Supporting Information

WATER ASSISTED AND CHOLINE CHLORIDE-DIMETHYLUREA DEEP EUTECTIC SALTS AS CATALYST TOWARDS THE ATTRACTIVE REACTION OF INDOLE, BENZALDEHYDE, AND MALONONITRILE

Hongli Ruan, Yue Lv, Shijun Yu, Chengwei Lv,* Yue An*

School of Chemistry and Chemical Engineering, Liaoning Normal University, Dalian 116029, People's Republic of China

*E-mail: chengweilv@126.com; 18018928980@163.com

General information

Commercial solvents and reagents were used as received, except for benzaldehyde, which was used as a fresh distilled sample. Melting points were measured on Beijing Tech X-5 melting point detector and were uncorrected. FT-IR spectras were determined on Bruker Shimadzu IR-460 spectrometer. ^{1}H and ^{13}C NMR spectras were recorded on Bruker Avance 500 MHz or Bruker Avance III 400 MHz. X-ray crystal spectra was obtained on Bruker Smart APEX II. High resolution mass spectra (HRMS) were obtained on an Agilent 6540 UHD Q-TOF mass spectrometer.

Deep eutectic solvent preparation

The catalyst was prepared in accordance with the literature 1. Choline chloride (4 mmol) and 1,3-dimethylurea (8 mmol) were added to a 50 mL round-bottom flask, then this mixture was stirred at 80 ^{o}C for 30 min. After slowly cooled to room temperature, the solid was dried at 50 ^{o}C for 6 h to afford the DES.

General procedure for the synthesis of 4a-4r

0.50 mmol Aldehyde, 0.50 mmol malononitrile, and 0.10 mmol catalyst were taken in 1 mL solvent (EtOH:H_2O 4:1, v/v). This solution was stirred in a 10 mL pressure tube at the stipulated temperature mentioned in Table 2 for 10 min, then 0.55 mmol indole was added and continuously reacted. After completion, 0.6 mL water and 0.4 mL ethanol was added and vigorously stirred for 10 min to remove the impurity and catalyst. This mixture was filtered and the precipitate was washed with 50% cold aqueous ethanol. Most of the desired products could be collected without further purification. When necessary, product was separated by silica gel column chromatography with petroleum ether/ethyl acetate as eluent.

General procedure for the synthesis of 5a-5i

0.50 mmol Aldehyde, 0.55 mmol Meldrum's acid, and 0.10 mmol catalyst were taken in 2 mL solvent (EtOH:H_2O 4:1, v/v). This solution was stirred in a 10 mL

pressure tube at 40 °C for 10 min, then 0.50 mmol indole was added and continuously reacted. After completion of the reaction, 1.0 mL 40% ethanol was added and vigorously stirred for 10 min to remove the impurity and catalyst. The mixture was filtered on Büchner funnel after cooling in ice bath. The precipitate was washed with 70% cold aqueous ethanol without further purification to afford the desired products.

1. (a) J.M. Pérez, and D.J. Ramón, *ACS Sustainable Chem. Eng*. 2015, **3**, 2343;
(b) M.A. Bakht, M.J. Ansari, Y. Riadi, et al., *J. Mol. Liq*., 2016, **224**, 1249;
(c) N. Azizi, and M. Edrisi, *Res. Chem. Intermed*., 2017, **43**, 379.

^{1}H NMR and ^{13}C NMR spectra data of 4a-4r

2-((1H-indol-3-yl)(phenyl)methyl)malononitrile, ***4a*** IR (KBr) *v*: 3348, 3039, 2885, 2260 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) *δ*: 8.27 (s, 1H), 7.31-7.48 (m, 9H), 7.10 (t, *J* = 7.5 Hz, 1H), 4.96 (d, *J* = 6.2 Hz, 1H), 4.47 (d, *J* = 6.2 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) *δ*: 131.9, 131.0, 123.9, 123.5, 122.9, 120.6, 117.9, 116.9, 115.1, 113.4, 107.3, 107.0, 106.9, 106.3, 38.9, 24.3.

2-((1H-indol-3-yl)(o-tolyl)methyl)malononitrile, ***4b*** IR (KBr) *v*: 3408, 3058, 2902, 2256 cm^{-1}; ^{1}H NMR (500 MHz, DMSO-d_6) *δ*: 11.18 (s, 1H), 7.50-7.37 (m, 4H), 7.25-7.17 (m, 3H), 7.09 (t, *J* = 7.6 Hz, 1H), 6.97 (t, *J* = 7.5 Hz, 1H), 5.80 (d, *J* = 9.4 Hz, 1H), 5.37 (d, *J* = 9.5 Hz, 1H), 2.45 (s, 3H); ^{13}C NMR (125 MHz, DMSO-d_6) *δ*: 137.3, 136.1, 136.0, 130.7, 127.4, 126.5, 126.2, 125.8, 123.8, 121.5, 118.9, 118.4, 114.0, 113.9, 112.0, 111.7, 38.4, 28.2, 19.3.

2-((1H-indol-3-yl)(m-tolyl)methyl)malononitrile, ***4c*** IR (KBr) *v*: 3350, 3057, 2883, 2221 cm^{-1}; ^{1}H NMR (500 MHz, DMSO-d_6) *δ*: 11.18 (s, 1H), 7.54 (s, 1H), 7.49 (d, *J* = 8.0 Hz, 1H), 7.39-7.24 (m, 4H), 7.09 (t, *J* = 7.8 Hz, 2H), 6.96 (t, *J* = 7.5 Hz, 1H), 5.81 (d, *J* = 9.3 Hz, 1H), 5.15 (d, *J* = 9.4 Hz, 1H), 2.28 (s, 3H); ^{13}C NMR (125 MHz, DMSO-d_6) *δ*: 139.2, 137.7, 136.1, 128.5, 128.4, 125.9, 125.0, 122.7, 121.6, 118.9, 118.5, 114.1, 113.8, 112.4, 111.6, 42.5, 28.7, 21.0.

2-((1H-indol-3-yl)(p-tolyl)methyl)malononitrile, ***4d*** IR (KBr) *v*: 3350, 3035, 2883, 2223 cm^{-1}; ^{1}H NMR (500 MHz, DMSO-d_6) *δ*: 11.17 (s, 1H), 7.52 (s, 1H), 7.44 (d, *J* = 8.0 Hz, 1H), 7.38 (d, *J* = 7.4 Hz, 3H), 7.17 (d, *J* = 7.7 Hz, 2H), 7.09 (t, *J* = 7.5 Hz, 1H), 6.95 (t, *J* = 7.4 Hz, 1H), 5.78 (d, *J* = 9.1 Hz, 1H), 5.14 (d, *J* = 9.1 Hz, 1H), 2.27 (s, 3H); ^{13}C NMR (125 MHz, DMSO-d_6) *δ*: 136.9, 136.2, 136.1, 129.1, 127.9, 125.9, 122.6, 121.6, 118.8, 118.6, 114.0, 113.8, 112.5, 111.6, 42.2, 28.7, 20.6.

2-((1H-indol-3-yl)(2-methoxyphenyl)methyl)malononitrile, ***4e*** IR (KBr) *v*: 3375, 3058, 2842, 2260 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) *δ*: 8.29(s, 1H), 7.59 (d, *J* = 2.0 Hz, 1H), 7.45-7.31 (m, 3H), 7.26-6.88 (m, 6H), 5.43 (d, *J* = 6.2 Hz, 1H), 4.74 (d, *J* = 6.2 Hz, 1H), 4.00 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) *δ*: 156.0, 135.6, 129.3, 129.2, 125.9, 124.7, 122.4, 121.9, 120.7, 119.6, 118.3, 112.2, 112.2, 111.1, 110.9, 110.2, 55.1, 37.1, 27.0.

2-((1H-indol-3-yl)(3-methoxyphenyl)methyl)malononitrile, ***4f*** IR (KBr) *v*: 3344, 3058, 2885, 2262 cm-1; ^{1}H NMR (500 MHz, $CDCl_3$) *δ*: 8.26 (s, 1H), 7.44-7.31

(m, 4H), 7.25-6.90 (m, 5H), 4.91 (d, *J* = 4.9 Hz, 1H), 4.44 (d, *J* = 4.4 Hz, 1H), 3.80 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) *δ*: 159.6, 138.2, 136.2, 135.7, 129.7, 122.5, 121.7, 121.4, 119.9, 119.8, 119.4, 118.8, 118.2, 113.8, 113.3, 111.8, 111.1, 54.8, 43.6, 29.1.

2-((2-chlorophenyl)(1H-indol-3-yl)methyl)malononitrile, ***4g*** IR (KBr) *v*: 3346, 3064, 2891, 2262 cm-1; ^{1}H NMR (500 MHz, $CDCl_3$) *δ*: 8.35 (s, 1H), 7.53 (d, *J* = 7.9 Hz, 2H), 7.41-7.21 (m, 6H), 7.12 (t, *J* = 7.5 Hz, 1H), 5.60 (d, *J* = 6.0 Hz, 1H), 4.57 (d, *J* = 6.1 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) *δ*: 135.7, 134.2, 133.1, 129.7, 129.6, 129.4, 127.2, 125.5, 122.7, 122.0, 119.9, 118.1, 111.7, 111.6, 111.2, 110.5, 39.6, 27.3.

2-((3-chlorophenyl)(1H-indol-3-yl)methyl)malononitrile, ***4h*** IR (KBr) *v*: 3356, 3060, 2879, 2262 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) *δ*: 8.38 (s, 1H), 7.44-7.31 (m, 7H), 7.27-7.25 (m, 1H), 7.13-7.10 (m, 1H), 4.93 (d, *J* = 6.4 Hz, 1H), 4.45 (d, *J* = 6.4 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) *δ*: 138.6, 135.8, 134.6, 129.9, 128.6, 127.9, 125.9, 125.2, 122.8, 121.7, 120.0, 117.9, 111.4, 111.4, 111.3, 111.2, 43.2, 28.9.

2-((4-chlorophenyl)(1H-indol-3-yl)methyl)malononitrile, ***4i*** IR (KBr) *v*: 3329, 3035, 2915, 2223 cm^{-1}; ^{1}H NMR (500 MHz, DMSO-d_6) *δ*: 11.25 (s, 1H), 7.59-7.58 (m, 2H), 7.50 (t, *J* = 6.4 Hz, 2H), 7.43-7.36 (m, 3H), 7.11 (t, *J* = 6.4 Hz, 1H), 6.98 (t, *J* = 7.5 Hz, 1H), 5.89 (d, *J* = 9.5 Hz, 1H), 5.30 (d, *J* = 9.5 Hz, 1H); ^{13}C NMR (125 MHz, DMSO-d_6) *δ*: 141.7, 136.0, 133.2, 130.5, 127.9, 127.8, 126.8, 125.8, 122.8, 121.8, 119.0, 118.4, 113.8, 113.6, 111.7, 111.7, 43.9, 28.4.

2-((2-bromophenyl)(1H-indol-3-yl)methyl)malononitrile, ***4j*** IR (KBr) *v*: 3348, 3062, 2887, 2256 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) *δ*: 8.36 (s, 1H), 7.71 (d, *J* = 7.7 Hz, 1H), 7.56 (s, 1H), 7.42-7.28 (m, 4H), 7.25-7.21 (m, 2H), 7.12 (t, *J* = 7.5 Hz, 1H), 5.58 (d, *J* = 5.8 Hz, 1H), 4.57 (d, *J* = 5.9 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) *δ*: 135.7, 133.0, 129.8, 129.6, 127.9, 125.6, 123.8, 122.7, 122.0, 119.9, 118.2, 111.6, 111.5, 111.1, 110.6, 42.3, 27.3.

2-((3-bromophenyl)(1H-indol-3-yl)methyl)malononitrile, ***4k*** IR (KBr) *v*: 3356, 3060, 2881, 2260 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) *δ*: 8.35 (s, 1H), 7.57-7.28 (m, 8H), 7.13 (t, *J* = 6.7 Hz, 1H), 4.89 (s, 1H), 4.40 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) *δ*: 138.9, 135.8, 131.5, 130.7, 130.2, 126.3, 125.2, 122.8, 122.7, 121.7, 120.0, 118.0, 111.5, 111.2, 43.2, 28.9.

2-((1H-indol-3-yl)(3-nitrophenyl)methyl)malononitrile, ***4l*** IR (KBr) *v*: 3417, 3064, 2902, 2264 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) *δ*: 8.43 (s, 1H), 8.33 (s, 1H), 8.25 (d, *J* = 8.5 Hz, 1H), 7.85 (d, *J* = 7.7 Hz, 1H), 7.61 (t, *J* = 8.0 Hz, 1H), 7.45 (d, *J* = 10.1 Hz, 2H), 7.29-7.26 (m, 2H), 7.11 (t, *J* = 7.5 Hz, 1H), 5.07 (d, *J* = 6.4 Hz, 1H), 4.53 (d, *J* = 6.4 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) *δ*: 138.7, 135.8, 133.8, 129.8, 125.0, 123.4, 123.0, 122.8, 121.7, 120.2, 117.7, 111.3, 111.2, 111.1, 110.7, 43.2, 28.8.

2-((1H-indol-3-yl)(4-nitrophenyl)methyl)malononitrile, ***4m*** IR (KBr) *v*: 3424, 3051, 2891, 2227 cm^{-1}; ^{1}H NMR (500 MHz, DMSO-d_6) *δ*: 11.30 (s, 1H), 8.26 (d, *J* = 8.5 Hz, 2H), 7.80 (d, *J* = 8.5 Hz, 2H), 7.60 (s, 1H), 7.48 (t, *J* = 8.0 Hz, 1H), 7.40 (d, *J* = 8.2 Hz, 1H), 7.11 (t, *J* = 7.5 Hz, 1H), 6.97 (t, *J* = 7.5 Hz, 1H), 5.97 (d, *J* = 9.4 Hz, 1H), 5.50 (d, *J* = 9.4 Hz, 1H); ^{13}C NMR (125 MHz, DMSO-d_6) *δ*: 147.0, 146.6, 136.1, 129.4, 125.7, 123.8, 123.1, 121.8, 119.1, 118.3, 113.6, 113.5, 111.8, 111.2, 41.8, 28.1.

2-((2-methyl-1H-indol-3-yl)(phenyl)methyl)malononitrile, ***4n*** IR (KBr) *v*: 3384, 3057, 2908, 2256 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) *δ*: 8.07 (s, 1H), 7.47-7.30 (m, 8H), 7.18-7.15 (m, 1H), 7.08-7.05 (m, 1H), 4.98 (d, *J* = 9.4 Hz, 1H), 4.70 (d, *J* = 9.4 Hz, 1H), 2.46 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) *δ*: 136.7, 134.9, 133.5, 128.5, 127.5, 126.9, 125.7, 121.3, 119.6, 117.8, 112.3, 112.0, 110.5, 107.4, 43.7, 27.3, 11.8.

2-((2-methyl-1H-indol-3-yl)(m-tolyl)methyl)malononitrile, ***4o*** IR (KBr) *v*: 3369, 3068, 2916, 2254 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) *δ*: 8.03 (s, 1H), 7.40 (d, *J* = 8.0 Hz, 1H), 7.32-7.24 (m, 4H), 7.19-7.14 (m, 2H), 7.09 (t, *J* = 7.5 Hz, 1H), 4.94 (d, *J* = 9.5 Hz, 1H), 4.69 (d, *J* = 9.5 Hz, 1H), 2.44 (s, 3H), 2.36 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) *δ*: 138.3, 136.6, 134.9, 133.4, 128.3, 128.3, 127.8, 125.7, 123.7, 121.3, 119.6, 117.8, 112.3, 112.1, 110.5, 107.5, 43.7, 27.2, 21.0, 11.9.

2-((3-chlorophenyl)(2-methyl-1H-indol-3-yl)methyl)malononitrile, ***4p*** IR (KBr) *v*: 3404, 3057, 2918, 2256 cm^{-1}; ^{1}H NMR (500 MHz, DMSO-d_6) *δ*: 11.14 (s, 1H), 7.54 (d, *J* = 9.2 Hz, 2H), 7.48 (d, *J* = 7.8 Hz, 1H), 7.42 (t, *J* = 7.8 Hz, 1H), 7.35 (d, *J* = 8.0 Hz, 1H), 7.28 (d, *J* = 8.0 Hz, 1H), 7.02 (t, *J* = 7.5 Hz, 1H), 6.92 (t, *J* = 7.5 Hz, 1H), 6.02 (d, *J* = 10.7 Hz, 1H), 5.28 (d, *J* = 10.7 Hz, 1H), 2.49 (s, 3H); ^{13}C NMR (125 MHz, DMSO-d_6) *δ*: 141.3, 135.4, 134.6, 133.2, 130.4, 127.5, 127.3, 126.2, 125.6, 120.5, 118.9, 118.2, 114.0, 113.7, 111.0, 106.8, 42.1, 27.0, 11.7.

2-((3-bromophenyl)(2-methyl-1H-indol-3-yl)methyl)malononitrile, ***4q*** IR (KBr) *v*: 3394, 3064, 2912, 2256 cm^{-1}; ^{1}H NMR (500 MHz, DMSO-d_6) δ: 11.14 (s, 1H), 7.69 (s, 1H), 7.54 (t, *J* = 7.1 Hz, 2H), 7.48 (d, *J* = 8.0 Hz, 1H), 7.35 (t, *J* = 7.9 Hz, 1H), 7.28 (d, *J* = 8.0 Hz, 1H), 7.02 (t, *J* = 7.5 Hz, 1H), 6.92 (t, *J* = 7.5 Hz, 1H), 6.02 (d, *J* = 10.8 Hz, 1H), 5.27 (d, *J* = 10.7 Hz, 1H), 2.49 (s, 3H); ^{13}C NMR (125 MHz, DMSO-d_6) δ: 141.5, 135.4, 134.6, 130.6, 130.3, 130.2, 126.5, 125.6, 121.8, 120.5, 118.9, 118.2, 114.0, 113.7, 111.0, 106.8, 42.0, 27.0, 11.7; HRMS (ESI-MS) calcd. for $C_{19}H_{14}BrN_3$ $[M+H]^+$: 364.0444, found: 364.0444.

