Electronic Supplementary Information

Borane-Catalyzed Dehydrogenative C–C Bond Formation of Indoles with *N*-Tosylhydrazones: An Experimental and Computational Study

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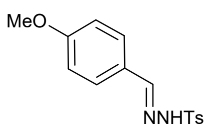
I. General Information

Reactions were performed under inert atmosphere using Schlenk techniques or under nitrogen glovebox. ^{1}H and ^{13}C NMR spectra were recorded on a JEOL-ECS400 spectrometer at 400 MHz and 100 MHz respectively. The ^{1}H NMR and ^{13}C NMR chemical shifts were assigned in reference to tetramethylsilane (TMS) or residual solvent peak as an internal standard. High-resolution mass spectra (HRMS) were recorded on Agilent–6545Q-TOF micro mass spectrometer. Aldehydes, ketones, tosylhydrazine, indole derivatives, boron compounds and other chemicals were purchased from Sigma-Aldrich, Alfa-Aesar, Acros Organics and used as received. Solvents used in the reactions were collected from M-Braun Solvent Purification System. *N*-Tosylhydrazones were prepared according to standard procedure reported in literature.[1]

II. Table for the numbering of *N*-tosylhydrazones and indoles



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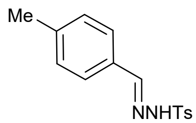

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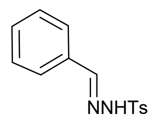

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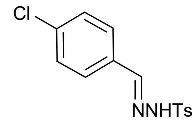

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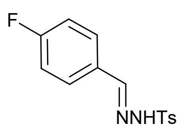

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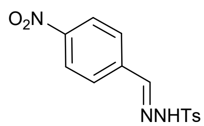

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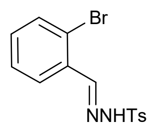

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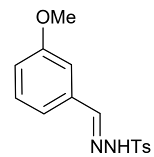

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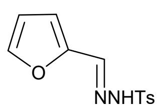

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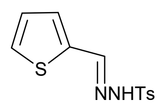

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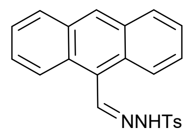

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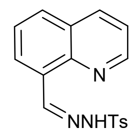

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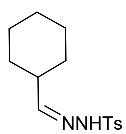

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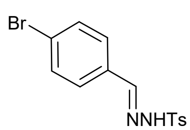

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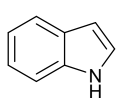

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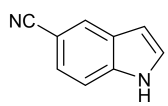

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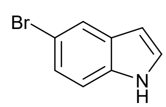

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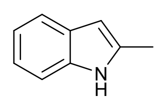

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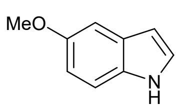

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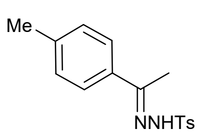

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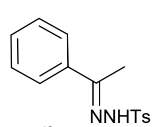

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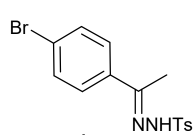

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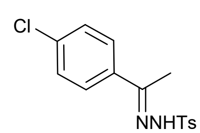

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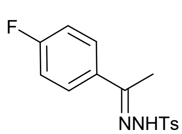

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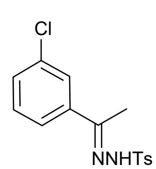

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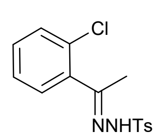
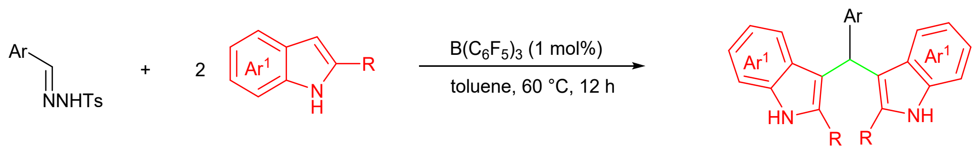


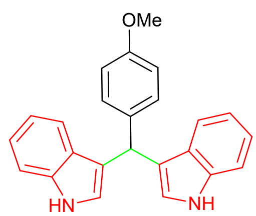
4g

III. $B(C_6F_5)_3$ catalyzed synthesis of symmetrical di(indolyl)methane (DIM) 3 from *N*-tosylhydrazone 1 and indole 2



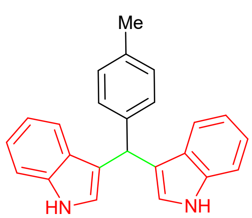
Representative Procedure: *N*-tosylhydrazone **1a** (76.1 mg, 0.25 mmol, 1.0 equiv) and indole **2a** (58.6 mg, 0.5 mmol, 2.0 equiv) were dissolved in 2 mL toluene in a 10 mL Schlenk tube. Next, $B(C_6F_5)_3$ catalyst (1.3 mg, 0.0025 mmol, 1 mol%) was added to that solution under nitrogen at room temperature with continuous stirring for 10 minutes. The reaction mixture was heated at 60 °C for 12 h in an oil bath. after completion of reaction the solvent was evaporated under reduced pressure. Pure compound was isolated with the aid of column chromatography using 2:8 ethyl acetate/hexane as eluent to afford symmetrical di(indolyl)methane **3aaa** as an orange solid in 85% (74.9 mg) yield.

3,3'-((4-Methoxyphenyl)methylene)bis(1*H*-indole) (3aaa).[2] Analytical TLC on silica gel 2:8 ethyl acetate/hexane R_f = 0.25; Yield 85% (74.9 mg, 0.212 mmol). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.82 (brs, 2H), 7.41 (d, J = 8.0 Hz, 2H), 7.33 (d, J = 8.0 Hz, 2H), 7.27-7.19 (m, 2H), 7.18-7.05 (m, 2H), 7.04-7.01 (m, 2H), 6.85-6.82 (m, 2H), 6.59 (d, J = 4.0 Hz, 2H), 5.85 (s, 1H), 3.80 (s, 3H)); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 158.0, 136.8, 136.4, 129.7, 127.2, 123.7, 122.0, 120.1, 119.3, 113.7, 111.2, 55.3, 39.4; **HRMS** [M - H^+] calcd for $C_{24}H_{19}N_2O$: (m/z) = 351.1492, found = 351.1502.



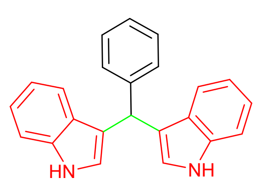
3aaa

3,3'-(*p*-Tolylmethylene)bis(1*H*-indole) (3baa).[3] Analytical TLC in silica gel 1:9 ethyl acetate/hexane R_f = 0.25; Yield 87% (72.9 mg, 0.217 mmol). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.59 (brs, 2H), 7.46 (d, J = 8.0 Hz, 2H), 7.29-7.26 (m, 4H), 7.23-7.19 (m, 2H), 7.14 (d, J = 8.0 Hz, 2H), 7.08-7.04 (m, 2H), 6.52 (s, 2H), 5.89 (s, 1H), 2.39 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 141.1, 136.7, 135.6, 129.0, 128.6, 127.1, 123.7, 121.9, 120.0, 119.7, 119.2, 111.2, 39.8, 21.2; **HRMS** [M - H^+] calcd for $C_{24}H_{19}N_2$: (m/z) = 335.1543, found = 335.1528.



3baa

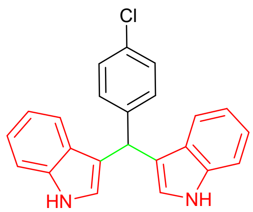
3,3'-(Phenylmethylene)bis(1*H*-indole) (3caa).[4] Analytical TLC in silica gel 2:8 ethyl acetate/hexane R_f = 0.33; Yield 89% (71.7 mg, 0.222 mmol). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.59 (brs, 2H), 7.52 (d, J = 7.9 Hz, 2H), 7.45 (d, J = 6.8 Hz, 2H), 7.40-7.28 (m, 7H), 7.13 (t, J = 8.0 Hz, 2H), 6.55 (s, 2H), 5.99 (s, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 144.1, 136.7, 128.8, 128.3, 127.1,



3caa

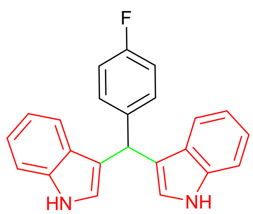
126.2, 123.8, 122.0, 120.0, 119.7, 119.3, 111.2, 40.3. **HRMS** [M - H$^+$] calcd for $C_{23}H_{17}N_2$: (m/z) = 321. 1387, found = 321.1405.

3,3'-((4-Chlorophenyl)methylene)bis(1*H*-indole) (3daa).[5] Analytical TLC on silica gel 2:8 ethyl acetate/hexane R_f = 0.20; Yield 92% (81.9 mg, 0.23 mmol). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.69 (brs, 2H), 7.43 (d, *J* = 8.0 Hz, 2H), 7.30-7.22 (m, 8H), 7.11-7.07 (m, 2H), 6.53 (s, 2H), 5.89 (s, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 142.8, 136.8, 131.9, 130.3, 128.6, 127.0, 123.9, 122.2, 120.0, 119.5, 119.2, 111.4, 39.8; **HRMS** [M - H$^+$] calcd for $C_{23}H_{16}{}^{35}ClN_2$: (m/z) = 355.0997, found = 355.1004.



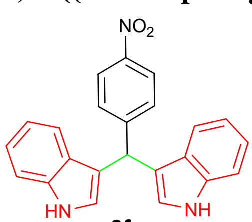
3daa

3,3'-((4-Fluorophenyl)methylene)bis(1*H*-indole) (3eaa).[6] Analytical TLC in silica gel 2:8 ethyl acetate/hexane R_f = 0.35; Yield 90% (76.5 mg, 0.225 mmol). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.93 (brs, 2H), 7.38-7.31 (m, 4H), 7.30-7.20 (m, 2H), 7.18-7.02 (m, 2H), 7.01-6.98 (m, 2H), 6.96-6.94 (m, 2H), 6.64 (s, 2H), 5.87 (s, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 162.8 (d, *J* = 242.0 Hz), 139.8 (d, *J* = 3.0 Hz), 136.8, 130.2 (d, *J* = 7.6 Hz), 127.1, 123.7, 122.2, 120.0, 119.7, 119.4, 115.2 (d, *J* = 21.0 Hz), 111.2, 39.6; **^{19}F NMR** (376 MHz, $CDCl_3$): δ -117.3 (m, 1F) **HRMS** [M - H$^+$] calcd for $C_{23}H_{16}FN_2$: (m/z) = 339.1293, found = 339.1310.



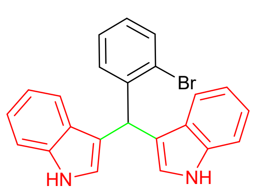
3eaa

3,3'-((4-Nitrophenyl)methylene)bis(1*H*-indole) (3faa).[7] Analytical TLC in silica gel 2:8 ethyl acetate/hexane R_f = 0.20; Yield 72% (66.1 mg, 0.18 mmol). **^{1}H NMR** (400 MHz, $(CD_3)_2SO$): δ 10.92 (brs, 2H), 8.15 (d, *J* = 8.0 Hz, 2H), 7.61 (d, *J* = 8.0 Hz, 2H), 7.36 (d, *J* = 8.0 Hz, 2H), 7.29 (d, *J* = 8.0Hz, 2H), 7.07-7.03 (m, 2H), 6.90-6.86 (m, 4H), 6.03 (s, 1H); **^{13}C NMR** (100 MHz, $(CD_3)_2SO$): δ 153.7, 146.2, 137.1, 130.0, 126.9, 124.4, 124.0, 121.6, 119.4, 118.9, 117.2, 112.1; **HRMS** [M - H$^+$] calcd for $C_{23}H_{16}N_3O_2$: (m/z) = 366.1238, found = 366.1231.



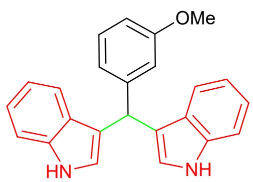
3faa

3,3'-((2-Bromophenyl)methylene)bis(1*H*-indole) (3gaa).[8] Analytical TLC in silica gel 3:7 ethyl acetate/hexane R_f = 0.35; Yield 75% (75.2 mg, 0.187 mmol). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.70 (brs, 2H), 7.66 (d, *J* = 8.0 Hz, 1H), 7.45 (d, *J* = 8.0 Hz, 2H), 7.31 (d, *J* = 8.0 Hz, 2H), 7.25-7.20 (m, 3H), 7.15-7.09 (m, 1H), 7.07-7.05 (m, 3H), 6.52 (s, 2H), 6.35 (s, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 143.1, 136.8, 132.9, 130.6, 127.9, 127.4, 127.0, 124.9, 124.0, 122.1, 119.9, 119.4, 118.4, 111.2, 39.6; **HRMS** [M - H$^+$] calcd for $C_{23}H_{16}{}^{81}BrN_2$: (m/z) = 401.0471, found = 401.0490.



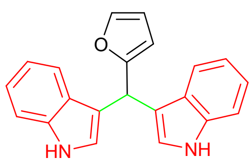
3gaa

3,3'-((3-Methoxyphenyl)methylene)bis(1*H*-indole) (3haa).[8] Analytical TLC in silica gel 2:8 ethyl acetate/hexane R_f = 0.20; Yield 81% (71.4 mg, 0.202 mmol). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.87 (brs, 2H), 7.41 (d, *J* = 8.0 Hz, 2H), 7.34 (d, *J* = 8.0 Hz, 2H), 7.22-7.15 (m, 3H), 7.03-6.99 (m, 2H), 6.97-6.93 (m, 2H), 6.78-6.75 (m, 1H), 6.65 (s, 2H), 5.86 (s, 1H), 3.74 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 159.7, 145.9, 136.9, 129.3, 127.2, 123.7, 122.0, 121.4, 120.0, 119.7, 119.4, 114.9, 111.4, 111.1, 55.3, 40.4; **HRMS** [M - H^+] calcd for $C_{24}H_{19}N_2O$: (m/z) = 351.1492, found = 351.1506.



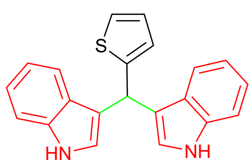
3haa

3,3'-(Furan-2-ylmethylene)bis(1*H*-indole) (3iaa).[9] Analytical TLC in silica gel 1:9 ethyl acetate/hexane R_f = 0.35; Yield 78% (60.9 mg, 0.195 mmol). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.70 (brs, 2H), 7.55 (d, *J* = 8.0 Hz, 2H), 7.38-7.38 (m, 1H), 7.27-7.20 (m, 4H), 7.13-7.09 (m, 2H) 6.69 (d, *J* = 4.0 Hz, 2H), 6.34 (s, 1H), 6.10 (s, 1H), 5.98 (s, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 157.2, 141.3, 136.5, 126.7, 123.3, 121.9, 119.7, 119.4, 116.9, 111.3, 110.3, 106.7, 34.1; **HRMS** [M - H^+] calcd for $C_{21}H_{15}N_2O$: (m/z) = 311.1179, found = 311.1169.



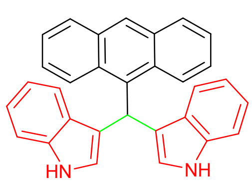
3iaa

3,3'-(Thiophen-2-ylmethylene)bis(1*H*-indole) (3jaa).[10] Analytical TLC in silica gel 2:8 ethyl acetate/hexane R_f = 0.35; Yield 80% (65.7 mg, 0.20 mmol). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.89 (brs, 2H), 7.48 (d, *J* = 8.0 Hz, 2H), 7.35 (d, *J* = 8.0 Hz, 2H), 7.21-7.15 (m, 3H), 7.07-7.03 (m, 2H), 6.94-6.91 (m, 2H), 6.81-6.80 (m, 2H), 6.17 (s, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 148.8, 136.7, 126.9, 126.6, 125.3, 123.7, 123.3, 122.1, 119.9, 119.8, 119.5, 111.3, 35.4; **HRMS** [M - H^+] calcd for $C_{21}H_{15}N_2S$: (m/z) = 327.0951, found = 327.0963.



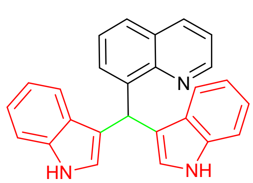
3jaa

3,3'-(Anthracen-9-ylmethylene)bis(1*H*-indole) (3kaa).[4] Analytical TLC in silica gel 2:8 ethyl acetate/hexane R_f = 0.30; Yield 68% (71.8 mg, 0.17 mmol). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.64 (d, *J* = 9.1 Hz, 2H), 8.46 (s, 1H), 8.01 (d, *J* = 8.2 Hz, 2H), 7.82 (s, 2H), 7.43-7.29 (m, 6H), 7.14-7.18 (m, 5H), 6.90-6.86 (m, 2H), 6.75 (s, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 136.7, 135.3, 132.1, 129.3, 127.5, 127.4, 124.8, 124.1, 122.0, 120.1, 119.3, 119.0, 111.1, 35.2; **HRMS** [M - H^+] calcd for $C_{31}H_{21}N_2$: (m/z) = 421.1700, found = 421.1680.



3kaa

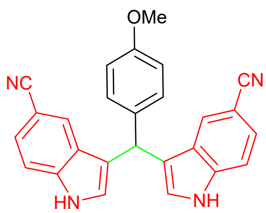
8-(Di(1*H*-indol-3-yl)methyl)quinoline (3laa). Analytical TLC in silica gel 3:7 ethyl acetate/hexane R_f = 0.40; Yield 70% (65.4 mg, 0.175 mmol). **^{1}H NMR** (400 MHz, CD_3OD): δ 8.86 (d, *J* = 4.0 Hz, 1H), 8.33 (d, *J* = 8.0 Hz,



3laa

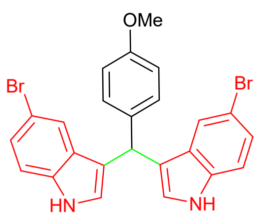
1H), 7.78 (d, *J* = 8.0.0 Hz, 1H), 7.60 (d, *J* = 8.0 Hz, 1H), 7.51-7.43 (m, 2H), 7.32-7.24 (m, 5H), 7.05-7.01 (m, 2H), 6.84-6.80 (m, 2H), 6.57 (d, *J* = 4.0 Hz, 2H); **^{13}C NMR** (100 MHz, CD_3OD): δ 150.5, 147.2, 144.1, 138.6, 138.3, 131.1, 130.1, 128.5, 127.5, 127.4, 125.0, 122.2, 122.1, 120.6, 120.3, 119.3, 112.1, 34.5; **HRMS** [M + H^+] calcd for $C_{26}H_{20}N_3$: (m/z) = 374.1657, found = 374.1660.

3,3'-((4-Methoxyphenyl)methylene)bis(1*H*-indole-5-carbonitrile) (3abb).[3] Analytical TLC in silica gel 4:6 ethyl acetate/hexane R_f = 0.40; Yield 77% (77.5 mg, 0.193 mmol). **^{1}H NMR** (400 MHz, CD_3OD): δ 7.60 (brs, 2H), 7.48 (d, *J* = 12 Hz, 2H), 7.33-7.31 (m, 2H), 7.18 (d, *J* = 8 Hz, 2H), 6.84-6.82 (m, 4H), 5.82 (s, 1H), 4.60 (s, 2H), 3.74 (s, 3H); **^{13}C NMR** (100 MHz, CD_3OD): δ 159.8, 140.3, 136.8, 130.5, 128.0, 127.3, 126.1, 125.2, 121.9, 121.0, 114.8, 113.6, 102.1, 55.7, 40.2; **HRMS** [M - H^+] calcd for $C_{26}H_{17}N_4O$: (m/z) = 401.1397, found = 401.1381.



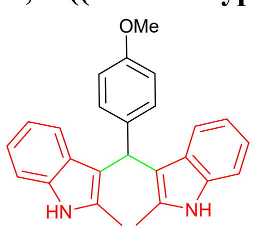
3abb

3,3'-((4-Methoxyphenyl)methylene)bis(5-bromo-1*H*-indole) (3acc).[11] Analytical TLC in silica gel 2:8 ethyl acetate/hexane R_f = 0.30; Yield 75% (95.7 mg, 0.187 mmol). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.02 (brs, 2H), 7.47 (s, 2H), 7.23-7.17 (m, 6H), 6.83 (d, *J* = 8.0 Hz, 2H), 6.63-6.62 (m, 2H), 5.69 (s, 1H), 3.79 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 158.3, 135.5, 135.4, 129.6, 128.8, 125.0, 124.8, 122.4, 119.5, 113.9, 112.7, 55.4, 39.2; **HRMS** [M - H^+] calcd for $C_{24}H_{17}{}^{79}Br_2N_2O$: (m/z) = 508.9682, found = 508.9668.



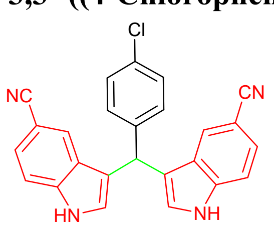
3acc

3,3'-((4-Methoxyphenyl)methylene)bis(2-methyl-1*H*-indole) (3add).[4] Analytical TLC in silica gel 3:7 ethyl acetate/hexane R_f = 0.50; Yield = 74% (70.4 mg, 0.185 mmol). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.71 (brs, 2H), 7.23 (d, *J* = 8.0 Hz, 2H),7.18 (d, *J* = 8.0 Hz, 2H), 7.05-6.99 (m, 4H), 6.87-6.84 (m, 2H), 6.80-6.78 (m, 2H), 5.95 (s, 1H), 3.79 (s, 3H), 2.05 (s, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 158.0, 136.0, 135.2, 131.8, 130.1, 129.1, 120.7, 119.5, 119.2, 113.8, 113.6, 110.1, 55.4, 38.6, 12.6; **HRMS** [M - H^+] calcd for $C_{26}H_{23}N_2O$: (m/z) = 379.1805, found = 379.1810.



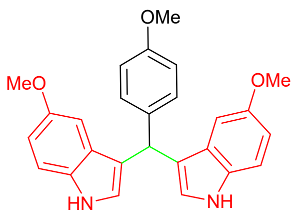
3add

3,3'-((4-Chlorophenyl)methylene)bis(1*H*-indole-5-carbonitrile) (3dbb). Analytical TLC in silica gel 4:6 ethyl acetate/hexane R_f = 0.50; Yield = 80% (81,4 mg, 0.20 mmol). **^{1}H NMR** (400 MHz, CD_3OD): δ 7.63 (brs, 2H), 7.49 (d, *J* = 8.0Hz, 2H), 7.34 (d, *J* = 8.0Hz, 2H), 7.27-7.27 (m, 4H), 6.86 (s, 2H), 5.91 (s, 1H); **^{13}C NMR** (100 MHz, CD_3OD): δ 143.6, 140.3, 133.3, 131.2, 129.5, 127.9, 127.5, 125.9, 125.3, 121.8, 120.2, 113.7, 102.4, 40.3; **HRMS** [M + H^+] calcd for $C_{25}H_{14}{}^{35}ClN_4$: (m/z) = 407.1063, found = 407.1037.



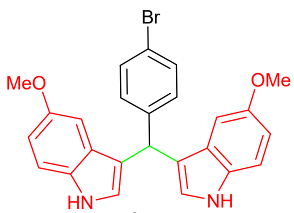
3dbb

3,3'-((4-Methoxyphenyl)methylene)bis(5-methoxy-1*H*-indole) (3aee).[11] Analytical TLC in silica gel 2:3 ethyl acetate/hexane R_f = 0.50; Yield = 93% (95.9 mg, 0.233 mmol). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.84 (brs, 2H), 7.26-7.21 (m, 4H), 6.84-6.81 (m, 6H), 6.62 (s, 2H), 5.73 (s, 1H), 3.78 (s, 3H), 3.70 (s, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 158.0, 153.7, 136.3, 132.0, 129.7, 127.6, 124.5, 119.7, 113.7, 111.9, 111.8, 102.2, 56.0, 55.4, 39.5; **HRMS** [M - H^+] calcd for $C_{26}H_{23}N_2O_3$: (m/z) = 411.1704, found = 411.1710.



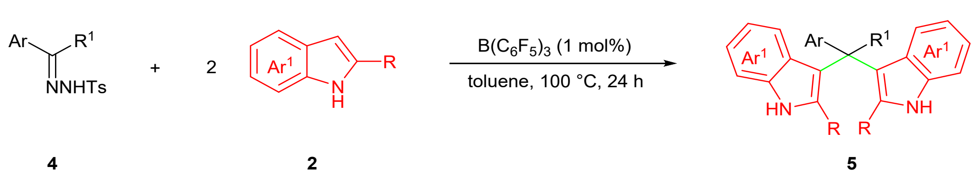
3aee

3,3'-((4-Bromophenyl)methylene)bis(5-methoxy-1*H*-indole) (3nee). Analytical TLC in silica gel 2:3 ethyl acetate/hexane R_f = 0.45; Yield = 95% (109.6 mg, 0.237 mmol). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.87 (brs, 2H), 7.39 (d, J = 8.4 Hz, 2H), 7.24-7.20 (m, 4H), 6.86-6.79 (m, 4H), 6.60 (s, 2H), 5.74 (s, 1H), 3.71 (s, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 153.8, 143.1, 132.0, 131.4, 130.6, 130.1, 128.4, 127.4, 124.6, 120.0, 118.7, 112.0, 111.9, 102.0, 56.0, 39.8; **HRMS** [M - H^+] calcd for $C_{25}H_{20}{}^{79}BrN_2O_2$: (m/z) = 459.0703, found = 459.0698.

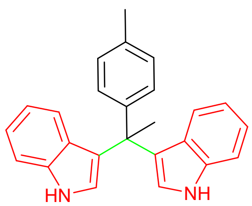


3nee

IV. $B(C_6F_5)_3$ catalyzed synthesis of symmetrical DIM's 5 from hydrazones of aryl ketone 4 and indole 2



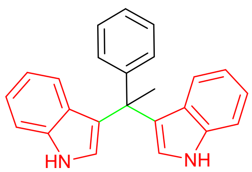
Representative Procedure: *N*-Tosylhydrazone **4a** (75.6 mg, 0.25 mmol, 1.0 equiv) and indole **2a** (58.6 mg, 0.5 mmol, 2.0 equiv) were dissolved in 2 mL toluene in a 10 mL Schlenk tube. $B(C_6F_5)_3$ catalyst (1.3 mg, 0.0025 mmol, 1 mol%) was added to that solution under nitrogen at room temperature with continuous stirring for 10 minutes. The reaction mixture was heated at 100 °C for 24 hours. The completion of reaction was monitored by TLC and the solvent was removed under reduced pressure to get crude reaction mixture. The compound was purified with the aid of column chromatography using 1:9 ethyl acetate/hexane as eluent to afford symmetrical DIM **5aaa** in 71% yield (62.2 mg, 0.177 mmol).



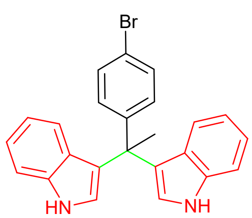
5aaa

3,3'-(1-(*p*-Tolyl)ethane-1,1-diyl)bis(1*H*-indole) (5aaa). Analytical TLC in silica gel 2:8 ethyl acetate/hexane R_f = 0.35; Yield 71% (62.2 mg, 0.178 mmol). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.68 (brs, 2H), 7.38 (d, *J* = 8.0 Hz, 2H), 7.33-7.30 (m, 4H), 7.17 (t, *J* = 8.0 Hz, 2H), 7.08 (d, *J* = 12 Hz, 2H), 7.00-6.96 (m, 2H), 6.57 (d, *J* = 4.0 Hz, 2H), 2.38-2.36 (m, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 145.1, 137.2, 135.2, 128.6, 128.0, 126.6, 124.9, 123.5, 122.2, 121.6, 119.0, 111.3, 43.5, 28.9, 21.1; **HRMS** [M^+] calcd for $C_{25}H_{22}N_2$: (m/z) = 350.1783, found = 350.1795.

3,3'-(1-Phenylethane-1,1-diyl)bis(1*H*-indole) (5baa).[12] Analytical TLC in silica gel 2:8 ethyl acetate/hexane R_f = 0.40; Yield 80% (67.3 mg, 0.20 mmol). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.78 (brs, 2H), 7.42 (d, *J* = 8.0 Hz, 2H), 7.36-7.32 (m, 4H), 7.29-7.23 (m, 3H), 7.18-7.14 (m, 2H), 6.98-6.94 (m, 2H), 6.59 (s, 2H), 2.38 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 148.1, 137.1, 128.2, 127.9, 126.5, 125.9, 124.7, 123.5, 122.2, 121.6, 119.0, 111.3, 43.8, 28.8; **HRMS** [$M + H^+$] calcd for $C_{24}H_{21}N_2$: (m/z) = 337.1705, found = 337.1676.

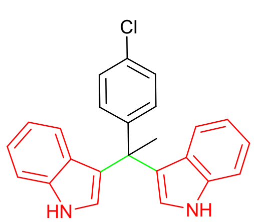


5baa



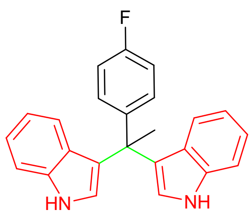
5caa

3,3'-(1-(4-Bromophenyl)ethane-1,1-diyl)bis(1*H*-indole) (5caa). Analytical TLC in silica gel 3:7 ethyl acetate/hexane R_f = 0.35; Yield 75% (77.9 mg, 0.188 mmol). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.91 (brs, 2H), 7.37-7.35 (m, 4H), 7.32-7.27 (m, 4H), 7.17-7.13 (m, 2H), 6.97-6.93 (m, 2H), 6.64 (s, 2H), 2.34 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 147.3, 137.3, 131.0, 130.1, 126.4, 124.3, 123.5, 122.1, 121.8, 119.9, 119.2, 111.4, 43.7, 28.8; **HRMS** [M^+] calcd for $C_{24}H_{19}{}^{37}BrN_2$: (m/z) = 416.0711, found = 416.0684.

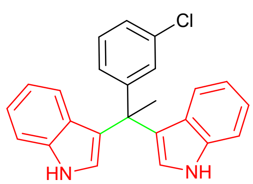


5daa

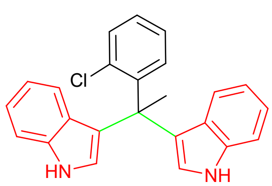
3,3'-(1-(4-Chlorophenyl)ethane-1,1-diyl)bis(1*H*-indole) (5daa). Analytical TLC in silica gel 2:8 ethyl acetate/hexane R_f = 0.30; Yield 84% (77.9 mg, 0.21 mmol). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.62 (brs, 2H), 7.40-7.31 (m, 6H), 7.25-7.21 (m, 4H), 7.07-7.03 (m, 2H), 6.53 (d, *J* = 4.0 Hz, 2H), 2.39 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 146.6, 137.1, 131.6, 129.6, 128.0, 126.2, 124.1, 123.5, 122.0, 121.7, 119.1, 111.4, 43.4, 28.8; **HRMS** [M - H$^+$] calcd for $C_{24}H_{18}{}^{35}ClN_2$: (m/z) = 369.1164, found = 369.1179.


5eaa

3,3'-(1-(4-Fluorophenyl)ethane-1,1-diyl)bis(1*H*-indole) (5eaa). Analytical TLC in silica gel 3:7 ethyl acetate/hexane R_f = 0.50; Yield 72% (64.0 mg, 0.18 mmol). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.88 (brs, 2H), 7.37-7.30 (m, 6H), 7.15 (m, 2H), 6.97-6.91 (m, 4H), 6.62 (s, 2H), 2.35 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 161.2 (d, *J* = 242 Hz), 143.9 (d, *J* = 3.0 Hz), 137.3, 129.7 (d, *J* = 7.0 Hz), 126.4, 124.7, 123.4, 122.1, 121.8, 119.2, 114.6 (d, *J* = 20 Hz), 111.3, 102.8, 43.4, 29.0; **^{19}F NMR** (376 MHz, $CDCl_3$): δ -117.8 (td, *J* = 8.0, 4.2 Hz, 1F); **HRMS** [M - H$^+$] calcd for $C_{24}H_{18}FN_2$: (m/z) = 353.1454, found = 353.1478.


5faa

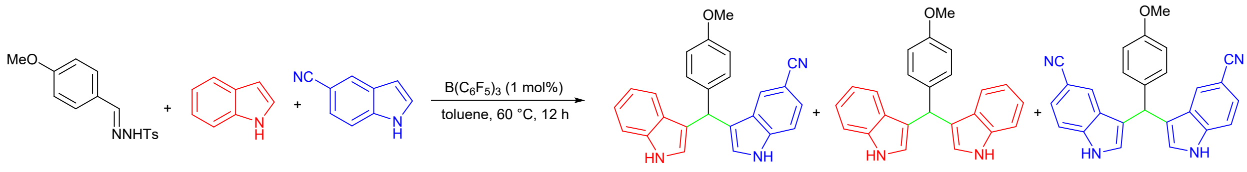
3,3'-(1-(3-Chlorophenyl)ethane-1,1-diyl)bis(1*H*-indole) (5faa). Analytical TLC in silica gel 3:7 ethyl acetate/hexane R_f = 0.40; Yield 74% (68.6 mg, 0.185 mmol). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.89 (brs, 2H), 7.42 (s, 1H), 7.37-7.31 (m, 4H), 7.18-7.13 (m,4H), 6.98-6.94 (m, 3H), 6.63 (d, *J* = 4.0 Hz, 2H), 2.35 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 150.4, 137.3, 133.9, 129.1, 128.3, 126.6, 126.3, 126.2, 124.1, 123.5, 122.0, 121.8, 119.2, 111.4, 43.9, 28.7; **HRMS** [M - H$^+$] calcd for $C_{24}H_{18}{}^{35}ClN_2$: (m/z) = 369.1145, found = 369.1138.


5gaa

3,3'-(1-(2-chlorophenyl)ethane-1,1-diyl)bis(1*H*-indole) (5gaa). Analytical TLC in silica gel 3:7 ethyl acetate/hexane R_f = 0.35; Yield = 65% (60.1 mg, 0.163 mmol). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.82 (brs, 2H), 7.52 (d, *J* = 8.0 Hz, 1H), 7.35-7.28 (m, 5H), 7.19-7.15 (m, 4H), 6.99-6.95 (m, 2H), 6.66 (s, 2H), 2.57 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 144.4, 137.1, 134.7, 132.1, 131.4, 127.8, 126.7, 126.3, 123.9, 123.3, 121.9, 121.6, 119.2, 111.4, 45.0, 27.3; **HRMS** [M - H$^+$] calcd for $C_{24}H_{18}{}^{35}ClN_2$: (m/z) = 369.1164, found = 369.1138.

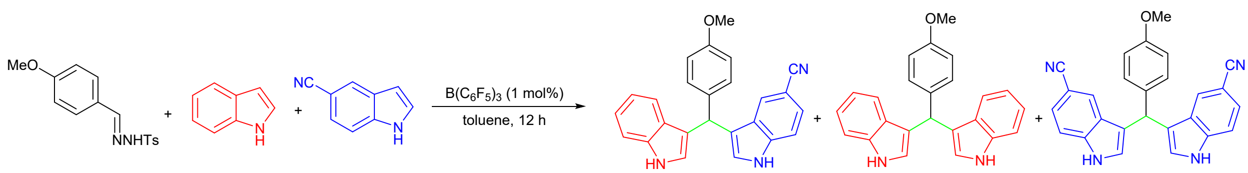
V. $B(C_6F_5)_3$ catalyzed synthesis of unsymmetrical DIM 6 from hydrazone of aryl aldehyde 1 and indoles 2

Va. Table S1. Optimization of reactant ratio for unsymmetrical DIMs synthesis



entry	reactant ratio (**1a**:**2a**:**2b**)	yield (%)		
		6aab	**3aaa**	**3abb**
1.	1:1:1	75	10	7
2.	1:2:1	23	62	5
3.	1:1:2	73	12	10

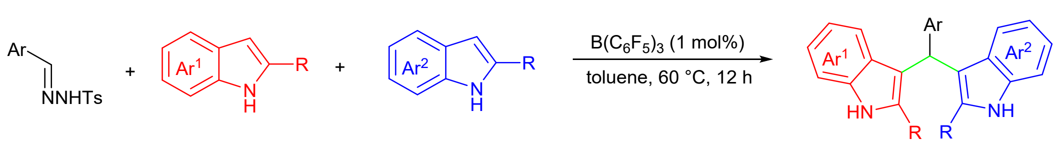
Vb. Table S2. Optimization of temperature for unsymmetrical DIMs synthesis



entry	reactant ratio (**1a**:**2a**:**2b**)	Temperature (°C)	yield (%)		
			6aab	**3aaa**	**3abb**
1.	1:1:1	40	n.d.	n.d.	n.d.
2.	1:1:1	60	75	10	7
3.	1:1:1	80	45	25	20

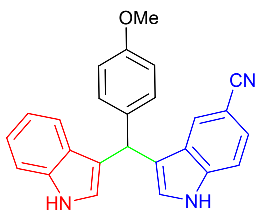
n.d. = not detected

Vc. Procedure for synthesis of unsymmetrical DIM's



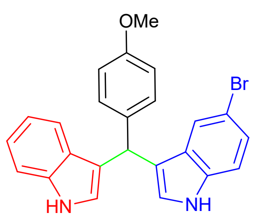
Representative Procedure: *N*-tosylhydrazone **1a** (76.1 mg, 0.25 mmol, 1.0 equiv), indole **2a** (29.3 mg, 0.25 mmol, 1.0 equiv) and indole **2b** (35.5 mg, 0.25mmol, 1.0 equiv) were dissolved in 2 mL toluene in a 15 mL Schlenk tube. $B(C_6F_5)_3$ catalyst (1.3 mg, 0.0025 mmol, 1 mol%) was added to that solution under nitrogen at room temperature with continuous stirring. Next, the reaction mixture was heated at 60°C for 12 h. The completion of reaction was monitored by TLC. The solvent was removed under reduced pressure and the analytically pure compound was isolated by column chromatography using 3:7 ethyl acetate/hexane as eluent to afford unsymmetrical bis(indolyl)methane **6aab** as solid compound in 75% yield (70.7 mg, 0.187 mmol).

