Supporting Information

Convenient synthesis of 6,7,12,13-tetrahydro-5*H*-cyclohepta[2,1-*b*:3,4-*b*']diindole derivatives mediated by hypervalent iodine (III) reagent

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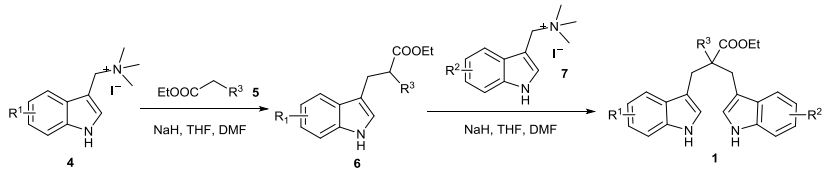
General

All the chemical reagents were commercial products and used without purification in all cases. TLC was performed on silica gel plates (0.15-0.2 mm thickness, Yantai Huiyou Company, China) and detected with UV light at 254 nM, Column chromatography was carried out on silica gel (200-300 mesh). Proton and carbon magnetic resonance spectra (^{1}H NMR and ^{13}C NMR) were recorded on Varian Mercury-300, Varian Mercury-400, Varian Mercury-500 and/or Varian Mercury-600 spectrometers. NMR experiments were conducted in CD_3OD and DMSO-d_6. Tetramethylsilane (TMS) was used as internal standard. Chemical shifts (δ) are reported in parts per million (ppm). Data are reported as follows: chemical shift, multiplicity (br s = broad singlet, d = doublet, dd = doublet of doublet, dt = doublet of triplet, m = multiple, s = singlet and t = triplet), coupling constants (Hz). Low-resolution mass spectra (ESI) were obtained using Agilent HPLC-MS (1200-6110). High resolution mass spectra (HRMS) were obtained using Agilent 1290-6545 UHPLC-QTOF. Melting points (mp) were measured by Büchi 510 melting point apparatus without further corrected.

General procedure for preparation of the substrates (both symmetric and asymmetric ones) ***1***



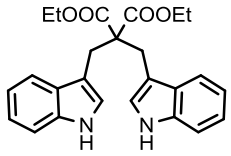
Ester **5** (3.3 mmol, 1.1 eq) was dissolved in tetrahydrofuran, sodium hydride (3.9 mmol, 1.3 eq) was added slowly at 0 ℃, and the mixture was moved to room temperature and stirred for 30 minutes, quaternary ammonium salt **4** (3 mmol, 1 eq) was dissolved in DMF and the solution was added to the reaction mixture, and stirred for 4 h at room temperature. After completion of the reaction, the resulting mixture was poured into water and extracted with ethyl acetate, the organic layer was washed with brine and dried over anhydrous sodium sulfate and concentrated in vacuum. The resulting residue was purified by silica gel chromatography (petroleum ether/ethyl acetate, v/v, 10:1 to 5:1) to afford **6**.

Ethyl R^3-substituted-3-(1*H*-indol-3-yl)propanoate **6** (1 mmol, 1 eq) was dissolved in tetrahydrofuran, sodium hydride (1.5 mmol, 1.5 eq) was added slowly at 0 ℃, and the mixture was

moved to room temperature and stirred for 30 minutes, quaternary ammonium salt **7** (1.5 mmol, 1.5 eq) was dissolved in DMF and the solution was added to the reaction mixture, and stirred for 4 h at room temperature. After completion of the reaction, the resulting mixture was poured into water and extracted with ethyl acetate, The organic layer was washed with brine and dried over anhydrous sodium sulfate and concentrated in vacuum. The resulting residue was purified by silica gel chromatography (petroleum ether/ethyl acetate, v/v, 8:1 to 4:1) to give 1,3-di(1*H*-indol-3-yl)propanes **1**.

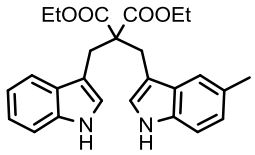
*Experiment data for substrates **1***

Diethyl 2,2-bis((1*H*-indol-3-yl)methyl)malonate (1a)



Yellow solid. (Yield of two steps, 82%). mp 120-122 ℃. ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.97 (s, 2H, NH), 7.41 (d, *J* = 7.9 Hz, 2H, Ar-H), 7.35 (d, *J* = 8.1 Hz, 2H, Ar-H), 7.16 (d, *J* = 2.4 Hz, 2H, Ar-H), 7.06 (t, *J* = 7.5 Hz, 2H, Ar-H), 6.95 (t, *J* = 7.4 Hz, 2H, Ar-H), 3.90 (q, *J* = 7.1 Hz, 4H, -$CO_2CH_2CH_3$), 3.34 (s, 4H, C_q-CH_2Ar), 1.00 (t, *J* = 7.1 Hz, 6H, -$CO_2CH_2CH_3$). ^{13}C NMR (125 MHz, DMSO-d_6) δ 170.92 (C=O), 135.73 (C), 127.81 (C), 124.00 (CH), 120.86 (CH), 118.24 (CH), 118.20 (CH), 111.30 (CH), 108.19 (C), 60.62 (OCH_2), 58.67 (C), 28.12 (CH_2), 13.53 (CH_3). HRMS (ESI): *m/z* calcd for $C_{25}H_{27}N_2O_4$ $[M + H]^+$: 419.1965, found: 419.1973.

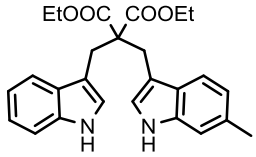
Diethyl 2-((1*H*-indol-3-yl)methyl)-2-((5-methyl-1*H*-indol-3-yl)methyl)malonate (1b)



Yellow solid. (Yield of two steps, 84%). mp 132-134 ℃. ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.97 (d, *J* = 2.7 Hz, 1H, NH), 10.83 (d, *J* = 2.6 Hz, 1H, NH), 7.40 (d, *J* = 7.9 Hz, 1H, Ar-H), 7.36 (d, *J* = 8.1 Hz, 1H, Ar-H), 7.22 (d, *J* = 8.2 Hz, 1H, Ar-H), 7.16 (d, *J* = 2.4 Hz, 1H, Ar-H), 7.14 – 7.09 (m, 2H, Ar-H), 7.06 (ddd, *J* = 8.1, 6.9, 1.2 Hz, 1H, Ar-H), 6.95 (ddd, *J* = 8.0, 6.9, 1.1 Hz, 1H, Ar-H), 6.87 (dd, *J* = 8.2, 1.6 Hz, 1H, Ar-H), 3.92 (q, *J* = 7.1 Hz, 4H, -$CO_2CH_2CH_3$), 3.32 (s, 4H, C_q-CH_2Ar), 2.29 (s, 3H, Ar-CH_3), 1.04 (t, *J* = 7.1 Hz, 6H, -$CO_2CH_2CH_3$). ^{13}C NMR (125 MHz, DMSO-d_6) δ 170.96 (C=O), 135.75 (C), 134.12 (C), 128.05 (C), 127.83 (C), 126.62 (C), 124.10 (CH), 123.85 (CH), 122.47 (CH), 120.90 (CH), 118.26 (CH), 118.22 (CH), 117.86 (CH), 111.30 (CH), 110.97 (CH), 108.27 (C), 107.60 (C), 60.65 (OCH_2), 58.54 (C), 27.96 (CH_2), 21.16 ($ArCH_3$), 13.57 (CH_3). HRMS (ESI): *m/z*

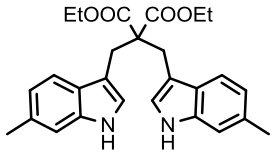
calcd for $C_{26}H_{29}N_2O_4$ [M + H]$^+$: 433.2122, found: 433.2130.

Diethyl 2-((1*H*-indol-3-yl)methyl)-2-((6-methyl-1*H*-indol-3-yl)methyl)malonate (1c)



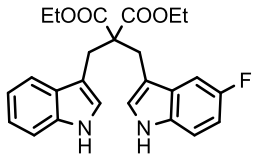
Yellow solid. (Yield of two steps, 87%). mp 119-121 ℃. ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.97 (s, 1H, NH), 10.81 (s, 1H, NH), 7.41 (d, *J* = 8.0 Hz, 1H, Ar-H), 7.35 (d, *J* = 8.1 Hz, 1H, Ar-H), 7.29 (d, *J* = 8.1 Hz, 1H, Ar-H), 7.15 (d, *J* = 2.5 Hz, 1H, Ar-H), 7.13 (s, 1H, Ar-H), 7.09 – 7.03 (m, 2H, Ar-H), 6.98 – 6.91 (m, 1H, Ar-H), 6.78 (d, *J* = 8.0 Hz, 1H, Ar-H), 3.90 (q, *J* = 7.1 Hz, 4H, -$CO_2CH_2CH_3$), 3.33 (s, 2H, C_q-CH_2Ar), 3.31 (s, 2H, C_q-CH_2Ar), 2.37 (s, 3H, Ar-CH_3), 1.02 (t, *J* = 7.1 Hz, 6H, -$CO_2CH_2CH_3$). ^{13}C NMR (125 MHz, DMSO-d_6) δ 170.93 (C=O), 136.18 (C), 135.73 (C), 129.84 (C), 127.81 (C), 125.82 (C), 124.00 (CH), 123.25 (CH), 120.87 (CH), 120.05 (CH), 118.24 (CH), 118.21 (CH), 117.95 (CH), 111.30 (CH), 111.12 (CH), 108.22 (C), 108.01 (C), 60.61 (OCH_2), 58.64 (C), 28.16 (CH_2), 28.03 (CH_2), 21.32 ($ArCH_3$), 13.57 (CH_3). HRMS (ESI): *m/z* calcd for $C_{26}H_{29}N_2O_4$ [M + H]$^+$: 433.2122, found: 433.2134.

Diethyl 2,2-bis((6-methyl-1*H*-indol-3-yl)methyl)malonate (1d)



Yellow solid. (Yield of two steps, 80%). mp 147-149 ℃. ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.79 (d, *J* = 2.5 Hz, 2H, NH), 7.28 (d, *J* = 8.1 Hz, 2H, Ar-H), 7.13 (s, 2H, Ar-H), 7.05 (d, *J* = 2.4 Hz, 2H, Ar-H), 6.78 (dd, *J* = 8.2, 1.5 Hz, 2H, Ar-H), 3.90 (q, *J* = 7.1 Hz, 4H, -$CO_2CH_2CH_3$), 3.29 (s, 4H, C_q-CH_2Ar), 2.37 (s, 6H, Ar-CH_3), 1.03 (t, *J* = 7.1 Hz, 6H, -$CO_2CH_2CH_3$). ^{13}C NMR (150 MHz, DMSO-d_6) δ 171.41 (C=O), 136.66 (C), 130.31 (C), 126.29 (C), 123.72 (CH), 120.52 (CH), 118.42 (CH), 111.59 (CH), 108.51 (C), 61.08 (OCH_2), 59.07 (C), 28.53 (CH_2), 21.81 ($ArCH_3$), 14.07 (CH_3). HRMS (ESI): *m/z* calcd for $C_{27}H_{31}N_2O_4$ [M + H]$^+$: 447.2278, found: 447.2290.

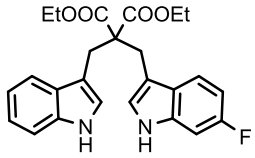
Diethyl 2-((1*H*-indol-3-yl)methyl)-2-((5-fluoro-1*H*-indol-3-yl)methyl)malonate (1e)



Yellow solid. (Yield of two steps, 83%). mp 119-121 ℃. ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.09 (s, 1H, NH), 10.98 (s, 1H, NH), 7.41 (dd, *J* = 8.1, 4.1 Hz, 1H, Ar-H), 7.37 – 7.30 (m, 2H, Ar-H), 7.25 (d, *J* = 2.3 Hz, 1H, Ar-H), 7.18 (d, *J* = 2.1 Hz, 1H, Ar-H), 7.14 – 7.08 (m, 1H, Ar-H), 7.06 (t, *J* = 7.6 Hz, 1H, Ar-H), 6.95 (t, *J* = 7.5 Hz, 1H, Ar-H), 6.90 (td, *J* = 9.3, 2.5 Hz, 1H, Ar-H), 3.89 (q, *J* = 7.1 Hz, 4H, -$CO_2CH_2CH_3$), 3.33 (s, 2H, C_q-CH_2Ar), 3.29 (s, 2H, C_q-CH_2Ar), 1.00 (t, *J* = 7.1 Hz, 6H, -$CO_2CH_2CH_3$). ^{13}C NMR

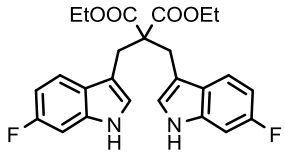
(125 MHz, DMSO-d_6) δ 170.89 (C=O), 156.69 (d, J = 230.9 Hz, CF), 135.74 (C), 132.39 (C), 128.08 (d, J = 9.7 Hz, C), 127.80 (C), 126.30 (CH), 124.03 (CH), 120.88 (CH), 118.26 (CH), 118.22 (CH), 112.22 (d, J = 9.9 Hz, CH), 111.30 (CH), 108.99 (d, J = 26.2 Hz, CH), 108.55 (d, J = 5.2 Hz, C), 108.12 (C), 102.91 (d, J = 23.1 Hz, CH), 60.65 (OCH_2), 58.70 (C), 28.31 (CH_2), 28.23 (CH_2), 13.50 (CH_3). HRMS (ESI): *m/z* calcd for $C_{25}H_{25}FN_2NaO_4$ [M + Na]$^+$: 459.1691, found: 459.1703.

Diethyl 2-((1*H*-indol-3-yl)methyl)-2-((6-fluoro-1*H*-indol-3-yl)methyl)malonate (1f)



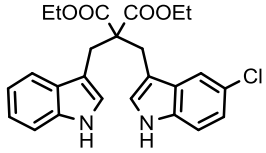
Yellow solid. (Yield of two steps, 81%). mp 124-126 ℃. ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.04 (d, J = 2.5 Hz, 1H, NH), 10.97 (s, 1H, NH), 7.43 – 7.36 (m, 2H, Ar-H), 7.34 (d, J = 7.9 Hz, 1H, Ar-H), 7.18 (d, J = 2.4 Hz, 1H, Ar-H), 7.16 (d, J = 2.4 Hz, 1H, Ar-H), 7.12 (dd, J = 10.1, 2.4 Hz, 1H, Ar-H), 7.05 (ddd, J = 8.0, 6.8, 1.1 Hz, 1H, Ar-H), 6.94 (t, J = 7.5 Hz, 1H, Ar-H), 6.85 – 6.76 (m, 1H, Ar-H), 3.89 (q, J = 7.1 Hz, 4H, -$CO_2CH_2CH_3$), 3.33 (s, 2H, C_q-CH_2Ar), 3.31 (s, 2H, C_q-CH_2Ar), 1.00 (t, J = 7.1 Hz, 6H, -$CO_2CH_2CH_3$). ^{13}C NMR (125 MHz, DMSO-d_6) δ 170.87 (C=O), 158.68 (d, J = 234.0 Hz, CF), 135.73 (C), 135.51 (d, J = 12.7 Hz, C), 127.79 (C), 124.66 (CH), 124.63 (d, J = 3.1 Hz, C), 124.04 (CH), 120.87 (CH), 119.24 (d, J = 10.3 Hz, CH), 118.25 (CH), 118.20 (CH), 111.31 (CH), 108.51 (C), 108.11 (C), 106.73 (d, J = 24.4 Hz, CH), 97.18 (d, J = 25.2 Hz, CH), 60.65 (OCH_2), 58.66 (C), 28.21 (CH_2), 28.06 (CH_2), 13.53 (CH_3). HRMS (ESI): *m/z* calcd for $C_{25}H_{26}FN_2O_4$ [M + H]$^+$: 437.1871, found: 437.1878.

Diethyl 2,2-bis((6-fluoro-1*H*-indol-3-yl)methyl)malonate (1g)



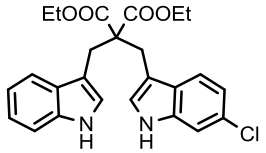
Yellow solid. (Yield of two steps, 80%). mp 119-121 ℃. ^{1}H NMR (600 MHz, DMSO-d_6) δ 11.01 (s, 2H, NH), 7.37 (dd, J = 8.7, 5.4 Hz, 2H, Ar-H), 7.16 (d, J = 2.4 Hz, 2H, Ar-H), 7.11 (dd, J = 10.1, 2.4 Hz, 2H, Ar-H), 6.80 (ddd, J = 9.8, 8.7, 2.4 Hz, 2H, Ar-H), 3.89 (q, J = 7.1 Hz, 4H, -$CO_2CH_2CH_3$), 3.31 (s, 4H, C_q-CH_2Ar), 0.99 (t, J = 7.1 Hz, 6H, -$CO_2CH_2CH_3$). ^{13}C NMR (125 MHz, DMSO-d_6) δ 170.85 (C=O), 158.71 (d, J = 233.8 Hz, CF), 135.54 (d, J = 12.7 Hz, C), 124.70 (d, J = 3.4 Hz, C), 124.67 (CH), 119.26 (d, J = 10.2 Hz, CH), 108.44 (C), 106.79 (d, J = 24.5 Hz, CH), 97.22 (d, J = 25.3 Hz, CH), 60.72 (OCH_2), 58.65 (C), 28.16 (CH_2), 13.55 (CH_3). HRMS (ESI): *m/z* calcd for $C_{25}H_{25}F_2N_2O_4$ [M + H]$^+$: 455.1777, found: 455.1782.

Diethyl 2-((1*H*-indol-3-yl)methyl)-2-((5-chloro-1*H*-indol-3-yl)methyl)malonate (1h)



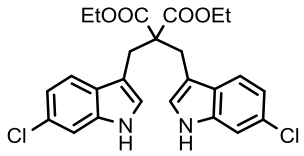
Yellow solid. (Yield of two steps, 82%). mp 122-124 ℃. ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.18 (s, 1H, NH), 10.99 (s, 1H, NH), 7.43 (d, J = 8.0 Hz, 1H, Ar-H), 7.38 (d, J = 2.0 Hz, 1H, Ar-H), 7.36 (d, J = 8.7 Hz, 1H, Ar-H), 7.35 (d, J = 8.0 Hz, 1H, Ar-H), 7.27 (d, J = 2.5 Hz, 1H, Ar-H), 7.19 (d, J = 2.4 Hz, 1H, Ar-H), 7.09 – 7.02 (m, 2H, Ar-H), 6.95 (t, J = 7.4 Hz, 1H, Ar-H), 3.89 (q, J = 7.1 Hz, 4H, -$CO_2CH_2CH_3$), 3.32 (s, 2H, C_q-CH_2Ar), 3.30 (s, 2H, C_q-CH_2Ar), 1.01 (t, J = 7.1 Hz, 6H, -$CO_2CH_2CH_3$). ^{13}C NMR (125 MHz, DMSO-d_6) δ 170.84 (C=O), 135.75 (C), 134.18 (C), 128.90 (C), 127.78 (C), 126.20 (CH), 124.08 (CH), 123.09 (C), 120.89 (CH), 120.76 (CH), 118.28 (CH), 118.23 (CH), 117.57 (CH), 112.84 (CH), 111.31 (CH), 108.18 (C), 108.05 (C), 60.68 (OCH_2), 58.65 (C), 28.34 (CH_2), 28.06 (CH_2), 13.50 (CH_3). HRMS (ESI): *m/z* calcd for $C_{25}H_{26}ClN_2O_4$ $[M + H]^+$: 453.1576, found: 453.1582.

Diethyl 2-((1*H*-indol-3-yl)methyl)-2-((6-chloro-1*H*-indol-3-yl)methyl)malonate (1i)



Yellow solid. (Yield of two steps, 80%). mp 129-131 ℃. ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.11 (s, 1H, NH), 10.98 (s, 1H, NH), 7.44 – 7.37 (m, 3H, Ar-H), 7.35 (d, J = 8.1 Hz, 1H, Ar-H), 7.23 (d, J = 2.4 Hz, 1H, Ar-H), 7.16 (d, J = 2.4 Hz, 1H, Ar-H), 7.06 (ddd, J = 8.1, 6.9, 1.2 Hz, 1H, Ar-H), 6.99 – 6.91 (m, 2H, Ar-H), 3.89 (q, J = 7.1 Hz, 4H, -$CO_2CH_2CH_3$), 3.33 (s, 2H, C_q-CH_2Ar), 3.31 (s, 2H, C_q-CH_2Ar), 1.00 (t, J = 7.1 Hz, 6H, -$CO_2CH_2CH_3$). ^{13}C NMR (125 MHz, DMSO-d_6) δ 170.85 (C=O), 136.08 (C), 135.75 (C), 127.79 (C), 126.64 (C), 125.60 (C), 125.27 (CH), 124.08 (CH), 120.89 (CH), 119.65 (CH), 118.61 (CH), 118.28 (CH), 118.20 (CH), 111.33 (CH), 110.91 (CH), 108.63 (C), 108.07 (C), 60.68 (OCH_2), 58.68 (C), 28.27 (CH_2), 28.03 (CH_2), 13.54 (CH_3). HRMS (ESI): *m/z* calcd for $C_{25}H_{26}ClN_2O_4$ $[M + H]^+$: 453.1576, found: 453.1577.

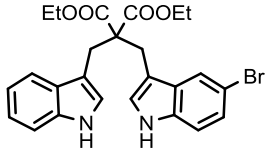
Diethyl 2,2-bis((6-chloro-1*H*-indol-3-yl)methyl)malonate (1j)



Yellow solid. (Yield of two steps, 81%). mp 172-174 ℃. ^{1}H NMR (600 MHz, DMSO-d_6) δ 11.10 (d, J = 2.5 Hz, 2H, NH), 7.42 – 7.37 (m, 4H, Ar-H), 7.21 (d, J = 2.4 Hz, 2H, Ar-H), 6.96 (dd, J = 8.4, 2.0 Hz, 2H, Ar-H), 3.89 (q, J = 7.1 Hz, 4H, -$CO_2CH_2CH_3$), 3.31 (s, 4H, C_q-CH_2Ar), 0.99 (t, J = 7.1 Hz, 6H, -$CO_2CH_2CH_3$). ^{13}C NMR (125 MHz, DMSO-d_6) δ 170.78 (C=O), 136.10 (C), 126.63 (C), 125.63 (C), 125.37 (CH), 119.67 (CH), 118.65 (CH), 110.95 (CH), 108.51 (C), 60.75 (OCH_2), 58.67

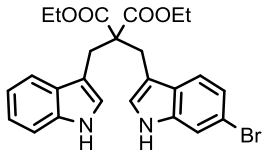
(C), 28.16 (CH_2), 13.55 (CH_3). HRMS (ESI): *m/z* calcd for $C_{25}H_{23}Cl_2N_2O_4$ $[M - H]^-$: 485.1040, found: 485.1028.

Diethyl 2-((1*H*-indol-3-yl)methyl)-2-((5-bromo-1*H*-indol-3-yl)methyl)malonate (1k)



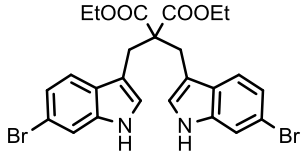
Yellow solid. (Yield of two steps, 82%). mp 124-126 ℃. ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.20 (s, 1H, NH), 10.99 (s, 1H, NH), 7.53 (d, *J* = 2.0 Hz, 1H, Ar-H), 7.43 (d, *J* = 8.0 Hz, 1H, Ar-H), 7.35 (d, *J* = 8.2 Hz, 1H, Ar-H), 7.32 (d, *J* = 8.6 Hz, 1H, Ar-H), 7.26 (d, *J* = 2.5 Hz, 1H, Ar-H), 7.20 (d, *J* = 2.4 Hz, 1H, Ar-H), 7.16 (dd, *J* = 8.6, 1.9 Hz, 1H, Ar-H), 7.06 (t, *J* = 7.6 Hz, 1H, Ar-H), 6.96 (t, *J* = 7.4 Hz, 1H, Ar-H), 3.89 (q, *J* = 7.1 Hz, 4H, -$CO_2CH_2CH_3$), 3.32 (s, 2H, C_q-CH_2Ar), 3.30 (s, 2H, C_q-CH_2Ar), 1.02 (t, *J* = 7.1 Hz, 6H, -$CO_2CH_2CH_3$). ^{13}C NMR (125 MHz, DMSO-d_6) δ 170.83 (C=O), 135.76 (C), 134.41 (C), 129.59 (C), 127.78 (C), 126.08 (CH), 124.09 (CH), 123.27 (CH), 120.89 (CH), 120.61 (CH), 118.29 (CH), 118.23 (CH), 113.32 (CH), 111.32 (CH), 111.03 (C), 108.08 (C), 108.04 (C), 60.69 (OCH_2), 58.61 (C), 28.33 (CH_2), 28.04 (CH_2), 13.52 (CH_3). HRMS (ESI): *m/z* calcd for $C_{25}H_{26}BrN_2O_4$ $[M + H]^+$: 497.1070, found: 497.1072.

Diethyl 2-((1*H*-indol-3-yl)methyl)-2-((6-bromo-1*H*-indol-3-yl)methyl)malonate (1l)



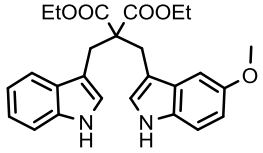
Yellow solid. (Yield of two steps, 81%). mp 132-134 ℃. ^{1}H NMR (600 MHz, DMSO-d_6) δ 11.10 (s, 1H, NH), 10.95 (s, 1H, NH), 7.53 (d, *J* = 1.8 Hz, 1H, Ar-H), 7.41 (d, *J* = 7.4 Hz, 1H, Ar-H), 7.36 (d, *J* = 2.4 Hz, 1H, Ar-H), 7.34 (d, *J* = 2.0 Hz, 1H, Ar-H), 7.21 (d, *J* = 2.4 Hz, 1H, Ar-H), 7.15 (d, *J* = 2.4 Hz, 1H, Ar-H), 7.09 – 7.03 (m, 2H, Ar-H), 6.95 (ddd, *J* = 8.0, 6.9, 1.0 Hz, 1H, Ar-H), 3.90 (q, *J* = 7.1 Hz, 4H, -$CO_2CH_2CH_3$), 3.33 (s, 2H, C_q-CH_2Ar), 3.31 (s, 2H, C_q-CH_2Ar), 1.00 (t, *J* = 7.1 Hz, 6H, -$CO_2CH_2CH_3$). ^{13}C NMR (125 MHz, DMSO-d_6) δ 170.82 (C=O), 136.56 (C), 135.72 (C), 127.76 (C), 126.85 (C), 125.21 (CH), 124.08 (CH), 121.13 (CH), 120.88 (CH), 120.05 (CH), 118.26 (CH), 118.19 (CH), 113.85 (CH), 113.60 (C), 111.31 (CH), 108.62 (C), 108.03 (C), 60.67 (OCH_2), 58.64 (C), 28.23 (CH_2), 27.96 (CH_2), 13.52 (CH_3). HRMS (ESI): *m/z* calcd for $C_{25}H_{26}BrN_2O_4$ $[M + H]^+$: 497.1070, found: 497.1077.

Diethyl 2,2-bis((6-bromo-1*H*-indol-3-yl)methyl)malonate (1m)



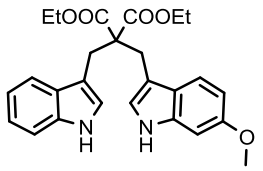
Yellow solid. (Yield of two steps, 81%). mp 183-185 ℃. ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.13 (d, J = 2.6 Hz, 2H, NH), 7.53 (d, J = 1.8 Hz, 2H, Ar-H), 7.35 (d, J = 8.5 Hz, 2H, Ar-H), 7.22 (d, J = 2.5 Hz, 2H, Ar-H), 7.07 (dd, J = 8.5, 1.9 Hz, 2H, Ar-H), 3.89 (q, J = 7.1 Hz, 4H, -$CO_2CH_2CH_3$), 3.30 (s, 4H, C_q-CH_2Ar), 0.99 (t, J = 7.1 Hz, 6H, -$CO_2CH_2CH_3$). ^{13}C NMR (125 MHz, DMSO-d_6) δ 170.73 (C=O), 136.59 (C), 126.84 (C), 125.28 (CH), 121.16 (CH), 120.05 (CH), 113.88 (CH), 113.63 (C), 108.53 (C), 60.73 (OCH_2), 58.65 (C), 28.14 (CH_2), 13.53 (CH_3). HRMS (ESI): *m/z* calcd for $C_{25}H_{23}Br_2N_2O_4$ $[M - H]^-$: 573.0030, found: 573.0013.

Diethyl 2-((1*H*-indol-3-yl)methyl)-2-((5-methoxy-1*H*-indol-3-yl)methyl)malonate (1n)



Yellow solid. (Yield of two steps, 81%). mp 95-97 ℃. ^{1}H NMR (400 MHz, Methanol-d_4) δ 7.42 (d, J = 8.0 Hz, 1H, Ar-H), 7.32 (d, J = 8.1 Hz, 1H, Ar-H), 7.20 (d, J = 8.8 Hz, 1H, Ar-H), 7.11 (s, 1H, Ar-H), 7.08 (ddd, J = 8.1, 7.0, 1.2 Hz, 1H, Ar-H), 7.03 (s, 1H, Ar-H), 6.96 (ddd, J = 8.0, 7.0, 1.0 Hz, 1H, Ar-H), 6.83 (d, J = 2.4 Hz, 1H, Ar-H), 6.71 (dd, J = 8.7, 2.4 Hz, 1H, Ar-H), 3.98 (q, J = 7.2 Hz, 4H, -$CO_2CH_2CH_3$), 3.57 (s, 3H, -OCH_3), 3.46 (s, 2H, C_q-CH_2Ar), 3.45 (s, 2H, C_q-CH_2Ar), 1.05 (t, J = 7.1 Hz, 6H, -$CO_2CH_2CH_3$). ^{13}C NMR (150 MHz, Methanol-d_4) δ 173.52 (C=O), 154.87 (C), 137.60 (C), 132.78 (C), 129.88 (C), 129.54 (C), 125.43 (CH), 124.37 (CH), 122.37 (CH), 119.59 (CH), 119.50 (CH), 112.77 (CH), 112.70 (CH), 112.09 (CH), 110.41 (C), 110.12 (C), 101.34 (CH), 62.36 (OCH_2), 60.84 (C), 55.98 (OCH_3), 29.79 (CH_2), 29.69 (CH_2), 14.08 (CH_3). HRMS (ESI): *m/z* calcd for $C_{26}H_{29}N_2O_5$ $[M + H]^+$: 449.2071, found: 449.2082.

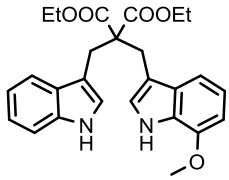
Diethyl 2-((1*H*-indol-3-yl)methyl)-2-((6-methoxy-1*H*-indol-3-yl)methyl)malonate (1o)



Yellow solid. (Yield of two steps, 84%). mp 114-116 ℃. ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.96 (d, J = 2.4 Hz, 1H, NH), 10.76 (s, 1H, NH), 7.40 (d, J = 7.9 Hz, 1H, Ar-H), 7.34 (d, J = 8.1 Hz, 1H, Ar-H), 7.26 (d, J = 8.7 Hz, 1H, Ar-H), 7.14 (d, J = 2.4 Hz, 1H, Ar-H), 7.08 – 7.03 (m, 1H, Ar-H), 7.02 (d, J = 2.3 Hz, 1H, Ar-H), 6.97 – 6.91 (m, 1H, Ar-H), 6.84 (d, J = 2.3 Hz, 1H, Ar-H), 6.60 (dd, J = 8.7, 2.3 Hz, 1H, Ar-H), 3.90 (q, J = 7.1 Hz, 4H, -$CO_2CH_2CH_3$), 3.75 (s, 3H, -OCH_3), 3.32 (s, 2H, C_q-CH_2Ar), 3.28 (s, 2H, C_q-CH_2Ar), 1.02 (t, J = 7.1 Hz, 6H, -$CO_2CH_2CH_3$). ^{13}C NMR (125 MHz, DMSO-d_6) δ 170.94 (C=O), 155.39 (C), 136.43 (C), 135.74 (C), 127.82 (C), 124.00 (CH), 122.55 (CH), 122.22 (C),

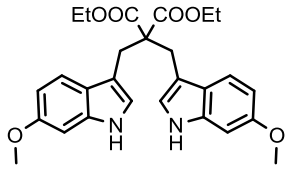
120.88 (CH), 118.84 (CH), 118.25 (CH), 118.21 (CH), 111.31 (CH), 108.56 (CH), 108.21 (C), 108.18 (C), 94.31 (CH), 60.63 (OCH_2), 58.64 (C), 55.11 (OCH_3), 28.15 (CH_2), 28.02 (CH_2), 13.58 (CH_3). HRMS (ESI): *m/z* calcd for $C_{26}H_{29}N_2O_5$ $[M + H]^+$: 449.2071, found: 449.2084.

Diethyl 2-((1*H*-indol-3-yl)methyl)-2-((7-methoxy-1*H*-indol-3-yl)methyl)malonate (1p)



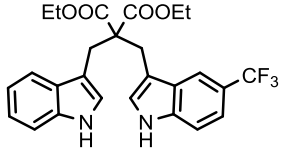
Yellow solid. (Yield of two steps, 78%). mp 159-161 ℃. ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.08 (d, *J* = 2.5 Hz, 1H, NH), 10.96 (s, 1H, NH), 7.40 (d, *J* = 7.9 Hz, 1H, Ar-H), 7.34 (d, *J* = 8.1 Hz, 1H, Ar-H), 7.14 (d, *J* = 2.4 Hz, 1H, Ar-H), 7.08 – 7.03 (m, 2H, Ar-H), 7.01 (d, *J* = 8.1 Hz, 1H, Ar-H), 6.97 – 6.91 (m, 1H, Ar-H), 6.87 (t, *J* = 7.8 Hz, 1H, Ar-H), 6.63 (d, *J* = 7.6 Hz, 1H, Ar-H), 3.90 (q, *J* = 7.1 Hz, 4H, -$CO_2CH_2CH_3$), 3.90 (s, 3H, -OCH_3), 3.32 (s, 2H, C_q-CH_2Ar), 3.31 (s, 2H, C_q-CH_2Ar), 1.01 (t, *J* = 7.1 Hz, 6H, -$CO_2CH_2CH_3$). ^{13}C NMR (125 MHz, DMSO-d_6) δ 170.92 (C=O), 146.03 (C), 135.73 (C), 129.38 (C), 127.81 (C), 125.82 (C), 123.98 (CH), 123.48 (CH), 120.88 (CH), 118.84 (CH), 118.26 (CH), 118.19 (CH), 111.31 (CH), 111.13 (CH), 108.76 (C), 108.19 (C), 101.41 (CH), 60.64 (OCH_2), 58.66 (C), 55.03 (OCH_3), 28.29 (CH_2), 28.07 (CH_2), 13.56 (CH_3). HRMS (ESI): *m/z* calcd for $C_{26}H_{29}N_2O_5$ $[M + H]^+$: 449.2071, found: 449.2082.

Diethyl 2,2-bis((6-methoxy-1*H*-indol-3-yl)methyl)malonate (1q)



Yellow solid. (Yield of two steps, 80%). mp 129-131 ℃. ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.75 (d, *J* = 2.5 Hz, 2H, NH), 7.25 (d, *J* = 8.7 Hz, 2H, Ar-H), 7.00 (d, *J* = 2.4 Hz, 2H, Ar-H), 6.84 (d, *J* = 2.3 Hz, 2H, Ar-H), 6.60 (dd, *J* = 8.7, 2.3 Hz, 2H, Ar-H), 3.91 (q, *J* = 7.0 Hz, 4H, -$CO_2CH_2CH_3$), 3.74 (s, 6H, -OCH_3), 3.27 (s, 4H, C_q-CH_2Ar), 1.03 (t, *J* = 7.1 Hz, 6H, -$CO_2CH_2CH_3$). ^{13}C NMR (150 MHz, DMSO-d_6) δ 170.92 (C=O), 155.38 (C), 136.42 (C), 122.53 (CH), 122.21 (C), 118.82 (CH), 108.54 (CH), 108.18 (C), 94.29 (CH), 60.61 (OCH_2), 58.59 (C), 55.10 (OCH_3), 28.03 (CH_2), 13.59 (CH_3). HRMS (ESI): *m/z* calcd for $C_{27}H_{31}N_2O_6$ $[M + H]^+$: 479.2177, found: 479.2189.

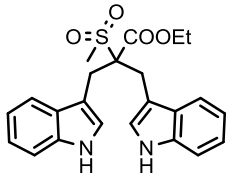
Diethyl 2-((1*H*-indol-3-yl)methyl)-2-((5-(trifluoromethyl)-1*H*-indol-3-yl)methyl)malonate (1r)



Yellow solid. (Yield of two steps, 84%). mp 127-129 ℃. ^{1}H NMR (400 MHz, Methanol-d_4) δ 7.75 (d, *J* = 1.7 Hz, 1H, Ar-H), 7.50 – 7.43 (m, 2H, Ar-H), 7.36 – 7.30 (m, 2H, Ar-H), 7.25 (s, 1H, Ar-H), 7.12 (s, 1H, Ar-H), 7.08 (t, *J* = 7.4 Hz, 1H, Ar-H), 6.97 (td, *J* = 7.4, 7.0, 1.0 Hz, 1H, Ar-H), 3.93 (q, *J* = 7.2 Hz,

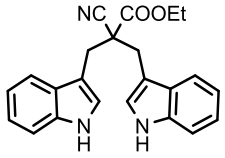
4H, -$CO_2CH_2CH_3$), 3.48 (s, 2H, C_q-CH_2Ar), 3.45 (s, 2H, C_q-CH_2Ar), 1.03 (t, *J* = 7.1 Hz, 6H, -$CO_2CH_2CH_3$). ^{13}C NMR (125 MHz, DMSO-d_6) δ 170.82 (C=O), 137.25 (C), 135.77 (C), 127.76 (C), 127.04 (C), 126.86 (CH), 125.64 (q, *J* = 271.1 Hz, CF_3), 124.10 (CH), 120.90 (CH), 119.24 (q, *J* = 30.9 Hz, CCF_3), 118.28 (CH), 118.21 (CH), 117.23 (d, *J* = 3.7 Hz, CH), 115.85 (d, *J* = 4.6 Hz, CH), 112.13 (CH), 111.32 (CH), 109.50 (C), 107.99 (C), 60.67 (OCH_2), 58.61 (C), 28.37 (CH_2), 27.99 (CH_2), 13.43 (CH_3). HRMS (ESI): *m/z* calcd for $C_{26}H_{26}F_3N_2O_4$ $[M + H]^+$: 487.1839, found: 487.1842.

Ethyl 2-((1*H*-indol-3-yl)methyl)-3-(1*H*-indol-3-yl)-2-(methylsulfonyl)propanoate (1s)



Yellow solid. (Yield of two steps, 78%). mp 194-196 ℃. ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.00 (d, *J* = 2.6 Hz, 2H, NH), 7.54 (d, *J* = 7.9 Hz, 2H, Ar-H), 7.34 (d, *J* = 8.0 Hz, 2H, Ar-H), 7.14 (d, *J* = 2.5 Hz, 2H, Ar-H), 7.06 (ddd, *J* = 8.1, 6.9, 1.3 Hz, 2H, Ar-H), 6.98 (ddd, *J* = 7.4, 7.0, 1.2 Hz, 2H, Ar-H), 4.02 (q, *J* = 7.1 Hz, 2H, -$CO_2CH_2CH_3$), 3.64 (d, *J* = 15.0 Hz, 2H, C_q-C*H*HAr), 3.47 (d, *J* = 15.1 Hz, 2H, C_q-CH*H*Ar), 2.80 (s, 3H, - SO_2CH_3), 0.96 (t, *J* = 7.1 Hz, 3H, -$CO_2CH_2CH_3$). ^{13}C NMR (125 MHz, DMSO-d_6) δ 168.16 (C=O), 135.56 (C), 127.95 (C), 125.29 (CH), 120.91 (CH), 118.66 (CH), 118.46 (CH), 111.33 (CH), 107.06 (C), 75.68 (C), 61.78 (OCH_2), 40.29 (SO_2CH_3), 27.97 (CH_2), 13.29 (CH_3). HRMS (ESI): *m/z* calcd for $C_{23}H_{25}N_2O_4S$ $[M + H]^+$: 425.1530, found: 425.1541.

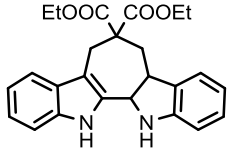
Ethyl 2-((1*H*-indol-3-yl)methyl)-2-cyano-3-(1*H*-indol-3-yl)propanoate (1t)



Yellow solid. (Yield of two steps, 85%). mp 100-102 ℃. ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.06 (s, 2H, NH), 7.58 (d, *J* = 7.9 Hz, 2H, Ar-H), 7.36 (d, *J* = 8.1 Hz, 2H, Ar-H), 7.22 (d, *J* = 2.5 Hz, 2H, Ar-H), 7.08 (ddd, *J* = 8.2, 6.9, 1.2 Hz, 2H, Ar-H), 6.99 (ddd, *J* = 8.0, 6.9, 1.1 Hz, 2H, Ar-H), 3.89 (q, *J* = 7.1 Hz, 2H, -$CO_2CH_2CH_3$), 3.53 (d, *J* = 14.5 Hz, 2H, C_q-C*H*HAr), 3.44 (d, *J* = 14.5 Hz, 2H, C_q-CH*H*Ar), 0.86 (t, *J* = 7.1 Hz, 3H, -$CO_2CH_2CH_3$). ^{13}C NMR (125 MHz, DMSO-d_6) δ 168.84 (C=O), 135.79 (C), 127.19 (C), 124.62 (CH), 121.07 (CH), 120.07 (CN), 118.54 (CH), 118.50 (CH), 111.41 (CH), 107.71 (C), 62.06 (OCH_2), 53.90 (C), 32.87 (CH_2), 13.39 (CH_3). HRMS (ESI): *m/z* calcd for $C_{23}H_{22}N_3O_2$ $[M + H]^+$: 372.1707, found: 372.1717.

*Experiment data for compound **3a***

Diethyl 4b,5,7,12,12b,13-hexahydro-6*H*-cyclohepta[2,1-*b*:3,4-*b'*]diindole-6,6-dicarboxylate (3a)



Yellow solid. mp 90-92 ℃. ^{1}H NMR (500 MHz, Methanol-d_4) δ 7.51 (d, J = 7.6 Hz, 1H, Ar-H), 7.29 (d, J = 7.9 Hz, 1H, Ar-H), 7.13 (d, J = 7.4 Hz, 1H, Ar-H), 7.06 – 7.01 (m, 2H, Ar-H), 6.99 (ddd, J = 8.0, 7.0, 1.2 Hz, 1H, Ar-H), 6.75 (td, J = 7.4, 1.0 Hz, 1H, Ar-H), 6.71 (d, J = 7.8 Hz, 1H, Ar-H), 5.14 (d, J = 8.5 Hz, 1H, -NHC*H*), 4.32 – 4.21 (m, 2H, -$CO_2CH_2CH_3$), 4.00 (q, J = 7.1 Hz, 2H, -$CO_2CH_2CH_3$), 3.84 (ddd, J = 11.1, 8.9, 1.6 Hz, 1H, -NHCHC*H*), 3.57 (d, J = 15.1 Hz, 1H, C_q-C*H*HAr), 3.31 – 3.27 (m, 1H, C_q-C*H*HAr), 2.27 (dd, J = 14.9, 11.4 Hz, 1H, C_q-CH*H*Ar), 2.13 (d, J = 14.8 Hz, 1H, C_q-CH*H*Ar), 1.29 (t, J = 7.1 Hz, 3H, -$CO_2CH_2CH_3$), 1.10 (t, J = 7.1 Hz, 3H, -$CO_2CH_2CH_3$). ^{13}C NMR (125 MHz, Methanol-d_4) δ 173.48 (C=O), 173.04 (C=O), 150.92 (C), 137.21 (C), 136.21 (C), 134.88 (C), 129.41 (C), 128.97 (CH), 125.34 (CH), 121.81 (CH), 120.76 (CH), 119.82 (CH), 119.12 (CH), 111.72 (CH), 111.30 (CH), 106.21 (C), 62.66 (OCH_2), 62.53 (OCH_2), 60.79 (NHCH), 57.84 (C), 41.70 (CH), 36.69 (CH_2), 27.53 (CH_2), 14.51 (CH_3), 14.27 (CH_3). HRMS (ESI): *m/z* calcd for $C_{25}H_{27}N_2O_4$ $[M + H]^+$: 419.1965, found: 419.1964.

