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Supporting Information associated with the paper

Water-tuned tautomer-selective tandem synthesis of the 5,6-dihydropyrimidin-4(3H)-ones driven under the umbrella of the sustainable chemistry

Nenad Janković,[†*] Srđan Stefanović,[§] Jelena Petronijević, [†] Nenad Joksimović,[†] Sladjana B. Novaković,[‡] Goran A. Bogdanović,[‡] Jovana Muškinja,[†] Milan Vraneš,[‖] Zoran Ratković[†] and Zorica Bugarčić[†]

[†]Department of Chemistry, University of Kragujevac, Faculty of Science, Radoja Domanovića 12, 34000 Kragujevac, Serbia

E-mail: nenad.jankovic@kg.ac.rs

[§]Institute of Meat Hygiene and Technology Kaćanskog 13, 11000 Belgrade, Serbia

[‡]Vinča Institute of Nuclear Science University of Belgrade, P.O. Box 522, 11001, Belgrade, Serbia

[‖]Department of Chemistry, Biochemistry and Environmental Protection University of Novi Sad, Faculty of Science, Trg Dositeja Obradovića 3, 21000 Novi Sad

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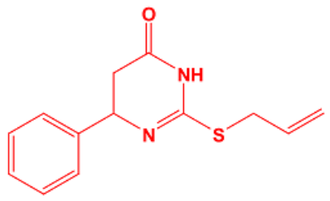
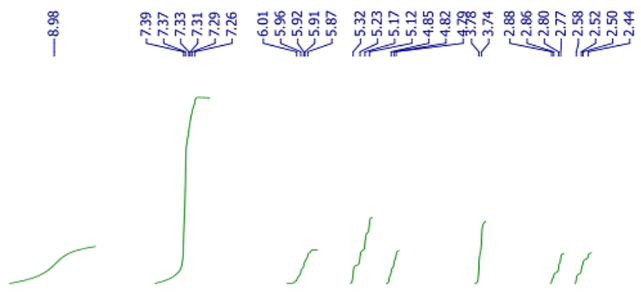
1. ^{1}H and ^{13}C NMR spectrums of 4a-t

2-allylthio-6-phenyl-5,6-dihydropyrimidin-4(3H)-one (4a)

White powder; yield: 91%, reaction time: 90 min.; mp = 140˚C; IR (KBr): ν 3182, 3086, 2922, 1698, 1634, 1481, 1357, 1321, 1298, 1143, 1080 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.44-2.88 (m, 2H, CH_2CO), 3.76 (d, 2H, *J* = 6.8 Hz, CH_2S), 4.84 (dd, 1H, *J* = 12.2, 5.3 Hz, CH_{Bn}), 5.12-5.32 (m, 2H, CH_2=), 5.87-6.01 (m, 1H, CH=), 7.26-7.39 (m, 5H, CH_{Ar}), 8.98 (br. s, 1H, NH) ppm; ^{13}C NMR (50 MHz, $CDCl_3$): δ = 33.3, 38.1, 58.5, 126.3, 127.4, 128.6, 132.7, 141.9 and 170.2 ppm; ESI-MS: m/z (100 %) = 247 $[M+1]^{+}$.





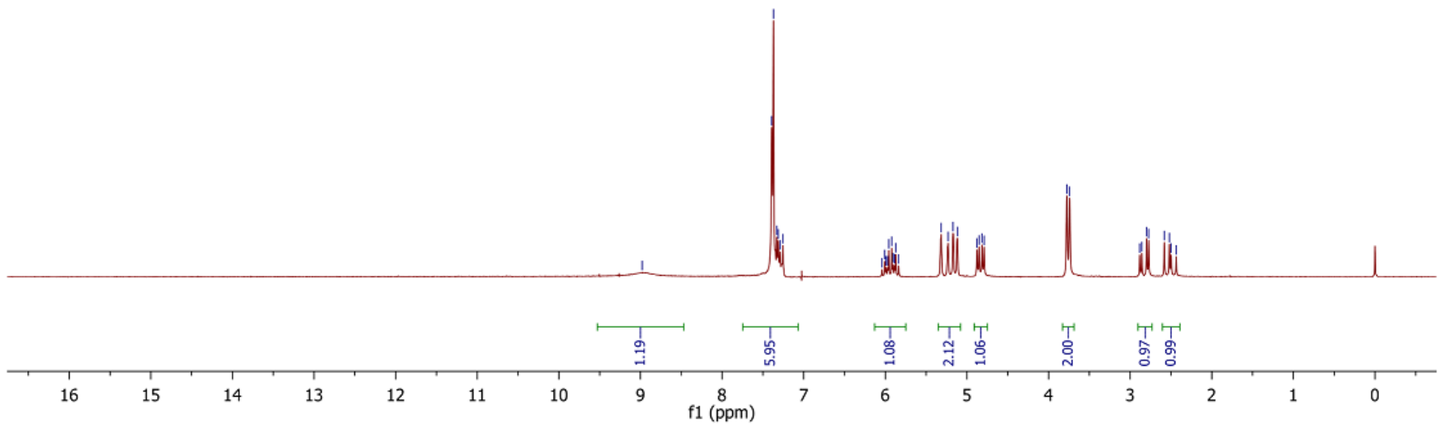
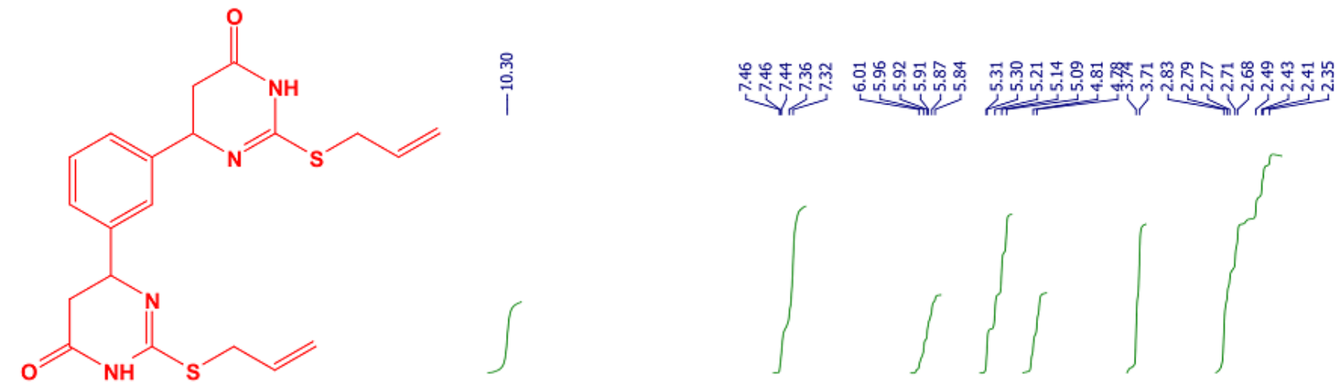


Figure S1 ^{1}H NMR spectrum of **4a**

Figure S2 ^{13}C NMR spectrum of **4a**

6,6'-(1,3-phenylene)bis(2-allylthio-5,6-dihydropyrimidin-4(3H)-one) (4b)

White powder; yield: 88%, reaction time: 110 min.; mp = 196˚C; IR (KBr): ν 3185, 3095, 2918, 1701, 1629, 1476, 1356, 1240, 1242, 1037 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$ + DMSO-d_6): δ = 2.35-2.83 (m, 4H, 2×CH_2CO), 3.73 (d, 4H, *J* = 6.9 Hz, 2×CH_2S), 4.79 (dd, 2H, *J* = 12.4, 5.1 Hz, 2×CH_{Bn}), 5.09-5.31 (m, 4H, 2×CH_2=), 5.84-6.01 (m, 2H, 2×CH=), 7.32-7.46 (m, 4H, CH_{Ar}), 10.30 (br. s, 2H, 2×NH); ^{13}C NMR (50 MHz, $CDCl_3$ + DMSO-d_6): δ = 32.5, 37.9, 58.1, 117.6, 123.9, 124.7, 128.2, 132.6, 142.5, 142.6, 152.0 and 169.1 ppm; ESI-MS: m/z (100 %) = 415 $[M + 1]^+$.



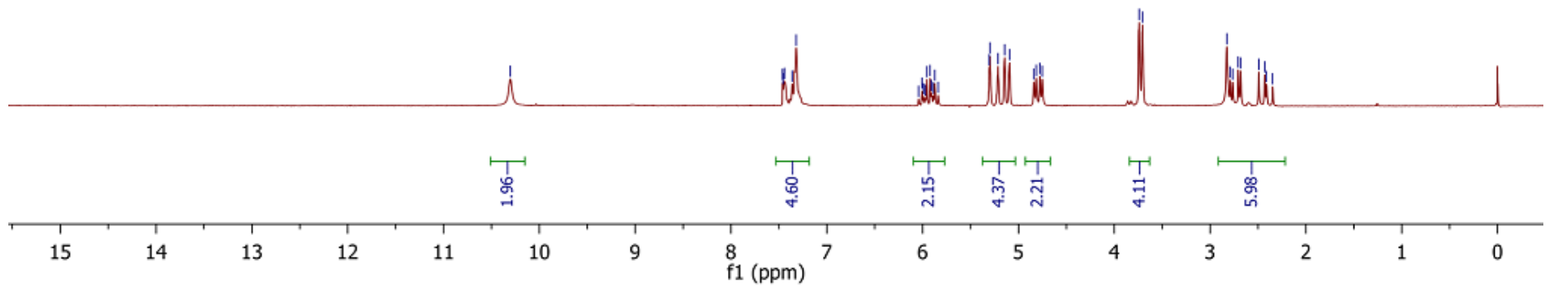


Figure S3 ^{1}H NMR spectrum of **4b**

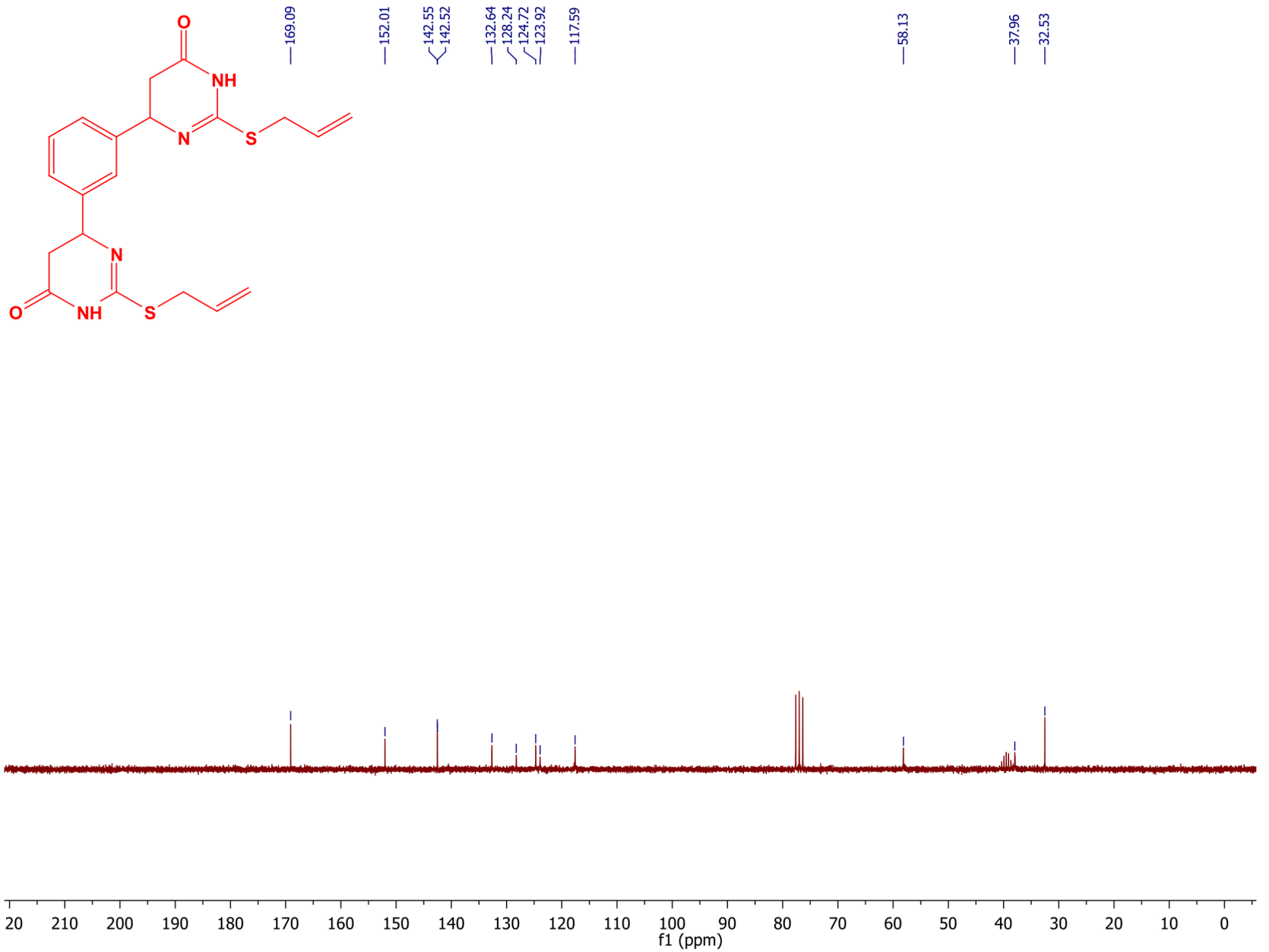
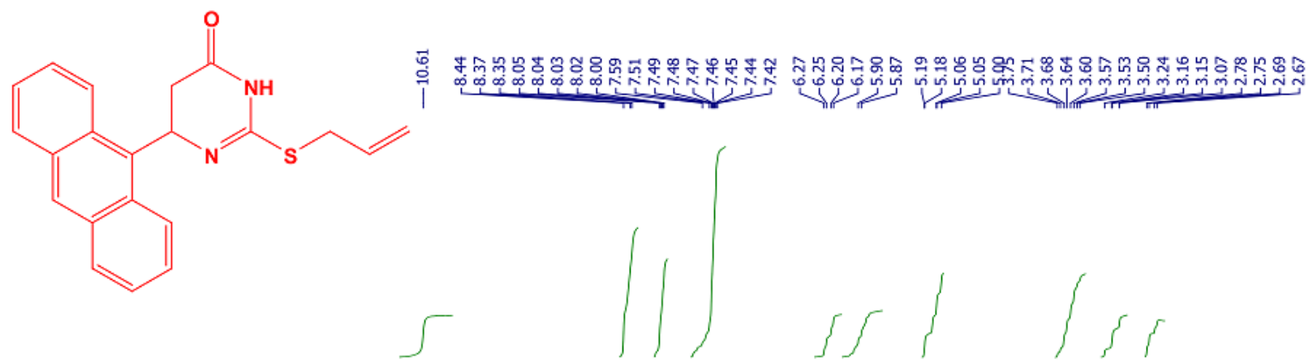


Figure S4 ^{13}C NMR spectrum of **4b**

2-allylthio-6-(9'-anthracenyl)-5,6-dihydropyrimidin-4(3H)-one (4c)

Orange crystals; yield: 73%, reaction time: 140 min.; mp = 204˚C; IR (KBr): ν 3185, 3082, 2917, 1697, 1628, 1474, 1328, 1298, 1137, 1083 cm^{-1}; ^1H NMR (200 MHz, DMSO-d_6 +$CDCl_3$): δ = 2.73 (dd, 1H, *J* = 17.2, 5.3 Hz, CH_2CO), 3.16 (dd, 1H, *J* = 17.1, 15.3 Hz, CH_2CO), 3.63 (qd, 2H, *J* = 13.9, 6.9 Hz, CH_2S), 5.00-5.19 (m, 2H, CH_2=), 5.87-5.90 (m, 1H, CH=), 6.22 (dd, 1H, *J* = 15.2, 5.3 Hz, CH_{Bn}), 7.42-7.59 (m, 5H, CH_{Ar}), 8.00-8.05 (m, 2H, CH_{Ar}), 8.35-8.44 (m, 3H, CH_{Ar}), 10.61 (br. s, 1H, NH) ppm; ^{13}C NMR (50 MHz, DMSO-d_6 +$CDCl_3$): δ = 32.4, 36.7, 55.2, 117.5, 123.1, 124.4, 125.2, 127.6, 128.8, 129.1, 131.4, 132.5, 133.1, 150.7 and 169.6 ppm; ESI-MS: m/z (100 %) = 347 $[M + 1]^+$.



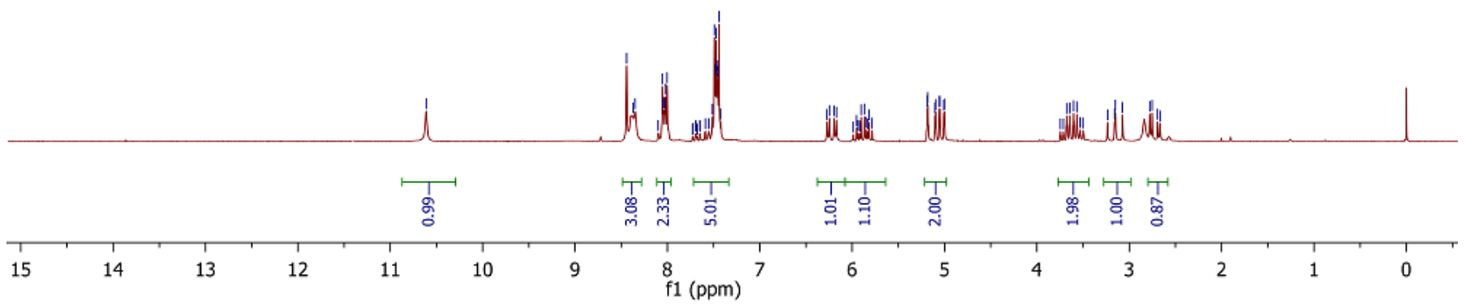


Figure S5 ^1H NMR spectrum of **4c**

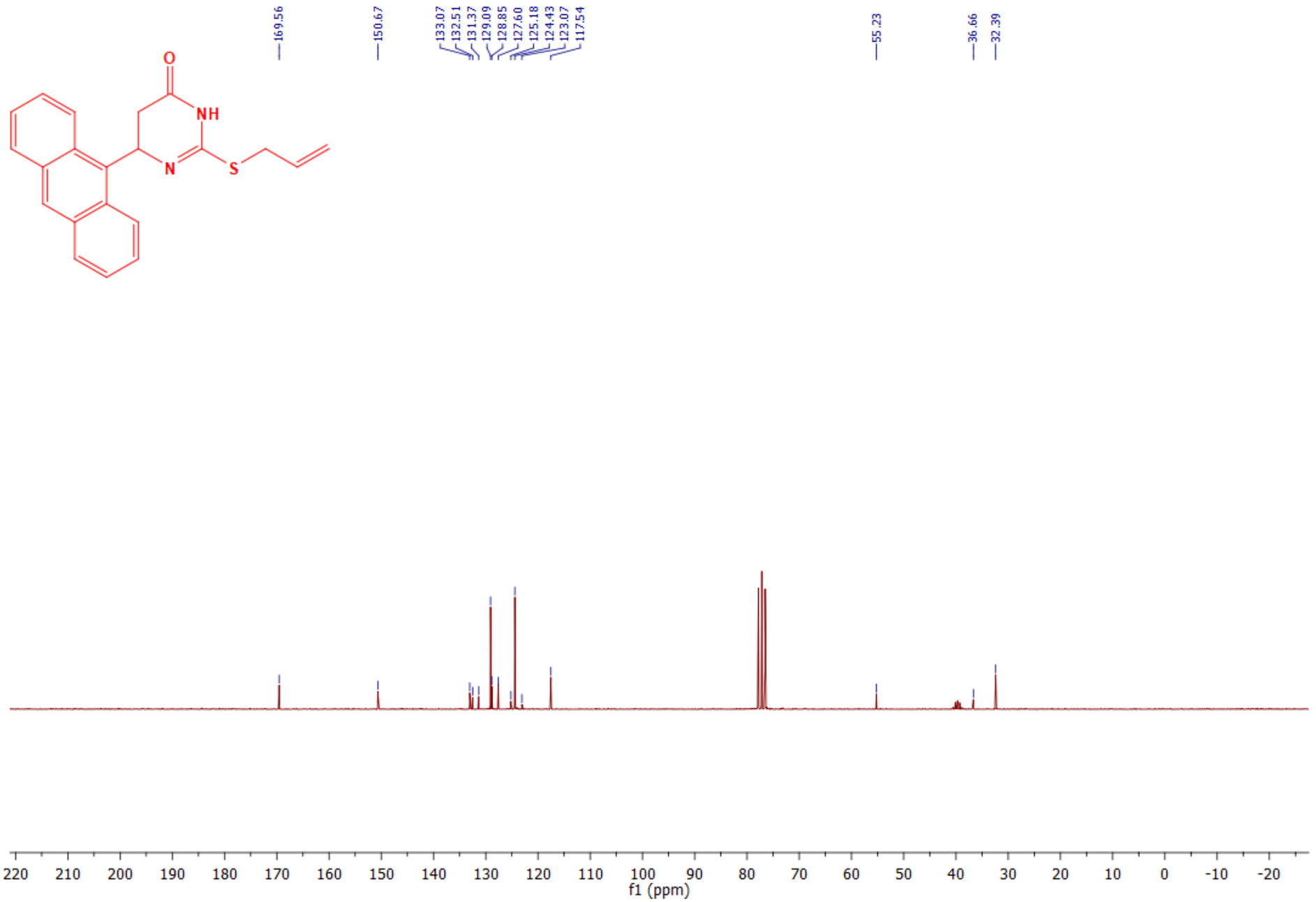


Figure S6 ^{13}C NMR spectrum of **4c**

2-allylthio-6-(4'-chlorophenyl)-5,6-dihydropyrimidin-4(3H)-one (4d)

Colourless crystals; yield: 93%, reaction time: 75 min.; mp = 128˚C; IR (KBr): ν 3191, 3083, 2922, 1695, 1624, 1475, 1332, 1289, 1233, 1137, 1090 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.45 (dd, 1H, *J* = 16.7, 12.5 Hz, CH_2CO), 2.80 (dd, 1H, *J* = 16.7, 5.2 Hz, CH_2CO), 3.74 (dt, 2H, *J* = 6.9, 1.1 Hz, CH_2S), 4.80 (dd, 1H, *J* = 12.5, 5.2 Hz, CH_{Bn}), 5.17-5.32 (m, 2H, CH_2=), 5.83-6.03 (m, 1H, CH=), 7.34 (s, 4H, CH_{Ar}), 8.85 (br. s, 1H, NH) ppm; ^{13}C NMR (50 MHz, $CDCl_3$): δ = 33.3, 38.1, 58.0, 118.6, 127.7, 128.7, 132.6, 133.1, 140.7, 151.7 and 169.7 ppm; ESI-MS: m/z (100 %) = 281 $[M + 1]^+$.

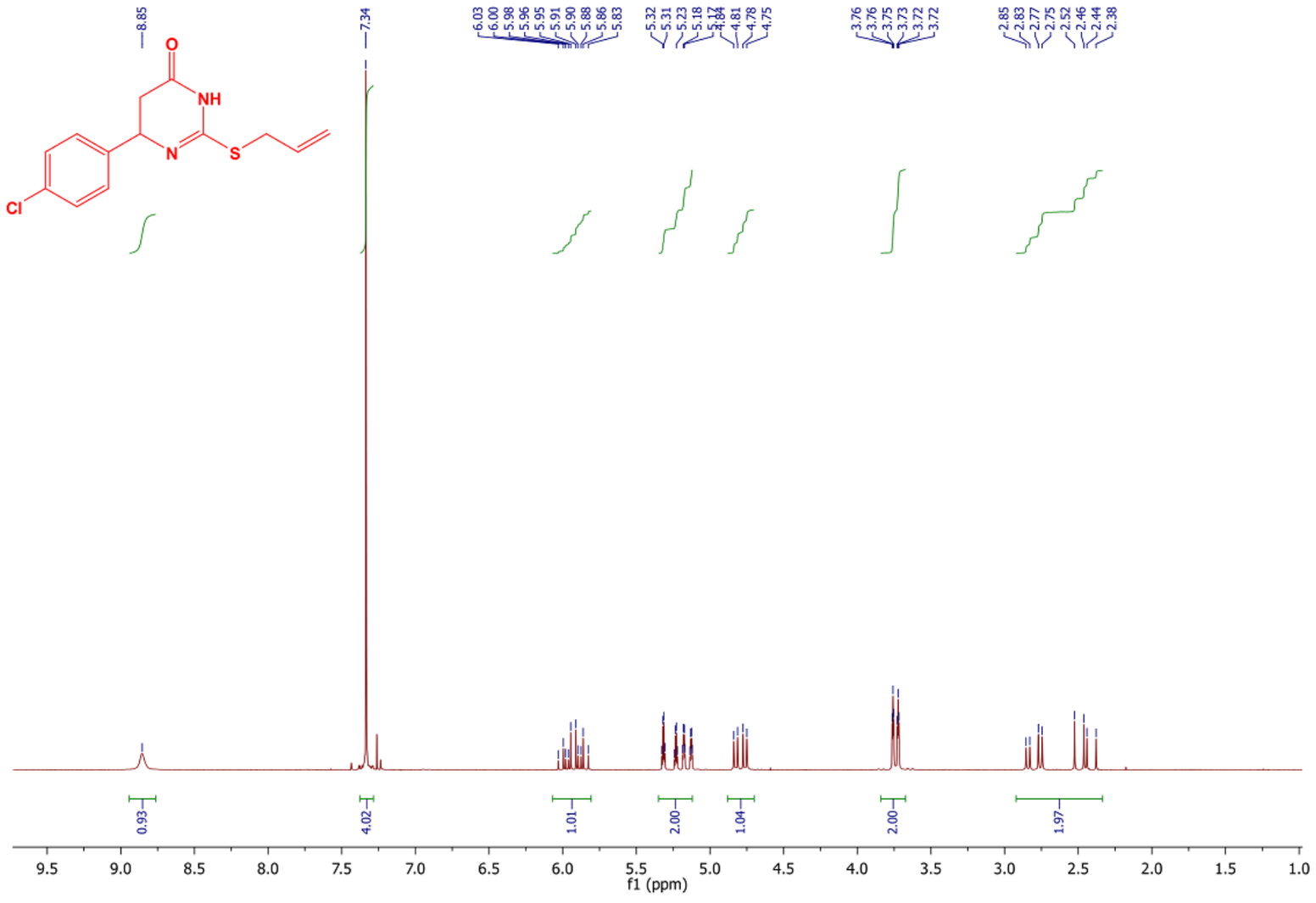


Figure S7 ^{1}H NMR spectrum of **4d**

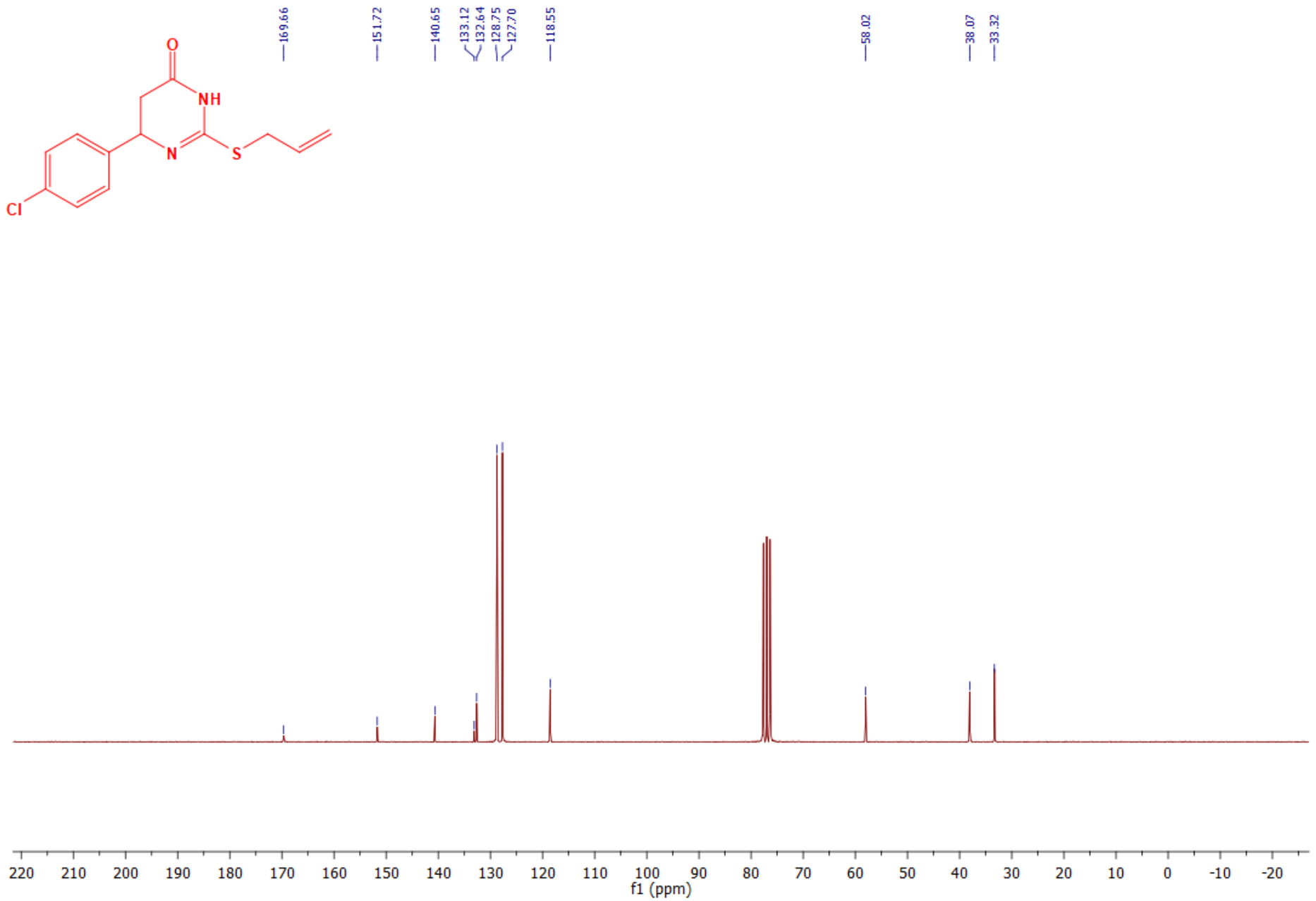


Figure S8 ^{13}C NMR spectrum of **4d**

2-allylthio-6-(3'-chlorophenyl)-5,6-dihydropyrimidin-4(3H)-one (4e)

Colourless crystals; yield: 90%, reaction time: 95 min.; mp = 126˚C; IR (KBr): ν 3184, 3086, 2918, 1698, 1631, 1571, 1472, 1352, 1299, 1246, 1145, 1078 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.46 (dd, 1H, *J* = 16.7, 12.7 Hz, CH_2CO), 2.81 (dd, 1H, *J* = 16.7, 5.2 Hz, CH_2CO), 3.76 (dt, 2H, *J* = 6.9, 1.0 Hz, CH_2S), 4.81 (dd, 1H, *J* = 12.7, 5.1 Hz, CH_{Bn}), 5.14-5.35 (m, 2H, CH_2=), 5.83-6.04 (m, 1H, CH=), 7.22-7.32 (m, 3H, CH_{Ar}), 7.43 (d, 1H, *J* = 2.3 Hz, CH_{Ar}), 8.88 (br. s, 1H, NH) ppm; ^{13}C NMR (50 MHz, $CDCl_3$): δ = 33.3, 38.0, 58.1, 118.6, 124.4, 126.7, 127.5, 129.9, 132.6, 134.5, 144.2, 151.9 and 169.6 ppm; ESI-MS: m/z (100 %) = 281 $[M + 1]^+$.

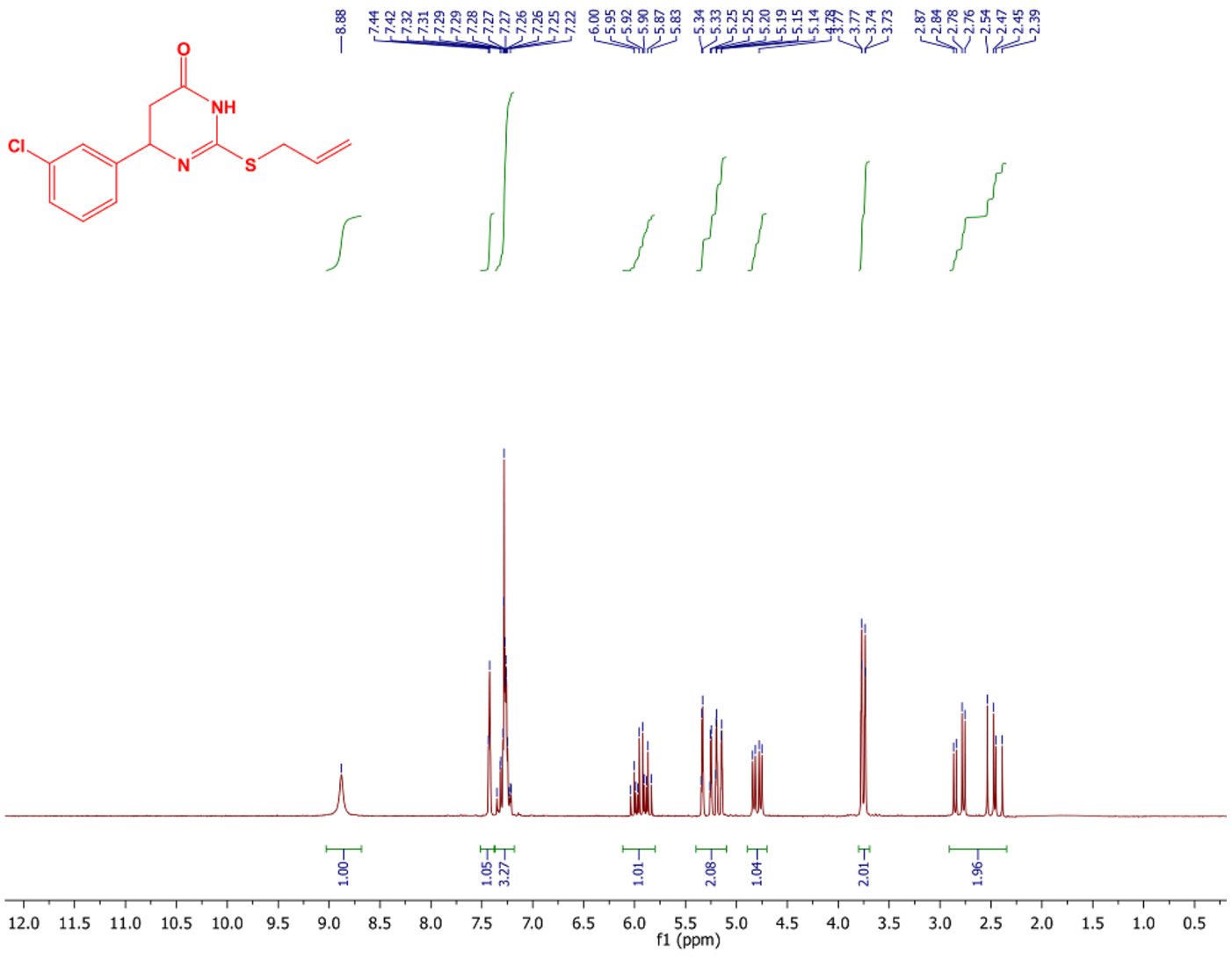


Figure S9 ^{1}H NMR spectrum of **4e**

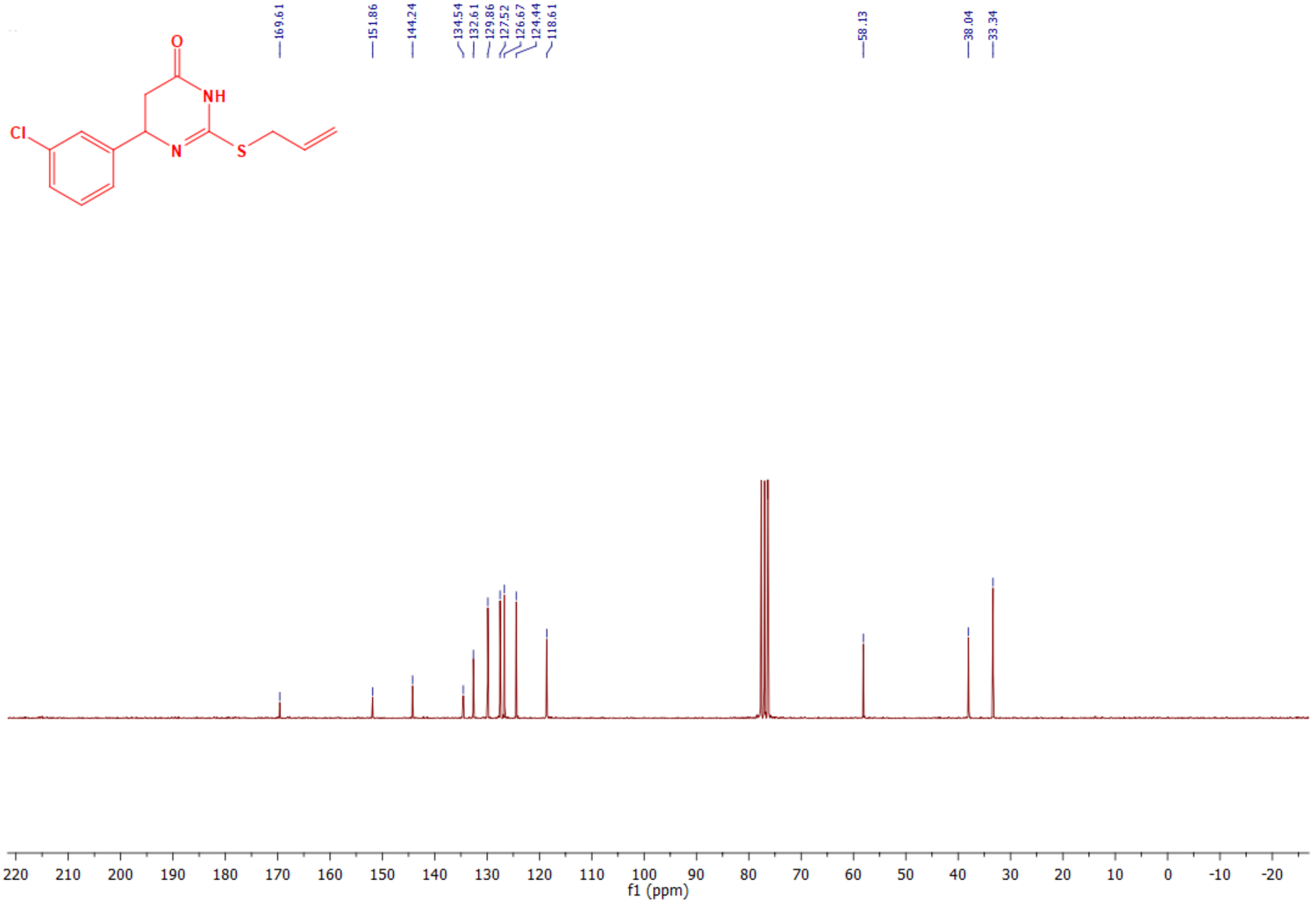


Figure S10 ^{13}C NMR spectrum of **4e**

2-allylthio-6-(2'-chlorophenyl)-5,6-dihydropyrimidin-4(3H)-one (4f)

White crystals; yield: 85%, reaction time: 90 min.; mp = 119˚C; IR (KBr): ν 3195, 3098, 2912, 1696, 1635, 1468, 1316, 1166, 1140, 1064 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ = 2.31 (dd, 1H, *J* = 16.8, 12.8 Hz, CH_2CO), 2.98 (dd, 1H, *J* = 16.8, 5.0 Hz, CH_2CO), 3.75 (d, 2H, *J* = 6.8 Hz, CH_2S), 5.14-5.33 (m, 3H, CH_2= + CH_{Bn}), 5.88-6.01 (m, 1H, CH=), 7.23-7.35 (m, 3H, CH_{Ar}), 7.56 (dd, 1H, *J* = 7.4, 1.8 Hz, CH_{Ar}), 8.92 (br. s, 1H, NH) ppm; ^{13}C NMR (50 MHz, $CDCl_3$): δ = 33.3, 36.4, 56.4, 118.5, 127.3, 128.3, 128.6, 129.5, 132.2, 132.7, 139.8, 152.0 and 169.8 ppm; ESI-MS: m/z (100 %) = 281 $[M + 1]^+$.

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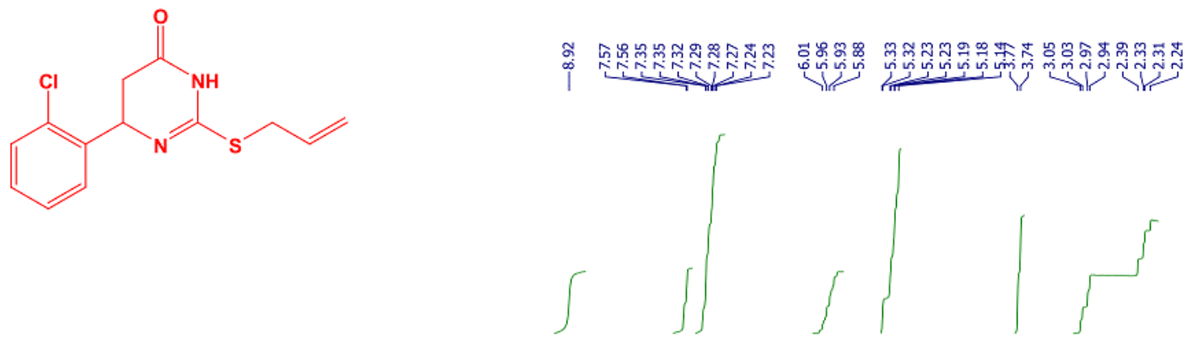

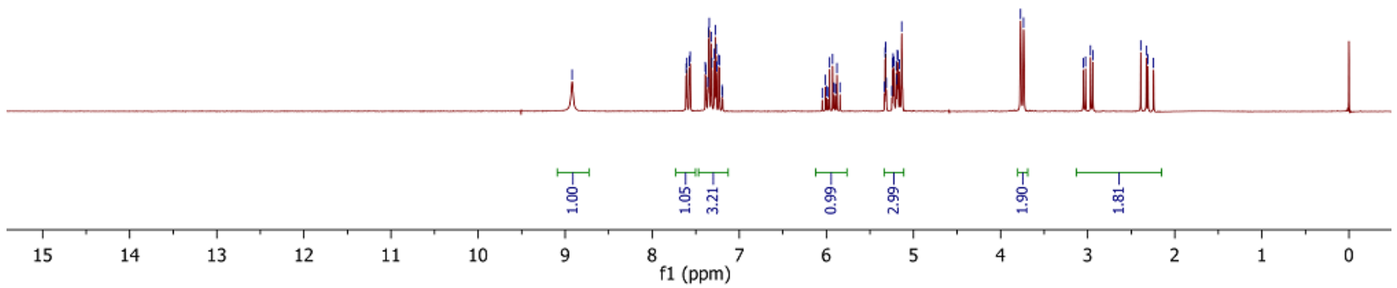

Figure S11 ^{1}H NMR spectrum of **4f**

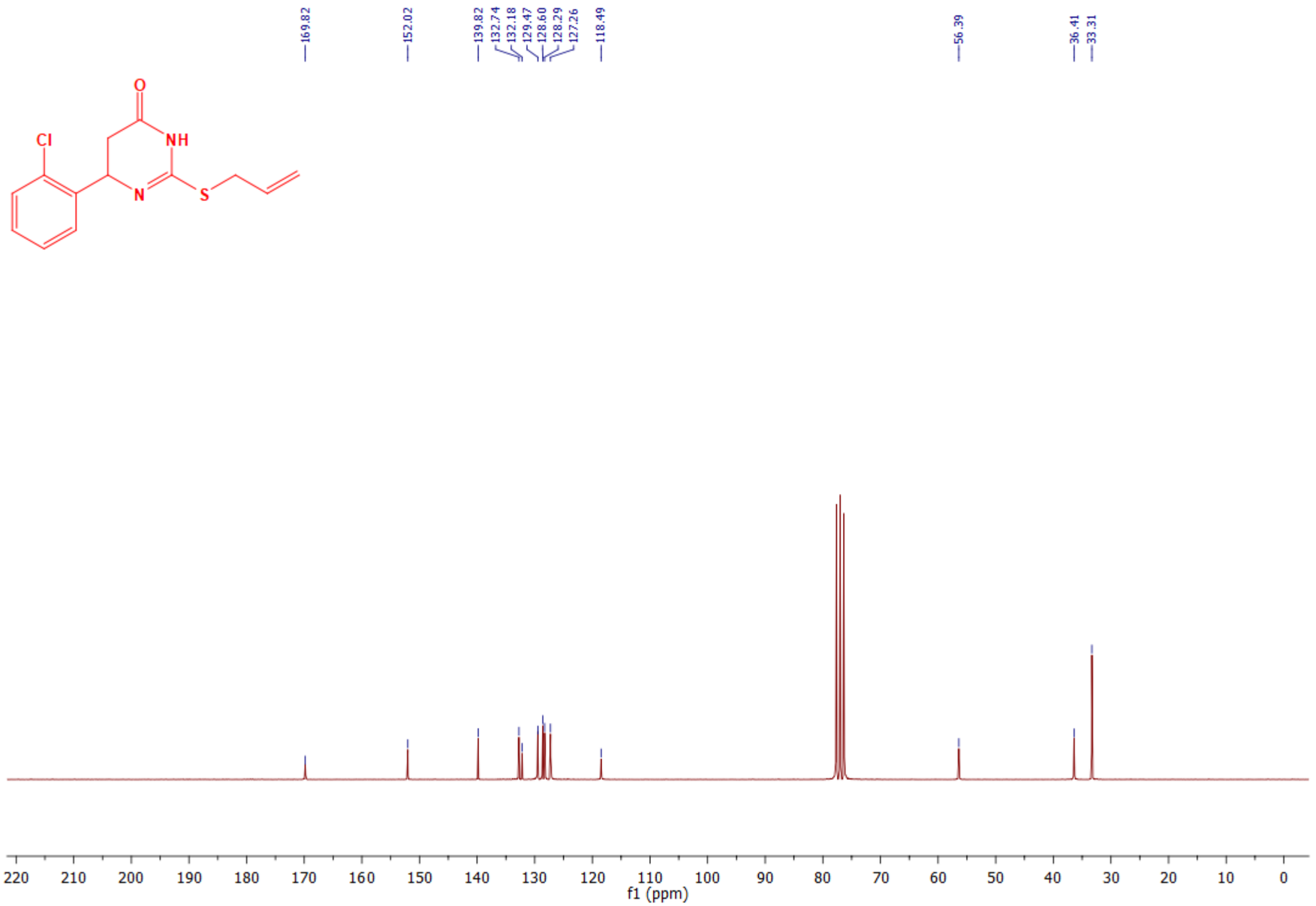

Figure S12 ^{13}C NMR spectrum of **4f**

2-allylthio-6-(4'-methylthiophenyl)-5,6-dihydropyrimidin-4(3H)-one (4g)

Colourless crystals; yield: 90%, reaction time: 60 min; mp = 132˚C; IR (KBr): v 3185, 3096, 2918, 1698, 1627, 1476, 1354, 1291, 1142, 1034 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.39-2.58 (m, 4H, CH_2CO + SCH_3), 2.81 (dd, 1H, *J* = 16.7, 5.2 Hz, CH_2CO), 3.74 (dd, 2H, *J* = 4.5, 3.4 Hz, CH_2S), 4.77 (dd, 1H, *J* = 12.3, 5.2 Hz, CH_{Bn}), 5.16-5.31 (m, 2H, CH_2=), 5.83-6.00 (m, 1H, CH=), 7.24-7.38 (m, 4H, CH_{Ar}), 8.97 (br. s, 1H, NH) ppm; ^{13}C NMR (50 MHz, $CDCl_3$): δ = 15.9, 33.3, 38.0, 58.2, 118.4, 126.8, 126.9, 132.7, 137.4, 139.1, 151.4 and 170.0 ppm; ESI-MS: m/z (100 %) = 293 $[M + 1]^+$.

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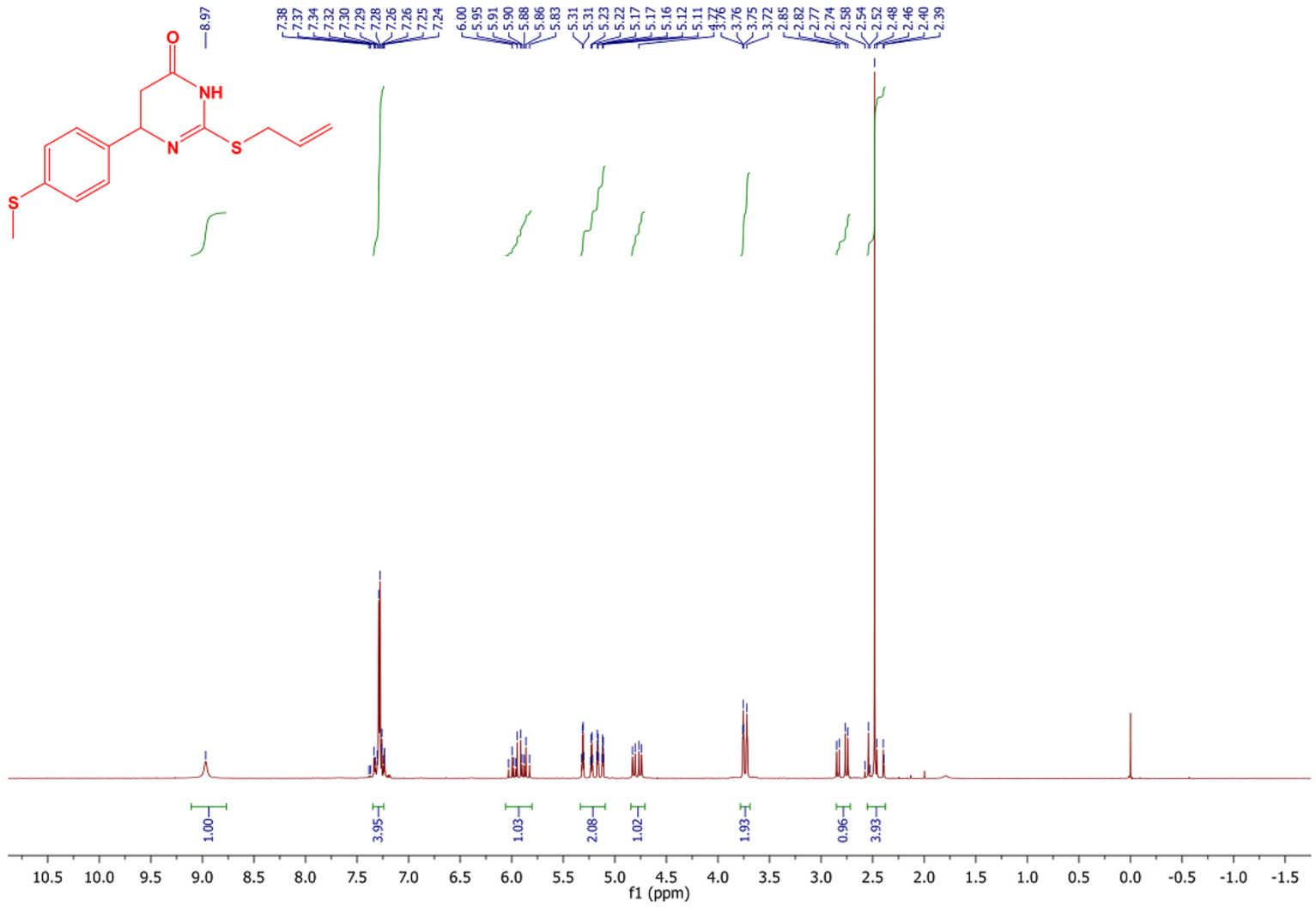


Figure S13 ^{1}H NMR spectrum of **4g**

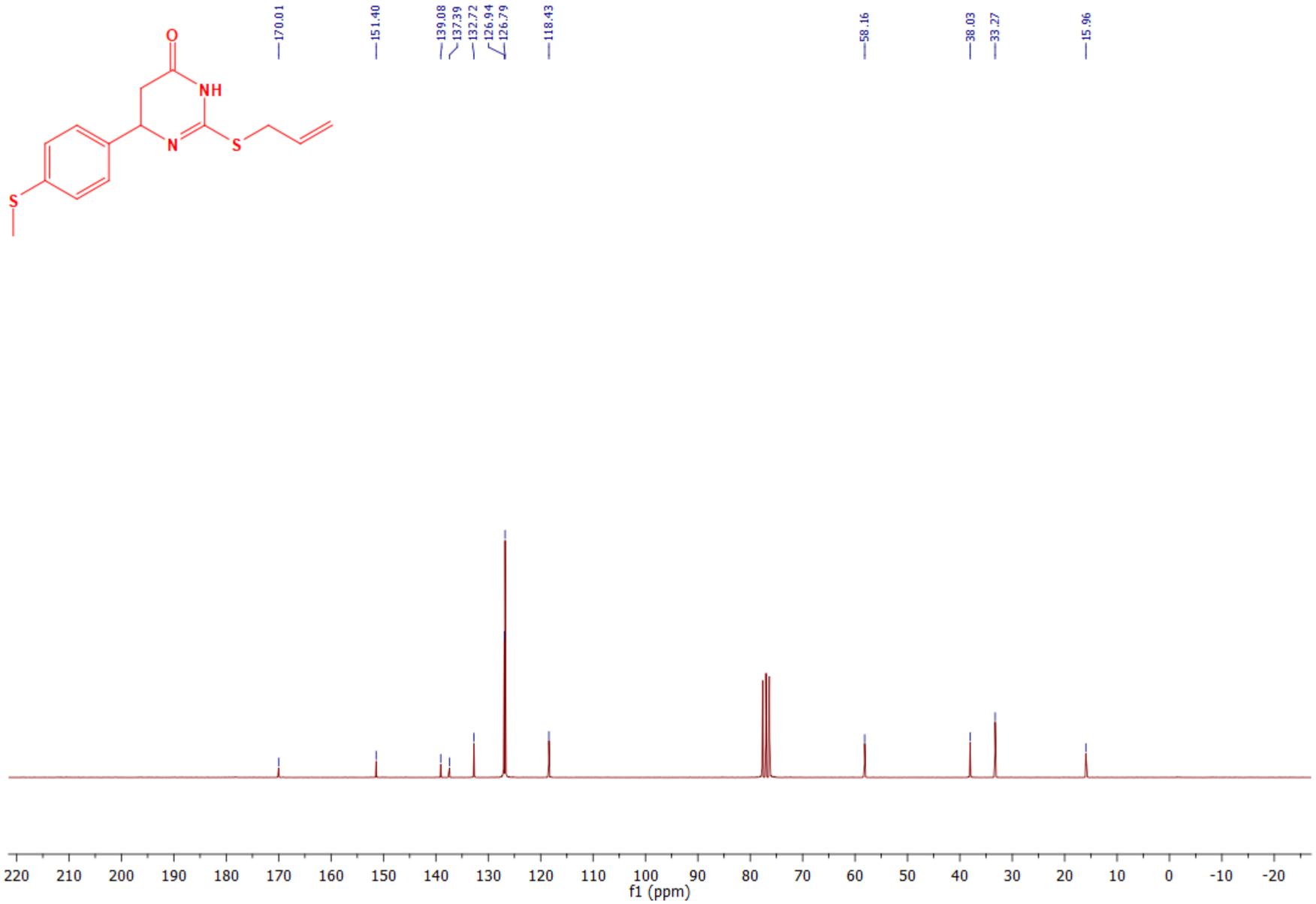


Figure S14 ^{13}C NMR spectrum of **4g**

2-allylthio-6-(4'-fluorophenyl)-5,6-dihydropyrimidin-4(3H)-one (4h)

Colourless crystals; yield: 89%, reaction time: 120 min.; mp = 136 ˚C; IR (KBr): ν 3182, 3083, 2921, 1696, 1626, 1516, 1477, 1338, 1261, 1232, 1139, 1038 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.47 (dd, 1H, *J* = 16.7, 12.5 Hz, CH_2CO), 2.81 (dd, 1H, *J* = 16.7, 5.2 Hz, CH_2CO), 3.75 (dt, 2H, *J* = 6.9, 1.1 Hz, CH_2S), 4.77 (dd, 1H, *J* = 12.5, 5.1 Hz, CH_{Bn}), 5.12-5.33 (m, 2H, CH_2=), 5.83-6.04 (m, 1H, CH=), 7.00-7.12 (m, 2H, CH_{Ar}), 7.32-7.39 (m, 2H, CH_{Ar}), 8.88 (br. s, 1H, NH) ppm; ^{13}C NMR (50 MHz, $CDCl_3$): δ = 33.3, 38.2, 57.9, 115.2, 115.6, 118.5, 127.8, 127.9, 132.7, 137.8, 151.5, 159.6, 164.5 and 169.9 ppm; ESI-MS: m/z (100 %) = 265 $[M + 1]^+$.

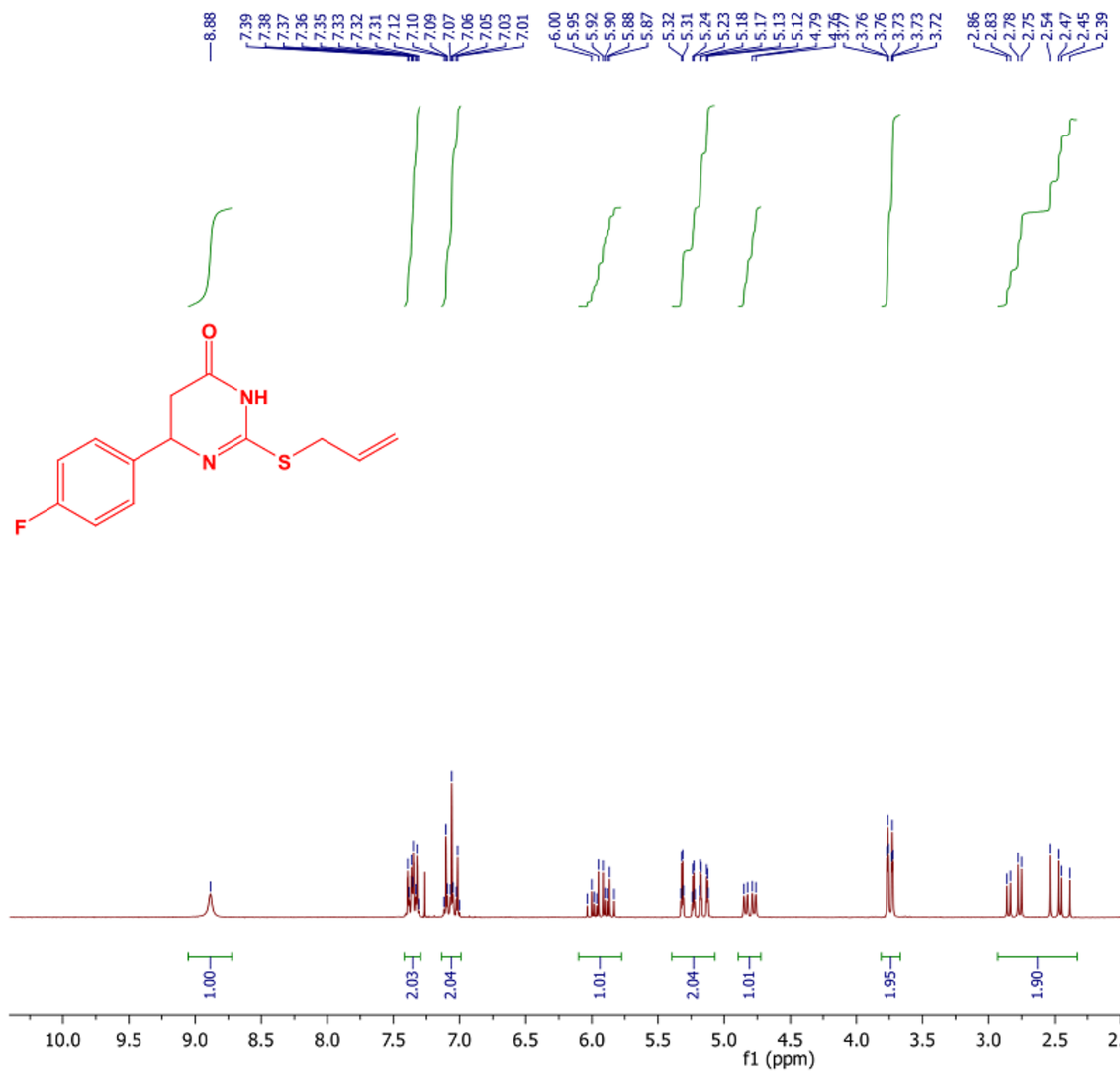


Figure S15 ^{1}H NMR spectrum of **4h**

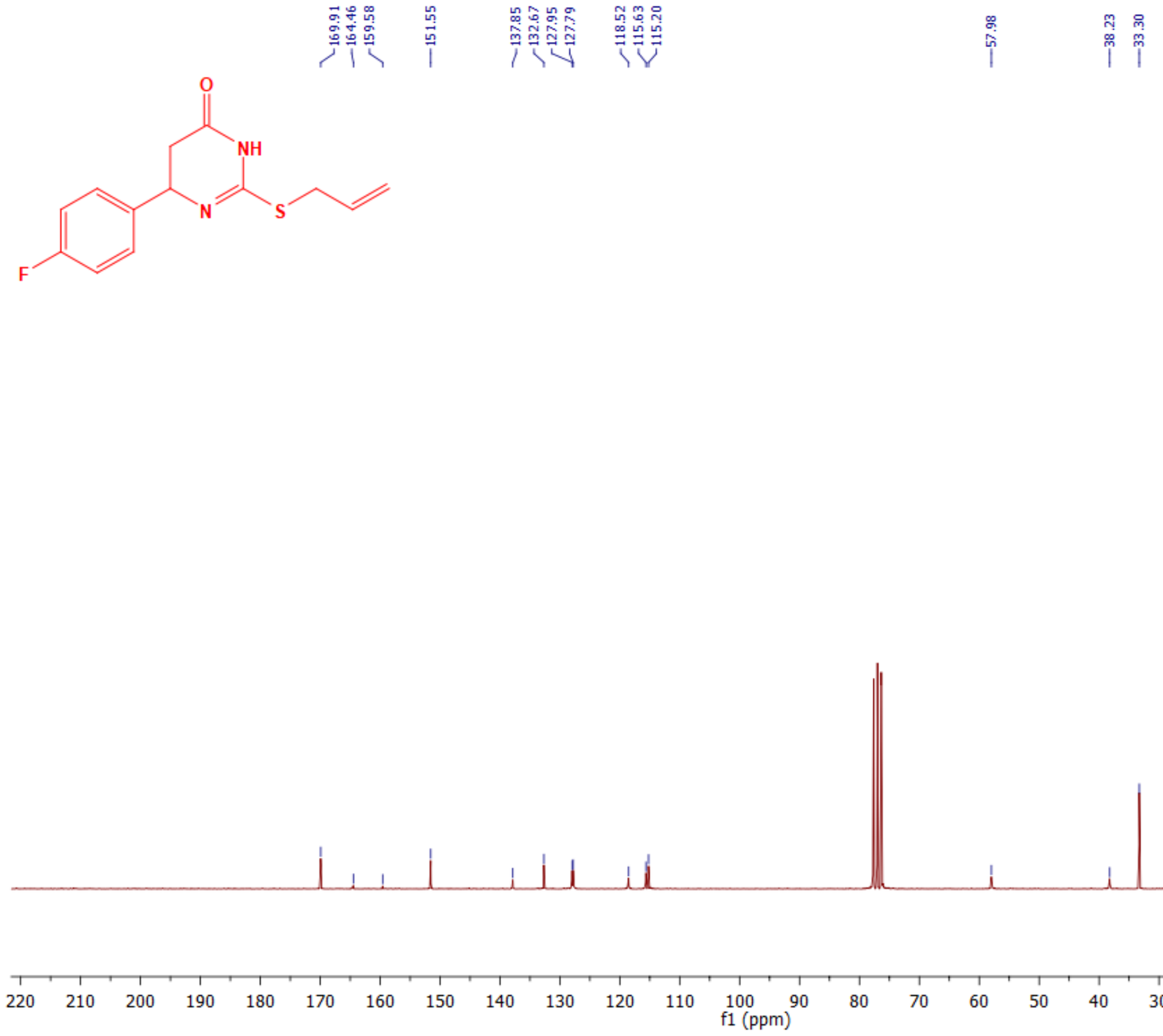
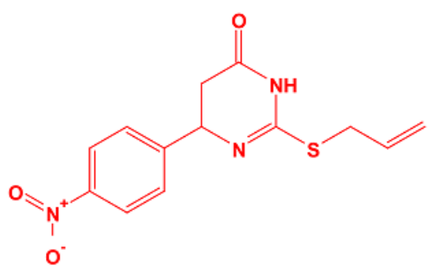
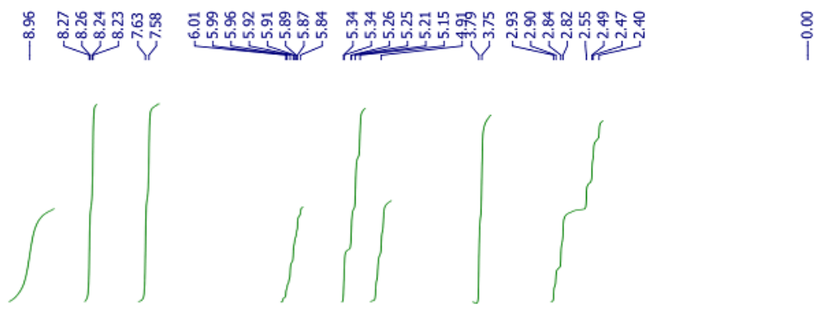


Figure S16 ^{13}C NMR spectrum of **4h**

2-allylthio-6-(4'-nitrophenyl)-5,6-dihydropyrimidin-4(3H)-one (4i)

Yellow amorphous solid; yield: 90%, reaction time: 175 min.; mp = 133˚C; IR (KBr): ν 3189, 3082, 2901, 1699, 1624, 1516, 1467, 1346, 1286, 1144, 1034 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.47 (dd, 1H, *J* = 16.7, 13.0 Hz, CH_2CO), 2.87 (dd, 1H, *J* = 16.6, 5.1 Hz, CH_2CO), 3.77 (d, 2H, *J* = 6.9 Hz, CH_2S), 4.91 (dd, 1H, *J* = 12.9, 5.0 Hz, CH_{Bn}), 5.15-5.34 (m, 2H, CH_2=), 5.84-6.04 (m, 1H, CH=), 7.60 (d, 2H, *J* = 8.5 Hz, CH_{Ar}), 8.23-8.27 (m, 2H, CH_{Ar}), 8.96 (br. s, 1H, NH) ppm; ^{13}C NMR (50 MHz, $CDCl_3$): δ = 33.4, 37.8, 58.1, 118.7, 123.9, 127.3, 130.5, 132.4, 147.3, 149.4, 152.7 and 169.1 ppm; ESI-MS: m/z (100 %) = 292 $[M + 1]^+$.





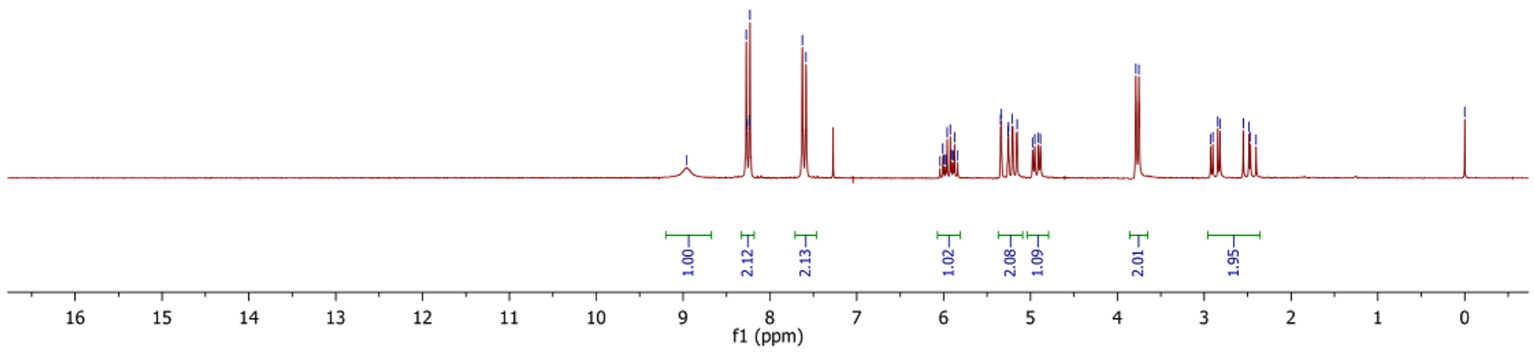


Figure S17 ^{1}H NMR spectrum of **4i**

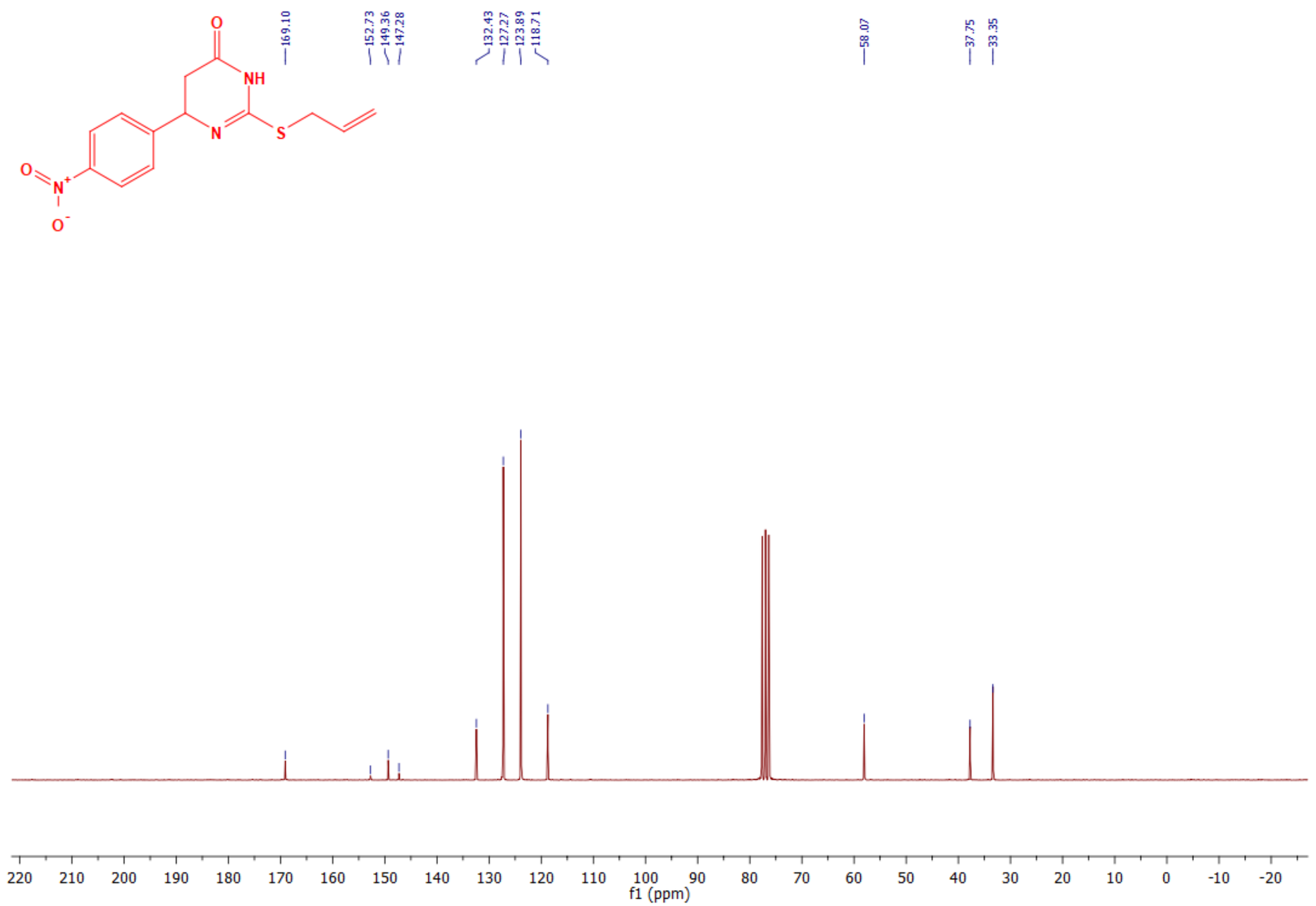


Figure S18 ^{13}C NMR spectrum of **4i**

2-allylthio-6-(4'-methoxyphenyl)-5,6-dihydropyrimidin-4(3H)-one (4j)

White crystals; yield: 93%, reaction time: 105 min.; mp = 122˚C; IR (KBr): ν 3179, 3096, 2930, 1697, 1629, 1514, 1466, 1358, 1248, 1141, 1028 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.48 (dd, 1H, *J* = 16.7, 12.1 Hz, CH_2CO), 2.74-2.87 (m, 1H, CH_2CO), 3.74 (d, 2H, *J* = 6.9 Hz, CH_2S), 3.81 (s, 3H, OCH_3), 4.78 (dd, 1H, *J* = 12.1, 5.3 Hz, CH_{Bn}), 5.11-5.32 (m, 2H, CH_2=), 5.83-6.00 (m, 1H, CH=), 6.84-6.94 (m, 2H, CH_{Ar}), 7.24-7.33 (m, 2H, CH_{Ar}), 8.86 (br. s, 1H, NH) ppm; ^{13}C NMR (50 MHz, $CDCl_3$): δ = 33.3, 38.2, 55.3, 58.1, 113.9, 118.4, 127.3, 132.8, 134.2, 151.0, 158.8 and 170.2 ppm; ESI-MS: m/z (100 %) = 277 $[M + 1]^+$.

