

Supplementary Information

Design, synthesis, and herbicidal activity of *sec-p*-menthane-7-amine derivatives as botanical herbicides

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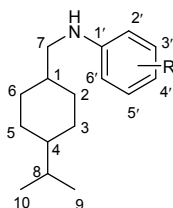
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Table S1 The preparation of *sec-p*-menthane-7-amine derivatives

Compd.	Yield (%)	Purity(%)	Compd.	Yield (%)	Purity(%)
3a	56.3	97.7	3n	81.1	95.6
3b	79.0	97.3	3o	95.5	96.6
3c	73.6	97.0	3p	93.6	97.0
3d	51.3	97.3	3q	95.8	96.6
3e	50.2	98.5	3r	94.0	98.9
3f	40.0	98.6	3s	71.5	98.6
3g	65.4	98.8	3t	92.2	95.4
3h	70.2	96.8	3u	91.6	96.5
3i	40.5	99.0	3v	92.7	94.9
3j	49.8	99.9	3w	98.1	99.9
3k	70.1	98.9	3x	94.3	97.0
3l	47.5	99.9	3y	80.3	98.6
3m	47.7	94.4			

2, *p*-menthane-7-aldehyde, colourless liquid, *cis*- and *trans*-isomers mixture. ¹H NMR (500 MHz, CDCl₃) δ (ppm): 9.65 (s, 1H, H-7), 9.55 (s, 1H, H-7'), 2.35 (d, *J* = 2.9 Hz, 1H, H-1), 2.13 – 2.09 (m, 3H, H-1, Ha-2', 6'), 1.95 (d, *J* = 12.4 Hz, 2H, Ha-3', 5'), 1.78 (d, *J* = 9.7 Hz, 2H, Ha-3, 5), 1.52 (t, *J* = 12.4 Hz, 4H, Ha-2, 6, He-2', 6'), 1.42 – 1.33 (m, 2H, H-8, 8'), 1.19 (d, *J* = 12.4 Hz, 2H, He-3' 5'), 0.99 (dd, *J* = 6.9, 6.4 Hz, 6H, H-4, 4', He-2,3,5,6), 0.82 (s, 3H, H-9), 0.81 (s, 3H, H-9'), 0.78 (s, 3H, H-10), 0.76 (s, 3H, H-10'). ¹³C NMR (126 MHz, CDCl₃) δ (ppm): 205.65 (C-7), 204.75 (C-7'), 50.54 (C-1), 47.03 (C-1'), 43.46 (C-4), 43.17 (C-4'), 32.68 (C-8), 31.98 (C-8'), 28.46 (C-3, 5), 26.38 (C-3', 5'), 26.13 (C-2, 6), 24.60 (C-2', 6'), 19.69 (C-9, 9', 10, 10'). FT-IR(ν /cm⁻¹): 2925, 2856 (s, ν_{C-H}); 1724 (s, $\nu_{C=O}$); 1448 (m, δ_{C-H}). HRMS (ESI) for C₁₀H₁₉O, calcd 155.1436, found 155.1438 [M+H]⁺.



3a, N-((4-isopropylcyclohexyl)methyl)aniline, light yellow oil. ¹H NMR (500 MHz, CDCl₃) δ (ppm): 7.24 (dd, *J* = 8.5, 7.4 Hz, 2H, H-3', 5'), 6.75 (t, *J* = 7.3 Hz, 1H, H-4'), 6.66 (d, *J* = 7.5 Hz, 2H, H-2', 6'), 3.76 (s, 1H, NH), 3.02 (d, *J* = 7.0 Hz, 2H, H-7), 1.95 (d, *J* = 8.7 Hz, 2H, Ha-3, 5), 1.83 (d, *J* = 9.0 Hz, 2H, Ha-2, 6), 1.64–1.55 (m, 1H, H-1), 1.50 (dd, *J* = 11.8, 6.8 Hz, 1H, H-8), 1.11–1.02 (m, 4H, He-2,3,5,6), 0.96 (s, 1H, H-4), 0.95 (s, 3H, H-9), 0.94 (s, 3H, H-10). ¹³C NMR (126 MHz, CDCl₃) δ (ppm): 148.70 (C-1'), 129.27 (C-3', 5'), 116.93 (C-4'), 112.67 (C-2', 6'), 50.67 (C-7), 44.27 (C-4), 37.84 (C-1), 32.94 (C-8), 31.52 (C-3, 5), 29.37 (C-2, 6), 19.93 (C-9, 10). FT-IR(ν /cm⁻¹): 3419 (w, ν_{N-H}); 3050 (w, ν_{C-H}); 2916, 2848 (m, ν_{C-H}); 1600, 1503, 1469, 1446 (s, $\nu_{C=C}$ of aromatic ring); 1319 (w, ν_{C-N}); 1257 (w, δ_{C-N}); 744, 689 (s, δ_{C-H}). HRMS (ESI) for C₁₆H₂₆N, calcd 232.2065, found 232.2066 [M+H]⁺.

3b, N-((4-isopropylcyclohexyl)methyl)-4-methylaniline, light yellow oil. ^1H NMR (500 MHz, CDCl_3) δ (ppm): 7.03 (d, $J=8.0$ Hz, 2H, H-3', 5'), 6.58 (d, $J=8.5$ Hz, 2H, H-2', 6'), 5.31 (s, 1H, NH), 2.98 (d, $J=6.5$ Hz, 2H, H-7), 2.29 (s, 3H, 4'- CH_3), 1.92 (d, $J=9.0$ Hz, 2H, Ha-3, 5), 1.80 (d, $J=9.0$ Hz, 2H, Ha-2, 6), 1.59–1.52 (m, 1H, H-1), 1.48 (dd, $J=11.9, 6.7$ Hz, 1H, H-8), 1.08–1.00 (m, 4H, He-2,3,5,6), 0.95 (d, $J=5.6$ Hz, 1H, H-4), 0.93 (s, 3H, H-9), 0.91 (s, 3H, H-10). ^{13}C NMR (126 MHz, CDCl_3) δ (ppm): 146.48 (C-1'), 129.77 (C-3',5'), 126.08 (C-4'), 112.88 (C-2',6'), 51.07 (C-7), 44.29 (C-4), 37.83 (C-1), 32.95 (C-8), 31.53 (C-3, 5), 29.38 (C-2, 6), 20.45 (4'- CH_3), 19.93 (C-9, 10). FT-IR(ν/cm^{-1}): 3414 (w, $\nu_{\text{N-H}}$); 2916, 2850 (m, $\nu_{\text{C-H}}$); 1618, 1518, 1470, 1446 (s, $\nu_{\text{C=C}}$ of aromatic ring); 1316 (w, $\nu_{\text{C-N}}$); 1253 (w, $\delta_{\text{C-N}}$); 803 (s, $\delta_{\text{C-H}}$). HRMS (ESI) for $\text{C}_{17}\text{H}_{28}\text{N}$, calcd 246.2222, found 246.2224 $[\text{M}+\text{H}]^+$.

3c, N-((4-isopropylcyclohexyl)methyl)-3-methylaniline, light yellow oil. ^1H NMR (500 MHz, CDCl_3) δ (ppm): 7.14 (t, $J=7.0$ Hz, 1H, H-5'), 6.59 (d, $J=7.5$ Hz, 1H, H-2'), 6.53–6.47 (t, $J=6.5$ Hz, 2H, H-4', 6'), 5.34 (s, 1H, NH), 3.02 (d, $J=6.5$ Hz, 2H, H-7), 2.37 (s, 3H, 3'- CH_3), 1.96 (d, $J=9.2$ Hz, 2H, Ha-3, 5), 1.84 (d, $J=8.9$ Hz, 2H, Ha-2, 6), 1.65–1.57 (m, 1H, H-1), 1.51 (dd, $J=11.8, 6.8$ Hz, 1H, H-8), 1.07 (dt, $J=12.3, 9.5$ Hz, 4H, He-2, 3, 5, 6), 0.98 (d, $J=5.4$ Hz, 1H, H-4), 0.96 (s, 3H, H-9), 0.95 (s, 3H, H-10). ^{13}C NMR (126 MHz, CDCl_3) δ (ppm): 148.77 (C-1'), 139.00 (C-3'), 129.16 (C-5'), 117.92 (C-4'), 113.48 (C-2'), 109.87 (C-6'), 50.72 (C-7), 44.29 (C-4), 37.89 (C-1), 32.96 (C-8), 31.54 (C-3, 5), 29.39 (C-2, 6), 21.74 (3'- CH_3), 19.94 (C-9, 10). FT-IR(ν/cm^{-1}): 3415 (w, $\nu_{\text{N-H}}$); 2915, 2848 (m, $\nu_{\text{C-H}}$); 1603, 1589, 1509, 1490 (s, $\nu_{\text{C=C}}$ of aromatic ring); 1326 (w, $\nu_{\text{C-N}}$); 1305 (w, $\delta_{\text{C-N}}$); 764, 690 (s, $\delta_{\text{C-H}}$). HRMS (ESI) for $\text{C}_{17}\text{H}_{28}\text{N}$, calcd 246.2222, found 246.2219 $[\text{M}+\text{H}]^+$.

3d, 3-fluoro-N-((4-isopropylcyclohexyl)methyl)aniline, light yellow oil. ^1H NMR (500 MHz, CDCl_3) δ (ppm): 7.09 (t, $J=8.0$ Hz, 1H, H-5'), 6.78 (dd, $J=7.8, 1.5$ Hz, 1H, H-2'), 6.72 (t, $J=2.0$ Hz, 1H, H-6'), 6.49 (dd, $J=8.2, 1.5$ Hz, 1H, H-4'), 3.85 (s, 1H, NH), 2.92 (d, $J=6.6$ Hz, 2H, H-7), 1.88 (d, $J=9.4$ Hz, 2H, Ha-3, 5), 1.78 (d, $J=8.9$ Hz, 2H, Ha-2, 6), 1.57–1.54 (m, 1H, H-1), 1.45 (dd, $J=11.8, 6.7$ Hz, 1H, H-8), 1.04–0.97 (m, 5H, He-2, 3, 5, 6, H-4), 0.89 (s, 3H, H-9), 0.88 (s, 3H, H-10). ^{13}C NMR (126 MHz, CDCl_3) δ (ppm): 165.21 (C-3'), 150.51 (C-1'), 130.24 (C-5'), 108.57 (C-6'), 103.27 (C-4'), 99.18 (C-2'), 50.51 (C-7), 44.19 (C-4), 37.75 (C-1), 32.75 (C-8), 31.42 (C-3, 5), 29.29 (C-2, 6), 19.87 (C-9, 10). FT-IR(ν/cm^{-1}): 3427 (w, $\nu_{\text{N-H}}$); 2919, 2849 (m, $\nu_{\text{C-H}}$); 1620, 1587, 1509, 1495 (s, $\nu_{\text{C=C}}$ of aromatic ring); 1334 (w, $\nu_{\text{C-N}}$); 1283 (w, $\delta_{\text{C-N}}$); 1175, 1147 (s, $\nu_{\text{C-F}}$); 754, 680 (s, $\delta_{\text{C-H}}$). HRMS (ESI) for $\text{C}_{16}\text{H}_{25}\text{FN}$, calcd. 250.1971, found 250.1968 $[\text{M}+\text{H}]^+$.

3e, 4-fluoro-N-((4-isopropylcyclohexyl)methyl)aniline, light yellow oil. ^1H NMR (500 MHz, CDCl_3) δ (ppm): 6.90 (t, $J=8.0$ Hz, 1H, H-2', 6'), 6.55 (dd, $J=7.8, 1.5$ Hz, 1H, H-3', 5'), 5.32 (s, 1H, NH), 2.94 (d, $J=6.6$ Hz, 2H, H-7), 1.90 (d, $J=9.4$ Hz, 2H, Ha-3, 5), 1.78 (d, $J=8.9$ Hz, 2H, Ha-2, 6), 1.60–1.52 (m, 1H, H-1), 1.46 (dd, $J=11.9, 6.6$ Hz, 1H, H-8), 1.05–0.99 (m, 5H, He-2, 3, 5, 6, H-4), 0.90 (s, 3H, H-9), 0.89 (s, 3H, H-10). ^{13}C NMR (126 MHz, CDCl_3) δ (ppm): 156.51 (C-4'), 145.06 (C-1'), 115.68 (C-2', 6'), 113.41 (C-3', 5'), 50.37 (C-7), 44.21 (C-4), 37.80 (C-1), 32.88 (C-8), 31.46 (C-3, 5), 29.31 (C-2, 6), 19.86 (C-9, 10). FT-IR(ν/cm^{-1}): 3424 (w, $\nu_{\text{N-H}}$); 2917, 2850 (m, $\nu_{\text{C-H}}$); 1612, 1580, 1470, 1447 (s, $\nu_{\text{C=C}}$ of aromatic ring); 1316 (w, $\nu_{\text{C-N}}$); 1257 (w, $\delta_{\text{C-N}}$); 1219 (s, $\nu_{\text{C-F}}$); 815 (s, $\delta_{\text{C-H}}$). HRMS (ESI) for $\text{C}_{16}\text{H}_{25}\text{FN}$, calcd. 250.1971, found 250.1969 $[\text{M}+\text{H}]^+$.

3f, 2-chloro-N-((4-isopropylcyclohexyl)methyl)aniline, light yellow oil. ^1H NMR (500 MHz, CDCl_3) δ (ppm): 7.30–7.25 (m, 1H, H-3'), 7.17 (dd, $J=11.7, 7.7$ Hz, 1H, H-5'), 6.68 (t, $J=8.7$ Hz, 1H, H-6'), 6.63 (t, $J=7.6$ Hz, 1H, H-4'), 5.33 (s, 1H, NH), 3.15 (d, $J=6.5$ Hz, 1H, Ha-7), 3.04 (d, $J=3.9$ Hz, 1H, He-7), 1.93 (d, $J=5.1$ Hz, 1H, Ha-3), 1.80 (d, $J=4.7$ Hz, 1H, Ha-5), 1.60 (dd, $J=11.2, 6.1$ Hz, 2H, Ha-2, 6), 1.54–1.49 (m, 1H, H-1), 1.45–1.39 (m, 1H, H-8), 1.19–1.14 (m, 1H, H-4), 1.07–1.02 (m, 4H, He-2, 3, 5, 6), 0.91 (t, $J=6.9$ Hz, 6H, H-9, 10). ^{13}C NMR (126 MHz, CDCl_3) δ (ppm): 144.30 (C-1'), 129.08 (C-3', 5'), 127.79 (C-4'), 116.64 (C-2'), 111.10 (C-6'), 50.27 (C-7), 44.17 (C-4), 37.60 (C-1), 32.88 (C-8), 31.41 (C-3), 29.27 (C-5), 27.56 (C-2), 25.61 (C-6), 20.31 (C-9), 19.87 (C-10). FT-IR(ν/cm^{-1}): 3425 (w, $\nu_{\text{N-H}}$); 2918, 2851 (m, $\nu_{\text{C-H}}$); 1597, 1511, 1459, 1431 (s, $\nu_{\text{C=C}}$ of aromatic ring); 1323 (w, $\nu_{\text{C-N}}$); 1290 (w, $\delta_{\text{C-N}}$); 1032 (s, $\nu_{\text{C-Cl}}$); 736 (s, $\delta_{\text{C-H}}$). HRMS (ESI) for $\text{C}_{16}\text{H}_{25}\text{ClN}$, calcd. 266.1676, found 266.1677 [$\text{M}+\text{H}$] $^+$.

3g, 3-chloro-N-((4-isopropylcyclohexyl)methyl)aniline, light yellow oil. ^1H NMR (500 MHz, CDCl_3) δ (ppm): 7.09 (t, $J=8.0$ Hz, 1H, H-5'), 6.67 (dd, $J=7.8, 1.5$ Hz, 1H, H-2'), 6.59 (t, $J=2.0$ Hz, 1H, H-4'), 6.48 (dd, $J=8.2, 1.5$ Hz, 1H, H-6'), 5.32 (s, 1H, NH), 2.96 (d, $J=6.6$ Hz, 2H, H-7), 1.90 (d, $J=9.4$ Hz, 2H, Ha-3, 5), 1.80 (d, $J=8.9$ Hz, 2H, Ha-2, 6), 1.60–1.53 (m, 1H, H-1), 1.47 (dd, $J=11.9, 6.8$ Hz, 1H, H-8), 1.08–0.98 (m, 4H, He-2, 3, 5, 6), 0.94 (d, $J=4.4$ Hz, 1H, H-4), 0.92 (s, 3H, H-9), 0.91 (s, 3H, H-10). ^{13}C NMR (126 MHz, CDCl_3) δ (ppm): 149.79 (C-1'), 135.02 (C-3'), 130.16 (C-5'), 116.64 (C-4'), 112.09 (C-2'), 111.02 (C-6'), 50.41 (C-7), 44.18 (C-4), 37.71 (C-1), 32.90 (C-8), 31.41 (C-3, 5), 29.28 (C-2, 6), 19.90 (C-9, 10). FT-IR(ν/cm^{-1}): 3422 (w, $\nu_{\text{N-H}}$); 2916, 2849 (m, $\nu_{\text{C-H}}$); 1595, 1574, 1501, 1485 (s, $\nu_{\text{C=C}}$ of aromatic ring); 1325 (w, $\nu_{\text{C-N}}$); 1086 (m, $\nu_{\text{C-Cl}}$); 759, 680 (s, $\delta_{\text{C-H}}$). HRMS (ESI) for $\text{C}_{16}\text{H}_{25}\text{ClN}$, calcd. 266.1676, found 266.1678 [$\text{M}+\text{H}$] $^+$.

3h, 4-chloro-N-((4-isopropylcyclohexyl)methyl)aniline, light yellow oil. ^1H NMR (500 MHz, CDCl_3) δ (ppm): 7.14 (d, $J=8.8$ Hz, 2H, H-3', 5'), 6.54 (d, $J=8.8$ Hz, 2H, H-2', 6'), 5.33 (s, 1H, NH), 2.95 (d, $J=6.7$ Hz, 2H, H-7), 1.90 (d, $J=8.9$ Hz, 2H, Ha-3, 5), 1.80 (d, $J=8.8$ Hz, 2H, Ha-2, 6), 1.59–1.44 (m, 2H, H-1, 8), 1.02 (dt, $J=11.4, 9.2$ Hz, 4H, He-2, 3, 5, 6), 0.93 (s, 1H, H-4), 0.92 (s, 3H, H-9), 0.90 (s, 3H, H-10). ^{13}C NMR (126 MHz, CDCl_3) δ (ppm): 147.23 (C-1'), 129.02 (C-3', 5'), 121.31 (C-4'), 113.67 (C-2', 6'), 50.73 (C-7), 44.19 (C-4), 37.73 (C-1), 32.90 (C-8), 31.43 (C-3, 5), 29.30 (C-2, 6), 19.90 (C-9, 10). FT-IR(ν/cm^{-1}): 3422 (w, $\nu_{\text{N-H}}$); 2916, 2849 (m, $\nu_{\text{C-H}}$); 1600, 1498, 1470, 1446 (s, $\nu_{\text{C=C}}$ of aromatic ring); 1315 (w, $\nu_{\text{C-N}}$); 1175 (w, $\delta_{\text{C-N}}$); 1093 (s, $\nu_{\text{C-Cl}}$); 811 (s, $\delta_{\text{C-H}}$). HRMS (ESI) for $\text{C}_{16}\text{H}_{25}\text{ClN}$, calcd. 266.1676, found 266.1674 [$\text{M}+\text{H}$] $^+$.

3i, 2-bromo-N-((4-isopropylcyclohexyl)methyl)aniline, light yellow oil. ^1H NMR (500 MHz, CDCl_3) δ (ppm): 7.41 (d, $J=7.9$ Hz, 1H, H-3'), 7.20–7.14 (m, 1H, H-5'), 6.63 (t, $J=8.3$ Hz, 1H, H-6'), 6.54 (t, $J=7.6$ Hz, 1H, H-4'), 5.30 (s, 1H, NH), 3.14–3.09 (t, $J=5.5$ Hz, 1H, Ha-7), 3.00 (t, $J=6.0$ Hz, 1H, He-7), 1.90 (d, $J=5.1$ Hz, 1H, Ha-3), 1.77 (d, $J=4.6$ Hz, 1H, Ha-5), 1.57 (dd, $J=11.1, 6.0$ Hz, 2H, Ha-2, 6), 1.51–1.45 (m, 1H, H-1), 1.44–1.37 (m, 1H, H-8), 1.17–1.11 (m, 1H, H-4), 1.02 (q, $J=10.5, 19$ Hz, 4H, He-2, 3, 5, 6), 0.88 (t, $J=6.8$ Hz, 6H, H-9, 10). ^{13}C NMR (126 MHz, CDCl_3) δ (ppm): 145.22 (C-1'), 132.35 (C-3', 5'), 128.46 (C-4'), 117.21 (C-2'), 111.21 (C-6'), 50.44 (C-7), 44.16 (C-4), 37.53 (C-1), 32.88 (C-8), 31.41 (C-3), 29.27 (C-5), 27.56 (C-2), 25.62 (C-6), 20.32 (C-9), 19.88 (C-10). FT-IR(ν/cm^{-1}): 3415 (w, $\nu_{\text{N-H}}$); 2917, 2850 (m, $\nu_{\text{C-H}}$); 1596, 1508, 1454 (s, $\nu_{\text{C=C}}$ of aromatic ring); 1321 (w, $\nu_{\text{C-N}}$); 1071 (s, $\nu_{\text{C-Br}}$); 736 (s, $\delta_{\text{C-H}}$). HRMS (ESI) for $\text{C}_{16}\text{H}_{25}\text{BrN}$, calcd. 310.1170, found 310.1174 [$\text{M}+\text{H}$] $^+$.

3j, 3-bromo-N-((4-isopropylcyclohexyl)methyl)aniline, light yellow oil. ¹H NMR (500 MHz, CDCl₃) δ (ppm): 7.00 (t, *J*=8.0 Hz, 1H, H-5'), 6.78 (dd, *J*=7.8, 1.5 Hz, 1H, H-2'), 6.72 (t, *J*=2.0 Hz, 1H, H-4'), 6.49 (dd, *J*=8.2, 1.5 Hz, 1H, H-6'), 3.78(s, 1H, NH), 2.92 (d, *J*=6.6 Hz, 2H, H-7), 1.87 (d, *J*=9.4 Hz, 2H, Ha-3, 5), 1.77 (d, *J*=8.9 Hz, 2H, Ha-2, 6), 1.56–1.52 (m, 1H, H-1), 1.44–1.40 (m, 1H, H-8), 1.06–0.94 (m, 5H, He-2, 3, 5, 6, H-4), 0.92 (s, 3H, H-9), 0.87 (s, 3H, H-10). ¹³C NMR (126 MHz, CDCl₃) δ (ppm): 149.93 (C-1'), 130.45 (C-3'), 123.34 (C-5'), 119.56 (C-4'), 115.02 (C-2'), 111.41 (C-6'), 50.39 (C-7), 44.18 (C-4), 37.74 (C-1), 32.88 (C-8), 31.41 (C-3, 5), 29.28 (C-2, 6), 19.89 (C-9, 10). FT-IR(*ν*/cm⁻¹): 3422 (w, *ν*_{N-H}); 2953, 2916, 2848 (m, *ν*_{C-H}); 1593, 1571, 1498, 1481 (s, *ν*_{C=C of aromatic ring}); 1323 (w, *ν*_{C-N}); 984 (s, *ν*_{C-Br}); 757, 679 (s, *δ*_{C-H}). HRMS (ESI) for C₁₆H₂₅BrN, calcd. 310.1170, found 310.1173 [M+H]⁺.

3k, N-((4-isopropylcyclohexyl)methyl)-4-methoxyaniline, light yellow oil. ¹H NMR (500 MHz, CDCl₃) δ (ppm): 6.82 (d, *J*=8.9 Hz, 2H, C-2', 5'), 6.61 (d, *J*=8.9 Hz, 2H, C-3', 6'), 3.78 (s, 3H, 4'-OCH₃), 2.94 (d, *J*=6.6 Hz, 2H, H-7), 1.91 (d, *J*=8.3 Hz, 2H, Ha-3, 5), 1.79 (d, *J*=6.2 Hz, 2H, Ha-2, 6), 1.54 (dd, *J*=8.0, 4.7 Hz, 1H, H-1), 1.51–1.43 (m, 1H, H-8), 1.10–0.98 (m, 5H, He-2, 3, 5, 6, H-4), 0.91 (s, 3H, H-9), 0.90 (s, 3H, H-10). ¹³C NMR (126 MHz, CDCl₃) δ (ppm): 151.81 (C-4'), 143.03 (C-1'), 114.91 (C-3', 5'), 113.92 (C-2', 6'), 55.85 (4'-OCH₃), 51.69 (C-7), 44.25 (C-4), 37.83 (C-1), 32.92 (C-8), 31.51 (C-3, 5), 29.35 (C-2, 6), 19.89(C-9, 10). FT-IR(*ν*/cm⁻¹): 3406 (w, *ν*_{N-H}); 2915, 2848 (m, *ν*_{C-H}); 1618, 1510, 1464 (s, *ν*_{C=C of aromatic ring}); 1232 (s, *ν*_{C-N}); 1037 (s, *ν*_{C-O}); 815 (s, *δ*_{C-H}). HRMS (ESI) for C₁₇H₂₈NO, calcd. 262.2171, found 262.2170 [M+H]⁺.

3l, N-((4-isopropylcyclohexyl)methyl)-3-(trifluoromethoxy)aniline, light yellow oil. ¹H NMR (500 MHz, CDCl₃) δ (ppm): 7.13 (t, *J*=8.2 Hz, 1H, H-5'), 6.50 (dd, *J*=14.9, 8.6 Hz, 2H, H-2', 6'), 3.86 (s, 1H, NH), 2.94 (d, *J*=6.6 Hz, 2H, H-7), 1.87 (d, *J*=9.4 Hz, 2H, Ha-3, 5), 1.77 (d, *J*=8.9 Hz, 2H, Ha-2, 6), 1.56–1.51 (m, 1H, H-1), 1.44 (dd, *J*=13.4, 5.1 Hz, 1H, H-8), 1.04–0.98 (m, 5H, He-2, 3, 5, 6, H-4), 0.88 (s, 3H, H-9), 0.87 (s, 3H, H-10). ¹³C NMR (126 MHz, CDCl₃) δ (ppm): 150.94 (C-3'), 150.42 (C-1'), 130.44 (OCF₃), 111.32 (C-2', 6'), 108.91 (C-5'), 104.98 (C-4'), 50.82 (C-7), 44.55 (C-4), 38.15 (C-1), 33.24 (C-8), 31.78 (C-3, 5), 29.65 (C-2, 6), 20.21 (C-9, 10). FT-IR(*ν*/cm⁻¹): 3432 (w, *ν*_{N-H}); 2919, 2852 (m, *ν*_{C-H}); 1614, 1587, 1510 (m, *ν*_{C=C of aromatic ring}); 1248, 1215 (s, *ν*_{C-O}); 1152 (s, *ν*_{C-N}); 699 (m, *δ*_{C-H}). HRMS (ESI) for C₁₇H₂₅F₃NO, calcd. 316.1888, found 316.1888 [M+H]⁺.

3m, N-((4-isopropylcyclohexyl)methyl)-4-(trifluoromethoxy)aniline, light yellow oil. ¹H NMR (500 MHz, CDCl₃) δ (ppm): 7.05 (d, *J*=8.7 Hz, 2H, H-2', 6'), 6.56 (d, *J*=8.9 Hz, 2H, H-3', 5'), 3.80 (s, 1H, NH), 2.96 (d, *J*=6.6 Hz, 2H, H-7), 1.90 (d, *J*=9.4 Hz, 2H, Ha-3, 5), 1.79 (d, *J*=8.9 Hz, 2H, Ha-2, 6), 1.54–1.52 (m, 1H, H-1), 1.46 (dd, *J*=11.8, 6.7 Hz, 1H, H-8), 1.06–0.99 (m, 5H, He-2, 3, 5, 6, H-4), 0.91 (s, 3H, H-9), 0.89 (s, 3H, H-10). ¹³C NMR (126 MHz, CDCl₃) δ (ppm): 147.42 (C-1', 4'), 140.05 (OCF₃), 122.40 (C-3', 5'), 112.69 (C-2', 6'), 50.79 (C-7), 44.19 (C-4), 37.75 (C-1), 32.87 (C-8), 31.42 (C-3, 5), 29.27 (C-2, 6), 19.84 (C-9, 10). FT-IR(*ν*/cm⁻¹): 3436 (w, *ν*_{N-H}); 2920, 2852 (m, *ν*_{C-H}); 1612, 1513, 1471 (s, *ν*_{C=C of aromatic ring}); 1248, 1190 (s, *ν*_{C-O}); 1154 (s, *ν*_{C-N}); 826 (m, *δ*_{C-H}). HRMS (ESI) for C₁₇H₂₅F₃NO, calcd. 316.1888, found 316.1889 [M+H]⁺.

3n, N-((4-isopropylcyclohexyl)methyl)butan-1-amine, light yellow oil. ¹H NMR (500 MHz, CDCl₃) δ (ppm): 2.56–2.50 (t, *J*=7.2 Hz, 2H, H-1'), 2.39 (d, *J*=6.7 Hz, 2H, H-7), 1.93 (s, 1H, NH), 1.75 (d, *J*=11.9 Hz, 2H, Ha-3, 5), 1.67 (d, *J*=8.7 Hz, 2H, Ha-2, 6), 1.42 (dd, *J*=14.9, 7.7 Hz, 4H, H-2', 3'), 1.39–1.33 (m,

1H, H-1), 1.29 (dd, $J=14.8, 7.2$ Hz, 1H, H-8), 0.96-0.91 (m, 5H, He-2, 3, 5, 6, H-4), 0.87 (t, $J=7.3$ Hz, 3H, H-4'), 0.82 (s, 3H, H-9), 0.80 (s, 3H, H-10). ^{13}C NMR (126 MHz, CDCl_3) δ (ppm): 56.79 (C-7), 49.87 (C-1'), 44.25 (C-4), 38.00 (C-1), 32.88 (C-8), 32.14 (C-2'), 31.58 (C-3, 5), 29.36 (C-2, 6), 20.50 (C-3'), 19.81 (C-9, 10), 13.99 (C-4'). FT-IR(ν/cm^{-1}): 2955, 2915, 2850 (s, $\nu_{\text{C-H}}$); 1461, 1447 (s, $\delta_{\text{C-H}}$ of aliphatic chain); 1338 (m, $\nu_{\text{C-N}}$); 1129 (m, $\delta_{\text{C-N}}$); 733 (s, $\nu_{\text{C-C}}$). HRMS (ESI) for $\text{C}_{14}\text{H}_{30}\text{N}$, calcd. 212.2378, found 212.2375 $[\text{M}+\text{H}]^+$.

3o, N-((4-isopropylcyclohexyl)methyl)pentan-1-amine, light yellow oil. ^1H NMR (500 MHz, CDCl_3) δ (ppm): 2.56–2.51 (t, $J=7.2$ Hz, 2H, H-1'), 2.39 (d, $J=6.7$ Hz, 2H, H-7), 1.94 (s, 1H, NH), 1.76 (d, $J=12.0$ Hz, 2H, Ha-3, 5), 1.68 (d, $J=7.7$ Hz, 2H, Ha-2, 6), 1.49–1.41 (m, 2H, H-2'), 1.40–1.33 (m, 1H, H-1), 1.29-1.24 (m, 5H, H-8, 3', 4'), 0.96-0.92 (m, 5H, He-2, 3, 5, 6, H-4), 0.86 (t, $J=6.4$ Hz, 3H, H-5'), 0.82 (s, 3H, H-9), 0.81 (s, 3H, H-10). ^{13}C NMR (126 MHz, CDCl_3) δ (ppm): 56.78 (C-7), 50.18 (C-1'), 44.26 (C-4), 37.99 (C-1), 32.88 (C-8), 31.58 (C-3, 5), 29.69 (C-2'), 29.59 (C-3'), 29.37 (C-2, 6), 22.61 (C-4'), 19.81 (C-9, 10), 14.03 (C-5'). FT-IR(ν/cm^{-1}): 2954, 2917, 2851 (s, $\nu_{\text{C-H}}$); 1447 (s, $\delta_{\text{C-H}}$ of aliphatic chain); 1383 (w, $\delta_{\text{C-N}}$); 1128 (m, $\nu_{\text{C-N}}$); 729 (m, $\nu_{\text{C-C}}$). HRMS (ESI) for $\text{C}_{15}\text{H}_{32}\text{N}$, calcd. 226.2535, found 226.2532 $[\text{M}+\text{H}]^+$.

3p, N-((4-isopropylcyclohexyl)methyl)hexan-1-amine, light yellow oil. ^1H NMR (500 MHz, CDCl_3) δ (ppm): 2.53 (t, $J=7.2$ Hz, 2H, H-1'), 2.39 (d, $J=6.7$ Hz, 2H, H-7), 1.76 (d, $J=12.3$ Hz, 2H, Ha-3, 5), 1.69 (d, $J=8.1$ Hz, 2H, Ha-2, 6), 1.45–1.41 (m, 2H, H-2'), 1.38-1.35 (m, 1H, H-1), 1.26 (s, 7H, H-8, 3', 4', 5'), 1.19 (s, 1H, NH), 0.96-0.89 (m, 5H, He-2, 3, 5, 6, H-4), 0.86 (t, $J=6.1$ Hz, 3H, H-6'), 0.83 (s, 3H, H-9), 0.81 (s, 3H, H-10). ^{13}C NMR (126 MHz, CDCl_3) δ (ppm): 56.95 (C-7), 50.37 (C-1'), 44.38 (C-4), 38.15 (C-1), 33.00 (C-8), 31.91 (C-4'), 31.71 (C-3, 5), 30.16 (C-2'), 29.49 (C-2, 6), 27.20 (C-3'), 22.73 (C-5'), 19.93 (C-9, 10), 14.14 (C-6'). FT-IR(ν/cm^{-1}): 2954, 2918, 2851 (s, $\nu_{\text{C-H}}$); 1447 (s, $\delta_{\text{C-H}}$ of aliphatic chain); 1366 (w, $\delta_{\text{C-N}}$); 1129 (m, $\nu_{\text{C-N}}$); 725 (m, $\nu_{\text{C-C}}$). HRMS (ESI) for $\text{C}_{16}\text{H}_{34}\text{N}$, calcd. 240.2691, found 240.2692 $[\text{M}+\text{H}]^+$.

3q, N-((4-isopropylcyclohexyl)methyl)heptan-1-amine, light yellow oil. ^1H NMR (500 MHz, CDCl_3) δ (ppm): 2.57-2.51 (m 2H, H-1'), 2.40 (d, $J=6.7$ Hz, 2H, H-7), 1.77 (d, $J=11.8$ Hz, 2H, Ha-3, 5), 1.69 (d, $J=7.8$ Hz, 2H, Ha-2, 6), 1.48–1.41 (m, 3H, H-1, 2'), 1.41–1.33 (m, 1H, H-8), 1.26 (s, 9H, H-4, 3', 4', 5', 6'), 1.00–0.89 (m, 4H, He-2, 3, 5, 6), 0.86 (t, $J=6.1$ Hz, 3H, H-7'), 0.83 (s, 3H, H-9), 0.82 (s, 3H, H-10). ^{13}C NMR (126 MHz, CDCl_3) δ (ppm): 57.07 (C-7), 50.46 (C-1'), 44.42 (C-4), 38.30 (C-1), 33.03 (C-8), 31.96 (C-5'), 31.75 (C-3, 5), 30.34 (C-2'), 29.53 (C-2, 6), 29.39 (C-4'), 27.51 (C-3'), 22.74 (C-6'), 19.96 (C-9, 10), 14.19 (C-7'). FT-IR(ν/cm^{-1}): 2954, 2919, 2805 (s, $\nu_{\text{C-H}}$); 1448 (s, $\delta_{\text{C-H}}$ of aliphatic chain); 1366 (w, $\delta_{\text{C-N}}$); 1129 (m, $\nu_{\text{C-N}}$); 724 (m, $\nu_{\text{C-C}}$). HRMS (ESI) for $\text{C}_{17}\text{H}_{36}\text{N}$, calcd. 254.2848, found 254.2847 $[\text{M}+\text{H}]^+$.

3r, N-((4-isopropylcyclohexyl)methyl)octan-1-amine, light yellow oil. ^1H NMR (500 MHz, CDCl_3) δ (ppm): 2.56 (t, $J=7.2$ Hz, 2H, H-1'), 2.42 (d, $J=6.7$ Hz, 2H, H-7), 1.79 (d, $J=11.5$ Hz, 2H, Ha-3, 5), 1.72 (d, $J=9.6$ Hz, 2H, Ha-2, 6), 1.47-1.42 (m, 3H, H-1, H-2'), 1.42-1.38 (m, 1H, H-8), 1.28 (s, 11H, H-4, 3', 4', 5', 6', 7'), 1.02–0.91 (m, 4H, He-2, 3, 5, 6), 0.89 (t, $J=6.7$ Hz, 3H, H-8'), 0.86 (s, 3H, H-9), 0.84 (s, 3H, H-10). ^{13}C NMR (126 MHz, CDCl_3) δ (ppm): 56.93 (C-7), 50.32 (C-1'), 44.31 (C-4), 38.15 (C-1), 32.92 (C-8), 31.85 (C-5'), 31.64 (C-3, 5), 30.18 (C-2'), 29.42 (C-2, 6), 29.29 (C-3'), 27.44 (C-6'), 22.67 (C-7'), 19.85 (C-9, 10), 14.10 (C-8'). FT-IR(ν/cm^{-1}): 2954, 2919, 2851 (s, $\nu_{\text{C-H}}$); 1447 (s, $\delta_{\text{C-H}}$ of aliphatic

chain); 1366 (m, ν_{C-N}); 1130 (m, δ_{C-N}); 722 (m, ν_{C-C}). HRMS (ESI) for $C_{18}H_{38}N$, calcd. 268.3004, found 268.3004 $[M+H]^+$.

