Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information
Copper-Catalyzed Oxidative Intermolecular 1,2-Alkylarylation of Styrenes with Ethers and Indoles

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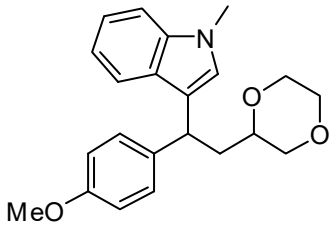
(A) Typical experimental procedure

To a Schlenk tube were added alkenes **1** (0.2 mmol), ethers **2** (2 mL), indole **3** (0.4 mmol), $Cu(MeCN)_4PF_6$ (10 mol%; 0.02 mmol), TBPB (3 equiv; 0.6 mmol). Then the tube was charged with argon, and was stirred at 110 ºC for 16 h until complete consumption of starting material as monitored by TLC and/or GC-MS analysis. After the reaction was finished, the concentrated in vacuum, and the resulting residue was purified by silica gel column chromatography (hexane/ethyl acetate) to afford the desired products **4**.

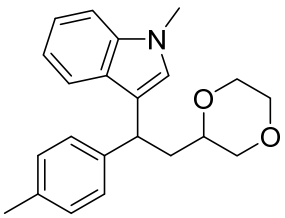
(B) Analytical data

3-(2-(1,4-Dioxan-2-yl)-1-(4-methoxyphenyl)ethyl)-1-methyl-1*H*-indole (4aaa):



dr =1:1

Brown oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.48-7.42 (m, 1H), 7.25-7.13 (m, 4H), 7.03-6.97 (m, 1H), 6.81-6.77 (m, 3H), 4.41-4.35 (m, 1H), 3.79-3.49 (m, 11.45H), 3.43-3.38 (m, 0.51H), 3.34-3.28 (m, 1H), 2.28-2.21 (m, 0.47H), 2.10-2.04 (m, 1H), 1.90-1.84 (m, 0.47H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 158.0, 157.9, 137.5, 137.3, 137.3, 136.5, 129.0, 128.6, 127.5, 127.3, 126.0, 125.6, 121.6, 119.8, 119.7, 119.2, 118.8, 118.7, 118.0, 113.9, 113.8, 109.2, 109.1, 73.5, 73.2, 71.5, 71.4, 66.8, 66.7, 66.6 (2C), 55.3, 38.6, 38.0, 37.3, 37.2, 32.8, 32.7; LRMS (EI, 70 eV) *m/z* (%): 351 (M^+, 18), 250 (100), 235 (9), 206 (29); HRMS *m/z* (ESI) calcd for $C_{22}H_{26}NO_3$ ($[M+H]^+$) 352.1907, found 352.1901.

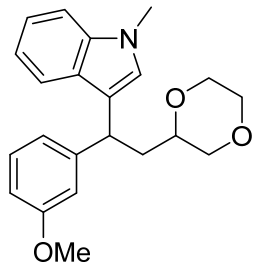


3-(2-(1,4-Dioxan-2-yl)-1-(p-tolyl)ethyl)-1-methyl-1H-indole (4baa):

dr = 1.2:1

Brown oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.49 (d, *J* = 8.0 Hz, 0.61H), 7.45 (d, *J* = 8.0 Hz, 0.52H), 7.26-7.13 (m, 4H), 7.09-6.97 (m, 3H), 6.82 (d, *J* = 6.0 Hz, 1H), 4.43-4.37 (m, 1H), 3.79-3.27 (m, 13H), 2.12-2.08 (m, 3.66H), 2.10 (t, *J* = 7.2 Hz, 1H), 1.94-1.87 (m, 0.63H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 142.2, 141.2, 137.2, 137.2, 135.6, 135.4, 129.1, 129.1, 127.9, 127.5, 127.4, 127.2, 126.0, 125.6, 121.5, 119.6, 119.5, 119.0, 118.7, 118.6, 117.8, 109.1, 109.0, 73.4, 73.1, 71.4, 71.3, 66.7, 66.6, 66.5, 66.5, 38.5, 37.9, 37.6, 37.4, 32.7, 32.6, 21.0, 20.9; LRMS (EI, 70 eV) *m/z* (%): 335 (M^+, 26), 234 (100), 218 (11); HRMS *m/z* (ESI) calcd for $C_{22}H_{26}NO_2$ ($[M+H]^+$) 336.1958, found 336.1966.

3-(2-(1,4-Dioxan-2-yl)-1-(3-methoxyphenyl)ethyl)-1-methyl-1*H*-indole (4daa):

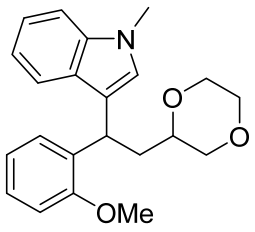


dr = 1.2:1

Brown oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.51 (d, *J* = 8.0 Hz, 1H), 7.46 (d, *J* = 8.0 Hz, 1H), 7.27-7.23 (m, 1H), 7.21-7.15 (m, 2H), 7.05-6.98 (m, 1H), 6.93-6.84 (m, 3H), 6.73-6.69 (m, 1H), 4.45-4.39 (m, 1H), 3.85-3.70 (m, 8H), 3.67-3.51 (m, 4H), 3.36-3.29 (m, 1H), 2.30-2.21 (m, 0.61H), 2.12-2.09 (m, 1H), 1.96-1.89 (m, 0.55H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 159.6, 159.6, 147.1, 146.1, 137.2, 137.2, 129.3 (2C), 126.0, 125.6, 121.6, 121.6, 120.6, 120.1, 119.6, 119.5, 118.8, 118.7, 118.6, 117.5, 114.3, 113.7, 111.1, 111.0, 109.1, 109.0, 73.4, 73.1, 71.4 (2C), 66.7, 66.6, 66.5, 66.5, 55.1, 38.4, 38.1, 37.9,

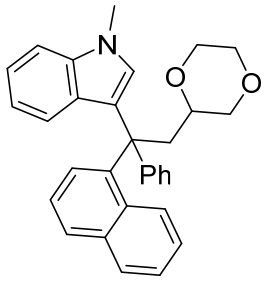
37.8, 32.7, 32.7, 29.7; LRMS (EI, 70 eV) *m/z* (%): 351 (M^+, 24), 250 (100), 206 (18), 144 (16); HRMS *m/z* (ESI) calcd for $C_{22}H_{26}NO_3$ ($[M+H]^+$) 352.1907, found 352.1918.

3-(2-(1,4-Dioxan-2-yl)-1-(2-methoxyphenyl)ethyl)-1-methyl-1*H*-indole (4eaa):



dr = 1.1:1

Brown oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.51 (t, *J* = 8.4 Hz, 1H), 7.24-7.10 (m, 4H), 7.03-6.98 (m, 1H), 6.87-6.80 (m, 3H), 4.89-4.82 (m, 1H), 3.87-3.45 (m, 12H), 3.35-3.29 (m, 1H), 2.28-2.21 (m, 0.50H), 2.14 (t, *J* = 7.2 Hz, 1H), 2.04-1.97 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 157.0, 156.6, 137.1, 137.0, 133.3, 133.0, 128.3, 128.0, 127.7, 127.5, 127.0 (2C), 126.1, 126.0, 121.4, 120.6, 119.6, 119.6, 118.6, 118.5, 118.1, 118.0, 110.7, 110.5, 109.0, 108.9, 74.0, 73.6, 71.5, 71.4, 66.8, 66.7, 66.5, 55.5, 37.8, 37.6, 32.6, 30.8, 29.8; LRMS (EI, 70 eV) *m/z* (%): 351 (M^+, 24), 250 (73), 234 (22), 144 (100); HRMS *m/z* (ESI) calcd for $C_{22}H_{26}NO_3$ ($[M+H]^+$) 352.1907, found 352.1917.

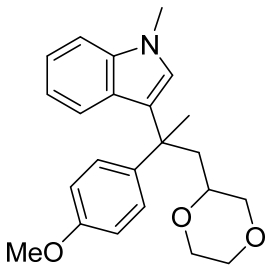


3-(2-(1,4-Dioxan-2-yl)-1-(naphthalen-1-yl)-1-phenylethyl)-1-methyl-1*H*-indole (4faa):

dr = 1.2:1

Light yellow oil; 1H NMR (400 MHz, CDCl3) δ: 8.10 (s, 0.47H), 7.89 (s, 0.56H), 7.80-7.65 (m, 3H), 7.51-7.37 (m, 5H), 7.26-7.03 (m, 6H), 6.89-6.81 (m, 2H), 3.79-3.48 (m, 8H), 3.18 (d, *J* = 14.8 Hz, 1H), 2.91 (t, *J* = 10.8 Hz, 1H), 2.52-2.47 (m, 1H), 2.36 (t, *J* = 12.0 Hz, 1H); ^{13}C NMR (100 MHz, CDCl3) δ: 146.5, 145.9, 144.2, 143.6, 137.6, 133.2, 133.1, 131.8, 131.7, 129.1, 128.8, 128.8, 128.7, 128.3, 128.3, 128.2, 128.0, 127.9, 127.6, 127.4, 127.3, 127.2, 126.8, 126.7, 126.1, 126.0, 125.8, 125.7, 125.7, 125.7, 125.6, 122.1, 121.4, 120.1, 119.6, 118.7,

109.4, 109.3, 74.3, 74.2, 71.8, 67.0, 66.0, 51.7, 43.2, 43.1, 32.8, 32.8; HRMS m/z (ESI) calcd for $C_{31}H_{30}NO_2$ ($[M+H]^+$) 448.2271, found 448.2260.

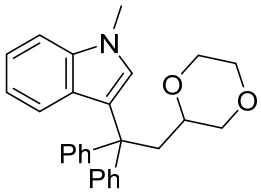


3-(1-(1,4-Dioxan-2-yl)-2-(4-methoxyphenyl)propan-2-yl)-1-methyl-1*H*-indole (4gaa):

dr = 1.1:1

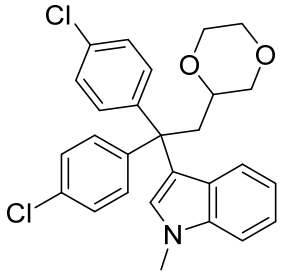
Brown oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.27-6.99 (m, 5H), 6.93-6.74 (m, 4H), 3.78-3.45 (m, 11H), 3.19-3.06 (m, 1.69H), 2.92-2.89 (m, 0.42H), 2.34-2.26 (m, 1H), 2.19-2.14 (m, 0.42H), 2.03-1.98 (m, 0.59H), 1.82 (s, 1.70H), 1.71 (s, 1.49H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 157.6, 157.4, 141.1, 139.5, 137.8, 137.6, 128.1, 127.6, 126.7, 126.3, 126.1, 125.2, 124.6, 121.4, 121.3, 121.3, 121.2, 118.4, 118.3, 113.3, 113.3, 109.2, 109.0, 73.8, 73.4, 71.7, 71.6, 66.6, 66.2, 66.2, 55.1, 44.8, 43.0, 41.2, 40.7, 32.7, 32.6, 29.6, 27.0; (EI, 70 eV) *m/z* (%): 365 (M^+, 15), 264 (100), 133 (23); HRMS *m/z* (ESI) calcd for $C_{23}H_{28}NO_3$ ($[M+H]^+$) 366.2064, found 366.2075.

3-(2-(1,4-Dioxan-2-yl)-1,1-diphenylethyl)-1-methyl-1*H*-indole (4haa)：



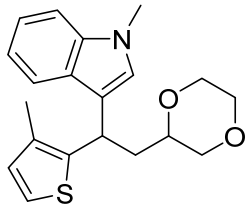
Brown oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.48 (d, *J* = 8.0 Hz, 2H), 7.36 (d, *J* = 8.0 Hz, 2H), 7.27-7.11 (m, 8H), 7.01 (d, *J* = 8.0 Hz, 1H), 6.89-6.85 (m, 2H), 3.75-3.72 (m, 4H), 3.62-3.45 (m, 4H), 3.06 (d, *J* = 14.8 Hz, 1H), 2.88 (t, *J* = 10.4 Hz, 1H), 2.41-2.30 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 146.8, 146.1, 137.6, 128.7, 128.7, 128.5, 127.9, 127.9, 126.7, 126.0, 125.9, 122.1, 121.4, 120.2, 118.6, 109.3, 74.2, 71.8, 67.0, 66.0, 51.5, 43.3, 32.8; (EI, 70 eV) *m/z* (%): 397 (M^+, 8), 276 (100), 218 (7), 165 (8); HRMS *m/z* (ESI) calcd for $C_{27}H_{28}NO_2$ ($[M+H]^+$) 398.2115, found 398.2123.

3-(1,1-bis(4-chlorophenyl)-2-(1,4-Dioxan-2-yl)ethyl)-1-methyl-1*H*-indole (4iaa):



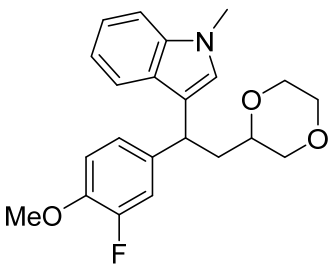
Brown oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.39 (d, *J* = 8.4 Hz, 2H), 7.28-7.14 (m, 8H), 6.97-6.90 (m, 2H), 6.79 (s, 1H), 3.73-3.71 (m, 4H), 3.58-3.43 (m, 4H), 2.98-2.88 (m, 2H), 2.43-2.32 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 144.9, 144.5, 137.6, 132.1, 131.9, 129.9, 129.9, 128.8, 128.2, 128.1, 126.3, 121.7, 119.2, 118.9, 109.6, 73.9, 71.6, 67.0, 66.0, 50.9, 42.9, 32.8; (EI, 70 eV) *m/z* (%): 467 (M^++2, 2), 465 (M^+, 7), 364 (100), 146 (13); HRMS *m/z* (ESI) calcd for $C_{27}H_{26}{}^{35}Cl_2NO_2$ ($[M+H]^+$) 466.1335, found 466.1346.

3-(2-(1,4-Dioxan-2-yl)-1-(3-methylthiophen-2-yl)ethyl)-1-methyl-1*H*-indole (4jaa):



dr = 1.3:1

Brown oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.61 (d, *J* = 8.0 Hz, 0.58H), 7.51 (d, *J* = 8.0 Hz, 0.44H), 7.26-7.16 (m, 2H), 7.08-6.99 (m, 2H), 6.85 (s, 1H), 6.77-6.73 (m, 1H), 4.85-4.75 (m, 1H), 3.80-3.44 (m, 9H), 3.34-3.28 (m, 1H), 2.27-2.08 (m, 4.59H), 1.95-1.89 (t, *J* = 12.4 Hz, 0.52H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 143.1, 142.1, 137.1, 136.9, 133.2, 132.1, 130.0, 129.7, 127.4, 127.0, 126.2, 125.6, 121.8, 121.6, 121.6, 120.9, 119.3, 119.2, 118.8, 118.8, 117.3, 109.2, 109.1, 73.2, 73.1, 71.3, 71.2, 66.6 (2C), 66.5, 39.7, 39.5, 32.7, 32.6, 31.1, 31.1, 13.9, 13.7; LRMS (EI, 70 eV) *m/z* (%): 341 (M^+, 21), 240 (100), 224 (13), 207 (14); HRMS *m/z* (ESI) calcd for $C_{20}H_{24}NO_2S$ ($[M+H]^+$) 342.1522, found 342.1510.

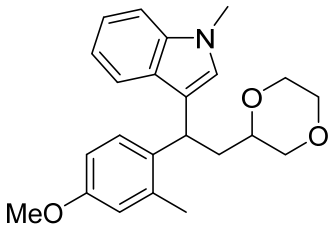


3-(2-(1,4-Dioxan-2-yl)-1-(3-fluoro-4-methoxyphenyl)ethyl)-1-methyl-1*H*-indole (4kaa):

dr = 1.1:1

Brown oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.45-7.39(m, 1H), 7.26-7.15 (m, 2H), 7.04-6.98 (m, 3H), 6.89-6.82 (m, 2H), 4.42-4.36 (m, 1H), 3.85-3.51 (m, 12H), 3.38-3.29 (m, 1H), 2.26-2.19 (m, 0.41H), 2.06 (t, *J* = 6.8 Hz, 1H), 1.89-1.82 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 153.66, 151.1, 145.9, 145.8, 145.7, 145.6, 138.7, 138.7, 137.7, 137.6, 137.2, 137.2, 127.3, 127.0, 125.9, 125.5, 123.6, 123.6, 123.0 (2C), 121.7, 119.5, 119.4, 118.8, 118.7, 118.4, 117.2, 115.6, 115.5, 115.3, 115.1, 113.3, 109.2, 109.1, 73.3, 72.9, 71.4, 71.3, 66.7, 66.6, 66.5, 66.5, 56.3, 38.3, 37.7, 37.1, 37.0, 32.7, 32.6; ^{19}F NMR (376 MHz, CDCl3) δ -135.23; LRMS (EI, 70 eV) *m/z* (%): 369 (M^+, 21), 269 (100), 253 (18), 224 (24); HRMS *m/z* (ESI) calcd for $C_{22}H_{25}FNO_3$ ($[M+H]^+$) 370.1813, found 370.1821.

