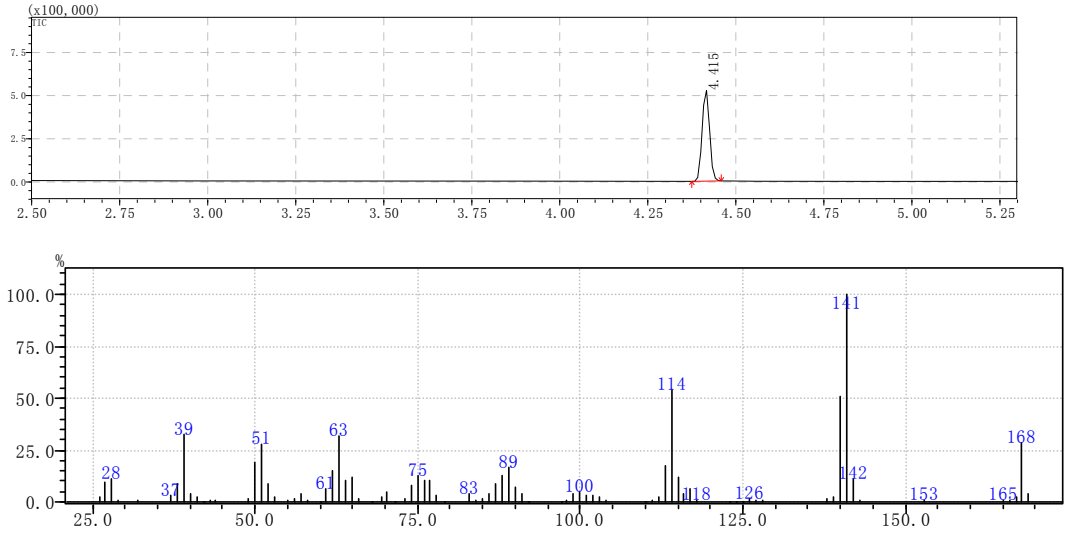


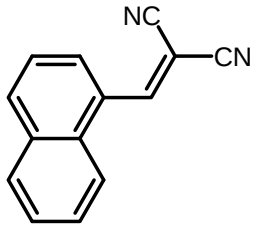
2i: White solid; m.p. 101-102 °C (lit.,[7] 101-104 °C); ^{1}H NMR (300MHz, $CDCl_3$) δ 2.45 (s, 3H), 7.31–7.38 (m, 2H), 7.50 (m, *J* = 9.0 Hz, *J* = 6.0 Hz, 1H), 8.08 (d, J = 9.0 Hz, 1H), 8.10 (s, 1H) ppm. GC-MS retention time 4.415 min., m/z (EI) 168 (M+, 29), 141 (100), 114 (54), 89 (17), 63 (31), 51 (28).

