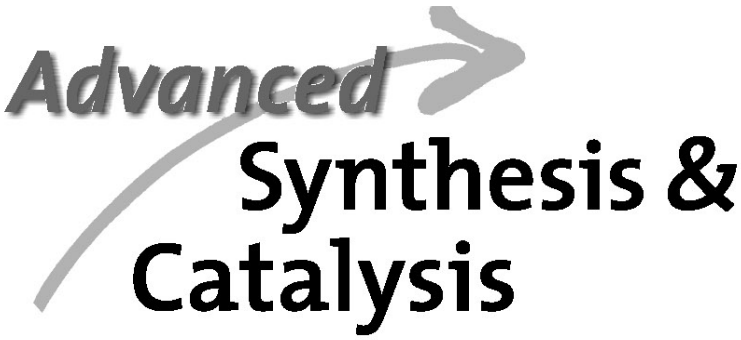

Supporting Information

Supporting Information

Triarylaminium salt Initiated Aerobic Double Friedel-Crafts Reaction of Glycine Derivatives with Indoles

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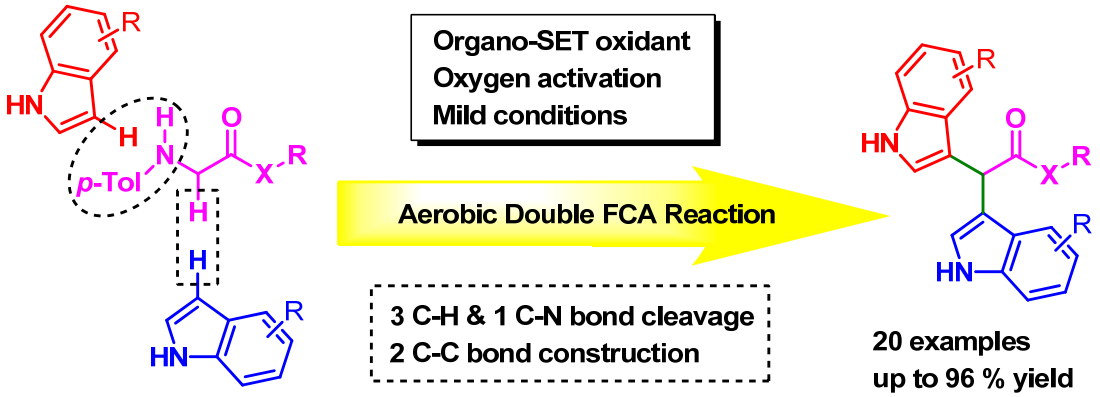


Table of Contents

General information. The starting materials, reagents and solvents, purchased from commercial suppliers, were used without further purification. Literature procedures were used for the preparation of glycine derivatives (*Angew. Chem. Int. Ed.* **2008**, *47*, 7075). $TBPA^{+\cdot}SbCl_6^-$ was synthesized according to literatures and used as freshly prepared (*J. Org. Chem.* **1992**, *57*, 6178). Analytical TLC was performed with silica gel GF254 plates, and the products were visualized by UV detection. Flash chromatography was carried out using silica gel 200−300. ^{1}HNMR (400 MHz) and ^{13}CNMR (100 MHz) spectra were measured with TMS as internal standard when $CDCl_3$, acetone-d_6 or DMSO-d_6 was used as solvent. High-resolution electrospray ionization (HRESI) mass spectra were recorded by a QTOF-2 Micromass spectrometer.

General experimental methods

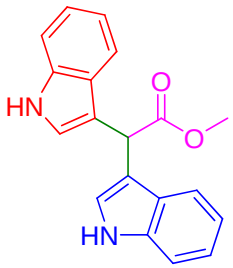
General procedure for $TBPA^{+\cdot}SbCl_6^-$ induced reaction of glycine esters with indoles.

Glycine esters (2, 1 mmol) and indoles (3, 2 mmol) were dissolved in CH_2Cl_2 (15 mL) at ambient temperature; $TBPA^{+\cdot}SbCl_6^-$ (0.2 mmol) was then added in one portion under stirring. The reactions were performed under an air atmosphere (open flask) at room temperature and completed within 5-8 hour as monitored by TLC. The products were isolated by column chromatographic separation.

General procedure for $TBPA^{+\cdot}SbCl_6^-$ induced reaction of glycine amides or short peptides with indoles.

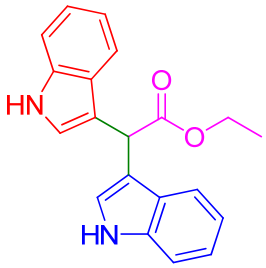
Glycine amides or short peptides (2, 1 mmol) and indoles (3, 2 mmol) were dissolved in $ClCH_2CH_2Cl$ (15 mL) at ambient temperature; $TBPA^{+\cdot}SbCl_6^-$ (0.2 mmol) was then added in one portion under stirring. The reactions were performed under an oxygen atmosphere (oxygen balloon) at room temperature and completed within 10-16 hour as monitored by TLC. The products were isolated by column chromatographic separation.

Characterization of the products



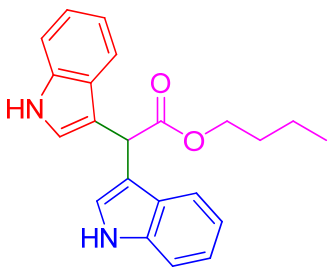
Compound 4aa, methyl 2,2-di(1H-indol-3-yl)acetate

Pale red powder, mp 58-60 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (s, 2H), 7.50 (d, *J* = 7.6 Hz, 2H), 7.14-6.96 (m, 6H), 6.77 (s, 2H), 5.40 (s, 1H), 3.75 (s, 3H). ^{13}C NMR (100 MHz, acetone-d_6) δ 173.4, 136.9, 126.9, 123.7, 121.4, 119.0, 118.8, 113.2, 111.4, 51.3, 40.5. HRMS (ESI) exact mass calcd for $C_{19}H_{17}N_2O_2$ [M+H] *m/z* 305.1290, found 305.1295.



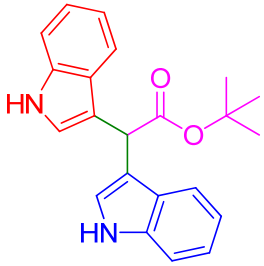
Compound 4ba, ethyl 2,2-di(1H-indol-3-yl)acetate

Pale red powder, mp 60-62 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (s, 2H), 7.66 (d, *J* = 7.9 Hz, 2H), 7.32 (d, *J* = 8.1 Hz, 2H), 7.20 (m, 2H), 7.12 (m, 2H), 7.02 (d, *J* = 2.0 Hz, 2H), 5.52 (s, 1H), 4.24 (q, *J* = 7.1 Hz, 2H), 1.29 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, acetone-d_6) δ 173.8, 137.8, 127.9, 124.6, 122.3, 120.0, 119.7, 114.2, 112.3, 61.2, 41.7, 14.6. HRMS (ESI) exact mass calcd for $C_{20}H_{19}N_2O_2$ [M+H] *m/z* 319.1447, found 319.1446.



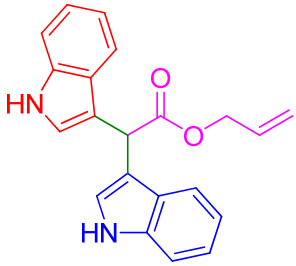
Compound 4ca, butyl 2,2-di(1H-indol-3-yl)acetate

Pale red powder, mp 45-47 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (s, 2H), 7.61 (d, *J* = 8.0 Hz, 2H), 7.28-7.05 (m, 6H), 6.98 (s, 2H), 5.49 (s, 1H), 4.15 (t, *J* = 6.4 Hz, 2H), 1.60 (m, 2H), 1.31 (m, 2H), 0.85 (t, *J* = 6.8 Hz, 2H). ^{13}C NMR (100 MHz, acetone-d_6) δ 173.9, 137.8, 127.9, 124.6, 122.3, 120.0, 119.6, 114.2, 112.3, 65.0, 41.7, 19.8, 14.0. HRMS (ESI) exact mass calcd for $C_{22}H_{23}N_2O_2$ [M+H] *m/z* 347.1760, found 347.1762.



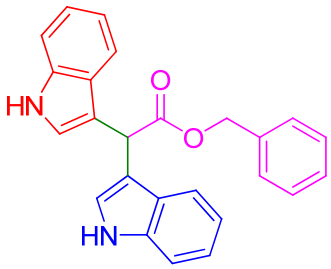
Compound 4da, *tert*-butyl 2,2-di(1H-indol-3-yl)acetate

Pale red powder, mp 74-76 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (s, 2H), 7.47 (d, *J* = 7.6 Hz, 2H), 7.19-6.98 (m, 6H), 6.85 (s, 2H), 5.31 (s, 1H), 1.37 (s, 9H). ^{13}C NMR (100 MHz, acetone-d_6) δ 172.2, 136.9, 127.0, 123.5, 121.3, 119.2, 118.7, 113.6, 111.4, 79.9, 41.9, 27.4. HRMS (ESI) exact mass calcd for $C_{22}H_{23}N_2O_2$ [M+H] *m/z* 347.1760, found 347.1757.



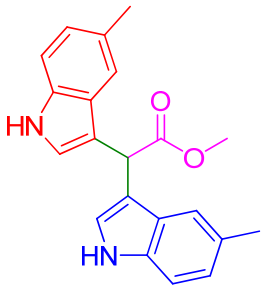
Compound 4ea, allyl 2,2-di(1H-indol-3-yl)acetate

Red powder, mp 46-48 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (s, 2H), 7.52 (d, *J* = 8.0 Hz, 2H), 7.16-7.05 (m, 4H), 6.83 (s, 2H), 5.80 (m, 1H), 5.44 (s, 1H), 5.16-5.06 (m, 2H), 4.55 (m, 2H). ^{13}C NMR (100 MHz, acetone-d_6) δ 172.6, 136.9, 132.8, 126.9, 123.7, 121.4, 119.1, 118.8, 117.1, 113.1, 111.4, 64.9, 40.7. HRMS (ESI) exact mass calcd for $C_{21}H_{19}N_2O_2$ [M+H] *m/z* 331.1447, found 331.1451.



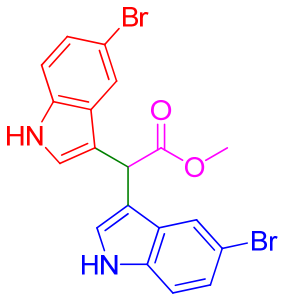
Compound 4fa, benzyl 2,2-di(1H-indol-3-yl)acetate

Pale green powder, mp 49-51 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (s, 2H), 7.51 (d, *J* = 7.6 Hz, 2H), 7.27-6.96 (m, 13H), 5.50 (s, 1H), 5.12 (s, 2H). ^{13}C NMR (100 MHz, acetone-d_6) δ 172.8, 136.9, 136.6, 128.3, 128.0, 127.9, 126.9, 123.7, 121.4, 119.1, 118.8, 113.1, 111.4, 66.0, 40.8. HRMS (ESI) exact mass calcd for $C_{25}H_{21}N_2O_2$ [M+H] *m/z* 381.1603, found 381.1610.



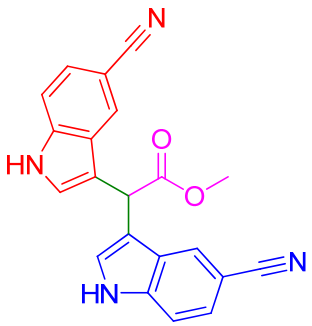
Compound 4ab, methyl 2,2-bis(5-methyl-1H-indol-3-yl)acetate

Purple powder, mp 77-79 ^{o}C. ^{1}H NMR (400 MHz, Acetone-d_6) δ 10.07 (brs, 1H), 7.42 (s, 2H), 7.29 (d, *J* = 8.3 Hz, 2H), 7.20 (s, 2H), 6.94 (d, *J* = 8.3 Hz, 2H), 5.48 (s, 1H), 3.70 (s, 3H), 2.38 (s, 6H). ^{13}C NMR (100 MHz, Acetone-d_6) δ 173.6, 135.3, 135.1, 127.6, 127.2, 127.2, 123.8, 123.6, 123.0, 118.6, 112.7, 112.6, 111.1, 111.1, 51.3, 40.5, 20.9. HRMS (ESI) exact mass calcd for $C_{21}H_{21}N_2O_2$ [M+H] *m/z* 333.1603, found 333.1604.



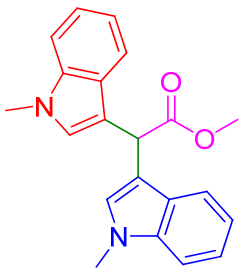
Compound 4ac, methyl 2,2-bis(5-bromo-1H-indol-3-yl)acetate

Pale red powder, mp 78-80 °C. ^{1}H NMR (400 MHz, Acetone-d_6) δ 10.49 (brs, 1H), 7.78 (s, 2H), 7.39 (m, 4H), 7.21 (d, J = 8.6Hz, 2H), 5.54 (s, 1H), 3.72 (s, 3H). ^{13}C NMR (100 MHz, Acetone-d_6) δ 173.0, 135.6, 135.4, 128.5, 125.4, 125.2, 124.1, 121.6, 113.4, 113.3, 112.5, 112.5, 111.8, 51.5, 40.2. HRMS (ESI) exact mass calcd for $C_{19}H_{15}Br_2N_2O_2$ [M+H] *m/z* 460.9500, found 460.9496.



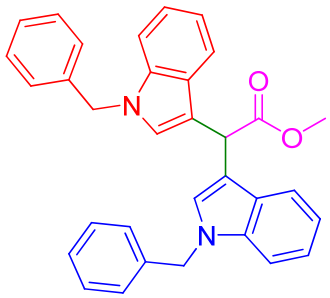
Compound 4ad, methyl 2,2-bis(5-cyano-1H-indol-3-yl)acetate

Pale yellow powder, mp 97-99 °C. ^{1}H NMR (400 MHz, Acetone-d_6) δ 8.08 (s, 2H), 7.61 (m, 4H), 7.40 (d, J = 8.6Hz, 2H), 5.73 (s, 1H), 3.76 (s, 3H). ^{13}C NMR (100 MHz, Acetone-d_6) δ 172.6, 138.4, 130.0, 126.4, 126.3, 124.8, 124.3, 124.1, 120.3, 113.6, 112.8, 101.9, 51.7, 40.0. HRMS (ESI) exact mass calcd for $C_{21}H_{15}N_4O_2$ [M+H] *m/z* 355.1195, found 355.1201.



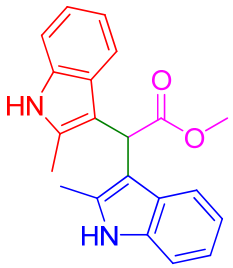
Compound 4ae, methyl 2,2-bis(1-methyl-1H-indol-3-yl)acetate

Pale red powder, mp 134-136 °C. ^{1}H NMR (400 MHz, Acetone-d_6) δ 10.07 (brs, 1H), 7.30 (m, 4H), 6.98 (d, J = 5.4 Hz, 2H), 6.86 (d, J = 5.5 Hz, 2H), 5.51 (s, 1H), 3.72 (s, 3H), 2.26 (s, 6H). ^{13}C NMR (100 MHz, Acetone-d_6) δ 173.8, 135.4, 132.5, 128.5, 120.2, 118.6, 118.5, 110.3, 108.3, 51.3, 39.8, 11.4. HRMS (ESI) exact mass calcd for $C_{21}H_{21}N_2O_2$ [M+H] m/z 333.1603, found 333.1600.



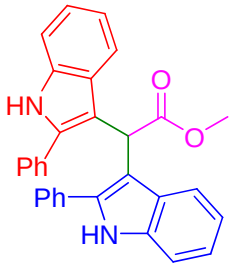
Compound 4af, methyl 2,2-bis(1-benzyl-1H-indol-3-yl)acetate

Pale yellow powder, mp 131-133 °C. ^{1}H NMR (400 MHz, Acetone-d_6) δ 10.55 (brs, 1H), 7.37 (m, 14H), 7.07 (m, 2H), 6.86 (m, 2H), 5.67 (s, 1H), 3.53 (s, 3H). ^{13}C NMR (100 MHz, Acetone-d_6) δ 173.8, 136.5, 136.3, 136.2, 133.1, 128.5, 128.4, 127.6, 121.4, 120.4, 119.1, 111.2, 111.1, 109.9, 51.2, 41.6. HRMS (ESI) exact mass calcd for $C_{33}H_{29}N_2O_2$ [M+H] m/z 485.2229, found 485.2230.



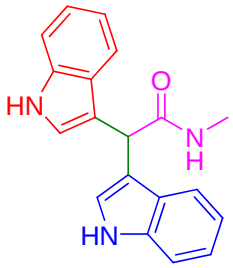
Compound 4ag, methyl 2,2-bis(2-methyl-1H-indol-3-yl)acetate

Blue powder, mp 210-212 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, J = 7.8 Hz, 2H), 7.41 – 7.00 (m, 18H), 5.61 (s, 1H), 5.30 (s, 4H), 3.80 (s, 3H). ^{13}C NMR (100 MHz, Acetone-d_6) δ 173.1, 138.4, 136.8, 128.5, 127.6, 127.5, 127.3, 126.8, 121.6, 119.5, 119.0, 112.7, 110.0, 51.4, 49.4, 40.4. HRMS (ESI) exact mass calcd for $C_{21}H_{21}N_2O_2$ [M+H] m/z 333.1603, found 333.1605.