3-(2-(1,4-Dioxan-2-yl)-1-(4-methoxy-2-methylphenyl)ethyl)-1-methyl-1*H*-indole (4laa):

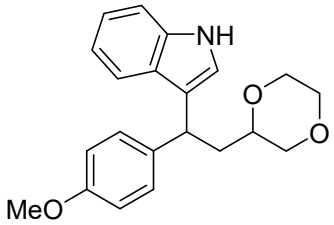


dr = 1.2:1

Brown oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ:7.54 (d, *J* = 8.0 Hz, 1H), 7.44 (d, *J* = 8.0 Hz, 1H), 7.27-7.11 (m, 3H), 7.07-6.99 (m, 1H), 6.72-6.67 (m, 3H), 4.67-4.59 (m, 1H), 3.78-3.53 (m, 11.62H), 3.44-3.27 (m, 1.54H), 2.41 (s, 1H), 2.31-2.22 (m, 2.17H), 2.07-1.95 (m, 1H), 1.92-1.85 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 157.5, 137.6, 137.2, 137.0, 135.8, 134.4, 128.0, 127.9, 127.2, 127.1, 126.5, 126.0, 121.5, 119.5, 119.3, 118.7, 118.6,

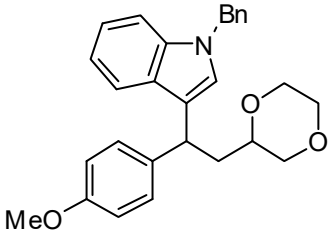
118.0, 116.0, 115.7, 111.4, 110.9, 109.1, 109.0, 73.3, 73.3, 71.5, 71.5, 66.7, 66.6, 66.5, 66.5, 55.1, 38.5, 38.2, 32.7, 32.6, 32.5, 32.4, 19.9, 19.9; LRMS (EI, 70 eV) *m/z* (%): 365 (M^+, 22), 264 (100), 248 (5), 220 (8); HRMS *m/z* (ESI) calcd for $C_{23}H_{28}NO_3$ ($[M+H]^+$) 366.2064, found 366.2074.

3-(2-(1,4-Dioxan-2-yl)-1-(4-methoxyphenyl)ethyl)-1*H*-indole (4aba):



dr = 1.1:1

Brown oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.04 (s, 0.50H), 7.98 (s, 0.50H), 7.47-7.41 (m, 1H), 7.30 (t, *J* = 8.0 Hz, 1H), 7.24-7.20 (m, 2H), 7.16-7.10 (m, 1H), 7.03-6.96 (m, 2H), 6.80 (t, *J* = 8.4 Hz, 2H), 4.43-4.36 (m, 1H), 3.81-3.71 (m, 5H), 3.67-3.51 (m, 3.51H), 3.41-3.29 (m, 1.53H), 2.25 (m, 0.52H), 2.13-2.07 (m, 1H), 1.94-1.83 (m, 0.51H); ^{13}C NMR (100 MHz, $CDCl_3$) δ:158.0, 157.8, 137.2, 136.6, 136.5, 136.3, 129.0, 128.5, 127.0, 126.8, 122.0 (2C), 121.1, 120.6, 120.6, 119.6, 119.5, 119.4, 119.3, 119.2, 113.8 (2C), 111.1, 110.9, 73.5, 73.1, 71.4, 71.3, 66.7, 66.6, 66.5, 55.2, 38.4, 37.8, 37.2, 37.1; LRMS (EI, 70 eV) *m/z* (%): 337 (M^+, 17), 236 (100), 207 (26), 192 (24); HRMS *m/z* (ESI) calcd for $C_{21}H_{24}NO_3$ ($[M+H]^+$) 338.1751, found 338.1760.

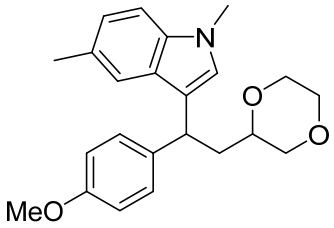


3-(2-(1,4-Dioxan-2-yl)-1-(4-methoxyphenyl)ethyl)-1-benzyl-1*H*-indole (4aca):

dr = 1:1

Brown oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.47-7.40 (m, 1H), 7.27-7.17 (m, 6H), 7.12-6.92 (m, 5H), 6.82-6.77 (m, 2H), 5.24 (d, *J* = 5.2 Hz, 2H), 4.44-4.36 (m, 1H), 3.79-3.50 (m, 7.63H), 3.42-3.27 (m, 1.67H), 2.26-2.21 (m, 0.51H), 2.11-2.07 (m, 1H),

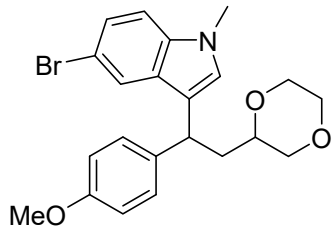
1.89-1.83 (m, 0.58H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 1157.9, 157.8, 137.8, 137.6, 137.2, 136.9, 136.3, 128.9, 128.7, 128.7, 128.5, 127.6, 127.5, 127.4, 126.6, 126.6, 125.4, 124.9, 121.8, 121.7, 119.8, 119.8, 119.7, 119.0, 118.9, 118.5, 113.8, 113.7, 109.6, 109.5, 73.4, 73.0, 71.4, 71.2, 66.7, 66.6, 66.5, 55.1, 49.8, 49.8, 38.4, 37.9, 37.2, 37.1; LRMS (EI, 70 eV) *m/z* (%): 427 (M^+, 5), 326 (100), 91 (89); HRMS *m/z* (ESI) calcd for $C_{28}H_{30}NO_3$ ($[M+H]^+$) 428.2220, found 428.2228.



3-(1-(4-methoxyphenyl)-2-(tetrahydrofuran-2-yl)ethyl)-1,5-dimethyl-1*H*-indole (4ada):

dr = 1:1

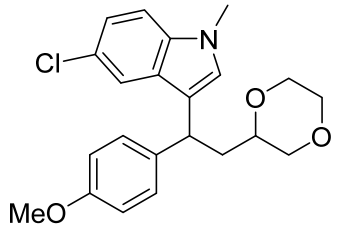
Brown oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.27-7.20 (m, 3H), 7.13 (t, *J* = 8.0 Hz, 1H), 6.99 (t, *J* = 8.0 Hz, 1H), 6.83-6.76 (m, 3H), 4.38-4.33 (m, 1H), 3.80-3.52 (m, 11.56H), 3.43-3.28 (m, 1.58H), 2.39 (s, 3H), 2.24-2.19 (m, 0.56H), 2.07 (t, *J* = 7.2 Hz, 1H), 1.91-1.84 (m, 0.56H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 157.9, 157.8, 137.6, 136.5, 135.7, 135.6, 128.9, 128.4, 127.9, 127.8, 127.7, 127.3, 126.0, 125.7, 123.2, 119.2, 119.1, 118.4, 117.4, 113.8, 113.7, 108.8, 108.7, 73.5, 73.2, 71.4, 71.3, 66.7, 66.6, 66.5 (2C), 55.2, 38.7, 38.1, 37.1, 37.0, 32.7, 32.7, 21.5 (2C); (EI, 70 eV) *m/z* (%): 365 (M^+, 78), 264 (100), 207 (38); HRMS *m/z* (ESI) calcd for $C_{23}H_{28}NO_3$ ($[M+H]^+$) 366.2064, found 366.2075.



3-(2-(1,4-Dioxan-2-yl)-1-(4-methoxyphenyl)ethyl)-5-bromo-1-methyl-1*H*-indole (4aea):

dr = 1.2:1

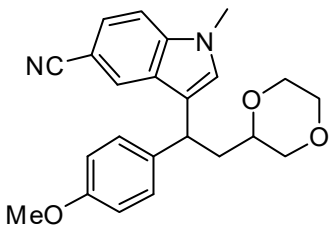
Brown oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.63 (s, 0.54H), 7.54 (s, 0.45H), 7.24-7.17 (m, 3H), 7.08 (t, *J* = 8.8 Hz, 1H), 6.83-6.79 (m, 3H), 4.35-4.32 (m, 1H), 3.84-3.27 (m, 13H), 2.20-2.01 (m, 1.56H), 1.89-1.82 (m, 0.55H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 158.0, 157.9, 136.9, 135.9, 135.7, 129.1, 128.8, 128.3, 127.1, 126.7, 124.4, 122.0 (2C), 118.8, 117.8, 113.8, 113.8, 112.2, 112.1, 110.6, 110.5, 73.2, 72.9, 71.3, 71.3, 66.6, 66.6, 66.5, 55.2, 38.5, 37.9, 36.9, 36.6, 32.8, 32.8; LRMS (EI, 70 eV) *m/z* (%): 431 (M^++2, 18), 429 (M^+, 19), 330 (100), 249 (11), 207 (23); HRMS *m/z* (ESI) calcd for $C_{22}H_{25}BrNO_3$ ([M+H]$^+$) 430.1012, found 430.1019.



3-(2-(1,4-Dioxan-2-yl)-1-(4-methoxyphenyl)ethyl)-5-chloro-1-methyl-1*H*-indole (4afa):

dr = 1.1:1

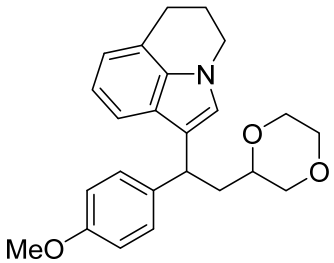
Brown oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.46 (s, 0.45H), 7.38 (s, 0.49H), 7.21-7.09 (m, 4H), 6.85-6.80 (m, 3H), 4.36-4.32 (m, 1H), 3.82-3.76 (m, 4H), 3.72-3 (m, 3H), 3.68-3.56 (m, 4H), 3.49-3.45 (m, 0.51H), 3.40-3.29 (m, 1.46H), 2.18 (m, 0.52H), 2.07-2.02 (m, 1H), 1.89-1.83 (m, 0.53H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 158.01, 157.9, 137.0, 135.9, 135.6, 135.5, 128.8, 128.4, 128.3, 128.1, 127.3, 126.8, 124.6, 124.5, 121.9, 119.0, 118.9, 118.9, 117.8, 113.9, 113.8, 110.2, 110.1, 73.2, 72.9, 71.4, 71.3, 66.7, 66.6, 66.5, 66.5, 55.2, 38.5, 37.9, 37.0, 36.7, 32.9, 32.9; LRMS (EI, 70 eV) *m/z* (%): 387 (M^++2, 8), 385 (M^+, 21), 284 (100), 206 (7); HRMS *m/z* (ESI) calcd for $C_{22}H_{25}{}^{35}ClNO_3$ ([M+H]$^+$) 386.1517, found 386.1528.



3-(2-(1,4-Dioxan-2-yl)-1-(4-methoxyphenyl)ethyl)-1-methyl-1*H*-indole-5-carbonitrile (4aga):

dr = 1:1

Brown oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ:1H N7.83 (s, 0.52H), 7.73 (s, 0.52H), 7.37 (t, *J* = 8.8 Hz, 1H), 7.30-7.24 (m, 1H), 7.18 (t, *J* = 7.2 Hz, 2H), 6.96 (s, 1H), 6.83 (t, *J* = 7.6 Hz, 2H), 4.42-4.36 (m, 1H), 3.82-3.56 (m, 11H), 3.46-3.30 (m, 2H), 2.20-2.00 (m, 1.54H), 1.90-1.83 (m, 0.59H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 158.2, 158.0, 138.7, 138.5, 136.4, 135.3, 128.8, 128.3, 128.1, 127.6, 127.2, 126.9, 125.3, 125.2, 124.5, 120.9, 120.8, 120.5, 119.4, 114.0, 113.9, 110.0, 109.9, 101.8, 101.6, 73.1, 72.7, 71.3, 71.2, 66.6 (2C), 66.6, 66.5, 66.4, 55.2, 38.3, 37.7, 36.8, 36.5, 32.9, 32.8; LRMS (EI, 70 eV) *m/z* (%):376 (M^+, 17), 275 (100), 231 (16), 206 (26); HRMS *m/z* (ESI) calcd for $C_{23}H_{25}N_2O_3$ ($[M+H]^+$) 377.1860, found 377.1869.



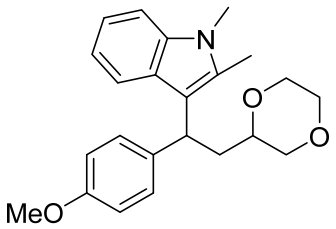
1-(2-(1,4-Dioxan-2-yl)-1-(4-methoxyphenyl)ethyl)-5,6-dihydro-4*H*-pyrrolo[3,2,1-*ij*]quinoline (4aha):

dr = 1.1:1

Brown oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.28-7.21 (m, 3H), 6.93-6.78 (m, 5H), 4.40-4.33 (m, 1H), 4.10-4.06 (m, 2H), 3.79-3.70 (m, 5H), 3.65-3.54 (m, 3.58H), 3.42-3.39 (m, 0.54H), 3.34-3.28 (m, 1H), 2.97-2.92 (m, 2H), 2.31-2.15 (m, 2.59H), 2.13-2.05 (m, 1H), 1.94-1.87 (m, 0.59H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 157.9, 157.8, 137.6, 136.7, 134.7 (2C), 129.0, 128.5, 124.8, 124.6, 123.3, 122.9, 121.6, 121.5, 119.2, 119.1, 119.0, 118.4, 118.0, 117.3, 117.2, 113.8, 113.7, 73.5, 73.2, 71.5, 71.3, 66.7, 66.6, 66.5 (2C), 55.2, 43.9, 43.9, 38.5, 38.0, 37.7, 37.6,

24.7, 22.8 (2C); LRMS (EI, 70 eV) *m/z* (%): 377 (M^+, 23), 276 (100), 232 (6), 204 (9); HRMS *m/z* (ESI) calcd for $C_{24}H_{28}NO_3$ ($[M+H]^+$) 378.2064, found 378.2074.

3-(2-(1,4-Dioxan-2-yl)-1-(4-methoxyphenyl)ethyl)-1,2-dimethyl-1*H*-indole (4aia):

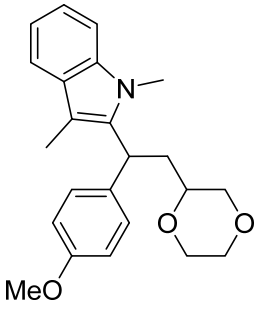


dr = 1:1

Brown oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.34 (d, *J* = 7.6 Hz, 1H), 7.25-7.23 (m, 3H), 7.10 (t, *J* = 7.6 Hz, 1H), 6.93 (t, *J* = 7.6 Hz, 1H), 6.77 (d, *J* = 8.0 Hz, 2H), 4.53-4.49 (m, 1H), 3.79-3.74 (m, 4H), 3.67 (s, 3H), 3.63-3.49 (m, 4H), 3.34-3.27 (m, 2H), 2.38 (s, 3H), 2.18-2.17 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 157.5, 137.2, 137.0, 133.8, 128.5, 126.6, 120.3, 119.4, 118.5, 113.4, 112.5, 108.6, 73.6, 71.5, 66.6, 66.5, 55.2, 36.0, 35.8, 29.5, 10.3;

Brown oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.60 (d, *J* = 7.6 Hz, 1H), 7.23 (d, *J* = 6.8 Hz, 2H), 7.12 (t, *J* = 7.6 Hz, 1H), 7.02 (t, *J* = 7.6 Hz, 1H), 6.77 (d, *J* = 8.4 Hz, 2H), 4.32 (t, *J* = 8.0 Hz, 1H), 3.76-3.74 (m, 5H), 3.65-3.47 (m, 7H), 3.36-3.31 (m, 1H), 2.36-2.31 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 157.7, 137.1, 136.9, 132.7, 128.5, 126.8, 120.3, 119.4, 118.8, 113.7, 108.7, 73.6, 71.4, 66.7, 66.6, 55.2, 37.1, 36.9, 29.5, 10.7;

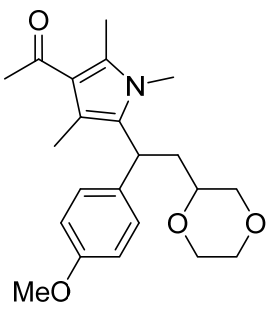
(EI, 70 eV) *m/z* (%): 365 (M^+, 24), 264 (100), 220 (16), 145 (15); HRMS *m/z* (ESI) calcd for $C_{23}H_{28}NO_3$ ($[M+H]^+$) 366.2064, found 366.2072.



