Supporting Material

for

Reactions of β-Diketone Compounds with Nitriles Catalyzed by Lewis Acids: a simple approach to β-enaminone synthesis

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Experimental details and characterization data of synthesized compounds, ^{1}H NMR and ^{13}C NMR

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General

Unless otherwise noted, materials were obtained from commercial suppliers and were used without further purification. All manipulations involving air-sensitive materials were performed under argon.

TLC was performed using precoated silica gel GF254 (0.2mm), while column chromatography was performed using silica gel (100-200 mesh). The melting point was measured on a YRT-3 melting point apparatus (Shantou Keyi instrument & Equipment Co. Ltd, Shantou, China). IR spectra were obtained on a Perkin Elmer983 (Perkin Elmer, Norwalk, CT, USA). 1H-NMR spectra were taken on a Varian INOVA400 (Varian, Palo Alto, CA, USA) using $CDCl_3$, as solvent. Chemical shifts are expressed in δ (ppm), with tetramethylsilane (TMS) functioning as the internal reference, and coupling constants (*J*) were expressed in Hz. Mass spectra were recorded on an Agilent 1946B ESI-MS instrument (Agilent, Palo Alto, CA, USA).

Characterization data

3-(amino(phenyl)methylene)pentane-2,4-dione (3a)

Yellow oil; ^{1}H NMR ($CDCl_3$, 400 MHz, δ ppm): 10.94 (brs, 1H), 7.54-7.27 (m, 5H), 5.50 (brs, 1H), 2.29 (s, 3H), 1.64 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz, δ ppm): 197.60, 196.99, 168.19, 134.33, 128.65, 128.04, 127.83, 110.83, 29.74, 29.66. HRMS: m/z (+ESI) Calcd for $C_{12}H_{13}NO_2$, 204.1025, Found: 204.2306 $[M+H]^+$.

3-(amino(4-nitrophenyl)methylene)pentane-2,4-dione (3b)

Yellow oil; ^{1}H NMR ($CDCl_3$, 400 MHz, δ ppm): 9.94 (brs, 1H), 8.32 (d, 2H, *J* = 8.8 Hz), 7.74 (d, 2H, *J*= 8.8 Hz), 5.19 (brs, 1H), 2.46 (s, 3H), 2.20 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz, δ ppm): 198.90, 196.99, 166.18, 147.14, 140.04, 126.36, 123.04, 112.84, 29.97, 29.75. HRMS: m/z (+ESI) Calcd for $C_{12}H_{12}N_2O_4$, 249.0797, Found: 249.1906 $[M+H]^+$.

3-(amino(2-nitrophenyl)methylene)pentane-2,4-dione (3c)

Yellow oil; ^{1}H NMR ($CDCl_3$, 400 MHz, δ ppm): 9.87 (brs, 1H), 7.95-7.94 (m, 1H), 7.70-7.46 (m, 3H), 5.08 (brs, 1H), 2.20 (s, 3H), 2.08 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz, δ ppm): 199.30, 198.77, 167.19, 145.05, 134.74, 130.14, 128.87, 127.20, 123.80, 112.86, 29.74, 29.25. HRMS: m/z (+ESI) Calcd for $C_{12}H_{12}N_2O_4$, 249.0797, Found: 249.1906 $[M+H]^+$

3-(1-amino-2-phenylethylidene)pentane-2,4-dione (3d)

Yellow oil; ^{1}H NMR ($CDCl_3$, 400 MHz, δ ppm): 11.11 (brs, 1H), 7.40-7.18 (m, 5H), 5.64 (brs, 1H), 3.79 (s, 2H), 2.28 (s, 3H), 2.04 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz, δ ppm): 198.18, 197.30, 163.18, 135.63, 128.04, 127.85, 125.37, 110.80, 38.61, 32.04, 31.96. HRMS: m/z (+ESI) Calcd for $C_{13}H_{15}NO_2$, 218.1103, Found: 218.1082 $[M+H]^+$

3-(1-amino-3-phenylallylidene)pentane-2,4-dione (3e)

Yellow oil; ^{1}H NMR ($CDCl_3$, 400 MHz, δ ppm): 10.12 (brs, 2H), 7.48-7.32 (m, 5H), 7.10 (d, 1H, *J* = 16.4 Hz), 6.80 (d, 1H, *J* = 16.4 Hz), 2.34 (s, 3H), 2.14 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz, δ

ppm): 197.92, 197.35, 169.26, 135.38, 135.02, 129.31, 128.72, 127.28, 124.32, 103.58, 30.19, 29.98. HRMS: m/z (+ESI) Calcd for $C_{14}H_{15}NO_2$, 230.1103, Found: 230.1783 $[M+H]^+$.

3-(amino(furan-2-yl)methylene)pentane-2,4-dione (3f)

Yellow oil; ^1H NMR ($CDCl_3$, 400 MHz, δ ppm): 10.46(brs, 2H), 7.56(s, 1H), 6.78 (s, 1H), 6.51 (s, 1H), 2.11 (s, 3H), 1.96 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz, δ ppm): 198.57, 198.46, 165.62, 155.32, 143.83, 124.13, 112.78, 111.60, 30.48, 30.33. HRMS: m/z (+ESI) Calcd for $C_{10}H_{11}NO_3$, 194.0739, Found: 194.1452 $[M+H]^+$.

3-(amino(2-methoxyphenyl)methylene)pentane-2,4-dione (3g)

Yellow oil; ^1H NMR ($CDCl_3$, 400 MHz, δ ppm): 10.17 (brs, 1H), 7.46-7.37 (m, 4H), 5.98 (brs, 1H), 3.87 (s, 3H), 2.12 (s, 3H), 1.26 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz, δ ppm): 197.30, 197.27, 169.18, 155.63, 130.65, 128.04, 127.13, 120.37, 110.80, 104.05, 59.50, 29.64, 29.25. HRMS: m/z (+ESI) Calcd for $C_{13}H_{15}NO_3$, 234.1052, Found: 234.2187 $[M+H]^+$

3-(1-aminoethylidene)pentane-2,4-dione (3h)

Yellow oil; ^1H NMR ($CDCl_3$, 400 MHz, δ ppm): 8.61 (brs, 2H), 2.29 (s, 6H), 2.20 (s, 3H); HRMS: m/z (+ESI) Calcd for $C_7H_{11}NO_2$, 142.0790, Found: 142.2203 $[M+H]^+$.
The observed data was consistent with that previously reported.[1]

ethyl 4-acetyl-3-amino-5-oxohex-3-enoate (3i)

Yellow oil; ^1H NMR ($CDCl_3$, 400 MHz, δ ppm): 15.11 (brs, 2H), 4.19 (q, 2H, J = 7.2 Hz), 3.22 (s, 2H), 2.24 (s, 3H), 2.07 (s, 3H), 1.27 (t, 3H, J = 7.2 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz, δ ppm): 198.77, 197.97, 168.03, 163.19, 116.71, 61.43, 32.04, 31.97, 29.89, 14.32. HRMS: m/z (+ESI) Calcd for $C_{10}H_{15}NO_4$, 214.1001, Found: 214.1546 $[M+H]^+$.

2-(amino(phenyl)methylene)-1-phenylbutane-1,3-dione (3j)

Yellow oil; ^1H NMR ($CDCl_3$, 400 MHz, δ ppm): 15.61 (brs, 1H), 8.12-7.99 (m, 4H), 7.63-7.51 (m, 6H), 6.75 (brs, 1H), 2.20 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz, δ ppm): 198.63, 191.22, 166.50, 135.38, 133.58, 132.68, 132.35, 130.37, 129.40, 128.68, 128.65, 128.56, 128.19, 127.05, 109.65, 30.21. HRMS: m/z (+ESI) Calcd for $C_{17}H_{15}NO_2$, 266.1103, Found: 266.1912 $[M+H]^+$.

3-(amino(2-chlorophenyl)methylene)pentane-2,4-dione (3m)

Yellow oil; ^1H NMR ($CDCl_3$, 400 MHz, δ ppm): 9.61 (brs, 1H), 7.69-7.38 (m, 4H), 5.53 (brs, 1H), 3.29 (s, 3H), 2.11 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz, δ ppm): 196.98, 196.10, 167.18, 136.58, 136.56, 133.85, 129.88, 127.09, 115.82, 113.11, 29.75, 29.24. HRMS: m/z (+ESI) Calcd for $C_{12}H_{12}NO_2Cl$, 238.0557, Found: 238.1139 $[M+H]^+$.

3-(1-amino-3-bromopropylidene)pentane-2,4-dione (3n)

Yellow oil; ^1H NMR ($CDCl_3$, 400 MHz, δ ppm): 5.41 (brs, 2H), 3.53 (t, 2H, J = 6.4 Hz), 2.99 (t, 2H, J = 6.4 Hz), 2.27 (s, 3H), 2.01 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz, δ ppm): 198.70, 198.65, 167.71, 115.69, 38.50, 30.15, 29.98, 27.21. HRMS: m/z (+ESI) Calcd for $C_8H_{12}NO_2Br$, 234.0051, Found: 234.1671 $[M+H]^+$.

3-(amino(4-hydroxyphenyl)methylene)pentane-2,4-dione (3o)

Yellow oil; ^{1}H NMR (DMSO-d_6, 400 MHz, δ ppm): 11.05 (brs, 1H), 10.64 (s, 1H), 7.59 (d, 2H, J = 8.8 Hz), 6.89 (d, 2H, J = 8.8 Hz), 5.40 (brs, 1H), 2.26 (s, 3H), 1.71 (s, 3H). ^{13}C NMR (DMSO-d_6, 100 MHz, δ ppm): 199.01, 197.59, 167.28, 161.96, 134.52, 128.13, 116.74, 112.09, 29.97, 29.75. HRMS: m/z (+ESI) Calcd for $C_{12}H_{13}NO_3$, 220.0895, Found: 220.1901 $[M+H]^+$.

3-(1-amino-2-(4-hydroxyphenyl)ethylidene)pentane-2,4-dione (3p)

Yellow oil; ^{1}H NMR (DMSO-d_6, 400 MHz, δ ppm): 9.54 (s, 1H), 7.14 (d, 2H, J = 8.4 Hz), 6.79 (d, 2H, J = 8.4 Hz), 5.24 (brs, 2H), 3.85 (s, 2H), 2.29 (s, 3H), 2.11 (s, 3H). ^{13}C NMR (DMSO-d_6, 100 MHz, δ ppm): 198.97, 198.76, 163.17, 155.51, 130.47, 128.19, 115.87, 112.01, 38.65, 29.10, 28.87. HRMS: m/z (+ESI) Calcd for $C_{13}H_{15}NO_3$, 234.1052, Found: 234.1787 $[M+H]^+$.

methyl 4-(2-acetyl-1-amino-3-oxobut-1-en-1-yl)benzoate (3q)

Yellow oil; ^{1}H NMR ($CDCl_3$, 400 MHz, δ ppm): 10.02 (brs, 1H), 8.20 (d, 2H, J = 5.6 Hz), 7.96 (d, 2H, J = 5.6 Hz), 5.52 (brs, 1H), 3.97 (s, 3H), 2.11 (s, 3H), 1.94 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz, δ ppm): 198.90, 196.99, 166.18, 165.97, 138.54, 129.85, 129.36, 126.34, 112.84, 51.51, 29.97, 29.75. HRMS: m/z (+ESI) Calcd for $C_{14}H_{15}NO_4$, 262.1001, Found: 262.1625 $[M+H]^+$.

4-amino-4-phenylbut-3-en-2-one (4a)

White solid; m.p 84-86 ^{o}C (lit.[2] 84-87 ^{o}C); ^{1}H NMR ($CDCl_3$, 400 MHz, δ ppm): 9.93 (brs, 1H), 7.55-7.26 (m, 5H), 5.45 (s, 1H), 5.25 (brs, 1H), 2.15 (s, 3H); HRMS: m/z (+ESI) Calcd for $C_{10}H_{11}NO$, 162.0841, Found: 162.1431 $[M+H]^+$.

4-amino-4-(4-nitrophenyl)but-3-en-2-one (4b)

Yellow oil; ^{1}H NMR ($CDCl_3$, 400 MHz, δ ppm):9.83 (brs, 1H), 8.29 (d, 2H, J = 8.8 Hz), 7.72 (d, 2H, J = 8.8 Hz), 5.47 (s, 1H), 5.08 (brs, 1H), 2.20 (s, 3H); HRMS: m/z (+ESI) Calcd for $C_{10}H_{10}N_2O_3$, 207.0691, Found: 207.1983 $[M+H]^+$.

The observed data was consistent with that previously reported.[3]

4-amino-4-(2-nitrophenyl)but-3-en-2-one (4c)

Colorless oil; ^{1}H NMR ($CDCl_3$, 400 MHz, δ ppm): 9.79 (brs, 1H), 7.96-7.94 (s 1H), 7.69-7.51 (m, 3H), 5.11 (s, 1H), 2.08 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz, δ ppm): 199.30, 155.88, 145.07, 134.75, 130.07, 128.88, 127.30, 123.85, 100.82, 29.22. HRMS: m/z (+ESI) Calcd for $C_{10}H_{10}N_2O_3$, 207.0691, Found: 207.1983 $[M+H]^+$

4-amino-5-phenylpent-3-en-2-one (4d)

Yellow oil; ^{1}H NMR ($CDCl_3$, 400 MHz, δ ppm): 9.70 (brs, 1H), 7.46-7.24 (m, 5H), 5.11 (s, 1H), 5.01 (brs, 1H), 3.46 (s, 2H), 2.09 (s, 3H); HRMS: m/z (+ESI) Calcd for $C_{11}H_{13}NO$, 176.0997, Found: 176.2143 $[M+H]^+$

The observed data was consistent with that previously reported.[4]

4-amino-6-phenylhexa-3,5-dien-2-one (4e)

Yellow oil; ^{1}H NMR ($CDCl_3$, 400 MHz, δ ppm): 9.87 (brs, 2H), 7.51-7.47 (m, 5H), 7.04 (d, 1H, J = 16.4 Hz), 6.43 (d, 1H, J = 16.4 Hz), 5.32 (s, 1H), 2.17 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz, δ

ppm): 197.94, 153.76, 135.43, 134.98, 129.31, 128.73, 127.28, 124.39, 103.20, 30.16. HRMS: m/z (+ESI) Calcd for $C_{12}H_{13}NO$, 188.0997, Found: 188.0464 $[M+H]^+$

4-amino-4-(furan-2-yl)but-3-en-2-one (4f)

White solid; m.p 80-82 ^oC (lit.[5] 80.0-80.5 ^oC); ^1H NMR ($CDCl_3$, 400 MHz, δ ppm): 9.69 (brs, 1H), 7.49 (s, 1H), 6.82 (s, 1H), 6.47 (s, 1H), 5.80 (brs, 1H), 5.56 (s, 1H), 2.11 (s, 3H); HRMS: m/z (+ESI) Calcd for $C_6H_9NO_2$, 152.0633, Found: 152.1872 $[M+H]^+$

4-amino-4-(2-methoxyphenyl)but-3-en-2-one (4g)

Colorless oil; ^1H NMR ($CDCl_3$, 400 MHz, δ ppm): 11.08 (brs, 1H), 7.21-6.96 (m, 4H), 5.66 (brs, 1H), 5.35 (s, 1H), 3.86 (s, 3H), 1.30 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz, δ ppm): 190.31, 169.20, 155.64, 131.57, 128.04, 127.13, 120.38, 110.83, 104.05, 59.51, 29.63. HRMS: m/z (+ESI) Calcd for $C_{11}H_{13}NO_2$, 192.0946, Found: 192.2021 $[M+H]^+$.

4-aminopent-3-en-2-one (4h)

White solid; m.p 30-32 ^oC (lit.[6] 31-32 ^oC); ^1H NMR ($CDCl_3$, 400 MHz, δ ppm): 8.59 (brs, 2H), 5.01 (s, 1H), 2.26 (s, 3H), 1.97 (s, 3H); HRMS: m/z (+ESI) Calcd for C_5H_9NO, 100.0684, Found: 100.1197 $[M+H]^+$.

ethyl 3-amino-5-oxohex-3-enoate (4i)

Yellow oil; ^1H NMR ($CDCl_3$, 400 MHz, δ ppm): 15.03 (brs, 2H), 5.60 (s, 1H), 4.20 (q, 2H, J = 7.2 Hz), 3.34 (s, 2H), 1.99 (s, 3H), 1.29 (t, 3H, J = 7.2 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz, δ ppm): 196.90, 169.54, 167.54, 102.70, 59.85, 32.41, 30.35, 13.99. HRMS: m/z (+ESI) Calcd for $C_8H_{13}NO_3$, 172.0895, Found: 172.2547 $[M+H]^+$.

3-amino-1,3-diphenylprop-2-en-1-one (4j / 4l)

Yellow oil; ^1H NMR ($CDCl_3$, 400 MHz, δ ppm): 16.8 (brs, 1H), 8.00-7.98 (m, 4H), 7.57-7.47 (m, 6H), 6.86 (s, 1H), 6.83 (brs, 1H); HRMS: m/z (+ESI) Calcd for $C_{15}H_{13}NO$, 224.0997, Found: 224.3112 $[M+H]^+$.

The observed data was consistent with that previously reported.[7]

1-amino-4,4-dimethyl-1-phenylpent-1-en-3-one (4k)

White solid; m.p 73-75 ^oC (lit.[7] 72-74 ^oC); ^1H NMR ($CDCl_3$, 400 MHz, δ ppm): 7.55-7.41 (m, 5H), 5.45 (s, 1H), 2.03 (brs, 2H), 1.27 (s, 9H); HRMS: m/z (+ESI) Calcd for $C_{13}H_{17}NO$, 204.1310, Found: 204.3212 $[M+H]^+$.