2-((2-methyl-1H-indol-3-yl)(4-nitrophenyl)methyl)malononitrile, ***4r*** IR (KBr) *v*: 3425, 3082, 2908, 2254 cm^{-1}; ^{1}H NMR (500 MHz, DMSO-d_6) δ: 11.19 (s, 1H), 8.25 (d, *J* = 8.4 Hz, 2H), 7.77 (d, *J* = 8.4 Hz, 2H), 7.51 (d, *J* = 8.0 Hz, 1H), 7.28 (d, *J* = 8.1 Hz, 1H), 7.02 (t, *J* = 7.5 Hz, 1H), 6.91 (t, *J* = 7.5 Hz, 1H), 6.10 (d, *J* = 10.6 Hz, 1H), 5.48 (d, *J* = 10.6 Hz, 1H), 2.51 (s, 3H); ^{13}C NMR (125 MHz, DMSO-d_6) δ: 146.6, 146.3, 135.4, 134.9, 128.8, 125.6, 123.70, 120.6, 118.9, 118.1, 113.9, 113.6, 111.0, 106.3, 42.2, 26.8, 11.7.

^{1}H NMR spectra data of 5a-5i

5-((1H-indol-3-yl)(phenyl)methyl)-2,2-dimethyl-1,3-dioxane-4,6-dione, ***5a*** m.p. 144-146 ^{o}C; IR (KBr) *v*: 3409, 3052, 2946, 1789, 1744 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 11.02 (s, 1H), 7.36 (d, *J* = 8.1 Hz, 1H), 7.30 (d, *J* = 7.4 Hz, 2H), 7.15-7.25 (m, 5H), 7.03 (t, *J* = 7.5 Hz, 1H), 6.87 (t, *J* = 7.4 Hz, 1H), 5.41 (d, *J* = 2.0 Hz, 1H), 5.24 (d, *J* = 2.8 Hz, 1H), 1.82 (s, 3H), 1.54 (s, 3H).

5-((1H-indol-3-yl)(m-tolyl)methyl)-2,2-dimethyl-1,3-dioxane-4,6-dione, ***5b*** m.p. 120-122 ^{o}C; IR (KBr) *v*: 3417, 3014, 2931, 1745, 1605 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 11.00 (s, 1H), 7.35 (d, *J* = 8.1 Hz, 1H), 7.19 (d, *J* = 7.0 Hz, 2H), 7.03-7.15 (m, 4H), 6.98 (d, *J* = 6.6 Hz, 1H), 6.87 (t, *J* = 7.4 Hz, 1H), 5.37 (d, *J* = 2.2 Hz, 1H), 5.20 (d, *J* = 2.8 Hz, 1H), 2.22 (s, 3H), 1.81 (s, 3H), 1.52 (s, 3H).

5-((1H-indol-3-yl)(p-tolyl)methyl)-2,2-dimethyl-1,3-dioxane-4,6-dione, ***5c*** m.p. 135-137 ^{o}C; IR (KBr) *v*: 3417, 3068, 2911, 1769, 1738 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 11.00 (s, 1H), 7.35 (d, *J* = 8.1 Hz, 1H), 7.15-7.21 (m, 4H), 7.02 (t, *J* = 8.2 Hz, 3H), 6.86 (t, *J* = 7.4 Hz, 1H), 5.37 (s, 1H), 5.20 (d, *J* = 2.8 Hz, 1H), 2.23 (s, 3H), 1.81, (s, 3H), 1.53 (s, 3H).

5-((1H-indol-3-yl)(3-methoxyphenyl)methyl)-2,2-dimethyl-1,3-dioxane-4,6-dione, ***5d*** m.p. 129-131 ºC; IR (KBr) *v*: 3427, 3065, 2938, 1790, 1746 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6) δ: 11.02 (s, 1H), 7.37 (d, *J* = 8.0 Hz, 1H), 7.22 (d, *J* = 8.1 Hz, 2H), 7.13 (t, *J* = 7.8 Hz, 1H), 7.04 (t, *J* = 7.4 Hz, 1H), 6.87-6.92 (m, 3H), 6.74 (d, *J* = 7.3 Hz, 1H), 5.40 (s, 1H), 5.24 (d, *J* = 2.3 Hz, 1H), 3.66 (s, 3H), 1.82 (s, 3H), 1.54 (s, 3H).

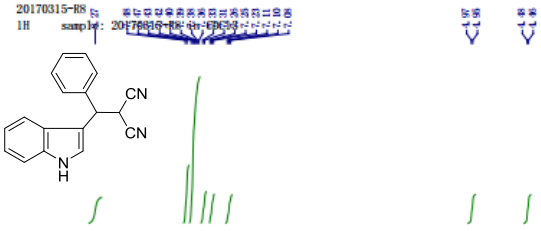
5-((2-chlorophenyl)(1H-indol-3-yl)methyl)-2,2-dimethyl-1,3-dioxane-4,6-dione, ***5e*** m.p. 140-142 ºC; IR (KBr) *v*: 3420, 3049, 2944, 1776, 1739 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6) δ: 11.08 (s, 1H), 7.46 (d, *J* = 7.6 Hz, 1H), 7.35-7.40 (m, 2H), 7.02-7.27 (m, 5H), 6.88 (t, *J* = 7.4 Hz, 1H), 5.78 (t, *J* = 3.2 Hz, 1H), 4.97 (t, *J* = 3.4 Hz, 1H), 1.82 (s, 3H), 1.64 (s, 3H).

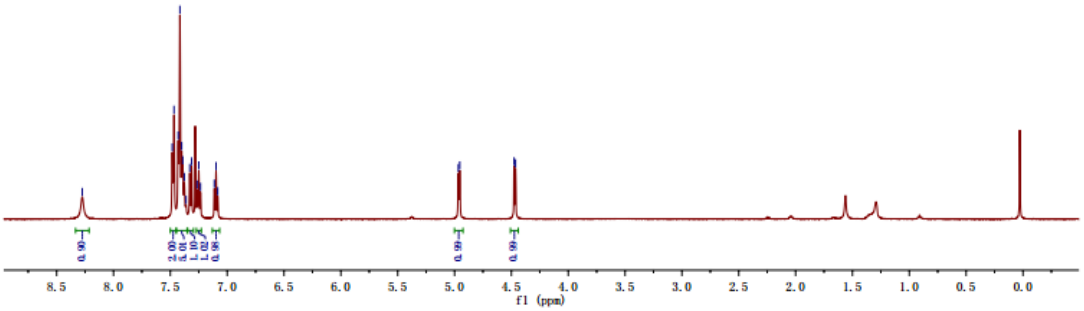
5-((3-chlorophenyl)(1H-indol-3-yl)methyl)-2,2-dimethyl-1,3-dioxane-4,6-dione, ***5f*** m.p. 140-142 ºC; IR (KBr) *v*: 3445, 3078, 2925, 1784, 1745 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6) δ: 11.08 (s, 1H), 7.36-7.39 (m, 2H), 7.18-7.29 (m, 5H), 7.07 (t, *J* = 7.5 Hz, 1H), 6.91 (t, *J* = 7.4 Hz, 1H), 5.41 (d, *J* = 2.8 Hz, 1H), 5.34 (d, *J* = 3.2 Hz, 1H), 1.85 (s, 3H), 1.60 (s, 3H).

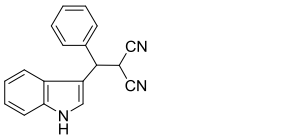
5-((3-bromophenyl)(1H-indol-3-yl)methyl)-2,2-dimethyl-1,3-dioxane-4,6-dione, ***5g*** m.p. 141-143 ºC; IR (KBr) *v*: 3444, 3075, 2992, 1759, 1640 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6) δ: 11.06 (s, 1H), 7.50 (s, 1H), 7.32-7.39 (m, 3H), 7.18-7.23 (m, 3H), 7.05 (t, *J* = 7.3 Hz, 1H), 6.89 (t, *J* = 7.3 Hz, 1H), 5.40 (s, 1H), 5.33 (d, *J* = 2.4 Hz, 1H), 1.85 (s, 3H), 1.60 (s, 3H).

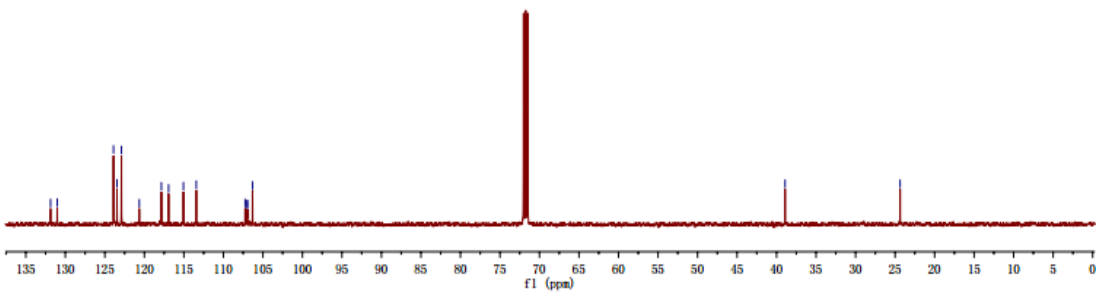
5-((3-nitrophenyl)(1H-indol-3-yl)methyl)-2,2-dimethyl-1,3-dioxane-4,6-dione, ***5h*** m.p. 155-157 ºC; IR (KBr) *v*: 3444, 3064, 2998, 1775, 1737 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6) δ: 11.13 (s, 1H), 8.24 (s, 1H), 8.05 (d, *J* = 7.9 Hz, 1H), 7.80 (d, *J* = 7.7 Hz, 1H), 7.53 (t, *J* = 8.0 Hz, 1H), 7.39 (d, *J* = 8.1 Hz, 1H), 7.22-7.25 (m, 2H), 7.06 (t, *J* = 7.5 Hz, 1H), 6.90 (t, *J* = 7.5 Hz, 1H), 5.54 (d, *J* = 2.4 Hz, 1H), 5.46 (d, *J* = 3.1 Hz, 1H), 1.87 (s, 3H), 1.63 (s, 3H).

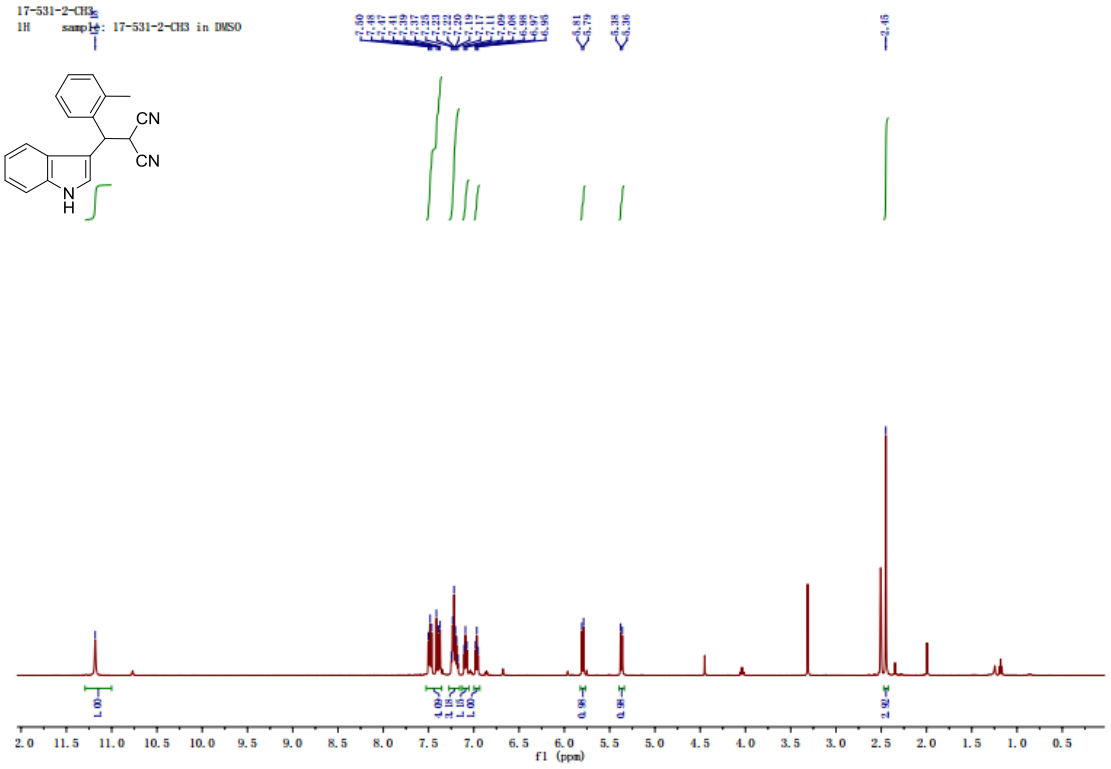
5-((4-nitrophenyl)(1H-indol-3-yl)methyl)-2,2-dimethyl-1,3-dioxane-4,6-dione, ***5i*** m.p. 145-147 ºC; IR (KBr) *v*: 3442, 3066, 3005, 1781, 1737 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6) δ: 11.13 (s, 1H), 8.12 (d, *J* = 8.5 Hz, 2H), 7.58 (d, *J* = 8.4 Hz, 2H), 7.38 (d, *J* = 8.0 Hz, 1H), 7.19 (t, *J* = 8.0 Hz, 2H), 7.06 (t, *J* = 7.4 Hz, 1H), 6.90 (t, *J* = 7.3 Hz, 1H), 5.52 (s, 1H), 5.45 (d, *J*═2.8 Hz, 1H), 1.87 (s, 3H), 1.63 (s, 3H).

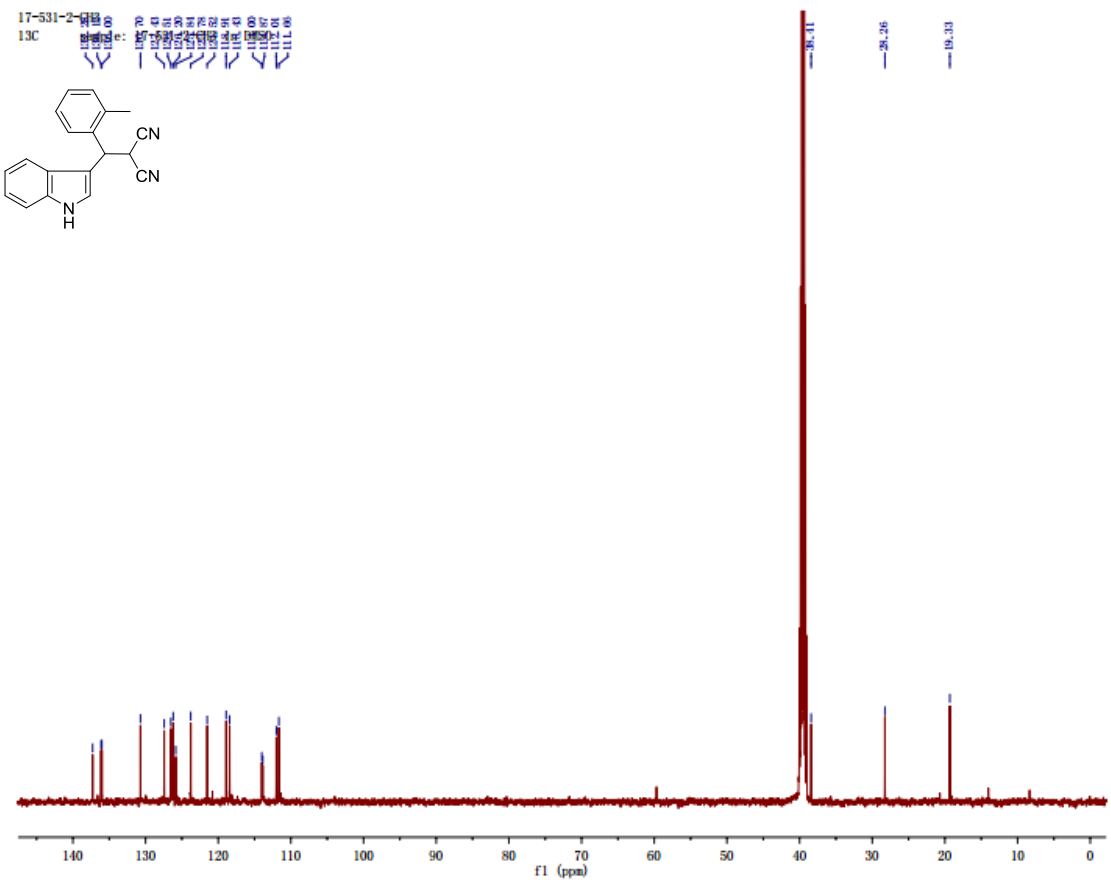

CN
CN
N
H

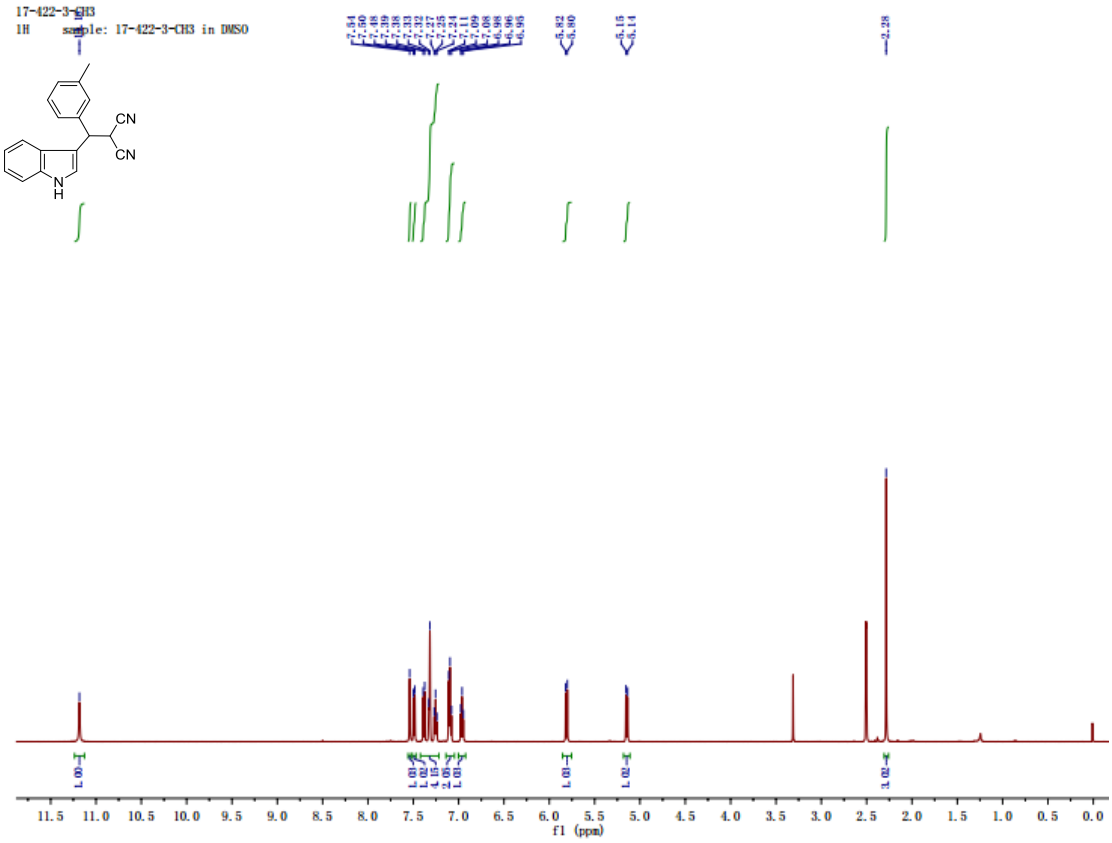

f1 (ppm)

