Supporting Information

A FACILE SYNTHESIS OF INDOLO[2,3-*b*]CARBAZOLES FROM THE REACTION OF DI(2-INDOLYL)METHANE AND AROMATIC ALDEHYDES CATALYZED BY OXALIC ACID

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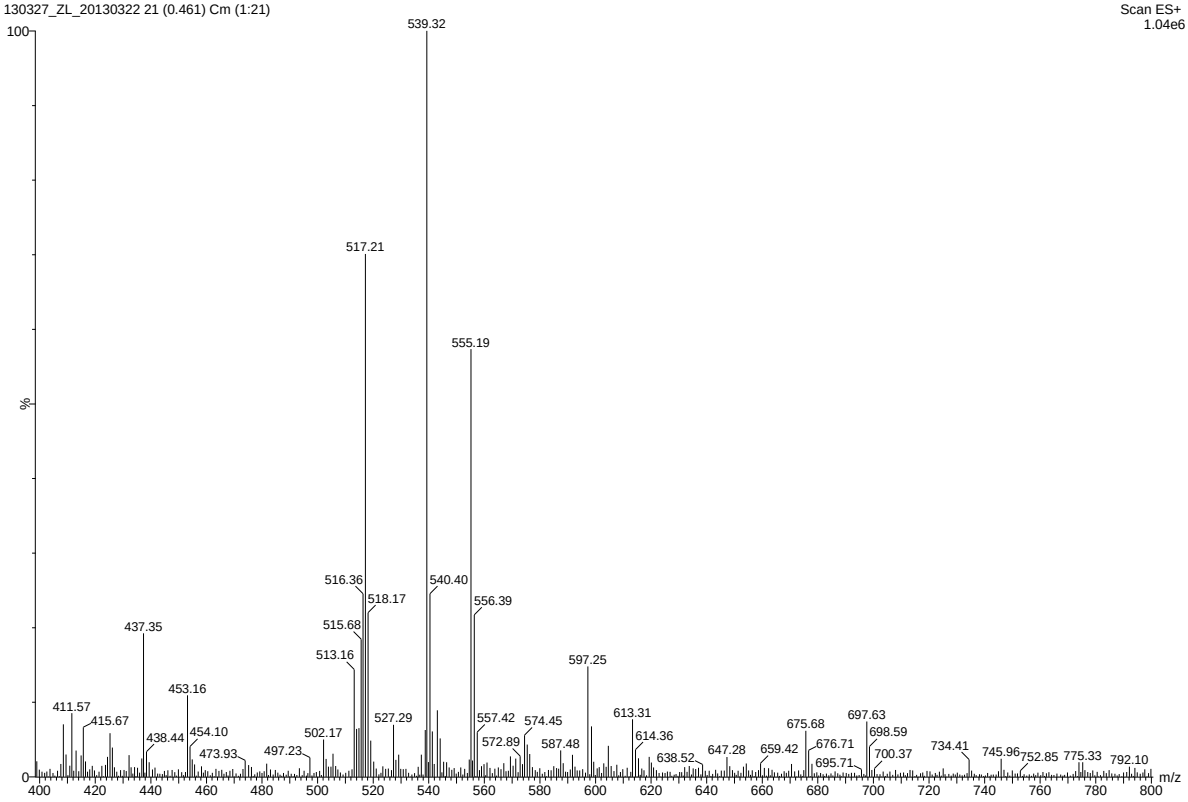
I. Experimental procedure

Preparation of di(2-indolyl)methane: To a mixture of indole-2-carbinol (0.45 g, 3.06 mmol) and 3-methylthioindole (0.5 g, 3.06 mmol) in CH_2Cl_2 (10 mL) was added $(CF_3SO_3)_3Sc$ (0.2 g, 0.49 mmol) and stirred for 3 h under argon. The solvent was evaporated to give a crude product. The crude product was dissolved in EtOH (10 mL) and Raney Ni was added at room temperature until no starting material was observed from TLC. The Raney Ni was removed by filtration and washed with ethyl acetate. The filtrate was dried ($MgSO_4$) and concentrated to give a solid. Flash chromatography (10 percent EtOAc/hexane) yielded di(2-indolyl)methane as a white solid (0.49 g, 65 percent): ^{1}H NMR (400 MHz, DMSO-d_6): δ = 10.99 (s, 2H), 7.42 (d, *J* = 4.0Hz, 2H), 7.29 (d, *J* = 4.0Hz, 2H), 6.98-7.02 (m, 2H), 6.91-6.94 (m, 2H), 6.21 (s, 2H), 4.22 (s, 2H).

Typical Procedure for the Preparation of Products: All synthetic processes were performed in argon atmosphere. To a solution of di(2-indolyl)methane (1mmol) in ethanol (2mL) was added aldehyde (0.5 mmol) and oxalic acid (0.05 mmol) at room temperature. The mixture was stirred at room temperature for 5 hours, and a lot of solid was precipitated. Upon completion, the reaction mixture was filtered and the filtrate was washed with cold ethanol (5 mL) to afford the desired product. The ^{1}H and ^{13}C spectra were recorded on Bruker Avance II-400 MHz with reference to TMS as the internal standard. Mass spectra were recorded with an AMD40223 (Interambulacra) spectrometer.

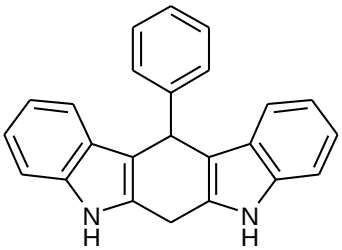
Procedure for the Reaction of Di(2-indolyl)methane and Formaldehyde: To a solution of di(2-indolyl)methane (1 mmol) in EtOH (2mL) was added formaldehyde (1 mmol) and oxalic acid (0.05 mmol) at room temperature. The mixture was stirred at

room temperature for 5 h and a white solid was precipitated. Then the mixture was filtered and the white solid was detected by mass spectral analysis. MS[M+Na^+] calcd. for $[C_{36}H_{28}N_4Na]^+$, 539.22; found, 539.32.

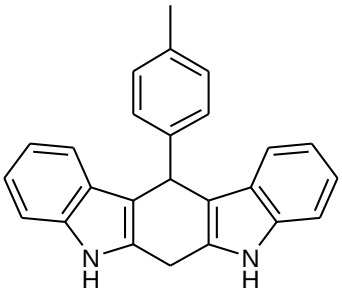


MS[M+Na^+] calcd. for $[C_{36}H_{28}N_4Na]^+$, 539.22; found, 539.32.

