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Halogenation Effects in Intramolecular Furan Diels-Alder Reactions: Broad Scope Synthetic and Computational Studies

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General Information

^{1}H NMR spectra were recorded on Bruker AV 300, DPX 400 and AV 400 spectrometers at 300 and 400 MHz respectively and referenced to residual solvent. ^{13}C NMR spectrum were recorded using the same spectrometers at 75 and 100 MHz respectively. Chemical shifts (δ in ppm) were referenced to tetramethylsilane (TMS) or to residual solvent peaks ($CDCl_3$ at δH 7.26). *J* values are given in Hz and s, d, dd, ddd, t, dt, q, m, br and app. abbreviations correspond to singlet, doublet, doublet of doublet, doublet of doublet of doublet, triplet, triplet of doublet, quartet, multiplet, broad and apparent respectively. Mass spectra were obtained at the EPSRC National Mass Spectrometry Service Centre in Swansea. Infrared spectra were obtained on Perkin-Elmer Spectrum 100 FT-IR Universal ATR Sampling Accessory, deposited neat or as a chloroform solution to a diamond/ZnSe plate.

Flash column chromatography was carried out using Matrix silica gel 60 from Fisher Chemicals and TLC was performed using Merck silica gel 60 F254 precoated sheets and visualised by UV (254 nm) and stained by the use of aqueous acidic $KMnO_4$. Anhydrous dichloromethane (DCM) was distilled from CaH_2.

Experimental Section

Substrates **1a**[1], **1b**, **1c**, **1d**, **1i**, **1j**, **1k**, **1l**, **1r**, **1s**, **1t**, **1u**, **1v**, **1w**, **1x**, **1y** and **1z** were prepared by reaction of the corresponding acyl chloride (generated from the carboxylic acid if necessary) with the corresponding amines.

Substrates **1e**, **1f**, **1g**, and **1h** were prepared by reaction of the corresponding amine with acryloyl chloride.

Substrates **1m**, **1n**[2], **1o**[3], **1p** and **1q** were prepared by reaction of the corresponding amine with $(Boc)_2O$.

Cycloadducts **2a**[1]**-2z** were prepared in intra-molecular Diels-Alder processes by heating the corresponding substrate to reflux in toluene for lengths of time detailed below. Cycloadducts **2n**[2] and **2o**[3] have been synthesised previously. In the majority of cases, remaining starting material

eluted just before the cycloadduct (amounts of recovered starting material are detailed in the main manuscript).

With regards to the substrates detailed below, the following starting materials are commercially available: 5-bromo-2-furoic acid, *N*-allyl aniline, 2-furoyl chloride, acryloyl chloride and $(Boc)_2O$.

4-Bromo-2-furoic acid was synthesised from 4,5-dibromo-2-furoic acid *via* know methods.[4]

3-Bromo-2-furoic acid was synthesised from 3-bromofuran *via* known methods.[5]

Secondary amines (*Z*)-*N*-(3-chloroallyl)aniline, (*E*)-*N*-(3-chloroallyl)aniline, *N*-(2-chloroallyl)aniline, *N*-(2-bromoallyl)aniline, (*Z*)-3-chloro-*N*-(furan-2-ylmethyl)prop-2-en-1-amine and (*E*)-3-chloro-*N*-(furan-2-ylmethyl)prop-2-en-1-amine were synthesised by reaction of the corresponding, commercially available dihalopropenes with furfurylamine or aniline (both also commercially available) *via* known methods.[6]

Secondary amines *N*-(furan-2-ylmethyl)aniline, *N*-((5-bromofuran-2-yl)methyl)aniline, *N*-((4-bromofuran-2-yl)methyl)aniline, *N*-((3-bromofuran-2-yl)methyl)aniline and *N*-(furan-2-ylmethyl)prop-2-en-1-amine were synthesised by reductive amination reactions of the corresponding, commercially available 2-furaldehydes with aniline or *N*-allylamine (both also commercially available) *via* known methods.[7]

***N*-allyl-5-bromo-*N*-phenylfuran-2-carboxamide (1b):** To a solution of 5-bromo-2-furoic acid (1.0 g, 5.2 mmol) in dry dichloromethane (6.5 ml) containing *N*,*N*-dimethylformamide (1 drop) was carefully added oxalyl chloride (1.0 g, 7.9 mmol) at 0 °C. The solution was allowed to rise to room temperature while stirring for 1.5 hours before the reaction mixture was concentrated *in vacuo*. Dry dichloromethane (2.0 ml) was introduced before a solution of *N*-allyl aniline (759 mg, 5.7 mmol) and triethylamine (1.5 ml, 10.0 mmol) in dry dichloromethane (2.0 ml) was then carefully added at 0 °C with stirring. The reaction mixture was then allowed to rise to room temperature while stirring overnight. Water (10 ml) was then added to the reaction mixture and extracted with dichloromethane (3 x 25 ml). Combined organic layers were dried (Na_2SO_4) and concentrated *in vacuo*. Purification by column chromatography (3:7 ethyl acetate/ petroleum ether) afforded the title compound: Wt 1.29 g; 81%; white solid; m.p. 104-106 °C; δ_H (300 MHz, $CDCl_3$) 7.49 – 7.33 (m, 3H), 7.26 – 7.13 (m, 2H), 6.15 (d, *J* = 3.5 Hz, 1H), 5.96 (ddt, *J* = 16.7, 10.4, 6.3 Hz, 1H), 5.81 (d, *J* = 3.5 Hz, 1H), 5.21 – 5.15 (m, 1H), 5.19 – 5.11 (m, 1H), 4.44 (dt, *J* =

6.3, 1.2 Hz, 2H); δ_C (75 MHz, $CDCl_3$) 157.7, 148.9, 142.2, 132.5, 129.5, 128.3, 128.2, 125.4, 118.8, 118.5, 112.9, 53.4; ν_{max}/cm^{-1} 3115, 3094, 3051, 1633, 1594, 1492, 1455, 1425, 1398, 1302, 1285, 1214, 1178, 1036; m/z HRMS (NSI+) found 306.0128, $C_{14}H_{13}BrNO_2$ $[M + H]^+$ requires 306.0124.

***N*-allyl-4-bromo-*N*-phenylfuran-2-carboxamide (1c):** To a solution of 4-bromo-2-furoic acid (200 mg, 1.05 mmol) in dry dichloromethane (1.3 ml) containing *N*,*N*-dimethylformamide (1 drop) was carefully added oxalyl chloride (201 mg, 1.58 mmol) at 0 °C. The solution was allowed to rise to room temperature while stirring for 1.5 hours before the reaction mixture was concentrated *in vacuo*. Dry dichloromethane (0.8 ml) was introduced before a solution of *N*-allyl aniline (152 mg, 1.14 mmol) and triethylamine (0.28 ml, 2.0 mmol) in dry dichloromethane (0.8 ml) was then carefully added at 0 °C with stirring. The reaction mixture was then allowed to rise to room temperature while stirring overnight. Water (2 ml) was then added to the reaction mixture and extracted with dichloromethane (3 x 5ml). Combined organic layers were dried (Na_2SO_4) and concentrated *in vacuo*. Purification by column chromatography (1:4 ethyl acetate/ petroleum ether) afforded the title compound: Wt 197 mg; 62%; white solid: m.p. 74-76 °C; δ_H (300 MHz, $CDCl_3$) 7.46 – 7.37 (m, 3H), 7.32 (d, *J* = 0.8 Hz, 1H), 7.22 – 7.10 (m, 2H), 5.93 (ddt, *J* = 16.6, 10.3, 6.3 Hz, 1H), 5.73 (app. s, 1H), 5.20 – 5.13 (m, 1H), 5.17 – 5.09 (m, 1H), 4.43 (dt, *J* = 6.3, 1.3 Hz, 2H); δ_C (75 MHz, $CDCl_3$) 157.8, 147.4, 142.6, 141.9, 132.3, 129.6, 128.4, 128.2, 118.8, 118.6, 100.3, 53.4; ν_{max}/cm^{-1} 3121, 3058, 1636, 1594, 1479, 1399, 1294, 1283, 1196; m/z HRMS (NSI+) found 306.0131, $C_{14}H_{13}BrNO_2$ $[M + H]^+$ requires 306.0124.

***N*-allyl-3-bromo-*N*-phenylfuran-2-carboxamide (1d):** To a solution of 3-bromo-2-furoic acid (382 mg, 2.0 mmol) in dry dichloromethane (0.8 ml) containing *N*,*N*-dimethylformamide (1 drop) was carefully added oxalyl chloride (381 mg, 3.0 mmol) at 0 °C. The solution was allowed to rise to room temperature while stirring for 1.5 hours before the reaction mixture was concentrated *in vacuo*. Dry dichloromethane (0.8 ml) was introduced before a solution of *N*-allyl aniline (266 mg, 2.0 mmol) and triethylamine (0.28 ml, 2.0 mmol) in dry dichloromethane (0.8 ml) was then carefully added at 0 °C with stirring. The reaction mixture was then allowed to rise to room temperature while stirring overnight. Water (4 ml) was then added to the reaction mixture and extracted with dichloromethane (3 x 10 ml). Combined organic layers were dried (Na_2SO_4) and concentrated *in vacuo*. Purification by column chromatography (1:4 diethyl ether/ petroleum ether) afforded the title compound: Wt 274 mg; 45%; white solid: m.p. 129-131 °C; δ_H (300 MHz, $CDCl_3$) 7.33 – 7.18 (m, 3H), 7.12 – 7.06 (m, 2H), 7.03 (d, *J* = 1.9 Hz, 1H), 6.35 (d, *J* = 1.9 Hz, 1H), 5.96 (ddt, *J* = 16.2, 10.2, 6.0 Hz, 1H), 5.25 – 5.17 (m, 1H), 5.20 – 5.14 (m, 1H), 4.47 (dt, *J* = 6.0, 1.3 Hz, 2H); δ_C (75 MHz, $CDCl_3$) 159.0, 144.2, 143.2, 142.4, 132.6, 128.9, 126.9,

126.7, 118.1, 115.4, 104.5, 53.0; ν_{max}/cm^{-1} 3123, 1642, 1595, 1493, 1388, 1299, 1282, 1199 ; m/z HRMS (NSI+) found 306.0123, $C_{14}H_{13}BrNO_2$ $[M + H]^+$ requires 306.0124.

***N*-(furan-2-ylmethyl)-*N*-phenylacrylamide (1e):** Acryloyl chloride (157 mg, 1.73 mmol) was added carefully to a solution of *N*-(furan-2-ylmethyl)aniline (300 mg, 1.73 mmol), triethylamine (0.23 ml. 3.2 mmol) and DMAP (5 mg) in dry dichloromethane (1.3 ml) at 0 °C with stirring. The reaction mixture was allowed to rise to r.t. and stirred overnight. The reaction mixture was then diluted with dichloromethane (5 ml) and water (5 ml) was added. The mixture was further extracted with dichloromethane (2 x 5 ml) and the combined organic phase dried (Na_2SO_4). Purification by column chromatography (3:7 ethyl acetate/ petroleum ether) afforded the title compound: Wt 278 mg; 71%; golden viscous oil: δ_H (300 MHz, $CDCl_3$) 7.43 – 7.27 (m, 3H), 7.32 (dd, *J* = 1.8, 0.8 Hz, 1H), 7.10 – 7.00 (m, 2H), 6.41 (dd, *J* = 16.8, 2.0 Hz, 1H), 6.26 (dd, *J* = 3.2, 1.8 Hz, 1H), 6.17 (dd, *J* = 3.2, 0.8 Hz, 1H), 5.99 (dd, *J* = 16.8, 10.3 Hz, 1H), 5.52 (dd, *J* = 10.3, 2.0 Hz, 1H), 4.94 (s, 2H); δ_C (75 MHz, $CDCl_3$) 165.4, 150.6, 142.1, 141.6, 129.5, 128.5, 128.3, 128.1, 128.0, 110.3, 109.0, 45.8; ν_{max}/cm^{-1} 3118, 3062, 1655, 1594, 1494, 1407, 1364, 1253, 1181, 1147, 1014; m/z HRMS (NSI+) found 228.1018, $C_{14}H_{14}NO_2$ $[M + H]^+$ requires 228.1019.

***N*-((5-bromofuran-2-yl)methyl)-*N*-phenylacrylamide (1f):** Acryloyl chloride (462 mg, 5.1 mmol) was added carefully to a solution of *N*-((5-bromofuran-2-yl)methyl)aniline (1.29 g, 5.1 mmol), triethylamine (0.72 ml. 5.1 mmol) and DMAP (14 mg) in dry dichloromethane (5 ml) at 0 °C with stirring. The reaction mixture was allowed to rise to r.t. and stirred overnight. The reaction mixture was then diluted with dichloromethane (20 ml) and water (20 ml) was added. The mixture was further extracted with dichloromethane (2 x 20 ml) and the combined organic phase dried (Na_2SO_4). Purification by column chromatography (1:4 ethyl acetate/ petroleum ether) afforded the title compound: Wt 1.29 g; 82%; colourless oil: δ_H (300 MHz, $CDCl_3$) 7.44 – 7.27 (m, 3H), 7.14 – 7.04 (m, 2H), 6.39 (dd, *J* = 16.8, 2.0 Hz, 1H), 6.18 (d, *J* = 3.5 Hz, 1H), 6.17 (d, *J* = 3.5 Hz, 1H), 5.99 (dd, *J* = 16.8, 10.3 Hz, 1H), 5.52 (dd, *J* = 10.3, 2.0 Hz, 1H), 4.88 (s, 2H); δ_C (75 MHz, $CDCl_3$) 165.4, 152.7, 141.5, 129.6, 128.3, 128.2, 128.1, 121.0, 112.1, 111.8, 45.8; ν_{max}/cm^{-1} 3063, 3039, 2984, 2933, 1656, 1594, 1494, 1407, 1253, 1172, 1123, 1016; m/z HRMS (NSI+) found 306.0132, $C_{14}H_{13}BrNO_2$ $[M + H]^+$ requires 306.0124.

***N*-((4-bromofuran-2-yl)methyl)-*N*-phenylacrylamide (1g):** Acryloyl chloride (41 mg, 1.0 mmol) was added carefully to a solution of *N*-((4-bromofuran-2-yl)methyl)aniline (115 mg, 0.46 mmol), triethylamine (0.07 ml. 0.5 mmol) and DMAP (2 mg) in dry dichloromethane (2 ml) at 0 °C with stirring. The reaction mixture was allowed to rise to r.t. and stirred overnight. The reaction mixture was then diluted with dichloromethane (5 ml) and water (5 ml) was added. The mixture was further extracted with dichloromethane (2 x 5 ml) and the combined organic phase

dried (Na_2SO_4). Purification by column chromatography (15:85 ethyl acetate/ petroleum ether) afforded the title compound: Wt 49 mg; 35%; colourless oil: δ_H (300 MHz, $CDCl_3$) 7.43 – 7.33 (m, 3H), 7.31 (d, *J* = 0.8 Hz, 1H), 7.13 – 7.02 (m, 2H), 6.41 (dd, *J* = 16.8, 2.0 Hz, 1H), 6.27 (d, *J* = 0.8 Hz, 1H), 5.99 (dd, *J* = 16.8, 10.3 Hz, 1H), 5.54 (dd, *J* = 10.3, 2.0 Hz, 1H), 4.89 (s, 2H); δ_C (75 MHz, $CDCl_3$) 165.5, 151.8, 141.5, 140.3, 129.6, 128.4, 128.2, 128.2, 128.1, 112.3, 100.1, 45.8; ν_{max}/cm^{-1} 3147, 1656, 1593, 1493, 1406, 1256, 1218, 1172, 1122; m/z HRMS (NSI+) found 306.0131, $C_{14}H_{13}BrNO_2$ $[M + H]^+$ requires 306.0124.

***N*-((3-bromofuran-2-yl)methyl)-*N*-phenylacrylamide (1h):** Acryloyl chloride (91 mg, 1.0 mmol) was added carefully to a solution of *N*-((3-bromofuran-2-yl)methyl)aniline (252 mg, 1.0 mmol), triethylamine (0.15 ml. 1.0 mmol) and DMAP (4 mg) in dry dichloromethane (5 ml) at 0 °C with stirring. The reaction mixture was allowed to rise to r.t. and stirred overnight. The reaction mixture was then diluted with dichloromethane (10 ml) and water (10 ml) was added. The mixture was further extracted with dichloromethane (2 x 10 ml) and the combined organic phase dried (Na_2SO_4). Purification by column chromatography (1:4 diethyl ether/ petroleum ether) afforded the title compound: Wt 162 mg; 53%; colourless oil: δ_H (300 MHz, $CDCl_3$) 7.39 – 7.31 (m, 3H), 7.30 (d, *J* = 2.0 Hz, 1H), 7.10 – 6.98 (m, 2H), 6.43 (dd, *J* = 16.8, 2.0 Hz, 1H), 6.29 (d, *J* = 2.0 Hz, 1H), 5.99 (dd, *J* = 16.8, 10.3 Hz, 1H), 5.53 (dd, *J* = 10.3, 2.0 Hz, 1H), 5.01 (s, 2H); δ_C (75 MHz, $CDCl_3$) 165.5, 147.5, 142.7, 140.9, 129.5, 128.4, 128.3, 128.2, 128.1, 113.7, 100.0, 43.4; ν_{max}/cm^{-1} 3121, 1657, 1594, 1494, 1407, 1253, 1075; m/z HRMS (NSI+) found 306.0133, $C_{14}H_{13}BrNO_2$ $[M + H]^+$ requires 306.0124.

***N*-(2-chloroallyl)-*N*-phenylfuran-2-carboxamide (1i):** 2-Furoyl chloride (506 mg, 3.9 mmol) in dry dichloromethane (1.0 ml) was added carefully to a stirring solution of *N*-(2-chloroallyl)aniline (650 mg, 3.9 mmol), triethylamine (0.54 ml, 3.9 mmol) and DMAP (13 mg) in dry dichloromethane (3 ml) at 0 °C. The solution was then allowed to rise to room temperature and stirred overnight. The solution was then diluted with dichloromethane (10 ml) and water (10 ml) was added. The mixture was extracted further with dichloromethane (2 x 10 ml) and the combined organic layers were dried (Na_2SO_4) and concentrated *in vacuo*. Purification by column chromatography (1:19 ethyl acetate/ petroleum ether) afforded the title compound: Wt 770 mg; 76%; off-white solid: m.p. 100-102 °C δ_H (300 MHz, $CDCl_3$) 7.44 – 7.36 (m, 3H), 7.33 (dd, *J* = 1.7, 0.7 Hz, 1H), 7.30 – 7.23 (m, 2H), 6.21 (dd, *J* = 3.5, 1.7 Hz, 1H), 5.84 (app. d, *J* = 3.5 Hz, 1H), 5.33 (s, 2H), 4.67 (s, 2H); δ_C (75 MHz, $CDCl_3$) 159.1, 146.6, 144.7, 142.0, 137.1, 129.5, 128.3, 128.1, 117.0, 115.4, 111.1, 55.7; ν_{max}/cm^{-1} 3111, 1627, 1595, 1560, 1472, 1404, 1278, 1187, 1032; m/z HRMS (NSI+) found 262.0623, $C_{14}H_{13}ClNO_2$ $[M + H]^+$ requires 262.0629.

***N*-(2-bromoallyl)-*N*-phenylfuran-2-carboxamide (1j):** 2-Furoyl chloride (261 mg, 2.0 mmol) in dry dichloromethane (0.5 ml) was added carefully to a stirring solution of *N*-(2-bromoallyl)aniline (424 mg, 2.0 mmol), triethylamine (0.27 ml, 2.0 mmol) and DMAP (5 mg) in dry dichloromethane (1.5 ml) at 0 °C. The solution was then allowed to rise to room temperature and stirred overnight. The solution was then diluted with dichloromethane (10 ml) and water (10 ml) was added. The mixture was extracted further with dichloromethane (2 x 10 ml) and the combined organic layers were dried (Na_2SO_4) and concentrated *in vacuo*. Purification by column chromatography (3:7 ethyl acetate/ petroleum ether) afforded the title compound: Wt 440 mg; 72%; white solid; m.p. 106-108 °C; δ_H (300 MHz, $CDCl_3$) 7.44 – 7.35 (m, 3H), 7.33 (dd, *J* = 1.7, 0.7 Hz, 1H), 7.31 – 7.24 (m, 2H), 6.21 (dd, *J* = 3.5, 1.7 Hz, 1H), 5.85 (d, *J* = 3.5 Hz, 1H), 5.77 (dt, *J* = 2.0, 1.3 Hz, 1H), 5.63 – 5.54 (m, 1H), 4.80 – 4.67 (m, 2H); δ_C (75 MHz, $CDCl_3$) 159.1, 146.6, 144.7, 142.0, 129.5, 128.3, 128.1, 128.1, 119.6, 117.1, 111.1, 57.4; ν_{max}/cm^{-1} 3112, 3066, 3042, 2946, 1630, 1595, 1561, 1472, 1403, 1370, 1277, 1187, 1141, 1032; m/z HRMS (NSI+) found 306.0130, $C_{14}H_{13}BrNO_2$ $[M + H]^+$ requires 306.0124.

(*Z*)-N-(3-chloroallyl)-*N*-phenylfuran-2-carboxamide (1k): 2-Furoyl chloride (389 mg, 3.0 mmol) in dry dichloromethane (0.5 ml) was added carefully to a stirring solution of (*Z*)-*N*-(3-chloroallyl)aniline (500 mg, 3.0 mmol), triethylamine (0.4 ml, 3.0 mmol) and DMAP (7 mg) in dry dichloromethane (2.0 ml) at 0 °C. The solution was then allowed to rise to room temperature and stirred overnight. The solution was then diluted with dichloromethane (10 ml) and water (10 ml) was added. The mixture was extracted further with dichloromethane (2 x 10 ml) and the combined organic layers were dried (Na_2SO_4) and concentrated *in vacuo*. Purification by column chromatography (3:7 ethyl acetate/ petroleum ether) afforded the title compound: Wt 716 mg; 61%; white solid; m.p. 98-100 °C; δ_H (300 MHz, $CDCl_3$) 7.44 – 7.34 (m, 3H), 7.32 (dd, *J* = 1.7, 0.7 Hz, 1H), 7.23 – 7.15 (m, 2H), 6.19 (dd, *J* = 3.5, 1.7 Hz, 1H), 6.15 (dt, *J* = 7.2, 1.5 Hz, 1H), 6.02 (dt, *J* = 7.2, 6.5 Hz, 1H), 5.81 (app. d, *J* = 3.5 Hz, 1H), 4.66 (dd, *J* = 6.5, 1.5 Hz, 2H); δ_C (75 MHz, $CDCl_3$) 159.2, 146.8, 144.5, 142.4, 129.6, 128.2, 128.1, 126.7, 121.2, 116.7, 111.0, 47.3; ν_{max}/cm^{-1} 3109, 3087, 1628, 1561, 1473, 1435, 1410, 1298, 1227, 1182, 1026; m/z HRMS (NSI+) found 262.0633, $C_{14}H_{13}ClNO_2$ $[M + H]^+$ requires 262.0629.

(*E*)-N-(3-chloroallyl)-*N*-phenylfuran-2-carboxamide (1l): 2-Furoyl chloride (389 mg, 3.0 mmol) in dry dichloromethane (0.5 ml) was added carefully to a stirring solution of (*E*)-*N*-(3-chloroallyl)aniline (500 mg, 3.0 mmol), triethylamine (0.4 ml, 3.0 mmol) and DMAP (7 mg) in dry dichloromethane (2.0 ml) at 0 °C. The solution was then allowed to rise to room temperature and stirred overnight. The solution was then diluted with dichloromethane (10 ml) and water (10 ml) was added. The mixture was extracted further with dichloromethane (2 x 10 ml) and the

combined organic layers were dried (Na_2SO_4) and concentrated *in vacuo*. Purification by column chromatography (3:7 ethyl acetate/ petroleum ether) afforded the title compound: Wt 637 mg; 54%; off-white solid; m.p. 58-60 °C; δ_H (300 MHz, $CDCl_3$) 7.47 – 7.35 (m, 3H), 7.34 – 7.29 (m, 1H), 7.21 – 7.12 (m, 2H), 6.18 (dd, *J* = 3.5, 1.7 Hz, 1H), 6.13 (d, *J* = 13.3 Hz, 1H), 6.07 (dt, *J* = 13.3, 6.1 Hz, 1H), 5.77 (d, *J* = 3.5 Hz, 1H), 4.40 (dd, *J* = 6.1, 1.2 Hz, 2H); δ_C (75 MHz, $CDCl_3$) 158.9, 146.7, 144.6, 142.1, 129.7, 128.4, 128.4, 127.7, 122.5, 116.7, 111.0, 50.4; ν_{max}/cm^{-1} 3111, 3067, 1631, 1561, 1473, 1408, 1302, 1283, 1227, 1183, 1026; m/z HRMS (NSI+) found 262.0633, $C_{14}H_{13}ClNO_2$ $[M + H]^+$ requires 262.0629.

***tert*-butyl allyl(furan-2-ylmethyl)carbamate (1m):** To a solution of *N*-(furan-2-ylmethyl)prop-2-en-1-amine (823 mg, 6.0 mmol) and $(Boc)_2O$ (1.310 g, 6.0 mmol) in dry dichloromethane (11.2 ml) was added DMAP (7.3 mg, 1 mol %) at 0 °C with stirring. The solution was allowed to rise to r.t. and left stirring for 24 hours. The solvent was then removed *in vacuo* to afford the title compound with no further purification necessary: Wt 907 mg; 64%; colourless oil: δ_H (300 MHz, $CDCl_3$) 7.34 (dd, *J* = 1.8, 0.8 Hz, 1H), 6.30 (dd, *J* = 3.2, 1.8 Hz, 1H), 6.18 (br s, 1H), 5.72 (br s, 1H), 5.14 (br s, 1H), 5.11 (br s, 1H), 4.36 (br s, 2H), 3.84 (br s, 2H), 1.46 (s, 9H); δ_C (75 MHz, $CDCl_3$) 155.3, 151.9, 141.9, 133.6, 116.7 (br), 110.2, 107.7 (br), 79.9, 48.8, 42.5, 28.4; ν_{max}/cm^{-1} 2977, 2931, 1693, 1454, 1406, 1366, 1249, 1161, 1011; m/z HRMS (NSI+) found 238.1437, $C_{13}H_{20}NO_3$ $[M + H]^+$ requires 238.1438.

(*Z*)-*tert*-butyl (3-chloroallyl)(furan-2-ylmethyl)carbamate (1p): To a solution of (*Z*)-3-chloro-*N*-(furan-2-ylmethyl)prop-2-en-1-amine (172 mg, 1.0 mmol) and $(Boc)_2O$ (219 mg, 1.0 mmol) in dry dichloromethane (1.9 ml) was added DMAP (0.6 mg, 1 mol %) at 0 °C with stirring. The solution was allowed to rise to r.t. and left stirring for 72 hours. More $(Boc)_2O$ (219 mg, 1.0 mmol) was then added and the solution left to stir for 30 mins. Solvent was then removed *in vacuo* and ethanol (5 ml) was then added to the crude reaction mixture. Imidazole (204 mg, 3 mmol) was then added and the reaction allowed to stir for 20 mins. Solvent was then removed *in vacuo* and dichloromethane (20 ml) added. The solution was then rinsed with 1% HCl solution (2 x 30 ml), the organic phase was then dried (Na_2SO_4) and the solvent removed *in vacuo* to afford the pure title compound: Wt 238 mg; 88%; colourless oil: δ_H (300 MHz, $CDCl_3$) 7.38 (dd, *J* = 1.8, 0.8 Hz, 1H), 6.34 (dd, *J* = 3.2, 1.8 Hz, 1H), 6.25 (br s, 1H), 6.14 (br d, *J* = 6.4 Hz, 1H), 5.75 (br s, 1H), 4.40 (br s, 2H), 4.08 (br s, 2H), 1.50 (s, 9H); δ_C (75 MHz, $CDCl_3$) 155.2, 151.5, 142.1, 128.2, 119.9 (br), 110.3, 108.0 (br), 80.3, 43.5, 43.3, 28.4; ν_{max}/cm^{-1} 2978, 2934, 1690, 1456, 1410, 1394, 1367, 1250, 1155, 1029; m/z HRMS (NSI+) found 294.0870, $C_{13}H_{18}ClNO_3Na$ $[M + Na]^+$ requires 294.0867.