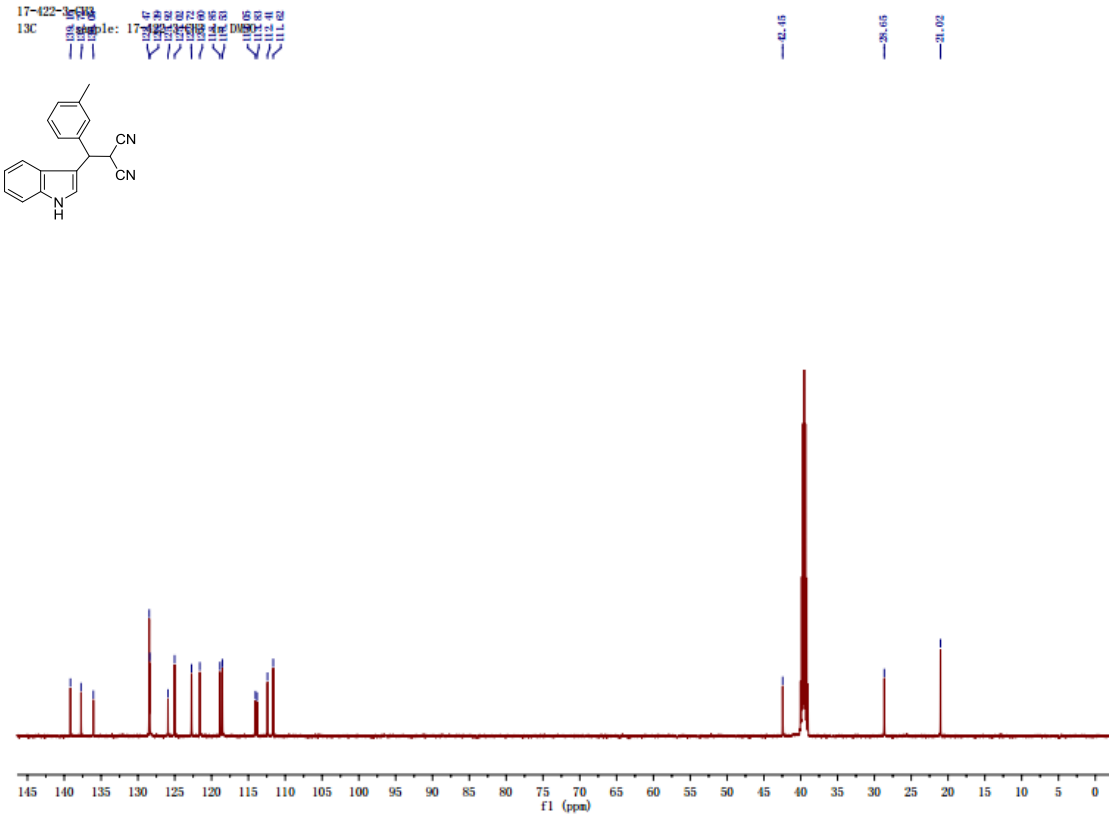

CN
CN
N
H

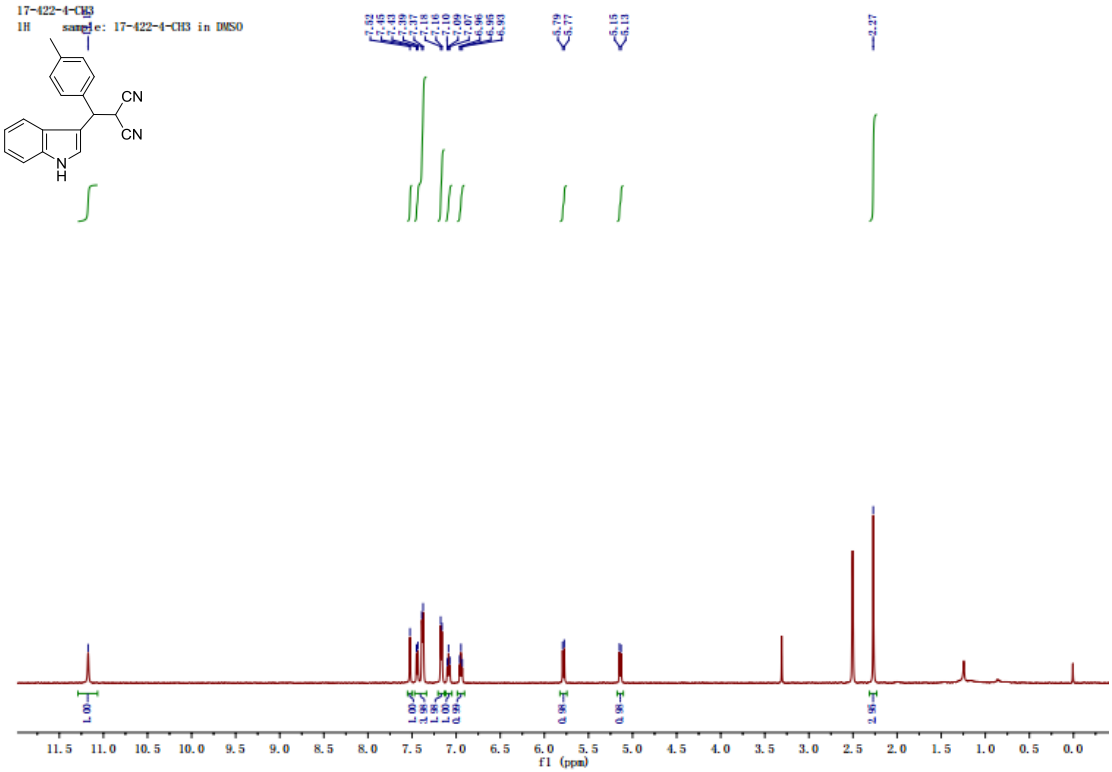

f1 (ppm)

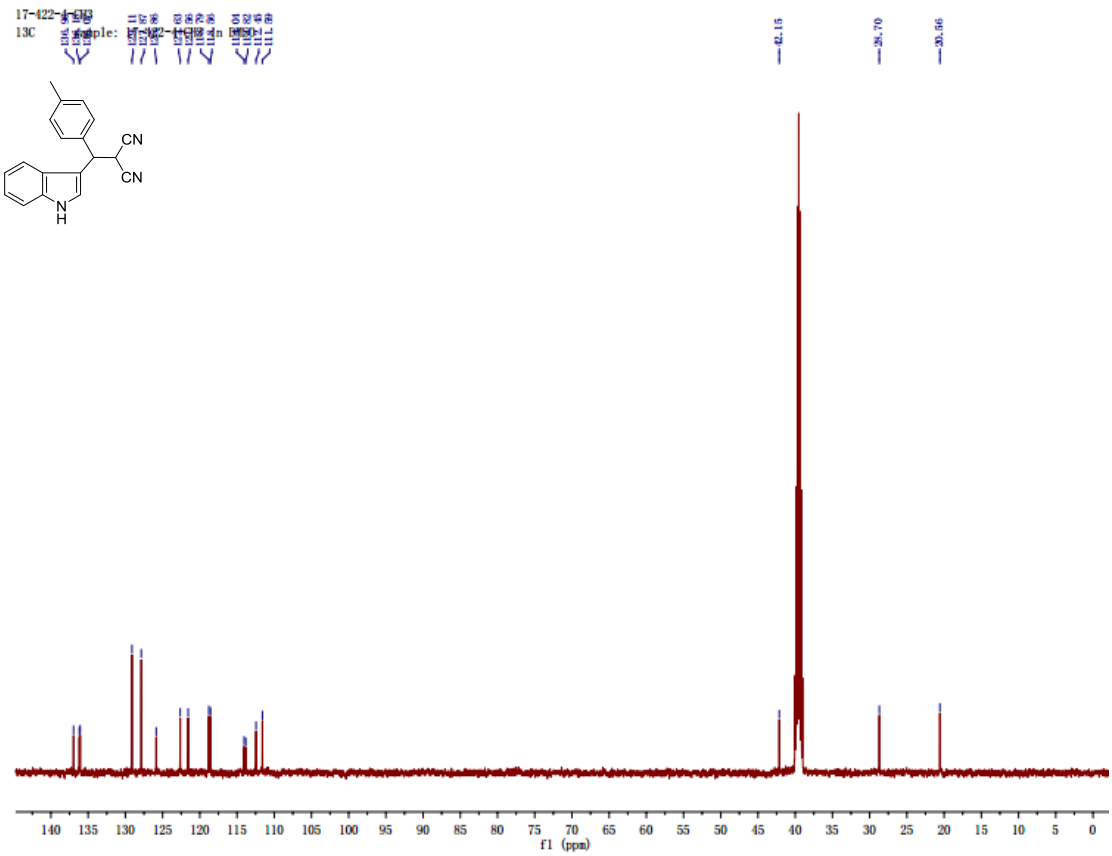

17-531-2-CH3
1H sample: 17-531-2-CH3 in DMSO
CN
CN
N
H
f1 (ppm)

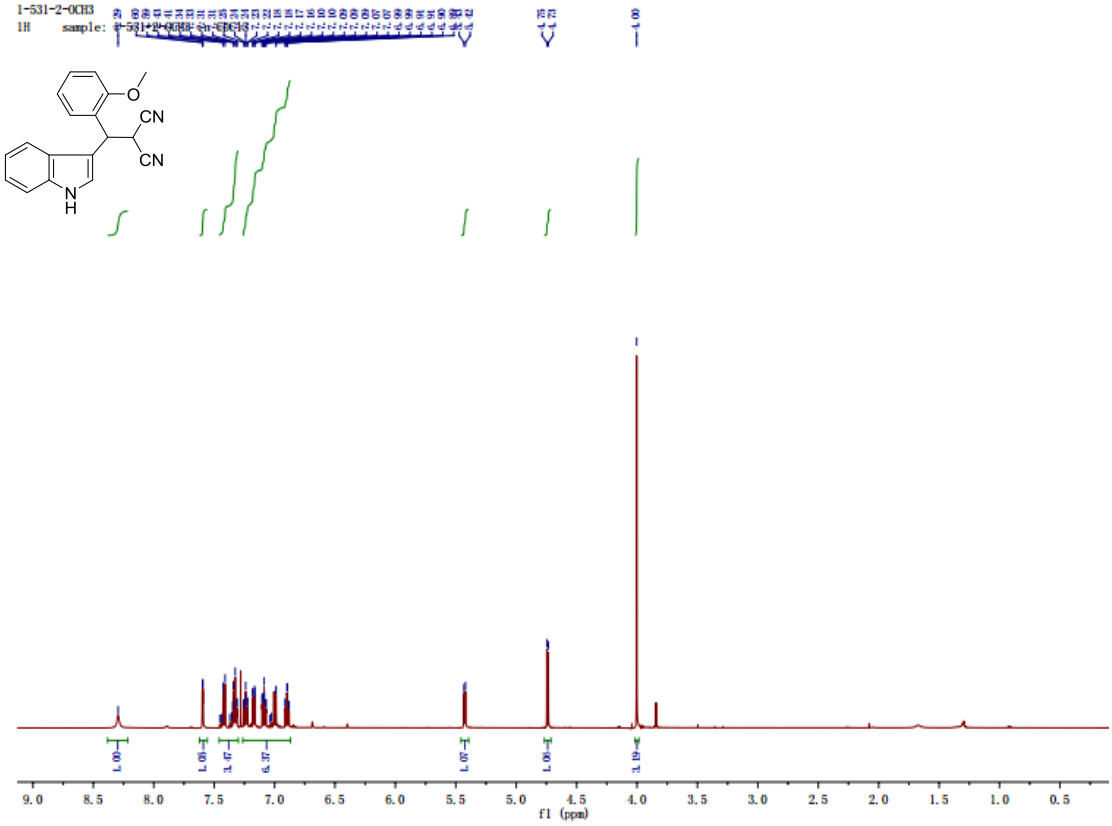

17-531-2-CH3
13C
CN
CN
N
H
f1 (ppm)

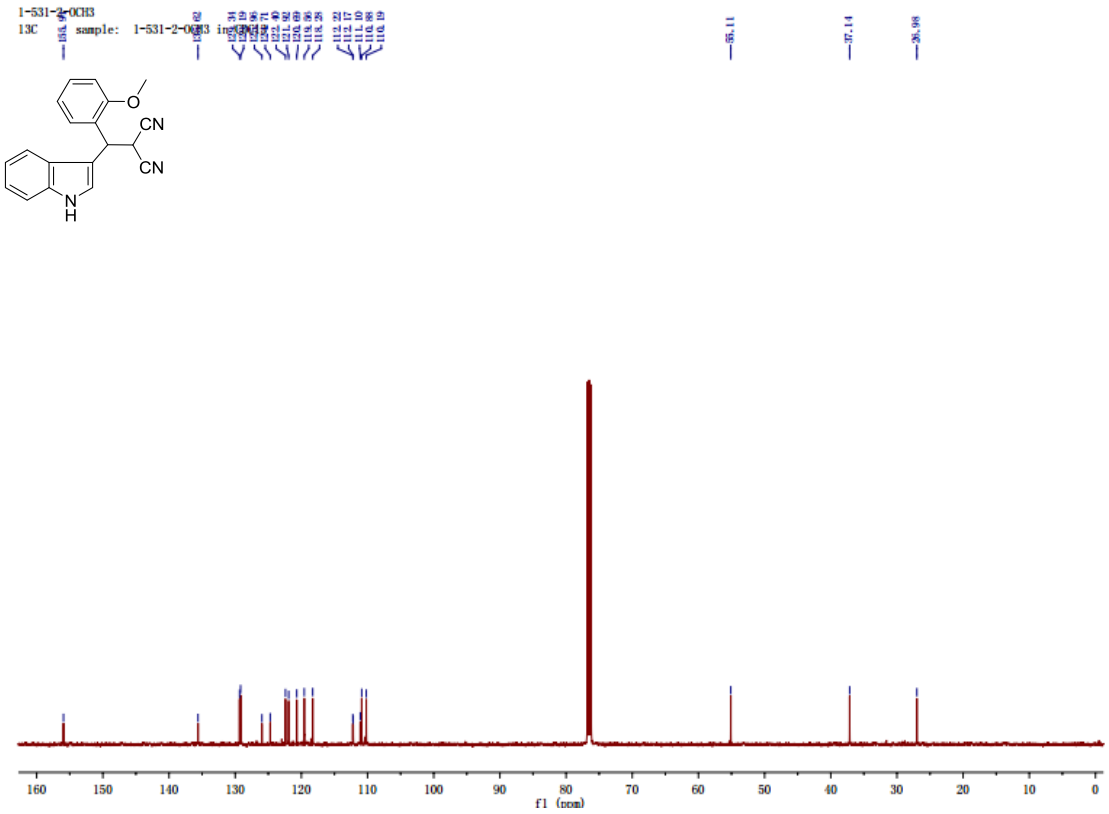

17-422-3-CH3
1H sample: 17-422-3-CH3 in DMSO
CN
CN
N
H
f1 (ppm)


17-422-3-CH3
13C
CN
CN
N
H
f1 (ppm)

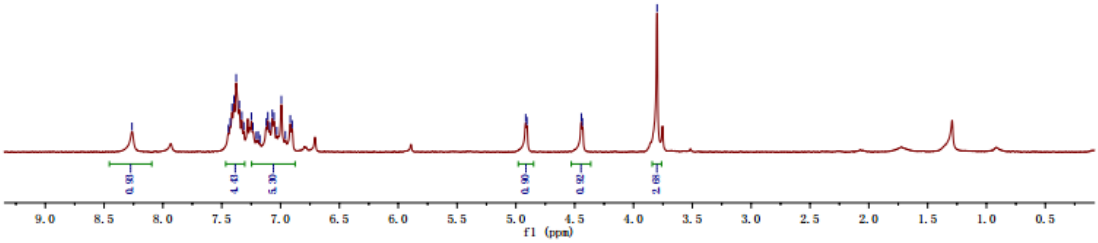

17-422-4-CH3
1H sample: 17-422-4-CH3 in DMSO
CN
CN
N
H
f1 (ppm)

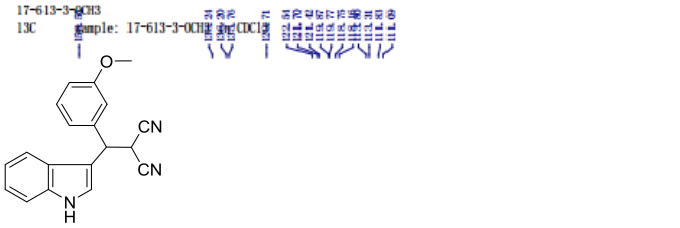

17-422-4-CH3
13C
CN
CN
N
H
f1 (ppm)

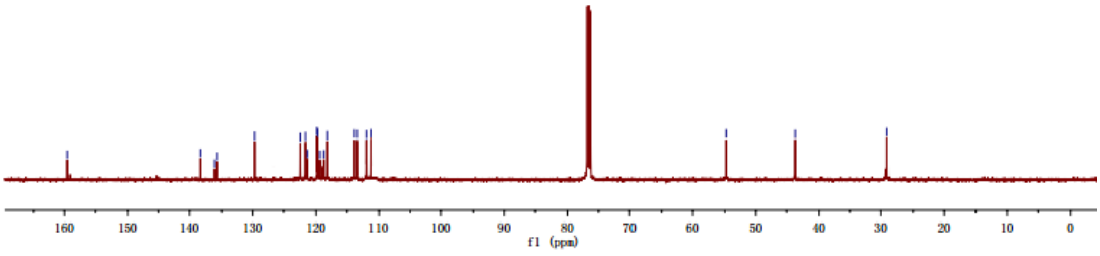

1-531-2-OCH3
1H
O
CN
CN
N
H
1.00
1.05
3.47
6.37
1.07
1.06
3.19
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

