Electronic Supplementary Material (ESI) for ChemComm.

SUPPORTING INFORMATION

Electrochemical oxidative *Z*-Selective C(sp^2)-H chlorination of acrylamides

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Contents

1. General Information

Unless otherwise stated, all non-electrochemical reactions were conducted in flame-dried glassware under an atmosphere of dry nitrogen or argon, sealed with septum seals and were stirred with Teflon coated magnetic stirrer bars. Unless stated otherwise, all electrochemical reactions were performed using oven-dried 10 mL ElectraSyn vials under an atmosphere of dry nitrogen, sealed with an ElectraSyn Teflon cap fitted with a graphite anode and platinum cathode and were stirred with Teflon-coated magnetic stirrer bars. Dry tetrahydrofuran (THF), diethyl ether (Et_2O) and acetonitrile (MeCN) were obtained after passing these previously degassed solvents through activated alumina columns (Mbraun, SPS-800). Tetra-n-butylammonium hexafluorophosphate ($TBAPF_6$) and tetra-n-butylammonium tetrafluoroborate ($TBABF_4$) were recrystallised from ethanol or water, respectively, and dried in the oven before use. All other solvents and commercial reagents were used as supplied without further purification unless stated otherwise.

All electrochemical reactions were conducted using an ElectraSyn 2.0 apparatus, purchased from IKA. Graphite, reticulated vitreous carbon (RVC), glassy carbon (GC) and Pt electrodes were purchased from IKA and are of uniform dimensions. Graphite electrodes were used as supplied from IKA or were cut from a sheet of carbon foil (2 mm thickness) purchased from Goodfellow. The electrodes were cut to the dimension of 8 mm × 52 mm using a Startrite Bandsaw (model 18-T-5) with a Starrett, Durate SFB high carbon steel blade (2870 mm x 10 mm x 0.65 mm, 3 mm pitch, regular tooth). Graphite electrodes could be used several times by renewing the top surface of the graphite. This was achieved by scraping away the top layer with a razor blade, sonicating in MeCN for 5 minutes, followed by oven-drying for 30 mins.

Cyclic voltammetry (CV) experiments were conducted using an Autolab PGSTAT204, controlled using Nova 2.1 software. The working electrode was a GC disc (3 mm dia., BASi part number MF-2012), the counter electrode was a Pt-wire (BASi part number MW-4130) and a Ag/AgCl reference electrode was used (BASi part number – MF-2052).

Room temperature (rt) refers to 20-25 °C. Ice/water and CO_2(s)/acetone baths were used to obtain temperatures of 0 °C and -78 °C respectively. All reactions involving heating were conducted using DrySyn blocks and a contact thermometer. In vacuo refers to reduced pressure through the use of a rotary evaporator.

Analytical thin layer chromatography was carried out using aluminium plates coated with silica (Kieselgel 60 F254 silica) and visualisation was achieved using ultraviolet light (254 nm), followed by

staining with a 1% aqueous $KMnO_4$ solution, or a 10% w/v solution of phosphomolybdic acid in ethanol. Flash column chromatography was performed using Kieselgel 60 silica in the solvent system stated using head-pressure by means of a compressed air line. Melting points were recorded on an a Gallenkamp melting point apparatus and are reported corrected by linear calibration to benzophenone (47 - 49 °C) and benzoic acid (121 - 123 °C).

Infrared spectra were recorded on a Shimadzu IRAffinity-1 Fourier Transform ATR spectrometer as thin films using a Pike MIRacle ATR accessory. The most intense peaks and structurally important peaks are quoted. Absorption maxima (vmax) are recorded in wavenumbers (cm^{-1}).

^{1}H, ^{13}C and ^{19}F NMR spectra were obtained on a Bruker Avance 300 (300 MHz 1H, 75 MHz 13C), Bruker Avance 400 (400 MHz ^{1}H, 101 MHz ^{13}C, 376 MHz ^{19}F) or a Bruker Avance 500 (500 MHz ^{1}H, 126 MHz ^{13}C, 471 MHz ^{19}F) spectrometer at rt in the solvent stated. Chemical shifts are reported in parts per million (ppm) relative to the residual solvent signal. All coupling constants, J, are quoted in Hz. Multiplicites are reported with the following symbols: br = broad, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet and combinations of these were used to denote higher order multiplicities.

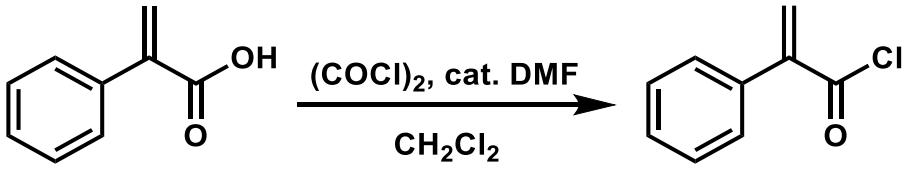
High resolution mass spectrometry (HRMS, m/z) data was acquired at Cardiff University on a Micromass LCT Spectrometer.

“Petrol” and ‘’hexanes’’ refers to the fraction boiling in the range of 40-60 °C unless otherwise stated

2. Experimental and Characterisation Data of Substrates

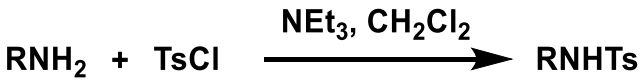
2.1 General Procedures

2.1.1 General Procedure A: Synthesis of 2-phenacryloyl chloride



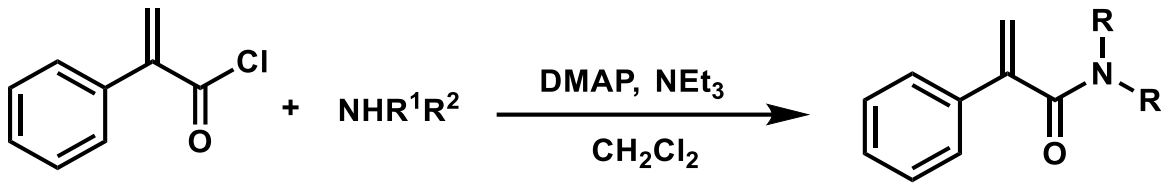
To a 250 mL round bottom flask was added phenacrylic acid (5.48 g, 37.0 mmol, 1 equiv.), DMF (5 drops) and CH_2Cl_2 (60 mL). The solution was cooled to 0 °C using an ice/water bath before oxalyl chloride (4.80 mL, 55.5 mmol, 1.5 equiv.) was added dropwise over 25 minutes. The mixture was allowed to warm slowly to room temperature with concurrent gas evolution. After 2.5 h stirring at rt the mixture was heated to 35 °C for 30 mins until gas evolution had ceased. The mixture was cooled to room temperature and then concentrated *in vacuo* affording crude product as a yellow oil. The crude material was used directly in the subsequent steps.

2.1.2 General Procedure B: Synthesis of *N*-alkyl-*N*-tosylamines:



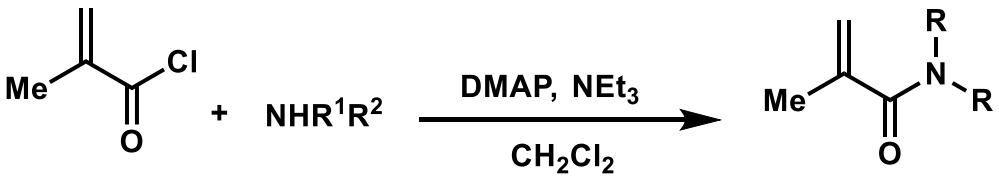
To a 250 mL round bottom was added tosyl chloride (1 equiv.), triethylamine (2 equiv.) and CH_2Cl_2 (3.75 mL/mmol). After the solution was cooled using an ice bath, amine (1 equiv.) was added rapid dropwise over 5 minutes. The mixture was warmed naturally up to room temperature and stirred for 2 h. The reaction mixture was sampled for TLC to confirm full consumption of tosyl chloride. The reaction was then quenched into water (3.75 mL/mmol) and layers separated. The organic layer was dried over $MgSO_4$ and concentrated *in vacuo* forming crude product. Where the crude product was an oil, the crude material was redissolved in a minimum amount of CH_2Cl_2 precipitated from hexanes to form a crystalline solid. The solid was used crude in subsequent steps without any further purification.

2.1.3 General Procedure C: Synthesis of 2-phenylacrylamides



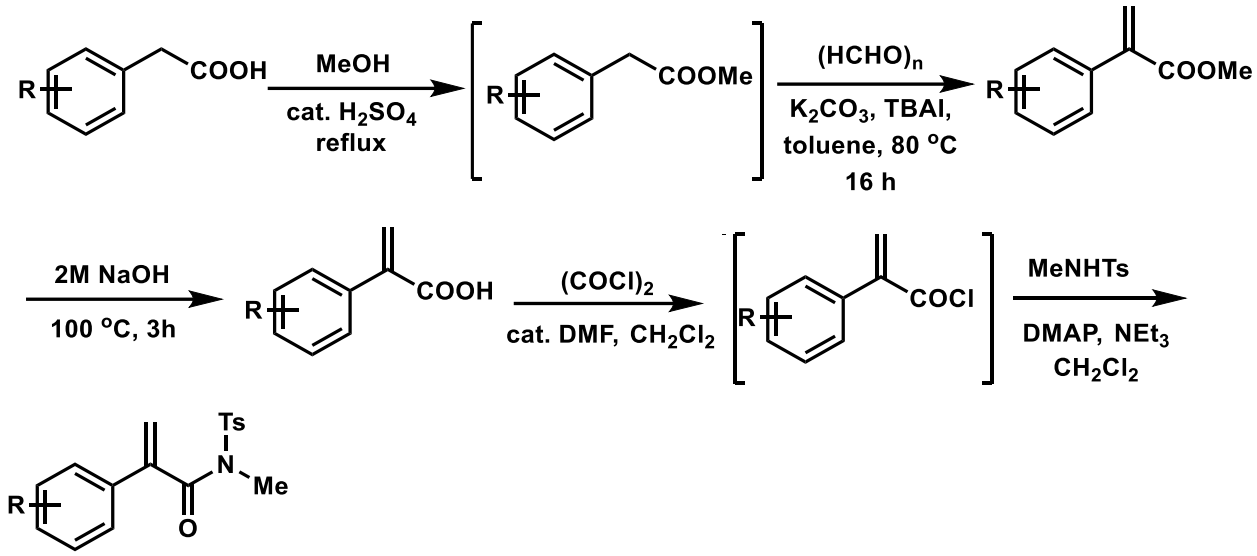
To a 250 mL round bottom was added amine (1 equiv.), 4-dimethylaminopyridine (10 mol %), triethylamine (2 equiv.) and CH_2Cl_2 (8 mL/mmol). The solution was stirred then cooled to 0 °C using an ice bath. 2-phenacryloyl chloride (2 equiv.) was added dropwise by syringe over 15 minutes turning the solution bright yellow. The mixture was stirred at 0 °C for 30 mins before being allowed to warm to room temperature and stir overnight. The mixture was quenched with saturated sodium bicarbonate solution (50 mL), layers separated, and organics washed with saturated sodium bicarbonate solution (2 x 50 mL). The aqueous was extracted CH_2Cl_2 (2 x 50 mL) and organics combined. The organics were washed with water (50 mL), dried over $MgSO_4$, filtered, and concentrated *in vacuo* to crude product. Purification by flash column chromatography was then undertaken to give pure product.

2.1.4 General Procedure D: Synthesis of methacrylamides



To a 250 mL round bottom was added amine (1 equiv.), 4-dimethylaminopyridine (10 mol %), triethylamine (2 equiv.) and CH_2Cl_2 (8 mL/mmol). The solution was stirred then cooled to 0 °C using an ice bath. Methacryloyl chloride (2 equiv.) was added dropwise by syringe over 15 minutes turning the solution bright yellow. The mixture was stirred at 0 °C for 30 mins before being allowed to warm to room temperature and stir overnight. The mixture was quenched with saturated sodium bicarbonate solution (50 mL), layers separated, and organics washed with saturated sodium bicarbonate solution (2 x 50 mL). The aqueous was extracted CH_2Cl_2 (2 x 50 mL) and organics combined. The organics were washed with water (50 mL), dried over $MgSO_4$, filtered and concentrated *in vacuo* to crude product. Purification by flash column chromatography was then undertaken to give pure product.

2.1.5 General Procedure E: Synthesis of Functionalised 2-arylacrylamides



Following a modified literature procedure:[1]

Step 1:

To a solution of 2-aryl acetic acid (20 mmol) in MeOH (25 mL) was added 5 drops of concentrated H_2SO_4. The solution was then heated at reflux for 16 h. Upon completion of the mixture was concentrated *in vacuo*. The residue was diluted with EtOAc (50 mL) and then neutralized with saturated sodium bicarbonate solution (50 mL). The organic phase was dried over $MgSO_4$, filtered, and concentrated under reduced pressure to afford the corresponding methyl ester, which was used for the next step without further purification.

Step 2:

Methyl ester (20 mmol), paraformaldehyde (40 mmol, 2 equiv.), TBAI (4 mmol, 0.2 equiv.) and K_2CO_3 (40 mmol, 2 equiv.) in toluene (30 mL) was heated to 80 °C overnight as a viscous suspension. Upon cooling the mixture was diluted with EtOAc (120 mL) and quenched with water (120 mL). The layers were separated and the aqueous re-extracted with EtOAc (120 mL). The organics were combined and dried over $MgSO_4$ and concentrated yielding crude methyl acrylate. The residue was purified by flash column chromatography unless stated otherwise (eluent = 3 to 10% EtOAc in hexanes, silica gel) to yield pure methyl acrylate products.

Step 3:

To a 50 mL round bottom flask was added prepared methyl acrylates and a 2M NaOH solution (3 mL/ mmol). The mixture was heated at reflux for 2 h before being cooled to room temperature. The

aqueous was extracted with Et_2O (3 mL/ mmol) then acidified to pH 1 using 2M HCl. The acidified aqueous suspension was then extracted with CH_2Cl_2 (3 x 30 mL), organics combined and dried over $MgSO_4$, filtered and concentrated to afford crude acrylic acids.

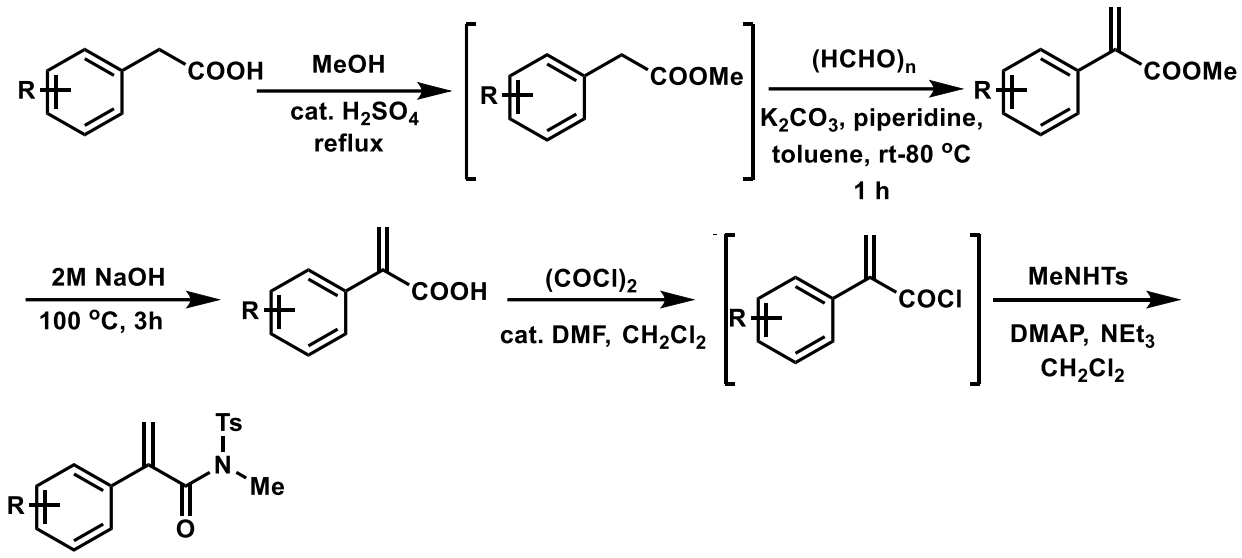
Step 4, part A:

A solution of the 2-acrylacrylic acid derivatives (1.1 equiv.) in CH_2Cl_2 (3 mL/ mmol) and DMF (3 drops) was prepared. Oxalyl chloride (1.5 equiv.) was added dropwise at room temperature and the mixture was allowed to stir for 3 h until no gas evolution was observed. The solution was concentrated *in vacuo* and redissolved in CH_2Cl_2 (1 mL/mmol).

Step 4, part B:

A solution of N-methyl-N-tosylamine (0.9 equiv.), DMAP (10 mol %) and triethylamine (2 equiv.) in CH_2Cl_2 (8 mL/mmol) was prepared and cooled to 0 ^oC using an salt/ice bath. The crude acyl chloride solution prepared in **Step 4, part A** was added dropwise and the mixture was stirred at 0 ^oC for 15 mins before being allowed to warm to room temperature and stir overnight. The reaction mixture was quenched with a saturated sodium bicarbonate solution (8 mL/mmol), layers separated and aqueous phase extracted with CH_2Cl_2 (2 x 40 mL). The organics were combined and dried over $MgSO_4$, filtered and concentrated *in vacuo* yielding crude product. The crude residue was purified by flash column chromatography (silica gel) to yield pure product.

2.1.6 General Procedure F: Modified Synthesis of Functionalised 2-arylacrylamides



Following a modified literature procedure:[1]

Step 1:

To a solution of 2-aryl acetic acid (20 mmol) in MeOH (25 mL) was added 5 drops of concentrated H_2SO_4. The solution was then heated at reflux for 16 h. Upon completion of the mixture was concentrated *in vacuo*. The residue was diluted with EtOAc (50 mL) and then neutralized with saturated sodium bicarbonate solution (50 mL). The organic phase was dried over $MgSO_4$, filtered, and concentrated under reduced pressure to afford the corresponding methyl ester, which was used for the next step without further purification.

Step 2:

To a 100 mL round bottom flask was added crude phenylacetic acid methyl ester (20 mmol), piperidine (0.6 mL, 6 mmol, 0.3 equiv.), paraformaldehyde (1.80 g, 60 mmol, 3 equiv.), potassium carbonate (5.50 g, 40 mmol, 2 equiv.) and DMF (60 mL). The mixture was stirred at room temperature for 10 minutes before heating to 70 °C for 15 minutes. Completion was judged by TLC and the reaction mixture was cooled to room temperature then poured onto a mixture of water (100 mL) and EtOAc (50 mL). The mixture was stirred for 5 minutes, organics separated and washed with water (5 x 100 mL), dried over $MgSO_4$ and concentrated *in vacuo* to yield crude product as an oil. The crude residue was purified by column chromatography.

Step 3:

To a 50 mL round bottom flask was added prepared methyl acrylates and a 2M NaOH solution (3 mL/ mmol). The mixture was heated at reflux for 2 h before being cooled to room temperature. The aqueous was extracted with Et_2O (3 mL/ mmol) then acidified to pH 1 using 2M HCl. The acidified aqueous suspension was then extracted with CH_2Cl_2 (3 x 30 mL), organics combined and dried over $MgSO_4$, filtered and concentrated *in vacuo* to afford crude acrylic acids.

Step 4, part A:

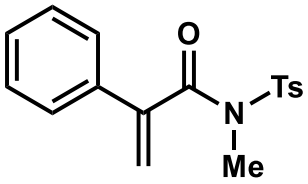
A solution of the 2-acrylacrylic acid derivatives (1.1 equiv.) in CH_2Cl_2 (3 mL/ mmol) and DMF (3 drops) was prepared. Oxalyl chloride (1.5 equiv.) was added dropwise at room temperature and the mixture was allowed to stir for 3 h until no gas evolution was observed. The solution was concentrated *in vacuo* and redissolved in CH_2Cl_2 (1 mL/mmol).

Step 4, part B:

A solution of N-methyl-N-tosylamine (0.9 equiv.), DMAP (10 mol %) and triethylamine (2 equiv.) in CH_2Cl_2 (8 mL/mmol) was prepared and cooled to 0 ^oC using an salt/ice bath. The crude acyl chloride solution prepared in **Step 4, part A** was added dropwise and the mixture was stirred at 0 ^oC for 15 mins before being allowed to warm to room temperature and stir overnight. The reaction mixture was quenched with a saturated sodium bicarbonate solution (8 mL/mmol), layers separated and aqueous phase extracted with CH_2Cl_2 (2 x 40 mL). The organics were combined and dried over $MgSO_4$, filtered and concentrated *in vacuo* yielding crude product. The crude residue was purified by flash column chromatography (silica gel) to yield pure product.

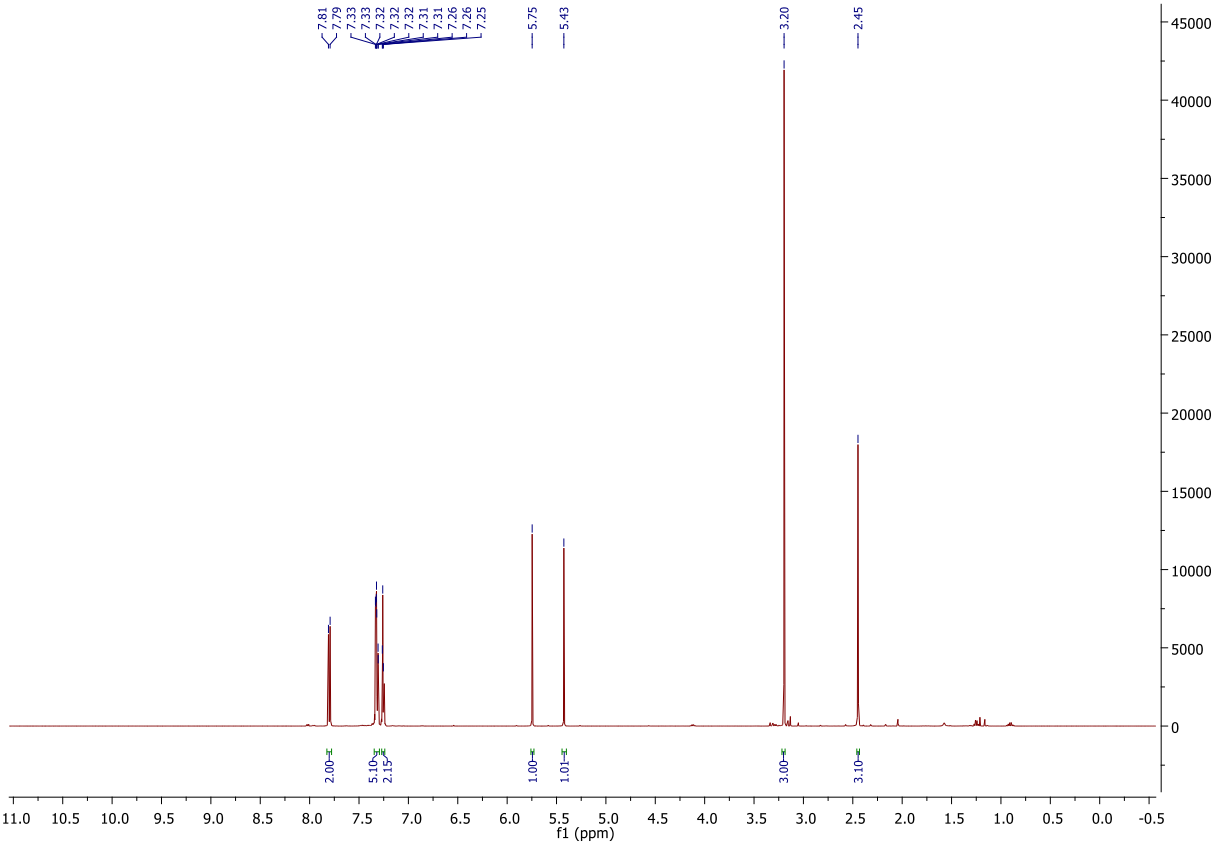
2.2 Characterisation of Substrates

(1)



Prepared according to General Procedure C using N-methyl-p-toluenesulfonamide (1.85 g, 10.0 mmol), 4-dimethylaminopyridine (112 mg, 1.00 mmol), triethylamine (3.0 mL, 20.0 mmol), CH_2Cl_2 (80 mL) and phenacryloyl chloride (3.33 g, 20.0 mmol). The crude residue was purified by flash column chromatography (eluent = 10 to 20% EtOAc in hexanes, silica gel) to afford product **(1)** as a yellow solid (1.94 g, 62% yield).

Mp: 101-103 °C; $\mathbf{R_f}$ = 0.33 (eluent = 20% EtOAc in hexanes); $\boldsymbol{\nu_{max}}$ **/ cm^{-1}**(thin film) 3250, 1695, 1425, 1342, 1167, 1142, 1082, 1069, 926, 860, 812, 777, 748, 702, 656, 576, 549, 530, 513, 488, 478, 468, 422, 401; **^{1}H NMR (500 MHz, $CDCl_3$)** δ_H: 2.45 (3H, s), 3.20 (3H, s), 5.43 (1H, s), 5.75 (1H, s), 7.24-7.27 (2H, m), 7.29-7.35 (5H, m), 7.78-7.82 (2H, m); **^{13}C NMR (126 MHz, $CDCl_3$)** δ_C: 21.7, 34.2, 117.5, 125.9, 128.4, 128.9, 128.9, 129.5, 134.7, 135.6, 144.8, 145.0, 170.2; **HRMS (ES$^+$)** [$C_{17}H_{17}NO_3S$] requires $[M+H]^+$ 316.1007, found 316.1008 (+ 0.30 ppm).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7.33
7.32
7.32
7.32
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7.26
7.26
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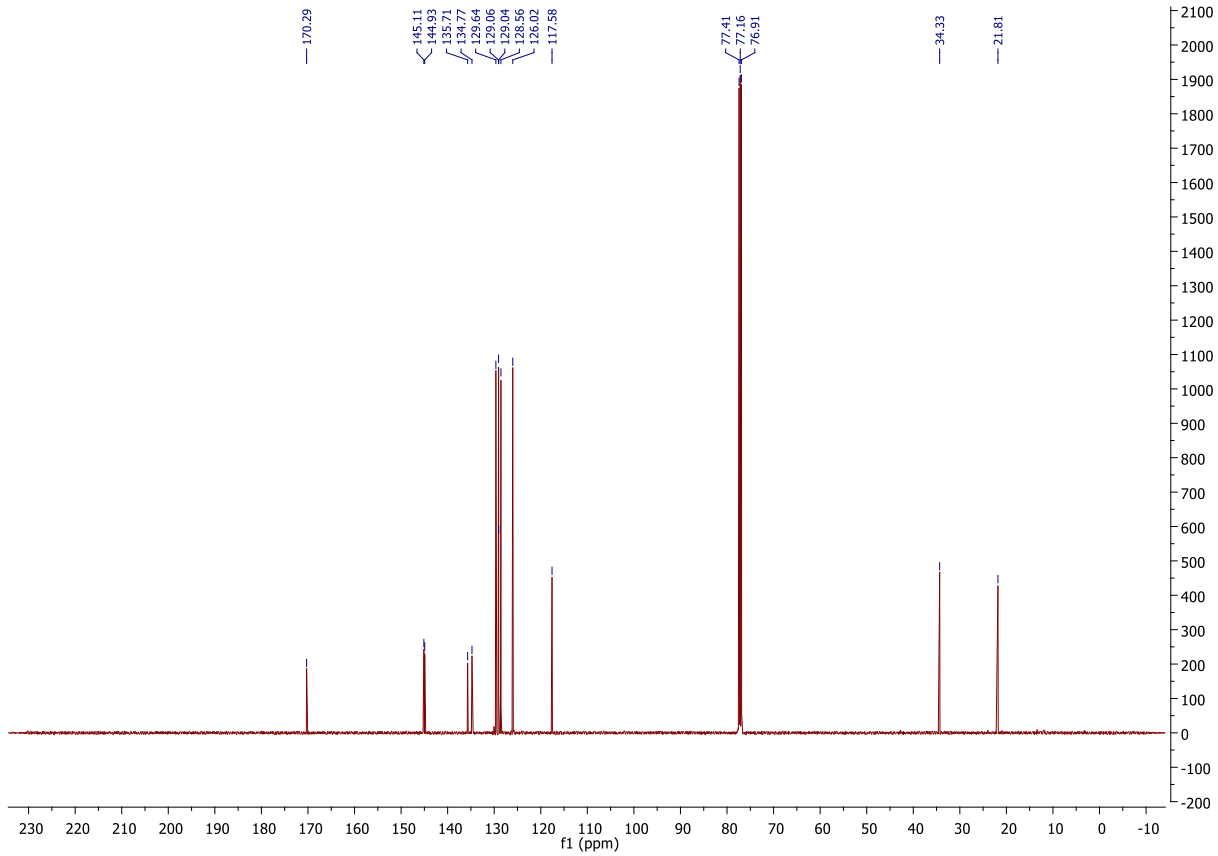
1.01
3.00
3.10
f1 (ppm)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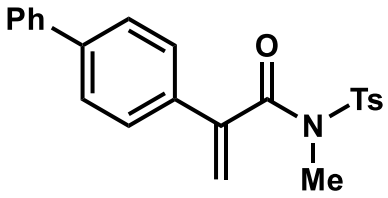
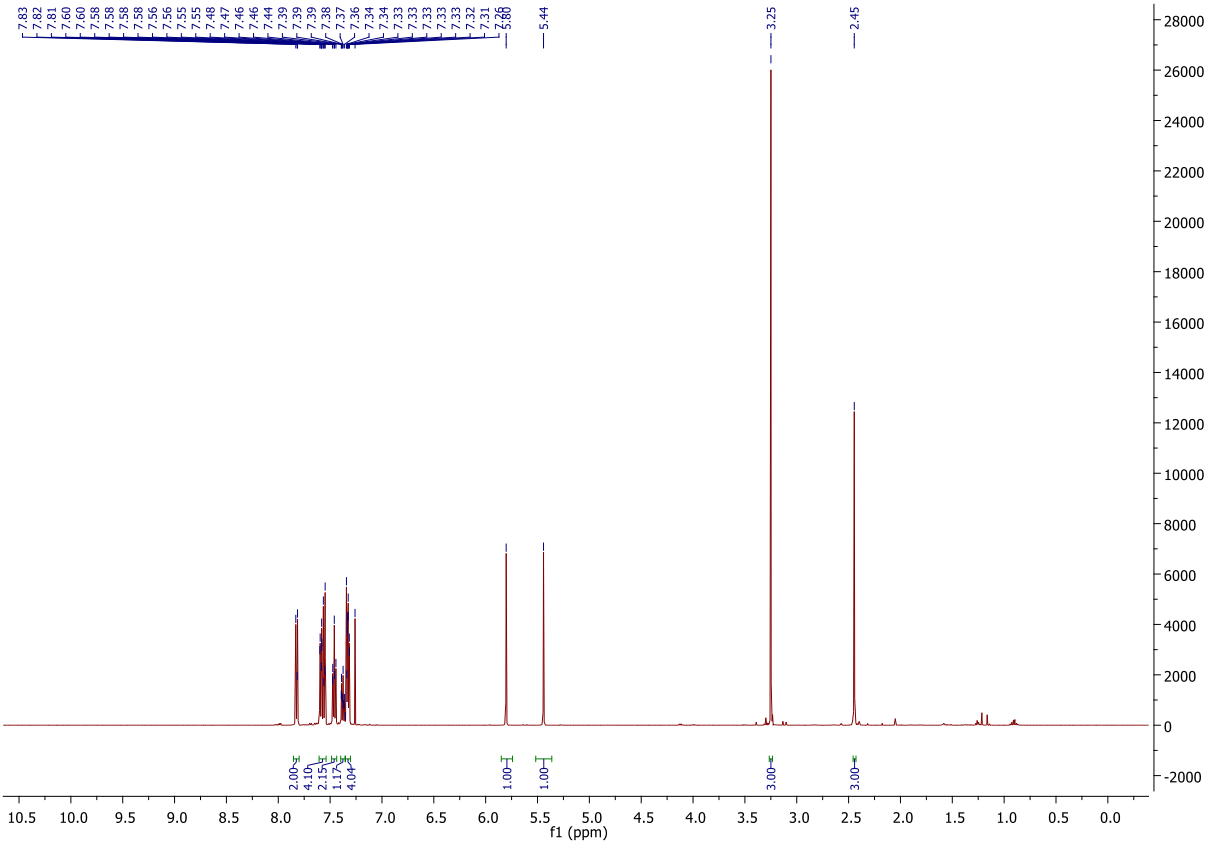
21.81
f1 (ppm)

(S3)



Prepared according to General procedure E using 4-biphenylacetic acid (4.25 g, 20.0 mmol). Step 4B was carried out using N-methyl-p-toluenesulfonamide (930 mg, 5.00 mmol), dimethylaminopyridine (61.0 mg, 0.50 mmol), triethylamine (1.50 mL, 10.0 mmol), CH_2Cl_2 (40 mL) and acyl chloride (5.50 mmol). The crude residue was purified by flash column chromatography (eluent = 15 to 25% EtOAc in hexanes, silica gel) to afford product **(S3)** as a white solid (1.40, 72% yield), (Step 1- 4B overall yield = 18%).

Mp.: 143-145 °C; $\mathbf{R_f}$ = 0.29 (eluent = 25% EtOAc in hexanes); $\mathbf{\nu_{max}}$ **/ cm^{-1}** (thin film) 1694, 1595, 1485, 1402, 1341, 1244, 1165, 1055, 855; **^{1}H NMR (500 MHz, $CDCl_3$)** δ_H: 2.45 (3H, s), 3.25 (3H, s), 5.44 (1H, s), 5.80 (1H, s), 7.31-7.34 (4H, m), 7.36-7.41 (1H, m), 7.43-7.49 (2H, m), 7.53-7.62 (4H, m) 7.79-7.85 (2H, m); **^{13}C NMR (126 MHz, $CDCl_3$)** δ_C: 21.9, 34.4, 117.4, 126.4, 127.1, 127.7, 127.8, 128.5, 129.0, 129.7, 133.6, 135.6, 140.3, 141.8, 144.4, 145.2, 170.3; **HRMS (ES$^+$)** [$C_{23}H_{21}NO_3S$] requires $[M+H]^+$ 392.1320, found 392.1320 (+ 0.0 ppm).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7.38
7.37
7.36
7.34
7.34
7.33
7.33
7.33
7.33
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7.26
5.80
5.44
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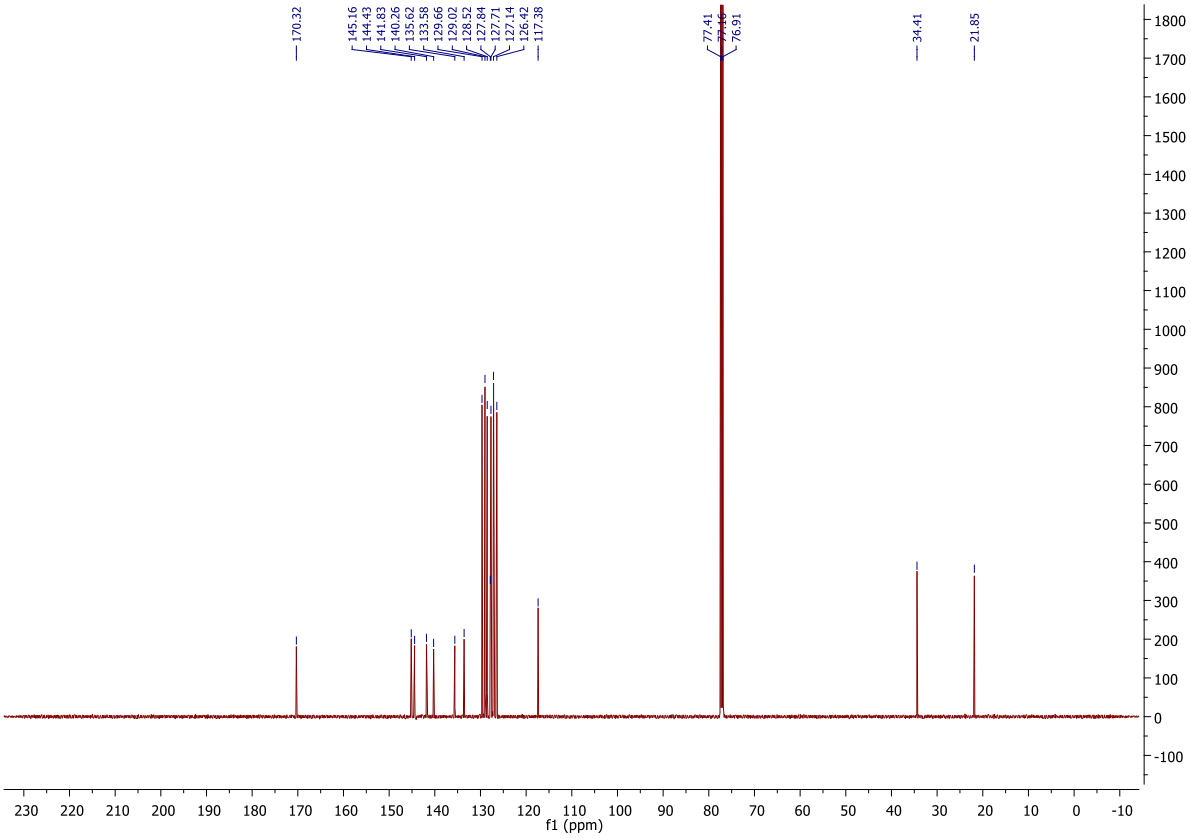
1.00
3.00
3.00
f1 (ppm)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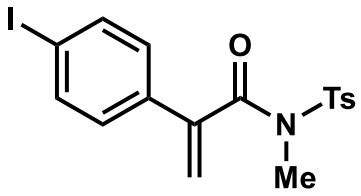
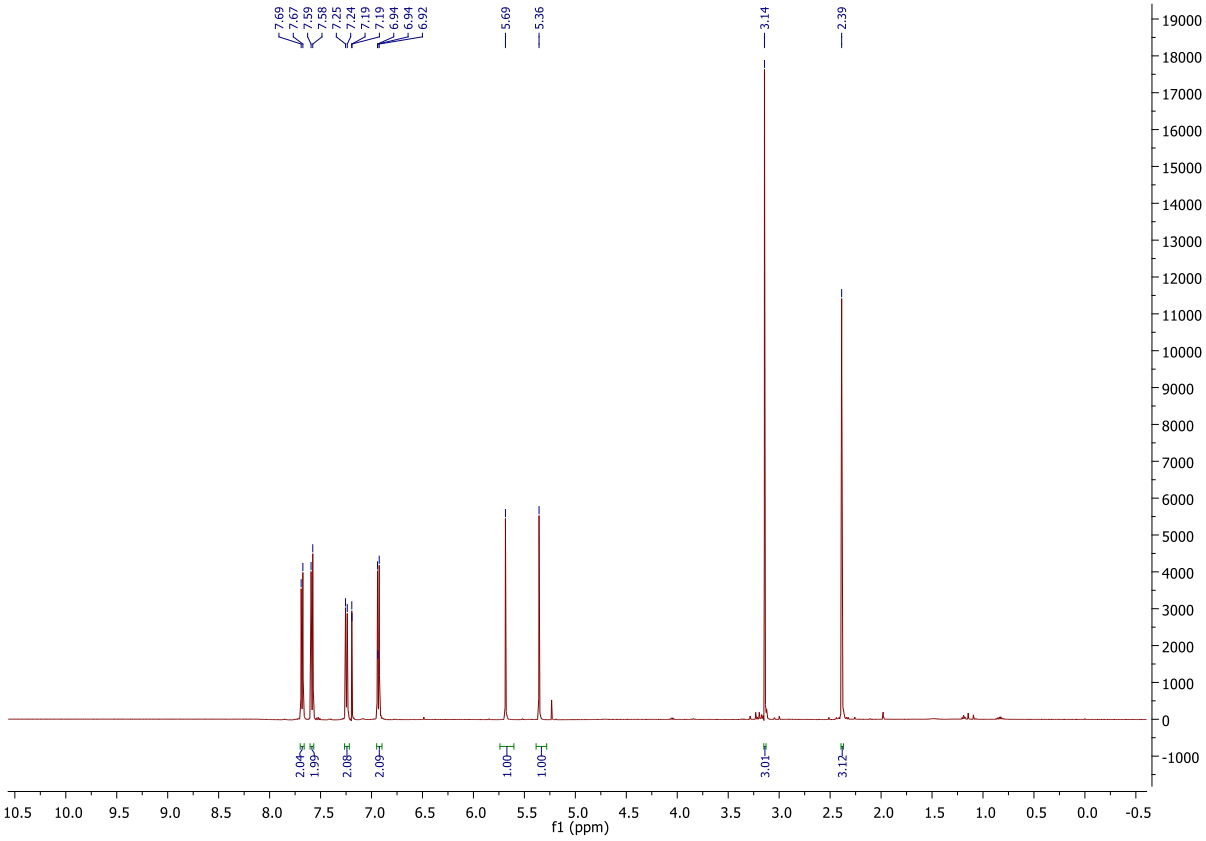
21.85
f1 (ppm)

(S4)



Prepared according to General procedure E using 4-iodophenylacetic acid (5.24 g, 20.0 mmol). Step 4B was carried out using N-methyl-p-toluenesulfonamide (260 mg, 1.36 mmol), dimethylaminopyridine (17.0 mg, 0.14 mmol), triethylamine (0.38 mL, 2.72 mmol), CH_2Cl_2 (11 mL) and acyl chloride (1.50 mmol). The crude residue was purified by flash column chromatography (eluent = 15 to 25% EtOAc in hexanes, silica gel) to afford product **(S4)** as a white solid (400 mg, 66% yield), (Step 1- 4B overall yield = 5%).

Mp.: 130-133 °C; $\mathbf{R_f}$ = 0.22 (eluent = 20% EtOAc in hexanes); $\boldsymbol{\nu_{max}}$ **/ cm^{-1}** (thin film) 2949, 1717, 1613, 1583, 1485, 1435, 1388, 1317, 1199, 1174, 1087, 1004; **^{1}H NMR (500 MHz, $CDCl_3$)** δ_H: 2.45 (3H, s), 3.21 (3H, s), 5.42 (1H, s), 5.75 (1H, s), 7.00 (2H, d, *J* 8.3 Hz), 7.31 (2H, d, *J* 8.4 Hz), 7.65 (2H, d, *J* 8.3 Hz), 7.75 (2H, d, *J* 8.4 Hz); **^{13}C NMR (126 MHz, $CDCl_3$)** δ_C: 21.9, 34.2, 95.0, 118.1, 127.8, 128.4, 129.7, 134.4, 135.5, 138.1, 140.0, 145.3, 169.8; **HRMS (ES$^+$)** [$C_{17}H_{16}NO_3SI$] requires $[M+H]^+$ 441.9974 found 441.9982 (+ 1.8 ppm).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7.24
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7.19
6.94
6.94
6.92
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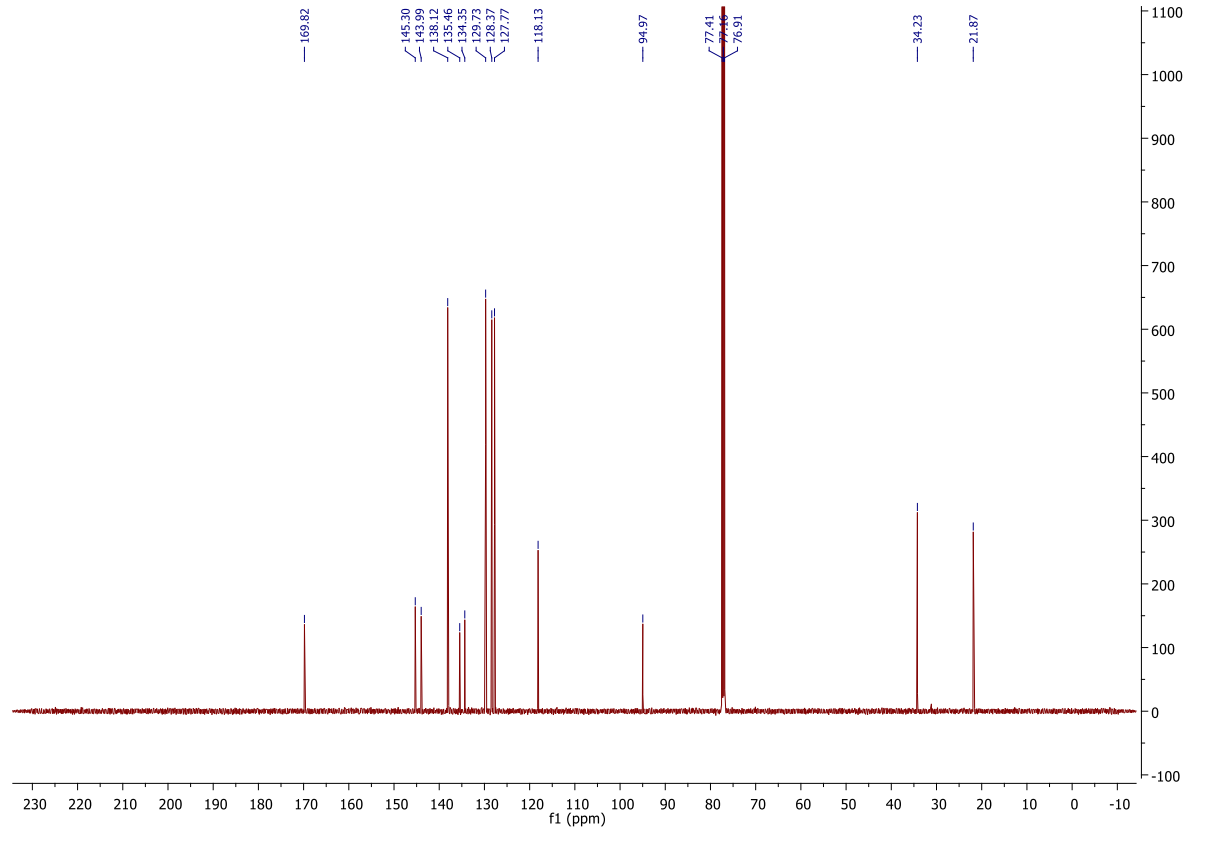
1.00
3.01
3.12
f1 (ppm)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143.99
138.12
135.46
134.35
129.73
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118.13
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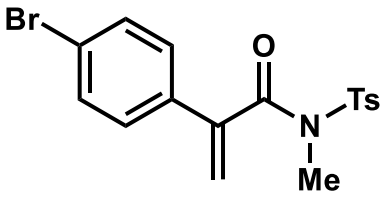
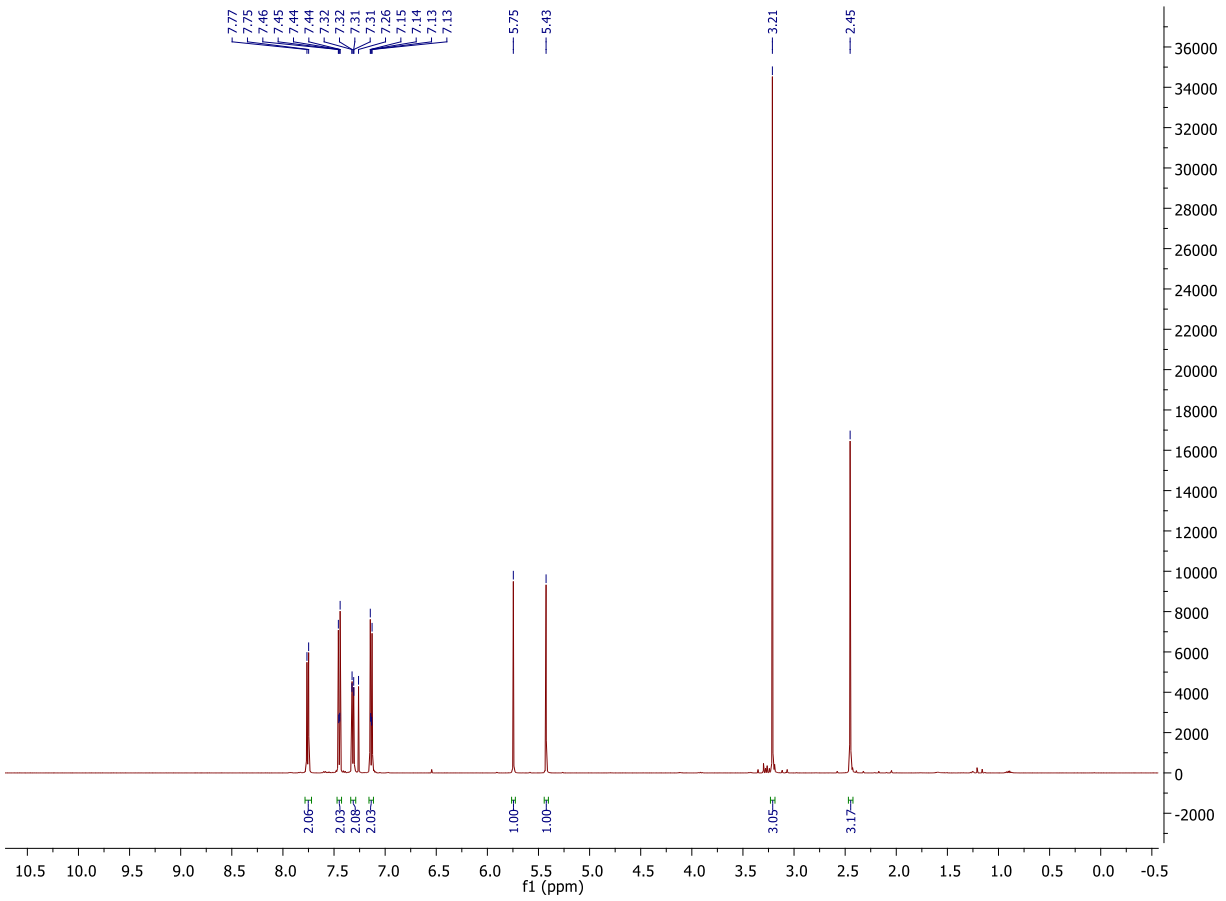
76.91
34.23
21.87
f1 (ppm)

(S5)



Prepared according to General procedure E using 4-bromophenylacetic acid (4.30 g, 20.0 mmol). Step 4B was carried out using N-methyl-p-toluenesulfonamide (480 mg, 2.60 mmol), dimethylaminopyridine (32.0 mg, 0.26 mmol), triethylamine (0.72 mL, 5.20 mmol), CH_2Cl_2 (21 mL) and acyl chloride (2.90 mmol). The crude residue was purified by flash column chromatography (eluent = 15 to 25% EtOAc in hexanes, silica gel) to afford product **(S5)** as a white solid (602 mg, 53% yield), (Step 1- 4B overall yield = 8%).

Mp.: 125-127 °C; $\mathbf{R_f}$ = 0.34 (eluent = 30% EtOAc in hexanes); $\mathbf{\nu_{max}}$ **/ cm^{-1}** (thin film) 2950, 1696, 1595, 1490, 1420, 1340, 1310, 1244, 1165, 1057, 855; **^{1}H NMR (500 MHz, $CDCl_3$)** δ_H: 2.45 (3H, s), 3.21 (3H, s), 5.43 (1H, s), 5.75 (1H, s), 7.11-7.17 (2H, m), 7.32 (2H, dd, *J* 8.5, 0.6 Hz), 7.42-7.48 (2H, m), 7.76 (2H, d, *J* 8.5 Hz); **^{13}C NMR (126 MHz, $CDCl_3$)** δ_C: 21.9, 34.2, 118.1, 123.2, 127.7, 128.4, 129.7, 132.2, 133.8, 135.5, 143.9, 145.3, 169.9; ; **HRMS (ES$^+$)** [$C_{17}H_{16}NO_3SBr$] requires $[M+H]^+$ 394.0113, found 394.0116 (+ 0.80 ppm).


7.77
7.75
7.46
7.45
7.44
7.44
7.32
7.32
7.31
7.31
7.26
7.15
7.14
7.13
7.13
5.75
5.43
3.21
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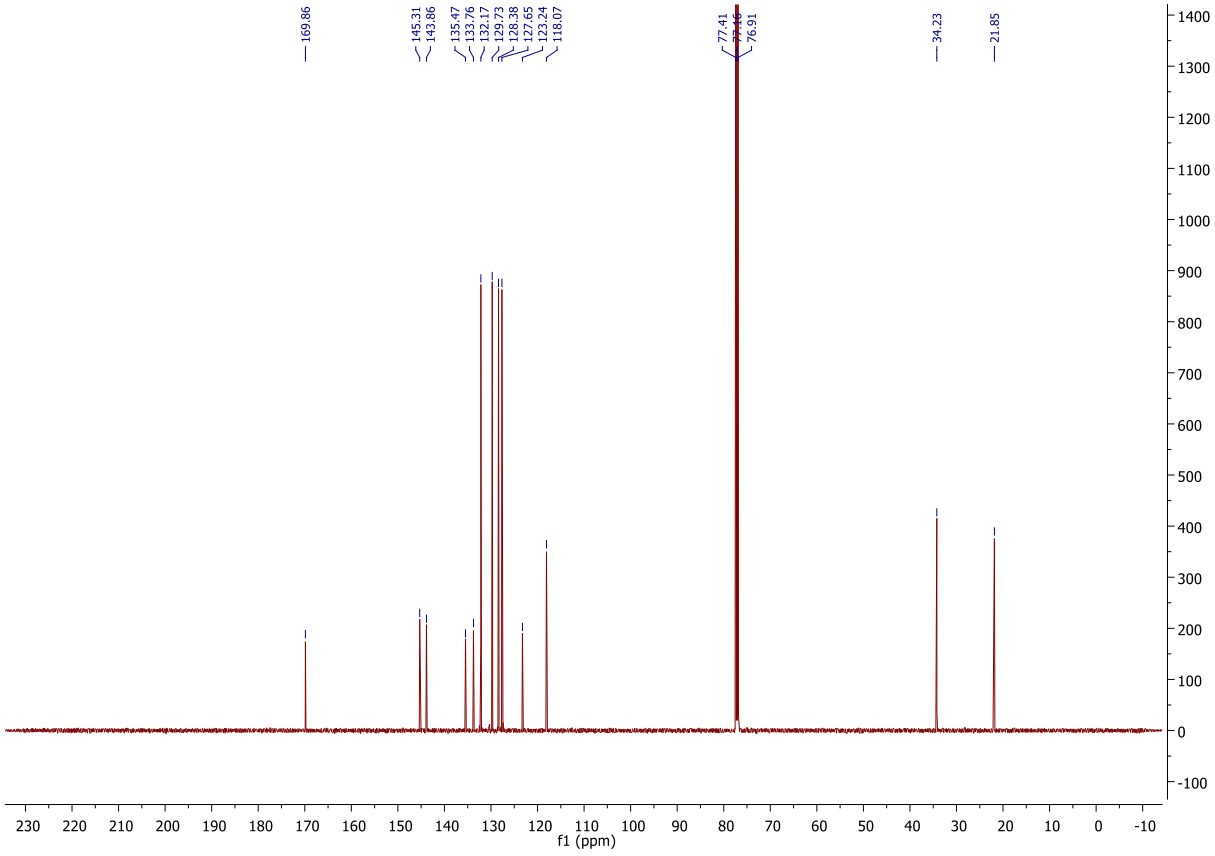
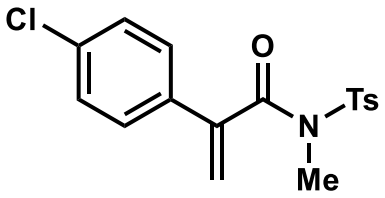
2.03
2.08
2.03
1.00
1.00
3.05
3.17
f1 (ppm)

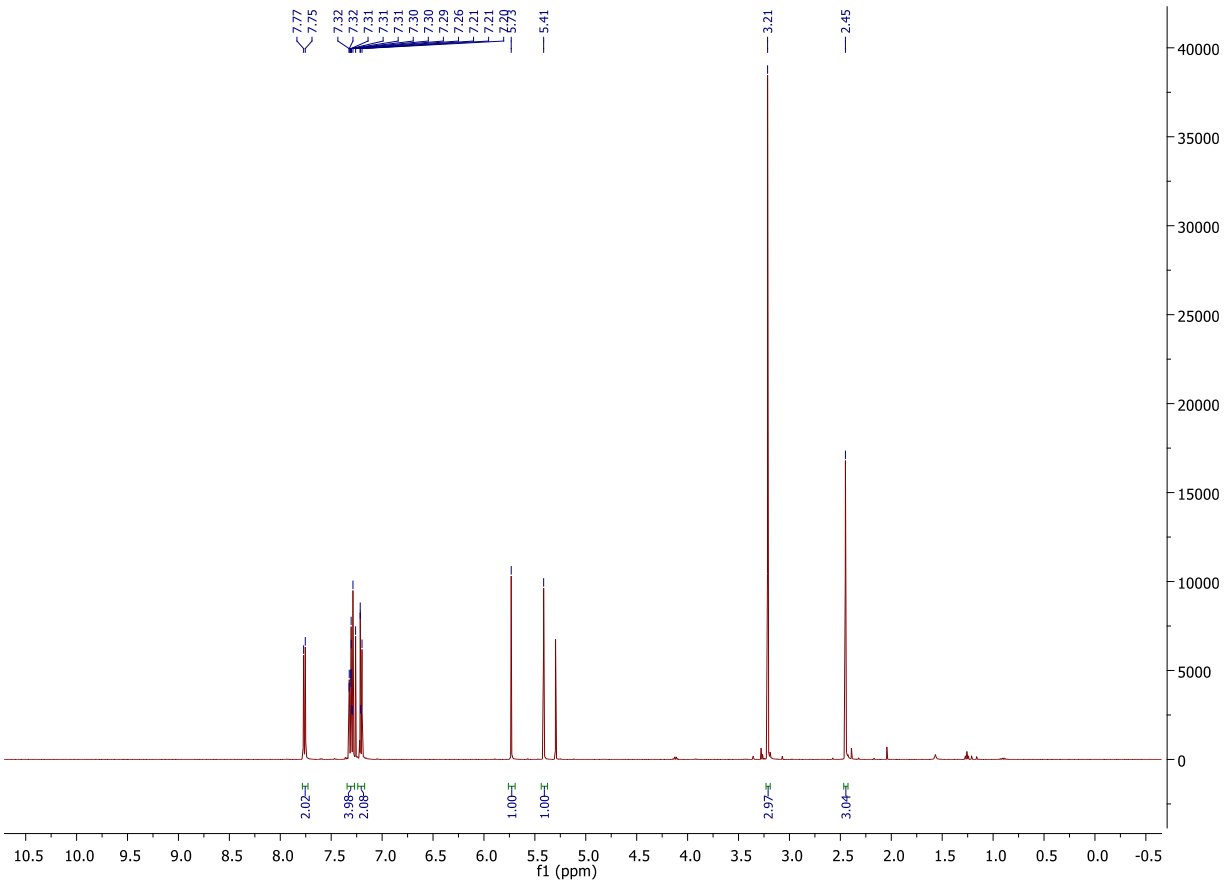

169.86
145.31
143.86
135.47
133.76
132.17
129.73
128.38
127.65
123.24
118.07
77.41
77.16
76.91
34.23
21.85
f1 (ppm)

(S6)



Prepared according to General procedure F using 4-chlorophenylacetic acid (3.41 g, 20.0 mmol). Step 4B was carried out using N-methyl-p-toluenesulfonamide (960 mg, 5.20 mmol), dimethylaminopyridine (64.0 mg, 0.52 mmol), triethylamine (1.44 mL, 10.4 mmol), CH_2Cl_2 (40 mL) and acyl chloride (5.70 mmol). The crude residue was purified by flash column chromatography (eluent = 15 to 25% EtOAc in hexanes, silica gel) to afford product **(S6)** as a white solid (1.28 g, 63% yield), (Step 1- 4B overall yield = 18%).

Mp.: 108-110 °C**;** $\mathbf{R_f}$ = 0.27 (eluent = 15% EtOAc in hexanes); $\mathbf{\nu_{max}}$ **/ cm^{-1}** (thin film) 1685, 1595, 1492, 1355, 1163, 1088; **^{1}H NMR (500 MHz, $CDCl_3$)** δ_H: 2.45 (3H, s), 3.21 (3H, s), 5.41 (1H, s), 5.73 (1H, s), 7.18-7.22 (2H, m), 7.27-7.34 (4H, m), 7.76 (2H, d, *J* 8.3 Hz); **^{13}C NMR (126 MHz, $CDCl_3$)** δ_C: 21.8, 34.2,, 117.9, 127.4, 128.4, 129.2, 129.7, 133.4, 135.0, 135.6, 143.9, 145.3, 169.9; **HRMS (ES$^+$)** [$C_{17}H_{16}NO_3SCl$] requires $[M+H]^+$ 350.0618 found 350.0614 (- 1.1 ppm).