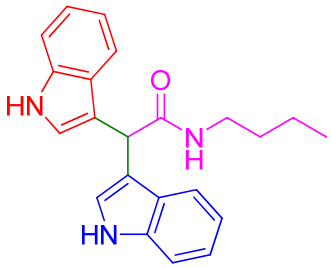
Compound 4ah, methyl 2,2-bis(2-phenyl-1H-indol-3-yl)acetate

Colorless block crystals, mp 220-222 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, *J* = 7.9 Hz, 2H), 7.29 (d, *J* = 8.2 Hz, 2H), 7.22 (t, *J* = 7.4 Hz, 2H), 7.09 (t, *J* = 7.4 Hz, 2H), 7.01 (s, 2H), 5.51 (s, 1H), 3.74 (s, 3H), 3.71 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.1, 137.2, 128.0, 127.2, 121.8, 119.4, 119.2, 112.2, 109.4, 77.5, 77.2, 76.8, 52.3, 40.3, 32.8. HRMS (ESI) exact mass calcd for $C_{31}H_{25}N_2O_2$ [M+H] *m/z* 457.1916, found 457.1917.



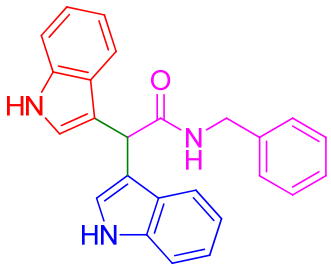
Compound 4ga, 2,2-di(1H-indol-3-yl)-N-methylacetamide

Pale red powder, mp 162-164 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.37 (brs, 2H), 7.46 (d, *J* = 7.9 Hz, 2H), 7.23 (d, *J* = 7.9 Hz, 3H), 7.12 (t, *J* = 7.5 Hz, 2H), 7.02 (t, *J* = 7.5 Hz, 2H), 6.62 (s, 2H), 6.03 (brs, 1H), 5.30 (s, 1H), 2.70 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.1, 136.6, 126.7, 123.9, 121.8, 119.3, 119.0, 113.8, 111.5, 60.4, 26.5. HRMS (ESI) exact mass calcd for $C_{19}H_{18}N_3O$ [M+H] *m/z* 304.1450, found 304.1448.



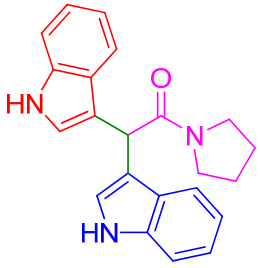
Compound 4ha, N-butyl-2,2-di(1H-indol-3-yl)acetamide

Red powder, mp 208-210 °C. ^{1}H NMR (400 MHz, Acetone-d_6) δ 10.13 (s, 2H), 7.61 (m, 2H), 7.37 (m, 3H), 7.21 (s, 2H), 7.10 (m, 2H), 7.00 (m, 2H), 5.41 (s, 1H), 3.24 (m, 2H), 1.46 (m, 2H), 1.25 (m, 2H), 0.87 (m, 3H). ^{13}C NMR (100 MHz, Acetone-d_6) δ 172.5, 136.9, 127.2, 123.8, 121.2, 119.1, 118.5, 114.7, 111.3, 42.2, 39.0, 31.7, 19.8, 13.2. HRMS (ESI) exact mass calcd for $C_{22}H_{24}N_3O$ [M+H] *m/z* 346.1919, found 346.1924.



Compound 4ia, N-benzyl-2,2-di(1H-indol-3-yl)acetamide

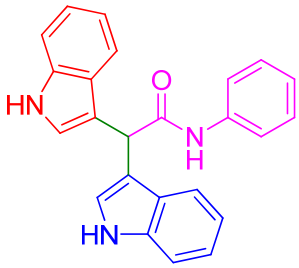
White powder, mp 143-145 °C. ^{1}H NMR (400 MHz, Acetone-d_6) δ 10.08 (brs, 2H), 7.72 (brs, 1H), 7.64 (d, J = 7.9 Hz, 2H), 7.39 (d, J = 8.1 Hz, 2H), 7.21 (m, 7H), 7.09 (t, J = 7.5 Hz, 2H), 6.97 (t, J = 7.4 Hz, 2H), 5.50 (s, 1H), 4.46 (d, J = 5.9 Hz, 2H). ^{13}C NMR (100 MHz, Acetone-d_6) δ 172.7, 139.7, 136.9, 128.2, 127.5, 127.2, 126.7, 123.8, 121.2, 119.2, 118.6, 114.5, 111.4, 42.9, 42.1. HRMS (ESI) exact mass calcd for $C_{25}H_{22}N_3O$ [M+H] *m/z* 380.1763, found 380.1766.



Compound 4ja, 2,2-di(1H-indol-3-yl)-1-(pyrrolidin-1-yl)ethanone

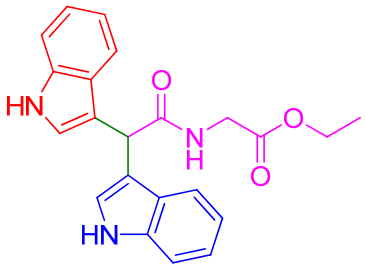
Pale red powder, mp 143-145 °C. ^{1}H NMR (400 MHz, Acetone-d_6) δ 10.09 (s, 2H), 7.67 (m, 2H), 7.35 (m, 2H), 7.20 (m, 2H), 7.05 (d, J = 5.9 Hz, 2H), 6.95 (d, J = 5.5 Hz, 2H), 5.67 (s, 1H), 3.72 (m, 2H), 3.46 (m, 2H), 1.86 (m, 4H). ^{13}C NMR (100 MHz,

Acetone-d_6) δ 170.8, 136.8, 127.3, 123.9, 121.1, 119.2, 118.5, 114.3, 111.3, 46.5, 45.9, 39.2, 26.0, 24.1. HRMS (ESI) exact mass calcd for $C_{22}H_{22}N_3O$ [M+H] *m/z* 344.1763, found 344.1759.



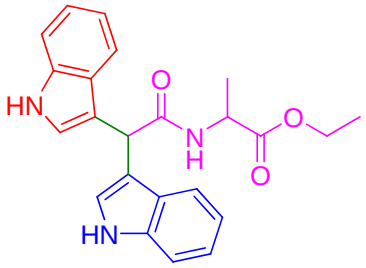
Compound 4ka, 2,2-di(1H-indol-3-yl)-N-phenylacetamide

Yellow powder, mp 118-120 °C. ^{1}H NMR (400 MHz, Acetone-d_6) δ 10.13 (brs, 2H), 9.47 (brs, 1H), 7.70 (m, 4H), 7.43 (m, 2H), 7.27 (m, 4H), 7.10 (t, *J* = 7.3 Hz, 2H), 7.02 (m, 3H), 5.62 (s, 1H). ^{13}C NMR (100 MHz, Acetone-d_6) δ 171.3, 139.7, 136.9, 128.6, 127.2, 123.9, 123.3, 121.3, 119.4, 119.1, 118.7, 114.2, 111.4, 43.0. HRMS (ESI) exact mass calcd for $C_{24}H_{20}N_3O$ [M+H] *m/z* 366.1606, found 366.1602.



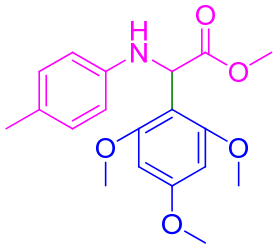
Compound 4la, ethyl 2-(2,2-di(1H-indol-3-yl)acetamido)acetate

Colorless block crystals, mp 207-209 °C. ^{1}H NMR (400 MHz, Acetone-d_6) δ 10.11 (brs, 2H), 7.61 (d, *J* = 7.9 Hz, 2H), 7.53 (brs, 1H), 7.39 (d, *J* = 8.1 Hz, 2H), 7.26 (s, 2H), 7.09 (t, *J* = 7.4 Hz, 2H), 6.98 (t, *J* = 7.4 Hz, 2H), 5.49 (s, 1H), 4.12 (q, *J* = 7.1 Hz, 2H), 3.98 (s, 2H), 1.19 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 173.3, 170.5, 136.7, 127.1, 124.2, 121.3, 119.5, 118.7, 114.2, 111.8, 60.8, 41.5, 41.2, 14.5. HRMS (ESI) exact mass calcd for $C_{22}H_{22}N_3O_3$ [M+H] *m/z* 376.1661, found 376.1664.



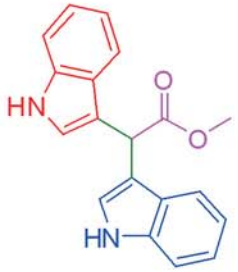
Compound 4ma, ethyl 2-(2,2-di(1H-indol-3-yl)acetamido)propanoate

White powder, mp 96-98 °C. ^{1}H NMR (400 MHz, Acetone-d_6) δ 10.08 (brs, 2H), 7.62-6.96 (m, 11H), 5.47 (s, 1H), 4.70 (q, J = 7.2 Hz, 2H), 4.08 (q, J = 7.1 Hz, 2H), 1.33 (t, J = 7.2 Hz, 3H) , 1.16 (t, J = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, Acetone-d_6) δ 172.6, 172.2, 136.9, 127.2, 123.9, 121.2, 119.2, 118.6, 114.4, 111.3, 60.5, 48.3, 41.8, 17.1, 13.5. HRMS (ESI) exact mass calcd for $C_{23}H_{24}N_3O_3$ [M+H] *m/z* 390.1818, found 390.1819.