(*E*)-*tert*-butyl (3-chloroallyl)(furan-2-ylmethyl)carbamate (1q): To a solution of (*E*)-3-chloro-*N*-(furan-2-ylmethyl)prop-2-en-1-amine (514mg, 3.0 mmol) and $(Boc)_2O$ (953 mg, 4.5 mmol) in dichloromethane (4.9 ml) was added DMAP (1.9 mg, 1 mol %) at 0 °C with stirring. The solution was allowed to rise to r.t. and left stirring overnight. Solvent was then removed *in vacuo* and ethanol (5 ml) was then added to the crude reaction mixture. Imidazole (204 mg, 3 mmol) was then added and the reaction allowed to stir for 30 mins. Solvent was then removed *in vacuo* and chloroform (20 ml) added. The solution was then rinsed with 1% HCl solution (2 x 30 ml), the organic phase was then dried (Na_2SO_4) and the solvent removed *in vacuo* to afford the pure title compound: Wt 500 mg; 61%; colourless oil: δ_H (300 MHz, $CDCl_3$) 7.43 – 7.32 (m, 1H), 6.33 (dd, *J* = 3.1, 1.9 Hz, 1H), 6.21 (br s, 1H), 6.10 (br d, *J* = 12.4 Hz, 1H), 5.87 (br s, 1H), 4.38 (br s, 2H), 3.84 (br s, 2H), 1.49 (s, 9H); δ_C (75 MHz, $CDCl_3$) 155.0, 151.4, 142.1, 128.9, 120.8 (br), 110.3, 108.1 (br), 80.4, 46.2, 42.7, 28.4.; ν_{max}/cm^{-1} 2978, 2932, 1692, 1454, 1408, 1366, 1269, 1253, 1223, 1159, 1115, 1011; m/z HRMS (NSI+) found 272.1049, $C_{13}H_{19}ClNO_3$ $[M + H]^+$ requires 272.1048.

5-bromo-*N*-(2-chloroallyl)-*N*-phenylfuran-2-carboxamide (1r): To a solution of 5-bromo-2-furoic acid (115 mg, 0.6 mmol) in dry dichloromethane (0.8 ml) containing *N*,*N*-dimethylformamide (1 drop) was carefully added oxalyl chloride (114 mg, 0.9 mmol) at 0 °C. The solution was allowed to rise to room temperature while stirring for 1 hour before the reaction mixture was concentrated *in vacuo*. A solution of (*E*)-*N*-(3-chloroallyl)aniline (100 mg, 0.6 mmol) and triethylamine (0.18 ml, 1.3 mmol) in dry dichloromethane (0.25 ml) was then carefully added at 0 °C and allowed to rise to room temperature while stirring overnight. If the solution became too viscous to stir efficiently, more dry dichloromethane was added until the reaction mixture dissolved. Water (10 ml) added to the reaction mixture and extracted with dichloromethane (3 x 10 ml). Combined organic layers were dried (Na_2SO_4) and concentrated *in vacuo*. Purification by column chromatography (1:9 ethyl acetate/ petroleum ether) afforded the title compound: Wt 84 mg; 77%; clear golden oil: δ_H (300 MHz, $CDCl_3$) 7.47 – 7.33 (m, 3H), 7.32 – 7.20 (m, 2H), 6.14 (d, *J* = 3.6 Hz, 1H), 5.82 (d, *J* = 3.6 Hz, 1H), 5.32 (s, 1H), 5.31 (s, 1H), 4.64 (s, 2H); δ_C (75 MHz, $CDCl_3$) 157.9, 148.4, 141.6, 136.9, 129.6, 128.6, 128.1, 125.9, 119.4, 115.7, 113.1, 55.7; ν_{max}/cm^{-1} 3063, 2926, 1644, 1595, 1494, 1462, 1382, 1281, 1210, 1154, 1125, 1008; m/z HRMS (NSI+) found 339.9736, $C_{14}H_{12}BrClNO_2$ $[M + H]^+$ requires 339.9734.

(*Z*)-5-bromo-*N*-(3-chloroallyl)-*N*-phenylfuran-2-carboxamide (1s): To a solution of 5-bromo-2-furoic acid (191 mg, 1.0 mmol) in dry dichloromethane (2.6 ml) containing *N*,*N*-dimethylformamide (1 drop) was carefully added oxalyl chloride (191 mg, 1.5 mmol) at 0 °C. The solution was allowed to rise to room temperature while stirring for 1 hour before the reaction

mixture was concentrated *in vacuo*. A solution of (*Z*)-*N*-(3-chloroallyl)aniline (168 mg, 1.0 mmol) and triethylamine (0.15 ml, 1.0 mmol) in dry dichloromethane (1.6 ml) was then carefully added at 0 °C and allowed to rise to room temperature while stirring overnight. If the solution became too viscous to stir efficiently, more dry dichloromethane was added until the reaction mixture dissolved. Water (10 ml) added to the reaction mixture and extracted with dichloromethane (3 x 10 ml). Combined organic layers were dried (Na_2SO_4) and concentrated *in vacuo*. Purification by column chromatography (1:4 diethyl ether/ petroleum ether) afforded the title compound: Wt 282 mg; 83%; white solid; m.p. 80-82 °C; δ_H (300 MHz, $CDCl_3$) 7.48 – 7.35 (m, 1H), 7.21 – 7.11 (m, 1H), 6.14 (d, *J* = 13.3 Hz, 1H), 6.13 (d, *J* = 3.6 Hz, 1H), 6.07 (dt, *J* = 13.3, 6.1 Hz, 1H), 5.78 (d, *J* = 3.6 Hz, 1H), 4.38 (d, *J* = 6.1 Hz, 1H); δ_C (75 MHz, $CDCl_3$) 157.7, 148.5, 141.6, 129.7, 128.6, 128.4, 127.5, 125.7, 122.7, 119.0, 113.0, 50.4; ν_{max}/cm^{-1} 3064, 2931, 1640, 1594, 1494, 1462, 1391, 1295, 1209, 1168, 1013; m/z HRMS (NSI+) found 339.9741, $C_{14}H_{12}BrClNO_2$ $[M + H]^+$ requires 339.9734.

(*E*)-5-bromo-*N*-(3-chloroallyl)-*N*-phenylfuran-2-carboxamide (1t): To a solution of 5-bromo-2-furoic acid (115 mg, 0.6 mmol) in dry dichloromethane (0.8 ml) containing *N*,*N*-dimethylformamide (1 drop) was carefully added oxalyl chloride (114 mg, 0.9 mmol) at 0 °C. The solution was allowed to rise to room temperature while stirring for 1 hour before the reaction mixture was concentrated *in vacuo*. A solution of (*E*)-*N*-(3-chloroallyl)aniline (100 mg, 0.6 mmol) and triethylamine (0.18 ml, 1.3 mmol) in dry dichloromethane (0.25 ml) was then carefully added at 0 °C and allowed to rise to room temperature while stirring overnight. If the solution became too viscous to stir efficiently, more dry dichloromethane was added until the reaction mixture dissolved. Water (10 ml) added to the reaction mixture and extracted with dichloromethane (3 x 10 ml). Combined organic layers were dried (Na_2SO_4) and concentrated *in vacuo*. Purification by column chromatography (1:4 diethyl ether/ petroleum ether) afforded the title compound: Wt 263 mg; 77%; white solid: m.p. 54-56 °C; δ_H (300 MHz, $CDCl_3$) 7.45 – 7.35 (m, 3H), 7.22 – 7.14 (m, 2H), 6.16 (dt, *J* = 7.2, 1.5 Hz, 1H), 6.13 (d, *J* = 3.6 Hz, 1H), 6.01 (dt, *J* = 7.2, 6.6 Hz, 1H), 5.80 (d, *J* = 3.6 Hz, 1H), 4.64 (dd, *J* = 6.6, 1.5 Hz, 2H); δ_C (75 MHz, $CDCl_3$) 157.9, 148.6, 142.0, 129.6, 128.4, 128.1, 126.5, 125.7, 121.5, 119.0, 113.0, 47.3; ν_{max}/cm^{-1} 3118, 3070, 2926, 1632, 1460, 1430, 1404, 1317, 1294, 1215, 1170, 1028; m/z HRMS (NSI+) found 339.9740, $C_{14}H_{12}BrClNO_2$ $[M + H]^+$ requires 339.9734.

4-bromo-*N*-(2-chloroallyl)-*N*-phenylfuran-2-carboxamide (1u): To a solution of 4-bromo-2-furoic acid (115 mg, 0.6 mmol) in dry dichloromethane (0.8 ml) containing *N*,*N*-dimethylformamide (1 drop) was carefully added oxalyl chloride (114 mg, 0.9 mmol) at 0 °C. The solution was allowed to rise to room temperature while stirring for 1 hour before the reaction

mixture was concentrated *in vacuo*. A solution of *N*-(2-chloroallyl)aniline (100 mg, 0.6 mmol) and triethylamine (0.18 ml, 1.3 mmol) in dry dichloromethane (0.25 ml) was then carefully added at 0 °C and allowed to rise to room temperature while stirring overnight. If the solution became too viscous to stir efficiently, more dry dichloromethane was added until the reaction mixture dissolved. Water (10 ml) added to the reaction mixture and extracted with dichloromethane (3 x 10 ml). Combined organic layers were dried (Na_2SO_4) and concentrated *in vacuo*. Purification by column chromatography (1:4 diethyl ether/ petroleum ether) afforded the title compound: Wt 88 mg; 43%; white solid; m.p. 53-55 °C; δ_H (300 MHz, $CDCl_3$) 7.48 – 7.35 (m, 3H), 7.33 (d, *J* = 0.7 Hz, 1H), 7.31 – 7.18 (m, 2H), 5.78 (app. s, 1H), 5.34 (d, *J* = 1.5 Hz, 1H), 5.31 (d, *J* = 1.5 Hz, 1H), 4.65 (s, 2H); δ_C (75 MHz, $CDCl_3$) 158.1, 147.0, 142.9, 141.3, 136.8, 129.7, 128.7, 128.1, 119.4, 115.8, 100.45, 55.7 ν_{max}/cm^{-1} 2967, 2938, 1639, 1594, 1494, 1476, 1392, 1302, 1279, 1196, 1142, 1017; m/z HRMS (NSI+) found 339.9727, $C_{14}H_{12}BrClNO_2$ $[M + H]^+$ requires 339.9734.

(*Z*)-4-bromo-*N*-(3-chloroallyl)-*N*-phenylfuran-2-carboxamide (1v): To a solution of 4-bromo-2-furoic acid (115 mg, 0.6 mmol) in dry dichloromethane (0.8 ml) containing *N*,*N*-dimethylformamide (1 drop) was carefully added oxalyl chloride (114 mg, 0.9 mmol) at 0 °C. The solution was allowed to rise to room temperature while stirring for 1 hour before the reaction mixture was concentrated *in vacuo*. A solution of (*Z*)-*N*-(3-chloroallyl)aniline (100 mg, 0.6 mmol) and triethylamine (0.18 ml, 1.3 mmol) in dry dichloromethane (0.25 ml) was then carefully added at 0 °C and allowed to rise to room temperature while stirring overnight. If the solution became too viscous to stir efficiently, more dry dichloromethane was added until the reaction mixture dissolved. Water (10 ml) added to the reaction mixture and extracted with dichloromethane (3 x 10 ml). Combined organic layers were dried (Na_2SO_4) and concentrated *in vacuo*. Purification by column chromatography (1:4 diethyl ether/ petroleum ether) afforded the title compound: Wt 103 mg; 51%; white solid; m.p. 69-71 °C; δ_H (300 MHz, $CDCl_3$) δ 7.47 – 7.36 (m, 3H), 7.32 (d, *J* = 0.8 Hz, 1H), 7.22 – 7.14 (m, 2H), 6.17 (dt, *J* = 7.2, 1.5 Hz, 1H), 6.00 (dt, *J* = 7.2, 6.6 Hz, 1H), 5.77 (app. s, 1H), 4.65 (dd, *J* = 6.6, 1.5 Hz, 2H); δ_C (75 MHz, $CDCl_3$) 158.1, 147.1, 142.7, 141.7, 129.8, 128.6, 128.1, 126.3, 121.61, 119.1, 100.4, 47.3; ν_{max}/cm^{-1} 3146, 3128, 3052, 2923, 1640, 1595, 1556, 1494, 1476, 1424, 1400, 1287, 1200, 1186, 1139, 1027; m/z HRMS (NSI+) found 339.9737, $C_{14}H_{12}BrClNO_2$ $[M + H]^+$ requires 339.9734.

(*E*)-4-bromo-*N*-(3-chloroallyl)-*N*-phenylfuran-2-carboxamide (1w): To a solution of 4-bromo-2-furoic acid (115 mg, 0.6 mmol) in dry dichloromethane (0.8 ml) containing *N*,*N*-dimethylformamide (1 drop) was carefully added oxalyl chloride (114 mg, 0.9 mmol) at 0 °C. The solution was allowed to rise to room temperature while stirring for 1 hour before the reaction

mixture was concentrated *in vacuo*. A solution of (*E*)-*N*-(3-chloroallyl)aniline (100 mg, 0.6 mmol) and triethylamine (0.18 ml, 1.3 mmol) in dry dichloromethane (0.25 ml) was then carefully added at 0 °C and allowed to rise to room temperature while stirring overnight. If the solution became too viscous to stir efficiently, more dry dichloromethane was added until the reaction mixture dissolved. Water (10 ml) added to the reaction mixture and extracted with dichloromethane (3 x 10 ml). Combined organic layers were dried (Na_2SO_4) and concentrated *in vacuo*. Purification by column chromatography (3:7 diethyl ether/ petroleum ether) afforded the title compound: Wt 104 mg; 51%; white solid; m.p. 60-62 °C; δ_H (300 MHz, $CDCl_3$) δ 7.49 – 7.37 (m, 3H), 7.32 (d, *J* = 0.8 Hz, 1H), 7.21 – 7.12 (m, 2H), 6.14 (d, *J* = 13.4 Hz, 1H), 6.11 – 6.01 (m, 1H), 5.73 (app. s, 1H), 4.39 (d, *J* = 6.2 Hz, 2H); δ_C (75 MHz, $CDCl_3$) δ 157.8, 147.0, 142.8, 141.4, 129.9, 128.8, 128.3, 127.4, 122.8, 119.09, 100.4, 50.5; ν_{max}/cm^{-1} 3144, 3065, 2926, 2852, 1644, 1595, 1493, 1481, 1394, 1298, 1074; m/z HRMS (NSI+) found 339.9737, $C_{14}H_{12}BrClNO_2$ $[M + H]^+$ requires 339.9734.

3-bromo-*N*-(2-chloroallyl)-*N*-phenylfuran-2-carboxamide (1x): To a solution of 3-bromo-2-furoic acid (229 mg, 1.2 mmol) in dry dichloromethane (1.6 ml) containing *N*,*N*-dimethylformamide (1 drop) was carefully added oxalyl chloride (228 mg, 1.8 mmol) at 0 °C. The solution was allowed to rise to room temperature while stirring for 1 hour before the reaction mixture was concentrated *in vacuo*. A solution of *N*-(2-chloroallyl)aniline (200 mg, 1.2 mmol) and triethylamine (0.36 ml, 2.6 mmol) in dry dichloromethane (0.5 ml) was then carefully added at 0 °C and allowed to rise to room temperature while stirring overnight. If the solution became too viscous to stir efficiently, more dry dichloromethane was added until the reaction mixture dissolved. Water (15 ml) added to the reaction mixture and extracted with dichloromethane (3 x 15 ml). Combined organic layers were dried (Na_2SO_4) and concentrated *in vacuo*. Purification by column chromatography (1:4 diethyl ether/ petroleum ether) afforded the title compound: Wt 286 mg; 70%; golden, viscous oil: δ_H (300 MHz, $CDCl_3$) δ 7.44 – 7.28 (m, 3H), 7.28 – 7.21 (m, 2H), 7.14 (d, *J* = 1.9 Hz, 1H), 6.46 (d, *J* = 1.9 Hz, 1H), 5.51 (dt, *J* = 2.9, 1.3 Hz, 1H), 5.49 – 5.43 (m, 1H), 4.75 (s, 2H); δ_C (75 MHz, $CDCl_3$) δ 159.3, 143.7, 143.5, 142.1, 136.7, 129.0, 127.2, 126.5, 115.6, 115.0, 105.2, 55.5; ν_{max}/cm^{-1} 3126, 3040, 1646, 1595, 1492, 1384, 1301, 1280, 1229, 1199, 1157, 1071, 1015; m/z HRMS (NSI+) found 339.9736, $C_{14}H_{12}BrClNO_2$ $[M + H]^+$ requires 339.9734.

(*Z*)-3-bromo-*N*-(3-chloroallyl)-*N*-phenylfuran-2-carboxamide (1y): To a solution of 3-bromo-2-furoic acid (229 mg, 1.2 mmol) in dry dichloromethane (1.6 ml) containing *N*,*N*-dimethylformamide (1 drop) was carefully added oxalyl chloride (228 mg, 1.8 mmol) at 0 °C. The solution was allowed to rise to room temperature while stirring for 1 hour before the reaction

mixture was concentrated *in vacuo*. A solution of (*Z*)-*N*-(3-chloroallyl)aniline (200 mg, 1.2 mmol) and triethylamine (0.36 ml, 2.6 mmol) in dry dichloromethane (0.5 ml) was then carefully added at 0 °C and allowed to rise to room temperature while stirring overnight. If the solution became too viscous to stir efficiently, more dry dichloromethane was added until the reaction mixture dissolved. Water (15 ml) added to the reaction mixture and extracted with dichloromethane (3 x 15 ml). Combined organic layers were dried (Na_2SO_4) and concentrated *in vacuo*. Purification by column chromatography (1:4 diethyl ether/ petroleum ether) afforded the title compound: Wt 343 mg; 84%; clear, yellow, viscous oil: δ_H (300 MHz, $CDCl_3$) 7.34 – 7.20 (m, 3H), 7.14 – 7.05 (m, 2H), 7.03 (d, *J* = 1.9 Hz, 1H), 6.36 (d, *J* = 1.9 Hz, 1H), 6.16 (dt, *J* = 7.2, 1.5 Hz, 1H), 6.02 (dt, *J* = 7.2, 6.4 Hz, 1H), 4.68 (dd, *J* = 6.4, 1.5 Hz, 2H); δ_C (75 MHz, $CDCl_3$) δ 159.3, 143.9, 143.4, 142.1, 129.0, 127.2, 126.74, 126.7, 121.2, 115.6, 105.0, 47.2; ν_{max}/cm^{-1} 3124, 3039, 1643, 1595, 1563, 1492, 1387, 1367, 1293, 1180, 1075; m/z HRMS (NSI+) found 339.9732, $C_{14}H_{12}BrClNO_2$ $[M + H]^+$ requires 339.9734.

(*E*)-3-bromo-*N*-(3-chloroallyl)-*N*-phenylfuran-2-carboxamide (1z): To a solution of 3-bromo-2-furoic acid (229 mg, 1.2 mmol) in dry dichloromethane (1.6 ml) containing *N*,*N*-dimethylformamide (1 drop) was carefully added oxalyl chloride (228 mg, 1.8 mmol) at 0 °C. The solution was allowed to rise to room temperature while stirring for 1 hour before the reaction mixture was concentrated *in vacuo*. A solution of (*E*)-*N*-(3-chloroallyl)aniline (200 mg, 1.2 ml) and triethylamine (0.36 ml, 2.6 mmol) in dry dichloromethane (0.5 ml) was then carefully added at 0 °C and allowed to rise to room temperature while stirring overnight. If the solution became too viscous to stir efficiently, more dry dichloromethane was added until the reaction mixture dissolved. Water (15 ml) added to the reaction mixture and extracted with dichloromethane (3 x 15 ml). Combined organic layers were dried (Na_2SO_4) and concentrated *in vacuo*. Purification by column chromatography (1:4 diethyl ether/ petroleum ether) afforded the title compound: Wt 331 mg; 81%; clear, yellow, viscous oil: δ_H ((300 MHz, $CDCl_3$) δ 7.30 – 7.13 (m, 3H), 7.06 – 6.97 (m, 2H), 6.94 (d, *J* = 1.9 Hz, 1H), 6.29 (d, *J* = 1.9 Hz, 1H), 6.10 (d, *J* = 13.4 Hz, 1H), 6.07 – 5.95 (m, 1H), 4.36 (d, *J* = 6.0 Hz, 2H); δ_C (75 MHz, CDCl3) 156.0, 143.8, 143.4, 141.9, 129.2, 127.6, 127.3, 127.0, 122.5, 115.6, 105.2, 50.3; ν_{max}/cm^{-1} 3125, 3066, 1639, 1595, 1563, 1492, 1388, 1367, 1298, 1282, 1181, 1066; m/z HRMS (NSI+) found 339.9736, $C_{14}H_{12}BrClNO_2$ $[M + H]^+$ requires 339.9734.

(3aR,6S,7aR)-6-bromo-2-phenyl-1,6,7,7a-tetrahydro-3a,6-epoxyisoindol-3(2H)-one (2b): A solution of **1b** (202 mg, 0.66 mmol) in toluene (7 ml) was heated to reflux with stirring for 24 hours. Toluene was then removed *in vacuo* to afford the pure title compound: Wt 202 mg; 100%; white solid; m.p. 151-153 °C; δ_H (300 MHz, $CDCl_3$) 7.68 – 7.54 (m, 2H), 7.46 – 7.30 (m, 2H),

7.24 – 7.15 (m, 1H), 6.71 (d, *J* = 5.7 Hz, 1H), 6.55 (d, *J* = 5.7 Hz, 1H), 4.05 (dd, *J* = 9.6, 8.4 Hz, 1H), 3.91 (dd, *J* = 9.6, 8.4 Hz, 1H), 2.62-2.48 (m, 1H), 2.39 (dd, *J* = 11.9, 3.1 Hz, 1H), 2.30 (dd, *J* = 11.9, 7.3 Hz, 1H); δ_C (75 MHz, $CDCl_3$) 164.9, 141.4, 138.7, 134.3, 129.0, 125.5, 120.4, 91.4, 90.8, 53.6, 43.2, 41.3; ν_{max}/cm^{-1} 3070, 2957, 1695, 1594, 1492, 1473, 1403, 1299, 1255, 1164, 1073, 1018; m/z HRMS (NSI+) found 306.0128, $C_{14}H_{13}BrNO_2$ $[M + H]^+$ requires 306.0124.

(3aS,6R,7aR)-5-bromo-2-phenyl-1,6,7,7a-tetrahydro-3a,6-epoxyisoindol-3(2H)-one (2c): A solution of **1c** (173 mg, 0.57 mmol) in toluene (6 ml) was heated to reflux with stirring for 24 hours. Toluene was then removed *in vacuo* and purification by column chromatography (3:7 ethyl acetate/petroleum ether) afforded the title compound: Wt 133 mg; 77%; white solid; m.p. 207-209 °C; δ_H (300 MHz, $CDCl_3$) 7.70 – 7.61 (m, 2H), 7.46 – 7.38 (m, 2H), 7.26 – 7.19 (m, 1H), 6.73 (s, 1H), 5.11 (d, *J* = 4.3 Hz, 1H), 4.06 (dd, *J* = 9.5, 8.4 Hz, 1H), 3.82 (dd, *J* = 9.5, 8.4 Hz, 1H), 2.64-2.51 (m, 1H), 2.08 (ddd, *J* = 12.0, 4.3, 2.9 Hz, 1H), 1.85 (dd, *J* = 12.0, 7.7 Hz, 1H); δ_C (75 MHz, $CDCl_3$) 165.8, 138.9, 132.0, 129.0, 127.6, 125.3, 120.3, 94.6, 86.6, 53.4, 39.6, 31.1; ν_{max}/cm^{-1} 3088, 3001, 2975, 2948, 1686, 1597, 1567, 1494, 1407, 1390, 1301, 1200, 1152, 1043; m/z HRMS (NSI+) found 306.0132, $C_{14}H_{13}BrNO_2$ $[M + H]^+$ requires 306.0124.

(3aR,6R,7aR)-4-bromo-2-phenyl-1,6,7,7a-tetrahydro-3a,6-epoxyisoindol-3(2H)-one (2d): A solution of **1d** (274 mg, 0.89 mmol) in toluene (18.25 ml) was heated to reflux with stirring for 24 hours. Toluene was then removed *in vacuo* and purification by column chromatography (3:7 ethyl acetate/petroleum ether) afforded the title compound: Wt 211 mg; 77%; white solid; m.p. 168-170 °C; δ_H (300 MHz, $CDCl_3$) δ 7.69 – 7.63 (m, 2H), 7.43 – 7.34 (m, 2H), 7.23 – 7.15 (m, 1H), 6.51 (d, *J* = 1.8 Hz, 1H), 5.23 (dd, *J* = 4.2, 1.8 Hz, 1H), 4.05 (dd, *J* = 9.5, 8.5 Hz, 1H), 3.77 (dd, *J* = 9.5, 8.5 Hz, 1H), 2.63 – 2.50 (m, 1H), 2.10 (ddd, *J* = 11.8, 4.2, 3.3 Hz, 1H), 1.79 (dd, *J* = 11.8, 7.7 Hz, 1H); δ_C (75 MHz, $CDCl_3$) 164.5, 138.9, 136.1, 128.91, 125.3, 123.4, 120.2, 93.7, 83.4, 53.1, 37.8, 33.2; ν_{max}/cm^{-1} 3120, 2956, 1698, 1596, 1495, 1408, 1286, 1213, 1157, 1050, 1016; m/z HRMS (NSI+) found 306.0123, $C_{14}H_{13}BrNO_2$ $[M + H]^+$ requires 306.0124.

(3aR,6R,7aS)-2-phenyl-2,3,7,7a-tetrahydro-3a,6-epoxyisoindol-1(6H)-one (2e): A solution of **1e** (150 mg, 0.66 mmol) in toluene (7.0 ml) was heated to reflux with stirring for 24 hours. Toluene was then removed *in vacuo* and purification by column chromatography (3:7 ethyl acetate/petroleum ether) afforded the title compound: Wt 93 mg; 62%; white solid; m.p. 133-135 °C; δ_H (300 MHz, $CDCl_3$) δ 7.62 – 7.49 (m, 2H), 7.37 – 7.24 (m, 2H), 7.14 – 7.02 (m, 1H), 6.41 (d, *J* = 5.8 Hz, 1H), 6.38 (dd, *J* = 5.8, 1.5 Hz, 1H), 5.05 (dd, *J* = 4.5, 1.5 Hz, 1H), 4.40 (d, *J* = 11.5 Hz, 1H), 4.08 (d, *J* = 11.5 Hz, 1H), 2.58 (dd, *J* = 8.8, 3.5 Hz, 1H), 2.26 (ddd, *J* = 11.9, 4.5, 3.5 Hz, 1H), 1.62 (dd, *J* = 11.9, 8.8 Hz, 1H); δ_C (75 MHz, $CDCl_3$) 173.4, 139.4, 137.5, 133.0, 128.9, 124.7, 120.3, 88.1, 79.3, 50.9, 48.8, 28.9; ν_{max}/cm^{-1} 3135, 3010, 2982, 2953, 1686, 1600,

1495, 1396, 1358, 1196, 1125, 1047; m/z HRMS (NSI+) found 228.1022, $C_{14}H_{14}NO_2$ $[M + H]^+$ requires 228.1019.

