

Direct Synthesis of Carbamates, Thiocarbamates, and Ureas from Boc-Protected Amines: A Sustainable and Efficient Approach

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2.1 General information

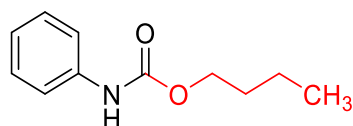
All solvents were distilled from appropriate drying agents prior to use. Flash column chromatography was performed using silica gel (300-400 mesh). All reactions conducted at 110 °C were performed on a DF-101D collector thermostatic magnetic stirrer pan. ¹H NMR and ¹³C NMR (400 and 101 MHz, respectively) spectra were recorded on a Bruker 400 MHz NMR spectrometer in CDCl₃ or DMSO-*d*₆. ¹H NMR chemical shifts were reported in ppm (δ) relative to tetramethylsilane (TMS) with the solvent resonance employed as the internal standard (CDCl₃, 7.26 ppm, DMSO-*d*₆, 2.50 ppm). ¹³C NMR chemical shifts were reported in ppm from TMS with the solvent resonance as the internal standard (CDCl₃, 77.0 ppm, DMSO-*d*₆, 39.5 ppm). HRMS data were recorded on a SCIEX X500R QTOF HRMS apparatus. Melting points were recorded on a MP430 automatic melting point apparatus.

2.2 General procedure for the synthesis of carbamates, thiocarbamates and ureas

Into a dry 10-mL round-bottom flask equipped with a magnetic stirring bar were added successively a N-Boc aniline (0.26 mmol, 1.0 equiv.), Lithium tert-butoxide (0.31 mmol, 1.2 equiv.), 1 mL of toluene and alcohol, mercaptan or amine substrate (1.3 mmol, 5.0 equiv.). Stir at 110 °C for 2h, the mixture was cooled to room temperature and then concentrated under reduced pressure. Purification by flash chromatography on silica gel to give the corresponding carbamates, thiocarbamates and ureas.

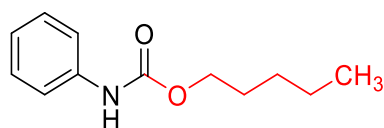
2.3 Characterization data

butyl phenylcarbamate (**8a**)



Prepared according to general procedure; 95% yield; White crystal; M.p. 60-62 °C; ¹H NMR (400 MHz, CDCl₃): δ 7.41 (d, *J* = 8.0 Hz, 2H), 7.37 – 7.26 (m, 2H), 7.14 – 7.01 (m, 1H), 6.78 (d, *J* = 4.7 Hz, 1H), 4.20 (t, *J* = 6.7 Hz, 2H), 1.75 – 1.61 (m, 2H), 1.52 – 1.37 (m, 2H), 0.98 (t, *J* = 7.4 Hz, 3H). All analytical data were in good accordance with data reported in the literature^[1].

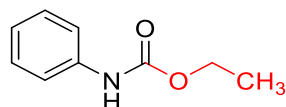
pentyl phenylcarbamate (**8b**)



Prepared according to general procedure; 93% yield; White solid; M.p. 46-48 °C; ¹H NMR (400 MHz, CDCl₃): δ 7.38 (d, *J* = 8.1 Hz, 2H), 7.30 (t, *J* = 7.8 Hz, 2H), 7.05 (t,

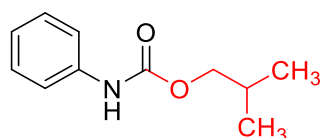
$J = 7.4$ Hz, 1H), 6.63 (s, 1H), 4.16 (t, $J = 6.7$ Hz, 2H), 1.74 – 1.61 (m, 2H), 1.41 – 1.32 (m, 4H), 0.92 (t, 3H). All analytical data were in good accordance with data reported in the literature^[2].

ethyl phenylcarbamate (**8c**)



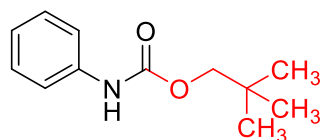
Prepared according to general procedure; 95% yield; White crystal; M.p. 49-50 °C; ¹H NMR (400 MHz, CDCl₃): δ 7.29 (d, $J = 8.0$ Hz, 2H), 7.24 – 7.17 (m, 2H), 7.00 – 6.94 (m, 1H), 6.50 (s, 1H), 4.14 (q, $J = 7.1$ Hz, 2H), 1.23 (t, $J = 7.1$ Hz, 3H). All analytical data were in good accordance with data reported in the literature^[1].

isobutyl phenylcarbamate (**8d**)



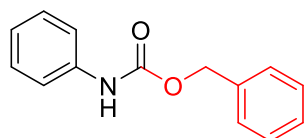
Prepared according to general procedure; 73% yield; White crystal; M.p. 84-86 °C; ¹H NMR (400 MHz, DMSO-*d*₆): δ 9.59 (s, 1H), 7.56 – 7.42 (m, 2H), 7.40 – 7.21 (m, 2H), 7.01 – 6.94 (m, 1H), 3.87 (d, $J = 6.7$ Hz, 2H), 2.00 – 1.83 (m, 1H), 0.94 (d, $J = 6.7$ Hz, 6H). All analytical data were in good accordance with data reported in the literature^[1].

neopentyl phenylcarbamate (**8e**)



Prepared according to general procedure; 98% yield; White solid; M.p. 72-74 °C; ¹H NMR (400 MHz, DMSO-*d*₆): δ 9.56 (s, 1H), 7.54 – 7.40 (m, 2H), 7.32 – 7.21 (m, 2H), 6.98 (m, $J = 7.3, 1.2$ Hz, 1H), 3.79 (s, 2H), 0.95 (s, 9H). All analytical data were in good accordance with data reported in the literature^[3].

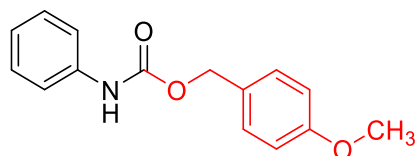
benzyl phenylcarbamate (**8f**)



Prepared according to general procedure; 60% yield; White crystal; M.p. 70-72 °C; ¹H NMR (400 MHz, DMSO-*d*₆): δ 9.75 (s, 1H), 7.48 (d, $J = 7.8$ Hz, 2H), 7.45 – 7.31 (m, 5H), 7.28 (dd, $J = 10.8, 5.1$ Hz, 2H), 6.99 (t, $J = 7.4$ Hz, 1H),

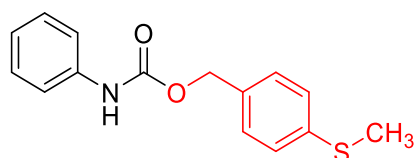
5.15 (s, 2H). All analytical data were in good accordance with data reported in the literature^[1].

4-methoxybenzyl phenylcarbamate (**8g**)



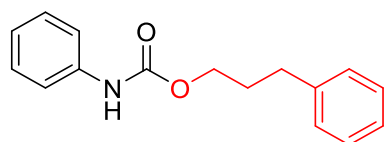
Prepared according to general procedure; 59% yield; White solid; M.p. 88-90 °C; ¹H NMR (400 MHz, CDCl₃): δ 7.46 – 7.20 (m, 6H), 7.05 (d, *J* = 7.8 Hz, 1H), 6.93 – 6.85 (m, 2H), 6.73 (s, 1H), 5.12 (s, 2H), 3.80 (s, 3H). All analytical data were in good accordance with data reported in the literature^[4].

4-(methylthio)benzyl phenylcarbamate (**8h**)



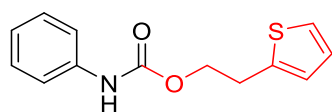
Prepared according to general procedure; 93% yield; White solid; M.p. 89-90 °C; ¹H NMR (400 MHz, CDCl₃): δ 7.37 (d, *J* = 8.0 Hz, 2H), 7.30 (d, *J* = 6.7 Hz, 4H), 7.24 (dd, *J* = 8.2, 2.4 Hz, 2H), 7.06 (t, *J* = 7.6 Hz, 1H), 6.67 (s, 1H), 5.14 (s, 2H), 2.48 (s, 3H). ¹³C NMR (101 MHz, CDCl₃): δ 153.48, 139.17, 137.92, 132.99, 129.23 (d, *J* = 6.2 Hz), 126.84, 123.75, 118.93, 66.84, 15.94. HRMS (ESI): calcd for C₁₅H₁₅NO₂S⁺ (M + Na)⁺: 296.0721, found 296.0727.

3-phenylpropyl phenylcarbamate (**8i**)



Prepared according to general procedure; 70% yield; White solid; M.p. 47-48 °C; ¹H NMR (400 MHz, DMSO-*d*₆): δ 9.64 (s, 1H), 7.51 – 7.43 (m, 2H), 7.33 – 7.17 (m, 7H), 7.02 – 6.92 (m, 1H), 4.08 (t, *J* = 6.6 Hz, 2H), 2.69 (dd, *J* = 8.6, 6.9 Hz, 2H), 2.03 – 1.87 (m, 2H). All analytical data were in good accordance with data reported in the literature^[5].

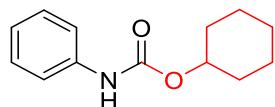
2-(thiophen-2-yl)ethyl phenylcarbamate (**8j**)



Prepared according to general procedure; 83% yield; White solid; M.p. 60-61 °C; ¹H NMR (400 MHz, CDCl₃): δ 7.44 – 7.22 (m, 4H), 7.16 (d, *J* = 4.4 Hz, 1H),

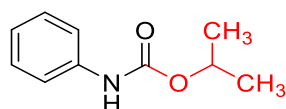
7.07 (d, $J = 8.2$ Hz, 1H), 6.95 (d, $J = 4.4$ Hz, 1H), 6.88 (s, 1H), 6.69 (s, 1H), 4.39 (t, $J = 7.8$ Hz, 2H), 3.20 (t, $J = 7.6$ Hz, 2H). ^{13}C NMR (101 MHz, CDCl_3): δ 153.46, 140.14, 137.94, 129.24, 127.11, 125.72, 124.21, 123.72, 118.95, 65.54, 29.81. HRMS (ESI): calcd for $\text{C}_{13}\text{H}_{13}\text{NO}_2\text{S}^+$ ($\text{M} + \text{Na}$) $^+$: 270.0565, found 270.0569.

cyclohexyl phenylcarbamate (**8k**)



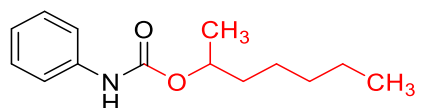
Prepared according to general procedure; 95% yield; White crystal; M.p. 79-80 °C; ^1H NMR (400 MHz, $\text{DMSO}-d_6$): δ 9.53 (s, 1H), 7.46 (d, $J = 7.8$ Hz, 2H), 7.26 (dd, $J = 10.7, 5.1$ Hz, 2H), 6.96 (t, $J = 7.4$ Hz, 1H), 4.62 (td, $J = 9.0, 4.0$ Hz, 1H), 1.95 – 1.82 (m, 2H), 1.71 (dd, $J = 9.2, 4.1$ Hz, 2H), 1.59 – 1.47 (m, 1H), 1.46 – 1.28 (m, 4H), 1.28 – 1.15 (m, 1H). All analytical data were in good accordance with data reported in the literature^[1].

isopropyl phenylcarbamate (**8l**)



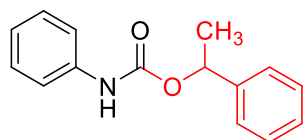
Prepared according to general procedure; 90% yield; White crystal; M.p. 83-85 °C; ^1H NMR (400 MHz, $\text{DMSO}-d_6$): δ 9.53 (s, 1H), 7.52 – 7.44 (m, 2H), 7.30 – 7.21 (m, 2H), 7.04 – 6.87 (m, 1H), 4.89 (p, $J = 6.3$ Hz, 1H), 1.25 (d, $J = 6.4$ Hz, 6H). All analytical data were in good accordance with data reported in the literature^[1].

heptan-2-yl phenylcarbamate (**8m**)



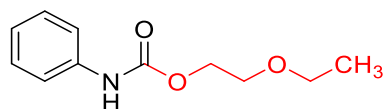
Prepared according to general procedure; 90% yield; Yellow oil; ^1H NMR (400 MHz, $\text{DMSO}-d_6$): δ 9.49 (s, 1H), 7.48 – 7.38 (m, 2H), 7.30 – 7.15 (m, 2H), 7.01 – 6.89 (m, 1H), 4.82 – 4.70 (m, 1H), 1.61 – 1.43 (m, 2H), 1.38 – 1.22 (m, 6H), 1.20 (d, $J = 6.3$ Hz, 3H), 0.89 – 0.80 (m, 3H). ^{13}C NMR (101 MHz, $\text{DMSO}-d_6$): δ 153.30, 139.32, 128.63, 122.13, 118.05, 70.49, 35.57, 31.07, 24.53, 21.98, 20.16, 13.84. HRMS (ESI): calcd for $\text{C}_{14}\text{H}_{21}\text{NO}_2^+$ ($\text{M} + \text{Na}$) $^+$: 258.1470, found 258.1474.

1-phenylethyl phenylcarbamate (**8n**)



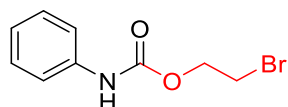
Prepared according to general procedure; 50% yield; White crystal; M.p. 90-92 °C; $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.37 (d, $J = 10.0$ Hz, 6H), 7.33 – 7.24 (m, 3H), 7.05 (d, $J = 7.6$ Hz, 1H), 6.66 (s, 1H), 5.90 (q, $J = 7.2$ Hz, 1H), 1.60 (d, $J = 4.2$ Hz, 3H). All analytical data were in good accordance with data reported in the literature^[1].

2-ethoxyethyl phenylcarbamate (8o)



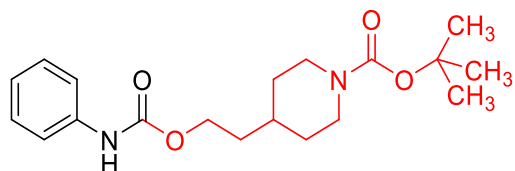
Prepared according to general procedure; 80% yield; Yellow oil; $^1\text{H NMR}$ (400 MHz, $\text{DMSO}-d_6$): δ 9.73 (s, 1H), 7.52 – 7.41 (m, 2H), 7.35 – 7.19 (m, 2H), 7.08 – 6.93 (m, 1H), 4.30 – 4.10 (m, 2H), 3.65 – 3.53 (m, 2H), 3.47 (q, $J = 7.0$ Hz, 2H), 1.12 (t, $J = 7.0$ Hz, 3H). $^{13}\text{C NMR}$ (101 MHz, $\text{DMSO}-d_6$): δ 153.95, 139.63, 129.17, 122.79, 118.60, 68.54, 65.99, 64.01, 15.51. **HRMS (ESI)**: calcd for $\text{C}_{11}\text{H}_{15}\text{NO}_3^+$ ($\text{M} + \text{Na}$) $^+$: 270.0950, found 232.0954.

2-bromoethyl phenylcarbamate (8p)



Prepared according to general procedure; 70% yield; Pale yellow oil; M.p. 73-75 °C; $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.12 (t, $J = 7.9$ Hz, 2H), 6.67 (t, $J = 7.3$ Hz, 1H), 6.60 (d, $J = 8.0$ Hz, 2H), 3.77 (t, $J = 5.2$ Hz, 2H), 3.24 (t, $J = 5.2$ Hz, 2H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3): δ 147.91, 129.51, 118.44, 113.71, 61.27, 46.55, 29.85. **HRMS (ESI)**: calcd for $\text{C}_9\text{H}_{10}\text{NO}_2\text{Br}^+$ ($\text{M} + \text{Na}$) $^+$: 265.9793, found 265.9791.

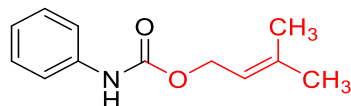
tert-butyl 4-(2-((phenylcarbamoyl)oxy)ethyl)piperidine-1-carboxylate (8q)



Prepared according to general procedure; 80% yield; Pale yellow oil; $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.31 (d, $J = 8.0$ Hz, 2H), 7.26 – 7.18 (m, 2H), 7.05 – 6.95 (m, 1H), 6.62 (s, 1H), 4.15 (t, $J = 6.5$ Hz, 2H), 4.10 – 3.95 (m, 2H), 2.62 (t, $J = 12.9$ Hz, 2H), 1.62 (d, $J = 12.9$ Hz, 2H), 1.55 (t, $J = 6.4$ Hz, 2H), 1.38 (s, 9H), 1.23 – 1.16 (m, 1H), 1.13 – 1.01 (m, 2H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3): δ 154.96, 138.17 (d, $J = 2.2$ Hz),

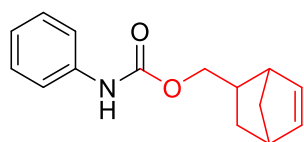
129.07, 123.41, 118.83, 79.43, 62.89, 39.34, 35.56, 32.99, 32.06, 28.54, 14.25. **HRMS (ESI):** calcd for $C_{19}H_{28}N_2O_4^+$ ($M + Na$) $^+$: 371.1947, found 371.1952.

3-methylbut-2-en-1-yl phenylcarbamate (**8r**)



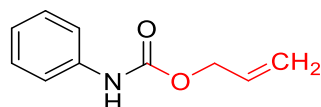
Prepared according to general procedure; 80% yield; White solid; M.p. 63-65 °C **1H NMR (400 MHz, $CDCl_3$):** δ 7.33 – 7.25 (m, 2H), 7.24 – 7.17 (m, 2H), 6.97 (tt, $J = 7.2, 1.3$ Hz, 1H), 6.51 (s, 1H), 5.32 (tdt, $J = 7.3, 2.9, 1.4$ Hz, 1H), 4.58 (d, $J = 7.3$ Hz, 2H), 1.70 (d, $J = 1.4$ Hz, 3H), 1.67 (d, $J = 1.4$ Hz, 3H). All analytical data were in good accordance with data reported in the literature^[6].

bicyclo[2.2.1]hept-5-en-2-ylmethyl phenylcarbamate (**8s**)



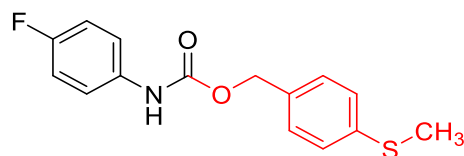
Prepared according to general procedure; 95% yield; White solid; M.p. 123-125 °C; **1H NMR (400 MHz, $CDCl_3$):** δ 7.42 – 7.25 (m, 4H), 7.05 (t, $J = 7.4$ Hz, 1H), 6.65 (d, $J = 12.3$ Hz, 1H), 6.23 – 5.94 (m, 2H), 4.33 – 3.70 (m, 2H), 2.96 – 2.68 (m, 2H), 2.52 – 2.33 (m, 1H), 1.93 – 1.72 (m, 1H), 1.52 – 0.51 (m, 4H). **^{13}C NMR (101 MHz, $CDCl_3$):** δ 153.84, 137.82, 136.38, 132.36, 129.23, 123.54 (d, $J = 5.5$ Hz), 118.84, 68.88, 49.59, 44.08, 42.40, 38.26, 29.11. **HRMS (ESI):** calcd for $C_{15}H_{17}NO_2^+$ ($M + Na$) $^+$: 266.1157, found 266.1161.

allyl phenylcarbamate (**8t**)



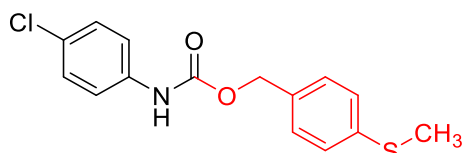
Prepared according to general procedure; 20% yield; White crystal; M.p. 67-68 °C; **1H NMR (400 MHz, $DMSO-d_6$):** δ 9.70 (s, 1H), 7.49 – 7.42 (m, 2H), 7.35 – 7.20 (m, 2H), 7.05 – 6.94 (m, 1H), 6.07 – 5.89 (m, 1H), 5.47 – 5.10 (m, 2H), 4.64 – 4.56 (m, 2H). All analytical data were in good accordance with data reported in the literature^[1].

4-(methylthio)benzyl (4-fluorophenyl)carbamate (**8u**)



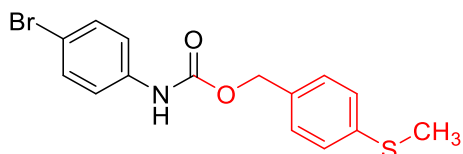
Prepared according to general procedure; 80% yield; White solid; M.p. 113-114 °C; **¹H NMR (400 MHz, CDCl₃)**: δ 7.31 (d, *J* = 7.9 Hz, 4H), 7.28 – 7.22 (m, 2H), 6.99 (t, *J* = 8.4 Hz, 2H), 6.63 (s, 1H), 5.14 (s, 2H), 2.48 (s, 3H). **¹³C NMR (101 MHz, CDCl₃)**: δ 160.48, 153.66, 139.25, 133.89, 132.87, 129.21, 126.80, 120.73, 115.88 (d, *J* = 22.6 Hz), 66.94, 15.90. **HRMS (ESI)**: calcd for C₁₅H₁₄NO₂SF⁺ (M + Na)⁺: 314.0627, found 314.0630.

4-(methylthio)benzyl (4-chlorophenyl)carbamate (**8v**)



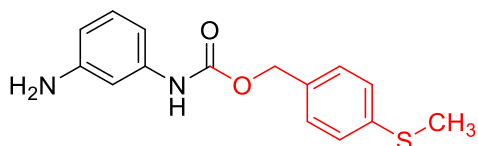
Prepared according to general procedure; 80% yield; White solid; M.p. 133-134 °C; **¹H NMR (400 MHz, CDCl₃)**: δ 7.38 – 7.28 (m, 4H), 7.28 – 7.22 (m, 4H), 6.68 (s, 1H), 5.14 (s, 2H), 2.48 (s, 3H). **¹³C NMR (101 MHz, CDCl₃)**: δ 153.35, 139.31, 136.52, 132.69, 129.24, 128.74, 126.74, 120.08, 67.02, 15.86. **HRMS (ESI)**: calcd for C₁₅H₁₄NO₂SCI⁺ (M + Na)⁺: 330.0331, found 330.0334.