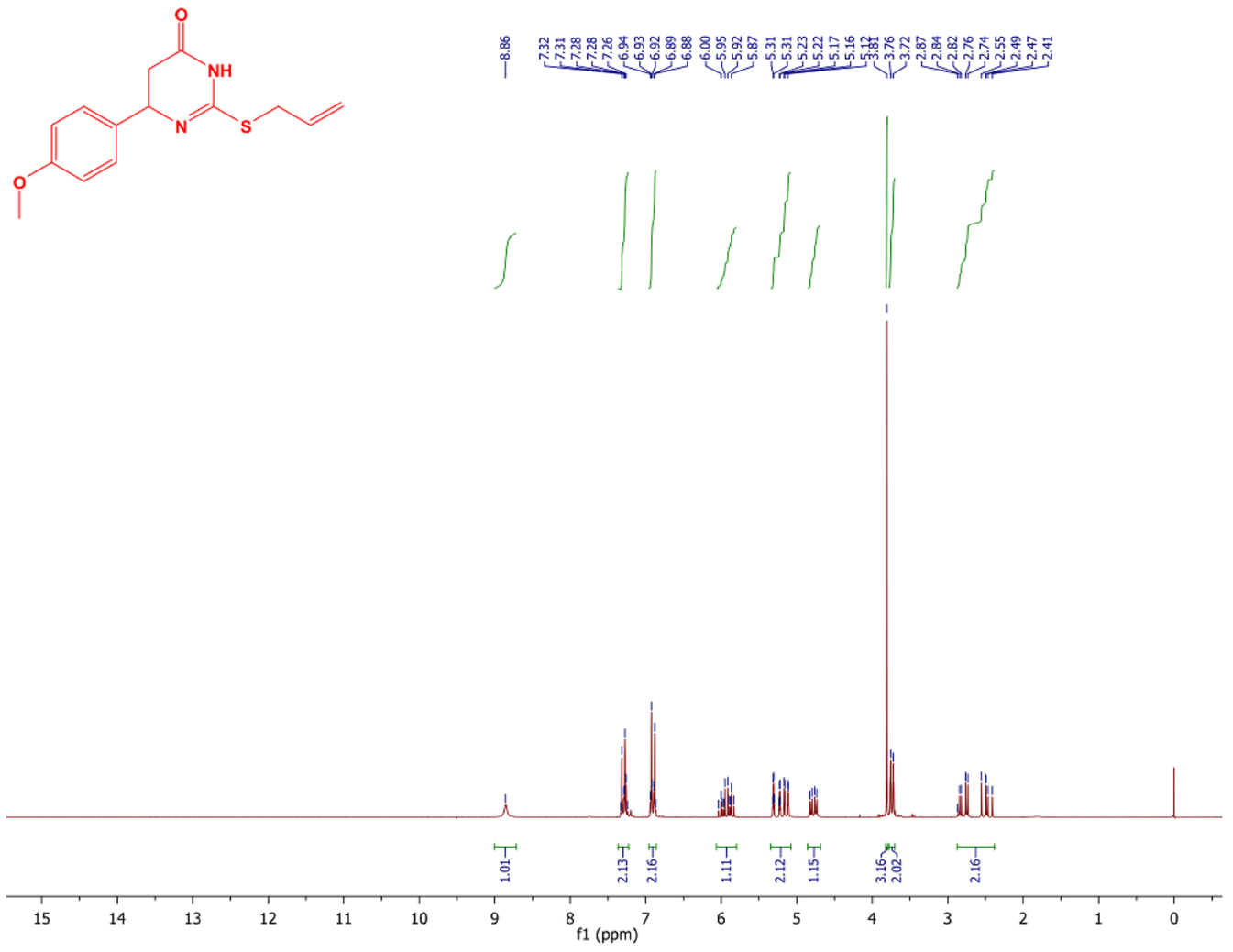


Figure S19 ^{1}H NMR spectrum of **4j**

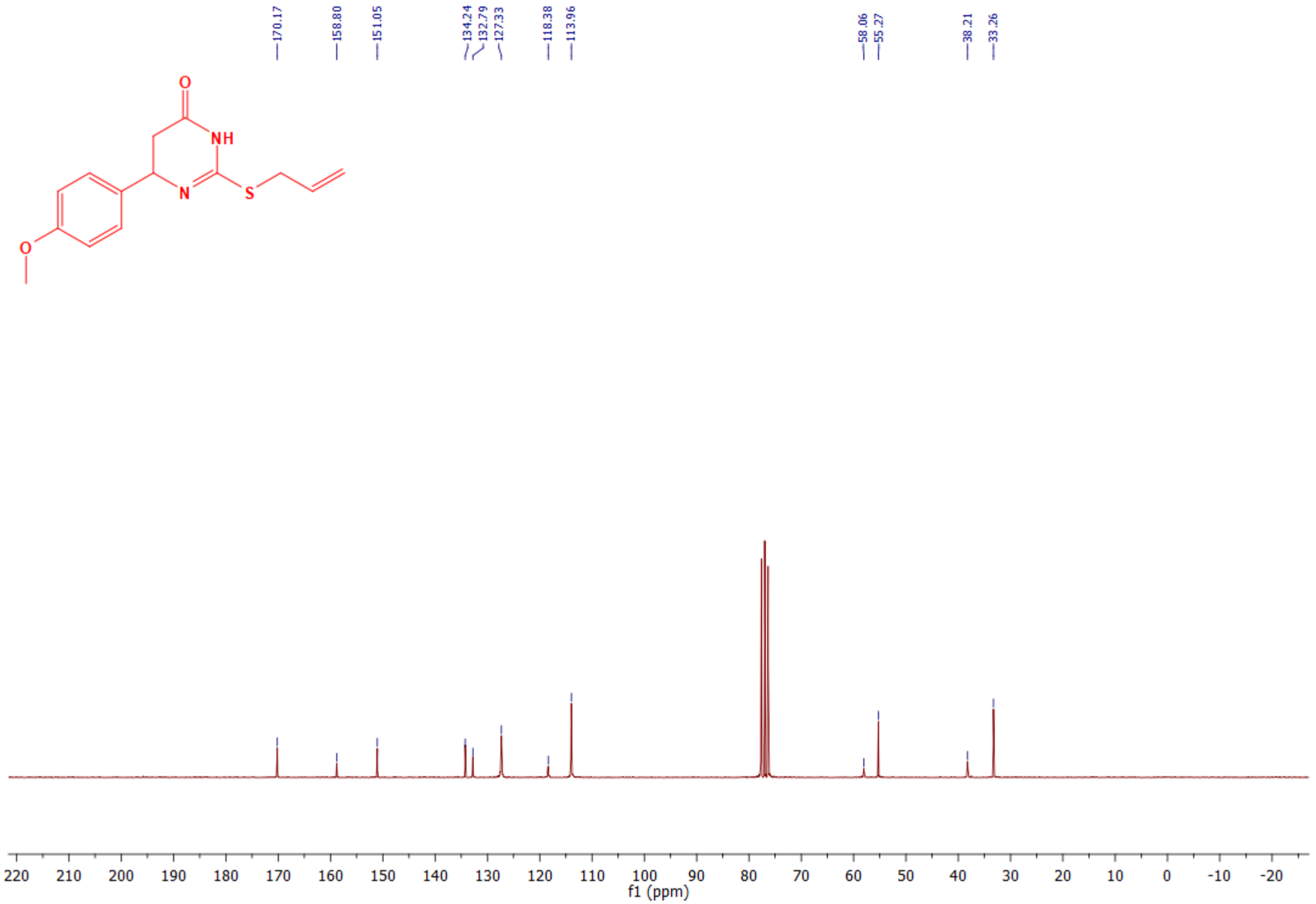
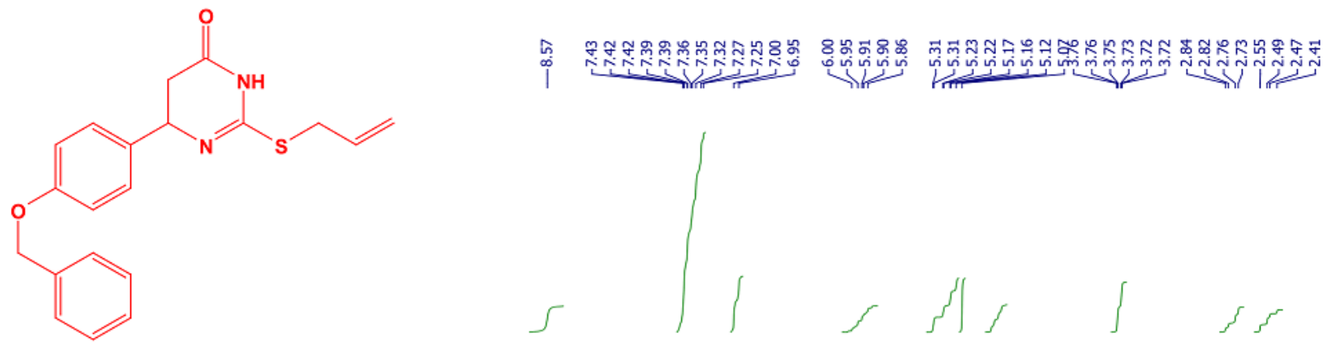


Figure S20 ^{13}C NMR spectrum of **4j**

2-allylthio-6-(4'-benzyloxyphenyl)-5,6-dihydropyrimidin-4(3H)-one (4k)

White amorphous solid; yield: 95%, reaction time: 155 min.; mp = 216 ˚C; IR (KBr): ν 3293, 3089, 2928, 1700, 1631, 1517, 1463, 1259, 1236, 1137, 1025 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$): δ = 2.48 (dd, 1H, *J* = 16.7, 12.1 Hz, CH_2CO), 2.78 (dd, 1H, *J* = 16.7, 5.2 Hz, CH_2CO), 3.74 (dt, 2H, *J* = 6.9, 1.0 Hz, CH_2S), 4.77 (dd, 1H, *J* = 12.1, 5.3 Hz, CH_{Bn}), 5.07 (s, 2H,OCH_2), 5.17-5.31 (m, 2H, CH_2=), 5.83-6.00 (m, 1H, CH=), 6.94-7.01 (m, 2H, CH_{Ar}), 7.25-7.43 (m, 7H, CH_{Ar}), 8.57 (br. s, 1H, NH) ppm; ^{13}C NMR (50 MHz, $CDCl_3$): δ = 33.3, 38.3, 58.1, 70.1, 114.9, 118.4, 127.4, 127.9, 128.6, 132.8, 134.5, 136.9, 150.9, 158.1 and 169.8 ppm; ESI-MS: m/z (100 %) = 353 $[M + 1]^+$.



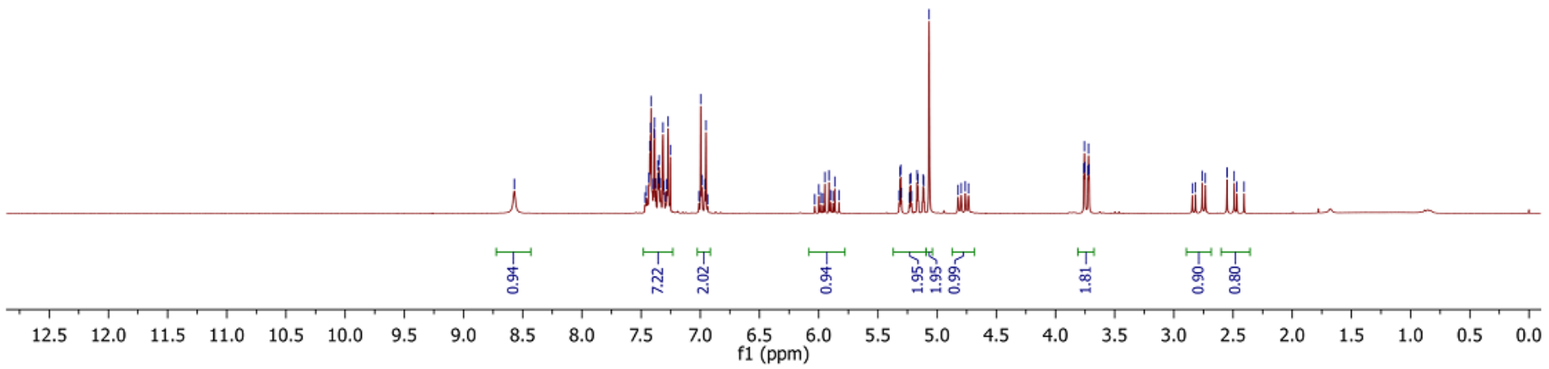


Figure S21 ^1H NMR spectrum of **4k**

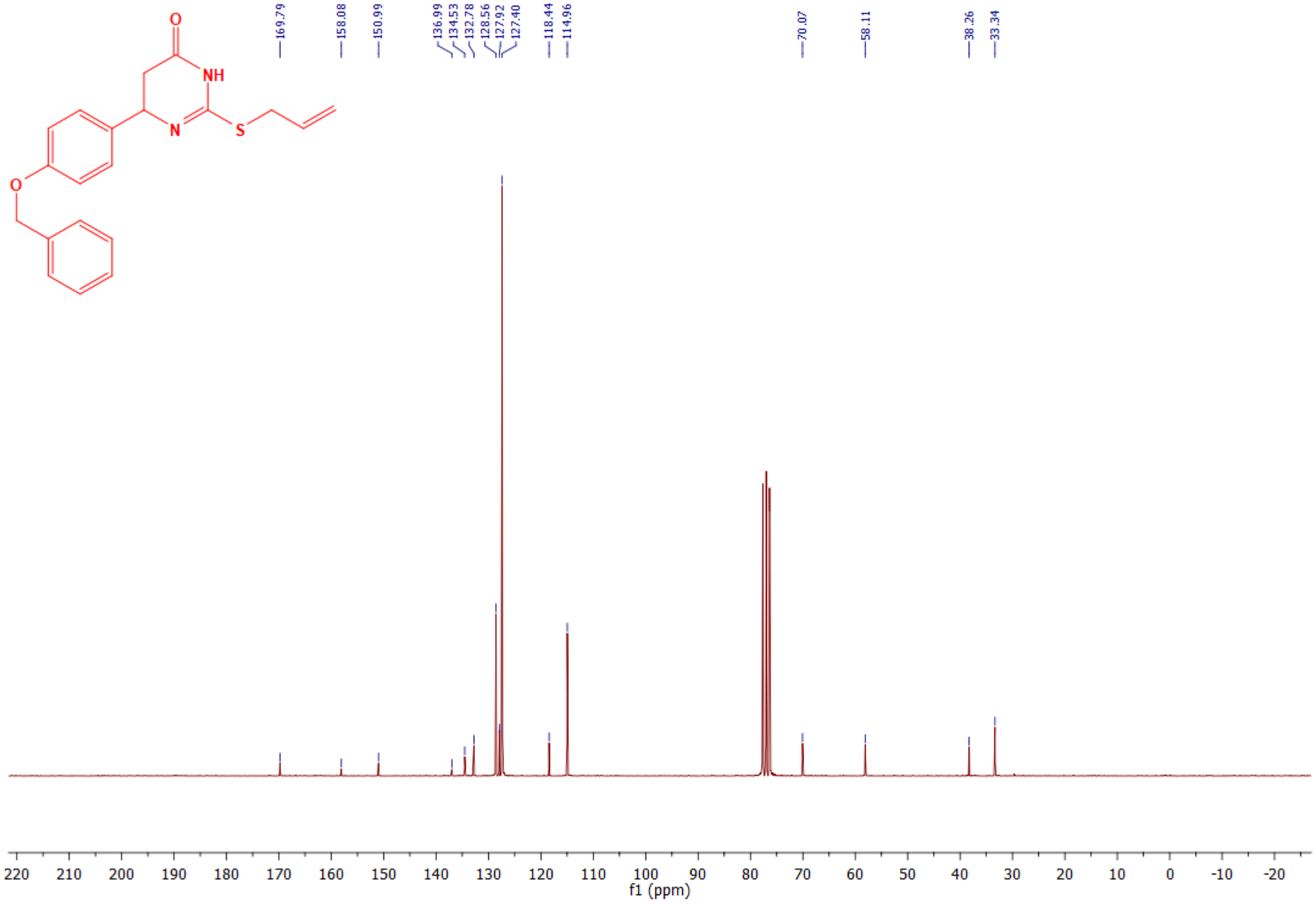


Figure S22 ^{13}C NMR spectrum of **4k**

2-allylthio-6-[4'-(4"-methylbenzyloxy)-3'-methoxyphenyl]-5,6-dihydropyrimidin-4(3H)-one (4l)

White powder; yield: 89%, reaction time: 180 min.; mp = 163˚C; IR (KBr): ν 3179, 3094, 2925, 1697, 1638, 1517, 1464, 1335, 1260, 1227, 1156, 1139, 1029 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.34 (s, 3H, CH_3), 2.48 (dd, 1H, *J* = 16.7, 12.4 Hz, CH_2CO), 2.78 (dd, 1H, *J* = 16.7, 5.2 Hz, CH_2CO), 3.75 (m, 2H, CH_2S), 3.89 (s, 3H, OCH_3), 4.76 (dd, 1H, *J* = 12.3, 5.2 Hz, CH_{Bn}), 5.12-5.32 (m, 4H, CH_2= + OCH_2), 5.88-5.96 (m, 1H, CH=), 6.83-6.89 (m, 2H, CH_{Ar}), 6.96 (d, 1H, *J* = 1.6 Hz, CH_{Ar}), 7.17 (d, 2H, *J* = 7.8 Hz, CH_{Ar}), 7.33 (d, 2H, *J* = 8.1 Hz, CH_{Ar}), 8.72 (br. s, 1H, NH) ppm; ^{13}C NMR (50 MHz, $CDCl_3$): δ = 21.2, 33.2, 38.2, 55.9, 58.3, 70.9, 110.3, 114.0, 118.2, 127.3, 129.2, 132.8, 134.1, 135.2, 137.5, 147.5, 149.7, 151.1 and 169.9 ppm; ESI-MS: m/z (100 %) = 397 $[M + 1]^+$.

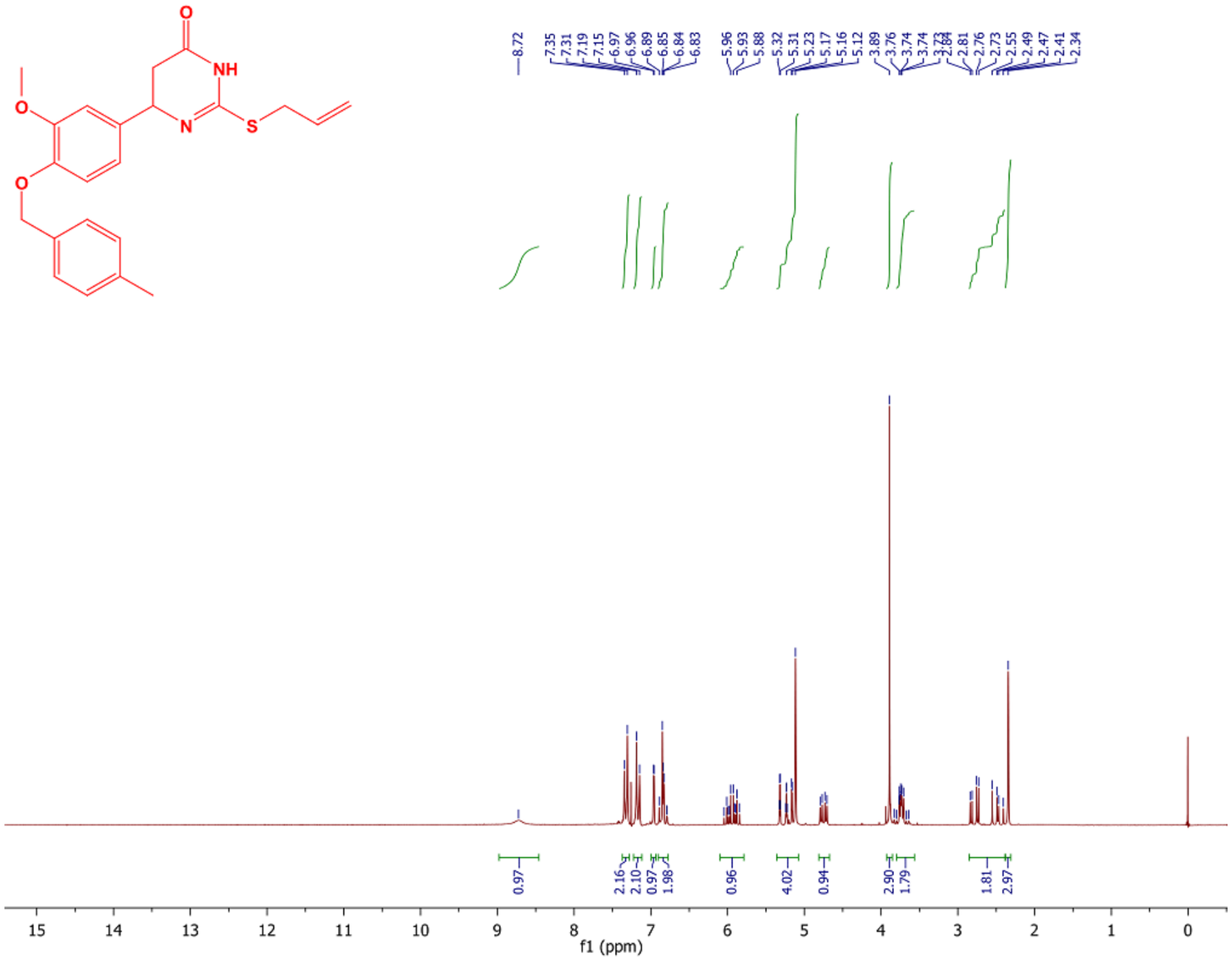


Figure S23 ^{1}H NMR spectrum of **4l**

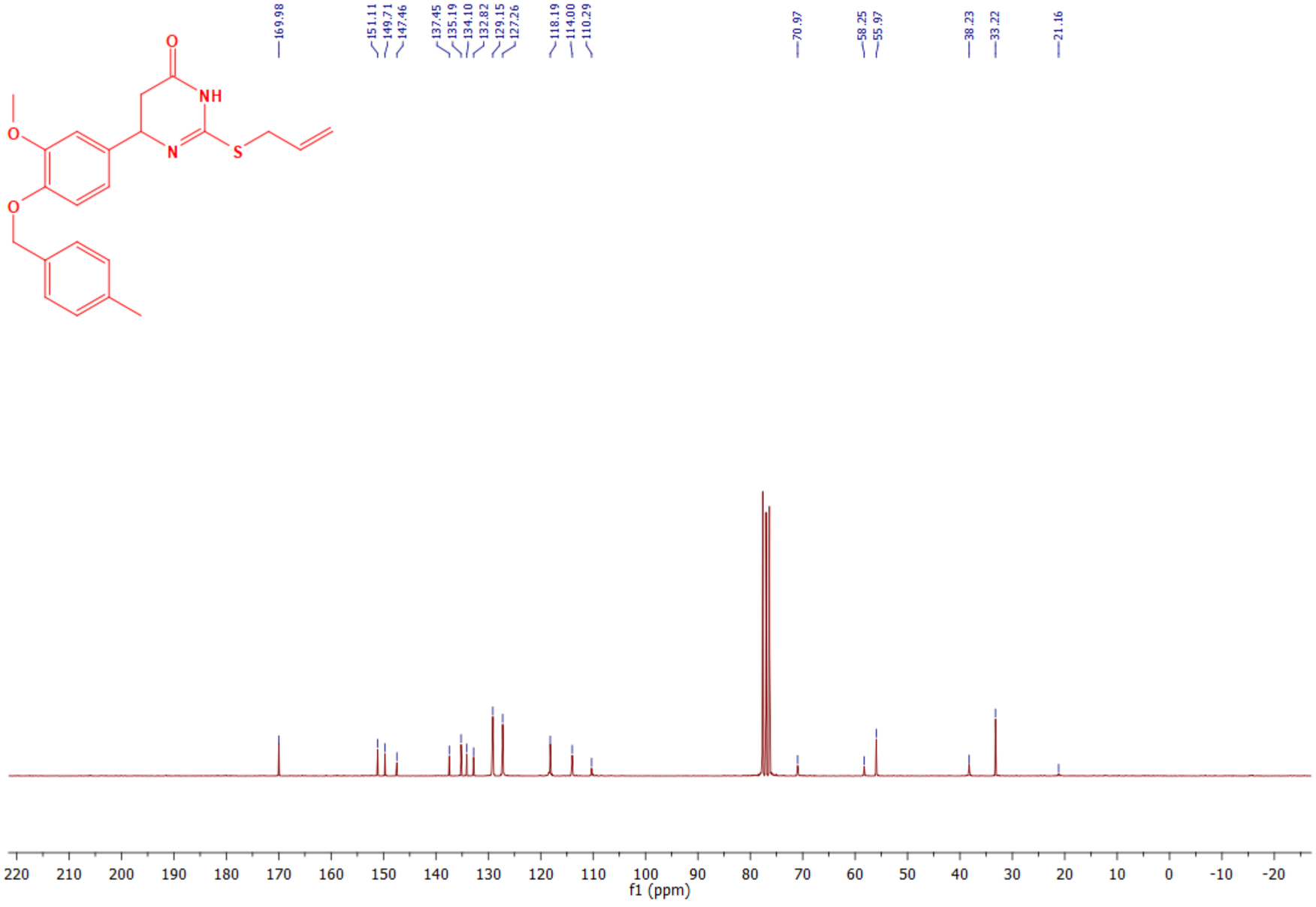
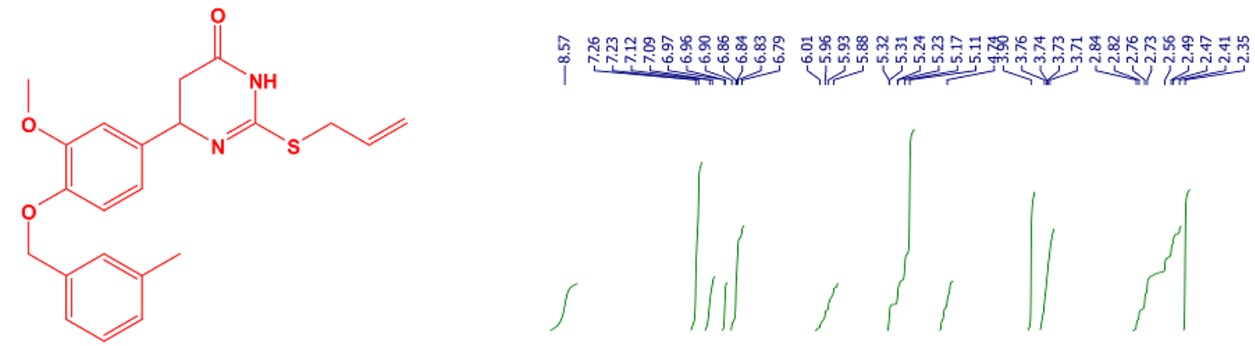


Figure S24 ^{13}C NMR spectrum of **4l**

2-allylthio-6-[4'-(3"-methylbenzyloxy)-3'-methoxyphenyl]-5,6-dihydropyrimidin-4(3H)-one (4m)

White powder; yield: 87%, reaction time: 180 min.; mp = 111˚C; IR (KBr): ν 3184, 3104, 2931, 1699, 1644, 1515, 1464, 1328, 1276, 1139 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.35 (s, 3H, CH_3), 2.49 (dd, 1H, *J* = 16.7, 12.3 Hz, CH_2CO), 2.78 (dd, 1H, *J* = 16.7, 5.2 Hz, CH_2CO), 3.75 (m, 2H, CH_2S), 3.90 (s, 3H, OCH_3), 4.74 (dd, 1H, *J* = 12.3, 5.2 Hz, CH_{Bn}), 5.11-5.32 (m, 4H, CH_2= + OCH_2), 5.88-6.01 (m, 1H, CH=), 6.79-6.83 (m, 2H, CH_{Ar}), 6.96 (d, 1H, *J* = 1.6 Hz, CH_{Ar}), 7.09-7.12 (m, 1H, CH_{Ar}), 7.23-7.26 (m, 3H, CH_{Ar}), 8.57 (br. s, 1H, NH) ppm; ^{13}C NMR (50 MHz, $CDCl_3$): δ = 21.4, 33.3, 38.3, 55.9, 58.3, 71.2, 110.3, 114.0, 118.2, 124.3, 127.9, 128.5, 132.8, 135.3, 137.0, 138.1, 147.5, 149.7, 151.0 and 169.8 ppm; ESI-MS: m/z (100 %) = 397 $[M + 1]^+$.



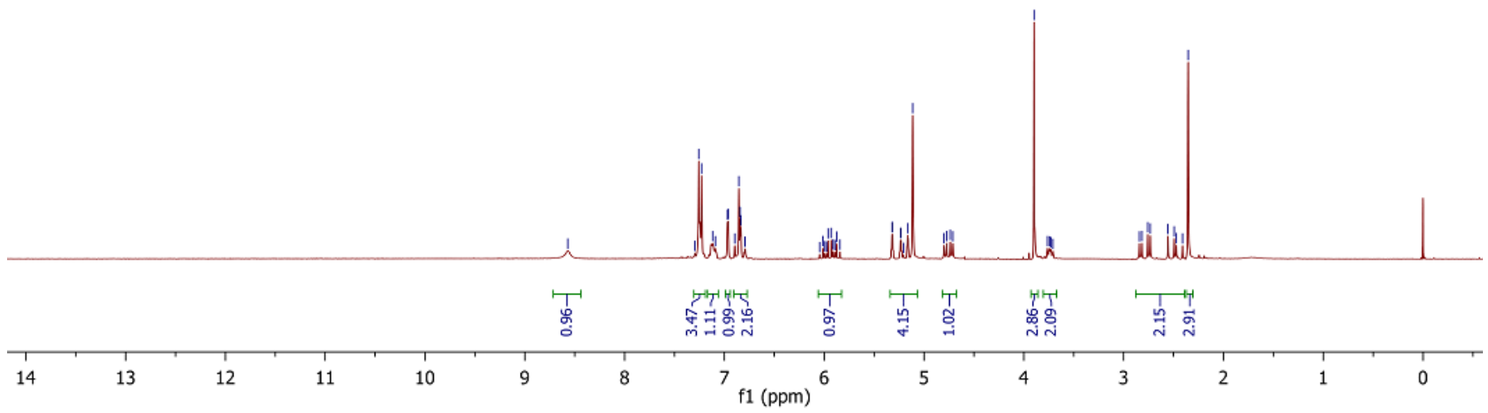


Figure S25 ^{1}H NMR spectrum of **4m**

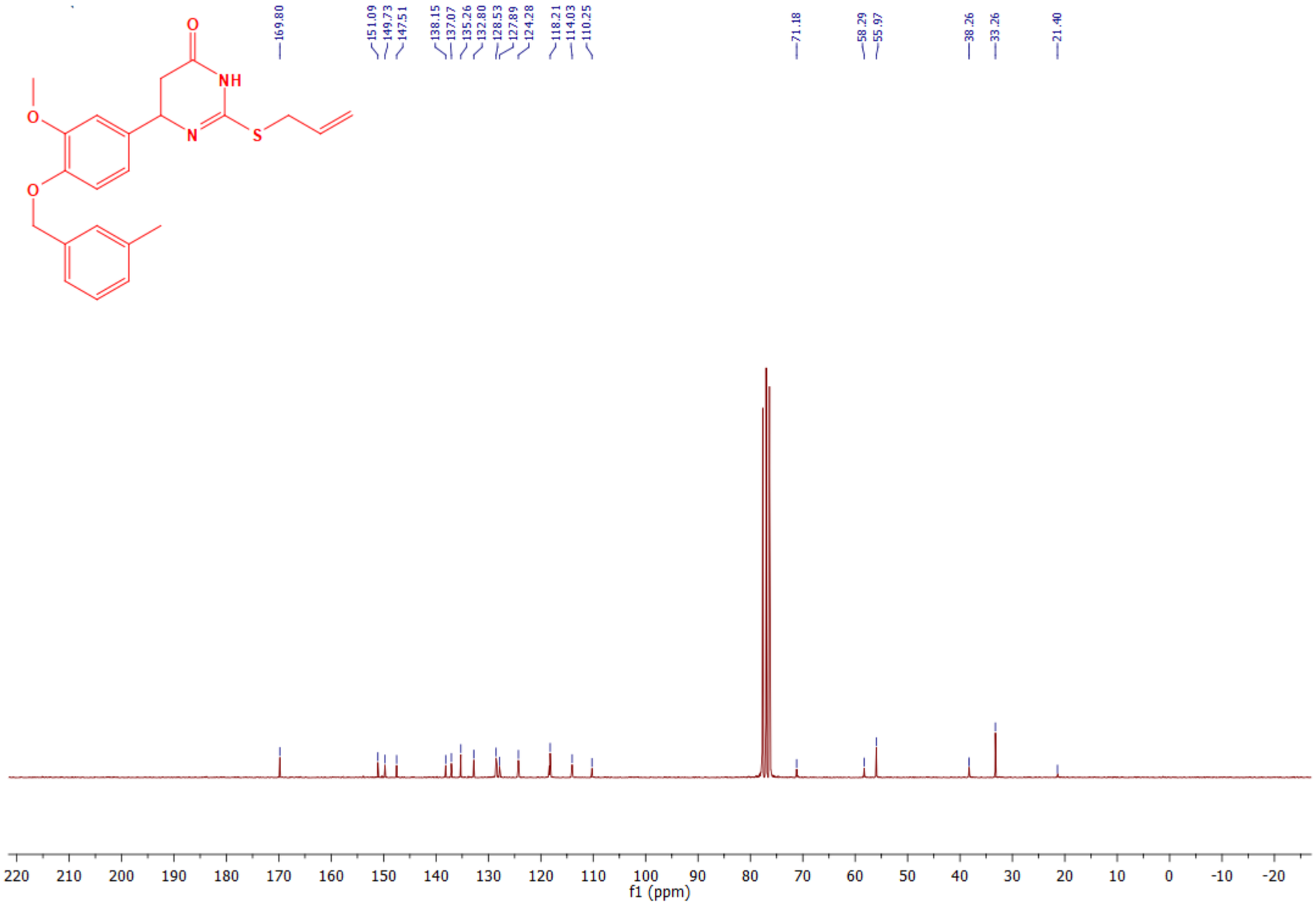
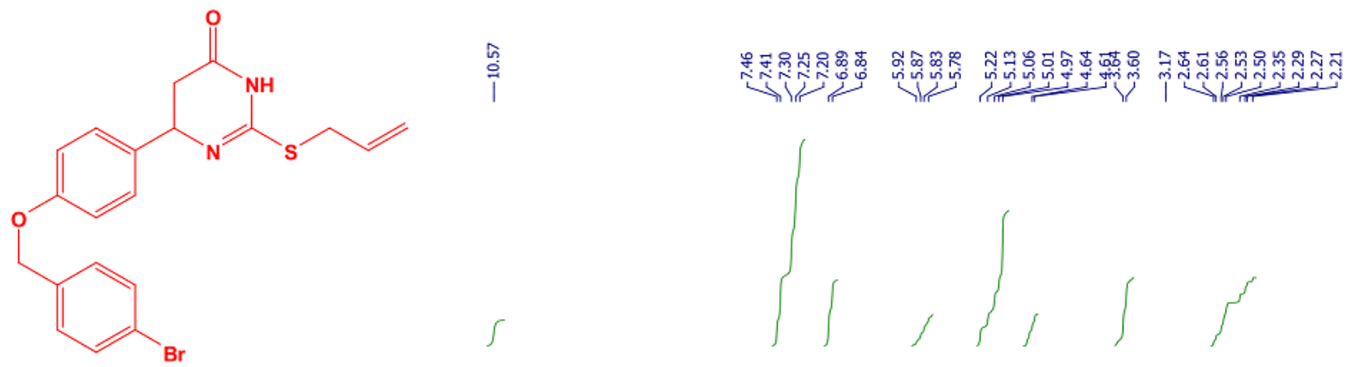


Figure S26 ^{13}C NMR spectrum of **4m**

2-allylthio-6-[4'-(4"-bromobenzyloxy)phenyl]-5,6-dihydropyrimidin-4(3H)-one (4n)

White solid; yield: 94%, reaction time: 115 min.; mp = 194˚C; IR (KBr): ν 3186, 3099, 2918, 1705, 1631, 1508, 1479, 1356, 1239, 1144 cm^{-1}; ^1H NMR (200 MHz, DMSO-d_6 +$CDCl_3$): δ = 2.21-2.64 (m, 2H, CH_2CO), 3.62 (d, 2H, *J* = 6.9 Hz, CH_2S), 4.65 (dd, 1H, *J* = 11.8, 5.2 Hz, CH_{Bn}), 4.97 (s, 2H, OCH_2), 5.01-5.22 (m, 2H, CH_2=), 5.75-5.95 (m, 1H, CH=), 6.86 (d, 2H, *J* = 8.6 Hz, CH_{Ar}), 7.20-7.30 (m, 4H, CH_{Ar}), 7.44 (d, 2H, *J* = 8.4 Hz, CH_{Ar}), 10.57 (br. s, 1H, NH) ppm; ^{13}C NMR (50 MHz, DMSO-d_6 +$CDCl_3$): δ = 32.4, 38.0, 57.5, 68.7, 114.4, 117.5, 121.1, 127.1, 128.9, 131.1, 133.0, 135.1, 136.0, 152.0, 157.1 and 168.9 ppm; ESI-MS: m/z (100 %) = 431 $[M]^+$.



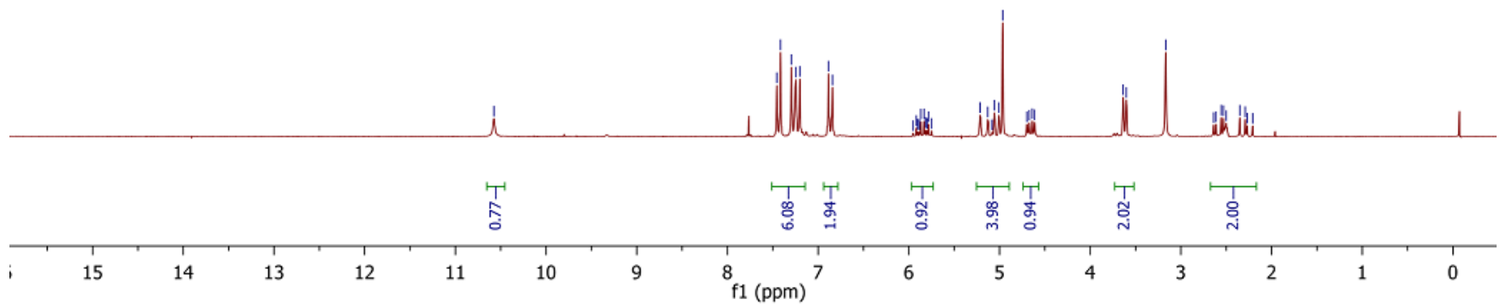


Figure S27 ^1H NMR spectrum of **4n**

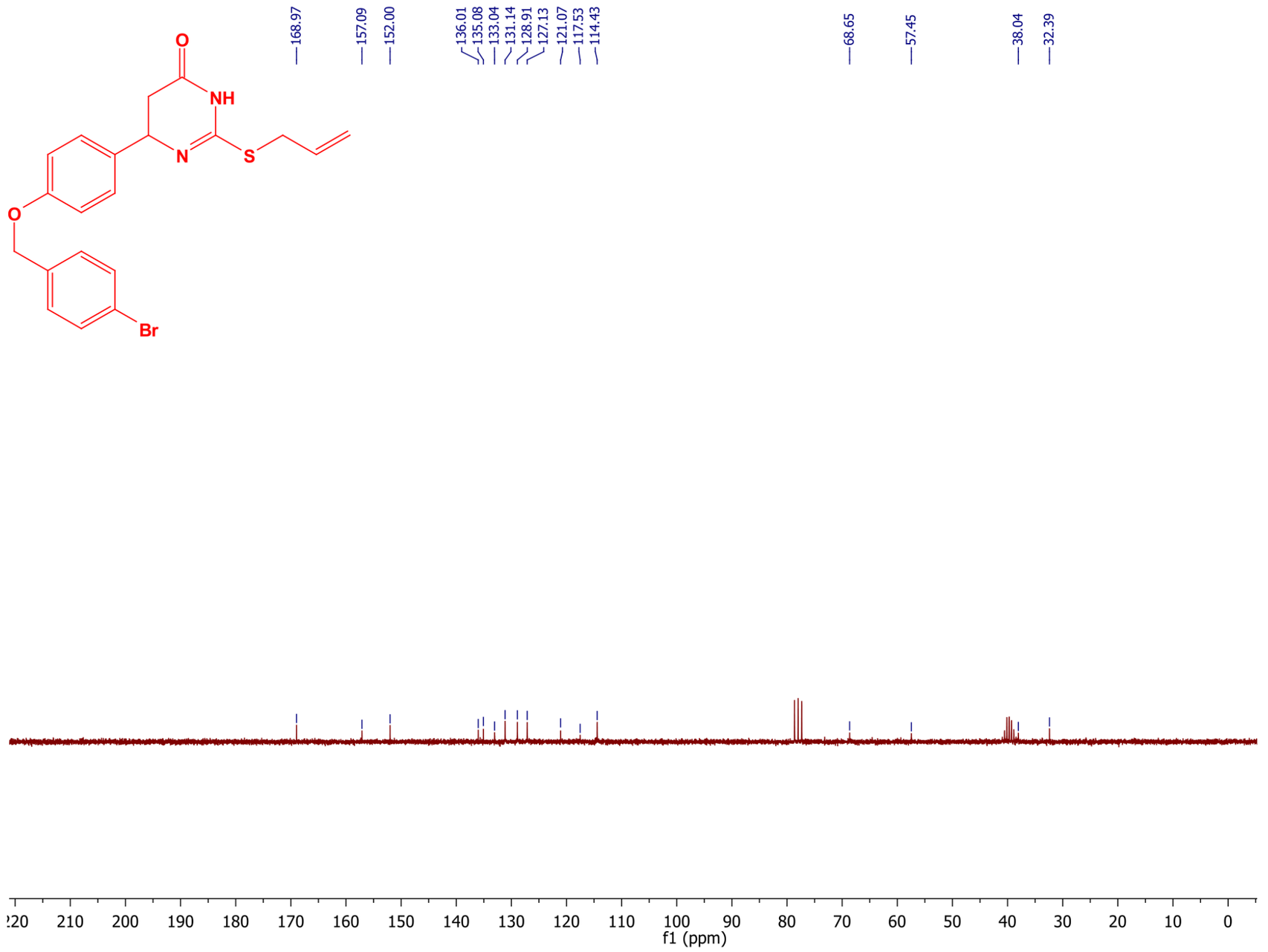


Figure S28 ^{13}C NMR spectrum of **4n**

2-allylthio-6-(4'-benzyloxy-3'-methoxyphenyl)-5,6-dihydropyrimidin-4(3H)-one (4o)

White solid; yield: 88%, reaction time: 180 min.; mp = 136˚C; IR (KBr): ν 3179, 3088, 2869, 1697, 1637, 1515, 1465, 1335, 1259, 1227, 1156, 1138, 1029 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$): δ = 2.47 (dd, 1H, *J* = 16.7, 12.4 Hz, CH_2CO), 2.79 (dd, 1H, *J* = 16.7, 5.2 Hz, CH_2CO), 3.75 (m, 2H, CH_2S), 3.90 (s, 3H,OCH_3), 4.74 (dd, 1H, *J* = 12.4, 5.1 Hz, CH_{Bn}), 5.11-5.32 (m, 4H, CH_2= + OCH_2), 5.87-5.96 (m, 1H, CH=), 6.84-6.96 (m, 2H, CH_{Ar}), 6.96 (d, 1H, *J* = 1.6 Hz, CH_{Ar}), 7.32-7.42 (m, 5H, CH_{Ar}), 8.74 (br. s, 1H, NH) ppm; ^{13}C NMR (50 MHz, $CDCl_3$): δ = 33.3, 38.3, 56.0, 58.3, 71.1, 110.4, 114.2, 118.2, 118.3, 127.2, 127.8, 128.5, 132.8, 135.4, 137.2, 147.5, 149.8, 151.1 and 169.9 ppm; ESI-MS: m/z (100 %) = 383 $[M + 1]^+$.

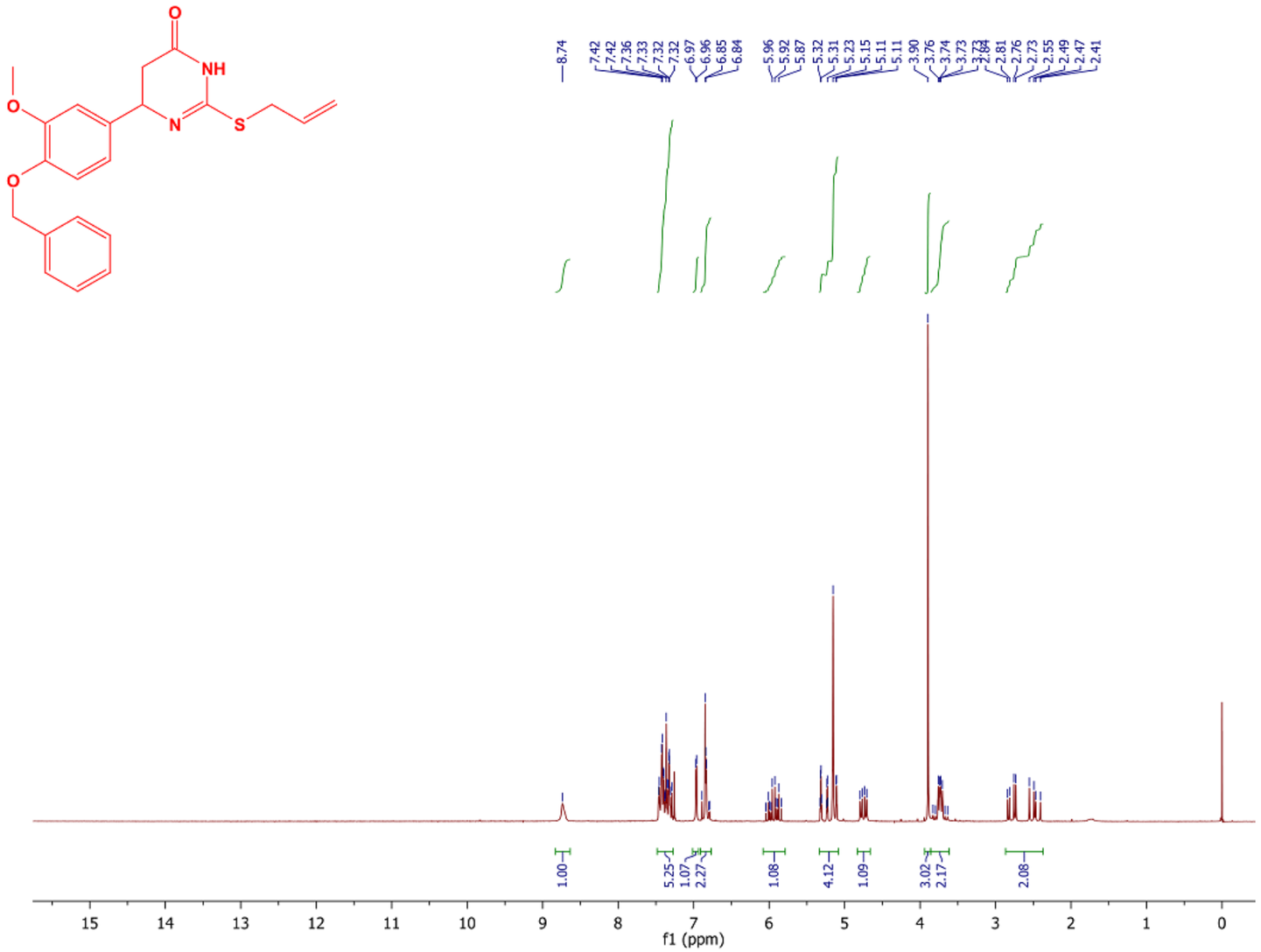


Figure S29 ^1H NMR spectrum of **4o**

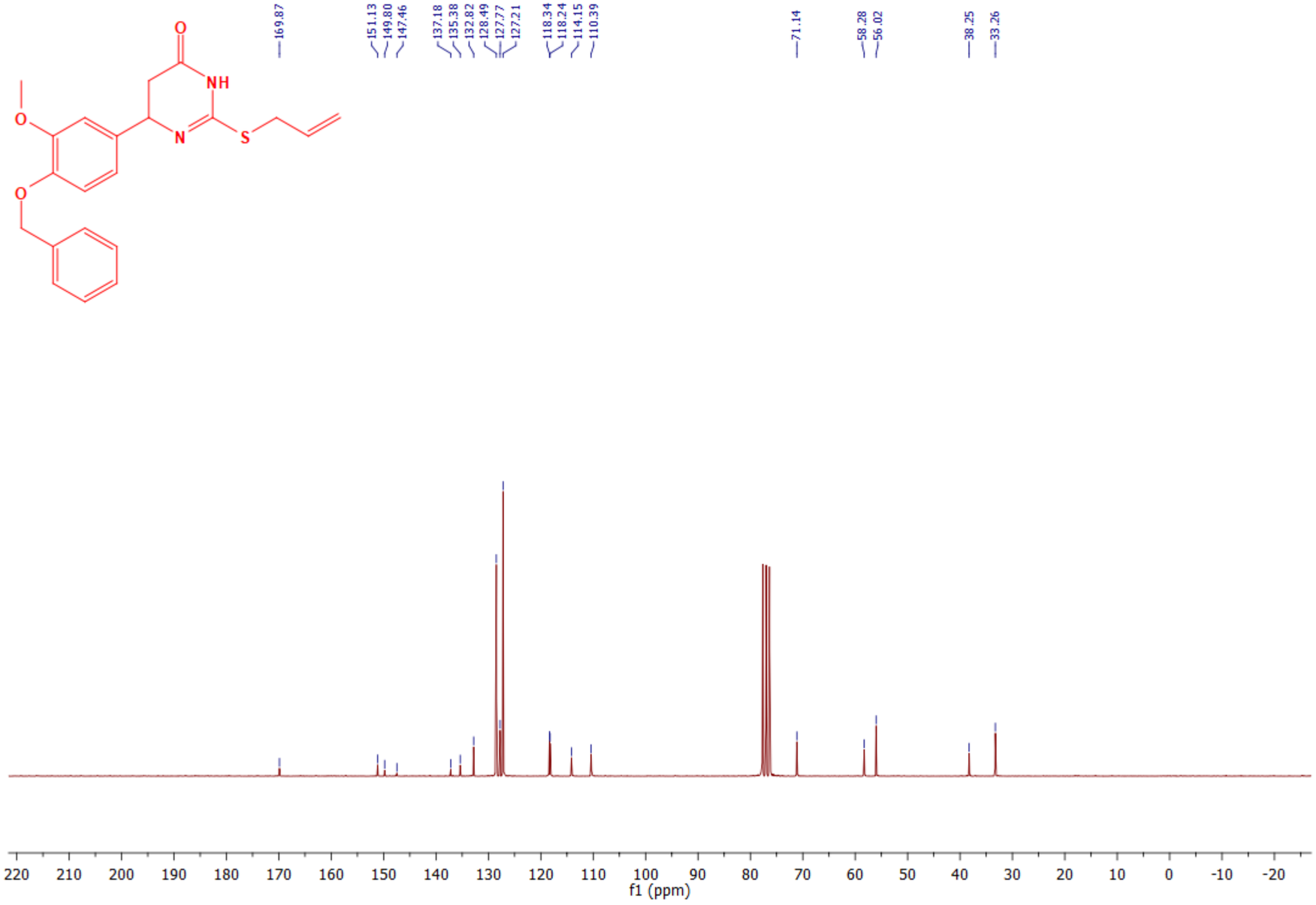


Figure S30 ^{13}C NMR spectrum of **4o**

2-allylthio-6-(3',4',5'-trimethoxyphenyl)-5,6-dihydropyrimidin-4(3H)-one (4p)

White solid; yield: 79%, reaction time: 180 min.; mp = 118˚C; IR (KBr): ν 3196, 3098, 2929, 1699, 1630, 1591, 1462, 1332, 1232 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.501(dd, 1H, *J* = 16.7, 12.8 Hz, CH_2CO), 2.82 (dd, 1H, *J* = 16.7, 5.1 Hz, CH_2CO), 3.61-3.95 (m, 11H, 3×OCH_3 + CH_2S), 4.75 (dd, 1H, *J* = 12.8, 5.1 Hz, CH_{Bn}), 5.12-5.35 (m, 2H, CH_2=), 5.86-6.07 (m, 1H, CH=), 6.63 (s, 2H, CH_{Ar}), 8.95 (br. s, 1H, NH) ppm; ^{13}C NMR (50 MHz, $CDCl_3$): δ = 33.2, 38.4, 56.1, 58.7, 60.8, 103.4, 118.3, 132.8, 137.2, 137.9, 151.4, 153.3 and 169.9 ppm; ESI-MS: m/z (100 %) = 337 $[M + 1]^+$.

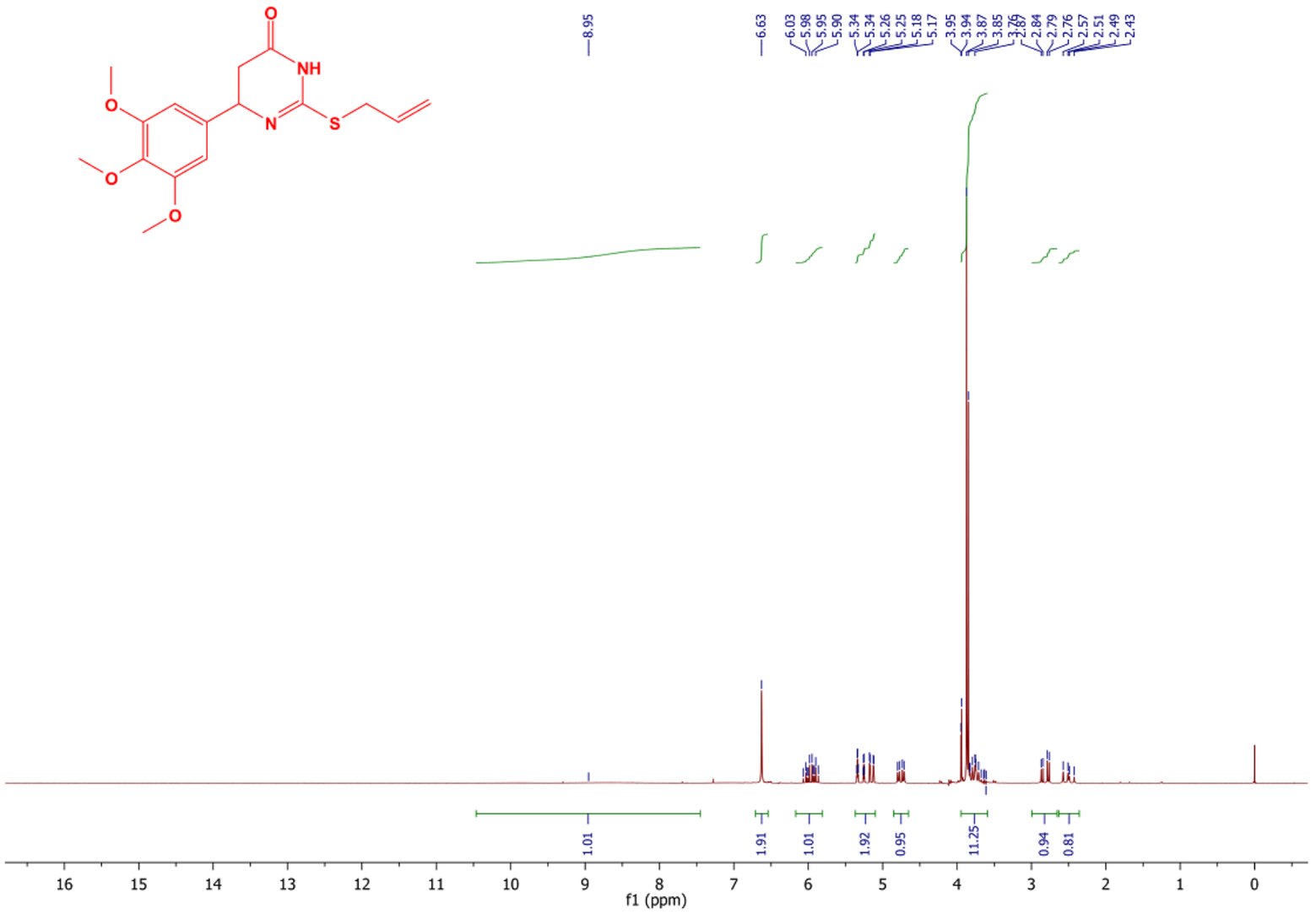


Figure S31 ^{1}H NMR spectrum of **4p**

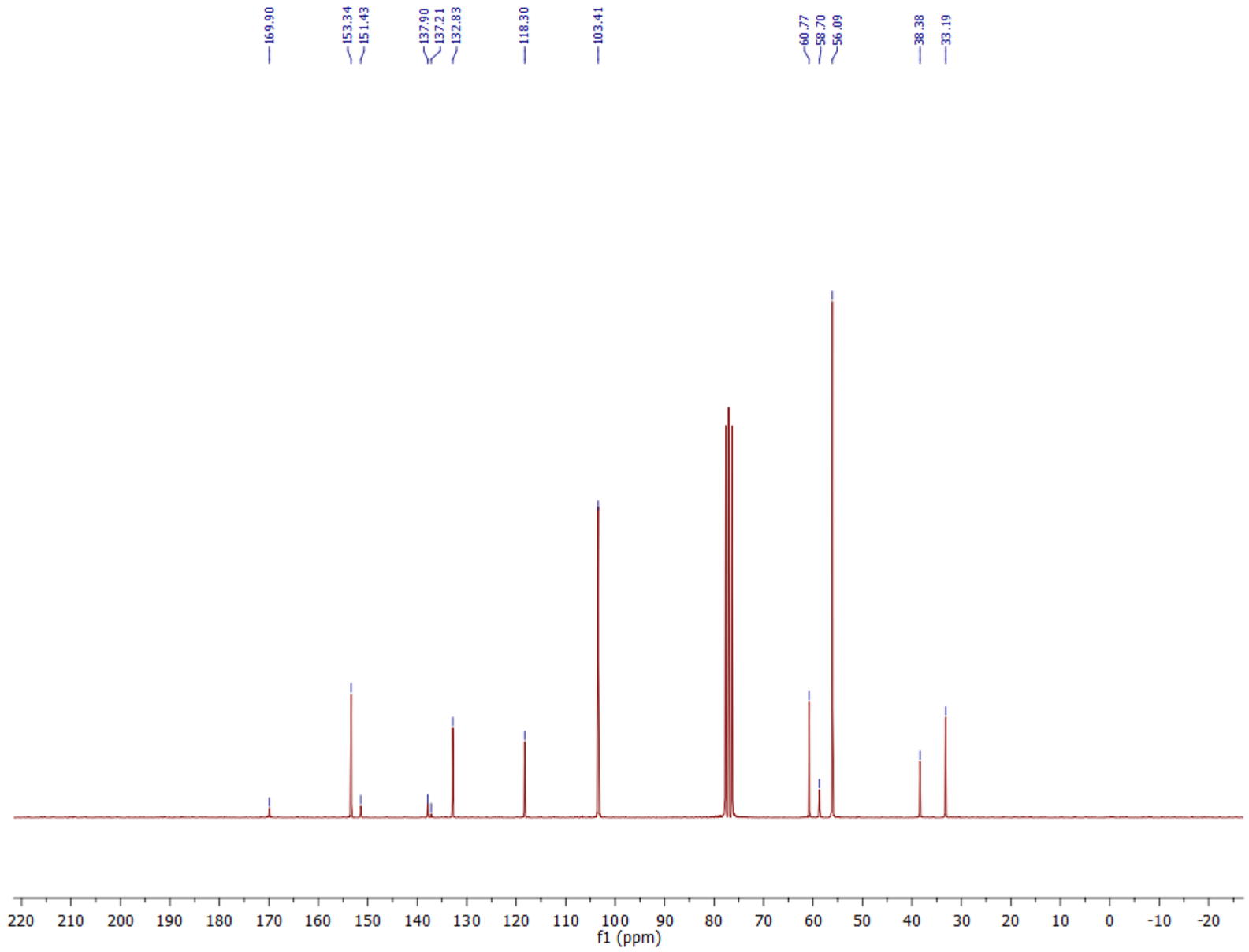
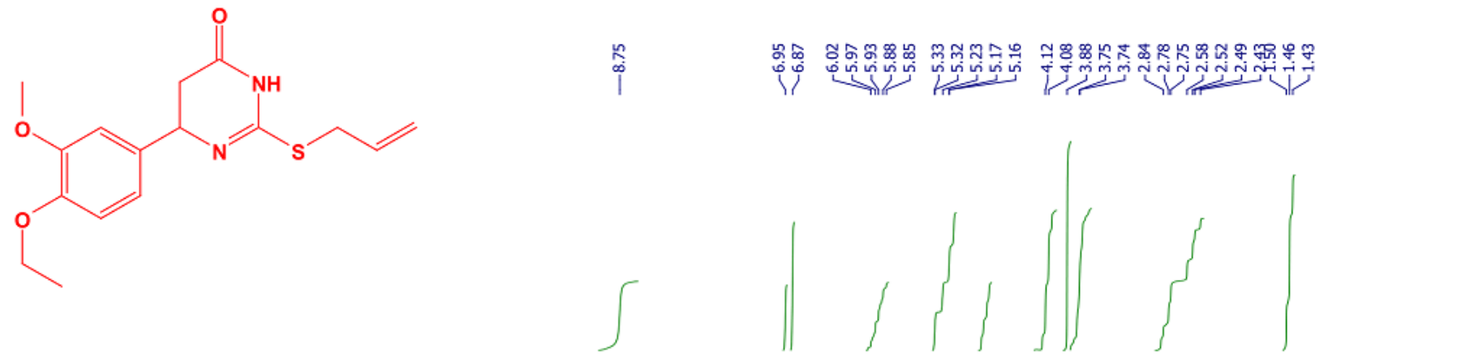


Figure S32 ^{13}C NMR spectrum of **4p**

2-allylthio-6-(4'-ethoxy-3'-methoxyphenyl)-5,6-dihydropyrimidin-4(3H)-one (4q)

Yellow powder; yield: 74%, reaction time: 180 min.; mp = 119˚C; IR (KBr): ν 3181, 3083, 2913, 1698, 1623, 1517, 1477, 1333, 1262, 1243, 1138, 1041 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.46 (t, 3H, *J* = 7.0, CH_3) 2.51 (dd, 1H, *J* = 16.7, 12.3 Hz, CH_2CO), 2.79 (dd, 1H, *J* = 16.7, 5.2 Hz, CH_2CO), 3.74-3.75 (m, 2H, CH_2S), 3.88 (s, 3H, OCH_3), 4.12 (q, 2H, *J* = 7.0 Hz, OCH_2), 4.78 (dd, 1H, *J* = 12.3, 5.2 Hz, CH_{Bn}), 5.16-5.33 (m, 2H, CH_2=), 5.85-6.02 (m, 1H, CH=), 6.87 (s, 2H, CH_{Ar}), 6.95 (s, 1H, CH_{Ar}), 8.75 (br. s, 1H, NH) ppm; ^{13}C NMR (50 MHz, $CDCl_3$): δ = 14.8, 33.2, 38.3, 55.9, 58.3, 64.4, 110.0, 112.8, 118.2, 118.3, 132.8, 134.7, 147.6, 149.4, 151.1 and 170.0 ppm; ESI-MS: m/z (100 %) = 321 $[M + 1]^+$.



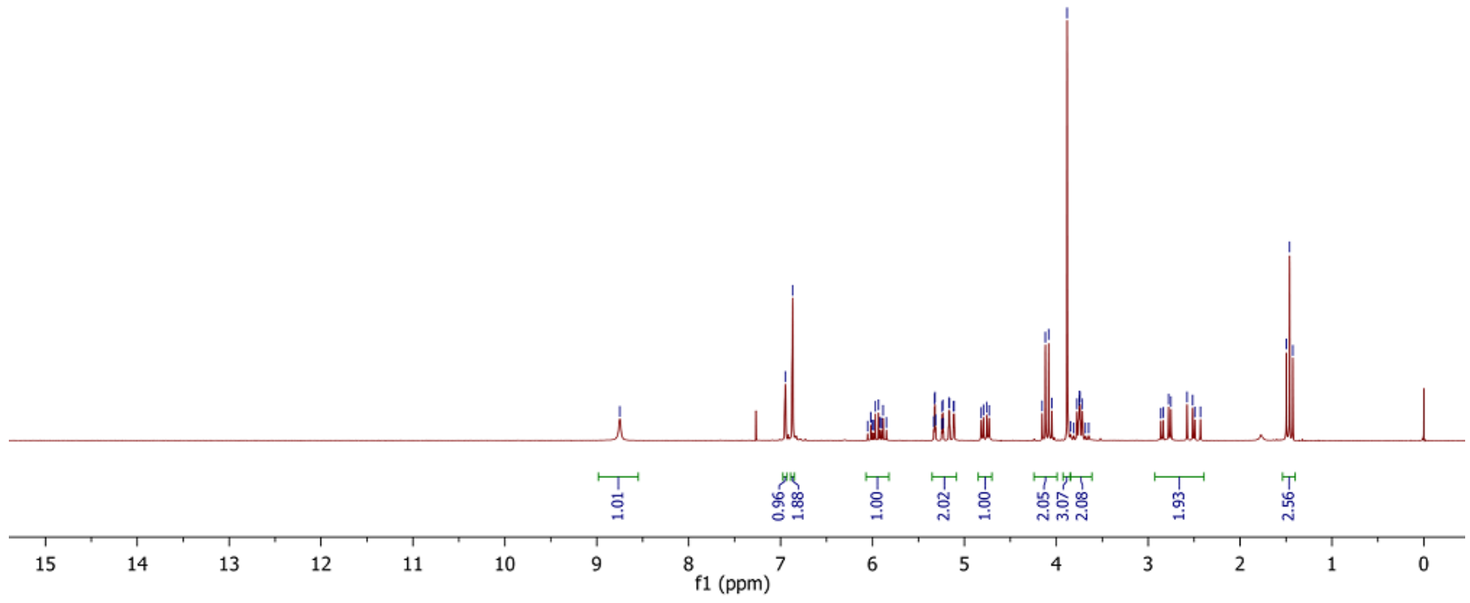


Figure S33 ^{1}H NMR spectrum of **4q**

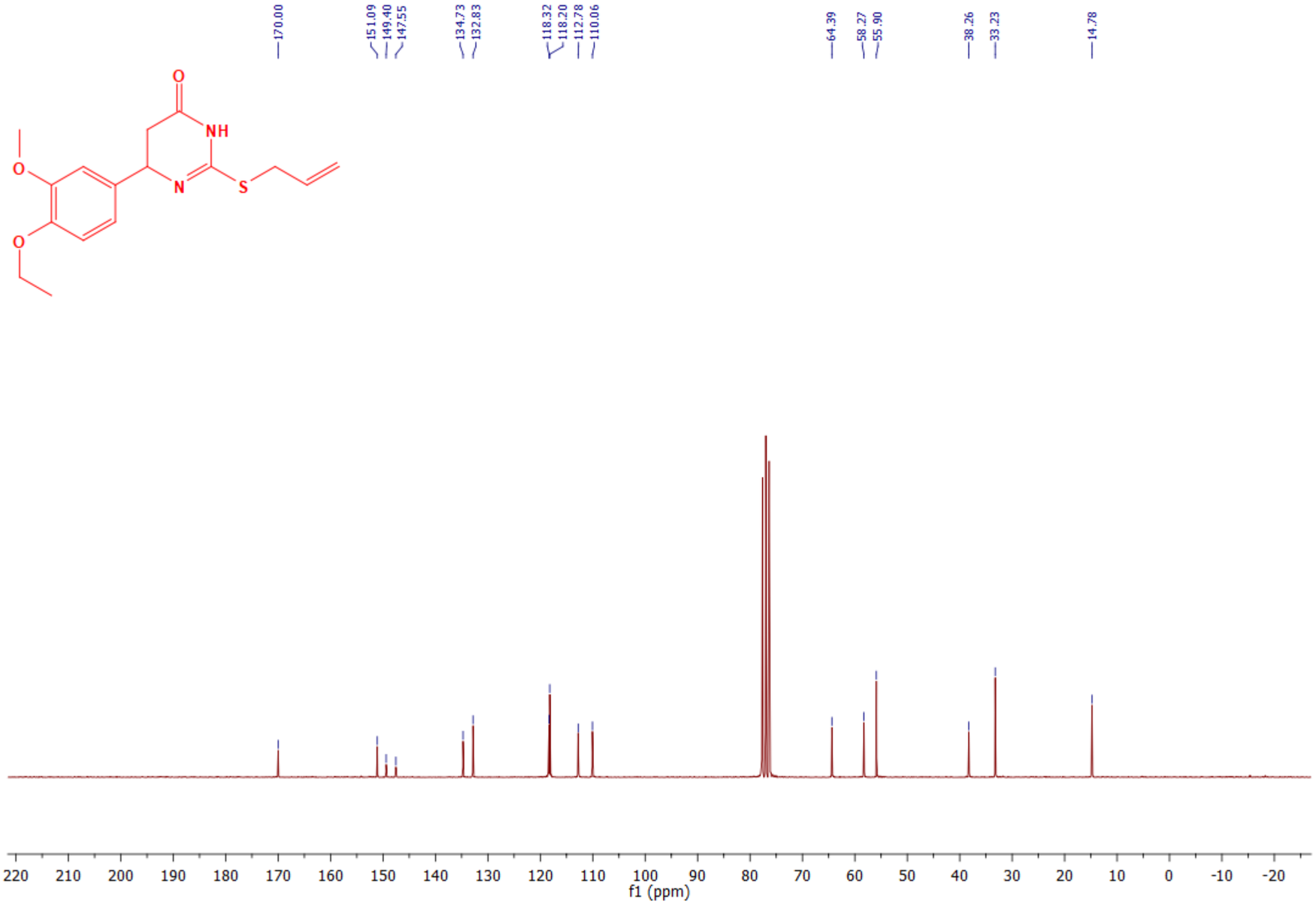
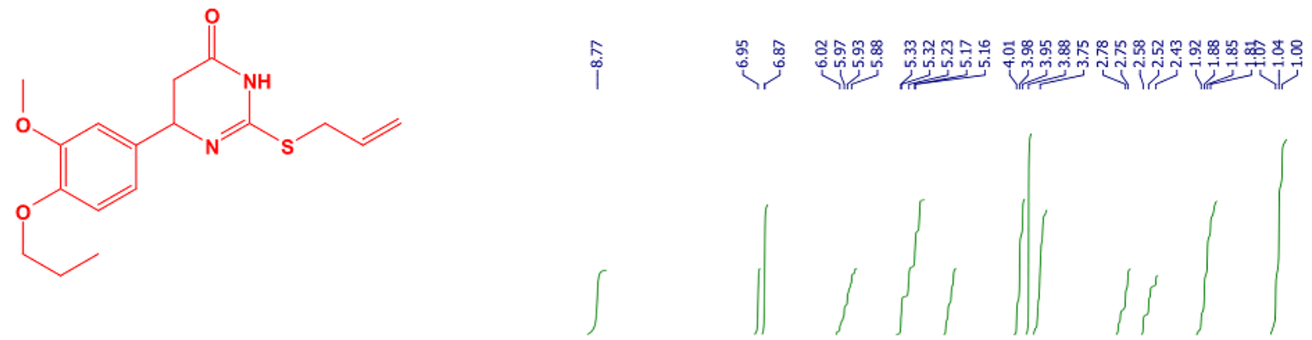


Figure S34 ^{13}C NMR spectrum of **4q**

2-allylthio-6-(3'-methoxyphenyl-4'-propoxy)-5,6-dihydropyrimidin-4(3H)-one (4r)

Yellow powder; yield: 91%, reaction time: 125 min.; mp = 100˚C; IR (KBr): ν 3185, 3085, 2969, 2916, 1700, 1619, 1517, 1467, 1327, 1261, 1237, 1135 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$): δ = 1.00-1.07 (t, 3H, *J* = 7.4, CH_3) 1.78-1.96 (m, 2H, CH_2), 2.51 (dd, 1H, *J* = 16.7, 12.3 Hz, CH_2CO), 2.81 (dd, 1H, *J* = 16.7, 5.2 Hz, CH_2CO), 3.65-3.81 (m, 2H, CH_2S), 3.88 (s, 3H, OCH_3), 3.98 (t, 2H, *J* = 6.9 Hz, OCH_2), 4.78 (dd, 1H, *J* = 12.3, 5.2 Hz, CH_{Bn}), 5.11-5.33 (m, 2H, CH_2=), 5.88-6.02 (m, 1H, CH=), 6.87 (s, 2H, CH_{Ar}), 6.95 (s, 1H, CH_{Ar}), 8.77 (br. s, 1H, NH) ppm; ^{13}C NMR (50 MHz, $CDCl_3$): δ = 10.4, 22.4, 33.2, 38.3, 55.9, 58.3, 70.6, 110.3, 113.0, 118.2, 132.8, 134.7, 147.8, 149.5, 151.1 and 170.1 ppm; ESI-MS: m/z (100 %) = 335 $[M + 1]^+$.