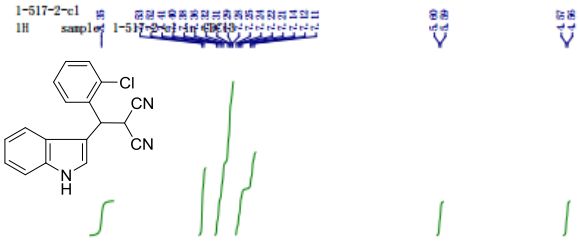

1-531-2-OCH3
13C
55.11
37.14
26.98
O
CN
CN
N
H
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

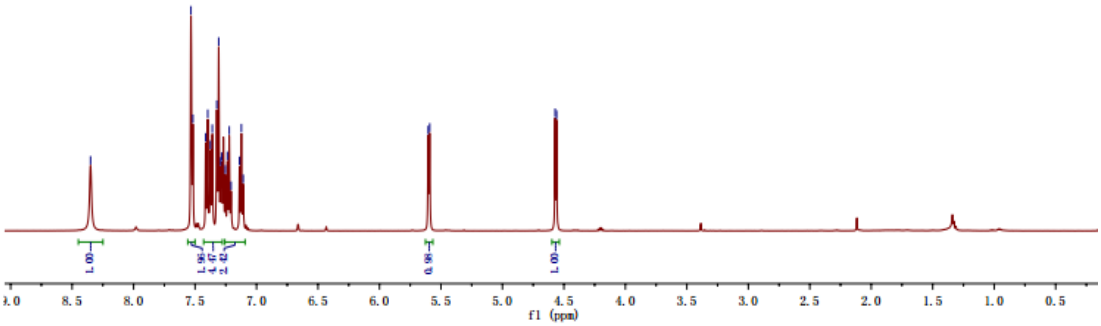

17-613-3-OCH3
1H
sample: 17-613-3-OCH3
O
CN
CN
N
H

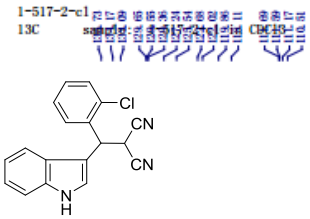

f1 (ppm)

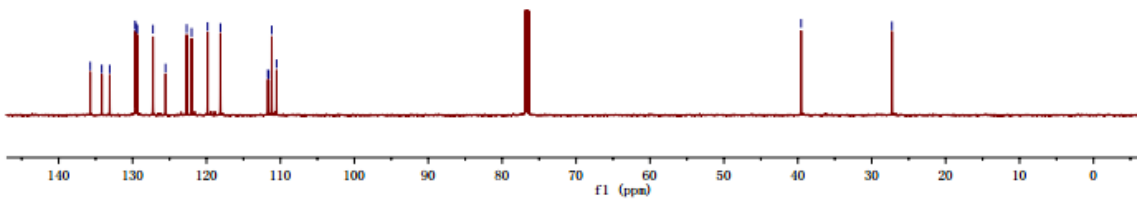

17-613-3-OCH3
13C
sample: 17-613-3-OCH3
O
CN
CN
N
H

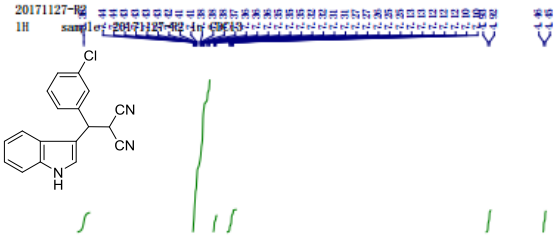

f1 (ppm)

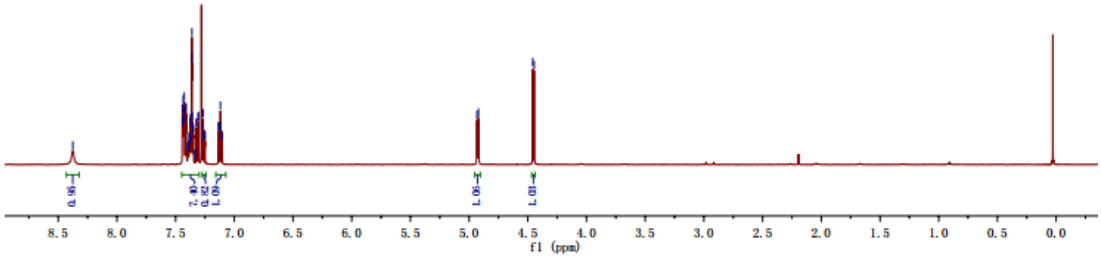

1-517-2-c1
1H
Cl
CN
CN
N
H

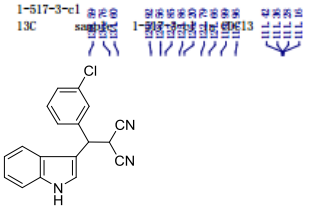

f1 (ppm)

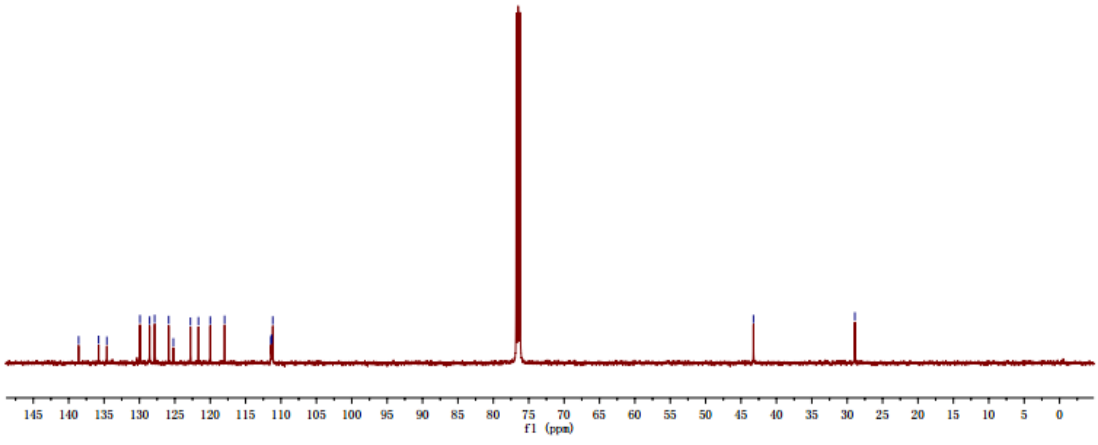

1-517-2-c1
13C
Cl
CN
CN
N
H

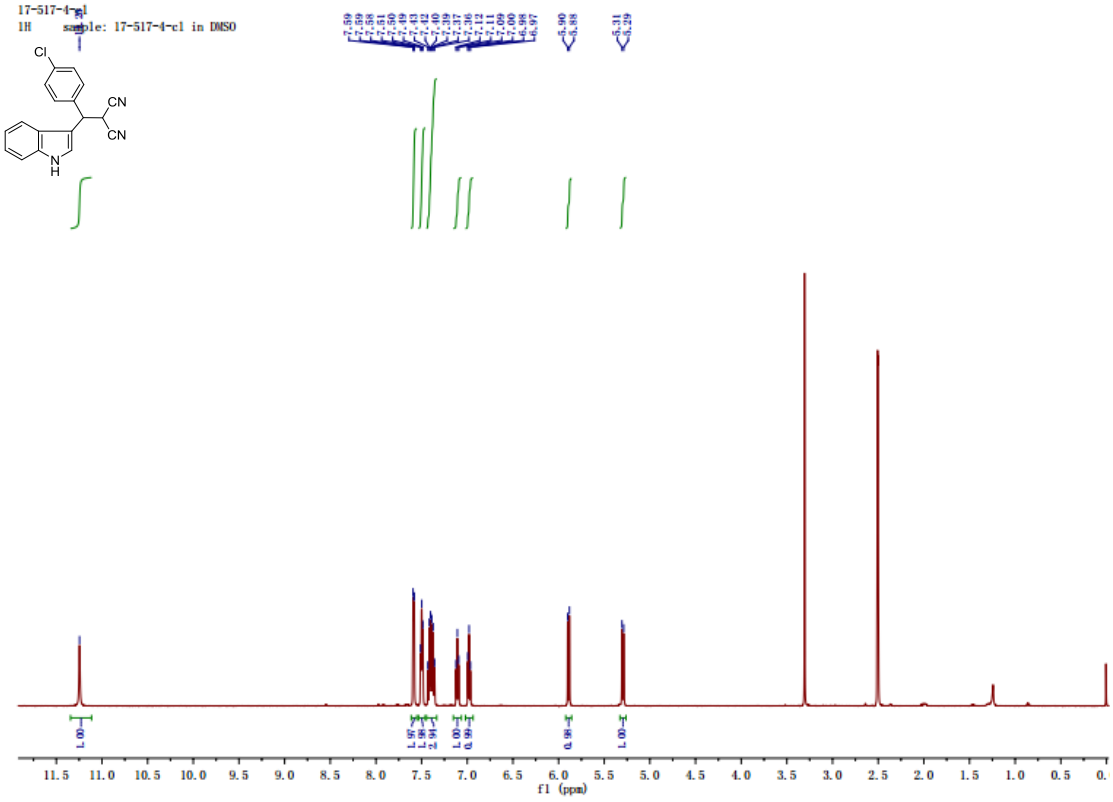

f1 (ppm)

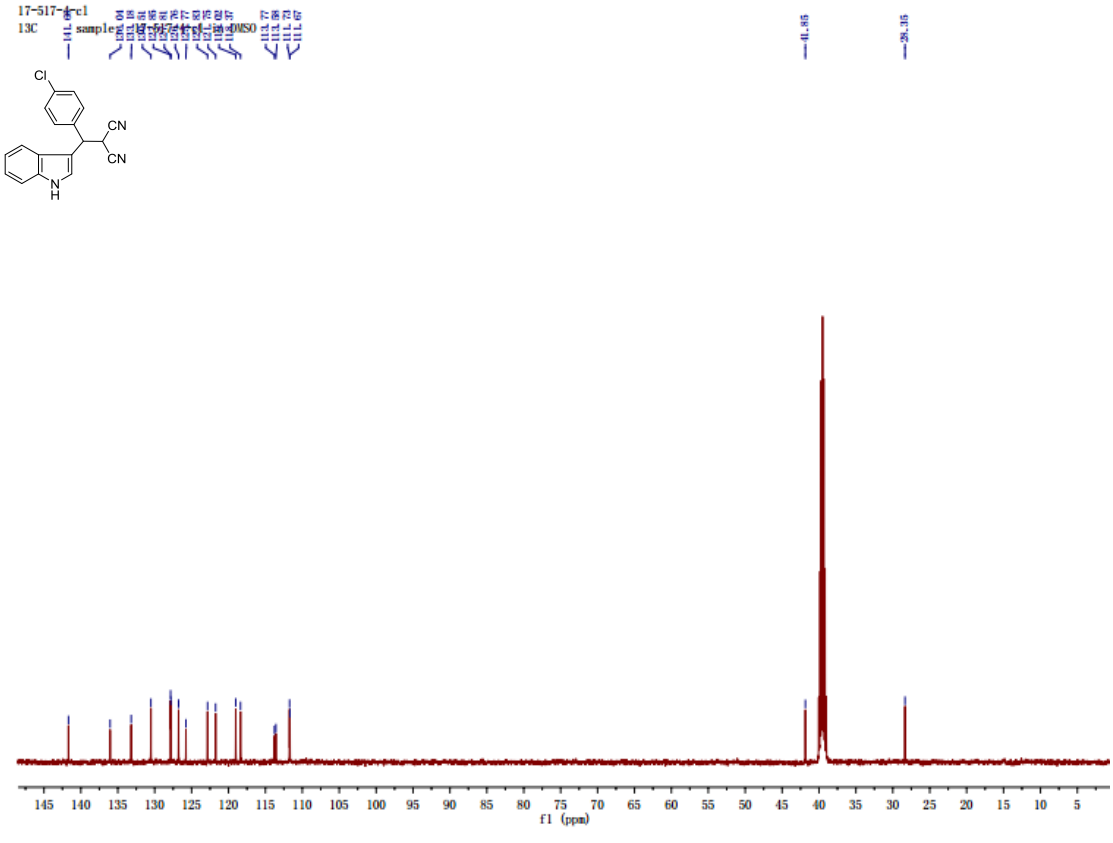

Cl
CN
CN
N
H

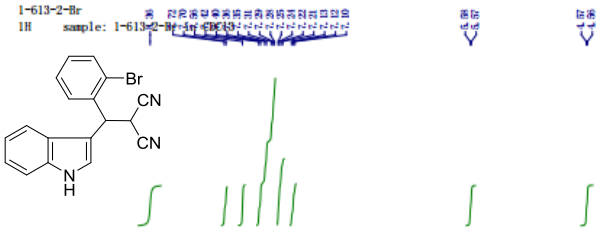

8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

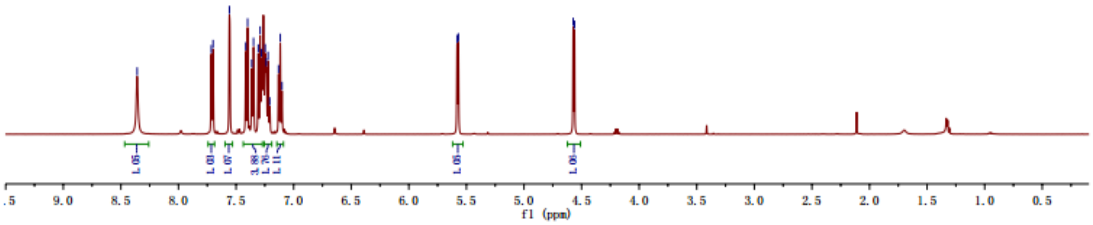

Cl
CN
CN
N
H

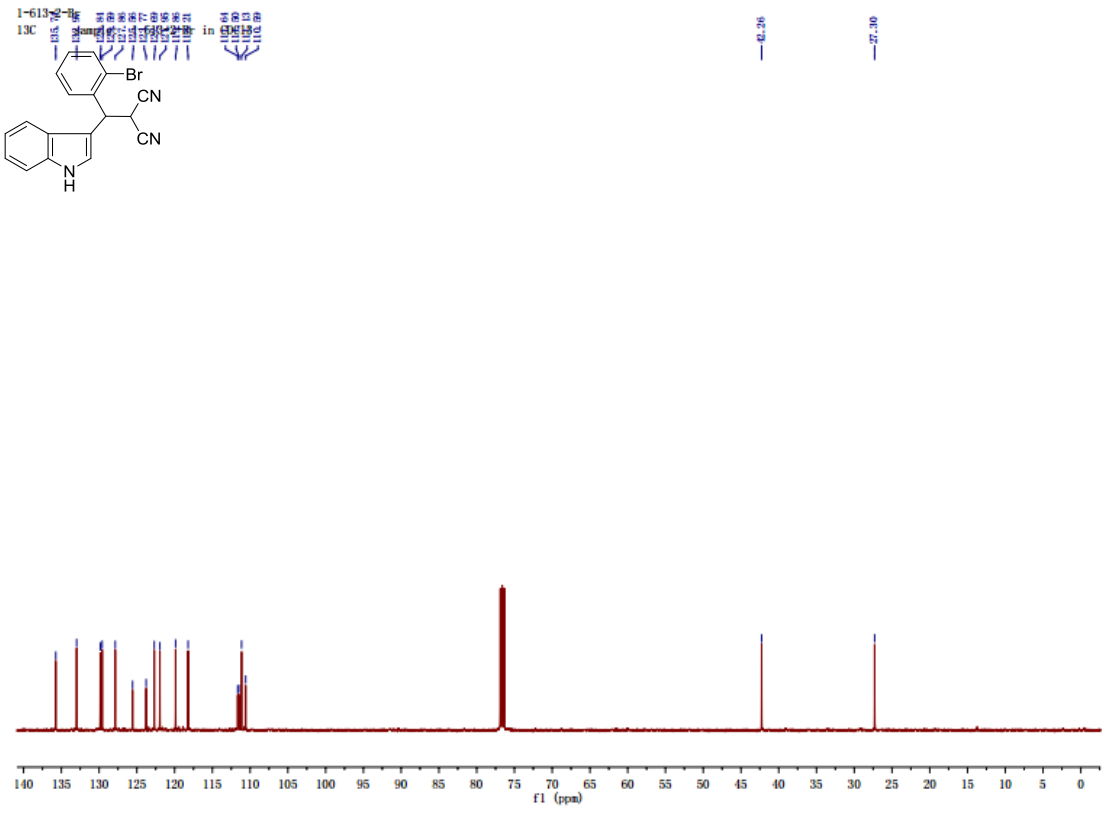

145
140
135
130
125
120
115
110
105
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
0
f1 (ppm)

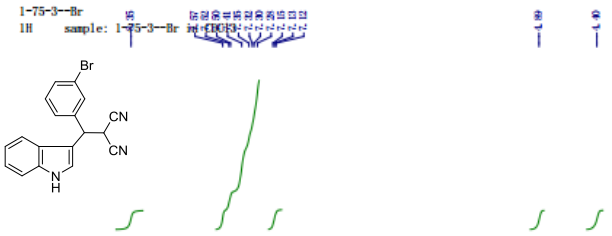

17-517-4-cl
1H sample: 17-517-4-cl in DMSO
Cl
CN
CN
N
H
f1 (ppm)

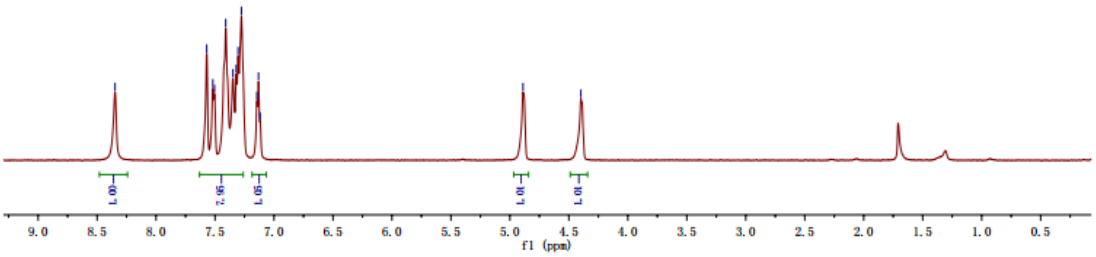

17-517-4-cl
13C sample
DMSO
Cl
CN
CN
N
H
f1 (ppm)


