

Supporting Information

Base-Promoted Synthesis of α,β -Unsaturated Amides via C-N Bond Formation Using α,β -Unsaturated Acids and Isothiocyanates

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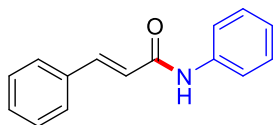
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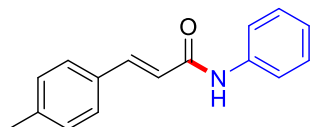
1. Physical and Spectral Data of the Products 3.

N-Phenylcinnamamide (3a)¹:



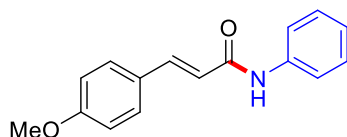
White solid; Yield = 102 mg (91%); Purification by column chromatography (ethyl acetate/hexane, v/v = 10:90); ¹H NMR (500 MHz, CDCl₃): δ 8.64 (brs, 1H), 7.75 (d, *J* = 16.0 Hz, 2H), 7.70 (s, 1H), 7.38 (d, *J* = 7.5 Hz, 2H), 7.30-7.23 (m, 5H), 7.09 (t, *J* = 7.5 Hz, 1H), 6.74 (d, *J* = 16.0 Hz, 1H); ¹³C {¹H} NMR (126 MHz, CDCl₃): δ 164.9, 142.2, 138.3, 134.7, 129.9, 129.1, 128.8, 128.0, 124.5, 121.3, 120.5.

(*E*)-*N*-Phenyl-3-(*p*-tolyl)acrylamide (3b)¹:



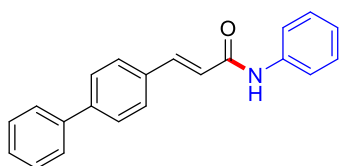
White solid; Yield = 108 mg (91%); Purification by column chromatography (ethyl acetate/hexane, v/v = 10:90); ¹H NMR (500 MHz, CDCl₃): δ 7.78 (brs, 1H), 7.74 (d, *J* = 15.0 Hz, 1H), 7.65 (d, *J* = 6.0 Hz, 2H), 7.38 (d, *J* = 8.0 Hz, 2H), 7.33 (t, *J* = 8.0 Hz, 2H), 7.15-7.10 (m, 3H), 6.58 (d, *J* = 15.0 Hz, 1H), 2.36 (s, 3H); ¹³C {¹H} NMR (126 MHz, CDCl₃): δ 164.5, 142.5, 140.4, 138.3, 132.0, 129.7, 129.2, 128.1, 124.5, 120.2, 120.0, 21.6.

(*E*)-3-(4-Methoxyphenyl)-*N*-phenylacrylamide (3c)³:



White solid; Yield = 117 mg (92%); Purification by column chromatography (ethyl acetate/hexane, v/v = 15:85); ¹H NMR (500 MHz, CDCl₃): δ 7.77 (brs, 1H), 7.70 (d, *J* = 16.0 Hz, 1H), 7.62 (brs, 2H), 7.41 (d, *J* = 8.5 Hz, 2H), 7.31 (t, *J* = 7.5 Hz, 2H), 7.10 (t, *J* = 7.0 Hz, 1H), 6.85 (d, *J* = 8.5 Hz, 2H), 6.47 (d, *J* = 15.5 Hz, 1H), 3.80 (s, 3H); ¹³C {¹H} NMR (126 MHz, CDCl₃): δ 164.8, 161.2, 142.2, 138.3, 129.7, 129.2, 127.5, 124.5, 120.2, 118.5, 114.4, 55.5.

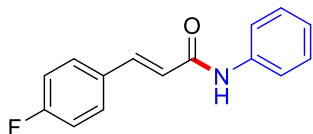
(*E*)-3-([1,1'-Biphenyl]-4-yl)-*N*-phenylacrylamide (3d)¹:



Light yellow solid; Yield = 112 mg (75%); Purification by column chromatography (ethyl acetate/hexane, v/v = 10:90); ¹H NMR (500 MHz, CDCl₃): δ 7.82 (d, *J* = 15.5 Hz, 1H), 7.64-7.60 (m, 8H), 7.46 (t, *J* = 7.5 Hz, 2H), 7.42 (brs, 1H), 7.39 (q, *J* = 7.5 Hz, 3H), 7.14 (t, *J* = 7.5 Hz, 1H), 6.61 (d, *J* = 16.0 Hz, 1H);

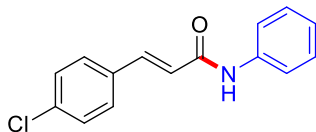
$^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3): δ 164.1, 142.9, 142.2, 140.3, 138.2, 133.7, 129.2, 129.0, 128.6, 128.0, 127.7, 127.2, 124.6, 120.8, 120.1.

(E)-3-(4-Fluorophenyl)-N-phenylacrylamide (3e)³:



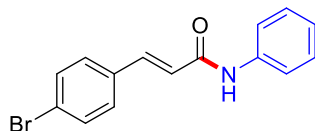
White solid; Yield = 105 mg (87%); Purification by column chromatography (ethyl acetate/hexane, v/v = 10:90); ^1H NMR (500 MHz, CDCl_3): δ 7.71 (d, J = 15.5 Hz, 2H), 7.63 (d, J = 8.0 Hz, 2H), 7.46-7.43 (m, 2H), 7.33 (t, J = 8.0 Hz, 2H), 7.13 (t, J = 7.5 Hz, 1H), 7.03 (t, J = 8.5 Hz, 2H), 6.52 (d, J = 15.0 Hz, 1H); $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3): δ 164.9, 164.2 (d, J = 165.3 Hz), 141.2, 138.3, 131.2 (d, J = 2.9 Hz), 129.9 (d, J = 8.3 Hz), 129.2, 124.7, 120.9, 120.5, 116.2 (d, J = 21.9 Hz); ^{19}F NMR (471 MHz, CDCl_3): δ -110.2.

(E)-3-(4-Chlorophenyl)-N-phenylacrylamide (3f)³:



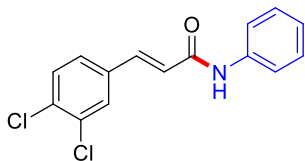
Light yellow solid; Yield = 114 mg (88%); Purification by column chromatography (ethyl acetate/hexane, v/v = 10:90); ^1H NMR (500 MHz, CDCl_3): δ 7.82 (brs, 1H), 7.69 (d, J = 15.5 Hz, 1H), 7.64 (d, J = 6.0 Hz, 2H), 7.38-7.29 (m, 6H), 7.13 (t, J = 7.0 Hz, 1H), 6.58 (d, J = 16.0 Hz, 1H); $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3): δ 163.9, 141.2, 138.1, 136.0, 133.2, 130.2, 129.3, 129.2, 124.7, 121.6, 120.2.

(E)-3-(4-Bromophenyl)-N-phenylacrylamide (3g)¹:



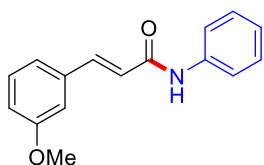
White solid; Yield = 129 mg (85%); Purification by column chromatography (ethyl acetate/hexane, v/v = 10:90); ^1H NMR (500 MHz, CDCl_3): δ 7.68 (d, J = 16.0 Hz, 1H), 7.61 (d, J = 7.0 Hz, 2H), 7.55 (brs, 1H), 7.50 (d, J = 7.5 Hz, 2H), 7.35-7.34 (m, 4H), 7.13 (t, J = 7.0 Hz, 1H), 6.56 (d, J = 15.0 Hz, 1H); $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3): δ 163.8, 141.3, 138.0, 133.7, 132.3, 129.5, 129.3, 124.7, 124.3, 121.6, 120.1.

(E)-3-(3,4-Dichlorophenyl)-N-phenylacrylamide (3h):



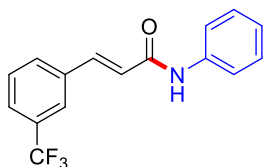
Light brown solid; Yield = 126 mg (86%); Purification by column chromatography (ethyl acetate/hexane, v/v = 10:90); ^1H NMR (500 MHz, CDCl_3): δ 7.84 (brs, 1H), 7.63 (s, 1H), 7.62 (d, $J = 16.0$ Hz, 2H), 7.52 (s, 1H), 7.40 (d, $J = 8.5$ Hz, 1H), 7.33 (t, $J = 8.0$ Hz, 2H), 7.26 (d, $J = 7.0$ Hz, 1H), 7.13 (t, $J = 7.0$ Hz, 1H), 6.58 (d, $J = 15.0$ Hz, 1H); $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3): δ 163.6, 139.9, 138.1, 135.1, 134.1, 133.5, 131.1, 129.6, 129.3, 127.2, 125.0, 123.1, 120.6. HRMS (ESI-TOF) m/z: $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{15}\text{H}_{12}\text{Cl}_2\text{NO}^+$ 292.0290; found 292.0288.

(E)-3-(3-Methoxyphenyl)-N-phenylacrylamide (3i):



Colorless liquid; Yield = 107 mg (84%); Purification by column chromatography (ethyl acetate/hexane, v/v = 15:85); ^1H NMR (500 MHz, CDCl_3): δ 7.86 (brs, 1H), 7.72 (d, $J = 15.5$ Hz, 1H), 7.65 (d, $J = 6.5$ Hz, 2H), 7.32 (t, $J = 8.0$ Hz, 2H), 7.25 (t, $J = 8.0$ Hz, 1H), 7.12 (t, $J = 7.5$ Hz, 1H), 7.08 (d, $J = 7.5$ Hz, 1H), 6.99 (s, 1H), 6.91 (dd, $J = 2.0$ Hz, $J' = 2.0$ Hz, 1H), 6.61 (d, $J = 15.5$ Hz, 1H), 3.78 (s, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3): δ 164.3, 160.0, 142.4, 138.2, 136.1, 130.0, 129.2, 124.6, 121.4, 120.6, 120.2, 115.9, 113.2, 55.4. HRMS (ESI-TOF) m/z: $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{16}\text{H}_{16}\text{NO}_2^+$ 254.1176; found 254.1171.

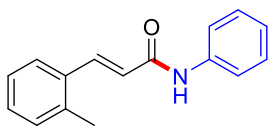
(E)-N-Phenyl-3-(3-(trifluoromethyl)phenyl)acrylamide (3j):



Yellow solid; Yield = 115 mg (79%); Purification by column chromatography (ethyl acetate/hexane, v/v = 10:90); ^1H NMR (500 MHz, CDCl_3): δ 8.03 (brs, 1H), 7.76 (d, $J = 15.5$ Hz, 1H), 7.70 (s, 1H), 7.67 (d, $J = 7.5$ Hz, 2H), 7.58 (d, $J = 7.5$ Hz, 2H), 7.44 (t, $J = 8.0$ Hz, 1H), 7.33 (t, $J = 8.0$ Hz, 2H), 7.13 (t, $J = 7.5$ Hz, 1H), 6.71 (d, $J = 15.5$ Hz, 1H); $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3): δ 163.8, 140.7, 138.0, 135.5, 131.6, 131.3, 129.5, 129.2, 126.4 (d, $J = 2.9$ Hz), 125.0, 124.8, 124.3 (d, $J = 3.0$ Hz), 123.0, 122.8, 120.3; ^{19}F NMR (471 MHz, CDCl_3): δ -62.7. HRMS

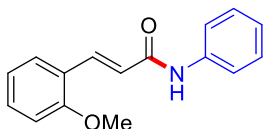
(ESI-TOF) m/z : $[M + H]^+$ calcd for $C_{16}H_{13}F_3NO^+$ 292.0944; found 292.0944.

(E)-N-Phenyl-3-(*o*-tolyl)acrylamide (3k)¹:



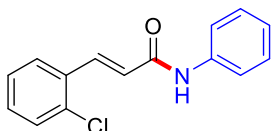
Light yellow solid; Yield = 103 mg (87%); Purification by column chromatography (ethyl acetate/hexane, v/v = 10:90); ¹H NMR (600 MHz, CDCl₃): δ 8.06 (d, J = 12.5 Hz, 1H), 7.96 (brs, 1H), 7.68 (d, J = 5.5 Hz, 2H), 7.50 (d, J = 6.5 Hz, 1H), 7.33 (t, J = 7.0 Hz, 2H), 7.24 (t, J = 6.0 Hz, 1H), 7.18 (d, J = 6.0 Hz, 1H), 7.15-7.10 (m, 2H), 6.54 (d, J = 13.0 Hz, 1H), 2.38 (s, 3H); ¹³C{¹H} NMR (151 MHz, CDCl₃): δ 164.5, 140.2, 138.3, 137.9, 133.7, 130.9, 129.8, 129.2, 126.3, 126.3, 124.5, 122.1, 120.2, 19.9.

(E)-3-(2-Methoxyphenyl)-N-phenylacrylamide (3l)¹:



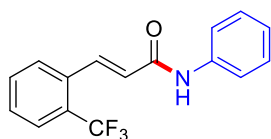
White solid; Yield = 115 mg (91%); Purification by column chromatography (ethyl acetate/hexane, v/v = 15:85); ¹H NMR (500 MHz, CDCl₃): δ 8.28 (brs, 1H), 8.07 (d, J = 15.5 Hz, 1H), 7.71 (d, J = 7.0 Hz, 2H), 7.42 (d, J = 7.0 Hz, 1H), 7.31 (q, J = 8.0 Hz, 3H), 7.08 (t, J = 7.5 Hz, 1H), 6.85-6.83 (m, 2H), 6.82 (d, J = 15.5 Hz, 1H), 3.77 (s, 3H); ¹³C{¹H} NMR (126 MHz, CDCl₃): δ 165.2, 158.7, 138.7, 137.7, 131.0, 129.1, 129.0, 124.3, 124.2, 122.1, 120.9, 120.5, 111.6, 55.6.

(E)-3-(2-Chlorophenyl)-N-phenylacrylamide (3m):



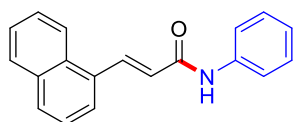
Yellow solid; Yield = 104 mg (81%); Purification by column chromatography (ethyl acetate/hexane, v/v = 12:88); ¹H NMR (500 MHz, CDCl₃): δ 8.14 (d, J = 16.0 Hz, 1H), 7.65 (d, J = 7.0 Hz, 3H), 7.58 (d, J = 7.5 Hz, 1H), 7.42 (d, J = 8.0 Hz, 1H), 7.34 (t, J = 8.0 Hz, 2H), 7.29 (t, J = 7.0 Hz, 1H), 7.24 (t, J = 7.5 Hz, 1H), 7.13 (t, J = 7.5 Hz, 1H), 6.60 (d, J = 15.0 Hz, 1H); ¹³C{¹H} NMR (126 MHz, CDCl₃): δ 163.7, 138.4, 138.0, 135.1, 133.1, 130.8, 130.4, 129.2, 127.8, 127.1, 124.7, 123.9, 120.1. HRMS (ESI-TOF) m/z : $[M + H]^+$ calcd for $C_{15}H_{13}ClNO^+$ 258.0680; found 258.0676.

(E)-N-Phenyl-3-(2-(trifluoromethyl)phenyl)acrylamide (3n):



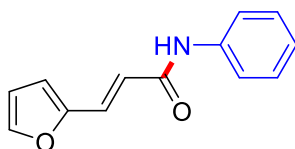
Light yellow solid; Yield = 108 mg (74%); Purification by column chromatography (ethyl acetate/hexane, v/v = 15:85); ^1H NMR (500 MHz, CDCl_3): δ 8.13 (d, $J = 15.0$ Hz, 1H), 7.75 (brs, 1H), 7.70 (d, $J = 7.5$ Hz, 1H), 7.64 (d, $J = 6.5$ Hz, 3H), 7.51 (t, $J = 7.5$ Hz, 1H), 7.45 (t, $J = 7.5$ Hz, 1H), 7.33 (t, $J = 7.5$ Hz, 2H), 7.12 (t, $J = 7.0$ Hz, 1H), 6.56 (d, $J = 15.5$ Hz, 1H); $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3): δ 163.4, 138.0 (d, $J = 17.3$ Hz), 133.9, 132.1, 129.4, 129.2, 128.0, 126.4 (q, $J = 4.8$ Hz), 125.6, 125.2, 124.8, 124.7 (q, $J = 108.9$ Hz), 120.7, 120.2; ^{19}F NMR (471 MHz, CDCl_3): δ -58.9. HRMS (ESI-TOF) m/z: $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{16}\text{H}_{13}\text{F}_3\text{NO}^+$ 292.0944; found 292.0939.

(E)-3-(Naphthalen-1-yl)-N-phenylacrylamide (3o)³:



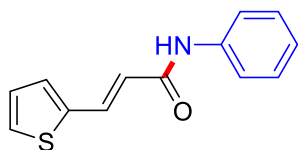
Light yellow solid; Yield = 97 mg (71%); Purification by column chromatography (ethyl acetate/hexane, v/v = 10:90); ^1H NMR (500 MHz, CDCl_3): δ 8.62 (d, $J = 15.0$ Hz, 1H), 8.24 (d, $J = 8.0$ Hz, 1H), 7.90-7.87 (m, 2H), 7.74 (d, $J = 6.5$ Hz, 1H), 7.66 (s, 2H), 7.58-7.52 (m, 3H), 7.47 (t, $J = 7.0$ Hz, 2H), 7.37 (t, $J = 8.0$ Hz, 2H), 7.15 (t, $J = 7.0$ Hz, 1H), 6.65 (d, $J = 14.5$ Hz, 1H); $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3): δ 164.0, 139.9, 138.2, 133.8, 132.3, 131.7, 130.4, 129.3, 128.8, 127.0, 126.4, 125.5, 124.9, 124.7, 123.8, 120.1.

(E)-3-(Furan-2-yl)-N-phenylacrylamide (3p)¹:



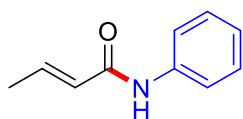
Light brown solid; Yield = 88 mg (83%); Purification by column chromatography (ethyl acetate/hexane, v/v = 12:88); ^1H NMR (500 MHz, CDCl_3): δ 8.17 (brs, 1H), 7.64 (d, $J = 7.0$ Hz, 2H), 7.52 (d, $J = 15.0$ Hz, 1H), 7.37 (s, 1H), 7.28 (t, $J = 8.0$ Hz, 2H), 7.09 (t, $J = 7.5$ Hz, 1H), 6.59 (d, $J = 15.0$ Hz, 1H), 6.48 (d, $J = 3.0$ Hz, 1H), 6.42 (d, $J = 4.0$ Hz, 1H); $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3): δ 164.6, 151.3, 144.3, 138.3, 129.0, 128.9, 124.4, 120.3, 119.0, 114.4, 112.3.

(E)-N-Phenyl-3-(thiophen-2-yl)acrylamide (3q)¹:



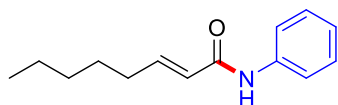
White solid; Yield = 100 mg (87%); Purification by column chromatography (ethyl acetate/hexane, v/v = 12:88); ¹H NMR (500 MHz, CDCl₃): δ 8.06 (brs, 1H), 7.87 (d, *J* = 15.5 Hz, 1H), 7.65 (d, *J* = 7.0 Hz, 2H), 7.32-7.28 (m, 3H), 7.14 (d, *J* = 3.5 Hz, 1H), 7.10 (t, *J* = 7.5 Hz, 1H), 7.01-6.99 (m, 1H), 6.47 (d, *J* = 16.0 Hz, 1H); ¹³C{¹H} NMR (126 MHz, CDCl₃): δ 164.3, 139.9, 138.2, 135.0, 130.8, 129.1, 128.2, 127.8, 124.5, 120.3, 120.0.

(E)-N-Phenylbut-2-enamide (3r)⁴:



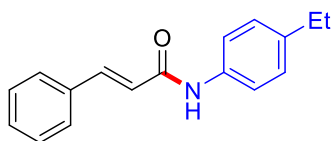
White solid; Yield = 64 mg (79%); Purification by column chromatography (ethyl acetate/hexane, v/v = 10:90); ¹H NMR (500 MHz, CDCl₃): δ 7.74 (brs, 1H), 7.58 (d, *J* = 7.5 Hz, 2H), 7.30 (t, *J* = 8.0 Hz, 2H), 7.09 (t, *J* = 7.5 Hz, 1H), 7.00-6.93 (m, 1H), 6.01-5.97 (m, 1H), 1.87-1.86 (m, 3H); ¹³C{¹H} NMR (126 MHz, CDCl₃): δ 164.4, 141.6, 138.2, 129.0, 125.6, 124.3, 120.2, 17.9.

(E)-N-Phenyl-oct-2-enamide (3s):



Brown oil; Yield = 77 mg (71%); Purification by column chromatography (ethyl acetate/hexane, v/v = 15:85); ¹H NMR (500 MHz, CDCl₃): δ 7.58 (d, *J* = 7.0 Hz, 2H), 7.41 (brs, 1H), 7.31 (t, *J* = 8.0 Hz, 2H), 7.10 (t, *J* = 7.5 Hz, 1H), 7.01-6.95 (m, 1H), 5.95 (d, *J* = 14.5 Hz, 1H), 2.23 (q, *J* = 7.0 Hz, 2H), 1.49-1.44 (m, 2H), 1.32-1.29 (m, 4H), 0.90 (t, *J* = 7.0 Hz, 3H); ¹³C{¹H} NMR (126 MHz, CDCl₃): δ 164.3, 146.8, 138.2, 129.1, 124.3, 124.0, 120.0, 32.2, 31.5, 28.0, 22.6, 14.1. HRMS (ESI-TOF) *m/z*: [M + H]⁺ calcd for C₁₄H₂₀NO⁺ 218.1539; found 218.1529.

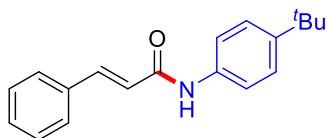
N-(4-Ethylphenyl)cinnamamide (3t)²:



Yellow solid; Yield = 113 mg (90%); Purification by column chromatography (ethyl acetate/hexane, v/v = 10:90); ¹H NMR (500 MHz, CDCl₃): δ 8.27 (brs, 1H), 7.74 (d, *J* = 16.0 Hz, 1H), 7.60 (d, *J* = 8.0 Hz, 2H), 7.42 (d, *J* = 8.0 Hz, 2H), 7.33-7.27 (m,

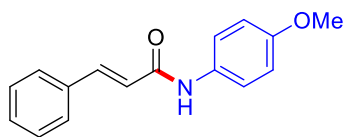
3H), 7.14 (d, $J = 8.0$ Hz, 2H), 6.69 (d, $J = 15.5$ Hz, 1H), 2.62 (q, $J = 7.5$ Hz, 2H), 1.22 (t, $J = 8.0$ Hz, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3): δ 164.5, 142.0, 140.6, 135.9, 134.8, 129.9, 128.9, 128.4, 128.0, 121.3, 120.5, 28.4, 15.7.

***N*-(4-(*Tert*-butyl)phenyl)cinnamamide (3u):**



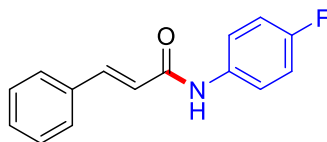
Light yellow solid; Yield = 127 mg (91%); Purification by column chromatography (ethyl acetate/hexane, v/v = 10:90); ^1H NMR (500 MHz, CDCl_3): δ 8.93 (brs, 1H), 7.75 (d, $J = 16.0$ Hz, 1H), 7.69 (d, $J = 8.5$ Hz, 2H), 7.36 (d, $J = 7.5$ Hz, 2H), 7.32 (d, $J = 8.0$ Hz, 2H), 7.28 (d, $J = 7.5$ Hz, 1H), 7.24-7.19 (m, 2H), 6.82 (d, $J = 16.0$ Hz, 1H), 1.28 (s, 9H); $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3): δ 164.9, 147.4, 141.9, 135.8, 134.8, 129.8, 128.8, 128.0, 125.9, 121.5, 120.4, 34.4, 31.4. HRMS (ESI-TOF) m/z : $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{19}\text{H}_{22}\text{NO}^+$ 280.1696; found 280.1686.

***N*-(4-Methoxyphenyl)cinnamamide (3v)²:**



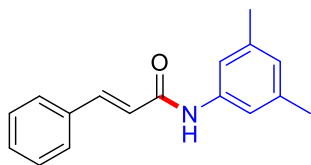
Light brown solid; Yield = 115 mg (91%); Purification by column chromatography (ethyl acetate/hexane, v/v = 15:85); ^1H NMR (500 MHz, CDCl_3): δ 7.81 (brs, 1H), 7.74 (d, $J = 15.5$ Hz, 1H), 7.55 (d, $J = 8.5$ Hz, 2H), 7.47-7.46 (m, 2H), 7.34-7.32 (m, 3H), 6.86 (d, $J = 8.5$ Hz, 2H), 6.60 (d, $J = 15.5$ Hz, 1H), 3.77 (s, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3): δ 164.2, 156.6, 142.0, 134.8, 131.4, 130.0, 129.0, 128.0, 122.0, 121.2, 114.3, 55.6.

***N*-(4-Fluorophenyl)cinnamamide (3w)²:**



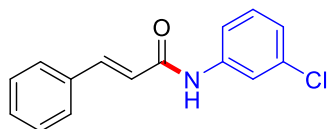
Light brown solid; Yield = 106 mg (88%); Purification by column chromatography (ethyl acetate/hexane, v/v = 10:90); ^1H NMR (500 MHz, CDCl_3): δ 7.88 (brs, 1H), 7.76 (d, $J = 16.0$ Hz, 1H), 7.59 (brs, 2H), 7.47-7.46 (m, 2H), 7.35 (d, $J = 7.0$ Hz, 3H), 7.01 (t, $J = 9.0$ Hz, 2H), 6.61 (d, $J = 16.0$ Hz, 1H); $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3): δ 164.3, 160.6 (d, $J = 243.5$ Hz), 142.6, 134.6, 134.2, 130.2, 129.0, 128.1, 122.0 (d, $J = 6.8$ Hz), 120.8, 115.9 (d, $J = 22.3$ Hz); ^{19}F NMR (471 MHz, CDCl_3): δ -117.6.

***N*-(3,5-Dimethylphenyl)cinnamamide (3x)⁶:**



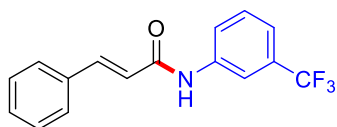
Yellow solid; Yield = 111 mg (88%); Purification by column chromatography (ethyl acetate/hexane, v/v = 10:90); ¹H NMR (500 MHz, CDCl₃): δ 8.02 (brs, 1H), 7.75 (d, *J* = 15.0 Hz, 1H), 7.46 (d, *J* = 8.5 Hz, 2H), 7.33-7.31 (m, 5H), 6.75 (s, 1H), 6.66 (d, *J* = 15.5 Hz, 1H), 2.26 (s, 6H); ¹³C{¹H} NMR (126 MHz, CDCl₃): δ 164.4, 142.1, 138.8, 138.1, 134.8, 129.9, 128.9, 128.0, 126.3, 121.3, 118.1, 21.4.

***N*-(3-Chlorophenyl)cinnamamide (3y)⁵:**



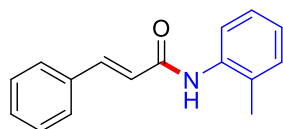
Yellow solid; Yield = 108 mg (84%); Purification by column chromatography (ethyl acetate/hexane, v/v = 10:90); ¹H NMR (500 MHz, CDCl₃): δ 8.33 (brs, 1H), 7.77 (s, 1H), 7.75 (d, *J* = 15.0 Hz, 1H), 7.54 (d, *J* = 8.0 Hz, 1H), 7.42 (d, *J* = 7.5 Hz, 2H), 7.33-7.28 (m, 3H), 7.21 (t, *J* = 8.0 Hz, 1H), 7.08 (d, *J* = 8.0 Hz, 1H), 6.66 (d, *J* = 15.0 Hz, 1H); ¹³C{¹H} NMR (126 MHz, CDCl₃): δ 164.8, 143.0, 139.4, 134.8, 134.5, 130.2, 130.1, 129.0, 128.1, 124.6, 120.6, 120.4, 118.4.

***N*-(3-(Trifluoromethyl)phenyl)cinnamamide (3z)⁵:**



White solid; Yield = 118 mg (81%); Purification by column chromatography (ethyl acetate/hexane, v/v = 10:90); ¹H NMR (500 MHz, CDCl₃): δ 8.54 (brs, 1H), 7.96 (s, 1H), 7.89 (d, *J* = 8.0 Hz, 1H), 7.78 (d, *J* = 16.0 Hz, 1H), 7.42 (d, *J* = 7.0 Hz, 2H), 7.38 (d, *J* = 8.0 Hz, 1H), 7.34-7.32 (m, 2H), 7.29 (t, *J* = 7.5 Hz, 2H), 6.70 (d, *J* = 15.0 Hz, 1H); ¹³C{¹H} NMR (126 MHz, CDCl₃): δ 165.0, 143.3, 138.7, 134.4, 131.9 (q, *J* = 32.2 Hz), 130.3, 129.7, 129.0, 128.1, 127.2 (q, *J* = 272.9 Hz), 123.4, 122.9, 121.1, 120.5, 117.1; ¹⁹F NMR (471 MHz, CDCl₃): δ -62.6.

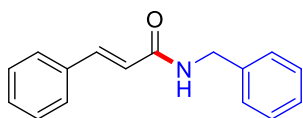
***N*-(*o*-Tolyl)cinnamamide (3aa)²:**



White solid; Yield = 102 mg (86%); Purification by column chromatography (ethyl acetate/hexane, v/v = 10:90); ¹H NMR (500 MHz, CDCl₃): δ 7.94 (brs, 1H), 7.77 (d, *J* = 15.5 Hz, 1H), 7.52 (s, 2H), 7.37 (s, 3H), 7.28 (brs, 1H), 7.25-7.20 (m, 2H), 7.10

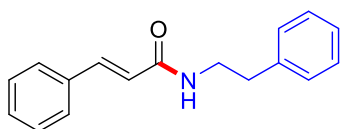
(brs, 1H), 6.62 (d, $J = 15.0$ Hz, 1H), 2.31 (s, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3): δ 164.4, 142.3, 135.9, 134.8, 130.6, 130.0, 128.9, 128.1, 126.8, 125.5, 123.6, 121.0, 18.0.

***N*-Benzylcinnamamide (3ab):**



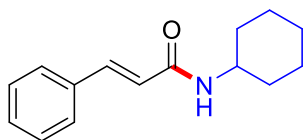
White solid; Yield = 101 mg (85%); Purification by column chromatography (ethyl acetate/hexane, v/v = 12:88); ^1H NMR (500 MHz, CDCl_3): δ 7.68 (d, $J = 16.0$ Hz, 1H), 7.49-7.47 (m, 2H), 7.35-7.28 (m, 8H), 6.45 (d, $J = 16.0$ Hz, 1H), 6.12 (brs, 1H), 4.56 (d, $J = 5.5$ Hz, 2H); $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3): δ 166.1, 141.3, 138.3, 134.9, 129.8, 128.9, 128.8, 127.9, 127.9, 127.6, 120.7, 43.8. HRMS (ESI-TOF) m/z : $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{16}\text{H}_{16}\text{NO}^+$ 238.1226; found 238.1224.

***N*-Phenethylcinnamamide (3ac):**



Light yellow solid; Yield = 99 mg (79%); Purification by column chromatography (ethyl acetate/hexane, v/v = 20:80); ^1H NMR (500 MHz, CDCl_3): δ 7.64 (d, $J = 15.5$ Hz, 1H), 7.48 (dd, $J = 3.5$ Hz, $J' = 2.0$ Hz, 2H), 7.36-7.34 (m, 3H), 7.32 (d, $J = 7.5$ Hz, 2H), 7.26-7.22 (m, 3H), 6.37 (d, $J = 15.5$ Hz, 1H), 5.86 (brs, 1H), 3.68 (q, $J = 7.0$ Hz, 2H), 2.90 (t, $J = 7.0$ Hz, 2H); $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3): δ 166.0, 141.1, 139.0, 134.9, 129.8, 128.9, 128.8, 127.9, 126.7, 120.8, 41.0, 35.8. HRMS (ESI-TOF) m/z : $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{17}\text{H}_{18}\text{NO}^+$ 252.1383; found 252.1382.

***N*-Cyclohexylcinnamamide (3ad):**



White solid; Yield = 89 mg (78%); Purification by column chromatography (ethyl acetate/hexane, v/v = 12:88); ^1H NMR (500 MHz, CDCl_3): δ 7.62 (d, $J = 16.0$ Hz, 1H), 7.48-7.47 (m, 2H), 7.35-7.32 (m, 3H), 6.42 (d, $J = 15.0$ Hz, 1H), 5.76 (d, $J = 7.5$ Hz, 1H), 3.95-3.87 (m, 1H), 2.00-1.97 (m, 2H), 1.74-1.70 (m, 2H), 1.64-1.60 (m, 1H), 1.43-1.34 (m, 2H), 1.23-1.15 (m, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3): δ 165.1, 140.7, 135.1, 129.6, 128.9, 127.8, 121.4, 48.5, 33.3, 25.7, 25.0. HRMS (ESI-TOF) m/z : $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{15}\text{H}_{20}\text{NO}^+$ 230.1539; found 230.1537.