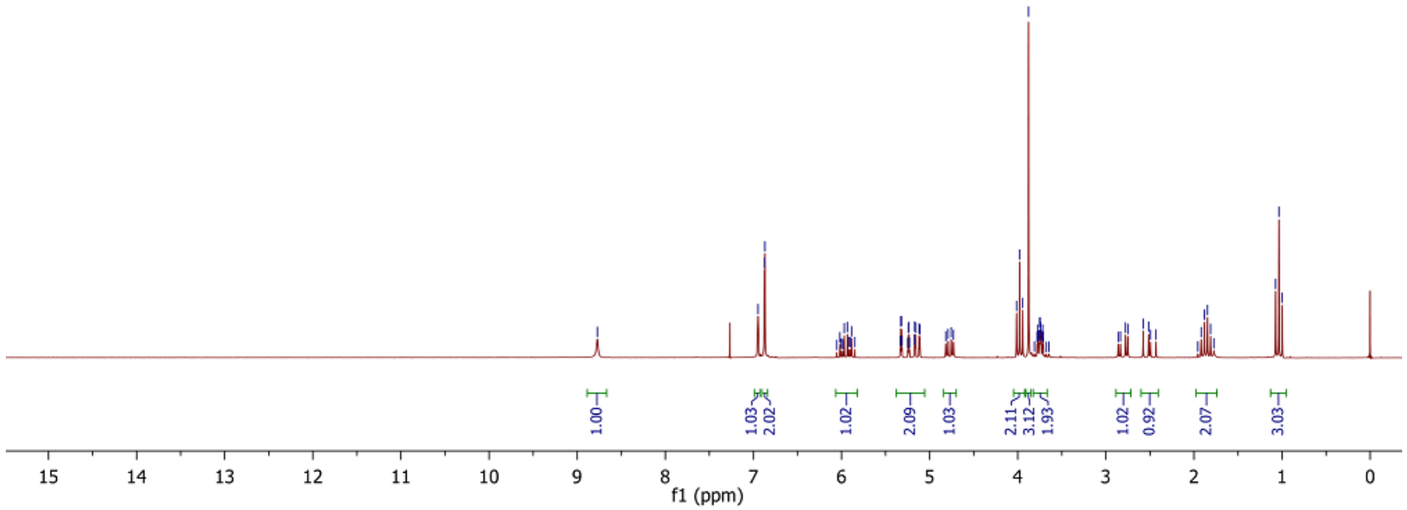


Figure S35 ^1H NMR spectrum of **4r**

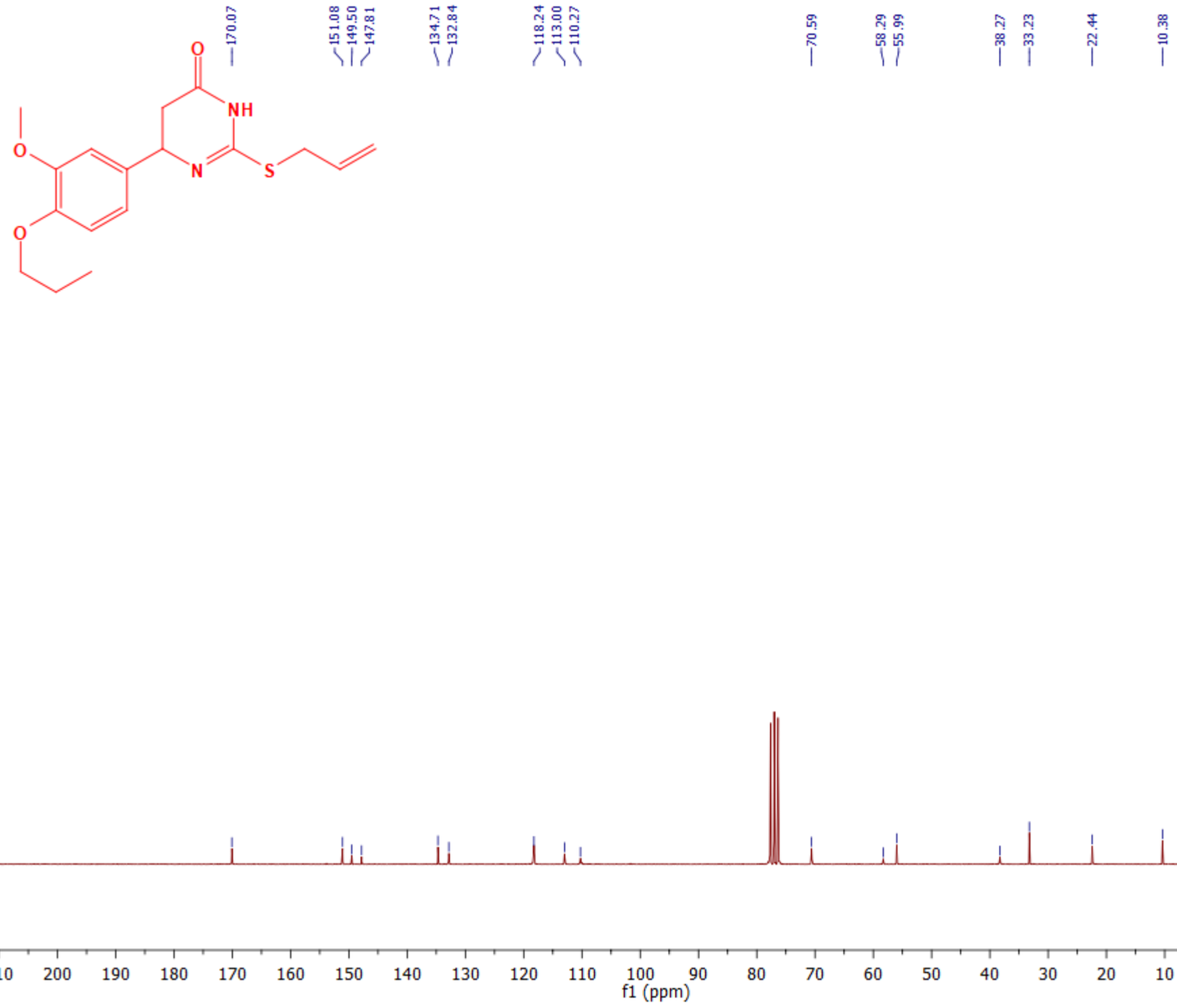


Figure S36 ^{13}C NMR spectrum of **4r**

2-allylthio-6-(4'-butoxy-3'-methoxyphenyl)-5,6-dihydropyrimidin-4(3H)-one (4s)

Yellow powder; yield: 85%, reaction time: 115 min.; mp = 93˚C; IR (KBr): ν 3181, 3088, 2934, 1698, 1639, 1518, 1475, 1335, 1260, 1139 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.97 (t, 3H, *J* = 7.3, CH_3) 1.41-1.59 (m, 2H, CH_2), 1.76-1.90 (m, 2H, CH_2), 2.51 (dd, 1H, *J* = 16.7, 12.3 Hz, CH_2CO), 2.81 (dd, 1H, *J* = 16.7, 5.2 Hz, CH_2CO), 3.65-3.82 (m, 2H, CH_2S), 3.87 (s, 3H, OCH_3), 4.02 (t, 2H, *J* = 6.8 Hz, OCH_2), 4.77 (dd, 1H, *J* = 12.3, 5.2 Hz, CH_{Bn}), 5.16-5.33 (m, 2H, CH_2=), 5.88-6.02 (m, 1H, CH=), 6.87 (s, 2H, CH_{Ar}), 6.94 (s, 1H, CH_{Ar}), 8.74 (br. s, 1H, NH) ppm; ^{13}C NMR (50 MHz, $CDCl_3$): δ = 13.8, 19.3, 31.2, 33.3, 38.3, 56.0, 58.3, 68.9, 110.4, 113.1, 118.3, 118.3, 132.9, 134.7, 147.9, 149.6, 151.1 and 169.9 ppm; ESI-MS: m/z (100 %) = 349 $[M + 1]^+$.

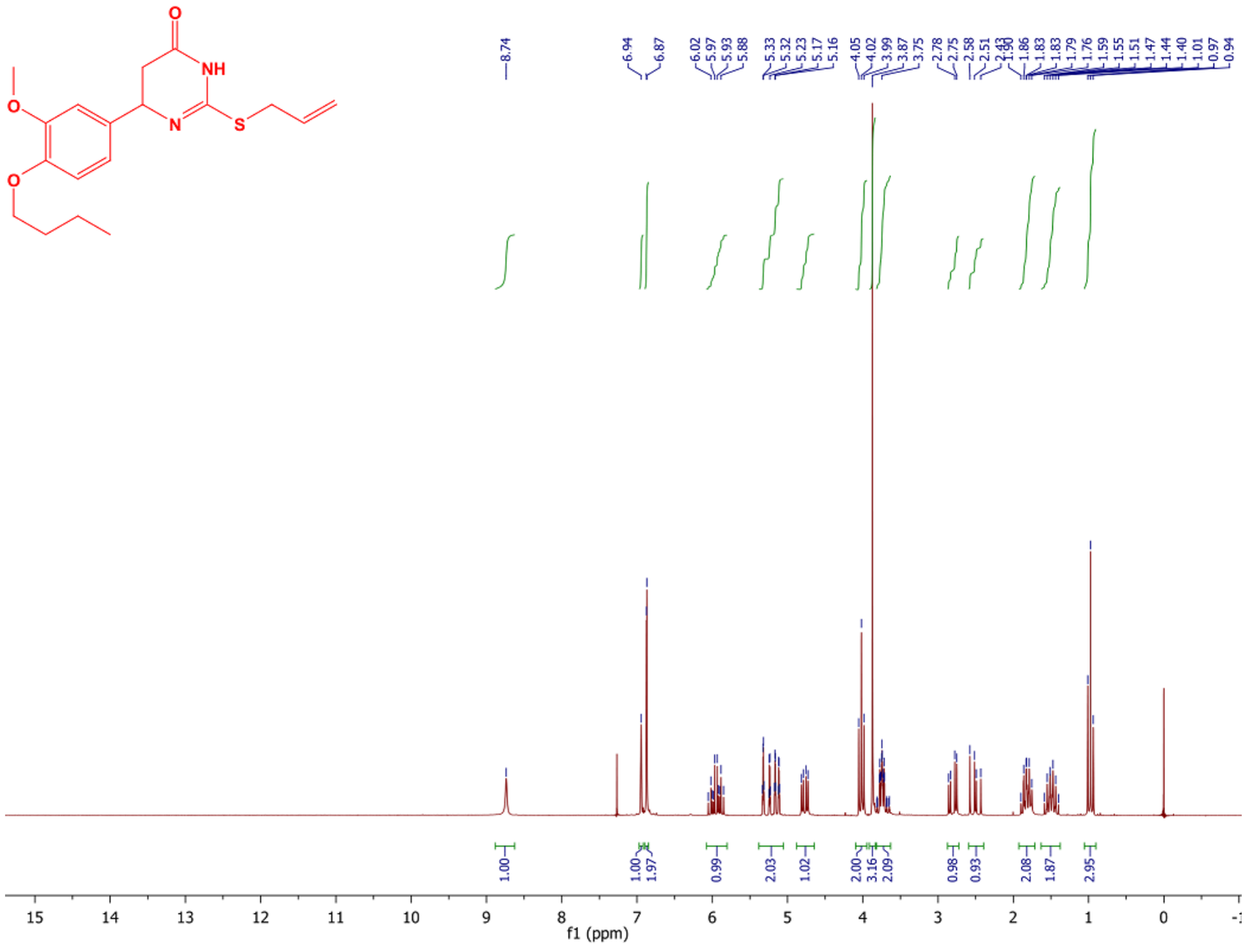


Figure S37 ^{1}H NMR spectrum of **4s**

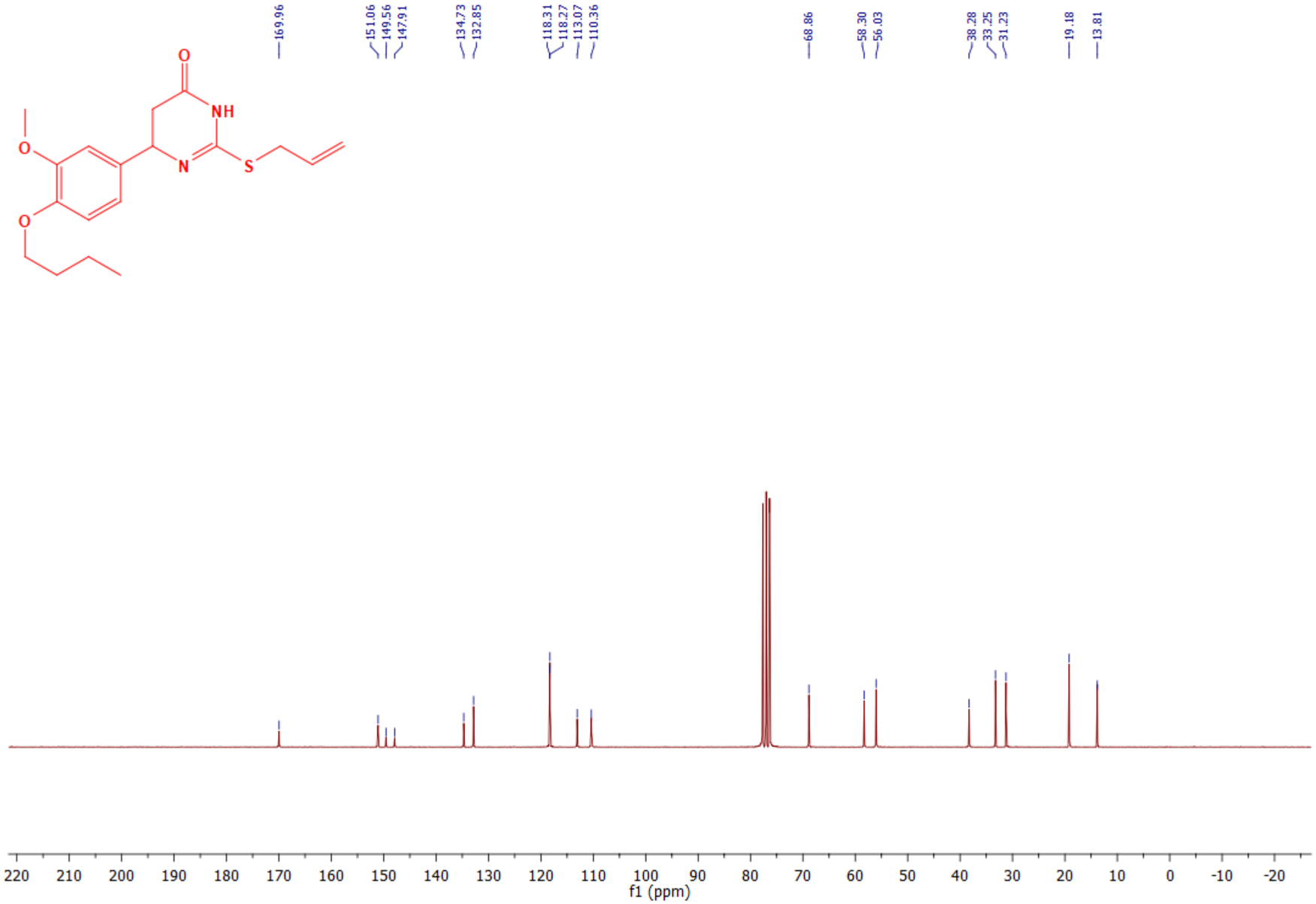
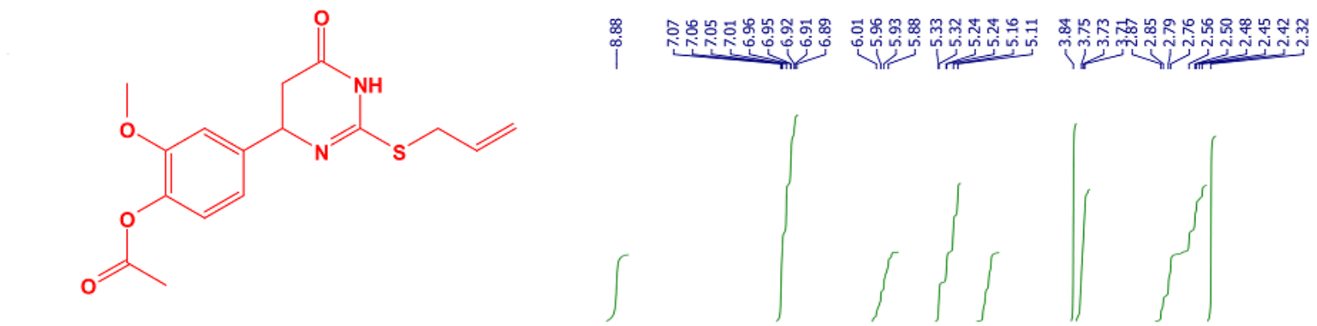


Figure S38 ^{13}C NMR spectrum of **4s**

2-allylthio-6-(4'-acetoxy-3'-methoxyphenyl)-5,6-dihydropyrimidin-4(3H)-one (4t)

White solid; yield: 94%, reaction time: 145 min.; mp =183˚C; IR (KBr): ν 3183, 3083, 2919, 1760, 1697, 1633, 1515, 1478, 1353, 1283, 1220, 1156, 1116 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.32 (s, 3H, $COCH_3$), 2.51 (dd, 1H, *J* = 16.7, 12.9 Hz, CH_2CO), 2.82 (dd, 1H, *J* = 16.7, 5.1 Hz, CH_2CO), 3.71-3.80 (m, 2H, CH_2S), 3.84 (s, 3H, OCH_3), 4.79 (dd, 1H, *J* = 12.8, 5.1 Hz, CH_{Bn}), 5.11-5.33 (m, 2H, CH_2), 5.85-6.05 (m, 1H, CH=), 6.89-7.07 (m, 3H, CH_{Ar}), 8.88 (br. s, 1H, NH) ppm; ^{13}C NMR (50 MHz, $CDCl_3$): δ = 20.5, 33.1, 38.1, 55.7, 58.2, 110.6, 118.3, 122.6, 132.7, 138.7, 141.0, 151.1, 168.9 and 169.8 ppm; ESI-MS: m/z (100 %) = 335 $[M + 1]^+$.



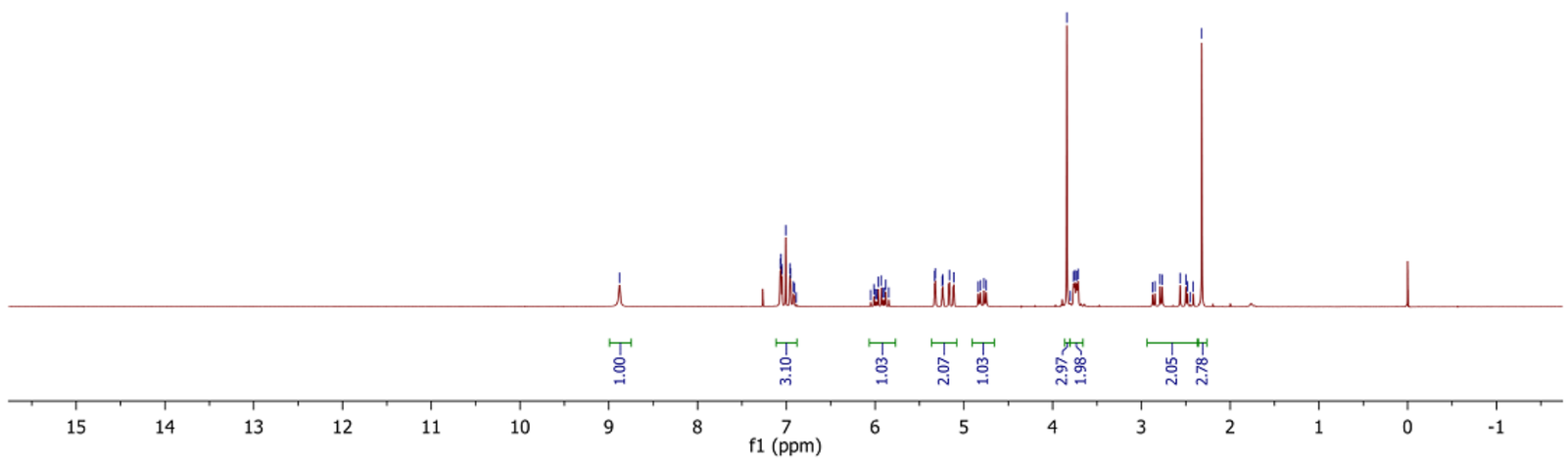


Figure S39 ^{1}H NMR spectrum of **4t**

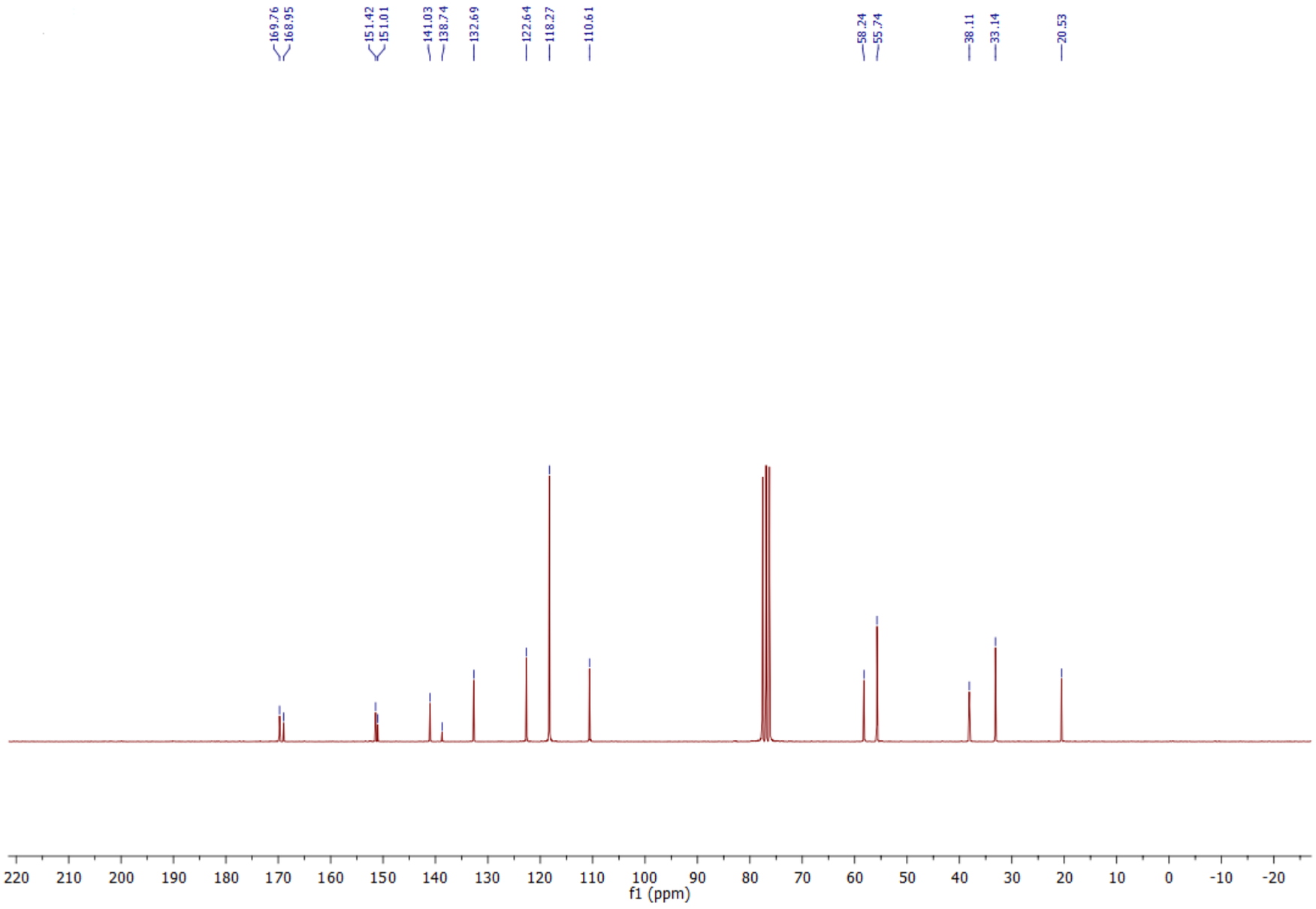
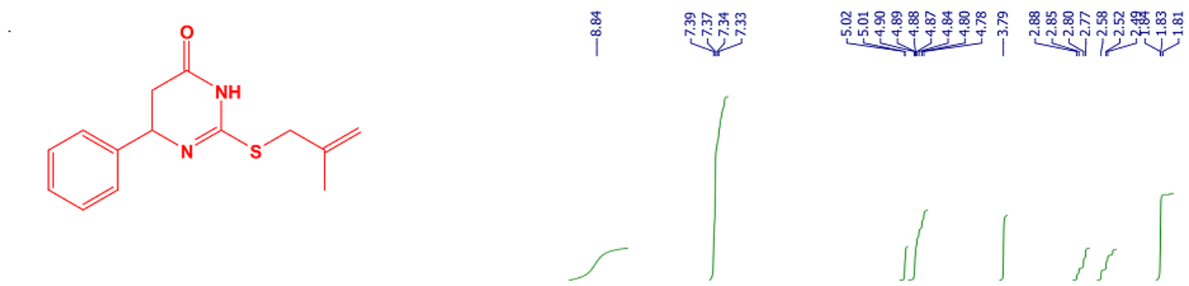


Figure S40 ^{13}C NMR spectrum of **4t**

2. ^{1}H and ^{13}C NMR spectrums of 4'a-t

2-methallylthio-6-phenyl-5,6-dihydropyrimidin-4(3H)-one (4'a)

White powder; yield: 92%, reaction time: 85 min.; mp = 120˚C; IR (KBr): ν 3182, 3087, 2923, 1701, 1633, 1482, 1357, 1322, 1298, 1145, 1079 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.81-1.84 (m, 3H, CH_3C=), 2.51 (dd, 1H, *J* = 16.7, 12.4 Hz, CH_2CO), 2.83 (dd, 1H, *J* = 16.7, 5.2 Hz, CH_2CO), 3.79 (d, 2H, *J* = 0.8 Hz SCH_2), 4.78-5.02 (m, 3H, CH_{Bn} + $C=CH_2$), 7.33-7.39 (m, 5H, CH_{Ar}), 8.84 (br. s, 1H, NH) ppm; ^{13}C NMR (50 MHz, $CDCl_3$): δ = 21.3, 37.4, 38.2, 58.5, 114.7, 126.3, 127.4, 128.6, 140.3, 142.1 and 170.1 ppm; ESI-MS: m/z (100 %) = 261 $[M + 1]^{+}$.



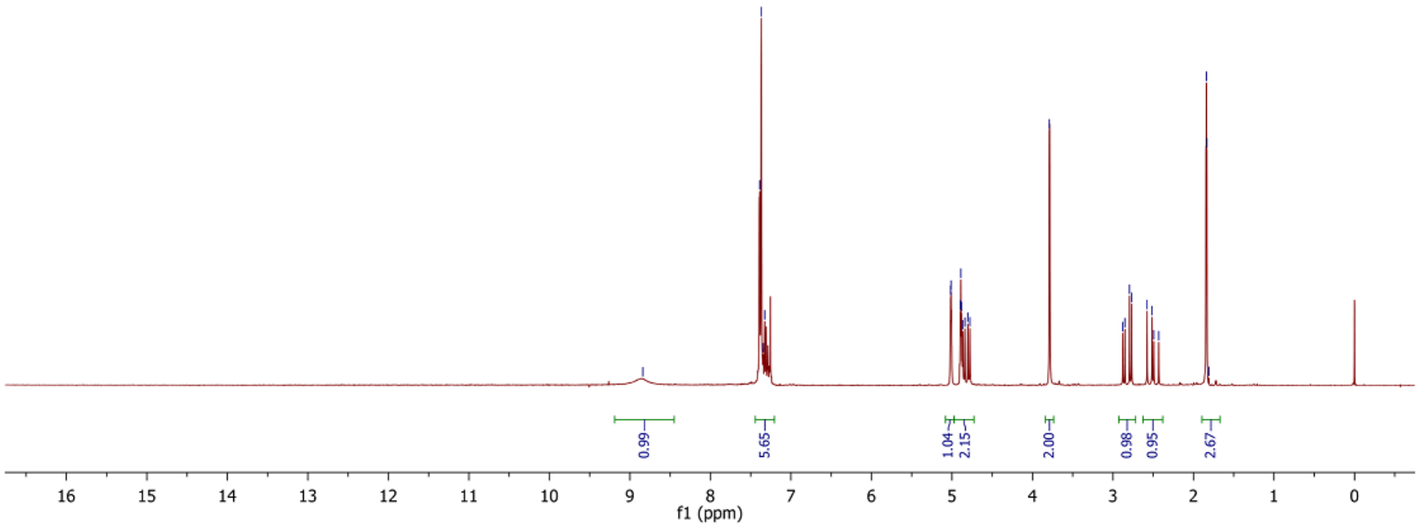


Figure S41 ^{1}H NMR spectrum of **4'a**

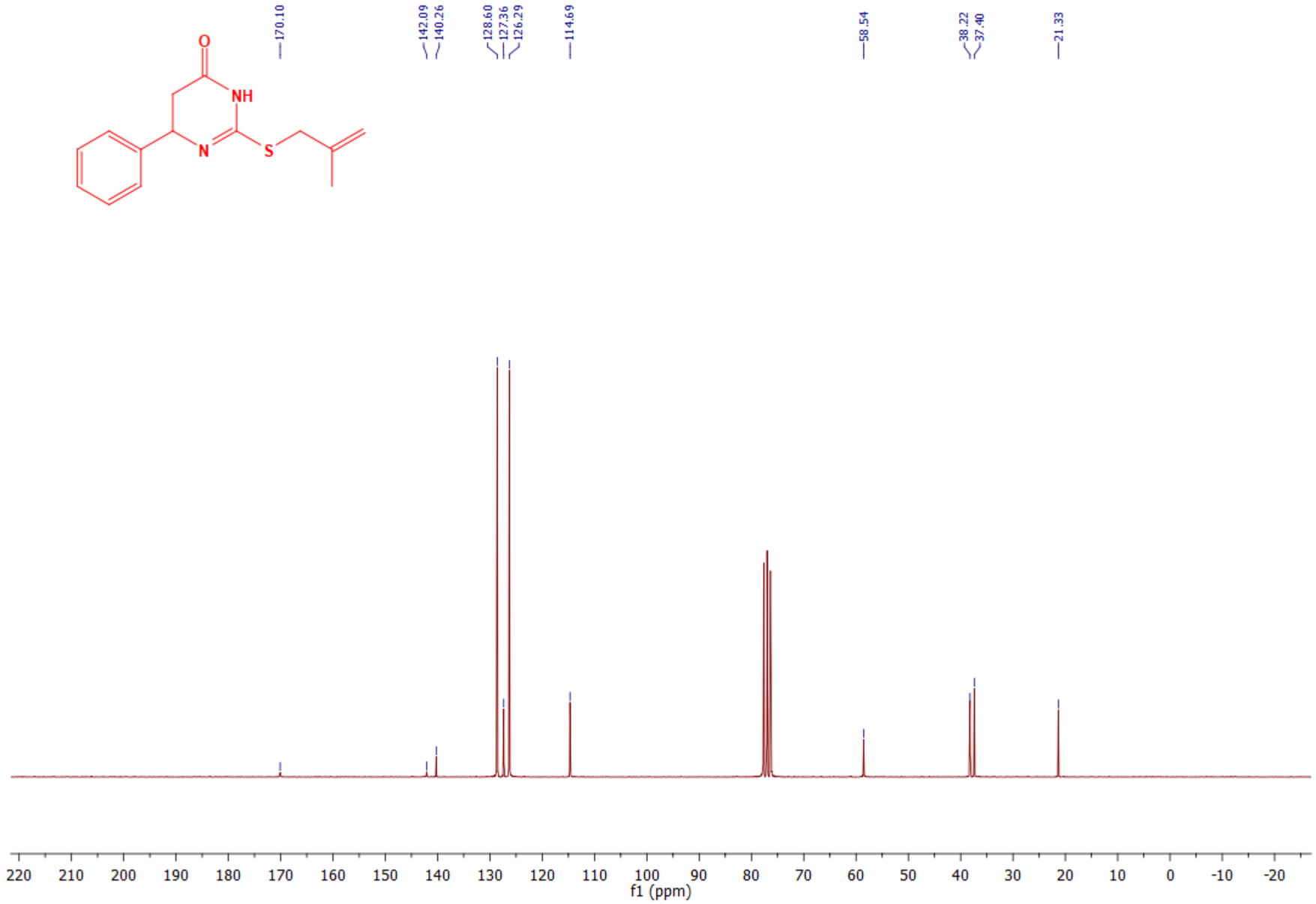


Figure S42 ^{13}C NMR spectrum of **4'a**

6,6'-(1,3-phenylene)bis[2-methallylthio-5,6-dihydropyrimidin-4(3H)-one] (4'b)

White solid; yield: 90%, reaction time: 160 min.; mp = 179˚C; IR (KBr): ν 3186, 3088, 2912, 1694, 1631, 1464, 1321, 1154, 1131, 1038 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$ + DMSO-d_6): δ = 1.83 (s, 6H, 2×CH_3C=), 2.40-2.75 (m, 4H, 2×CH_2CO), 3.67-3.85 (m, 4H, 2×CH_2S), 4.73-4.99 (m, 6H, 2×CH_{Bn} + 2×C=CH_2), 7.31-7.44 (m, 4H, CH_{Ar}), 10.60 (br. s, 2H, 2×NH); ^{13}C NMR (50 MHz, $CDCl_3$ + DMSO-d_6): δ = 20.3, 35.7, 37.3, 57.4, 113.2, 123.3, 124.0, 127.5, 139.5, 142.0, 151.8 and 168.3 ppm; ESI-MS: m/z (100 %) = 443 $[M + 1]^+$.

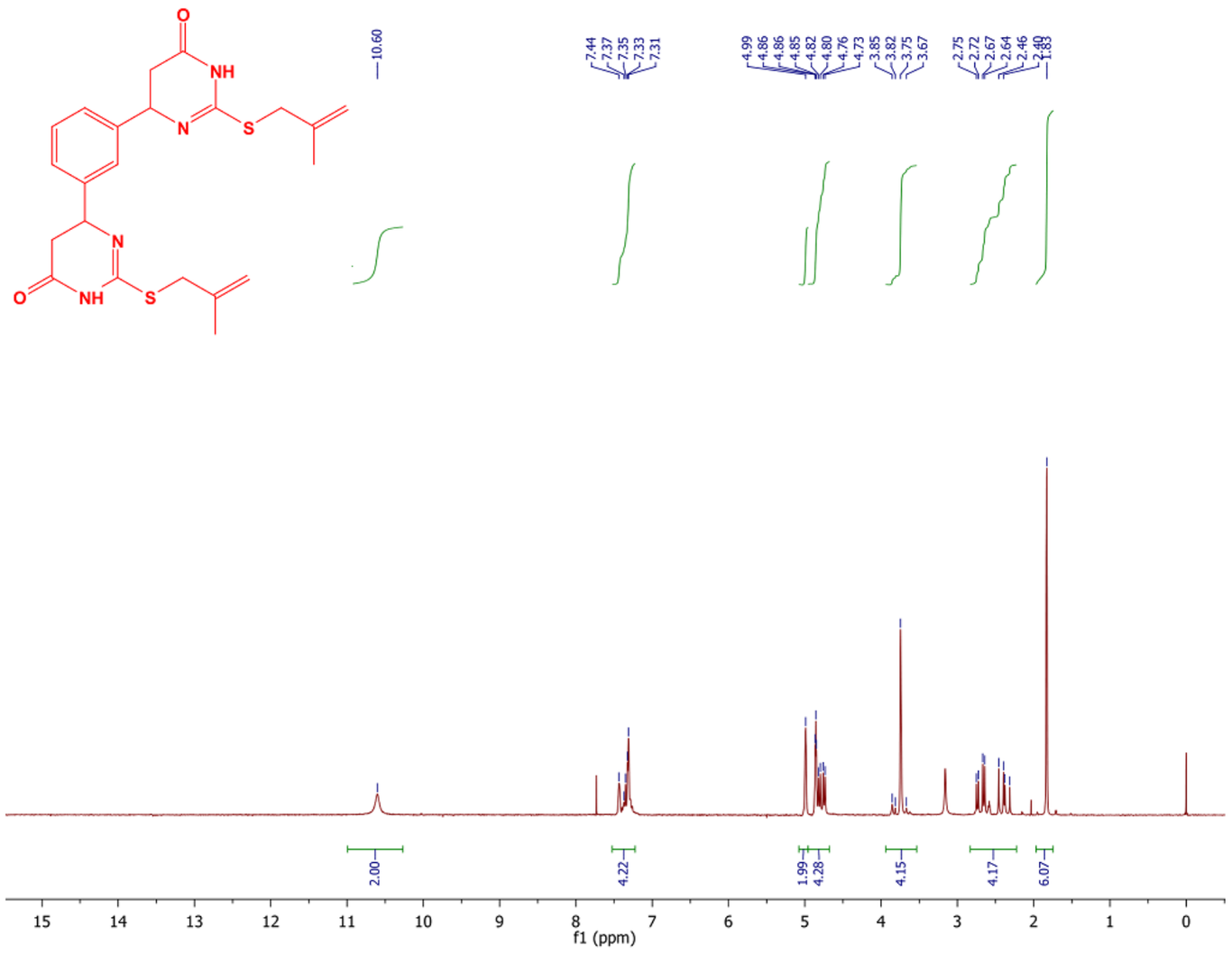


Figure S43 ^{1}H NMR spectrum of **4'b**

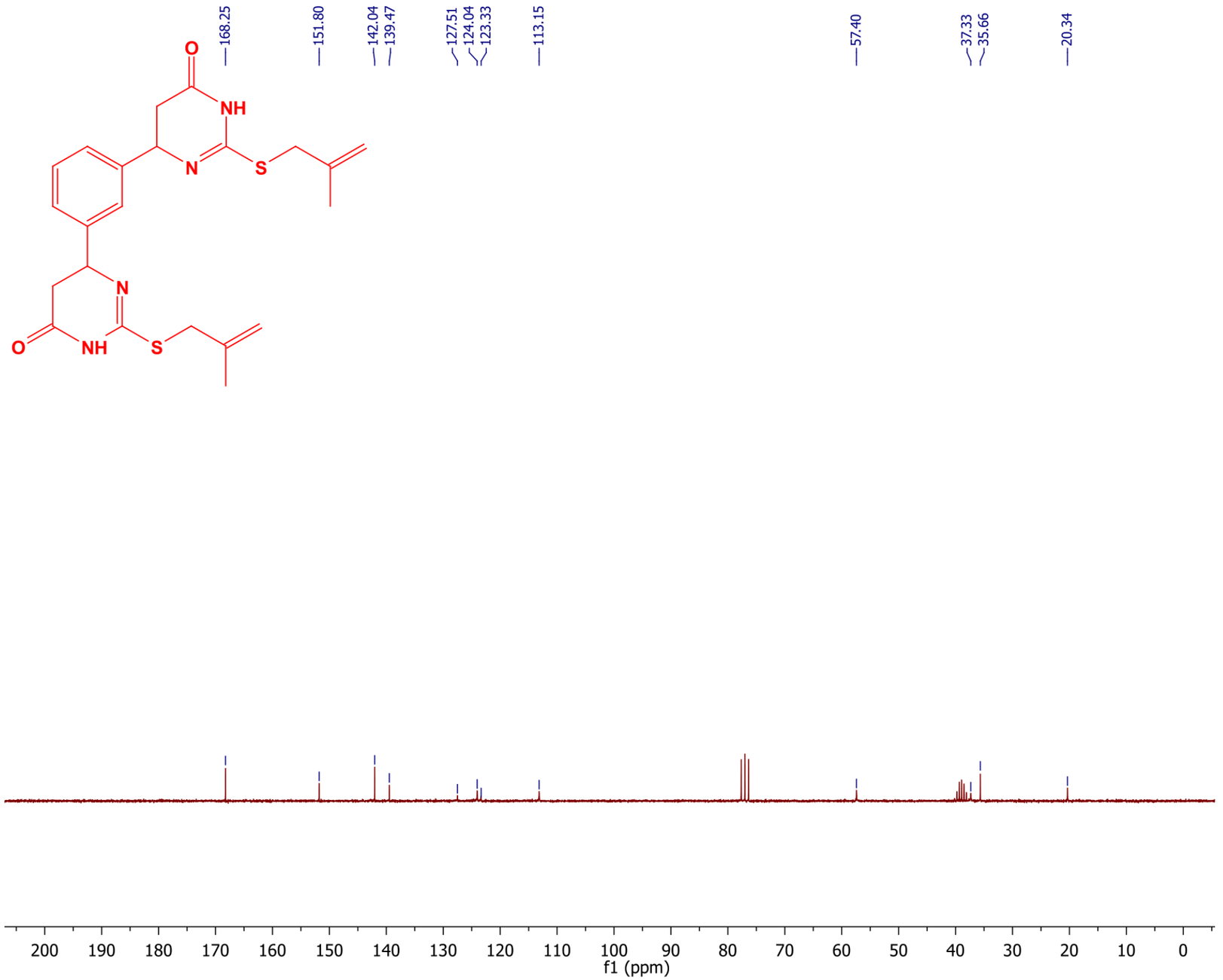
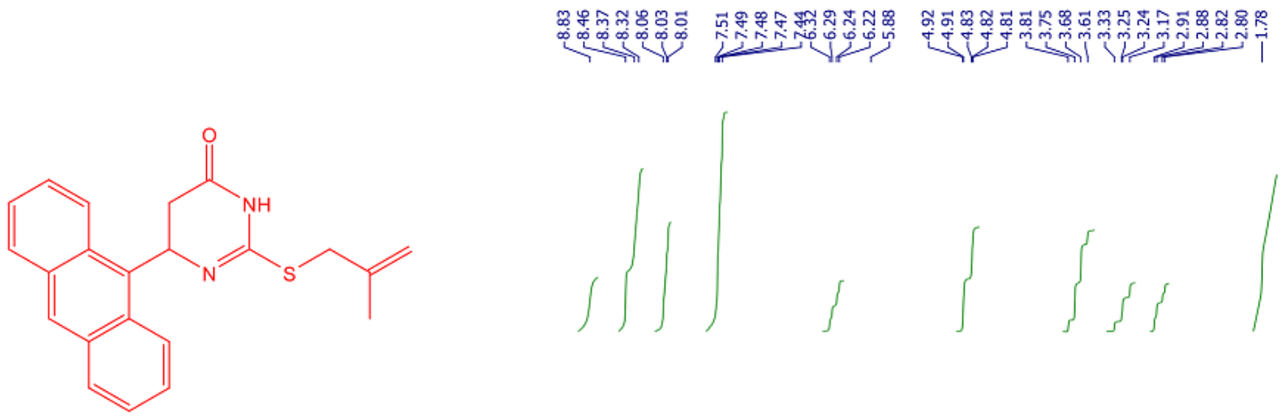


Figure S44 ^{13}C NMR spectrum of **4'b**

2-methallylthio-6-(9'-anthracenyl)-5,6-dihydropyrimidin-4(3H)-one (4'c)

Yellow crystals; yield: 68%, reaction time: 170 min.; mp = 201˚C; IR (KBr): ν 3184, 3083, 2916, 1696, 1629, 1445, 1373, 1334, 1298, 1138, 1086 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.78 (s, 3H, CH_3C=), 2.86 (dd, 1H, *J* = 17.5, 5.3 Hz, CH_2CO), 3.25 (dd, 1H, *J* = 17.5, 15.2 Hz, CH_2CO), 3.71 (qd, 2H, *J* = 13.6, 1.0 Hz, CH_2S), 4.81-4.92 (m, 2H, CH_2=), 6.27 (dd, 1H, *J* = 15.2, 5.3 Hz, CH_{Bn}), 7.44-7.51 (m, 4H, CH_{Ar}), 8.01-8.06 (m, 2H, CH_{Ar}), 8.32-8.46 (m, 3H, CH_{Ar}), 8.83 (br. s, 1H, NH) ppm; ^{13}C NMR (50 MHz, $CDCl_3$): δ = 21.4, 36.9, 37.2, 55.7, 114.7, 124.8, 125.7, 128.3, 129.3, 129.6, 131.8, 132.2, 140.2, 149.9 and 170.3 ppm; ESI-MS: m/z (100 %) = 361 $[M + 1]^+$.



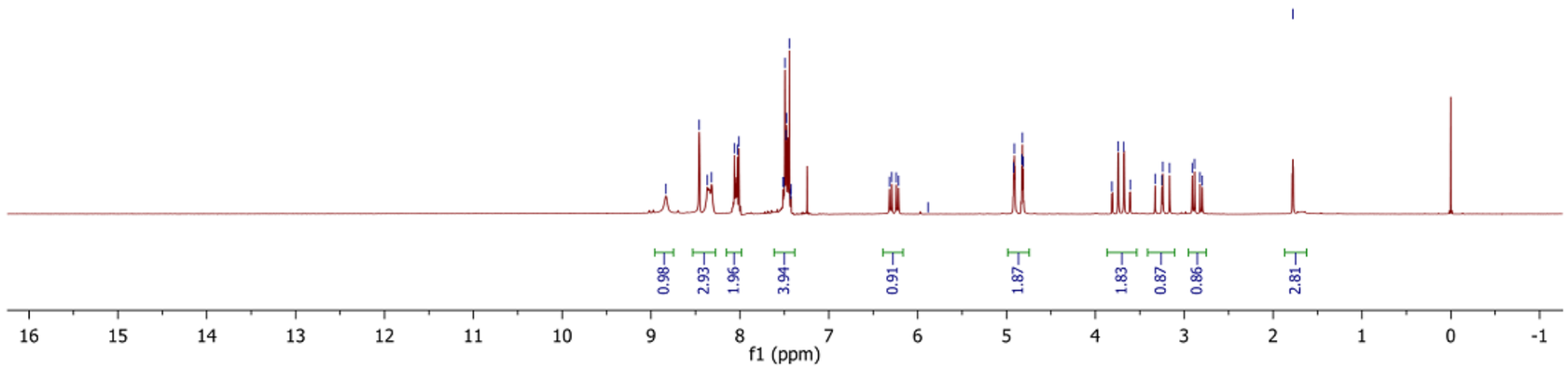


Figure S45 ^{1}H NMR spectrum of **4'c**

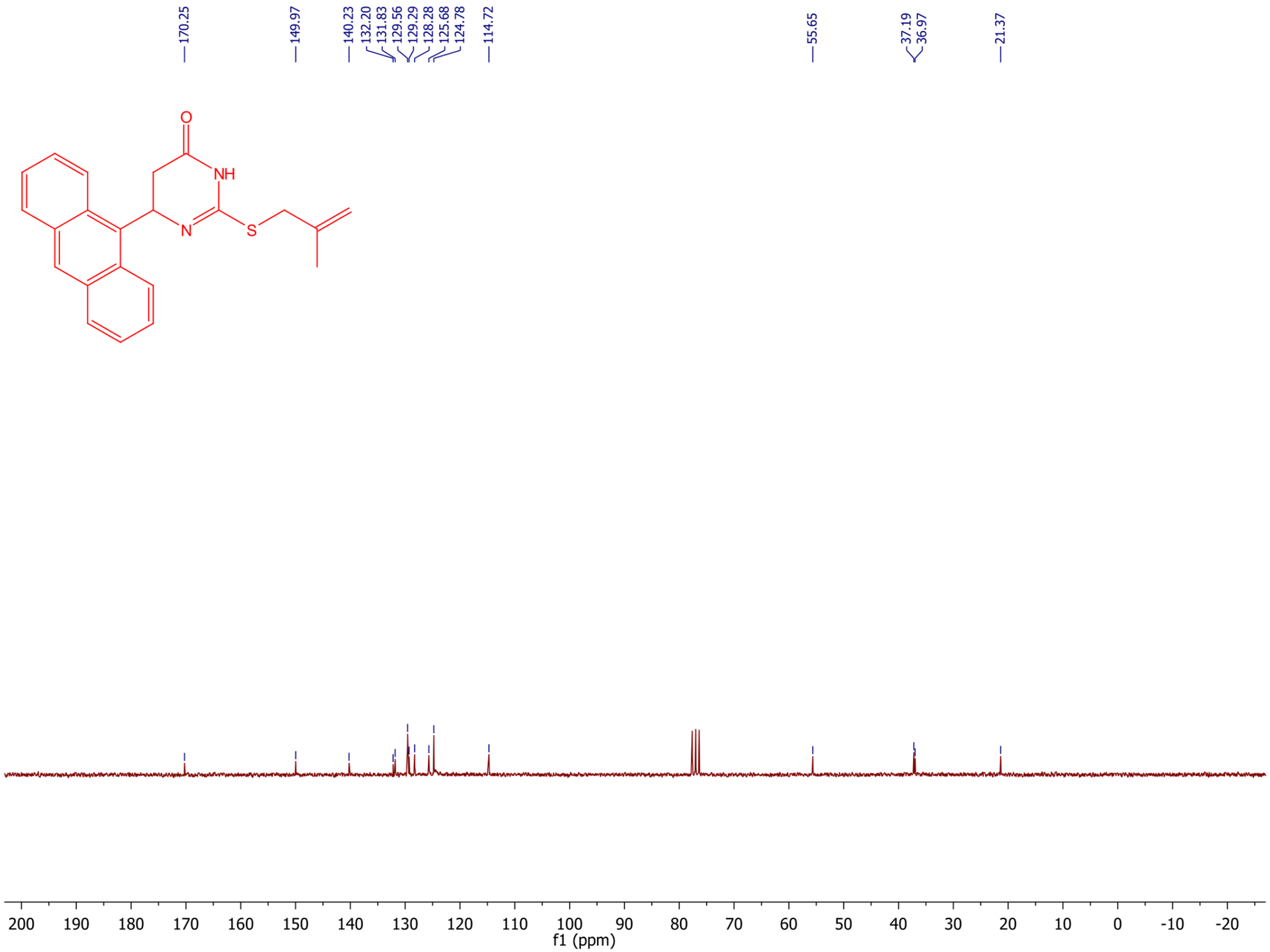


Figure S46 ^{13}C NMR spectrum of **4'c**

2-methallylthio-6-(4'-chlorophenyl)-5,6-dihydropyrimidin-4(3H)-one (4'd)

White crystals; yield: 91%, reaction time: 80 min.; mp = 111˚C; IR (KBr): ν 3183, 3089, 2920, 1698, 1626, 1487, 1348, 1289, 1142, 1089 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.83 (s, 3H, *J* = Hz, CH_3=C), 2.45 (dd, 1H, *J* = 16.2, 12.2 Hz, CH_2CO), 2.78 (dd, 1H, *J* = 16.7, 5.2 Hz, CH_2CO), 3.76 (d, 2H, *J* = 0.7 Hz, CH_2S), 4.78 (dd, 1H, *J* = 12.6, 5.1 Hz, CH_{Bn}), 4.89-5.01 (m, 2H, CH_2=), 7.33 (s, 4H, CH_{Ar}), 8.92 (br. s, 1H, NH) ppm; ^{13}C NMR (50 MHz, $CDCl_3$): δ =21.3, 37.4, 38.1, 58.0, 114.7, 127.7, 128.7, 133.1, 140.1, 140.7, 152.1 and 169.7 ppm; ESI-MS: m/z (100 %) = 295 $[M + 1]^+$.

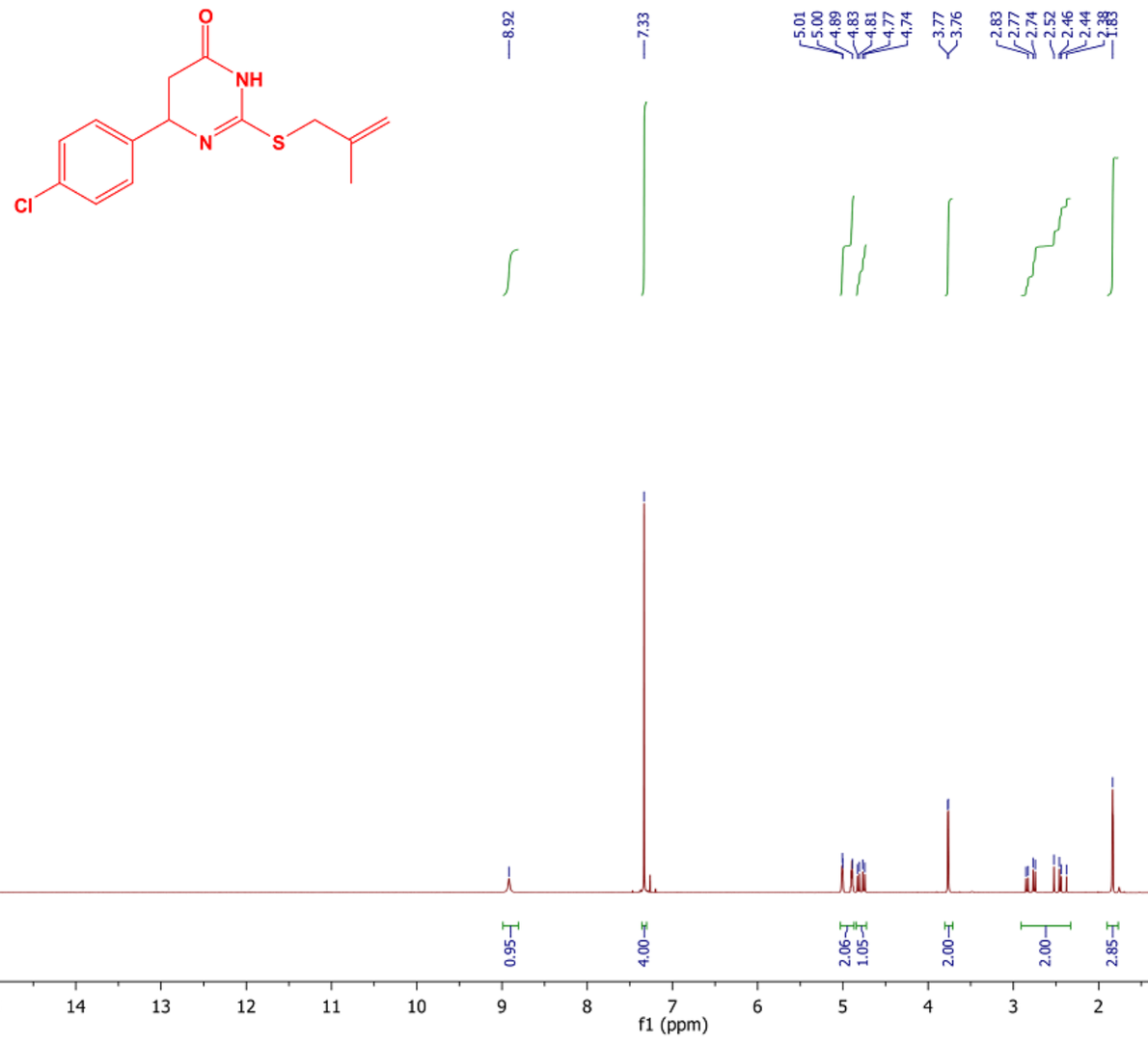


Figure S47 ^{1}H NMR spectrum of **4'd**

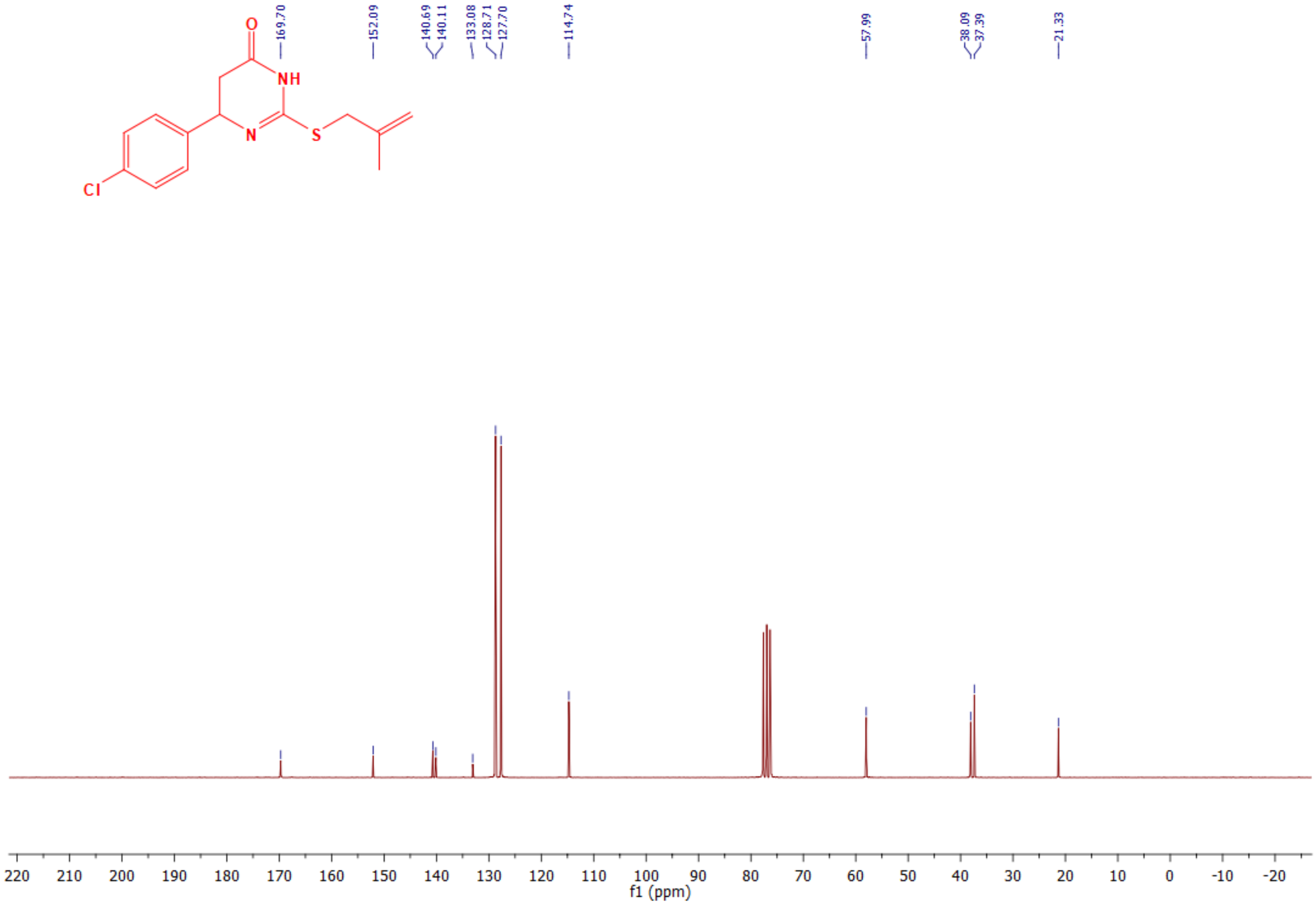
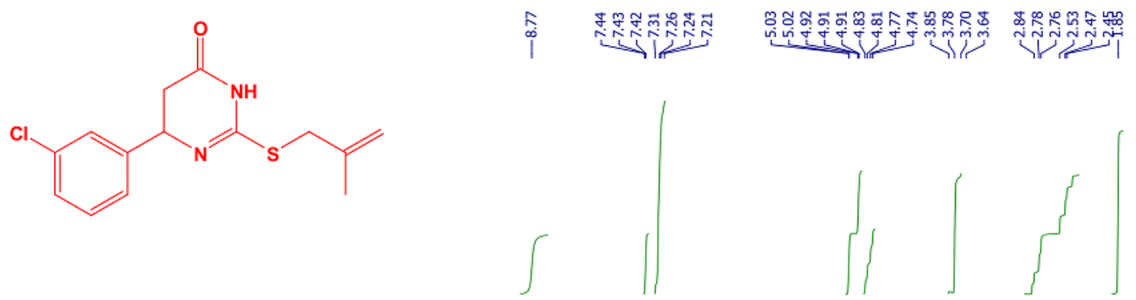


Figure S48 ^{13}C NMR spectrum of **4'd**

2-methallylthio-6-(3'-chlorophenyl)-5,6-dihydropyrimidin-4(3H)-one (4'e)

White crystals; yield: 94%, reaction time: 110 min.; mp = 133˚C; IR (KBr): ν 3183, 3088, 2916, 1698, 1631, 1597, 1472, 1351, 1298, 1245, 1144, 1078 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.85 (d, 3H, *J* = 0.7 Hz CH_3C=), 2.49 (dd, 1H, *J* = 16.7, 12.7 Hz, CH_2CO), 2.80 (dd, 1H, *J* = 16.7, 5.1 Hz, CH_2CO), 3.64-3.85 (m, 2H, CH_2S), 4.78 (dd, 1H, *J* = 12.7, 5.1 Hz, CH_{Bn}), 4.91-5.03 (m, 2H, =CH_2), 7.21-7.31 (m, 3H, CH_{Ar}), 7.42-7.44 (m, 1H, CH_{Ar}), 8.77 (br. s, 1H, NH) ppm; ^{13}C NMR (50 MHz, $CDCl_3$): δ = 21.3, 37.4, 38.0, 58.1, 114.8, 124.4, 126.7, 127.5, 129.8, 134.5, 140.1, 144.3, 152.2 and 169.5 ppm; ESI-MS: m/z (100 %) = 295 $[M + 1]^+$.



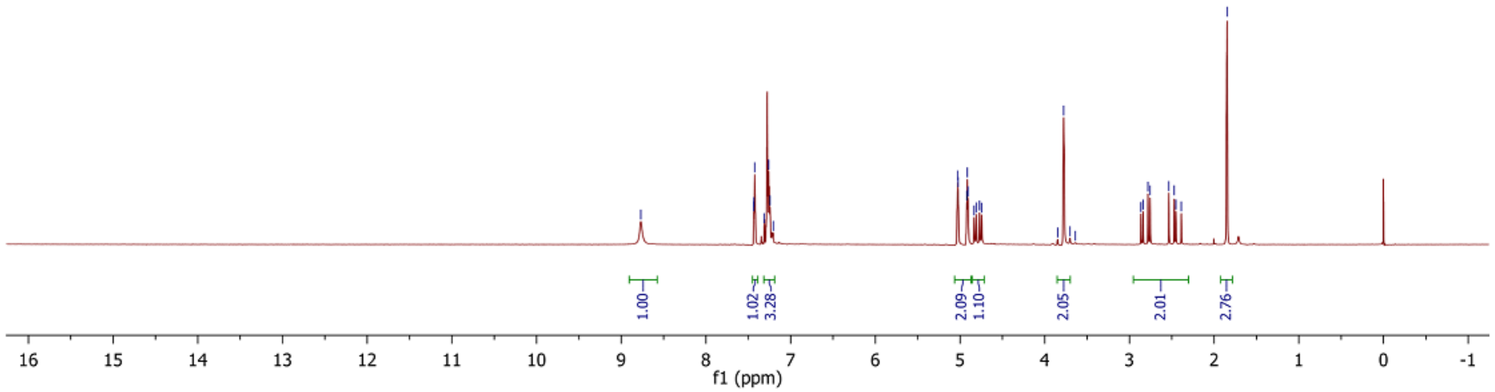


Figure S49 ^{1}H NMR spectrum of **4'e**

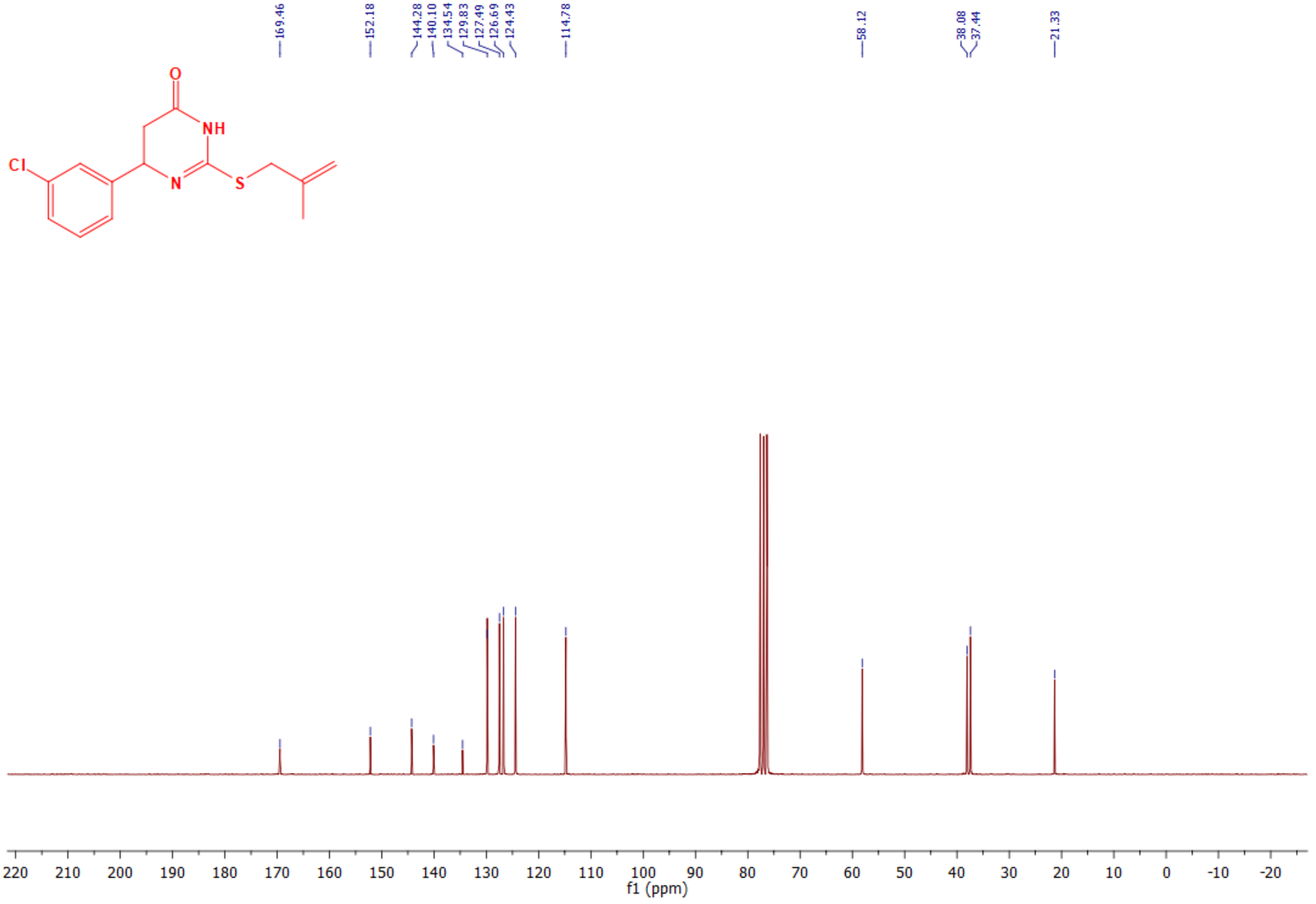
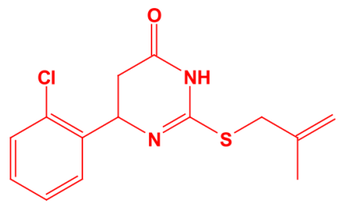
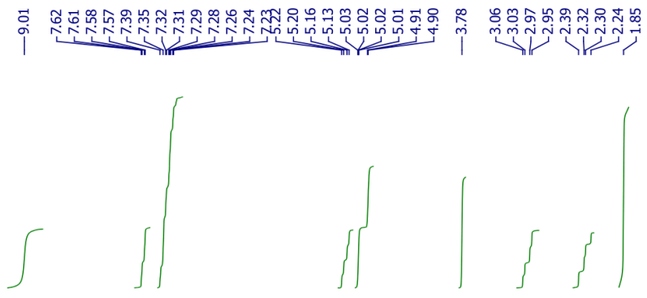


Figure S50 ^{13}C NMR spectrum of **4'e**

2-methallylthio-6-(2'-chlorophenyl)-5,6-dihydropyrimidin-4(3H)-one (4'f)

White crystals; yield: 92%, reaction time: 95 min.; mp = 131˚C; IR (KBr): ν 3184, 3096, 2926, 1702, 1632, 1469, 1354, 1313, 1267, 1162, 1147, 1062 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ = 1.85 (s, 3H, CH_3C=), 2.32 (dd, 1H, *J* = 16.9, 12.9 Hz, CH_2CO), 3.01 (dd, 1H, *J* = 16.8, 5.0 Hz, CH_2CO), 3.78 (s, 2H, CH_2S), 4.90-5.03 (m, 2H, CH_2=), 5.18 (dd, *J* = 12.9, 5.0 Hz, CH_{Bn}), 7.23-7.35 (m, 3H, CH_{Ar}), 7.60 (dd, 1H, *J* = 1.9 Hz, CH_{Ar}), 9.01 (br. s, 1H, NH) ppm; ^{13}C NMR (50 MHz, $CDCl_3$): δ = 21.4, 36.4, 37.4, 56.4, 114.7, 127.2, 128.3, 128.6, 129.4, 132.2, 139.9, 140.2, 152.4 and 169.8 ppm; ESI-MS: m/z (100 %) = 295 $[M + 1]^+$.





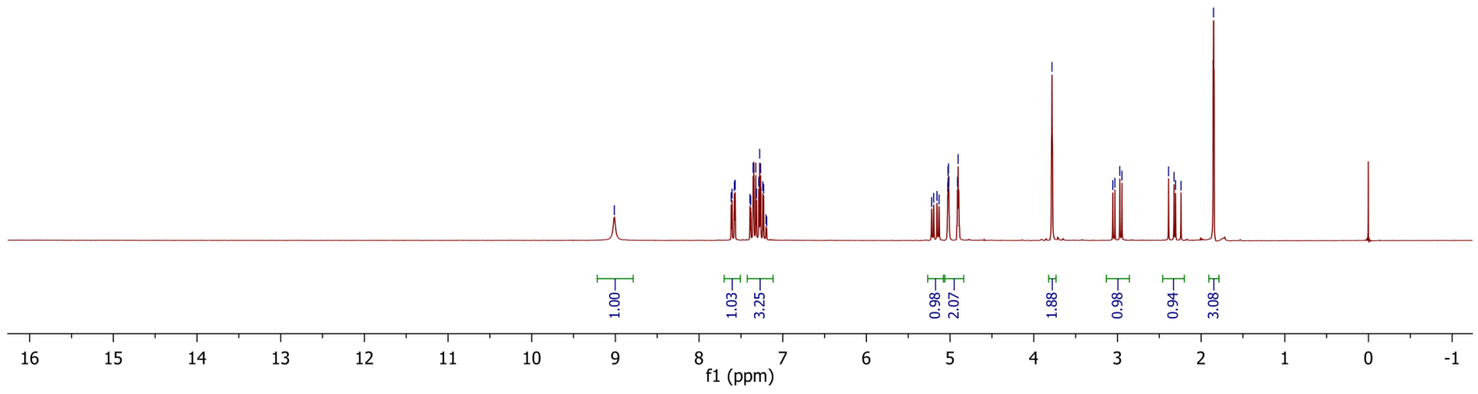


Figure S51 ^1H NMR spectrum of **4'f**

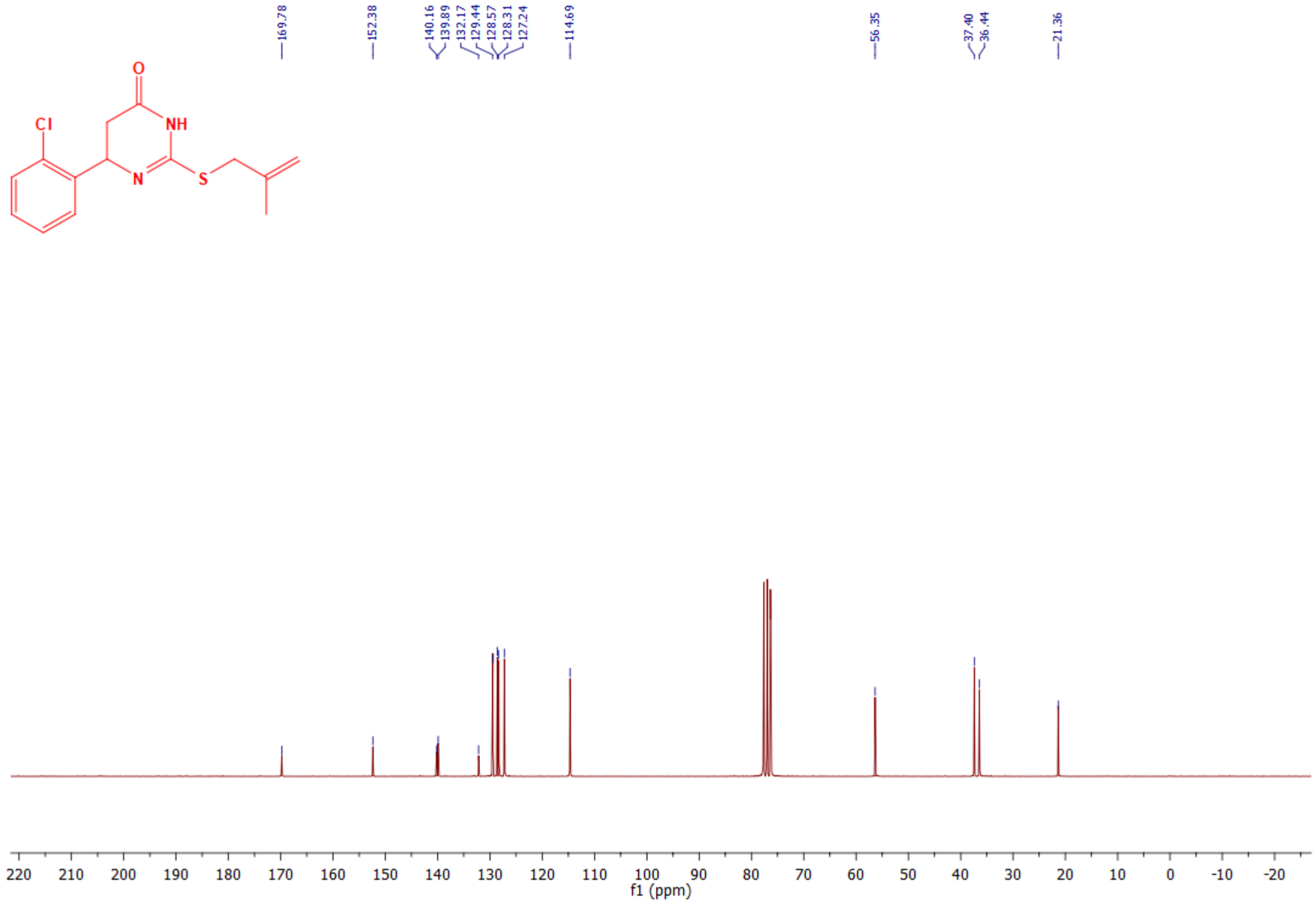


Figure S52 ^{13}C NMR spectrum of **4'f**

2-methallylthio-6-(4'-methylthiophenyl)-5,6-dihydropyrimidin-4(3H)-one (4'g)

White crystals; yield: 88%, reaction time: 60 min.; mp = 110˚C; IR (KBr): ν 3185, 3078, 2921, 1694, 1631, 1476, 1351, 1245, 1136, 1031 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.83-1.85 (m, 3H, CH_3C=), 2.40-2.54 (m, 4H, CH_2CO + SCH_3), 2.78 (dd, 1H, *J* = 16.7, 5.2 Hz, CH_2CO), 3.77 (s, 2H, CH_2S), 4.78 (dd, 1H, *J* = 12.3, 5.2 Hz, CH_{Bn}), 4.89-5.01 (m, 2H, CH_2=), 7.23-7.33 (m, 4H, CH_{Ar}), 8.73 (br. s, 1H, NH) ppm; ^{13}C NMR (50 MHz, $CDCl_3$): δ = 16.0, 21.3, 37.4, 38.1, 58.2, 114.7, 126.8, 126.9, 137.4, 139.2, 140.2, 151.7 and 169.8 ppm; ESI-MS: m/z (100 %) = 307 $[M + 1]^+$.