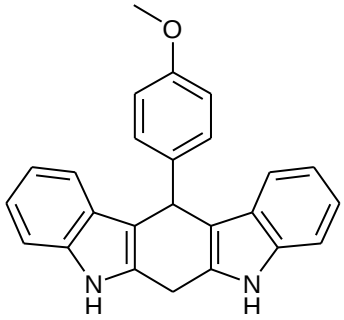
Ⅱ. Characterization data



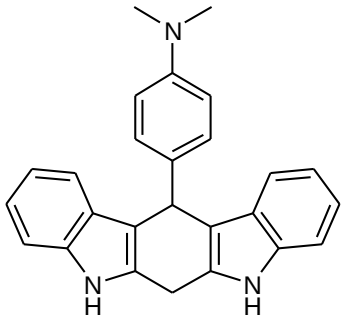
12-phenyl-5,6,7,12-tetrahydro-indolo[2,3-*b*]carbazole (**2a**)**:** White solid, 94.5% yield. ^{1}H NMR (400 MHz, DMSO-d_6): δ = 11.08 (s, 2H), 7.36 (d, *J* = 2.0Hz, 2H), 7.31 (d, *J* = 4.0Hz, 2H), 7.16-7.20 (m, 4H), 7.04-7.08 (m, 1H), 6.95-6.99 (m, 2H), 6.79-6.83 (m, 2H), 5.47 (s, 1H), 4.18-4.42 (m, 2H); ^{13}C NMR (100 MHz, DMSO-d_6): δ =146.81, 137.03, 131.72, 128.79, 128.46, 126.65, 126.16, 120.85, 118.69, 118.65, 112.34, 111.26, 39.05, 23.28; HRMS (ESI): [M+H$^+$] calcd. For $[C_{24}H_{19}N_2]^+$, 335.1548; found, 335.1557.



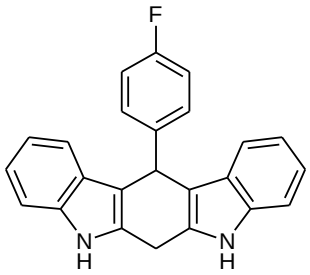
12-p-tolyl-5,6,7,12-tetrahydro-indolo[2,3-*b*]carbazole (**2b**): White solid, 94% yield. ^{1}H NMR (400 MHz, DMSO-d_6): δ = 11.05 (s, 2H), 7.30 (d, *J* = 4.0Hz, 2H), 7.23 (d, *J* = 4.0Hz, 2H), 7.17 (d, *J* = 4.0Hz, 2H), 6.95-6.99 (m, 4H), 6.79-6.83 (m, 2H), 5.42 (s, 1H), 4.16-4.41 (m, 2H), 2.18 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6): δ =143.78, 137.02, 134.92, 131.63, 129.06, 128.65, 126.67, 120.82, 118.76, 118.61, 112.46, 111.23, 38.63, 23.27, 21.10; HRMS (ESI): [M+H$^+$] calcd. For $[C_{25}H_{21}N_2]^+$, 349.1705; found,349.1701 .



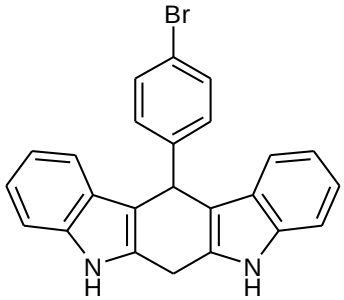
12-(4-Methoxy-phenyl)-5,6,7,12-tetrahydro-indolo[2,3-*b*]carbazole (**2c**): white solid, 93.7% yield. ^{1}H NMR (400 MHz, DMSO-d_6): δ = 11.04 (s, 2H), 7.31 (d, *J* = 4.0Hz, 2H), 7.25 (d, *J* = 6.0Hz, 2H), 7.18 (d, *J* = 4.0Hz, 2H), 6.96-7.00 (m, 2H), 6.80-6.84 (m, 2H), 6.74 (d, *J* = 4.0Hz, 2H), 5.42 (s, 1H), 4.16-4.40 (m, 2H), 3.65 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6): δ =157.62, 138.73, 137.04, 131.56, 129.61, 126.69, 120.79, 118.76, 118.59, 113.77, 112.59, 111.21, 55.26, 38.18, 23.26; HRMS (ESI): [M+H$^+$] calcd. For $[C_{25}H_{21}N_2O]^+$, 365.1654; found, 365.1660.



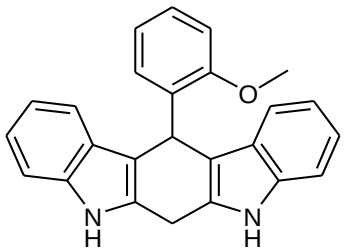
dimethyl-[4-(5,6,7,12-tetrahydro-indolo[2,3-*b*]carbazol-12-yl)-phenyl]-amine (**2d**): light yellow solid, 91% yield. ^{1}H NMR (400 MHz, DMSO-d_6): δ = 11.00 (s, 2H), 7.30 (d, *J* = 4.0Hz, 2H), 7.20 (d, *J* = 4.0Hz, 2H), 7.14 (d, *J* = 4.0Hz, 2H), 6.95-6.99 (m, 2H), 6.79-6.83 (m, 2H), 6.55 (d, *J* = 4.0Hz, 2H), 5.34 (s, 1H), 4.15-4.39 (m, 2H), 2.78 (s, 6H); ^{13}C NMR (100 MHz, DMSO-d_6): δ =148.98, 137.05, 134.51, 131.43, 129.17, 126.83, 120.74, 118.94, 118.54, 112.96, 112.69, 111.17, 40.74, 38.11, 23.31; HRMS (ESI): [M+H$^+$] calcd. For $[C_{26}H_{24}N_3]^+$, 378.1970; found, 378.1968.