2-(2-(1,4-Dioxan-2-yl)-1-(4-methoxyphenyl)ethyl)-1,3-dimethyl-1*H*-indole (4aja):

dr = 1.2:1

Brown oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.56-7.53 (m, 1H), 7.24-7.07 (m, 5H), 6.82-6.78 (m, 2H), 4.77-4.73 (m, 0.51H), 4.53 (t, *J* = 7.6 Hz, 0.43H), 3.76-3.34 (m, 13H), 2.38 (s, 1.38H), 2.30-2.23 (m, 3H), 2.06 (t, *J* = 12.8 Hz, 0.62H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 158.1, 157.9, 137.6, 136.9, 136.7, 136.7, 134.3, 133.9, 128.7, 128.6, 128.5, 128.3, 121.0 (2C), 118.6, 118.6, 118.2, 118.2, 113.9, 113.7, 108.6, 108.5, 107.9, 107.3, 73.2, 73.0, 71.4, 71.3, 66.7, 66.6, 66.5, 66.5, 55.2, 36.4, 35.9, 35.4, 34.5, 30.4, 30.2, 29.7, 9.7, 9.2; (EI, 70 eV) *m/z* (%): 365 (M^+, 66), 250 (23), 217 (18), 158 (100); HRMS *m/z* (ESI) calcd for $C_{23}H_{28}NO_3$ ($[M+H]^+$) 366.2064, found 366.2075.

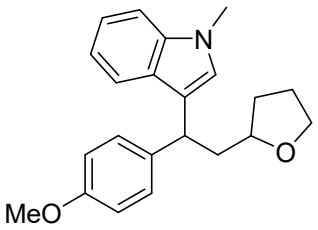


1-(5-(2-(1,4-Dioxan-2-yl)-1-(4-methoxyphenyl)ethyl)-1,2,4-trimethyl-1*H*-pyrrol-3-yl)ethan-1-one (4aka):

dr = 1.8:1

Brown oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.07 (d, *J* = 8.0 Hz, 2H), 6.84-6.80 (m, 2H), 4.59-4.55 (m, 0.61H), 4.36 (t, *J* = 7.6 Hz, 0.34H), 3.78-3.58 (m, 9H), 3.40-3.14 (m, 4H), 2.45-2.40 (m, 5H), 2.30-2.01 (m, 4H), 2.07-1.83 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 196.1 (2C), 158.0, 157.8, 135.2, 134.9, 134.5, 134.0, 130.7, 129.5, 128.3, 128.0, 121.6, 121.6, 116.9, 115.6, 113.9, 113.8, 73.3, 73.2, 71.4, 71.2, 66.7, 66.6, 66.5, 55.2, 35.5, 34.9, 34.3, 34.0, 31.5, 31.4, 31.1, 29.7, 12.6, 12.4, 12.4, 12.3; (EI, 70 eV) *m/z* (%): 371 (M^+, 33), 270 (100), 228 (14), 152 (24); HRMS *m/z* (ESI) calcd for $C_{22}H_{30}NO_4$ ($[M+H]^+$) 372.2169, found 372.2179.

3-(1-(4-methoxyphenyl)-2-(tetrahydrofuran-2-yl)ethyl)-1-methyl-1*H*-indole



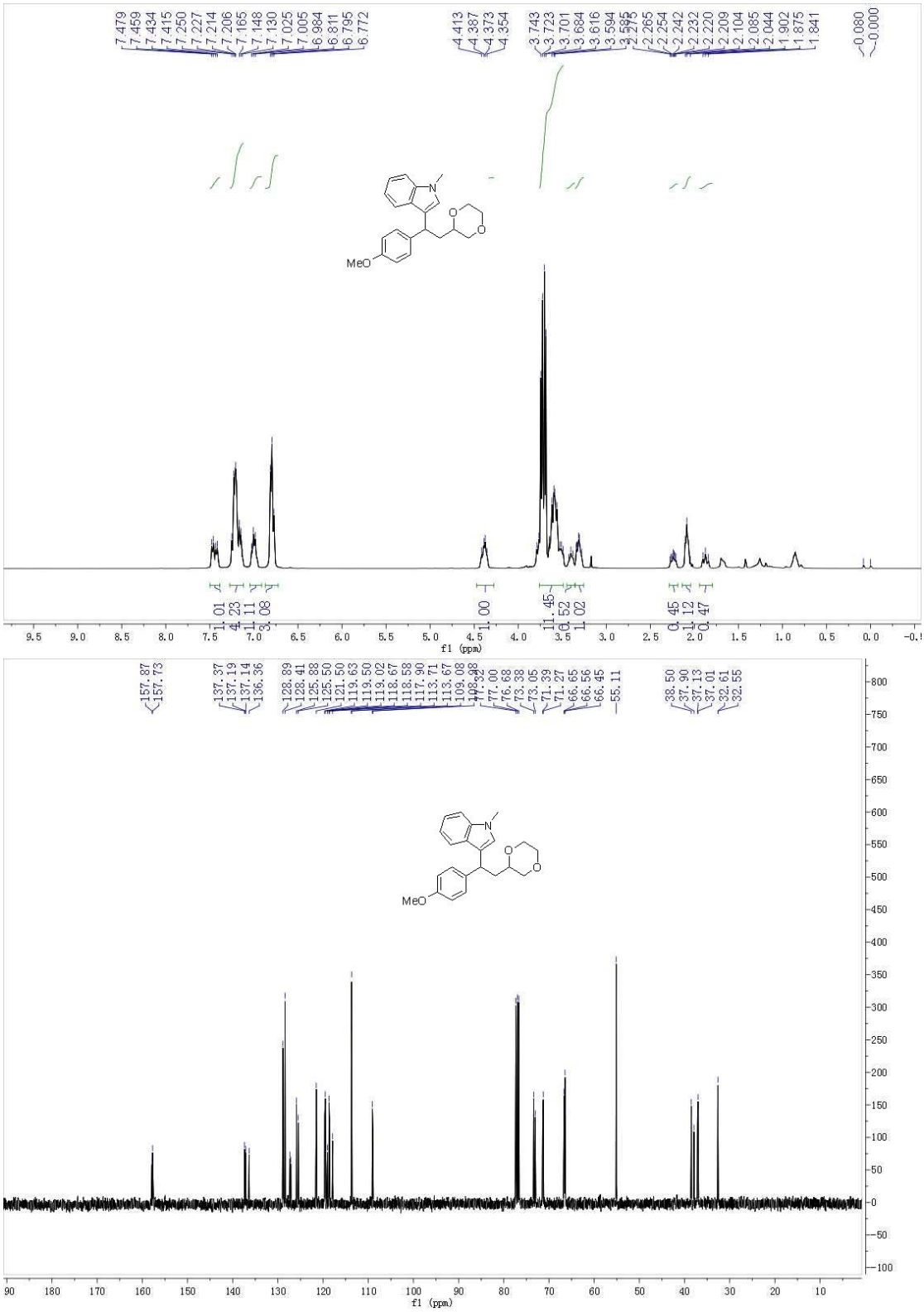
(4aab):

dr = 1.1:1

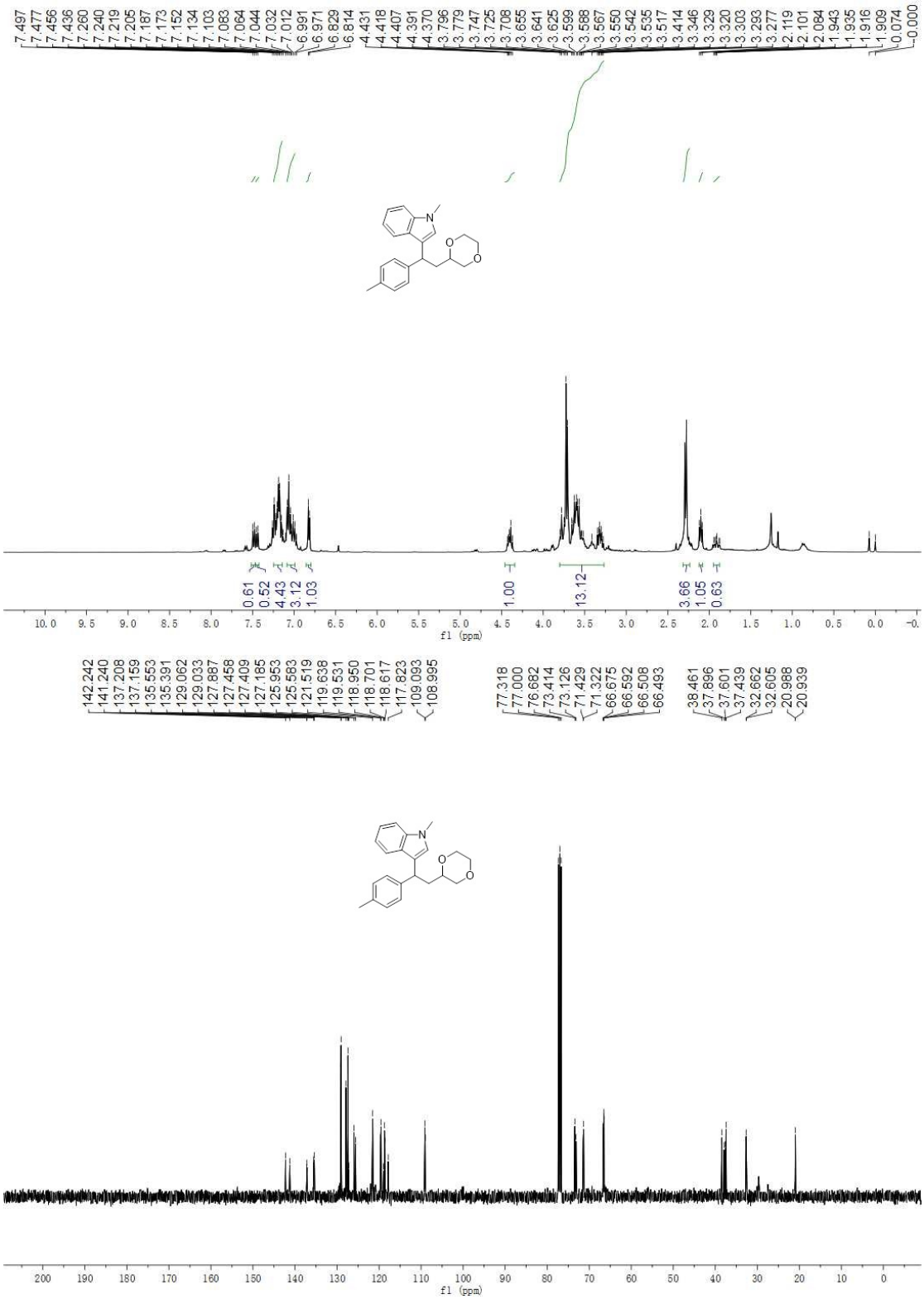
Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.50-7.45 (m, 1H), 7.25-7.22 (m, 3H), 7.15 (t, *J* = 7.6 Hz, 1H), 7.01-6.99 (m, 1H), 6.85 (s, 1H), 6.81-6.78 (m, 2H), 4.38-4.34 (m, 0.48H), 4.29 (t, *J* = 7.6 Hz, 0.50H), 3.88-3.83 (m, 1H), 3.74-3.64 (m, 8H), 2.43-2.35 (m, 0.51H), 2.33-2.22 (m, 1.05H), 2.11-1.93 (m, 1.50H), 1.89-1.77(m, 2H), 1.54-1.43 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 157.8, 157.7, 137.5, 137.2, 137.1, 128.9, 128.5, 127.3, 126.0, 125.5, 121.4, 121.4, 119.7, 119.6, 119.3, 118.6, 113.7, 113.6, 109.0 (2C), 67.4, 55.1, 55.1, 42.5, 42.2, 39.1, 39.0, 32.6, 31.6, 31.3, 25.7, 25.7; LRMS (EI, 70 eV) m/z (%): 335 (M^+, 19), 250 (100), 205 (30), 145 (15); HRMS *m/z* (ESI) calcd for $C_{22}H_{26}NO_2$ ($[M+H]^+$) 336.1958, found 336.1965.

(D) Spectra

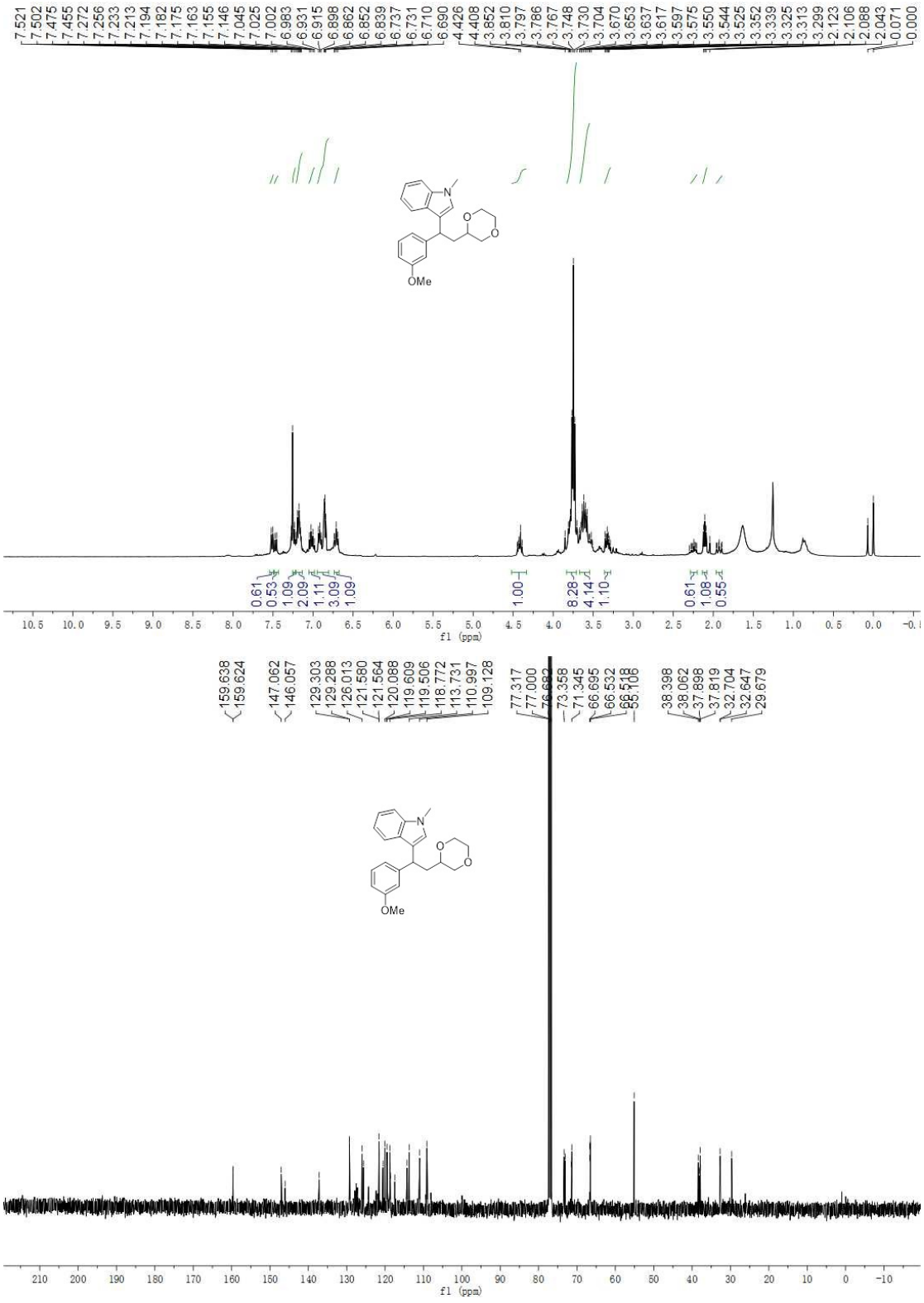
3-(2-(1,4-Dioxan-2-yl)-1-(4-methoxyphenyl)ethyl)-1-methyl-1*H*-indole (4aaa)



3-(2-(1,4-Dioxan-2-yl)-1-(*p*-tolyl)ethyl)-1-methyl-1H-indole (4baa)

