

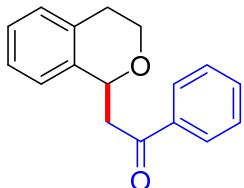
Supporting Information

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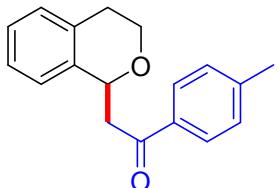
General procedure for CBr₄-mediated CDC reaction of isochromans with ketones. Isochromans (**1**, 1.5 mmol), ketones (**1**, 0.5 mmol) and CBr₄ (0.1 mmol) were mixed under air atmosphere. The reactions were performed at 100°C and completed within 48 hours. The products were isolated by column chromatographic separation.

Characterization of the products



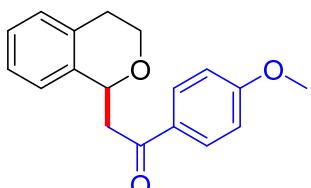
2-(isochroman-1-yl)-1-phenylethanone (**3aa**)¹

¹H NMR (400 MHz, CDCl₃) δ 8.01 (d, *J* = 7.4 Hz, 1H), 7.58 (t, *J* = 7.4 Hz, 1H), 7.47 (t, *J* = 7.6 Hz, 2H), 7.23 – 7.06 (m, 4H), 5.51 (dd, *J* = 8.7, 2.9 Hz, 1H), 4.12 (ddd, *J* = 11.3, 5.3, 3.7 Hz, 1H), 3.81 (ddd, *J* = 11.4, 9.7, 3.8 Hz, 1H), 3.62 (dd, *J* = 16.2, 8.8 Hz, 1H), 3.32 (dd, *J* = 16.2, 3.5 Hz, 1H), 3.11 – 2.94 (m, 1H), 2.72 (m, 1H).



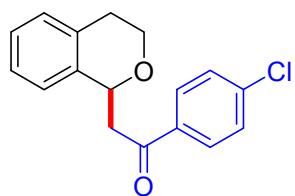
2-(isochroman-1-yl)-1-(p-tolyl)ethanone (**3ab**)¹

¹H NMR (400 MHz, CDCl₃) δ 7.91 (d, *J* = 8.0 Hz, 2H), 7.26 (d, *J* = 8.2 Hz, 2H), 7.21 – 6.99 (m, 4H), 5.50 (m, 1H), 4.11 (m, 1H), 3.80 (m, 1H), 3.58 (dd, *J* = 16.2, 8.7 Hz, 1H), 3.29 (dd, *J* = 16.2, 3.6 Hz, 1H), 3.00 (m, 1H), 2.71 (m, 1H), 2.40 (s, 3H).



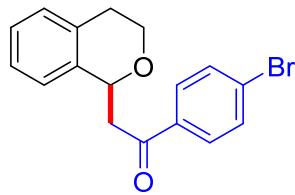
2-(isochroman-1-yl)-1-(4-methoxyphenyl)ethanone (**3ac**)¹

¹H NMR (400 MHz, CDCl₃) δ 7.99 (d, *J* = 8.4 Hz, 2H), 7.14 (m, 4H), 6.93 (d, *J* = 8.5 Hz, 2H), 5.48 (d, *J* = 7.4 Hz, 1H), 4.11 (m, 1H), 3.95 – 3.73 (m, 4H), 3.56 (dd, *J* = 16.0, 8.8 Hz, 1H), 3.25 (dd, *J* = 16.0, 3.1 Hz, 1H), 3.01 (m, 1H), 2.70 (d, *J* = 16.3 Hz, 1H).



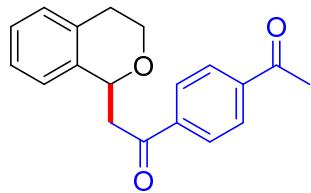
1-(4-chlorophenyl)-2-(isochroman-1-yl)ethanone (3ad)

¹H NMR (400 MHz, CDCl₃) δ 7.95 (d, *J* = 8.3 Hz, 2H), 7.44 (d, *J* = 8.2 Hz, 2H), 7.31 – 7.01 (m, 4H), 5.47 (d, *J* = 8.7 Hz, 1H), 4.10 (m, 1H), 3.80 (m, 1H), 3.58 (dd, *J* = 16.0, 9.0 Hz, 1H), 3.28 (d, *J* = 15.9 Hz, 1H), 3.01 (m, 1H), 2.71 (d, *J* = 16.3 Hz, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 197.0, 139.6, 137.4, 135.7, 134.0, 129.8, 129.1, 128.8, 126.7, 126.3, 124.5, 72.8, 63.6, 45.4, 28.9. HRMS (ESI) exact mass calcd for C₁₇H₁₆ClO₂ [M+H]⁺ 287.0839, found 287.0836.



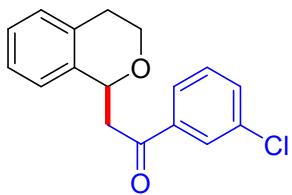
1-(4-bromophenyl)-2-(isochroman-1-yl)ethanone (3ae)¹

¹H NMR (400 MHz, CDCl₃) δ 7.87 (d, *J* = 8.4 Hz, 2H), 7.61 (d, *J* = 8.2 Hz, 2H), 7.37 – 6.95 (m, 4H), 5.46 (d, *J* = 6.4 Hz, 1H), 4.10 (m, 1H), 3.79 (m, 1H), 3.57 (dd, *J* = 16.0, 8.9 Hz, 1H), 3.27 (dd, *J* = 16.0, 3.3 Hz, 1H), 3.01 (m, 1H), 2.70 (d, *J* = 16.3 Hz, 1H).



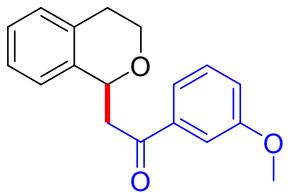
1-(4-acetylphenyl)-2-(isochroman-1-yl)ethanone (3af)

¹H NMR (400 MHz, CDCl₃) δ 8.08 (d, *J* = 8.6 Hz, 2H), 8.04 (d, *J* = 8.1 Hz, 2H), 7.25 – 7.04 (m, 4H), 5.48 (d, *J* = 6.6 Hz, 1H), 4.11 (m, 1H), 3.80 (m, 1H), 3.63 (dd, *J* = 16.1, 9.0 Hz, 1H), 3.34 (dd, *J* = 16.1, 3.3 Hz, 1H), 3.03 (m, 1H), 2.78 – 2.56 (m, 4H). ¹³C NMR (101 MHz, CDCl₃) δ 197.7, 197.4, 140.4, 140.1, 137.2, 134.0, 129.1, 128.5, 128.4, 126.7, 126.3, 124.4, 72.8, 63.5, 45.8, 28.8, 26.8. HRMS (ESI) exact mass calcd for C₁₉H₁₉O₃ [M+H]⁺ 295.1334, found 295.1341.



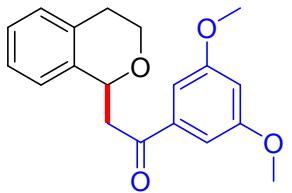
1-(3-chlorophenyl)-2-(isochroman-1-yl)ethanone (3ag)

¹H NMR (400 MHz, CDCl₃) δ 7.98 (s, 1H), 7.88 (d, *J* = 7.8 Hz, 1H), 7.54 (d, *J* = 7.9 Hz, 1H), 7.41 (t, *J* = 7.9 Hz, 1H), 7.24 – 7.02 (m, 4H), 5.47 (d, *J* = 8.6 Hz, 1H), 4.11 (m, 1H), 3.80 (m, 1H), 3.58 (dd, *J* = 16.1, 9.0 Hz, 1H), 3.28 (dd, *J* = 16.1, 2.1 Hz, 1H), 3.02 (m, 1H), 2.71 (d, *J* = 16.2 Hz, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 197.0, 138.9, 137.3, 134.9, 134.0, 133.0, 129.9, 129.1, 128.5, 126.7, 126.4, 126.3, 124.5, 72.7, 63.5, 45.6, 28.9. HRMS (ESI) exact mass calcd for C₁₇H₁₆ClO₂ [M+H]⁺ 287.0839, found 287.0845.



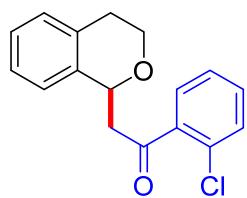
2-(isochroman-1-yl)-1-(3-methoxyphenyl)ethanone (3ah)

¹H NMR (400 MHz, CDCl₃) δ 7.57 (m, 2H), 7.37 (t, *J* = 7.9 Hz, 1H), 7.24 – 6.93 (m, 5H), 5.50 (d, *J* = 6.7 Hz, 1H), 4.11 (m, 1H), 3.97 – 3.72 (m, 4H), 3.60 (dd, *J* = 16.2, 8.8 Hz, 1H), 3.32 (dd, *J* = 16.2, 2.9 Hz, 1H), 3.02 (m, 1H), 2.72 (d, *J* = 16.3 Hz, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 197.9, 159.7, 138.5, 137.5, 133.9, 129.5, 129.0, 126.5, 126.2, 124.5, 120.9, 119.7, 112.3, 72.6, 63.4, 55.3, 45.5, 28.8. HRMS (ESI) exact mass calcd for C₁₈H₁₉O₃ [M+H]⁺ 283.1334, found 283.1338.



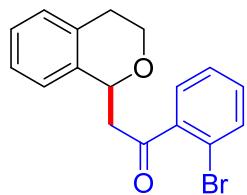
1-(3,5-dimethoxyphenyl)-2-(isochroman-1-yl)ethanone (3ai)

¹H NMR (400 MHz, CDCl₃) δ 7.18 (m, 6H), 6.66 (s, 1H), 5.49 (d, *J* = 7.6 Hz, 1H), 4.11 (m, 1H), 3.85 (s, 6H), 3.57 (m, 1H), 3.29 (d, *J* = 16.1 Hz, 1H), 3.00 (m, 1H), 2.72 (d, *J* = 16.1 Hz, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 197.8, 160.9, 139.2, 137.6, 134.1, 129.1, 126.6, 126.3, 124.6, 106.2, 105.6, 72.8, 63.4, 55.6, 45.7, 28.9. HRMS (ESI) exact mass calcd for C₁₉H₂₁O₄ [M+H]⁺ 313.1440, found 313.1447.



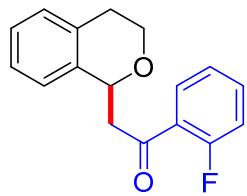
1-(2-chlorophenyl)-2-(isochroman-1-yl)ethanone (3aj)¹

¹H NMR (400 MHz, CDCl₃) δ 7.54 (d, *J* = 7.8 Hz, 1H), 7.45 – 7.31 (m, 3H), 7.22 – 7.07 (m, 4H), 5.30 (t, *J* = 7.2 Hz, 1H), 4.08 (m, 1H), 3.77 (m, 1H), 3.47 (m, 2H), 2.95 (m, 1H), 2.71 (m, 1H).



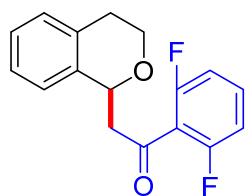
1-(2-bromophenyl)-2-(isochroman-1-yl)ethanone (3ak)¹

¹H NMR (400 MHz, CDCl₃) δ 7.60 (d, *J* = 7.9 Hz, 1H), 7.48 (d, *J* = 7.6 Hz, 1H), 7.37 (t, *J* = 7.5 Hz, 1H), 7.30 (t, *J* = 7.9 Hz, 1H), 7.20 – 7.10 (m, 4H), 5.35 (dd, *J* = 8.3, 3.9 Hz, 1H), 4.08 (m, 1H), 3.77 (m, 1H), 3.55 – 3.37 (m, 2H), 2.90 (m, 1H), 2.71 (d, *J* = 16.3 Hz, 1H).



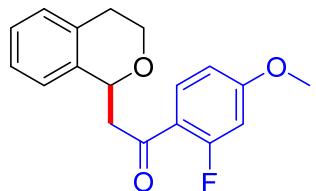
1-(2-fluorophenyl)-2-(isochroman-1-yl)ethanone (3al)

¹H NMR (400 MHz, CDCl₃) δ 7.92 (t, *J* = 6.9 Hz, 1H), 7.52 (dd, *J* = 12.4, 6.5 Hz, 1H), 7.35 – 6.99 (m, 6H), 5.47 (m, 1H), 4.10 (m, 1H), 3.79 (m, 1H), 3.63 – 3.31 (m, 2H), 2.97 (m, 1H), 2.71 (d, *J* = 16.3 Hz, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 196.3, 163.0, 160.4, 137.3, 134.5, 134.4, 134.0, 130.9, 129.0, 126.5, 126.2, 125.8, 124.6, 124.5, 116.6, 116.4, 72.2, 63.0, 50.4, 28.8. HRMS (ESI) exact mass calcd for C₁₇H₁₆FO₂ [M+H]⁺ 271.1134, found 271.1129.



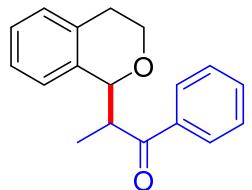
1-(2,6-difluorophenyl)-2-(isochroman-1-yl)ethanone (3am)

¹H NMR (400 MHz, CDCl₃) δ 7.16 (m, 7H), 5.37 (s, 1H), 4.08 (m, 1H), 3.77 (m, 1H), 3.39 (m, 2H), 2.93 (m, 1H), 2.69 (d, *J* = 16.1 Hz, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 195.6, 161.3, 161.2, 158.8, 158.7, 136.6, 133.9, 132.6, 132.5, 132.4, 129.0, 126.7, 126.2, 124.5, 112.2, 112.1, 112.0, 111.9, 111.9, 72.4, 63.1, 51.3, 28.6. HRMS (ESI) exact mass calcd for C₁₇H₁₅F₂O₂ [M+H]⁺ 289.1040, found 289.1038.



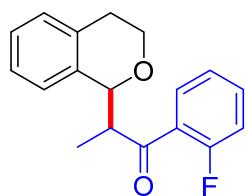
1-(2-fluoro-4-methoxyphenyl)-2-(isochroman-1-yl)ethanone (3an)

¹H NMR (400 MHz, CDCl₃) δ 7.96 (t, *J* = 8.6 Hz, 1H), 7.16 (m, 4H), 6.77 (d, *J* = 8.6 Hz, 1H), 6.61 (d, *J* = 13.2 Hz, 1H), 5.48 (s, 1H), 4.11 (m, 1H), 3.95 – 3.69 (m, 4H), 3.59 – 3.29 (m, 2H), 2.98 (m, 1H), 2.72 (d, *J* = 15.9 Hz, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 197.0, 139.6, 137.4, 135.7, 134.0, 129.8, 129.1, 128.8, 126.7, 126.3, 124.5, 72.8, 63.6, 45.4, 28.9. HRMS (ESI) exact mass calcd for C₁₈H₁₈FO₃ [M+H]⁺ 301.1240, found 301.1245.



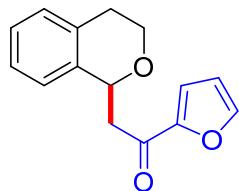
2-(isochroman-1-yl)-1-phenylpropan-1-one (3ao)¹

¹H NMR (400 MHz, CDCl₃) δ 7.96 (m, 2H), 7.63 – 7.36 (m, 3H), 7.23 – 6.81 (m, 4H), 5.26 (m, 1H), 4.06 (m, 2H), 3.61 (m, 1H), 3.00 (m, 1H), 2.60 (m, 1H), 1.15 (m, 3H).



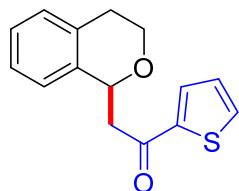
1-(2-fluorophenyl)-2-(isochroman-1-yl)propan-1-one (3ap)

¹H NMR (400 MHz, CDCl₃) δ 7.86 – 6.98 (m, 8H), 5.26 – 5.11 (m, 1H), 4.09 – 3.92 (m, 2H), 3.62 – 3.53 (m, 1H), 3.01 – 2.86 (m, 1H), 2.58 – 2.50 (m, 1H), 1.30 – 1.03 (m, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 200.4, 161.9, 159.4, 135.8, 135.1, 133.8, 133.7, 131.3, 128.9, 126.4, 126.4, 125.9, 125.8, 124.8, 124.8, 124.5, 116.3, 116.1, 64.2, 51.7, 28.9, 8.4. HRMS (ESI) exact mass calcd for C₁₈H₁₈FO₂ [M+H]⁺ 285.1291, found 285.1283.



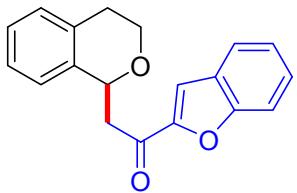
1-(furan-2-yl)-2-(isochroman-1-yl)ethanone (3aq)¹

¹H NMR (400 MHz, CDCl₃) δ 7.60 (s, 1H), 7.39 – 6.99 (m, 5H), 6.64 – 6.42 (m, 1H), 5.46 (d, *J* = 7.0 Hz, 1H), 4.11 (m, 1H), 3.80 (m, 1H), 3.44 (dd, *J* = 15.4, 9.4 Hz, 1H), 3.19 (dd, *J* = 15.4, 3.3 Hz, 1H), 3.00 (m, 1H), 2.72 (d, *J* = 16.3 Hz, 1H).



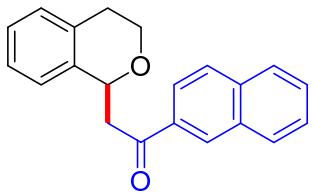
2-(isochroman-1-yl)-1-(thiophen-2-yl)ethanone (3ar)

¹H NMR (400 MHz, CDCl₃) δ 7.75 (d, *J* = 3.7 Hz, 1H), 7.66 (d, *J* = 4.9 Hz, 1H), 7.24 – 7.06 (m, 5H), 5.47 (d, *J* = 7.9 Hz, 1H), 4.12 (m, 1H), 3.81 (m, 1H), 3.52 (dd, *J* = 15.6, 9.1 Hz, 1H), 3.26 (dd, *J* = 15.6, 2.4 Hz, 1H), 3.02 (m, 1H), 2.71 (d, *J* = 16.4 Hz, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 190.8, 144.7, 137.3, 134.0, 133.9, 132.4, 129.1, 128.1, 126.6, 126.3, 124.6, 72.9, 63.4, 46.3, 28.9. HRMS (ESI) exact mass calcd for C₁₅H₁₅O₂S [M+H]⁺ 259.0793, found 259.0799.