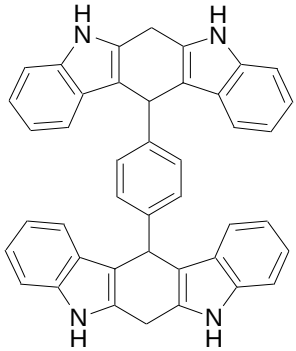
12-(4-fluoro-phenyl)-5,6,7,12-tetrahydro-indolo[2,3-*b*]carbazole (**2e**): White solid, 90% yield. ^{1}H NMR (400 MHz, DMSO-d_6): δ = 11.10 (s, 2H), 7.37-7.40 (m, 2H), 7.32 (d, *J* = 4.0Hz, 2H), 7.17 (d, *J* = 4.0Hz, 2H), 6.97-7.02 (m, 2H), 6.81-6.85 (m, 2H), 5.49 (s, 1H), 4.17-4.42 (m, 2H); ^{13}C NMR (100 MHz, DMSO-d_6): δ =142.94, 137.04, 131.74, 130.45, 126.54, 120.92, 118.73, 118.60, 115.22, 115.01, 112.17, 111.32, 38.16, 23.24; HRMS (ESI): [M+H$^+$] calcd. For $[C_{24}H_{18}FN_2]^+$, 353.1454; found, 353.1454.



12-(4-bromo-phenyl)-5,6,7,12-tetrahydro-indolo[2,3-*b*]carbazole (**2f**): White solid, 91% yield. ^{1}H NMR (400 MHz, DMSO-d_6): δ = 11.12 (s, 2H), 7.37 (d, *J* = 4.0Hz, 2H), 7.31-7.34 (m, 4H), 7.17 (d, *J* = 4.0Hz, 2H), 6.97-7.01 (m, 2H), 6.82-6.86 (m, 2H), 5.49 (s, 1H), 4.18-4.42 (m, 2H); ^{13}C NMR (100 MHz, DMSO-d_6): δ =146.40, 137.07, 131.91, 131.40, 131.07, 126.51, 121.02, 119.07, 118.84, 118.57, 111.84, 111.40, 38.37, 23.26; HRMS (ESI): [M+H$^+$] calcd. For $[C_{24}H_{18}BrN_2]^+$, 413.0653; found, 413.0640.

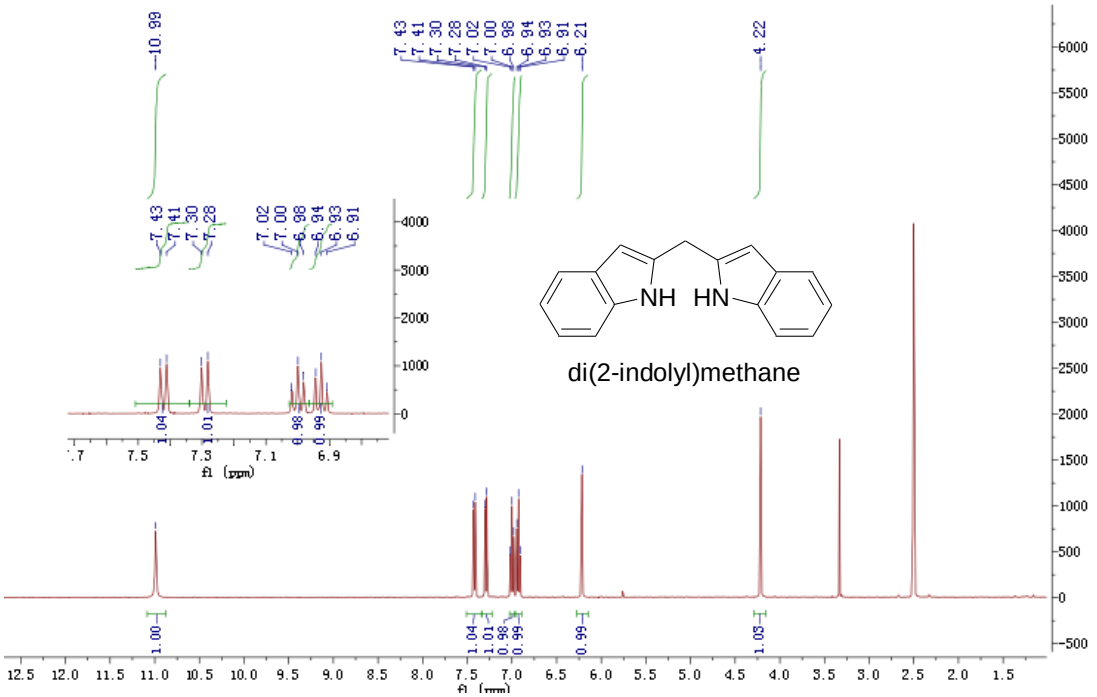


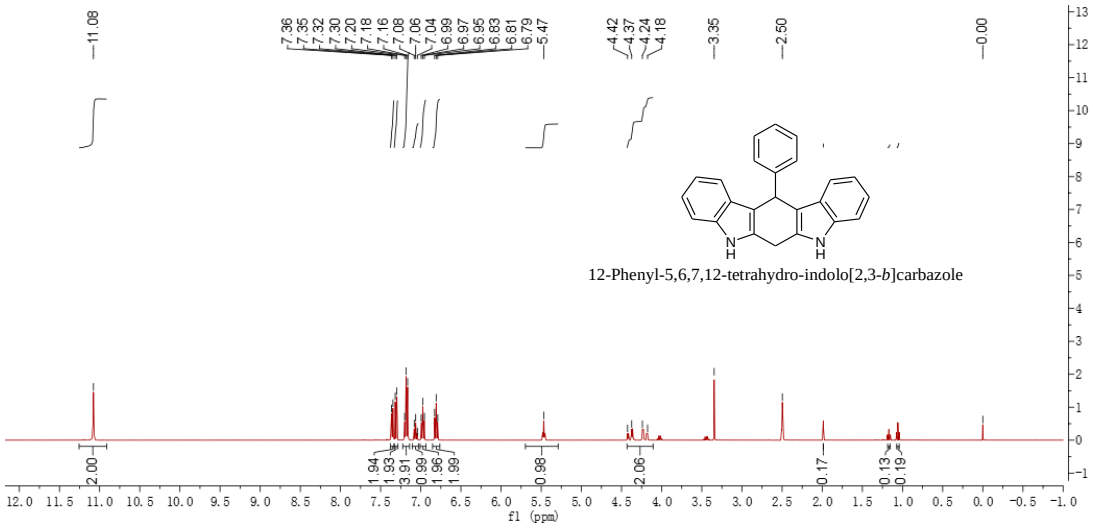
12-(2-Methoxy-phenyl)-5,6,7,12-tetrahydro-indolo[2,3-*b*]carbazole (**2g**): white solid, 85% yield. ^{1}H NMR (400 MHz, DMSO-d_6): δ = 11.02 (s, 2H), 7.30 (d, *J* = 4.0Hz, 2H), 7.10-7.13 (m, 3H), 7.01-7.05 (m, 1H), 6.95-6.99 (m, 2H), 6.79-6.83 (m, 2H), 6.66 (d, *J* = 4.0Hz, 1H), 6.54-6.58 (m, *J* = 4.0Hz, 1H), 5.98 (s, 1H), 4.17-4.42 (m, 2H), 4.12 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6): δ =156.61, 136.95, 134.46, 131.88, 129.98, 127.07, 126.57, 120.92, 120.83, 118.66, 118.55, 118.38, 112.77, 111.18, 56.34, 39.36, 23.25; HRMS (ESI): [M+H$^+$] calcd. For $[C_{25}H_{21}N_2O]^+$, 365.1654; found, 365.1658.