Compound 4ai, methyl 2-(p-tolylamino)-2-(2,4,6-trimethoxyphenyl)acetate

^{1}H NMR (400 MHz, $CDCl_3$) δ6.95 (d, J = 8.2 Hz, 2H), 6.68 (d, J = 8.4 Hz, 2H), 6.12 (s, 2H), 5.66 (s, 1H), 4.81 (brs, 1H), 4.17 (m, 2H), 3.84 (s, 6H), 3.80 (s, 3H), 2.21 (s, 3H), 1.18 (t, J = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.0, 160.8, 158.7, 145.0, 129.4, 126.8, 114.0, 108.7, 90.9, 77.3, 77.0, 76.7, 60.9, 55.8, 55.2, 51.3, 20.4, 14.2. HRMS (ESI) exact mass calcd for $C_{19}H_{24}NO_5$ [M+H] *m/z* 346.1654, found 346.1653.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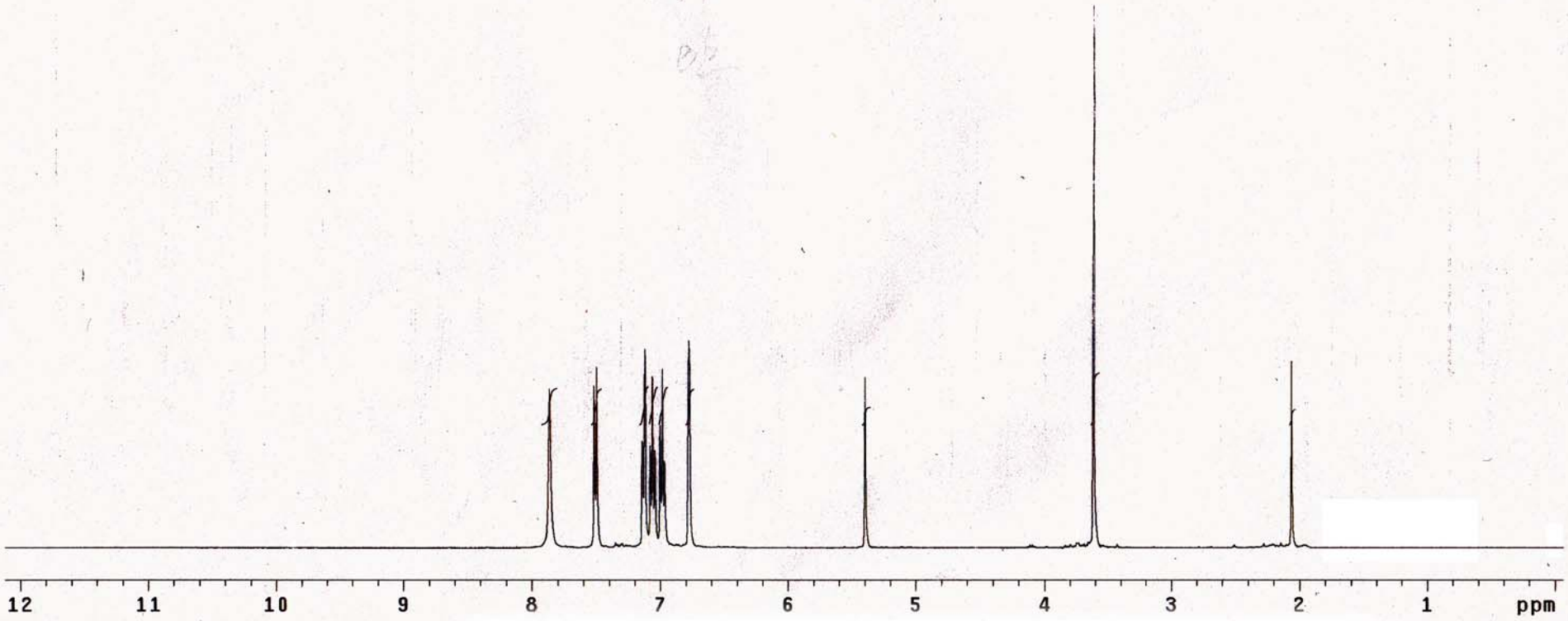
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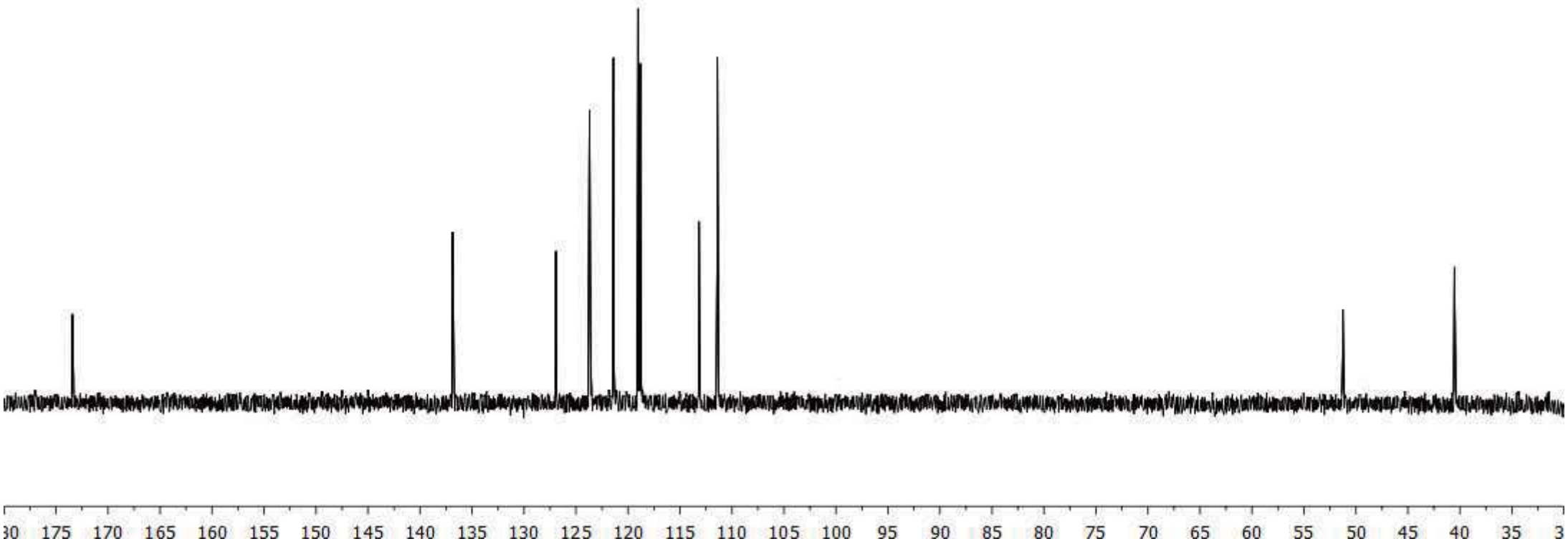
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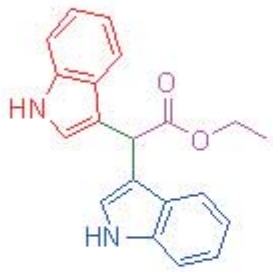
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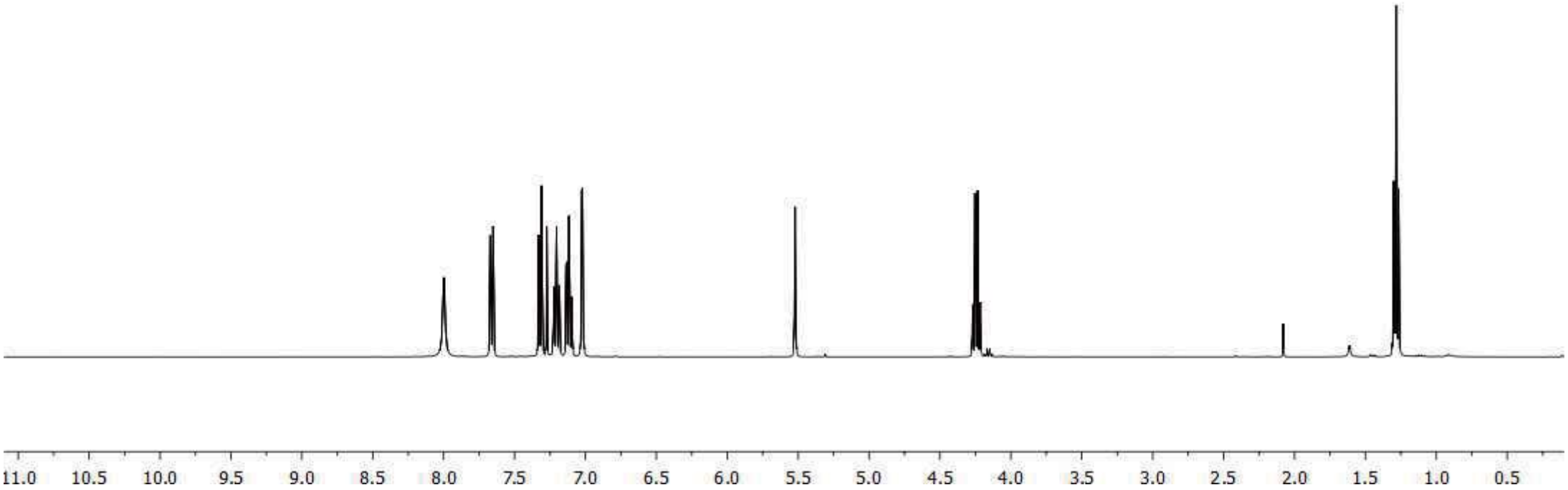
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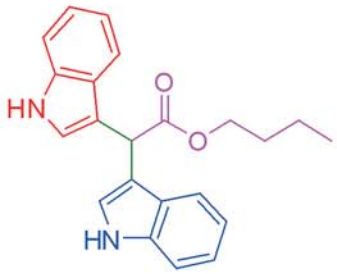
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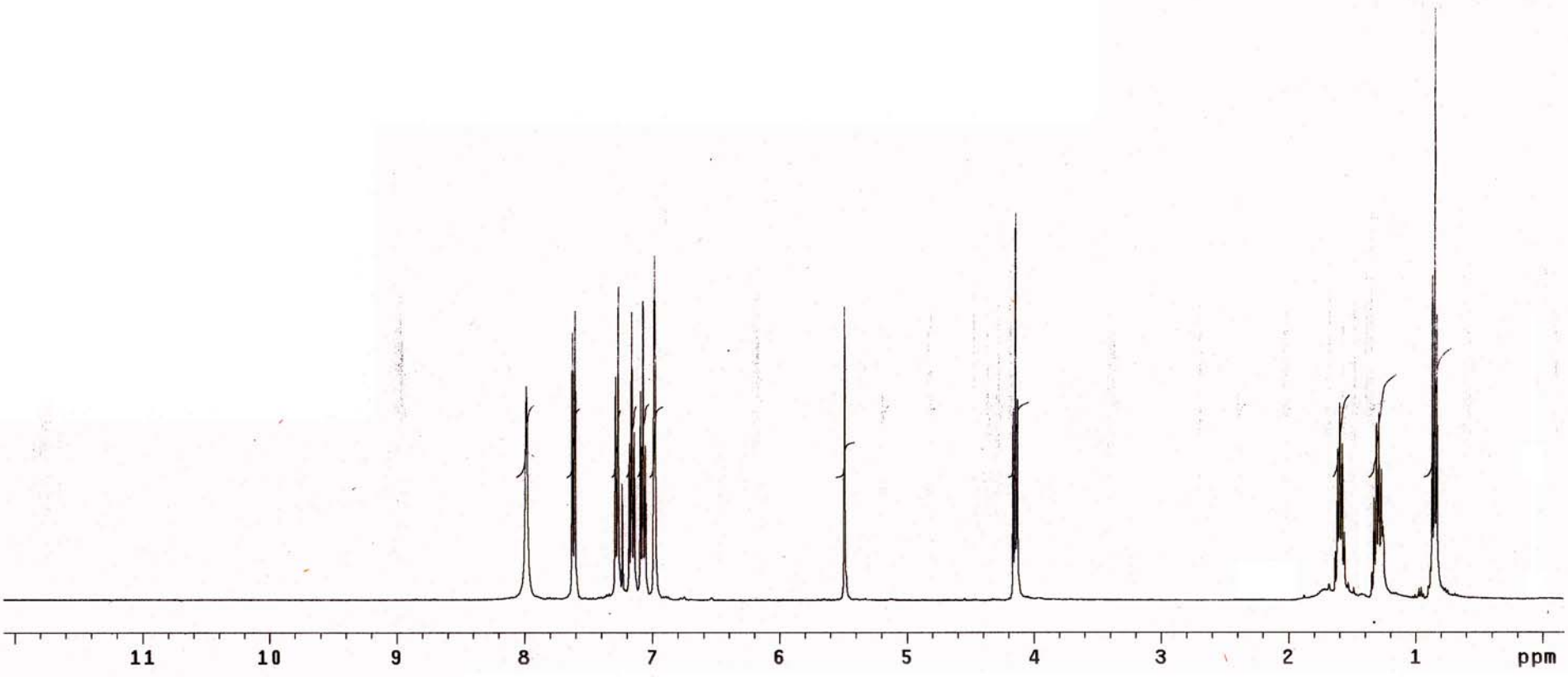
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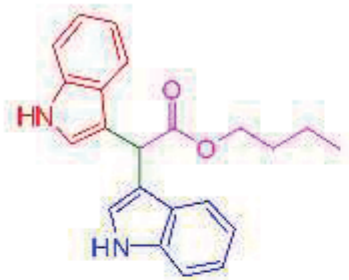
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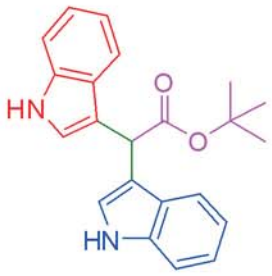
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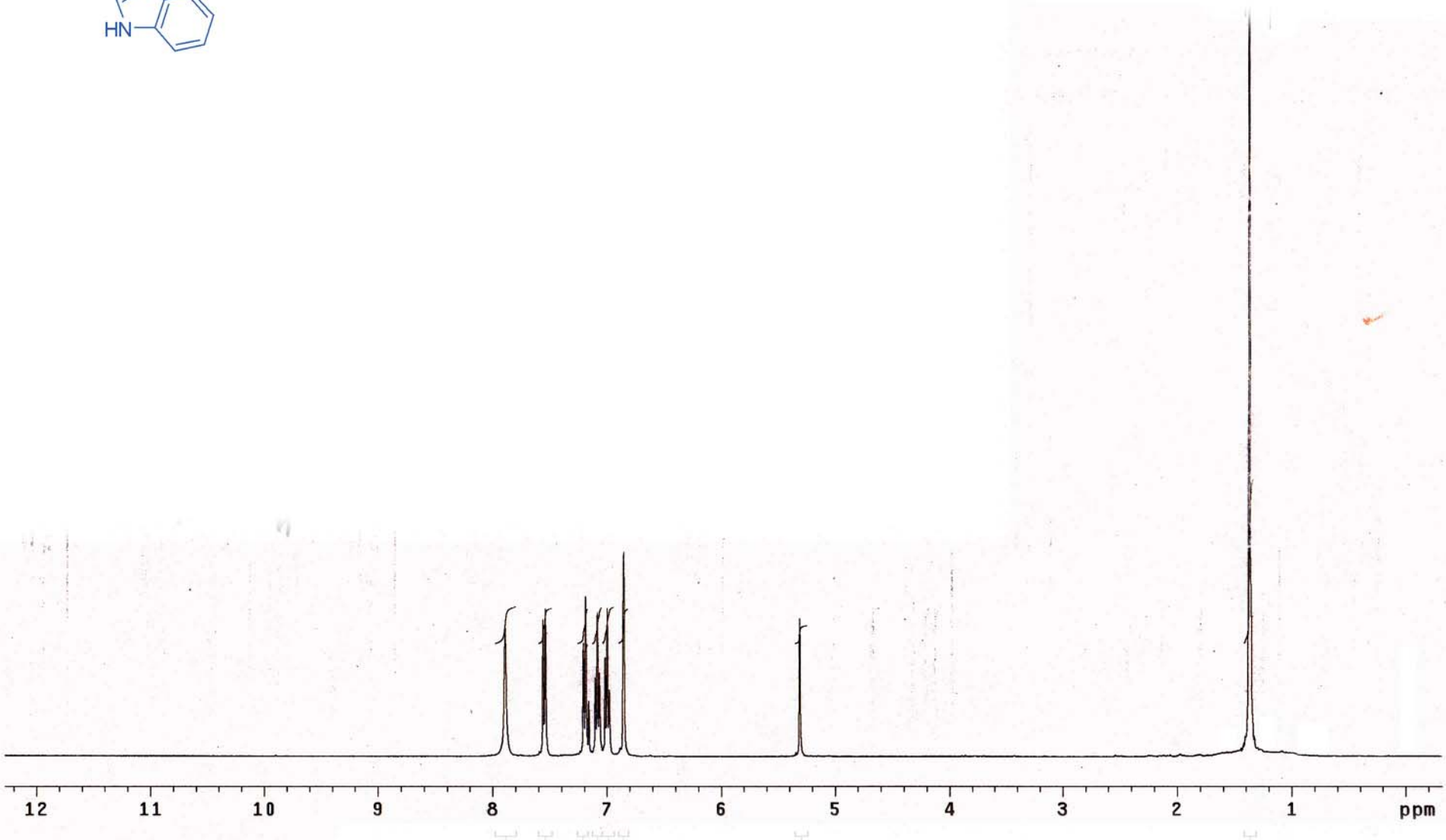