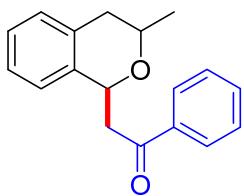
1-(benzofuran-2-yl)-2-(isochroman-1-yl)ethanone (3as)

¹H NMR (400 MHz, CDCl₃) δ 7.71 (d, *J* = 7.7 Hz, 1H), 7.64 – 7.41 (m, 3H), 7.38 – 7.07 (m, 5H), 5.51 (d, *J* = 8.1 Hz, 1H), 4.12 (m, 1H), 3.80 (m, 1H), 3.58 (dd, *J* = 15.3, 9.4 Hz, 1H), 3.33 (d, *J* = 15.3 Hz, 1H), 3.01 (m, 1H), 2.72 (d, *J* = 16.2 Hz, 1H). ¹³C NMR (101 MHz, DMSO) δ 188.8, 155.6, 152.8, 137.1, 133.9, 129.0, 128.2, 127.0, 126.6, 126.2, 124.5, 123.8, 123.3, 113.4, 112.4, 72.6, 63.2, 45.7, 28.7. HRMS (ESI) exact mass calcd for C₁₉H₁₇O₃ [M+H]⁺ 293.1178, found 293.1181.



2-(isochroman-1-yl)-1-(naphthalen-2-yl)ethanone (3at)

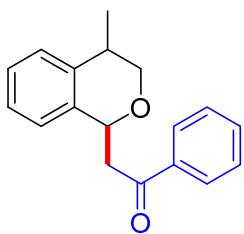
¹H NMR (400 MHz, CDCl₃) δ 8.51 (s, 1H), 8.10 (d, *J* = 8.6 Hz, 1H), 8.02 – 7.77 (m, 3H), 7.62 – 7.53 (mz, 2H), 7.21 – 7.16 (m, 4H), 5.57 (d, *J* = 8.4 Hz, 1H), 4.13 (m, 1H), 3.80 (m, 2H), 3.44 (dd, *J* = 16.1, 3.1 Hz, 1H), 3.04 (m, 1H), 2.72 (d, *J* = 16.3 Hz, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 198.0, 137.6, 135.6, 134.0, 132.5, 130.1, 129.6, 129.1, 128.4, 128.4, 127.7, 126.7, 126.6, 126.3, 124.6, 124.0, 72.8, 63.5, 45.5, 28.9. HRMS (ESI) exact mass calcd for C₂₁H₁₉O₂ [M+H]⁺ 303.1385, found 303.1390.



2-(3-methylisochroman-1-yl)-1-phenylethanone (3ba)

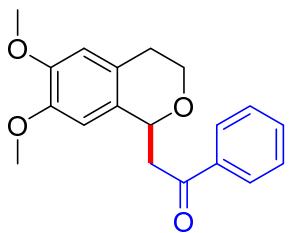
¹H NMR (400 MHz, CDCl₃) δ 8.02 (d, *J* = 7.6 Hz, 2H), 7.60 (t, *J* = 7.4 Hz, 1H), 7.51 (t, *J* = 7.5 Hz, 2H), 7.18 (m, 4H), 5.65 (dd, *J* = 9.2, 3.9 Hz, 1H), 4.11 (m, 1H), 3.76 (dd, *J* = 15.6, 9.2 Hz, 1H), 3.25 (dd, *J* = 15.6, 3.9 Hz, 1H), 2.79 (dd, *J* = 16.2, 3.4 Hz, 1H), 2.68 (dd, *J* = 16.2, 9.8 Hz, 1H), 1.23 (d, *J* = 6.2 Hz, 3H). diastereoisomer: ¹H NMR (400 MHz, CDCl₃) δ 8.04 (d, *J* = 7.6 Hz, 2H), 7.59 (t, *J* = 7.4 Hz, 1H), 7.49 (t, *J* = 7.6 Hz, 2H), 7.16 (m, 4H), 5.52 (dd, *J* = 7.3, 4.0 Hz, 1H), 3.87 (m, 1H), 3.60 (dd, *J* = 16.3, 7.7 Hz, 1H), 3.40 (dd, *J* = 16.2, 4.1 Hz, 1H), 2.74 (m, 2H), 1.30 (d, *J* = 6.2 Hz, 3H). ¹³C NMR

(101 MHz, CDCl₃) δ 198.1, 137.4, 137.1, 133.6, 133.1, 129.0, 128.6, 128.3, 126.7, 126.2, 125.1, 71.7, 64.7, 45.3, 35.8, 21.1. HRMS (ESI) exact mass calcd for C₁₈H₁₉O₂ [M+H]⁺ 267.1385, found 267.1377.



2-(4-methylisochroman-1-yl)-1-phenylethanone (3ca)

¹H NMR (400 MHz, CDCl₃) δ 8.02 – 7.28 (m, 9H), 5.56 – 5.47 (m, 1H), 4.07 – 3.03 (m, 6H), 1.31 (m, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 198.2, 198.1, 139.6, 139.4, 137.4, 137.0, 133.2, 128.6, 128.6, 128.4, 128.4, 127.3, 126.9, 126.8, 126.3, 126.2, 124.5, 124.4, 73.0, 73.0, 69.3, 69.1, 45.8, 45.5, 32.8, 32.0, 21.0, 17.6. HRMS (ESI) exact mass calcd for C₁₈H₁₉O₂ [M+H]⁺ 267.1385, found 267.1379.

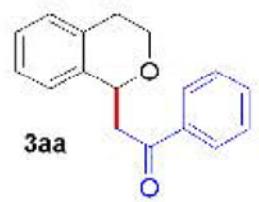


2-(6,7-dimethoxyisochroman-1-yl)-1-phenylethanone (3da)

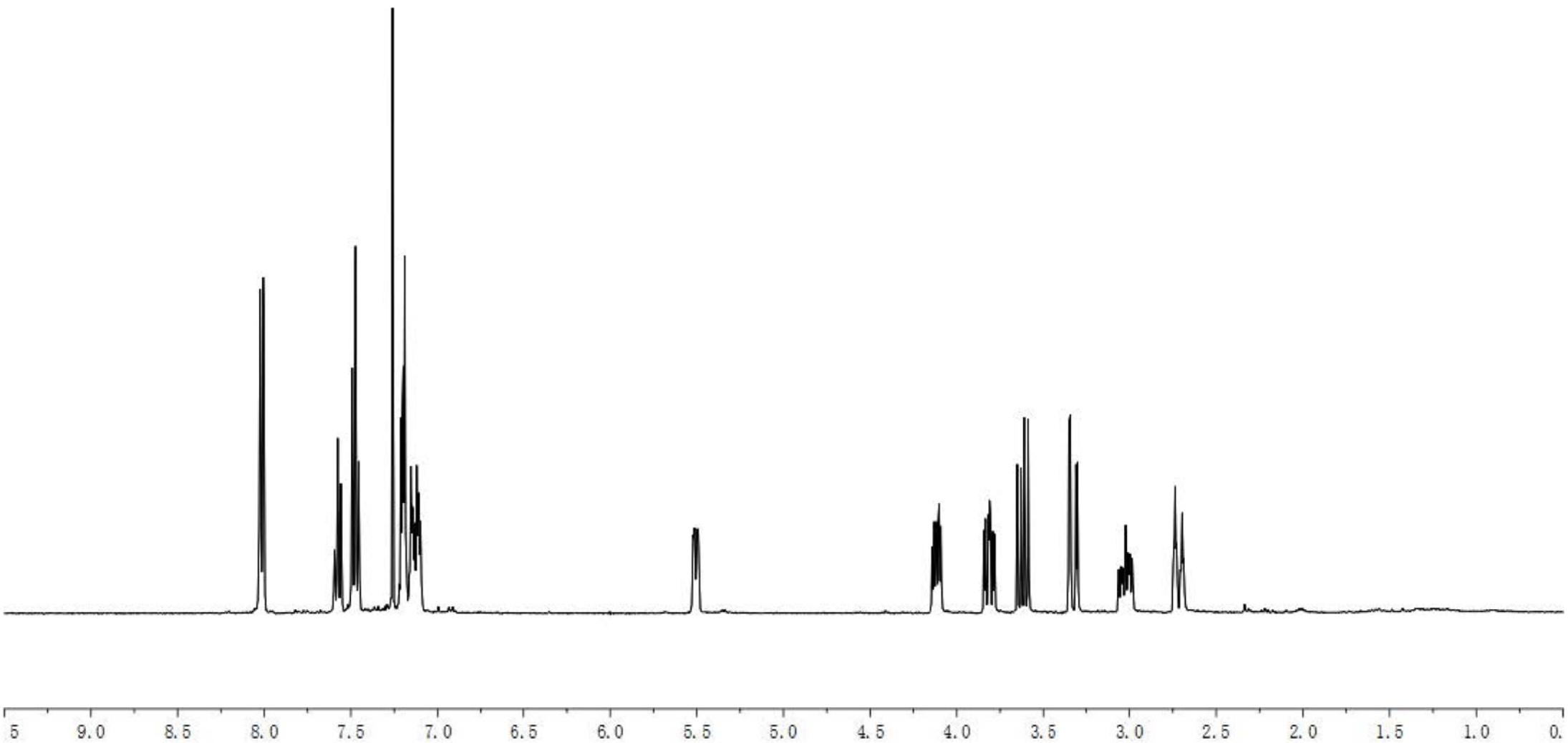
¹H NMR (400 MHz, CDCl₃) δ 8.01 (d, *J* = 7.6 Hz, 2H), 7.68 – 7.39 (m, 3H), 6.62 (s, 1H), 6.58 (s, 1H), 5.44 (d, *J* = 4.6 Hz, 1H), 4.09 (m, 1H), 3.87 (s, 3H), 3.78 (s, 3H), 3.61 (m, 1H), 3.27 (m, 1H), 2.92 (m, 1H), 2.63 (m, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 198.6, 147.8, 147.6, 137.4, 133.3, 129.3, 128.7, 128.5, 126.2, 111.6, 107.7, 72.6, 63.5, 56.1, 56.0, 45.7, 28.5. HRMS (ESI) exact mass calcd for C₁₉H₂₁O₄ [M+H]⁺ 313.1440, found 313.1444.

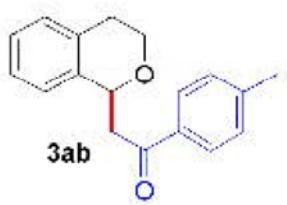
Reference:

- Zhang, Y.; Li, C.-J. *J. Am. Chem. Soc.* **2006**, 128, 4242.

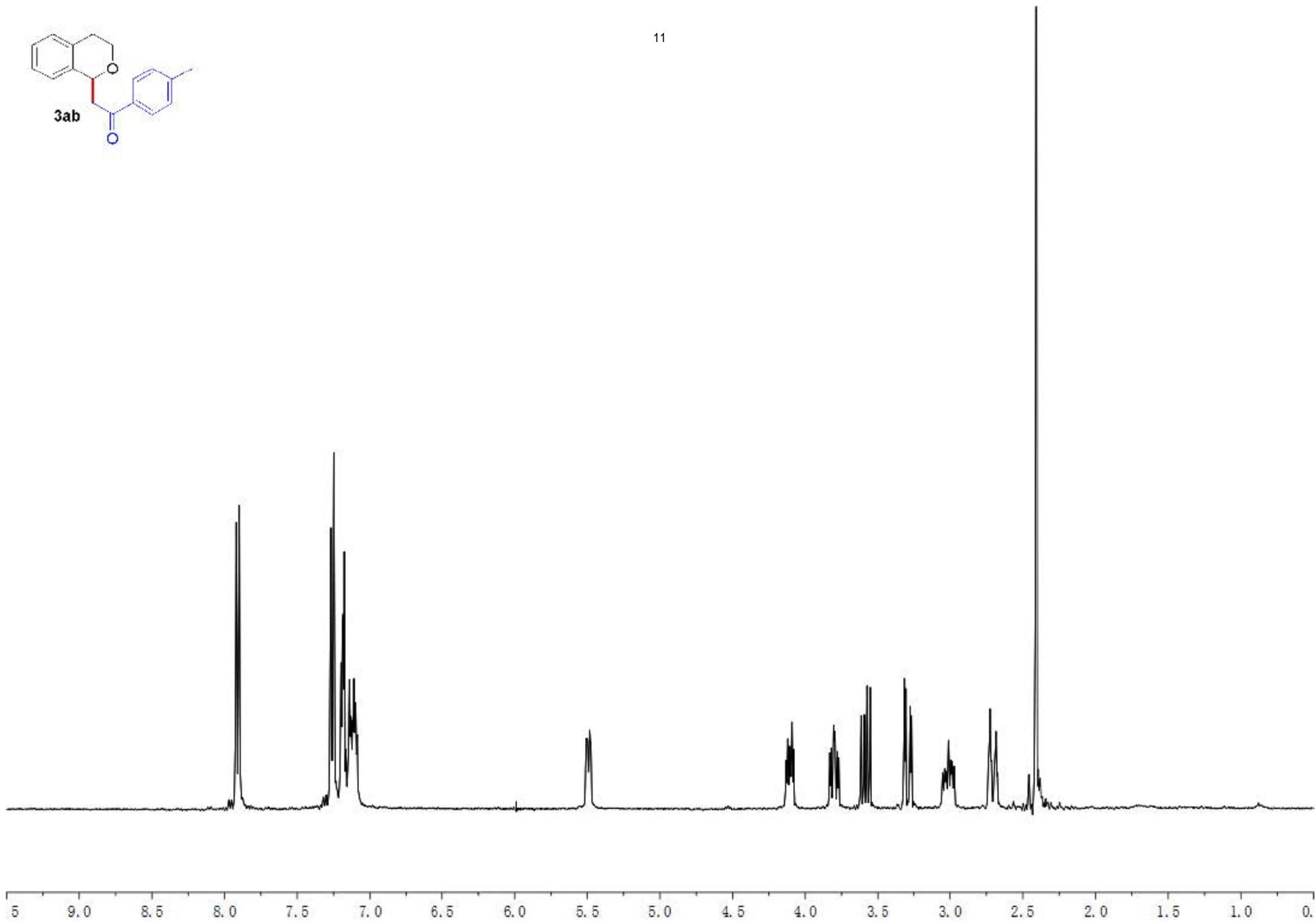


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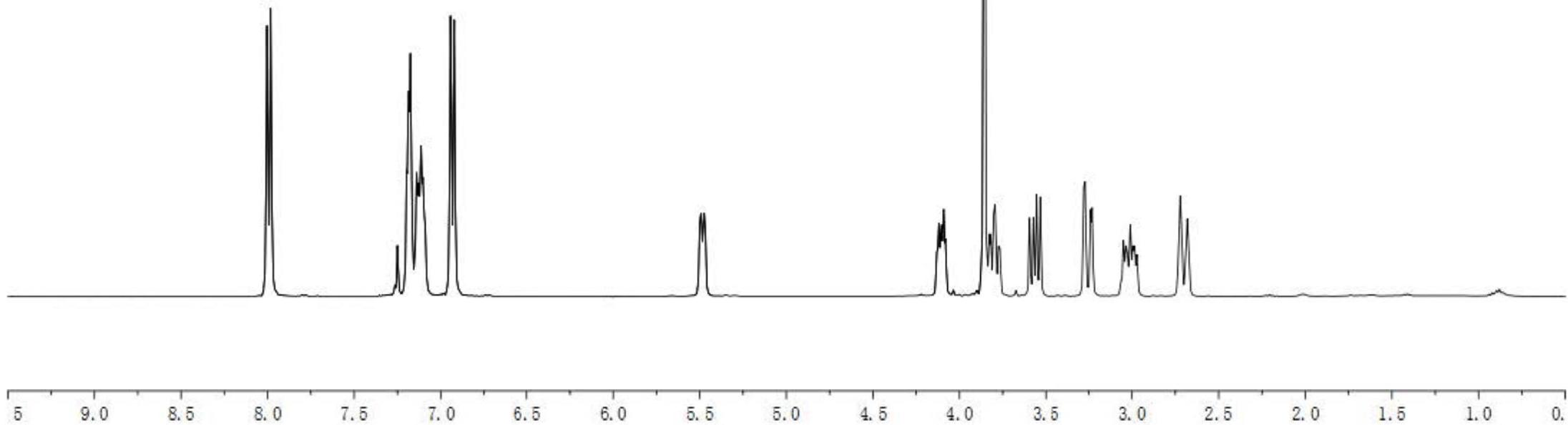