4-(methylthio)benzyl (4-bromophenyl)carbamate (**8w**)



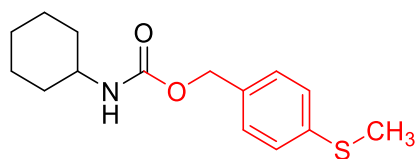
Prepared according to general procedure; 90% yield; Yellow solid; M.p. 133-135 °C; **¹H NMR (400 MHz, CDCl₃)**: δ 7.43 – 7.37 (m, 2H), 7.34 – 7.22 (m, 6H), 6.71 (s, 1H), 5.14 (s, 2H), 2.48 (s, 3H). **¹³C NMR (101 MHz, CDCl₃)**: δ 153.14, 139.17, 136.89, 132.49, 132.03, 129.09, 126.56, 120.25, 116.08, 66.88, 15.70. **HRMS (ESI)**: calcd for C₁₅H₁₄NO₂SBr⁺ (M + Na)⁺: 373.9826, found 373.9828.

4-(methylthio)benzyl (3-aminophenyl)carbamate (**8x**)



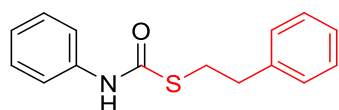
Prepared according to general procedure; 93% yield; Yellow solid; M.p. 68-70 °C; **¹H NMR (400 MHz, CDCl₃)**: δ 7.32 (d, *J* = 8.0 Hz, 2H), 7.25 (d, *J* = 7.9 Hz, 3H), 7.05 (t, *J* = 8.0 Hz, 1H), 6.94 (s, 1H), 6.62 – 6.54 (m, 2H), 6.45 – 6.33 (m, 1H), 5.13 (s, 2H), 3.68 (s, 2H), 2.48 (s, 3H). **¹³C NMR (101 MHz, CDCl₃)**: δ 153.38, 147.50, 139.09, 138.95, 133.05, 129.98, 129.15, 126.82, 110.53, 108.96, 105.45, 66.73, 15.93. **HRMS (ESI)**: calcd for C₁₅H₁₆N₂O₂S⁺ (M + Na)⁺: 311.0830, found 311.0834.

4-(methylthio)benzyl cyclohexylcarbamate (**8y**)



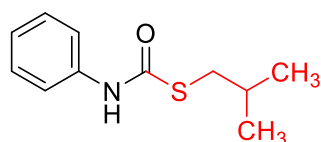
Prepared according to general procedure; 50% yield; White solid; M.p. 93-95 °C; **¹H NMR (400 MHz, CDCl₃):** δ 7.32 – 7.20 (m, 4H), 5.03 (s, 2H), 4.61 (s, 1H), 3.49 (d, *J* = 10.5 Hz, 1H), 2.48 (s, 3H), 2.01 – 1.86 (m, 2H), 1.77 – 1.64 (m, 2H), 1.63 – 1.54 (m, 2H), 1.42 – 1.26 (m, 2H), 1.16 – 1.09 (m, 2H). **¹³C NMR (101 MHz, CDCl₃)** δ 155.70, 138.67, 133.74, 129.00, 126.85, 66.26, 50.08, 33.57, 25.65, 24.93, 16.01. **HRMS (ESI):** calcd for C₁₅H₂₁NO₂S⁺ (M + Na)⁺:302.1191, found 302.1196.

S-phenethyl phenylcarbamothioate (**8z**)



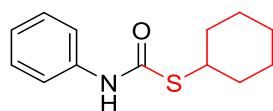
Prepared according to general procedure; 80% yield; White solid; M.p. 108-110 °C; **¹H NMR (400 MHz, CDCl₃):** δ 7.46 – 7.39 (m, 2H), 7.38 – 7.28 (m, 4H), 7.26 – 7.20 (m, 3H), 7.13 (ddt, *J* = 8.6, 7.3, 1.2 Hz, 1H), 7.01 (s, 1H), 3.29 – 3.18 (m, 2H), 2.99 (dd, *J* = 8.8, 6.5 Hz, 2H). All analytical data were in good accordance with data reported in the literature^[7].

S-isobutyl phenylcarbamothioate (**8aa**)



Prepared according to general procedure; 90% yield; White solid; M.p. 105-107 °C; **¹H NMR (400 MHz, CDCl₃):** δ 7.42 – 7.37 (m, 2H), 7.32 – 7.23 (m, 2H), 7.14 – 7.00 (m, 2H), 2.88 (d, *J* = 6.7 Hz, 2H), 1.86 (dq, *J* = 13.3, 6.7 Hz, 1H), 0.98 (d, *J* = 6.7 Hz, 6H). **¹³C NMR (101 MHz, CDCl₃)** δ 166.19, 137.98, 129.24, 124.44, 119.80, 38.82, 29.31, 28.47, 21.80. **HRMS (ESI):** calcd for C₁₁H₁₅NOS⁺ (M + Na)⁺: 232.0772, found 232.0775.

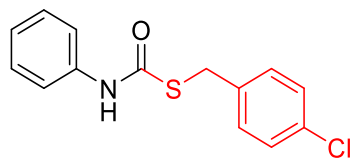
S-cyclohexyl phenylcarbamothioate (**8ab**)



Prepared according to general procedure; 70% yield; Yellow solid; M.p. 106-107 °C; **¹H NMR (400 MHz, CDCl₃):** δ 7.43 – 7.38 (m, 2H), 7.33 – 7.27 (m, 2H), 7.10 (d, *J* = 7.4 Hz, 1H), 7.08 – 7.04 (m, 1H), 3.60 – 3.50 (m, 1H), 2.09 –

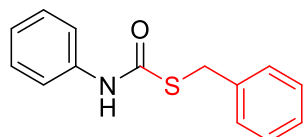
1.96 (m, 2H), 1.73 (dq, $J = 12.1, 3.9$ Hz, 2H), 1.45 (dddd, $J = 21.9, 16.0, 9.5, 4.5$ Hz, 5H), 1.34 – 1.19 (m, 1H). All analytical data were in good accordance with data reported in the literature^[8].

S-(4-chlorobenzyl) phenylcarbamothioate (**8ac**)



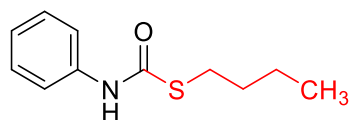
Prepared according to general procedure; 90% yield; Yellow solid; M.p. 119-121 °C; ¹H NMR (400 MHz, CDCl₃): δ 7.40 (d, $J = 8.1$ Hz, 2H), 7.31 (dd, $J = 17.6, 7.1$ Hz, 6H), 7.12 (t, $J = 7.4$ Hz, 1H), 7.03 (s, 1H), 4.17 (s, 2H). All analytical data were in good accordance with data reported in the literature^[8].

S-benzyl phenylcarbamothioate (**8ad**)



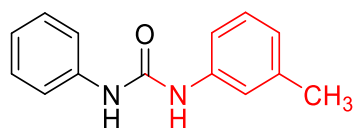
Prepared according to general procedure; 70% yield; Yellow solid; M.p. 93-95 °C; ¹H NMR (400 MHz, CDCl₃): δ 7.45 – 7.28 (m, 9H), 7.27 – 7.20 (m, 1H), 7.11 (t, $J = 7.3$ Hz, 1H), 7.05 (s, 1H), 4.23 (s, 2H). All analytical data were in good accordance with data reported in the literature^[8].

S-butyl phenylcarbamothioate (**8ae**)



Prepared according to general procedure; 90% yield; White solid; M.p. 73-74 °C; ¹H NMR (400 MHz, CDCl₃): δ 7.44 – 7.37 (m, 2H), 7.35 – 7.27 (m, 2H), 7.10 (tt, $J = 7.2, 1.2$ Hz, 2H), 2.98 (t, $J = 7.3$ Hz, 2H), 1.65 (tt, $J = 8.8, 6.7$ Hz, 2H), 1.43 (dq, $J = 14.5, 7.3$ Hz, 2H), 0.93 (t, $J = 7.4$ Hz, 3H). All analytical data were in good accordance with data reported in the literature^[8].

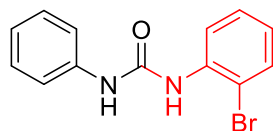
1-phenyl-3-(m-tolyl)urea (**8af**)



Prepared according to general procedure; 87% yield; White solid; M.p. 230-235 °C; ¹H NMR (400 MHz, DMSO-*d*₆): δ 8.65 (s, 1H), 8.56 (d, $J = 6.8$ Hz,

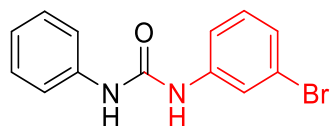
1H), 7.49 – 7.42 (m, 3H), 7.33 – 7.29 (m, 2H), 7.19 – 7.10 (m, 1H), 7.00 – 6.92 (m, 2H), 6.79 (d, $J = 7.4$ Hz, 1H), 2.28 (s, 3H). All analytical data were in good accordance with data reported in the literature^[9].

1-(2-bromophenyl)-3-phenylurea (**8ag**)



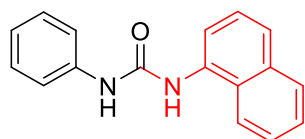
Prepared according to general procedure; 70% yield; White solid; M.p. 171-173 °C; ¹H NMR (400 MHz, DMSO-*d*₆): δ 9.46 (s, 1H), 8.14 (s, 1H), 8.09 – 8.03 (m, 1H), 7.63 – 7.59 (m, 1H), 7.47 (d, $J = 7.9$ Hz, 2H), 7.32 (dt, $J = 15.7, 7.7$ Hz, 3H), 6.97 (dt, $J = 8.7, 4.2$ Hz, 2H). All analytical data were in good accordance with data reported in the literature^[10].

1-(3-bromophenyl)-3-phenylurea (**8ah**)



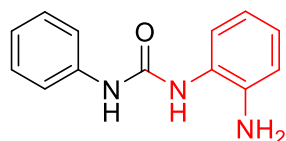
Prepared according to general procedure; 81% yield; White crystal; M.p. 171-173 °C; ¹H NMR (400 MHz, DMSO-*d*₆): δ 8.98 – 8.70 (m, 1H), 8.64 (s, 1H), 7.48 – 7.43 (m, 3H), 7.34 – 7.21 (m, 4H), 6.98 (qt, $J = 7.4, 1.3$ Hz, 2H). All analytical data were in good accordance with data reported in the literature^[10].

1-(naphthalen-1-yl)-3-phenylurea (**8ai**)



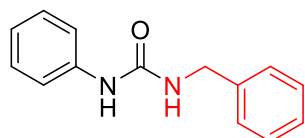
Prepared according to general procedure; 95% yield; Pale purple solid; M.p. 242-246 °C; ¹H NMR (400 MHz, DMSO-*d*₆): δ 8.84 (d, $J = 115.3$ Hz, 1H), 8.58 (s, 1H), 8.12 – 7.81 (m, 2H), 7.60 – 7.49 (m, 1H), 7.49 – 7.40 (m, 2H), 7.42 – 7.33 (m, 2H), 7.29 – 7.15 (m, 3H), 6.98 – 6.86 (m, 1H). All analytical data were in good accordance with data reported in the literature^[11].

1-(2-aminophenyl)-3-phenylurea (**8aj**)



Prepared according to general procedure; 80% yield; White solid; M.p. 183–184 °C; $^1\text{H NMR}$ (400 MHz, $\text{DMSO-}d_6$): δ 8.68 (s, 2H), 7.45 (dd, $J = 8.5, 1.0$ Hz, 4H), 7.34 – 7.20 (m, 4H), 7.01 – 6.83 (m, 2H). All analytical data were in good accordance with data reported in the literature^[12].

1-benzyl-3-phenylurea (8ak)



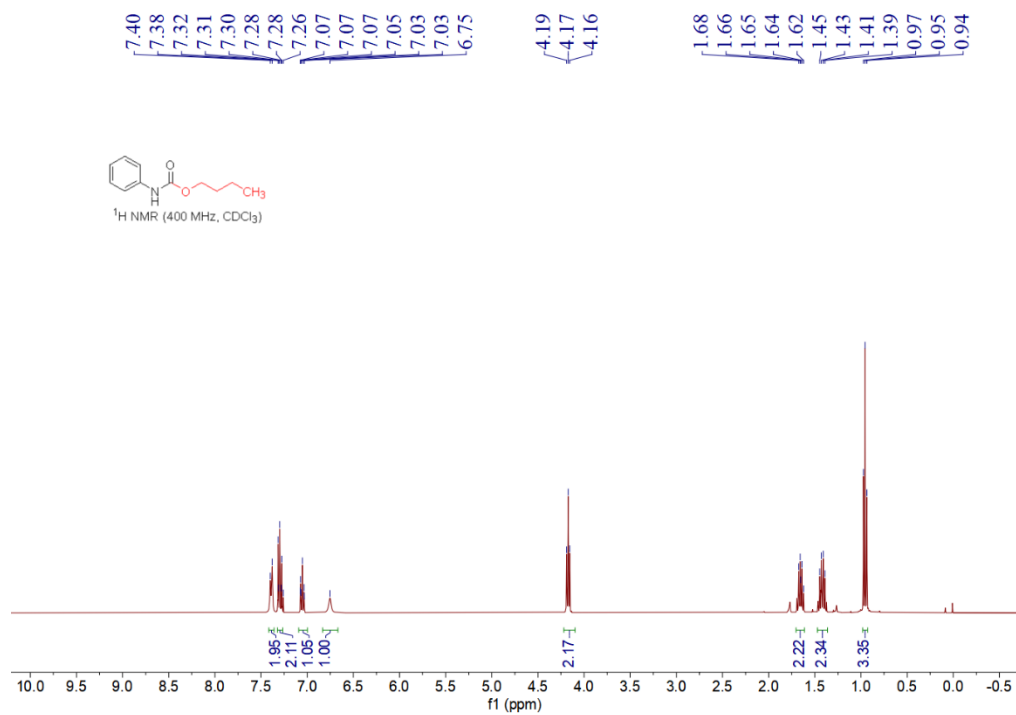
Prepared according to general procedure; 81% yield; White solid; M.p. 171–172 °C; $^1\text{H NMR}$ (400 MHz, $\text{DMSO-}d_6$): δ 8.54 (s, 1H), 7.44 – 7.37 (m, 2H), 7.36 – 7.27 (m, 4H), 7.27 – 7.19 (m, 3H), 6.94 – 6.85 (m, 1H), 6.60 (t, $J = 6.0$ Hz, 1H), 4.31 (d, $J = 5.9$ Hz, 2H). All analytical data were in good accordance with data reported in the literature^[12].

2.3 References

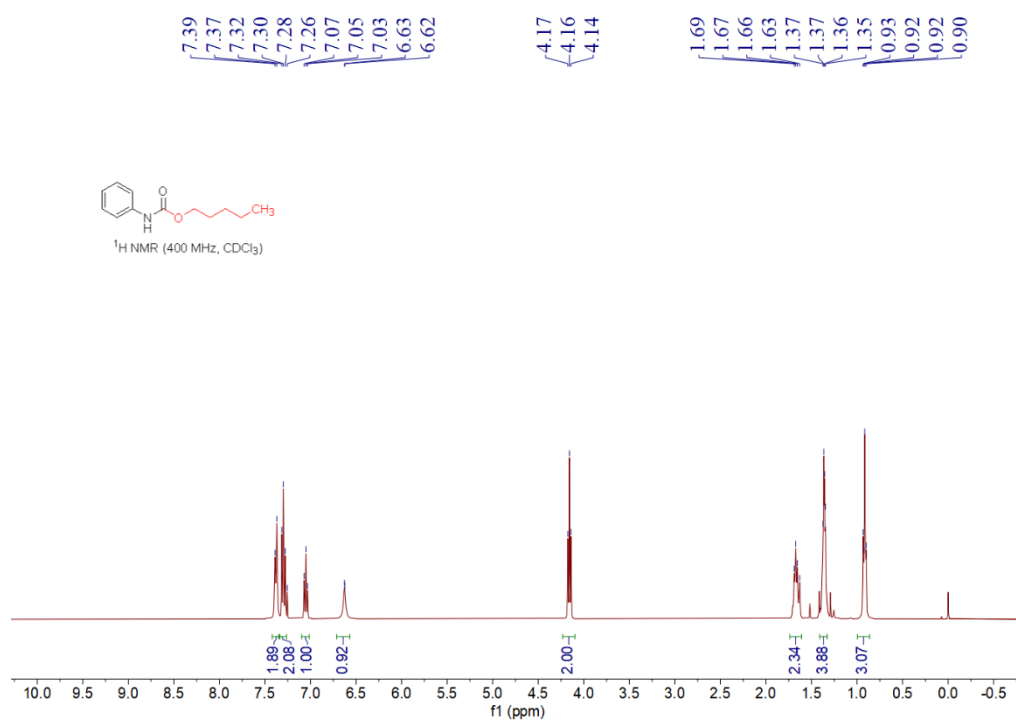
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1. ^1H , ^{13}C NMR and HRMS spectra