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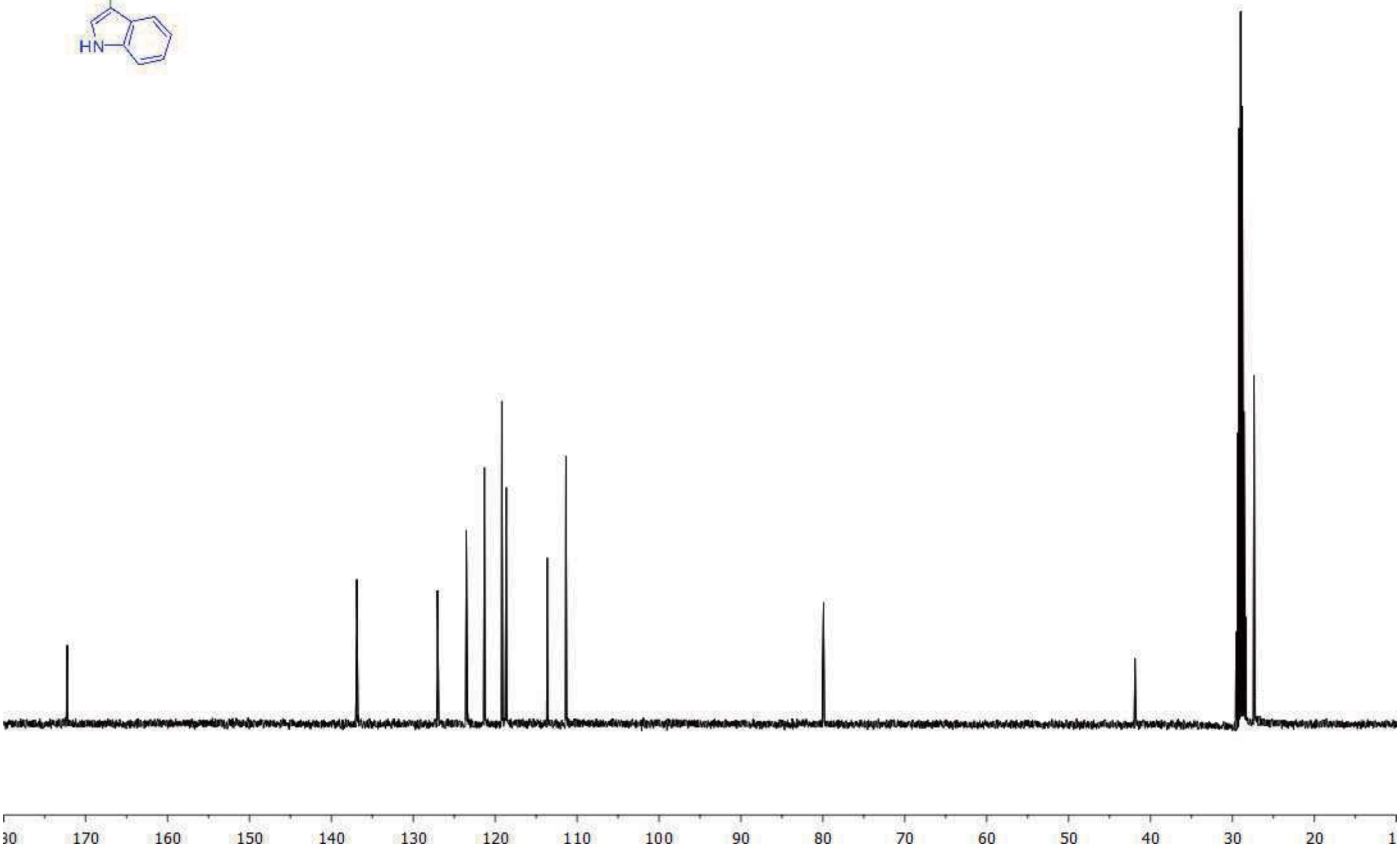
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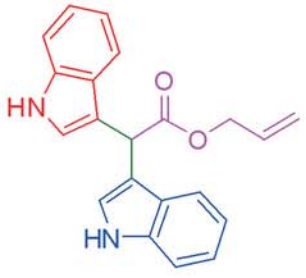
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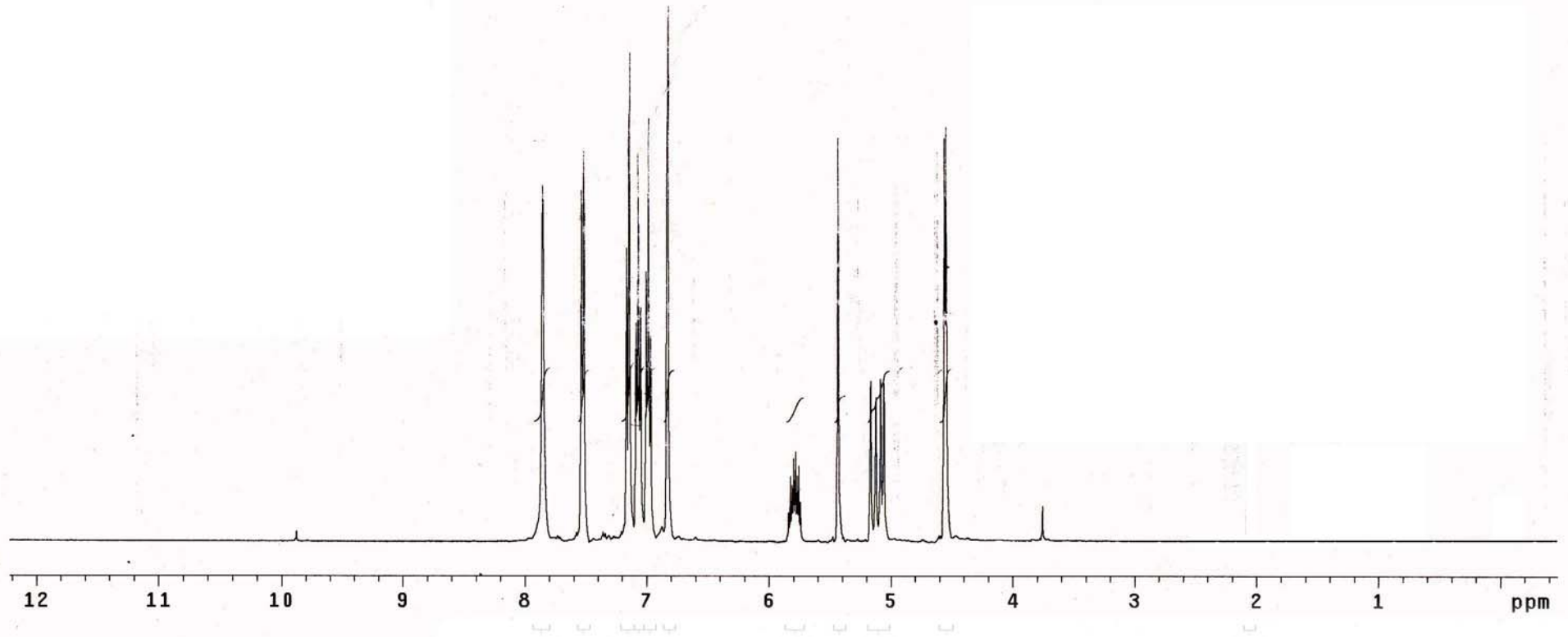
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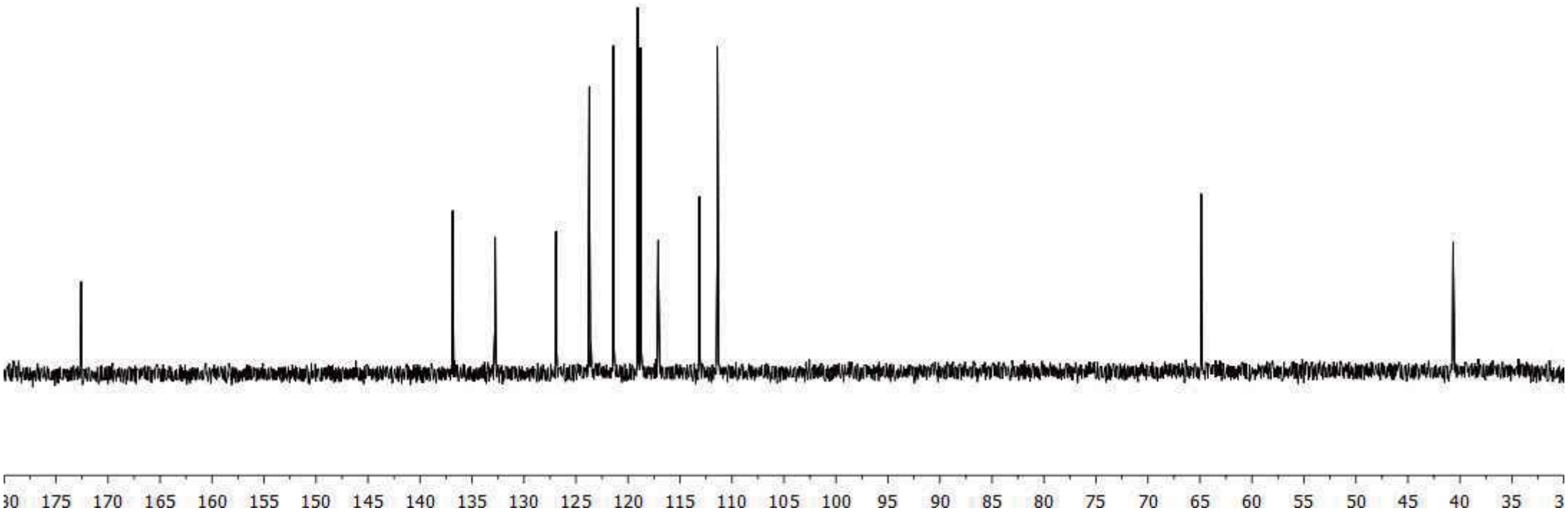
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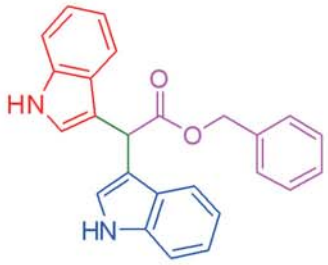
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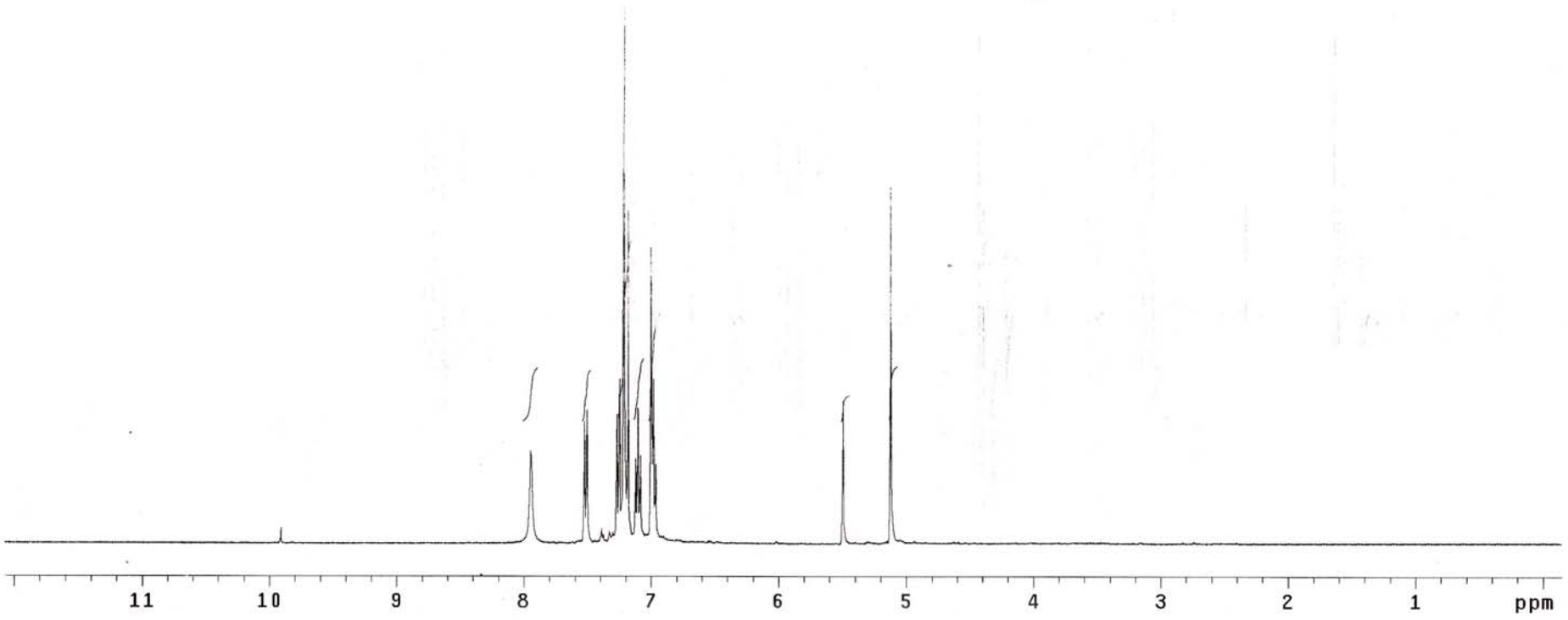
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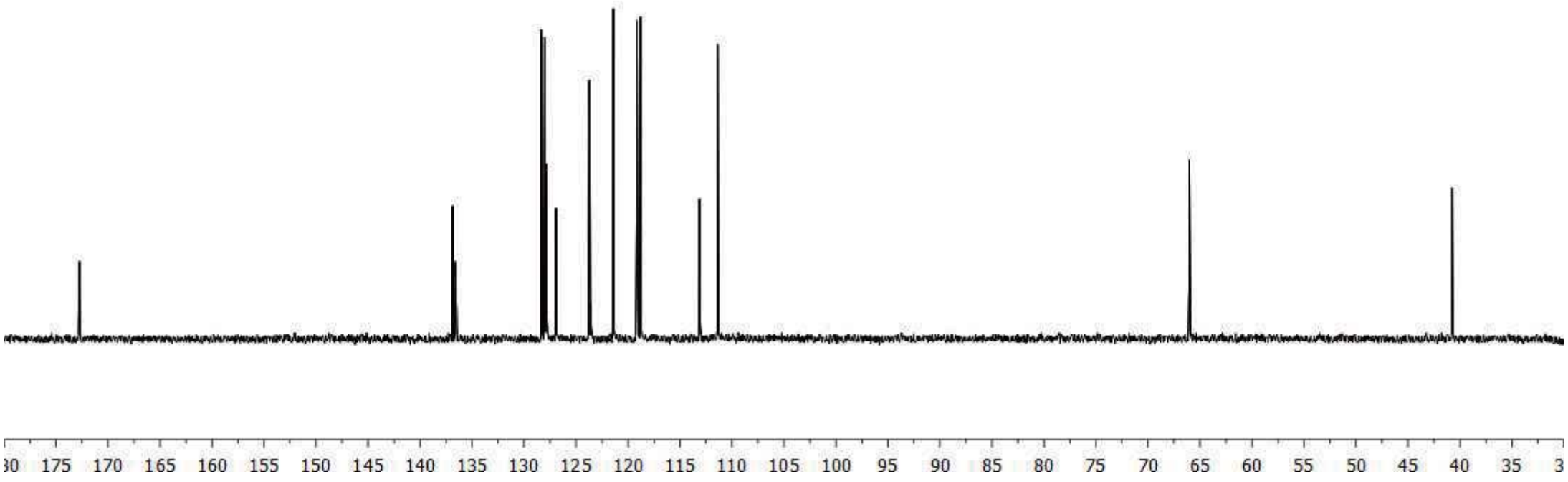
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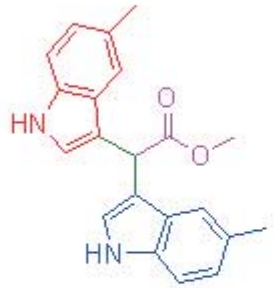
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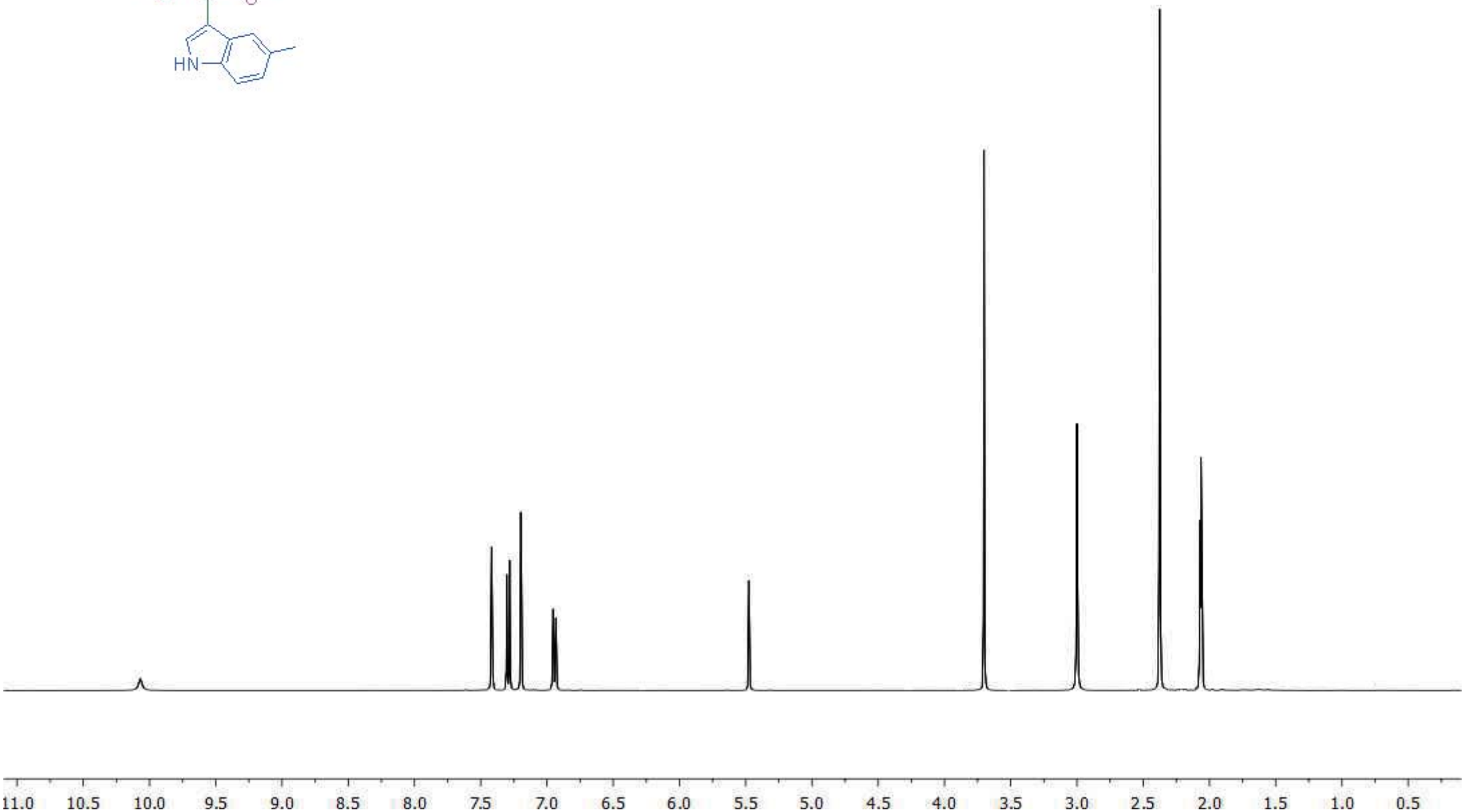
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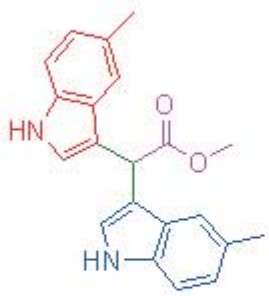
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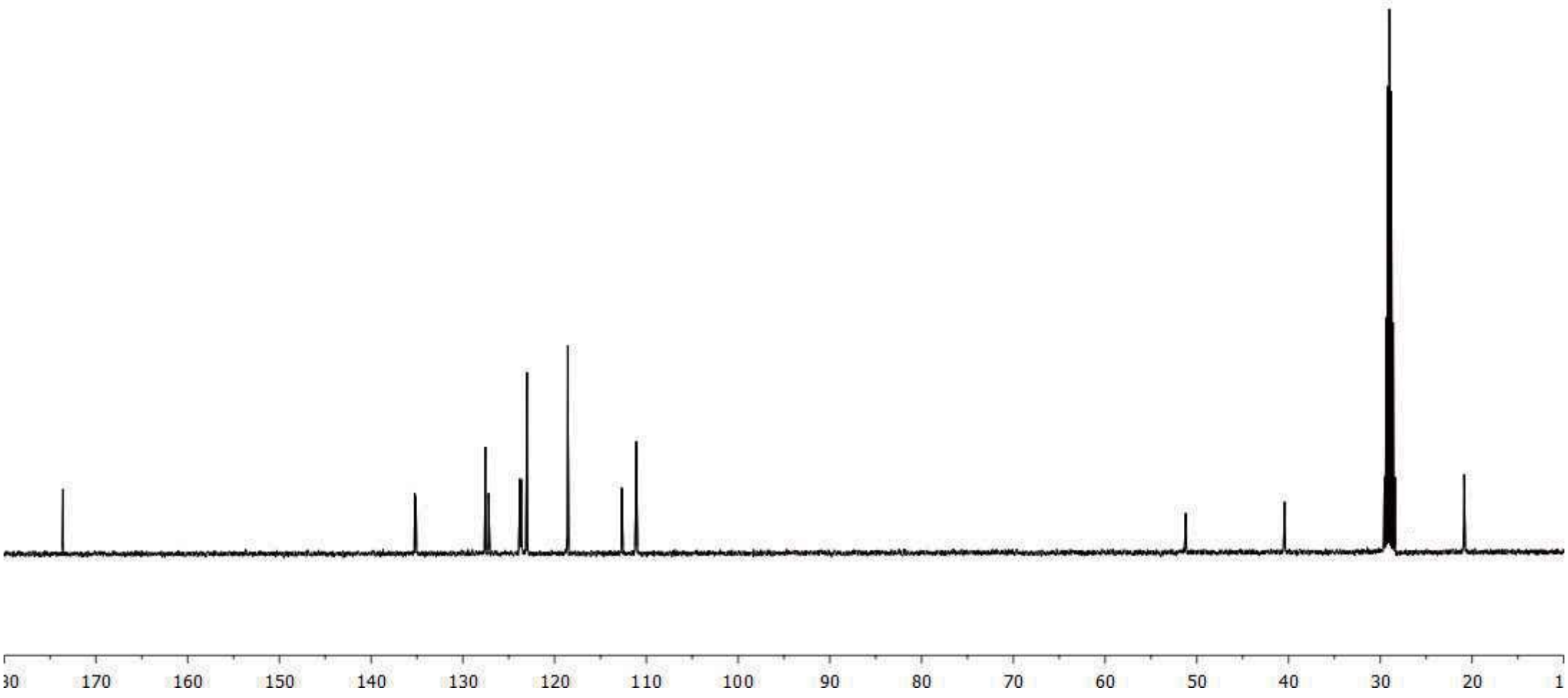
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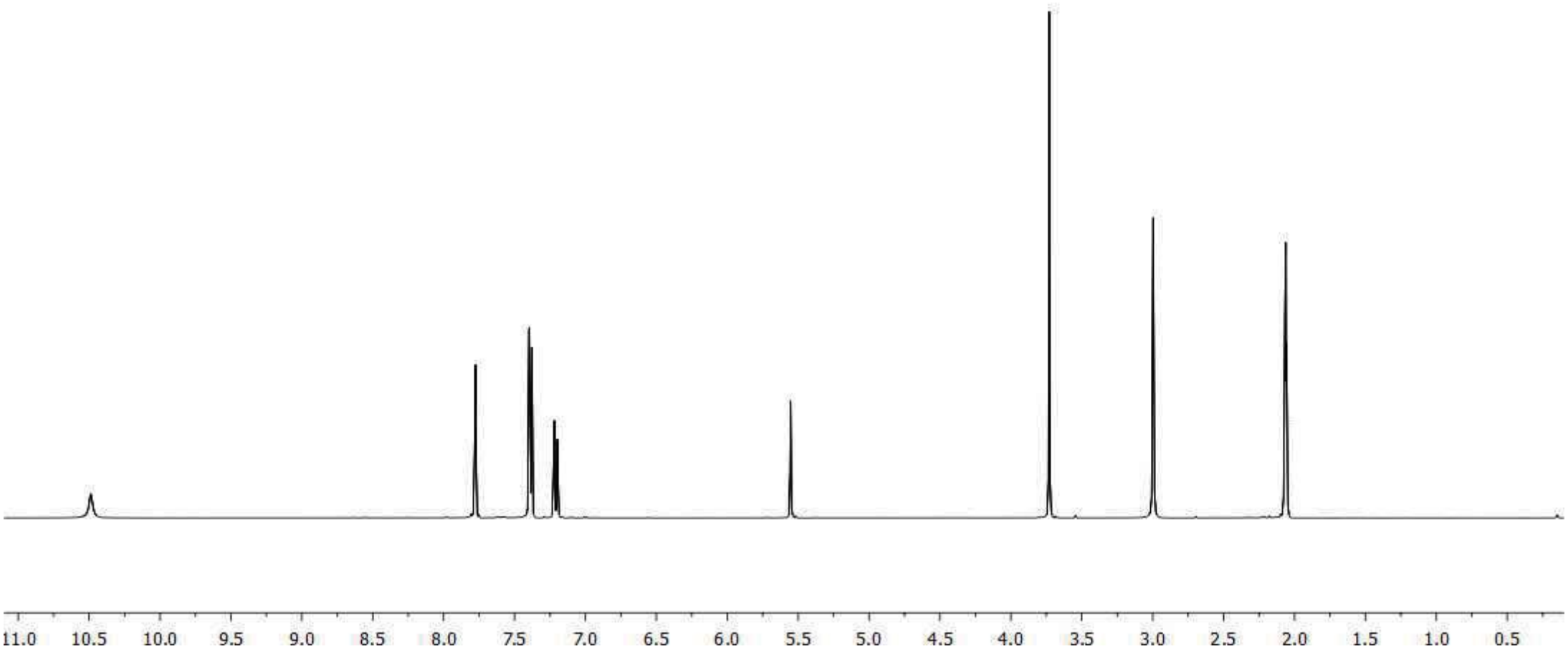
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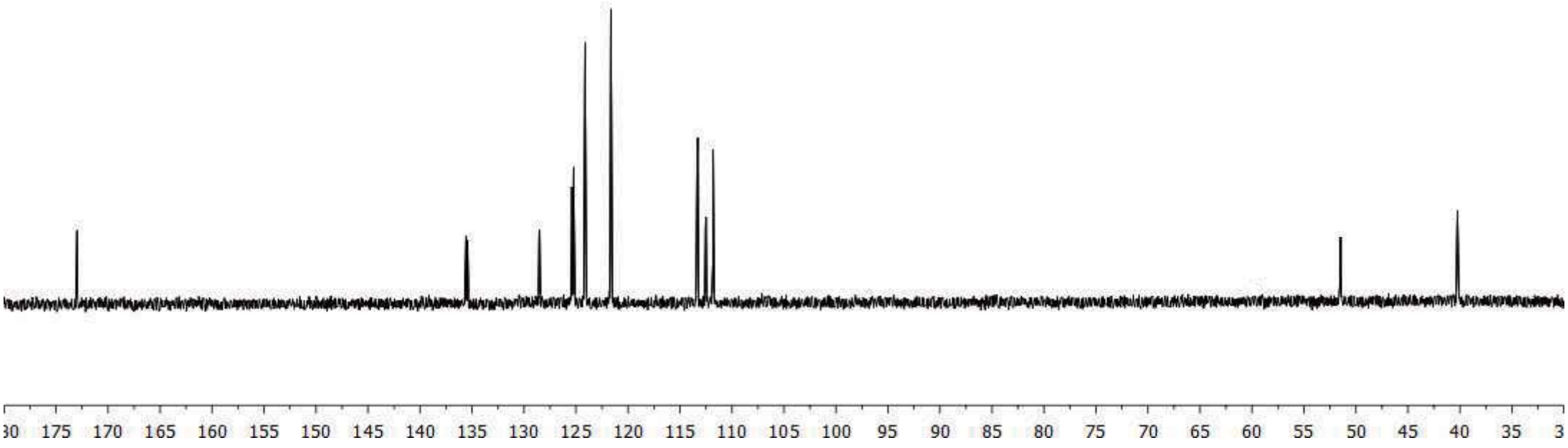
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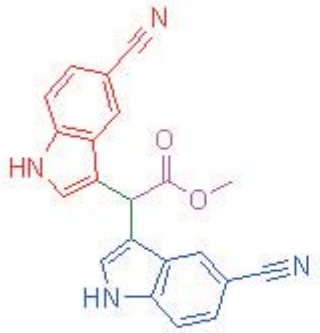
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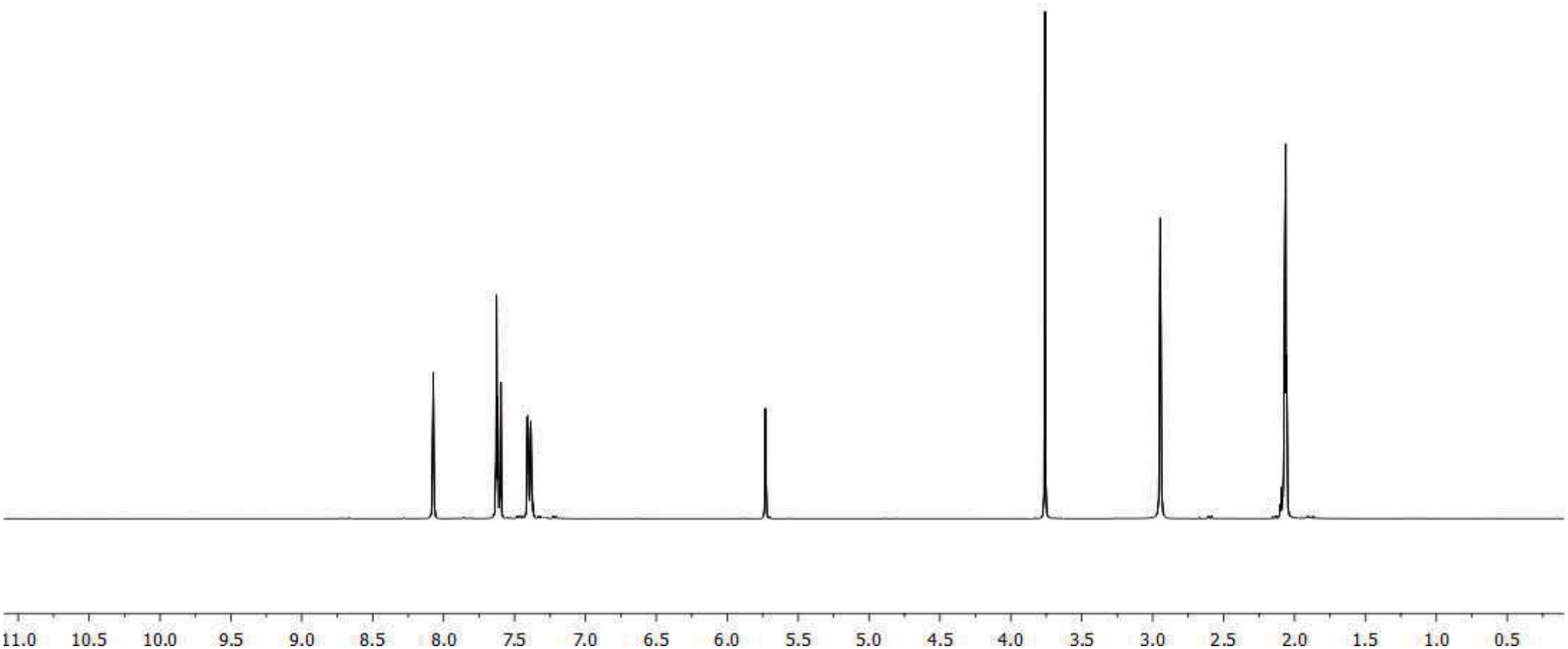