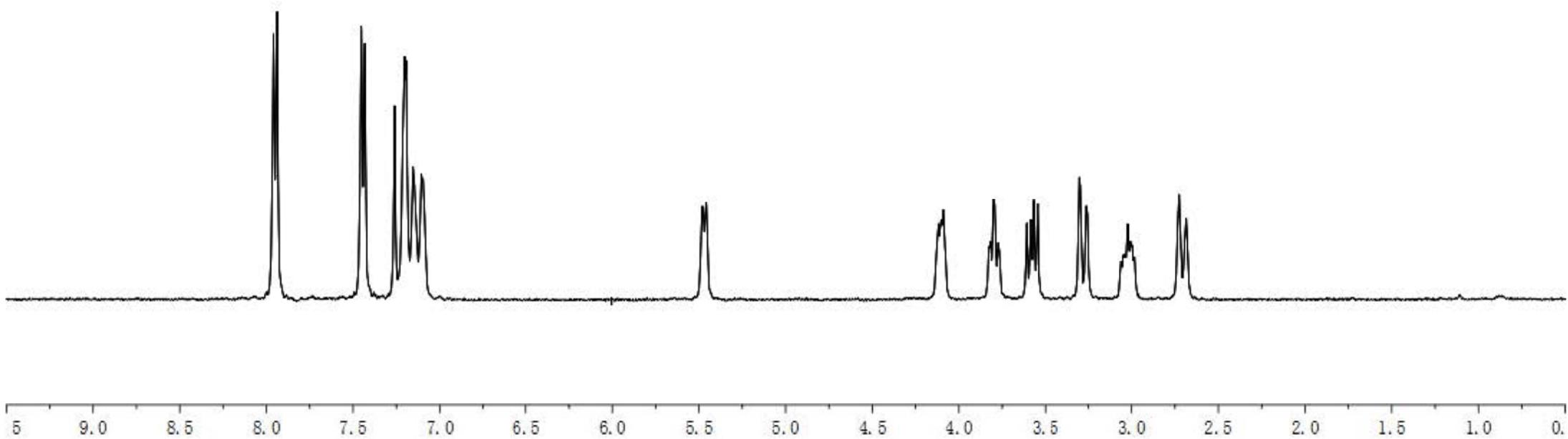
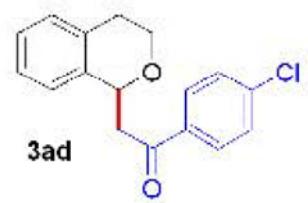
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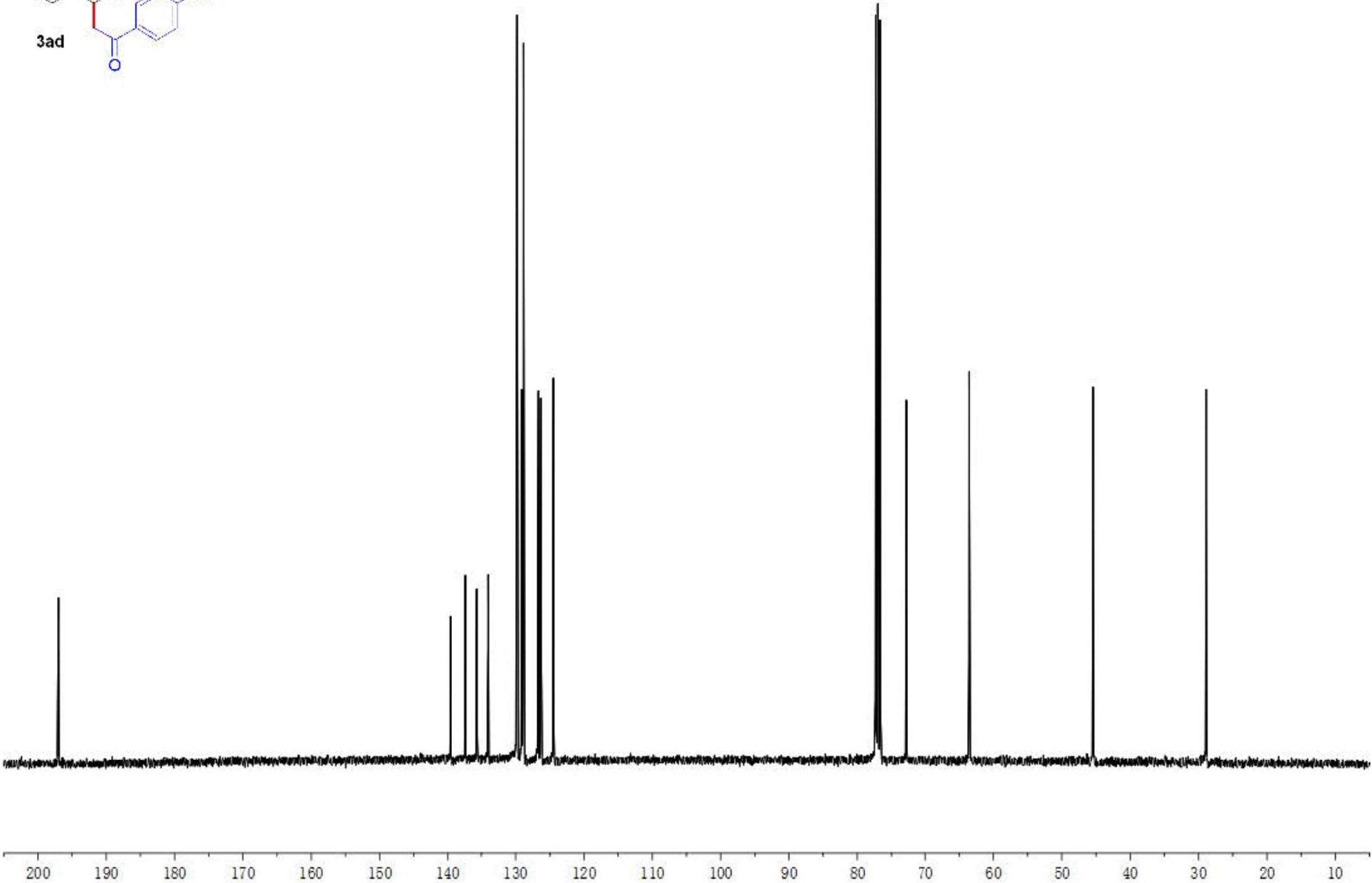
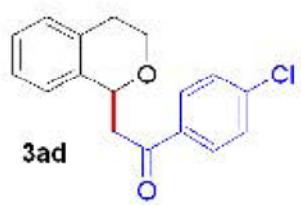


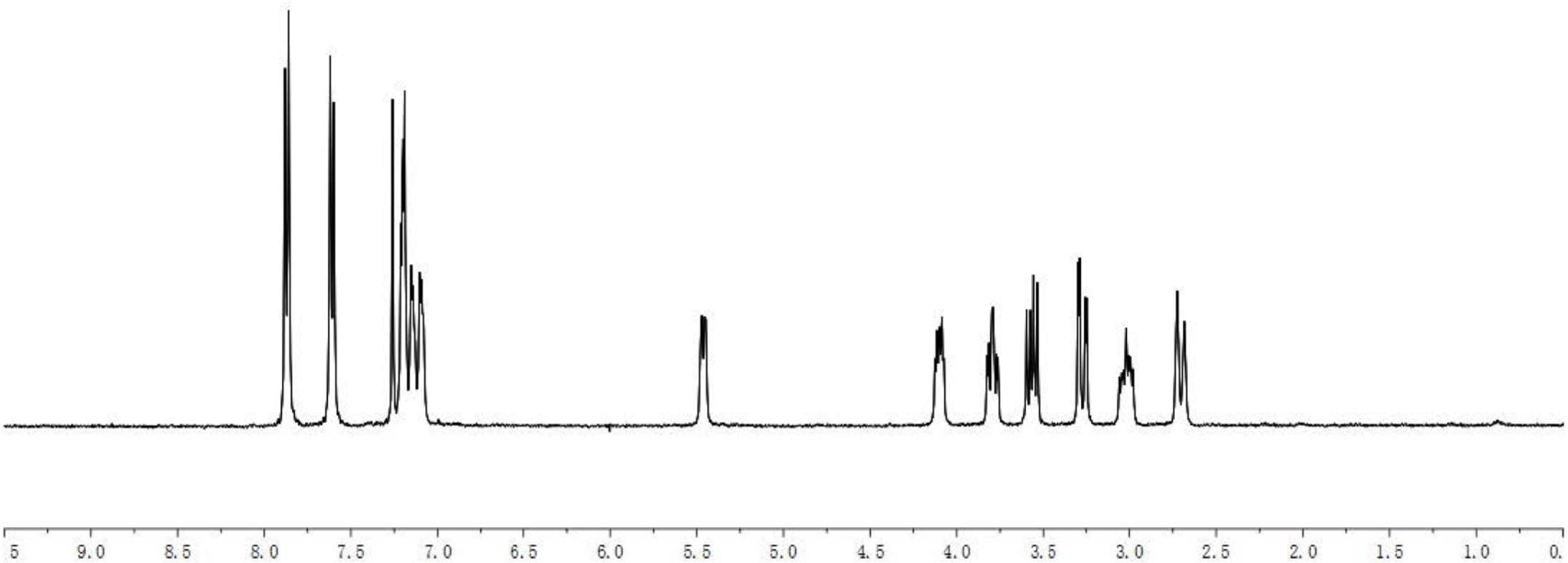
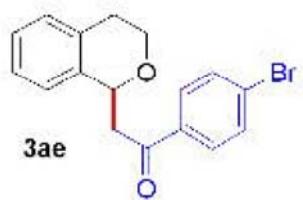


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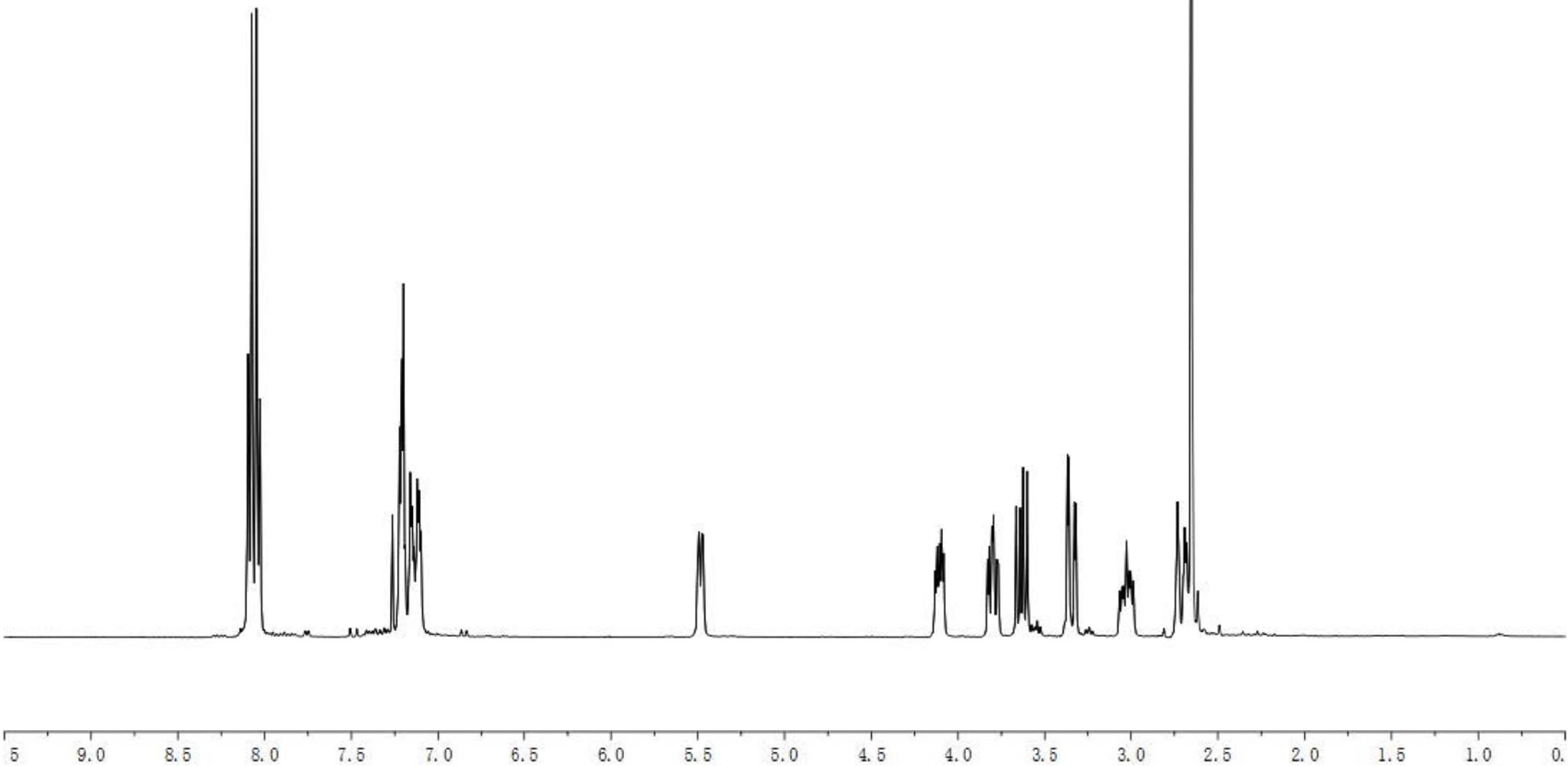


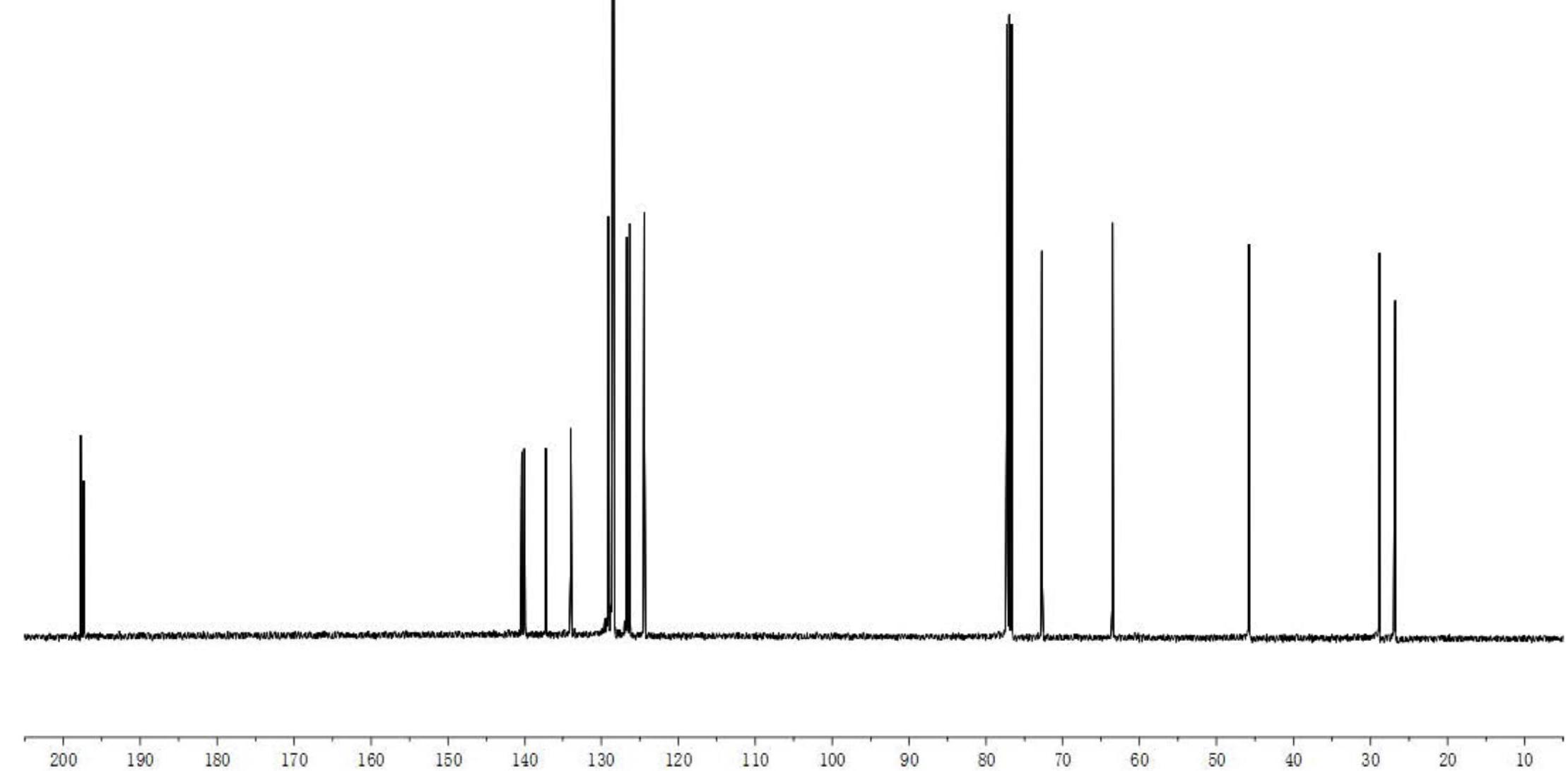
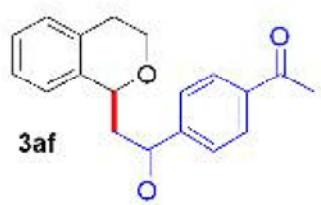


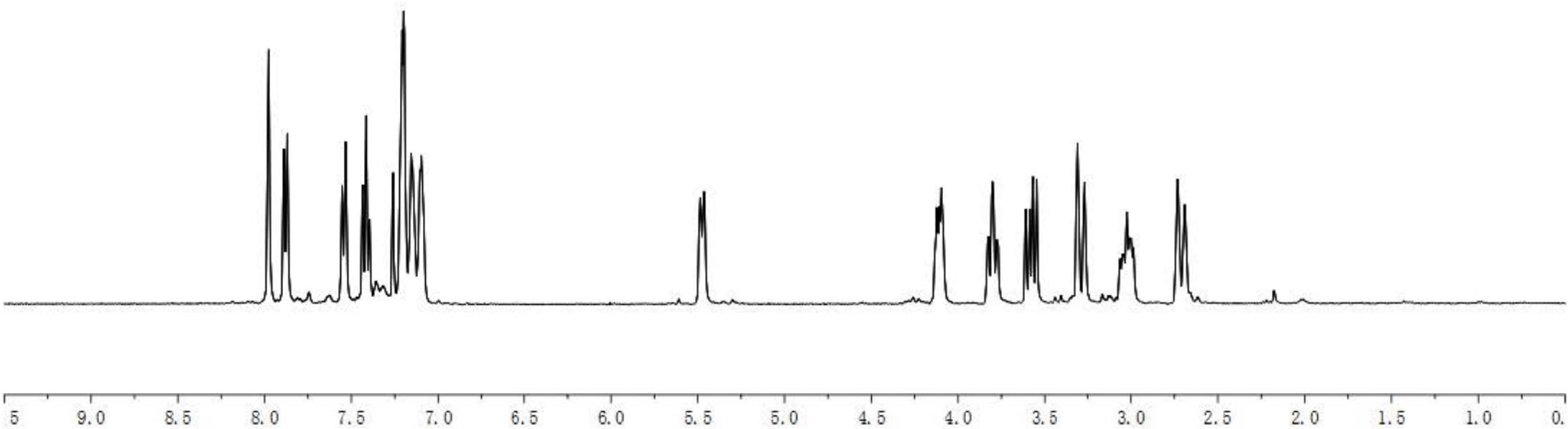
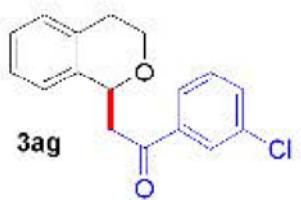