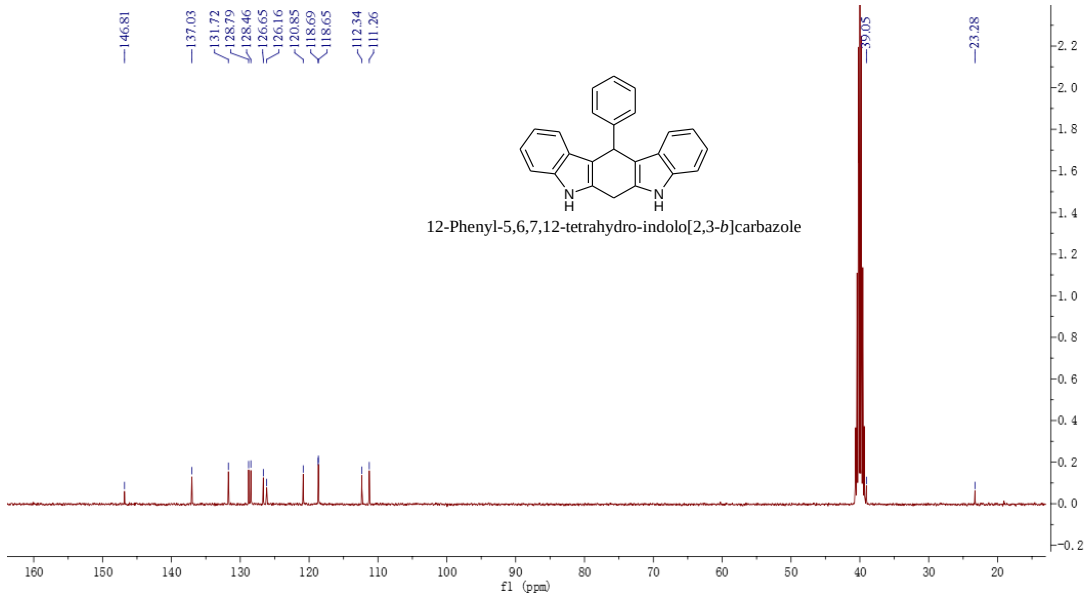
2h: white solid, 80% yield. ^{1}H NMR (400 MHz, DMSO-d_6): δ = 10.92 (s, 4H), 7.19 (d, *J* = 2.0Hz,4H), 7.13 (s, 4H), 6.93 (d, *J* = 4.0Hz, 4H), 6.84-6.88 (m, 4H), 6.61-6.65 (m, 4H), 5.29 (s, 2H), 4.06-4.25 (m, 4H); ^{13}C NMR (100 MHz, DMSO-d_6): δ = 143.72, 137.08, 131.59, 128.82, 126.89, 120.76, 118.97, 118.53, 112.31, 111.18, 39.27, 23.32; HRMS (ESI): [M+H$^+$] calcd. For $[C_{42}H_{31}N_4]^+$, 591.2549; found, 591.2548

Ⅲ. Copies of ^{1}H and ^{13}C-NMR





12-Phenyl-5,6,7,12-tetrahydro-indolo[2,3-*b*]carbazole



12-Phenyl-5,6,7,12-tetrahydro-indolo[2,3-*b*]carbazole

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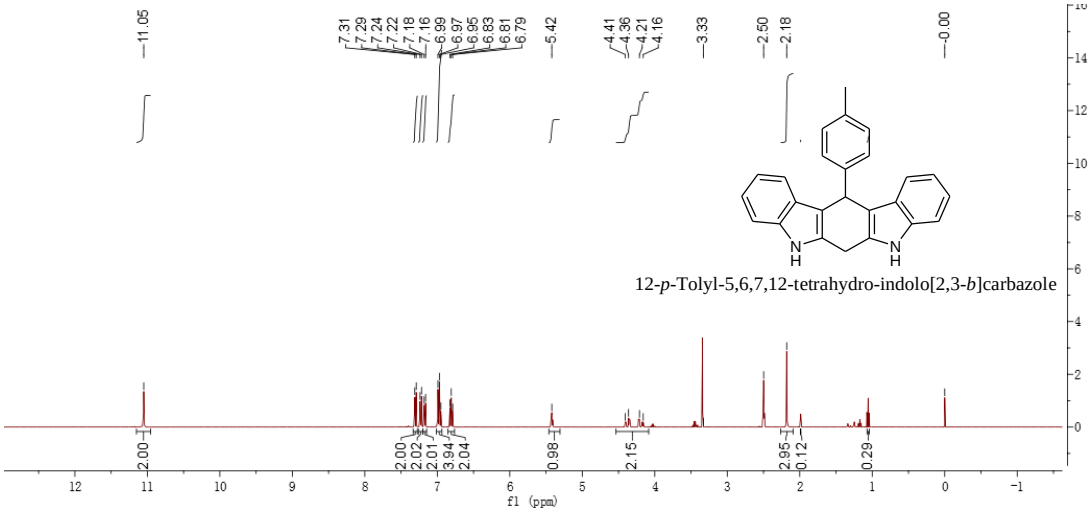