(3aR,6S,7aS)-6-bromo-2-phenyl-2,3,7,7a-tetrahydro-3a,6-epoxyisoindol-1(6H)-one (2f): A solution of **1f** (100 mg, 0.33 mmol) in toluene (6.5 ml) was heated to reflux with stirring for 2 hours. Toluene was then removed *in vacuo* and purification by column chromatography (7:3 diethyl ether/petroleum ether) afforded the title compound: Wt 70 mg; 70%; white solid; m.p. 138-140 °C; δ_H (300 MHz, $CDCl_3$) δ 7.63 – 7.55 (m, 2H), 7.44 – 7.32 (m, 2H), 7.18 (ddd, *J* = 8.5, 2.2, 1.1 Hz, 1H), 6.52 (d, *J* = 5.7 Hz, 1H), 6.49 (d, *J* = 5.7 Hz, 1H), 4.43 (d, *J* = 11.8 Hz, 1H), 4.17 (d, *J* = 11.8 Hz, 1H), 2.82 (dd, *J* = 8.6, 3.5 Hz, 1H), 2.66 (dd, *J* = 12.0, 3.5 Hz, 1H), 2.30 (dd, *J* = 12.0, 8.6 Hz, 1H); δ_C (75 MHz, $CDCl_3$) δ 171.6, 141.4, 138.9, 133.9, 129.0, 125.2, 120.4, 88.8, 87.6, 51.7, 50.7, 39.8; ν_{max}/cm^{-1} 3064, 2954, 1687, 1499, 1400, 1355, 1243, 1200, 1186, 1064; m/z HRMS (NSI+) found 306.0129, $C_{14}H_{13}BrNO_2$ $[M + H]^+$ requires 306.0124.

(3aS,6R,7aS)-5-bromo-2-phenyl-2,3,7,7a-tetrahydro-3a,6-epoxyisoindol-1(6H)-one (2g): A solution of **1g** (100 mg, 0.33 mmol) in toluene (6.5 ml) was heated to reflux with stirring for 12 hours. Toluene was then removed *in vacuo* and purification by column chromatography (2:3 diethyl ether/petroleum ether) afforded the title compound: Wt 76 mg; 76%; white solid; m.p. 145-147 °C; δ_H (300 MHz, $CDCl_3$) 7.67 – 7.54 (m, 2H), 7.47 – 7.29 (m, 2H), 7.23 – 7.11 (m, 1H), 6.52 (s, 1H), 4.95 (d, *J* = 4.5 Hz, 1H), 4.43 (d, *J* = 11.6 Hz, 1H), 4.14 (d, *J* = 11.6 Hz, 1H), 2.81 (dd, *J* = 8.8, 3.4 Hz, 1H), 2.34 (ddd, *J* = 12.2, 4.5, 3.4 Hz, 1H), 1.85 (dd, *J* = 12.2, 8.8 Hz, 1H); δ_C (75 MHz, $CDCl_3$) 172.4, 139.1, 131.7, 129.0, 127.7, 125.0, 120.3, 90.1, 84.3, 50.6, 49.9, 28.4; ν_{max}/cm^{-1} 3064, 2952, 1695, 1597, 1499, 1397, 1353, 1297, 1203, 1124, 1034; m/z HRMS (NSI+) found 306.0132, $C_{14}H_{13}BrNO_2$ $[M + H]^+$ requires 306.0124.

(3aR,6R,7aS)-4-bromo-2-phenyl-2,3,7,7a-tetrahydro-3a,6-epoxyisoindol-1(6H)-one (2h): A solution of **1h** (100 mg, 0.33 mmol) in toluene (6.5 ml) was heated to reflux with stirring for 6 hours. Toluene was then removed *in vacuo* and purification by column chromatography (1:1 diethyl ether/petroleum ether) afforded the title compound: Wt 83 mg; 83%; white solid; m.p. 144-146 °C; δ_H (300 MHz, $CDCl_3$)7.73 – 7.60 (m, 2H), 7.49 – 7.33 (m, 2H), 7.27 – 7.13 (m, 1H), 6.52 (d, *J* = 1.9 Hz, 1H), 5.14 (dd, *J* = 4.4, 1.9 Hz, 1H), 4.56 (d, *J* = 11.6 Hz, 1H), 4.10 (d, *J* = 11.6 Hz, 1H), 2.82 (dd, *J* = 8.8, 3.7 Hz, 1H), 2.41 (ddd, *J* = 12.0, 4.4, 3.7 Hz, 1H), 1.86 (dd, *J* = 12.0, 8.8 Hz, 1H); δ_C (75 MHz, $CDCl_3$) 172.1, 139.1, 135.9, 129.0, 125.0, 123.7, 120.3, 90.3, 80.7, 49.4, 48.1, 30.3; ν_{max}/cm^{-1} 3035, 2960, 2930, 1700, 1593, 1571, 1493, 1392, 1346, 1274, 1189, 1124, 1066; m/z HRMS (NSI+) found 306.0123, $C_{14}H_{13}BrNO_2$ $[M + H]^+$ requires 306.0124.

(3aS,6R,7aS)-7a-chloro-2-phenyl-1,6,7,7a-tetrahydro-3a,6-epoxyisoindol-3(2H)-one (2i): A solution of **1i** (173 mg, 0.66 mmol) in toluene (7.0 ml) was heated to reflux with stirring for 24 hours. Toluene was then removed *in vacuo* and purification by column chromatography (1:9 ethyl acetate/petroleum ether) afforded the title compound: Wt 47 mg; 27%; white solid; m.p. 126-128 °C; δ_H (300 MHz, $CDCl_3$) 7.64 – 7.56 (m, 2H), 7.46 – 7.36 (m, 2H), 7.25 – 7.18 (m, 1H), 6.80 (d, *J* = 5.9 Hz, 1H), 6.68 (dd, *J* = 5.9, 1.8 Hz, 1H), 5.32 (dd, *J* = 4.5, 1.8 Hz, 1H), 4.36 (d, *J* = 11.0 Hz, 1H), 4.24 (d, *J* = 11.0 Hz, 1H), 2.81 (dd, *J* = 12.5, 4.5 Hz, 1H), 1.87 (d, *J* = 12.5 Hz, 1H); δ_C (75 MHz, $CDCl_3$) 164.8, 138.6, 137.6, 132.5, 129.1, 125.6, 120.6, 94.2, 83.1, 68.4, 63.5, 42.5; ν_{max}/cm^{-1} 3042, 2957, 1709, 1594, 1494, 1465, 1400, 1303, 1212, 1162, 1092, 1048; m/z HRMS (NSI+) found 262.0635, $C_{14}H_{13}ClNO_2$ $[M + H]^+$ requires 262.0629.

(3aS,6R,7aS)-7a-bromo-2-phenyl-1,6,7,7a-tetrahydro-3a,6-epoxyisoindol-3(2H)-one (2j): A solution of **1j** (153 mg, 0.5 mmol) in toluene (1.0 ml) was heated to reflux with stirring for 24 hours. Toluene was then removed *in vacuo* and purification by column chromatography (1:9 ethyl acetate/petroleum ether) afforded the title compound: Wt 68 mg; 44%; white solid; m.p. 137-139 °C; δ_H (300 MHz, $CDCl_3$) 7.59 (ddd, *J* = 4.5, 3.3, 1.8 Hz, 2H), 7.45 – 7.36 (m, 2H), 7.25 – 7.18 (m, 1H), 6.81 (d, *J* = 5.9 Hz, 1H), 6.62 (dd, *J* = 5.9, 1.8 Hz, 1H), 5.32 (dd, *J* = 4.5, 1.8 Hz, 1H), 4.41 (d, *J* = 11.3 Hz, 1H), 4.31 (d, *J* = 11.3 Hz, 1H), 2.78 (dd, *J* = 12.7, 4.5 Hz, 1H), 1.95 (d, *J* = 12.7 Hz, 1H); δ_C (75 MHz, $CDCl_3$) 164.7, 138.6, 136.96, 133.70, 129.1, 125.6, 120.7, 94.48, 83.1, 64.7, 59.7, 42.2; ν_{max}/cm^{-1} 3036, 2954, 2925, 1708, 1494, 1464, 1400, 1302, 1210, 1160, 1092, 1046, ; m/z HRMS (APCI+) found 306.0128, $C_{14}H_{13}BrNO_2$ $[M + H]^+$ requires 306.0124.

(3aR,6S,7R,7aR)-7-chloro-2-phenyl-1,6,7,7a-tetrahydro-3a,6-epoxyisoindol-3(2H)-one (2k): A solution of **1k** (262 mg, 1.0 mmol) in toluene (20.4 ml) was heated to reflux with stirring for 24 hours. Toluene was then removed *in vacuo* and purification by column chromatography (3:7 ethyl acetate/petroleum ether) afforded the title compound: Wt 19 mg; 7%; white solid; m.p. 122-124 °C; δ_H (300 MHz, $CDCl_3$) 7.75 – 7.59 (m, 2H), 7.47 – 7.33 (m, 2H), 7.24-7.17 (m, 1H), 6.81 (d, *J* = 5.9 Hz, 1H), 6.57 (dd, *J* = 5.9, 1.7 Hz, 1H), 5.13 (d, *J* = 1.7 Hz, 1H), 4.35 (dd, *J* = 10.0, 8.5 Hz, 1H), 4.17 (d, *J* = 7.0 Hz, 1H), 3.85 (dd, *J* = 10.0, 8.8 Hz, 1H), 2.78-2.68 (m, 1H); δ_C (75 MHz, $CDCl_3$) 165.3, 138.8, 136.7, 136.1, 129.0, 125.4, 120.4, 93.3, 89.3, 59.1, 49.52, 42.0; ν_{max}/cm^{-1} 3086, 3010, 2967, 1699, 1597, 1493, 1403, 1320, 1285, 1254, 1158, 1048; m/z HRMS (NSI+) found 262.0632, $C_{14}H_{13}ClNO_2$ $[M + H]^+$ requires 262.0629.

(3aR,6S,7S,7aR)-7-chloro-2-phenyl-1,6,7,7a-tetrahydro-3a,6-epoxyisoindol-3(2H)-one (2l): A solution of **1l** (99 mg, 0.66 mmol) in toluene (4 ml) was heated to reflux with stirring for 24 hours. Toluene was then removed *in vacuo* and purification by column chromatography (1:4 ethyl acetate/petroleum ether) afforded the title compound: Wt 42 mg; 42%; white solid; m.p.

160-161 °C; δ_H (300 MHz, $CDCl_3$) 7.70 – 7.54 (m, 2H), 7.47 – 7.33 (m, 2H), 7.25 – 7.16 (m, 1H), 6.88 (d, *J* = 5.9 Hz, 1H), 6.61 (dd, *J* = 5.9, 1.7 Hz, 1H), 5.32 (dd, *J* = 4.1, 1.7 Hz, 1H), 4.33 (dd, *J* = 4.1, 2.4 Hz, 1H), 4.21 (dd, *J* = 9.8, 8.8 Hz, 1H), 3.87 (dd, *J* = 9.8, 8.5 Hz, 1H), 2.51 (app. td, *J* = 8.5, 2.3 Hz, 1H); δ_C (75 MHz, $CDCl_3$) 165.6, 138.7, 135.4, 135.0, 129.0, 125.5, 120.3, 93.8, 84.3, 55.9, 54.0, 52.2, 51.51, 48.8; ν_{max}/cm^{-1} 3063, 2897, 1694, 1596, 1495, 1468, 1406, 1298, 1206, 1157, 1019; m/z HRMS (NSI+) found 262.0631, $C_{14}H_{13}ClNO_2$ $[M + H]^+$ requires 262.0629.

(3aR,6R,7aR)-*tert*-butyl 1,6,7,7a-tetrahydro-3a,6-epoxyisoindole-2(3H)-carboxylate (2m): A solution of **1m** (593 mg, 2.5 mmol) in toluene (5 ml) was heated to reflux with stirring for 24 hours. Toluene was then removed *in vacuo* and purification by column chromatography (1:4 ethyl acetate/petroleum ether) afforded the title compound: Wt 272 mg; 7%; white solid; m.p. 63-65 °C; δ_H (300 MHz, $CDCl_3$) 6.40 (dd, *J* = 5.8, 1.5 Hz, 1H), 6.36 (d, *J* = 5.8 Hz, 1H), 5.08 (dd, *J* = 4.5, 1.5 Hz, 1H), 3.98 – 3.86 (m, 1H), 3.86 – 3.81 (m, 1H), 3.81 – 3.72 (m, 1H), 3.06 – 2.89 (m, 1H), 2.18 – 2.00 (m, 1H), 1.87 – 1.70 (m, 1H), 1.48 (s, 9H), 1.47 – 1.40 (m, 1H); δ_C (75 MHz, $CDCl_3$, pairs of rotomeric signals observed for certain C atoms) 154.3 and 154.1, 137.2 and 137.1, 134.4 and 134.2, 95.4 and 94.6, 80.3, 79.4, 51.6 and 51.1, 47.9 and 47.5, 42.2 and 41.3, 31.3 and 31.2, 28.5; ν_{max}/cm^{-1} 2973, 2873, 1687, 1400, 1364, 1262, 1221, 1177, 1155, 1109, 1084, 1062, 1009; m/z HRMS (NSI+) found 238.1438, $C_{13}H_{20}NO_3$ $[M + H]^+$ requires 238.1438.

(3aR,6S,7R,7aR)-*tert*-butyl 7-chloro-1,6,7,7a-tetrahydro-3a,6-epoxyisoindole-2(3H)-carboxylate (2p): A solution of **1p** (272 mg, 1.0 mmol) in toluene (2 ml) was heated to reflux with stirring for 48 hours. Toluene was then removed *in vacuo* and purification by column chromatography (1:9 ethyl acetate/petroleum ether) afforded the title compound: Wt 20 mg; 7%; off-white solid; m.p. 106-108 °C; δ_H (300 MHz, $CDCl_3$) 6.46 – 6.40 (m, 1H), 6.39 (dd, *J* = 5.8, 1.7 Hz, 1H), 4.90 (d, *J* = 1.7 Hz, 1H), 4.00 – 3.91 (m, 1H), 3.87 – 3.78 (m, 1H), 3.77 – 3.68 (m, 1H), 3.68 – 3.55 (m, 1H), 3.54 – 3.43 (m, 1H), 2.43 – 2.28 (m, 1H), 1.41 (s, 9H); δ_C (100 MHz, $CDCl_3$, pairs of rotomeric signals observed for certain C atoms) 153.4, 134.0 and 136.8, 134.8 and 134.7, 95.4 and 94.6, 86.9, 78.8, 58.1 and 58.3, 47.2 and 46.8, 46.5 and 46.1, 44.5 and 43.8, 27.5; ν_{max}/cm^{-1} 3006, 2973, 2920, 2850, 1678, 1405, 1380, 1363, 1258, 1243, 1167, 1118, 1086, 1065, 1025; m/z HRMS (NSI+) found 294.0869, $C_{13}H_{18}ClNO_3Na$ $[M + Na]^+$ requires 294.0867.

(3aR,6S,7S,7aR)-*tert*-butyl 7-chloro-1,6,7,7a-tetrahydro-3a,6-epoxyisoindole-2(3H)-carboxylate (2q): A solution of **1q** (272 mg, 1.0 mmol) in toluene (2 ml) was heated to reflux with stirring for 24 hours. Toluene was then removed *in vacuo* and purification by column chromatography (1:4 ethyl acetate/petroleum ether) afforded the title compound: Wt 83 mg; 31%; white solid; m.p. 138-140 °C; δ_H (300 MHz, $CDCl_3$) 6.51 (app. t, *J* = 6.2, 1H), 6.42 (dd, *J* =

5.8, 1.7, 1H), 5.08 (dd, *J*=4.3, 1.7, 1H), 4.08 – 4.01 (m, 1H), 4.01 – 3.90 (m, 1H), 3.76 (app. t, *J* = 12.9, 1H), 3.66 (app. t, *J* = 13.2, 1H), 3.02 (app. t, *J* = 9.6, 1H), 2.16 (app. qd, *J* = 9.2, 1.8, 1H), 1.40 (s, 9H); δ_C (75 MHz, $CDCl_3$, pairs of rotomeric signals observed for certain C atoms) 154.0, 136.0 and 135.7, 135.2 and 135.0, 97.0 and 96.2, 82.7, 79.8, 56.4 and 56.3, 53.3 and 52.4, 49.8 and 49.3, 48.0 and 47.6, 28.5; ν_{max}/cm^{-1} 2978, 2934, 2901, 1683, 1477, 1402, 1364, 1317, 1248, 1168, 1112, 1077, 1057, 1021; m/z HRMS (NSI+) found 294.0869, $C_{13}H_{18}ClNO_3Na$ $[M + Na]^+$ requires 294.0867.

(3aS,6S,7aS)-6-bromo-7a-chloro-2-phenyl-1,6,7,7a-tetrahydro-3a,6-epoxyisoindol-3(2H)-one (2r): A solution of **1r** (49 mg, 0.14 mmol) in toluene (3.0 ml) was heated to reflux with stirring for 24 hours. Toluene was then removed *in vacuo* and purification by column chromatography (1:9 diethyl ether/petroleum ether) afforded the title compound: Wt 30 mg; 61%; white solid; m.p. 141-143 °C; δ_H (300 MHz, $CDCl_3$) δ 7.62 – 7.52 (m, 2H), 7.47 – 7.36 (m, 2H), 7.28 – 7.20 (m, 1H), 6.81 (d, *J* = 5.7 Hz, 1H), 6.70 (d, *J* = 5.7 Hz, 1H), 4.47 (d, *J* = 11.1 Hz, 1H), 4.26 (d, *J* = 11.1 Hz, 1H), 3.07 (d, *J* = 12.7 Hz, 1H), 2.51 (d, *J* = 12.7 Hz, 1H); δ_C (75 MHz, $CDCl_3$) 162.6, 141.4, 138.1, 133.6, 129.2, 126.0, 120.8, 92.8, 90.8, 69.3, 63.2, 53.4; ν_{max}/cm^{-1} 3078, 2955, 1710, 1494, 1408, 1308, 1285, 1219, 1177, 1101, 1041; m/z HRMS (NSI+) found 339.9738, $C_{14}H_{12}BrClNO_2$ $[M + H]^+$ requires 339.9734.

(3aR,6R,7R,7aR)-6-bromo-7-chloro-2-phenyl-1,6,7,7a-tetrahydro-3a,6-epoxyisoindol-3(2H)-one (2s): A solution of **1s** (66 mg, 0.19 mmol) in toluene (4 ml) was heated to reflux with stirring for 24 hours. Toluene was then removed *in vacuo* and purification by column chromatography (30:70 ethyl acetate/petroleum ether) afforded the title compound: Wt 8 mg; 12%; white solid; m.p. 179-181 °C; δ_H (300 MHz, CDCl3) 7.60 – 7.51 (m, 2H), 7.38 – 7.29 (m, 2H), 7.18 – 7.11 (m, 1H), 6.77 (d, *J* = 5.6 Hz, 1H), 6.56 (d, *J* = 5.6 Hz, 1H), 4.22 (d, *J* = 7.0 Hz, 1H), 4.28 (dd, *J* = 10.1, 8.6 Hz, 1H), 3.79 (dd, *J* = 10.1, 8.7 Hz, 1H), 2.85 (app. t, *J* = 8.6, 7.0 Hz, 1H); δ_C (75 MHz, CDCl3) 163.4, 140.9, 138.4, 137.1, 129.1, 125.8, 120.5, 96.3, 91.4, 63.9, 49.8, 43.6; ν_{max}/cm^{-1} 3136, 3094, 3076, 2915, 1690, 1595, 1491, 1477, 1405, 1294, 1275, 1259, 1172, 1061, 1033; m/z HRMS (NSI+) found 339.9729, $C_{14}H_{12}BrClNO_2$ $[M + H]^+$ requires 339.9734.

(3aR,6S,7S,7aR)-6-bromo-7-chloro-2-phenyl-1,6,7,7a-tetrahydro-3a,6-epoxyisoindol-3(2H)-one (2t): A solution of **1t** (100 mg, 0.29 mmol) in toluene (5.9 ml) was heated to reflux with stirring for 8 hours. Toluene was then removed *in vacuo* and purification by column chromatography (1:4 diethyl ether/petroleum ether) afforded the title compound: Wt 60 mg; 60%; white solid; m.p. 196-198 °C; δ_H (300 MHz, CDCl3) 7.58 – 7.46 (m, 2H), 7.41 – 7.28 (m, 2H), 7.18 – 7.11 (m, 1H), 6.79 (d, *J* = 5.7, 1H), 6.56 (d, *J* = 5.7, 1H), 4.31 (d, *J* = 2.4, 1H), 4.17 (dd, *J* = 9.9, 8.7, 1H), 3.93 (dd, *J* = 9.9, 8.4, 1H), 2.62 (app. td, *J* = 8.5, 2.4, 1H); δ_C (75 MHz,

CDCl3) 163.7, 139.6, 138.2, 135.3, 129.1, 125.9, 120.5, 93.8, 91.9, 77.5, 77.0, 76.6, 65.1, 52.0, 51.0; ν_{max}/cm^{-1} 3098, 3075, 2997, 2897, 1707, 1497, 1472, 1402, 1301, 1284, 1240, 1161, 1091, 1050, 1008; m/z HRMS (APCI+) found 339.9739, $C_{14}H_{12}BrClNO_2$ $[M + H]^+$ requires 339.9734.

(3aS,6R,7aS)-5-bromo-7a-chloro-2-phenyl-1,6,7,7a-tetrahydro-3a,6-epoxyisoindol-3(2H)-one (2u): A solution of **1u** (68 mg, 0.20 mmol) in toluene (4.1 ml) was heated to reflux with stirring for 24 hours. Toluene was then removed *in vacuo* and purification by column chromatography (1:5 diethyl ether/petroleum ether) afforded the title compound: Wt 34 mg; 50%; white solid; m.p. 162-164 °C; δ_H (300 MHz, CDCl3) 7.56 – 7.45 (m, 2H), 7.40 – 7.28 (m, 2H), 7.19 – 7.12 (m, 1H), 6.77 (s, 1H), 5.06 (d, *J* = 4.5 Hz, 1H), 4.29 (d, *J* = 11.0 Hz, 1H), 4.16 (d, *J* = 11.0 Hz, 1H), 2.73 (dd, *J* = 12.8, 4.5 Hz, 1H), 1.96 (d, *J* = 12.8 Hz, 1H); δ_C (75 MHz, CDCl3) 163.5, 138.3, 131.3, 129.1, 127.9, 125.9, 120.7, 95.9, 87.6, 69.3, 63.1, 42.0; ν_{max}/cm^{-1} 3093, 3068, 3046, 2958, 1708, 1596, 1567, 1493, 1465, 1408, 1302, 1199, 1157, 1045; m/z HRMS (NSI+) found 339.9729, $C_{14}H_{12}BrClNO_2$ $[M + H]^+$ requires 339.9734.

(3aS,6R,7R,7aR)-5-bromo-7-chloro-2-phenyl-1,6,7,7a-tetrahydro-3a,6-epoxyisoindol-3(2H)-one (2v): A solution of **1v** (29 mg, 0.09 mmol) in toluene (1.7 ml) was heated to reflux with for 24 hours. Toluene was then removed *in vacuo* and purification by column chromatography (30:70 diethyl ether/petroleum ether) afforded the title compound: Wt 9 mg; 31%; off-white solid; m.p. 188-190 °C; δ_H (300 MHz, $CDCl_3$) 7.65 – 7.53 (m, 2H), 7.41 – 7.26 (m, 2H), 7.18 – 7.10 (m, 1H), 6.75 (s, 1H), 4.90 (s, 1H), 4.27 (dd, *J* = 10.1, 8.5, 1H), 4.22 (d, *J* = 7.0, 1H), 3.79 (dd, *J* = 10.1, 8.8, 1H), 2.82 (app. td, *J* = 8.6, 7.0, 1H); δ_C (75 MHz, CDCl3) 164.0, 138.6, 134.7, 129.1, 126.5, 125.7, 120.4, 95.2, 93.3, 58.0, 49.1, 43.5; ν_{max}/cm^{-1} 3103, 3027, 2964, 2920, 1696, 1597, 1490, 1406, 1296, 1251, 1193, 1010; m/z HRMS (NSI+) found 339.9738, $C_{14}H_{12}BrClNO_2$ $[M + H]^+$ requires 339.9734.

(3aS,6R,7S,7aR)-5-bromo-7-chloro-2-phenyl-1,6,7,7a-tetrahydro-3a,6-epoxyisoindol-3(2H)-one (2w): A solution of **1w** (68 mg, 0.2 mmol) in toluene (4.0 ml) was heated to reflux with stirring for 24 hours. Toluene was then removed *in vacuo* and purification by column chromatography (1:4 diethyl ether/petroleum ether) afforded the title compound: Wt 37 mg; 54%; white solid; m.p. 167-169 °C; δ_H (300 MHz, CDCl3) (300 MHz, $CDCl_3$) 7.56 – 7.48 (m, 2H), 7.37 – 7.27 (m, 2H), 7.17 – 7.11 (m, 1H), 6.89 (s, 1H), 5.10 (d, *J* = 4.0, 1H), 4.39 (dd, *J* = 4.0, 2.3, 1H), 4.15 (dd, *J* = 9.9, 8.7, 1H), 3.80 (dd, *J*=9.9, 8.4, 1H), 2.63 (app. td, *J*=8.5, 2.3, 1H); δ_C (75 MHz, CDCl3) 164.4, 138.4, 133.6, 129.1, 126.0, 125.8, 120.4, 95.2, 88.0, 55.4, 52.0, 48.6; ν_{max}/cm^{-1} 3063, 2896, 1692, 1597, 1572, 1494, 1469, 1407, 1299, 1287, 1198, 1150, 1078, 1022, 1002; m/z HRMS (NSI+) found 339.9735, $C_{14}H_{12}BrClNO_2$ $[M + H]^+$ requires 339.9734.

(3aS,6R,7aS)-4-bromo-7a-chloro-2-phenyl-1,6,7,7a-tetrahydro-3a,6-epoxyisoindol-3(2H)-one (2x): A solution of **1x** (100 mg, 0.3 mmol) in toluene (6 ml) was heated to reflux with stirring for 5 hours. Toluene was then removed *in vacuo* and purification by column chromatography (30:70 diethyl ether/petroleum ether) afforded the title compound: Wt 20 mg; 20%; yellow solid; m.p. 172-174 °C; δ_H (300 MHz, CDCl3) 7.70 – 7.43 (m, 2H), 7.45 – 7.24 (m, 2H), 7.19 – 7.12 (m, 1H), 6.70 (d, *J* = 2.1 Hz, 1H), 5.19 (dd, *J* = 4.5, 2.1 Hz, 1H), 4.26 (d, *J* = 11.0 Hz, 1H), 4.18 (d, *J* = 11.0 Hz, 1H), 2.74 (dd, *J* = 12.6, 4.5 Hz, 1H), 1.99 (d, *J* = 12.6 Hz, 1H); δ_C (75 MHz, CDCl3) 162.3, 138.3, 136.5, 129.1, 125.8, 122.8, 120.6, 93.7, 83.9, 68.1, 63.1, 42.2; ν_{max}/cm^{-1} 3035, 2924, 1709, 1492, 1396, 1300, 1284, 1166, 1066; m/z HRMS (NSI+) found 339.9736, $C_{14}H_{12}BrClNO_2$ $[M + H]^+$ requires 339.9734.

(3aR,6S,7R,7aR)-4-bromo-7-chloro-2-phenyl-1,6,7,7a-tetrahydro-3a,6-epoxyisoindol-3(2H)-one (2y): A solution of **1y** (100 mg, 0.3 mmol) in toluene (6 ml) was heated to reflux with stirring for 16 hours. Toluene was then removed *in vacuo* and purification by column chromatography (30:70 diethyl ether/petroleum ether) afforded the title compound: Wt 67 mg; 67%; white solid; m.p. 195-197 °C; δ_H (300 MHz, CDCl3) 7.67 – 7.57 (m, 2H), 7.41 – 7.27 (m, 2H), 7.18 – 7.08 (m, 1H), 6.50 (d, *J* = 1.9, 1H), 5.03 (d, *J* = 1.9, 1H), 4.25 (dd, *J* = 10.0, 8.4, 1H), 4.17 (d, *J* = 7.0, 1H), 3.81 (dd, *J* = 10.0, 8.9, 1H), 2.78 (app. td, *J* = 8.6, 7.0, 1H); δ_C (75 MHz, CDCl3) 162.6, 138.6, 134.1, 129.0, 127.6, 125.6, 120.3, 94.1, 90.3, 58.9, 48.8, 41.2; ν_{max}/cm^{-1} 3001, 2980, 2924, 1702, 1597, 1575, 1493, 1403, 1284, 1238, 1164, 1056, 1016; m/z HRMS (NSI+) found 339.9734, $C_{14}H_{12}BrClNO_2$ $[M + H]^+$ requires 339.9734.