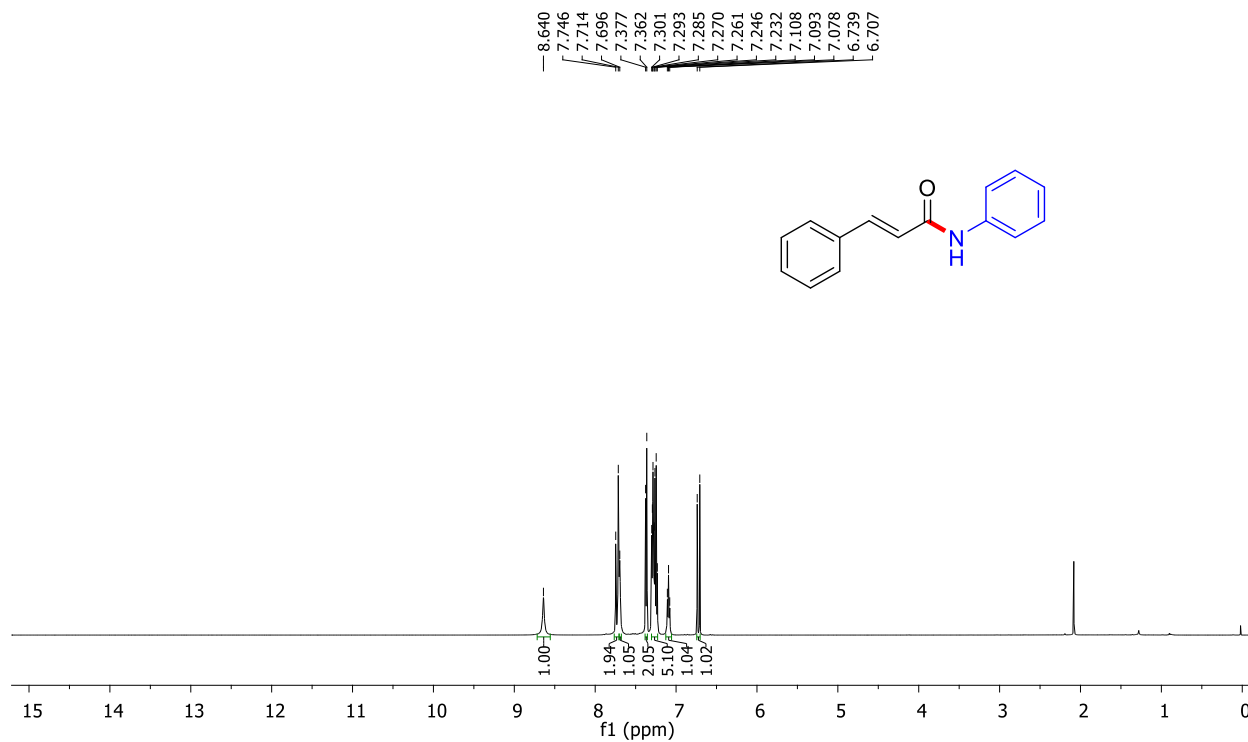
2. References

1. B. K. Pandia, C. Gunanathan, *J. Org. Chem.* 2021, **86**, 9994–10005.
2. J. B. Peng, H. Q. Geng, D. Li, X. Qi, J. Ying, X. F. Wu, *Org. Lett.* 2018, **20**, 4988–4993.
3. S. Verma, V. Singh, J. L. Jat, B. Tiwari *J. Org. Chem.* 2024, **89**, 8201–8207.
4. R. -H. A, J. Zhang, X. -F. Wu, *Chem. Sci.* 2025, **16**, 22168–22173.
5. Y. Luo, X. Wang, Q. Liu, Y. He, J. Li, S. Luo, Q. Zhu, *Green Chem.* 2023, **25**, 1120–1127.
6. T. T. S. Lew, D. S. W. Lim, Y. Zhang, *Green Chem.* 2015, **17**, 5140–5143.

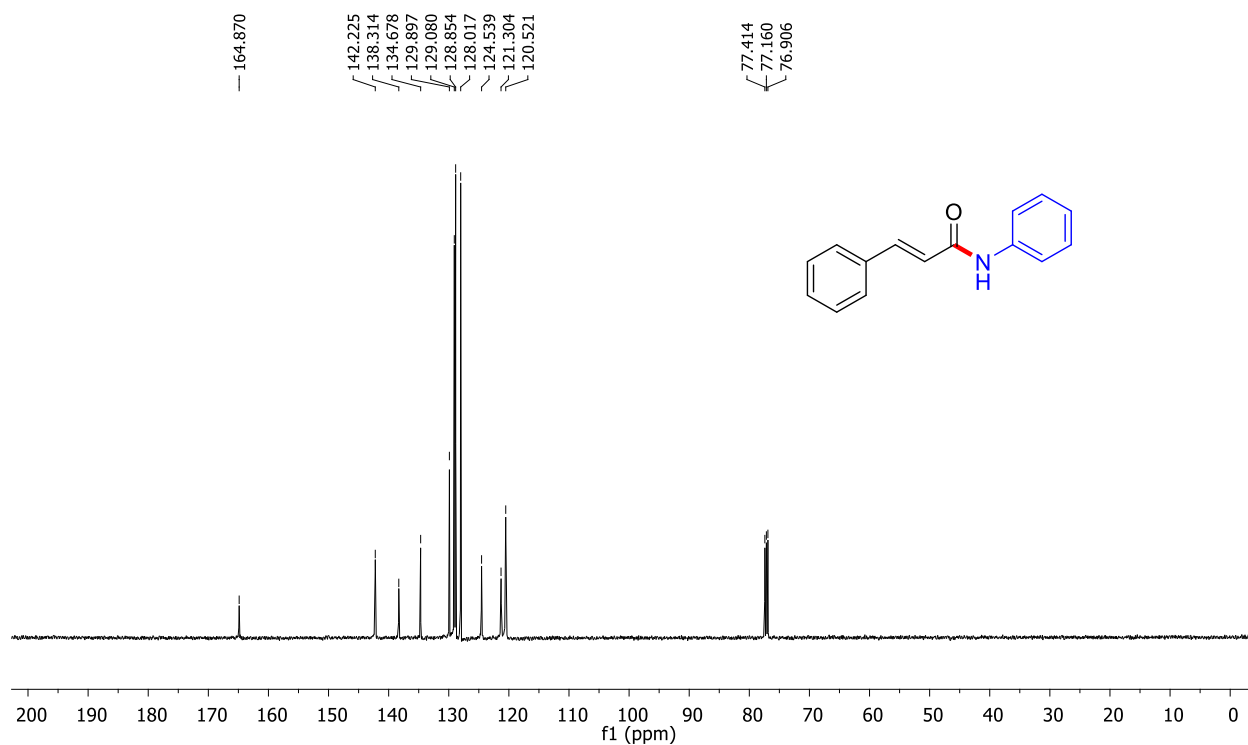
3. Copies of ^1H , $^{13}\text{C}\{^1\text{H}\}$, and ^{19}F Spectra of the Products 3.

N-Phenylcinnamamide (3a):

^1H NMR (500 MHz, CDCl_3)

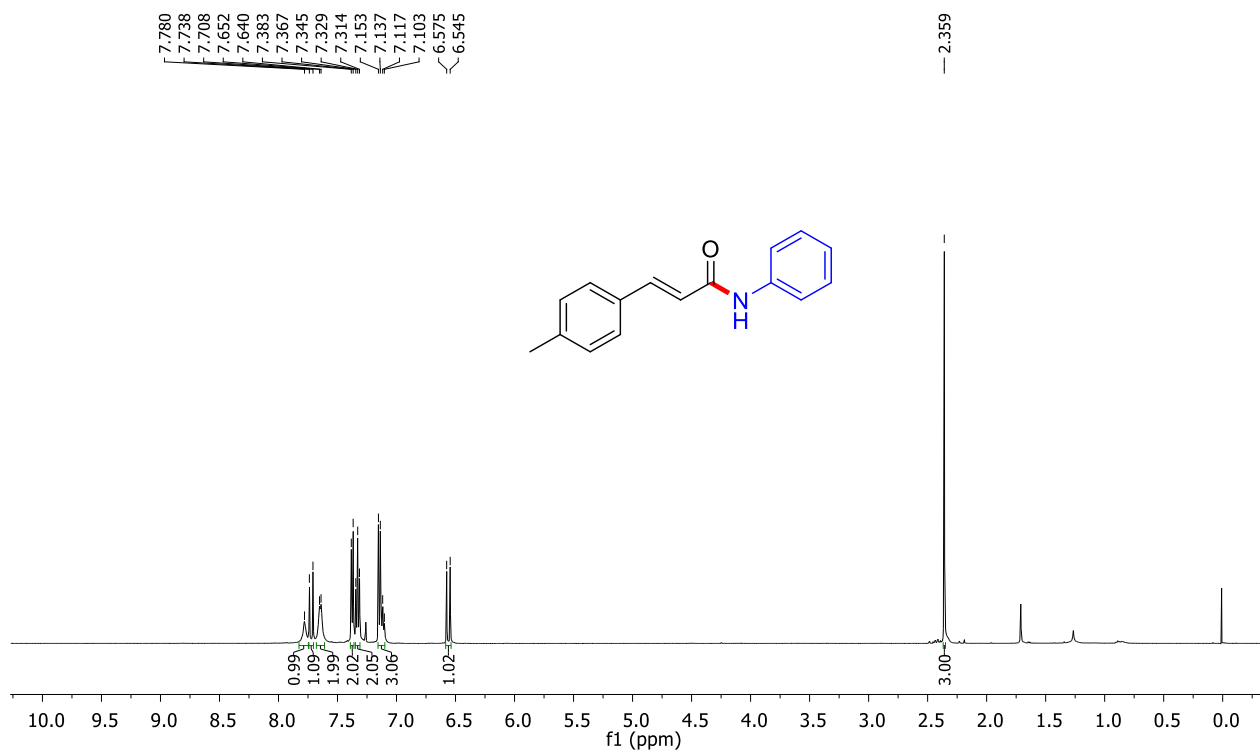


$^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3)

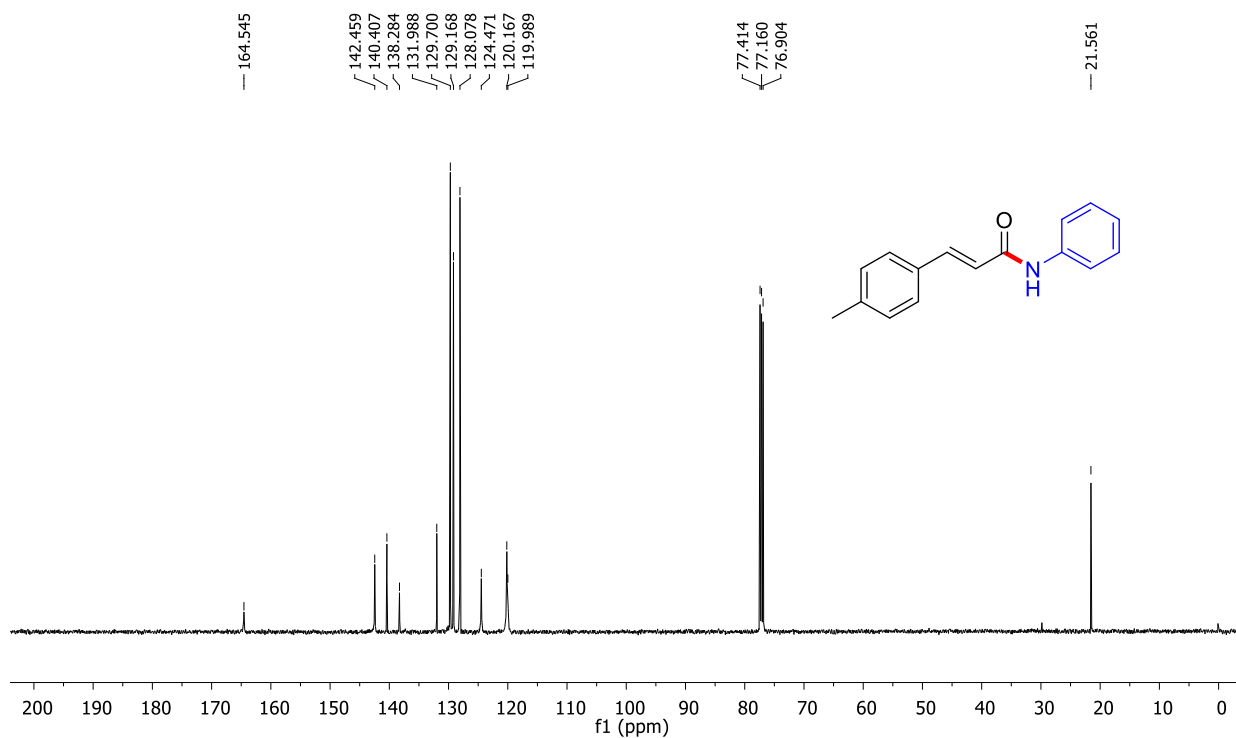


(E)-N-Phenyl-3-(p-tolyl)acrylamide (3b):

^1H NMR (500 MHz, CDCl_3)

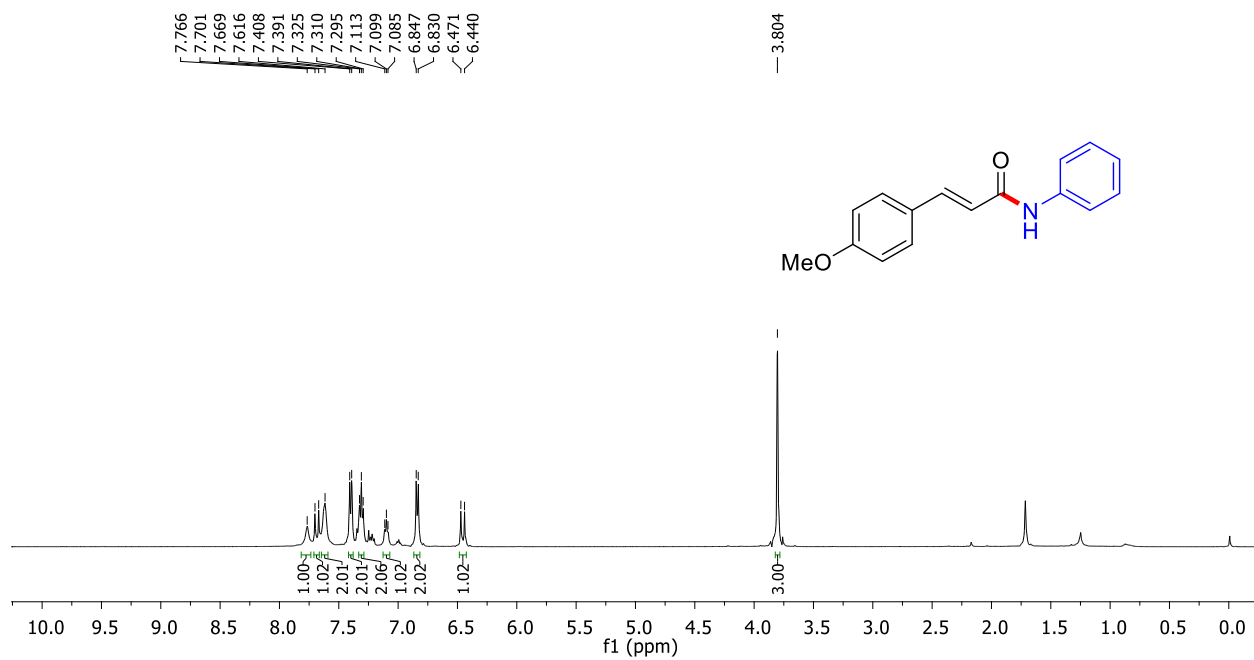


$^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3)

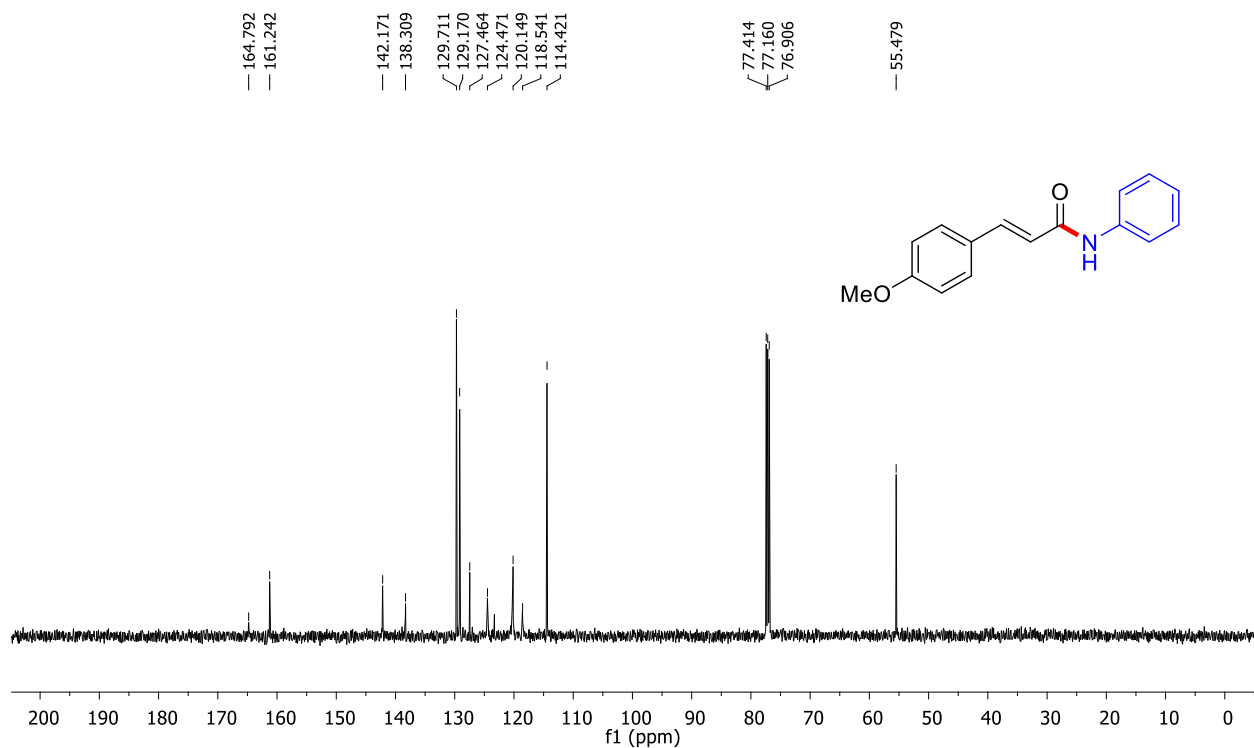


(E)-3-(4-Methoxyphenyl)-N-phenylacrylamide (3c):

^1H NMR (500 MHz, CDCl_3)

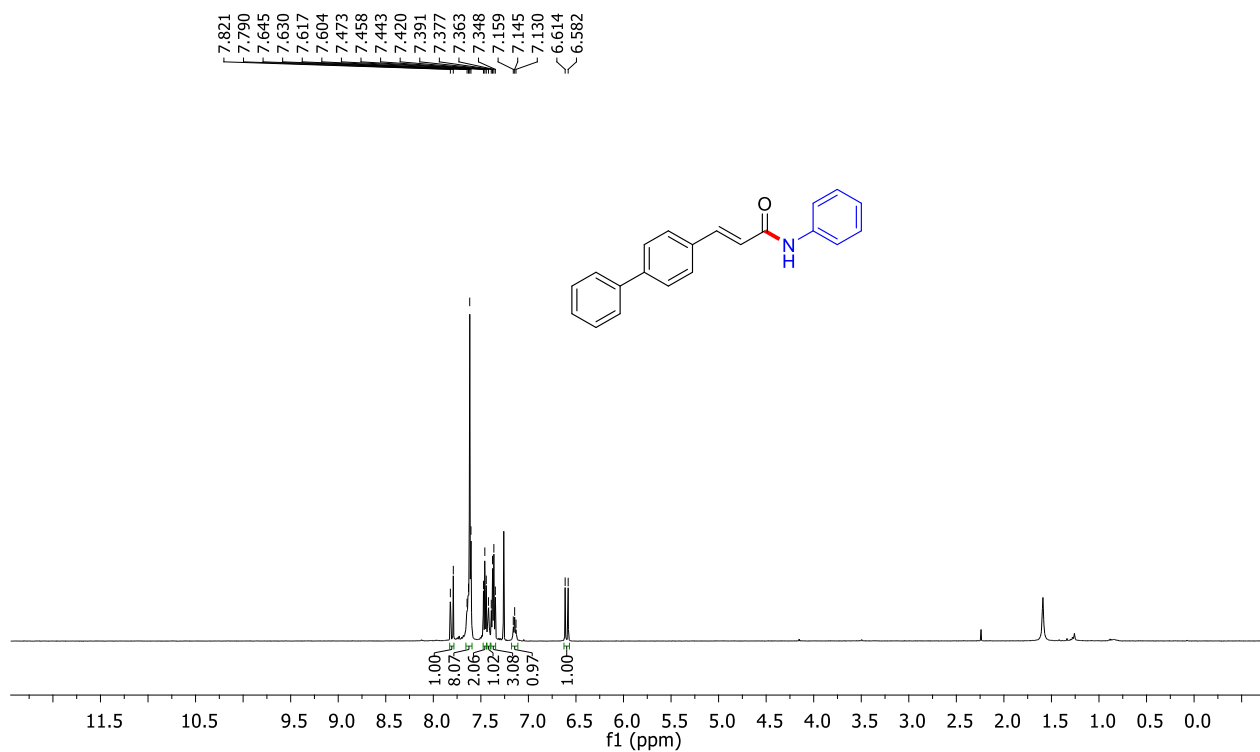


$^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3)

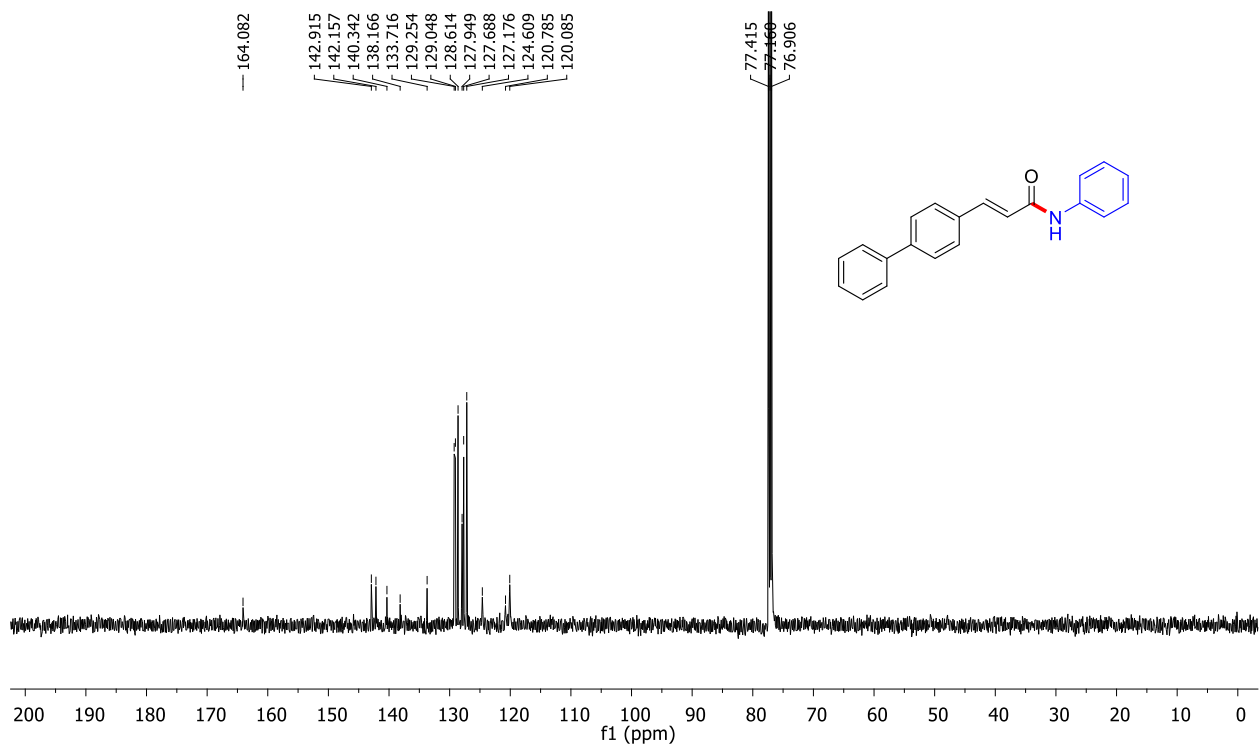


(E)-3-([1,1'-Biphenyl]-4-yl)-N-phenylacrylamide (3d):

¹H NMR (500 MHz, CDCl₃)

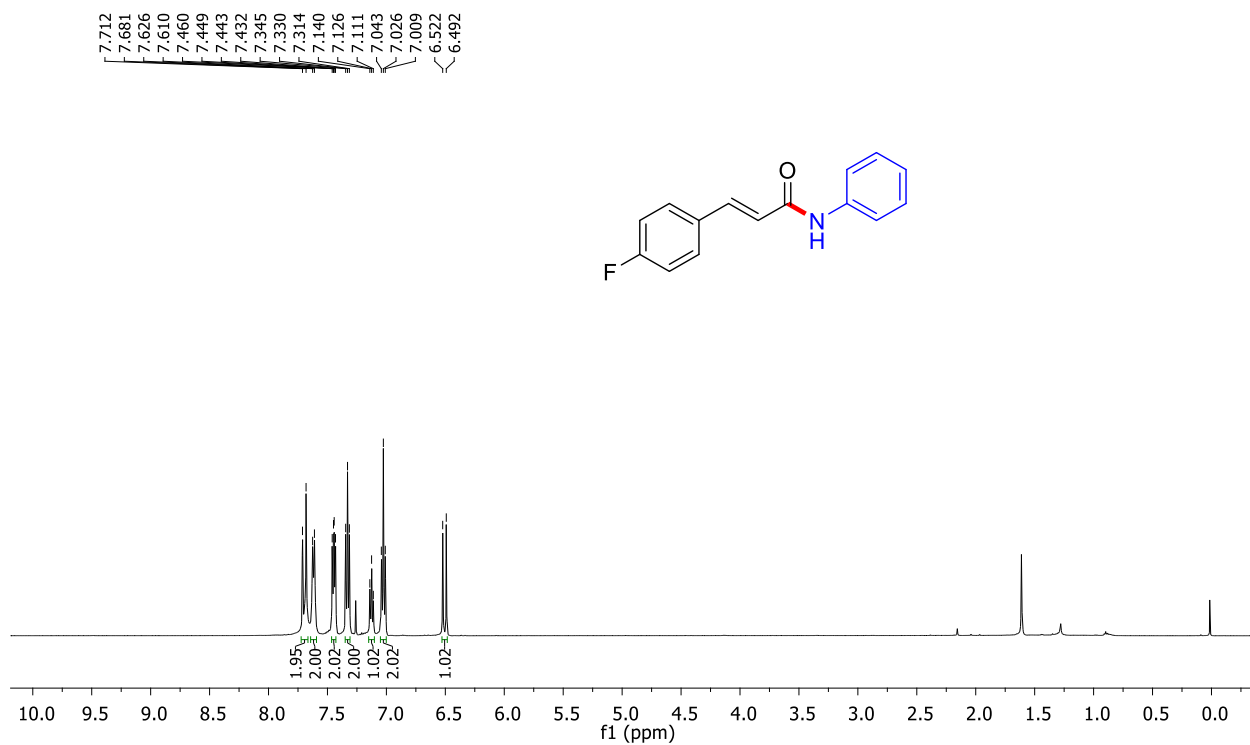


¹³C{¹H} NMR (126 MHz, CDCl₃)

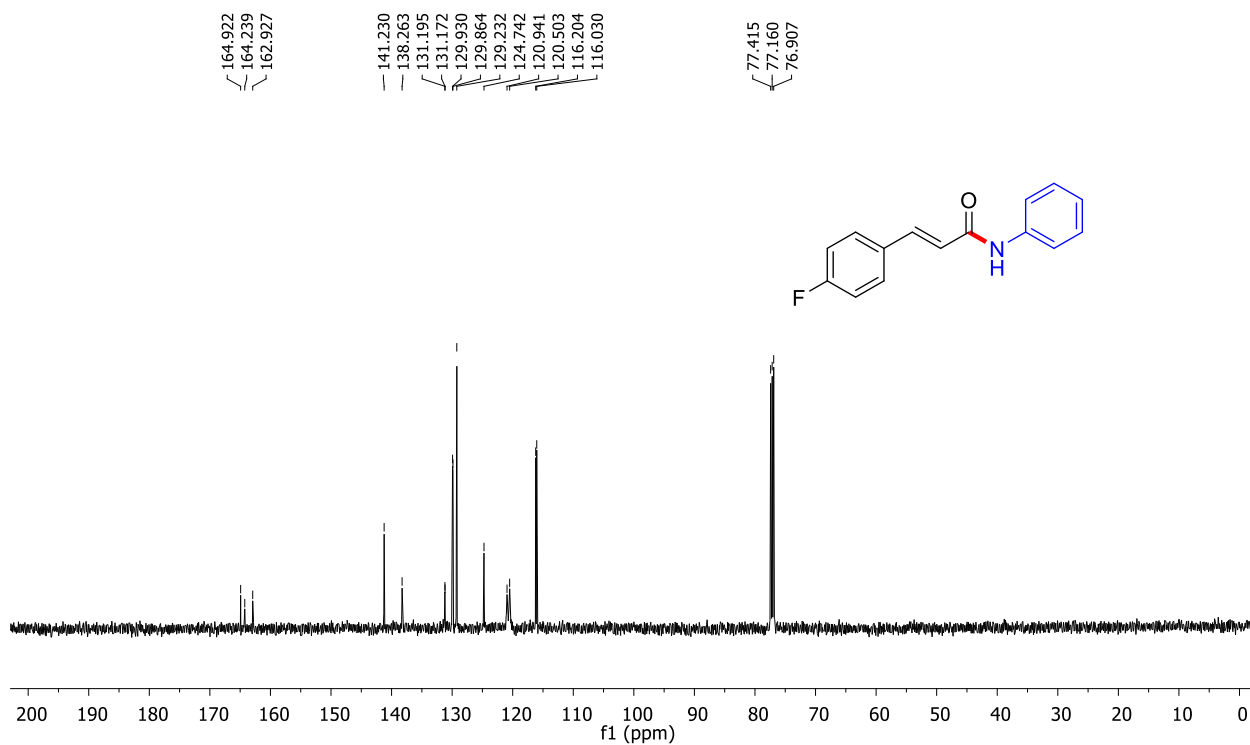


(E)-3-(4-Fluorophenyl)-N-phenylacrylamide (3e):

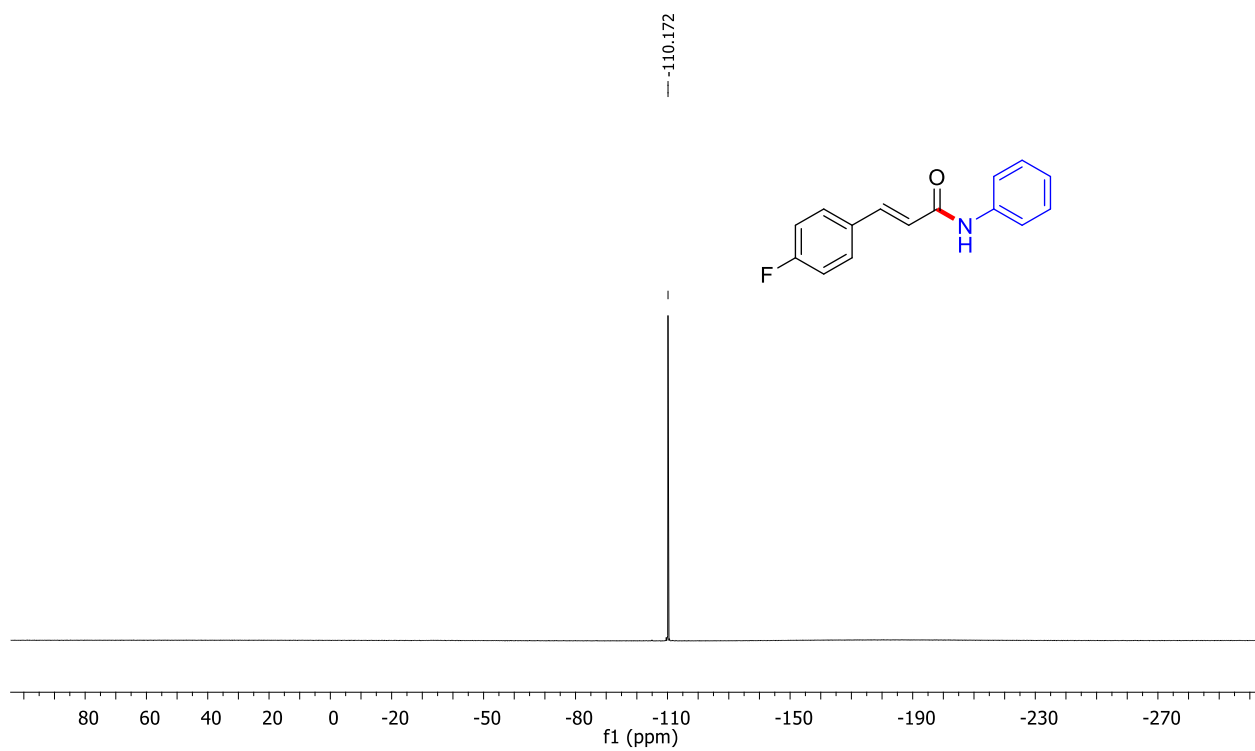
^1H NMR (500 MHz, CDCl_3)