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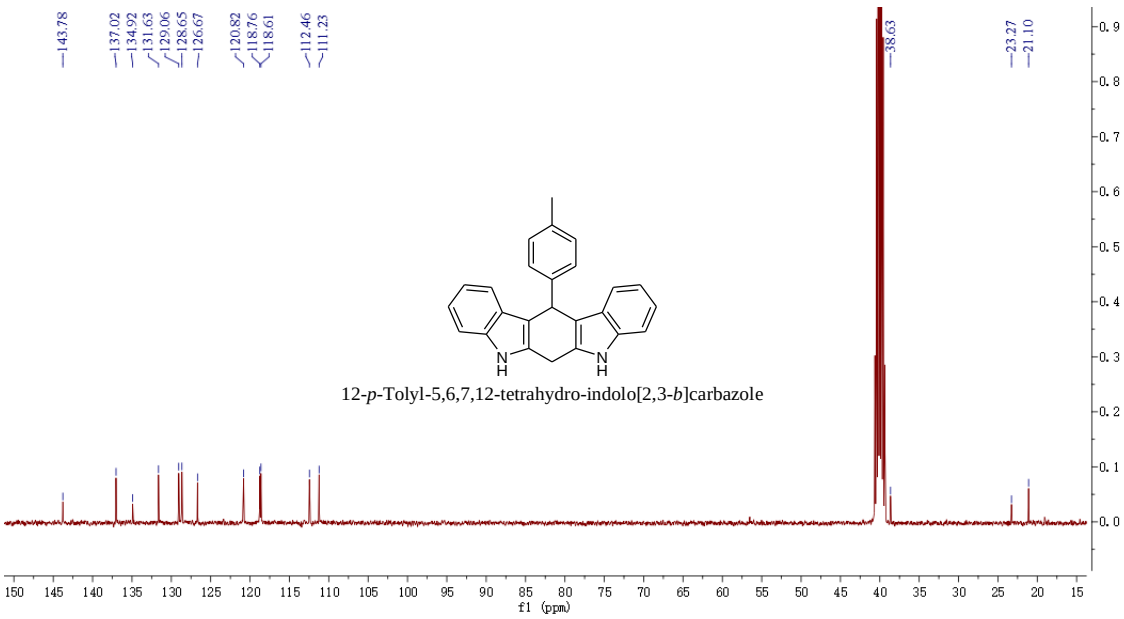
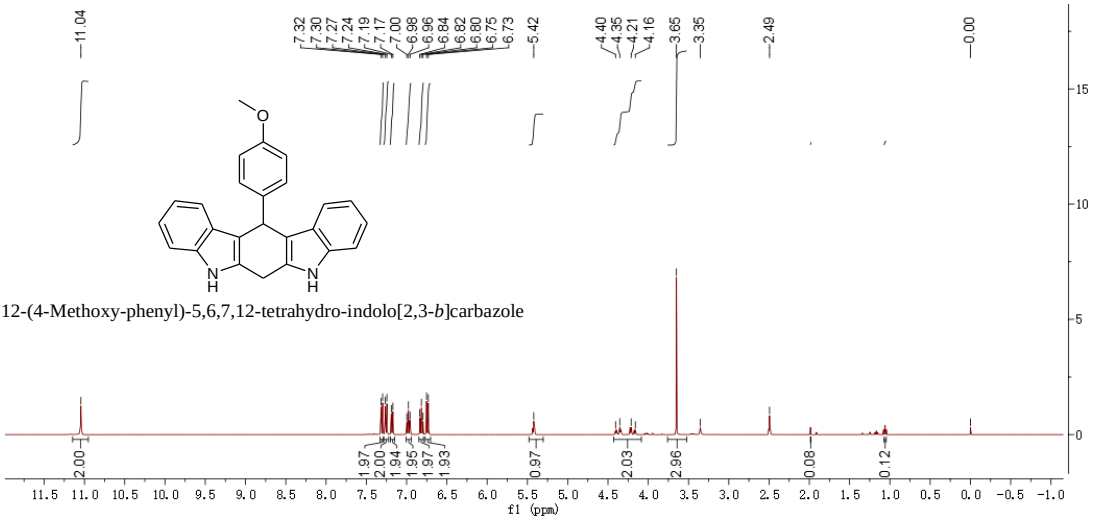