7.77
7.75
7.32
7.32
7.31
7.31
7.31
7.30
7.30
7.29
7.26
7.21
7.21
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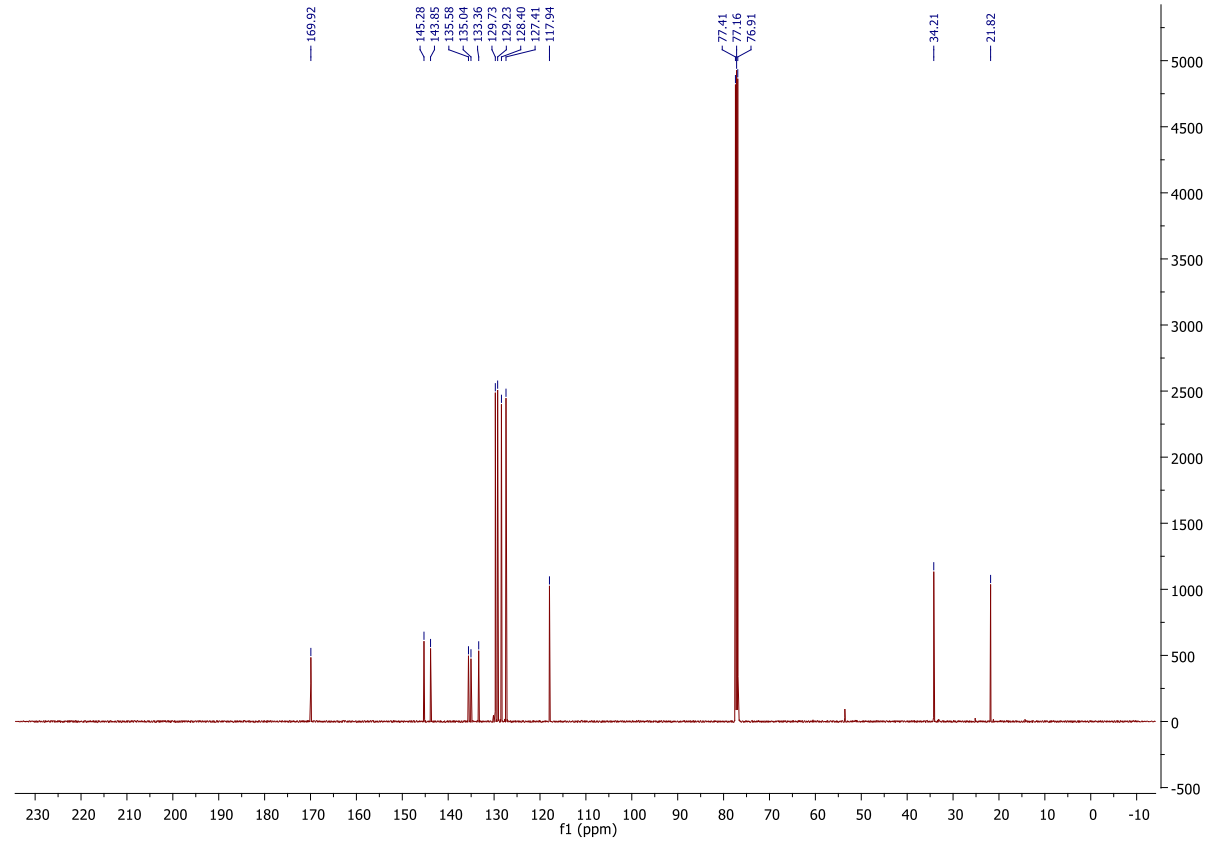
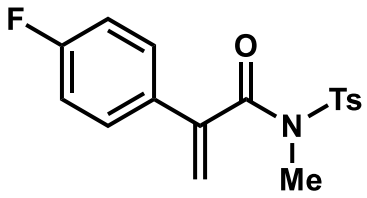
2.02
3.98
2.08
1.00
1.00
2.97
3.04
f1 (ppm)

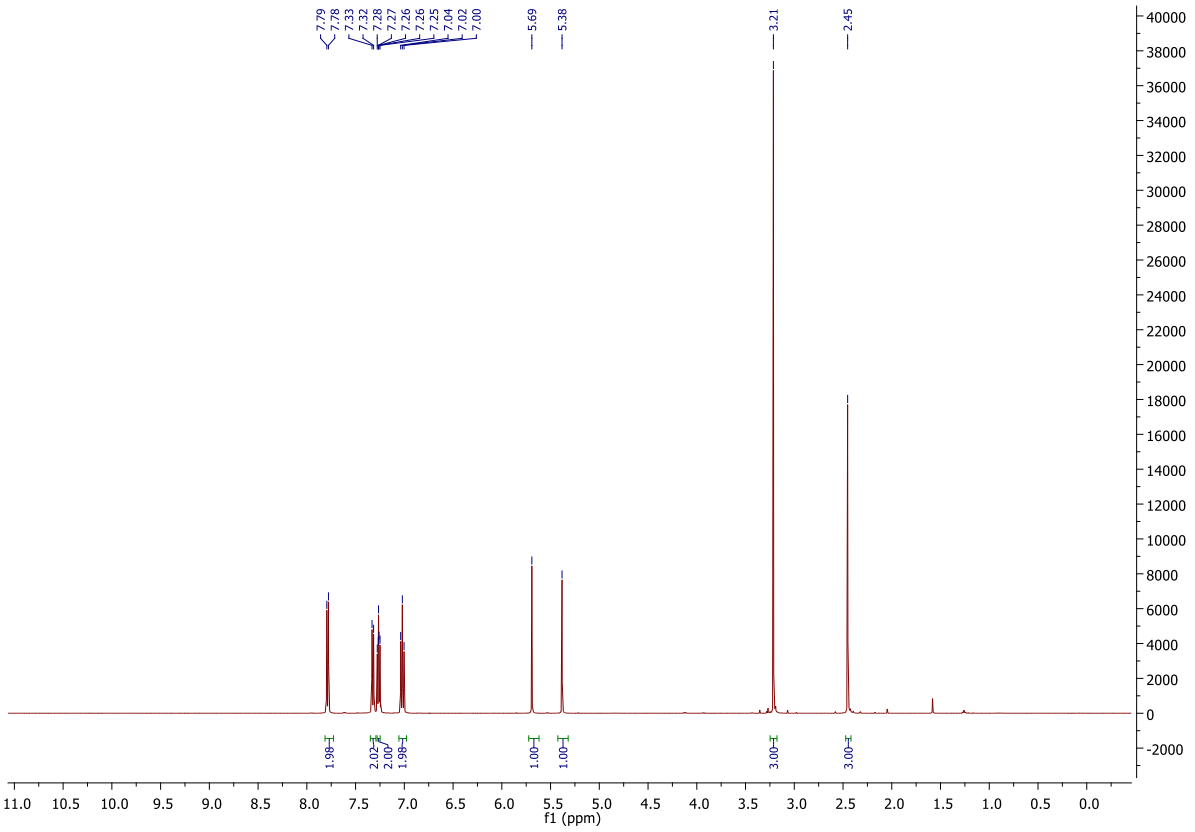

169.92
145.28
143.85
135.58
135.04
133.36
129.73
129.23
128.40
127.41
117.94
77.41
77.16
76.91
34.21
21.82
f1 (ppm)

(S7)



Prepared according to General procedure F using 4-fluorophenylacetic acid (3.08 g, 20.0 mmol). Step 4B was carried out using N-methyl-p-toluenesulfonamide (589 mg, 3.18 mmol), dimethylaminopyridine (38.8 mg, 0.32 mmol), triethylamine (0.95 mL, 6.36 mmol), CH_2Cl_2 (28 mL) and acyl chloride (3.50 mmol). The crude residue was purified by flash column chromatography (eluent = 10 to 20% EtOAc in hexanes, silica gel) to afford product **(S7)** as a colourless oil (510 mg, 43% yield), (Extrapolated Step 1- 4B overall yield = 16%).

Mp.: 56-58 ^{o}C **R_f** = 0.32 (eluent = 20% EtOAc in hexanes); **ν_{max} / cm^{-1}** (thin film) 2961, 1672, 1618, 1595, 1506, 1465, 1400, 1350, 1217, 1186, 1167, 1165, 1051, 921; **^{1}H NMR (500 MHz, $CDCl_3$)** δ_H: 2.45 (3H, s), 3.21 (3H, s), 5.38 (1H, s), 5.68 (1H, s), 6.98-7.04 (2H, m), 7.23-7.28 (2H, m), 7.32 (2H, dd, *J* 8.6 0.6 Hz), 7.78 (2H, d, *J* 8.3 Hz); **^{13}C NMR (126 MHz, $CDCl_3$)** δ_C: 21.8, 34.2, 116.0 (d, *J* 21.4 Hz), 117.4 (d, *J* 1.3 Hz), 128.0 (d, *J* 8.8 Hz), 128.4, 129.7, 131.0 (d, *J* 3.8 Hz), 135.6, 143.8, 145.2, 163.2 (d *J* 250 Hz), 170.1;**^{19}F NMR (471 MHz, $CDCl_3$)** δ_F:-112.3; **HRMS (ES$^+$)** [$C_{17}H_{16}NO_3SF$] requires $[M+H]^+$ 334.0913 found 334.0921 (+ 2.4 ppm).


7.79
7.78
7.33
7.32
7.28
7.27
7.26
7.26
7.25
7.04
7.02
7.00
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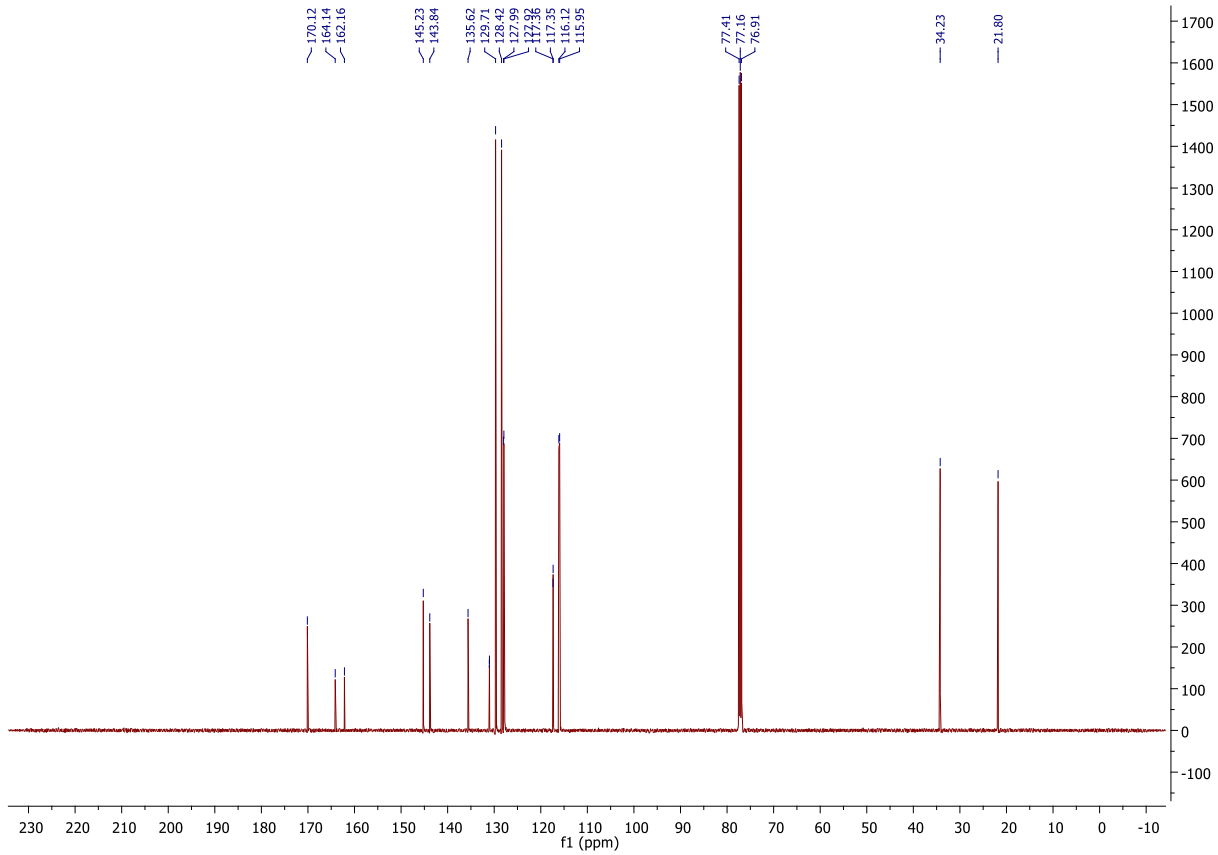
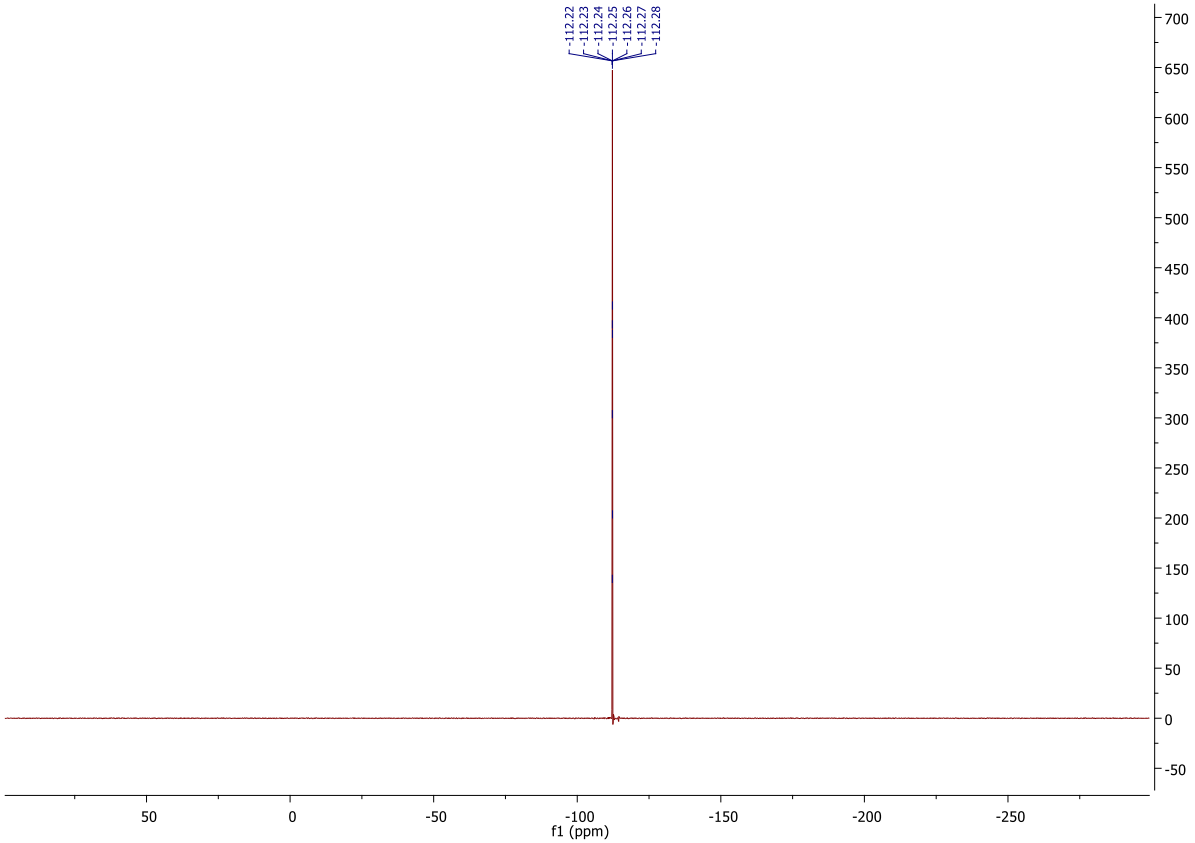
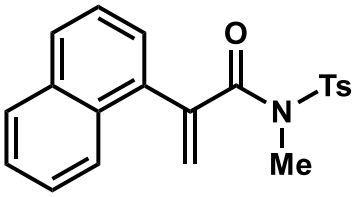
1.00
1.00
3.00
3.00
f1 (ppm)


170.12
164.14
162.16
145.23
143.84
135.62
129.71
128.42
127.99
127.92
117.36
117.35
116.12
115.95
77.41
77.16
76.91
34.23
21.80
f1 (ppm)

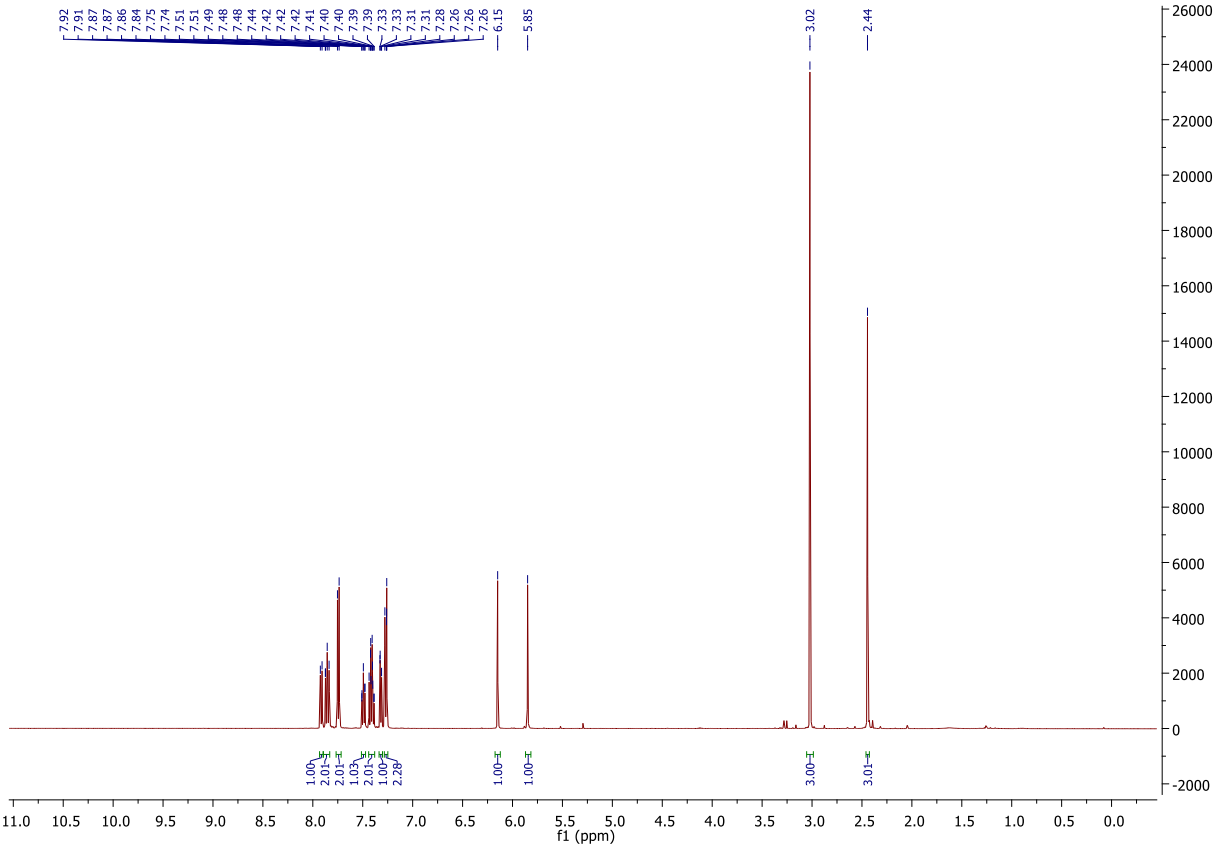

-112.22
-112.23
-112.24
-112.25
-112.26
-112.27
-112.28
700
650
600
550
500
450
400
350
300
250
200
150
100
50
0
-50
50
0
-50
-100
-150
-200
-250
f1 (ppm)

(S8)



Prepared according to General procedure F using 1-naphthaleneacetic acid (3.72 g, 20.0 mmol). Step 4B was carried out using N-methyl-p-toluenesulfonamide (894 mg, 4.84 mmol), dimethylaminopyridine (59.0 mg, 0.48 mmol), triethylamine (1.35 mL, 9.70 mmol), CH_2Cl_2 (37 mL) and acyl chloride (5.30 mmol). The crude residue was purified by flash column chromatography (eluent = 15 to 25% EtOAc in hexanes, silica gel) to afford product **(S8)** as a white solid (1.24 g, 64% yield), (Step 1- 4B overall yield = 17%).

Mp.: 102-104 ^{o}C **R_f** = 0.26 (eluent = 15% EtOAc in hexanes); **ν_{max} / cm^{-1}** (thin film) 1678, 1595, 1498, 1354, 1305, 1170, 1066; **^{1}H NMR (500 MHz, $CDCl_3$)** δ_H: 2.44 (3H, s), 3.02 (3H, s), 5.85 (1H, s), 6.15 (1H, s), 7.25-7.28 (2H, m), 7.32 (1H, dd, *J* 7.1, 1.0 Hz), 7.37-7.45 (2H, m), 7.46-7.52 (1H, m), 7.74 (2H, d, *J* 8.3 Hz), 7.83-7.88 (2H, m), 7.92 (1H, d, *J* 8.5 Hz); **^{13}C NMR (126 MHz, $CDCl_3$)** δ_C: 21.8, 34.6, 124.7, 125.4, 126.3, 126.9, 127.0, 127.1, 128.7, 128.8, 129.5, 129.5, 130.8, 133.6, 134.0, 135.5, 144.1, 144.9, 170.6; **HRMS (ES^{+})** [$C_{21}H_{19}NO_3S$] requires $[M+H]^+$ 366.1164 found 366.1168 (+ 1.1 ppm).


7.92
7.91
7.87
7.87
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7.84
7.75
7.74
7.51
7.51
7.49
7.48
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7.44
7.42
7.42
7.42
7.41
7.40
7.40
7.39
7.39
7.33
7.31
7.31
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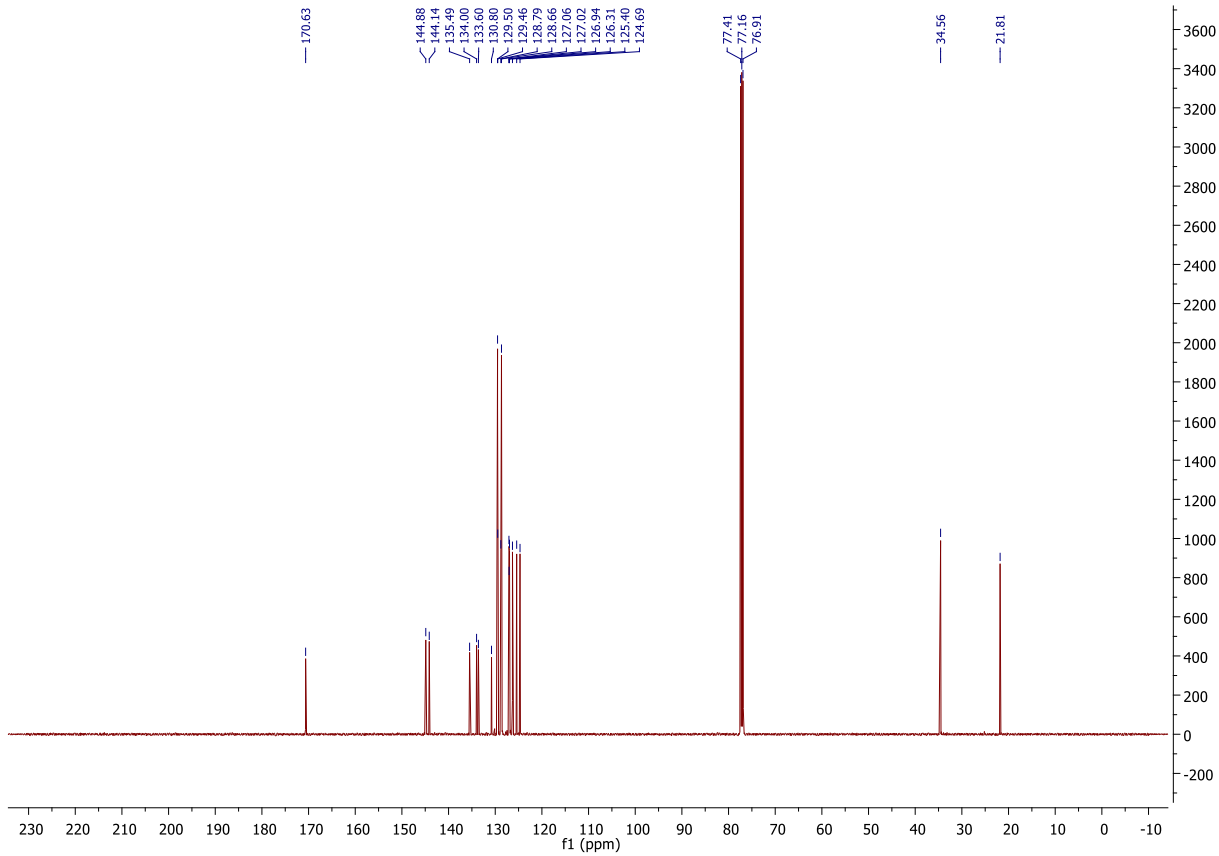
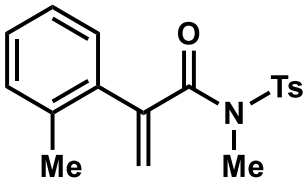
1.00
1.00
3.00
3.01
f1 (ppm)

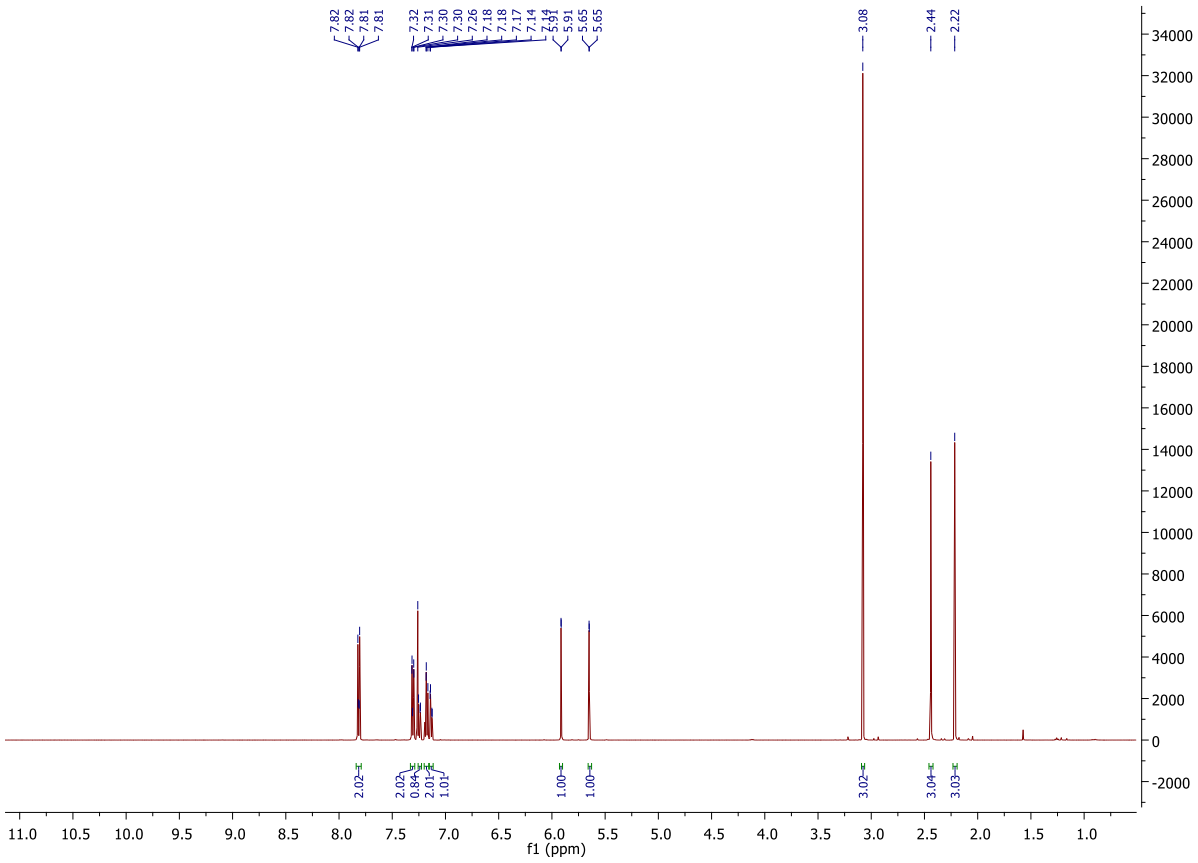

170.63
144.88
144.14
133.49
134.00
133.60
130.80
129.50
129.46
128.79
128.66
127.06
127.02
126.94
126.31
125.40
124.69
77.41
77.16
76.91
34.56
21.81
f1 (ppm)

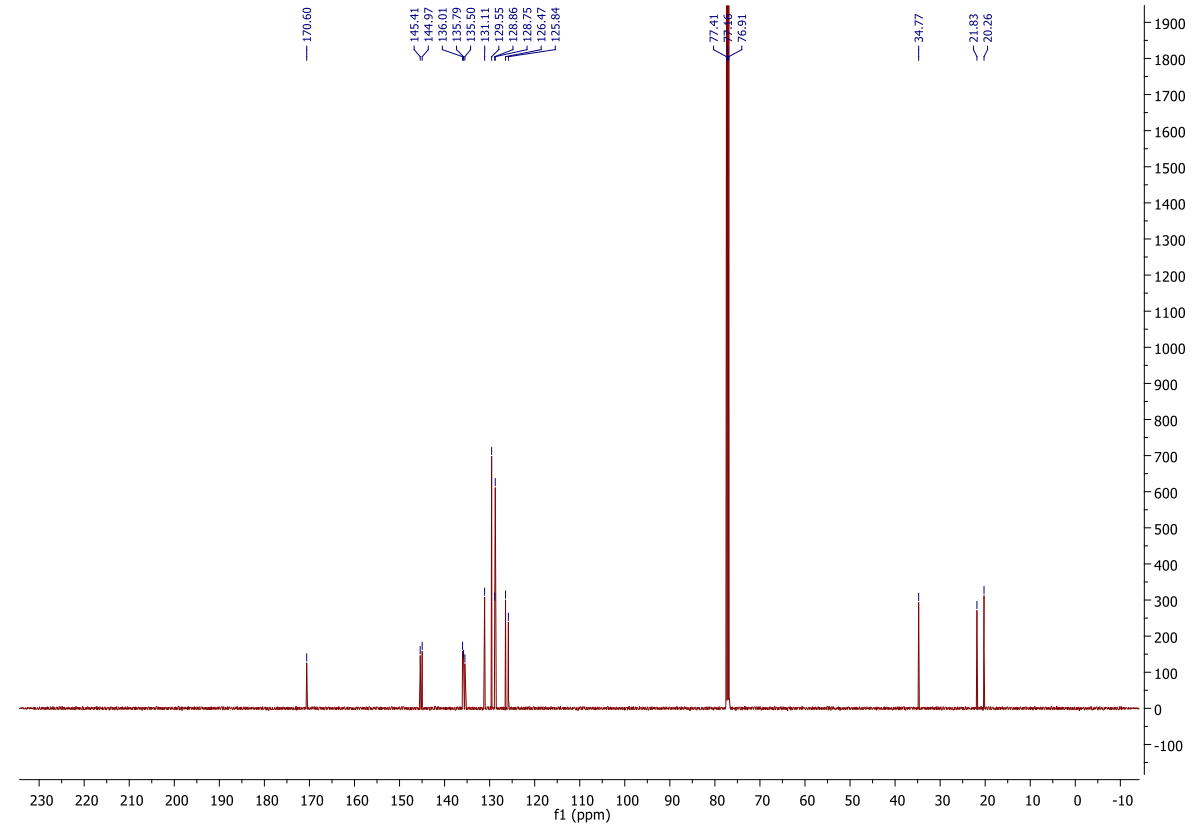
(S9)



Prepared according to General procedure E step using *o*-tolylphenylacetic acid (3.00 g, 20.0 mmol). Step 4B was carried out using N-methyl-p-toluenesulfonamide (930 mg, 5.00 mmol), dimethylaminopyridine (61.0 mg, 0.50 mmol), triethylamine (1.50 mL, 10.0 mmol), CH_2Cl_2 (40 mL) and acyl chloride (5.50 mmol). The crude residue was purified by flash column chromatography (eluent = 5 to 15% EtOAc in hexanes, silica gel) to afford product **(S9)** as a white solid (950 mg, 58% yield), (Step 1- 4B overall yield = 15%).

Mp.: 103-105 °C; $\mathbf{R_f}$ = 0.25 (eluent = 20% EtOAc in hexanes); $\mathbf{\nu_{max}}$ **/ cm^{-1}** (thin film) 2950, 1690, 1595, 1491, 1450, 1348, 1273, 1165, 1085, 1051; **^{1}H NMR (500 MHz, $CDCl_3$)** δ_H: 2.22 (3H, s), 2.44 (3H, s), 3.08 (3H, s), 5.65 (1H, d, *J* 0.8 Hz), 5.91 (1H, d, *J* 0.8 Hz), 7.12-7.14 (1H, m), 7.16-7.20 (2H, m), 7.23-7.26 (1H, m), 7.28-7.33 (2H, m), 7.78-7.84 (2H, m); **^{13}C NMR (126 MHz, $CDCl_3$)** δ_C: 20.3, 21.8, 34.8, 125.8, 126.5, 128.8, 128.9, 129.6, 131.1, 135.5, 135.8, 136.0, 145.0, 145.4, 170.6; **HRMS (ES$^+$)** [$C_{18}H_{19}NO_3S$] requires $[M+H]^+$ 330.1164, found 330.1175 (+ 3.3 ppm).


7.82
7.82
7.81
7.81
7.32
7.31
7.30
7.30
7.26
7.18
7.17
7.14
5.91
5.65
5.65
3.08
2.44
2.22
2.02
2.02
0.84
2.01
1.01
1.00
1.00
3.02
3.04
3.03
f1 (ppm)


170.60
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144.97
136.01
135.79
135.50
131.11
129.55
128.86
128.75
126.47
125.84
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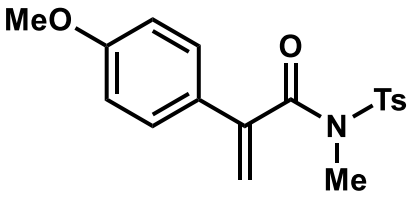
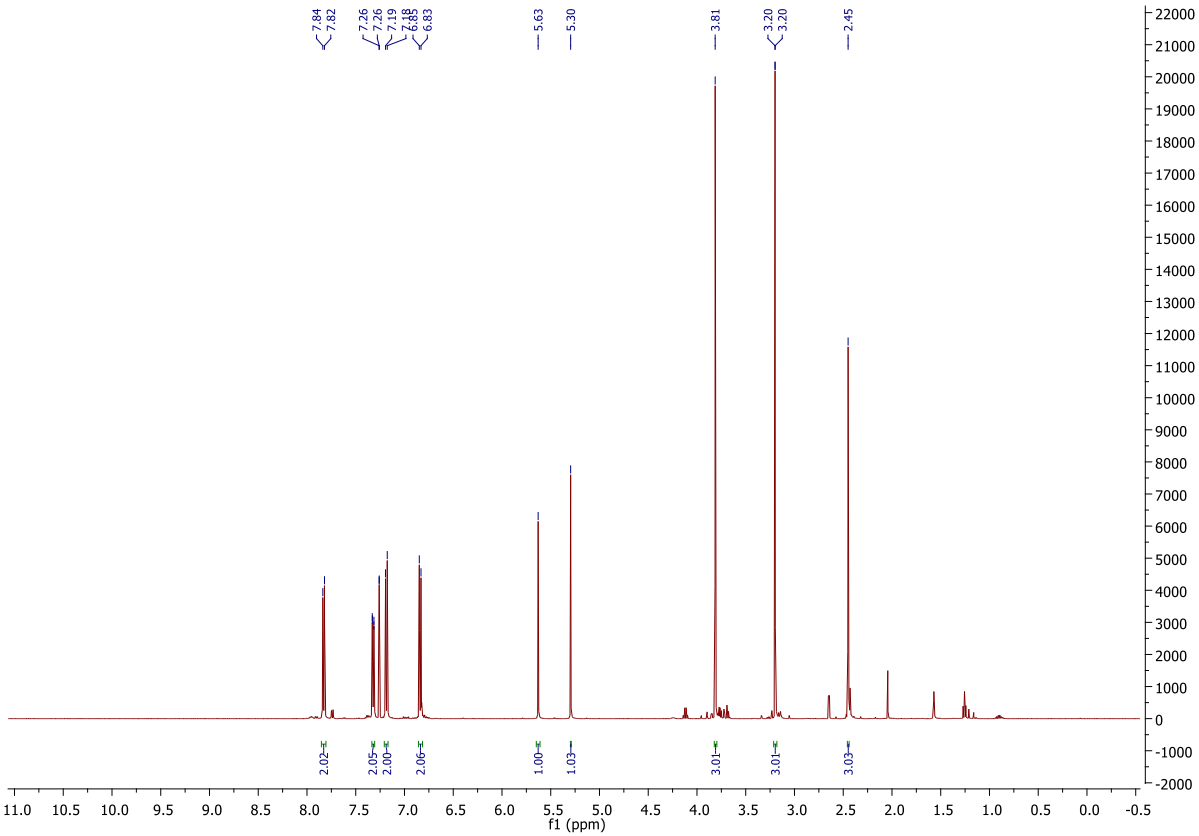
77.16
76.91
34.77
21.83
20.26
f1 (ppm)

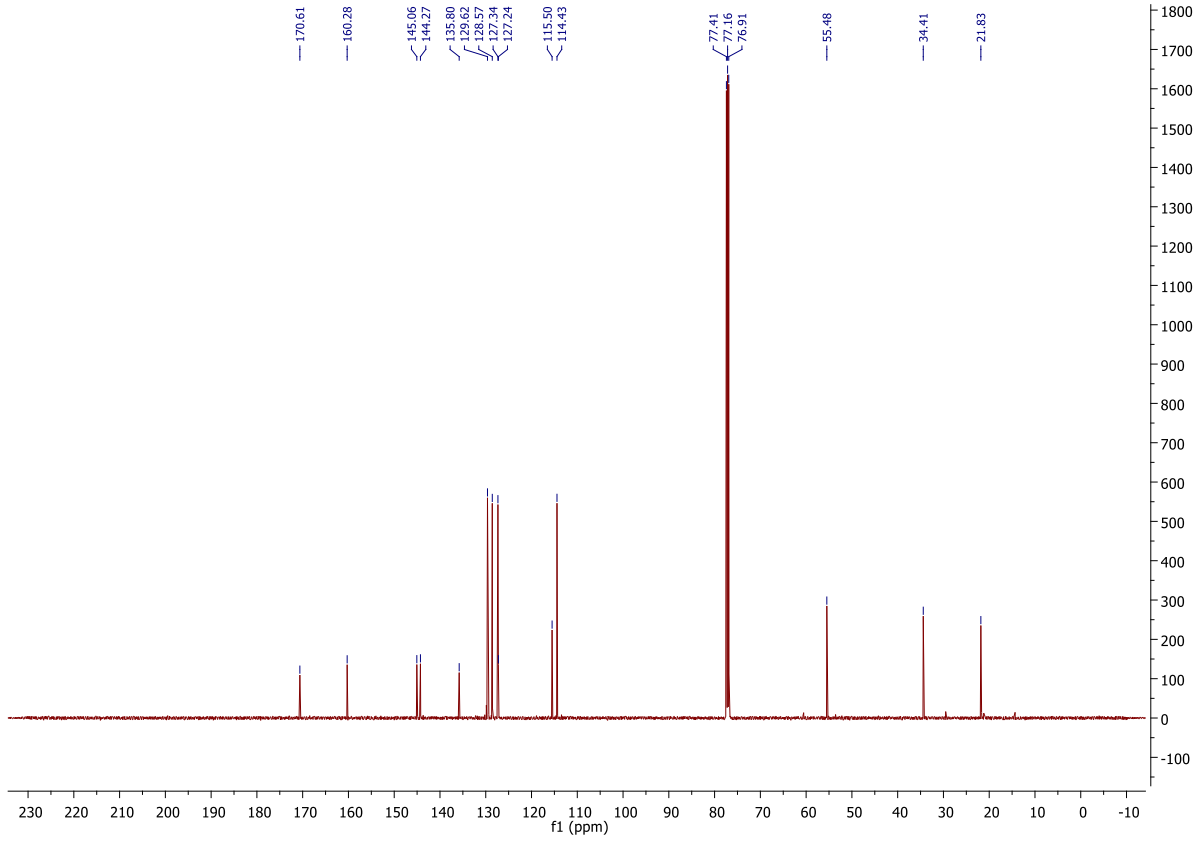
(S10)



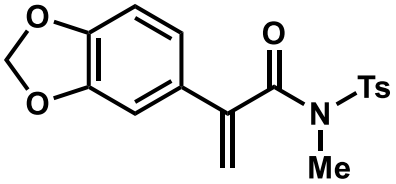
Prepared according to General procedure F using 4-methoxyphenylacetic acid (3.32 g, 20.0 mmol). Step 4B was carried out using N-methyl-p-toluenesulfonamide (460 mg, 2.50 mmol), dimethylaminopyridine (30.0 mg, 0.25 mmol), triethylamine (0.80 mL, 5.00 mmol), CH_2Cl_2 (25 mL) and acyl chloride (2.80 mmol). The crude residue was purified by flash column chromatography (eluent = 15 to 25% EtOAc in hexanes, silica gel) to afford product **(S10)** as a white solid (480 mg, 50% yield), (Step 1- 4B overall yield = 7%).

Mp.: 79-81 ^{o}C **R_f** = 0.14 (eluent = 15% EtOAc in hexanes); **ν_{max} / cm^{-1}** (thin film) 1686, 1606, 1512, 1355, 1290, 1251, 1168, 1056; **^{1}H NMR (500 MHz, $CDCl_3$)** δ_H: 2.45 (3H, s), 3.18-3.20 (3H, m), 3.81 (3H, s), 5.30 (1H, s), 5.63 (1H, s), 6.84 (2H, d, *J* 8.7 Hz), 7.19 (2H, d, *J* 8.7 Hz), 7.28-7.35 (2H, m), 7.83 (2H, d, *J* 8.5 Hz); **^{13}C NMR (126 MHz, $CDCl_3$)** δ_C: 21.8, 34.4, 55.5, 114.4, 115.5, 127.2, 127.3, 128.6, 129.6, 135.8, 144.3, 145.1, 160.3, 170.6; **HRMS (ES$^+$)** [$C_{18}H_{19}NO_4S$] requires $[M+H]^+$ 346.1113 found 346.1118 (+ 1.4 ppm).


7.84
7.82
7.26
7.26
7.19
6.85
6.83
5.63
5.30
3.81
3.20
3.20
2.45
2.02
2.05
2.00
2.06
1.00
1.03
3.01
3.01
3.03
f1 (ppm)

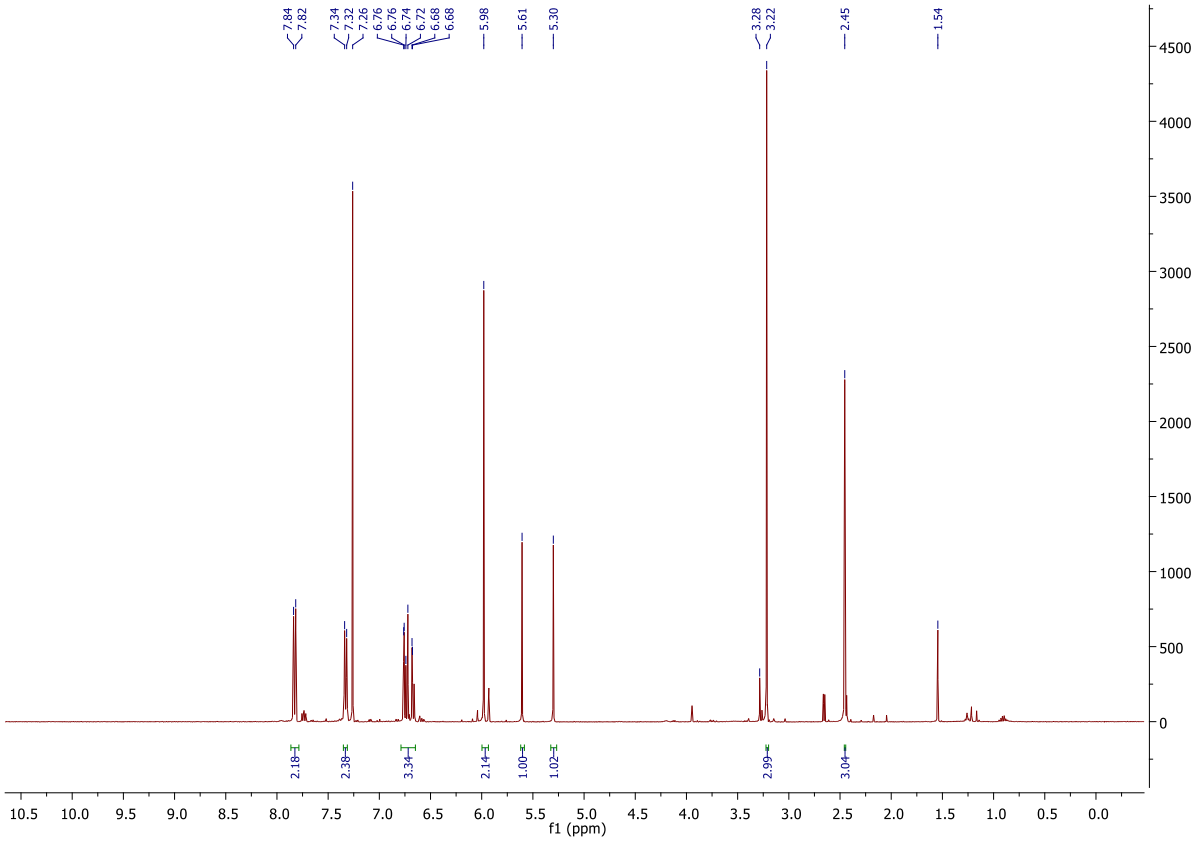

170.61
160.28
145.06
144.27
135.80
129.62
128.57
127.34
127.24
115.50
114.43
77.41
77.16
76.91
55.48
34.41
21.83
f1 (ppm)

(S11)



Prepared according General procedure E using 1,3-Benzodioxole-5-acetic acid (3.60 g, 20 mmol). Step 4B carried out using N-methyl-p-toluenesulfonamide (460 mg, 2.50 mmol), dimethylaminopyridine (30.0 mg, 0.25 mmol), triethylamine (0.80 mL, 5.00 mmol), CH_2Cl_2 (23 mL) and acyl chloride (2.80 mmol). The crude residue was purified by flash column chromatography (eluent = 15 to 30% EtOAc in hexanes, silica gel) to afford product **(S11)** as a yellow solid (250 mg, 28% yield), (Step 1-4B overall yield = 7%).

Mp.: 90-93 °C; **R_f** = 0.40 (eluent = 40% EtOAc in hexanes); **ν_{max} / cm^{-1}** (thin film) 2956, 1676, 1618, 1597, 1493, 1449, 1350, 1225, 1163, 1078; **^{1}H NMR (400 MHz, $CDCl_3$)** δ_H: 2.45 (3H, s), 3.22 (3H, s), 5.30 (1H, s); 5.61 (1H, s), 5.98 (2H, s), 6.64-6.78 (3H, m), 7.33 (2H, d, *J* 8.0 Hz), 7.83 (2H, d, *J* 8.0 Hz); **^{13}C NMR (101 MHz, $CDCl_3$)** δ_C: 21.8, 34.4, 101.6, 106.2, 108.7, 116.0, 120.3, 128.6, 128.9, 129.7, 135.8, 144.4, 145.1, 148.4, 148.5, 170.3; **HRMS (ES$^+$)** [$C_{18}H_{17}NO_5S$] requires $[M+H]^+$ 360.0906 found 360.0902 (- 1.1 ppm).


7.84
7.82
7.34
7.32
7.26
6.76
6.76
6.74
6.72
6.68
6.68
5.98
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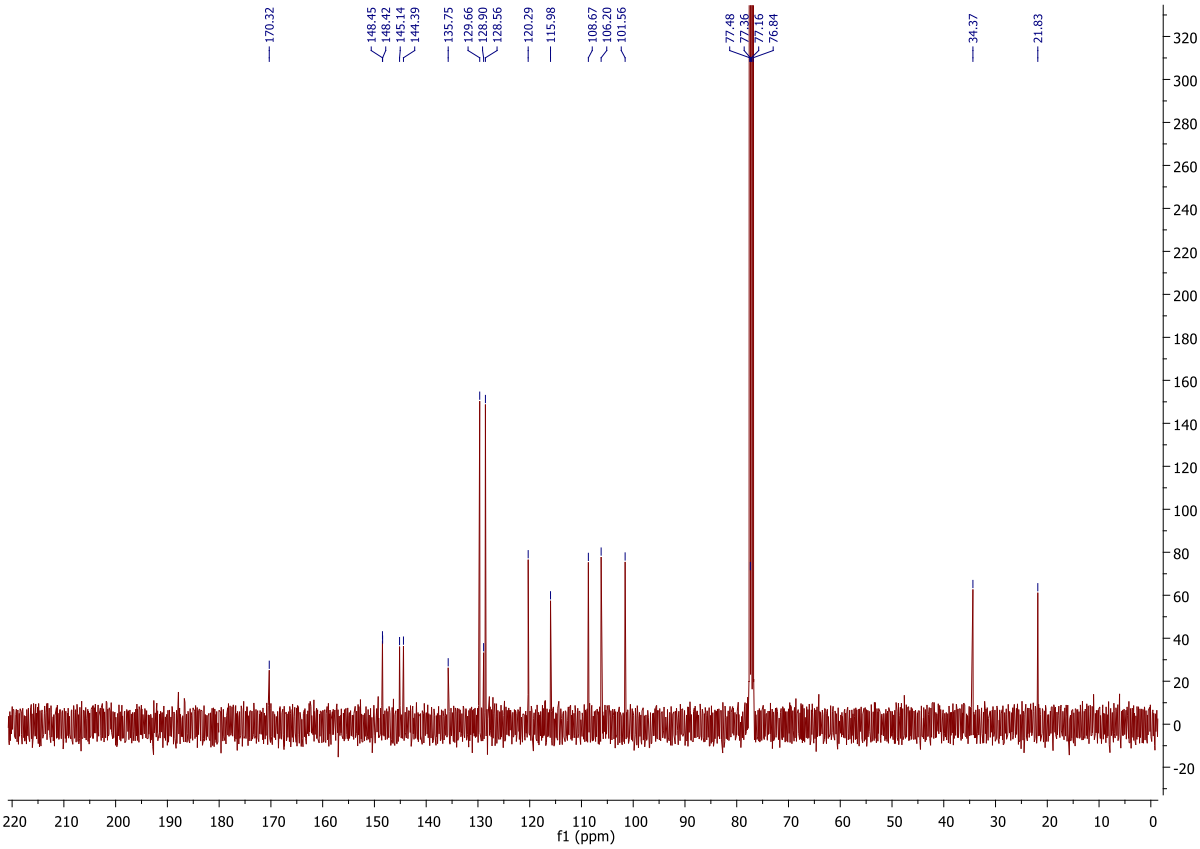
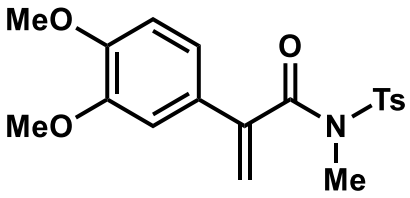
5.30
3.28
3.22
2.45
1.54
2.18
2.38
3.34
2.14
1.00
1.02
2.99
3.04
f1 (ppm)

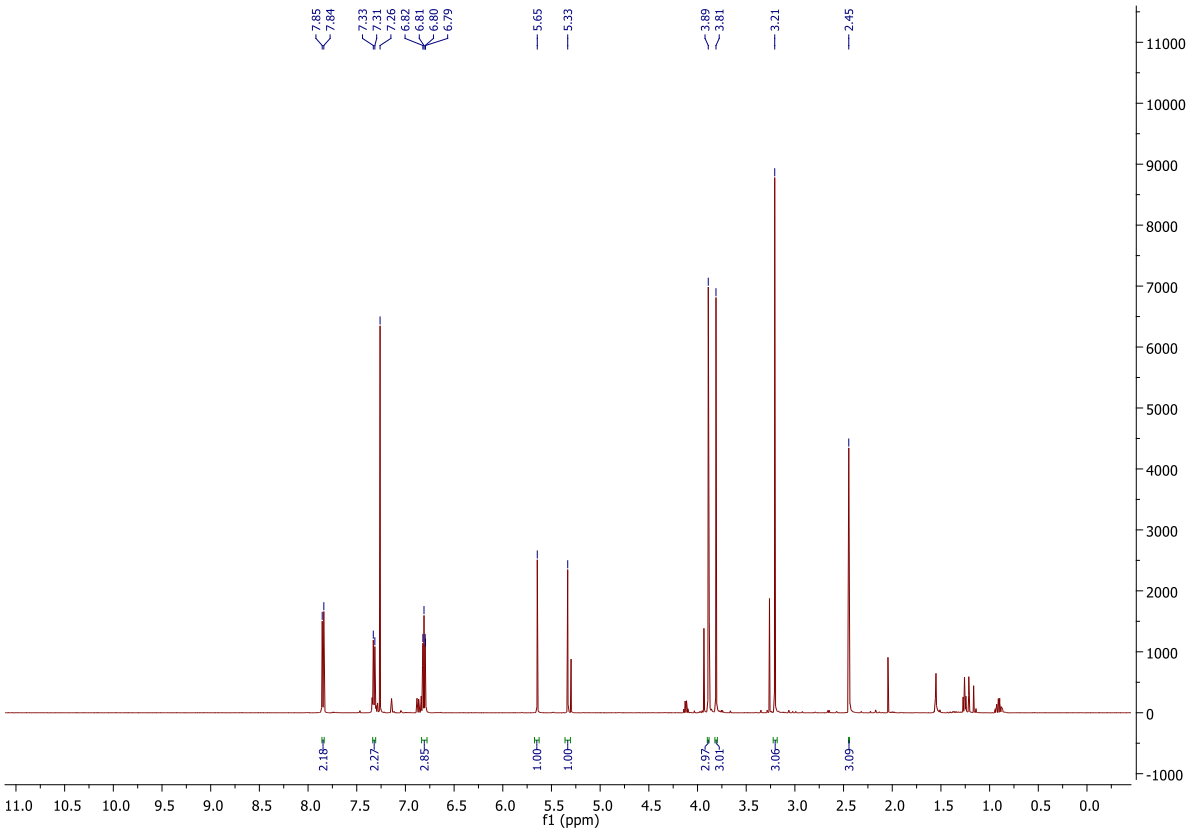

170.32
148.45
148.42
145.14
144.39
135.75
129.66
128.90
128.56
120.29
115.98
108.67
106.20
101.56
77.48
77.36
77.16
76.84
34.37
21.83
f1 (ppm)

(S12)



Prepared according to General procedure F using 3,4-dimethoxyphenylacetic acid (3.92 g, 20.0 mmol). Step 4B was carried out using N-methyl-p-toluenesulfonamide (386 mg, 2.10 mmol), dimethylaminopyridine (25.2 mg, 0.21 mmol), triethylamine (0.70 mL, 4.20 mmol), CH_2Cl_2 (20 mL) and acyl chloride (2.35 mmol). The crude residue was purified by flash column chromatography (eluent = 15 to 25% EtOAc in hexanes, silica gel) to afford product **(S12)** as a white solid (450 mg, 49% yield), (Step 1- 4B overall yield = 6%).

Mp.: 100-102 °C**;** $\mathbf{R_f}$ = 0.13 (eluent = 15% EtOAc in hexanes); $\mathbf{\nu_{max}}$ **/ cm^{-1}** (thin film) 1681, 1597, 1517, 1463, 1344, 1255, 1169, 1022; **^{1}H NMR (500 MHz, $CDCl_3$)** δ_H: 2.45 (3H, s), 3.21 (3H, s), 3.81 (3H, s), 3.89 (3H, s), 5.33 (1H, s), 5.65 (1H, s), 6.78-6.83 (3H, m), 7.30-7.34 (2H, m), 7.83-7.86 (2H, m); **^{13}C NMR (126 MHz, $CDCl_3$)** δ_C: 21.8, 34.5, 56.0, 56.1, 108.9, 111.4, 115.7, 119.0, 127.5, 128.6, 129.6, 135.9, 144.5, 145.1, 149.3, 149.9, 170.5; **HRMS (ES$^+$)** [$C_{19}H_{21}NO_5S$] requires $[M+H]^+$ 376.1219 found 376.1218 (- 0.3 ppm).


7.85
7.84
7.33
7.31
7.26
6.82
6.81
6.80
6.79
5.65
5.33
3.89
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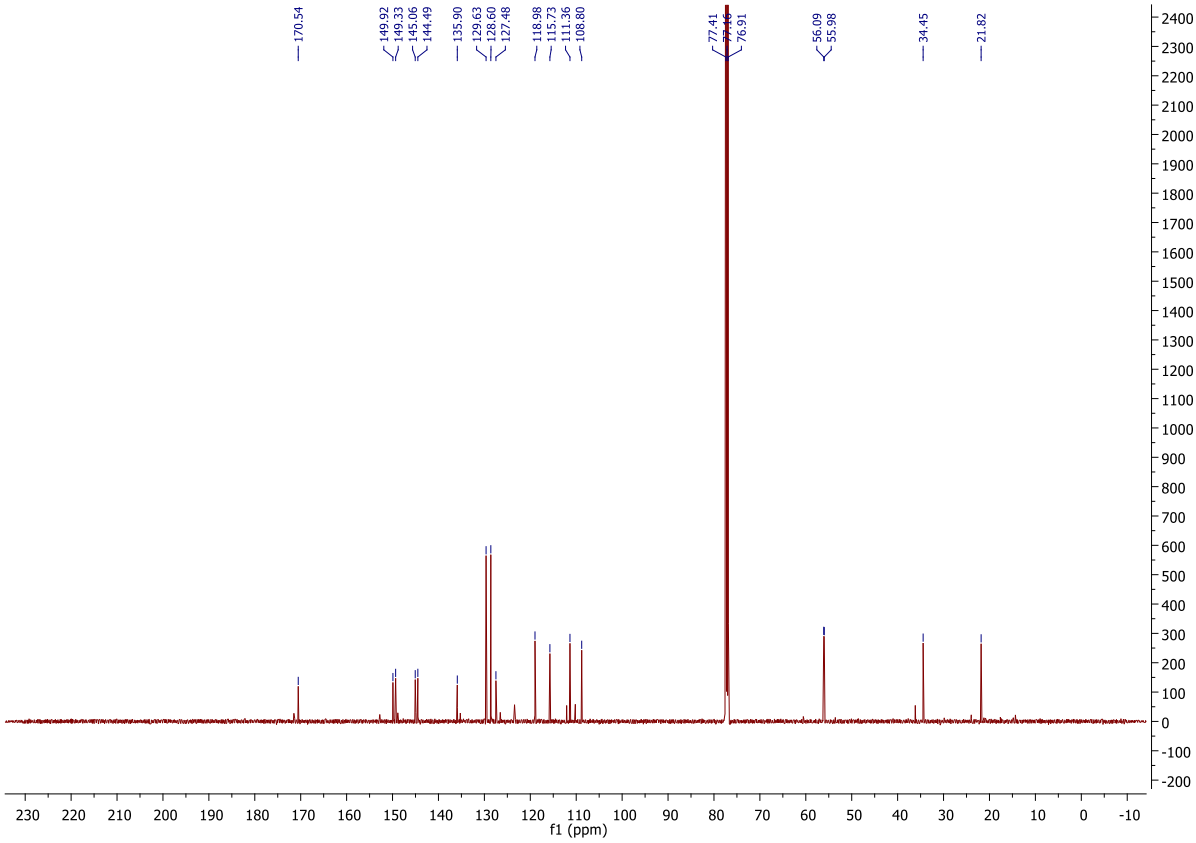
2.97
3.01
3.06
3.09
f1 (ppm)


170.54
149.92
149.33
145.06
144.49
135.90
129.63
128.60
127.48
118.98
115.73
111.36
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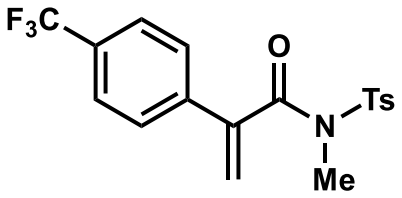
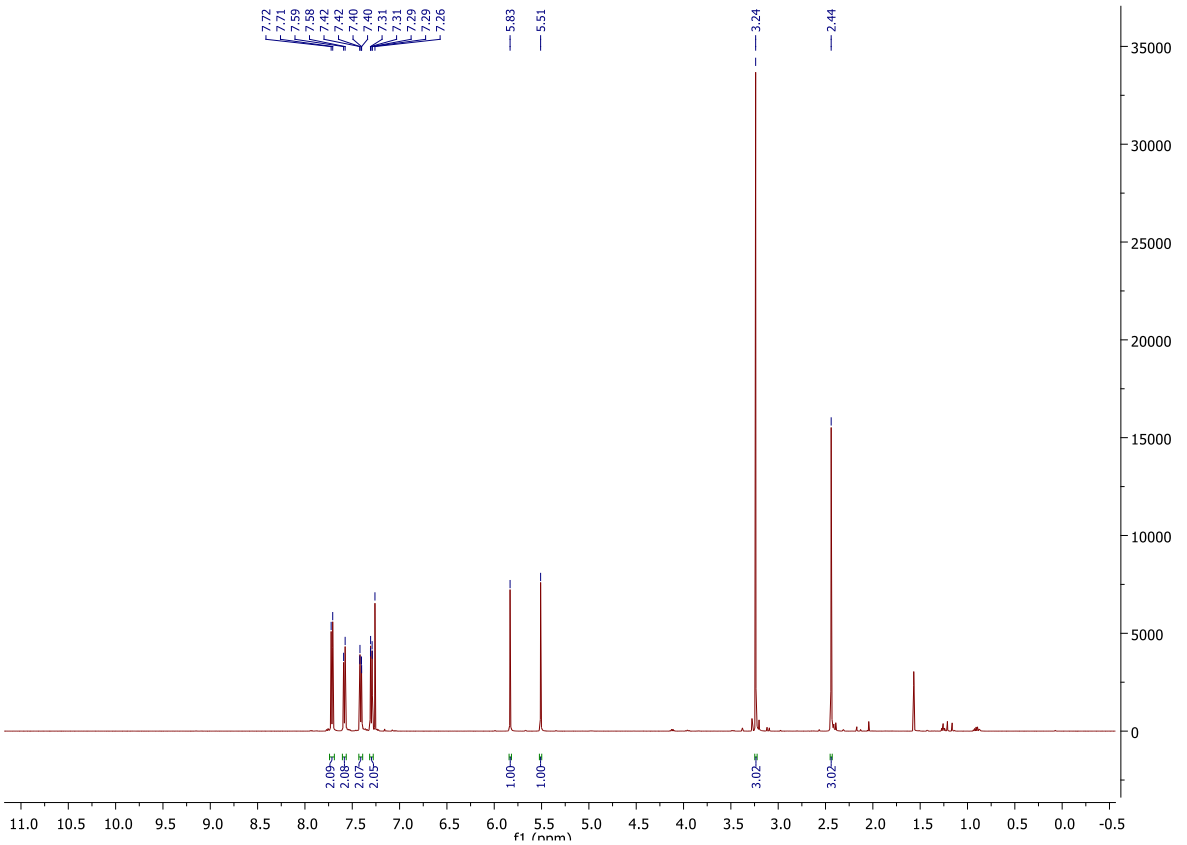
55.98
34.45
21.82
f1 (ppm)

(S13)



Prepared according to General procedure F using 4-trifluoromethylphenylacetic acid (4.10 g, 20.0 mmol). Step 4B was carried out using N-methyl-p-toluenesulfonamide (437 mg, 2.36 mmol), dimethylaminopyridine (29.0 mg, 0.24 mmol), triethylamine (0.72 mL, 5.20 mmol), CH_2Cl_2 (19 mL) and acyl chloride (2.60 mmol). The crude residue was purified by flash column chromatography (eluent = 10 to 20% EtOAc in hexanes, silica gel) to afford product **(S13)** as a white solid (502 mg, 50% yield), (Step 1- 4B overall yield = 7%).