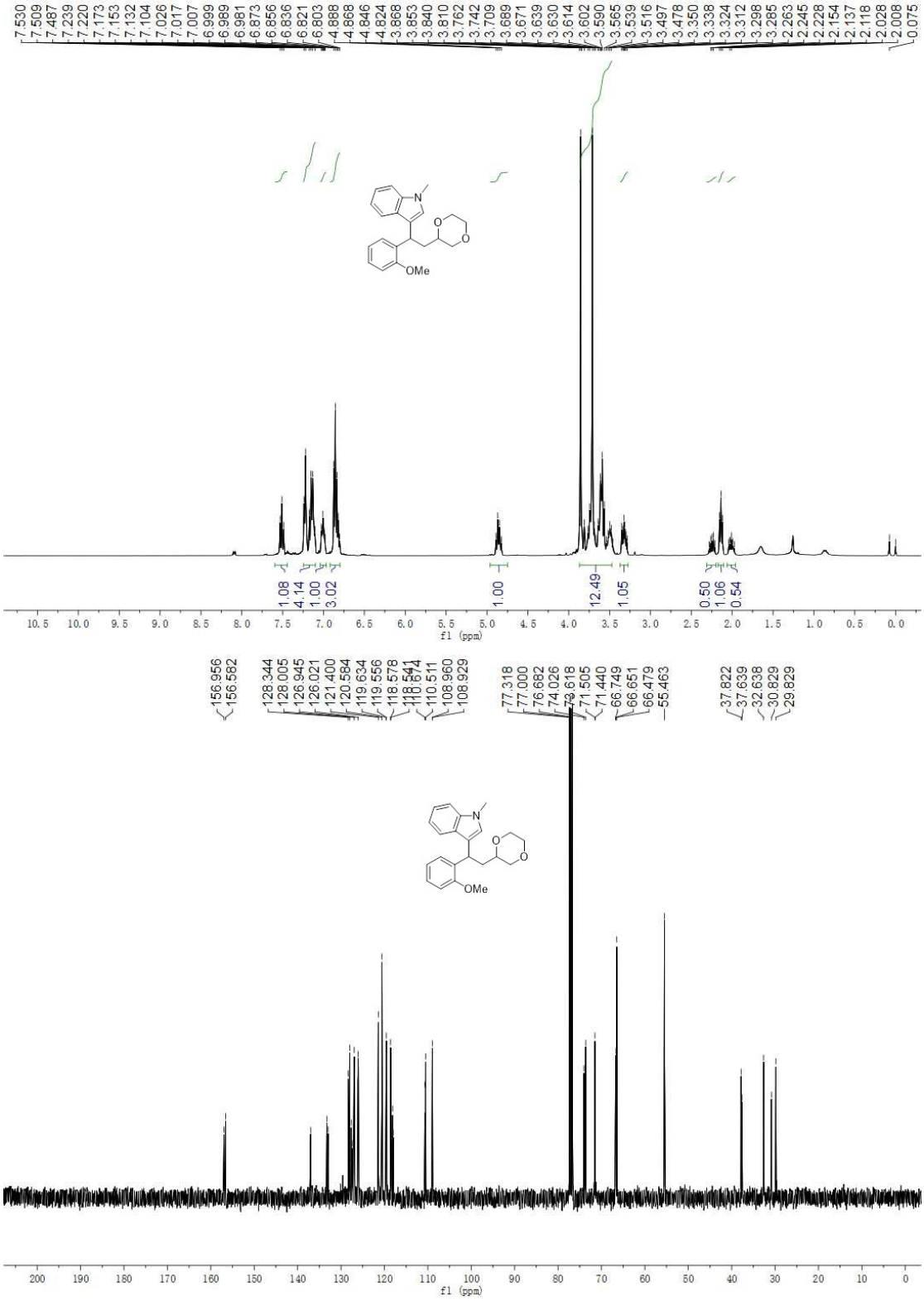


3-(2-(1,4-Dioxan-2-yl)-1-(3-methoxyphenyl)ethyl)-1-methyl-1*H*-indole (4daa)

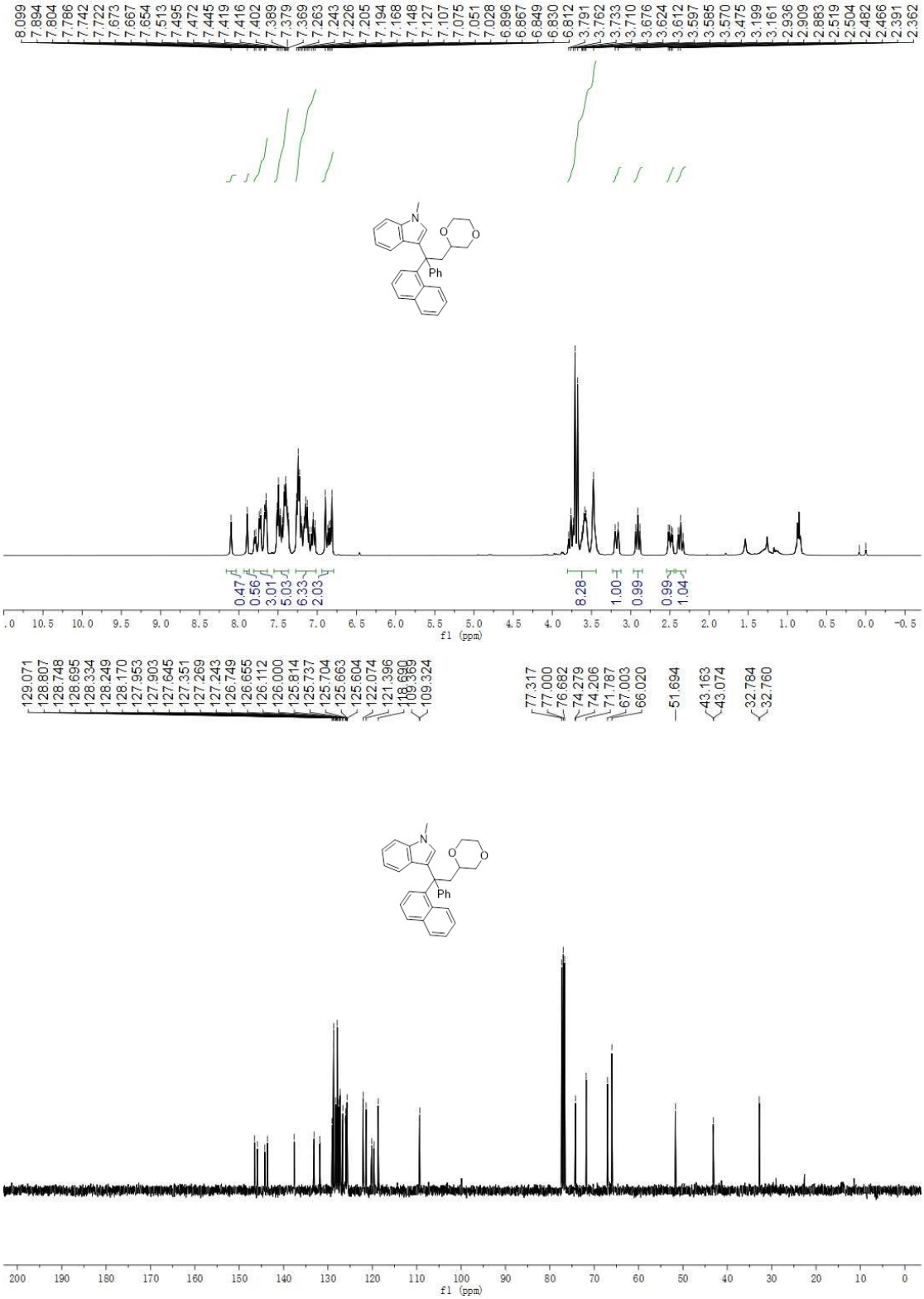


3-(2-(1,4-Dioxan-2-yl)-1-(2-methoxyphenyl)ethyl)-1-methyl-1*H*-indole

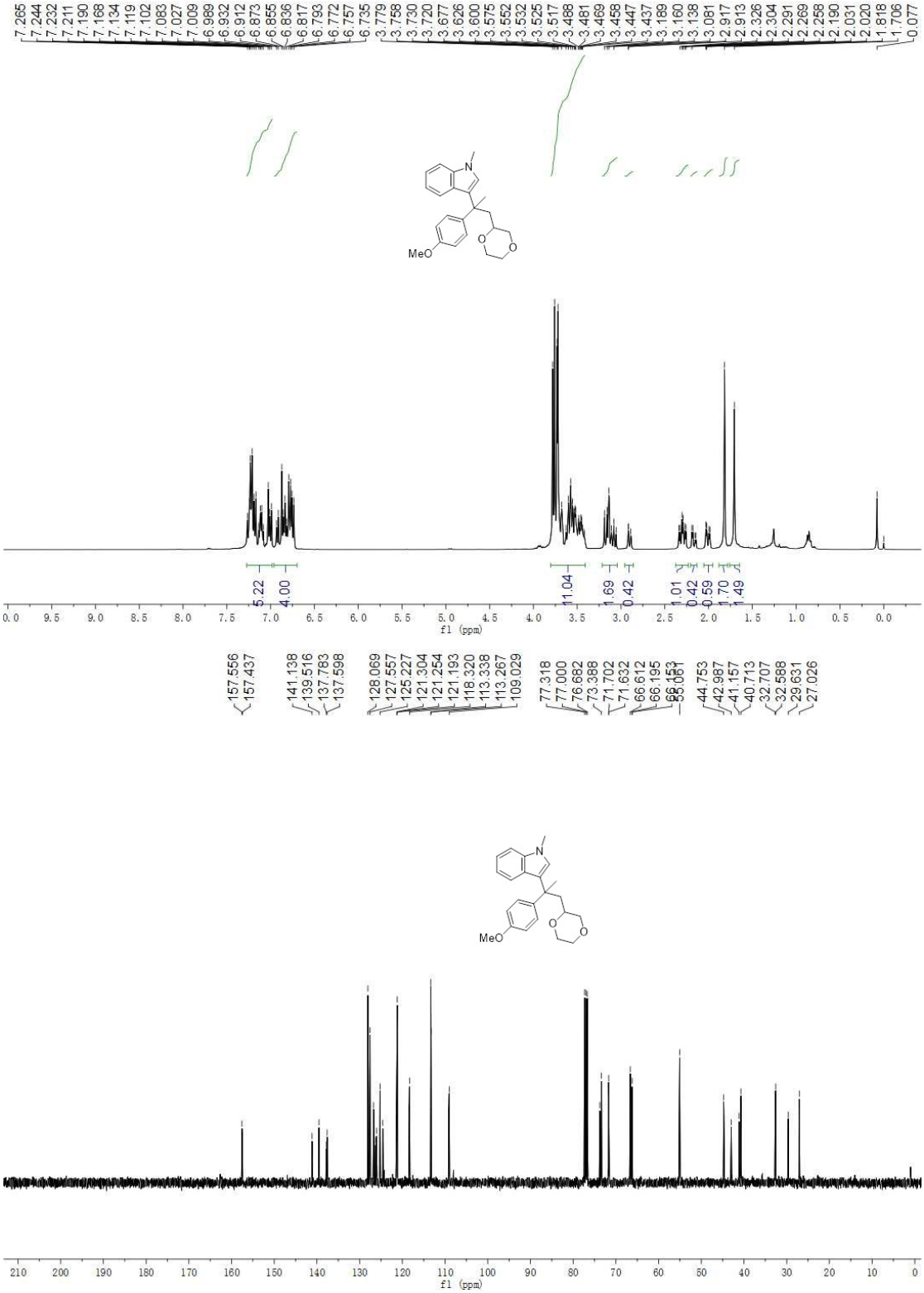
(4eaa)



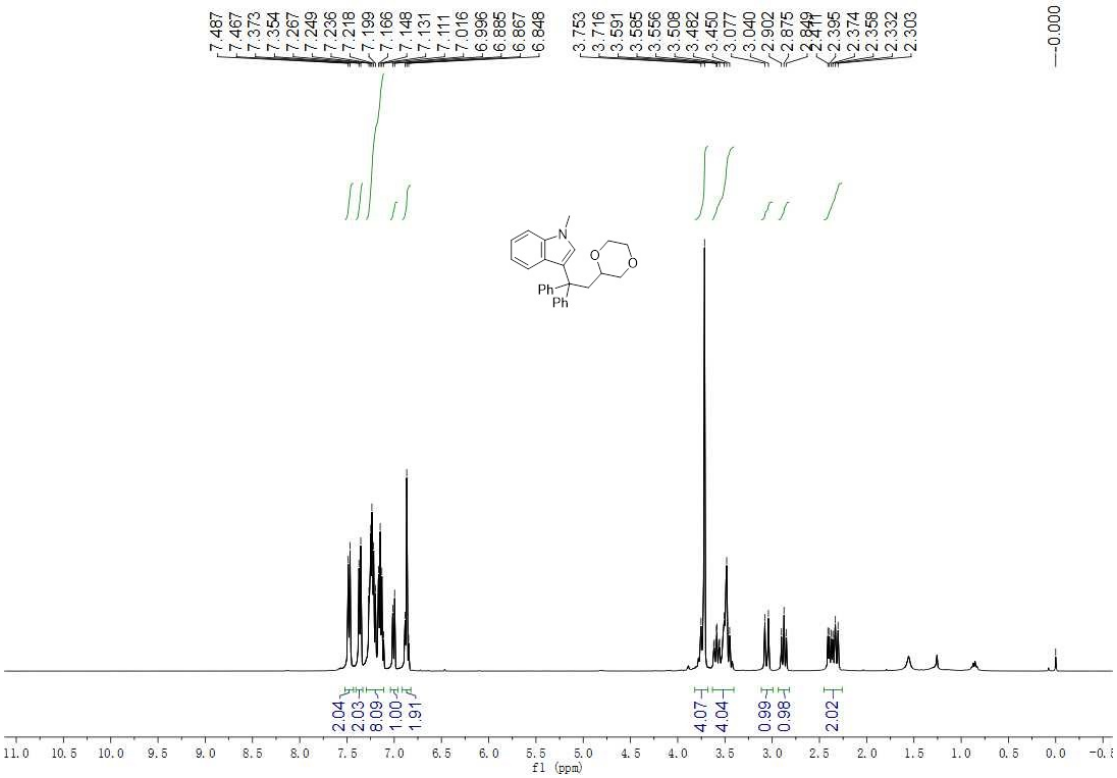
3-(2-(1,4-Dioxan-2-yl)-1-(naphthalen-1-yl)-1-phenylethyl)-1-methyl-1*H*-indole (4faa)

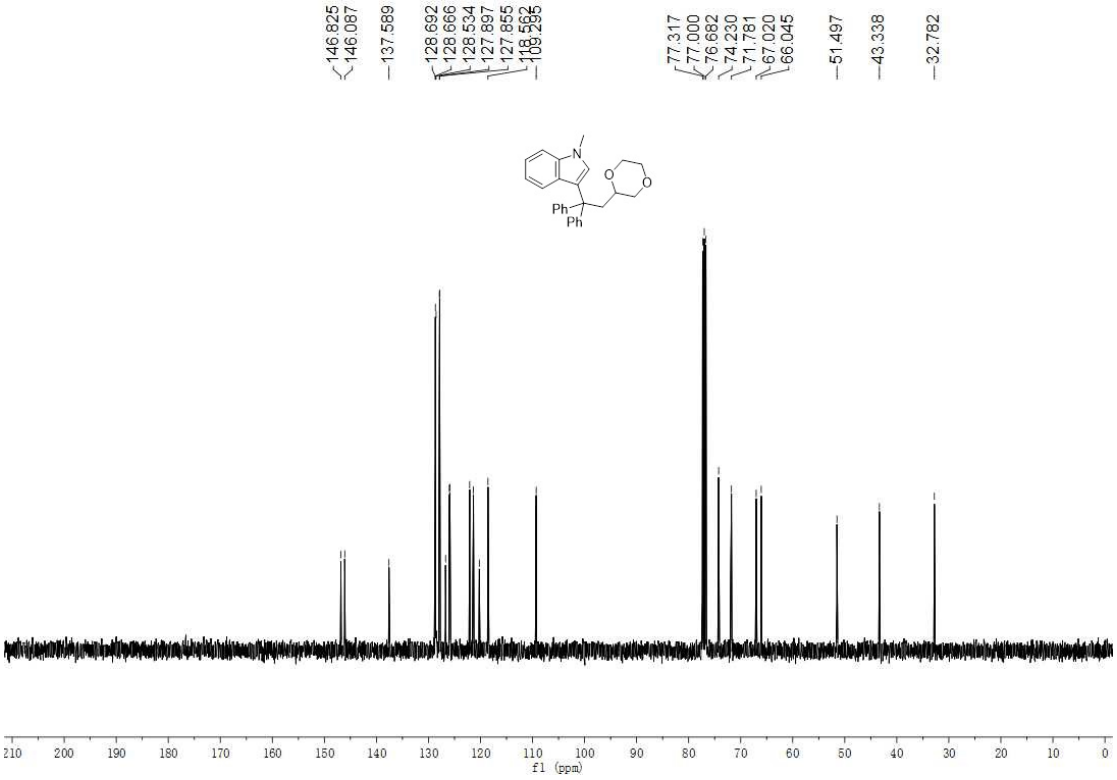


3-(1-(1,4-Dioxan-2-yl)-2-(4-methoxyphenyl)propan-2-yl)-1-methyl-1*H*-indole (4gaa)