3-((1*H*-Indol-3-yl)(4-methoxyphenyl)methyl)-1*H*-indole-5-carbonitrile (6aab). Analytical TLC in silica gel 3:7 ethyl acetate/hexane R_f = 0.50; Yield 75% (70.7 mg, 0.187 mmol). **^{1}H NMR** (400 MHz, CD_3OD): δ 7.61 (s, 1H), 7.47 (d, *J* = 8.0 Hz, 1H), 7.35-7.31 (m, 2H), 7.26-7.22 (m, 3H), 7.04-7.06 (m, 1H), 6.90-6.82 (m, 4H), 6.64 (s, 1H), 5.82 (s, 1H), 5.0 (s, 2H), 3.77 (s, 3H); **^{13}C NMR** (100 MHz, CD_3OD): δ 159.6, 138.5, 137.6, 130.7, 128.3, 128.1, 127.4, 126.3, 125.0, 124.6, 122.4, 122.0, 121.7, 120.3, 119.8, 119.5, 114.6, 113.4, 112.2, 101.9, 101.3, 55.7, 40.6; **HRMS** [M - H$^+$] calcd for $C_{25}H_{18}N_3O$: (m/z) = 376.1455, found = 376.1463.



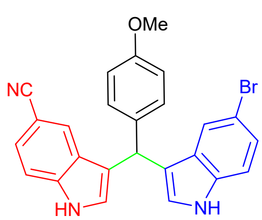
6aab

3-((1*H*-Indol-3-yl)(4-methoxyphenyl)methyl)-5-bromo-1*H*-indole (6aac). Analytical TLC in silica gel 3:7 ethyl acetate/hexane R_f = 0.35; Yield 67% (72.2 mg, 0.167 mmol). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.93 (brs, 2H), 7.53 (d, *J* = 4.0 Hz, 1H), 7.37-7.34 (m, 2H), 7.24-7.15 (m, 5H), 7.02-6.98 (m, 1H), 6.84-6.81 (m, 2H), 6.66-6.62 (m, 2H), 5.77 (s, 1H), 3.79 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 158.2, 136.9, 135.9, 135.5, 129.7, 128.9, 127.1, 125.0, 124.9, 123.6, 122.5, 122.2, 120.04, 120.00, 119.8, 119.4, 113.8, 112.7, 112.6, 111.2, 55.4, 39.3; **HRMS** [M - H$^+$] calcd for $C_{24}H_{18}{}^{79}BrN_2O$: (m/z) = 429.0598, found = 429.0582.



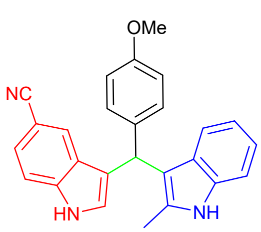
6aac

3-((5-Bromo-1*H*-indol-3-yl)(4-methoxyphenyl)methyl)-1*H*-indole-5-carbonitrile (6abc). Analytical TLC in silica gel 3:7 ethyl acetate/hexane R_f = 0.40; Yield 72% (82.1 mg, 0.18 mmol). **^{1}H NMR** (400 MHz, $(CD_3)_2CO$): δ 10.46 (m, 2H), 7.78 (s, 1H), 7.59 (d, *J* = 8.0 Hz, 1H), 7.50 (s, 1H), 7.38 (d, *J* = 8.0 Hz, 2H), 7.32-7.30 (m, 2H), 7.20-7.17 (m, 1H), 7.03-7.02 (m, 1H), 6.89-6.85 (m, 3H), 5.95 (s, 1H), 3.76 (s, 3H); **^{13}C NMR** (100 MHz, $(CD_3)_2CO$): δ 159.2, 139.8, 136.8, 130.3, 129.7, 127.8, 127.1, 126.2, 125.8, 124.88, 124.85, 122.6, 121.2, 121.1, 119.4, 114.5, 114.2, 114.1, 113.6, 112.4, 102.5, 55.4, 39.7; **HRMS** [M - H$^+$] calcd for $C_{25}H_{17}{}^{79}BrN_3O$: (m/z) = 454.0550, found = 454.0559 .



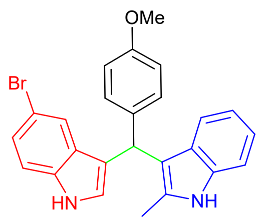
6abc

3-((4-Methoxyphenyl)(2-methyl-1*H*-indol-3-yl)methyl)-1*H*-indole-5-carbonitrile (6abd). Analytical TLC in silica gel 3:7 ethyl acetate/hexane R_f = 0.40; Yield 58% (56.8 mg, 0.145 mmol). **^{1}H NMR** (400 MHz, CD_3OD): δ 7.77 (m, 1H), 7.45-7.41 (m, 2H), 7.29-7.16 (m, 4H), 7.04 (d, *J* = 8.0 Hz, 1H), 6.94-6.89 (m, 1H), 6.77-6.71 (m, 4H), 5.81 (s, 1H), 3.69 (s, 3H), 3.35 (s, 1H), 2.21 (s, 3H); **^{13}C NMR** (100 MHz, CD_3OD): δ 159.4,



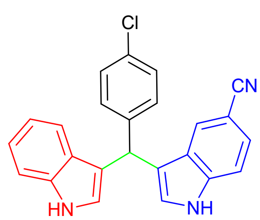
6abd

140.3, 137.4, 137.0, 132.9, 130.7, 129.5, 128.5, 127.4, 126.2, 125.0, 122.0, 121.6, 121.1, 119.8, 119.3, 114.5, 113.9, 113.4, 111.3, 101.8, 55.6, 39.8, 11.98; **HRMS** [M - H$^+$] calcd for $C_{26}H_{20}N_3O$: (m/z) = 390.1601, found = 390.1612.



6acd

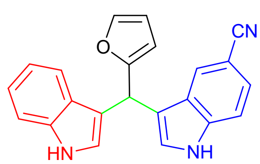
5-Bromo-3-((4-methoxyphenyl)(2-methyl-1*H*-indol-3-yl)methyl)-1*H*-indole (6acd). Analytical TLC in silica gel 2:8 ethyl acetate/hexane R_f = 0.35; Yield 52% (57.9 mg, 0.13 mmol). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.98 (brs, 1H), 7.78 (brs, 1H), 7.42 (s, 1H), 7.27 (s, 1H), 7.25-7.17 (m, 5H), 7.06-7.02 (m, 1H), 6.90-6.86 (m, 1H), 6.80-6.78 (m, 2H), 6.69-6.69 (m, 1H), 5.78 (s, 1H), 3.77 (s, 3H), 2.23 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 158.0, 135.9, 135.4, 131.4, 129.7, 129.4, 128.5, 125.02, 124.95, 122.4, 120.9, 119.6, 119.5, 119.2, 113.9, 113.7, 112.73, 112.71, 112.6, 110.2, 55.4, 38.5, 12.4; **HRMS** [M - H$^+$] calcd for $C_{25}H_{20}{}^{79}BrN_2O$: (m/z) = 443.0754, found = 443.0769.



6dab

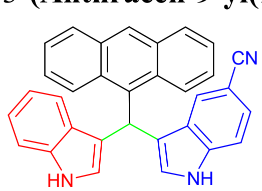
3-((4-Chlorophenyl)(1*H*-indol-3-yl)methyl)-1*H*-indole-5-carbonitrile (6dab). Analytical TLC in silica gel 3:7 ethyl acetate/hexane R_f = 0.40; Yield 78% (74.5 mg, 0.195 mmol). **^{1}H NMR** (400 MHz, CD_3OD): δ 7.78 (d, *J* = 8.0 Hz, 1H), 7.62 (s, 1H), 7.47 (d, *J* = 8.0 Hz, 1H), 7.36-7.32 (m, 3H), 7.28-7.23 (m, 5H), 7.07 (t, *J* = 8.0 Hz, 1H), 6.90-6.84 (m, 2H), 6.66 (s, 1H), 5.87 (s, 1H); **^{13}C NMR** (100 MHz, CD_3OD): δ 144.4, 140.3, 138.5, 132.9, 131.3, 130.5, 129.3, 128.1, 127.5, 127.1, 126.1, 125.2, 124.7, 122.5, 120.9, 120.2, 119.7, 118.9, 113.5, 112.3, 102.1, 40.7; **HRMS** [M - H$^+$] calcd for $C_{24}H_{15}ClN_3$: (m/z) = 380.0950, found = 380.0965.

3-(Furan-2-yl(1*H*-indol-3-yl)methyl)-1*H*-indole-5-carbonitrile (6iab). Analytical TLC in silica gel 3:7 ethyl acetate/hexane R_f = 0.45; Yield 70% (59.0 mg, 0.175 mmol). **^{1}H NMR** (400 MHz, CD_3OD): δ 7.78-7.70 (m, 2H), 7.45-7.28 (m, 6H), 7.08-7.04 (m, 2H), 6.91-6.88 (m, 2H), 6.33-6.31 (m, 1H), 6.02-6.00 (m, 1H), 5.90 (s, 1H); **^{13}C NMR** (100 MHz, CD_3OD): δ 158.5, 142.3, 140.1, 138.3, 130.5, 128.7, 127.9, 127.0, 126.1, 125.0, 124.2, 122.4, 120.2, 119.6, 118.9, 116.9, 113.5, 112.3, 111.1, 107.4, 102.0, 35.3; **HRMS** [M - H$^+$] calcd for $C_{22}H_{14}N_3O$: (m/z) = 336.1132 , found = 336.1140.



6iab

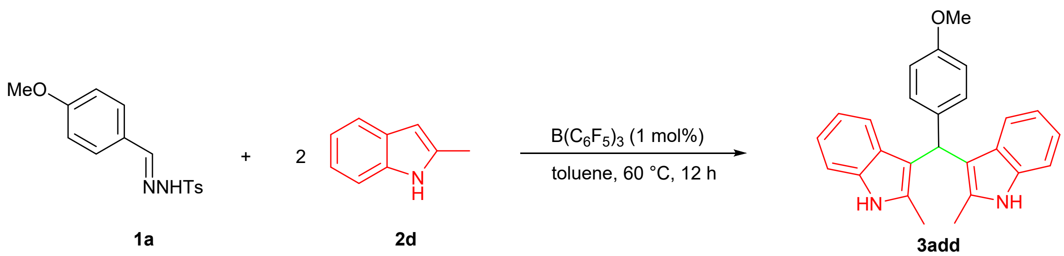
3-**(Anthracen-9-yl(1*H*-indol-3-yl)methyl)-1*H*-indole-5-carbonitrile (6kab).** Analytical TLC in silica gel 3:7 ethyl acetate/hexane R_f = 0.30; Yield 62% (69.4 mg, 0.155 mmol). **^{1}H NMR** (400 MHz, CD_3OD): δ 8.59-8.52 (m, 2H), 8.05 (d, *J* = 8.0 Hz, 1H), 7.90-7.60 (m, 2H), 7.44-7.24 (m, 9H), 7.15-7.04 (m, 4H), 6.92 (s, 1H), 6.85-6.81 (m, 1H), 6.70 (s, 1H); **^{13}C NMR** (100 MHz, CD_3OD): δ 140.2, 138.3, 136.3, 133.5, 130.3, 129.8, 129.3, 128.4, 128.3, 127.6, 127.2,



6kab

126.2, 126.0, 125.8, 125.1, 125.0, 122.5, 121.0, 120.2, 119.7, 118.4, 113.5, 112.3, 101.9, 101.3, 36.2; **HRMS** [M$^+$] calcd for $C_{32}H_{21}N_3$: (m/z) = 447.1735, found = 447.1707.

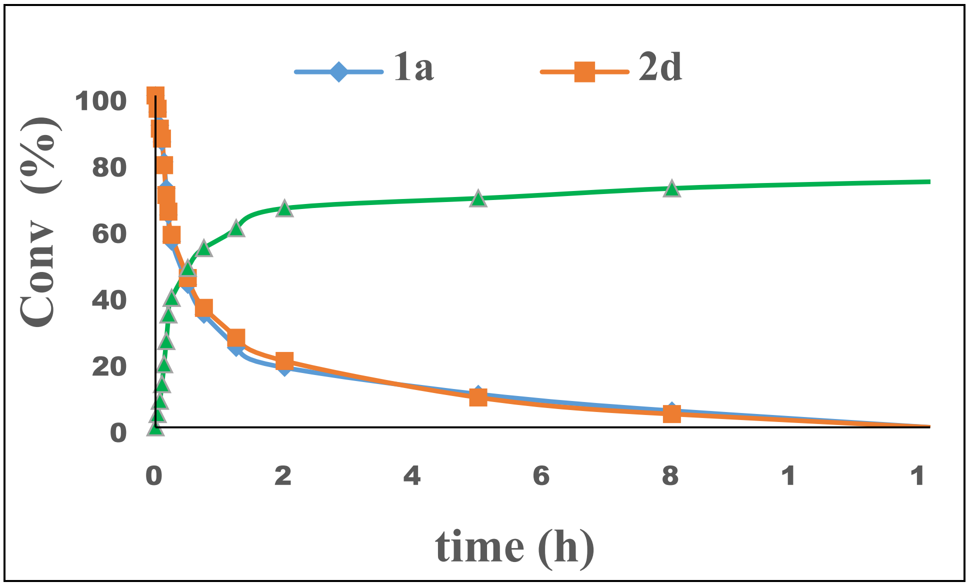
VI. Kinetic profile determination



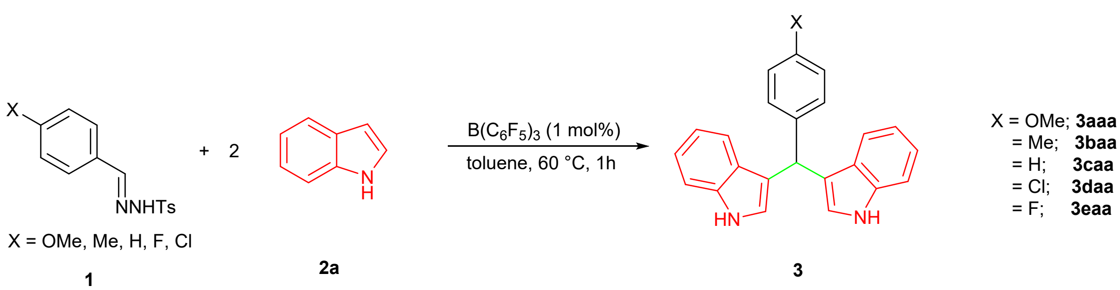
Experimental Procedure: *N*-Tosylhydrazone **1a** (19.02 mg, 0.0625 mmol, 1.0 equiv) and indole **2d** (16.4 mg, 0.125 mmol, 2.0 equiv) were dissolved in 0.6 mL benzene-d$_6$ in a NMR tube. $B(C_6F_5)_3$ catalyst (0.32 mg, 0.000625 mmol, 1 mol%) and 1,3,5-trimethoxybenzene (10.51 mg, 0.0625mmol, 1 equiv) was added to that solution under nitrogen at room temperature. The reaction tube was heated at 60°C. The yield of each component was determined by ^{1}H NMR taken at different time interval for kinetic measurement.

time (h)	**% yield**		
	1a	**2d**	**3add**
0	100	100	0
0.033	95	96	4
0.067	91	90	8
0.1	86	87	13
0.133	80	79	19
0.167	72	70	26
0.2	64	65	34
0.25	56	58	39
0.5	43	45	48
0.75	34	36	54
1.25	24	27	60
2	18	20	66
5	10	9	69
8	5	4	72
12	0	0	74

Kinetic Profile diagram



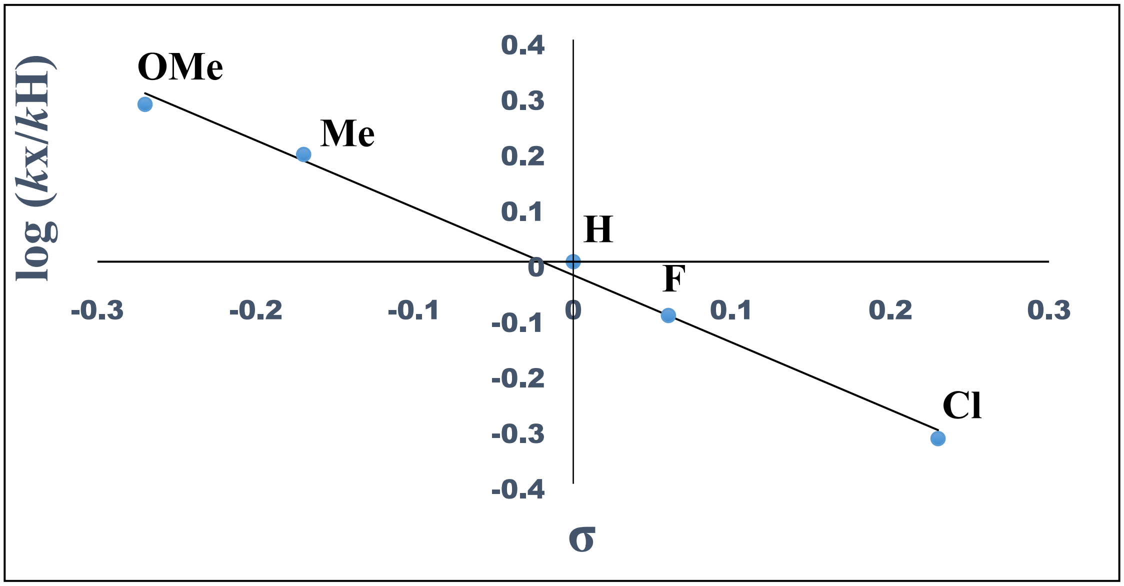
VII. Hammett analysis by varying *N*-tosylhydrazone 1



Experimental Procedure: In five different 15 mL Schlenk tubes *N*-tosylhydrazone **1a**, **1b**, **1c**, **1d** and **1e** (0.25 mmol, 1.0 equiv) and were dissolved in 2 mL toluene seperately. Next, indole **2a** (58.6 mg, 0.5 mmol, 2.0 equiv) and $B(C_6F_5)_3$ catalyst (1.3 mg, 0.0025 mmol, 1 mol%) were added to that solution in each of the tubes under nitrogen at room temperature with continuous stirring for 5 minutes. The reaction mixture was heated at 60°C for 1 h. The solvent was removed from the reaction mixture under reduced pressure and 1,3,5-trimethoxybenzene (42.0 mg, 0.25mmol, 1 equiv) was added to the crude residue as an external standard for the determination of the yield of the products by ^{1}H NMR. The ratio of the reaction rate was determined from the ratio of the yields of corresponding product for Hammett analysis.

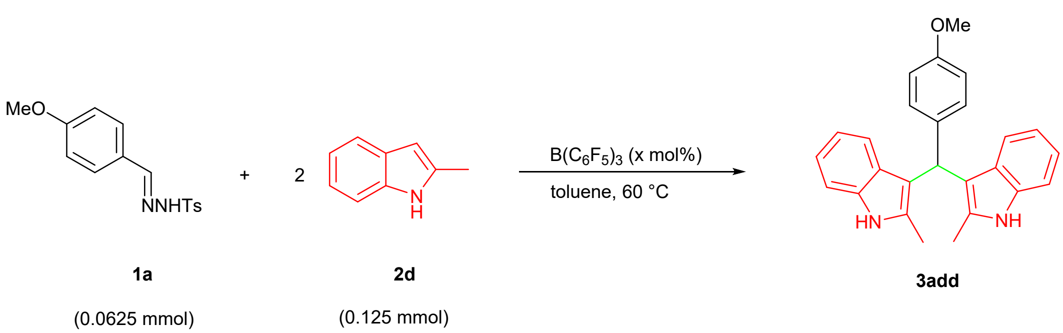
X	σ	log (kx/kH)

p-OMe	-0.27	0.2833
p-Me	-0.17	0.1931
H	0	0
p-F	0.06	-0.0969
p-Cl	0.23	-0.3186

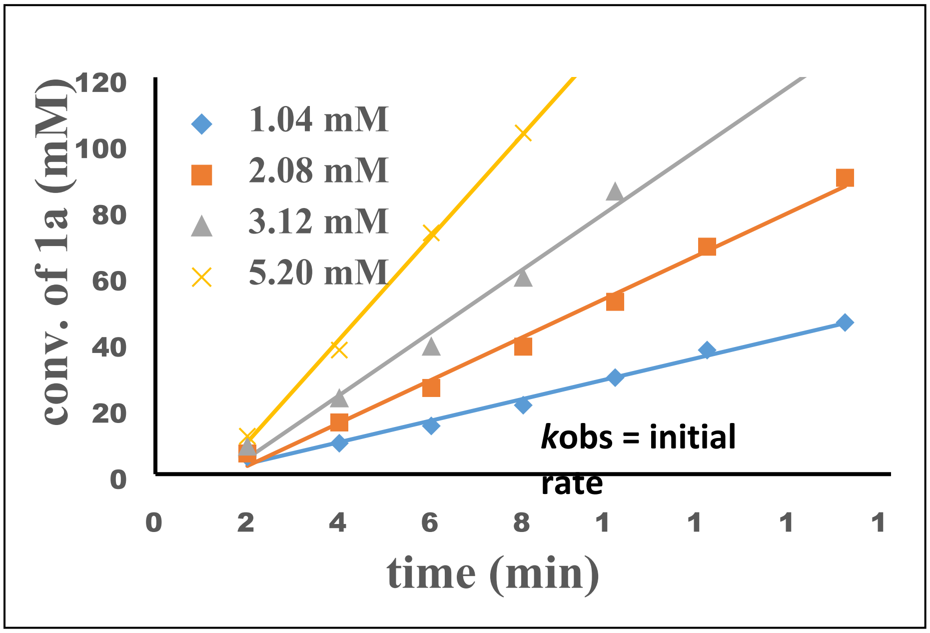


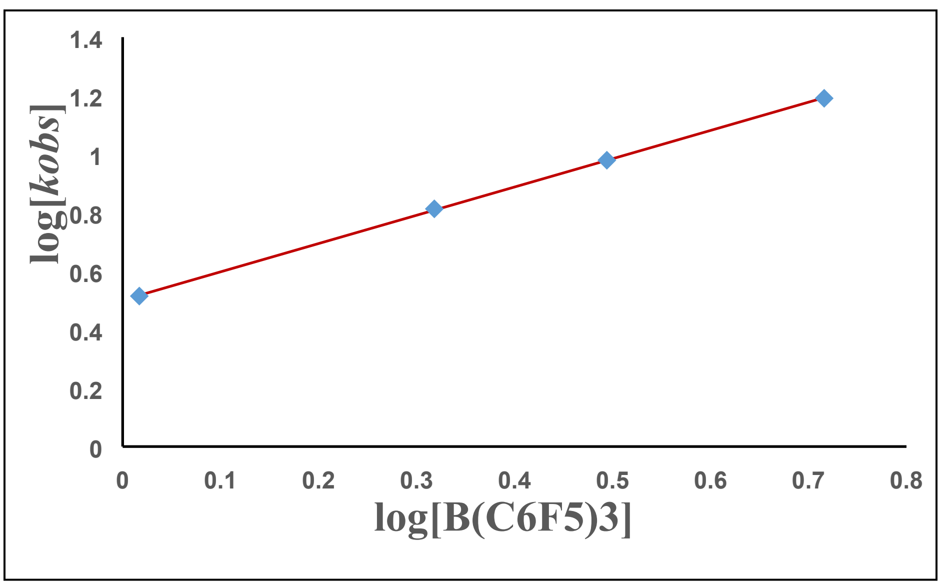
VII. Kinetic studies for determination of reaction order

VIIa. Reaction Order Determination by varying catalyst concentration

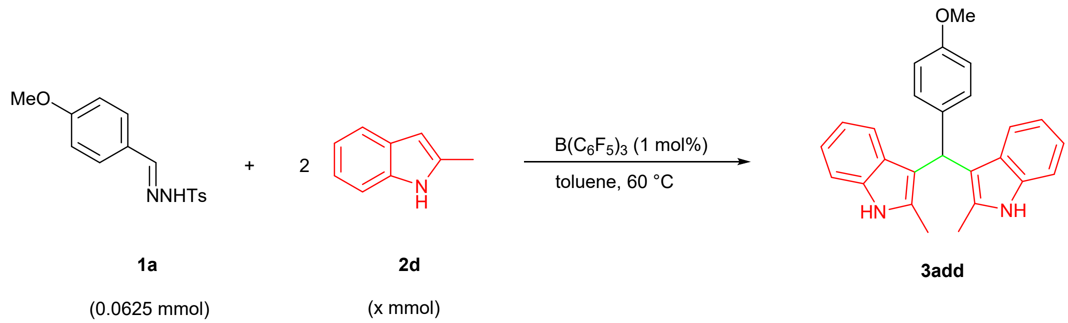


Experimental procedure: In four (1-4) different J-Young NMR tubes each of *N*-tosylhydrazone **1a** (19.02 mg, 0.0625 mmol, 1.0 equiv) and indole **2d** (16.4 mg, 0.125 mmol, 2.0 equiv) were dissolved in 0.6 mL benzene-d_6. Next, $B(C_6F_5)_3$ catalyst of 0.000625 mmol (1 mol%), 0.00125 mmol (2 mol%), 0.001875 mmol (3 mol%) and 0.003125 mmol (5 mol%) have been added serially from number 1 to 4 tubes respectively. Then, 1,3,5-trimethoxybenzene (10.51 mg, 0.0625 mmol, 1 equiv) was added to the reaction mixture as an internal standard and the reaction sets were heated at 60 °C. The conversion of *N*-tosylhydrazone **1a** was determined by [1]H NMR analysis at different time intervals.

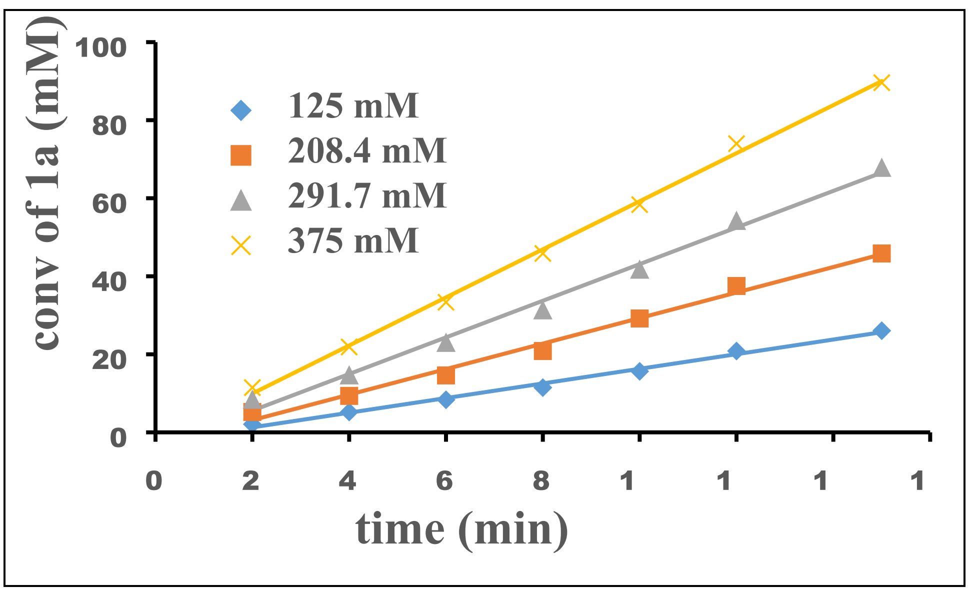


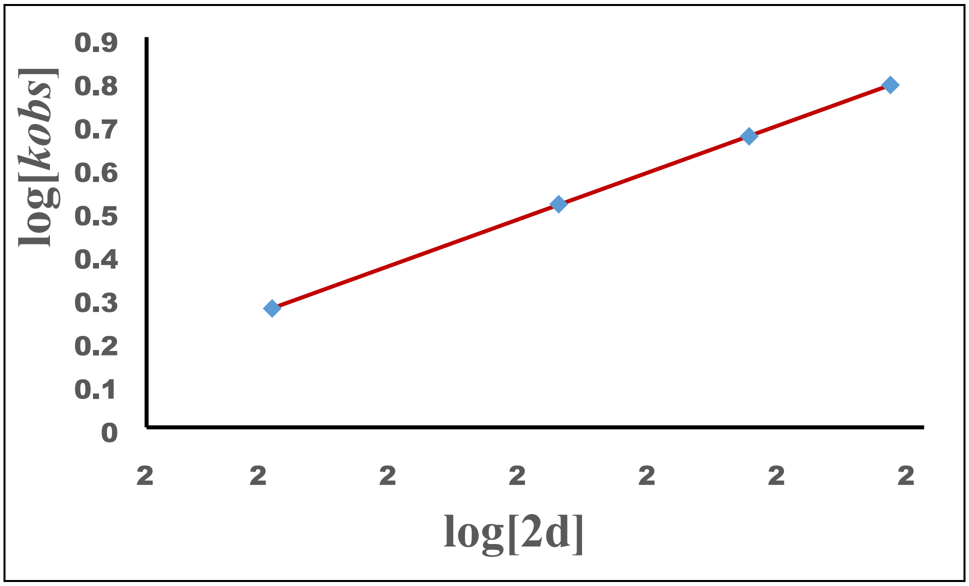


VIIb. Reaction Order Determination by varying concentration of indole 2d

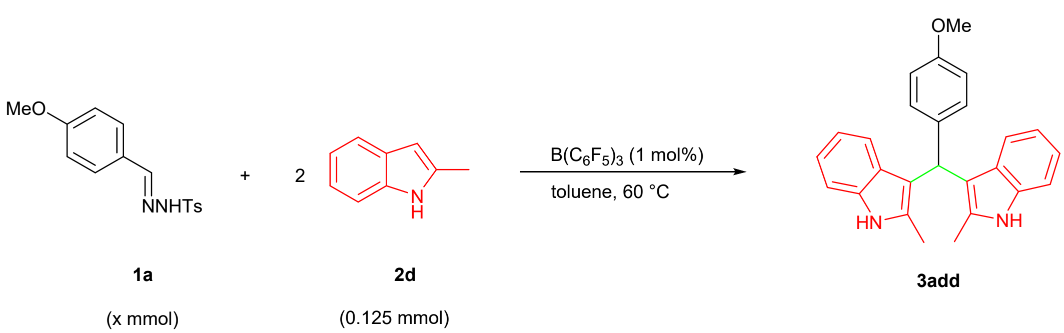


Experimental procedure: In four (1-4) different J-Young NMR tubes indole **2d** of 0.075 mmol, 0.125 mmol, 0.175 mmol, 0.225 mmol were added respectively. Next, in each tube *N*-tosylhydrazone **1a** (19.02 mg, 0.0625 mmol) was taken followed by addition of 0.6 mL benzene-d_6. After that, $B(C_6F_5)_3$ catalyst (0.32 mg, 0.000625 mmol, 1 mol%) and internal standard 1,3,5-trimethoxybenzene (10.51 mg, 0.0625mmol) were mixed to the solution under nitrogen. The reaction sets were heated at 60 °C and the conversion of *N*-tosylhydrazone **1a** was determined by ^{1}H NMR taken at different time intervals.

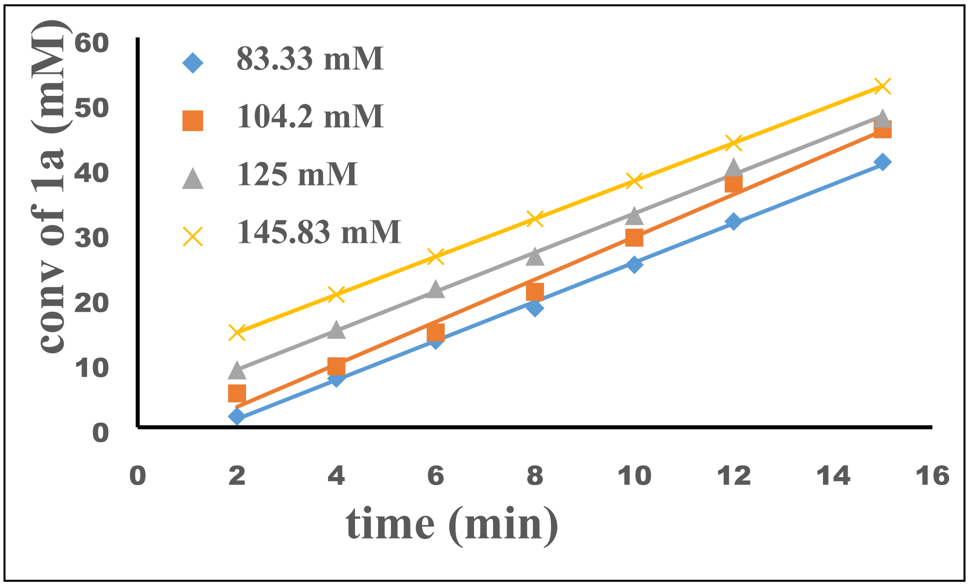


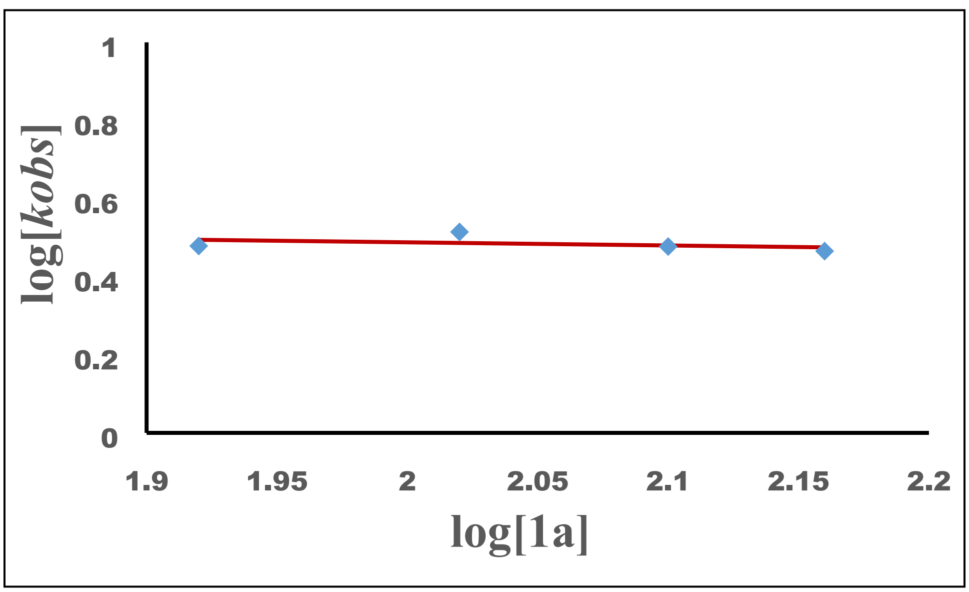


VIIc. Reaction Order Determination by varying concentration of *N*-Tosylhydrazone 1a

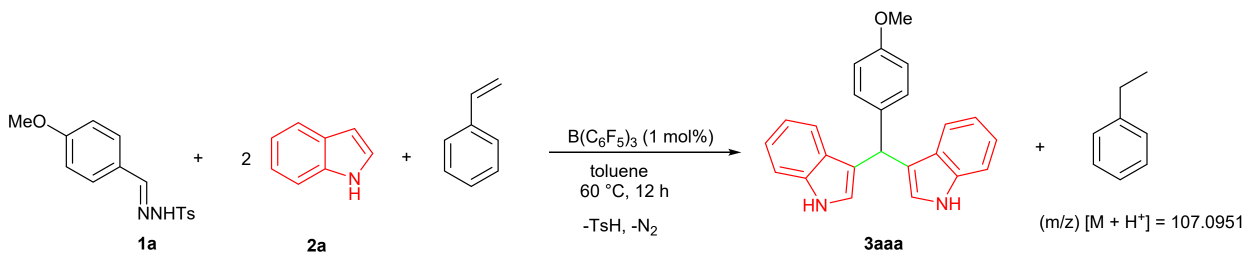


Experimental procedure: In four (1-4) different J-Young NMR tubes *N*-tosylhydrazone **1a** of 0.05 mmol, 0.0625 mmol, 0.075 mmol and 0.875 mmol have been added respectively. Next, in each tube indole **2d** (16.4 mg, 0.125 mmol) was taken followed by addition of 0.6 mL benzene-d_6. After that, $B(C_6F_5)_3$ catalyst (0.32 mg, 0.000625 mmol, 1 mol%) and internal standard 1,3,5-trimethoxybenzene (10.51 mg, 0.0625mmol) were mixed to the solution under nitrogen. The reaction sets were heated at 60 °C and the conversion of *N*-tosylhydrazone **1a** was determined by ^{1}H NMR taken at different time intervals.