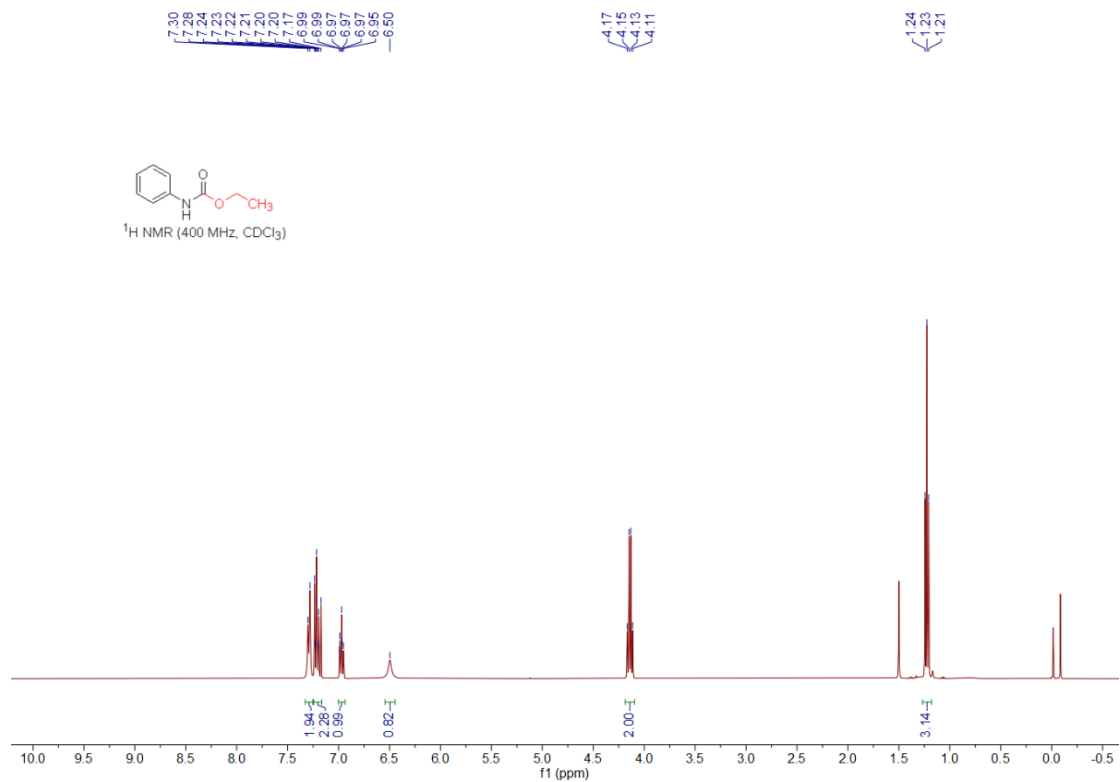
^1H NMR spectra of **8a**



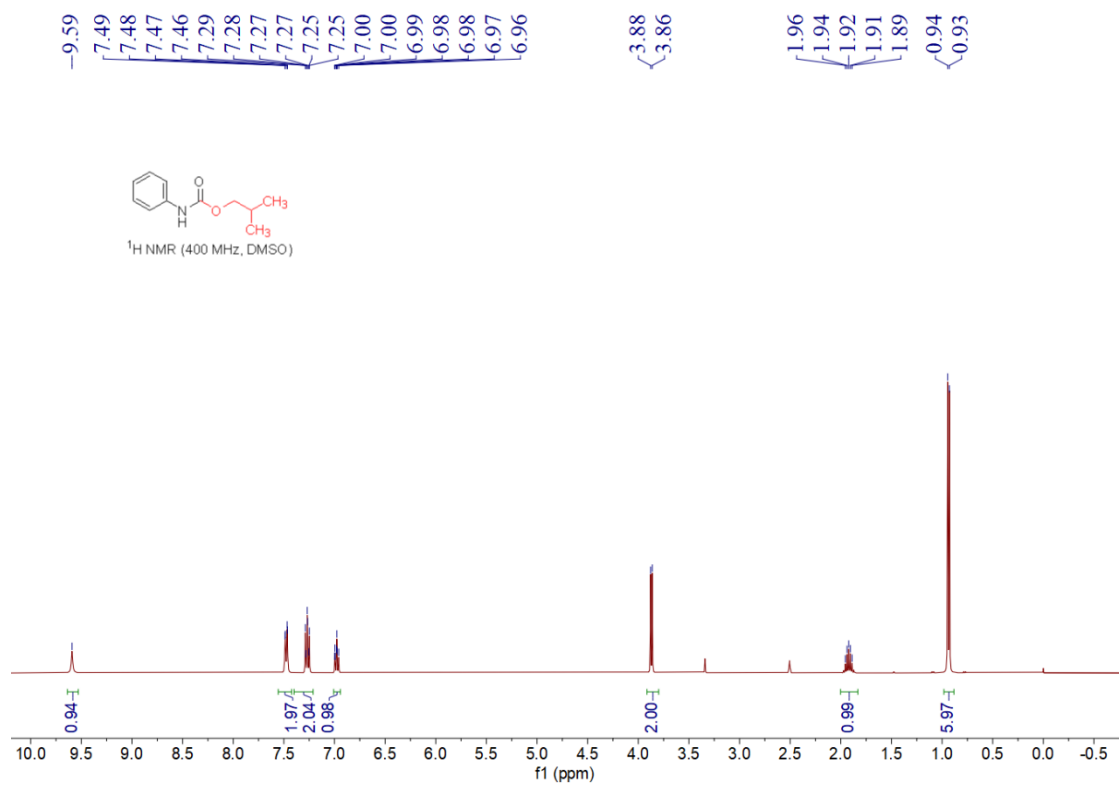
^1H NMR spectra of **8b**



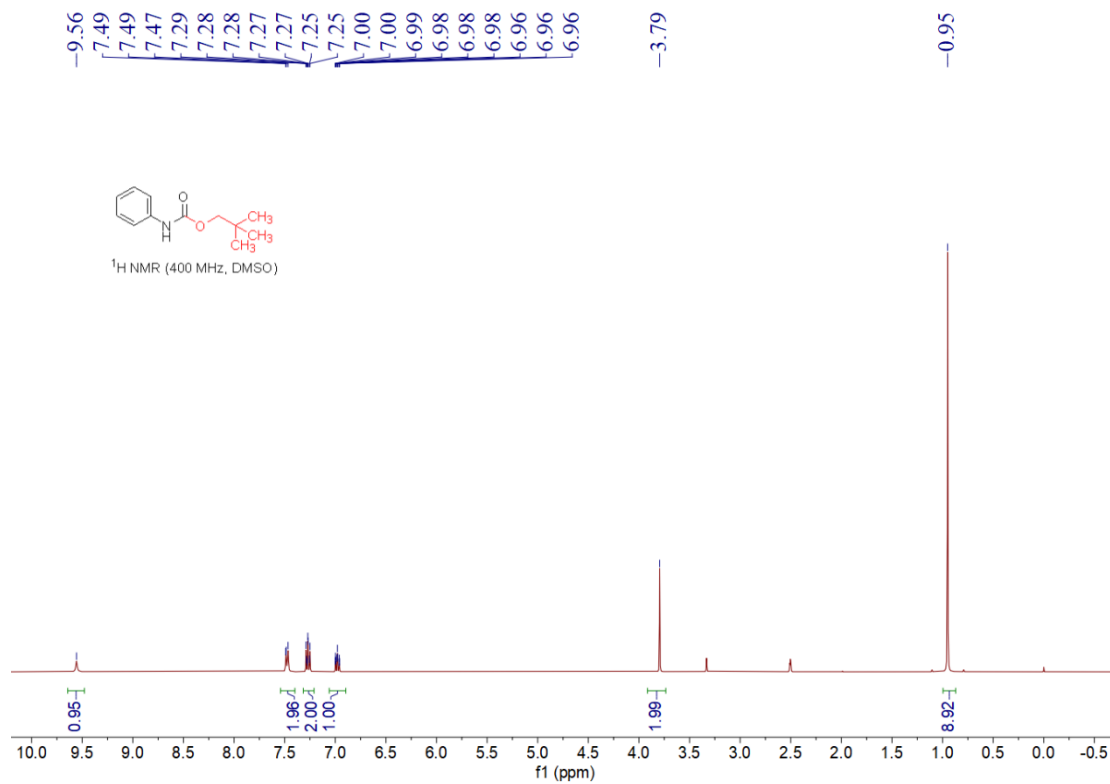
^1H NMR spectra of **8c**



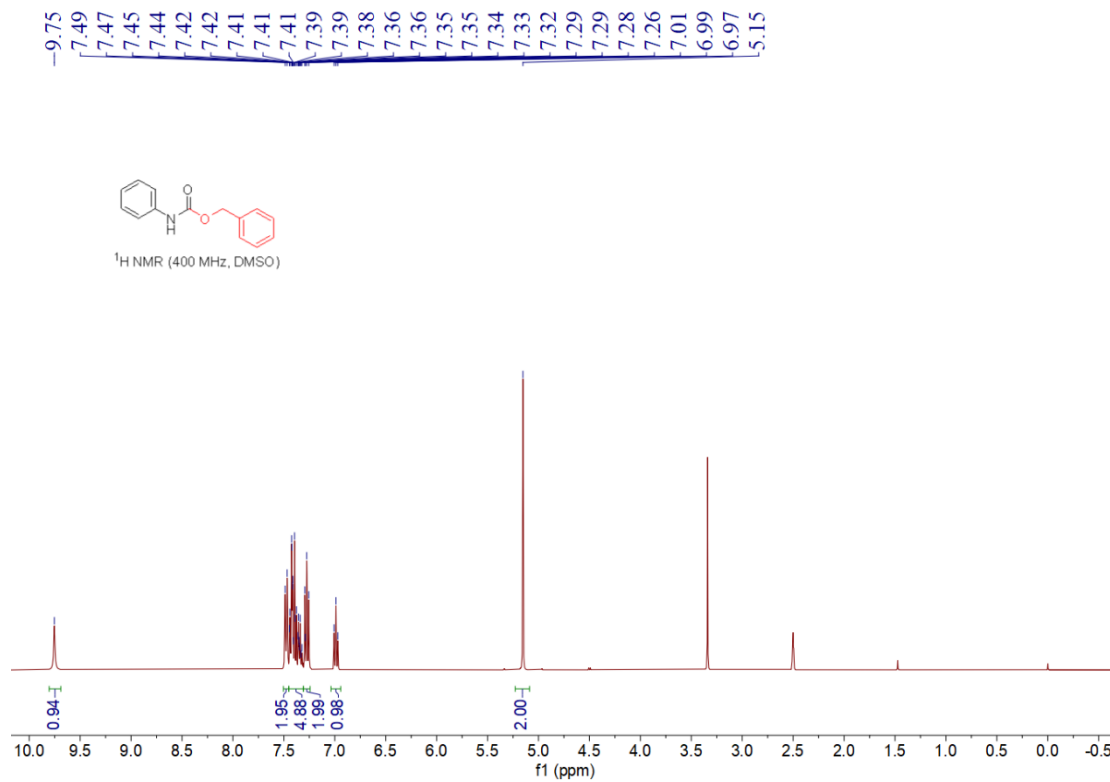
^1H NMR spectra of **8d**



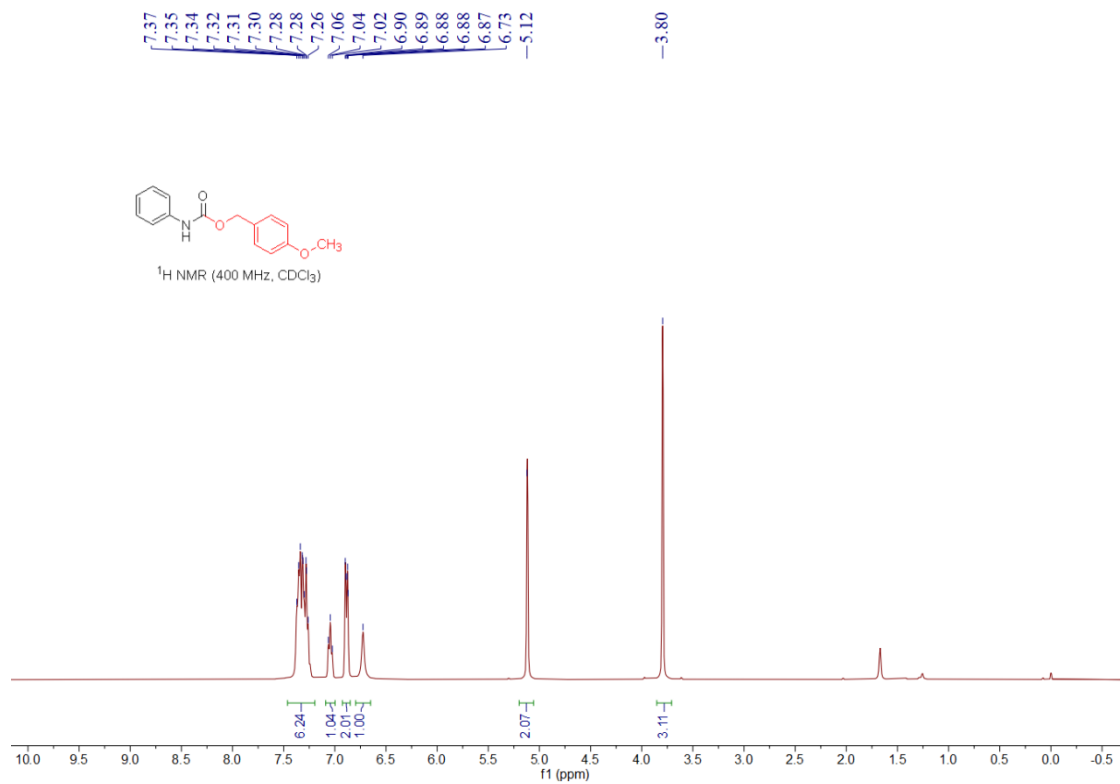
¹H NMR spectra of **8e**



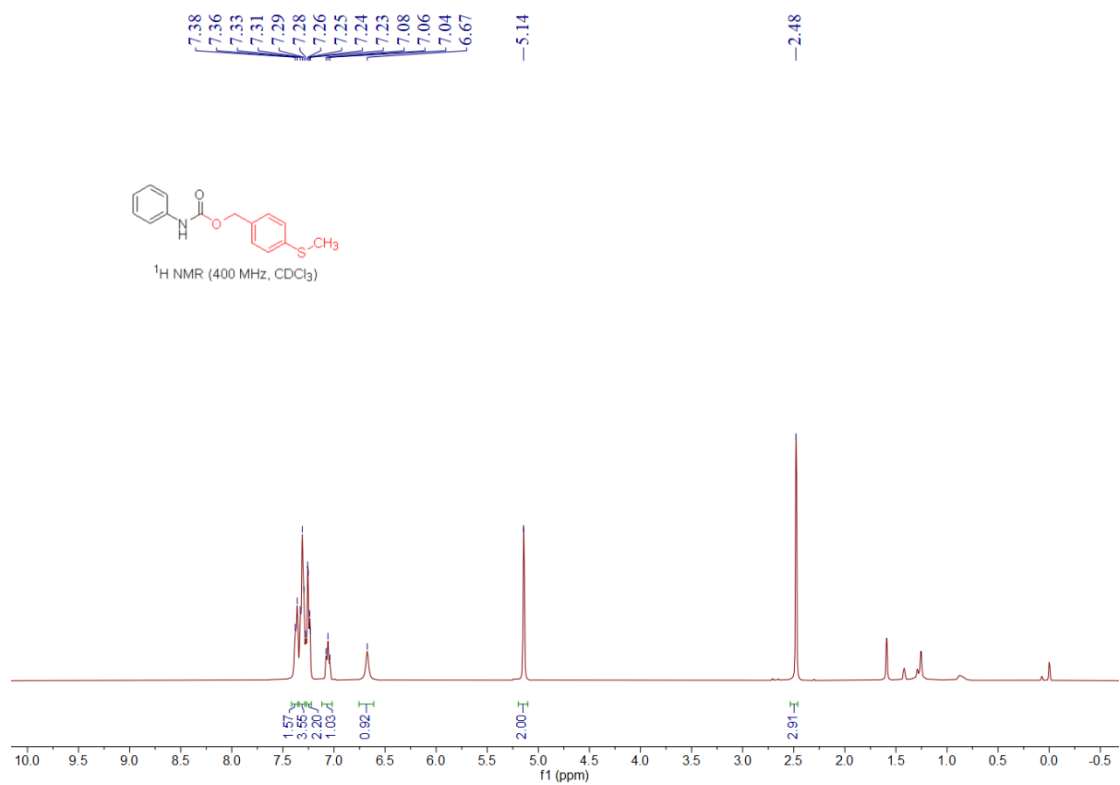
¹H NMR spectra of **8f**



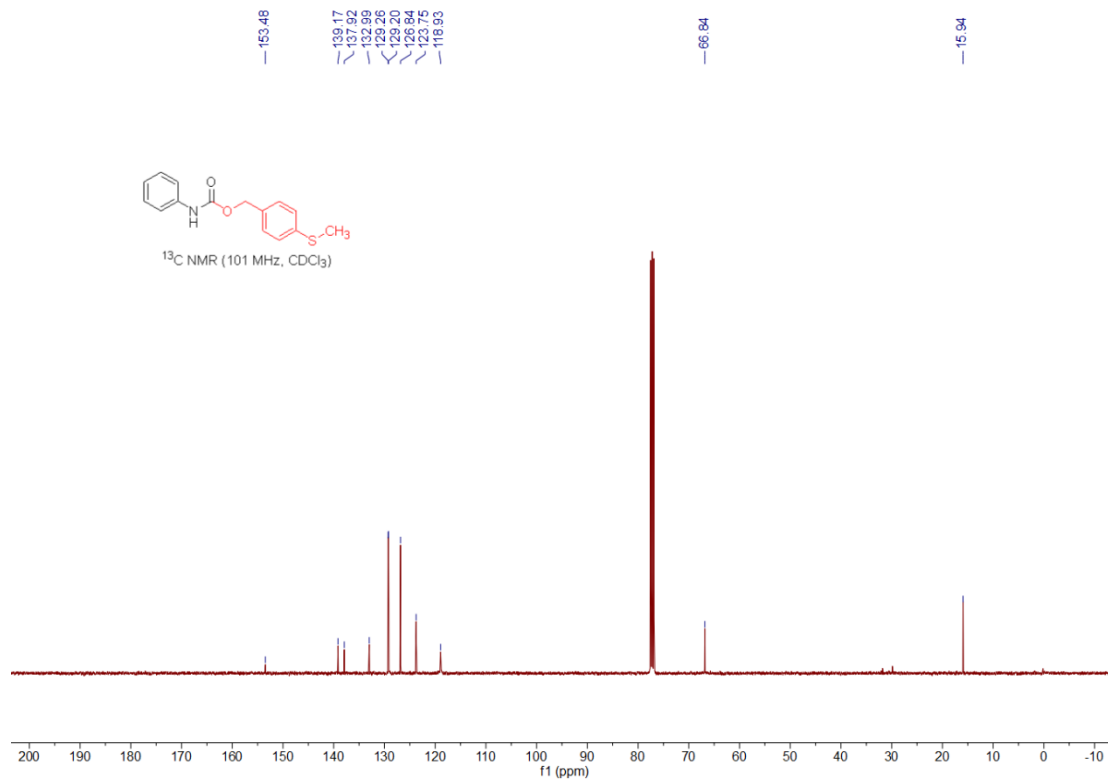
¹H NMR spectra of **8g**



¹H NMR spectra of **8h**



¹³C NMR spectra of **8h**



HRMS spectra of **8h**

Monoisotopic Mass, Even Electron Ions

836 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)

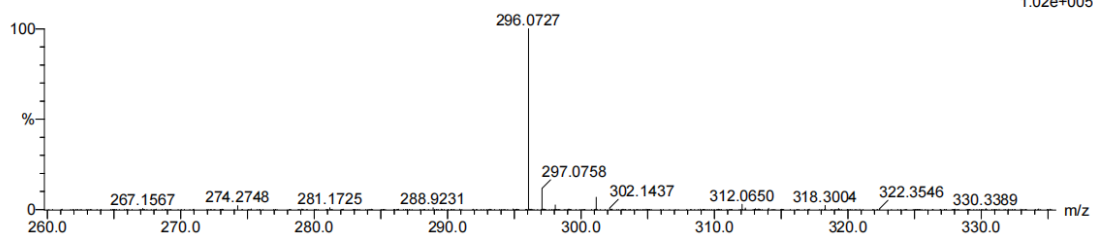
Elements Used:

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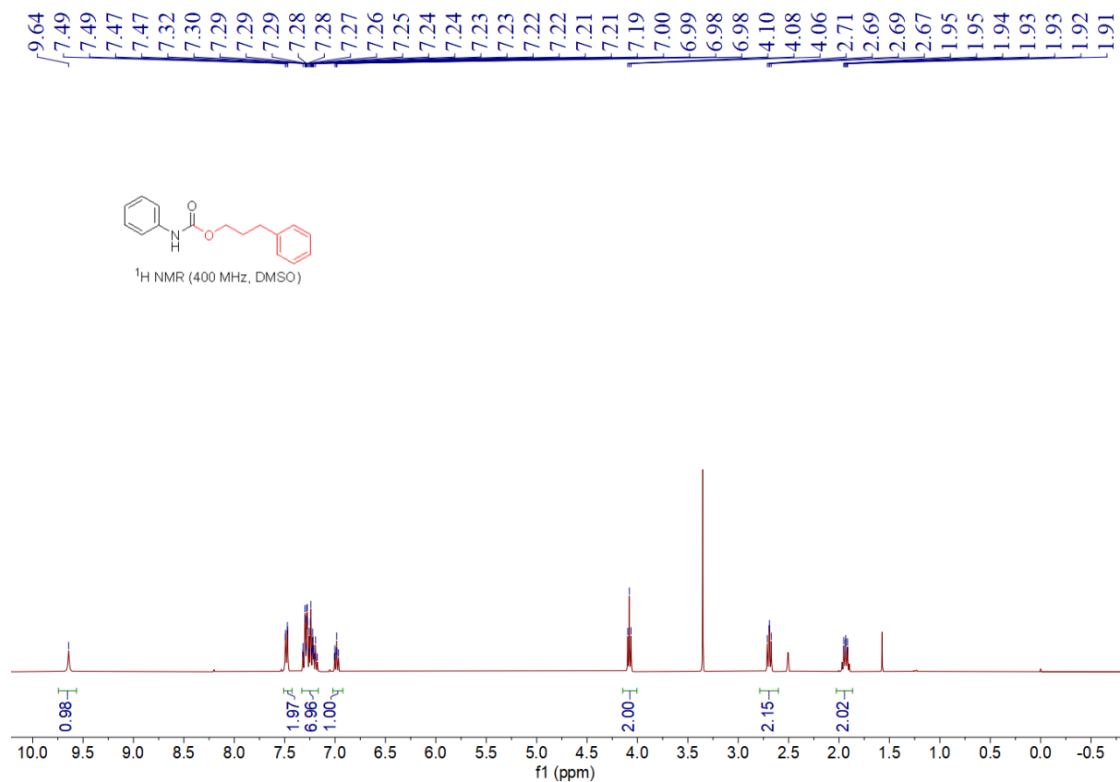
25

240403-13-8 11 (0.076)

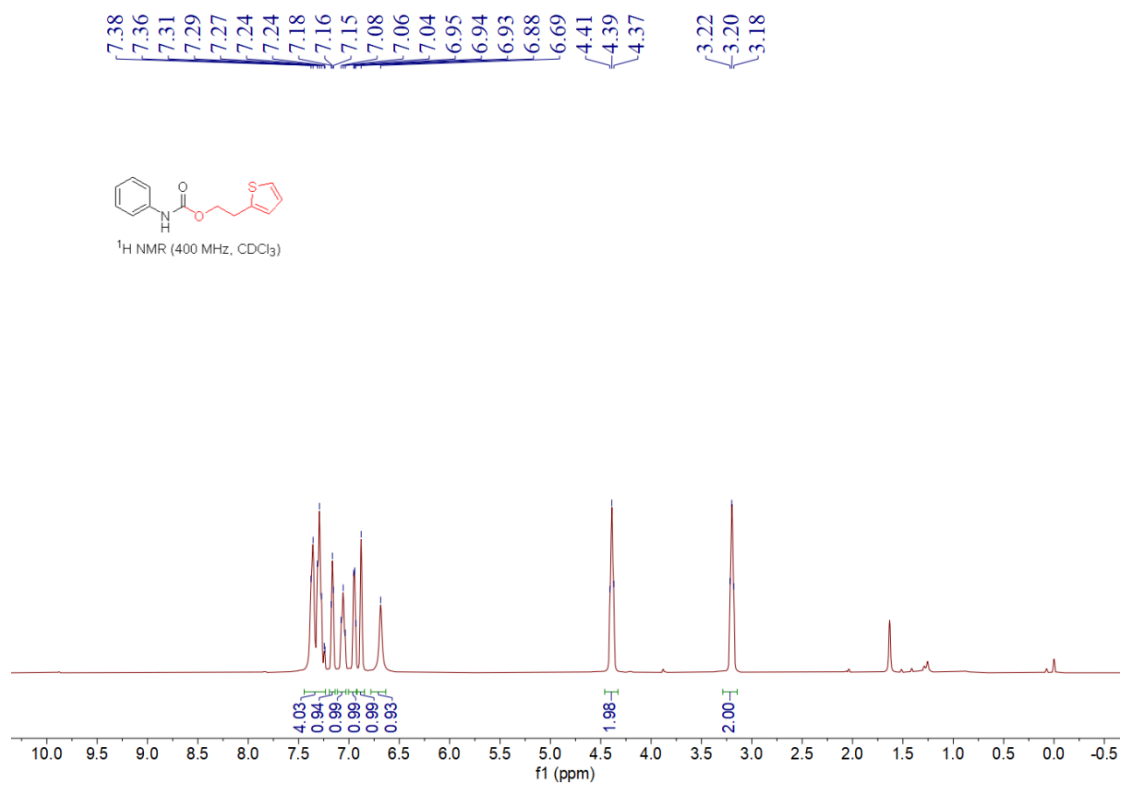
1: TOF MS ES+
1.02e+005



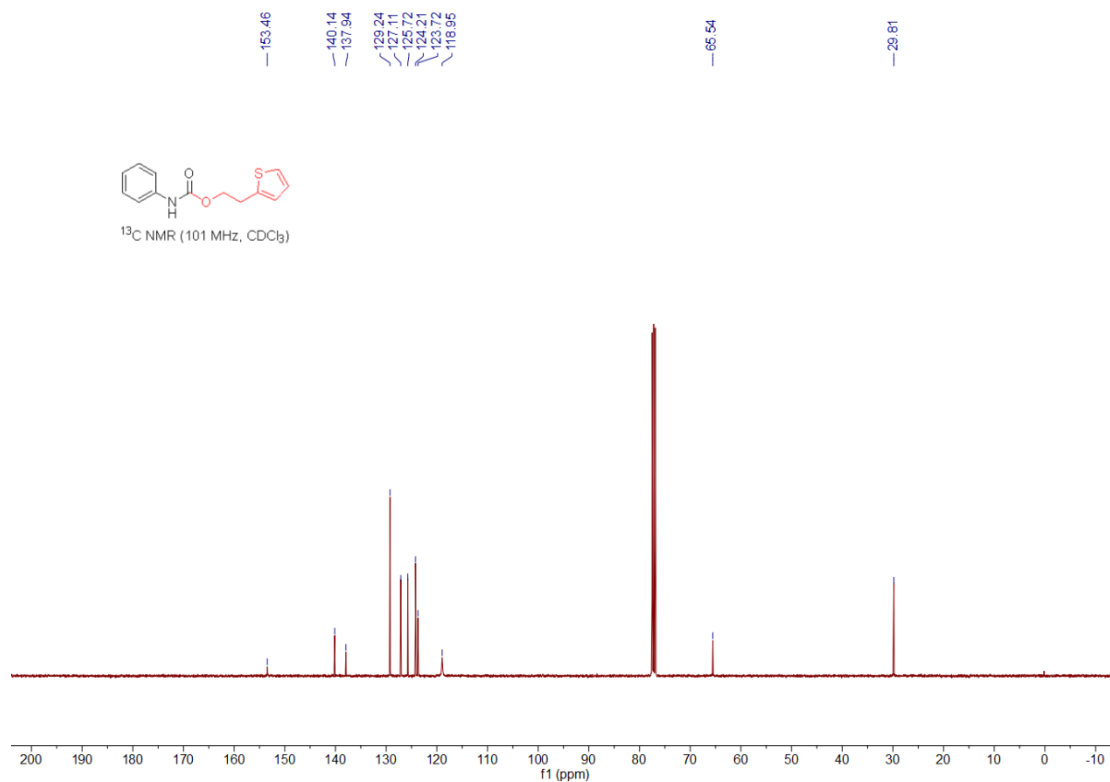
¹H NMR spectra of **8i**



¹H NMR spectra of **8j**



¹³C NMR spectra of **8j**



HRMS spectra of **8j**

Monoisotopic Mass, Even Electron Ions

647 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)