Copies of NMR spectra

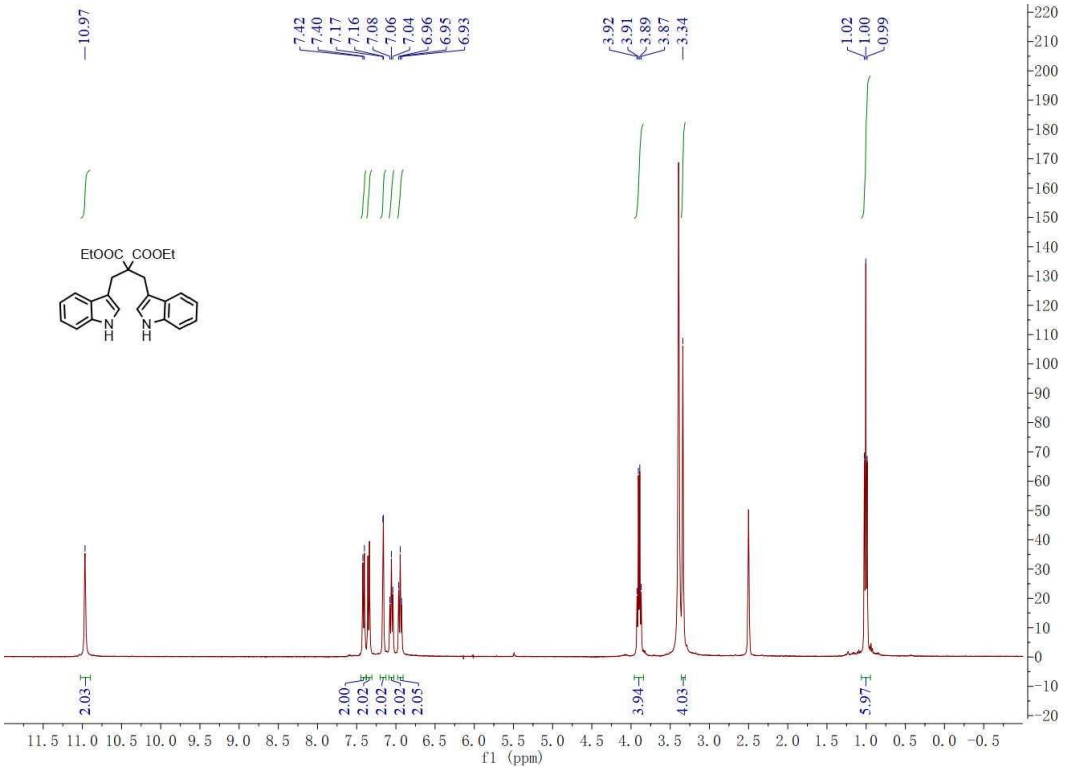


Figure S1. ^{1}H NMR spectrum of diethyl 2,2-bis((1*H*-indol-3-yl)methyl)malonate (**1a**) in DMSO-d_6

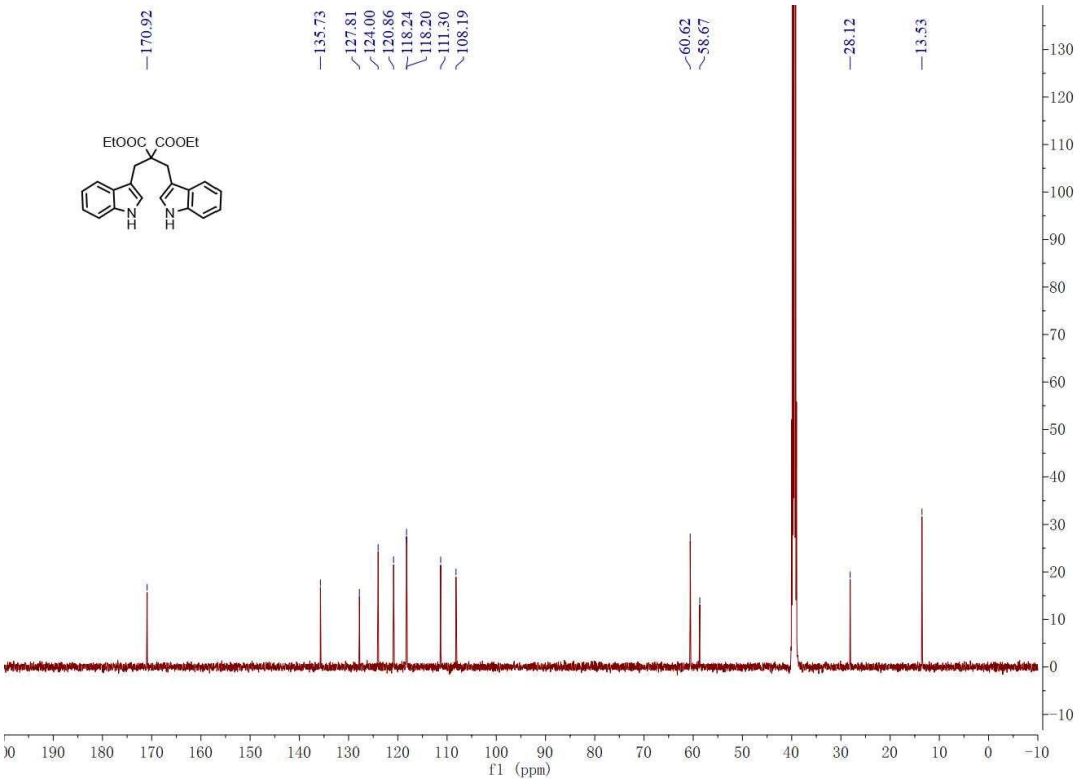


Figure S2. ^{13}C NMR spectrum of diethyl 2,2-bis((1*H*-indol-3-yl)methyl)malonate (**1a**) in DMSO-d_6

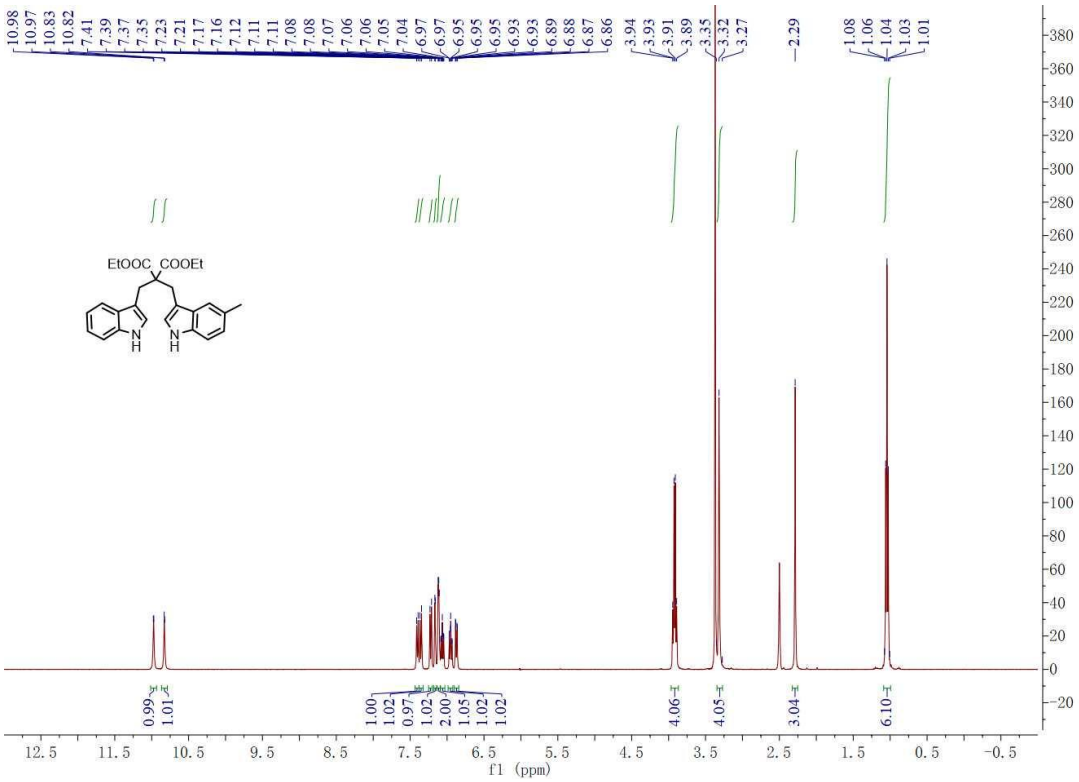


Figure S3. ^{1}H NMR spectrum of diethyl 2-((1*H*-indol-3-yl)methyl)-2-((5-methyl-1*H*-indol-3-yl)methyl)malonate (**1b**) in DMSO-d_6

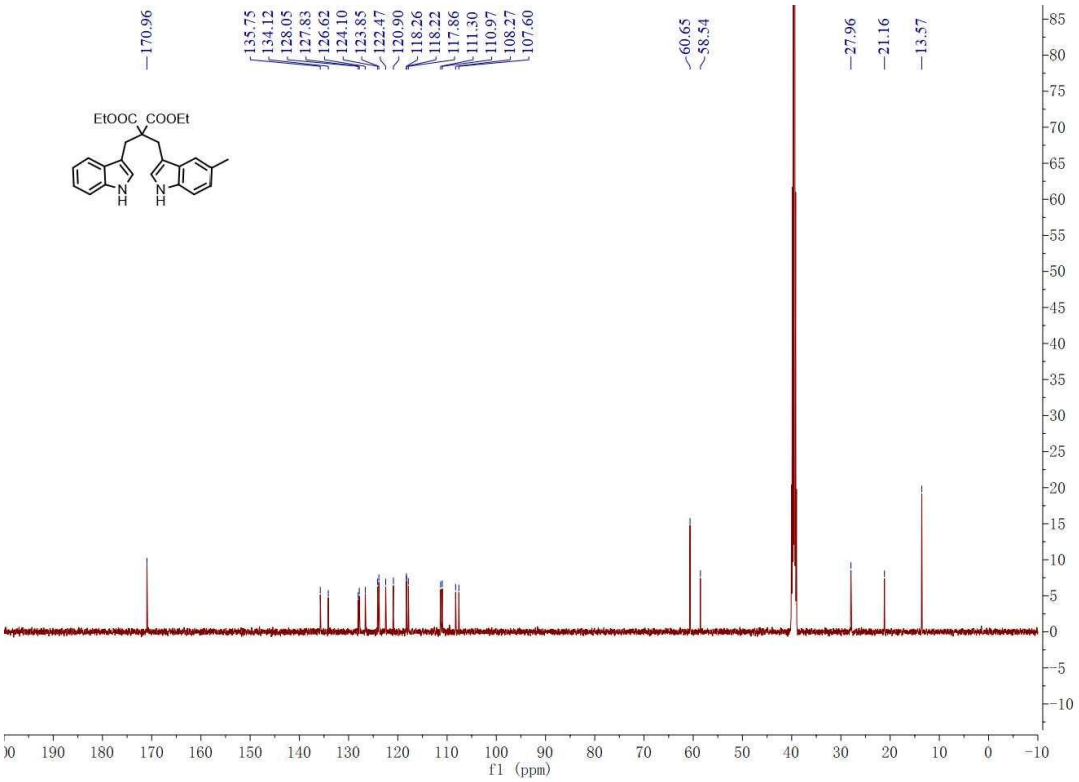


Figure S4. ^{13}C NMR spectrum of diethyl 2-((1*H*-indol-3-yl)methyl)-2-((5-methyl-1*H*-indol-3-yl)methyl)malonate (**1b**) in DMSO-d_6

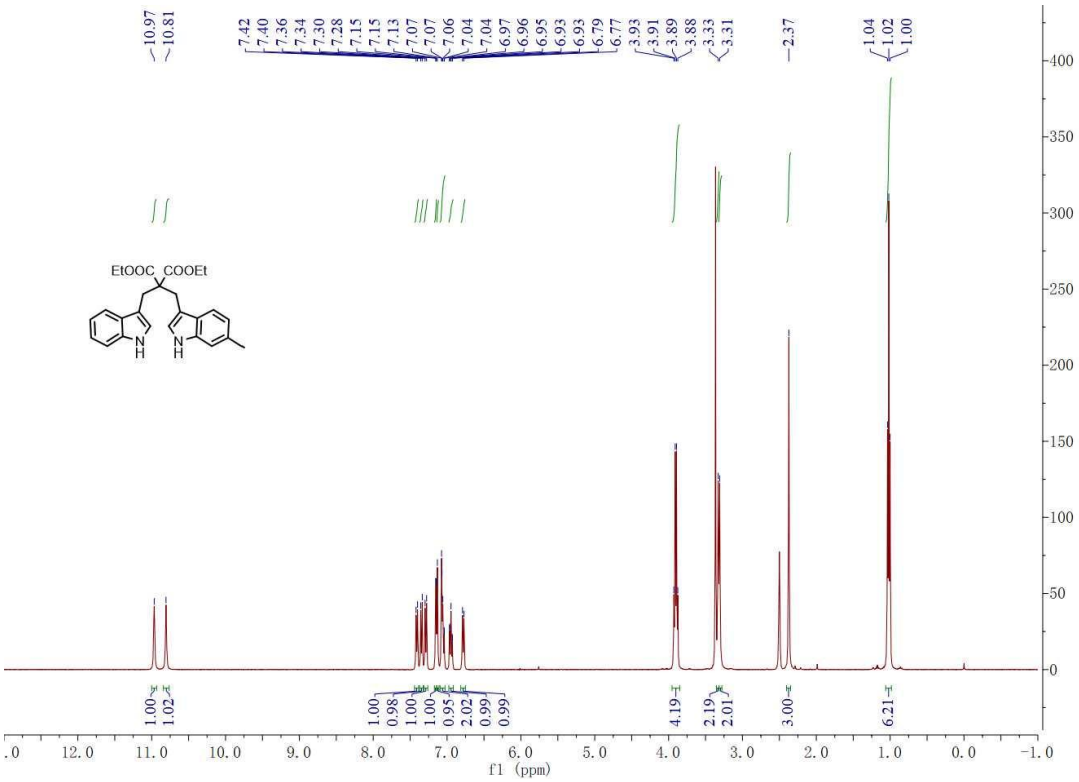


Figure S5. ^{1}H NMR spectrum of diethyl 2-((1*H*-indol-3-yl)methyl)-2-((6-methyl-1*H*-indol-3-yl)methyl)malonate (**1c**) in DMSO-d_6

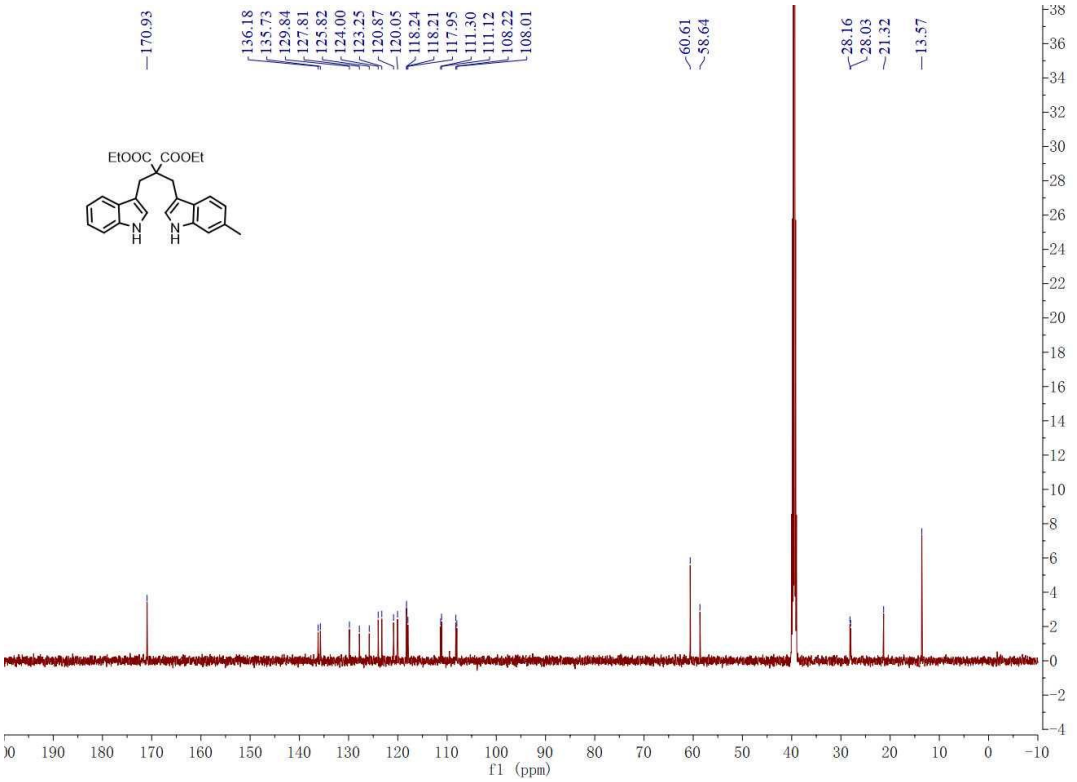


Figure S6. ^{13}C NMR spectrum of diethyl 2-((1*H*-indol-3-yl)methyl)-2-((6-methyl-1*H*-indol-3-yl)methyl)malonate (**1c**) in DMSO-d_6

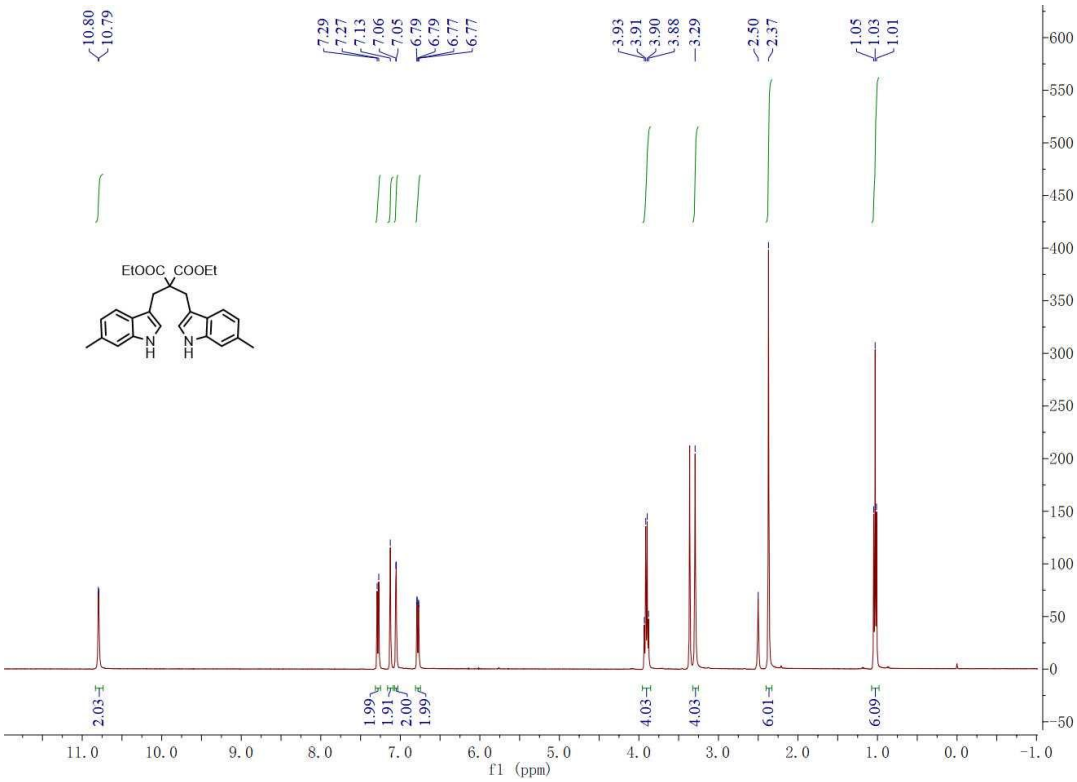


Figure S7. ^{1}H NMR spectrum of diethyl 2,2-bis((6-methyl-1*H*-indol-3-yl)methyl)malonate (**1d**) in DMSO-d_6

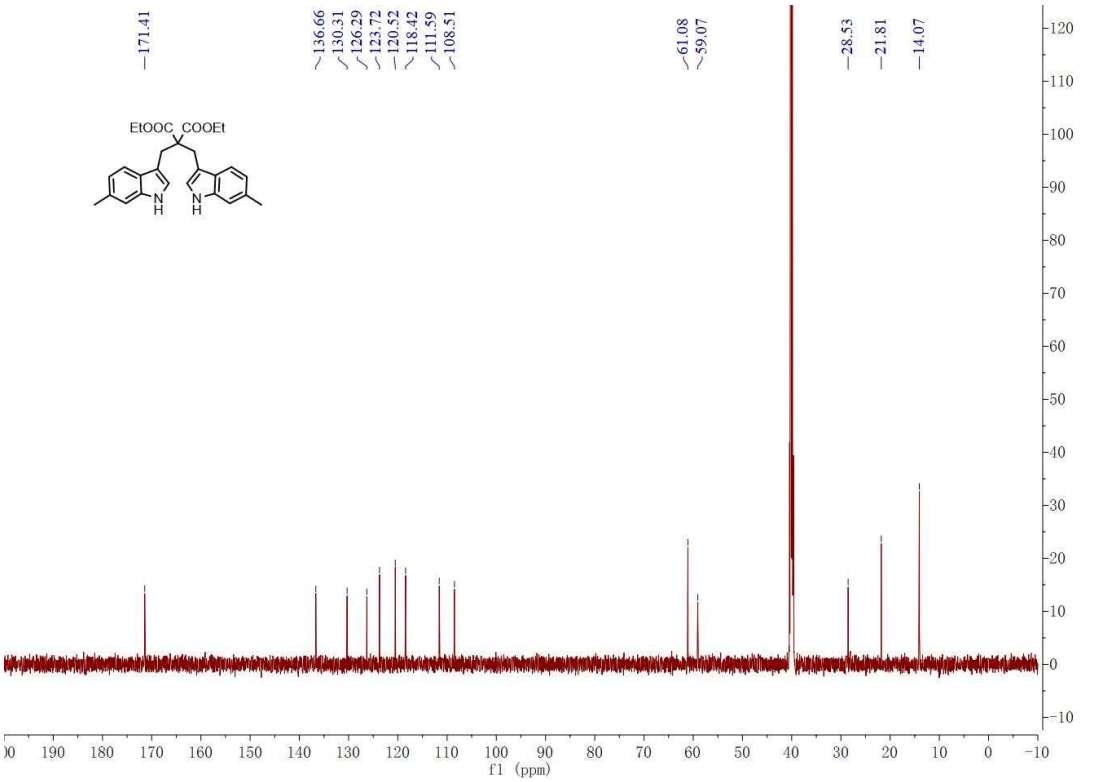


Figure S8. ^{13}C NMR spectrum of diethyl 2,2-bis((6-methyl-1*H*-indol-3-yl)methyl)malonate (**1d**) in DMSO-d_6

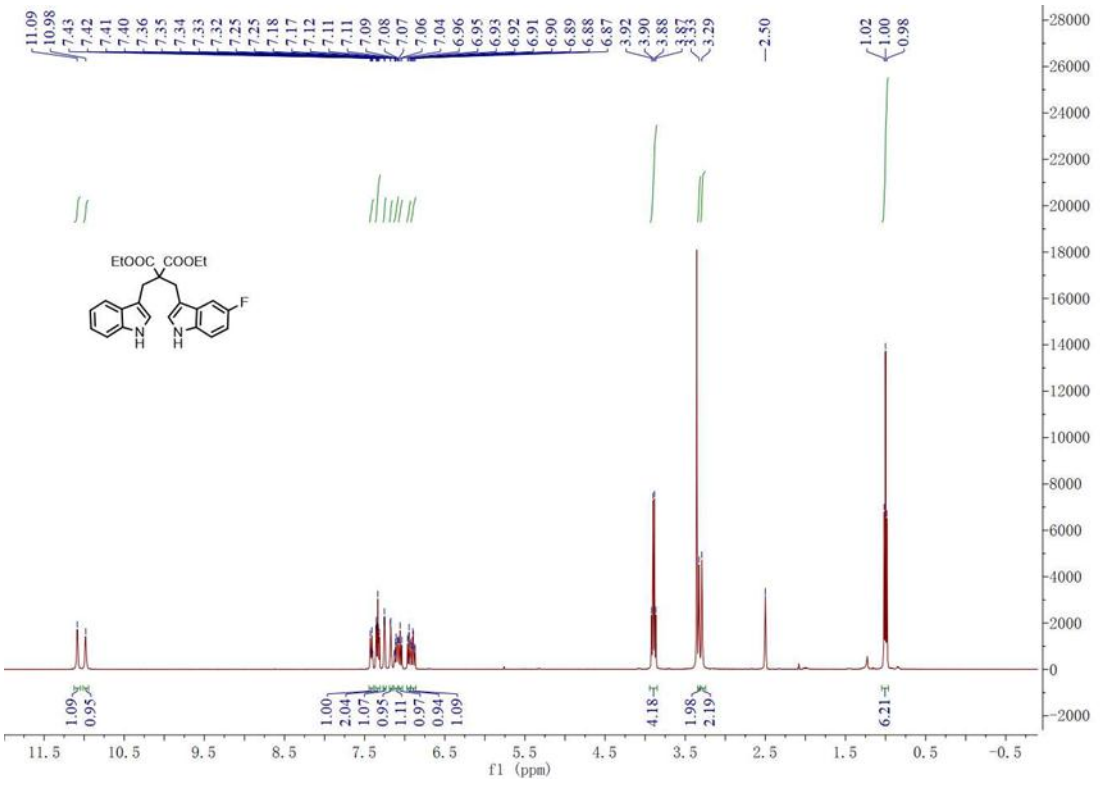


Figure S9. ^{1}H NMR spectrum of diethyl 2-((1*H*-indol-3-yl)methyl)-2-((5-fluoro-1*H*-indol-3-yl)methyl)malonate (**1e**) in DMSO-d_6

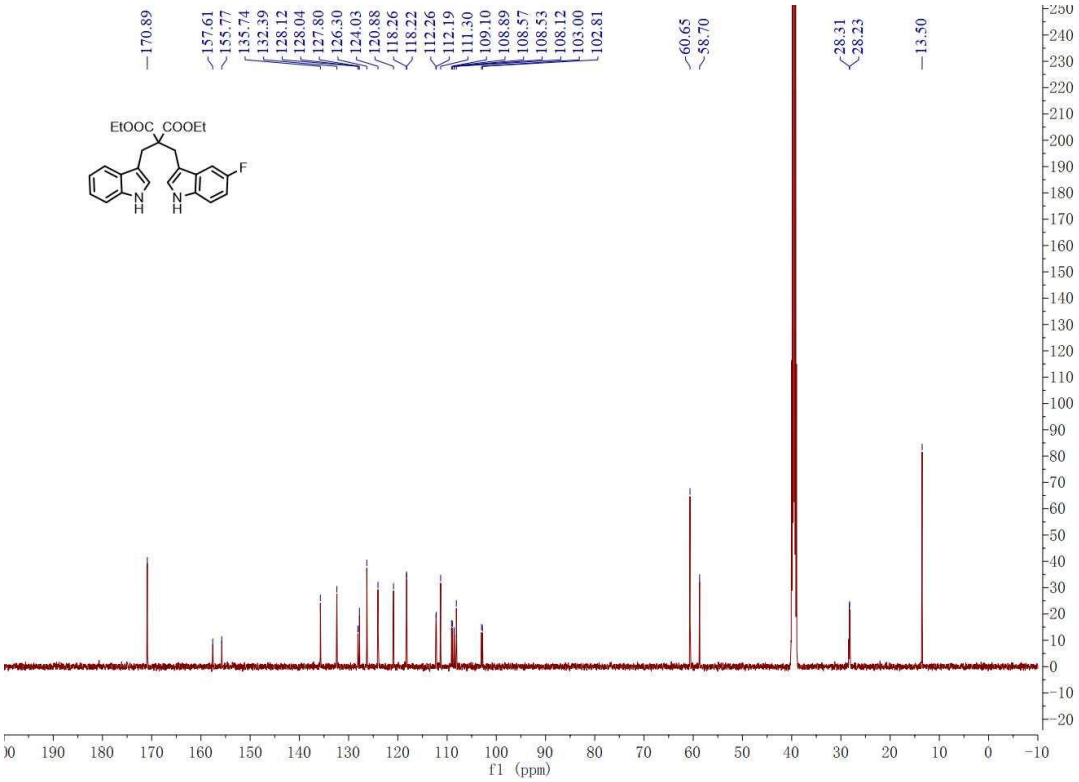


Figure S10. ^{13}C NMR spectrum of diethyl 2-((1*H*-indol-3-yl)methyl)-2-((5-fluoro-1*H*-indol-3-yl)methyl)malonate (**1e**) in DMSO-d_6

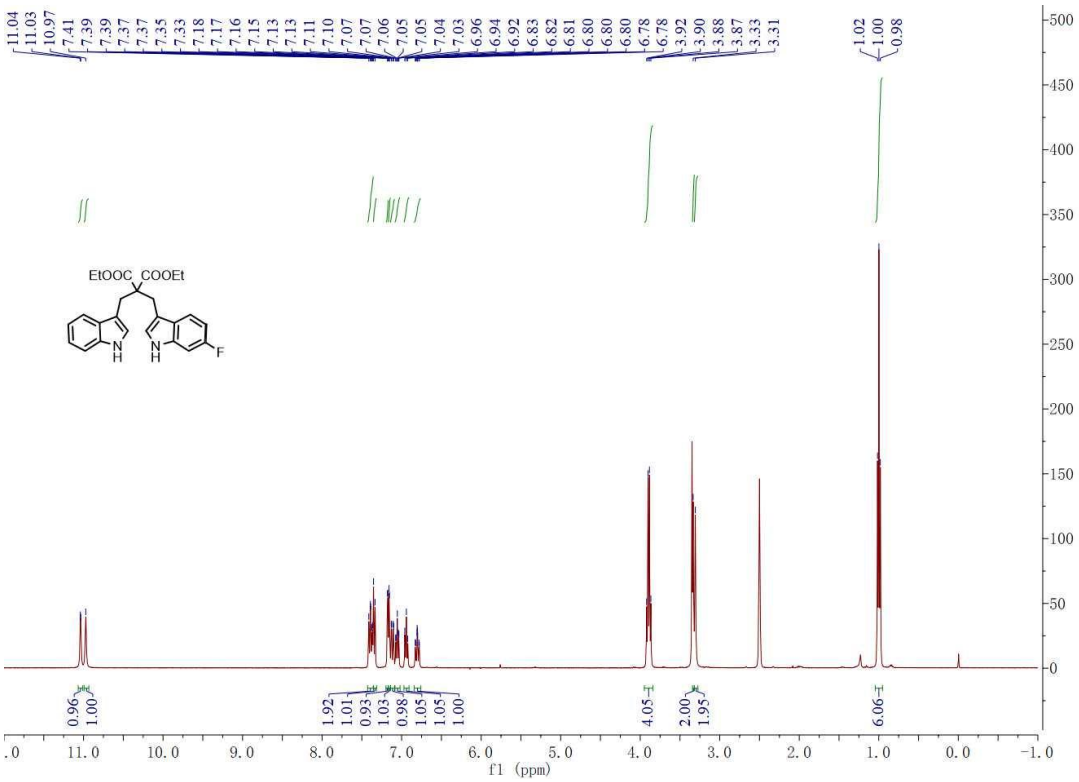


Figure S11. ^{1}H NMR spectrum of diethyl 2-((1*H*-indol-3-yl)methyl)-2-((6-fluoro-1*H*-indol-3-yl)methyl)malonate (**1f**) in DMSO-d_6

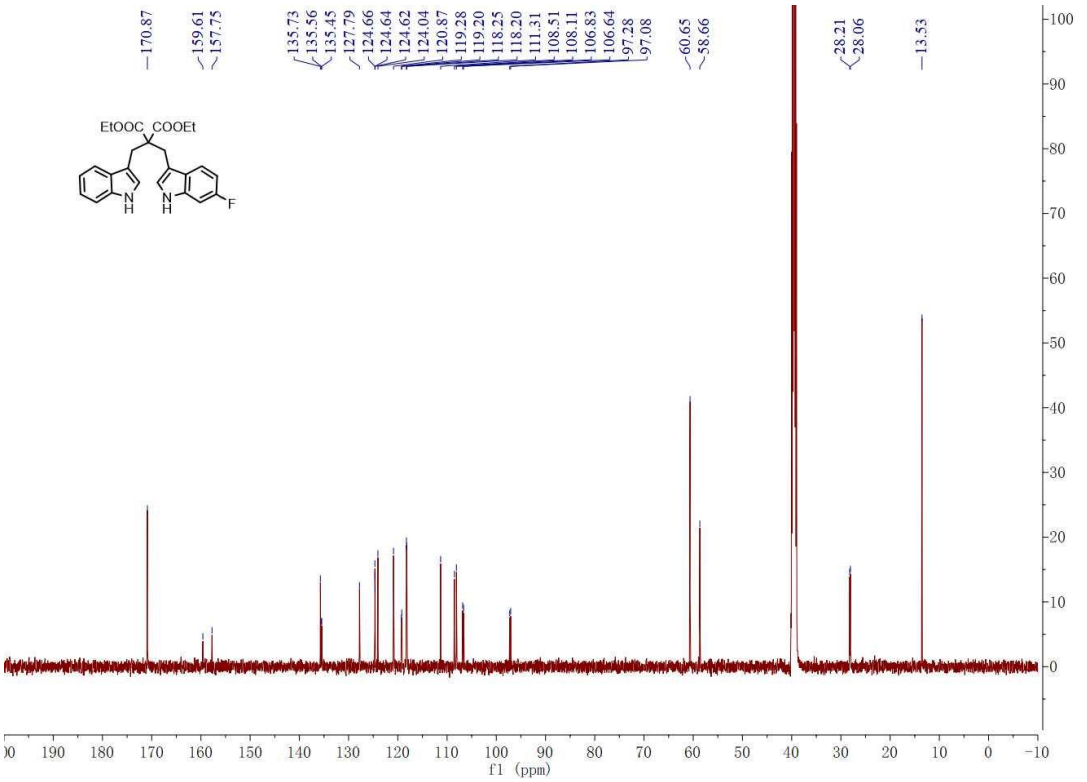


Figure S12. ^{13}C NMR spectrum of diethyl 2-((1*H*-indol-3-yl)methyl)-2-((6-fluoro-1*H*-indol-3-yl)methyl)malonate (**1f**) in DMSO-d_6

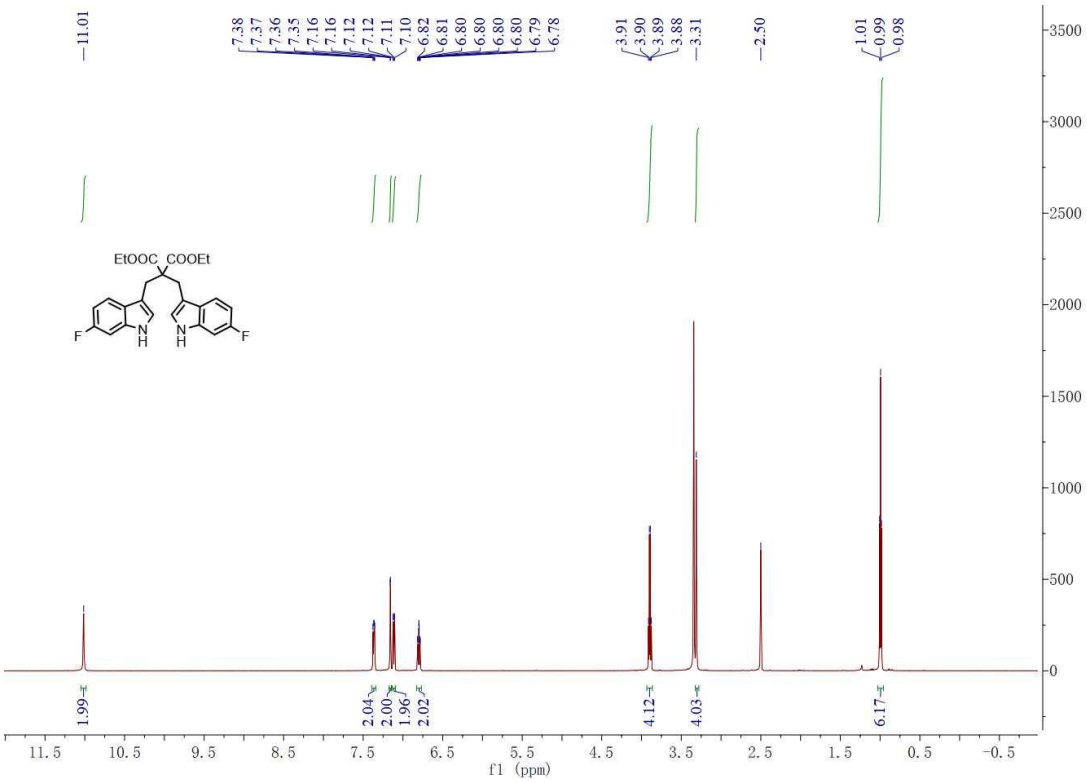


Figure S13. ^{1}H NMR spectrum of diethyl 2,2-bis((6-fluoro-1*H*-indol-3-yl)methyl)malonate (**1g**) in DMSO-d_6

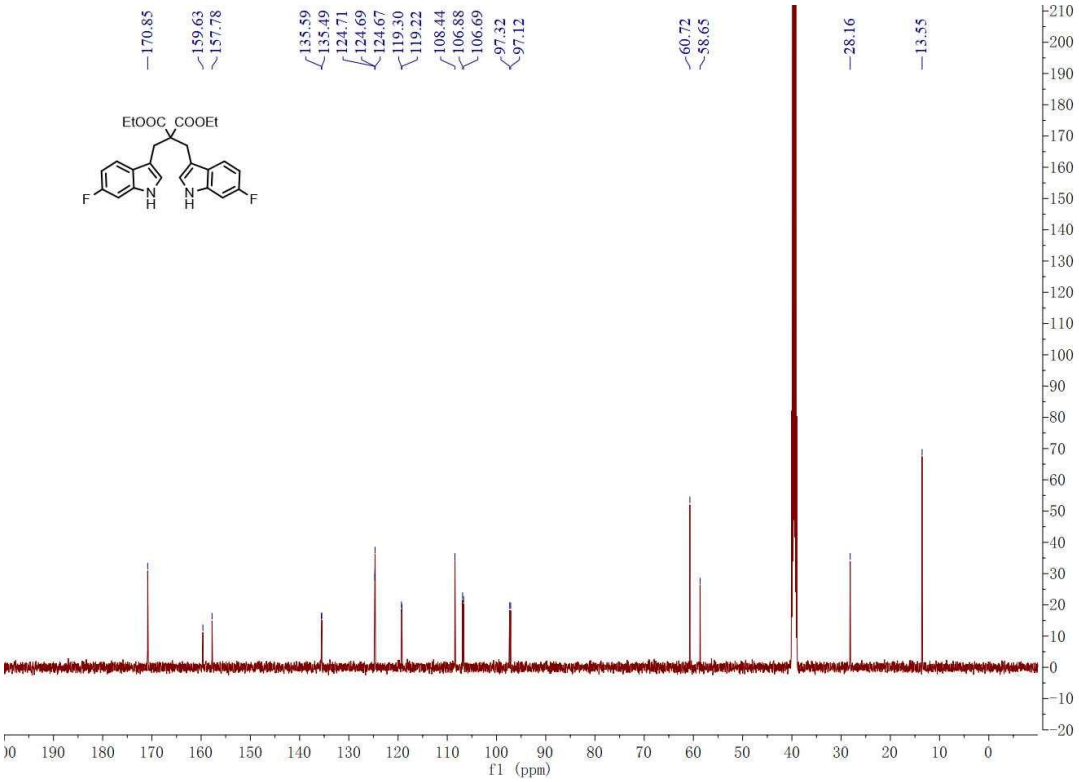


Figure S14. ^{13}C NMR spectrum of diethyl 2,2-bis((6-fluoro-1*H*-indol-3-yl)methyl)malonate (**1g**) in DMSO-d_6

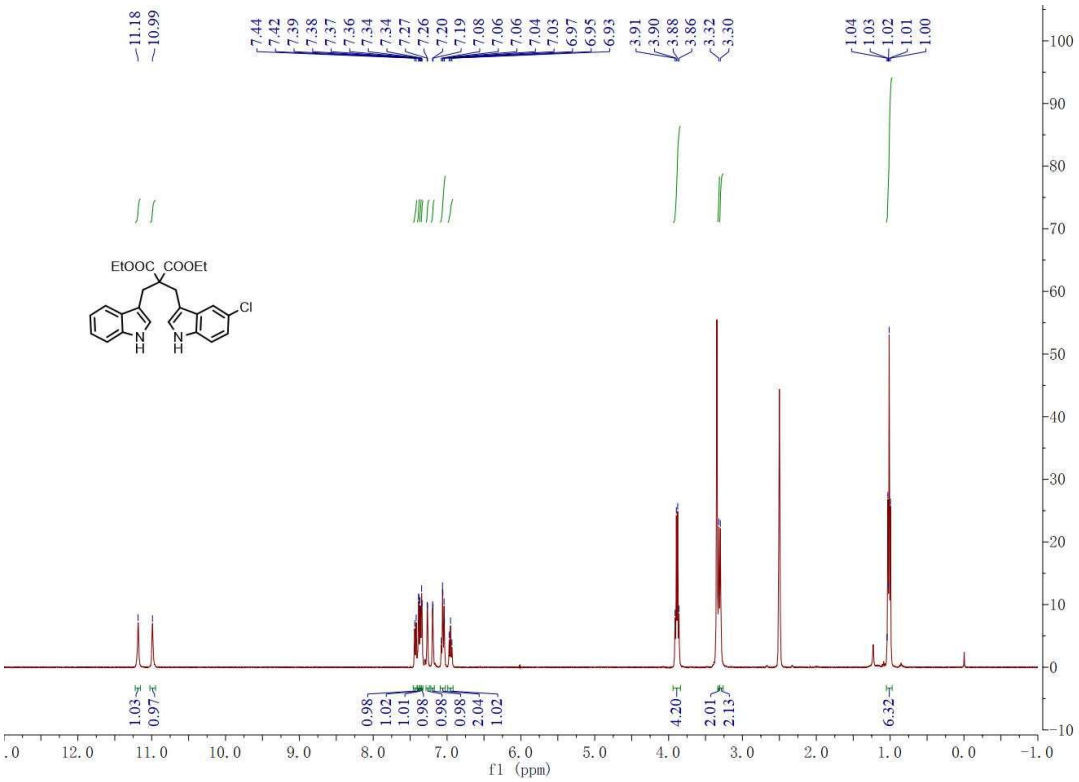


Figure S15. ^{1}H NMR spectrum of diethyl 2-((1*H*-indol-3-yl)methyl)-2-((5-chloro-1*H*-indol-3-yl)methyl)malonate (**1h**) in DMSO-d_6

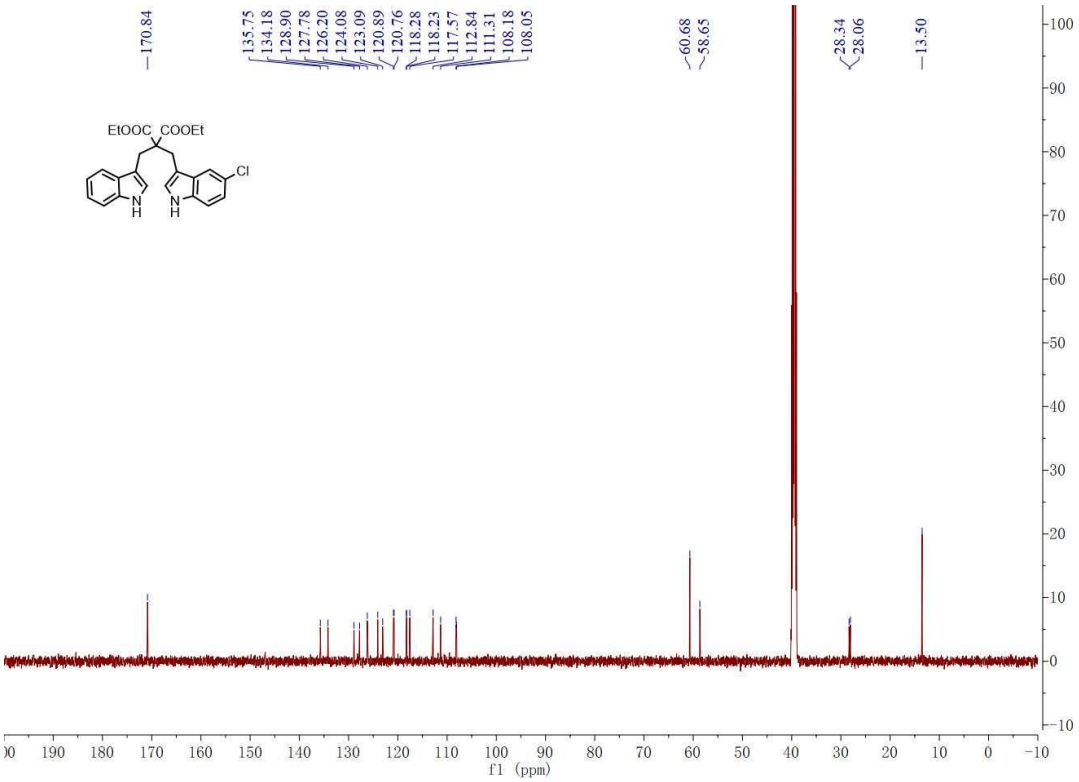


Figure S16. ^{13}C NMR spectrum of diethyl 2-((1*H*-indol-3-yl)methyl)-2-((5-chloro-1*H*-indol-3-yl)methyl)malonate (**1h**) in DMSO-d_6

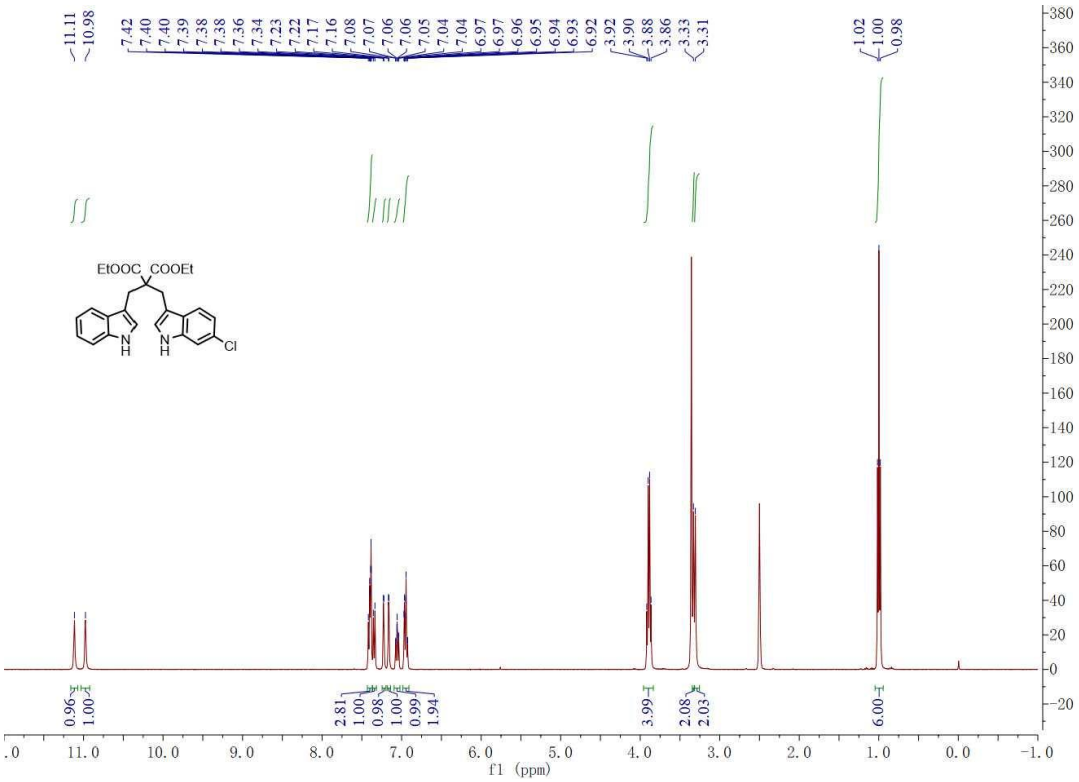


Figure S17. ^{1}H NMR spectrum of diethyl 2-((1*H*-indol-3-yl)methyl)-2-((6-chloro-1*H*-indol-3-yl)methyl)malonate (**1i**) in DMSO-d_6

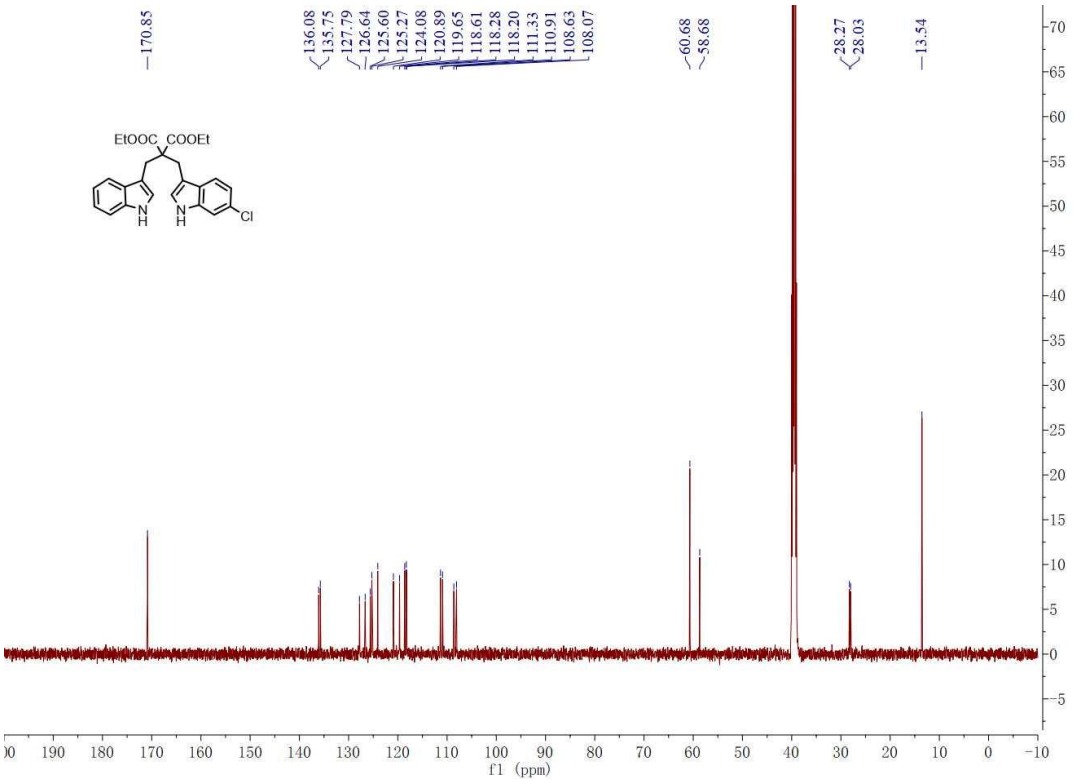


Figure S18. ^{13}C NMR spectrum of diethyl 2-((1*H*-indol-3-yl)methyl)-2-((6-chloro-1*H*-indol-3-yl)methyl)malonate (**1i**) in DMSO-d_6