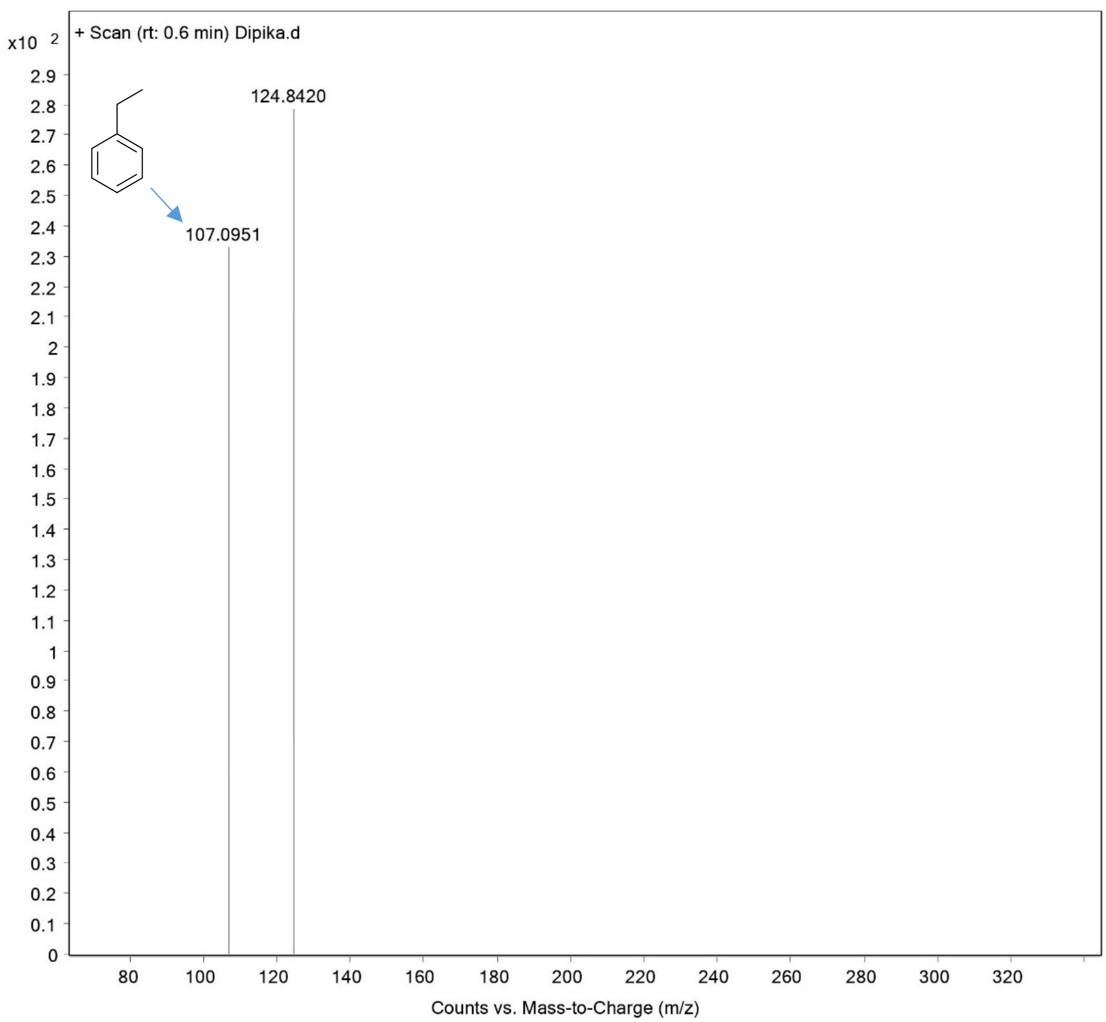




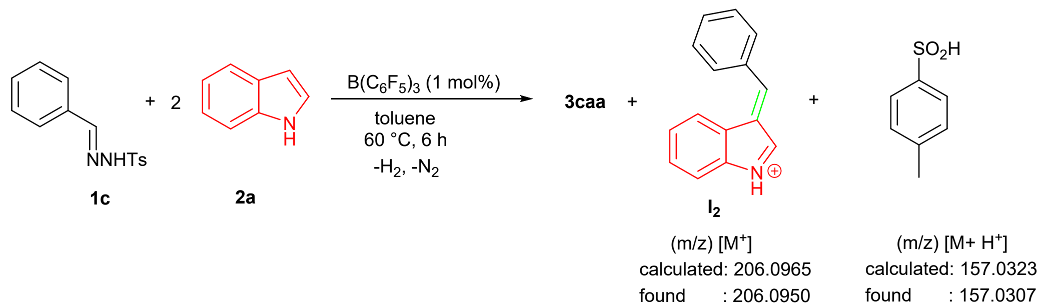
VIII. Hydrogen liberation experiment.



Experimental Procedure: *N*-Tosylhydrazone **1a** (76.1 mg, 0.25 mmol, 1.0 equiv), styrene (26.03 mg, 0.25 mmol, 1 equiv) and indole **2a** (58.6 mg, 0.5 mmol, 2.0 equiv) were dissolved in 2 mL toluene in a 15 mL sealed tube. $B(C_6F_5)_3$ catalyst (1.3 mg, 0.0025 mmol, 1 mol%) was added to that solution under nitrogen at room temperature with continuous stirring for 5 minutes. The reaction mixture was heated at 60 °C for 12 h and then the crude mixture was analyzed by HRMS.

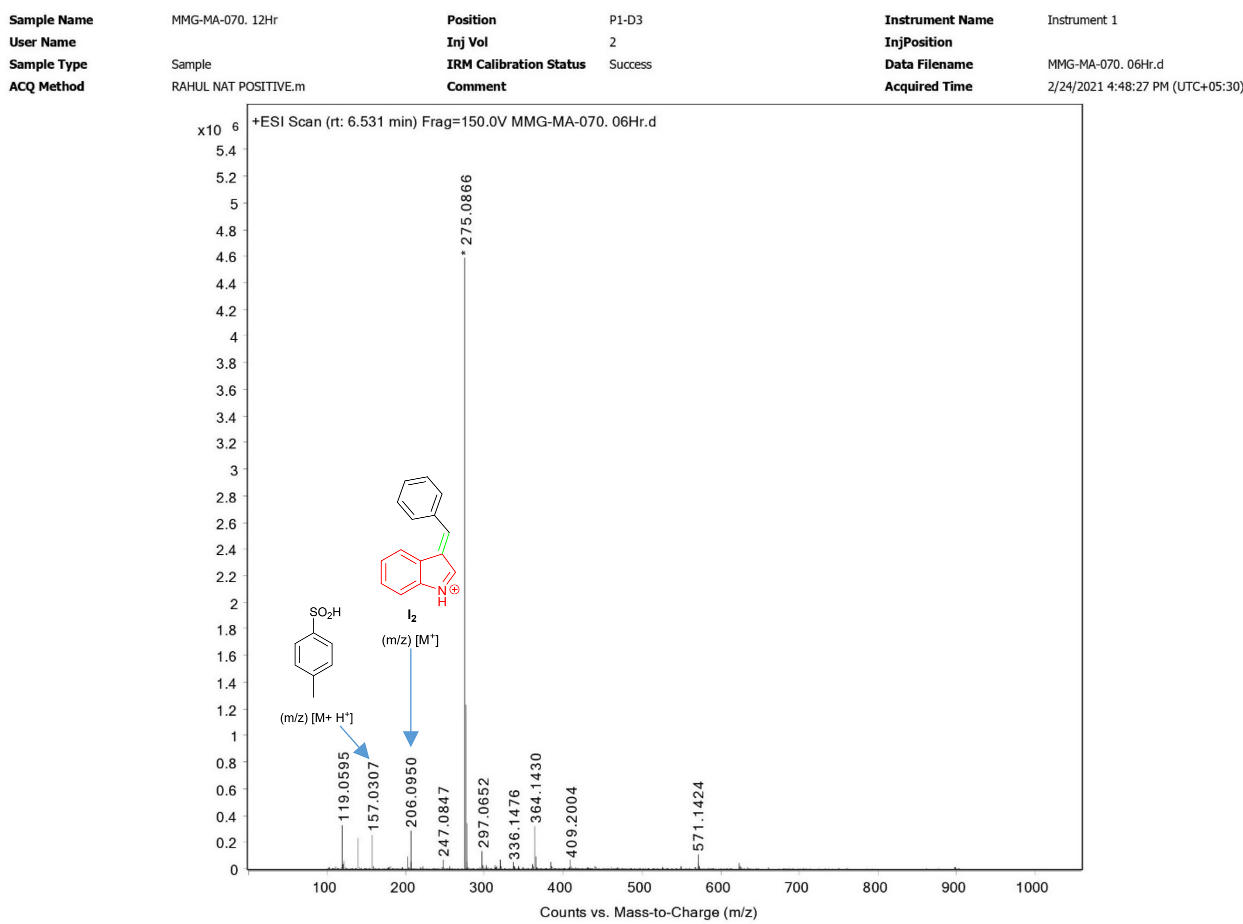


IX. Detection of reaction intermediate by HRMS



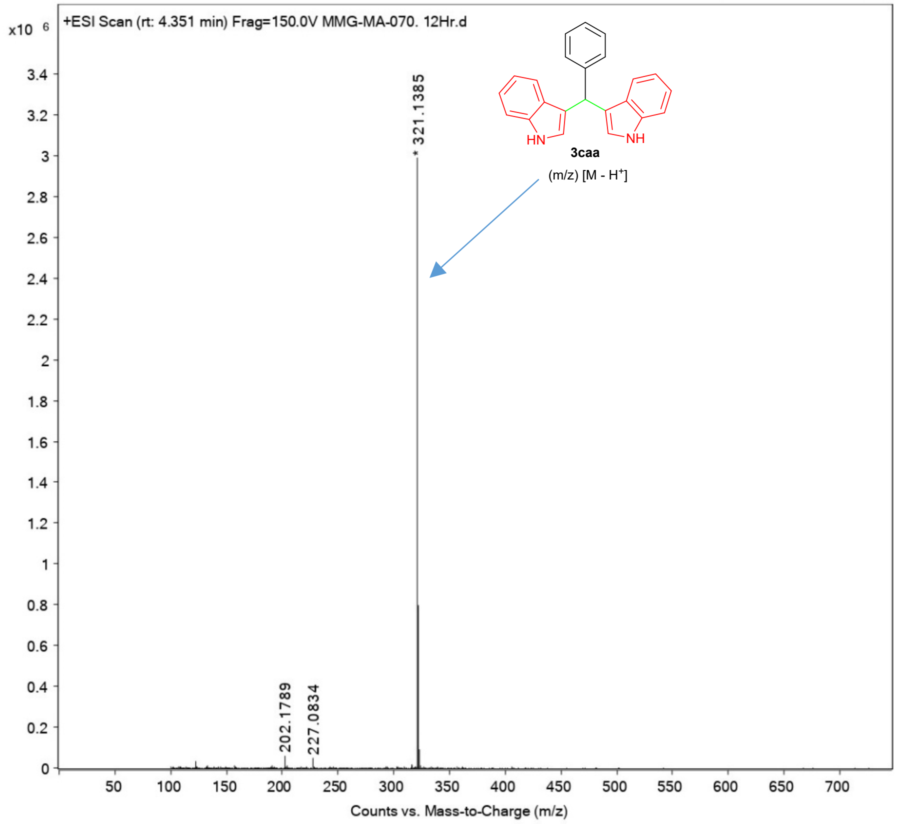
Experimental Procedure: *N*-tosylhydrazone **1c** (34.3 mg, 0.25 mmol, 1.0 equiv) and indole **2a** (R^2=H) (29.3 mg, 0.5 mmol, 2.0 equiv) were dissolved in 2 mL toluene in a 15 mL Schlenk tube. $B(C_6F_5)_3$ catalyst (1.3 mg, 0.0025 mmol, 1 mol%) was added to that solution under nitrogen at room temperature with continuous stirring for 5 minutes. The reaction mixture was heated at 60 °C for 6 h. After 6 h, a small portion of the crude reaction mixture was analyzed by HRMS. Again, the reaction was continued for 12 h and further analyzed by HRMS.

HRMS analysis of the crude mixture after 6 h of reaction



HRMS analysis of the crude mixture after 12 h of reaction

Sample Name	MMG-MA-070. 12Hr	**Position**	P1-D2	**Instrument Name**	Instrument 1
User Name		**Inj Vol**	2	**InjPosition**	
Sample Type	Sample	**IRM Calibration Status**	Success	**Data Filename**	MMG-MA-070. 12Hr.d
ACQ Method	RAHUL NAT POSITIVE.m	**Comment**		**Acquired Time**	2/24/2021 4:32:25 PM (UTC+05:30)



X. Computation studies

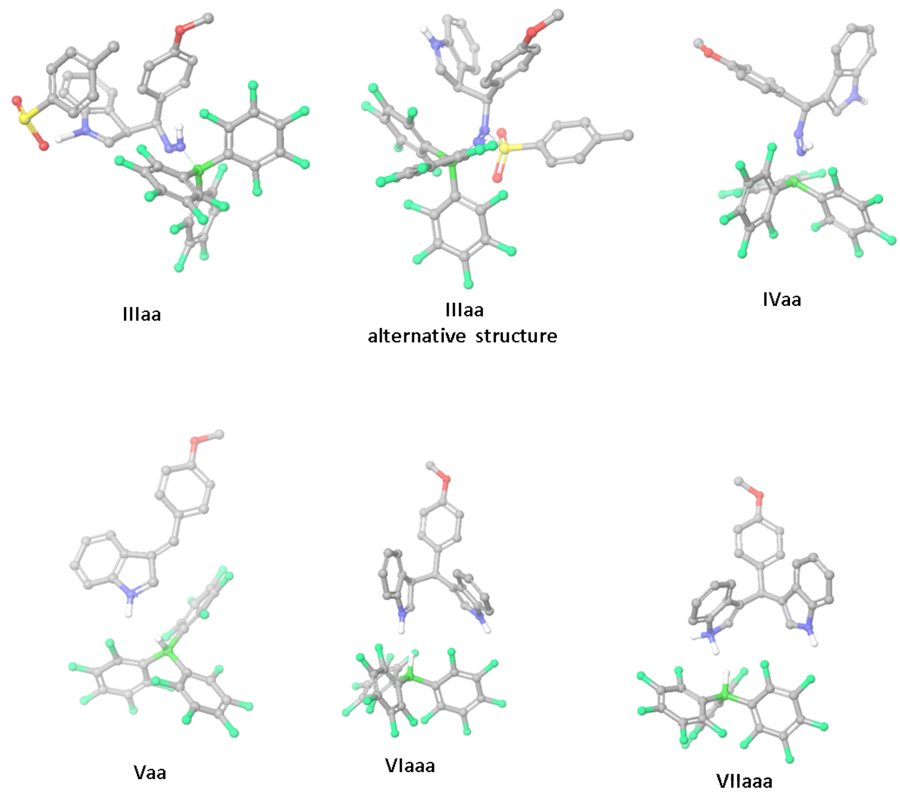


Figure S1. Optimized structures of pathway involving the formation of the symmetrical DIM (**3aaa**) (that involves unsubstituted indole in both transition states **TS1** and **TS2**).

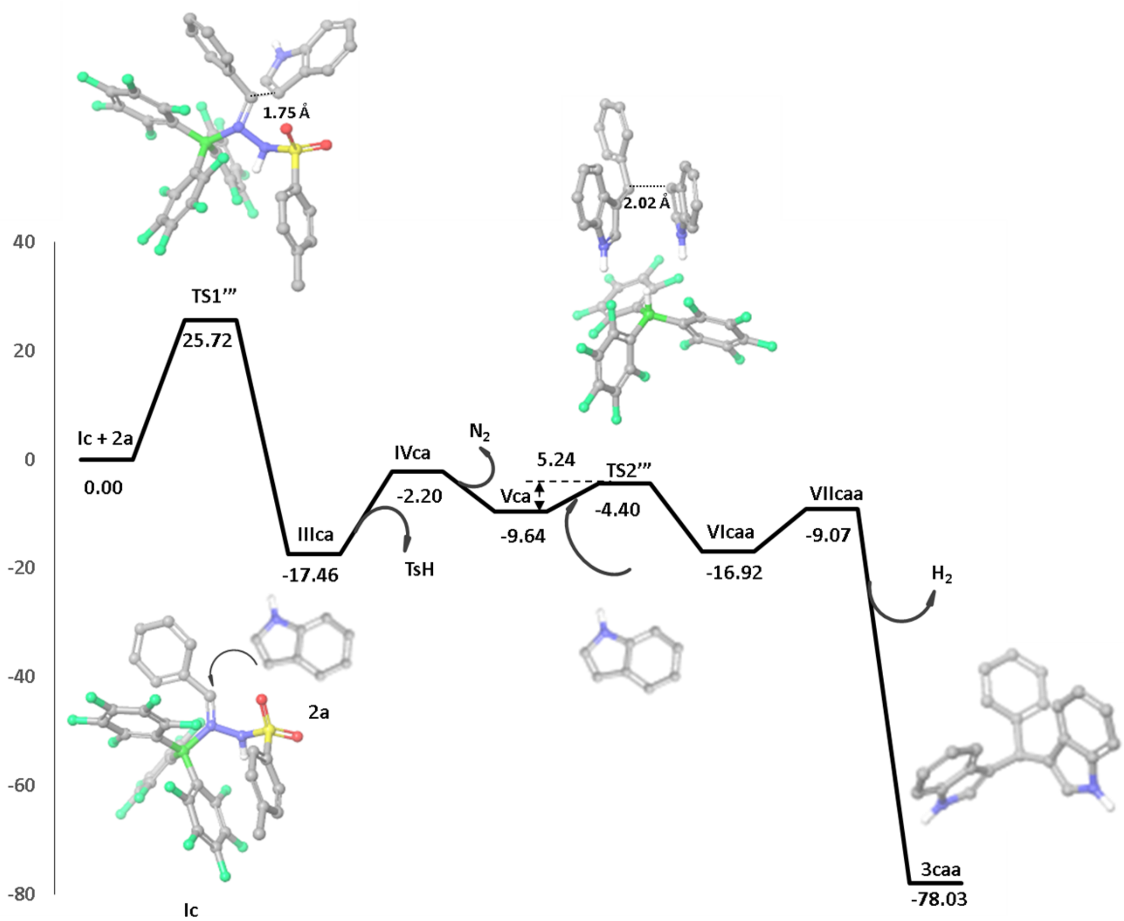


Figure S2. Potential energy surface for the formation of symmetrical product (**3caa**) with important optimized geometries at B3LYP/6-31G** level of theory. Nonpolar hydrogens were removed for clarity. Energies are in kcal/mol.

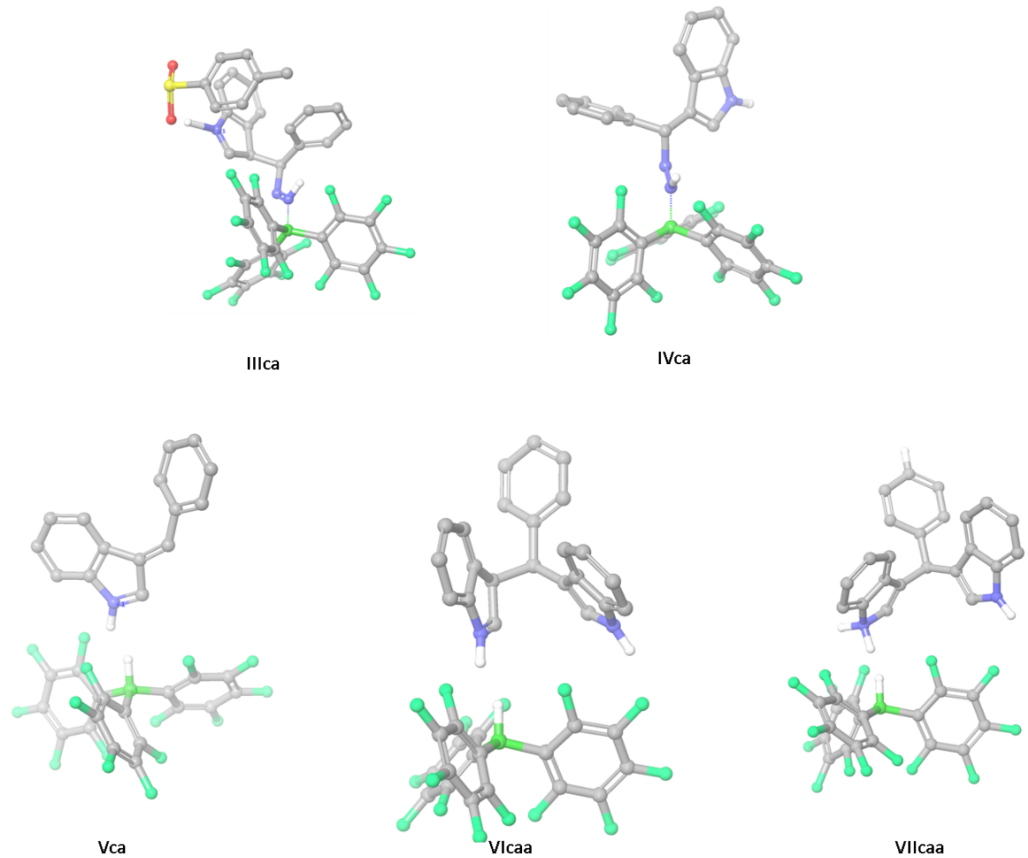


Figure S3. Optimized structures of pathway involving the formation of the symmetrical DIM (**3caa**) (that involves unsubstituted indole in both transition states **TS1** and **TS2**).

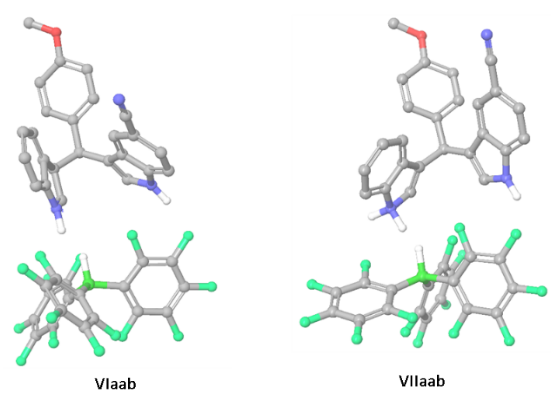


Figure S4. Optimized structures of the first possible pathway involving the formation of unsymmetrical DIM (**6aab**) (that involve unsubstituted indole in **TS1** and 5-cynoindole in the **TS2')**. Other common structures (**IIIaa**, **IVaa** and **Vaa**) are shown in **Figure S1**.

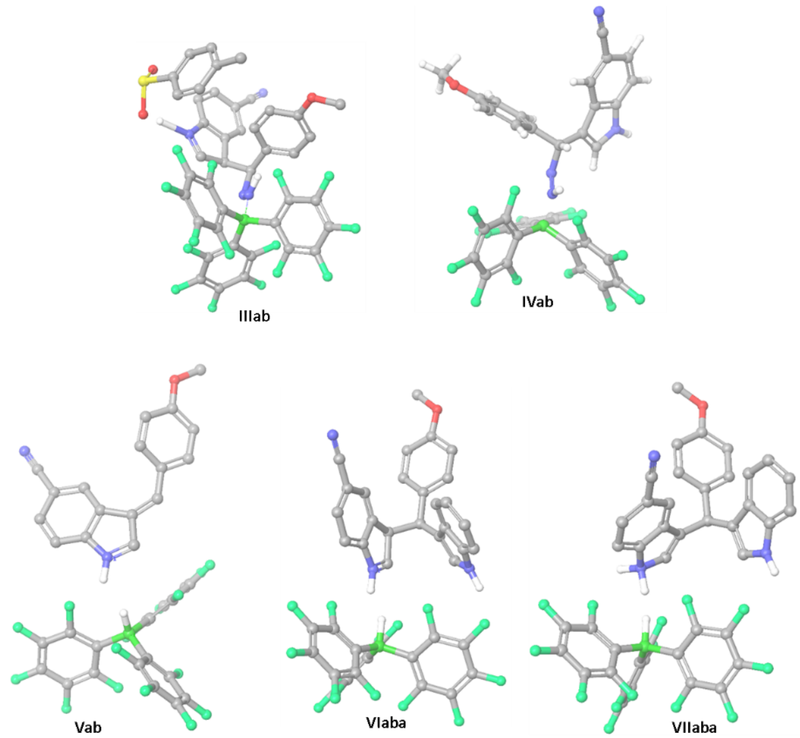


Figure S5. Optimized structures of the second possible pathway involving the formation of unsymmetrical DIM (**6aab**) (that involve 5-cynoindole in **TS″** and unsubstituted indole in the **TS″)**.

***References*:**

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XI. NMR spectra

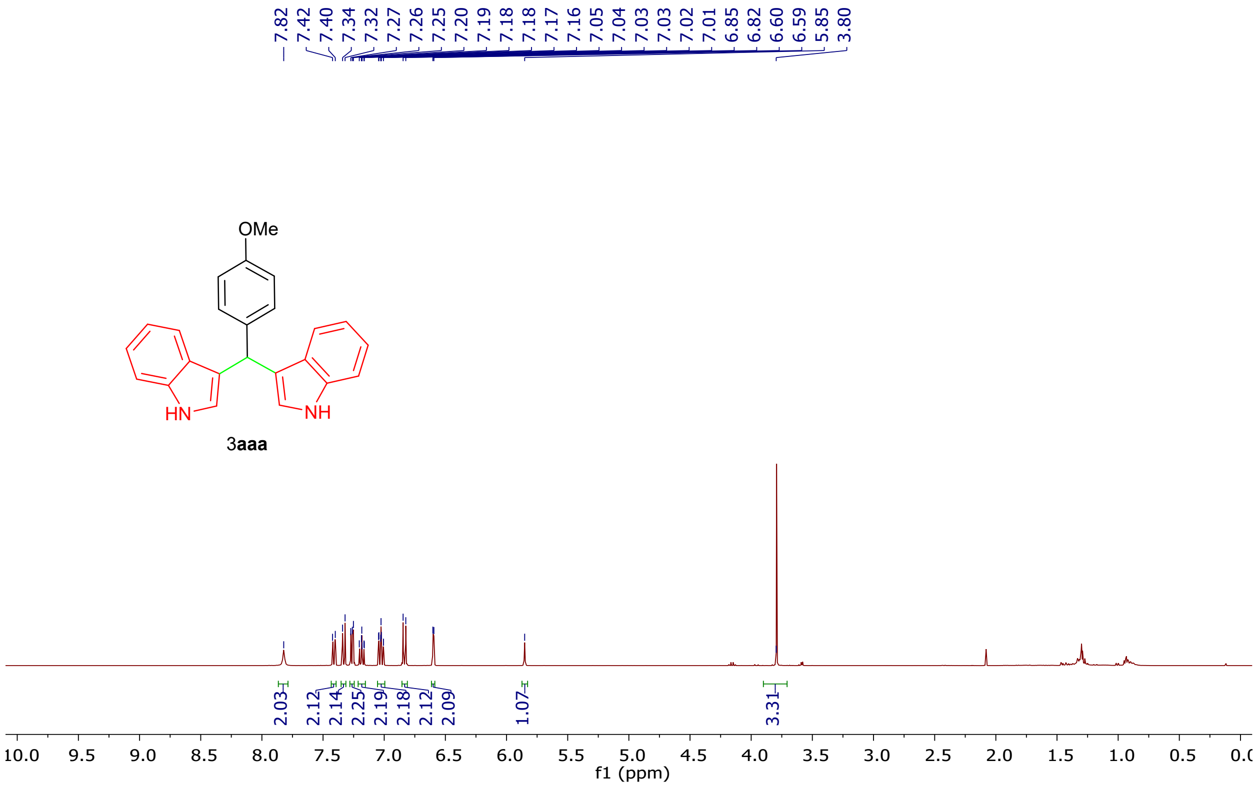


Figure. [1]H NMR of **3aaa** in $CDCl_3$

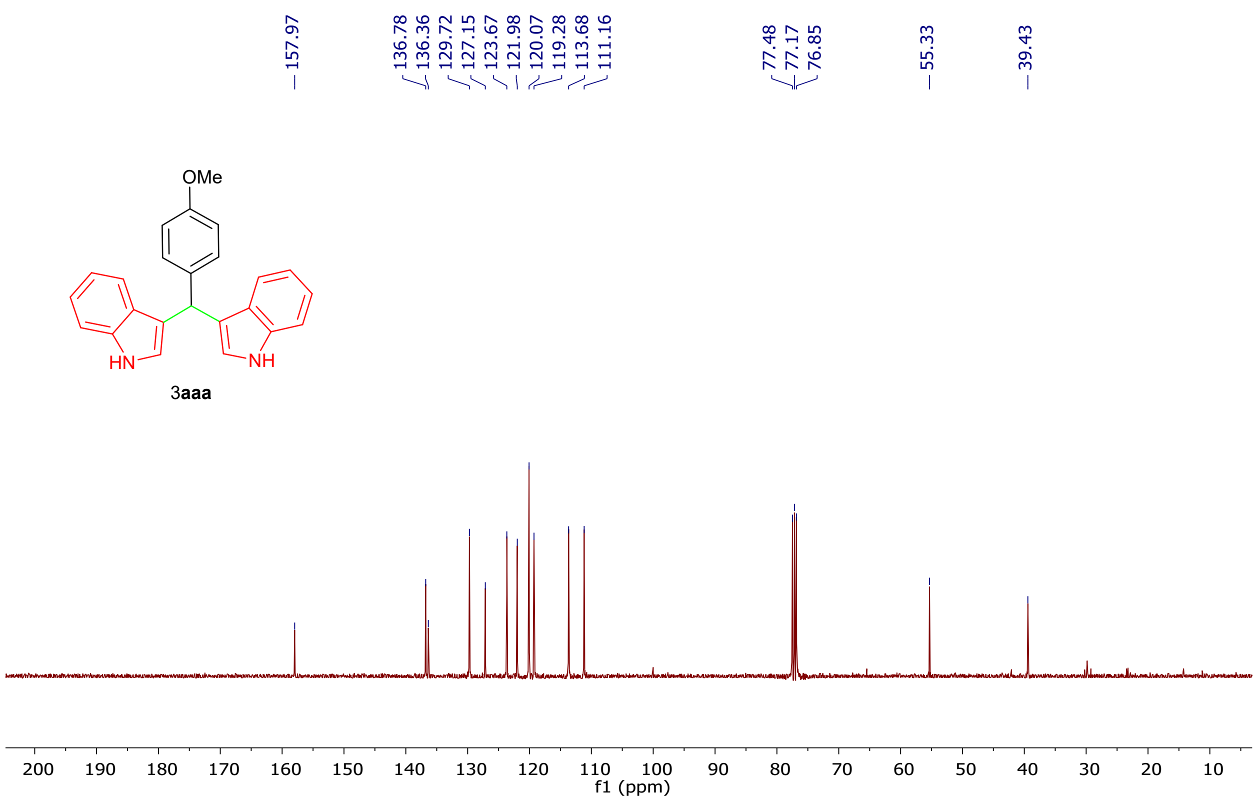
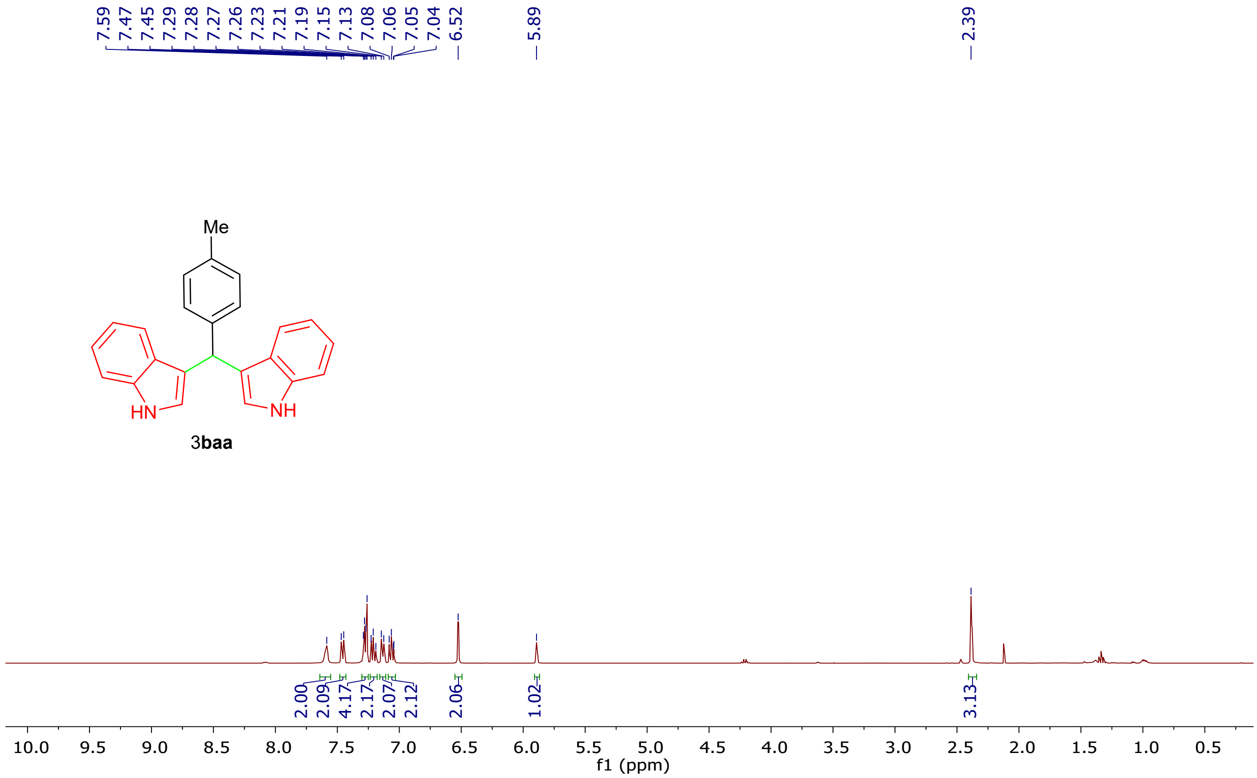


Figure. [13]C NMR of **3aaa** in $CDCl_3$



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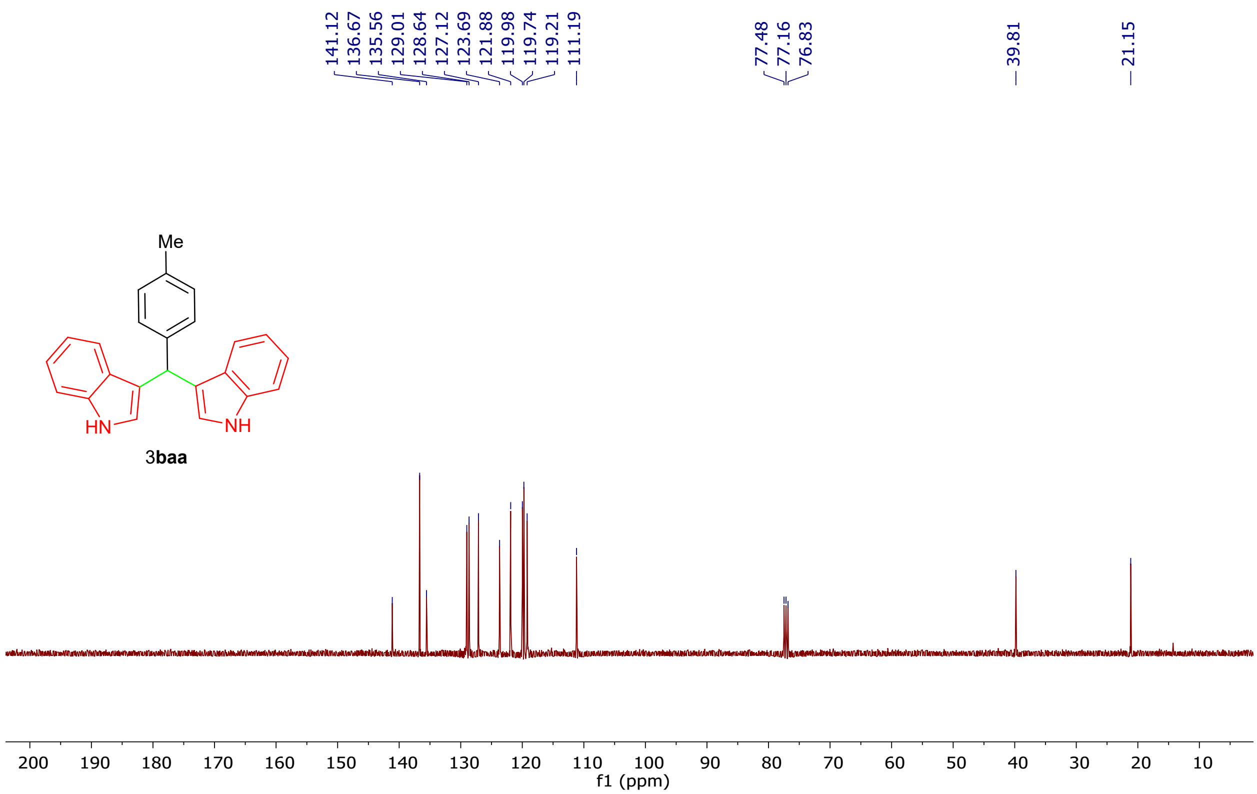

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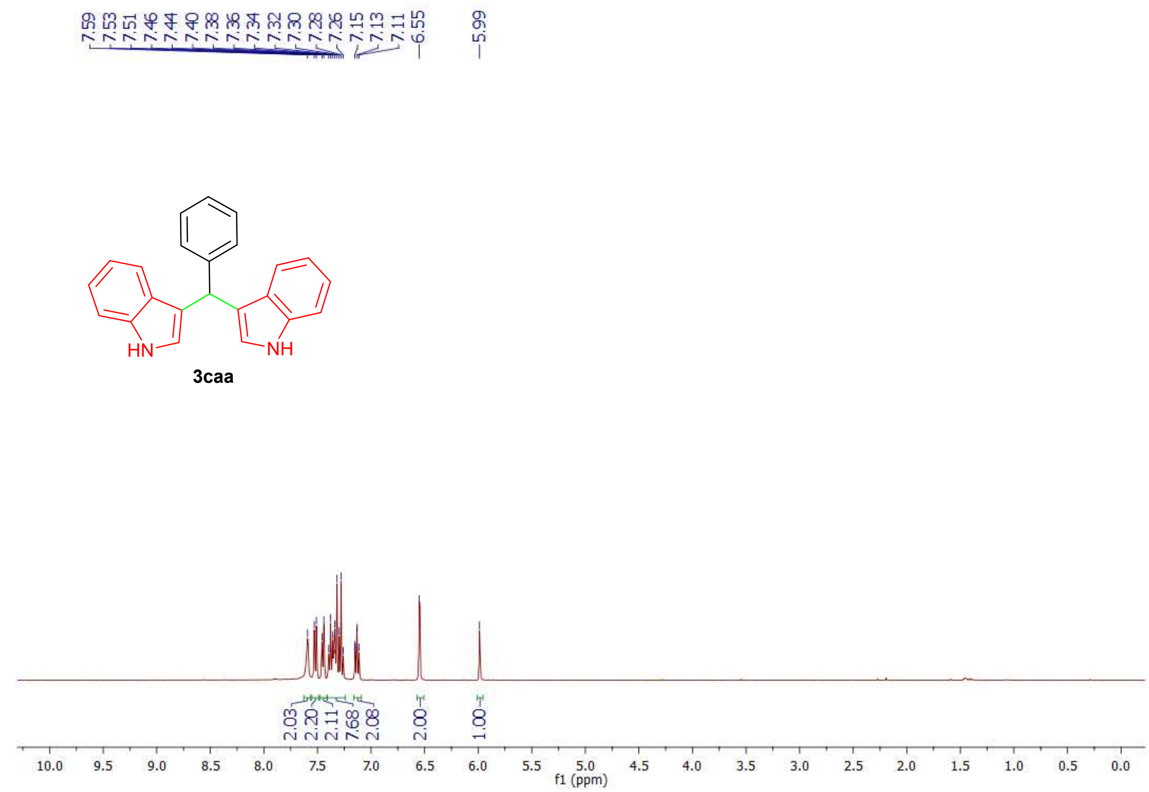