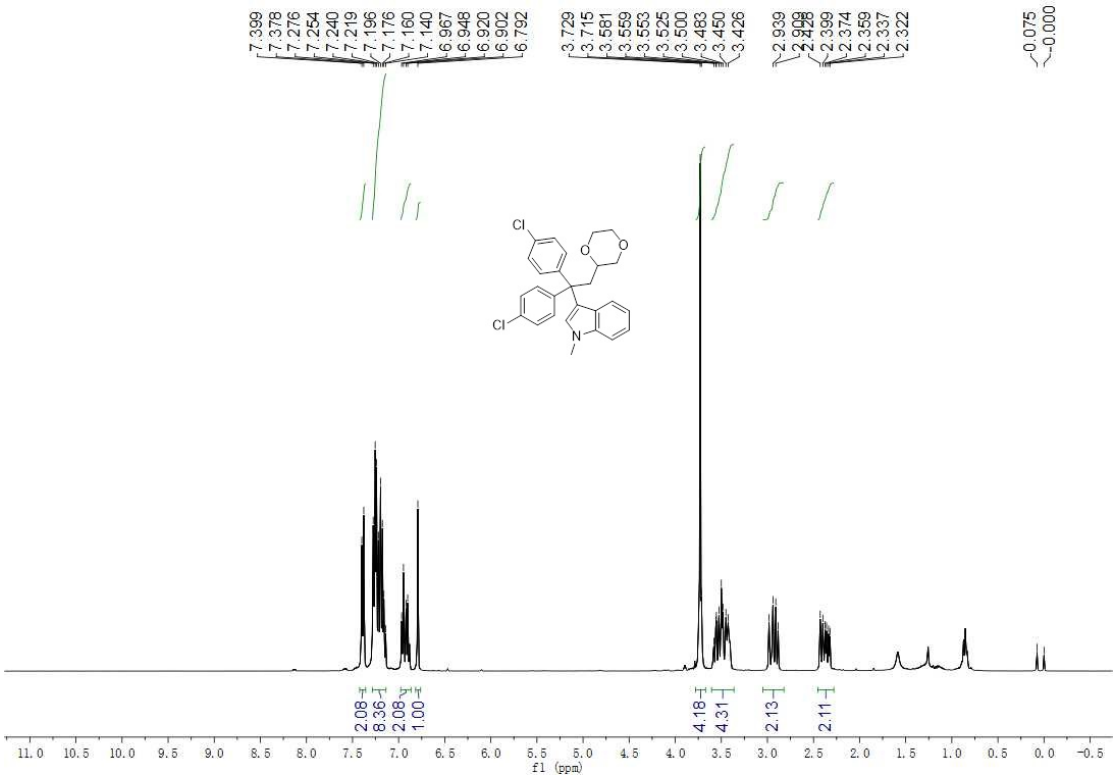


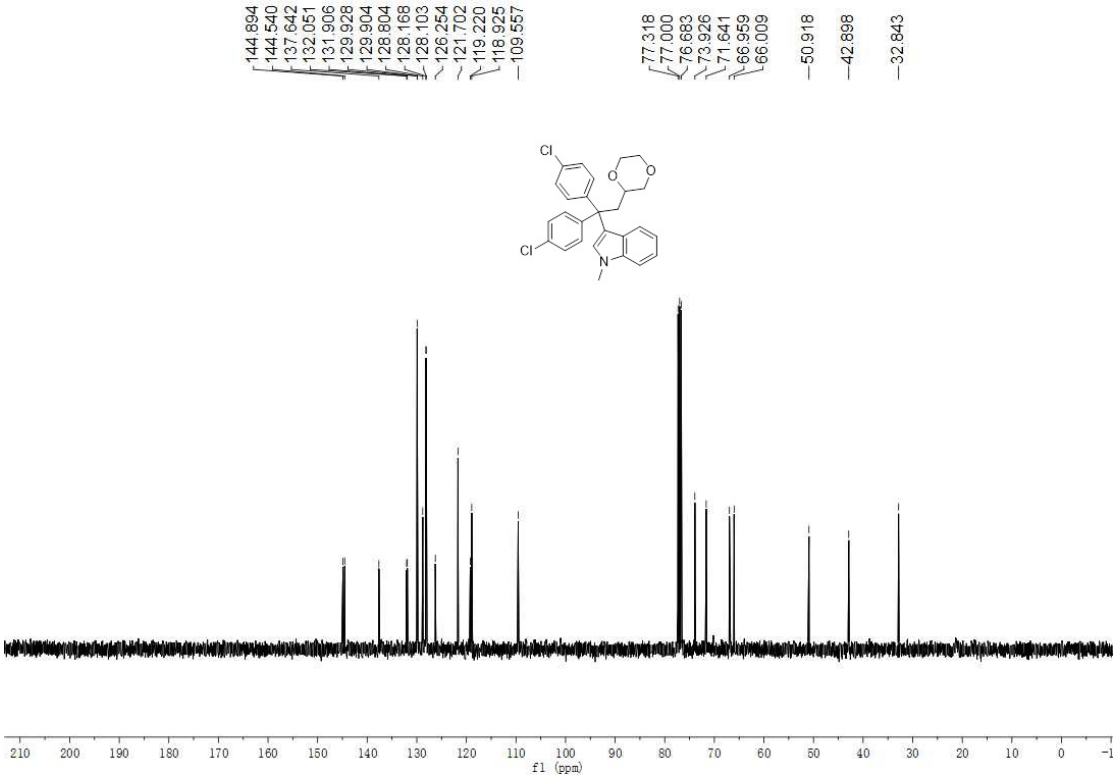
3-(2-(1,4-Dioxan-2-yl)-1,1-diphenylethyl)-1-methyl-1*H*-indole (4haa)



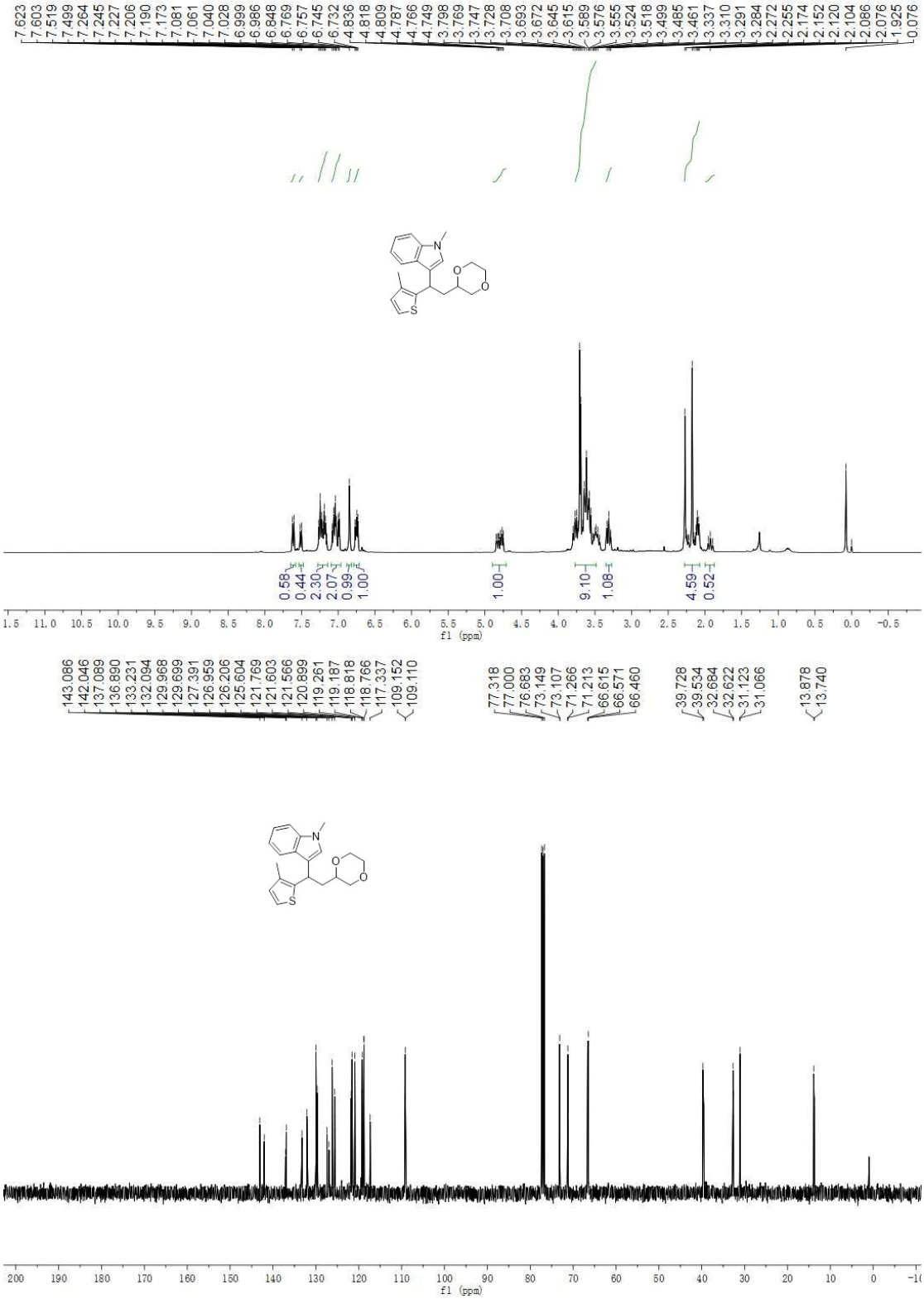


3-(1,1-bis(4-chlorophenyl)-2-(1,4-Dioxan-2-yl)ethyl)-1-methyl-1*H*-indole (4iaa)

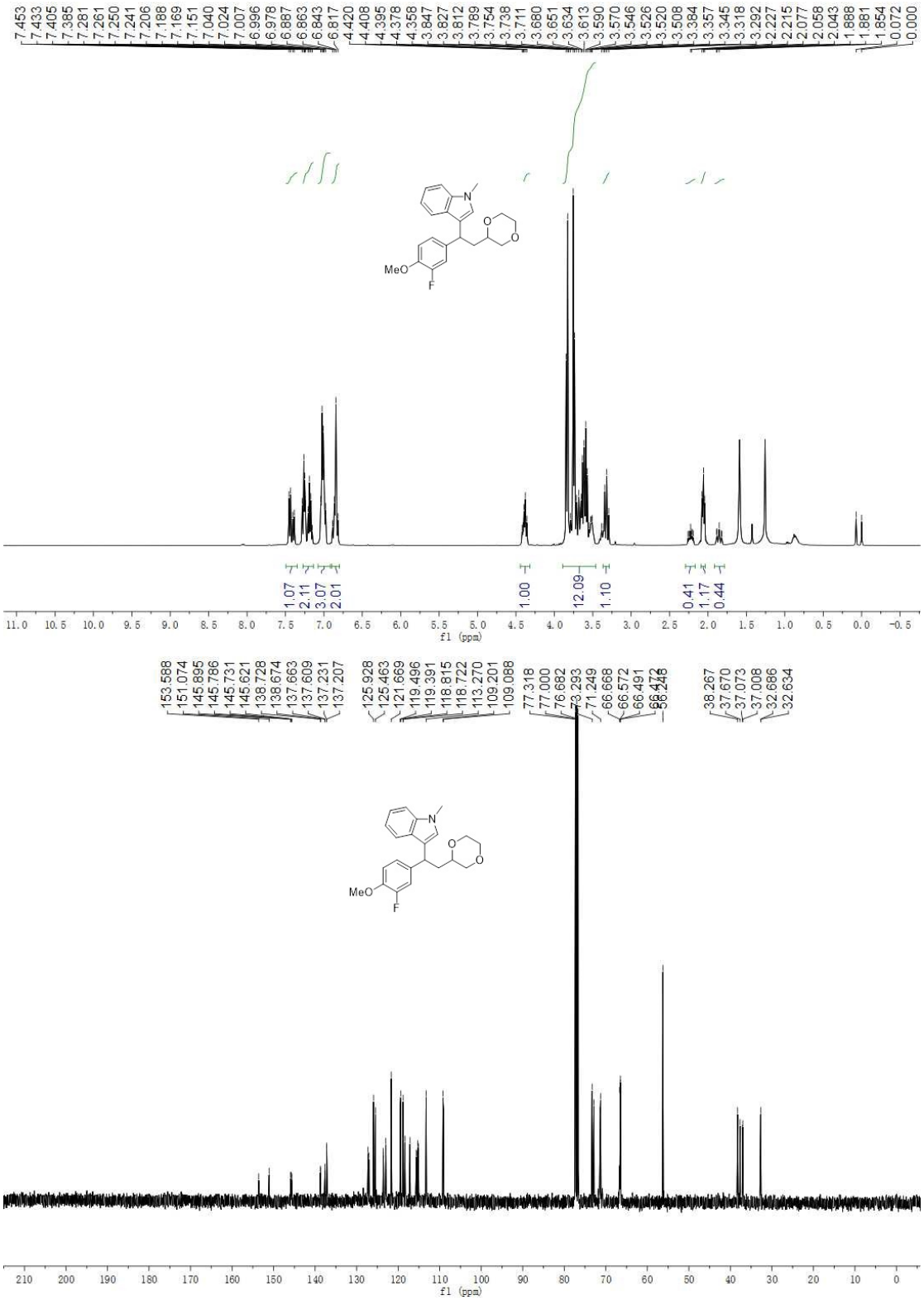


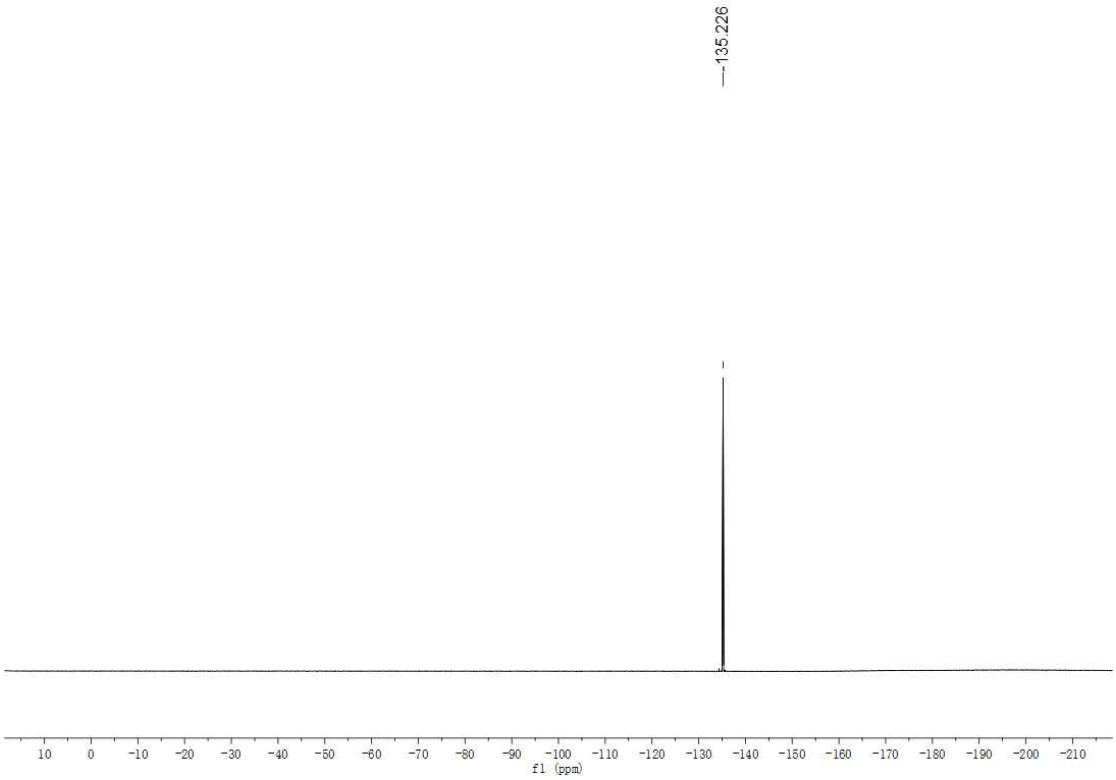


3-(2-(1,4-Dioxan-2-yl)-1-(3-methylthiophen-2-yl)ethyl)-1-methyl-1*H*-indole (4jaa)