1-613-2-Br
1H
Br
CN
CN
N
H

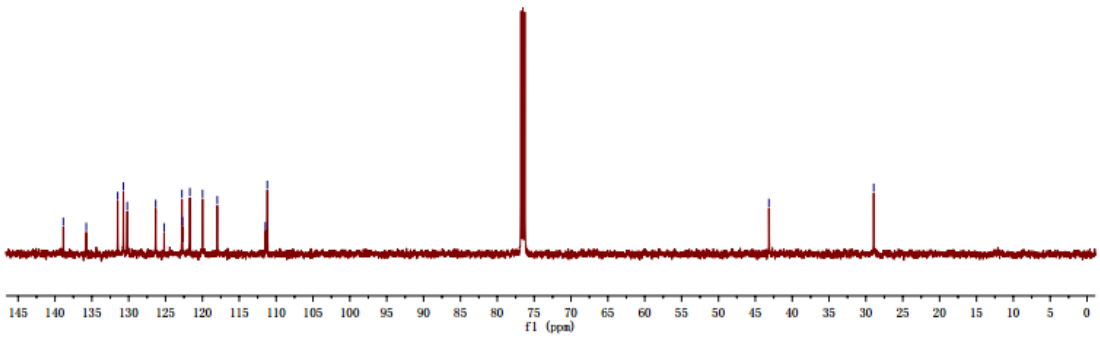

f1 (ppm)

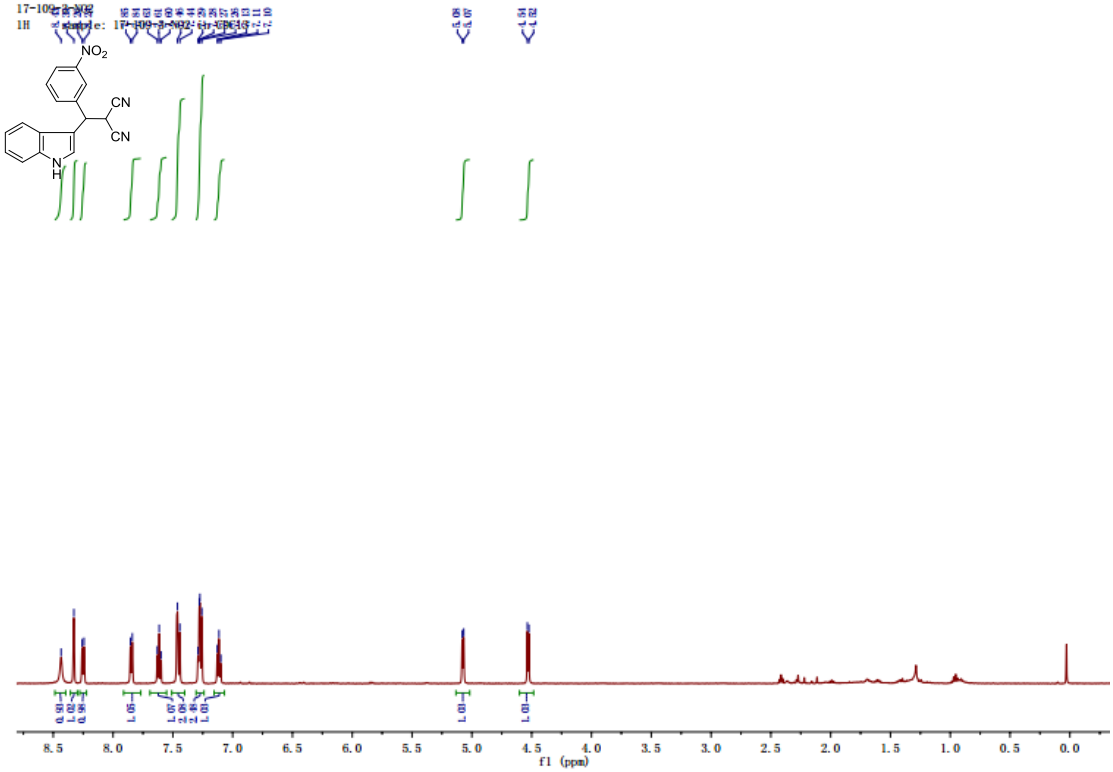

1-613-2-Br
13C
Br
CN
CN
N
H
42.26
27.30
f1 (ppm)

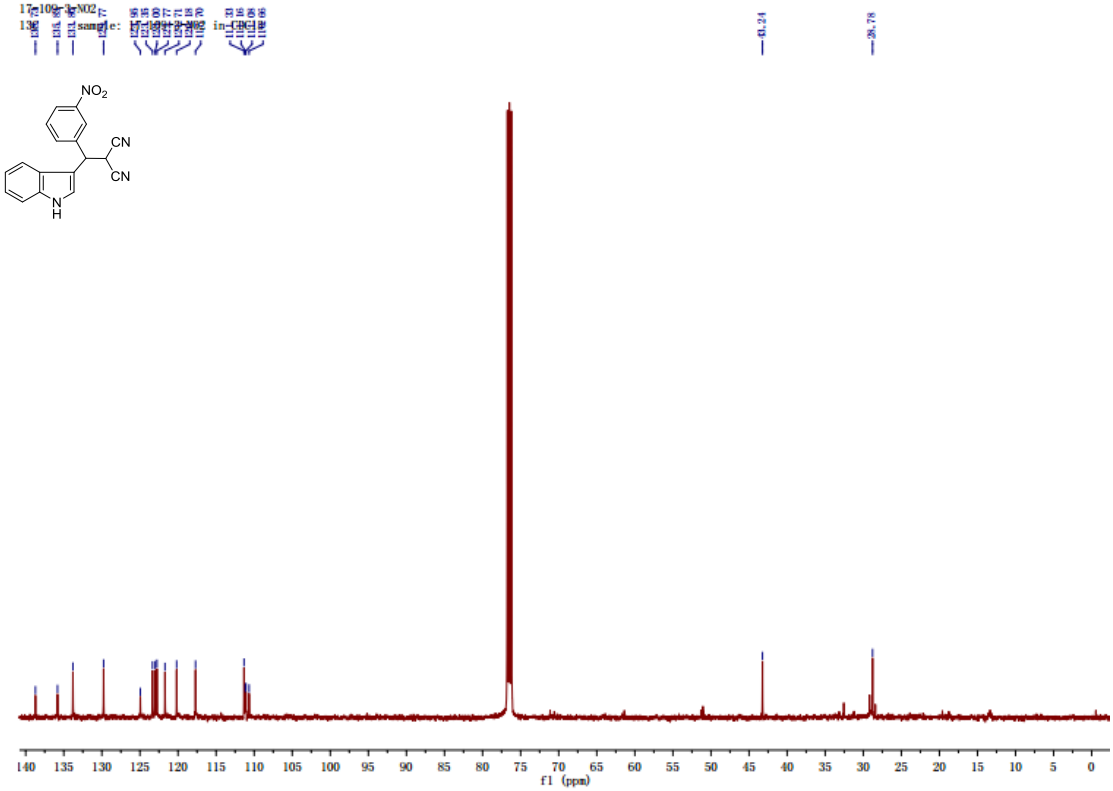

1-75-3--Br
1H
sample: 1-75-3--Br
Br
CN
CN
N
H

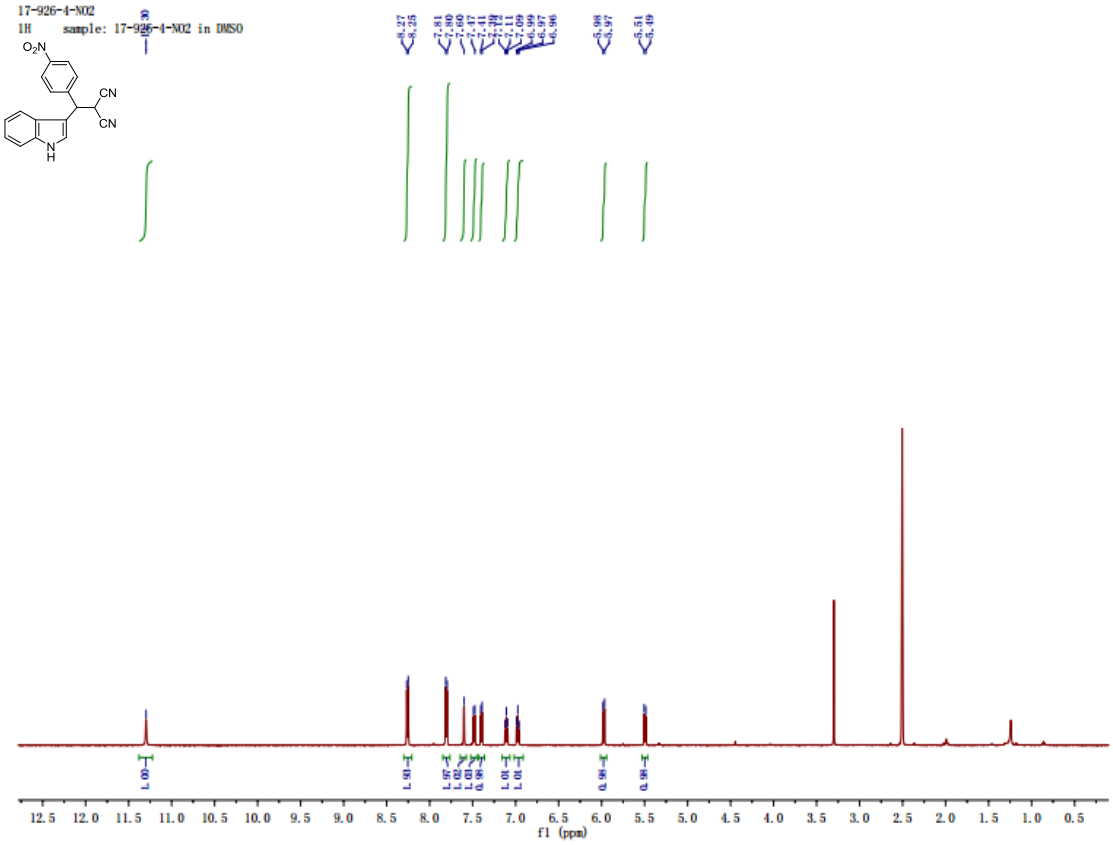

1.00
7.95
1.05
1.01
1.01
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

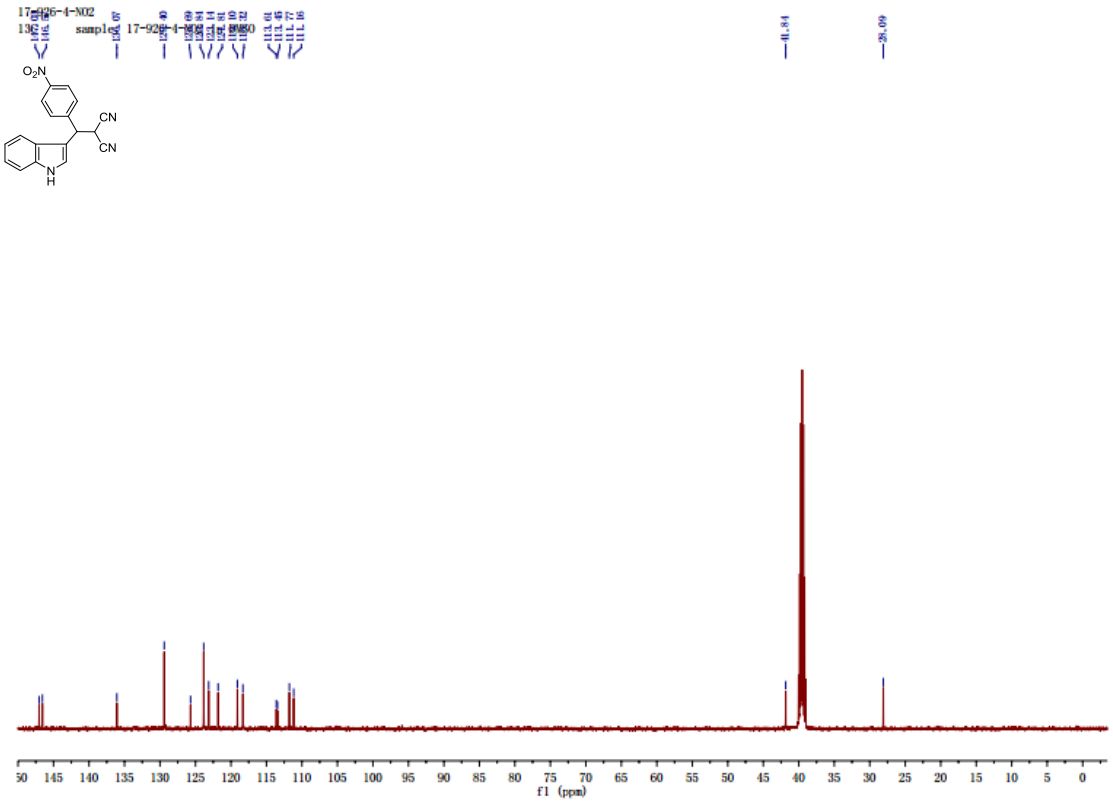

1-75-3--Br
13C
sample: 1-75-3--Br
Br
CN
CN
N
H

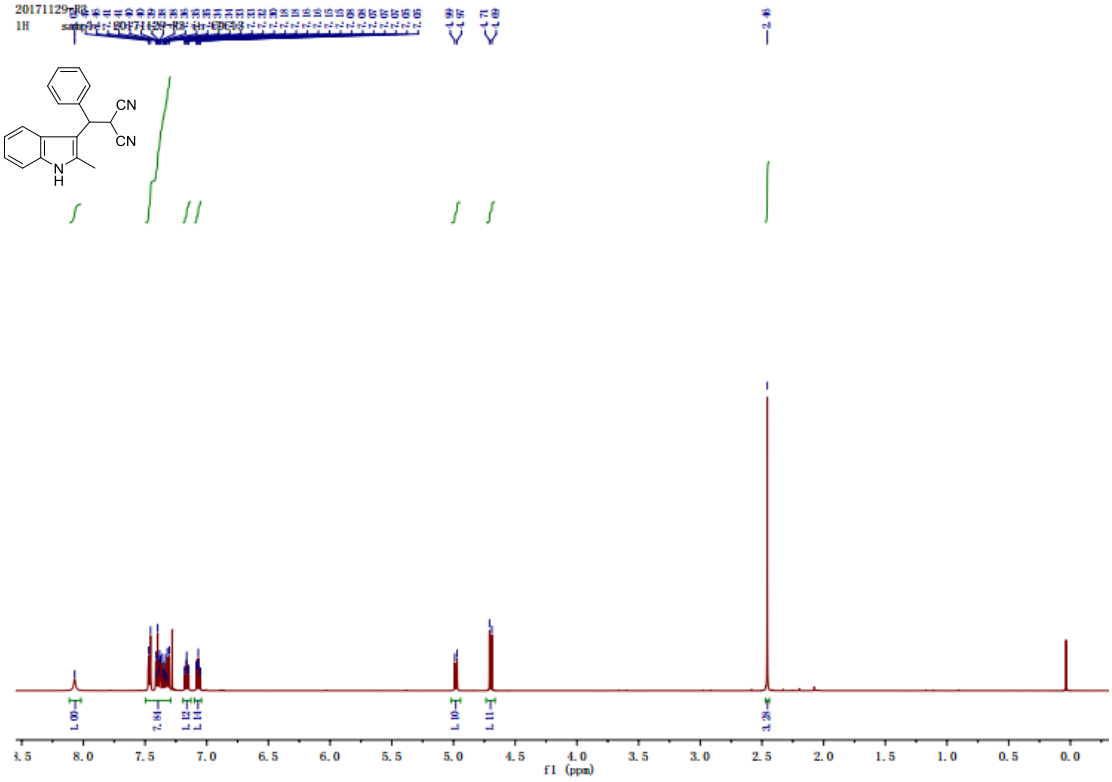

145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0
f1 (ppm)