12-*p*-Tolyl-5,6,7,12-tetrahydro-indolo[2,3-*b*]carbazole



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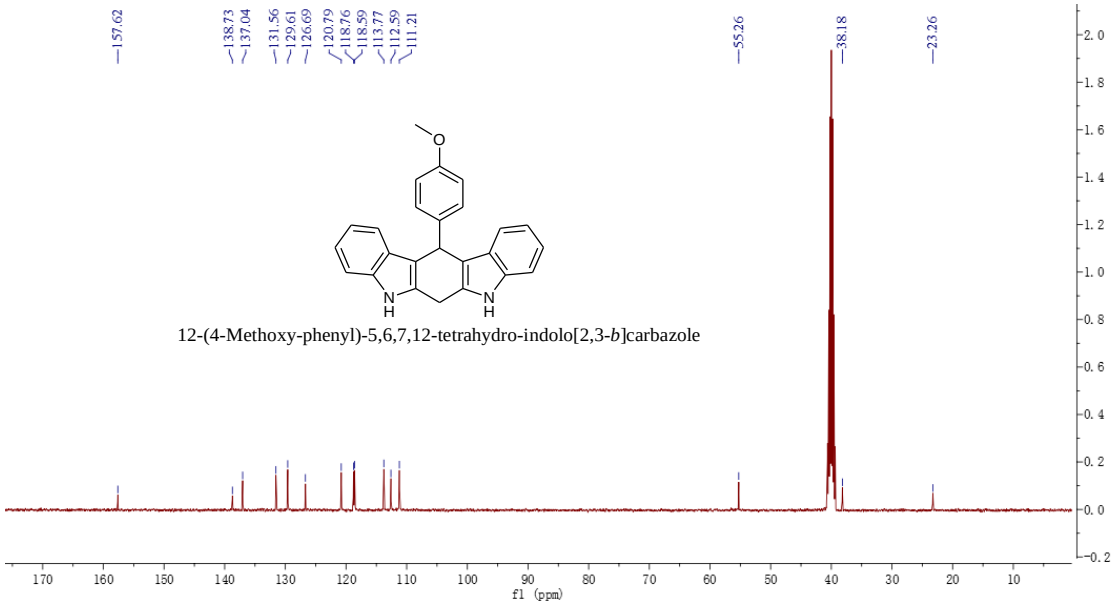
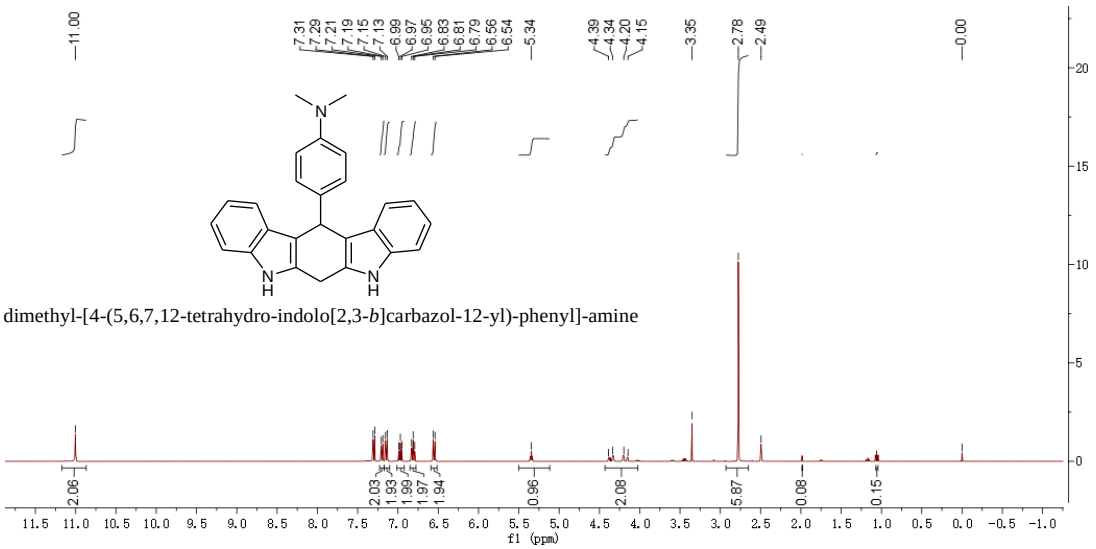
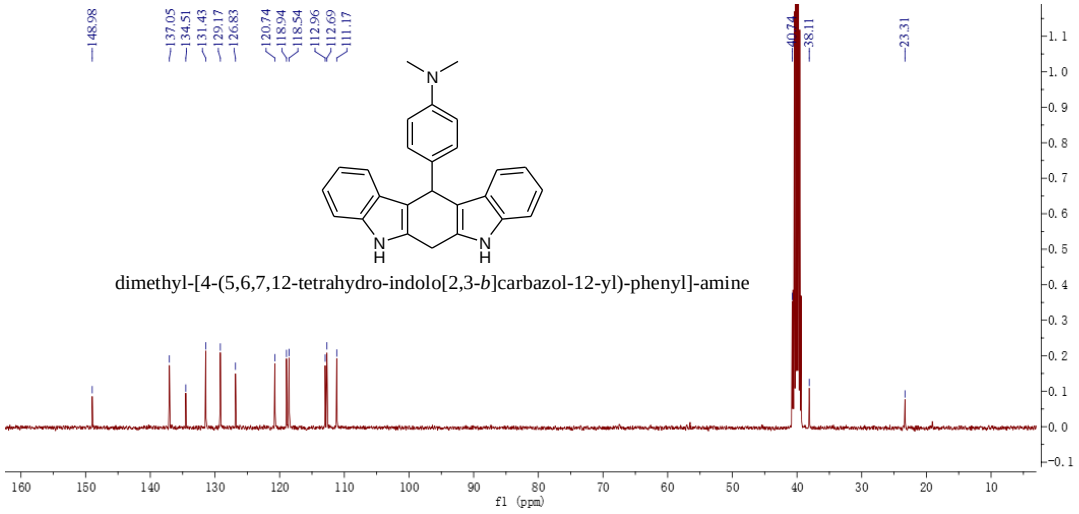


12-(4-Methoxy-phenyl)-5,6,7,12-tetrahydro-indolo[2,3-*b*]carbazole



dimethyl-[4-(5,6,7,12-tetrahydro-indolo[2,3-*b*]carbazol-12-yl)-phenyl]-amine



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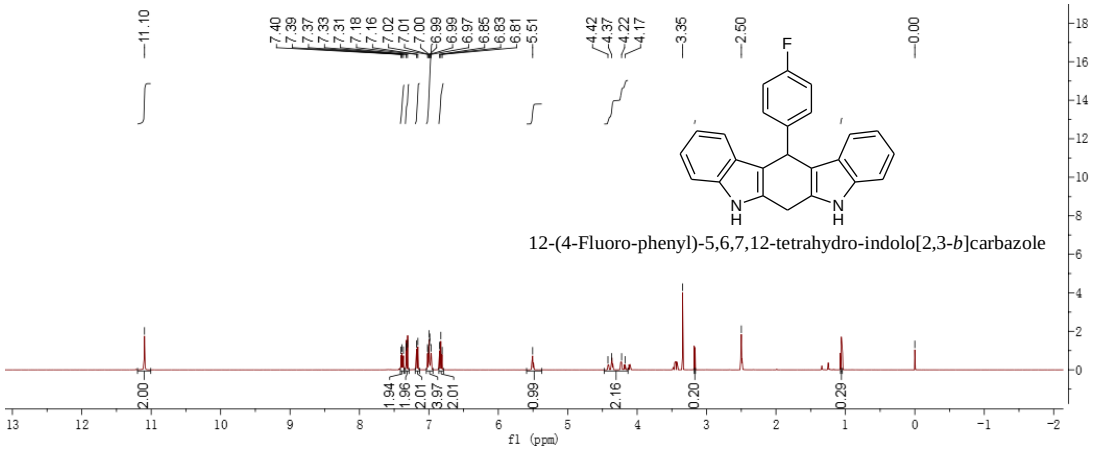

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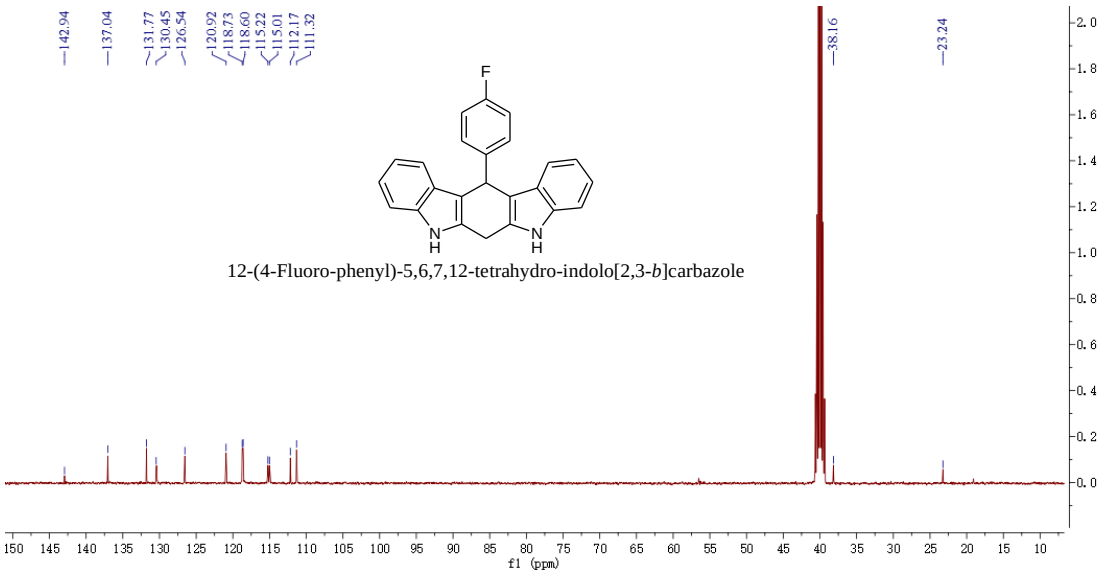