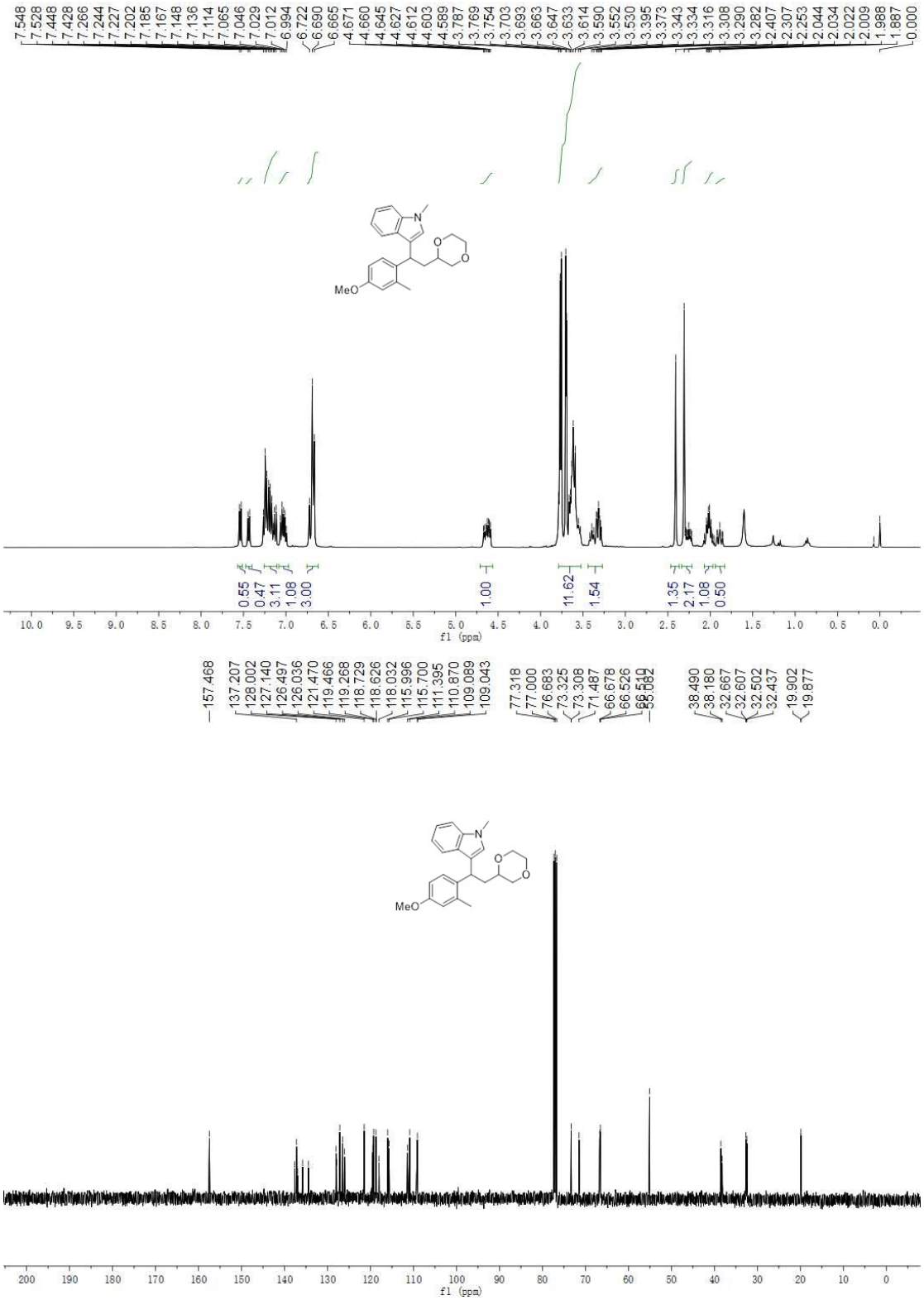


3-(2-(1,4-Dioxan-2-yl)-1-(3-fluoro-4-methoxyphenyl)ethyl)-1-methyl-1*H*-indole (4kaa)

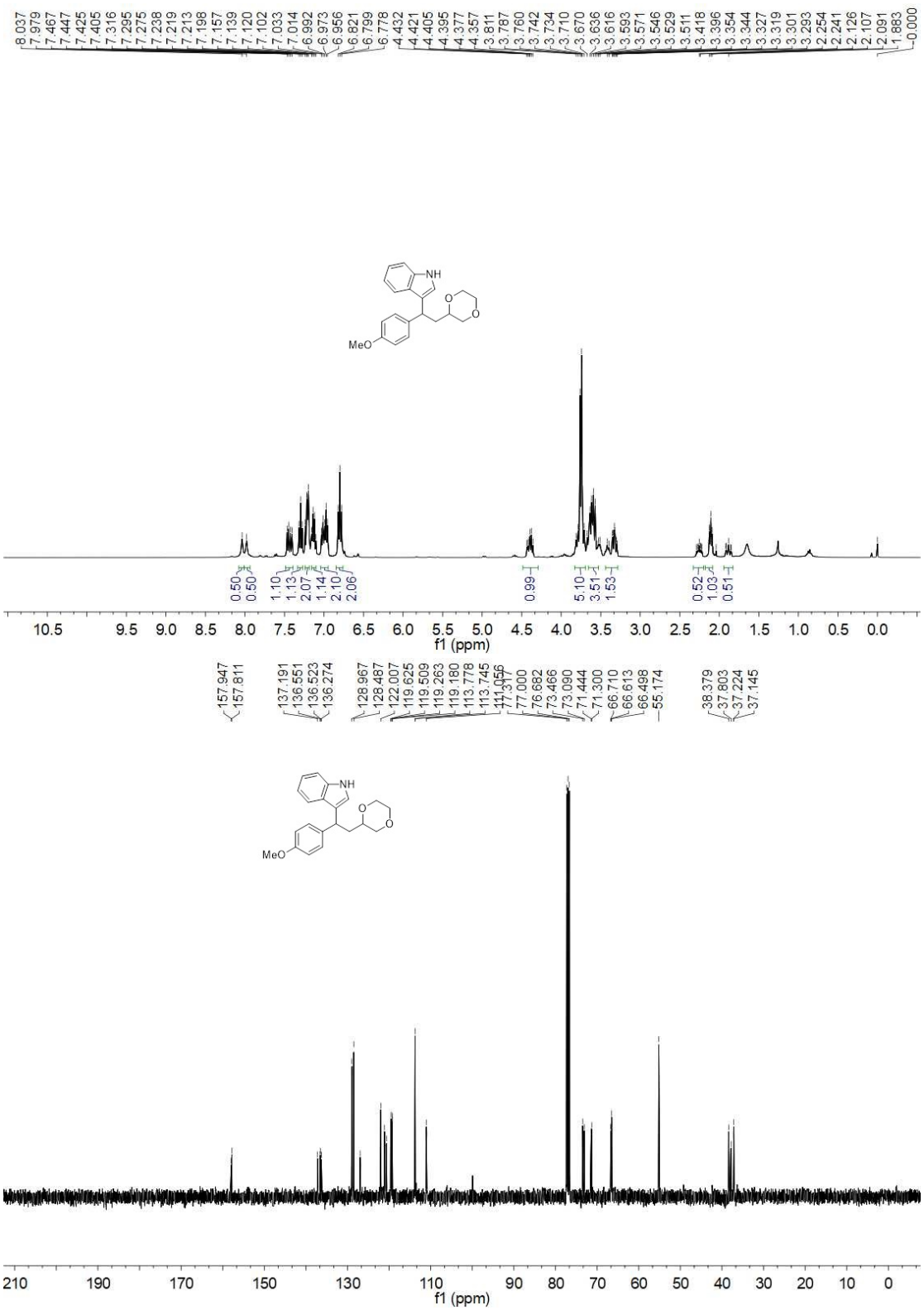



-135.226
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

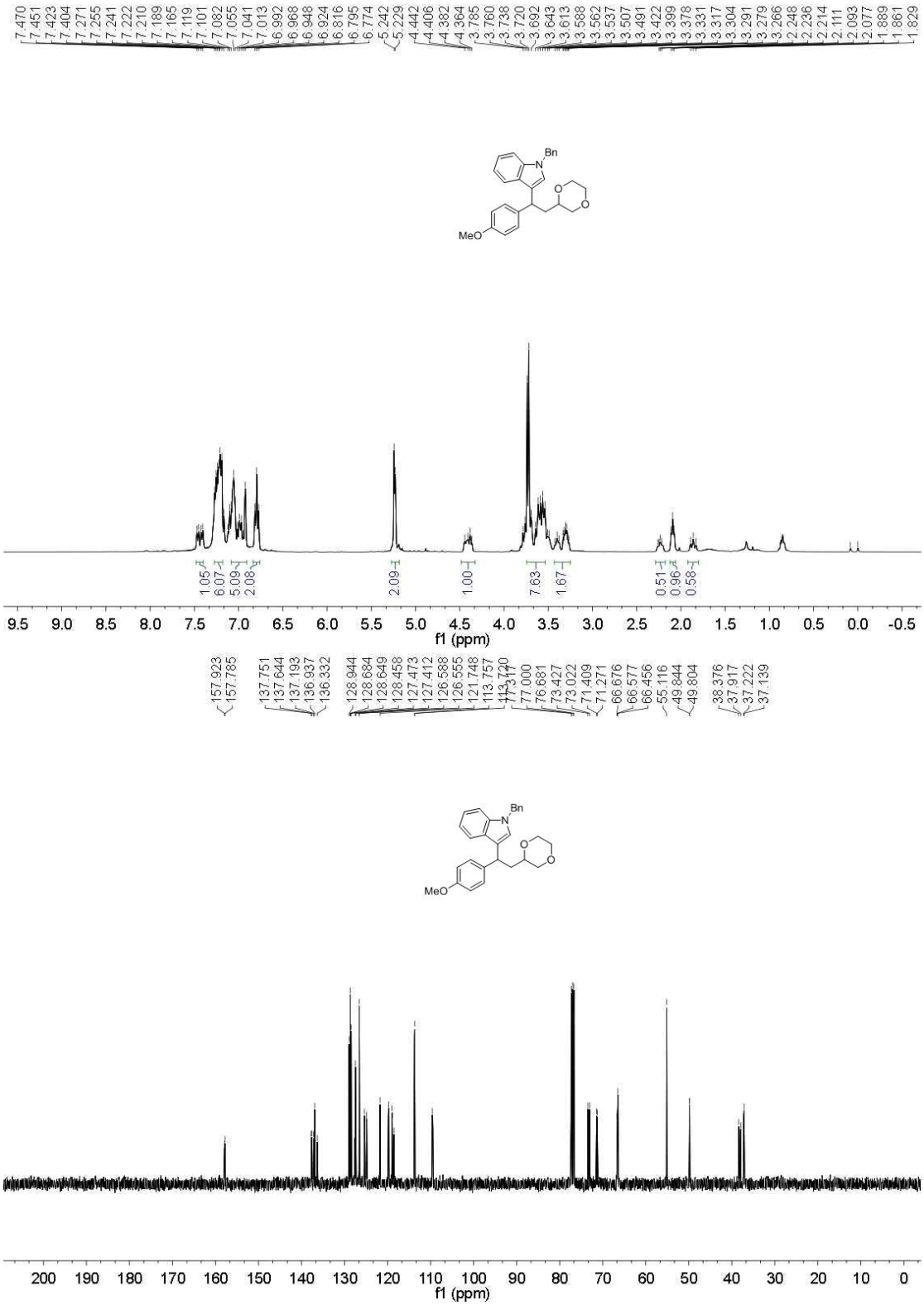
3-(2-(1,4-Dioxan-2-yl)-1-(4-methoxy-2-methylphenyl)ethyl)-1-methyl-1*H*-indole (4laa)



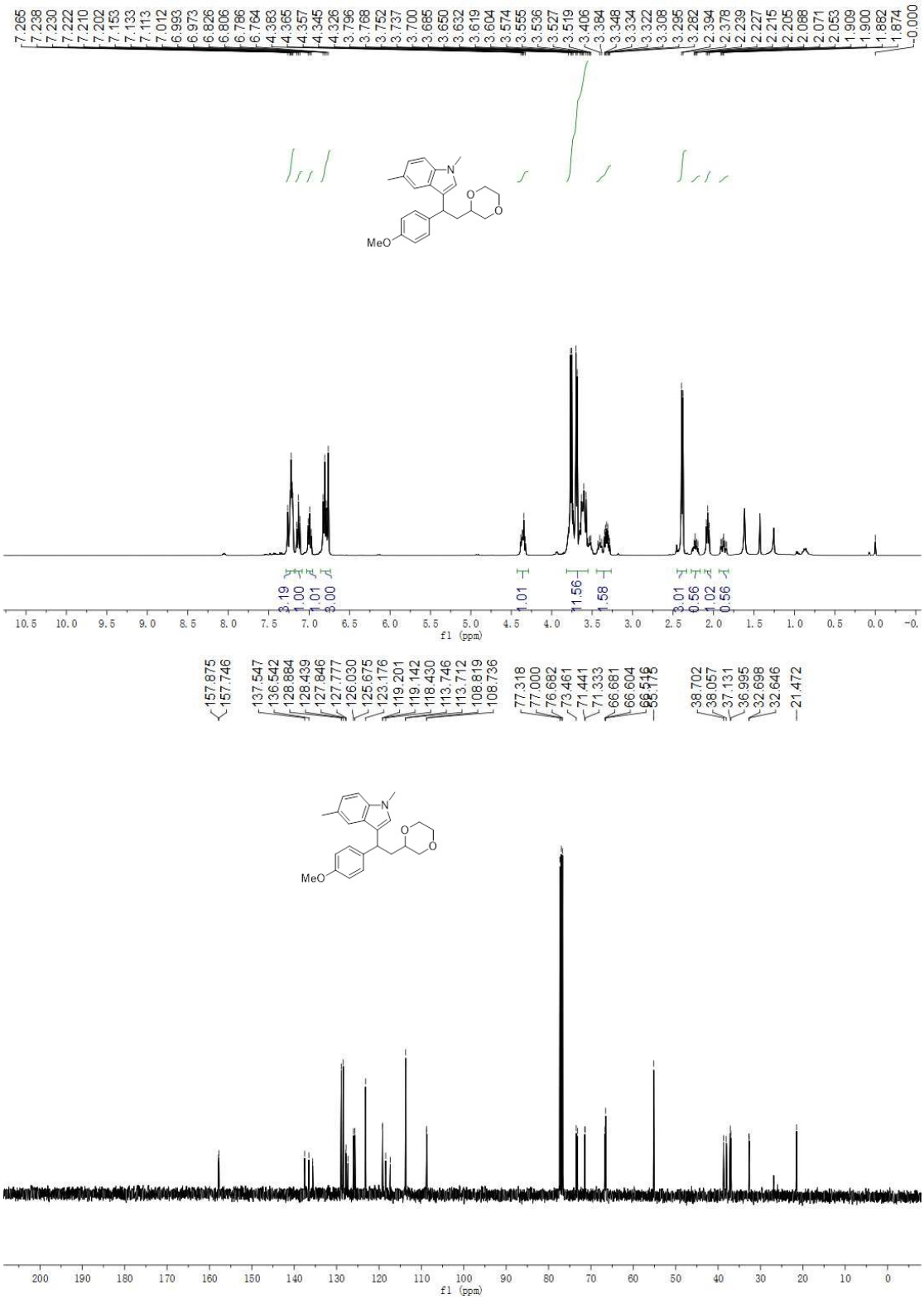
3-(2-(1,4-Dioxan-2-yl)-1-(4-methoxyphenyl)ethyl)-1*H*-indole (4aba)