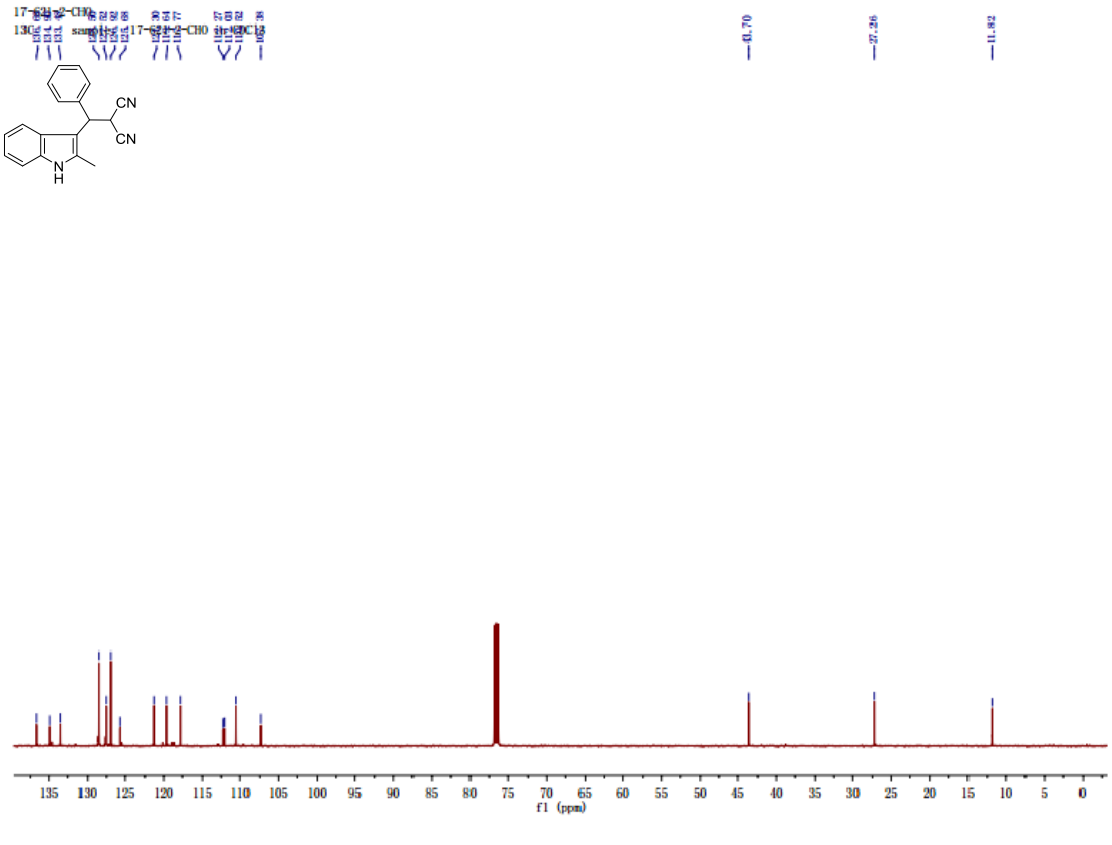

NO2
CN
CN
N
H
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

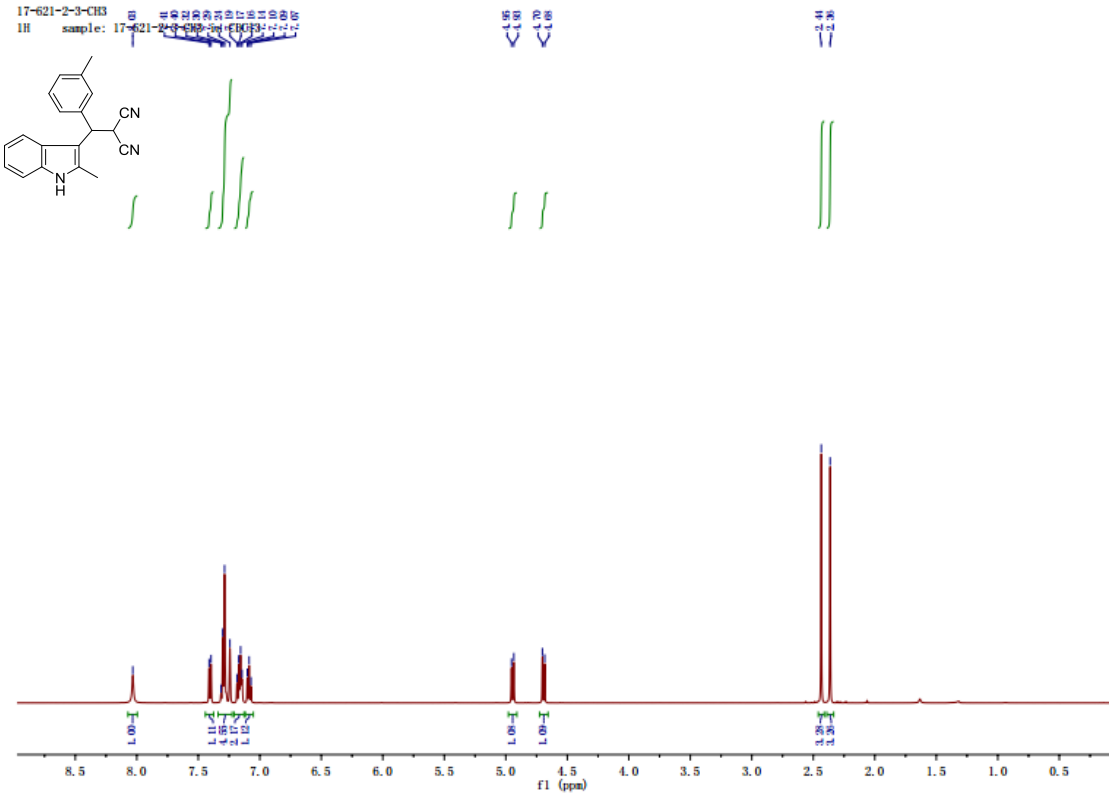

NO2
CN
CN
N
H
140
135
130
125
120
115
110
105
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
0
f1 (ppm)

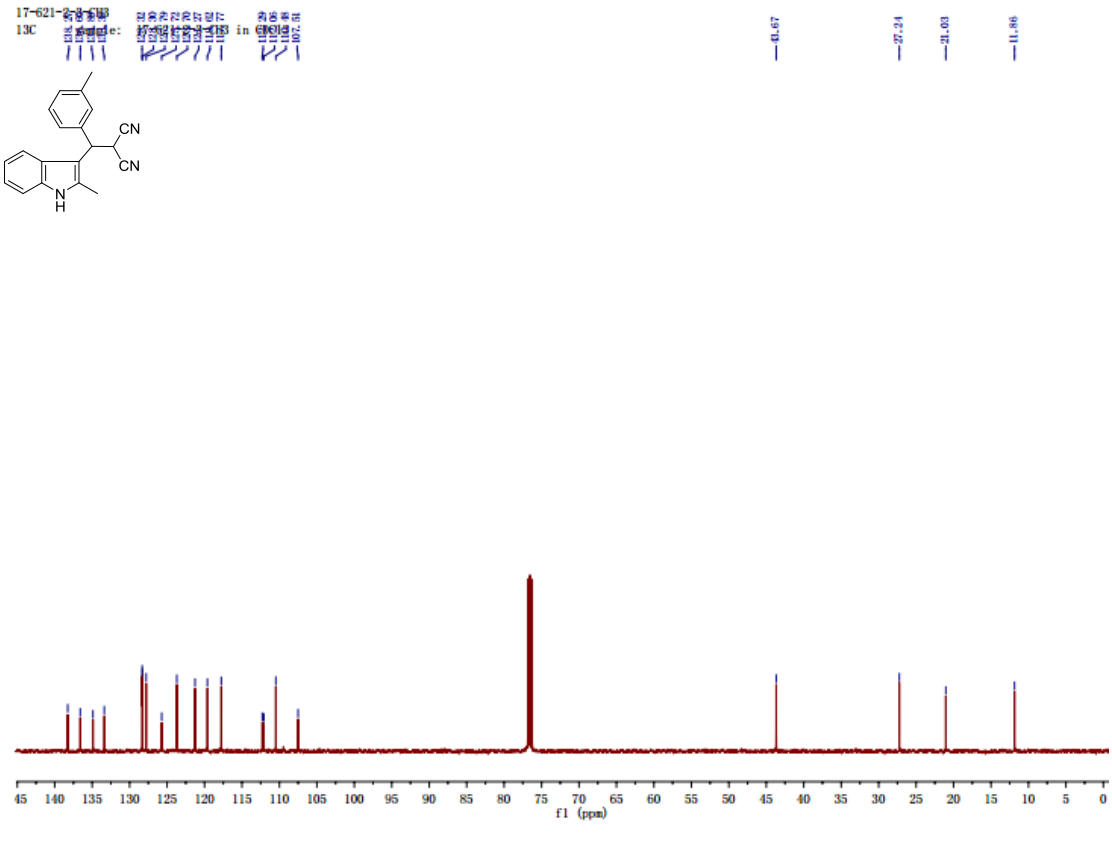

17-926-4-NO2
1H sample: 17-926-4-NO2 in DMSO
f1 (ppm)

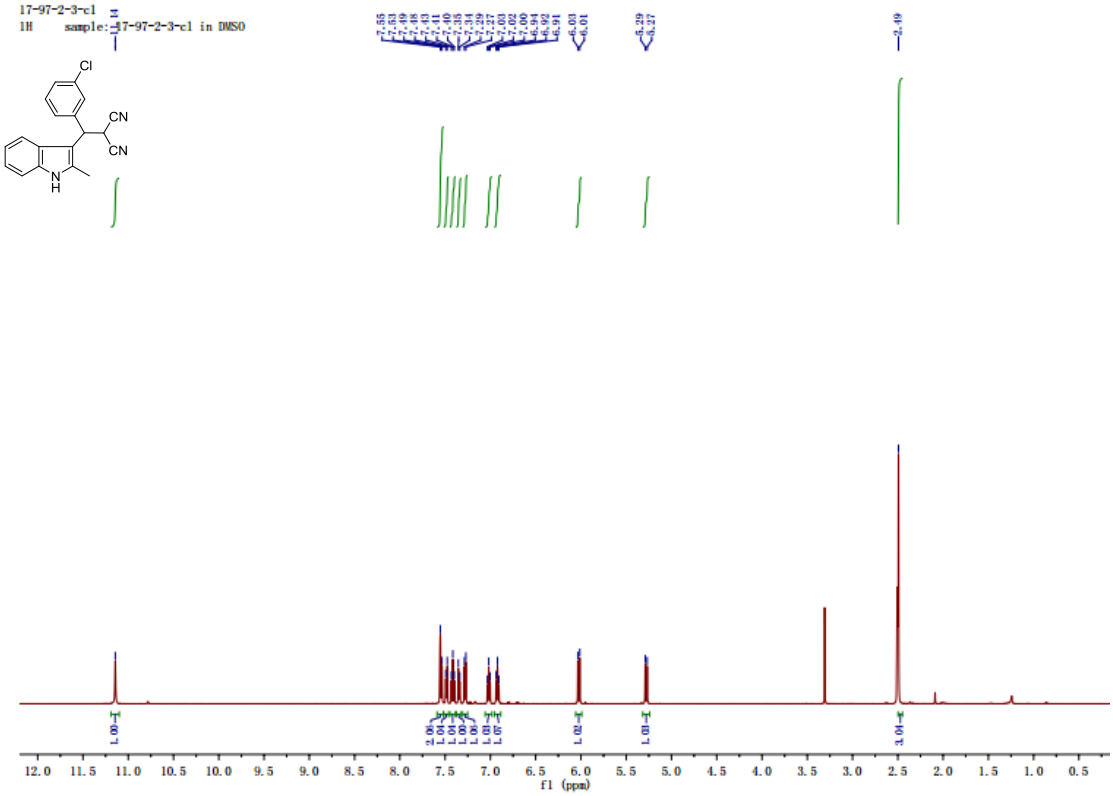

17-926-4-NO2
sample: 17-926-4-NO2 in DMSO
f1 (ppm)

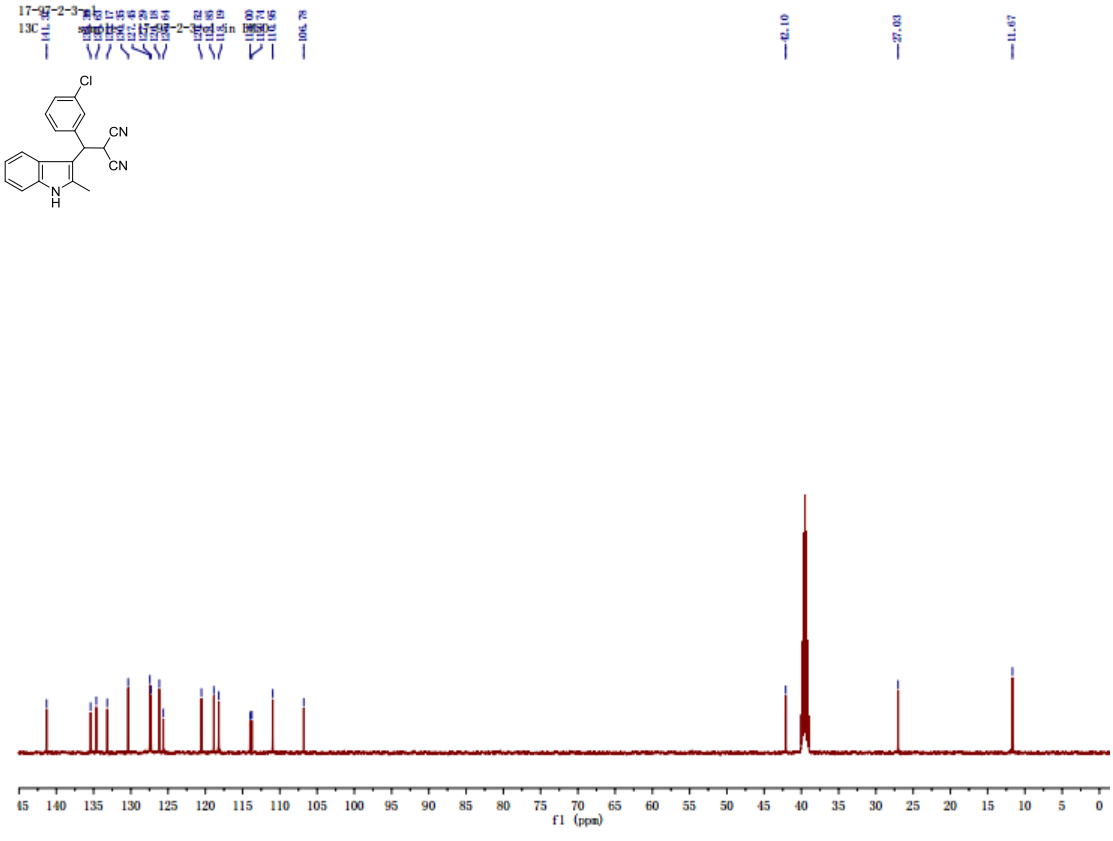

CN
CN
N
H
f1 (ppm)

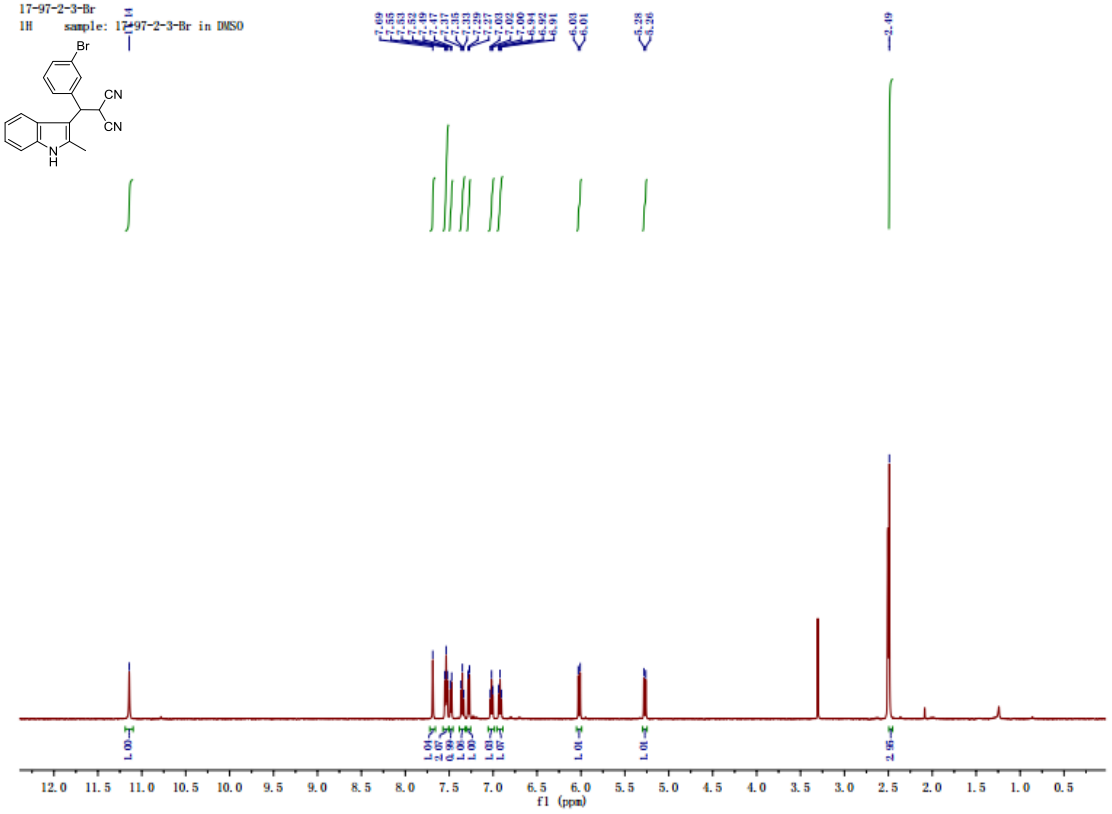

CN
CN
N
H
f1 (ppm)

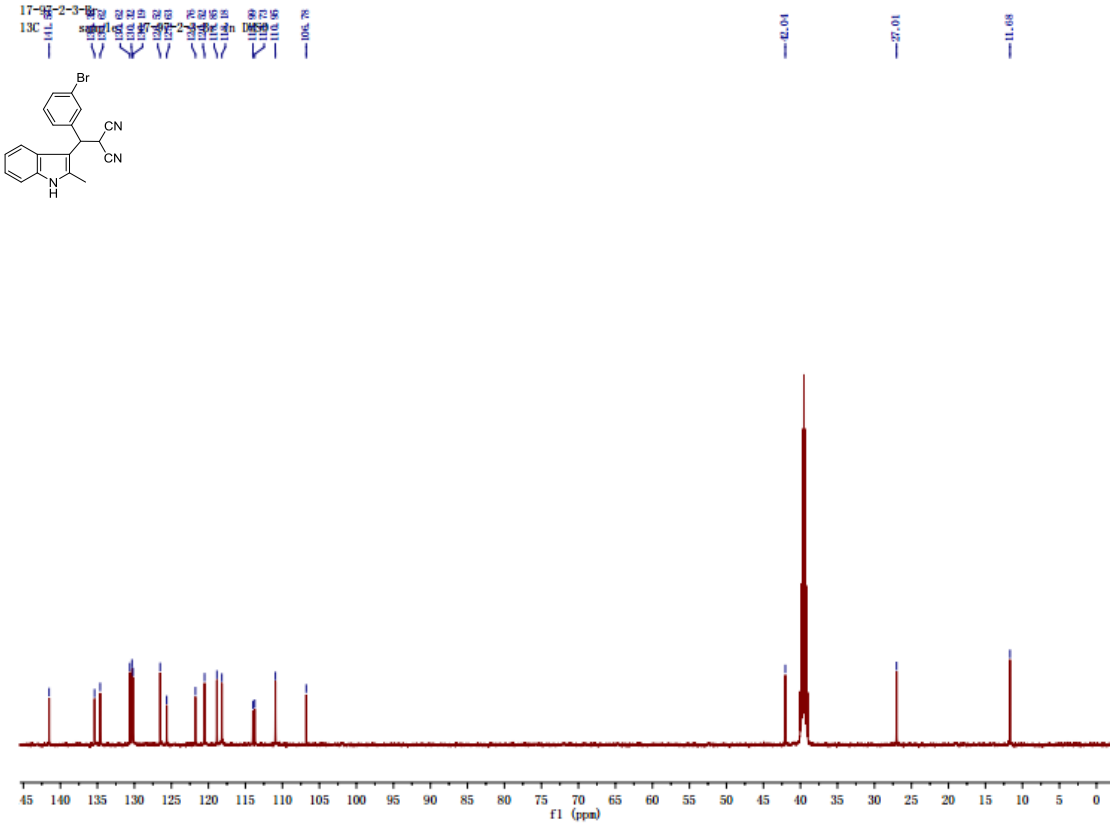

17-621-2-3-CH3
1H
CN
CN
N
H
f1 (ppm)