4-amino-4-(2-chlorophenyl)but-3-en-2-one (4m)

Yellow oil; ^1H NMR ($CDCl_3$, 400 MHz, δ ppm): 9.80 (brs, 1H), 7.68-7.37 (m, 4H), 5.70 (s, 1H), 5.53 (brs, 1H), 2.30 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz, δ ppm): 109.01, 167.17, 136.58, 136.57, 133.85, 129.89, 127.10, 116.73, 113.11, 29.25. HRMS: m/z (+ESI) Calcd for $C_{10}H_{10}NOCl$, 196.0451, Found: 196.1132 $[M+H]^+$.

4-amino-6-bromohex-3-en-2-one (4n)

Yellow oil; ^1H NMR ($CDCl_3$, 400 MHz, δ ppm): 5.42 (s, 1H), 5.31 (brs, 2H), 3.53 (t, 2H, J = 6.4

Hz), 2.99 (t, 2H, *J* = 6.4 Hz), 2.13 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz, δ ppm): 198.81, 167.70, 115.78, 38.41, 29.80, 27.30. HRMS: m/z (+ESI) Calcd for $C_6H_{10}NOBr$, 191.9946, Found: 192.0038 $[M+H]^+$.

4-amino-4-(4-hydroxyphenyl)but-3-en-2-one (4o)

Yellow oil; ^{1}H NMR (DMSO-d_6, 400 MHz, δ ppm): 11.06 (brs, 1H), 10.64 (s, 1H), 7.59 (d, 2H, *J* = 4.8 Hz), 6.89 (d, 2H, *J* = 4.8 Hz), 5.79 (s, 1H), 5.57 (brs, 1H), 2.27 (s, 3H). ^{13}C NMR (DMSO-d_6, 100 MHz, δ ppm): 199.10, 167.27, 162.02, 134.53, 128.21, 116.75, 112.10, 28.75. HRMS: m/z (+ESI) Calcd for $C_{10}H_{11}NO_2$, 178.0790, Found: 178.0920 $[M+H]^+$.

4-amino-5-(4-hydroxyphenyl)pent-3-en-2-one (4p)

Yellow oil; ^{1}H NMR (DMSO-d_6, 400 MHz, δ ppm): 9.55 (s, 1H), 7.15 (d, 2H, *J* = 8.0 Hz), 6.79 (d, 2H, *J* = 8.0 Hz), 5.47 (s, 1H), 5.20 (brs, 2H), 3.85 (s, 2H), 2.12 (s, 3H). ^{13}C NMR (DMSO-d_6, 100 MHz, δ ppm): 198.87, 163.21, 155.51, 130.56, 127.98, 116.01, 112.07, 38.70, 29.07. HRMS: m/z (+ESI) Calcd for $C_{11}H_{13}NO_2$, 192.0946, Found: 192.1405 $[M+H]^+$.

methyl 4-(1-amino-3-oxobut-1-en-1-yl)benzoate (4q)

Yellow oil; ^{1}H NMR ($CDCl_3$, 400 MHz, δ ppm): 10.03 (s, 1H), 8.20 (d, 2H, *J* = 5.6 Hz), 7.96 (d, 2H, *J* = 5.6 Hz), 5.71 (s, 1H), 5.50 (brs, 1H), 3.97 (s, 3H), 2.11 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz, δ ppm): 198.91, 166.20, 165.98, 138.54, 129.85, 129.36, 126.34, 112.85, 51.53, 29.76. HRMS: m/z (+ESI) Calcd for $C_{12}H_{13}NO_3$, 219.0895, Found: 219.1136 $[M+H]^+$.

2-(amino(phenyl)methylene)cyclohexane-1,3-dione (3r)

Yellow oil; ^{1}H NMR ($CDCl_3$, 400 MHz, δ ppm): 9.67 (brs, 2H), 7.96-7.94 (m, 2H), 7.47-7.39 (m, 3H), 2.55 (t, 2H, *J* = 6.4 Hz), 2.44 (t, 2H, *J* = 6.4 Hz), 2.07-2.03 (m, 2H); HRMS: m/z (+ESI) Calcd for $C_{13}H_{13}NO_2$, 216.0946, Found: 216.2211 $[M+H]^+$.
The observed data was consistent with that previously reported.[8]

7-amino-5-oxo-7-phenylhept-6-enoic acid (4r)

Yellow oil; ^{1}H NMR ($CDCl_3$, 400 MHz, δ ppm): 11.11 (s, 1H), 9.58 (brs, 2H), 7.41-7.30 (m, 5H), 5.35 (s, 1H), 2.40 (t, 2H, *J* = 6.4 Hz), 2.35 (t, 2H, *J* = 6.4 Hz), 2.01-1.95 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz, δ ppm): 201.29, 178.43, 160.71, 139.75, 128.31, 127.96, 126.97, 100.73, 42.35, 32.71, 18.29. HRMS: m/z (+ESI) Calcd for $C_{13}H_{15}NO_3$, 234.1052, Found: 234.2136 $[M+H]^+$.

Synthesis of (5-methylisoxazol-3-yl)methanamine (23)

2-(1,3-dioxoisoindolin-2-yl)acetonitrile (20)

To a stirring solution of glycinonitrile hydrochloride **19** (2g, 21.6mmol, 1.0eq) in chloroform (20ml) at 0 ^{o}C was added triethylamine (2.19g, 21.6mmol, 1.0eq) dropwise. The reaction mixture was allowed to attain room temperature for 30min and phthalic anhydride (3.2g, 21.6mmol, 1.0eq) was added. The reaction mixture was heat at 60 ^{o}C for a period of 6h. After cooling, the organic layer was washed with water and brine and dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was recrystallized from petroleum ether and ethyl acetate, to afford the pure white solid **20** (2.4g, 60%). M.p. 126-127^{o}C. ^{1}H NMR ($CDCl_3$, 400 MHz, δ ppm): 7.95-

7.94 (m, 2H), 7.83-7.80 (m, 2H), 4.59 (s, 2H).
The observed data was consistent with that previously reported. [9]

2-(2-amino-4-oxopent-2-en-1-yl)isoindoline-1,3-dione (21)

To a solution of **20** (500mg, 2.7mmol, 1.0eq), $AlCl_3$ (360mg, 2.7mmol, 1.0eq) and acetylacetone (323mg, 3.2mmol, 1.2eq) were added at room temperature with stirring. The mixture was heated at 100°C with stirring for 4 h. Afer cooling to room temperature, saturated sodium carbonate solution was added, and the mixture was extracted with EtOAc. The combined organic phases were washed with brine, dried over Na_2SO_4, and concentrated in vacuo. The residue was purified by flash column chromatography on silica gel to give **21** (495mg, 75.1%) as a white solid. M.p 150-152 °C. ^{1}H NMR ($CDCl_3$, 400 MHz, δ ppm): 14.63 (brs, 2H), 7.91-7.88 (m, 2H), 7.77-7.75 (m, 2H), 5.57 (s, 1H), 4.51 (s, 2H), 2.05 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz, δ ppm):196.38, 169.52, 167.75, 160.02, 132.25, 132.23, 132.21, 132.19, 123.74, 123.68, 98.83, 55.42, 27.53. HRMS: m/z (+ESI) Calcd for $C_{13}H_{12}N_2O_3$, 245.0848, Found: 245.1354 $[M+H]^+$

2-((5-methylisoxazol-3-yl)methyl)isoindoline-1,3-dione (22)

To a stirring solution of **21** (200mg, 0.82mmol, 1.0eq) in ethanol (10ml) was added hydroxylamine hydrochloride (69mg, 0.99mmol, 1.2eq). The mixture reaction was heated at 80°C with stirring for 2 h. Ethanol was removed under vacuo and the residue was extracted with ethyl acetate, the combined organic phases were washed with brine, dried over Na_2SO_4, and concentrated in vacuo. The crude product was used for the next reaction without any further purification.

(5-methylisoxazol-3-yl)methanamine (23)

To a stirring solution of **22** (150mg, 0.62mmol, 1.0eq) in ethanol (5ml) was added 80% hydrazine hydrate (78mg, 1.2mmol, 2.0eq). The mixture reaction was heated at 80°C with stirring for 2 h. Ethanol was removed under vacuo and the residue was extracted with ethyl acetate, the combined organic phases were washed with brine, dried over Na_2SO_4, and concentrated in vacuo. The residue was purified by flash column chromatography on silica gel to give **23** (53mg, 76.8%) as a yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz, δ ppm): 9.15 (brs, 2H), 6.33 (s, 1H), 3.83 (s, 2H), 2.39 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz, δ ppm): 169.36, 150.02, 102.32, 38.64, 11.85. HRMS: m/z (+ESI) Calcd for $C_5H_8N_2O$, 113.1298, Found: 113.2349 $[M+H]^+$

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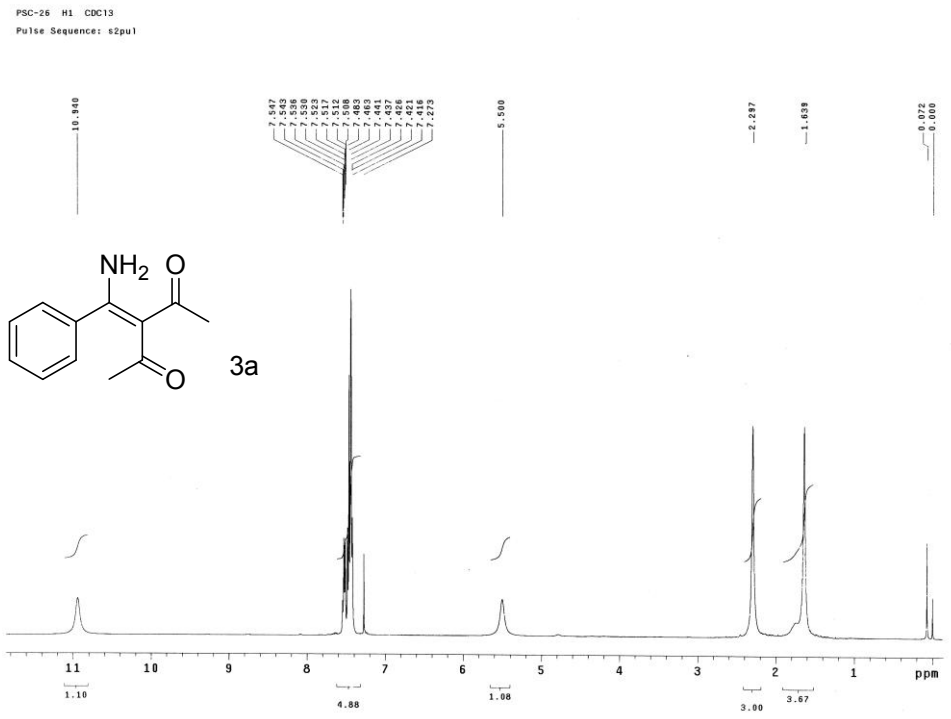
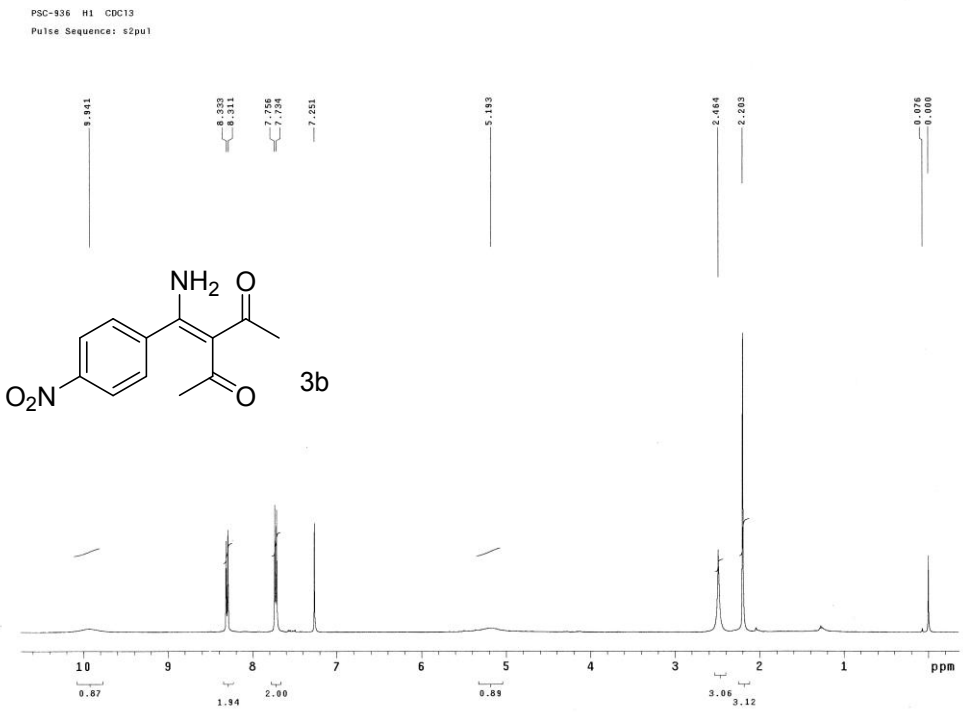
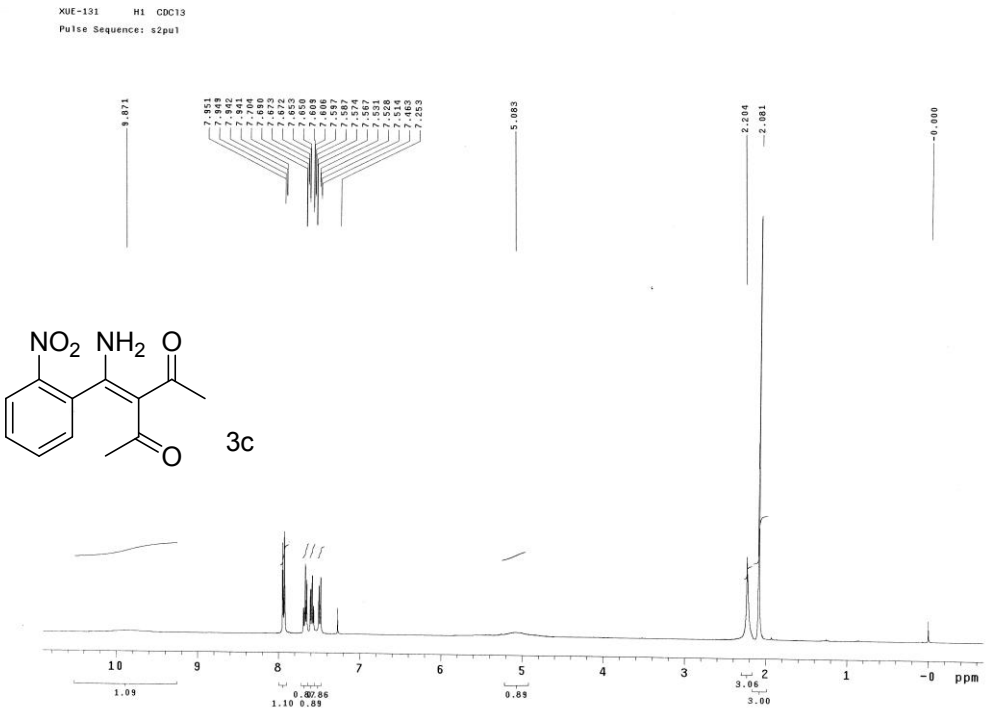
^{1}H NMR and ^{13}C NMR spectra for synthesized compounds