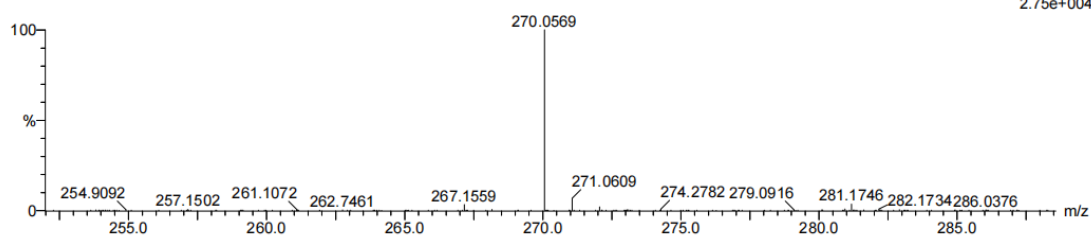
Elements Used:

C: 13-13 H: 13-13 N: 0-100 O: 0-100 Na: 0-1 S: 1-4

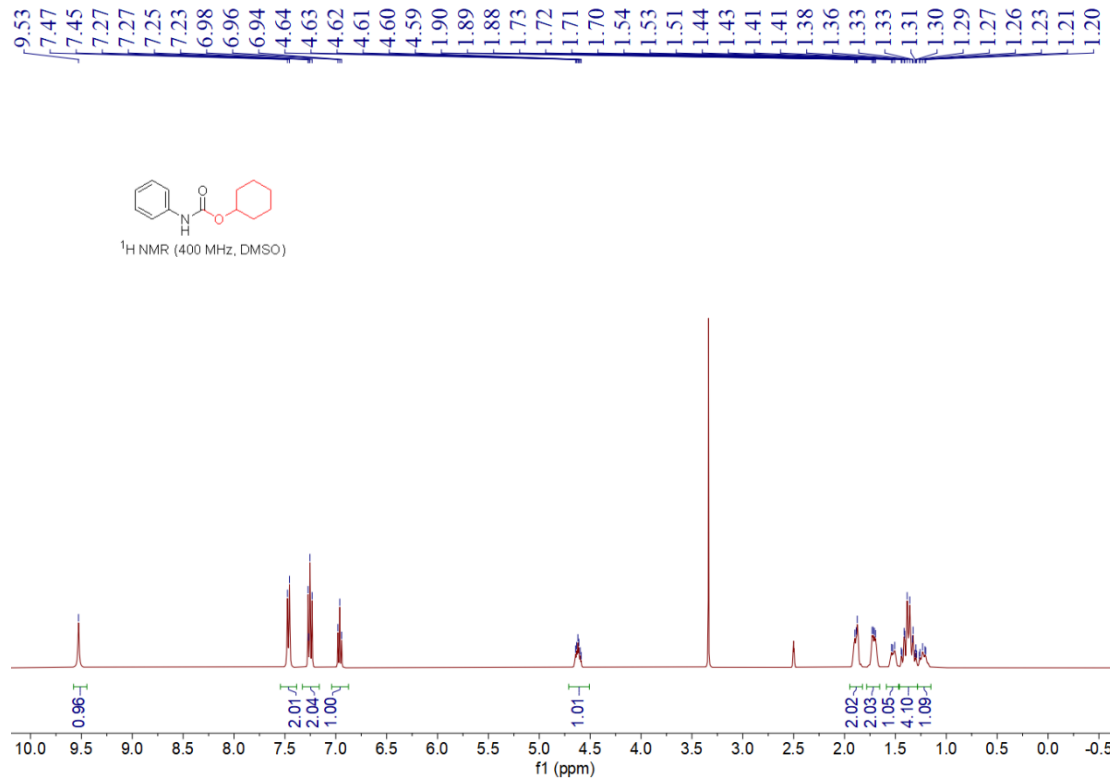
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240403-13-10 19 (0.105)

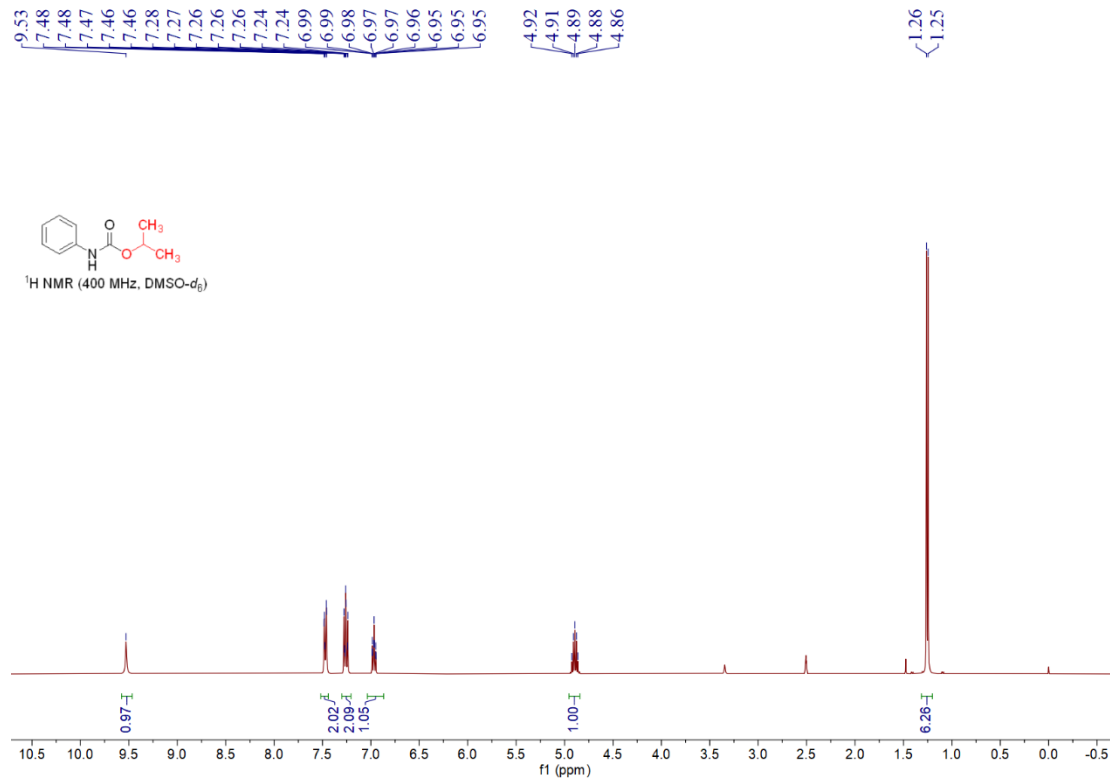
1: TOF MS ES+
2.75e+04



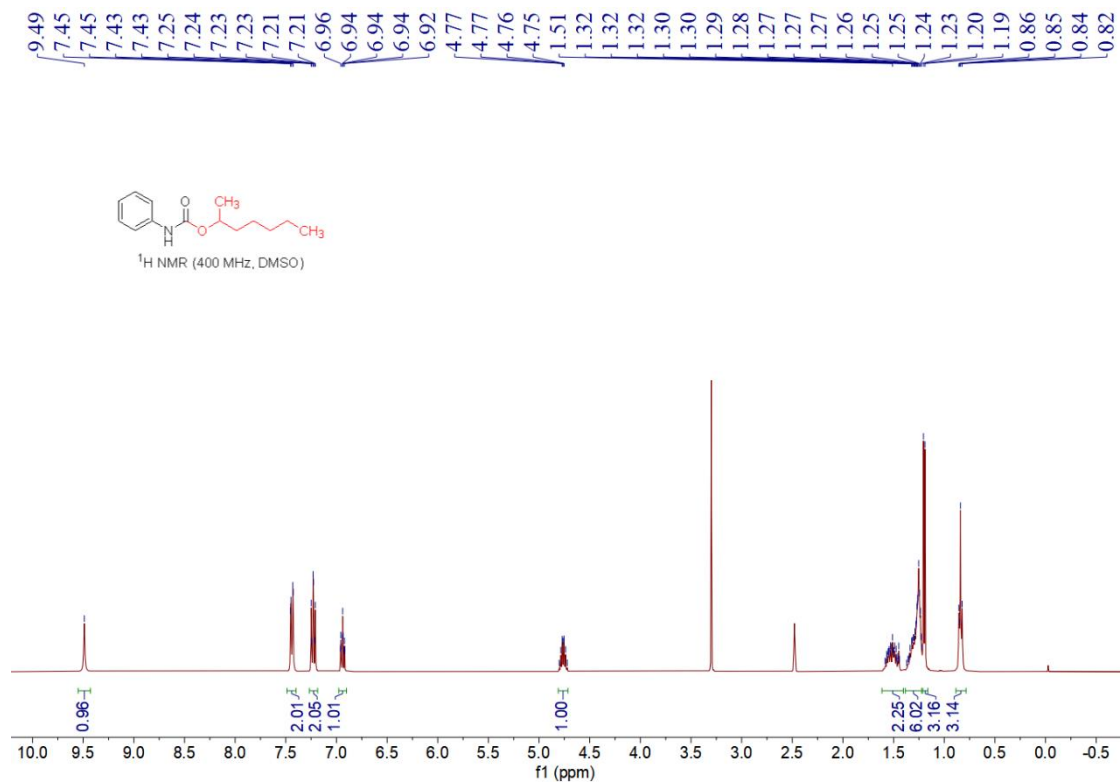
¹H NMR spectra of **8k**



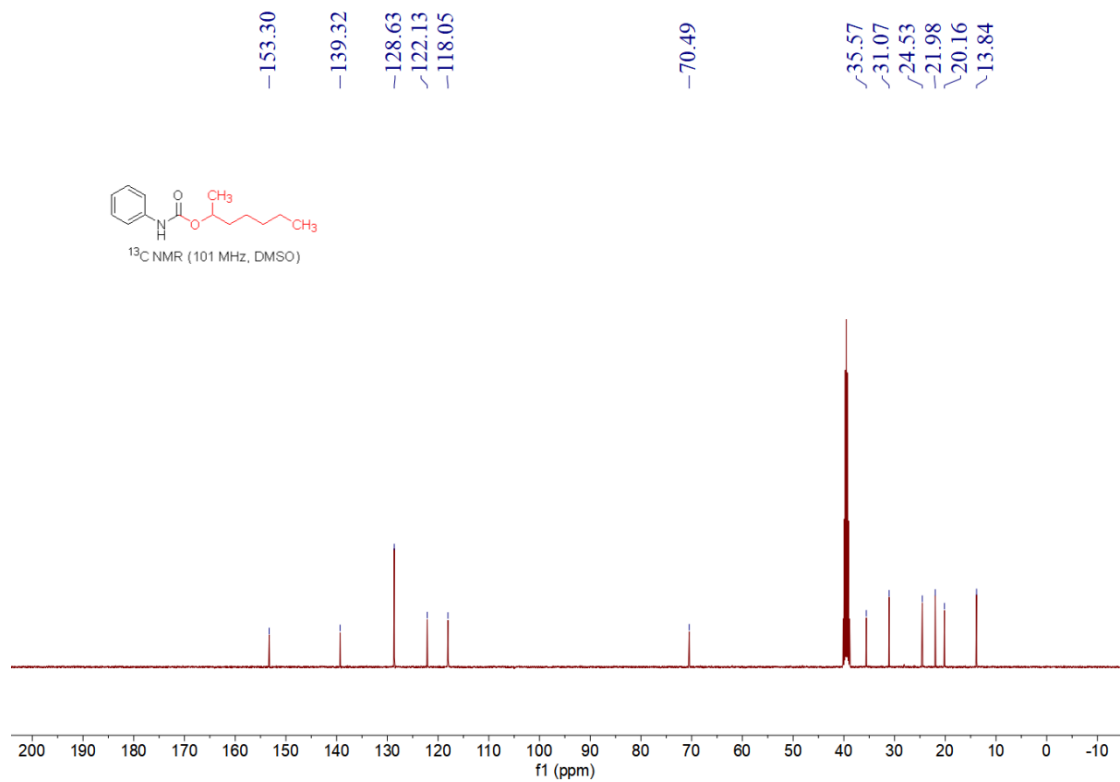
¹H NMR spectra of **8l**



^1H HRMS spectra of **8m**



^{13}C NMR spectra of **8m**



HRMS spectra of **8m**

Monoisotopic Mass, Even Electron Ions

270 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)

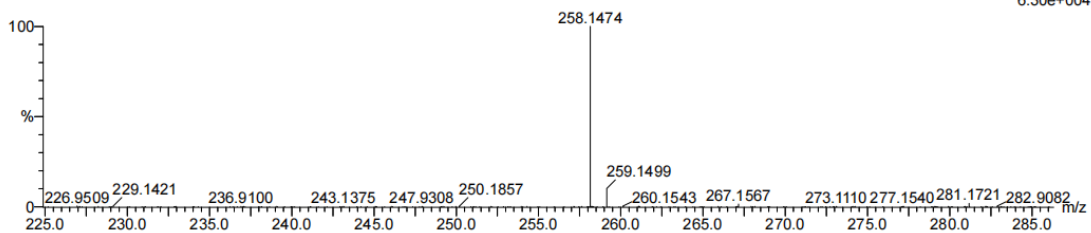
Elements Used:

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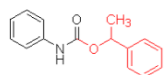
25

240403-13-13 51 (0.239)

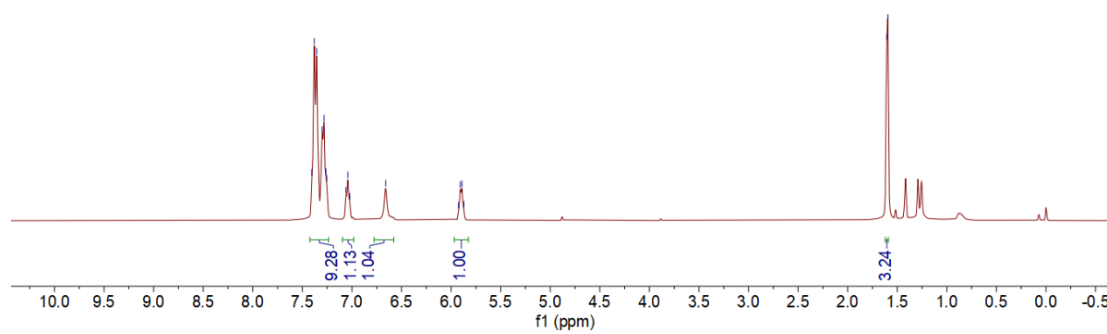
1: TOF MS ES+
6.30e+004



¹H NMR spectra of **8n**

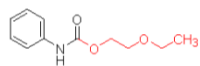


¹H NMR (400 MHz, CDCl₃)

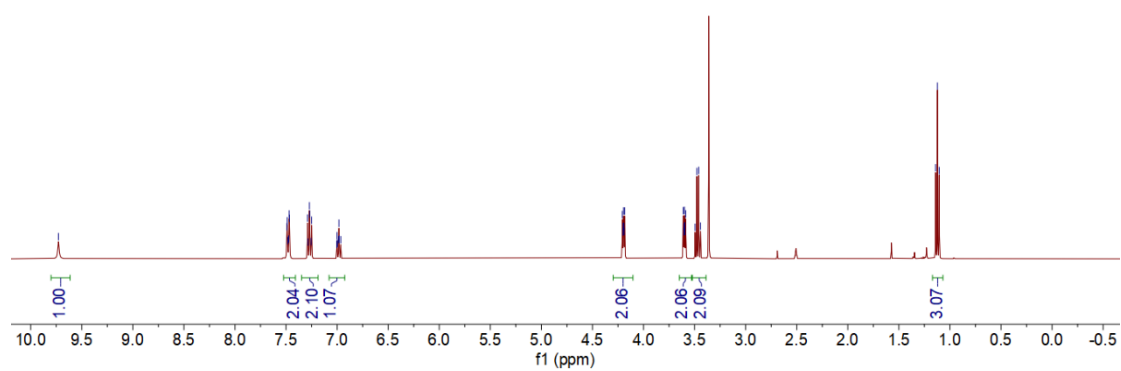


¹H NMR spectra of **80**

9.73
7.49
7.49
7.48
7.48
7.47
7.47
7.29
7.28
7.27
7.27
7.25
7.25
7.00
7.00
7.00
6.99
6.98
6.98
6.96
4.21
4.20
4.20
4.20
4.19
4.19
4.18
4.18
3.61
3.60
3.60
3.60
3.60
3.59
3.59
3.50
3.48
3.46
3.44
1.14
1.12
1.10

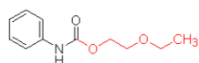


¹H NMR (400 MHz, DMSO)

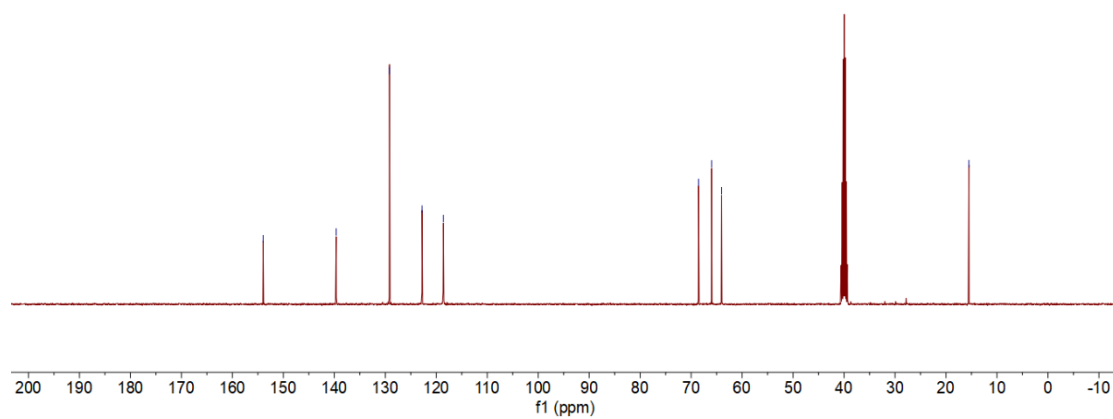


¹³C NMR spectra of **80**

-153.95
-139.63
-129.17
-122.79
-118.60
68.54
65.99
64.01
-15.51



¹³C NMR (101 MHz, DMSO)



HRMS spectra of **8o**

Monoisotopic Mass, Even Electron Ions

212 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)

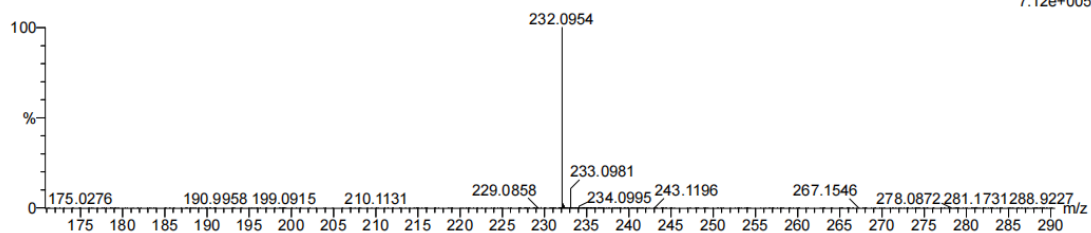
Elements Used:

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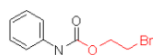
240403-13-15 22 (0.115)