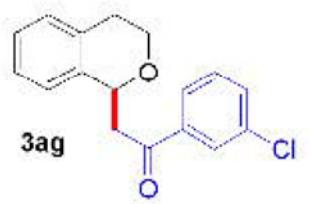


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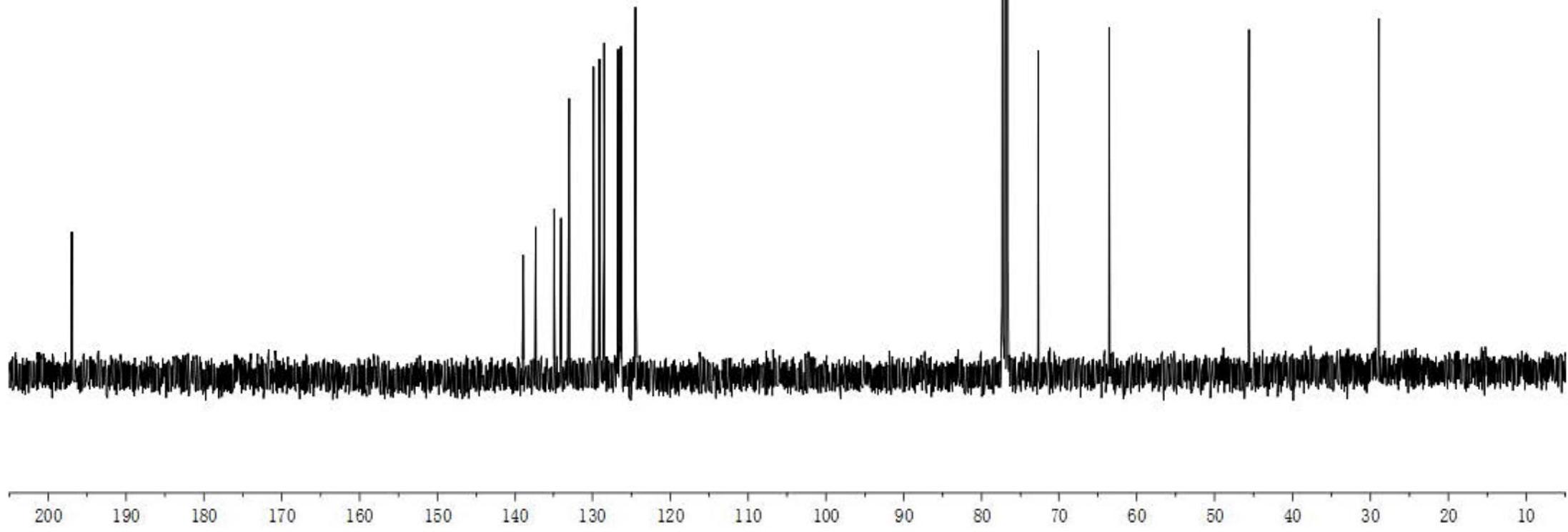


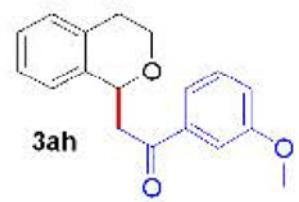




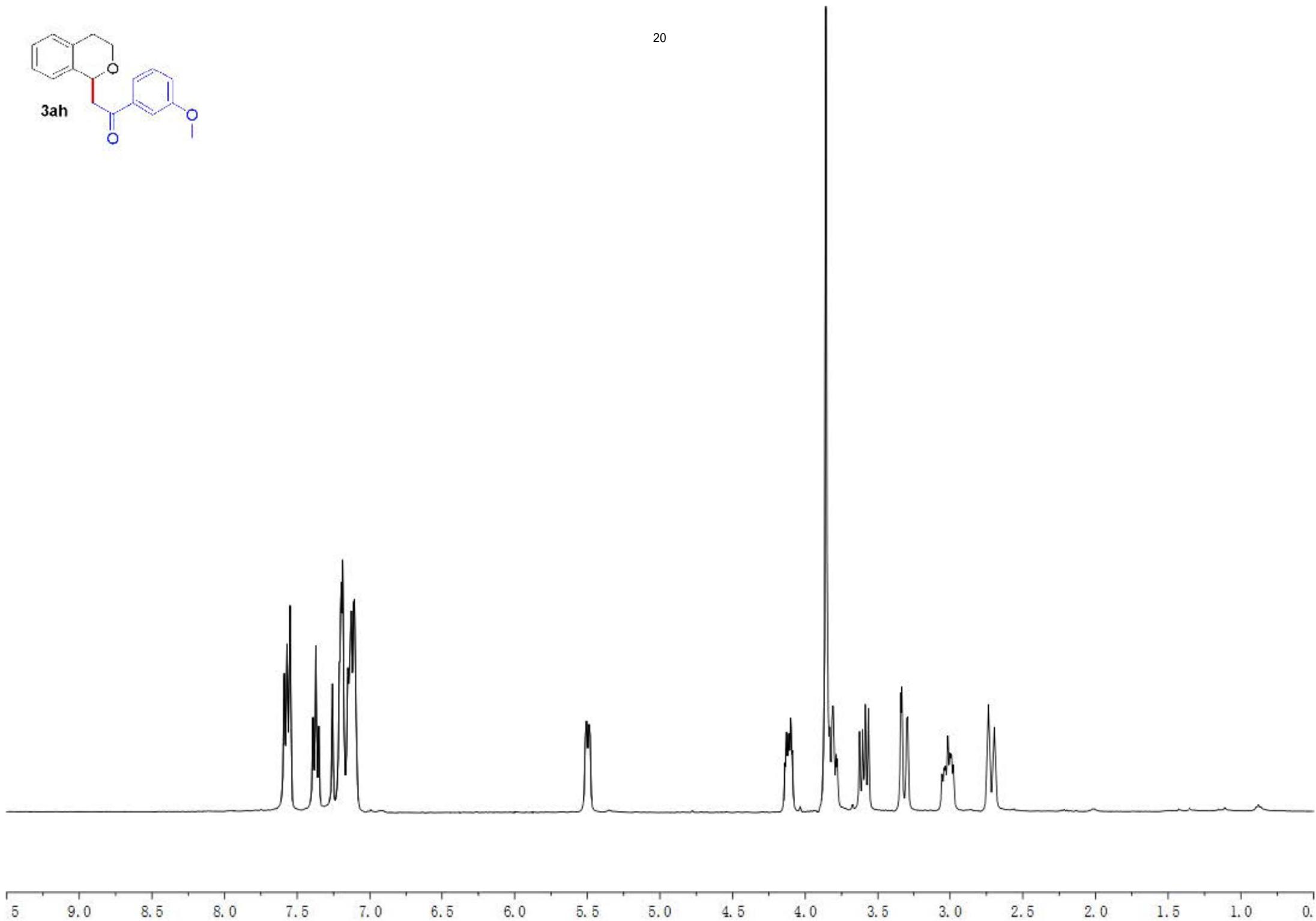


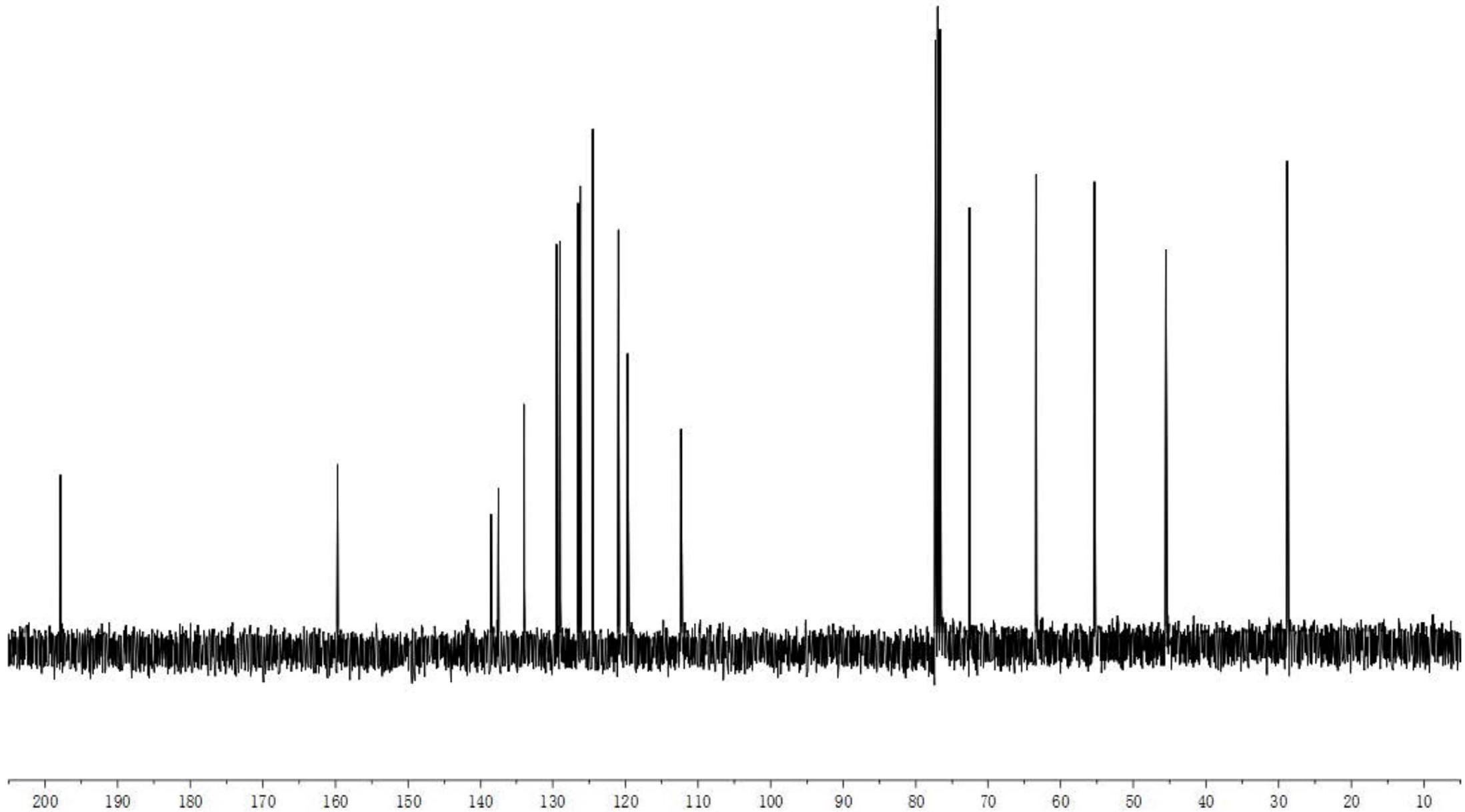
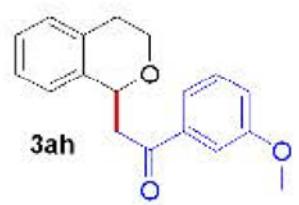
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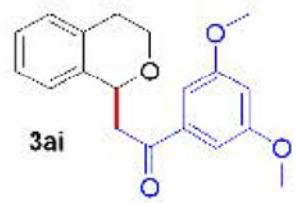




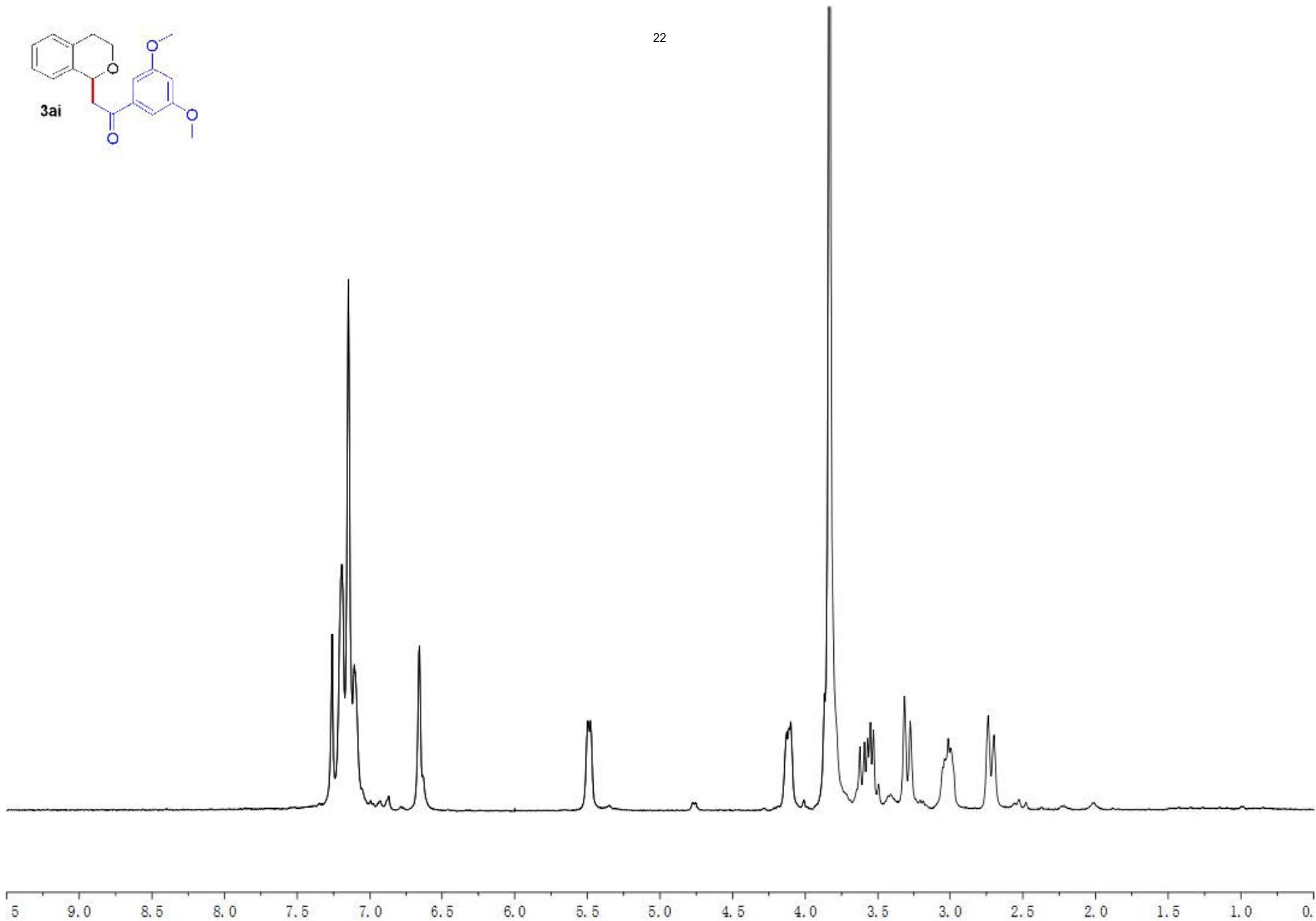
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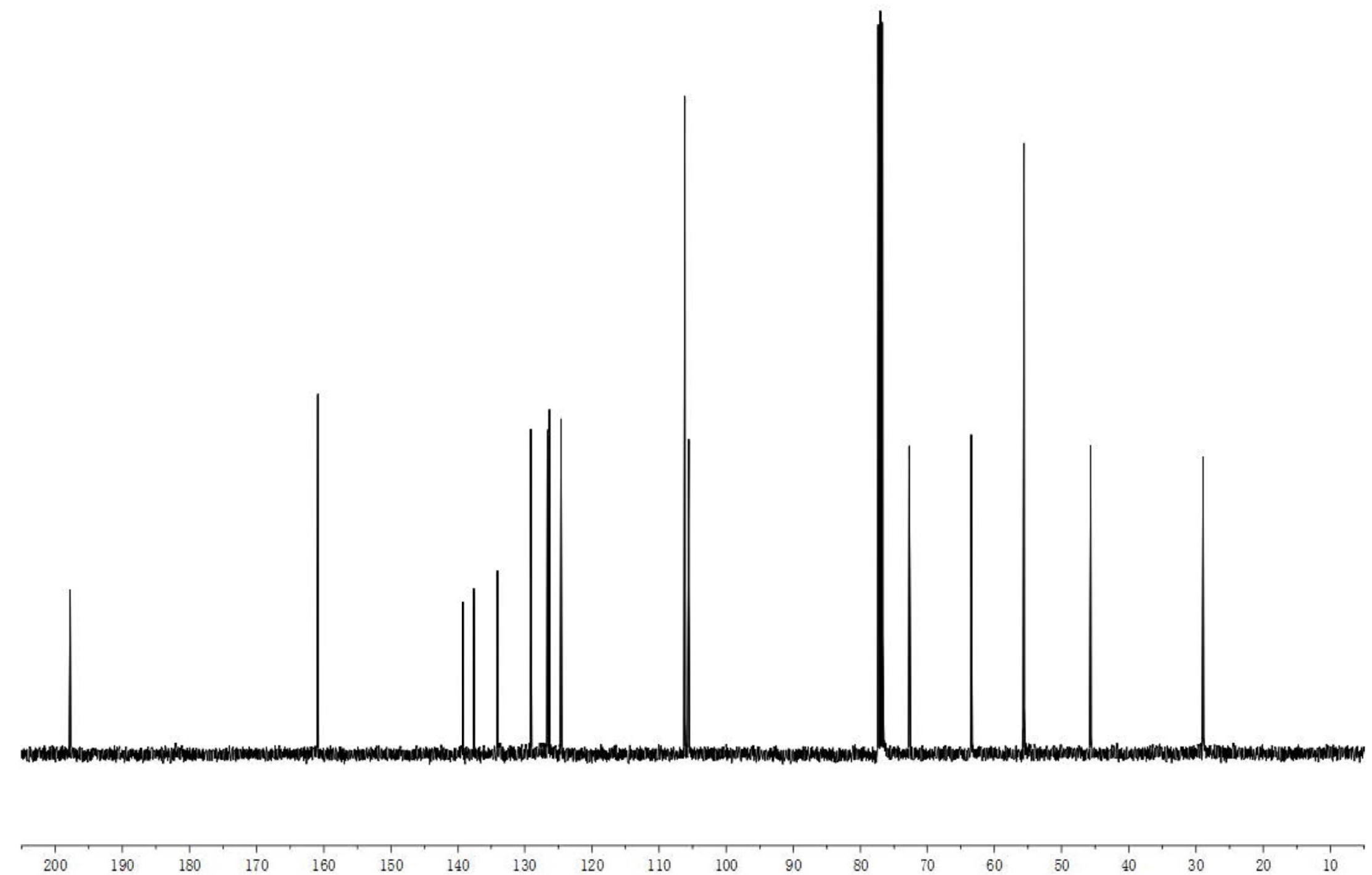