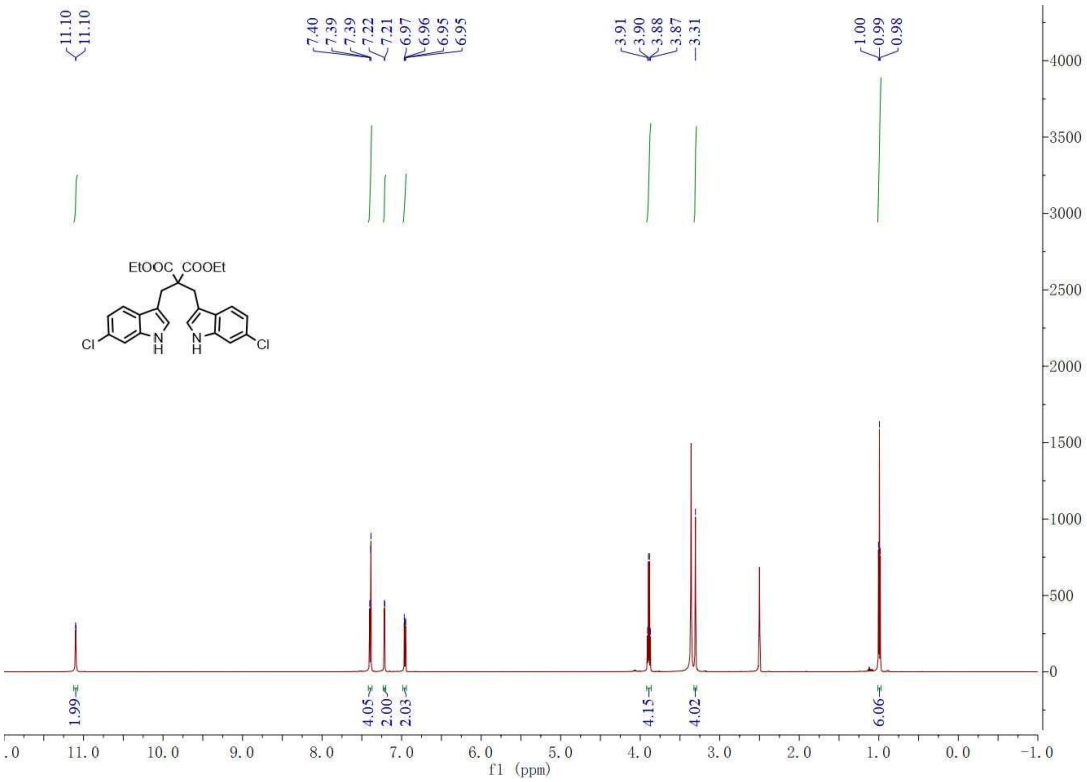


Figure S19. ^{1}H NMR spectrum of diethyl 2,2-bis((6-chloro-1*H*-indol-3-yl)methyl)malonate (**1j**) in DMSO-d_6

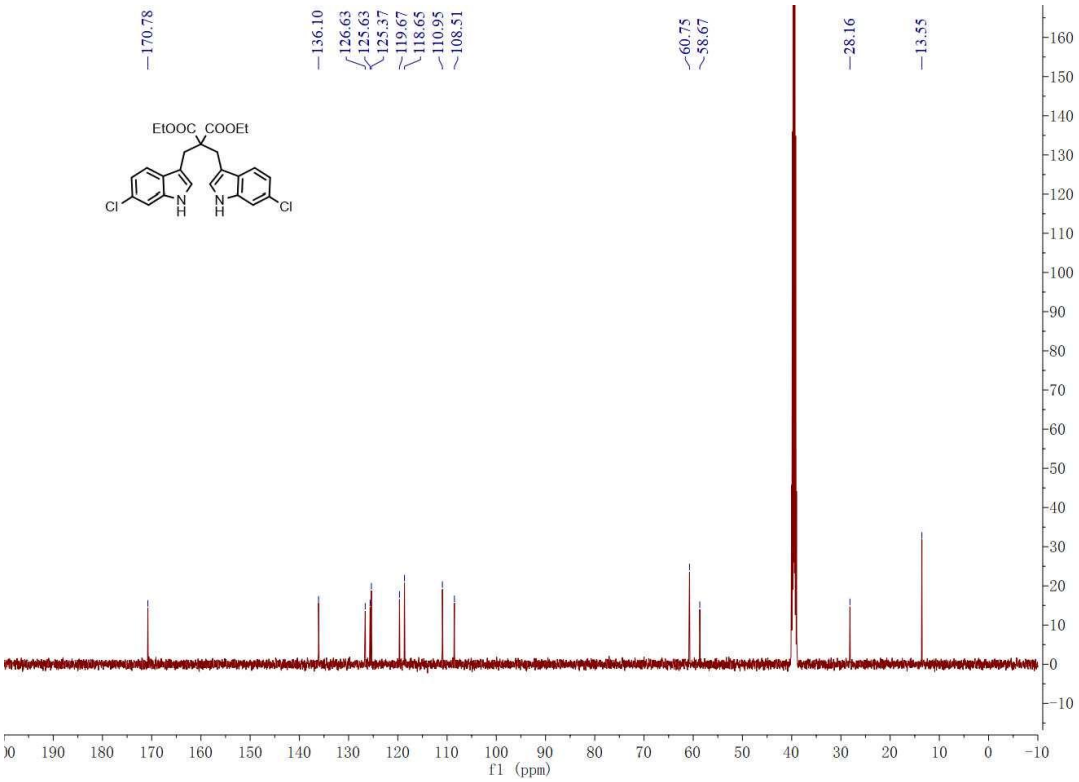


Figure S20. ^{13}C NMR spectrum of diethyl 2,2-bis((6-chloro-1*H*-indol-3-yl)methyl)malonate (**1j**) in DMSO-d_6

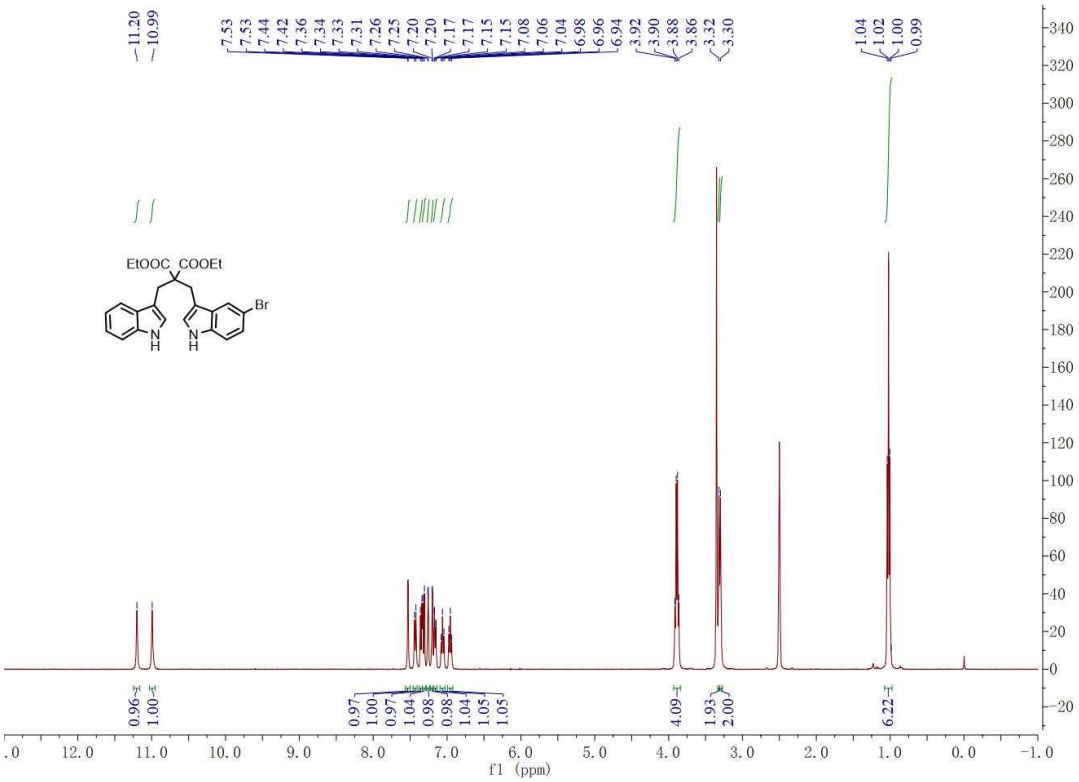


Figure S21. ^{1}H NMR spectrum of diethyl 2-((1*H*-indol-3-yl)methyl)-2-((5-bromo-1*H*-indol-3-yl)methyl)malonate (**1k**) in DMSO-d_6

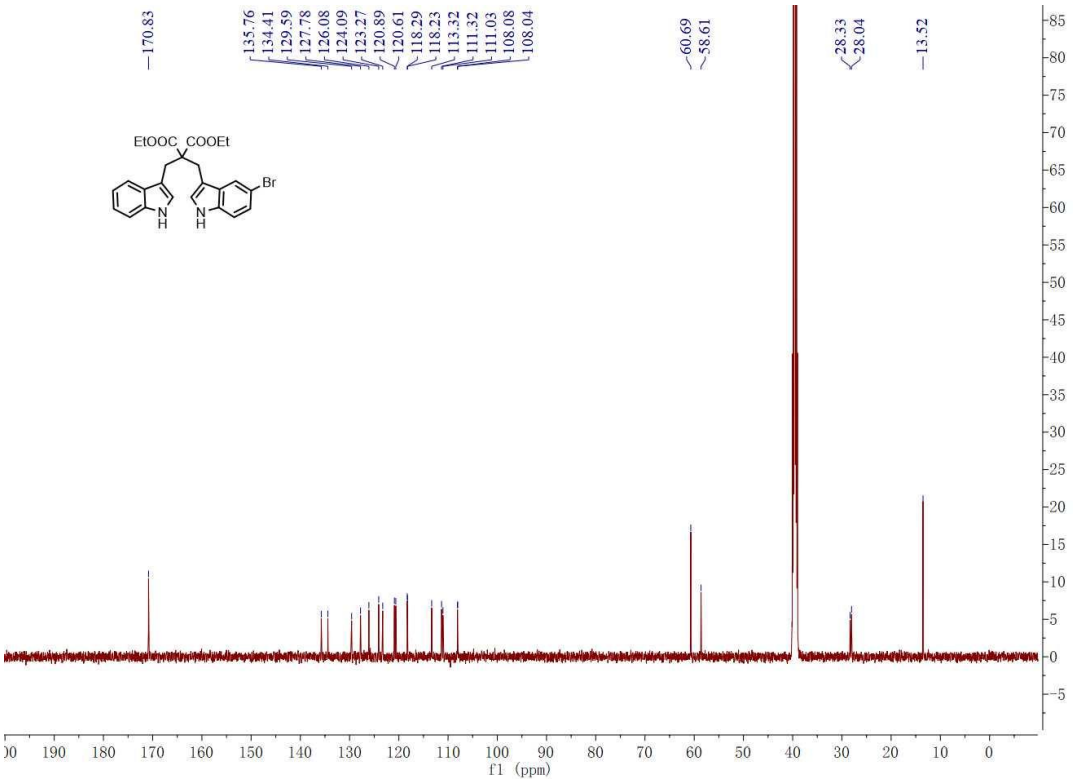


Figure S22. ^{13}C NMR spectrum of diethyl 2-((1*H*-indol-3-yl)methyl)-2-((5-bromo-1*H*-indol-3-yl)methyl)malonate (**1k**) in DMSO-d_6

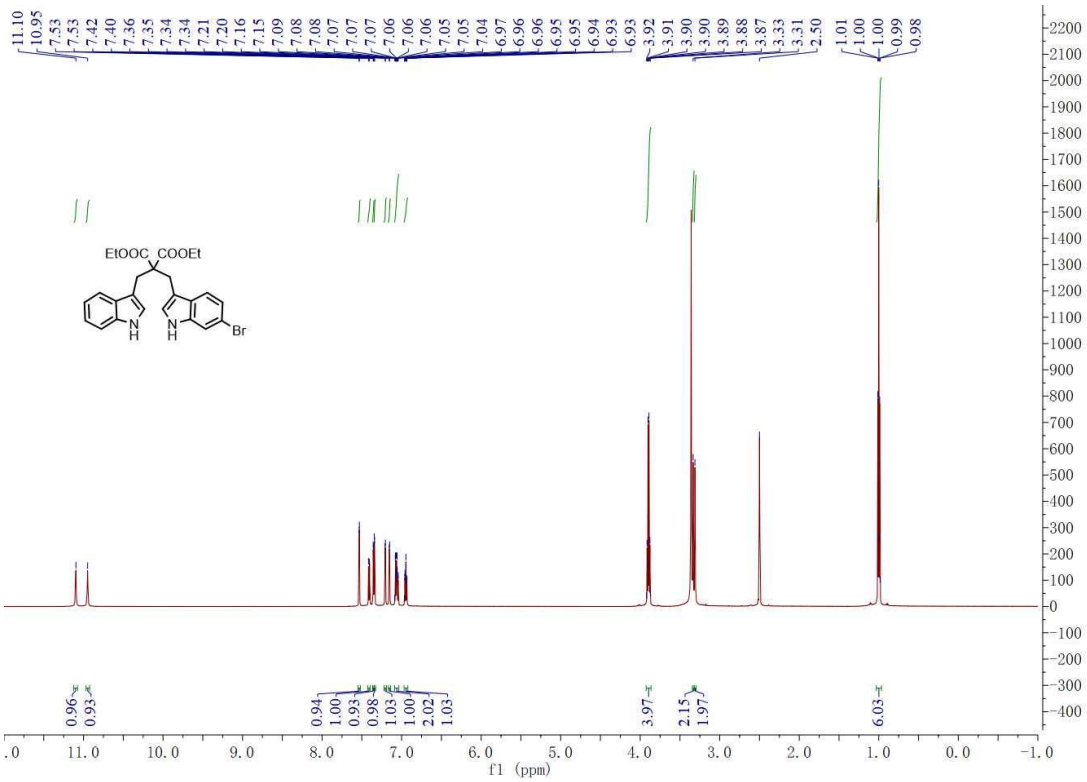


Figure S23. ^{1}H NMR spectrum of diethyl 2-((1*H*-indol-3-yl)methyl)-2-((6-bromo-1*H*-indol-3-yl)methyl)malonate (**1l**) in DMSO-d_6

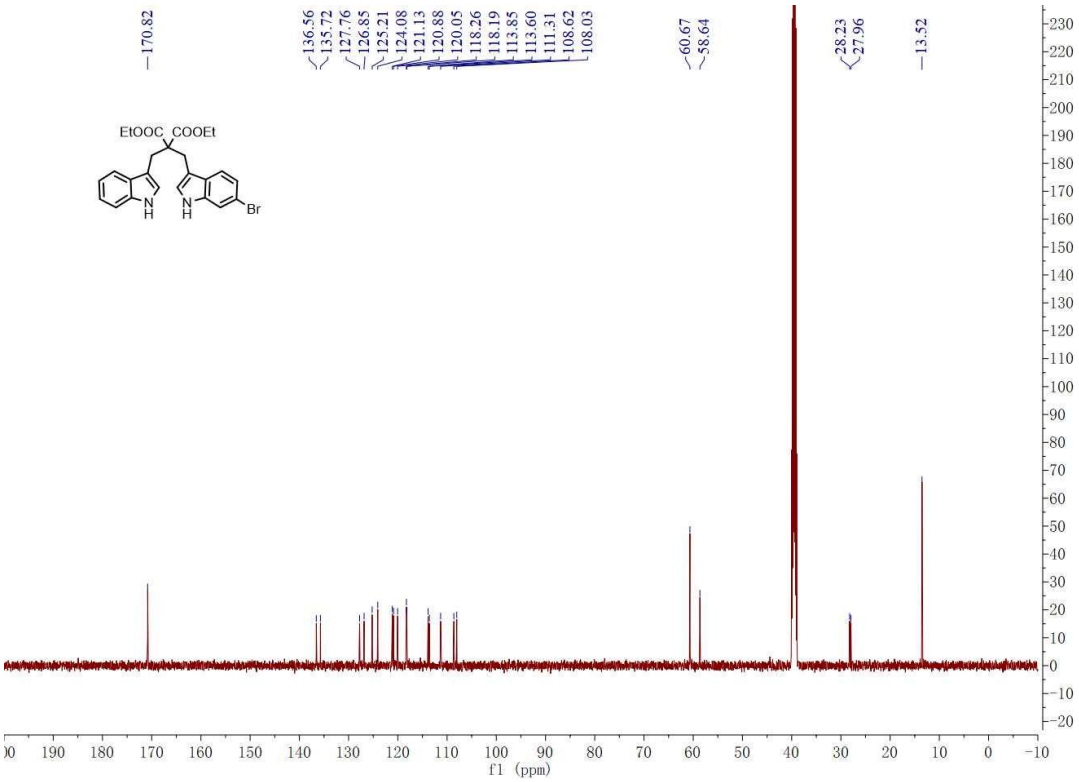


Figure S24. ^{13}C NMR spectrum of diethyl 2-((1*H*-indol-3-yl)methyl)-2-((6-bromo-1*H*-indol-3-yl)methyl)malonate (**1l**) in DMSO-d_6

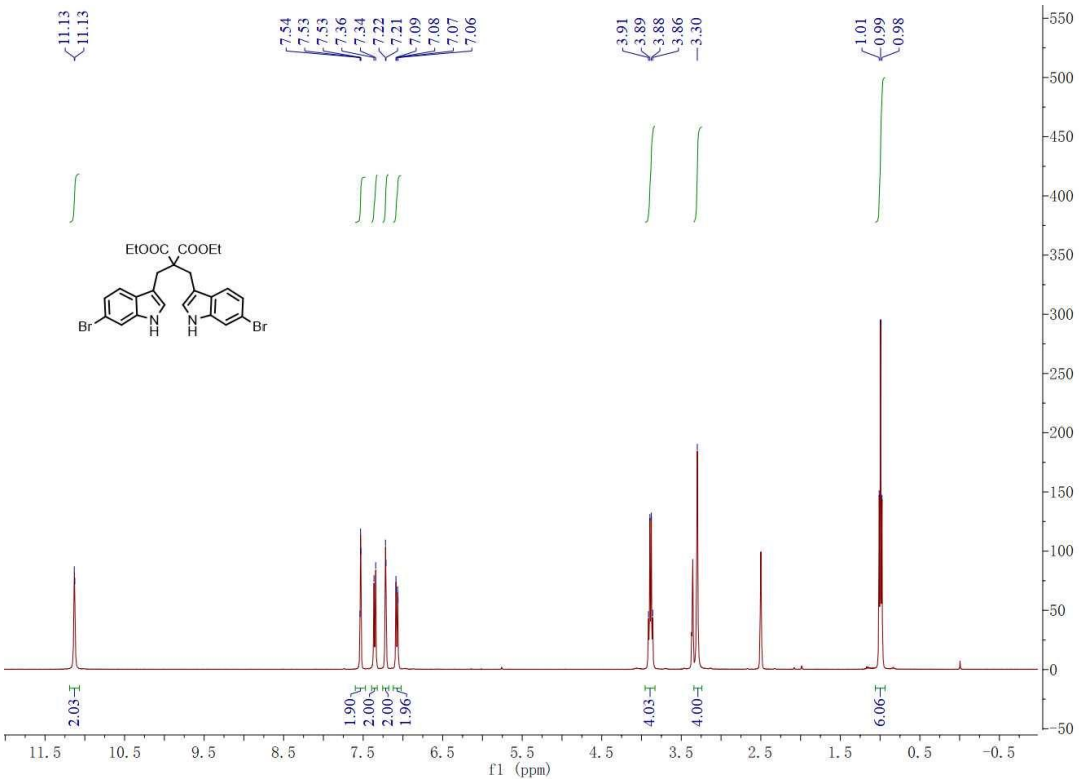


Figure S25. ^{1}H NMR spectrum of diethyl 2,2-bis((6-bromo-1*H*-indol-3-yl)methyl)malonate (**1m**) in DMSO-d_6

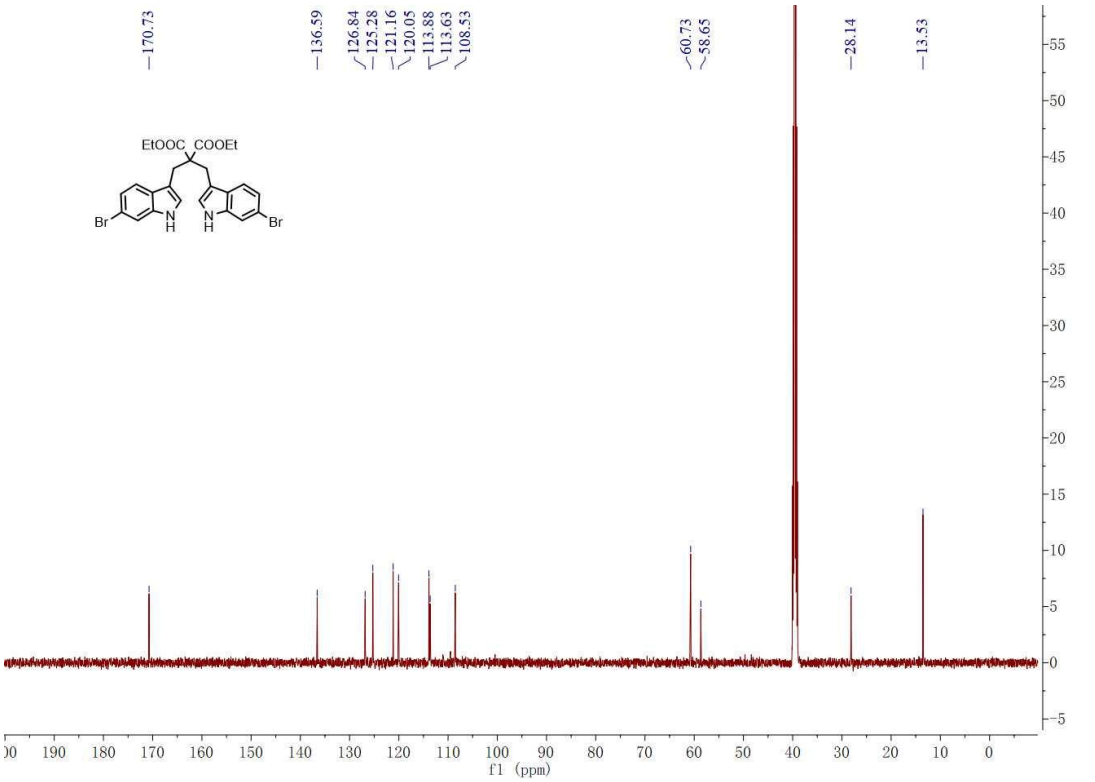


Figure S26. ^{13}C NMR spectrum of diethyl 2,2-bis((6-bromo-1*H*-indol-3-yl)methyl)malonate (**1m**) in DMSO-d_6

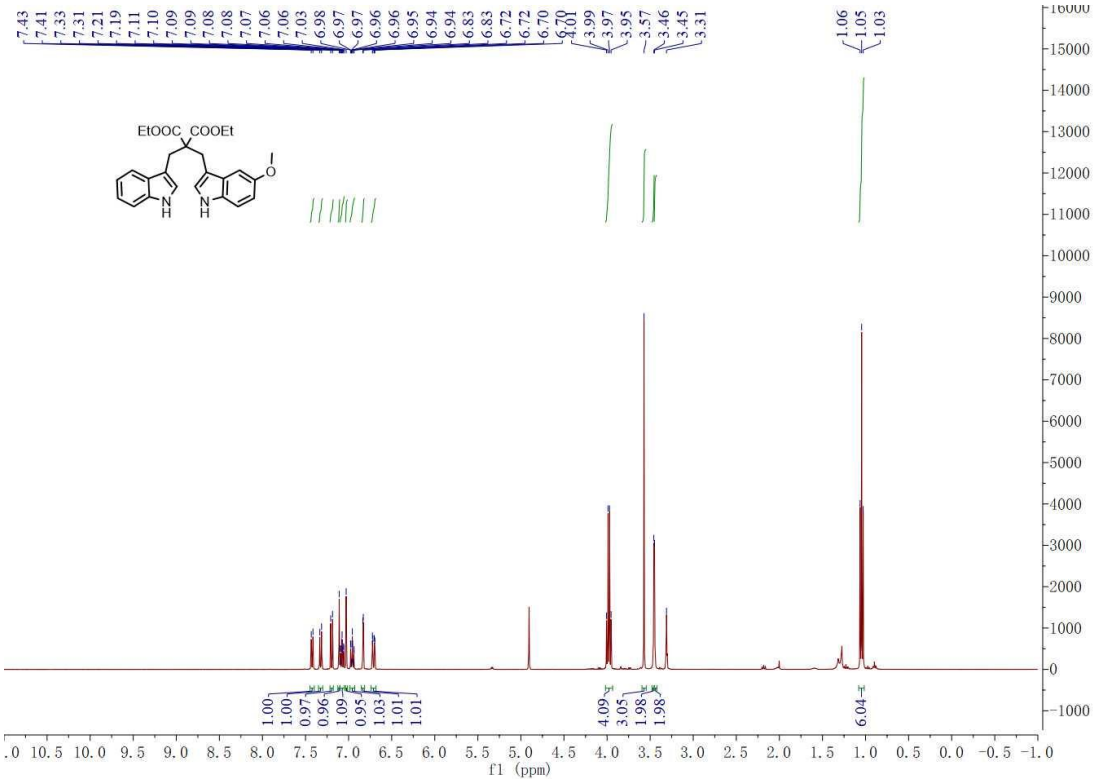


Figure S27. ^{1}H NMR spectrum of diethyl 2-((1*H*-indol-3-yl)methyl)-2-((5-methoxy-1*H*-indol-3-yl)methyl)malonate (**1n**) in Methanol-d_4

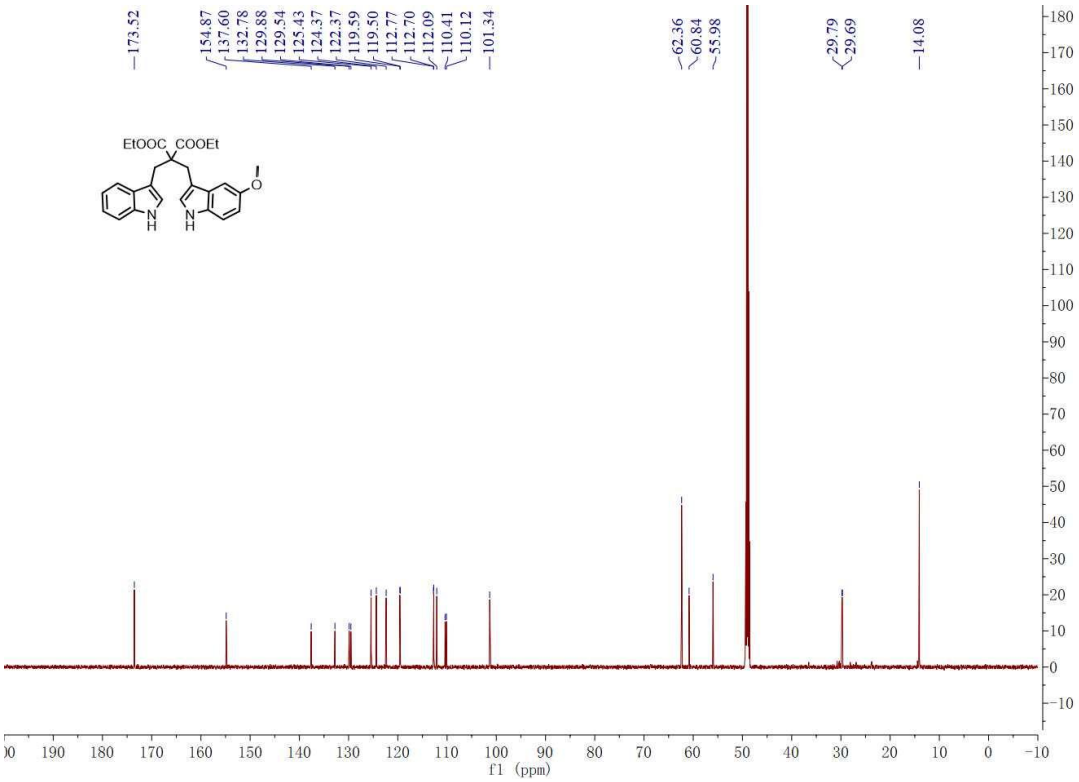


Figure S28. ^{13}C NMR spectrum of diethyl 2-((1*H*-indol-3-yl)methyl)-2-((5-methoxy-1*H*-indol-3-yl)methyl)malonate (**1n**) in Methanol-d_4

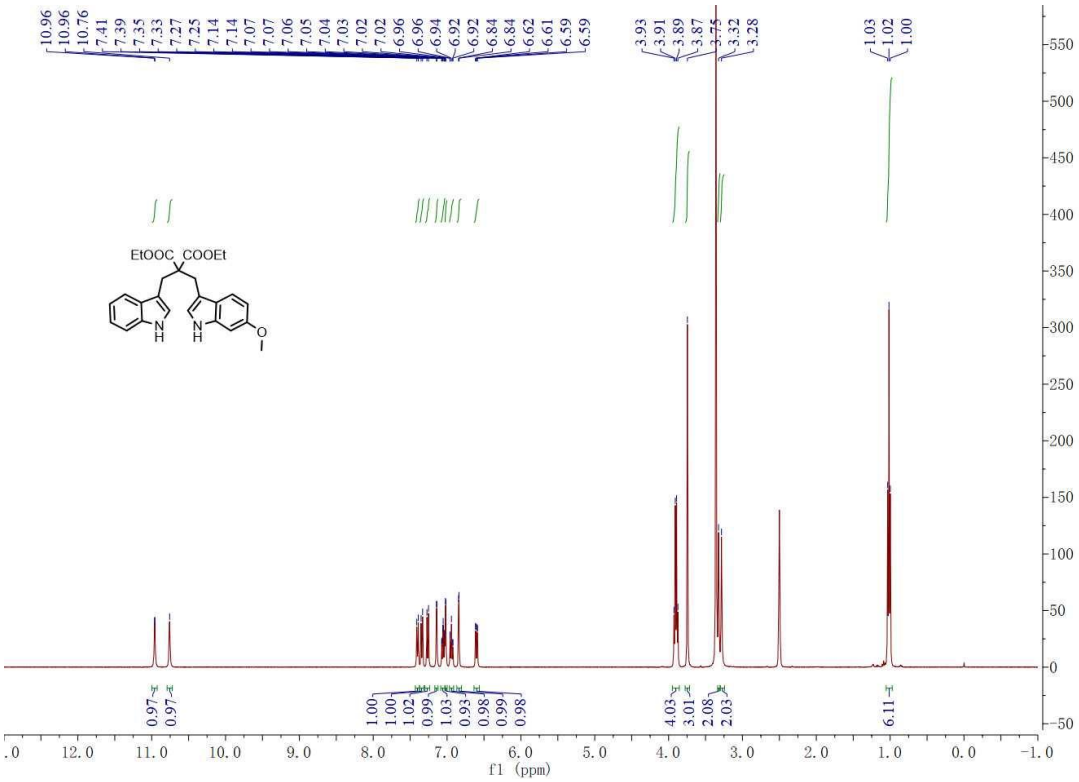


Figure S29. ^{1}H NMR spectrum of diethyl 2-((1*H*-indol-3-yl)methyl)-2-((6-methoxy-1*H*-indol-3-yl)methyl)malonate (**1o**) in DMSO-d_6

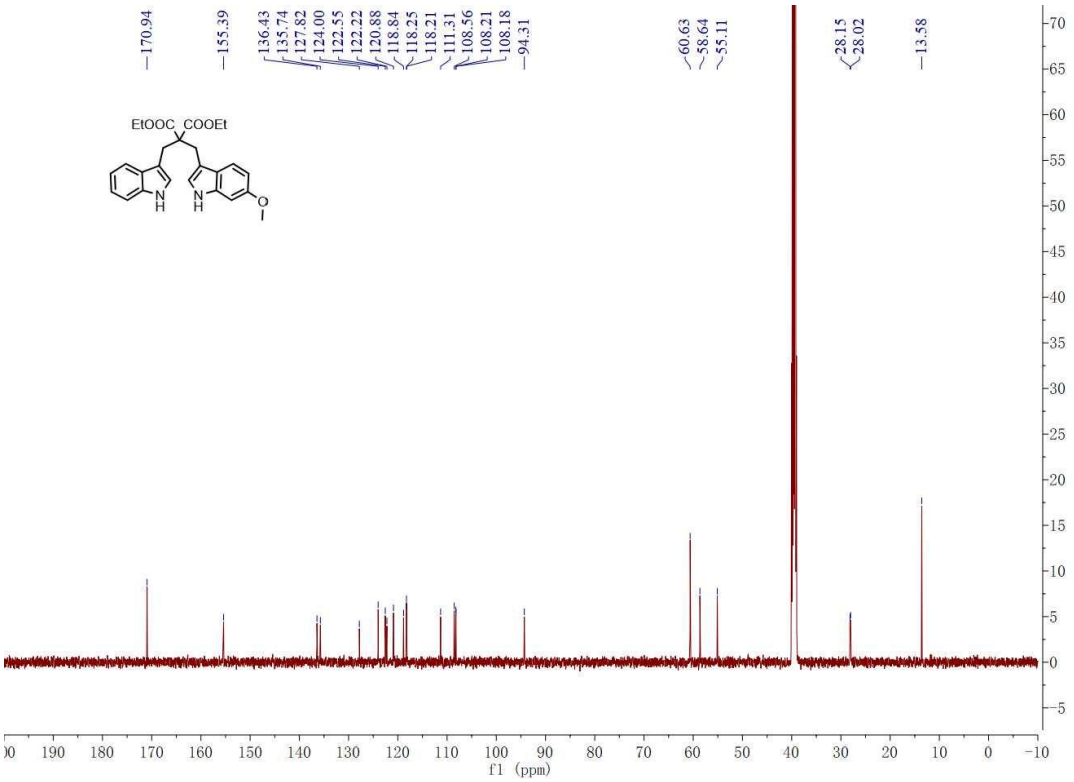


Figure S30. ^{13}C NMR spectrum of diethyl 2-((1*H*-indol-3-yl)methyl)-2-((6-methoxy-1*H*-indol-3-yl)methyl)malonate (**1o**) in DMSO-d_6

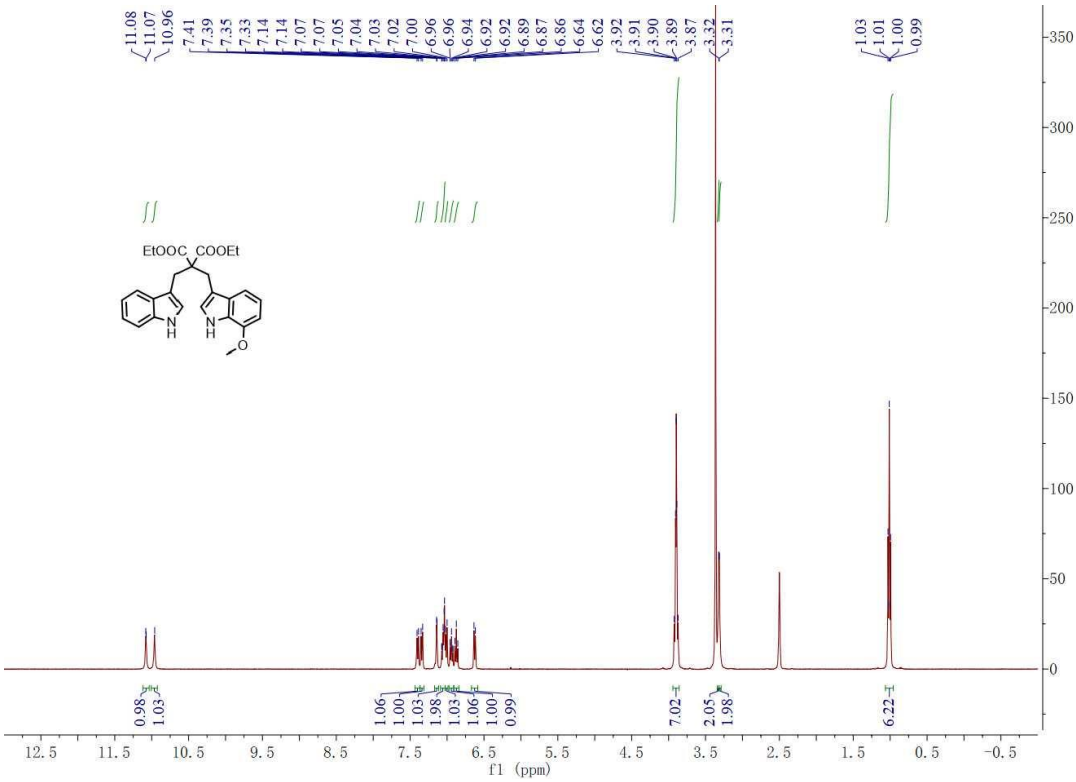


Figure S31. ^{1}H NMR spectrum of diethyl 2-((1*H*-indol-3-yl)methyl)-2-((7-methoxy-1*H*-indol-3-yl)methyl)malonate (**1p**) in DMSO-d_6

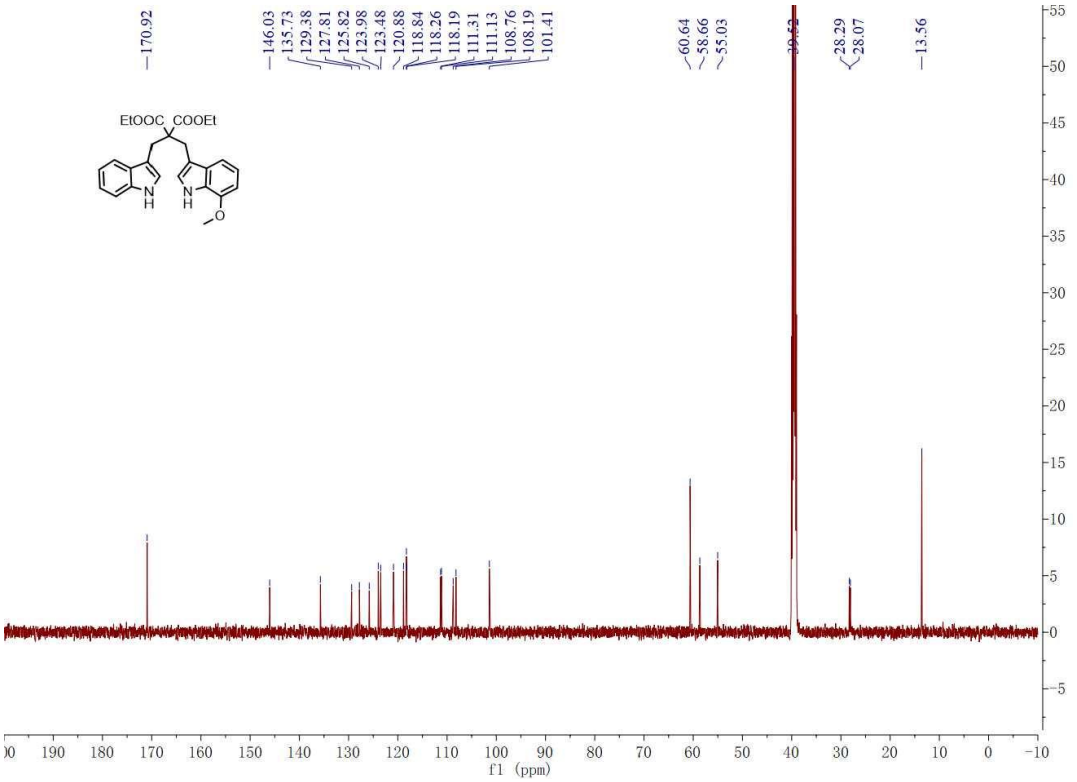


Figure S32. ^{13}C NMR spectrum of diethyl 2-((1*H*-indol-3-yl)methyl)-2-((7-methoxy-1*H*-indol-3-yl)methyl)malonate (**1p**) in DMSO-d_6

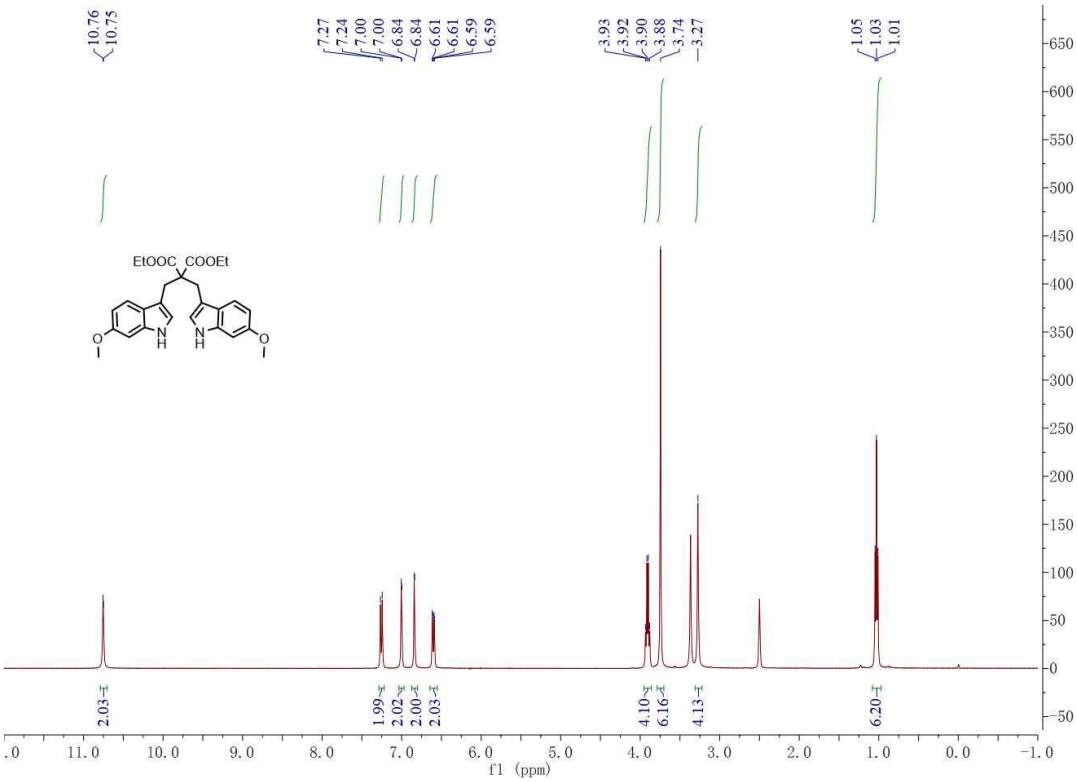


Figure S33. ^{1}H NMR spectrum of diethyl 2,2-bis((6-methoxy-1*H*-indol-3-yl)methyl)malonate (**1q**) in DMSO-d_6

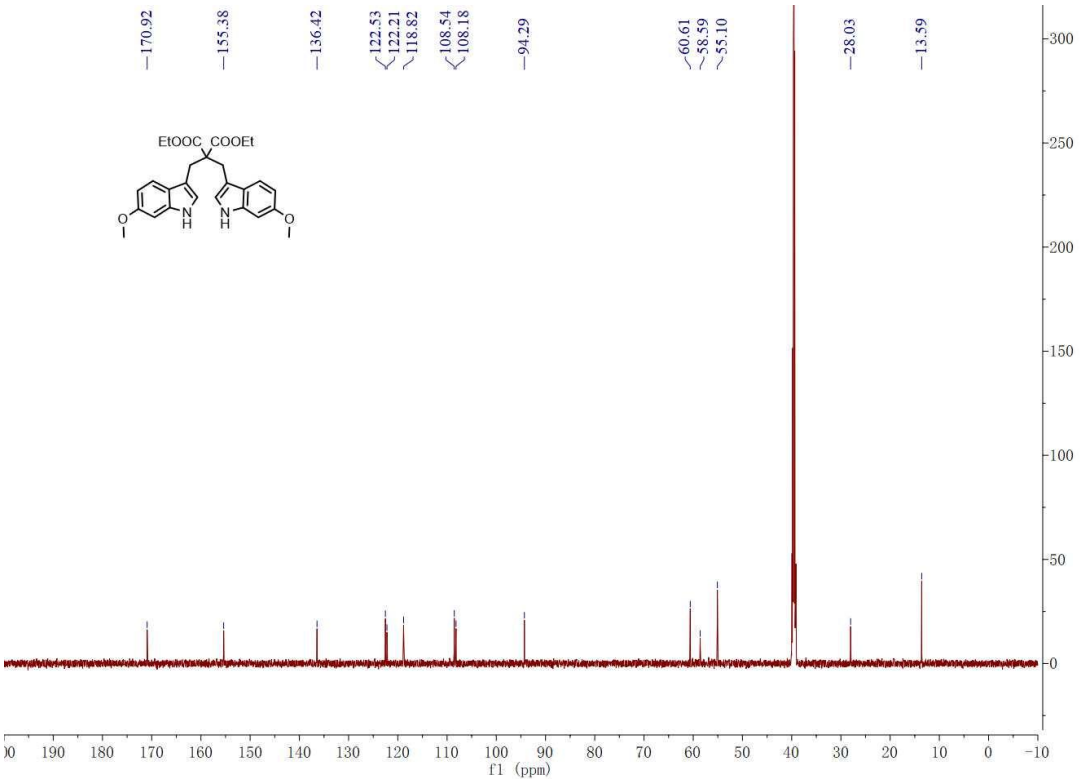


Figure S34. ^{13}C NMR spectrum of diethyl 2,2-bis((6-methoxy-1*H*-indol-3-yl)methyl)malonate (**1q**) in DMSO-d_6