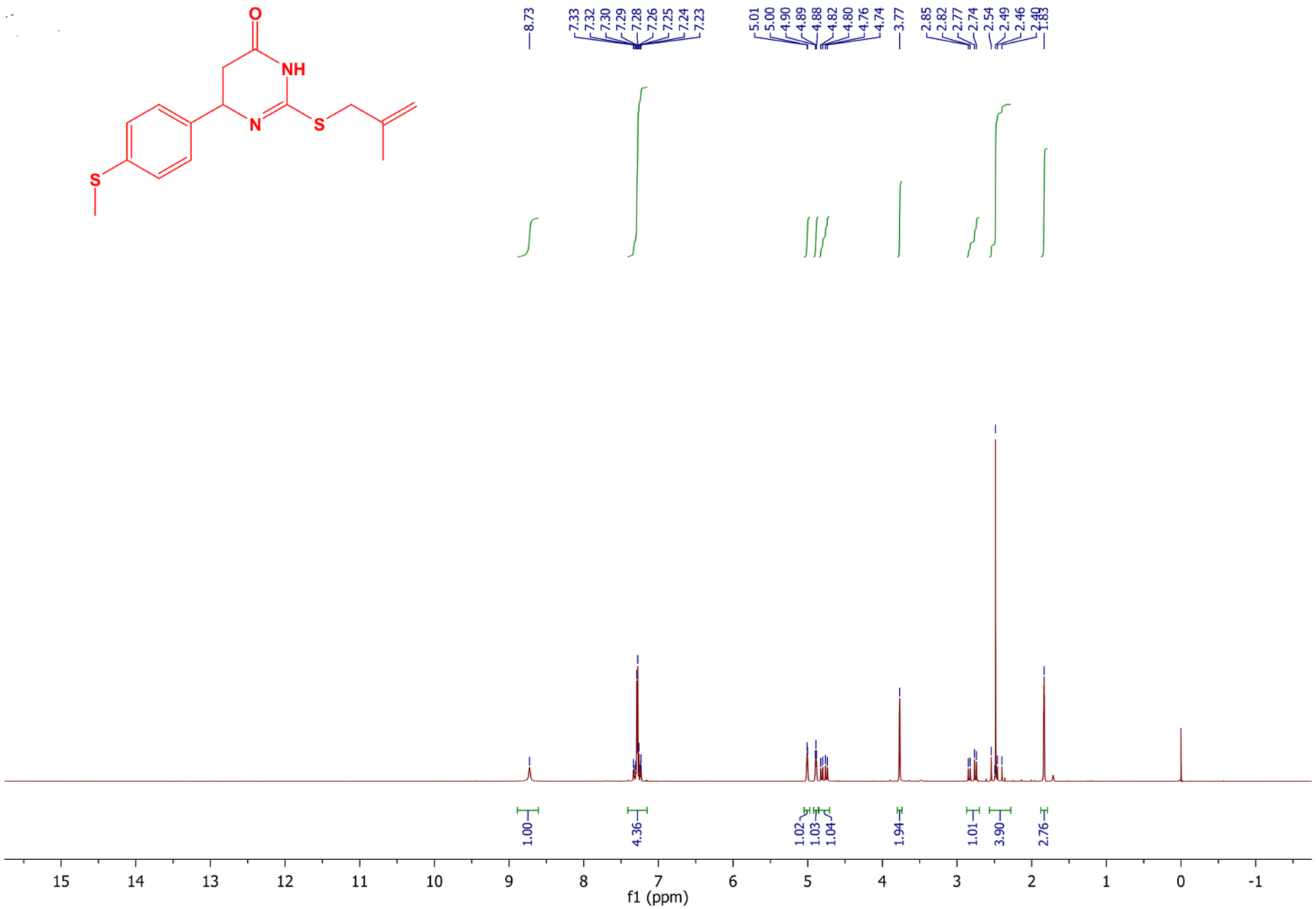


Figure S53 ^{1}H NMR spectrum of **4'g**

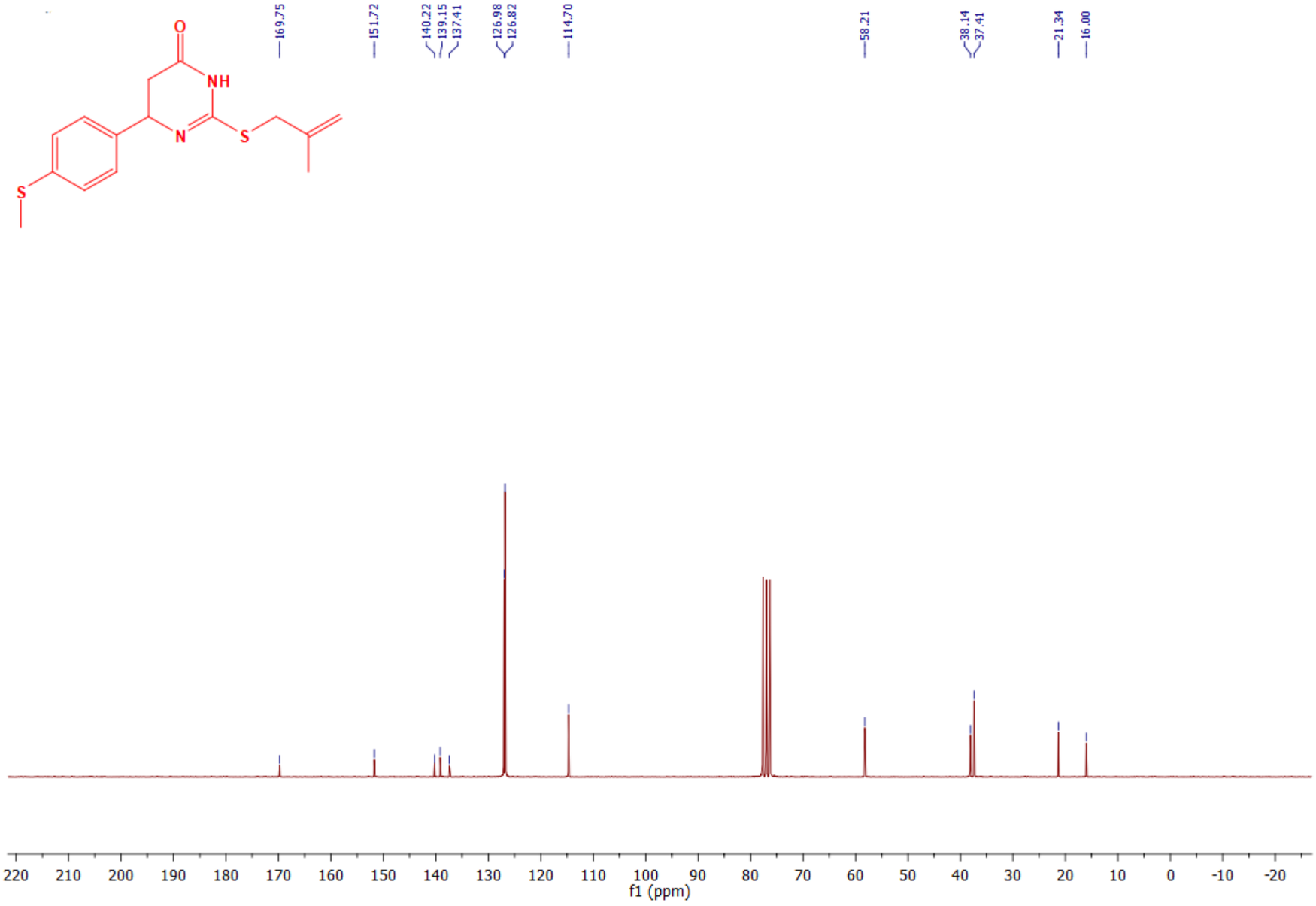
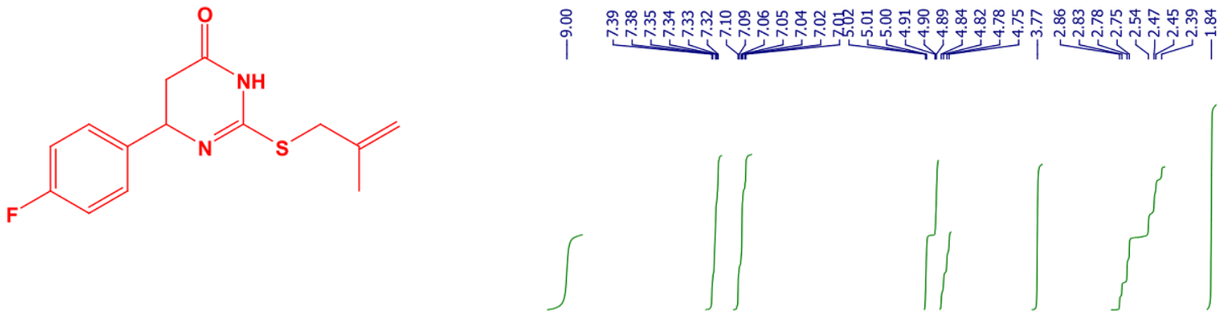


Figure S54 ^{13}C NMR spectrum of **4'g**

2-methallylthio-6-(4'-fluorophenyl)-5,6-dihydropyrimidin-4(3H)-one (4'h)

Colourless crystals; yield: 81%, reaction time: 135 min.; mp = 109˚C; IR (KBr): ν 3184, 3104, 2937, 1701, 1636, 1507, 1486, 1348, 1221, 1159, 1151, 1101 cm^{-1}; δ = 1.84 (s, 3H, CH_3C=), 2.47 (dd, 1H, *J* = 16.7, 12.0 Hz, CH_2CO), 2.81 (dd, 1H, *J* = 16.7, 5.2 Hz, CH_2CO), 3.77 (s, 2H, CH_2S), 4.81 (dd, 1H, *J* = 12.5, 5.1 Hz, CH_{Bn}), 4.89-5.02 (m, 2H, CH_2=), 7.01-7.10 (m, 2H, CH_{Ar}), 7.32-7.39 (m, 2H, CH_{Ar}), 9.00 (br. s, 1H, NH) ppm; ^{13}C NMR (50 MHz, $CDCl_3$): δ = 21.3, 37.4, 38.3, 57.9, 114.7, 115.2, 115.6, 127.8, 127.9, 137.9, 140.6, 151.9, 159.6, 164.5 and 170.0 ppm; ESI-MS: m/z (100 %) = 279 $[M + 1]^+$.



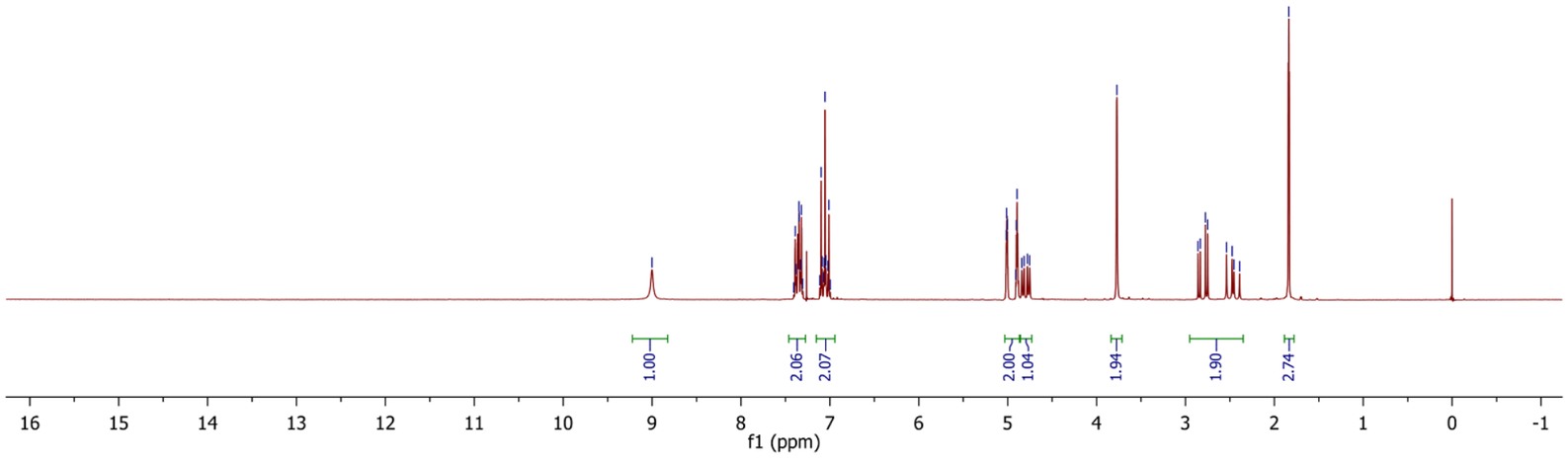


Figure S55 ^1H NMR spectrum of **4'h**

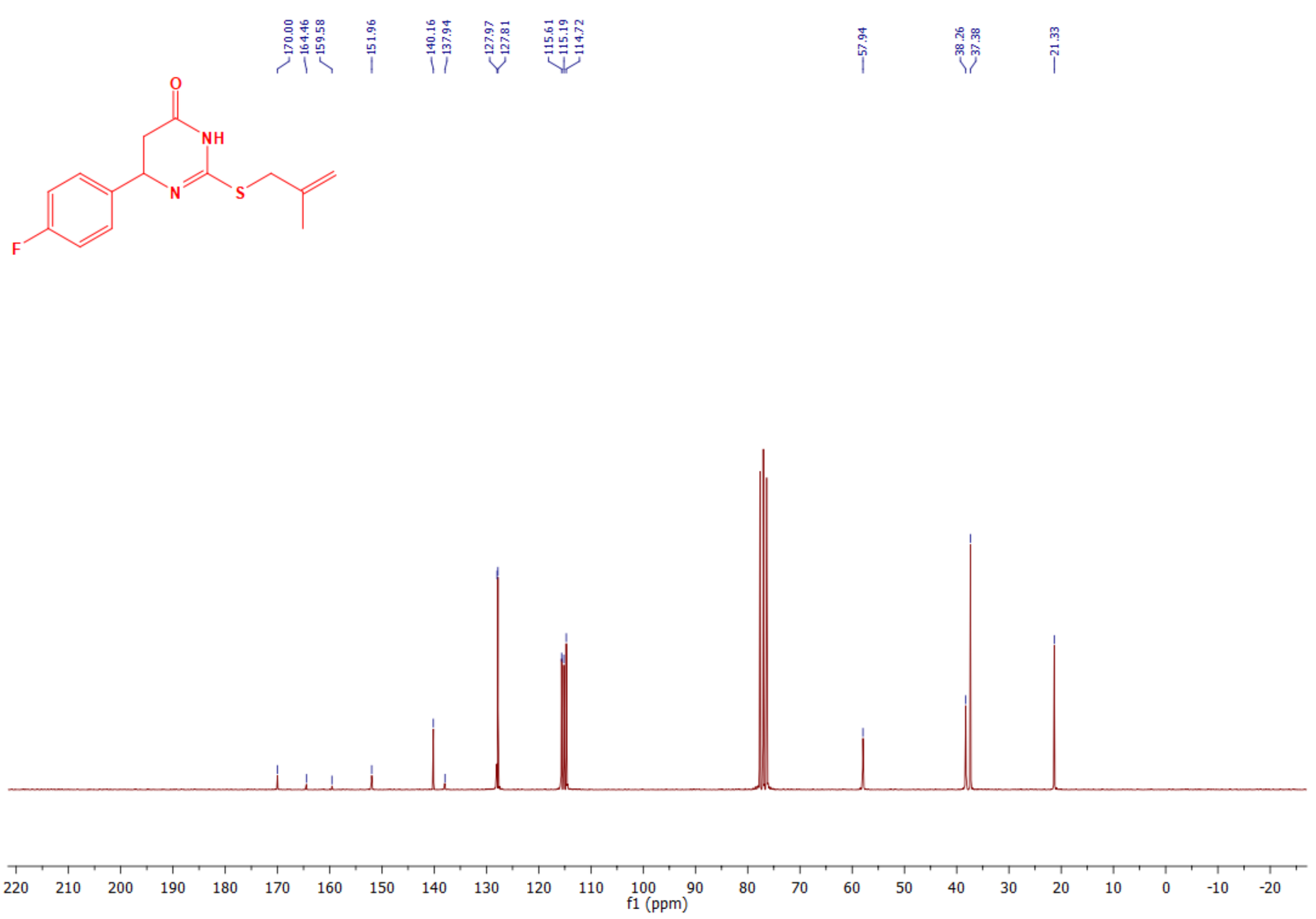
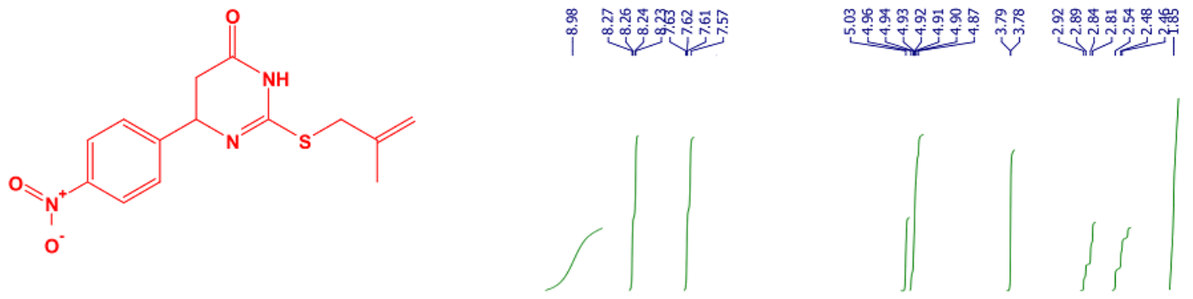


Figure S56 ^{13}C NMR spectrum of **4'h**

2-methallylthio-6-(4'-nitrophenyl)-5,6-dihydropyrimidin-4(3H)-one (4'i)

Yellow solid; yield: 86%, reaction time: 145 min.; mp = 130˚C; IR (KBr): ν 3186, 3088, 2914, 1703, 1634, 1516, 1456, 1346, 1284, 1146, 1137 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.85 (s, 3H, CH_3C=), 2.51 (dd, 1H, *J* = 16.7, 13.1 Hz, CH_2CO), 2.87 (dd, 1H, *J* = 16.7, 5.1 Hz, CH_2CO), 3.79 (d, 2H, *J* = 0.8 Hz, CH_2S), 4.87-5.03 (m, 3H, CH_{Bn} + CH_2=), 7.57-7.63 (m, 2H, CH_{Ar}), 8.23-8.27 (m, 2H, CH_{Ar}), 8.98 (br. s, 1H, NH) ppm; ^{13}C NMR (50 MHz, $CDCl_3$): δ = 21.3, 37.4, 37.8, 58.1, 114.8, 123.9, 127.3, 139.9, 147.3, 149.5, 152.9 and 169.2 ppm; ESI-MS: m/z (100 %) = 306 $[M + 1]^+$.



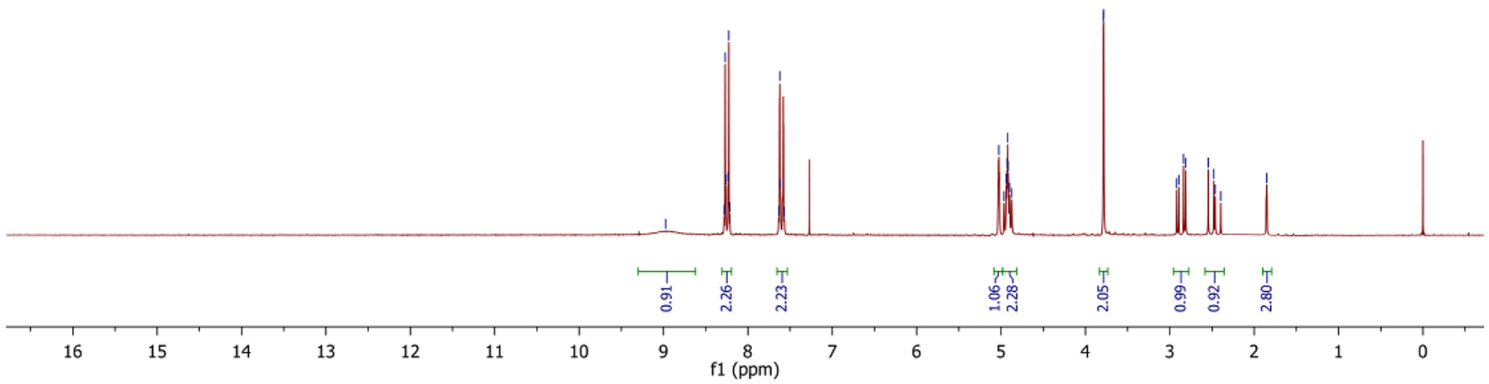


Figure S57 ^{1}H NMR spectrum of **4'i**

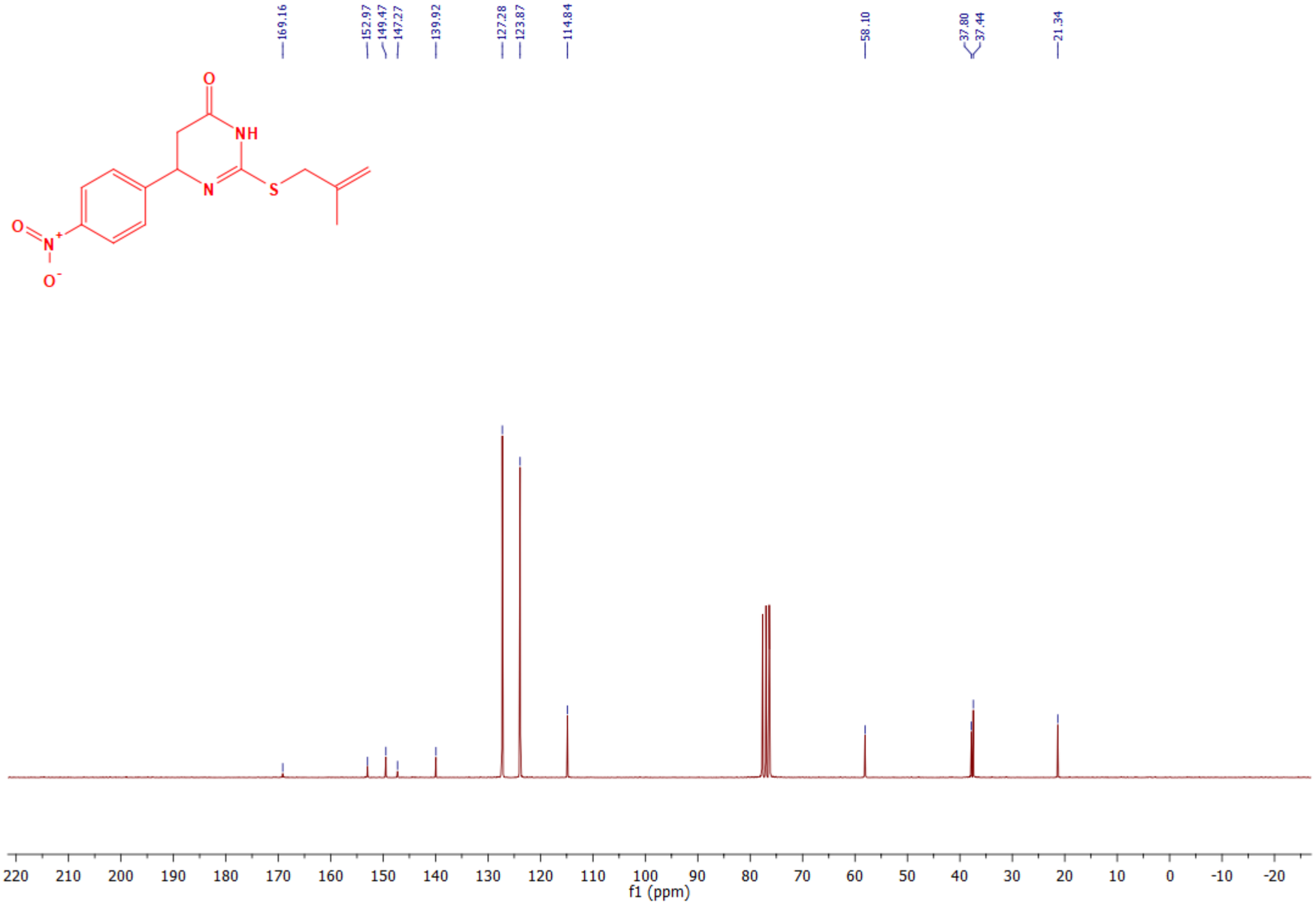
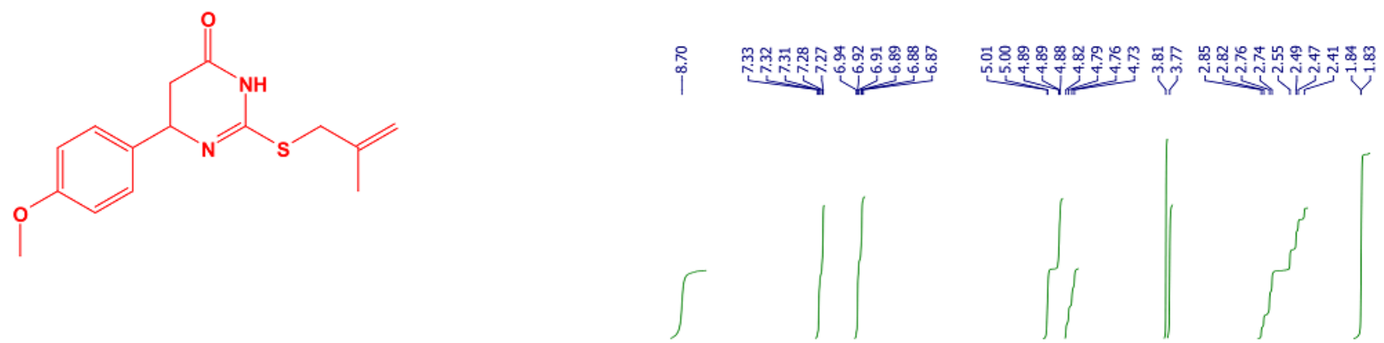


Figure S58 ^{13}C NMR spectrum of **4'i**

2-methallylthio-6-(4'-methoxyphenyl)-5,6-dihydropyrimidin-4(3H)-one (4'j)

White solid; yield: 87%, reaction time: 85 min.; mp = 110˚C; IR (KBr): ν 3185, 3089, 2920, 1694, 1638, 1514, 1464, 1358, 1242, 1178, 1133 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.83 (s, 3H, CH_3C=), 2.48 (dd, 1H, *J* = 16.7, 12.2 Hz, CH_2CO), 2.79 (dd, 1H, *J* = 16.7, 5.2 Hz CH_2CO), 3.77 (s, 2H, CH_2S), 3.81 (s, 3H,OCH_3), 4.78 (dd, 1H, *J* = 12.1, 5.2 Hz, CH_{Bn}), 4.88-5.01 (m, 2H, =CH_2), 6.87-6.94 (m, 2H, CH_{Ar}), 7.27-7.33 (m, 2H, CH_{Ar}), 8.70 (br. s, 1H, NH) ppm; ^{13}C NMR (50 MHz, $CDCl_3$): δ = 21.4, 37.4, 38.3, 55.3, 58.1, 113.9, 114.7, 127.3, 134.3, 140.3, 151.4, 158.8 and 170.0 ppm; ESI-MS: m/z (100 %) = 291 $[M + 1]^{+}$.



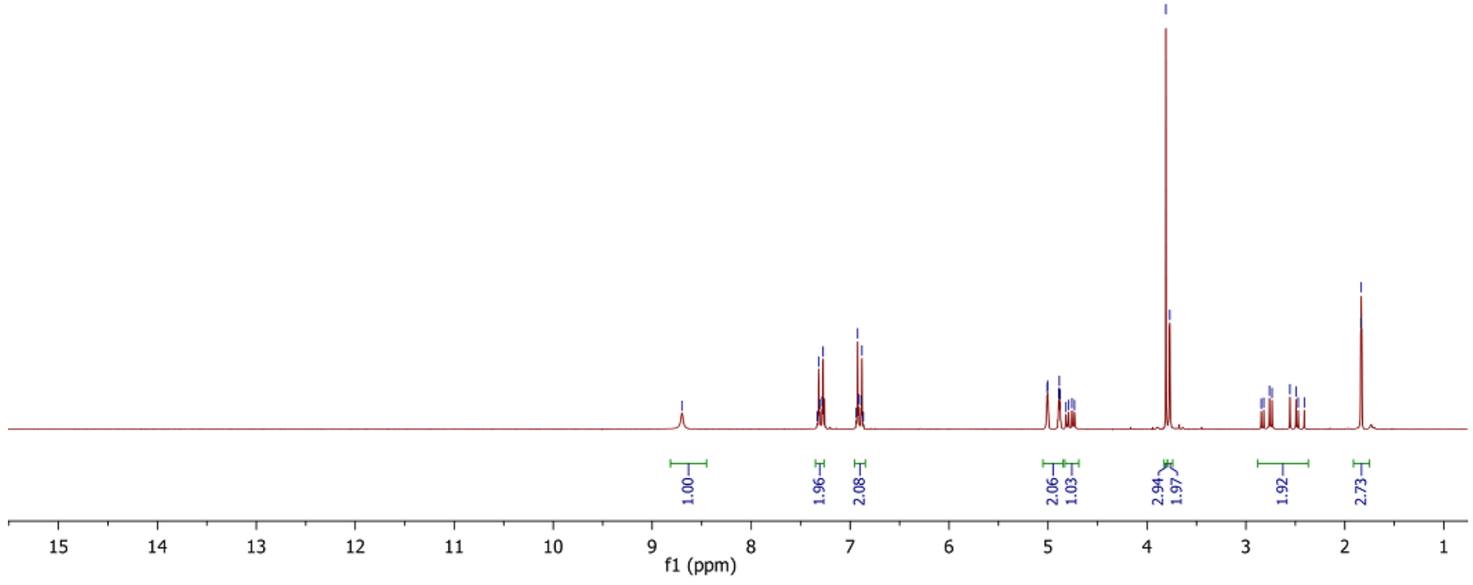


Figure S59 ^{1}H NMR spectrum of **4'j**

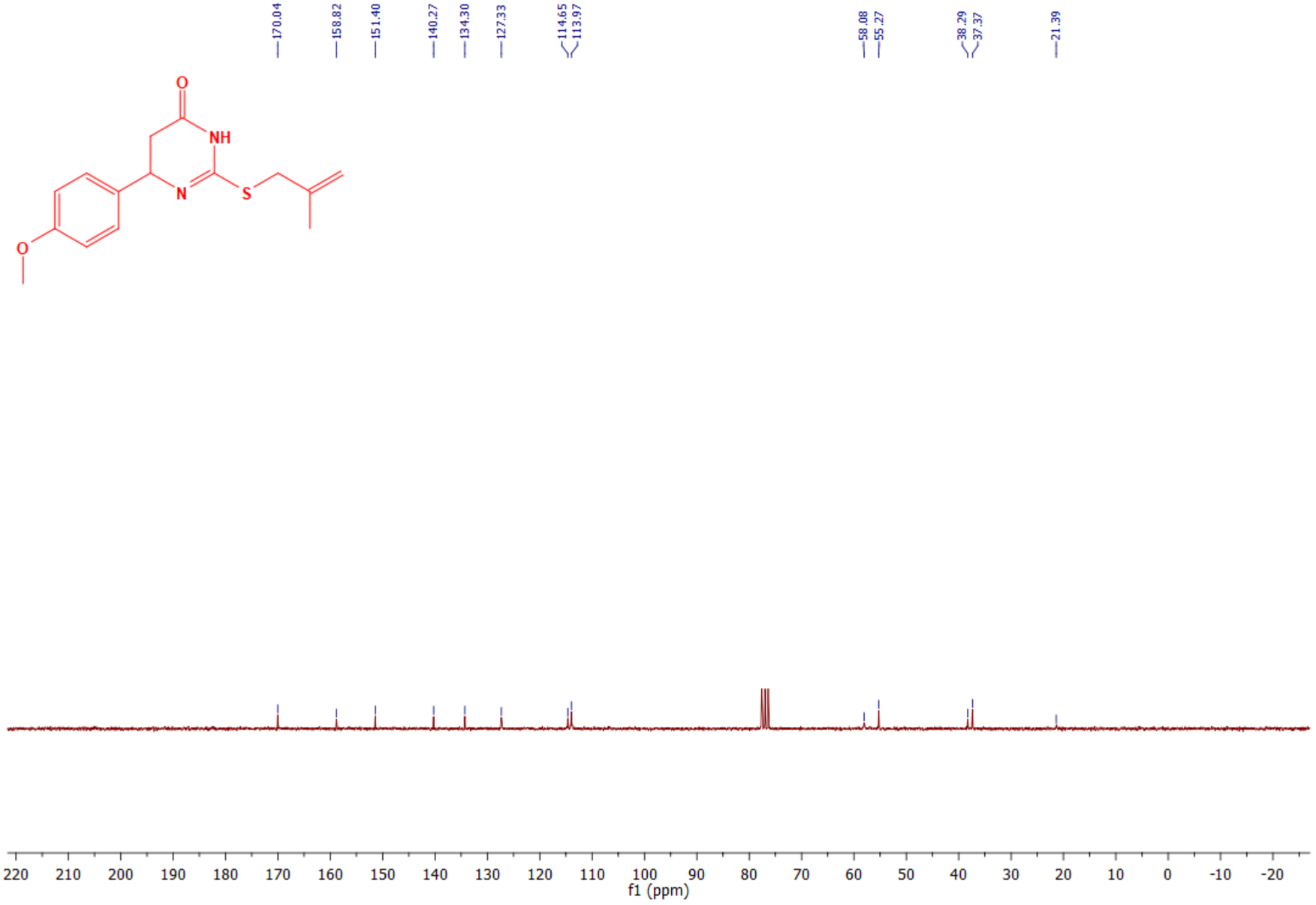
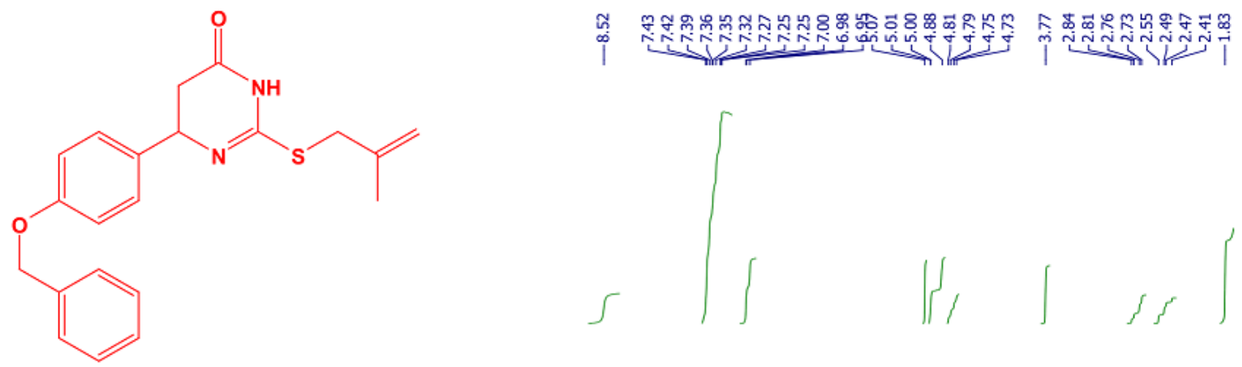


Figure S60 ^{13}C NMR spectrum of **4'j**

2-methallylthio-6-(4'-benzyloxyphenyl)-5,6-dihydropyrimidin-4(3H)-one (4'k)

White solid; yield: 91%, reaction time: 140 min.; mp = 143˚C; IR (KBr): ν 3184, 3090, 2928, 1699, 1634, 1512, 1480, 1356, 1289, 1239, 1146 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.83 (s, 3H, CH_3C=), 2.48 (dd, 1H, *J* = 16.7, 12.2 Hz, CH_2CO), 2.78 (dd, 1H, *J* = 16.7, 5.2 Hz, CH_2CO), 3.77 (s, 2H, CH_2S), 4.78 (dd, 1H, *J* = 12.1, 5.1 Hz, CH_{Bn}), 4.88-5.01 (m, 2H, =CH_2), 5.07 (s, 2H,OCH_2), 6.95-7.00 (m, 2H, CH_{Ar}), 7.25-7.43 (m, 7H, CH_{Ar}), 8.52 (br. s, 1H, NH) ppm; ^{13}C NMR (50 MHz, $CDCl_3$): δ = 21.3, 37.4, 38.3, 58.1, 70.1, 114.7, 114.9, 127.4, 127.9, 128.6, 134.6, 137.0, 140.3, 151.4, 158.1 and 169.8 ppm; ESI-MS: m/z (100 %) = 367 $[M + 1]^+$.



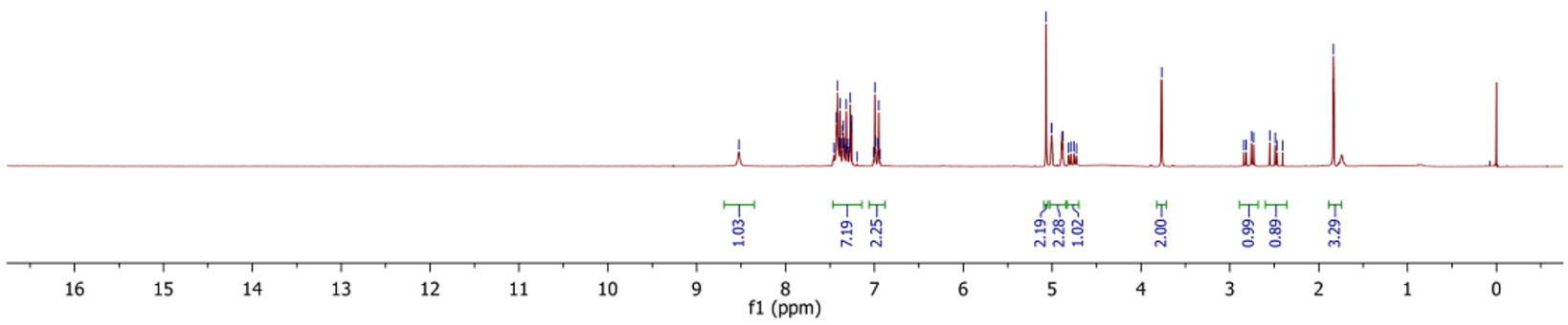


Figure S61 ^{1}H NMR spectrum of **4'k**

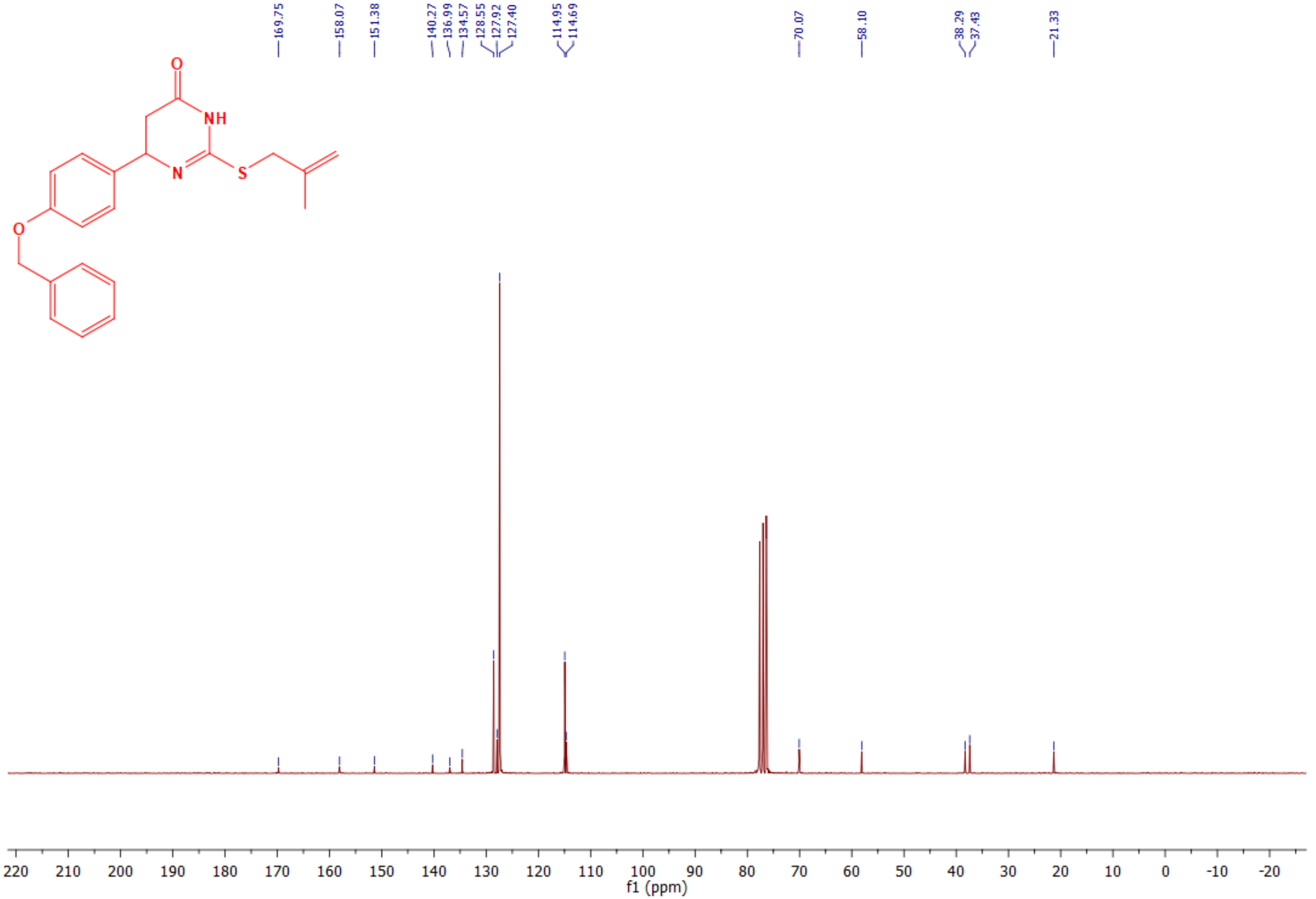
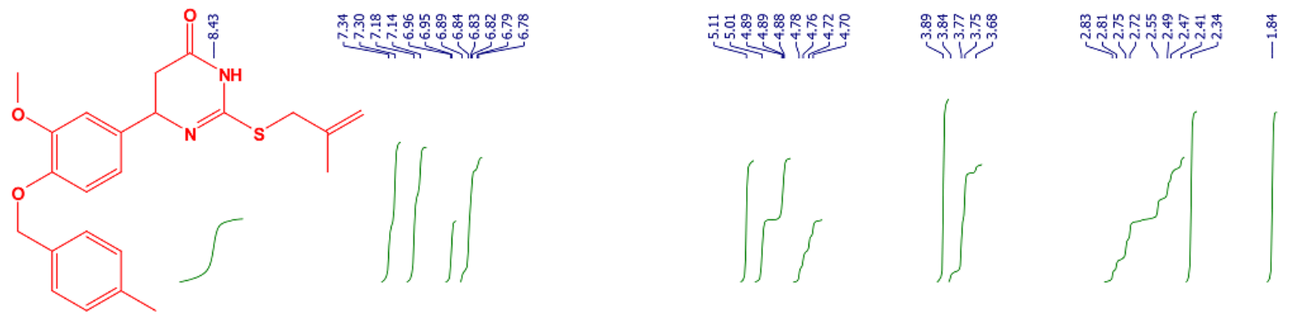


Figure S62 ^{13}C NMR spectrum of **4'k**

2-methallylthio-6-[4'-(4"-methylbenzyloxy)-3'-methoxyphenyl]-5,6-dihydropyrimidin-4(3H)-one (4'l)

White solid; yield: 94%, reaction time: 170 min.; mp = 142°C; IR (KBr): ν 3180, 3088, 2921, 1698, 1635, 1518, 1467, 1339, 1259, 1226, 1157, 1138 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$): δ = 1.84 (s, 3H, CH_3C=), 2.34 (s, 3H, Ar-CH_3), 2.48 (dd, 1H, *J* = 16.7, 12.2 Hz, CH_2CO), 2.76 (dd, 1H, *J* = 16.5, 5.1 Hz, CH_2CO), 3.75-3.77 (m, 2H, CH_2S), 3.89 (s, 3H, OCH_3), 4.70 (dd, 1H, *J* = 12.3, 5.1 Hz, CH_{Bn}), 4.88-5.01 (m, 2H, CH_2=), 5.11 (s, 2H, OCH_2), 6.79-6.96 (m, 3H, CH_{Ar}), 7.16 (d, 2H, *J* = 7.4 Hz, CH_{Ar}), 7.32 (d, 2H, *J* = 8.0 Hz, CH_{Ar}), 8.43 (br. s, 1H, NH) ppm; ^{13}C NMR (50 MHz, $CDCl_3$): δ = 21.3, 37.4, 38.4, 56.0, 58.3, 71.0, 110.3, 114.0, 114.6, 118.2, 127.3, 129.2, 134.1, 135.3, 137.5, 140.3, 147.5, 149.8, 151.4 and 169.7 ppm; ESI-MS: m/z (100 %) = 411 $[M + 1]^+$.



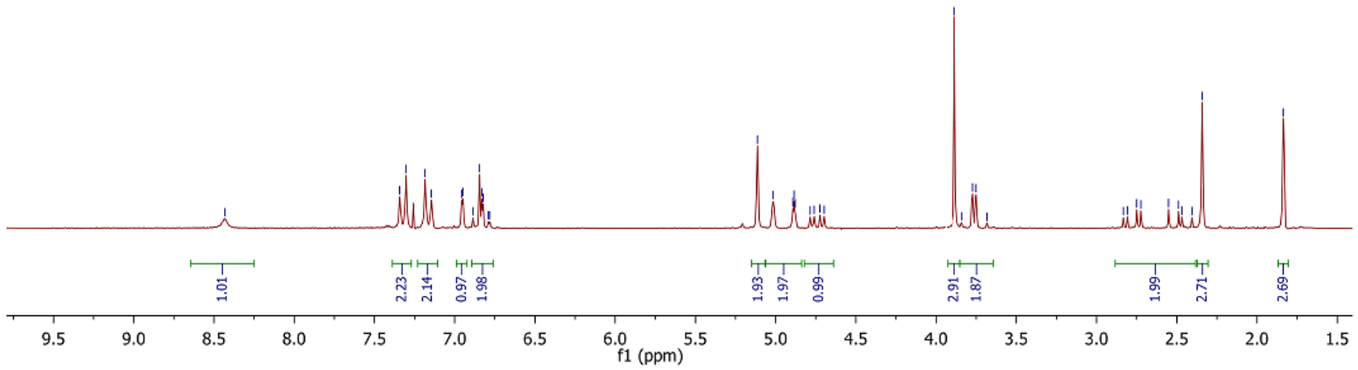


Figure S63 ^1H NMR spectrum of **4'l**

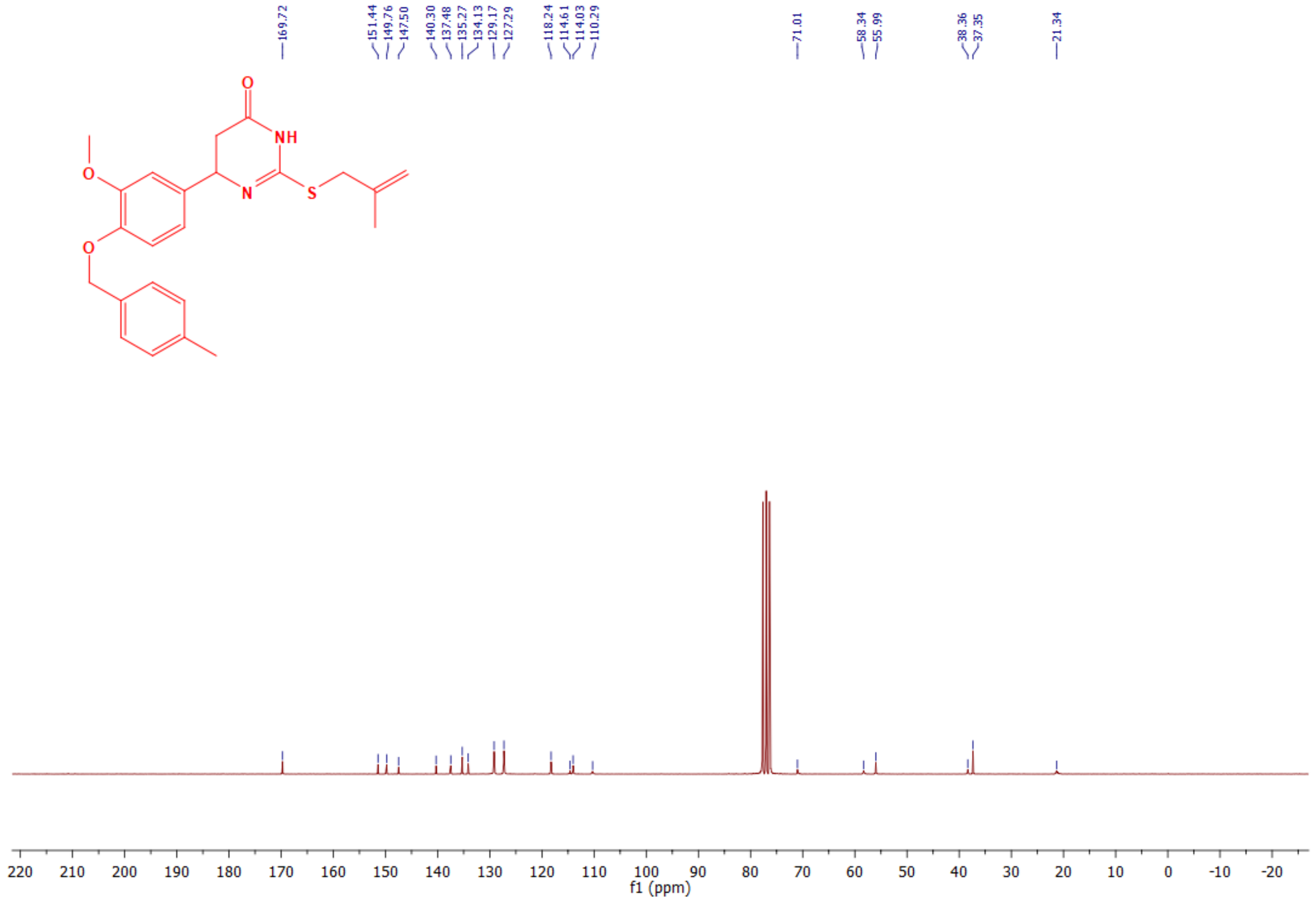


Figure S64 ^{13}C NMR spectrum of **4'l**

2-methallylthio-6-[4'-(3"-methylbenzyloxy)-3'-methoxyphenyl]-5,6-dihydropyrimidin-4(3H)-one (4'm)

White powder; yield: 90%, reaction time: 175 min.; mp = 106˚C; IR (KBr): ν 3184, 3089, 2915, 1691, 1633, 1516, 1365, 1342, 1262, 1226, 1134, 1041, 1029 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.84 (s, 3H, CH_3C=), 2.35 (s, 3H, CH_3), 2.52 (dd, 1H, *J* = 16.7, 12.4 Hz, CH_2CO), 2.79 (dd, 1H, *J* = 16.7, 5.2 Hz, CH_2CO), 3.75-3.78 (m, 2H, CH_2S), 3.89 (s, 3H, OCH_3), 4.75 (dd, 1H, *J* = 12.4, 5.1 Hz, CH_{Bn}), 4.88-5.02 (m, 2H, =CH_2), 5.11 (s, 1H, OCH_2), 6.79-6.85 (m, 2H, CH_{Ar}), 6.96 (m, 1H, CH_{Ar}), 7.09-7.12 (m, 1H, CH_{Ar}), 7.23-7.25 (m, 3H, CH_{Ar}), 8.63 (br. s, 1H, NH) ppm; ^{13}C NMR (50 MHz, $CDCl_3$): δ = 21.4, 37.3, 38.3, 56.0, 58.3, 71.2, 110.4, 114.1, 114.6, 118.3, 124.3, 128.4, 128.5, 135.4, 137.1, 138.1, 140.3, 147.5, 149.7, 151.5 and 169.8 ppm; ESI-MS: m/z (100 %) = 411 $[M + 1]^+$.

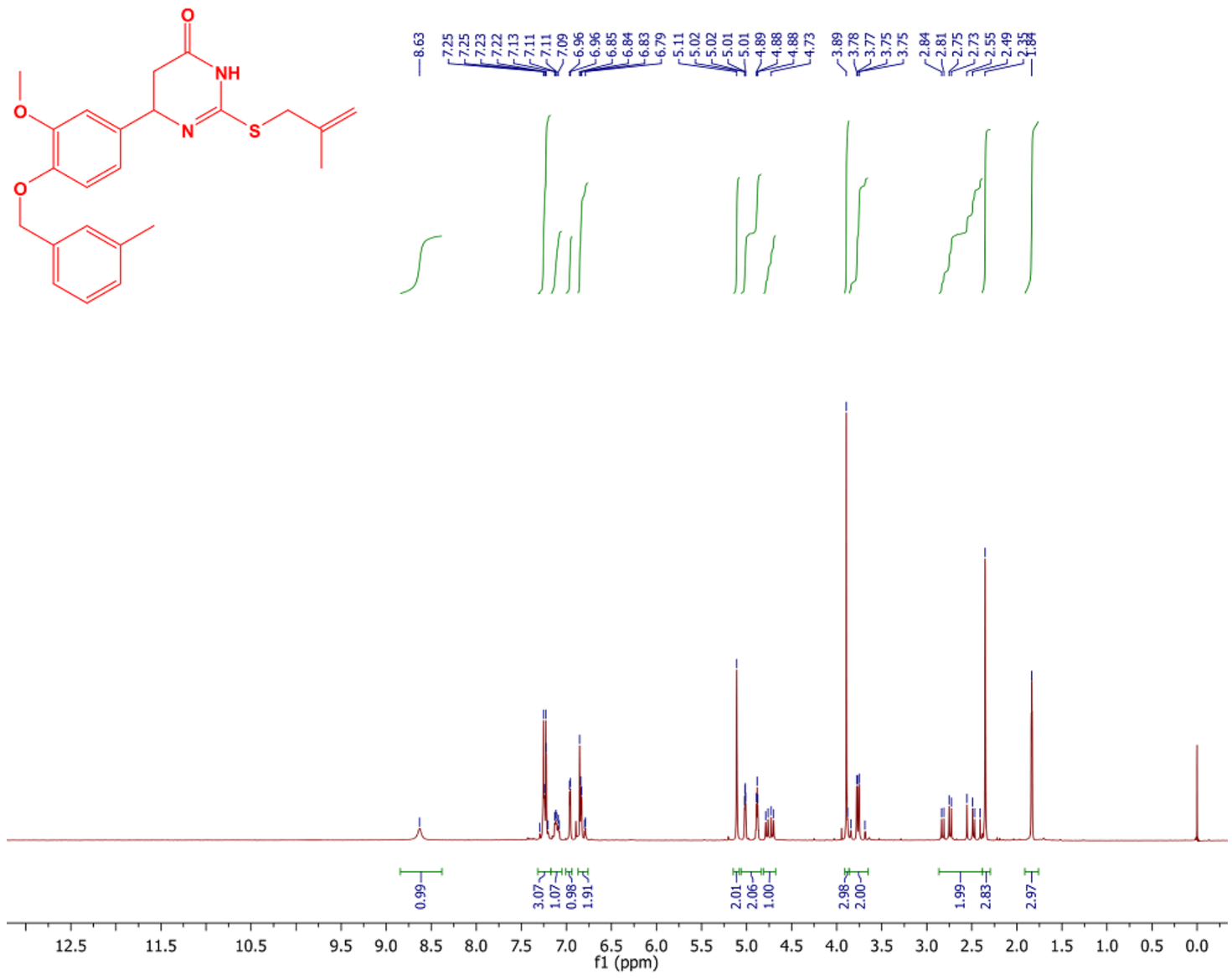


Figure S65 ^{1}H NMR spectrum of **4'm**

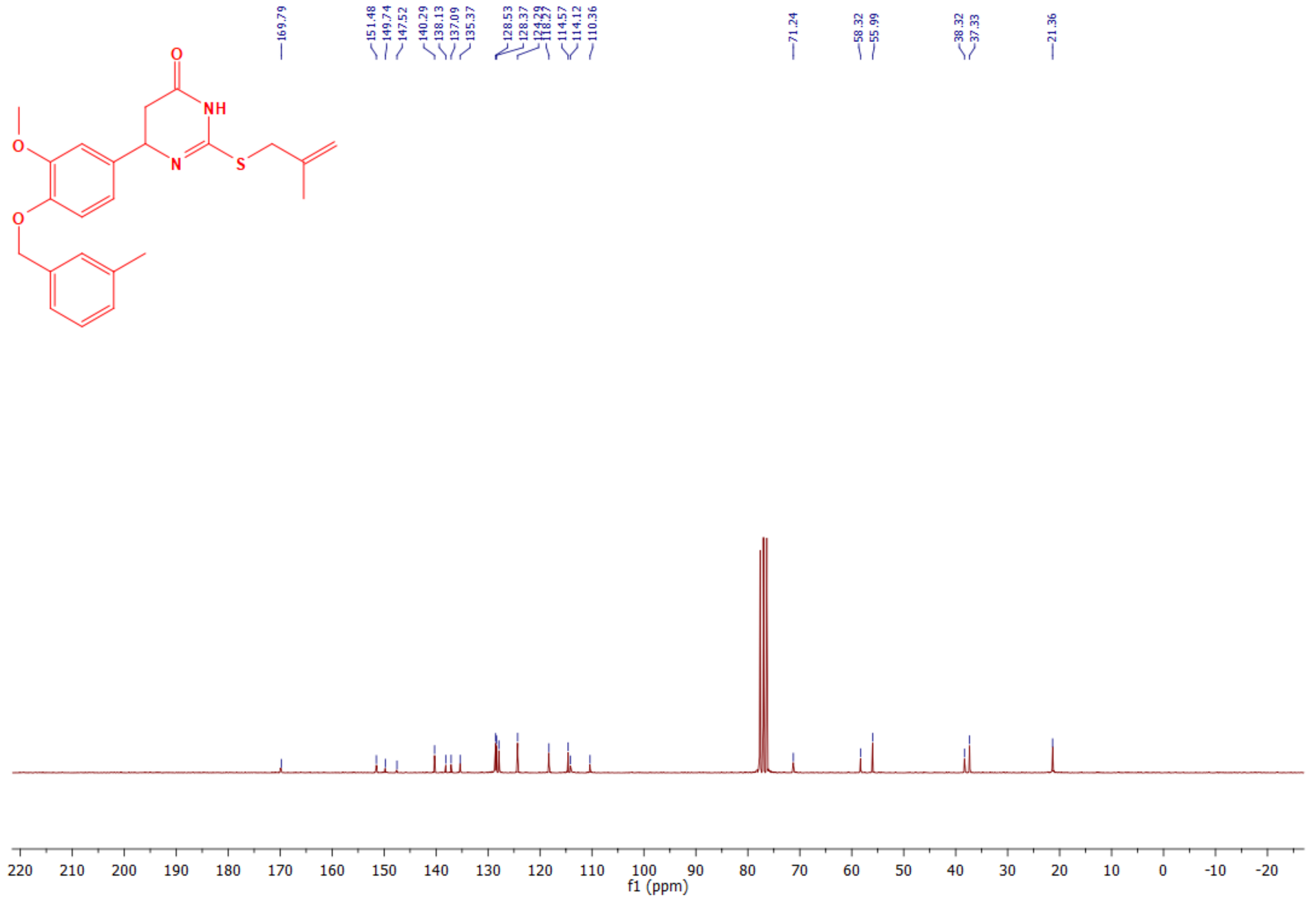
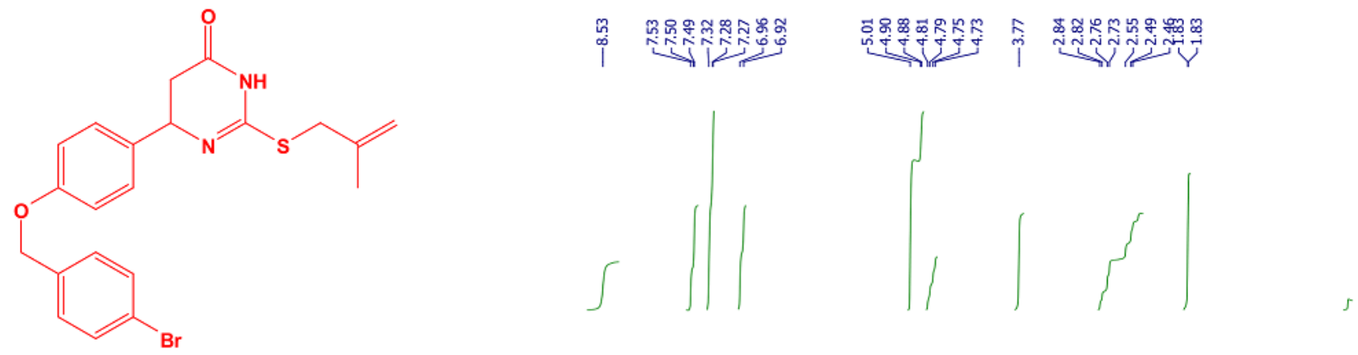


Figure S66 ^{13}C NMR spectrum of **4'm**

2-methallylthio-6-[4'-(4"-bromobenzyloxy)phenyl]-5,6-dihydropyrimidin-4(3H)-one (4'n)

White solid; yield: 87%, reaction time: 180 min.; mp = 146˚C; IR (KBr): ν 3184, 3089, 2922, 1698, 1630, 1509, 1487, 1358, 1287, 1237, 1141 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$): δ = 1.83 (s, 3H, CH_3C=), 2.52 (dd, 1H, *J* = 16.7, 12.3 Hz, CH_2CO), 2.78 (dd, 1H, *J* = 16.7, 5.3 Hz, CH_2CO), 3.77 (s, 2H, CH_2S), 4.77 (dd, 1H, *J* = 12.2, 5.2 Hz, CH_{Bn}), 4.88-5.01 (m, 4H, $=CH_2$ + OCH_2), 6.94 (d, 2H, *J* = 8.7 Hz, CH_{Ar}), 7.27-7.32 (m, 4H, CH_{Ar}), 7.51 (d, 2H, *J* = 8.3 Hz, CH_{Ar}), 8.53 (br. s, 1H, NH) ppm; ^{13}C NMR (50 MHz, $CDCl_3$): δ = 21.3, 37.4, 38.3, 58.1, 69.3, 114.7, 114.9, 121.8, 127.5, 128.9, 131.7, 134.8, 136.0, 140.2, 151.4, 157.8 and 169.7 ppm; ESI-MS: m/z (100 %) = 447 $[M + 2]^+$.



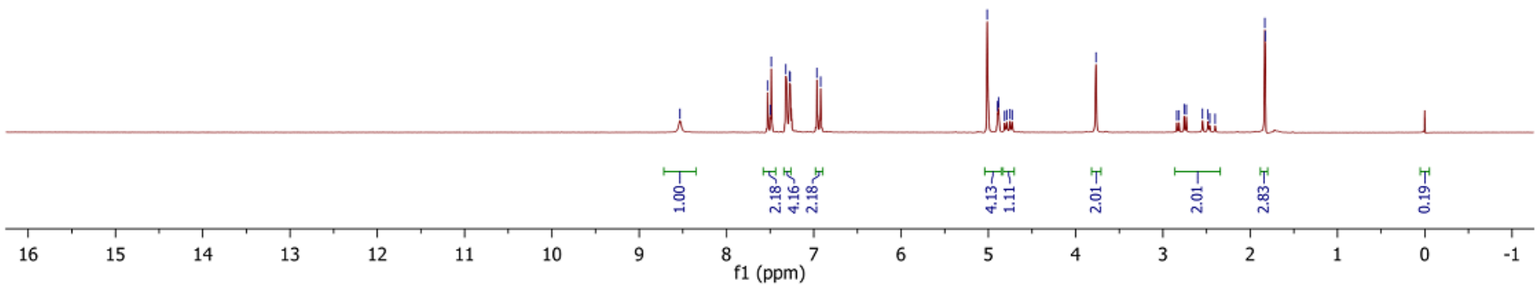


Figure S67 ^1H NMR spectrum of **4'n**

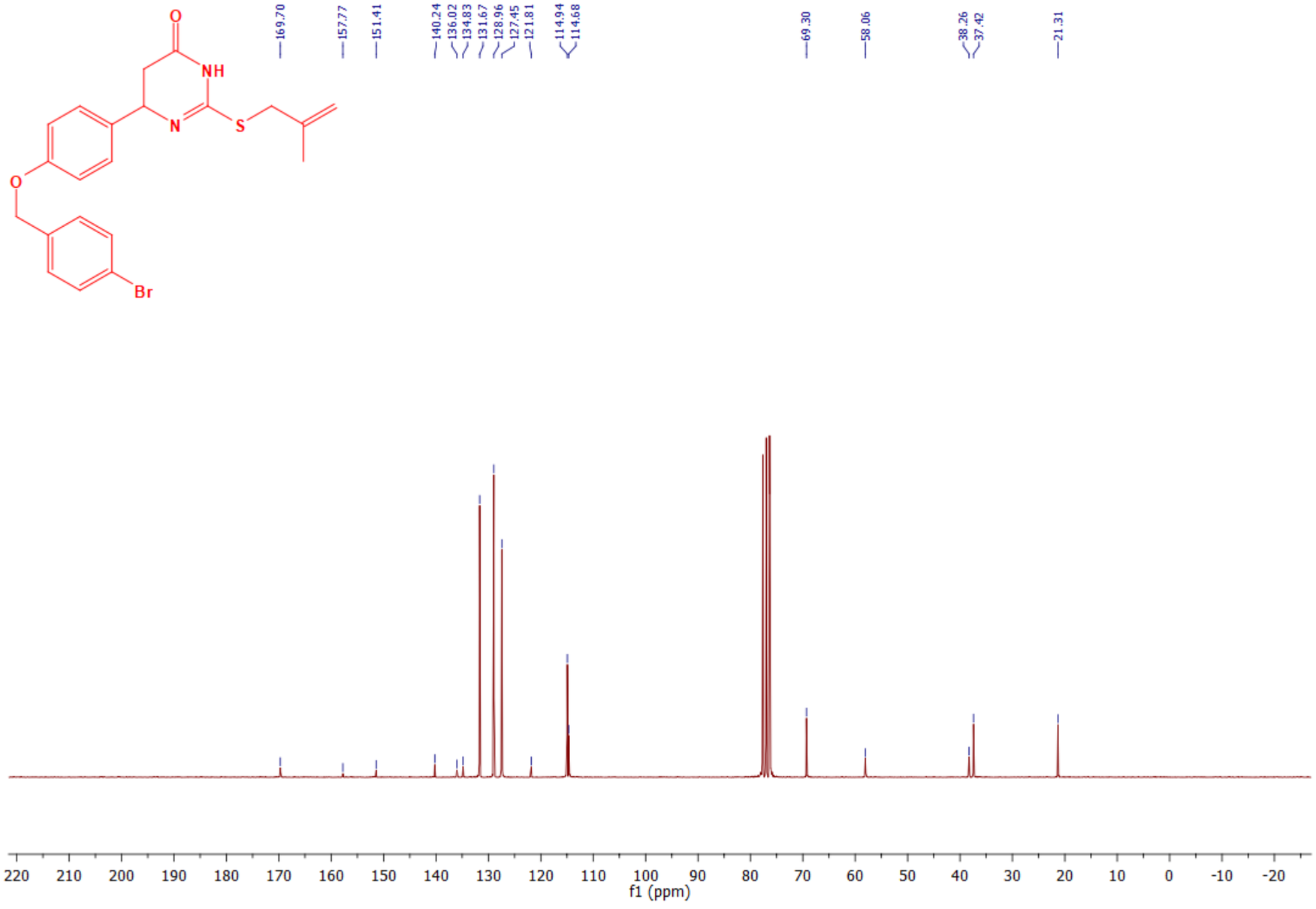


Figure S68 ^{13}C NMR spectrum of **4'n**

2-methallylthio-6-(4'-benzyloxy-3'-methoxyphenyl)-5,6-dihydropyrimidin-4(3H)-one (4'o)

White powder; yield: 92%, reaction time: 180 min.; mp = 134˚C; IR (KBr): ν 3184, 3088, 2916, 1699, 1624, 1515, 1467, 1336, 1260, 1236, 1139 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.84 (s, 3H, CH_3), 2.48 (dd, 1H, *J* = 16.7, 12.5 Hz, CH_2CO), 2.74 (dd, 1H, *J* = 16.7, 5.1 Hz, CH_2CO), 3.68-3.77 (m, 2H, CH_2S), 3.84 (s, 3H,OCH_3), 4.73 (dd, 1H, *J* = 12.4, 5.1 Hz, CH_{Bn}), 4.88-5.01 (m, 2H, $=CH_2$), 5.15 (s, 3H, OCH_3), 6.83-6.97 (m, 3H, CH_{Ar}), 7.26-7.46 (m, 5H, CH_{Ar}), 7.29-7.46 (m, 5H, CH_{Ar}), 8.61 (br. s, 1H, NH) ppm; ^{13}C NMR (50 MHz, $CDCl_3$): δ = 21.6, 37.3, 38.3, 56.0, 58.3, 71.2, 110.4, 114.2, 114.6, 118.3, 127.2, 127.8, 128.5, 135.5, 137.2, 140.3, 147.5, 149.8, 151.5 and 169.8 ppm; ESI-MS: m/z (100 %) = 397 $[M]^+$.

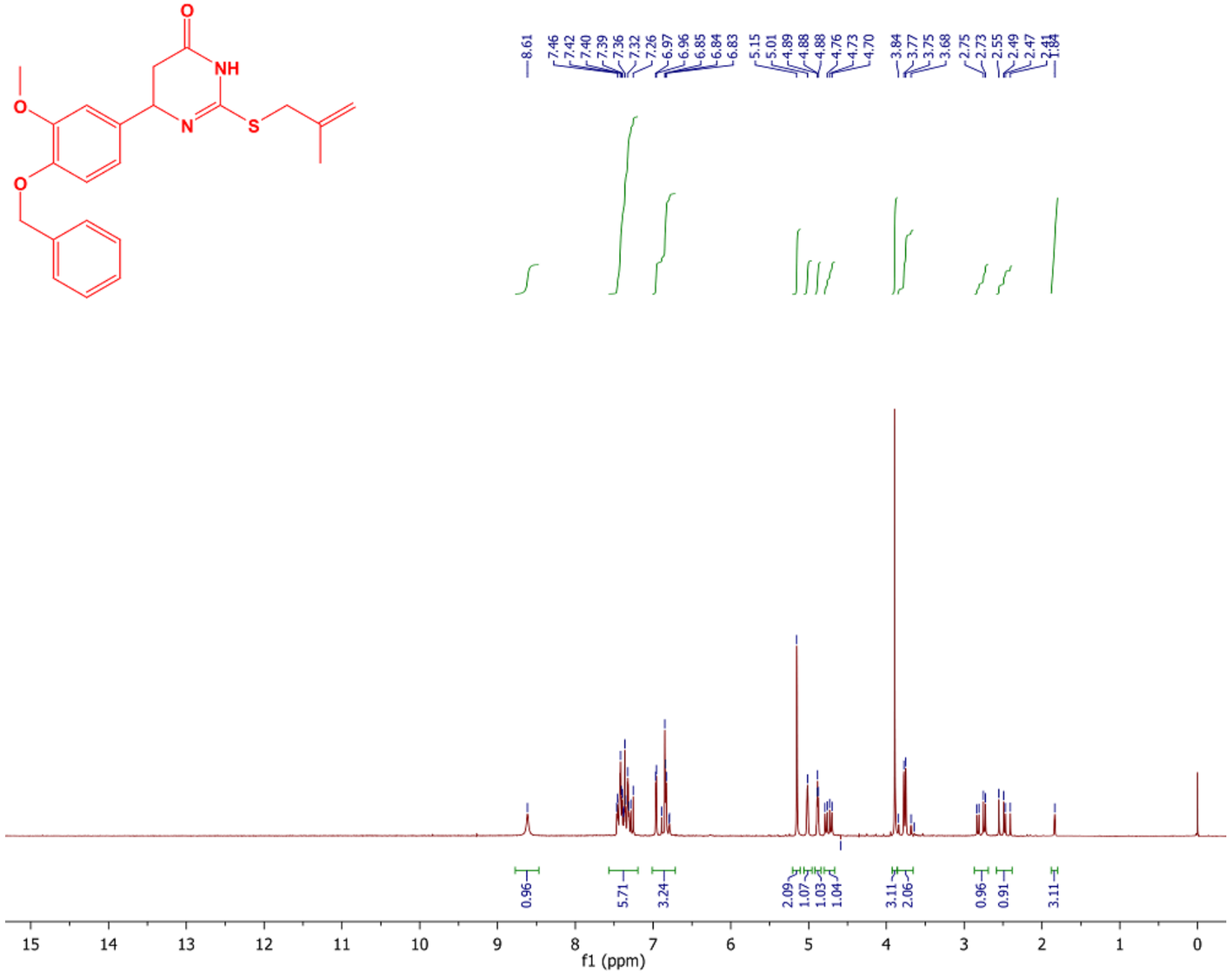


Figure S69 ^{1}H NMR spectrum of **4'o**

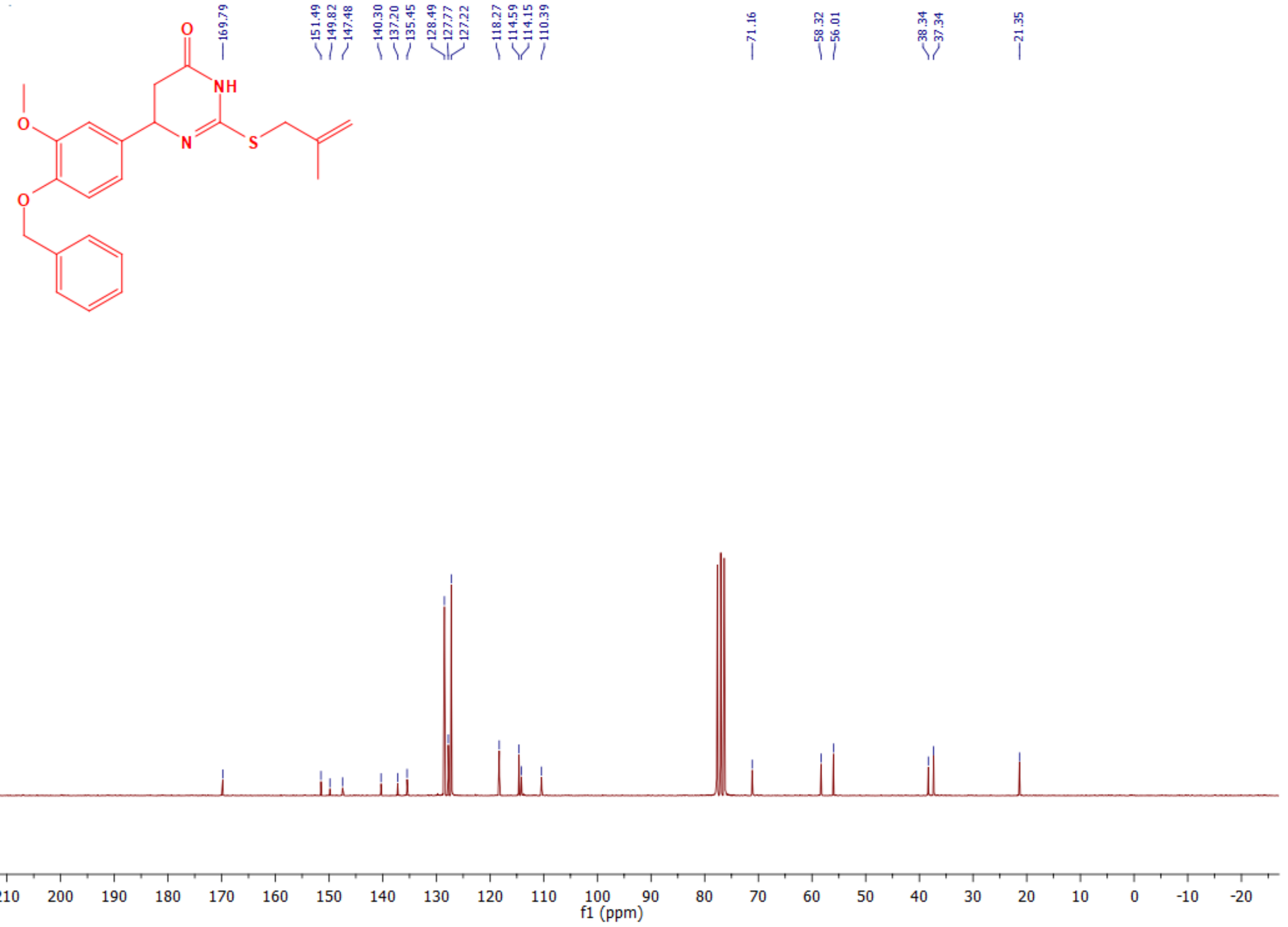


Figure S70 ^{13}C NMR spectrum of **4'o**

2-methallylthio-6-(3',4',5'-trimethoxyphenyl)-5,6-dihydropyrimidin-4(3H)-one (4'p)

White solid; yield: 83%, reaction time: 155 min.; mp = 132˚C; IR (KBr): ν 3185, 3097, 2935, 1701, 1635, 1594, 1511, 1461, 1335, 1230, 1153, 1128 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.85 (s, 3H, CH_3), 2.54 (dd, 1H, *J* = 16.7, 12.9 Hz, CH_2CO), 2.80 (dd, 1H, *J* = 16.7, 5.0 Hz, CH_2CO), 3.75-3.85 (m, 11H, 3×OCH_3 + CH_2S), 4.75 (dd, 1H, *J* = 12.8, 4.9 Hz, CH_{Bn}), 4.89-5.04 (m, 2H, =CH_2), 6.62 (s, 2H, CH_{Ar}), 8.53 (br. s, 1H, NH) ppm; ^{13}C NMR (50 MHz, $CDCl_3$): δ = 21.4, 37.3, 38.5, 56.1, 58.8, 60.8, 103.5, 114.6, 137.9, 140.3, 151.8, 153.4 and 169.7 ppm; ESI-MS: m/z (100 %) = 351 $[M + 1]^+$.