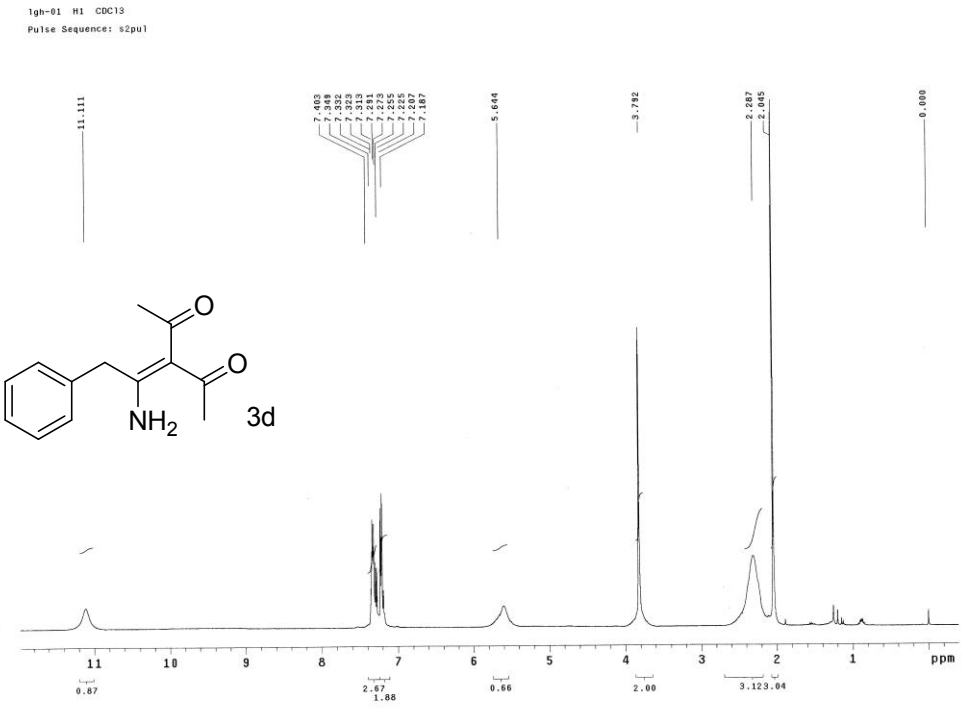
^{1}H NMR spectra for compound **3a**



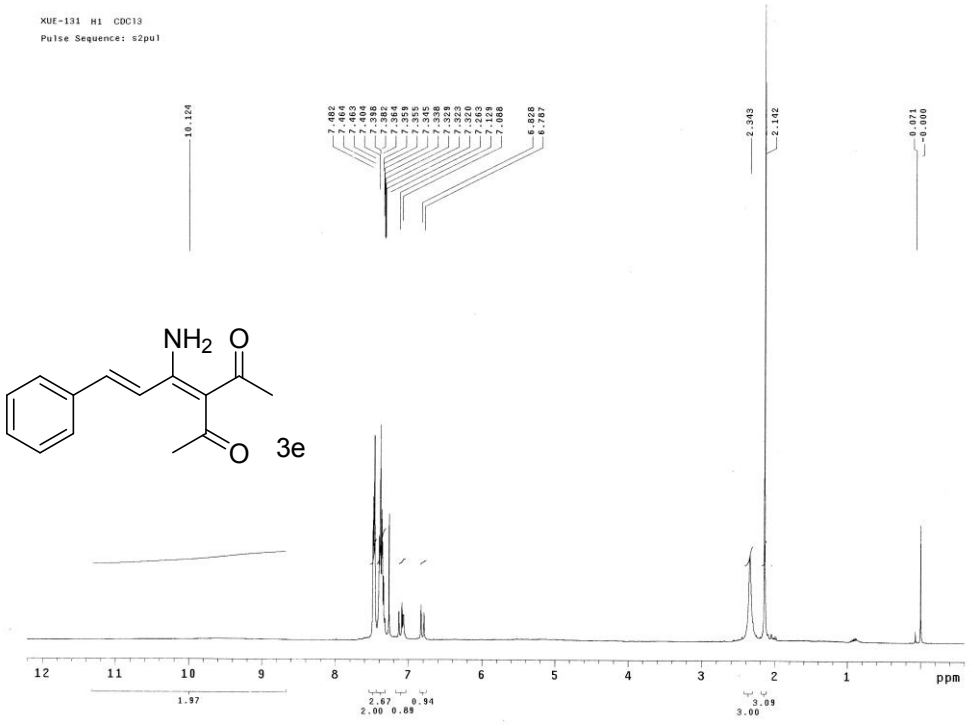
^{1}H NMR spectra for compound **3b**



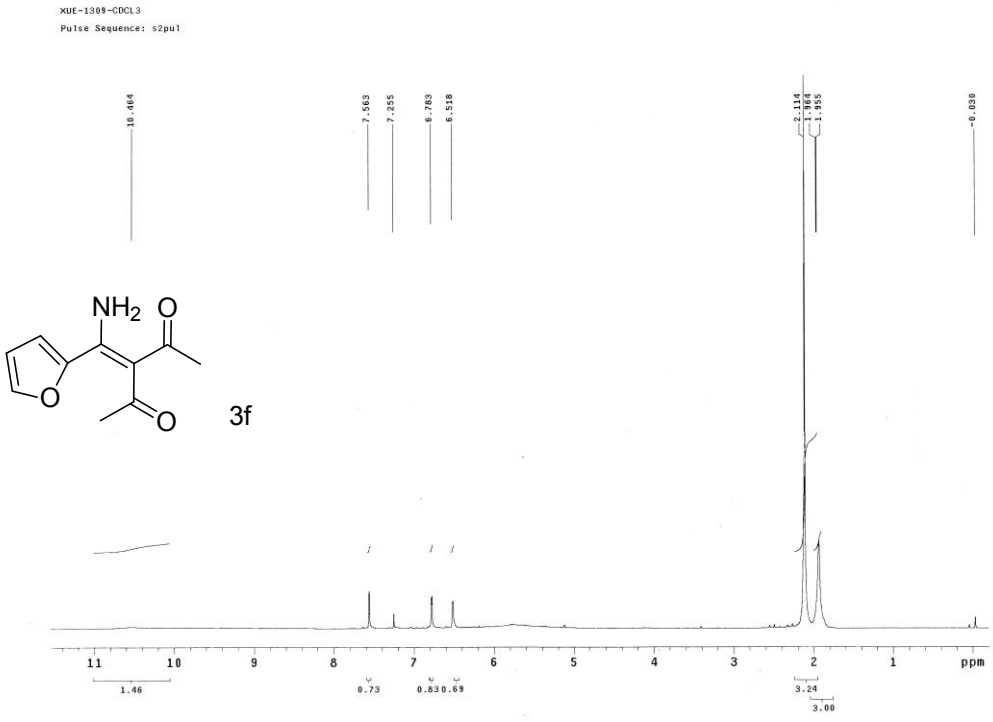
^{1}H NMR spectra for compound **3c**



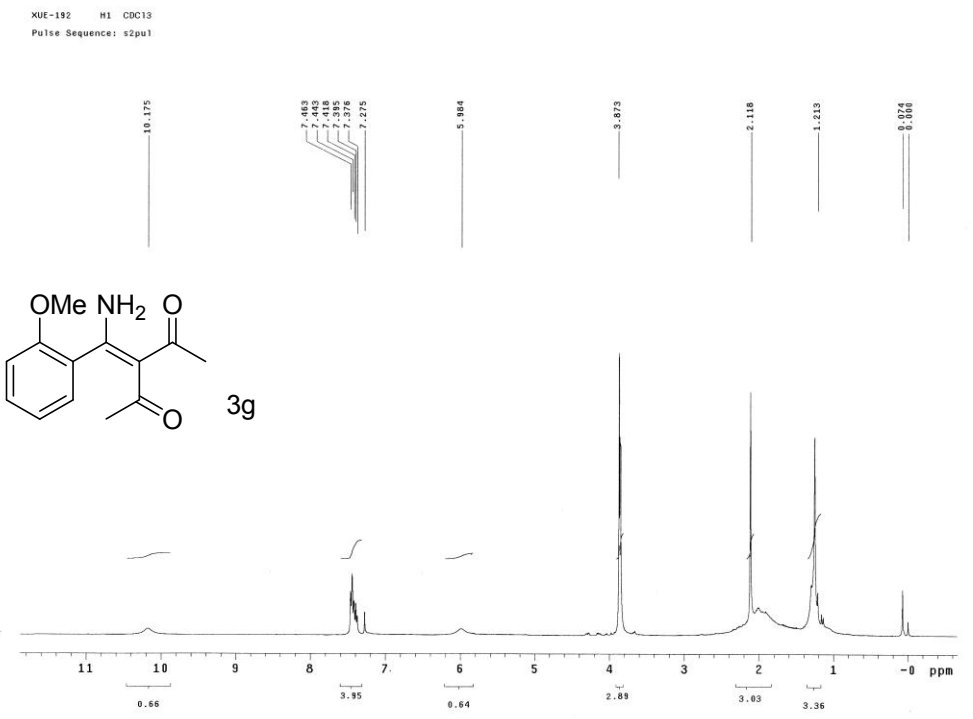
^{1}H NMR spectra for compound **3d**



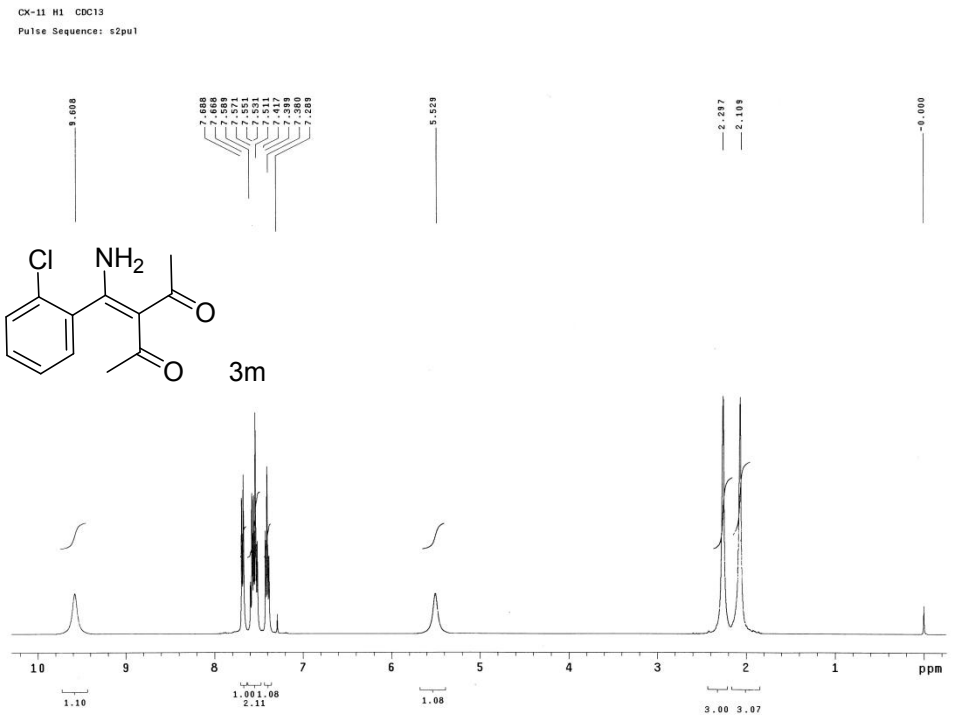
^{1}H NMR spectra for compound **3e**



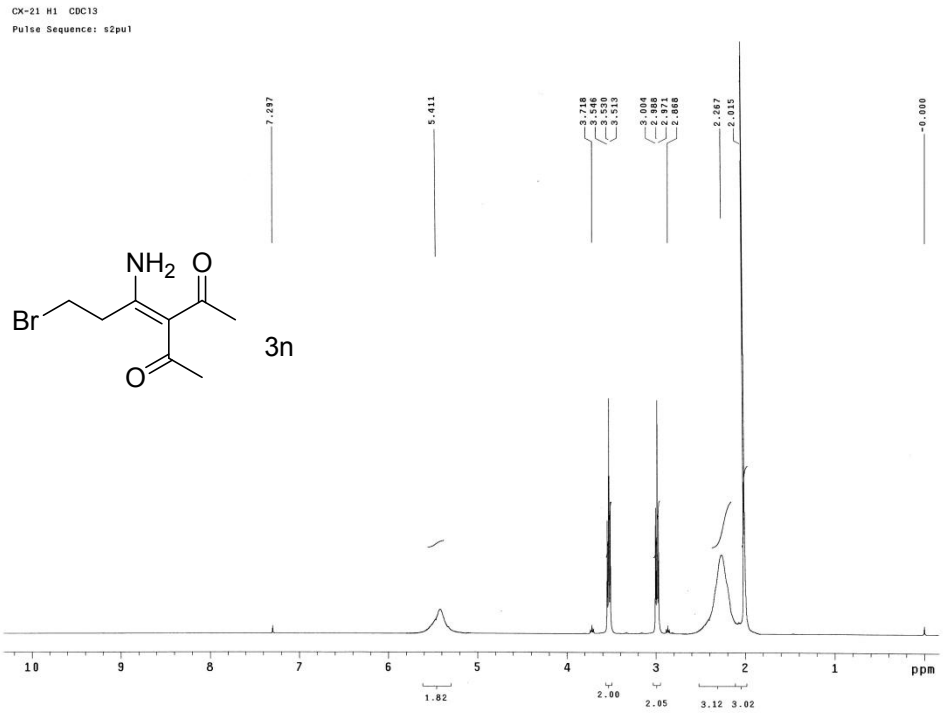
^{1}H NMR spectra for compound **3f**



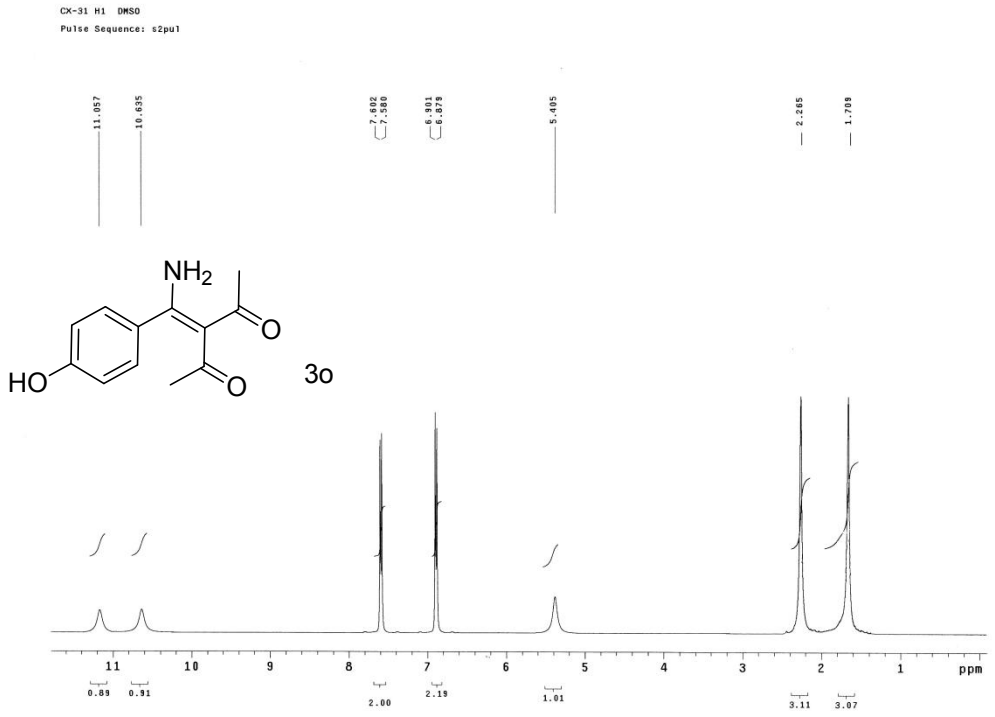
^{1}H NMR spectra for compound **3g**