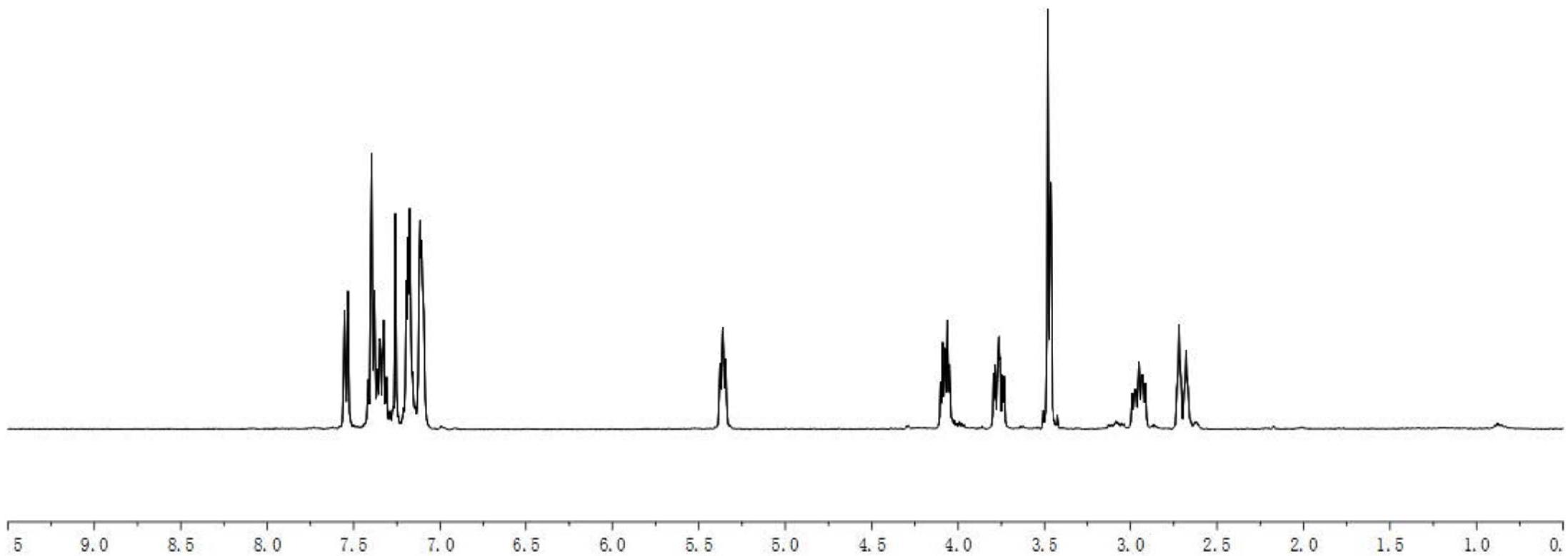
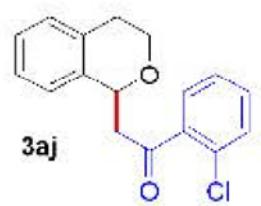


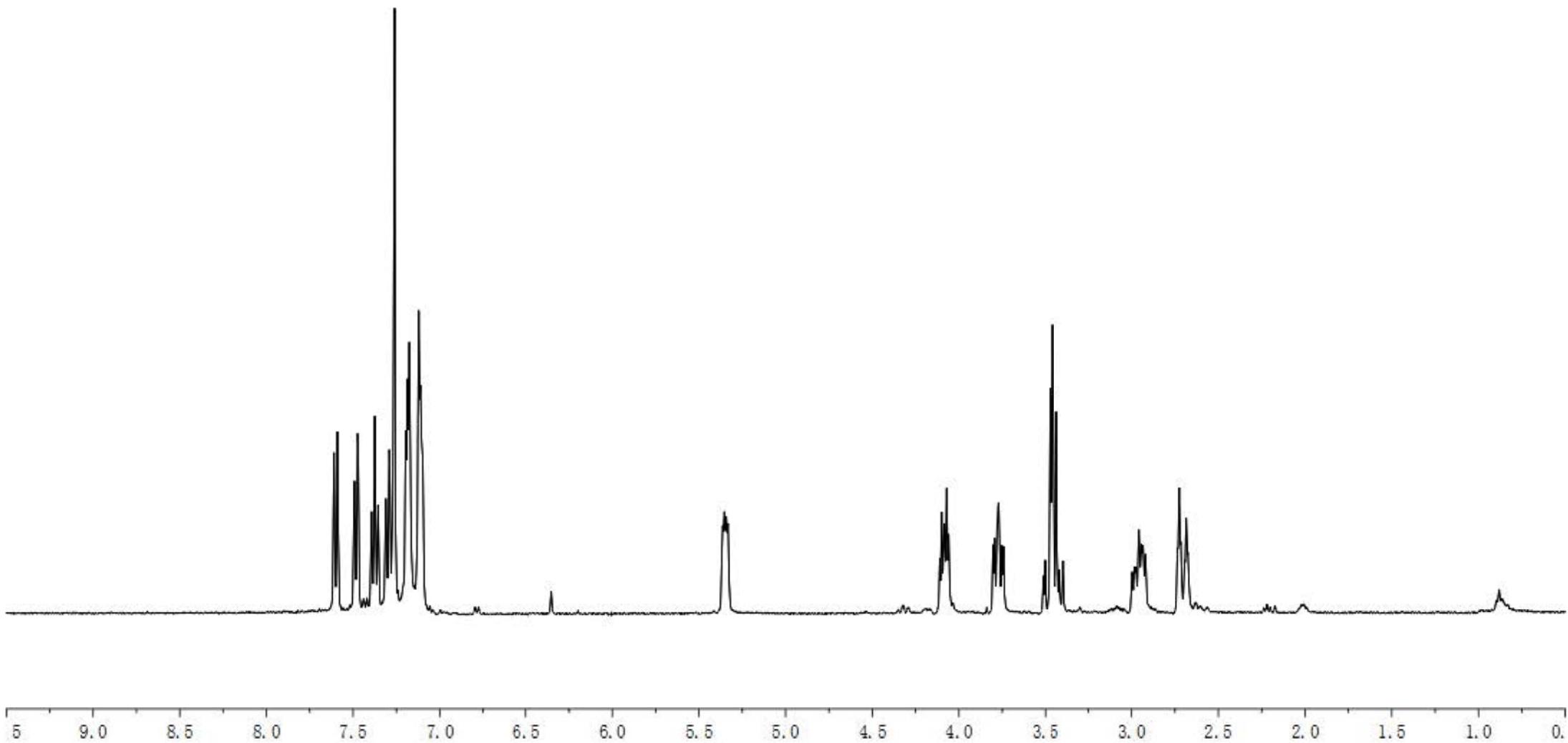
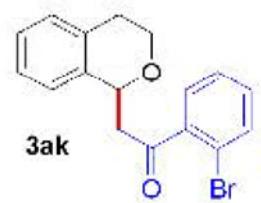


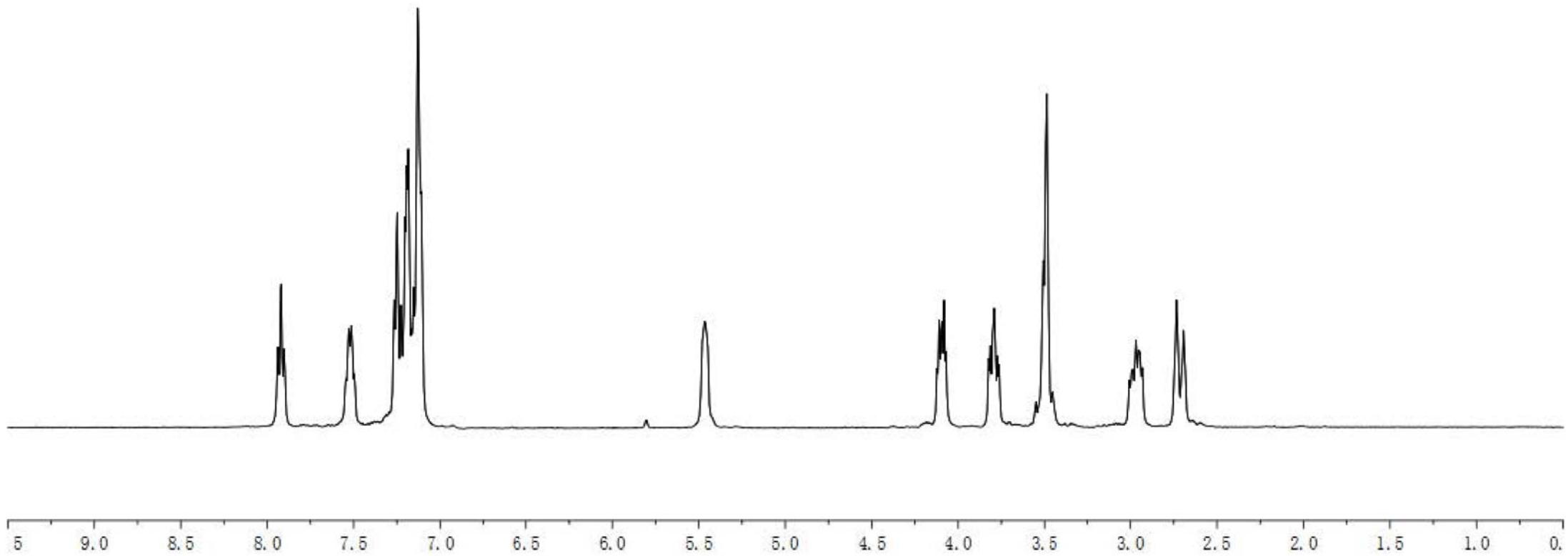
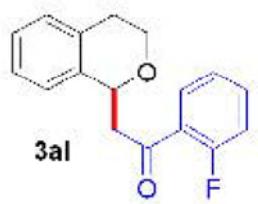
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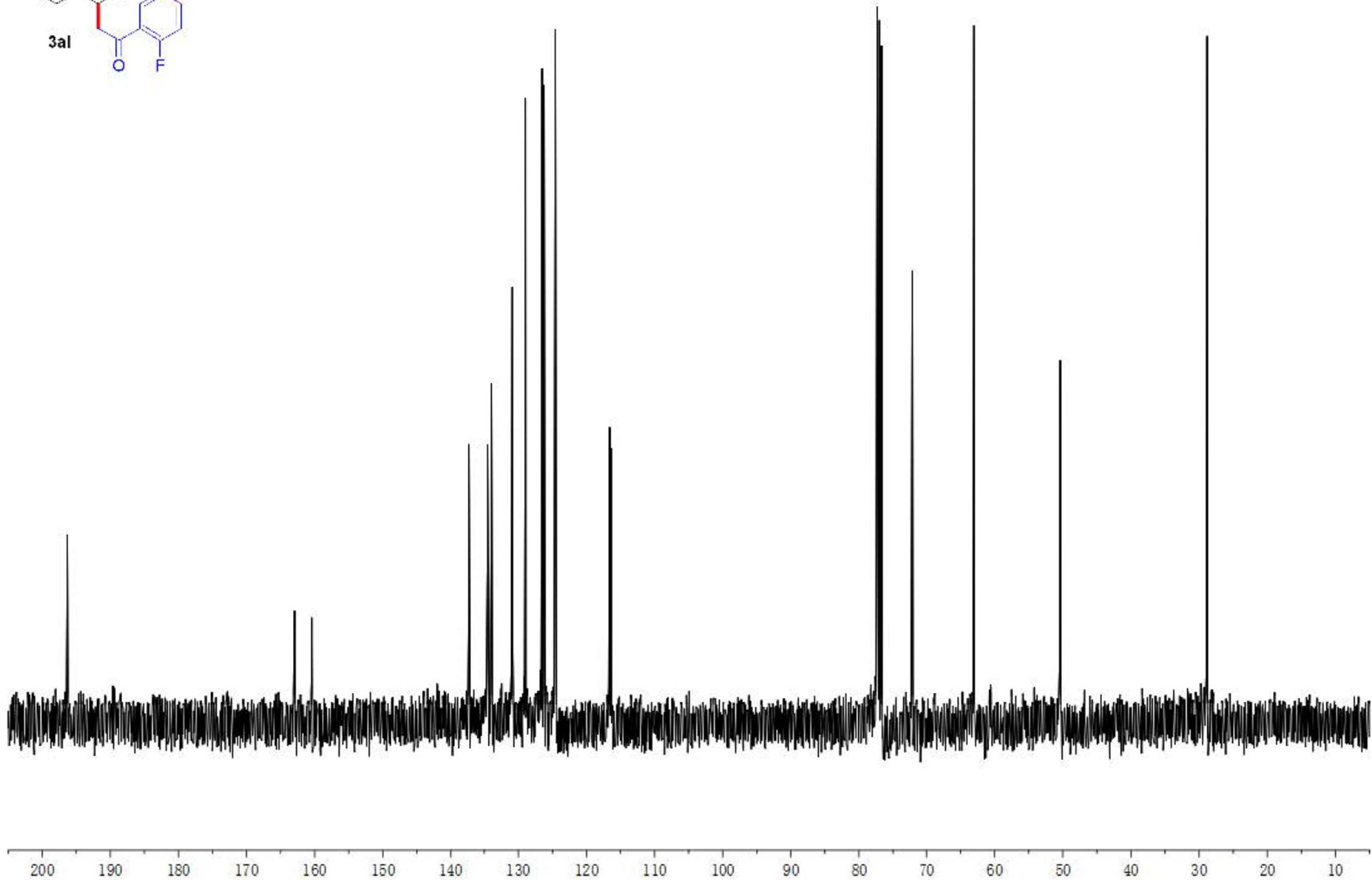
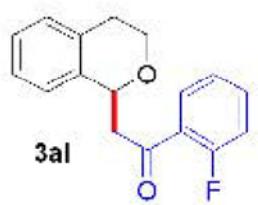


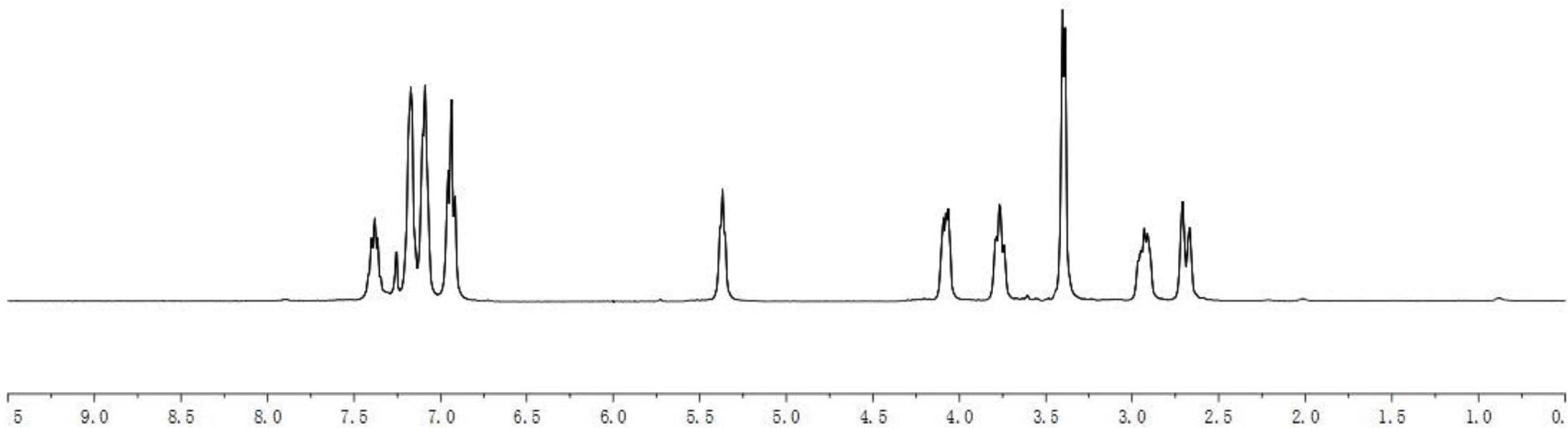
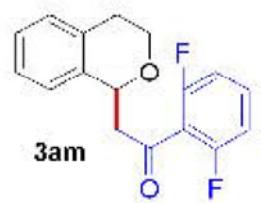


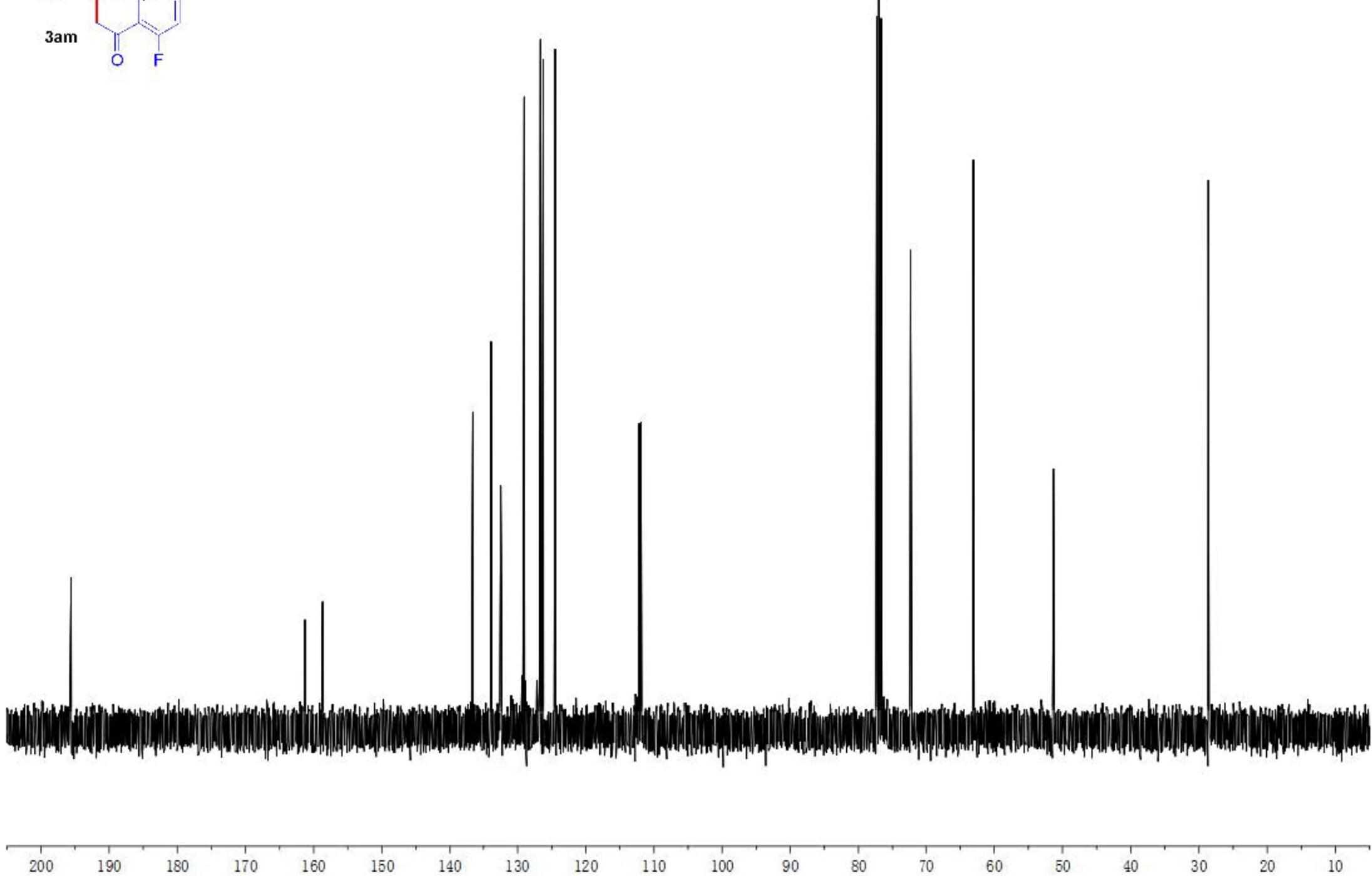
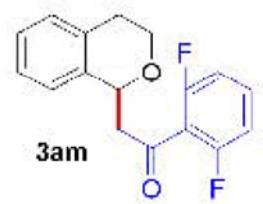