$^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3)

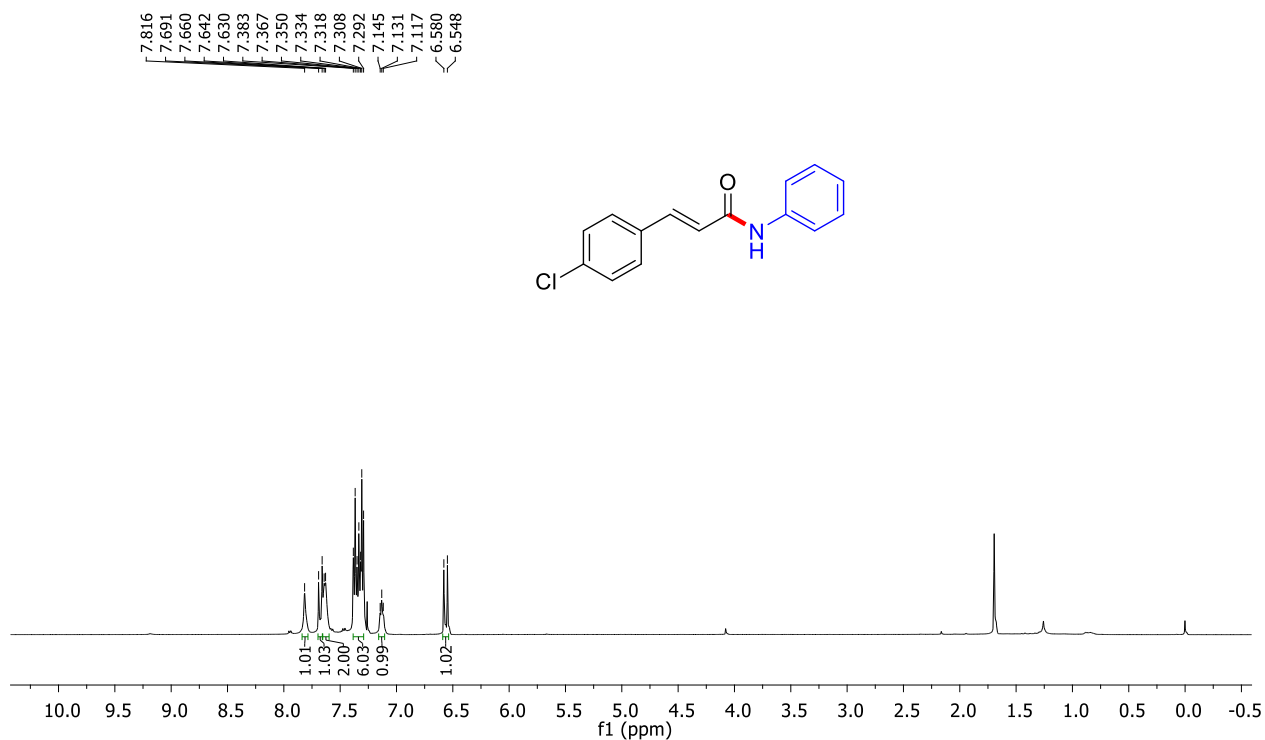


^{19}F NMR (471 MHz, CDCl_3)

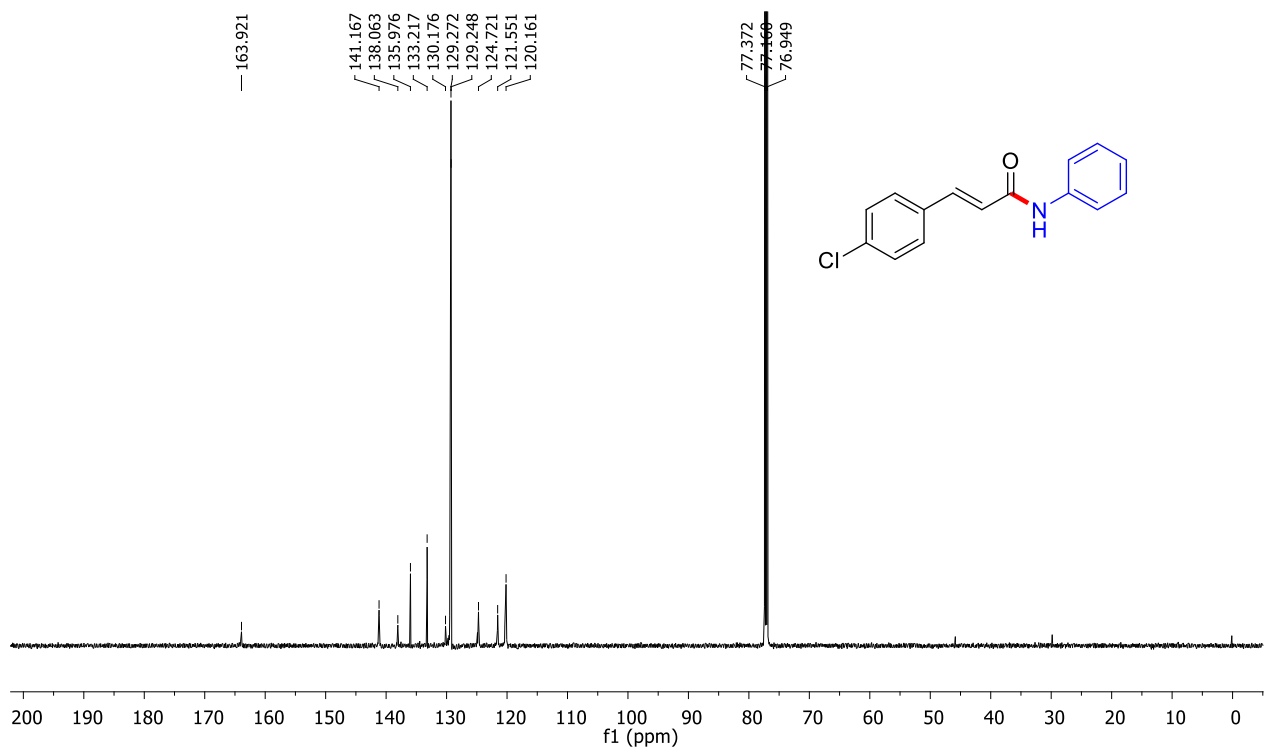


(E)-3-(4-Chlorophenyl)-N-phenylacrylamide (3f):

^1H NMR (500 MHz, CDCl_3)

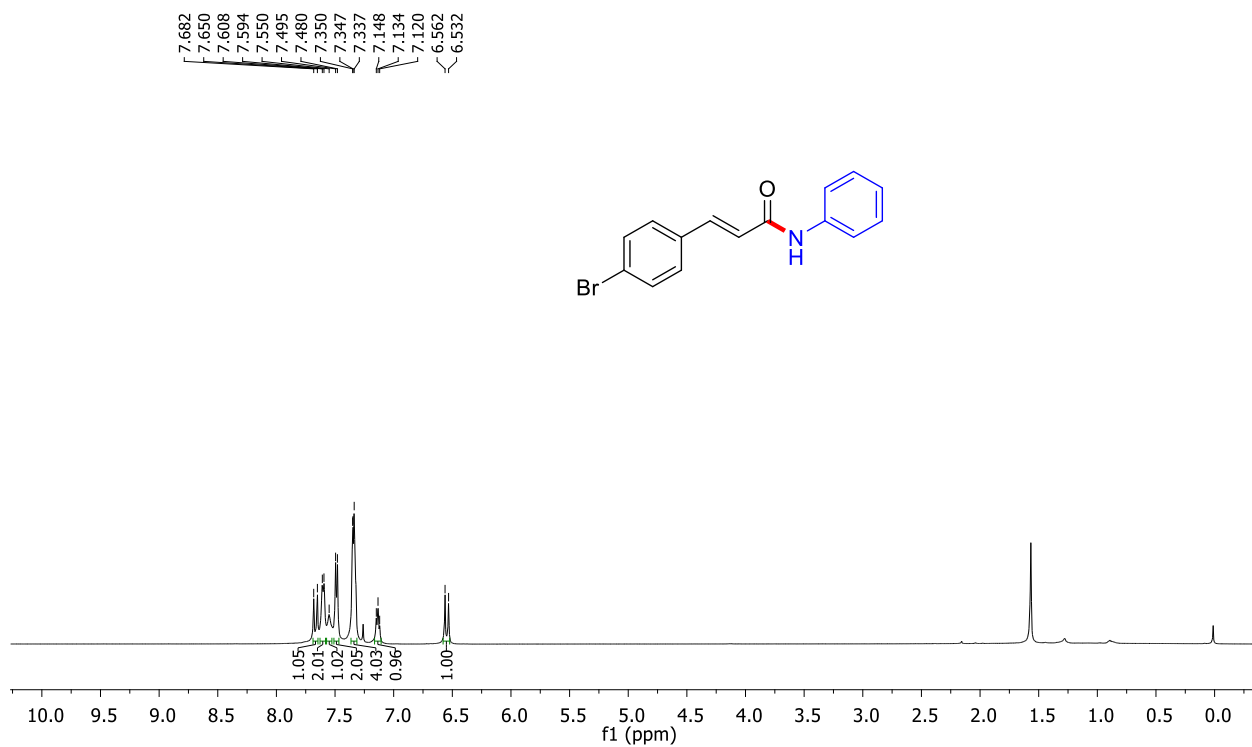


$^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3)

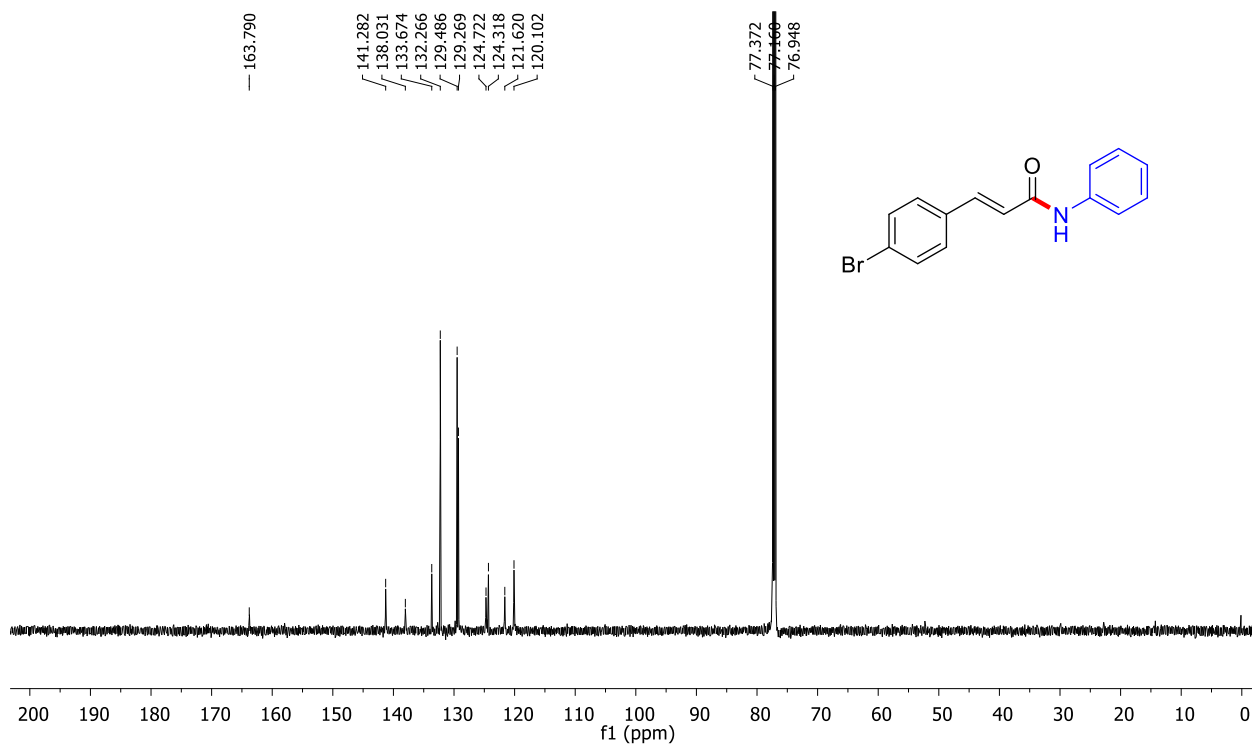


(E)-3-(4-Bromophenyl)-N-phenylacrylamide (3g):

^1H NMR (500 MHz, CDCl_3)

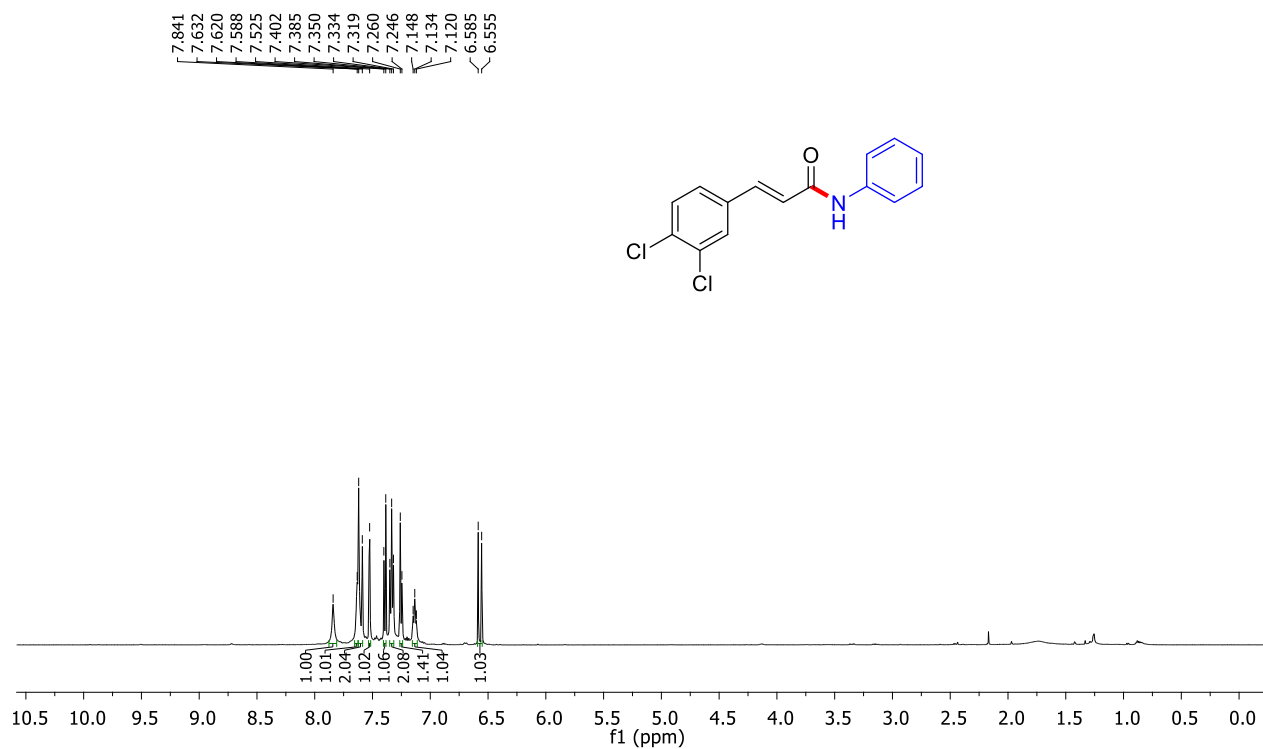


$^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3)

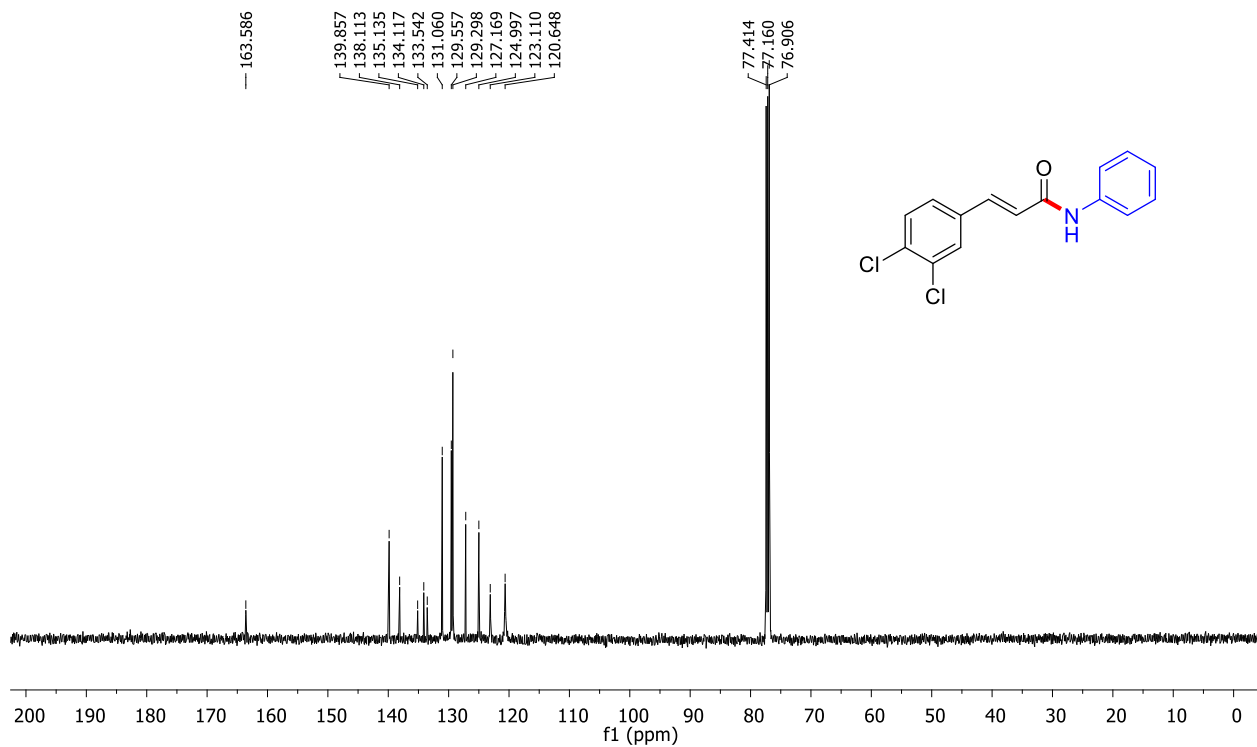


(E)-3-(3,4-Dichlorophenyl)-N-phenylacrylamide (3h):

^1H NMR (500 MHz, CDCl_3)

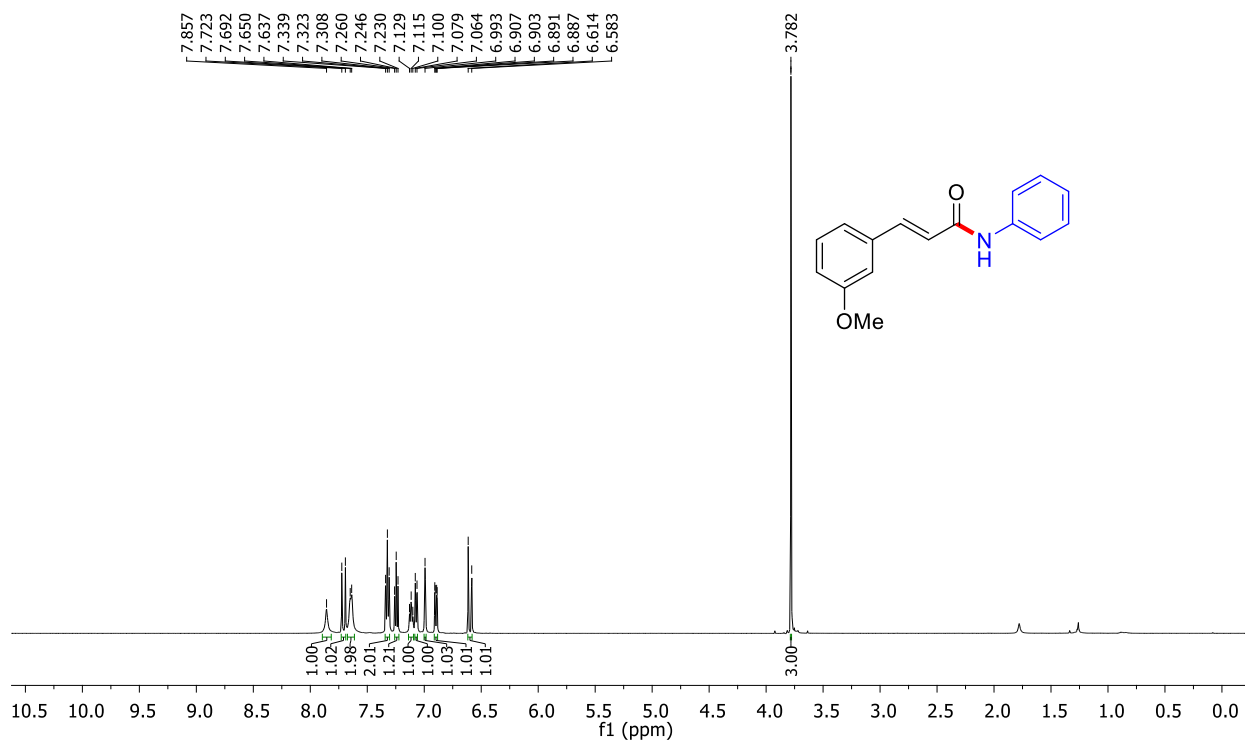


$^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3)

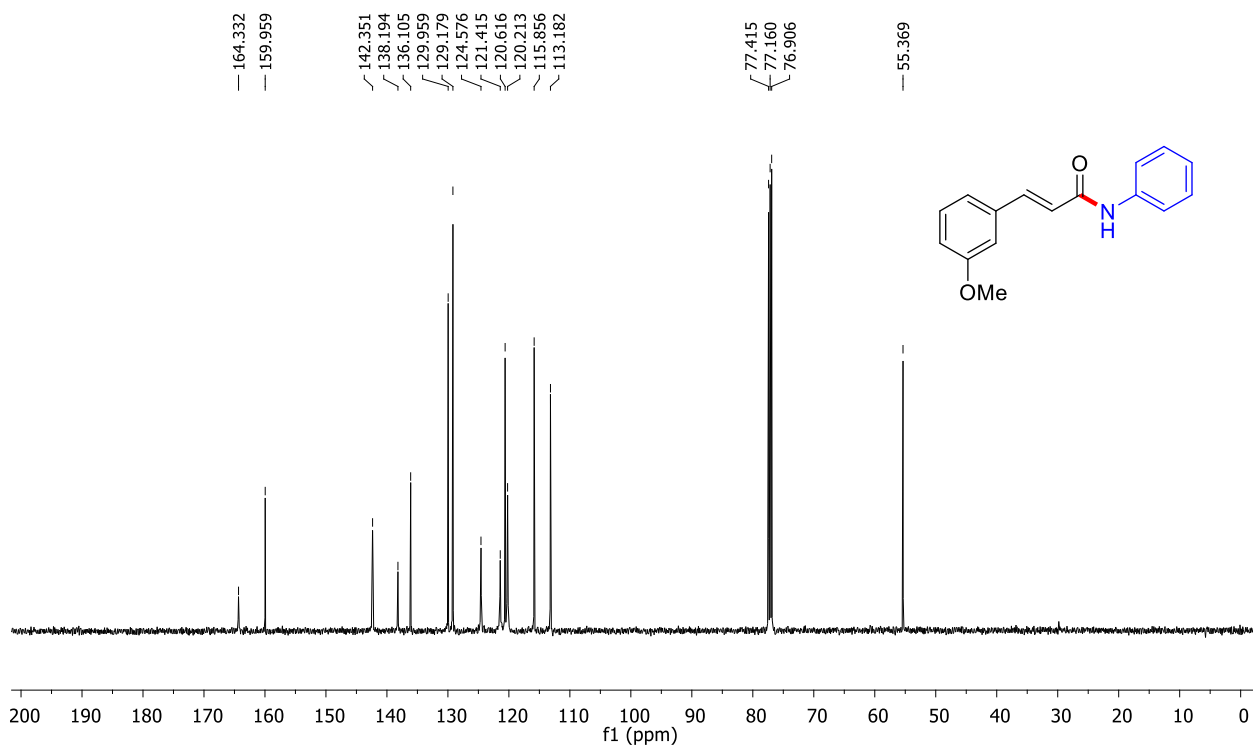


(E)-3-(3-Methoxyphenyl)-N-phenylacrylamide (3i):

^1H NMR (500 MHz, CDCl_3)

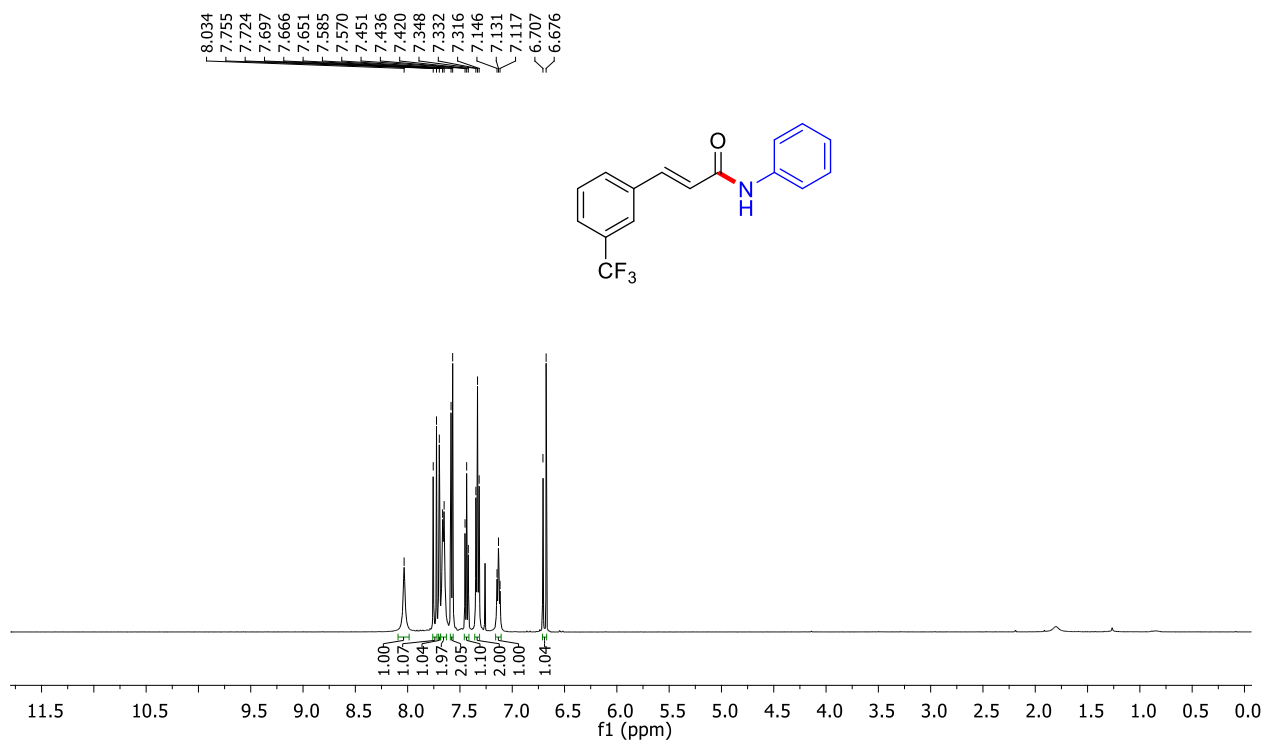


$^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3)

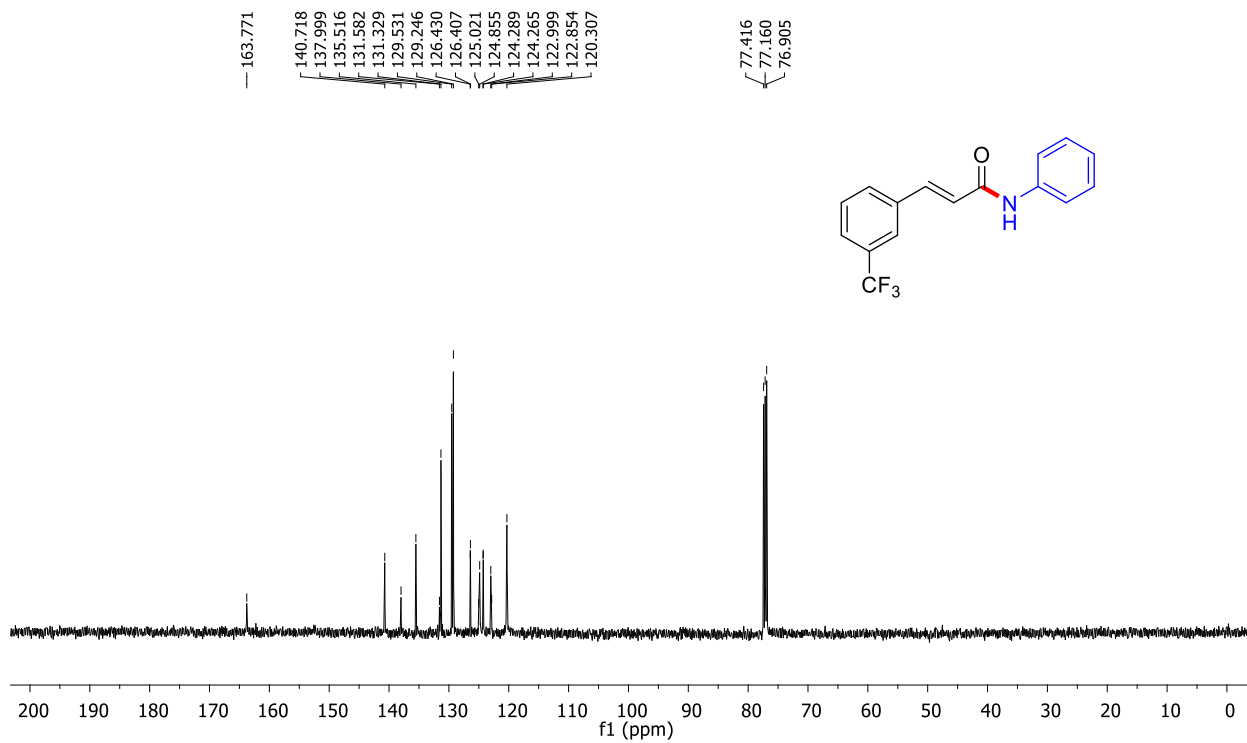


(E)-N-Phenyl-3-(3-(trifluoromethyl)phenyl)acrylamide (3j):

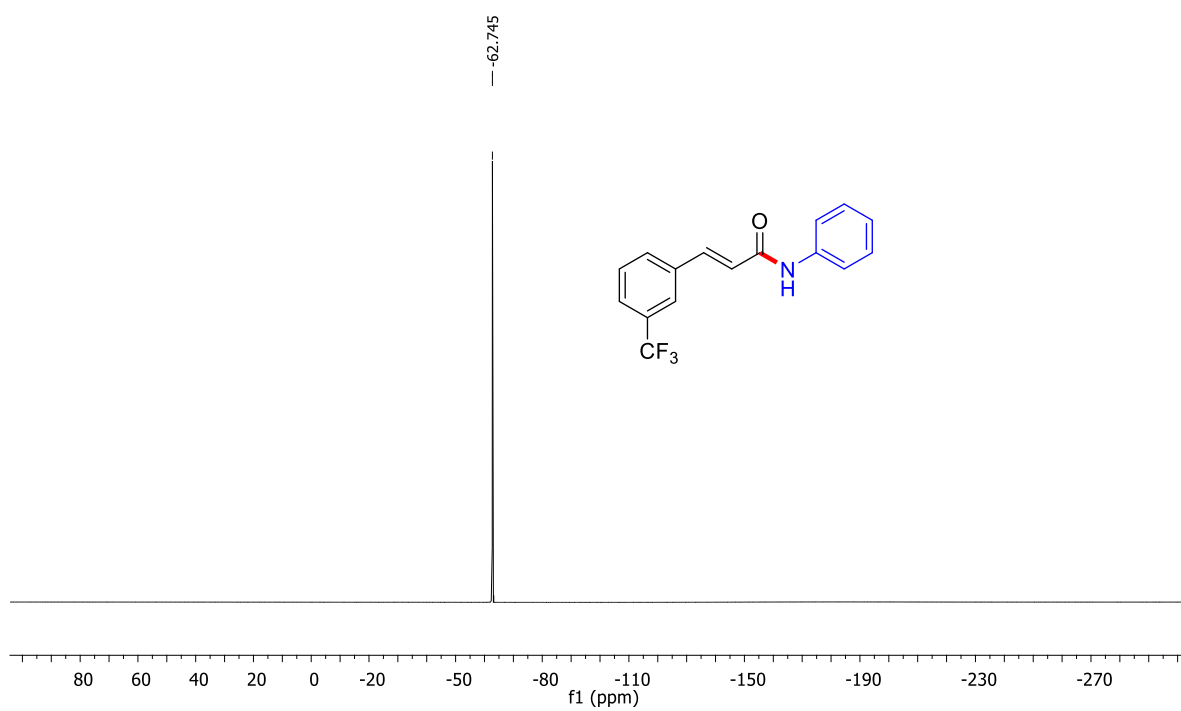
^1H NMR (500 MHz, CDCl_3)



$^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3)