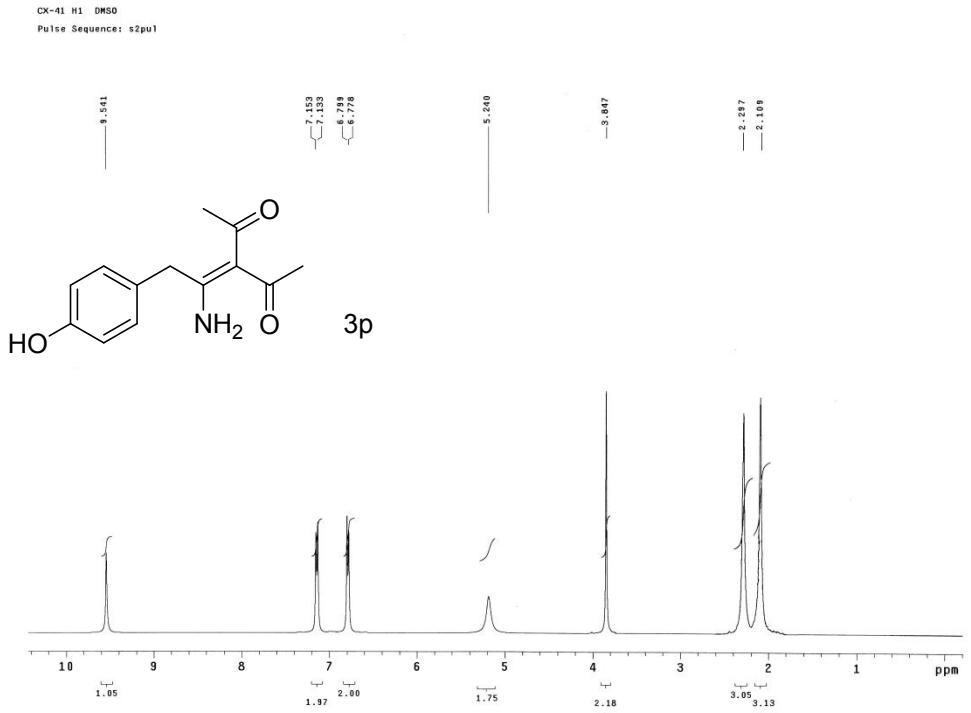
^{1}H NMR spectra for compound **3m**



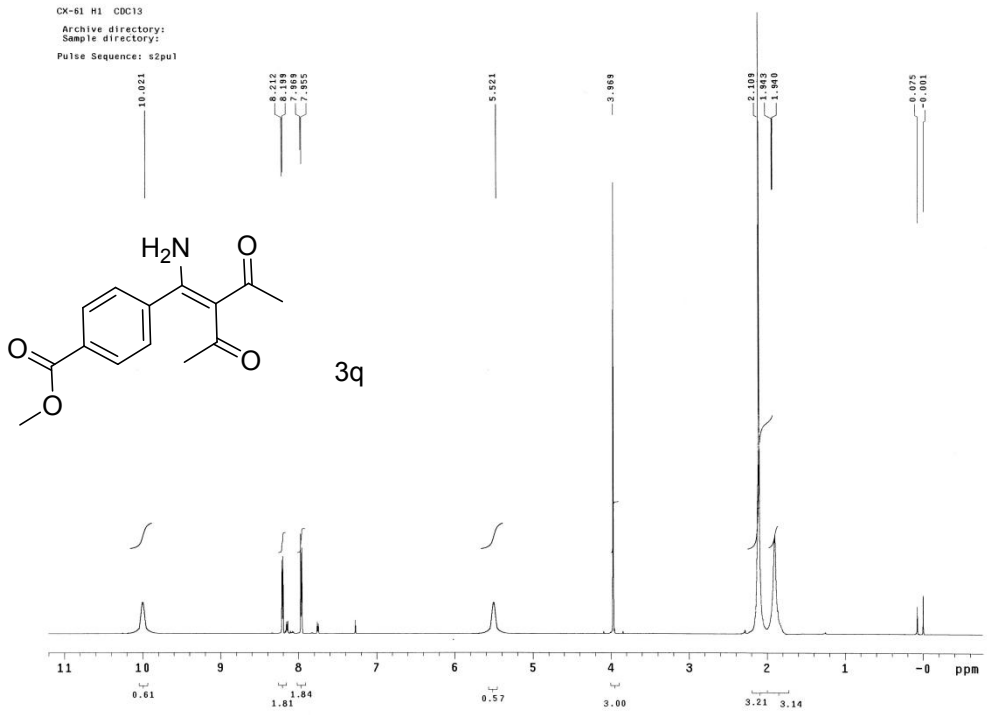
^{1}H NMR spectra for compound **3n**



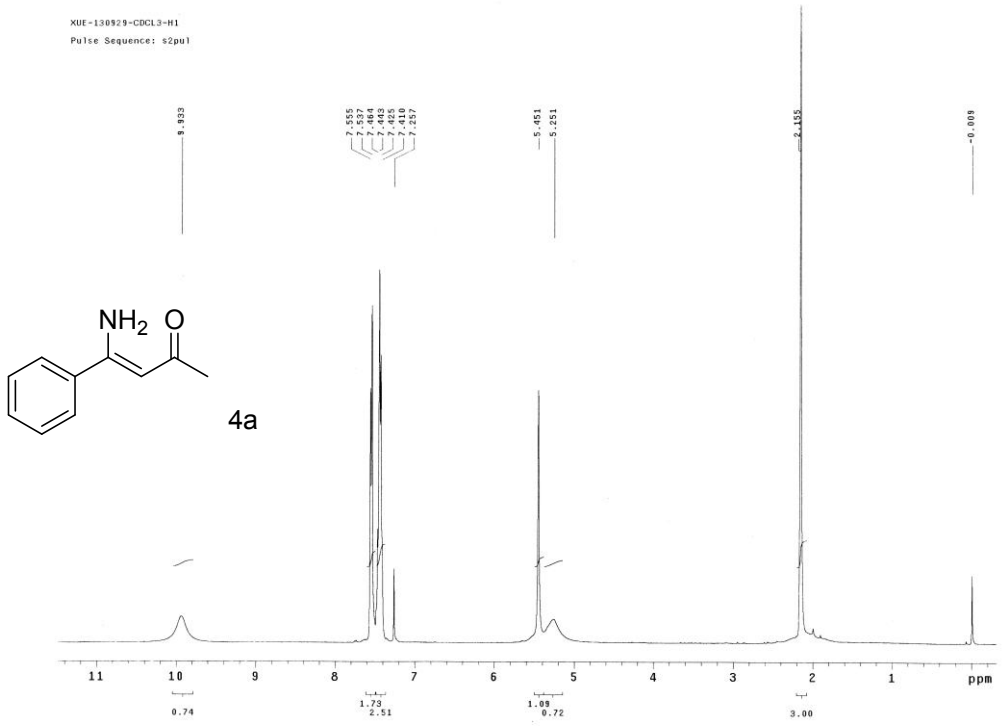
^{1}H NMR spectra for compound **3o**



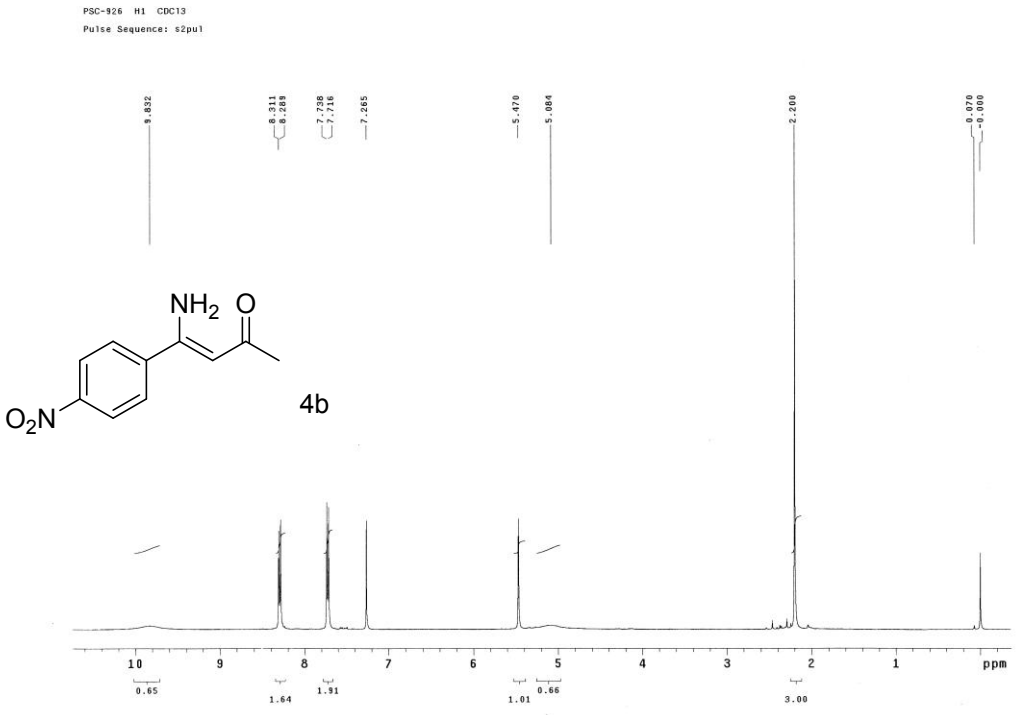
^{1}H NMR spectra for compound **3p**



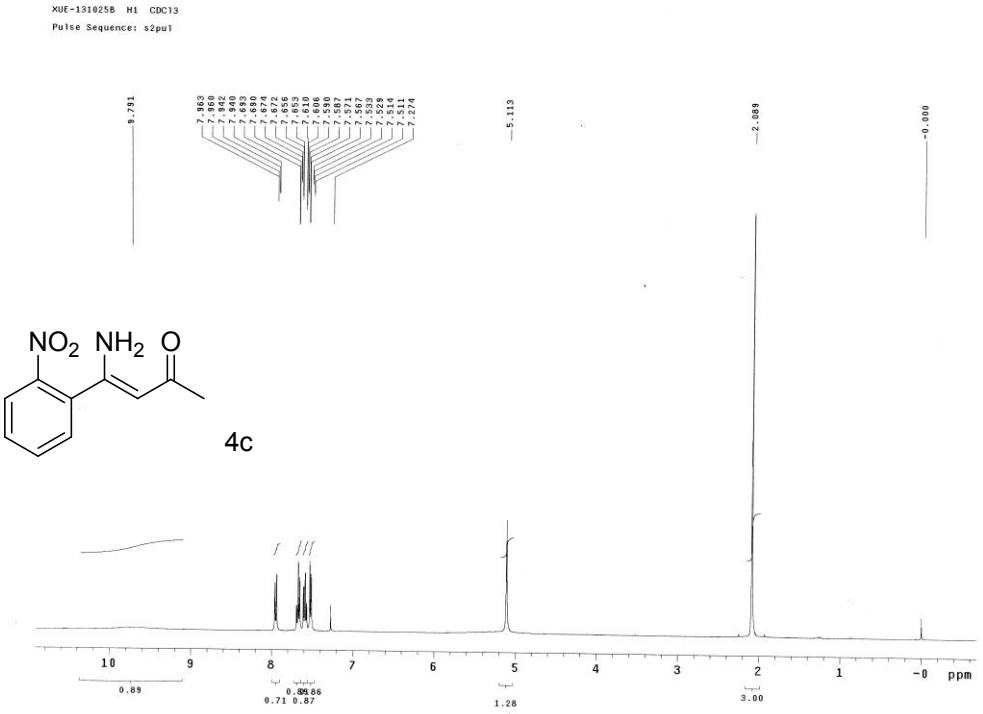
^{1}H NMR spectra for compound **3q**



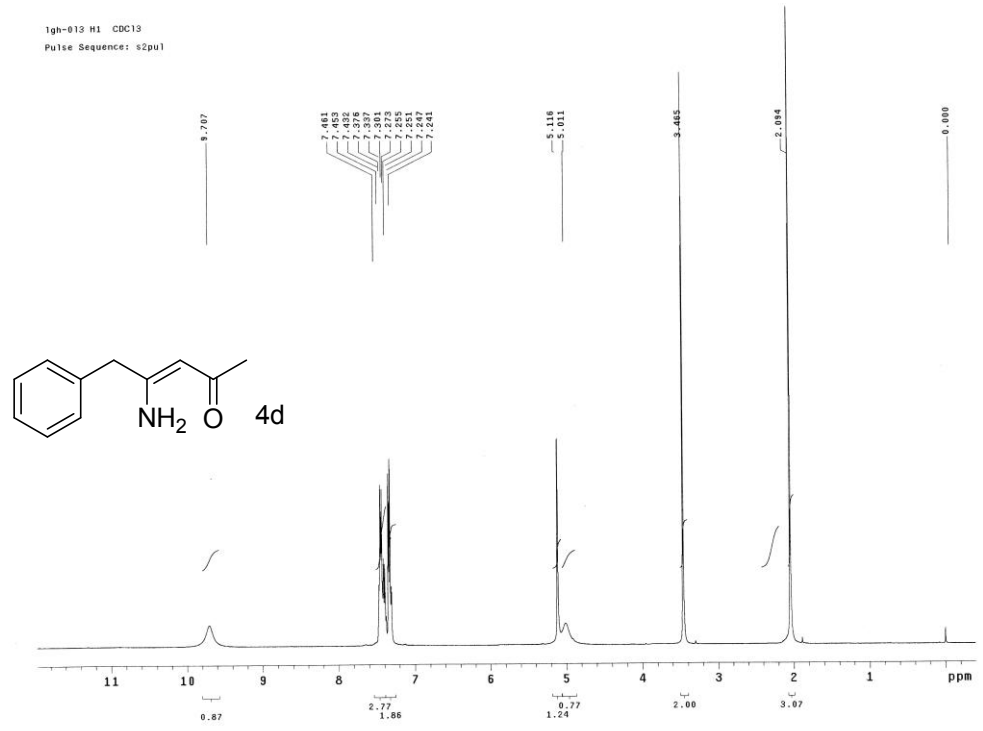
^{1}H NMR spectra for compound **4a**



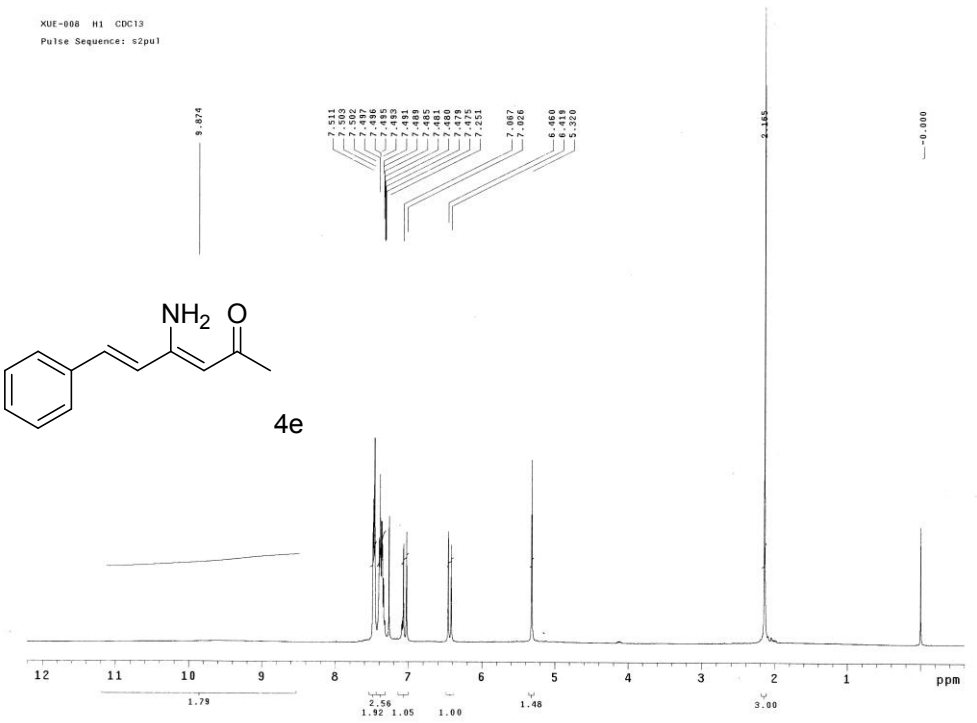
^{1}H NMR spectra for compound **4b**