^{1}H-NMR spectrum of 2i



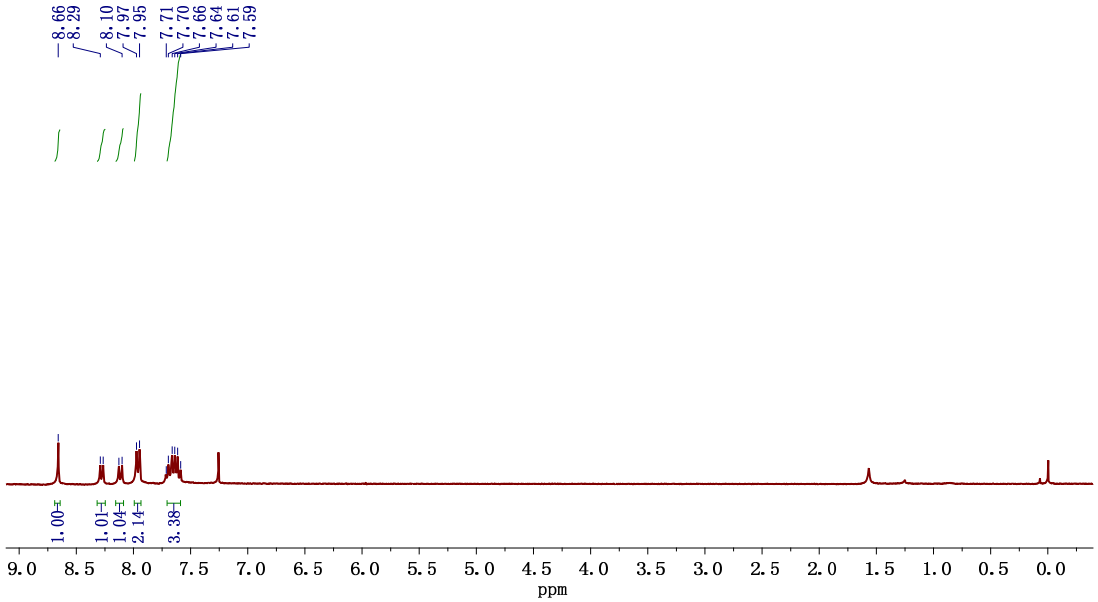
GC-MS spectra of 2i



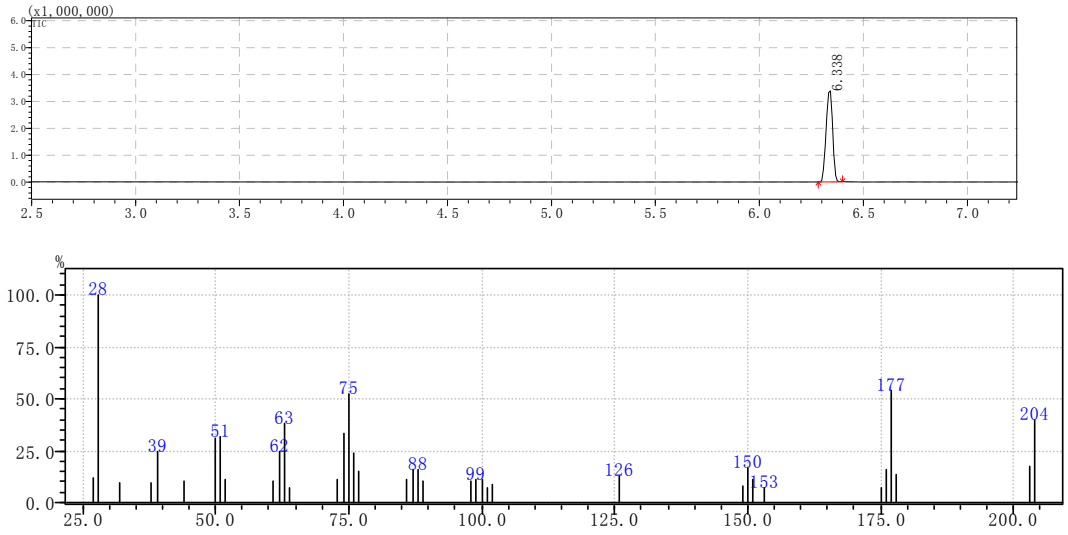


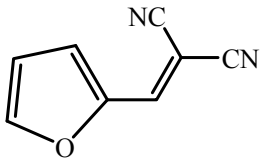
2j: Bright orange solid; m.p. 164-165 °C (lit.,[8] 168-169 °C); ^{1}H NMR (300MHz, $CDCl_3$) δ 7.59–7.71 (m, 3H), 7.96 (d, *J* = 6.0 Hz, 2H), 8.12 (d, 6.0 Hz, 1H), 8.28 (d, 6.0 Hz, 1H), 8.66 (s, 1H) ppm. GC-MS retention time 6.338 min., m/z (EI) 204 (M+, 40), 177 (54), 150 (17), 126 (13), 75 (52), 63 (38), 51 (32).