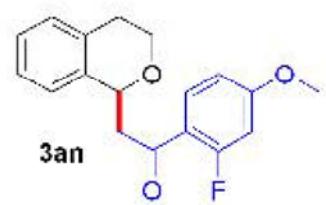




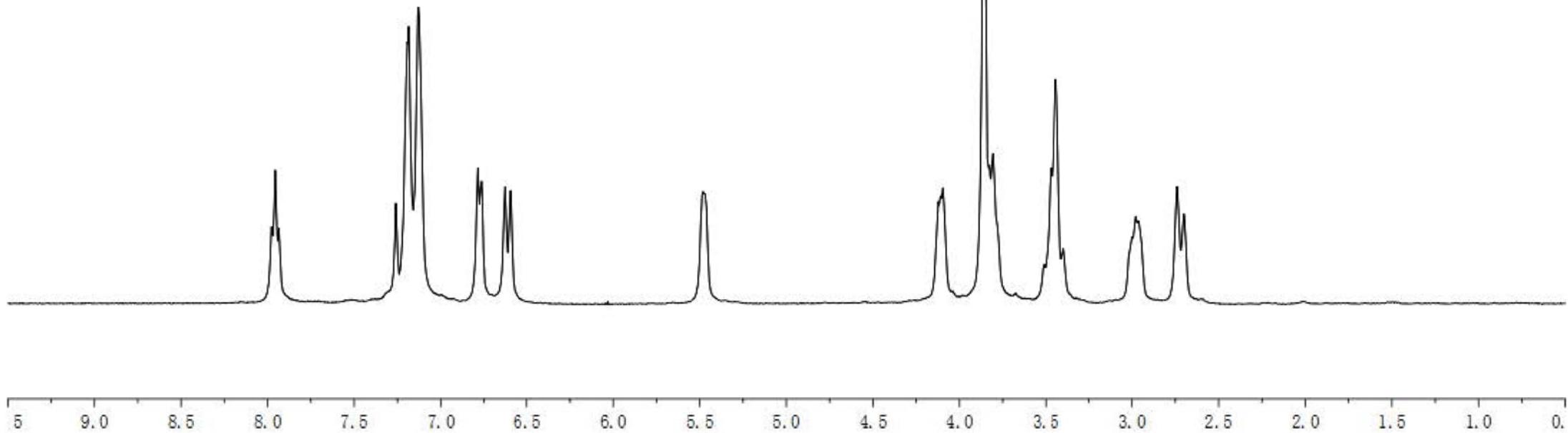


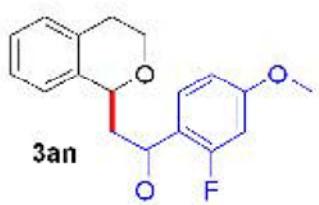




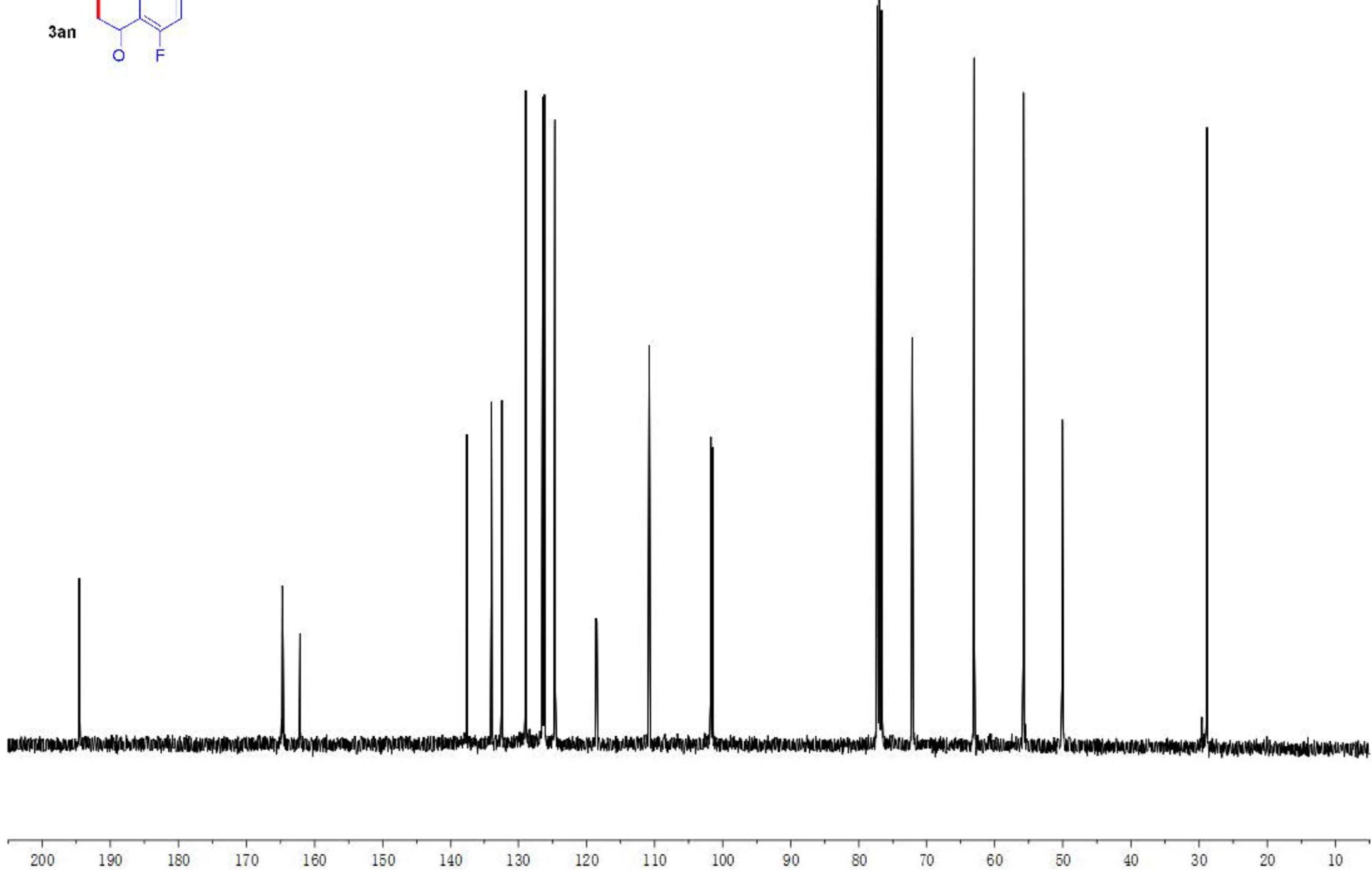


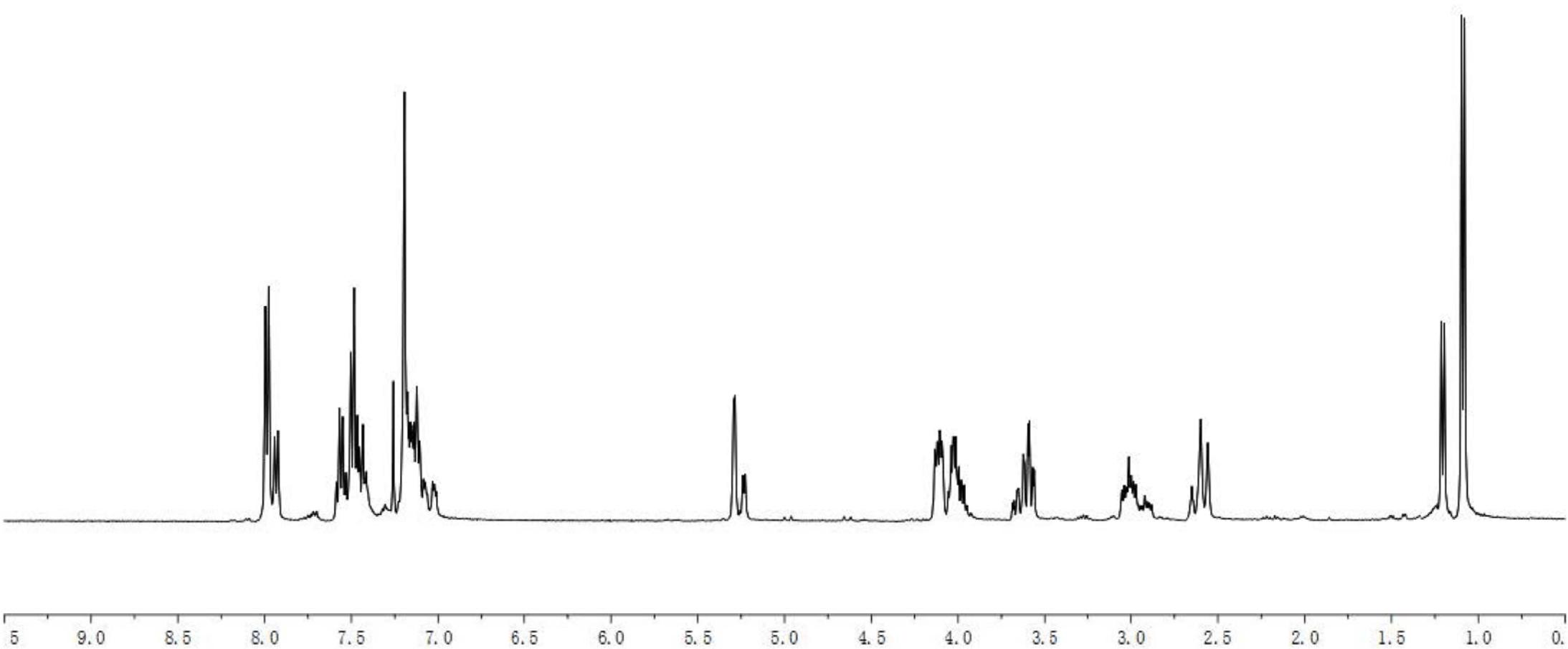
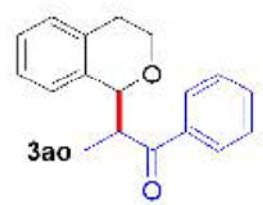
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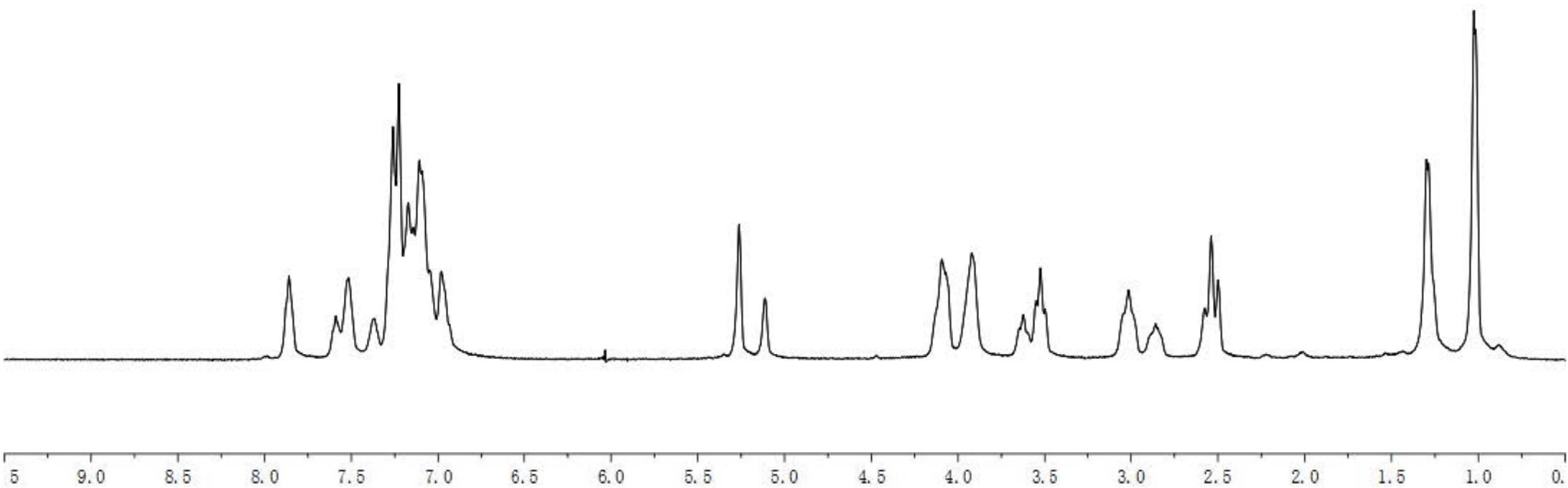
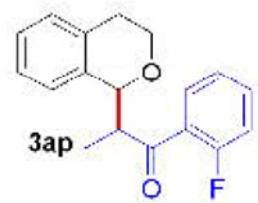


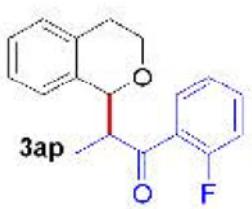


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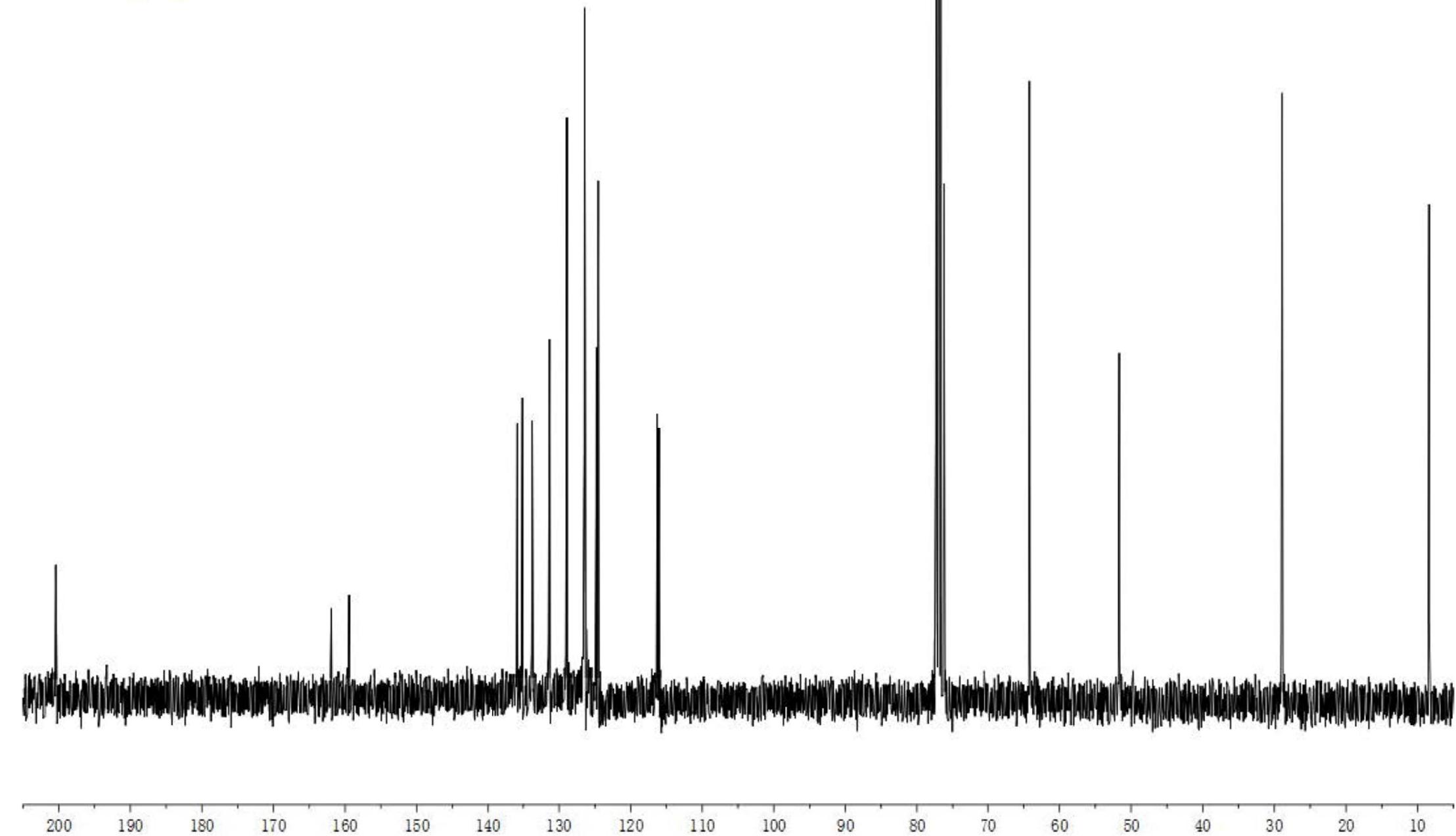