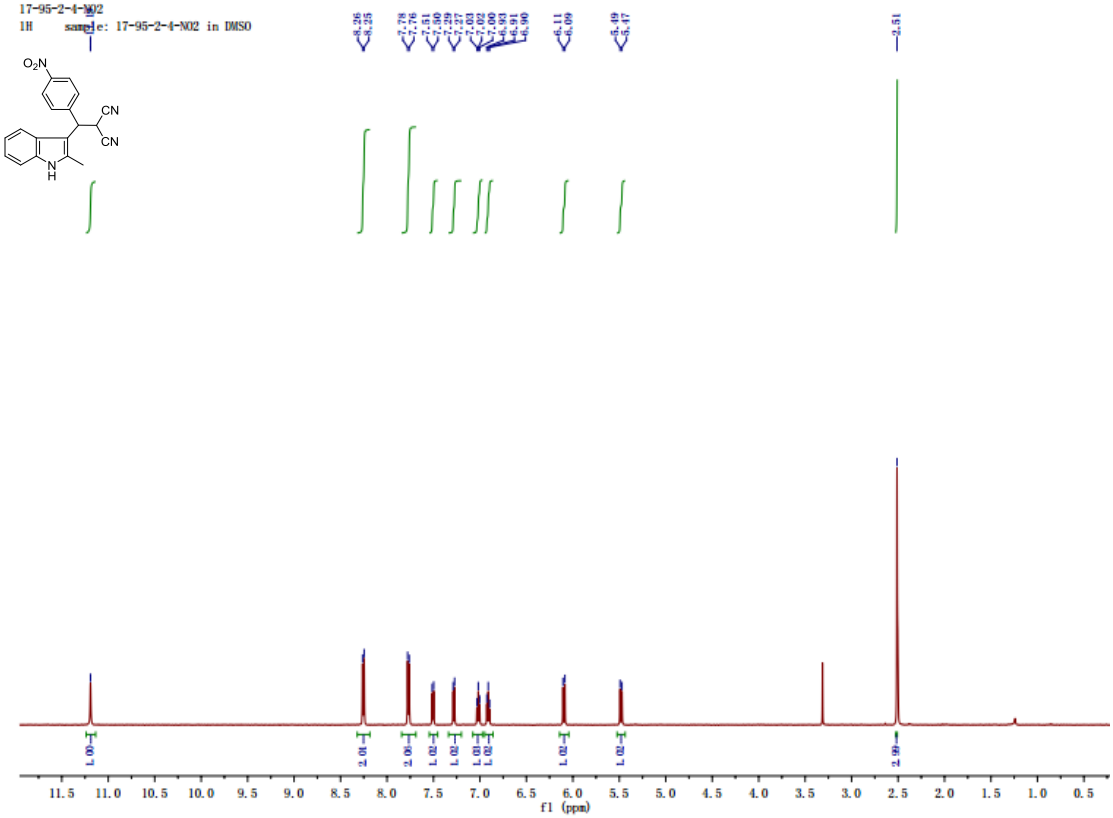

13C
CN
CN
N
H
f1 (ppm)

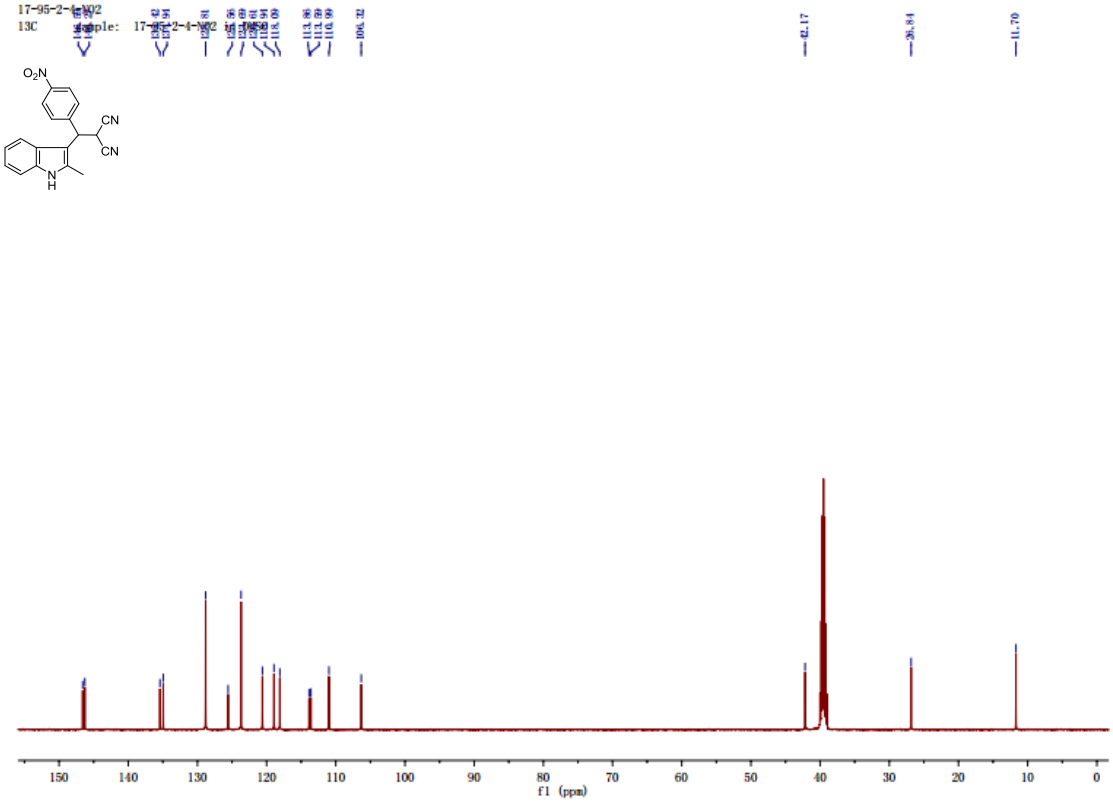

17-97-2-3-cl
1H sample: 17-97-2-3-cl in DMSO
Cl
CN
CN
N
H
f1 (ppm)

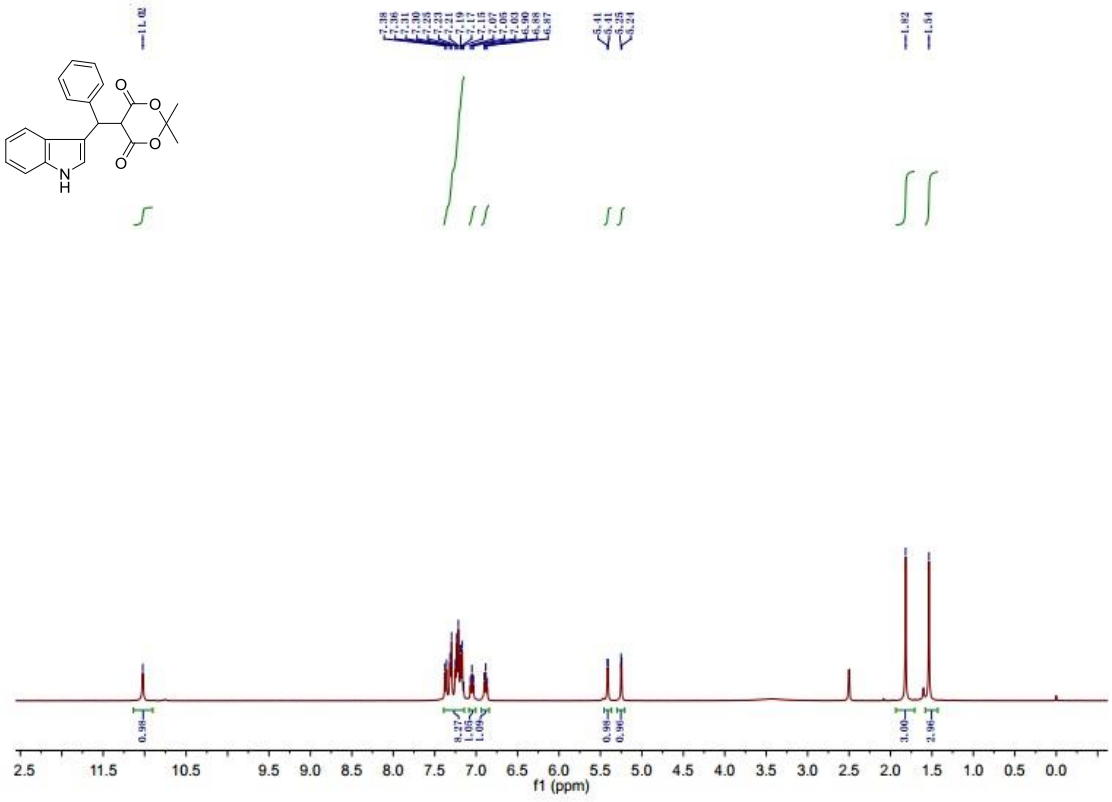

17-97-2-3-cl
13C
Cl
CN
CN
N
H
f1 (ppm)

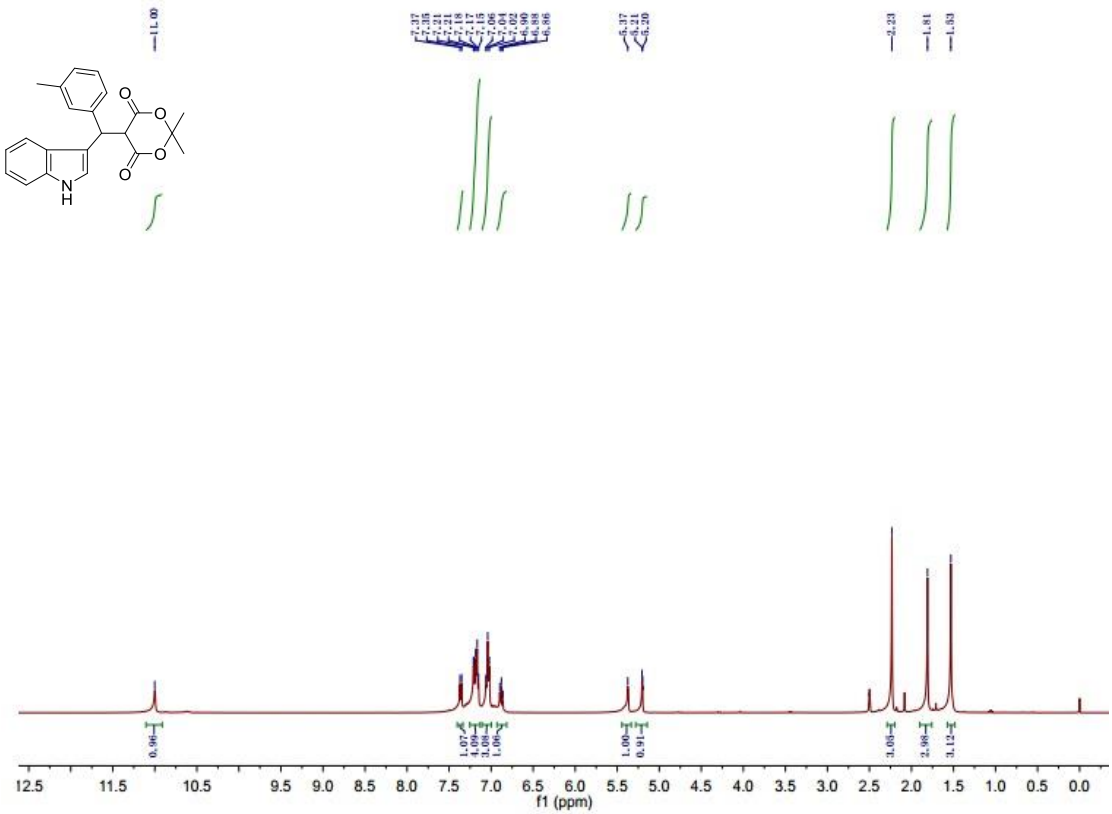

17-97-2-3-Br
1H sample: 17-97-2-3-Br in DMSO
Br
CN
CN
N
H
f1 (ppm)

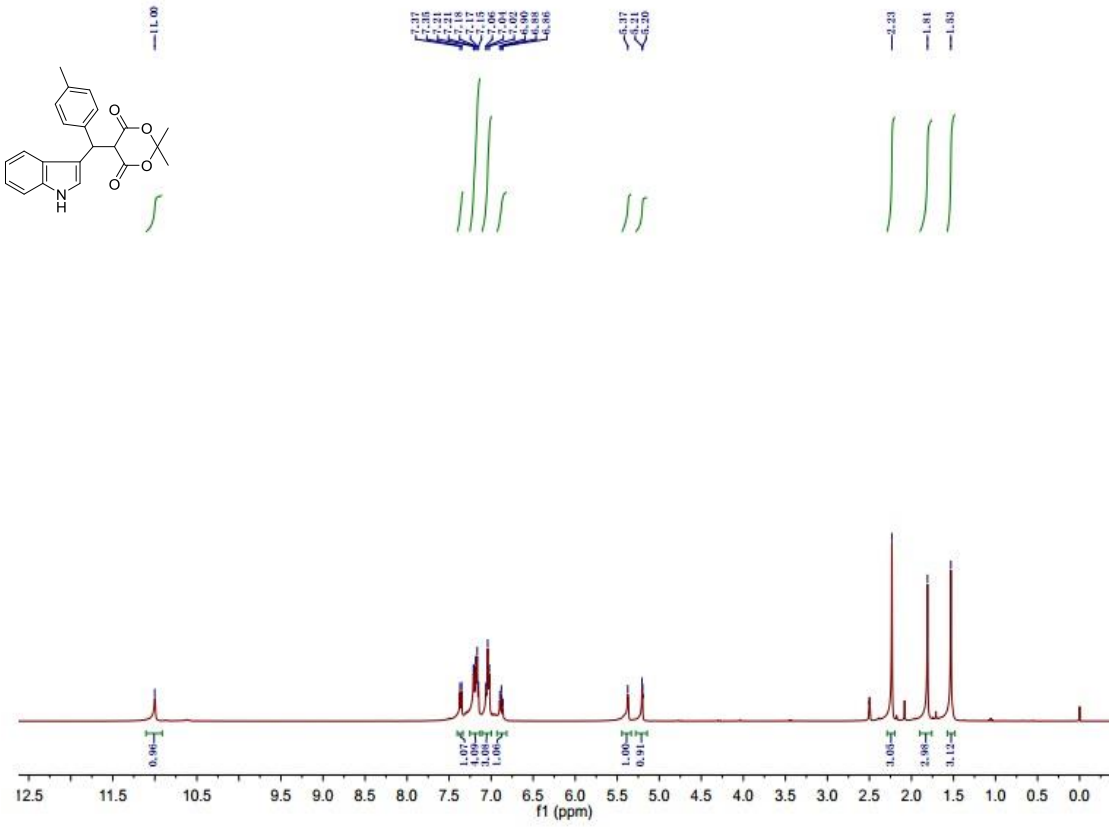

17-97-2-3-Br
13C
Br
CN
CN
N
H
f1 (ppm)

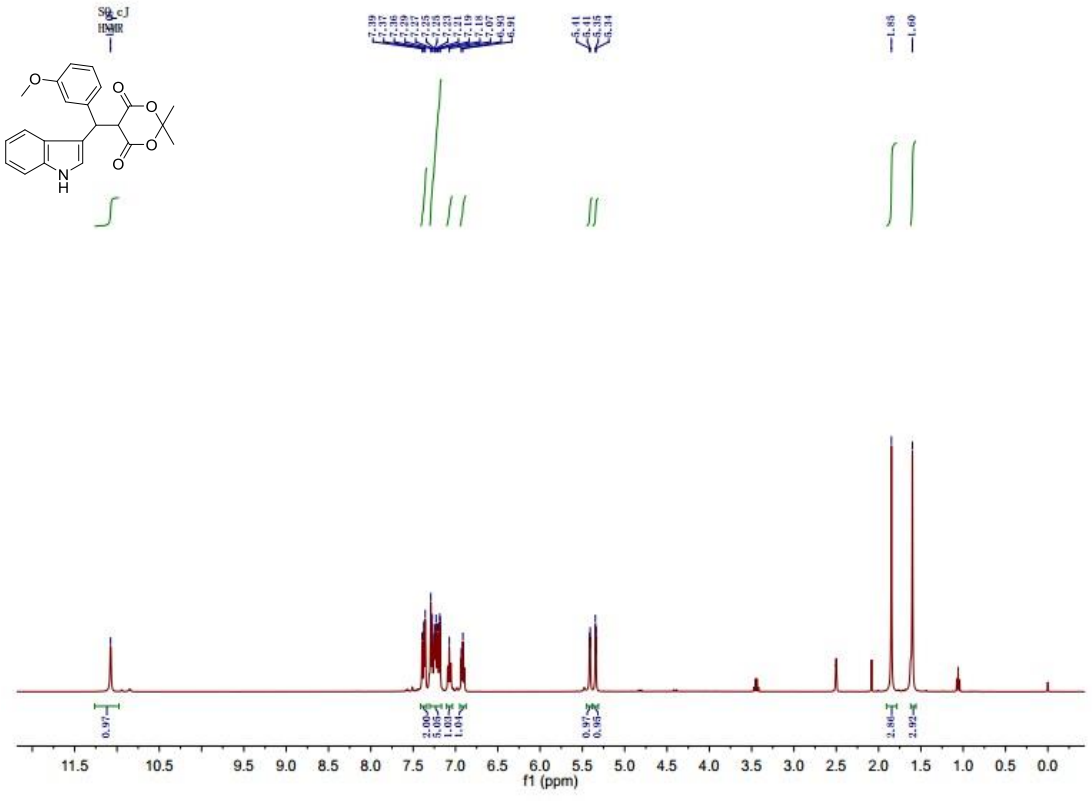

17-95-2-4-NO2
1H sample: 17-95-2-4-NO2 in DMSO
f1 (ppm)