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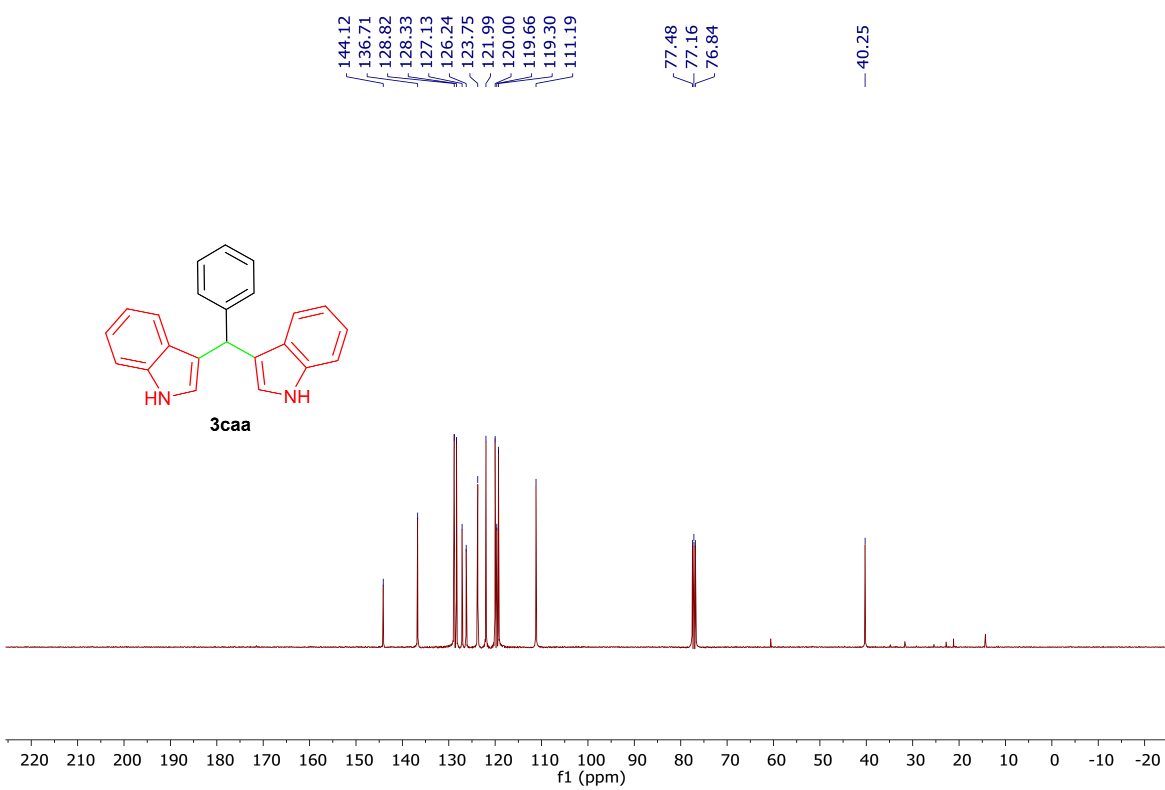

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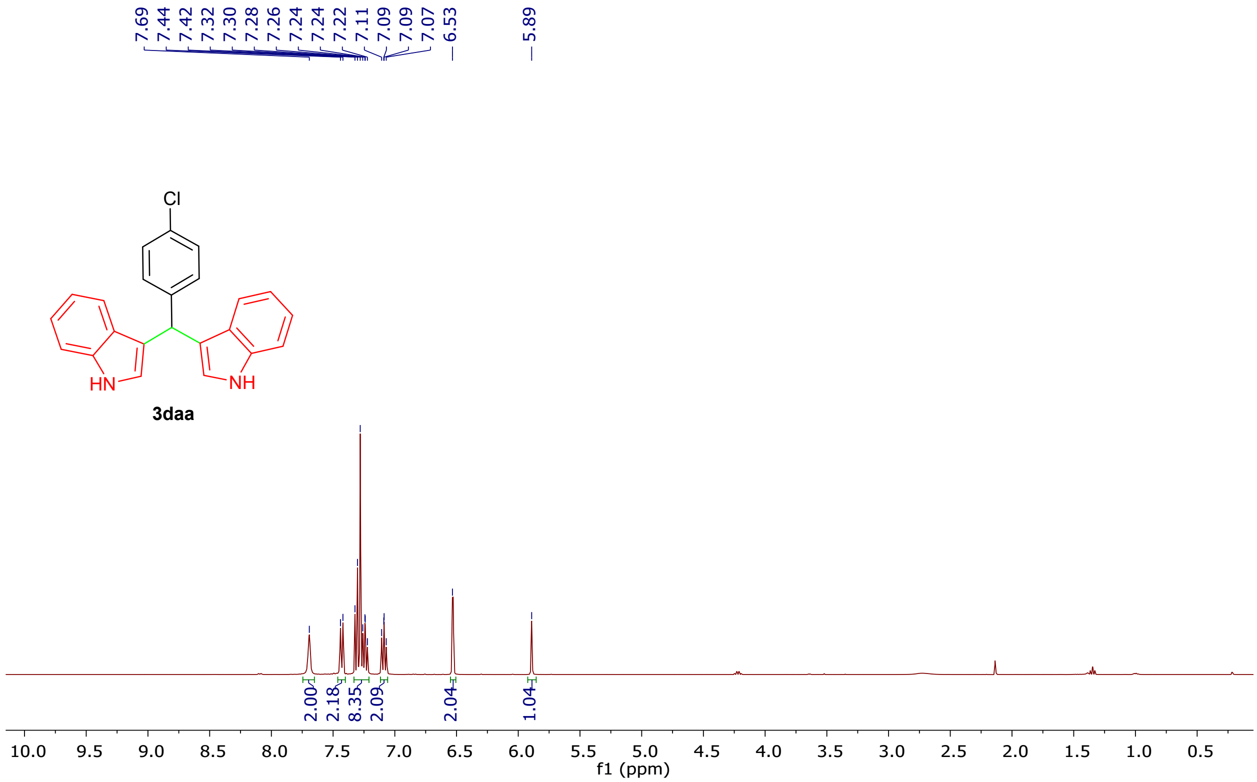

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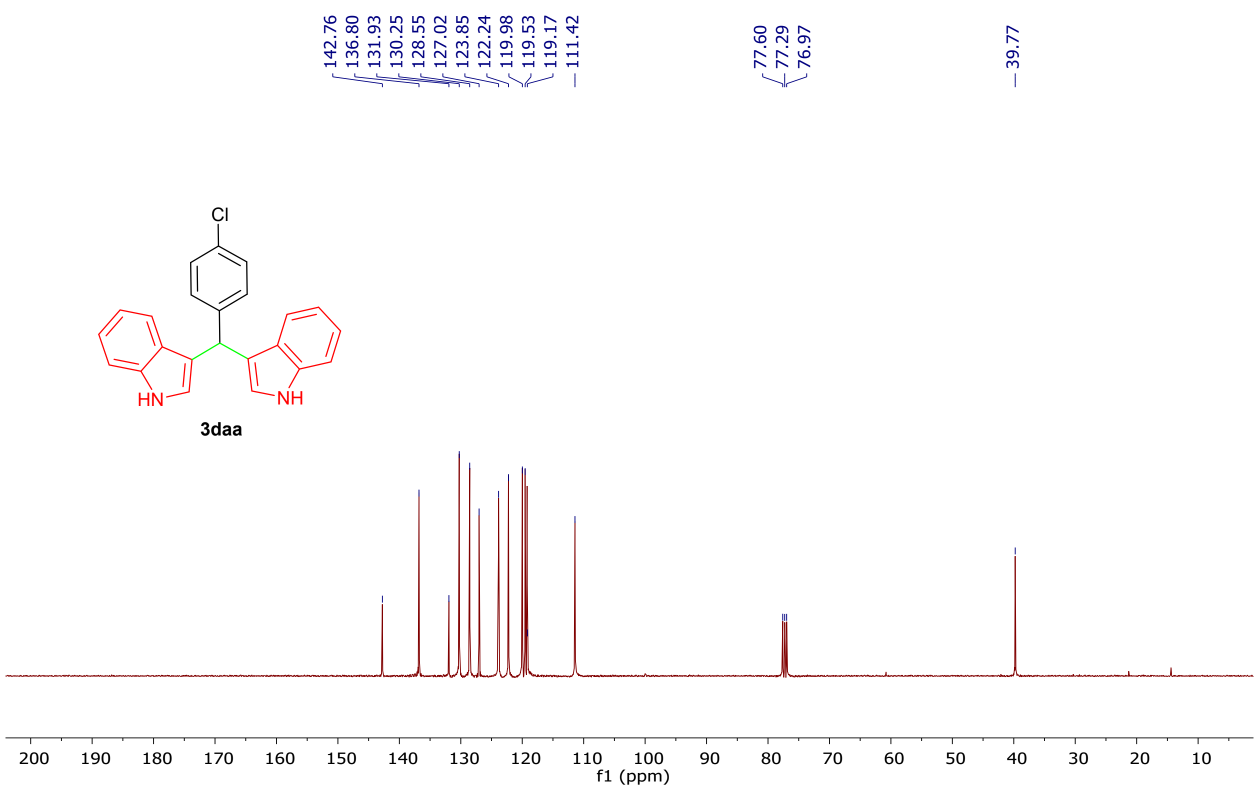

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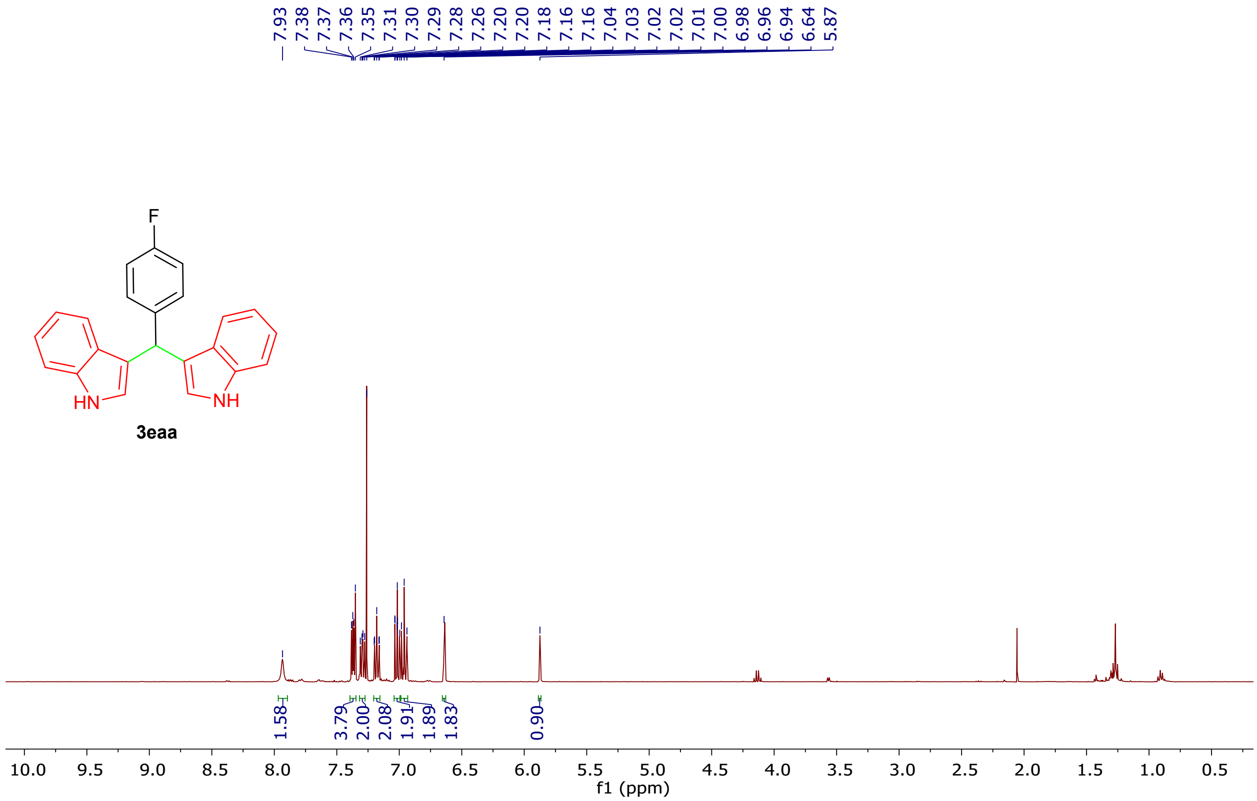

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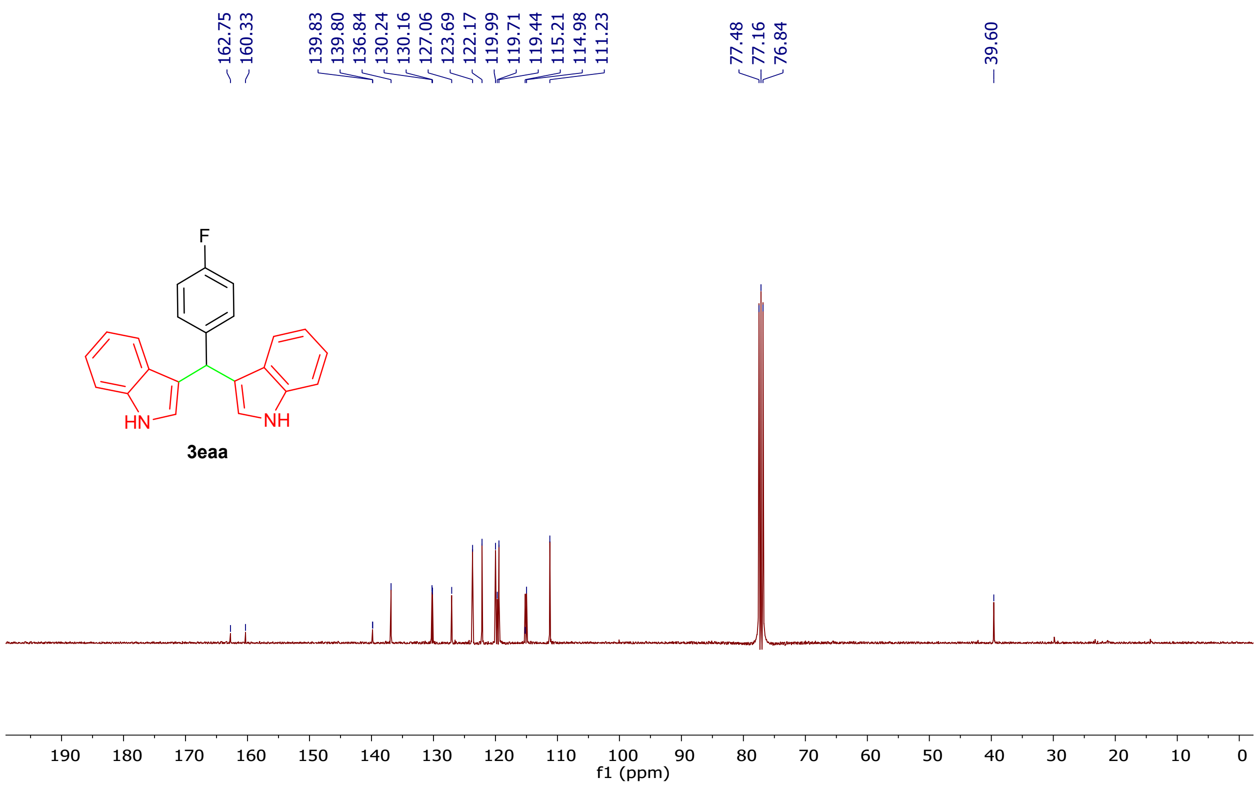

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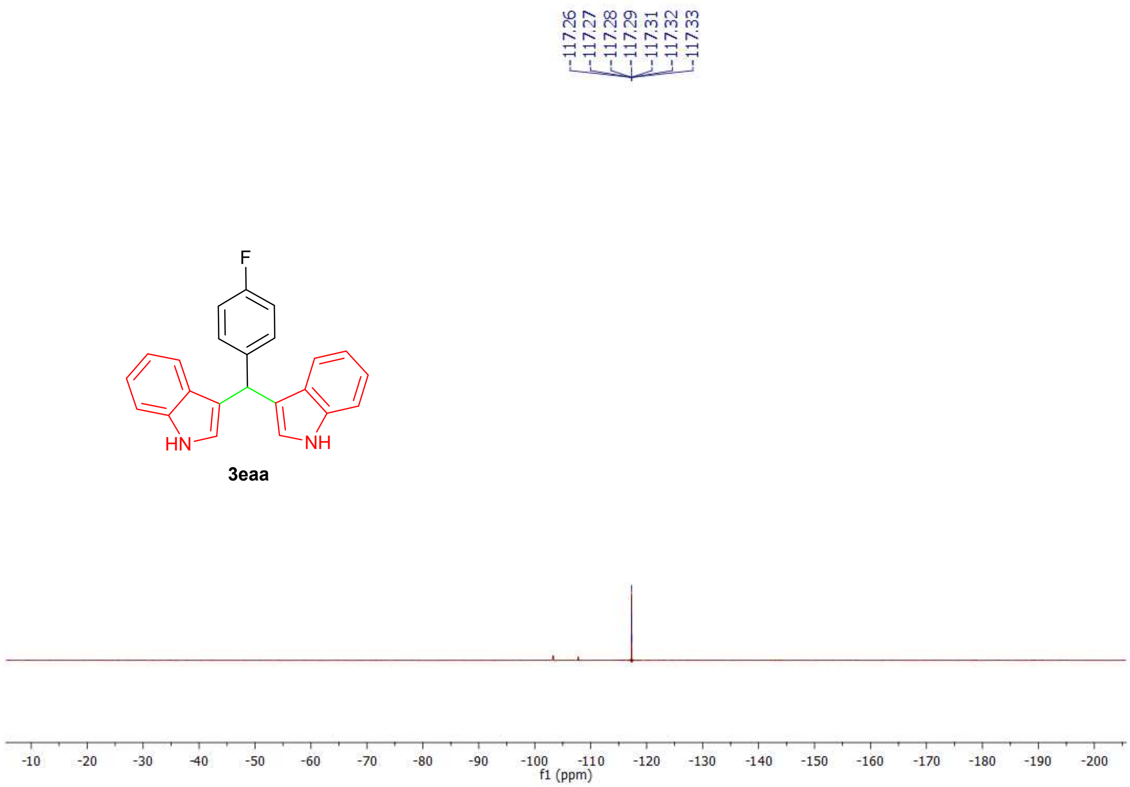

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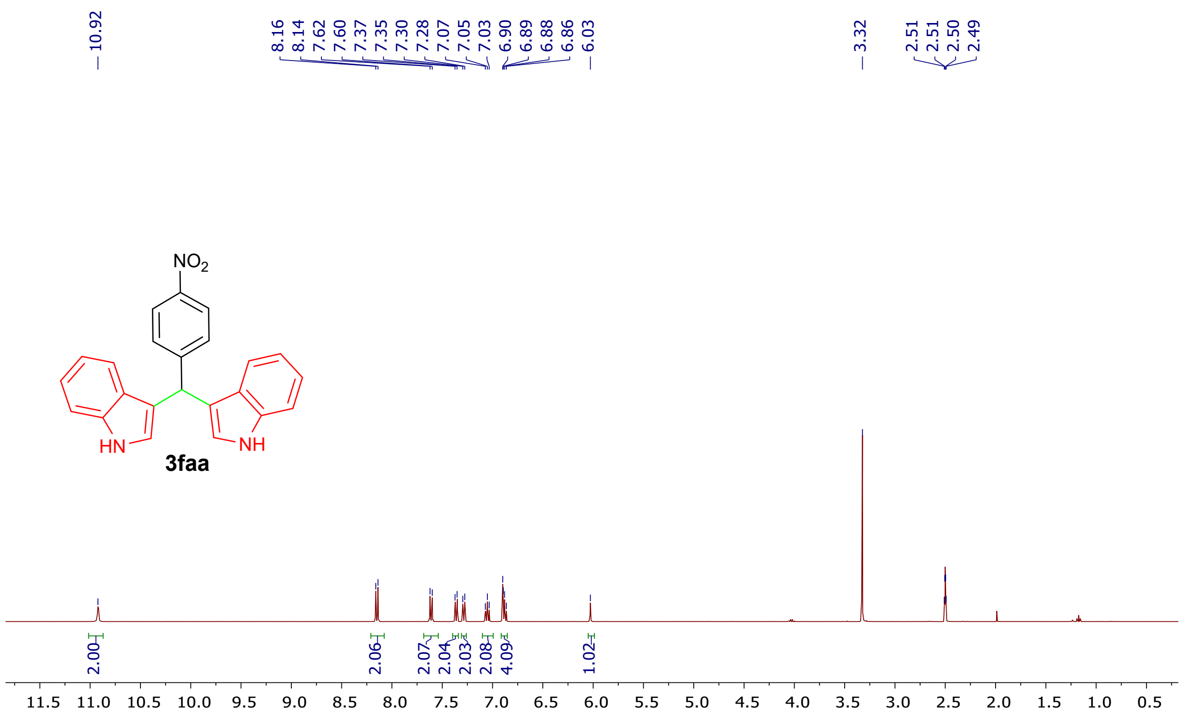


Figure.[1]H NMR of **3faa** in $(CD_3)_2SO$

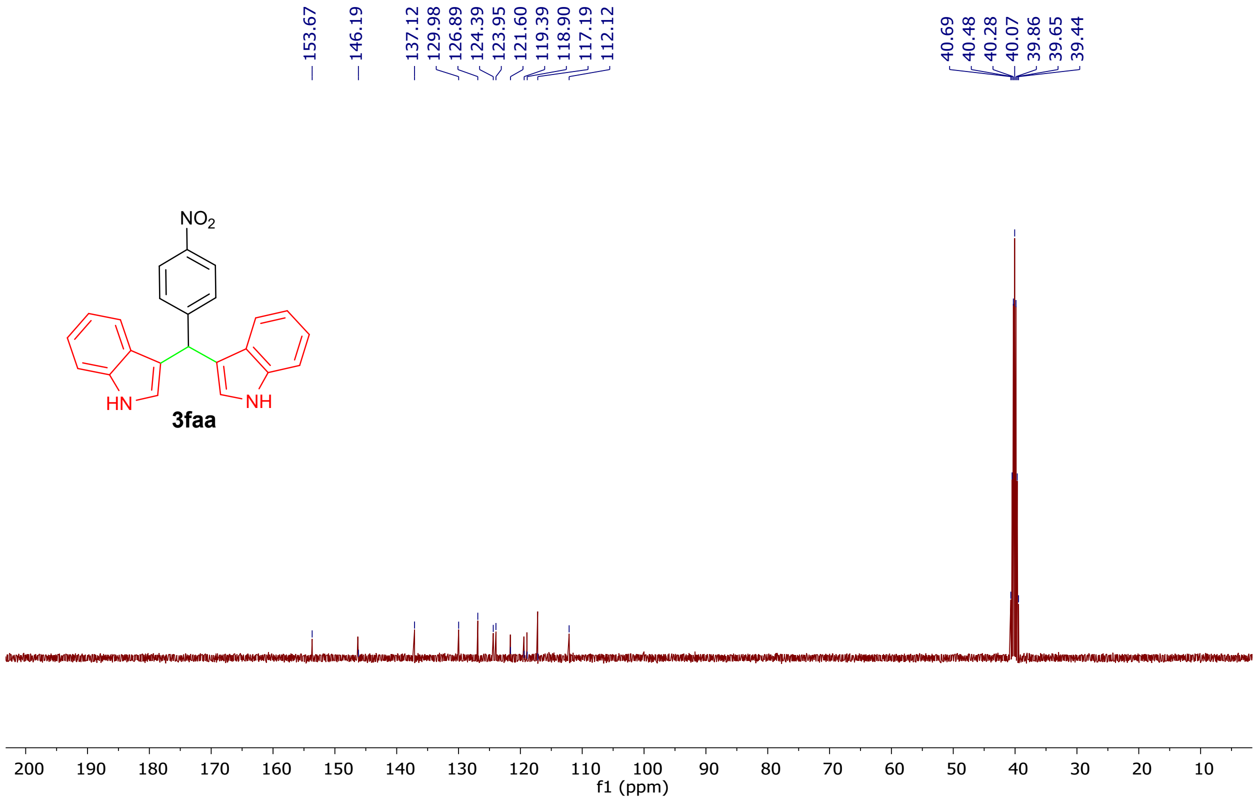
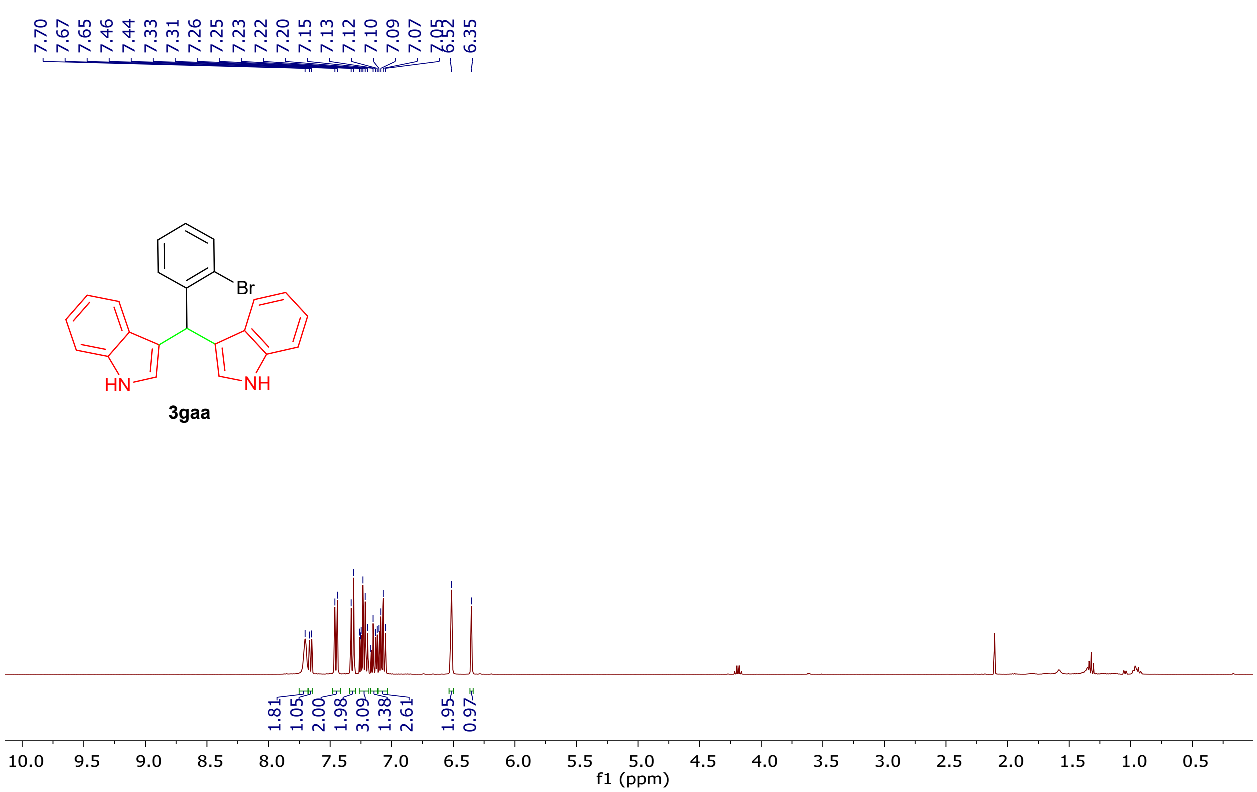


Figure. [13]C NMR of **3faa** in $(CD_3)_2SO$



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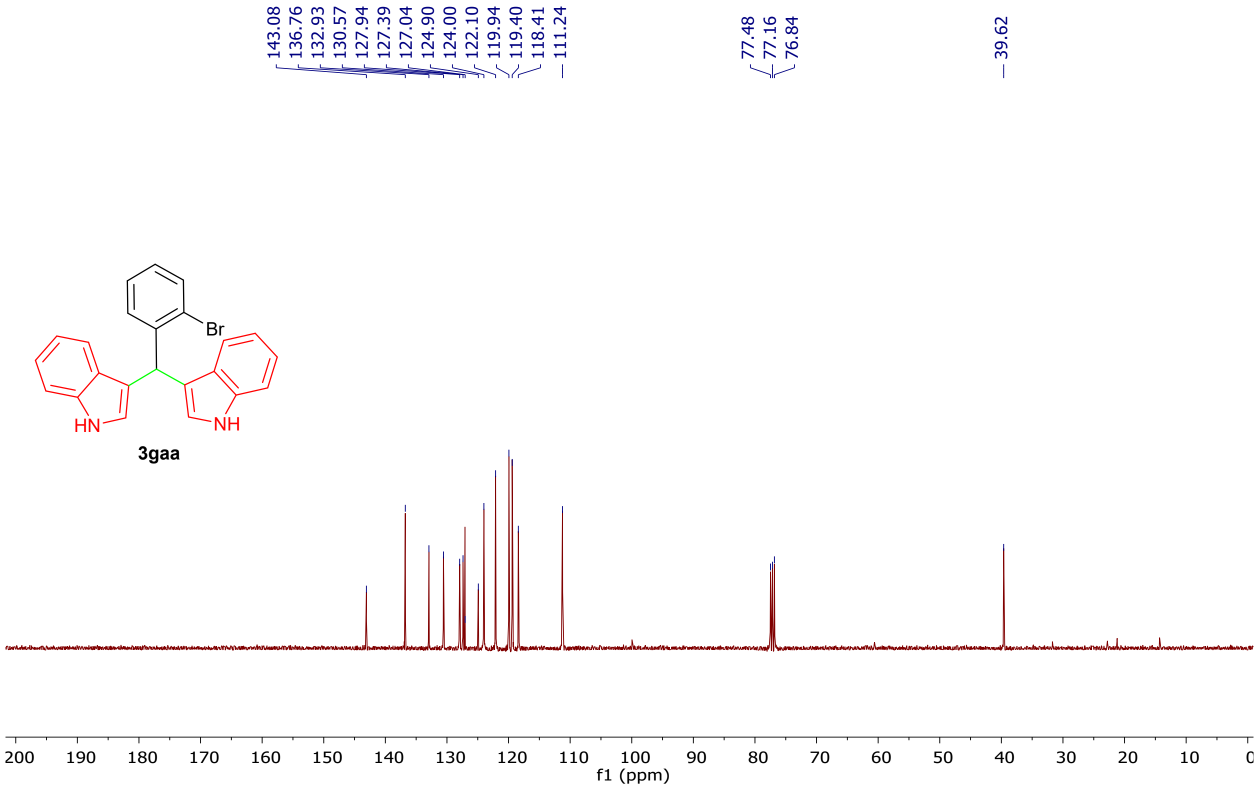

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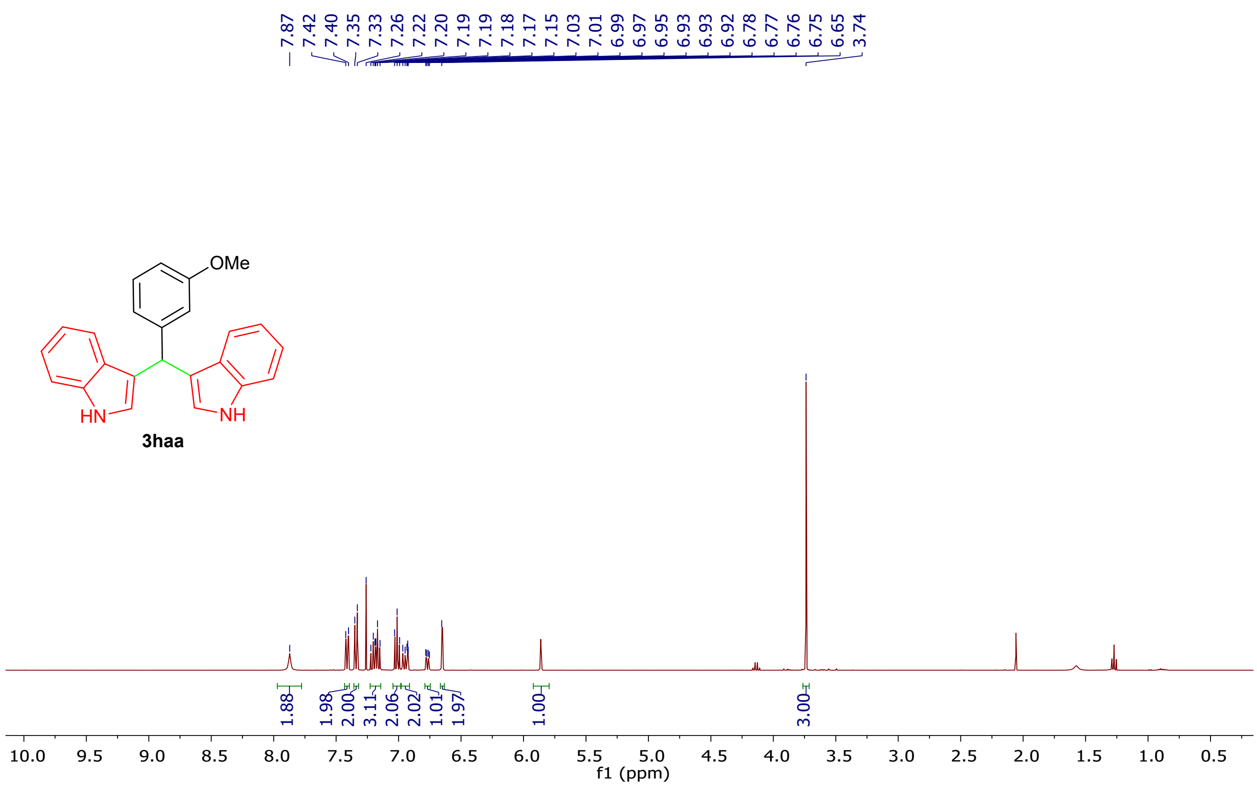

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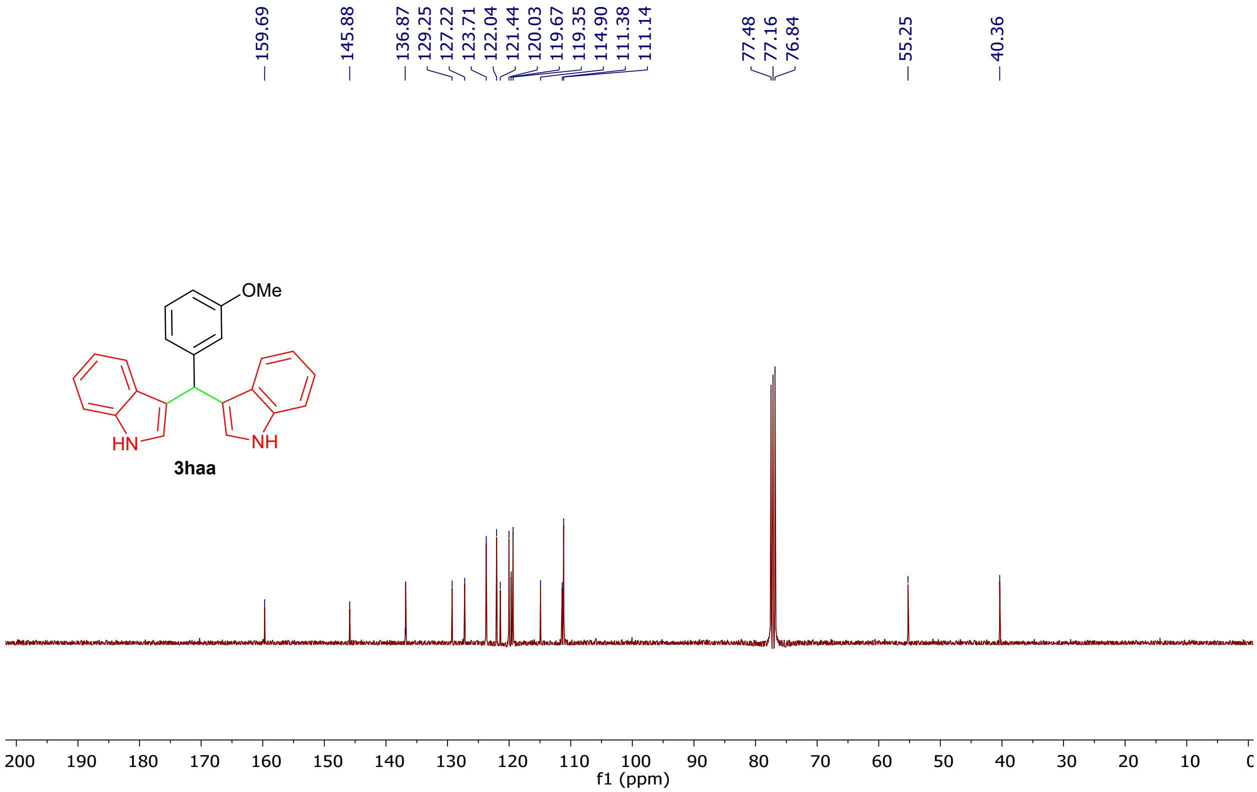

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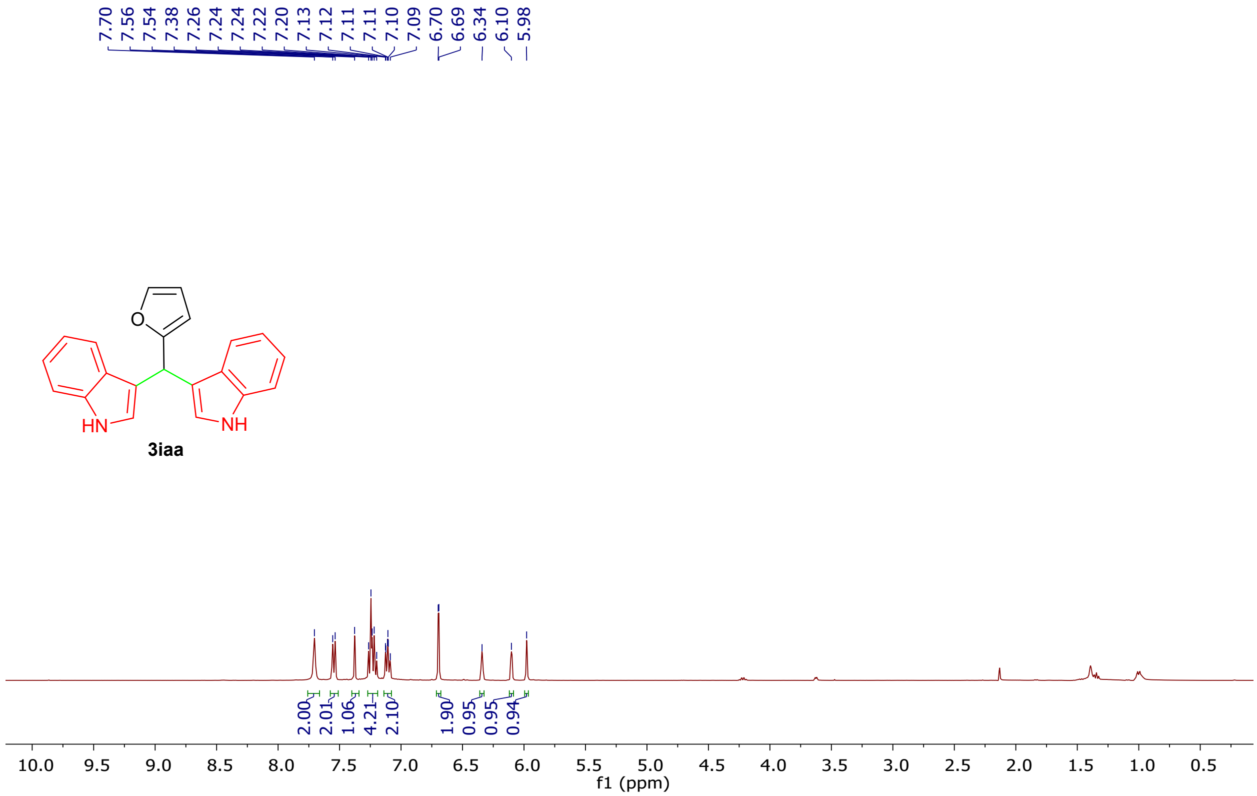