1: TOF MS ES+
7.12e+005

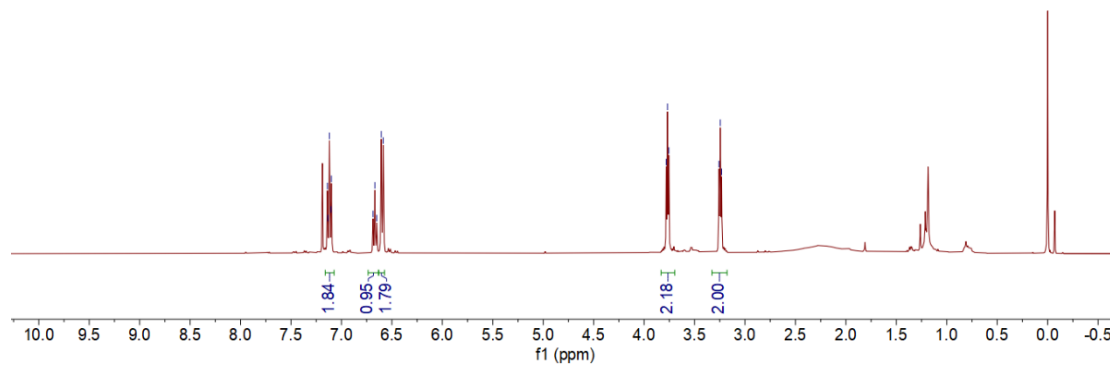


¹H NMR spectra of **8p**

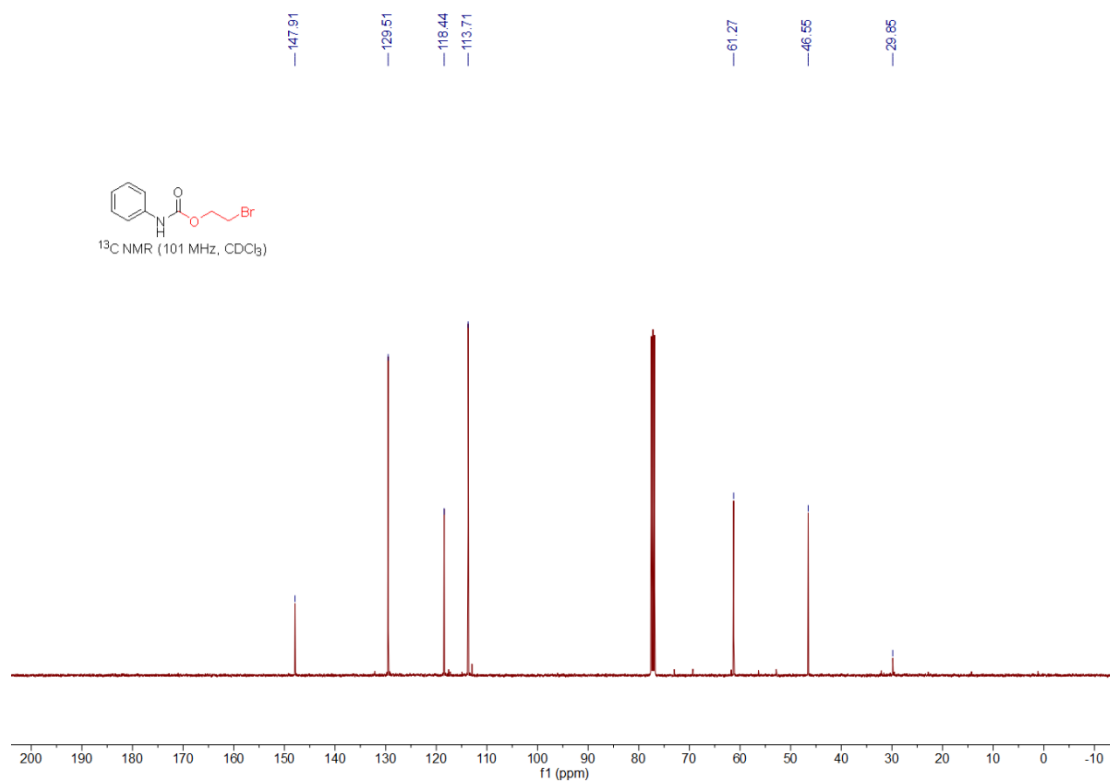
7.14
7.13
7.12
7.10
7.10
6.69
6.67
6.65
6.61
6.59
3.78
3.77
3.76
3.26
3.24
3.23



¹H NMR (400 MHz, CDCl₃)



¹³C NMR spectra of **8p**



HRMS spectra of **8p**

Monoisotopic Mass, Even Electron Ions

193 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)

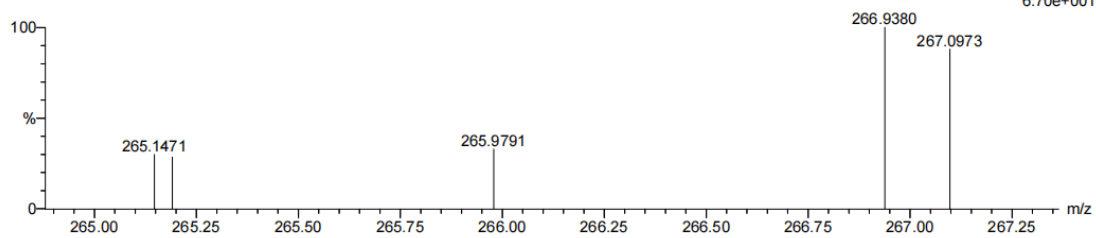
Elements Used:

C: 9-9 H: 10-10 N: 0-100 O: 0-100 Na: 0-1 Br: 1-2

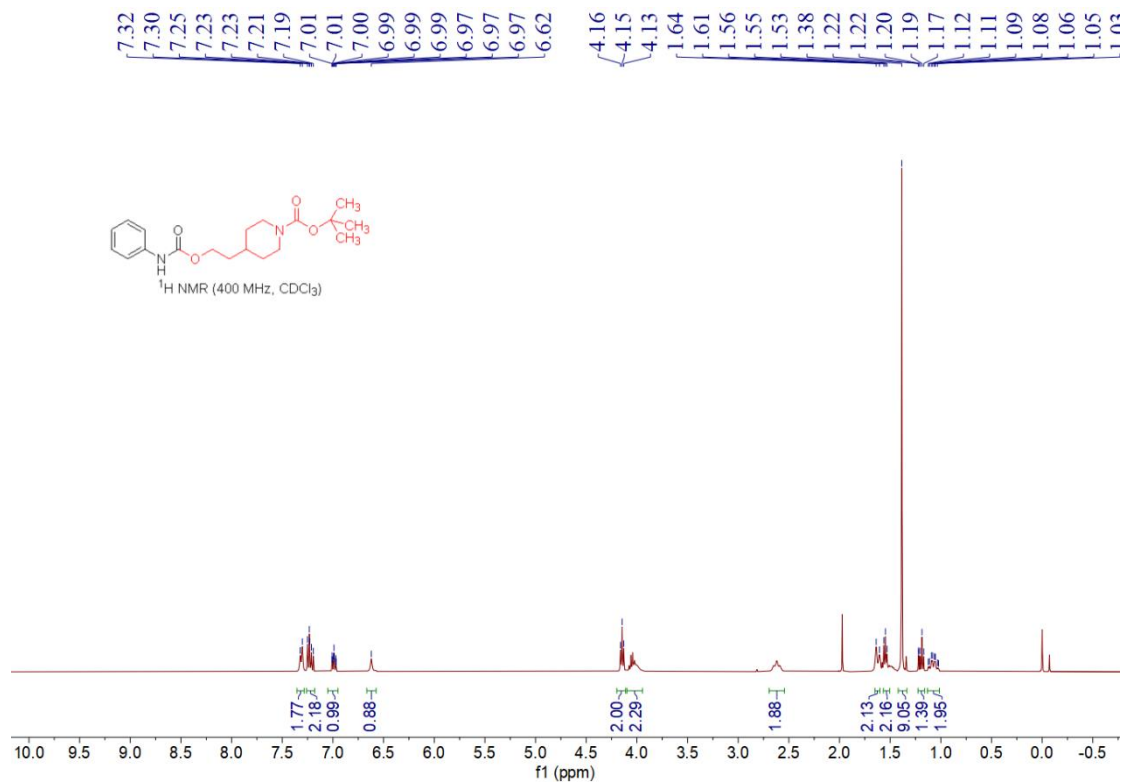
25

240403-13-16 91 (0.401)

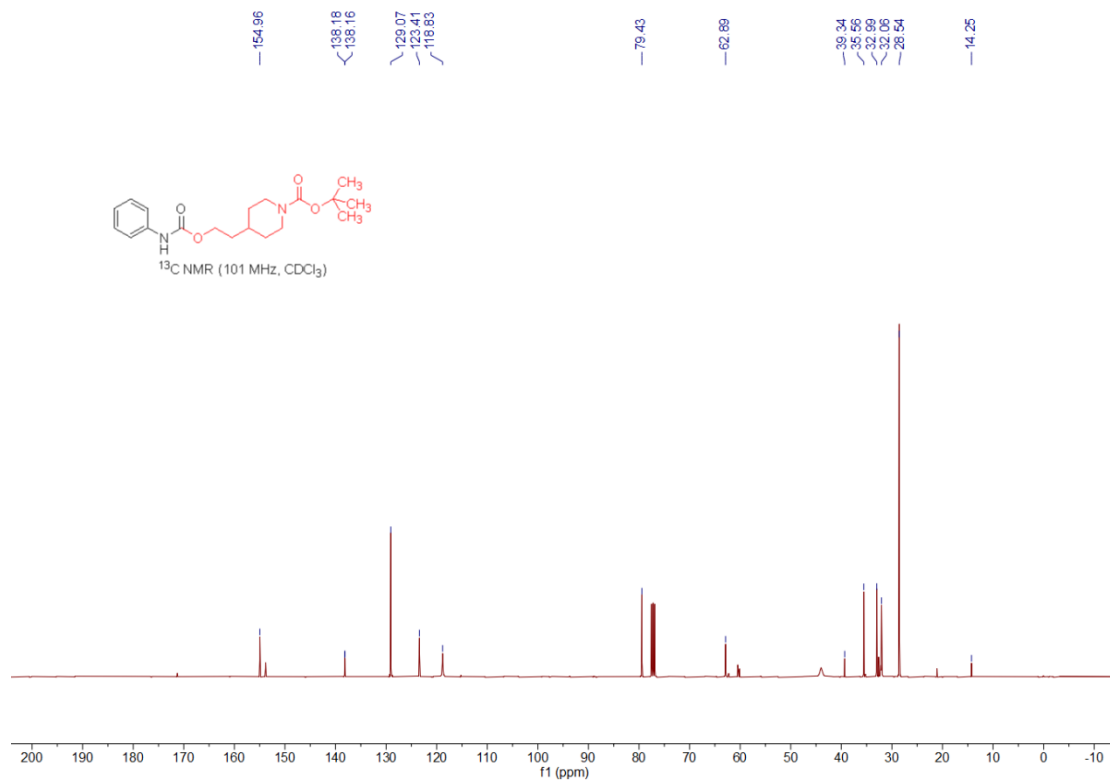
1: TOF MS ES+
6.70e+001



¹H NMR spectra of **8q**



¹³C NMR spectra of **8q**



HRMS spectra of **8q**

Monoisotopic Mass, Even Electron Ions

548 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)

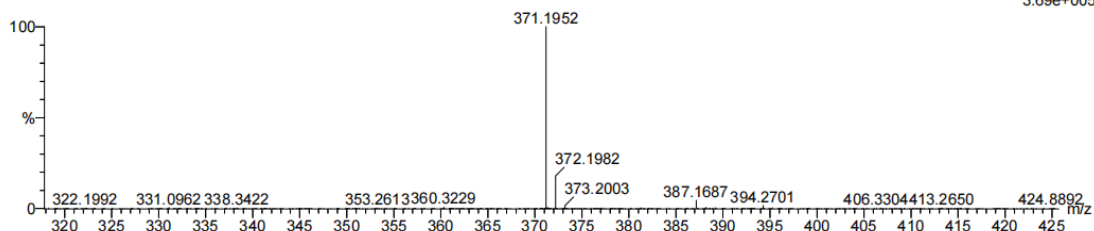
Elements Used:

C: 19-19 H: 28-28 N: 0-100 O: 0-100 Na: 0-1

25

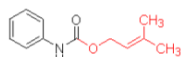
240403-13-17 19 (0.105)

1: TOF MS ES+
3.69e+005

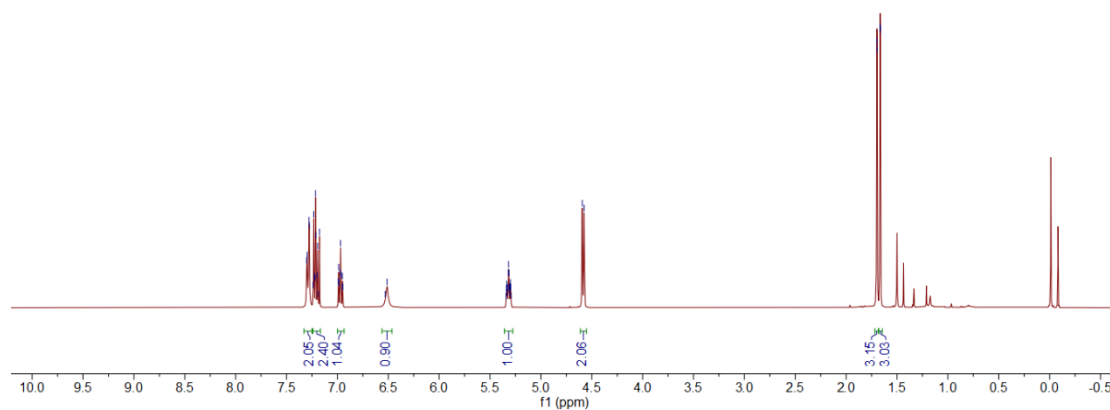


¹H NMR spectra of **8r**

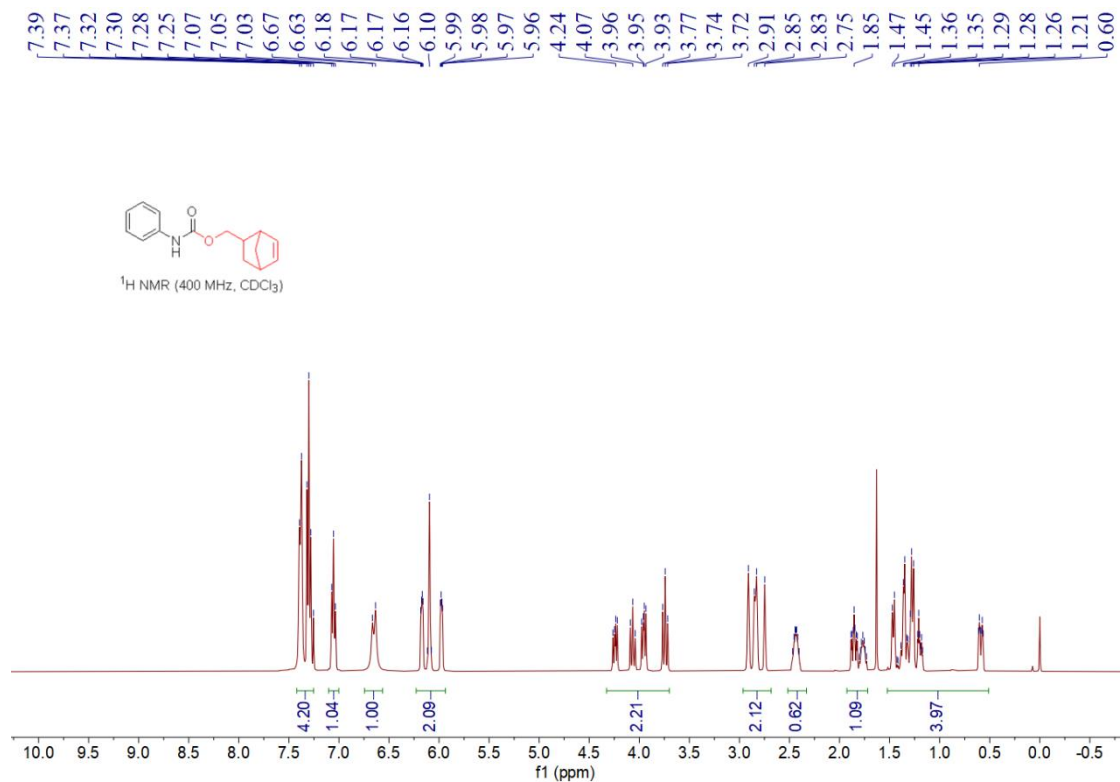
7.30
7.29
7.28
7.27
7.26
7.25
7.24
7.23
7.22
7.21
7.20
7.19
7.18
6.99
6.98
6.97
6.95
6.95
6.93
6.91
5.54
5.53
5.53
5.52
5.52
5.52
5.51
5.51
5.50
5.50
5.49
5.49
4.48
1.70
1.69
1.67
1.66



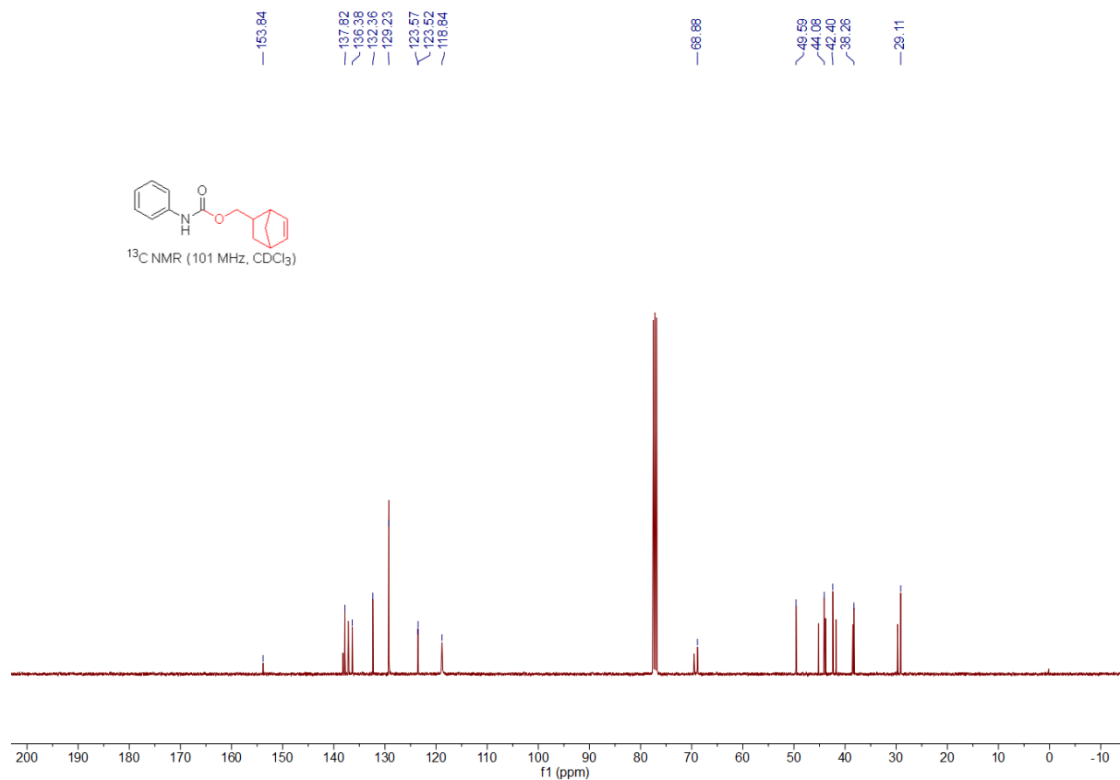
¹H NMR (400 MHz, CDCl₃)



¹H NMR spectra of **8s**



¹³C NMR spectra of **8s**



HRMS spectra of **8s**

Monoisotopic Mass, Even Electron Ions

292 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)

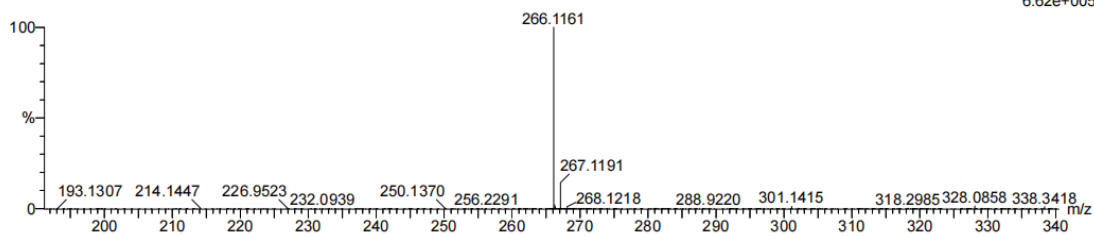
Elements Used:

C: 15-15 H: 17-17 N: 0-100 O: 0-100 Na: 0-1

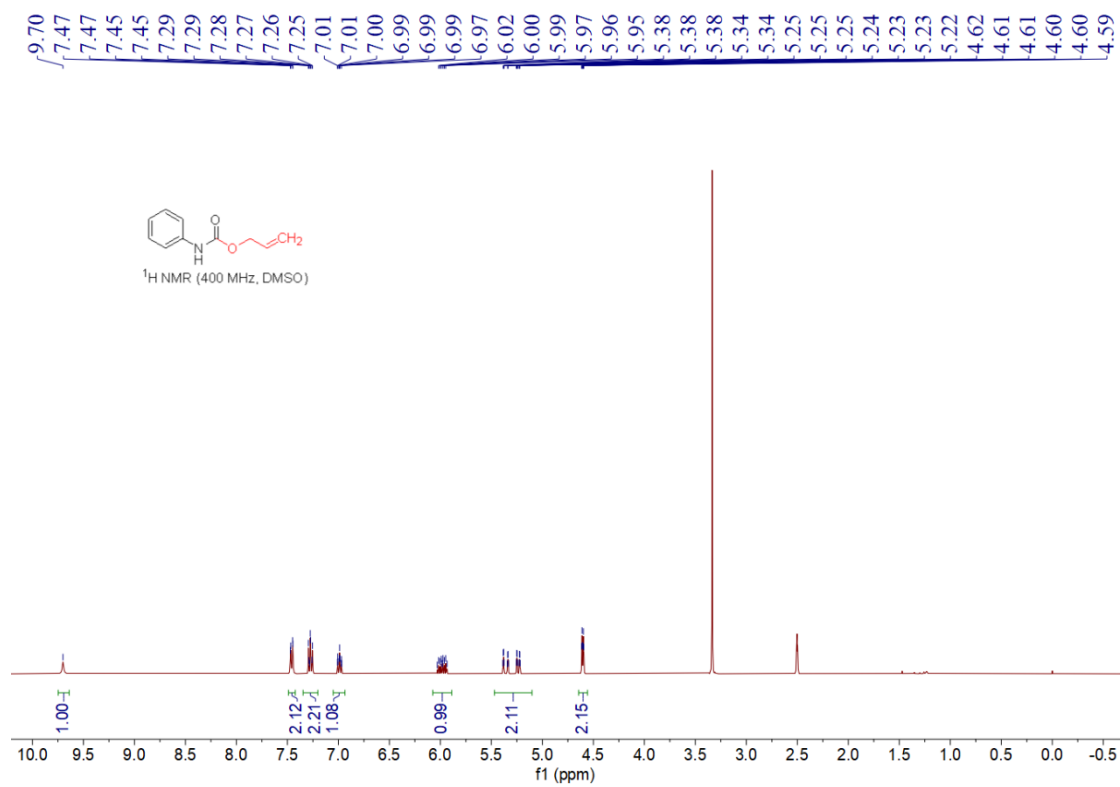
25

240403-13-19 13 (0.083)