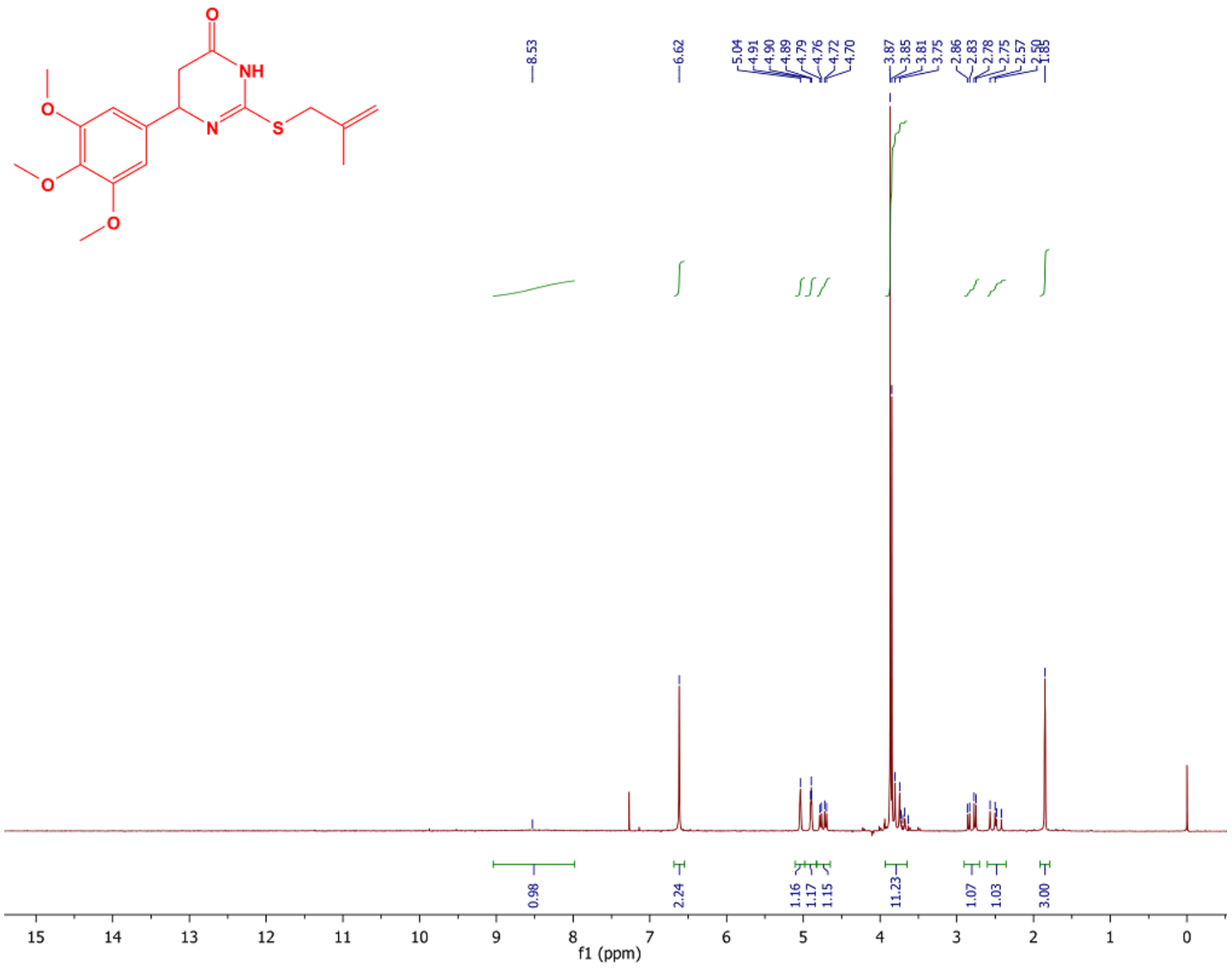


Figure S71 ^{1}H NMR spectrum of **4'p**

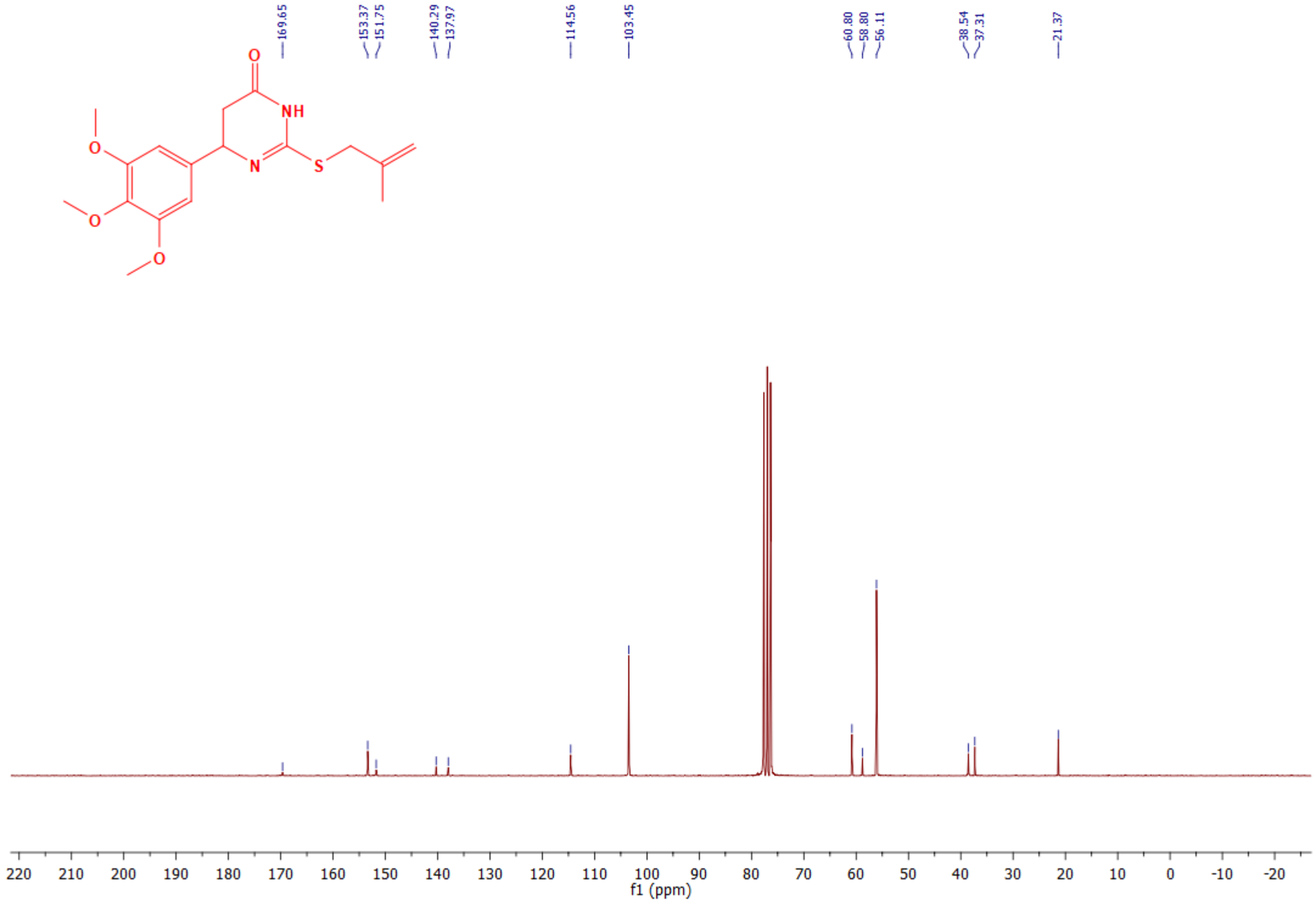
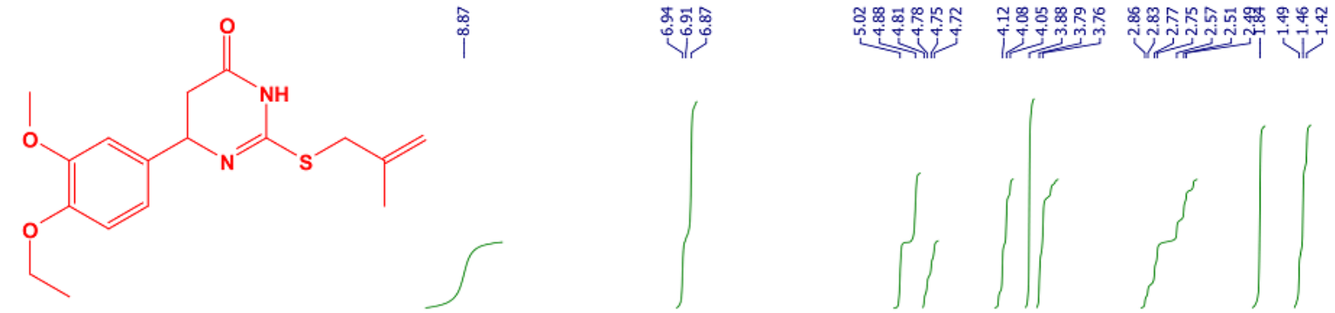


Figure S72 ^{13}C NMR spectrum of **4'p**

2-methallylthio-6-(4'-ethoxy-3'-methoxyphenyl)-5,6-dihydropyrimidin-4(3H)-one (4'q)

Yellow powder; yield: 88%, reaction time: 180 min.; mp = 108˚C; IR (KBr): ν 3182, 3083, 2921, 1696, 1626, 1516, 1477, 1338, 1261, 1232, 1139, 1038 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$): δ = 1.46 (t, 3H, *J* = 7.0, CH_3), 1.84 (s, 3H, CH_3C=), 2.53 (dd, 1H, *J* = 16.6, 12.5 Hz, CH_2CO), 2.80 (dd, 1H, *J* = 16.7, 5.2 Hz, CH_2CO), 3.76-3.79 (m, 2H, CH_2S), 3.88 (s, 3H, OCH_3), 4.08 (q, 2H, *J* = 7.0 Hz, OCH_2), 4.75 (dd, 1H, *J* = 12.4, 5.1 Hz, CH_{Bn}), 4.81-5.02 (m, 2H, =CH_2), 6.87-6.94 (m, 3H, CH_{Ar}), 8.87 (br. s, 1H, NH) ppm; ^{13}C NMR (50 MHz, $CDCl_3$): δ = 14.8, 21.3, 37.3, 38.3, 55.9, 58.3, 64.4, 110.1, 112.8, 114.5, 118.2, 134.8, 140.3, 147.6, 149.4, 151.5 and 170.0 ppm; ESI-MS: m/z (100 %) = 335 $[M + 1]^+$.



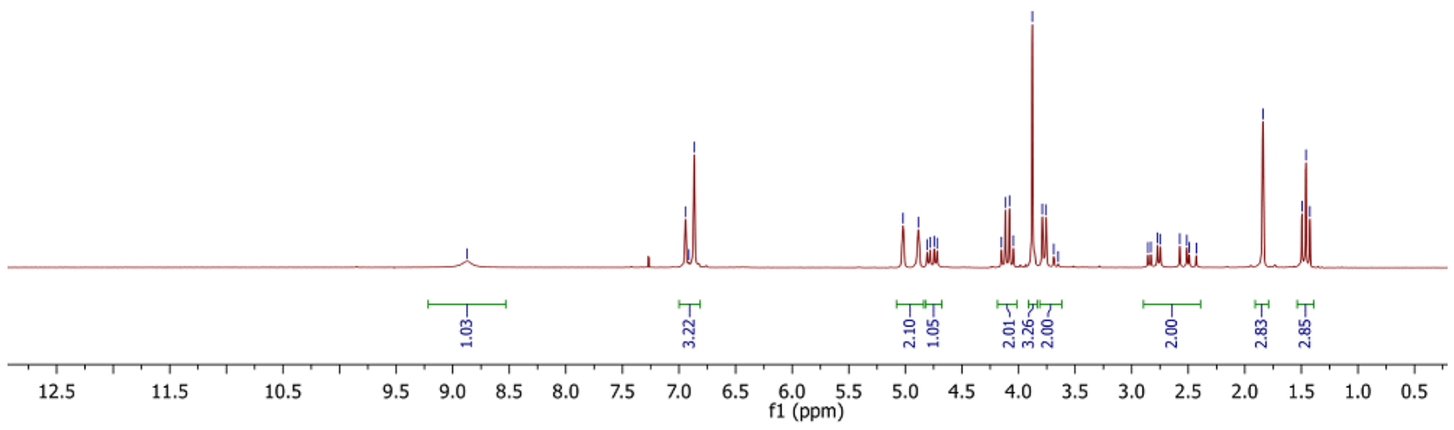


Figure S73 ^1H NMR spectrum of **4'q**

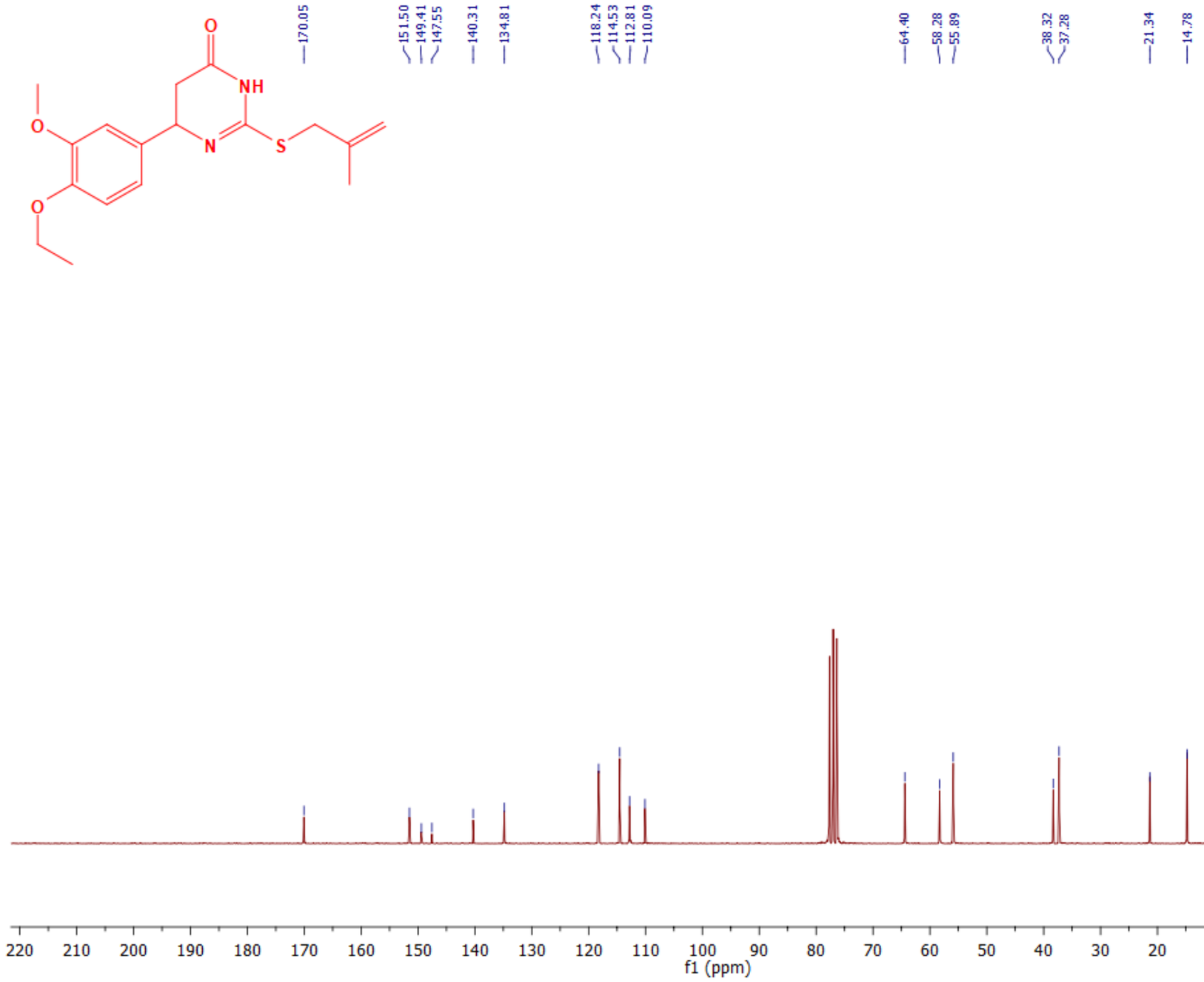
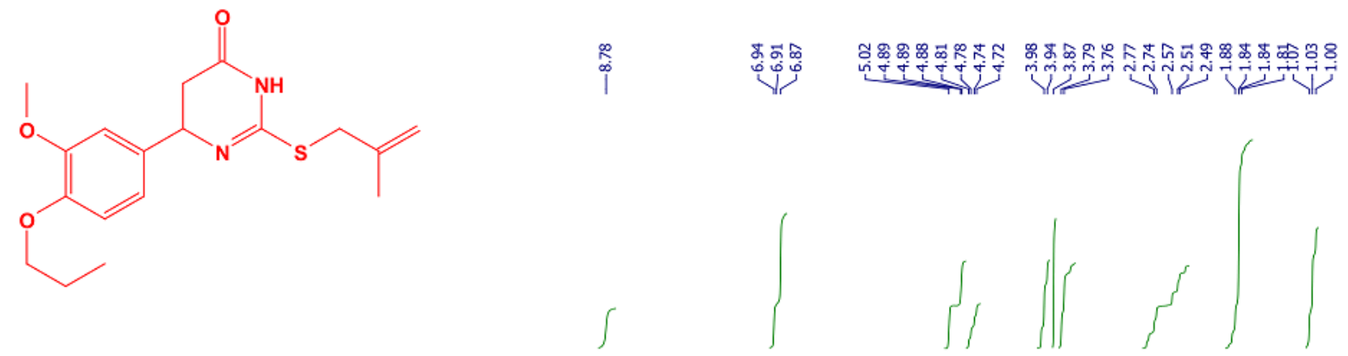


Figure S74 ^{13}C NMR spectrum of **4'q**

2-methallylthio-6-(4'-propoxy-3'-methoxyphenyl)-5,6-dihydropyrimidin-4(3H)-one (4'r)

Yellow powder; yield: 93%, reaction time: 165 min.; mp = 98˚C; IR (KBr): ν 3183, 3089, 2963, 2877, 1699, 1635, 1519, 1476, 1352, 1254, 1237, 1130 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.03 (t, 3H, *J* = 7.4, CH_3) 1.81-1.88 (m, 5H, CH_2 + CH_3C=), 2.53 (dd, 1H, *J* = 16.7, 12.4 Hz, CH_2CO), 2.76 (dd, 1H, *J* = 16.7, 5.2 Hz, CH_2CO), 3.76-3.79 (m, 2H, CH_2S), 3.87 (s, 3H, OCH_3), 3.96 (t, 2H, *J* = 6.8 Hz, OCH_2), 4.75 (dd, 1H, *J* = 12.3, 5.1 Hz, CH_{Bn}), 4.88-5.02 (m, 2H, =CH_2), 6.87-6.94 (m, 3H, CH_{Ar}), 8.78 (br. s, 1H, NH) ppm; ^{13}C NMR (50 MHz, $CDCl_3$): δ = 10.4, 21.4, 22.4, 37.3, 38.3, 56.0, 58.3, 70.6, 110.3, 113.0, 114.6, 118.3, 134.8, 140.3, 147.8, 149.5, 151.5 and 170.1 ppm; ESI-MS: m/z (100 %) = 349 $[M + 1]^+$.



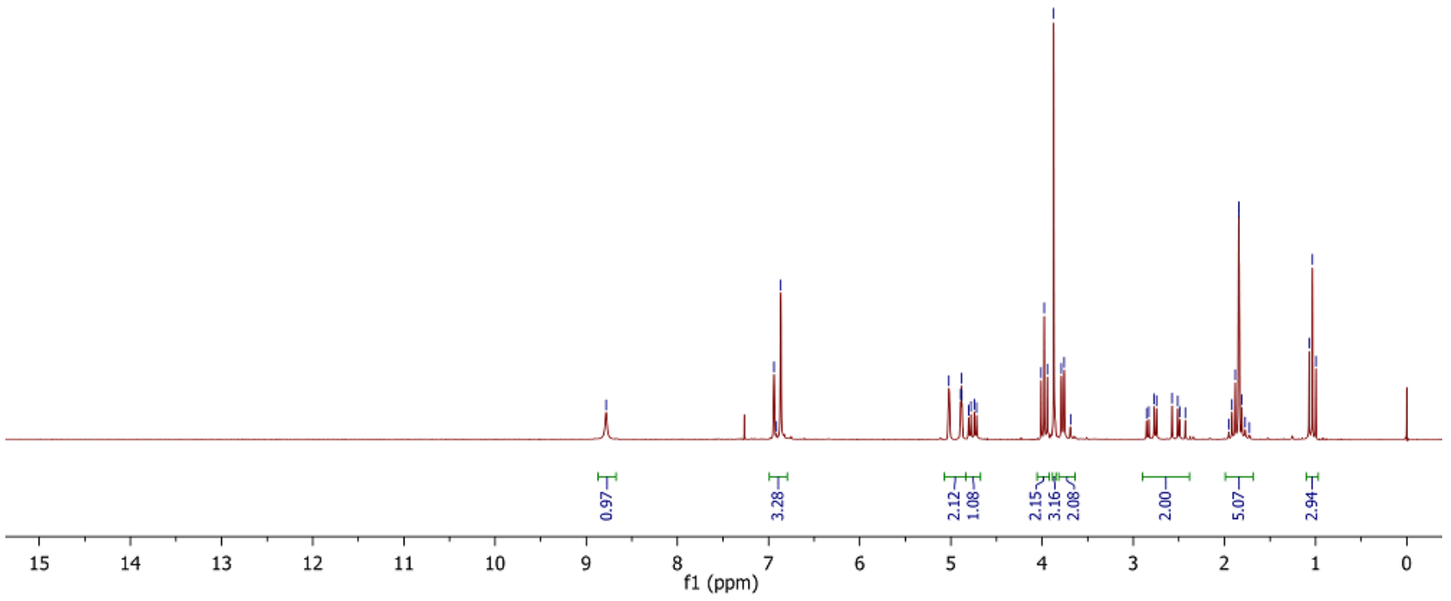


Figure S75 ^{1}H NMR spectrum of **4'r**

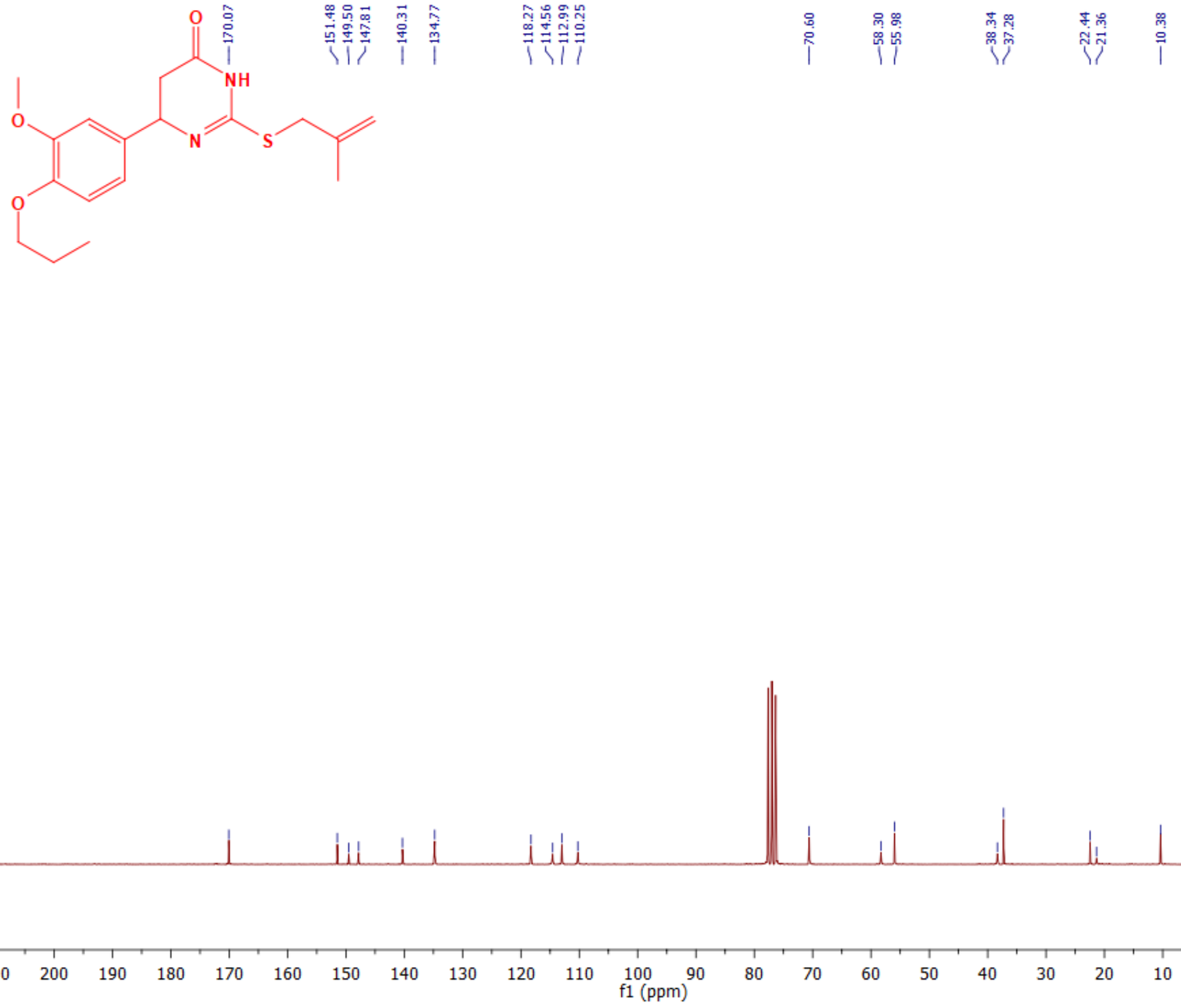
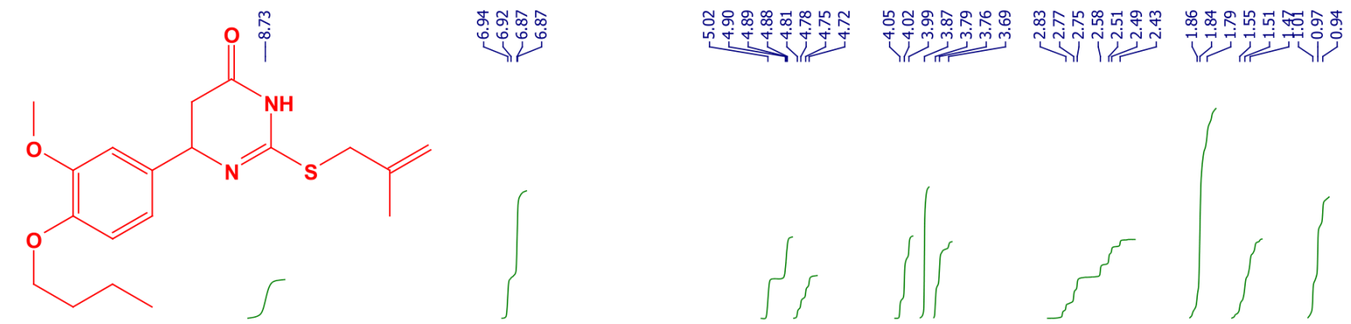


Figure S76 ^{13}C NMR spectrum of **4'r**

2-methallylthio-6-(4'-butoxy-3'-methoxyphenyl)-5,6-dihydropyrimidin-4(3H)-one (4's)

Yellow powder; yield: 81%, reaction time: 155 min.; mp = 97˚C; IR (KBr): ν 3179, 3086, 2958, 2870, 1694, 1634, 1518, 1476, 1341, 1259, 1231, 1139 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.97 (t, 3H, *J* = 7.3, CH_3) 1.47-1.55 (m, 2H, CH_2), 1.79-1.86 (m, 5H, $CH_2 + CH_3C=$), 2.51 (dd, 1H, *J* = 16.7, 12.4 Hz, CH_2CO), 2.78 (dd, 1H, *J* = 16.7, 5.2 Hz, CH_2CO), 3.69-3.79 (m, 2H, CH_2S), 3.87 (s, 3H, OCH_3), 4.02 (t, 2H, *J* = 6.8 Hz, OCH_2), 4.77 (dd, 1H, *J* = 12.4, 5.2 Hz, CH_{Bn}), 4.88-5.02 (m, 2H, $=CH_2$), 6.87-6.94 (m, 3H, CH_{Ar}), 6.94 (s, 1H, CH_{Ar}), 8.73 (br. s, 1H, NH) ppm; ^{13}C NMR (50 MHz, $CDCl_3$): δ = 13.8, 19.2, 21.3, 31.2, 37.3, 38.4, 56.0, 58.3, 68.8, 110.3, 113.0, 114.6, 118.3, 134.8, 140.3, 147.9, 149.6, 151.5 and 170.0 ppm; ESI-MS: m/z (100 %) = 363 $[M + 1]^+$.



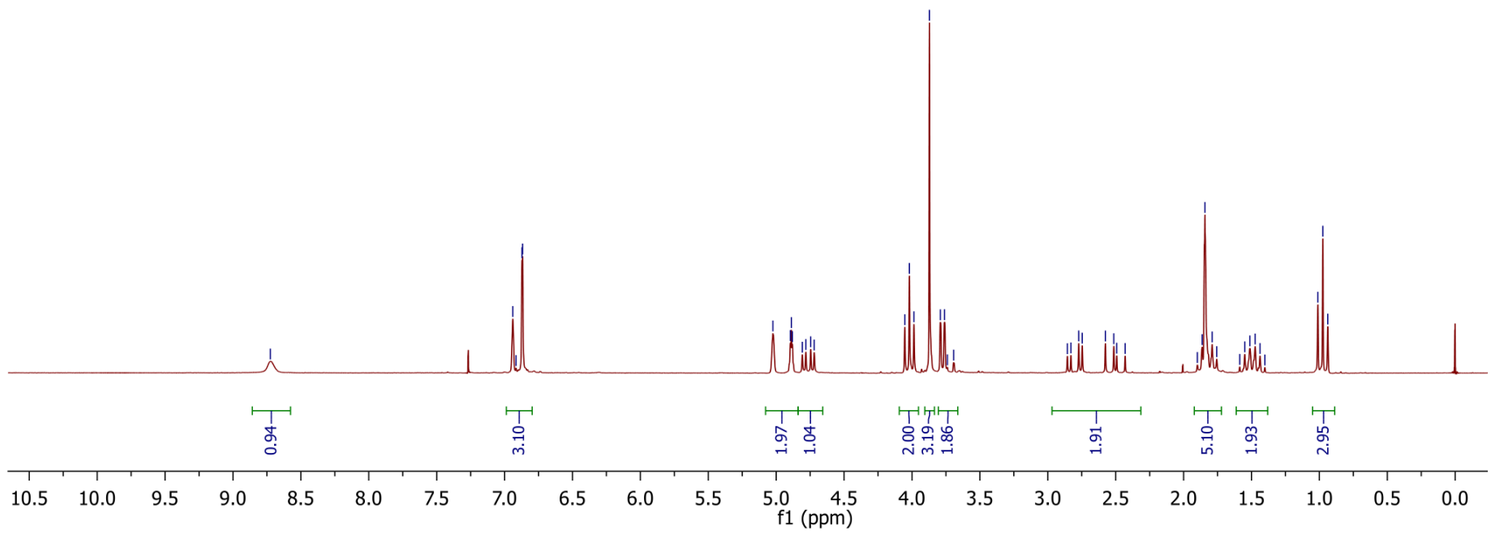


Figure S77 ^{1}H NMR spectrum of **4's**

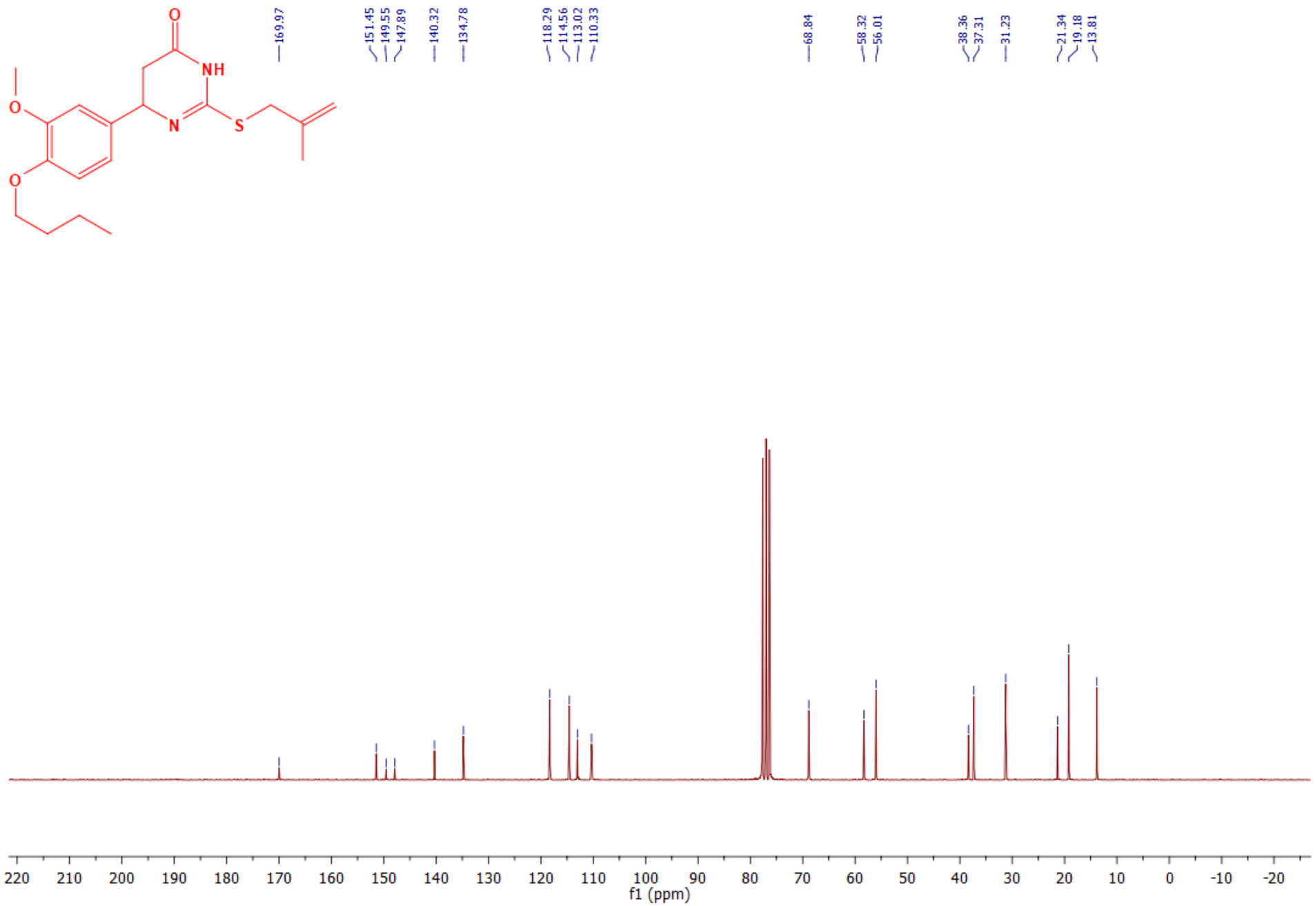


Figure S78 ^{13}C NMR spectrum of **4's**

2-methallylthio-6-(4'-acetoxy-3'-methoxyphenyl)-5,6-dihydropyrimidin-4(3H)-one (4't)

White solid; yield: 90%, reaction time: 150 min.; mp = 147˚C; IR (KBr): ν 3184, 3087, 2921, 1759, 1698, 1634, 1514, 1481, 1352, 1292,1223, 1155, 1115 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.84 (s, 3H, CH_3C=), 2.32 (s, 3H, $COCH_3$), 2.49 (dd, 1H, *J* = 16.7, 12.9 Hz, CH_2CO), 2.81 (dd, 1H, *J* = 16.7, 5.1 Hz, CH_2CO), 3.76-3.80 (m, 2H, CH_2S), 3.84 (s, 3H, OCH_3), 4.79 (dd, 1H, *J* = 12.9, 5.0 Hz, CH_{Bn}), 4.88-5.03 (m, 2H, $=CH_2$), 6.89-7.06 (m, 3H, CH_{Ar}), 8.72 (br. s, 1H, NH) ppm; ^{13}C NMR (50 MHz, $CDCl_3$): δ = 20.6, 21.4, 37.3, 38.3, 55.8, 58.4, 110.7, 115.0, 118.4, 122.7, 138.8, 140.2, 141.2, 151.1, 151.9, 169.1 and 169.8 ppm; ESI-MS: m/z (100 %) = 349 $[M + 1]^+$.

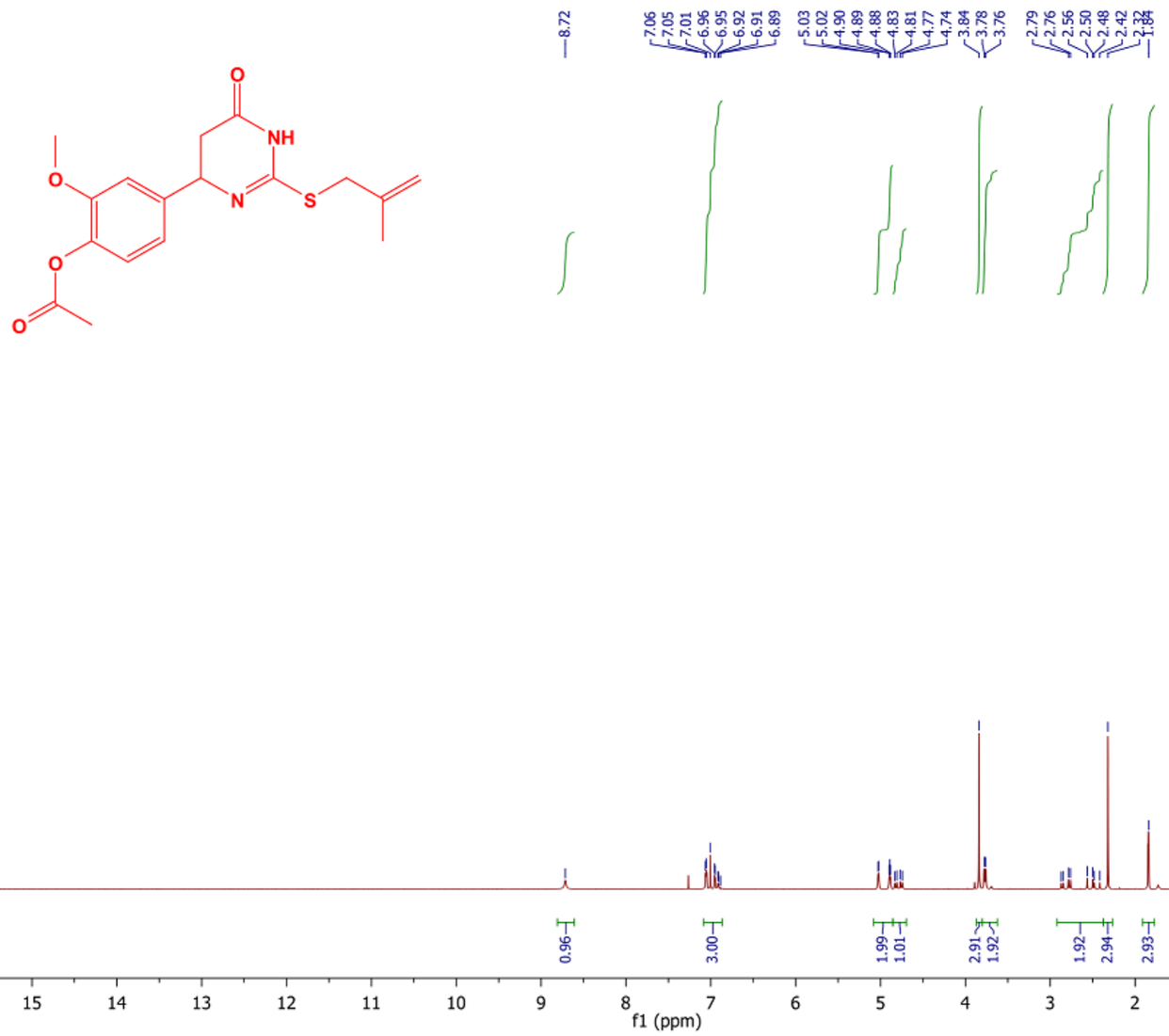


Figure S79 ^{1}H NMR spectrum of **4't**

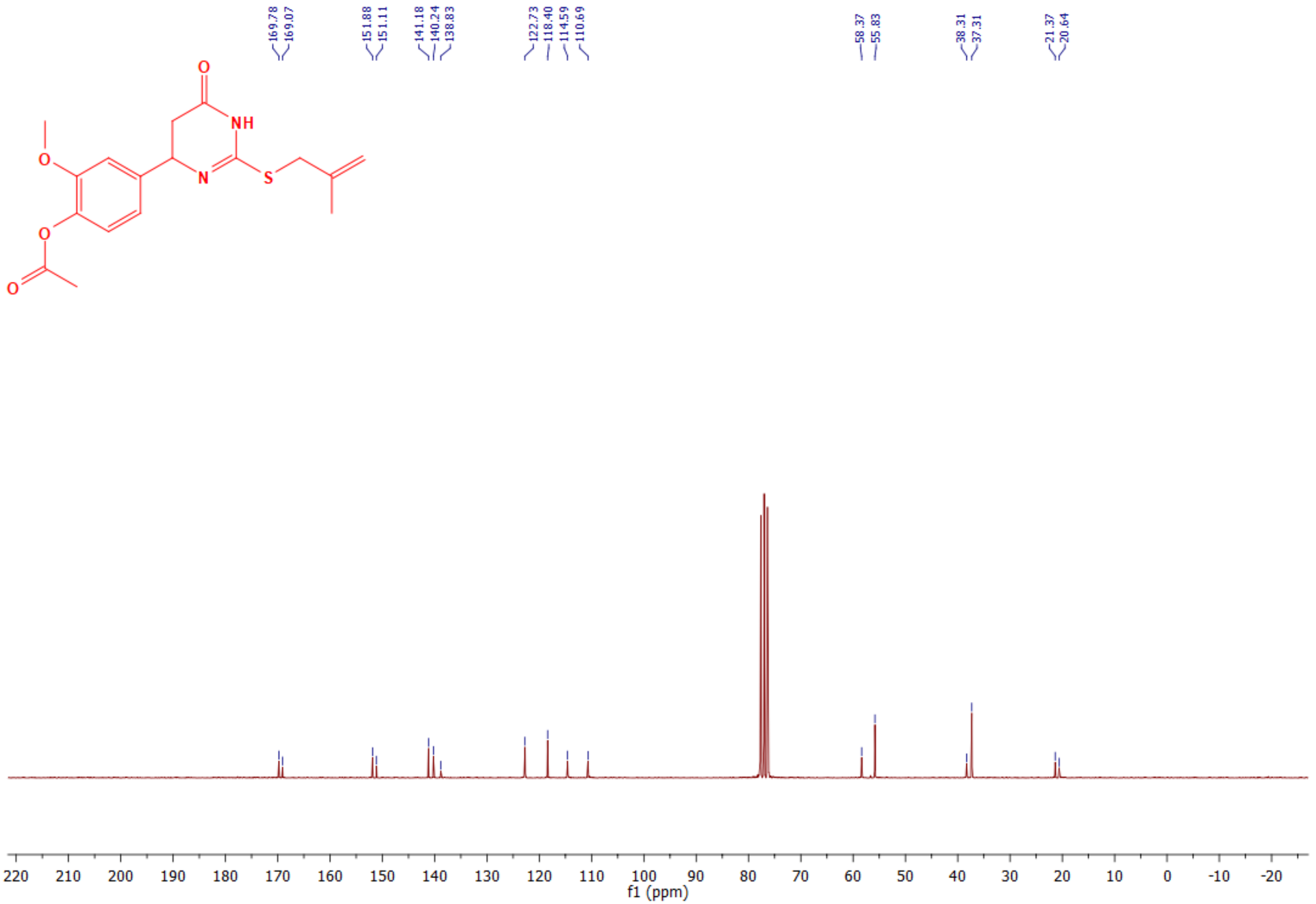


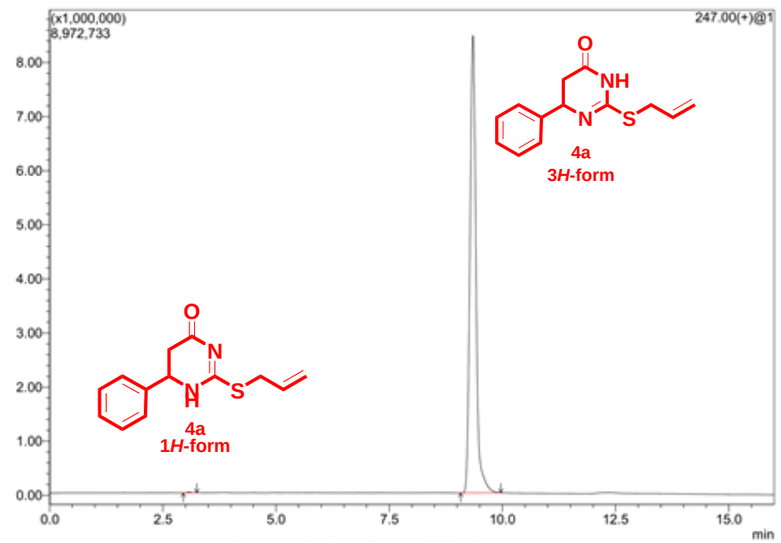
Figure S80 ^{13}C NMR spectrum of **4't**

3. LC/MS spectra of 4a-t

Princip of analysis. Analysis of major (**4a-t** and **4'a-t** are in 3*H*-form) and minor isomer (1*H*-form) was conducted in two steps. Initially, the mass spectra of each compound **4a-t** and **4'a-t** were recorded to determine their masses, and secondly, isomer specificity was determined chromatographically. Each compound **4a-t** and **4'a-t** (5 mg) was dissolved in 1 mL of MeOH and three consecutive dilutions were made in HPLC vials to the final concentration of 10 ng/µl for spectrum collection and 1 ng/µl for chromatographic separation. Flow injection analysis was used for spectra recording. HPLC column was replaced with 4 m long tubing 0.1 mm in diameter, in order to increase system pressure and delay the entrance of the compounds into the ion source. Mobile phase consisted of ACN : 0.1% HCOOH in water (50:50 v/v), isocratic flow rate was set to 0.2 mL/min. Injection volume for each compound was 1 µL. Total run time was 1 min. Spectrums were background corrected, averaging interval being 0.0-0.3 min for each data collection process. Determination of isomer specificity was carried-out chromatographically using the same LC-MS system described above. Final selection of HPLC column was made after conducting separation experiments with three RP columns (Phenomenex Luna® 5u NH_2, 250x4.6 mm, Supelco Discovery® C8 150x4.6mm, 5 µm and Warters Waters Symmetry® C18 150 x 4.6 mm, 5 µm. The last column was chosen since it produced symmetrical peaks and provided satisfactory separation of isomers with small overall baseline drift. Mobile phase consisted of 0.1% formic acid in water (A) and acetonitrile (B). Gradient elution program was set as follows: 0 min – 50% B; 12 min – 100% B (linear increase); 12.01 min – 50% B. Run time was 16 min, injection volume of methanolic solutions from spectra recording (described previously) was 1 µl corresponding to 1 ng of the compound on column. Mass spectrometer parameters (voltages and ion source parameters) were identical as in scan experiments, except for the operating mode. Instead of scanning, MS was collecting data in selected ion monitoring (SIM) mode, the monitored mass being different for each compound matching the masses (M+H) of each molecular ion found during full scan. Ionisation of compounds was efficient resulting in prominent peaks of the major isomer (3*H*). Lower peak was between 0.1% and 2.6% of the major peak area corresponding to the amounts in the order of few picograms which is at the detection limit of the instrument. In order to verify that lower peak originates from the minor isomer (1*H*) an additional experiment was conducted injecting different volumes (1, 2 and 3 µl) of the solution and observing the increase in area of the lower peak only, disregarding the principal peak which saturated the detector due to abundance of the major isomer in solution (Figure S121). It was evident that the increase in lower peak areas match the injection volumes confirming that the peak indeed originates from the minor isomer.

==== Shimadzu LabSolutions Browser Report ====

MS Chromatogram(180113 NJ 706_016.lcd)



MS Qualitative Table(180113 NJ 706_016.lcd)

247.00(Ev1)

Peak#	Ret. Time	Area	m/z	Area%
1	3.075	100130	247.00	0.127
2	9.347	78456707	247.00	99.873
Total		78556837		100.000

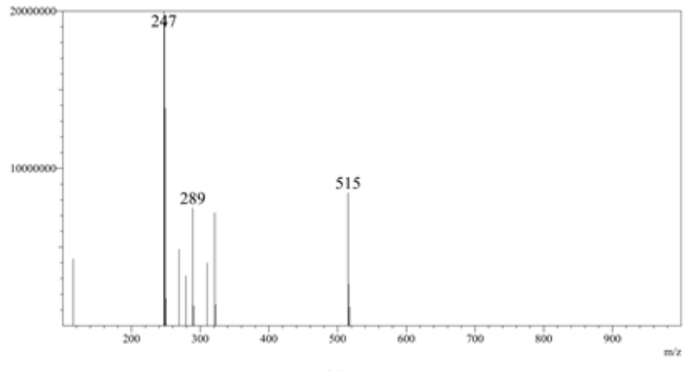
SHIMADZU LabSolutions **Analysis Report**

<Sample Information>

Sample Name	: 180113 NJ 706 Scan		
Sample ID	:		
Data Filename	: 180113 NJ 706 Scan.lcd		
Method Filename	: NNDKG.lcm		
Batch Filename	:		
Vial #	: 1-15	Sample Type	: Unknown
Injection Volume	: 1 uL		
Date Acquired	: 1/13/2018 1:32:45 PM	Acquired by	: System Administrator
Date Processed	: 1/13/2018 3:47:05 PM	Processed by	: System Administrator

MS Spectrum

Line#:1 R.Time:----(Scan#:----)
MassPeaks:15
Spectrum Mode:Averaged 0.367-0.533(23-33) Base Peak:247(20000000)
BG Mode:Averaged 0.000-0.300(1-19) Segment 1 - Event 1



MS Spectrum

Peak#:1 R.Time:0.461(Scan#:28)
MassPeaks:15
Spectrum Mode:Averaged 0.367-0.533(23-33)
BG Mode:Averaged 0.000-0.300(1-19) Segment 1 - Event 1

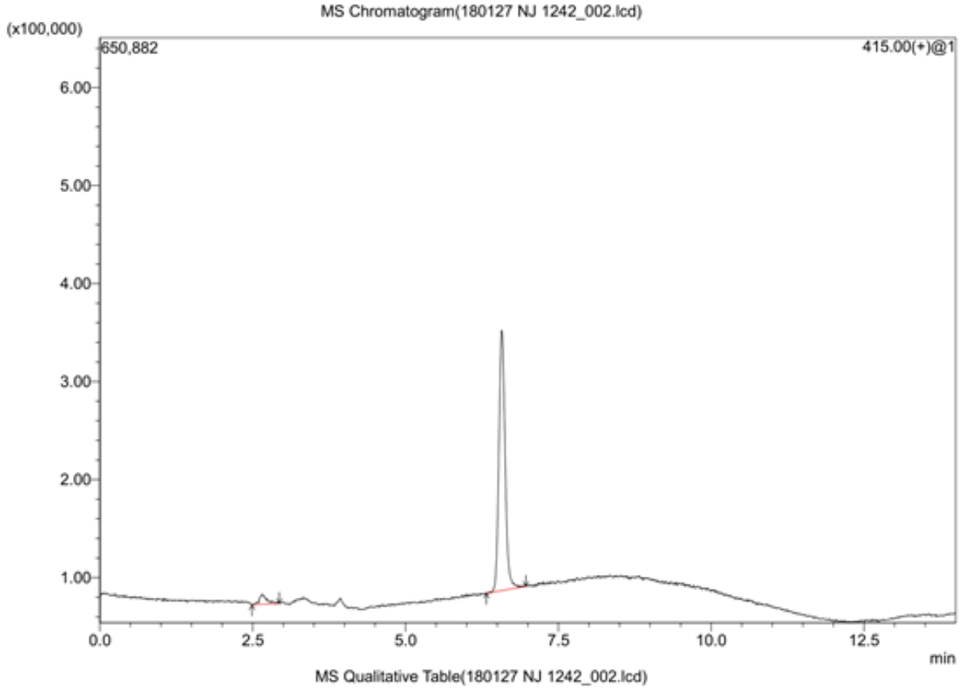
m/z	Absolute Intensity	Relative Intensity
115.20	4262241	21.31
247.10	20000000	100.00
248.10	19205716	96.03
249.15	13818381	69.09
250.15	1734321	8.67
269.10	4864368	24.32
279.15	3185399	15.93
289.15	7474863	37.37

C:\LabSolutions\Data\Nenad KG\NJ 180113 Scan\180113 NJ 706 Scan.lcd

Figure S81 Mass spectra of **4a**

==== Shimadzu LabSolutions Browser Report ====

MS Chromatogram(180127 NJ 1242_002.lcd)



MS Qualitative Table(180127 NJ 1242_002.lcd)

415.00(Ev1)

Peak#	Ret. Time	Area	m/z	Area%
1	2.664	89785	415.00	4.546
2	6.580	1885041	415.00	95.454
Total		1974826		100.000

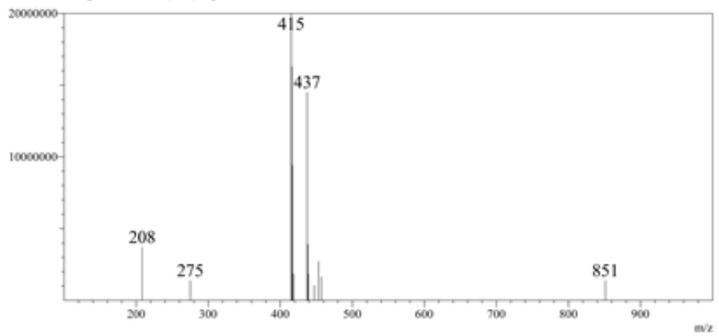
SHIMADZU LabSolutions Analysis Report

<Sample Information>

Sample Name	: 180125 NJ 1242 Spectrum		
Sample ID	:		
Data Filename	: 180125 NJ 1242 Spectrum.lcd		
Method Filename	: NNDKG.lcm		
Batch Filename	:		
Vial #	: 1-2	Sample Type	: Unknown
Injection Volume	: 1 uL		
Date Acquired	: 1/25/2018 11:20:45 AM	Acquired by	: System Administrator
Date Processed	: 1/25/2018 11:21:46 AM	Processed by	: System Administrator

MS Spectrum

Peak#:1 R.Time:0.429(Scan#:26)
MassPeaks:13
Spectrum Mode:Averaged 0.333-0.500(21-31)
BG Mode:Averaged 0.000-0.300(1-19) Segment 1 - Event 1



MS Spectrum

Peak#:1 R.Time:0.429(Scan#:26)
MassPeaks:13
Spectrum Mode:Averaged 0.333-0.500(21-31)
BG Mode:Averaged 0.000-0.300(1-19) Segment 1 - Event 1

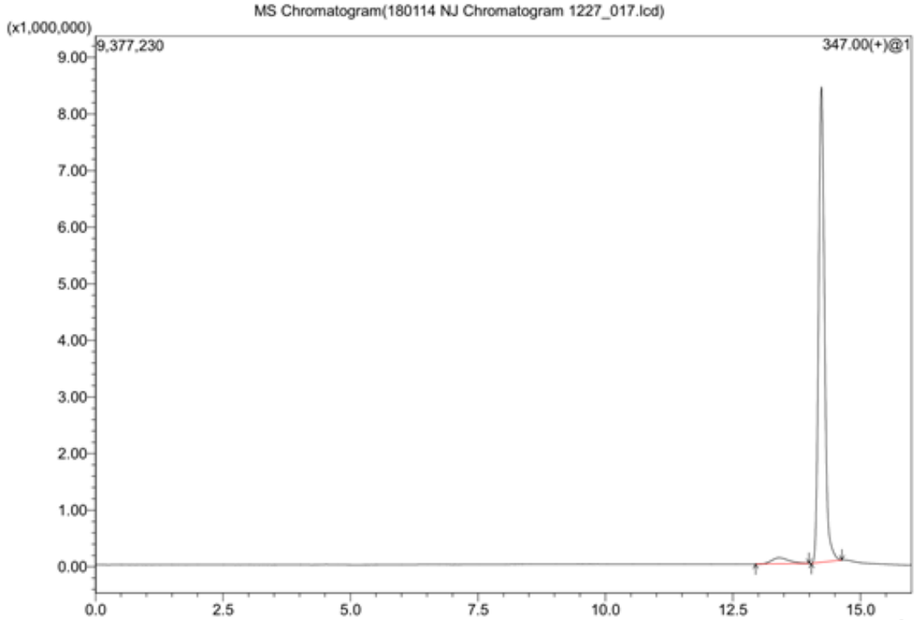
m/z	Absolute Intensity	Relative Intensity
208.20	3696435	18.48
275.15	1367642	6.84
415.15	20000000	100.00
416.20	16304100	81.52
417.20	9416423	47.08
418.20	1846056	9.23

C:\LabSolutions\Data\Nenad KG\180125 NJ 1242 Spectrum.lcd

Figure S82 Mass spectra of **4b**

==== Shimadzu LabSolutions Browser Report ====

MS Chromatogram(180114 NJ Chromatogram 1227_017.lcd)



MS Qualitative Table(180114 NJ Chromatogram 1227_017.lcd)

347.00(Ev1)

Peak#	Ret. Time	Area	m/z	Area%
1	13.409	2507325	347.00	3.538
2	14.237	68353677	347.00	96.462
Total		70861002		100.000

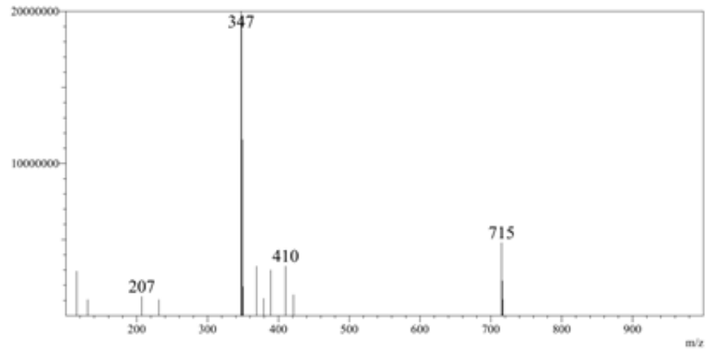
SHIMADZU LabSolutions Analysis Report

<Sample Information>

Sample Name	: 180114 NJ Spectrum 1227		
Sample ID	:		
Data Filename	: 180114 NJ Spectrum 1227_017.lcd		
Method Filename	: NNDKG.lcm		
Batch Filename	: 180114 NJ Spectrum.lcb		
Vial #	: 1-17	Sample Type	: Unknown
Injection Volume	: 1 uL		
Date Acquired	: 1/14/2018 3:24:08 PM	Acquired by	: System Administrator
Date Processed	: 1/14/2018 3:25:09 PM	Processed by	: System Administrator

MS Spectrum

Peak#:1 R.Time:0.456(Scan#:28)
MassPeaks:16
Spectrum Mode:Averaged 0.367-0.533(23-33)
BG Mode:Averaged 0.000-0.300(1-19) Segment 1 - Event 1



MS Spectrum

Peak#:1 R.Time:0.456(Scan#:28)
MassPeaks:16
Spectrum Mode:Averaged 0.367-0.533(23-33)
BG Mode:Averaged 0.000-0.300(1-19) Segment 1 - Event 1

m/z	Absolute Intensity	Relative Intensity
115.20	2935281	14.68
130.60	1056338	5.28
207.10	1268877	6.34
231.10	1055236	5.28
347.10	20000000	100.00
348.20	19242186	96.21
349.20	11570606	57.85
350.20	1907509	9.54

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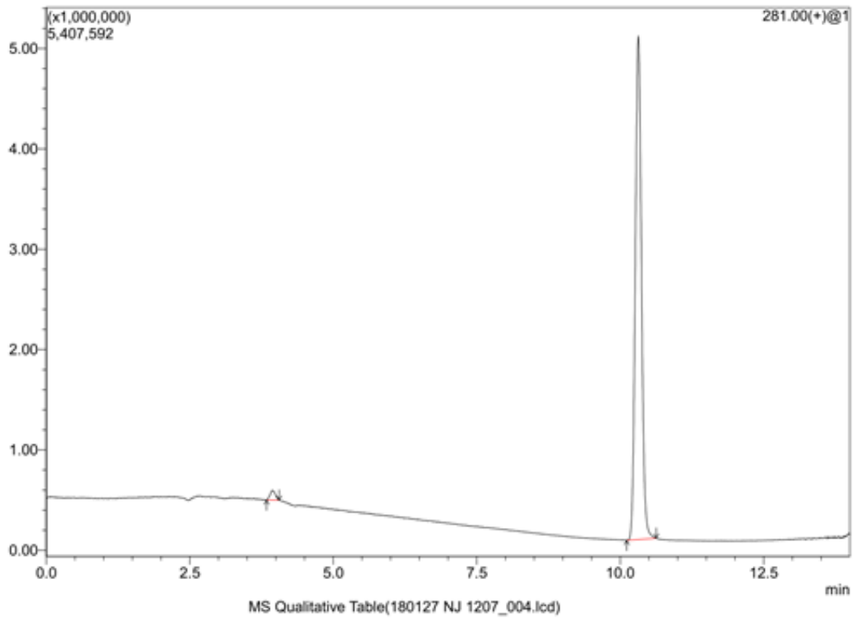
Figure S83 Mass spectra of **4c**

==== Shimadzu LabSolutions Browser Report ====

MS Chromatogram(180127 NJ 1207_004.lcd)



MS Qualitative Table(180127 NJ 1207_004.lcd)

281.00(Ev1)

Peak#	Ret. Time	Area	m/z	Area%
1	3.947	611806	281.00	1.606
2	10.314	37480087	281.00	98.394
Total		38091892		100.000

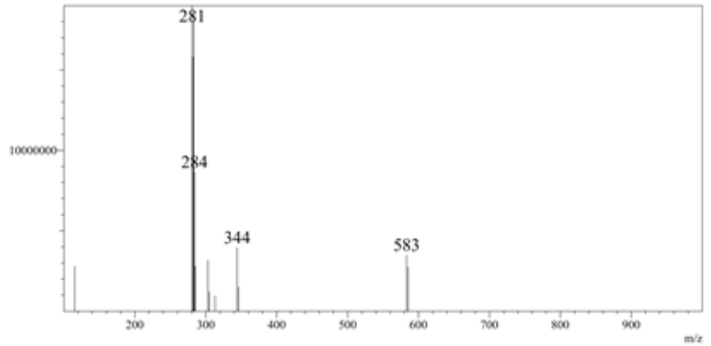
SHIMADZU LabSolutions **Analysis Report**

<Sample Information>

Sample Name	: 180114 NJ Spectrum 1207		
Sample ID	:		
Data Filename	: 180114 NJ Spectrum 1207_012.lcd		
Method Filename	: NNDKG.lcm		
Batch Filename	: 180114 NJ Spectrum.lcb		
Vial #	: 1-12	Sample Type	: Unknown
Injection Volume	: 1 uL		
Date Acquired	: 1/14/2018 3:16:19 PM	Acquired by	: System Administrator
Date Processed	: 1/14/2018 3:17:21 PM	Processed by	: System Administrator

MS Spectrum

Peak#:1 R.Time:0.448(Scan#:27)
MassPeaks:13
Spectrum Mode:Averaged 0.350-0.517(22-32)
BG Mode:Averaged 0.000-0.300(1-19) Segment 1 - Event 1



MS Spectrum

Peak#:1 R.Time:0.448(Scan#:27)
MassPeaks:13
Spectrum Mode:Averaged 0.350-0.517(22-32)
BG Mode:Averaged 0.000-0.300(1-19) Segment 1 - Event 1

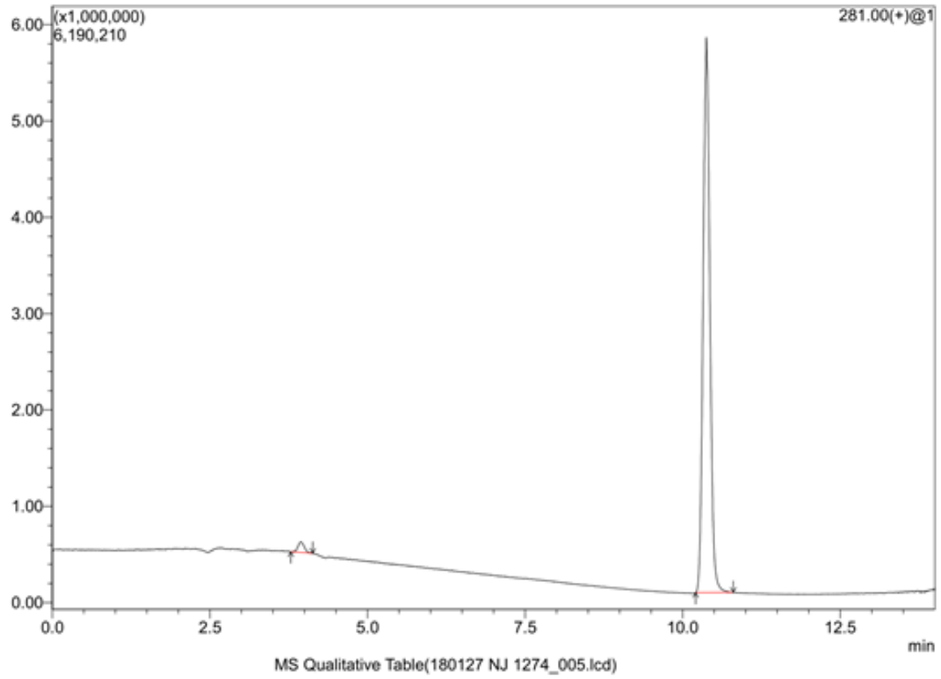
m/z	Absolute Intensity	Relative Intensity
115.20	2804054	14.76
281.05	18994307	100.00
282.10	15825474	83.32
283.05	18106211	95.32
284.10	8659659	45.59
285.10	2808817	14.79

C:\LabSolutions\Data\Nenad KG\NJ 180113 Scan\180114 NJ Spectrum 1207_012.lcd

Figure S84 Mass spectra of **4d**

==== Shimadzu LabSolutions Browser Report ====

MS Chromatogram(180127 NJ 1274_005.lcd)



MS Qualitative Table(180127 NJ 1274_005.lcd)

281.00(Ev1)

Peak#	Ret. Time	Area	m/z	Area%
1	3.949	757370	281.00	1.733
2	10.377	42954561	281.00	98.267
Total		43711932		100.000

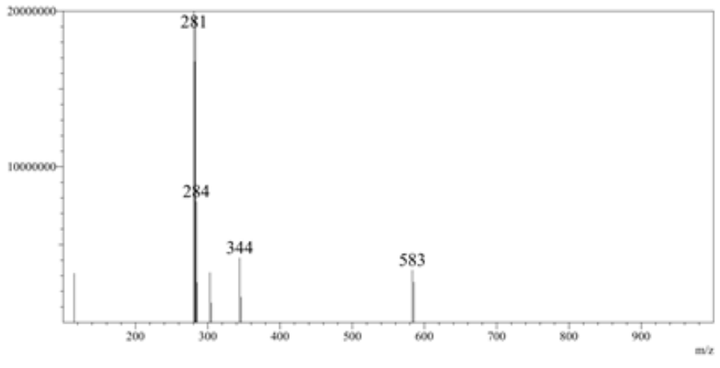
SHIMADZU LabSolutions Analysis Report

<Sample Information>

Sample Name	: 180114 NJ Spectrum 1274		
Sample ID	:		
Data Filename	: 180114 NJ Spectrum 1274_006.lcd		
Method Filename	: NNDKG.lcm		
Batch Filename	: 180114 NJ Spectrum.lcb		
Vial #	: 1-6	Sample Type	: Unknown
Injection Volume	: 1 uL		
Date Acquired	: 1/14/2018 3:06:57 PM	Acquired by	: System Administrator
Date Processed	: 1/14/2018 3:07:59 PM	Processed by	: System Administrator

MS Spectrum

Peak#:1 R.Time:0.467(Scan#:29)
MassPeaks:12
Spectrum Mode:Averaged 0.383-0.550(24-34)
BG Mode:Averaged 0.000-0.300(1-19) Segment 1 - Event 1



MS Spectrum

Peak#:1 R.Time:0.467(Scan#:29)
MassPeaks:12
Spectrum Mode:Averaged 0.383-0.550(24-34)
BG Mode:Averaged 0.000-0.300(1-19) Segment 1 - Event 1

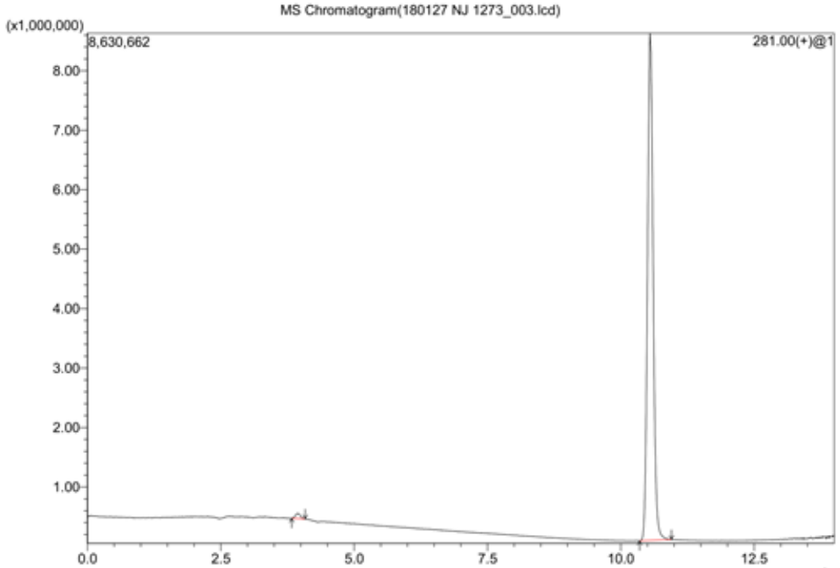
m/z	Absolute Intensity	Relative Intensity
115.20	3161600	15.81
281.05	20000000	100.00
282.10	16767942	83.84
283.05	19672346	98.36
284.10	7770752	38.85
285.10	2578137	12.89

C:\LabSolutions\Data\Nenad KG\NJ 180113 Scan\180114 NJ Spectrum 1274_006.lcd

Figure S85 Mass spectra of **4e**

==== Shimadzu LabSolutions Browser Report ====

MS Chromatogram(180127 NJ 1273_003.lcd)



MS Qualitative Table(180127 NJ 1273_003.lcd)

281.00(Ev1)

Peak#	Ret. Time	Area	m/z	Area%
1	3.947	543641	281.00	0.860
2	10.549	62706211	281.00	99.140
Total		63249852		100.000

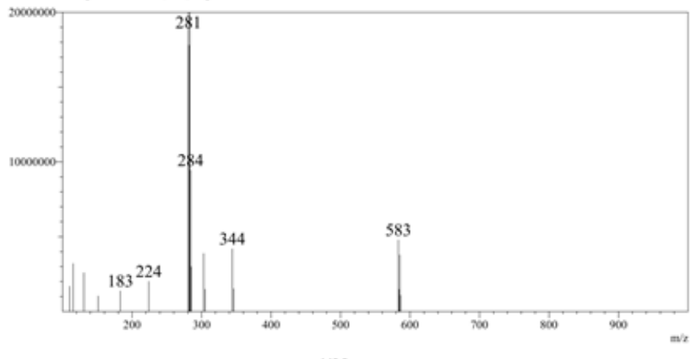
SHIMADZU LabSolutions **Analysis Report**

<Sample Information>

Sample Name	: 180114 NJ Spectrum 1273		
Sample ID	:		
Data Filename	: 180114 NJ Spectrum 1273_009.lcd		
Method Filename	: NNDKG.lcm		
Batch Filename	: 180114 NJ Spectrum.lcb		
Vial #	: 1-9	Sample Type	: Unknown
Injection Volume	: 1 uL		
Date Acquired	: 1/14/2018 3:11:38 PM	Acquired by	: System Administrator
Date Processed	: 1/14/2018 3:12:40 PM	Processed by	: System Administrator

MS Spectrum

Peak#:1 R.Time:0.454(Scan#:28)
MassPeaks:19
Spectrum Mode:Averaged 0.367-0.533(23-33)
BG Mode:Averaged 0.000-0.300(1-19) Segment 1 - Event 1



MS Spectrum

Peak#:1 R.Time:0.454(Scan#:28)
MassPeaks:19
Spectrum Mode:Averaged 0.367-0.533(23-33)
BG Mode:Averaged 0.000-0.300(1-19) Segment 1 - Event 1

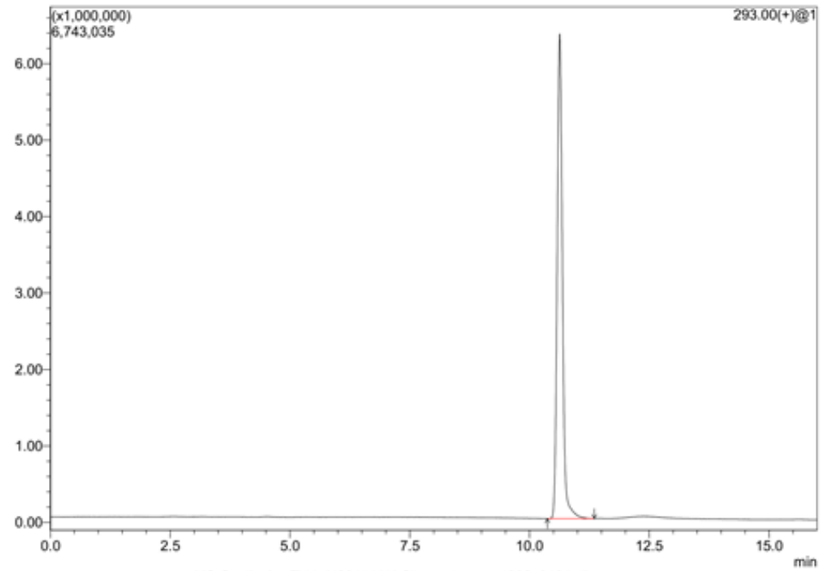
m/z	Absolute Intensity	Relative Intensity
110.10	1691926	8.46
115.20	3211351	16.06
130.65	2598042	12.99
151.15	1038287	5.19
183.05	1382970	6.91
224.05	2018597	10.09
281.05	20000000	100.00
282.10	17803122	89.02
283.05	20000000	100.00
284.10	9445673	47.23