(3aR,6S,7S,7aR)-4-bromo-7-chloro-2-phenyl-1,6,7,7a-tetrahydro-3a,6-epoxyisoindol-3(2H)-one (2z): A solution of **1z** (100 mg, 0.3 mmol) in toluene (6 ml) was heated to reflux with stirring for 7 hours. Toluene was then removed *in vacuo* and purification by column chromatography (30:70 diethyl ether/petroleum ether) afforded the title compound: Wt 75 mg; 75%; white solid; m.p. 208-210 °C: δ_H (300 MHz, $CDCl_3$) 7.72 – 7.60 (m, 2H), 7.47 – 7.31 (m, 2H), 7.22 (tt, *J* = 7.4, 1.1 Hz, 1H), 6.65 (d, *J* = 1.9 Hz, 1H), 5.28 (dd, *J* = 4.0, 1.9 Hz, 1H), 4.36 (dd, *J* = 4.0, 2.6 Hz, 1H), 4.24 (dd, *J* = 9.8, 8.8 Hz, 1H), 3.87 (dd, *J* = 9.8, 8.4 Hz, 1H), 2.65 (app. td, *J* = 8.8, 8.4, 2.6 Hz, 1H).; δ_C (75 MHz, CDCl3) 163.0, 138.4, 133.9, 129.0, 125.7, 120.3, 85.4, 57.1, 51.5, 48.3; ν_{max}/cm^{-1} 2973, 2896, 1697, 1597, 1497, 1473, 1410, 1300, 1242, 1204, 1160, 1049, 1019; m/z HRMS (NSI+) found 339.9735, $C_{14}H_{12}BrClNO_2$ $[M + H]^+$ requires 339.9734.

NMR Spectra

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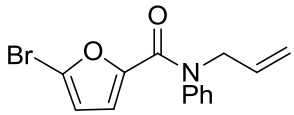

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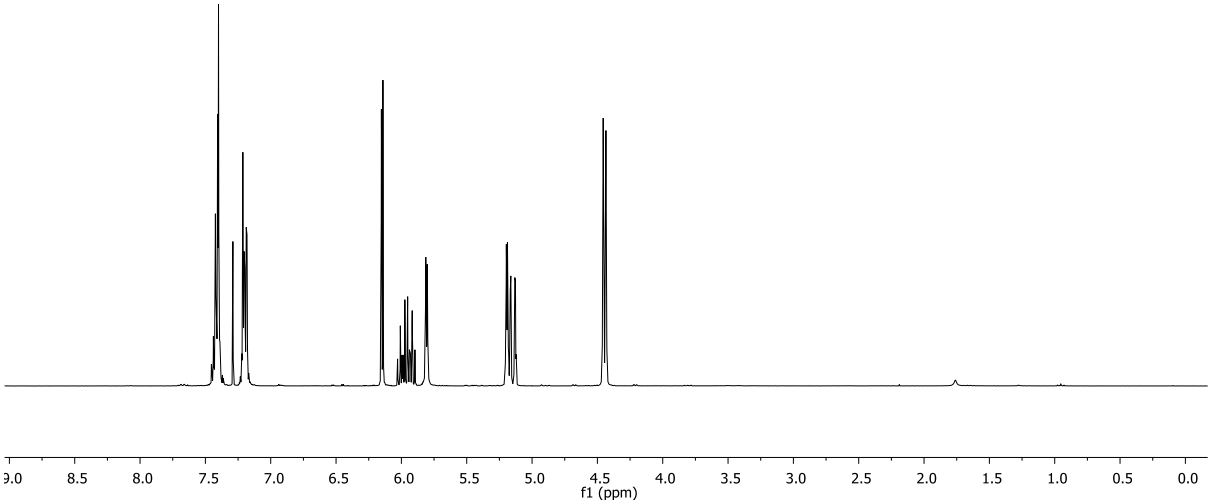

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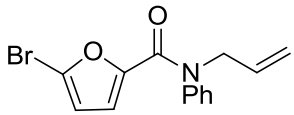

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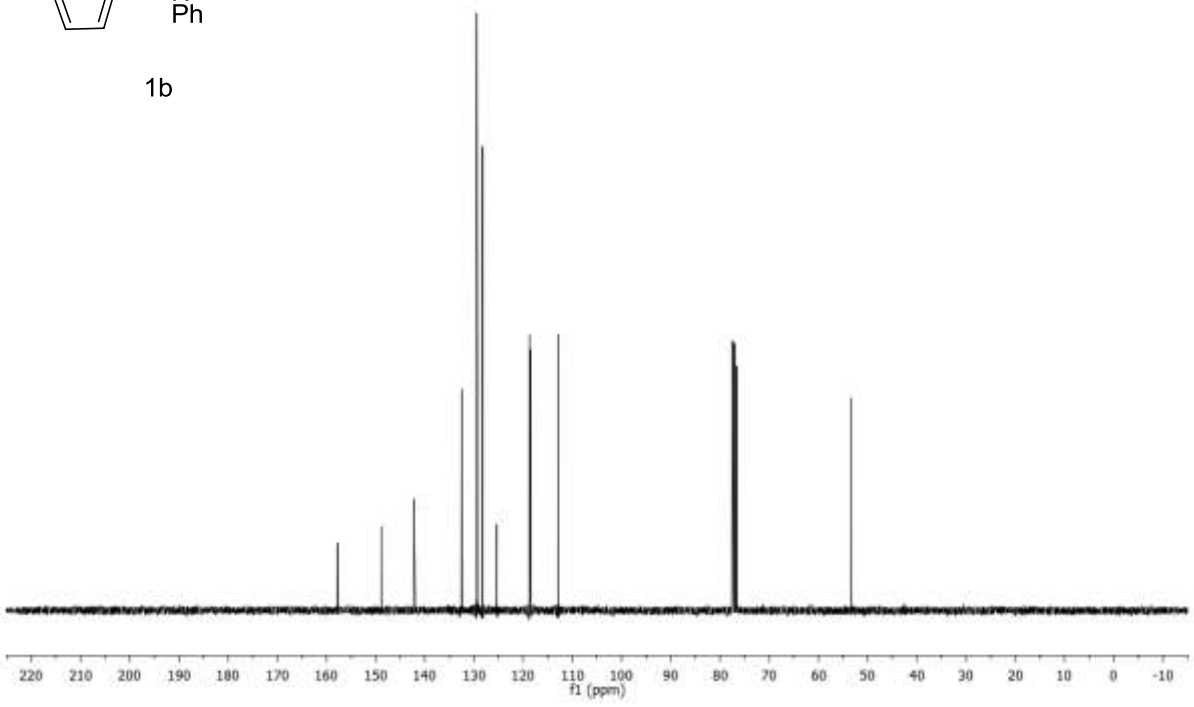

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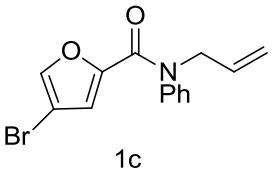

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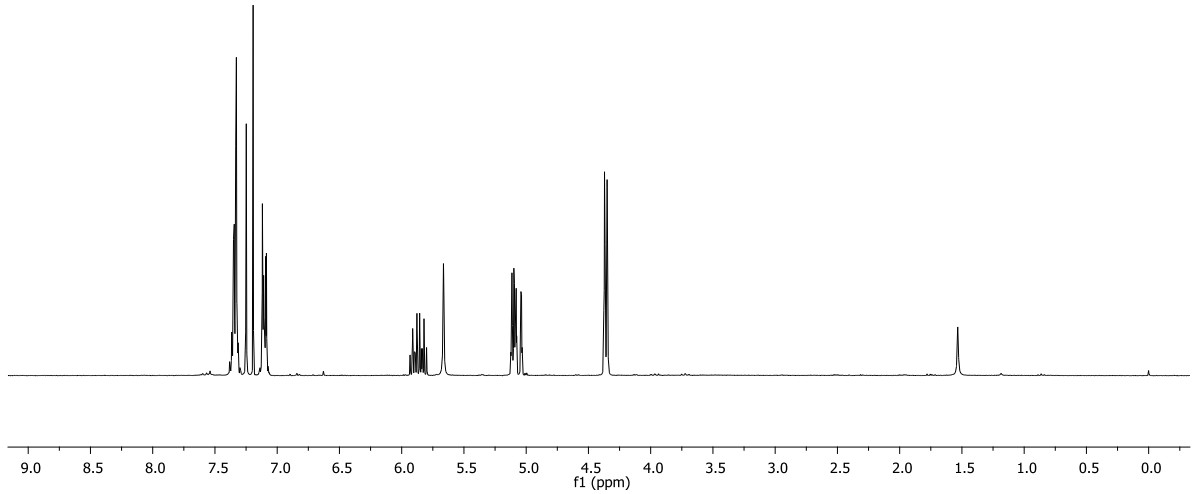

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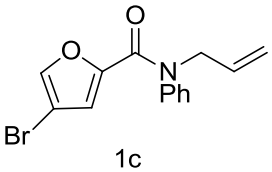

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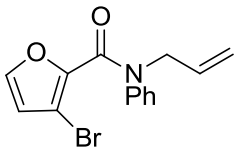

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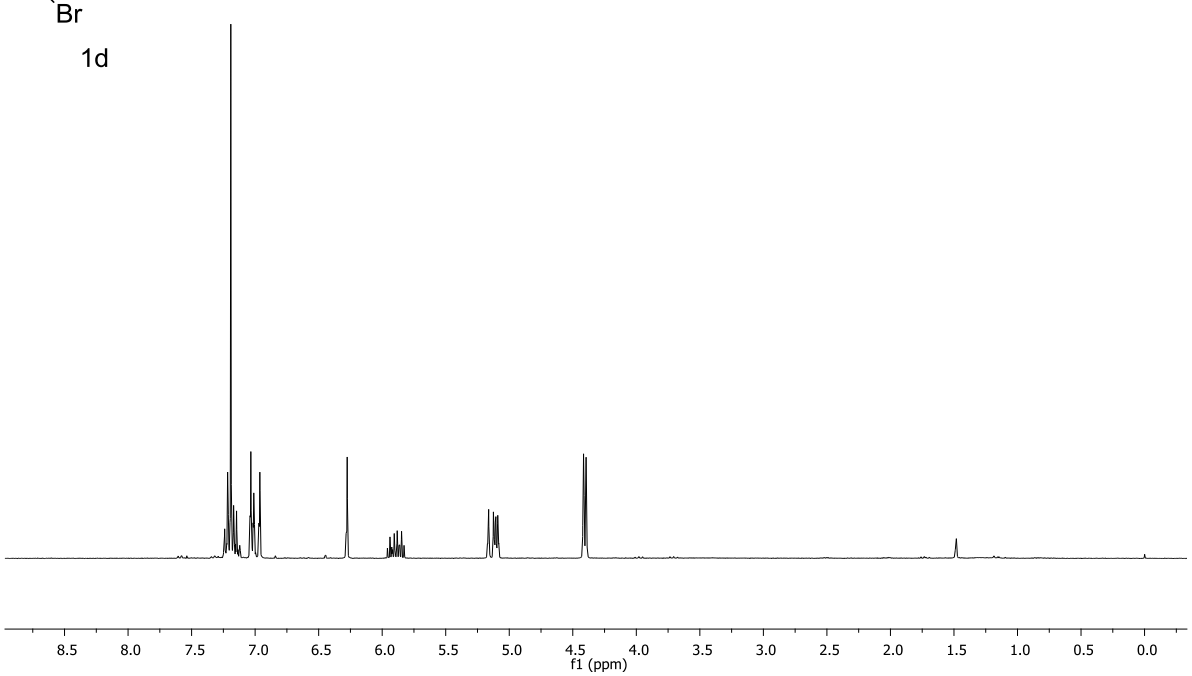

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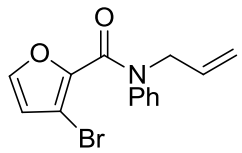

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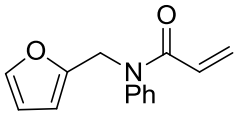

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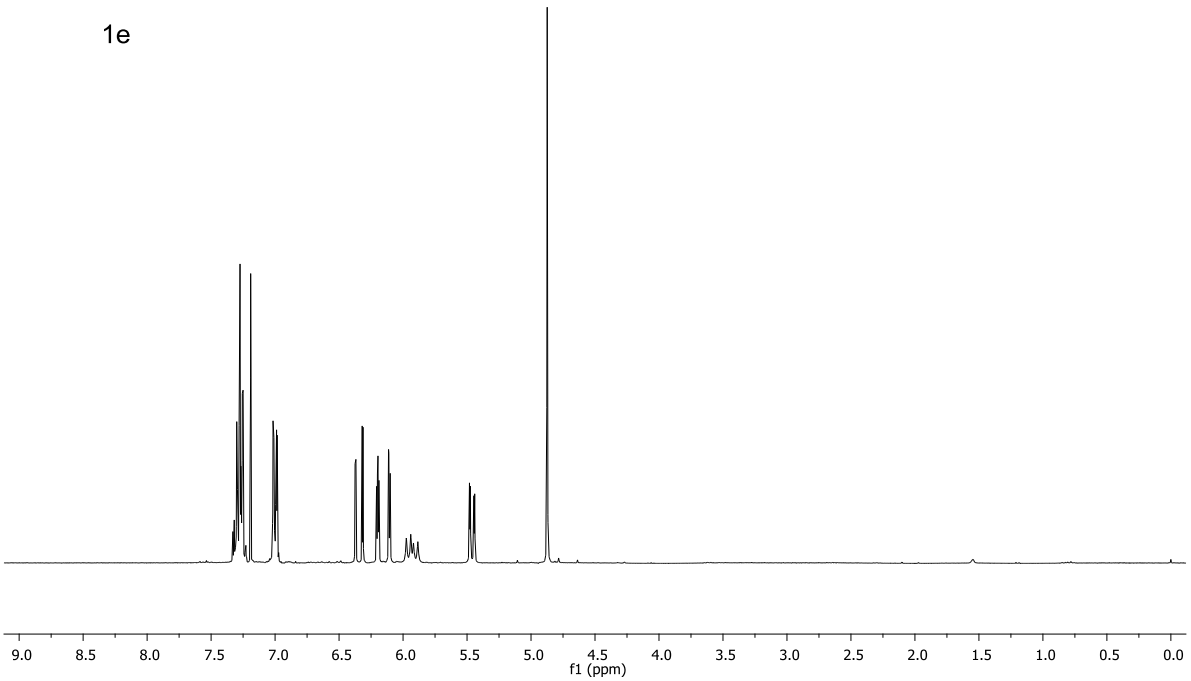

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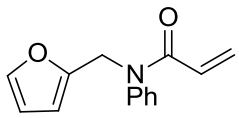

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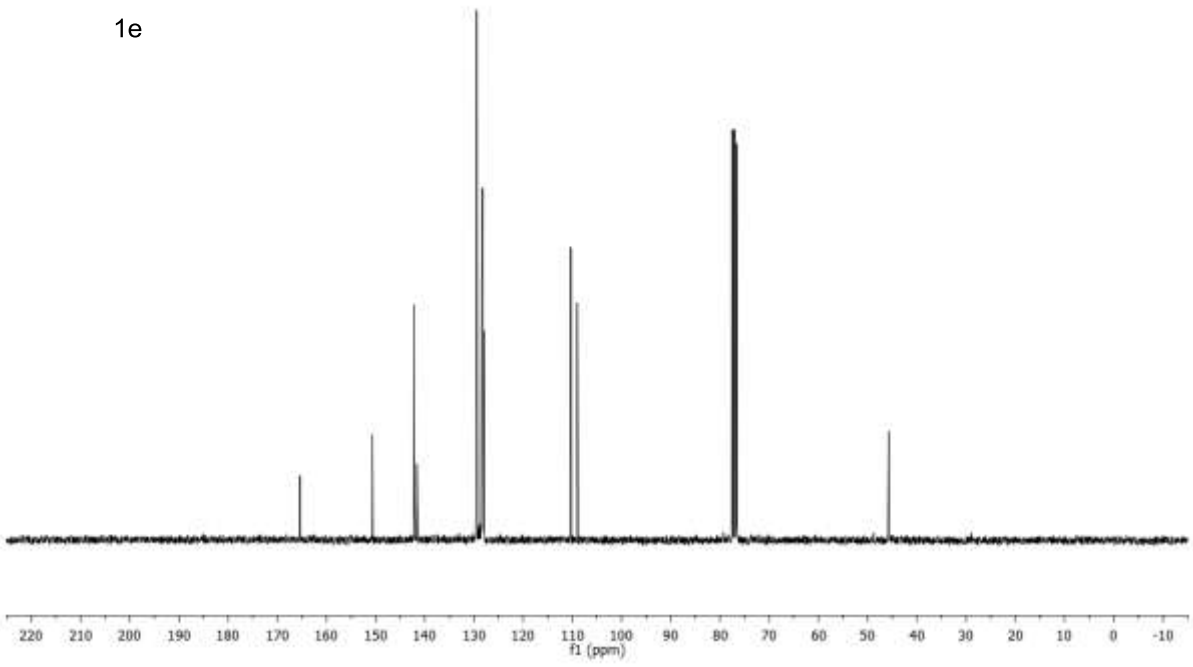

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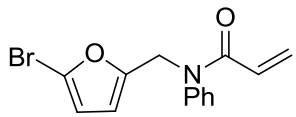

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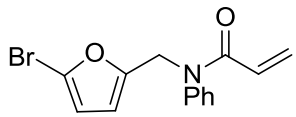

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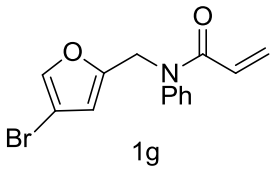

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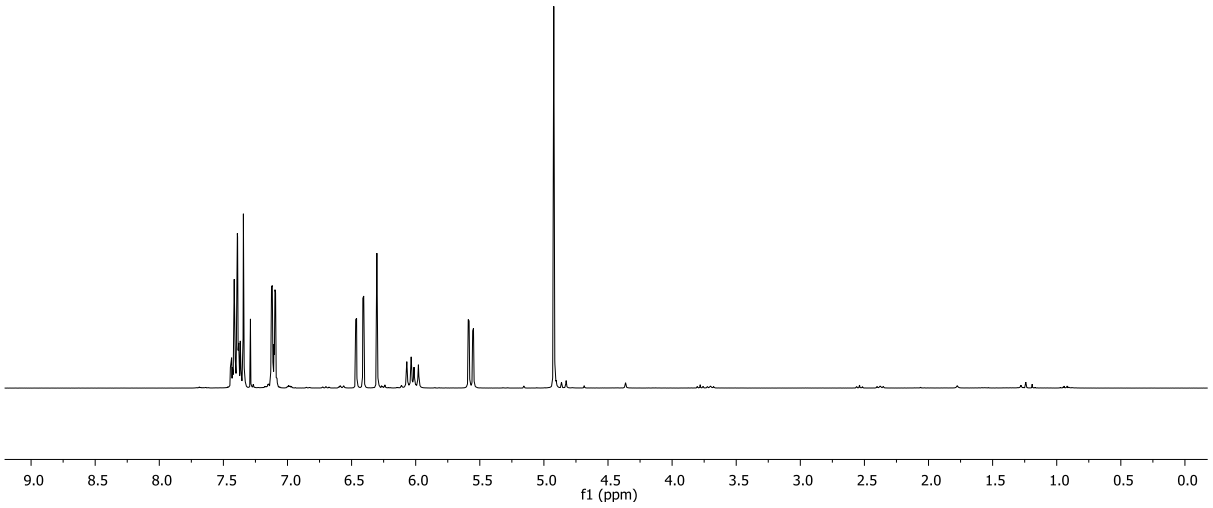

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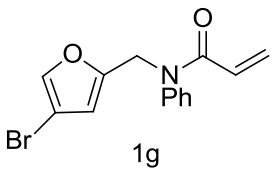

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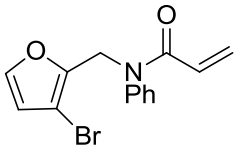

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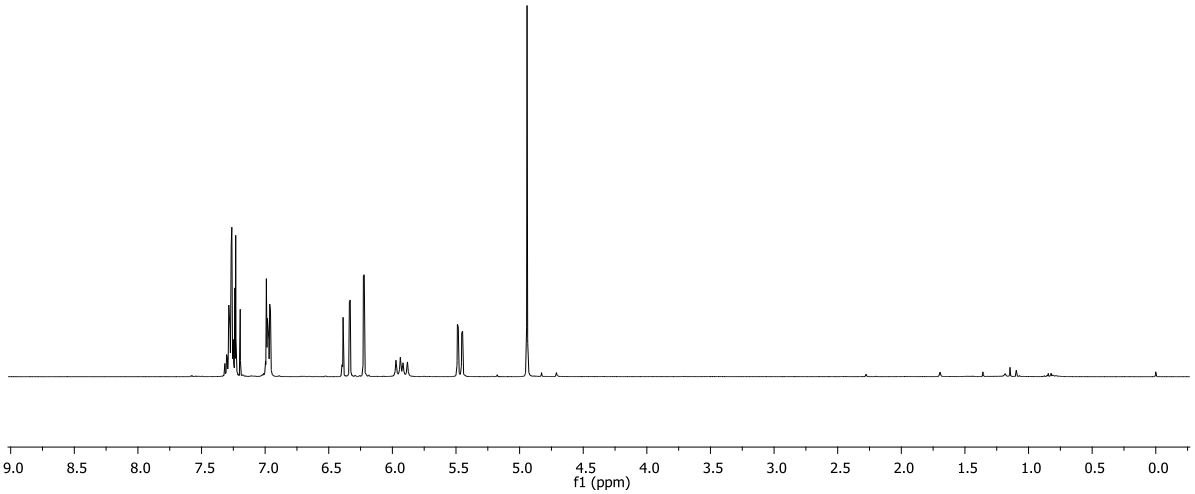

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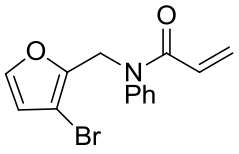

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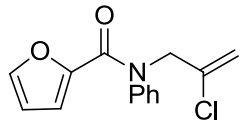

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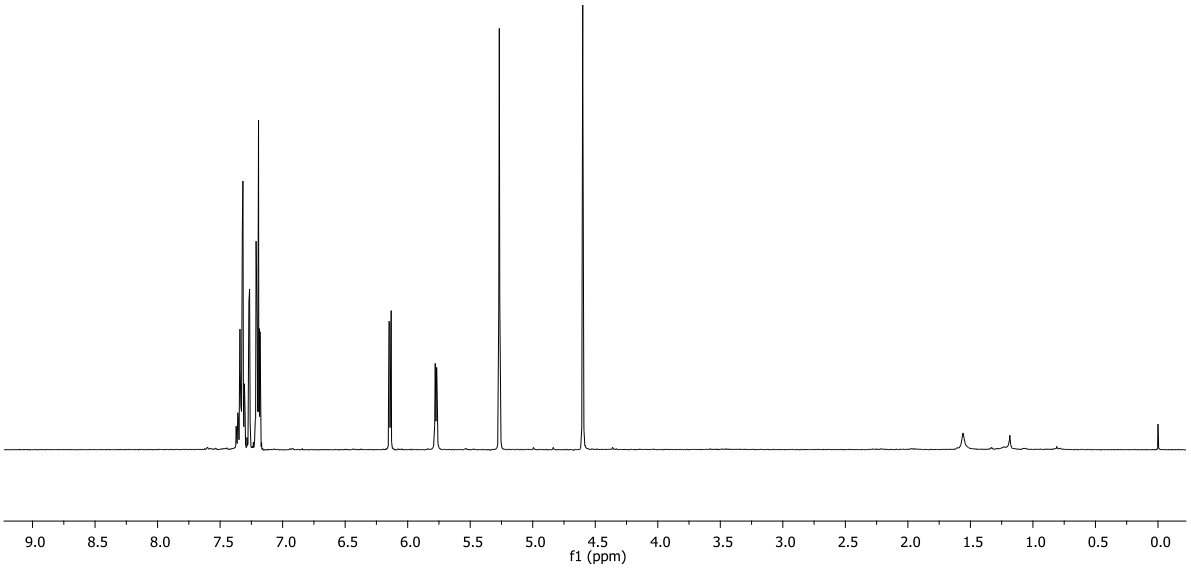

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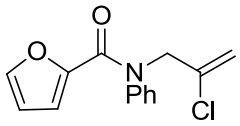

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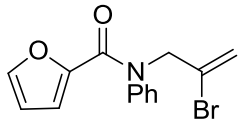

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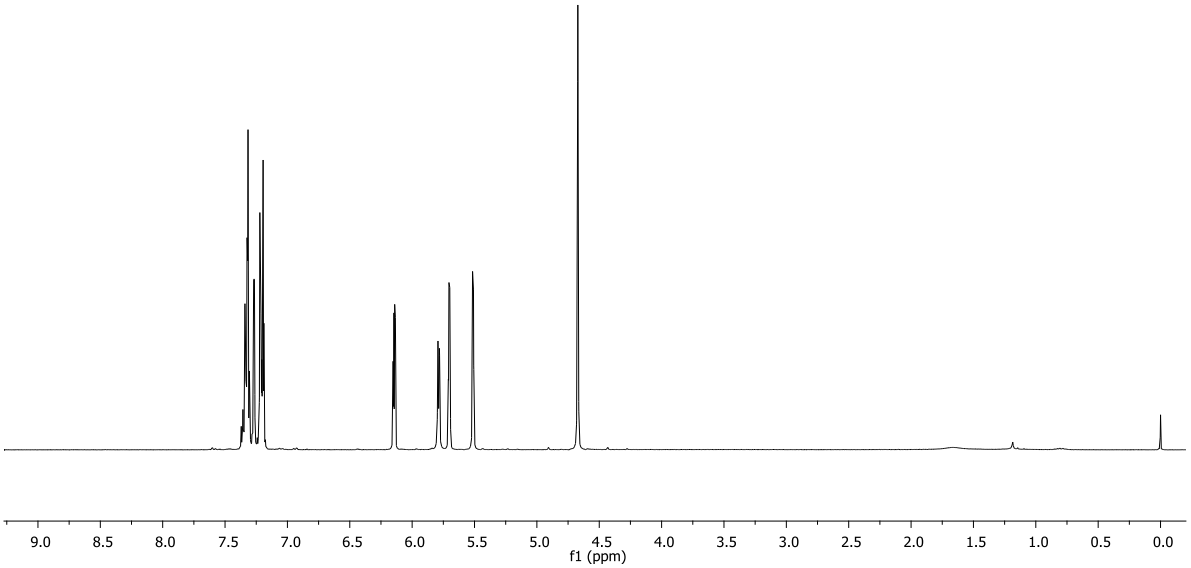

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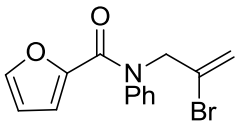

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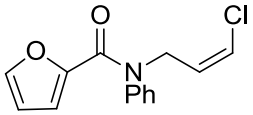