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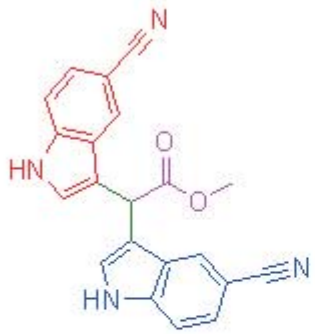
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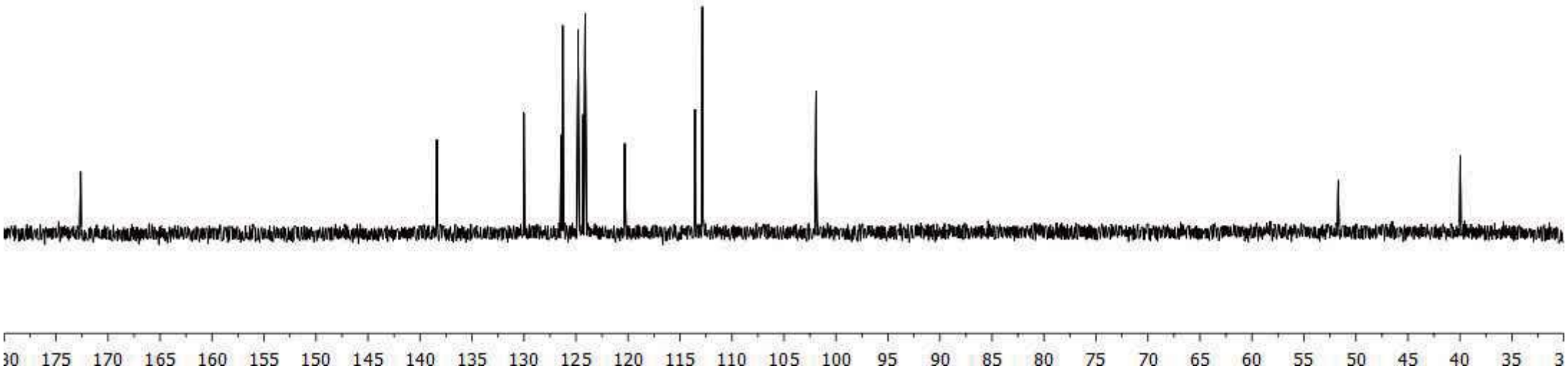
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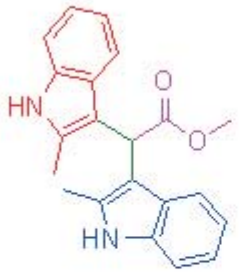
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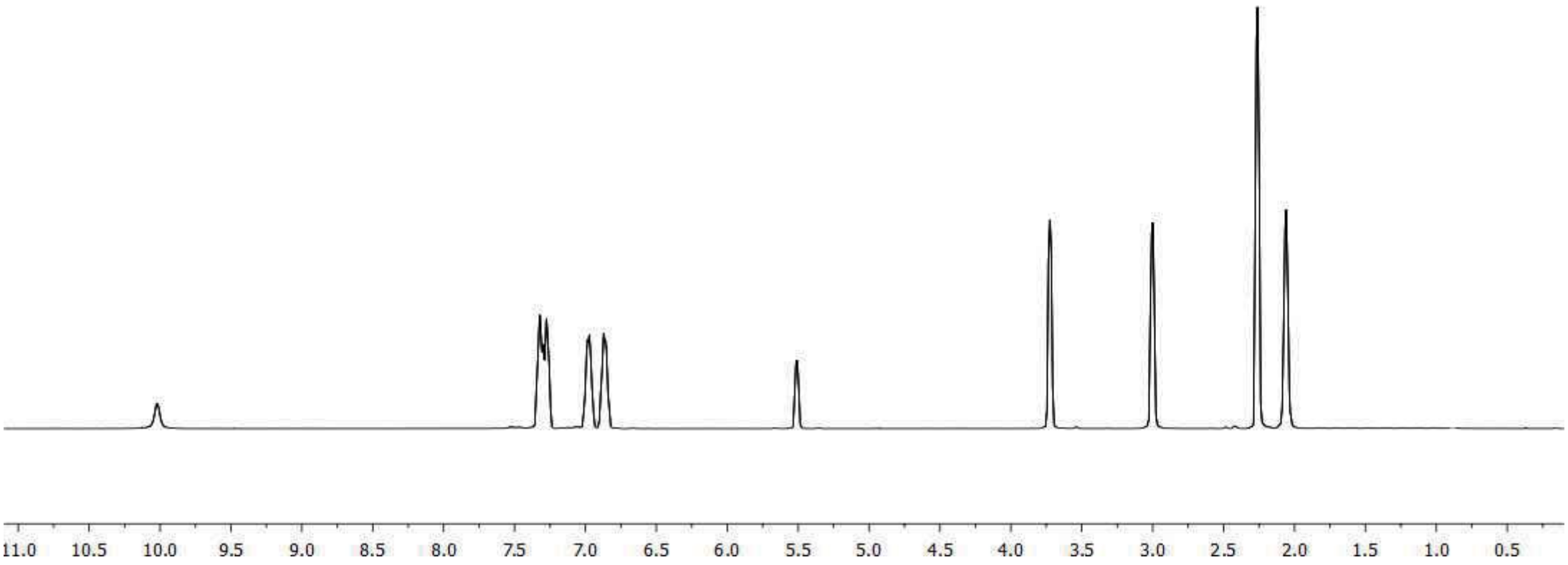
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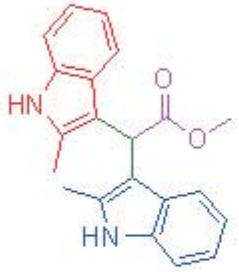
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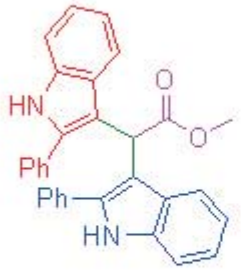
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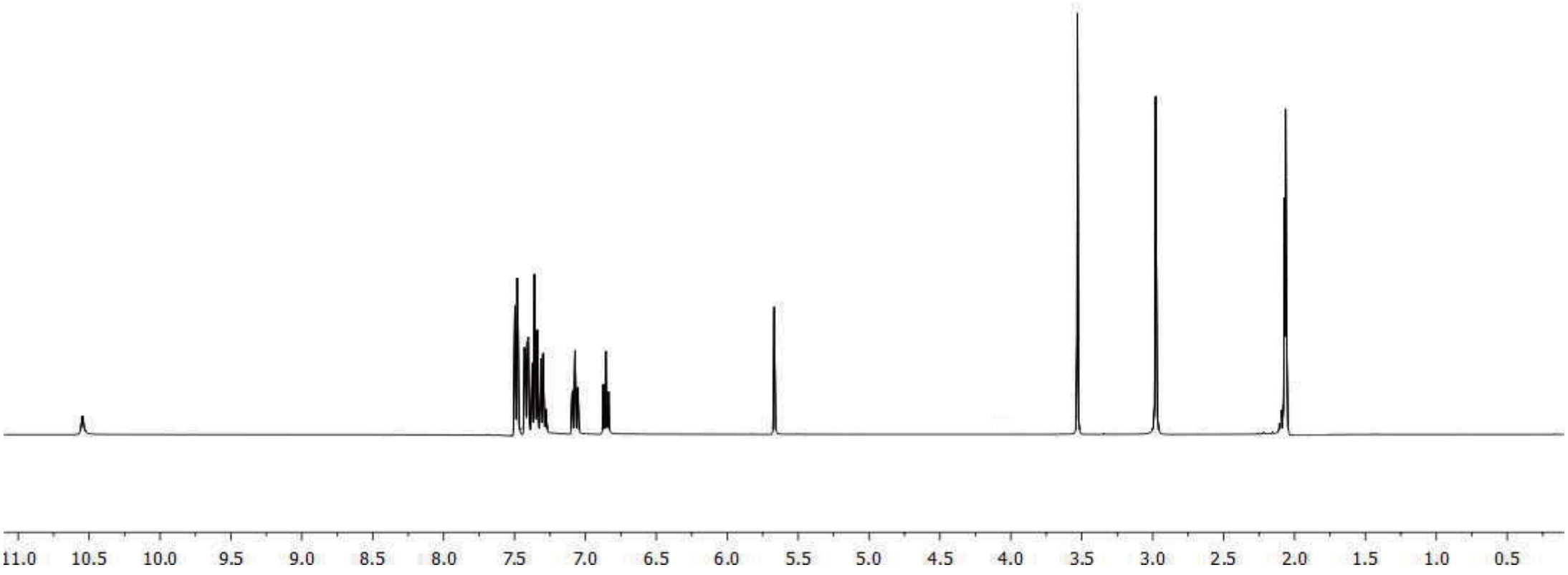
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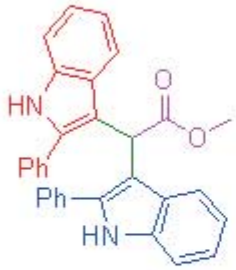
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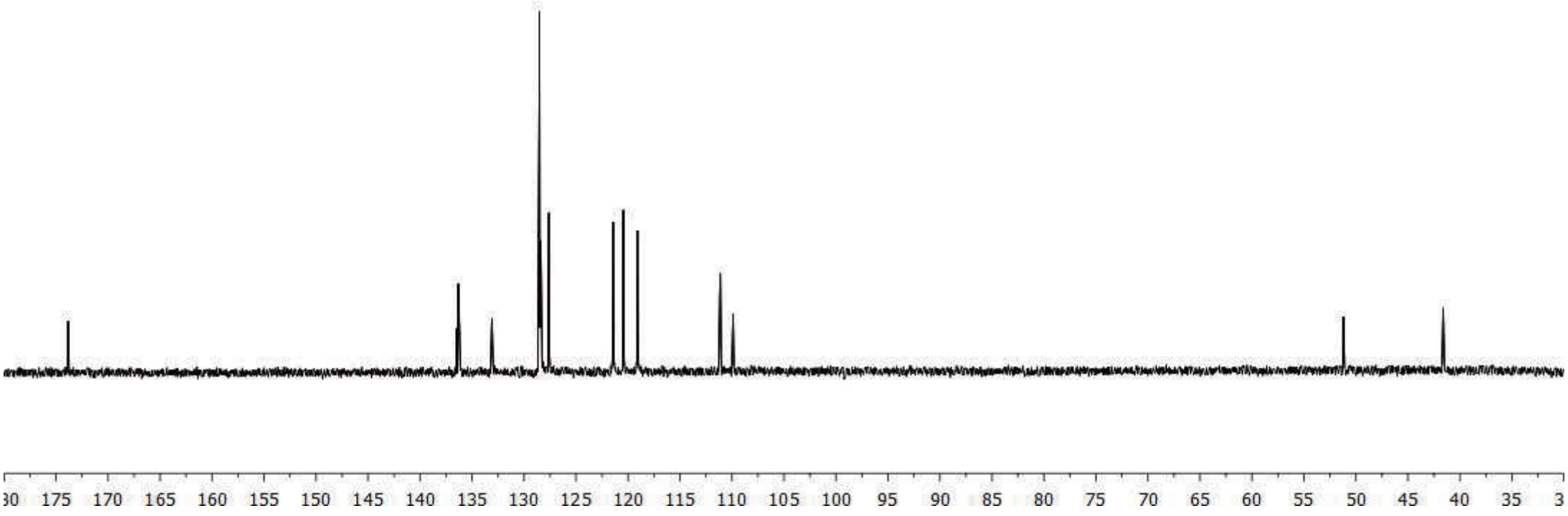
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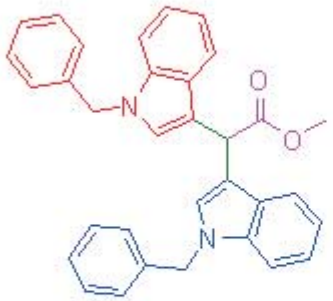
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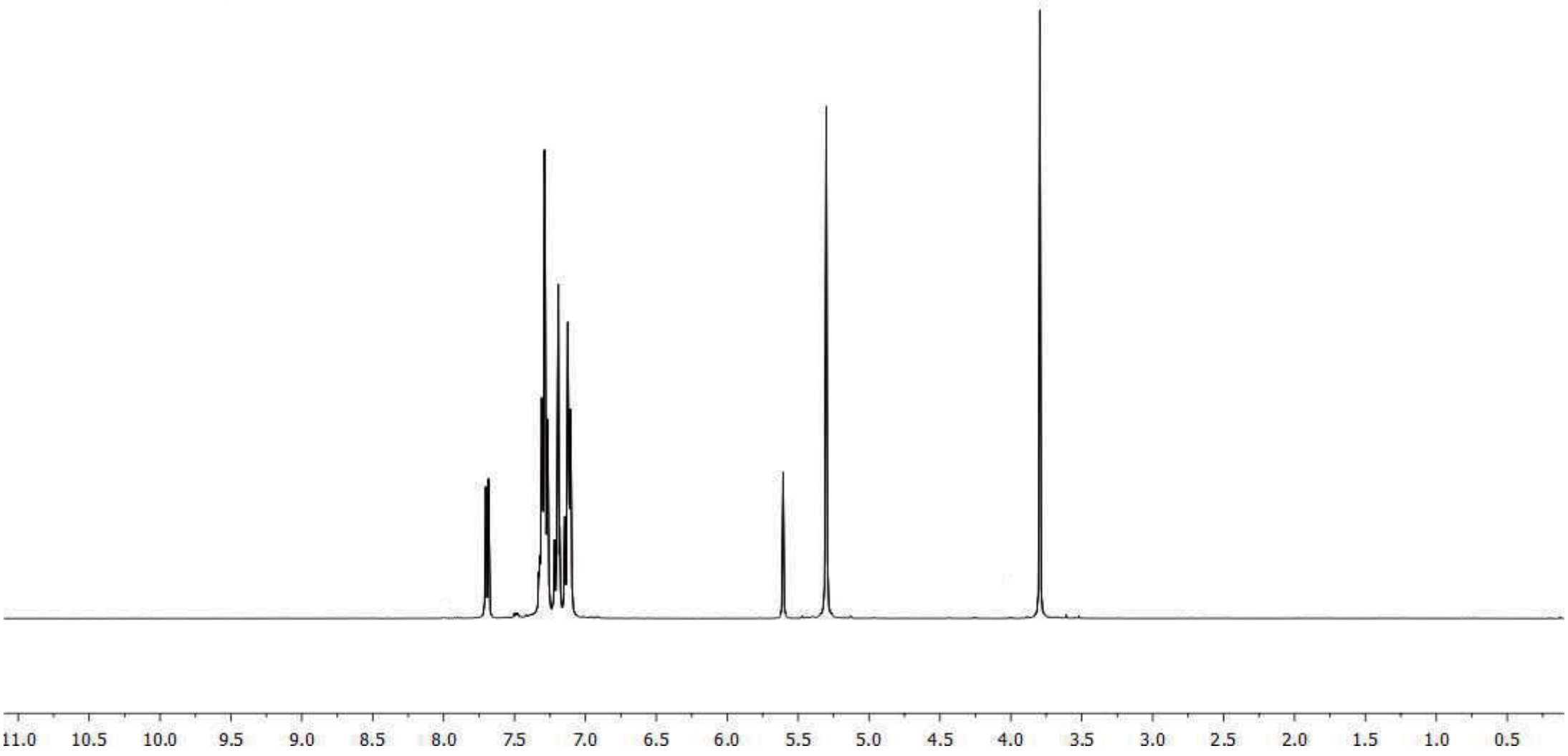
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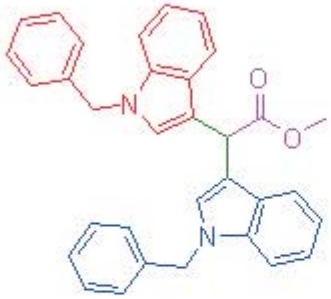
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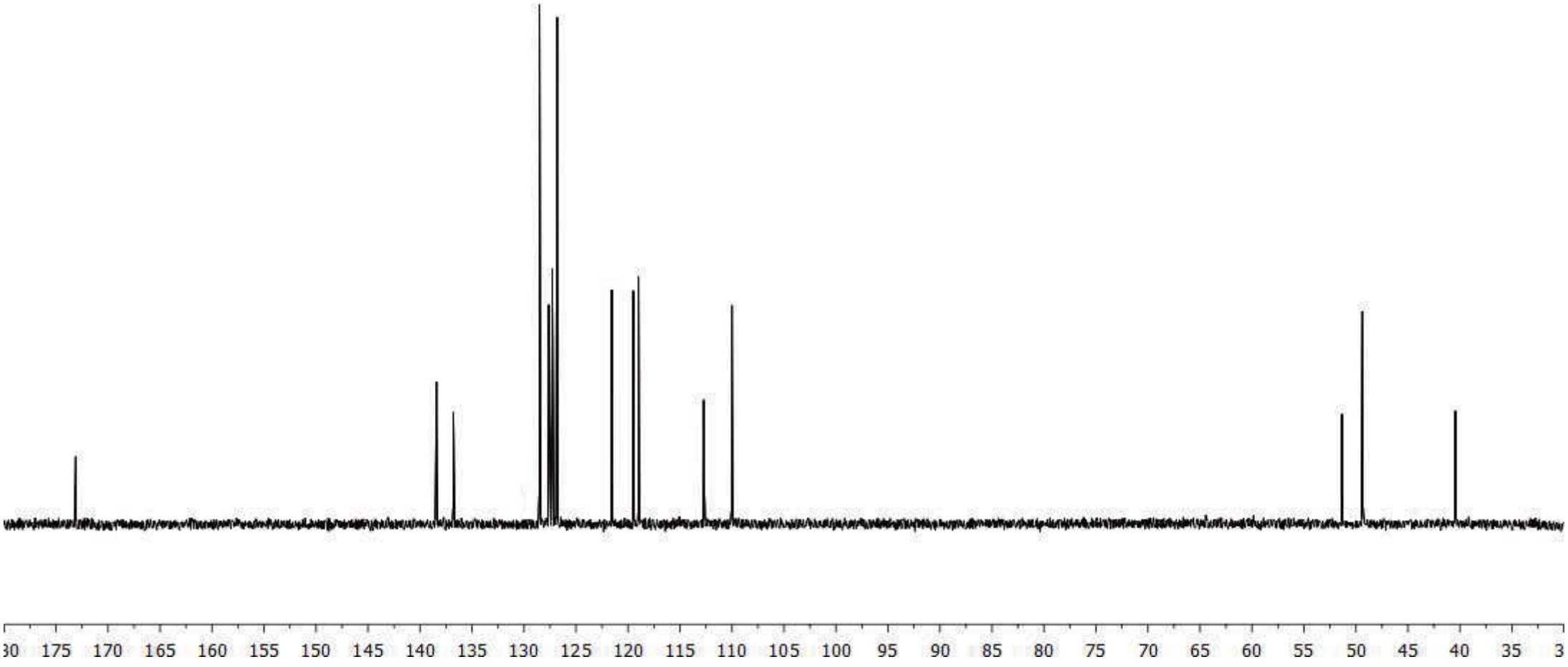
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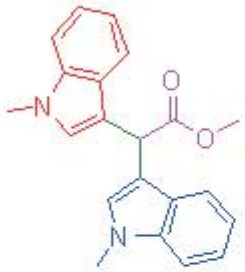
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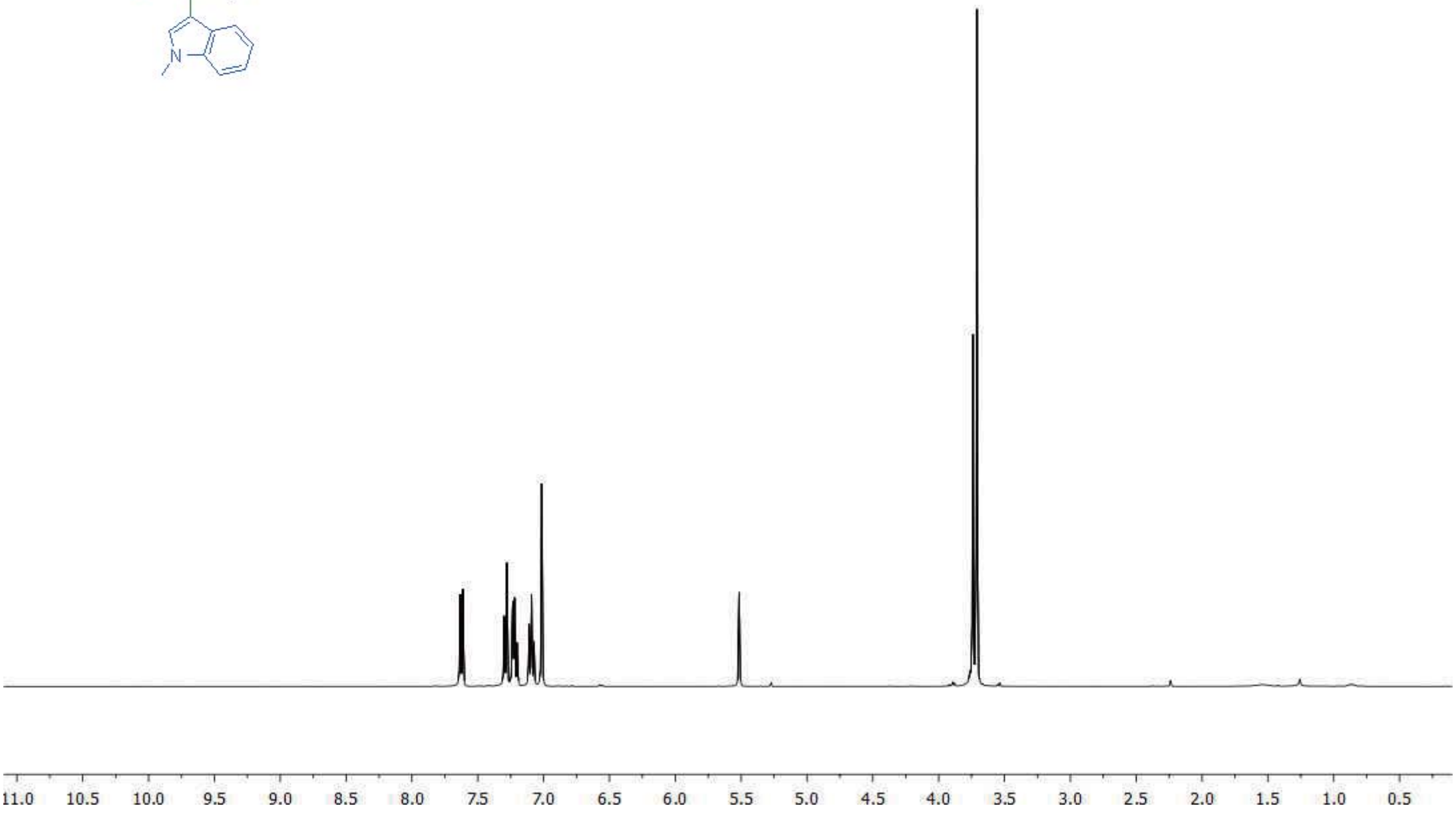