3s, N-((4-isopropylcyclohexyl)methyl)-2-methylpropan-1-amine, light yellow oil. 1H NMR (500 MHz, $CDCl_3$) δ (ppm): 2.41 (d, $J=6.7$ Hz, 2H, H-1'), 2.38 (d, $J=6.8$ Hz, 2H, H-7), 1.83–1.76 (m, 2H, Ha-3, 5), 1.75–1.71 (m, 3H, Ha-2, 6, H-2'), 1.46–1.36 (m, 2H, H-1, 8), 0.99–0.93 (m, 5H, He-2, 3, 5, 6, H-4), 0.90 (s, 3H, H-9), 0.89 (s, 3H, H-10), 0.86 (s, 3H, H-3'), 0.84 (s, 3H, H-4'). ^{13}C NMR (126 MHz, $CDCl_3$) δ (ppm): 58.36 (C-1'), 57.01 (C-7), 44.41 (C-4), 38.17 (C-1), 33.00 (C-8), 31.70 (C-3, 5), 29.50 (C-2, 6), 28.27 (C-2'), 20.75 (C-9, 10), 19.92 (C-3', 4'). FT-IR(ν/cm^{-1}): 2953, 2914, 2869 (s, ν_{C-H}); 1463, 1447 (s, δ_{C-H} of aliphatic chain); 1384 (m, ν_{C-N}); 1128 (m, δ_{C-N}); 743 (m, ν_{C-C}). HRMS (ESI) for $C_{14}H_{30}N$, calcd. 212.2378, found 212.2380 $[M+H]^+$.

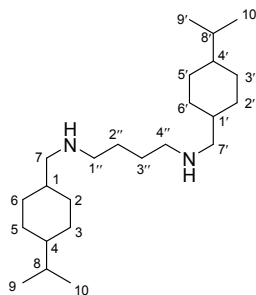
3t, N-((4-isopropylcyclohexyl)methyl)-3-methylbutan-1-amine, light yellow oil. 1H NMR (500 MHz, $CDCl_3$) δ (ppm): 2.58 (t, $J=7.2$ Hz, 2H, H-1'), 2.43 (d, $J=6.7$ Hz, 2H, H-7), 1.79 (d, $J=11.7$ Hz, 2H, Ha-3, 5), 1.72 (d, $J=9.5$ Hz, 2H, Ha-2, 6), 1.61 (dt, $J=13.4, 6.7$ Hz, 2H, H-3'), 1.40–1.35 (m, 4H, H-1, 8, 2'), 1.03 – 0.92 (m, 5H, He-2, 3, 5, 6, H-4), 0.90 (s, 3H, H-9), 0.89 (s, 3H, H-10), 0.86 (s, 3H, H-4'), 0.84 (s, 3H, H-5'). ^{13}C NMR (126 MHz, $CDCl_3$) δ (ppm): 57.01 (C-7), 48.40 (C-1'), 44.29 (C-4), 39.25 (C-2'), 38.14 (C-1), 32.90 (C-8), 31.62 (C-3, 5), 29.40 (C-2, 6), 26.24 (C-3'), 22.69 (C-4', 5'), 19.83 (C-9, 10). FT-IR(ν/cm^{-1}): 2953, 2913, 2868 (s, ν_{C-H}); 1464, 1447 (s, δ_{C-H} of aliphatic chain); 1366 (w, ν_{C-N}); 1127 (m, δ_{C-N}); 735 (m, ν_{C-C}). HRMS (ESI) for $C_{15}H_{32}N$, calcd. 226.2535, found 226.2535 $[M+H]^+$.

3u, N-((4-isopropylcyclohexyl)methyl)cyclohexanamine, light yellow oil. 1H NMR (500 MHz, $CDCl_3$) δ (ppm): 2.40 (d, $J=6.7$ Hz, 2H, H-7), 2.36–2.28 (m, 1H, H-1'), 1.82 (d, $J=10.5$ Hz, 2H, Ha-3, 5), 1.75 (d, $J=11.9$ Hz, 2H, Ha-2, 6), 1.67 (d, $J=9.5$ Hz, 4H, Ha-2', 6', H-4'), 1.60 (s, 1H, NH), 1.44–1.27 (m, 3H, H-1, He-2', 6'), 1.17 (m, 3H, H-8, Ha-3', 5'), 1.04 (dd, $J=24.7, 12.4$ Hz, 3H, H-4, He-3', 5'), 0.98–0.84 (m, 4H, He-2, 3, 5, 6), 0.82 (s, 3H, H-9), 0.80 (s, 3H, H-10). ^{13}C NMR (126 MHz, $CDCl_3$) δ (ppm): 56.92 (C-1'), 53.83 (C-7), 44.30 (C-4), 38.38 (C-1), 33.67 (C-2', 6'), 32.89 (C-8), 31.68 (C-3, 5), 29.39 (C-2, 6), 26.22 (C-4'), 25.12 (C-3', 5'), 19.83 (C-9, 10). FT-IR(ν/cm^{-1}): 2919, 2849 (s, ν_{C-H}); 1447 (s, δ_{C-H}); 1366 (m, ν_{C-N}); 1129 (m, δ_{C-N}); 733 (m, ν_{C-C}). HRMS (ESI) for $C_{16}H_{32}N$, calcd. 238.2535, found 238.2533 $[M+H]^+$.

3v, (*1R, 2R*)-N-((4-isopropylcyclohexyl)methyl)-2-methylcyclohexan-1-amine, light yellow oil. 1H NMR (500 MHz, $CDCl_3$) δ (ppm): 2.48 (dd, $J=11.3, 6.7$ Hz, 1H, Ha-7), 2.29 (dd, $J=11.4, 6.5$ Hz, 1H, He-7), 1.99–1.88 (m, 2H, Ha-3, 5), 1.82–1.73 (m, 2H, Ha-2, 6), 1.69 (d, $J=6.8$ Hz, 3H, H-1', Ha-3', 6'), 1.60 (dd, $J=12.4, 4.8$ Hz, 2H, H-1, 2'), 1.47–1.34 (m, 2H, H-4'), 1.34–1.23 (m, 3H, H-8, He-3', 6'), 1.19 (t, $J=11.1$ Hz, 3H, H-4, 5'), 0.99–0.96 (m, 4H, He-2, 3, 5, 6), 0.92 (d, $J=6.5$ Hz, 3H, $\underline{CH_3}$), 0.83 (s, 3H, H-9), 0.81 (s, 3H, H-10). ^{13}C NMR (126 MHz, $CDCl_3$) δ (ppm): 63.09 (C-1'), 53.81 (C-7), 44.34 (C-4), 38.42 (C-1), 37.79 (C-2'), 34.67 (C-3'), 32.90 (C-8), 32.30 (C-6'), 31.71 (C-3), 31.68 (C-5), 29.44 (C-2), 29.41 (C-6), 26.08 (C-4'), 25.61 (C-5'), 19.84 (C-9, 10), 19.27 ($\underline{CH_3}$). FT-IR(ν/cm^{-1}): 2916, 2850 (s, ν_{C-H}); 1446 (s, δ_{C-H}); 1366 (m, ν_{C-N}); 1126 (m, δ_{C-N}); 706 (m, ν_{C-C}). HRMS (ESI) for $C_{17}H_{34}N$, calcd. 252.2691, found 252.2691 $[M+H]^+$.

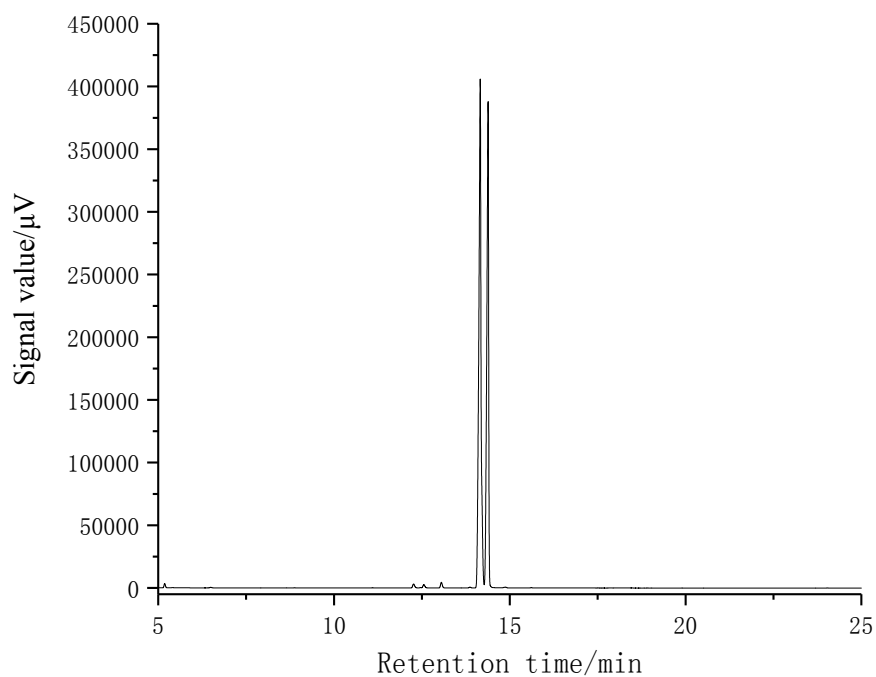
3w, (1R, 4R)-N-((4-isopropylcyclohexyl)methyl)-4-methylcyclohexan-1-amine, light yellow oil. ¹H NMR (500 MHz, CDCl₃) δ (ppm): 2.44 (d, *J*=6.7 Hz, 2H, H-7), 2.36–2.27 (m, 1H, H-1'), 1.88 (d, *J*=11.4 Hz, 2H, Ha-3, 5), 1.79 (d, *J*=11.7 Hz, 2H, Ha-2, 6), 1.69 (d, *J*=11.3 Hz, 5H, Ha-2', 3', 5', 6', H-4'), 1.42–1.27 (m, 2H, H-1, 8), 1.07 (d, *J*=11.3 Hz, 4H, He-2', 3', 5', 6'), 0.99–0.92 (m, 5H, He-2, 3, 5, 6, H-4), 0.87 (d, *J*=6.5 Hz, 3H, CH₃), 0.86 (s, 3H, H-9), 0.84 (s, 3H, H-10). ¹³C NMR (126 MHz, CDCl₃) δ (ppm): 57.04 (C-1'), 53.98 (C-7), 44.31 (C-4), 38.37 (C-1), 34.04 (C-3', 5'), 33.57 (C-2', 6'), 32.90 (C-4'), 32.54 (C-8), 31.69 (C-3, 5), 29.40 (C-2, 6), 22.33 (CH₃), 19.84 (C-9, 10). FT-IR(*ν*/cm⁻¹): 2913, 2846 (s, *ν*_{C-H}); 1447 (s, *δ*_{C-H}); 1367 (m, *ν*_{C-N}); 1131 (m, *δ*_{C-N}); 739 (w, *ν*_{C-C}). HRMS (ESI) for C₁₇H₃₄N, calcd. 252.2691, found 252.2688 [M+H]⁺.

3x, 4-isopropyl-N-((4-isopropylcyclohexyl)methyl)-1-methylcyclohex-3-en-1-amine, light yellow oil. ¹H NMR (400 MHz, CDCl₃) δ (ppm): ¹H NMR (500 MHz, CDCl₃) δ (ppm) 5.30 (s, 1H, H-3'), 2.42–2.28 (m, 2H, H-7), 2.19 (dt, *J*=13.7, 6.9 Hz, 1H, H-8'), 2.05–1.88 (m, 4H, H-2', 5'), 1.80 (d, *J*=9.3 Hz, 2H, Ha-2, 6), 1.71 (d, *J*=9.0 Hz, 2H, Ha-3, 5), 1.65 (dd, *J*=13.0, 6.3 Hz, 1H, Ha-6'), 1.48 (dt, *J*=13.2, 6.7 Hz, 1H, He-6'), 1.39 (dd, *J*=11.0, 6.5 Hz, 1H, H-8), 1.34–1.23 (m, 1H, H-1), 1.04 (s, 3H, H-7'), 0.99 (d, *J*=6.9 Hz, 8H, He-2, 6, H-9', 10'), 0.97–0.86 (m, 3H, He-3, 5, H-4), 0.85 (s, 3H, H-9), 0.83 (s, 3H, H-10). ¹³C NMR (126 MHz, CDCl₃) δ (ppm) 142.57 (C-4'), 116.59 (C-3'), 50.15 (C-1'), 48.50 (C-7), 44.35 (C-4), 38.92 (C-2'), 38.23 (C-1), 34.82 (C-6'), 32.99 (C-8'), 32.90 (C-8), 31.89 (C-3), 31.76 (C-5), 29.45 (C-2), 29.42 (C-6), 24.75 (C-7'), 23.37 (C-5'), 21.56 (C-9'), 21.50 (C-10'), 19.87 (C-9, 10). FT-IR(*ν*/cm⁻¹): 2956, 2912, 2869 (s, *ν*_{C-H}); 1466 (s, *δ*_{N-H}); 1447 (s, *δ*_{C-H}); 1366 (m, *δ*_{C-N}); 1132 (s, *ν*_{C-N}); 707 (m, *ν*_{C-C}). HRMS (ESI) for C₂₀H₃₈N, calcd. 292.3004, found 292.3001 [M+H]⁺.



3y

3y, N¹, N⁴-bis((4-isopropylcyclohexyl)methyl)butane-1,4-diamine, light yellow oil. ¹H NMR (500 MHz, CDCl₃) δ (ppm): 2.62–2.59 (m, 4H, H-1'', 4''), 2.42 (d, *J*=6.7 Hz, 4H, H-7, 7'), 2.04 (s, 2H, NH), 1.78 (d, *J*=11.6 Hz, 4H, Ha-3, 5, 3', 5'), 1.72 (d, *J*=9.3 Hz, 4H, Ha-2, 6, 2', 6'), 1.52–1.38 (m, 8H, H-1, 8, 1', 8', 2'', 3''), 1.02–0.88 (m, 10H, He-2, 3, 5, 6, 2', 3', 5', 6', H-4, 4'), 0.86 (s, 6H, H-9, 9'), 0.84 (s, 6H, H-10, 10'). ¹³C NMR (126 MHz, CDCl₃) δ (ppm): 56.81 (C-7), 50.06 (C-1'', 4''), 44.27 (C-4, 4'), 38.10 (C-1, 1'), 32.89 (C-8, 8'), 31.60 (C-3, 5, 3', 5'), 29.38 (C-2, 6, 2', 6'), 27.92 (C-2'', 3''), 19.83 (C-9, 10, 9', 10'). FT-IR(*ν*/cm⁻¹): 2914, 2849 (s, *ν*_{C-H}); 1741 (s, *δ*_{N-H}); 1447 (s, *δ*_{C-H} of aliphatic chain); 1367 (m, *ν*_{C-N}); 1137 (s, *δ*_{C-N}); 737 (m, *ν*_{C-C}). HRMS (ESI) for C₂₄H₄₉N₂, calcd. 365.3896, found 365.3893 [M+H]⁺.



Fig

re S1 The GC spectrum of compound **2**

Table S2 The GC relative contents of isomer of compound **2**

Peak#	Ret.Time	Aera	Conc.
1	12.264	12815.0	0.39297
2	12.555	10914.3	0.33469
3	13.054	16061.2	0.49252
4	14.159	1802396.0	55.27084
5	14.383	1409504.4	43.22274