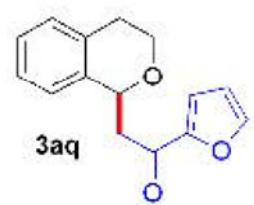




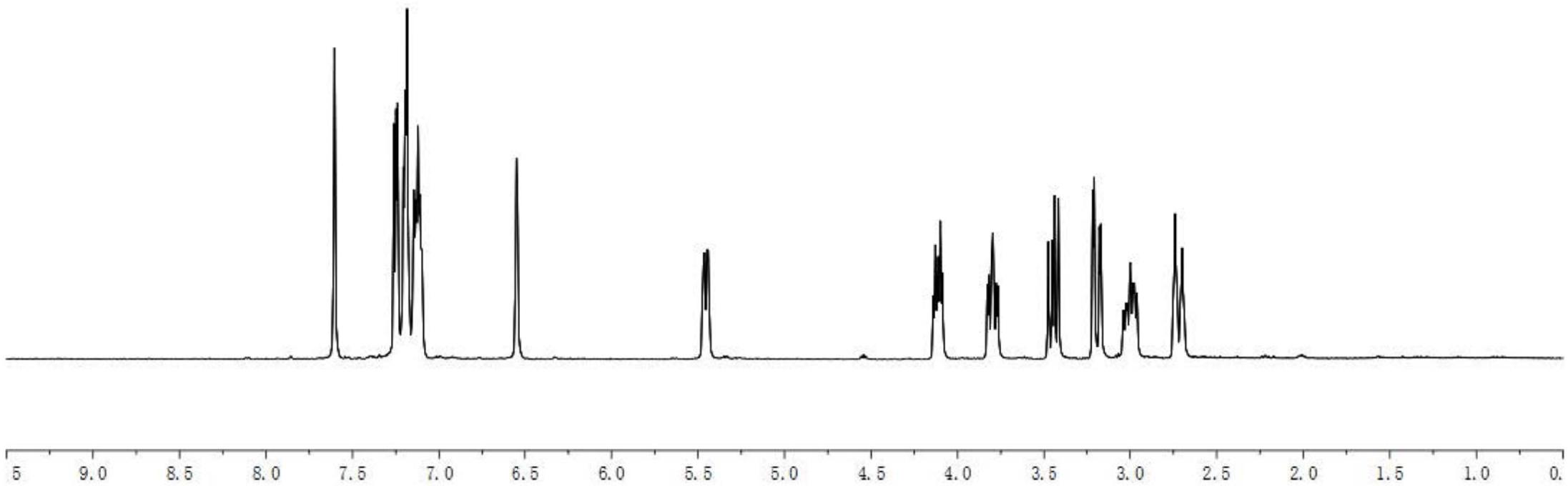


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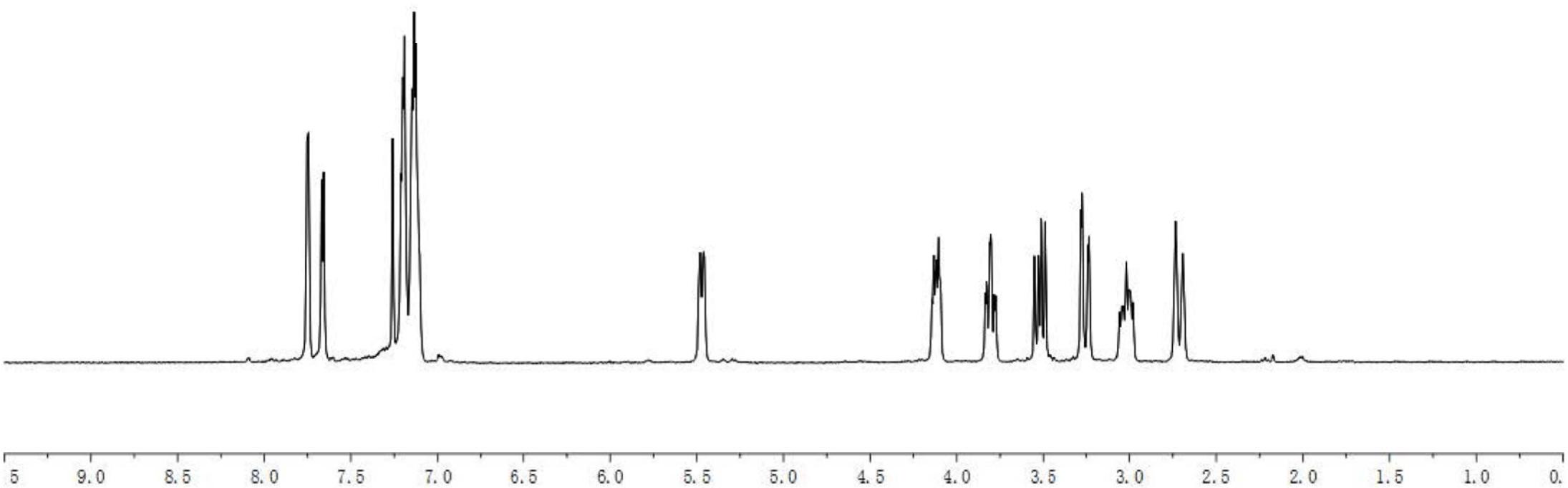


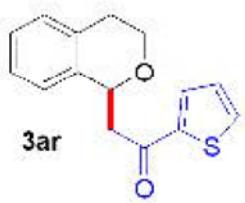
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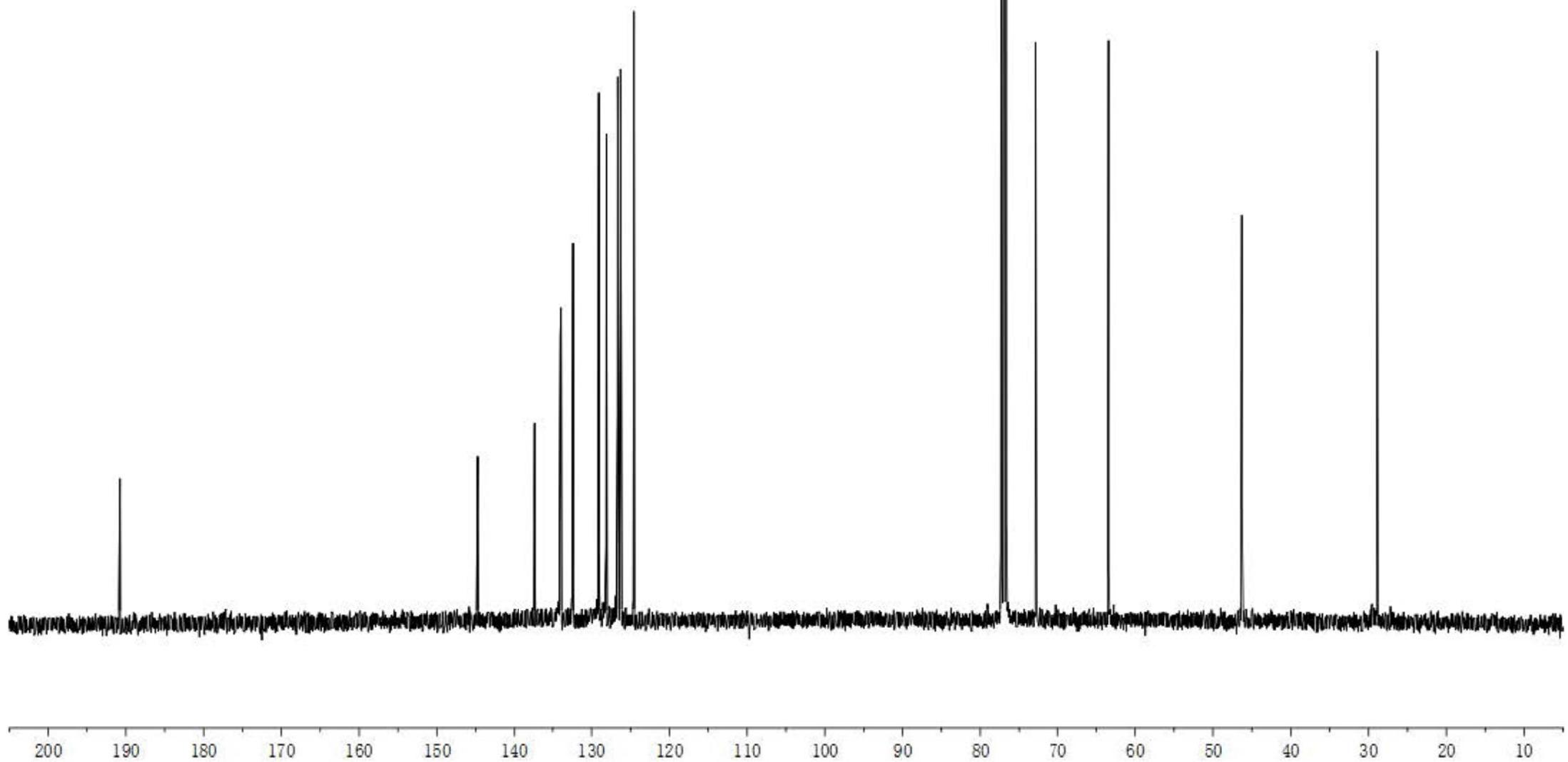


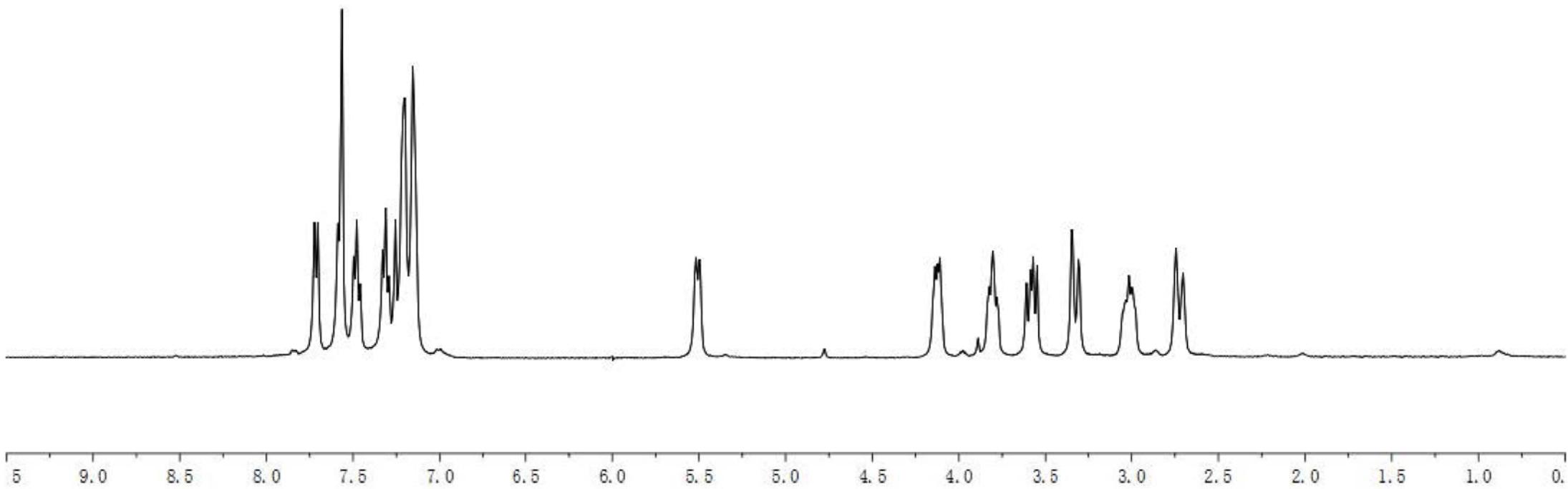
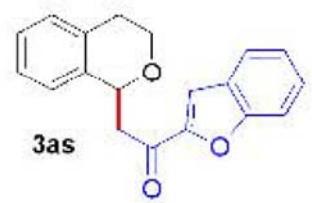
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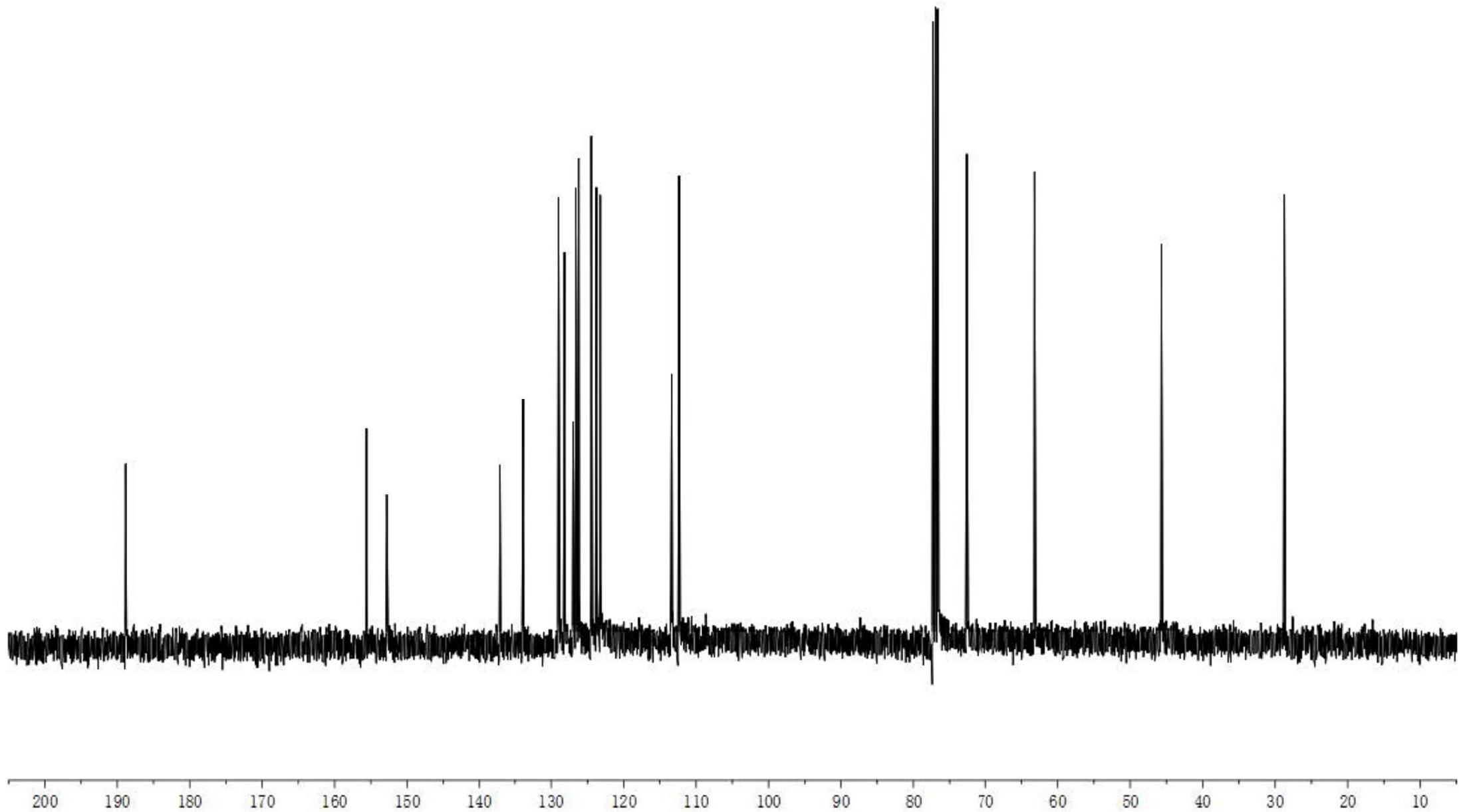
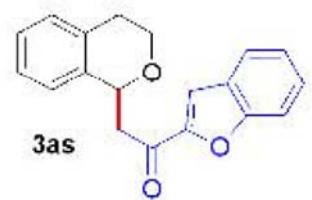


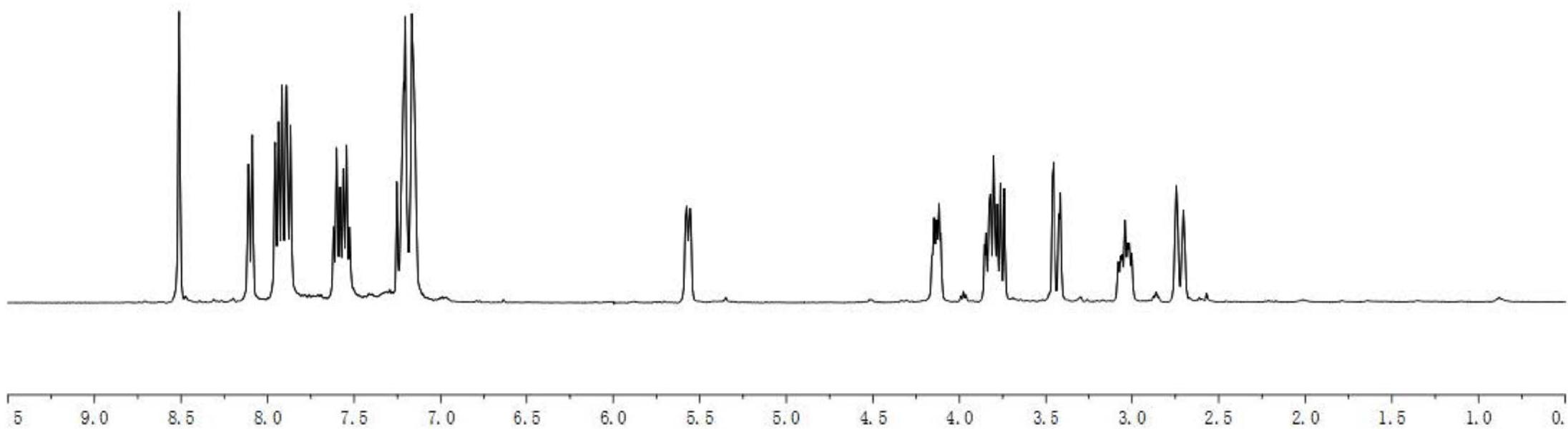
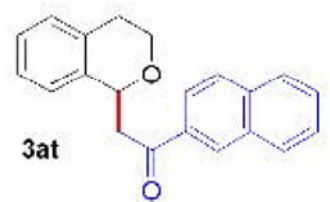