C:\LabSolutions\Data\Nenad KG\NJ 180113 Scan\180114 NJ Spectrum 1273_009.lcd

Figure S86 Mass spectra of **4f**

==== Shimadzu LabSolutions Browser Report ====

MS Chromatogram(180114 NJ Chromatogram 1206_016.lcd)



MS Qualitative Table(180114 NJ Chromatogram 1206_016.lcd)

293.00(Ev1)

Peak#	Ret. Time	Area	m/z	Area%
1	10.629	48812124	293.00	100.000
Total		48812124		100.000

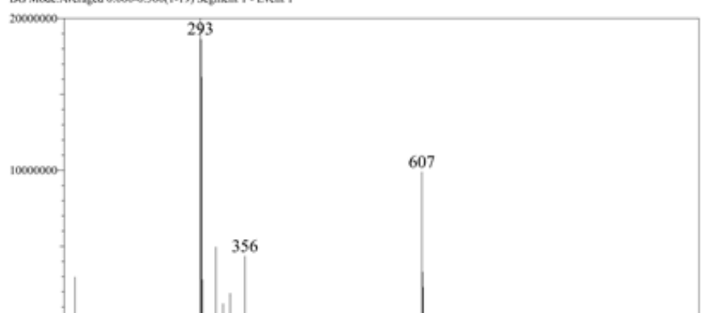
SHIMADZU LabSolutions **Analysis Report**

<Sample Information>

Sample Name	: 180114 NJ Spectrum 1206		
Sample ID	:		
Data Filename	: 180114 NJ Spectrum 1206_016.lcd		
Method Filename	: NNDKG.lcm		
Batch Filename	: 180114 NJ Spectrum.lcb		
Vial #	: 1-16	Sample Type	: Unknown
Injection Volume	: 1 uL		
Date Acquired	: 1/14/2018 3:22:34 PM	Acquired by	: System Administrator
Date Processed	: 1/14/2018 3:23:36 PM	Processed by	: System Administrator

MS Spectrum

Peak#:1 R.Time:0.454(Scan#:28)
MassPeaks:12
Spectrum Mode:Averaged 0.367-0.533(23-33)
BG Mode:Averaged 0.000-0.300(1-19) Segment 1 - Event 1



MS Spectrum

Peak#:1 R.Time:0.454(Scan#:28)
MassPeaks:12
Spectrum Mode:Averaged 0.367-0.533(23-33)
BG Mode:Averaged 0.000-0.300(1-19) Segment 1 - Event 1

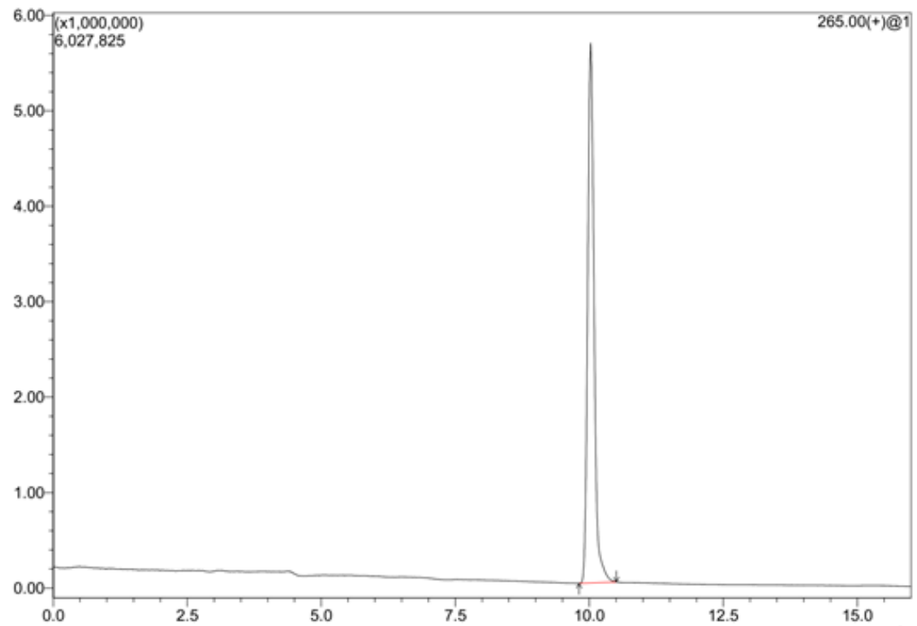
m/z	Absolute Intensity	Relative Intensity
115.20	2984002	14.92
293.10	20000000	100.00
294.10	18618501	93.09
295.10	16139220	80.70
296.15	2807384	14.04
315.10	4962650	24.81

C:\LabSolutions\Data\Nenad KG\NJ 180113 Scan\180114 NJ Spectrum 1206_016.lcd

Figure S87 Mass spectra of **4g**

==== Shimadzu LabSolutions Browser Report ====

MS Chromatogram(180113 NJ 1247_010.lcd)



MS Qualitative Table(180113 NJ 1247_010.lcd)

265.00(Ev1)

Peak#	Ret. Time	Area	m/z	Area%
1	10.026	47298868	265.00	100.000
Total		47298868		100.000

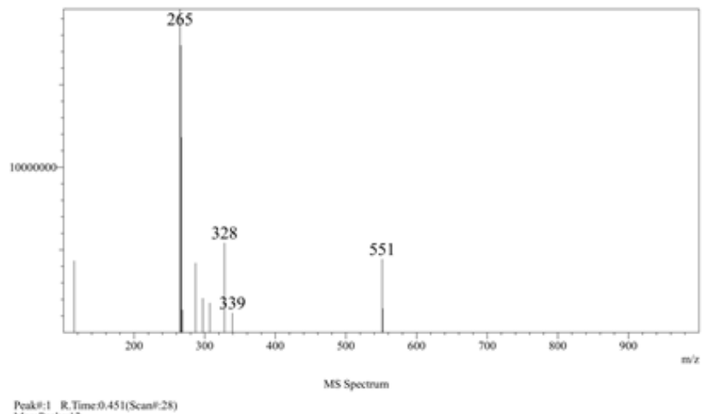
SHIMADZU LabSolutions Analysis Report

<Sample Information>

Sample Name	: 180113 NJ 1247 Scan		
Sample ID	:		
Data Filename	: 180113 NJ 1247 Scan.lcd		
Method Filename	: NNDKG.lcm		
Batch Filename	:		
Vial #	: 1-9	Sample Type	: Unknown
Injection Volume	: 1 uL		
Date Acquired	: 1/13/2018 12:53:11 PM	Acquired by	: System Administrator
Date Processed	: 1/13/2018 3:32:46 PM	Processed by	: System Administrator

MS Spectrum

Line#:1 R.Time:----(Scan#:----)
MassPeaks:12
Spectrum Mode:Averaged 0.367-0.533(23-33) Base Peak:265(19579278)
BG Mode:Averaged 0.000-0.300(1-19) Segment 1 - Event 1



MS Spectrum

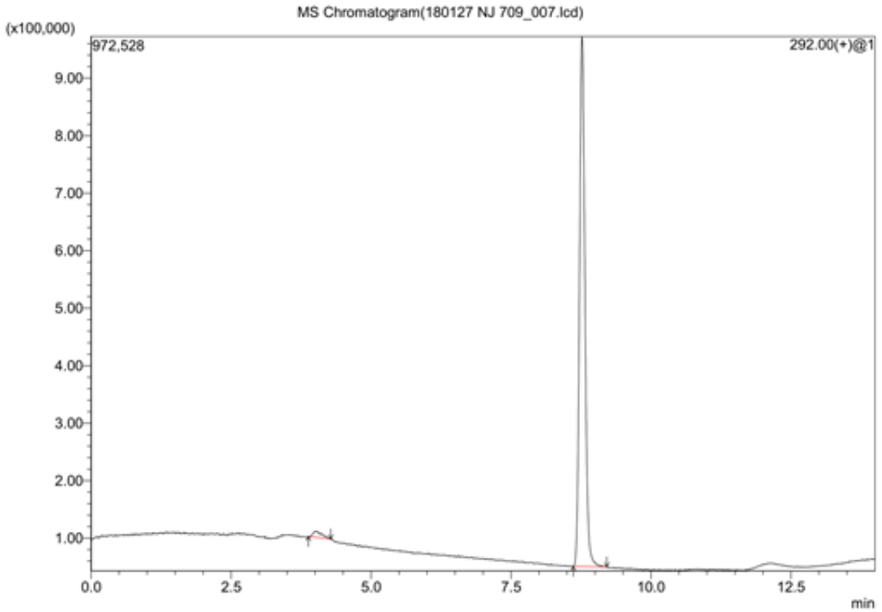
Peak#:1 R.Time:0.451(Scan#:28)
MassPeaks:12
Spectrum Mode:Averaged 0.367-0.533(23-33)
BG Mode:Averaged 0.000-0.300(1-19) Segment 1 - Event 1

m/z	Absolute Intensity	Relative Intensity
115.20	4340251	22.17
265.05	19579278	100.00
266.10	17384234	88.79
267.10	11808512	60.31
268.15	1370273	7.00
287.10	4201346	21.46

C:\LabSolutions\Data\Nenad KG\NJ 180113 Scan\180113 NJ 1247 Scan.lcd

Figure S88 Mass spectra of **4h**

==== Shimadzu LabSolutions Browser Report ====



MS Qualitative Table(180127 NJ 709_007.lcd)

292.00(Ev1)

Peak#	Ret. Time	Area	m/z	Area%
1	4.021	114378	292.00	1.795
2	8.772	6257860	292.00	98.205
Total		6372238		100.000

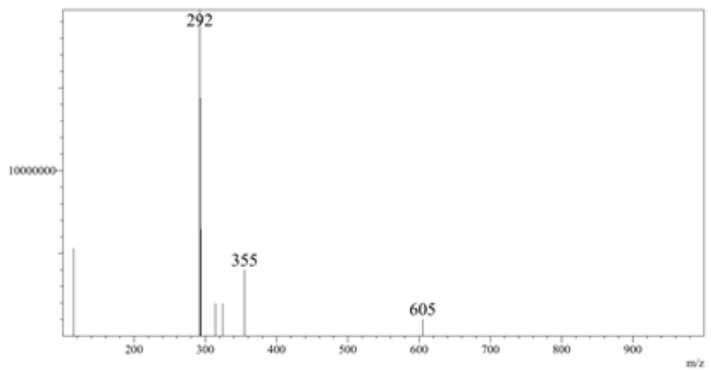
SHIMADZU LabSolutions **Analysis Report**

<Sample Information>

Sample Name	: 180113 NJ 709 Scan		
Sample ID	:		
Data Filename	: 180113 NJ 709 Scan.lcd		
Method Filename	: NNDKG.lcm		
Batch Filename	:		
Vial #	: 1-18	Sample Type	: Unknown
Injection Volume	: 1 uL		
Date Acquired	: 1/13/2018 1:41:38 PM	Acquired by	: System Administrator
Date Processed	: 1/13/2018 3:50:44 PM	Processed by	: System Administrator

MS Spectrum

Line#:1 R.Time:----(Scan#:----)
MassPeaks:8
Spectrum Mode:Averaged 0.367-0.533(23-33) Base Peak:292(19719938)
BG Mode:Averaged 0.000-0.300(1-19) Segment 1 - Event 1



MS Spectrum

Peak#:1 R.Time:0.459(Scan#:28)
MassPeaks:8
Spectrum Mode:Averaged 0.367-0.533(23-33)
BG Mode:Averaged 0.000-0.300(1-19) Segment 1 - Event 1

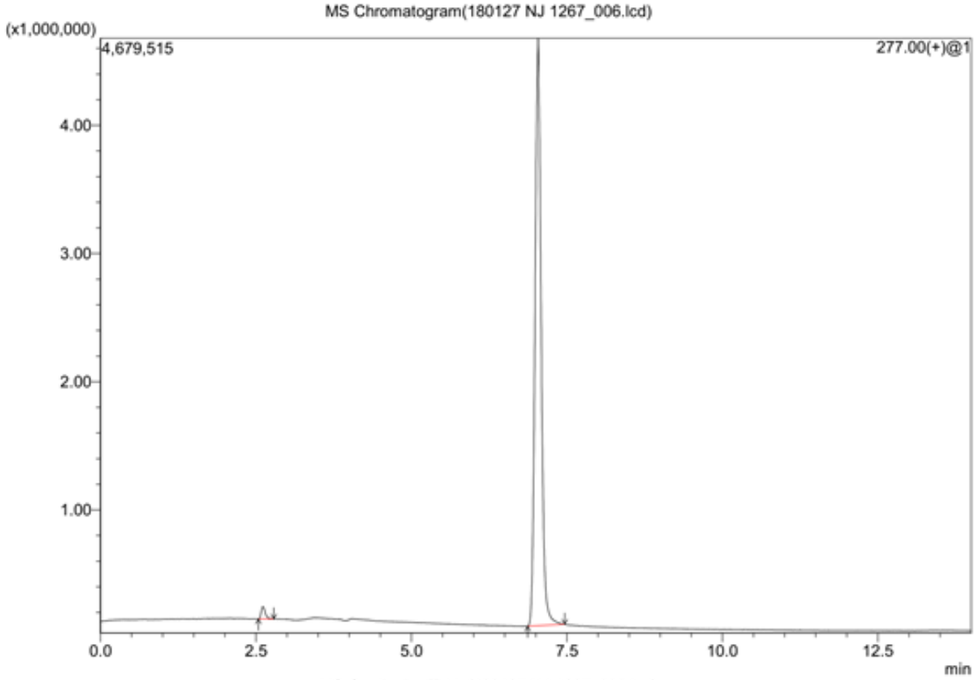
m/z	Absolute Intensity	Relative Intensity
115.15	5285923	26.80
292.10	19719938	100.00
293.10	14391005	72.98
294.10	6466465	32.79

C:\LabSolutions\Data\Nenad KG\NJ 180113 Scan\180113 NJ 709 Scan.lcd

Figure S89 Mass spectra of 4**i**

==== Shimadzu LabSolutions Browser Report ====

MS Chromatogram(180127 NJ 1267_006.lcd)



MS Qualitative Table(180127 NJ 1267_006.lcd)

277.00(Ev1)

Peak#	Ret. Time	Area	m/z	Area%
1	2.616	435906	277.00	1.375
2	7.039	31257696	277.00	98.625
Total		31693602		100.000

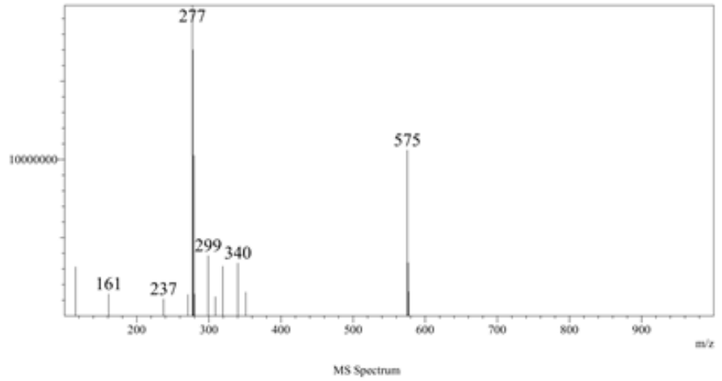
SHIMADZU LabSolutions Analysis Report

<Sample Information>

Sample Name	: 180114 NJ Spectrum 1267		
Sample ID	:		
Data Filename	: 180114 NJ Spectrum 1267_007.lcd		
Method Filename	: NNDKG.lcm		
Batch Filename	: 180114 NJ Spectrum.lcb		
Vial #	: 1-7	Sample Type	: Unknown
Injection Volume	: 1 uL		
Date Acquired	: 1/14/2018 3:08:31 PM	Acquired by	: System Administrator
Date Processed	: 1/14/2018 3:09:32 PM	Processed by	: System Administrator

MS Spectrum

Peak#:1 R.Time:0.449(Scan#:27)
MassPeaks:16
Spectrum Mode:Averaged 0.350-0.517(22-32)
BG Mode:Averaged 0.000-0.300(1-19) Segment 1 - Event 1



MS Spectrum

Peak#:1 R.Time:0.449(Scan#:27)
MassPeaks:16
Spectrum Mode:Averaged 0.350-0.517(22-32)
BG Mode:Averaged 0.000-0.300(1-19) Segment 1 - Event 1

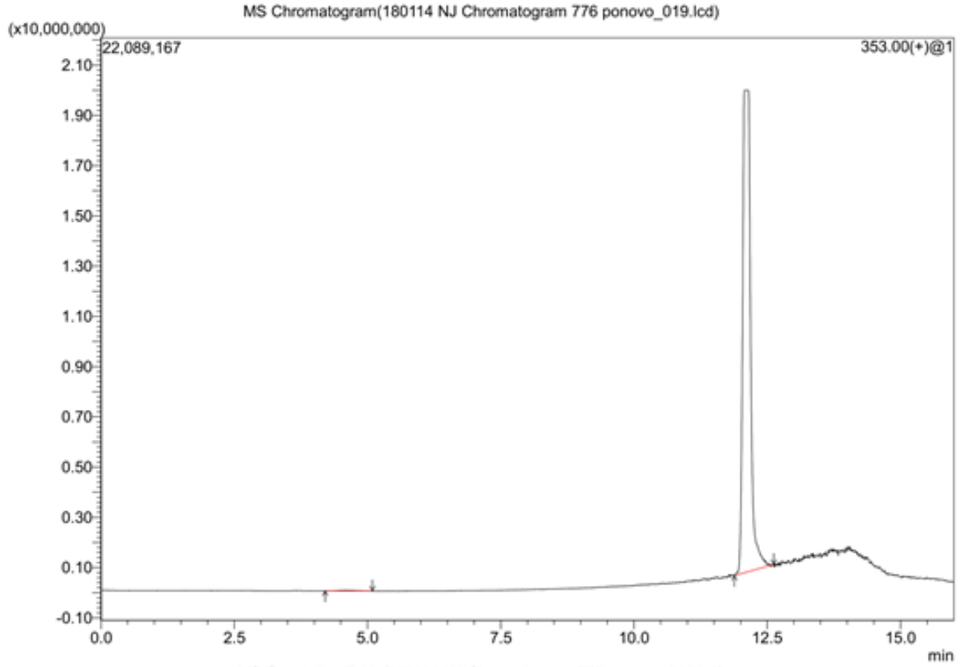
m/z	Absolute Intensity	Relative Intensity
115.20	3138950	15.82
161.10	1406179	7.09
237.10	1076767	5.43
271.15	1364400	6.88
277.10	19845159	100.00
278.15	17014602	85.74
279.15	10258672	51.69
280.15	1399747	7.05

C:\LabSolutions\Data\Nenad KG\NJ 180113 Scan\180114 NJ Spectrum 1267_007.lcd

Figure S90 Mass spectra of **4j**

==== Shimadzu LabSolutions Browser Report ====

MS Chromatogram(180114 NJ Chromatogram 776 ponovo_019.lcd)



MS Qualitative Table(180114 NJ Chromatogram 776 ponovo_019.lcd)

353.00(Ev1)

Peak#	Ret. Time	Area	m/z	Area%
1	4.611	619307	353.00	0.312
2	12.111	198158382	353.00	99.688
Total		198777689		100.000

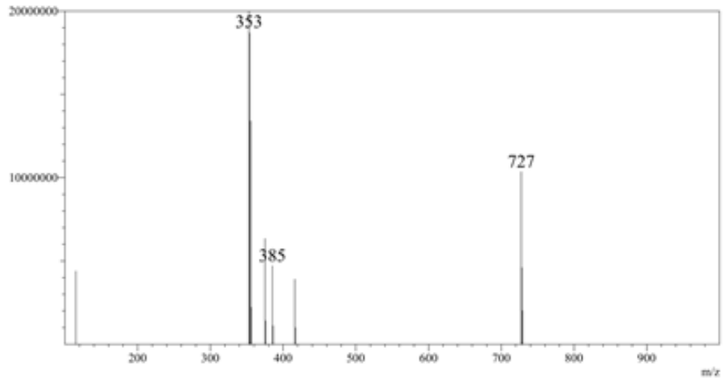
SHIMADZU LabSolutions **Analysis Report**

<Sample Information>

Sample Name	: 180113 NJ 776 Scan		
Sample ID	:		
Data Filename	: 180113 NJ 776 Scan.lcd		
Method Filename	: NNDKG.lcm		
Batch Filename	:		
Vial #	: 1-19	Sample Type	: Unknown
Injection Volume	: 1 uL		
Date Acquired	: 1/13/2018 1:43:54 PM	Acquired by	: System Administrator
Date Processed	: 1/13/2018 3:52:03 PM	Processed by	: System Administrator

MS Spectrum

Line#:1 R.Time:----(Scan#:----)
MassPeaks:14
Spectrum Mode:Averaged 0.367-0.533(23-33) Base Peak:353(20000000)
BG Mode:Averaged 0.000-0.300(1-19) Segment 1 - Event 1



MS Spectrum

Peak#:1 R.Time:0.466(Scan#:28)
MassPeaks:14
Spectrum Mode:Averaged 0.367-0.533(23-33)
BG Mode:Averaged 0.000-0.300(1-19) Segment 1 - Event 1

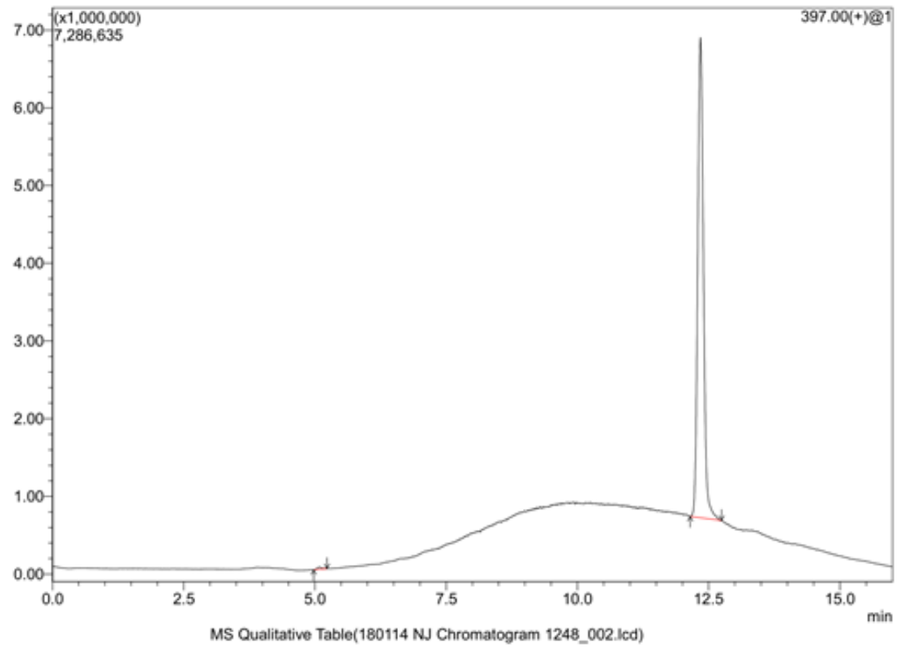
m/z	Absolute Intensity	Relative Intensity
115.20	4401858	22.01
353.10	20000000	100.00
354.20	18689724	93.45
355.20	13407699	67.04
356.20	2221201	11.11
375.15	6349307	31.75
376.15	1420636	7.10

C:\LabSolutions\Data\Nenad KG\NJ 180113 Scan\180113 NJ 776 Scan.lcd

Figure S91 Mass spectra of **4k**

==== Shimadzu LabSolutions Browser Report ====

MS Chromatogram(180114 NJ Chromatogram 1248_002.lcd)



MS Qualitative Table(180114 NJ Chromatogram 1248_002.lcd)

397.00(Ev1)

Peak#	Ret. Time	Area	m/z	Area%
1	5.092	158453	397.00	0.336
2	12.344	46940849	397.00	99.664
Total		47099302		100.000

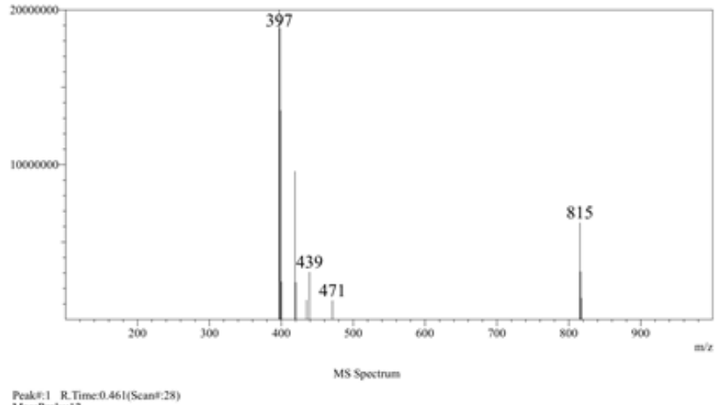
SHIMADZU LabSolutions **Analysis Report**

<Sample Information>

Sample Name	: 180114 NJ Spectrum 1248		
Sample ID	:		
Data Filename	: 180114 NJ Spectrum 1248_002.lcd		
Method Filename	: NNDKG.lcm		
Batch Filename	: 180114 NJ Spectrum.lcb		
Vial #	: 1-2	Sample Type	: Unknown
Injection Volume	: 1 uL		
Date Acquired	: 1/14/2018 3:00:26 PM	Acquired by	: System Administrator
Date Processed	: 1/14/2018 3:01:27 PM	Processed by	: System Administrator

MS Spectrum

Peak#:1 R.Time:0.461(Scan#:28)
MassPeaks:12
Spectrum Mode:Averaged 0.367-0.533(23-33)
BG Mode:Averaged 0.000-0.300(1-19) Segment 1 - Event 1



MS Spectrum

Peak#:1 R.Time:0.461(Scan#:28)
MassPeaks:12
Spectrum Mode:Averaged 0.367-0.533(23-33)
BG Mode:Averaged 0.000-0.300(1-19) Segment 1 - Event 1

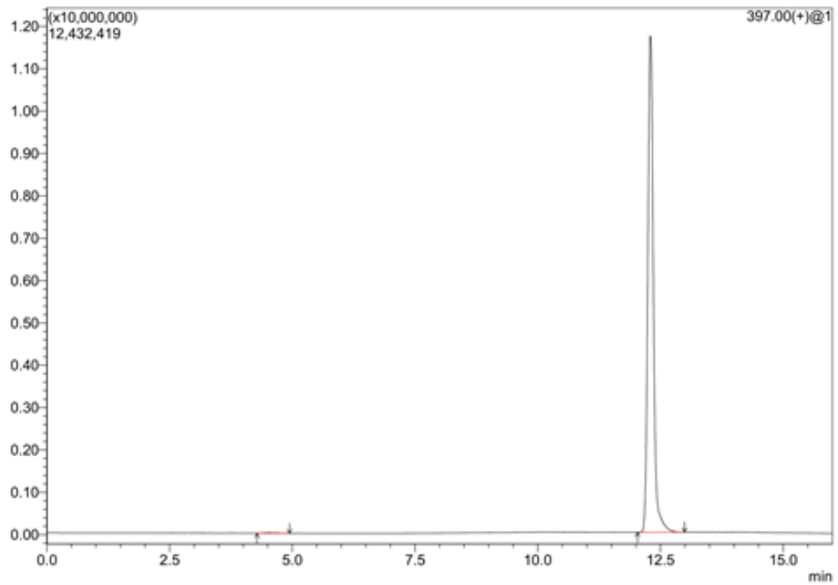
m/z	Absolute Intensity	Relative Intensity
397.15	20000000	100.00
398.20	18827475	94.14
399.20	13510403	67.55
400.25	2443339	12.22
419.15	9574069	47.87
420.20	2403342	12.02

C:\LabSolutions\Data\Nenad KG\NJ 180113 Scan\180114 NJ Spectrum 1248_002.lcd

Figure S92 Mass spectra of **4l**

==== Shimadzu LabSolutions Browser Report ====

MS Chromatogram(180114 NJ Chromatogram 1260_013.lcd)



MS Qualitative Table(180114 NJ Chromatogram 1260_013.lcd)

397.00(Ev1)

Peak#	Ret. Time	Area	m/z	Area%
1	4.532	169412	397.00	0.182
2	12.295	92710058	397.00	99.818
Total		92879470		100.000

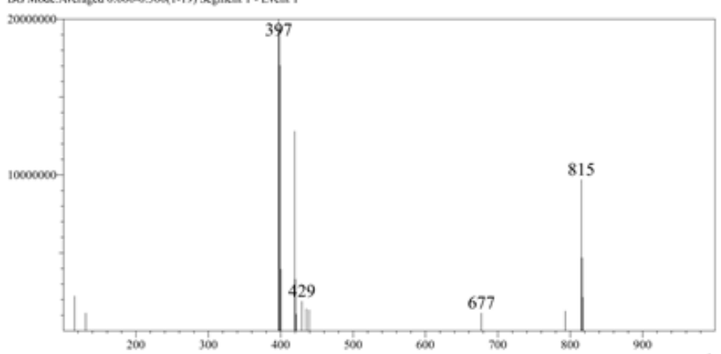
SHIMADZU LabSolutions Analysis Report

<Sample Information>

Sample Name	: 180114 NJ Spectrum 1260		
Sample ID	:		
Data Filename	: 180114 NJ Spectrum 1260_013.lcd		
Method Filename	: NNDKG.lcm		
Batch Filename	: 180114 NJ Spectrum.lcb		
Vial #	: 1-13	Sample Type	: Unknown
Injection Volume	: 1 uL		
Date Acquired	: 1/14/2018 3:17:53 PM	Acquired by	: System Administrator
Date Processed	: 1/14/2018 3:18:55 PM	Processed by	: System Administrator

MS Spectrum

Peak#:1 R.Time:0.439(Scan#:27)
MassPeaks:17
Spectrum Mode:Averaged 0.350-0.517(22-32)
BG Mode:Averaged 0.000-0.300(1-19) Segment 1 - Event 1



MS Spectrum

Peak#:1 R.Time:0.439(Scan#:27)
MassPeaks:17
Spectrum Mode:Averaged 0.350-0.517(22-32)
BG Mode:Averaged 0.000-0.300(1-19) Segment 1 - Event 1

m/z	Absolute Intensity	Relative Intensity
115.20	2241610	11.21
130.65	1146783	5.73
397.15	20000000	100.00
398.20	19417686	97.09
399.20	17027353	85.14
400.25	3962757	19.81
419.20	12817127	64.09
420.20	3320053	16.60
421.20	1072611	5.36

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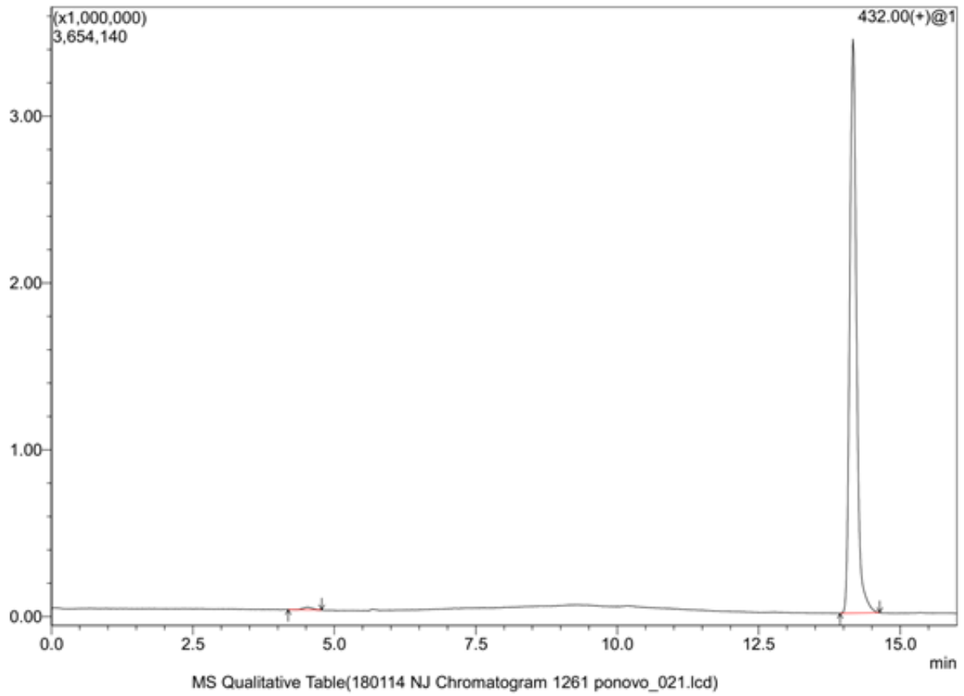
Figure S93 Mass spectra of **4m**

==== Shimadzu LabSolutions Browser Report ====

MS Chromatogram(180114 NJ Chromatogram 1261 ponovo_021.lcd)



MS Qualitative Table(180114 NJ Chromatogram 1261 ponovo_021.lcd)

432.00(Ev1)

Peak#	Ret. Time	Area	m/z	Area%
1	4.525	169909	432.00	0.588
2	14.166	28735362	432.00	99.412
Total		28905271		100.000

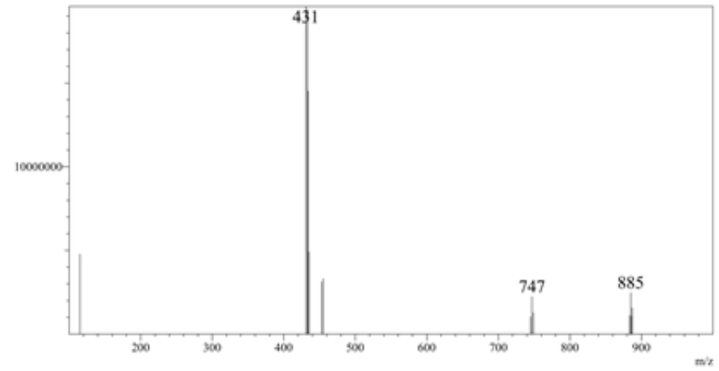
SHIMADZU LabSolutions Analysis Report

<Sample Information>

Sample Name	: 180113 NJ 1261 Scan		
Sample ID	:		
Data Filename	: 180113 NJ 1261 Scan.lcd		
Method Filename	: NNDKG.lcm		
Batch Filename	:		
Vial #	: 1-7	Sample Type	: Unknown
Injection Volume	: 1 uL		
Date Acquired	: 1/13/2018 12:48:51 PM	Acquired by	: System Administrator
Date Processed	: 1/13/2018 3:29:41 PM	Processed by	: System Administrator

MS Spectrum

Line#:1 R.Time:----(Scan#:----)
MassPeaks:14
Spectrum Mode:Averaged 0.367-0.533(23-33) Base Peak:431(19588924)
BG Mode:Averaged 0.000-0.300(1-19) Segment 1 - Event 1



MS Spectrum

Peak#:1 R.Time:0.463(Scan#:28)
MassPeaks:14
Spectrum Mode:Averaged 0.367-0.533(23-33)
BG Mode:Averaged 0.000-0.300(1-19) Segment 1 - Event 1

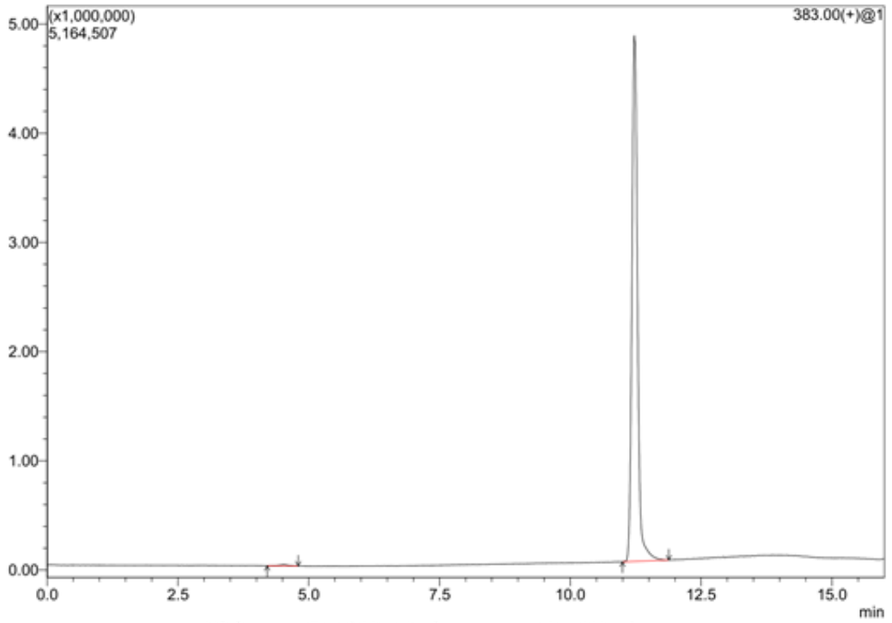
m/z	Absolute Intensity	Relative Intensity
115.20	4784047	24.42
431.05	19588924	100.00
433.05	19443618	99.26
434.05	14535709	74.20
435.10	4914293	25.09
453.05	3117547	15.91
455.05	3310085	16.90

C:\LabSolutions\Data\Nenad KG\NJ 180113 Scan\180113 NJ 1261 Scan.lcd

Figure S94 Mass spectra of **4n**

==== Shimadzu LabSolutions Browser Report ====

MS Chromatogram(180114 NJ Chromatogram 1214_008.lcd)



MS Qualitative Table(180114 NJ Chromatogram 1214_008.lcd)

383.00(Ev1)

Peak#	Ret. Time	Area	m/z	Area%
1	4.527	122652	383.00	0.338
2	11.234	36186909	383.00	99.662
Total		36309561		100.000

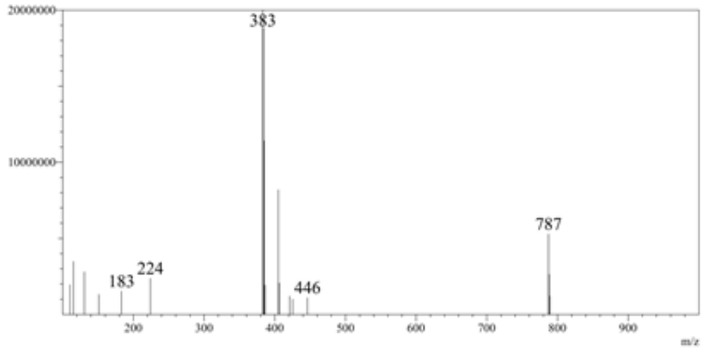
SHIMADZU LabSolutions Analysis Report

<Sample Information>

Sample Name	: 180114 NJ Spectrum 1214		
Sample ID	:		
Data Filename	: 180114 NJ Spectrum 1214_008.lcd		
Method Filename	: NNDKG.lcm		
Batch Filename	: 180114 NJ Spectrum.lcb		
Vial #	: 1-8	Sample Type	: Unknown
Injection Volume	: 1 uL		
Date Acquired	: 1/14/2018 3:10:04 PM	Acquired by	: System Administrator
Date Processed	: 1/14/2018 3:11:06 PM	Processed by	: System Administrator

MS Spectrum

Peak#:1 R.Time:0.451(Scan#:28)
MassPeaks:18
Spectrum Mode:Averaged 0.367-0.533(23-33)
BG Mode:Averaged 0.000-0.300(1-19) Segment 1 - Event 1



MS Spectrum

Peak#:1 R.Time:0.451(Scan#:28)
MassPeaks:18
Spectrum Mode:Averaged 0.367-0.533(23-33)
BG Mode:Averaged 0.000-0.300(1-19) Segment 1 - Event 1

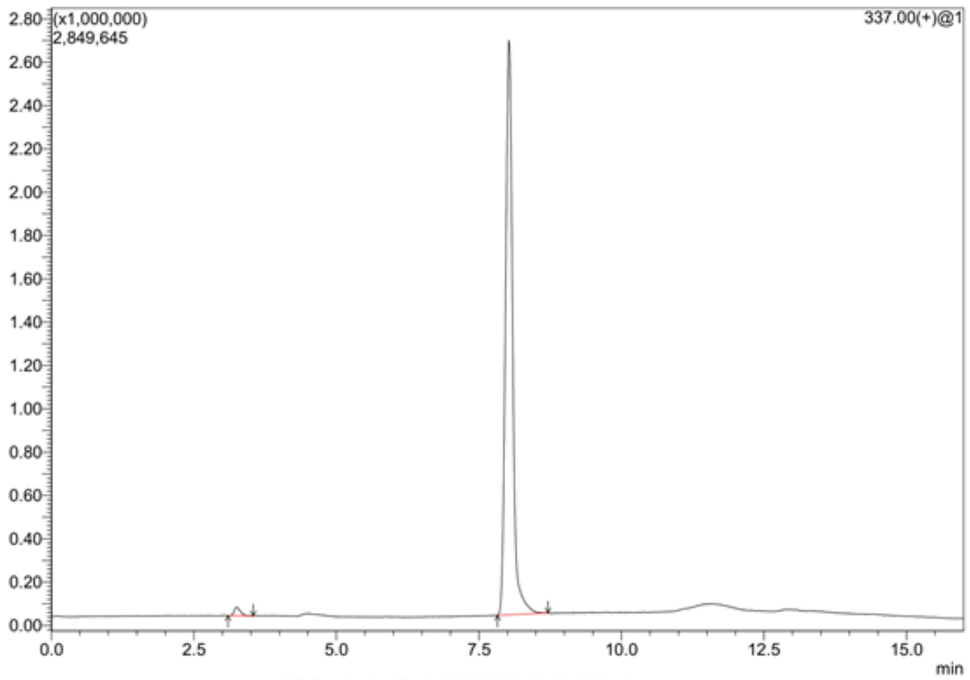
m/z	Absolute Intensity	Relative Intensity
110.15	1958475	9.79
115.15	3487410	17.44
130.60	2804201	14.02
151.15	1323954	6.62
183.05	1527973	7.64
224.05	2379511	11.90
383.15	20000000	100.00
384.20	18816702	94.08
385.20	11422948	57.11

C:\LabSolutions\Data\Nenad KG\NJ 180113 Scan\180114 NJ Spectrum 1214_008.lcd

Figure S95 Mass spectra of **4o**

==== Shimadzu LabSolutions Browser Report ====

MS Chromatogram(180113 NJ 1219_017.lcd)



MS Qualitative Table(180113 NJ 1219_017.lcd)

337.00(Ev1)

Peak#	Ret. Time	Area	m/z	Area%
1	3.263	292736	337.00	1.255
2	8.024	23040845	337.00	98.745
Total		23333581		100.000

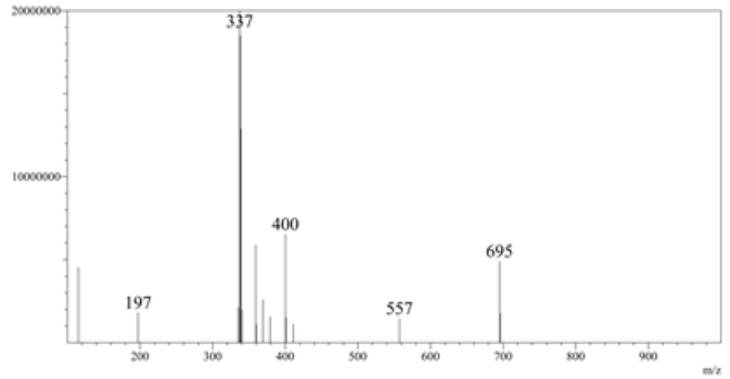
SHIMADZU LabSolutions Analysis Report

<Sample Information>

Sample Name	: 180113 NJ 1219 Scan		
Sample ID	:		
Data Filename	: 180113 NJ 1219 Scan.lcd		
Method Filename	: NNDKG.lcm		
Batch Filename	:		
Vial #	: 1-16	Sample Type	: Unknown
Injection Volume	: 1 uL		
Date Acquired	: 1/13/2018 1:35:01 PM	Acquired by	: System Administrator
Date Processed	: 1/13/2018 3:48:17 PM	Processed by	: System Administrator

MS Spectrum

Line#:1 R.Time:----(Scan#:----)
MassPeaks:17
Spectrum Mode:Averaged 0.367-0.533(23-33) Base Peak:337(20000000)
BG Mode:Averaged 0.000-0.300(1-19) Segment 1 - Event 1



MS Spectrum

Peak#:1 R.Time:0.455(Scan#:28)
MassPeaks:17
Spectrum Mode:Averaged 0.367-0.533(23-33)
BG Mode:Averaged 0.000-0.300(1-19) Segment 1 - Event 1

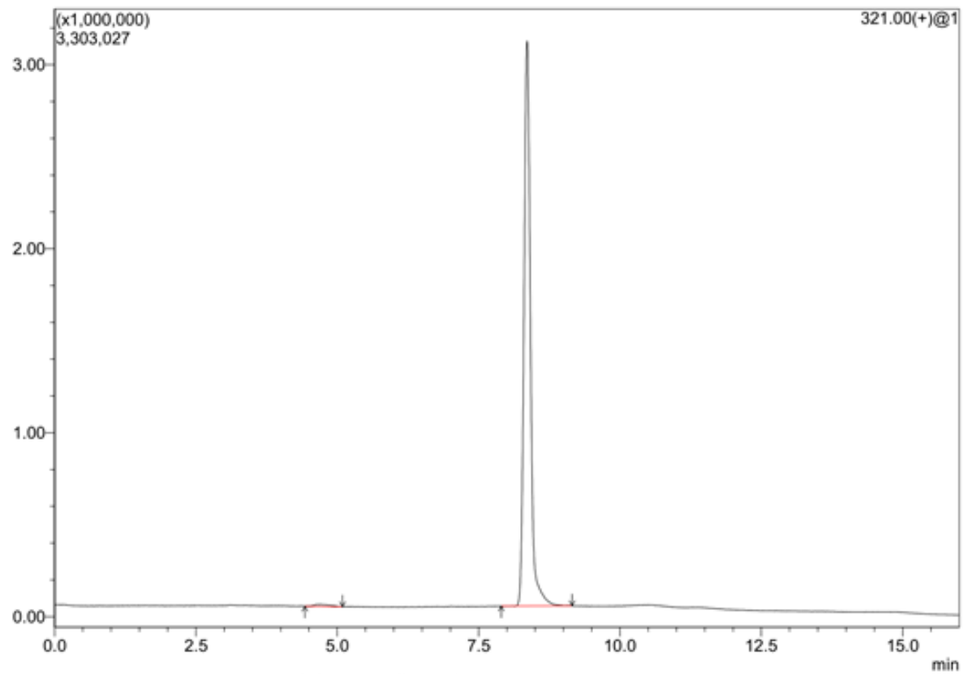
m/z	Absolute Intensity	Relative Intensity
115.20	4543843	22.72
197.15	1795841	8.98
335.15	2127692	10.64
337.10	20000000	100.00
338.15	18489954	92.45
339.15	12876534	64.38
340.20	1983479	9.92
359.15	5903233	29.52
360.20	1094054	5.47

C:\LabSolutions\Data\Nenad KG\NJ 180113 Scan\180113 NJ 1219 Scan.lcd

Figure S96 Mass spectra of **4p**

==== Shimadzu LabSolutions Browser Report ====

MS Chromatogram(180113 NJ 1249_006.lcd)



MS Qualitative Table(180113 NJ 1249_006.lcd)

321.00(Ev1)

Peak#	Ret. Time	Area	m/z	Area%
1	4.697	204071	321.00	0.826
2	8.364	24514949	321.00	99.174
Total		24719019		100.000

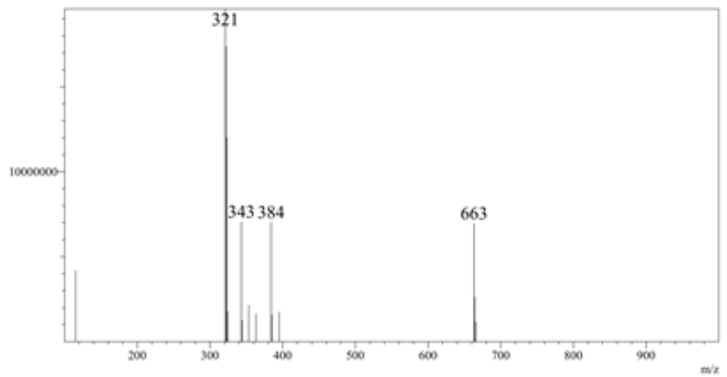
SHIMADZU LabSolutions Analysis Report

<Sample Information>

Sample Name	: 180113 NJ 1249 Scan		
Sample ID	:		
Data Filename	: 180113 NJ 1249 Scan.lcd		
Method Filename	: NNDKG.lcm		
Batch Filename	:		
Vial #	: 1-5	Sample Type	: Unknown
Injection Volume	: 1 uL		
Date Acquired	: 1/13/2018 12:41:10 PM	Acquired by	: System Administrator
Date Processed	: 1/13/2018 3:26:05 PM	Processed by	: System Administrator

MS Spectrum

Line#:1 R.Time:----(Scan#:----)
MassPeaks:15
Spectrum Mode:Averaged 0.367-0.533(23-33) Base Peak:321(19585199)
BG Mode:Averaged 0.000-0.300(1-19) Segment 1 - Event 1



MS Spectrum

Peak#:1 R.Time:0.465(Scan#:28)
MassPeaks:15
Spectrum Mode:Averaged 0.367-0.533(23-33)
BG Mode:Averaged 0.000-0.300(1-19) Segment 1 - Event 1

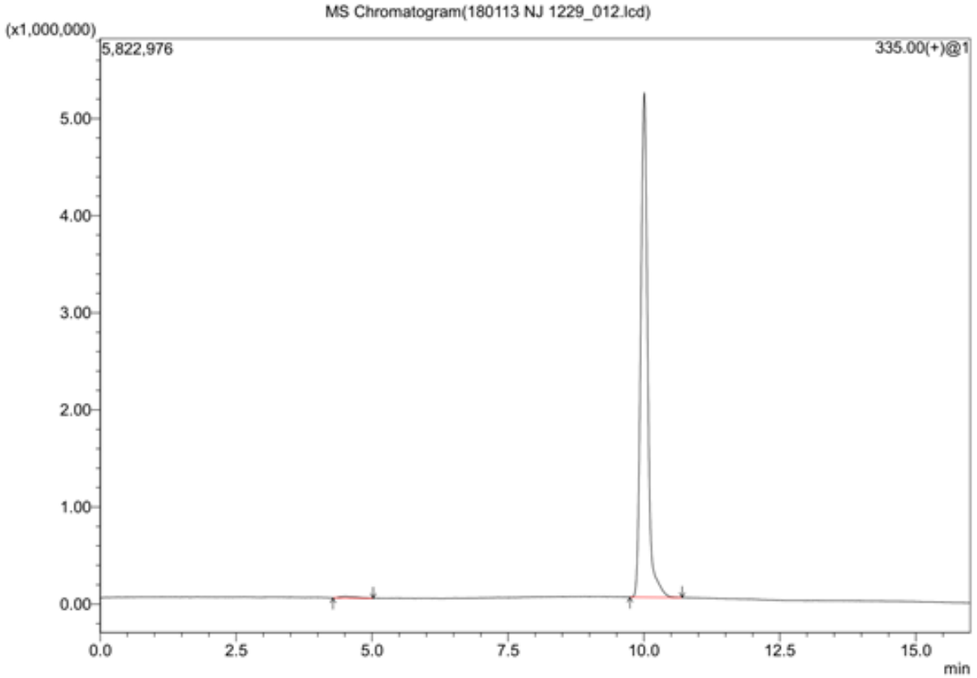
m/z	Absolute Intensity	Relative Intensity
115.20	4177209	21.33
321.10	19585199	100.00
322.15	17385314	88.77
323.15	12006030	61.30
324.15	1759025	8.98
343.15	7050127	36.00
344.20	1262409	6.45
353.20	2144068	10.95

C:\LabSolutions\Data\Nenad KG\NJ 180113 Scan\180113 NJ 1249 Scan.lcd

Figure S97 Mass spectra of **4q**

==== Shimadzu LabSolutions Browser Report ====

MS Chromatogram(180113 NJ 1229_012.lcd)



MS Qualitative Table(180113 NJ 1229_012.lcd)

335.00(Ev1)

Peak#	Ret. Time	Area	m/z	Area%
1	4.515	341878	335.00	0.734
2	10.007	46204186	335.00	99.266
Total		46546064		100.000

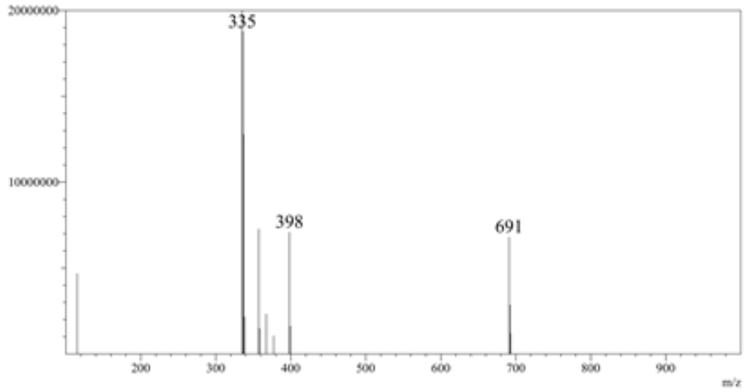
SHIMADZU LabSolutions **Analysis Report**

<Sample Information>

Sample Name	: 180113 NJ 1229 Scan		
Sample ID	:		
Data Filename	: 180113 NJ 1229 Scan.lcd		
Method Filename	: NNDKG.lcm		
Batch Filename	:		
Vial #	: 1-11	Sample Type	: Unknown
Injection Volume	: 1 uL		
Date Acquired	: 1/13/2018 12:58:18 PM	Acquired by	: System Administrator
Date Processed	: 1/13/2018 3:35:53 PM	Processed by	: System Administrator

MS Spectrum

Line#:1 R.Time:----(Scan#:----)
MassPeaks:14
Spectrum Mode:Averaged 0.367-0.533(23-33) Base Peak:335(20000000)
BG Mode:Averaged 0.000-0.300(1-19) Segment 1 - Event 1



MS Spectrum

Peak#:1 R.Time:0.457(Scan#:28)
MassPeaks:14
Spectrum Mode:Averaged 0.367-0.533(23-33)
BG Mode:Averaged 0.000-0.300(1-19) Segment 1 - Event 1

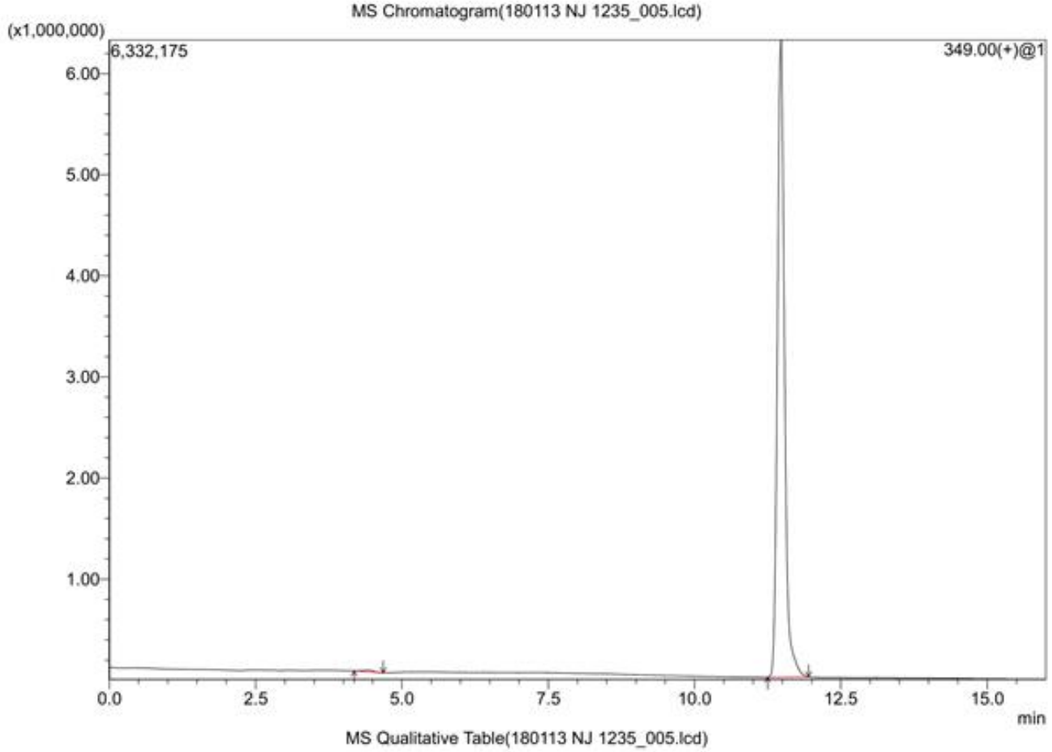
m/z	Absolute Intensity	Relative Intensity
115.20	4678587	23.39
335.15	20000000	100.00
336.15	18777432	93.89
337.20	12790121	63.95
338.20	2156987	10.78
357.15	7272395	36.36
358.20	1485917	7.43

C:\LabSolutions\Data\Nenad KG\NJ 180113 Scan\180113 NJ 1229 Scan.lcd

Figure S98 Mass spectra of **4r**

==== Shimadzu LabSolutions Browser Report ====

MS Chromatogram(180113 NJ 1235_005.lcd)



MS Qualitative Table(180113 NJ 1235_005.lcd)

349.00(Ev1)

Peak#	Ret. Time	Area	m/z	Area%
1	4.419	216681	349.00	0.404
2	11.476	53474436	349.00	99.596
Total		53691117		100.000

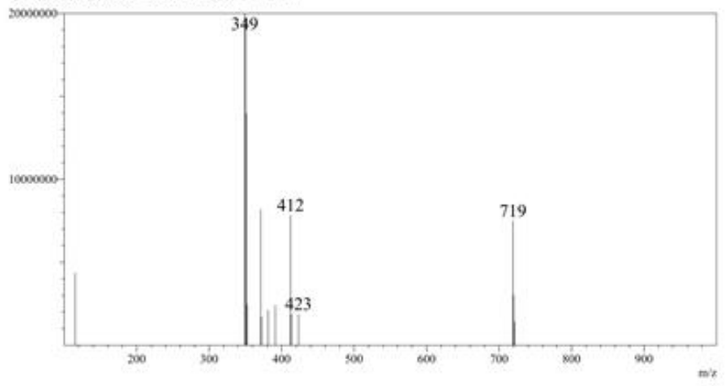
SHIMADZU LabSolutions **Analysis Report**

<Sample Information>

Sample Name	: 180113 NJ 1235 Scan		
Sample ID	:		
Data Filename	: 180113 NJ 1235.lcd		
Method Filename	: NNDKG.lcm		
Batch Filename	:		
Vial #	: 1-4	Sample Type	: Unknown
Injection Volume	: 1 uL		
Date Acquired	: 1/13/2018 12:25:48 PM	Acquired by	: System Administrator
Date Processed	: 1/13/2018 3:24:42 PM	Processed by	: System Administrator

MS Spectrum

Line#:1 R.Time:----(Scan#:----)
MassPeaks:15
Spectrum Mode:Averaged 0.383-0.550(24-34) Base Peak:349(20000000)
BG Mode:Averaged 0.000-0.300(1-19) Segment 1 - Event 1



MS Spectrum

Peak#:1 R.Time:0.467(Scan#:29)
MassPeaks:15
Spectrum Mode:Averaged 0.383-0.550(24-34)
BG Mode:Averaged 0.000-0.300(1-19) Segment 1 - Event 1

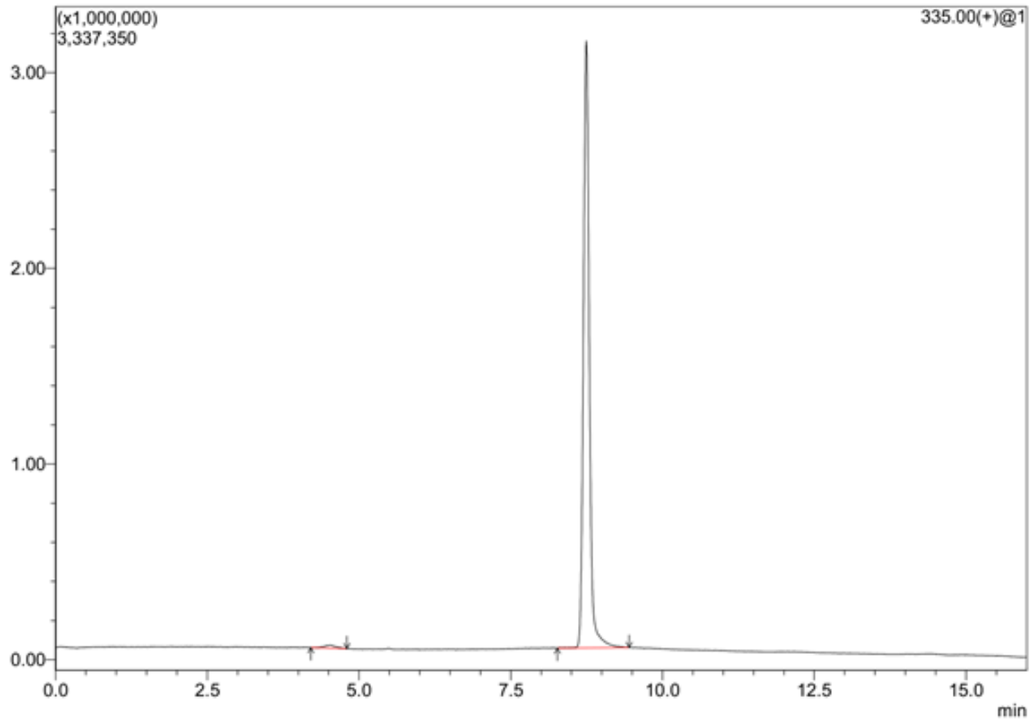
m/z	Absolute Intensity	Relative Intensity
115.20	4361725	21.81
349.15	20000000	100.00
350.20	19562654	97.81
351.20	13973116	69.87
352.20	2464209	12.32
371.15	8184328	40.92
372.20	1697496	8.49
381.20	2101660	10.51

C:\LabSolutions\Data\Nenad KG\NJ 180113 Scan\180113 NJ 1235.lcd

Figure S99 Mass spectra of **4s**

==== Shimadzu LabSolutions Browser Report ====

MS Chromatogram(180114 NJ Chromatogram 1208_010.lcd)



MS Qualitative Table(180114 NJ Chromatogram 1208_010.lcd)

335.00(Ev1)

Peak#	Ret. Time	Area	m/z	Area%
1	4.522	204622	335.00	0.967
2	8.745	20948743	335.00	99.033
Total		21153365		100.000

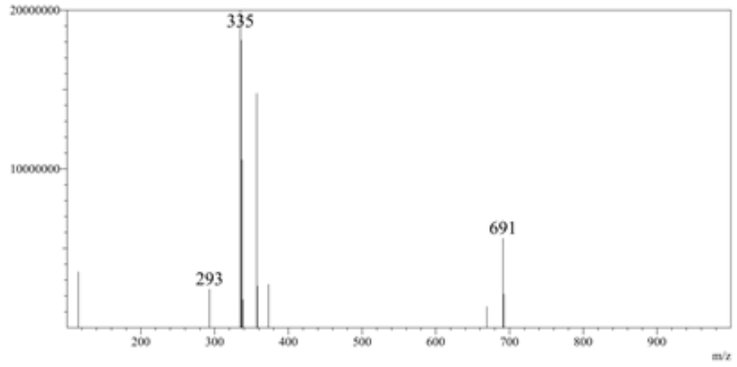
SHIMADZU LabSolutions Analysis Report

<Sample Information>

Sample Name	: 180114 NJ Spectrum 1208		
Sample ID	:		
Data Filename	: 180114 NJ Spectrum 1208_010.lcd		
Method Filename	: NNDKG.lcm		
Batch Filename	: 180114 NJ Spectrum.lcb		
Vial #	: 1-10	Sample Type	: Unknown
Injection Volume	: 1 uL		
Date Acquired	: 1/14/2018 3:13:12 PM	Acquired by	: System Administrator
Date Processed	: 1/14/2018 3:14:14 PM	Processed by	: System Administrator

MS Spectrum

Peak#:1 R.Time:0.465(Scan#:28)
MassPeaks:12
Spectrum Mode:Averaged 0.367-0.533(23-33)
BG Mode:Averaged 0.000-0.300(1-19) Segment 1 - Event 1



MS Spectrum

Peak#:1 R.Time:0.465(Scan#:28)
MassPeaks:12
Spectrum Mode:Averaged 0.367-0.533(23-33)
BG Mode:Averaged 0.000-0.300(1-19) Segment 1 - Event 1

m/z	Absolute Intensity	Relative Intensity
115.20	3519341	17.60
293.15	2420752	12.10
335.10	20000000	100.00
336.15	18119452	90.60
337.15	10586532	52.93
338.20	1771213	8.86

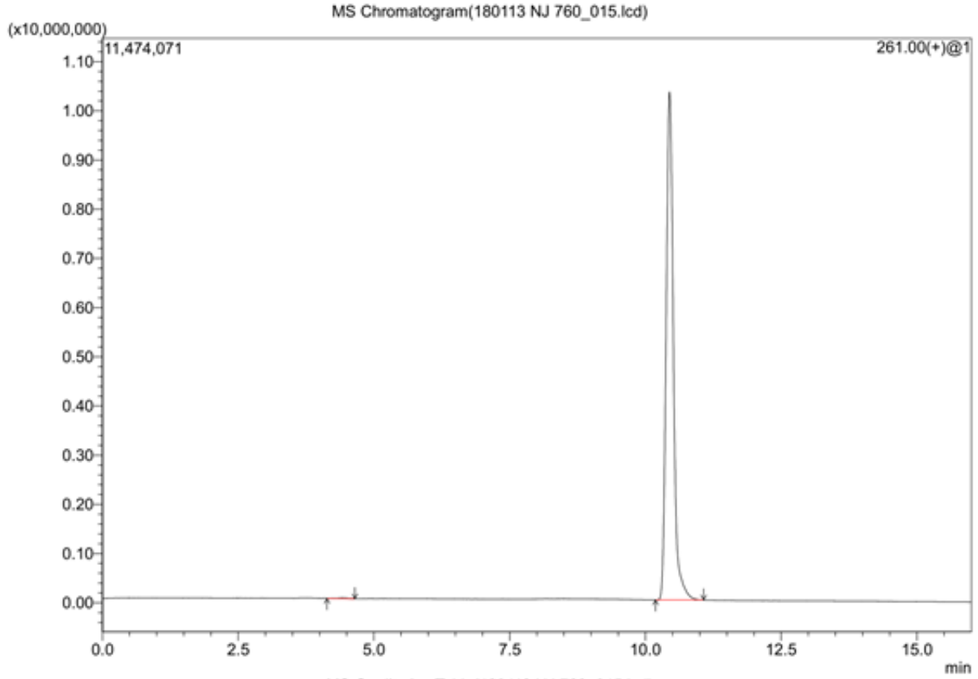
C:\LabSolutions\Data\Nenad KG\NJ 180113 Scan\180114 NJ Spectrum 1208_010.lcd

Figure S100 Mass spectra of **4t**

4. LC/MS spectra of 4’a-t

==== Shimadzu LabSolutions Browser Report ====

MS Chromatogram(180113 NJ 760_015.lcd)



MS Qualitative Table(180113 NJ 760_015.lcd)

261.00(Ev1)

Peak#	Ret. Time	Area	m/z	Area%
1	4.414	167041	261.00	0.174
2	10.446	95824641	261.00	99.826
Total		95991682		100.000

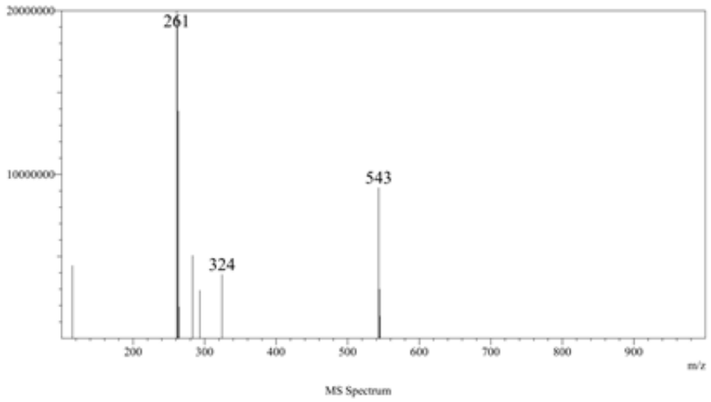
SHIMADZU LabSolutions **Analysis Report**

<Sample Information>

Sample Name	: 180113 NJ 760 Scan		
Sample ID	:		
Data Filename	: 180113 NJ 760 Scan.lcd		
Method Filename	: NNDKG.lcm		
Batch Filename	:		
Vial #	: 1-14	Sample Type	: Unknown
Injection Volume	: 1 uL		
Date Acquired	: 1/13/2018 1:30:41 PM	Acquired by	: System Administrator
Date Processed	: 1/13/2018 3:45:52 PM	Processed by	: System Administrator

MS Spectrum

Line#:1 R.Time:----(Scan#:----)
MassPeaks:11
Spectrum Mode:Averaged 0.367-0.533(23-33) Base Peak:261(20000000)
BG Mode:Averaged 0.000-0.300(1-19) Segment 1 - Event 1



MS Spectrum

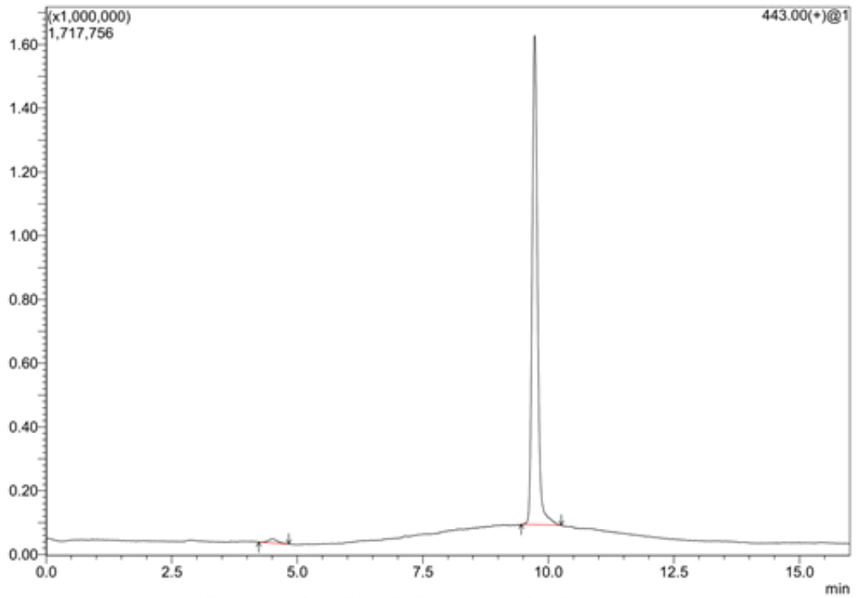
Peak#:1 R.Time:0.456(Scan#:28)
MassPeaks:11
Spectrum Mode:Averaged 0.367-0.533(23-33)
BG Mode:Averaged 0.000-0.300(1-19) Segment 1 - Event 1

m/z	Absolute Intensity	Relative Intensity
115.20	4440297	22.20
261.10	20000000	100.00
262.10	19654136	98.27
263.15	13876380	69.38
264.15	1921114	9.61

Figure S101 Mass spectra of **4’a**

==== Shimadzu LabSolutions Browser Report ====

MS Chromatogram(180114 NJ Chromatogram 1244_011.lcd)



MS Qualitative Table(180114 NJ Chromatogram 1244_011.lcd)

443.00(Ev1)

Peak#	Ret. Time	Area	m/z	Area%
1	4.508	167282	443.00	1.437
2	9.728	11471528	443.00	98.563
Total		11638810		100.000

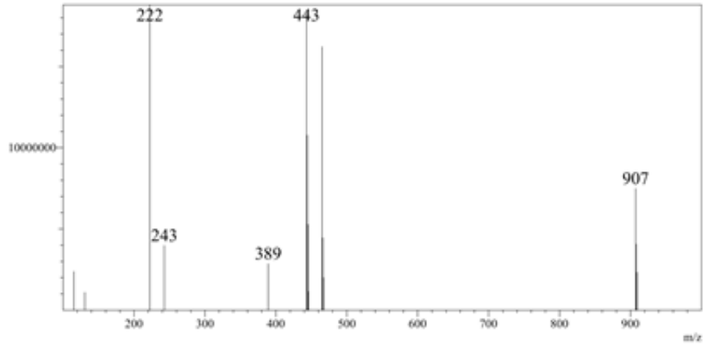
SHIMADZU LabSolutions Analysis Report

<Sample Information>

Sample Name	: 180114 NJ Spectrum 1244		
Sample ID	:		
Data Filename	: 180114 NJ Spectrum 1244_011.lcd		
Method Filename	: NNDKG.lcm		
Batch Filename	: 180114 NJ Spectrum.lcb		
Vial #	: 1-11	Sample Type	: Unknown
Injection Volume	: 1 uL		
Date Acquired	: 1/14/2018 3:14:45 PM	Acquired by	: System Administrator
Date Processed	: 1/14/2018 3:15:47 PM	Processed by	: System Administrator

MS Spectrum

Peak#:1 R.Time:0.449(Scan#:27)
MassPeaks:15
Spectrum Mode:Averaged 0.350-0.517(22-32)
BG Mode:Averaged 0.000-0.300(1-19) Segment 1 - Event 1



MS Spectrum

Peak#:1 R.Time:0.449(Scan#:27)
MassPeaks:15
Spectrum Mode:Averaged 0.350-0.517(22-32)
BG Mode:Averaged 0.000-0.300(1-19) Segment 1 - Event 1

m/z	Absolute Intensity	Relative Intensity
115.20	2388130	12.70
130.70	1097305	5.84
222.15	18799550	100.00
242.70	3987676	21.21
389.15	2864074	15.23
443.15	18275947	97.21
444.20	10775904	57.32
445.20	5283717	28.11