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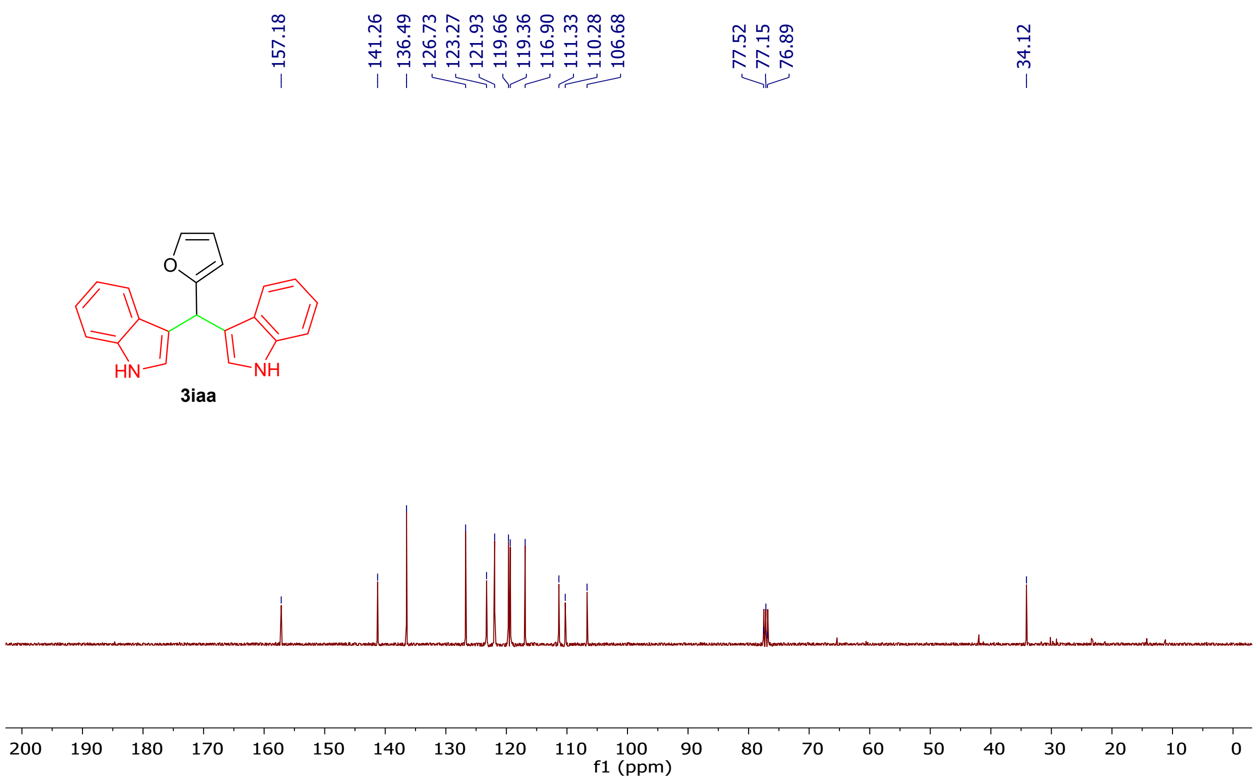

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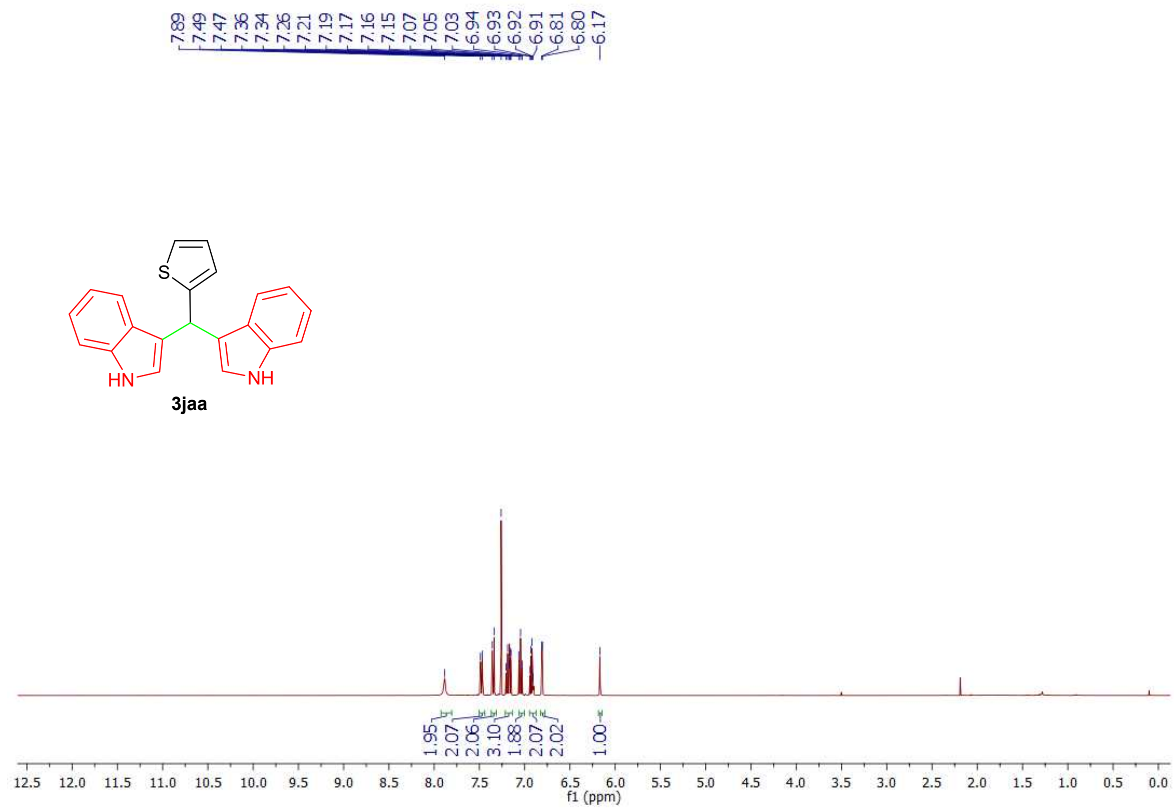

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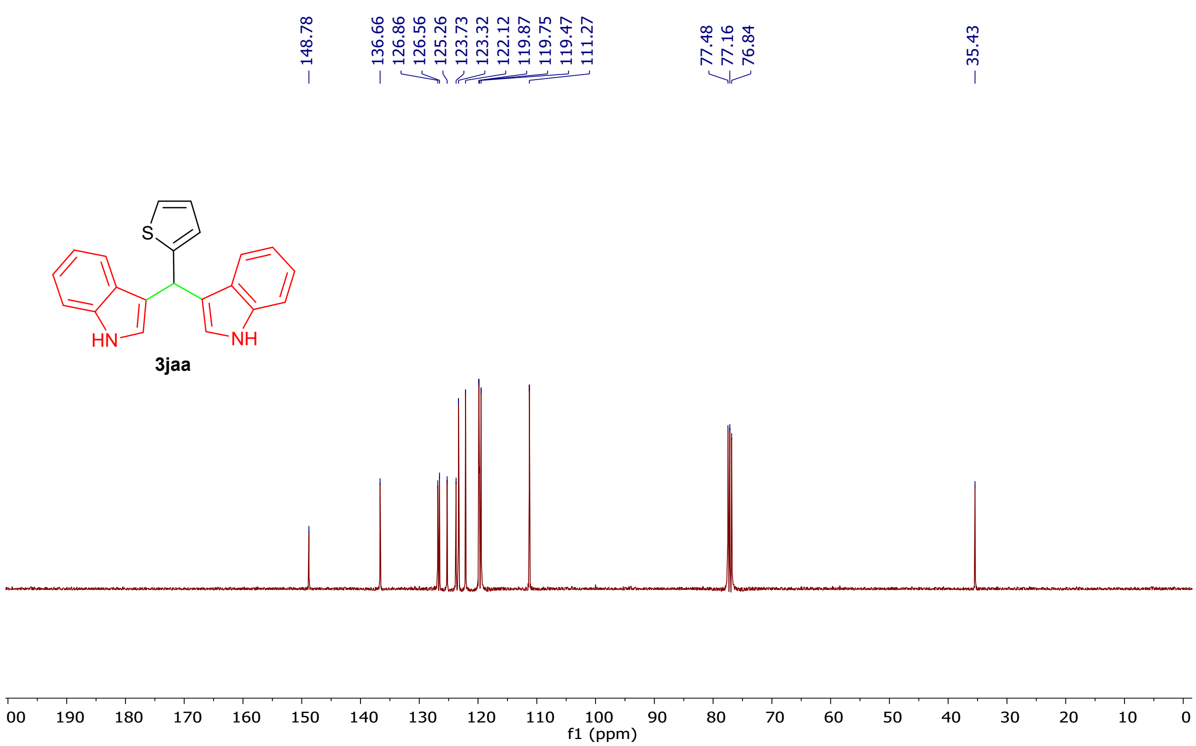

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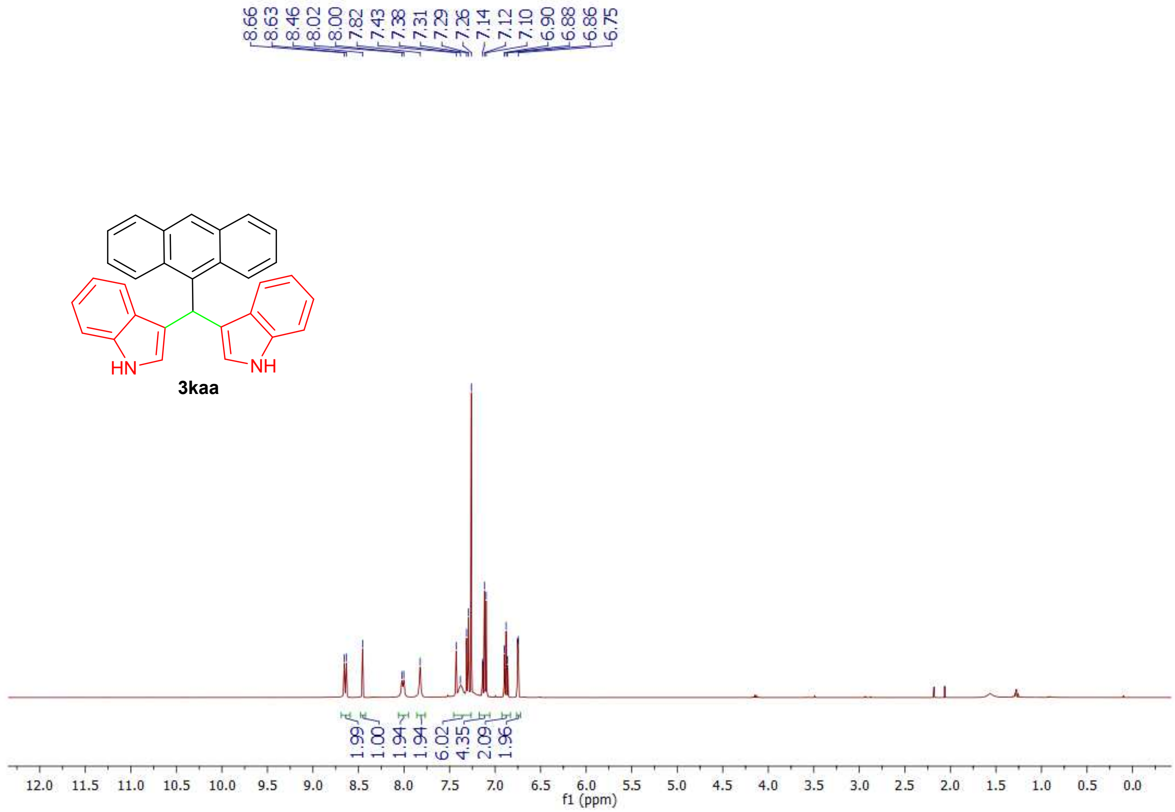

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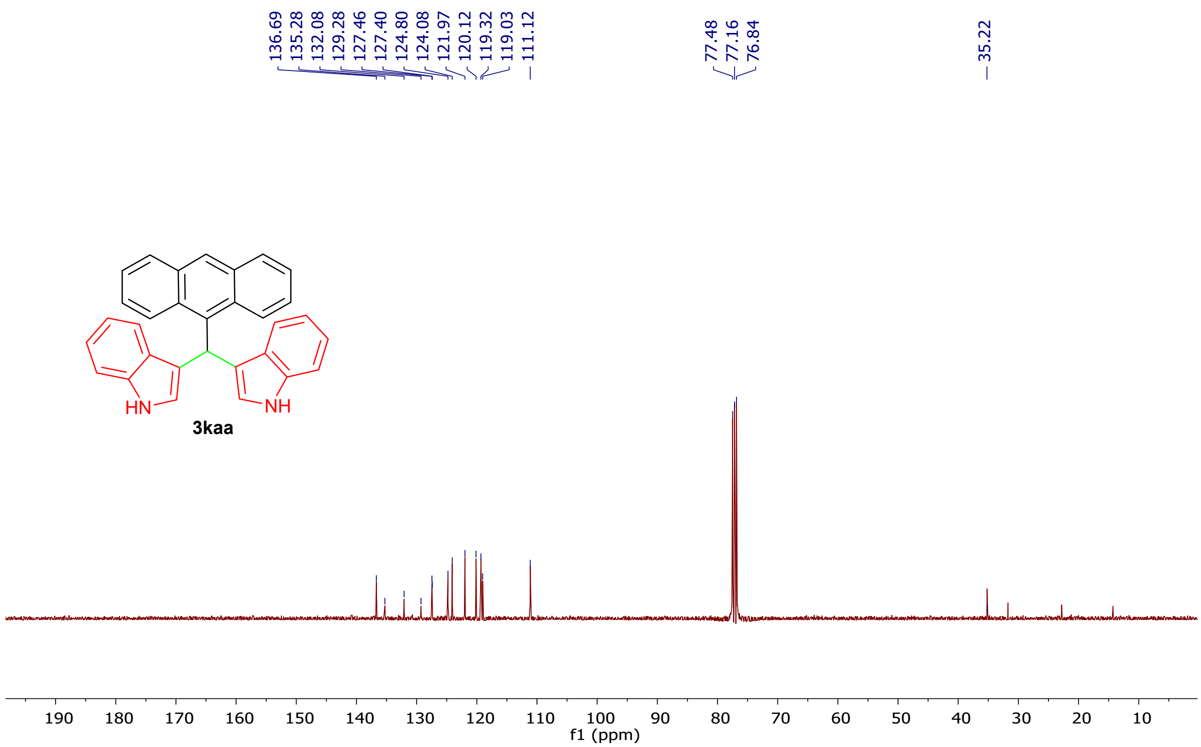

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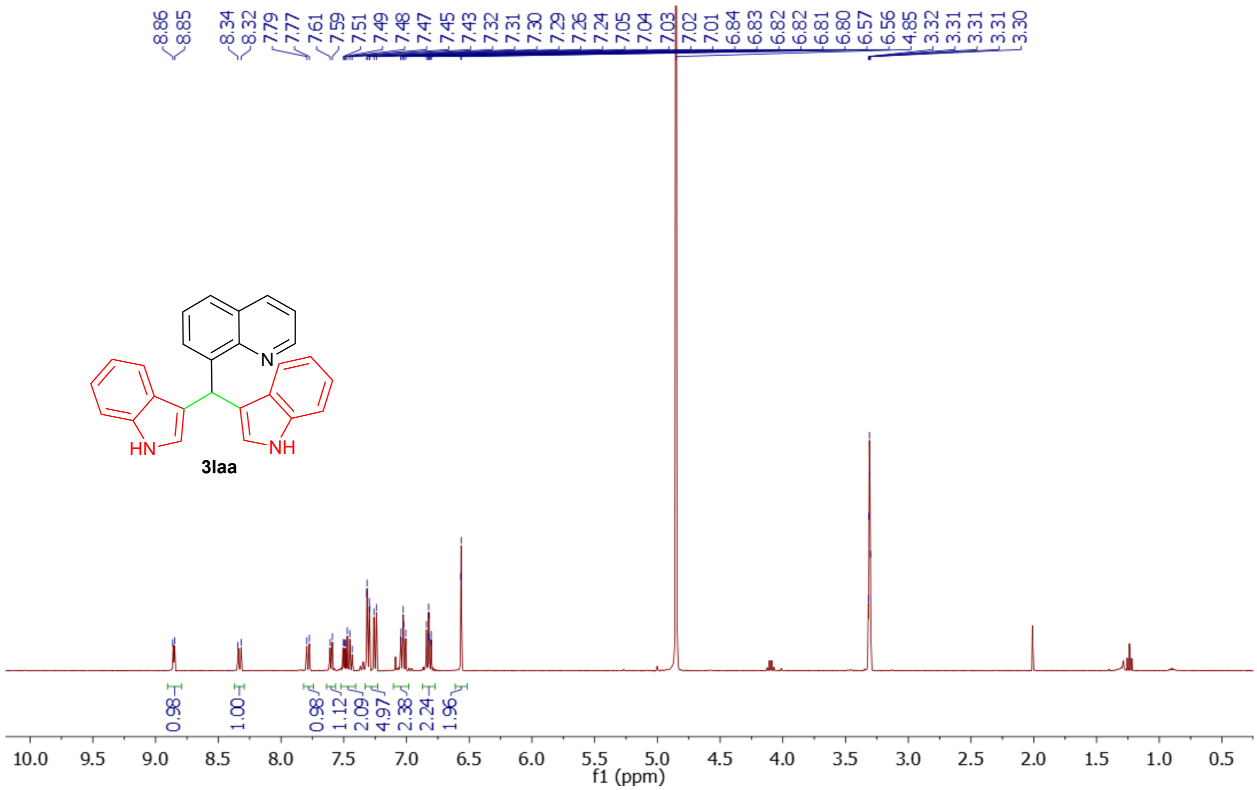

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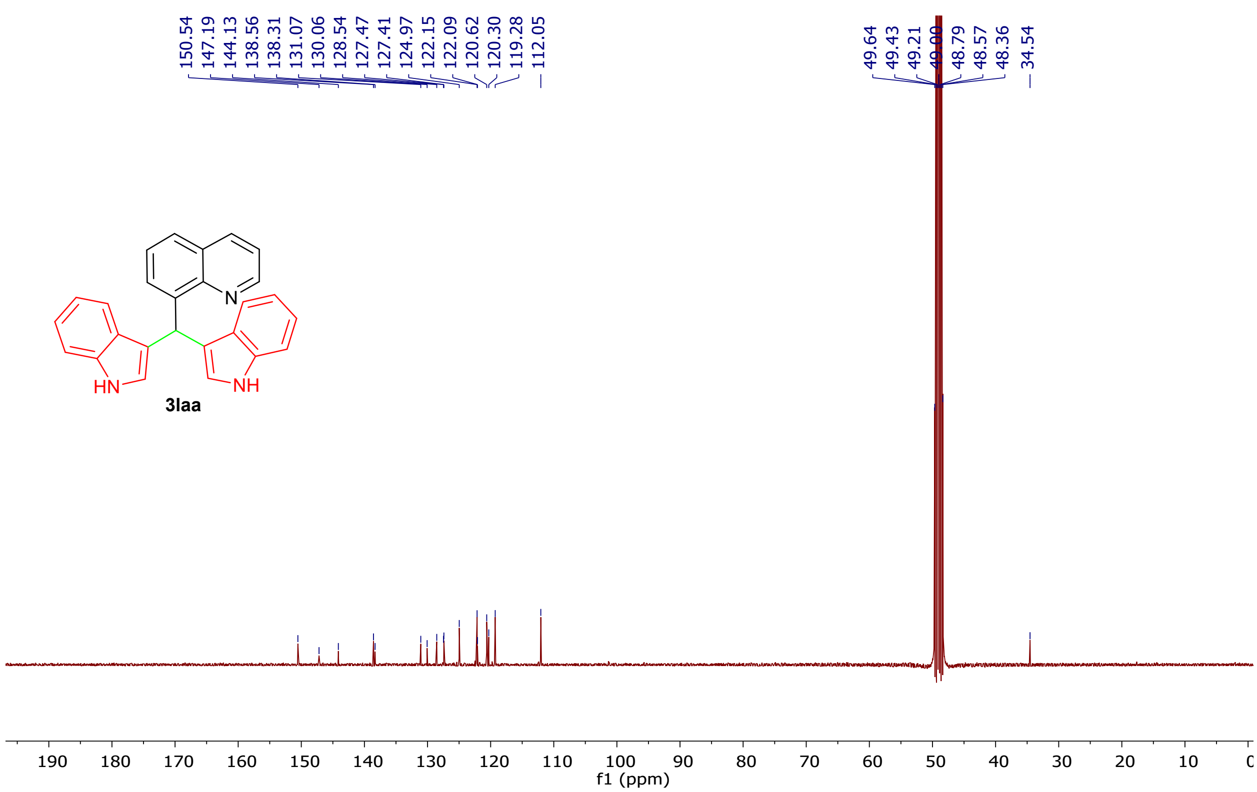

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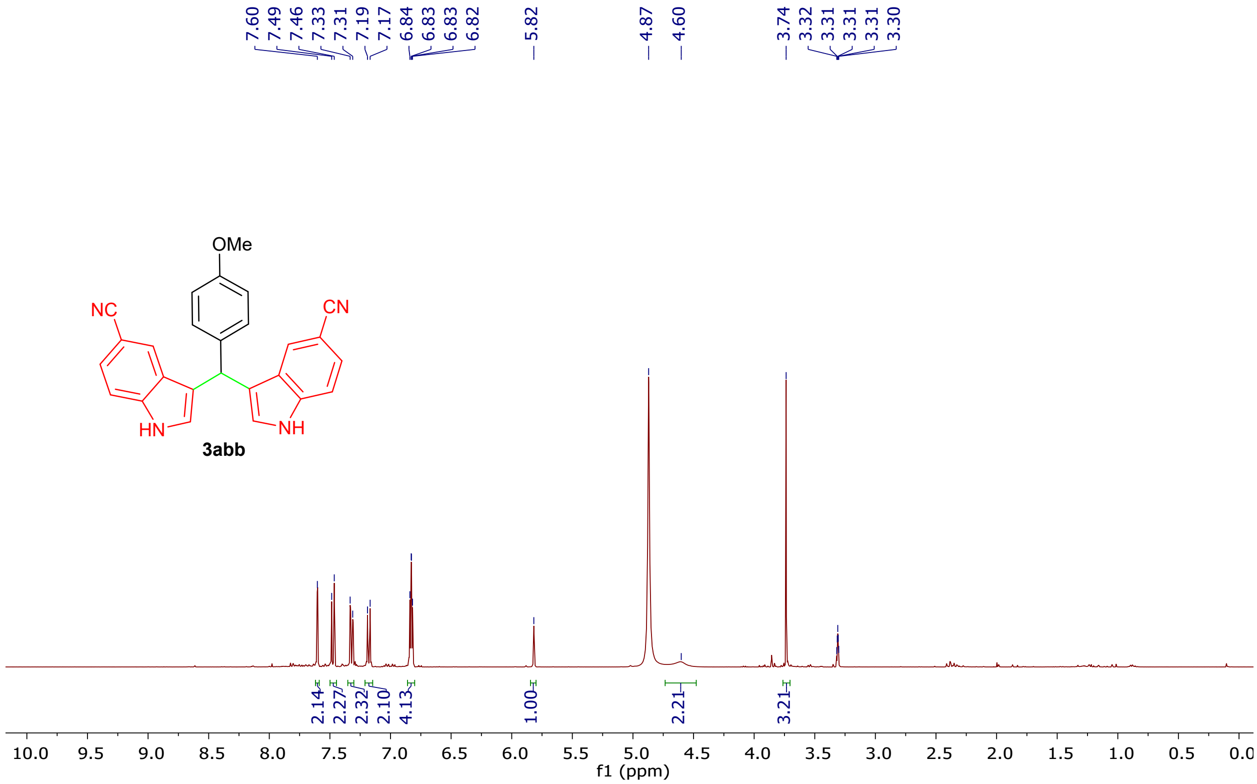

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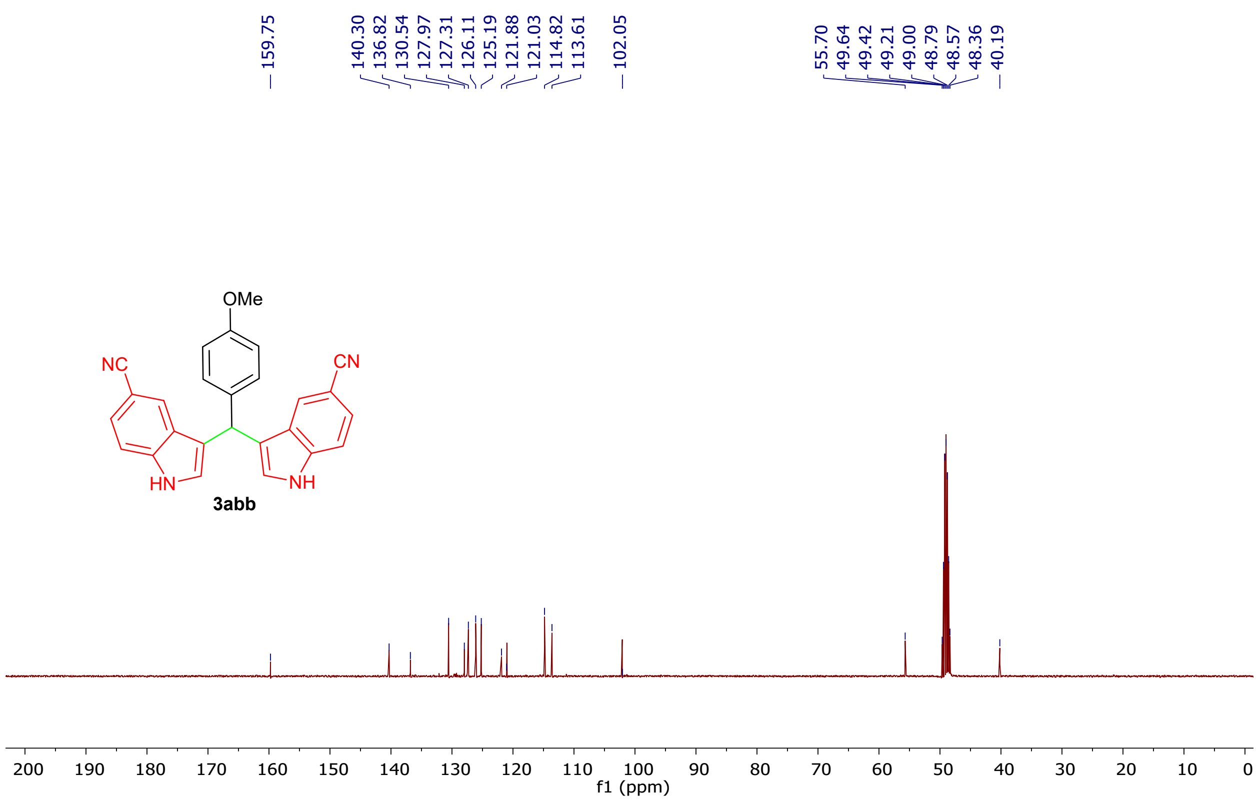

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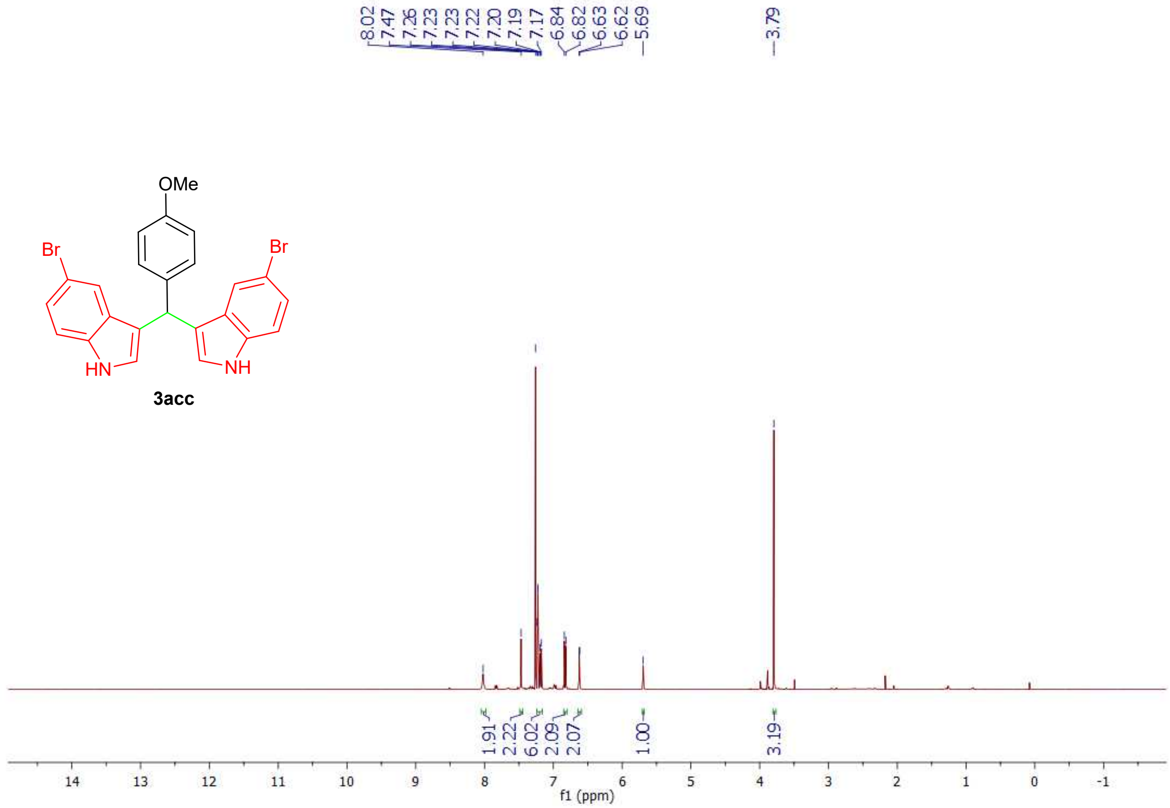

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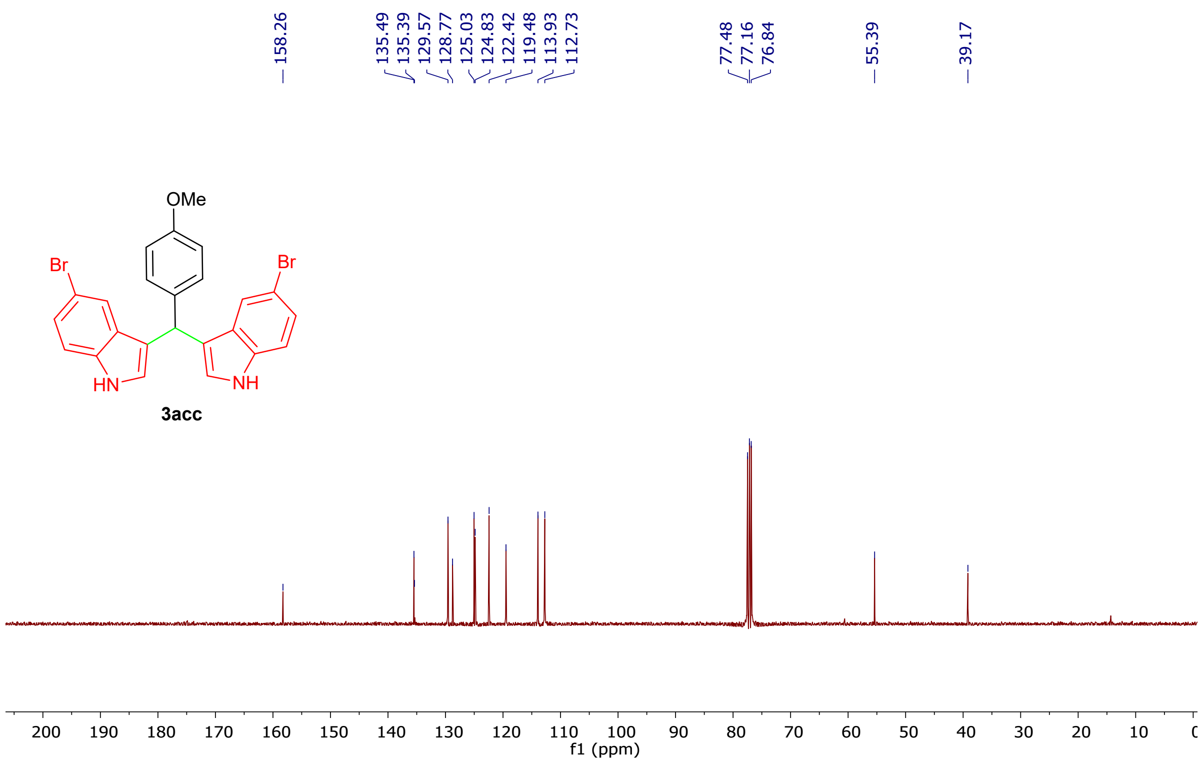

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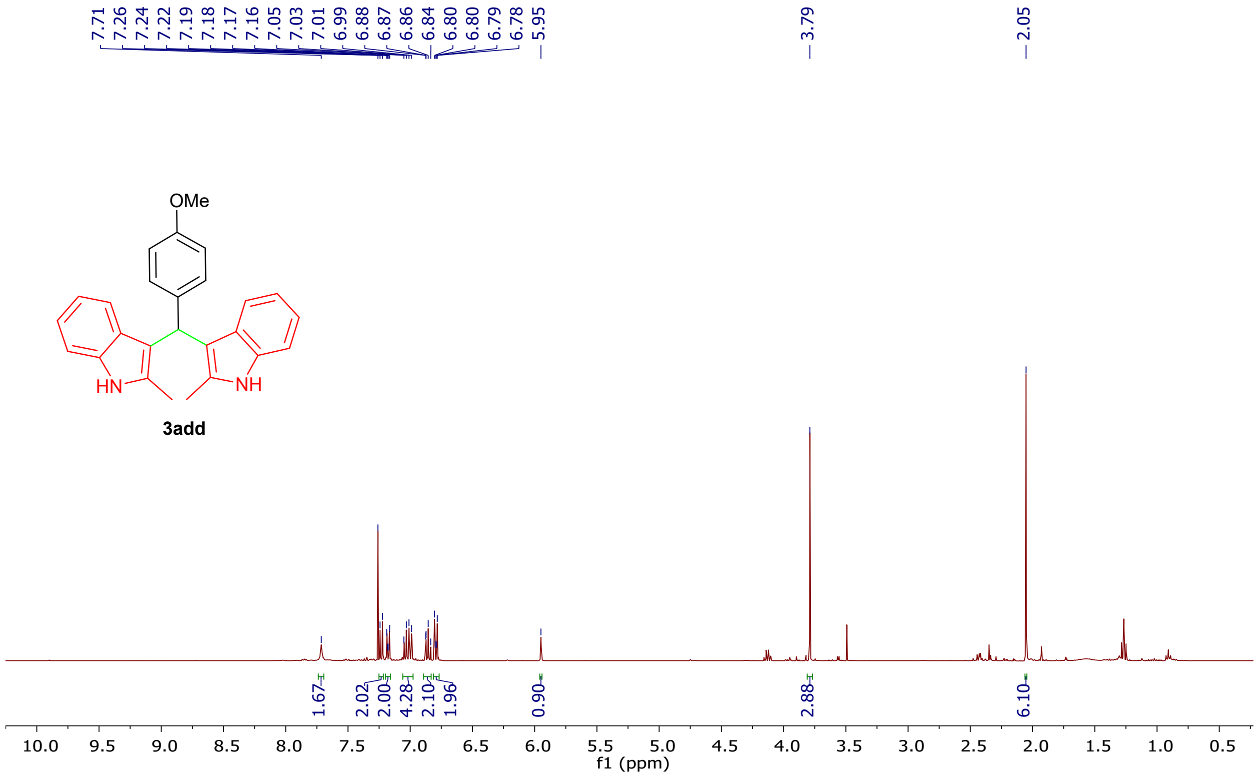