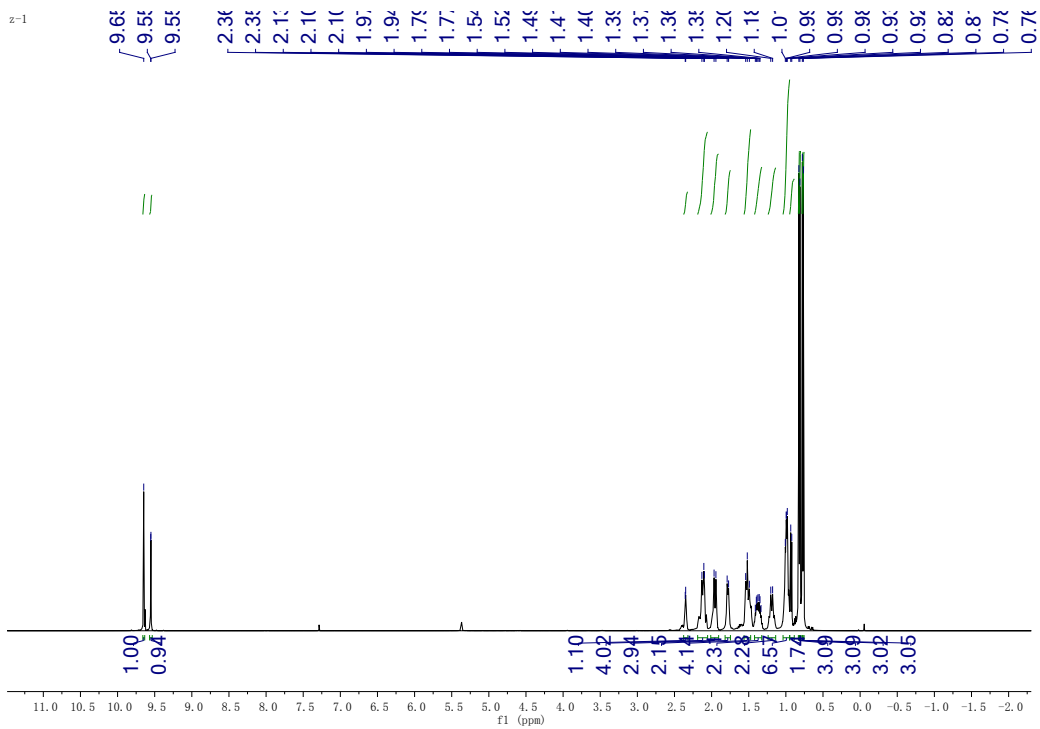


Figure S2 ^1H NMR spectrum of compound **2**

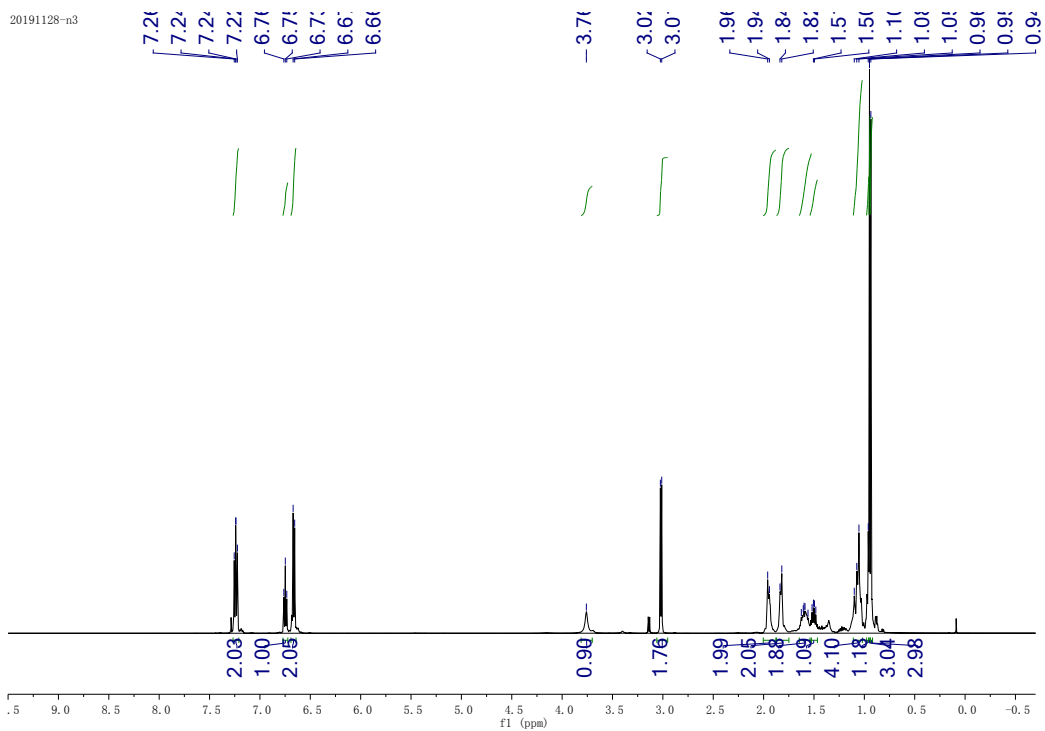


Figure S3 ^1H NMR spectrum of compound **3a**

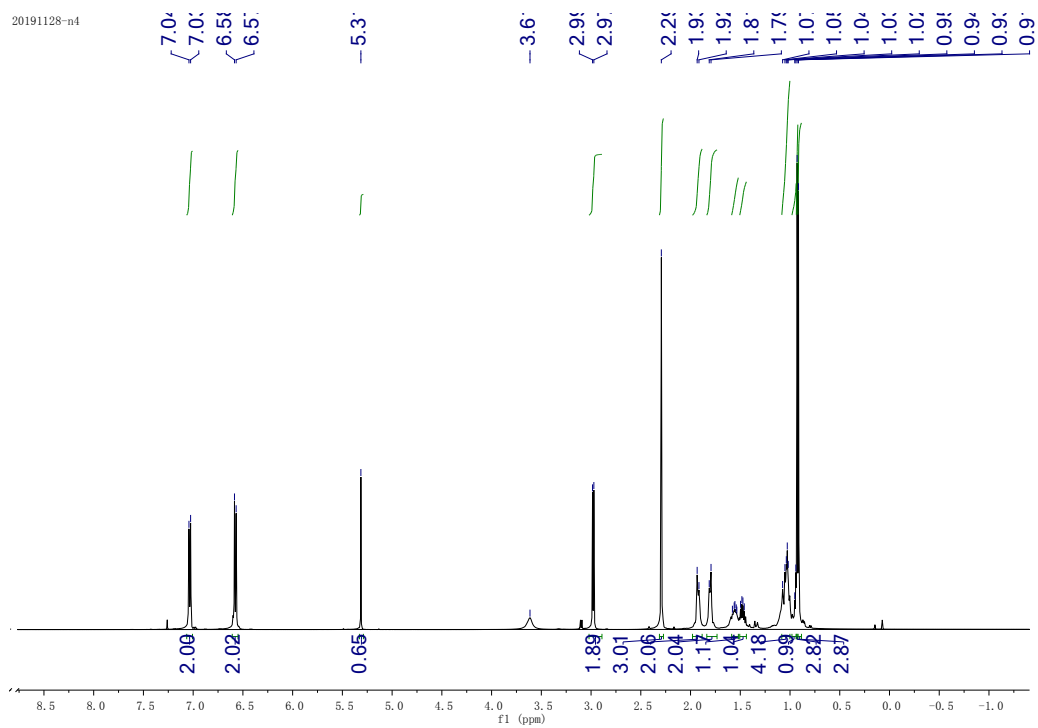


Figure S4 ^1H NMR spectrum of compound **3b**

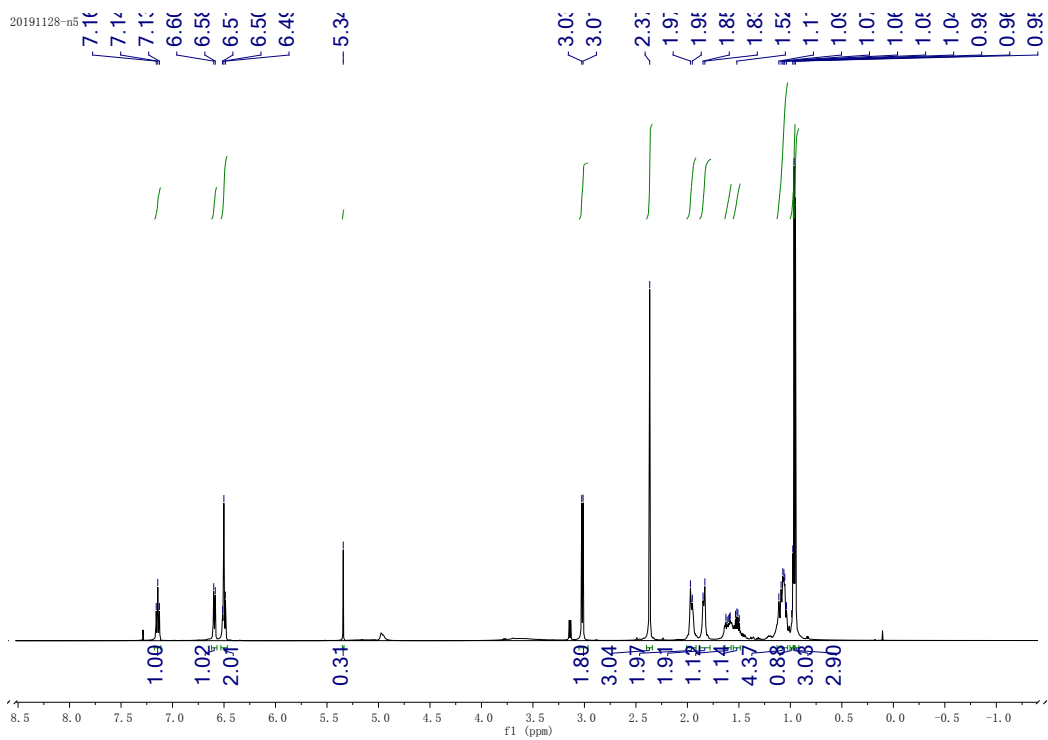


Figure S5 ^1H NMR spectrum of compound **3c**

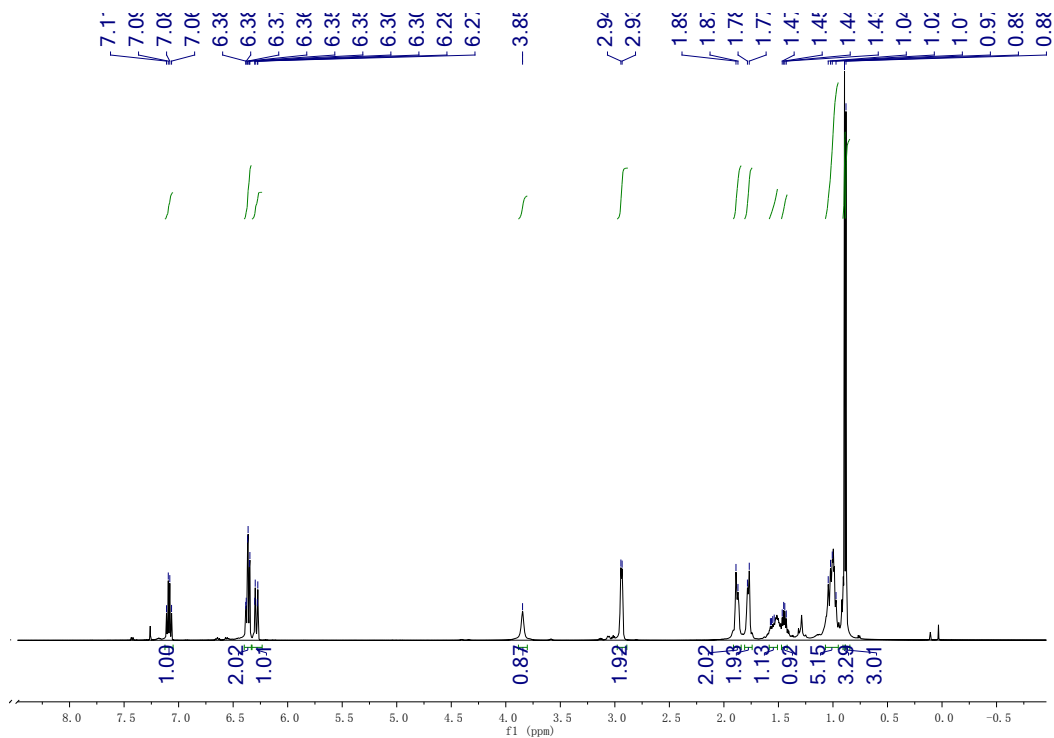


Figure S6 ^1H NMR spectrum of compound **3d**

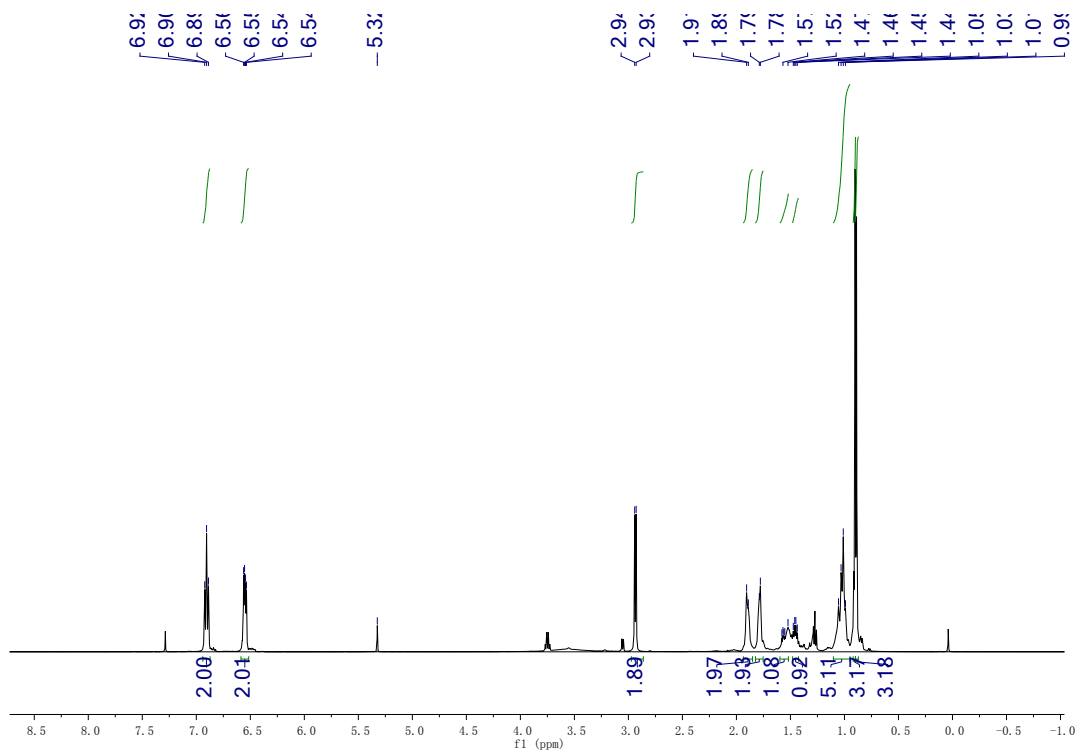


Figure S7 ^1H NMR spectrum of compound **3e**

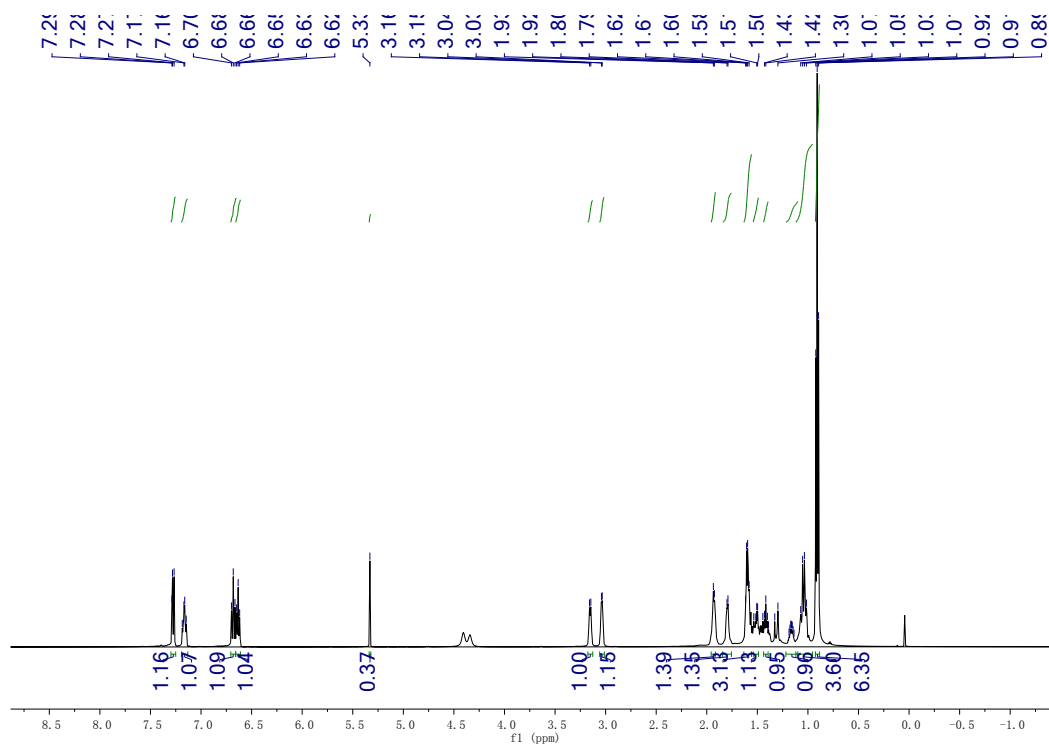


Figure S8 ^1H NMR spectrum of compound **3f**

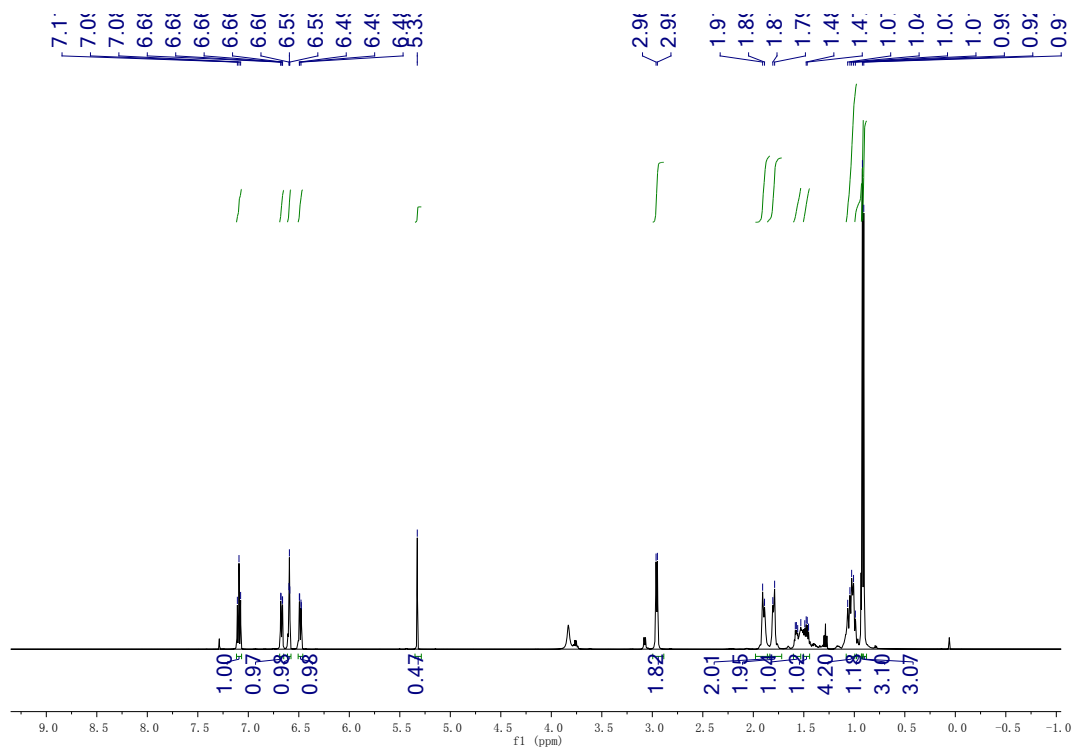


Figure S9 ^1H NMR spectrum of compound **3g**

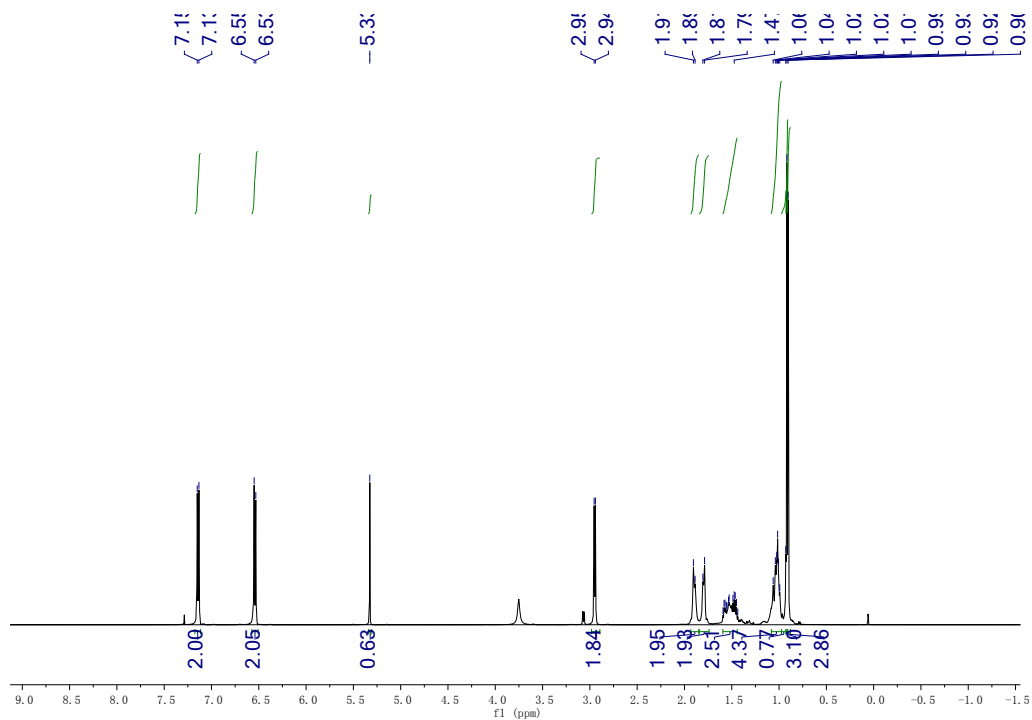


Figure S10 ^1H NMR spectrum of compound 3h

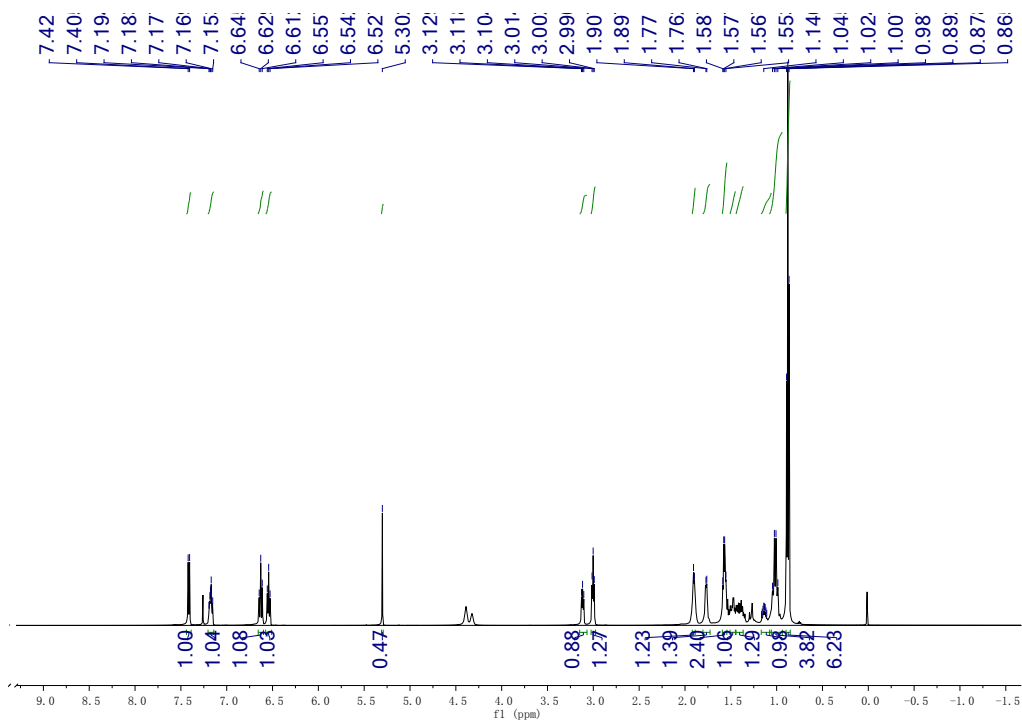


Figure S11 ^1H NMR spectrum of compound 3i

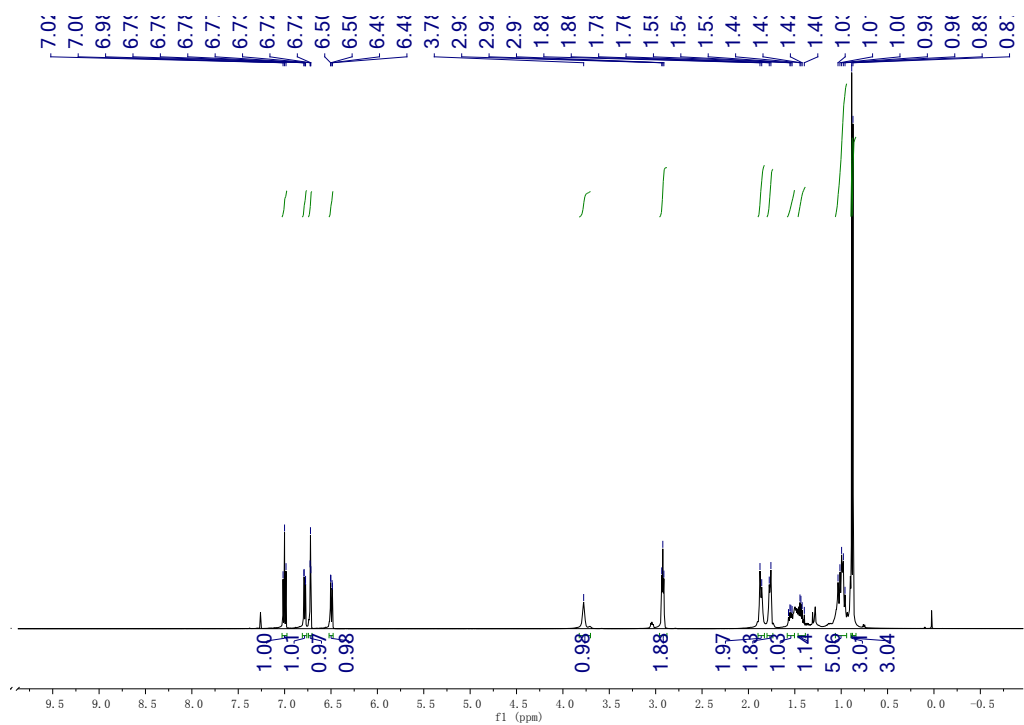


Figure S12 ¹H NMR spectrum of compound 3j

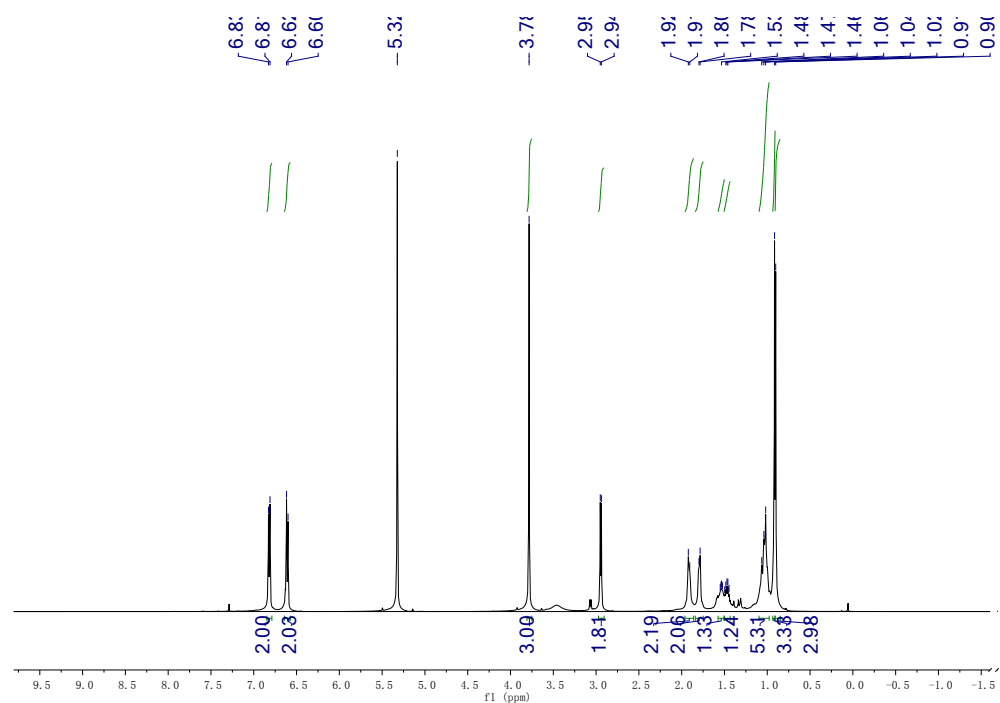


Figure S13 ¹H NMR spectrum of compound 3k

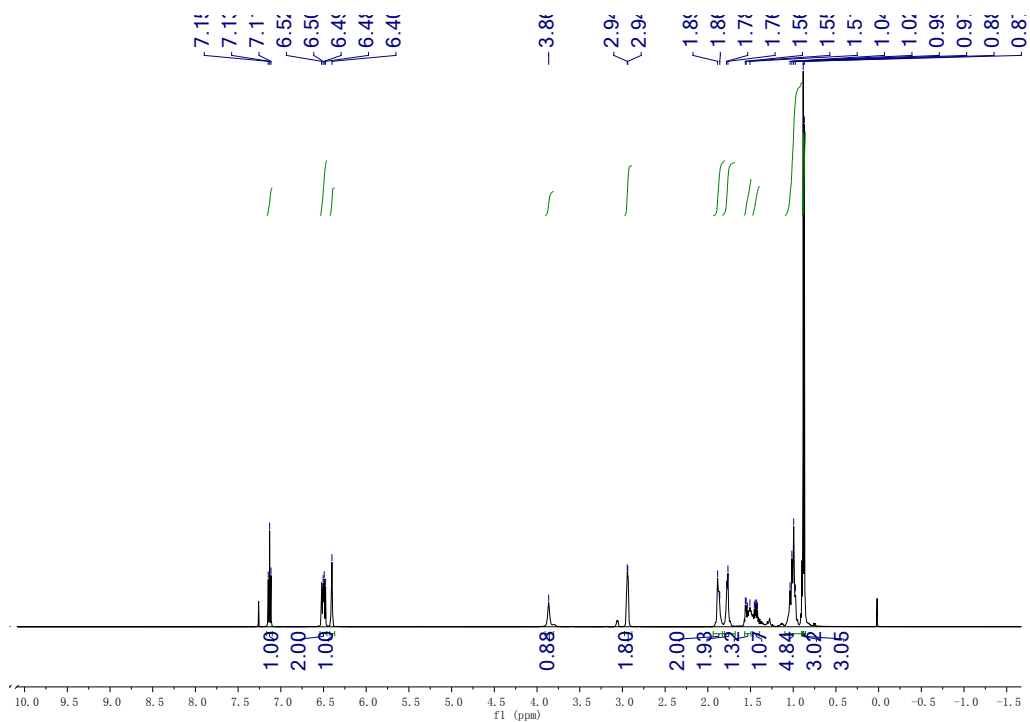


Figure S14 ^1H NMR spectrum of compound **3l**

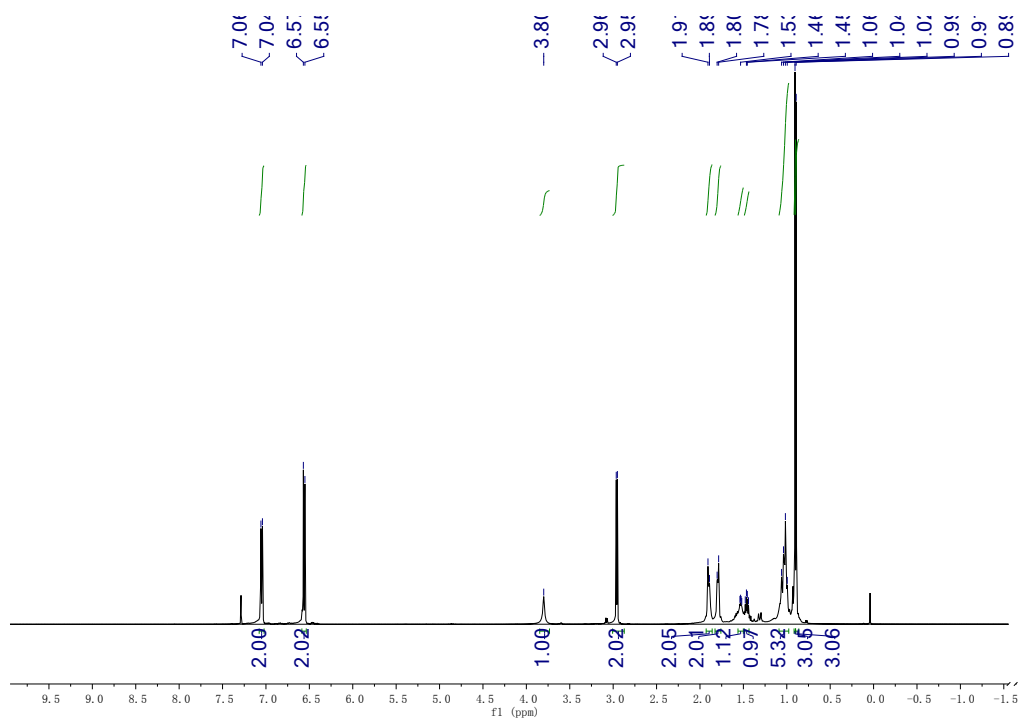


Figure S15 ^1H NMR spectrum of compound **3m**

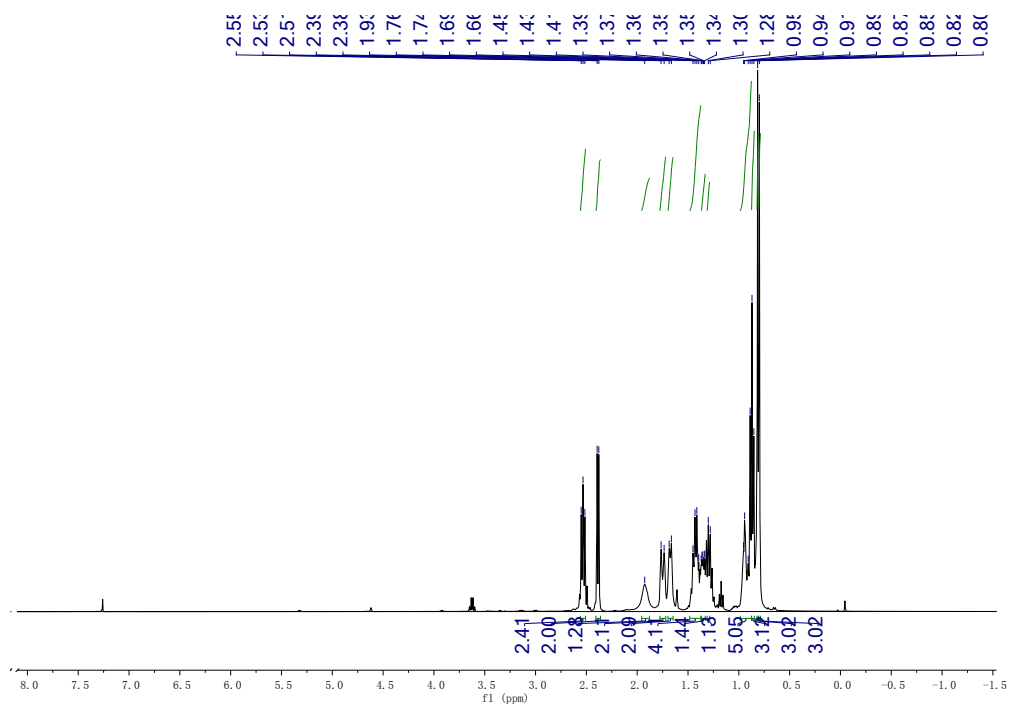


Figure S16 ^1H NMR spectrum of compound **3n**

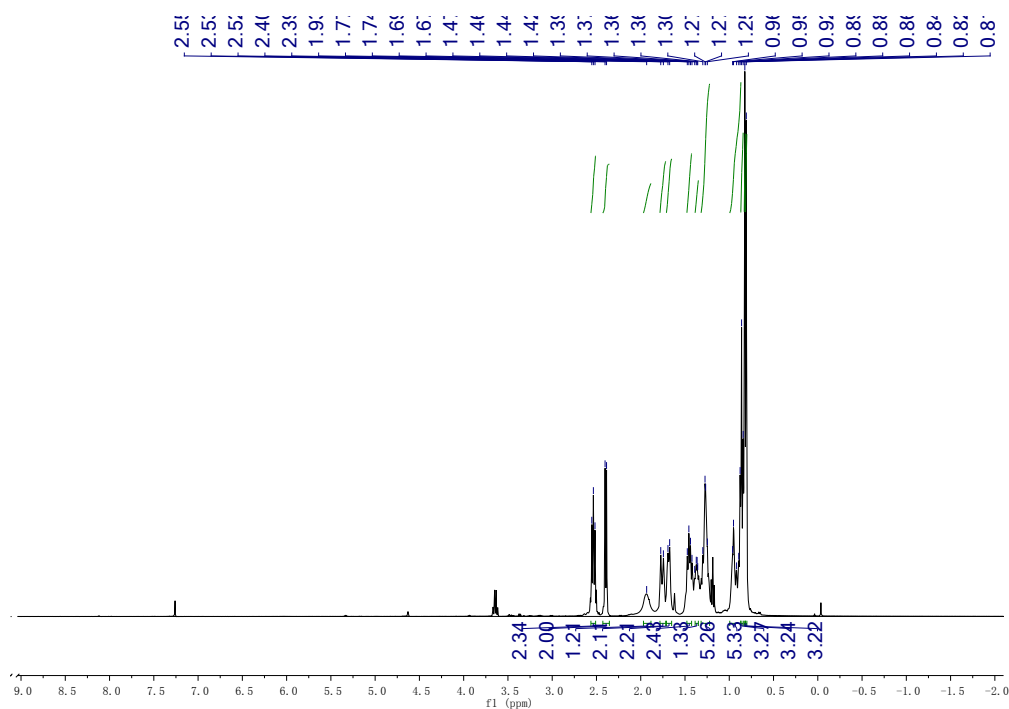


Figure S17 ^1H NMR spectrum of compound **3o**

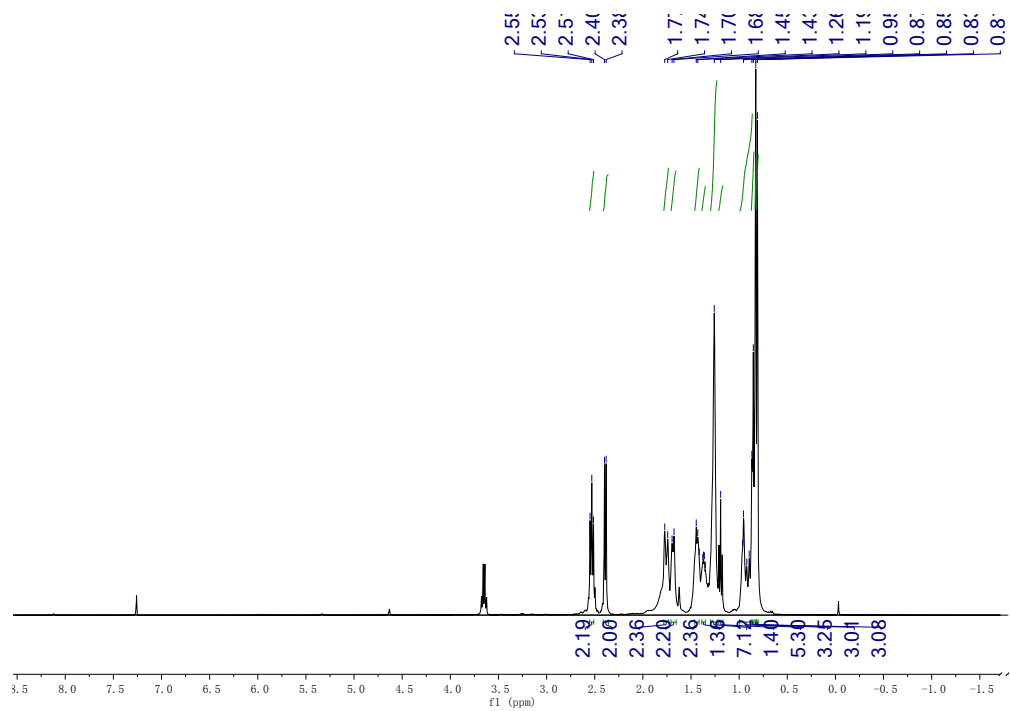


Figure S18 ¹H NMR spectrum of compound **3p**

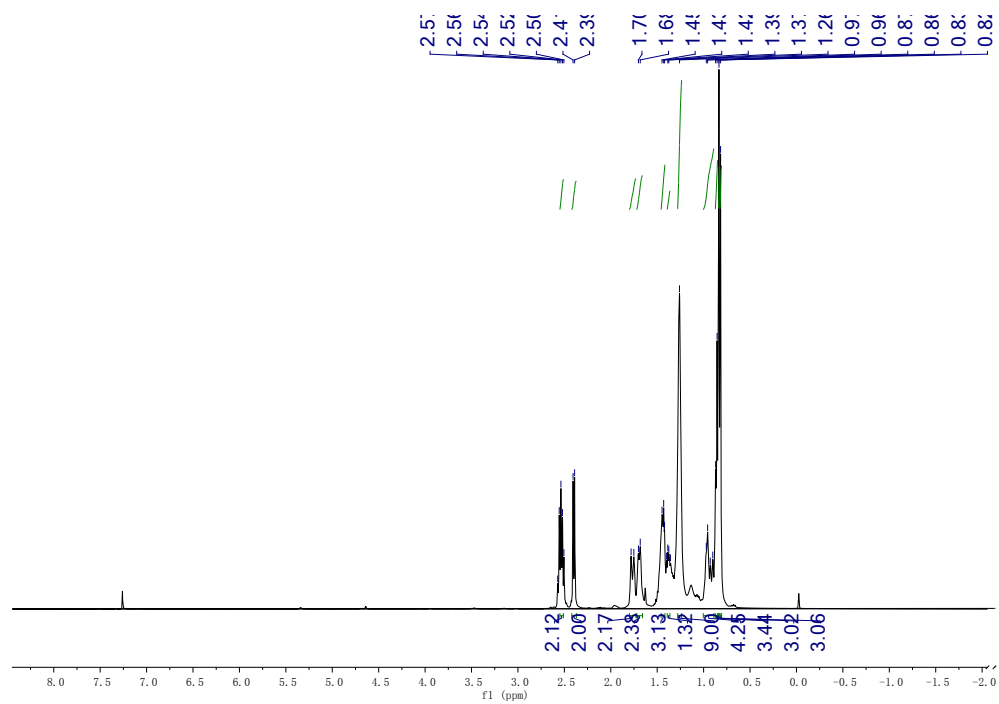


Figure S19 ¹H NMR spectrum of compound **3q**

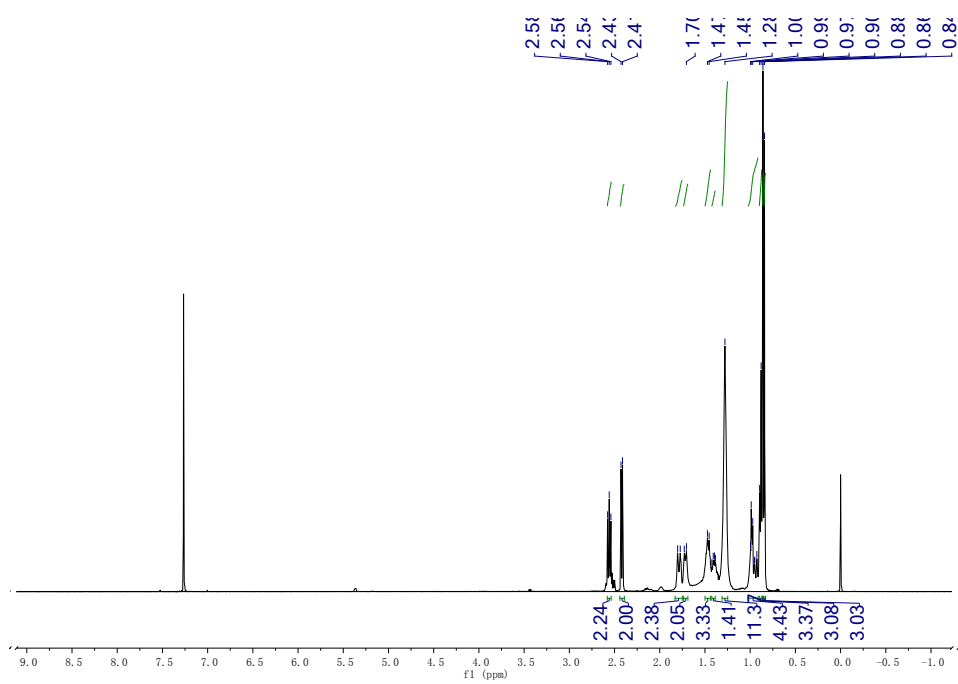


Figure S20 ^1H NMR spectrum of compound **3r**

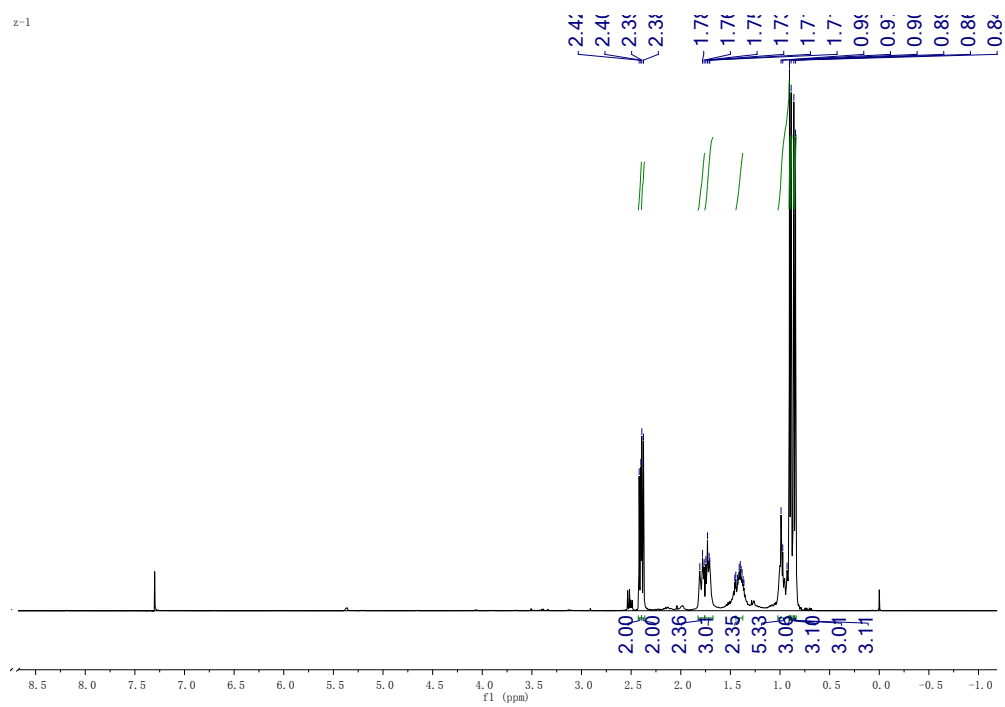


Figure S21 ^1H NMR spectrum of compound **3s**

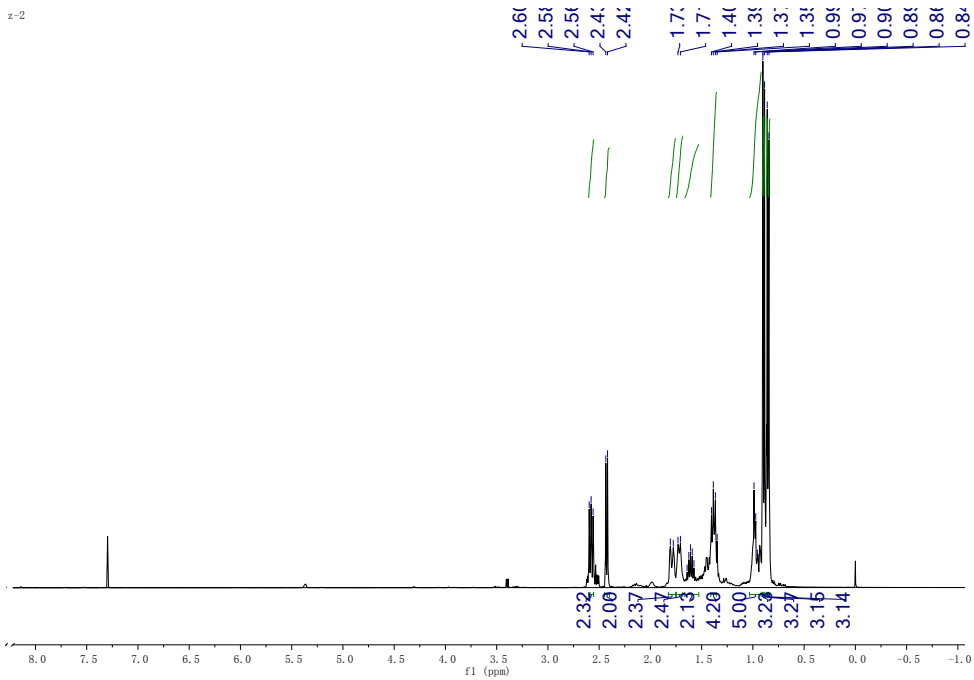


Figure S22 ^1H NMR spectrum of compound **3t**

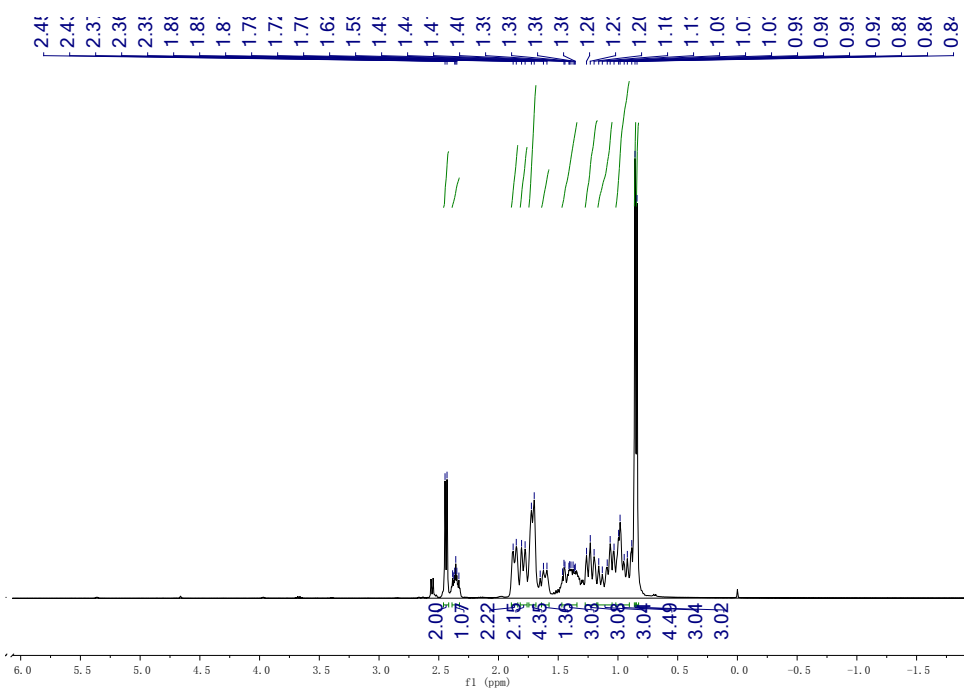


Figure S23 ^1H NMR spectrum of compound **3u**

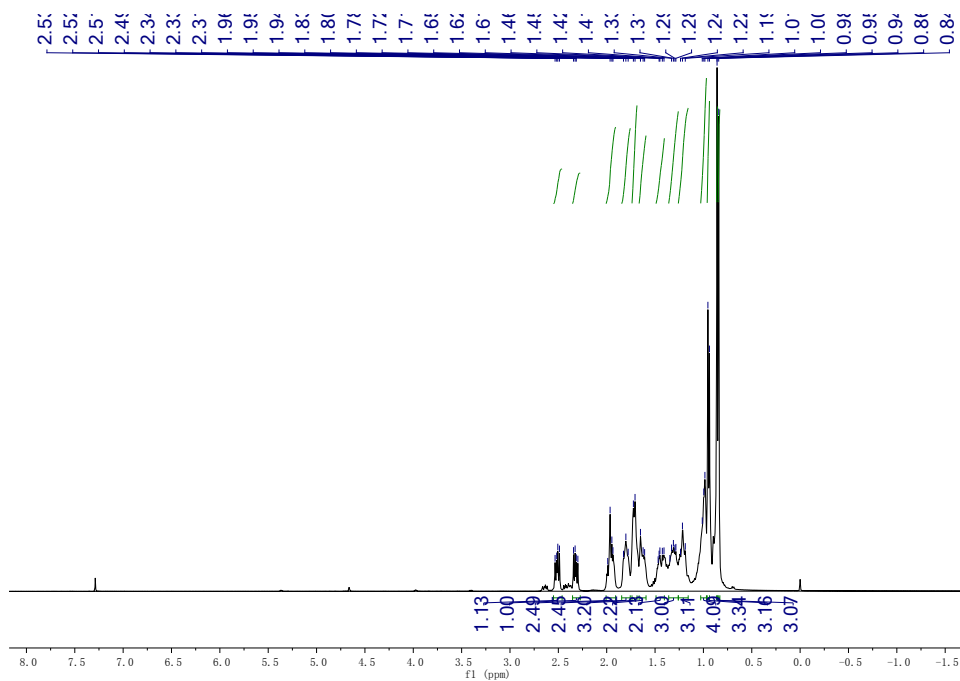


Figure S24 ^1H NMR spectrum of compound 3v

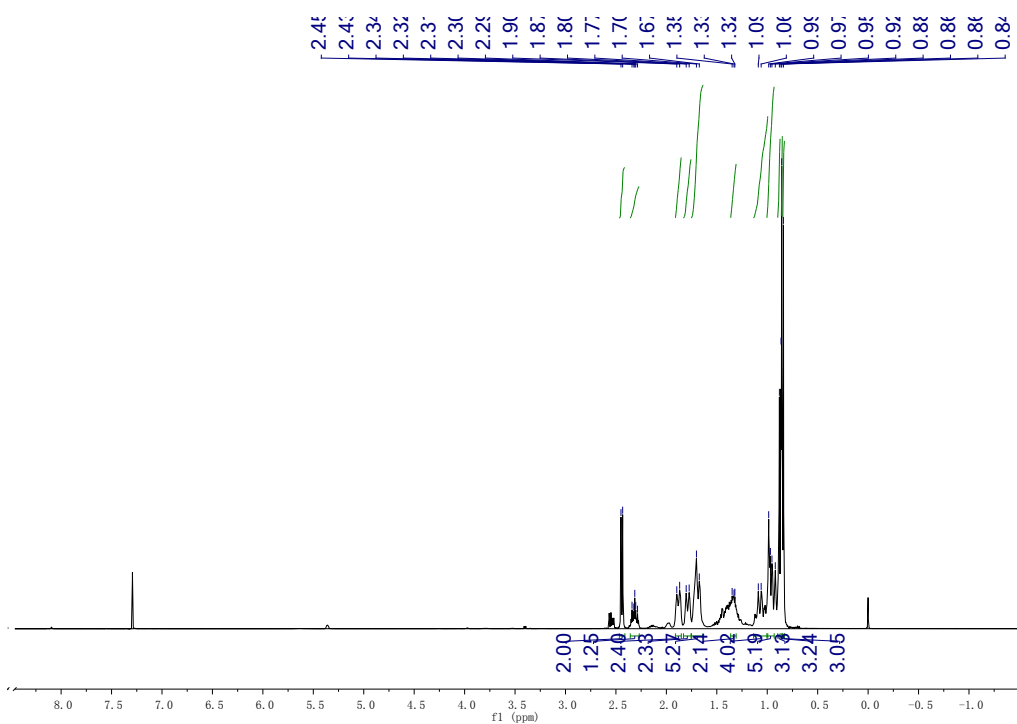


Figure S25 ^1H NMR spectrum of compound 3w

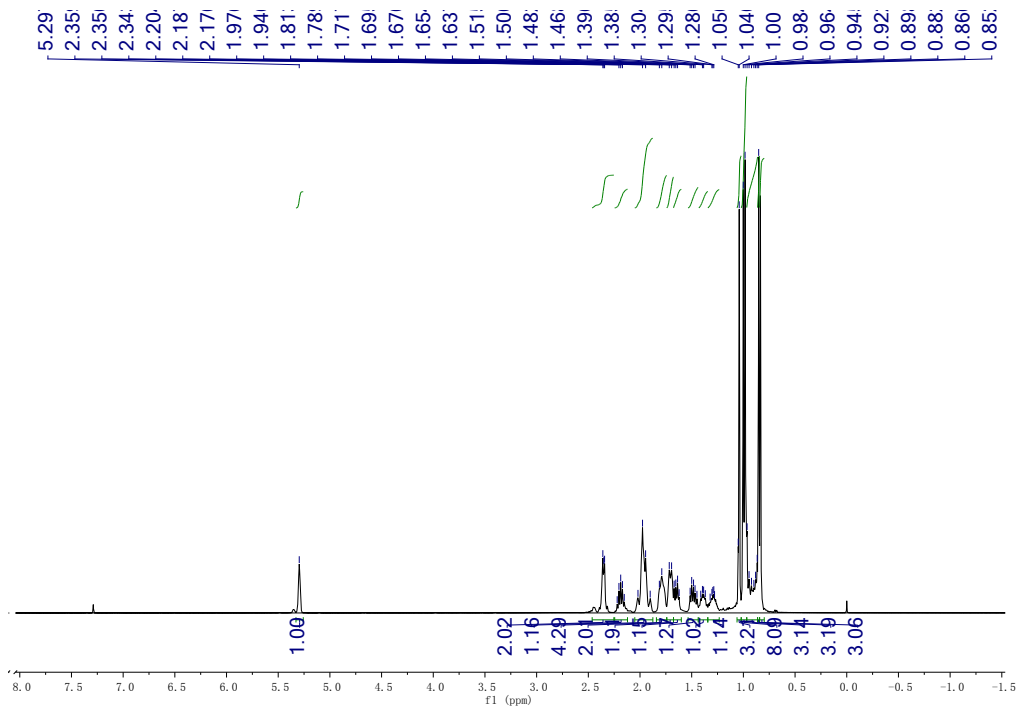


Figure S26 ¹H NMR spectrum of compound 3x

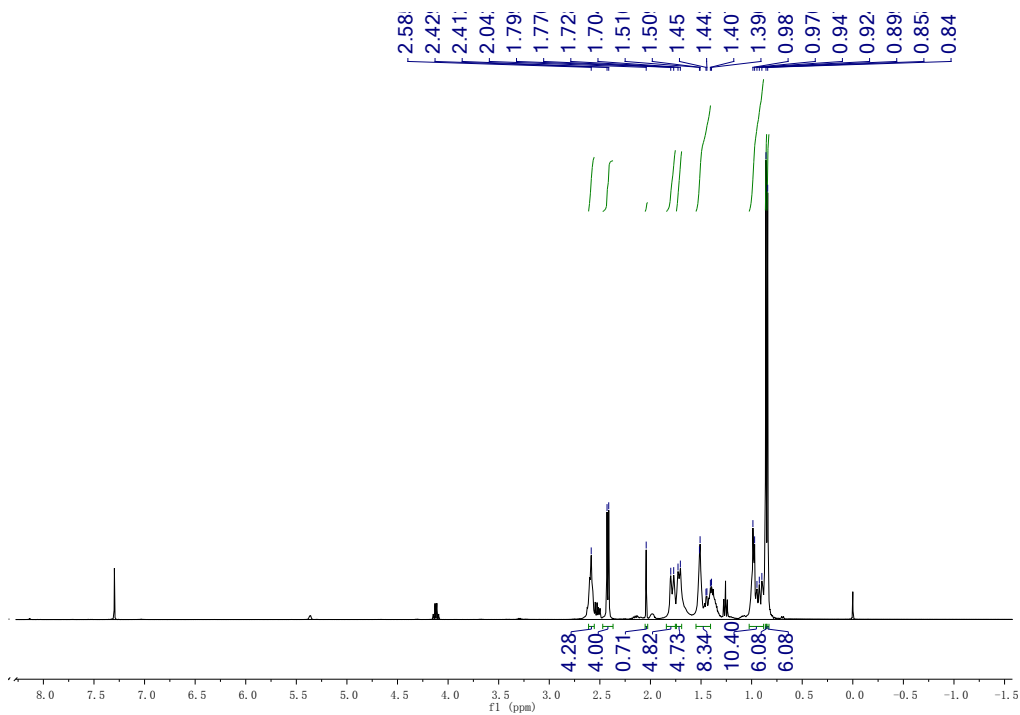


Figure S27 ¹H NMR spectrum of compound 3y

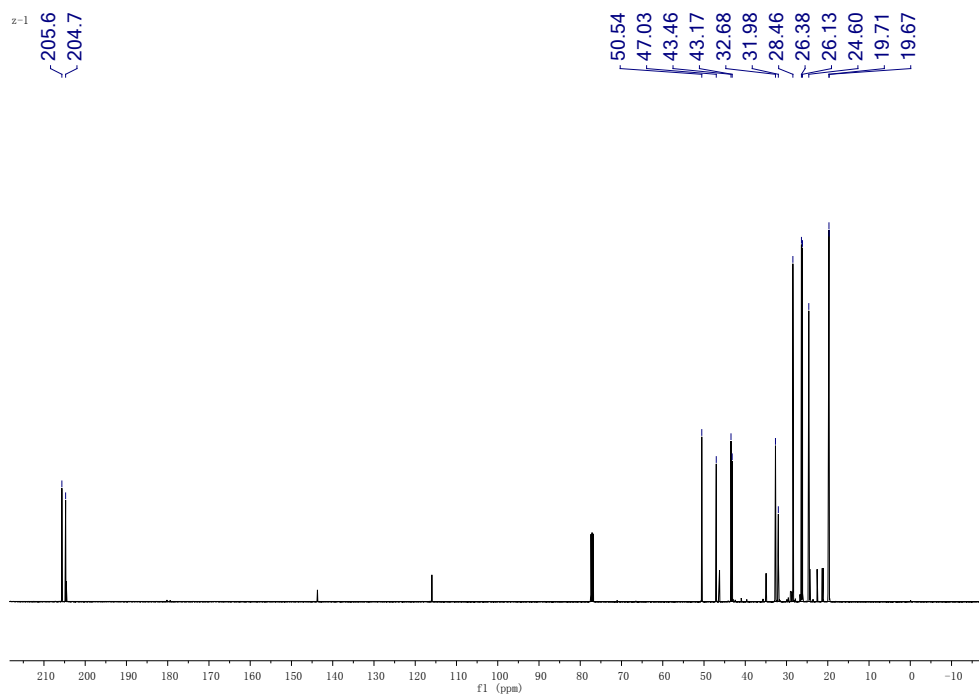


Figure S28 ^{13}C NMR spectrum of compound **2**

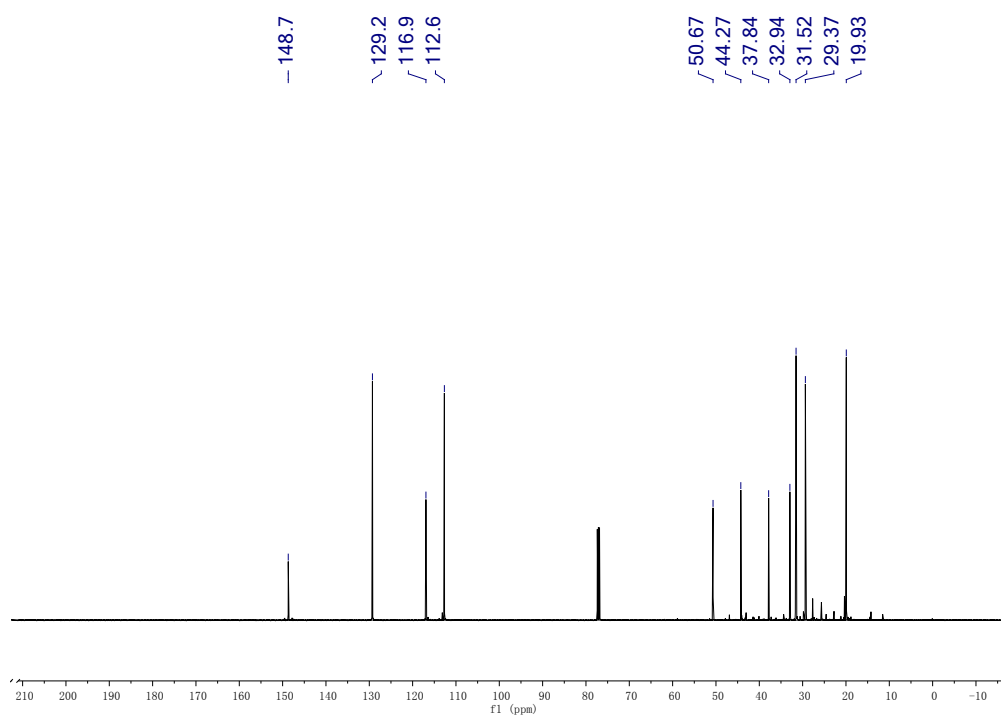


Figure S29 ^{13}C NMR spectrum of compound **3a**

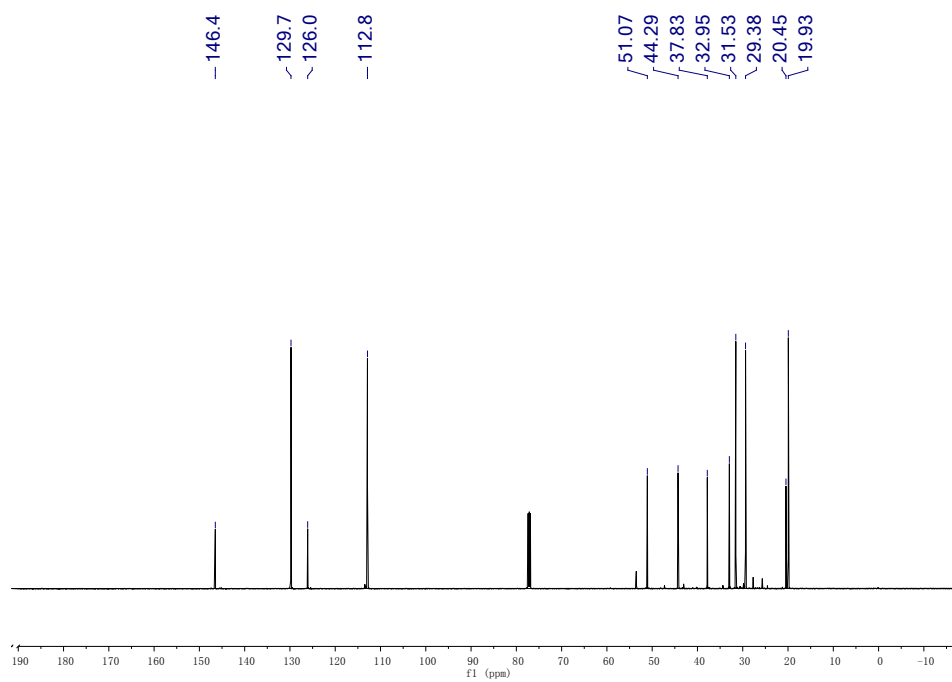


Figure S30 ^{13}C NMR spectrum of compound **3b**

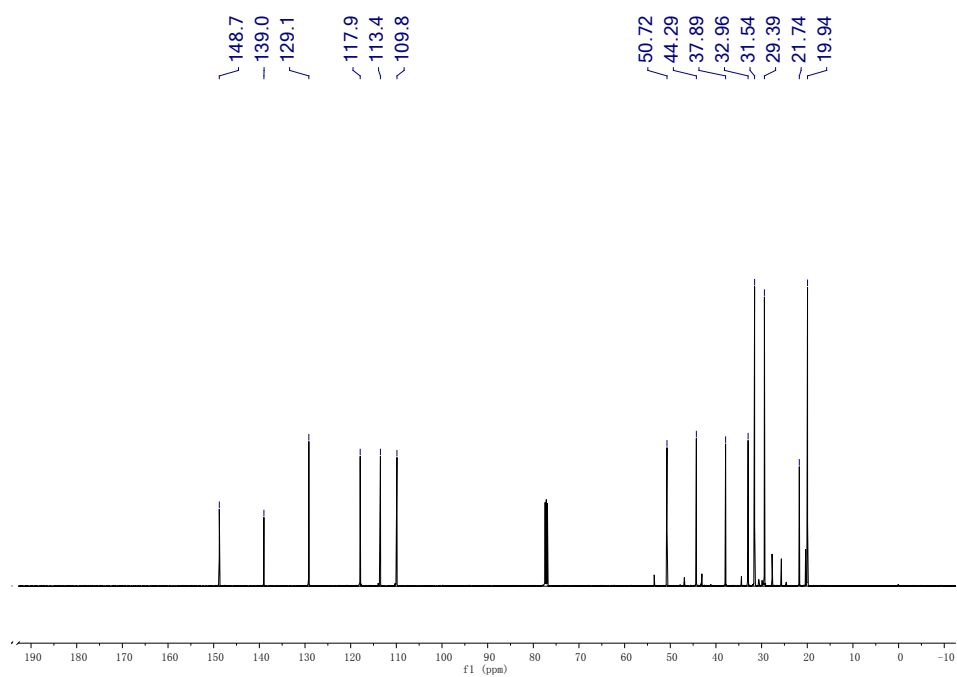


Figure S31 ^{13}C NMR spectrum of compound **3c**

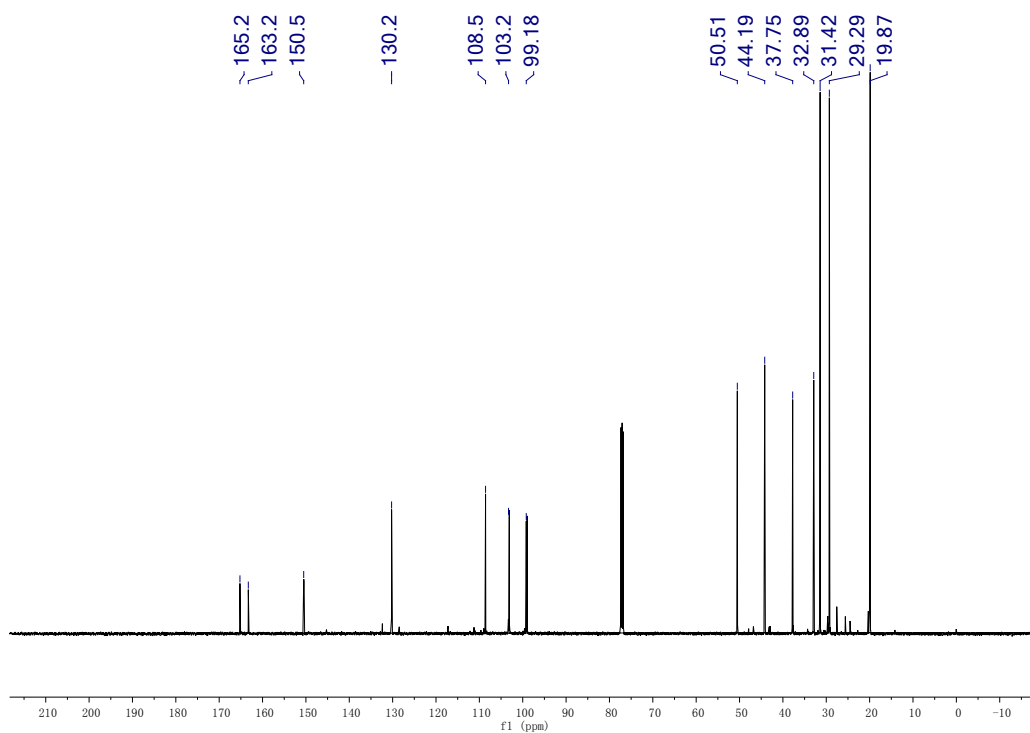


Figure S32 ^{13}C NMR spectrum of compound **3d**

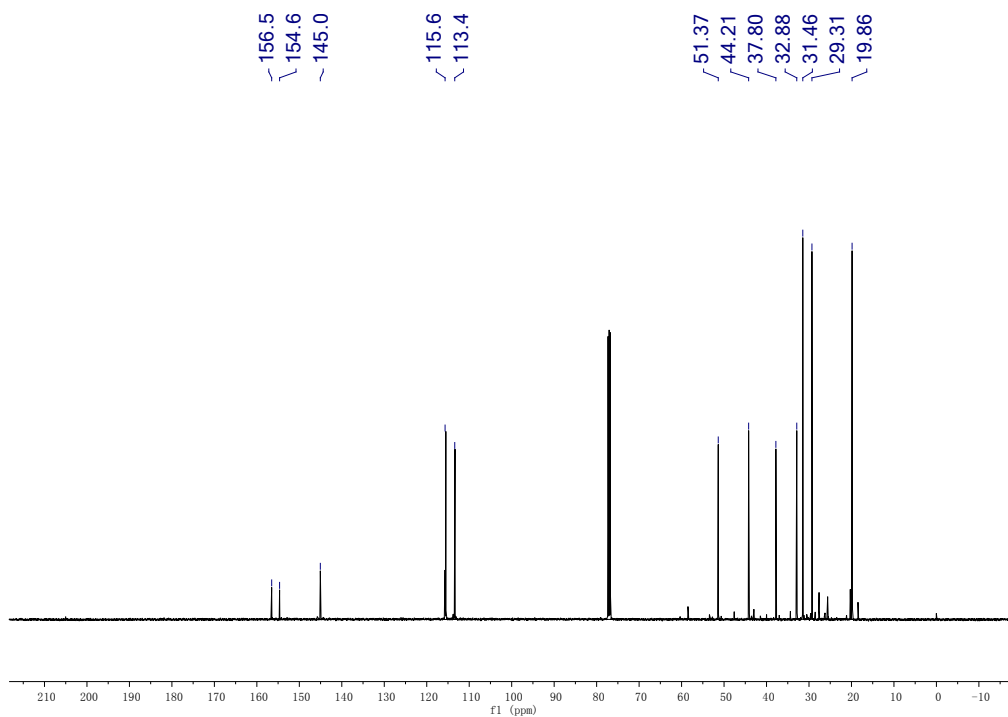