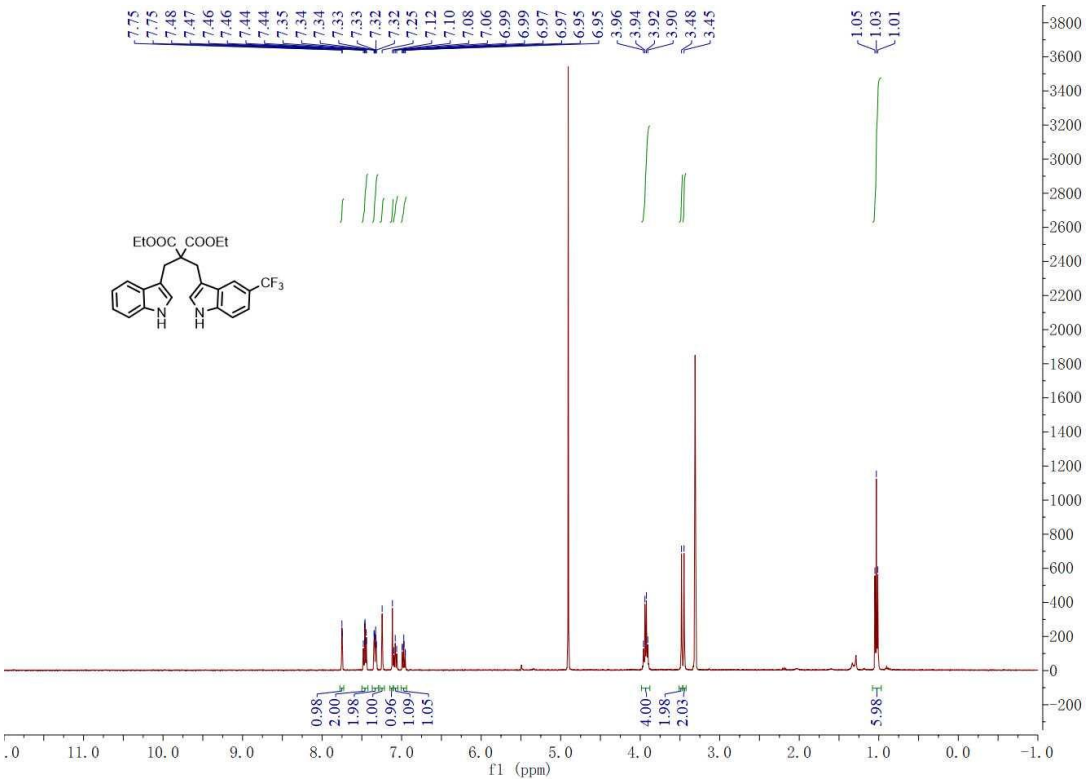


Figure S35. ^{1}H NMR spectrum of diethyl 2-((1*H*-indol-3-yl)methyl)-2-((5-(trifluoromethyl)-1*H*-indol-3-yl)methyl)malonate (**1r**) in Methanol-d_4

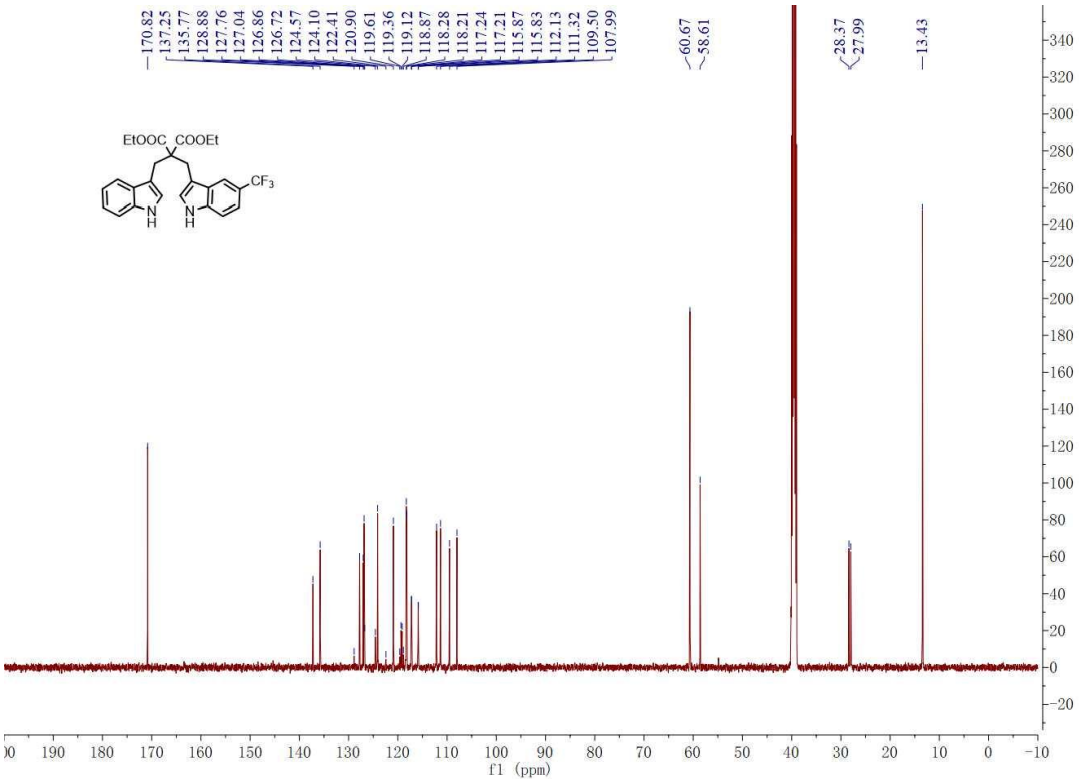


Figure S36. ^{13}C NMR spectrum of diethyl 2-((1*H*-indol-3-yl)methyl)-2-((5-(trifluoromethyl)-1*H*-indol-3-yl)methyl)malonate (**1r**) in DMSO-d_6

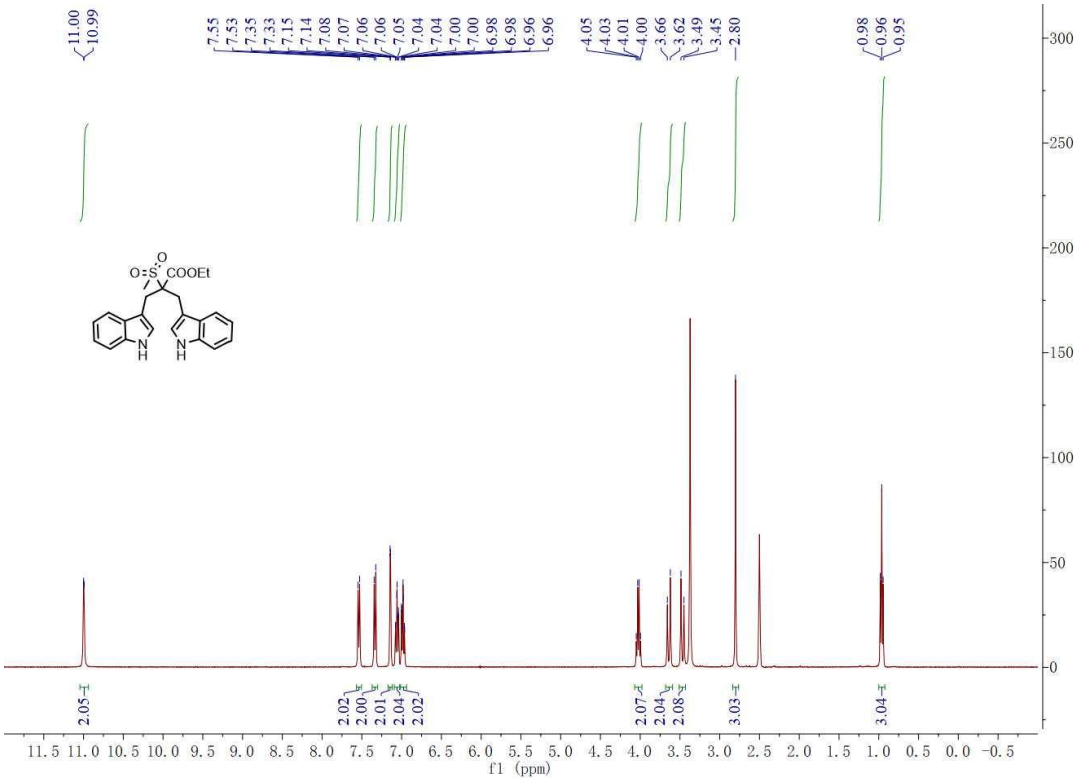


Figure S37. ^{1}H NMR spectrum of ethyl 2-((1*H*-indol-3-yl)methyl)-3-(1*H*-indol-3-yl)-2-(methylsulfonyl)propanoate (**1s**) in DMSO-d_6

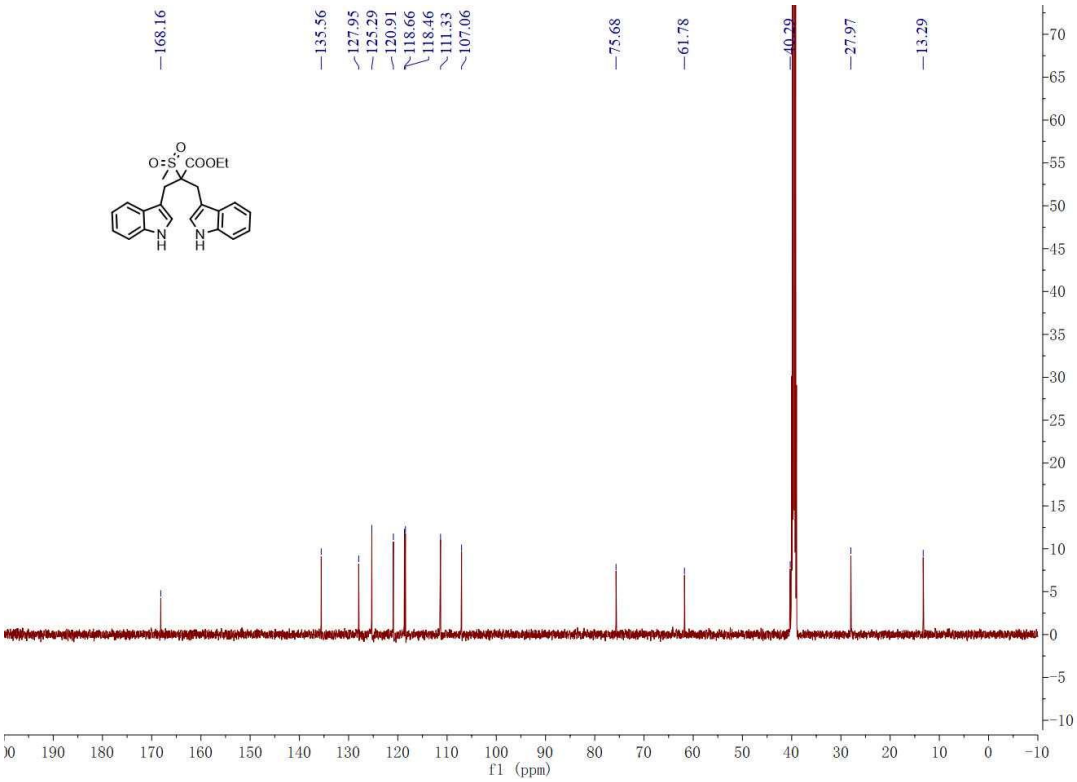


Figure S38. ^{13}C NMR spectrum of ethyl 2-((1*H*-indol-3-yl)methyl)-3-(1*H*-indol-3-yl)-2-(methylsulfonyl)propanoate (**1s**) in DMSO-d_6

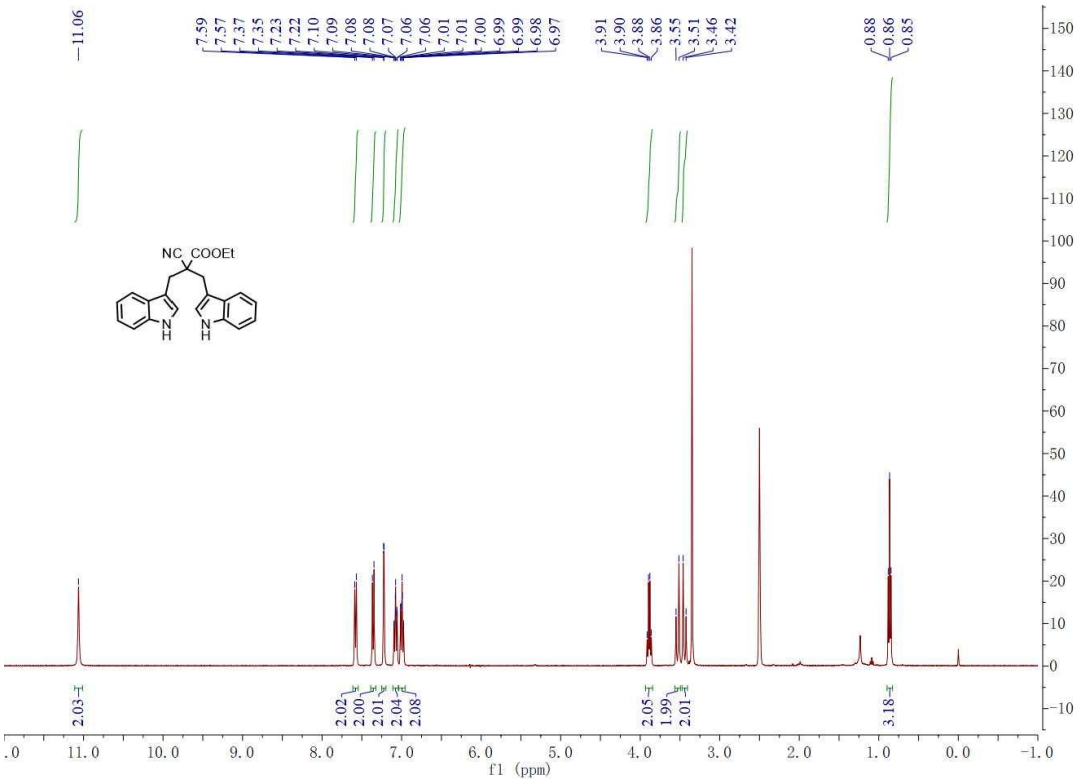


Figure S39. ^{1}H NMR spectrum of ethyl 2-((1*H*-indol-3-yl)methyl)-2-cyano-3-(1*H*-indol-3-yl)propanoate (**1t**) in DMSO-d_6

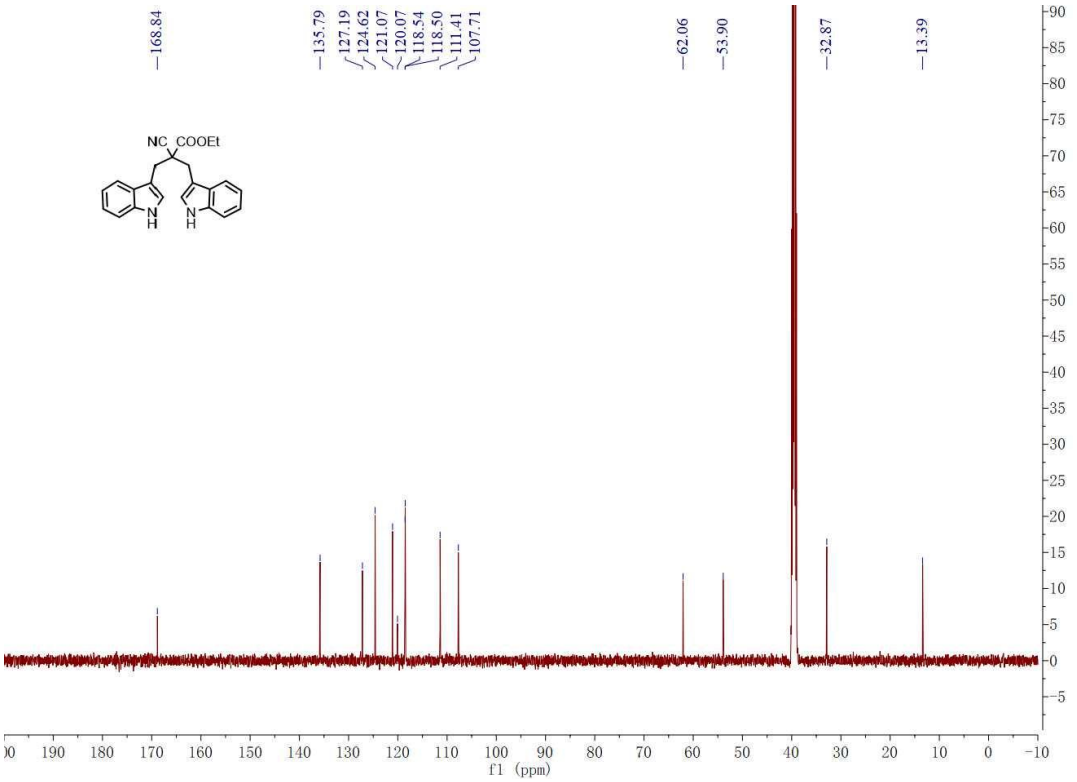


Figure S40. ^{13}C NMR spectrum of ethyl 2-((1*H*-indol-3-yl)methyl)-2-cyano-3-(1*H*-indol-3-yl)propanoate (**1t**) in DMSO-d_6

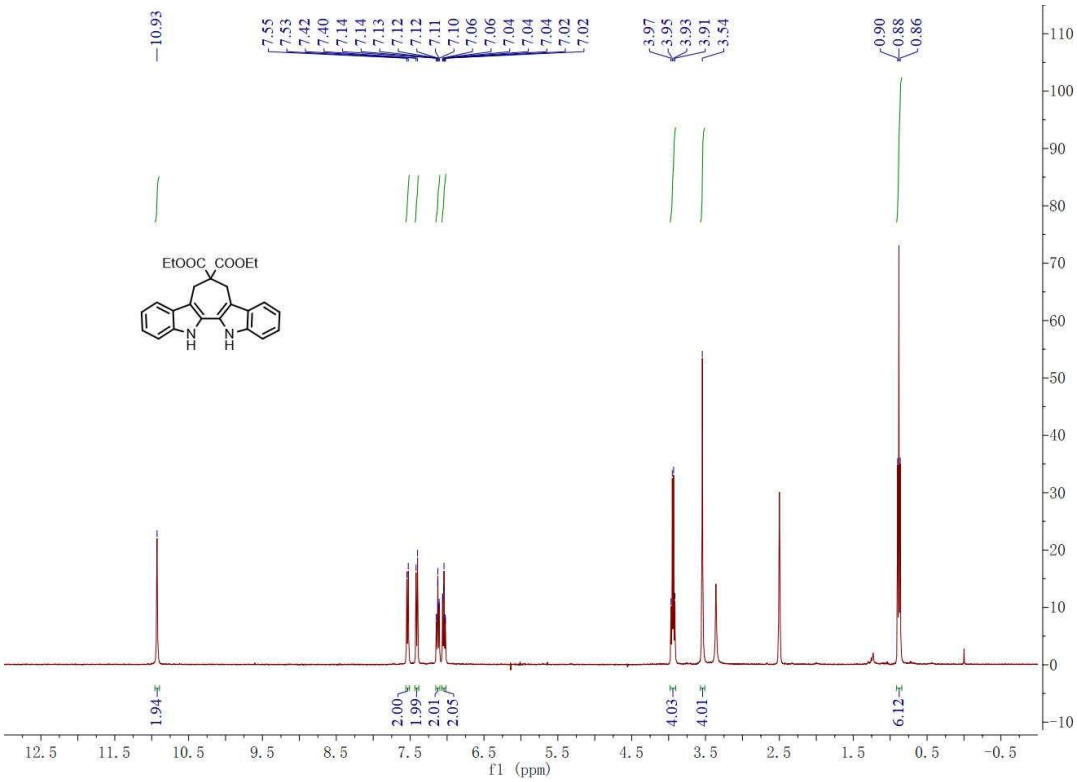


Figure S41. ^{1}H NMR spectrum of diethyl 5,7,12,13-tetrahydro-6*H*-cyclohepta[2,1-*b*:3,4-*b*′]diindole-6,6-dicarboxylate (**2a**) in DMSO-d_6

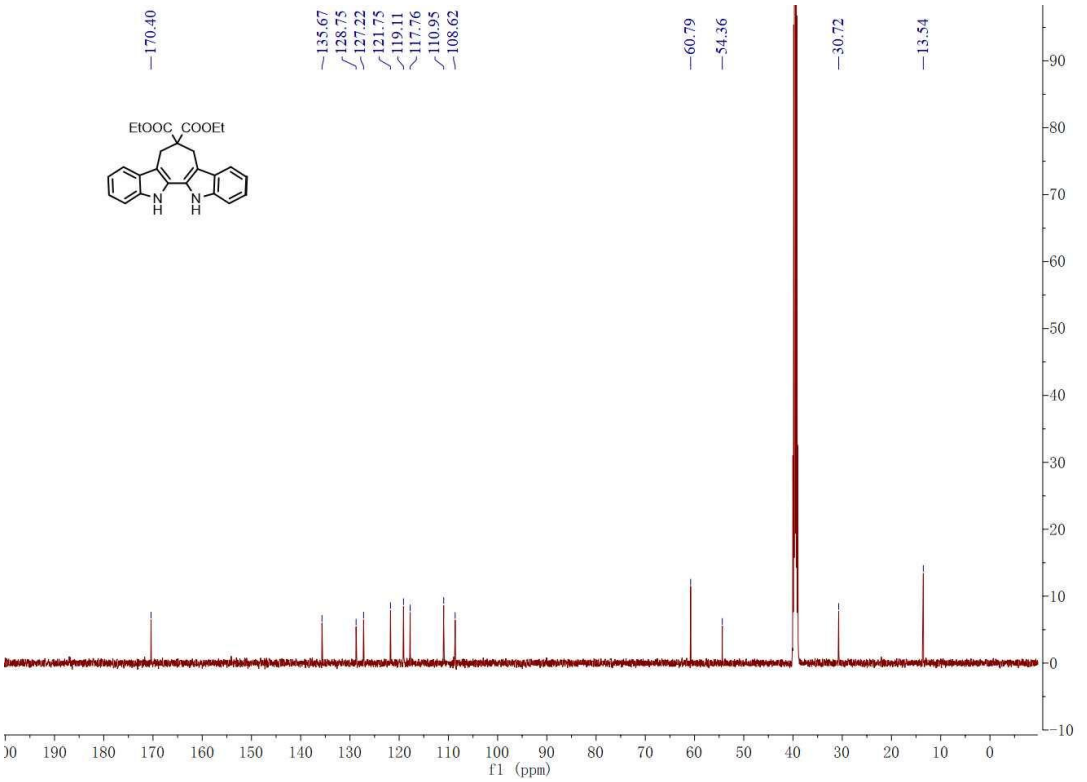


Figure S42. ^{13}C NMR spectrum of diethyl 5,7,12,13-tetrahydro-6*H*-cyclohepta[2,1-*b*:3,4-*b*′]diindole-6,6-dicarboxylate (**2a**) in DMSO-d_6

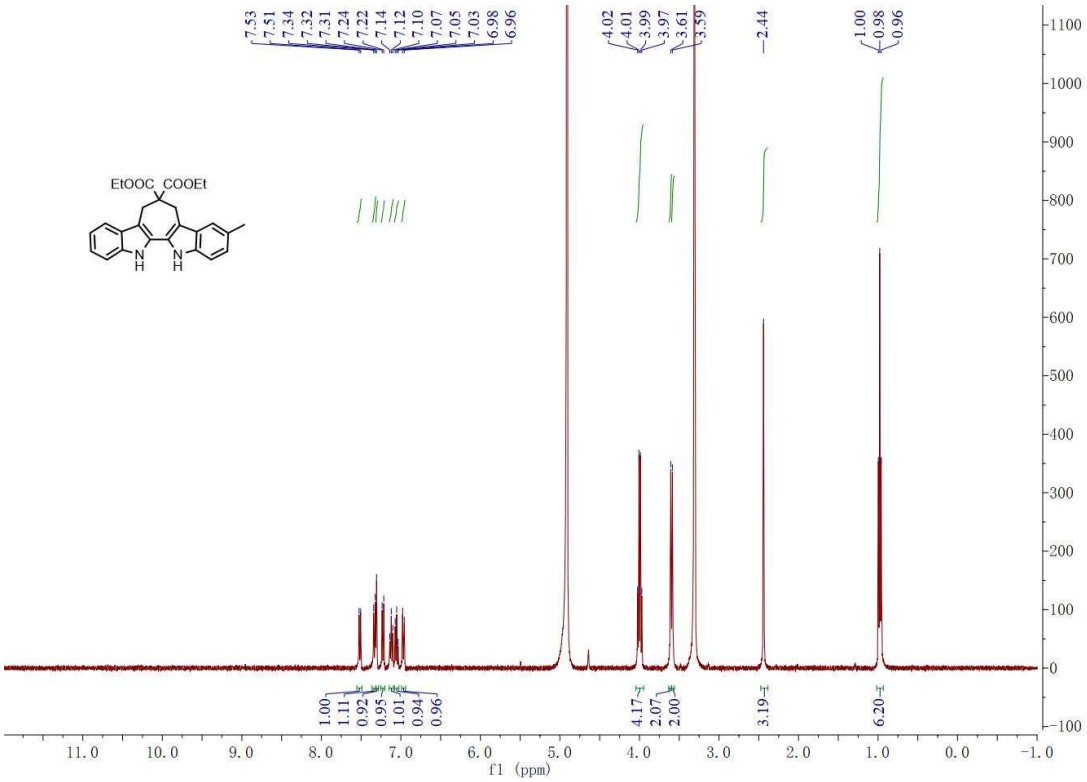


Figure S43. ^{1}H NMR spectrum of diethyl 3-methyl-5,7,12,13-tetrahydro-6*H*-cyclohepta[2,1-*b*:3,4-*b*′]diindole-6,6-dicarboxylate (**2b**) in Methanol-d_4

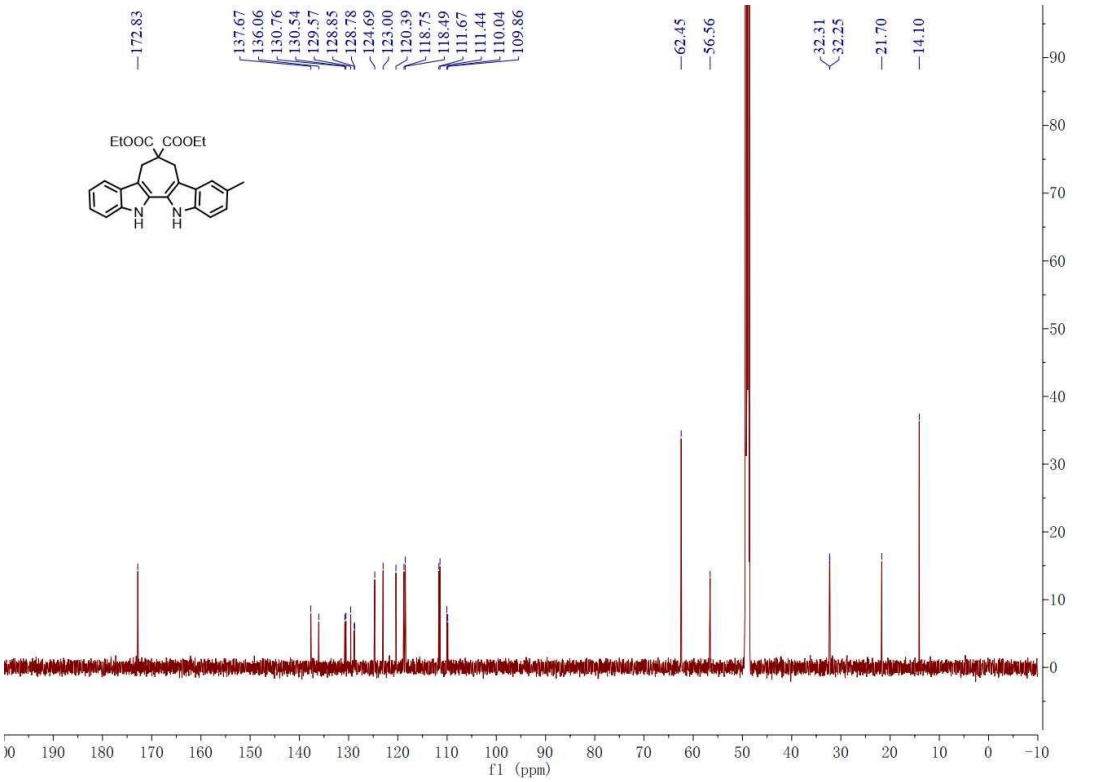


Figure S44. ^{13}C NMR spectrum of diethyl 3-methyl-5,7,12,13-tetrahydro-6*H*-cyclohepta[2,1-*b*:3,4-*b*′]diindole-6,6-dicarboxylate (**2b**) in Methanol-d_4

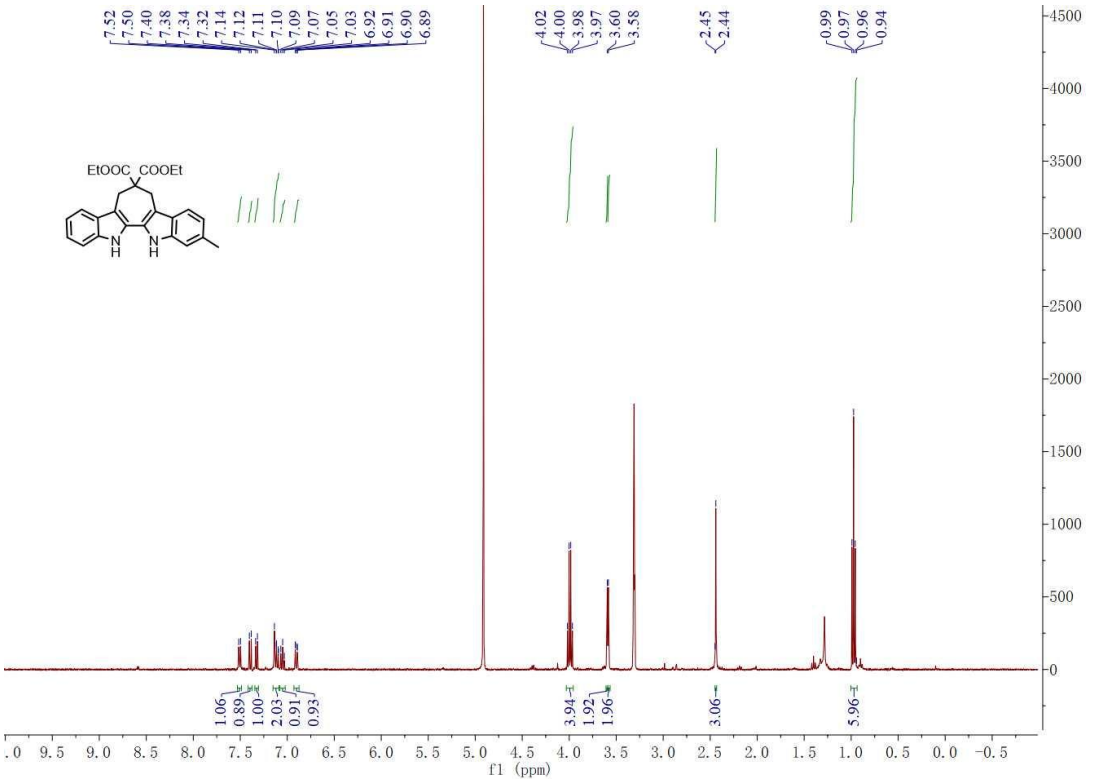


Figure S45. ^{1}H NMR spectrum of diethyl 2-methyl-5,7,12,13-tetrahydro-6*H*-cyclohepta[2,1-*b*:3,4-*b*′]diindole-6,6-dicarboxylate (**2c**) in Methanol-d_4

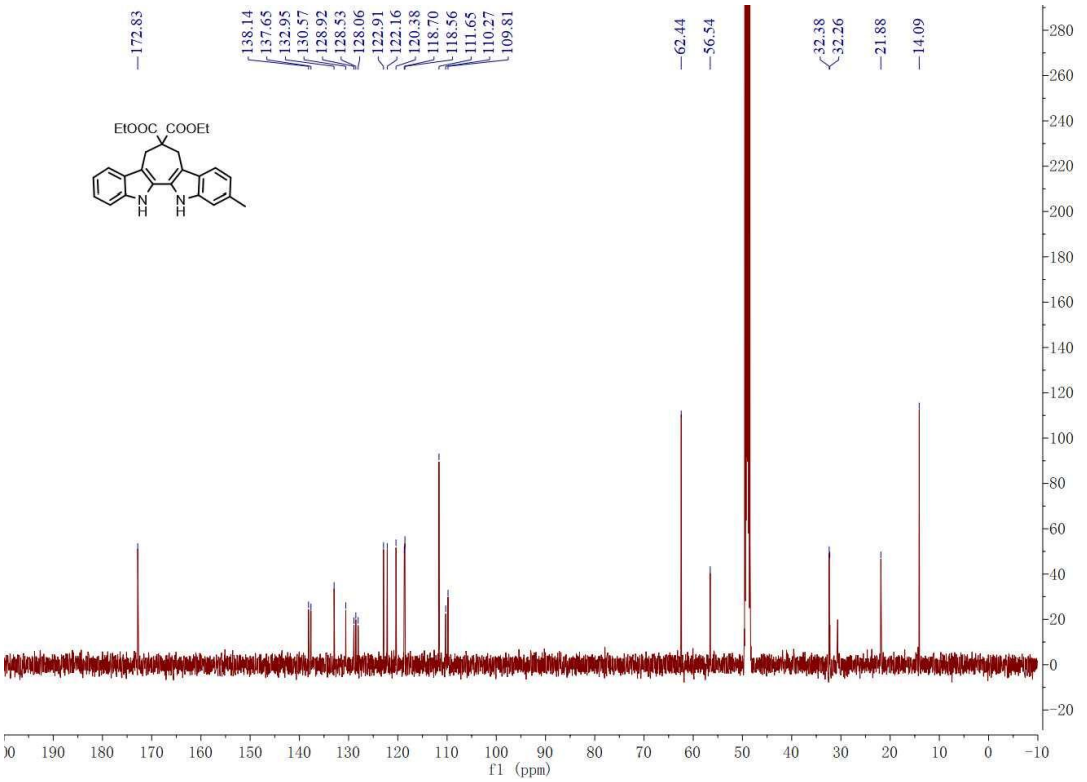


Figure S46. ^{13}C NMR spectrum of diethyl 2-methyl-5,7,12,13-tetrahydro-6*H*-cyclohepta[2,1-*b*:3,4-*b'*]diindole-6,6-dicarboxylate (**2c**) in Methanol-d_4

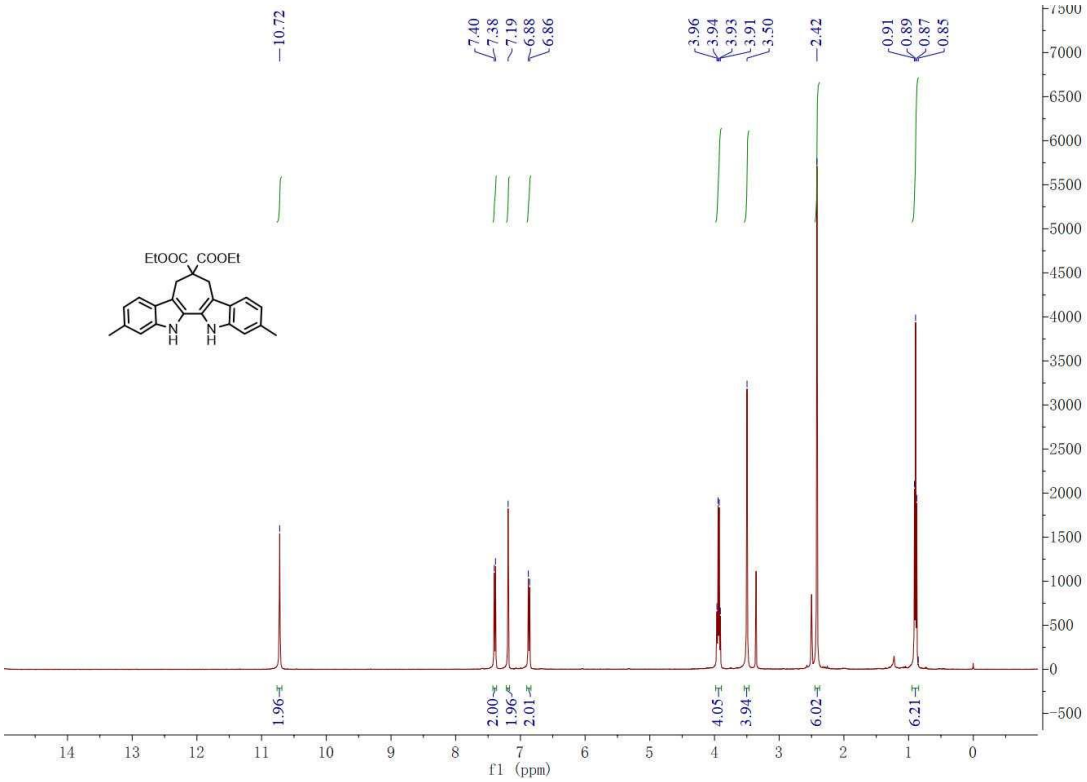


Figure S47. ^{1}H NMR spectrum of diethyl 2,10-dimethyl-5,7,12,13-tetrahydro-6*H*-cyclohepta[2,1-*b*:3,4-*b'*]diindole-6,6-di carboxylate (**2d**) in DMSO-d_6

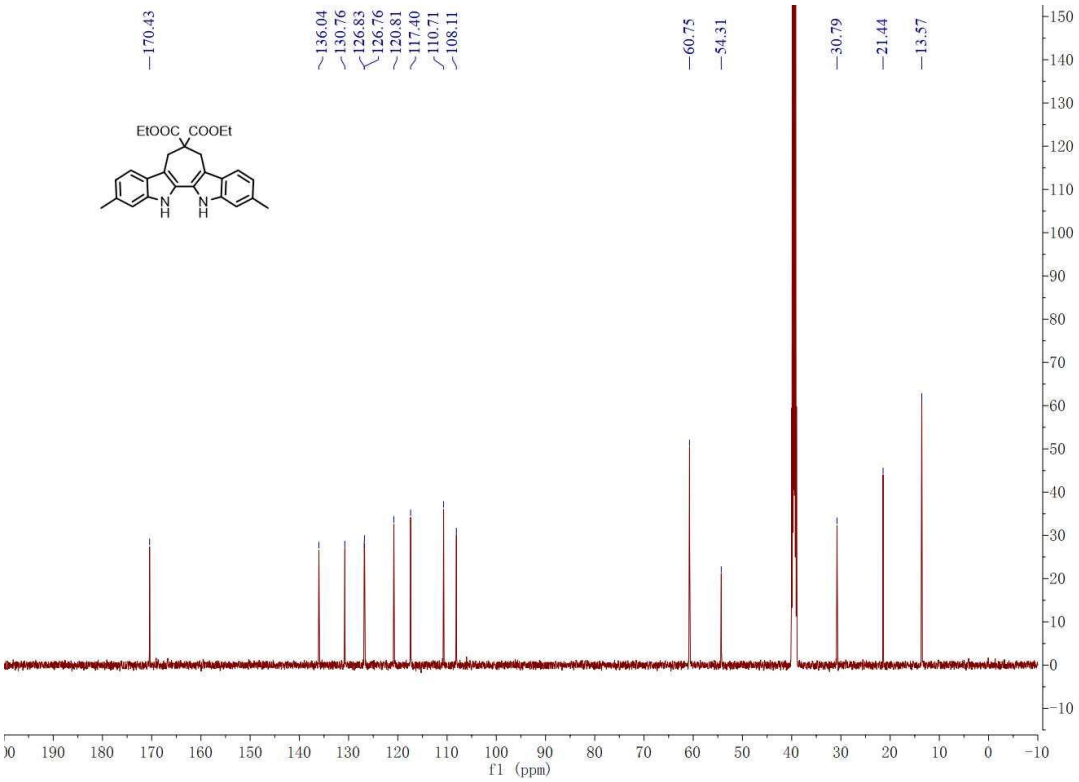


Figure S48. ^{13}C NMR spectrum of diethyl 2,10-dimethyl-5,7,12,13-tetrahydro-6*H*-cyclohepta[2,1-*b*:3,4-*b'*]diindole-6,6-di carboxylate (**2d**) in DMSO-d_6

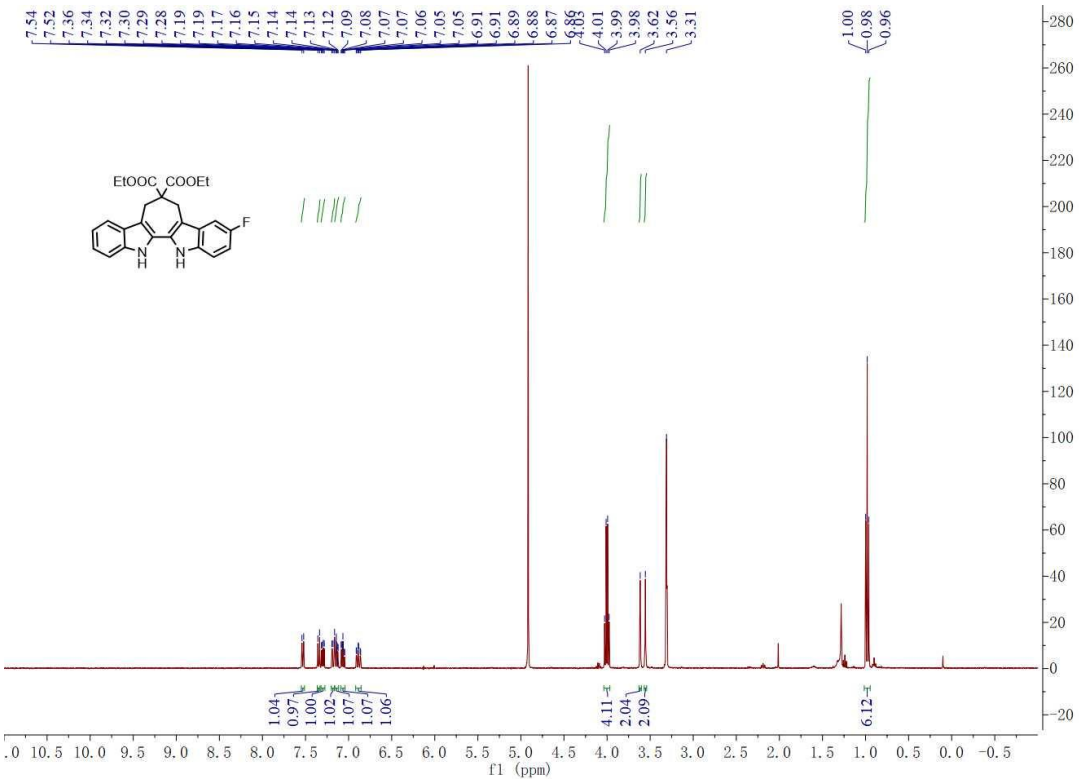


Figure S49. ^{1}H NMR spectrum of diethyl 3-fluoro-5,7,12,13-tetrahydro-6*H*-cyclohepta[2,1-*b*:3,4-*b'*]diindole-6,6-dicarboxylate (**2e**) in Methanol-d_4

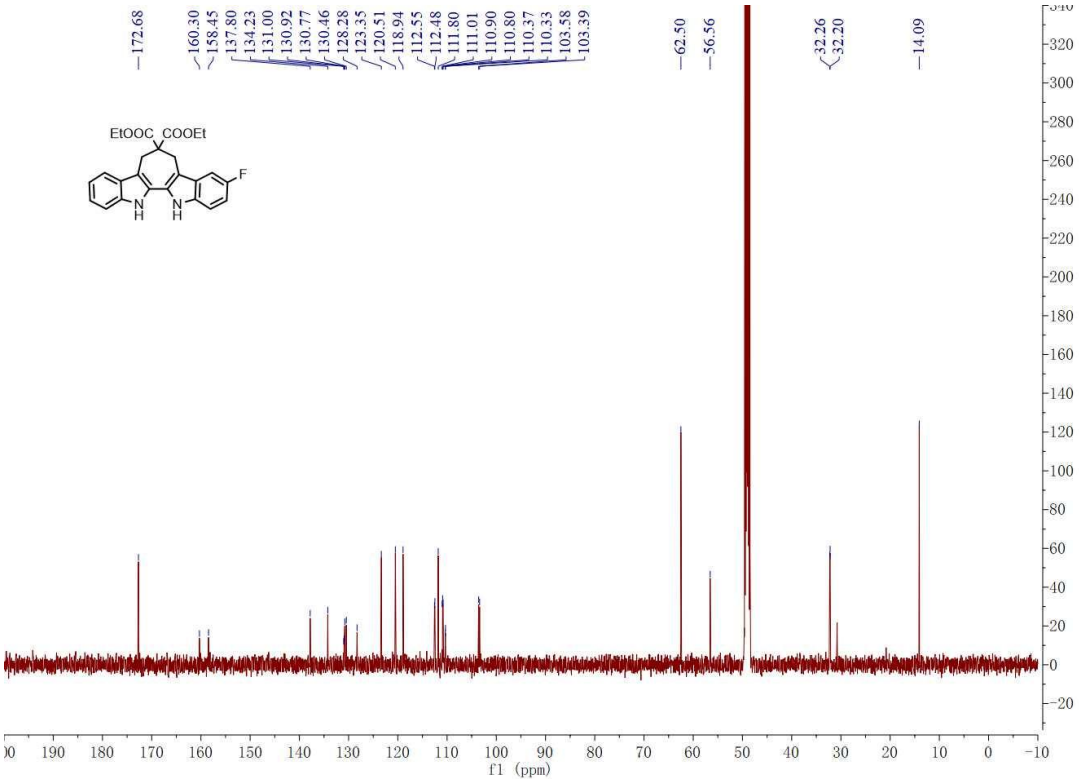


Figure S50. ^{13}C NMR spectrum of diethyl 3-fluoro-5,7,12,13-tetrahydro-6*H*-cyclohepta[2,1-*b*:3,4-*b'*]diindole-6,6-dicarboxylate (**2e**) in Methanol-d_4

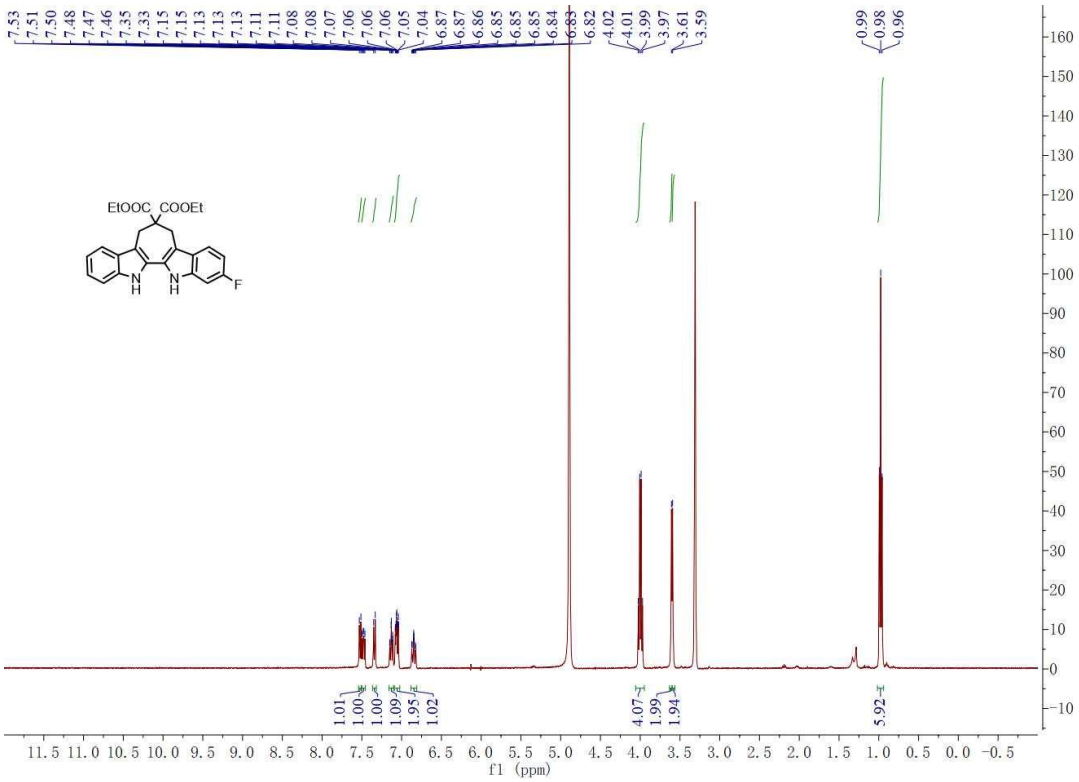


Figure S51. ^{1}H NMR spectrum of diethyl 2-fluoro-5,7,12,13-tetrahydro-6*H*-cyclohepta[2,1-*b*:3,4-*b'*]diindole-6,6-dicarboxylate (**2f**) in Methanol-d_4