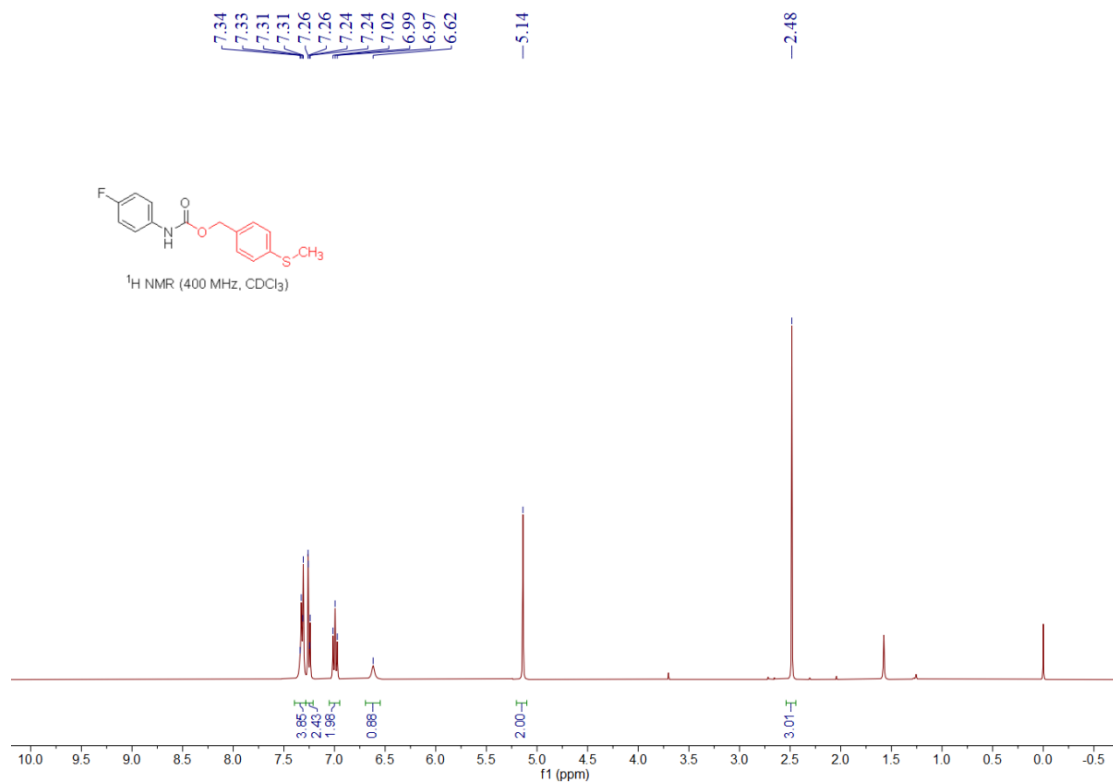
1: TOF MS ES+
6.62e+005



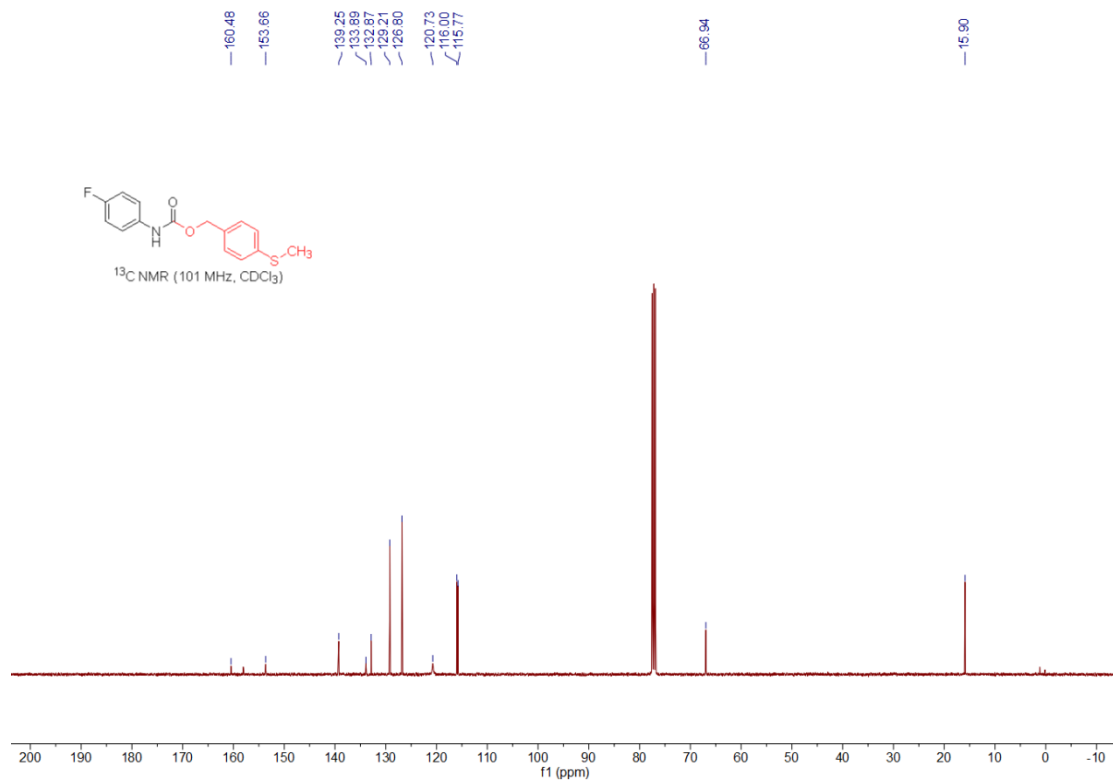
¹H NMR spectra of **8t**



^1H NMR spectra of **8u**



^{13}C NMR spectra of **8u**



HRMS spectra of **8u**

Monoisotopic Mass, Even Electron Ions

830 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)

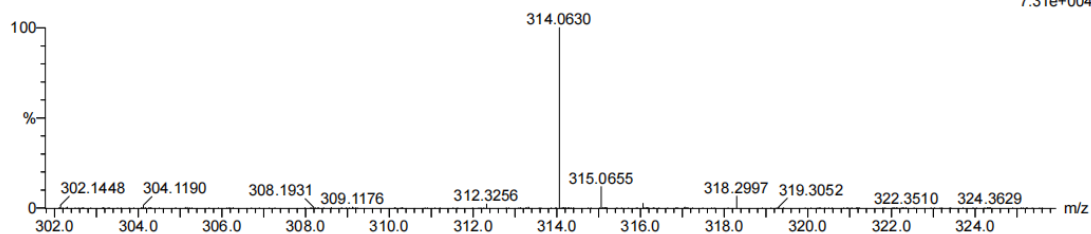
Elements Used:

C: 15-15 H: 14-14 N: 0-100 O: 0-100 Na: 0-1 S: 1-4 F: 1-1

25

240403-13-21 10 (0.072)

1: TOF MS ES+
7.31e+004

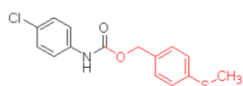


¹H NMR spectra of **8v**

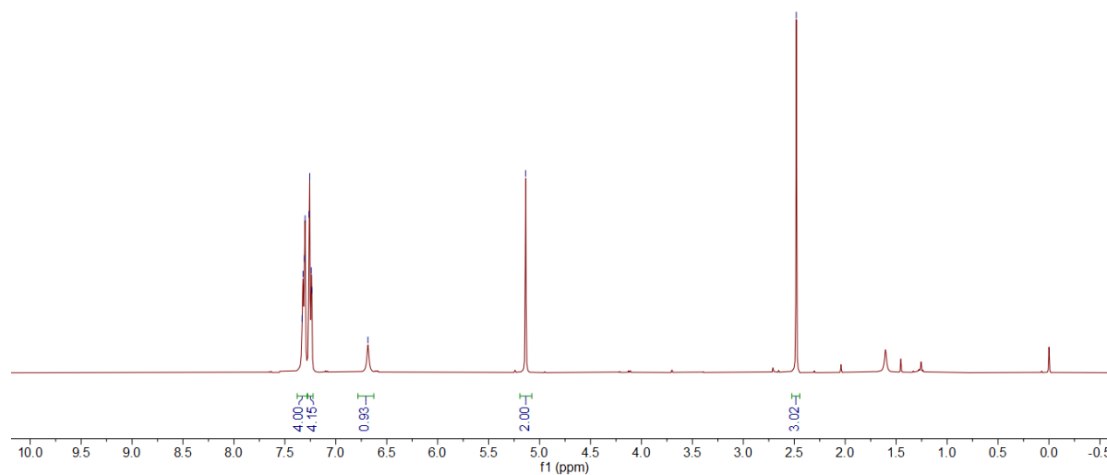
7.33
7.32
7.31
7.30
7.26
7.24
7.24
6.68

5.14

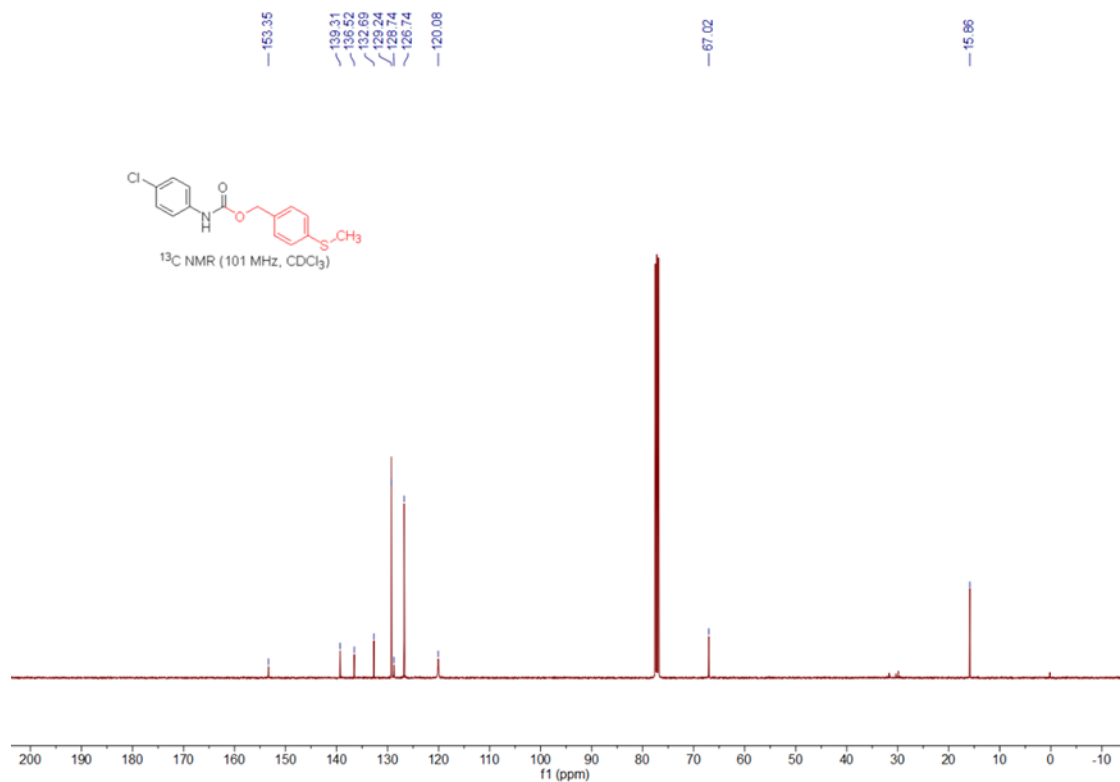
2.48



¹H NMR (400 MHz, CDCl₃)



¹³C NMR spectra of **8v**



HRMS spectra of **8v**

Monoisotopic Mass, Even Electron Ions

2251 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)

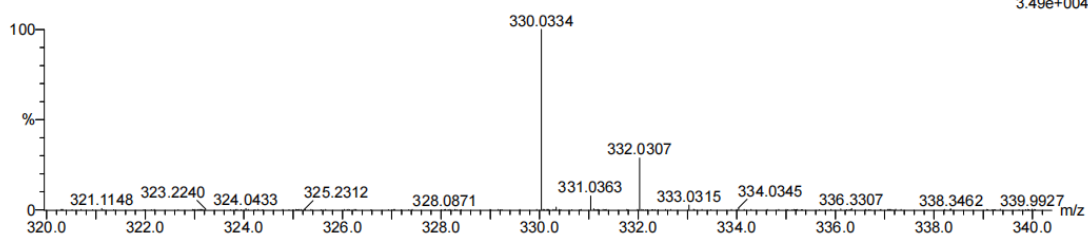
Elements Used:

C: 15-15 H: 14-14 N: 0-100 O: 0-100 Na: 0-1 S: 1-4 Cl: 1-5

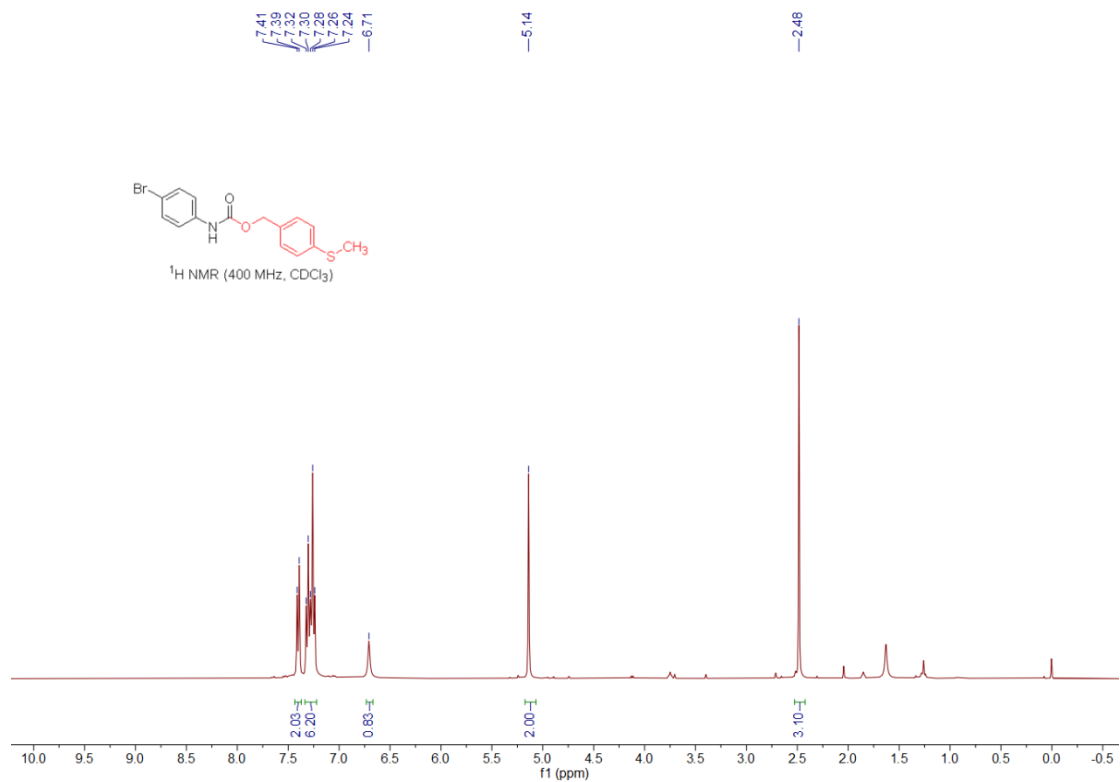
25

240403-13-22 10 (0.072)

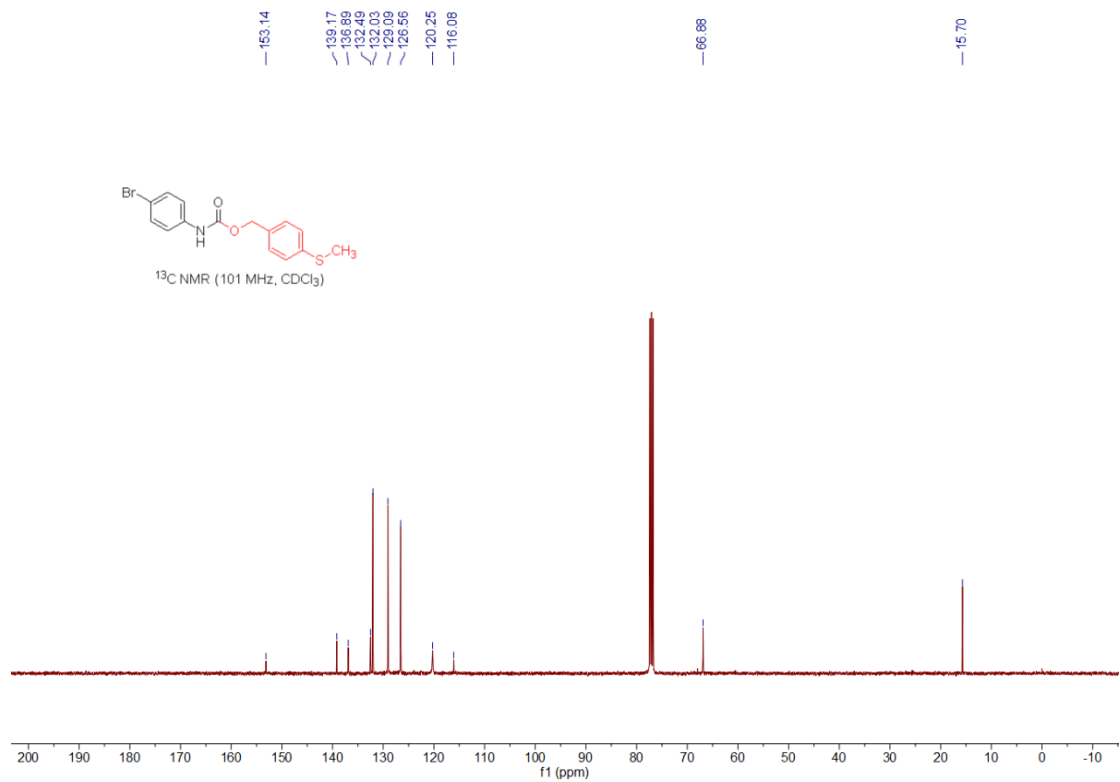
1: TOF MS ES+
3.49e+004



^1H NMR spectra of **8w**



^{13}C NMR spectra of **8w**



HRMS spectra of **8w**

Monoisotopic Mass, Even Electron Ions

1205 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)

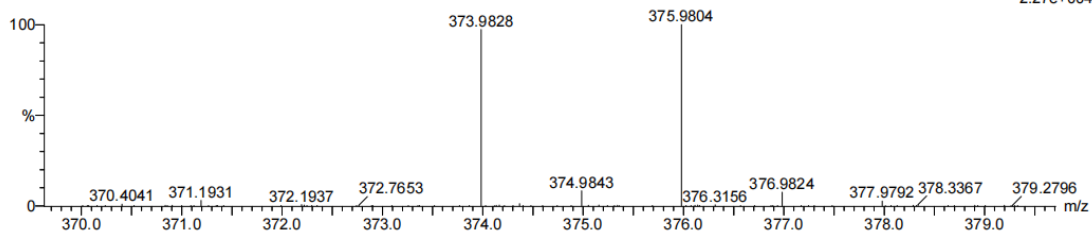
Elements Used:

C: 15-15 H: 14-14 N: 0-100 O: 0-100 Na: 0-1 S: 1-4 Br: 1-2

25

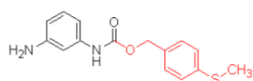
240403-13-23 11 (0.076)