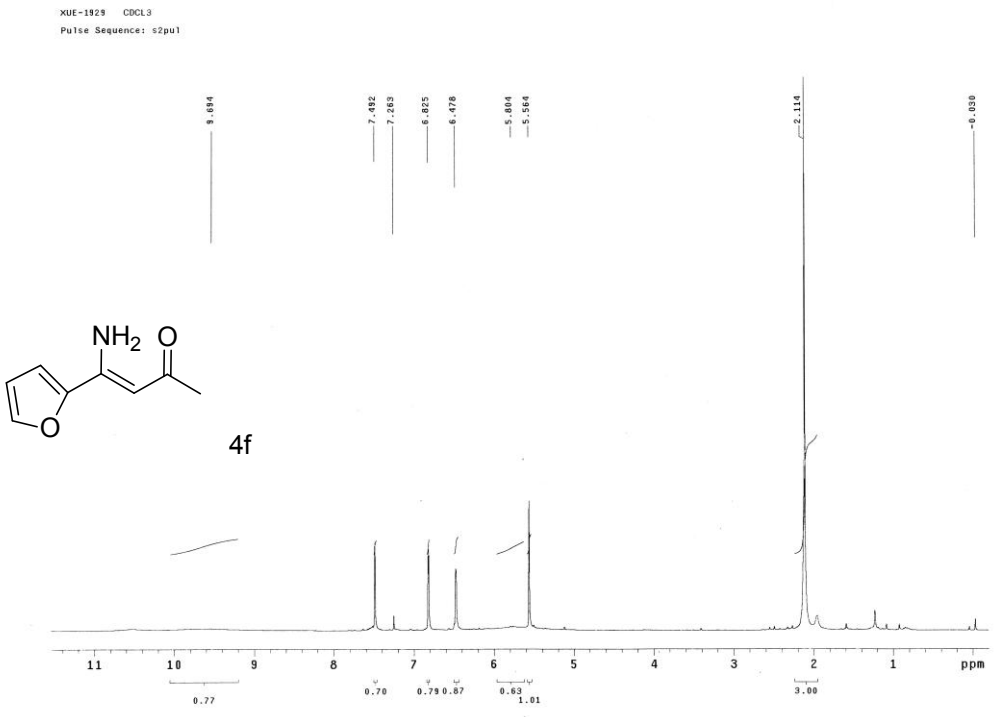
^{1}H NMR spectra for compound **4c**



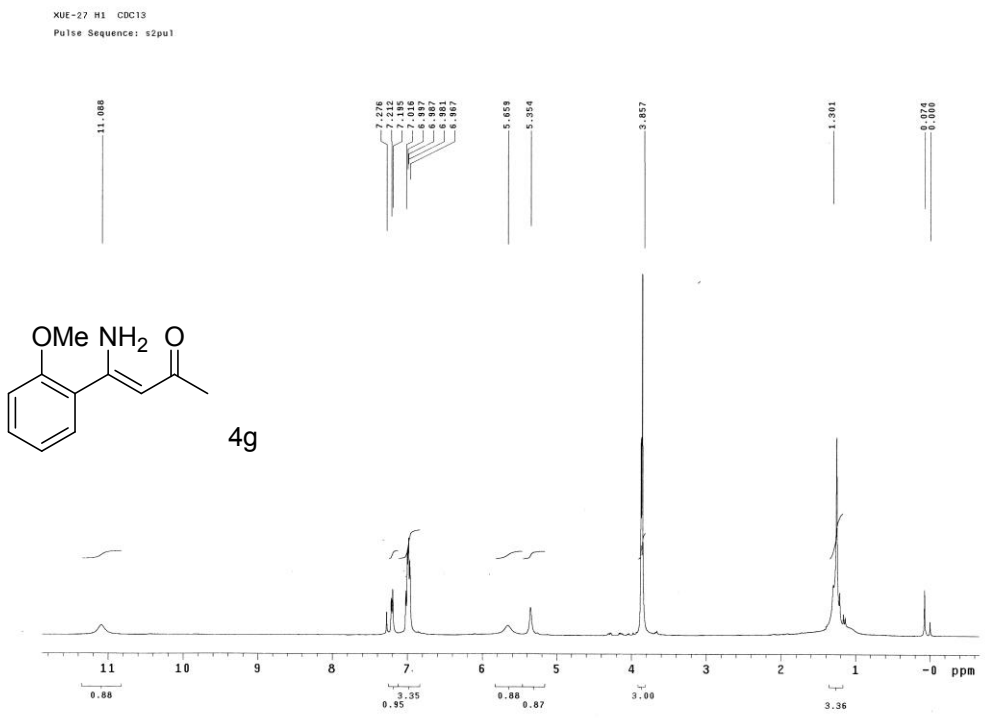
^{1}H NMR spectra for compound **4d**



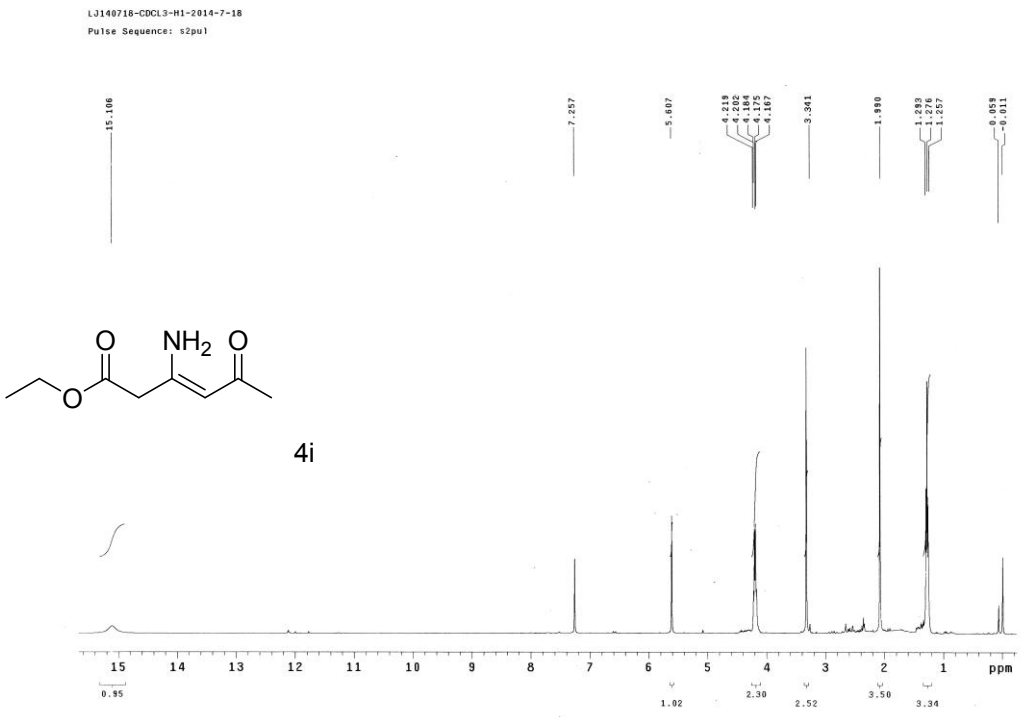
^{1}H NMR spectra for compound **4e**



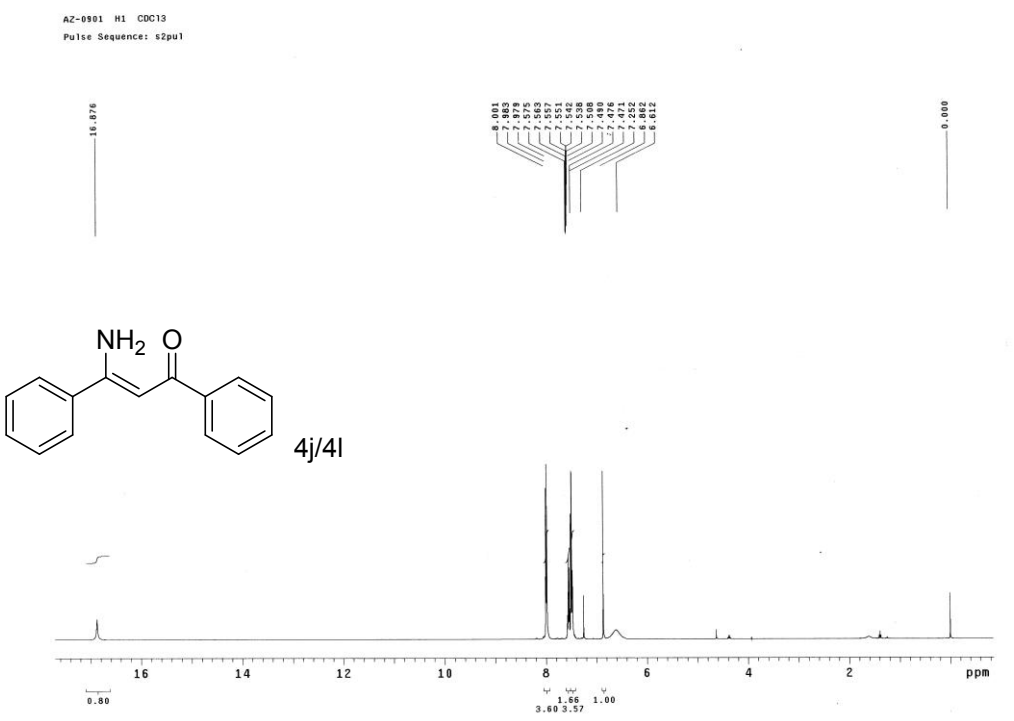
^{1}H NMR spectra for compound **4f**



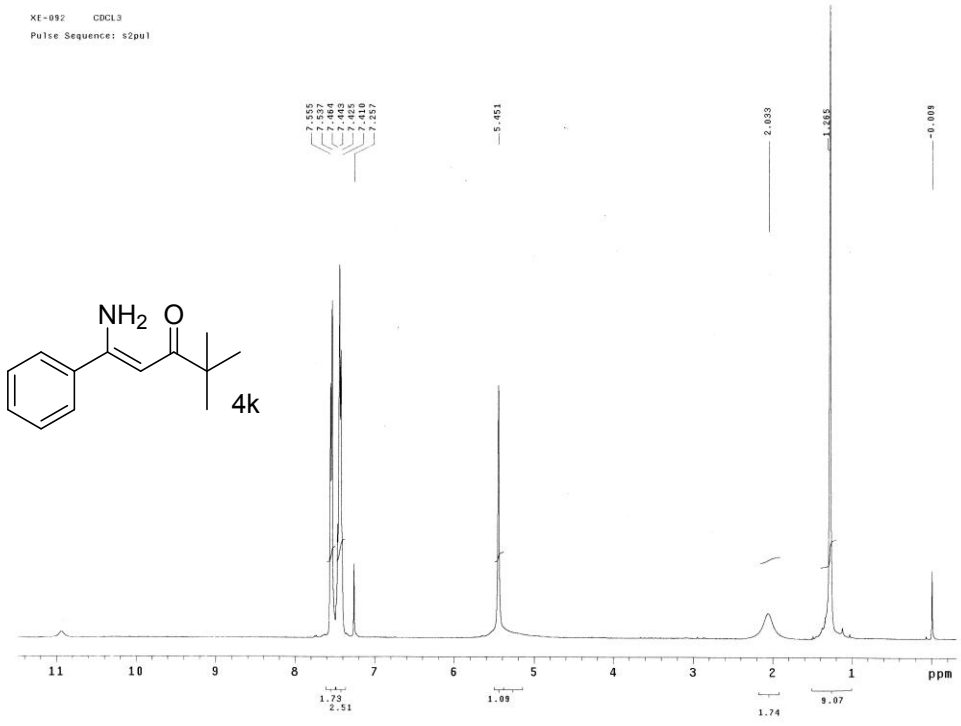
^{1}H NMR spectra for compound **4g**



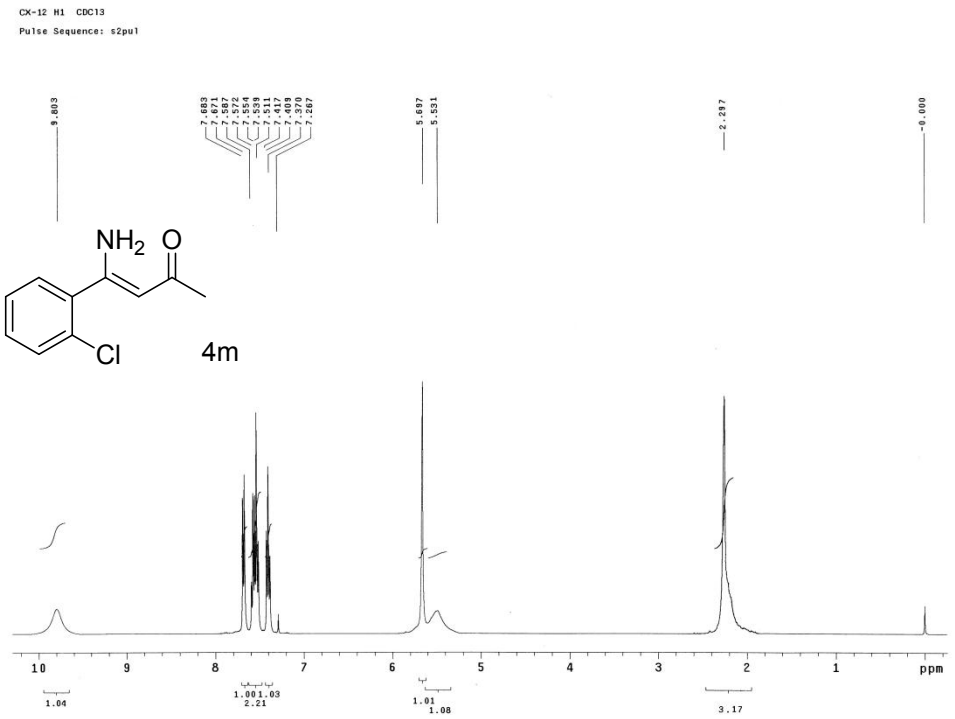
^{1}H NMR spectra for compound **4i**



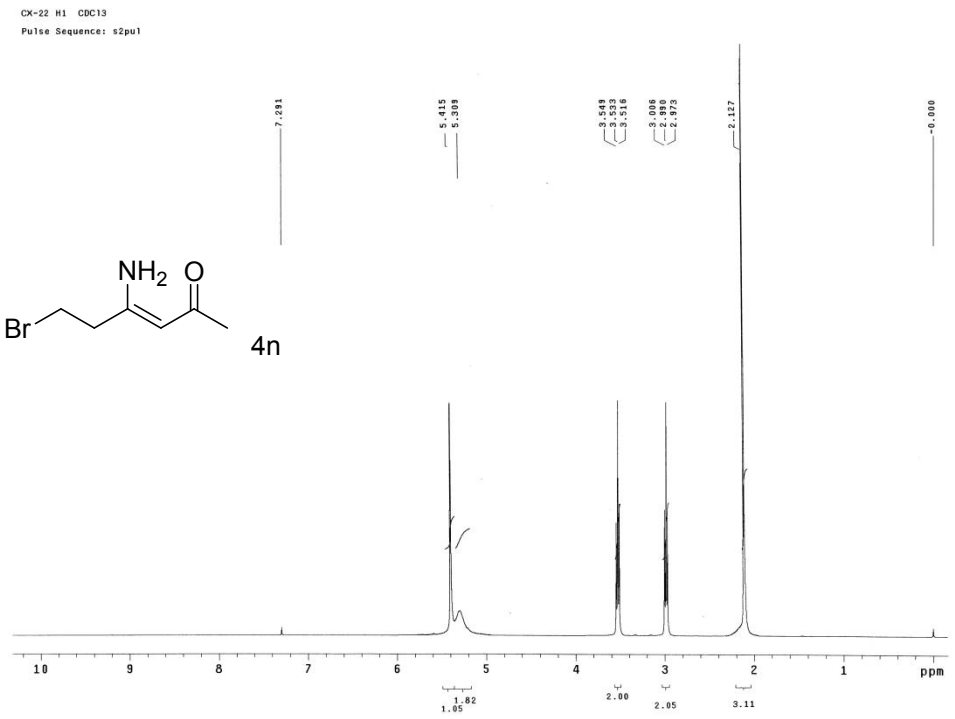
^{1}H NMR spectra for compound **4j (4l)**