Mp.: 88-90 ^{o}C **R_f** = 0.34 (eluent = 20% EtOAc in hexanes); **ν_{max} / cm^{-1}** (thin film) 3065, 1680, 1616, 1473, 1408, 1325, 1246, 1167, 1155, 1111, 1065, 1015, 962; **^{1}H NMR (500 MHz, $CDCl_3$)** δ_H: 2.44 (3H, s), 3.24 (3H, s), 5.51 (1H, s), 5.83 (1H, s), 7.30 (2H, dd, *J* 8.7, 0.7 Hz), 7.41 (2H, dd, *J* 8.7, 0.7 Hz), 7.58 (1H, d, *J* 8.2 Hz), 7.71 (2H, d, *J* 8.2 Hz); **^{13}C NMR (126 MHz, $CDCl_3$)** δ_C: 21.8, 34.1, 119.5, 124.0 (q, *J* 273 Hz), 126.0 (q, 3.8 Hz), 126.5, 128.3, 129.8, 130.8 (q, 32.8 Hz), 135.5, 138.5, 143.9, 145.4, 169.6; **^{19}F NMR (471 MHz, $CDCl_3$)** δ_F: -62.7; **HRMS (ES$^+$)** [$C_{18}H_{16}NO_3SF_3$] requires $[M+H]^+$ 384.0881 found 384.0887 (+ 1.6 ppm).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7.58
7.42
7.42
7.40
7.40
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7.29
7.29
7.26
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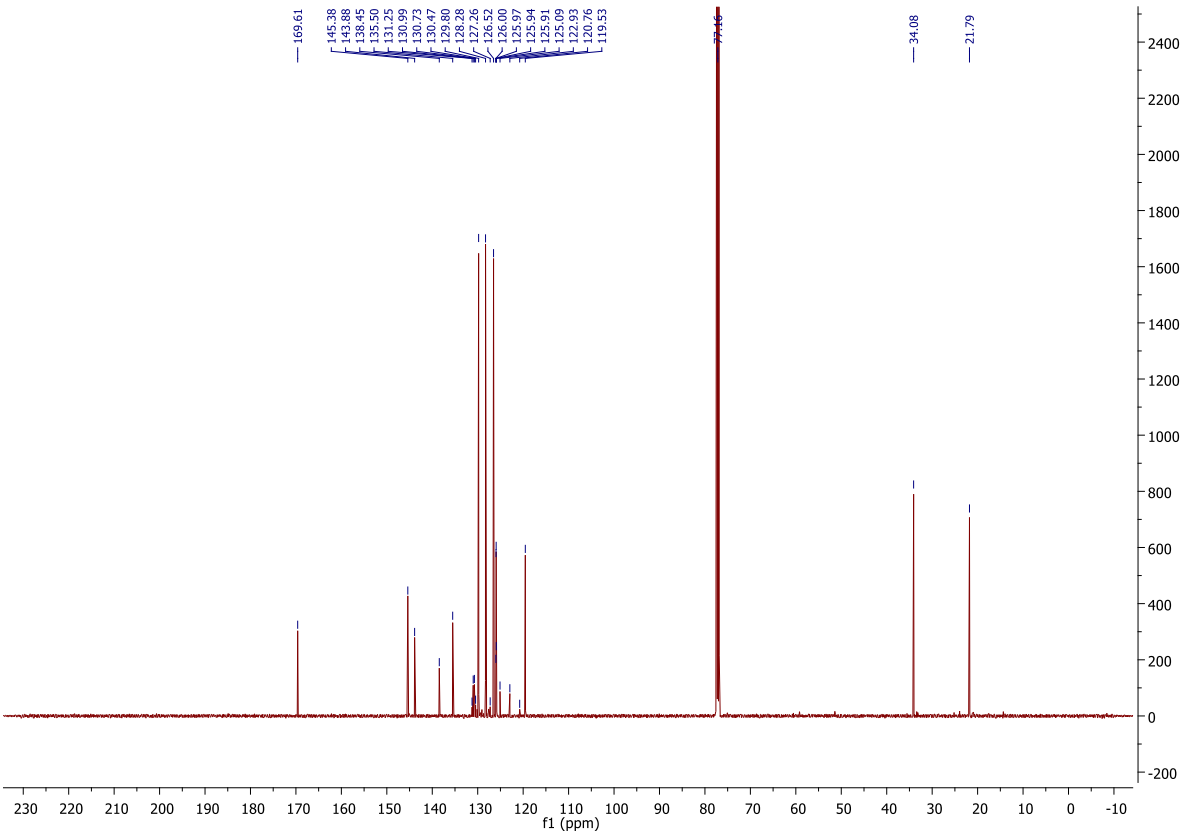
1.00
1.00
3.02
3.02
f1 (ppm)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130.73
130.47
129.80
128.28
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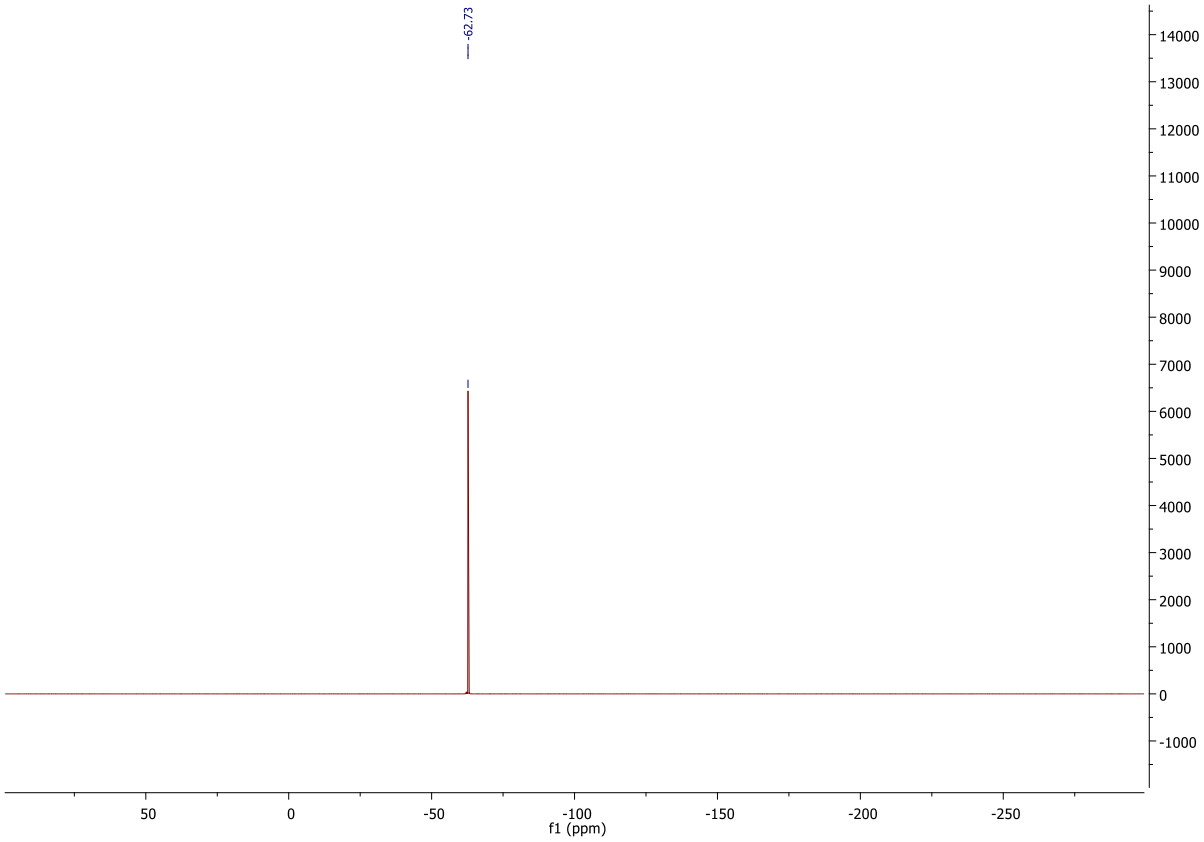
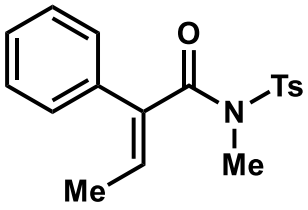
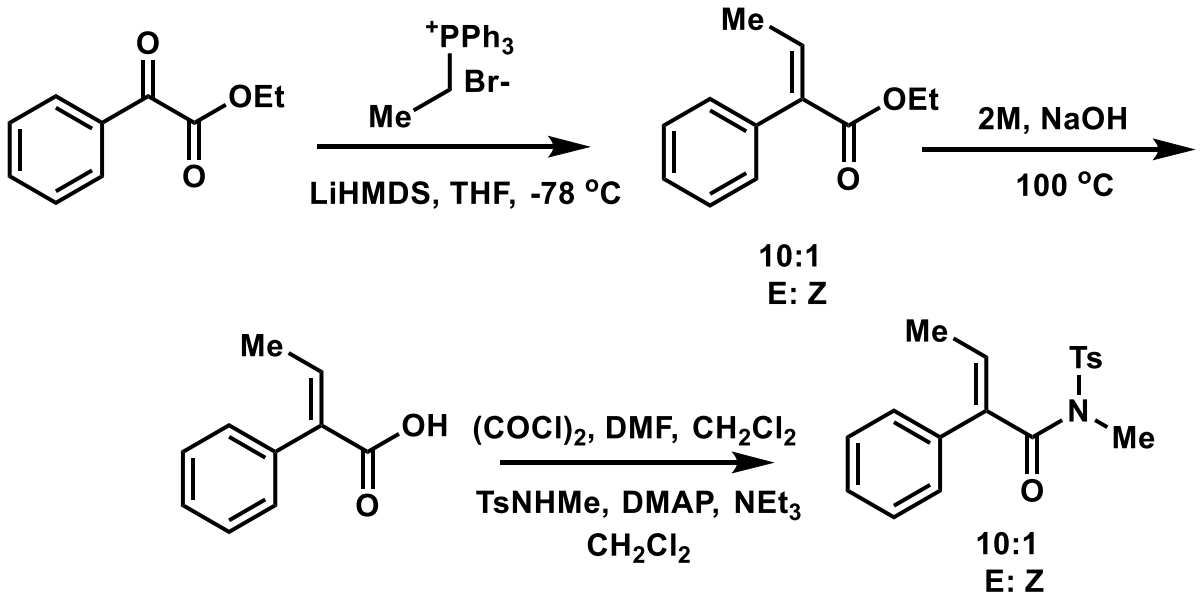
119.53
77.16
34.08
21.79
f1 (ppm)


-62.73
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
50
0
-50
-100
-150
-200
-250
f1 (ppm)

(S14)



Scheme:



Following a modified literature procedure:[2]

Methods:

Part 1:

To a suspension of ethyltriphenylphosphonium bromide (8.17 g, 22.0 mmol, 1.1 equiv.) in anhydrous THF (40 mL) cooled to –78 °C, LiHMDS (22 mL, 1M in THF, 22.0 mmol, 1.1 equiv.) was added dropwise and the resulting mixture was stirred at –78 °C for 5 minutes. The reaction was then allowed to warm to room temperature and stirred for an additional 30 minutes then was cooled back to –78 °C. A solution of ethyl phenylglyoxylate (3.56 g, 20.0 mmol, 1 equiv.) in anhydrous THF (10 mL) was added dropwise and the reaction was further stirred for 1 h at –78 °C, when the reaction was allowed to warm to room temperature overnight. The reaction was then quenched with 1M HCl, extracted with CH_2Cl_2, dried over $MgSO_4$, filtered and concentrated affording crude product as an orange oil which was used directly in the subsequent step.

Part 2:

Crude ethyl (E)-2-phenylbut-2-enoate in 2M NaOH solution (30 mL) was heated at reflux for 3 h before being cooled to room temperature. The aqueous was extracted with Et_2O (30 mL) then acidified to pH 1 using 2M HCl. The acidified aqueous suspension was then extracted with CH_2Cl_2 (3 x 30 mL), organics combined and dried over $MgSO_4$, filtered and concentrated *in vacuo* to afford crude acid (1.40 g, 43 % yield over 2 steps).

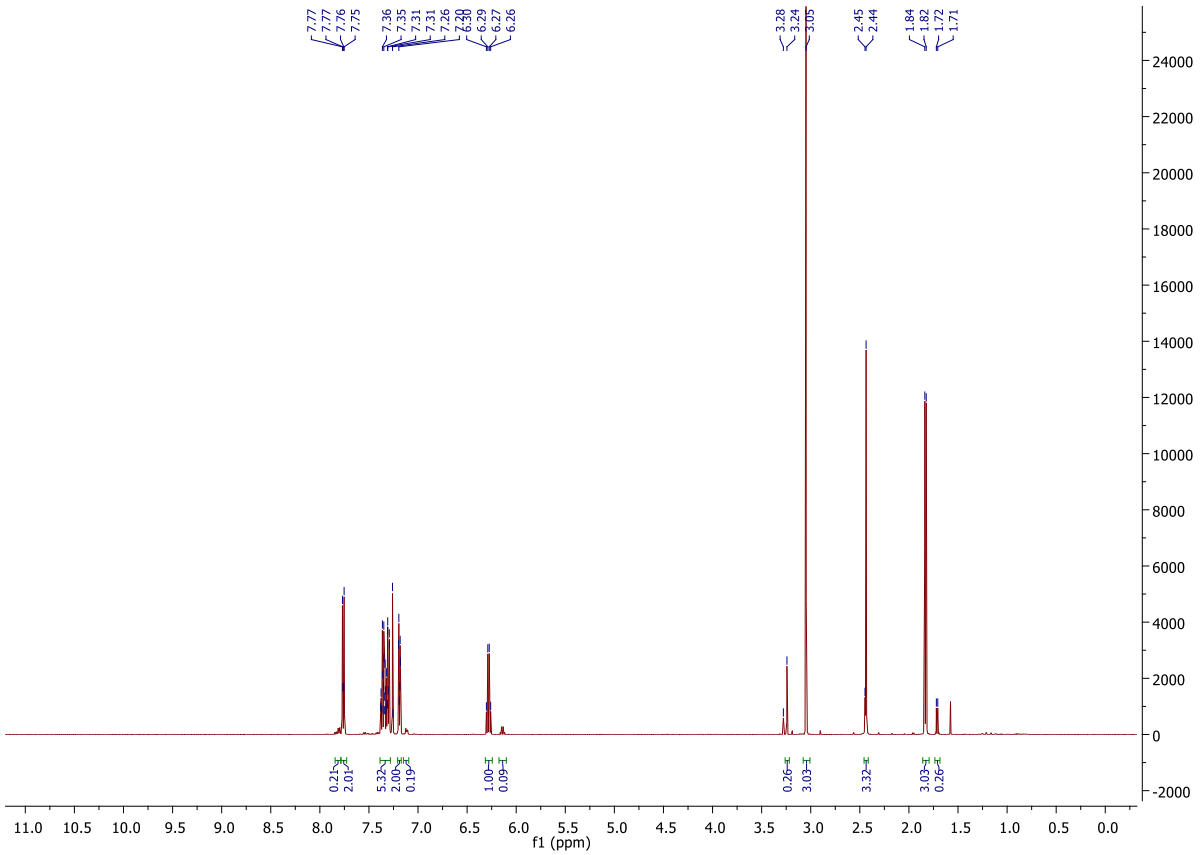
Part 3A:

To a solution of (E)-2-phenylbut-2-enoic acid (1.20 g, 7.40 mmol, 1 equiv.) in CH_2Cl_2 (22 mL) and DMF (3 drops) was added oxalyl chloride (1.40 g, 0.95 mL, 11.1 mmol, 1.5 equiv.) dropwise with concurrent gas evolution. The mixture was stirred at room temperature for 3 h until no gas evolution was observed. The solution was concentrated *in vacuo* and redissolved in CH_2Cl_2 (1 mL/mmol).

Part 3B:

A solution of N-methyl-N-tosylamine (1.24 g, 6.70 mmol, 1 equiv.), DMAP (82.0 mg, 0.67 mmol, 10 mol %) and triethylamine (2 equiv.) in CH_2Cl_2 (50 mL) was prepared and cooled to 0 ^oC using a salt/ice bath. The crude acyl chloride solution (1.1 equiv) prepared in **part 3A** was added dropwise and the mixture was stirred at 0 ^oC for 15 mins before being allowed to warm to room temperature and stir overnight. The reaction mixture was quenched with a saturated sodium bicarbonate solution (50 mL), layers separated and aqueous phase extracted with CH_2Cl_2 (2 x 40 mL). The organics were combined and dried over $MgSO_4$, filtered and concentrated *in vacuo* yielding crude product. The crude residue was purified by flash column chromatography (silica gel) to yield pure product **(S14)** as a yellow oil (1.10 g, 50% yield) as a 10:1 mixture of alkene stereoisomers. Data for (E)-alkene given.

R_f = 0.30 (eluent = 20% EtOAc in hexanes); **ν_{max} / cm^{-1}** (thin film) 2980, 1690, 1635, 1595, 1348, 1263, 1167, 1082; *Data for major (E) alkene stereoisomer:* **^{1}H NMR (500 MHz, $CDCl_3$)** δ_H: 1.83 (3H, d, *J* 7.2 Hz), 2.44 (3H, s), 3.05 (3H, s), 6.28 (1H, q, *J* 7.2 Hz), 7.17-7.20 (2H, m), 7.28-7.38 (5H, m), 7.74-7.78 (2H, m); **^{13}C NMR (126 MHz, $CDCl_3$)** δ_C: 15.1, 21.8, 34.6, 128.1, 128.5, 128.7, 129.2, 129.6, 133.8, 134.4, 135.7, 138.1, 144.8, 171.3; **HRMS (ES$^+$)** [$C_{18}H_{19}NO_3S$] requires $[M+H]^+$ 330.1164 found 330.1164 (+ 0.0 ppm).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7.31
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6.30
6.29
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3.28
3.24
3.05
2.45
2.44
1.84
1.82
1.72
1.71
0.21
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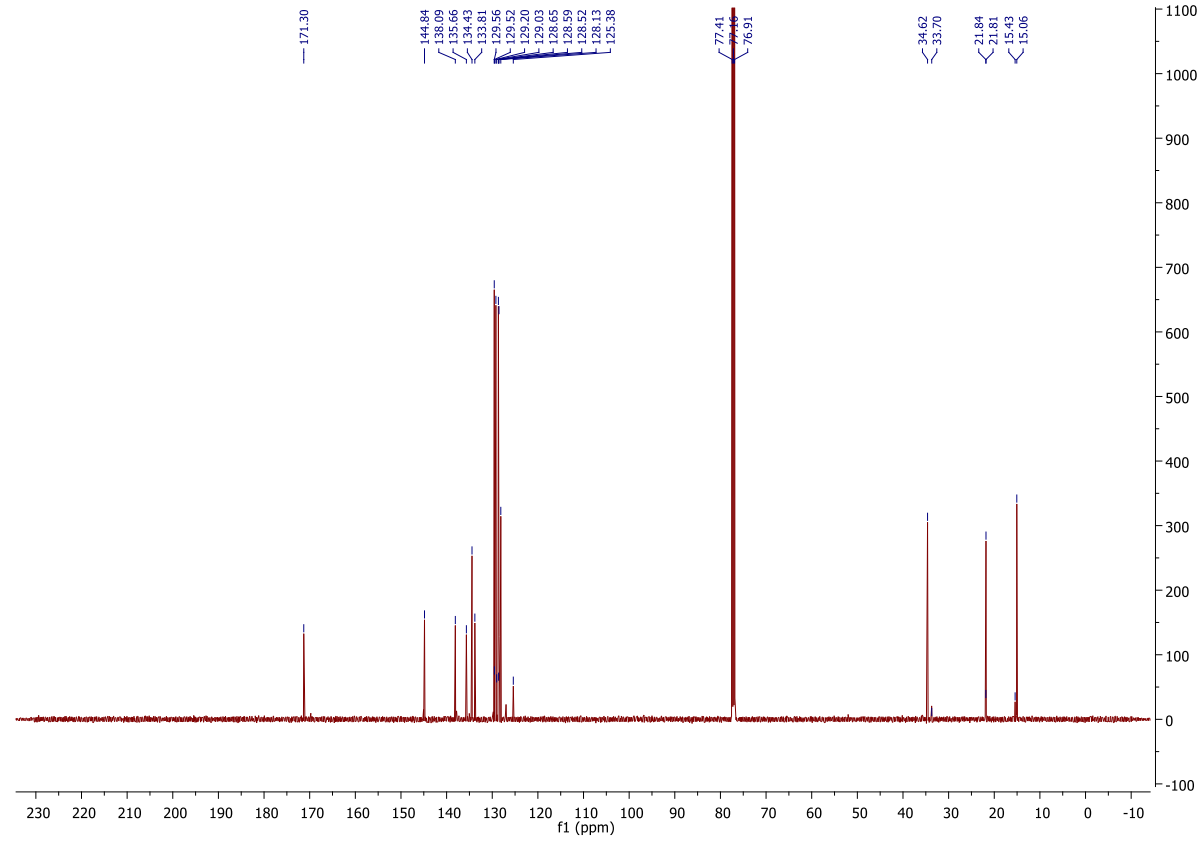
5.32
2.00
0.19
1.00
0.09
0.26
3.03
3.32
3.03
0.26
f1 (ppm)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129.03
128.65
128.59
128.52
128.13
125.38
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76.91
34.62
33.70
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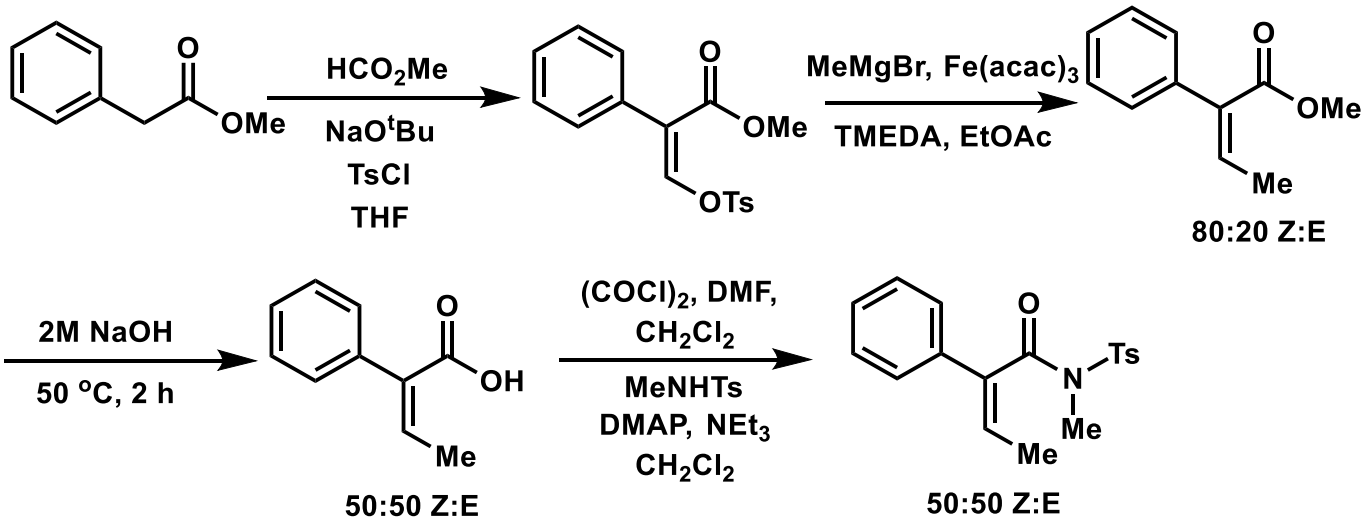
21.81
15.43
15.06
f1 (ppm)

(S14B)



Following a literature procedure.[3]

Part 1

To a solution of methyl-2-phenylacetate (5.27 g, 35 mmol) in THF (35 mL) was added methyl formate (3.26 mL, 52.5 mmol, 1.5 equiv.) and cooled to 0 °C with the aid of an ice bath. Sodium *tert*-butoxide (5.06 g, 52.5 mmol, 1.5 equiv.) was added portionwise to the solution over 10 minutes. A suspension formed which was left to stir for 1 h at 0 °C. Tosyl chloride (10.0 g, 52.5 mmol, 1.5 equiv.) was added portionwise over 10 minutes and the mixture was allowed to stir for 1 h at 0 °C. The reaction was quenched with water (35 mL) and diluted with EtOAc (20 mL). The layers were separated and the aqueous extracted with EtOAc (2 x 20 mL). The combined organic phases were washed with water (35 mL) and brine (35 mL), dried over $MgSO_4$ and concentrated *in vacuo* forming a yellow oil. To the oil was added 2-propanol (20 mL) resulting in precipitation of a white solid. The precipitate was stirred in 2-propanol for 30 minutes before being filtered. The crude (Z)-2-phenyl-3-(tosyloxy)acrylate was washed with cold 2-propanol before being vacuum dried overnight.

Part 2

Crude (Z)-2-phenyl-3-(tosyloxy)acrylate (5.76 g, 17 mmol, 1 equiv.), $Fe(acac)_3$ (353 mg, 1 mmol, 6 mol %), Tetramethylethylenediamine (3 mL, 17 mmol, 1 equiv.) and EtOAc (40 mL) were charged to a 250 mL round bottom flask. Methylmagnesium bromide (8.6 mL, 26 mmol, 1.5 equiv., 3M in Et_2O) was added to the orange solution dropwise maintaining 10-25 °C over 20 minutes and then the mixture was allowed to stir at room temperature for 1 h.

The reaction was then quenched with mixture of saturated solution of ammonium chloride (30 mL) and ice water (30 mL) and the mixture was then stirred for 5 minutes before 1M HCl (50 mL) was added and stirring continued for 10 minutes. The layers were then separated, the aqueous extracted with EtOAc (2 x 20 mL), organics combined, washed with brine (20 mL) and dried over $MgSO_4$. The organics were then concentrated *in vacuo* affording crude product as an orange oil. The crude residue was purified by flash column chromatography (eluent = 5 to 10 % EtOAc in hexanes, silica gel) to yield pure product as a colourless oil (2.41 g, 80% yield) as an 8:2 mixture of alkene stereoisomers.

Part 3

Crude methyl (Z)-2-phenylbut-2-enoate (2.0 g, 11 mmol) in 2M NaOH solution (33 mL) was heated at 50 °C for 2 h before being cooled to room temperature. The aqueous was extracted with Et_2O (30 mL) then acidified to pH 1 using 2M HCl. The acidified aqueous suspension was then extracted with CH_2Cl_2 (3 x 30 mL), organics combined and dried over $MgSO_4$, filtered and concentrated in vacuo to afford crude acid (1.83 g, 100 % yield).

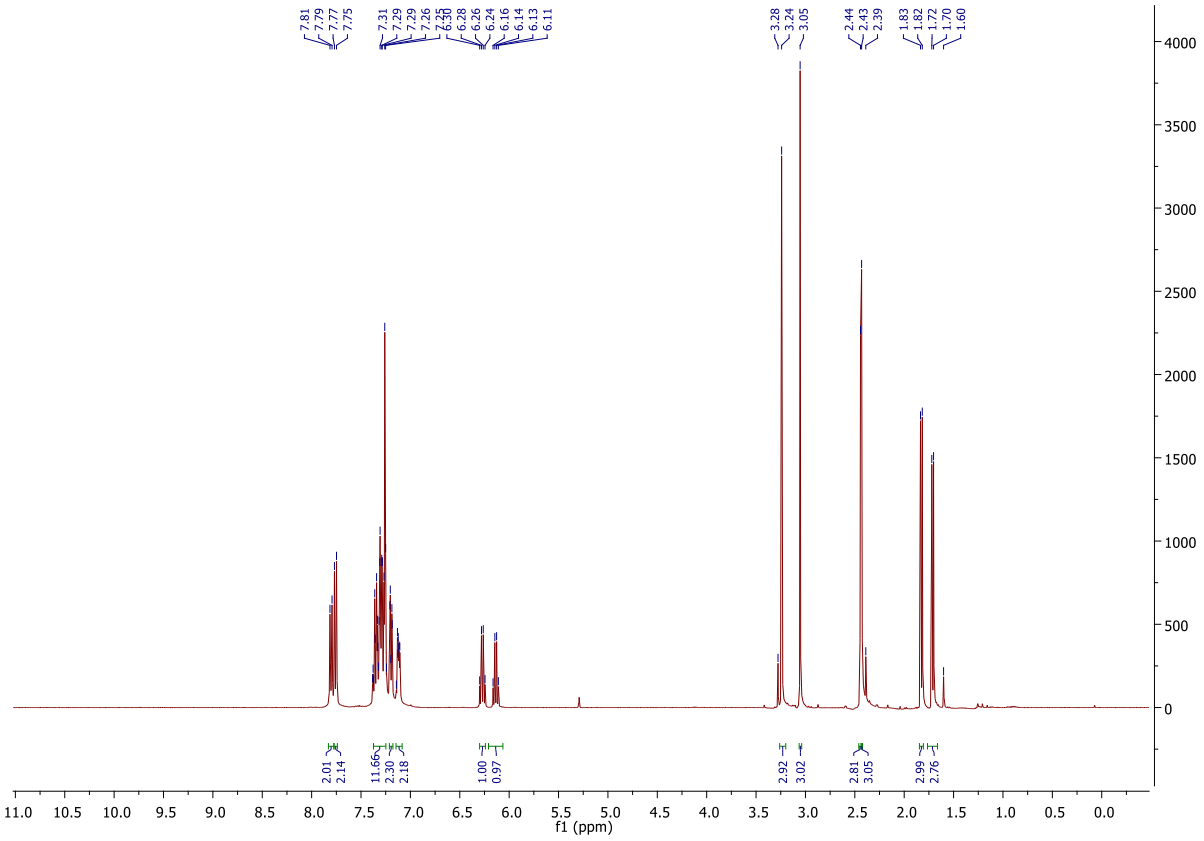
Part 4A:

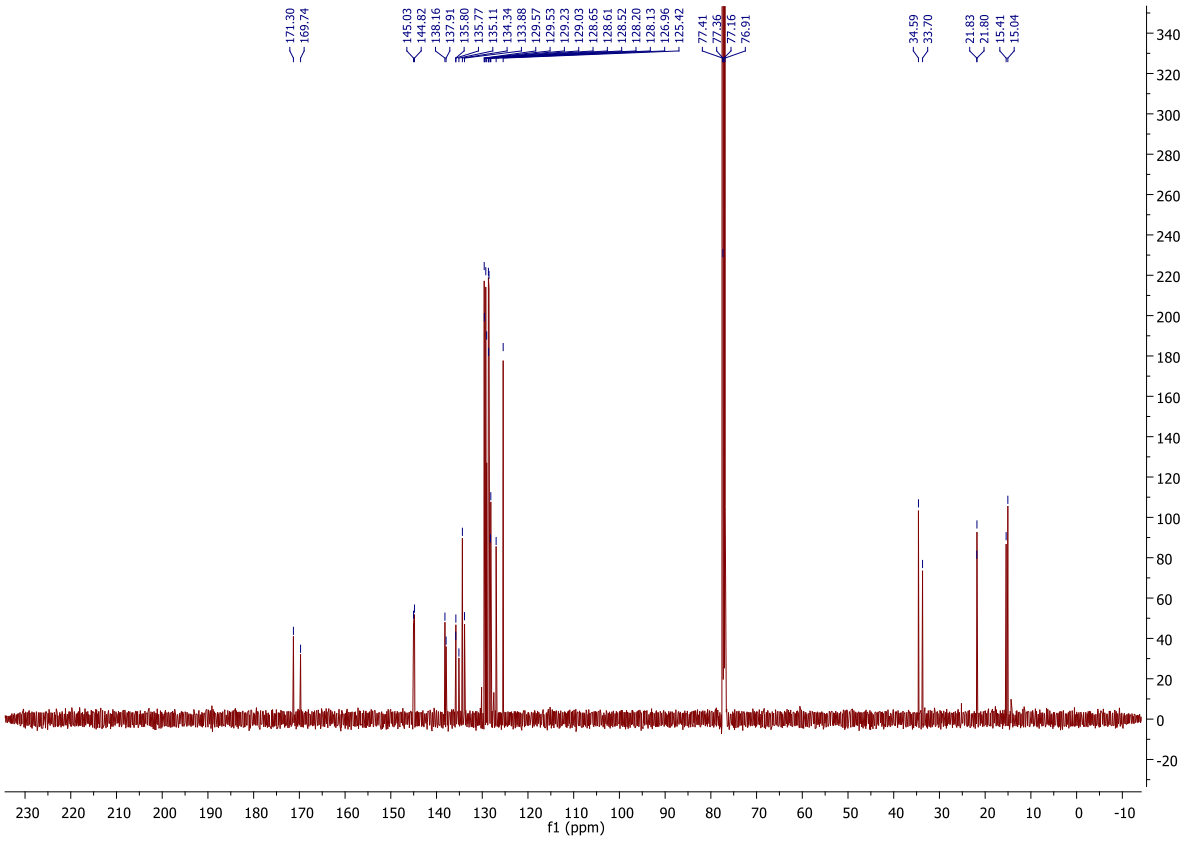
To a solution of (Z)-2-phenylbut-2-enoic acid (1.84 g, 11 mmol, 1 equiv.) in CH_2Cl_2 (33 mL) and DMF (3 drops) was added oxalyl chloride (2.16 g, 1.45 mL, 17 mmol, 1.5 equiv.) dropwise with concurrent gas evolution. The mixture was stirred at room temperature for 3 h until no gas evolution was observed. The solution was concentrated *in vacuo* and redissolved in CH_2Cl_2 (11 mL).

Part 4B:

A solution of N-methyl-N-tosylamine (1.85 g, 10 mmol, 1 equiv.), DMAP (122 mg, 1 mmol, 10 mol %) and triethylamine (3 mL, 2 equiv.) in CH_2Cl_2 (80 mL) was prepared and cooled to 0 °C using a salt/ice bath. The crude acyl chloride solution (1.1 equiv) prepared in **part 4A** was added dropwise and the mixture was stirred at 0 °C for 15 mins before being allowed to warm to room temperature and stir overnight. The reaction mixture was quenched with a saturated sodium bicarbonate solution (50 mL), layers separated and aqueous phase extracted with CH_2Cl_2 (2 x 40 mL). The organics were combined and dried over $MgSO_4$, filtered and concentrated *in vacuo* yielding crude product. The crude residue was purified by flash column chromatography (silica gel) to yield pure product **(S14B)** as a yellow oil (800 mg, 24% yield) as a 50:50 mixture of alkene stereoisomers.

R_f = 0.30 (eluent = 20% EtOAc in hexanes); *Data for (E) alkene stereoisomer:* **^{1}H NMR (400 MHz, $CDCl_3$)** δ_H: 1.83 (3H, d, *J* 7.2 Hz), 2.44 (3H, s), 3.05 (3H, s), 6.28 (1H, q, *J* 7.2 Hz), 7.17-7.20 (2H, m), 7.28-7.38 (5H, m), 7.74-7.78 (2H, m); **^{13}C NMR (126 MHz, $CDCl_3$)** δ_C: 15.0, 21.8, 34.6, 128.1, 128.5, 128.6, 129.2, 129.6, 133.8, 134.4, 135.8, 138.1, 144.8, 171.3; *Data for (Z) alkene stereoisomer:* **^{1}H NMR (400 MHz, $CDCl_3$)** δ_H: 1.71 (3H, d, *J* 7.2 Hz), 2.43 (3H, s), 3.24 (3H, s), 6.14 (1H, q, *J* 7.2 Hz), 7.08-7.14 (2H, m), 7.22-7.40 (5H, m), 7.80 (2H, d, *J* 8.3 Hz); **^{13}C NMR (126 MHz, $CDCl_3$)** δ_C: 15.4, 21.8, 33.7, 125.4, 126.9, 128.2, 128.6, 129.0, 129.5, 135.1, 135.8, 137.9, 145.0, 169.7.

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128.65
128.61
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128.13
126.96
125.42
77.41
77.36
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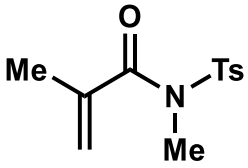
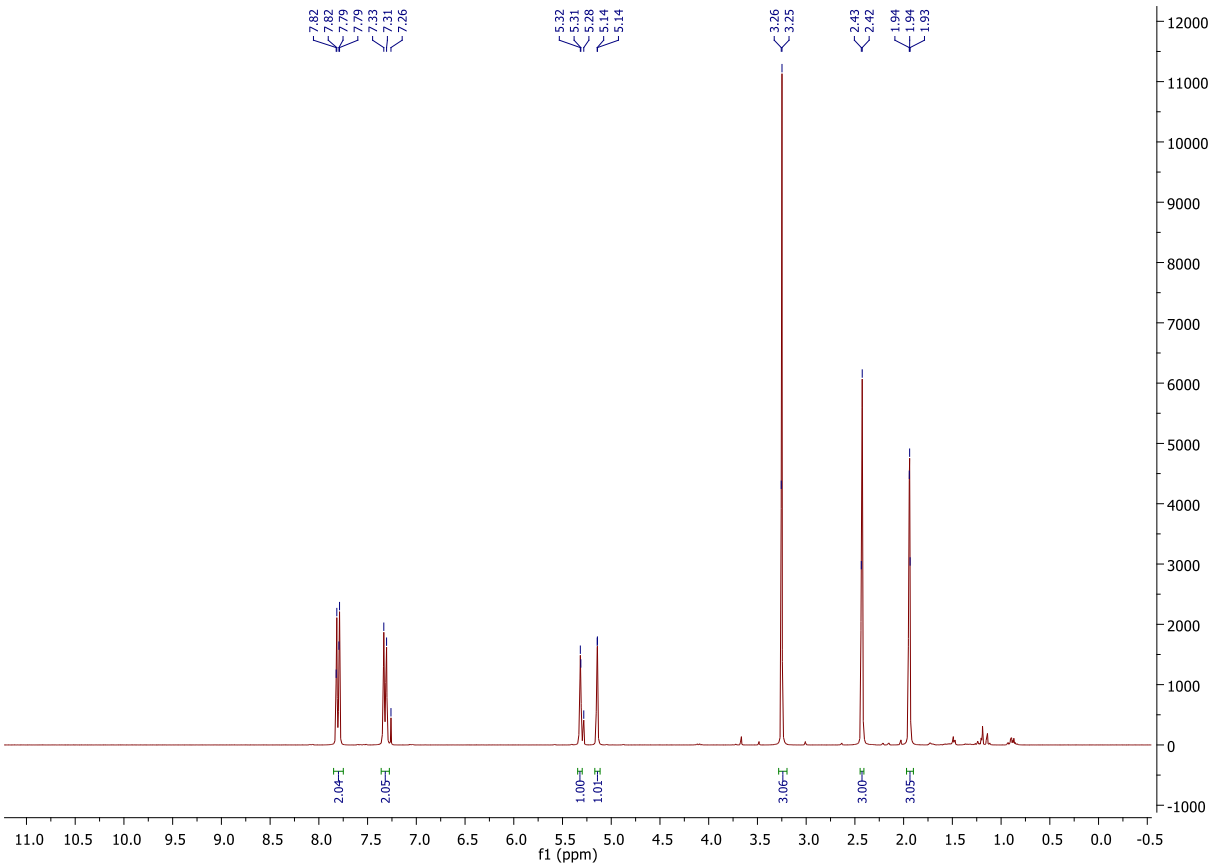
76.91
34.59
33.70
21.83
21.80
15.41
15.04
f1 (ppm)

(S15)



Prepared according to General Procedure D using N-methyl-p-toluenesulfonamide (1.85 g, 10.0 mmol), 4-dimethylaminopyridine (122 mg, 1.00 mmol), triethylamine (3.0 mL, 20.0 mmol), CH_2Cl_2 (80 mL) and methacryloyl chloride (2.09 g, 20.0 mmol). The crude residue was purified by flash column chromatography (eluent = 5 to 15% EtOAc in hexanes, silica gel) to afford product **(S15)** as a colourless oil (1.47 g, 58% yield).

R_f = 0.28 (eluent = 20% EtOAc in hexanes); **ν_{max} / cm^{-1}**(thin film) 2960, 1686, 1590, 1350, 1308, 1169, 1065, 935; **^{1}H NMR (300 MHz, $CDCl_3$)** δ_H: 1.89-1.98 (3H, m), 2.41-2.45 (3H, m), 3.24-3.26 (3H, m), 5.13-5.16 (1H, m), 5.30-5.34 (1H, m), 7.32 (2H, d, *J* 8.4 Hz), 7.80 (2H, d, *J* 8.4 Hz); **^{13}C NMR (75 MHz, $CDCl_3$)** δ_C: 19.7, 21.8, 34.4, 119.8, 128.3, 129.8, 135.8, 140.7, 145.0, 172.4; **HRMS (ES$^+$)** [$C_{12}H_{15}NO_3S$] requires [M^++ H^+] 254.0851, found 254.0861 (+ 3.9 ppm).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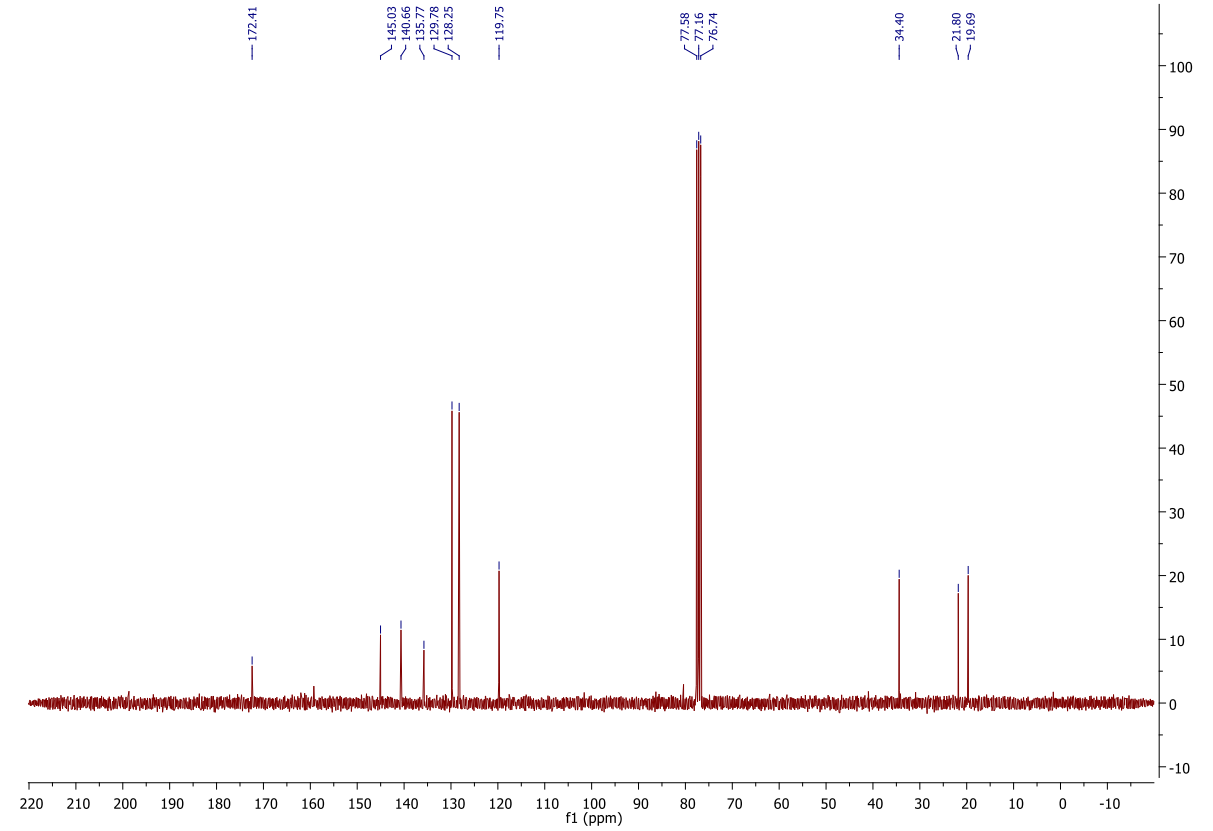
3.06
3.00
3.05
f1 (ppm)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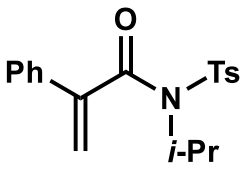
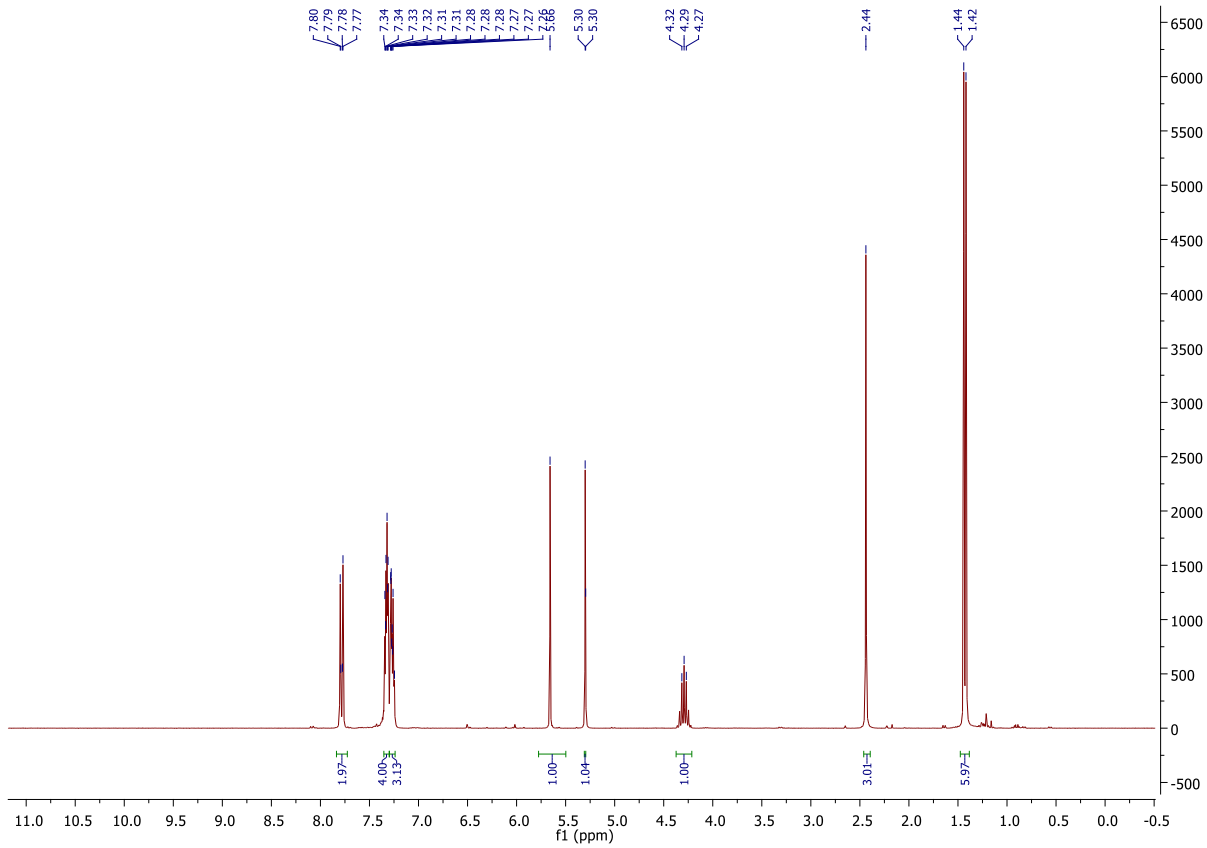
21.80
19.69
f1 (ppm)

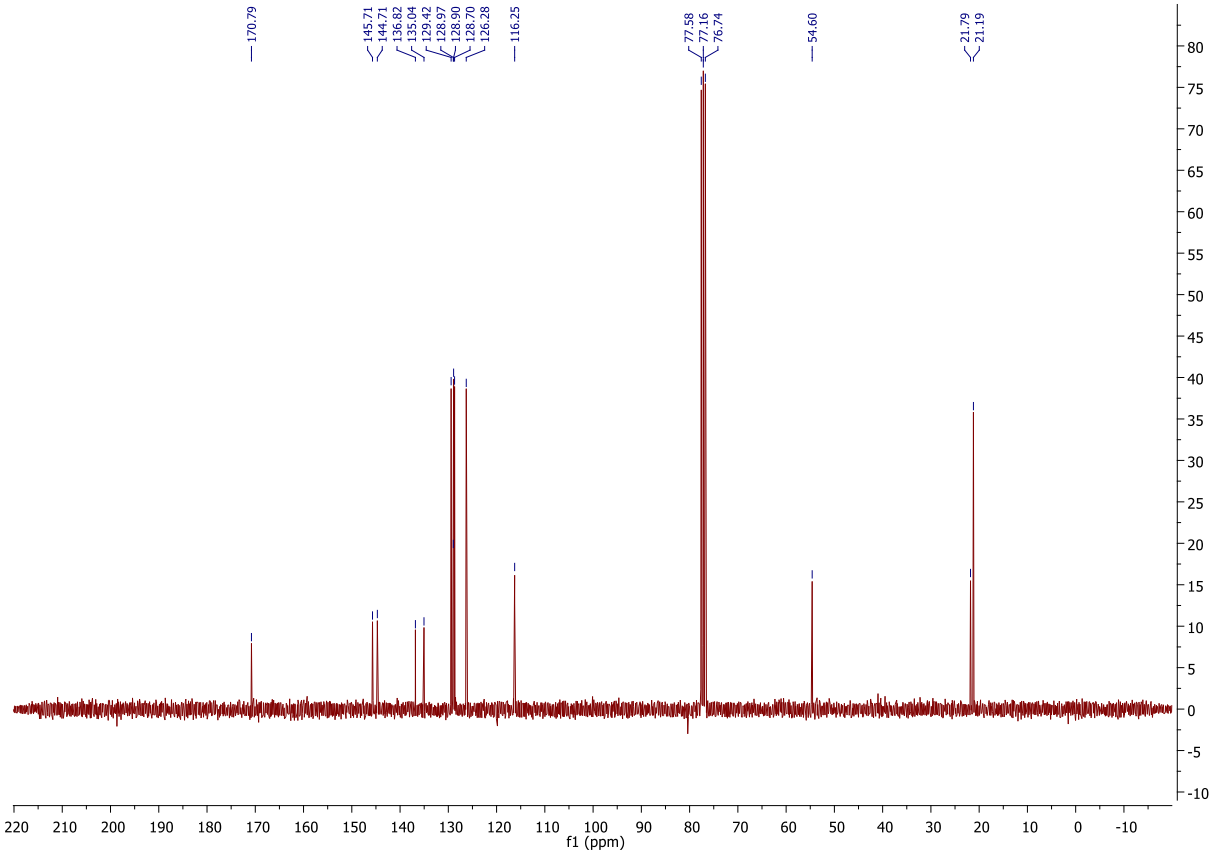
(S16)



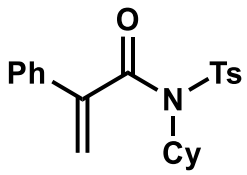
Prepared according to General Procedure C using N-isopropyl-p-toluenesulfonamide (1.07 g, 5.00 mmol), 4-dimethylaminopyridine (61.0 mg, 0.50 mmol), triethylamine (1.50 mL, 10.0 mmol), CH_2Cl_2 (40 mL) and phenacryloyl chloride (1.67 g, 10.0 mmol). The crude residue was purified by flash column chromatography (10 to 15% EtOAc in hexanes, silica gel) to afford product **(S16)** as a yellow oil (1.51 g, 88% yield).

R_f = 0.29 (eluent = 20% EtOAc in hexanes); **ν_{max} / cm^{-1}** (thin film) 2990, 1687, 1596, 1493, 1339, 1309, 1157, 1083 ; **^{1}H NMR (300 MHz, $CDCl_3$)** δ_H: 1.43 (6H, d, *J* 6.8 Hz), 2.44 (3H, s), 4.29 (1H, hept, *J* 6.8 Hz), 5.30 (1H, s), 5.66 (1H, s), 7.27 (3H, m), 7.30-7.38 (4H, m), 7.72-7.85 (2H, m); **^{13}C NMR (75 MHz, $CDCl_3$)** δ_C: 21.1, 21.7, 54.5, 116.2, 126.2, 128.6, 128.8, 128.9, 129.3, 134.9, 136.7, 144.6, 145.6, 170.7; **HRMS (ES$^+$)** [$C_{19}H_{22}NO_3S$] requires $[M+H]^+$ 344.1320, found 344.1316 (- 1.2 ppm).


7.80
7.79
7.78
7.77
7.34
7.34
7.33
7.32
7.31
7.28
7.28
7.28
7.27
7.27
7.26
5.66
5.30
5.30
4.32
4.29
4.27
2.44
1.44
1.42
1.97
4.00
3.13
1.00
1.04
1.00
3.01
5.97
f1 (ppm)

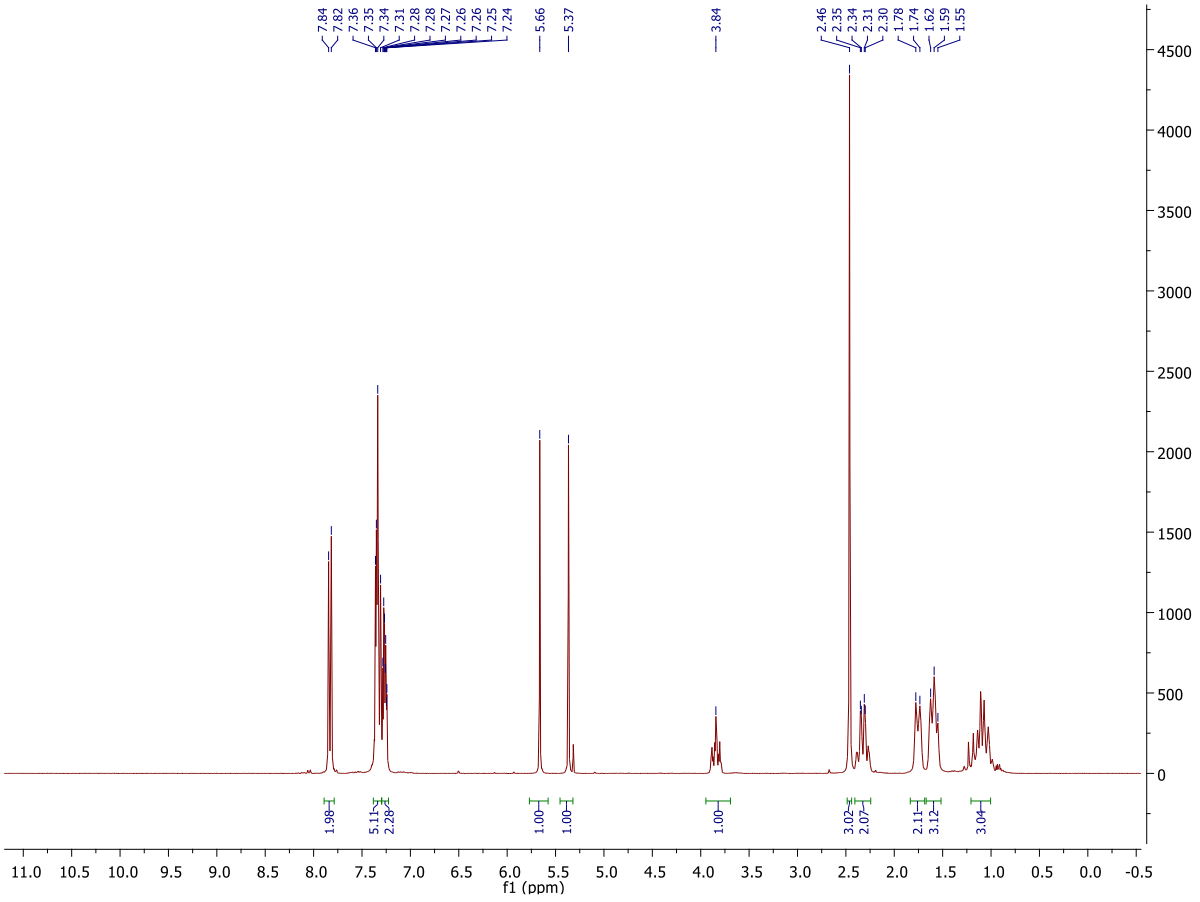

170.79
145.71
144.71
136.82
135.04
129.42
128.97
128.90
128.70
126.28
116.25
77.58
77.16
76.74
54.60
21.79
21.19
f1 (ppm)

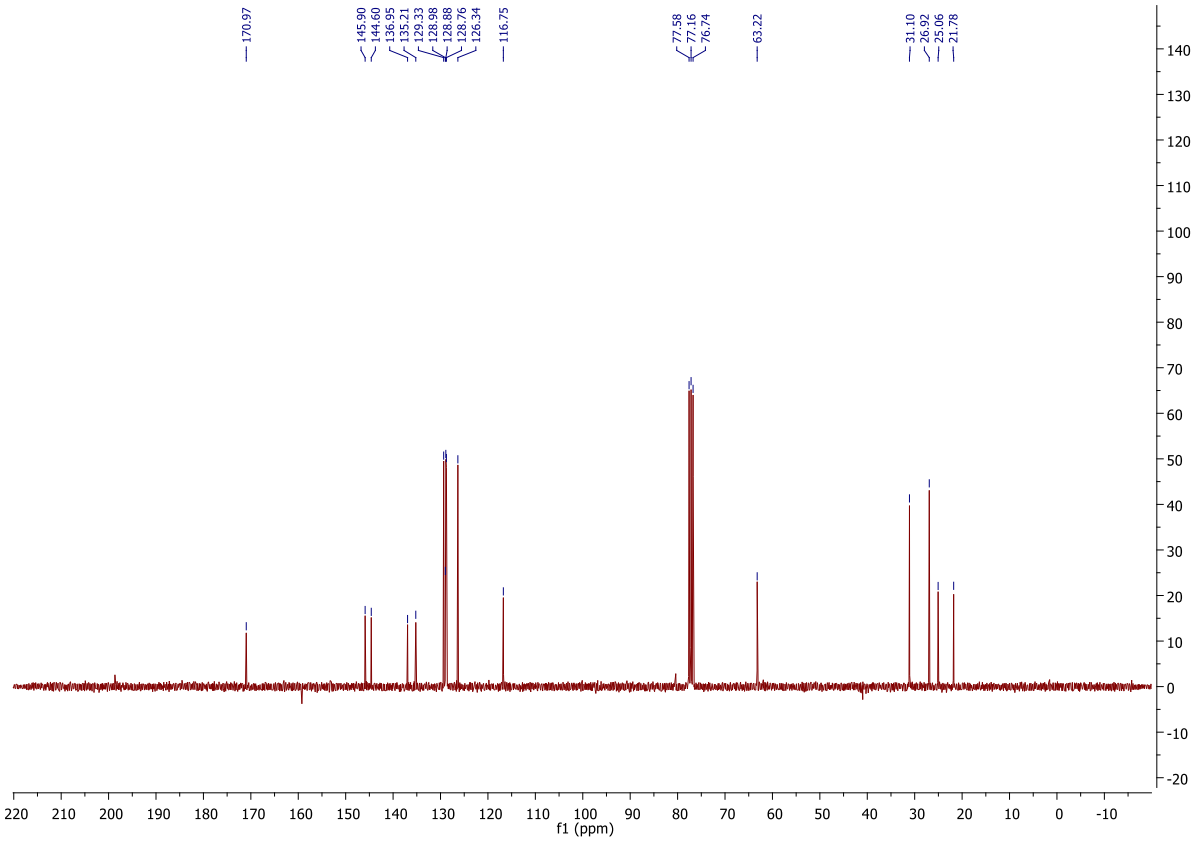
(S17)



Prepared according to General Procedure C using N-cyclohexyl-p-toluenesulfonamide (1.27 g, 5.00 mmol), 4-dimethylaminopyridine (61.0 mg, 0.50 mmol), triethylamine (1.50 mL, 10.0 mmol), CH_2Cl_2 (40 mL) and phenacryloyl chloride (1.67 g, 10.0 mmol). The crude residue was purified by flash column chromatography (eluent = 10 to 15% EtOAc in hexanes, silica gel) to afford product **(S17)** as an off white solid (902 mg, 47% yield).

Mp.: 105-107 °C; **R_f=** 0.30 (eluent = 20% EtOAc in hexanes); **ν_{max} / cm^{-1}**(thin film) 2945, 2850, 1682, 1596, 1496, 1456, 1449, 1385, 1350, 1330, 1305, 1287, 1204, 1163, 1139, 1075; **^{1}H NMR (300 MHz, $CDCl_3$)** δ_H: 0.97-1.25 (3H, m), 1.59 (3H, m), 1.76 (2H, d, *J* 12.7 Hz), 2.23-2.40 (2H, m), 2.46 (3H, s), 3.84 (1H, tt, *J* 12.0, 3.5 Hz), 5.37 (1H, s), 5.66 (1H, s), 7.22-7.39 (7H, m), 7.83 (2H, d, *J* 8.4Hz); **^{13}C NMR (75 MHz, $CDCl_3$)** δ_C: 21.8, 25.1, 26.9, 31.1, 63.2, 116.8, 126.3, 128.8, 128.9, 129.0, 129.3, 135.2, 137.0, 144.6, 145.9, 171.0; **HRMS (ES$^+$)** [$C_{22}H_{25}NO_3S$] requires $[M+H]^+$ 384.1633, found 384.1627 (- 1.6 ppm).


7.84
7.82
7.36
7.35
7.34
7.31
7.28
7.28
7.27
7.26
7.26
7.25
7.24
5.66
5.37
3.84
2.46
2.35
2.34
2.31
2.30
1.78
1.74
1.62
1.59
1.55
1.98
5.11
2.28
1.00
1.00
1.00
3.02
2.07
2.11
3.12
3.04
f1 (ppm)


170.97
145.90
144.60
136.95
135.21
129.33
128.98
128.88
128.76
126.34
116.75
77.58
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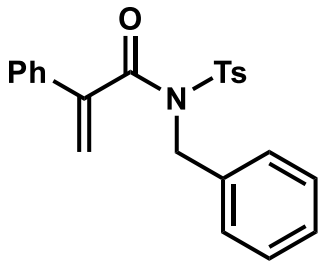
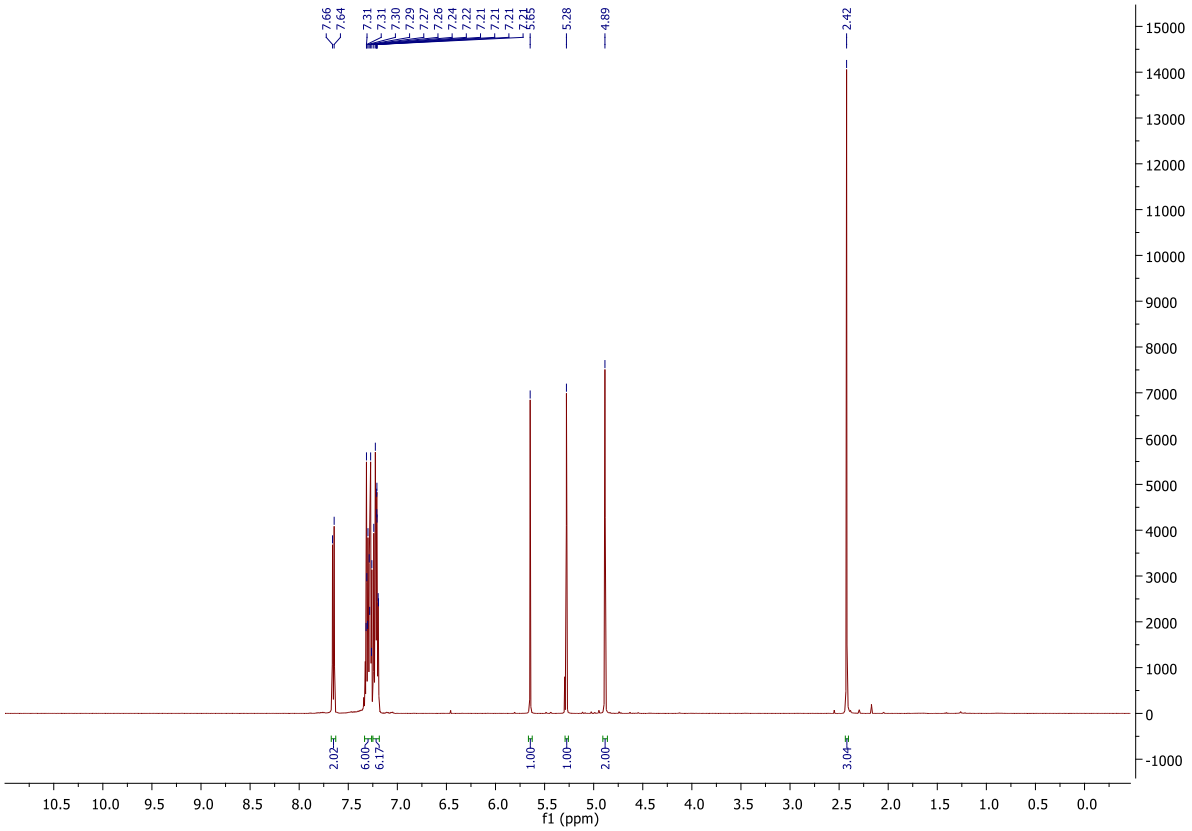
76.74
63.22
31.10
26.92
25.06
21.78
f1 (ppm)

(S18)



Prepared according to General Procedure C using N-benzyl-p-toluenesulfonamide (1.30 g, 5.00 mmol), 4-dimethylaminopyridine (61.0 mg, 0.50 mmol), triethylamine (1.50 mL, 10.0 mmol), CH_2Cl_2 (40 mL) and phenacryloyl chloride (1.67 g, 10.0 mmol). The crude residue was purified by flash column chromatography (eluent = 10 to 15% EtOAc in hexanes, silica gel) to afford product **(S18)** as a white solid (1.33 g, 68% yield).

Mp.: 126-129 °C; $\mathbf{R_f}$ = 0.26 (eluent = 20% EtOAc in hexanes); $\mathbf{\nu_{max}}$ **/ cm^{-1}** (thin film) 2982, 2971, 1683, 1558, 1495, 1458, 1352, 1162, 1078 ; **^{1}H NMR (500 MHz, $CDCl_3$)** δ_H: 2.42 (3H, s), 4.89 (2H, s), 5.28 (1H, s), 5.65 (1H, s), 7.19-7.24 (6H, m), 7.26-7.33 (6H, m), 7.65 (2H, d, *J* 8.3 Hz); **^{13}C NMR (126 MHz, $CDCl_3$)** δ_C: 21.7, 50.4, 118.1, 125.8, 127.6, 127.7, 128.6, 128.9, 128.9, 129.0, 129.3, 134.6, 136.0, 136.5, 144.2, 144.9, 170.4; **HRMS (ES$^+$)** [$C_{23}H_{21}NO_3S$] requires $[M+H]^+$ 392.1320, found 392.1315 (- 1.3 ppm).