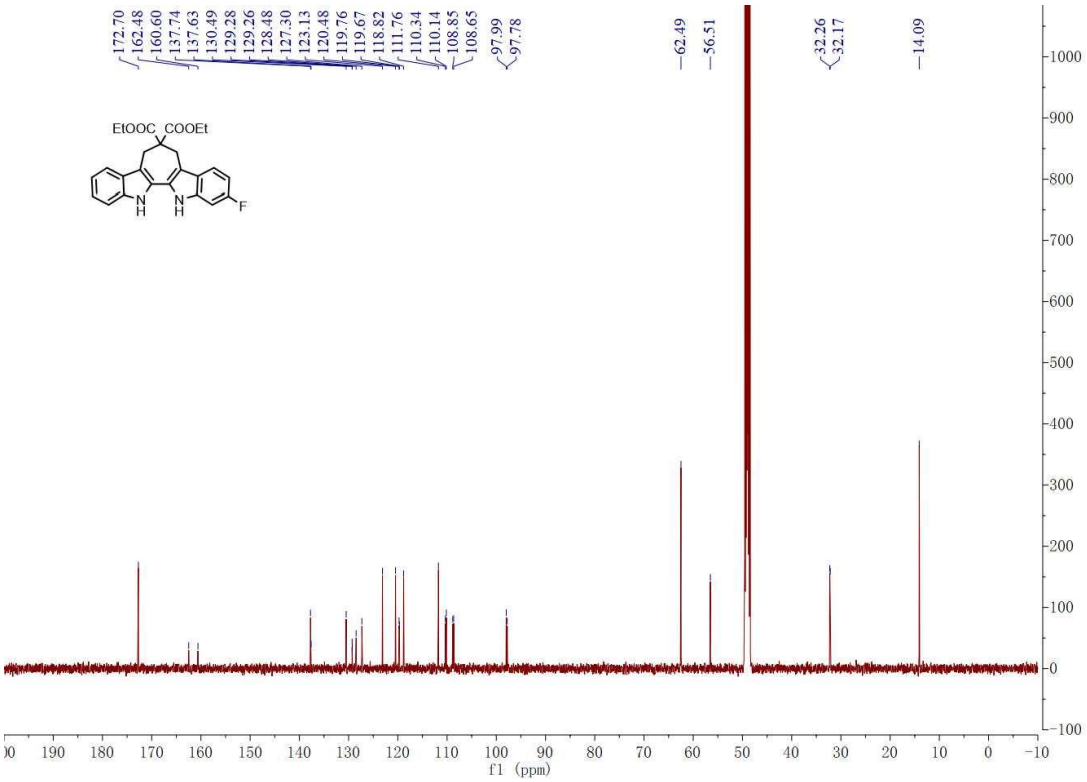


Figure S52. ^{13}C NMR spectrum of diethyl 2-fluoro-5,7,12,13-tetrahydro-6*H*-cyclohepta[2,1-*b*:3,4-*b'*]diindole-6,6-dicarboxylate (**2f**) in Methanol-d_4

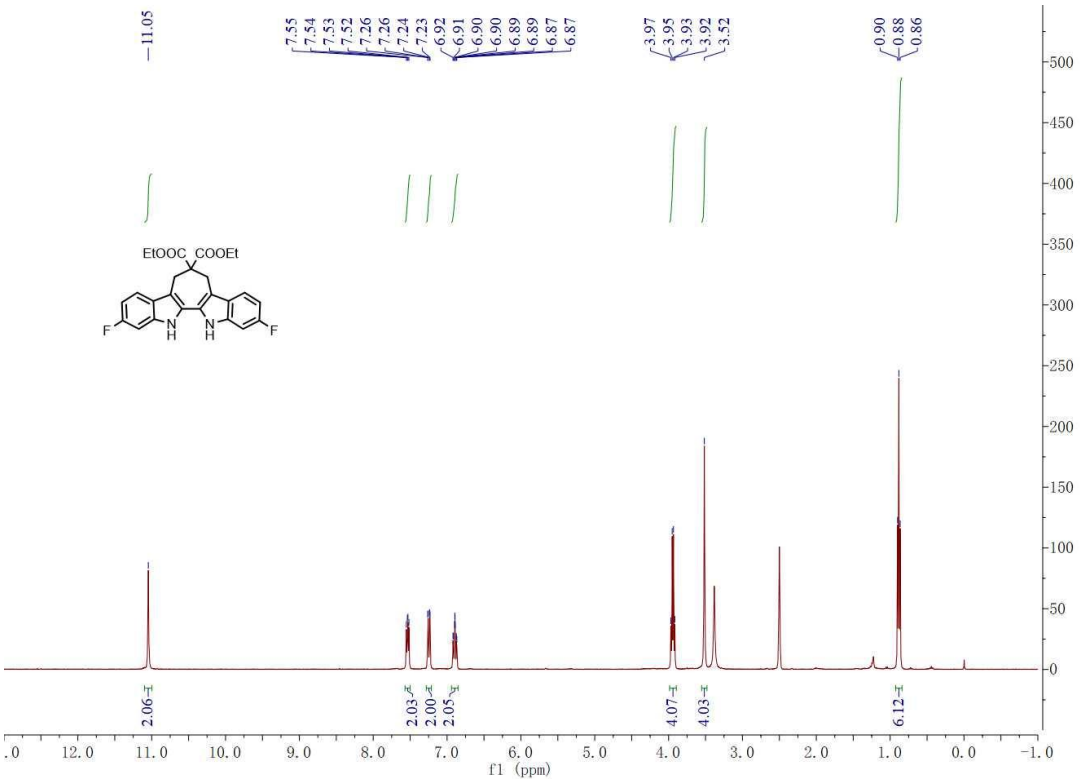


Figure S53. ^{1}H NMR spectrum of diethyl 2,10-difluoro-5,7,12,13-tetrahydro-6*H*-cyclohepta[2,1-*b*:3,4-*b'*]diindole-6,6-dicarboxylate (**2g**) in DMSO-d_6

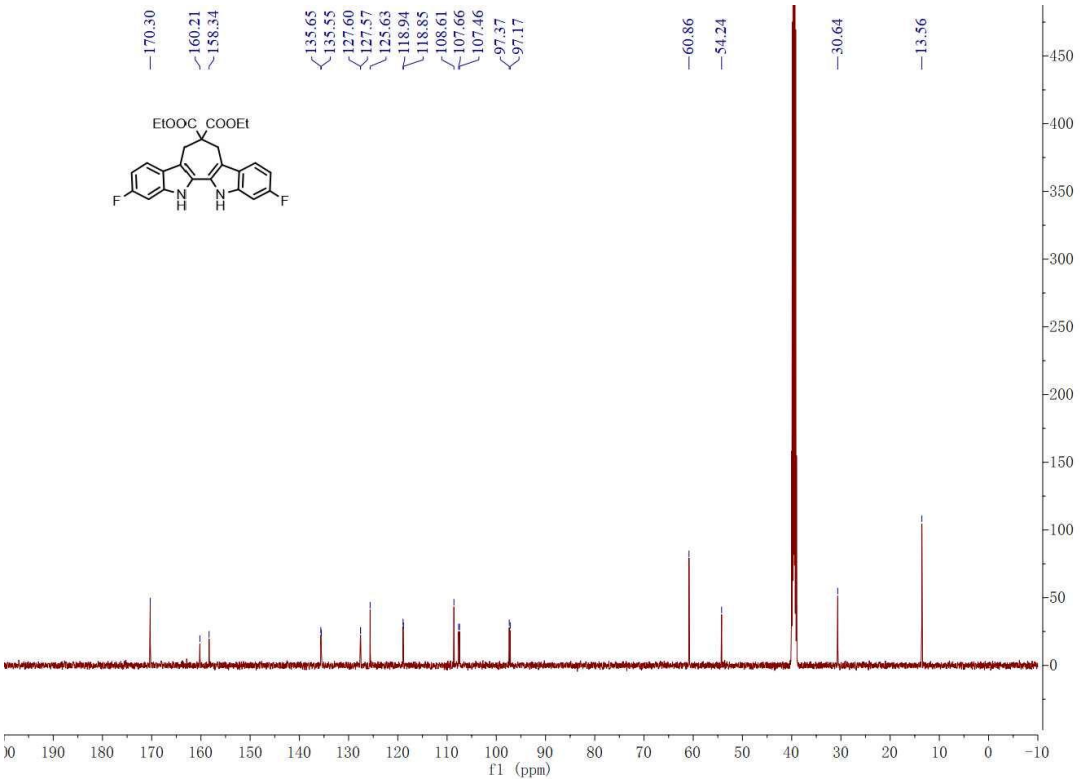


Figure S54. ^{13}C NMR spectrum of diethyl 2,10-difluoro-5,7,12,13-tetrahydro-6*H*-cyclohepta[2,1-*b*:3,4-*b*′]diindole-6,6-dicarboxylate (**2g**) in DMSO-d_6

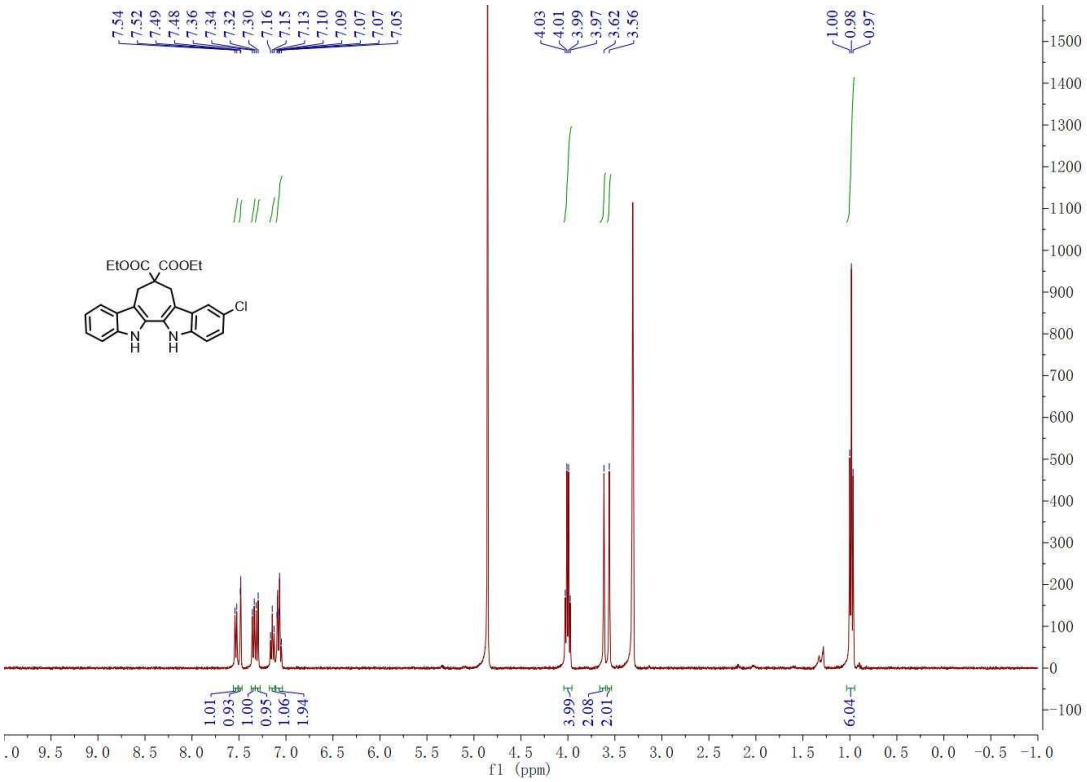


Figure S55. ^{1}H NMR spectrum of diethyl 3-chloro-5,7,12,13-tetrahydro-6*H*-cyclohepta[2,1-*b*:3,4-*b*′]diindole-6,6-dicarboxylate (**2h**) in Methanol-d_4

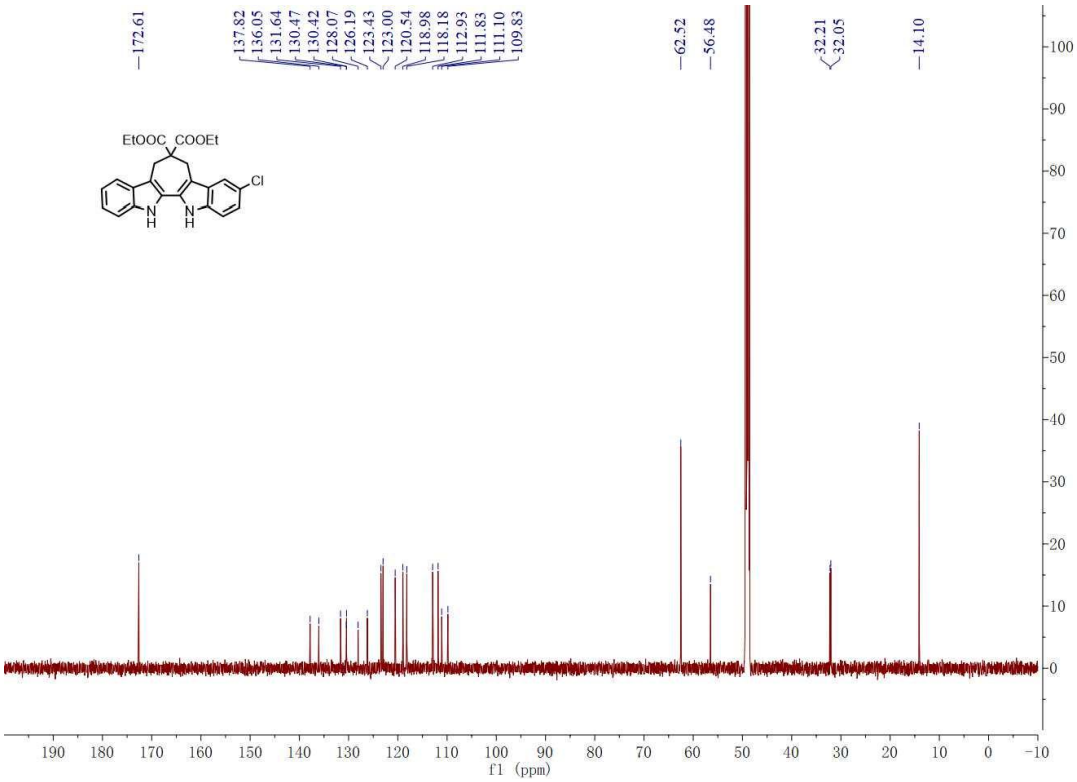


Figure S56. ^{13}C NMR spectrum of diethyl 3-chloro-5,7,12,13-tetrahydro-6*H*-cyclohepta[2,1-*b*:3,4-*b'*]diindole-6,6-dicarboxylate (**2h**) in Methanol-d_4

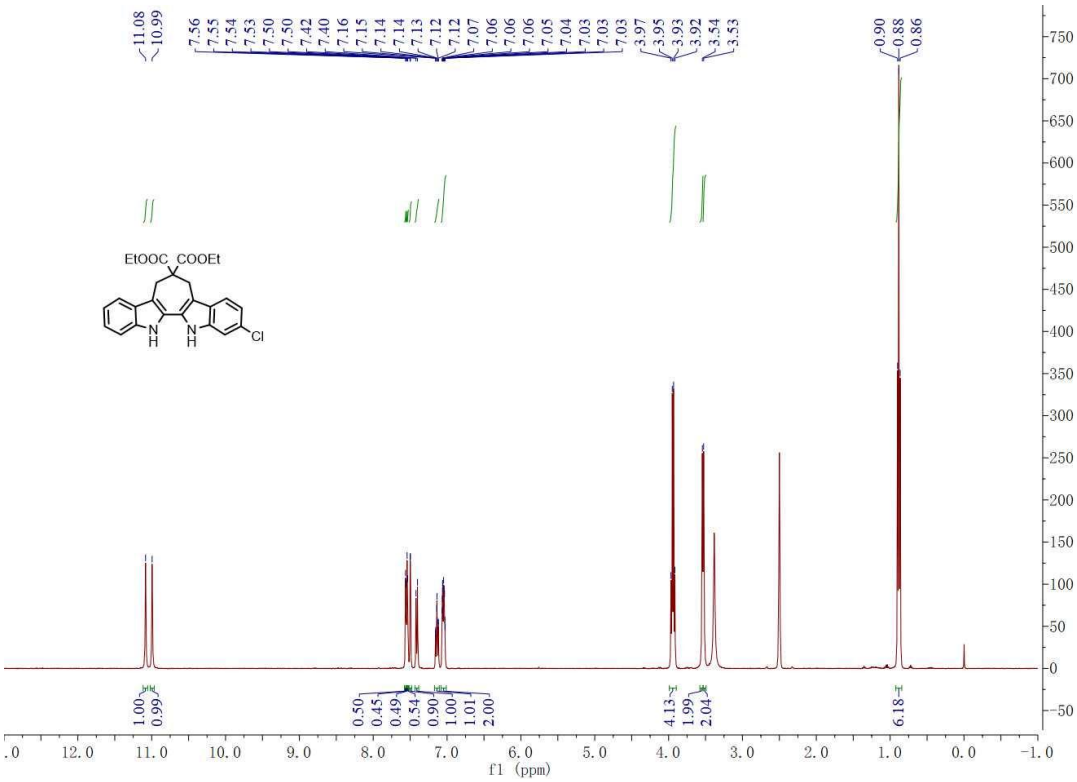


Figure S57. ^{1}H NMR spectrum of diethyl 2-chloro-5,7,12,13-tetrahydro-6*H*-cyclohepta[2,1-*b*:3,4-*b'*]diindole-6,6-dicarboxylate (**2i**) in DMSO-d_6

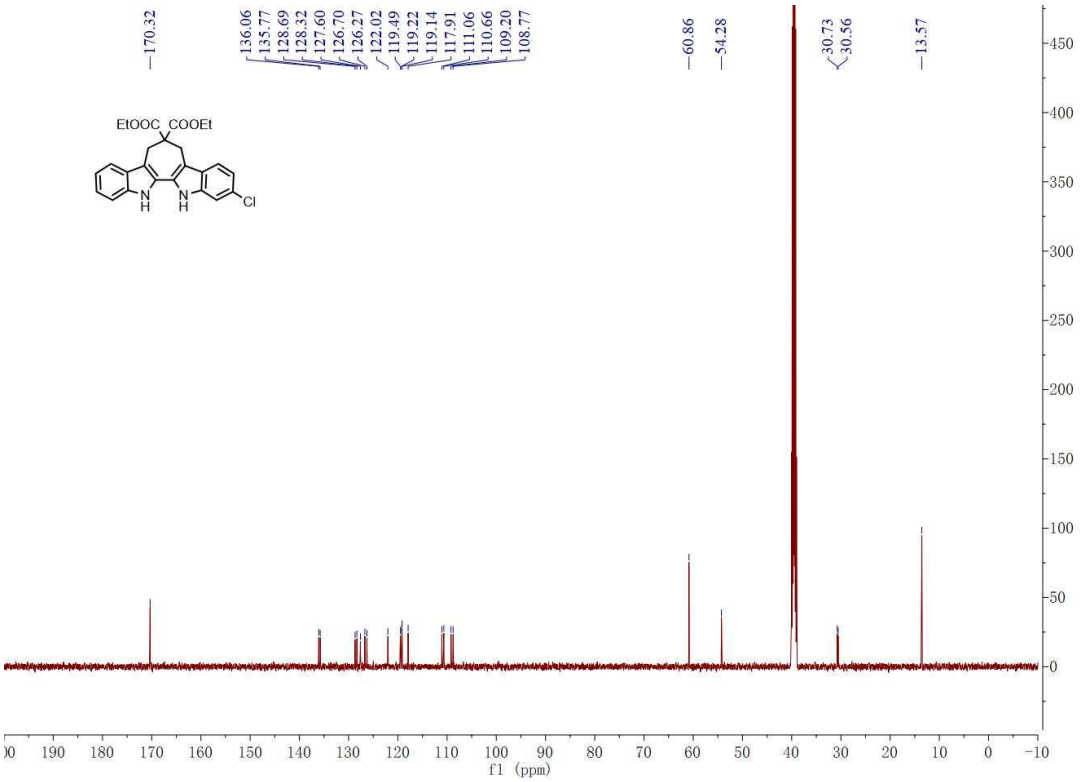


Figure S58. ^{13}C NMR spectrum of diethyl 2-chloro-5,7,12,13-tetrahydro-6*H*-cyclohepta[2,1-*b*:3,4-*b'*]diindole-6,6-dicarboxylate (**2i**) in DMSO-d_6

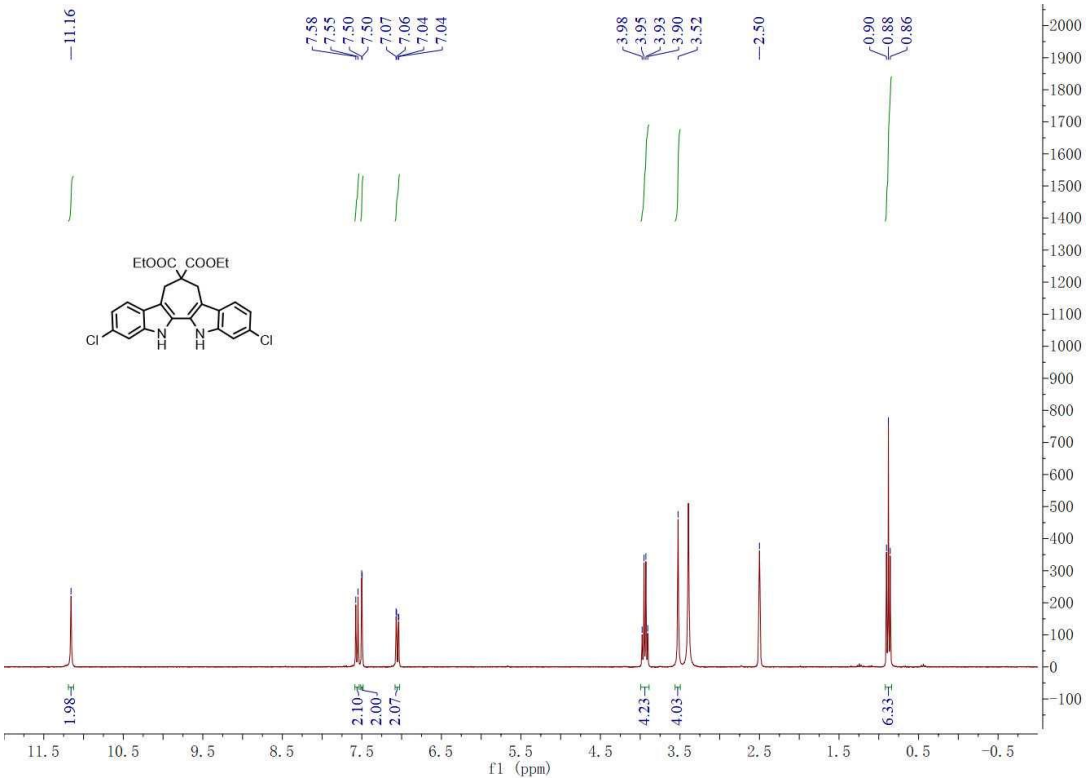


Figure S59. ^{1}H NMR spectrum of diethyl 2,10-dichloro-5,7,12,13-tetrahydro-6*H*-cyclohepta[2,1-*b*:3,4-*b'*]diindole-6,6-di carboxylate (**2j**) in DMSO-d_6

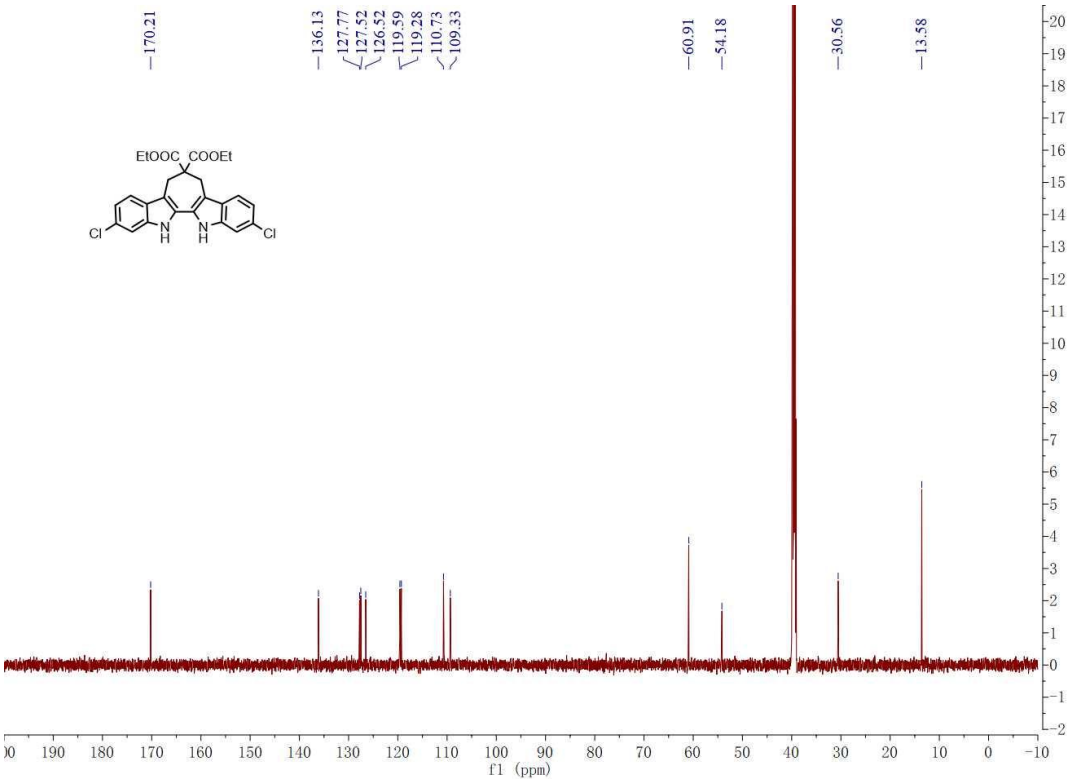


Figure S60. ^{13}C NMR spectrum of diethyl 2,10-dichloro-5,7,12,13-tetrahydro-6*H*-cyclohepta[2,1-*b*:3,4-*b'*]diindole-6,6-di carboxylate (**2j**) in DMSO-d_6

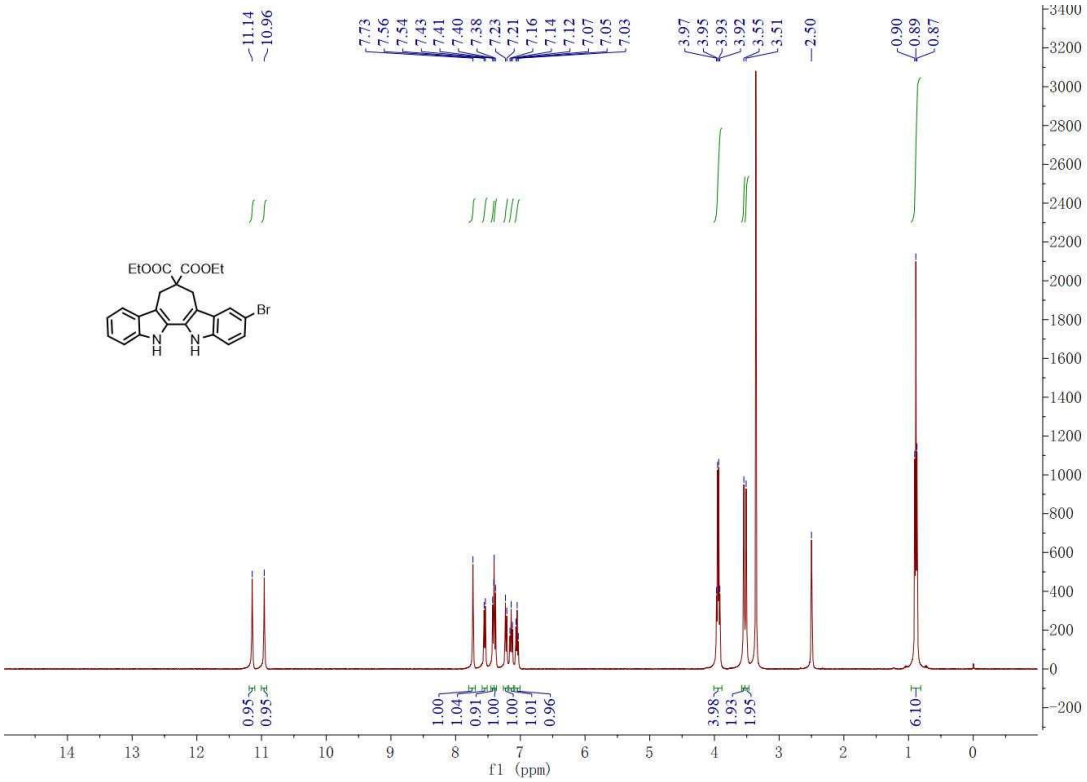


Figure S61. ^{1}H NMR spectrum of diethyl 3-bromo-5,7,12,13-tetrahydro-6*H*-cyclohepta[2,1-*b*:3,4-*b'*]diindole-6,6-dicarboxylate (**2k**) in DMSO-d_6

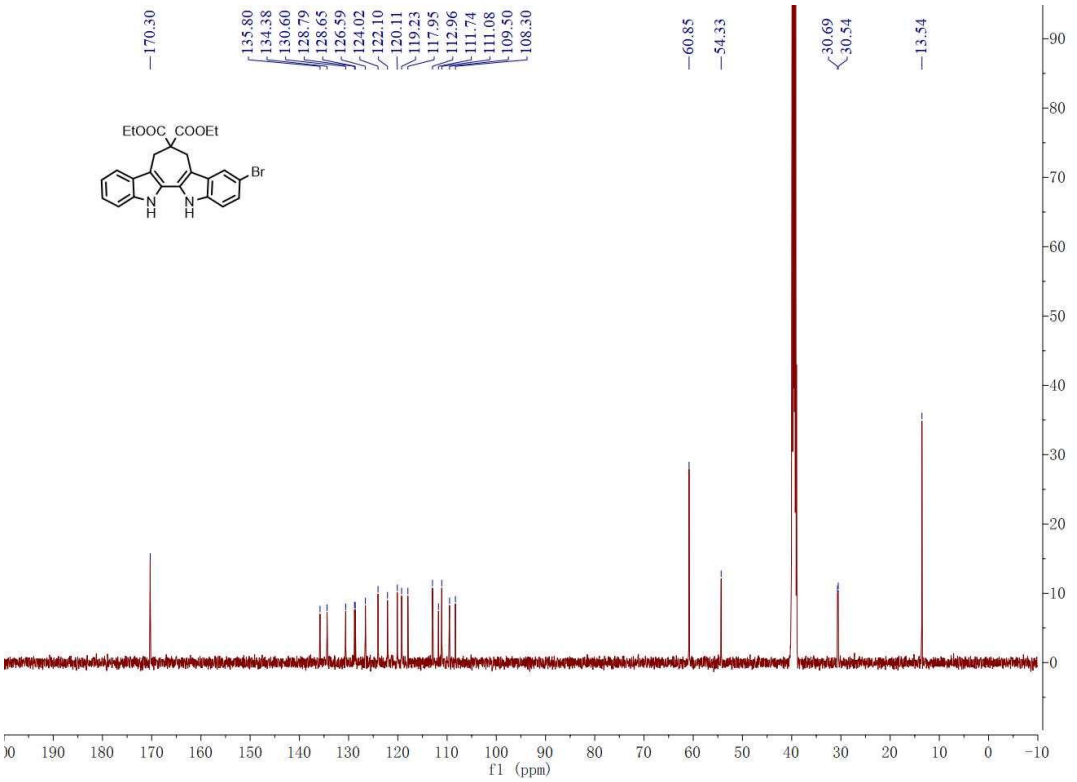


Figure S62. ^{13}C NMR spectrum of diethyl 3-bromo-5,7,12,13-tetrahydro-6*H*-cyclohepta[2,1-*b*:3,4-*b'*]diindole-6,6-dicarboxylate (**2k**) in DMSO-d_6

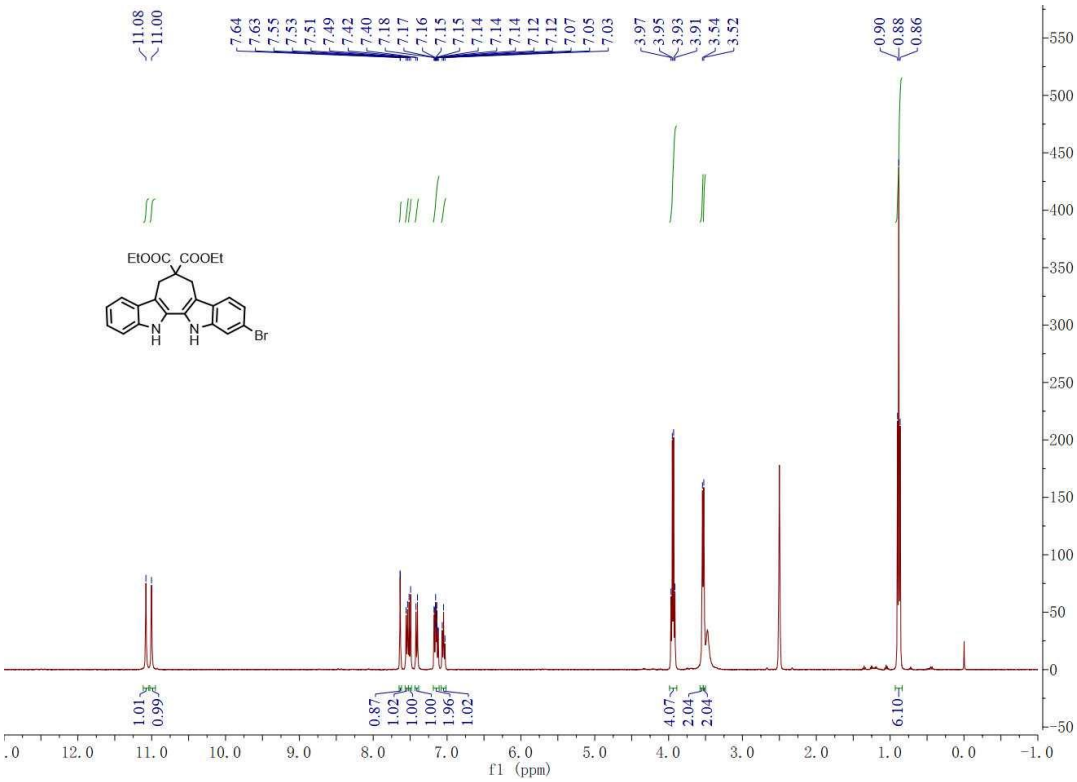


Figure S63. ^{1}H NMR spectrum of diethyl 2-bromo-5,7,12,13-tetrahydro-6*H*-cyclohepta[2,1-*b*:3,4-*b'*]diindole-6,6-dicarboxylate (**2l**) in DMSO-d_6

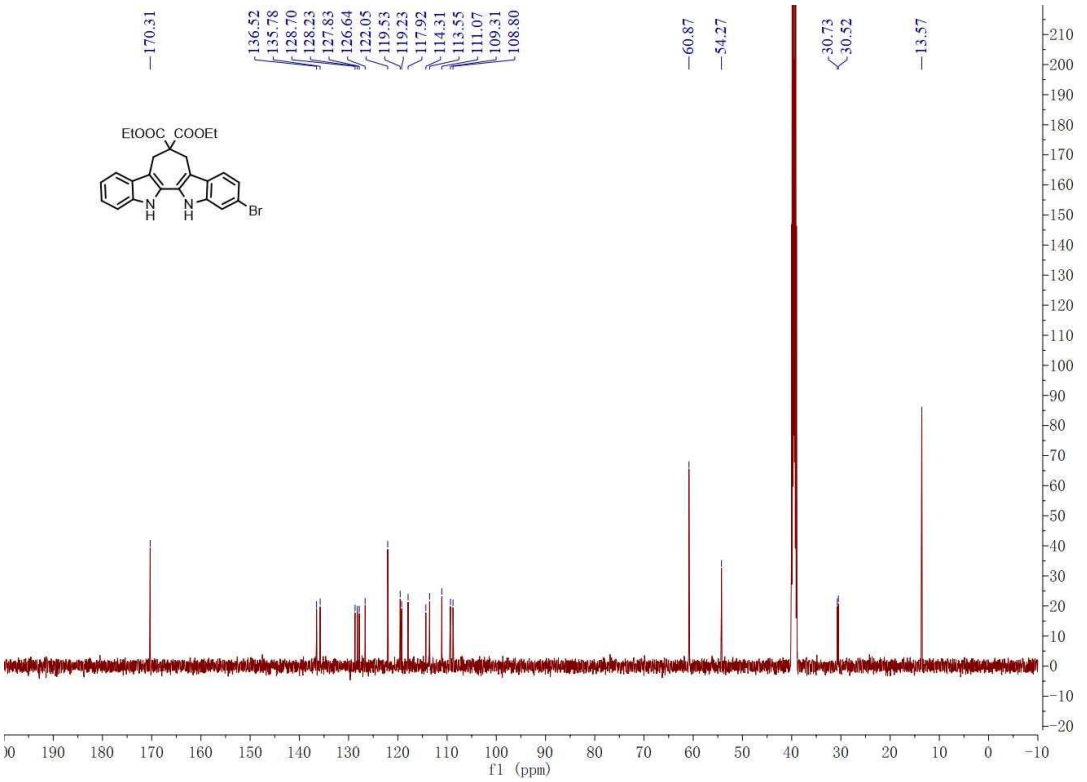


Figure S64. ^{13}C NMR spectrum of diethyl 2-bromo-5,7,12,13-tetrahydro-6*H*-cyclohepta[2,1-*b*:3,4-*b'*]diindole-6,6-dicarboxylate (**2l**) in DMSO-d_6

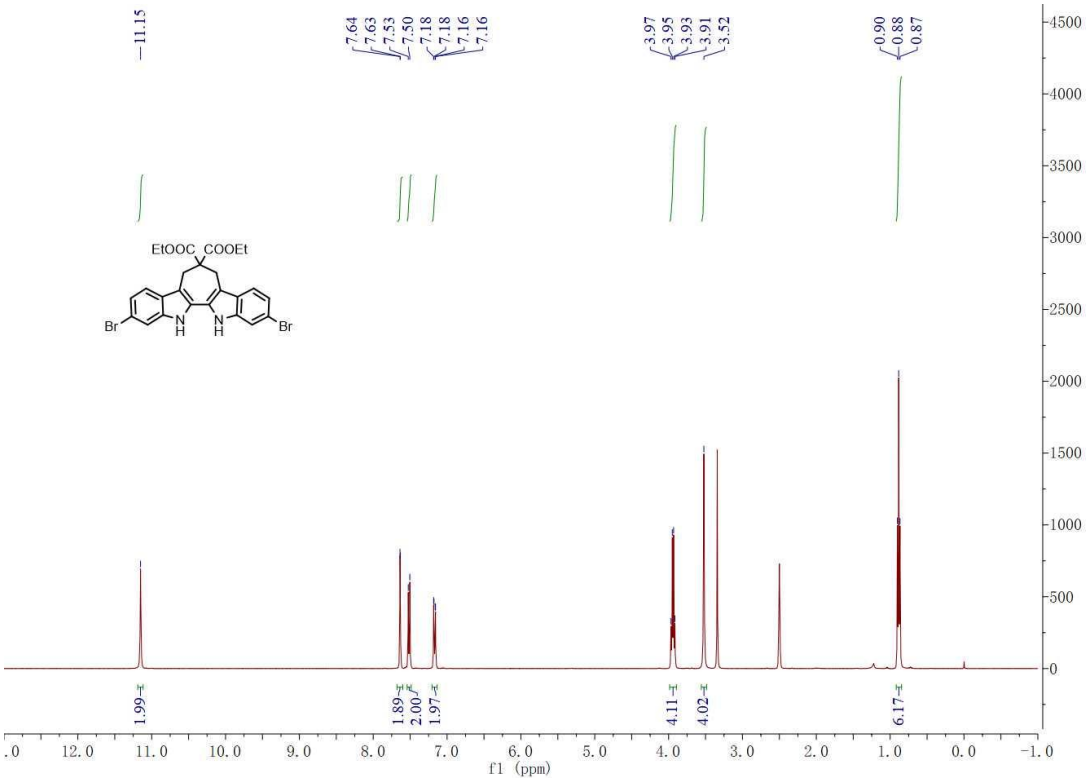


Figure S65. ^{1}H NMR spectrum of diethyl 2,10-dibromo-5,7,12,13-tetrahydro-6*H*-cyclohepta[2,1-*b*:3,4-*b'*]diindole-6,6-di carboxylate (**2m**) in DMSO-d_6

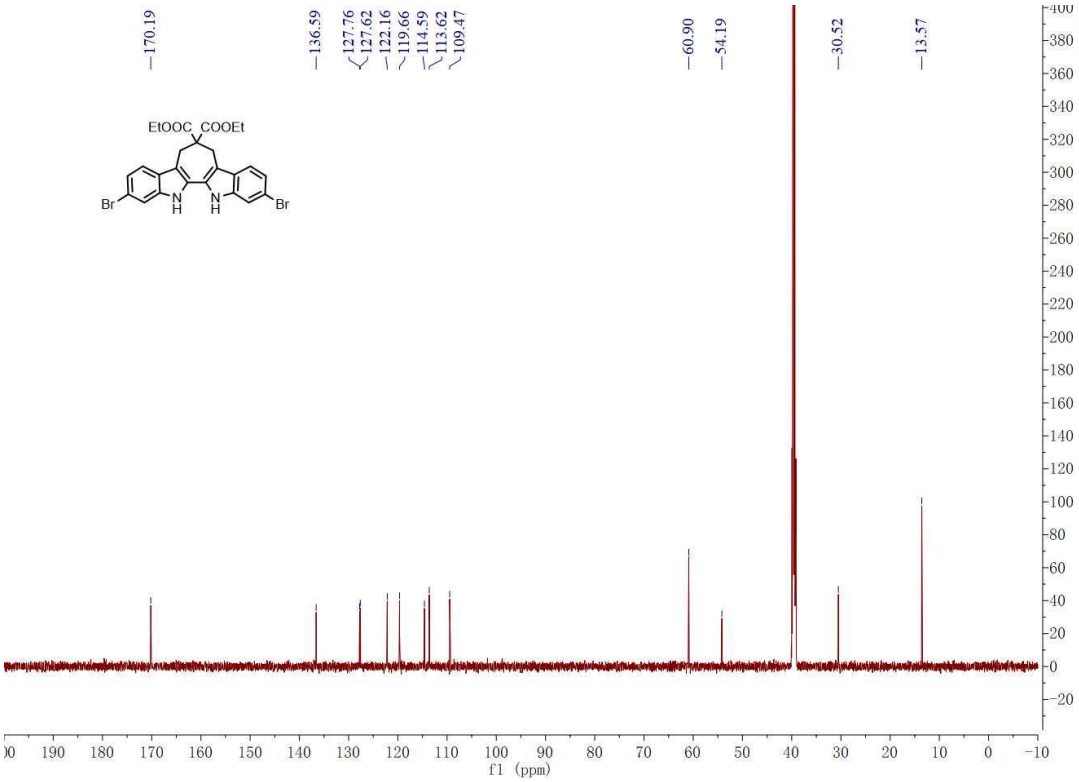


Figure S66. ^{13}C NMR spectrum of diethyl 2,10-dibromo-5,7,12,13-tetrahydro-6*H*-cyclohepta[2,1-*b*:3,4-*b*′]diindole-6,6-di carboxylate (**2m**) in DMSO-d_6

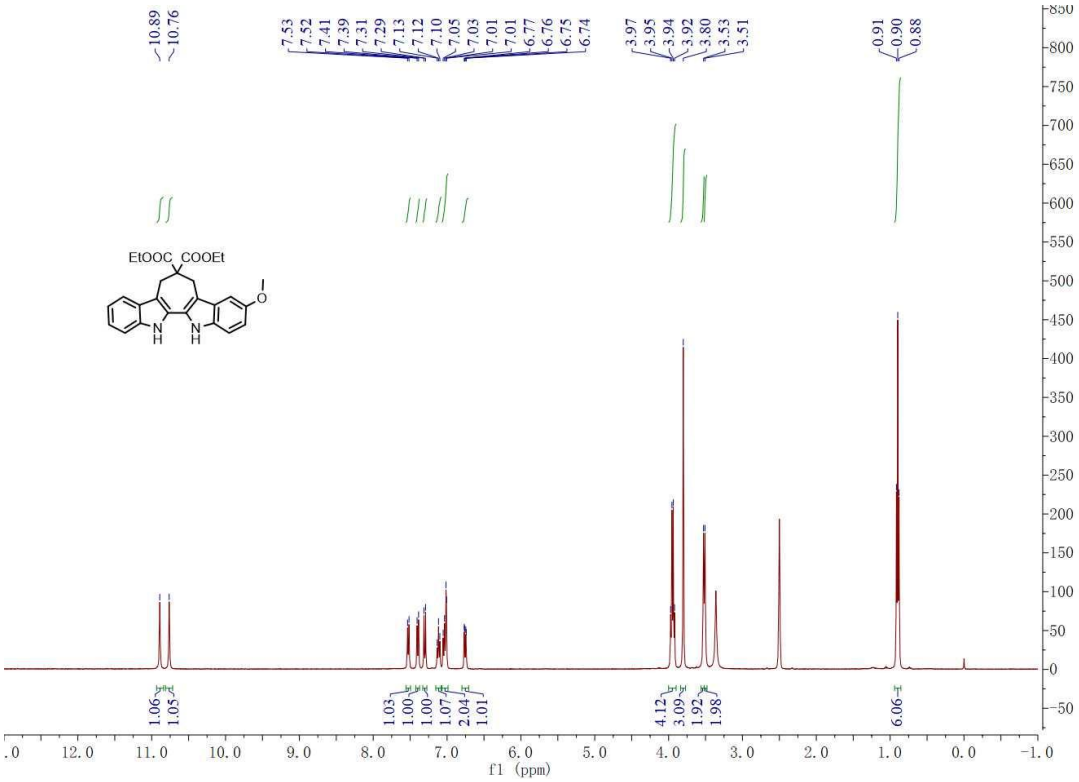


Figure S67. ^{1}H NMR spectrum of diethyl 3-methoxy-5,7,12,13-tetrahydro-6*H*-cyclohepta[2,1-*b*:3,4-*b*′]diindole-6,6-dicarboxylate (**2n**) in DMSO-d_6