1: TOF MS ES+
2.27e+004

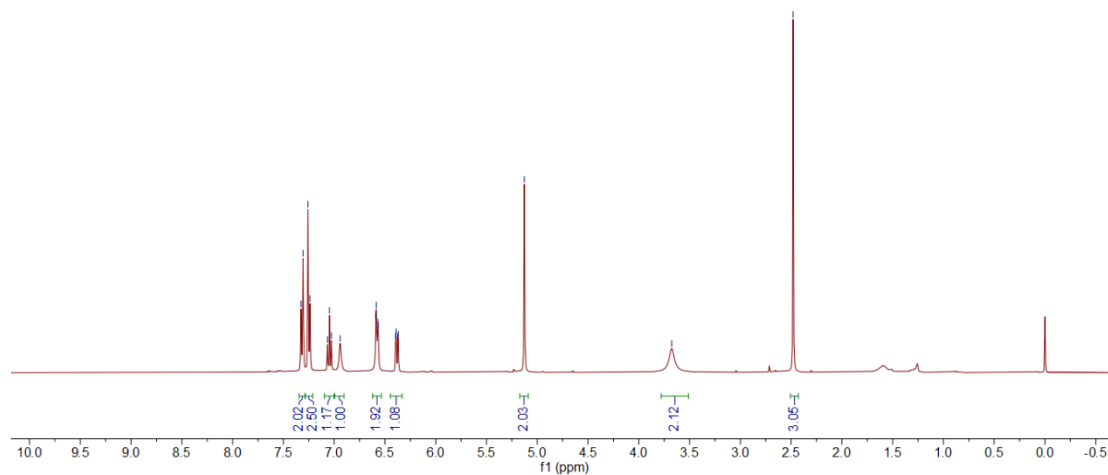


¹H NMR spectra of **8x**

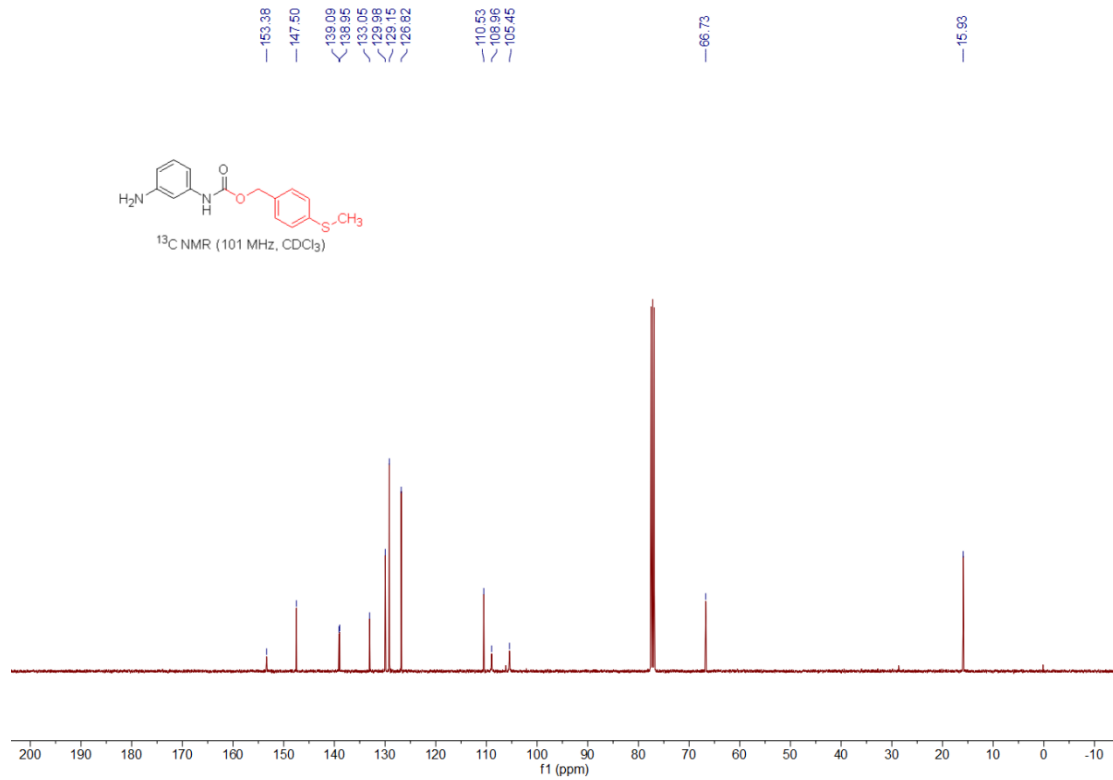
7.33
7.31
7.26
7.24
7.07
7.05
7.03
6.94
6.59
6.59
6.57
6.57
6.39
6.39
6.37
6.37
5.13
-3.68
-2.48



¹H NMR (400 MHz, CDCl₃)



¹³C NMR spectra of **8x**



HRMS spectra of **8x**

Monoisotopic Mass, Even Electron Ions

936 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)

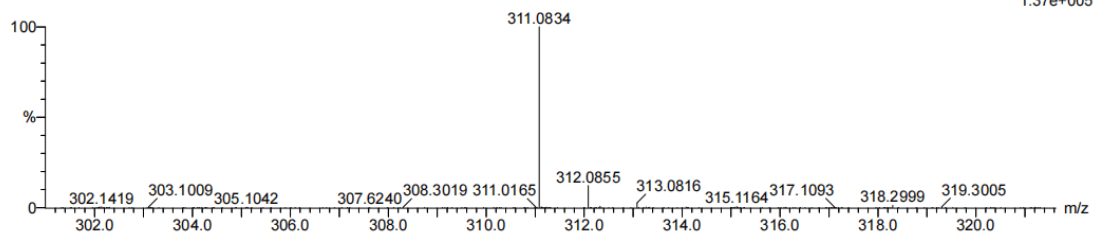
Elements Used:

C: 15-15 H: 16-16 N: 0-100 O: 0-100 Na: 0-1 S: 1-4

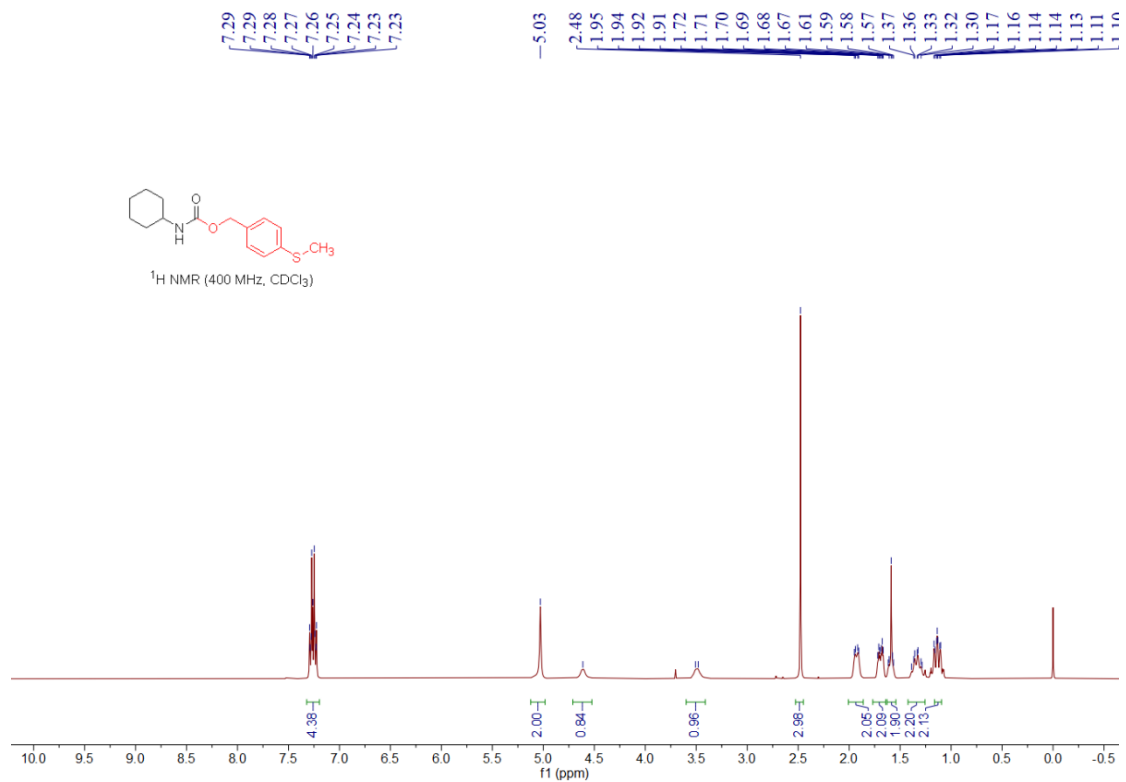
25

240403-13-24 12 (0.080)

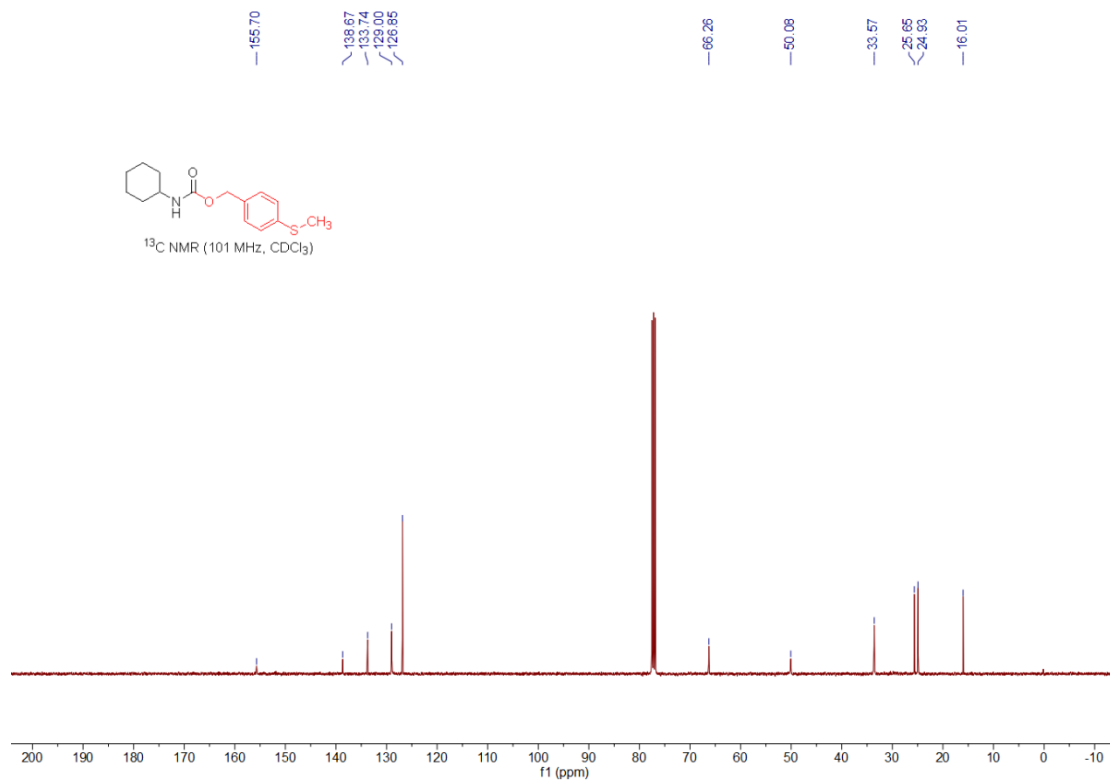
1: TOF MS ES+
1.37e+005



^1H NMR spectra of **8y**



^{13}C NMR spectra of **8y**



HRMS spectra of **8y**

Monoisotopic Mass, Even Electron Ions

871 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)

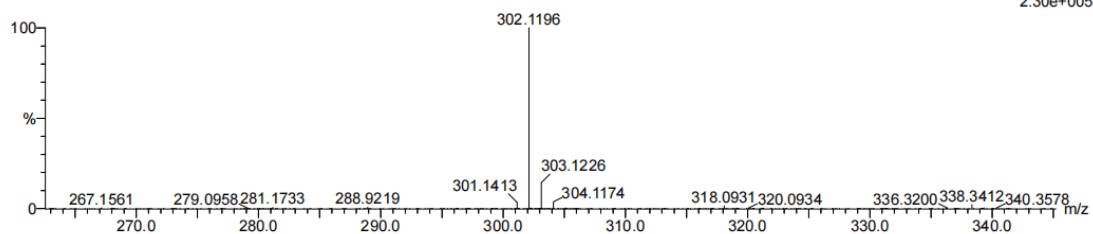
Elements Used:

C: 15-15 H: 21-21 N: 0-100 O: 0-100 Na: 0-1 S: 1-4

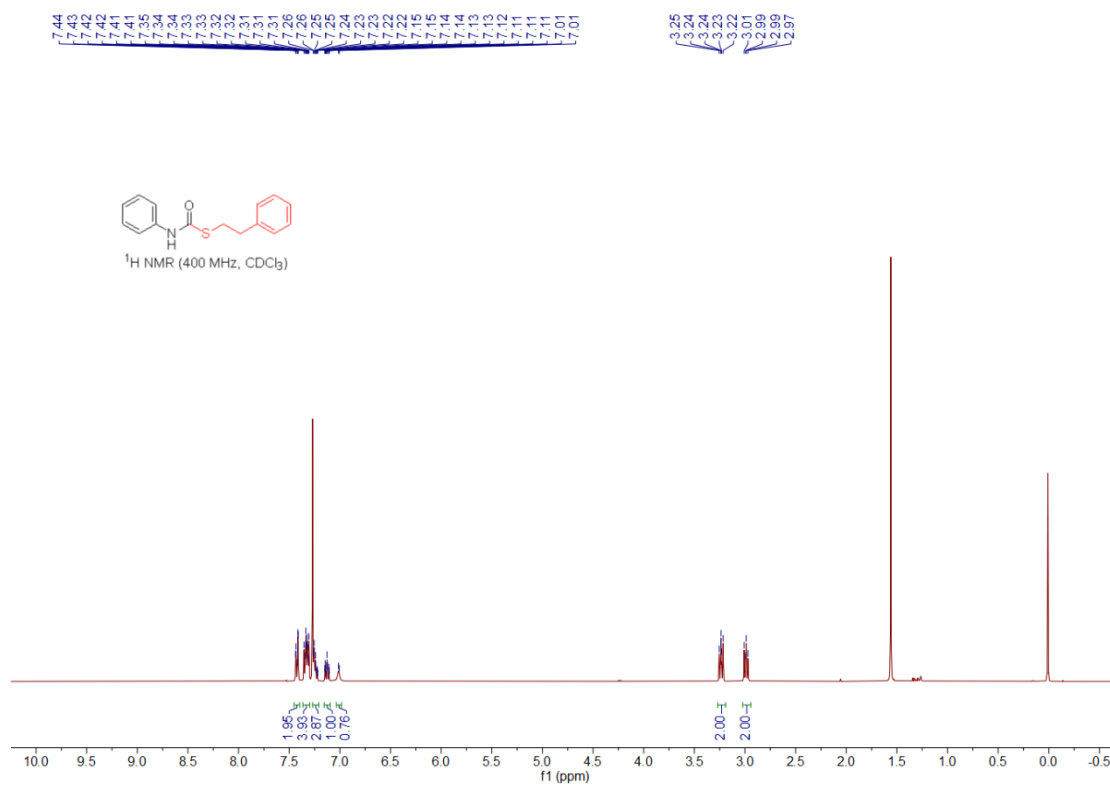
25

240403-13-25 17 (0.097)

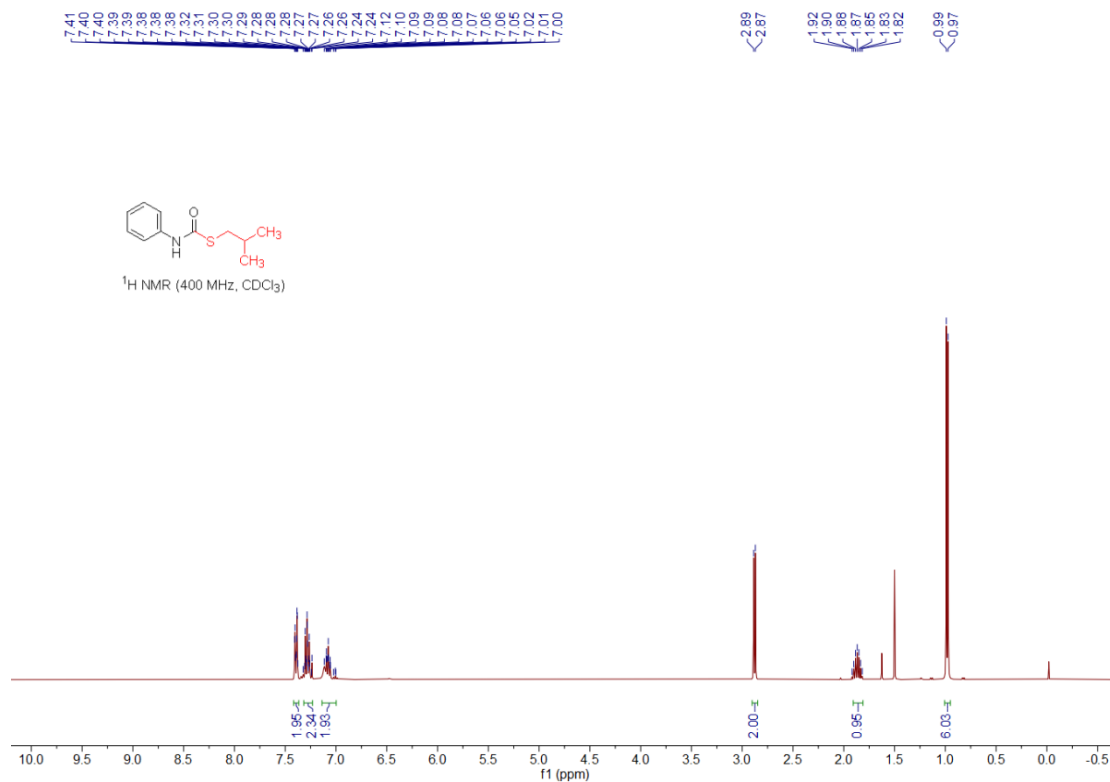
1: TOF MS ES+
2.30e+005



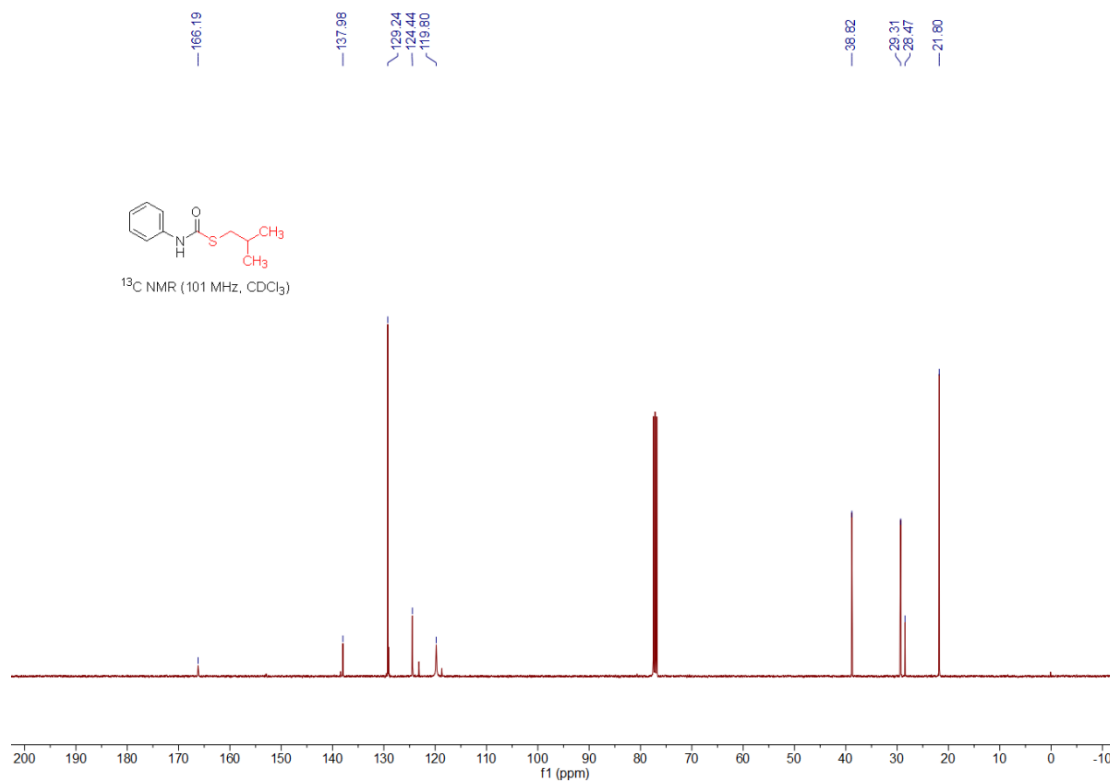
¹H NMR spectra of **8z**



¹H NMR spectra of **8aa**



¹³C NMR spectra of **8aa**



HRMS spectra of **8aa**

Monoisotopic Mass, Even Electron Ions

427 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)

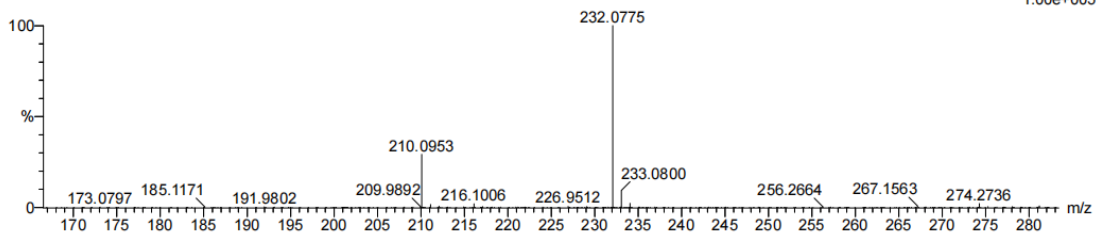
Elements Used:

C: 11-11 H: 15-15 N: 0-100 O: 0-100 Na: 0-1 S: 1-4

25

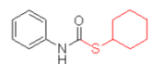
240403-13-27 10 (0.072)

1: TOF MS ES+
1.00e+005

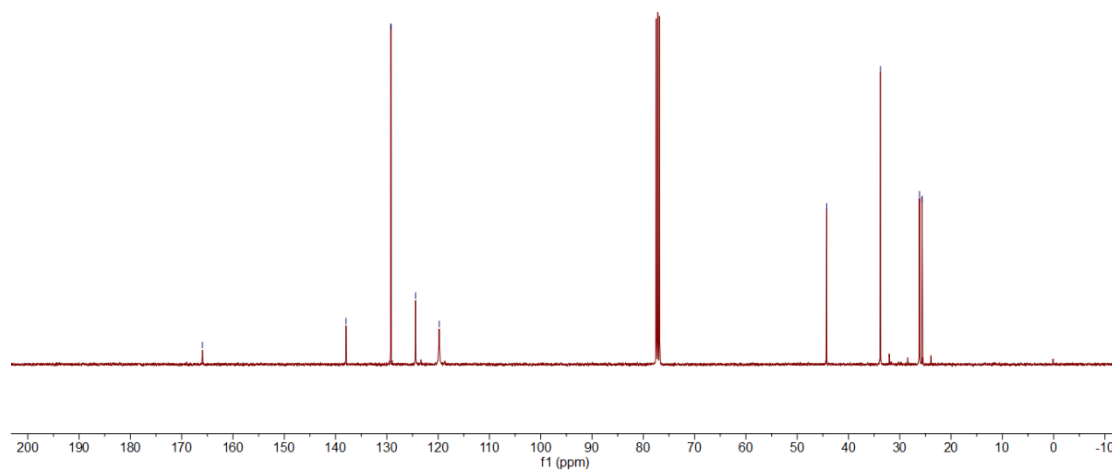


¹H NMR spectra of **8ab**

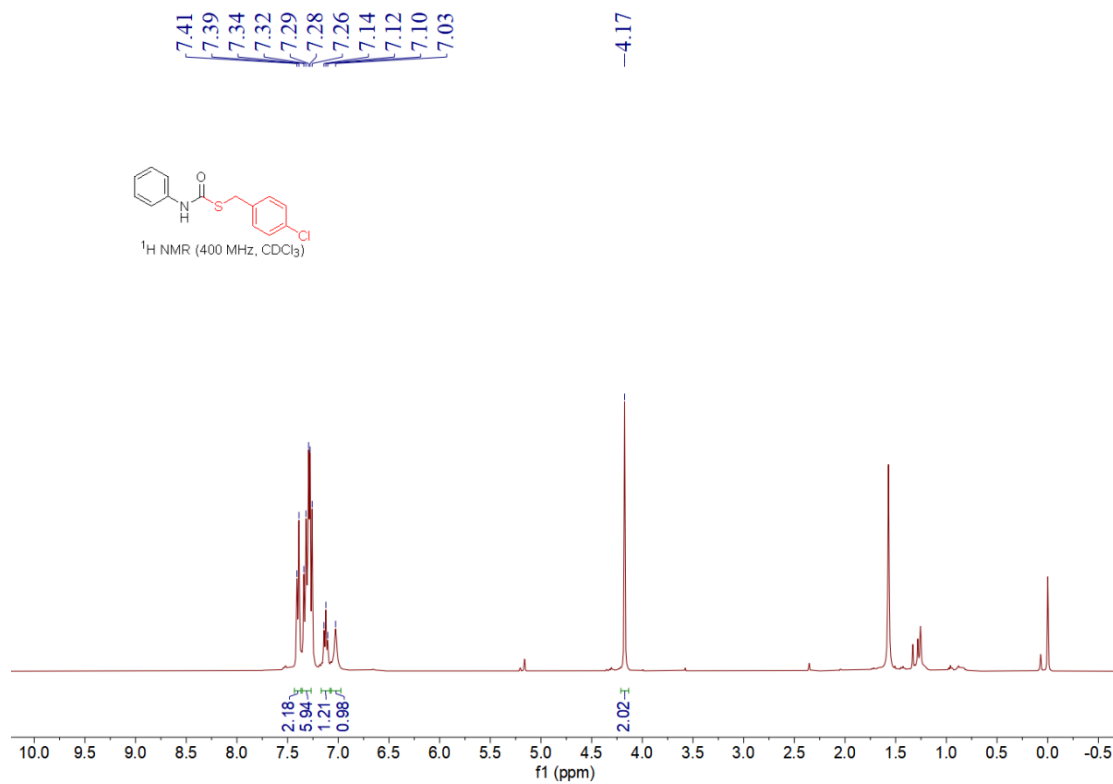
¹³C NMR (101 MHz, CDCl₃) chemical shifts (ppm): 165.96, 137.96, 129.22, 124.40, 119.80, 44.25, 33.77, 26.17, 25.65.