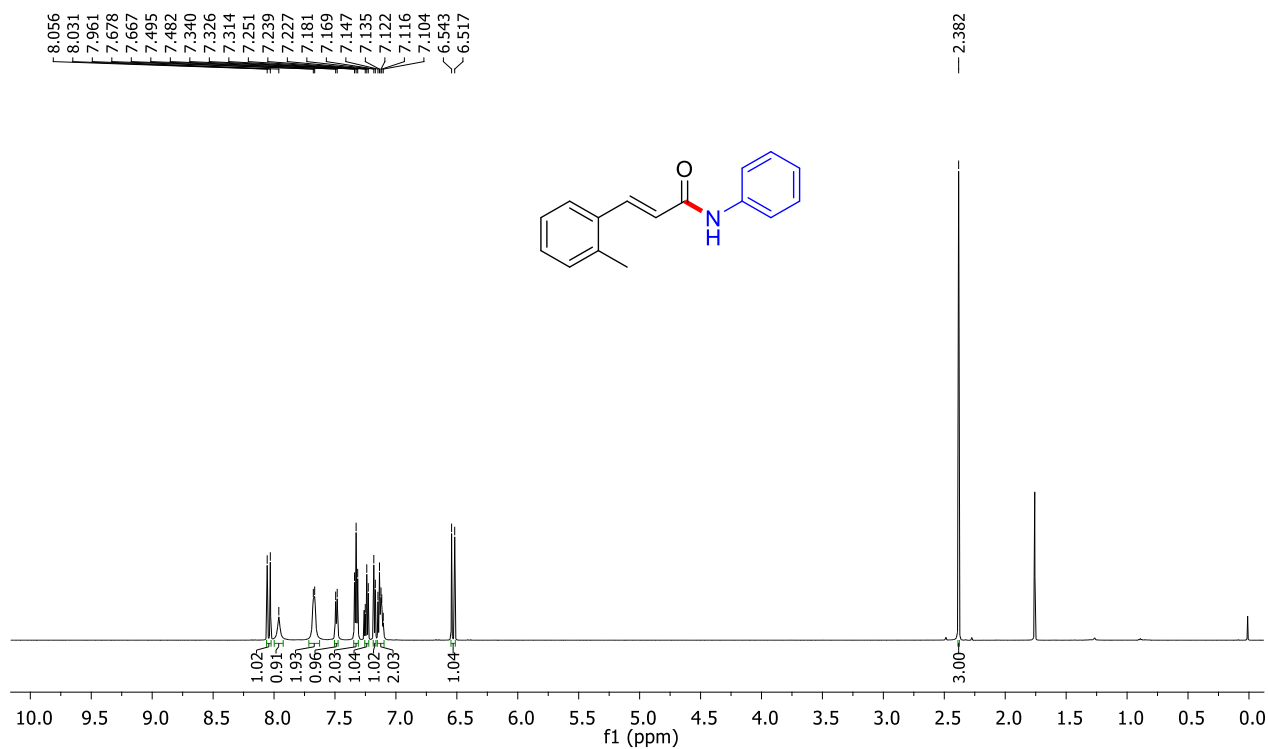


^{19}F NMR (471 MHz, CDCl_3)

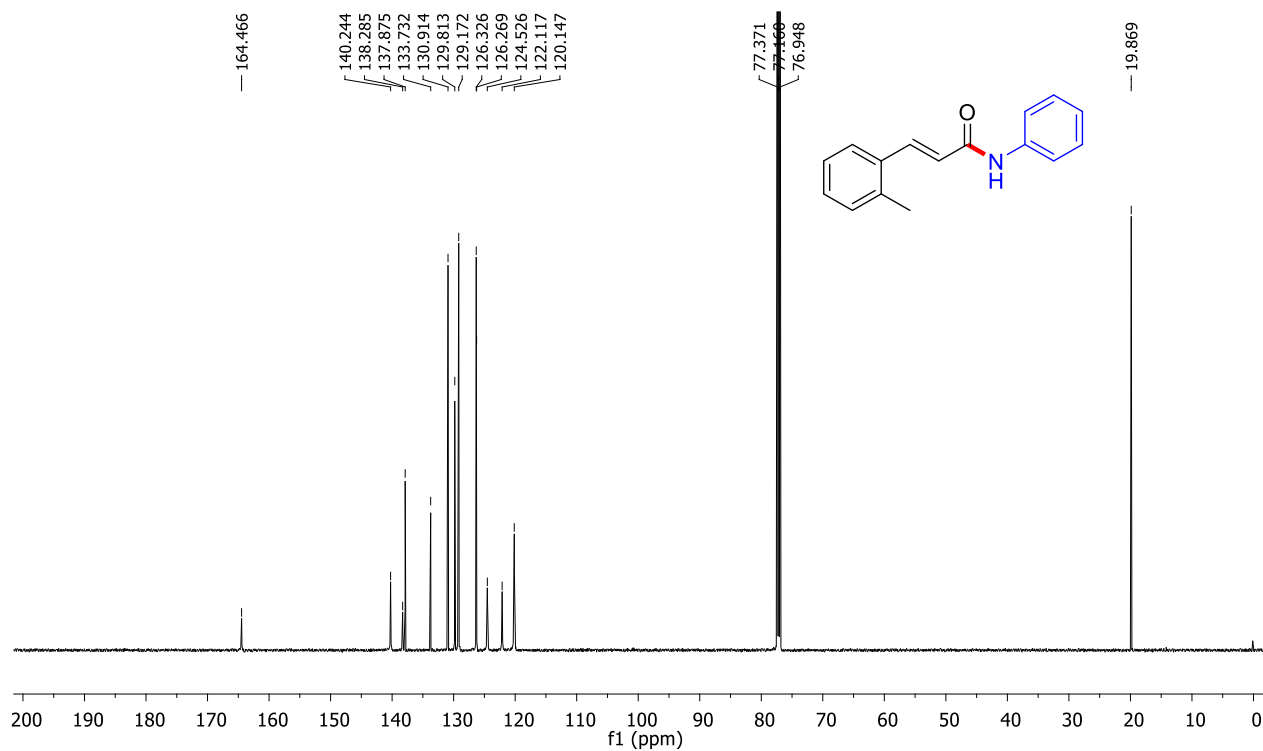


(E)-N-Phenyl-3-(*o*-tolyl)acrylamide (3k):

^1H NMR (600 MHz, CDCl_3)

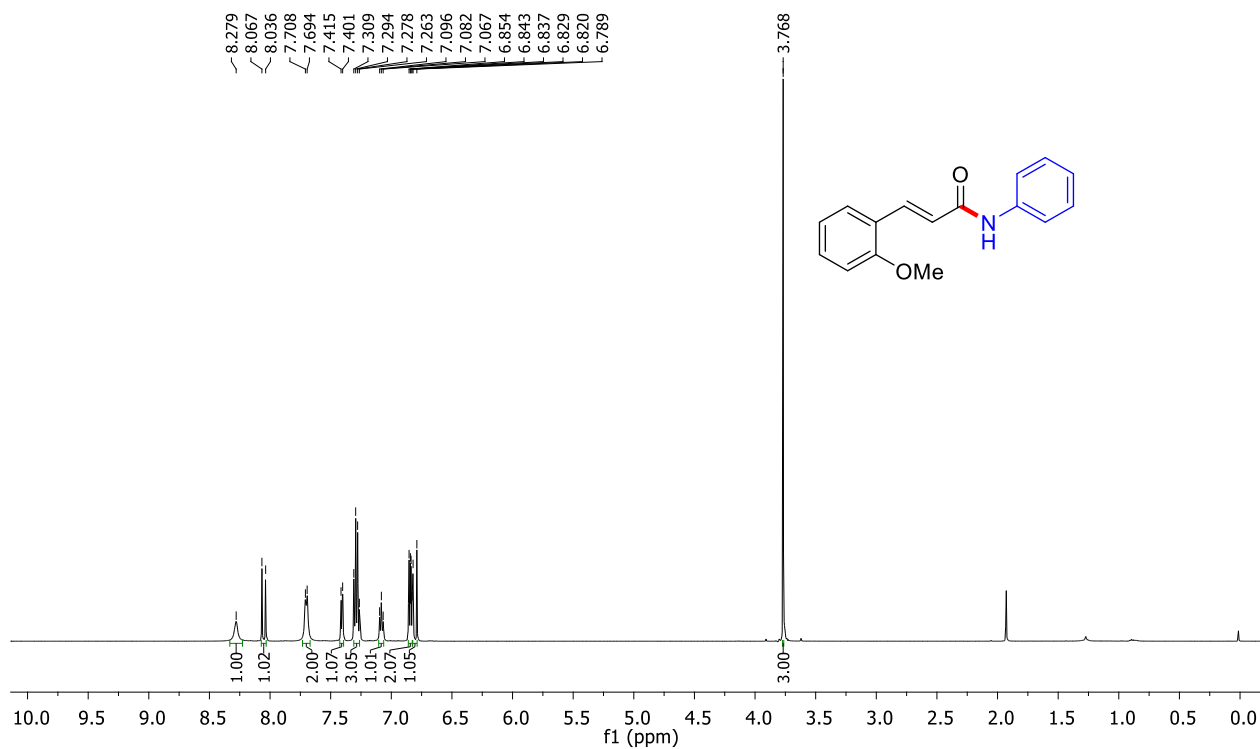


$^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3)

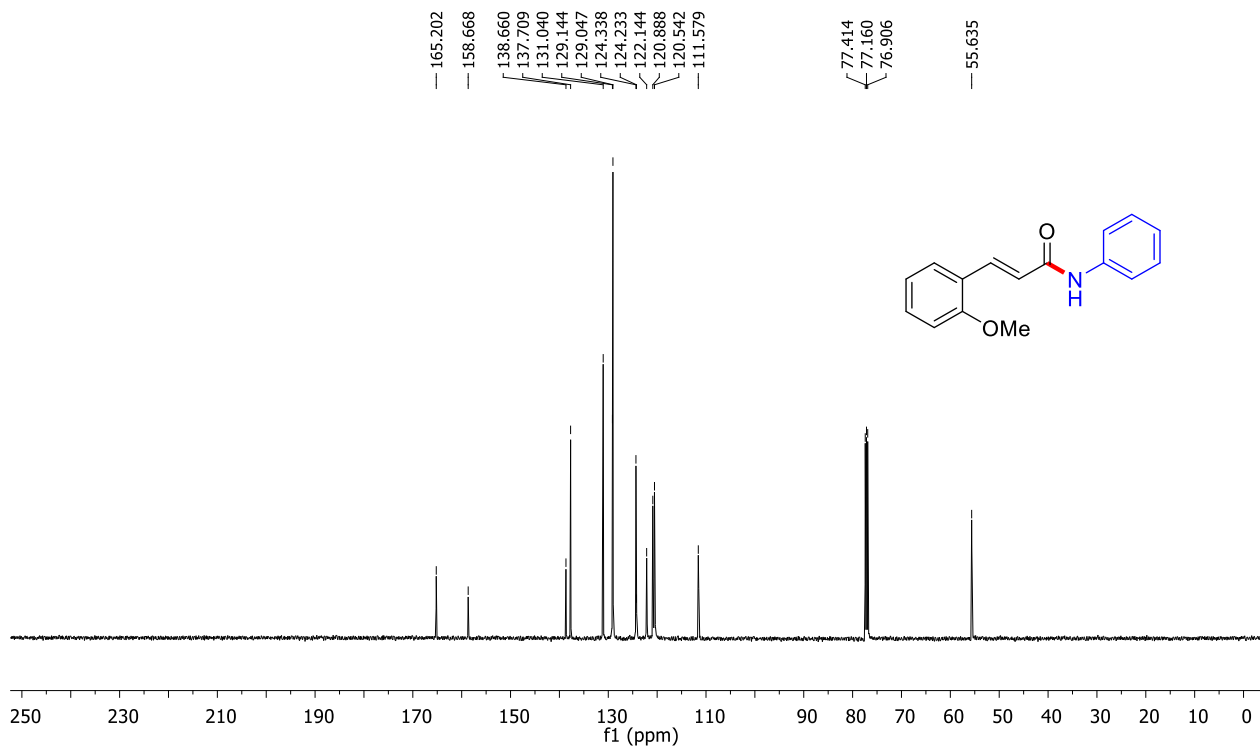


(E)-3-(2-Methoxyphenyl)-N-phenylacrylamide (3l):

^1H NMR (500 MHz, CDCl_3)

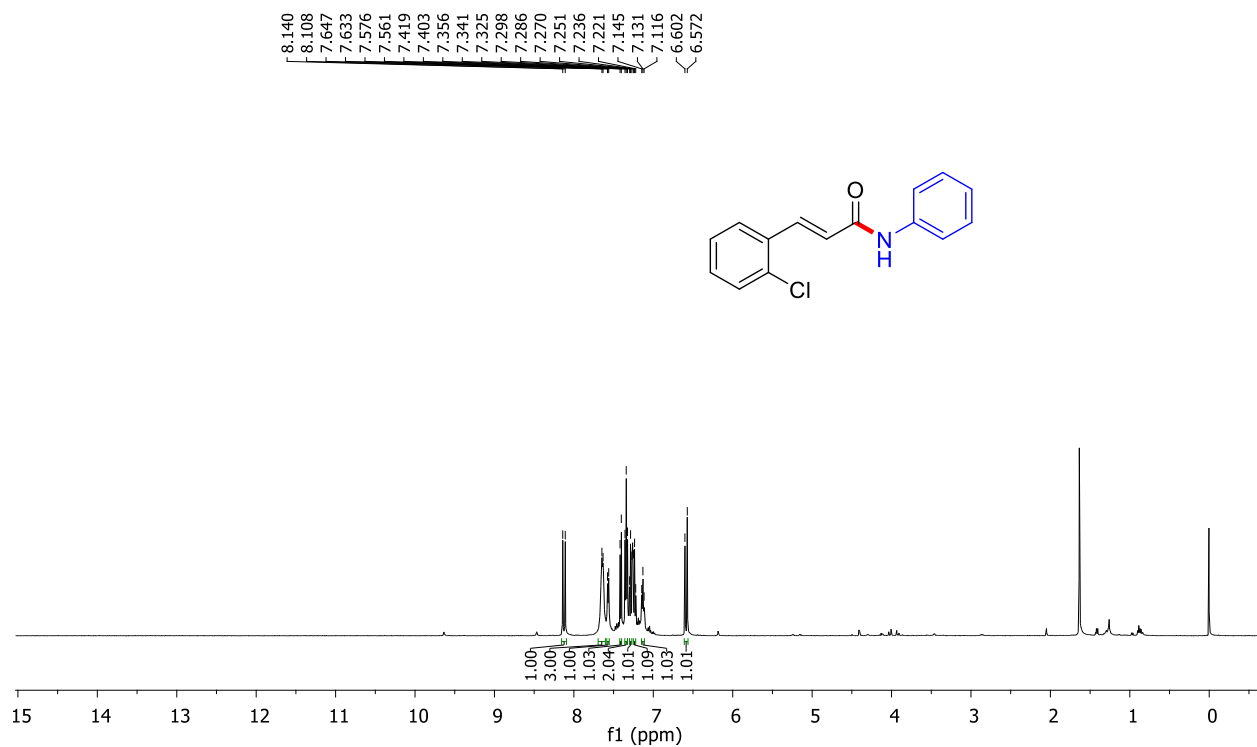


$^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3)

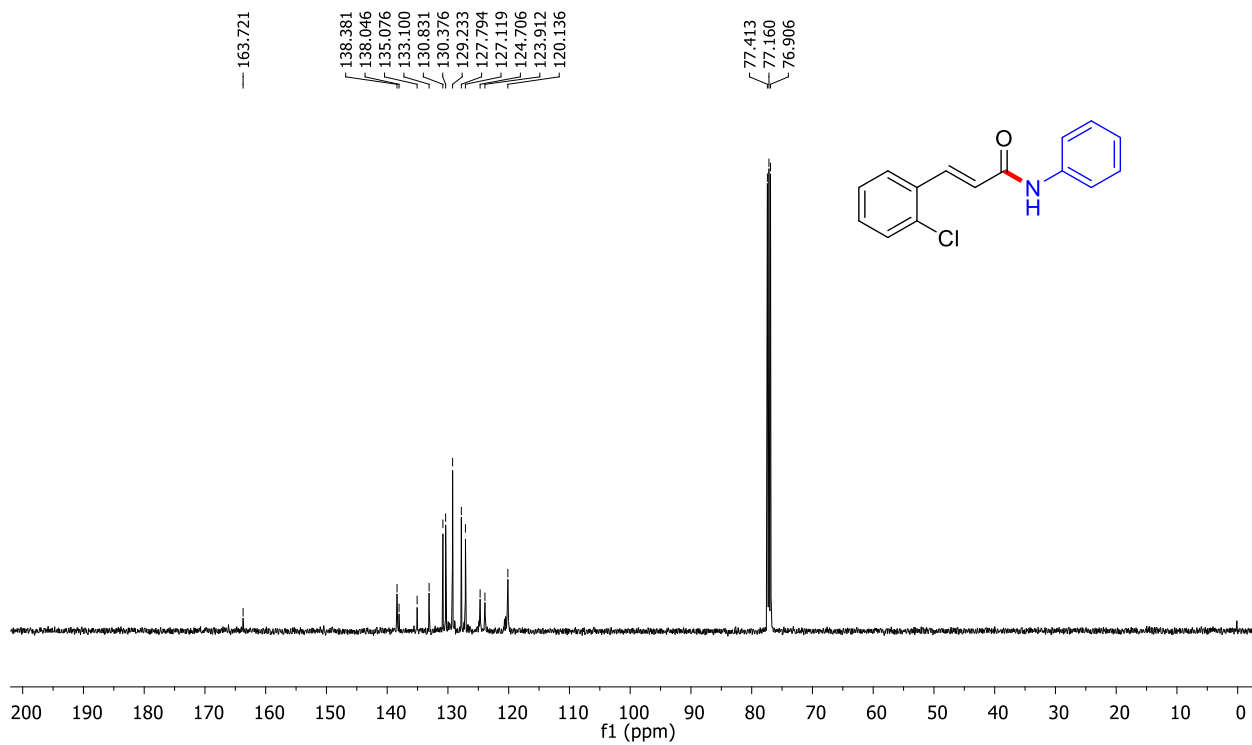


(E)-3-(2-Chlorophenyl)-N-phenylacrylamide (3m):

¹H NMR (500 MHz, CDCl₃)

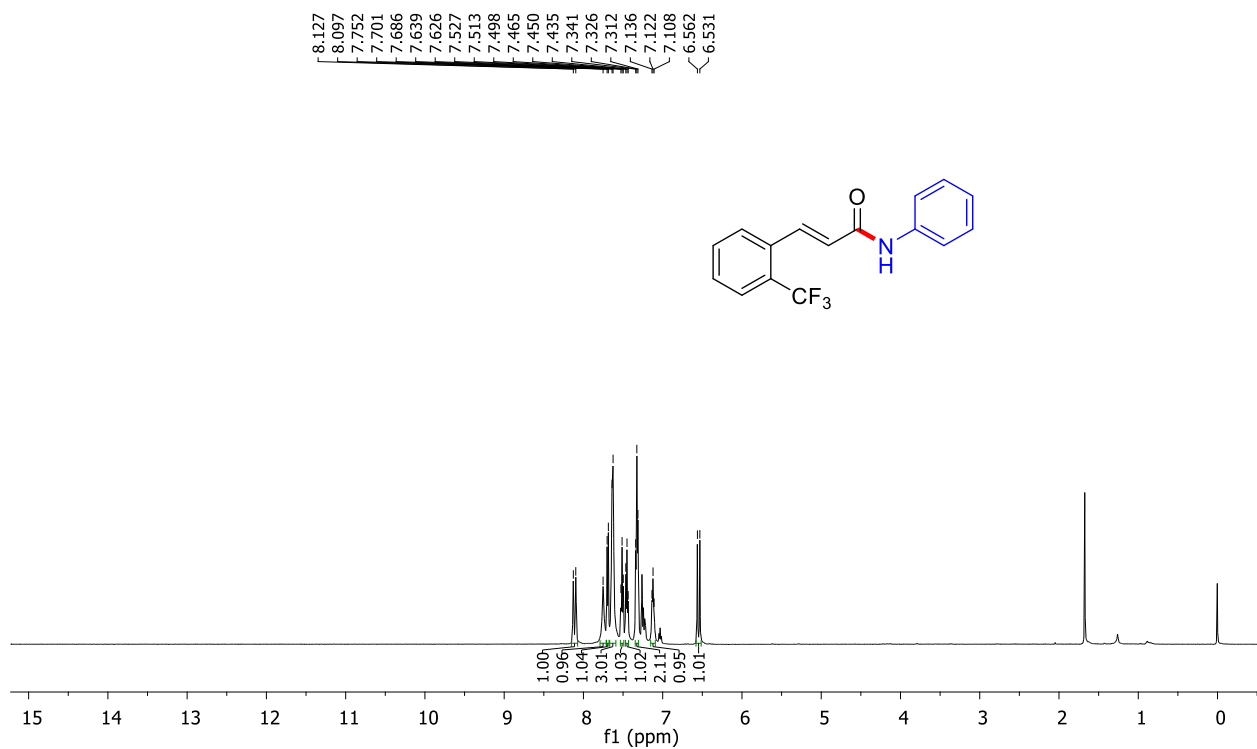


¹³C{¹H} NMR (126 MHz, CDCl₃)

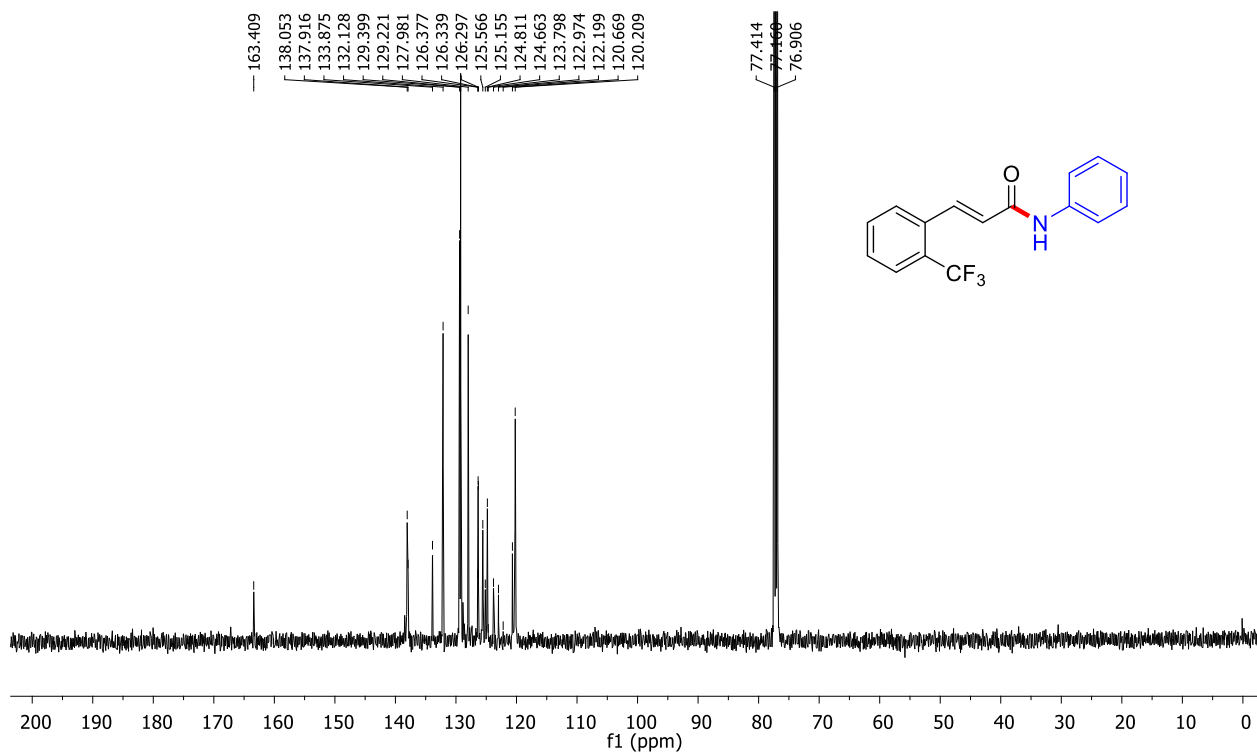


(E)-N-Phenyl-3-(2-(trifluoromethyl)phenyl)acrylamide (3n):

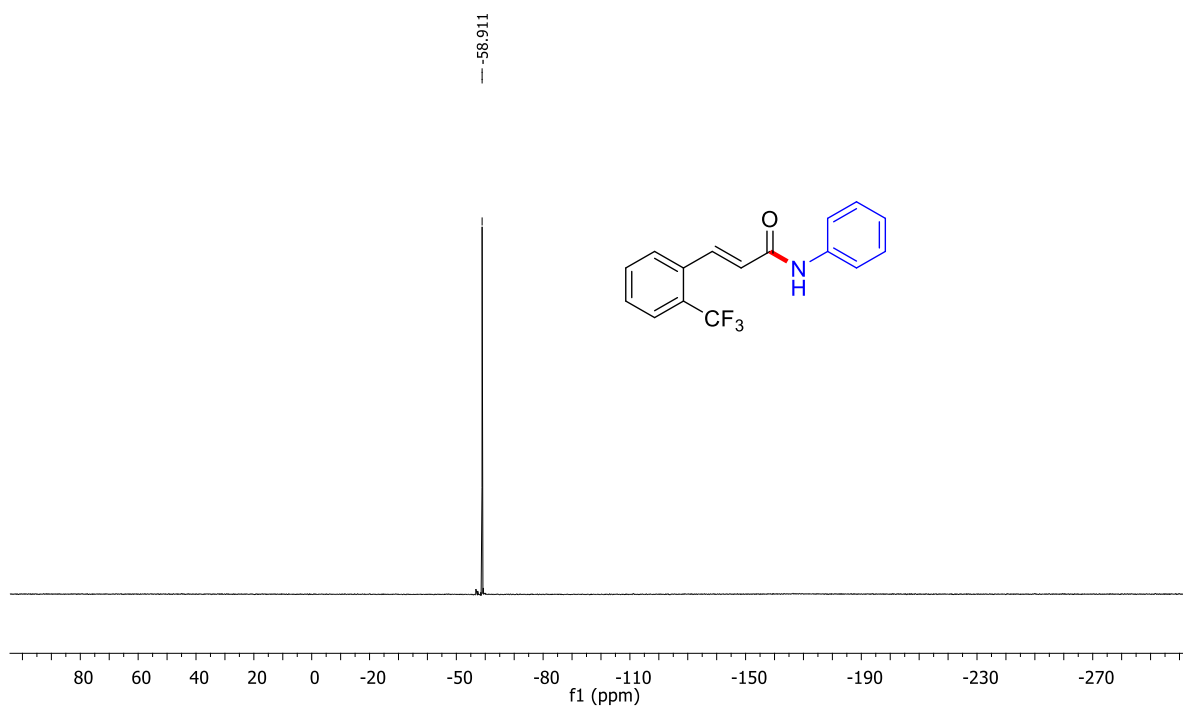
¹H NMR (500 MHz, CDCl₃)



¹³C{¹H} NMR (126 MHz, CDCl₃)

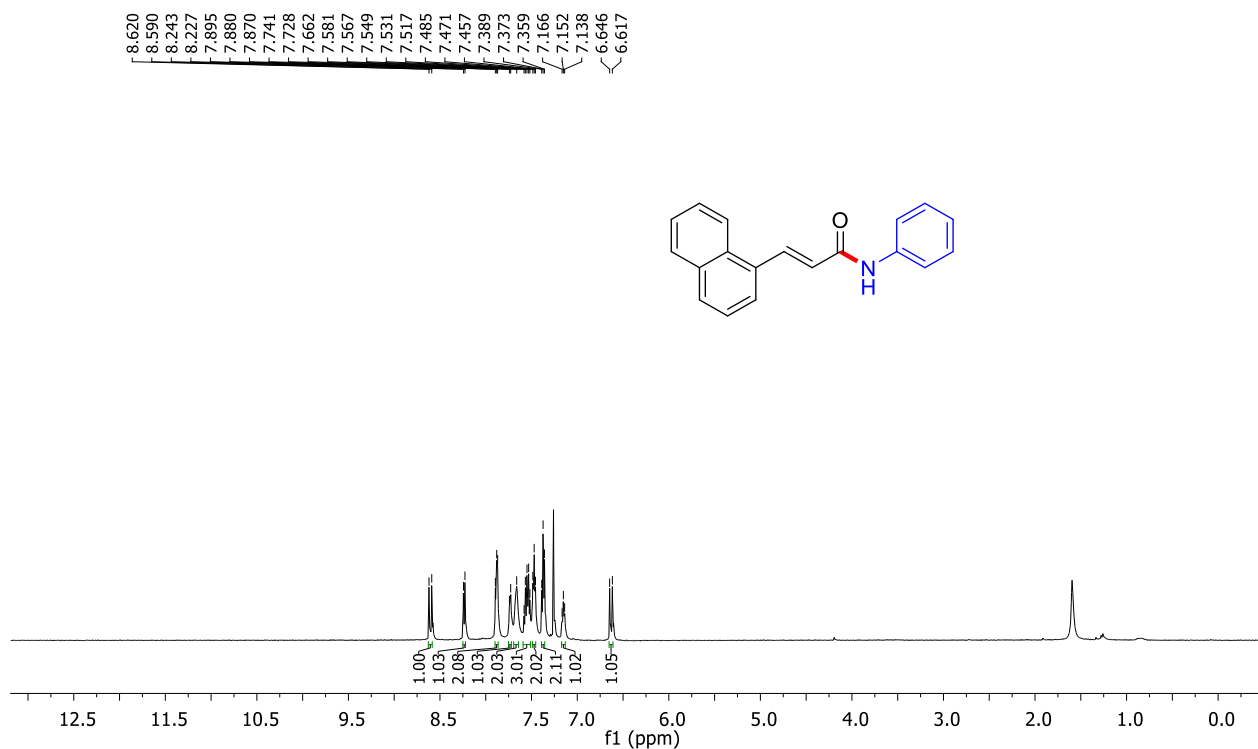


^{19}F NMR (471 MHz, CDCl_3)

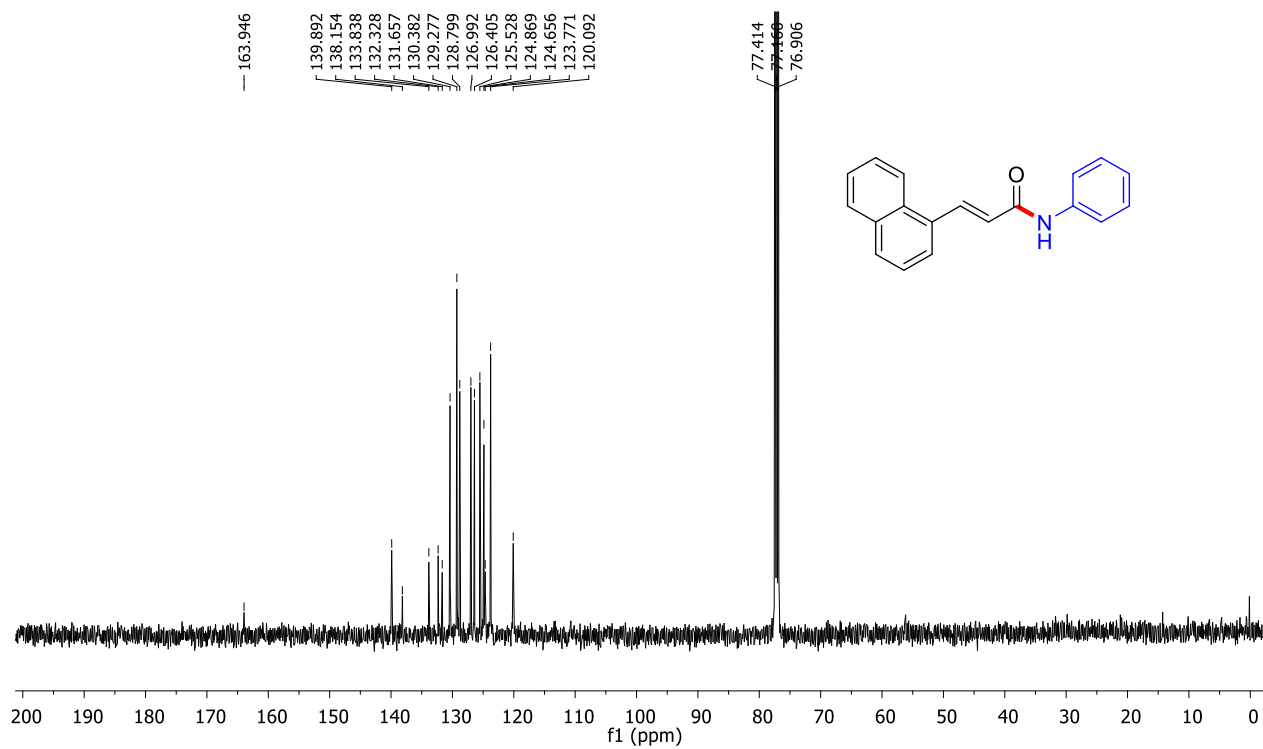


(E)-3-(Naphthalen-1-yl)-N-phenylacrylamide (3o):

^1H NMR (500 MHz, CDCl_3)