7.66
7.64
7.31
7.31
7.30
7.29
7.27
7.26
7.24
7.22
7.21
7.21
7.21
5.85
5.28
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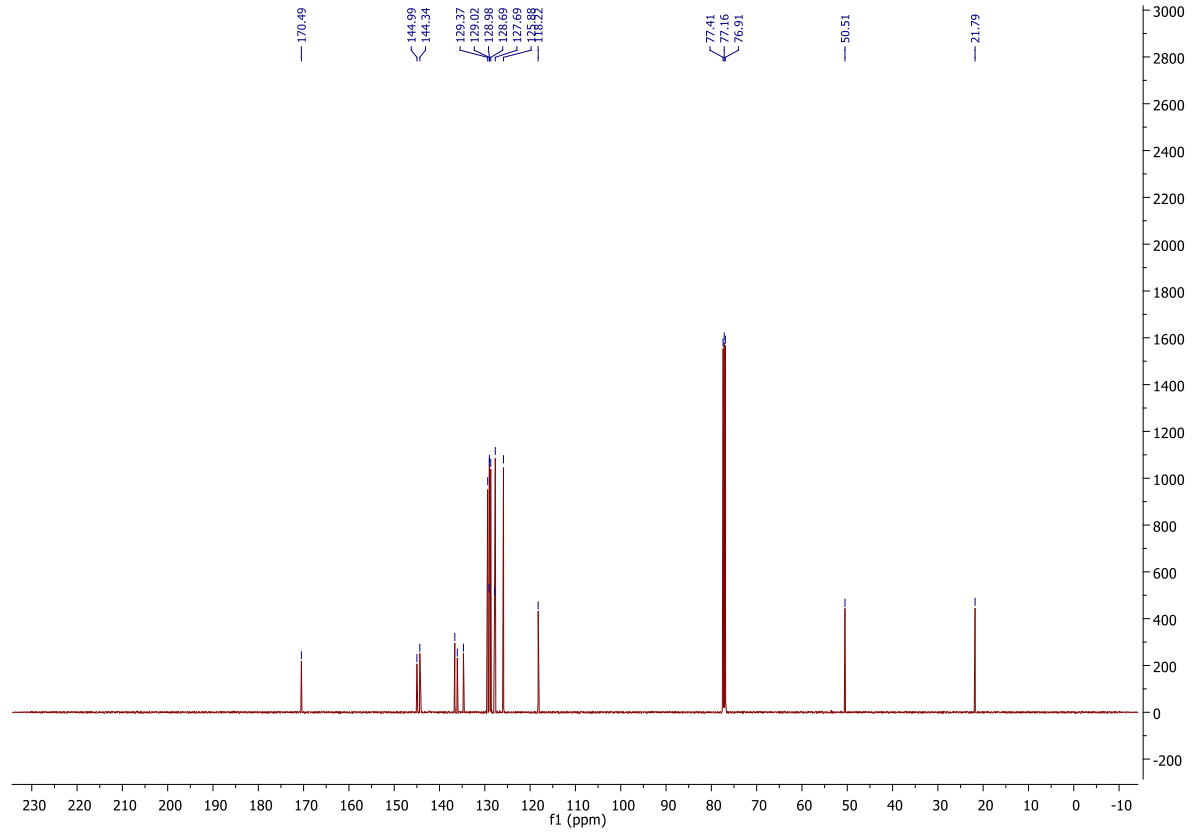
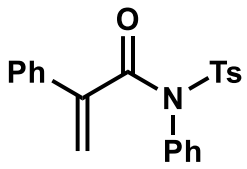
6.00
6.17
1.00
1.00
2.00
3.04
f1 (ppm)

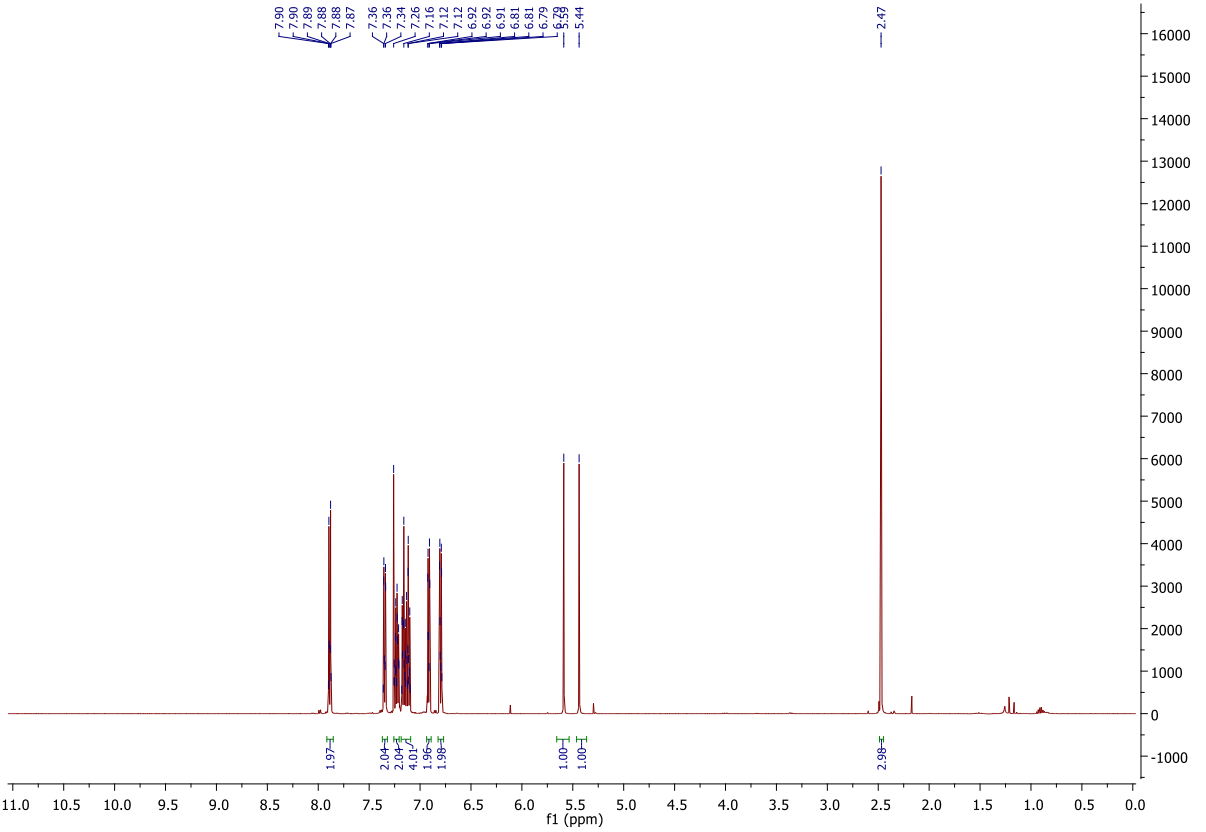

170.49
144.99
144.34
129.37
129.02
128.98
128.69
127.69
77.41
77.16
76.91
50.51
21.79
f1 (ppm)

(S19)



Prepared according to General Procedure C using N-phenyl-p-toluenesulfonamide (1.24 g, 5.00 mmol), 4-dimethylaminopyridine (61.0 mg, 0.50 mmol), triethylamine (1.50 mL, 10.0 mmol), CH_2Cl_2 (40 mL) and phenacryloyl chloride (1.67 g, 10.0 mmol). The crude residue was purified by flash column chromatography (eluent = 50-80% CH_2Cl_2 in hexanes, silica gel) to afford product **(S19)** as a yellow solid (1.45 g, 76% yield).

Mp.: 111-113 °C; $\mathbf{R_f}$ = 0.66 (eluent = 30% EtOAc in hexanes); $\mathbf{\nu_{max}}$ **/ cm^{-1}**(thin film) 2990, 1694, 1594, 1490, 1338, 1237, 1163, 1080 ; **^{1}H NMR (500 MHz, $CDCl_3$)** δ_H: 2.47 (3H, s), 5.44 (1H, s) 5.59 (1H, s), 6.77-6.82 (2H, m), 6.89-6.93 (2H, m), 7.08-7.20 (2H, m), 7.19-7.27 (3H, m), 7.33-7.37 (2H, m), 7.86-7.92 (2H, m); **^{13}C NMR (126 MHz, $CDCl_3$)** δ_C: 21.8, 122.1, 126.3, 128.4, 128.4, 128.5, 129.0, 129.3, 129.4, 130.7, 135.6, 135.7, 135.8, 144.9, 145.4, 169.7; **HRMS (ES$^+$)** [$C_{22}H_{19}NO_3S$] requires 378.1164 $[M+H]^+$, found 378.1159 (-1.3 ppm)


7.90
7.90
7.89
7.88
7.88
7.87
7.36
7.36
7.34
7.26
7.16
7.12
7.12
6.92
6.92
6.91
6.81
6.81
6.79
6.79
5.59
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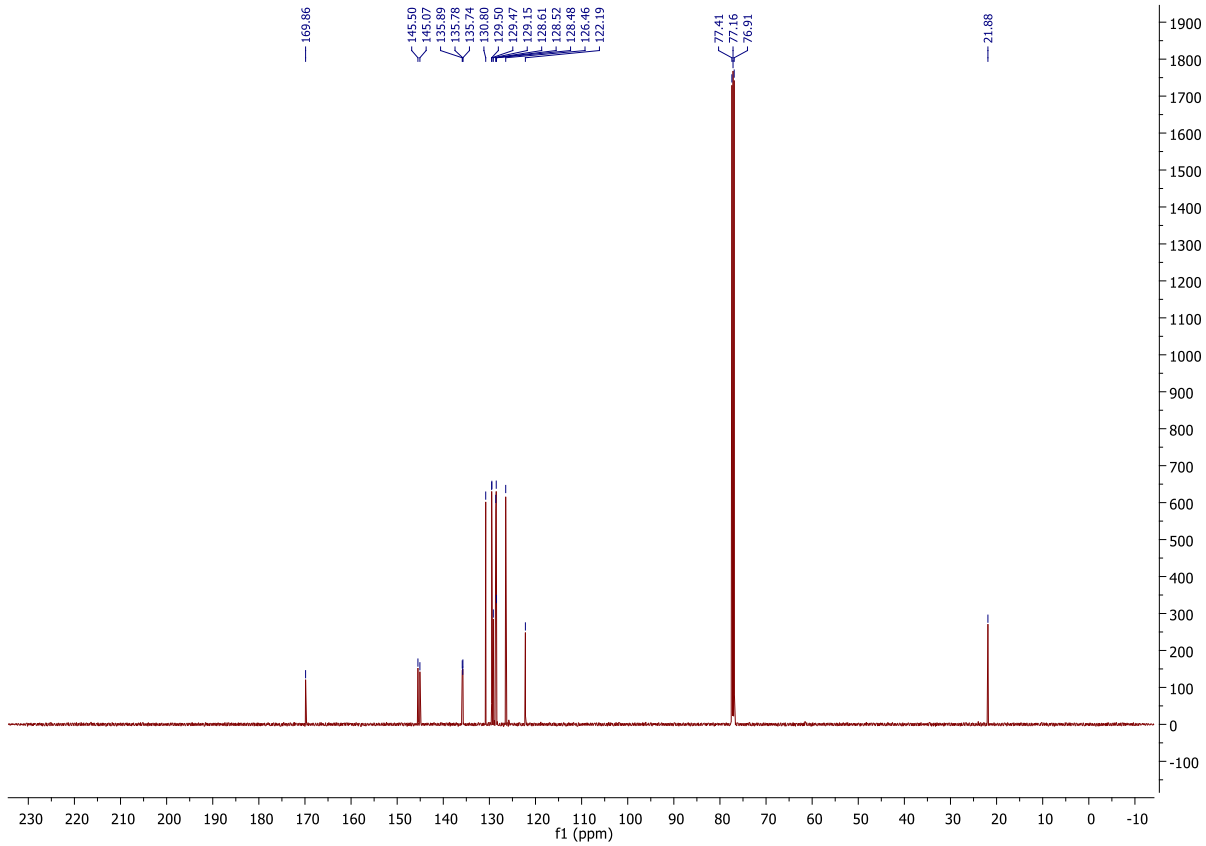
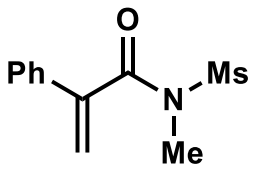
4.01
1.96
1.98
1.00
1.00
2.98
f1 (ppm)

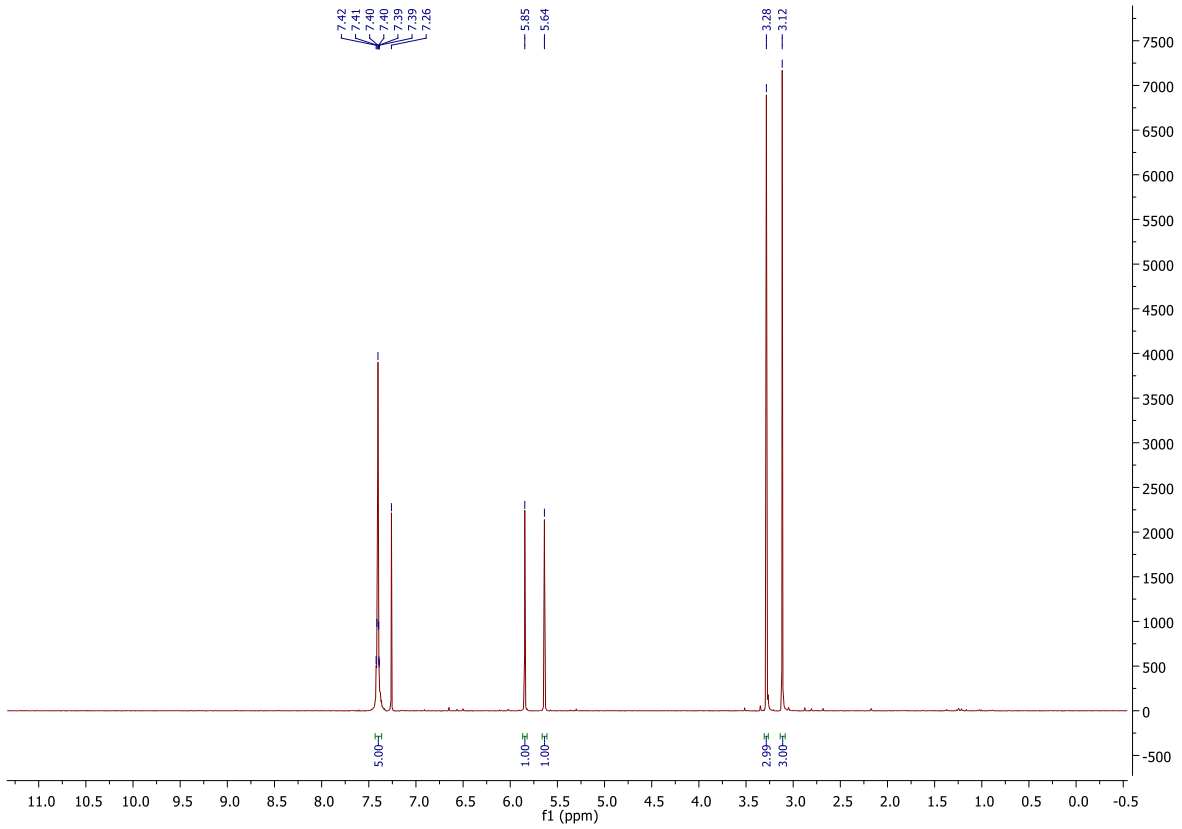

169.86
145.50
145.07
135.89
135.78
135.74
130.80
129.50
129.47
129.15
128.61
128.52
128.48
126.46
122.19
77.41
77.16
76.91
21.88
f1 (ppm)

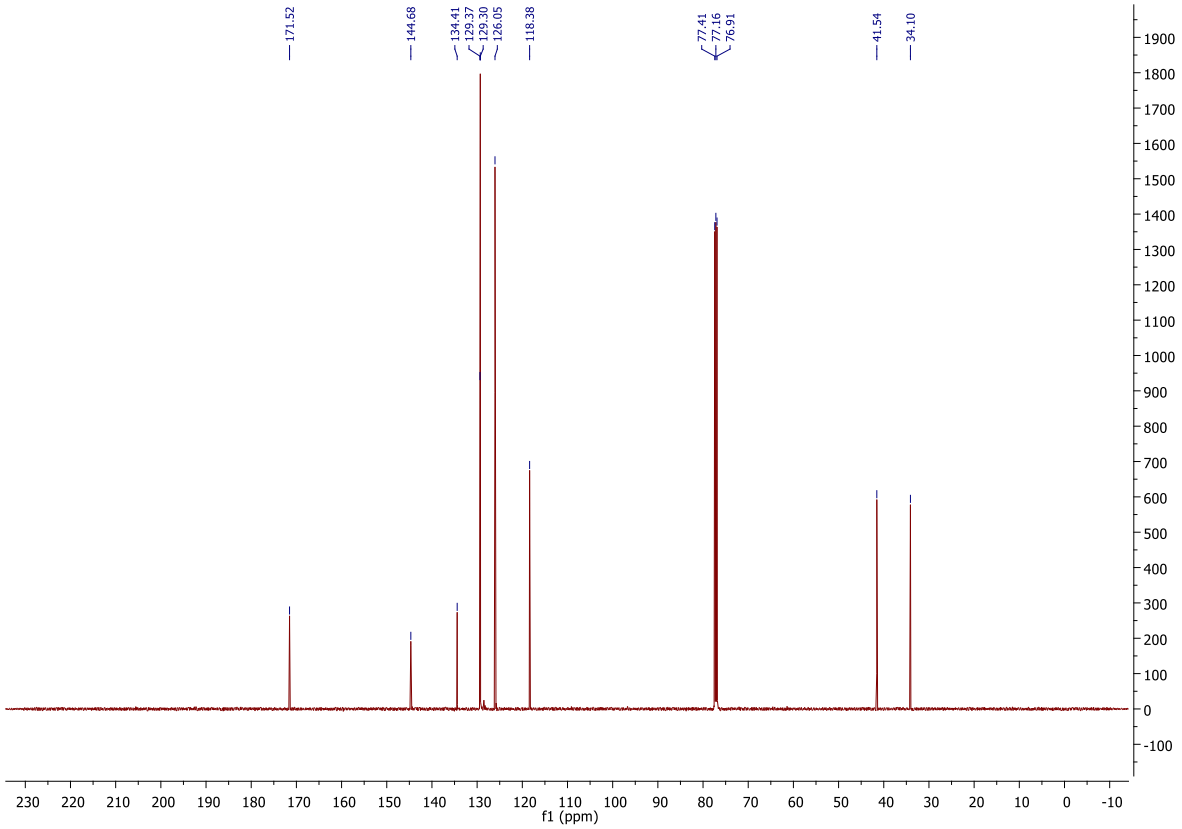
(S20)



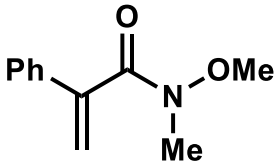
Prepared according to General Procedure C using N-methylmethanesulfonamide (550 mg, 5.00 mmol), 4-dimethylaminopyridine (61.0 mg, 1.00 mmol), triethylamine (1.50 mL, 10.0 mmol), CH_2Cl_2 (40 mL) and phenacryloyl chloride (1.67 g, 10.0 mmol). The crude residue was purified by flash column chromatography (eluent = 20 to 40% EtOAc in hexanes, silica gel) to afford product **(S20)** as an off-white solid (500 mg, 42% yield).

Mp.: 63-66 °C **R_f** = 0.28 (eluent = 30% EtOAc in hexanes); **ν_{max} / cm^{-1}** (thin film) 2990, 1682, 1495, 1460, 1342, 1323, 1246, 1167, 1121, 1049**; ^{1}H NMR (300 MHz, $CDCl_3$)** δ_H: 3.12 (3H, s), 3.28 (3H, s), 5.64 (1H, s), 5.85 (1H, s), 7.36-7.44 (5H, m); **^{13}C NMR (126 MHz, $CDCl_3$)** δ_C: 34.1, 41.5, 118.4, 126.1, 129.3, 129.4, 134.4, 144.7, 171.5; **HRMS (ES$^+$)** [$C_{21}H_{17}NO$] requires [M+ Na]$^+$ 262.0514, found 262.0519 (+ 1.9 ppm).


7.42
7.41
7.40
7.40
7.39
7.39
7.26
5.85
5.64
3.28
3.12
5.00
1.00
1.00
2.99
3.00
f1 (ppm)

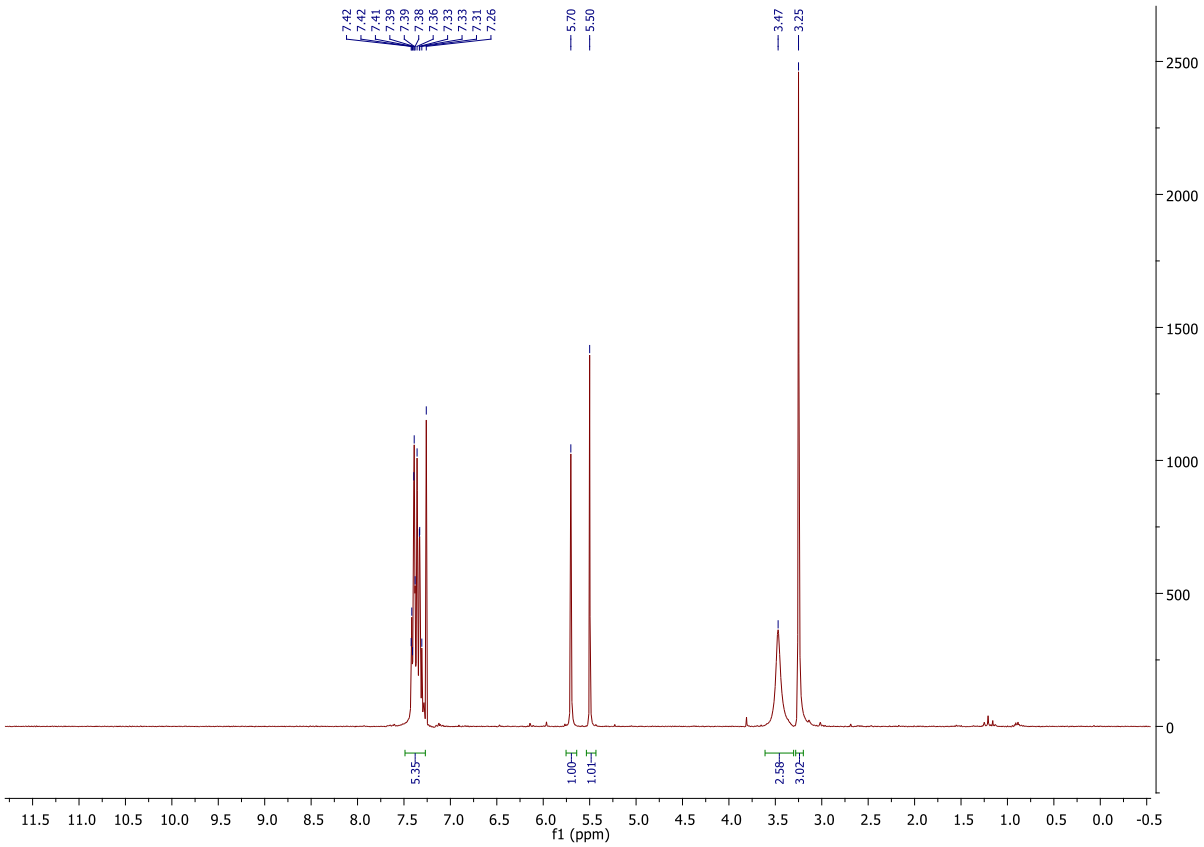

171.52
144.68
134.41
129.37
129.30
126.05
118.38
77.41
77.16
76.91
41.54
34.10
f1 (ppm)

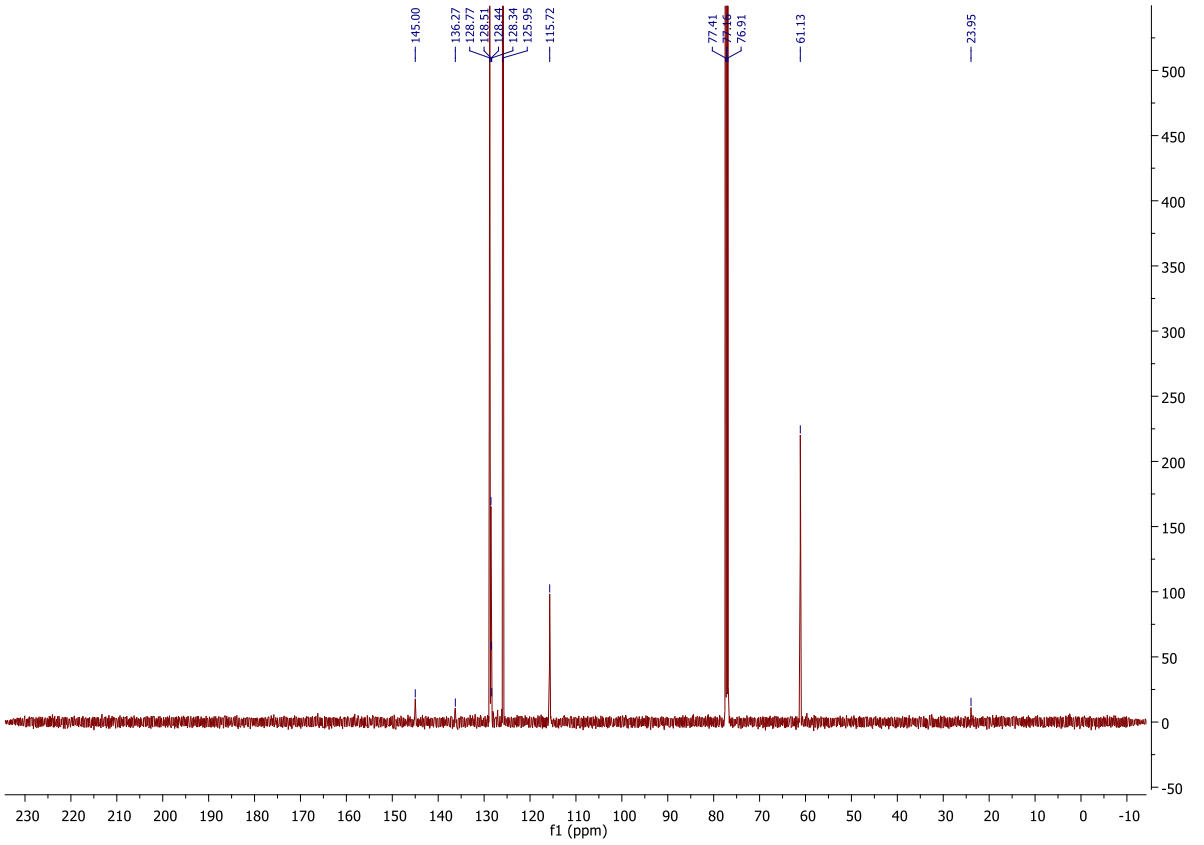
(S21)



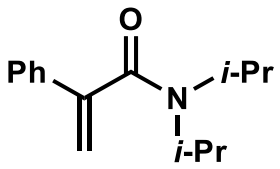
Prepared according to General Procedure using N,O-Dimethylhydroxylamine (490 mg, 5.00 mmol, 1 equiv.), 4-dimethylaminopyridine (61.0 mg, 1.00 mmol), triethylamine (1.50 mL, 10.0 mmol), CH_2Cl_2 (40 mL) and phenacryloyl chloride (1.67 g, 10.0 mmol). The crude residue was purified by flash column chromatography (eluent = 20 to 35% EtOAc in hexanes, silica gel) to afford product (**S21**) as a yellow oil (422 mg, 42% yield).

R_f = 0.30 (eluent = 35% EtOAc in hexanes); **ν_{max} / cm^{-1}** (thin film): 2934, 1651, 1497, 1421, 1377, 1177,1119, 1070, 995; **^{1}H NMR (300 MHz, $CDCl_3$)** δ_H: 3.25 (3H, s), 3.47 (3H, s), 5.50 (1H, s), 5.70 (1H, s), 7.27-7.48 (5H, m); **^{13}C NMR (126 MHz, $CDCl_3$)** δ_C: 24.0, 61.1, 115.7, 126.0, 128.3, 128.4, 128.5, 128.8, 136.3, 145.0; **HRMS (ES$^+$)** [$C_{11}H_{13}NO_2$] requires $[M+Na]^+$ 192.1025, found 192.1024 (-0.5 ppm).


7.42
7.42
7.41
7.39
7.39
7.38
7.36
7.33
7.33
7.31
7.26
5.70
5.50
3.47
3.25
5.35
1.00
1.01
2.58
3.02
f1 (ppm)

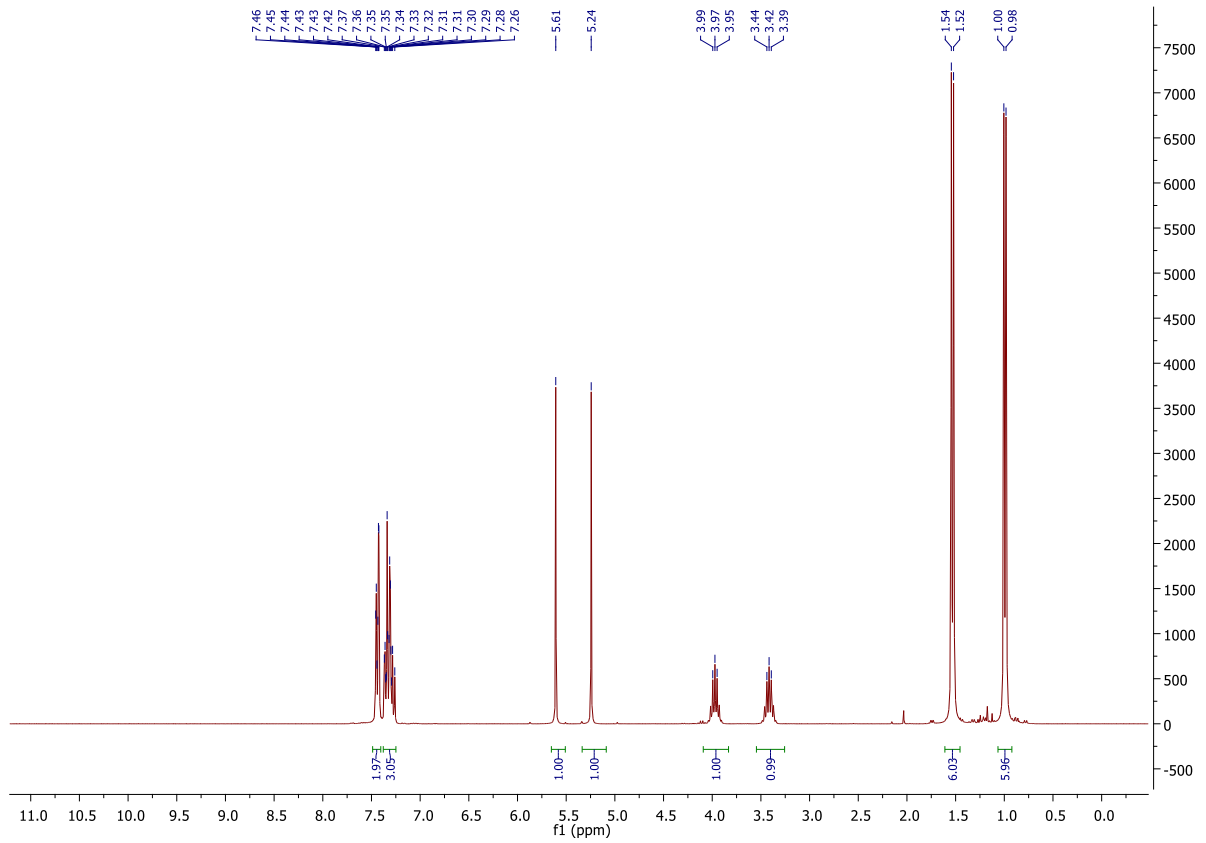

145.00
136.27
128.77
128.51
128.44
128.34
125.95
115.72
77.41
77.16
76.91
61.13
23.95
f1 (ppm)

(S22)



Prepared according to General Procedure C using diisopropylamine (1.52 g, 15.0 mmol, 1.5 equiv.), 4-dimethylaminopyridine (122 mg, 1.00 mmol), triethylamine (1.50 mL, 10.0 mmol), CH_2Cl_2 (40 mL) and phenacryloyl chloride (1.67 g, 10.0 mmol). The crude residue was purified by flash column chromatography (eluent = 5 to 15% EtOAc in hexanes, silica gel) to afford product **(S22)** (2.00 g, 86% yield).

Mp.: 80-83 °C (Lit. 81-82°C); $\mathbf{R_f}$ = 0.36 (eluent = 20% EtOAc in hexanes); $\mathbf{\nu_{max}}$ **/ cm^{-1}**(thin film) 2970, 1625, 1496, 1444, 1371, 1258, 1153, 1135, 1041, 903 ; **^{1}H NMR (300 MHz, $CDCl_3$)** δ_H: 0.99 (6H, d, *J* 6.7 Hz), 1.53 (6H, d, *J* 6.7 Hz), 3.42 (1H, hept, *J* 6.7 Hz), 3.97 (1H, hept, *J* 6.7 Hz), 5.61 (1H, s), 7.27-7.38 (3H, m), 7.40-7.48 (2H, m); **^{13}C NMR (75 MHz, $CDCl_3$)** δ_C : 20.4, 20.5, 45.6, 50.7, 111.5, 125.6, 128.4, 128.7, 135.9, 146.7, 170.1; **HRMS (ES$^+$)** [$C_{15}H_{21}NO$] requires $[M+H]^+$ 232.1701, found 232.1706 (+ 2.2 ppm).


7.46
7.45
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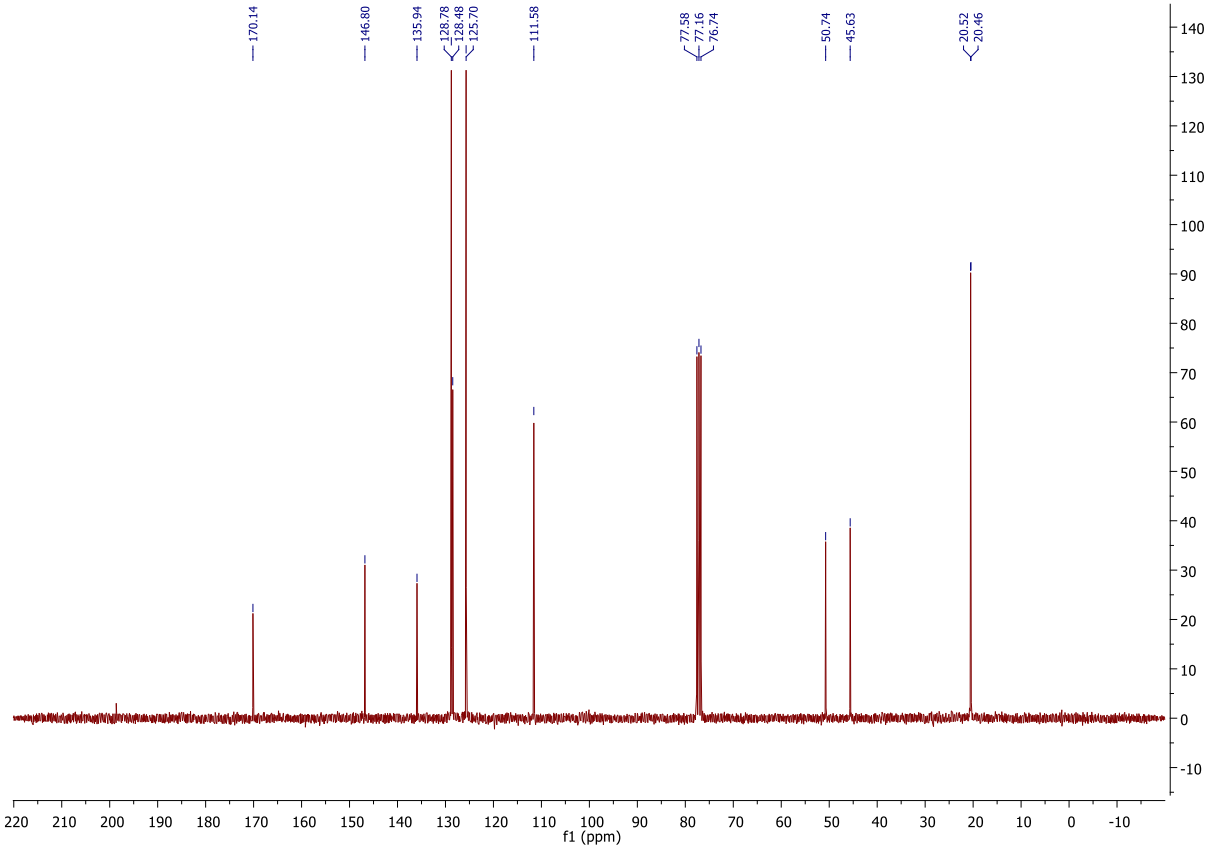
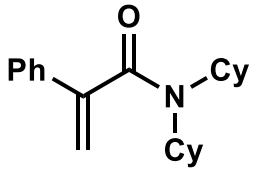
7.43
7.43
7.42
7.37
7.36
7.35
7.35
7.34
7.33
7.32
7.31
7.31
7.30
7.29
7.28
7.26
5.61
5.24
3.99
3.97
3.95
3.44
3.42
3.39
1.54
1.52
1.00
0.98
1.97
3.05
1.00
1.00
1.00
0.99
6.03
5.96
f1 (ppm)

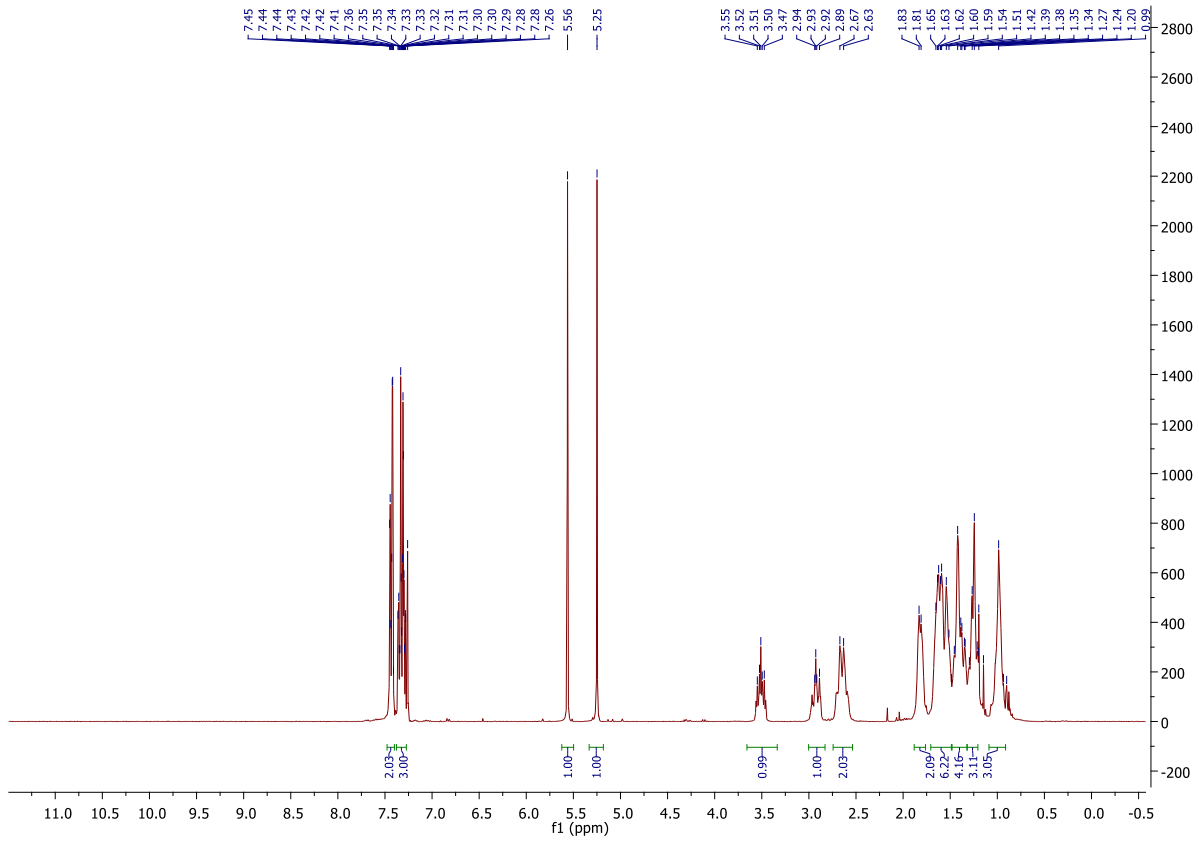

170.14
146.80
135.94
128.78
128.48
125.70
111.58
77.58
77.16
76.74
50.74
45.63
20.52
20.46
f1 (ppm)

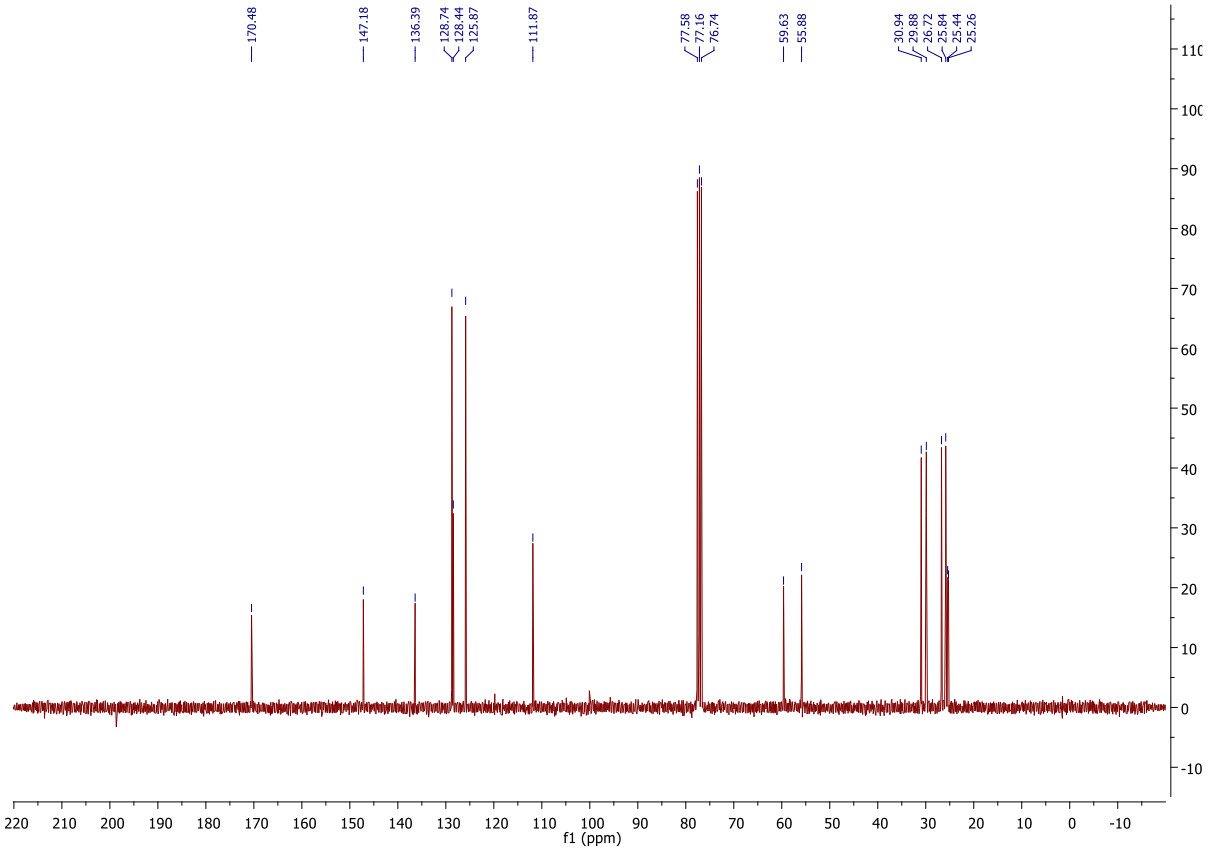
(S23)



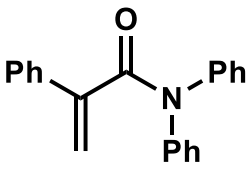
Prepared according to General Procedure C using dicyclohexylamine (1.81 g, 10.0 mmol), 4-dimethylaminopyridine (122 mg, 1.00 mmol), triethylamine (3.0 mL, 20.0 mmol), CH_2Cl_2 (80 mL) and phenacryloyl chloride (3.33 g, 20.0 mmol). The crude residue was purified by flash column chromatography (eluent = 5 to 15% EtOAc in hexanes, silica gel) to afford product **(S23)** as a white solid (2.58 g, 83% yield).

Mp.: 95-98 °C; **R_f** = 0.45 (eluent = 20% EtOAc in hexanes); **ν_{max} / cm^{-1}**(thin film) 2957, 2926, 2853, 1622, 1575, 1495, 1455, 1448, 1370, 1230, 1184, 1146, 1126 ; **^{1}H NMR (300 MHz, $CDCl_3$)** δ_H : 0.96 (3H, m), 1.20-1.30 (3H, m), 1.35-1.51 (4H, m), 1.54-1.69 (6H, m), 1.80 (2H, m), 2.65 (2H, m), 2.93 (1H, m), 3.42-3.60 (1H, m), 5.25 (1H, s), 5.56 (1H, s), 7.27-7.37 (3H, m), 7.38-7.48 (2H, m); **^{13}C NMR (75 MHz, $CDCl_3$)** δ_C : 25.2, 25.3, 25.7, 26.6, 29.8, 30.9, 55.8, 59.5, 111.8, 125.8, 128.3, 128.6, 136.3, 147.1, 170.4; **HRMS (ES$^+$)** [$C_{21}H_{30}NO$] requires $[M+H]^+$ 312.2327, found 312.2329 (+ 0.6 ppm)


7.45
7.44
7.44
7.43
7.42
7.42
7.41
7.36
7.35
7.35
7.34
7.33
7.33
7.32
7.31
7.31
7.30
7.30
7.29
7.28
7.28
7.26
5.56
5.25
3.55
3.52
3.51
3.50
3.47
2.94
2.93
2.92
2.89
2.67
2.63
1.83
1.81
1.65
1.63
1.62
1.60
1.59
1.54
1.51
1.42
1.39
1.38
1.35
1.34
1.27
1.24
1.20
0.99
2.03
3.00
1.00
1.00
0.99
1.00
2.03
2.09
6.22
4.16
3.11
3.05
f1 (ppm)

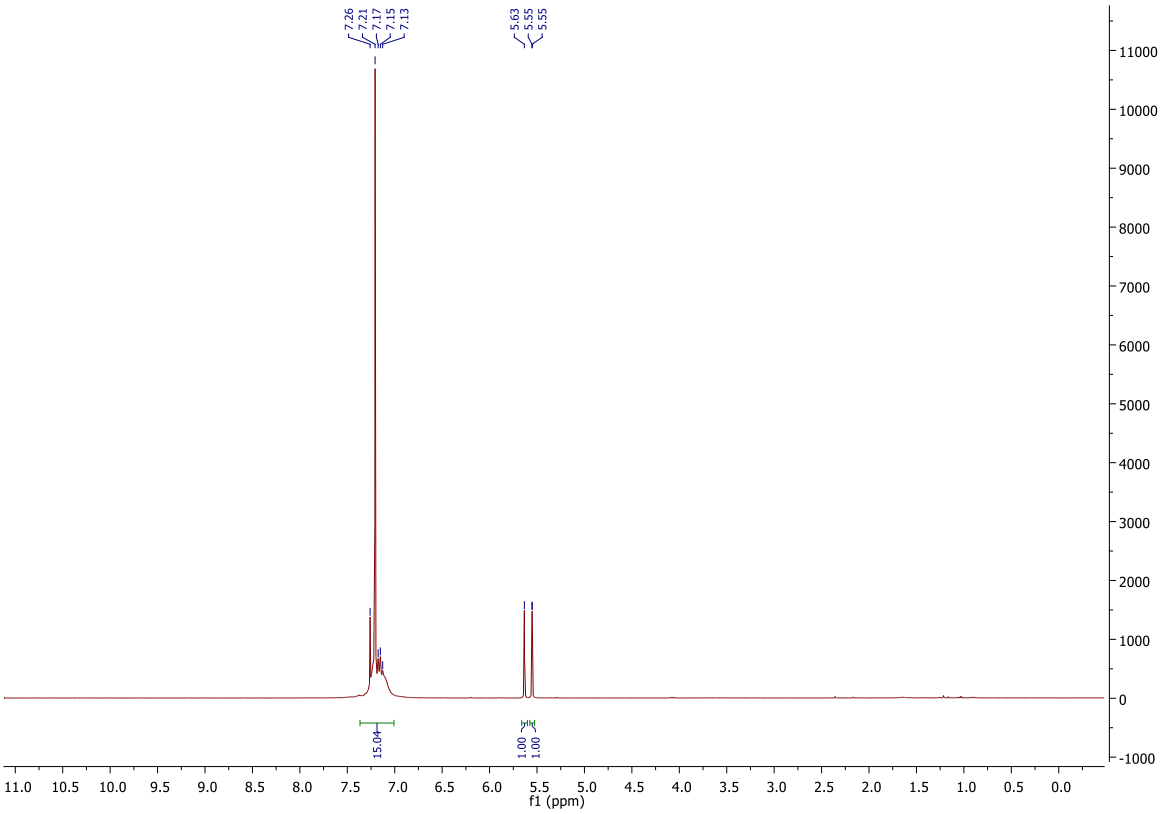

170.48
147.18
136.39
128.74
128.44
125.87
111.87
77.58
77.16
76.74
59.63
55.88
30.94
29.88
26.72
25.84
25.44
25.26
f1 (ppm)

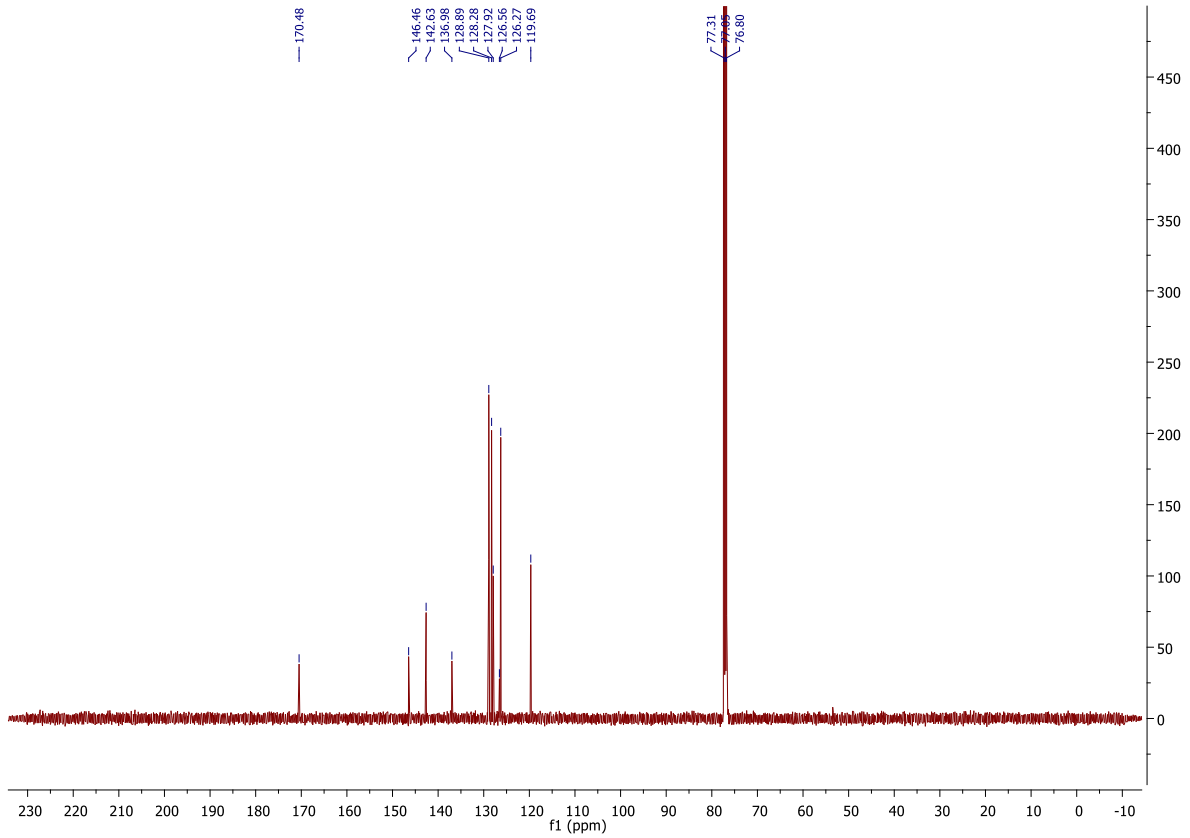
(24)



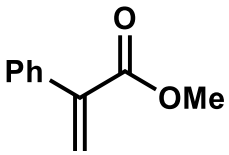
Prepared according to General Procedure C using diphenylamine (850 mg, 5.00 mmol), 4-dimethylaminopyridine (61.0 mg, 1.00 mmol), triethylamine (1.50 mL, 10.0 mmol), CH_2Cl_2 (40 mL) and phenacryloyl chloride (1.67 g, 10.0 mmol). The crude residue was purified by flash column chromatography (eluent = 5 to 10% EtOAc in hexanes, silica gel) to afford product **(24)** as a yellow solid (804 mg, 53% yield).

Mp.: 82-85 °C; **R_f** = 0.47 (eluent = 15% EtOAc in hexanes); **ν_{max} / cm^{-1}** (thin film) 3050, 1655, 1589, 1489, 1446, 1340, 1305, 1284, 1255, 1164, 1072, 926 **; ^{1}H NMR (300 MHz, $CDCl_3$)** δ_H: 5.55 (1H, s), 5.63 (1H, s), 6.93-7.53 (15H, m); **^{13}C NMR (126 MHz, $CDCl_3$)** δ_C: 119.7, 126.3, 126.6, 127.9, 128.3, 128.9, 137.0, 142.6, 146.5, 170.5; **HRMS (ES$^+$)** [$C_{21}H_{17}NO$] requires $[M+H]^+$ 300.1388, found 300.1389 (+ 0.3 ppm).



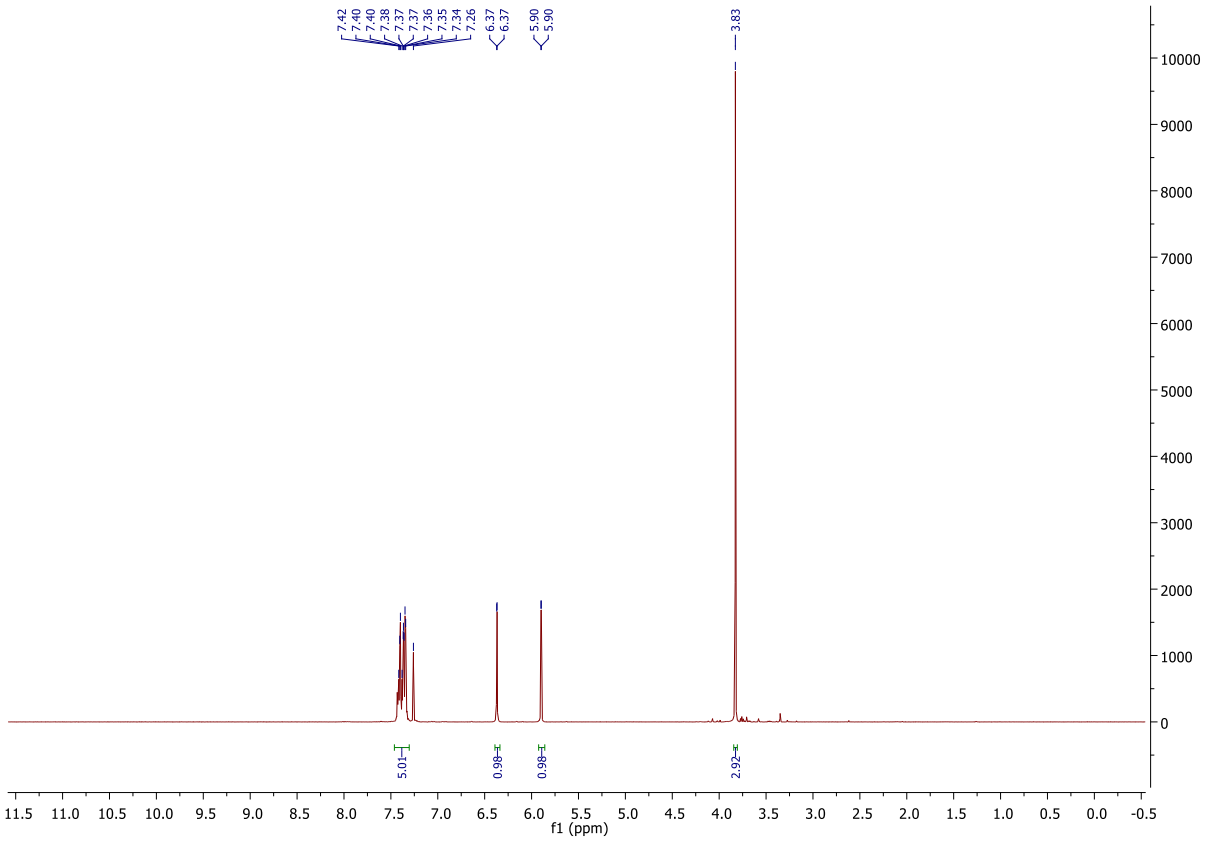


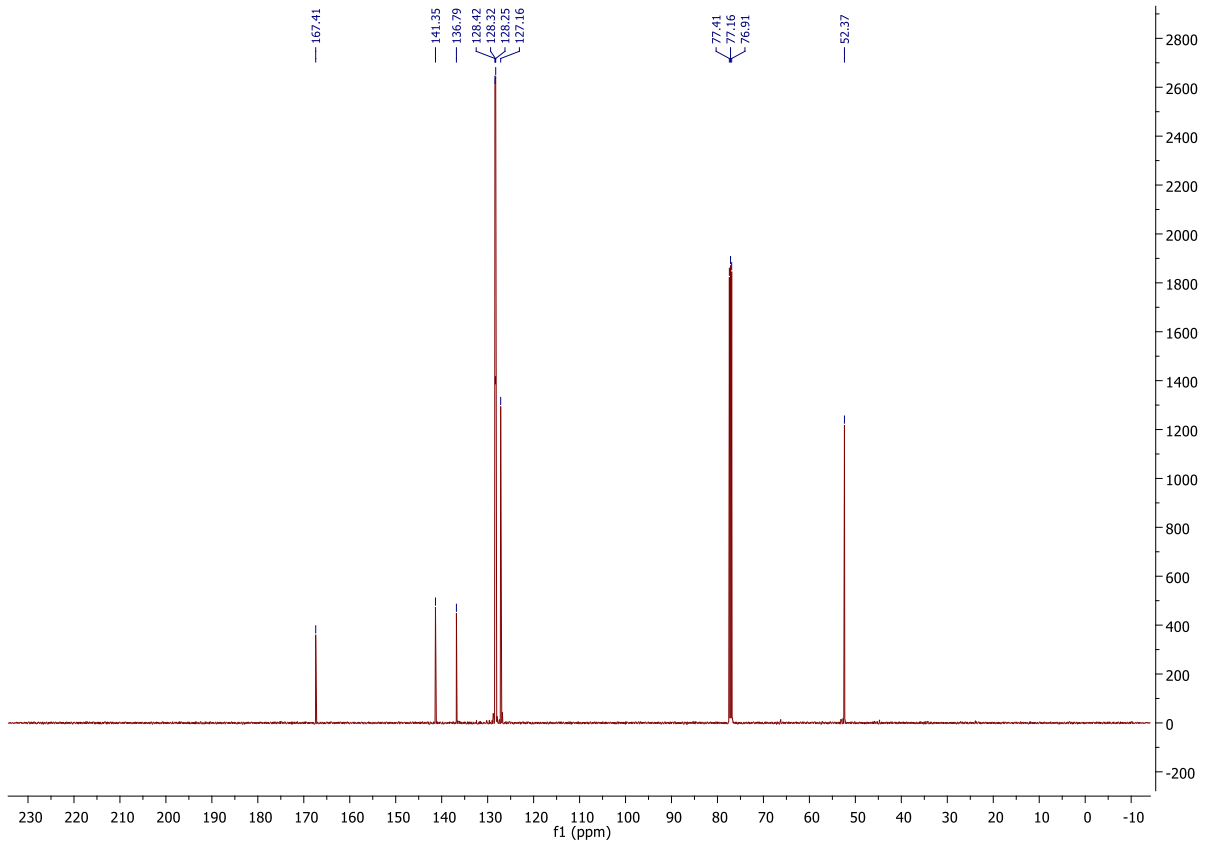
(26)



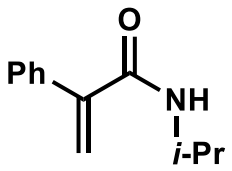
Prepared according to General procedure E step 1 using phenacrylic acid (740 mg, 5.00 mmol), MeOH (6.25 mL), and sulfuric acid (3 drops). The crude residue was afforded as a pale yellow oil **(26)** and used directly in the electrochemical chlorination (800 mg, 99% yield). Data consistent with the literature[6]

R_f = 0.50 (eluent = 10% EtOAc in hexanes); **^{1}H NMR (500 MHz, $CDCl_3$)** δ_H: 3.83 (3H, s), 5.90 (1H, d, *J* 1.2 Hz), 6.37 (1H, d, *J* 1.2 Hz), 7.32-7.45 (5H, m); **^{13}C NMR (126 MHz, $CDCl_3$)** δ_C: 52.4, 127.2, 128.3, 128.3, 128.4, 136.8, 141.4, 167.4.


7.42
7.40
7.40
7.38
7.37
7.37
7.36
7.35
7.34
7.26
6.37
6.37
5.90
5.90
3.83
5.01
0.98
0.98
2.92
f1 (ppm)

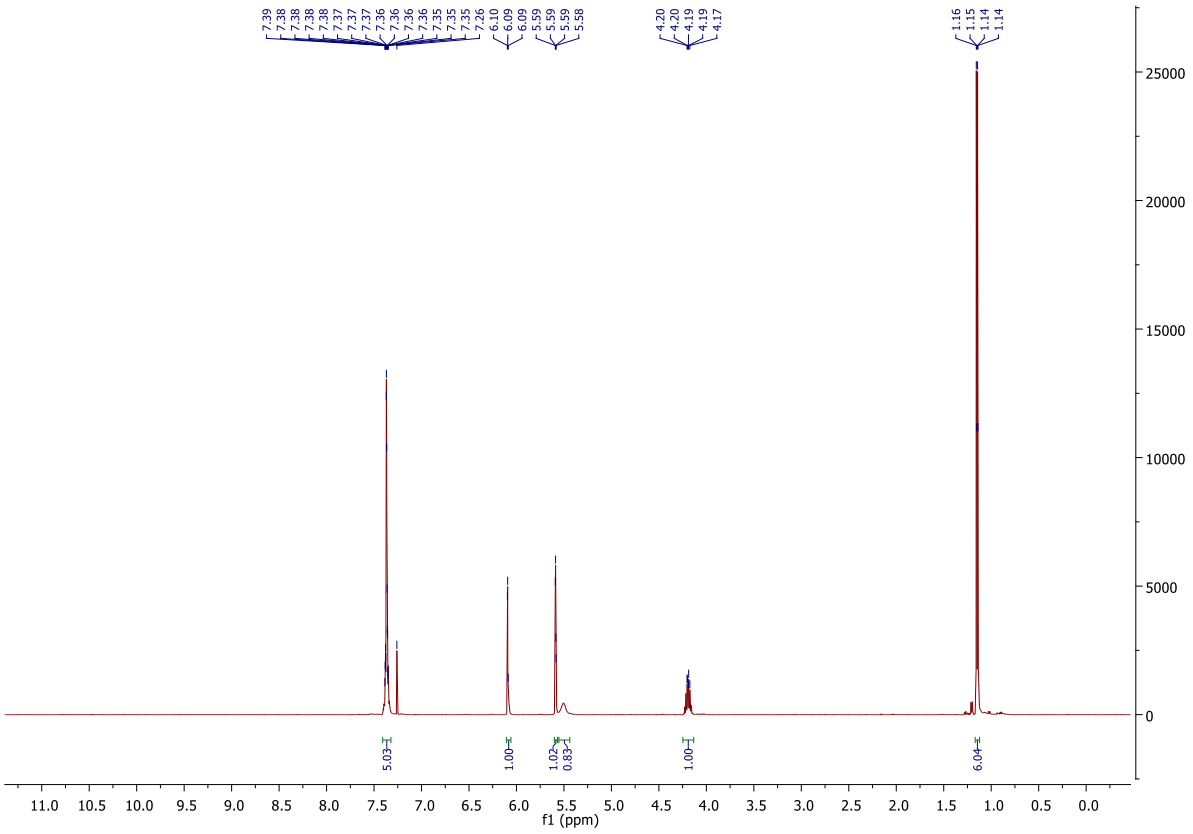

167.41
141.35
136.79
128.42
128.32
128.25
127.16
77.41
77.16
76.91
52.37
f1 (ppm)

(29)



Prepared according to General Procedure using isopropylamine (1.64 mL, 20.0 mmol, 2 equiv.), 4-dimethylaminopyridine (122 mg, 1.00 mmol), triethylamine (1.5 mL, 10.0 mmol), CH_2Cl_2 (40 mL) and phenacryloyl chloride (1.67 g, 10.0 mmol). The crude residue was purified by flash column chromatography (eluent = 10 to 35% EtOAc in hexanes, silica gel) to afford product **(29)** as a yellow oil (1.10 g, 58% yield).