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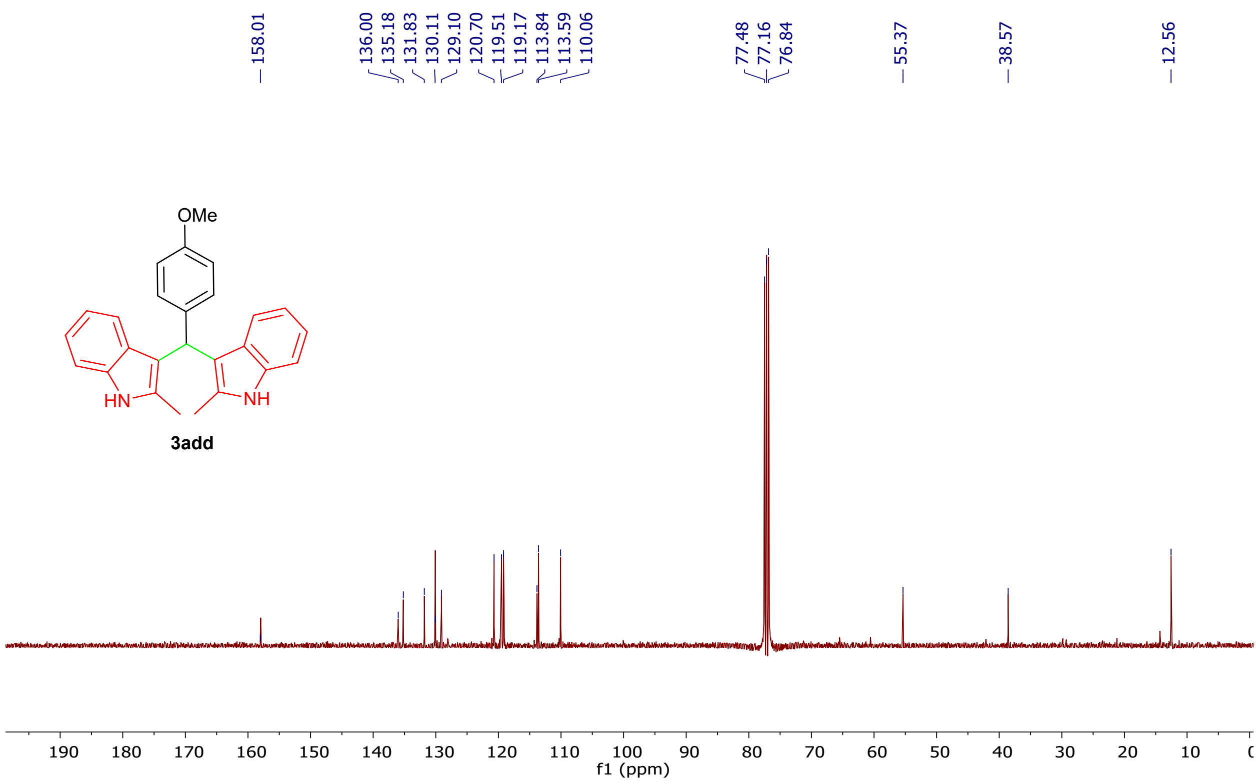

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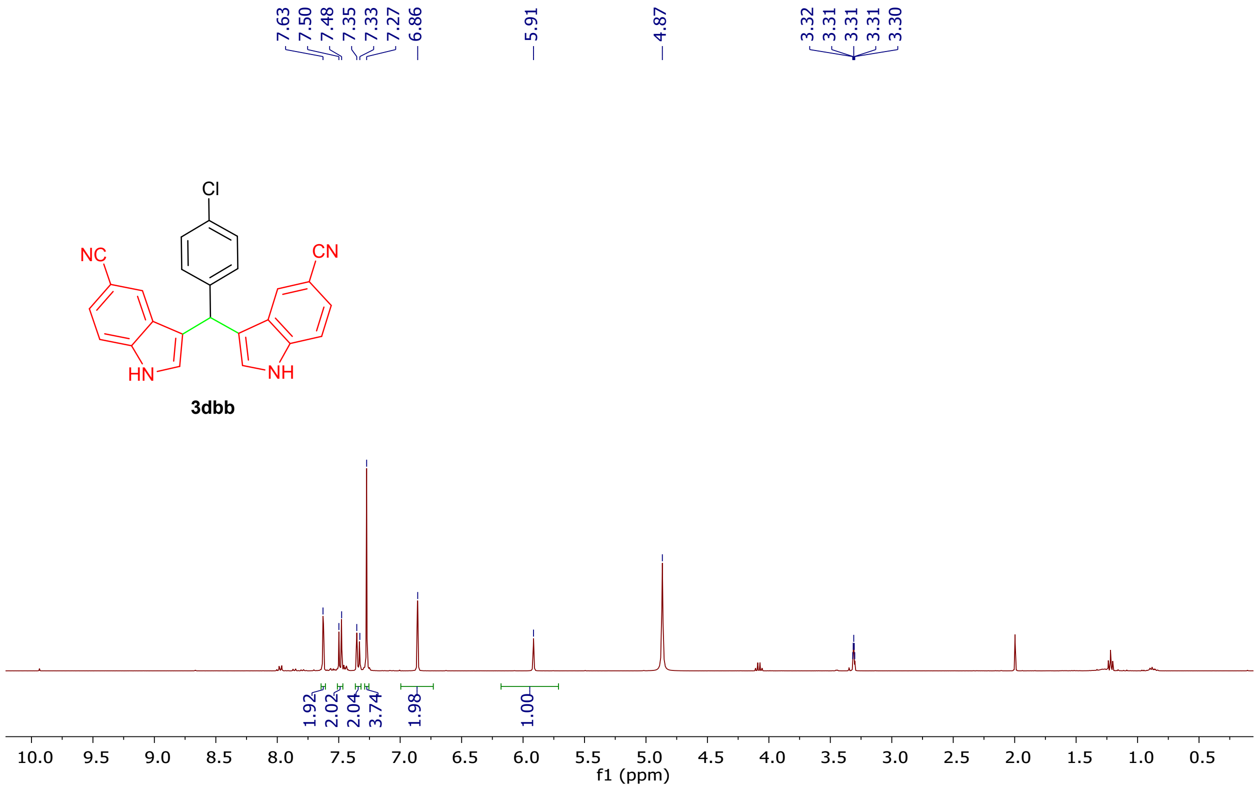

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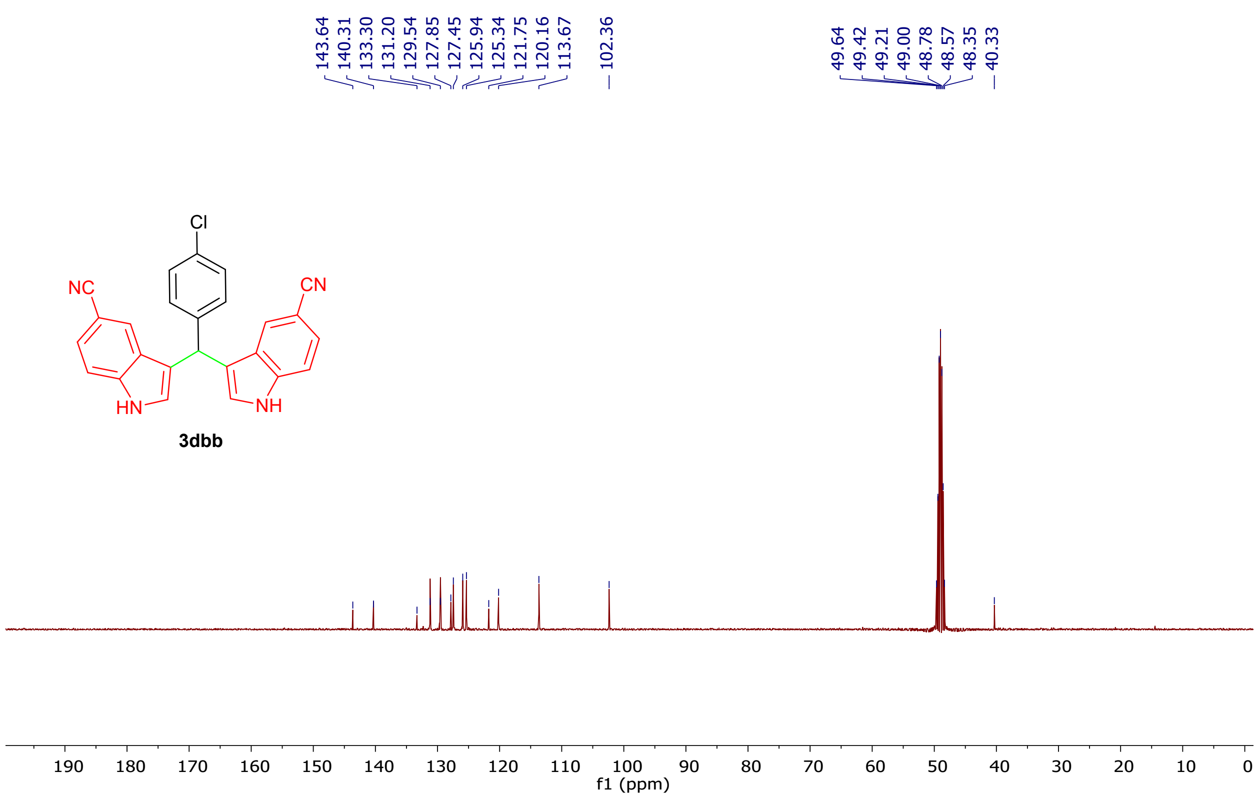

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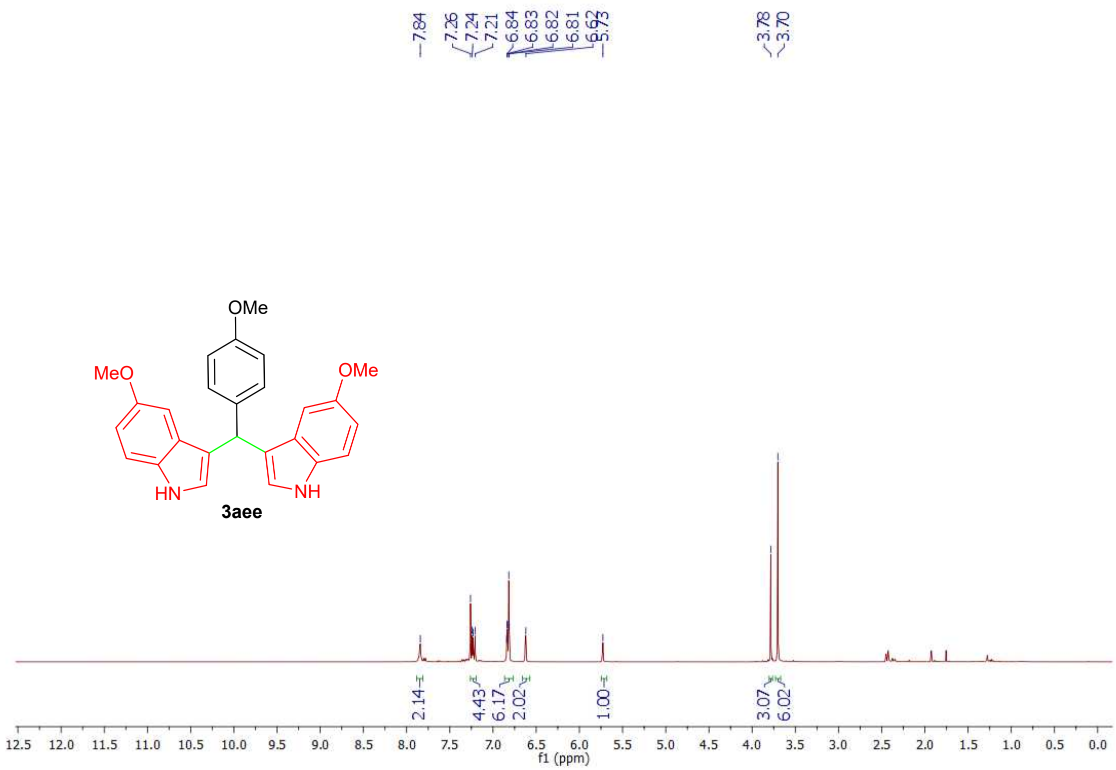

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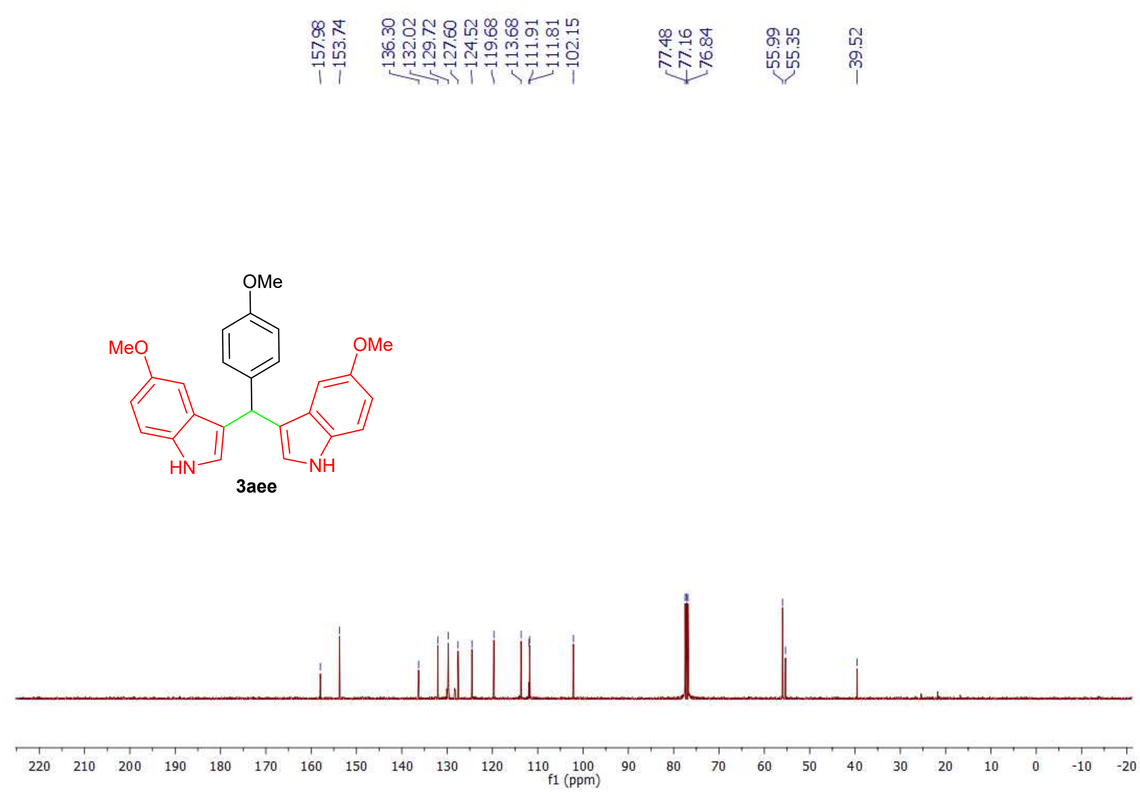

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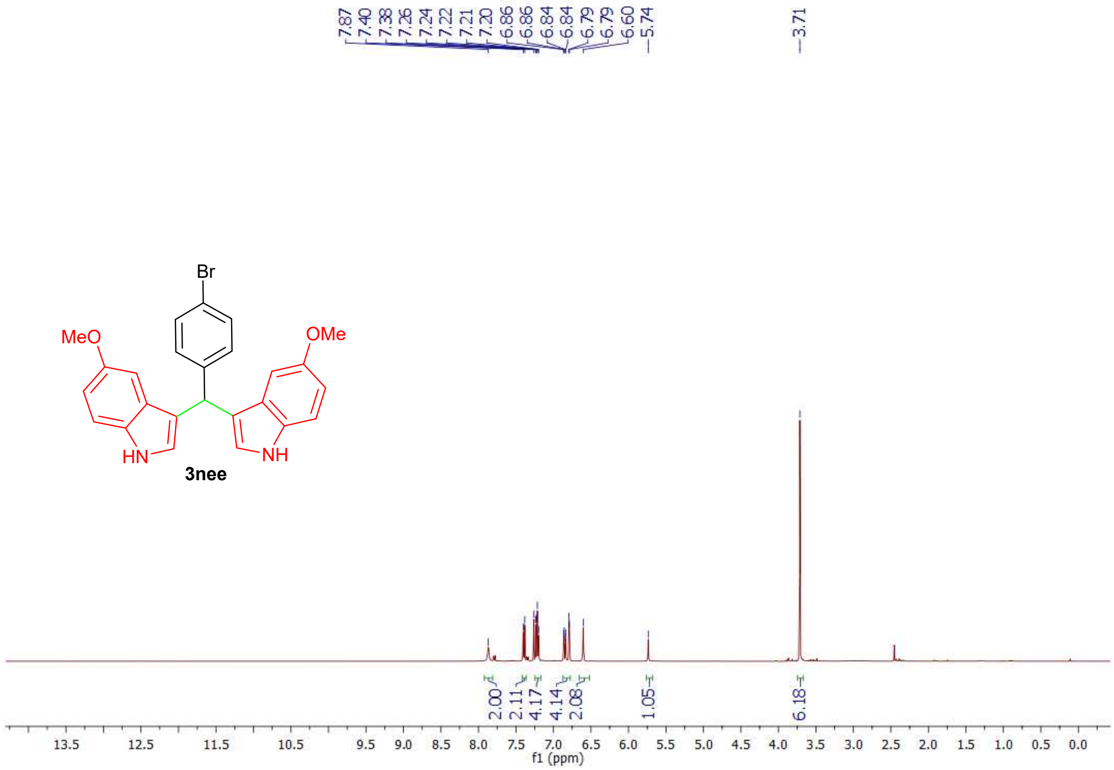

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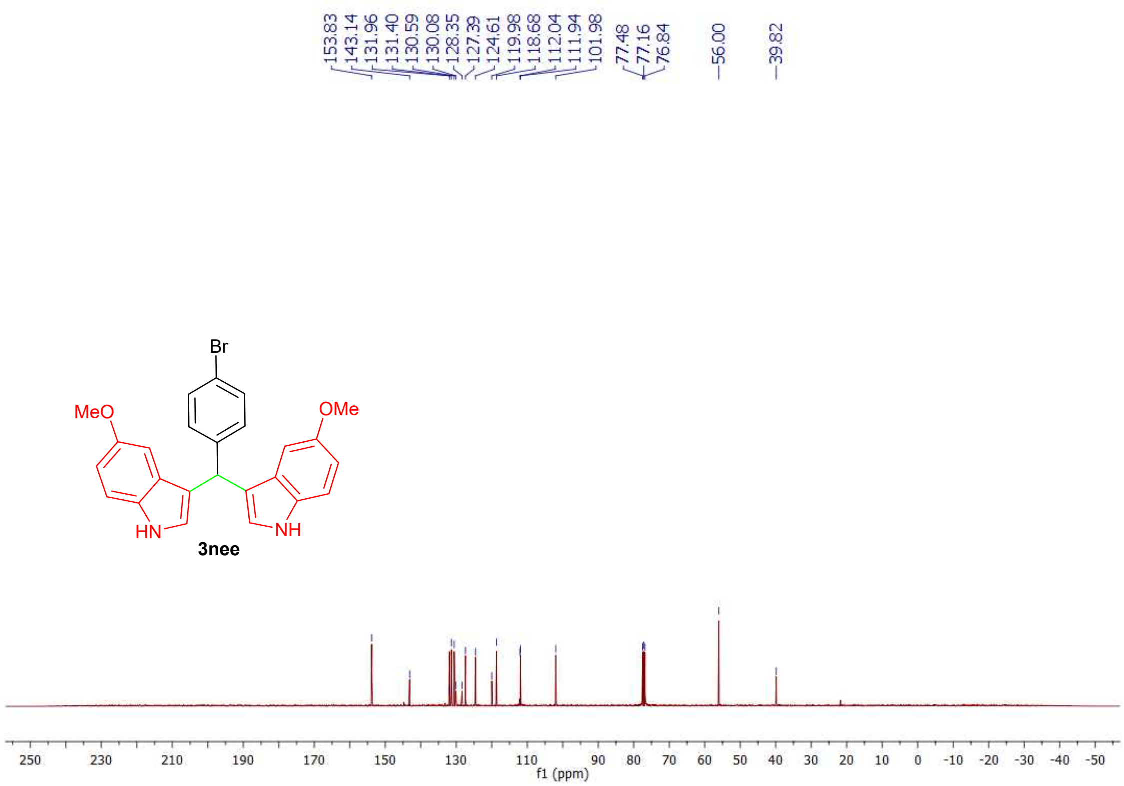

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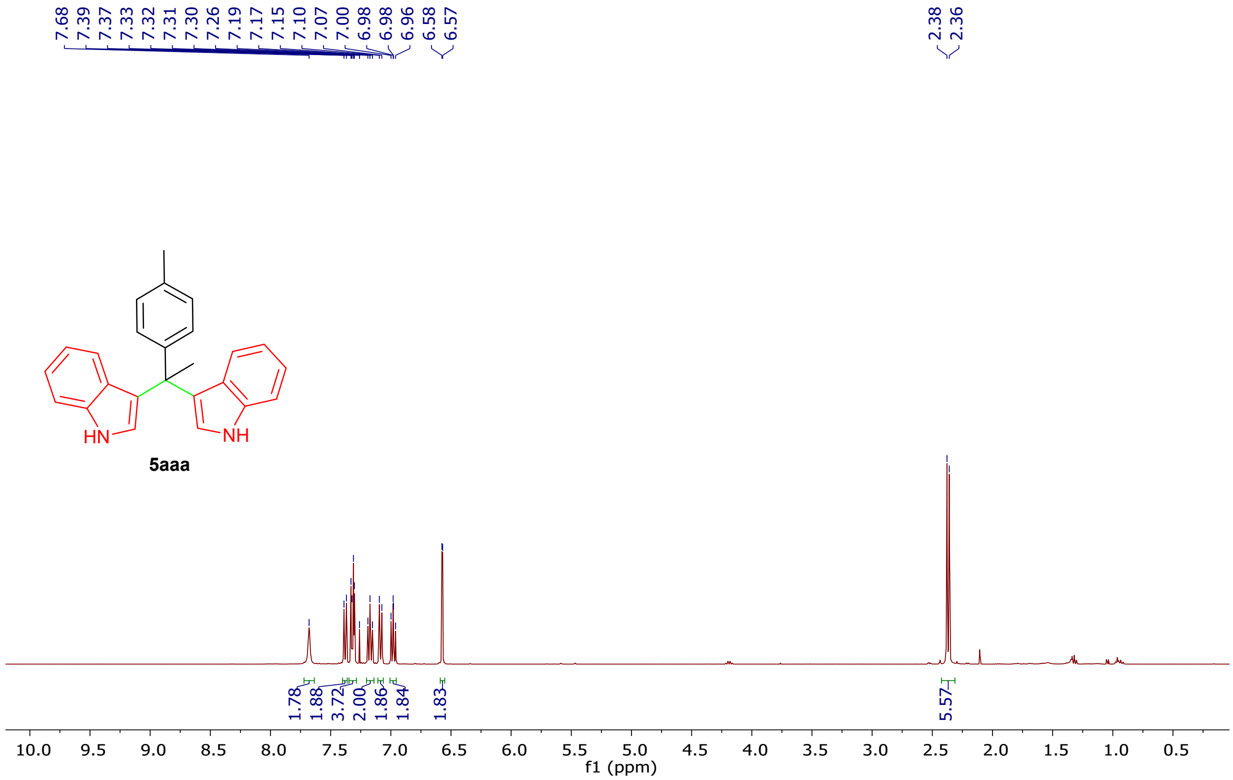

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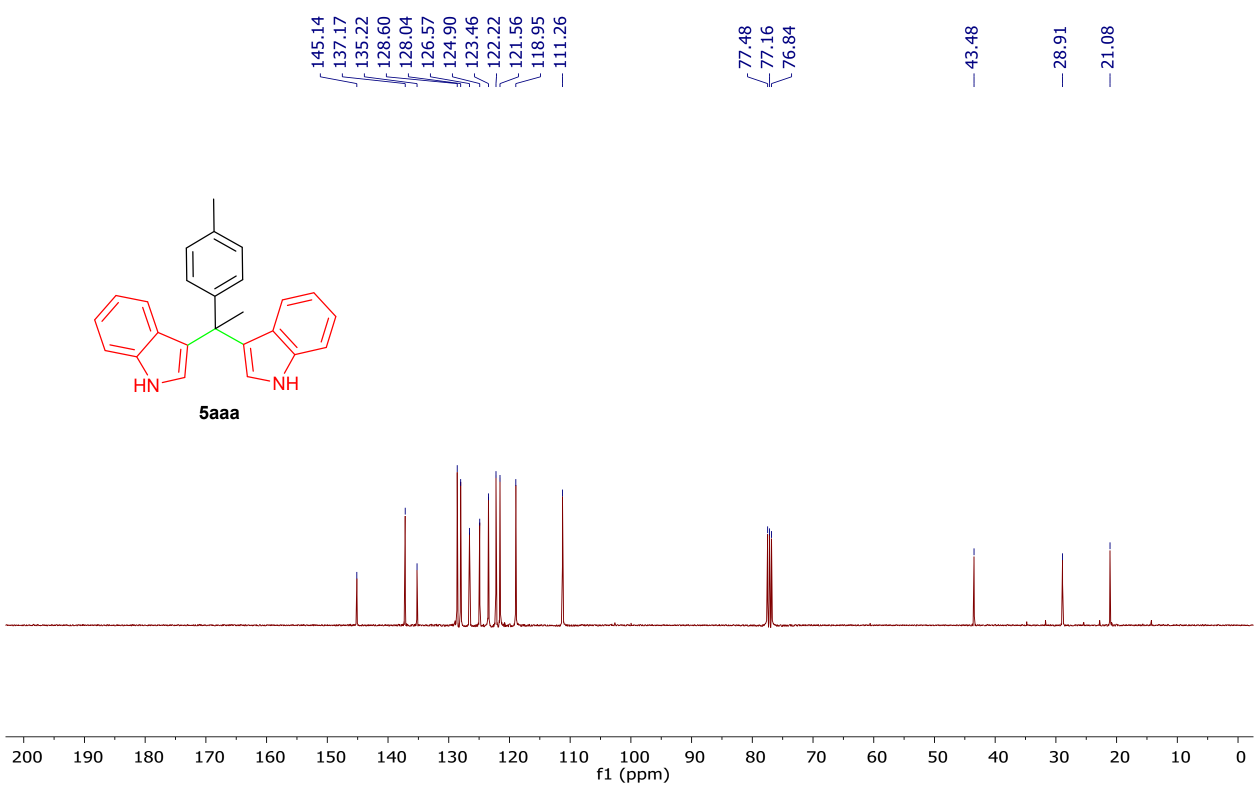

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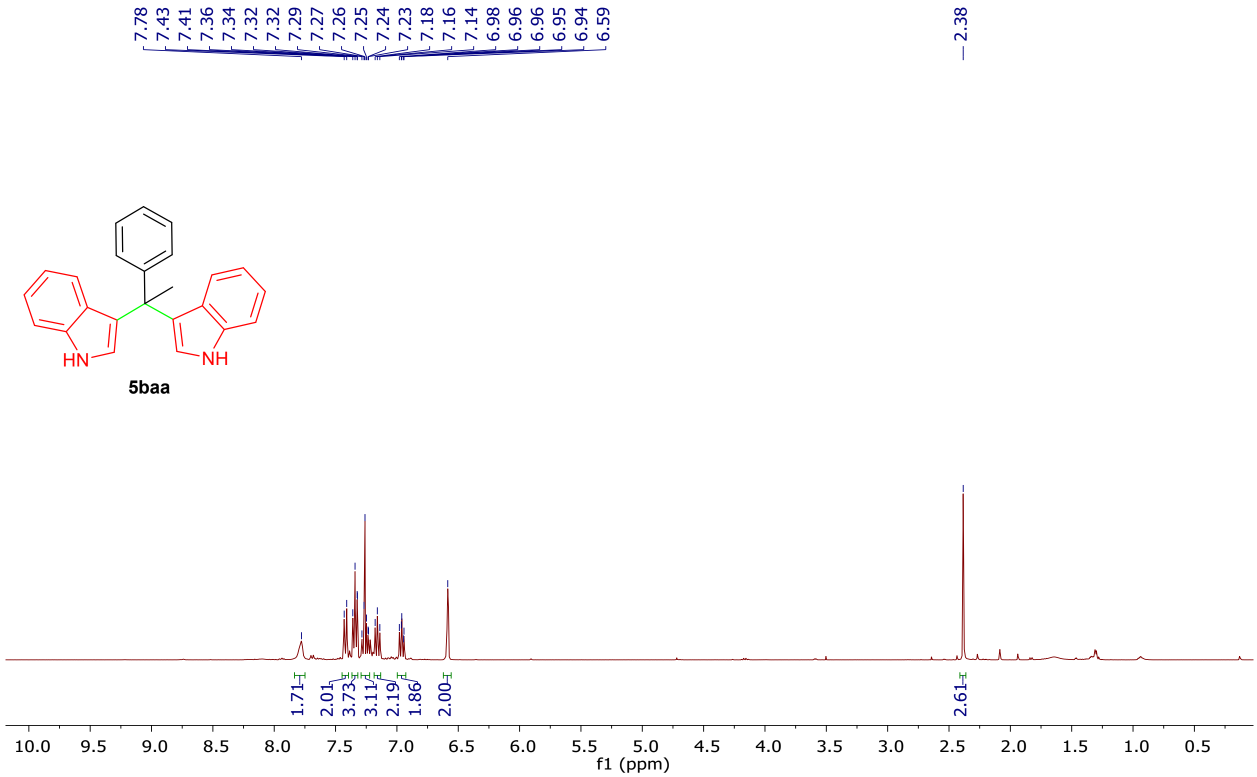

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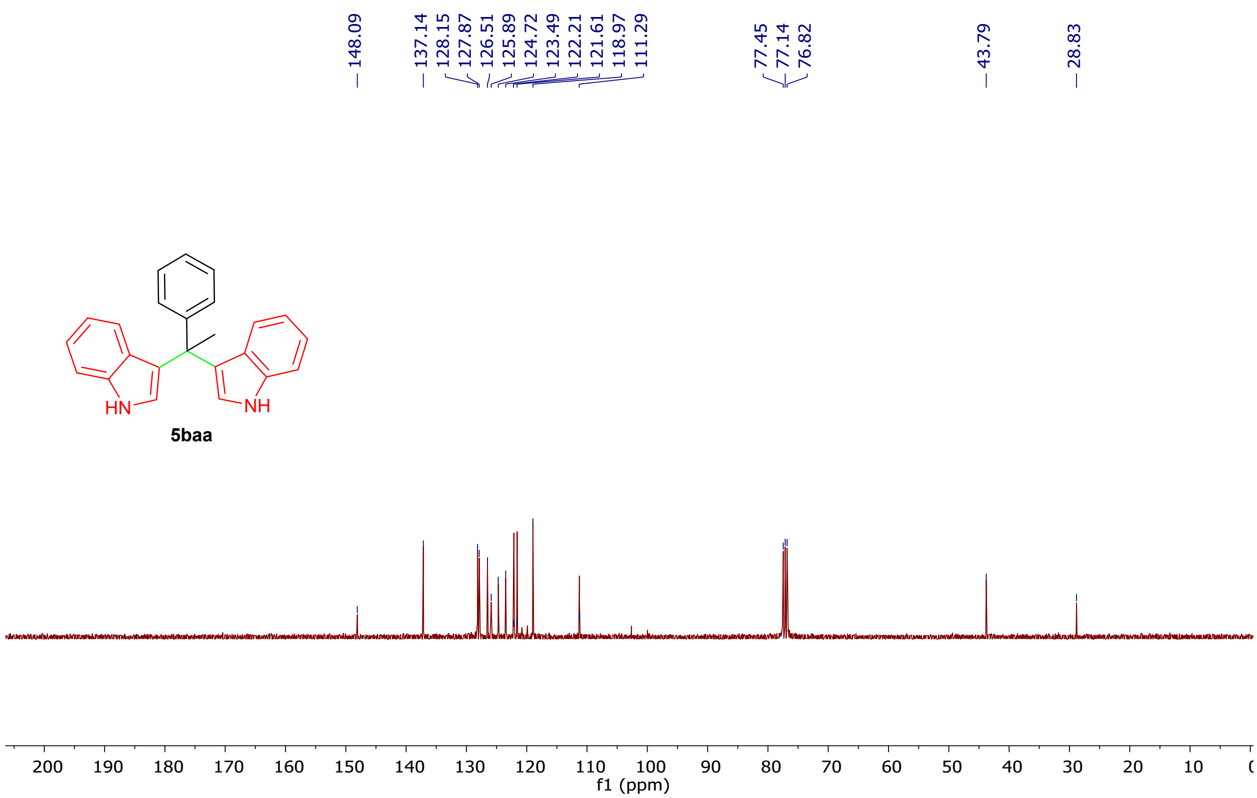

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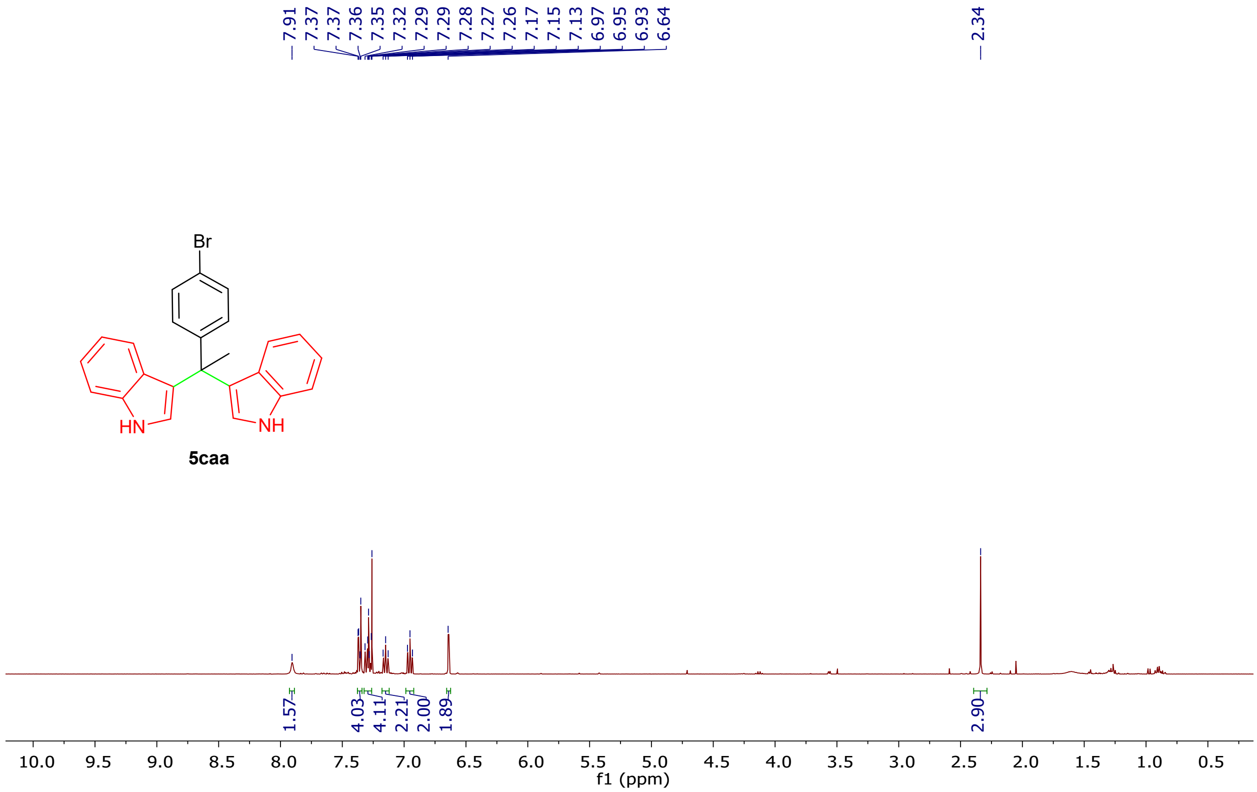

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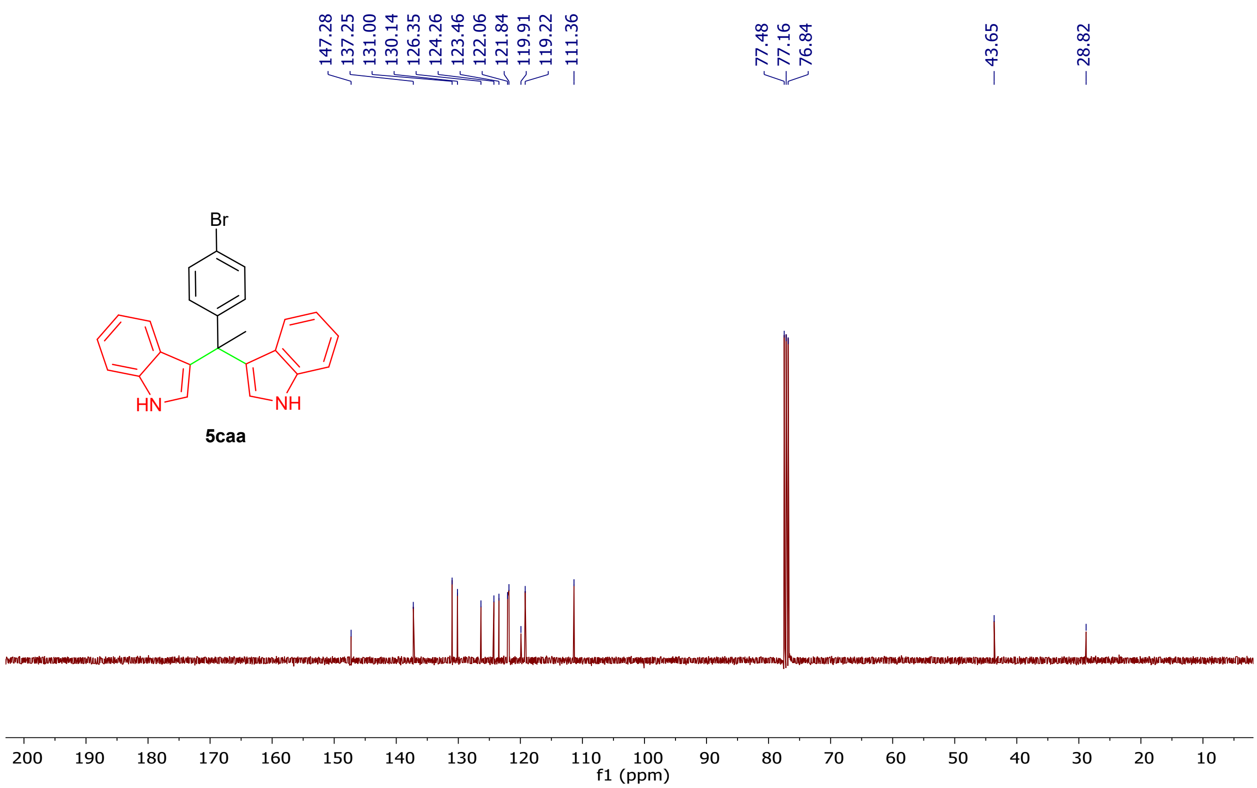