^{1}H-NMR spectrum of 2j



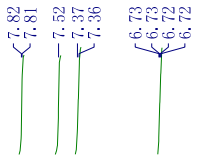
GC-MS spectra of 2j

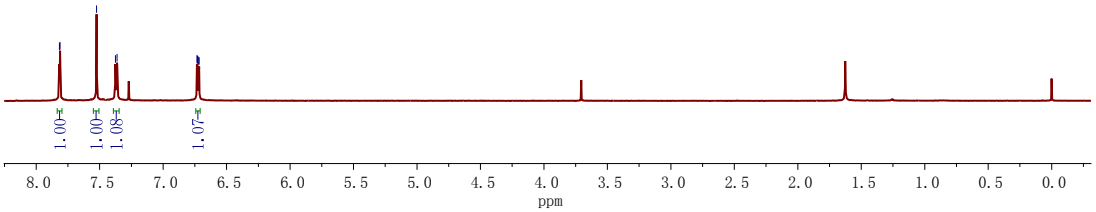




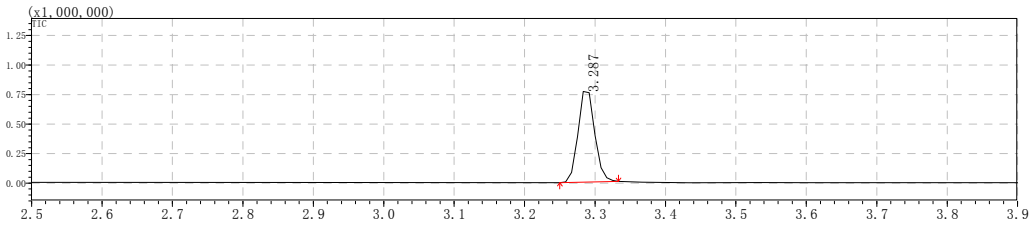
2k: Light pink solid; m.p. 70-71 °C (lit.,[9] 72-73 °C); ^{1}H NMR (300MHz, $CDCl_3$) δ 6.72 (dd, 1H), 7.36 (d, *J* = 3.0 Hz, 1H), 7.52 (s, 1H), 7.81 (d, 3.0 Hz, 1H) ppm. GC-MS retention time 3.287 min., m/z (EI) 144 (M+, 100), 115 (59), 89 (68), 62 (53).