R_f = 0.15 (eluent = 20% EtOAc in hexanes); **ν_{max} / cm^{-1}**(thin film) 3275, 2970, 1639, 1601, 1526, 1494, 1446, 1365, 1229, 1155, 1132, 936 **; ^{1}H NMR (500 MHz, $CDCl_3$)** δ_H: 1.07-1.23 (6H, m), 4.14- 4.27 (1H, m), 5.51 (1H, br s), 5.59 (1H, m), 6.09 (1H, m) 7.34-7.40 (5H, m); **^{13}C NMR (126 MHz, $CDCl_3$)** δ_C: 22.6, 41.8, 121.8, 128.1, 128.5, 128.7, 137.2, 145.0, 166.5; **HRMS (EI$^+$)** [$C_{12}H_{15}NO$] requires [M^+] 189.1154 , found 189.1149 (- 2.7 ppm)


7.39
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7.38
7.38
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7.37
7.37
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7.36
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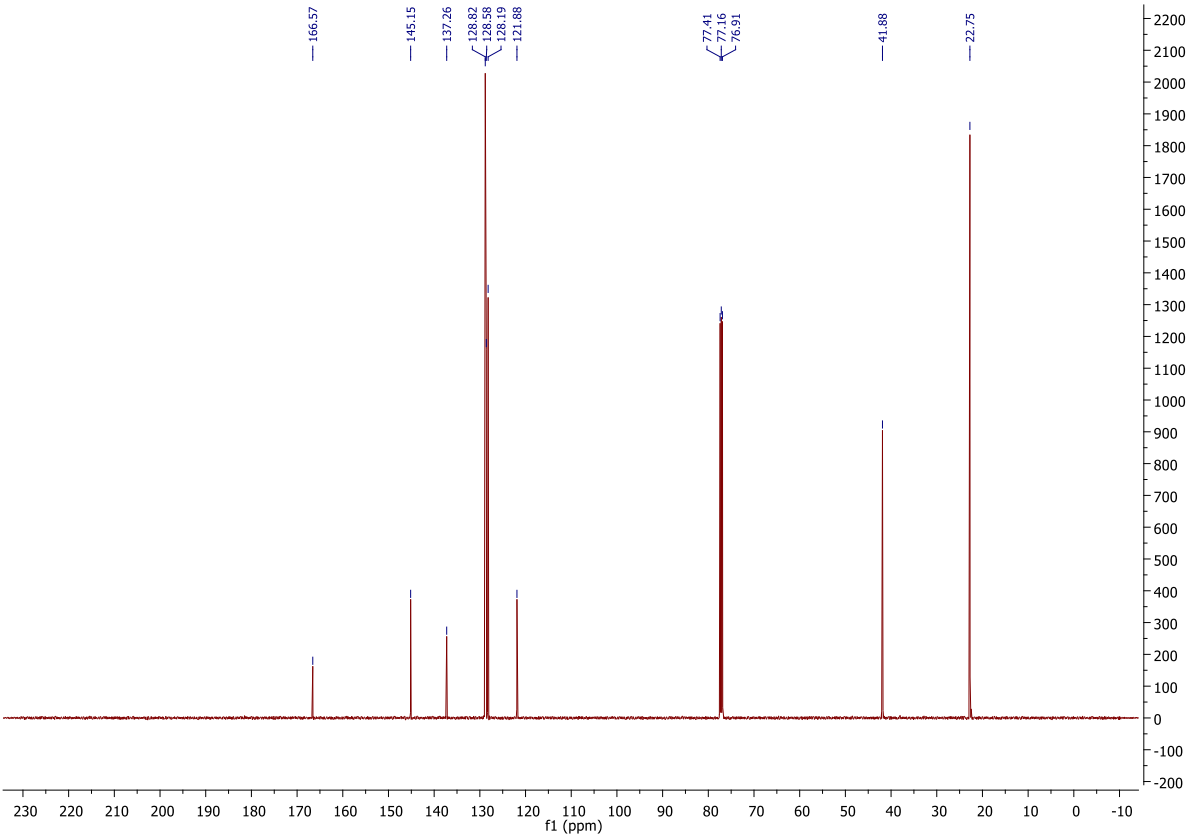
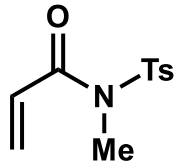
7.35
7.35
7.35
7.26
6.10
6.09
6.09
5.59
5.59
5.59
5.58
4.20
4.20
4.19
4.19
4.17
1.16
1.15
1.14
1.14
25000
20000
15000
10000
5000
0
5.03
1.00
1.02
0.83
1.00
6.04
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

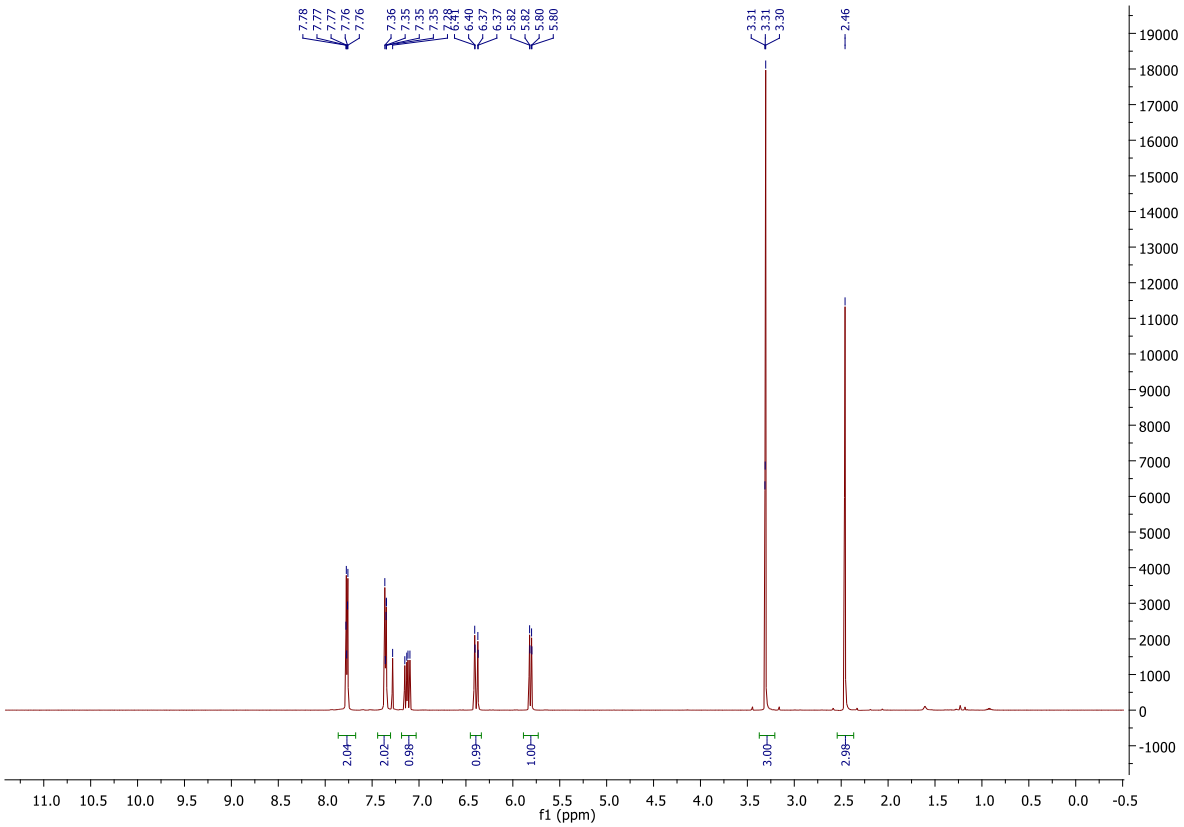

166.57
145.15
137.26
128.82
128.58
128.19
121.88
77.41
77.16
76.91
41.88
22.75
2200
2100
2000
1900
1800
1700
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
-200
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

(30)



Prepared according to a modified General Procedure D using N-methyl-p-toluenesulfonamide (1.85 g, 10.0 mmol), 4-dimethylaminopyridine (122 mg, 1.00 mmol), triethylamine (2.8 mL, 20.0 mmol), CH_2Cl_2 (80 mL) and acryloyl chloride (1.81 g, 20.0 mmol). The crude residue was purified by flash column chromatography (eluent =5-20% EtOAc in hexanes, silica gel) to afford product **(30)** as a colourless oil (0.50 g, 21% yield).

R_f = 0.28 (eluent = 20% EtOAc in hexanes); **ν_{max} / cm^{-1}** (thin film); **^{1}H NMR (500 MHz, $CDCl_3$)** δ_H: 2.44 (3H, s), 3.29 (3H, s), 5.79 (1H, dd, *J* 10.4, 1.7 Hz), 6.37 (1H, dd, *J* 16.7, 1.7 Hz), 7.10 (1H, dd, *J* 16.7, 10.4 Hz), 7.34 (2H, d, *J* 8.0 Hz), 7.67-7.81 (2H, m); **^{13}C NMR (126 MHz, $CDCl_3$)** δ_C: 21.8, 33.2, 127.4, 128.9, 130.1, 131.2, 136.2, 145.1, 166.3; **HRMS (ES$^+$)** [$C_{11}H_{13}NO_3S$] requires $[M+H]^+$ 240.0694, found 240.0685 (-3.7 ppm).


7.78
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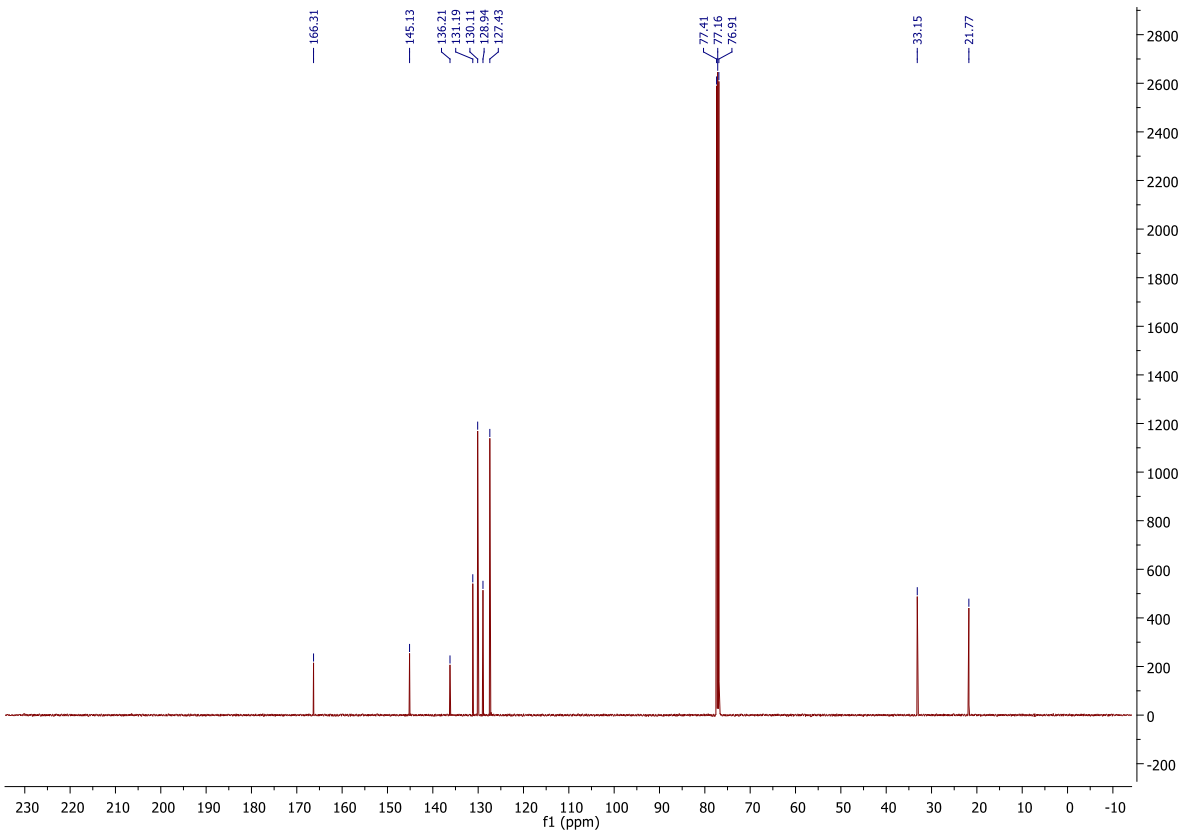
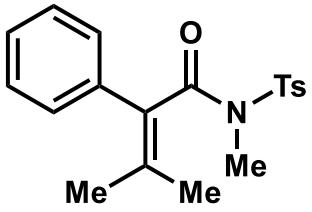
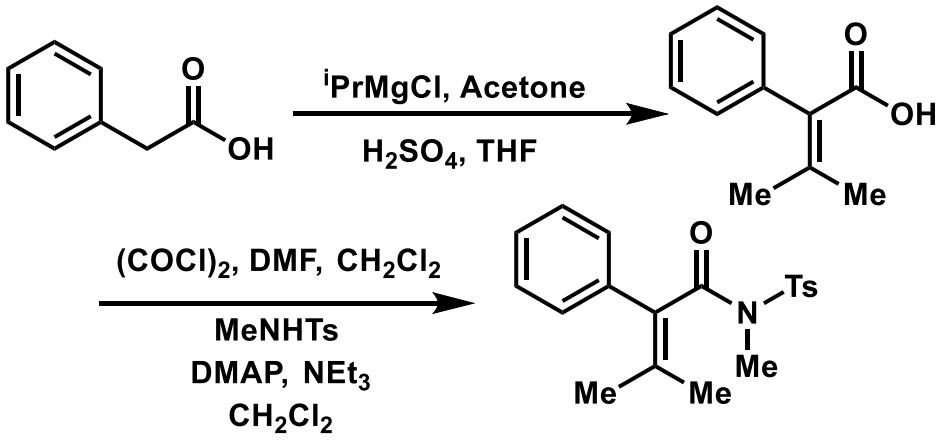
7.77
7.76
7.76
7.36
7.35
7.35
7.35
6.41
6.40
6.37
6.37
5.82
5.80
5.80
3.31
3.31
3.30
2.46
2.04
2.02
0.98
0.99
1.00
3.00
2.98
f1 (ppm)


166.31
145.13
136.21
131.19
130.11
128.94
127.43
77.41
77.16
76.91
33.15
21.77
f1 (ppm)

(31)



Scheme:



Following a literature procedure.[4]

Methods:

Step 1:

To a solution of phenylacetic acid (2.73 g, 20 mmol) in dry THF (40 mL) was added isopropylmagnesium bromide (40 mmol, 20 mL, 2M in THF) at room temperature. The brown solution was stirred at room temperature for 1 h before acetone (1.74 g, 2.2 mL, 30 mmol) was added dropwise and the mixture was heated to 40 °C for 1 h. The reaction solution was allowed to cool to room temperature and then cooled to 0 °C using an ice bath. Sulfuric acid (20 mL, 15 % v/v aqueous solution) was added and mixture stirred for 10 minutes. The mixture was extracted with Et_2O (3 x 40 mL), dried over $MgSO_4$, filtered and concentrated affording an orange oil. The orange oil was taken up in CH_2Cl_2 and concentrated sulfuric acid (3 mL) was added and the mixture stirred for 10 minutes before the mixture was concentrated *in vacuo* forming a red solution. This was stirred at room temperature for 1 h and

then quenched with ice water (30 mL). A white precipitate was formed which was collected by filtration, washed with water (3 x 30 mL) and hexane (3 x 30 mL) and dried overnight under vacuum.

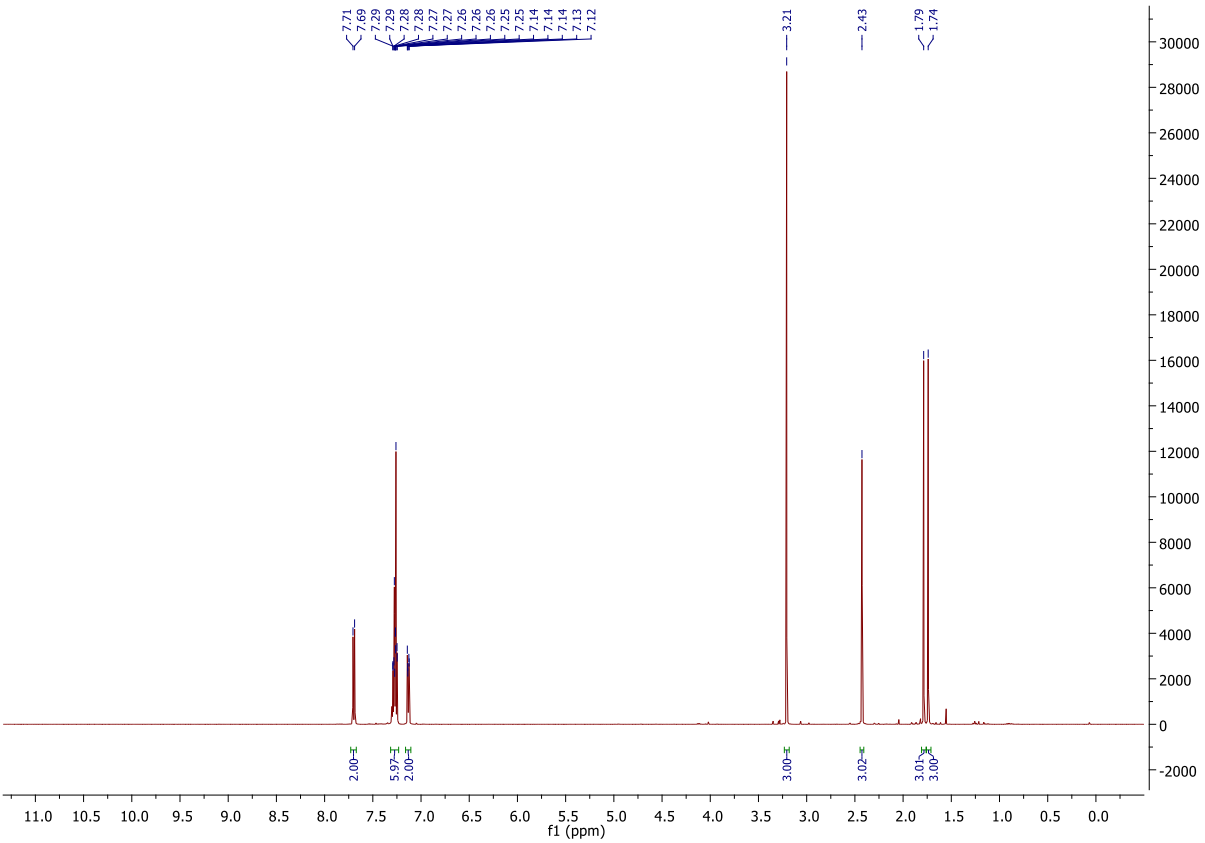
Step 2 Part A:

A solution of the 2-acrylacrylic acid derivative (1.50 g, 8.5 mmol, 1.1 equiv.) in CH_2Cl_2 (3 mL/ mmol) and DMF (3 drops) was prepared. Oxalyl chloride (1.52 g, 12 mmol, 1.5 equiv.) was added dropwise at room temperature and the mixture was allowed to stir for 3 h until no gas evolution was observed. The solution was concentrated *in vacuo* and redissolved in CH_2Cl_2 (1 mL/mmol).

Step 2, part B:

A solution of N-methyl-N-tosylamine (1.42 g, 7.70 mmol, 1 equiv.), DMAP (85 mg, 0.77 mmol, 10 mol %) and triethylamine (2.5 mL, 2 equiv.) in CH_2Cl_2 (8 mL/mmol) was prepared and cooled to 0 ^oC using an salt/ice bath. The crude acyl chloride solution prepared in **Step 2, part A** was added dropwise, and the mixture was stirred at 0 ^oC for 15 mins before being allowed to warm to room temperature and stir overnight. The reaction mixture was quenched with a saturated sodium bicarbonate solution (8 mL/mmol), layers separated, and aqueous phase extracted with CH_2Cl_2 (2 x 40 mL). The organics were combined and dried over $MgSO_4$, filtered and concentrated *in vacuo* yielding crude product. The crude residue was purified by flash column chromatography (silica gel) to yield pure product **(31)** as a yellow solid (1.19 g, 41%).

Mp.: 64-66°C; $\mathbf{R_f}$ = 0.24 (eluent = 15% EtOAc in hexanes); $\mathbf{\nu_{max}}$ **/ cm^{-1}** (thin film) 1674, 1598, 1442, 1344, 1293, 1275, 1170, 1146, 1055**; ^{1}H NMR (500 MHz, $CDCl_3$)** δ_H: 1.74 (3H, s), 1.79 (3H, s), 2.43 (3H, s), 3.21 (3H, s), 7.10-7.17 (2H, m), 7.21-7.31 (5H, m), 7.70 (2H, d, *J* 8.3 Hz); **^{13}C NMR (126 MHz, $CDCl_3$)** δ_C: 21.0, 21.8, 22.5, 33.7, 127.7, 128.5, 128.5, 129.3, 129.4, 132.4, 134.9, 135.7, 136.7, 144.8, 170.6; **HRMS (ES$^+$)** [$C_{19}H_{21}NO_3S$] requires $[M+H]^+$ 334.1320, found 344.1307 (-3.8 ppm)


7.71
7.69
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7.28
7.27
7.26
7.25
7.14
7.13
7.12
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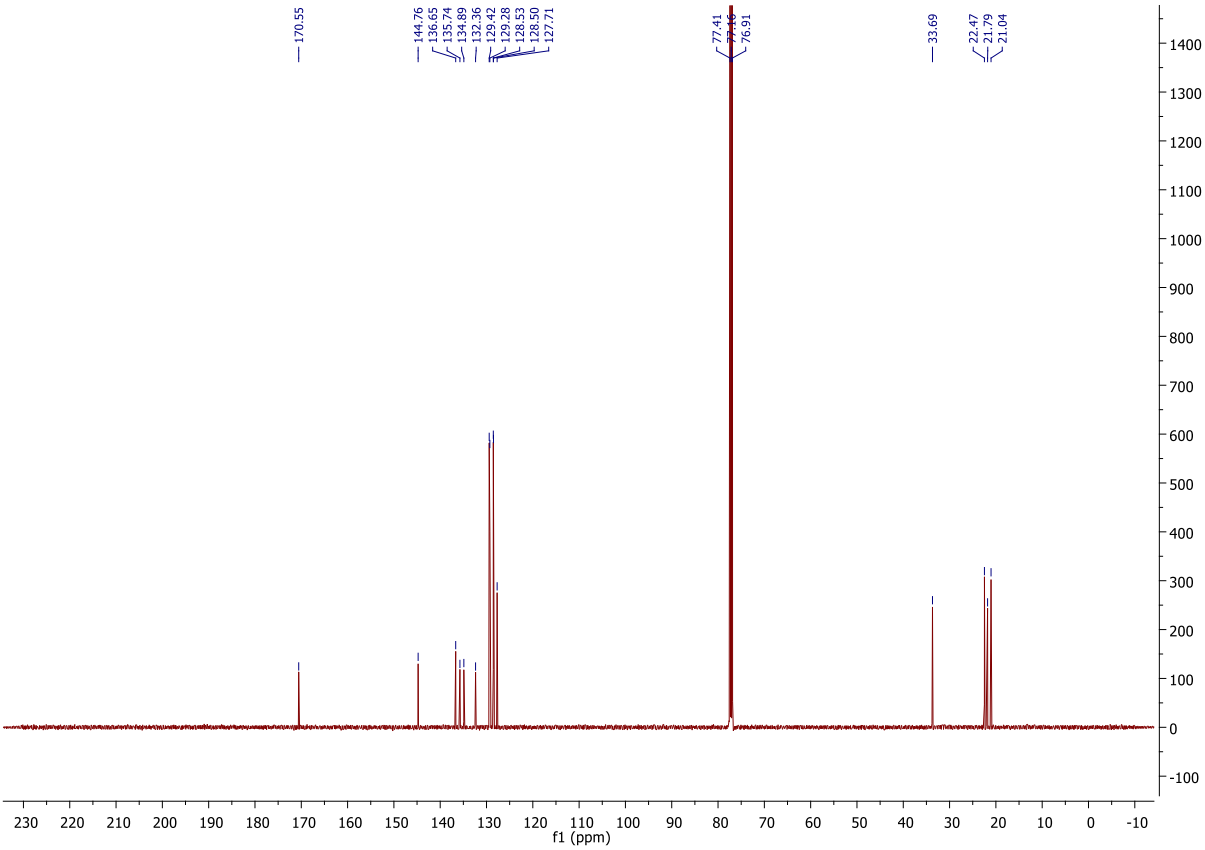
3.02
3.01
3.00
f1 (ppm)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129.28
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128.50
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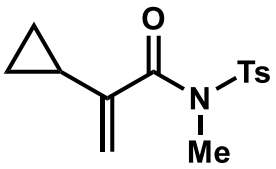
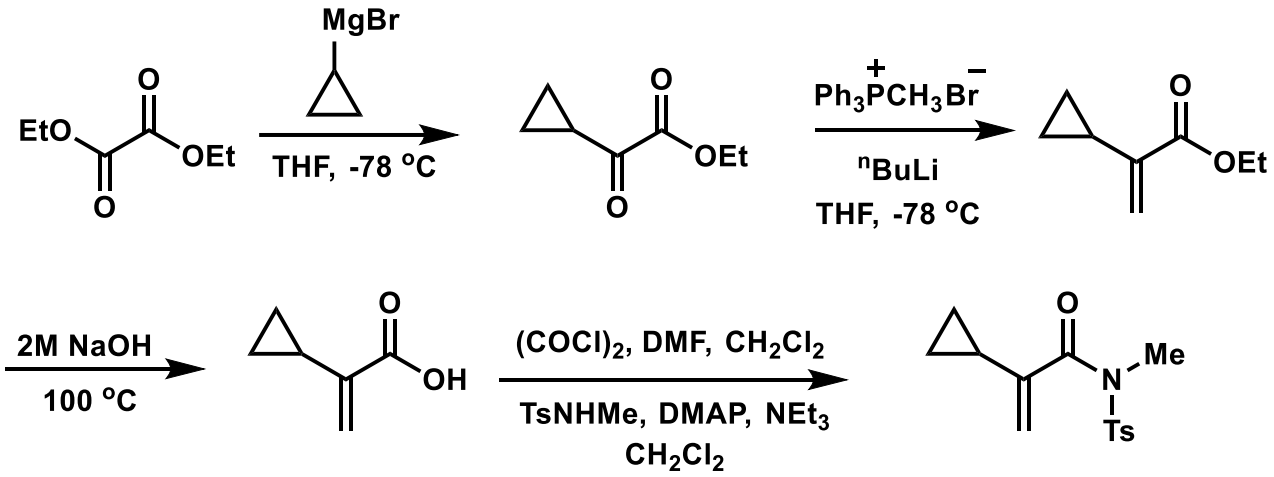
77.41
77.16
76.91
33.69
22.47
21.79
21.04
f1 (ppm)

(34)



Scheme:



Following a modified literature procedure:[5]

Methods:

Step 1:

To a solution of diethyl oxalate (50 mmol) in THF (50mL) at -78 °C was dropwise added freshly prepared cyclopropylmagnesium bromide (54 mmol, 0.9M) over 1 h with the help of syringe pump. After stirring for 1 h at -78 °C, the mixture was warmed to room temperature and quenched with 2N HCl (10 mL). The aqueous layer was extracted with ethyl acetate (3×10 mL) and the combined organic layers were dried over $MgSO_4$ and then filtered. The volatile compounds were removed *in vacuo* and the crude α-ketoester was directly used in the next step without further purification.

Step 2:

A stirred solution of methyl triphenylphosphonium bromide (35 mmol) in dry THF (70 mL) was cooled to -78 °C and n-butyllithium (35 mmol, 2.5M in THF) was dropwise added to the solution under N_2

atmosphere. After stirring 15 minutes, the resulting yellow reaction mixture was warmed up to room temperature and stirred for 1 hour, once the reaction mixture became transparent yellow, it was again cooled to -78 ^{o}C followed with the addition of crude α-ketoester obtained in last step. After stirring for 1 hour at -78 ^{o}C, the mixture was warmed up to room temperature and the progress of the reaction was monitored using TLC. Once the reaction was complete, 2N HCl (10 mL) was added followed by extraction with ethyl acetate (3 x 100 mL) and drying over $MgSO_4$. After filtration the organic solvent was removed *in vacuo*, and the residue was subjected to column chromatography on silica gel to deliver the α-substituted ethyl acrylate derivatives.

Step 3:

To a clean 50 mL round bottom flask was added prepared methyl acrylates and a 2M NaOH solution (3 mL/ mmol). The mixture was heated at reflux for 2 h before being cooled to room temperature. The aqueous was extracted with Et_2O (3 mL/ mmol) then acidified to pH 1 using 2M HCl. The acidified aqueous suspension was then extracted with CH_2Cl_2 (3 x 30 mL), organics combined and dried over $MgSO_4$, filtered and concentrated to afford crude acrylic acid.

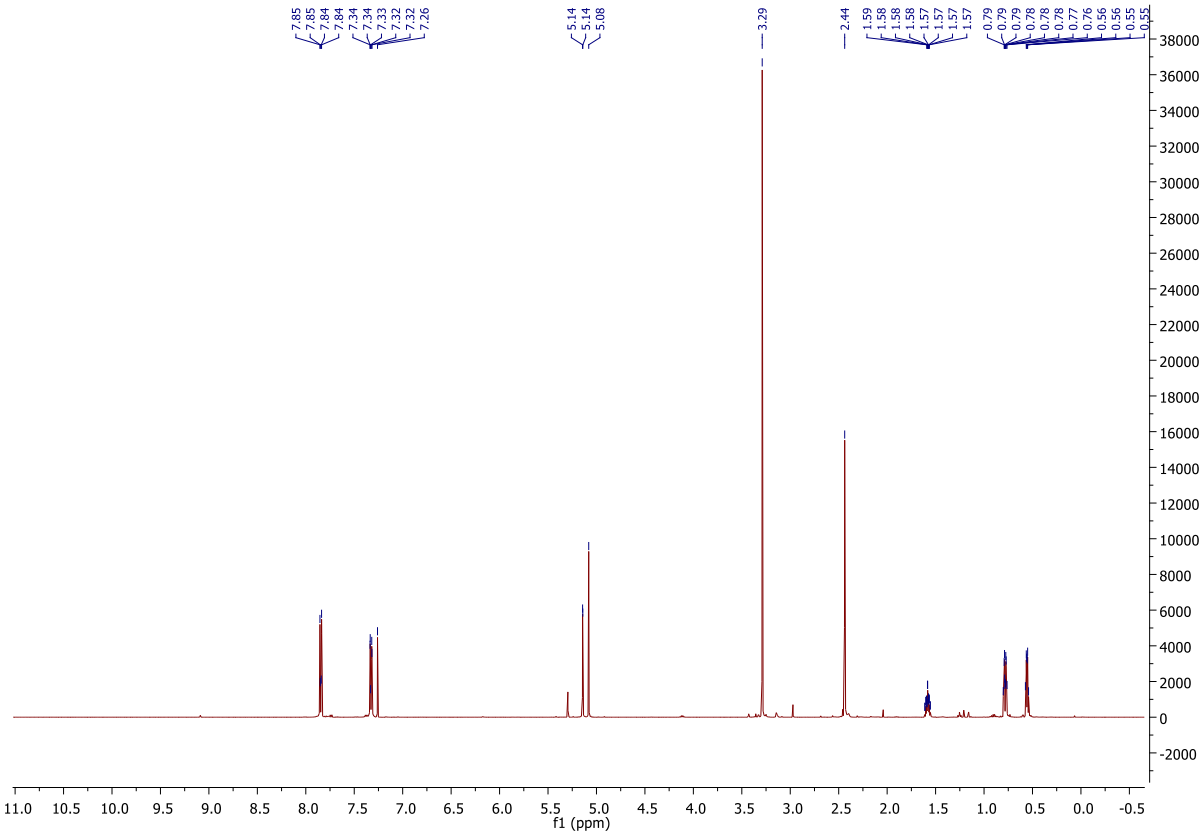
Step 4, part A:

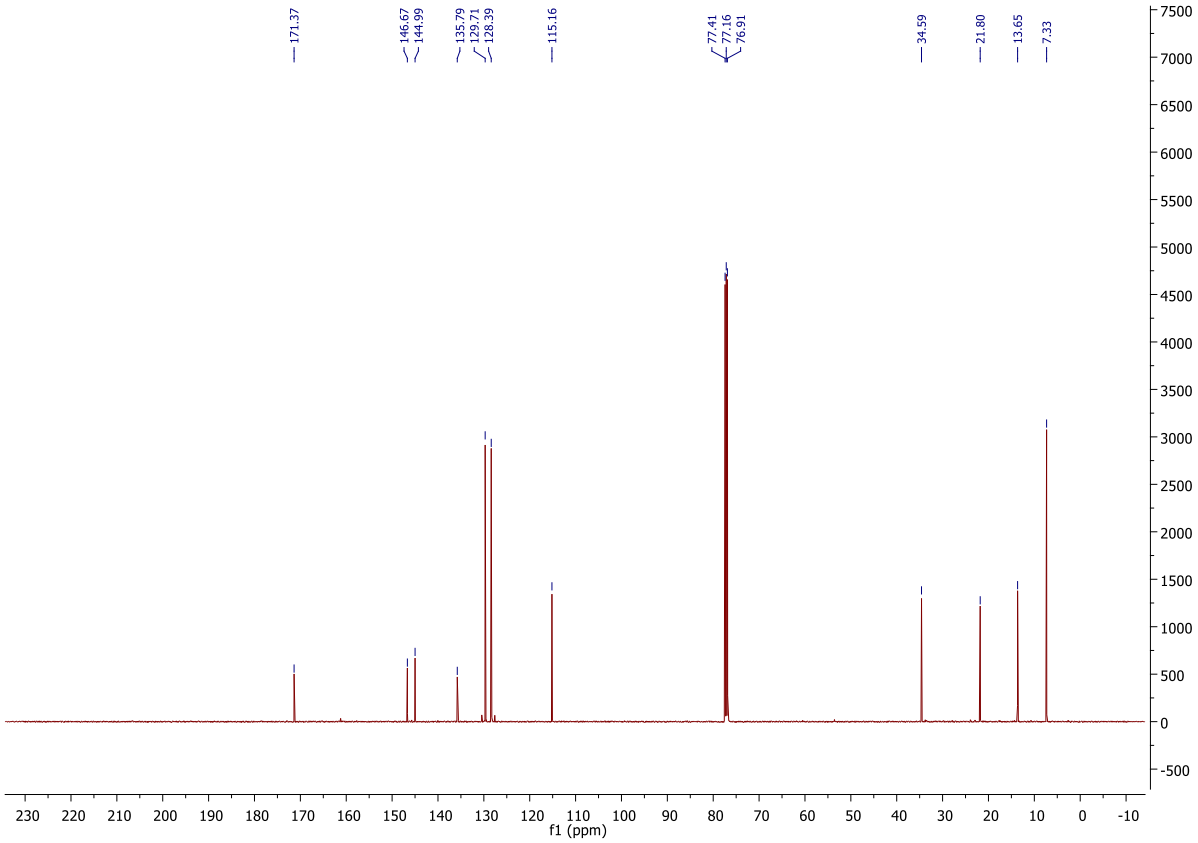
A solution of the 2-acrylacrylic acid derivative (1.1 equiv.) in CH_2Cl_2 (3 mL/ mmol) and DMF (3 drops) was prepared. Oxalyl chloride (1.5 equiv.) was added dropwise at room temperature and the mixture was allowed to stir for 3 h until no gas evolution was observed. The solution was concentrated *in vacuo* and redissolved in CH_2Cl_2 (1 mL/mmol).

Step 4, part B:

A solution of N-methyl-N-tosylamine (0.82 g, 4.42 mmol, 0.9 equiv.), DMAP (54 mg, 10 mol %) and triethylamine (1.2 mL, 2 equiv.) in CH_2Cl_2 (8 mL/mmol) was prepared and cooled to 0 ^{o}C using an salt/ice bath. The crude acyl chloride solution (0.58 g, 4.45 mmol) prepared in **Step 4, part A** was added dropwise, and the mixture was stirred at 0 ^{o}C for 15 mins before being allowed to warm to room temperature and stir overnight. The reaction mixture was quenched with a saturated sodium bicarbonate solution (8 mL/mmol), layers separated, and aqueous phase extracted with CH_2Cl_2 (2 x 40 mL). The organics were combined and dried over $MgSO_4$, filtered and concentrated *in vacuo* yielding crude product. The crude residue was purified by flash column chromatography (silica gel) to yield pure product **(33)** as a white solid (166 mg, 13%).

Mp.: 56-58 °C; **R_f** = 0.28 (eluent = 15% EtOAc in hexanes); **ν_{max} / cm^{-1}** (thin film) 3020, 1686, 1595, 1354, 1285, 1188, 1167, 1086, 1047 **; ^{1}H NMR (300 MHz, $CDCl_3$)** δ_H: 0.54-0.57 (2H, m), 0.72-0.82 (2H, m), 1.54-1.62 (1H, m), 2.44 (3H, s), 3.29 (3H, s), 5.08 (1H, s), 5.14 (1H, d, *J* 1.0 Hz), 7.30-7.35 (2H, m), 7.82-7.87 (2H, m); **^{13}C NMR (126 MHz, $CDCl_3$)** δ_C: 7.3, 13.7, 21.8, 34.6, 115.2, 128.4, 129.7, 135.8, 145.0, 146.7, 171.4; **HRMS (ES$^+$)** [$C_{14}H_{18}NO_3S$] requires $[M+H]^+$ 280.1007, found 280.1009 (+ 0.7 ppm).




171.37
146.67
144.99
135.79
129.71
128.39
115.16
77.41
77.16
76.91
34.59
21.80
13.65
7.33
f1 (ppm)

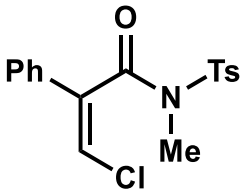
3. Experimental and Characterisation of the Electrochemical Chlorination

3.1 General Electrochemical Chlorination Procedure G

To an oven-dried 10 mL ElectraSyn vial equipped with a magnetic stirrer bar, was added substrate alkene (0.30 mmol) and $MgCl_2$ (143 mg, 1.50 mmol). The threaded glass of the vial was wrapped with PTFE tape and connected to the ElectraSyn cap, which was fitted with a graphite anode and a platinum foil cathode. The vial was purged with N_2 gas via evacuate-refill cycles (× 3). MeCN (5.25 mL) was added, followed by AcOH (0.75 mL) and the mixture was stirred for a minute to ensure solvation of the $MgCl_2$. The mixture was then purged via bubbling with N_2 gas for 10 minutes. The vial was then connected to an ElectraSyn. Electrolysis at 10 mA was conducted for 2 h under N_2 with continuous stirring. After electrolysis was complete, the reaction mixture was quenched with a saturated solution of aqueous $NaHCO_3$ (8 mL) and diluted with EtOAc (4 mL). Mesitylene internal standard (42 µL, 0.30 mmol) was added to the organic phase and the organic layer was sampled for crude ^1H NMR analysis. The aqueous and organic phases were separated and the aqueous extracted with EtOAc (2 x 10 mL), the combined extracts were dried over $MgSO_4$, filtered and concentrated *in vacuo*. The crude residue was purified by flash column chromatography on silica gel.

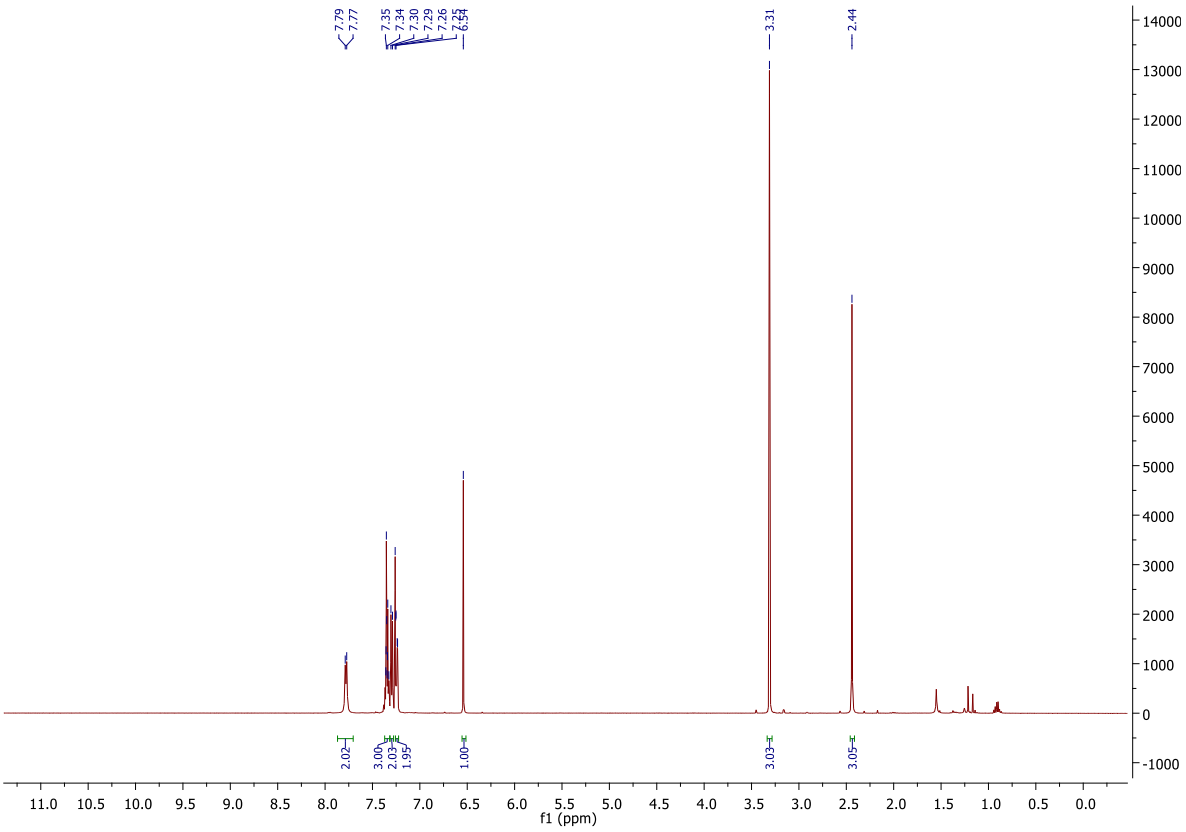
3.2 Characterisation of Electrochemical Products

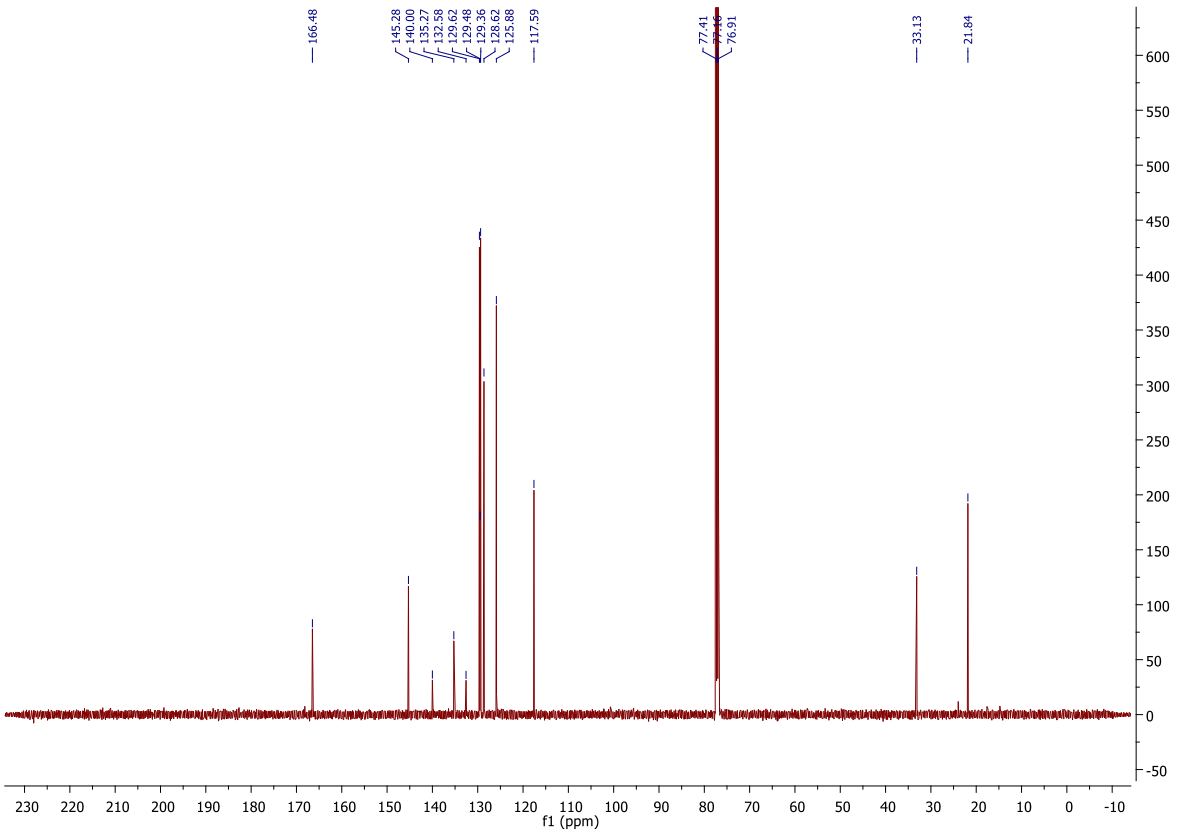
(2)



Prepared according to the General Procedure G using N-tosyl-N-methyl-2-phenacrylamide (94.6 mg, 0.30 mmol, 1 equiv.), magnesium chloride (143 mg, 1.50 mmol, 5 equiv.), acetonitrile (5.25 mL) and acetic acid (0.75 mL). Purification by flash column chromatography (eluent = 5 to 15% EtOAc in hexanes, silica gel) to afford pure product **(2)** as a white solid (99.0 mg, 92% yield).

Mp: 111-113 °C; $\mathbf{R_f}$ = 0.30 (eluent = 20% EtOAc in hexanes); $\mathbf{\nu_{max}}$ **/ cm^{-1}** (thin film) 3050, 1689, 1600, 1440, 1356, 1328, 1259, 1238, 1167, 1051; **^{1}H NMR (500 MHz, $CDCl_3$)** δ_H: 2.44 (3H, s), 3.31 (3H, s), 6.54 (1H, s), 7.24 (2H, dd, *J* 7.9, 1.7 Hz), 7.30 (2H, d, *J* 8.0 Hz), 7.32-7.37 (3H, m), 7.78 (2H, d, *J* 7.8 Hz); **^{13}C NMR (126 MHz, $CDCl_3$)** δ_C: 21.7, 33.0, 117.5, 125.8, 128.5, 129.2, 129.3, 129.5, 132.4, 135.1, 139.8, 145.1, 166.3; **HRMS (ES^+)** [$C_{17}H_{16}NO_3SCl$] requires $[M+H]^+$ 350.0618, found 350.0618 (+ 0.0 ppm).


7.79
7.77
7.35
7.34
7.30
7.29
7.26
7.25
6.54
3.31
2.44
2.02
3.00
2.03
1.95
1.00
3.03
3.05
f1 (ppm)


166.48
145.28
140.00
135.27
132.58
129.62
129.48
129.36
128.62
125.88
117.59
77.41
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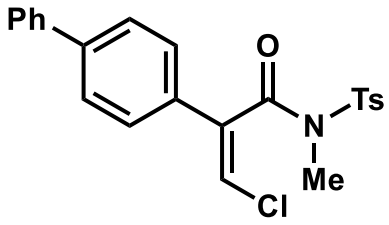
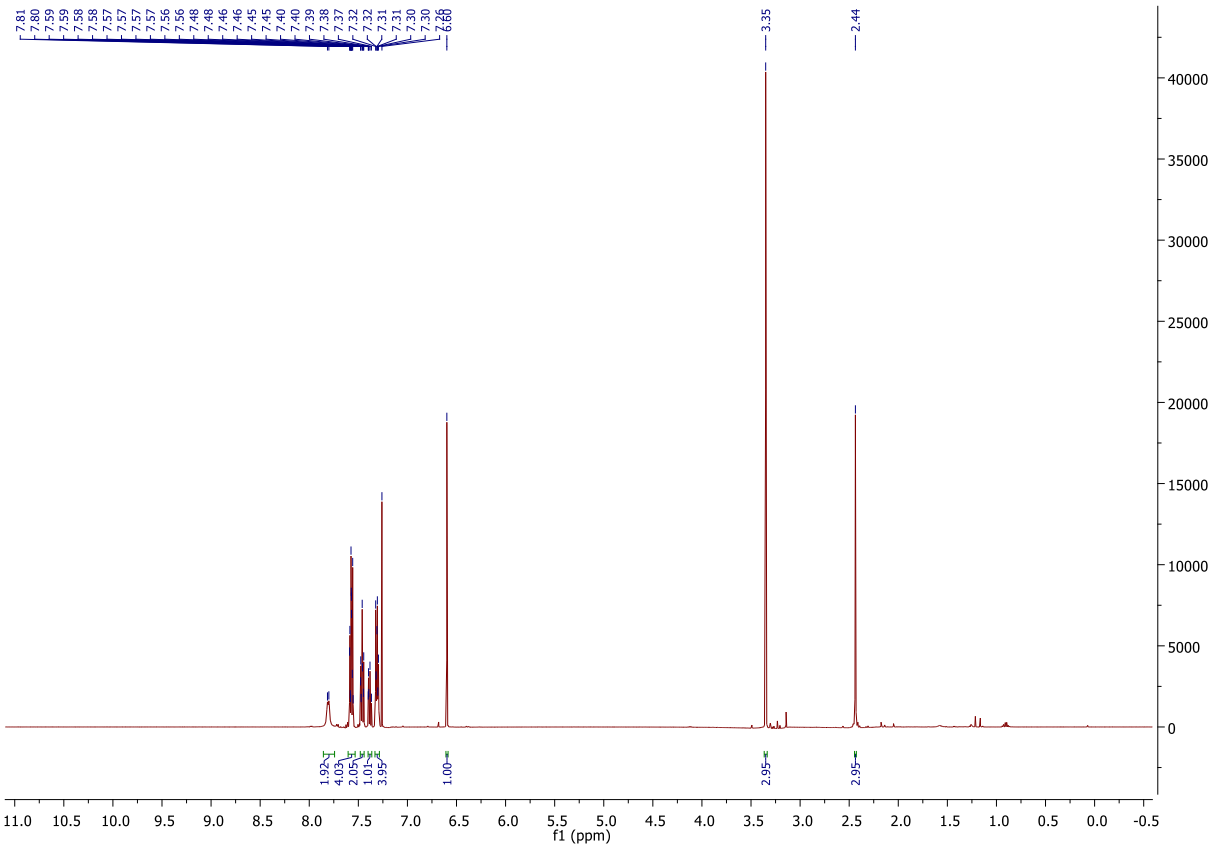
76.91
33.13
21.84
f1 (ppm)

(3)



Prepared according to the General Procedure G using 2-([1,1'-biphenyl]-4-yl)-N-methyl-N-tosylacrylamide (117 mg, 0.30 mmol, 1 equiv.), magnesium chloride (143 mg, 1.50 mmol, 5 equiv.), acetonitrile (5.25 mL) and acetic acid (0.75 mL). Purification by flash column chromatography (eluent = 5 to 15% EtOAc in hexanes, silica gel) to afford product **(3)** as a white foam solid (94.0 mg, 74% yield).

Mp: 157-159 ^{o}C; $\mathbf{R_f}$ = 0.35 (eluent = 20% EtOAc in hexanes); $\mathbf{\nu_{max}}$ **/ cm^{-1}** (thin film) 3050, 1695, 1595, 1487, 1406, 1354, 1248, 1163, 1082, 952; **^{1}H NMR (500 MHz, CDCl$_3$)** δ_H: 2.44 (3H, s), 3.35 (3H, s), 6.60 (1H, s), 7.27-7.34 (4H, m), 7.35-7.42 (1H, m), 7.42-7.49 (2H, m), 7.54-7.60 (4H, m), 7.81 (2H, br d, *J* 7.1 Hz); **^{13}C NMR (126 MHz, CDCl$_3$)** δ_C: 21.9, 33.2, 117.4, 126.2, 127.1, 127.2, 128.0, 128.6, 129.1, 129.6, 131.3, 135.2, 139.6, 140.0, 142.3, 145.3, 166.5; **HRMS (ES$^+$)** [$C_{23}H_{21}NO_3SCl$] requires $[M+H]^+$ 426.0931, found 426.0940 (+ 2.1 ppm).


7.81
7.80
7.59
7.59
7.58
7.58
7.57
7.57
7.57
7.56
7.56
7.48
7.48
7.46
7.46
7.45
7.45
7.40
7.40
7.39
7.38
7.37
7.32
7.32
7.31
7.31
7.30
7.30
7.26
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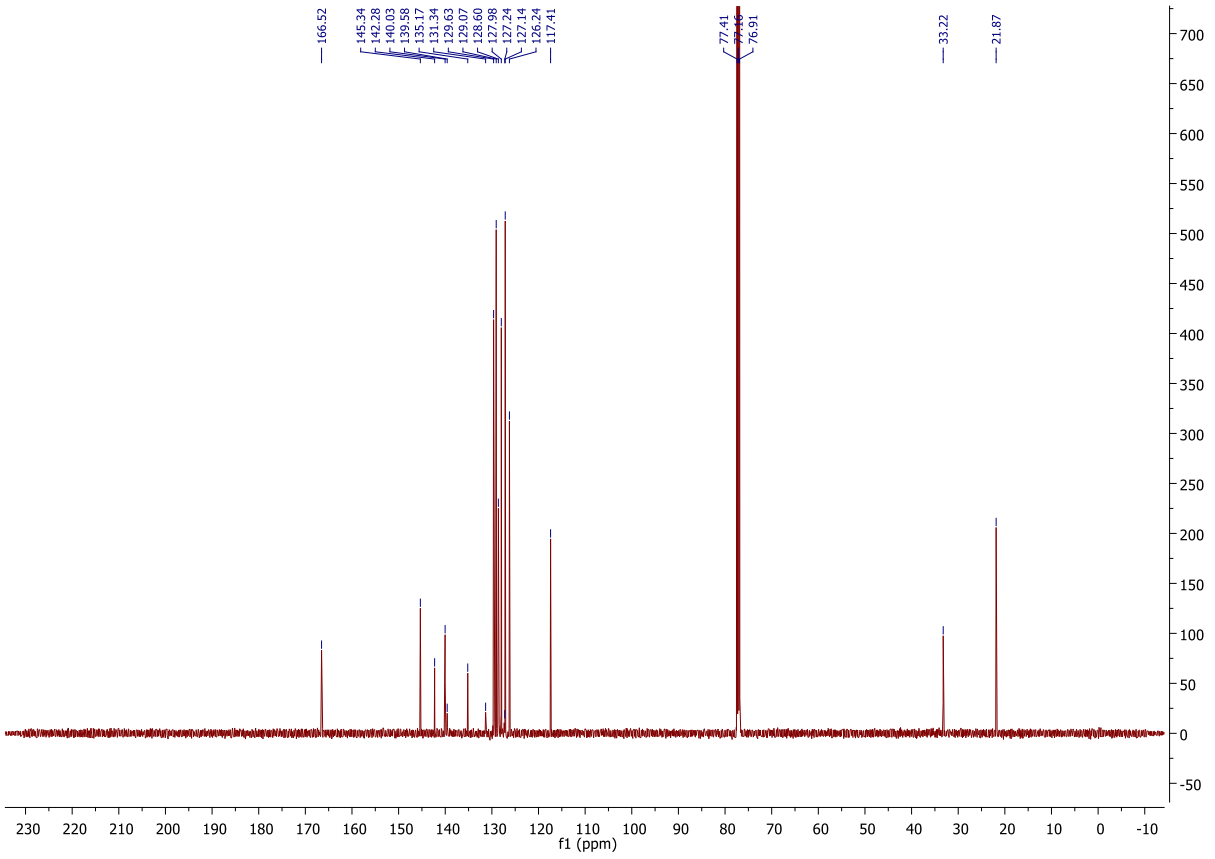
1.01
3.95
1.00
2.95
2.95
f1 (ppm)


166.52
145.34
142.28
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139.58
135.17
131.34
129.63
129.07
128.60
127.98
127.24
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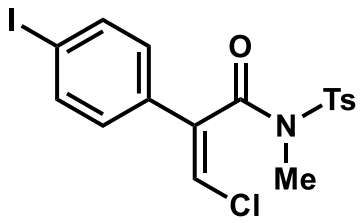
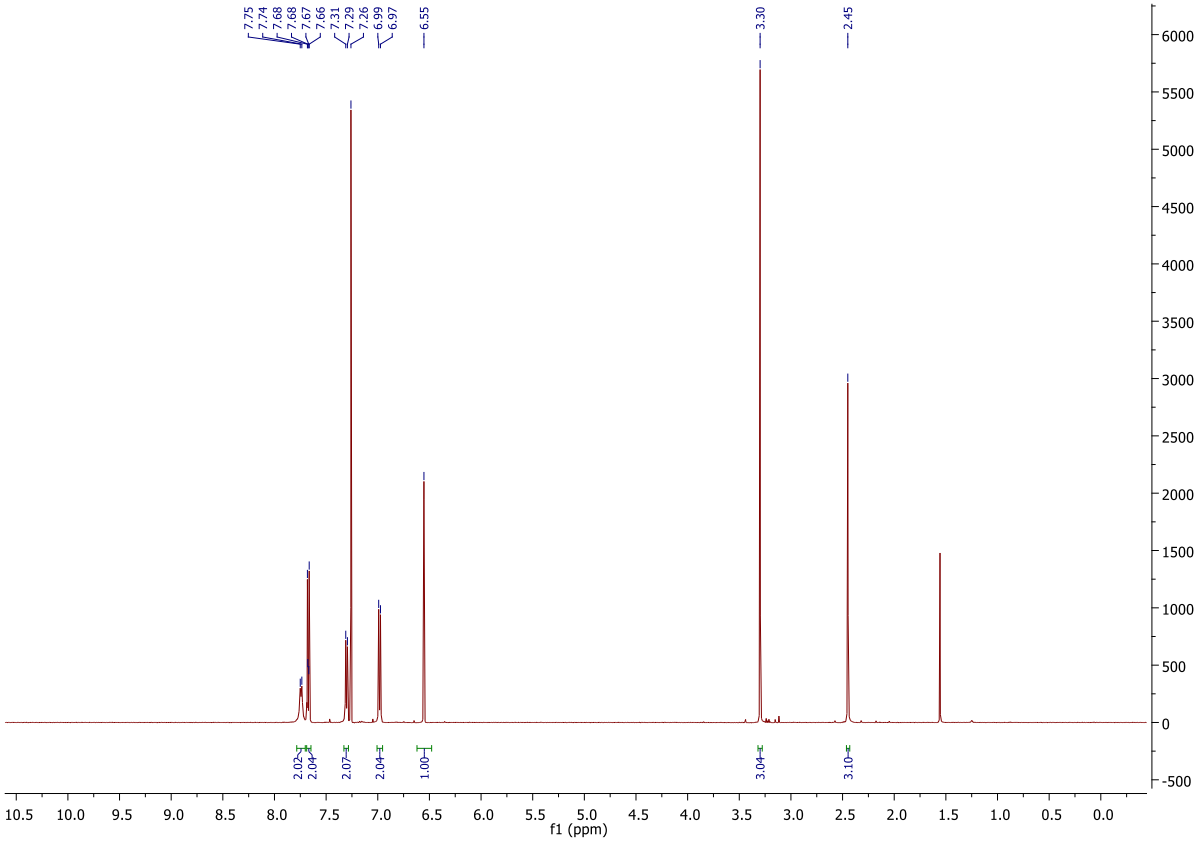
76.91
33.22
21.87
f1 (ppm)

(4)



Prepared according to the General Procedure G using 2-(4-iodophenyl)-N-methyl-N-tosylacrylamide (132 mg, 0.30 mmol, 1 equiv.), magnesium chloride (143 mg, 1.50 mmol, 5 equiv.), acetonitrile (5.25 mL) and acetic acid (0.75 mL). Purification by flash column chromatography (eluent = 5 to 15% EtOAc in hexanes, silica gel) to afford product **(4)** as a tacky solid residue (97.1 mg, 68% yield).

Mp: 138-139 ^{o}C; **R_f** = 0.28 (eluent = 20% EtOAc in hexanes); **ν_{max} / cm^{-1}** (thin film) 3072, 1674, 1593, 1483, 1348, 1303, 1296, 1165, 1082, 1058, 939; **^{1}H NMR (500 MHz, $CDCl_3$)** δ_H: 2.45 (3H, s), 3.30 (3H, s), 6.55 (1H, s), 6.97-7.00 (2H, m), 7.30 (2H, d, *J* 7.8 Hz), 7.64-7.69 (2H, m), 7.74 (2H, d, *J* 7.7 Hz); **^{13}C NMR (126 MHz, $CDCl_3$)** δ_C: 21.9, 33.1, 95.4, 118.2, 127.5, 128.5, 129.7, 132.2, 135.0, 138.5, 139.3, 145.5, 166.0; **HRMS (ES$^+$)** [$C_{17}H_{15}NO_3SClI$] requires $[M+H]^+$ 475.9584 found 475.9591 (+ 1.5 ppm).