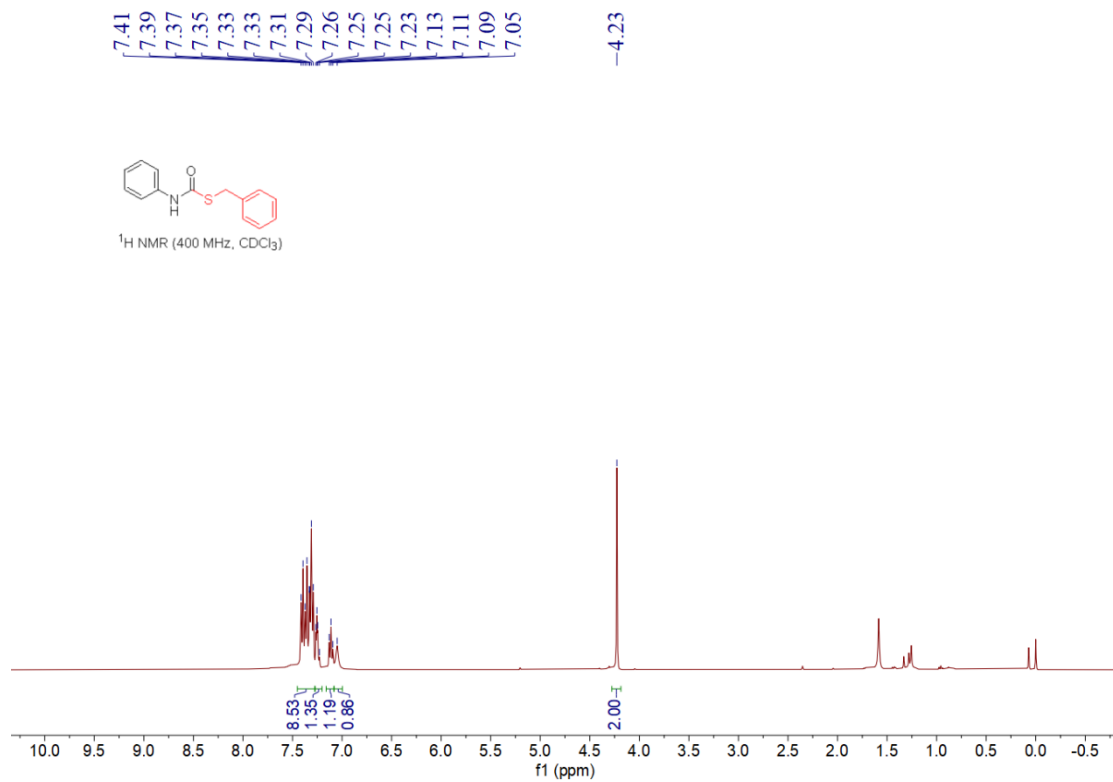
¹³C NMR (101 MHz, CDCl₃)



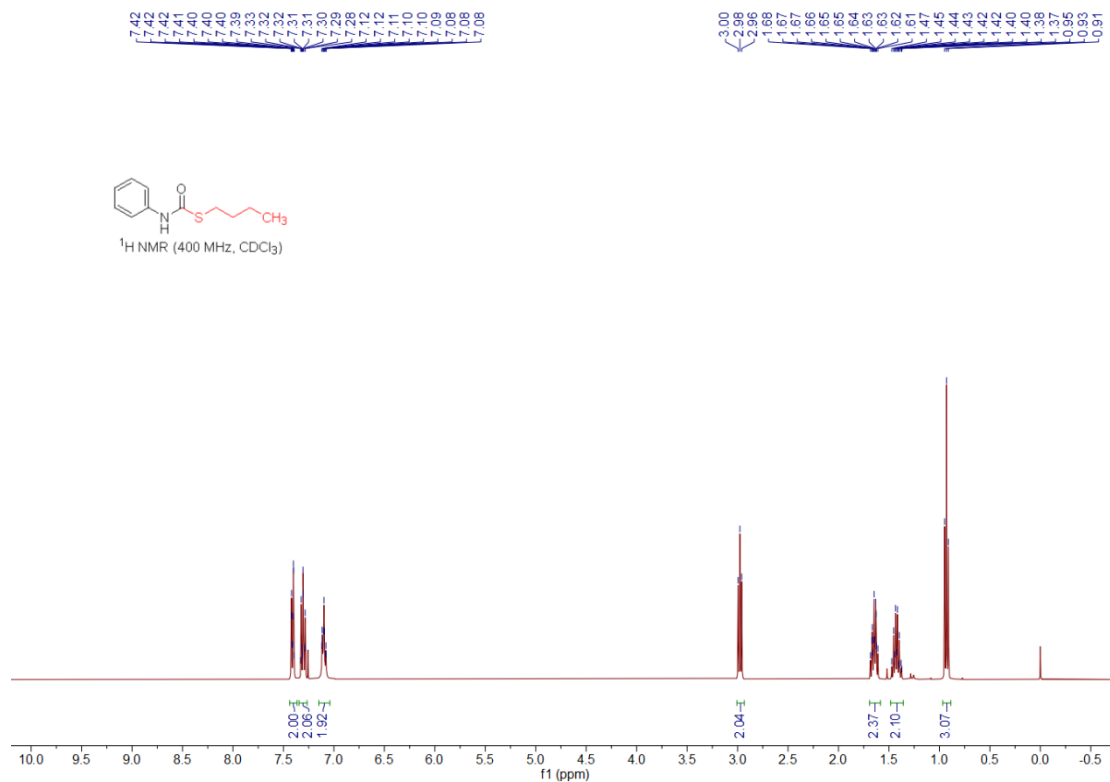
¹H NMR spectra of **8ac**



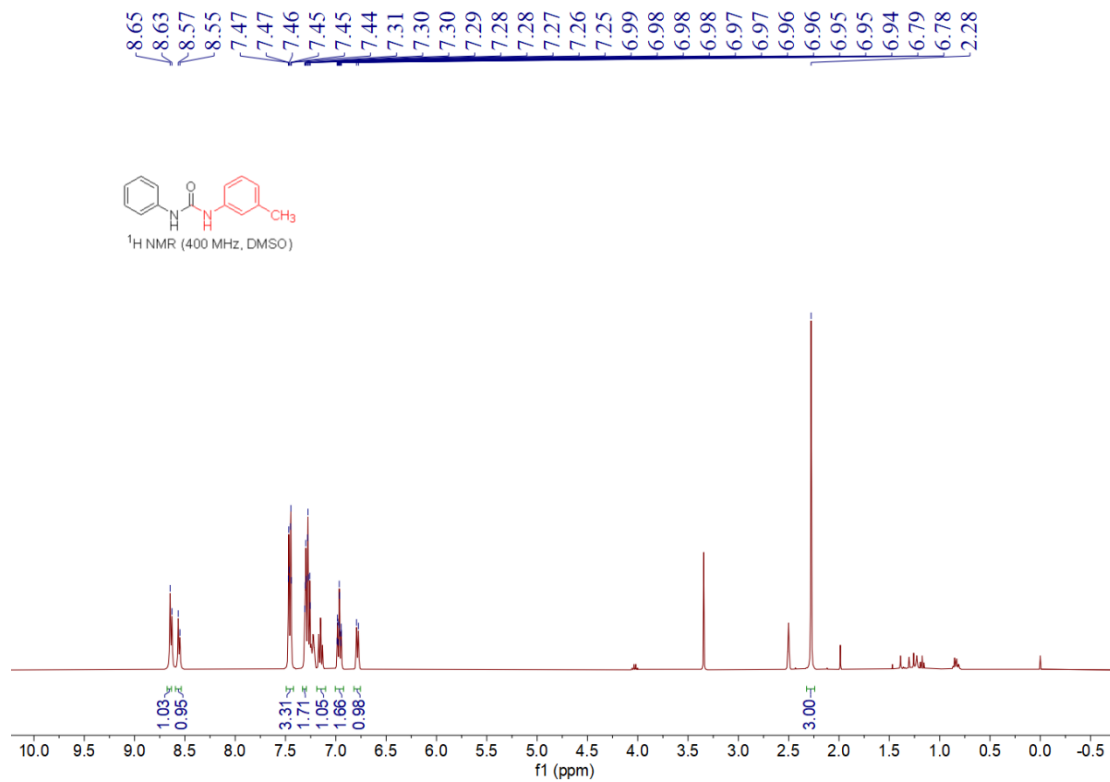
¹H NMR spectra of **8ad**



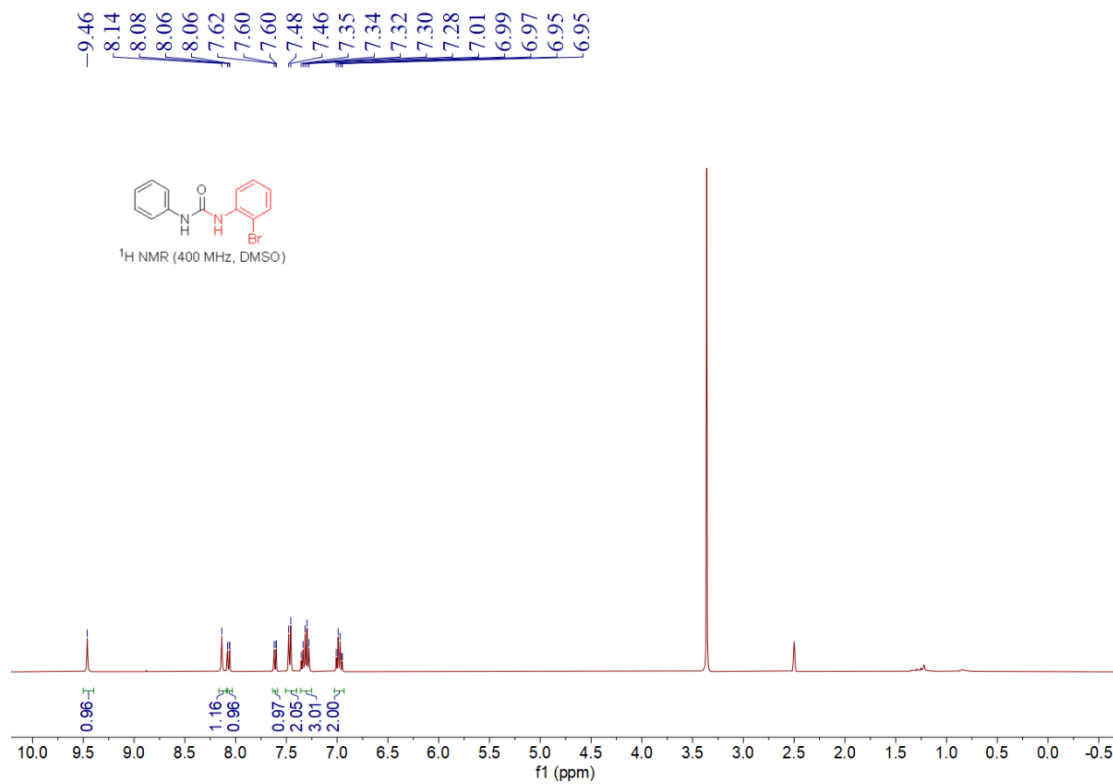
¹H NMR spectra of **8ae**



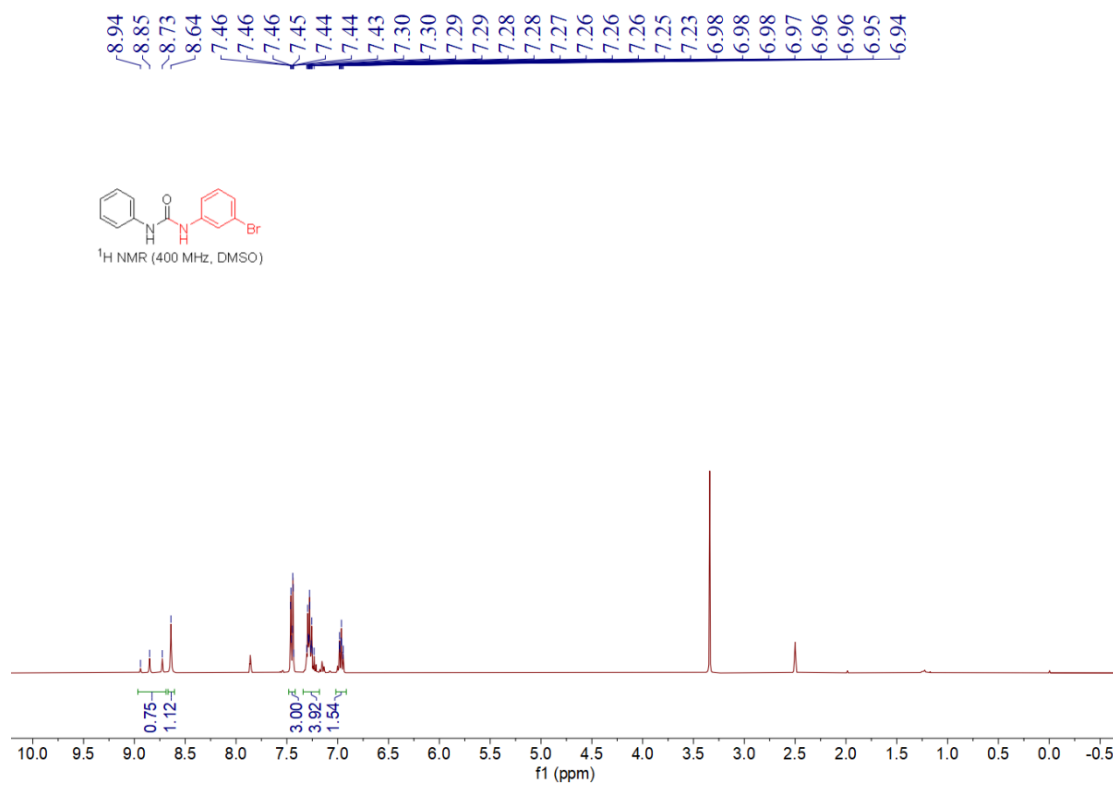
¹H NMR spectra of **8af**



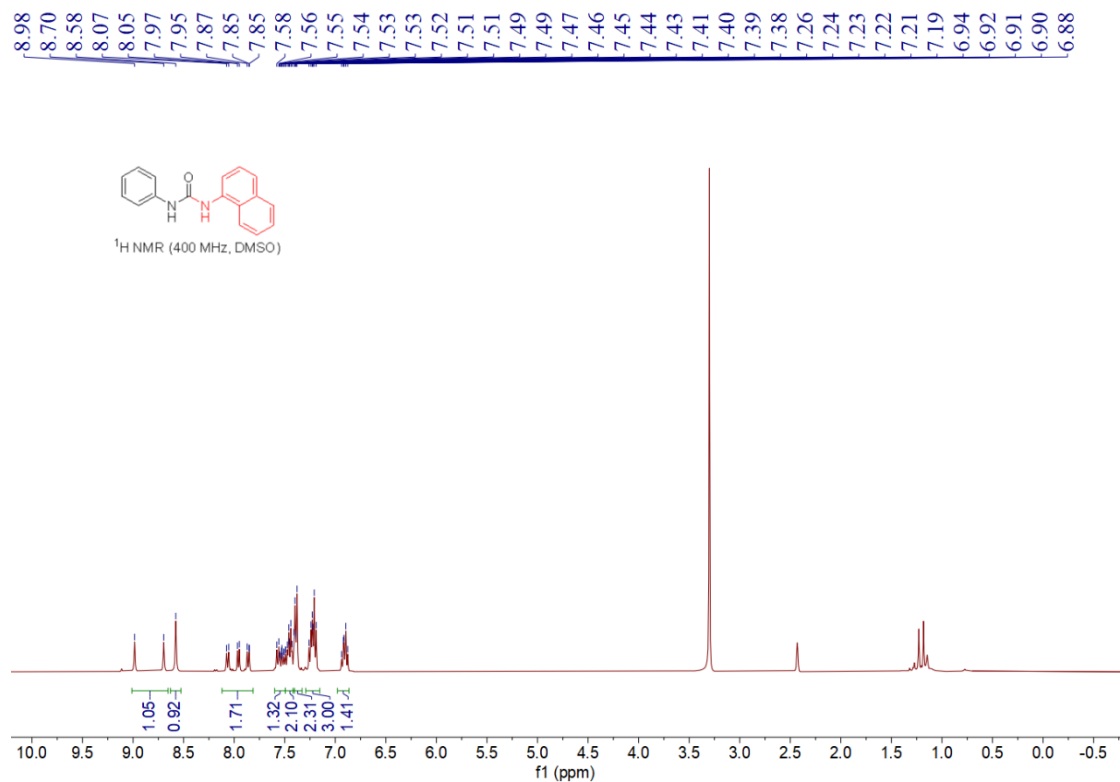
¹H NMR spectra of **8ag**



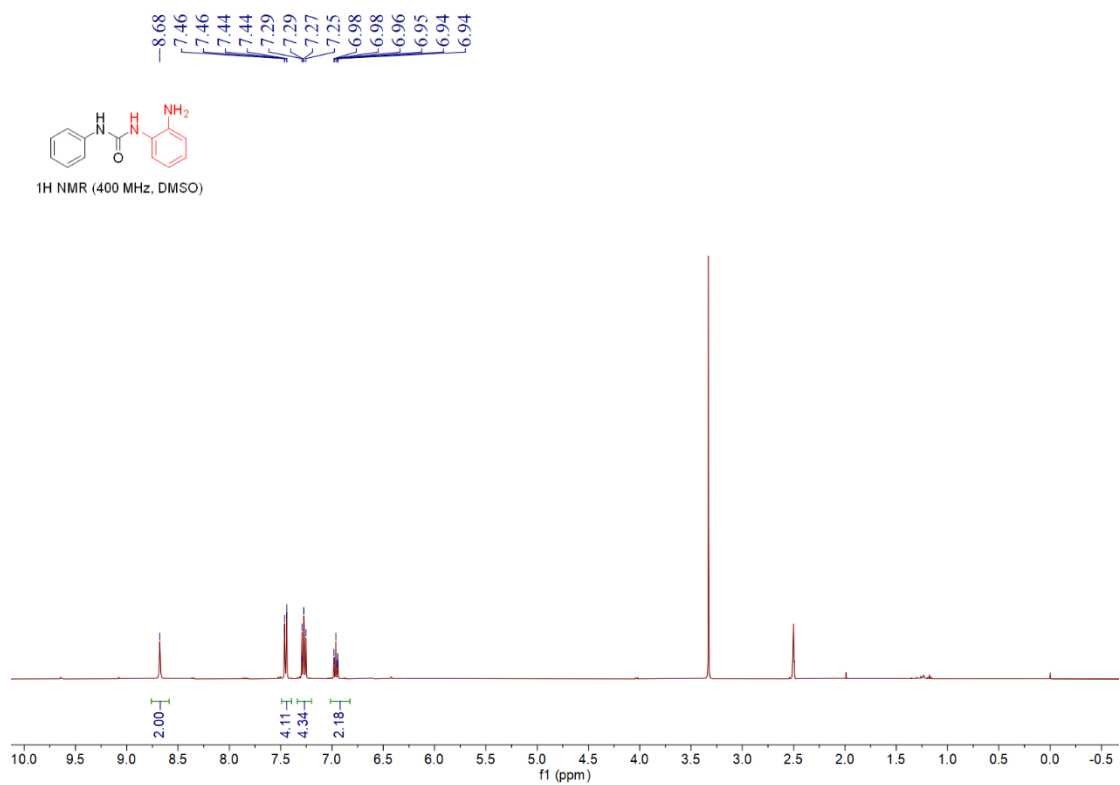
¹H NMR spectra of **8ah**



¹H NMR spectra of **8ai**



¹H NMR spectra of **8aj**



¹H NMR spectra of **ak**