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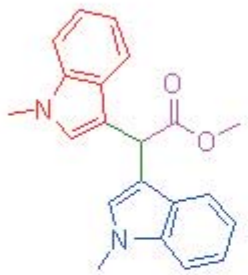
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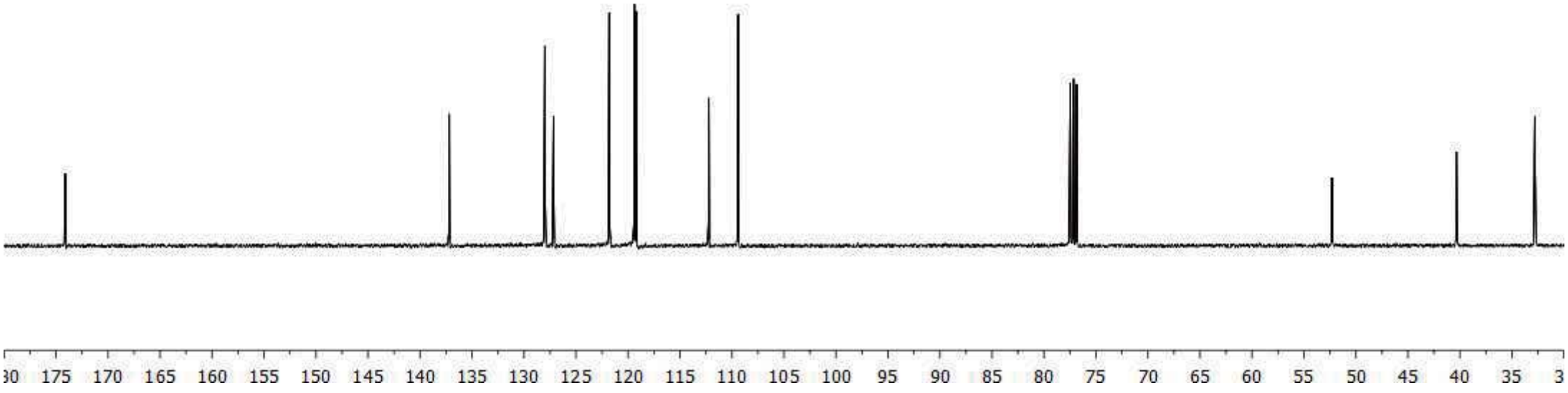
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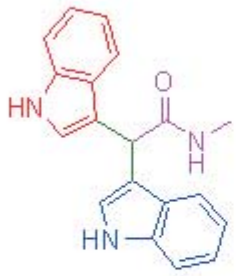
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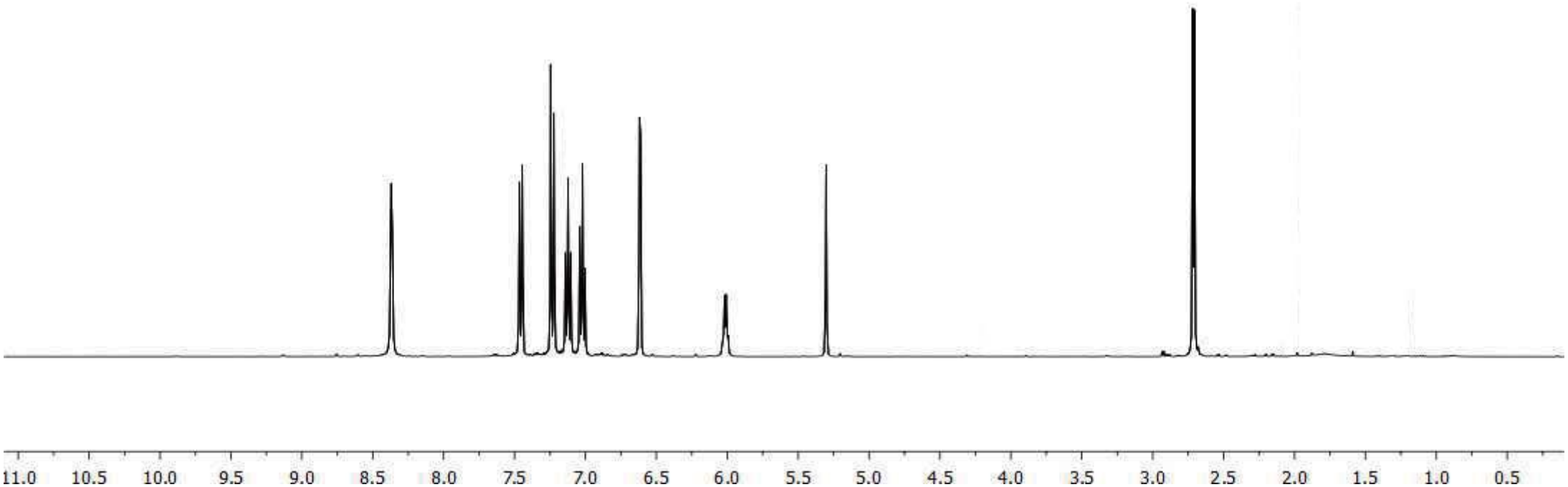
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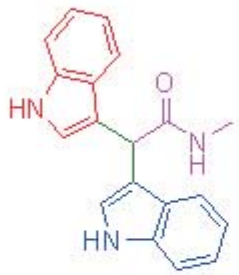
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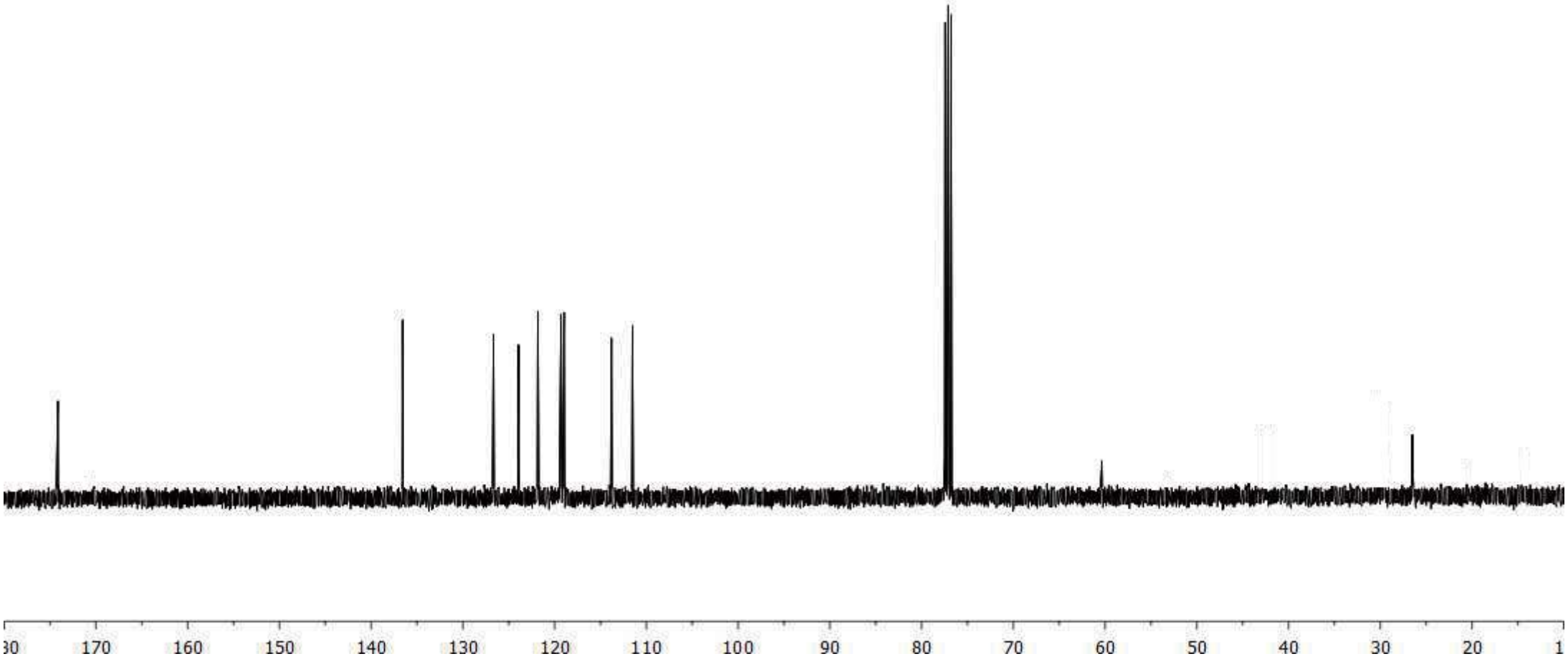
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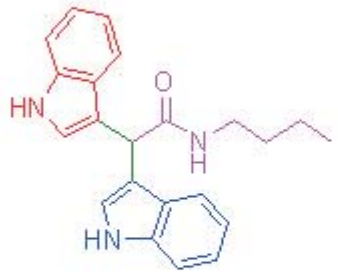
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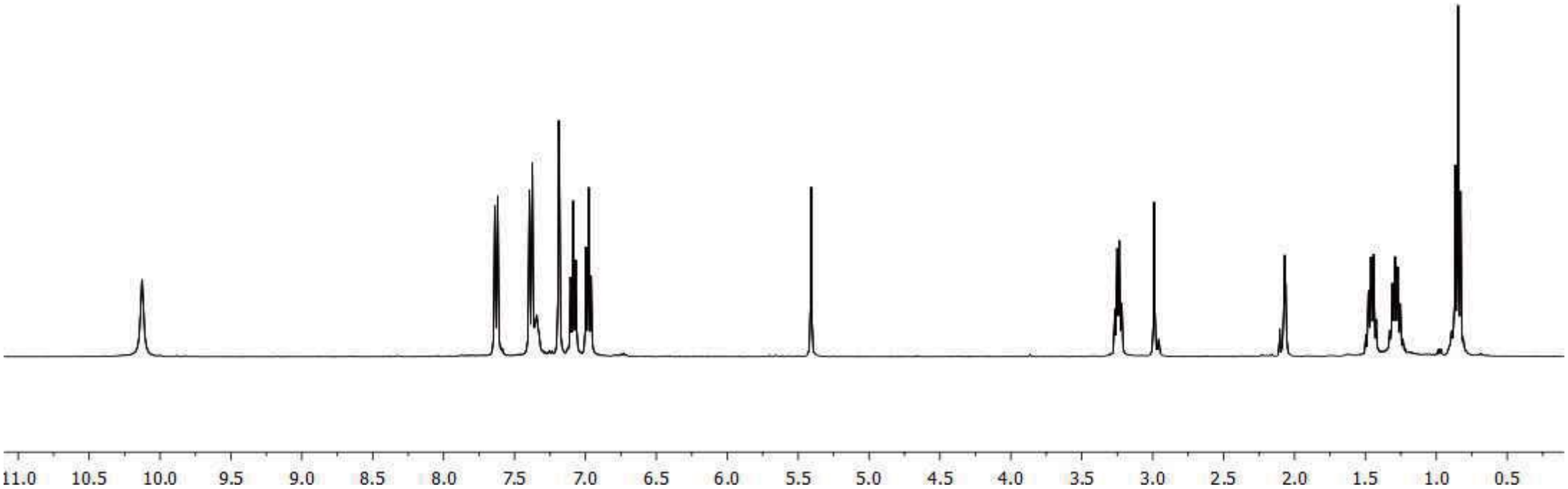
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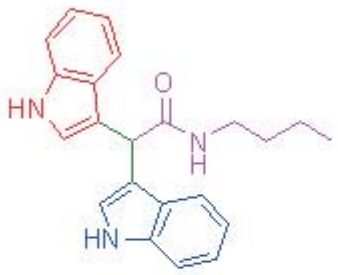
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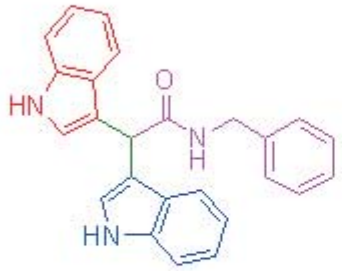
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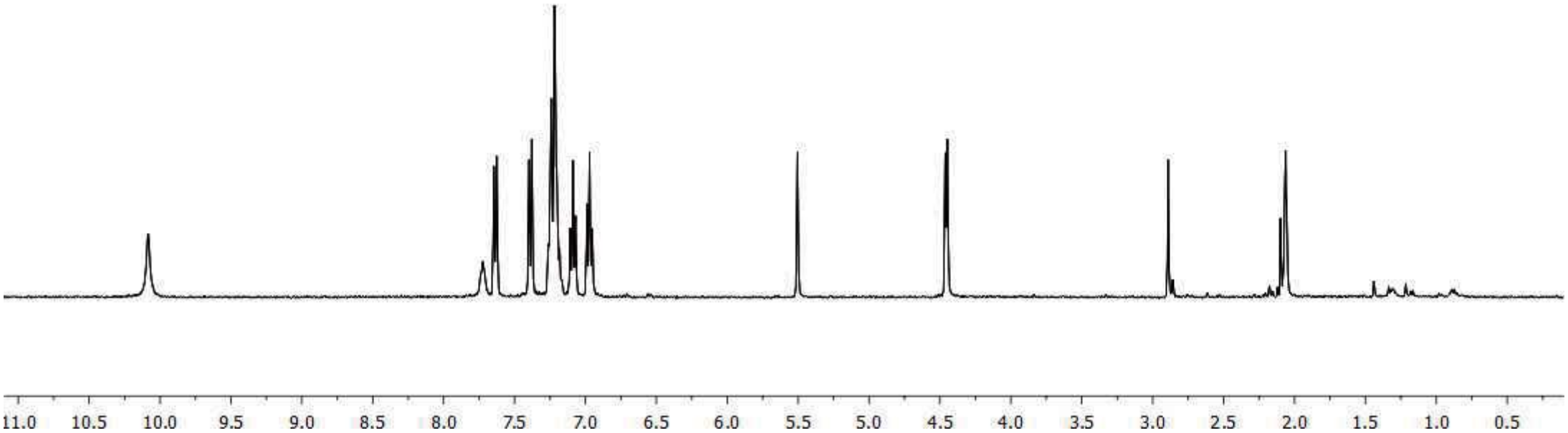
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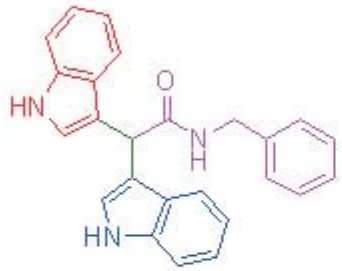
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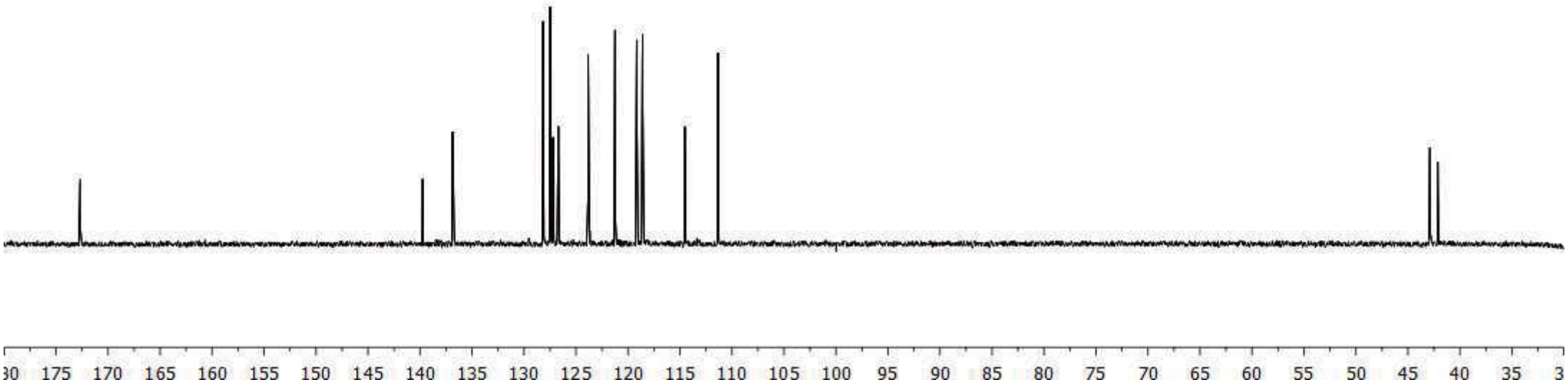
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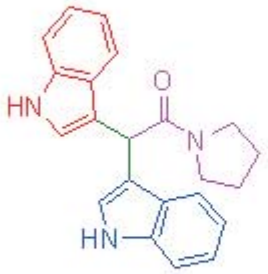