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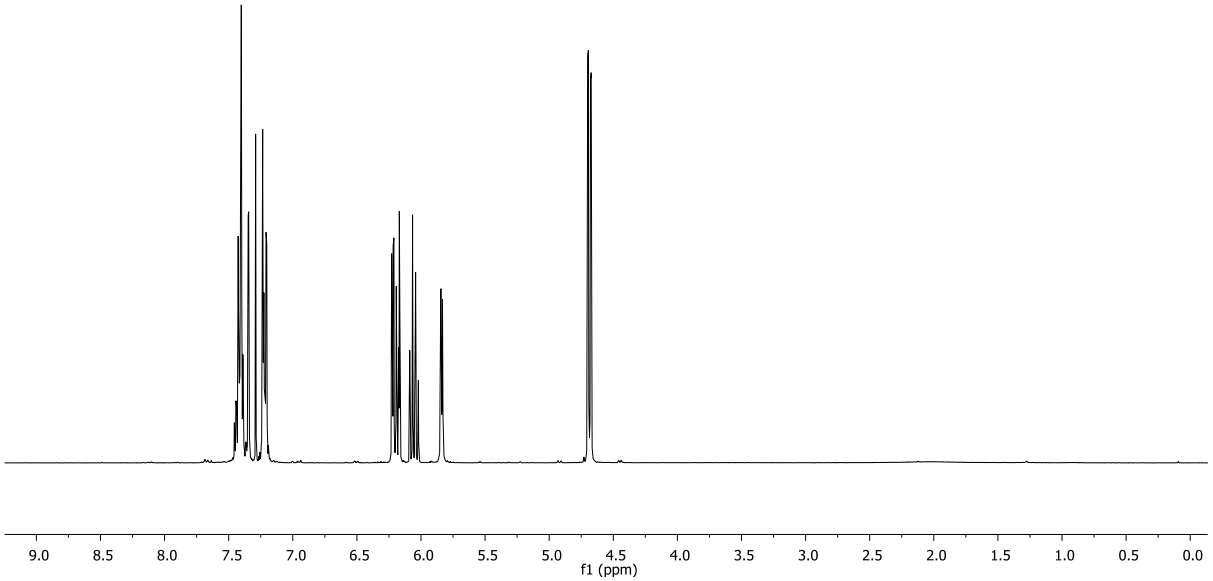

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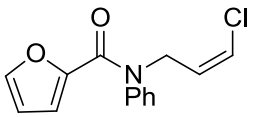

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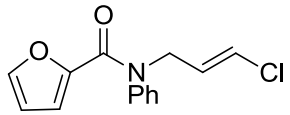

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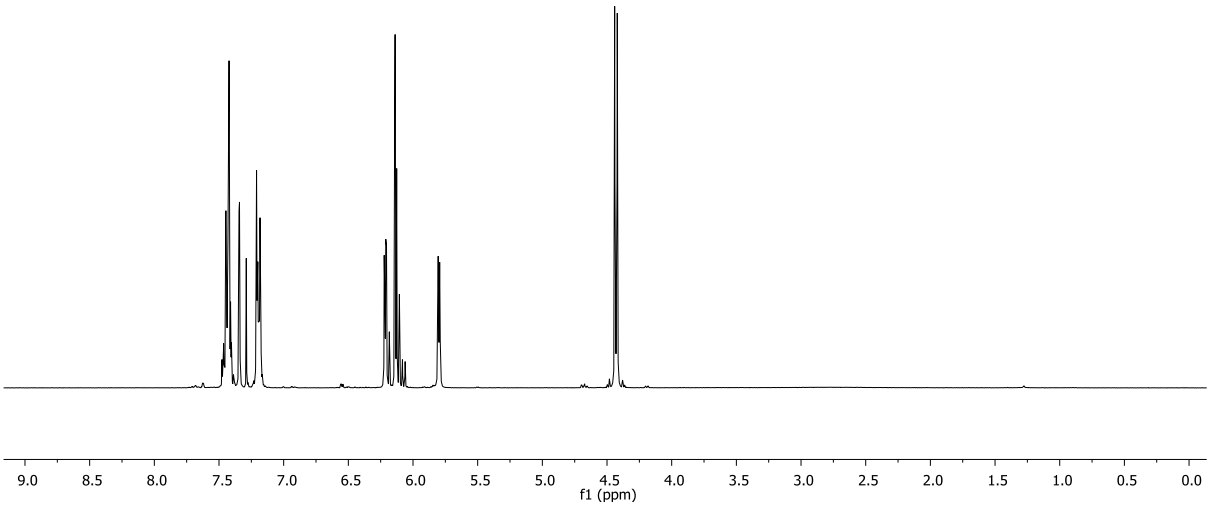

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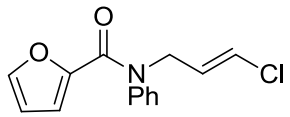

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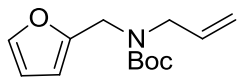

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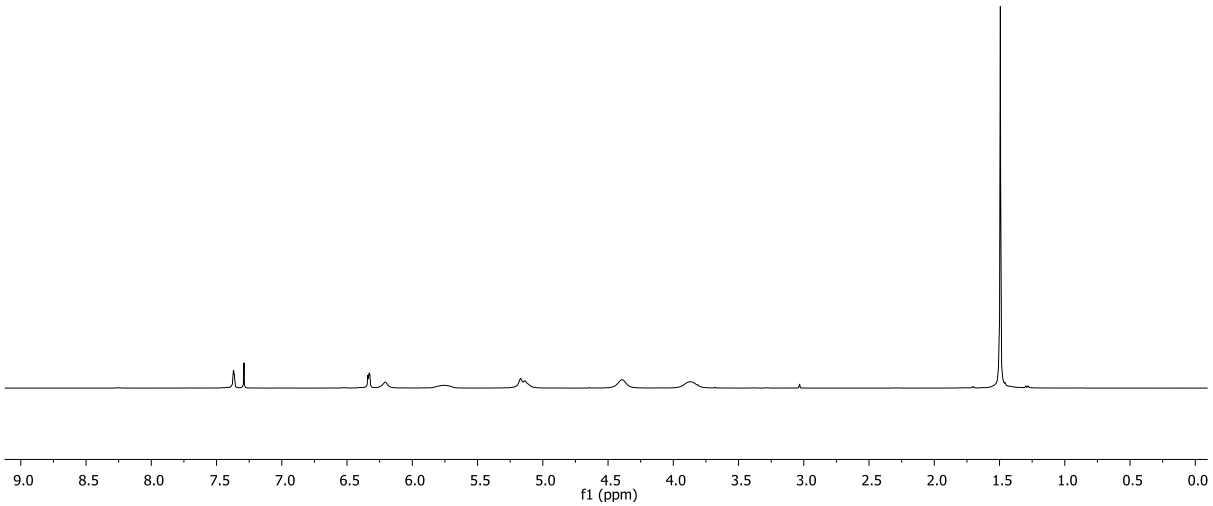

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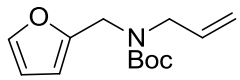

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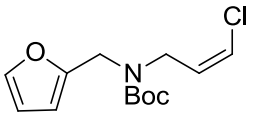

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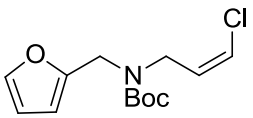

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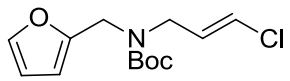

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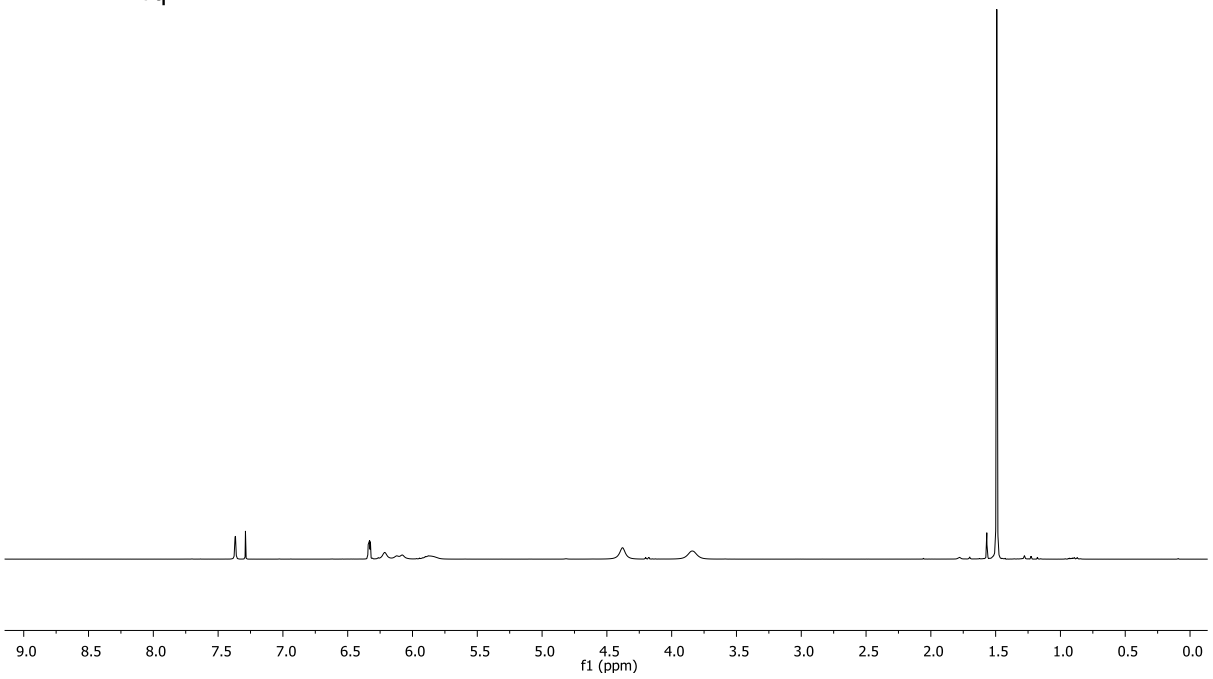

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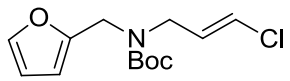

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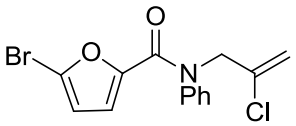

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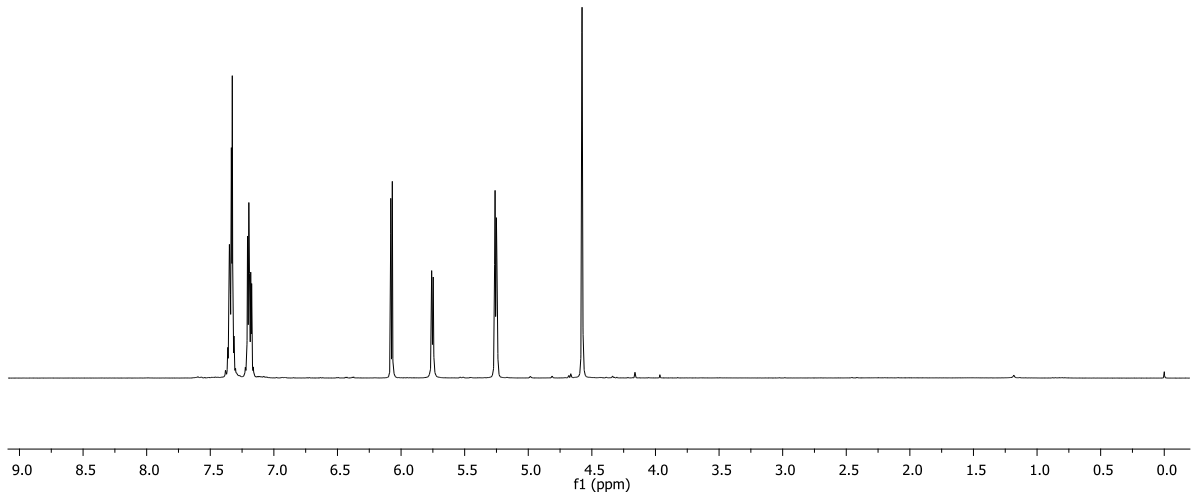

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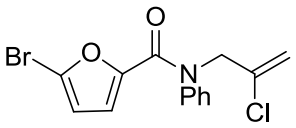

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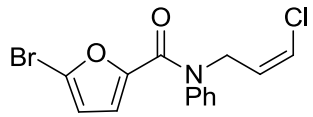

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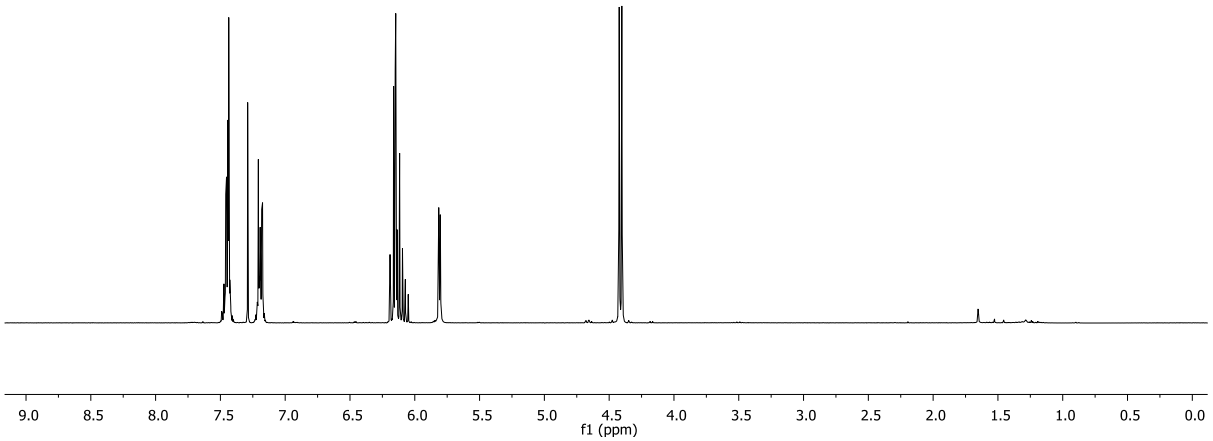

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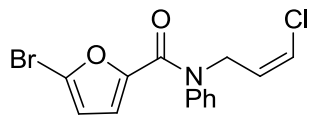

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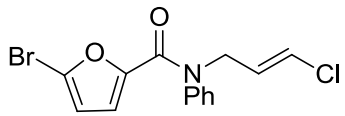

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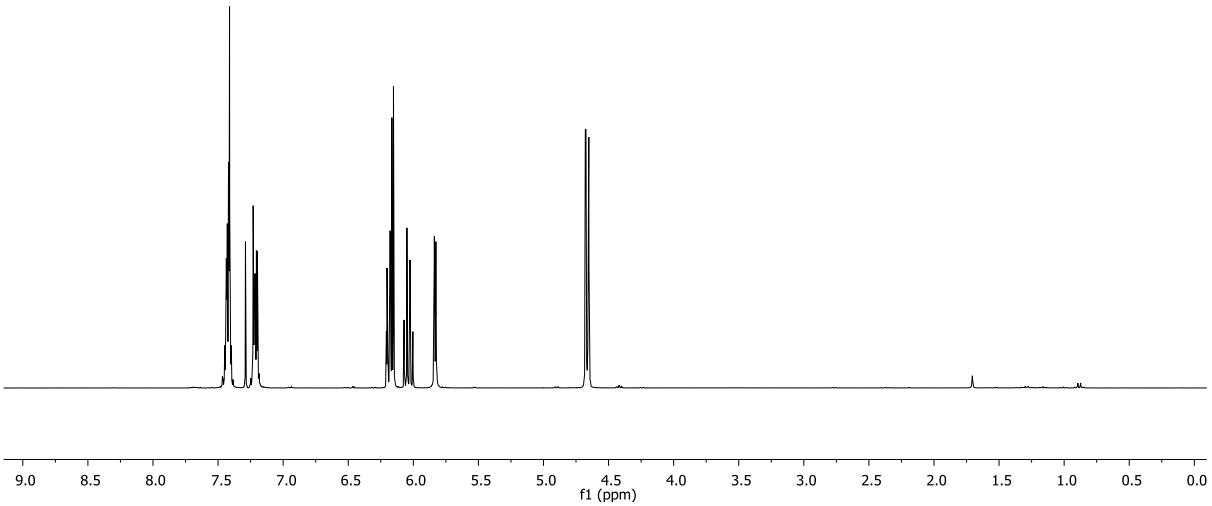

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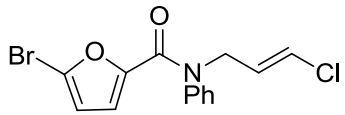

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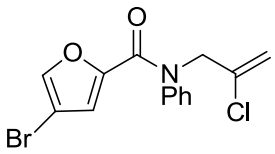

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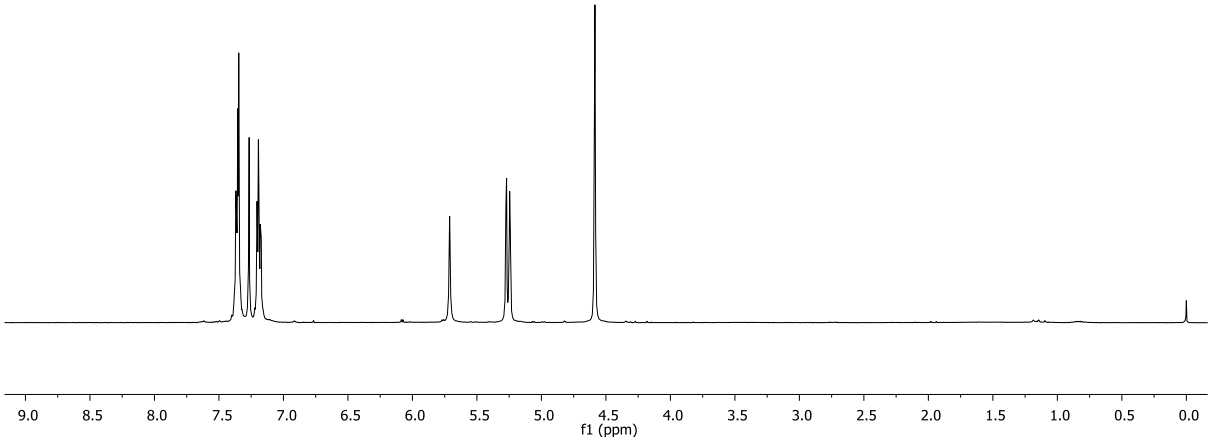

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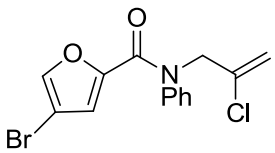

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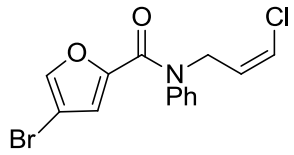

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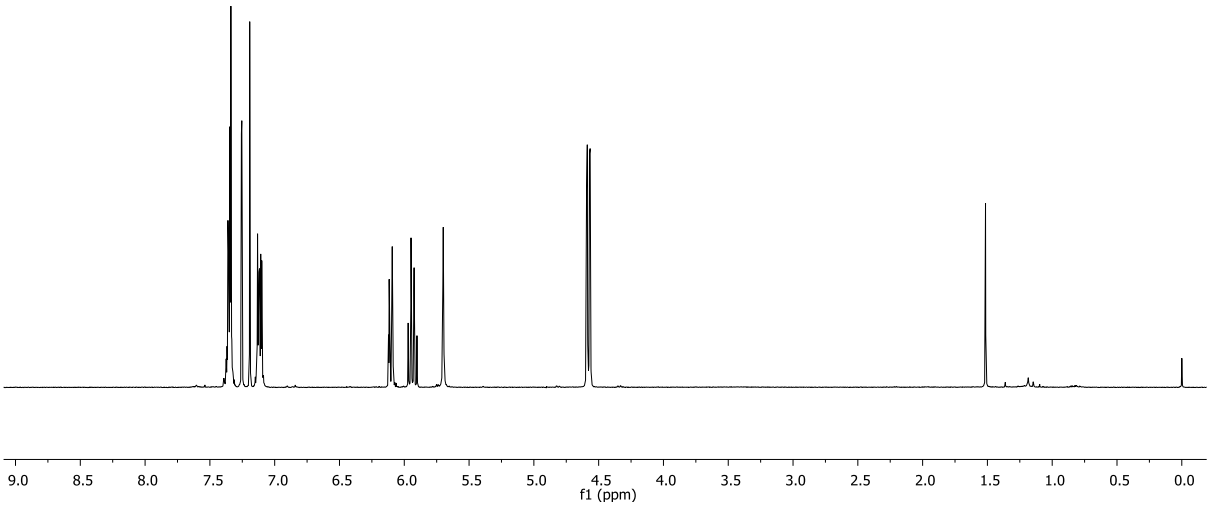

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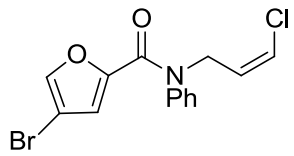

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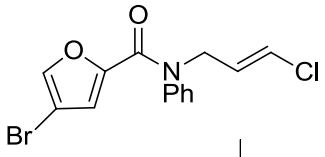

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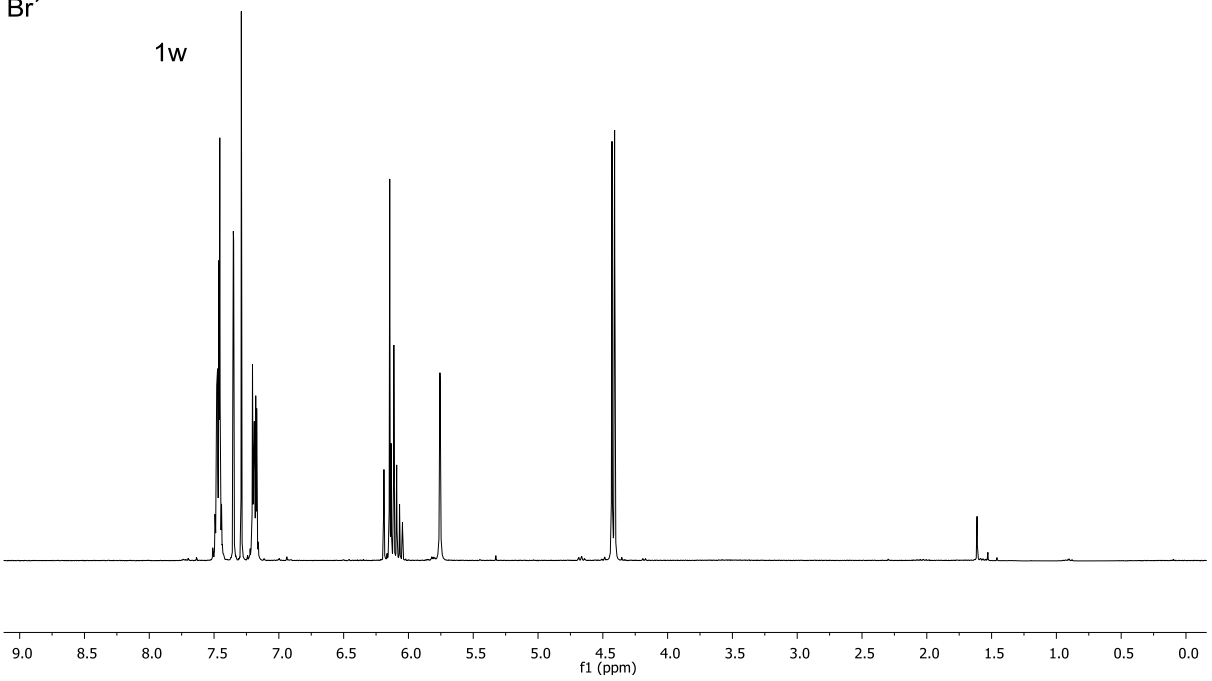

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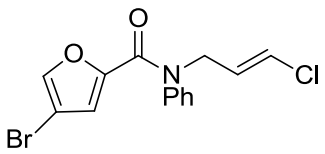

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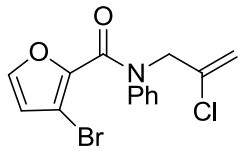

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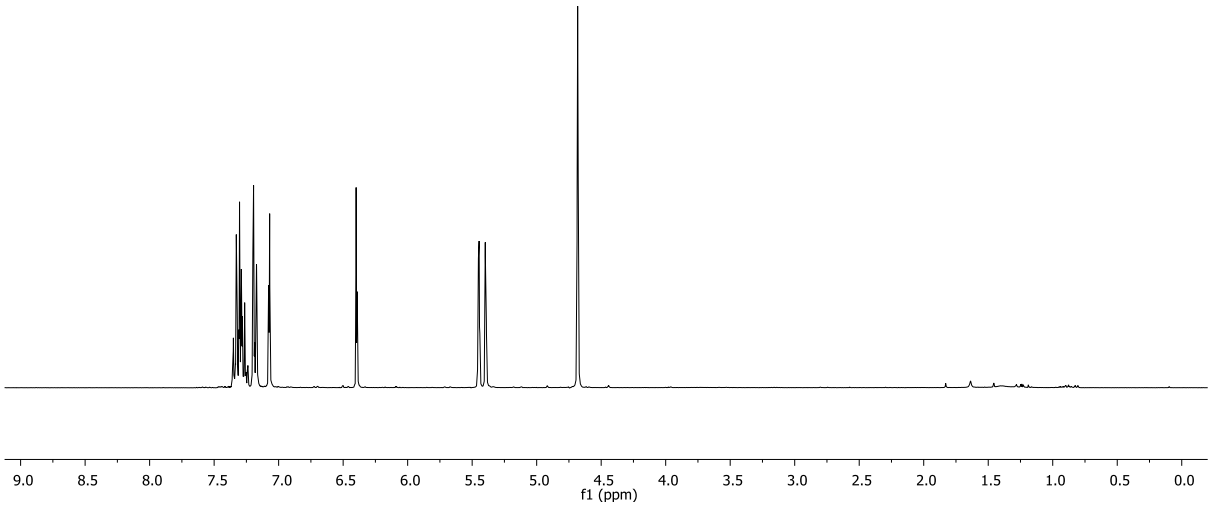

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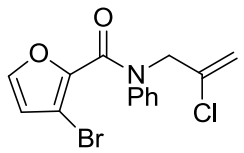

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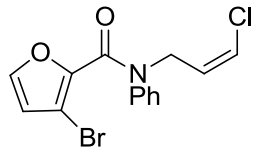

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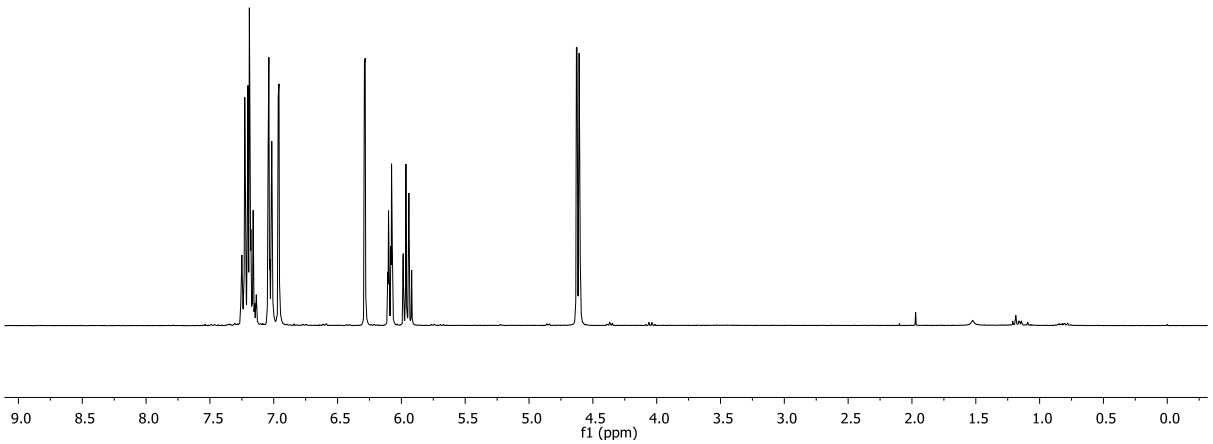

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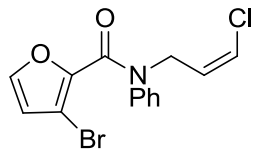

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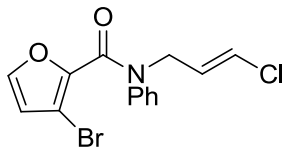