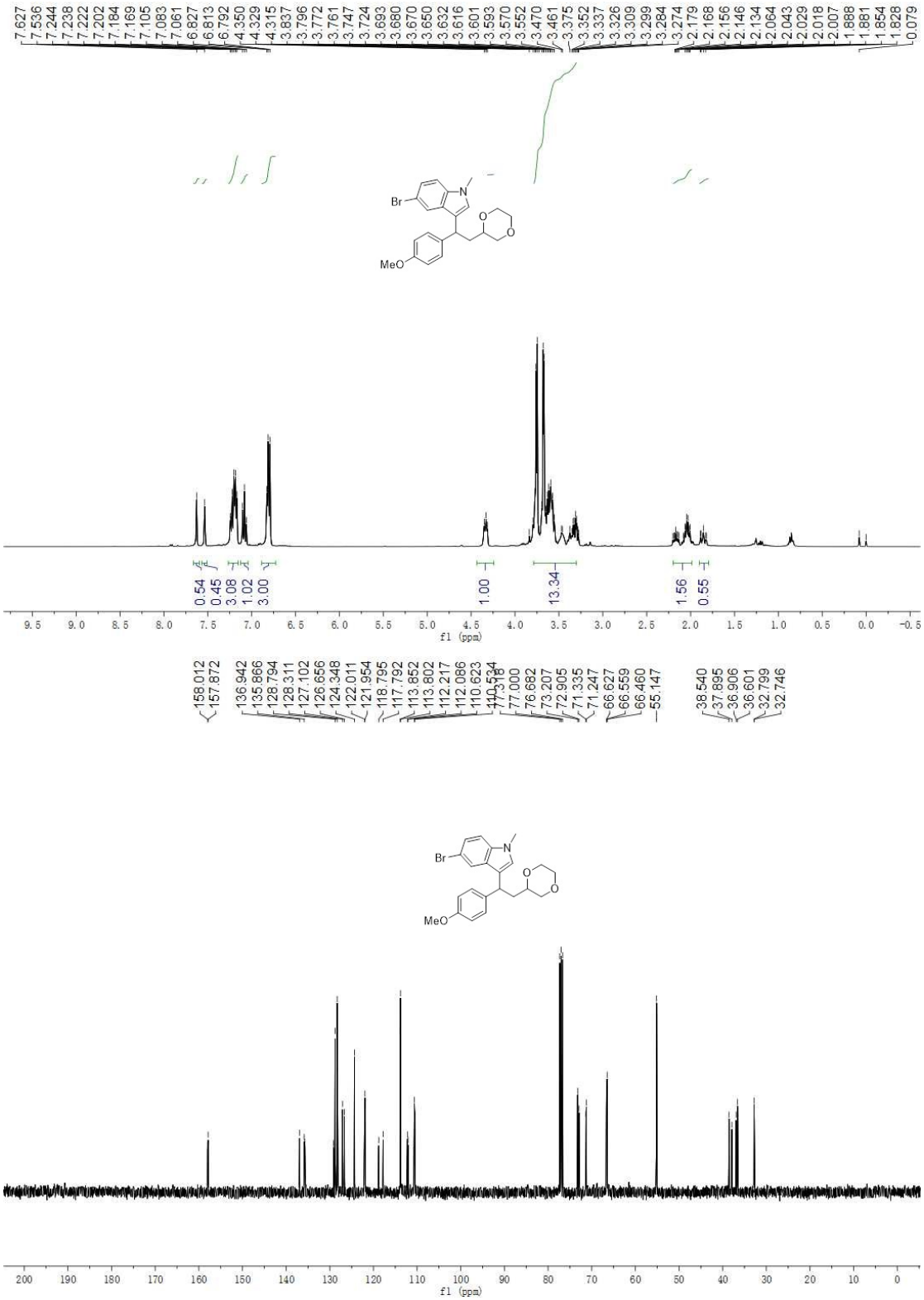
3-(2-(1,4-Dioxan-2-yl)-1-(4-methoxyphenyl)ethyl)-1-benzyl-1*H*-indole (4aca)



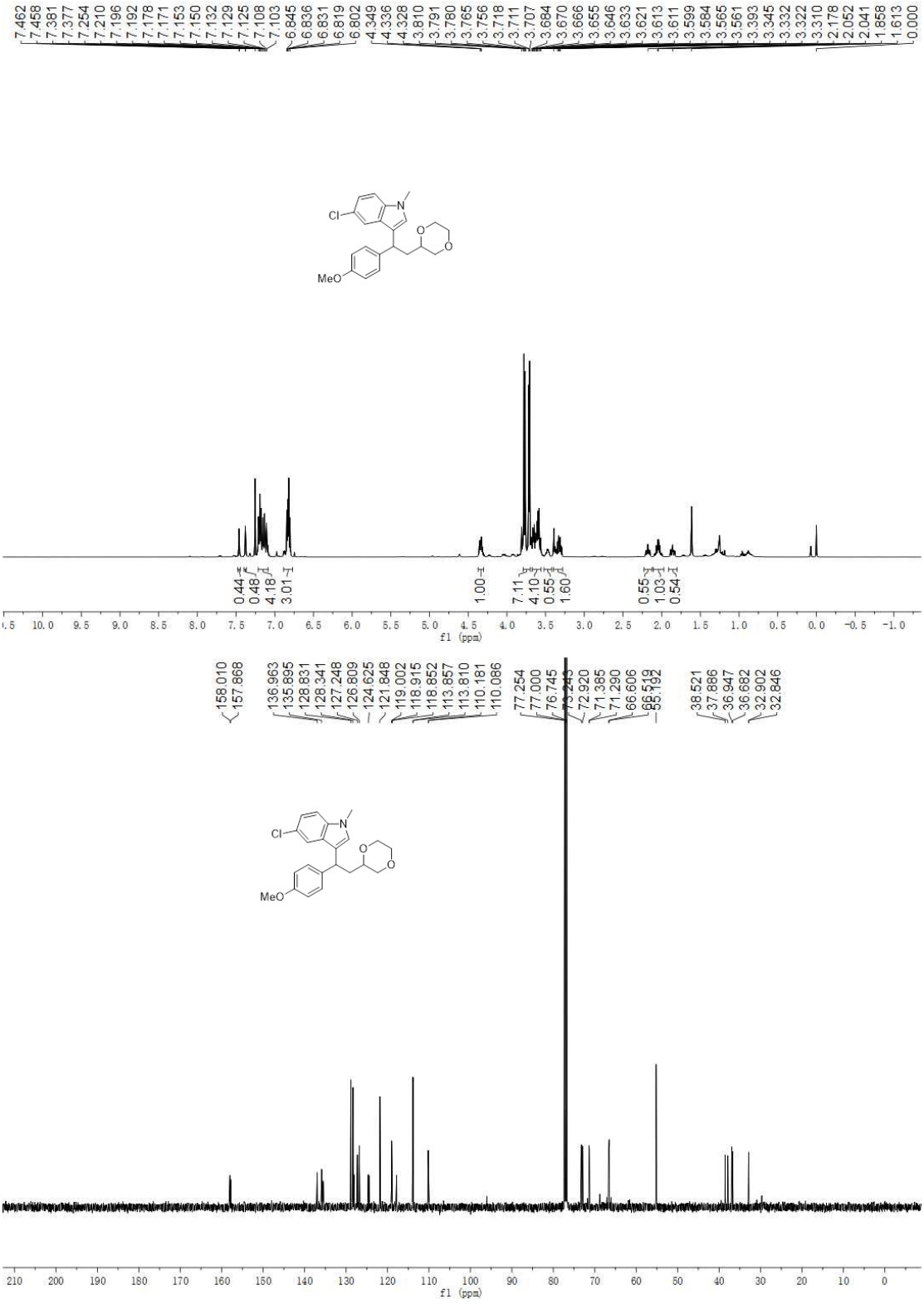
3-(1-(4-methoxyphenyl)-2-(tetrahydrofuran-2-yl)ethyl)-1,5-dimethyl-1*H*-indole (4ada)



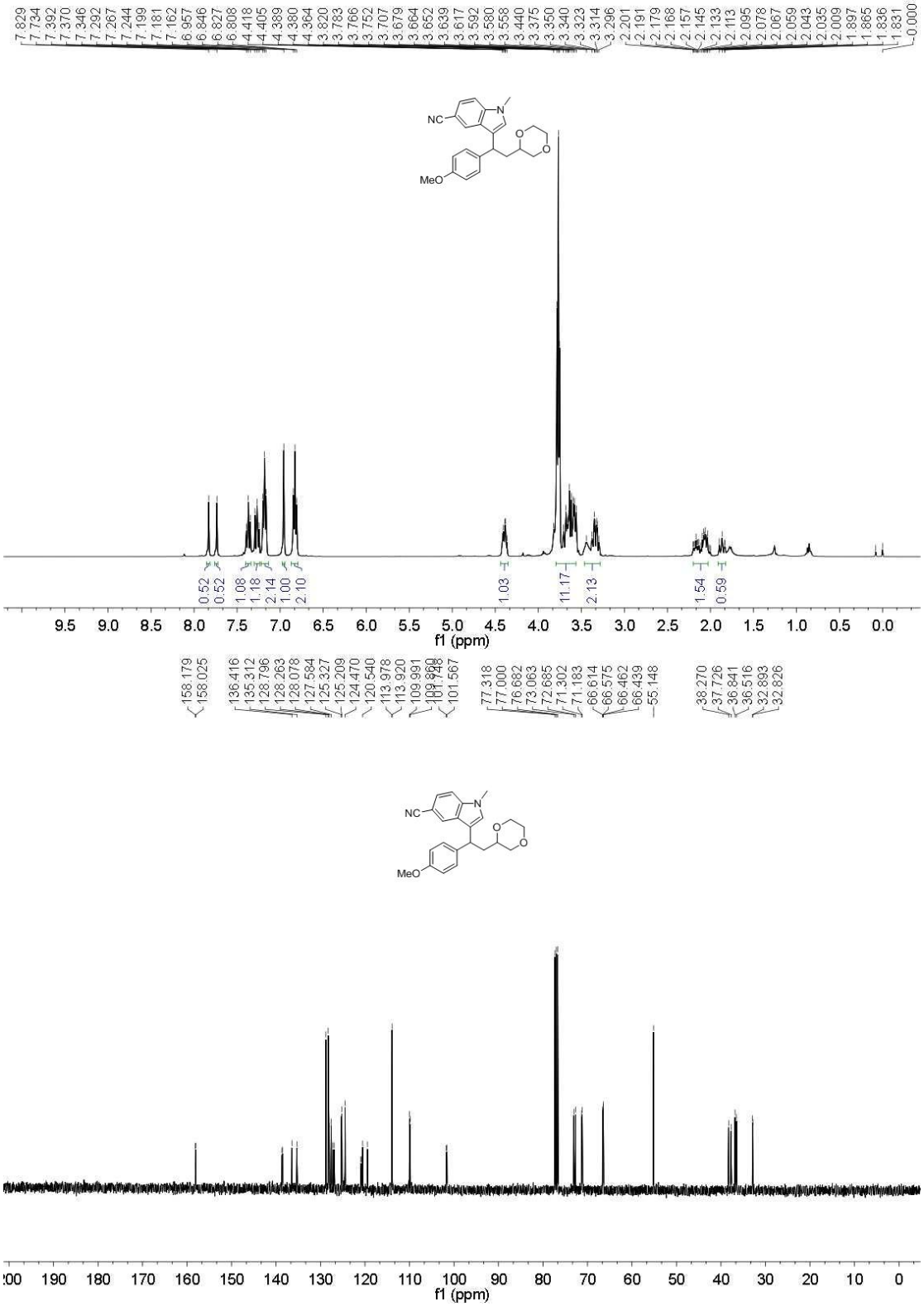
3-(2-(1,4-Dioxan-2-yl)-1-(4-methoxyphenyl)ethyl)-5-bromo-1-methyl-1*H*-indole (4aea)



3-(2-(1,4-Dioxan-2-yl)-1-(4-methoxyphenyl)ethyl)-5-chloro-1-methyl-1*H*-indole (4afa)

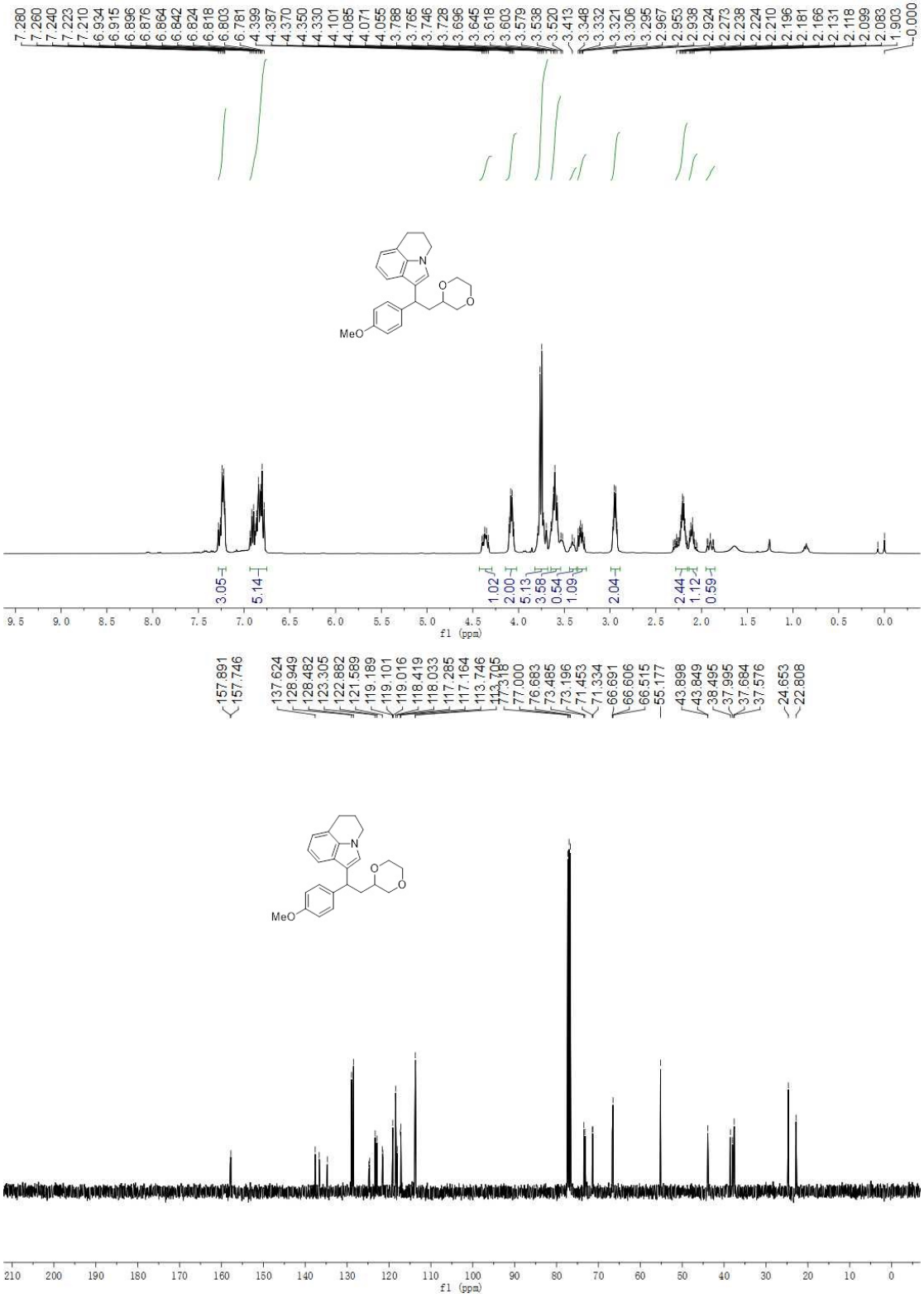


3-(2-(1,4-Dioxan-2-yl)-1-(4-methoxyphenyl)ethyl)-1-methyl-1*H*-indole-5-carbonitrile (4aga)