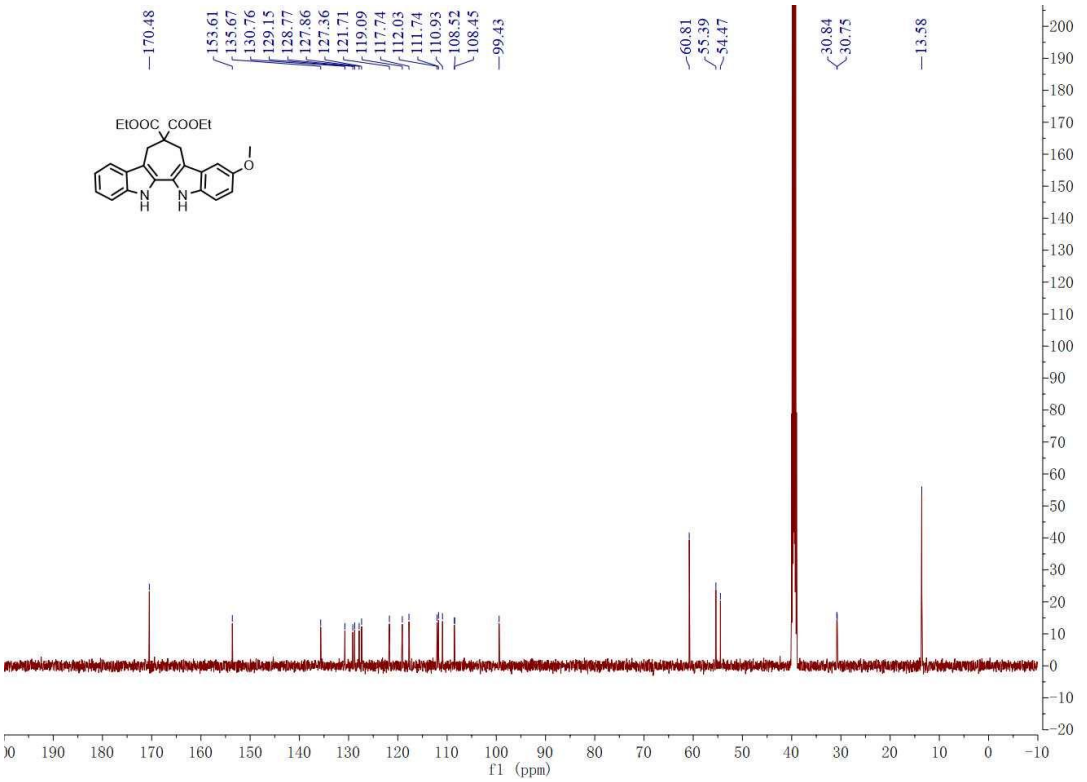


Figure S68. ^{13}C NMR spectrum of diethyl 3-methoxy-5,7,12,13-tetrahydro-6*H*-cyclohepta[2,1-*b*:3,4-*b*′]diindole-6,6-dicarboxylate (**2n**) in DMSO-d_6

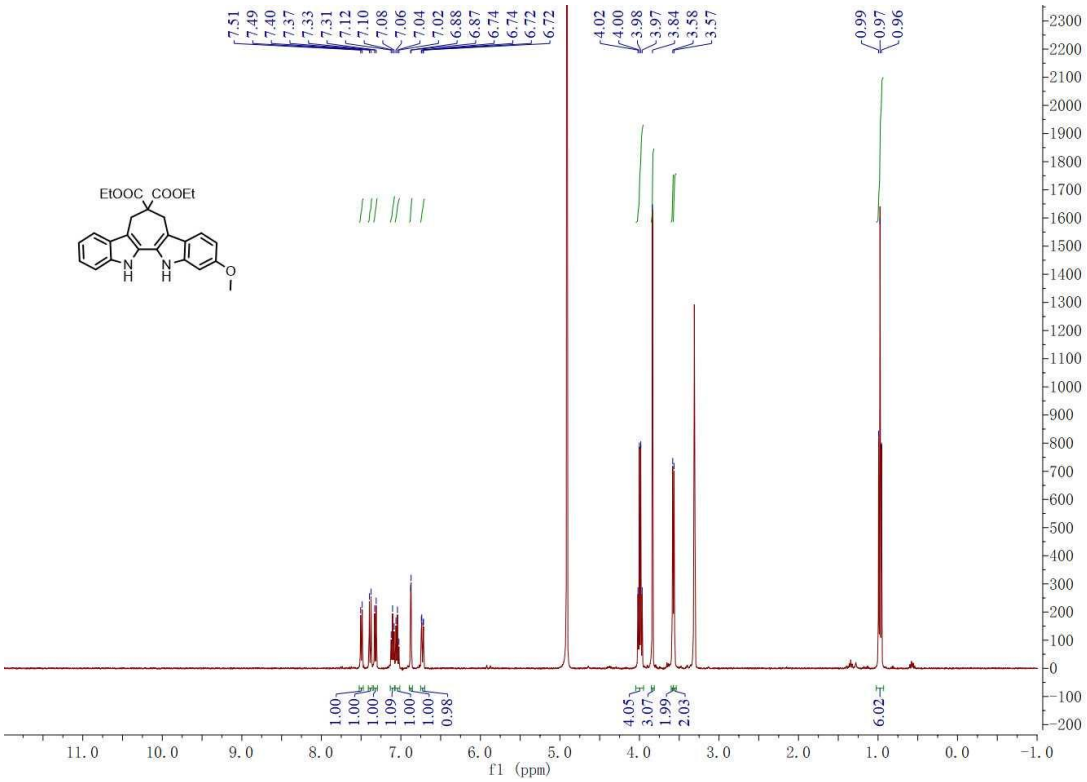


Figure S69. ^{1}H NMR spectrum of diethyl 2-methoxy-5,7,12,13-tetrahydro-6*H*-cyclohepta[2,1-*b*:3,4-*b*′]diindole-6,6-dicarboxylate (**2o**) in Methanol-d_4

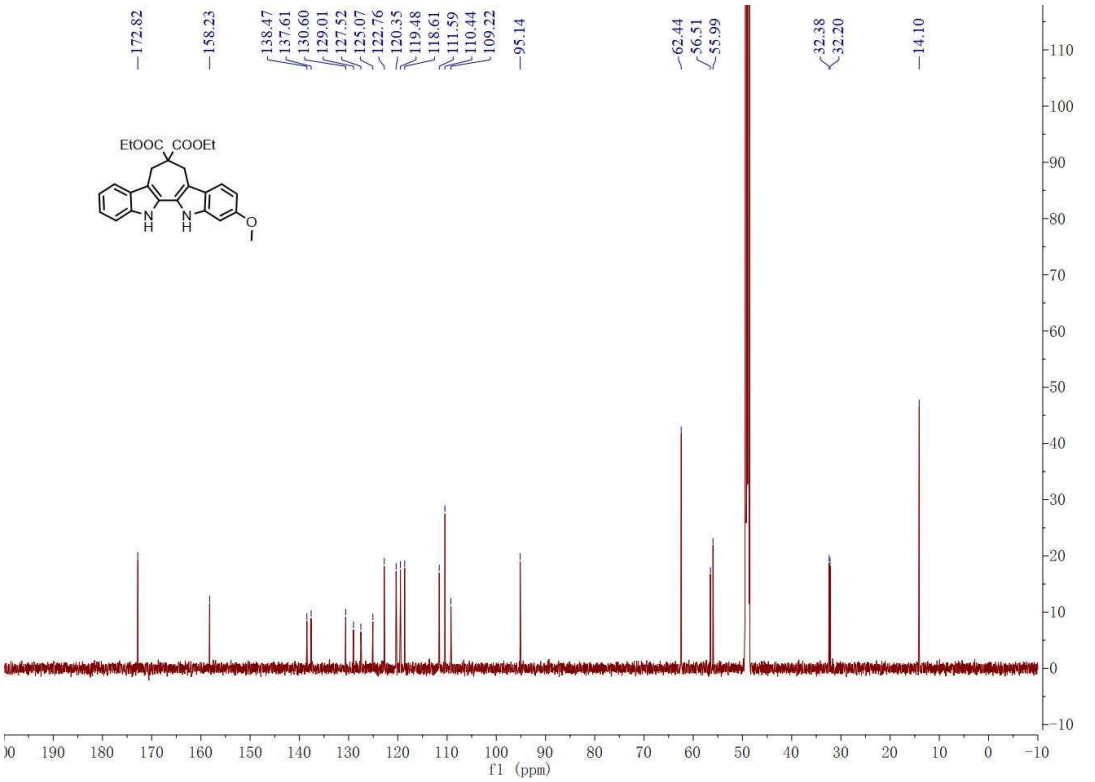


Figure S70. ^{13}C NMR spectrum of diethyl 2-methoxy-5,7,12,13-tetrahydro-6*H*-cyclohepta[2,1-*b*:3,4-*b*′]diindole-6,6-dicarboxylate (**2o**) in Methanol-d_4

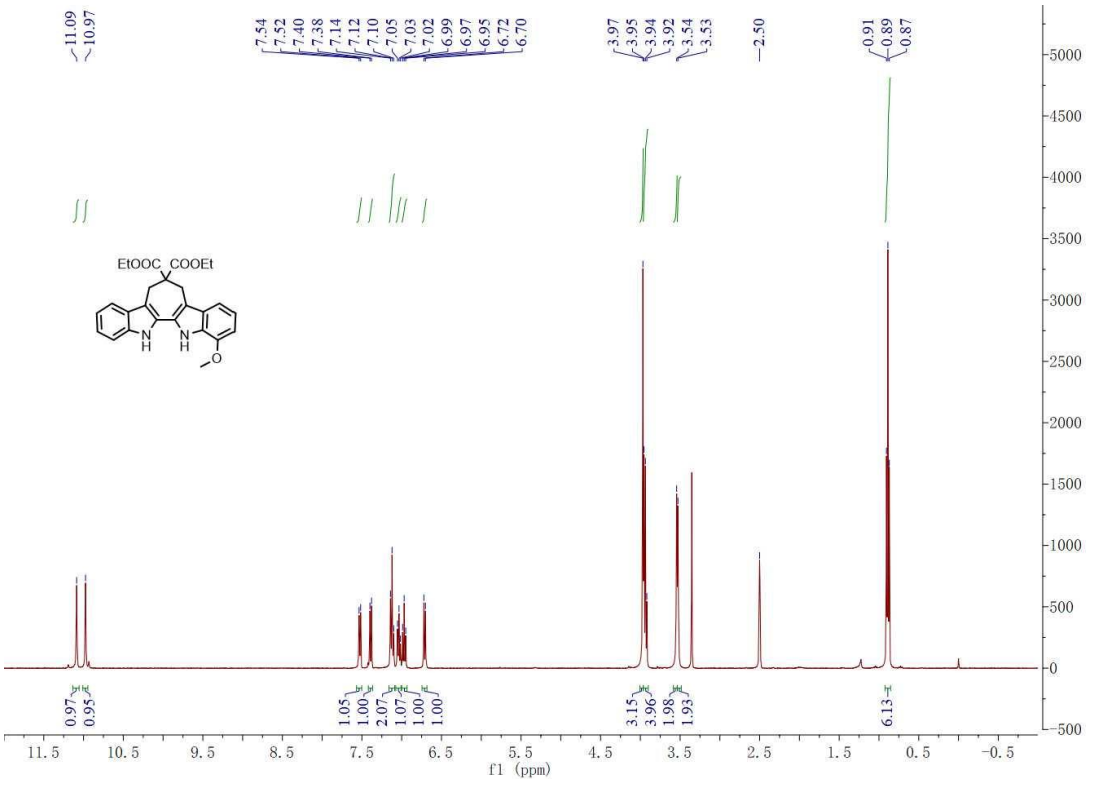


Figure S71. ^{1}H NMR spectrum of diethyl 1-methoxy-5,7,12,13-tetrahydro-6*H*-cyclohepta[2,1-*b*:3,4-*b*′]diindole-6,6-dicarboxylate (**2p**) in DMSO-d_6

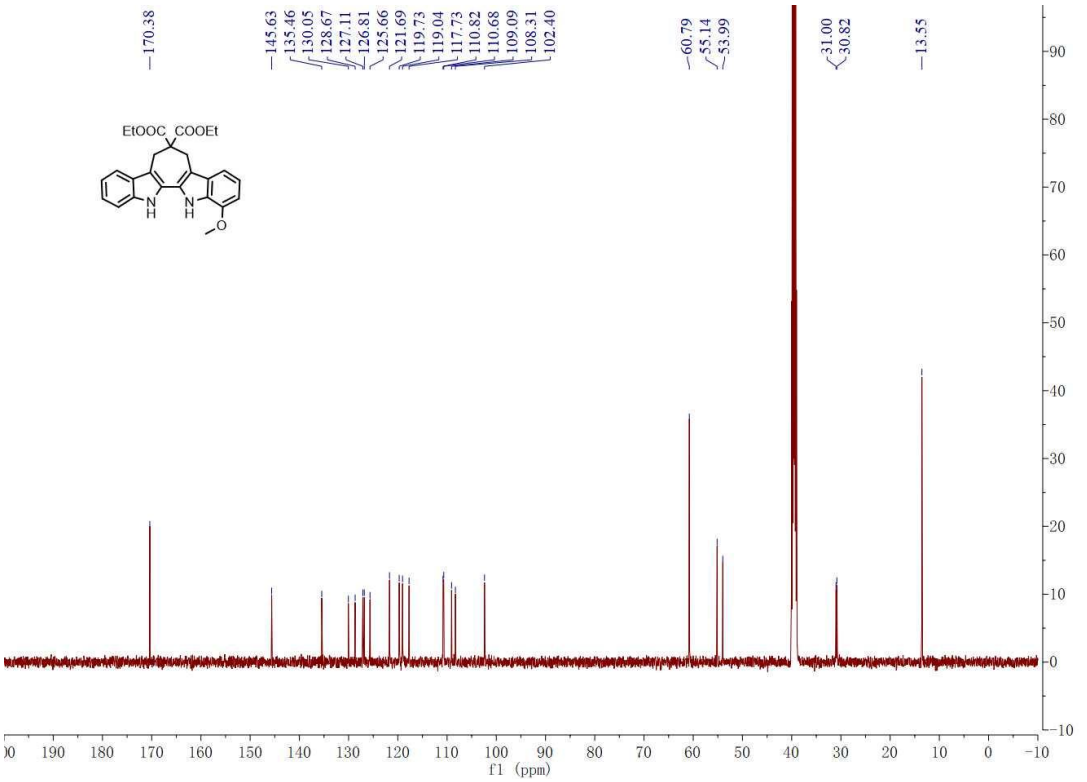


Figure S72. ^{13}C NMR spectrum of diethyl 1-methoxy-5,7,12,13-tetrahydro-6*H*-cyclohepta[2,1-*b*:3,4-*b'*]diindole-6,6-dicarboxylate (**2p**) in DMSO-d_6

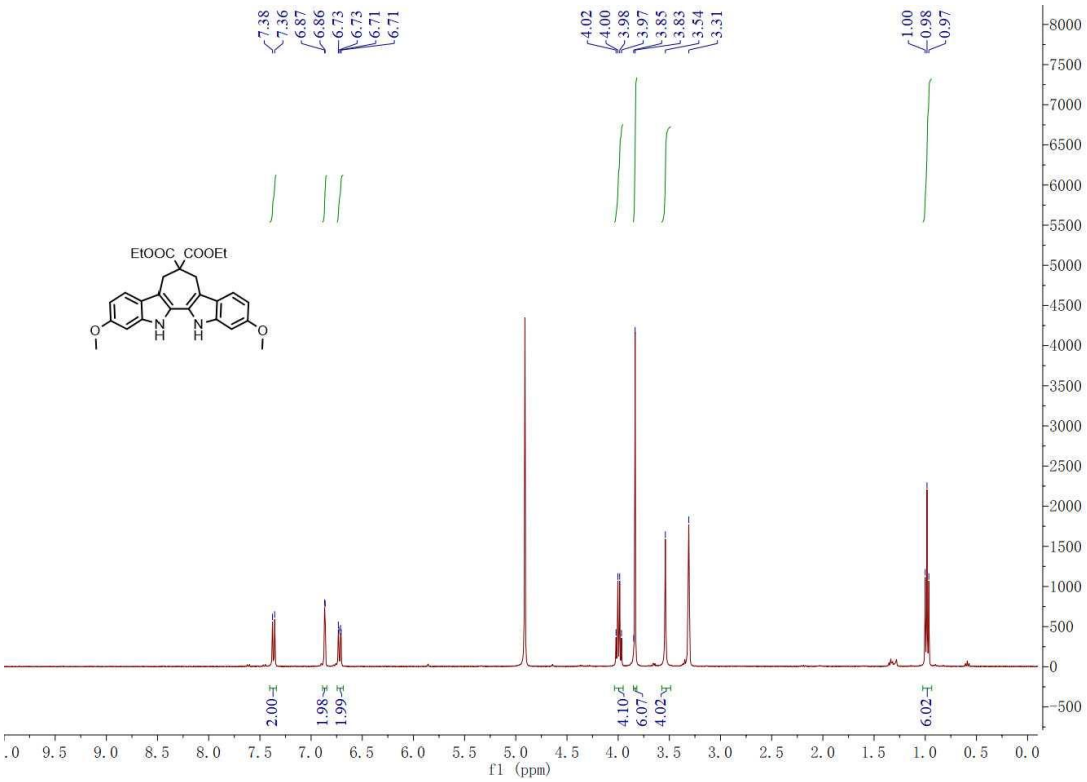


Figure S73. ^{1}H NMR spectrum of diethyl 2,10-dimethoxy-5,7,12,13-tetrahydro-6*H*-cyclohepta[2,1-*b*:3,4-*b'*]diindole-6,6-di carboxylate (**2q**) in Methanol-d_4

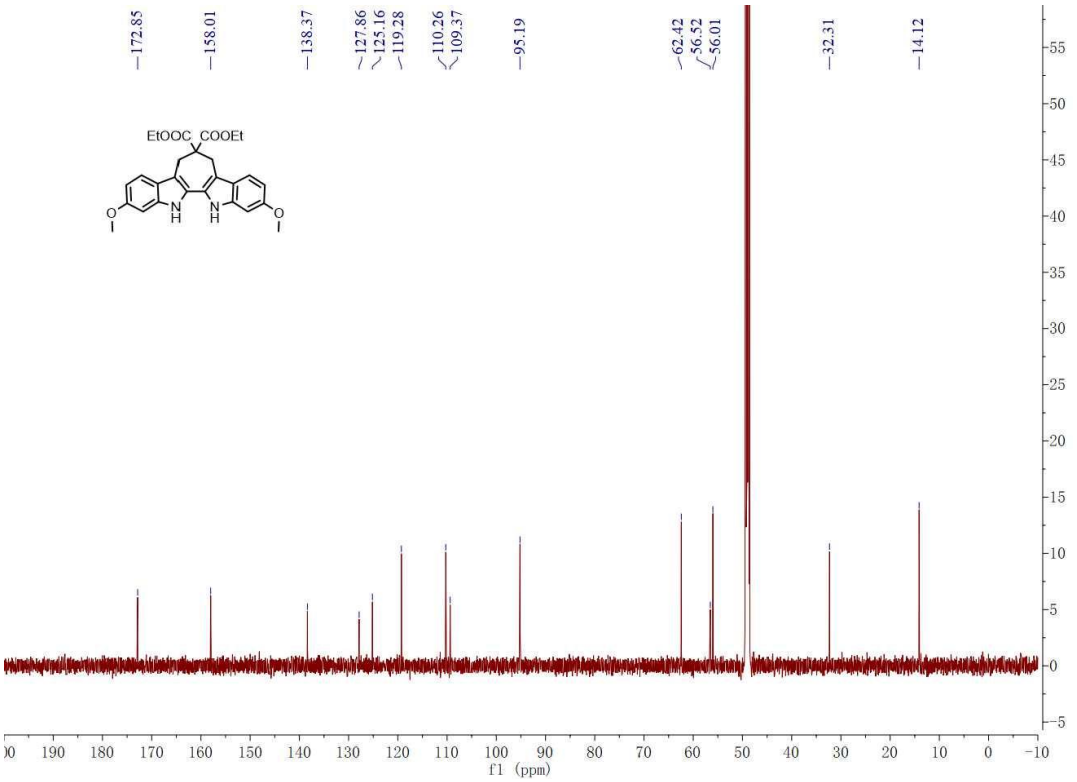


Figure S74. ^{13}C NMR spectrum of diethyl 2,10-dimethoxy-5,7,12,13-tetrahydro-6*H*-cyclohepta[2,1-*b*:3,4-*b'*]diindole-6,6-di carboxylate (**2q**) in Methanol-d_4

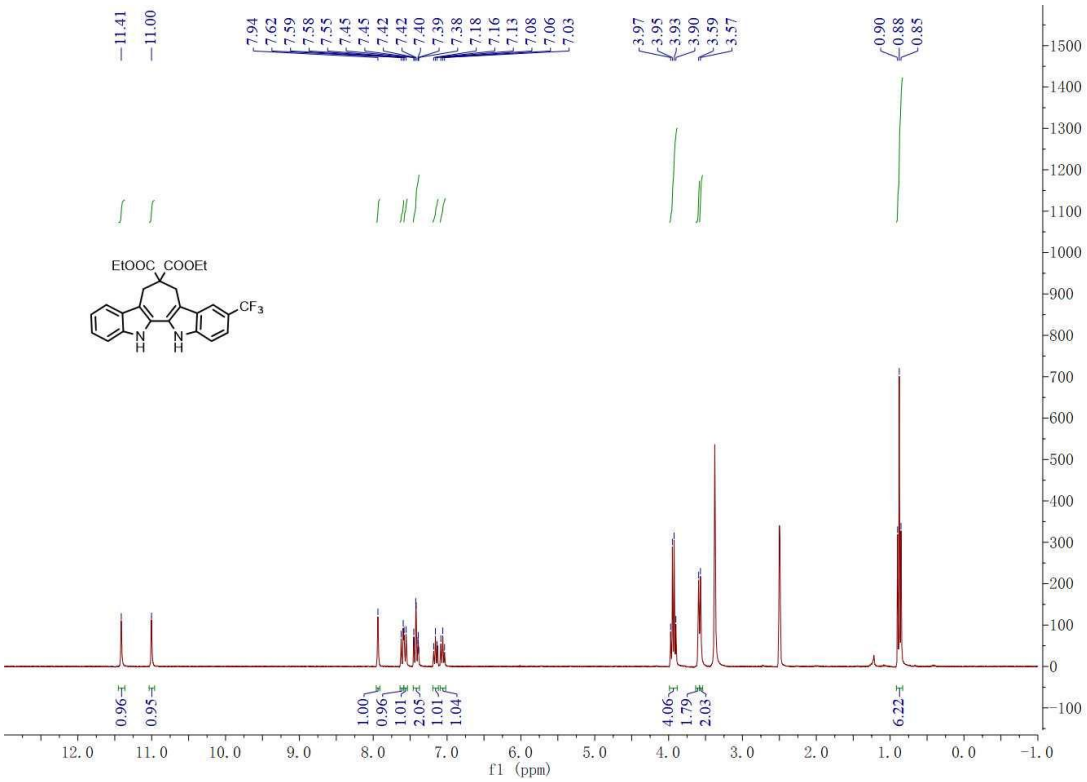


Figure S75. ^{1}H NMR spectrum of diethyl 3-(trifluoromethyl)-5,7,12,13-tetrahydro-6*H*-cyclohepta[2,1-*b*:3,4-*b'*]diindole-6,6-di carboxylate (**2r**) in DMSO-d_6

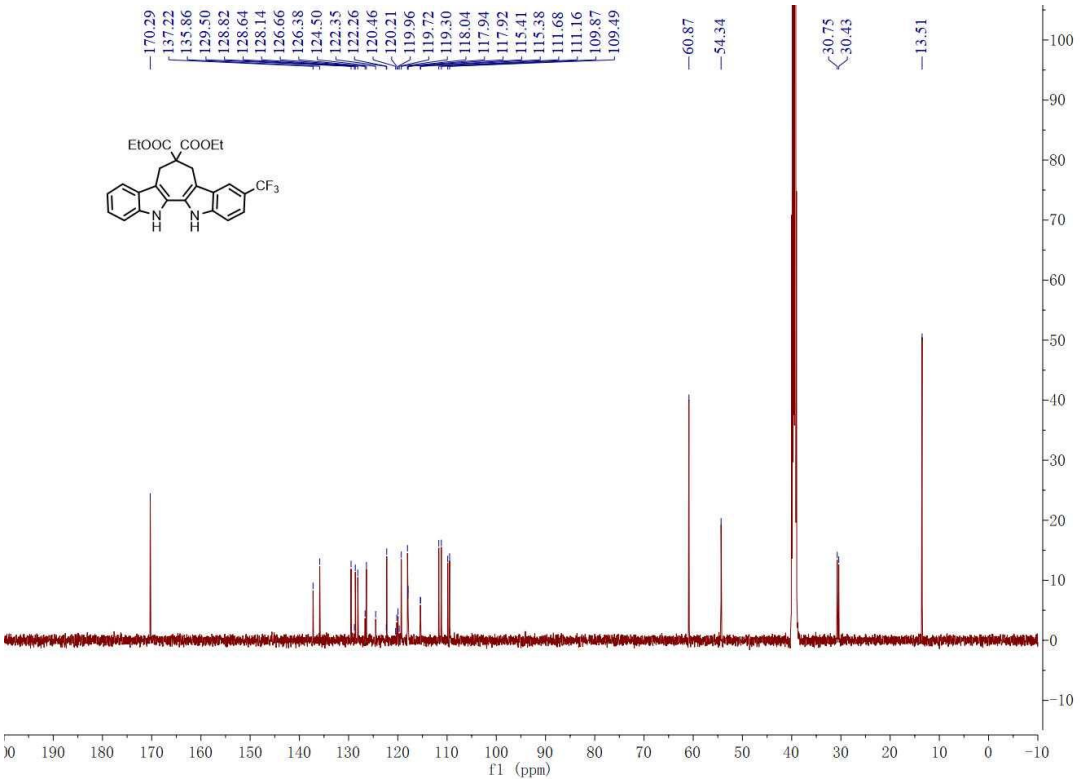


Figure S76. ^{13}C NMR spectrum of diethyl 3-(trifluoromethyl)-5,7,12,13-tetrahydro-6*H*-cyclohepta[2,1-*b*:3,4-*b'*]diindole-6,6-di carboxylate (**2r**) in DMSO-d_6

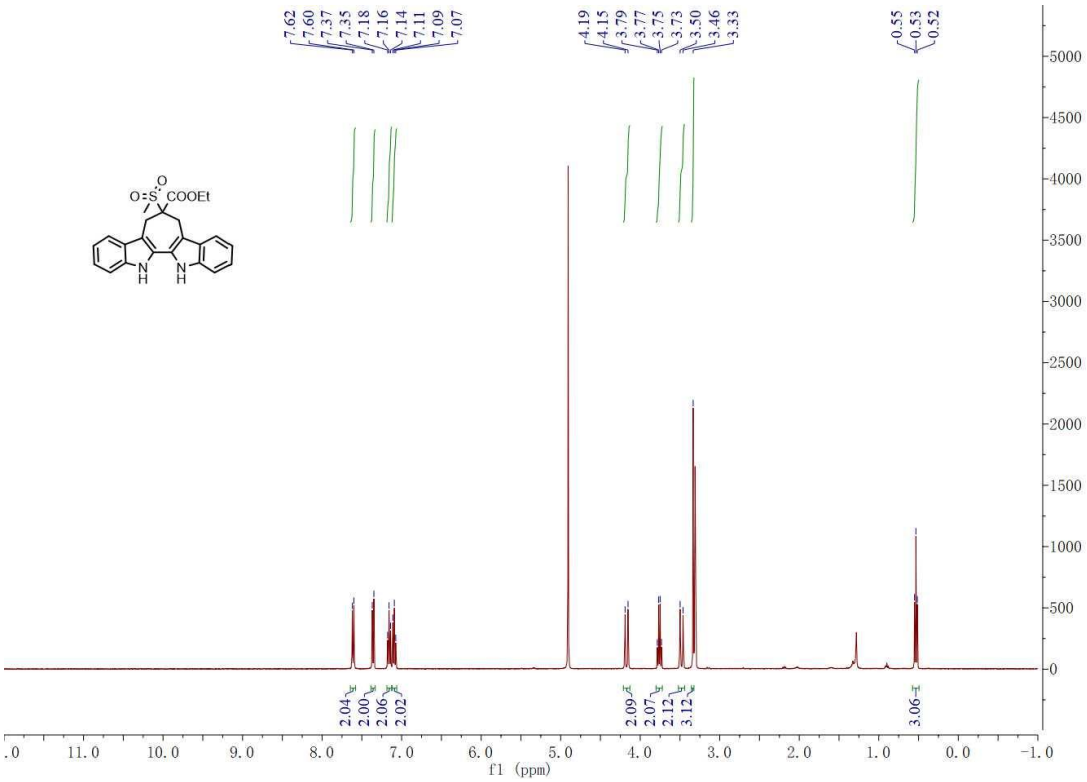


Figure S77. ^{1}H NMR spectrum of ethyl 6-(methylsulfonyl)-6,7,12,13-tetrahydro-5*H*-cyclohepta[2,1-*b*:3,4-*b'*]diindole-6-carboxylate (**2s**) in Methanol-d_4

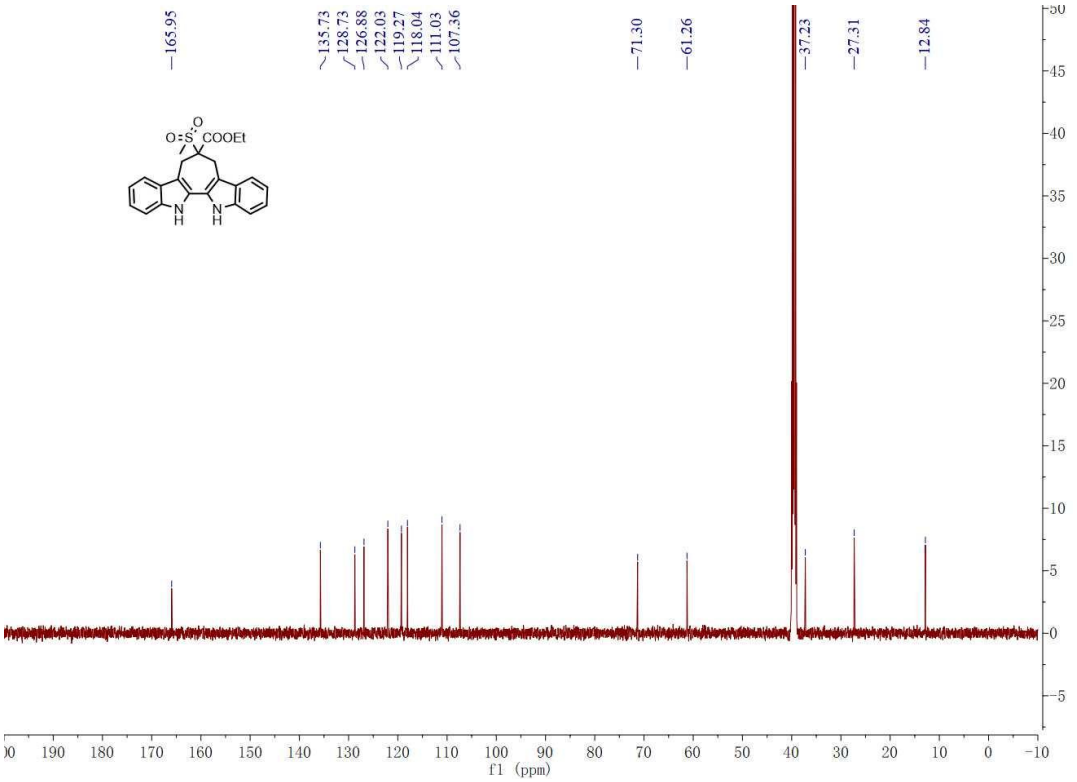


Figure S78. ^{13}C NMR spectrum of ethyl 6-(methylsulfonyl)-6,7,12,13-tetrahydro-5*H*-cyclohepta[2,1-*b*:3,4-*b'*]diindole-6-carboxylate (**2s**) in DMSO-d_6

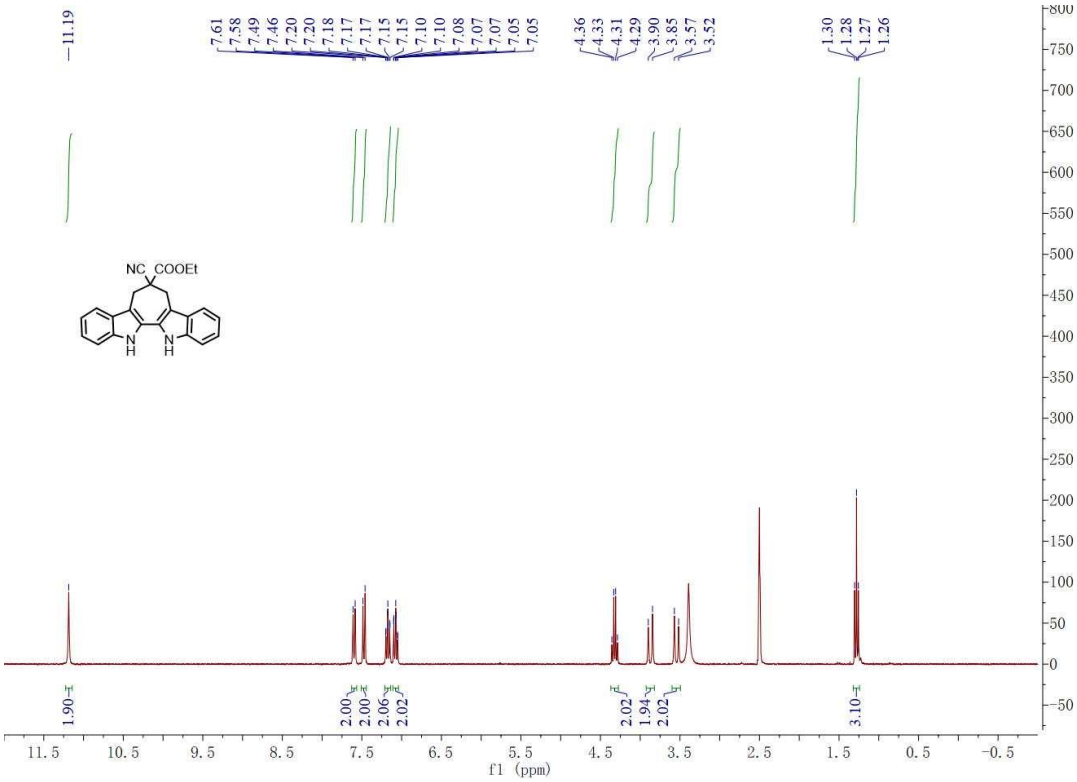


Figure S79. ^{1}H NMR spectrum of ethyl 6-cyano-6,7,12,13-tetrahydro-5*H*-cyclohepta[2,1-*b*:3,4-*b'*]diindole-6-carboxylate (**2t**) in DMSO-d_6

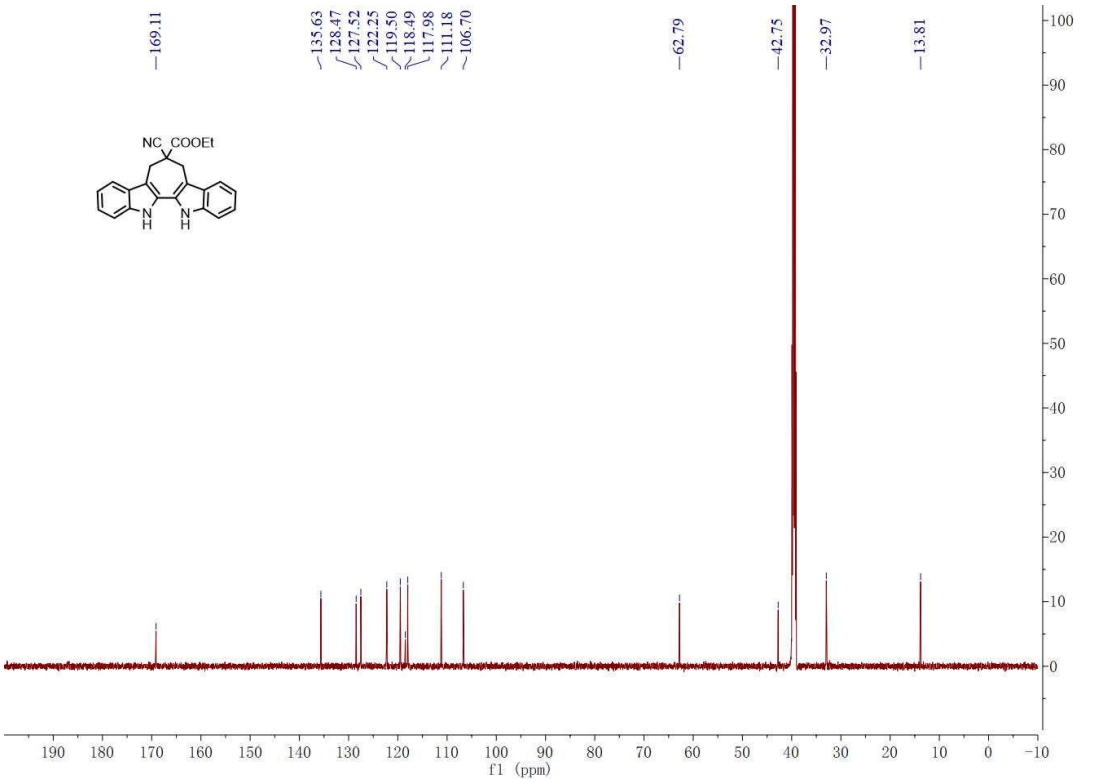


Figure S80. ^{13}C NMR spectrum of ethyl 6-cyano-6,7,12,13-tetrahydro-5*H*-cyclohepta[2,1-*b*:3,4-*b'*]diindole-6-carboxylate (**2t**) in DMSO-d_6

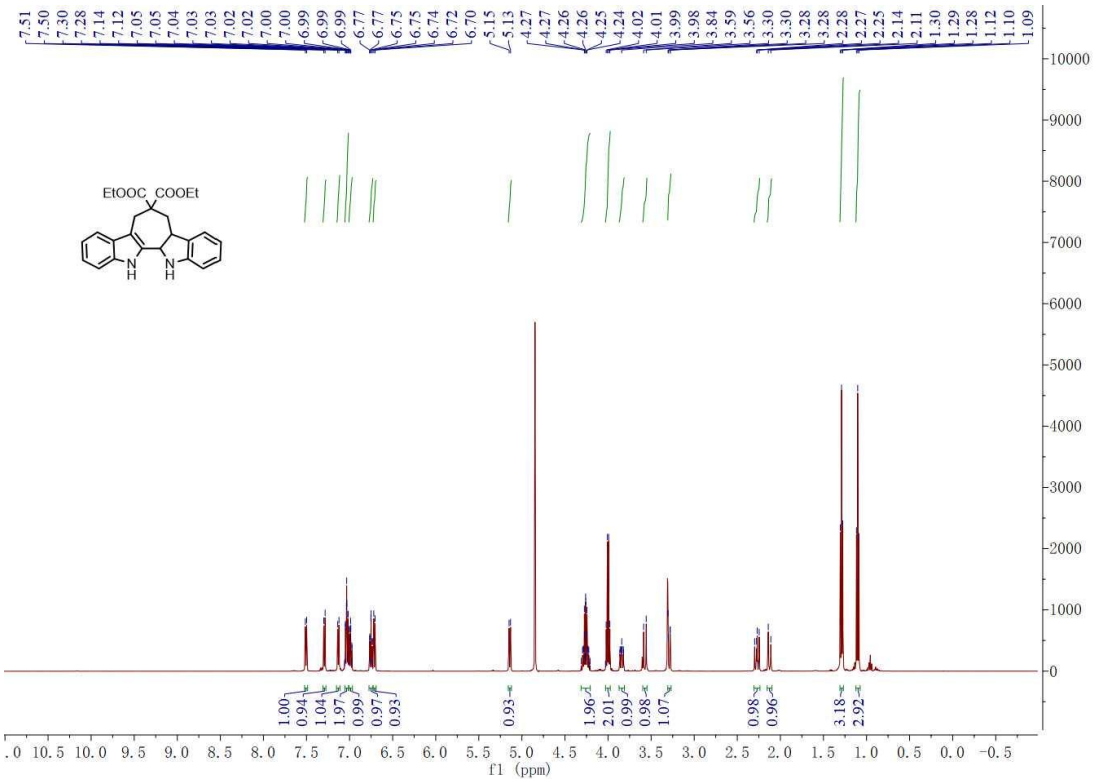


Figure S81. ^{1}H NMR spectrum of diethyl 4b,5,7,12,12b,13-hexahydro-6*H*-cyclohepta[2,1-*b*:3,4-*b'*]diindole-6,6-dicarboxylate (**3a**) in Methanol-d_4

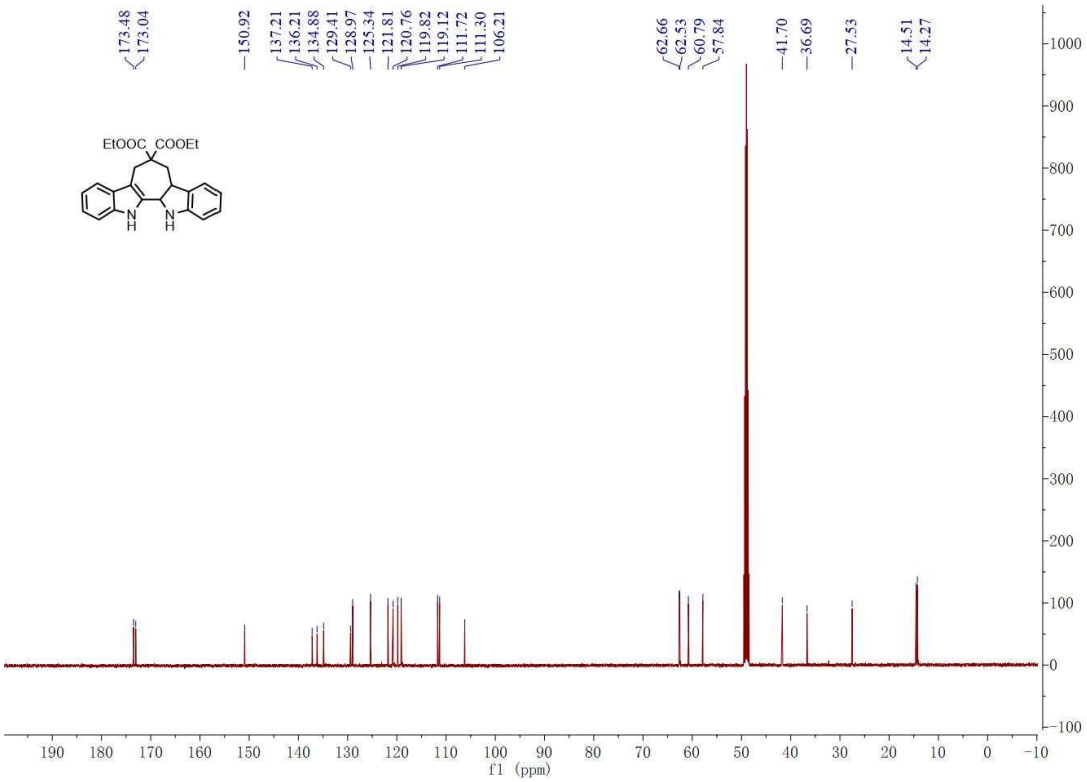


Figure S82. ^{13}C NMR spectrum of diethyl 4b,5,7,12,12b,13-hexahydro-6*H*-cyclohepta[2,1-*b*:3,4-*b'*]diindole-6,6-dicarboxylate (**3a**) in Methanol-d_4

Copies of HRMS chromatograms

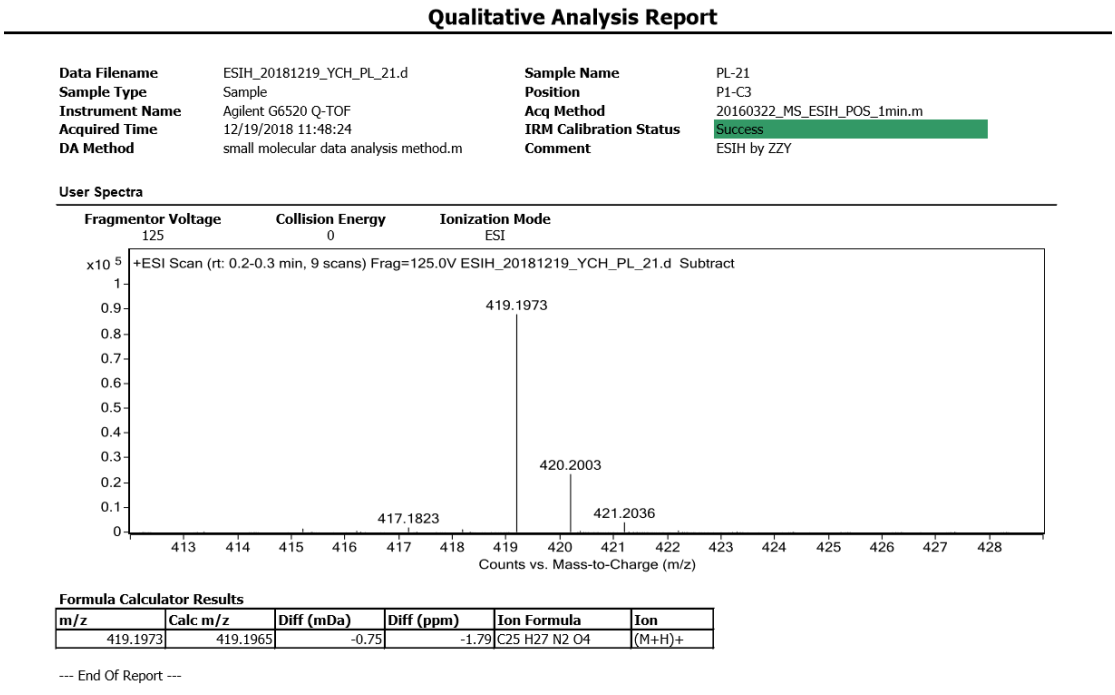


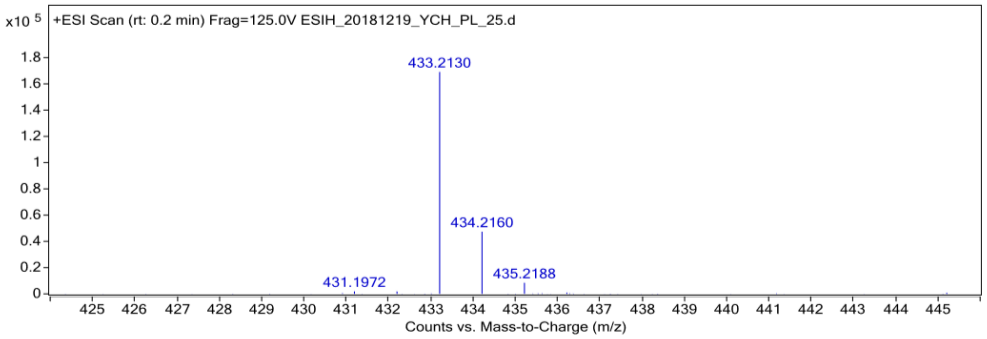
Figure S83. HRMS chromatogram of diethyl 2,2-bis((1*H*-indol-3-yl)methyl)malonate (**1a**)

Qualitative Analysis Report

Data Filename	ESIH_20181219_YCH_PL_25.d	**Sample Name**	PL-25
Sample Type	Sample	**Position**	P1-C7
Instrument Name	Agilent G6520 Q-TOF	**Acq Method**	20160322_MS_ESIH_POS_1min.m
Acquired Time	12/19/2018 11:55:44	**IRM Calibration Status**	Success
DA Method	small molecular data analysis method.m	**Comment**	ESIH by ZZY

User Spectra

Fragmentor Voltage	Collision Energy	Ionization Mode
125	0	ESI



Formula Calculator Results

m/z	Calc m/z	Diff (mDa)	Diff (ppm)	Ion Formula	Ion
433.213	433.2122	-0.83	-1.92	C26 H29 N2 O4	(M+H)+