Figure S33 ^{13}C NMR spectrum of compound **3e**

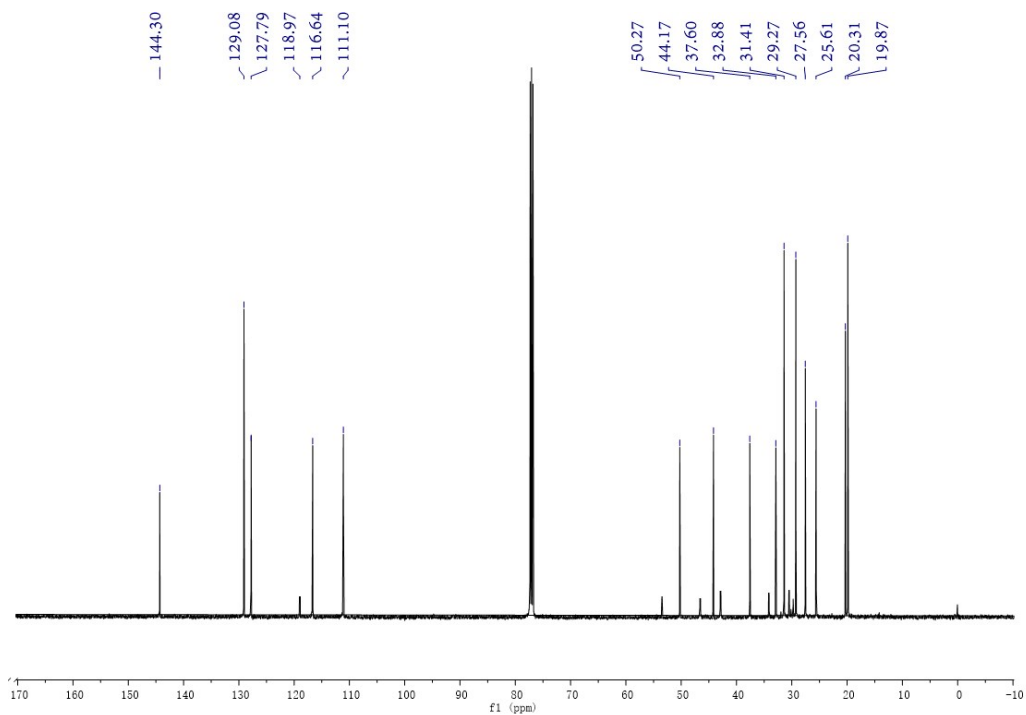


Figure S34 ^{13}C NMR spectrum of compound **3f**

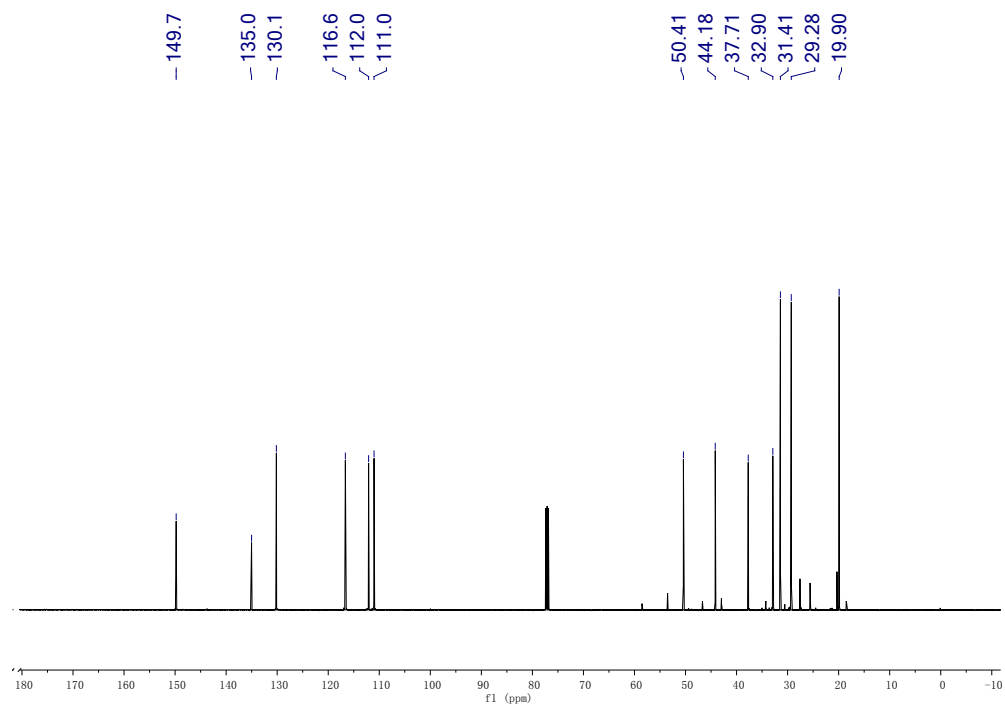


Figure S35 ^{13}C NMR spectrum of compound **3g**

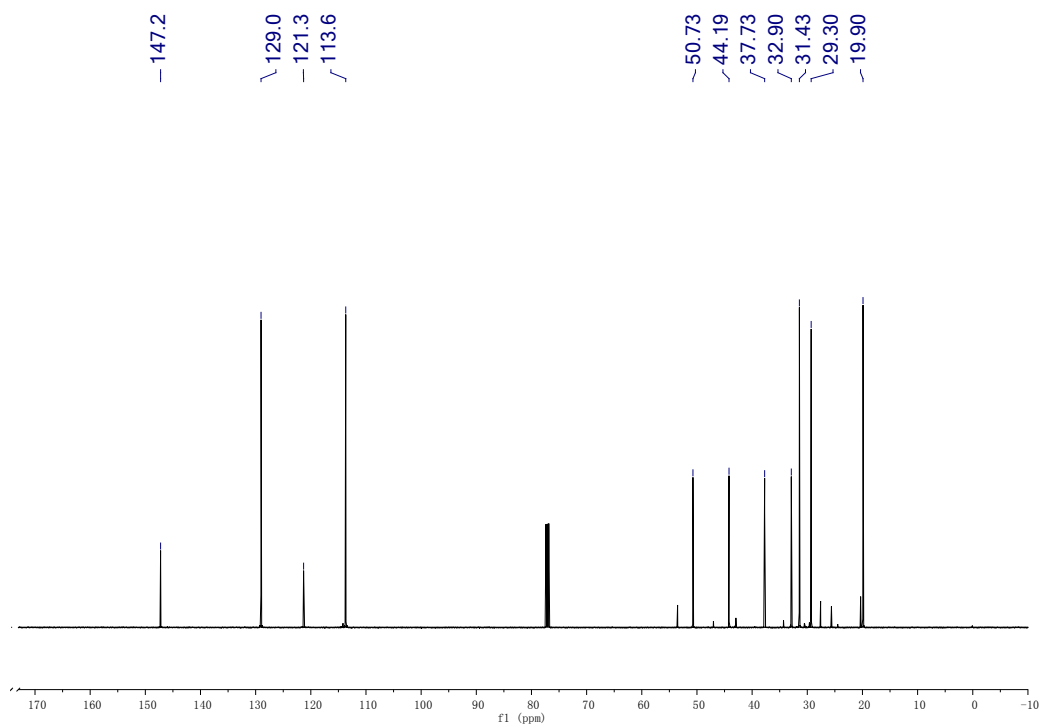


Figure S36 ^{13}C NMR spectrum of compound **3h**

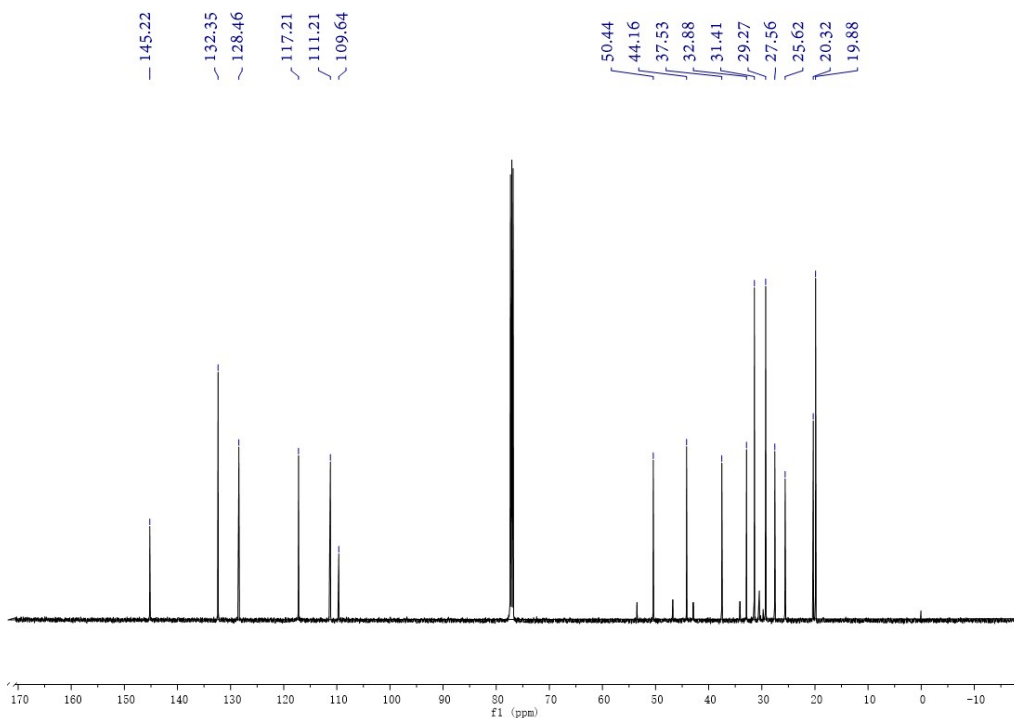


Figure S37 ^{13}C NMR spectrum of compound **3i**

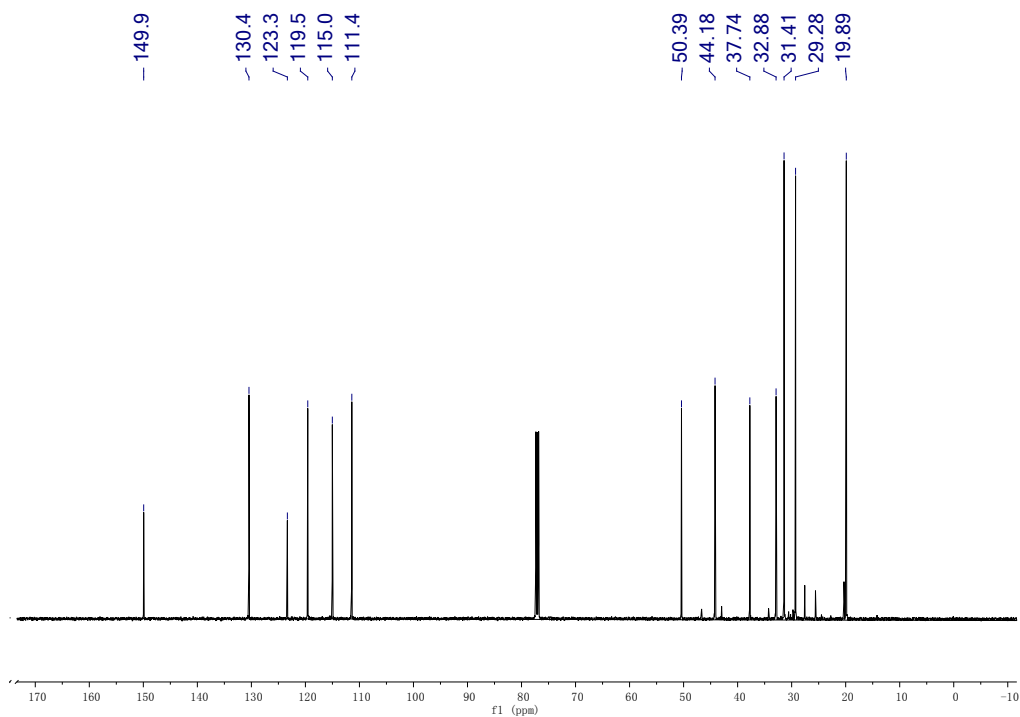


Figure S38 ^{13}C NMR spectrum of compound **3j**

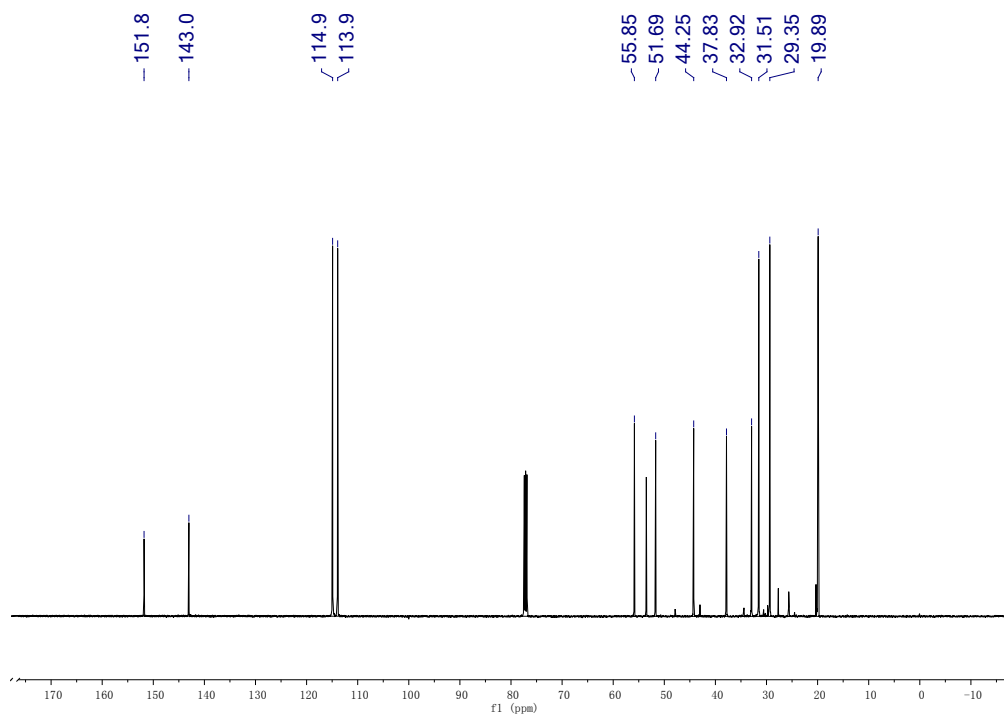


Figure S39 ^{13}C NMR spectrum of compound **3k**

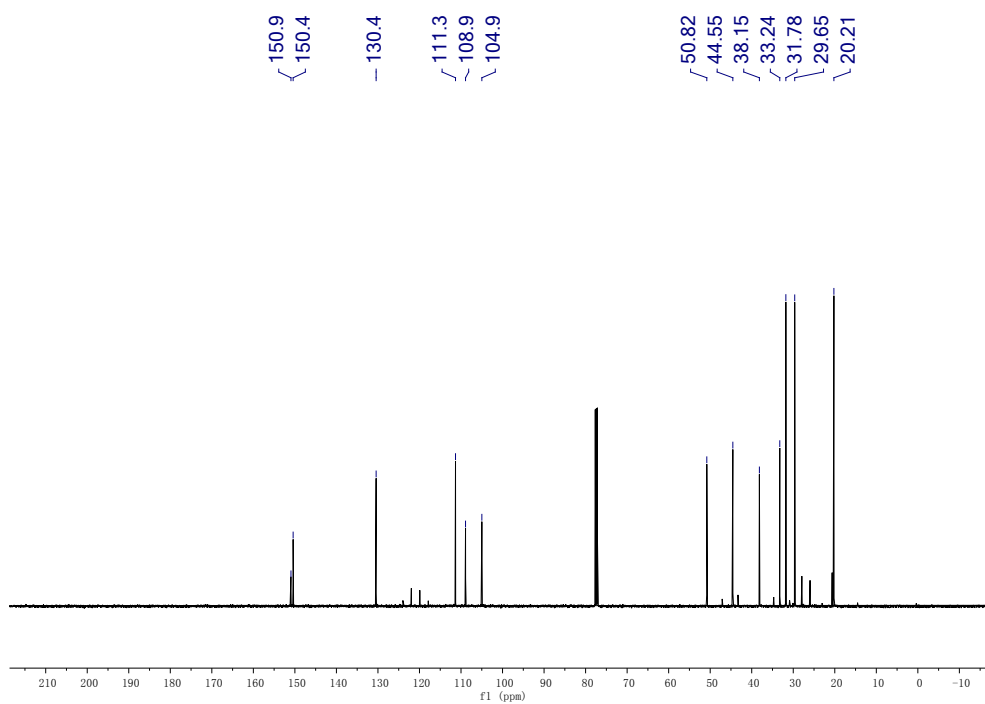


Figure S40 ^{13}C NMR spectrum of compound **3l**

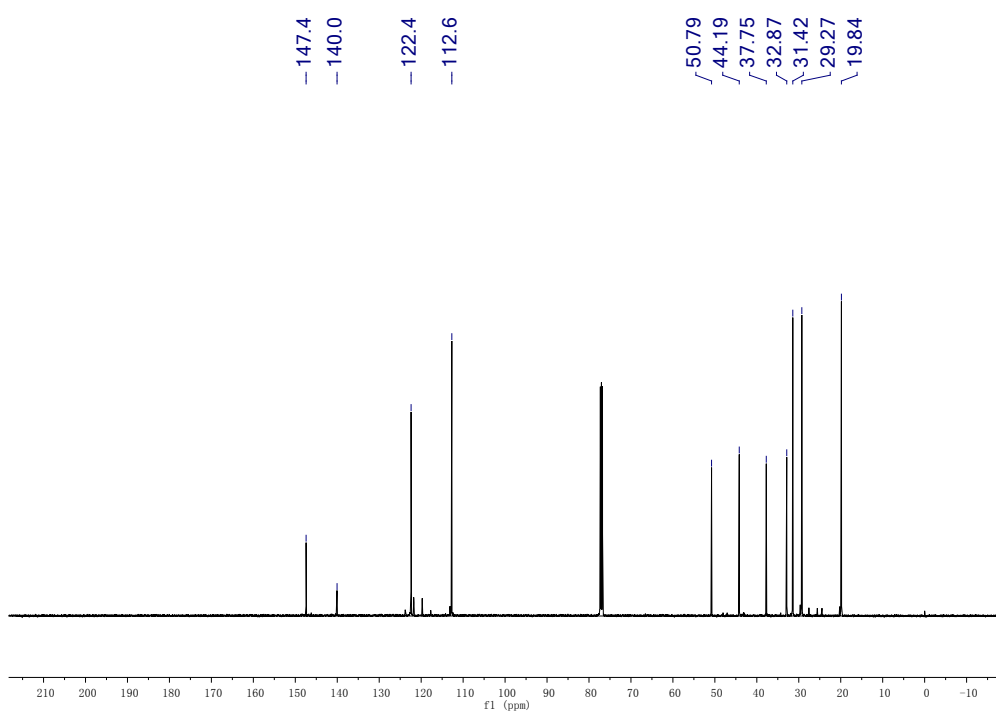


Figure S41 ^{13}C NMR spectrum of compound **3m**

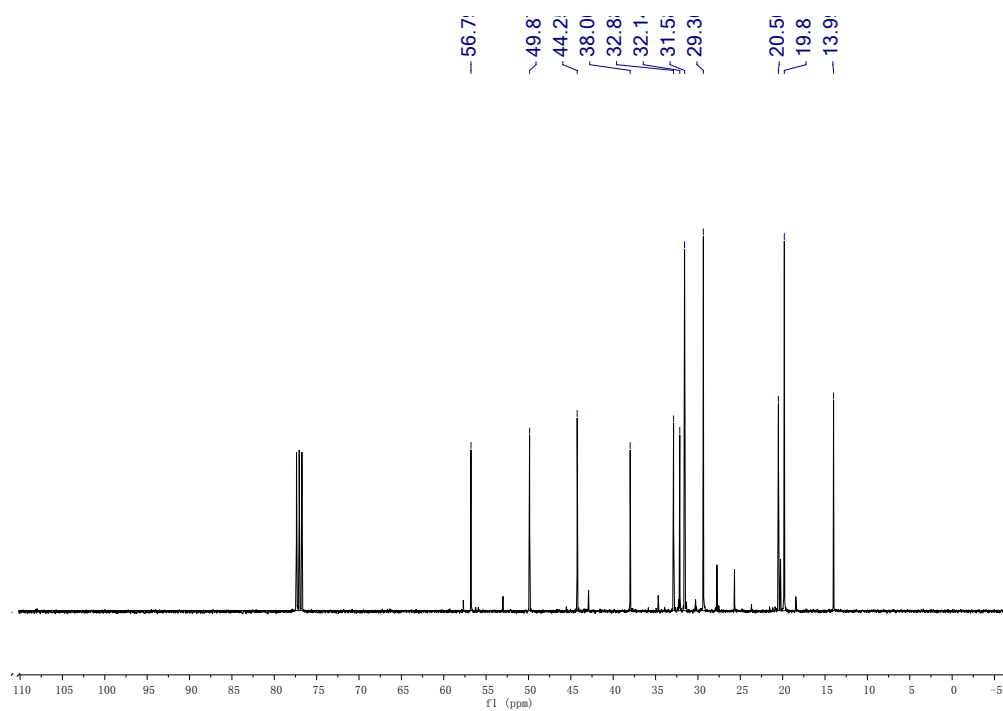


Figure S42 ^{13}C NMR spectrum of compound **3n**

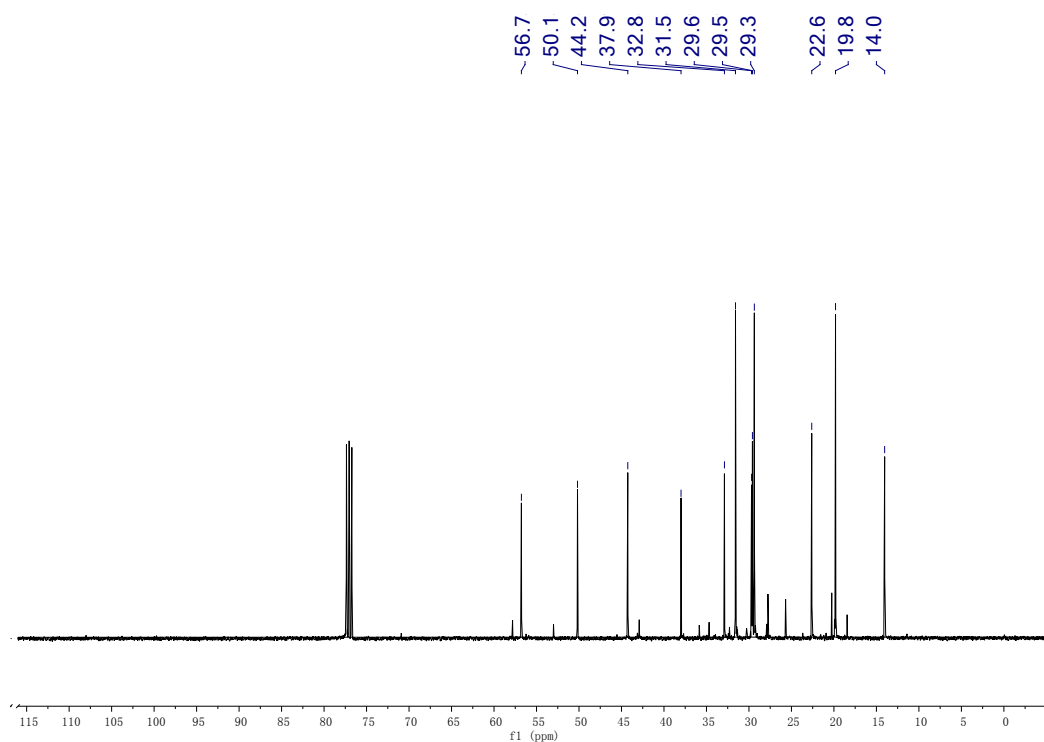


Figure S43 ^{13}C NMR spectrum of compound **3o**

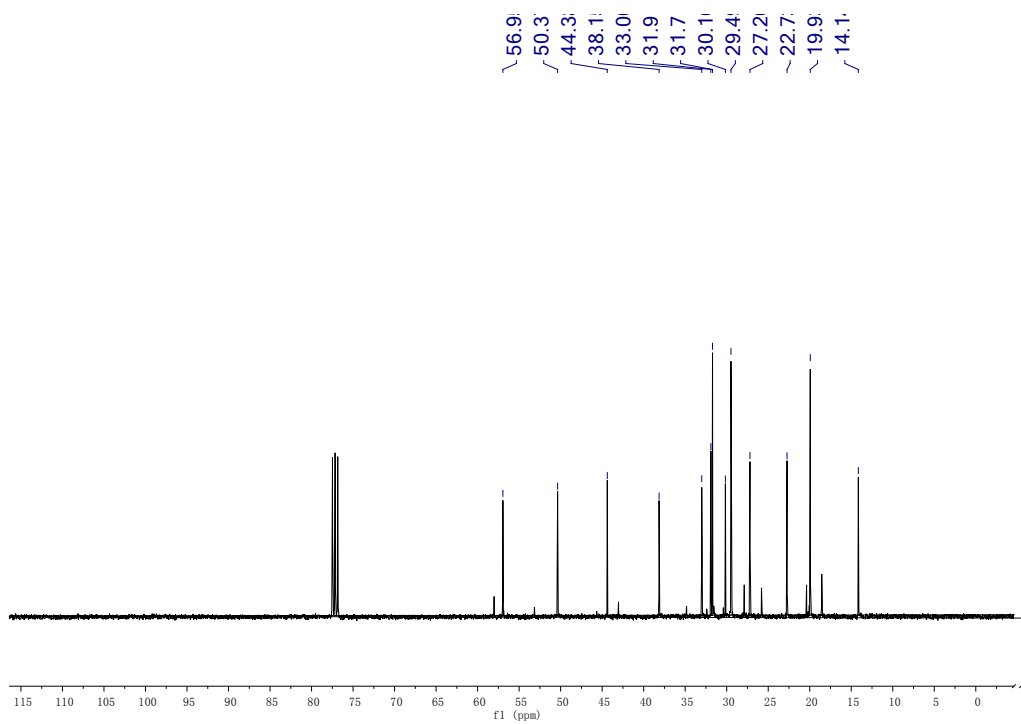


Figure S44 ^{13}C NMR spectrum of compound **3p**

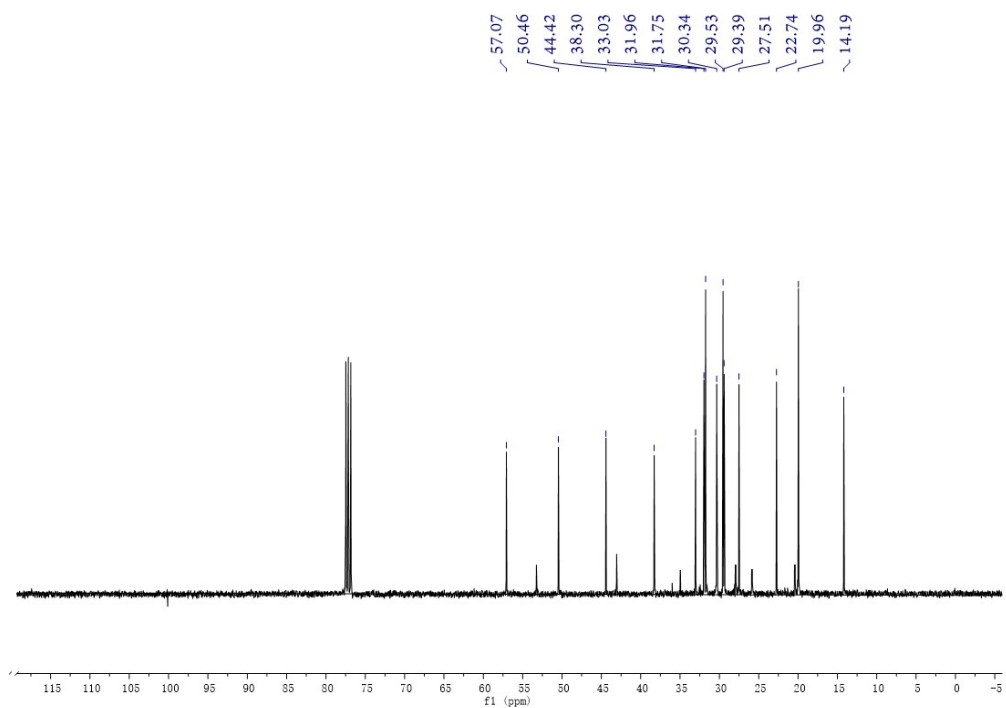


Figure S45 ^{13}C NMR spectrum of compound **3q**

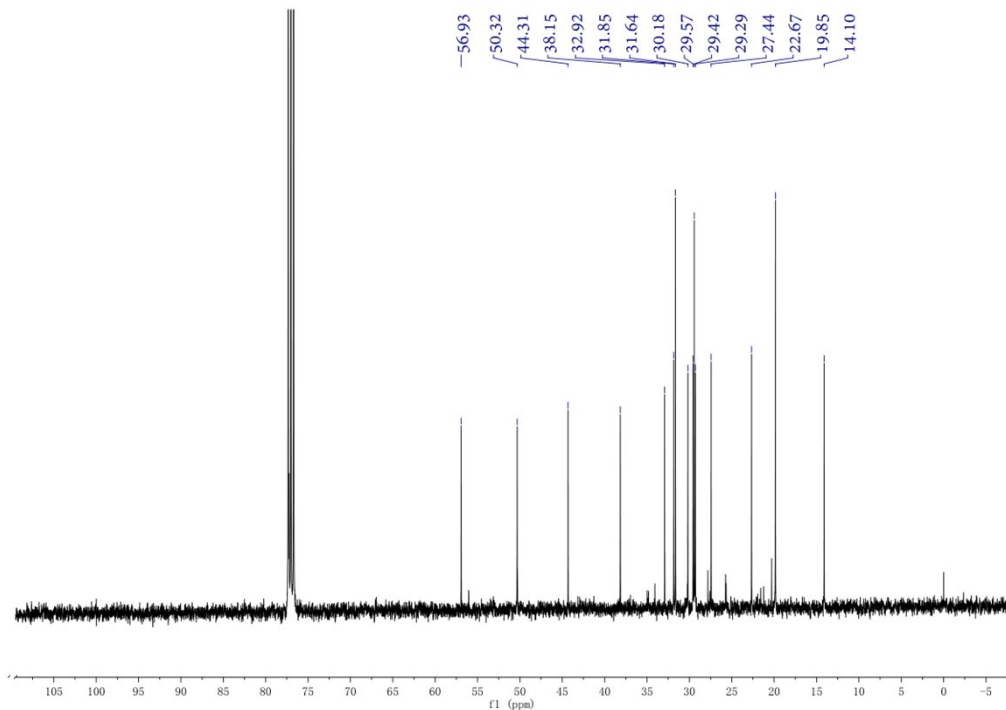


Figure S46 ^{13}C NMR spectrum of compound **3r**

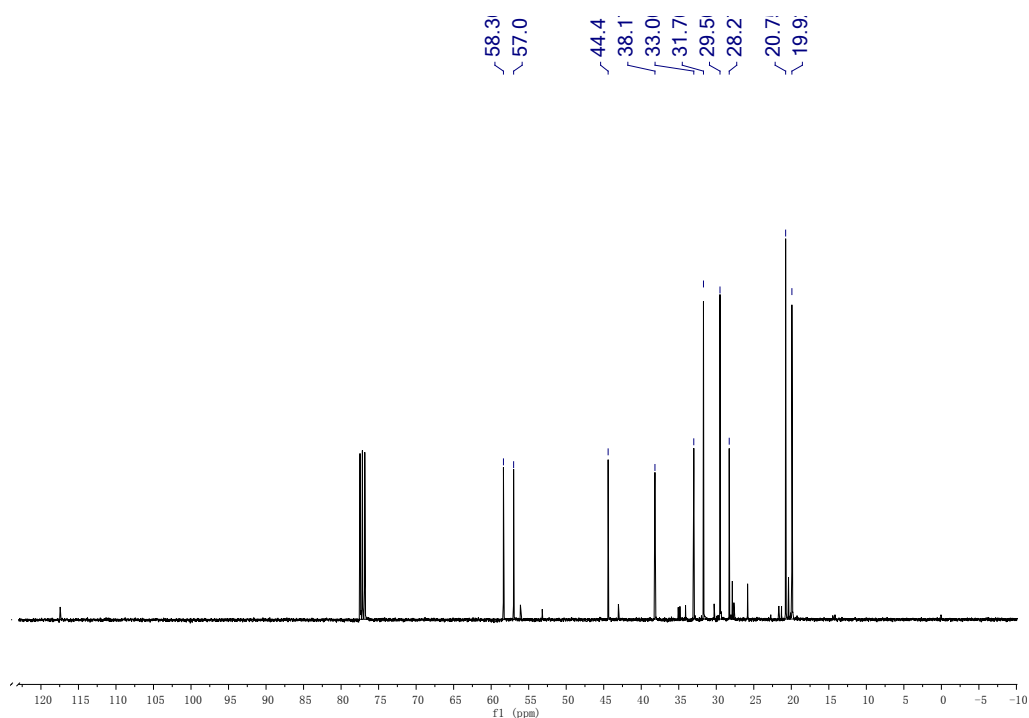


Figure S47 ^{13}C NMR spectrum of compound **3s**

z-2

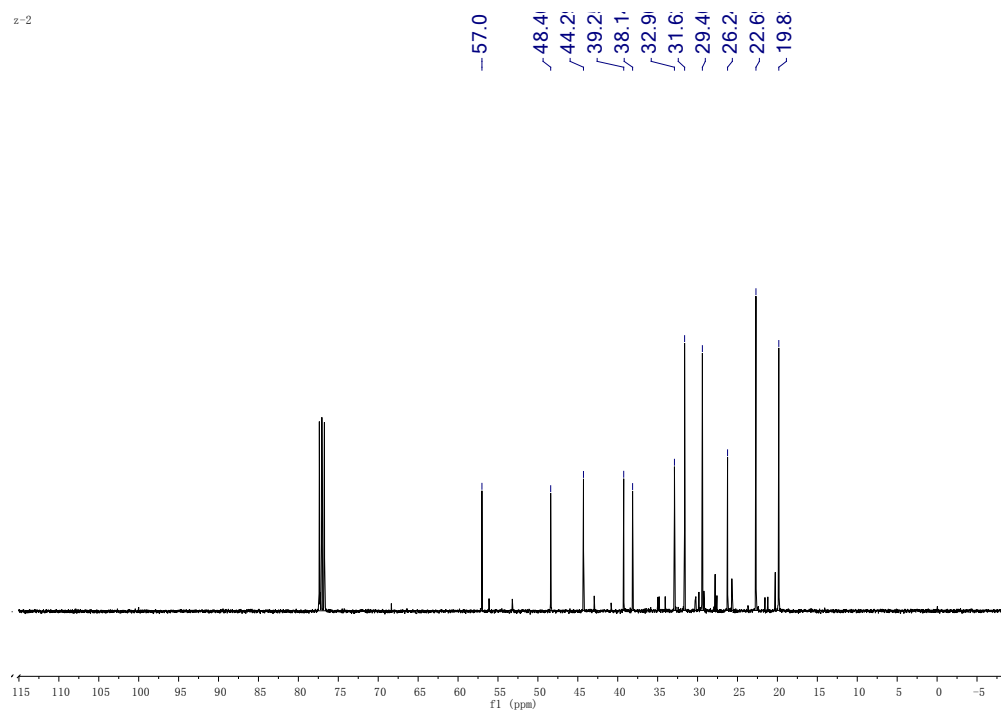


Figure S48 ^{13}C NMR spectrum of compound **3t**

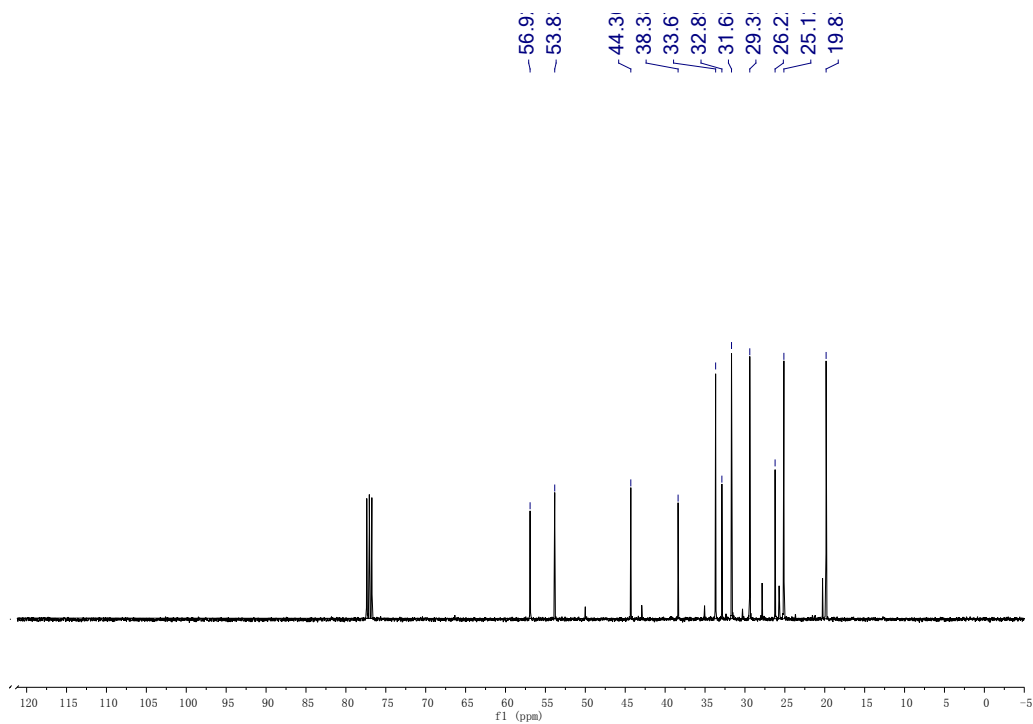


Figure S49 ^{13}C NMR spectrum of compound **3u**

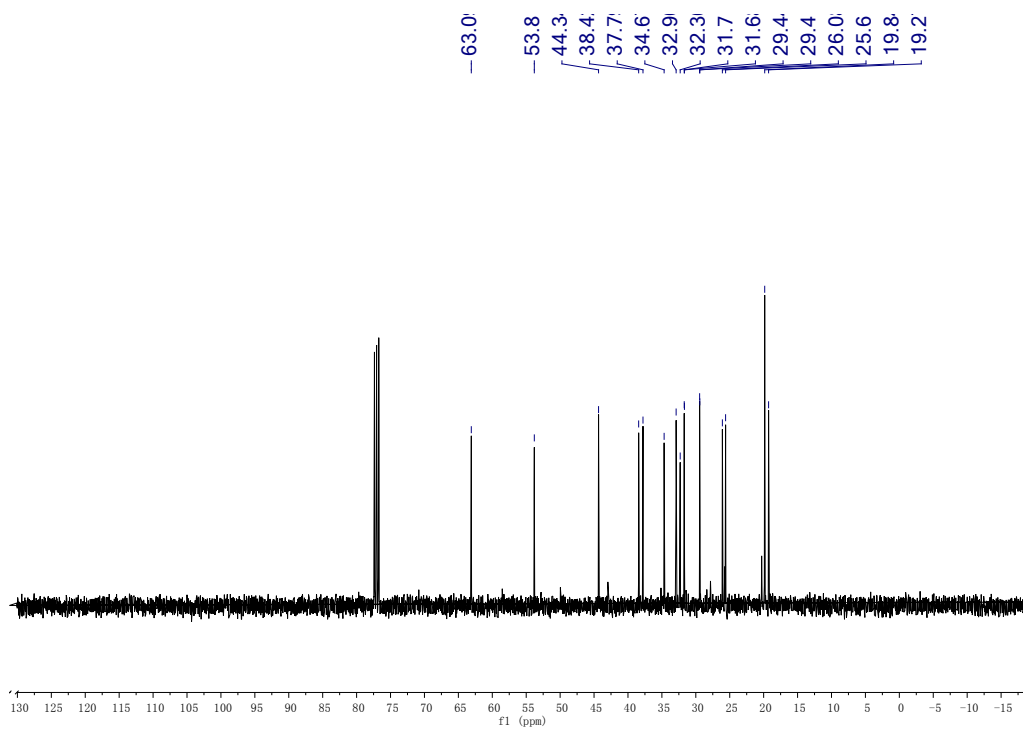


Figure S50 ^{13}C NMR spectrum of compound **3v**

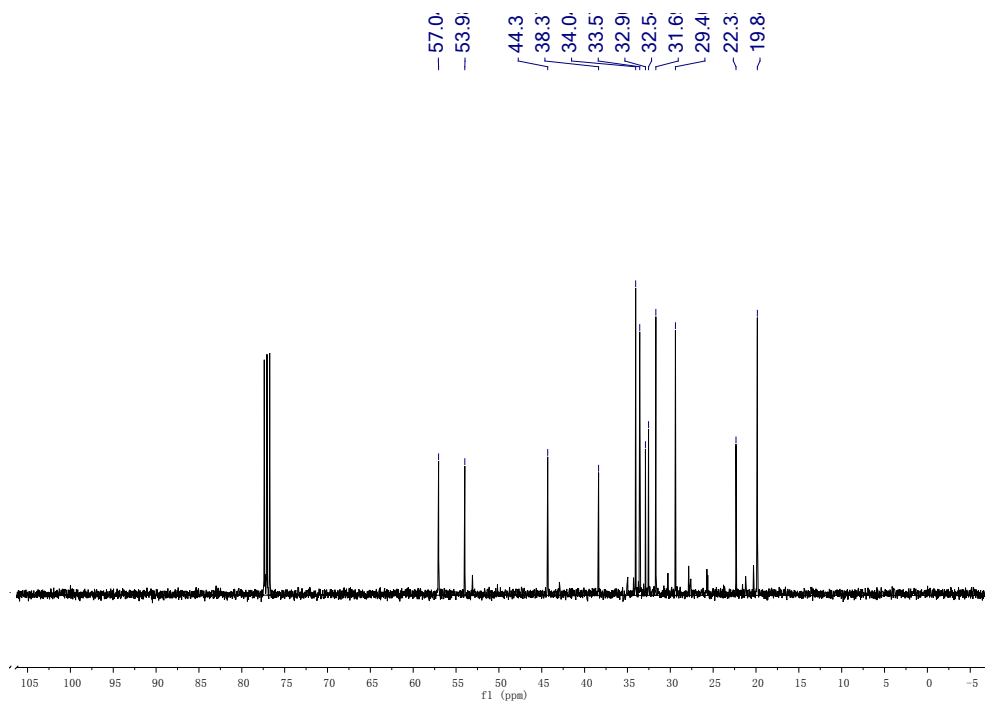


Figure S51 ^{13}C NMR spectrum of compound **3w**

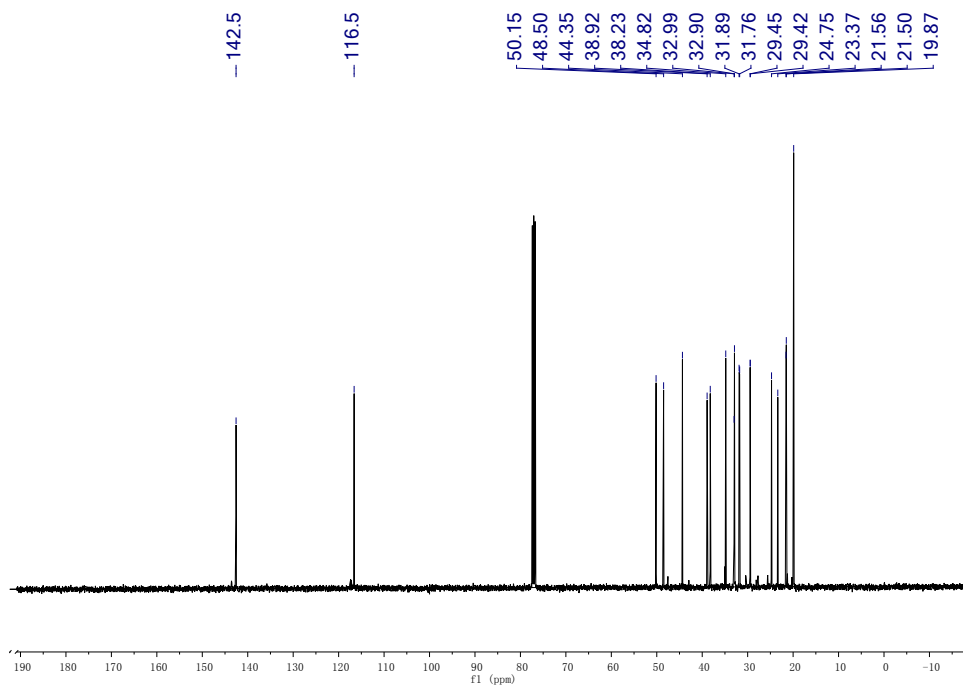


Figure S52 ^{13}C NMR spectrum of compound **3x**

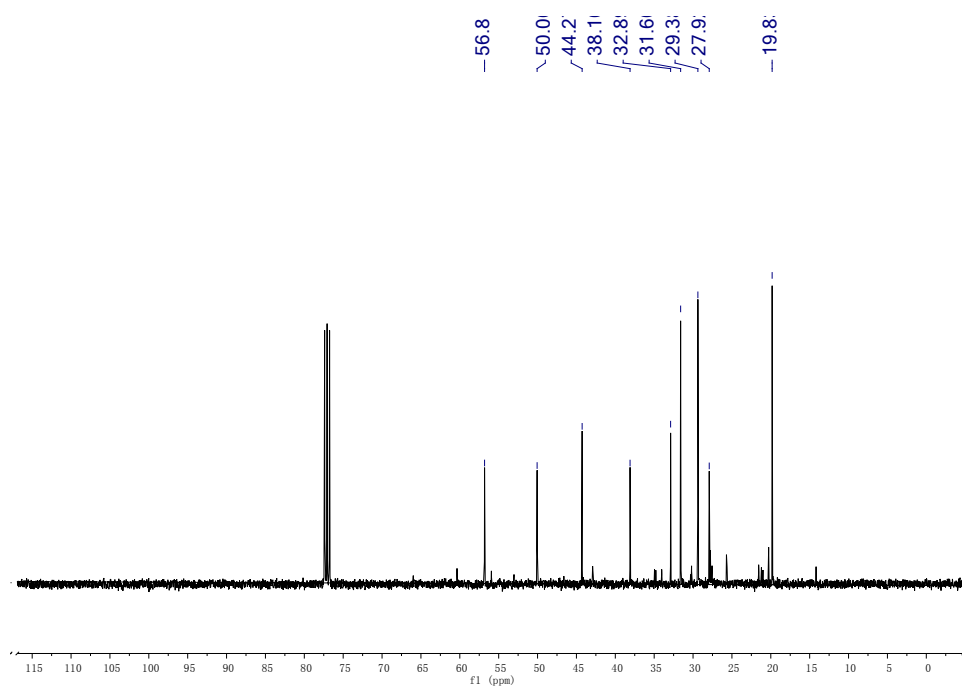


Figure S53 ^{13}C NMR spectrum of compound **3y**

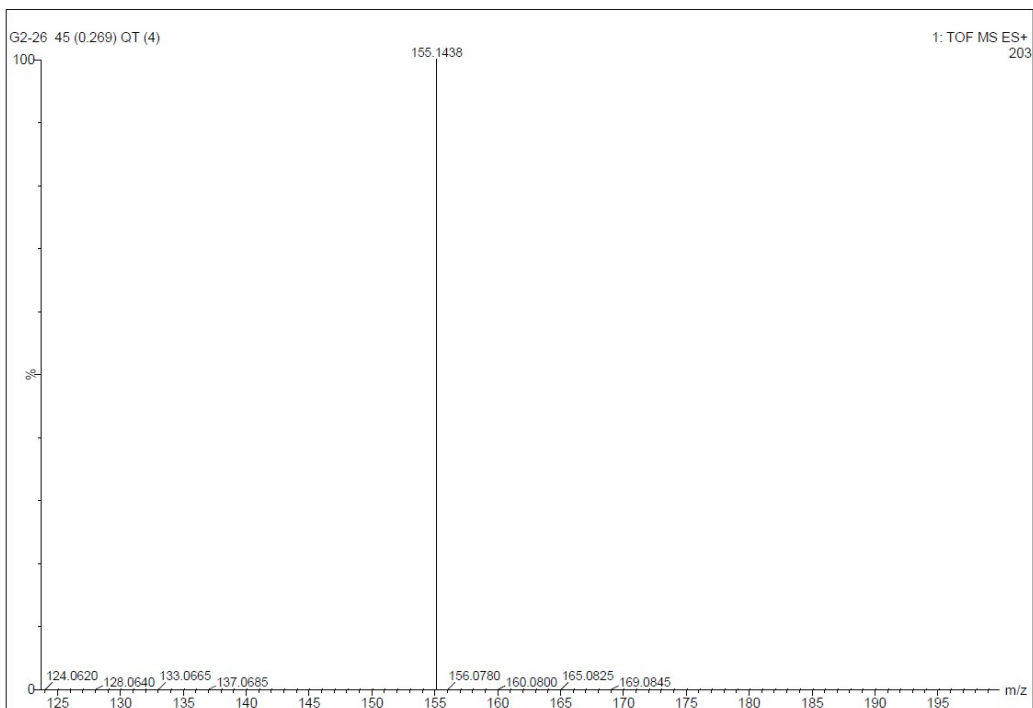


Figure 54 HRMS spectrum of compound **2**

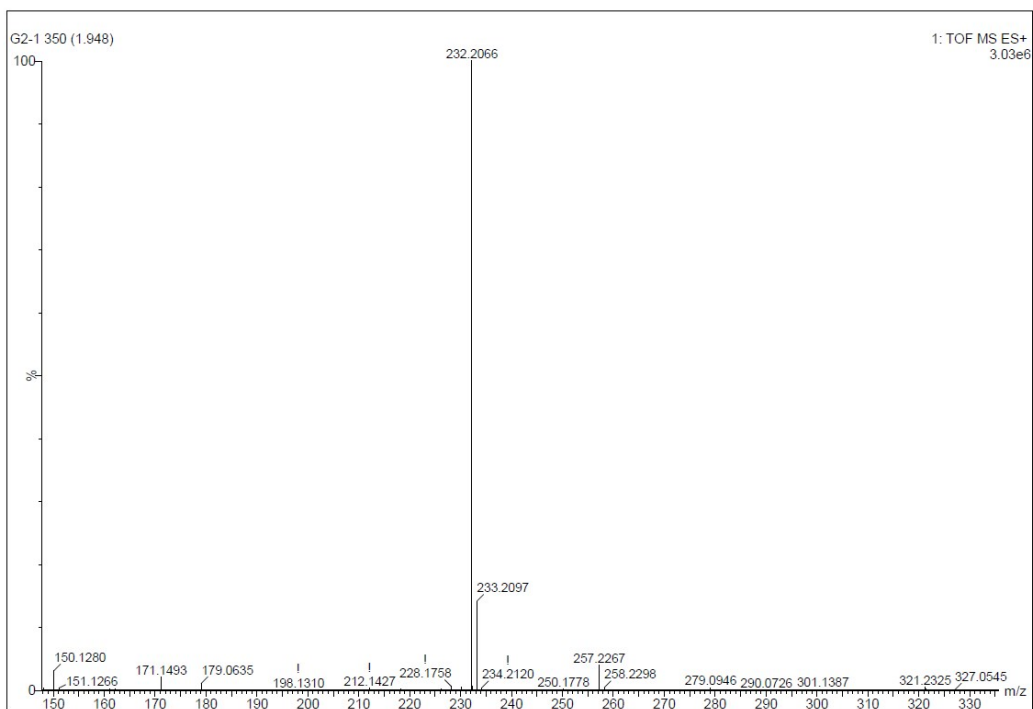


Figure 55 HRMS spectrum of compound **3a**

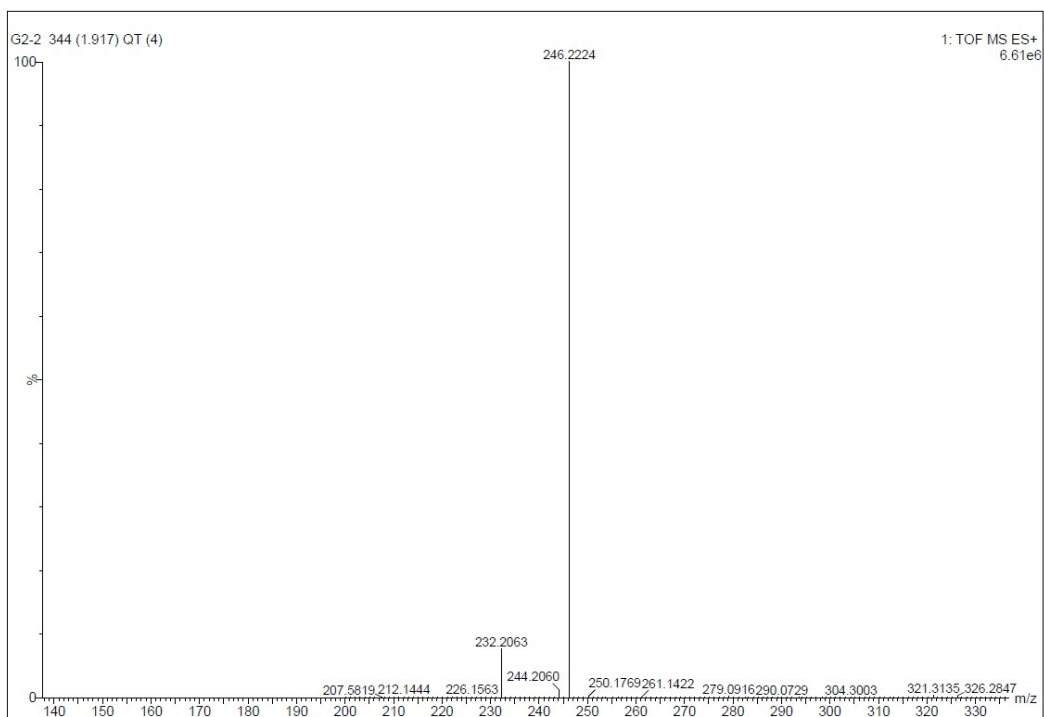


Figure 56 HRMS spectrum of compound **3b**

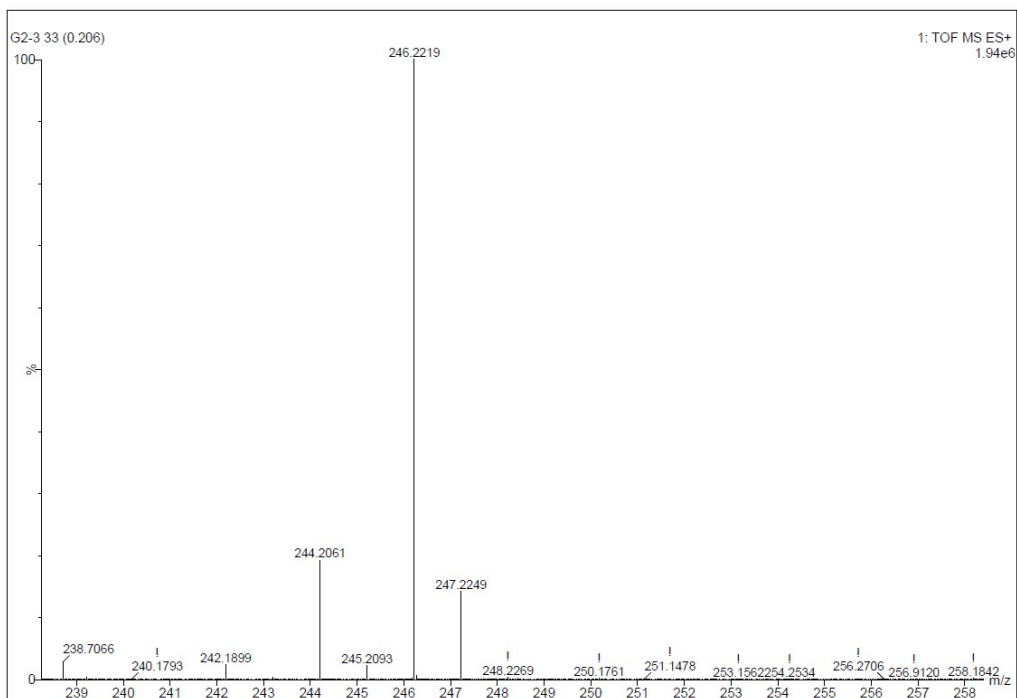


Figure 57 HRMS spectrum of compound **3c**

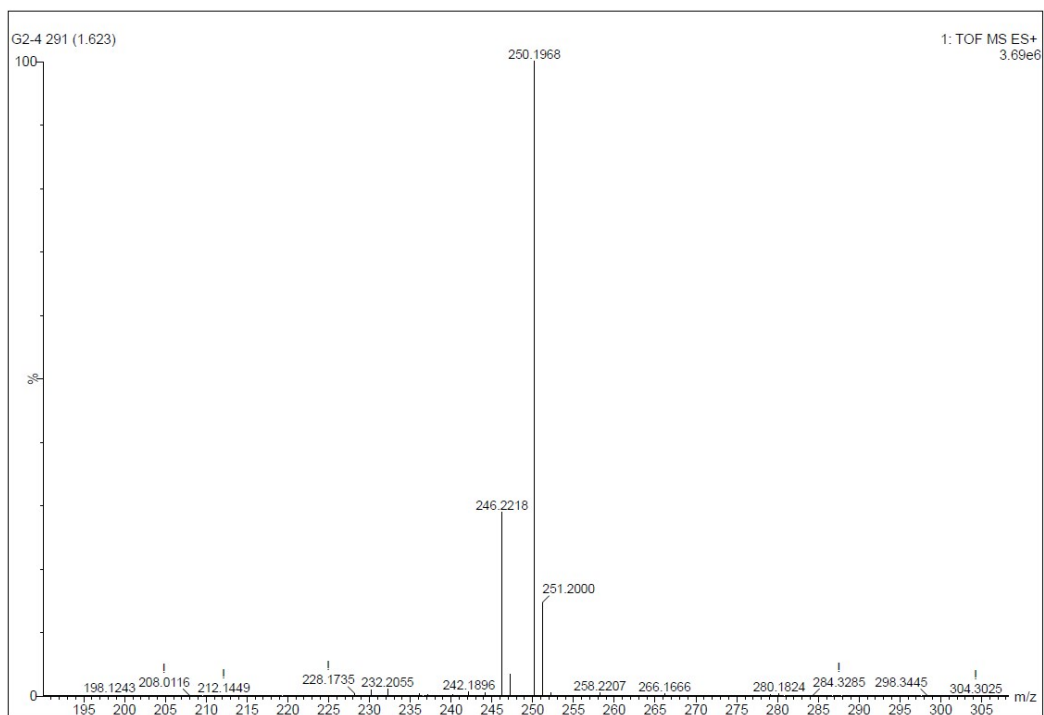


Figure 58 HRMS spectrum of compound **3d**

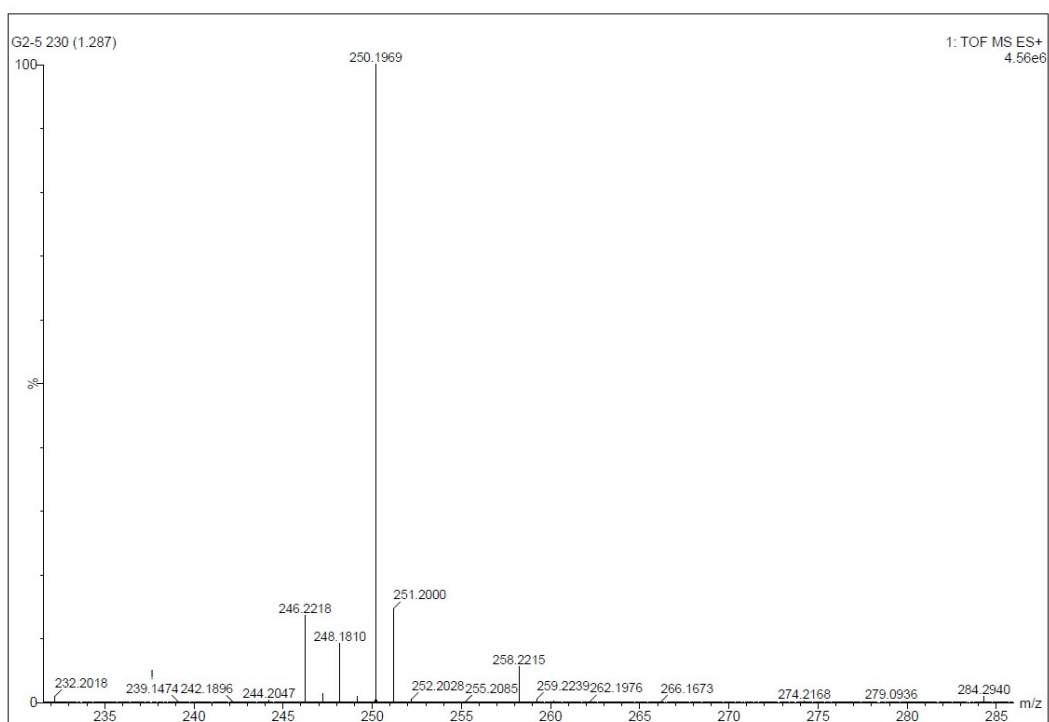


Figure 59 HRMS spectrum of compound **3e**

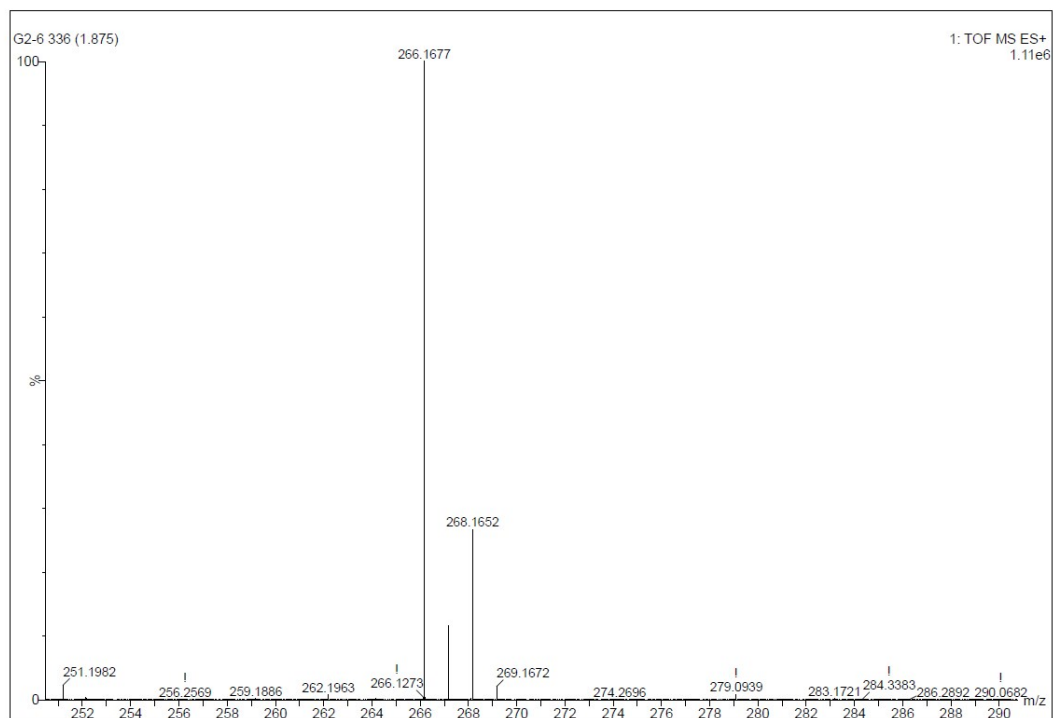


Figure 60 HRMS spectrum of compound **3f**

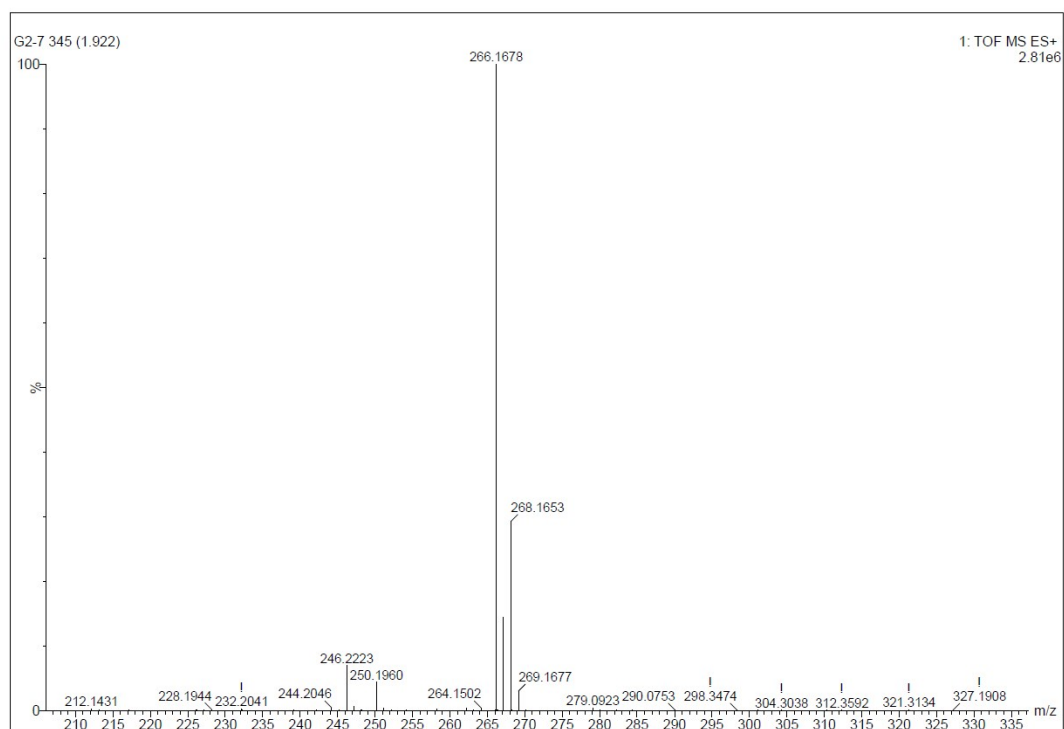


Figure 61 HRMS spectrum of compound **3g**

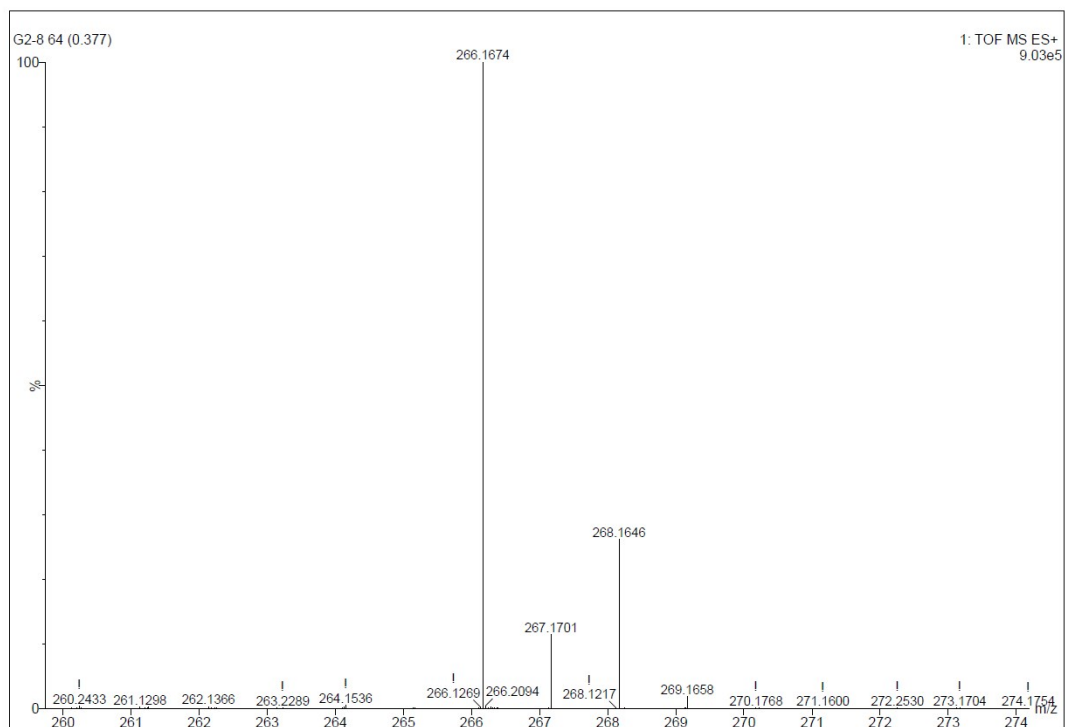


Figure 62 HRMS spectrum of compound **3h**

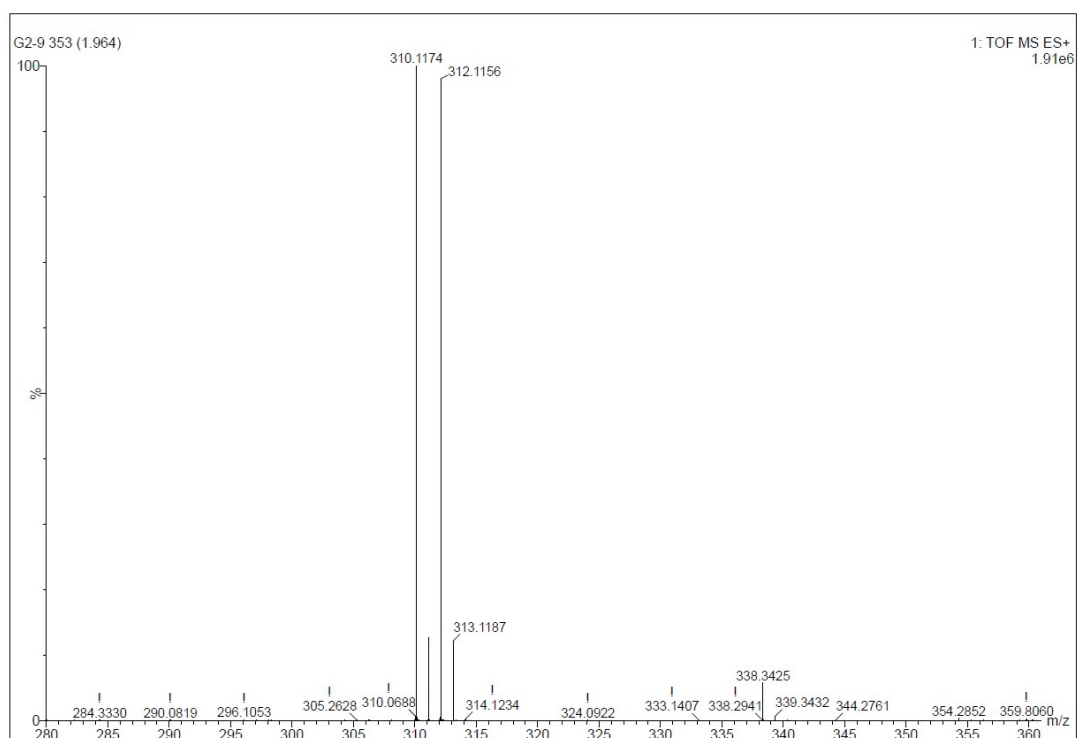


Figure 63 HRMS spectrum of compound **3i**