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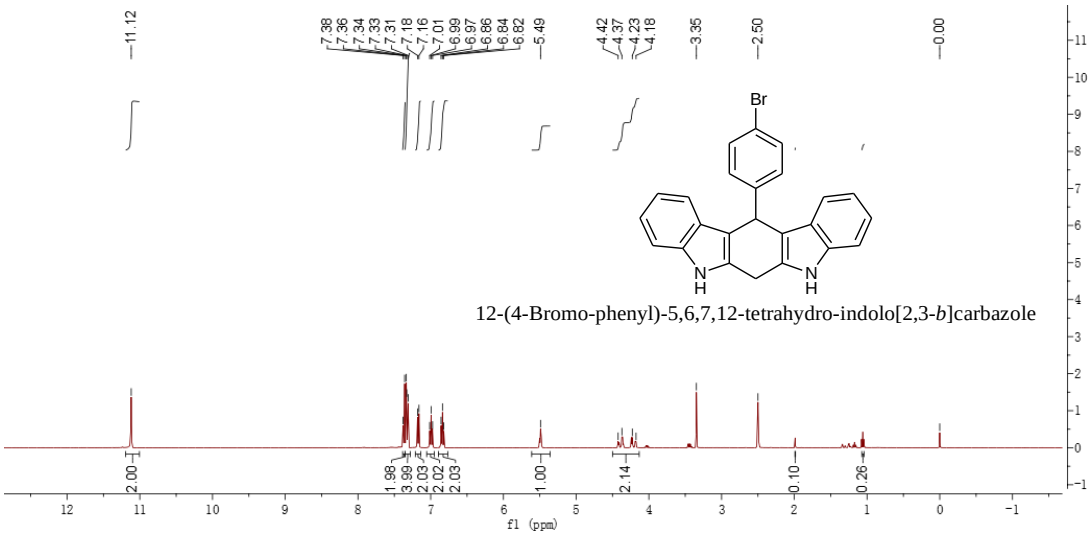

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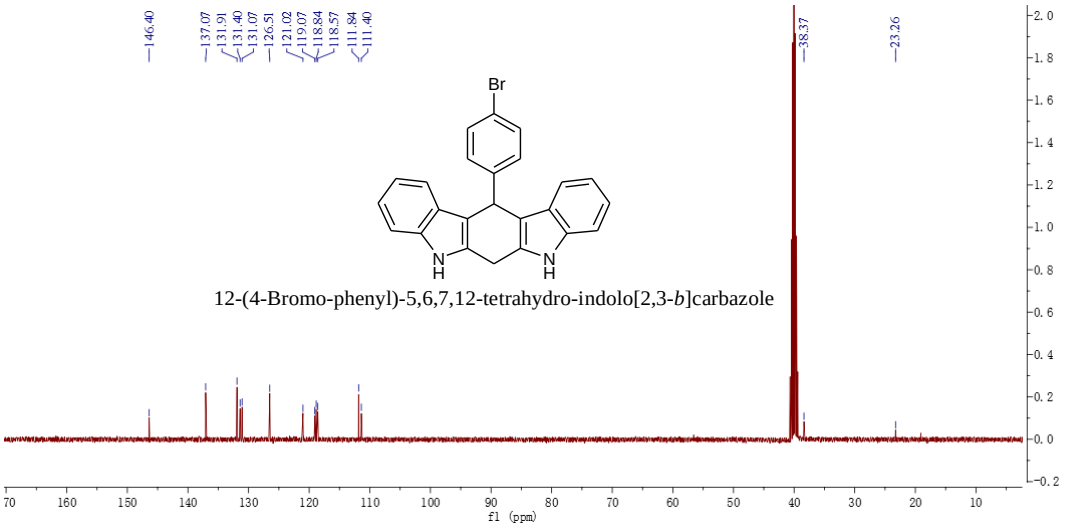
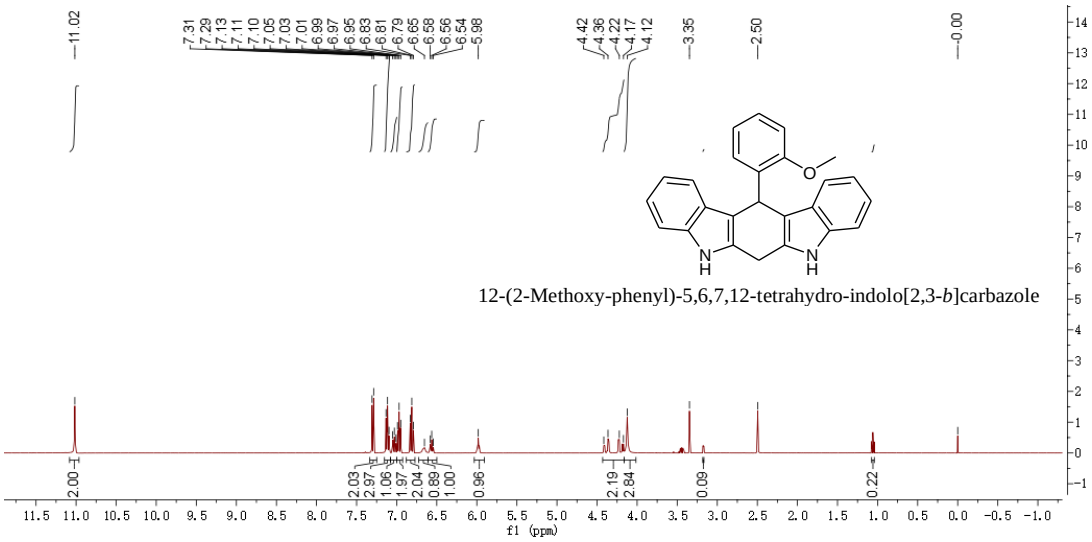
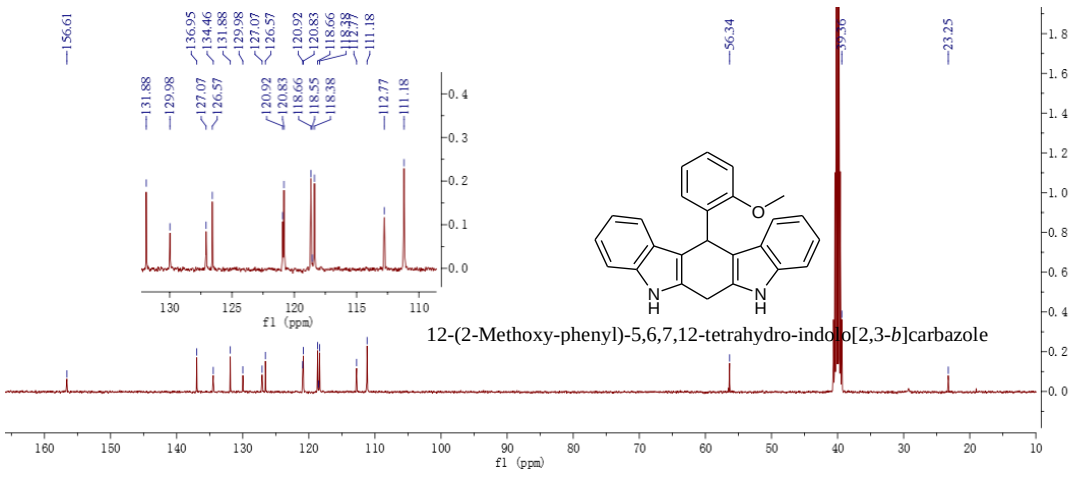