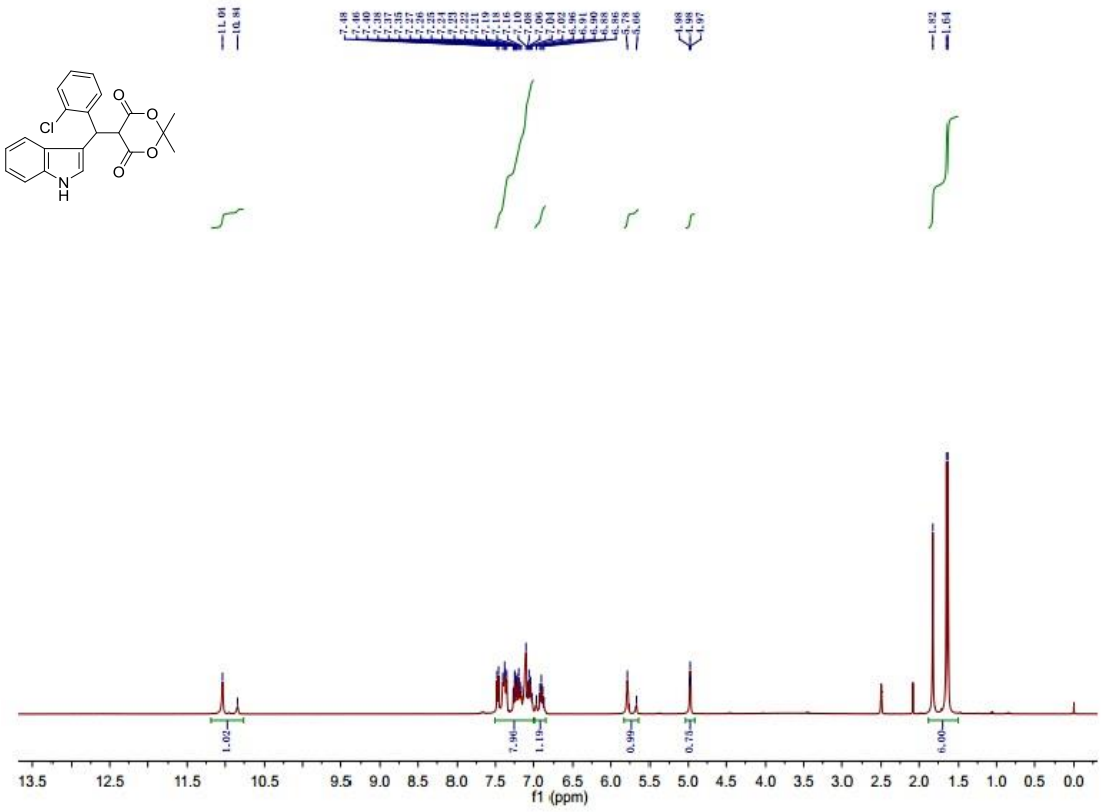

17-95-2-4-NO2
13C sample: 17-95-2-4-NO2 in DMSO
f1 (ppm)

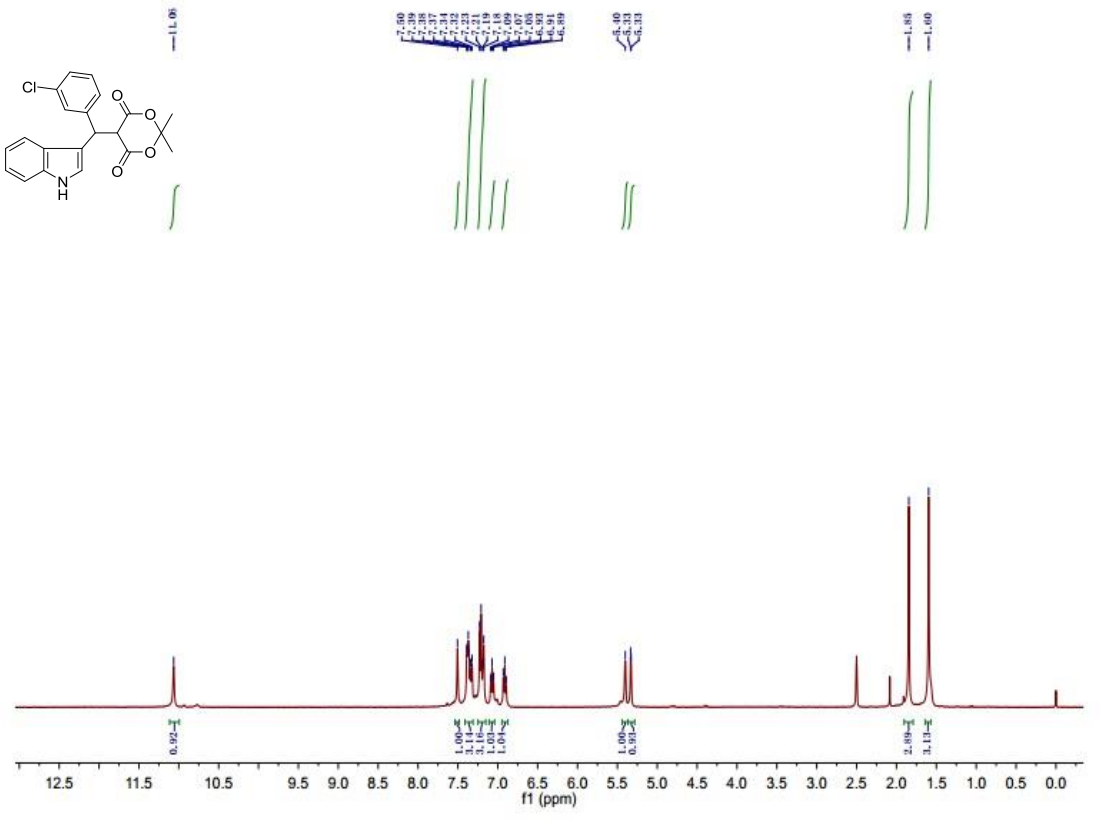


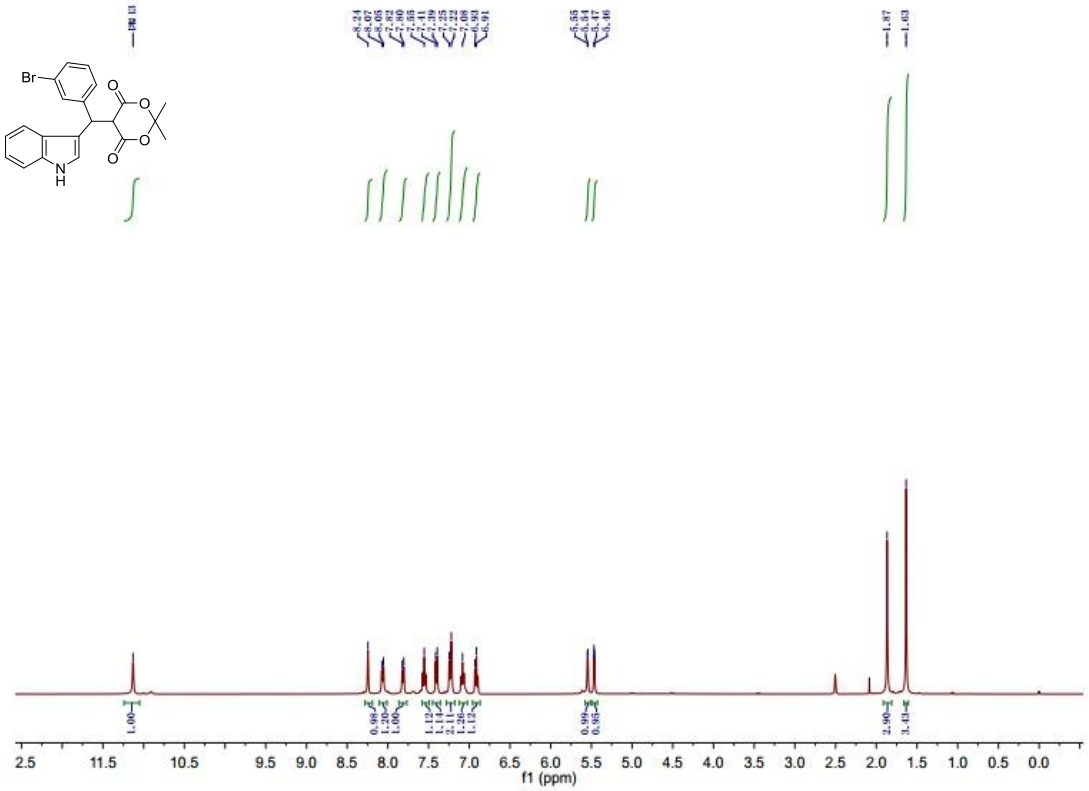


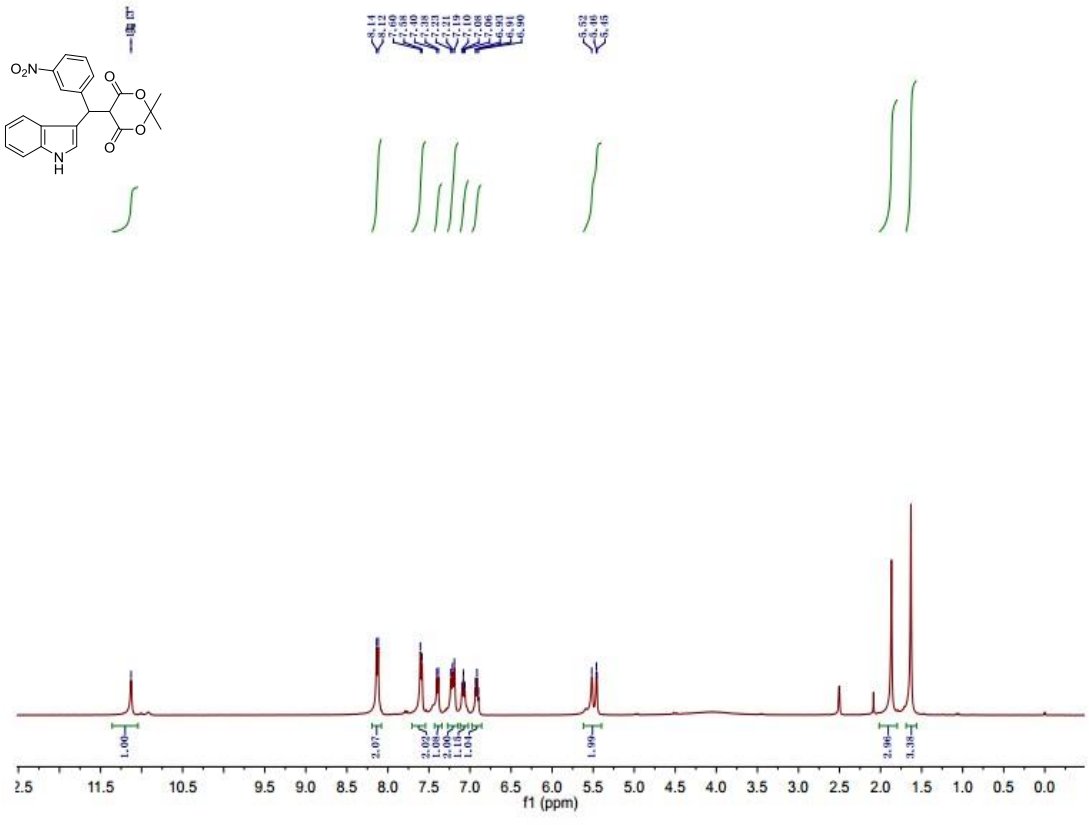

f1 (ppm)


f1 (ppm)


Cl
O
O
O
O
O
N
H
11.01
10.94
7.48
7.46
7.40
7.38
7.37
7.35
7.27
7.26
7.25
7.24
7.23
7.22
7.21
7.19
7.18
7.16
7.10
7.08
7.06
7.04
7.02
6.96
6.91
6.90
6.88
6.86
5.76
5.66
1.98
1.98
1.97
1.82
1.64
1.02
7.96
1.19
0.99
0.75
6.00
13.5
12.5
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


Cl
O
O
O
O
O
N
H
11.06
7.80
7.39
7.38
7.37
7.34
7.32
7.23
7.21
7.19
7.18
7.09
7.07
7.05
6.93
6.91
6.89
5.40
5.34
5.33
1.85
1.60
0.92
1.00
3.14
3.16
1.01
1.04
1.00
0.93
2.89
3.13
12.5
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


Br
O
O
O
O
O
N
H
8.24
8.07
8.05
7.82
7.80
7.55
7.41
7.39
7.25
7.22
7.09
6.93
6.91
5.55
5.54
5.47
5.46
1.87
1.63
1.00
0.98
1.20
1.00
1.12
1.14
2.14
1.16
1.12
0.99
0.95
2.90
3.43
2.5
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


O2N
O
O
O
O
O
N
H
8.14
8.12
7.69
7.58
7.40
7.38
7.23
7.21
7.19
7.10
7.08
7.06
6.93
6.91
6.90
5.52
5.46
5.45
1.00
2.07
2.02
1.08
1.10
1.04
1.99
2.96
3.38
2.5
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

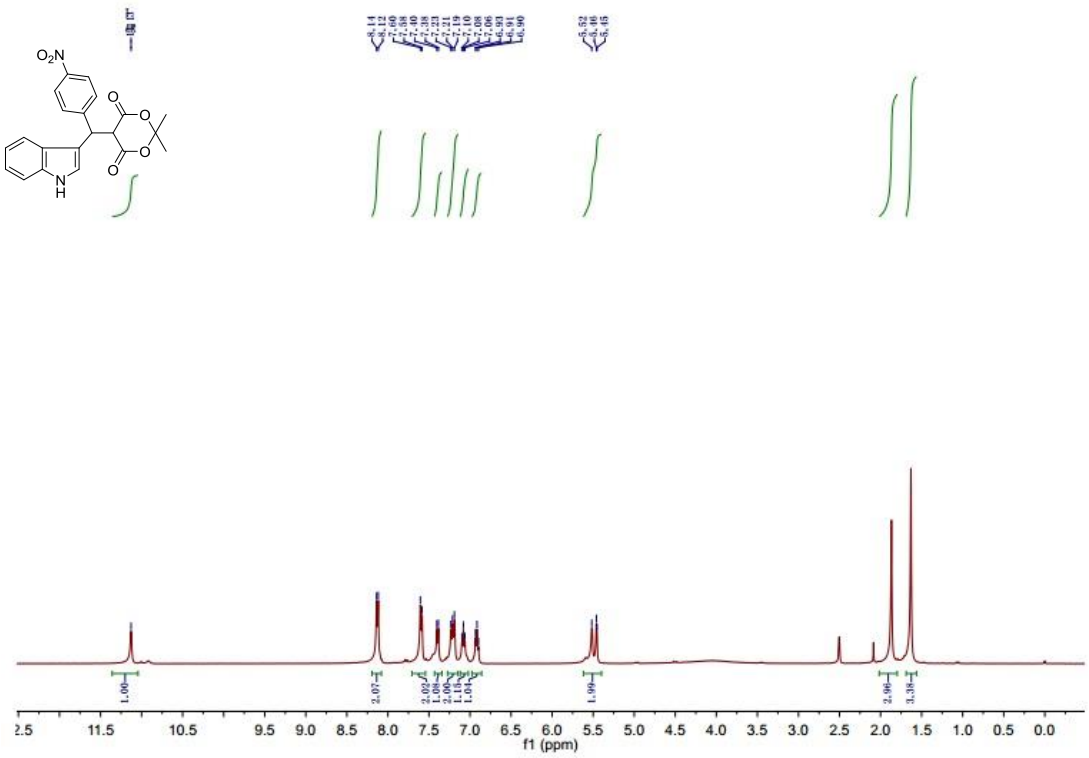
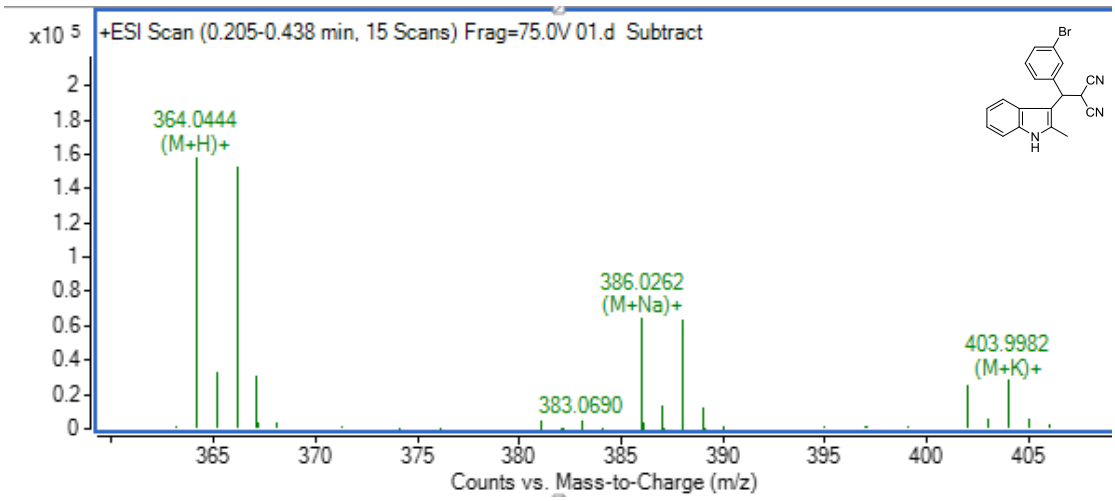


Table 1 The crystal structure date of **4a**

Empirical formula	$C_{18}H_{13}N_3$	γ(°)	107.406(11)
Formula weight	271.31	Volume(Å3)	736.4(9)
Temperature(K)	298.15	Z	2
Wavelength(Å)	0.71073	F(000)	284
Unit cell dimensions	a (Å) 6.727(5)	Completeness to $\theta = 25.00$	99.4 %
b (Å)	9.634(6)	Goodness-of-fit on F^2	1.097
c (Å)	12.094(8)	Final R indices [I>2σ(*I*)]	0.0504
α(°)	92.822(11)	R indices (all data)	0.0613
β(°)	98.356(10)	Largest diff. peak and hole (e. nm^{-3})	0.224 and -0.233


x10 5
+ESI Scan (0.205-0.438 min, 15 Scans) Frag=75.0V 01.d Subtract
364.0444
(M+H)+
386.0262
(M+Na)+
403.9982
(M+K)+
383.0690
Counts vs. Mass-to-Charge (m/z)
Br
CN
CN
N
H