--- End Of Report ---

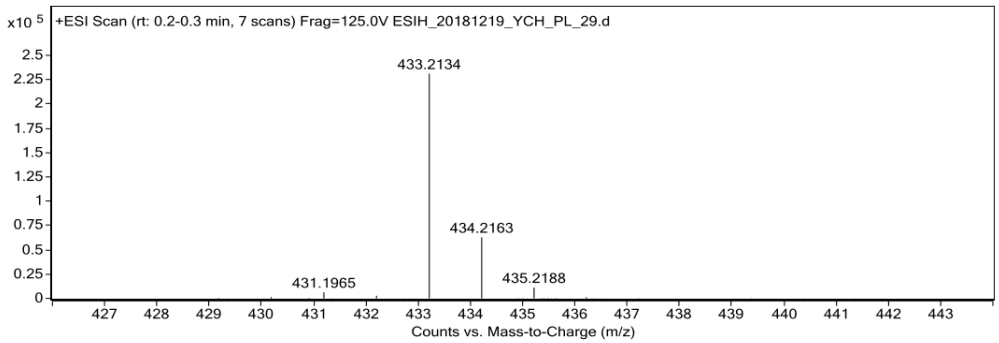
Figure S84. HRMS chromatogram of diethyl 2-((1*H*-indol-3-yl)methyl)-2-((5-methyl-1*H*-indol-3-yl)methyl)malonate (**1b**)

Qualitative Analysis Report

Data Filename	ESIH_20181219_YCH_PL_29.d	**Sample Name**	PL-29
Sample Type	Sample	**Position**	P1-D2
Instrument Name	Agilent G6520 Q-TOF	**Acq Method**	20160322_MS_ESIH_POS_1min.m
Acquired Time	12/19/2018 12:03:04	**IRM Calibration Status**	Success
DA Method	small molecular data analysis method.m	**Comment**	ESIH by ZZY

User Spectra

Fragmentor Voltage	Collision Energy	Ionization Mode
125	0	ESI



Formula Calculator Results

m/z	Calc m/z	Diff (mDa)	Diff (ppm)	Ion Formula	Ion
433.2134	433.2122	-1.17	-2.71	C26 H29 N2 O4	(M+H)+

--- End Of Report ---

Figure S85. HRMS chromatogram of diethyl 2-((1*H*-indol-3-yl)methyl)-2-((6-methyl-1*H*-indol-3-yl)methyl)malonate (**1c**)

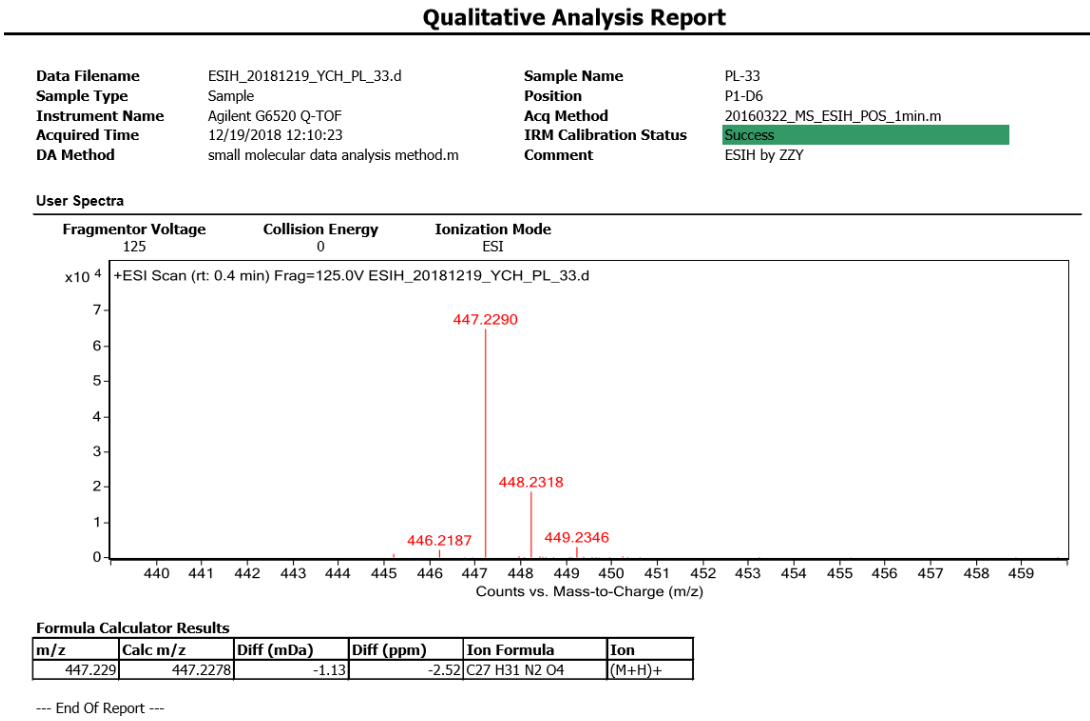


Figure S86. HRMS chromatogram of diethyl 2,2-bis((6-methyl-1*H*-indol-3-yl)methyl)malonate (**1d**)

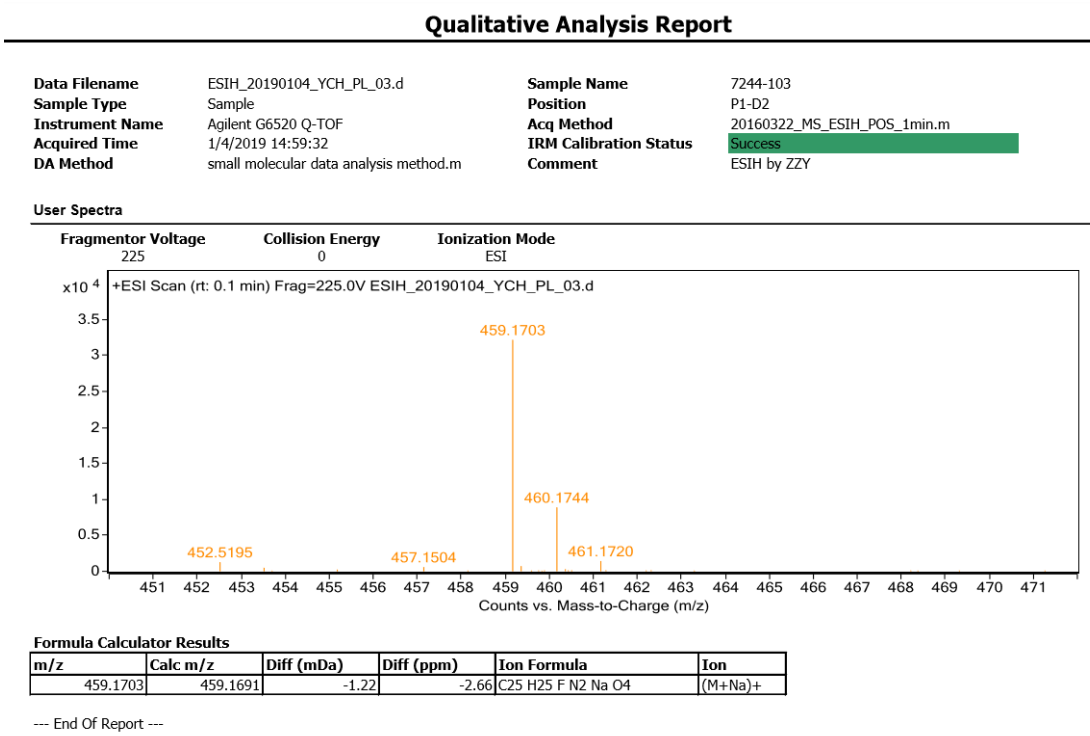


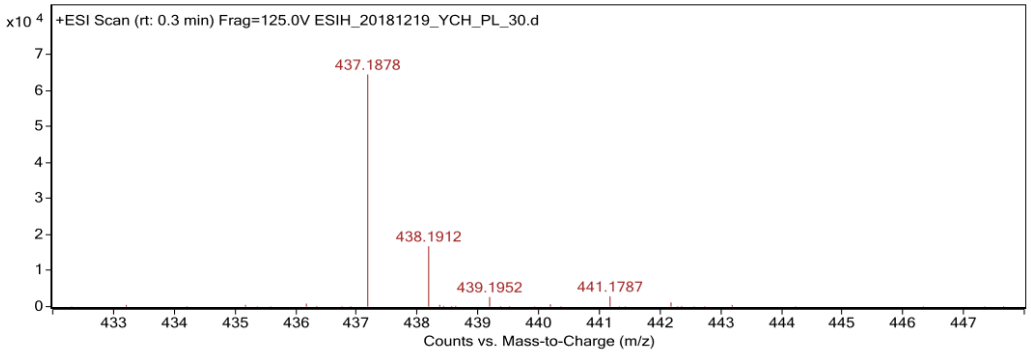
Figure S87. HRMS chromatogram of diethyl 2-((1*H*-indol-3-yl)methyl)-2-((5-fluoro-1*H*-indol-3-yl)methyl)malonate (**1e**)

Qualitative Analysis Report

Data Filename	ESIH_20181219_YCH_PL_30.d	**Sample Name**	PL-30
Sample Type	Sample	**Position**	P1-D3
Instrument Name	Agilent G6520 Q-TOF	**Acq Method**	20160322_MS_ESIH_POS_1min.m
Acquired Time	12/19/2018 12:04:53	**IRM Calibration Status**	Success
DA Method	small molecular data analysis method.m	**Comment**	ESIH by ZZY

User Spectra

Fragmentor Voltage	Collision Energy	Ionization Mode
125	0	ESI



Formula Calculator Results

m/z	Calc m/z	Diff (mDa)	Diff (ppm)	Ion Formula	Ion
437.1878	437.1871	-0.65	-1.49	C25 H26 F N2 O4	(M+H)+

--- End Of Report ---

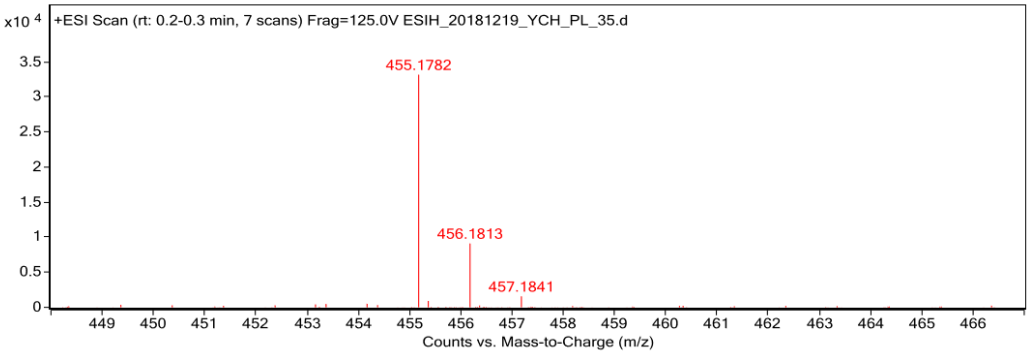
Figure S88. HRMS chromatogram of diethyl 2-((1*H*-indol-3-yl)methyl)-2-((6-fluoro-1*H*-indol-3-yl)methyl)malonate (**1f**)

Qualitative Analysis Report

Data Filename	ESIH_20181219_YCH_PL_35.d	**Sample Name**	PL-35
Sample Type	Sample	**Position**	P1-D8
Instrument Name	Agilent G6520 Q-TOF	**Acq Method**	20160322_MS_ESIH_POS_1min.m
Acquired Time	12/19/2018 12:14:04	**IRM Calibration Status**	Success
DA Method	small molecular data analysis method.m	**Comment**	ESIH by ZZY

User Spectra

Fragmentor Voltage	Collision Energy	Ionization Mode
125	0	ESI



Formula Calculator Results

m/z	Calc m/z	Diff (mDa)	Diff (ppm)	Ion Formula	Ion
455.1782	455.1777	-0.55	-1.21	C25 H25 F2 N2 O4	(M+H)+

--- End Of Report ---

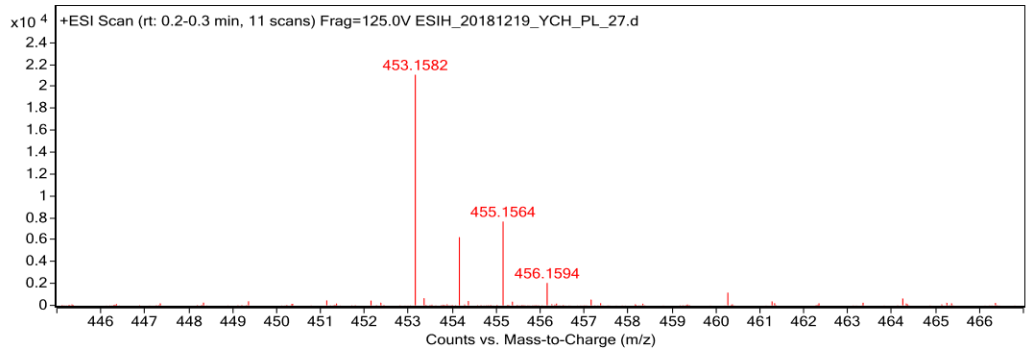
Figure S89. HRMS chromatogram of diethyl 2,2-bis((6-fluoro-1*H*-indol-3-yl)methyl)malonate (**1g**)

Qualitative Analysis Report

Data Filename	ESIH_20181219_YCH_PL_27.d	**Sample Name**	PL-27
Sample Type	Sample	**Position**	P1-C9
Instrument Name	Agilent G6520 Q-TOF	**Acq Method**	20160322_MS_ESIH_POS_1min.m
Acquired Time	12/19/2018 11:59:25	**IRM Calibration Status**	Success
DA Method	small molecular data analysis method.m	**Comment**	ESIH by ZZY

User Spectra

Fragmentor Voltage	Collision Energy	Ionization Mode
125	0	ESI



Formula Calculator Results

m/z	Calc m/z	Diff (mDa)	Diff (ppm)	Ion Formula	Ion
453.1582	453.1576	-0.62	-1.36	C25 H26 Cl N2 O4	(M+H)+

--- End Of Report ---

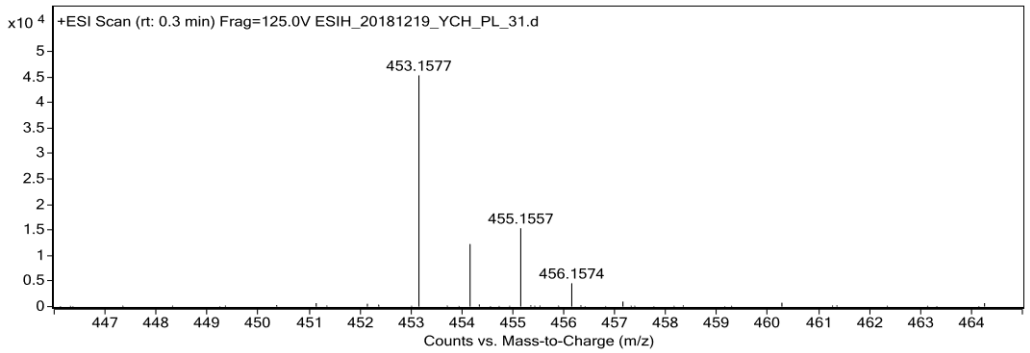
Figure S90. HRMS chromatogram of diethyl 2-((1*H*-indol-3-yl)methyl)-2-((5-chloro-1*H*-indol-3-yl)methyl)malonate (**1h**)

Qualitative Analysis Report

Data Filename	ESIH_20181219_YCH_PL_31.d	**Sample Name**	PL-31
Sample Type	Sample	**Position**	P1-D4
Instrument Name	Agilent G6520 Q-TOF	**Acq Method**	20160322_MS_ESIH_POS_1min.m
Acquired Time	12/19/2018 12:06:44	**IRM Calibration Status**	Success
DA Method	small molecular data analysis method.m	**Comment**	ESIH by ZZY

User Spectra

Fragmentor Voltage	Collision Energy	Ionization Mode
125	0	ESI



Formula Calculator Results

m/z	Calc m/z	Diff (mDa)	Diff (ppm)	Ion Formula	Ion
453.1577	453.1576	-0.12	-0.27	C25 H26 Cl N2 O4	(M+H)+

--- End Of Report ---

Figure S91. HRMS chromatogram of diethyl 2-((1*H*-indol-3-yl)methyl)-2-((6-chloro-1*H*-indol-3-

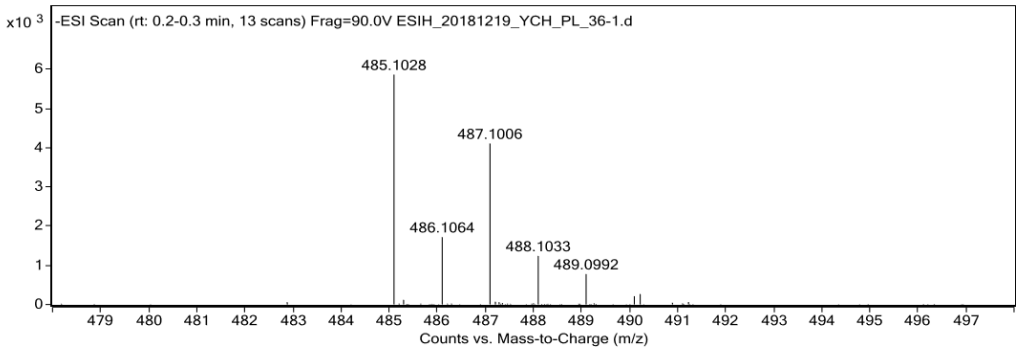
yl)methyl)malonate (**1i**)

Qualitative Analysis Report

Data Filename	ESIH_20181219_YCH_PL_36-1.d	**Sample Name**	PL-36
Sample Type	Sample	**Position**	P2-D9
Instrument Name	Agilent G6520 Q-TOF	**Acq Method**	20160324_MS_ESIH_NEG_1min.m
Acquired Time	12/19/2018 14:43:10	**IRM Calibration Status**	Success
DA Method	small molecular data analysis method.m	**Comment**	ESIH by ZZY

User Spectra

Fragmentor Voltage	Collision Energy	Ionization Mode
90	0	ESI



Formula Calculator Results

m/z	Calc m/z	Diff (mDa)	Diff (ppm)	Ion Formula	Ion
485.1028	485.104	1.21	2.5	C25 H23 Cl2 N2 O4	(M-H)-

--- End Of Report ---

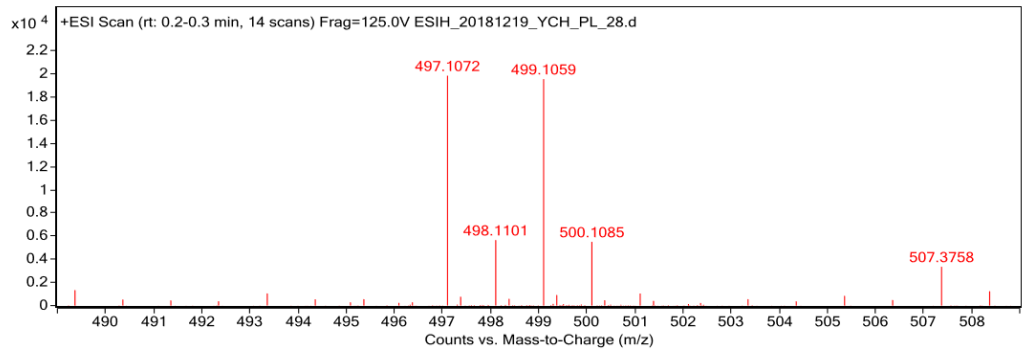
Figure S92. HRMS chromatogram of diethyl 2,2-bis((6-chloro-1*H*-indol-3-yl)methyl)malonate (**1j**)

Qualitative Analysis Report

Data Filename	ESIH_20181219_YCH_PL_28.d	**Sample Name**	PL-28
Sample Type	Sample	**Position**	P1-D1
Instrument Name	Agilent G6520 Q-TOF	**Acq Method**	20160322_MS_ESIH_POS_1min.m
Acquired Time	12/19/2018 12:01:13	**IRM Calibration Status**	Success
DA Method	small molecular data analysis method.m	**Comment**	ESIH by ZZY

User Spectra

Fragmentor Voltage	Collision Energy	Ionization Mode
125	0	ESI



Formula Calculator Results

m/z	Calc m/z	Diff (mDa)	Diff (ppm)	Ion Formula	Ion
497.1072	497.107	-0.17	-0.33	C25 H26 Br N2 O4	(M+H)+

--- End Of Report ---

Figure S93. HRMS chromatogram of diethyl 2-((1*H*-indol-3-yl)methyl)-2-((5-bromo-1*H*-indol-3-yl)methyl)malonate (**1k**)

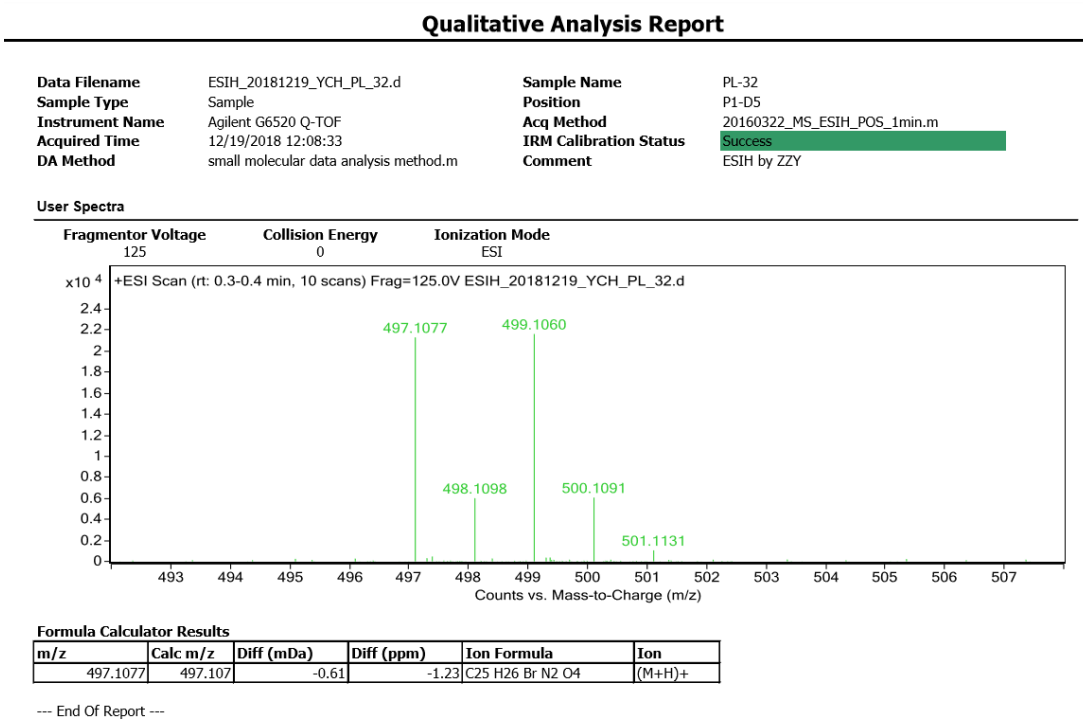


Figure S94. HRMS chromatogram of diethyl 2-((1*H*-indol-3-yl)methyl)-2-((6-bromo-1*H*-indol-3-yl)methyl)malonate (**1l**)

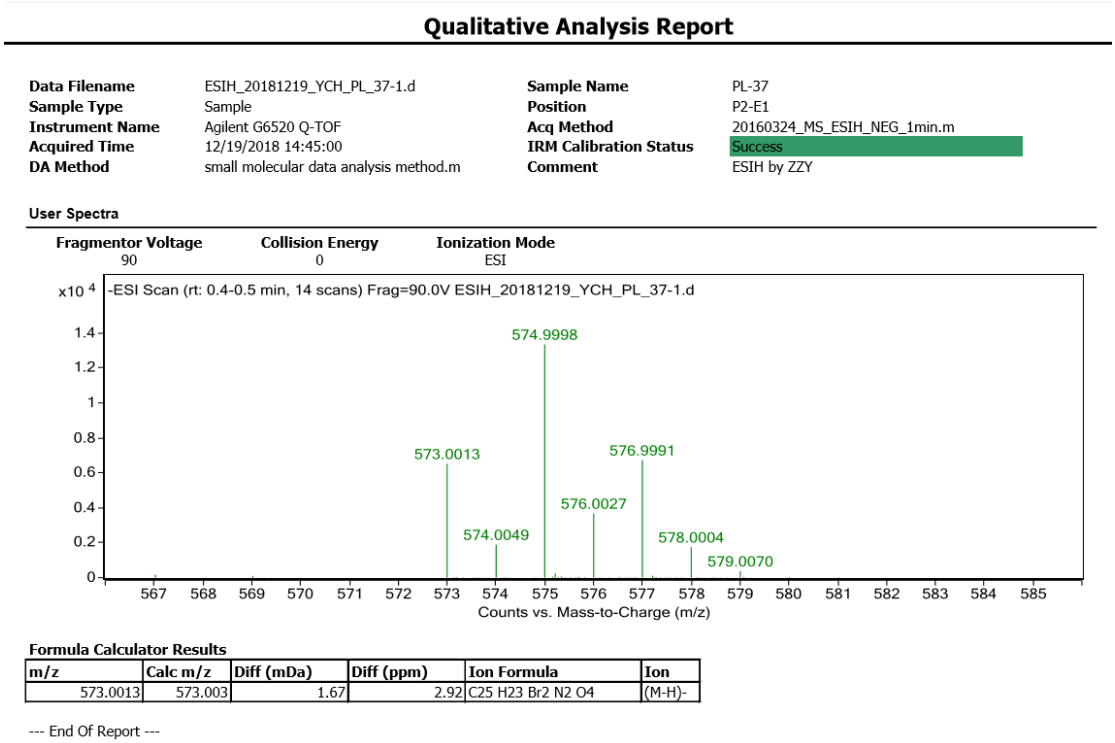


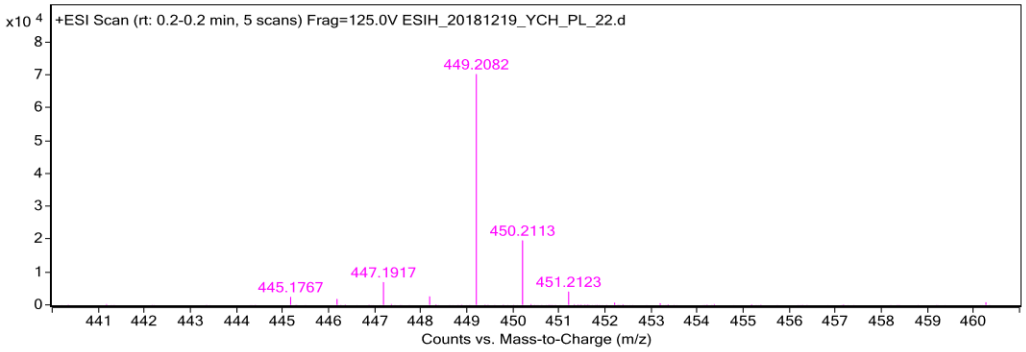
Figure S95. HRMS chromatogram of diethyl 2,2-bis((6-bromo-1*H*-indol-3-yl)methyl)malonate (**1m**)

Qualitative Analysis Report

Data Filename	ESIH_20181219_YCH_PL_22.d	**Sample Name**	PL-22
Sample Type	Sample	**Position**	P1-C4
Instrument Name	Agilent G6520 Q-TOF	**Acq Method**	20160322_MS_ESIH_POS_1min.m
Acquired Time	12/19/2018 11:50:14	**IRM Calibration Status**	Success
DA Method	small molecular data analysis method.m	**Comment**	ESIH by ZZY

User Spectra

Fragmentor Voltage	Collision Energy	Ionization Mode
125	0	ESI



Formula Calculator Results

m/z	Calc m/z	Diff (mDa)	Diff (ppm)	Ion Formula	Ion
449.2082	449.2071	-1.09	-2.44	C26 H29 N2 O5	(M+H)+

--- End Of Report ---

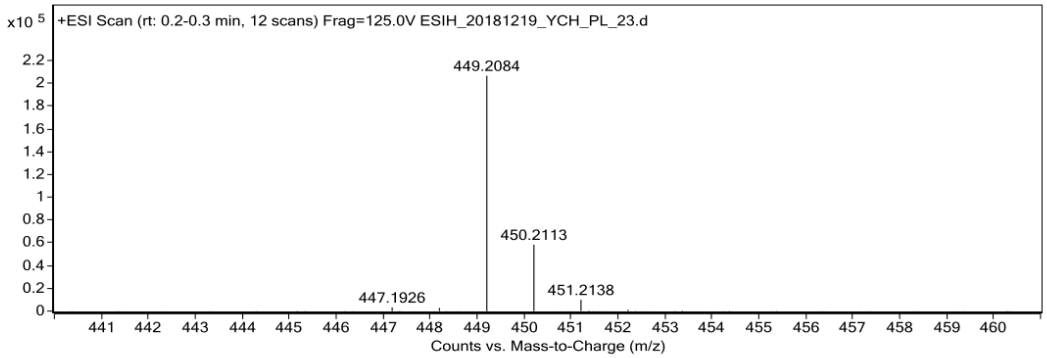
Figure S96. HRMS chromatogram of diethyl 2-((1*H*-indol-3-yl)methyl)-2-((5-methoxy-1*H*-indol-3-yl)methyl)malonate (**1n**)

Qualitative Analysis Report

Data Filename	ESIH_20181219_YCH_PL_23.d	**Sample Name**	PL-23
Sample Type	Sample	**Position**	P1-C5
Instrument Name	Agilent G6520 Q-TOF	**Acq Method**	20160322_MS_ESIH_POS_1min.m
Acquired Time	12/19/2018 11:52:04	**IRM Calibration Status**	Success
DA Method	small molecular data analysis method.m	**Comment**	ESIH by ZZY

User Spectra

Fragmentor Voltage	Collision Energy	Ionization Mode
125	0	ESI



Formula Calculator Results

m/z	Calc m/z	Diff (mDa)	Diff (ppm)	Ion Formula	Ion
449.2084	449.2071	-1.34	-2.99	C26 H29 N2 O5	(M+H)+

--- End Of Report ---

Figure S97. HRMS chromatogram of diethyl 2-((1*H*-indol-3-yl)methyl)-2-((6-methoxy-1*H*-indol-3-yl)methyl)malonate (**1o**)

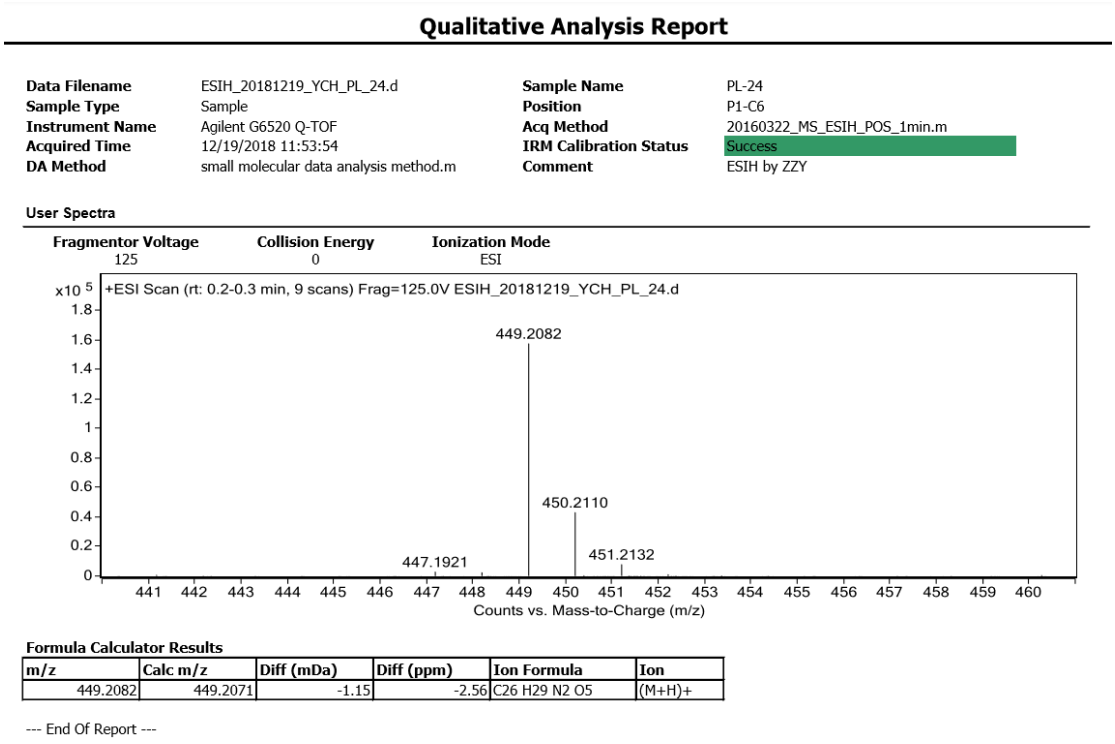


Figure S98. HRMS chromatogram of diethyl 2-((1*H*-indol-3-yl)methyl)-2-((7-methoxy-1*H*-indol-3-yl)methyl)malonate (**1p**)

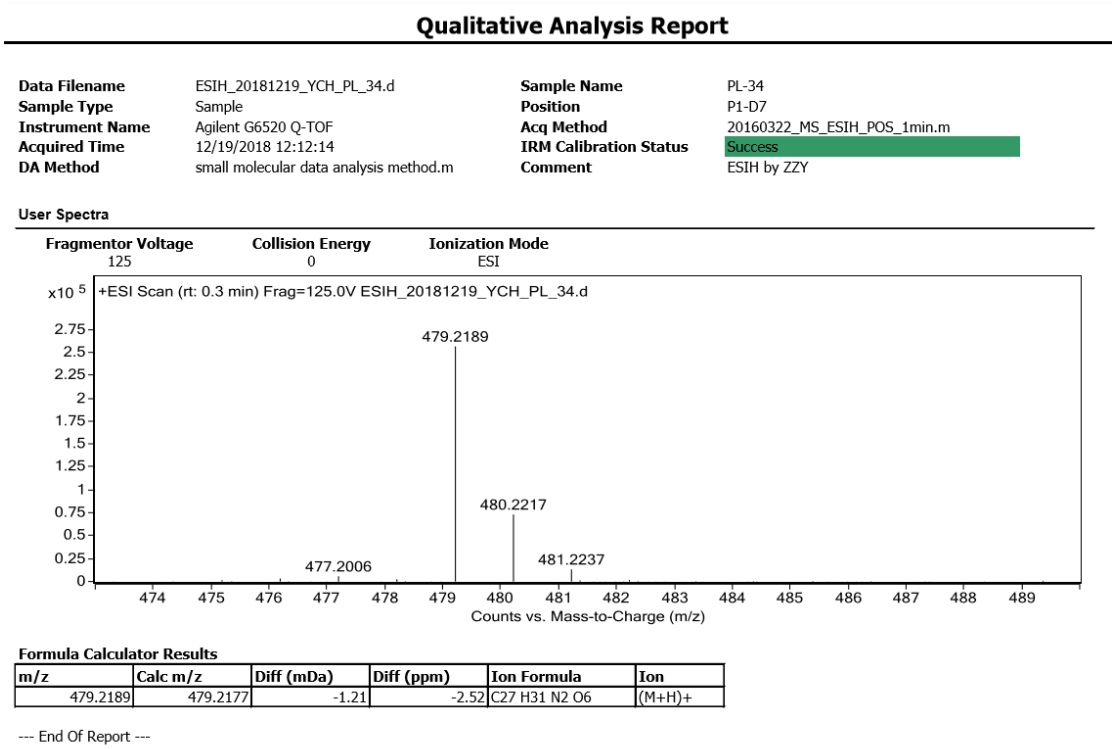


Figure S99. HRMS chromatogram of diethyl 2,2-bis((6-methoxy-1*H*-indol-3-yl)methyl)malonate (**1q**)

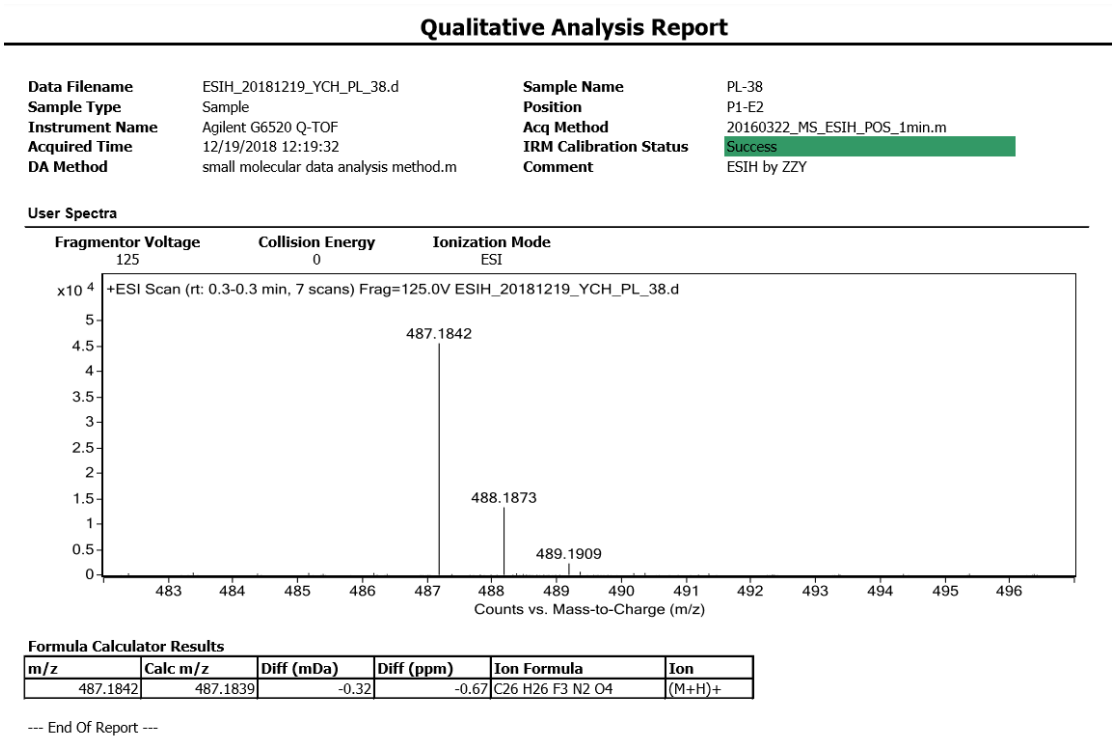


Figure S100. HRMS chromatogram of diethyl 2-((1*H*-indol-3-yl)methyl)-2-((5-(trifluoromethyl)-1*H*-indol-3-yl)methyl)malonate (**1r**)

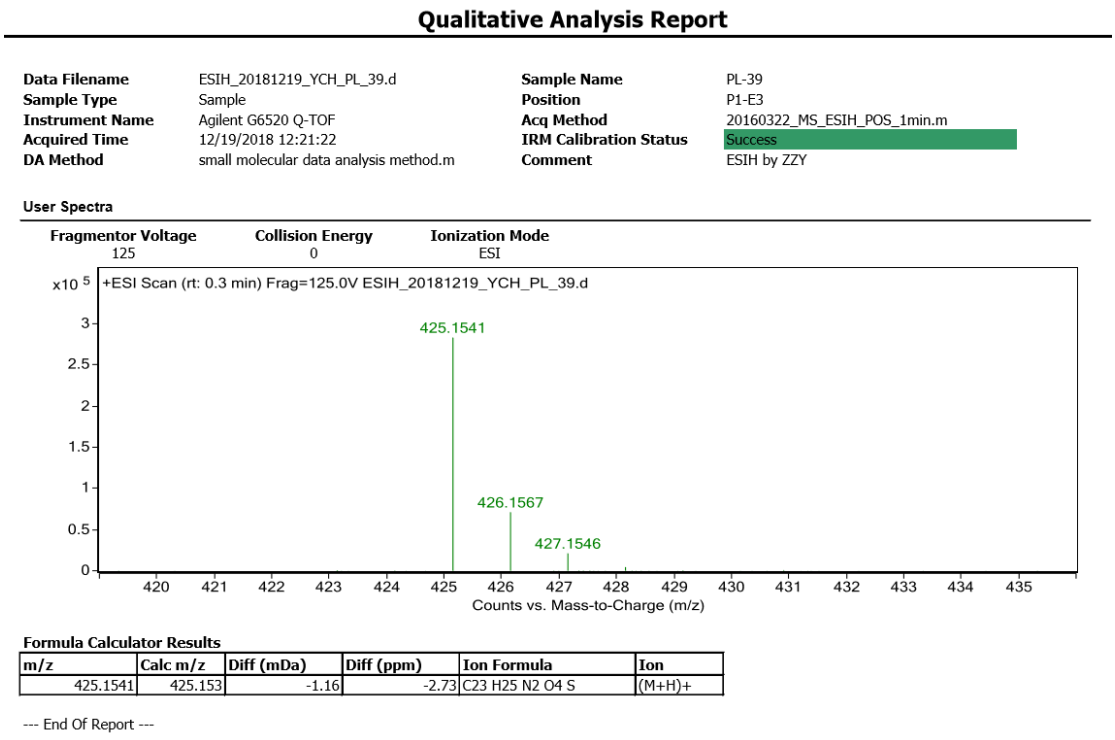


Figure S101. HRMS chromatogram of ethyl 2-((1*H*-indol-3-yl)methyl)-3-(1*H*-indol-3-yl)-2-(methylsulfonyl)propanoate (**1s**)

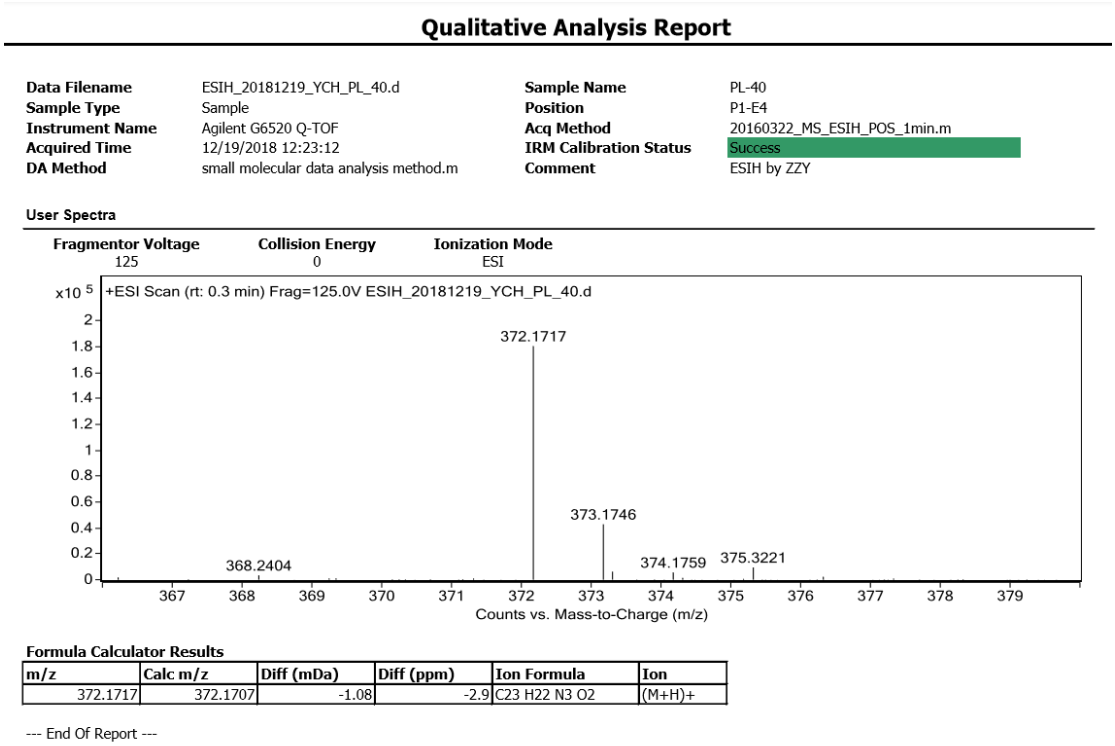


Figure S102. HRMS chromatogram of ethyl 2-((1*H*-indol-3-yl)methyl)-2-cyano-3-(1*H*-indol-3-yl)propanoate (**1t**)

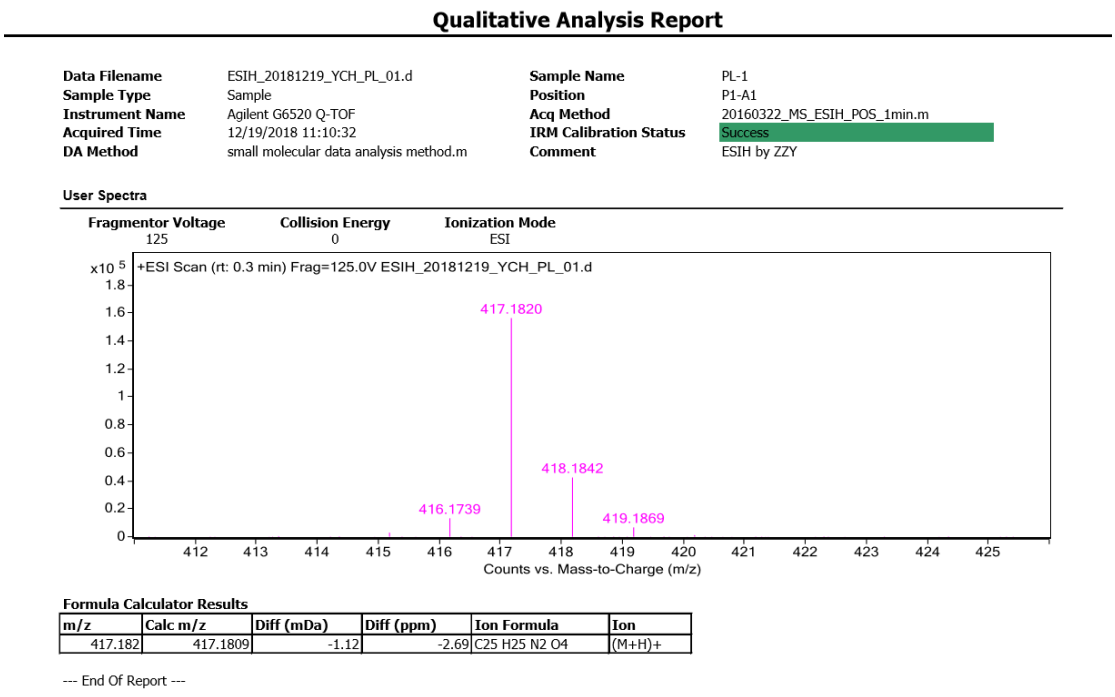


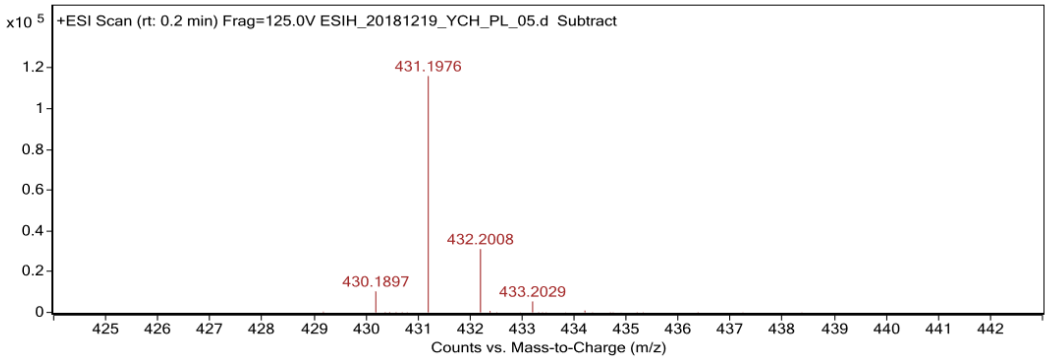
Figure S103. HRMS chromatogram of diethyl 5,7,12,13-tetrahydro-6*H*-cyclohepta[2,1-*b*:3,4-*b*′]diindole-6,6-dicarboxylate (**2a**)