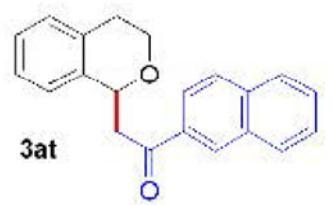
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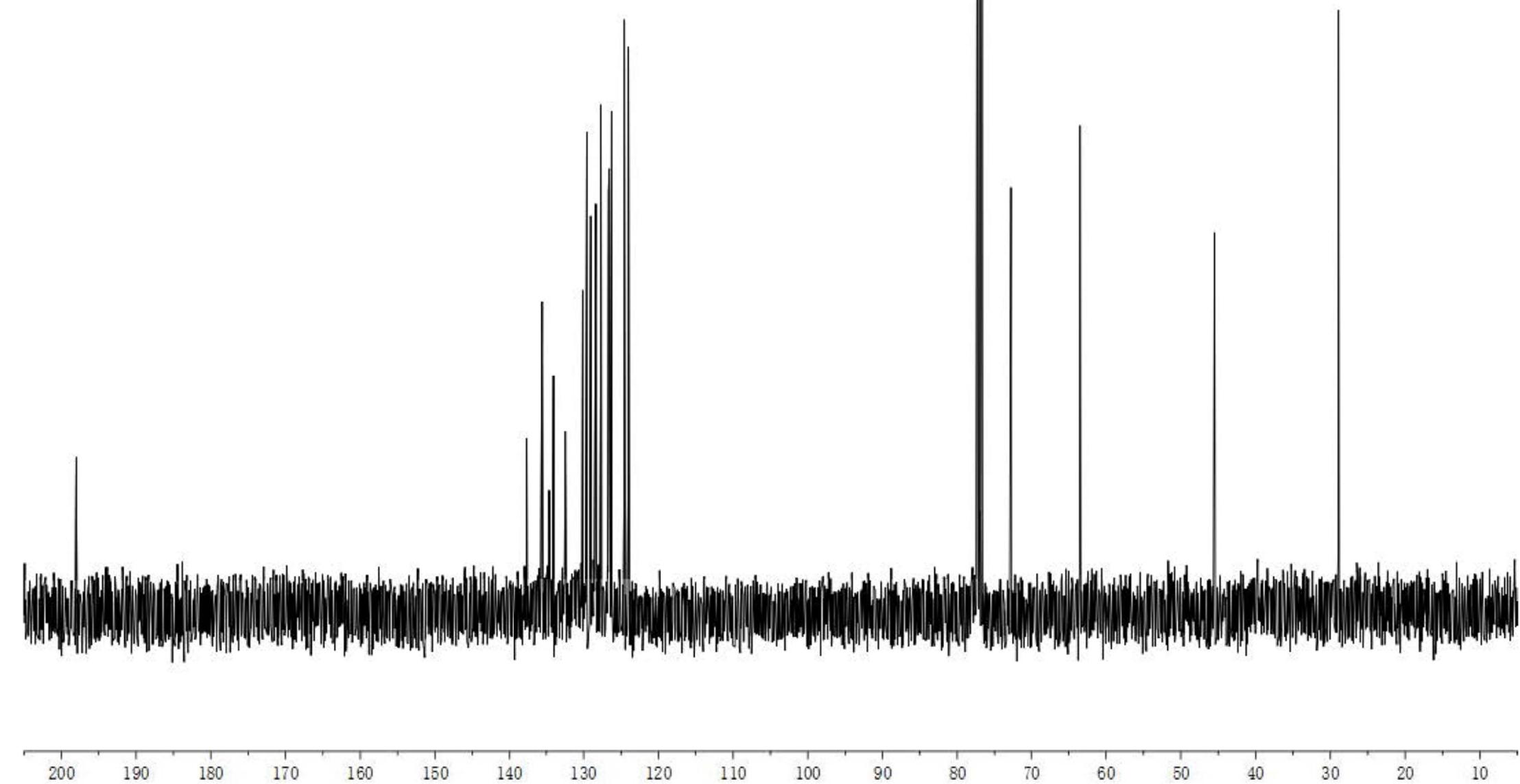


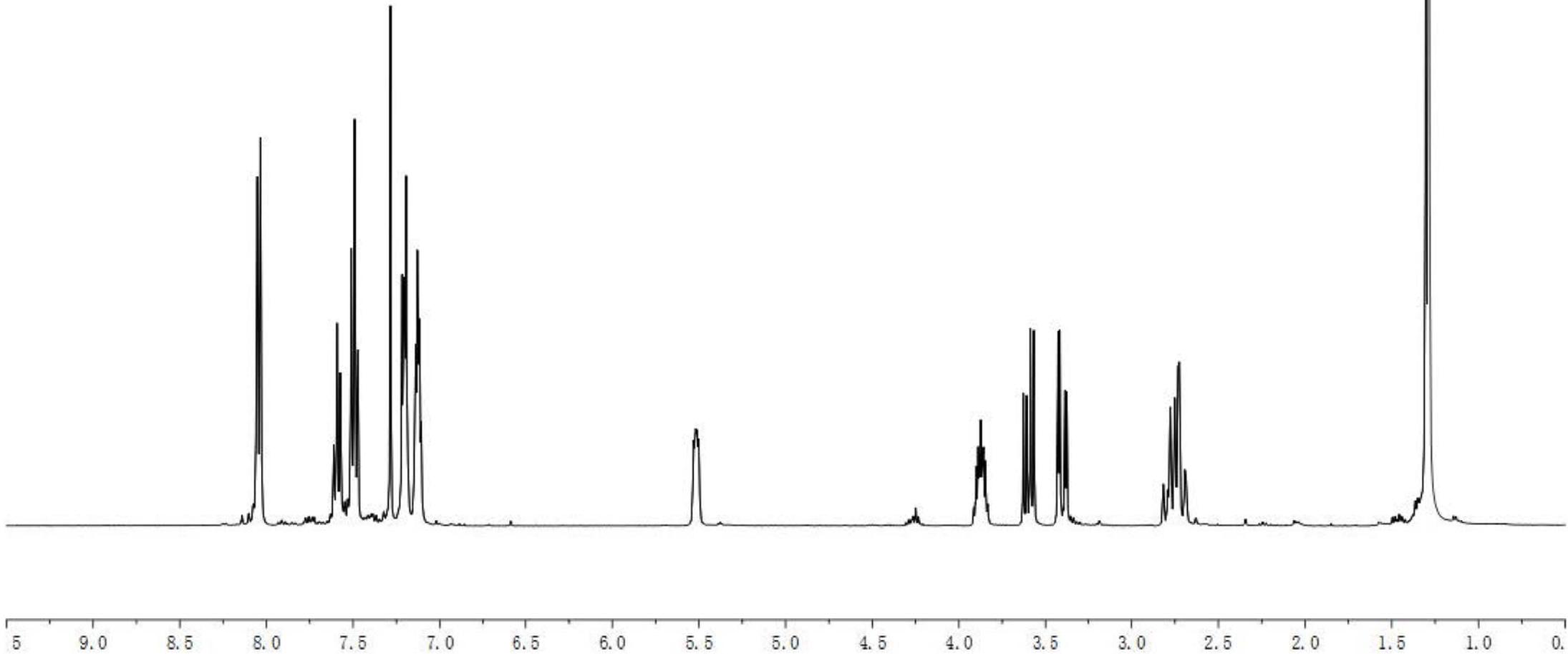
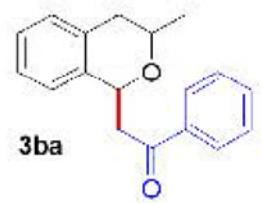


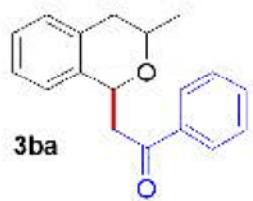




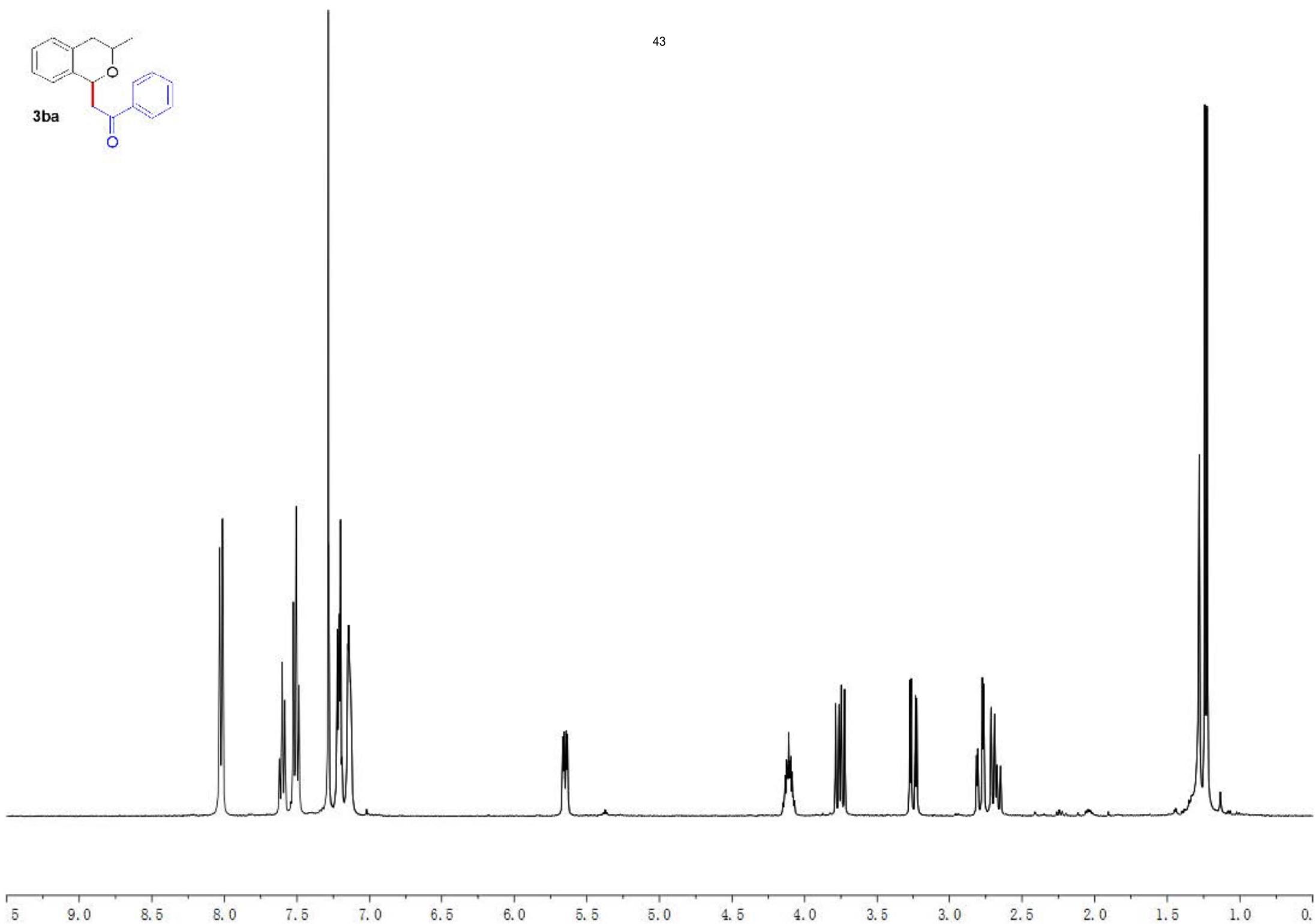
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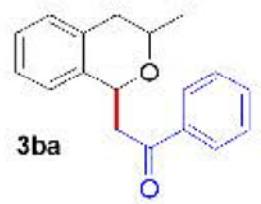




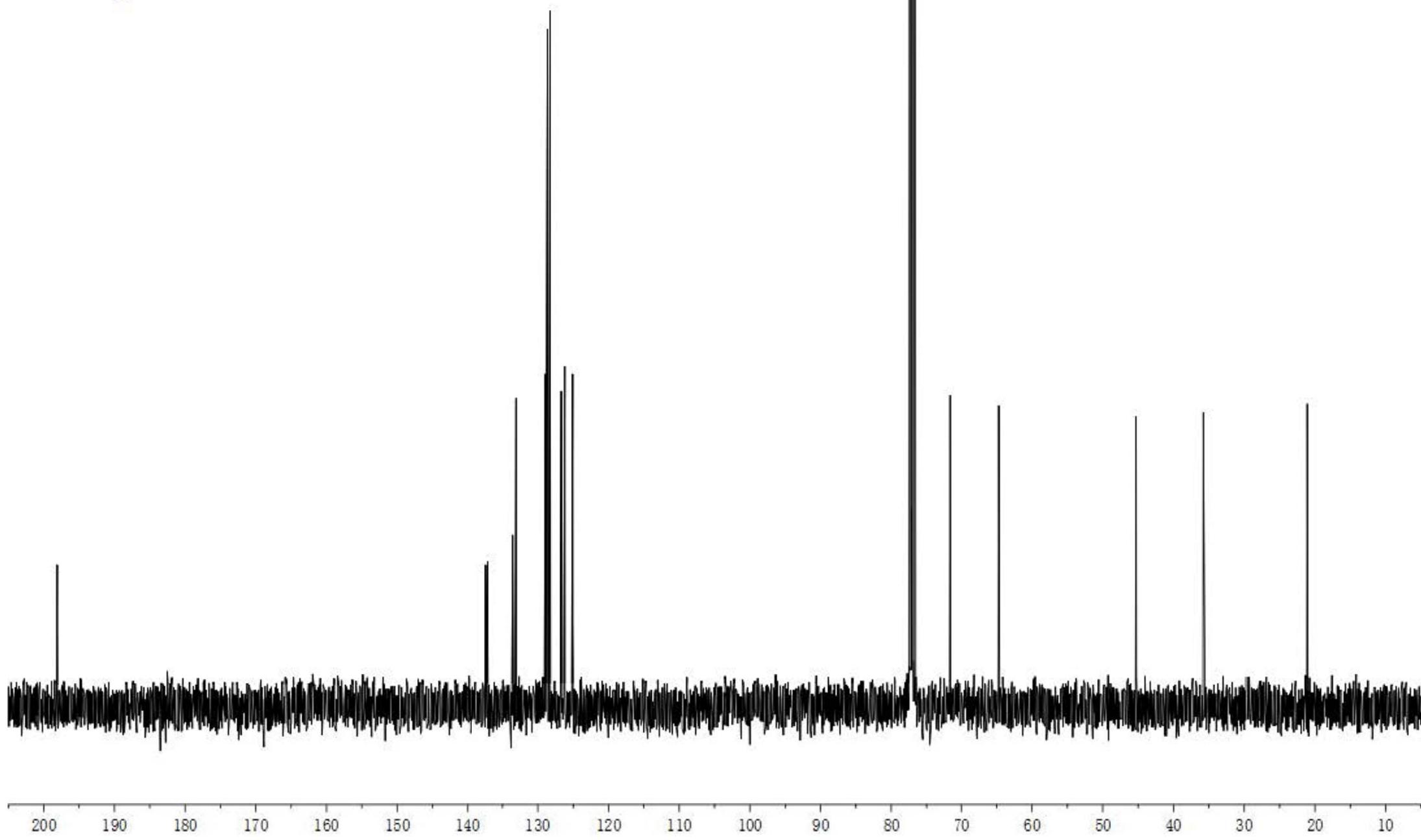


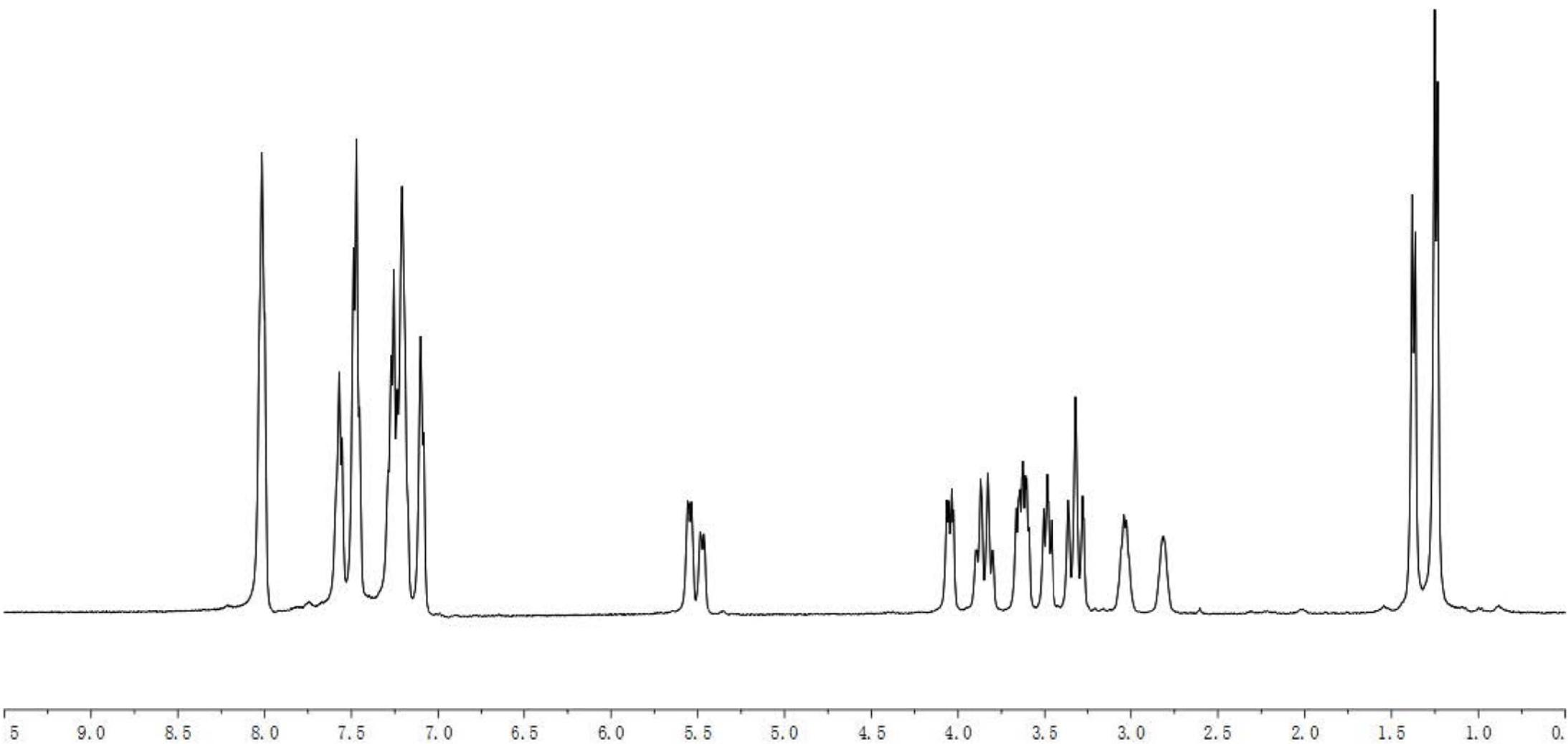
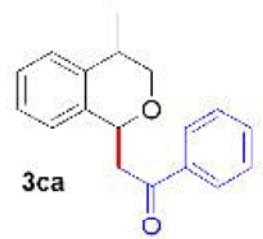
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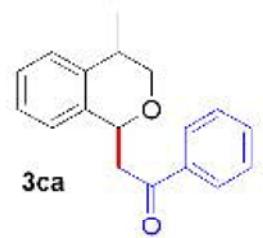




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3ca