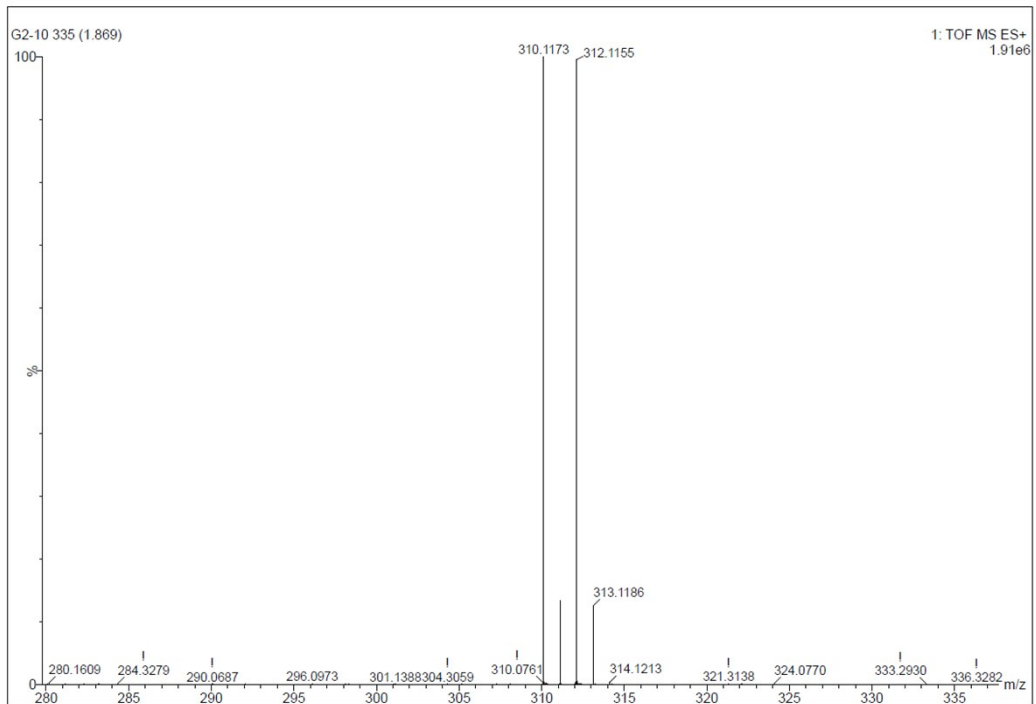


Figure 64 HRMS spectrum of compound **3j**

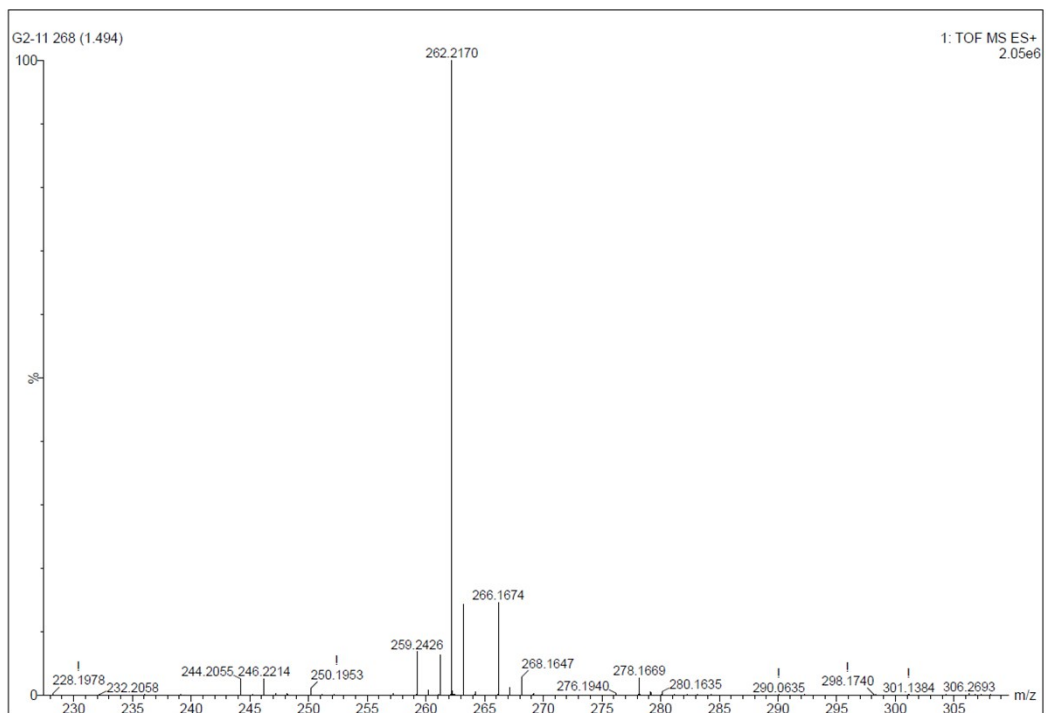


Figure 65 HRMS spectrum of compound **3k**

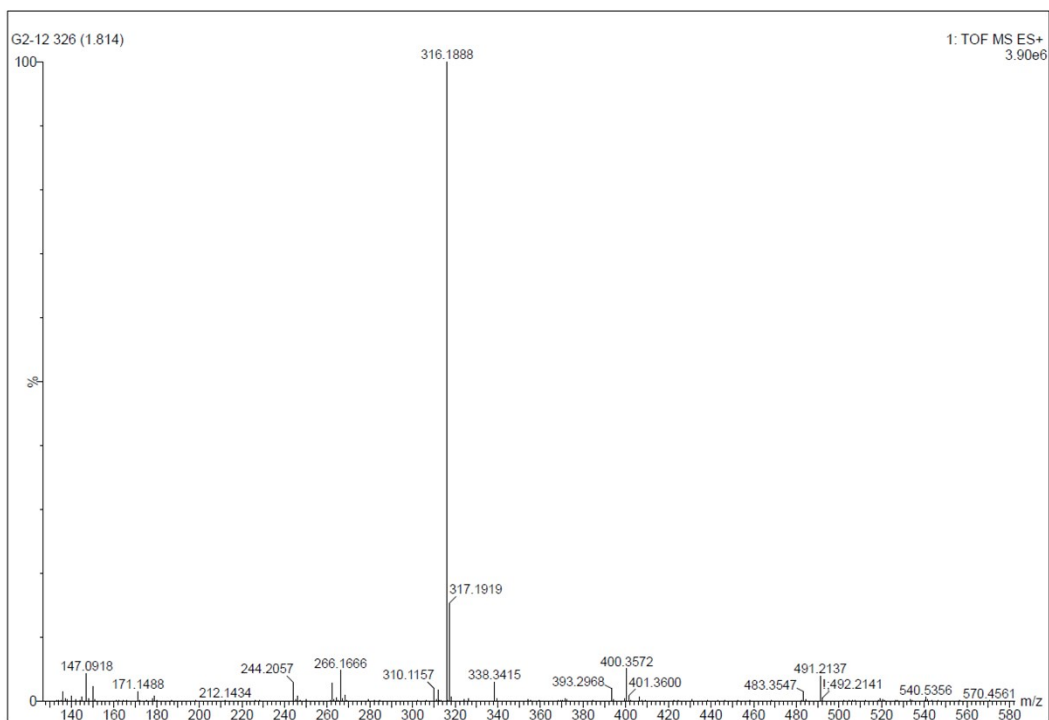


Figure 66 HRMS spectrum of compound **3l**

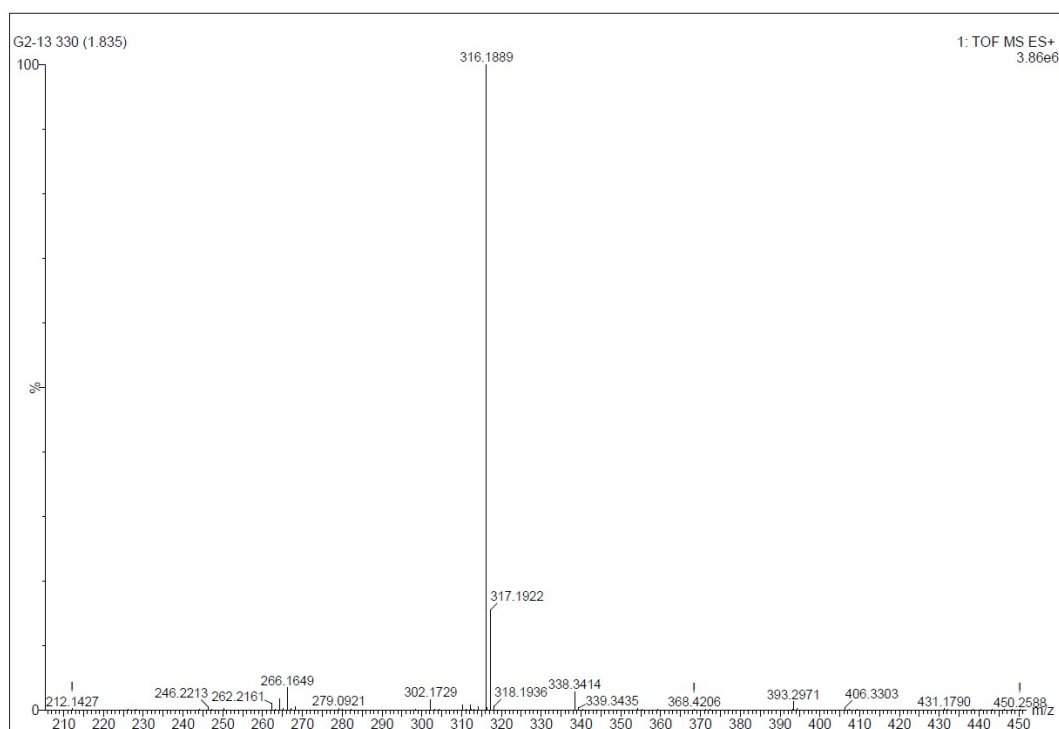


Figure 67 HRMS spectrum of compound **3m**

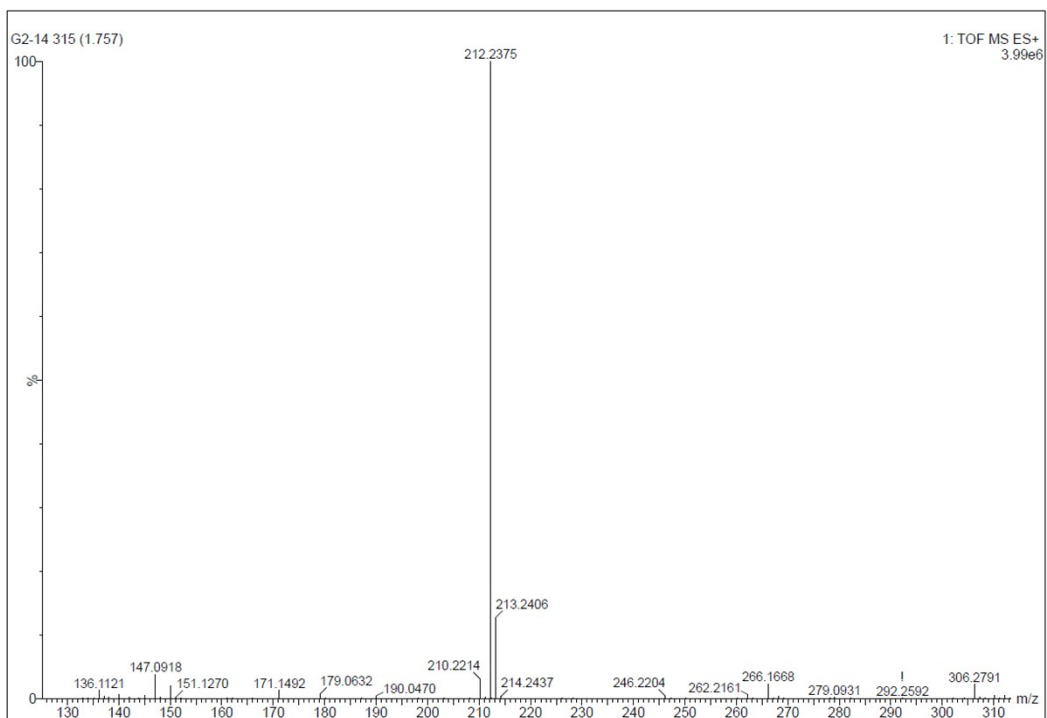


Figure 68 HRMS spectrum of compound **3n**

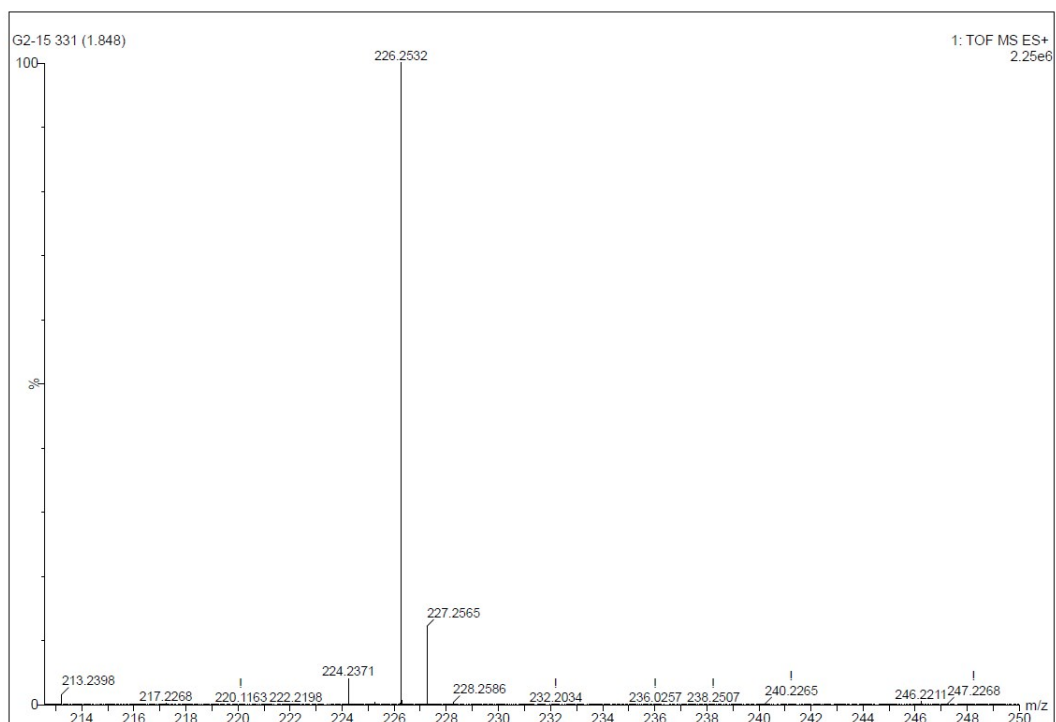


Figure 69 HRMS spectrum of compound **3o**

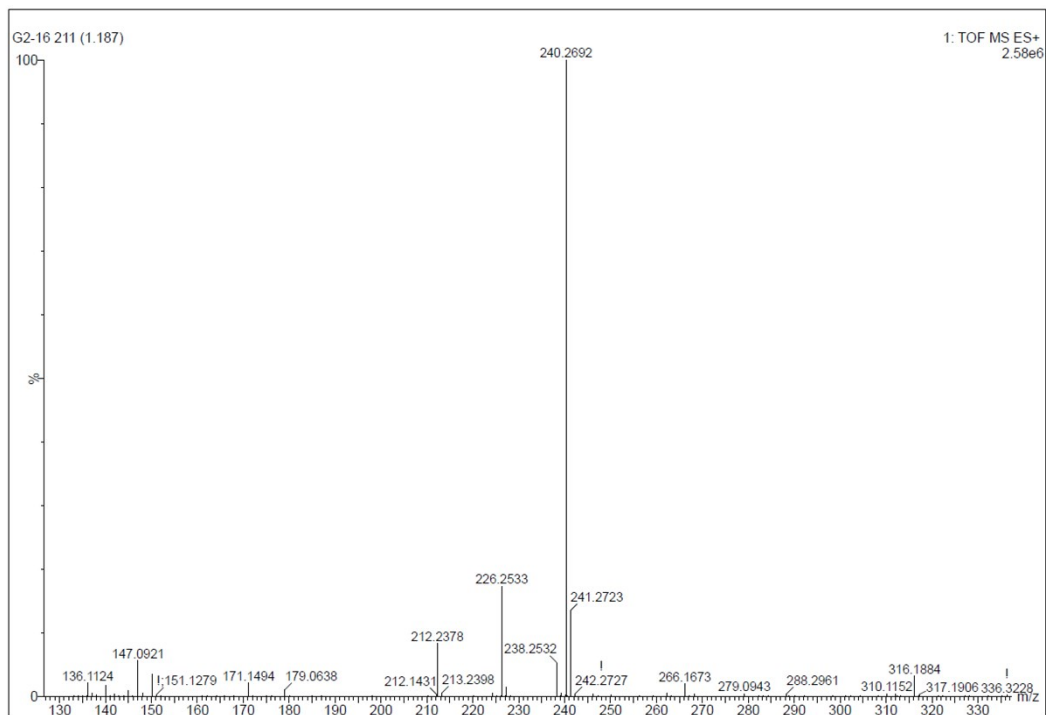


Figure 70 HRMS spectrum of compound **3p**

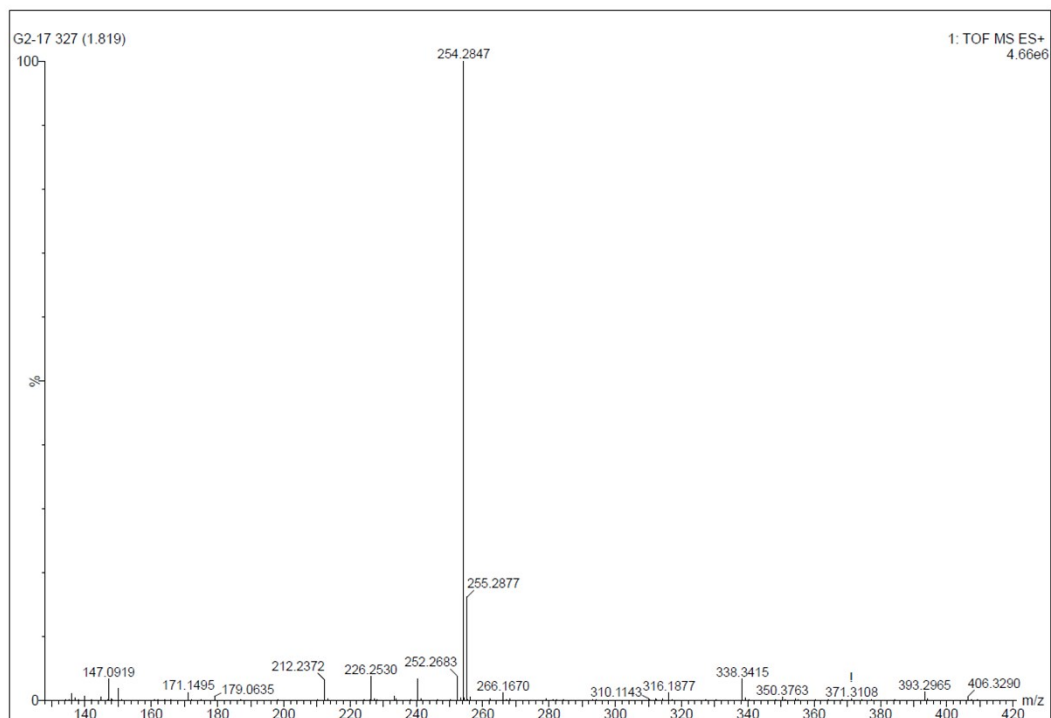


Figure 71 HRMS spectrum of compound **3q**

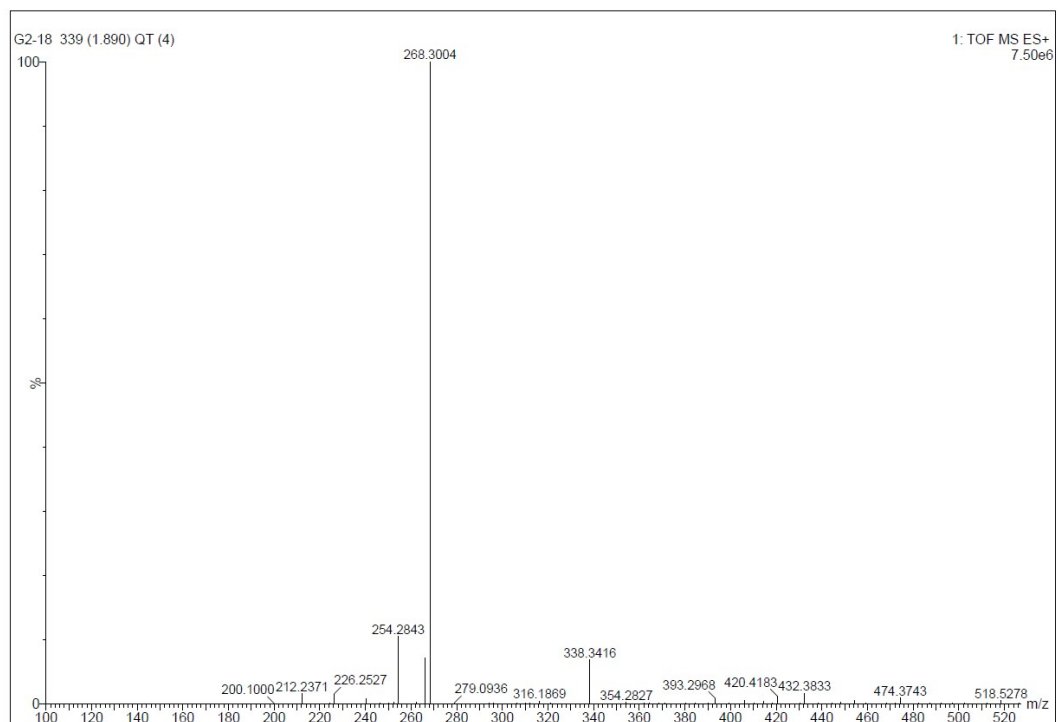


Figure 72 HRMS spectrum of compound **3r**

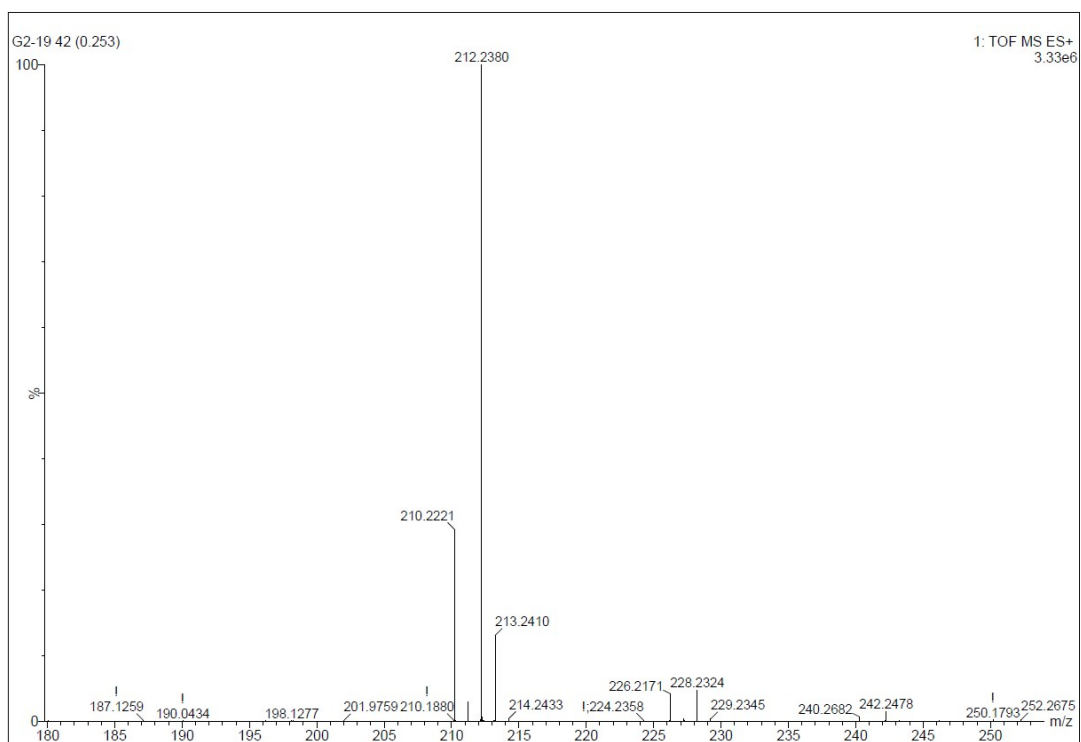


Figure 73 HRMS spectrum of compound **3s**

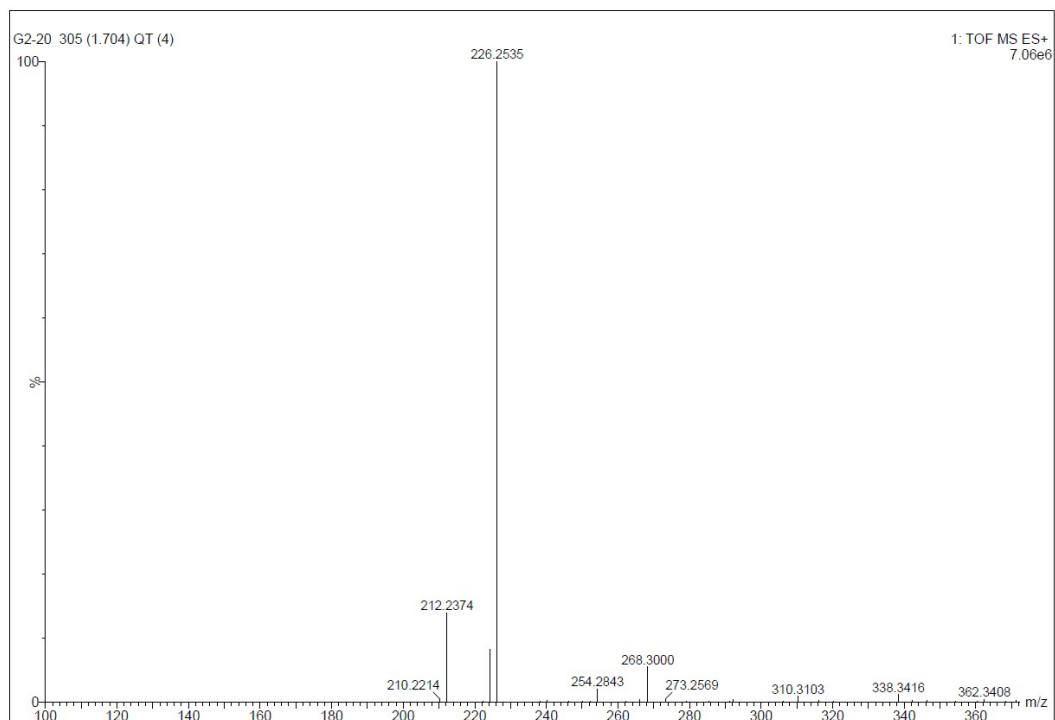


Figure 74 HRMS spectrum of compound **3t**

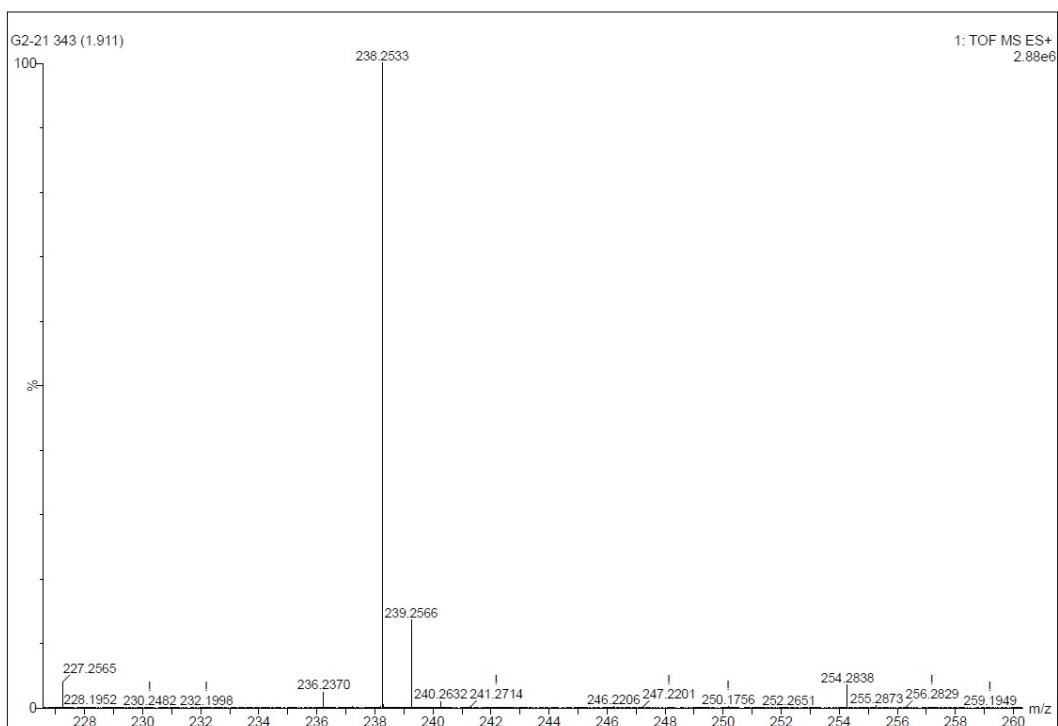


Figure 75 HRMS spectrum of compound **3u**

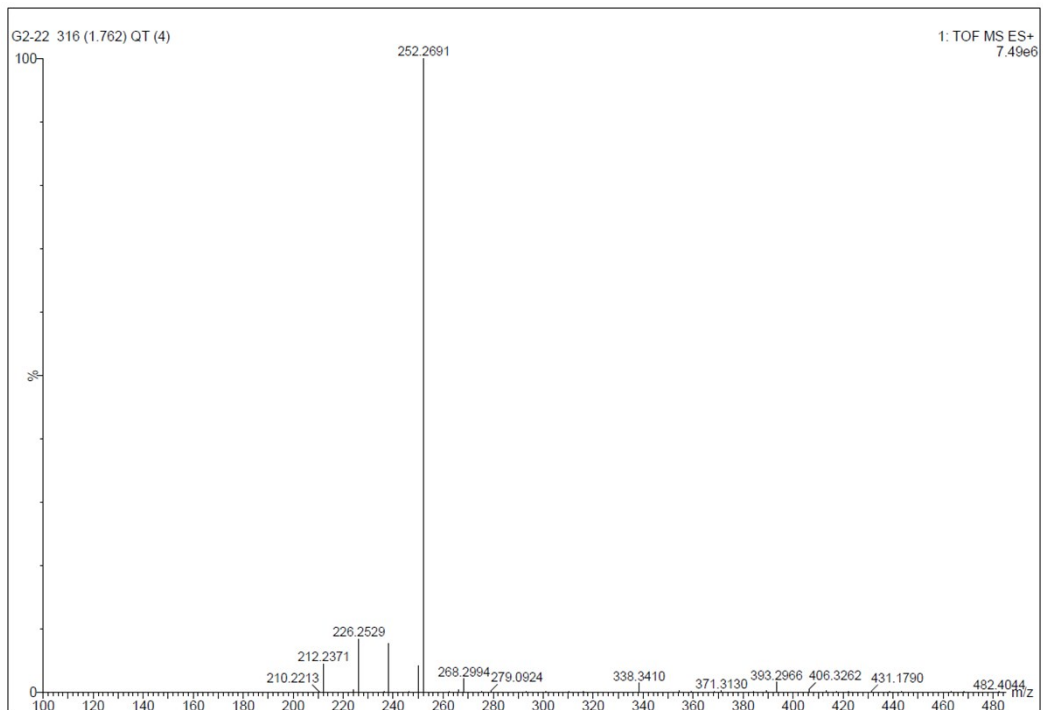


Figure 76 HRMS spectrum of compound **3v**

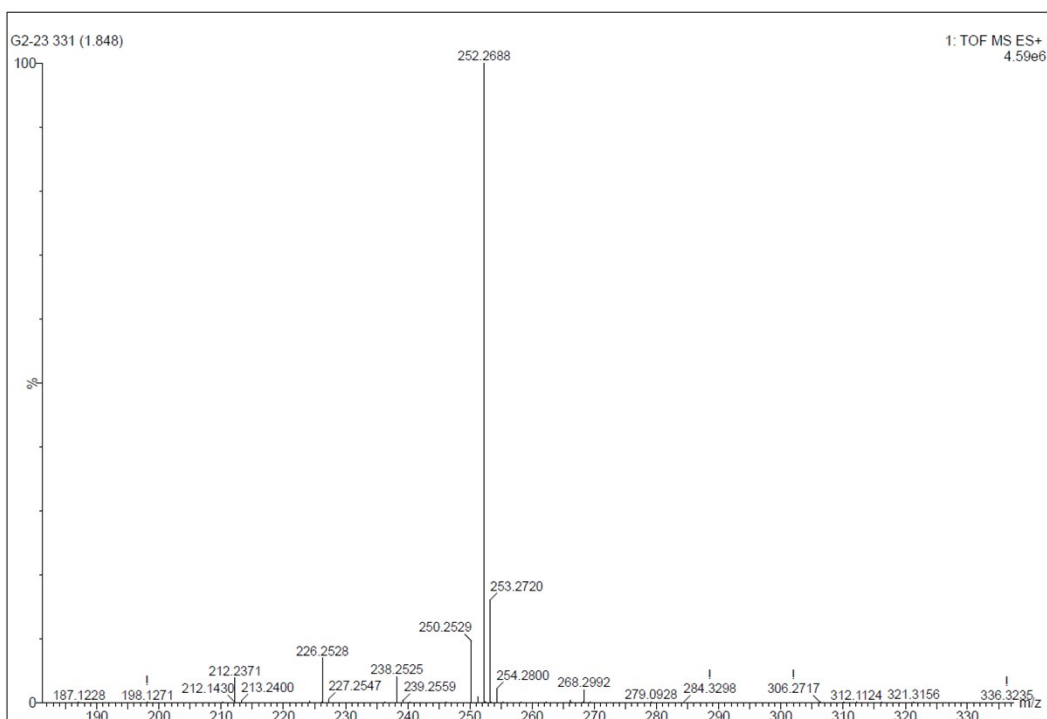


Figure 77 HRMS spectrum of compound **3w**

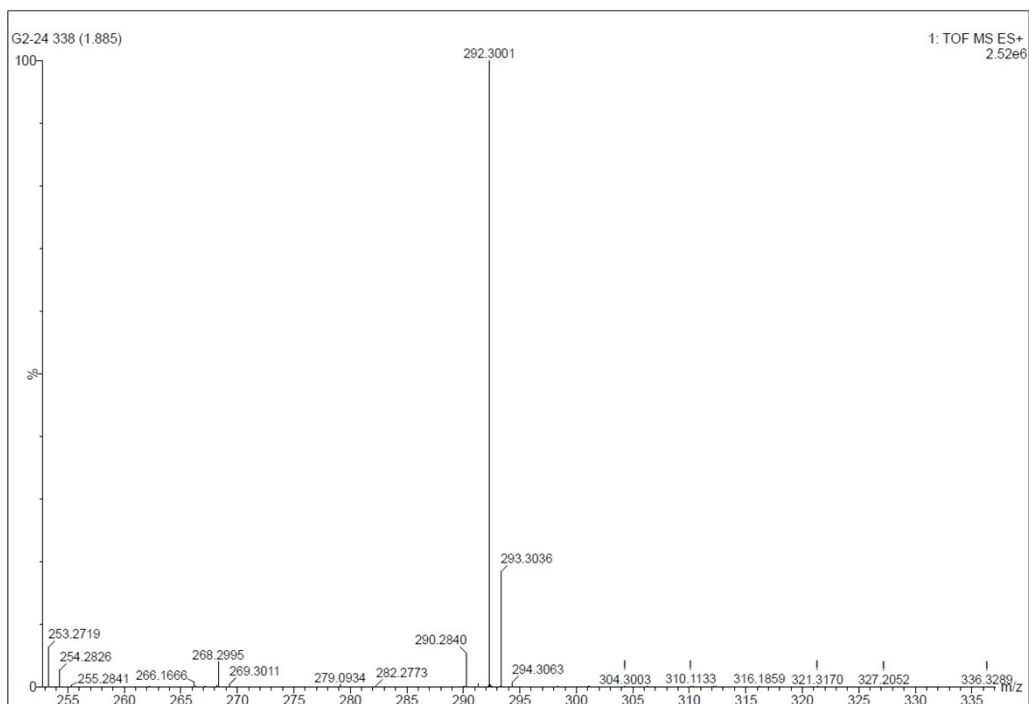


Figure 78 HRMS spectrum of compound **3x**

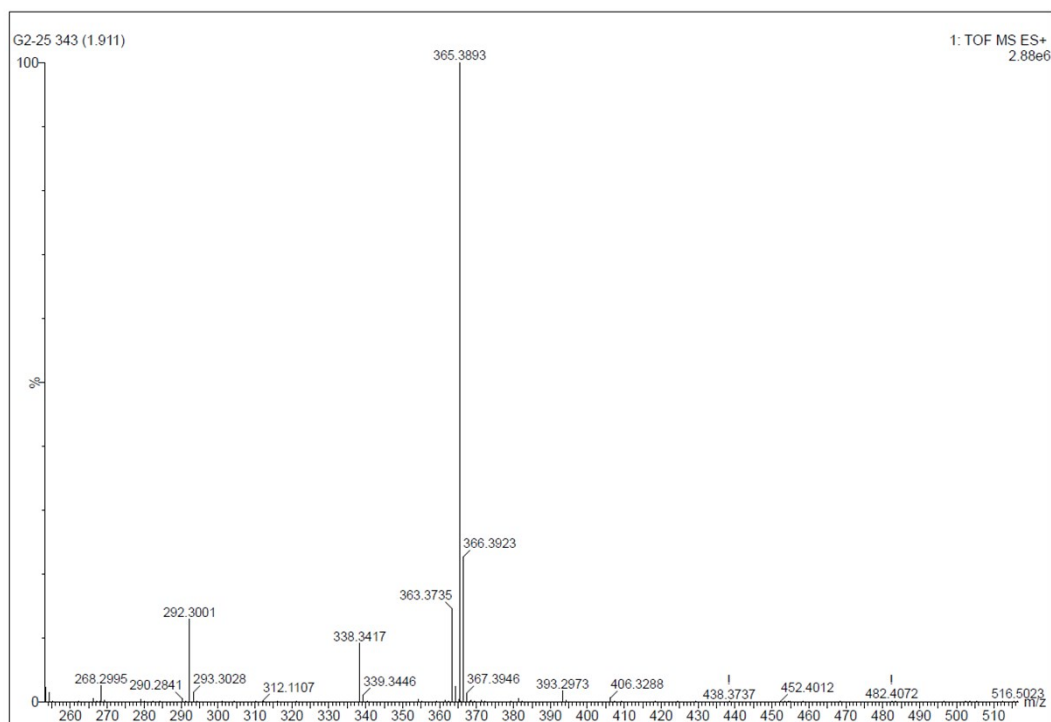


Figure 79 HRMS spectrum of compound **3y**

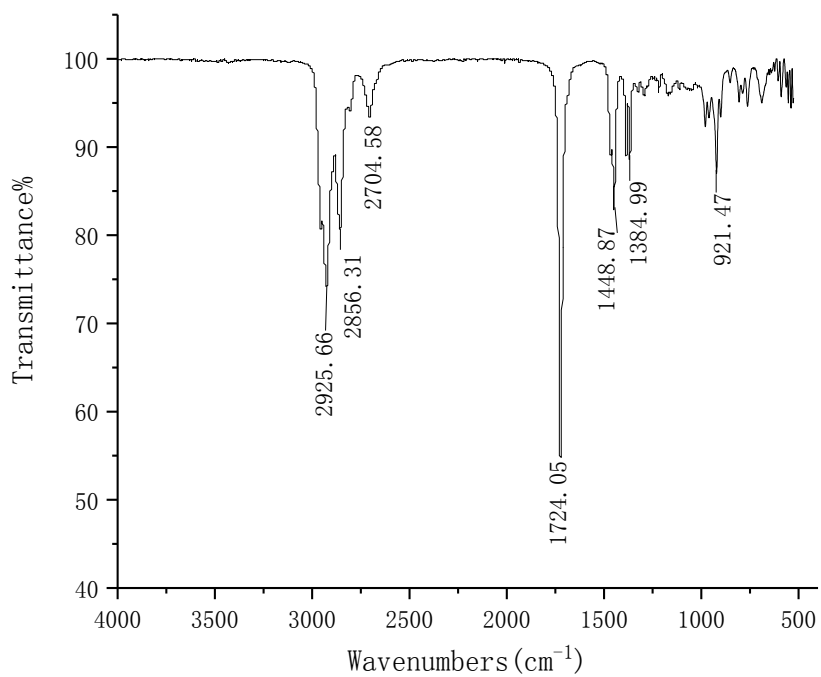


Figure S80 IR spectrum of compound **2**

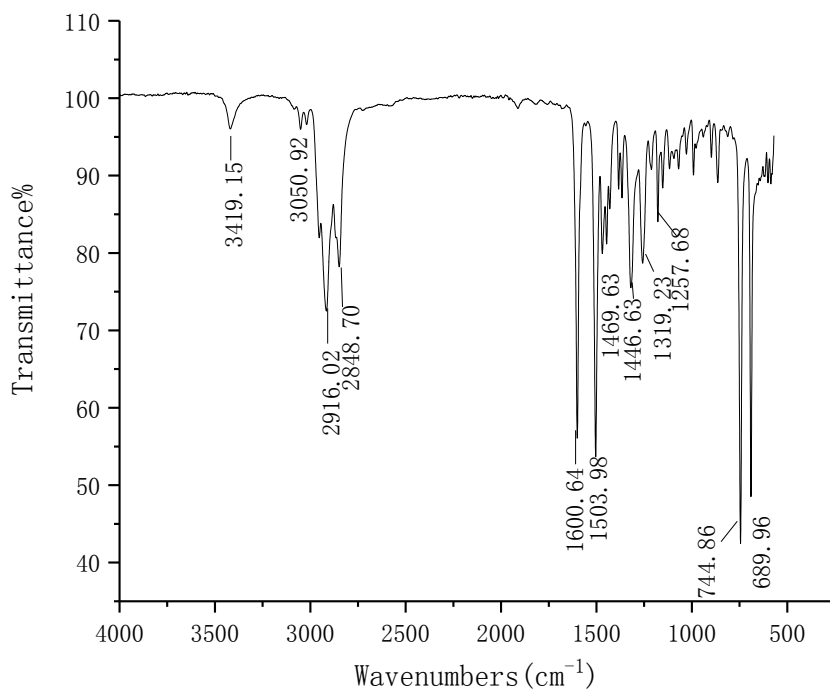


Figure S81 IR spectrum of compound **3a**

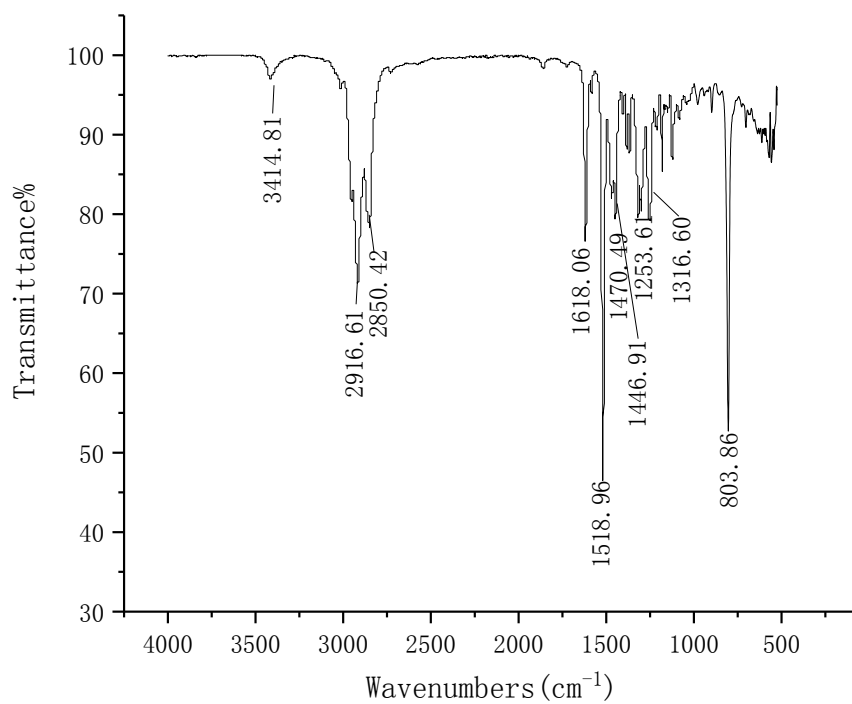


Figure S82 IR spectrum of compound **3b**

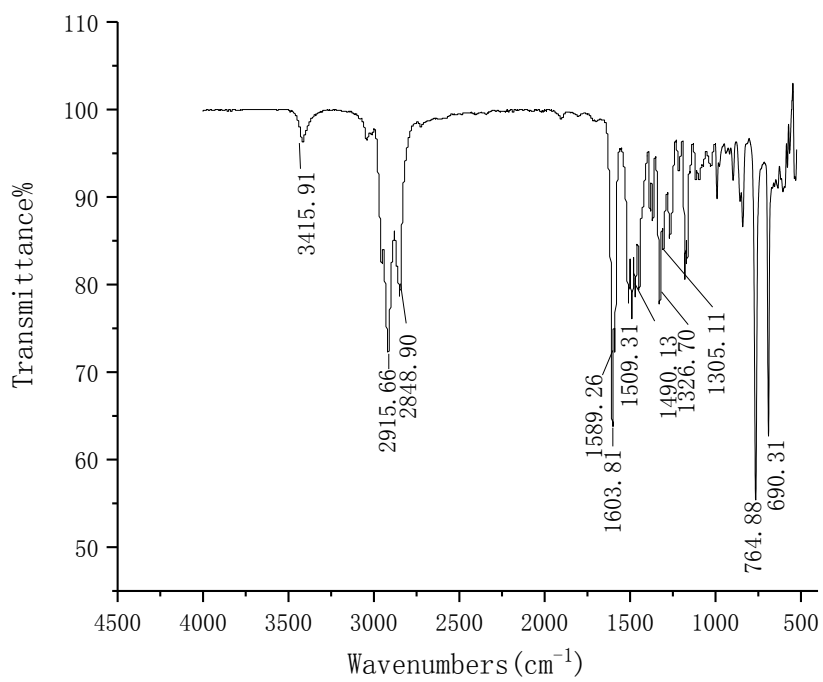


Figure S83 IR spectrum of compound **3c**

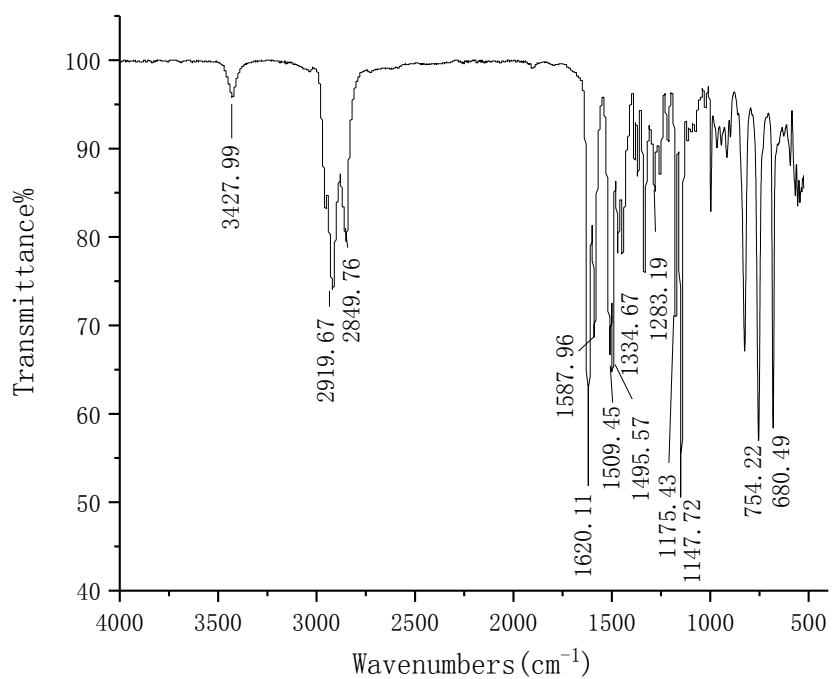


Figure S84 IR spectrum of compound **3d**

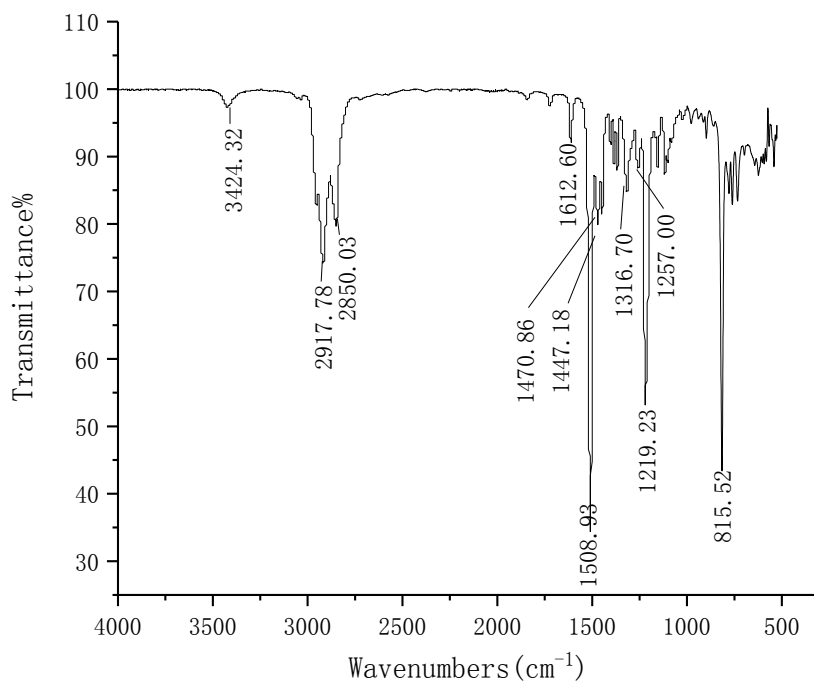


Figure 85 IR spectrum of compound **3e**

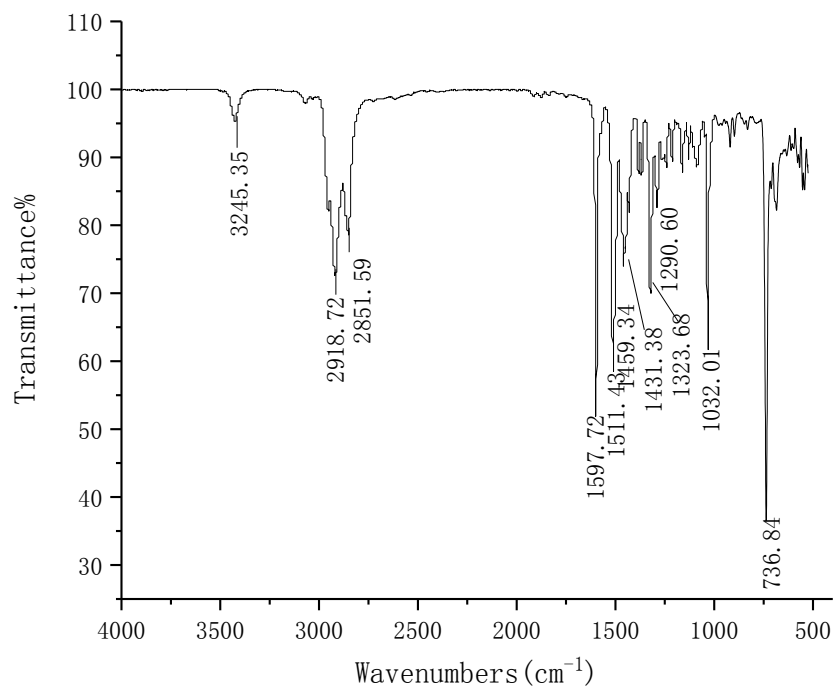


Figure S86 IR spectrum of compound **3f**

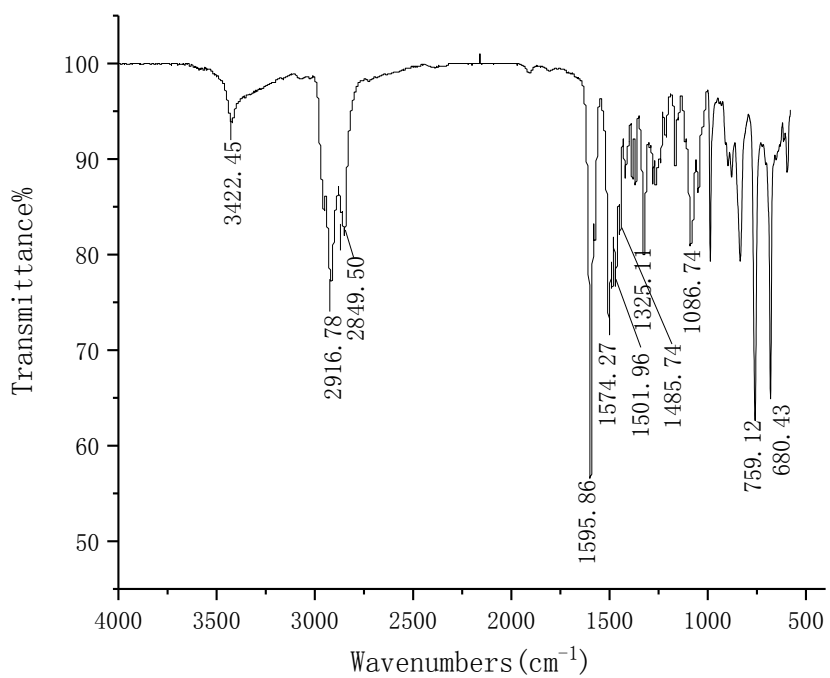


Figure S87 IR spectrum of compound **3g**

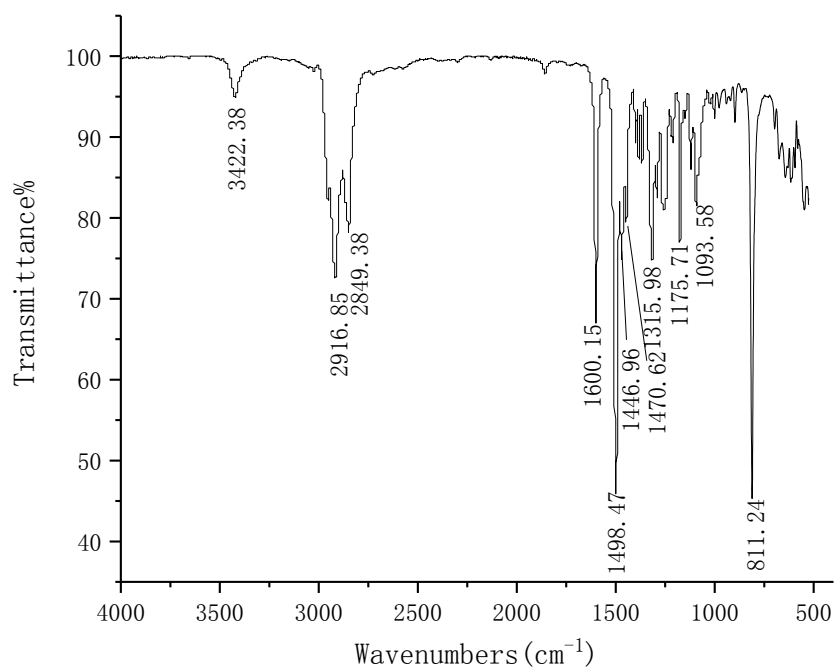


Figure S88 IR spectrum of compound **3h**

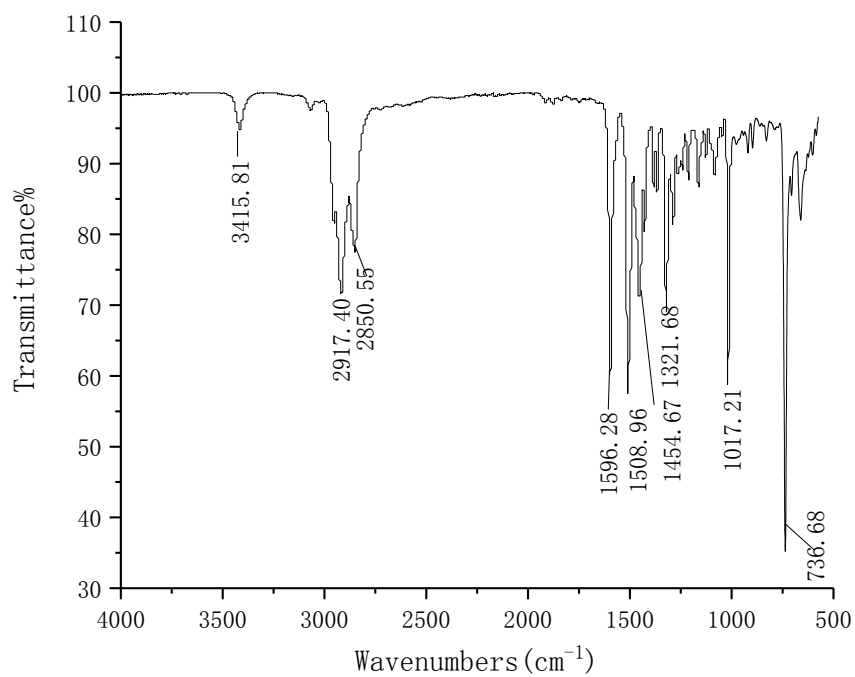


Figure S89 IR spectrum of compound **3i**

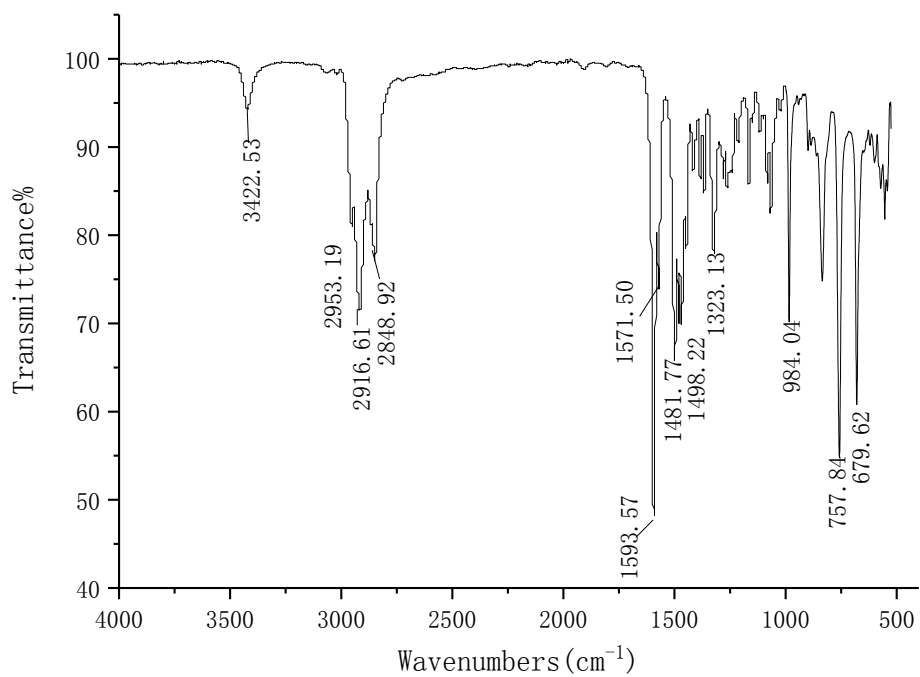


Figure S90 IR spectrum of compound **3j**

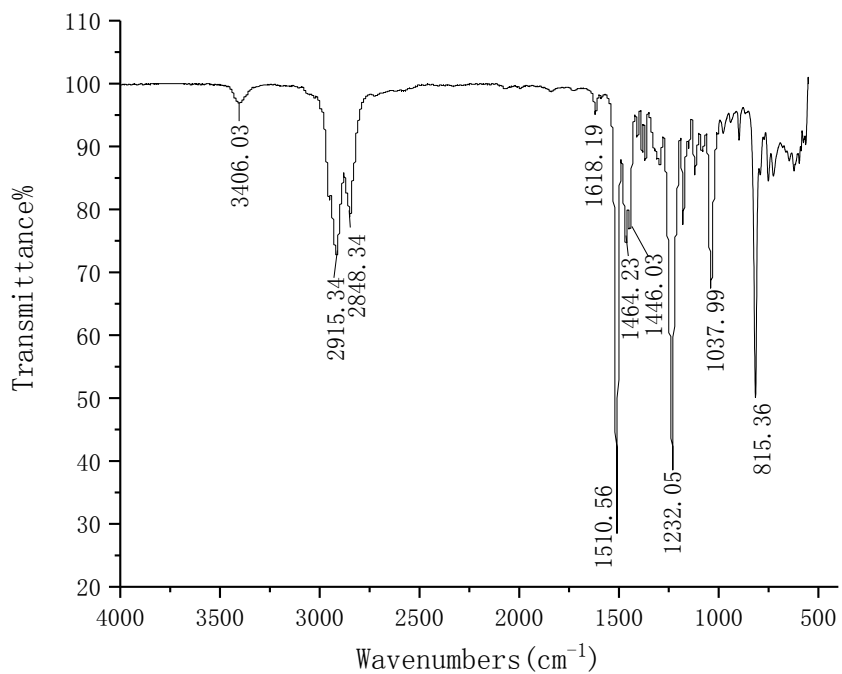


Figure S91 IR spectrum of compound **3k**

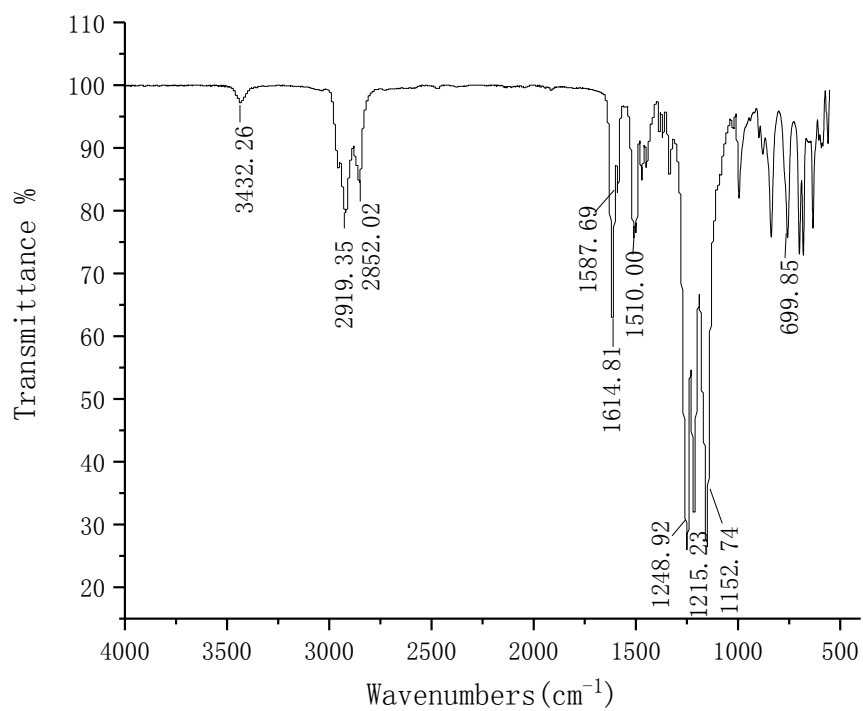


Figure S92 IR spectrum of compound **31**

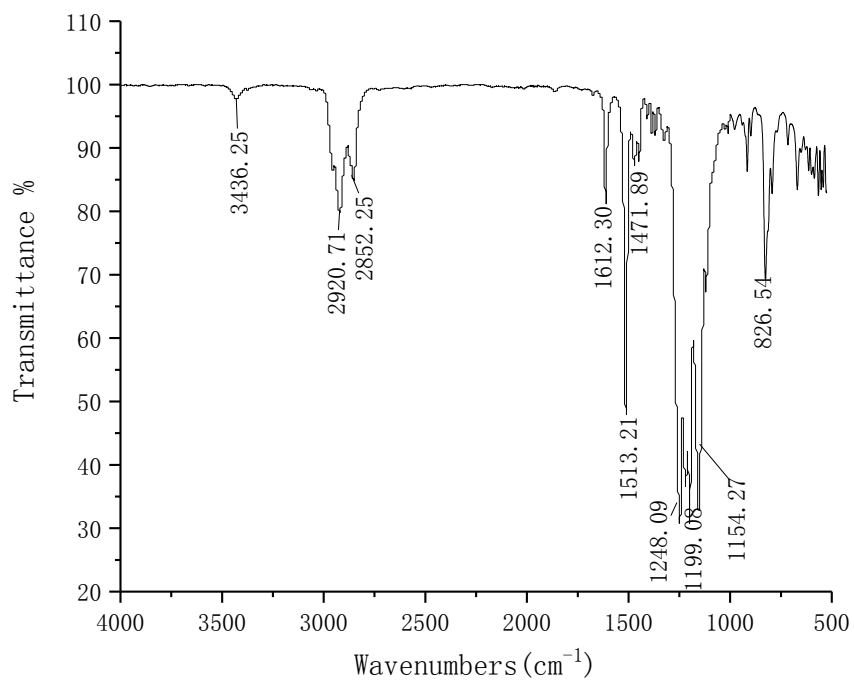


Figure S93 IR spectrum of compound **3m**

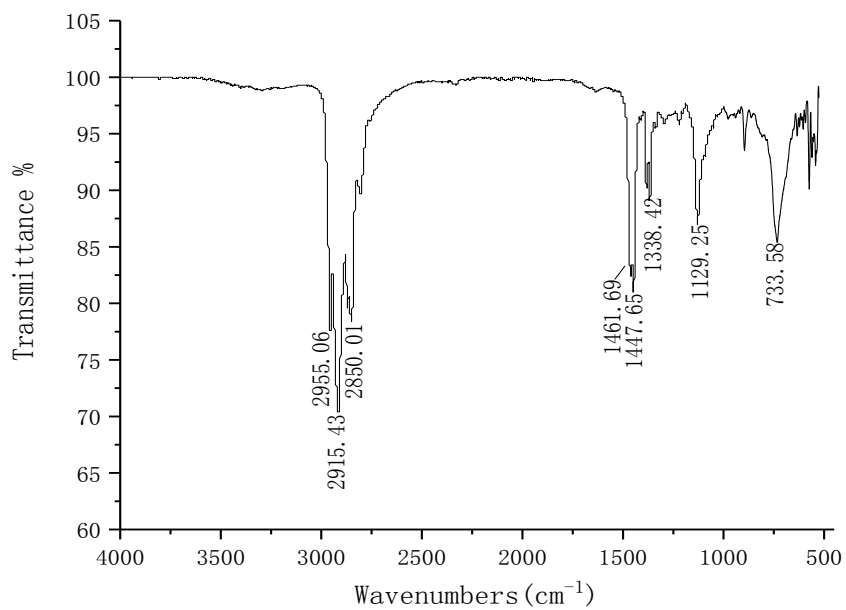


Figure S94 IR spectrum of compound **3n**

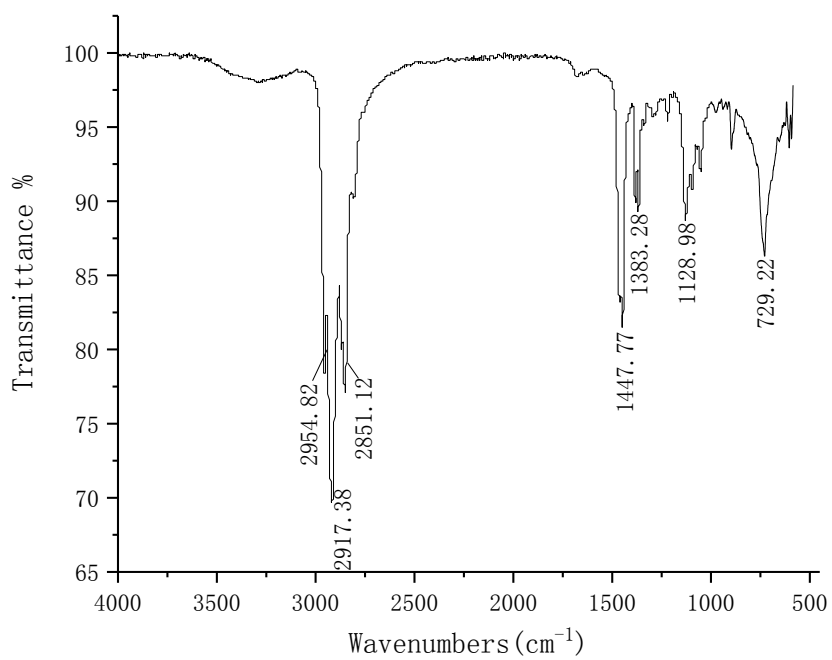


Figure S95 IR spectrum of compound **3o**

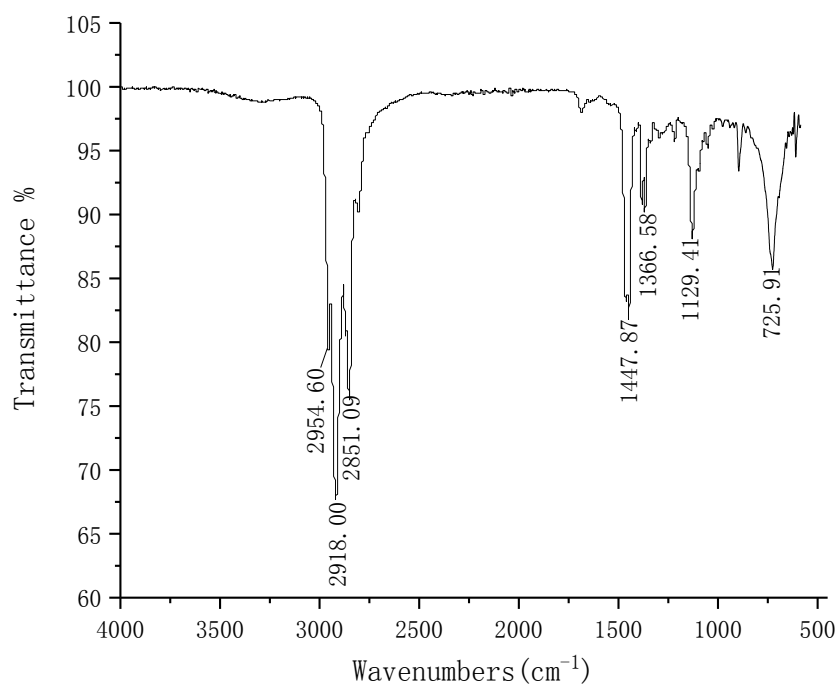