7.75
7.74
7.68
7.68
7.67
7.66
7.31
7.29
7.26
6.99
6.97
6.55
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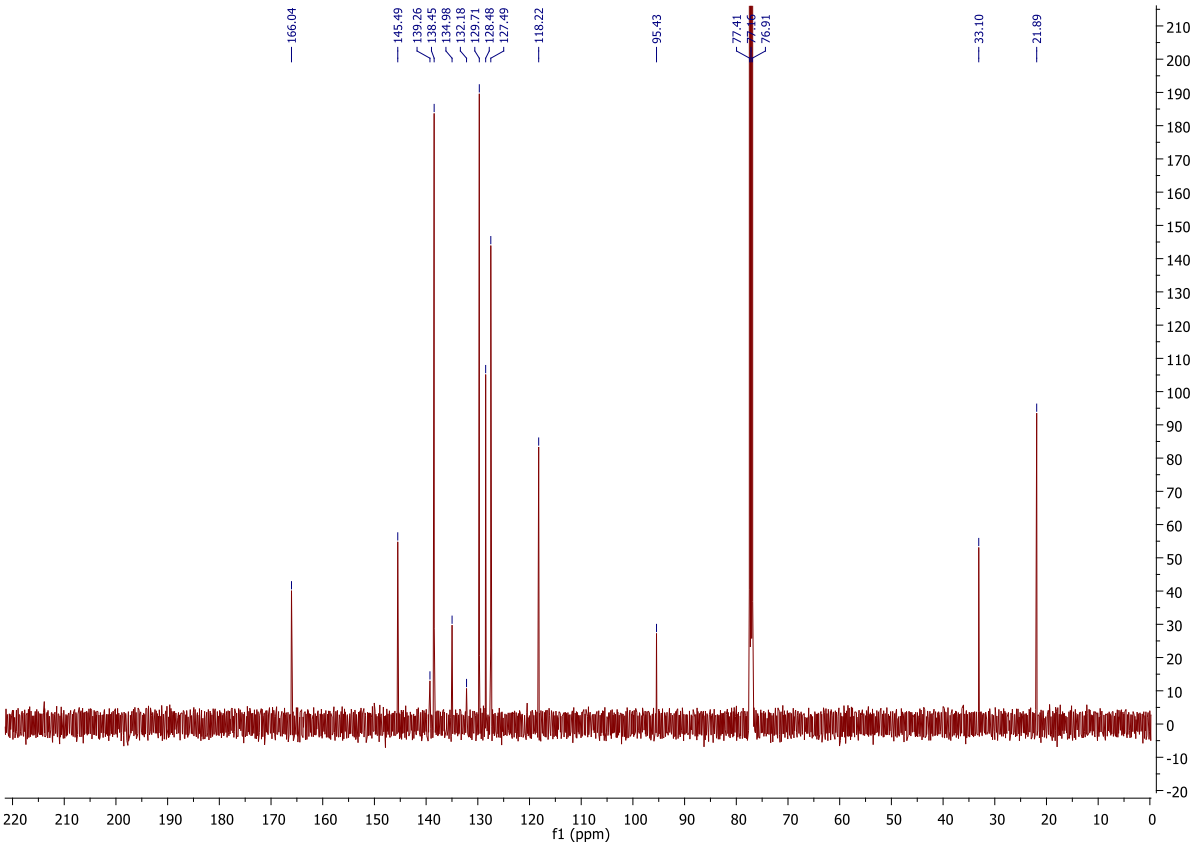
2.04
1.00
3.04
3.10
f1 (ppm)


166.04
145.49
139.26
138.45
134.98
132.18
129.71
128.48
127.49
118.22
95.43
77.41
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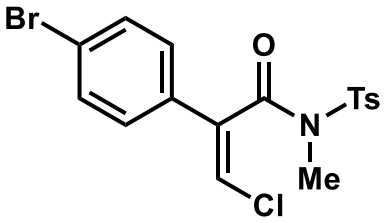
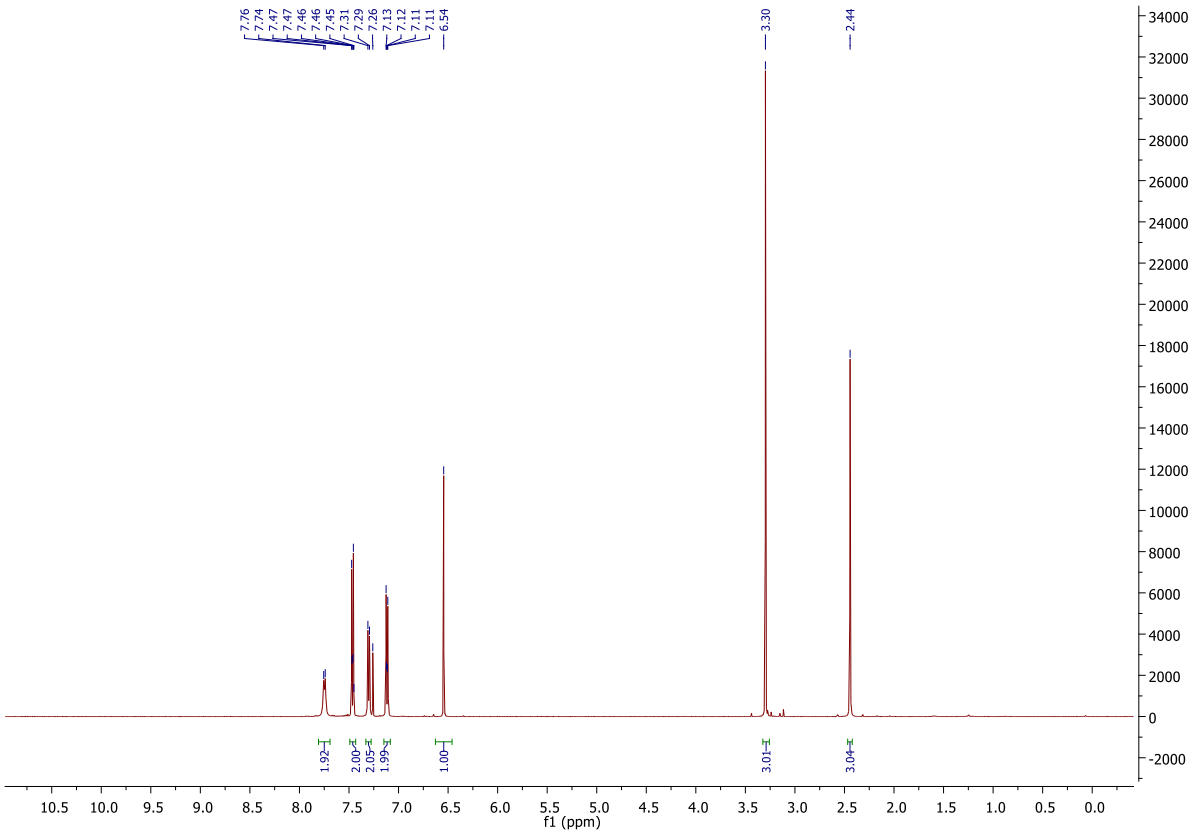
76.91
33.10
21.89
f1 (ppm)

(5)



Prepared according to the General Procedure G using 2-(4-bromophenyl)-N-methyl-N-tosylacrylamide (118 mg, 0.30 mmol, 1 equiv.), magnesium chloride (143 mg, 1.50 mmol, 5 equiv.), acetonitrile (5.25 mL) and acetic acid (0.75 mL). Purification by flash column chromatography (eluent = 5 to 15% EtOAc in hexanes, silica gel) to afford product **(5)** as a white foam solid (107 mg, 83% yield).

Mp: 160-162 ^{o}C; $\mathbf{R_f}$ = 0.50 (eluent = 30% EtOAc in hexanes); $\mathbf{\nu_{max}}$ **/ cm^{-1}** (thin film) 3064, 1674, 1593, 1487, 1352, 1281, 1165, 1083, 1070, 939 ; **^{1}H NMR (500 MHz, $CDCl_3$)** δ_H: 2.44 (3H, s), 3.30 (3H, s), 6.54 (1H, s), 7.06-7.16 (2H, m), 7.30 (2H, d, *J* 7.8 Hz), 7.42-7.50 (2H, m), 7.75 (2H, d, *J* 7.6 Hz); **^{13}C NMR (126 MHz, $CDCl_3$)** δ_C: 21.9, 33.1, 118.2, 123.7, 127.4, 128.5, 129.7, 131.6, 132.5, 135.0, 139.1, 145.5, 166.1; **HRMS (ES^{+})** [$C_{17}H_{15}NO_3SClBr$] requires $[M+H]^+$ 429.9693, found 429.9705 (+ 2.8 ppm).


7.76
7.74
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7.47
7.46
7.46
7.45
7.31
7.29
7.26
7.13
7.12
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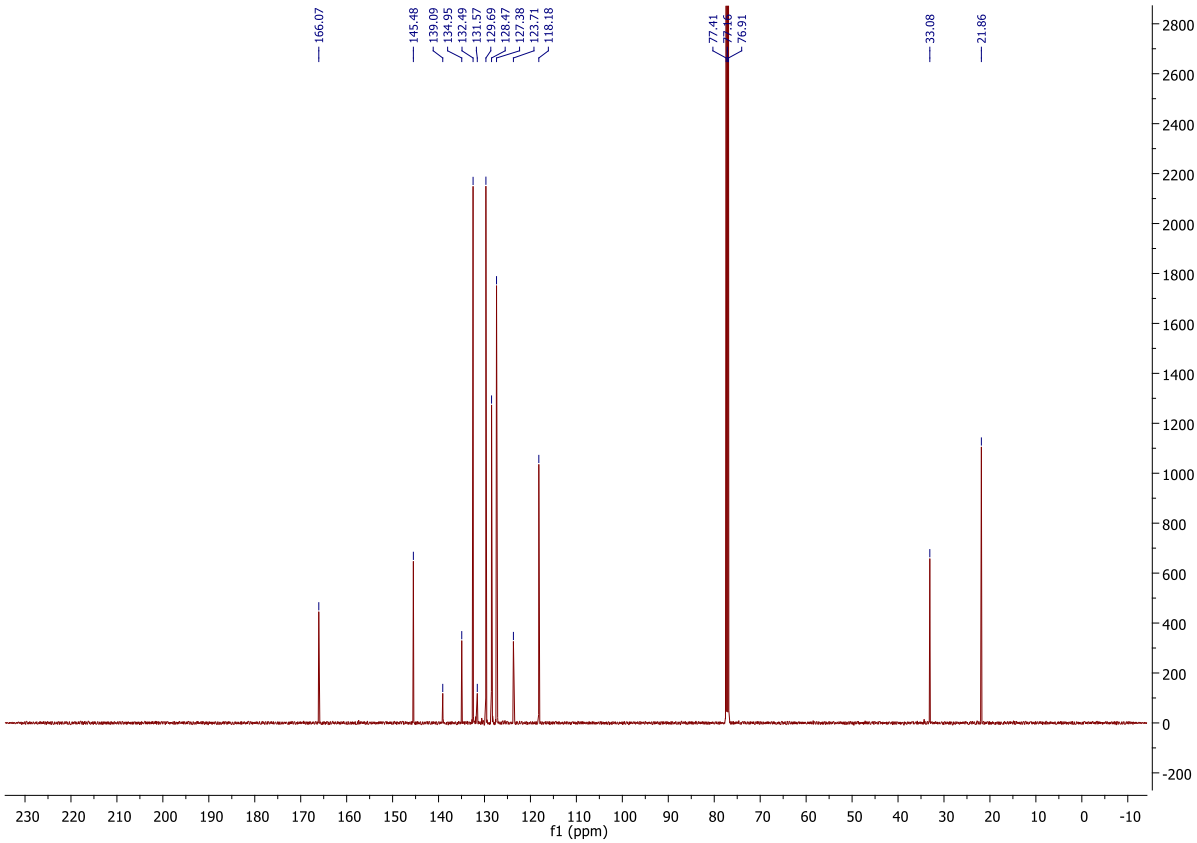
1.99
1.00
3.01
3.04
f1 (ppm)


166.07
145.48
139.09
134.95
132.49
131.57
129.69
128.47
127.38
123.71
118.18
77.41
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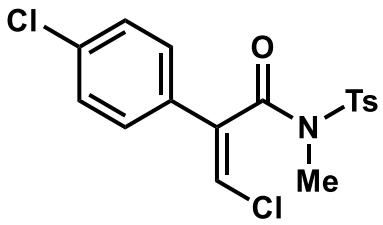
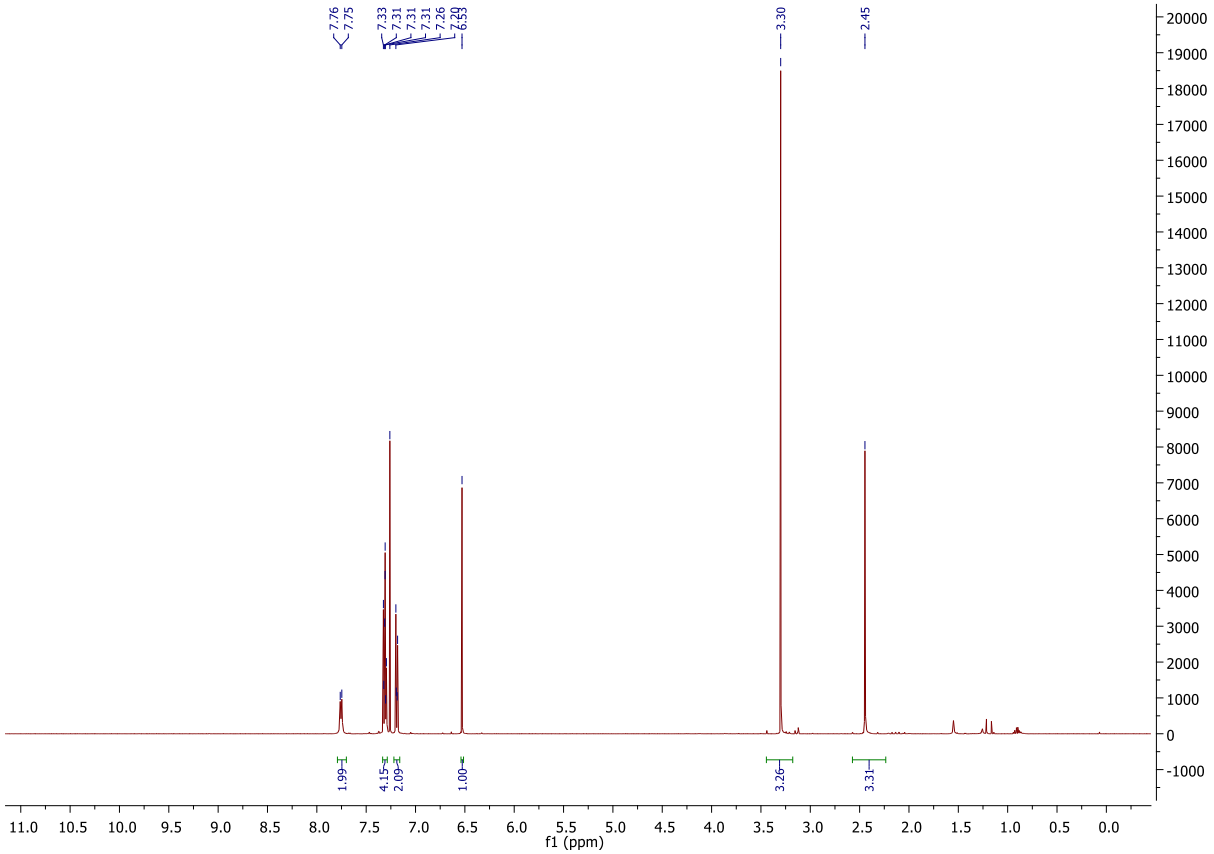
76.91
33.08
21.86
f1 (ppm)

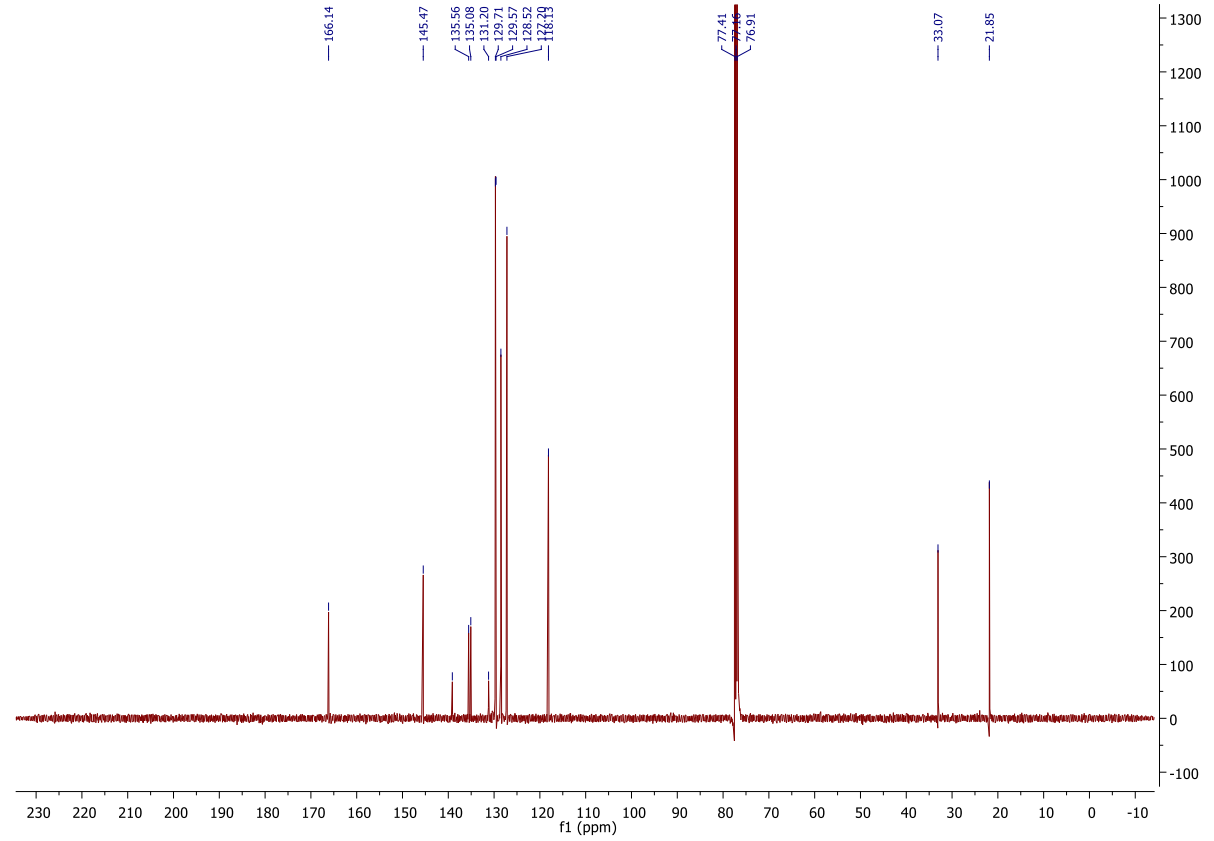
(6)



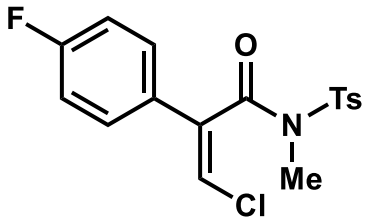
Prepared according to the General Procedure G using 2-(4-chlorophenyl)-N-methyl-N-tosylacrylamide (105 mg, 0.30 mmol, 1 equiv.), magnesium chloride (143 mg, 1.50 mmol, 5 equiv.), acetonitrile (5.25 mL) and acetic acid (0.75 mL). Purification by flash column chromatography (eluent = 5 to 15% EtOAc in hexanes, silica gel) to afford product as a white solid **(6)** (96.4 mg, 84% yield).

Mp.: 151-152 ^{o}C; $\mathbf{R_f}$ = 0.27 (eluent = 15% EtOAc in hexanes); $\mathbf{\nu_{max}}$ **/ cm^{-1}** (thin film) 3050, 1680, 1595, 1494, 1350, 1323, 1271, 1165, 1083, 952; **^{1}H NMR (500 MHz, CDCl$_3$)** δ_H: 2.45 (3H, s), 3.30 (3H, s), 6.53 (1H, s), 7.16-7.22 (2H, m), 7.28-7.34 (4H, m), 7.75 (2H, d, *J* 8.1 Hz); **^{13}C NMR (126 MHz, CDCl$_3$)** δ_C: 21.9, 33.1, 118.1, 127.2, 128.5, 129.6, 129.7, 131.2, 135.1, 135.6, 139.1, 145.5, 166.1; **HRMS (ES$^+$)** [$C_{17}H_{15}NO_3SCl_2$] requires 384.0228 $[M+H]^+$ found 384.0231 (+ 0.8 ppm).


7.76
7.75
7.33
7.31
7.31
7.31
7.26
7.20
6.53
3.30
2.45
1.99
4.15
2.09
1.00
3.26
3.31
f1 (ppm)

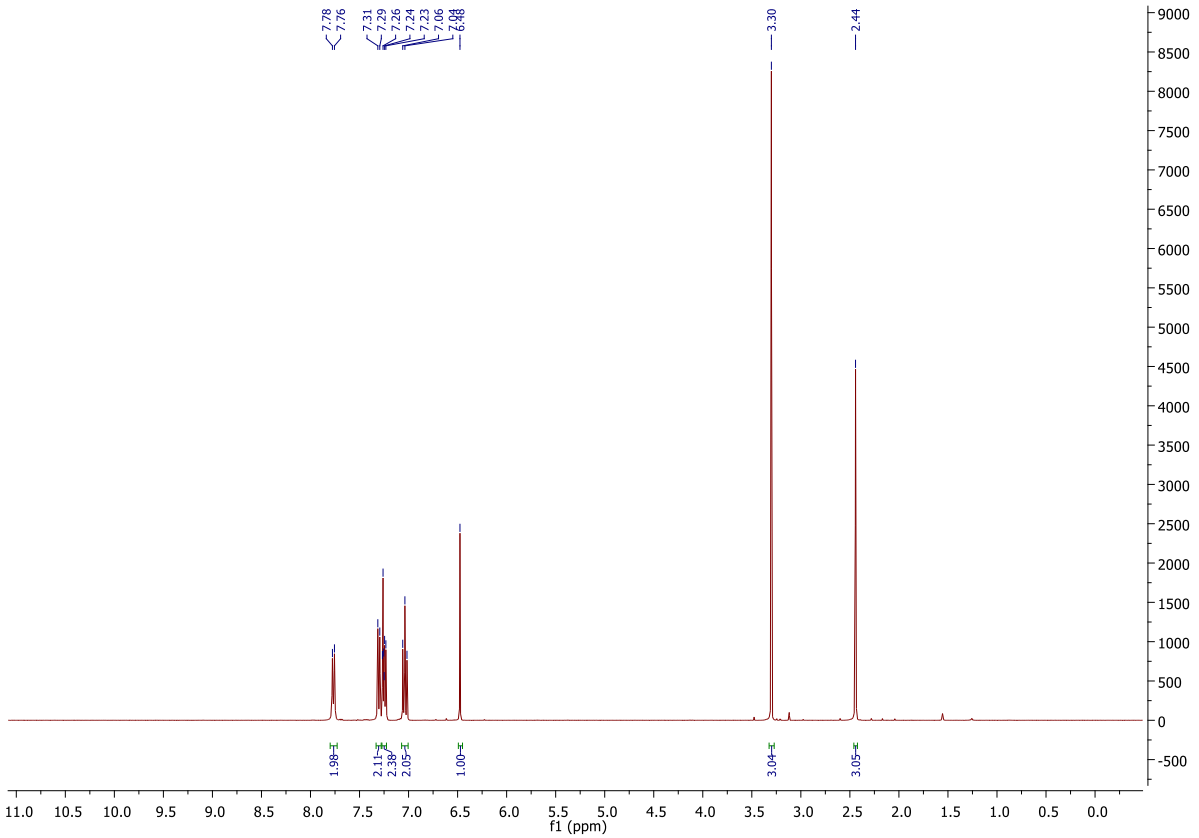

166.14
145.47
135.56
135.08
131.20
129.71
129.57
128.52
77.41
77.16
76.91
33.07
21.85
f1 (ppm)

(7)



Prepared according to General Procedure G using 2-(4-fluorophenyl)-N-methyl-N-tosylacrylamide (100 mg, 0.30 mmol, 1 equiv.), magnesium chloride (143 mg, 1.50 mmol, 5 equiv.), acetonitrile (5.25 mL) and acetic acid (0.75 mL). Purification by flash column chromatography (eluent = 10 to 15% EtOAc in hexanes, silica gel) to afford product **(7)** as a white solid (103 mg, 92% yield).

Mp.: 147-150 ^{o}C **R_f** = 0.26 (eluent = 20% EtOAc in hexanes); **ν_{max} / cm^{-1}**(thin film) 3071, 1682, 1602, 1593, 1506, 1467, 1352, 1286, 1220, 1167, 1157, 1101, 1084, 1014, 943 ; **^{1}H NMR (400 MHz, $CDCl_3$)** δ_H: 2.44 (3H, s), 3.30 (3H, s), 6.48 (1H, s), 7.04 (2H, app t, *J* 8.7 Hz), 7.22-7.27 (2H, m), 7.30 (2H, d, *J* 8.1 Hz), 7.77 (2H, d, *J* 8.1 Hz); **^{13}C NMR (126 MHz, $CDCl_3$)** δ_C: 21.8, 33.1, 116.4 (d, *J* 21.2 Hz), 117.5 (d, *J* 2.0 Hz), 127.9 (d, *J* 8.1 Hz), 128.6, 128.9 (d, *J* 4.0 Hz), 129.7, 135.2, 139.1, 145.4, 163.4 (d, *J* 251.5 Hz), 166.3; **^{19}F NMR (471 MHz, $CDCl_3$)** δ_F: -111.3; **HRMS (ES^{+})** [$C_{17}H_{15}NO_3SClF$] requires $[M+H]^+$ 368.0523 found 368.0525 (+ 0.50 ppm)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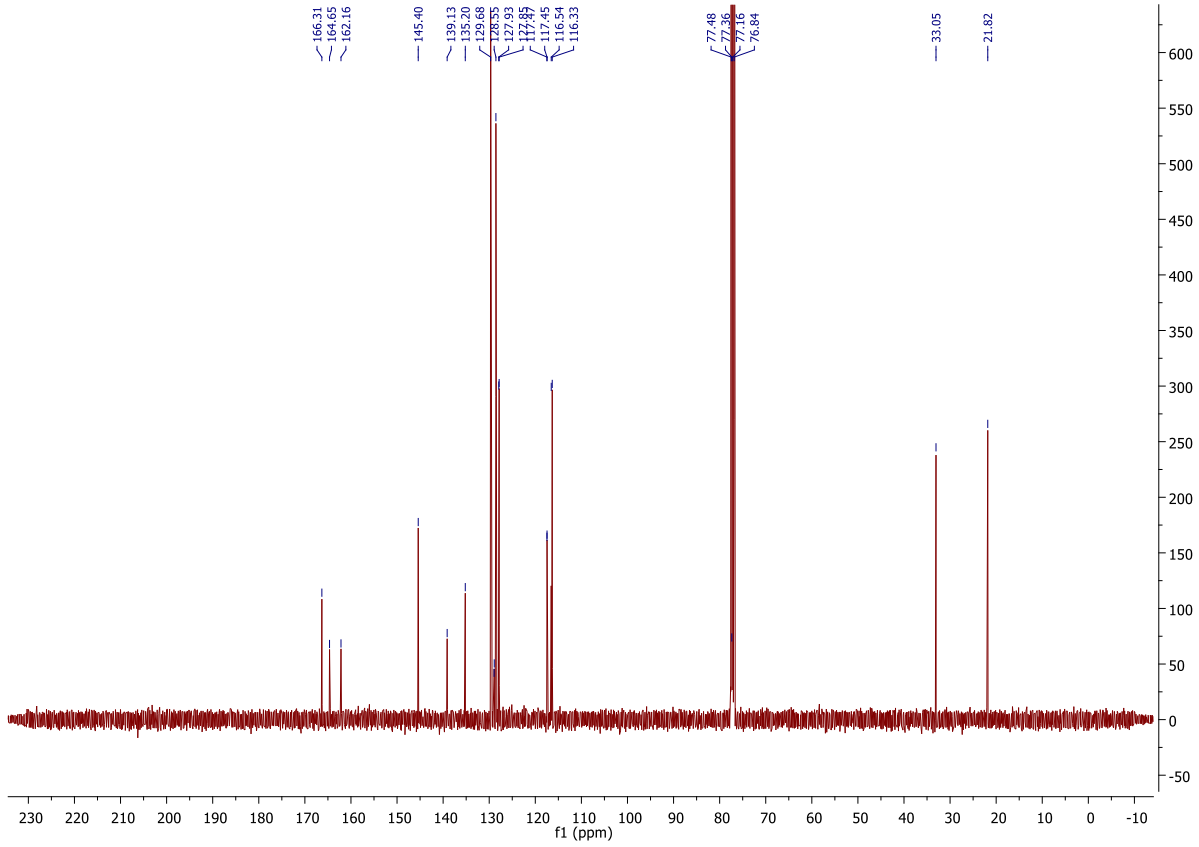
7.76
7.31
7.29
7.26
7.24
7.23
7.06
6.98
3.30
2.44
1.98
2.11
2.38
2.05
1.00
3.04
3.05
f1 (ppm)


166.31
164.65
162.16
145.40
139.13
135.20
129.68
128.55
127.93
117.45
116.54
116.33
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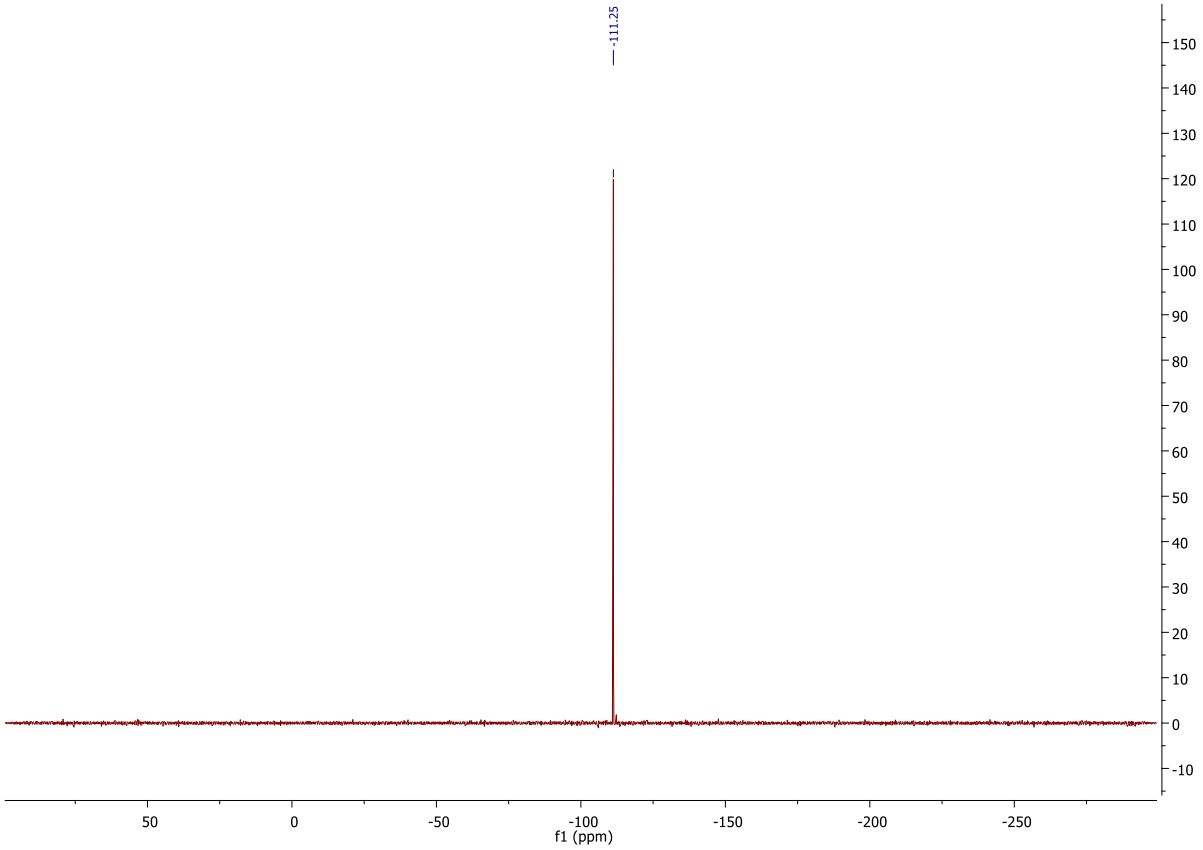
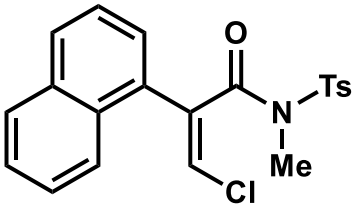
77.36
77.16
76.84
33.05
21.82
f1 (ppm)

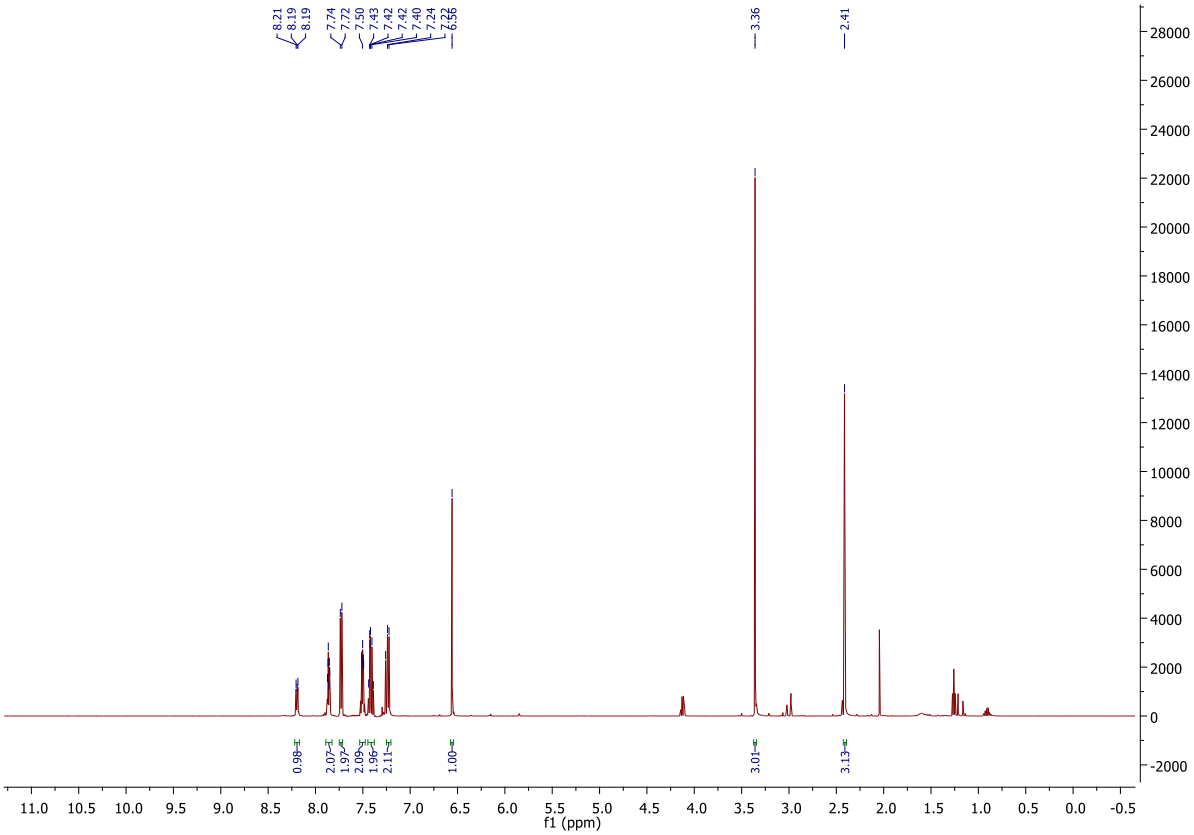

-111.25
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
50
0
-50
-100
-150
-200
-250
f1 (ppm)

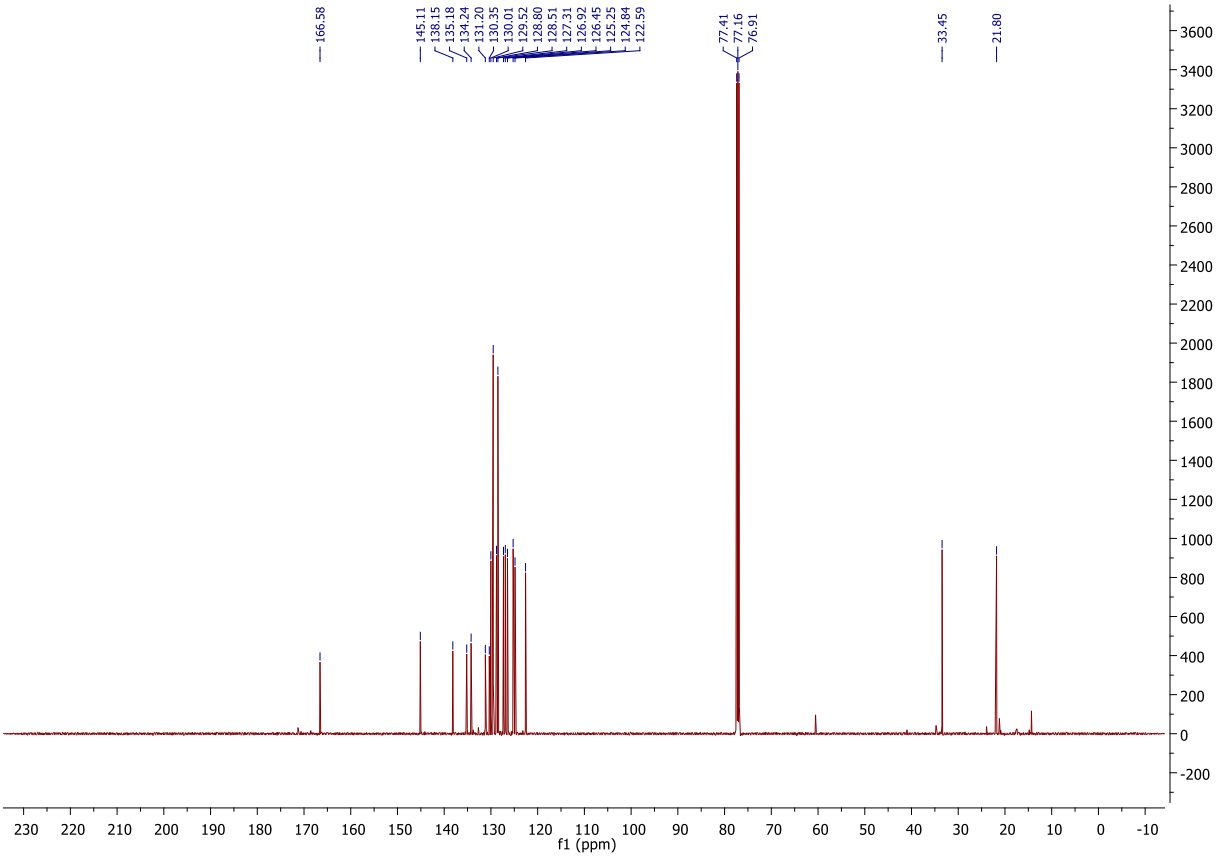
(8)



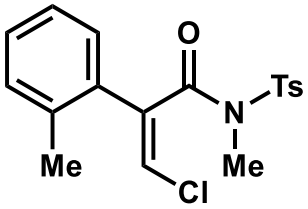
Prepared according to the General Procedure G using N-methyl-2-(naphthalen-1-yl)-N-tosylacrylamide (110 mg, 0.30 mmol, 1 equiv.), magnesium chloride (143 mg, 1.50 mmol, 5 equiv.), acetonitrile (5.25 mL) and acetic acid (0.75 mL). Purification by flash column chromatography (eluent = 5 to 15% EtOAc in hexanes, silica gel) to afford product **(8)** as a colourless oil (88.0 mg, 74% yield).

R_f = 0.27 (eluent = 15% EtOAc in hexanes); **ν_{max} / cm^{-1}** (thin film) 3040, 1688, 1594, 1358, 1317, 1188, 1168, 1087, 932; **^{1}H NMR (500 MHz, $CDCl_3$)** δ_H: 2.41 (3H, s), 3.36 (3H, s), 6.56 (1H, s), 7.23 (2H, d, *J* 8.1 Hz), 7.38-7.45 (2H, m), 7.48-7.53 (2H, m), 7.73 (2H, d, *J* 8.2 Hz), 7.82-7.89 (2H, m), 8.15-8.24 (1H, m); **^{13}C NMR (126 MHz, $CDCl_3$)** δ_C: 21.8, 33.5, 122.6, 124.8, 125.3, 126.5, 126.9, 127.3, 128.5, 128.8, 129.5, 130.0, 130.4, 131.2, 134.2, 135.2, 138.2, 145.1, 166.6; **HRMS (ES$^+$)** [$C_{21}H_{18}NO_3SCl$] requires $[M+H]^+$ 400.0774 found 400.0768 (-1.5 ppm).


8.21
8.19
8.19
7.74
7.72
7.50
7.43
7.42
7.42
7.40
7.24
6.56
3.36
2.41
0.98
2.07
1.97
2.09
1.96
2.11
1.00
3.01
3.13
f1 (ppm)

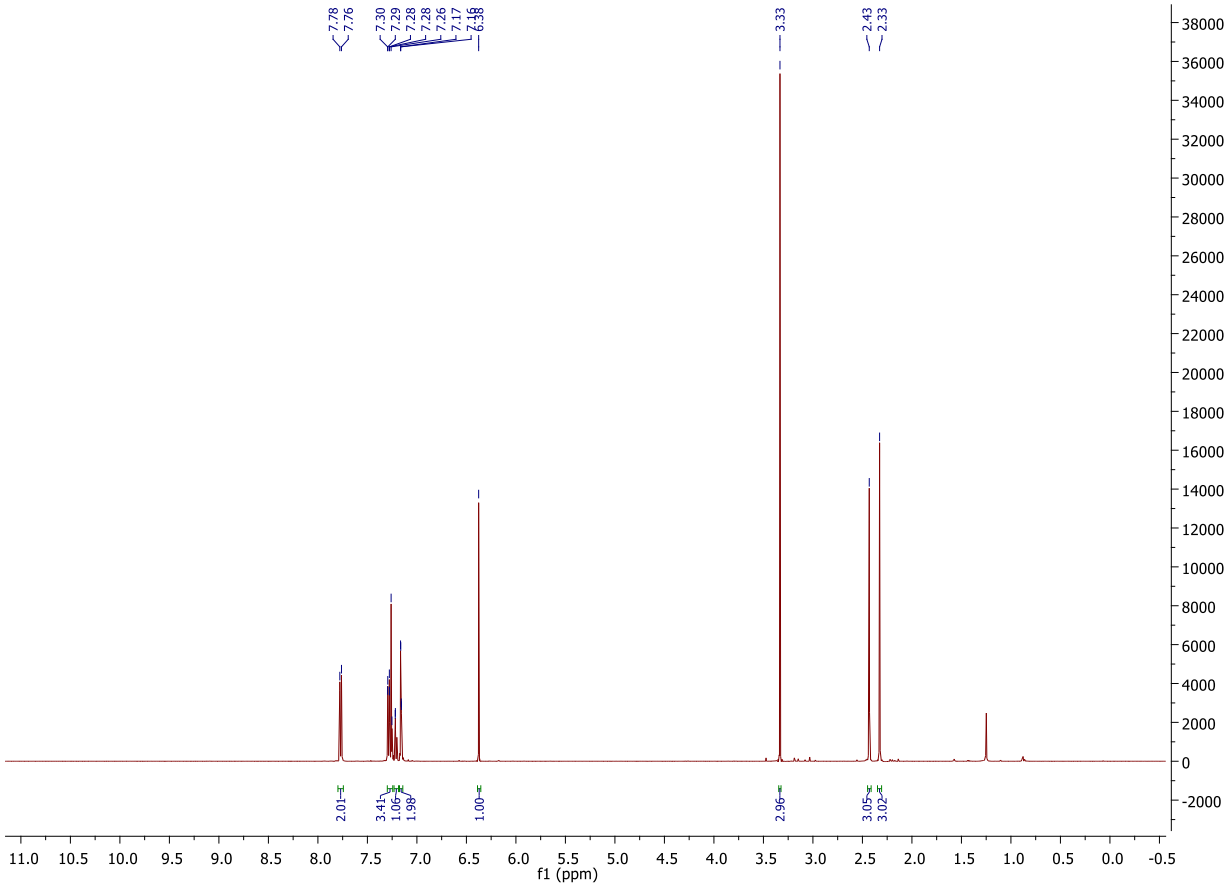

166.58
145.11
138.15
135.18
134.24
131.20
130.35
130.01
129.52
128.80
128.51
127.31
126.92
126.45
125.25
124.84
122.59
77.41
77.16
76.91
33.45
21.80
f1 (ppm)

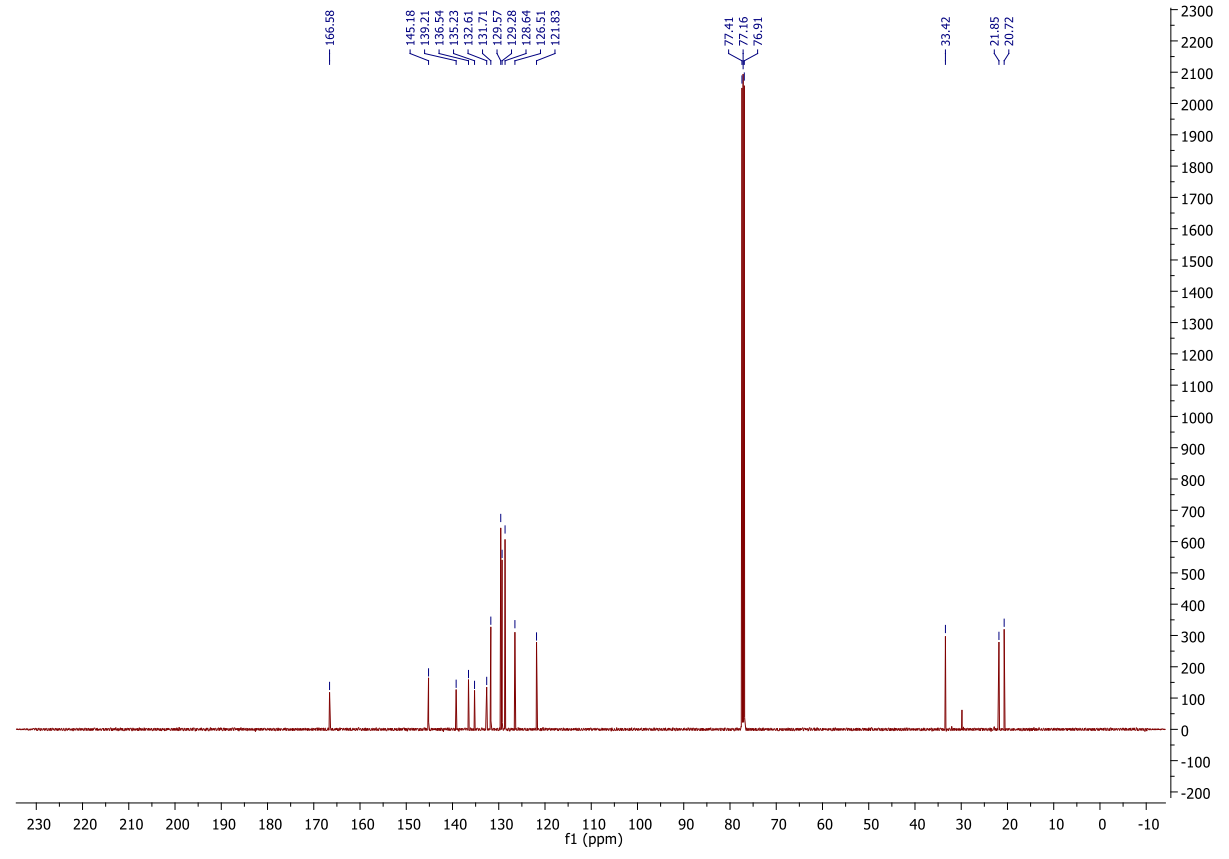
(9)



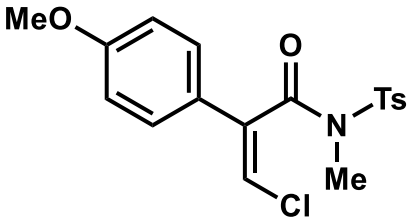
Prepared according to the General Procedure G using N-methyl-2-(o-tolyl)-N-tosylacrylamide (98.8 mg, 0.30 mmol, 1 equiv.), magnesium chloride (143 mg, 1.50 mmol, 5 equiv.), acetonitrile (5.25 mL) and acetic acid (0.75 mL). Purification by flash column chromatography (eluent = 5 to 15% EtOAc in hexanes, silica gel) to afford pure product **(9)** as a white solid (91.1 mg, 83% yield).

Mp: 107-109 °C; $\mathbf{R_f}$ = 0.32 (eluent = 20% EtOAc in hexanes); $\mathbf{\nu_{max}}$ **/ cm^{-1}** (thin film) 1689, 1595, 1450, 1350, 1244, 1167, 1074; **^{1}H NMR (500 MHz, $CDCl_3$)** δ_H: 2.33 (3H, s), 2.43 (3H, s), 3.33 (3H, s), 6.38 (1H, s), 7.13-7.18 (2H, m), 7.18-7.23 (1H, m), 7.24-7.31 (3H, m), 7.77 (2H, d, *J* 8.4 Hz); **^{13}C NMR (126 MHz, $CDCl_3$)** δ_C: 20.7, 21.9, 33.4, 121.8, 126.5, 128.6, 129.3, 129.6, 131.7, 132.6, 135.2, 136.5, 139.2, 145.2, 166.6; **HRMS (ES^{+})** [$C_{18}H_{18}NO_3SCl$] requires $[M+H]^+$ 364.0774, found 364.0776 (+ 0.50 ppm).


7.78
7.76
7.30
7.29
7.28
7.28
7.26
7.17
7.16
7.16
6.38
3.33
2.43
2.33
2.01
3.41
1.06
1.98
1.00
2.96
3.05
3.02
f1 (ppm)

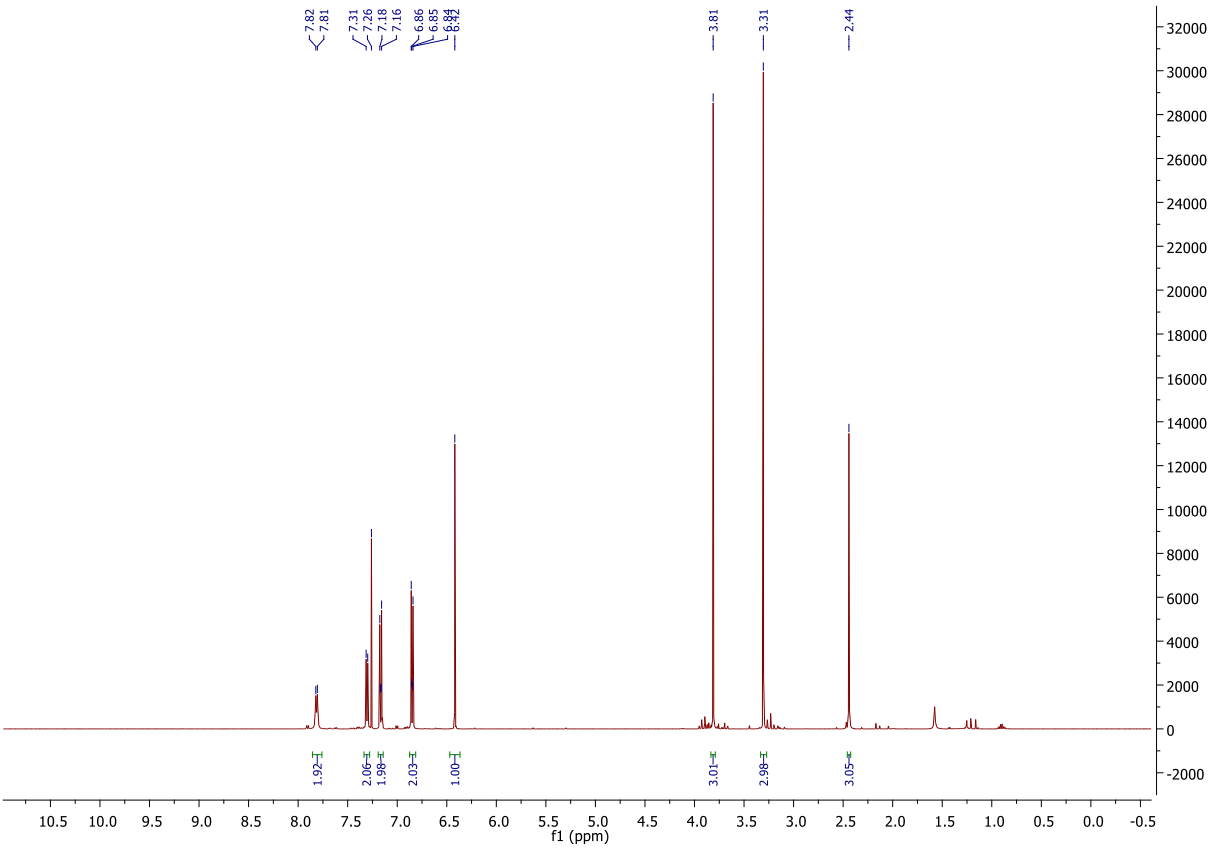

166.58
145.18
139.21
136.54
135.23
132.61
131.71
129.57
129.28
128.64
126.51
121.83
77.41
77.16
76.91
33.42
21.85
20.72
f1 (ppm)

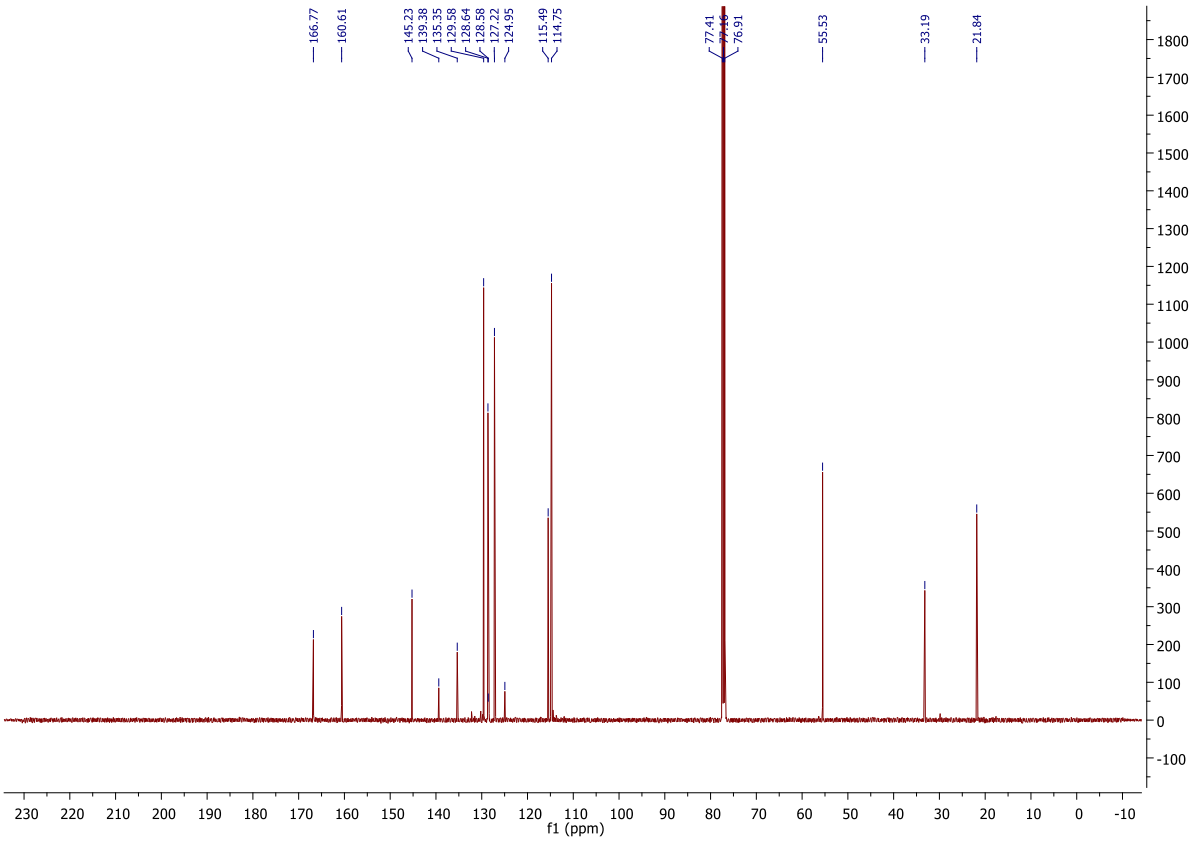
(10)



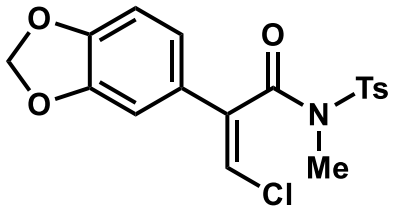
Prepared according to the General Procedure G using 2-(4-methoxyphenyl)-N-methyl-N-tosylacrylamide (104 mg, 0.30 mmol, 1 equiv.), magnesium chloride (143 mg, 1.50 mmol, 5 equiv.), acetonitrile (5.25 mL) and acetic acid (0.75 mL). Purification by flash column chromatography (eluent = 5 to 15% EtOAc in hexanes, silica gel) to afford product **(10)** as a colourless oil (52.1 mg, 46% yield).

R_f = 0.21 (eluent = 15% EtOAc in hexanes); **ν_{max} / cm^{-1}** (thin film) 3076, 1692, 1606, 1514, 1464, 1358, 1186, 1168, 1084, 952; **^{1}H NMR (500 MHz, $CDCl_3$)** δ_H: 2.44 (3H, s), 3.31 (3H, s), 3.81 (3H, s), 6.42 (1H, s), 6.82-6.88 (2H, m), 7.14-7.19 (2H, m), 7.31 (2H, d, *J* 8.0 Hz), 7.81 (2H, d, *J* 8.0 Hz); **^{13}C NMR (126 MHz, $CDCl_3$)** δ_C: 21.8, 33.2, 55.5, 114.8, 115.5, 125.0, 127.2, 128.6, 129.6, 135.4, 139.4, 145.2, 160.6, 166.8; **HRMS (ES$^+$)** [$C_{18}H_{18}NO_4SCl$] requires $[M+H]^+$ 380.0723 found 380.0720 (-0.8 ppm).


7.82
7.81
7.31
7.26
7.18
7.16
6.86
6.85
6.84
6.82
3.81
3.31
2.44
1.92
2.06
1.98
2.03
1.00
3.01
2.98
3.05
f1 (ppm)

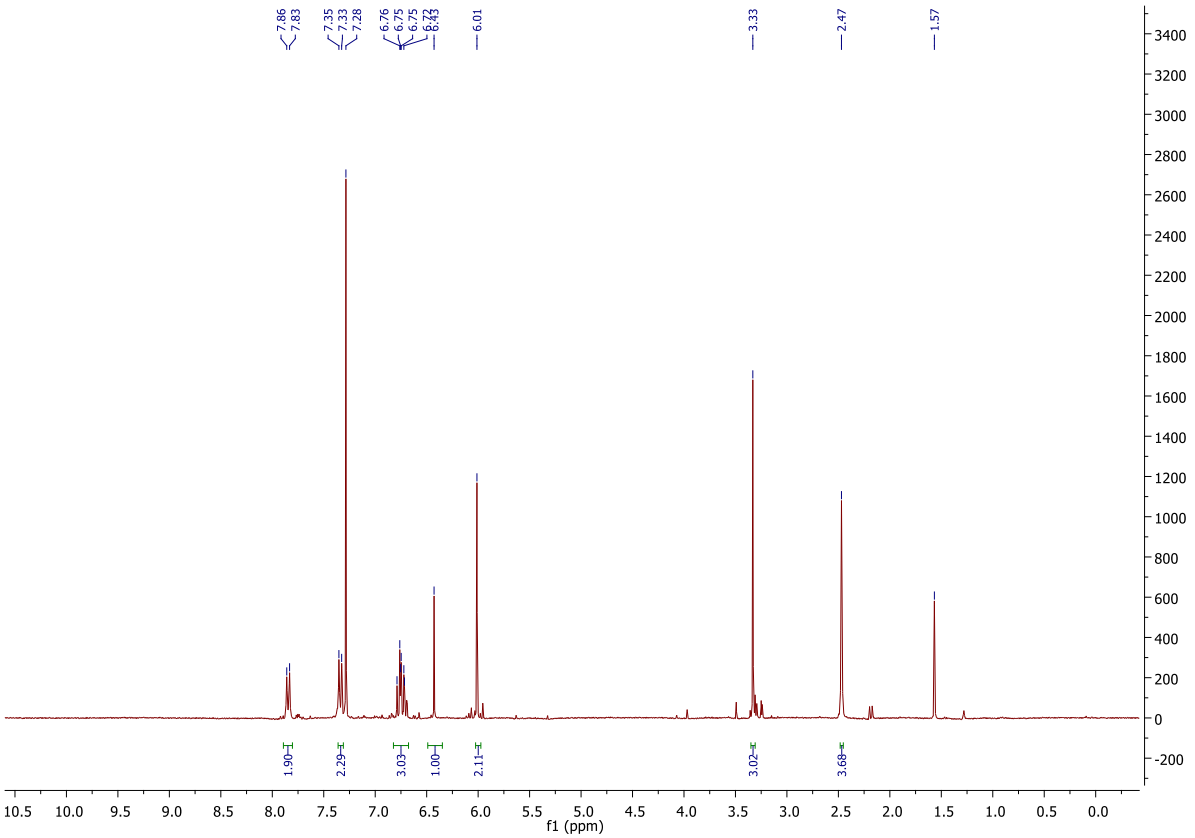

166.77
160.61
145.23
139.38
135.35
129.58
128.64
128.58
127.22
124.95
115.49
114.75
77.41
77.16
76.91
55.53
33.19
21.84
f1 (ppm)

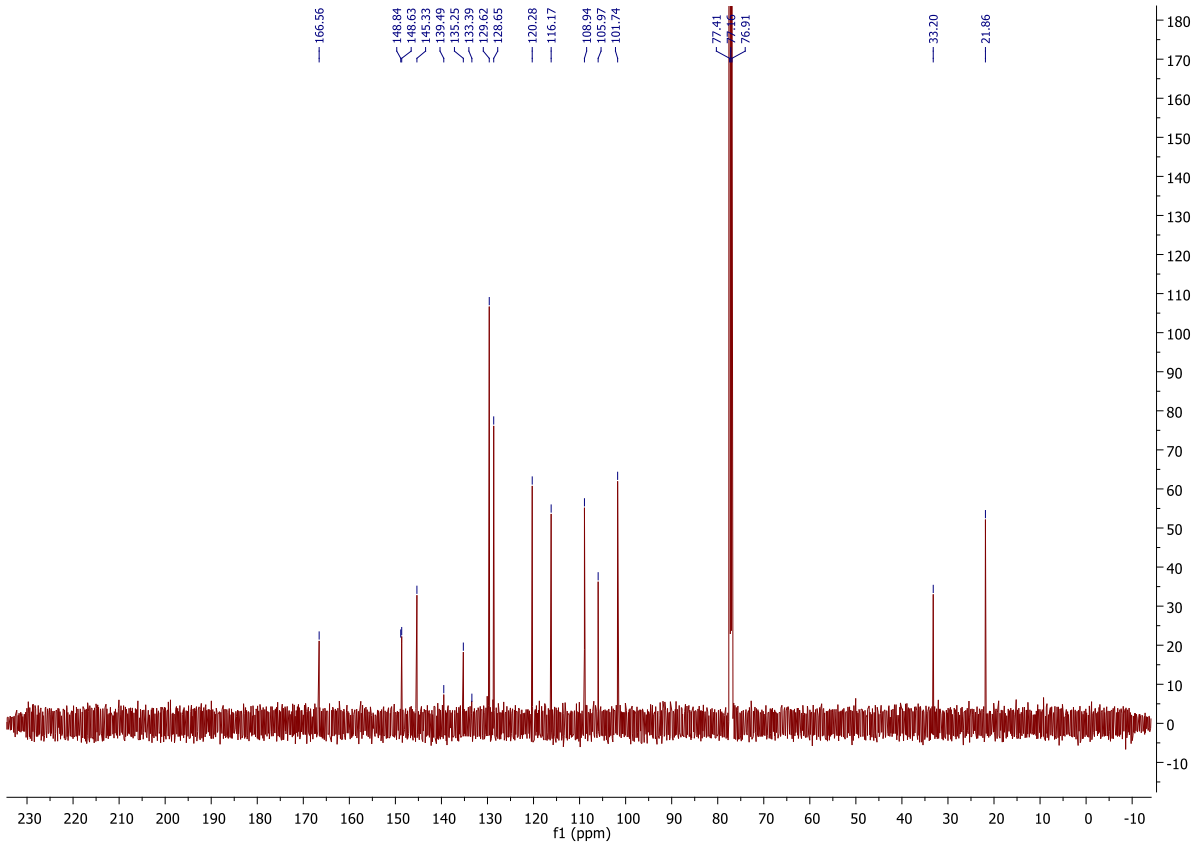
(11)



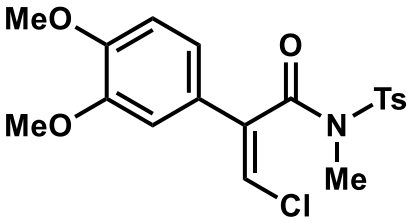
Prepared according to the General Procedure G using 2-(benzo[d][1,3]dioxol-5-yl)-N-methyl-N-tosylacrylamide (108 mg, 0.30 mmol, 1 equiv.), magnesium chloride (143 mg, 1.50 mmol, 5 equiv.), acetonitrile (5.25 mL) and acetic acid (0.75 mL). Purification by flash column chromatography (eluent = 10 to 20% EtOAc in hexanes, silica gel) to afford product **(11)** as a colourless oil (58.0 mg, 47% yield).