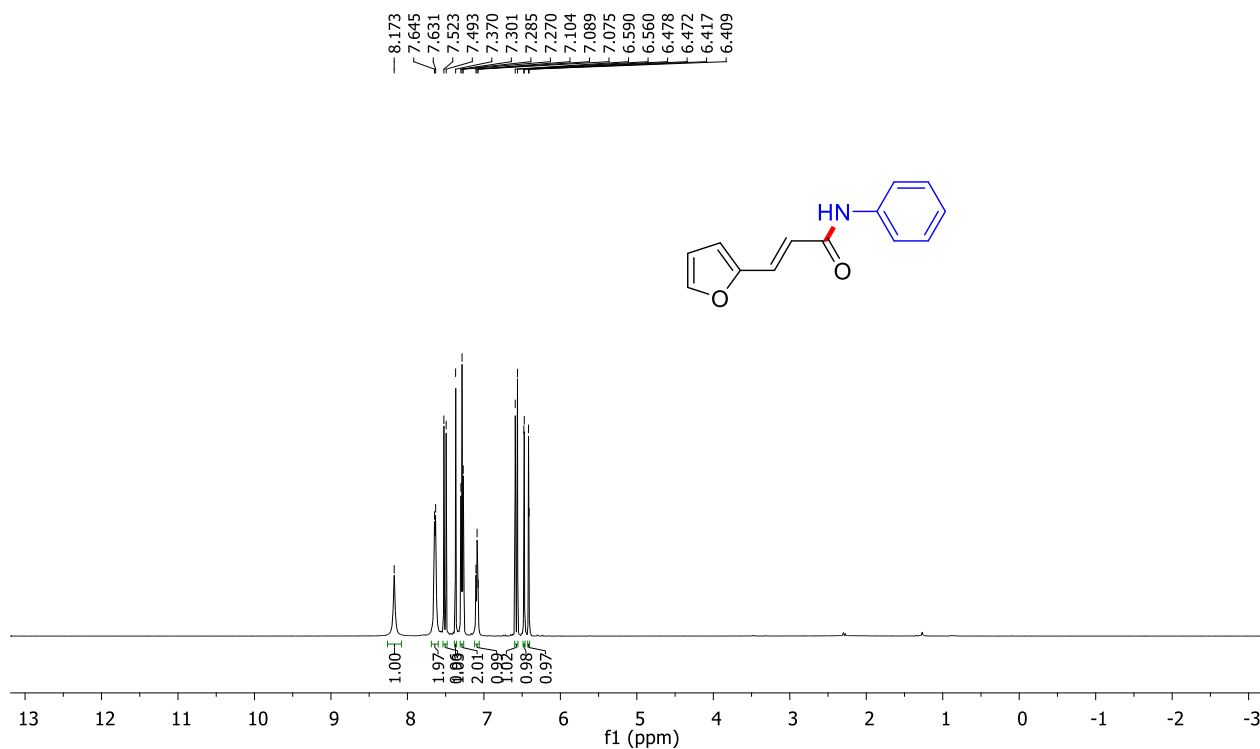


$^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3)

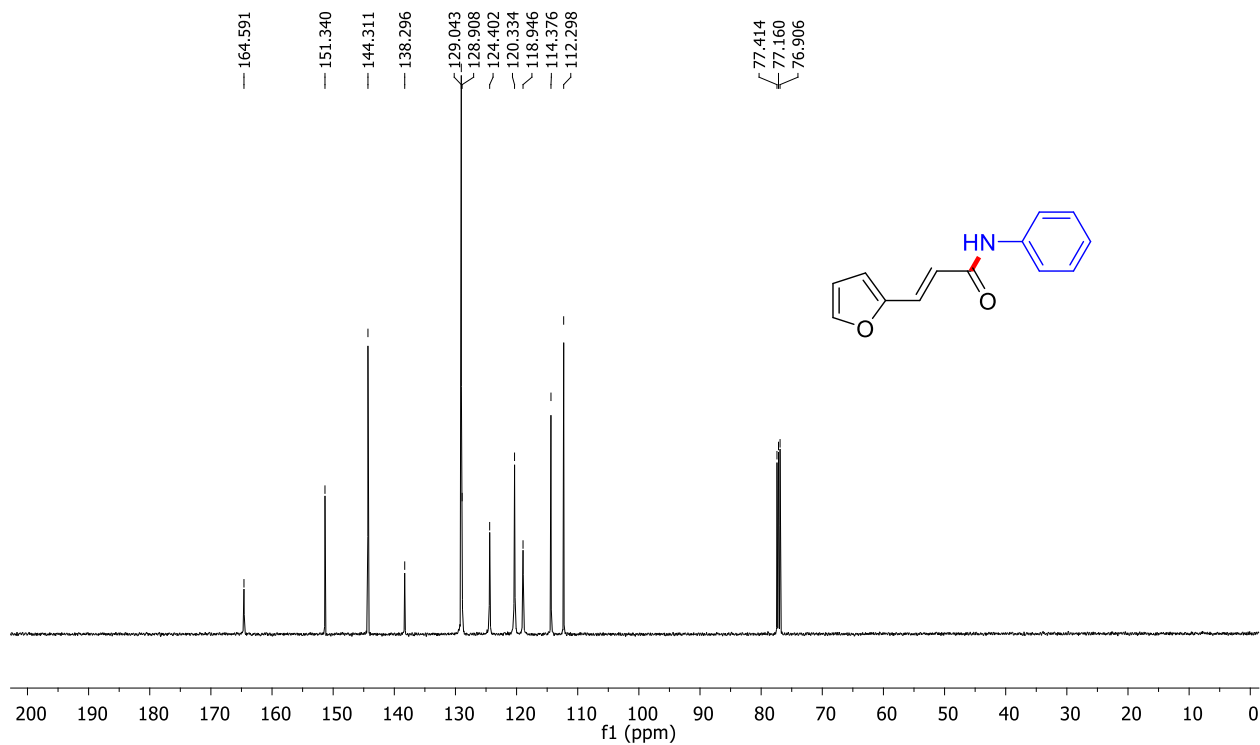


(E)-3-(Furan-2-yl)-N-phenylacrylamide (3p):

^1H NMR (500 MHz, CDCl_3)

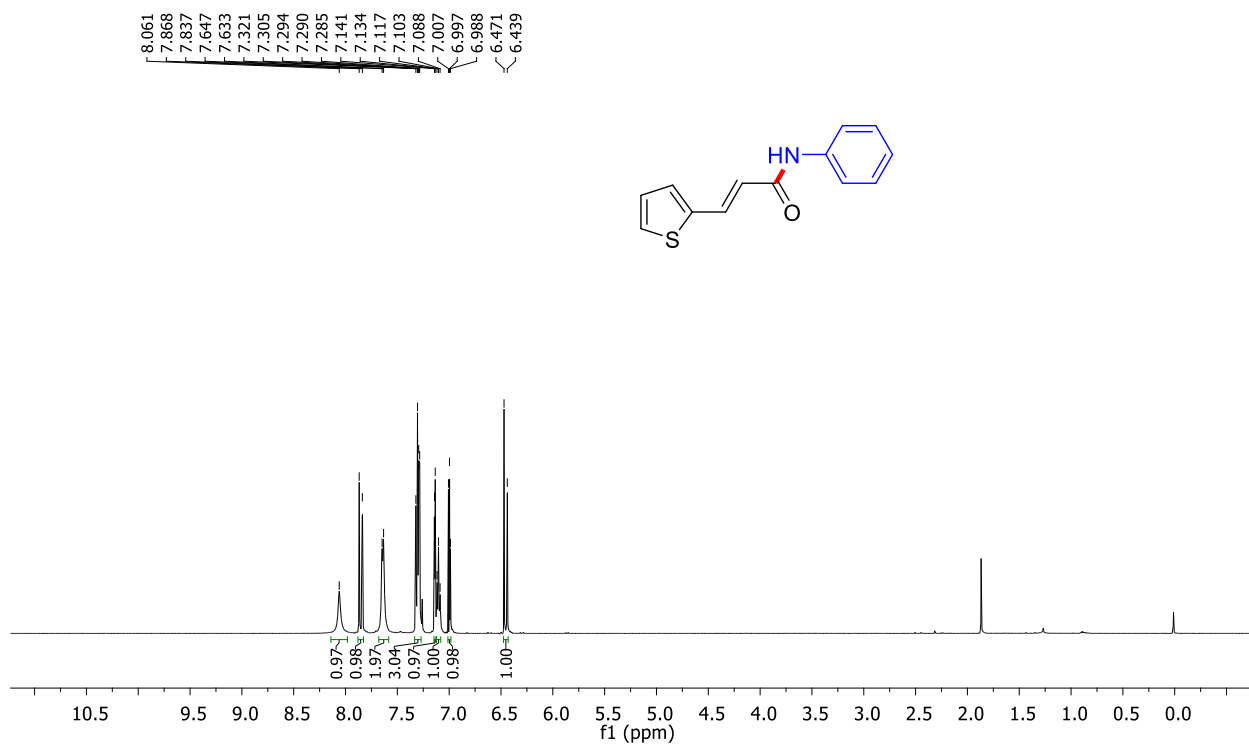


$^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3)

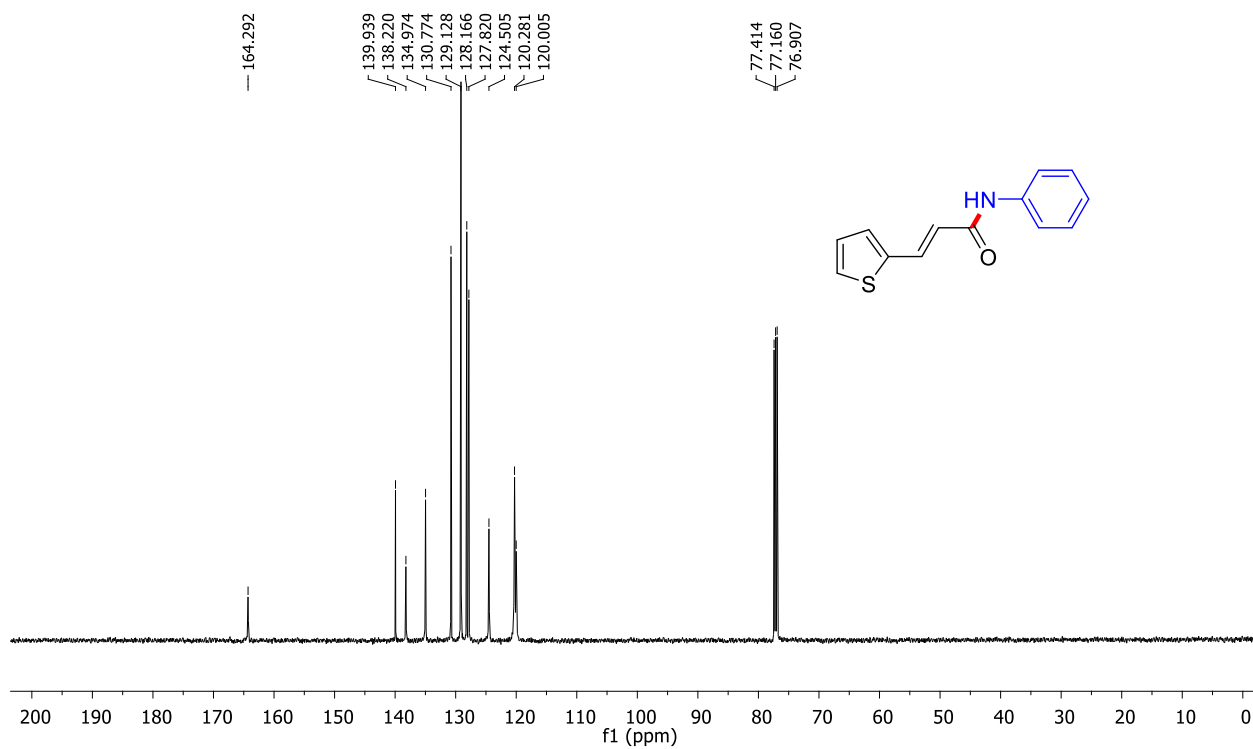


(E)-N-Phenyl-3-(thiophen-2-yl)acrylamide (3q):

^1H NMR (500 MHz, CDCl_3)

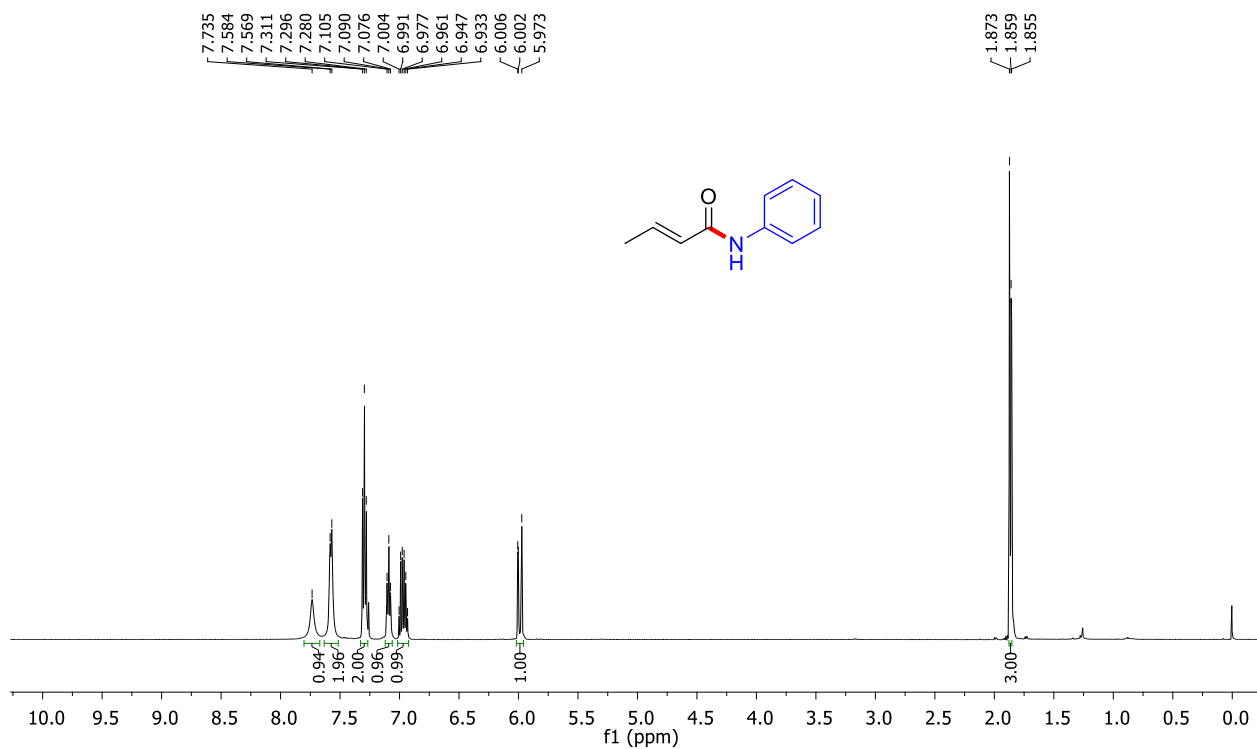


$^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3)

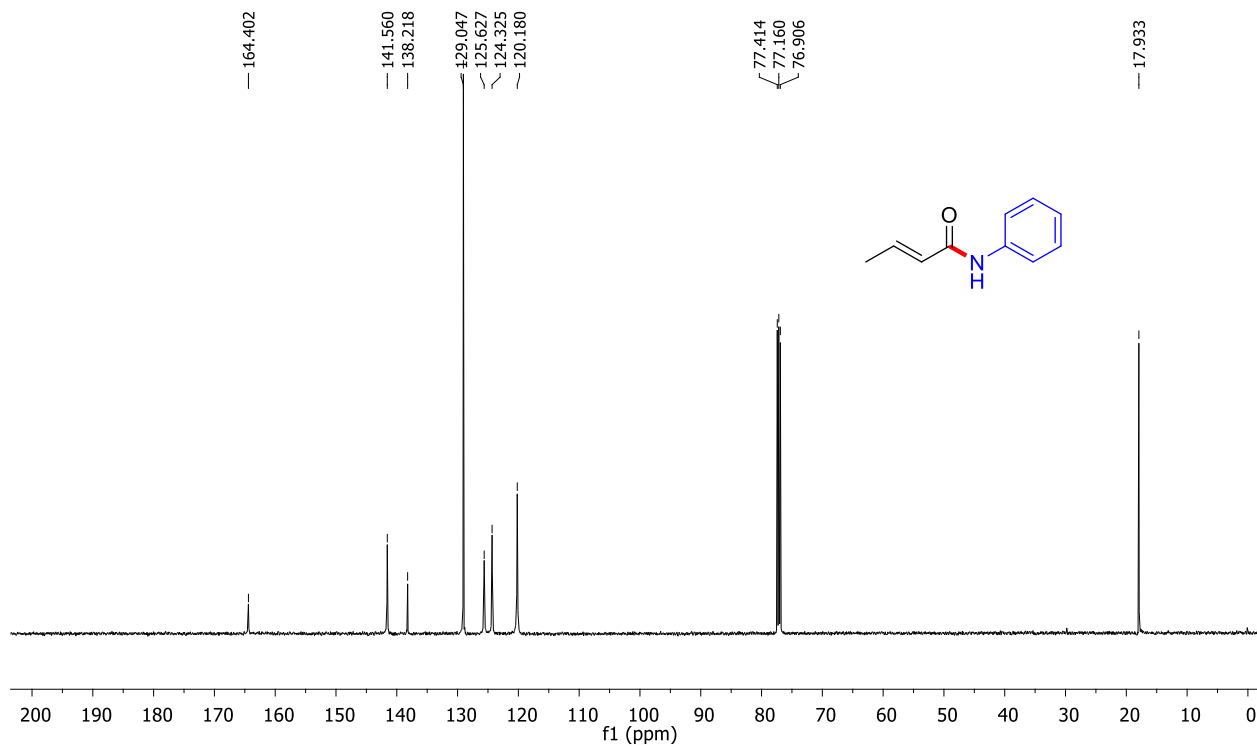


(E)-N-Phenylbut-2-enamide (3r):

^1H NMR (500 MHz, CDCl_3)

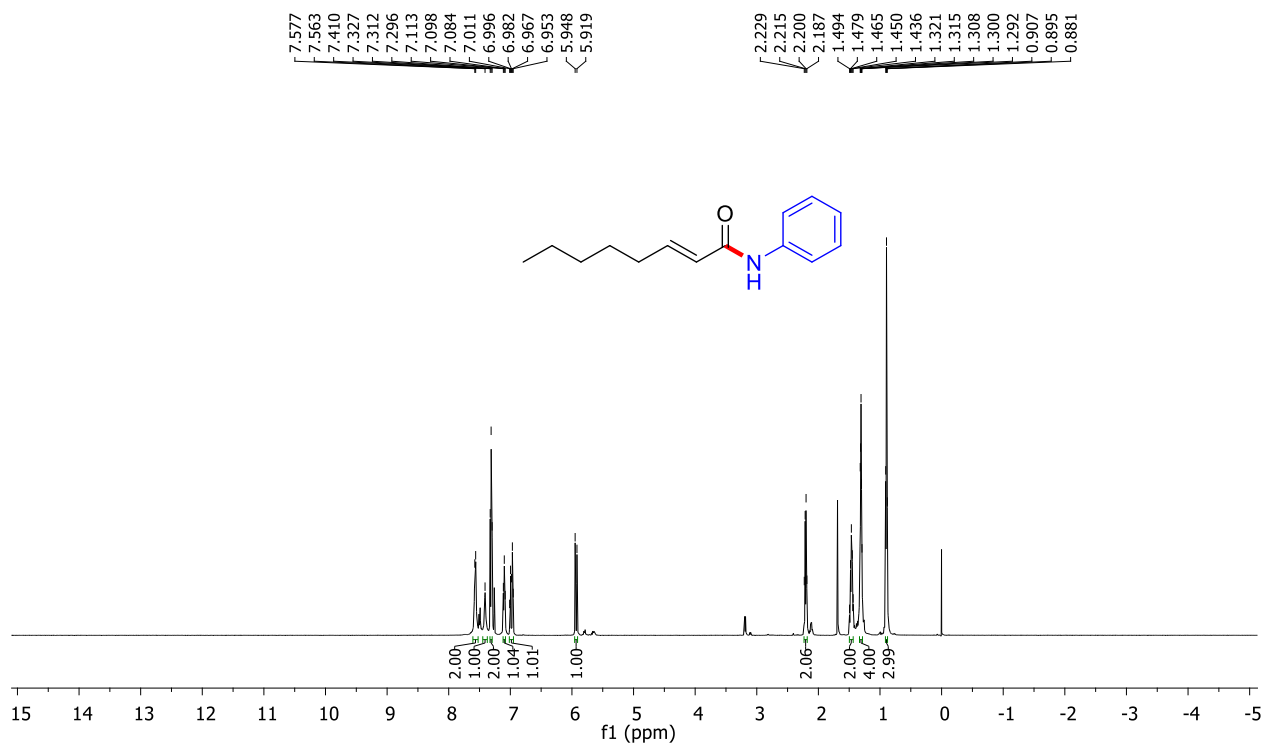


$^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3)

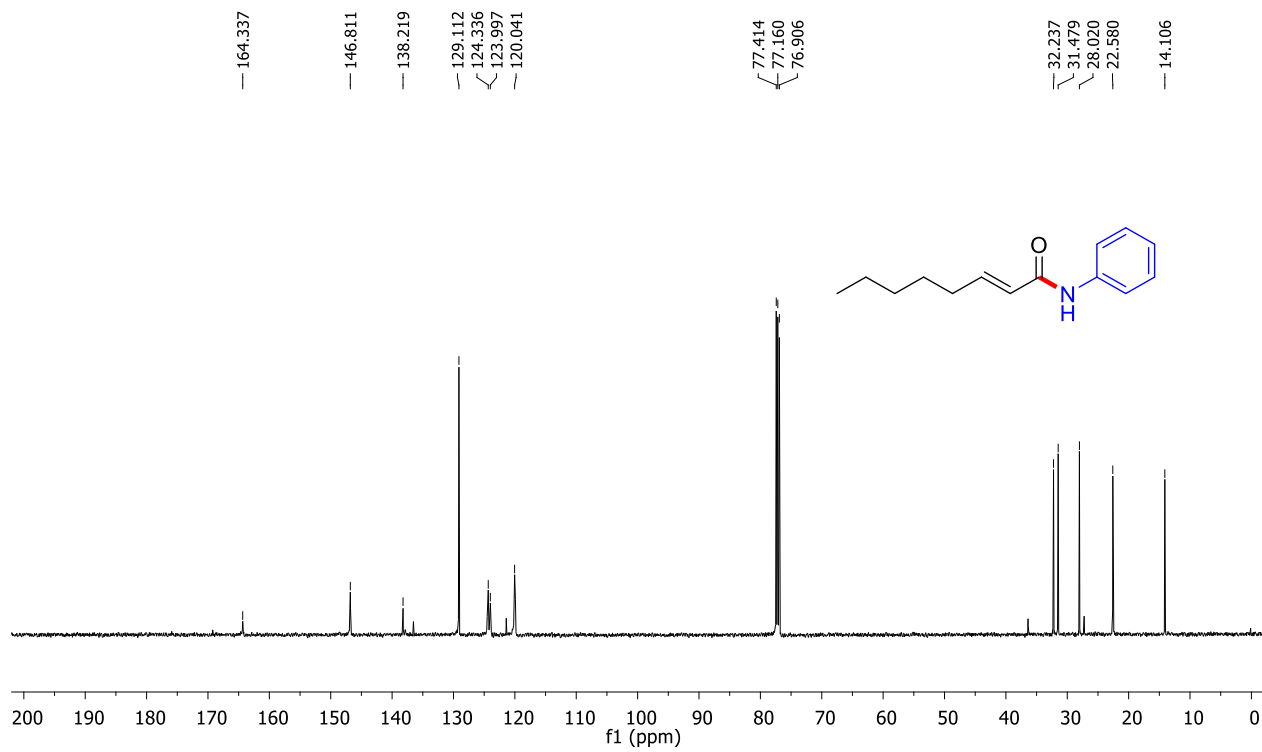


(E)-N-Phenyl-oct-2-enamide (3s):

^1H NMR (500 MHz, CDCl_3)

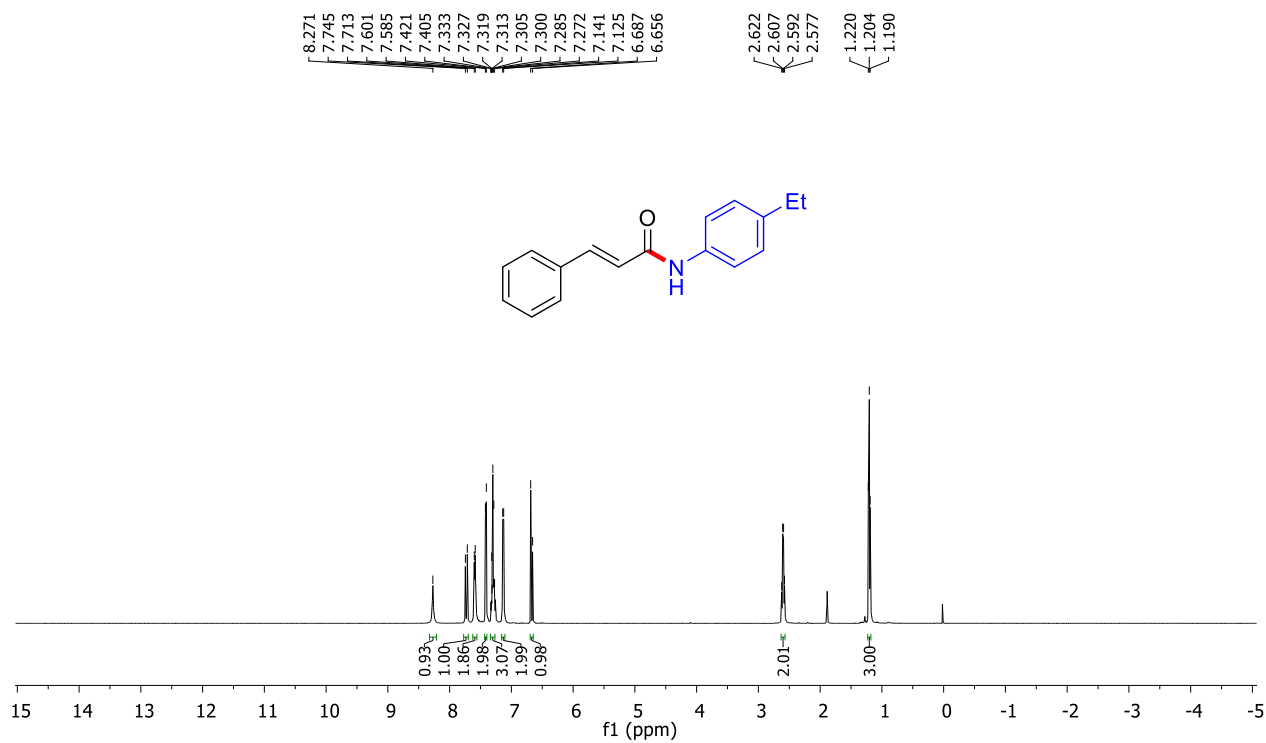


$^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3)

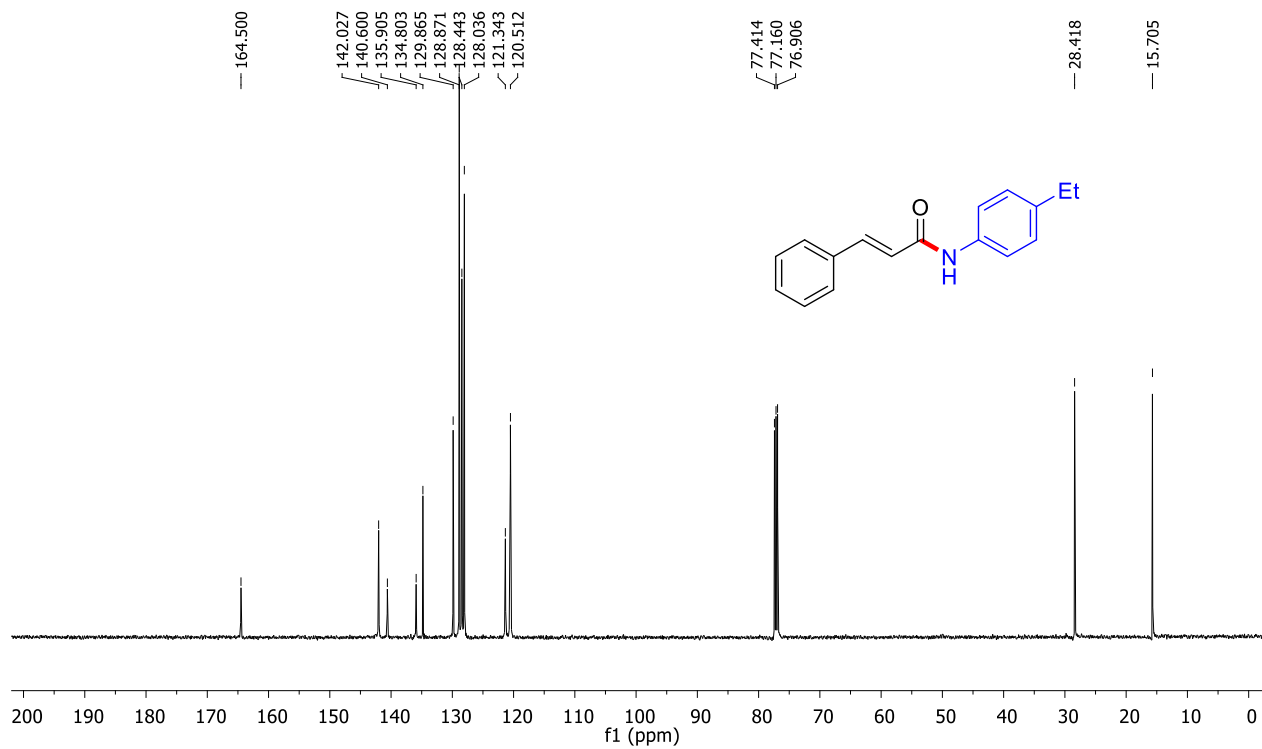


N-(4-Ethylphenyl)cinnamamide (3t):

^1H NMR (500 MHz, CDCl_3)

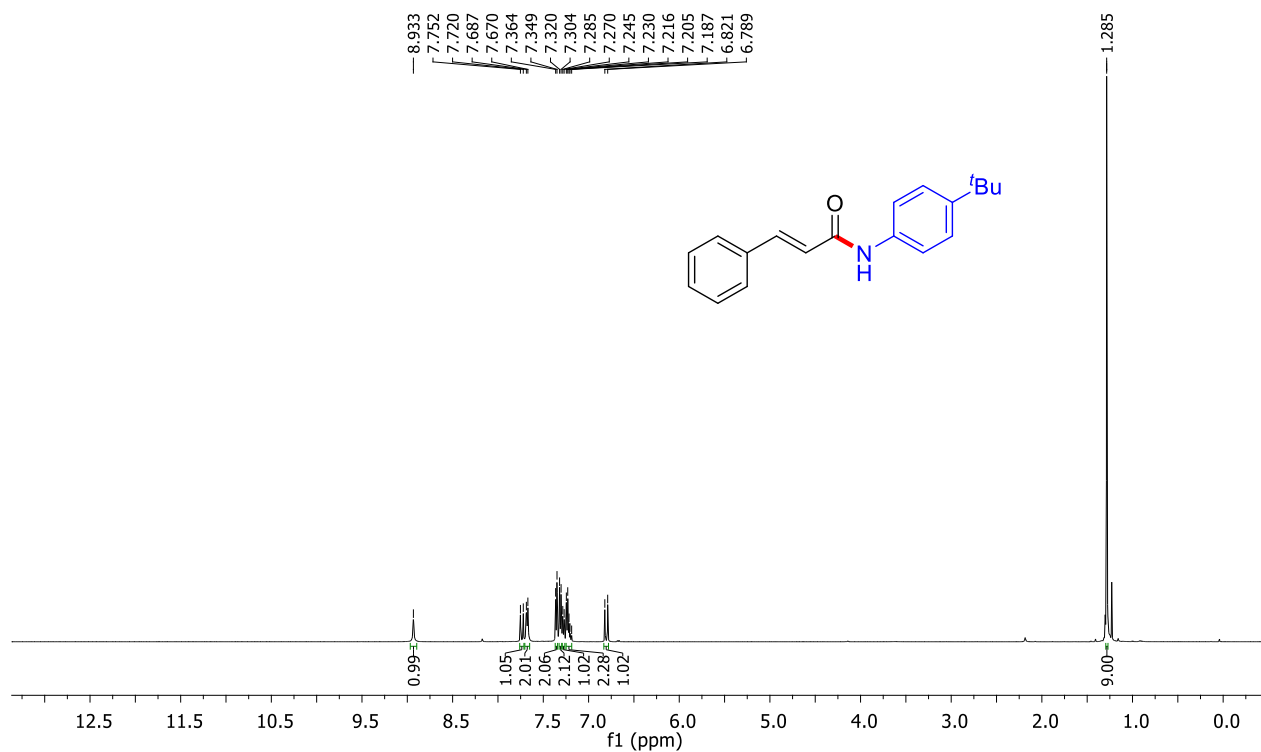


$^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3)