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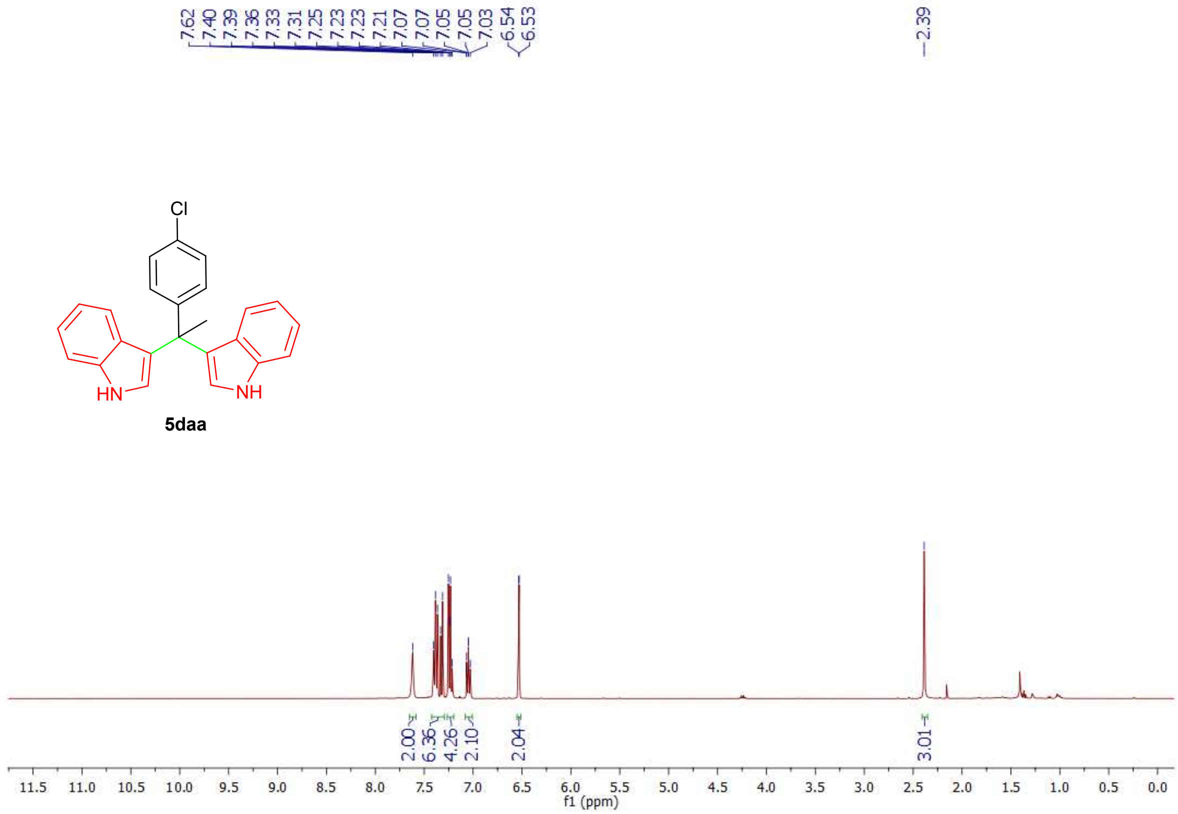

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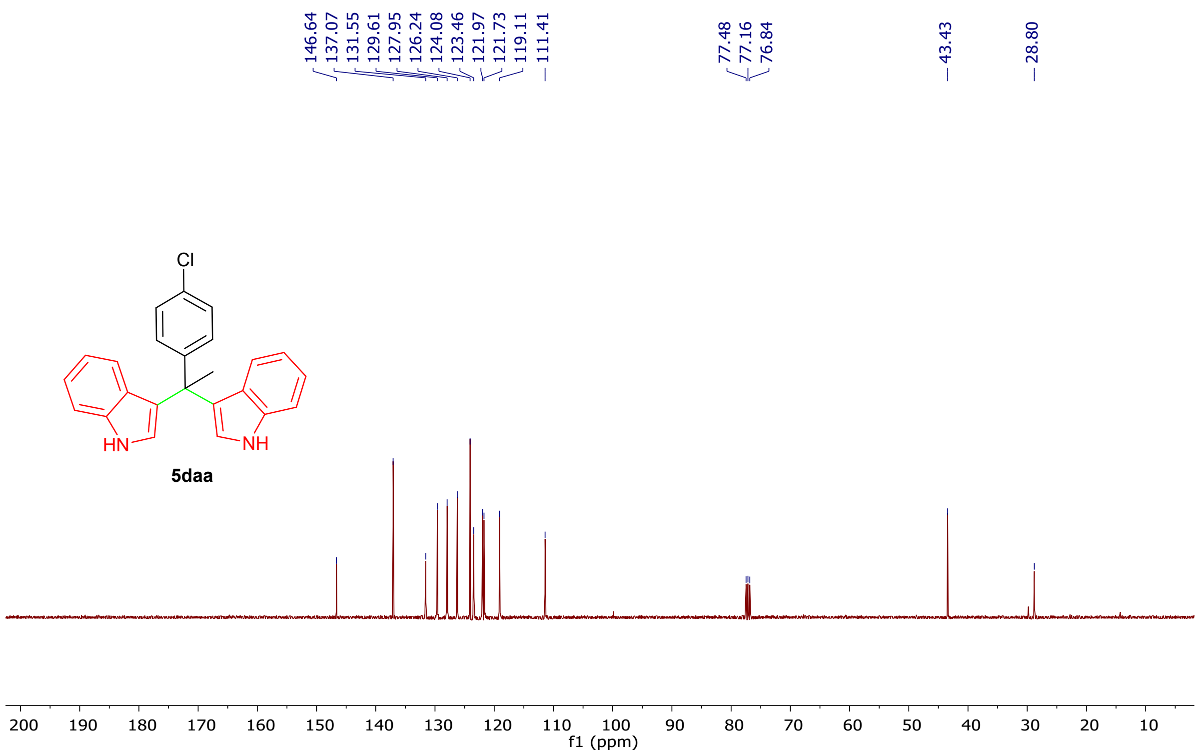

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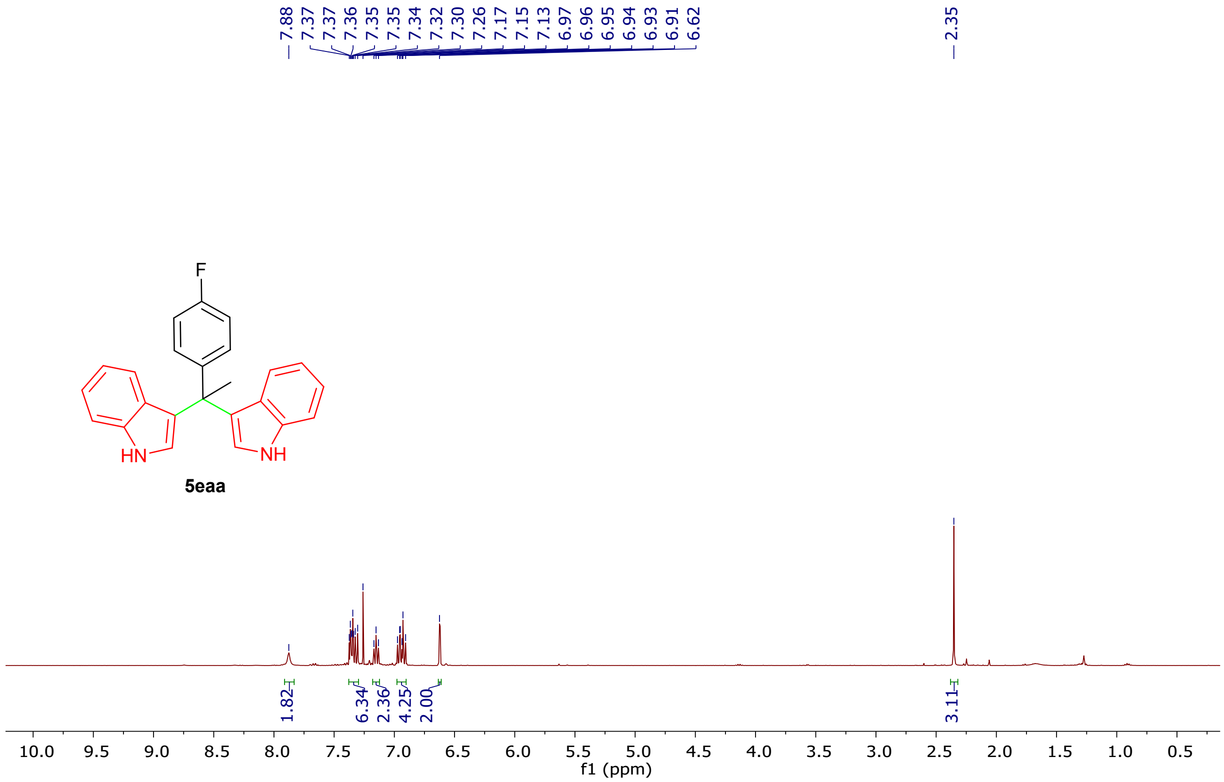

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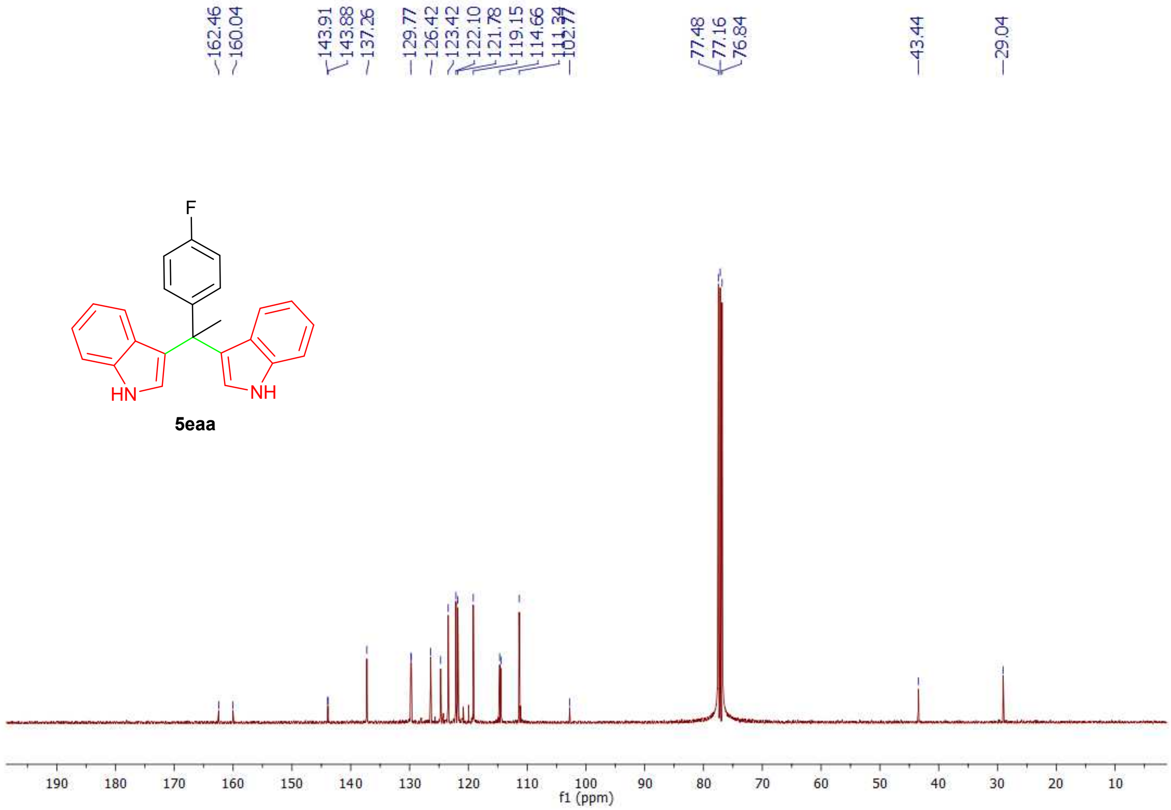

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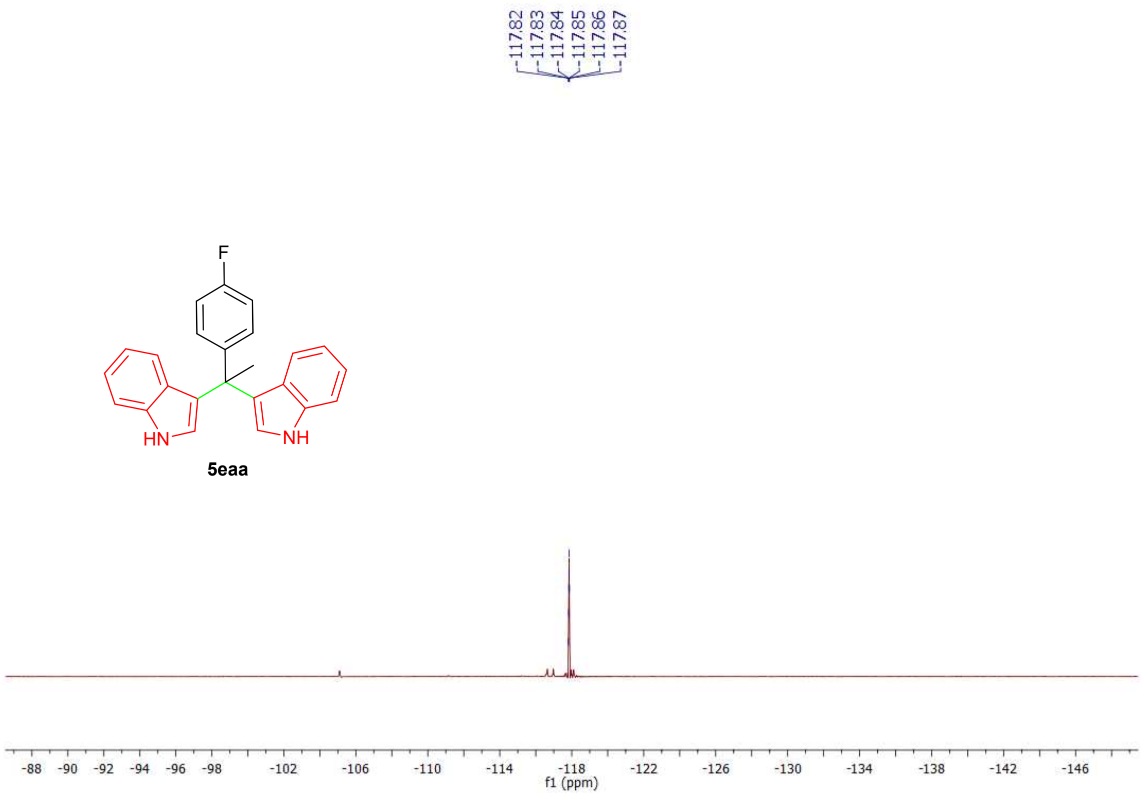

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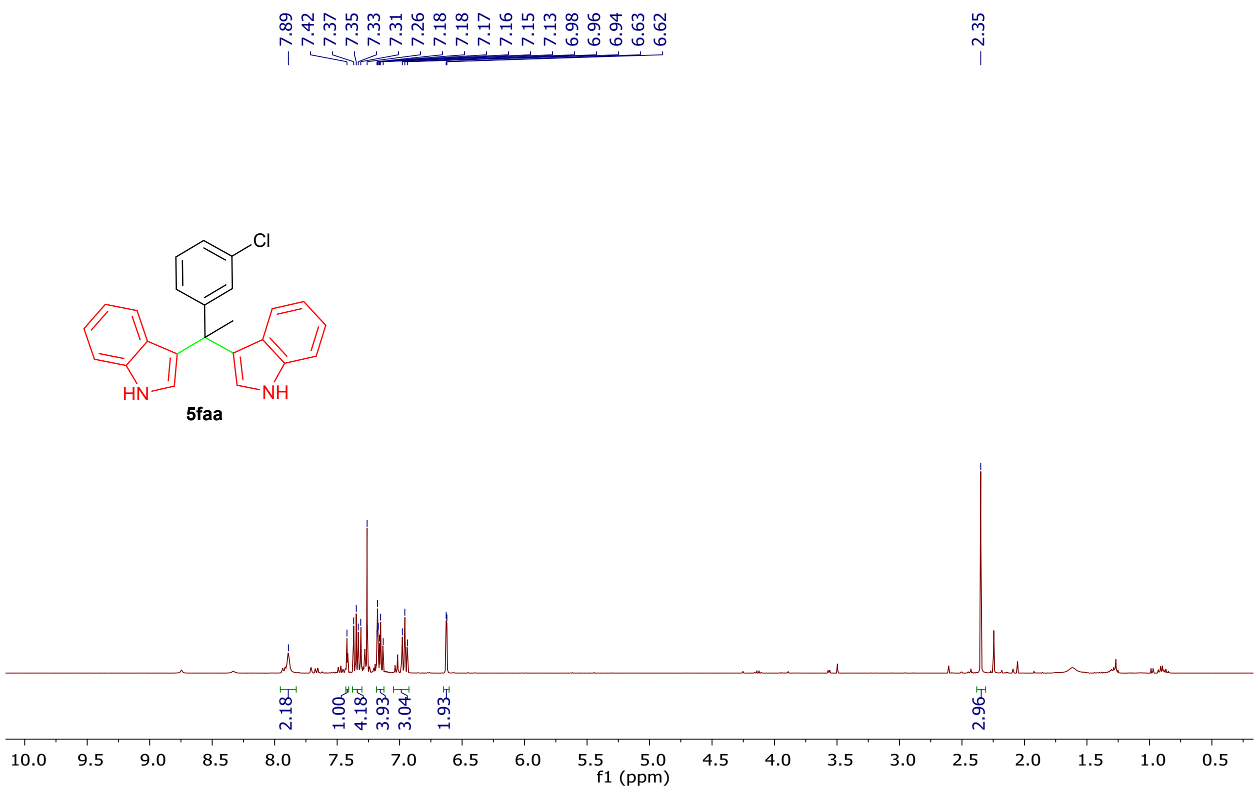

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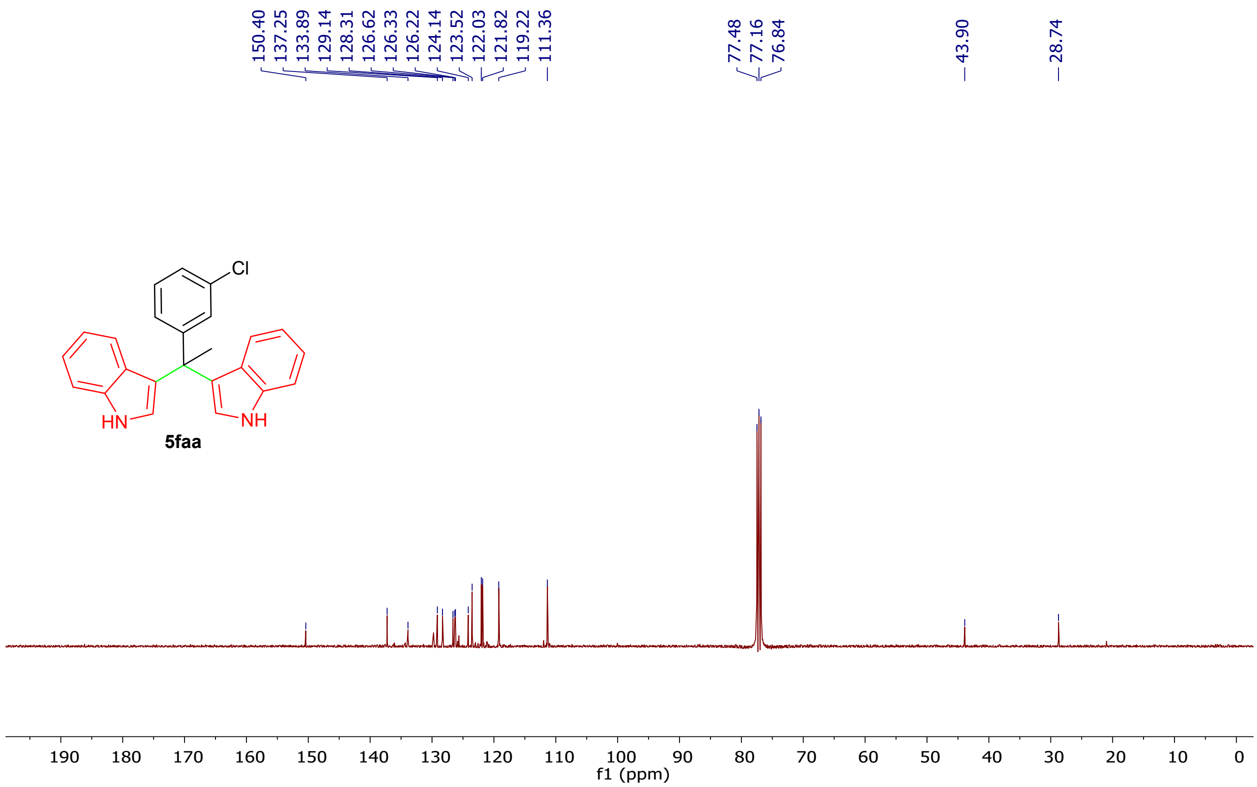

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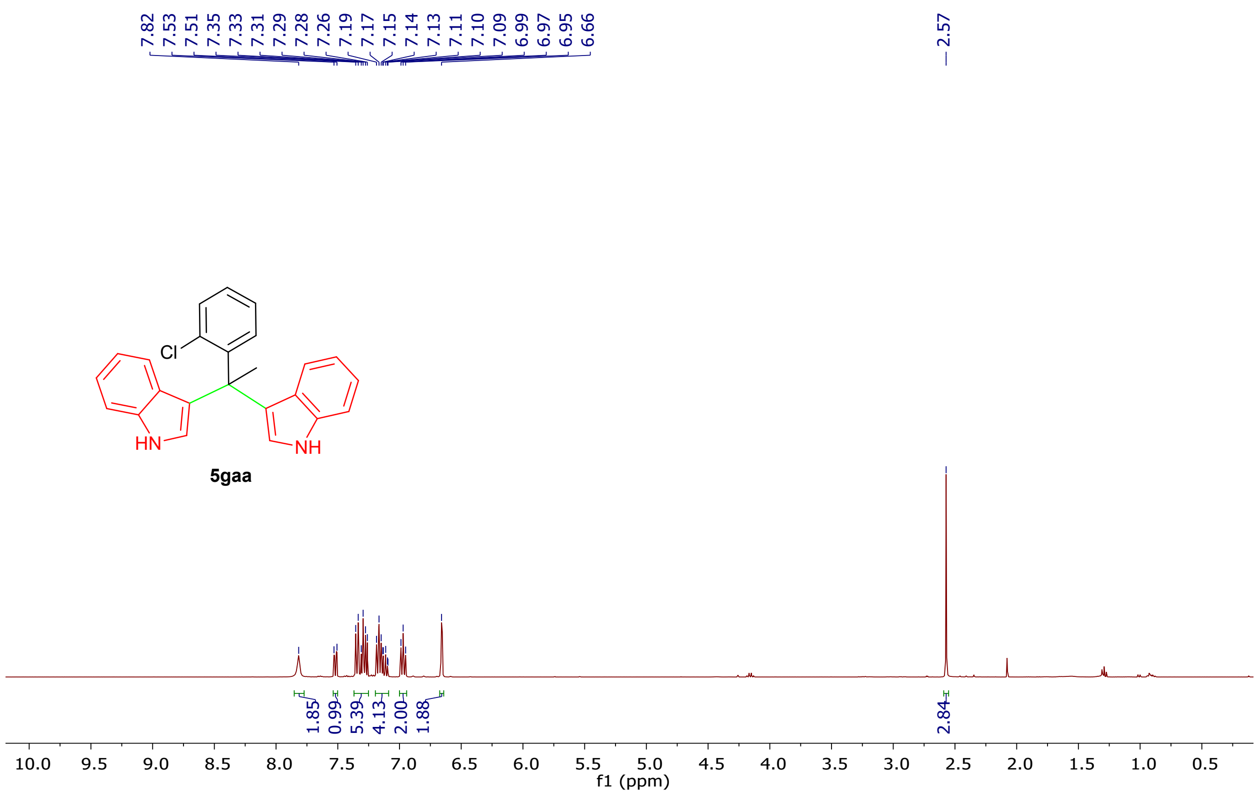

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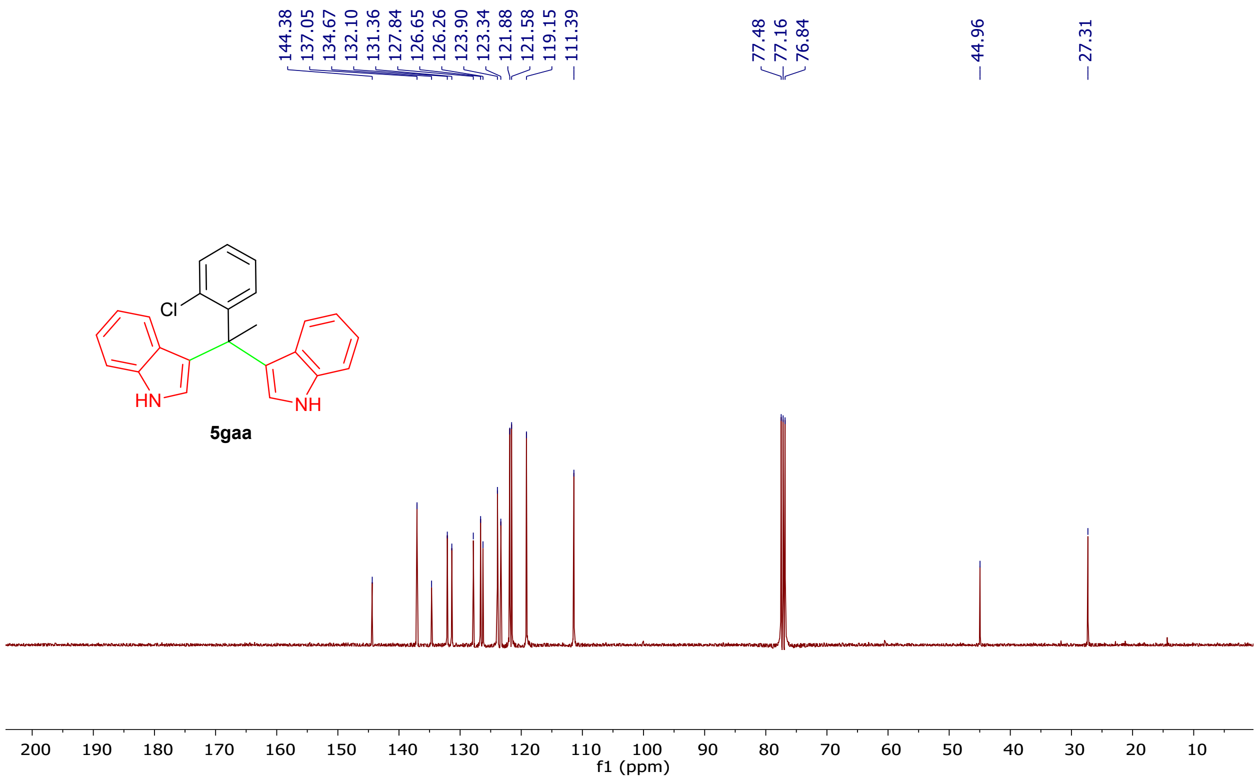

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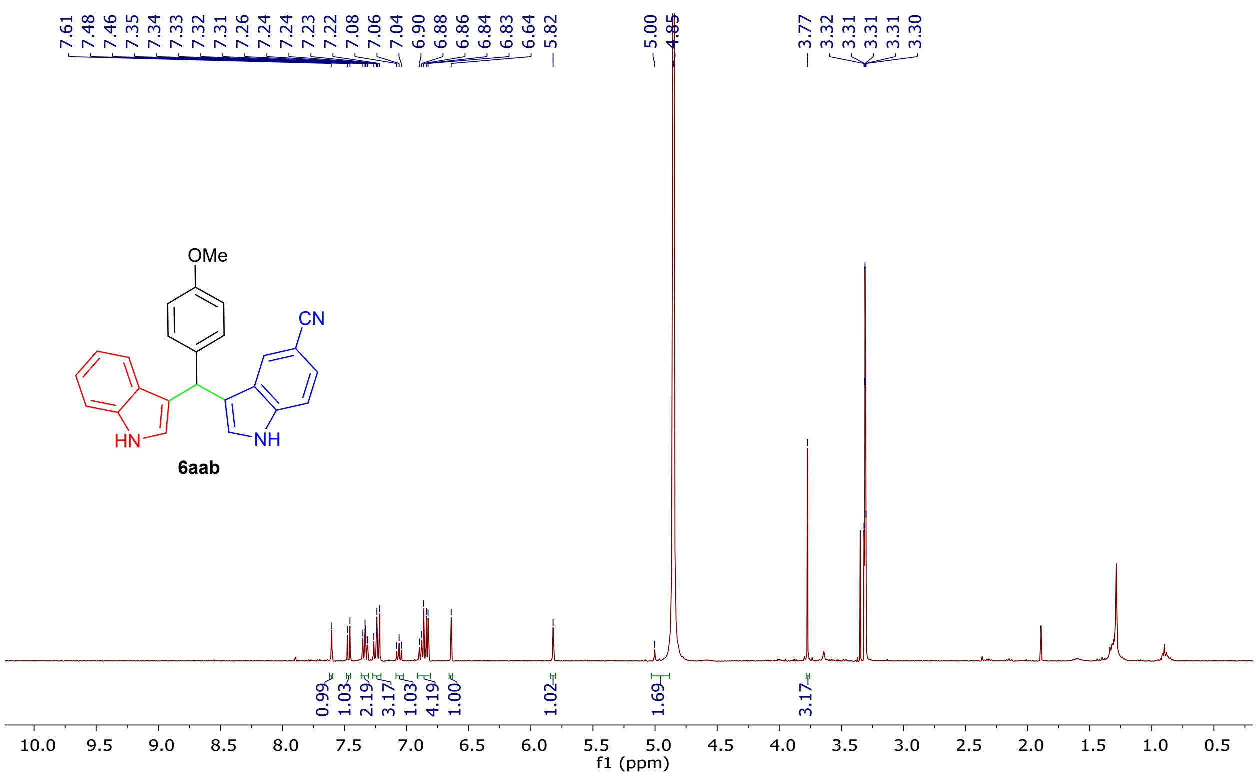

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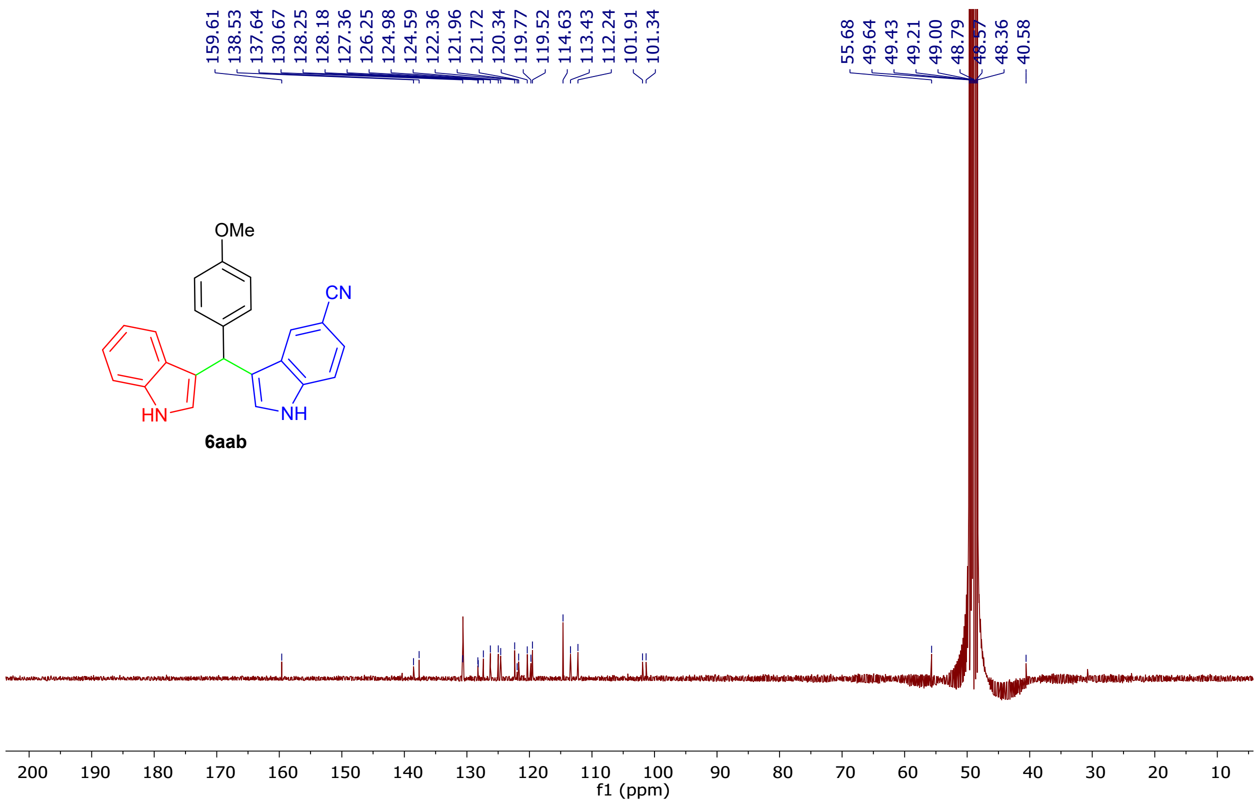

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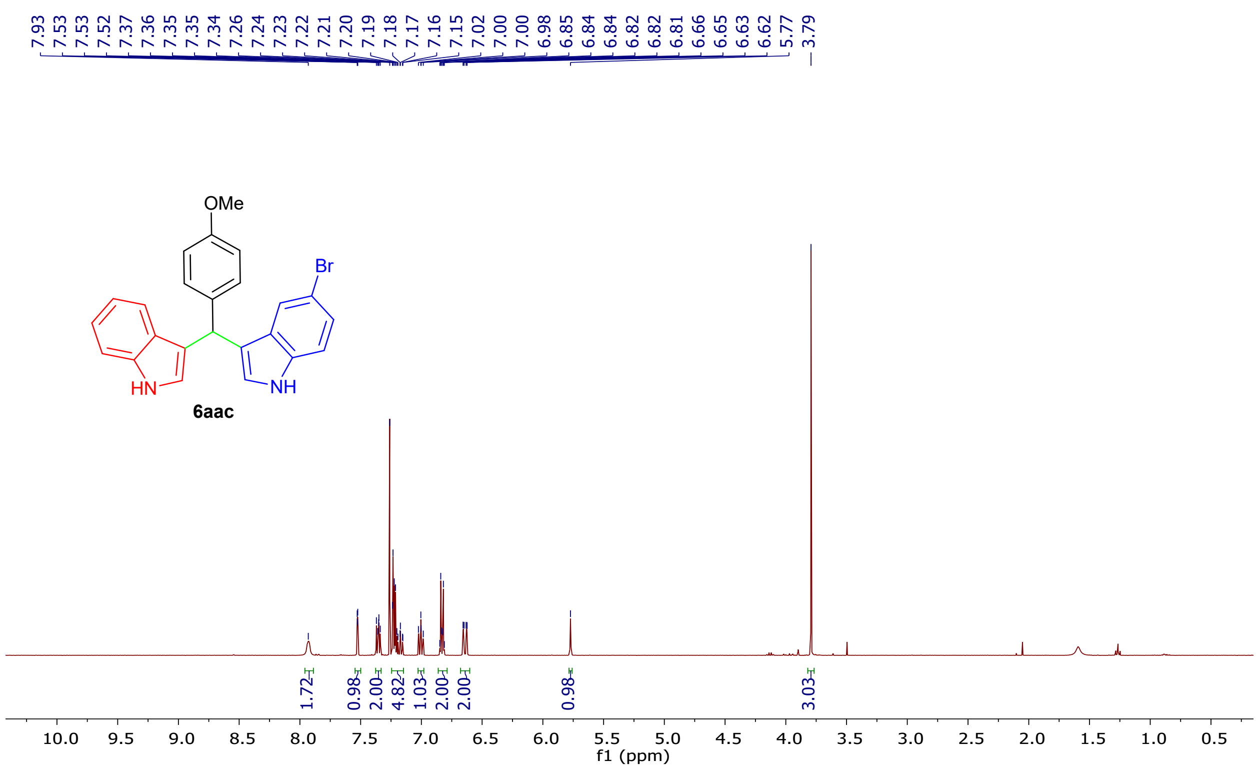

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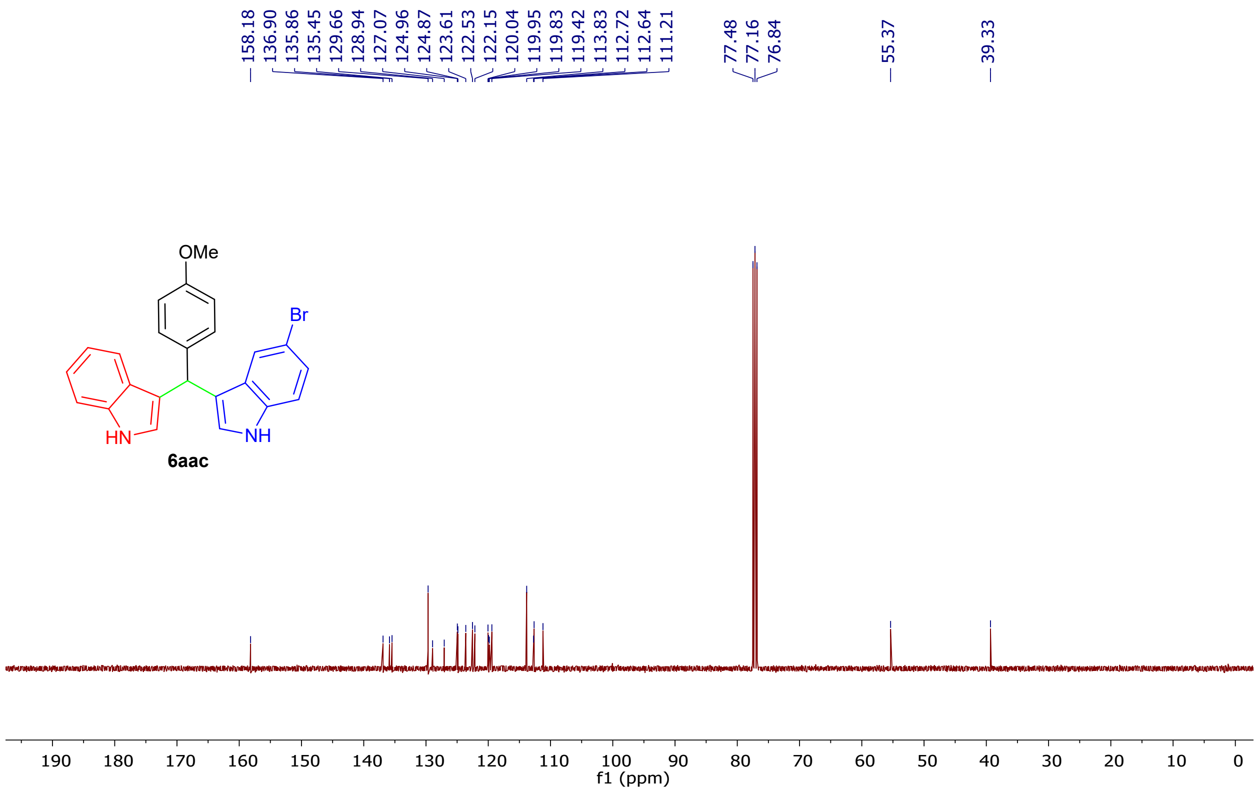