Qualitative Analysis Report

Data Filename	ESIH_20181219_YCH_PL_05.d	**Sample Name**	PL-5
Sample Type	Sample	**Position**	P1-A5
Instrument Name	Agilent G6520 Q-TOF	**Acq Method**	20160322_MS_ESIH_POS_1min.m
Acquired Time	12/19/2018 11:19:09	**IRM Calibration Status**	Success
DA Method	small molecular data analysis method.m	**Comment**	ESIH by ZZY

User Spectra

Fragmentor Voltage	Collision Energy	Ionization Mode
125	0	ESI



Formula Calculator Results

m/z	Calc m/z	Diff (mDa)	Diff (ppm)	Ion Formula	Ion
431.1976	431.1965	-1.09	-2.54	C26 H27 N2 O4	(M+H)+

--- End Of Report ---

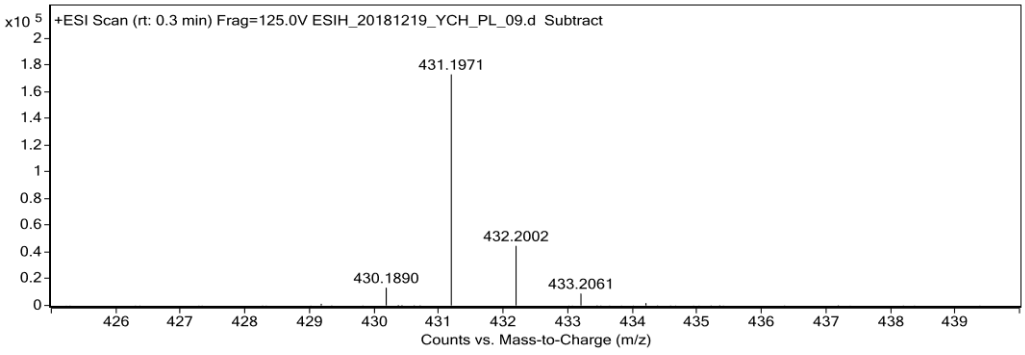
Figure S104. HRMS chromatogram of diethyl 3-methyl-5,7,12,13-tetrahydro-6*H*-cyclohepta[2,1-*b*:3,4-*b*']diindole-6,6-dicarboxylate (**2b**)

Qualitative Analysis Report

Data Filename	ESIH_20181219_YCH_PL_09.d	**Sample Name**	PL-9
Sample Type	Sample	**Position**	P1-A9
Instrument Name	Agilent G6520 Q-TOF	**Acq Method**	20160322_MS_ESIH_POS_1min.m
Acquired Time	12/19/2018 11:26:27	**IRM Calibration Status**	Success
DA Method	small molecular data analysis method.m	**Comment**	ESIH by ZZY

User Spectra

Fragmentor Voltage	Collision Energy	Ionization Mode
125	0	ESI



Formula Calculator Results

m/z	Calc m/z	Diff (mDa)	Diff (ppm)	Ion Formula	Ion
431.1971	431.1965	-0.58	-1.36	C26 H27 N2 O4	(M+H)+

--- End Of Report ---

Figure S105. HRMS chromatogram of diethyl 2-methyl-5,7,12,13-tetrahydro-6*H*-cyclohepta[2,1-*b*:3,4-*b*']diindole-6,6-dicarboxylate (**2c**)

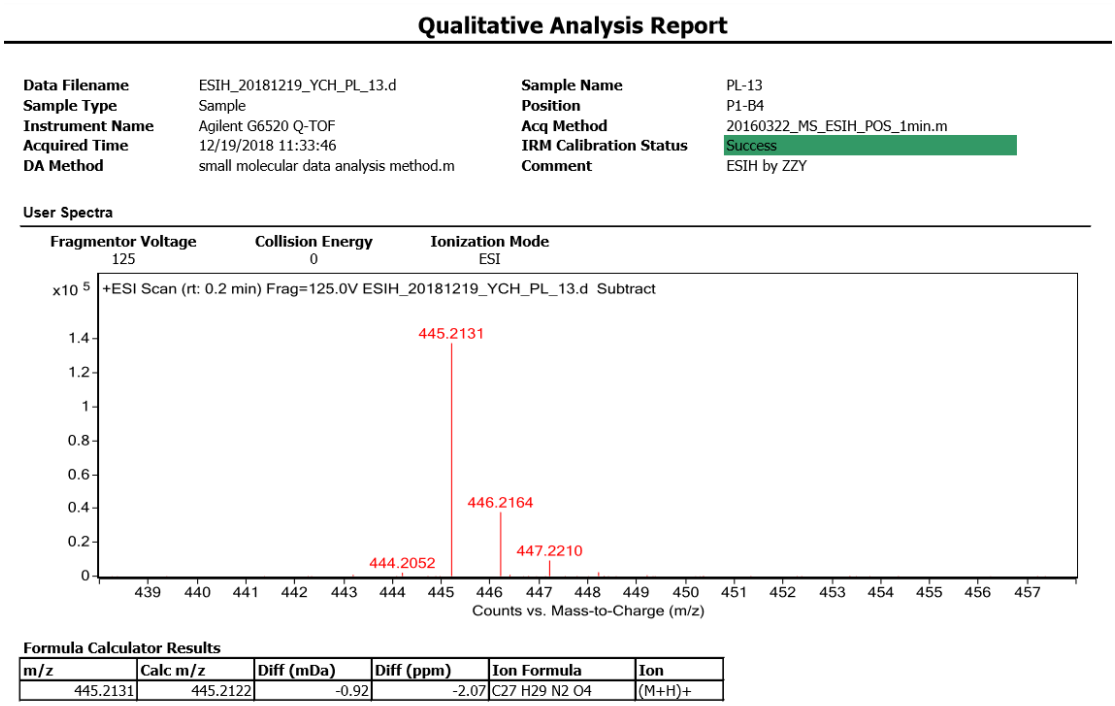


Figure S106. HRMS chromatogram of diethyl 2,10-dimethyl-5,7,12,13-tetrahydro-6*H*-cyclohepta[2,1-*b*:3,4-*b'*]diindole-6,6-di carboxylate (**2d**)

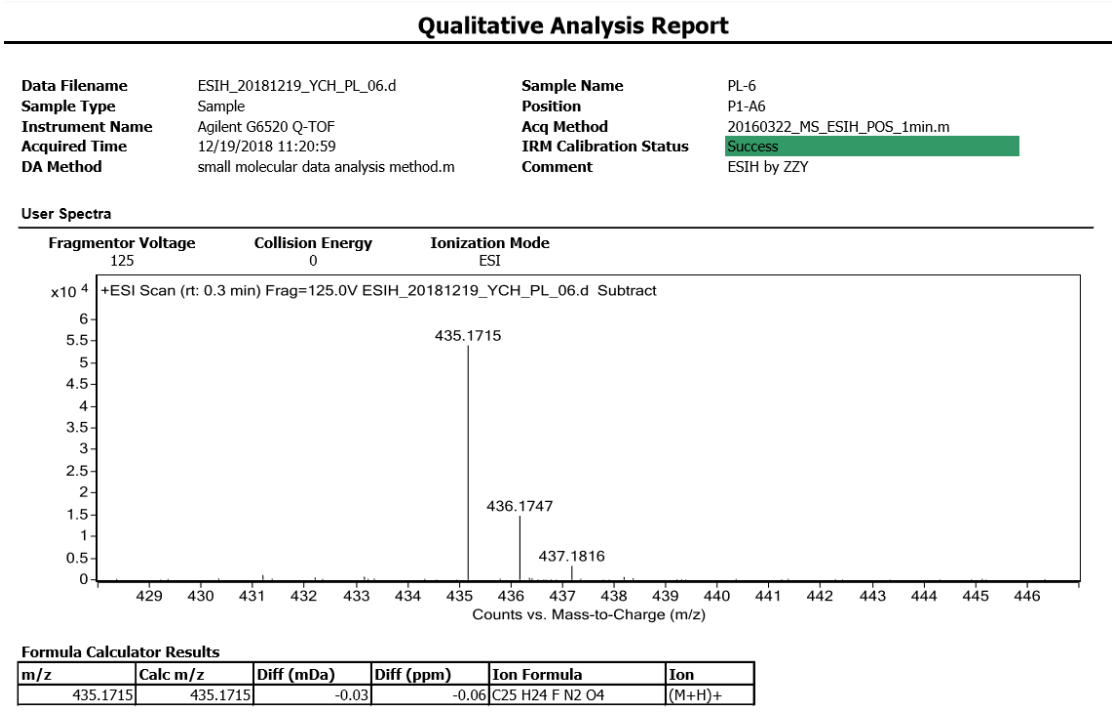


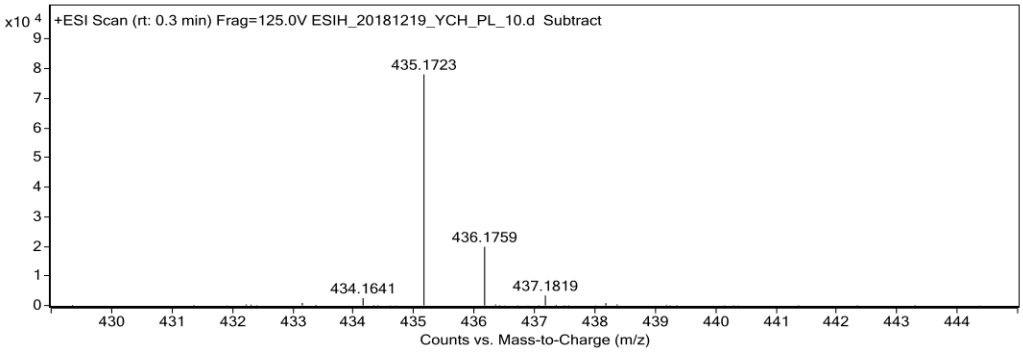
Figure S107. HRMS chromatogram of diethyl 3-fluoro-5,7,12,13-tetrahydro-6*H*-cyclohepta[2,1-*b*:3,4-*b'*]diindole-6,6-dicarboxylate (**2e**)

Qualitative Analysis Report

Data Filename	ESIH_20181219_YCH_PL_10.d	**Sample Name**	PL-10
Sample Type	Sample	**Position**	P1-B1
Instrument Name	Agilent G6520 Q-TOF	**Acq Method**	20160322_MS_ESIH_POS_1min.m
Acquired Time	12/19/2018 11:28:16	**IRM Calibration Status**	Success
DA Method	small molecular data analysis method.m	**Comment**	ESIH by ZZY

User Spectra

Fragmentor Voltage	Collision Energy	Ionization Mode
125	0	ESI



Formula Calculator Results

m/z	Calc m/z	Diff (mDa)	Diff (ppm)	Ion Formula	Ion
435.1723	435.1715	-0.81	-1.87	C25 H24 F N2 O4	(M+H)+

--- End Of Report ---

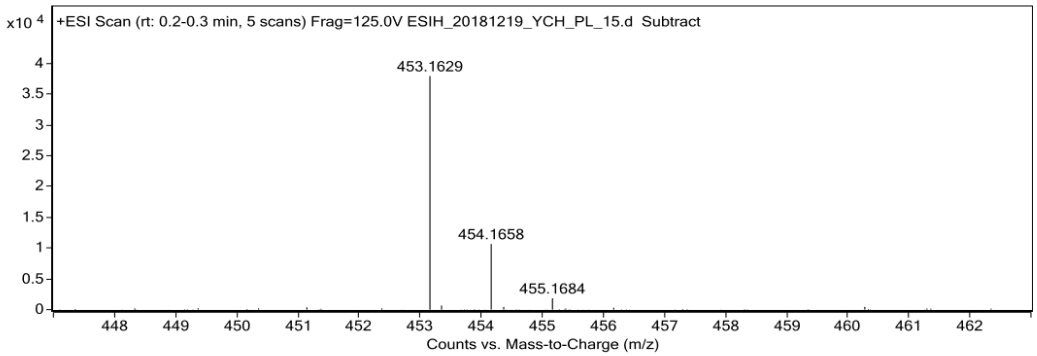
Figure S108. HRMS chromatogram of diethyl 2-fluoro-5,7,12,13-tetrahydro-6*H*-cyclohepta[2,1-*b*:3,4-*b'*]diindole-6,6-dicarboxylate (**2f**)

Qualitative Analysis Report

Data Filename	ESIH_20181219_YCH_PL_15.d	**Sample Name**	PL-15
Sample Type	Sample	**Position**	P1-B6
Instrument Name	Agilent G6520 Q-TOF	**Acq Method**	20160322_MS_ESIH_POS_1min.m
Acquired Time	12/19/2018 11:37:26	**IRM Calibration Status**	Success
DA Method	small molecular data analysis method.m	**Comment**	ESIH by ZZY

User Spectra

Fragmentor Voltage	Collision Energy	Ionization Mode
125	0	ESI



Formula Calculator Results

m/z	Calc m/z	Diff (mDa)	Diff (ppm)	Ion Formula	Ion
453.1629	453.162	-0.83	-1.83	C25 H23 F2 N2 O4	(M+H)+

--- End Of Report ---

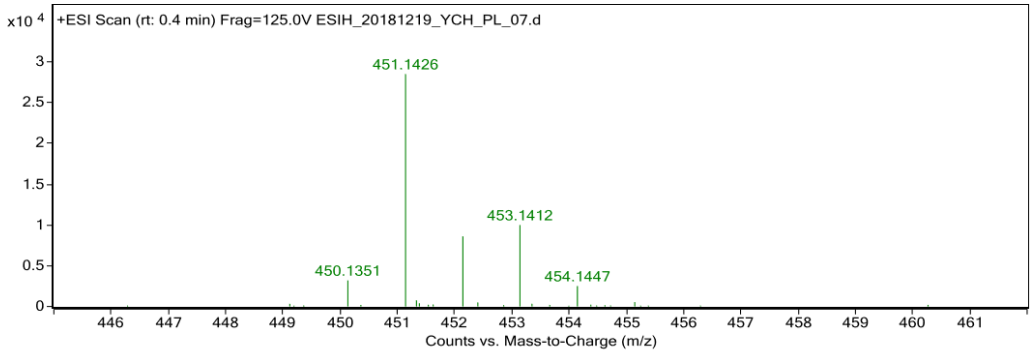
Figure S109. HRMS chromatogram of diethyl 2,10-difluoro-5,7,12,13-tetrahydro-6*H*-cyclohepta[2,1-*b*:3,4-*b'*]diindole-6,6-dicarboxylate (**2g**)

Qualitative Analysis Report

Data Filename	ESIH_20181219_YCH_PL_07.d	**Sample Name**	PL-7
Sample Type	Sample	**Position**	P1-A7
Instrument Name	Agilent G6520 Q-TOF	**Acq Method**	20160322_MS_ESIH_POS_1min.m
Acquired Time	12/19/2018 11:22:49	**IRM Calibration Status**	Success
DA Method	small molecular data analysis method.m	**Comment**	ESIH by ZZY

User Spectra

Fragmentor Voltage	Collision Energy	Ionization Mode
125	0	ESI



Formula Calculator Results

m/z	Calc m/z	Diff (mDa)	Diff (ppm)	Ion Formula	Ion
451.1426	451.1419	-0.72	-1.6	C25 H24 Cl N2 O4	(M+H)+

--- End Of Report ---

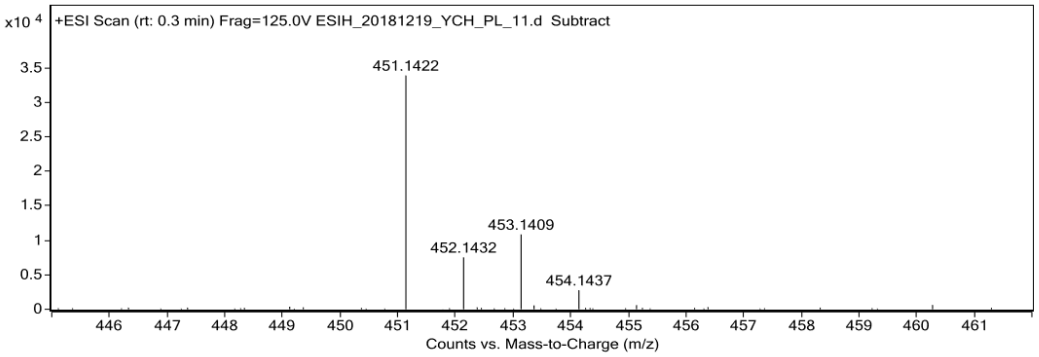
Figure S110. HRMS chromatogram of diethyl 3-chloro-5,7,12,13-tetrahydro-6*H*-cyclohepta[2,1-*b*:3,4-*b*']diindole-6,6-dicarboxylate (**2h**)

Qualitative Analysis Report

Data Filename	ESIH_20181219_YCH_PL_11.d	**Sample Name**	PL-11
Sample Type	Sample	**Position**	P1-B2
Instrument Name	Agilent G6520 Q-TOF	**Acq Method**	20160322_MS_ESIH_POS_1min.m
Acquired Time	12/19/2018 11:30:07	**IRM Calibration Status**	Success
DA Method	small molecular data analysis method.m	**Comment**	ESIH by ZZY

User Spectra

Fragmentor Voltage	Collision Energy	Ionization Mode
125	0	ESI



Formula Calculator Results

m/z	Calc m/z	Diff (mDa)	Diff (ppm)	Ion Formula	Ion
451.1422	451.1419	-0.29	-0.64	C25 H24 Cl N2 O4	(M+H)+

--- End Of Report ---

Figure S111. HRMS chromatogram of diethyl 2-chloro-5,7,12,13-tetrahydro-6*H*-cyclohepta[2,1-*b*:3,4-*b*']diindole-6,6-dicarboxylate (**2i**)

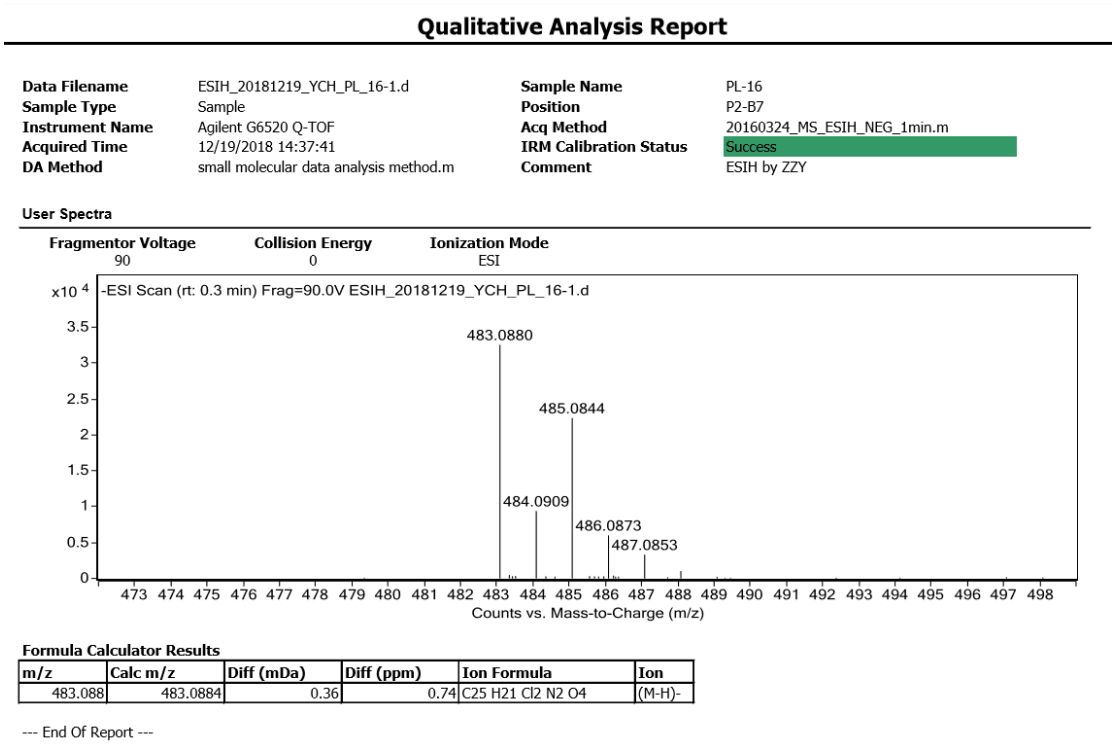


Figure S112. HRMS chromatogram of diethyl 2,10-dichloro-5,7,12,13-tetrahydro-6*H*-cyclohepta[2,1-*b*:3,4-*b'*]diindole-6,6-di carboxylate (**2j**)

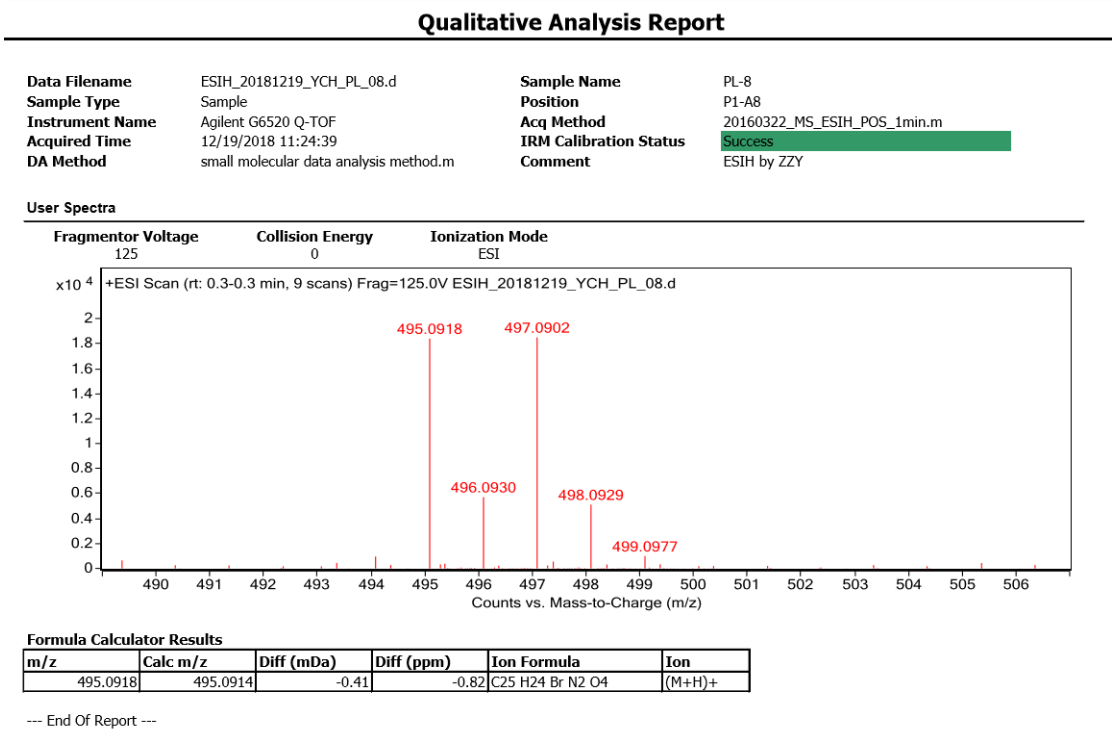


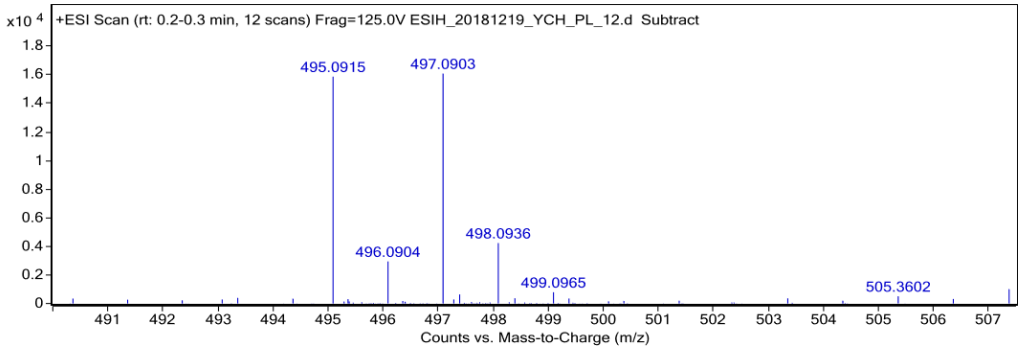
Figure S113. HRMS chromatogram of diethyl 3-bromo-5,7,12,13-tetrahydro-6*H*-cyclohepta[2,1-*b*:3,4-*b'*]diindole-6,6-dicarboxylate (**2k**)

Qualitative Analysis Report

Data Filename	ESIH_20181219_YCH_PL_12.d	**Sample Name**	PL-12
Sample Type	Sample	**Position**	P1-B3
Instrument Name	Agilent G6520 Q-TOF	**Acq Method**	20160322_MS_ESIH_POS_1min.m
Acquired Time	12/19/2018 11:31:56	**IRM Calibration Status**	Success
DA Method	small molecular data analysis method.m	**Comment**	ESIH by ZZY

User Spectra

Fragmentor Voltage	Collision Energy	Ionization Mode
125	0	ESI



Formula Calculator Results

m/z	Calc m/z	Diff (mDa)	Diff (ppm)	Ion Formula	Ion
495.0915	495.0914	-0.1	-0.2	C25 H24 Br N2 O4	(M+H)+

--- End Of Report ---

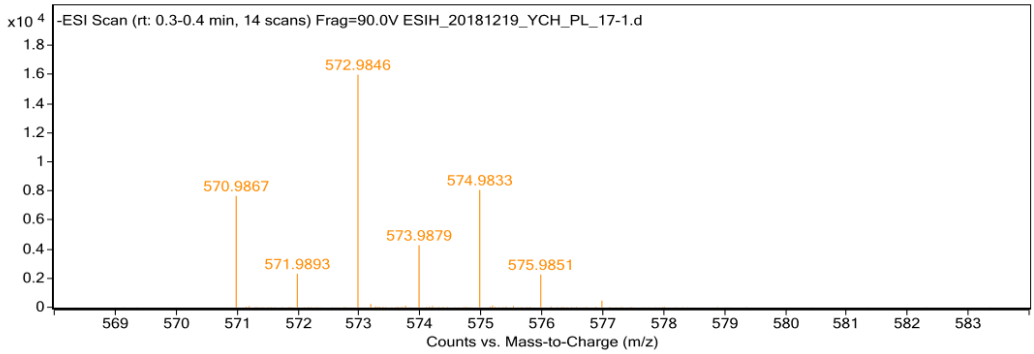
Figure S114. HRMS chromatogram of diethyl 2-bromo-5,7,12,13-tetrahydro-6*H*-cyclohepta[2,1-*b*:3,4-*b*']diindole-6,6-dicarboxylate (**2l**)

Qualitative Analysis Report

Data Filename	ESIH_20181219_YCH_PL_17-1.d	**Sample Name**	PL-17
Sample Type	Sample	**Position**	P2-B8
Instrument Name	Agilent G6520 Q-TOF	**Acq Method**	20160324_MS_ESIH_NEG_1min.m
Acquired Time	12/19/2018 14:39:30	**IRM Calibration Status**	Success
DA Method	small molecular data analysis method.m	**Comment**	ESIH by ZZY

User Spectra

Fragmentor Voltage	Collision Energy	Ionization Mode
90	0	ESI



Formula Calculator Results

m/z	Calc m/z	Diff (mDa)	Diff (ppm)	Ion Formula	Ion
570.9867	570.9874	0.65	1.14	C25 H21 Br2 N2 O4	(M-H)-

--- End Of Report ---

Figure S115. HRMS chromatogram of diethyl 2,10-dibromo-5,7,12,13-tetrahydro-6*H*-cyclohepta[2,1-*b*:3,4-*b*']diindole-6,6-di carboxylate (**2m**)

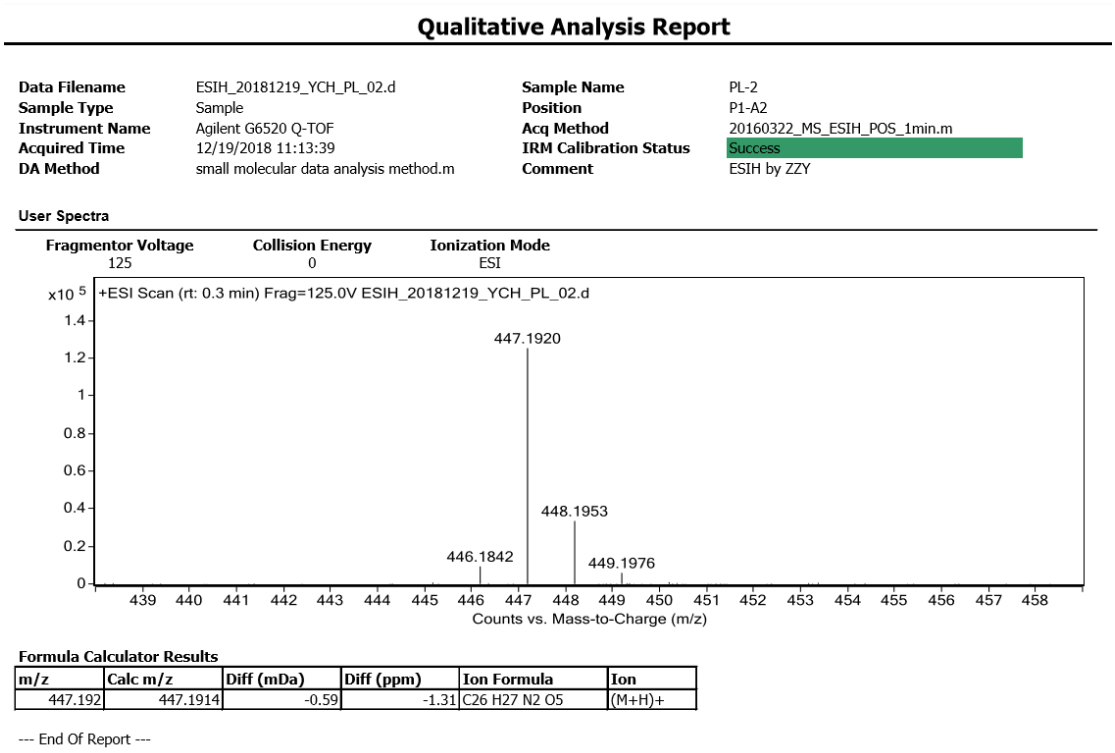


Figure S116. HRMS chromatogram of diethyl 3-methoxy-5,7,12,13-tetrahydro-6*H*-cyclohepta[2,1-*b*:3,4-*b'*]diindole-6,6-dicarboxylate (**2n**)

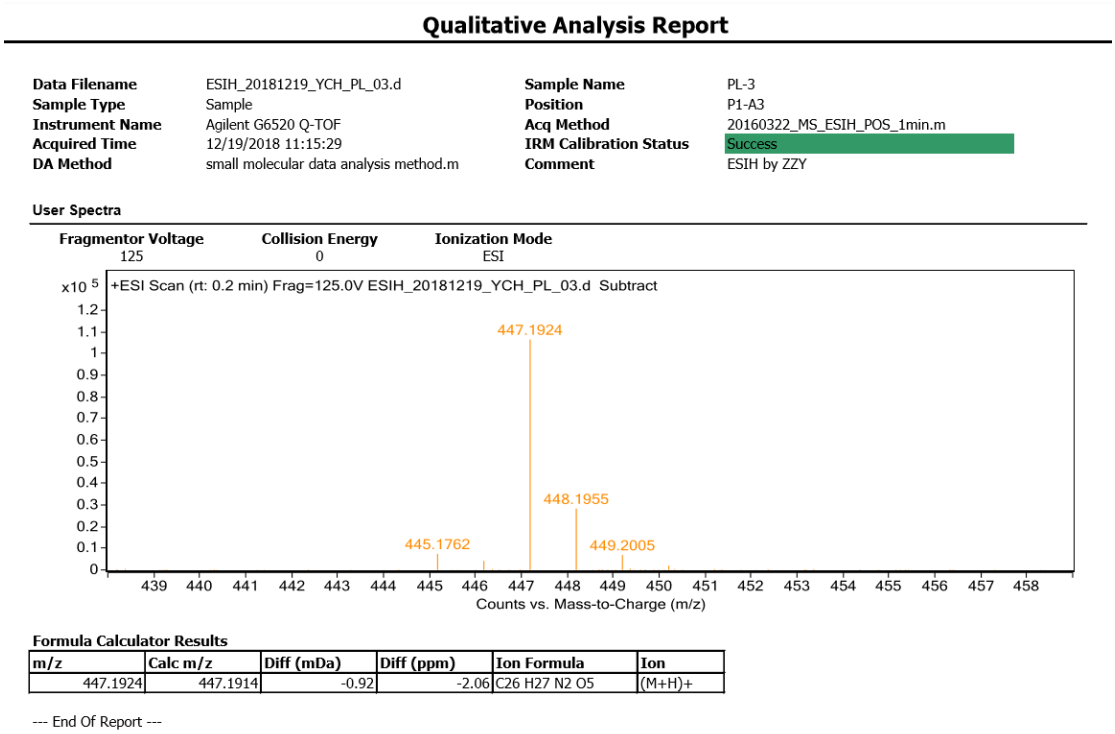


Figure S117. HRMS chromatogram of diethyl 2-methoxy-5,7,12,13-tetrahydro-6*H*-cyclohepta[2,1-*b*:3,4-*b'*]diindole-6,6-dicarboxylate (**2o**)

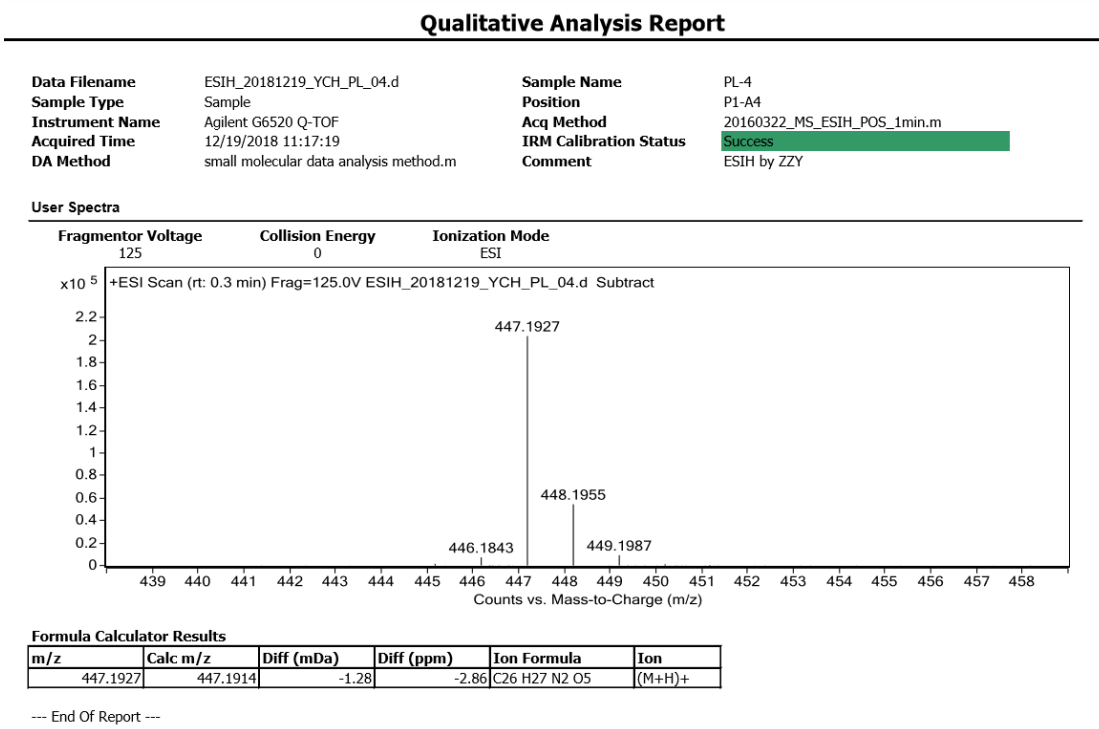


Figure S118. HRMS chromatogram of diethyl 1-methoxy-5,7,12,13-tetrahydro-6*H*-cyclohepta[2,1-*b*:3,4-*b'*]diindole-6,6-dicarboxylate (**2p**)

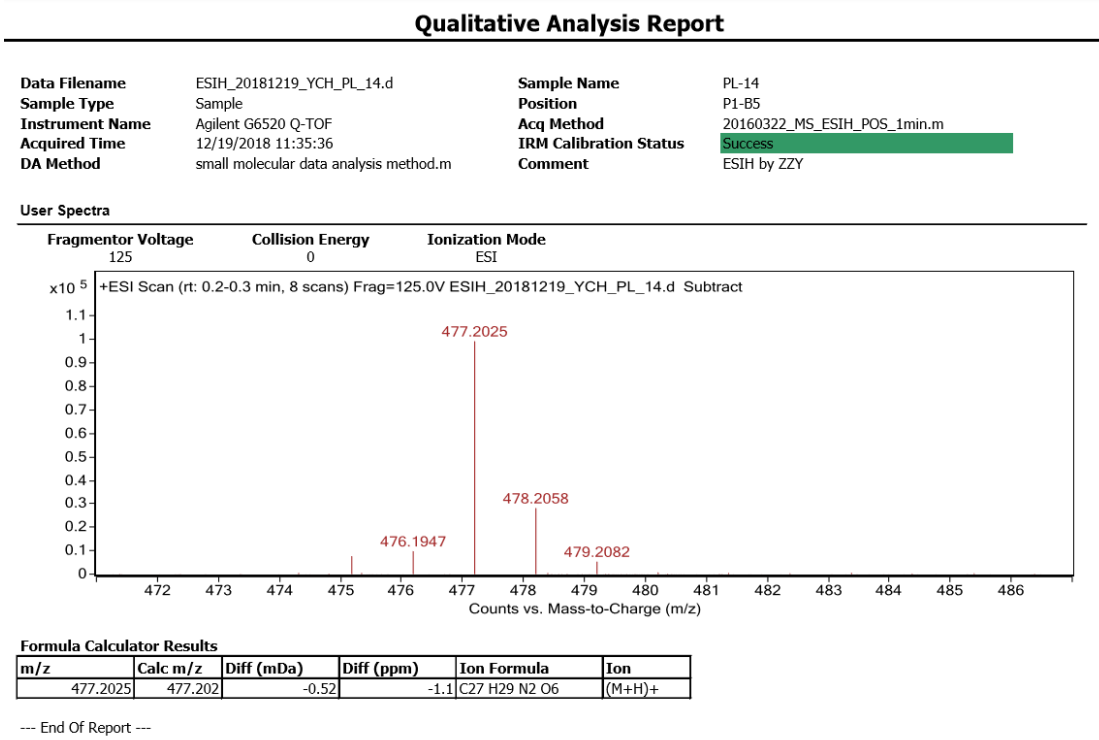


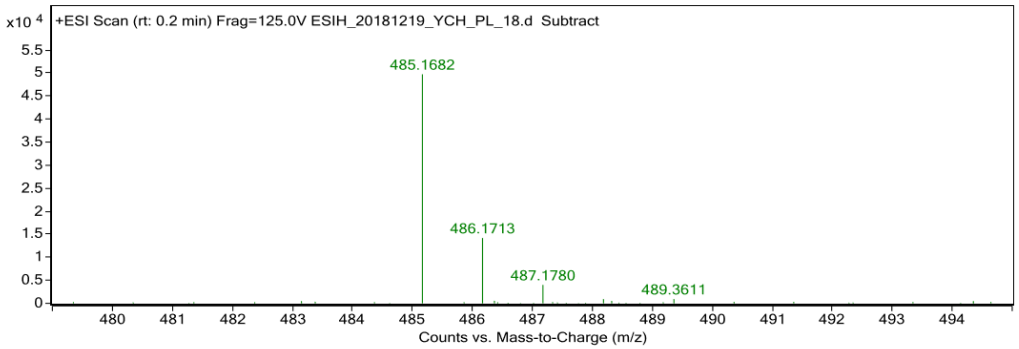
Figure S119. HRMS chromatogram of diethyl 2,10-dimethoxy-5,7,12,13-tetrahydro-6*H*-cyclohepta[2,1-*b*:3,4-*b'*]diindole-6,6-di carboxylate (**2q**)

Qualitative Analysis Report

Data Filename	ESIH_20181219_YCH_PL_18.d	**Sample Name**	PL-18
Sample Type	Sample	**Position**	P1-B9
Instrument Name	Agilent G6520 Q-TOF	**Acq Method**	20160322_MS_ESIH_POS_1min.m
Acquired Time	12/19/2018 11:42:55	**IRM Calibration Status**	Success
DA Method	small molecular data analysis method.m	**Comment**	ESIH by ZZY

User Spectra

Fragmentor Voltage	Collision Energy	Ionization Mode
125	0	ESI



Formula Calculator Results

m/z	Calc m/z	Diff (mDa)	Diff (ppm)	Ion Formula	Ion
485.1682	485.1683	0.07	0.15	C26 H24 F3 N2 O4	(M+H)+

--- End Of Report ---

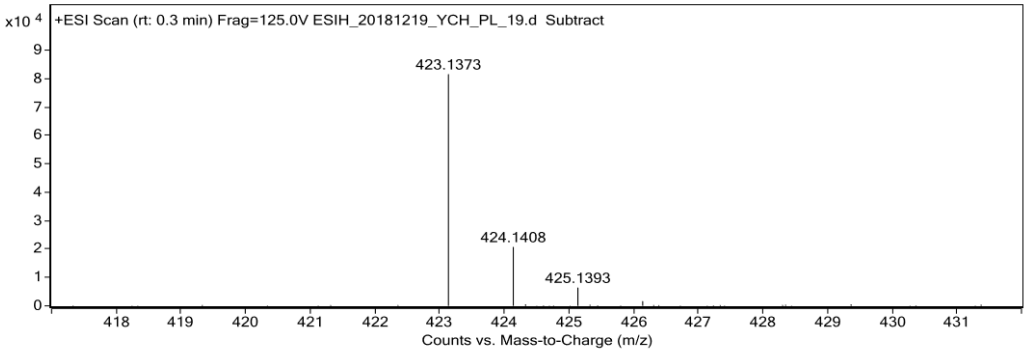
Figure S120. HRMS chromatogram of diethyl 3-(trifluoromethyl)-5,7,12,13-tetrahydro-6*H*-cyclohepta[2,1-*b*:3,4-*b'*]diindole-6,6-di carboxylate (**2r**)

Qualitative Analysis Report

Data Filename	ESIH_20181219_YCH_PL_19.d	**Sample Name**	PL-19
Sample Type	Sample	**Position**	P1-C1
Instrument Name	Agilent G6520 Q-TOF	**Acq Method**	20160322_MS_ESIH_POS_1min.m
Acquired Time	12/19/2018 11:44:44	**IRM Calibration Status**	Success
DA Method	small molecular data analysis method.m	**Comment**	ESIH by ZZY

User Spectra

Fragmentor Voltage	Collision Energy	Ionization Mode
125	0	ESI



Formula Calculator Results

m/z	Calc m/z	Diff (mDa)	Diff (ppm)	Ion Formula	Ion
423.1373	423.1373	0.03	0.07	C23 H23 N2 O4 S	(M+H)+

--- End Of Report ---

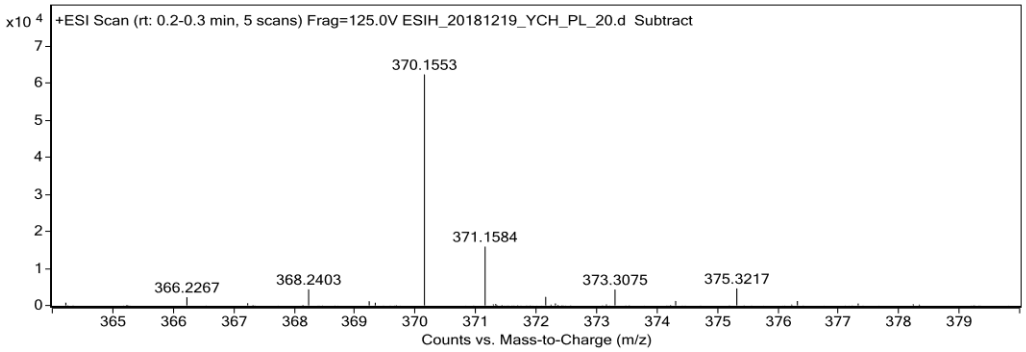
Figure S121. HRMS chromatogram of ethyl 6-(methylsulfonyl)-6,7,12,13-tetrahydro-5*H*-cyclohepta[2,1-*b*:3,4-*b'*]diindole-6-carboxylate (**2s**)

Qualitative Analysis Report

Data Filename	ESIH_20181219_YCH_PL_20.d	**Sample Name**	PL-20
Sample Type	Sample	**Position**	P1-C2
Instrument Name	Agilent G6520 Q-TOF	**Acq Method**	20160322_MS_ESIH_POS_1min.m
Acquired Time	12/19/2018 11:46:34	**IRM Calibration Status**	Success
DA Method	small molecular data analysis method.m	**Comment**	ESIH by ZZY

User Spectra

Fragmentor Voltage	Collision Energy	Ionization Mode
125	0	ESI



Formula Calculator Results

m/z	Calc m/z	Diff (mDa)	Diff (ppm)	Ion Formula	Ion
370.1553	370.155	-0.25	-0.67	C23 H20 N3 O2	(M+H)+

--- End Of Report ---

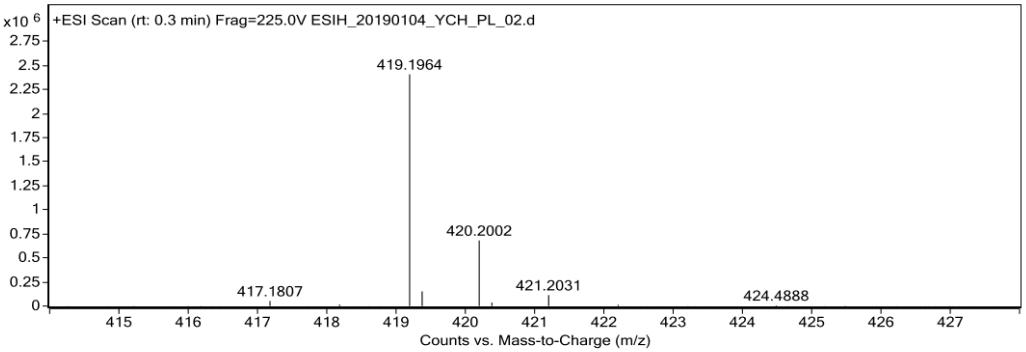
Figure S122. HRMS chromatogram of ethyl 6-cyano-6,7,12,13-tetrahydro-5*H*-cyclohepta[2,1-*b*:3,4-*b'*]diindole-6-carboxylate (**2t**)

Qualitative Analysis Report

Data Filename	ESIH_20190104_YCH_PL_02.d	**Sample Name**	PL-3a
Sample Type	Sample	**Position**	P1-D1
Instrument Name	Agilent G6520 Q-TOF	**Acq Method**	20160322_MS_ESIH_POS_1min.m
Acquired Time	1/4/2019 14:57:09	**IRM Calibration Status**	Success
DA Method	small molecular data analysis method.m	**Comment**	ESIH by ZZY

User Spectra

Fragmentor Voltage	Collision Energy	Ionization Mode
225	0	ESI



Formula Calculator Results

m/z	Calc m/z	Diff (mDa)	Diff (ppm)	Ion Formula	Ion
419.1964	419.1965	0.17	0.4	C25 H27 N2 O4	(M+H)+

--- End Of Report ---

Figure S123. HRMS chromatogram of diethyl 4b,5,7,12,12b,13-hexahydro-6*H*-cyclohepta[2,1-*b*:3,4-*b'*]diindole-6,6-dicarboxylate (**3a**)