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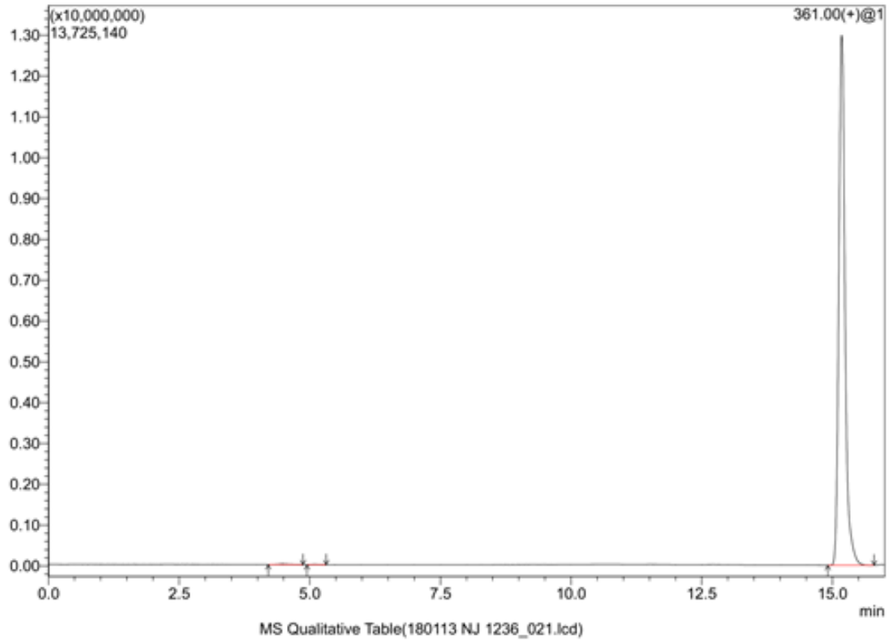
Figure S102 Mass spectra of **4'b**

==== Shimadzu LabSolutions Browser Report ====

MS Chromatogram(180113 NJ 1236_021.lcd)



MS Qualitative Table(180113 NJ 1236_021.lcd)

361.00(Ev1)

Peak#	Ret. Time	Area	m/z	Area%
1	4.484	271176	361.00	0.250
2	5.099	82524	361.00	0.076
3	15.177	108282306	361.00	99.674
Total		108636006		100.000

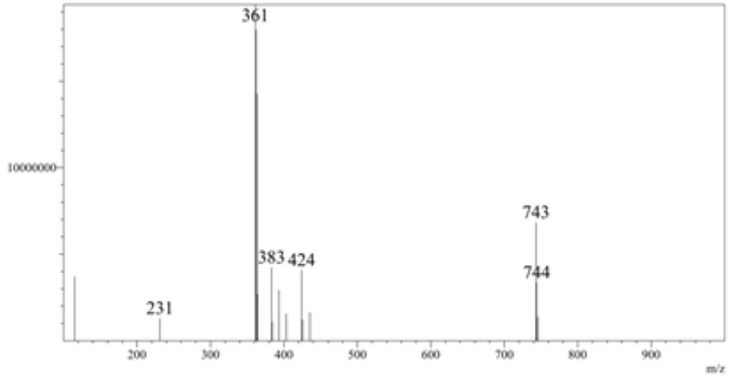
SHIMADZU LabSolutions Analysis Report

<Sample Information>

Sample Name	: 180113 NJ 1236 Scan		
Sample ID	:		
Data Filename	: 180113 NJ 1236 Scan.lcd		
Method Filename	: NNDKG.lcm		
Batch Filename	:		
Vial #	: 1-20	Sample Type	: Unknown
Injection Volume	: 1 uL		
Date Acquired	: 1/13/2018 1:45:52 PM	Acquired by	: System Administrator
Date Processed	: 1/13/2018 3:53:27 PM	Processed by	: System Administrator

MS Spectrum

Line#:1 R.Time:----(Scan#:----)
MassPeaks:16
Spectrum Mode:Averaged 0.350-0.517(22-32) Base Peak:361(19431149)
BG Mode:Averaged 0.000-0.300(1-19) Segment 1 - Event 1



MS Spectrum

Peak#:1 R.Time:0.447(Scan#:27)
MassPeaks:16
Spectrum Mode:Averaged 0.350-0.517(22-32)
BG Mode:Averaged 0.000-0.300(1-19) Segment 1 - Event 1

m/z	Absolute Intensity	Relative Intensity
115.20	3717944	19.13
231.10	1292078	6.65
361.15	19431149	100.00
362.20	17960600	92.43
363.20	14275712	73.47
364.20	2692561	13.86
383.15	4234514	21.79
384.20	1083295	5.58

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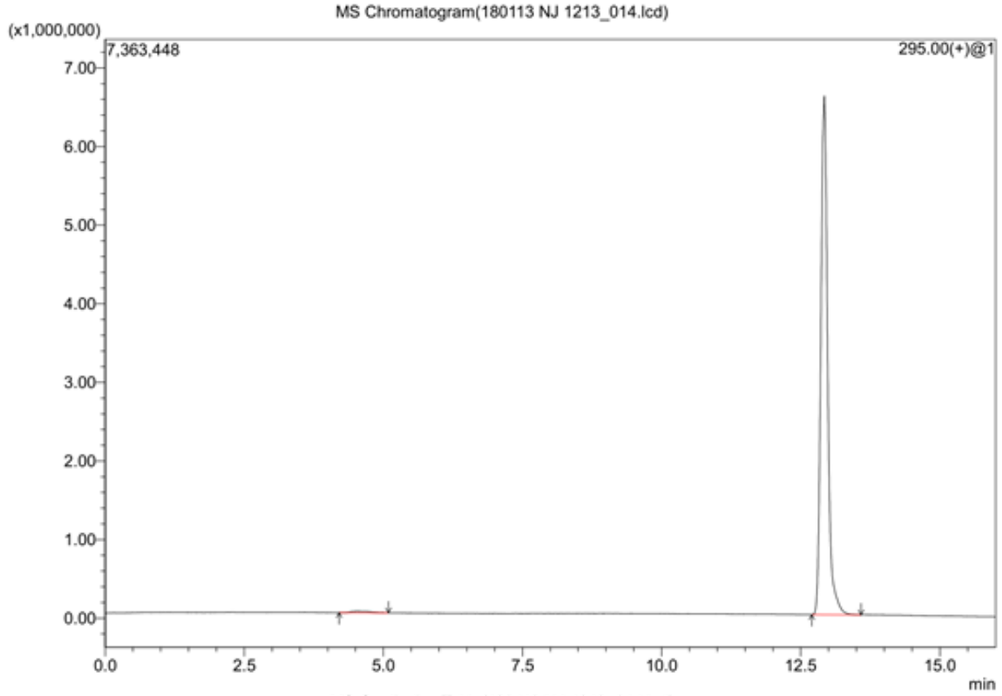
Figure S103 Mass spectra of **4'c**

==== Shimadzu LabSolutions Browser Report ====

MS Chromatogram(180113 NJ 1213_014.lcd)



MS Qualitative Table(180113 NJ 1213_014.lcd)

295.00(Ev1)

Peak#	Ret. Time	Area	m/z	Area%
1	4.549	476839	295.00	0.840
2	12.925	56314507	295.00	99.160
Total		56791346		100.000

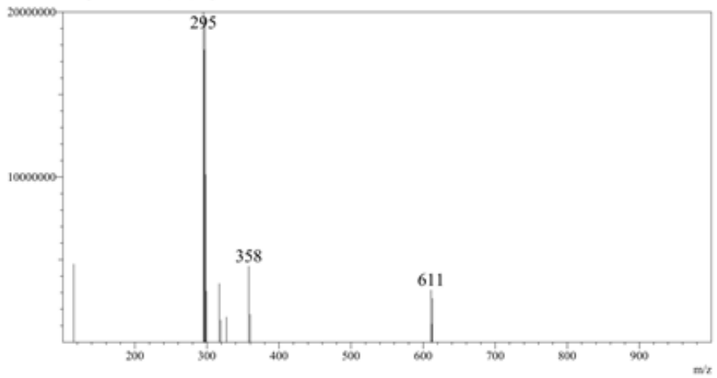
SHIMADZU LabSolutions Analysis Report

<Sample Information>

Sample Name	: 180113 NJ 1213 Scan		
Sample ID	:		
Data Filename	: 180113 NJ 1213 Scan.lcd		
Method Filename	: NNDKG.lcm		
Batch Filename	:		
Vial #	: 1-13	Sample Type	: Unknown
Injection Volume	: 1 uL		
Date Acquired	: 1/13/2018 1:02:53 PM	Acquired by	: System Administrator
Date Processed	: 1/13/2018 3:44:26 PM	Processed by	: System Administrator

MS Spectrum

Line#:1 R.Time:----(Scan#:----)
MassPeaks:14
Spectrum Mode:Averaged 0.367-0.533(23-33) Base Peak:295(20000000)
BG Mode:Averaged 0.000-0.300(1-19) Segment 1 - Event 1



MS Spectrum

Peak#:1 R.Time:0.461(Scan#:28)
MassPeaks:14
Spectrum Mode:Averaged 0.367-0.533(23-33)
BG Mode:Averaged 0.000-0.300(1-19) Segment 1 - Event 1

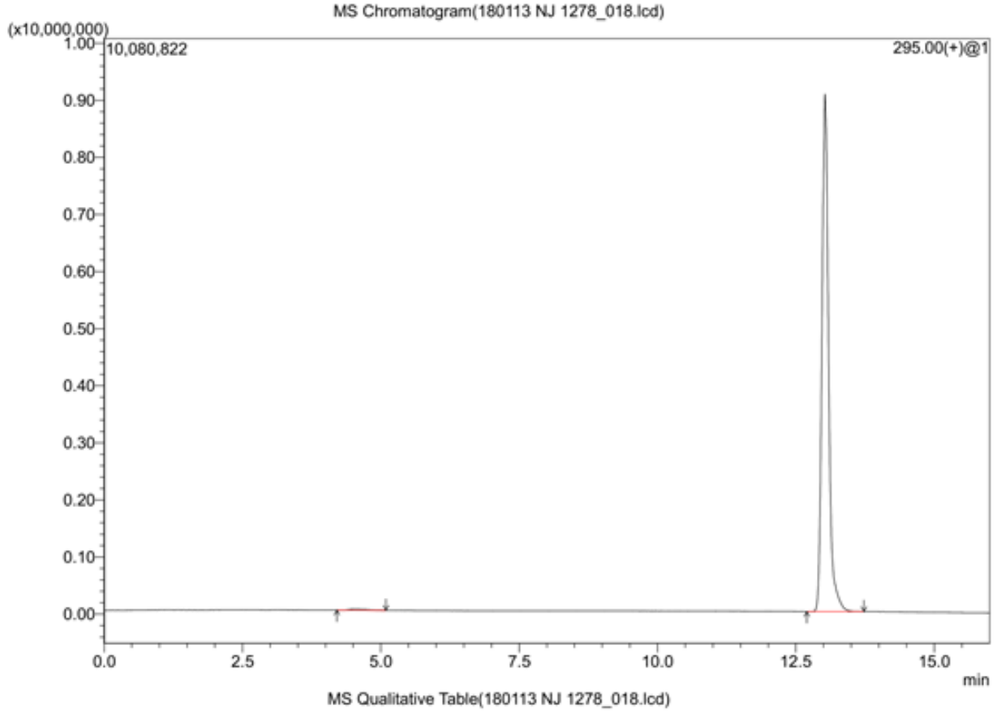
m/z	Absolute Intensity	Relative Intensity
115.20	4735244	23.68
295.05	20000000	100.00
296.10	17713947	88.57
297.10	19613637	98.07
298.10	10152078	50.76
299.10	3097343	15.49
317.10	3555703	17.78

C:\LabSolutions\Data\Nenad KG\NJ 180113 Scan\180113 NJ 1213 Scan.lcd

Figure S104 Mass spectra of **4'd**

==== Shimadzu LabSolutions Browser Report ====

MS Chromatogram(180113 NJ 1278_018.lcd)



MS Qualitative Table(180113 NJ 1278_018.lcd)

295.00(Ev1)

Peak#	Ret. Time	Area	m/z	Area%
1	4.546	477316	295.00	0.626
2	13.026	75811553	295.00	99.374
Total		76288869		100.000

SHIMADZU LabSolutions

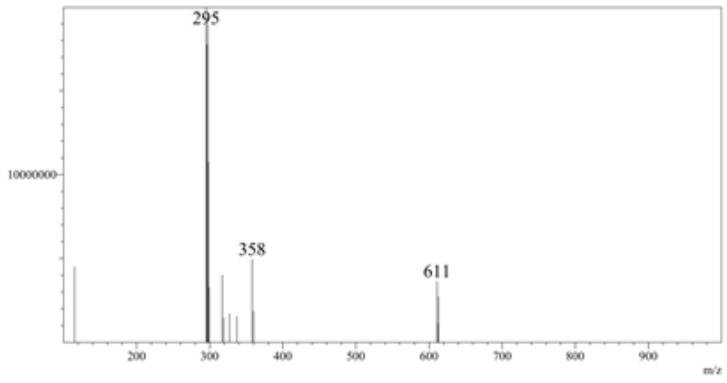
Analysis Report

<Sample Information>

Sample Name	: 180113 NJ 1278 Scan		
Sample ID	:		
Data Filename	: 180113 NJ 1278 Scan.lcd		
Method Filename	: NNDKG.lcm		
Batch Filename	:		
Vial #	: 1-17	Sample Type	: Unknown
Injection Volume	: 1 uL		
Date Acquired	: 1/13/2018 1:39:27 PM	Acquired by	: System Administrator
Date Processed	: 1/13/2018 3:49:22 PM	Processed by	: System Administrator

MS Spectrum

Line#:1 R.Time:----(Scan#:----)
MassPeaks:15
Spectrum Mode:Averaged 0.367-0.533(23-33) Base Peak:295(19970513)
BG Mode:Averaged 0.000-0.300(1-19) Segment 1 - Event 1



MS Spectrum

Peak#:1 R.Time:0.457(Scan#:28)
MassPeaks:15
Spectrum Mode:Averaged 0.367-0.533(23-33)
BG Mode:Averaged 0.000-0.300(1-19) Segment 1 - Event 1

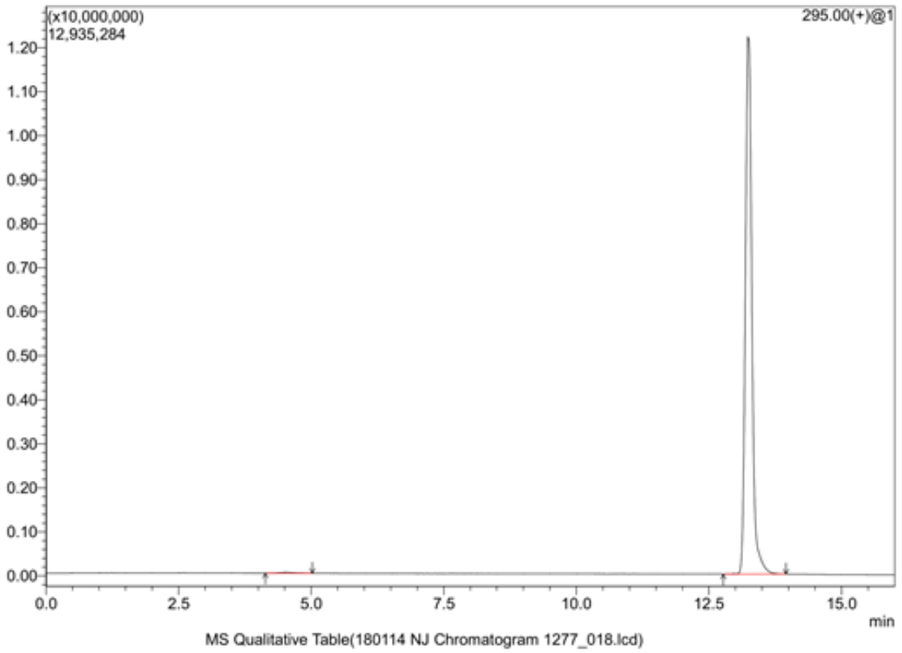
m/z	Absolute Intensity	Relative Intensity
115.20	4512994	22.60
295.05	19970513	100.00
296.10	17763947	88.95
297.10	18978464	95.03
298.10	10741376	53.79
299.10	3276159	16.40
317.10	4015027	20.10
319.10	1461316	7.32

C:\LabSolutions\Data\Nenad KG\NJ 180113 Scan\180113 NJ 1278 Scan.lcd

Figure S105 Mass spectra of **4'e**

==== Shimadzu LabSolutions Browser Report ====

MS Chromatogram(180114 NJ Chromatogram 1277_018.lcd)



MS Qualitative Table(180114 NJ Chromatogram 1277_018.lcd)

295.00(Ev1)

Peak#	Ret. Time	Area	m/z	Area%
1	4.530	324971	295.00	0.309
2	13.249	104935661	295.00	99.691
Total		105260633		100.000

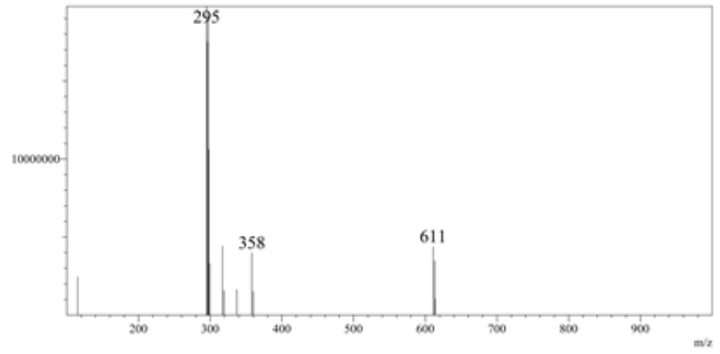
SHIMADZU LabSolutions **Analysis Report**

<Sample Information>

Sample Name	: 180114 NJ Spectrum 1277		
Sample ID	:		
Data Filename	: 180114 NJ Spectrum 1277_018.lcd		
Method Filename	: NNDKG.lcm		
Batch Filename	: 180114 NJ Spectrum.lcb		
Vial #	: 1-18	Sample Type	: Unknown
Injection Volume	: 1 uL		
Date Acquired	: 1/14/2018 3:25:41 PM	Acquired by	: System Administrator
Date Processed	: 1/14/2018 3:26:43 PM	Processed by	: System Administrator

MS Spectrum

Peak#:1 R.Time:0.447(Scan#:27)
MassPeaks:14
Spectrum Mode:Averaged 0.350-0.517(22-32)
BG Mode:Averaged 0.000-0.300(1-19) Segment 1 - Event 1



MS Spectrum

Peak#:1 R.Time:0.447(Scan#:27)
MassPeaks:14
Spectrum Mode:Averaged 0.350-0.517(22-32)
BG Mode:Averaged 0.000-0.300(1-19) Segment 1 - Event 1

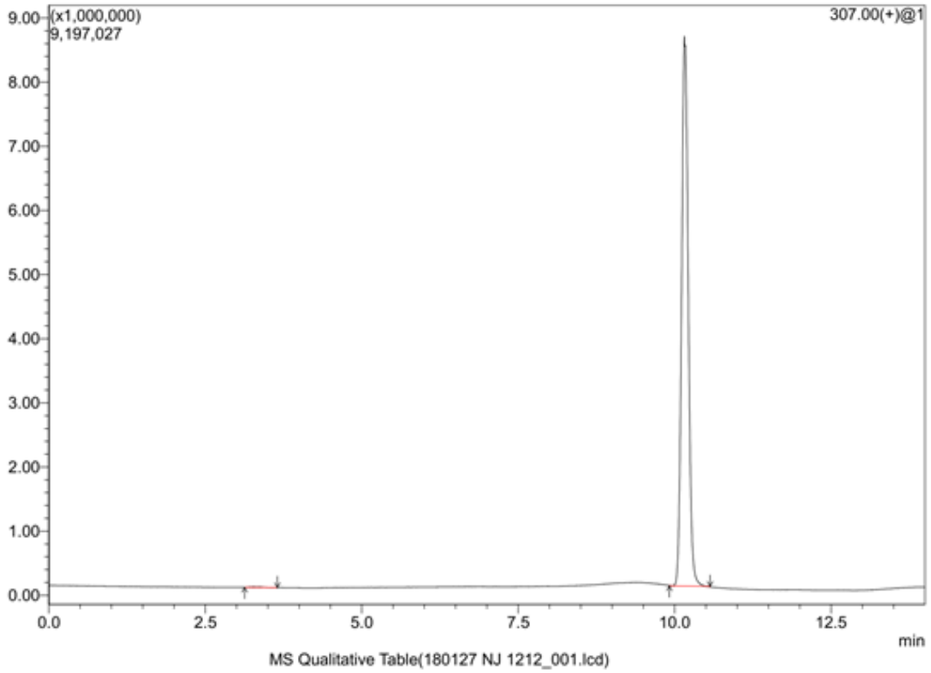
m/z	Absolute Intensity	Relative Intensity
115.20	2454041	12.41
295.05	19781165	100.00
296.10	17510959	88.52
297.10	18912435	95.61
298.10	10623838	53.71
299.10	3314923	16.76
317.05	4420682	22.35

C:\LabSolutions\Data\Nenad KG\NJ 180113 Scan\180114 NJ Spectrum 1277_018.lcd

Figure S106 Mass spectra of **4'f**

==== Shimadzu LabSolutions Browser Report ====

MS Chromatogram(180127 NJ 1212_001.lcd)



MS Qualitative Table(180127 NJ 1212_001.lcd)

307.00(Ev1)

Peak#	Ret. Time	Area	m/z	Area%
1	3.303	121102	307.00	0.191
2	10.159	63370280	307.00	99.809
Total		63491382		100.000

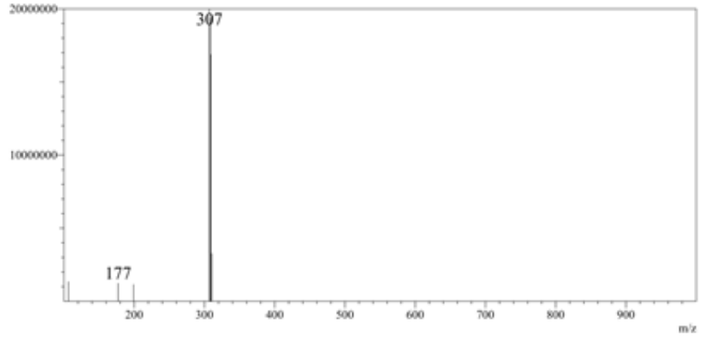
SHIMADZU LabSolutions **Analysis Report**

<Sample Information>

Sample Name	: 180125 NJ 1212 Spectrum		
Sample ID	:		
Data Filename	: 180125 NJ 1212 Spectrum.lcd		
Method Filename	: NNDKG.lcm		
Batch Filename	:		
Vial #	: 1-1	Sample Type	: Unknown
Injection Volume	: 1 uL		
Date Acquired	: 1/25/2018 11:10:54 AM	Acquired by	: System Administrator
Date Processed	: 1/25/2018 11:29:41 AM	Processed by	: System Administrator

MS Spectrum

Peak#:1 R.Time:0.375(Scan#:23)
MassPeaks:7
Spectrum Mode:Averaged 0.333-0.450(21-28)
BG Mode:Averaged 0.000-0.300(1-19) Segment 1 - Event 1



MS Spectrum

Peak#:1 R.Time:0.375(Scan#:23)
MassPeaks:7
Spectrum Mode:Averaged 0.333-0.450(21-28)
BG Mode:Averaged 0.000-0.300(1-19) Segment 1 - Event 1

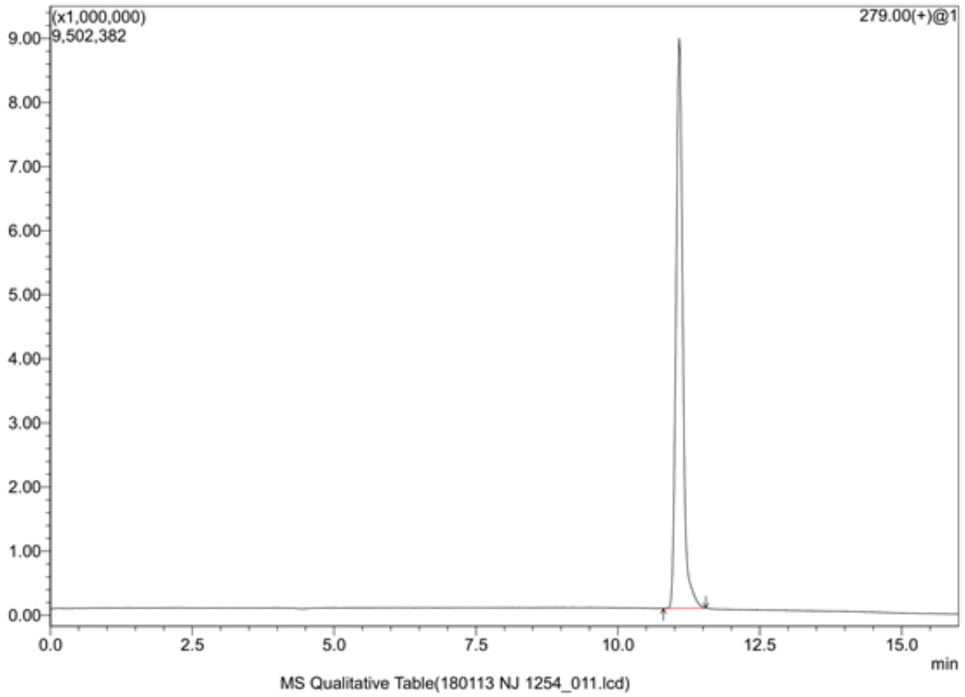
m/z	Absolute Intensity	Relative Intensity
106.20	1349003	6.75
177.10	1235087	6.18
199.05	1158413	5.79

C:\LabSolutions\Data\Nenad KG\180125 NJ 1212 Spectrum.lcd

Figure S107 Mass spectra of **4'g**

==== Shimadzu LabSolutions Browser Report ====

MS Chromatogram(180113 NJ 1254_011.lcd)



MS Qualitative Table(180113 NJ 1254_011.lcd)

279.00(Ev1)

Peak#	Ret. Time	Area	m/z	Area%
1	11.081	74086035	279.00	100.000
Total		74086035		100.000

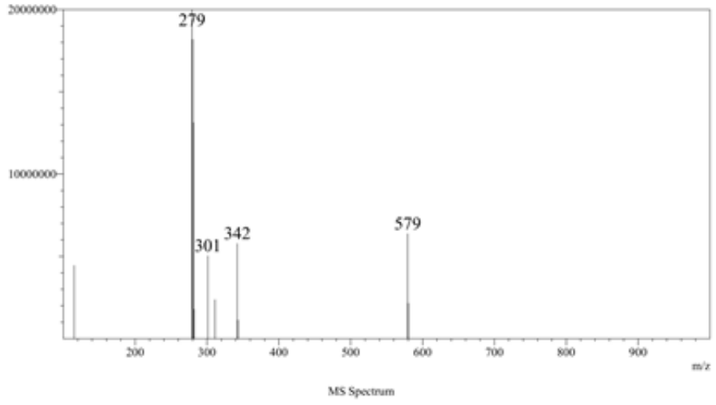
SHIMADZU LabSolutions Analysis Report

<Sample Information>

Sample Name	: 180113 NJ 1254 Scan		
Sample ID	:		
Data Filename	: 180113 NJ 1254 Scan.lcd		
Method Filename	: NNDKG.lcm		
Batch Filename	:		
Vial #	: 1-10	Sample Type	: Unknown
Injection Volume	: 1 uL		
Date Acquired	: 1/13/2018 12:56:18 PM	Acquired by	: System Administrator
Date Processed	: 1/13/2018 3:34:39 PM	Processed by	: System Administrator

MS Spectrum

Line#:1 R.Time:----(Scan#:----)
MassPeaks:11
Spectrum Mode:Averaged 0.367-0.533(23-33) Base Peak:279(20000000)
BG Mode:Averaged 0.000-0.300(1-19) Segment 1 - Event 1



MS Spectrum

Peak#:1 R.Time:0.463(Scan#:28)
MassPeaks:11
Spectrum Mode:Averaged 0.367-0.533(23-33)
BG Mode:Averaged 0.000-0.300(1-19) Segment 1 - Event 1

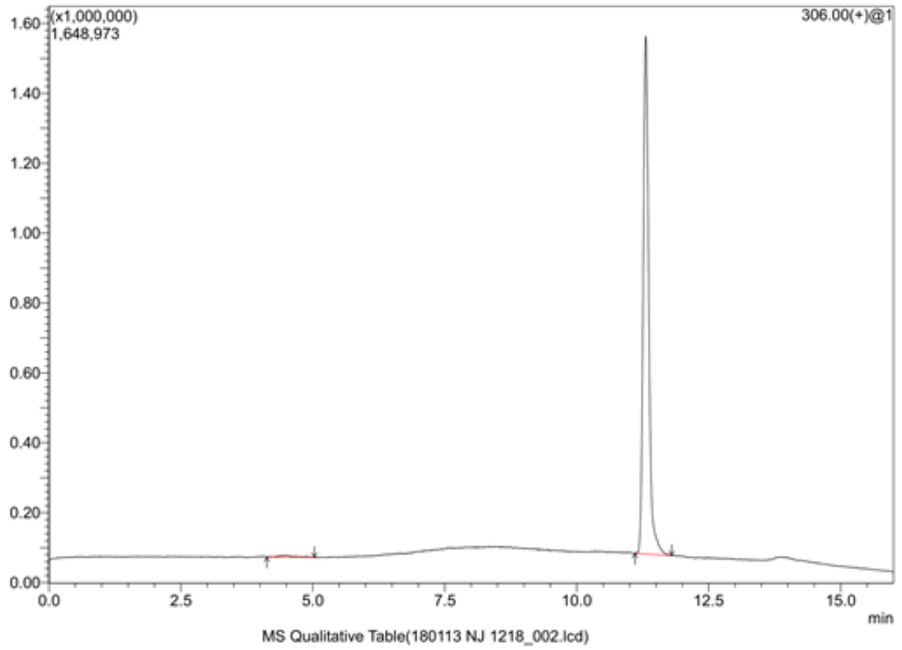
m/z	Absolute Intensity	Relative Intensity
115.20	4459893	22.30
279.10	20000000	100.00
280.10	18186698	90.93
281.15	13134405	65.67
282.15	1787611	8.94

C:\LabSolutions\Data\Nenad KG\NJ 180113 Scan\180113 NJ 1254 Scan.lcd

Figure S108 Mass spectra of **4'h**

==== Shimadzu LabSolutions Browser Report ====

MS Chromatogram(180113 NJ 1218_002.lcd)



MS Qualitative Table(180113 NJ 1218_002.lcd)

306.00(Ev1)

Peak#	Ret. Time	Area	m/z	Area%
1	4.482	101579	306.00	0.921
2	11.311	10922851	306.00	99.079
Total		11024430		100.000

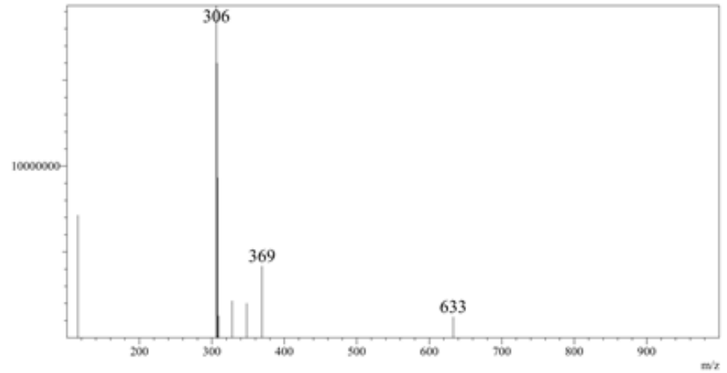
SHIMADZU LabSolutions Analysis Report

<Sample Information>

Sample Name	: 180113 NJ 1218 Scan		
Sample ID	:		
Data Filename	: 180113 NJ 1218 Scan.lcd		
Method Filename	: NNDKG.lcm		
Batch Filename	:		
Vial #	: 1-1	Sample Type	: Unknown
Injection Volume	: 1 uL		
Date Acquired	: 1/13/2018 11:09:39 AM	Acquired by	: System Administrator
Date Processed	: 1/13/2018 2:56:27 PM	Processed by	: System Administrator

MS Spectrum

Line#:1 R.Time:----(Scan#:----)
MassPeaks:9
Spectrum Mode:Averaged 0.367-0.533(23-33) Base Peak:306(19344999)
BG Mode:Calc Segment 1 - Event 1



MS Spectrum

Peak#:1 R.Time:0.461(Scan#:28)
MassPeaks:9
Spectrum Mode:Averaged 0.367-0.533(23-33)
BG Mode:Calc Segment 1 - Event 1

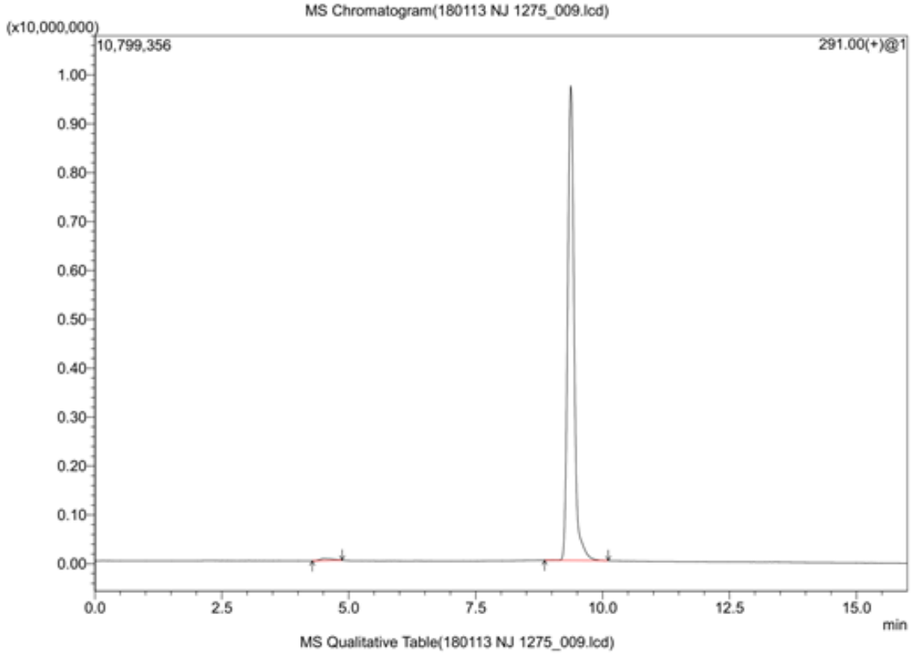
m/z	Absolute Intensity	Relative Intensity
115.20	7136143	36.89
306.10	19344999	100.00
307.10	16003105	82.72
308.15	9325692	48.21

C:\LabSolutions\Data\Nenad KG\NJ 180113 Scan\180113 NJ 1218 Scan.lcd

Figure S109 Mass spectra of **4'i**

==== Shimadzu LabSolutions Browser Report ====

MS Chromatogram(180113 NJ 1275_009.lcd)



MS Qualitative Table(180113 NJ 1275_009.lcd)

291.00(Ev1)

Peak#	Ret. Time	Area	m/z	Area%
1	4.549	720175	291.00	0.829
2	9.373	86141159	291.00	99.171
Total		86861334		100.000

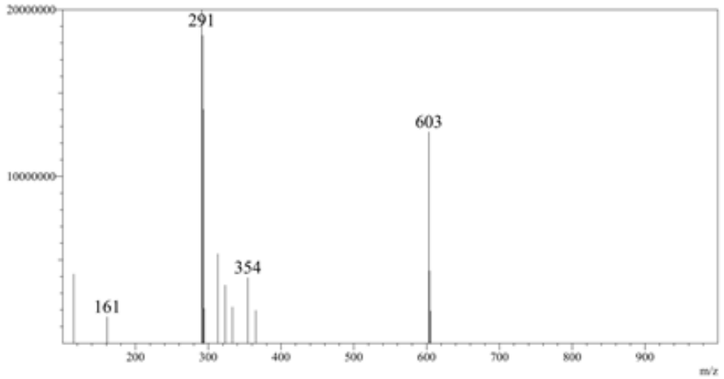
SHIMADZU LabSolutions **Analysis Report**

<Sample Information>

Sample Name	: 180113 NJ 1275 Scan		
Sample ID	:		
Data Filename	: 180113 NJ 1275 Scan.lcd		
Method Filename	: NNDKG.lcm		
Batch Filename	:		
Vial #	: 1-8	Sample Type	: Unknown
Injection Volume	: 1 uL		
Date Acquired	: 1/13/2018 12:50:55 PM	Acquired by	: System Administrator
Date Processed	: 1/13/2018 3:31:33 PM	Processed by	: System Administrator

MS Spectrum

Line#:1 R.Time:----(Scan#:----)
MassPeaks:14
Spectrum Mode:Averaged 0.367-0.533(23-33) Base Peak:291(20000000)
BG Mode:Averaged 0.000-0.300(1-19) Segment 1 - Event 1



MS Spectrum

Peak#:1 R.Time:0.457(Scan#:28)
MassPeaks:14
Spectrum Mode:Averaged 0.367-0.533(23-33)
BG Mode:Averaged 0.000-0.300(1-19) Segment 1 - Event 1

m/z	Absolute Intensity	Relative Intensity
115.20	4155837	20.78
161.10	1577421	7.89
291.10	20000000	100.00
292.15	18464073	92.32
293.15	14031076	70.16
294.20	2088345	10.44
313.15	5362907	26.81

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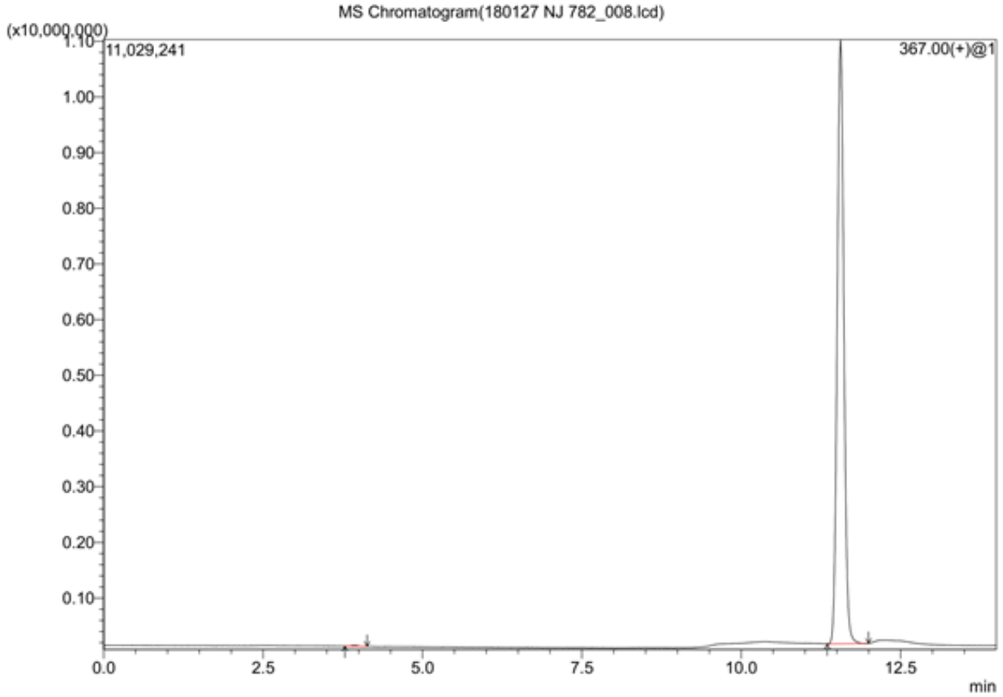
Figure S110 Mass spectra of **4'j**

==== Shimadzu LabSolutions Browser Report ====

MS Chromatogram(180127 NJ 782_008.lcd)



MS Qualitative Table(180127 NJ 782_008.lcd)

367.00(Ev1)

Peak#	Ret. Time	Area	m/z	Area%
1	3.941	98969	367.00	0.125
2	11.560	79252035	367.00	99.875
Total		79351004		100.000

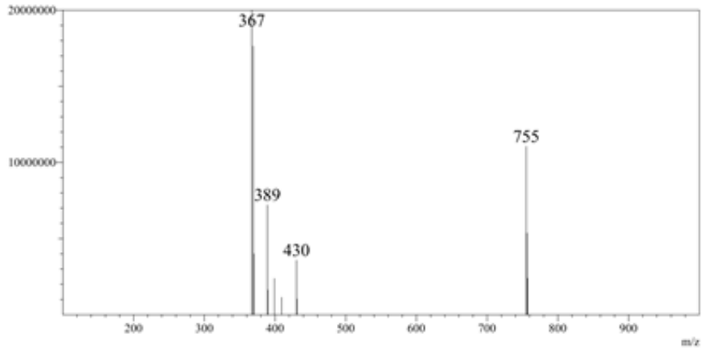
SHIMADZU LabSolutions **Analysis Report**

<Sample Information>

Sample Name	: 180114 NJ Spectrum 782		
Sample ID	:		
Data Filename	: 180114 NJ Spectrum 782_001.lcd		
Method Filename	: NNDKG.lcm		
Batch Filename	: 180114 NJ Spectrum.lcb		
Vial #	: 1-1	Sample Type	: Unknown
Injection Volume	: 1 uL		
Date Acquired	: 1/14/2018 2:58:51 PM	Acquired by	: System Administrator
Date Processed	: 1/14/2018 3:38:08 PM	Processed by	: System Administrator

MS Spectrum

Peak#:1 R.Time:0.454(Scan#:28)
MassPeaks:12
Spectrum Mode:Averaged 0.367-0.533(23-33)
BG Mode:Averaged 0.000-0.300(1-19) Segment 1 - Event 1



MS Spectrum

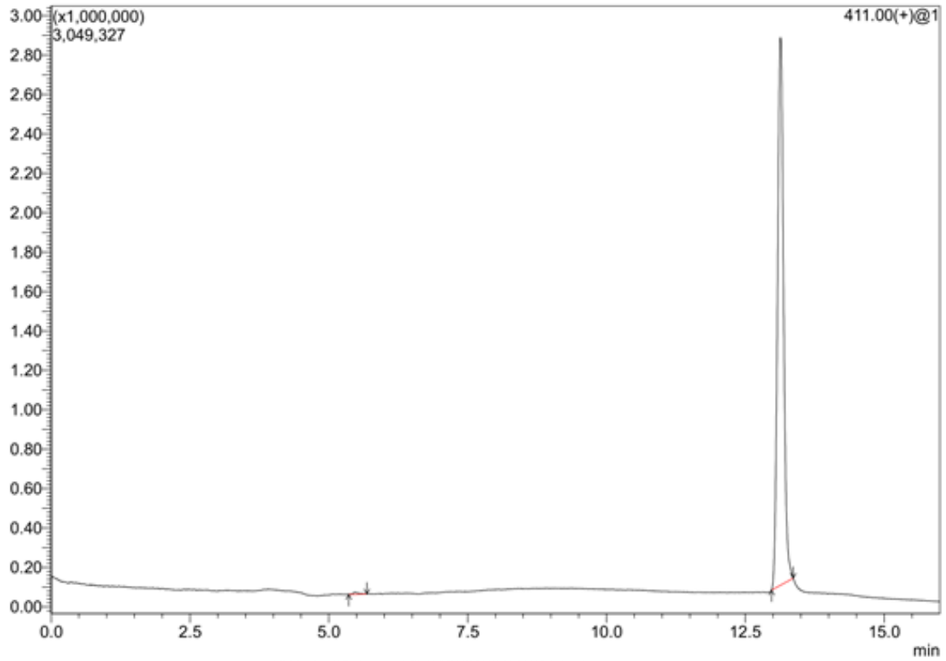
Peak#:1 R.Time:0.454(Scan#:28)
MassPeaks:12
Spectrum Mode:Averaged 0.367-0.533(23-33)
BG Mode:Averaged 0.000-0.300(1-19) Segment 1 - Event 1

m/z	Absolute Intensity	Relative Intensity
367.10	20000000	100.00
369.20	17642585	88.21
370.20	4008090	20.04
389.15	7212268	36.06
390.20	1634288	8.17
399.20	2390783	11.95

Figure S111 Mass spectra of **4'k**

==== Shimadzu LabSolutions Browser Report ====

MS Chromatogram(180113 NJ 1245_004.lcd)



MS Qualitative Table(180113 NJ 1245_004.lcd)

411.00(Ev1)

Peak#	Ret. Time	Area	m/z	Area%
1	5.472	75587	411.00	0.358
2	13.132	21017644	411.00	99.642
Total		21093231		100.000

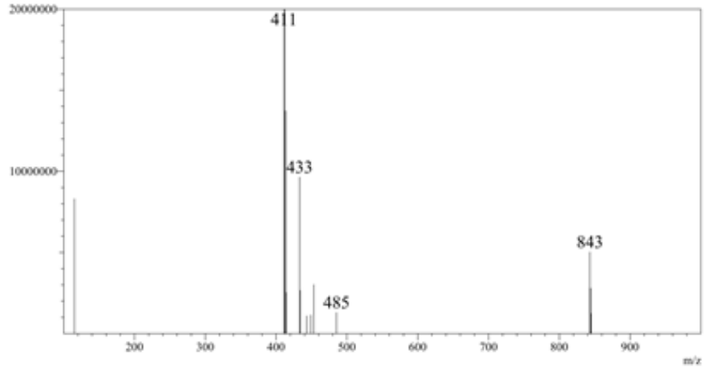
SHIMADZU LabSolutions Analysis Report

<Sample Information>

Sample Name	: 180113 NJ 1245 Scan		
Sample ID	:		
Data Filename	: 180113 NJ 1245.lcd		
Method Filename	: NNDKG.lcm		
Batch Filename	:		
Vial #	: 1-3	Sample Type	: Unknown
Injection Volume	: 1 uL		
Date Acquired	: 1/13/2018 11:27:42 AM	Acquired by	: System Administrator
Date Processed	: 1/13/2018 3:21:50 PM	Processed by	: System Administrator

MS Spectrum

Line#:1 R.Time:----(Scan#:----)
MassPeaks:14
Spectrum Mode:Averaged 0.433-0.467(27-29) Base Peak:411(20000000)
BG Mode:Calc Segment 1 - Event 1



MS Spectrum

Peak#:1 R.Time:0.096(Scan#:6)
MassPeaks:17
Spectrum Mode:Averaged 0.033-0.133(3-9)
BG Mode:Averaged 0.000-0.300(1-19) Segment 1 - Event 1

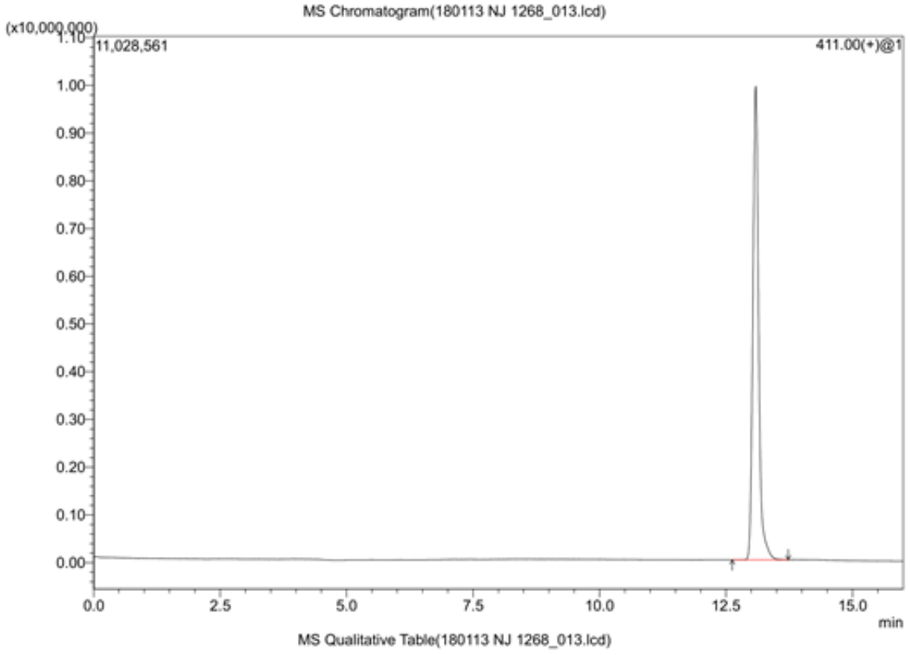
m/z	Absolute Intensity	Relative Intensity
104.90	275967	47.16
122.35	286531	48.97
134.85	48915	8.36
135.85	35404	6.05
142.85	388597	66.41
146.10	153736	26.27
159.05	32578	5.57
167.10	183811	31.41
180.00	60255	10.30

C:\LabSolutions\Data\Nenad KG\NJ 180113 Scan\180113 NJ 1245.lcd

Figure S112 Mass spectra of **4'l**

==== Shimadzu LabSolutions Browser Report ====

MS Chromatogram(180113 NJ 1268_013.lcd)



MS Qualitative Table(180113 NJ 1268_013.lcd)

411.00(Ev1)

Peak#	Ret. Time	Area	m/z	Area%
1	13.091	78819706	411.00	100.000
Total		78819706		100.000

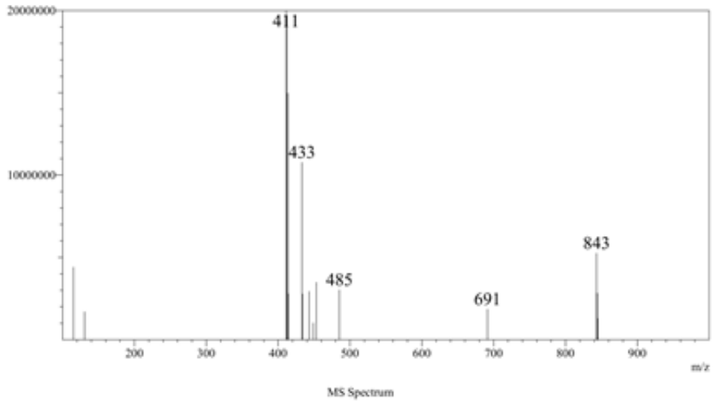
SHIMADZU LabSolutions **Analysis Report**

<Sample Information>

Sample Name	: 180113 NJ 1268 Scan		
Sample ID	:		
Data Filename	: 180113 NJ 1268 Scan.lcd		
Method Filename	: NNDKG.lcm		
Batch Filename	:		
Vial #	: 1-12	Sample Type	: Unknown
Injection Volume	: 1 uL		
Date Acquired	: 1/13/2018 1:00:18 PM	Acquired by	: System Administrator
Date Processed	: 1/13/2018 3:37:12 PM	Processed by	: System Administrator

MS Spectrum

Line#:1 R.Time:----(Scan#:----)
MassPeaks:16
Spectrum Mode:Averaged 0.367-0.533(23-33) Base Peak:411(20000000)
BG Mode:Averaged 0.000-0.300(1-19) Segment 1 - Event 1



MS Spectrum

Peak#:1 R.Time:0.452(Scan#:28)
MassPeaks:16
Spectrum Mode:Averaged 0.367-0.533(23-33)
BG Mode:Averaged 0.000-0.300(1-19) Segment 1 - Event 1

m/z	Absolute Intensity	Relative Intensity
115.15	4414582	22.07
130.60	1697723	8.49
411.15	20000000	100.00
412.20	19669003	98.35
413.20	14986327	74.93
414.25	2795167	13.98
433.20	10771071	53.86
434.20	2780771	13.90

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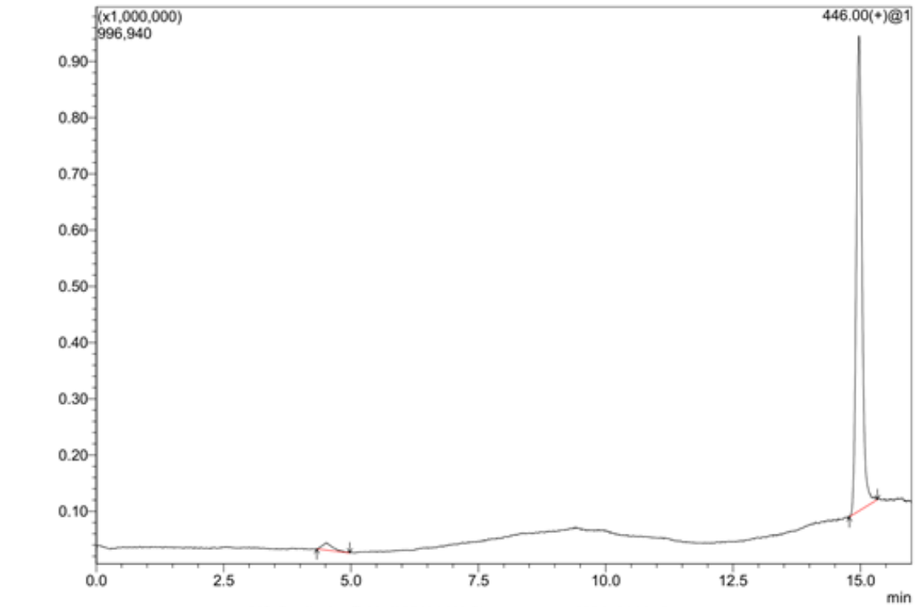
Figure S113 Mass spectra of **4'm**

==== Shimadzu LabSolutions Browser Report ====

MS Chromatogram(180114 NJ Chromatogram 1264_014.lcd)



MS Qualitative Table(180114 NJ Chromatogram 1264_014.lcd)

446.00(Ev1)

Peak#	Ret. Time	Area	m/z	Area%
1	4.510	178931	446.00	2.585
2	14.973	6743621	446.00	97.415
Total		6922552		100.000

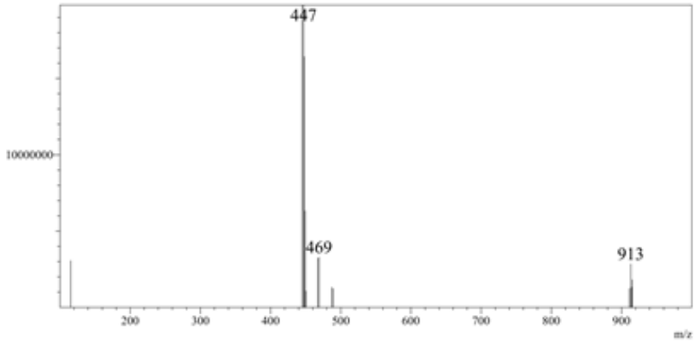
SHIMADZU LabSolutions Analysis Report

<Sample Information>

Sample Name	: 180114 NJ Spectrum 1264		
Sample ID	:		
Data Filename	: 180114 NJ Spectrum 1264_014.lcd		
Method Filename	: NNDKG.lcm		
Batch Filename	: 180114 NJ Spectrum.lcb		
Vial #	: 1-14	Sample Type	: Unknown
Injection Volume	: 1 uL		
Date Acquired	: 1/14/2018 3:19:27 PM	Acquired by	: System Administrator
Date Processed	: 1/14/2018 3:20:29 PM	Processed by	: System Administrator

MS Spectrum

Peak#:1 R.Time:0.464(Scan#:28)
MassPeaks:14
Spectrum Mode:Averaged 0.367-0.533(23-33)
BG Mode:Averaged 0.000-0.300(1-19) Segment 1 - Event 1



MS Spectrum

Peak#:1 R.Time:0.464(Scan#:28)
MassPeaks:14
Spectrum Mode:Averaged 0.367-0.533(23-33)
BG Mode:Averaged 0.000-0.300(1-19) Segment 1 - Event 1

m/z	Absolute Intensity	Relative Intensity
115.20	3072652	15.51
445.05	19797514	99.90
447.05	19816639	100.00
448.10	16433677	82.93
449.10	6332215	31.95
450.10	1078811	5.44
467.10	3224489	16.27

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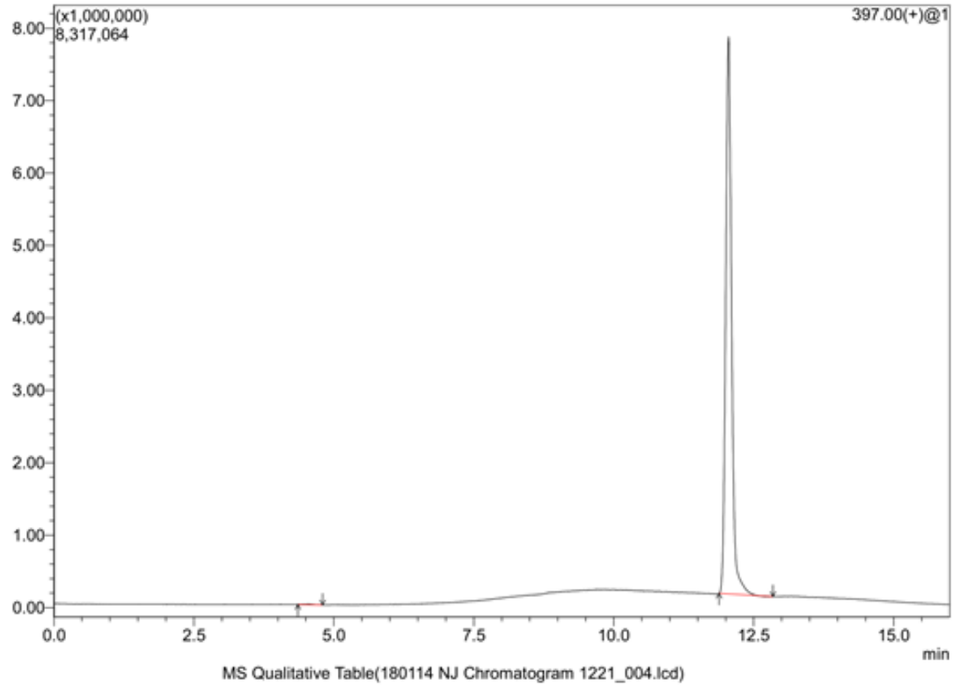
Figure S114 Mass spectra of **4'n**

==== Shimadzu LabSolutions Browser Report ====

MS Chromatogram(180114 NJ Chromatogram 1221_004.lcd)



MS Qualitative Table(180114 NJ Chromatogram 1221_004.lcd)

397.00(Ev1)

Peak#	Ret. Time	Area	m/z	Area%
1	4.529	84123	397.00	0.148
2	12.058	56596281	397.00	99.852
Total		56680405		100.000

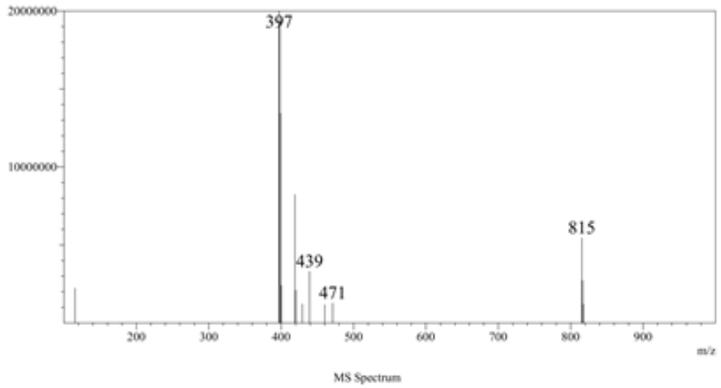
SHIMADZU LabSolutions Analysis Report

<Sample Information>

Sample Name	: 180114 NJ Spectrum 1221		
Sample ID	:		
Data Filename	: 180114 NJ Spectrum 1221_004.lcd		
Method Filename	: NNDKG.lcm		
Batch Filename	: 180114 NJ Spectrum.lcb		
Vial #	: 1-4	Sample Type	: Unknown
Injection Volume	: 1 uL		
Date Acquired	: 1/14/2018 3:03:51 PM	Acquired by	: System Administrator
Date Processed	: 1/14/2018 3:04:53 PM	Processed by	: System Administrator

MS Spectrum

Peak#:1 R.Time:0.451(Scan#:28)
MassPeaks:14
Spectrum Mode:Averaged 0.367-0.533(23-33)
BG Mode:Averaged 0.000-0.300(1-19) Segment 1 - Event 1



MS Spectrum

Peak#:1 R.Time:0.451(Scan#:28)
MassPeaks:14
Spectrum Mode:Averaged 0.367-0.533(23-33)
BG Mode:Averaged 0.000-0.300(1-19) Segment 1 - Event 1

m/z	Absolute Intensity	Relative Intensity
115.20	2241773	11.21
397.15	20000000	100.00
398.20	19385753	96.93
399.20	13454729	67.27
400.25	2409836	12.05
419.15	8240389	41.20
420.20	2097631	10.49

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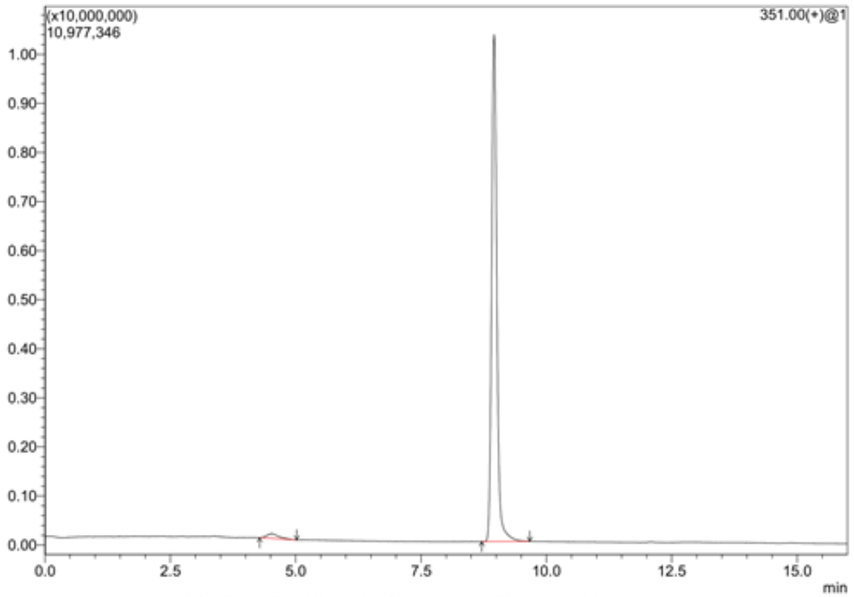
Figure S115 Mass spectra of **4'o**

==== Shimadzu LabSolutions Browser Report ====

MS Chromatogram(180114 NJ Chromatogram 1222 ponovo_020.lcd)



MS Qualitative Table(180114 NJ Chromatogram 1222 ponovo_020.lcd)

351.00(Ev1)

Peak#	Ret. Time	Area	m/z	Area%
1	4.523	1560862	351.00	2.044
2	8.963	74789561	351.00	97.956
Total		76350423		100.000

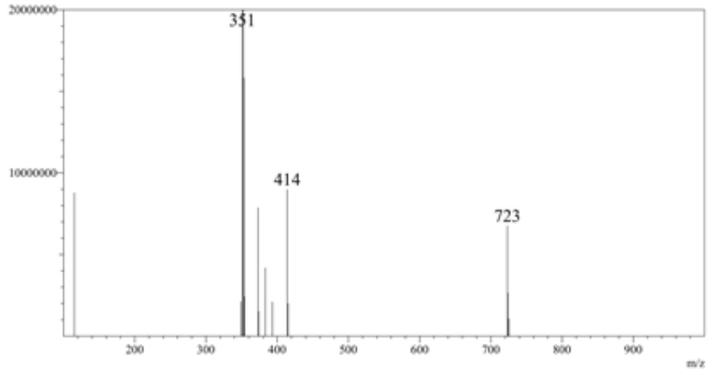
SHIMADZU LabSolutions **Analysis Report**

<Sample Information>

Sample Name	: 180113 NJ 1222 Scan		
Sample ID	:		
Data Filename	: 180113 NJ 1222 Scan.lcd		
Method Filename	: NNDKG.lcm		
Batch Filename	:		
Vial #	: 1-2	Sample Type	: Unknown
Injection Volume	: 1 uL		
Date Acquired	: 1/13/2018 11:14:49 AM	Acquired by	: System Administrator
Date Processed	: 1/13/2018 3:16:39 PM	Processed by	: System Administrator

MS Spectrum

Line#:1 R.Time:----(Scan#:----)
MassPeaks:15
Spectrum Mode:Averaged 0.433-0.467(27-29) Base Peak:351(20000000)
BG Mode:Averaged 0.000-0.300(1-19) Segment 1 - Event 1



MS Spectrum

Peak#:1 R.Time:0.462(Scan#:28)
MassPeaks:15
Spectrum Mode:Averaged 0.433-0.467(27-29)
BG Mode:Averaged 0.000-0.300(1-19) Segment 1 - Event 1

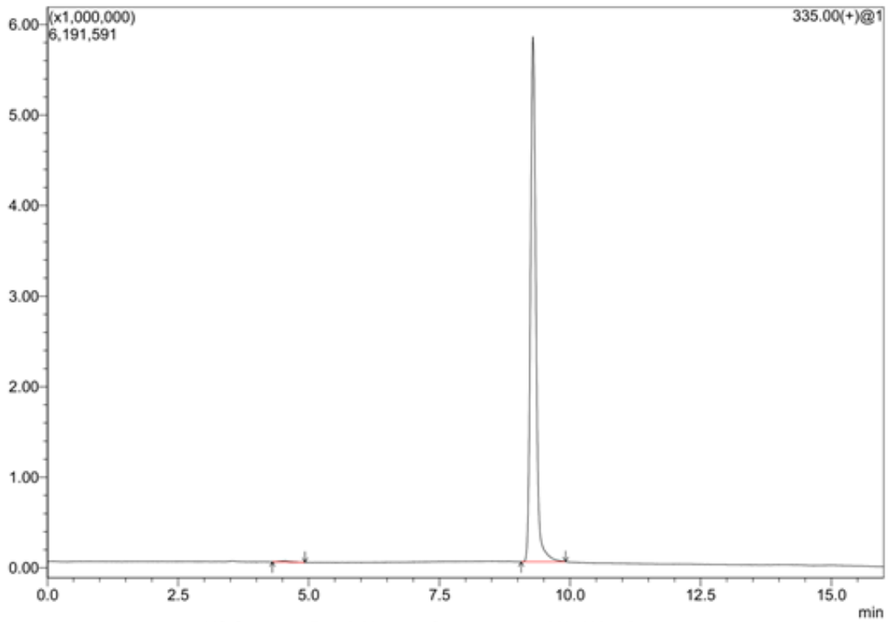
m/z	Absolute Intensity	Relative Intensity
115.20	8795072	43.98
349.15	2117196	10.59
351.15	20000000	100.00
352.20	20000000	100.00
353.20	15829018	79.15
354.20	2423398	12.12
373.15	7875223	39.38
374.20	1518560	7.59

C:\LabSolutions\Data\Nenad KG\NJ 180113 Scan\180113 NJ 1222 Scan.lcd

Figure S116 Mass spectra of **4'p**

==== Shimadzu LabSolutions Browser Report ====

MS Chromatogram(180114 NJ Chromatogram 1263_003.lcd)



MS Qualitative Table(180114 NJ Chromatogram 1263_003.lcd)

335.00(Ev1)

Peak#	Ret. Time	Area	m/z	Area%
1	4.542	183278	335.00	0.432
2	9.294	42254706	335.00	99.568
Total		42437984		100.000

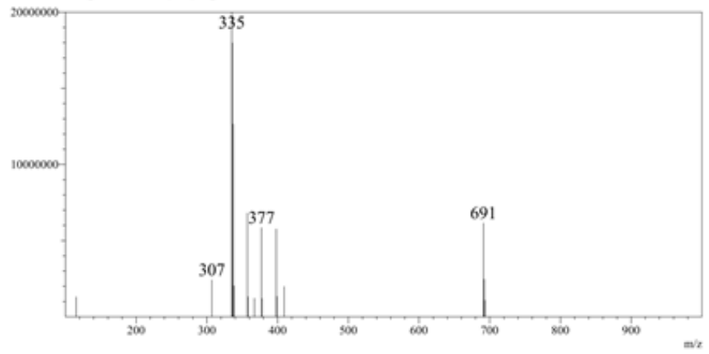
SHIMADZU LabSolutions Analysis Report

<Sample Information>

Sample Name	: 180114 NJ Spectrum 1263		
Sample ID	:		
Data Filename	: 180114 NJ Spectrum 1263_003.lcd		
Method Filename	: NNDKG.lcm		
Batch Filename	: 180114 NJ Spectrum.lcb		
Vial #	: 1-3	Sample Type	: Unknown
Injection Volume	: 1 uL		
Date Acquired	: 1/14/2018 3:02:17 PM	Acquired by	: System Administrator
Date Processed	: 1/14/2018 3:03:19 PM	Processed by	: System Administrator

MS Spectrum

Peak#:1 R.Time:0.460(Scan#:28)
MassPeaks:17
Spectrum Mode:Averaged 0.367-0.533(23-33)
BG Mode:Averaged 0.000-0.300(1-19) Segment 1 - Event 1



MS Spectrum

Peak#:1 R.Time:0.460(Scan#:28)
MassPeaks:17
Spectrum Mode:Averaged 0.367-0.533(23-33)
BG Mode:Averaged 0.000-0.300(1-19) Segment 1 - Event 1

m/z	Absolute Intensity	Relative Intensity
115.20	1315023	6.58
307.15	2422269	12.11
335.15	20000000	100.00
336.15	17991946	89.96
337.20	12657804	63.29
338.20	2044485	10.22
357.20	6815429	34.08
358.20	1318001	6.59
367.20	1218749	6.09

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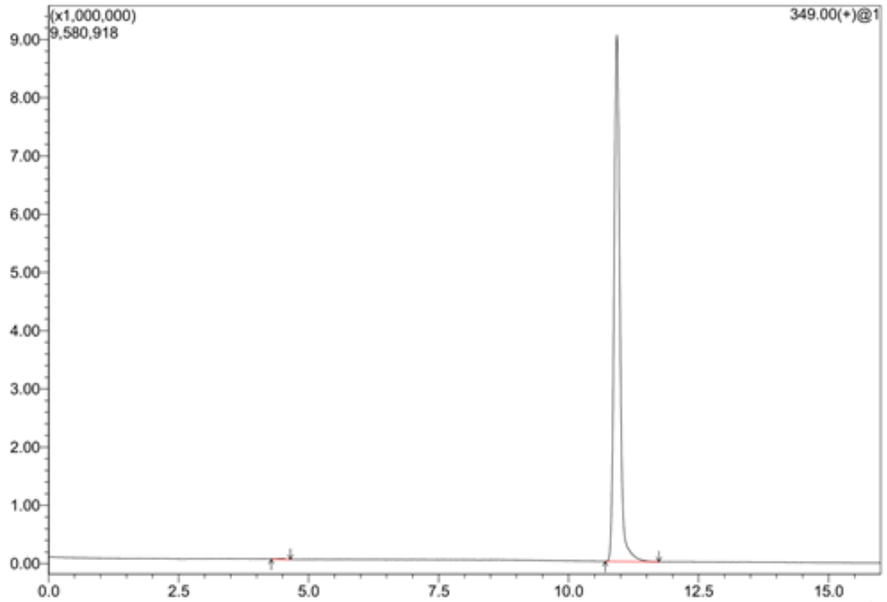
Figure S117 Mass spectra of **4'q**

==== Shimadzu LabSolutions Browser Report ====

MS Chromatogram(180114 NJ Chromatogram 1243_015.lcd)



MS Qualitative Table(180114 NJ Chromatogram 1243_015.lcd)

349.00(Ev1)

Peak#	Ret. Time	Area	m/z	Area%
1	4.465	122653	349.00	0.174
2	10.929	70384627	349.00	99.826
Total		70507280		100.000

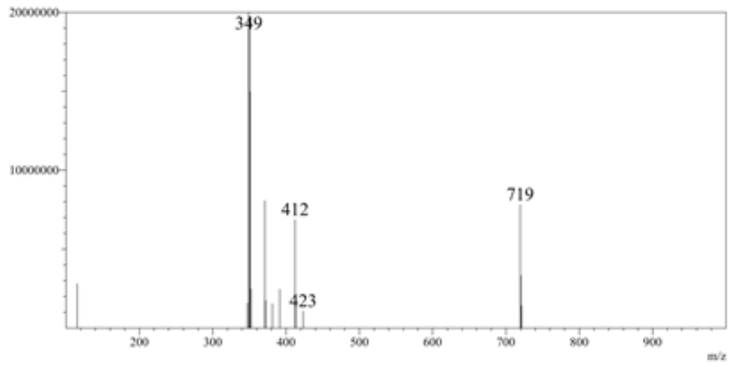
SHIMADZU LabSolutions Analysis Report

<Sample Information>

Sample Name	: 180114 NJ Spectrum 1243		
Sample ID	:		
Data Filename	: 180114 NJ Spectrum 1243_015.lcd		
Method Filename	: NNDKG.lcm		
Batch Filename	: 180114 NJ Spectrum.lcb		
Vial #	: 1-15	Sample Type	: Unknown
Injection Volume	: 1 uL		
Date Acquired	: 1/14/2018 3:21:01 PM	Acquired by	: System Administrator
Date Processed	: 1/14/2018 3:22:02 PM	Processed by	: System Administrator

MS Spectrum

Peak#:1 R.Time:0.466(Scan#:28)
MassPeaks:16
Spectrum Mode:Averaged 0.367-0.533(23-33)
BG Mode:Averaged 0.000-0.300(1-19) Segment 1 - Event 1



MS Spectrum

Peak#:1 R.Time:0.466(Scan#:28)
MassPeaks:16
Spectrum Mode:Averaged 0.367-0.533(23-33)
BG Mode:Averaged 0.000-0.300(1-19) Segment 1 - Event 1

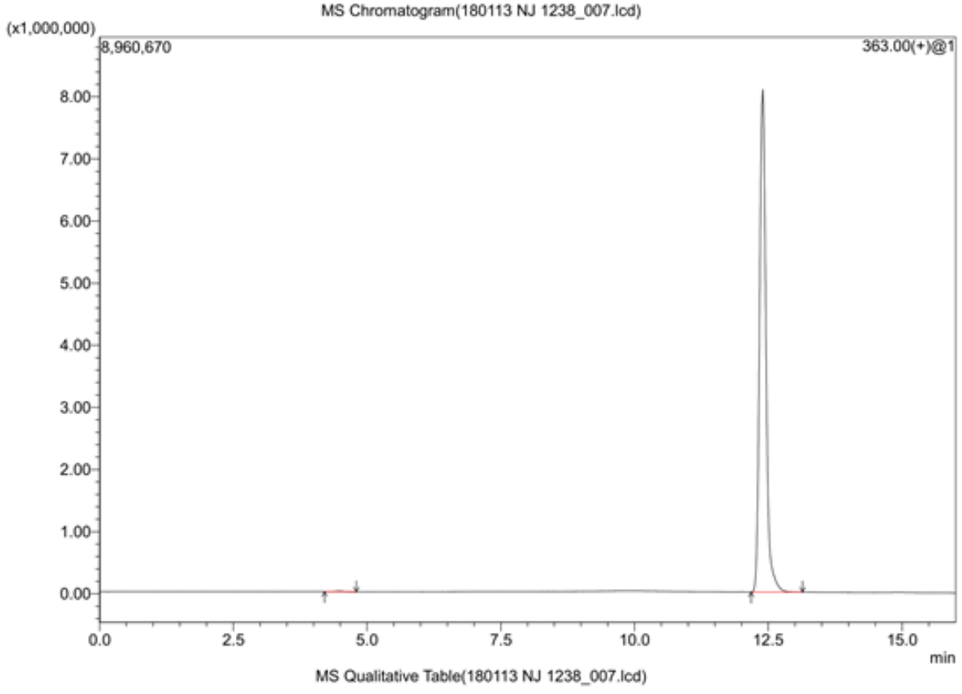
m/z	Absolute Intensity	Relative Intensity
115.20	2822207	14.11
347.20	1585426	7.93
349.15	20000000	100.00
350.20	19762234	98.81
351.20	14995102	74.98
352.25	2494270	12.47
371.15	8084195	40.42
372.20	1745191	8.73