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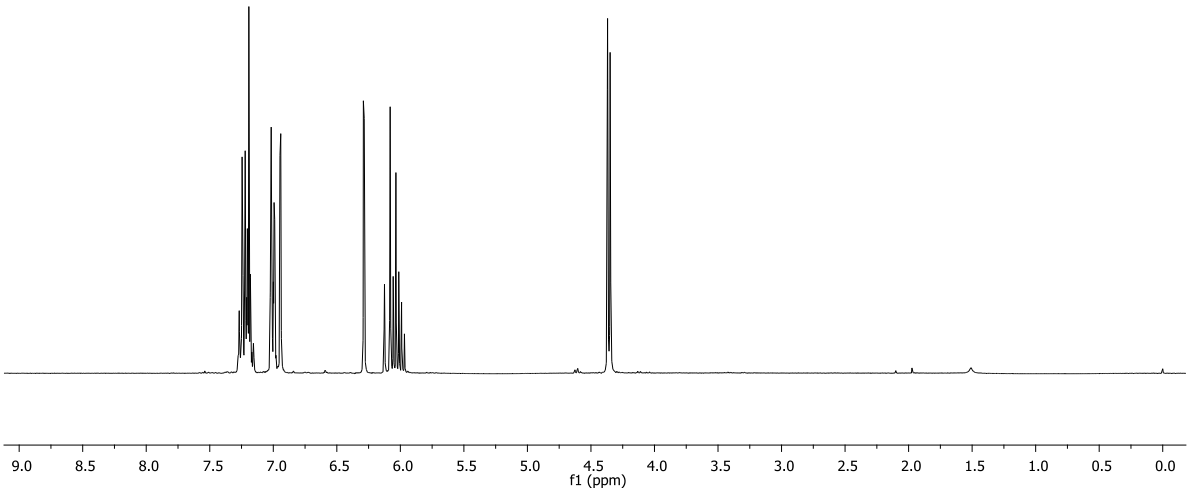

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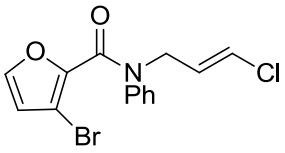

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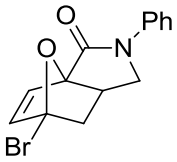

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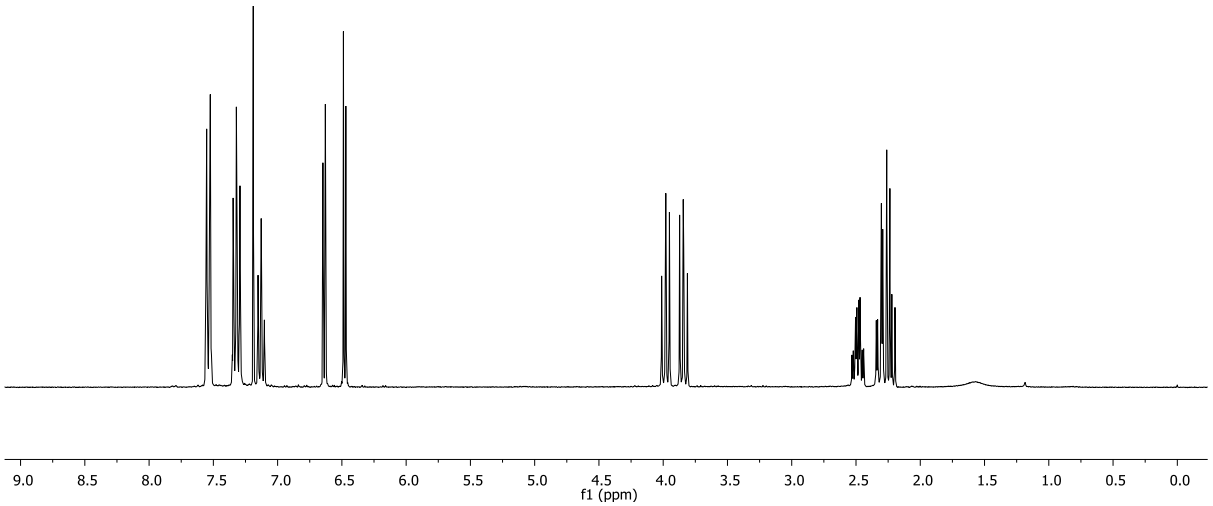

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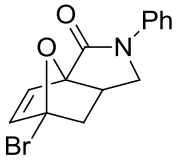

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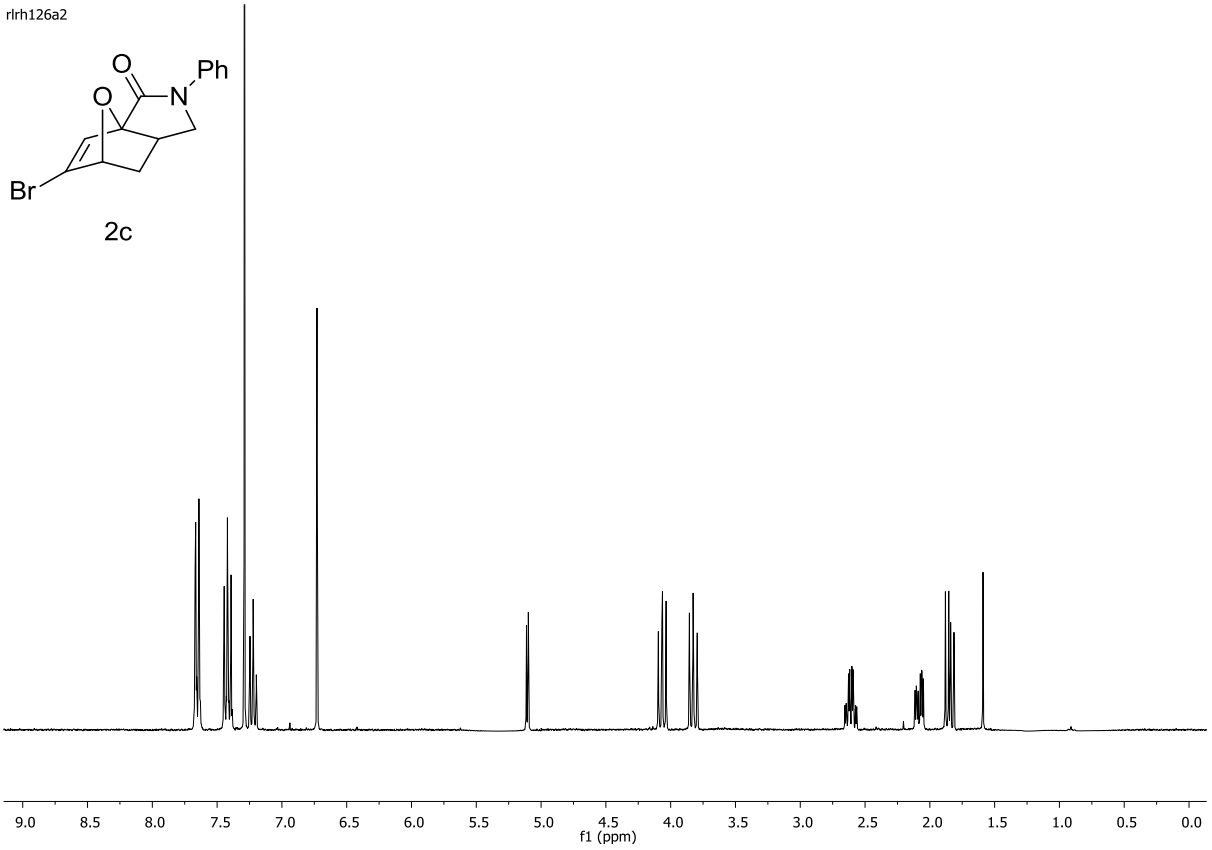

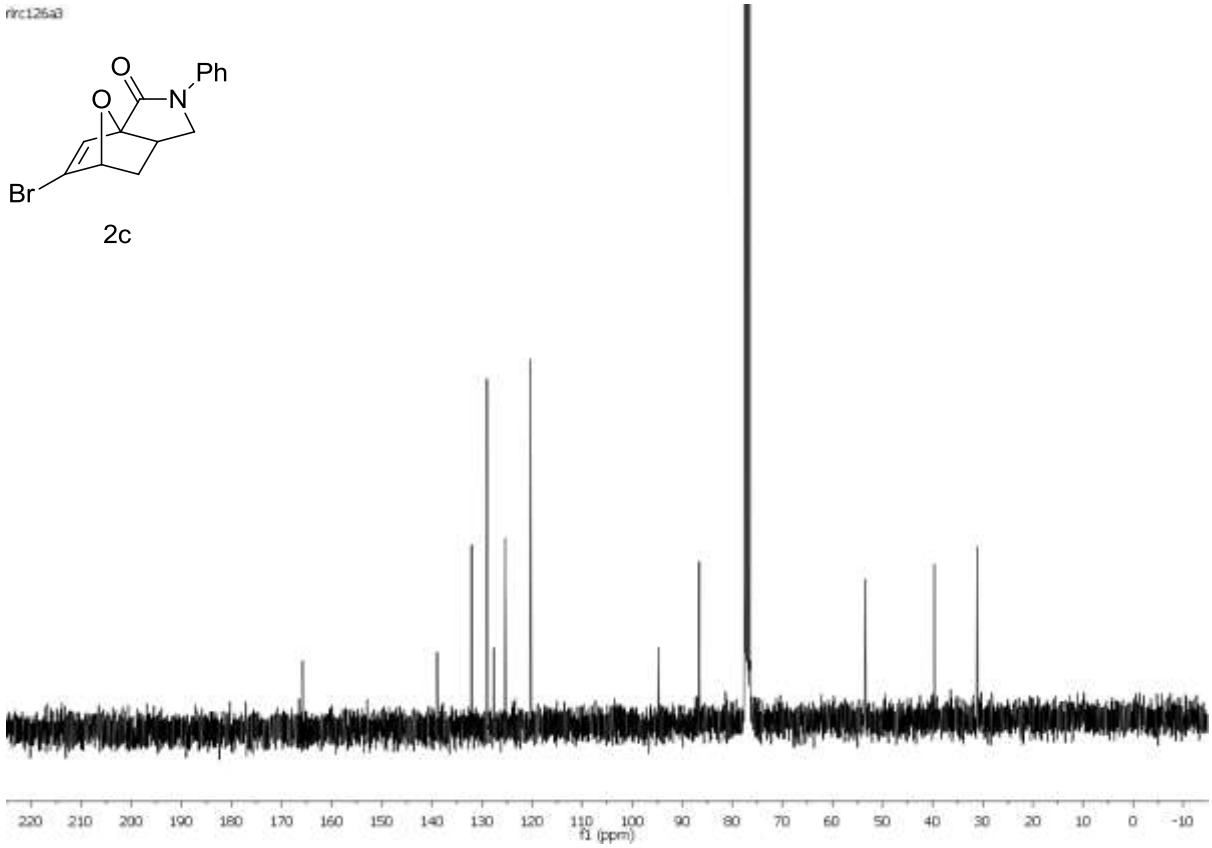

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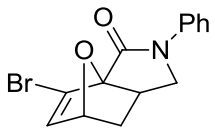

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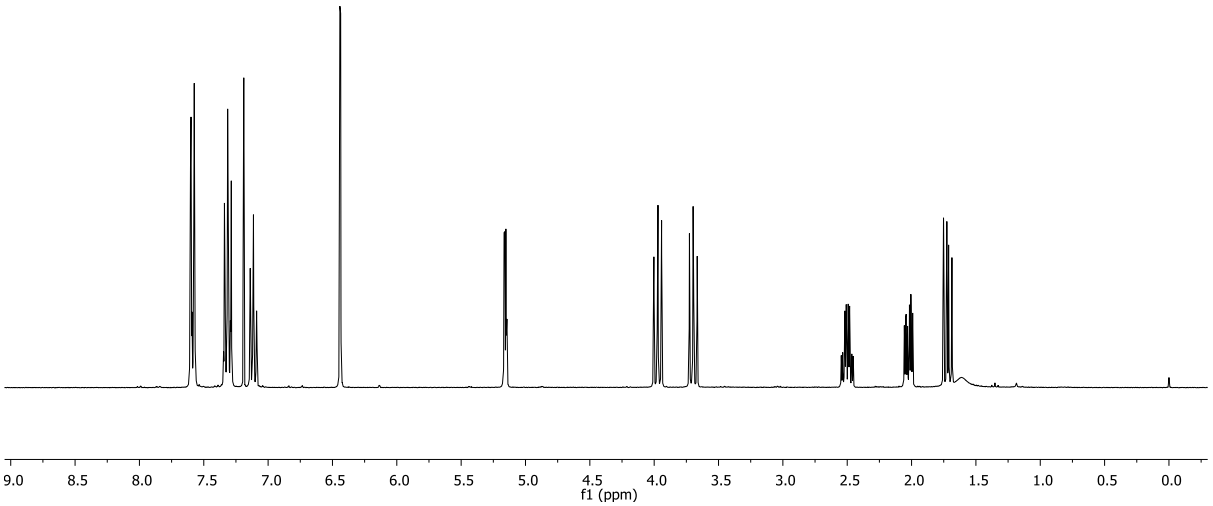

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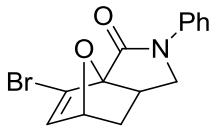

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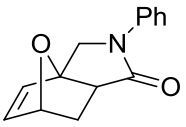

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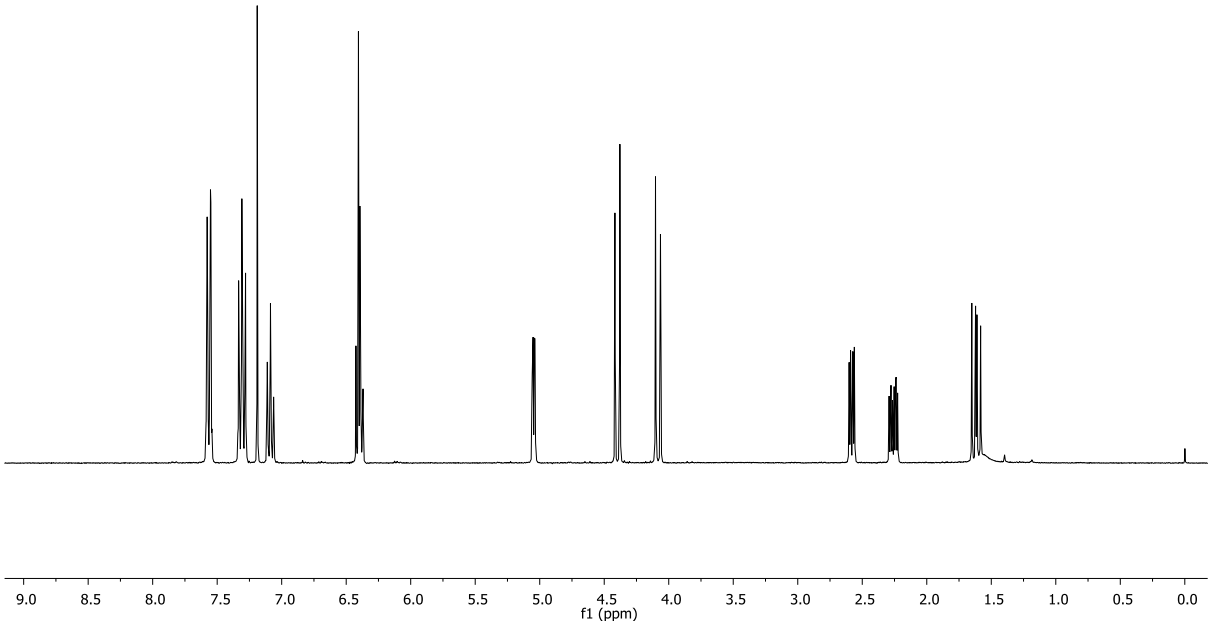

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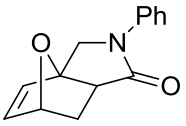

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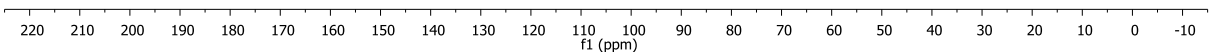

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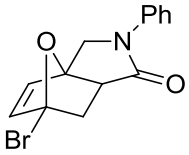

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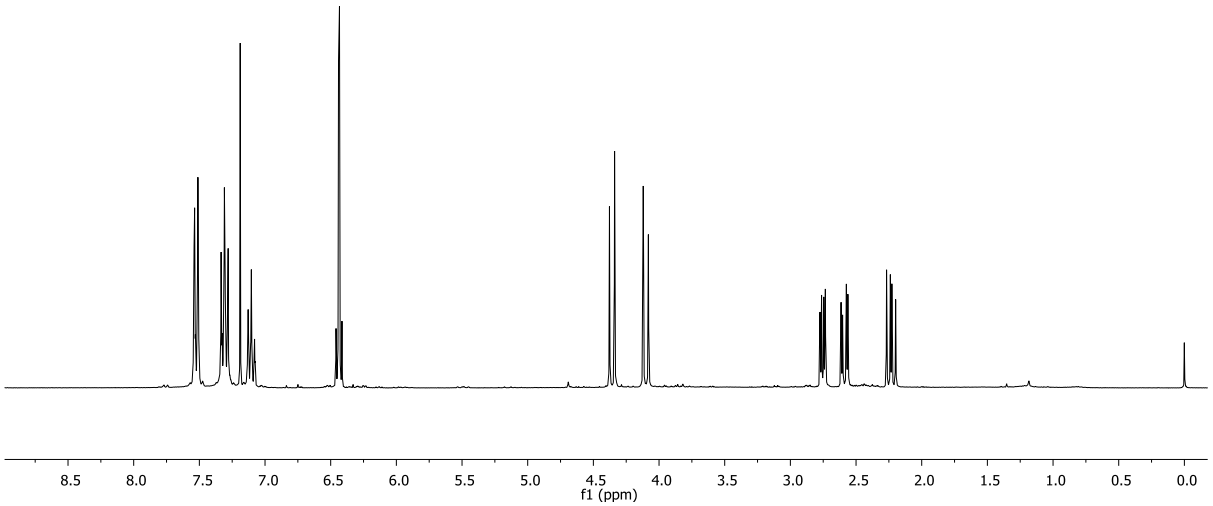

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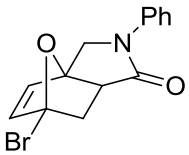

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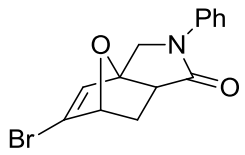

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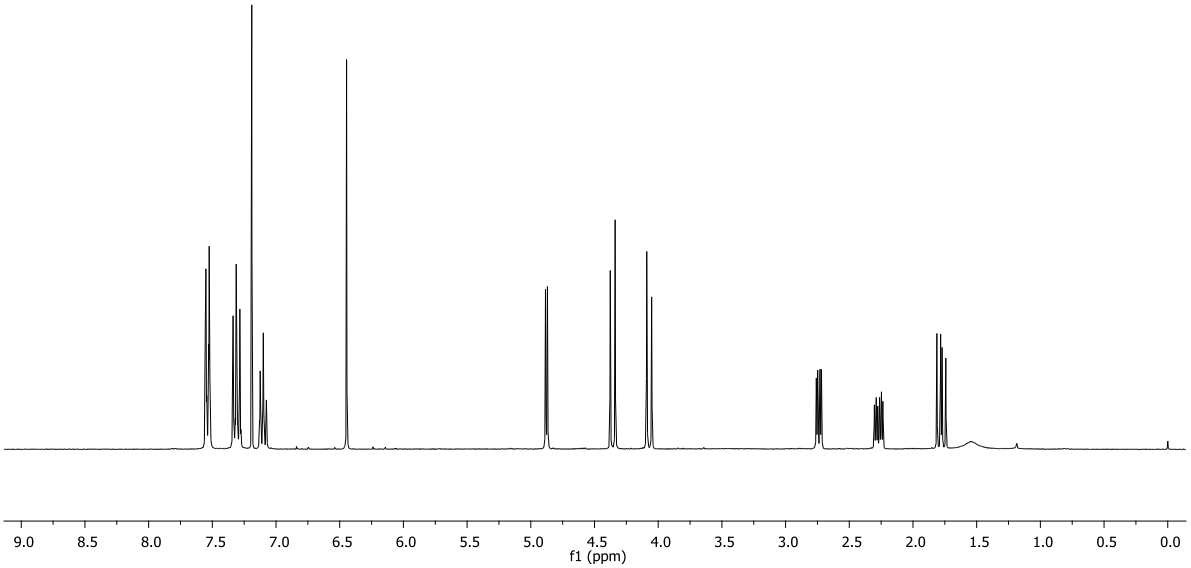

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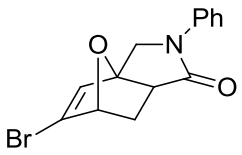

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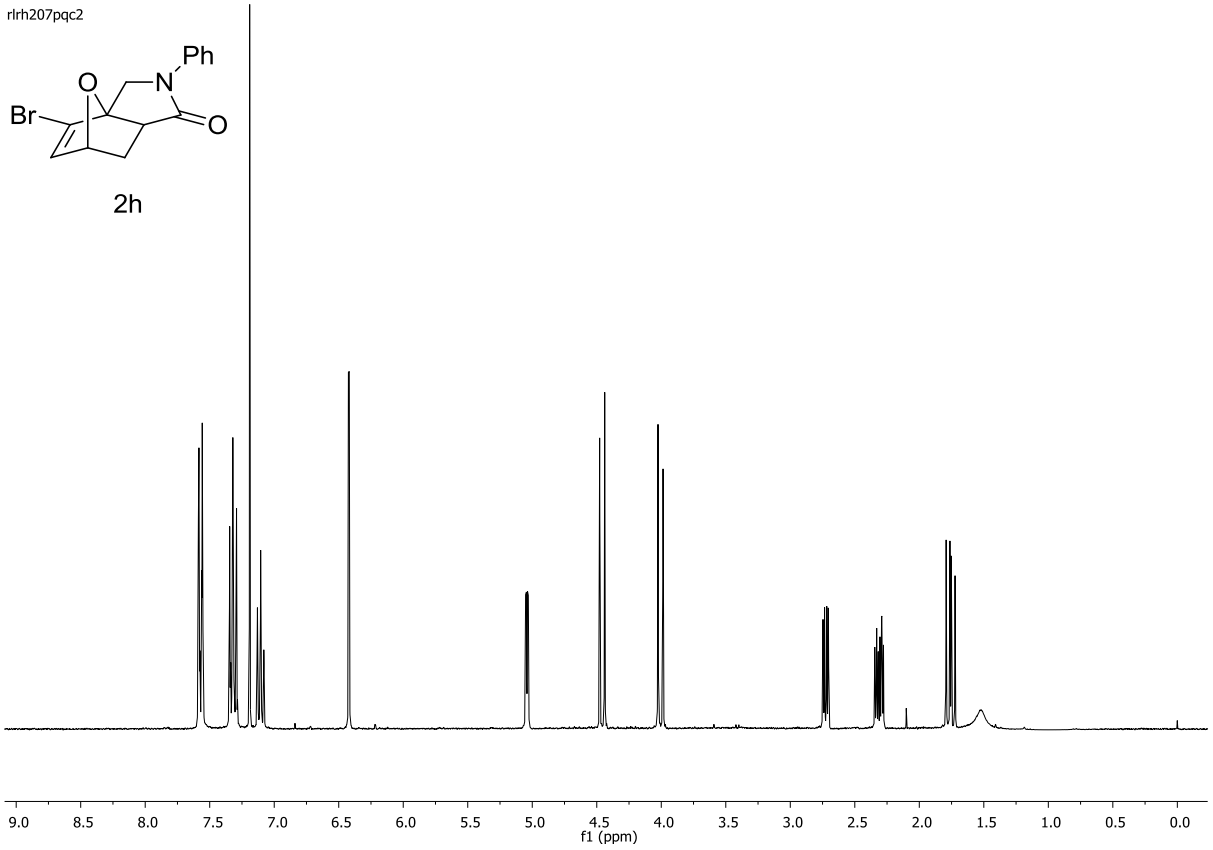

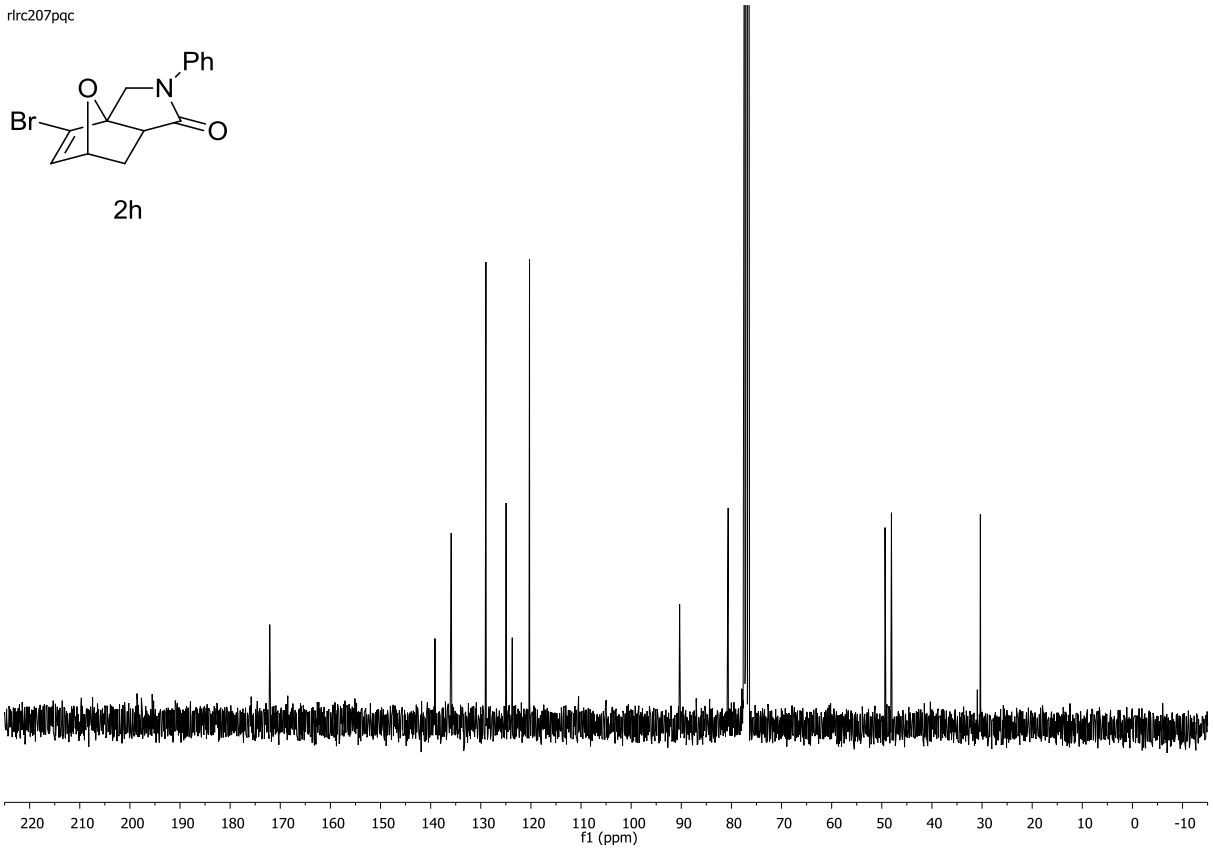

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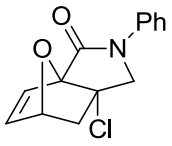