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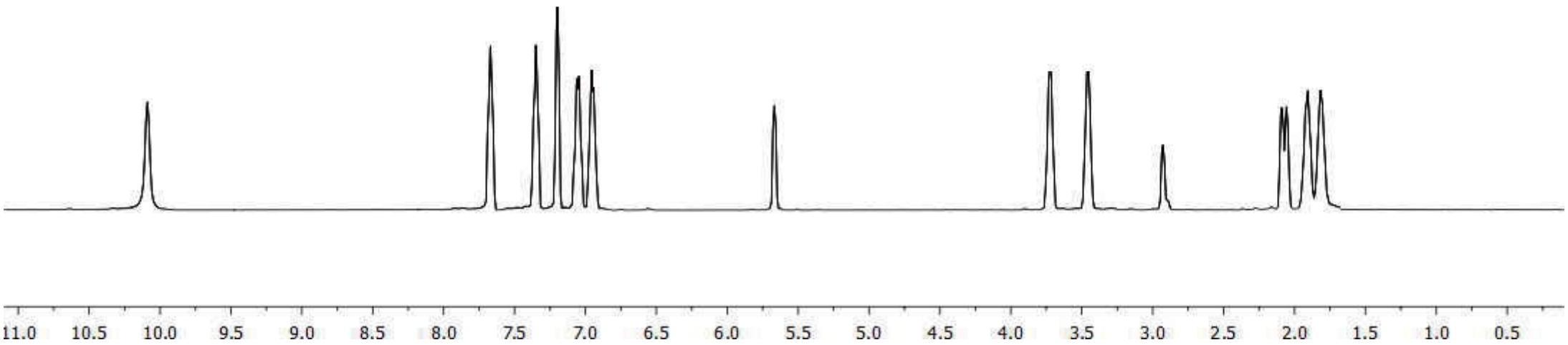
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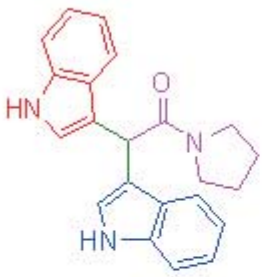
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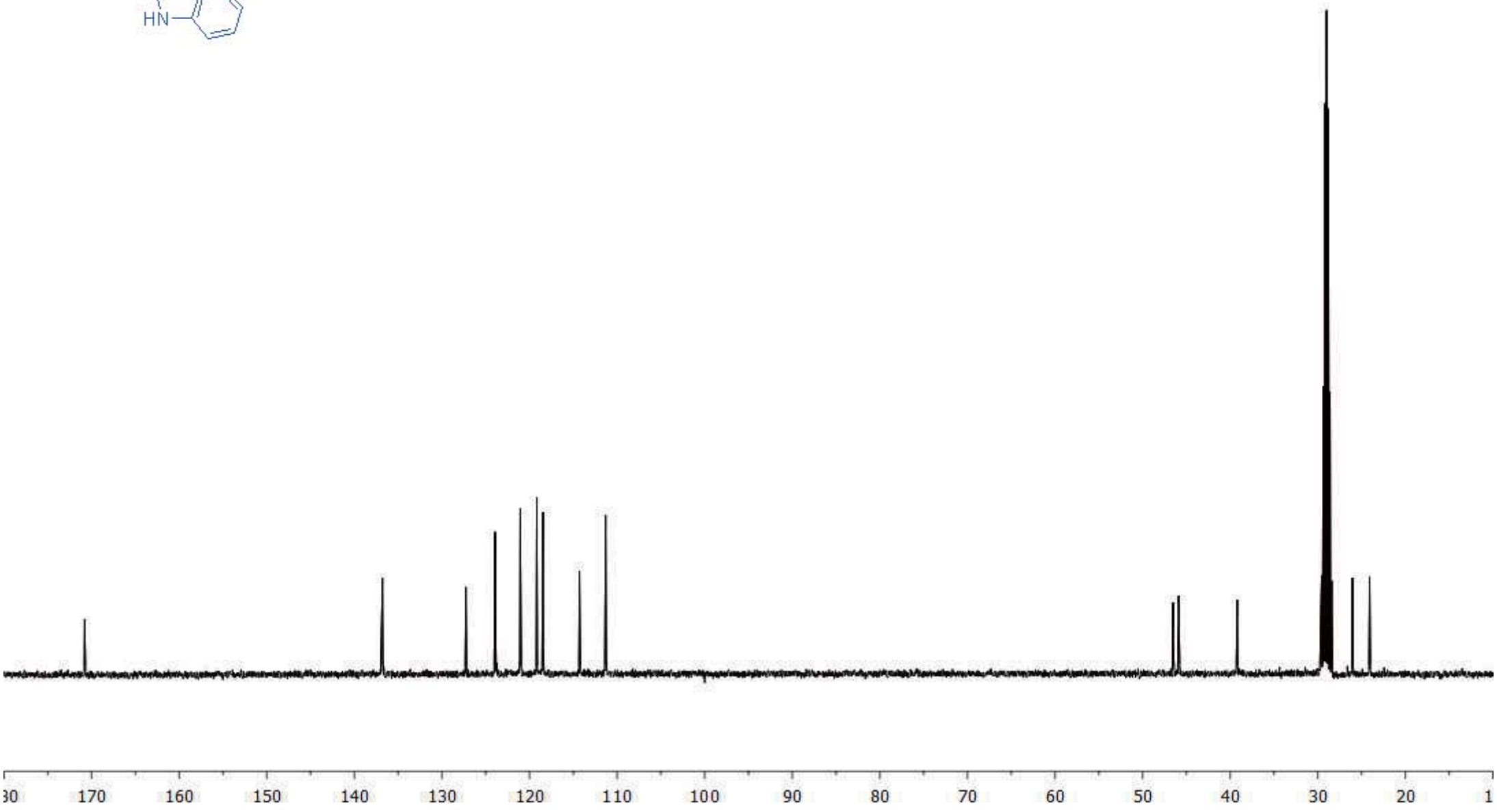
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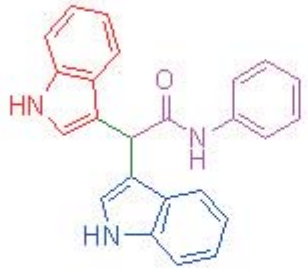
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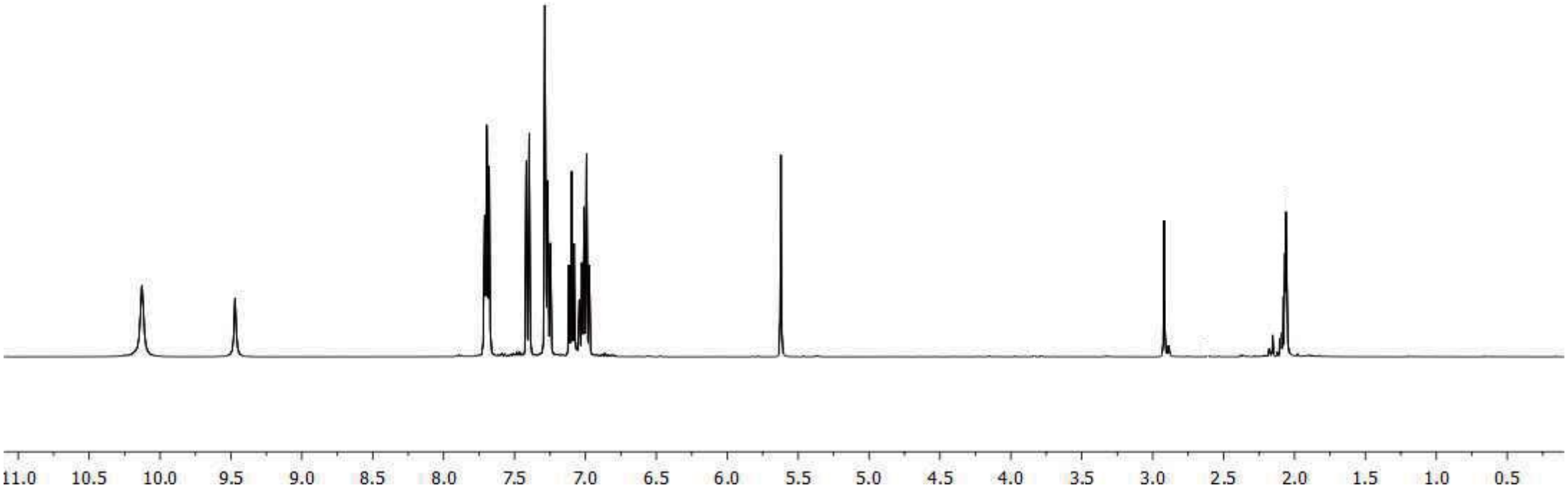
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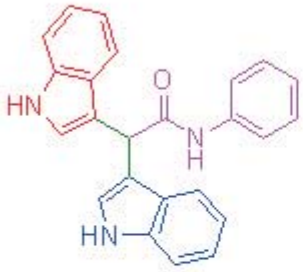
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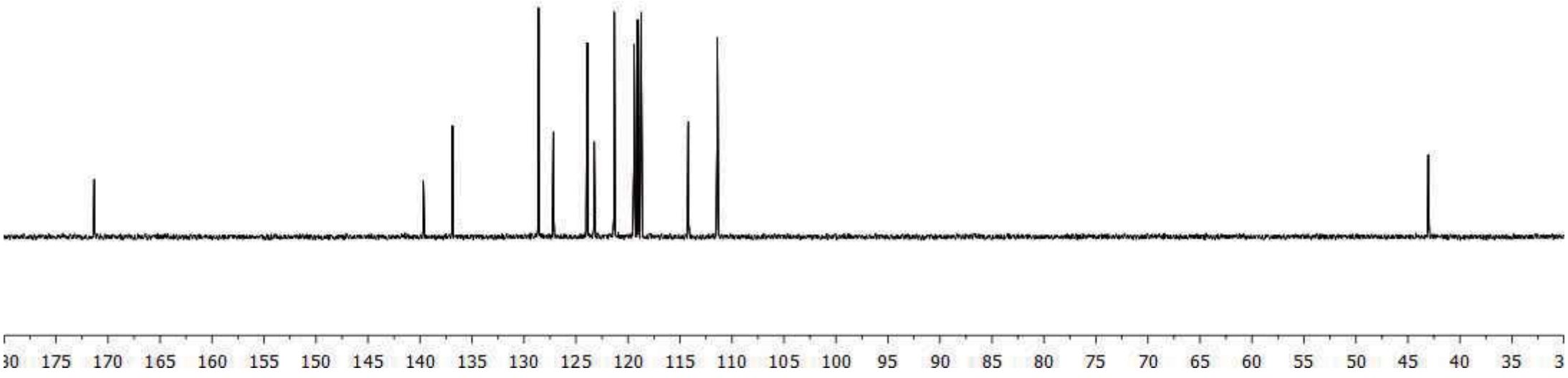
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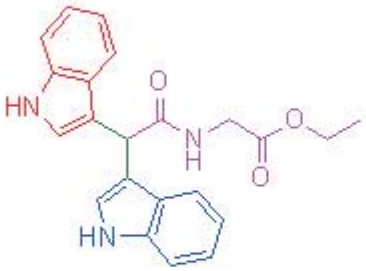
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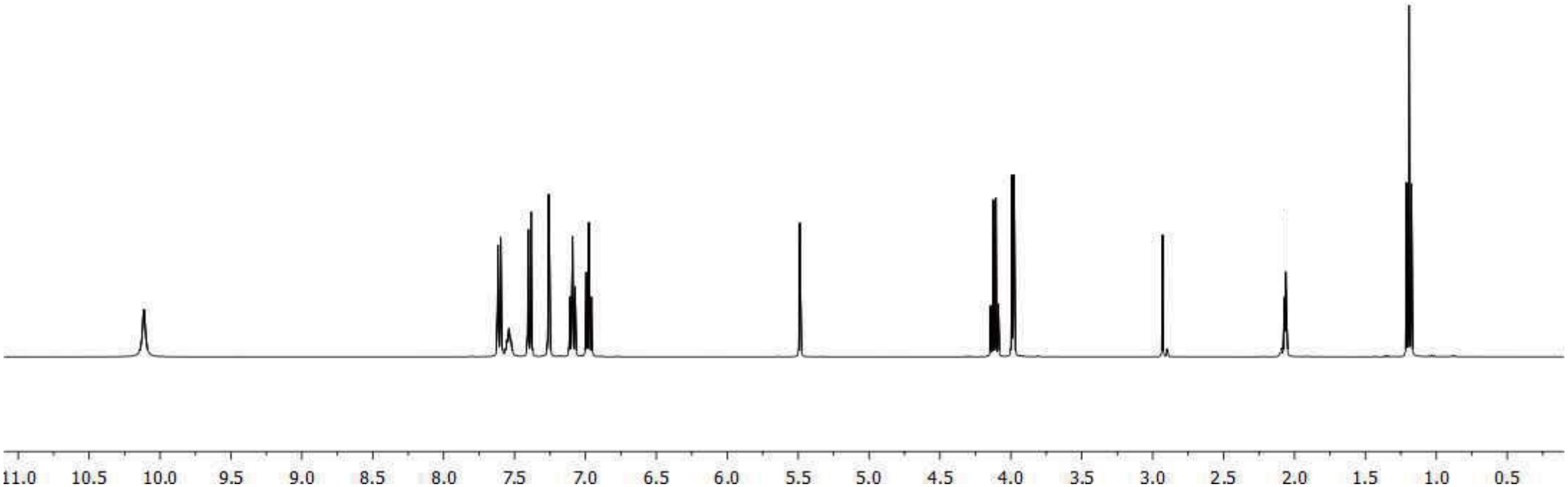
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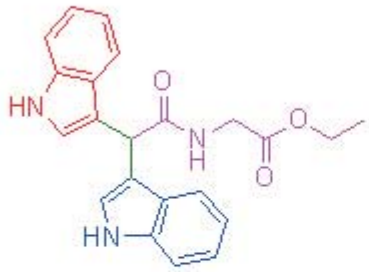
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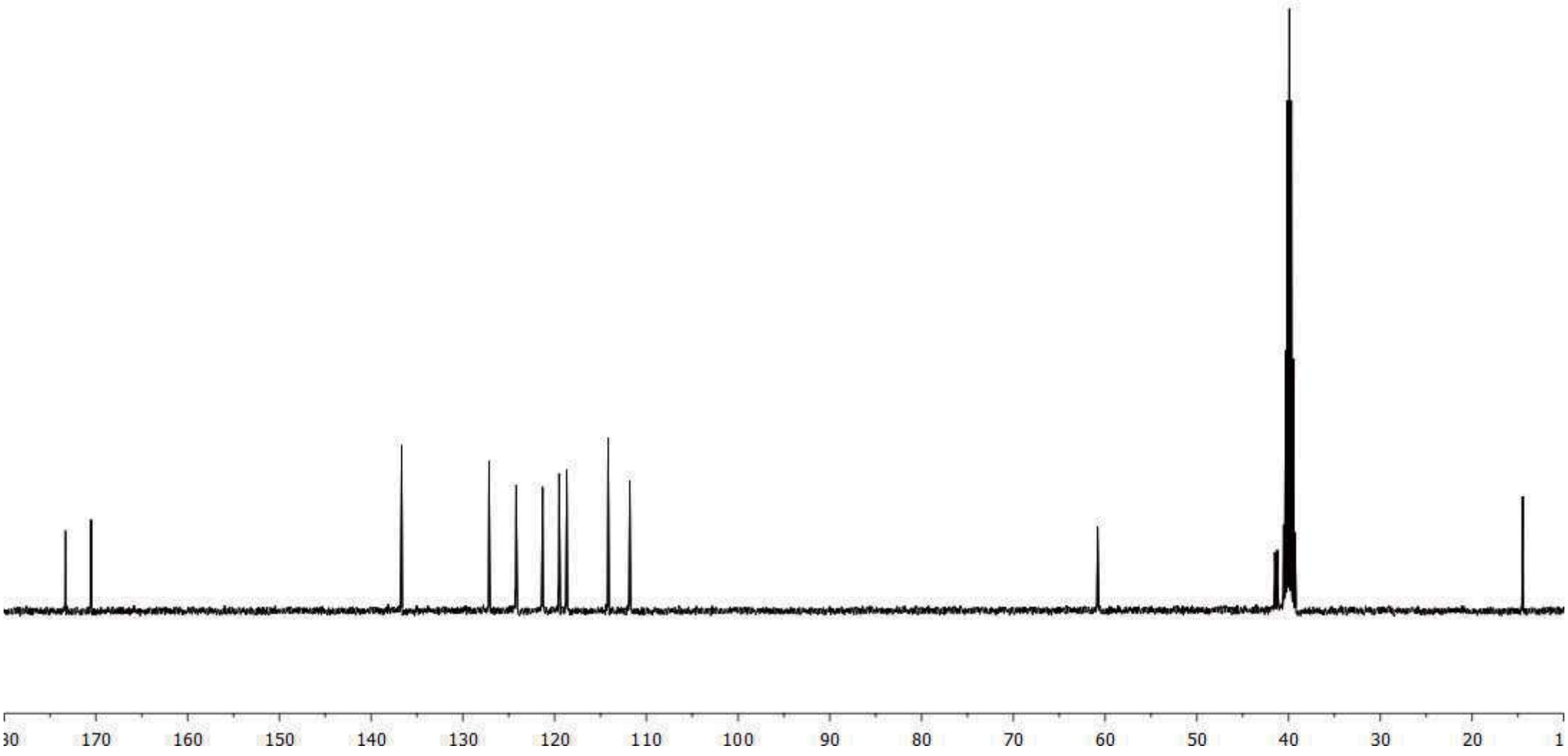
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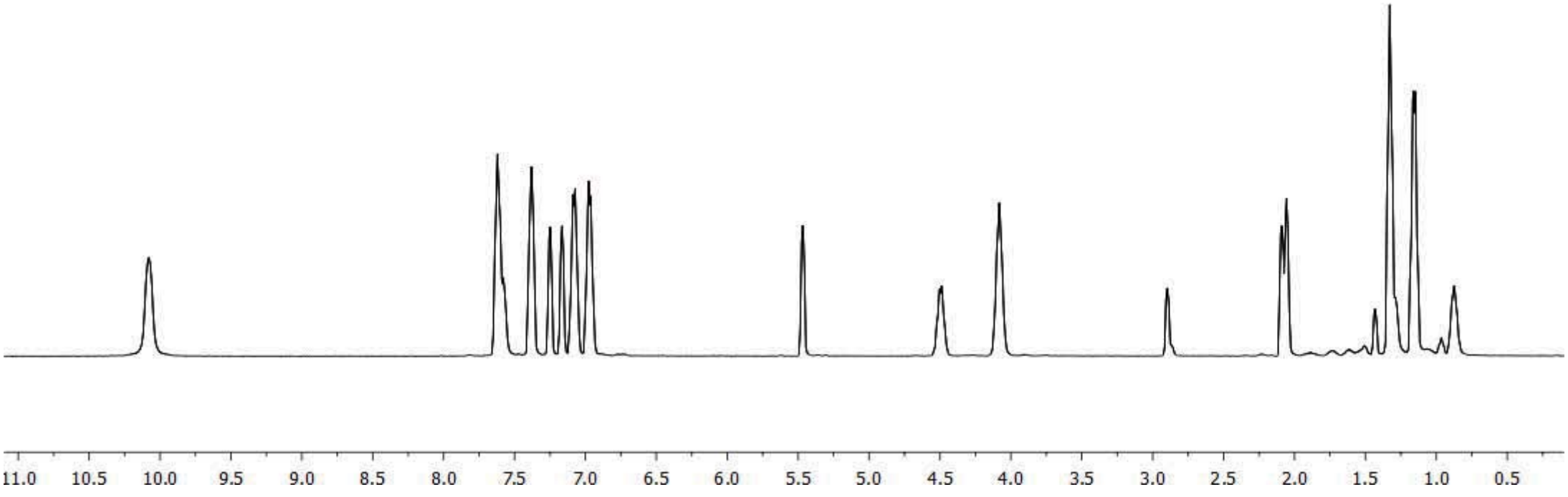
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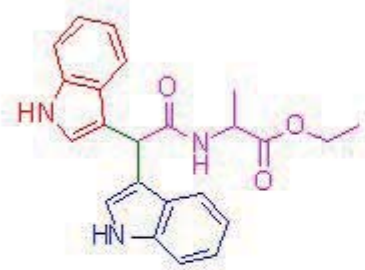
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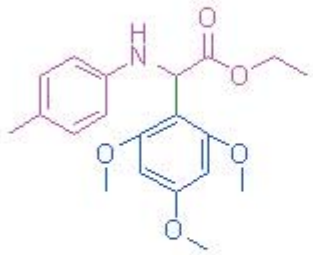
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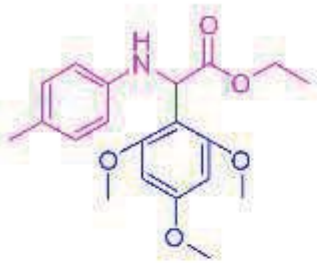