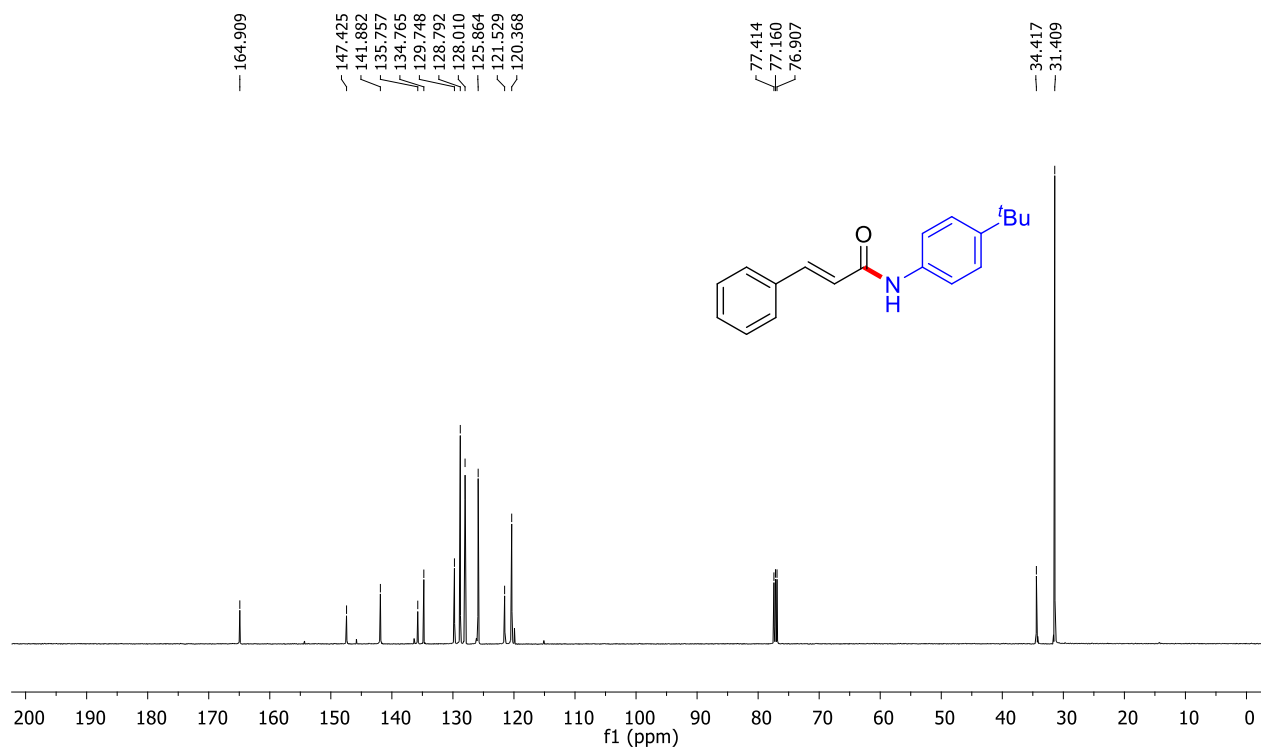


N-(4-(*Tert*-butyl)phenyl)cinnamamide (**3u**):

^1H NMR (500 MHz, CDCl_3)

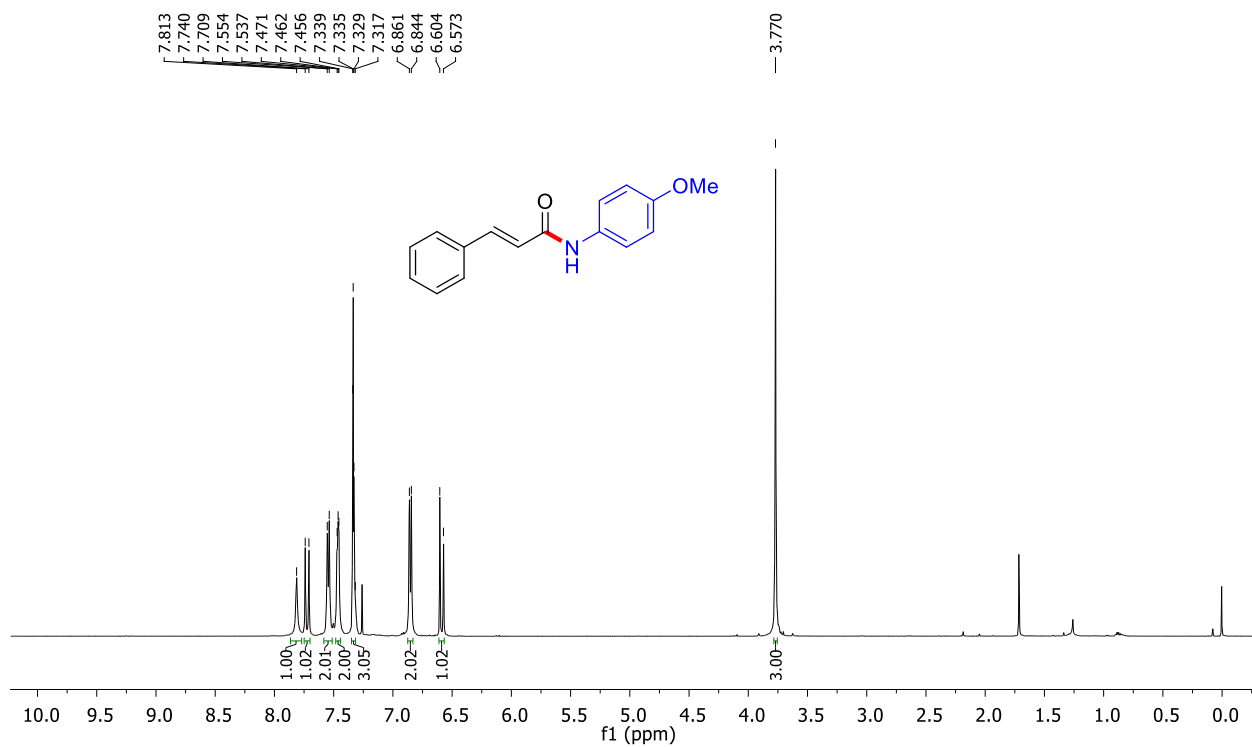


$^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3)

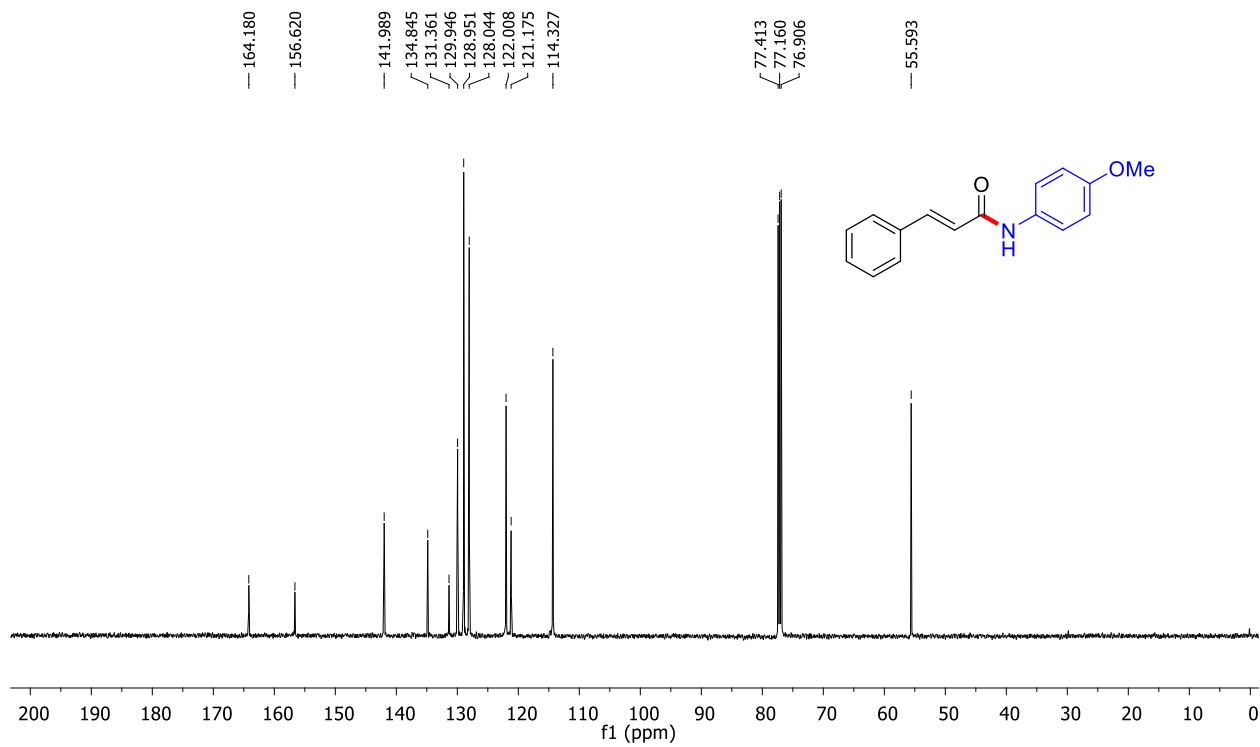


***N*-(4-Methoxyphenyl)cinnamamide (3v):**

¹H NMR (500 MHz, CDCl₃)

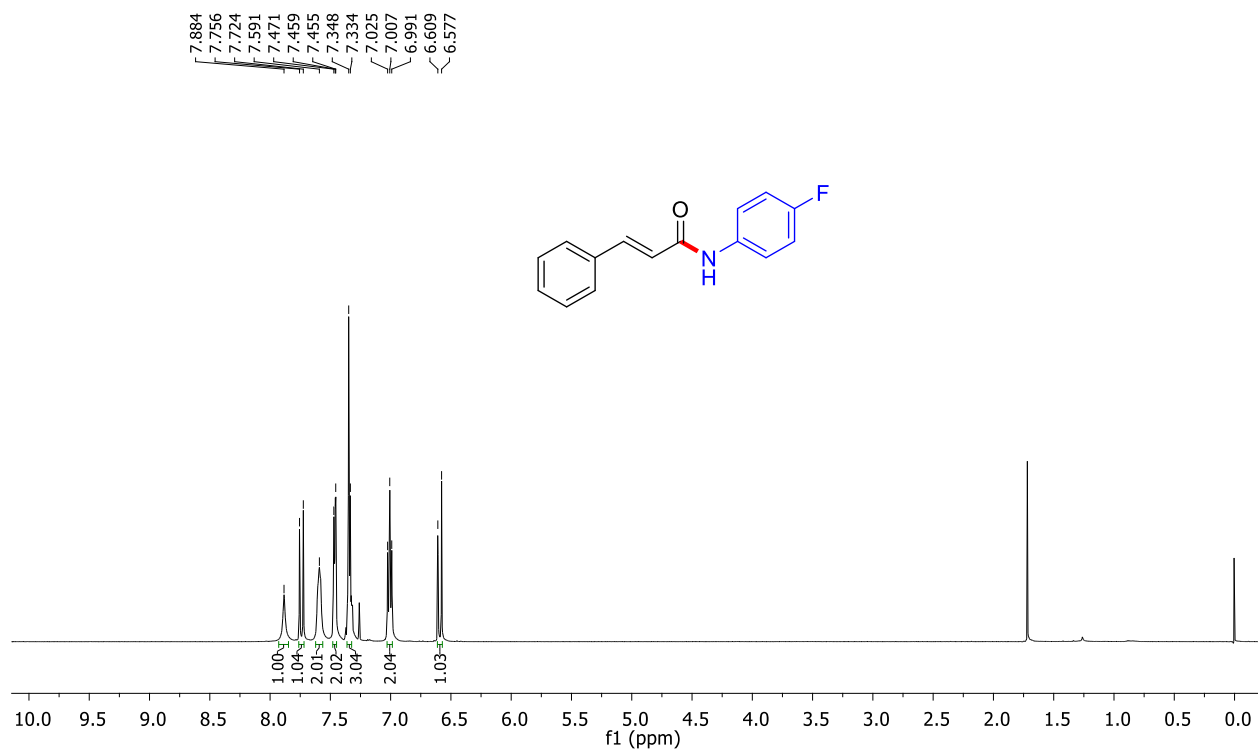


¹³C{¹H} NMR (126 MHz, CDCl₃)

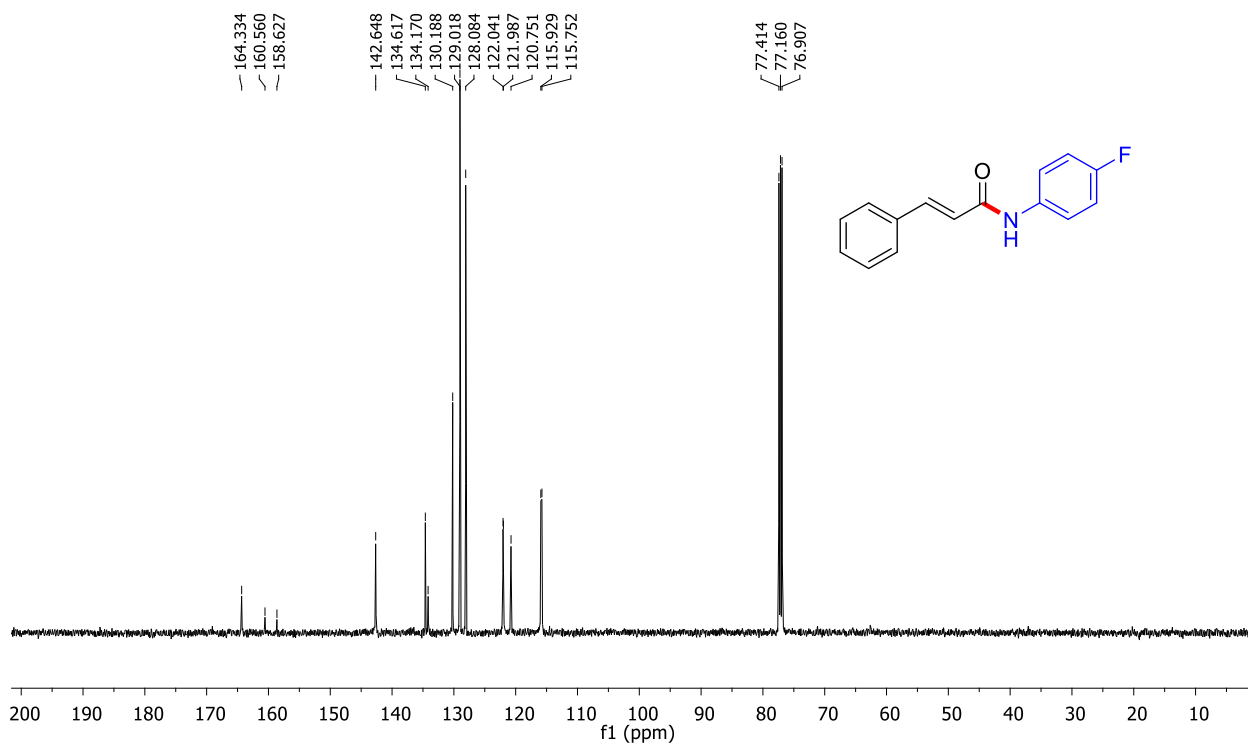


N-(4-Fluorophenyl)cinnamamide (**3w**):

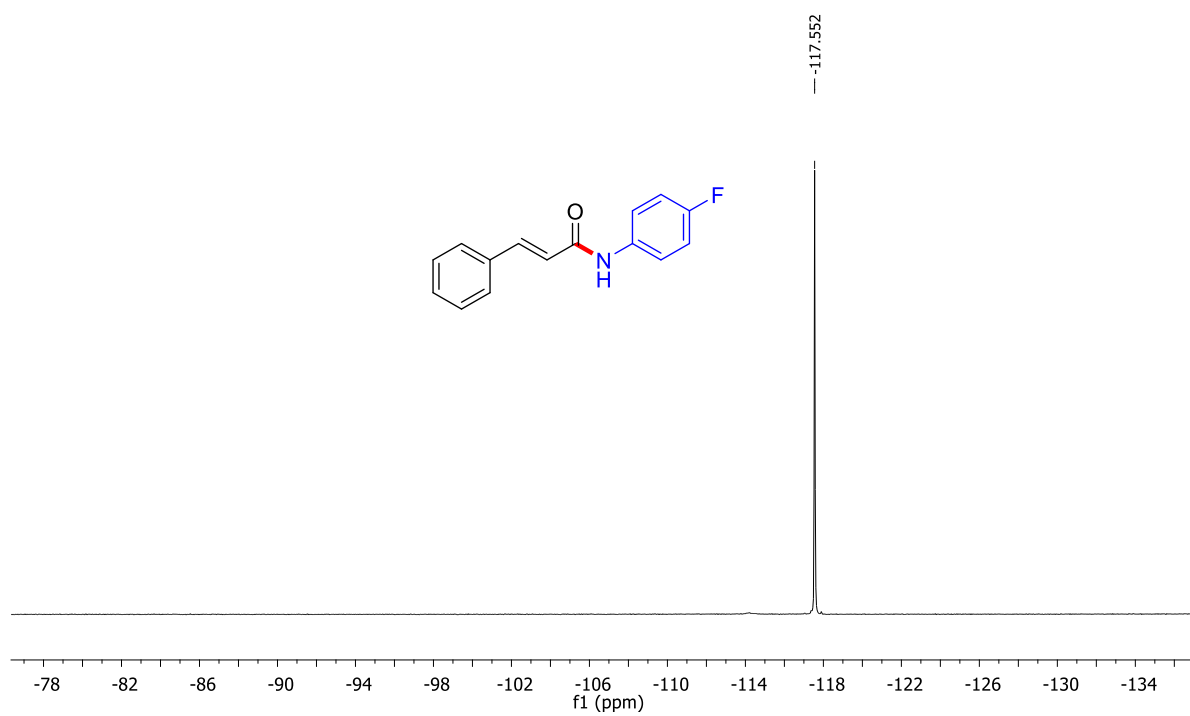
^1H NMR (500 MHz, CDCl_3)



$^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3)

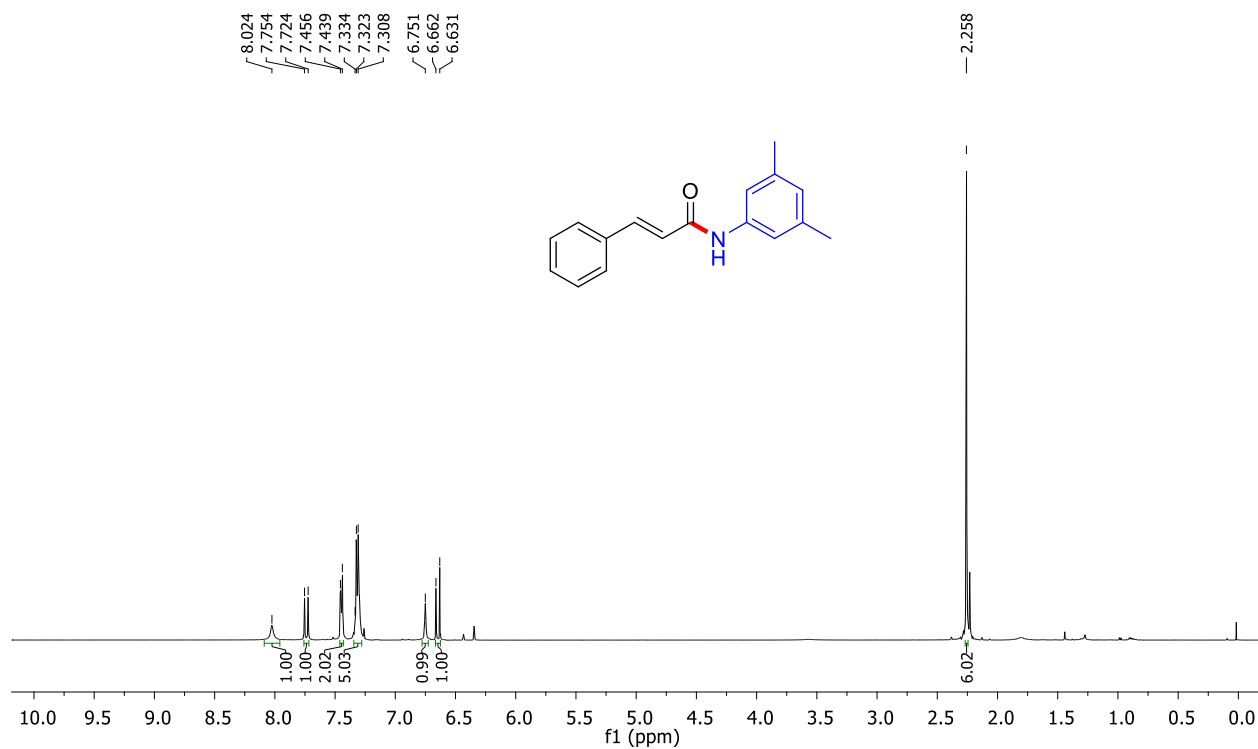


^{19}F NMR (471 MHz, CDCl_3)

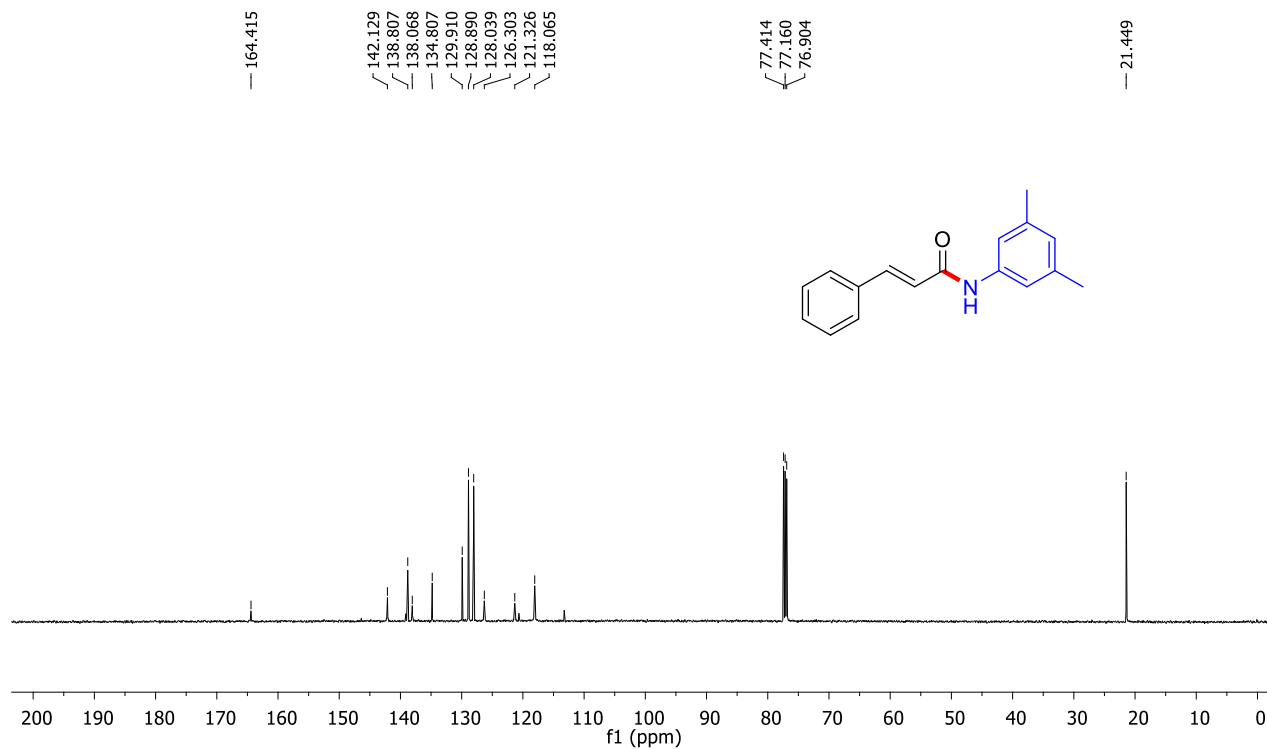


***N*-(3,5-Dimethylphenyl)cinnamamide (3x):**

^1H NMR (500 MHz, CDCl_3)

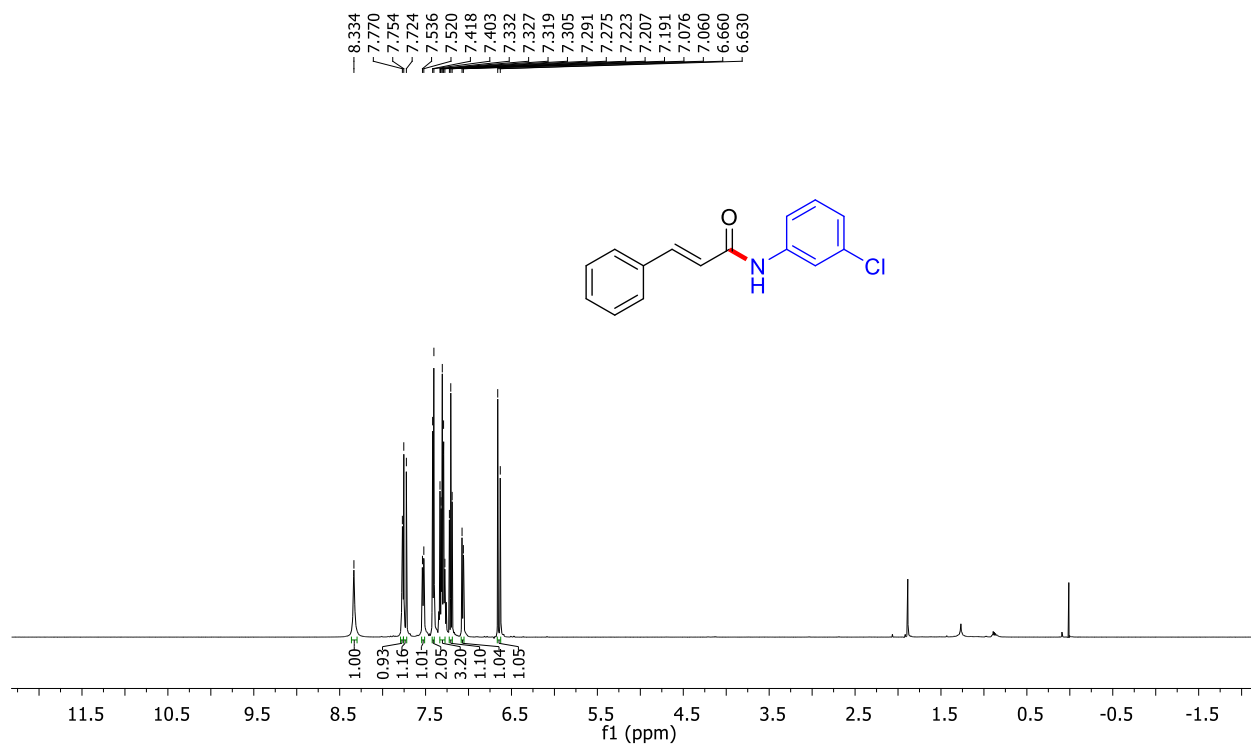


$^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3)

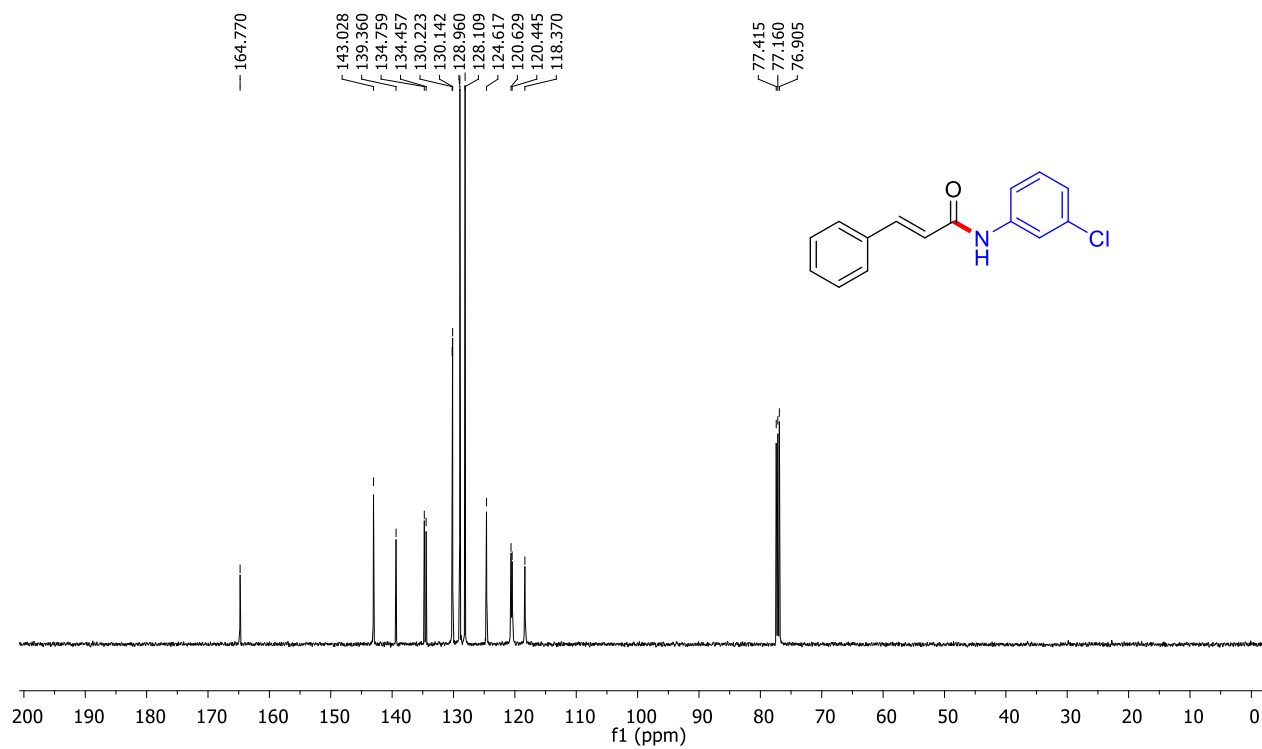


N-(3-Chlorophenyl)cinnamamide (3y):

^1H NMR (500 MHz, CDCl_3)

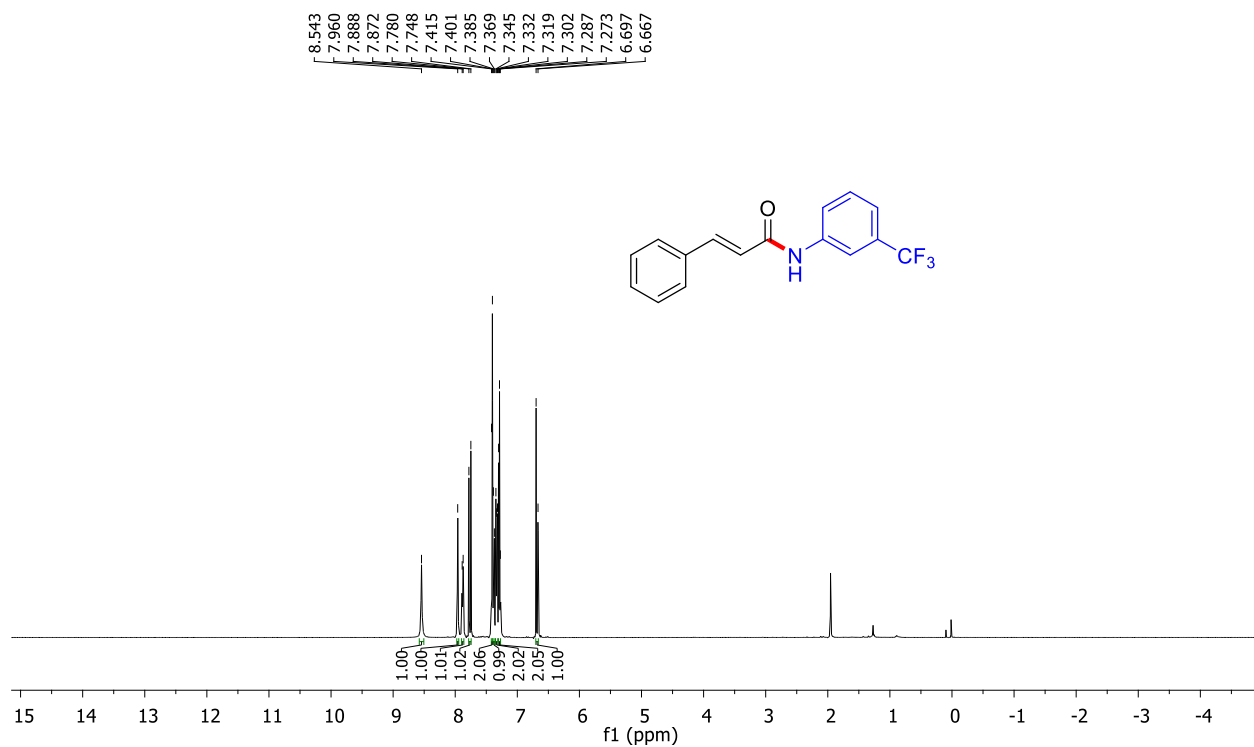


$^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3)