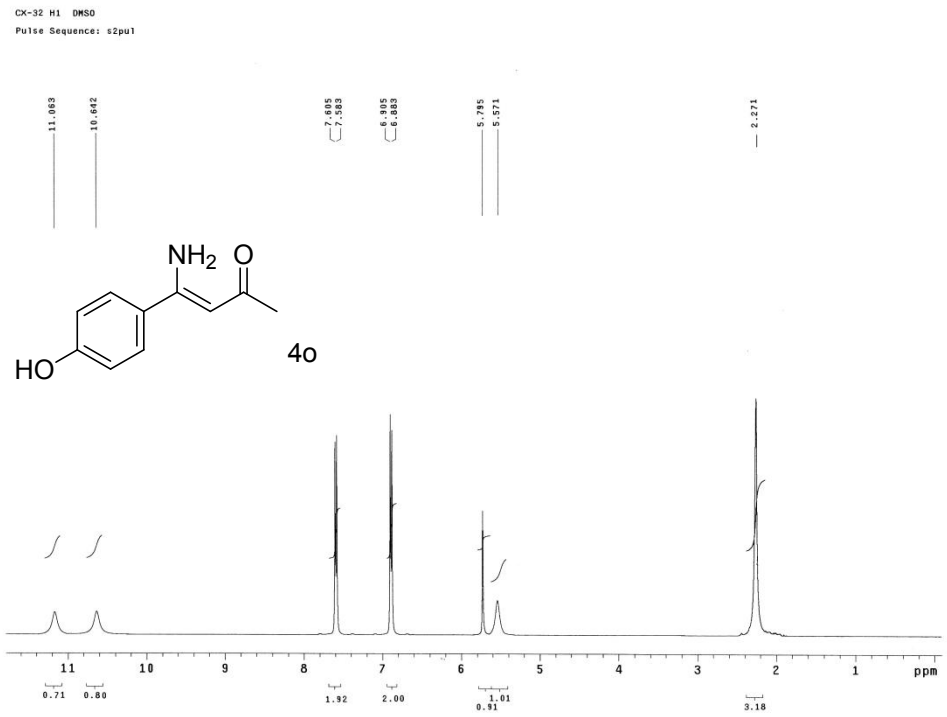
^{1}H NMR spectra for compound **4k**



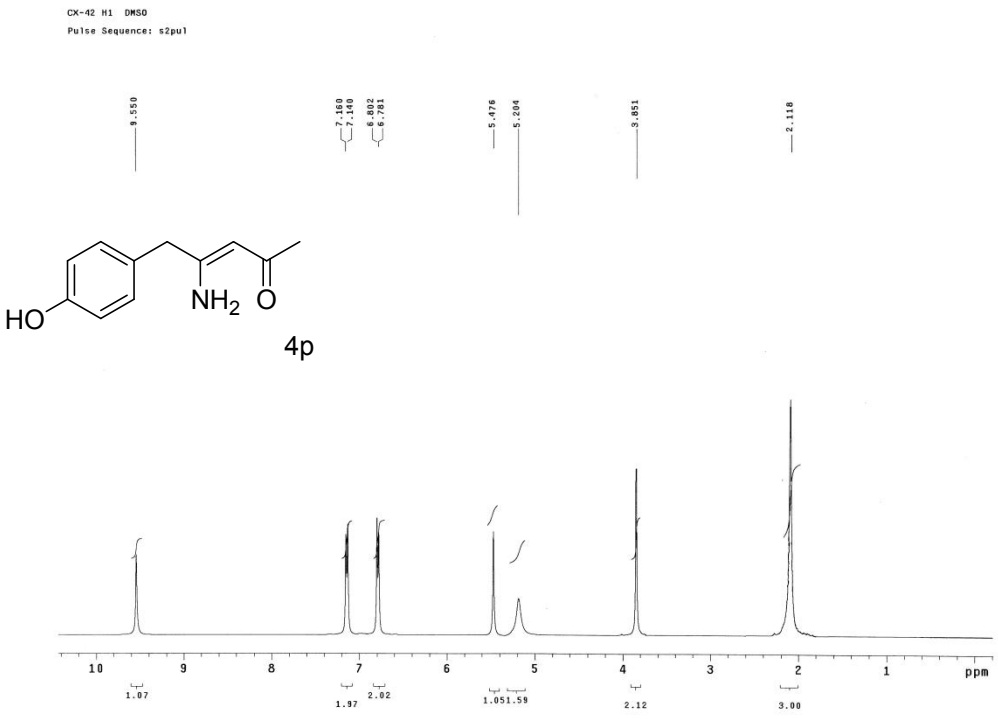
^{1}H NMR spectra for compound **4m**



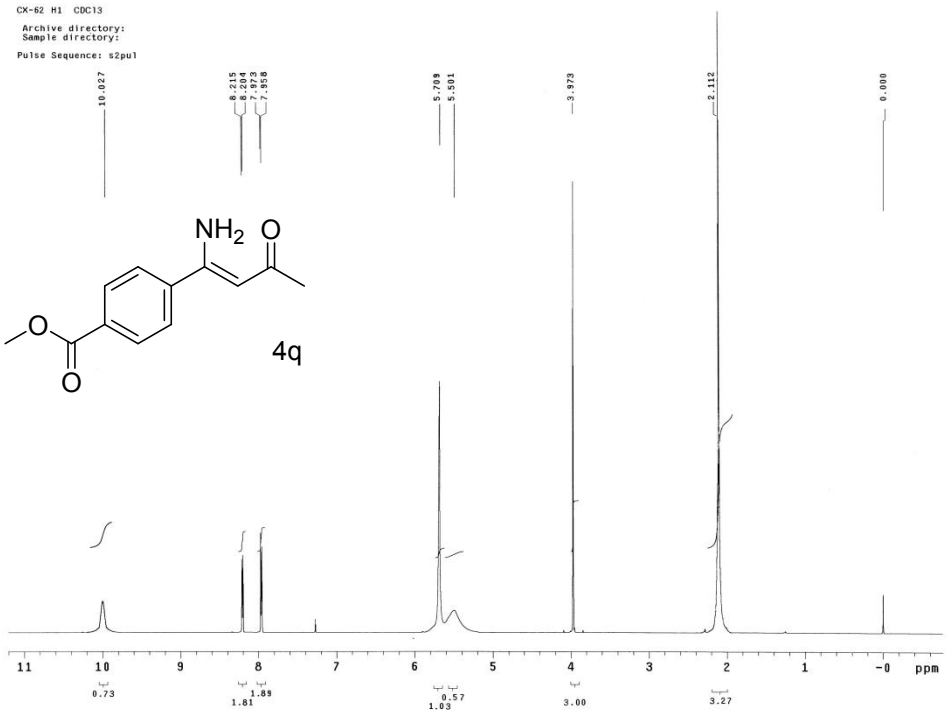
^{1}H NMR spectra for compound **4n**



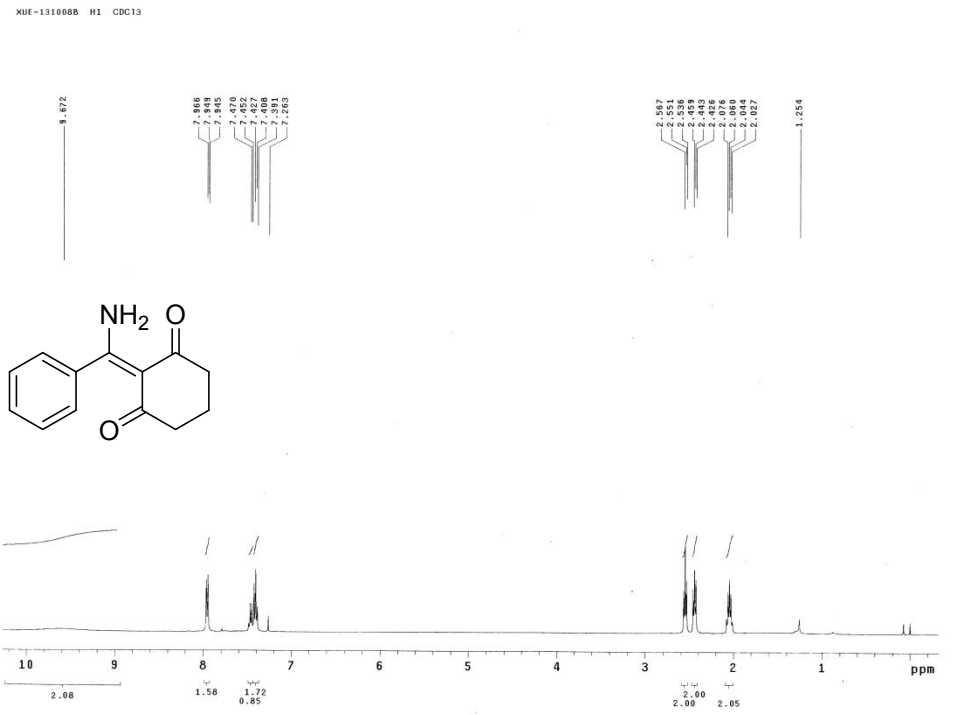
^{1}H NMR spectra for compound **4o**



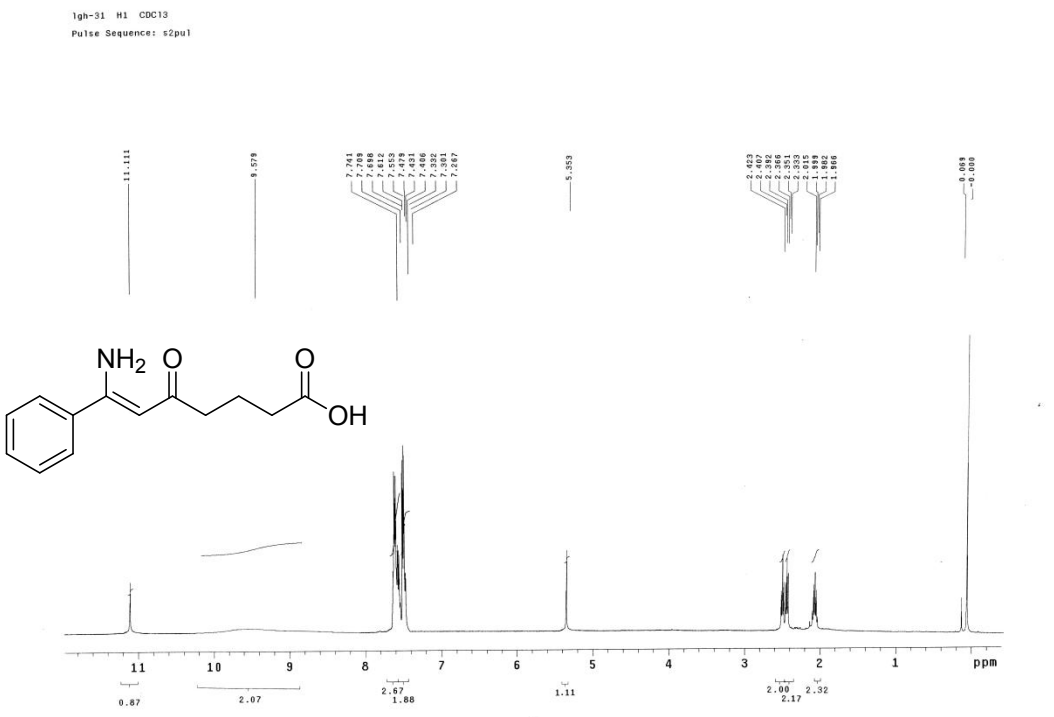
^{1}H NMR spectra for compound **4p**



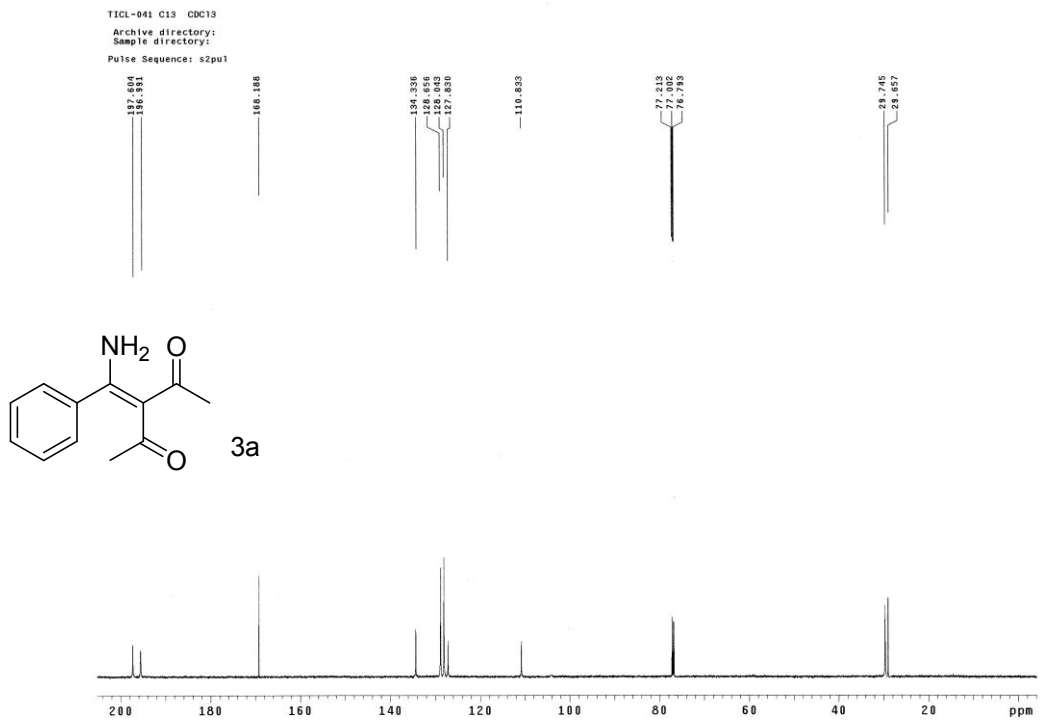
^{1}H NMR spectra for compound **4q**



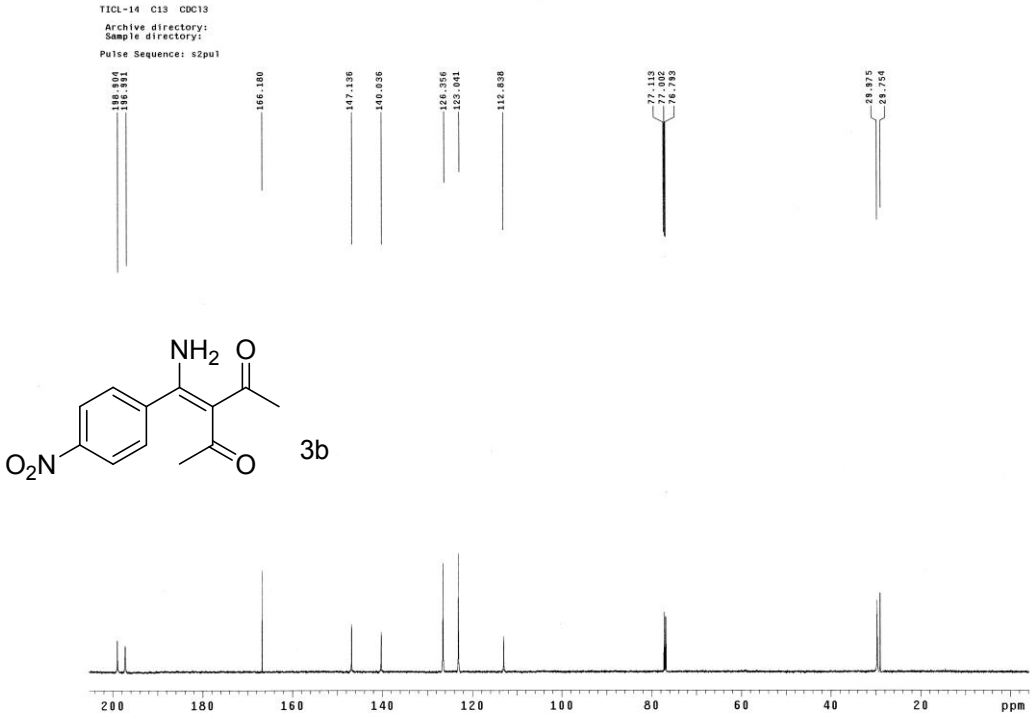
^{1}H NMR spectra for compound **3r**



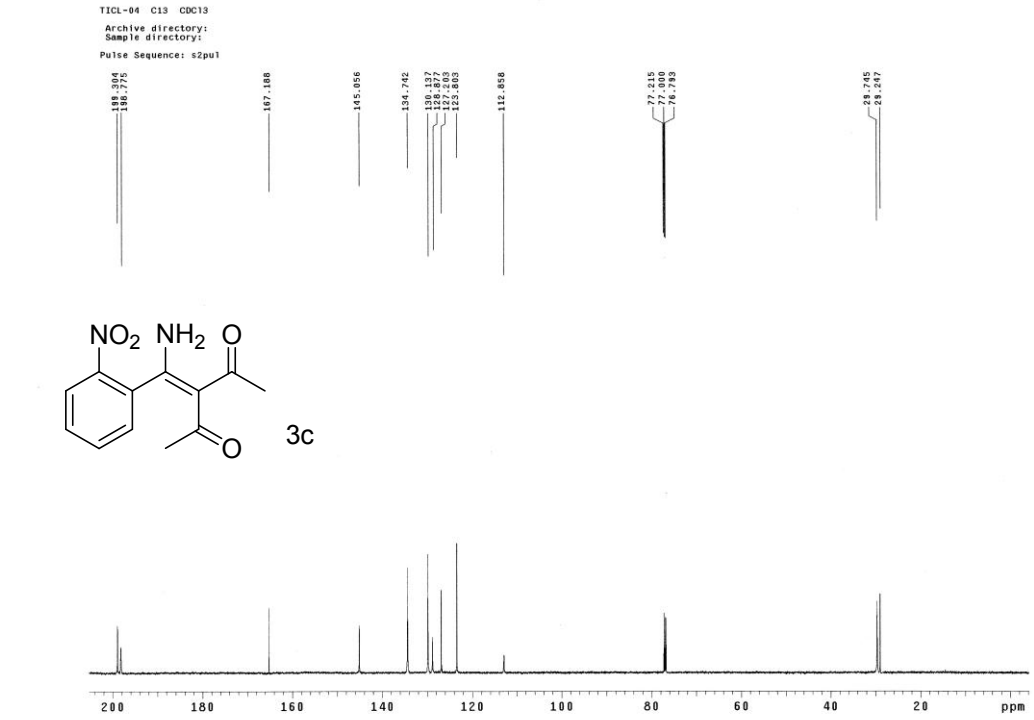
^{1}H NMR spectra for compound **4r**



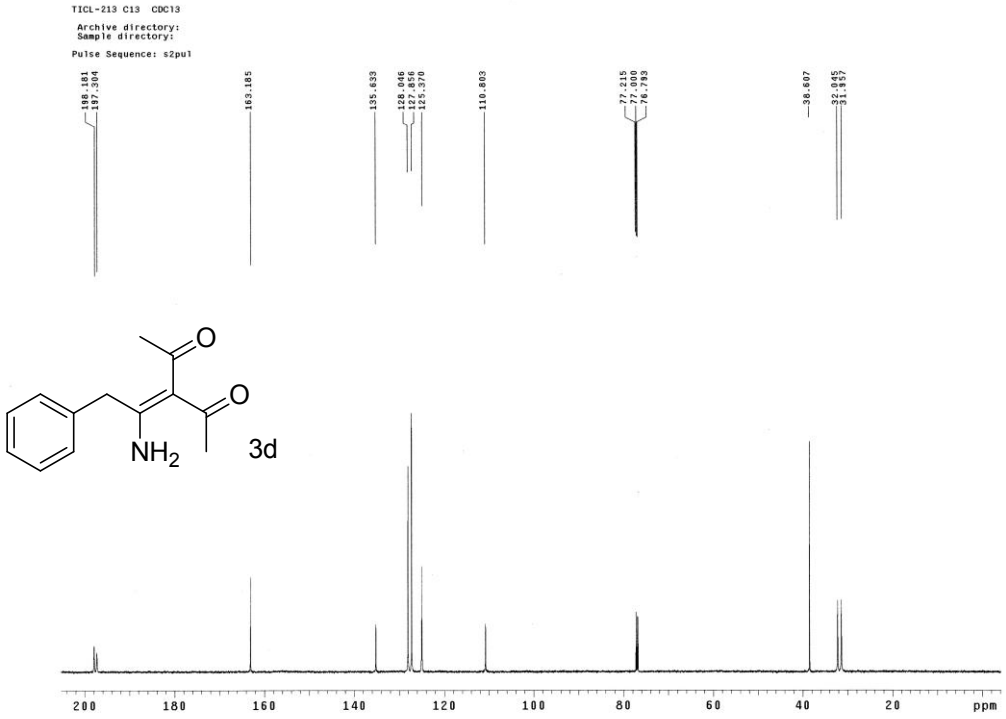
^{13}C NMR spectra for compound **3a**



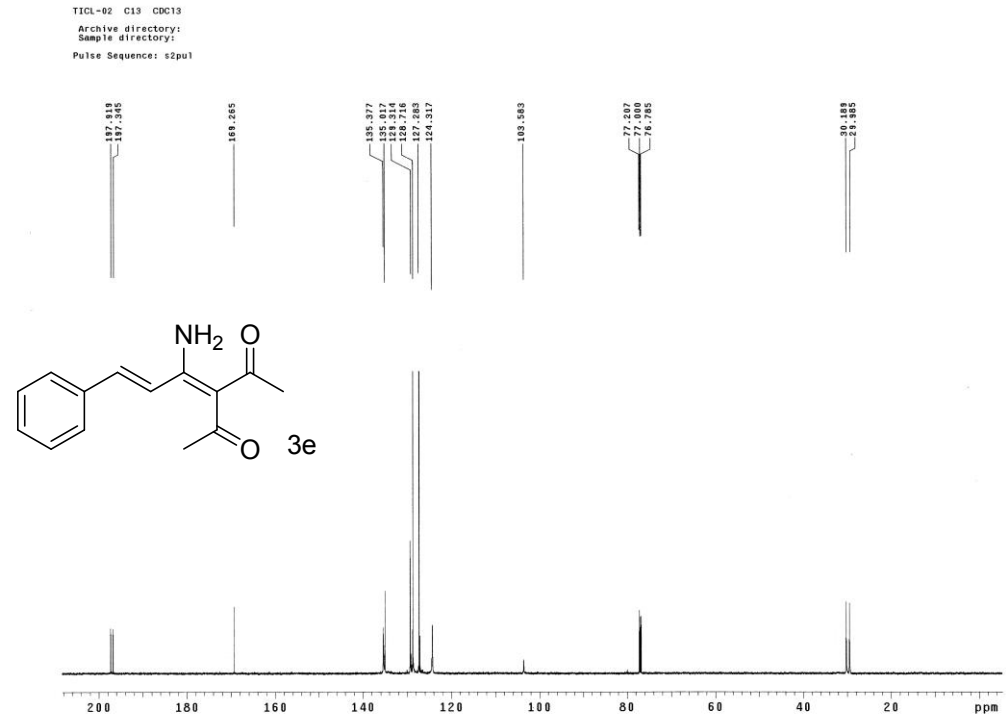