R_f = 0.33 (eluent = 35% EtOAc in hexanes); **ν_{max} / cm^{-1}** (thin film) 2995, 1676, 1597, 1489, 1446, 1352, 1248, 1167, 1076, 1062, 970; **^{1}H NMR (300 MHz, $CDCl_3$)** δ_H: 2.45 (3H, s), 3.31 (3H, s), 5.99 (2H, s), 6.40 (1H, s), 6.66-6.77 (3H, m), 7.31 (2H, d, *J* 8.2 Hz), 7.82 (2H, d, *J* 8.2 Hz); **^{13}C NMR (126 MHz, $CDCl_3$)** δ_C: 21.9, 33.2, 101.7, 106.0, 108.9, 116.2, 120.3, 128.7, 129.6, 133.4, 135.3, 139.5, 145.3, 148.6, 148.8, 166.6; **HRMS (ES$^+$)** [$C_{18}H_{17}NO_5SCl$] requires $[M+H]^+$ 394.0516 found 394.0516 (+ 0.0 ppm).


7.86
7.83
7.35
7.33
7.28
6.76
6.75
6.75
6.72
6.43
6.01
3.33
2.47
1.57
1.90
2.29
3.03
1.00
2.11
3.02
3.68
f1 (ppm)

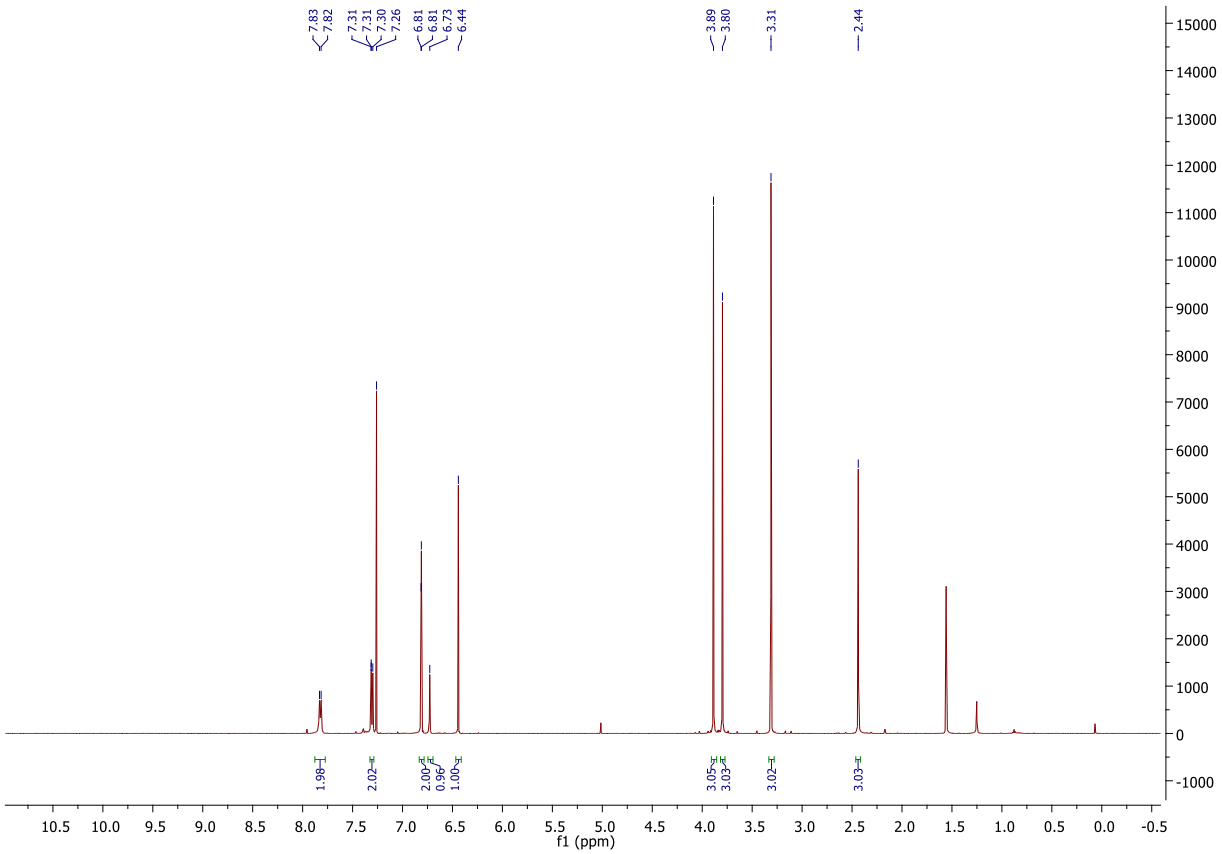

166.56
148.84
148.63
145.33
139.49
135.25
133.39
129.62
128.65
120.28
116.17
108.94
105.97
101.74
77.41
77.16
76.91
33.20
21.86
f1 (ppm)

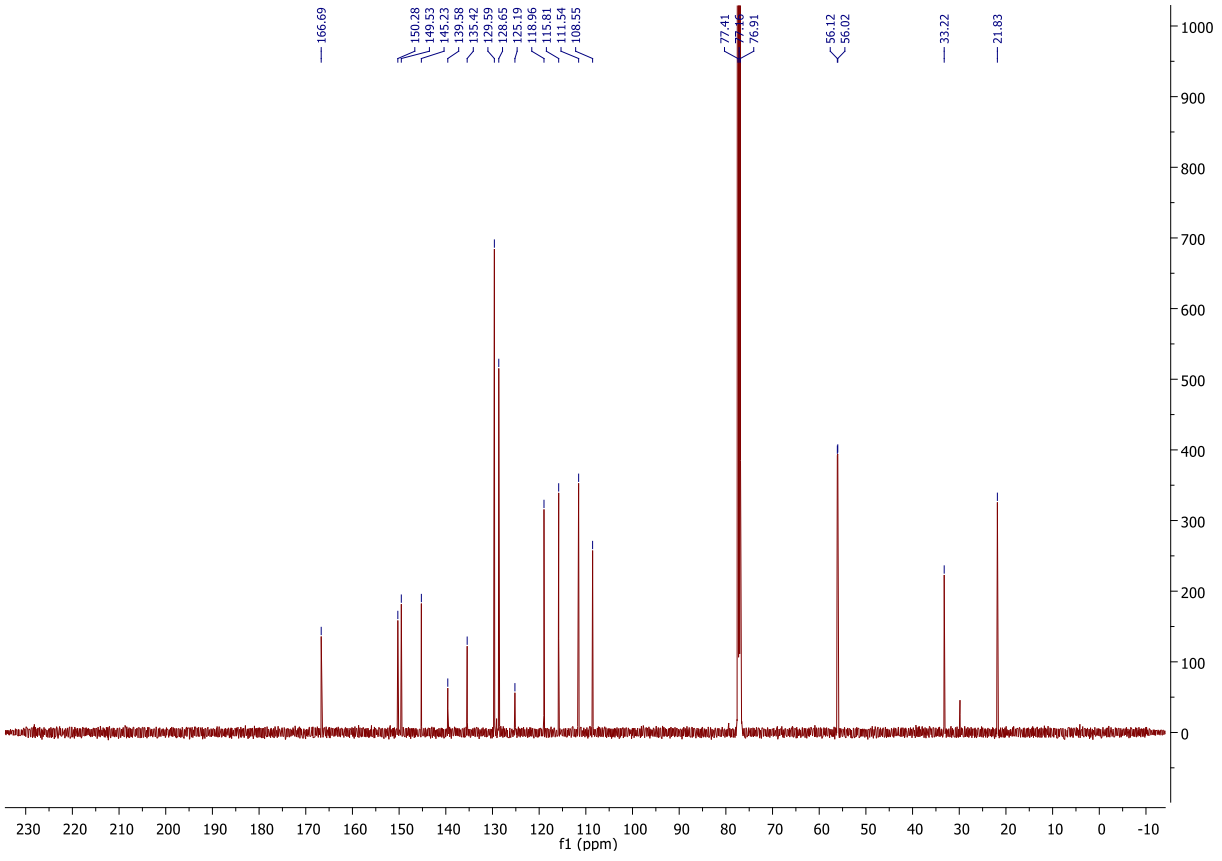
(12)



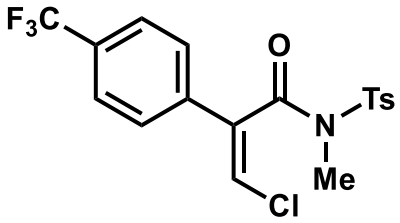
Prepared according to the General Procedure G using 2-(3,4-dimethoxyphenyl)-N-methyl-N-tosylacrylamide (113 mg, 0.30 mmol, 1 equiv.), magnesium chloride (143 mg, 1.50 mmol, 5 equiv.), acetonitrile (5.25 mL) and acetic acid (0.75 mL). Purification by flash column chromatography (eluent = 5 to 15% EtOAc in hexanes, silica gel) to afford product **(12)** as a colourless oil (42.0 mg, 34% yield).

R_f = 0.17 (eluent = 15% EtOAc in hexanes); **ν_{max} / cm^{-1}** (thin film) 3080, 1692, 1597, 1516, 1463, 1357, 1263, 1167, 1083; **^{1}H NMR (500 MHz, $CDCl_3$)** δ_H: 2.44 (3H, s), 3.31 (3H, s), 3.80 (3H, s), 3.89 (3H, s), 6.44 (1H, s), 6.73 (1H, s), 6.81 (2H, d, *J* 1.3 Hz), 7.28-7.33 (2H, m), 7.82 (2H, d, *J* 8.0 Hz); **^{13}C NMR (126 MHz, $CDCl_3$)** δ_C: 21.8, 33.2, 56.0, 56.1, 108.6, 111.5, 115.8, 119.0, 125.2, 128.7, 129.6, 135.4, 139.6, 145.2, 149.5, 150.3, 166.7; **HRMS (ES$^+$)** [$C_{19}H_{20}NO_5SCl$] requires $[M+H]^+$ 410.0829 found 410.0837 (+ 2.0 ppm).


7.83
7.82
7.31
7.31
7.30
7.26
6.81
6.81
6.73
6.44
3.89
3.80
3.31
2.44
1.98
2.02
2.00
0.96
1.00
3.05
3.03
3.02
3.03
f1 (ppm)

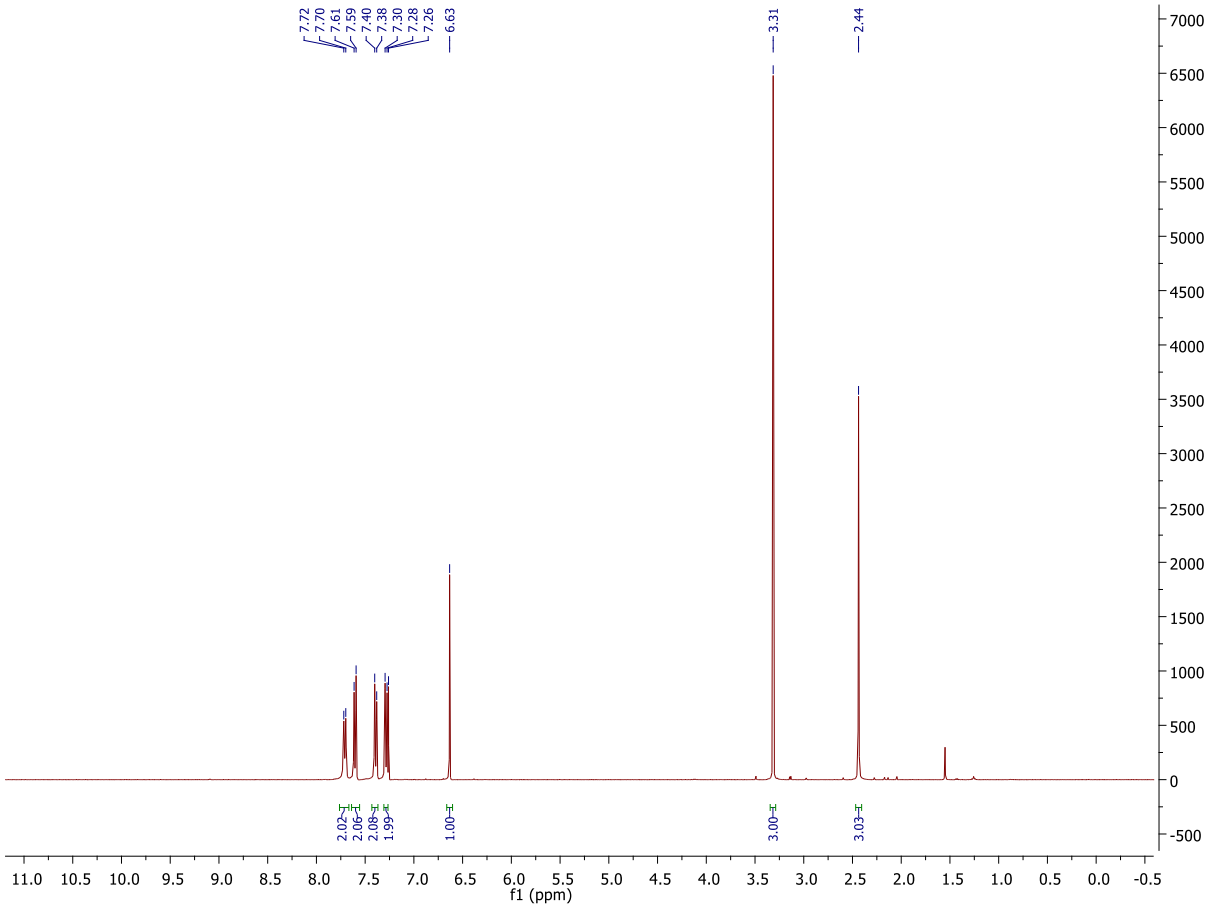

166.69
150.28
149.53
145.23
139.58
135.42
129.59
128.65
125.19
118.96
115.81
111.54
108.55
77.41
77.16
76.91
56.12
56.02
33.22
21.83
f1 (ppm)

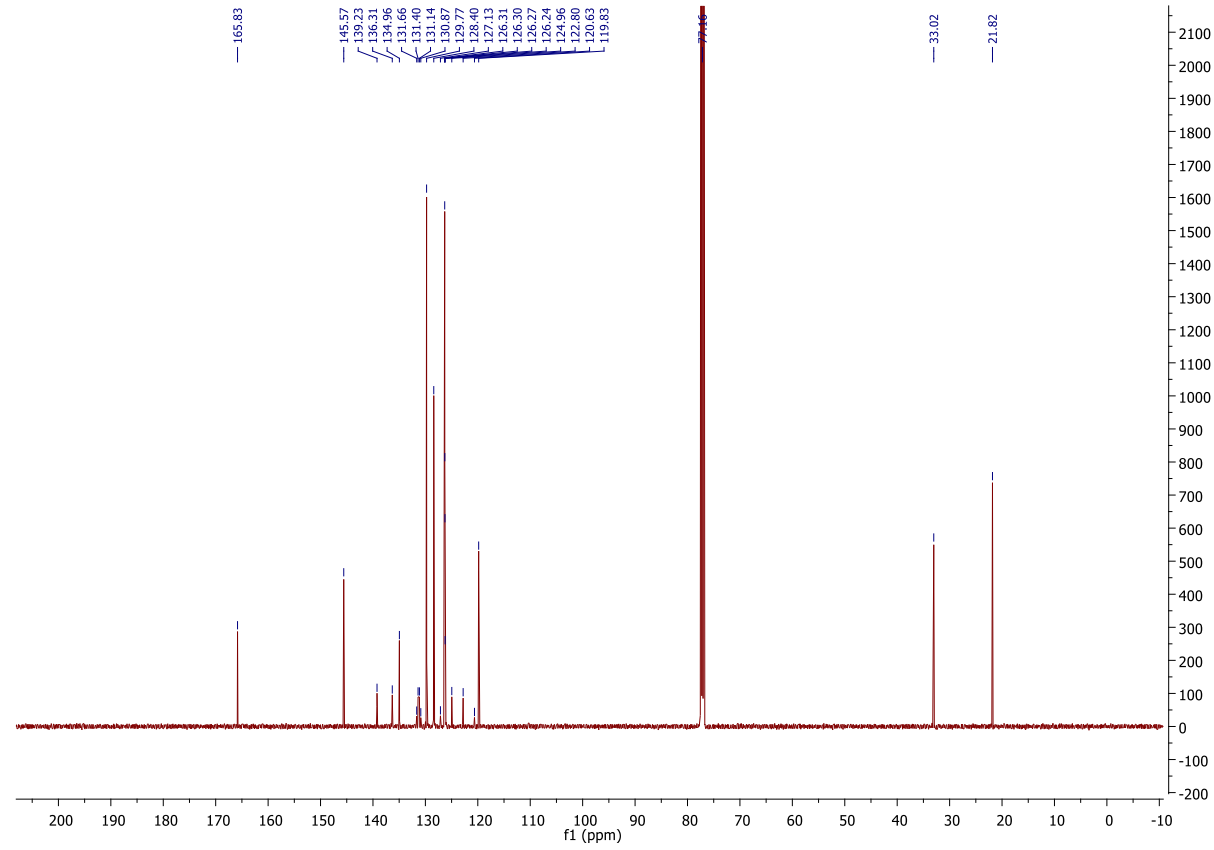
(13)



Prepared according to the General Procedure G using N-methyl-N-tosyl-2-(4-(trifluoromethyl)phenyl)acrylamide (115 mg, 0.30 mmol, 1 equiv.), magnesium chloride (143 mg, 1.50 mmol, 5 equiv.), acetonitrile (5.25 mL) and acetic acid (0.75 mL). Purification by flash column chromatography (eluent = 10 to 20% EtOAc in hexanes, silica gel) to afford product **(13)** as a white solid (85.1 mg, 67% yield).

Mp.: 132-135 °C; **R_f** = 0.42 (eluent = 20% EtOAc in hexanes); **ν_{max} / cm^{-1}** (thin film) 3065, 1674, 1614, 1593, 1468, 1410, 1323, 1170, 1105, 1084, 1017, 943; **^{1}H NMR (400 MHz, $CDCl_3$)** δ_H: 2.44 (3H, s), 3.31 (3H, s), 6.63 (1H, s), 7.29 (2H, d, *J* 8.1 Hz), 7.39 (2H, d, *J* 8.1 Hz), 7.60 (2H, d, *J* 8.1 Hz), 7.71 (2H, d, *J* 8.2 Hz); **^{13}C NMR (126 MHz, $CDCl_3$)** δ_C: 21.8, 33.0, 119.8, 122.8 (q, *J* 272.2), 126.3 (q, *J* 3.8 Hz), 126.3, 128.4, 129.8, 131.1 (q, *J* 32.8 Hz), 135.0, 136.3, 139.2, 145.6, 165.8; **^{19}F NMR (471 MHz, $CDCl_3$)** δ_F: -62.8; **HRMS (ES^+)** [$C_{18}H_{15}NO_3SClF_3$] requires $[M+H]^+$ 418.0492 found 418.0494 (+ 0.50 ppm).


7.72
7.70
7.61
7.59
7.40
7.38
7.30
7.28
7.26
6.63
3.31
2.44
2.02
2.06
2.08
1.99
1.00
3.00
3.03
f1 (ppm)


165.83
145.57
139.23
136.31
134.96
131.66
131.40
131.14
130.87
129.77
128.40
127.13
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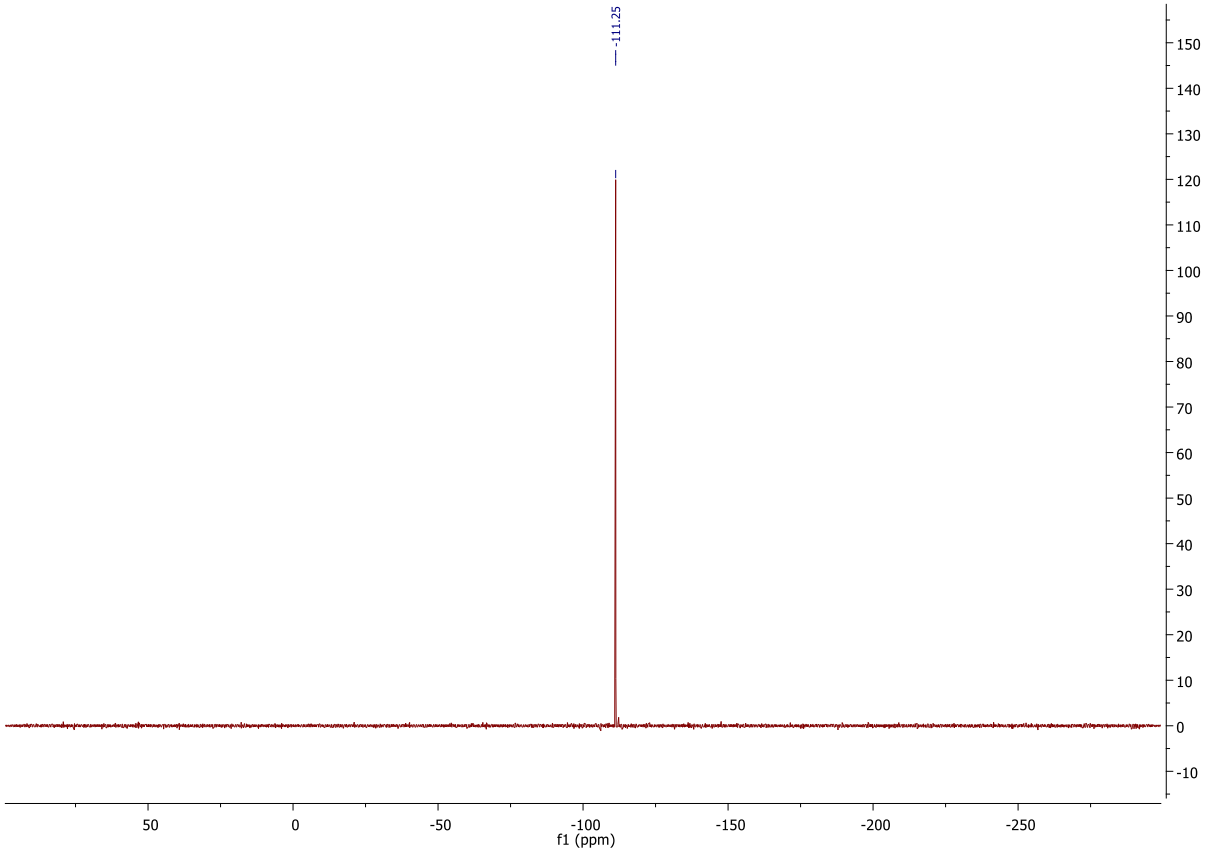
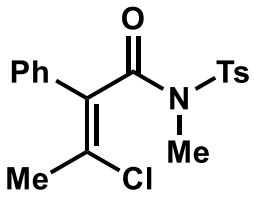
126.24
124.96
122.80
120.63
119.83
77.16
33.02
21.82
f1 (ppm)

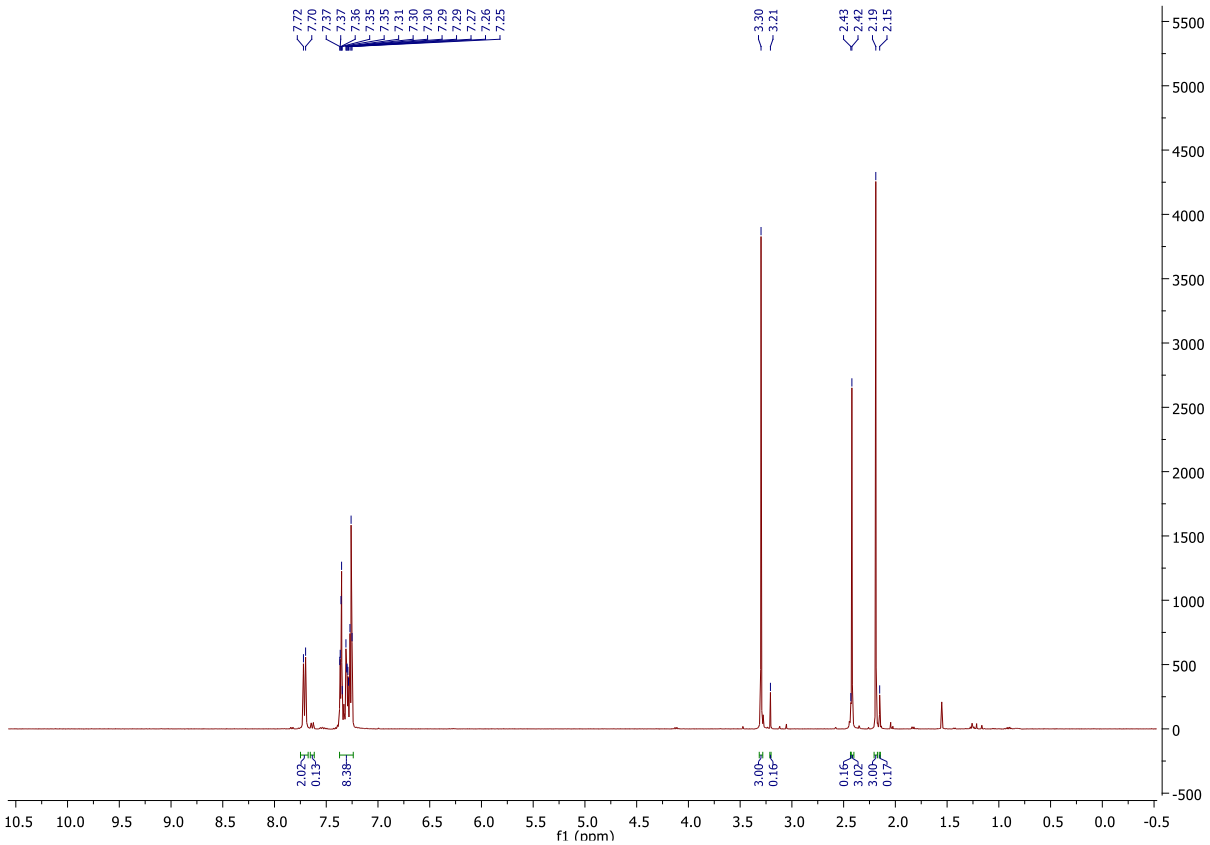

-111.25
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
50
0
-50
-100
-150
-200
-250
f1 (ppm)

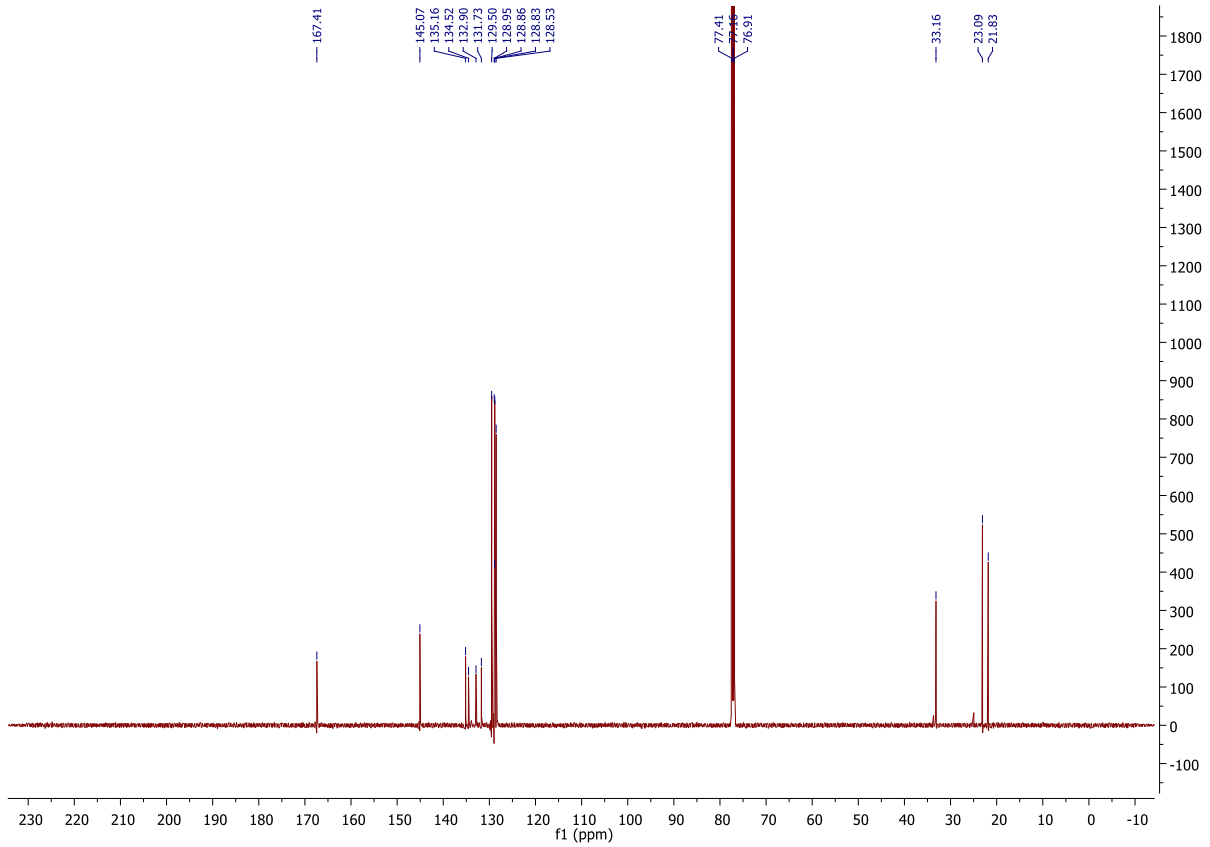
(14)



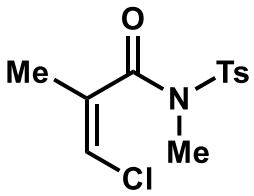
Prepared according to the General Procedure G using (E)-N-methyl-2-phenyl-N-tosylbut-2-enamide (98.9 mg, 0.30 mmol, 1 equiv.), magnesium chloride (143 mg, 1.50 mmol, 5 equiv.), acetonitrile (5.25 mL) and acetic acid (0.75 mL). Purification by flash column chromatography (eluent = 5 to 15% EtOAc in hexanes, silica gel) to afford product **(14)** as a colourless oil (82.1 mg, 75% yield).

R_f = 0.32 (eluent = 20% EtOAc in hexanes); **ν_{max} / cm^{-1}** (thin film) 2997, 1678, 1596, 1350, 1304, 1167, 1055, 1014; **^{1}H NMR (400 MHz, $CDCl_3$)** δ_H: 2.19 (3H, s), 2.43 (3H, s), 3.30 (3H, s), 7.23-7.39 (8H, m), 7.71 (2H, d, *J* 8.3 Hz); **^{13}C NMR (101 MHz, $CDCl_3$)** δ_C: 21.8, 23.1, 33.1, 128.5, 128.5, 128.8, 128.9, 129.0, 129.5, 131.7, 132.9, 134.5, 135.2, 145.1, 167.4; **HRMS (ES$^+$)** [$C_{18}H_{18}NO_3SCl$] requires $[M+H]^+$ 364.0768 found 364.0765 (- 1.0 ppm).


7.72
7.70
7.37
7.37
7.36
7.35
7.35
7.31
7.30
7.30
7.29
7.29
7.27
7.26
7.25
3.30
3.21
2.43
2.42
2.19
2.15
2.02
0.13
8.38
3.00
0.16
0.16
3.02
3.05
0.17
f1 (ppm)

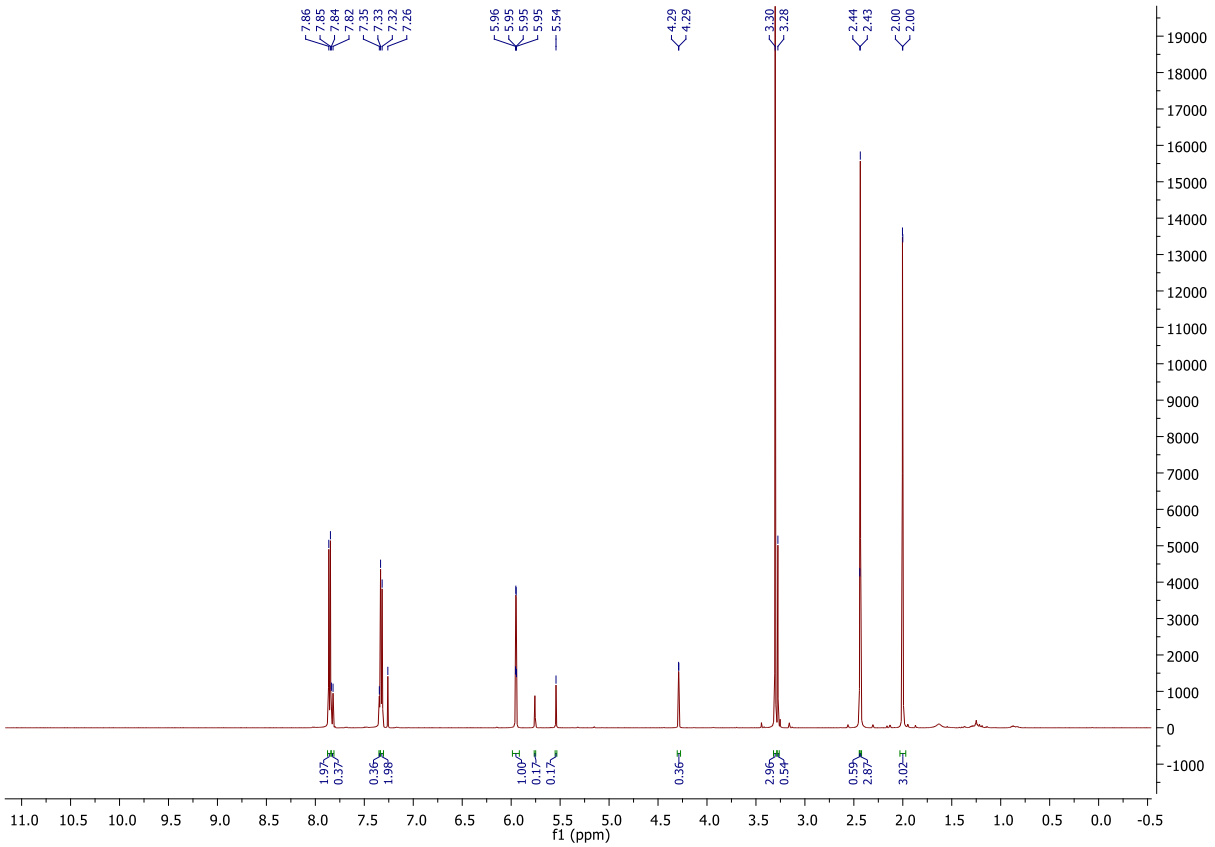

167.41
145.07
135.16
134.52
132.90
131.73
129.50
128.95
128.86
128.83
128.53
77.41
77.16
76.91
33.16
23.09
21.83
f1 (ppm)

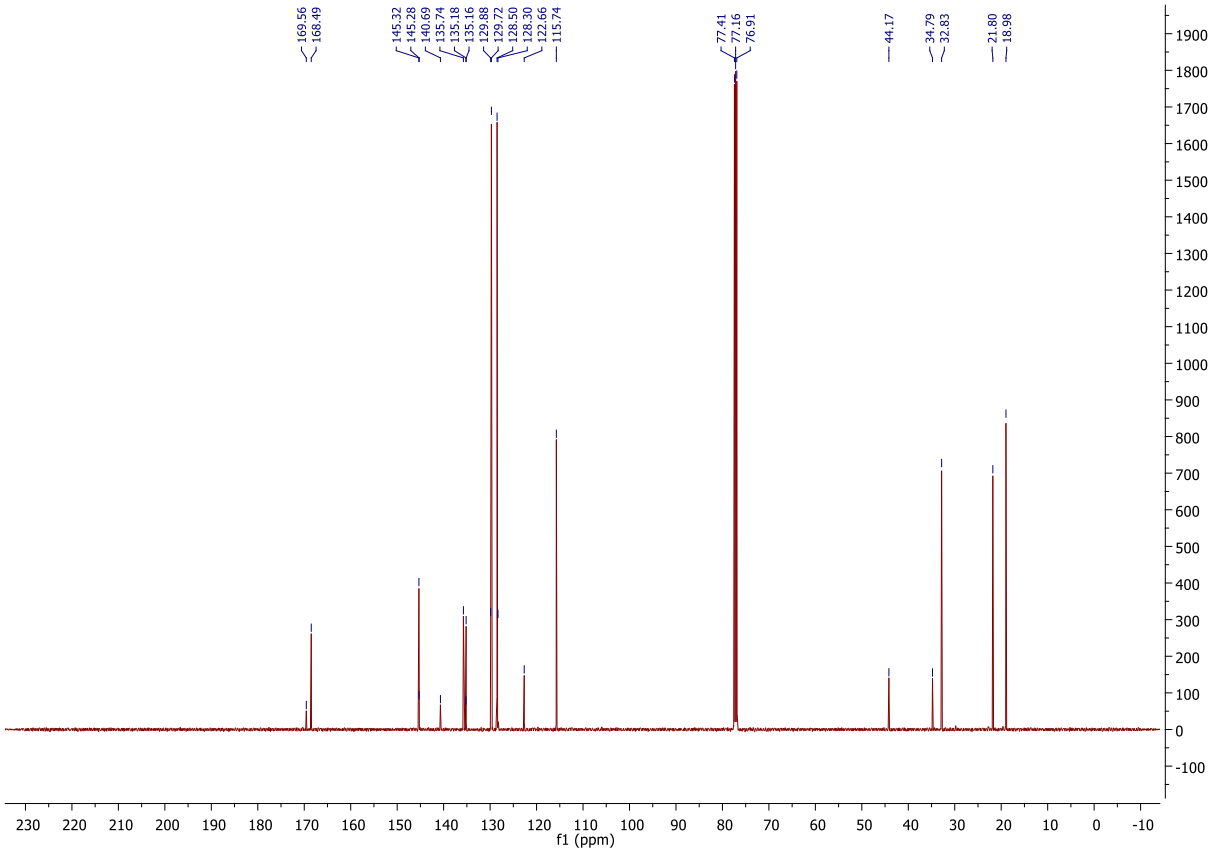
(15)



Prepared according to a modified General Procedure G using N-methyl-N-tosylmethacrylamide (76.0 mg, 0.30 mmol, 1 equiv.), magnesium chloride (143 mg, 1.50 mmol, 5 equiv.), acetonitrile (5.25 mL) and acetic acid (0.75 mL). Electrolysis was performed as per the general procedure (10 mA, constant current), however the passage of charge was increased from 2.5 F/mol to 3.5 F/mol. Purification by flash column chromatography (eluent = 5 to 15% EtOAc in hexanes, silica gel) to afford product as an inseperable mixture of alkene regioisomers **(15)** as a colourless oil (74.0 mg, 86% yield).

R_f = 0.27 (eluent = 20% EtOAc in hexanes); **ν_{max} / cm^{-1}**(thin film) 1685, 1595, 1436, 1356, 1256, 1165, 1051, 993; *Data for major alkene regioisomer:* **^{1}H NMR (500 MHz, $CDCl_3$)** δ_H: 2.00 (3H, d, *J* 1.6 Hz), 2.43 (3H, s), 3.30 (3H, s), 5.95 (1H, app. q, *J* 1.6 Hz), 7.33 (2H, d, *J* 8.2 Hz), 7.85 (2H, d, *J* 8.3 Hz); **^{13}C NMR (126 MHz, $CDCl_3$)** δ_C: 19.0, 21.8, 32.8, 115.7, 128.5, 129.7, 135.2, 135.7, 145.3, 168.5; *Data for minor alkene regioisomer:* **^{1}H NMR (500 MHz, $CDCl_3$)** δ_H: 2.44 (3H, s), 3.28 (3H, s), 4.29 (2H, m), 5.54 (1H, s), 5.76 (1H, app t, *J* 1.2 Hz), 7.33 (2H, m), 7.83 (2H, d, *J* 8.4 Hz); **^{13}C NMR (126 MHz, $CDCl_3$)** δ_C: 21.8, 34.8, 44.2, 122.7, 128.3, 129.9, 140.7, 145.3, 169.6; **HRMS (ES$^+$)** [$C_{12}H_{14}NO_3SCl$] requires $[M+H]^+$ 288.0461, found 288.0460 (-0.30 ppm).


7.86
7.85
7.84
7.82
7.35
7.33
7.32
7.26
5.96
5.95
5.95
5.95
5.54
4.29
4.29
3.30
3.28
2.44
2.43
2.00
2.00
1.97
0.37
0.36
1.98
1.00
0.17
0.17
0.36
2.96
0.54
0.59
2.87
3.02
f1 (ppm)


169.56
168.49
145.32
145.28
140.69
135.74
135.18
135.16
129.88
129.72
128.50
128.30
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77.16
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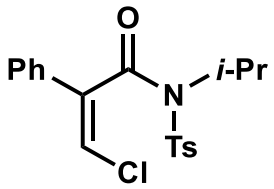
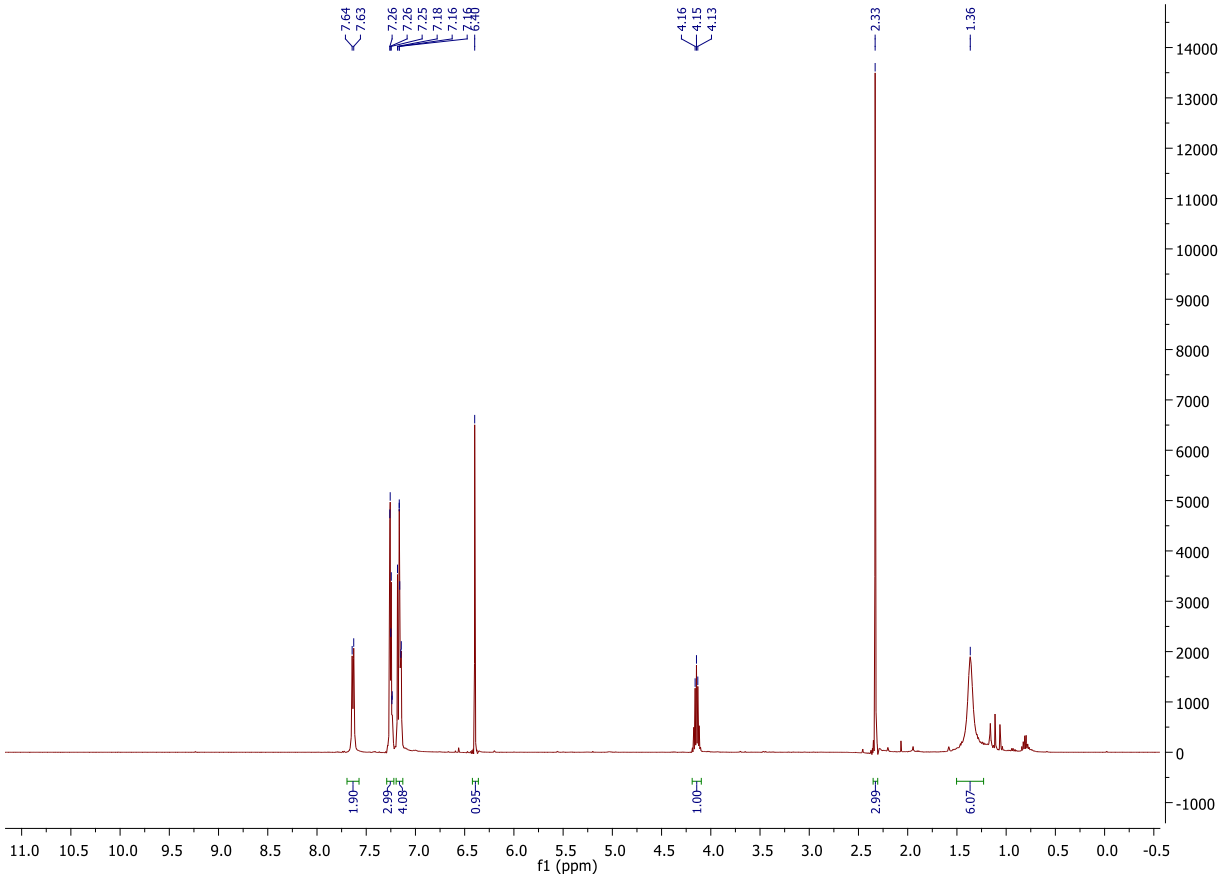
44.17
34.79
32.83
21.80
18.98
f1 (ppm)

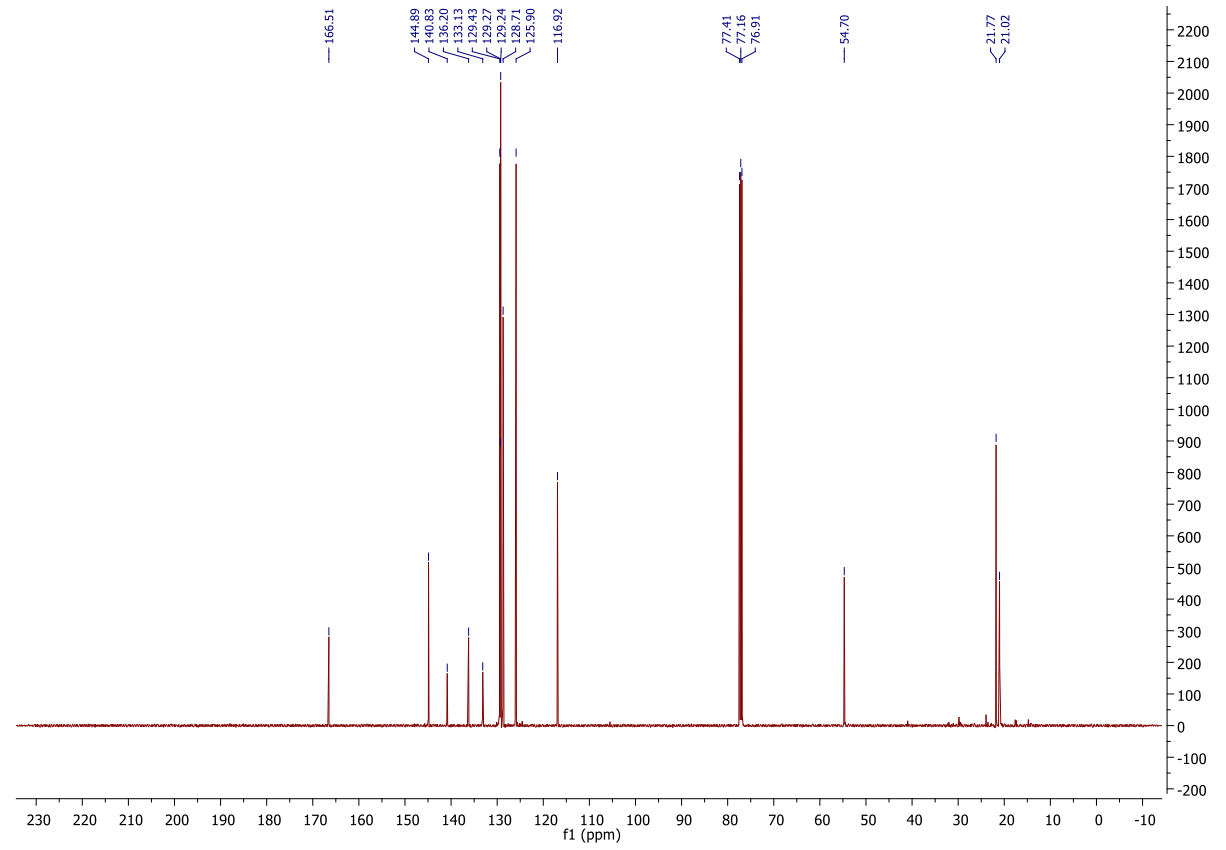
(16)



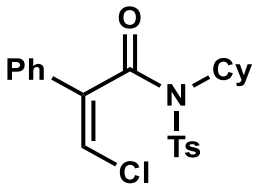
Prepared according to the General Procedure G using N-tosyl-N-isopropyl-2-phenacrylamide (103 mg, 0.30 mmol, 1 equiv.), magnesium chloride (143 mg, 1.50 mmol, 5 equiv.), acetonitrile (5.25 mL) and acetic acid (0.75 mL). Purification by flash column chromatography (eluent = 5 to 15% EtOAc in hexanes, silica gel) to afford pure product **(16)** as an orange oil (97.0 mg, 86% yield).

R_f = 0.50 (eluent = 25% EtOAc in hexanes); **ν_{max} / cm^{-1}**(thin film) 2990, 2920, 1681, 1597, 1494, 1445, 1352, 1330, 1217, 1161, 1055 ; **^{1}H NMR (500 MHz, $CDCl_3$)** δ_H: 1.35-1.60 (6H, s br), 2.33 (3H, s), 4.15 (1H, sept, *J* 7.5 Hz), 6.40 (1H, s), 7.14-7.18 (4H, m), 7.22-7.29 (3H, m), 7.63 (2H, d, *J* 8.0 Hz); **^{13}C NMR (126 MHz, $CDCl_3$)** δ_C: 20.9, 21.7, 54.6, 116.8, 125.8, 128.6, 129.1, 129.2, 129.3, 133.0, 136.1, 140.7, 144.8, 166.4; **HRMS (ES$^+$)** [$C_{19}H_{20}NO_3SCl$] requires $[M+H]^+$ 378.0931, found 378.0921 (- 2.6 ppm).


7.64
7.63
7.26
7.26
7.25
7.18
7.16
7.16
6.40
4.16
4.15
4.13
2.33
1.36
1.90
2.99
4.08
0.95
1.00
2.99
6.07
f1 (ppm)

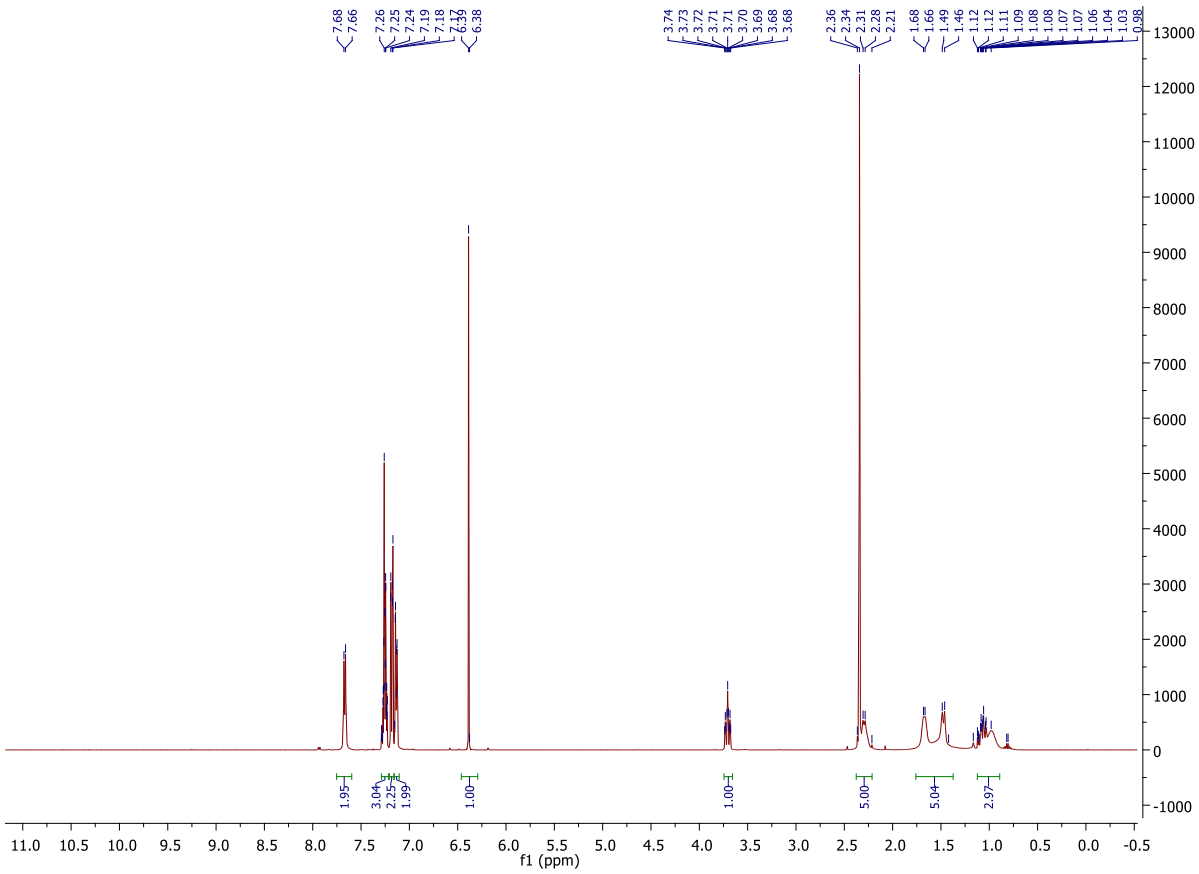

166.51
144.89
140.83
136.20
133.13
129.43
129.27
129.24
128.71
125.90
116.92
77.41
77.16
76.91
54.70
21.77
21.02
f1 (ppm)

(17)



Prepared according to the General Procedure G using N-tosyl-N-cyclohexyl-2-phenacrylamide (115 mg, 0.30 mmol, 1 equiv.), magnesium chloride (143 mg, 1.50 mmol, 5 equiv.), acetonitrile (5.25 mL) and acetic acid (0.75 mL). Purification by flash column chromatography (eluent = 5 to 15% EtOAc in hexanes, silica gel) to afford pure product **(17)** as a low melting solid (103 mg, 83% yield).

Mp.: 42-44 ^{o}C; **Rf** = 0.66 (eluent = 25% EtOAc in hexanes); **ν_{max} / cm^{-1}**(thin film) 3050, 2934, 1682, 1495, 1445, 1363, 1350, 1329, 1207, 1168, 1140, 1085 ; **^{1}H NMR (500 MHz, $CDCl_3$)** δ_H: 0.87-1.14 (3H, m), 1.37-1.79 (5H, m), 2.23-2.37 (5H, m), 3.71 (1H, tt, *J* 12.1, 3.6 Hz), 6.39 (1H, s), 7.14 (2H, m), 7.18 (2H, d, *J* 8.0 Hz), 7.22-7.29 (3H, m), 7.67 (2H, d, *J* 8.0 Hz); **^{13}C NMR (126 MHz, $CDCl_3$)** δ_C: 21.7, 24.9, 26.8, 30.8, 63.3, 116.9, 125.8, 128.7, 129.1, 129.2, 129.2, 133.1, 136.3, 140.9, 144.7, 166.5; **HRMS (ES^{+})** [$C_{22}H_{24}NO_3SCl$] requires $[M+H]^+$ 418.1244, found 418.1241 (- 0.70 ppm).


7.68
7.66
7.26
7.25
7.24
7.19
7.18
7.17
6.39
6.38
3.74
3.73
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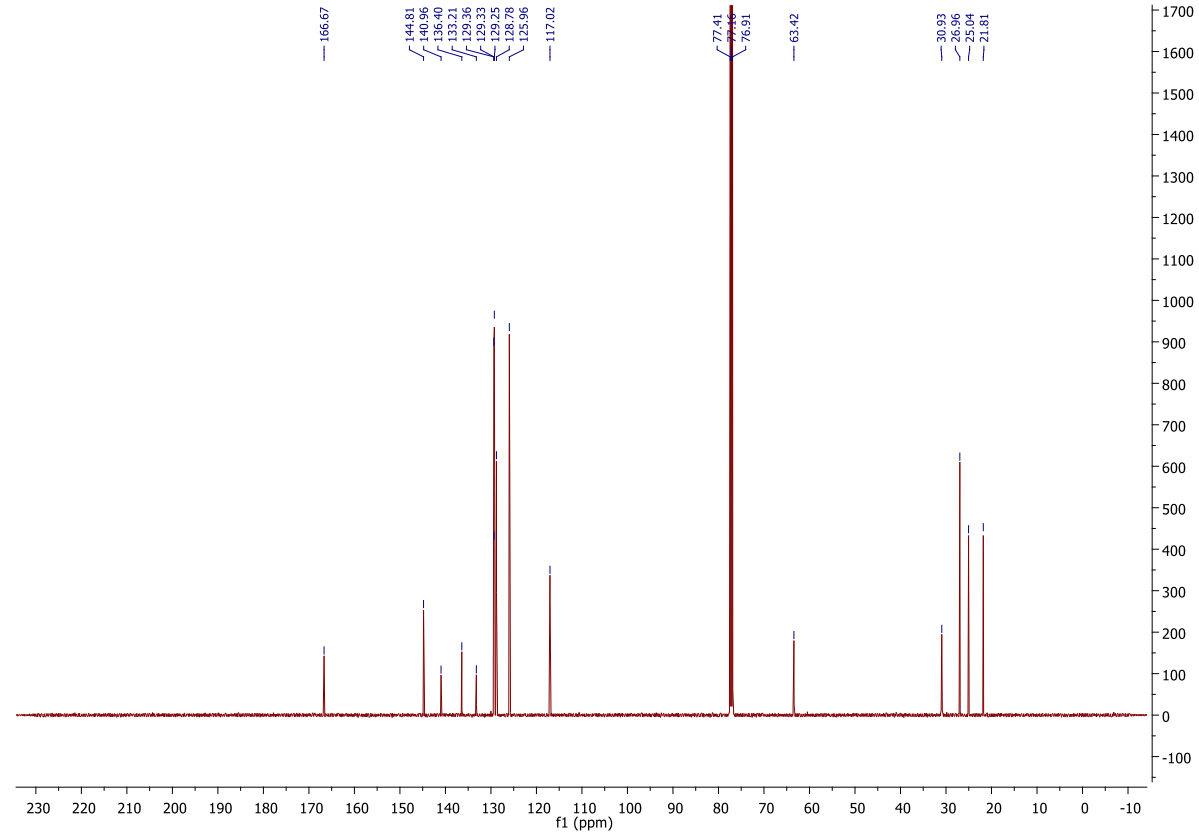
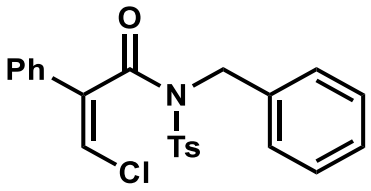
3.71
3.71
3.70
3.69
3.68
3.68
2.36
2.34
2.31
2.28
2.21
1.68
1.66
1.49
1.46
1.12
1.12
1.11
1.09
1.08
1.08
1.07
1.07
1.06
1.04
1.03
0.98
1.95
3.04
2.25
1.99
1.00
1.00
5.00
5.04
2.97
f1 (ppm)

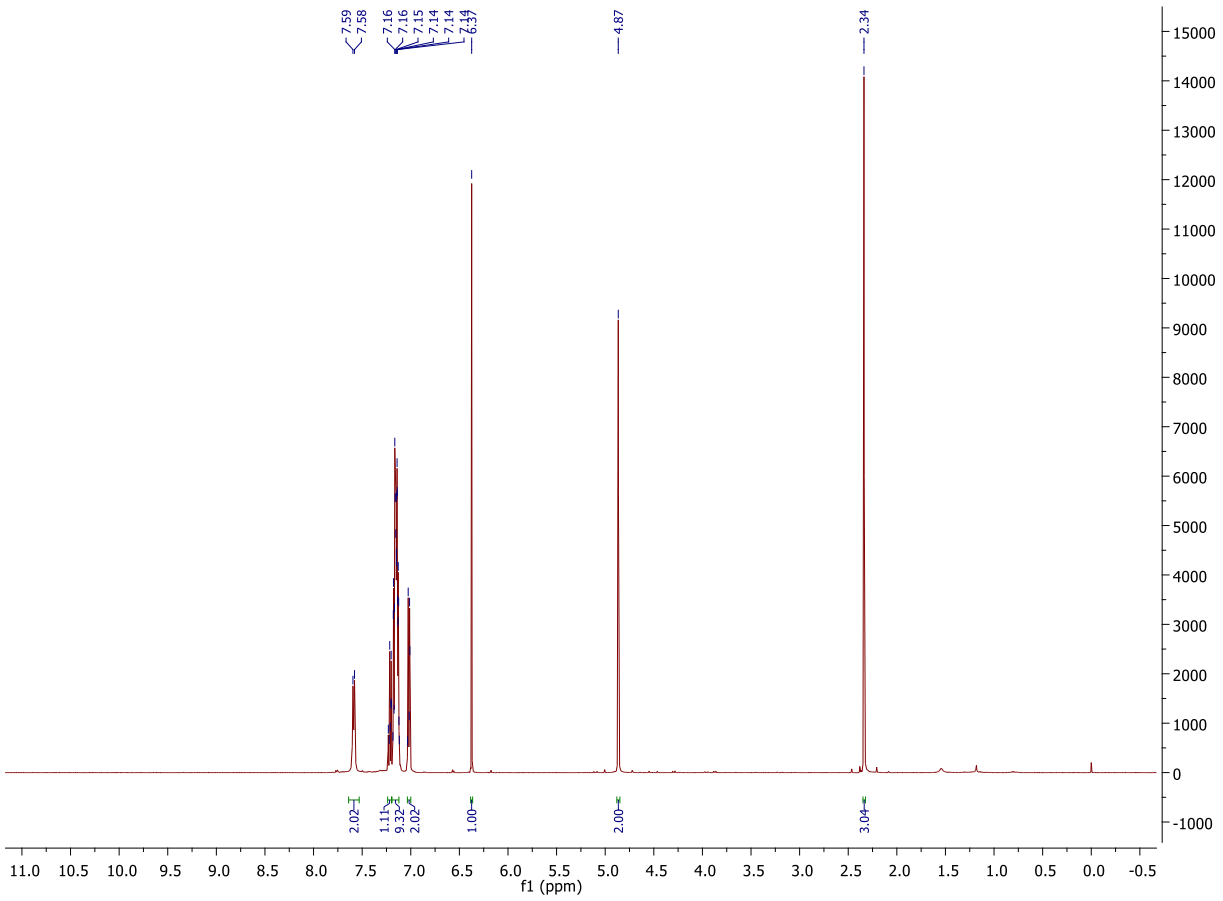

166.67
144.81
140.96
136.40
133.21
129.36
129.33
129.25
128.78
125.96
117.02
77.41
77.16
76.91
63.42
30.93
26.96
25.04
21.81
f1 (ppm)

(18)



Prepared according to the General Procedure G using N-tosyl-N-benzyl-2-phenacrylamide (117 mg, 0.30 mmol, 1 equiv.), magnesium chloride (143 mg, 1.50 mmol, 5 equiv.), acetonitrile (5.25 mL) and acetic acid (0.75 mL). Purification by flash column chromatography (eluent = 5 to 15% EtOAc in hexanes, silica gel) to afford pure product **(18)** as a yellow solid (101 mg, 81% yield).

Mp: 126-127 °C; $\mathbf{R_f}$ = 0.57 (eluent = 25% EtOAc in hexanes); $\mathbf{\nu_{max}}$ **/ cm^{-1}** (thin film) 3120, 1681, 1593, 1495, 1443, 1356, 1341, 1330, 1286, 1182, 1166, 1098, 1078; **^{1}H NMR (500 MHz, $CDCl_3$)** δ_H: 2.34 (3H, s), 4.87 (2H, s), 6.37 (1H, s), 6.99-7.05 (2H, m), 7.11-7.19 (9H, m), 7.19-7.24 (1H, m), 7.57 (2H, d, *J* 8.0 Hz); **^{13}C NMR (126 MHz, $CDCl_3$)** δ_C: 21.8, 50.4, 118.8, 125.8, 127.8, 128.0, 128.5, 128.8, 129.1, 129.1, 129.5, 133.0, 135.7, 135.8, 139.9, 145.2, 166.6; **HRMS (ES$^+$)** [$C_{23}H_{20}NO_3SCl$] requires $[M+H]^+$ 426.0931, found 426.0927 (- 0.90 ppm).