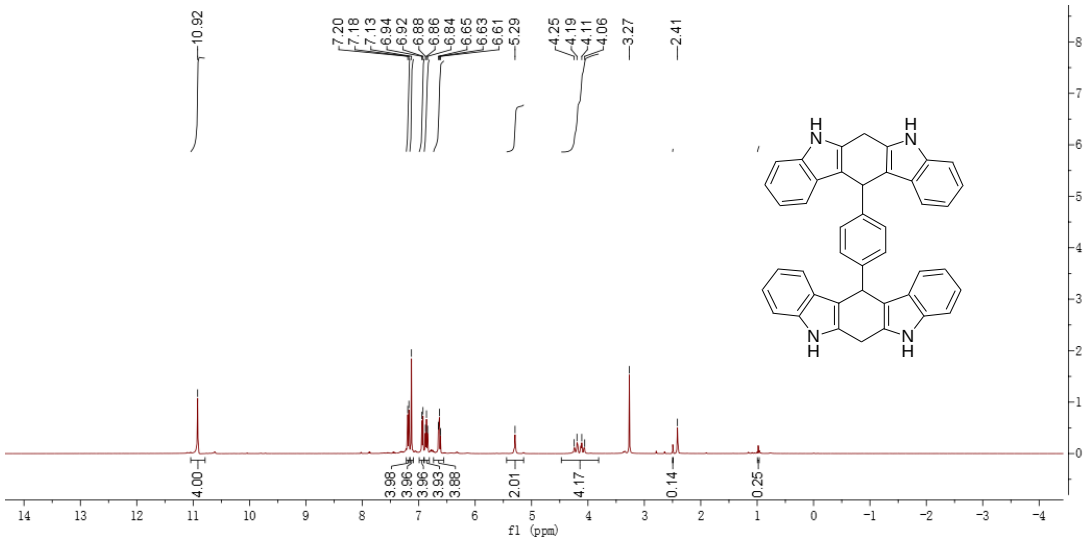
12-(4-Bromo-phenyl)-5,6,7,12-tetrahydro-indolo[2,3-*b*]carbazole



12-(2-Methoxy-phenyl)-5,6,7,12-tetrahydro-indolo[2,3-*b*]carbazole



12-(2-Methoxy-phenyl)-5,6,7,12-tetrahydro-indolo[2,3-*b*]carbazole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4.06
3.27
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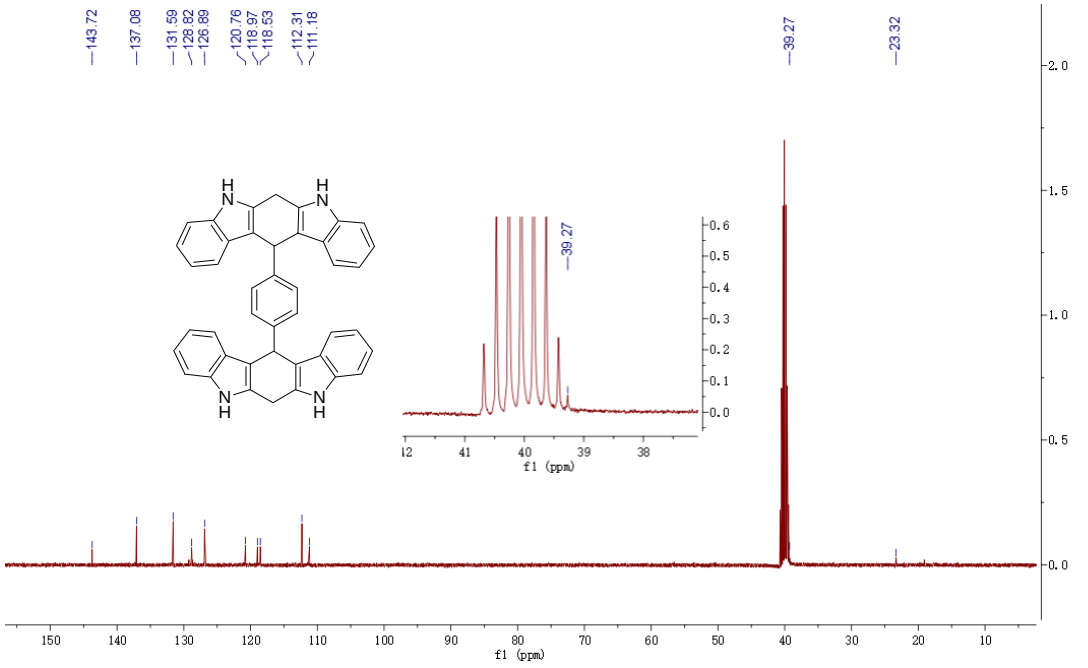
0.25
f1 (ppm)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39.27
f1 (ppm)
f1 (ppm)