^{13}C NMR spectra for compound **3b**



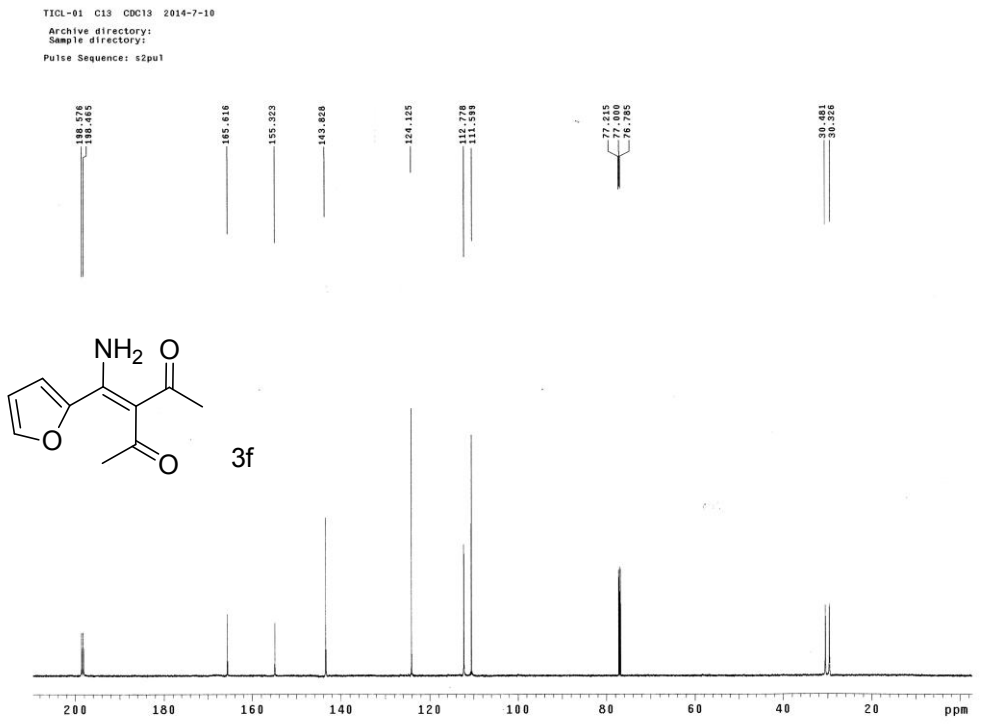
^{13}C NMR spectra for compound **3c**



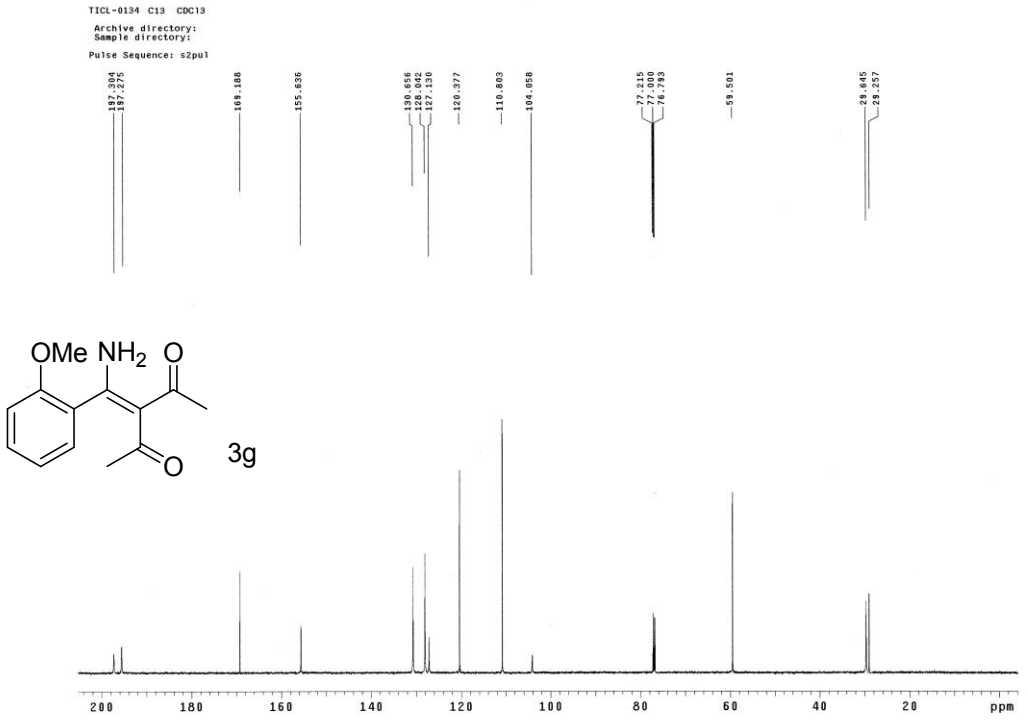
^{13}C NMR spectra for compound **3d**



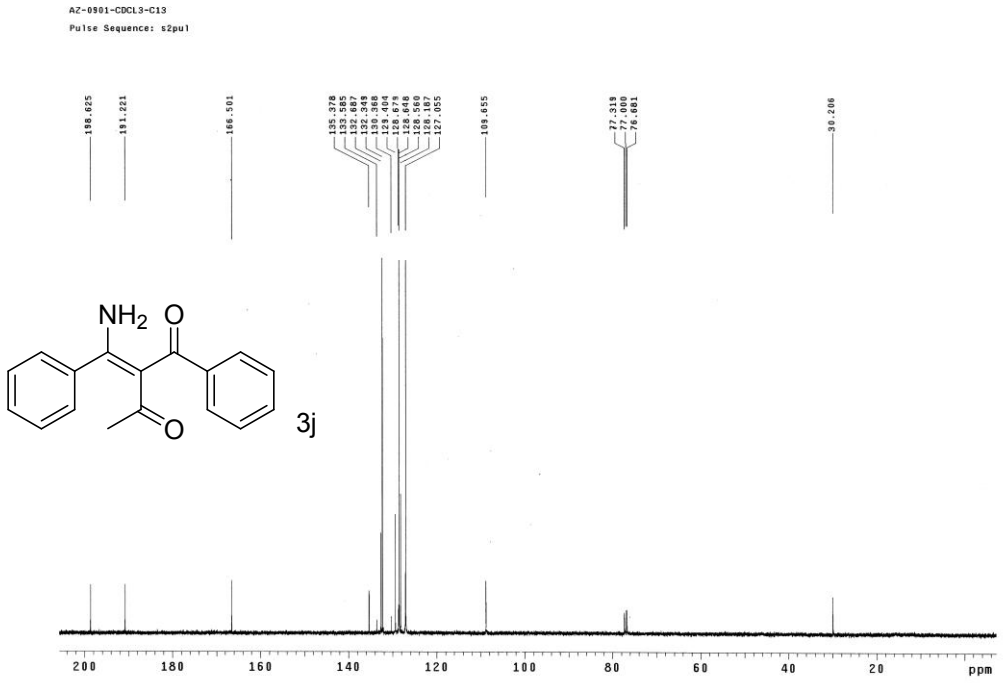
^{13}C NMR spectra for compound **3e**



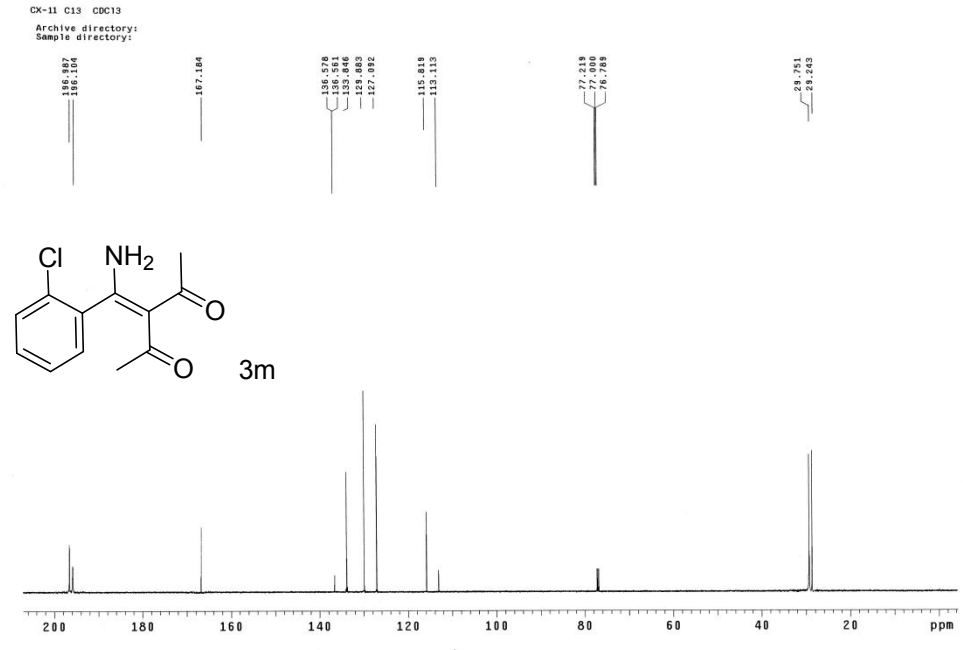
^{13}C NMR spectra for compound **3f**



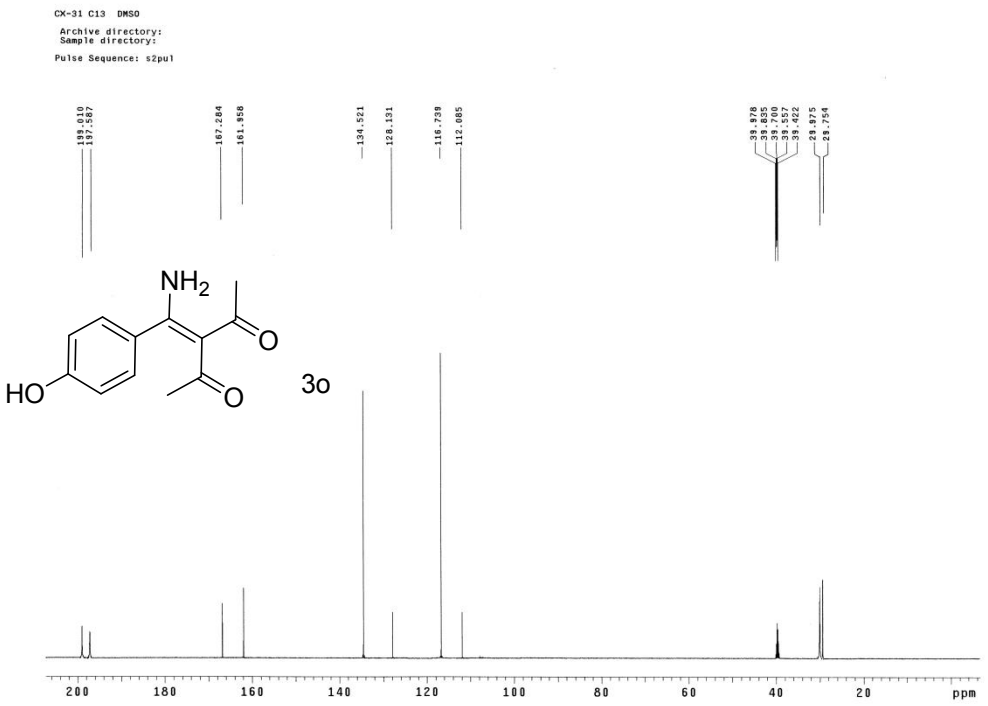
^{13}C NMR spectra for compound **3g**



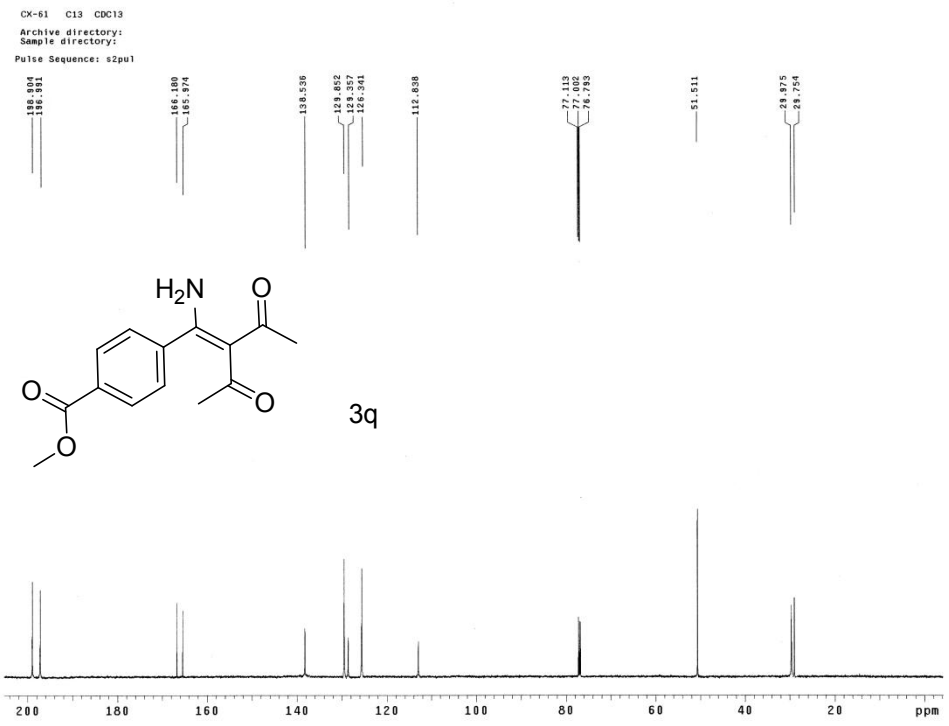
^{13}C NMR spectra for compound **3j**



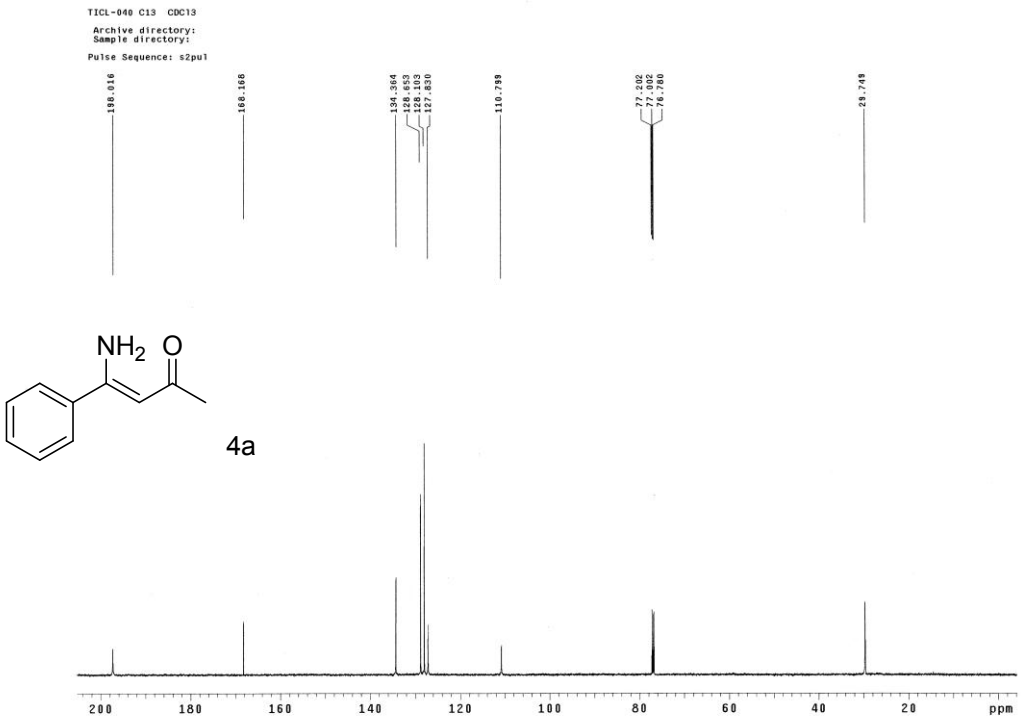
^{13}C NMR spectra for compound **3m**



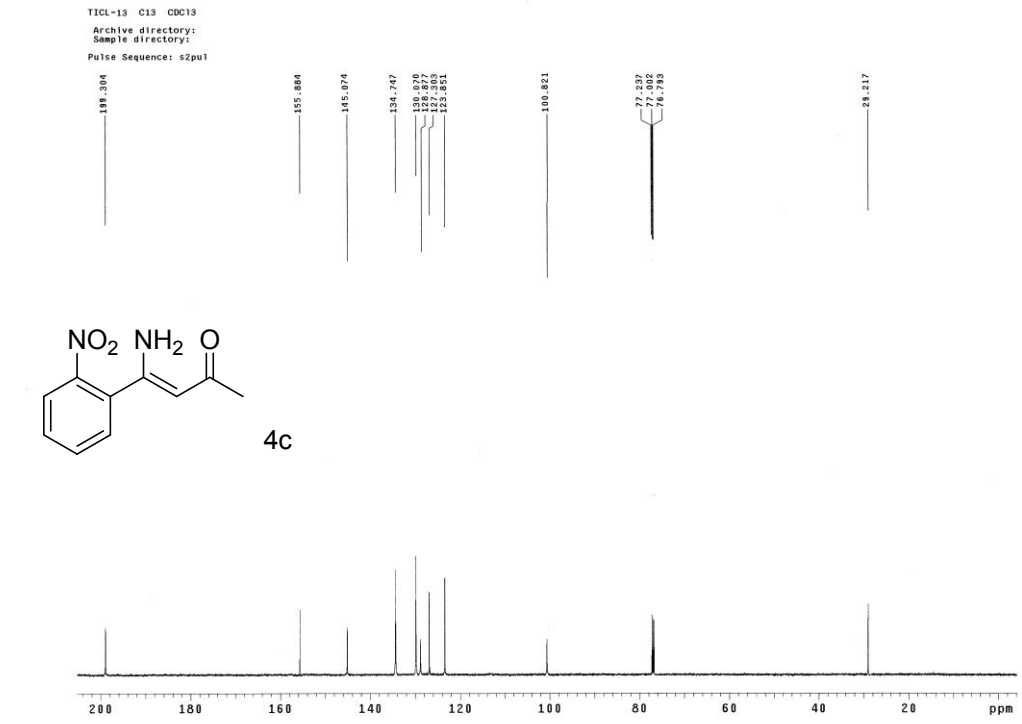
^{13}C NMR spectra for compound **3o**



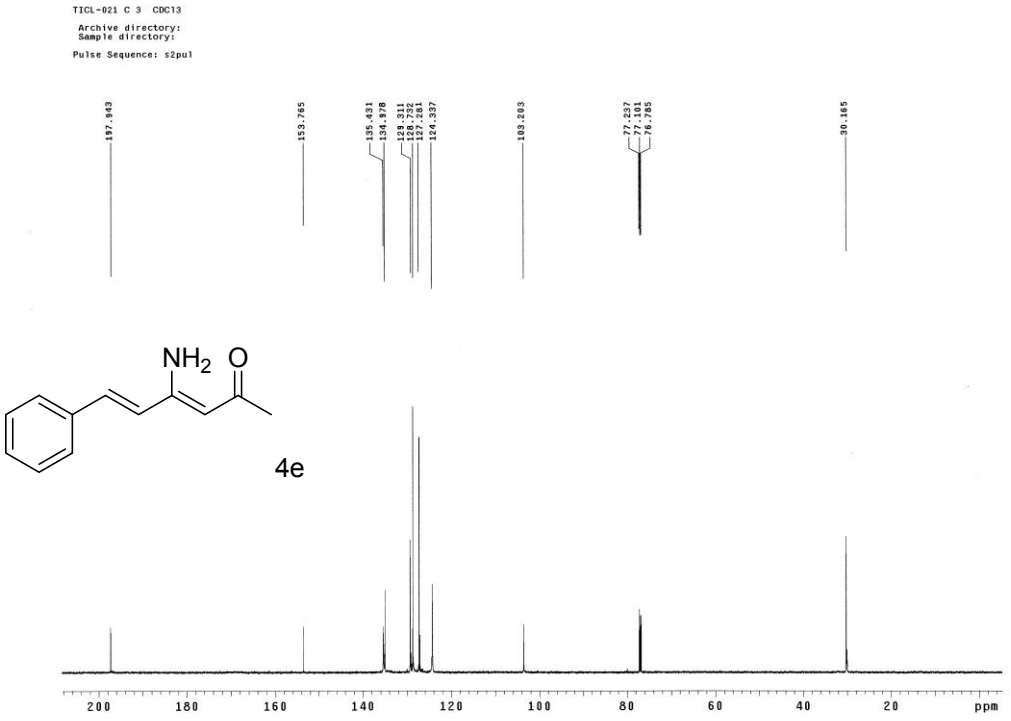
^{13}C NMR spectra for compound **3q**