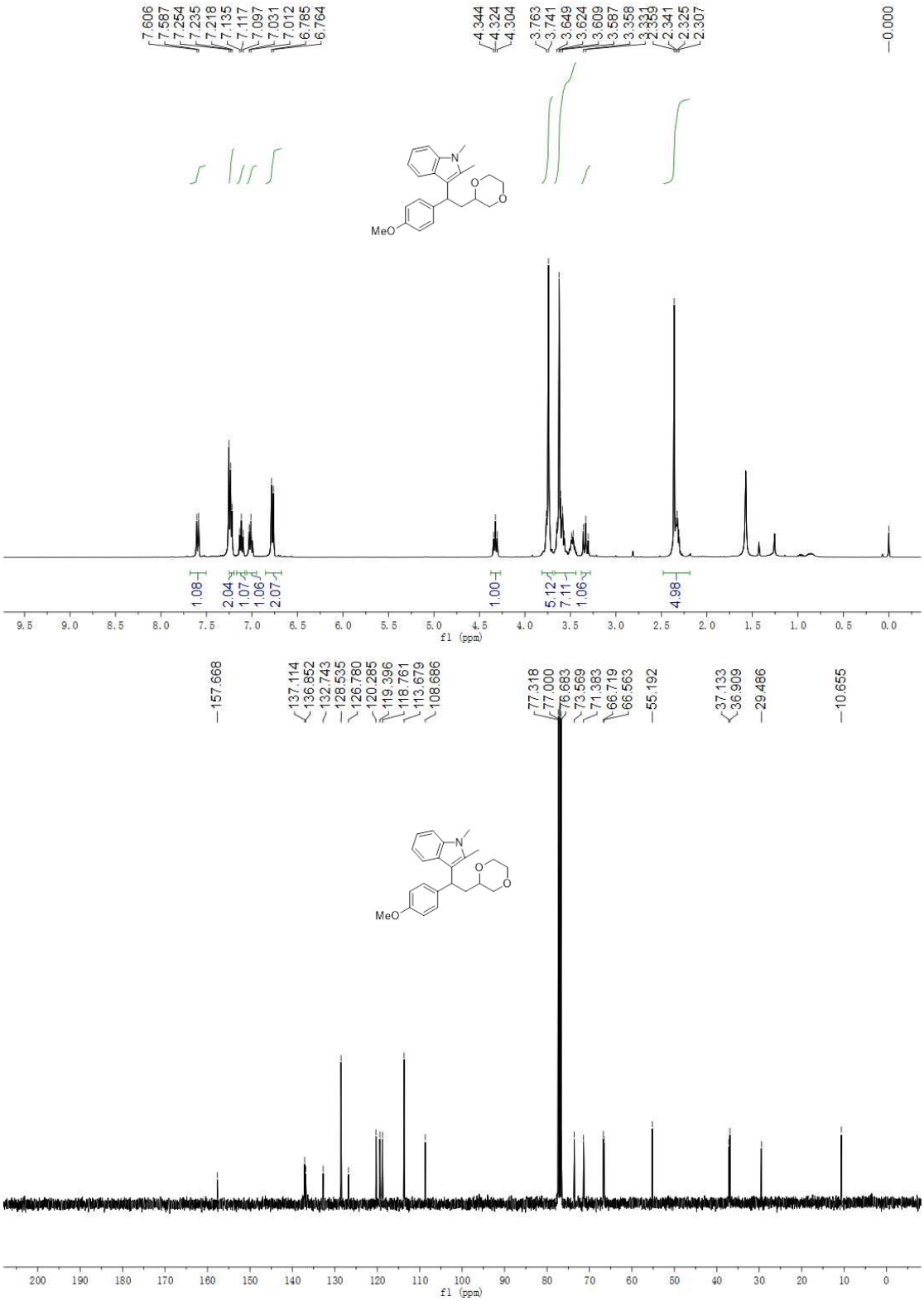


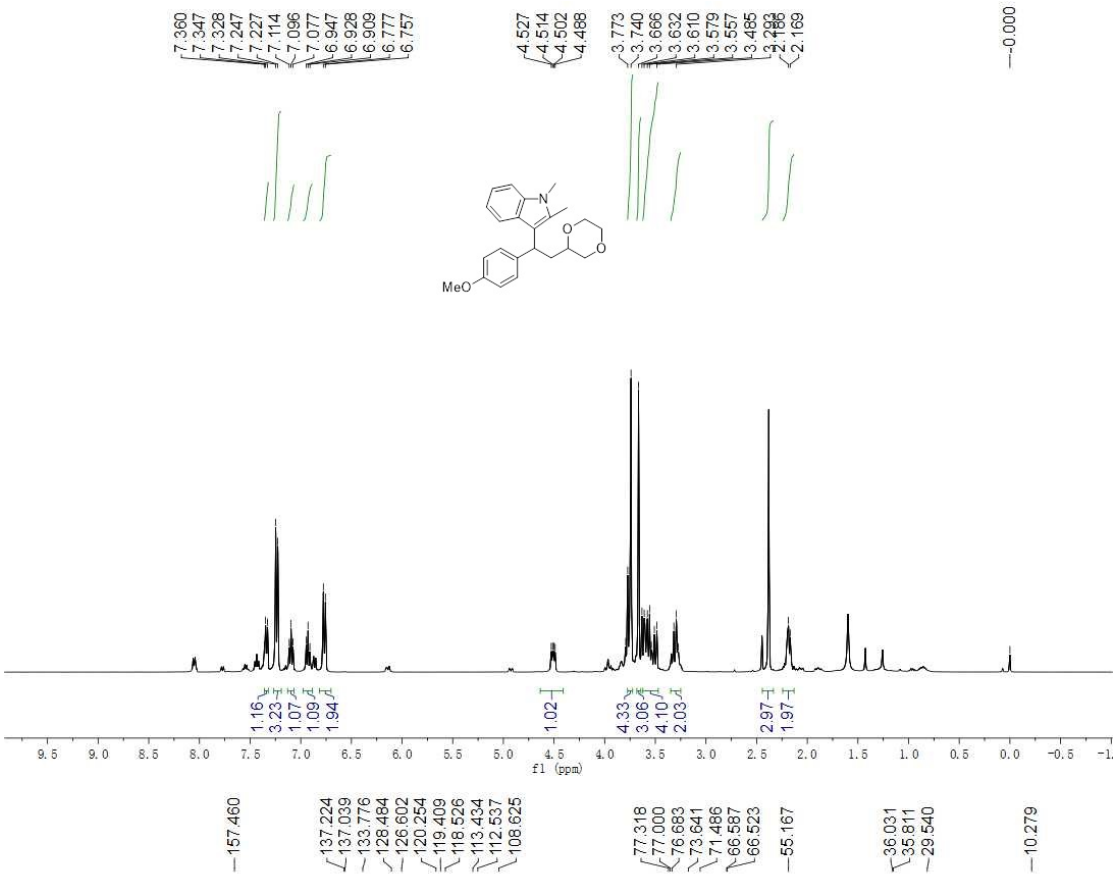
1-(2-(1,4-Dioxan-2-yl)-1-(4-methoxyphenyl)ethyl)-5,6-dihydro-4*H*-pyrrolo[3,2,1-*ij*]quinoline

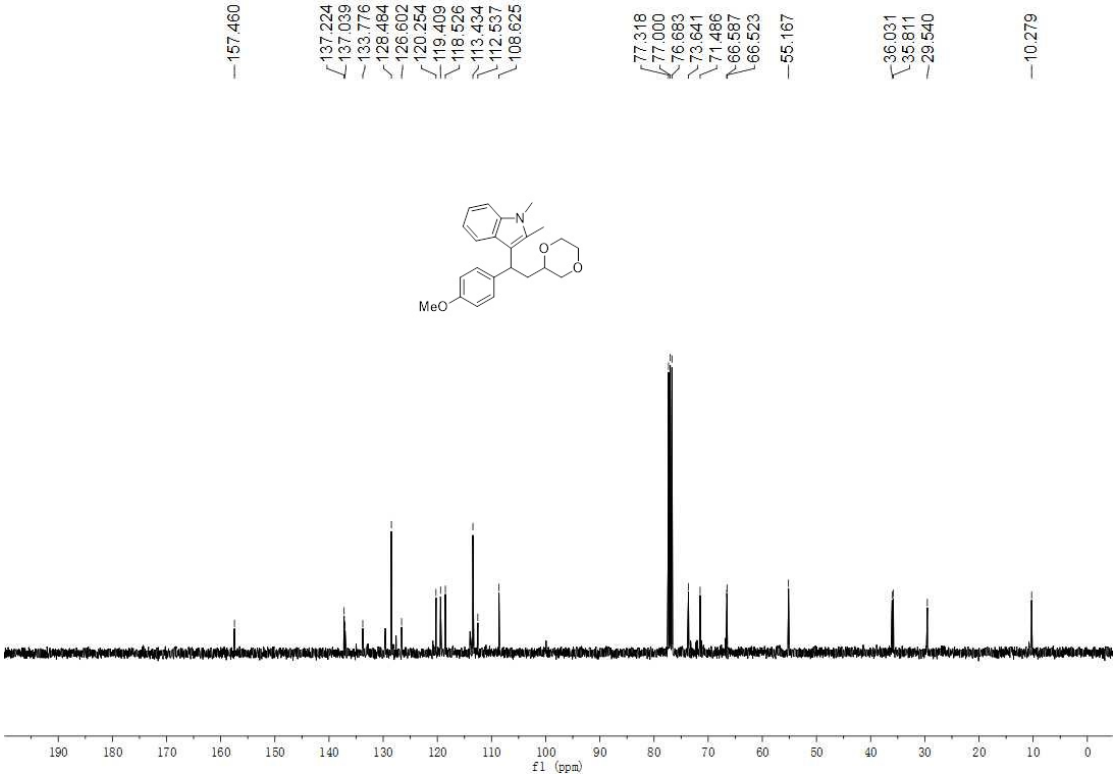
(4aha)



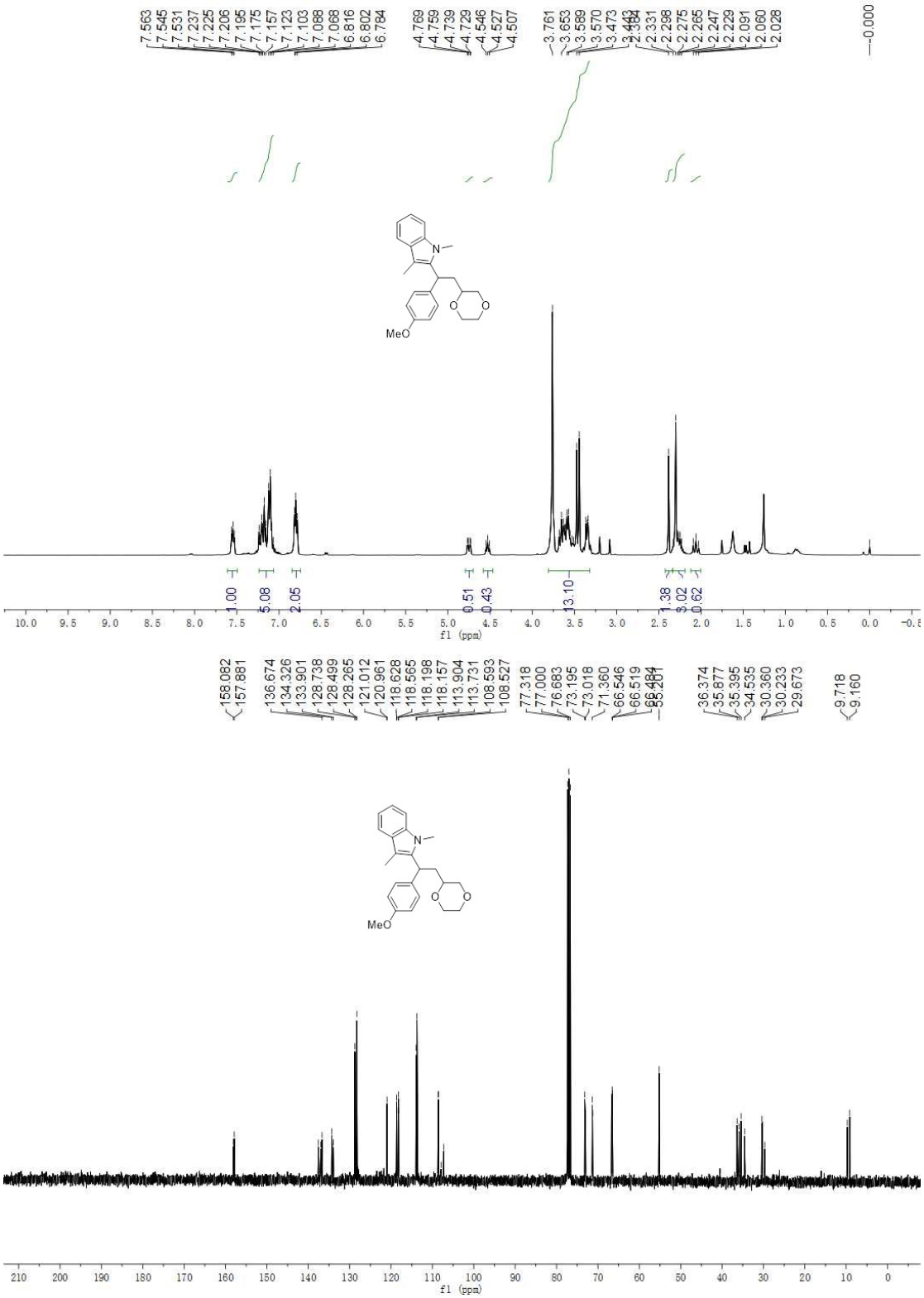
3-(2-(1,4-Dioxan-2-yl)-1-(4-methoxyphenyl)ethyl)-1,2-dimethyl-1*H*-indole (4aia)




7.360
7.347
7.328
7.247
7.227
7.114
7.096
7.077
6.947
6.928
6.909
6.777
6.757
4.527
4.514
4.502
4.488
3.773
3.740
3.666
3.632
3.610
3.579
3.557
3.485
2.169
0.000
MeO
1.16
3.23
1.07
1.09
1.94
1.02
4.33
3.06
4.10
2.03
2.97
1.97
f1 (ppm)

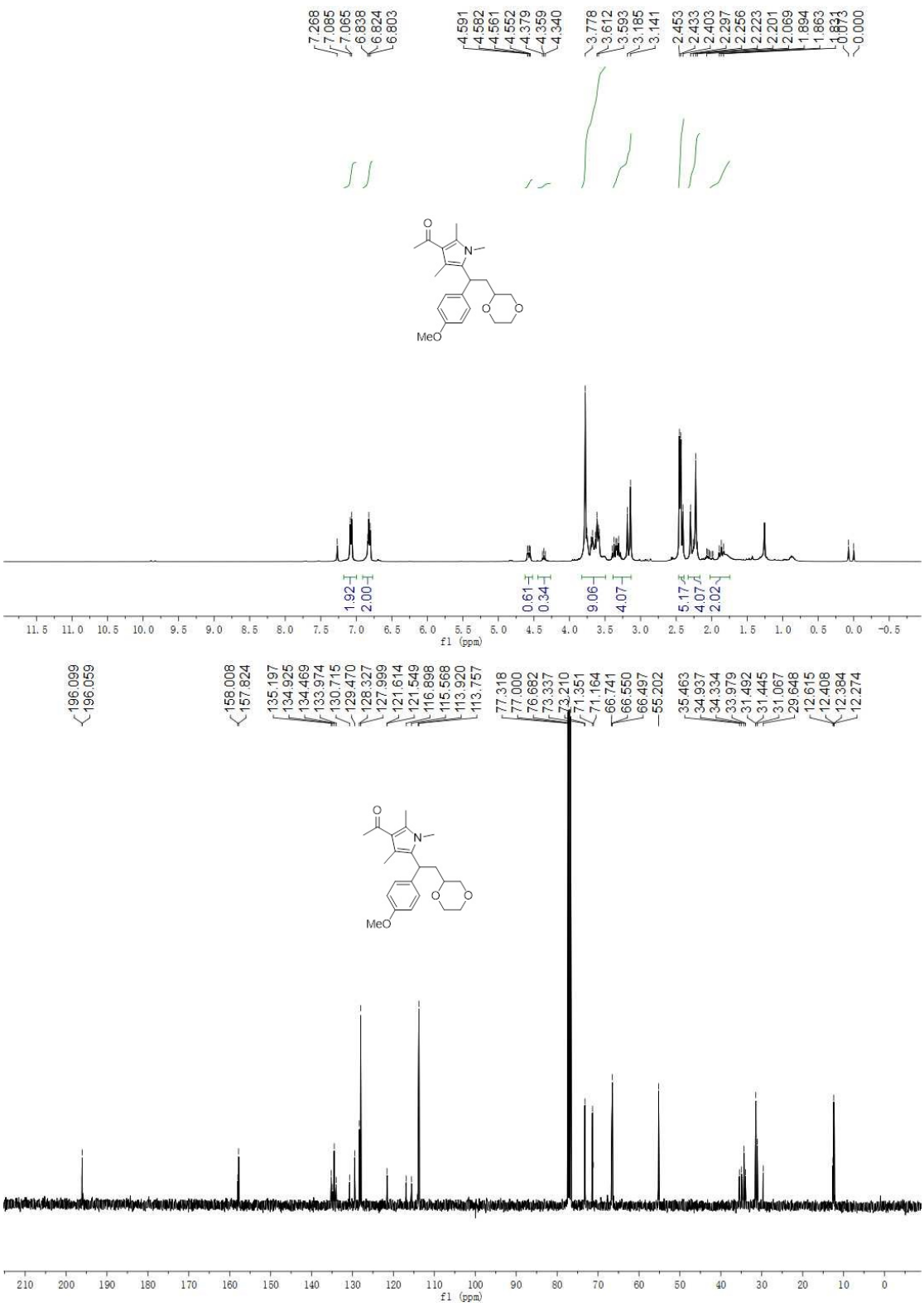

157.460
137.224
137.039
133.776
128.484
126.602
120.254
119.409
118.526
113.434
112.537
108.625
77.318
77.000
76.683
73.641
71.486
66.587
66.523
55.167
36.031
35.811
29.540
10.279
MeO
f1 (ppm)

2-(2-(1,4-Dioxan-2-yl)-1-(4-methoxyphenyl)ethyl)-1,3-dimethyl-1*H*-indole (4aja)



1-(5-(2-(1,4-Dioxan-2-yl)-1-(4-methoxyphenyl)ethyl)-1,2,4-trimethyl-1*H*-pyrrol-3-yl)ethan-1-one

(4aka)



3-(1-(4-methoxyphenyl)-2-(tetrahydrofuran-2-yl)ethyl)-1-methyl-1*H*-indole (4aab)