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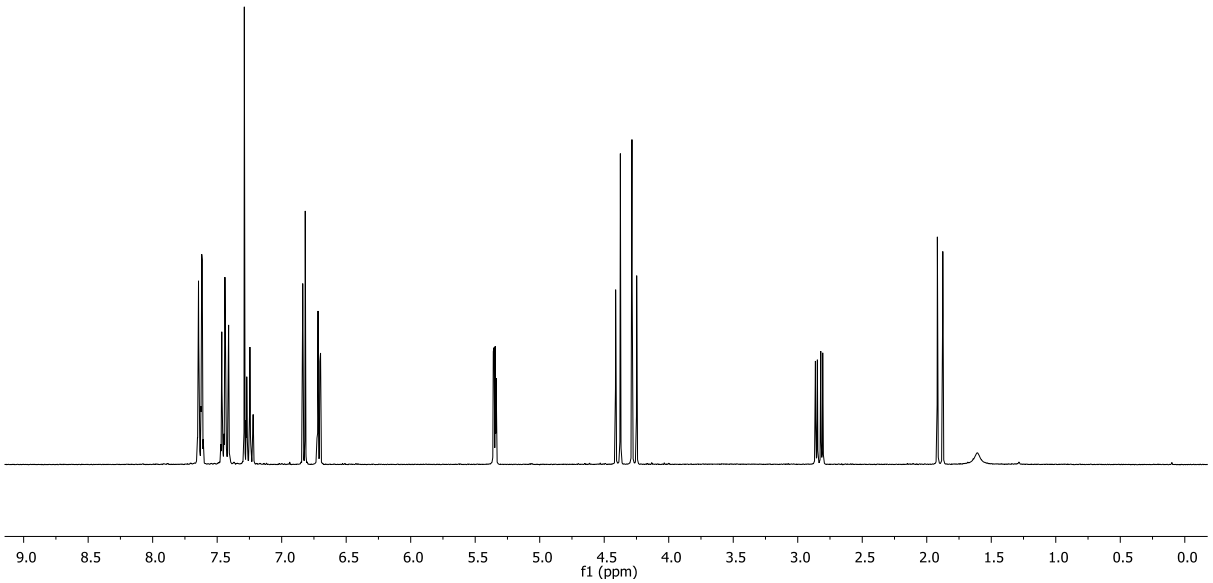

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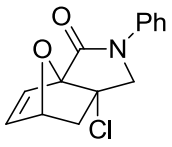

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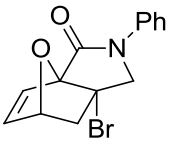

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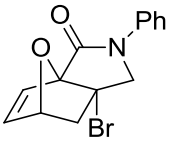

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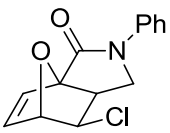

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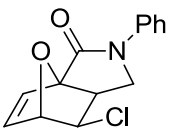

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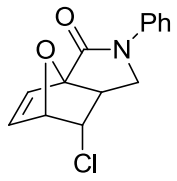

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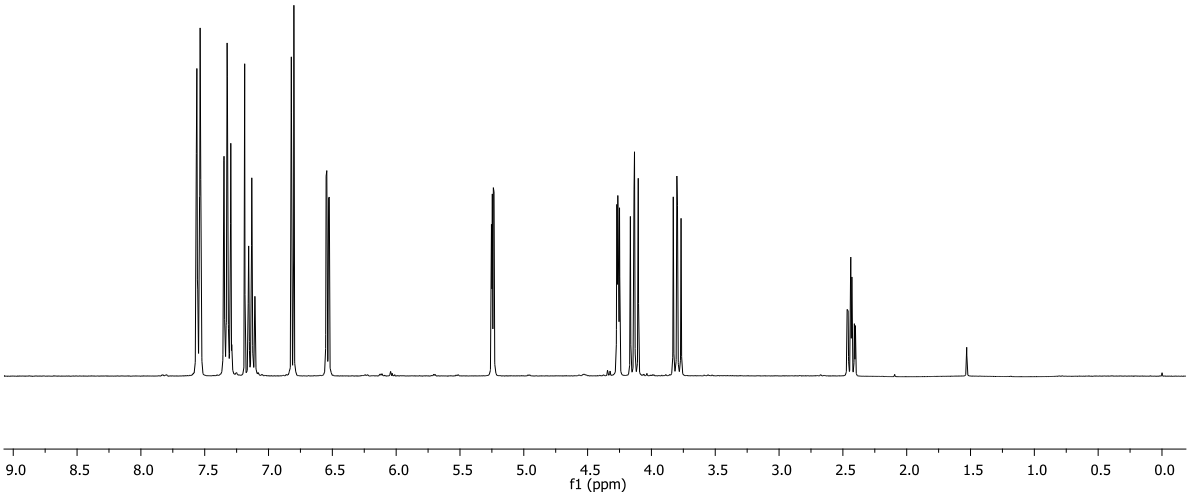

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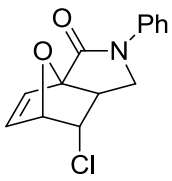

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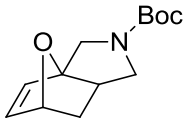

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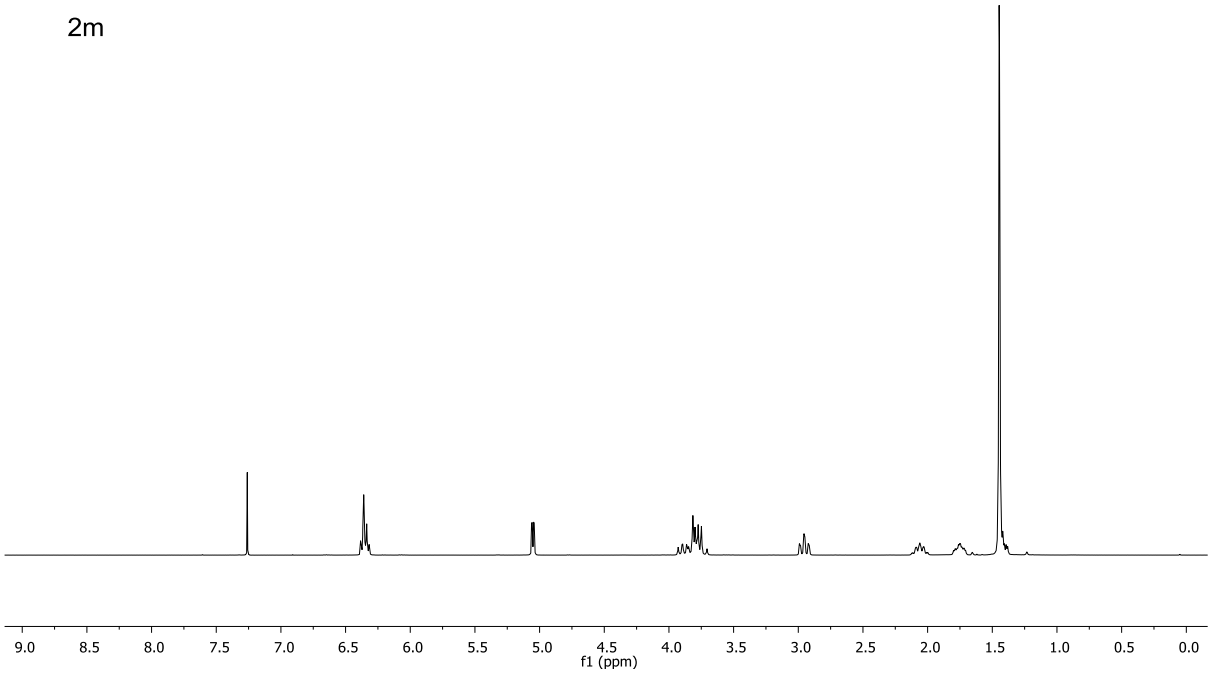

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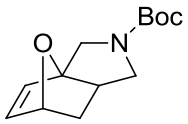

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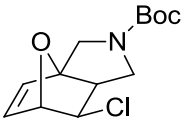

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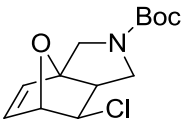

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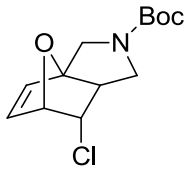

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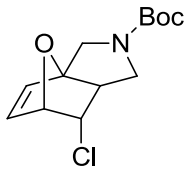

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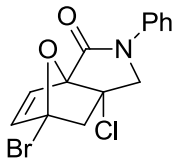

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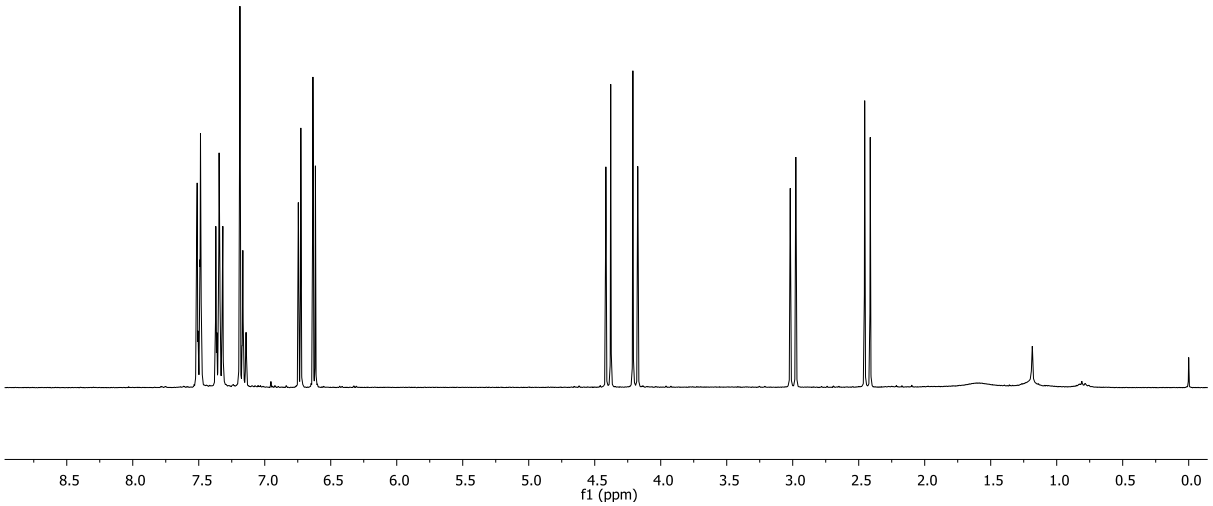

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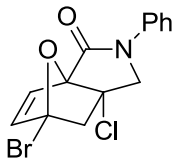

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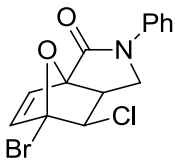

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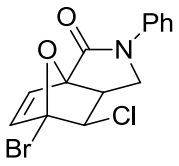

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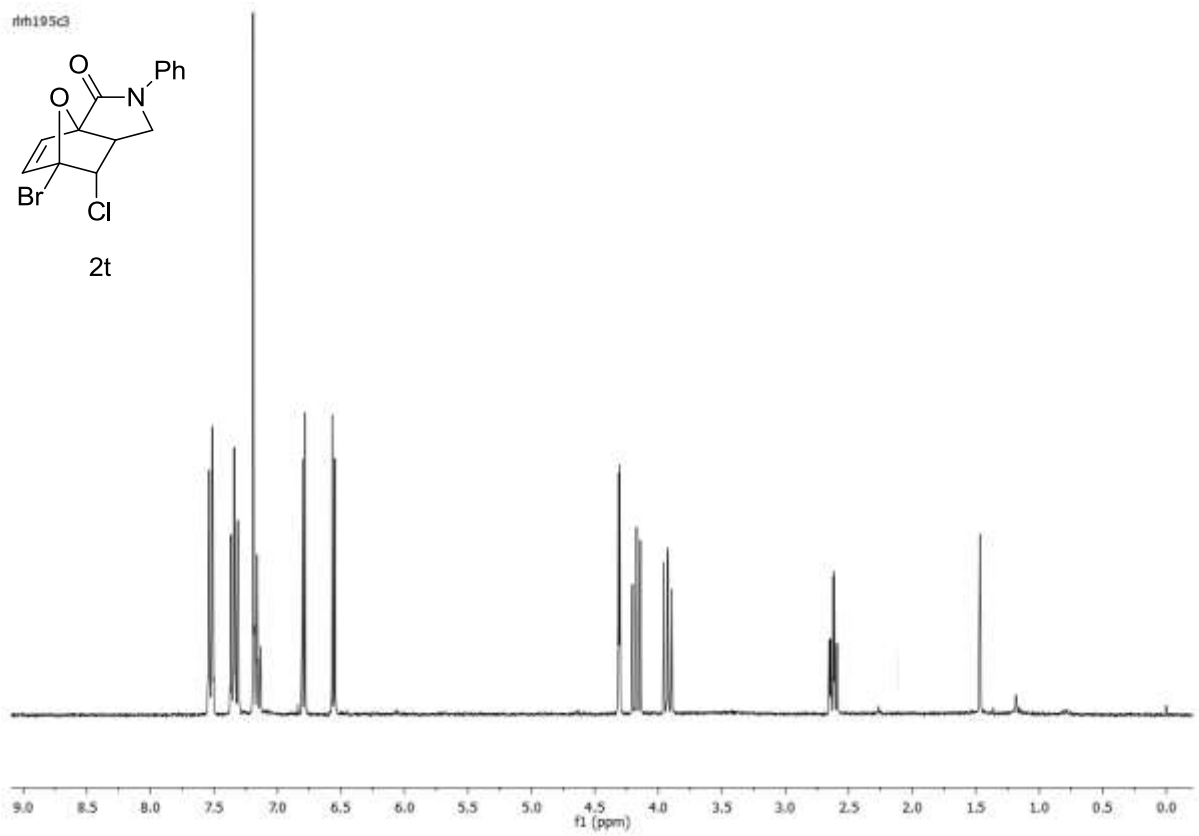

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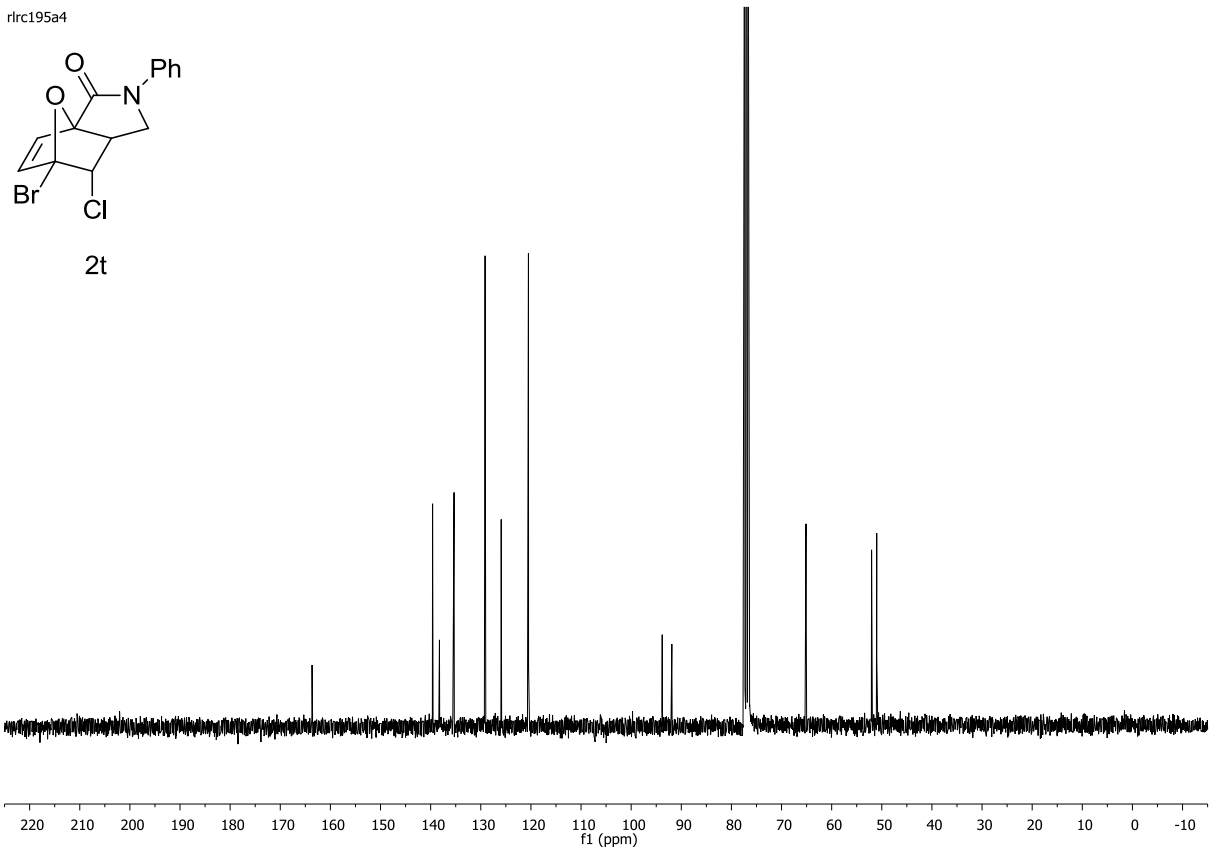

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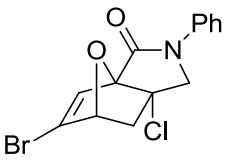

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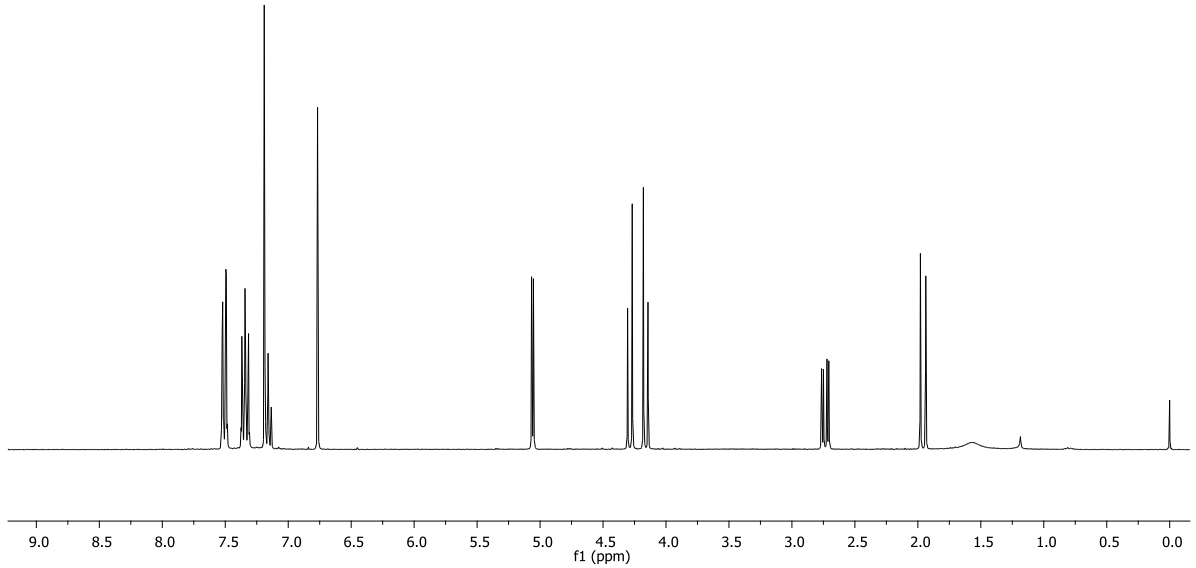

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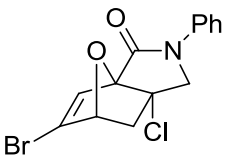

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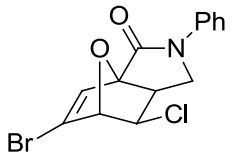

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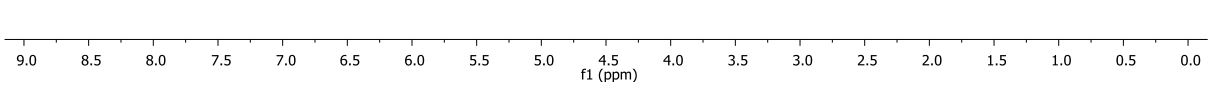

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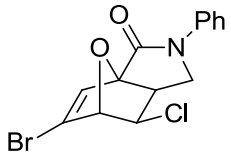

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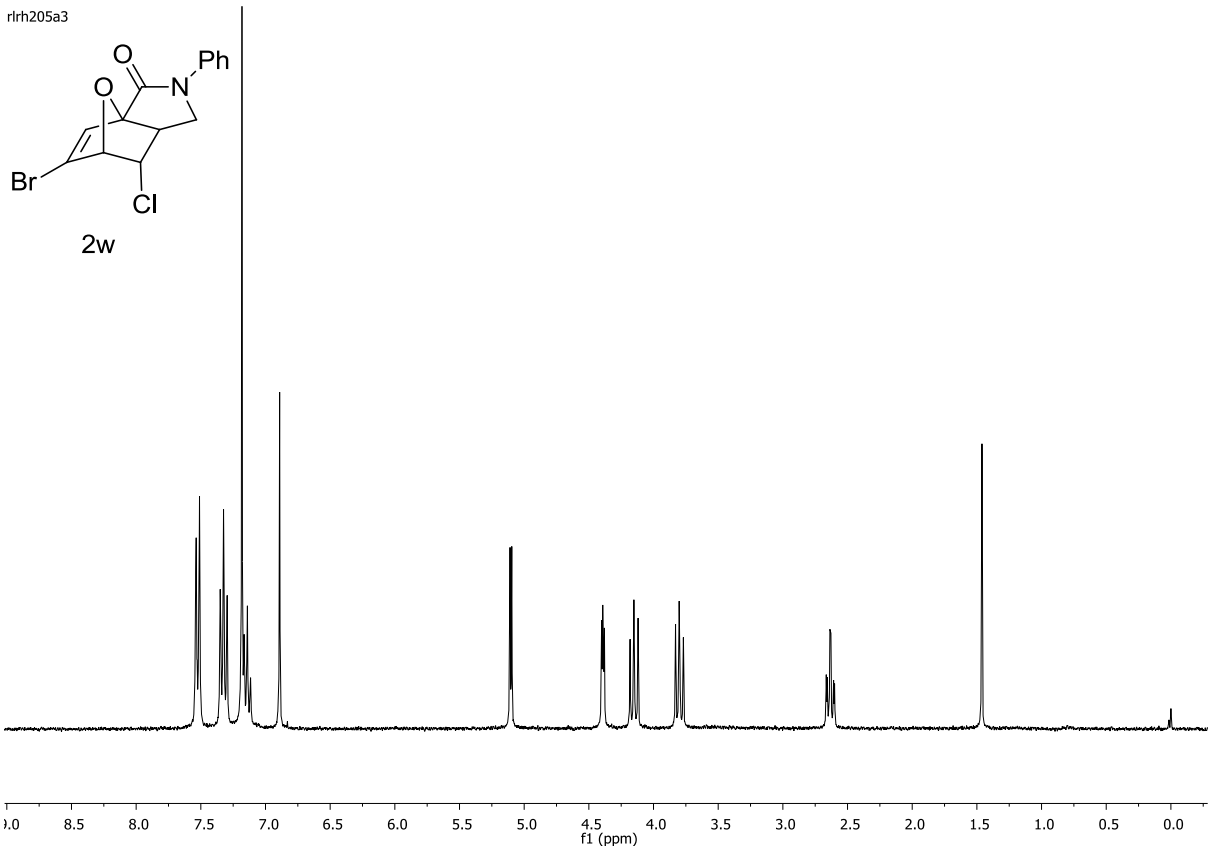

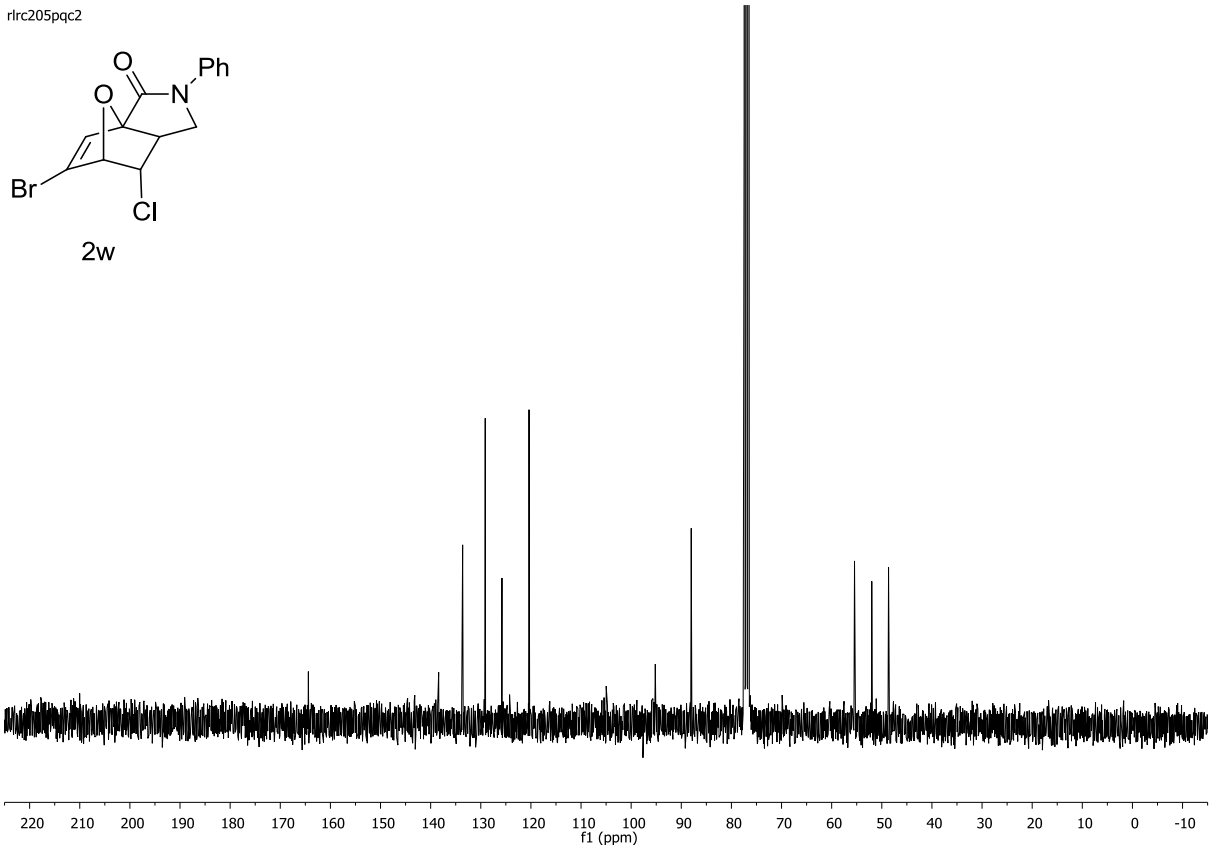

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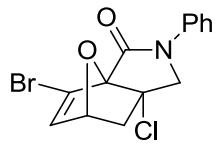

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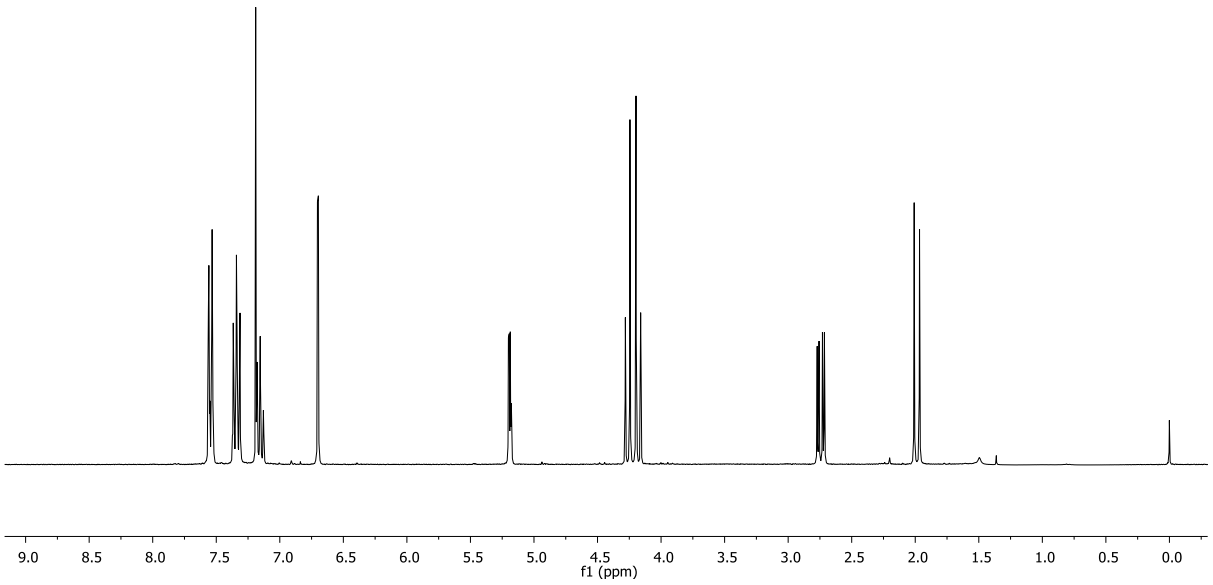