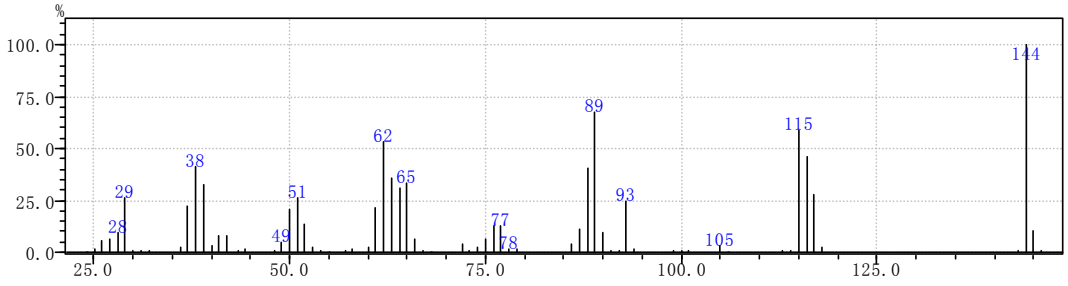
^{1}H-NMR spectrum of 2k

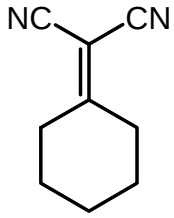




GC-MS spectra of 2k

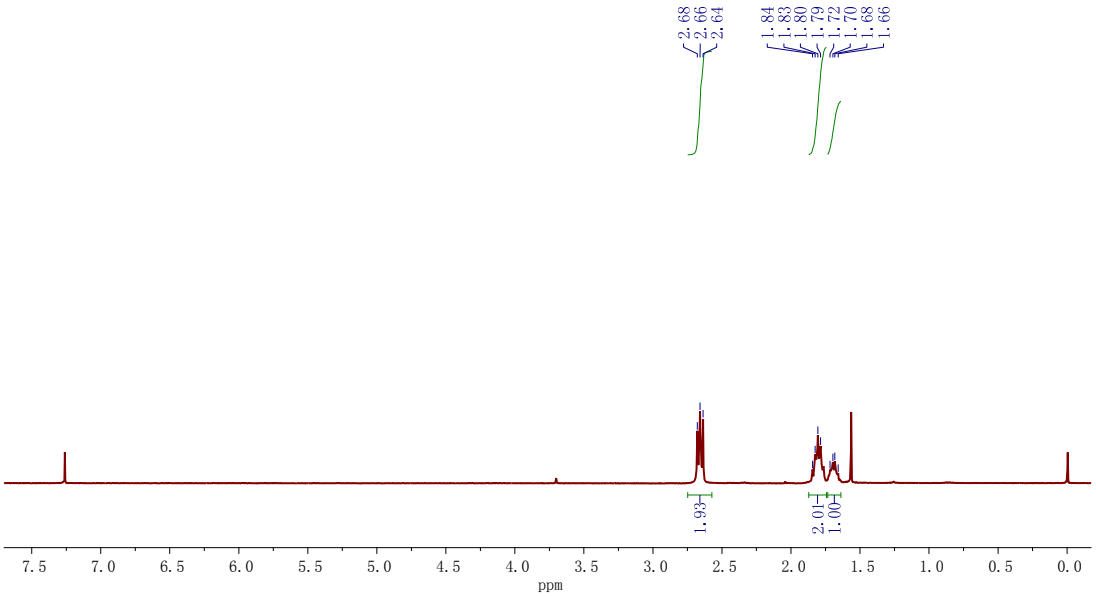




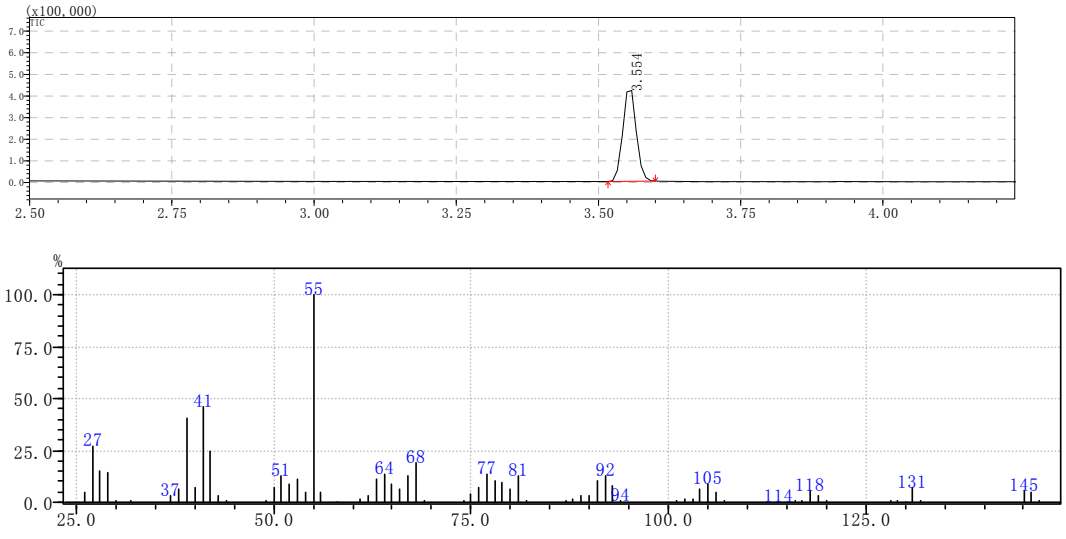


2l: Light yellow oil; ^{1}H NMR (300MHz, $CDCl_3$) δ 1.68 (t, 2H), 1.83 (t, 4H), 2.66 (t, J = 6.0 Hz, 4H) ppm. GC-MS retention time 3.554 min., m/z (EI) 146 (M+, 5.01), 92 (13), 81 (13), 68 (19), 55 (100).

^{1}H-NMR spectrum of 2l



GC-MS spectra of 2l



Section H. References

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