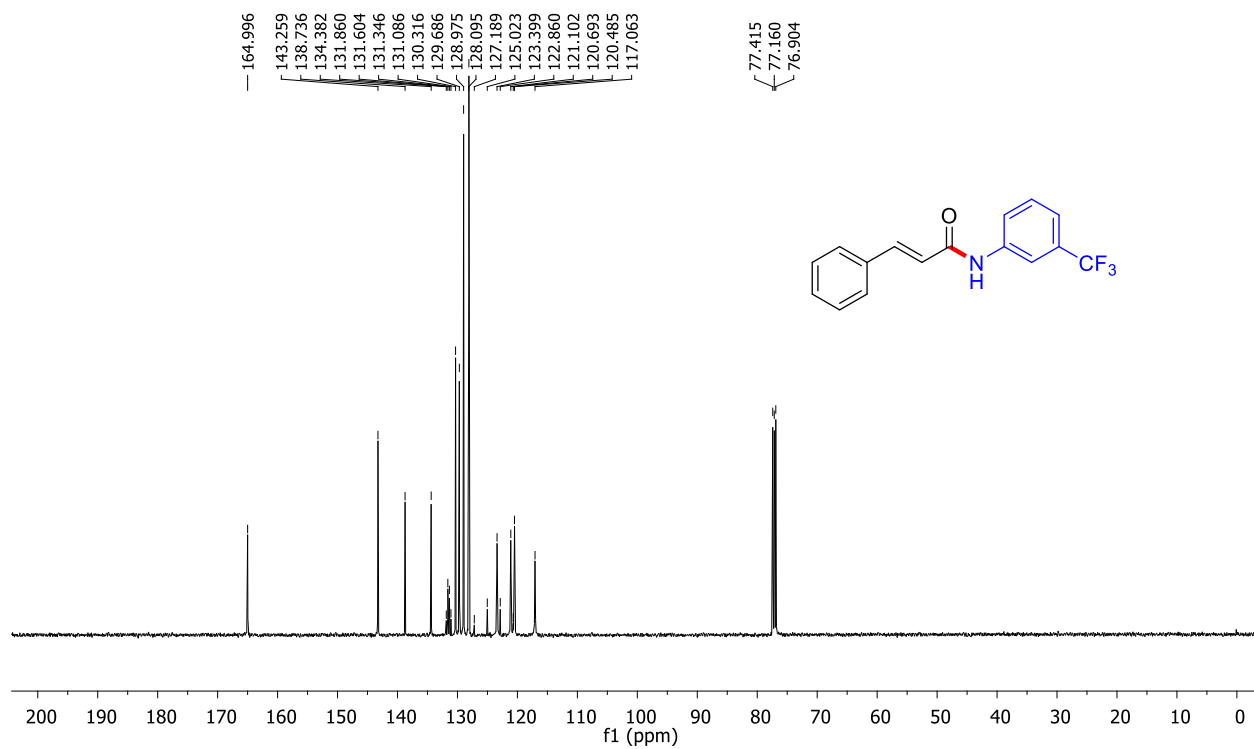


***N*-3-(Trifluoromethyl)phenylcinnamamide (3z):**

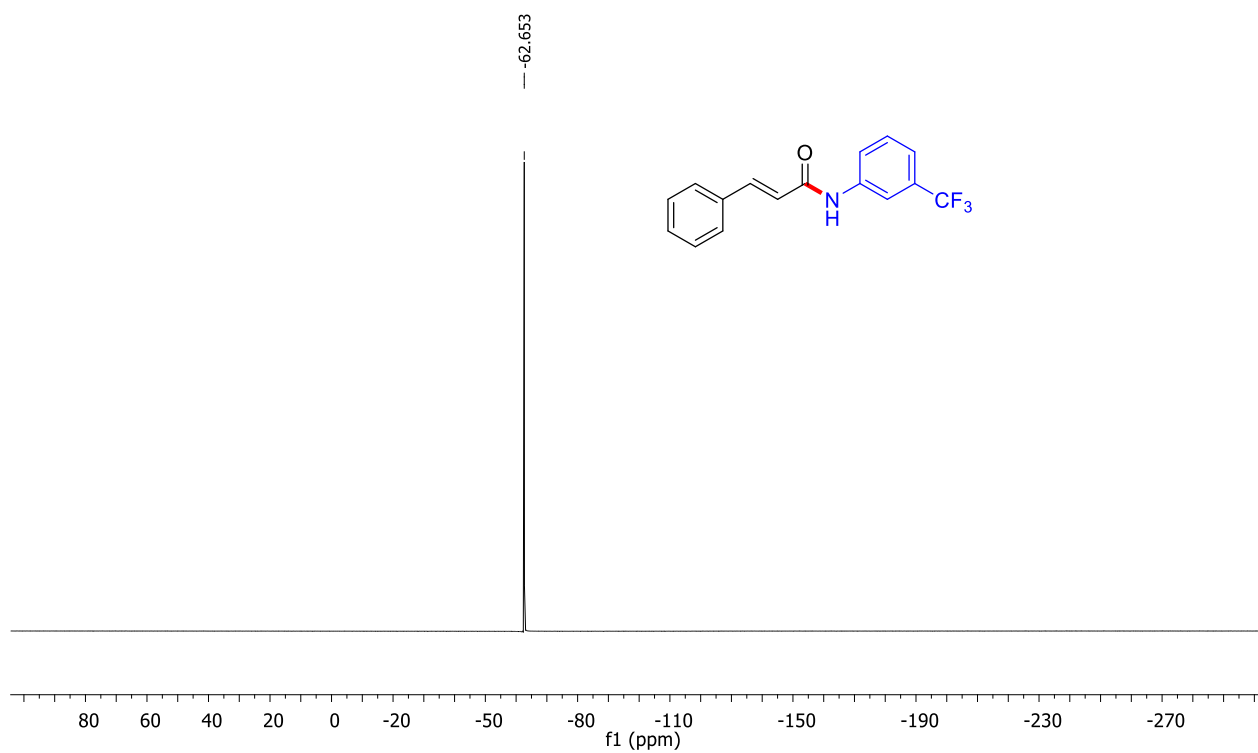
^1H NMR (500 MHz, CDCl_3)



$^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3)

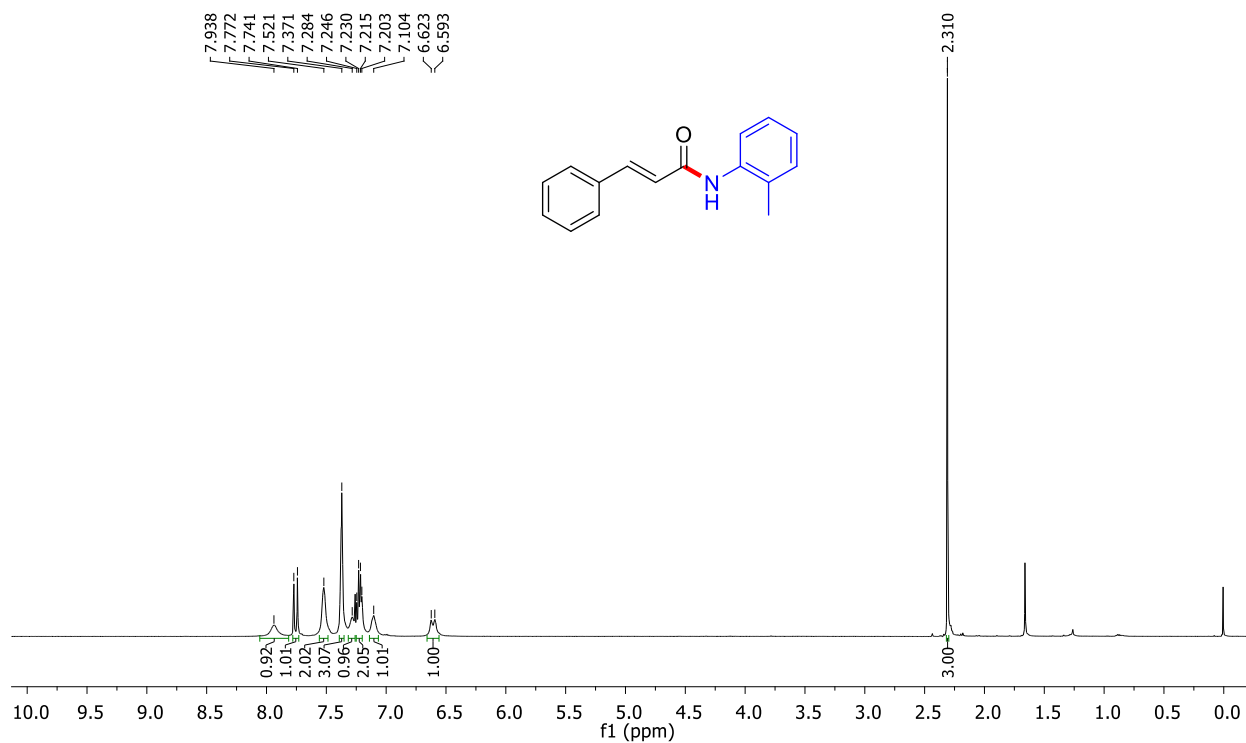


^{19}F NMR (471 MHz, CDCl_3)

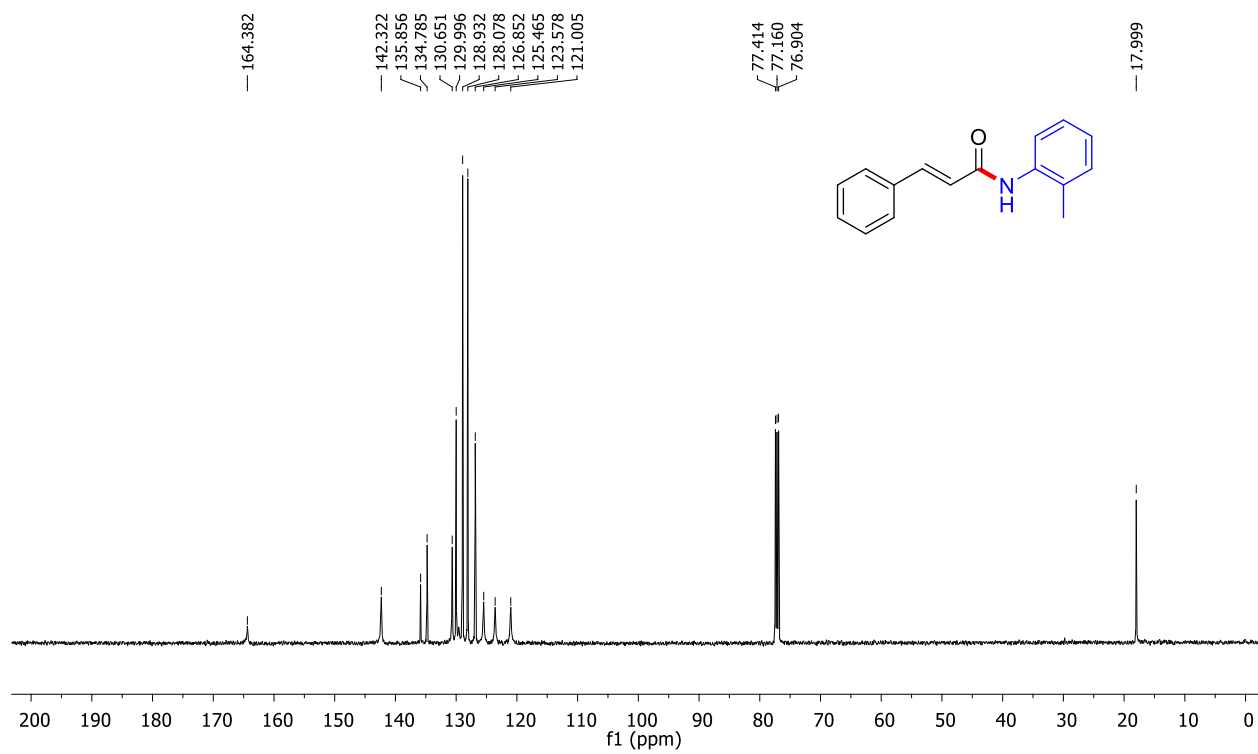


N-(*o*-Tolyl)cinnamamide (3aa):

^1H NMR (500 MHz, CDCl_3)

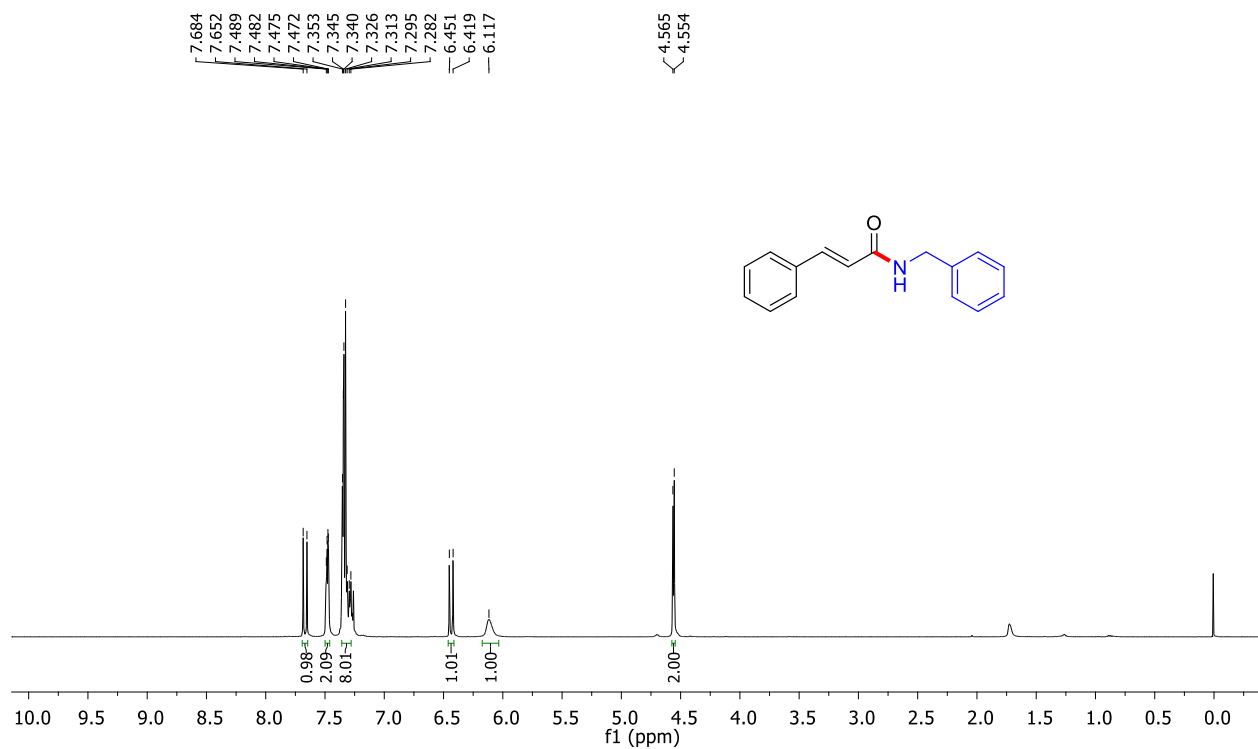


$^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3)

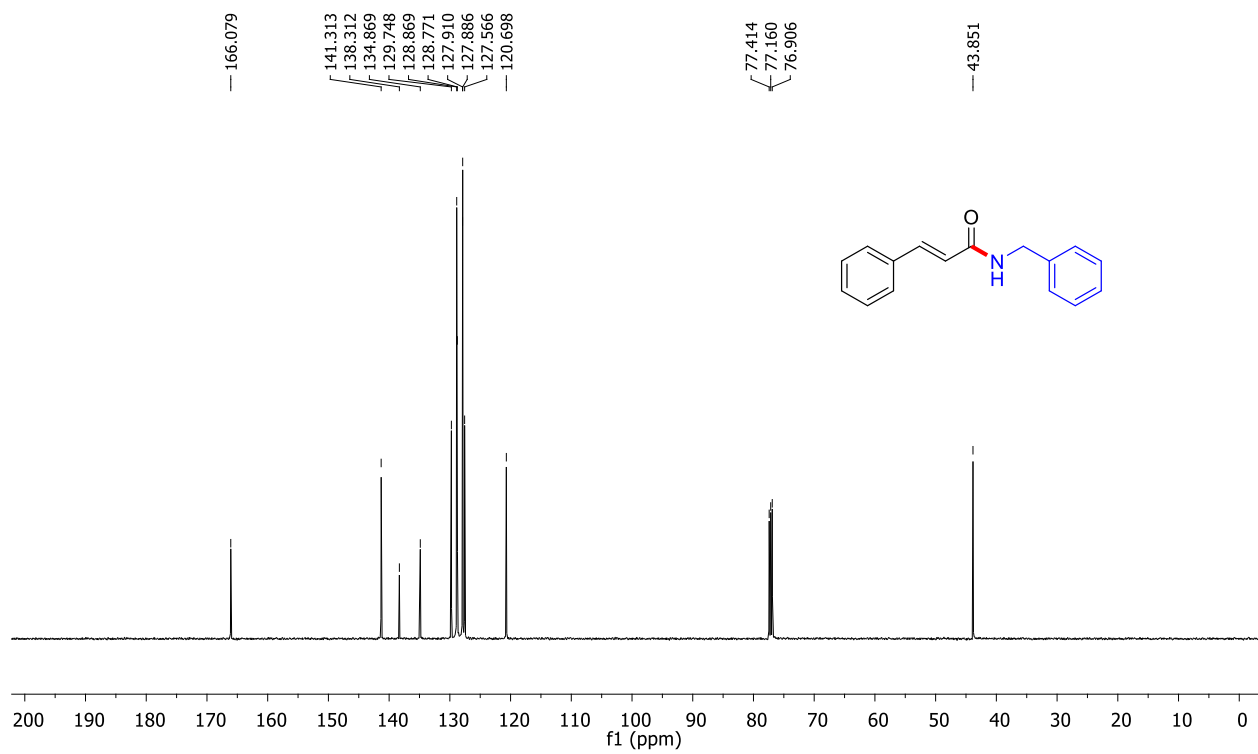


N-Benzylcinnamamide (3ab):

^1H NMR (500 MHz, CDCl_3)

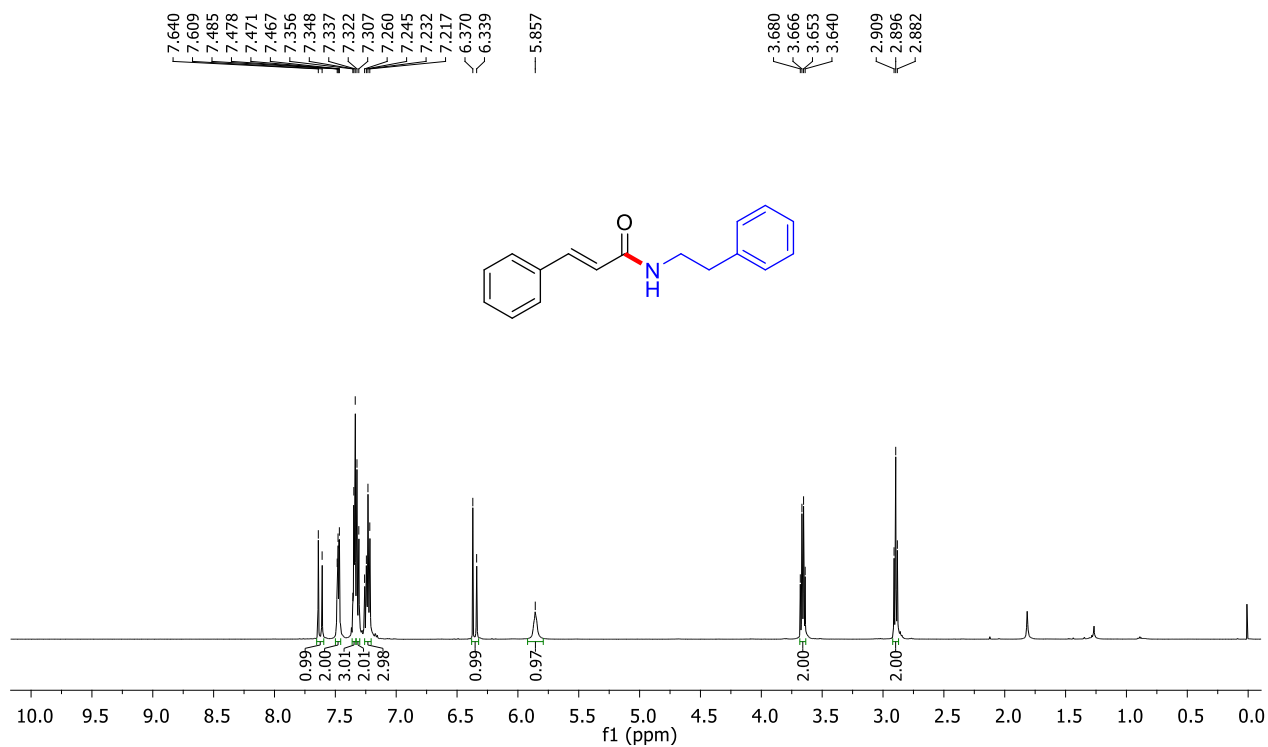


$^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3)

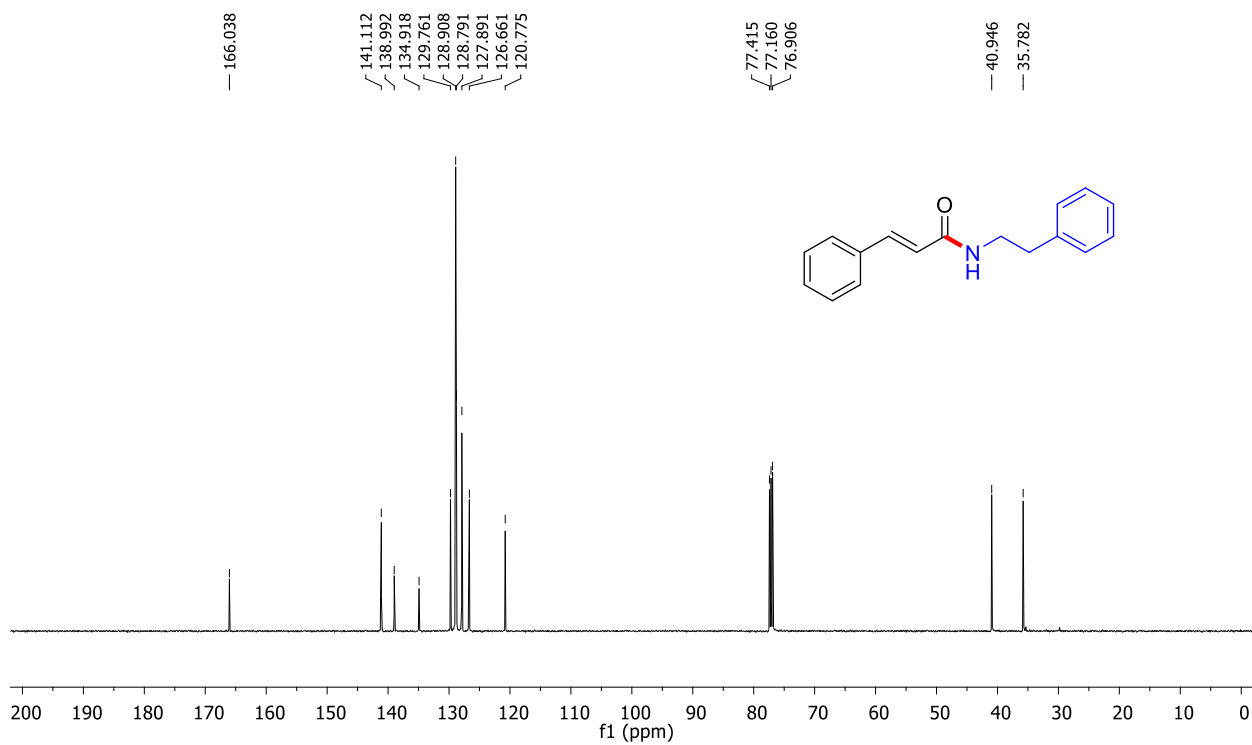


***N*-Phenethylcinnamamide (3ac):**

¹H NMR (500 MHz, CDCl₃)

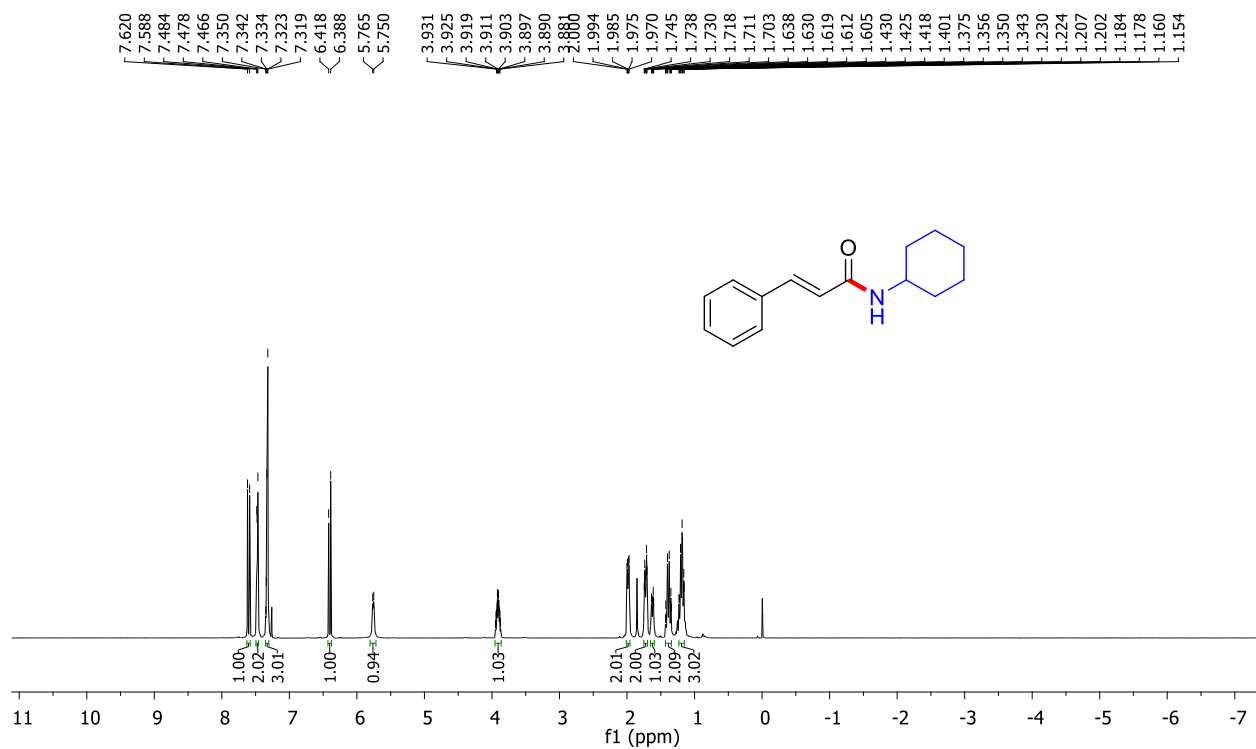


¹³C{¹H} NMR (126 MHz, CDCl₃)

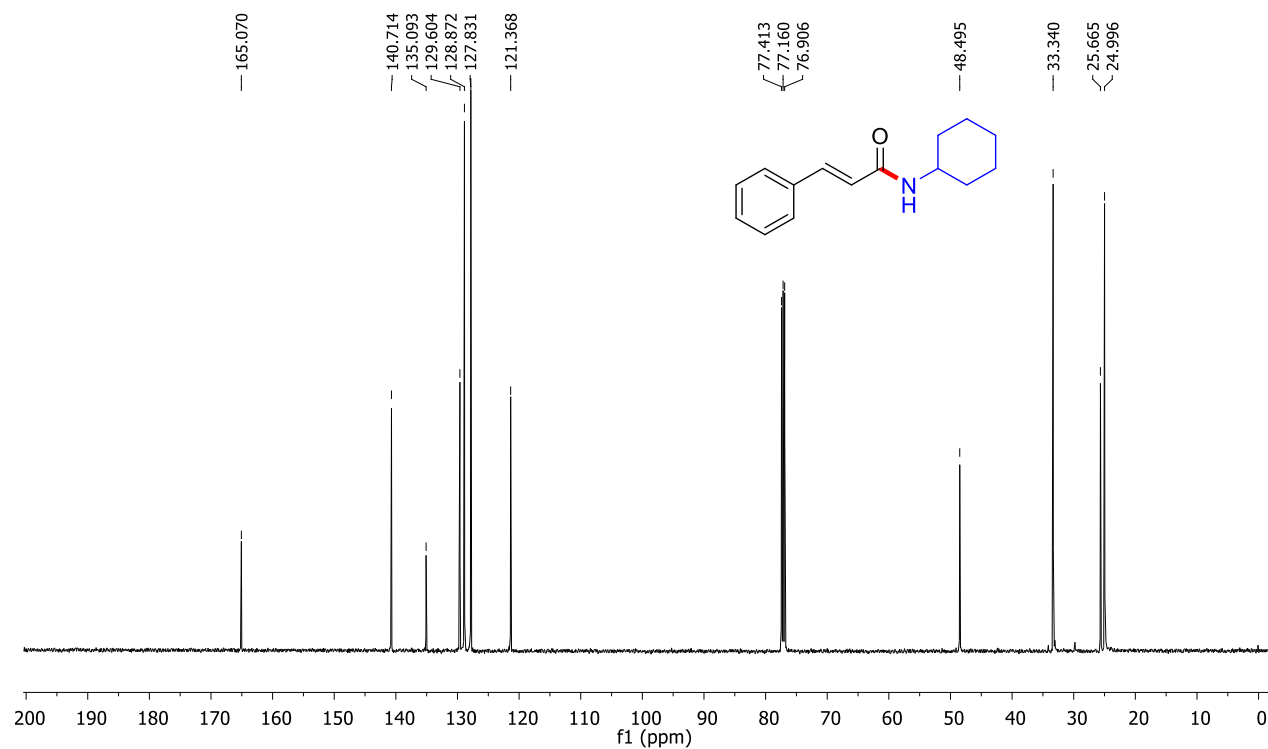


***N*-Cyclohexylcinnamamide (3ad):**

¹H NMR (500 MHz, CDCl₃)

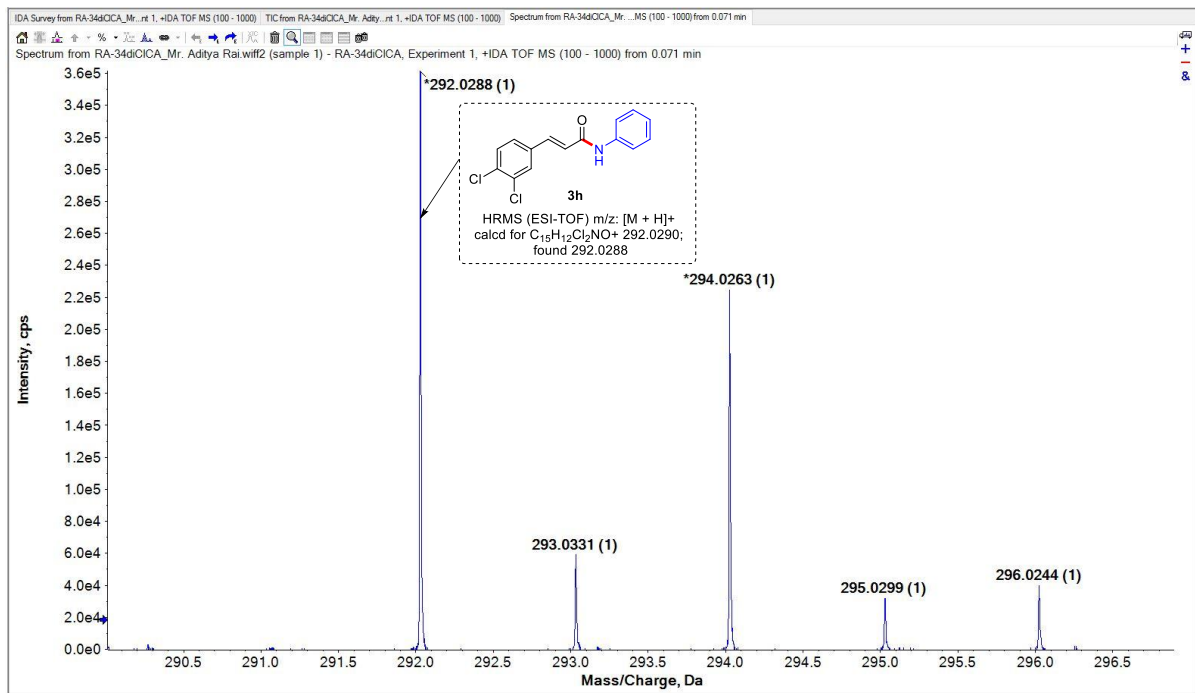


¹³C{¹H} NMR (126 MHz, CDCl₃)