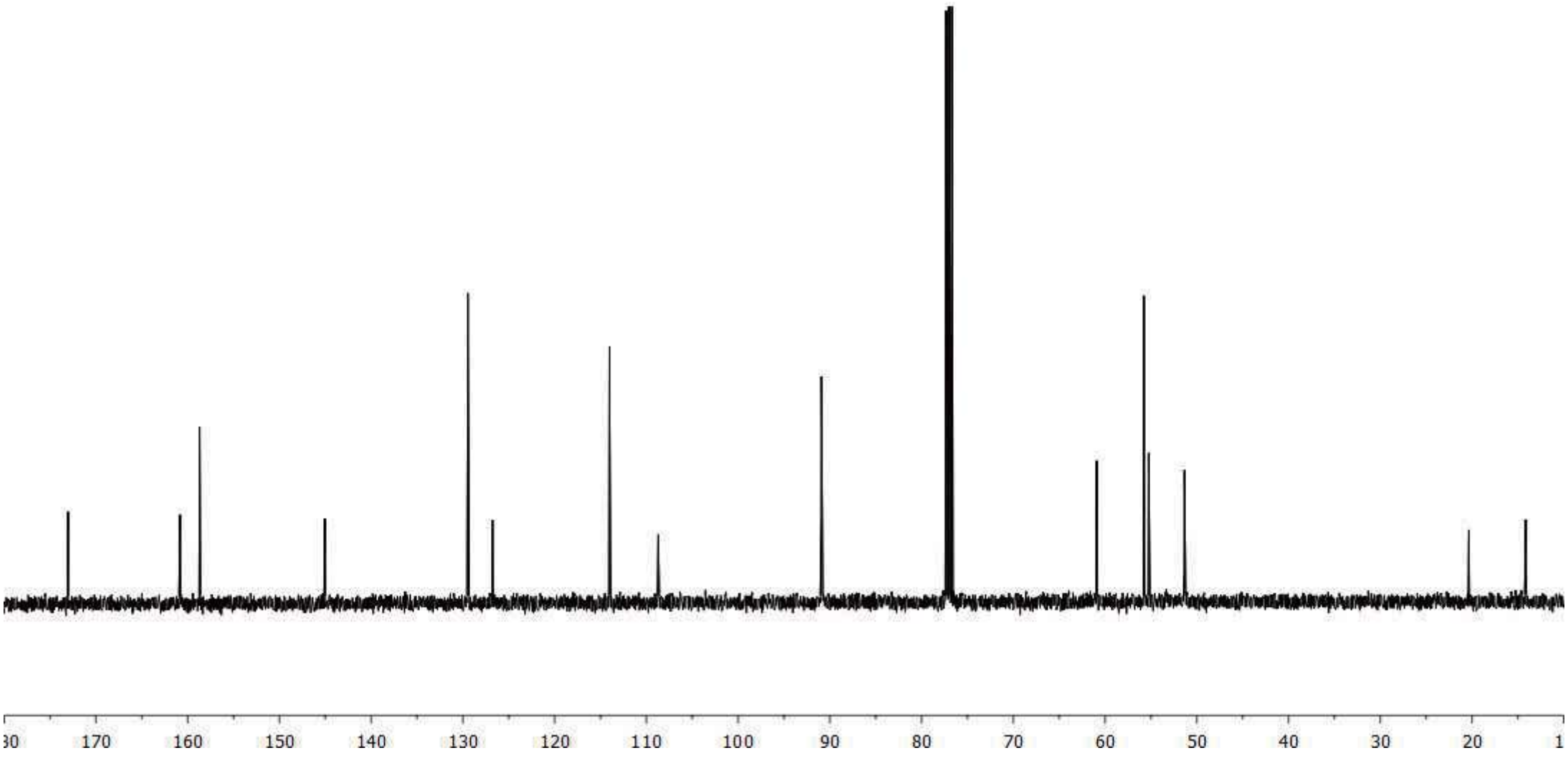
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