Figure S96 IR spectrum of compound **3p**

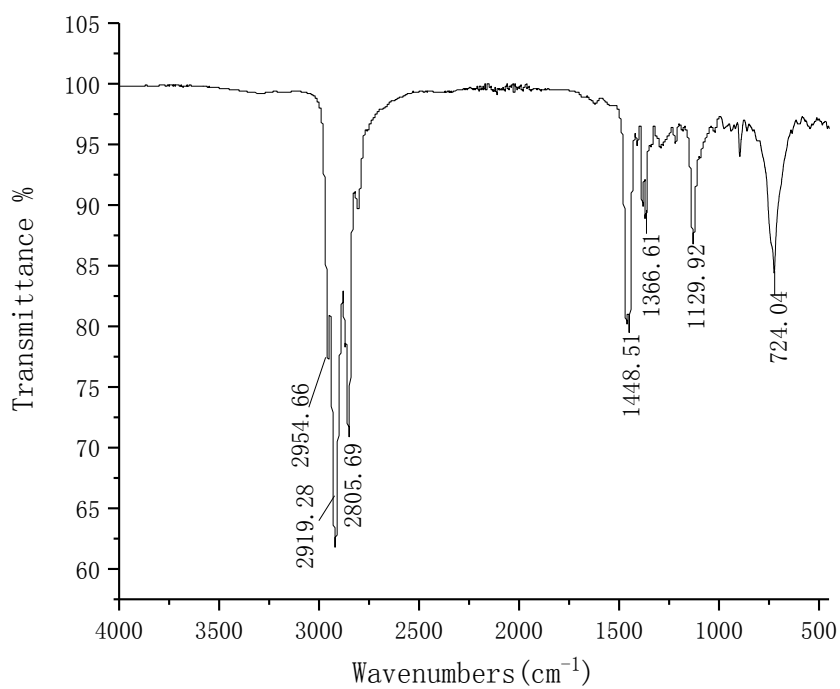


Figure S97 spectrum of compound **3q**

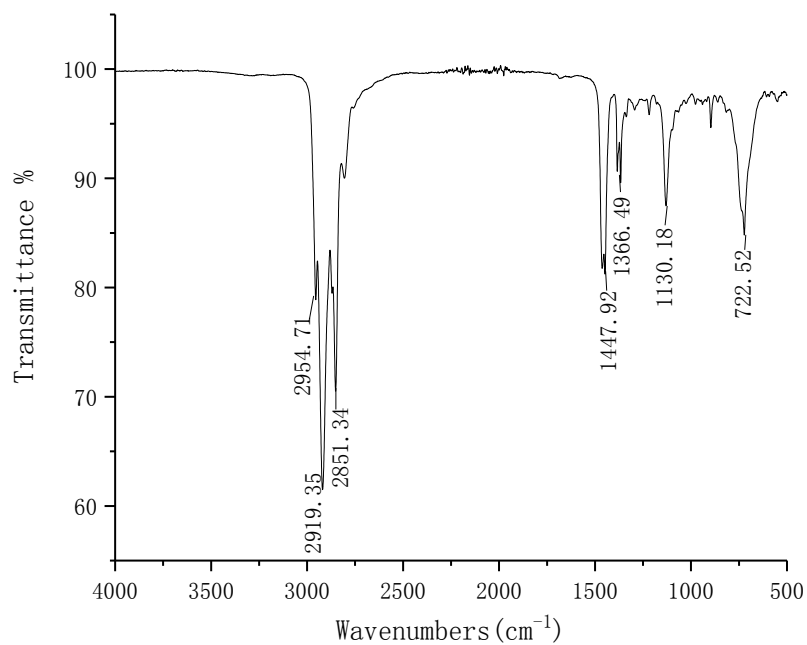


Figure S98 IR spectrum of compound **3r**

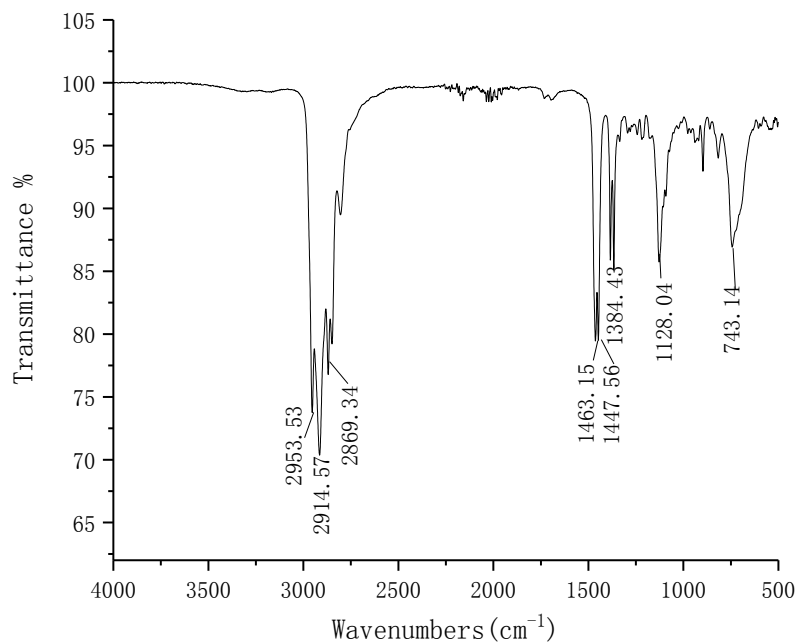


Figure S99 IR spectrum of compound **3s**

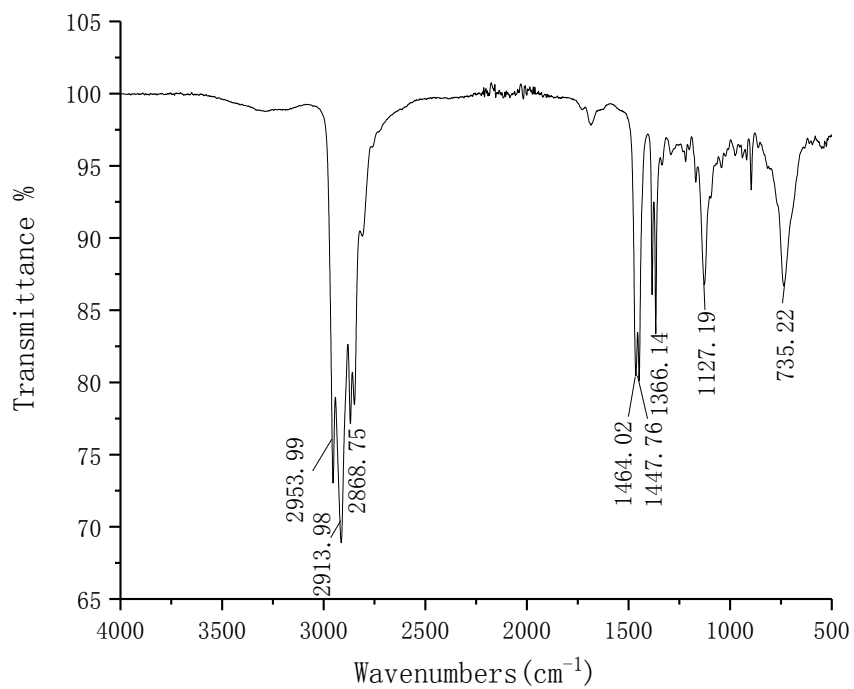


Figure S100 IR spectrum of compound **3t**

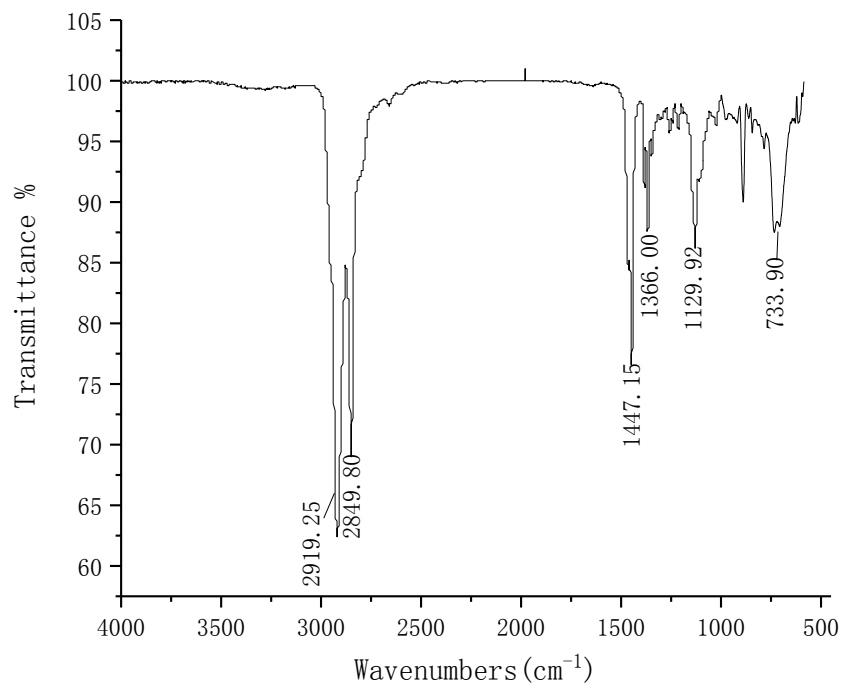


Figure S101 IR spectrum of compound **3u**

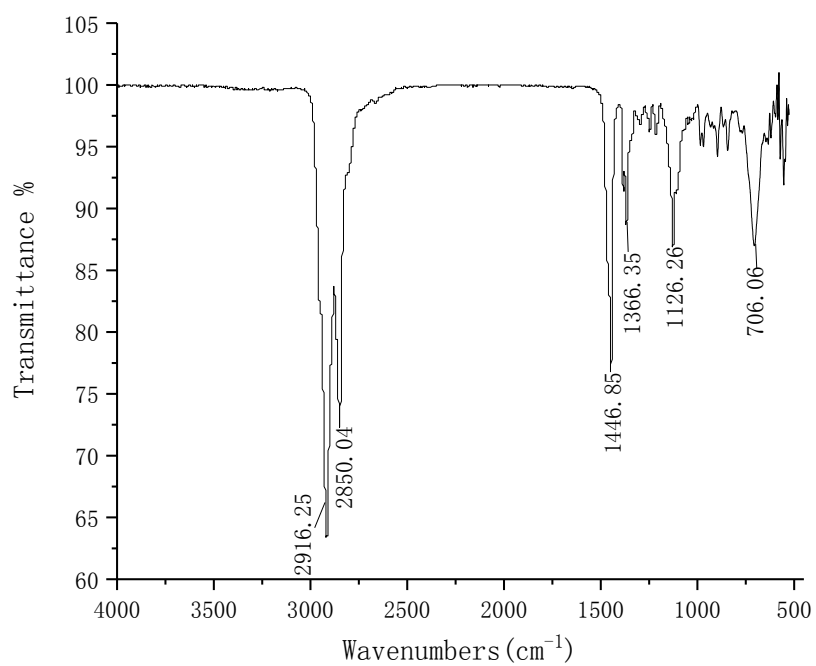


Figure S102 IR spectrum of compound **3v**

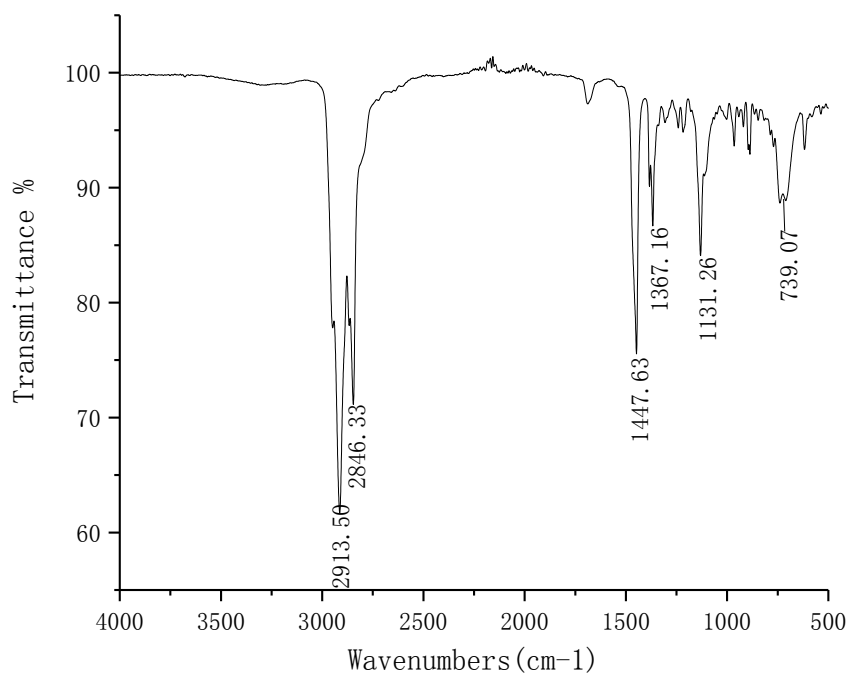


Figure S103 IR spectrum of compound **3w**

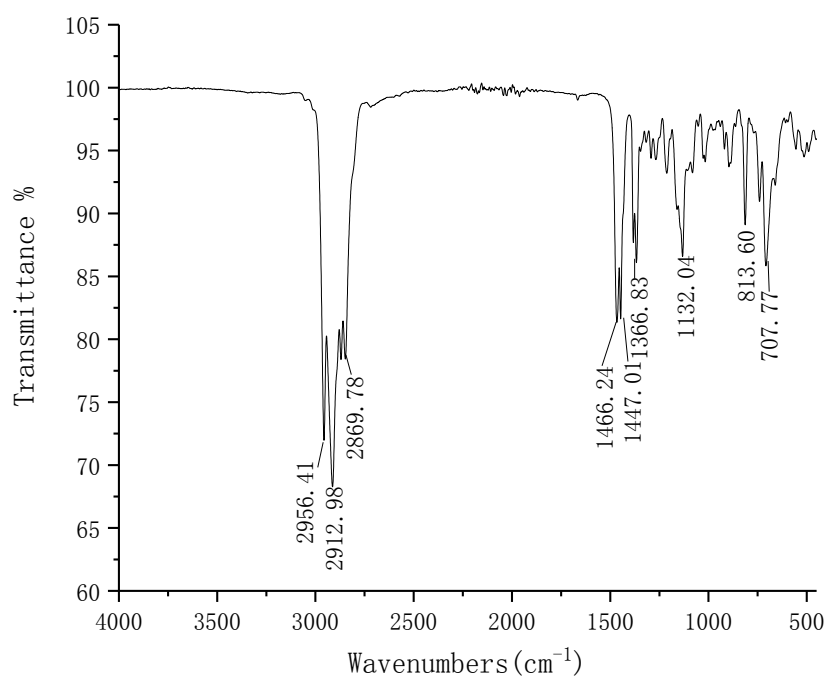


Figure S104 IR spectrum of compound **3x**

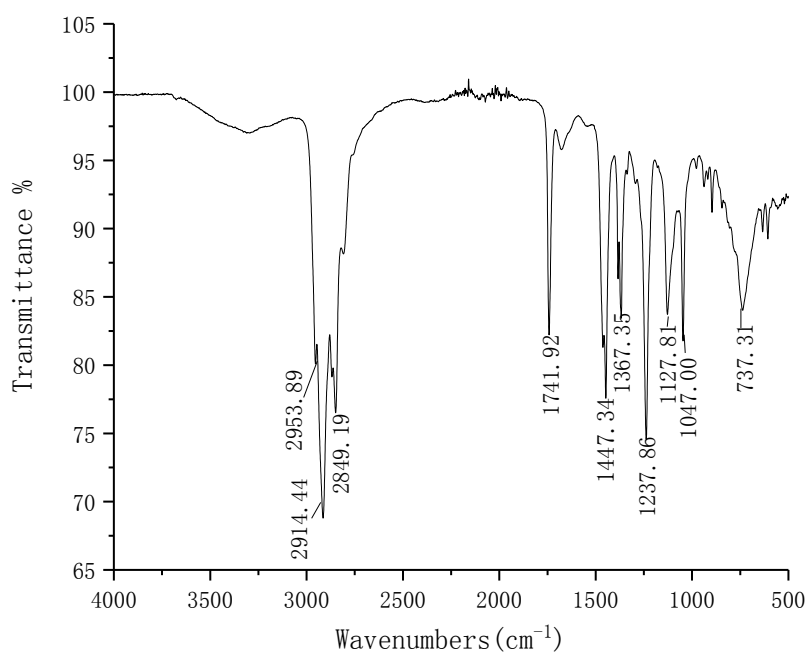


Figure S105 IR spectrum of compound **3y**

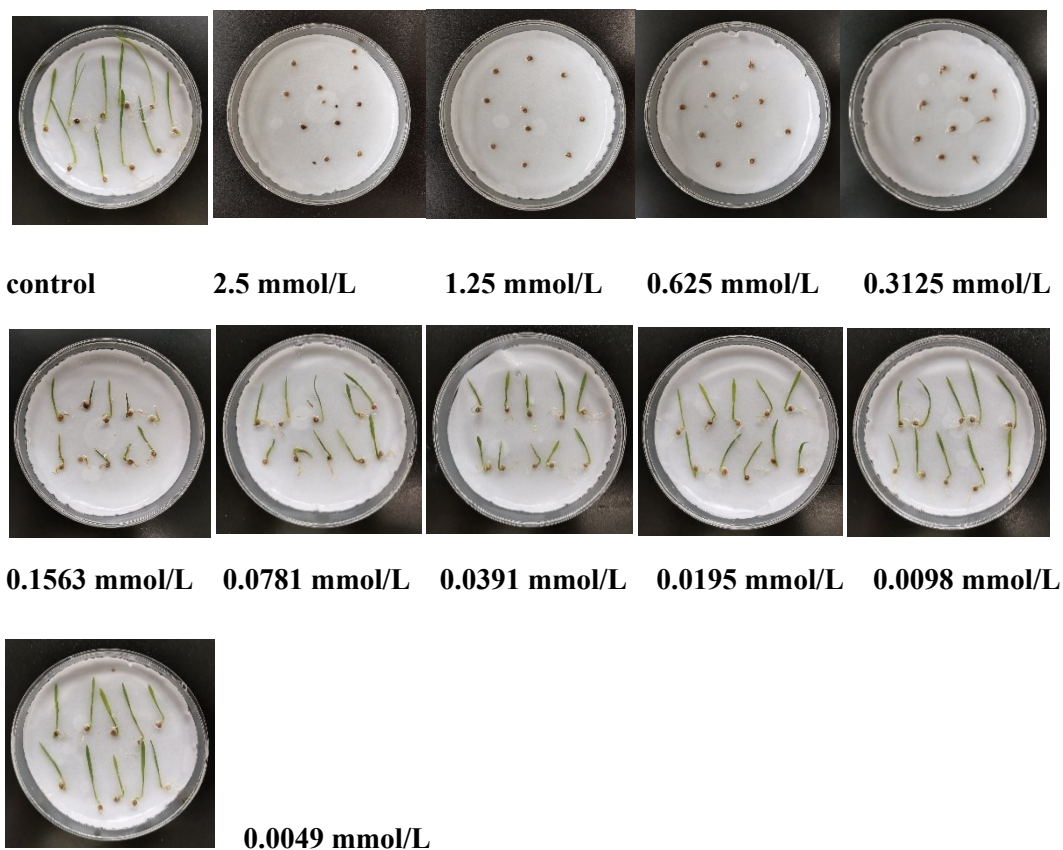
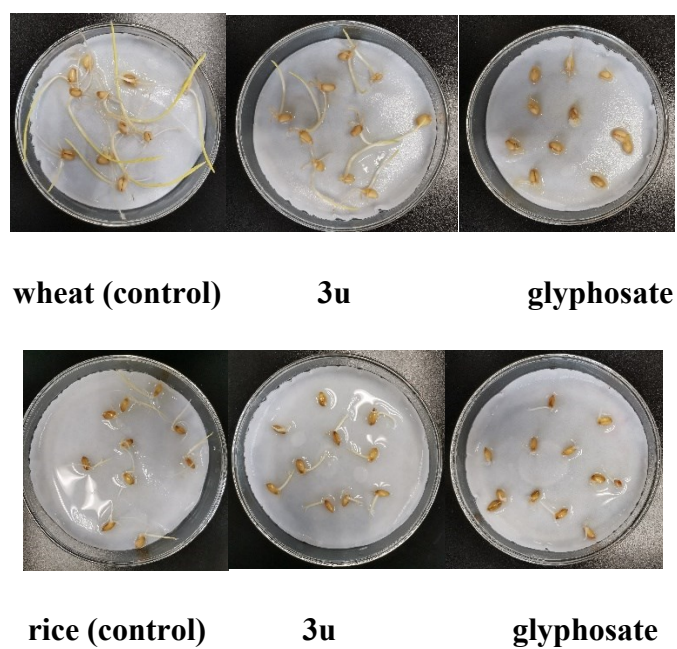
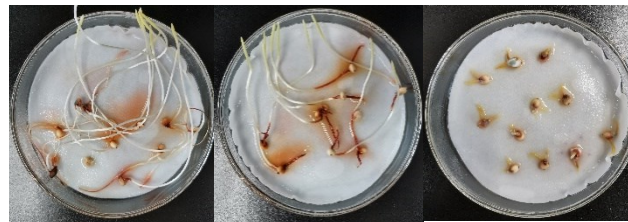


Figure 106 Herbicidal effect of compound **3u** on barnyard grass. (When the solution concentration was 0.1563, 0.0781, 0.0391, 0.0195, 0.0098 and 0.0049 mmol/L, the inhibition rates of root growth were 81.5%, 72.6%, 66.5%, 60.3%, 53.6%, 46.9% respectively, the inhibition rates of shoot growth were 54.1%, 50.3%, 35.5%, 26.2%, 19.3%, 0, respectively.)

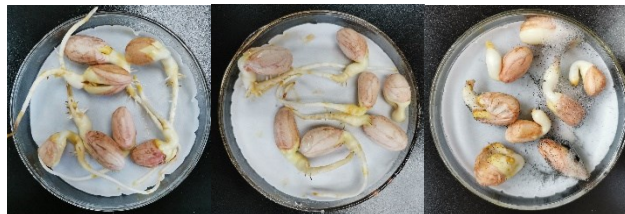




sorghum (control) 3u glyphosate



maize (control) 3u glyphosate



peanut (control) 3u glyphosate



cucumber (control) 3u glyphosate



radish (control) 3u glyphosate

Figure 107 Crop safety of 3u and glyphosate by preemergent application on wheat, rice, sorghum, maize, peanut, cucumber and radish at 100 mg/L.

Table S3 Inhibition rates of **3a-3m** against root growth of barnyard grass

Compd.	5.00 ^a	2.50	1.25	0.625	0.313	0.156	0.078	0.039	0.0195	0.0098	0.0049
1	100.0	81.2	54.3	53.4	48.5	21.5	20.2	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>
2	82.2	45.4	3.3	5.0	9.6	7.2	0.1	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>
3a	-12.6	-1.7	-2.5	-2.6	-6.7	-4.7	-5.5	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>
3b	16.2	16.1	14.5	13.3	17.6	13.8	17.3	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>
3c	23.5	26.1	17.2	16.2	19.6	14.6	17.9	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>
3d	-7.5	-6.6	-6.4	-2.6	-1.5	0.1	-1.1	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>
3e	22.5	-2.5	-2.0	-3.7	-1.2	-0.6	-5.5	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>
3f	-1.5	-1.8	-2.4	-1.1	-2.9	-0.5	-0.2	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>
3g	7.3	1.4	1.3	1.0	-0.9	-1.3	-0.6	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>
3h	-22.4	-35.4	-20.2	-21.6	-8.5	-17.5	-14.5	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>
3i	5.5	4.8	3.4	5.3	5.1	5.0	2.4	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>