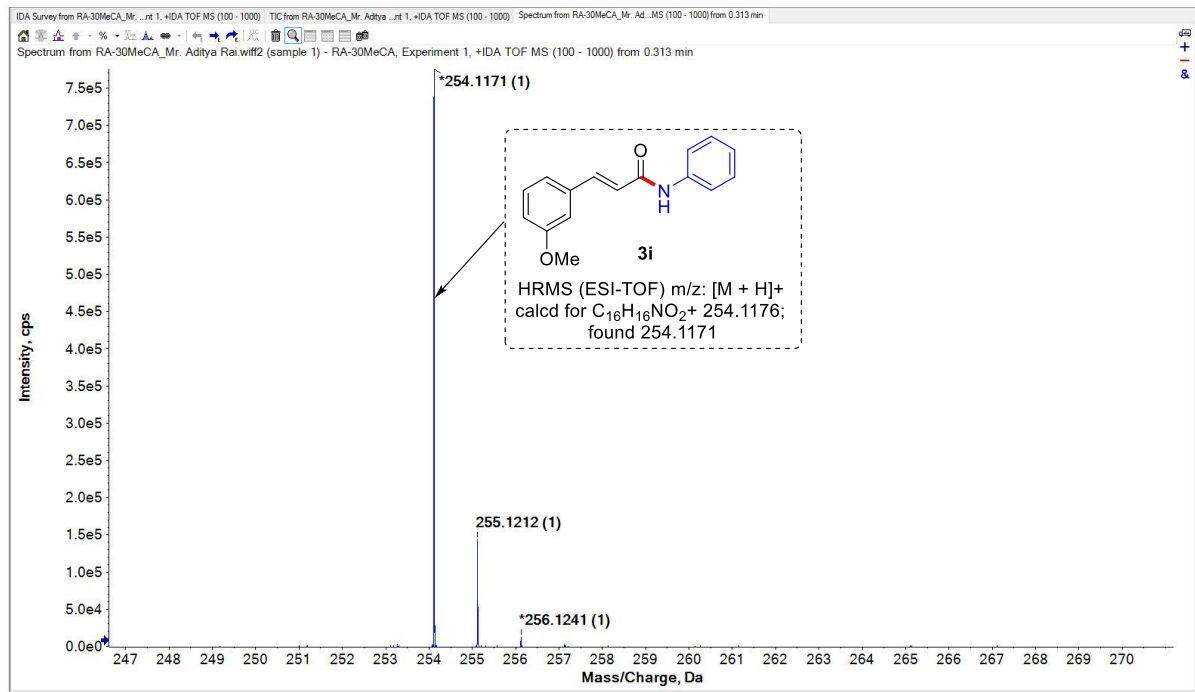


4. Copies of HRMS Spectra of the Unknown Products 3.

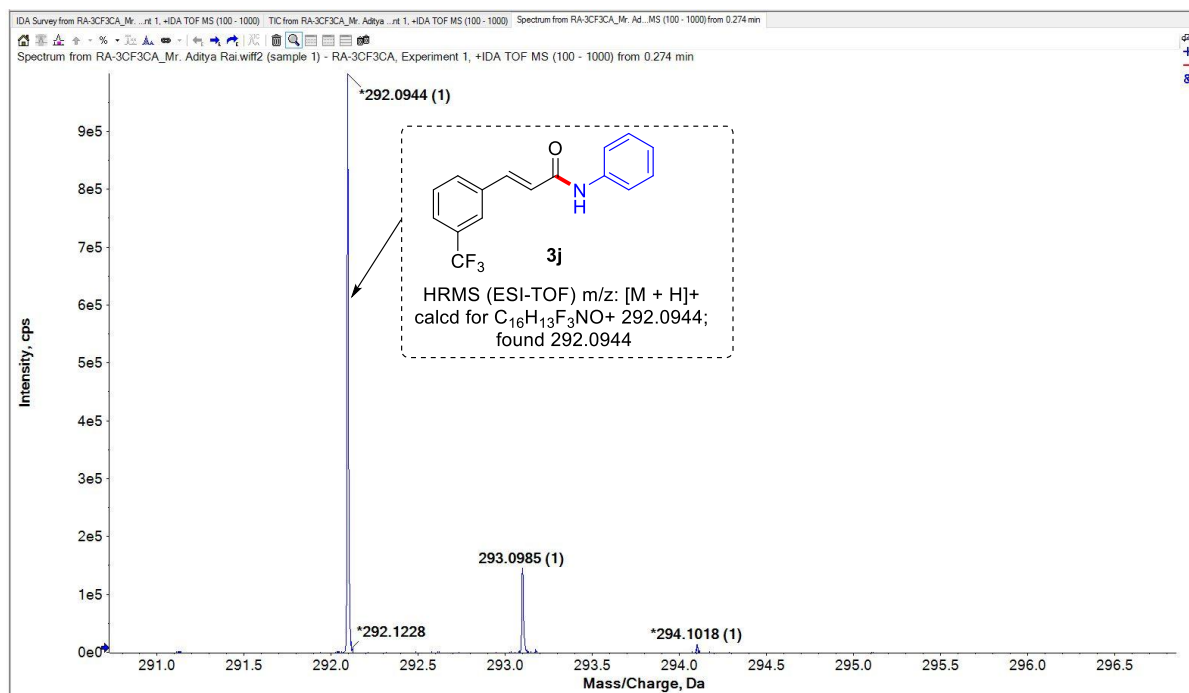
(*E*)-3-(3,4-Dichlorophenyl)-*N*-phenylacrylamide (3h):



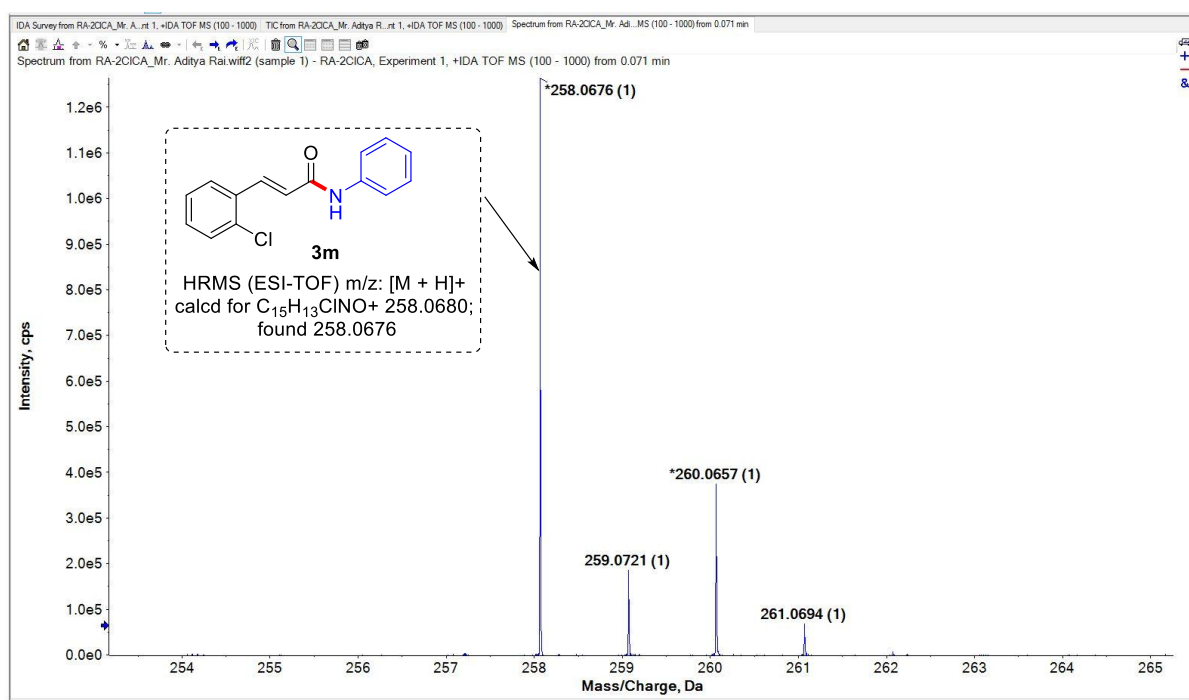
(*E*)-3-(3-Methoxyphenyl)-*N*-phenylacrylamide (3i):



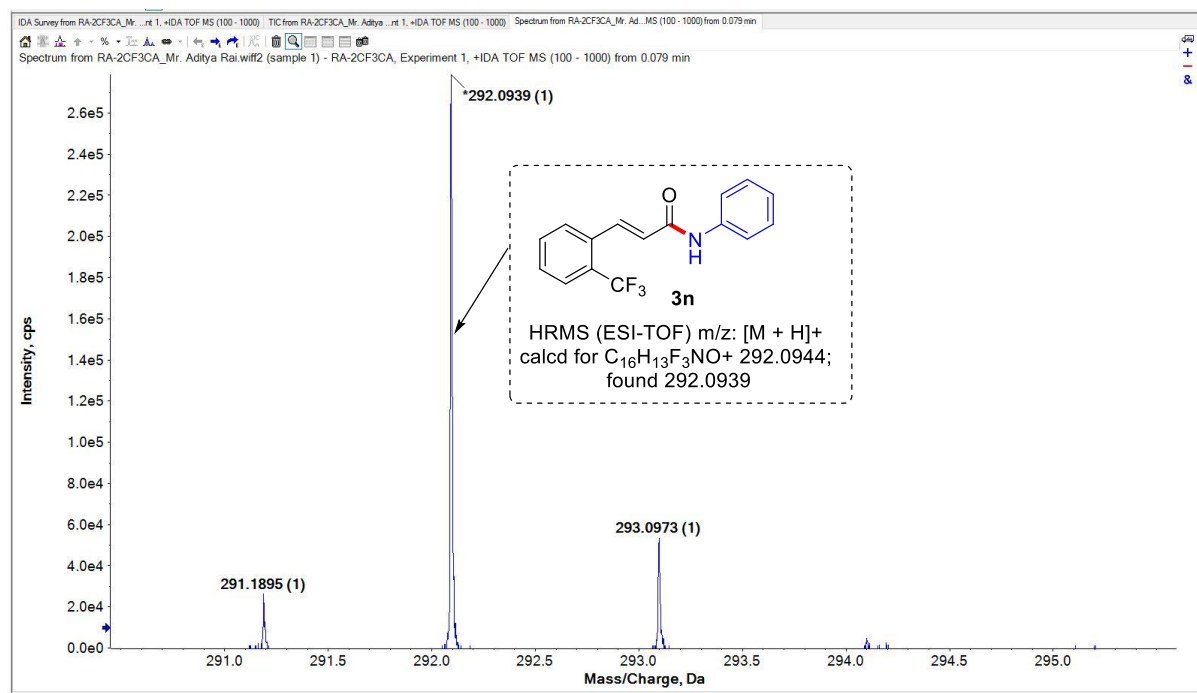
(E)-N-Phenyl-3-(3-(trifluoromethyl)phenyl)acrylamide (3j):



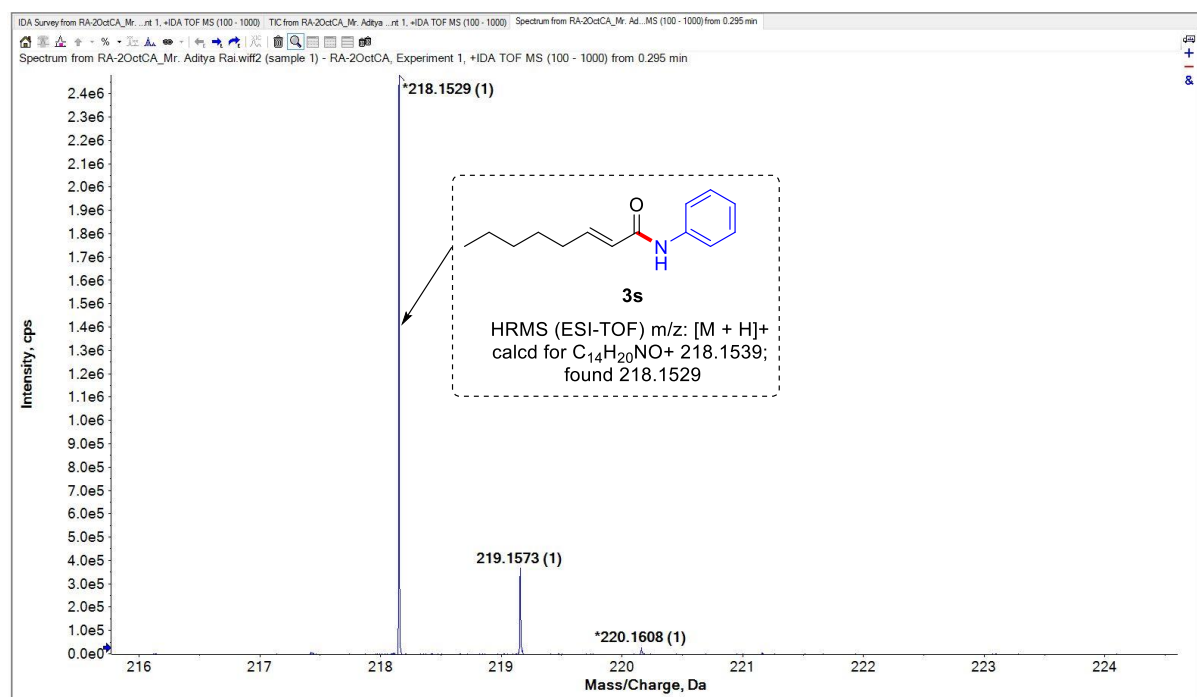
(E)-3-(2-Chlorophenyl)-N-phenylacrylamide (3m):



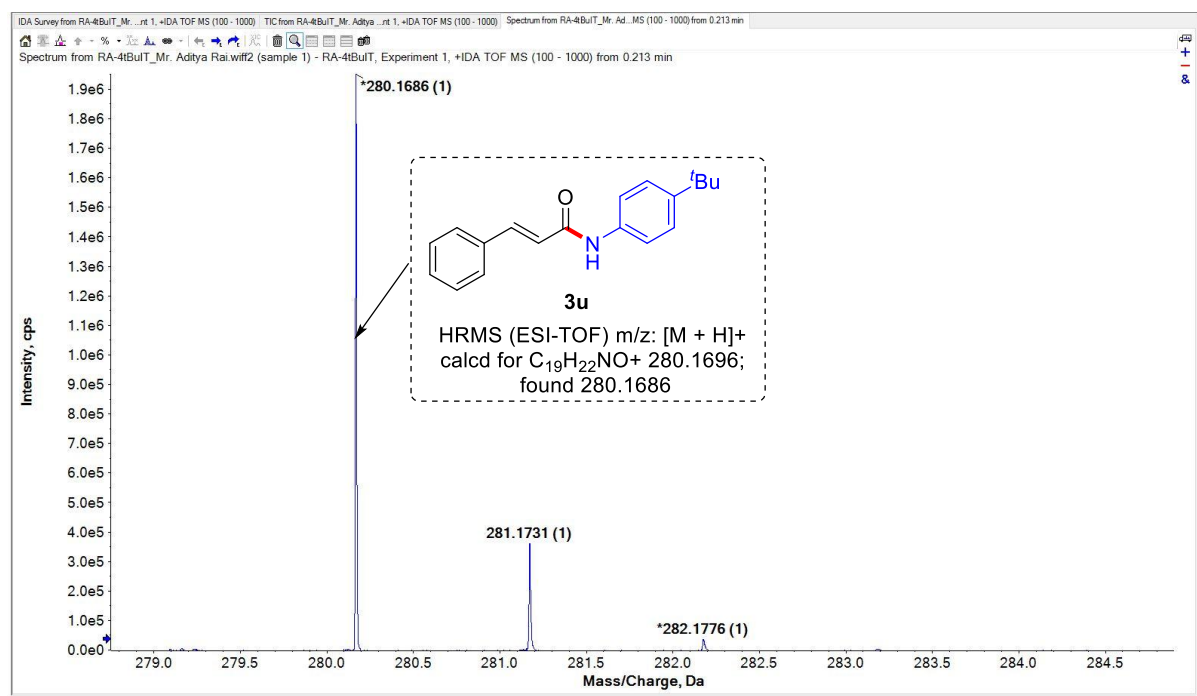
(E)-N-Phenyl-3-(2-(trifluoromethyl)phenyl)acrylamide (3n):



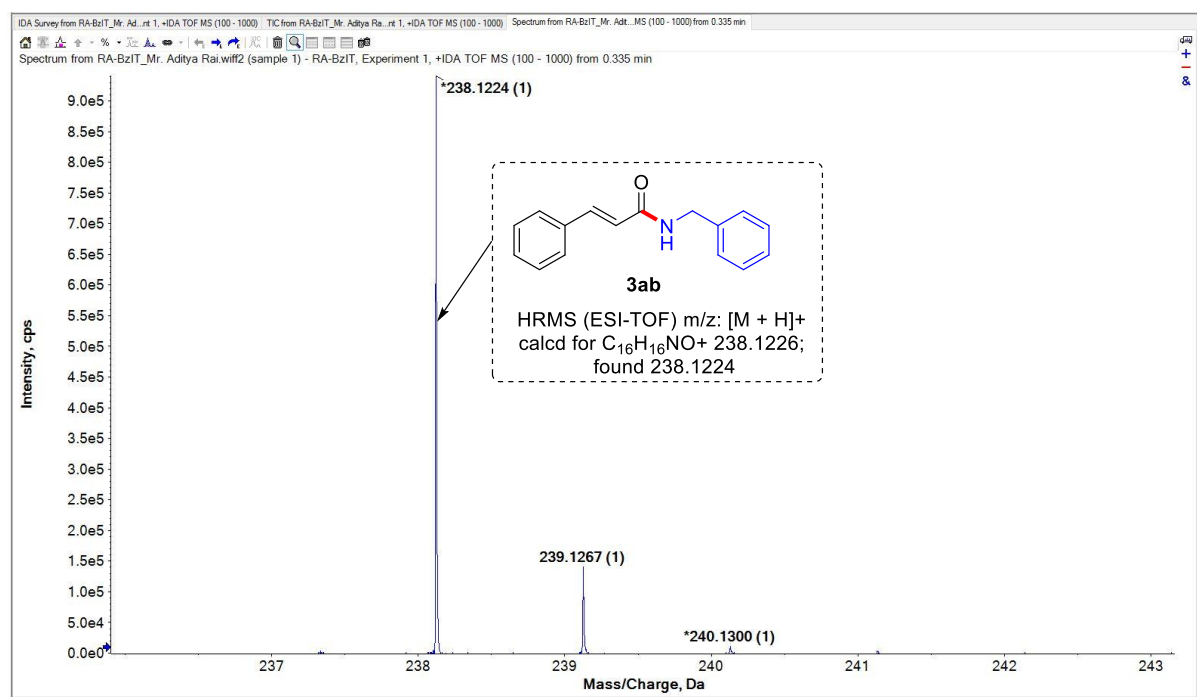
(E)-N-Phenyl-2-octenamide (3s):



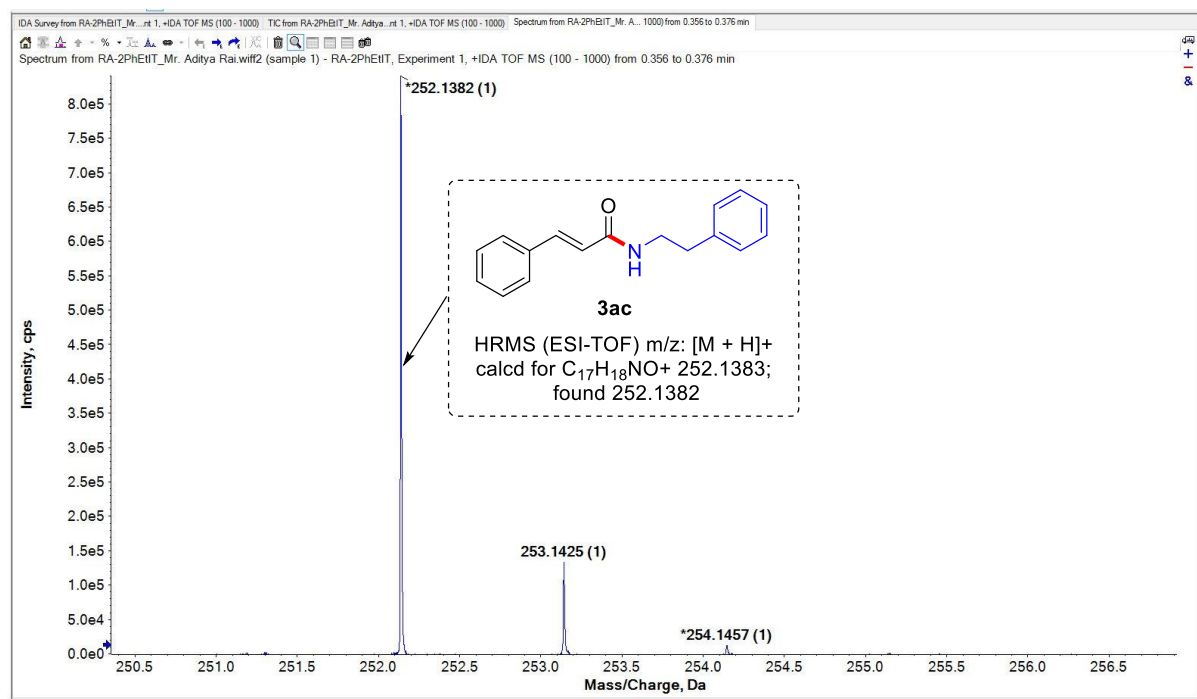
N-(4-(*Tert*-butyl)phenyl)cinnamamide (**3u**):



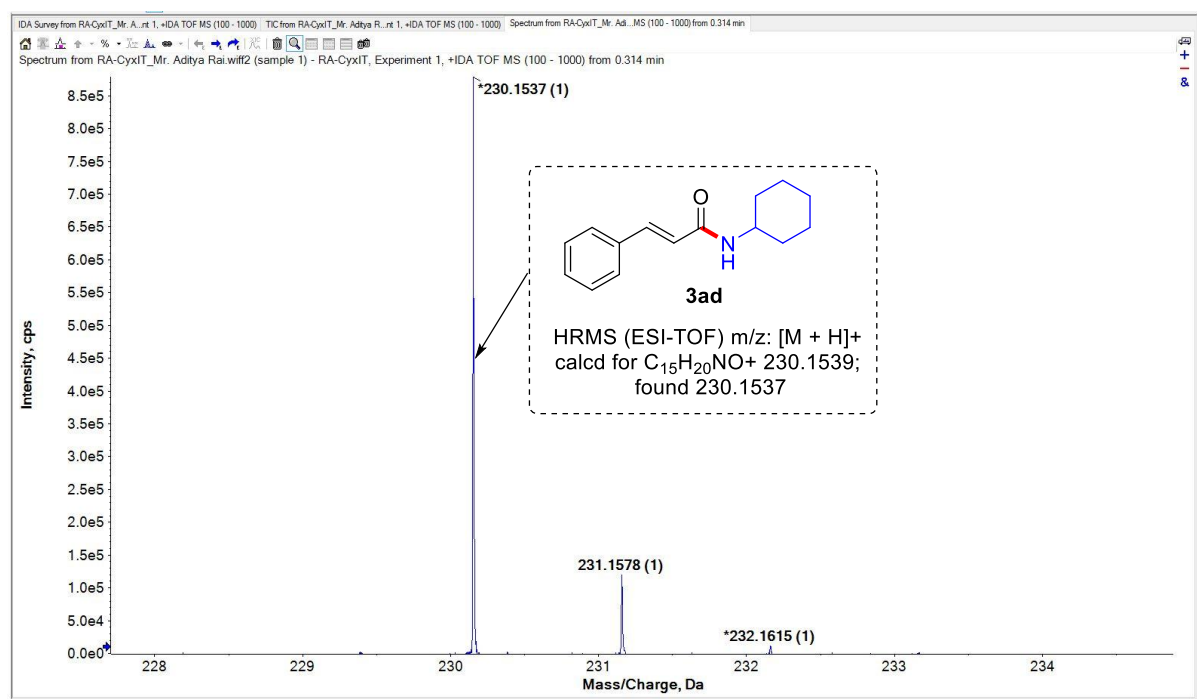
N-Benzylcinnamamide (**3ab**):



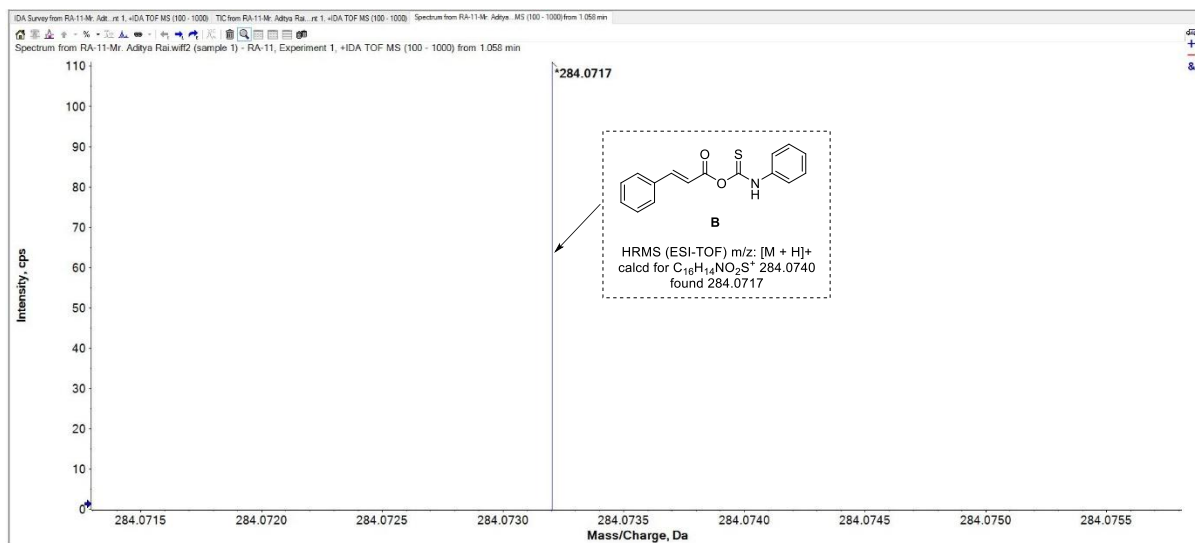
N-Phenethylcinnamamide (3ac):



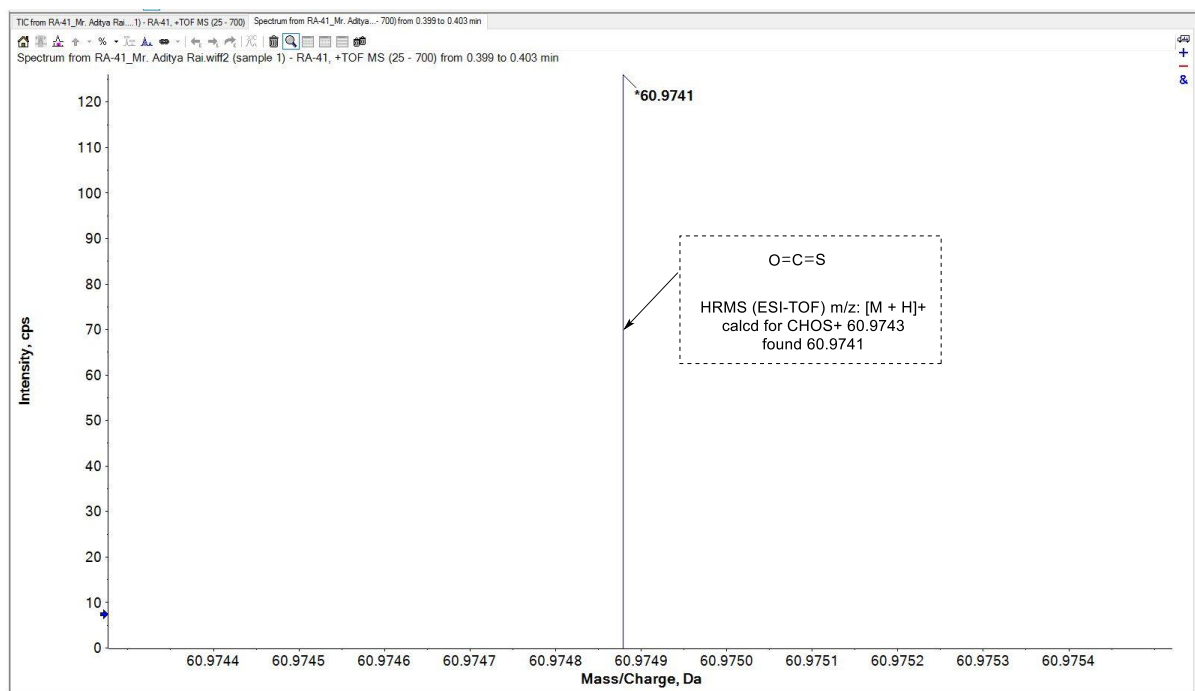
N-Cyclohexylcinnamamide (3ad):



5. HRMS Spectra of the Intermediate B.



6. HRMS Spectra of the Carbonyl Sulfide.



7. Crystallographic Data of the Product 3f.

Crystal of the product **3f** was grown by slow evaporation of a solution of the compound in CDCl₃.

Specification: Single crystal X-ray data of the compound was collected on the XtaLAB Synergy, Dualflex, HyPix3000 HPAD detector using Cu-K α ($\lambda = 1.54184 \text{ \AA}$) radiation source. The structure was solved using SHELXT-2018/2 and was refined by full-matrix least-squares procedures using the SHELXL-2019/3 software package through the OLEX2 suite.

Crystallized from	Chloroform
Empirical formula	C ₁₅ H ₁₂ ClNO
Formula weight [g mol ⁻¹]	257.71
Crystal color, habit	Light Yellow, Needle
Crystal dimensions/mm ³	0.16 × 0.14 × 0.13
Temperature [K]	293(2)
Crystal system	Orthorhombic
Space group	<i>Pbca</i>
a/Å	12.4472(2)
b/Å	9.62130(10)
c/Å	21.8930(2)
α /°	90°
β /°	90°
γ /°	90°
V[Å ³]	2621.87(6)
Z	8
ρ [g/cm ³]	1.306
μ [mm ⁻¹]	2.463
F(000)	1072
Radiation	Cu-K α ($\lambda = 1.54184 \text{ \AA}$)
Θ range for data collection/°	4.038 to 68.102°
Index ranges	-14 ≤ h ≤ 14, -11 ≤ k ≤ 8, -26 ≤ l ≤ 26
Reflections collected	23950
Independent reflections	2385 [R(int) = 0.0289]
Data/restraints/parameters	2385/0/167
Goodness-of-fit on F ²	0.915
Final R indexes [$I \geq 2\sigma(I)$]	R ₁ = 0.0345, wR ₂ = 0.1063
Final R indexes [all data]	R ₁ = 0.0398, wR ₂ = 0.1128
Largest diff. peak/hole / e Å ⁻³	0.124/-0.253

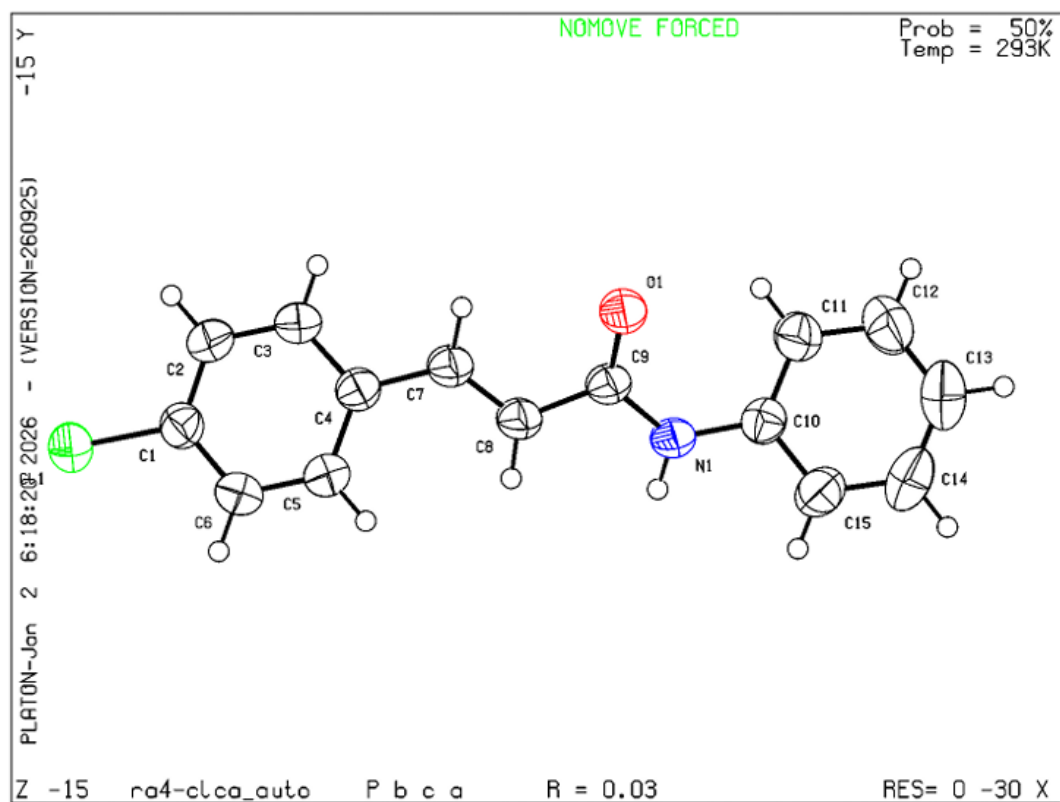
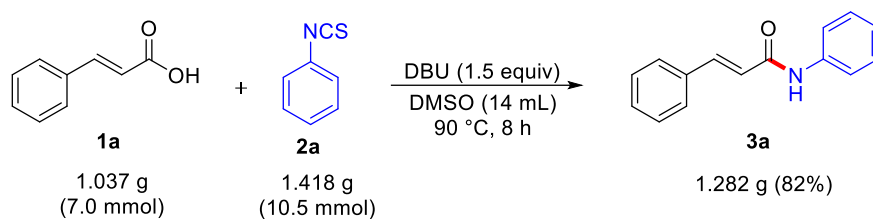


Figure S1: View of the molecular structure of the product **3f**. Displacement ellipsoids are drawn at the 50% probability level.

8. Procedure for Gram Scale Preparation of the Product **3a**.



A mixture of cinnamic acid **1a** (1.037 g, 7.0 mmol), phenyl isothiocyanate **2a** (1.418 g, 10.5 mmol), DBU (1.5 equiv), and DMSO (14 mL), contained in a 100-mL round-bottom flask, was stirred at 90 °C in an oil bath for 8 h. After completion of the reaction (monitored through TLC), a saturated aqueous NaHCO₃ solution (30 mL) was added to the reaction mixture, which was then extracted with ethyl acetate (3×30 mL). The combined organic phase was dried over anhydrous Na₂SO₄, filtered, and concentrated under reduced pressure. The resulting crude product was finally purified by silica gel column chromatography using *n*-hexane and ethyl acetate as eluent to afford the product **3a** (1.282 g, 82%).