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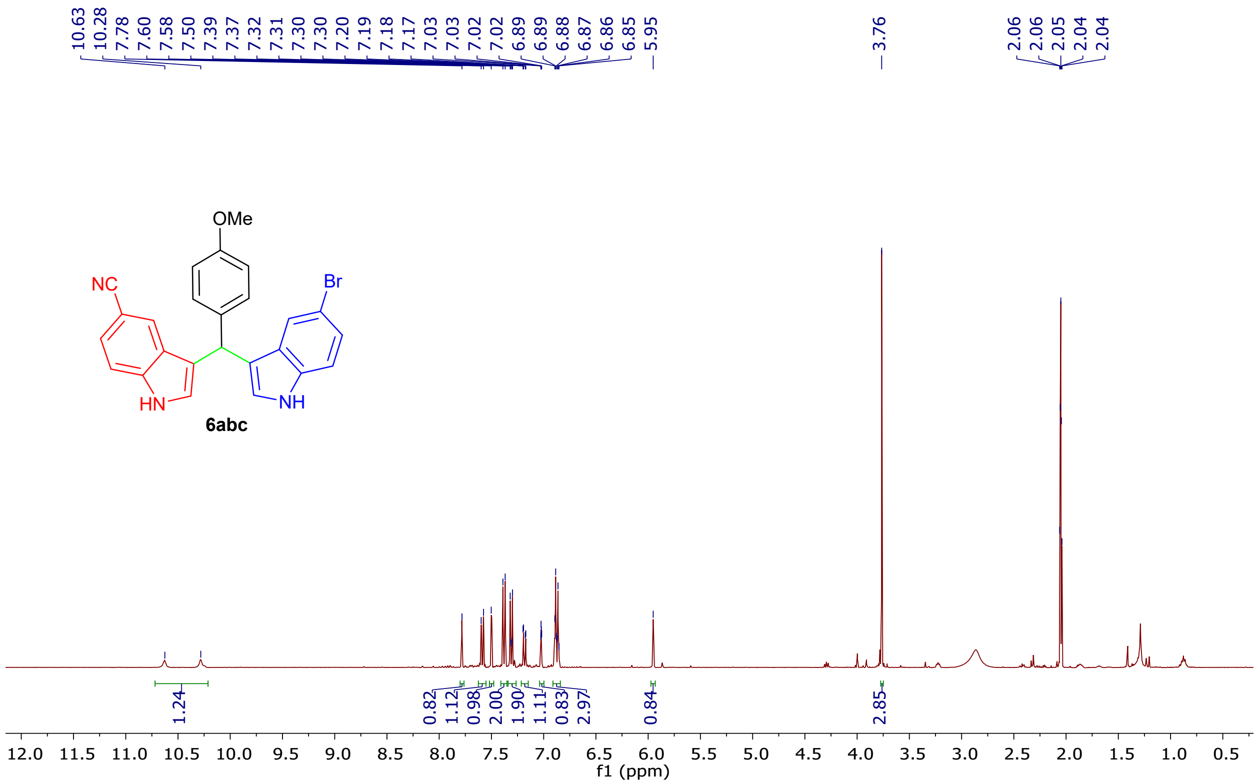

Figure.^{1}H NMR of **6abc** in $(CD_3)_2CO$

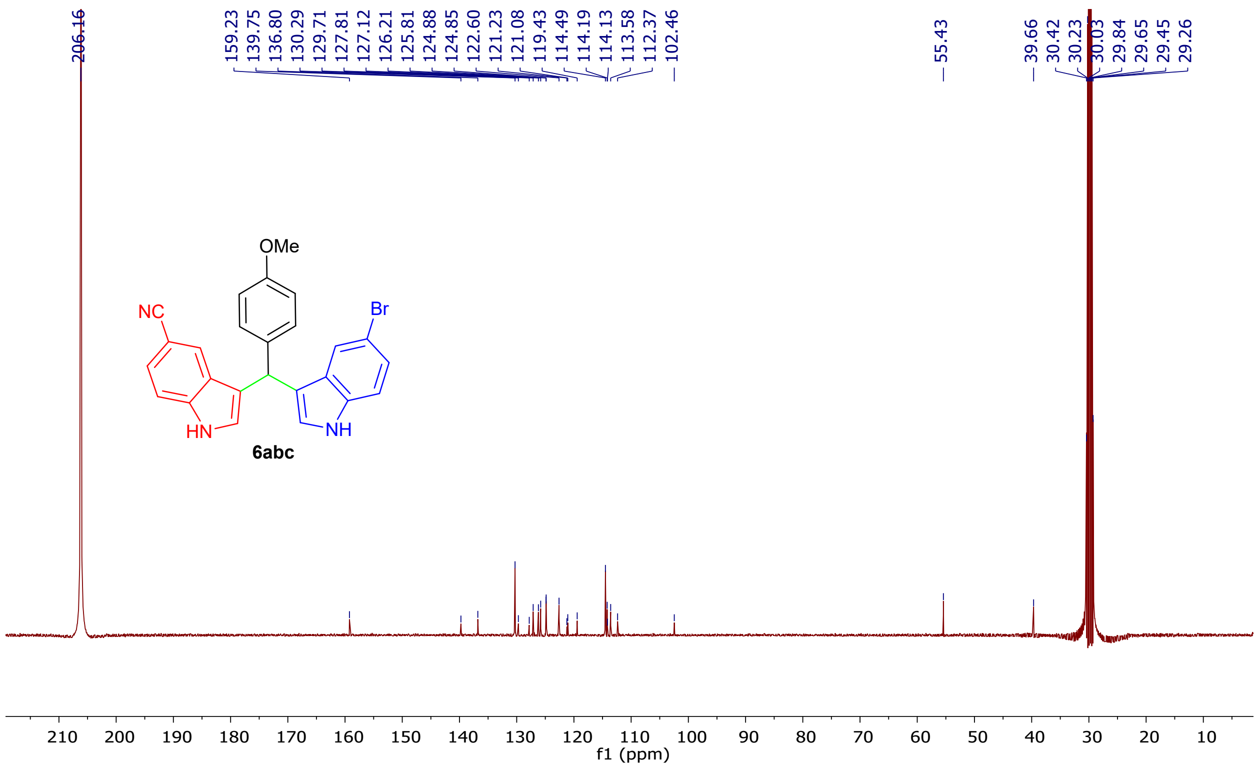

Figure.^{13}C NMR of **6abc** in $(CD_3)_2CO$

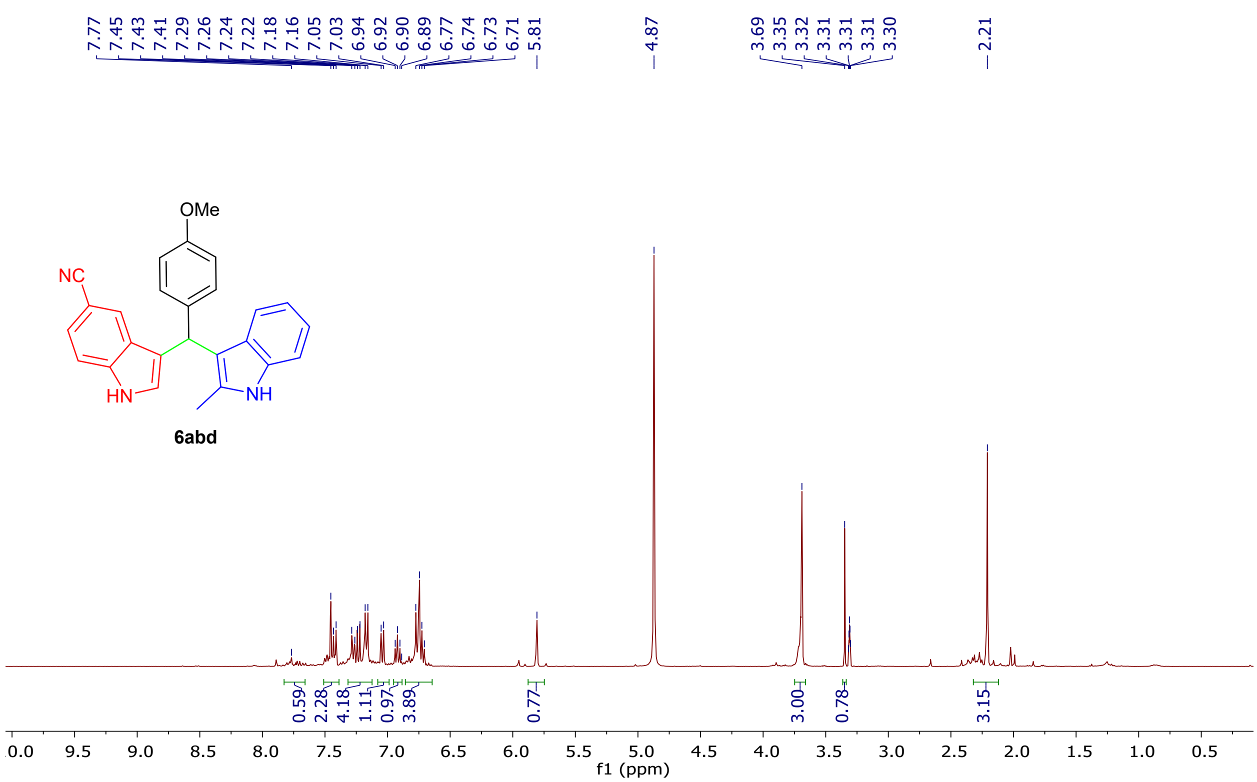

Figure.^{1}H NMR of **6abd** in CD_3OD

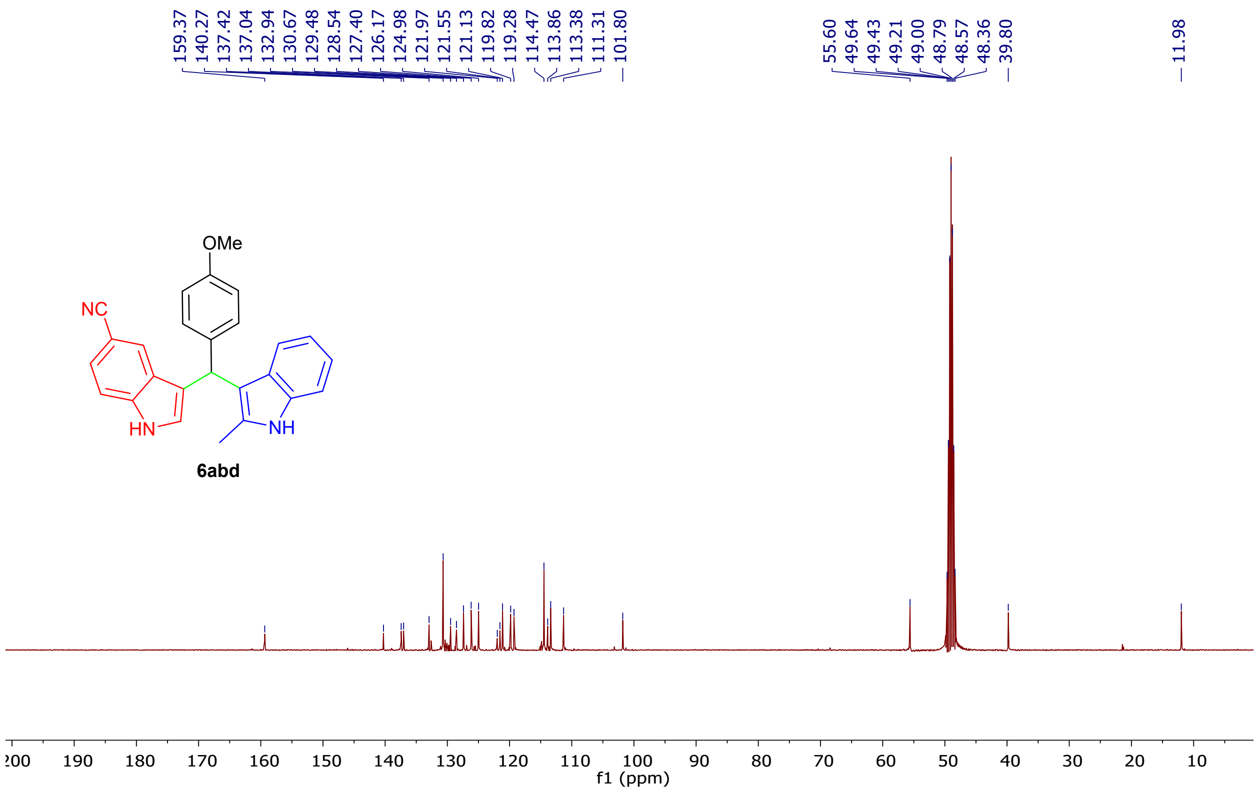

Figure.^{13}C NMR of **6abd** in CD_3OD

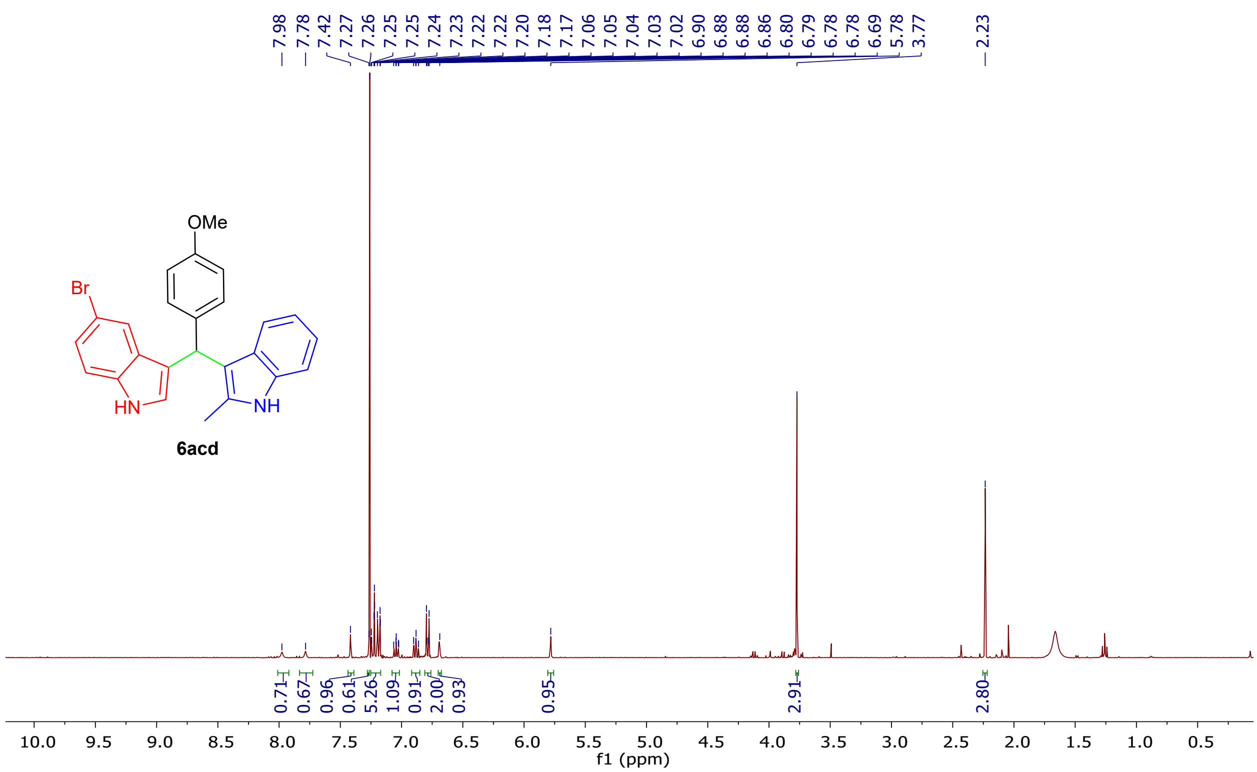

Figure.^{1}H NMR of **6acd** in $CDCl_3$

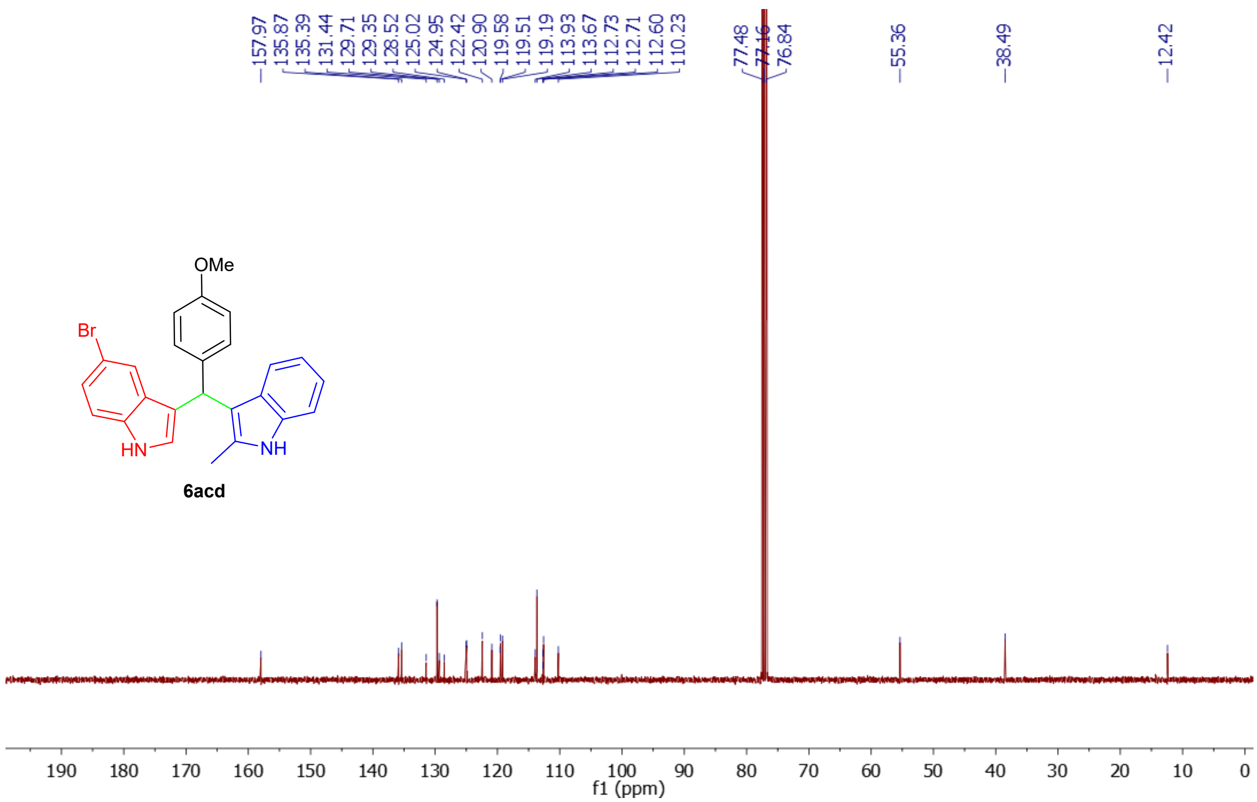

Figure.[13]C NMR of **6acd** in $CDCl_3$

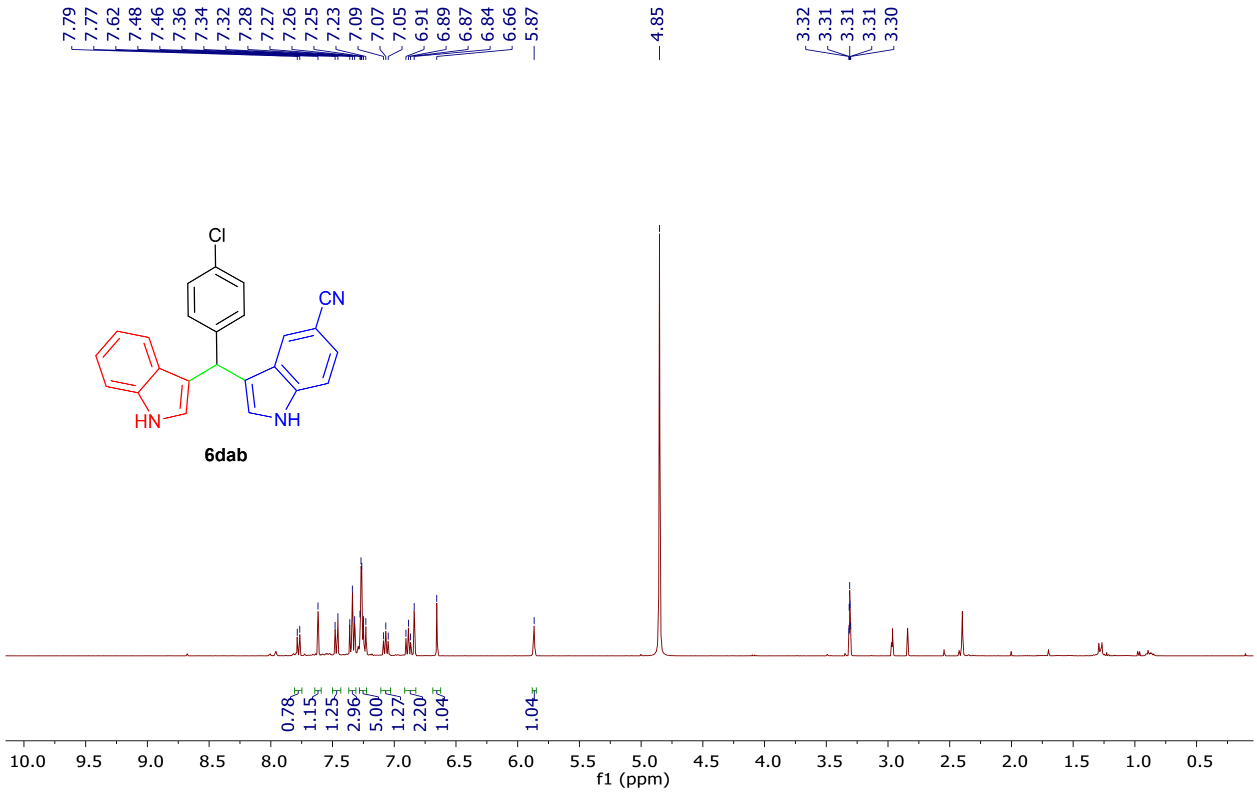

Figure.[1]H NMR of **6dab** in CD_3OD

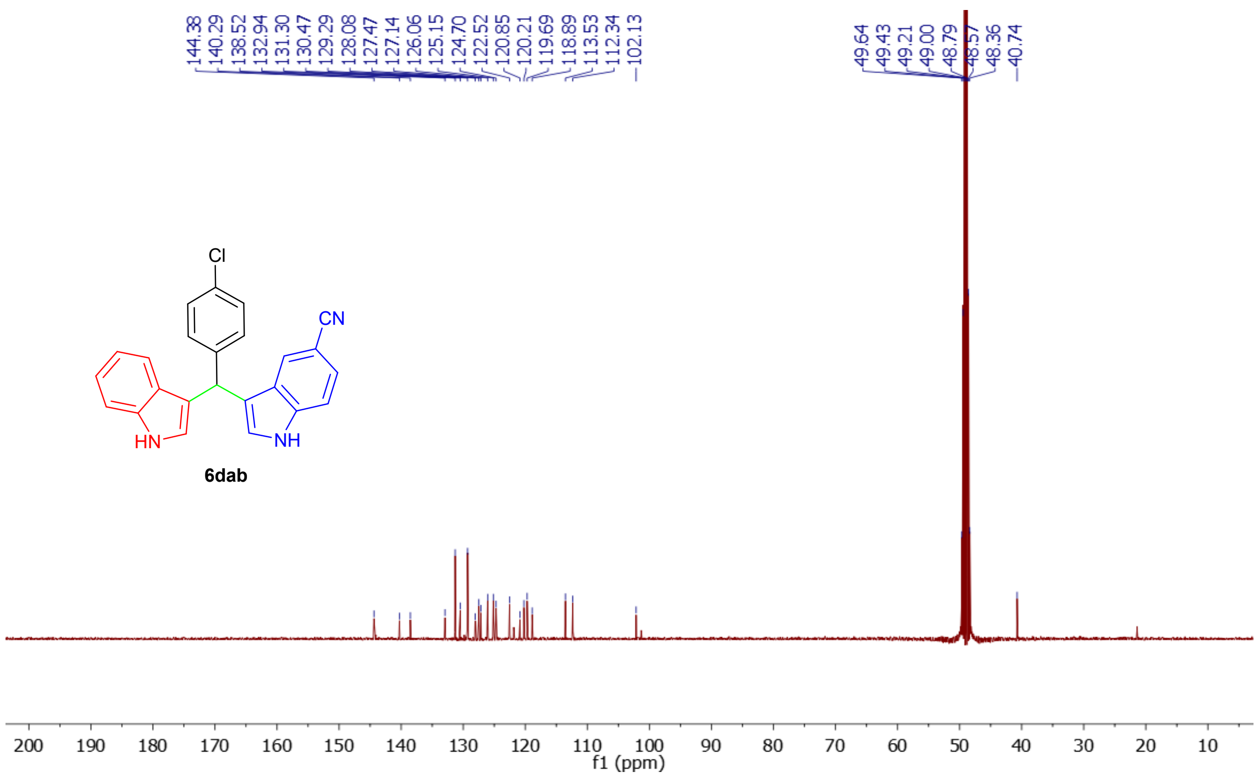

Figure.[13]C NMR of **6dab** in CD_3OD

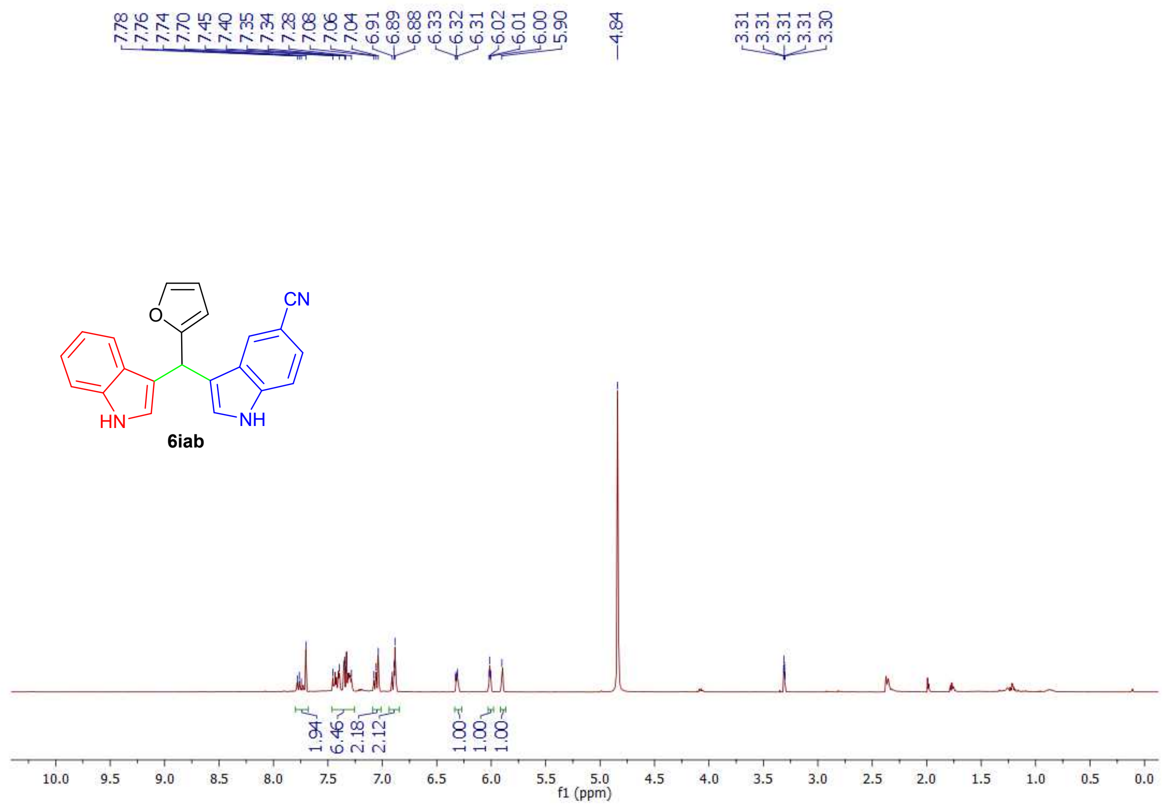

Figure. ^{1}H NMR of **6iab** in CD_3OD

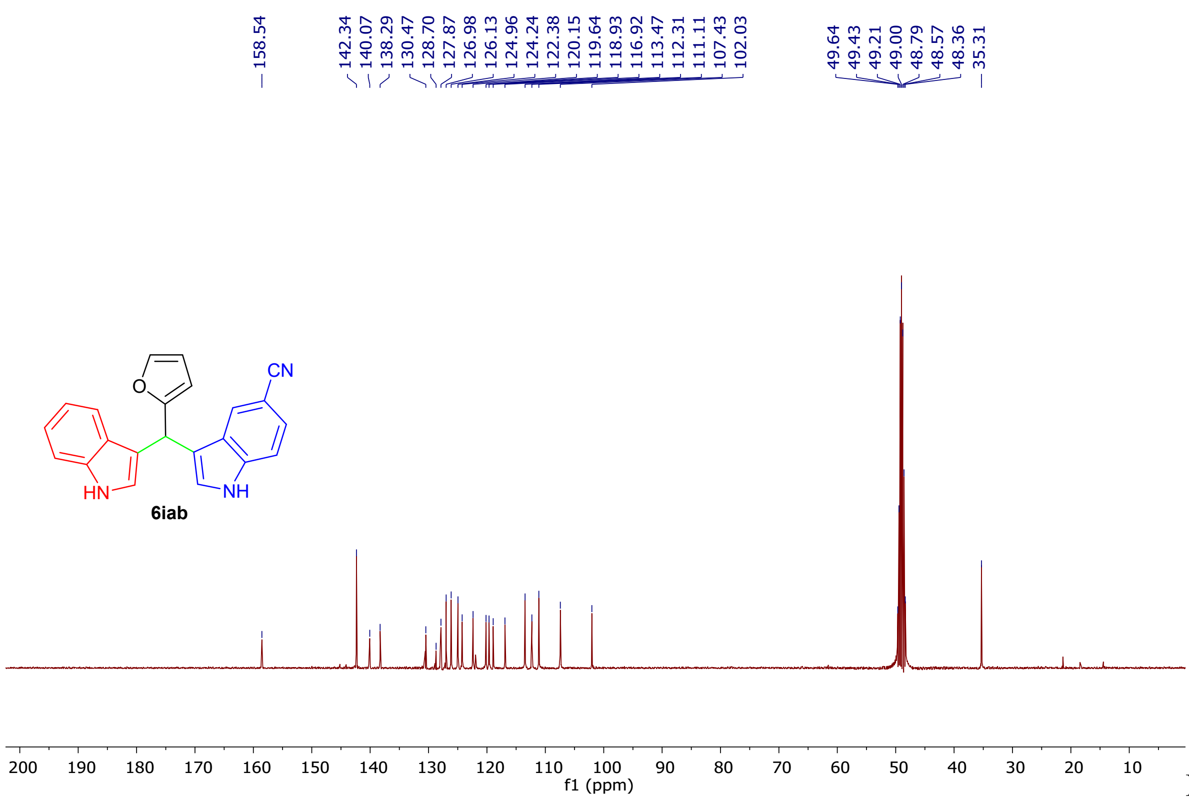

Figure. ^{13}C NMR of **6iab** in CD_3OD

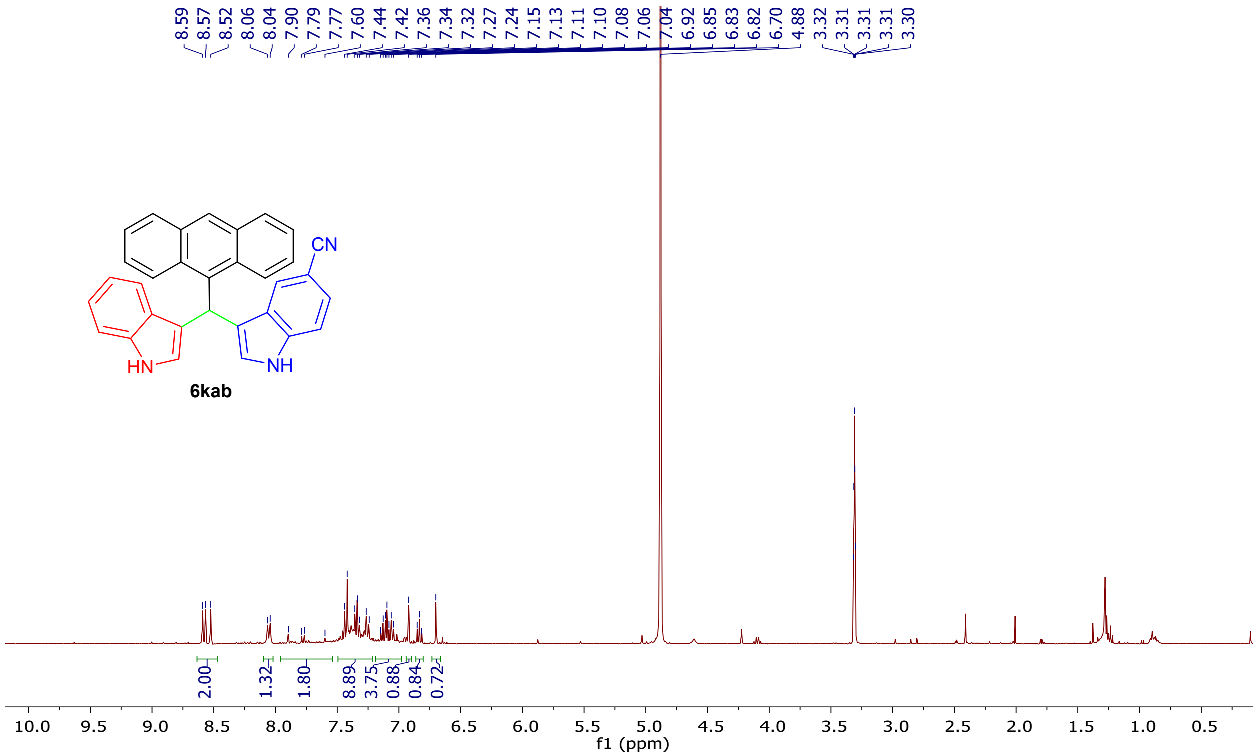

Figure.[1]H NMR of **6kab** in CD_3OD

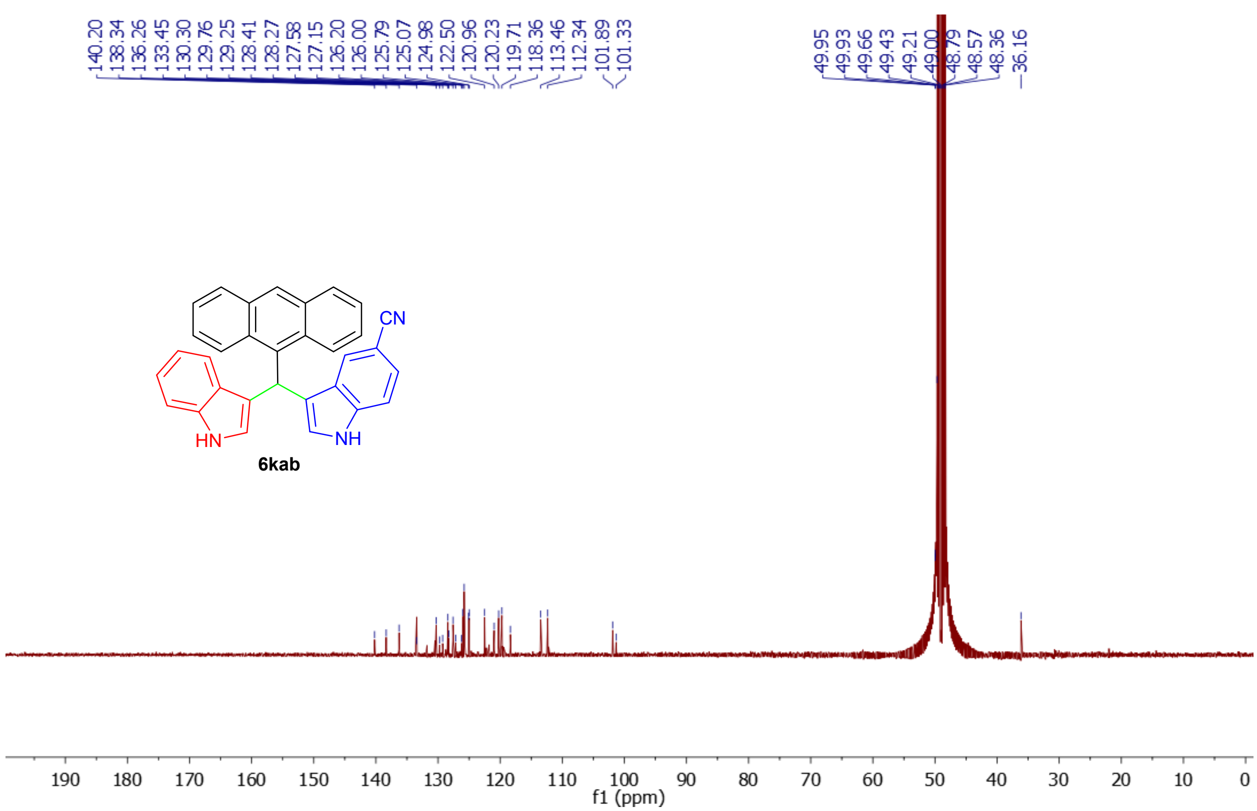

Figure. ^{13}C NMR of **6kab** in CD_3OD