3j	-7.7	-8.1	-9.0	-6.2	-7.6	-1.1	-3.1	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>
3k	13.1	12.1	-0.4	2.9	-1.5	-3.5	-2.7	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>
3l	5.6	7.7	5.1	8.9	9.3	10.2	9.8	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>
3m	-18.4	-17.0	-12.4	-12.8	-10.6	-6.7	-1.9	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>
Diuron	<i>c</i>	97.0	95.4	94.7	93.6	89.9	53.1	29.6	17.6	15.5	10.6
Glyphosate	<i>c</i>	100.0	99.8	92.3	83.9	79.6	69.5	43.9	24.9	16.6	8.9

a. The data in this line are the concentrations of different *sec-p*-menthane-7-amine derivatives solutions (mmol/L); b. Have no inhibition activity at this concentration; c. The data at this concentration were not determined.

Table S4 Inhibition rates of **3a-3m** against shoot growth of barnyard grass

Compd.	5.00 ^a	2.50	1.25	0.625	0.313	0.156	0.078	0.039	0.0195	0.0098	0.0049
1	100.0	76.4	59.5	32.1	25.1	20.1	17.5	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>
2	77.6	38.8	13.6	6.8	1.7	2.7	3.3	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>
3a	46.9	49.0	48.9	48.1	40.0	19.6	5.4	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>
3b	52.3	48.3	55.5	43.8	40.6	31.9	25.4	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>
3c	65.9	60.7	58.9	51.1	49.2	39.2	29.7	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>
3d	26.6	19.0	17.0	17.5	6.7	9.8	9.5	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>
3e	42.3	43.5	44.6	39.2	39.8	35.1	34.7	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>
3f	9.6	4.0	2.2	4.1	-1.5	-0.9	-0.5	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>
3g	21.6	20.1	26.6	29.9	24.2	26.1	23.4	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>
3h	39.8	33.4	29.2	23.0	18.9	18.2	17.0	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>
3i	7.1	6.5	3.4	4.2	3.7	5.7	2.2	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>
3j	16.7	12.2	18.3	14.6	17.7	17.6	16.3	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>
3k	64.0	56.9	48.9	43.1	43.0	28.7	15.3	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>
3l	23.0	24.2	20.0	23.8	23.2	14.1	11.6	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>
3m	34.4	34.3	29.7	29.6	28.8	28.0	20.2	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>
Diuron	<i>c</i>	27.3	26.3	20.8	24.9	14.0	12.3	13.4	10.5	<i>b</i>	<i>b</i>
Glyphosate	<i>c</i>	97.5	91.9	77.2	64.0	54.1	38.5	12.2	<i>b</i>	<i>b</i>	<i>b</i>

Table S5 Toxicity regression equations, IC₅₀ and IC₉₀ values of *sec-p*-menthane-7-amine derivatives against barnyard grass

Compd.	Root			Shoot		
	toxicity regression equation	IC ₅₀ (mmol/L)	IC ₉₀ (mmol/L)	toxicity regression equation	IC ₅₀ (mmol/L)	IC ₉₀ (mmol/L)
1	y=5.1897+1.1352x r=0.9676	0.6806	9.1576	y=5.0693+1.1110x r=0.9470	0.8663	>10