C:\LabSolutions\Data\Nenad KG\NJ 180113 Scan\180114 NJ Spectrum 1243_015.lcd

Figure S118 Mass spectra of **4'r**

==== Shimadzu LabSolutions Browser Report ====

MS Chromatogram(180113 NJ 1238_007.lcd)



MS Qualitative Table(180113 NJ 1238_007.lcd)

363.00(Ev1)

Peak#	Ret. Time	Area	m/z	Area%
1	4.470	135641	363.00	0.200
2	12.391	67677031	363.00	99.800
Total		67812671		100.000

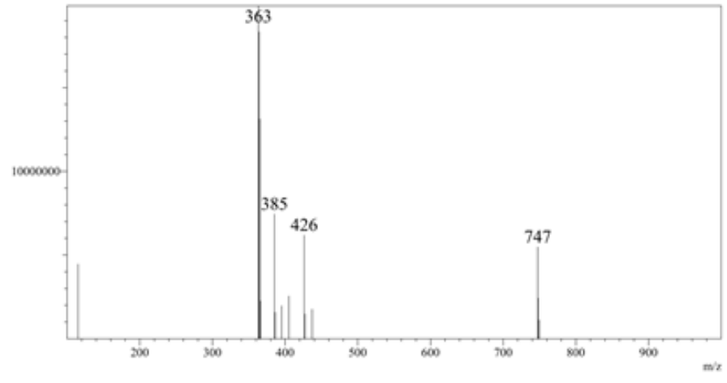
SHIMADZU LabSolutions **Analysis Report**

<Sample Information>

Sample Name	: 180113 NJ 1238 Scan		
Sample ID	:		
Data Filename	: 180113 NJ 1238 Scan.lcd		
Method Filename	: NNDKG.lcm		
Batch Filename	:		
Vial #	: 1-6	Sample Type	: Unknown
Injection Volume	: 1 uL		
Date Acquired	: 1/13/2018 12:44:25 PM	Acquired by	: System Administrator
Date Processed	: 1/13/2018 3:28:03 PM	Processed by	: System Administrator

MS Spectrum

Line#:1 R.Time:----(Scan#:----)
MassPeaks:15
Spectrum Mode:Averaged 0.367-0.533(23-33) Base Peak:363(19889807)
BG Mode:Averaged 0.000-0.300(1-19) Segment 1 - Event 1



MS Spectrum

Peak#:1 R.Time:0.464(Scan#:28)
MassPeaks:15
Spectrum Mode:Averaged 0.367-0.533(23-33)
BG Mode:Averaged 0.000-0.300(1-19) Segment 1 - Event 1

m/z	Absolute Intensity	Relative Intensity
115.20	4460672	22.43
363.15	19889807	100.00
364.20	18338954	92.20
365.20	13130773	66.02
366.20	2259015	11.36
385.20	7446488	37.44
386.20	1589030	7.99
395.25	1970384	9.91

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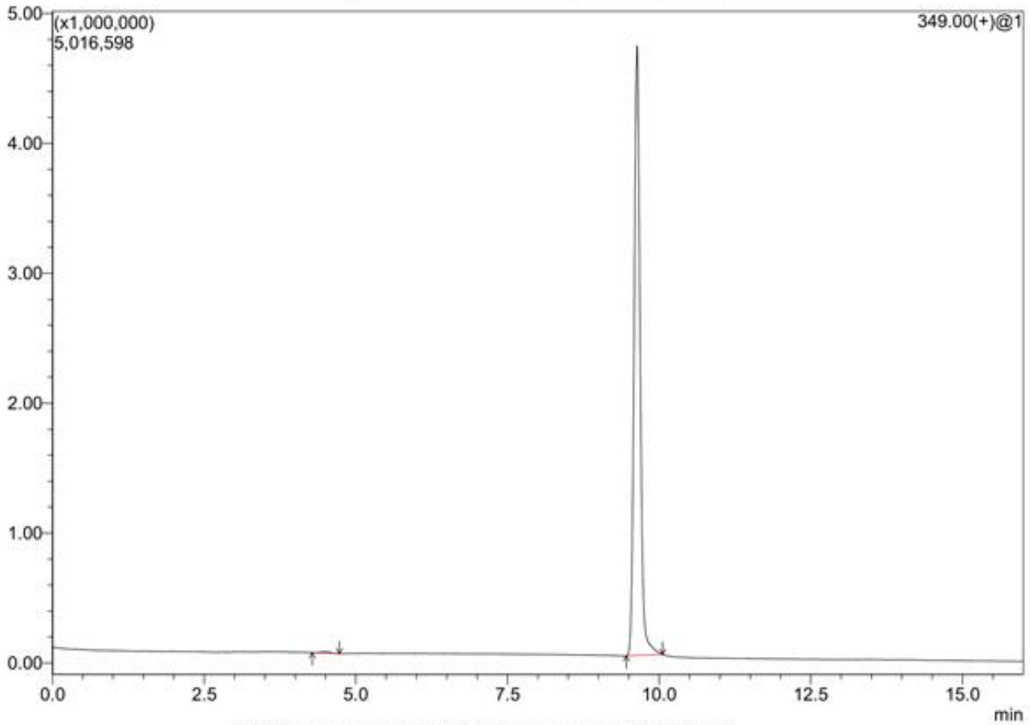
Figure S119 Mass spectra of **4's**

==== Shimadzu LabSolutions Browser Report ====

MS Chromatogram(180114 NJ Chromatogram 1253_005.lcd)



MS Qualitative Table(180114 NJ Chromatogram 1253_005.lcd)

349.00(Ev1)

Peak#	Ret. Time	Area	m/z	Area%
1	4.502	124260	349.00	0.381
2	9.637	32488664	349.00	99.619
Total		32612923		100.000

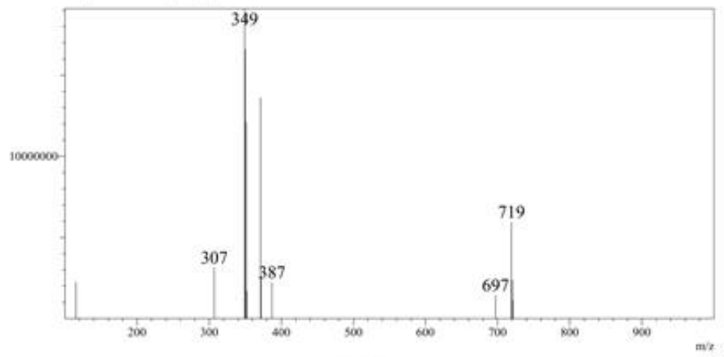
SHIMADZU LabSolutions Analysis Report

<Sample Information>

Sample Name	: 180114 NJ Spectrum 1253		
Sample ID	:		
Data Filename	: 180114 NJ Spectrum 1253_005.lcd		
Method Filename	: NNDKG.lcm		
Batch Filename	: 180114 NJ Spectrum.lcb		
Vial #	: 1-5	Sample Type	: Unknown
Injection Volume	: 1 uL		
Date Acquired	: 1/14/2018 3:05:24 PM	Acquired by	: System Administrator
Date Processed	: 1/14/2018 3:06:26 PM	Processed by	: System Administrator

MS Spectrum

Peak#:1 R.Time:0.448(Scan#:27)
MassPeaks:13
Spectrum Mode:Averaged 0.350-0.517(22-32)
BG Mode:Averaged 0.000-0.300(1-19) Segment 1 - Event 1



MS Spectrum

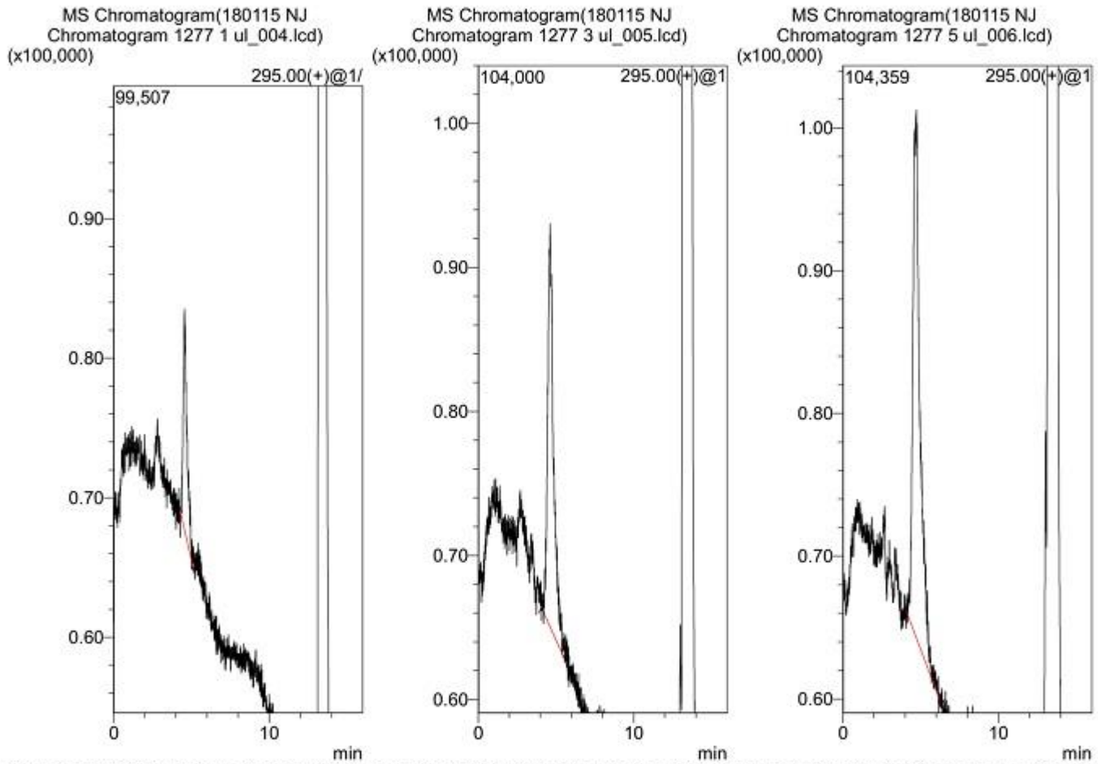
Peak#:1 R.Time:0.448(Scan#:27)
MassPeaks:13
Spectrum Mode:Averaged 0.350-0.517(22-32)
BG Mode:Averaged 0.000-0.300(1-19) Segment 1 - Event 1

m/z	Absolute Intensity	Relative Intensity
115.15	2237250	11.71
307.15	3120804	16.33
349.10	19108183	100.00
350.15	16569640	86.71
351.20	12115902	63.41
352.20	1690033	8.84

C:\LabSolutions\Data\Nenad KG\NJ 180113 Scan\180114 NJ Spectrum 1253_005.lcd

Figure S120 Mass spectra of **4't**

==== Shimadzu LabSolutions Browser Report ====



tive Table(180115 NJ Chromatogram 1277 1

295.00(Ev1)

Peak#	Ret. Time	Area
1	4.556	268173
2	13.310	101539902
Total		101808075

m/z
295.00
295.00

tive Table(180115 NJ Chromatogram 1277 3

295.00(Ev1)

Peak#	Ret. Time	Area
1	4.621	736396
2	13.285	234044920
Total		234781316

m/z
295.00
295.00

tive Table(180115 NJ Chromatogram 1277 5

295.00(Ev1)

Peak#	Ret. Time	Area
1	4.683	1185087
2	13.304	281769391
Total		282954478

m/z
295.00
295.00

Figure S121 Observed chromatograms upon variable injection of **4'f**

5. X-ray crystallography

X-ray diffraction experiments

Single-crystal X-ray diffraction data for compounds **4f**, **4'c**, **4'd**, **4'g** and **4's** were collected on an Oxford Gemini S diffractometer equipped with a CCD detector, using monochromatized Mo *K*α radiation (λ = 0.71073 Å). Data reduction and empirical absorption correction were performed with CrysAlisPRO.[1] The structures were solved by direct methods using SHELXS and refined on F^2 by full-matrix least-squares using SHELXL.[2] All non-H atoms were refined anisotropically. H atoms bonded to N atoms were located in difference Fourier maps and refined isotropically, with the exception of the disordered twin structure **4f** where these atoms were placed at geometrically calculated positions with the N–H distances fixed to 0.86 Å and U_{iso}(H) = 1.2U_{eq}(N). H atoms bonded to C atoms were placed at geometrically calculated positions with the C–H distances fixed to 0.93 from Csp^2 and 0.98, 0.97 and 0.96 Å from methine, methylene and methyl Csp^3, respectively. The corresponding isotropic displacement parameters were U_{iso}(H) = 1.2U_{eq}(C) for Csp^2, methine and methylene H atoms, while U_{iso}(H) = 1.5U_{eq}(C) for methyl H atoms.

In compound **4'g** the atoms C4, C6 and C7 belonging to heterocyclic and phenyl rings of molecule B were disordered over two sites with a site-occupation factor of 0.572(8) for the major occupied orientation. The thermal parameters of the corresponding carbon atoms were restrained by SIMU instruction from the SHELXL.[2]

The compound **4f** crystalized as nonmerohedral twin and was refined using an HKLF 5 reflection file with BASF value of 0.35822. In addition, the terminal C atoms of the S-allyl substituent in molecule B of **4f** were found disordered over two sites with a site-occupation factor of 0.54(2) for the major occupied orientation. Bond-length and bond-angle restraints were applied for the disordered fragment of S-allyl substituent in molecule B, while the disordered atoms were refined isotropically.

Crystallographic details for structure analysis of five compounds are summarized in **Table S1**. The crystal structures of compounds including the atom labelling schemes are presented in **Figure 3**, while selected geometrical parameters are listed in **Table S2** and **Table S3**. Figureures were produced using ORTEP-3[3] and MERCURY.[4] The software used for the preparation of the materials for publication: WINGX,[5] PLATON,[6] PARST.[7]

Description of crystal structures

The molecular structure of the compounds **4f**, **4'c**, **4'd**, **4'g** and **4's** (Figure 3) is determined by single-crystal X-ray analysis (Table S1). Compounds **4f**, **4'd** and **4'g** contain two crystallographically independent molecules per asymmetric unit. All molecules have chiral center in C4 position, but they crystallize in centrosymmetric space groups as racemic mixtures. Due to close structural resemblance of the pairs of independent molecules (comparison of A and B molecules in these crystal structures is given in Figure S122), only molecules A are used in structural analysis (Figure 4 and Figure S123).

Five molecules are characterized by a similar structural fragment which consists of the DHPM ring bearing the phenyl substituent at chiral C4 and the methylallylthio or allylthio group at atom C1 (Figure 3). The overlay of these fragments (Figures 4 and S122) reveals a very similar half-chair conformation of the central six-membered ring, where the C4 atom significantly deviates [0.510(3) to 0.623(3) Å] from the least-squares plane of the other five atoms [rms deviations of N2/C1/N1/C2/C3 atoms range from 0.053 to 0.078]. This is consistent with the fact that the largest torsion angles in each ring involve the C4 atom (the average values of C2–C3–C4–N2 and C3–C4–N2–C1 are 49.9 and -38.1°, respectively, Table S2). The five molecules mainly differ in two respects (Figures 4 and S123), i.e. the different inclination of the aromatic fragment relative to the heterocyclic ring and the dissimilar orientation of their S-substituents. In each molecule the aromatic fragment takes the equatorial position on C4 atom, nevertheless the dihedral angle between the mean planes of the above described heterocyclic fragment (N2/C1/N1/C2/C3) and the phenyl ring significantly increases when the latter belongs to more voluminous substituents. Thus in **4's** and **4'c** this dihedral angle is distinctly larger [82.4(1) and 57.2(1)°, respectively] in comparison to other structures which show a rather uniform twist of the corresponding aromatic substituents (35.5° in average. See also Figure S123). As evidenced by the different values of torsion angle C1–S1–C11–C12 (Table S2) the S-allyl fragment can change the orientation with respect to the heterocycle by a free rotation along the C1–S1 single bond, Figure 4. Thus in molecules **4'c**, the A molecule of **4'd** and **4's** the fragment lays close to the plane of the corresponding heterocycle (the average value of the C1–S1–C11–C12 torsion angle is 174.8°), while it is almost orthogonally positioned in **4'g** and **4f** (the average value of 87.0°). In the B molecule of **4'd** the torsion angle C1–S1–C11–C12 has intermediate value of 145.3(3)°.

A comparison of structural parameters given in Table S3 indicates similar bond lengths and angles for the five molecules. The double bond character decreases in C2–C3 bond involving the sp^3 carbon atom, while the C3–C4 and C4–N2 bonds are typically single bonds. It is interesting to notice that the all five molecules display very short length for the corresponding N2–C1 bond (average value of 1.26 Å); this can imply a highly localized electron density in this part of each heterocyclic ring. In order to examine the frequency of occurrence of such short N–C bonds a CSD search[8] is performed for heterocyclic structures comprising the N atom bonded only to two carbon atoms. The histogram plot in Figure 5 shows that in vast majority of structures the N–C bonds have the distance in range 1.31-1.38 Å, while less than 1% of the structures have the distances similar to N2–C1 bond in present compounds. Results of the CSD search also show that the difference between the bond lengths of two N-C bonds formed by the same N rarely reaches 0.21 Å as is the case with the N2–C1 and N2–C4 bonds in the present structures (see histogram plot in Figure S124).

The main structural feature of the crystal packing of **4f**, **4'd**, **4'g** and **4's** is the formation of discrete molecular dimers where the molecular components link by pairs of strong and nearly linear N1–H...O1 hydrogen bonds, Figure S125 [the average H...O distances and N–H...O angles are 2.02 Å and 171°, respectively, Table S4]. This common hydrogen bonding motif engages the most polar parts of the molecules, and it is formed either between the centrosymmetric molecular pairs (in **4f** and **4's**) or between the pairs of symmetry independent molecules (in **4'd** and **4'g**), Figure S125. The molecules of **4'c**, comprising the voluminous anthracene fragment, crystallize with DMSO solvent and do not form this type of dimers. Instead, each molecule of **4'c** engages the same hydrogen bonding sites in interactions with DMSO [N1–H1n...O2^{i}: H...O 1.97Å, N–H...O 175(2)°, symmetry code (i): -x+1,+y+0.5,-z+0.5; C23–H23B...O1^{ii}: H...O 2.47 Å, C–H...O 141°, symmetry code (ii): x,-y+0.5,+z-0.5] eventually forming the cyclic four-component unit consisting of **4'c**·DMSO pairs, Figure S126. The pyridine N2 acceptor is not involved in intermolecular interactions and no other significant hydrogen bonds can be observed in **4f**, **4'c**, **4'd**, **4'g** and **4's**.

On the other hand, the different aromatic substituents present at C4 atom of each compound give rise to numerous C-H...π and π...π interactions relevant for the crystal stabilization (Table S4). Thus the partial overlapping between the large antracene substituents in **4'c** results in π...π interaction with the interplanar distance between the adjacent ring systems of 3.45 Å and the distance between the closest ring centroids of 3.7899(2) Å. Additionally, the antracene substituents serve as donor and π acceptor in C–H...π interaction [C21–H21...Cg1^{i}: H...Cg 2.97 Å, C–H...Cg 149°, where Cg1 is centroid of C5/C10 ring, symmetry code (i): -x, y+0.5, -z+0.5]. The aromatic fragments of independent molecules in **4'd** also involve in numerous interactions. The above described N1–H...O1 bonded dimers mutually connect by rather short C–H...π interaction [C6b–H6b...Cg1^{i}: H...Cg 2.78 Å C–H...Cg 156°, where Cg1 is centroid of C5a/C10a ring, symmetry code (i): -x+1, -y+1, -z+1], while the parallel arrangement between the phenyl rings of molecule B results in π...π interactions with the interplanar distance of 3.56 Å and the distance between the ring centroids of 3.742(2) Å (symmetry code: -x, -y+2,-z). Ring B also forms additional weak C–H...π interaction with the S-allyl moiety [C13b–H13b...Cg2^{ii}: H...Cg 3.11 Å, C–H...Cg 152°, where Cg2 is centroid of C5b/C10b ring, symmetry code (ii): x, -y, 1-z]. Due to conformational disorder it is not possible to examine the role of the aromatic substituents in compound **4'g**, however it is worth noticing the engagement of the ordered S-allyl fragment in short and directional contacts to carbonyl O1 (Table S4), which could be related with the different orientation of the S- allyl fragment in these molecules (Figure 4). The structures **4's** and **4f** are both characterized by C–H...π interactions involving the phenyl substituents as the π

acceptors of donors from S-allyl and heterocyclic fragments, respectively [**4's:** C13–H13A...Cg1^{i}: H...Cg 2.95 Å, C–H... Cg 157°, symmetry code (i): -x, -y+2,-z; **4f:** C3a–H3a1...Cg1^{i}: H...Cg 2.94 Å, C–H...Cg 118°, symmetry code (i): x, -y+1.5, z-0.5.]. Full list of intermolecular interactions and the packing diagrams of the compounds are given in Table S4 and Figure S127.

1. Agilent, CrysAlis PRO, Agilent Technologies, Yarnton, Oxfordshire, England, 2013.
2. G. M. Sheldrick, *Acta Crystallogr., Sect. A*: Fundam. Crystallogr., 2008, **64**, 112.
3. L. J. Farrugia, *J. Appl. Crystallogr.*, 2012, **45**, 849.
4. C. F. Macrae, P. R. Edgington, P. McCabe, E. Pidcock, G. P. Shields, R. Taylor, M. Towler and J. van de Streek, *J. Appl. Crystallogr.*, 2006, **39**, 453.
5. L. J. Farrugia, *J. Appl. Crystallogr.*, 1999, **32**, 837.
6. A. L. Spek, *J. Appl. Crystallogr.*, 2003, **36**, 7.
7. M. Nardelli, *J. Appl. Crystallogr.*, 1995, **28**, 659.
8. F. H. Allen, *Acta Crystallogr., Sect. B*, 2002, **58**, 380. Cambridge Structural Database [CSD version 5.38, November 2016].

Table S1 Crystallographic data and refinement details.

	4f	**4'c**	**4'd**	**4'g**	**4's**
Empirical formula	$C_{13}H_{13}ClN_2OS$	$C_{24}H_{26}N_2O_2S_2$	$C_{14}H_{15}ClN_2OS$	$C_{15}H_{18}N_2OS_2$	$C_{19}H_{26}N_2O_3S$
Formula weight	280.76	438.59	294.79	306.43	362.48
Color, crystal shape	Colourless, prism	Colourless, plate	Colourless, prism	Colourless, plate	Yellow, prism
Crystal size (mm^3)	0.16 x 0.48 x 0.48	0.10 x 0.39 x 0.46	0.13x 0.24 x 0.36	0.09 x 0.19 x 0.50	0.14 x 0.20 x 0.34
Temperature (K)	293(2)	293(2)	293(2)	293(2)	293(2)
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073	0.71073
Crystal system	monoclinic	monoclinic	triclinic	monoclinic	triclinic
Space group	$P2_1/c$	$P2_1/c$	P-1	I2/a	P-1
Unit cell dimensions					
a (Å)	24.9132(13)	16.0134(7)	10.1382(6)	26.0519(12)	6.184(5)
b (Å)	10.5411(5)	9.3012(3)	11.3042(6)	9.2061(3)	9.994(5)
c (Å)	10.4984(4)	16.3406(8)	13.3643(13))	28.8160(15)	16.720(5)
α (°)	90	90	101.411(6)	90	77.369(5)
β (°)	101.545(5)	114.009(6)	113.893(4)	113.376(6)	85.008(5)
γ (°)	90	90	97.289(5)	90	80.707(5)
V (Å^3)	2701.2(2)	2223.26(19)	1483.59(19)	6343.9(6)	993.7(10)
Z	8	4	4	16	2
D_{calc} (Mg/m^3)	1.381	1.310	1.320	1.283	1.211
μ (mm^{-1})	0.426	0.263	0.391	0.333	0.182
ϑ range for data collection (°)	2.55-29.13	2.58-29.00	3.57-29.16	2.63-29.08	2.66-29.02
Reflections collected	24908	9736	12155	28462	7437
Independent reflections, R_{int}	0.0516	0.0256	0.0229	0.0286	0.0181
Data /parameters	5565/325	5089/278	6742263/	7546/401	4456/233
Goodness-of-fit	1.161	1.022	1. 018	1.071	1.034
Final R_1/wR_2 indices [$I > 2\sigma(I)$]	0.0870/0.2258	0.0460/0.0702	0. 0598/0.0984	0. 0649/0.1007	0.0526/0.0746
Final R_1/wR_2 indices (all data)	0.1052/0.2350	0.1019/0.1147	0. 1414/0.1661	0.1451/1622	0.1280/0.1442
Largest diff. peak and hole (e Å^{-3})	0.443/-0.365	0.234/-0.300	0.536/-0.424	0.753/-0.292	0.356/-0.167

Table S2 Selected torsion angles.

	4f		**4'c**	**4'd**		**4'g**	**4's**
	A	B		A	B	A**	
C1–N1–C2–C3	-1.1(8)	0.3(8)	-1.6(3)	-4.7(4)	5.7(4)	-0.9(4)	-0.4(3)
N1–C2–C3–C4	-33.0(7)	-33.2(7)	-32.3(2)	-28.8(4)	29.5(3)	-29.0(4)	-28.5(3)
C2–C3–C4–N2	53.8(6)	51.9(6)	52.2(2)	50.9(3)	-52.4(3)	48.9(4)	45.1(2)
C3–C4–N2–C1	-40.0(6)	-37.7(7)	-37.9(2)	-40.0(4)	40.9(3)	-38.3(4)	-33.2(3)
C4–N2–C1–N1	4.4(8)	3.5(8)	2.9(3)	5.9(5)	-5.5(4)	7.8(4)	4.0(3)
N2–C1–N1–C2	18.6(8)	17.4(9)	19.4(3)	18.8(5)	-20.6(4)	12.8(5)	14.9(3)
N2–C4–C5–C10	19.6(7)	19.5(8)	35.3(3)	7.8(4)	-3.1(4)	5.3(5)	-123.9(2)
N2–C1–S1–C11	0.94(6)	-0.52(6)	-0.7(2)	3.1(4)	-4.1(3)	-4.6(3)	4.8(2)
C1–S1–C11–C12	-89.1(8)	*	173.7(2)	177.6(3)	-145(2)	-84.8(3)	173.0(2)

* S-allyl substituent in molecule B of **4f** is partly disordered.

** Molecule B of **4'g** is partly disordered thus only the parameters for molecule A are presented in the Table.

Table S3 Selected bond distances and angles.

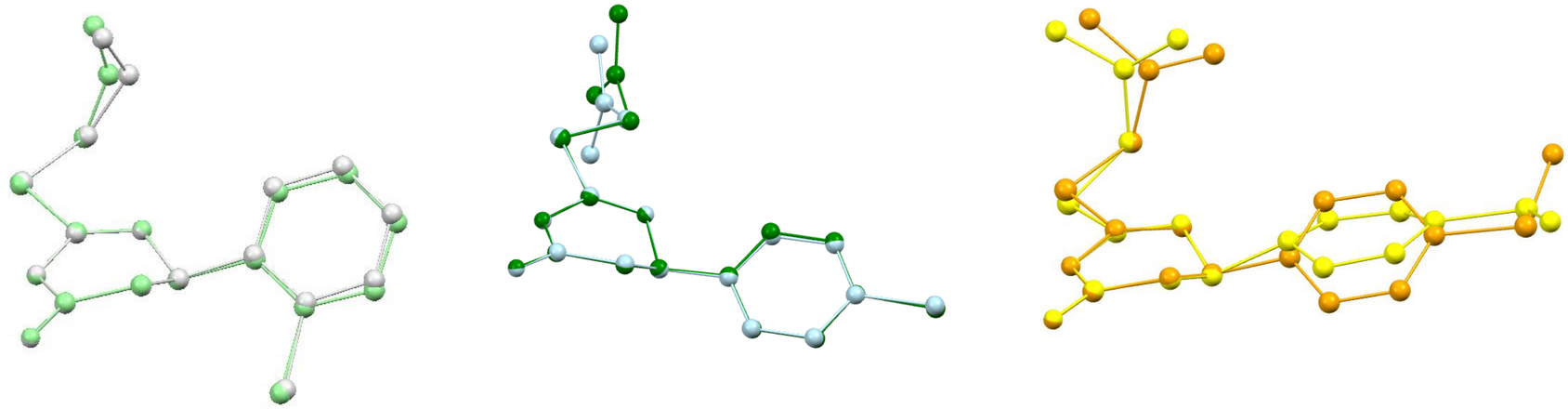
	4f		**4'c**	**4'd**		**4'g****	**4's**
	A	B		A	B	A	
N1–C1	1.406(6)	1.393(7)	1.395(2)	1.401(4)	1.405(3)	1.397(4)	1.399(3)
N1–C2	1.350(8)	1.352(8)	1.358(3)	1.349(4)	1.360(3)	1.352(3)	1.350(2)
N2–C1	1.257(7)	1.254(7)	1.268(2)	1.255(4)	1.258(3)	1.261(3)	1.266(2)
N2–C4	1.464(7)	1.462(7)	1.469(2)	1.464(4)	1.470(3)	1.471(4)	1.476(3)
C2–C3	1.500(8)	1.503(8)	1.500(3)	1.502(4)	1.495(4)	1.495(4)	1.495(3)
C3–C4	1.532(7)	1.519(7)	1.532(2)	1.512(4)	1.526(4)	1.451(5)	1.513(3)
C4–C5	1.520(7)	1.511(8)	1.528(2)	1.512(4)	1.507(3)	1.522(4)	1.523(3)
C2–O1	1.215(6)	1.219(7)	1.218(2)	1.219(3)	1.221(3)	1.215(3)	1.223(2)
C1–S1	1.757(6)	1.767(6)	1.762(2)	1.739(3)	1.757(3)	1.756(3)	1.755(2)
C11–S1	1.808(6)	1.802(8)	1.813(2)	1.820(4)	1.812(3)	1.802(3)	1.816(3)
N1–C1–N2	125.8(5)	125.7(5)	125.7(2)	125.6(3)	124.7(2)	125.2(2)	125.6(2)
N1–C2–C3	114.5(4)	114.1(5)	114.1(2)	114.8(2)	114.3(2)	113.4(3)	114.6(2)
N2–C4–C3	111.1(5)	111.2(5)	111.3(1)	111.2(2)	110.2(2)	113.7(3)	112.5(2)
C1–N1–C2	121.2(5)	121.5(5)	121.7(2)	121.0(3)	121.3(2)	122.5(2)	122.2(2)
C1–N2–C4	114.8(4)	115.8(5)	115.1(2)	115.5(2)	115.9(2)	114.3(2)	116.3(2)
C2–C3–C4	110.1(4)	110.9(5)	111.0(2)	111.5(2)	111.5(2)	113.2(3)	113.5(2)
C1–S1–C11	101.3(3)	101.1(3)	100.1(1)	100.4(2)	101.8(1)	102.9(1)	100.4(1)
N2–C4–C5	110.9(4)	110.4(4)	114.4(2)	111.2(2)	111.2(2)	111.2(3)	109.6(2)
C3–C4–C5	111.4(4)	111.2(5)	111.8(2)	113.2(2)	112.4(2)	113.6(3)	111.3(2)

** Molecule B of **4'g** is partly disordered thus only the parameters for molecule A are presented in the Table.

Table S4 Geometrical parameters for intermolecular interactions.

D–H...A	D–H (Å)	H...A (Å)	D–H...A (°)	Symmetry codes:
4f				
N1a–H1a...O1a	0.86	2.04	158	-x+1, -y+2, -z+1
N1b–H1b...O1b	0.86	2.03	161	-x, -y, -z
C3a–H3a1... Cg1	0.97	2.94	118	x, -y+1.5, z-0.5
4'c				
N1–H1n... O2	0.84(2)	1.97(3)	175(2)	-x+1, y+0.5, -z+0.5
C23–H23B...O1	0.96	2.47	141	x, -y+0.5, z-0.5
Cg1...Cg2		3.7899(2)		-x, 2-y, -z
C21–H21...Cg1	0.93	2.97	149	-x, y+0.5, -z+0.5
4'd				
N1a–H1a...O1b	0.86(3)	2.02(3)	173(3)	-x+1, -y+1, -z+2
N1b–H1b...O1a	0.86(3)	2.00(3)	178(3)	-x+1, -y+1, -z+2
C14a–H14c–O1a	0.96	2.57	170(4)	x, y-1, z
Cg1...Cg2		3.742(2)		-x+1, -y+1, -z+1
C6b–H6b...Cg1	0.93	2.78	156	-x+1,-y+1,-z+1
C13b–H13b...Cg1	0.93	3.11	152	-x+1, -y, -y+1
4'g				
N1a–H1a...O1b	0.79(3)	2.12(3)	175(4)	-x,-y+1,-z
N1b–H1b...O1a	0.86(3)	1.96(3)	177(4)	-x,-y+1,-z
C14a–H14c...O1b	0.96	2.59	148	x, y-1, z
C11b–H11c...O1a	0.97	2.45	164	x, y-1, z
4's				
N1–H1n...O1	0.81(2)	2.05(2)	175(2)	-x,-y+1,-z+2
C13–H13a...Cg1	0.93	2.95	157	-x, -y+2, -z

In **4f**: Cg1 is centroid of ring C5a/C10a. In **4'c**: Cg1 and Cg2 are centroid of rings C5/C10 and C6/C18, respectively.
In **4'd**: Cg1 and Cg2 are centroids of rings C5a/C10a and C5b/C10b, respectively. In **4's**: Cg1 is centroid of ring C5/C10.



4f **4'd** **4'g**

Figure S122 The overlay of crystallographically independent molecules in **4f**, **4'd** and **4'g** based on a least-squares fit of the atoms from heterocyclic rings. In the case of disordered molecules **4f** and **4'g** (B molecules) the major component is used for structural overlapping.

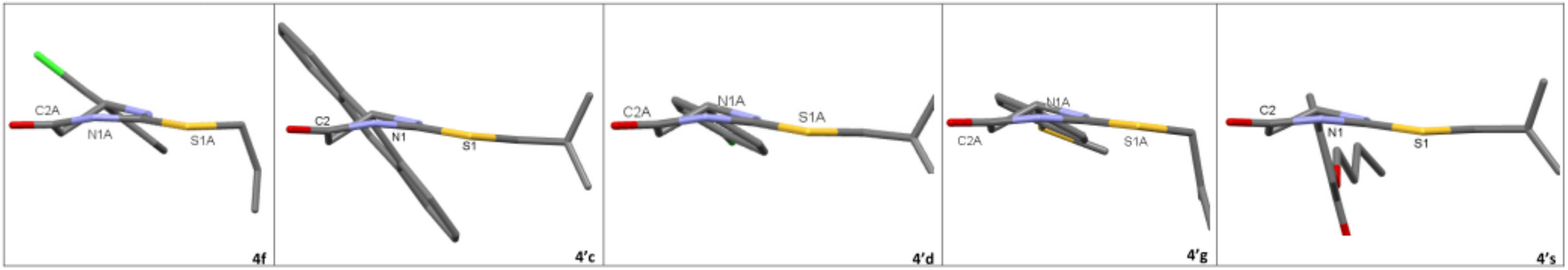


Figure S123 Different orientation of the aromatic and the S-allyl substituents with respect to the heterocyclic ring.

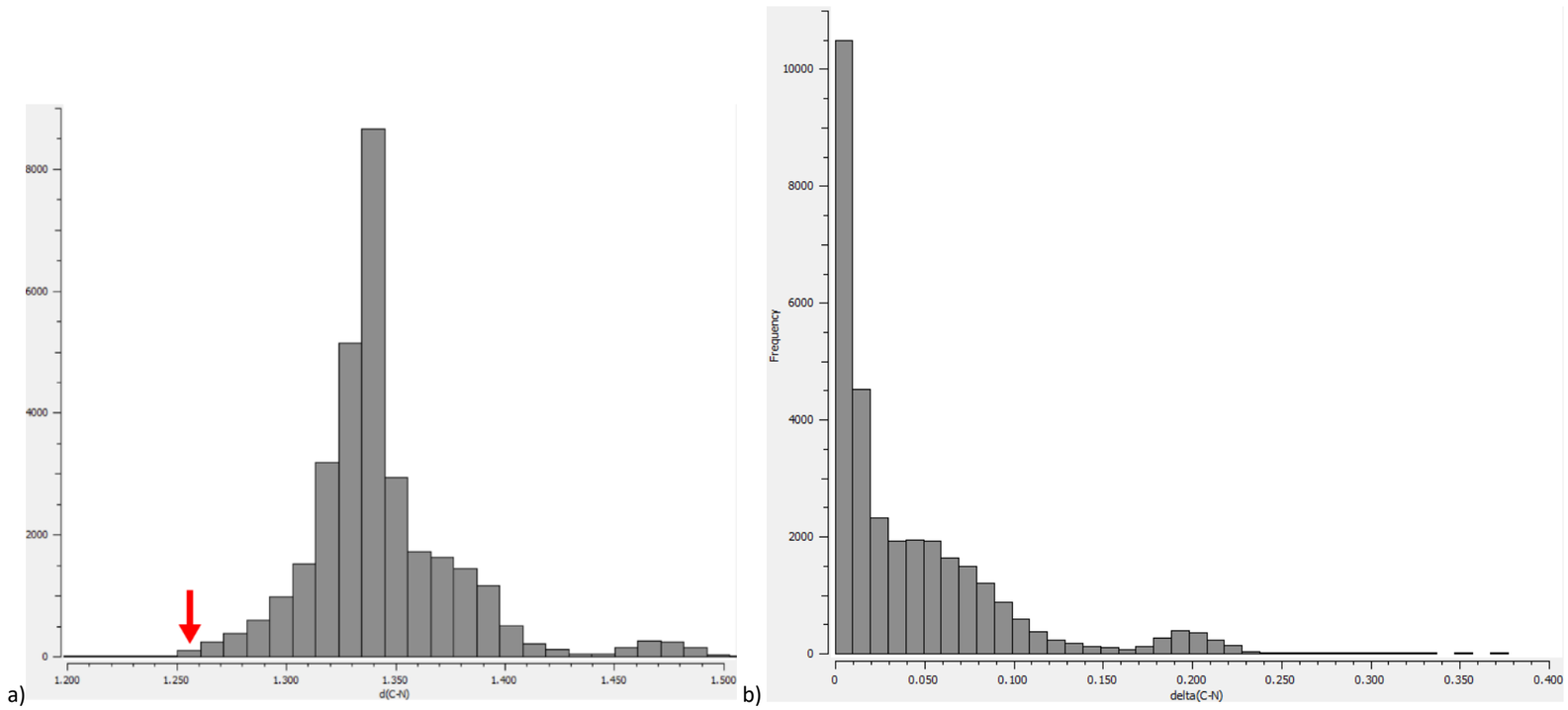
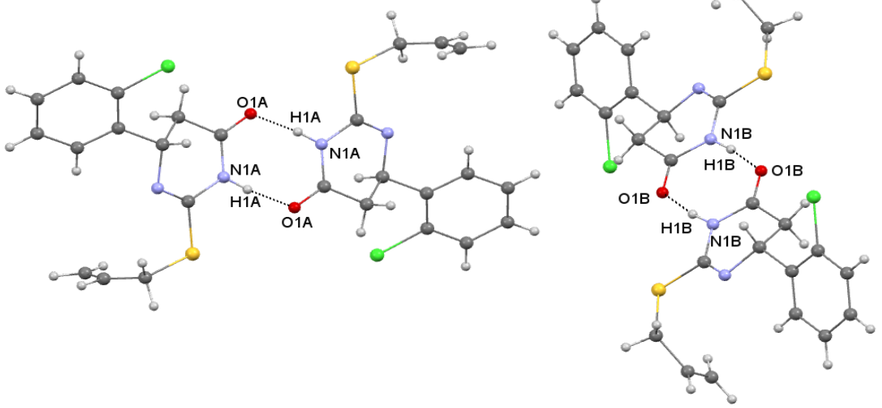
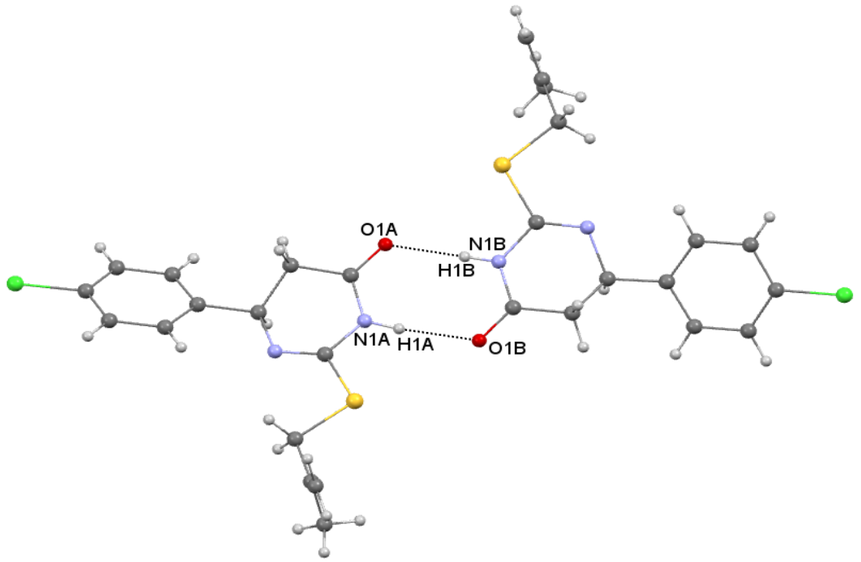


Figure S124 Result of the CSD analysis: a) Distribution of N–C bond lengths in heterocyclic structures extracted from CSD, where N atom belongs to heterocycle and forms only two bonds with C atoms. Red arrow indicates the portion of structures containing the N–C bonds with the distances similar to N2–C1 bond in the five molecules. b) Difference in lengths of the pairs of N–C bonds formed by a single N atom in heterocyclic structures.

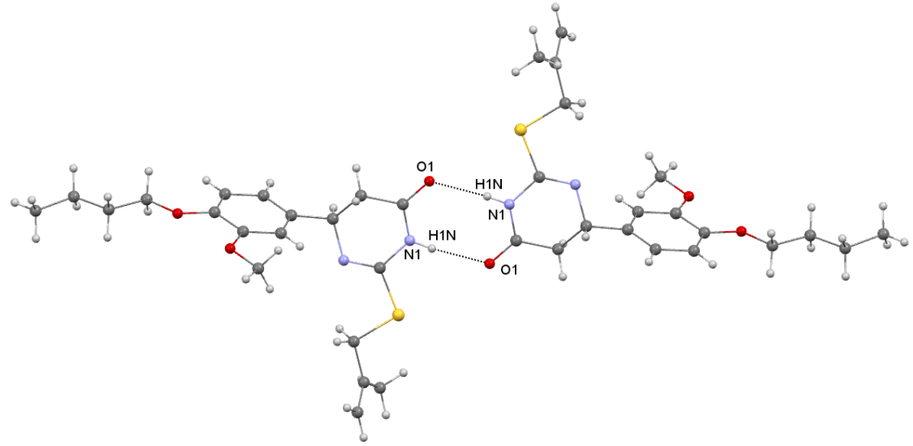


4f



4’d

4’g



4’s

Figure S125 Similar N1–H…O1 hydrogen bonded dimers formed in crystal structures of **4f**, **4’d**, **4’g** and **4’s**.

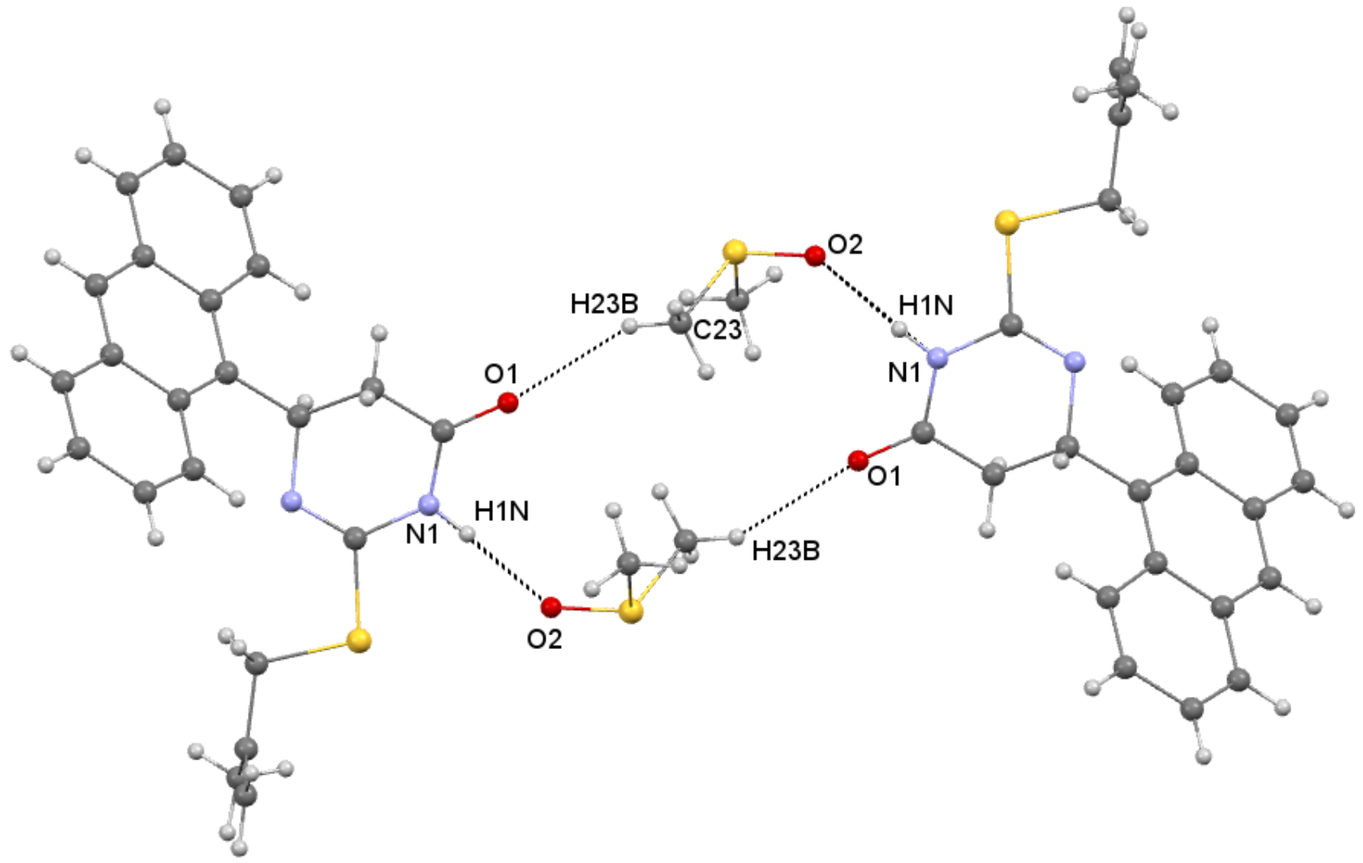
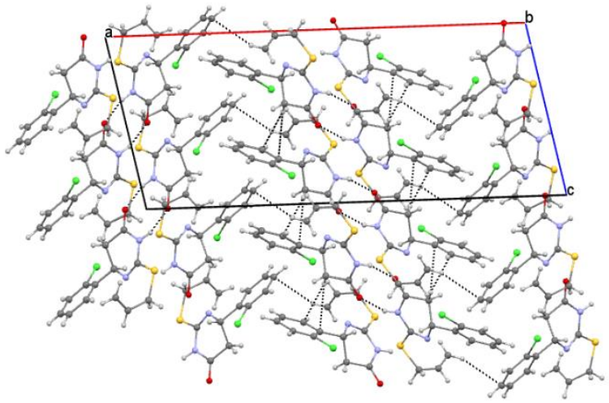
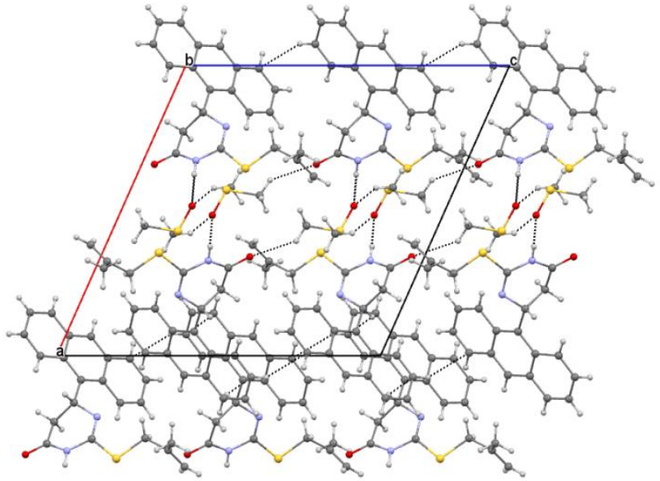


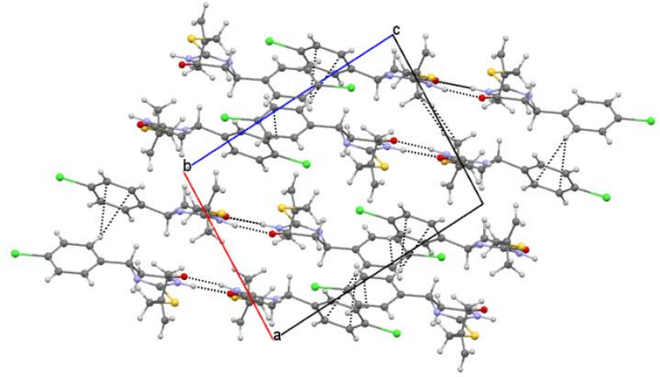
Figure S126 Four component hydrogen bonding motif in crystal structure of **4'c**·DMSO.



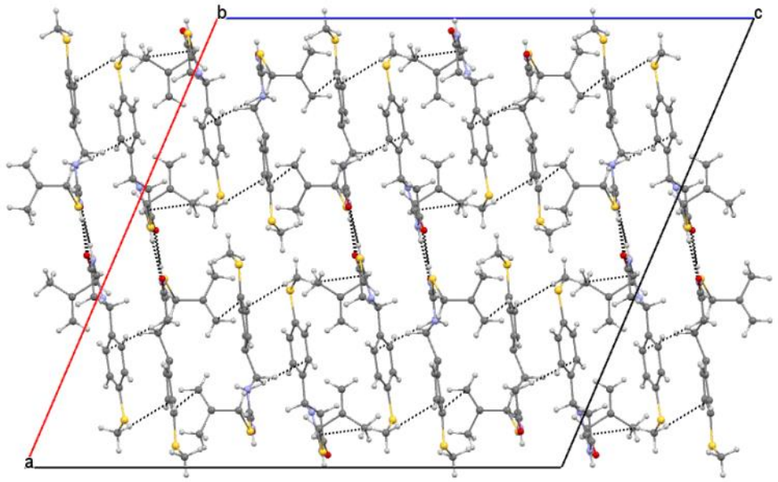
4f



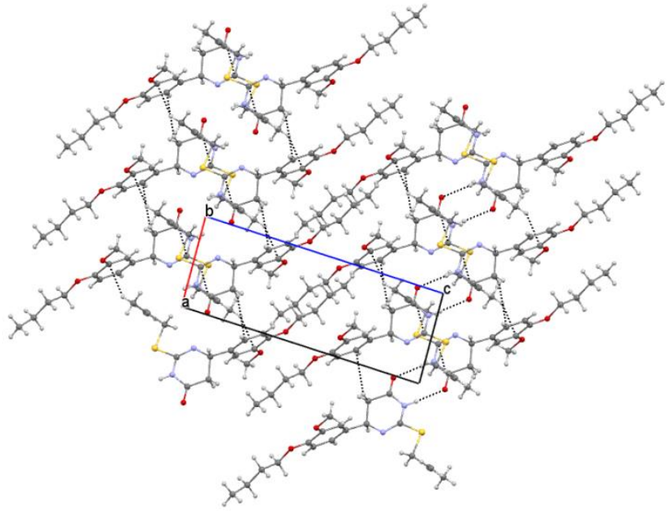
4’c



4’d



4’g



4’s

Figure S127. Crystal packing diagram of the structures as viewed down *b* crystallographic axis. N-H...O and relevant C-H...π interactions are indicated by dashed lines.

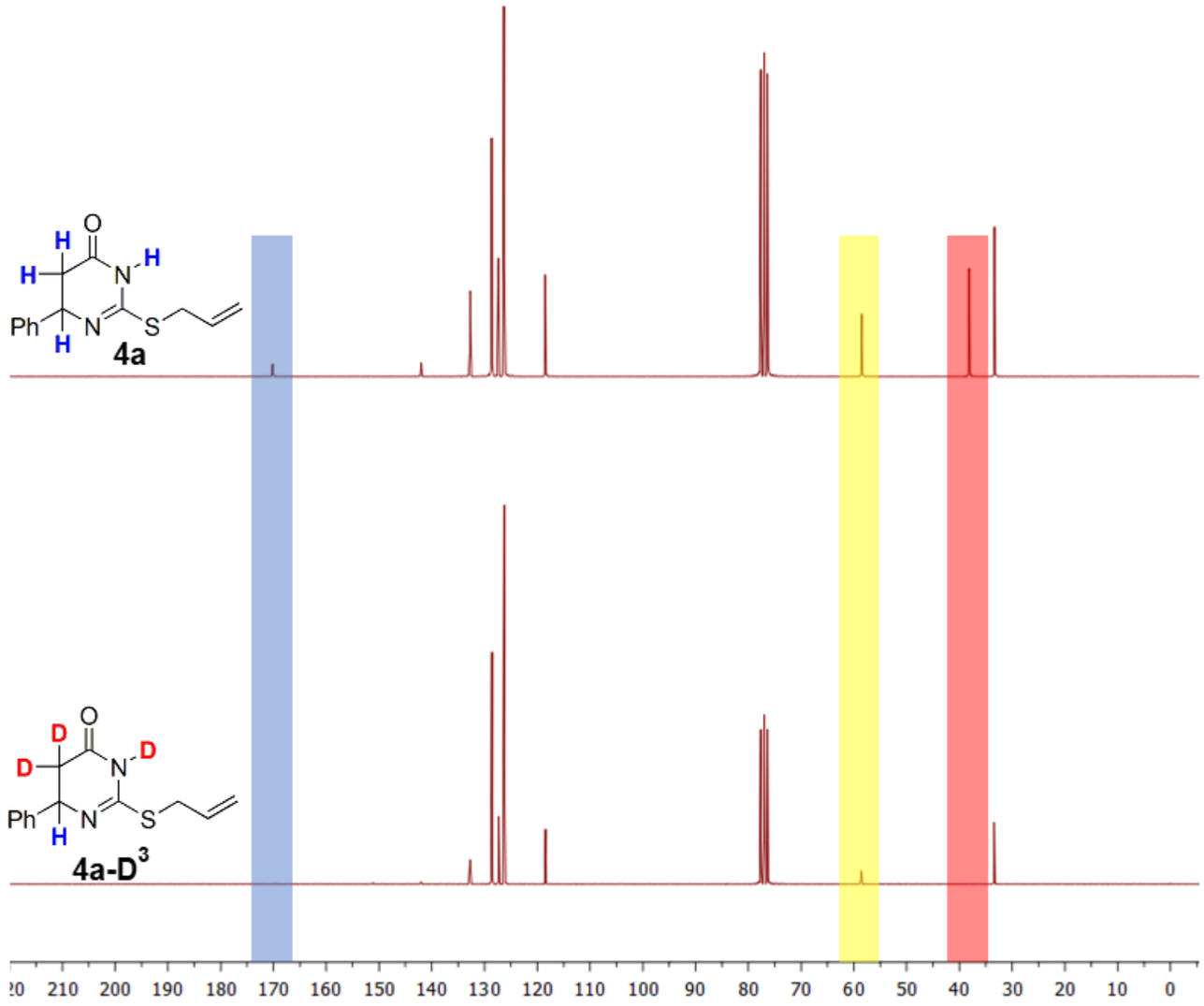


Figure S128. A) Overlap of ^{13}C NMR spectra of **4a** (top) and **4a-D^3** (bottom)

6. NOESY spectra of 4a and 4a-d_3

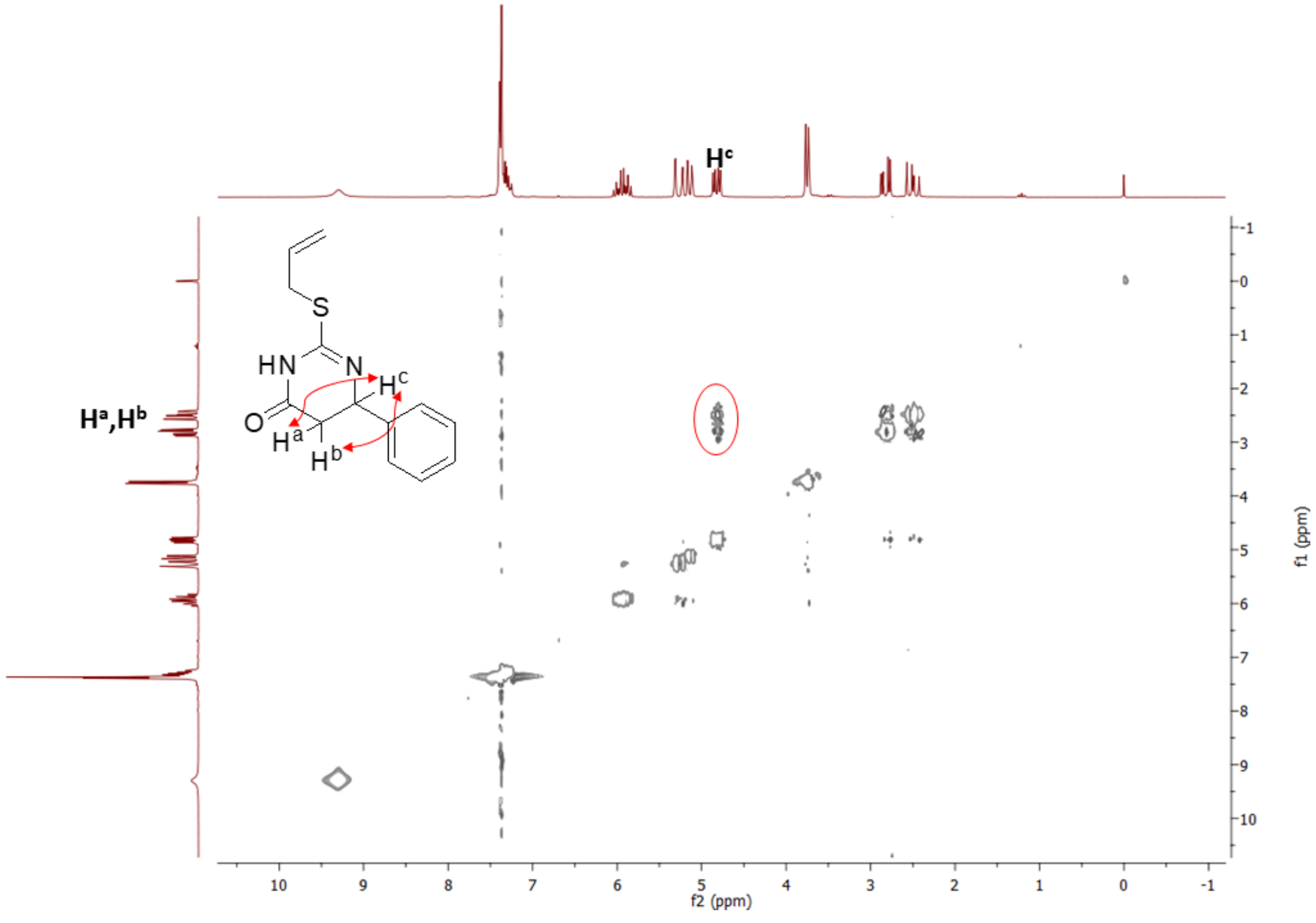


Figure S129. NOESY spectrum of **4a**

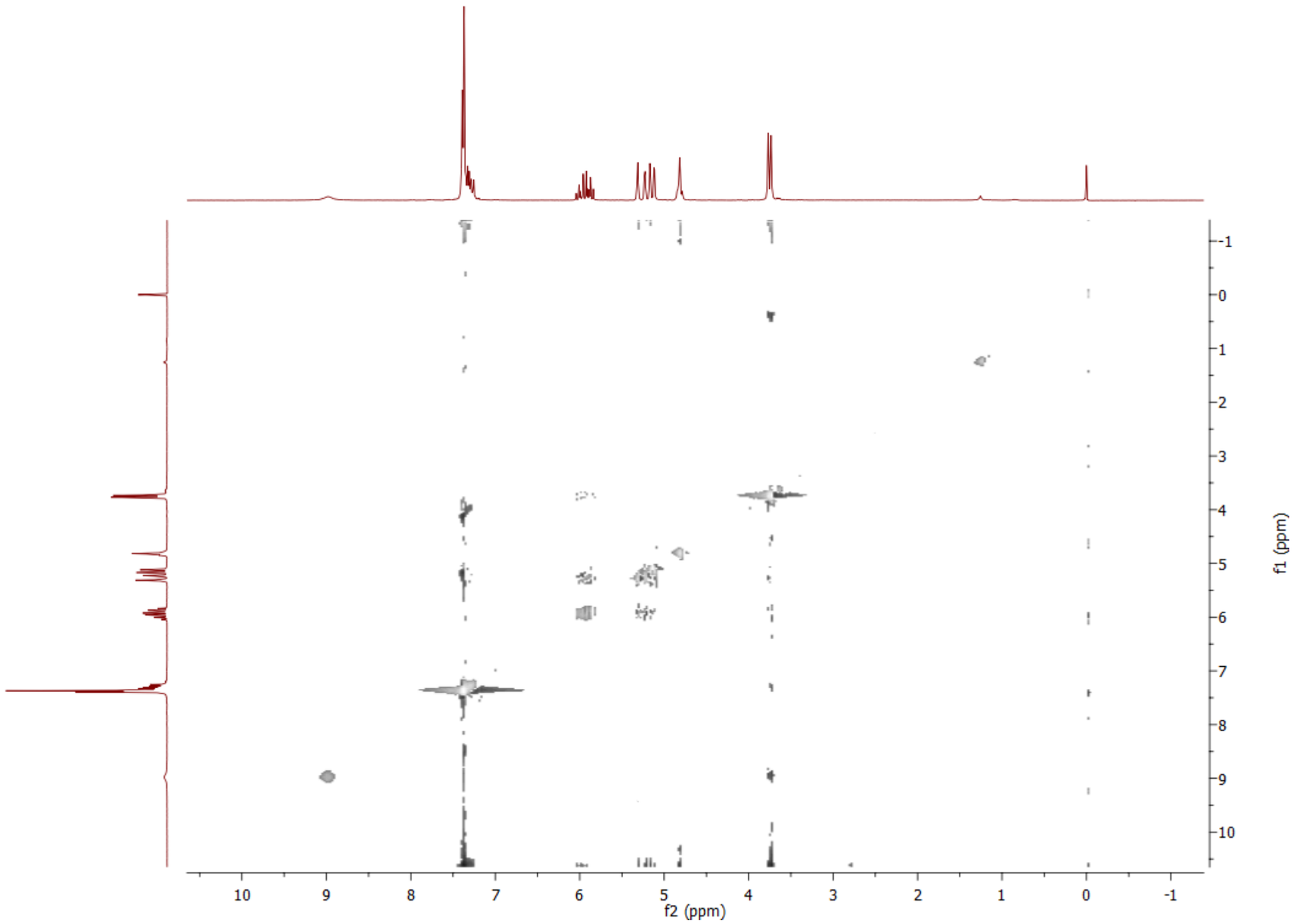


Figure S130. NOESY spectrum of **4a-*d*₃**

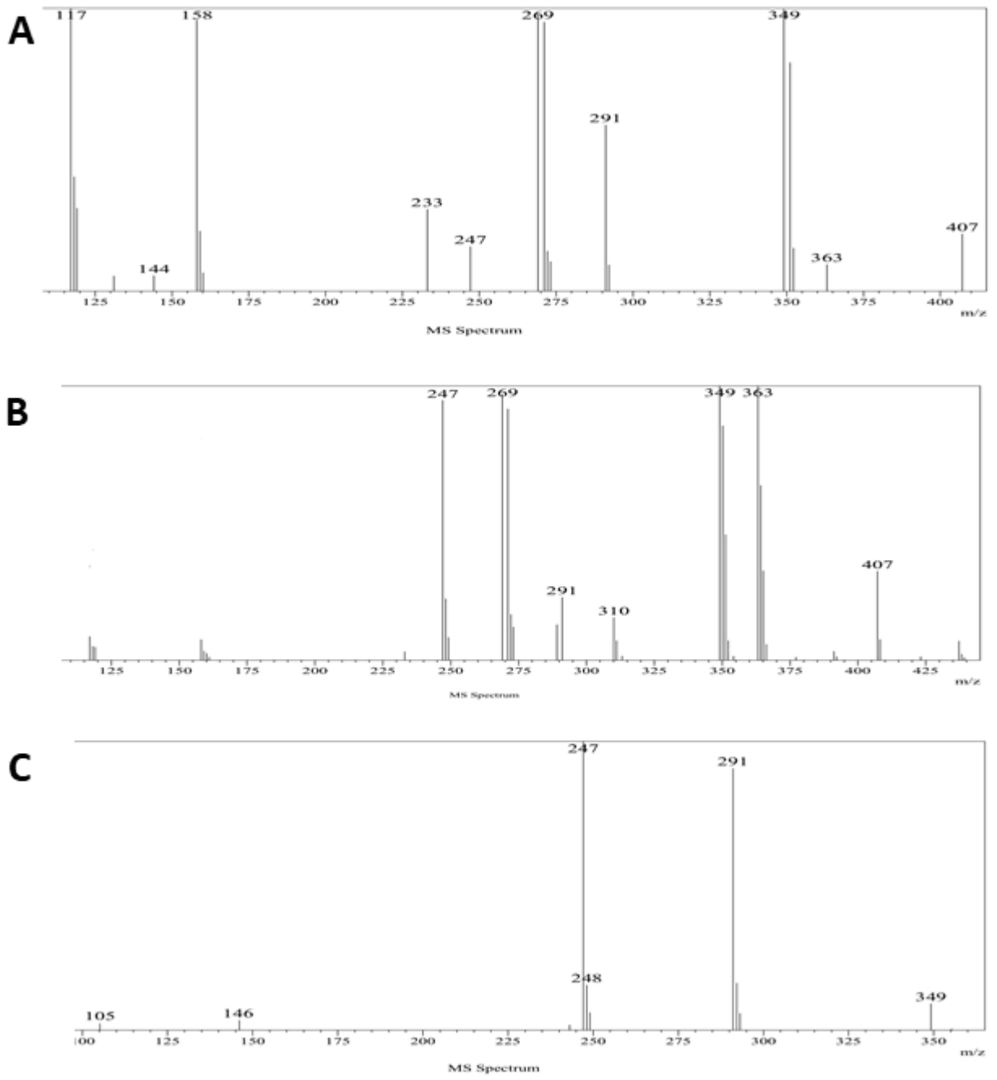


Figure S131. ESI-MS spectra of reaction mixture that recorded after 15 (A), 30 (B) and 45 minutes (C)

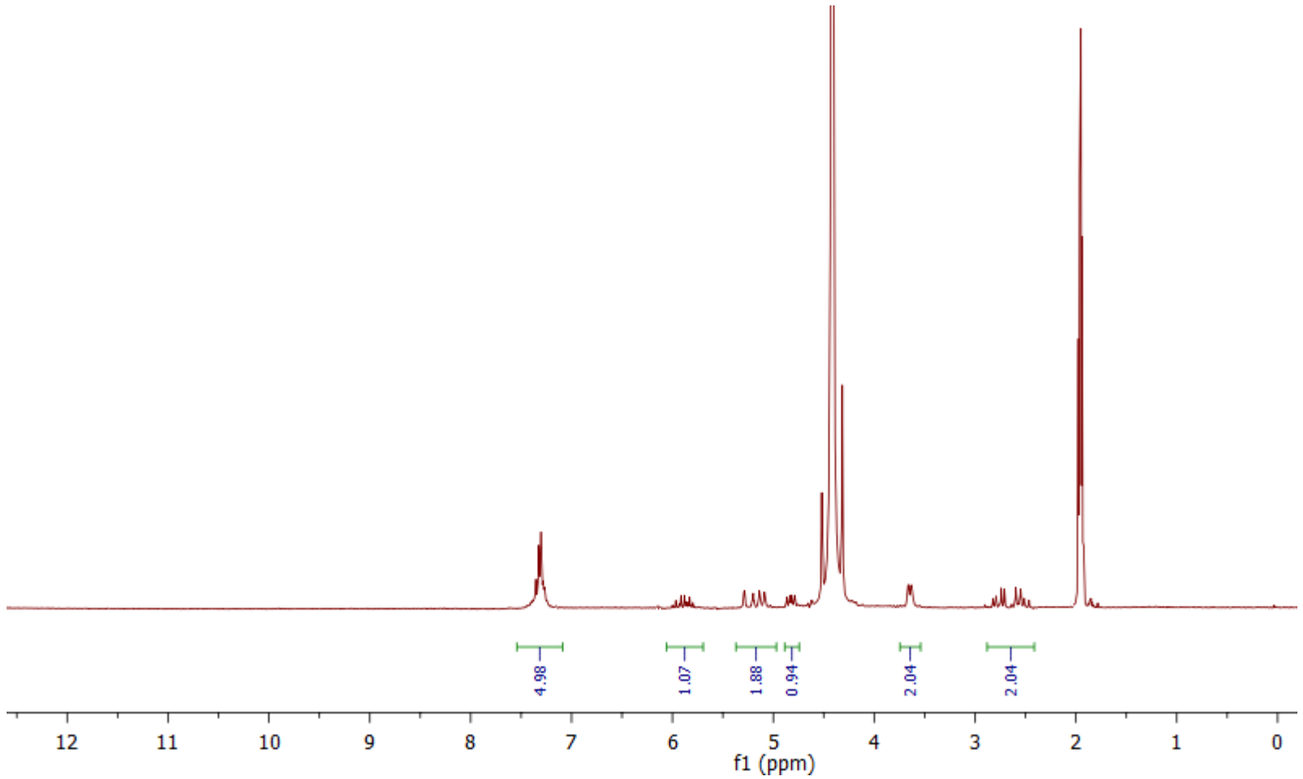


Figure S132. ^{1}H NMR spectra of **4a**. Isotopic exchange in basic conditions.

7. Green metrics

Complete E-factor (cEF)[9] = $\sum \boldsymbol{m}(\boldsymbol{raw\ materials}) + \sum \boldsymbol{m}(\boldsymbol{reactants}) + \sum \boldsymbol{m}(\boldsymbol{solvents}) + \sum \boldsymbol{m}(\boldsymbol{water}) - \sum \boldsymbol{m}(\boldsymbol{product})/\boldsymbol{m}(\boldsymbol{product})$

EcoScale [10] = 100 - penalty points*

* For detailed description of penalty points see ref. 10

1. E. Pair, V. Levacher, and J-F. Brière, *RSC Advances*, 2015, 5, 46267. (0.5 mmol scale, chromatography purification)

Synthesis of 2-methoxy-6-phenyl-5,6-dihydropyrimidin-4-one, yield = 79% (purity 3*H* : 1*H* = 86:14)

cEF = [0.0721 g (Meldrum's acid) + 0.053 g (benzaldehyde) + 0.0618 g (*O*-methylisourea hemisulfate salt) + 0.0584 g (sodiumcarbonate) + 1.42 g (acetonitrile) + 0.2 g (water)- 0.0809 g (product)]/ 0.0809 g (produckt) = **22.1**

cEF scaling to 10 mmol = **22.1** * 20 = **442**

EcoScale = 100 - (10.5 + 3 + 10 + 1) = **75.5**

yield penalty	10.5
heating, > 1 h	3
classical chromatography	10
inert atmosphere	1

2. L. Strekowski, R. A. Watson, M. A. Faunce, *SYNTHESIS*, 1987, 579. (10 mmol scale, chromatography purification)

Synthesis of 2-methylthio-6-phenyl-5,6-dihydropyrimidin-4-one, yield = 48%

cEF = [0.840 g (phenyllitium) + 1.651 g (2,4-bis(methylthio)pyrimidine) + 35.65 g (diethylether) + 19.72 g (ethanol) + 25 g (water) – 1.056 g (product)]/ 1.056 g (produckt) = **77.5**

EcoScale = 100 - (26 + 3 + 10 + 1 + 5 + 3) = **52**

yield penalty	26
heating, > 1 h	3
classical chromatography	10
inert atmosphere	1
cooling, < 0 C	5
liquid-liquid extraction	3

3. Our method- solvent-free versus solvent (5 mmol scale, no chromatography purification)

3.1. Synthesis of 2-allyl-6-phenyl-5,6-dihydropyrimidin-4(3H)-one (**4a**) under solvent-free grindstone chemistry, yield = 91% (purity 3H : 1H = 99.9 : 0.1)

cEF = [0.721 g (Meldrum's acid) + 0.53 g (benzaldehyde) + 1.21 g (*S*-allylisothiourea) + 0.082 g (sodiumacetate) + 0.5 g (water) + 8.8 g (methanol) + 3.8 g (water) - 1.1193 g (product)]/ 1.1193 g (product) = **12.97**

cEF scaling to 10 mmol = **12.97** * 2 = **25.95**

EcoScale = 100 - (4.5 + 3 + 1) = **91.5**

yield penalty	4.5
heating, > 1 h	3

crystallization and filtration 1

3.2. For comparation we done control experiment to produces of 2-allyl-6-phenyl-5,6-dihydropyrimidin-4(3H)-one (**4a**) carried out in solvent mixture acetonitrile + water = 18ml + 0.5ml , yield = 71% (purity 3H : 1H = 81 : 19)

cEF = [0.721 g (Meldrum's acid) + 0.53 g (benzaldehyde) + 1.21 g (*S*-allylisothiourea) + 0.082 g (sodiumacetate) + 14.2 g (acetonitrile, 18 ml) + 0.5 g (water) + 8.8 g (methanol) + 3.8 g (water) - 0.8734 g (product)]/ 0.8734 g (product) = **33.16**

cEF scaling to 10 mmol = **33.16** * 2 = **66.34**

References:

9. F. Roschangar, Y. Zhou, D. J. C. Constable, J. Colberg, D. P. Dickson, P. J. Dunn, M. D. Eastgate, F. Gallou, J. D. Hayler, S. G. Koenig, M. E. Kopach, D. K. Leahy, I. Mergelsberg, U. Scholz, A. G. Smith, M. Henry, J. Mulder, J. Brandenburg, J. R. Dehli, D. R. Fandrick, K. R. Fandrick, F. Gnad-Badouin, G. Zerban, K. Groll, P. T. Anastas, R. A. Sheldons, C. H. Senanayake, *Green Chem*. 2018, doi: 10.1039/C8GC00616D
10. K. Van Aken, L. Strekowski, L. Patiny, *Beilstein J. Org. Chem.* **2006**, *2*, 3.