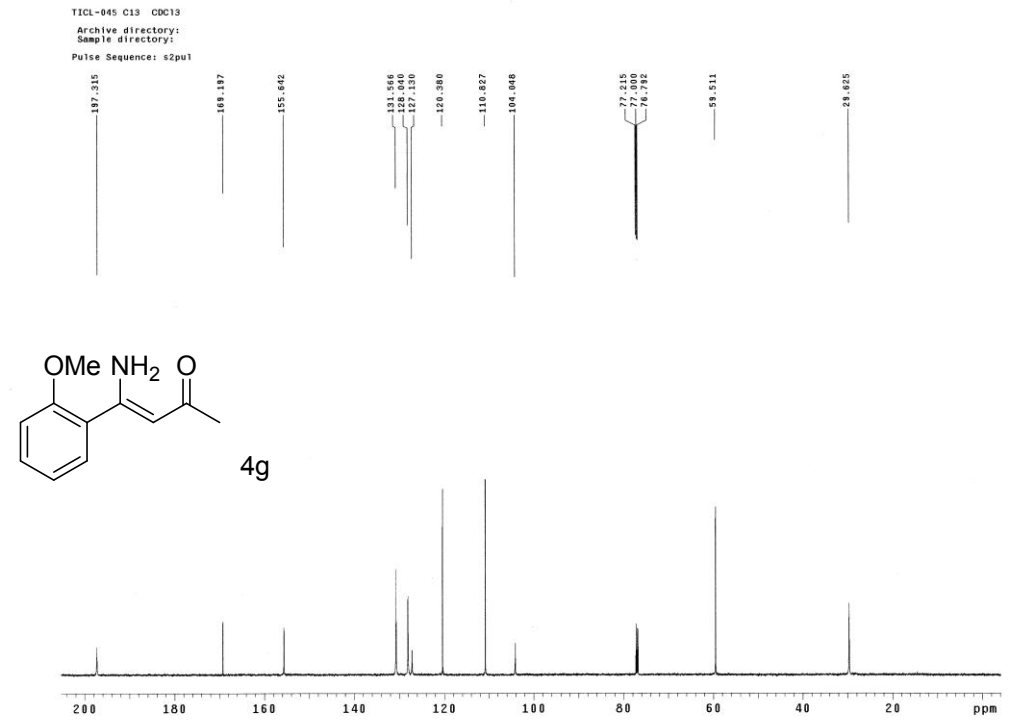
^{13}C NMR spectra for compound **4a**



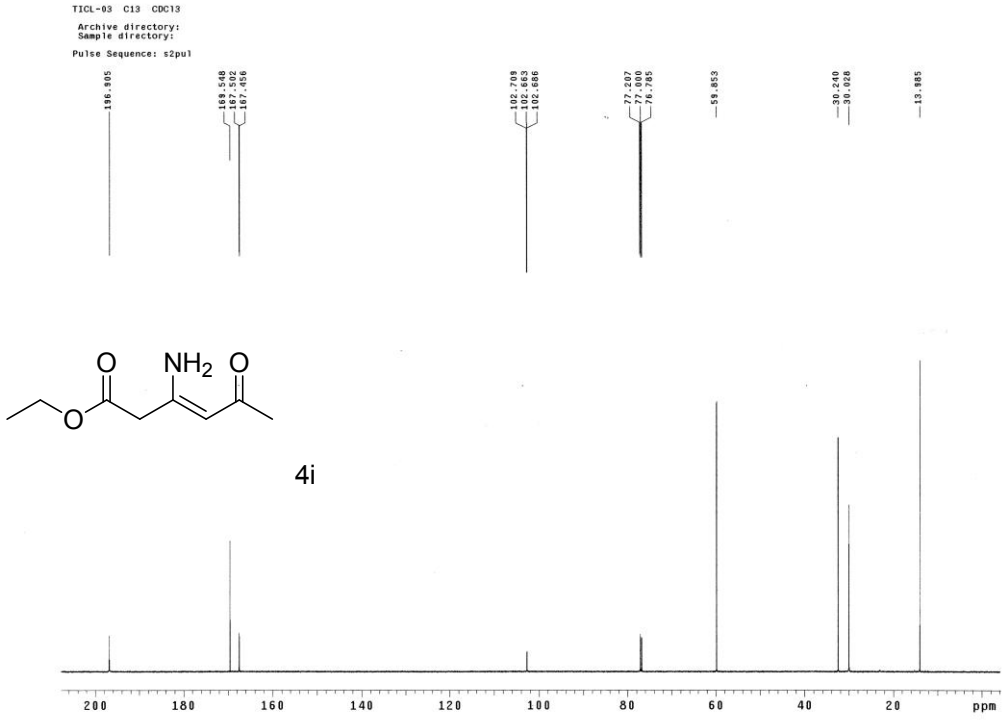
^{13}C NMR spectra for compound **4c**



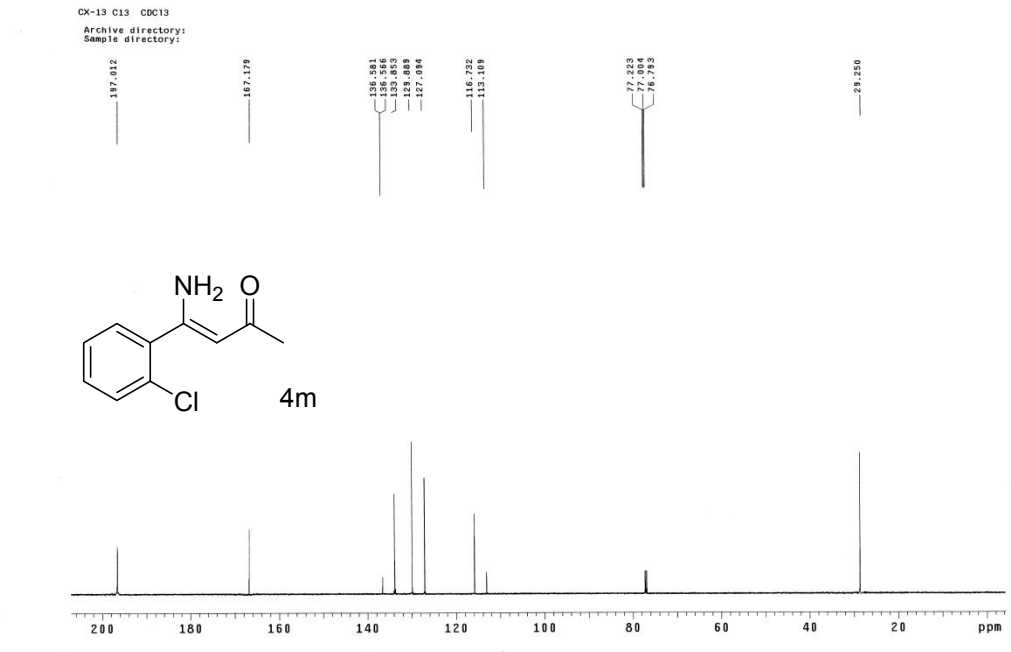
^{13}C NMR spectra for compound **4e**



^{13}C NMR spectra for compound **4g**

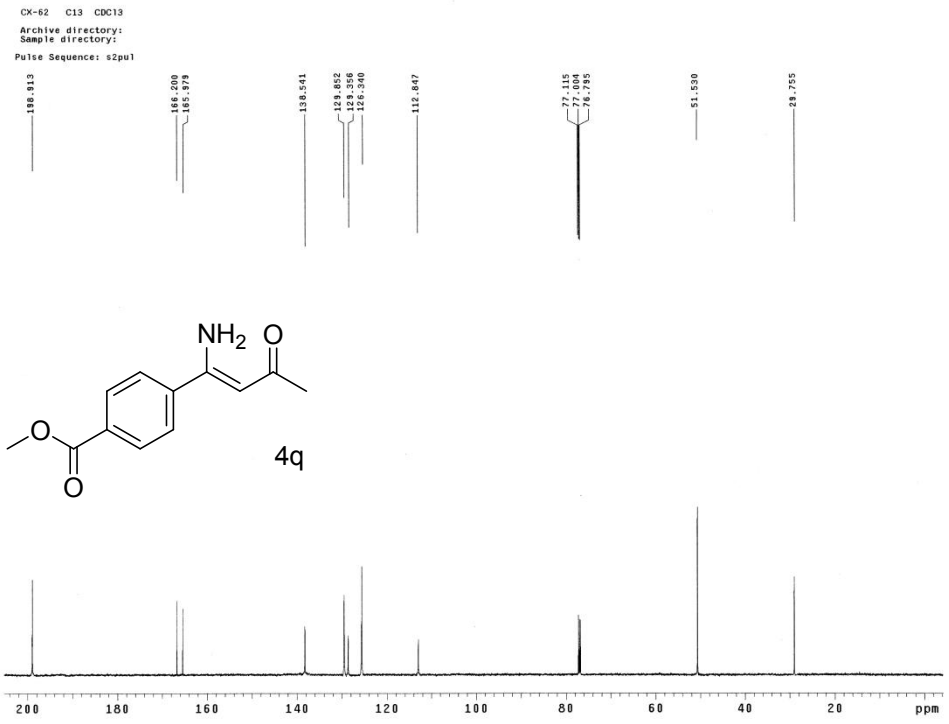


^{13}C NMR spectra for compound **4i**

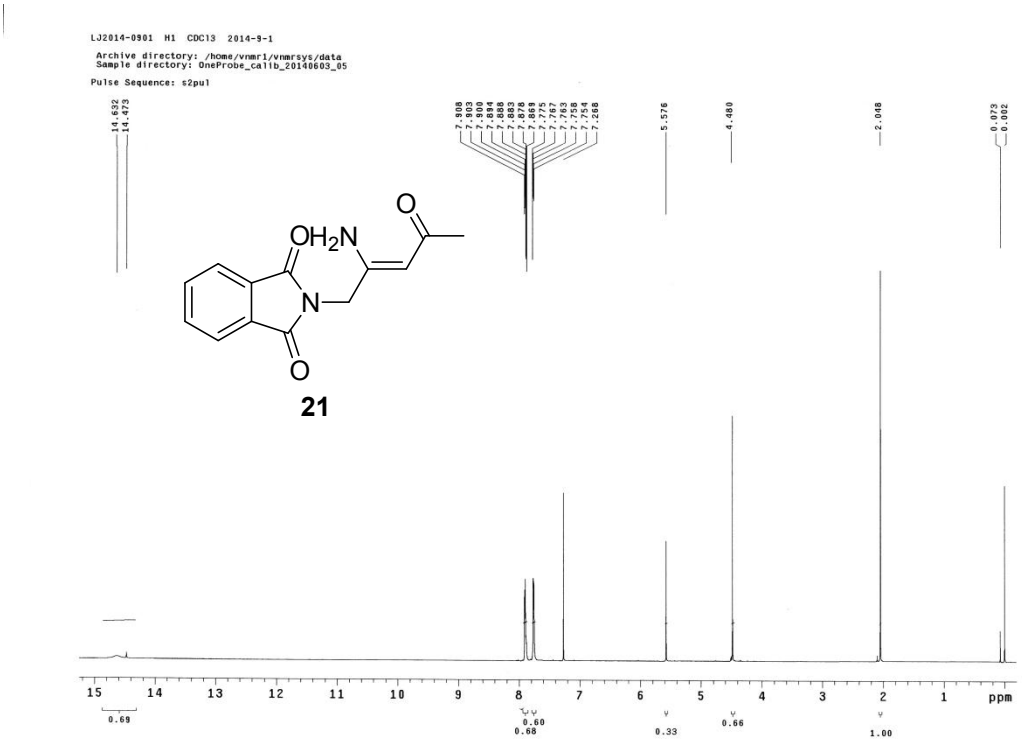


^{13}C NMR spectra for compound **4m**

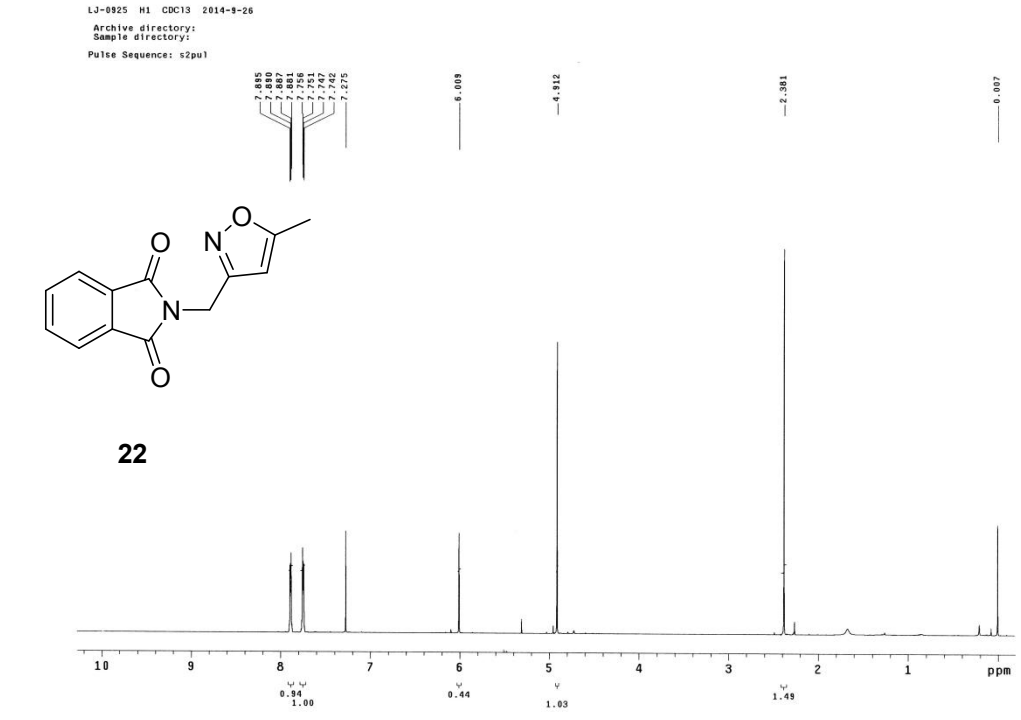
^{13}C NMR spectra for compound **4o**



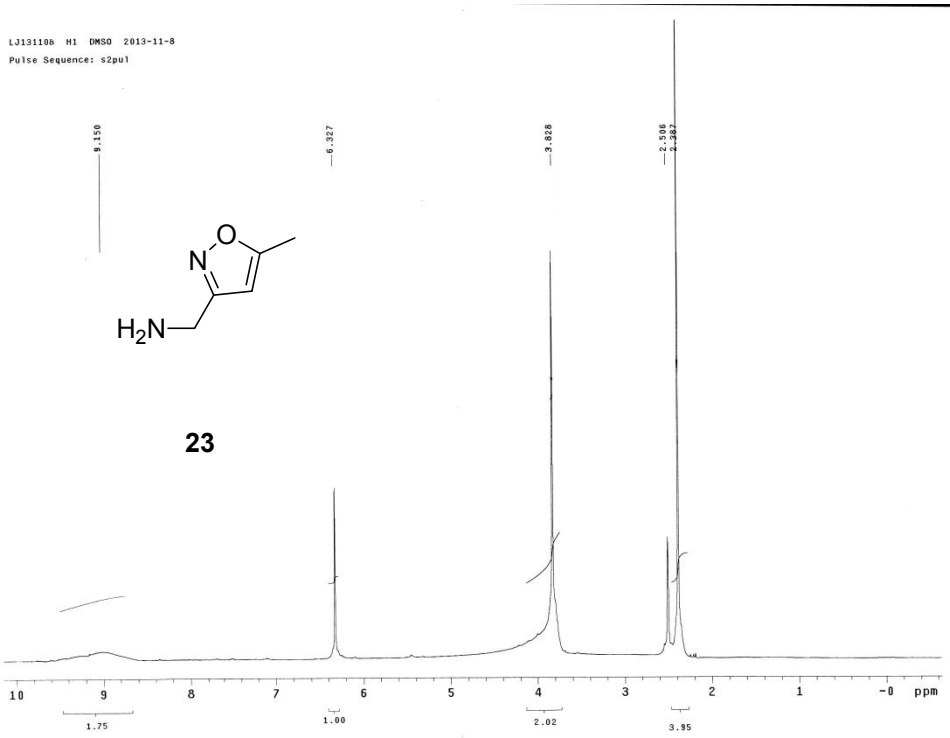
^{13}C NMR spectra for compound **4q**



^{1}H NMR spectra for compound **21**



^{1}H NMR spectra for compound **22**



^{1}H NMR spectra for compound **23**

^{13}C NMR spectra for compound **23**