2	y=2.8311+4.5866x r=0.9899	2.9707	5.6529	y=3.8474+2.5079x r=0.9810	2.8812	9.3447
3n	y=6.8004+1.0800x r=0.9111	0.0215	0.3308	y=6.2555+1.5618x r=0.9422	0.1571	1.0391
3o	y=6.6758+0.9094x r=0.9199	0.0144	0.3685	y=7.0860+2.0230x r=0.8991	0.0931	0.4002
3p	y=7.1306+1.0353x r=0.9644	0.0088	0.1513	y=6.8404+1.8018x r=0.9500	0.0952	0.4896
3q	y=7.1881+1.1279x r=0.9616	0.0115	0.1571	y=6.6932+1.7347x r=0.9517	0.1057	0.5790
3r	y=7.2005+1.0730x r=0.9952	0.0088	0.1392	y=6.7264+1.8163x r=0.9482	0.1121	0.5690
3s	y=6.8905+1.1140x r=0.9630	0.0201	0.2840	y=6.7917+1.8527x r=0.9404	0.1079	0.5305
3t	y=7.2191+1.2369x r=0.9290	0.0161	0.1746	y=6.3324+1.4714x r=0.9754	0.1243	0.9235
3u	y=6.7652+0.8596x r=0.9411	0.0088	0.2738	y=6.5213+1.2899x r=0.9543	0.0662	0.6518
3v	y=7.2372+1.1474x r=0.9250	0.0112	0.1469	y=6.5438+1.1813x r=0.9743	0.0493	0.5998
3w	y=6.9051+0.9267x r=0.9737	0.0088	0.2124	y=6.5685+1.4290x r=0.9870	0.0799	0.6298
3x	y=7.6525+1.3639x r=0.9641	0.0119	0.1035	y=6.2278+1.0400x r=0.9722	0.0701	0.9822
3y	y=7.9422+2.3376x r=0.9937	0.0551	0.1948	y=5.4980+2.0469x r=0.9676	0.5711	2.4142
Diuron	y=6.7262+1.3525x r=0.9612	0.0529	0.4690	y=4.3081+0.3752x r=0.9296	>10	>10
Glyphosate	y=7.1288+1.5735x r=0.9755	0.0444	0.2894	y=6.2470+1.5890x r=0.9890	0.1642	1.0514

Table S6 Toxicity regression equations, IC₅₀ and IC₉₀ values of *sec-p*-menthane-7-amine derivatives against rape

Compd.	Root			Shoot		
	toxicity regression equation	IC ₅₀ (mmol/L)	IC ₉₀ (mmol/L)	toxicity regression equation	IC ₅₀ (mmol/L)	IC ₉₀ (mmol/L)
1	y=5.9863+2.12498x r=0.9875	0.3434	1.3771	y=5.2749+1.2792x r=0.9705	0.6097	6.1230
2	y=5.9569+1.6144x r=0.9566	0.2554	1.5888	y=5.2536+1.0121x r=0.9230	0.5616	>10
3n	y=7.4501+1.6788x r=0.9852	0.0347	0.2014	y=6.5488+1.5931x r=0.9447	0.1066	0.6796
3o	y=7.7051+1.9394x r=0.9694	0.0403	0.1845	y=7.6037+3.2981x r=0.9768	0.1624	0.3973
3p	y=8.1376+2.1619x r=0.9916	0.0354	0.1385	y=6.9255+2.3133x r=0.9694	0.1471	0.5268
3q	y=7.9299+1.7905x r=0.9746	0.0231	0.1201	y=6.4436+1.5669x r=0.9712	0.1199	0.7881
3r	y=7.7781+2.0589x r=0.9717	0.0447	0.1876	y=6.7737+2.1097x r=0.9615	0.1443	0.5844
3s	y=6.9838+1.7680x r=0.9936	0.0755	0.4007	y=6.3232+1.6040x r=0.9734	0.1497	0.9420
3t	y=7.4794+1.7783x r=0.9757	0.0403	0.2120	y=6.6947+2.7736x r=0.9617	0.2449	0.7097
3u	y=7.8366+1.9685x r=0.9908	0.0362	0.1622	y=6.7703+1.8486x r=0.9684	0.1102	0.5440
3v	y=7.9037+1.8256x r=0.9816	0.0257	0.1292	y=6.9022+1.7451x r=0.9858	0.0813	0.4409
3w	y=7.8582+1.8000x r=0.9897	0.0258	0.1331	y=7.3168+2.6545x r=0.9505	0.1338	0.4068
3x	y=7.6402+1.6251x r=0.9881	0.0237	0.1459	y=6.4681+1.4131x r=0.9872	0.0914	0.7379
3y	y=7.8569+1.9504x r=0.9913	0.0343	0.1557	y=6.7860+2.2165x r=0.9771	0.1564	0.5921
Diuron	y=5.8184+1.0029x r=0.9850	0.1527	2.8964	y=5.1418+0.9150x r=0.9962	0.6999	>10
Glyphosate	y=6.4596+0.9099x r=0.9784	0.0249	0.6372	y=5.2477+1.1454x r=0.9909	0.6078	7.9915