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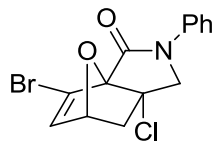

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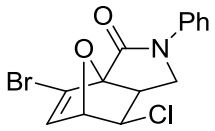

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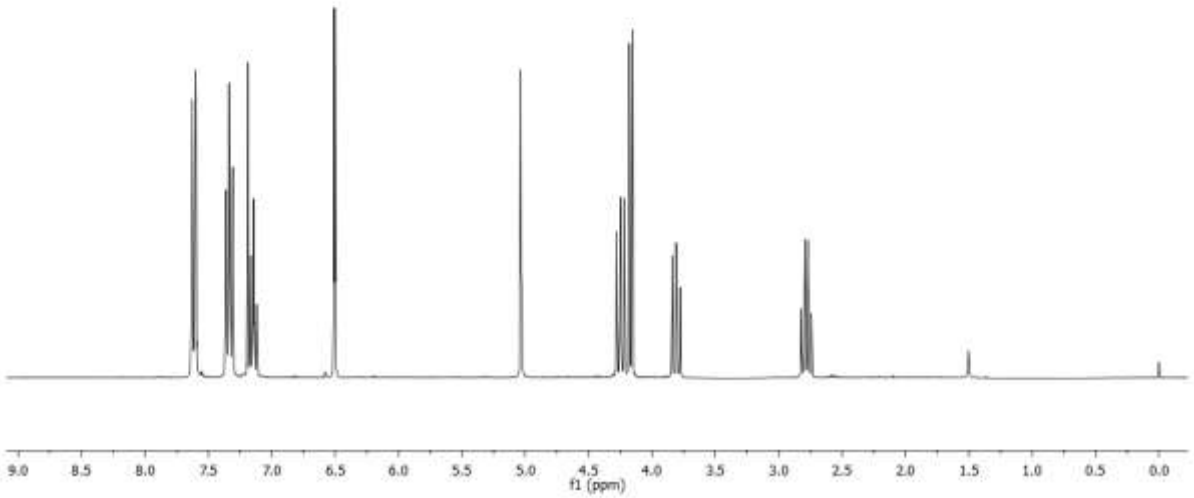

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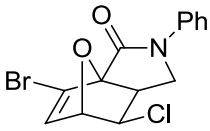

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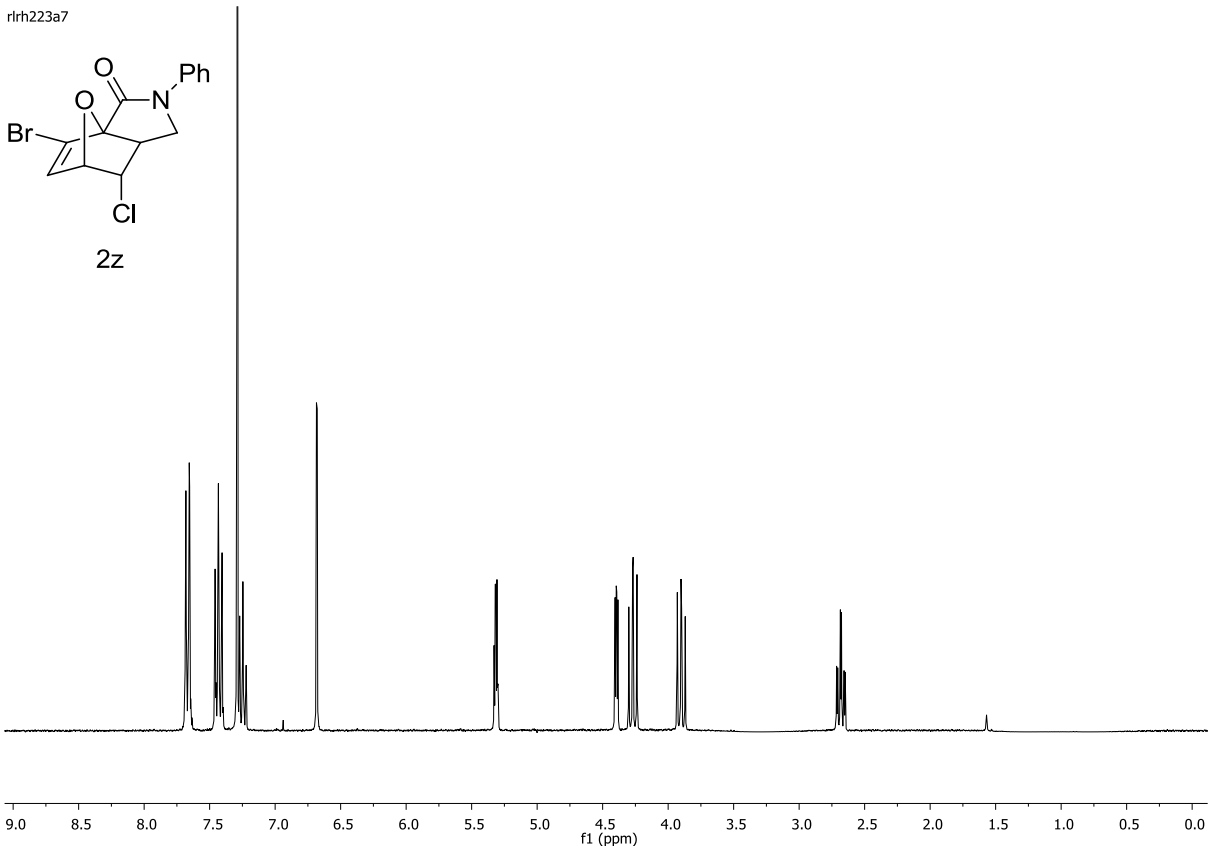
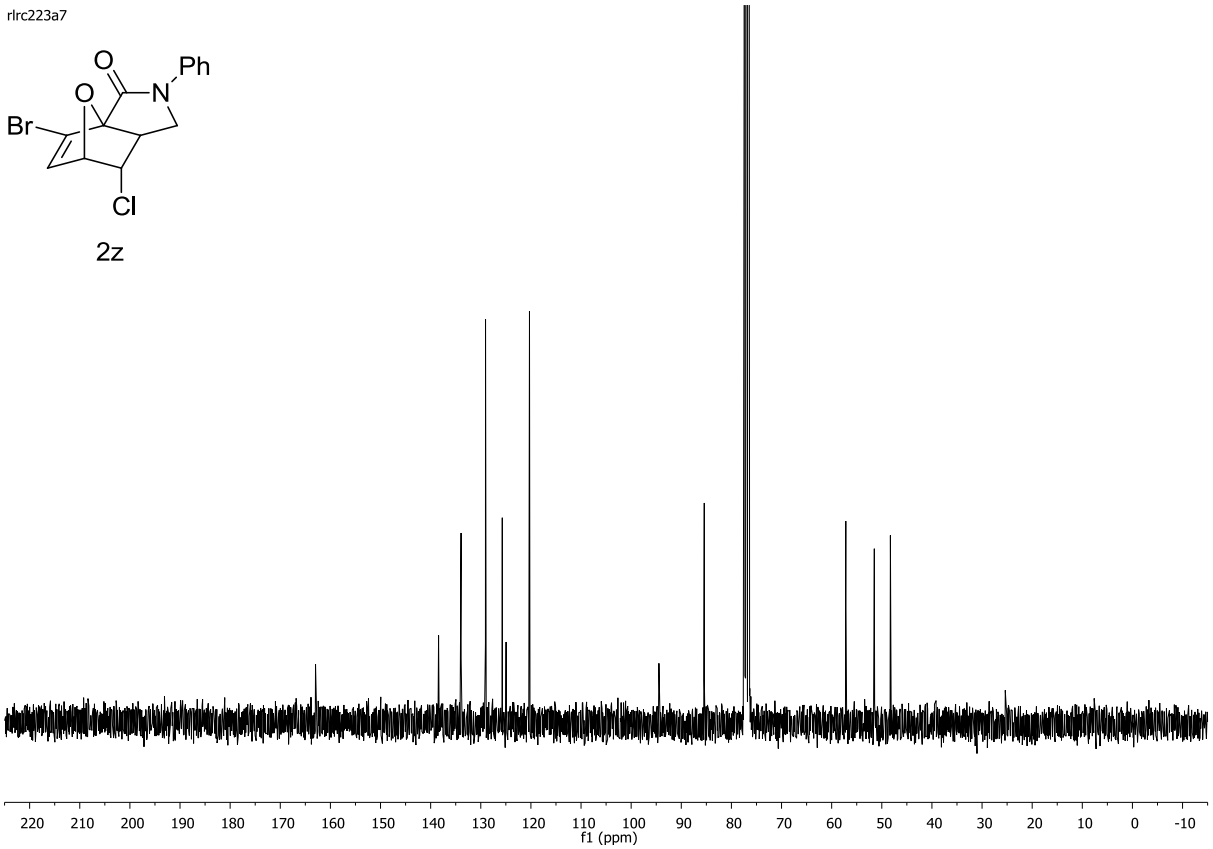


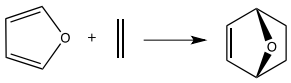
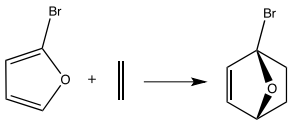


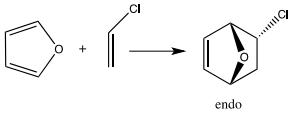
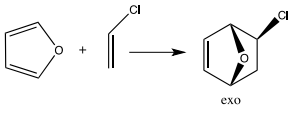
Computational supporting information:

(i) CBS Calculations

Two complete basis set (CBS) models, CBS-QB3 and CBS-4M, have been used to obtain the thermochemical data of studied Diels-Alder reactions. These results, compared also against the DFT-B3LYP/6-31G(*d*) basis for four of the simplest DA reactions are presented in *Table S1*. Free energies for both CBS models were calculated for two temperatures: 298K and 383K (temperature of experimental studies) and 298 K for B3LYP. It should be noted that 6-31G(*d*) basis set used for DFT-B3LYP studies can be poorer for elements such as halogens, thus the thermochemical values obtained here may not be of great accuracy and they are presented only for a qualitative comparison of a relatively cheap quantum chemical model with more expensive high accuracy ones.

Table S1. Thermochemical data of chosen Diels-Alder reactions using CBS-QB3, CBS-4M and DFT-B3LYP with 6-31g* basis set methods (T=298.15 K; 383 K).

Reaction	Method	Temp. (K)	$\Delta_r H°$ (kcal/mol)	$\Delta_r G°$ (kcal/mol)	$\Delta_{activ} H$ (kcal/mol)	$\Delta_{activ} G$ (kcal/mol)
	**CBS-QB3**	298.15	-12.2	1.6	20.5	33.35
		383.00	-12.35	5.5	20.5	37.0
	CBS-4M	298.15	-13.9	-0.3	17.9	30.85
		383.00	-14.0	3.65	15.5	41.2
	B3LYP	298.15	-5.25	8.6	25.85	38.8
		383.00	-5.4	12.5	25.85	42.4
	**CBS-QB3**	298.15	-17.2	-3.3	18.3	31.3
		383.00	-17.3	0.7	18.4	35.0
	CBS-4M	298.15	-20.4	-6.6	4.3	17.3
		383.00	-20.5	-2.7	4.3	21.1

	B3LYP	298.15 383.00	-9.6 -9.7	4.4 8.4	24.4 23.6	37.3 41.0
 endo	**CBS-QB3**	298.15 383.00	-13.3 -13.4	1.1 5.2	19.8 19.9	33.3 37.1
	CBS-4M	298.15 383.00	-15.1 -15.1	-0.7 3.4	17.4 17.4	31.0 34.9
	B3LYP	298.15 383.00	-4.1 -4.2	10.4 14.5	27.2 27.3	40.7 44.6
 exo	**CBS-QB3**	298.15 383.00	-12.8 -12.9	1.6 5.7	20.8 20.8	34.2 38.1
	CBS-4M	298.15 383.00	-14.6 -14.6	-0.3 3.8	18.2 18.3	31.9 35.8
	B3LYP	298.15 383.00	-3.8 -3.9	10.7 14.8	27.9 28.0	41.5 45.3

The CBS models employed in this paper use N^{-1} asymptotic convergence of second-order Moller-Plesset pair energies calculated from pair natural orbital expansions to extrapolate to the CBS limit. Application of CBS extrapolations enables the use of smaller basis sets at second-order, which reduces the calculation time and allows such methods to be used on wider range of systems. Low levels of theory are used for geometries and vibrational zero-point energies. To obtain a total molecular energy they are combined with higher-level calculations of the total electronic energy.[11] The CBS-QB3 model consists of following calculations:

a) B3LYP/6-311G(*2d,d,p*) - geometry optimisation and frequencies
b) CCSD(T)/6-31+G(*d'*) - energy
c) MP4(SDQ)/CBSB4 - energy
d) MP2/CBSB3 - energy and CBS extrapolation (with the G09c, default number of minimum 10 pair natural orbitals for this specific basis set used)

Geometries and frequencies in CBS-QB3 model are obtained with DFT-B3LYP calculations, unlike the original CBS-Q method. The CBS-Q model uses UHF with the 6-31G basis set for initial geometry and frequency calculations and then MP2(FC) with the same basis set for the final geometry optimisation. Changing to DFT-B3LYP with a larger basis set in CSB-QB3 method gives more reliable geometries and zero-point energies of stable molecules included in G2 test set relative to MP2, and gives more consistent structures for transition states.[12]

Early work showed that such CBS models would fail in some cases (e.g., some polycyclic systems, perchlorates etc.).[11-13] As it was found later the reason for it was the use of Mulliken analysis in Pipek and Mezey occupied orbital localisation methods, which due to its unphysical behaviour in some cases, obtained from the extended basis sets, results in unphysical energy contributions. A new algorithm for localisation was since then employed in which the populations are measured in a minimal basis (minimum population localisation) and not extended ones. This population method is now implemented in both CBS-QB3 and CBS-4M methods. It improves their reliability and sorts the previous anomalies caused by the abnormal behaviour of the older population method.[13]

The CBS-4M model is composed of following calculations:

a) HF/3-21G(*d*) - geometry optimisation and frequencies
b) MP4SDQ/6-31G - energy
c) MP2/(6-31+G(*d',p'*)) - energy and CBS extrapolation (with the G09c, default number of minimum 5 pair natural orbitals for this specific basis set used)
d) HF/CBSB1 with tight convergence of SCF energy

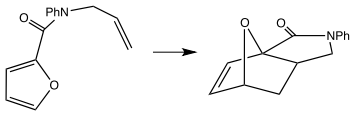
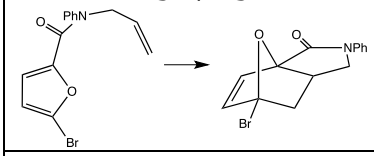
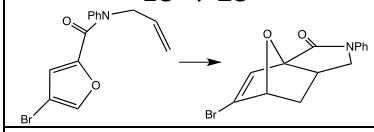
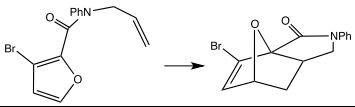
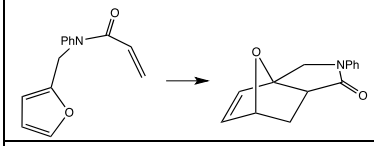
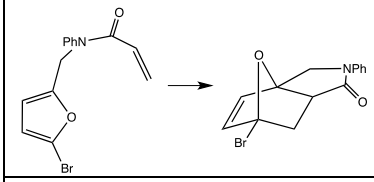
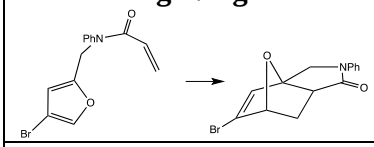
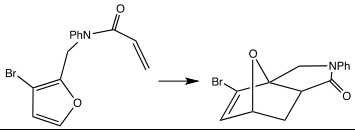
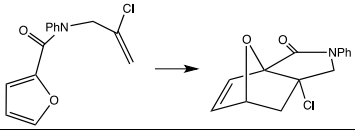
CBS methods are found to be very accurate for thermochemical studies with the mean absolute deviation of around 1.1 kcal/mol for the CBS-QB3 model and around 3.26 kcal/mol for CBS-4M method comparing to experimental data on G2/97 test set.[13, 14, 15] The accuracy of CBS-4M model is compromised here due to the use of HF with very small basis set 3-21G(*d*) for geometries. The CBS-QB3 model when used on larger systems can be computationally very expensive and unpractical. If this is the case CBS-4M model can be used as an alternative, which is much less expensive, thus can be used on larger systems with reasonable accuracy.

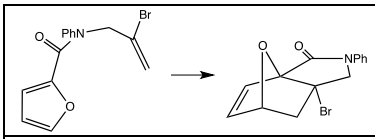
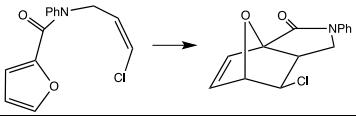
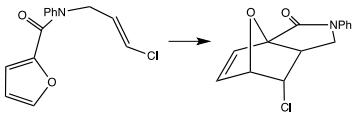
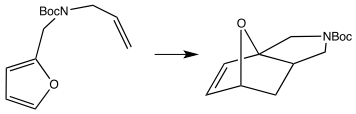
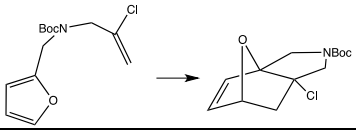
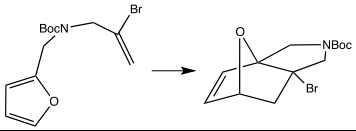
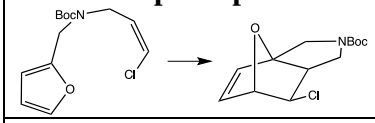
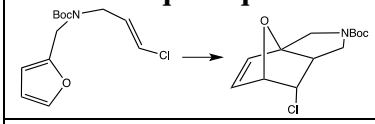
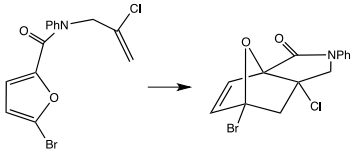
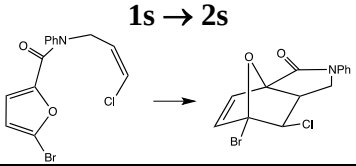
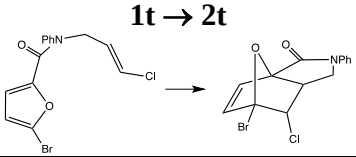
There have been other so-called "black box" methods, which offer very accurate results for thermochemical data. One popular and often used for benchmark data of small and medium sized molecules is W1 theory. It belongs to the hierarchy of W*n* computational protocols of Martin and co-workers in which cost and accuracy increases in a sequence (*n*={1-4.4}).[16-19] W1 theory returns a 0.44 kcal/mol mean absolute deviation for 220 total atomisation energies, electron affinities, ionisation potentials and proton affinities of the G2/97 test set. Due to the high cost of these methods such studies on all the reactions presented here could not be performed. The W1 model with unrestricted Brueckner doubles (W1BD) was chosen to obtain thermochemical data of the simplest Diels-Alder reaction between furan and ethylene as a benchmark for the other CBS models used. These results together with data obtained from CBS models discussed before, and DFT-B3LYP, have been compared in *Table S2*. The difference between free energies of the reaction obtained for W1BD and CBS-QB3 models is only 0.9 kcal/mol and around 3 kcal/mol for activation energies. The computational time of W1BD method for this reaction is around 3000 times higher than CBS-QB3 model, around 6000 times higher than CBS-4M model and around 8000 higher than DFT-B3LYP method. Thus the CBS-QB3 model provides an excellent balance between computational cost and accuracy for the series of reactions studied.

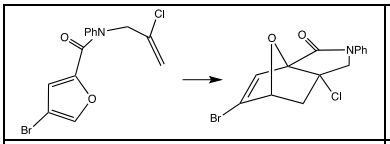
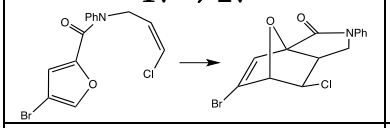
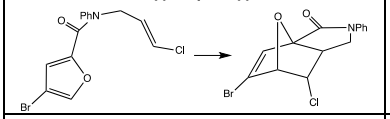
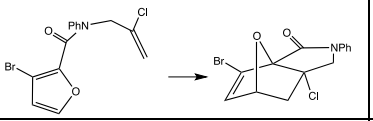
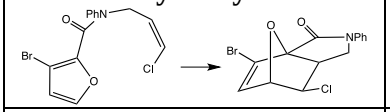
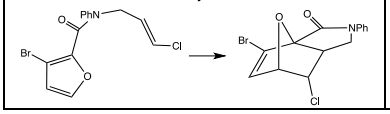
Table S2. Thermochemical data of furan plus ethylene Diels-Alder reaction comparing various theoretical methodologies (T=298.15 K).

Thermochemical data (in kcal/mole)	DFT-B3LYP 6-31G(*d*)	CBS-4M	CBS-QB3	W1BD
$\Delta_r H°$	-5.25	-13.9	-12.2	-11.3
$\Delta_r G°$	8.6	-0.3	1.6	2.5
$\Delta_{activ} H$	25.85	17.9	20.5	24.1
$\Delta_{activ} G$	38.8	30.85	33.35	36.9

Table S3. CBS-QB3 calculated thermochemical data of a-z Diels-Alder reactions for 298.15K.

Reaction	$\Delta_r H°$ (kcal/mole)	$\Delta_r G°$ (kcal/mole)	$\Delta_{activ} H$ (kcal/mole)	$\Delta_{activ} G$ (kcal/mole)
1a → 2a 	-11.0	-6.2	18.9	23.0
1b → 2b 	-14.3	-10.3	18.1	21.4
1c → 2c 	-13.6	-9.8	17.6	20.8
1d → 2d 	-13.7	-9.35	16.6	20.2
1e → 2e 	-16.8	-11.5	15.9	20.4
1f→ 2f 	-20.35	-15.8	15.2	18.8
1g → 2g 	-19.4	-15.0	14.7	18.1
1h → 2h 	-18.45	-14.1	15.0	18.4
1i → 2i 	-9.3	-5.2	20.7	24.1
1j → 2j	-9.6	-5.5	20.6	24.0

				
1k → 2k 	-11.3	-7.1	19.6	22.9
1l → 2l 	-11.8	-6.8	18.3	22.6
1m → 2m 	-7.9	-3.9	20.1	23.5
1n → 2n 	-7.9	-3.65	20.6	24.15
1o → 2o 	-8.3	-4.3	20.4	24.1
1p → 2p 	-6.9	-1.6	21.7	26.2
1q → 2q 	-8.1	-3.9	20.2	23.7
1r → 2r 	-13.3	-9.0	19.0	22.4
1s → 2s 	-13.5	-9.2	18.55	21.9
1t → 2t 	-14.6	-10.4	17.2	17.0
1u → 2u	-12.7	-8.5	18.9	22.4

				
1v → 2v 	-14.1	-9.8	18.0	21.4
1w → 2w 	-13.5	-9.2	17.8	21.5
1x → 2x 	-12.3	-7.6	18.9	22.8
1y → 2y 	-15.0	-11.2	15.85	18.8
1z → 2z 	-14.3	-9.8	16.4	20.3

(ii) Dipolar Interactions At Transition Structures

The dipolar orientational interaction term between the C-O and the dienophile C-X dipoles was calculated from the given formula (using the TS geometry):

$$f_1(\theta_A,\theta_B,\omega) = \sin\theta_A \sin\theta_B \cos\omega - 2\cos\theta_A \cos\theta_B$$

where:

θ_A – angle between O-C-C

θ_B – angle between C-C-X

ω – dihedral angle O-C-C-X

The values for reactions i-q are given in *Table S4* below.

Table S4. Data on dipolar orientational interaction term for reactions i-q.

Reaction	θ_A O-C-C	θ_B C-C-Cl	ω Cl-C-C-O	Dipolar orientational term
1i – 2i	90.09	106.53	160.14	-0.906
1j – 2j *	90.46	107.36	160.8	-0.902
1k – 2k	87.37	99.68	86.95	0.068
1l – 2l	87.11	109.51	-158.94	-0.845
1p – 2p	90.005	100.55	85.08	0.084
1q – 2q	89.675	108.59	-161.28	-0.894

*Br atom rather than Cl

Table S5. Selected data from calculated transition state and product structures

	Transition state		Product						
Reaction	**C-C distance *a***	**C-C distance *b***	**C-C Bond length *a***	**C-C Bond length *b***	**Δl(a)**	**Δl(b)**	**Δl(a)/% from TS**	**Δl(b)/% from TS**	**Av%age change from TS**
1a → 2a	2.029	2.178	1.558	1.571	0.471	0.607	-23.21	-27.89	-25.55
1b → 2b	2.044	2.199	1.558	1.565	0.486	0.634	-23.77	-28.82	-26.30
1c → 2c	2.053	2.179	1.556	1.568	0.497	0.611	-24.22	-28.04	-26.13
1d → 2d	2.004	2.227	1.555	1.570	0.449	0.657	-22.39	-29.51	-25.95
1e → 2e	2.035	2.223	1.556	1.569	0.480	0.654	-23.57	-29.42	-26.50
1f → 2f	2.056	2.241	1.556	1.563	0.500	0.678	-24.33	-30.26	-27.30
1g → 2g	2.061	2.221	1.553	1.566	0.507	0.655	-24.62	-29.50	-27.06
1h → 2h	2.022	2.259	1.553	1.567	0.469	0.691	-23.21	-30.61	-26.91
1i → 2i	2.064	2.153	1.563	1.570	0.501	0.583	-24.27	-27.08	-25.67
1j → 2j	2.067	2.152	1.562	1.570	0.505	0.582	-24.43	-27.04	-25.74
1k → 2k	1.995	2.225	1.557	1.569	0.438	0.656	-21.96	-29.50	-25.73
1l → 2l	1.987	2.231	1.555	1.570	0.431	0.661	-21.71	-29.65	-25.68
1m → 2m	2.095	2.111	1.576	1.572	0.519	0.540	-24.77	-25.56	-25.17
1n → 2n	2.137	2.076	1.581	1.570	0.556	0.506	-26.03	-24.35	-25.19
1o → 2o	2.139	2.077	1.579	1.571	0.560	0.507	-26.18	-24.39	-25.29
1p → 2p	2.061	2.137	1.574	1.570	0.487	0.567	-23.63	-26.52	-25.08
1q → 2q	2.067	2.146	1.574	1.570	0.493	0.576	-23.84	-26.84	-25.34
1r → 2r	2.079	2.165	1.563	1.565	0.515	0.600	-24.80	-27.72	-26.26
1s → 2s	1.950	2.332	1.553	1.583	0.397	0.749	-20.37	-32.13	-26.25
1t → 2t	2.031	2.235	1.554	1.572	0.476	0.663	-23.44	-29.67	-26.56
1u → 2u	2.095	2.146	1.562	1.566	0.533	0.580	-25.43	-27.03	-26.23
1v → 2v	2.016	2.222	1.554	1.567	0.461	0.654	-22.89	-29.45	-26.17
1w → 2w	1.986	2.253	1.552	1.570	0.434	0.683	-21.87	-30.30	-26.08
1x → 2x	2.086	2.150	1.565	1.566	0.521	0.585	-24.97	-27.19	-26.08
1y → 2y	1.962	2.278	1.554	1.569	0.409	0.709	-20.83	-31.12	-25.97
1z → 2z	1.968	2.275	1.553	1.570	0.416	0.704	-21.11	-30.97	-26.04

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