7.59
7.58
7.16
7.16
7.15
7.14
7.14
7.14
6.37
4.87
2.34
2.02
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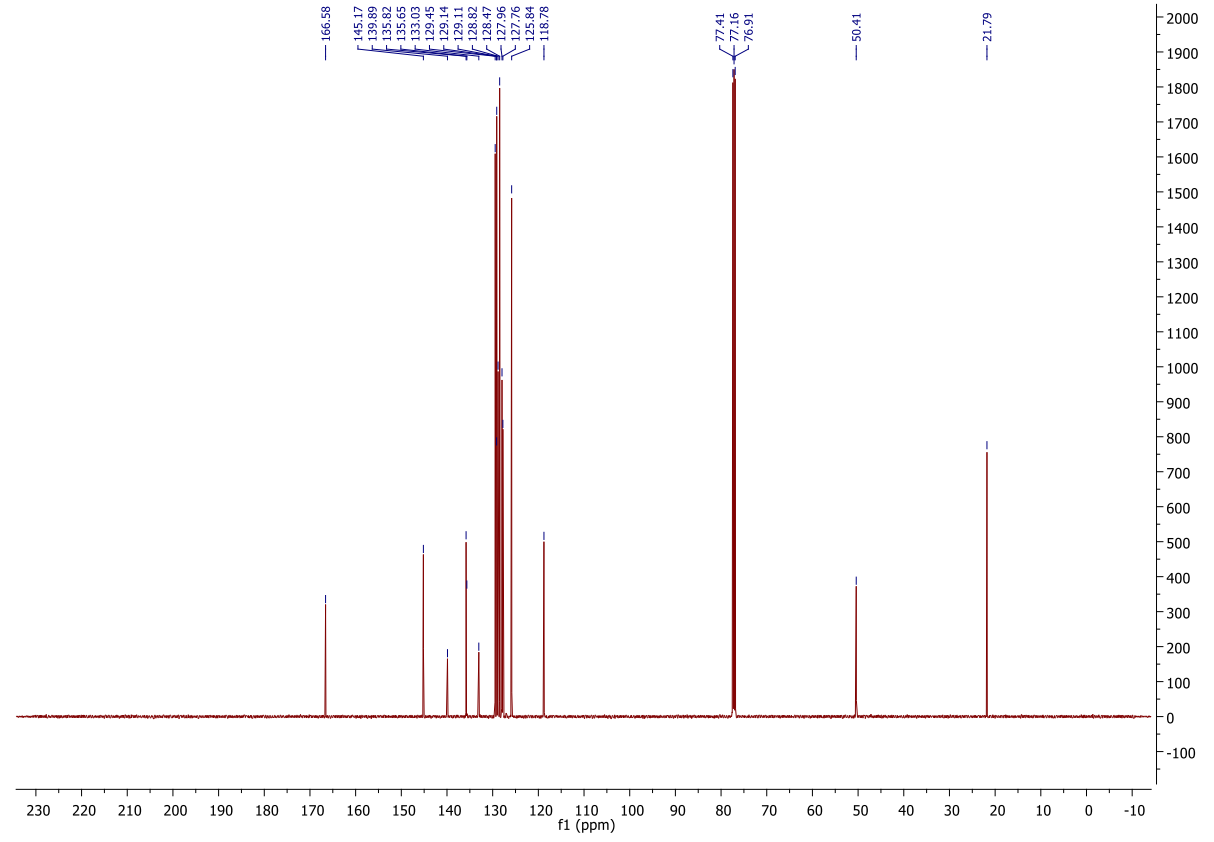
9.32
2.02
1.00
2.00
3.04
f1 (ppm)


166.58
145.17
139.89
135.82
135.65
133.03
129.45
129.14
129.11
128.82
128.47
127.96
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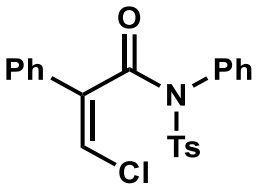
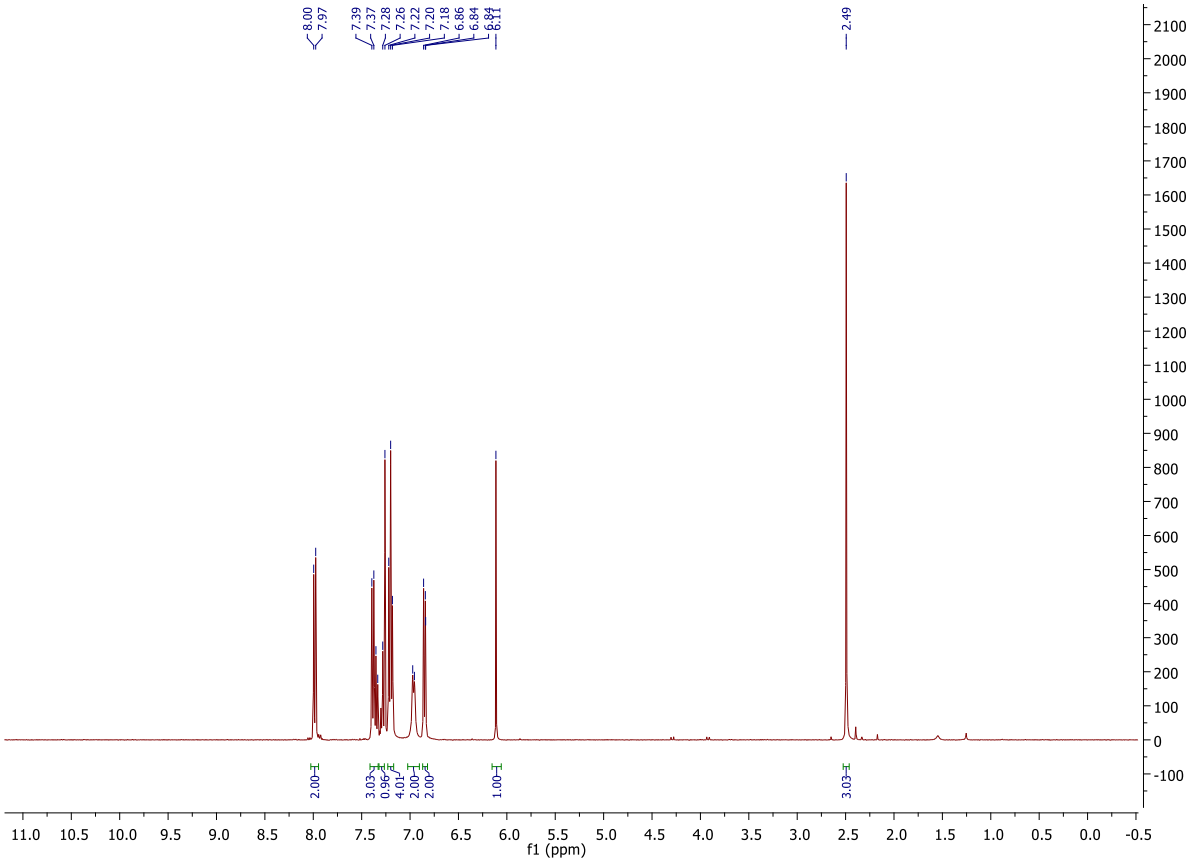
77.41
77.16
76.91
50.41
21.79
f1 (ppm)

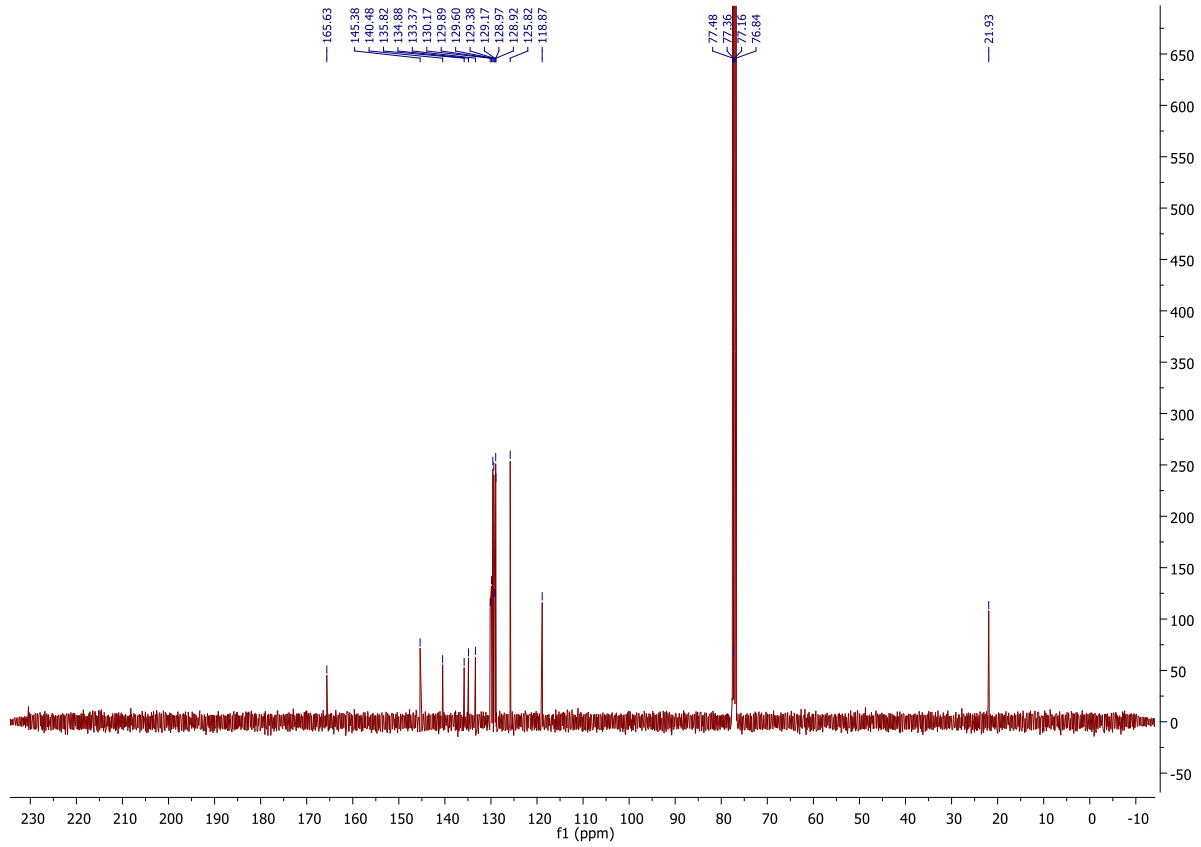
(19)



Prepared according to the General Procedure G using N,2-diphenyl-N-tosylacrylamide (113 mg, 0.30 mmol, 1 equiv.), magnesium chloride (143 mg, 1.50 mmol, 5 equiv.), acetonitrile (5.25 mL) and acetic acid (0.75 mL). Purification by flash column chromatography (eluent = 5 to 15% EtOAc in hexanes, silica gel) to afford pure product **(19)** as a white solid (92.9 mg, 75% yield).

Mp: 119-121 °C**;** $\mathbf{R_f}$ = 0.20 (eluent = 10% EtOAc in hexanes); $\mathbf{\nu_{max}}$ **/ cm**$^{-1}$(thin film) 3080, 1695, 1595, 1489, 1365, 1259, 1190, 1178, 1167, 1086 ; **^{1}H NMR (500 MHz, $CDCl_3$)** δ_H: 2.49 (3H, s), 6.11 (1H, s), 6.80-6.89 (2H, m), 6.94-7.02 (2H, m), 7.17-7.23 (4H, m), 7.29 (1H, m), 7.34 (1H, d, *J* 7.5 Hz), 7.38 (2H, d, *J* 8.3 Hz), 7.99 (2H, d, *J* 8.3 Hz); **^{13}C NMR (126 MHz, $CDCl_3$)** δ_C: 21.8, 118.7, 125.7, 128.8, 128.8, 129.0, 129.2, 129.5, 129.8, 130.0, 133.2, 134.7, 135.7, 140.4, 145.2, 165.5; **HRMS (ES$^+$)** [$C_{22}H_{18}NO_3SCl$] requires $[M+H]^+$ 412.0774, found 412.0789 (+3.6 ppm).


8.00
7.97
7.39
7.37
7.28
7.26
7.22
7.20
7.18
6.86
6.84
6.84
6.11
2.49
2.00
3.03
0.96
4.01
2.00
2.00
1.00
3.03
f1 (ppm)


165.63
145.38
140.48
135.82
134.88
133.37
130.17
129.89
129.60
129.38
129.17
128.97
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118.87
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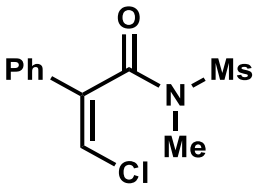
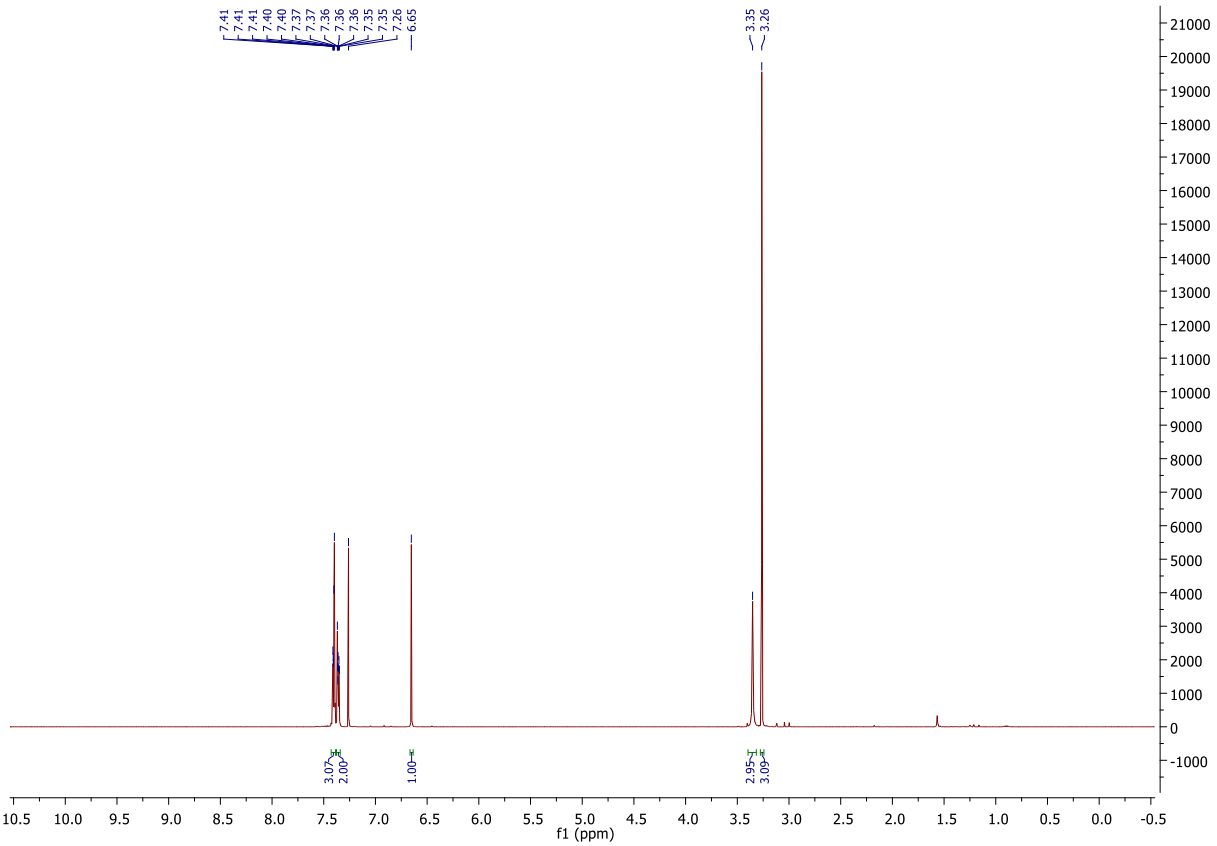
77.36
77.16
76.84
21.93
f1 (ppm)

(20)



Prepared according to the General Procedure G using N-mesyl-N-methyl-2-phenylacrylamide (71.8 mg, 0.30 mmol, 1 equiv.), magnesium chloride (143 mg, 1.50 mmol, 5 equiv.), acetonitrile (5.25 mL) and acetic acid (0.75 mL). Purification by flash column chromatography (eluent = 10 to 25% EtOAc in hexanes, silica gel) to afford pure product **(20)** as a colourless oil (71.0 mg, 86% yield).

R_f = 0.24 (eluent = 25% EtOAc in hexanes); **ν_{max} / cm^{-1}**(thin film) 1688, 1601, 1496, 1440, 1348, 1314, 1252, 1167, 1099, 949 ; **^{1}H NMR (500 MHz, $CDCl_3$)** δ_H: 3.26 (3H, s), 3.35 (3H, s br), 6.65 (1H, s), 7.34-7.38 (2H, m), 7.38-7.42 (3H, m); **^{13}C NMR (126 MHz, $CDCl_3$)** δ_C: 32.7, 41.5, 117.7, 125.8, 129.6, 129.8, 132.0, 139.7, 167.8; **HRMS (ASAP$^+$)** [$C_{11}H_{12}NO_3SCl$] requires $[M+H]^+$ 274.0305, found 274.0309 (+ 1.5 ppm).


7.41
7.41
7.41
7.40
7.40
7.37
7.37
7.36
7.36
7.36
7.35
7.35
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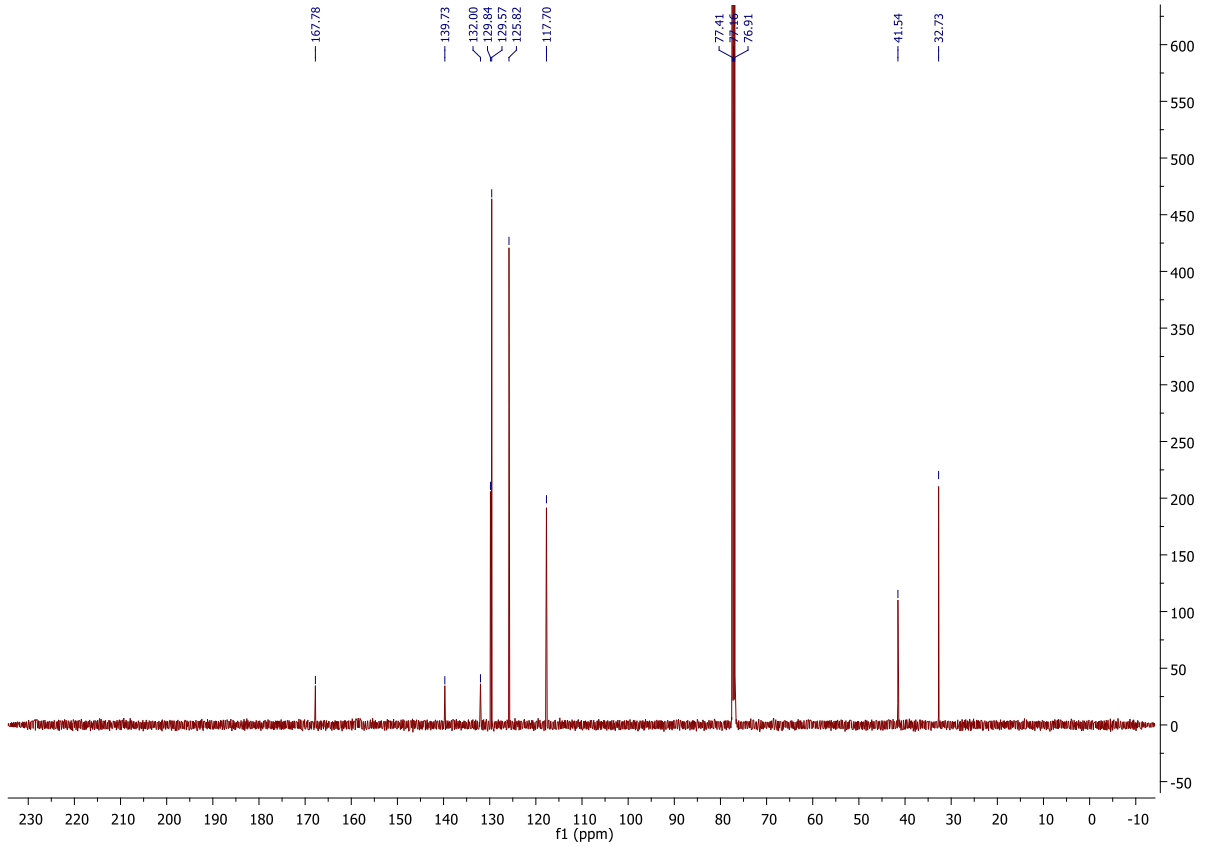
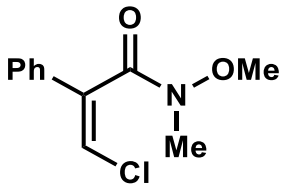
2.00
1.00
2.95
3.09
f1 (ppm)

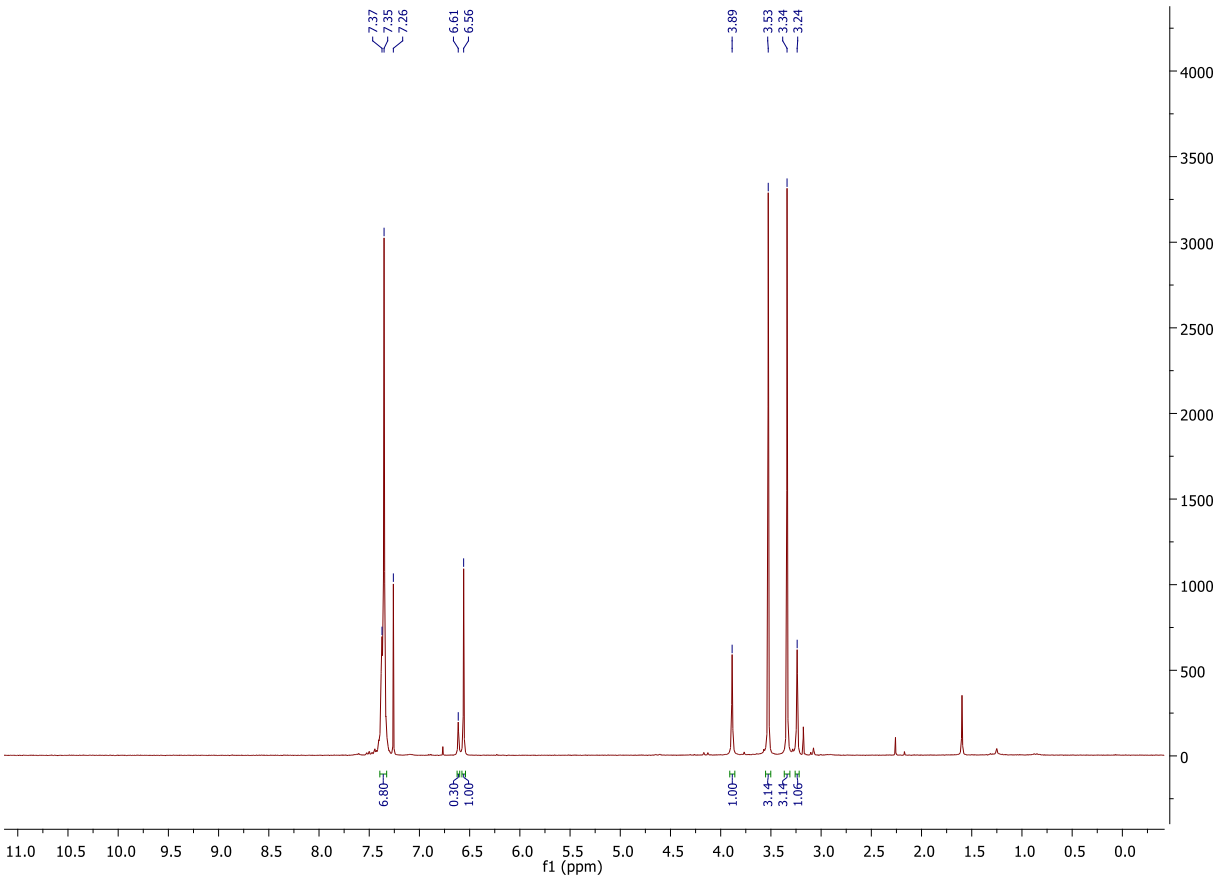

167.78
139.73
132.00
129.84
129.57
125.82
117.70
77.41
77.16
76.91
41.54
32.73
f1 (ppm)

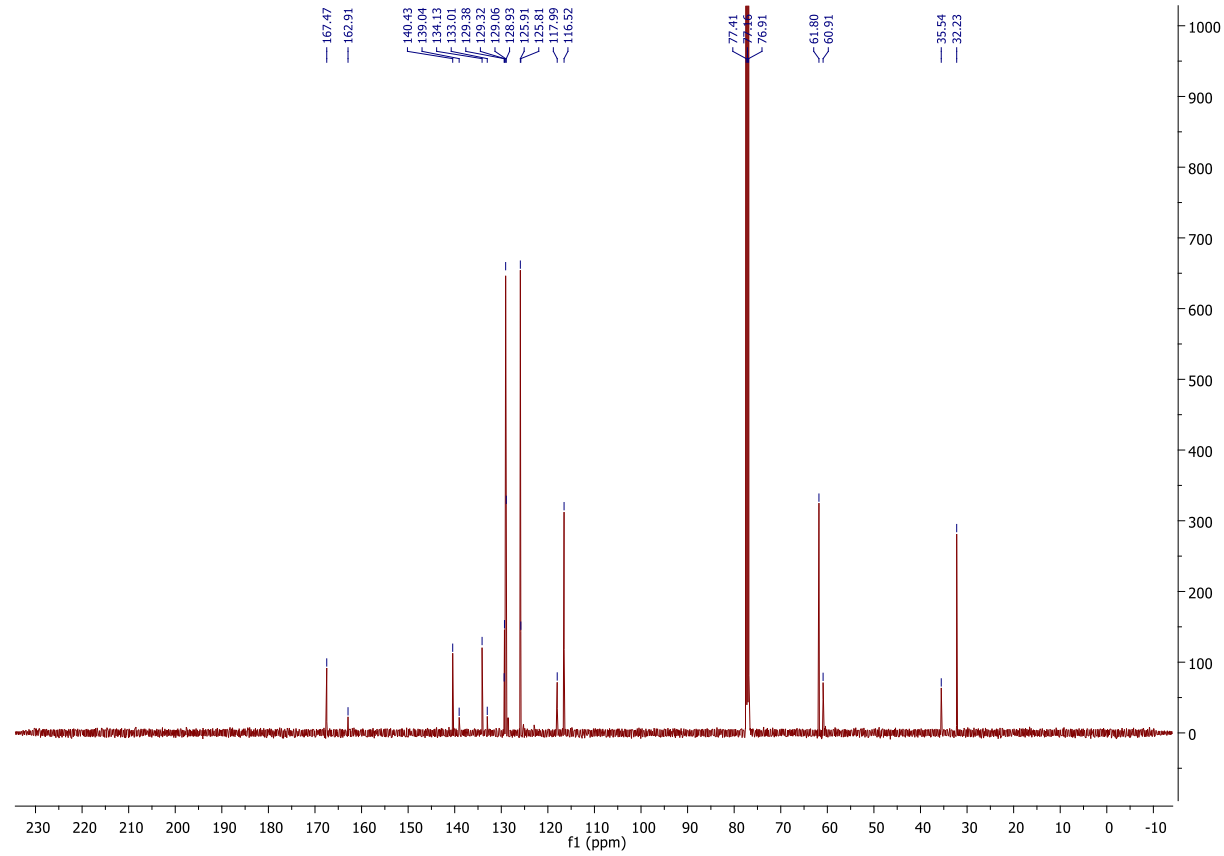
(21)



Prepared according to the General Procedure G using N-methoxy-N-methyl-2-phenylacrylamide (57.4 mg, 0.30 mmol, 1 equiv.), magnesium chloride (143 mg, 1.50 mmol, 5 equiv.), acetonitrile (5.25 mL) and acetic acid (0.75 mL). Purification by flash column chromatography (eluent = 10 to 20% EtOAc in hexanes, silica gel) to afford product **(21)** as an inseperable mixture of alkene stereoisomers (2:1) as a colourless oil (41.0 mg, 61% yield).

R_f = 0.45 (eluent = 40% EtOAc in hexanes); **ν_{max} / cm^{-1}** (thin film) 3080, 1651, 1445, 1420, 1383, 1179, 1107, 1011, 962; *Data for major alkene stereoisomer:* **^{1}H NMR (300 MHz, $CDCl_3$)** δ_H: 3.34 (3H, s), 3.53 (3H, s), 6.56 (1H, s), 7.36 (5H, m); **^{13}C NMR (126 MHz, $CDCl_3$)** δ_C: 32.2, 61.8, 116.5, 125.9, 129.1, 129.3, 134.1, 140.4, 167.5; *Data for minor alkene stereoisomer:* **^{1}H NMR (300 MHz, $CDCl_3$)** δ_H: 3.24 (3H, s), 3.89 (3H, s), 6.61 (1H, s), 7.36 (5H, m); **^{13}C NMR (126 MHz, $CDCl_3$)** δ_C: 35.5, 60.9, 118.0, 125.8, 128.9, 129.4, 133.0, 139.0, 162.9; **HRMS (ES$^+$)** [$C_{11}H_{12}NO_2Cl$] requires $[M+H]^+$ 226.0635, found 226.0638 (+ 1.3 ppm).


7.37
7.35
7.26
6.61
6.56
3.89
3.53
3.34
3.24
6.80
0.30
1.00
1.00
3.14
3.14
1.06
f1 (ppm)


167.47
162.91
140.43
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134.13
133.01
129.38
129.32
129.06
128.93
125.91
125.81
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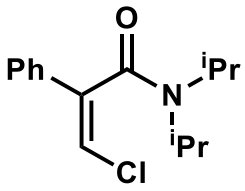
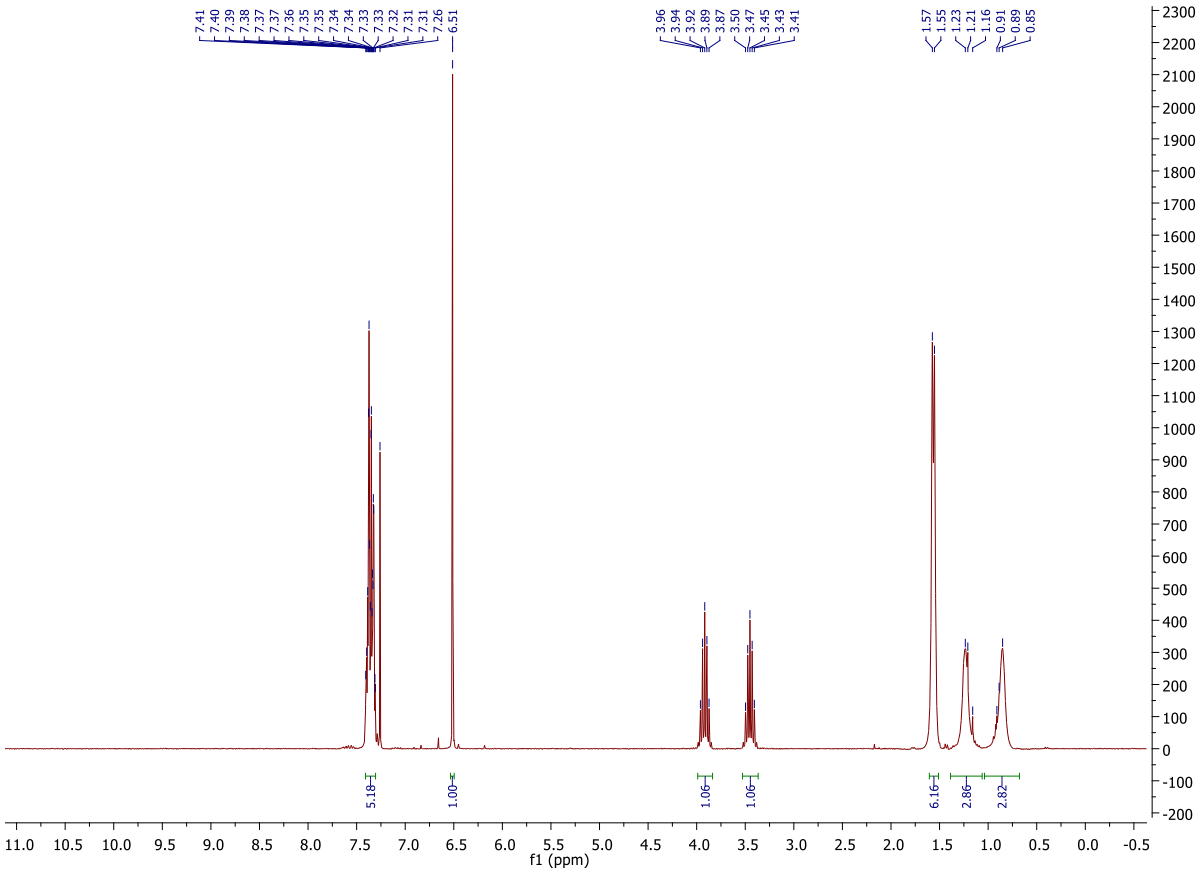
76.91
61.80
60.91
35.54
32.23
f1 (ppm)

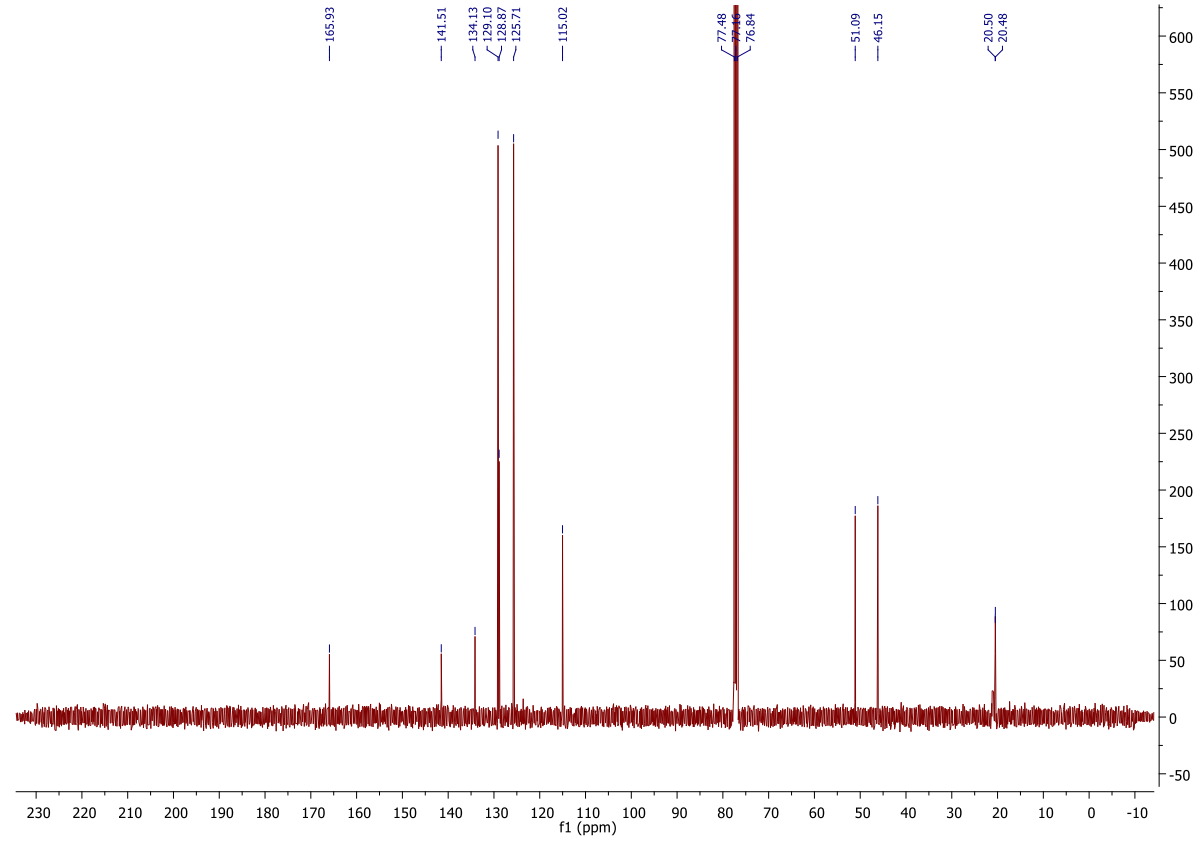
(22)



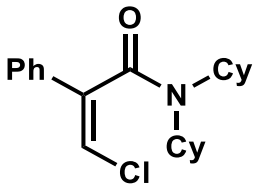
Prepared according to the General Procedure G using N,N-diisopropyl-2-phenylacrylamide (69.4 mg, 0.30 mmol, 1 equiv.), magnesium chloride (143 mg, 1.50 mmol, 5 equiv.), acetonitrile (5.25 mL) and acetic acid (0.75 mL). Purification by flash column chromatography (eluent = 2 to 10% EtOAc in hexanes, silica gel) to afford pure product **(22)** as a colourless oil (49.4 mg, 61% yield).

R_f = 0.30 (eluent = 10% EtOAc in hexanes); **ν_{max} / cm^{-1}** (thin film); 3075, 2990, 1622, 1597, 1441, 1367, 1350, 1290, 1167, 1086, 1042; **^{1}H NMR (300 MHz, $CDCl_3$)** δ_H: 0.73-0.98 (3H, m), 1.12-1.36 (3H, m), 1.56 (6H, d, *J* 6.6 Hz), 3.45 (1H, hept, *J* 6.7 Hz), 3.92 (1H, hept, *J* 6.6 Hz), 6.51 (1H, s), 7.28-7.45 (5H, m); **^{13}C NMR (101 MHz, $CDCl_3$)** δ_C: 20.5, 20.5, 46.2, 51.1, 115.0, 125.7, 128.9, 129.1, 134.1, 141.5, 165.9; **HRMS (ESP$^+$)** [$C_{16}H_{24}NOCl$] requires $[M+H]^+$ 266.1312, found 266.1314 (+ 0.80 ppm).


7.41
7.40
7.39
7.38
7.37
7.37
7.36
7.35
7.35
7.34
7.34
7.33
7.33
7.32
7.31
7.31
7.26
6.51
3.96
3.94
3.92
3.89
3.87
3.50
3.47
3.45
3.43
3.41
1.57
1.55
1.23
1.21
1.16
0.91
0.89
0.85
5.18
1.00
1.06
1.06
6.16
2.86
2.82
f1 (ppm)

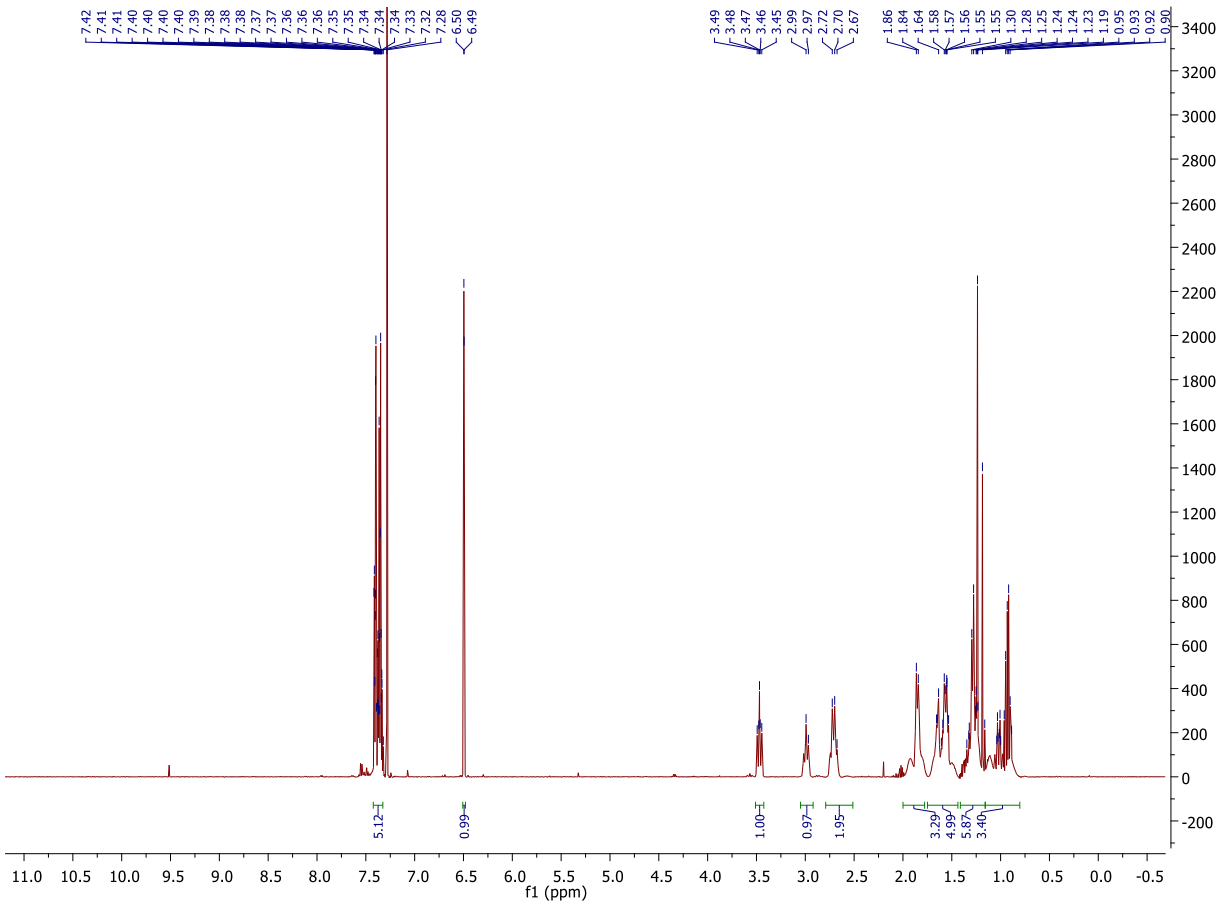

165.93
141.51
134.13
129.10
128.87
125.71
115.02
77.48
77.16
76.84
51.09
46.15
20.50
20.48
f1 (ppm)

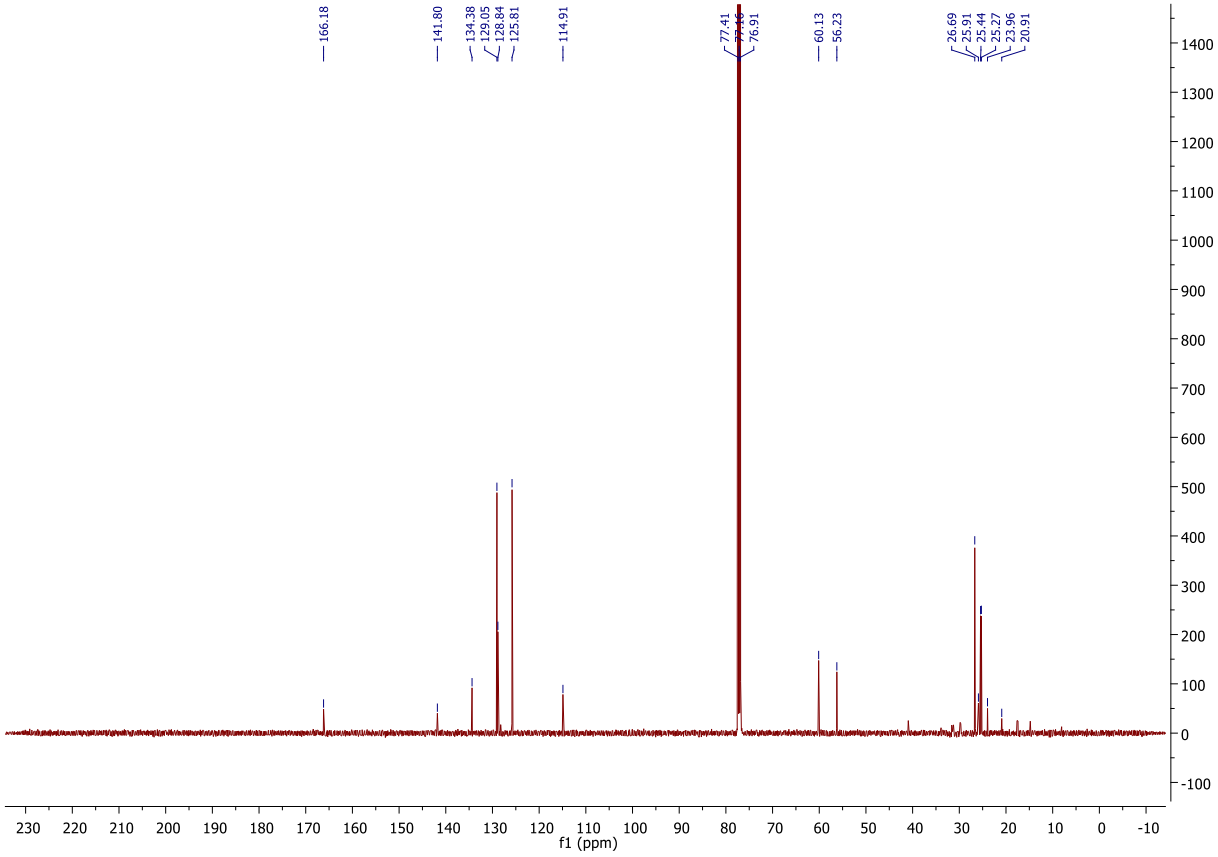
(23)



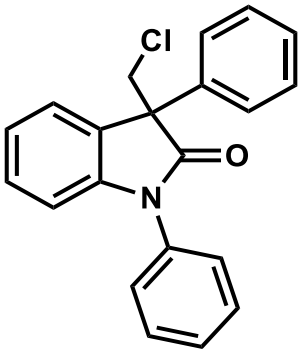
Prepared according to the General Procedure G using N,N-dicyclohexyl-2-phenylacrylamide (90.0 mg, 0.30 mmol, 1 equiv.), magnesium chloride (143 mg, 1.50 mmol, 5 equiv.), acetonitrile (5.25 mL) and acetic acid (0.75 mL). Purification by flash column chromatography (eluent = 3 to 10% EtOAc in hexanes, silica gel) to afford pure product **(23)** as a colourless oil (76.7 mg, 73% yield).

R_f = 0.29 (eluent = 10% EtOAc in hexanes); **ν_{max} / cm^{-1}** (thin film) 2930, 2853, 1628, 1468, 1437, 1370, 1327, 1230, 1182, 1126; **^{1}H NMR (500 MHz, $CDCl_3$)** δ_H: 0.78-1.11 (3H, m), 1.10-1.40 (6H, m), 1.40-1.72 (5H, m), 1.75-1.95 (3H, m), 2.60-2.75 (2H, m), 2.93-3.00 (1H, m), 3.41-3.48 (1H, m), 6.47 (1H, s), 7.29-7.42 (5H, m); **^{13}C NMR (126 MHz, $CDCl_3$)** δ_C: 20.9, 24.0, 25.3, 25.4, 25.9, 26.7, 56.2, 60.1, 114.9, 125.8, 128.8, 129.1, 134.4, 141.8, 166.2; **HRMS (ES$^+$)** [$C_{21}H_{28}NOCl$] requires $[M+H]^+$ 346.1938, found 346.1939 (+ 0.30 ppm).


7.42 7.41 7.41 7.40 7.40 7.40 7.40 7.39 7.38 7.38 7.37 7.37 7.36 7.36 7.35 7.35 7.34 7.34 7.34 7.33 7.32 7.28 6.50 6.49
3.49 3.48 3.47 3.46 3.45 2.99 2.97 2.72 2.70 2.67
1.86 1.84 1.64 1.58 1.57 1.56 1.55 1.55 1.30 1.28 1.25 1.24 1.24 1.23 1.19 0.95 0.93 0.92 0.90
5.12 0.99 1.00 0.97 1.95 3.29 4.99 5.87 3.40
f1 (ppm)

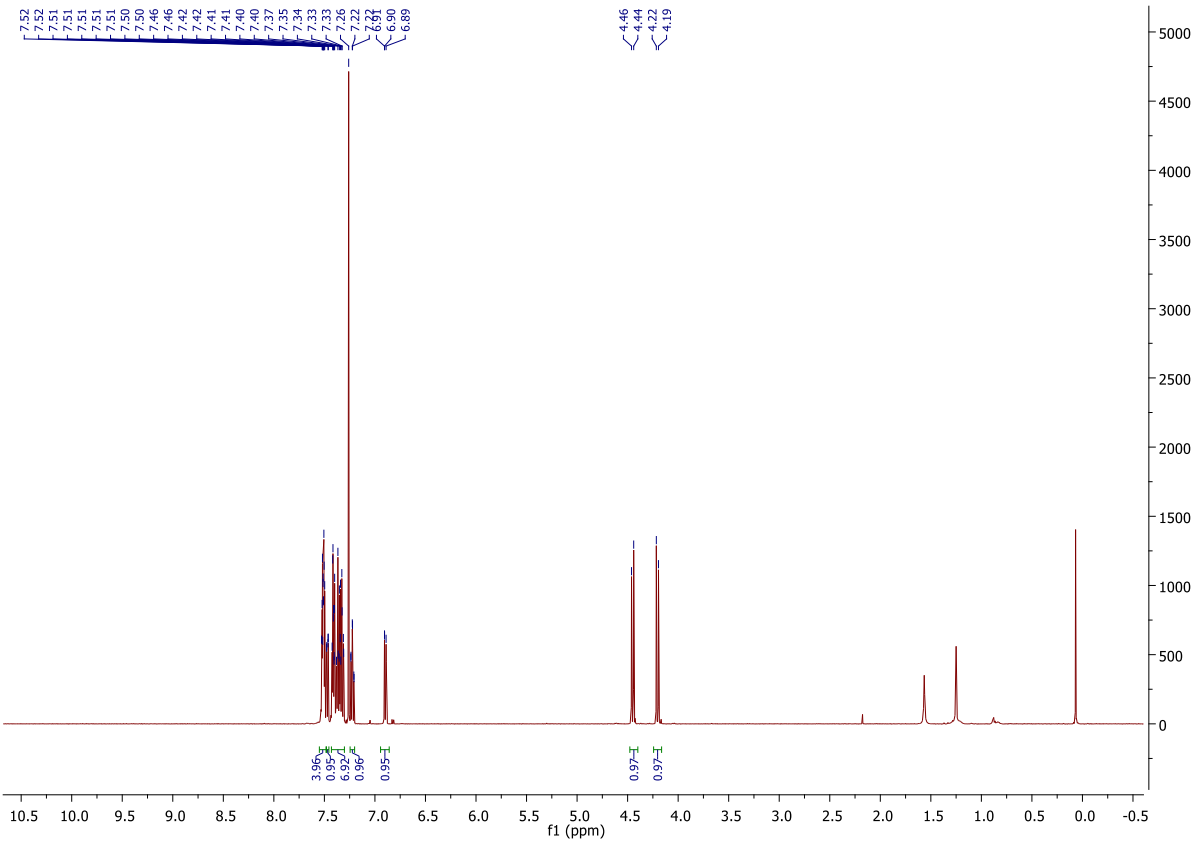

166.18 141.80 134.38 129.05 128.84 125.81 114.91 77.41 77.16 76.91 60.13 56.23 26.69 25.91 25.44 25.27 23.96 20.91
f1 (ppm)

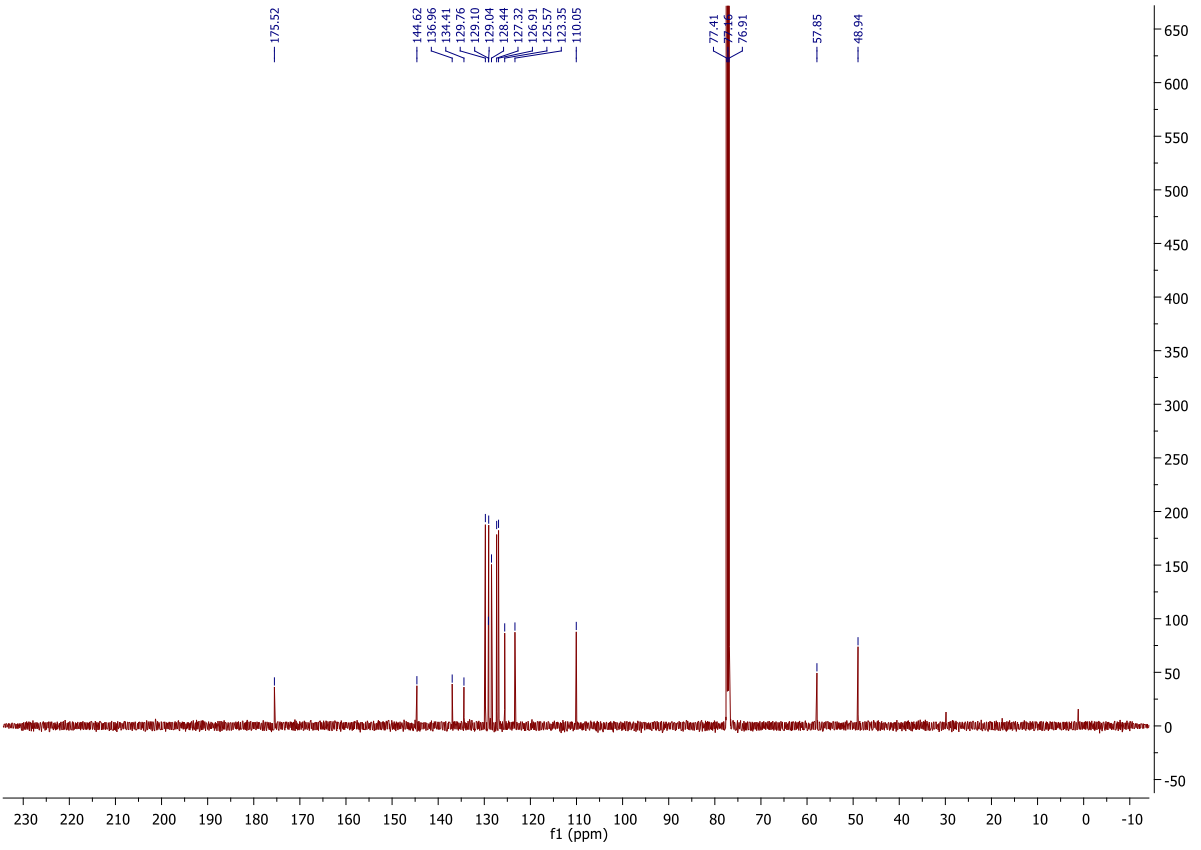
(25)



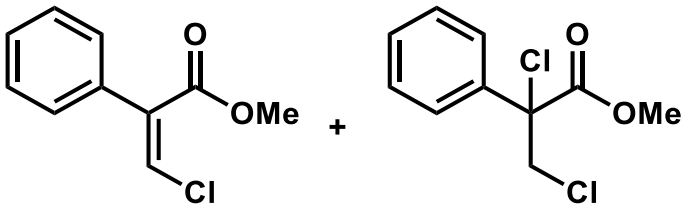
Prepared according to General Procedure G using N,N,2-triphenylacrylamide (89.8 mg, 0.30 mmol, 1 equiv.), magnesium chloride (143 mg, 1.50 mmol, 5 equiv.), acetonitrile (5.25 mL) and acetic acid (0.75 mL). Purification by flash column chromatography (eluent = 5 to 10% EtOAc in hexanes, silica gel) to afford product **(25)** as a colourless oil (64.3 mg, 64% yield).

R_f = 0.45 (eluent = 15% EtOAc in hexanes); **ν_{max} / cm^{-1}** (thin film) 3058, 1716, 1659, 1591, 1491, 1364, 1290, 1265, 1219, 1159 **; ^{1}H NMR (500 MHz, $CDCl_3$)** δ_H: 4.21 (1H, d, *J* 10.7 Hz), 4.45 (1H, d, *J* 10.7 Hz), 6.88-6.91 (1H, m), 7.22 (1H, td, *J* 7.6 Hz), 7.30-7.44 (7H, m), 7.45-7.49 (1H, m), 7.49-7.55 (4H, m); **^{13}C NMR (126 MHz, $CDCl_3$)** δ_C: 48.9, 57.9, 110.1, 123.4, 125.6, 126.9, 127.3, 128.4, 129.0, 129.1, 129.8, 134.4, 137.0, 144.6, 175.5; **HRMS (ASAP$^+$)** [$C_{21}H_{16}NOCl$] requires $[M+H]^+$ 334.0999, found 334.0998 (-0.3 ppm).


7.52
7.52
7.51
7.51
7.51
7.51
7.50
7.50
7.46
7.46
7.42
7.42
7.41
7.41
7.40
7.40
7.37
7.35
7.34
7.33
7.33
7.26
7.22
7.22
6.91
6.90
6.89
4.46
4.44
4.22
4.19
3.96
0.95
6.92
0.96
0.95
0.97
0.97
f1 (ppm)


175.52
144.62
136.96
134.41
129.76
129.10
129.04
128.44
127.32
126.91
125.57
123.35
110.05
77.41
77.16
76.91
57.85
48.94
f1 (ppm)

(27)&(28)



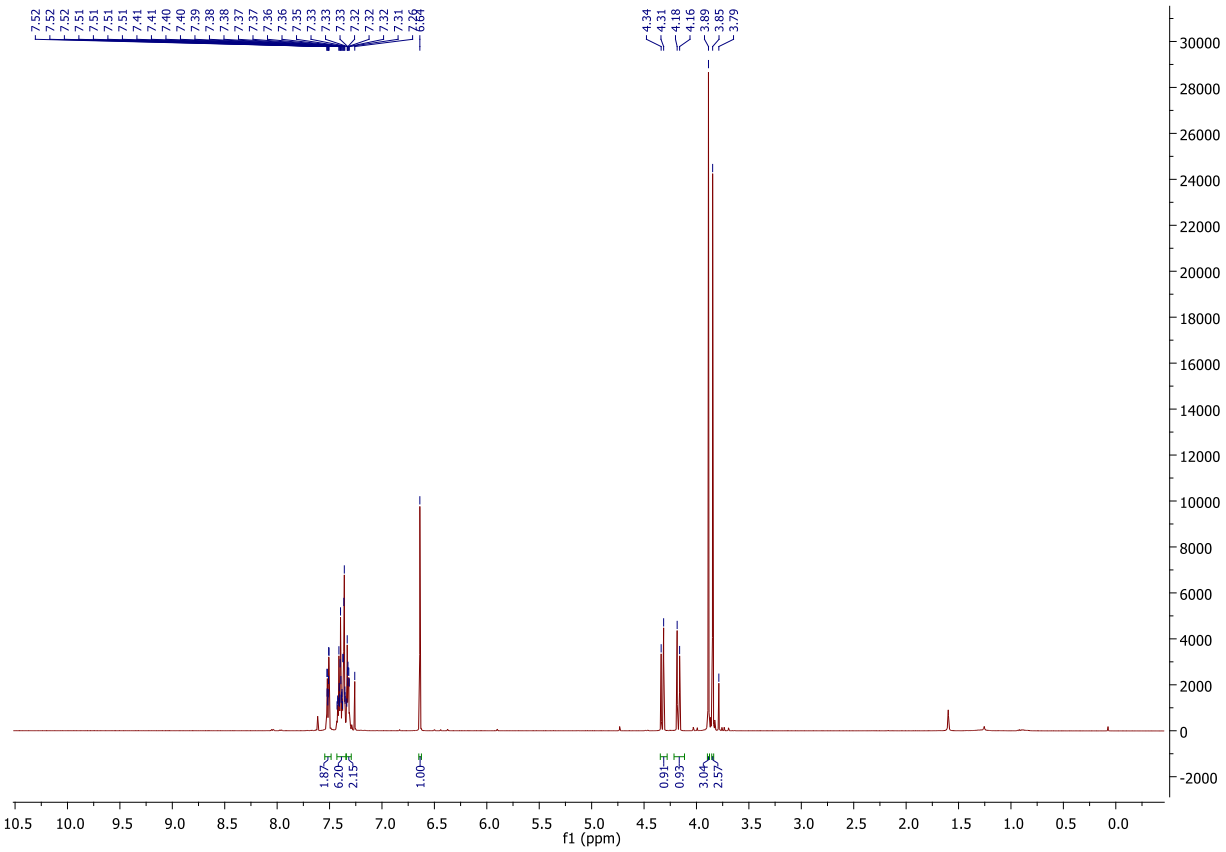
44% ^{1}H NMR yield **32% ^{1}H NMR yield**

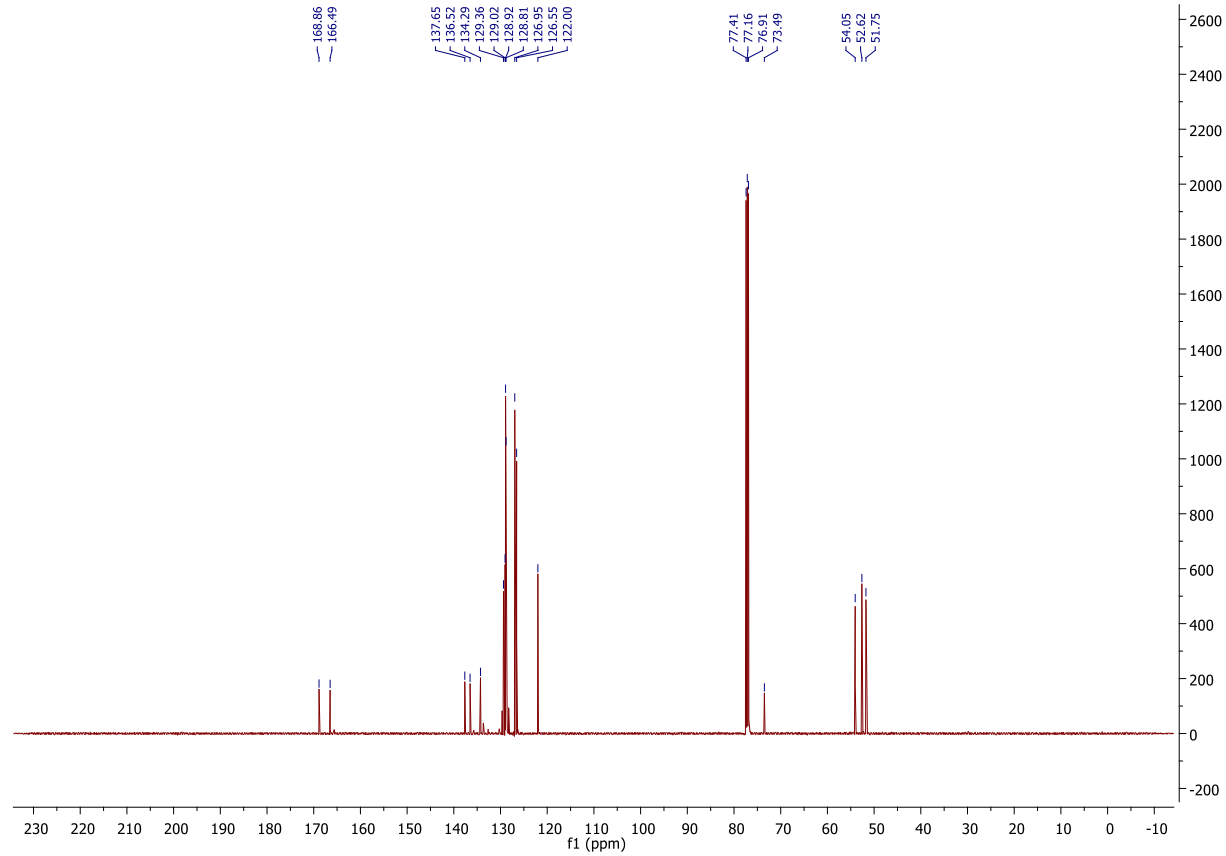
1.4 : 1

inseperable mixture

Mixture prepared according to General Procedure G using methyl 2-phenylacrylate (48.6 mg, 0.30 mmol, 1 equiv.), magnesium chloride (143 mg, 1.50 mmol, 5 equiv.), acetonitrile (5.25 mL) and acetic acid (0.75 mL). Attempted purification by flash column chromatography (eluent = 5 to 10% EtOAc in hexanes, silica gel) to afford the mixture of products as a colourless oil (31.3 mg).

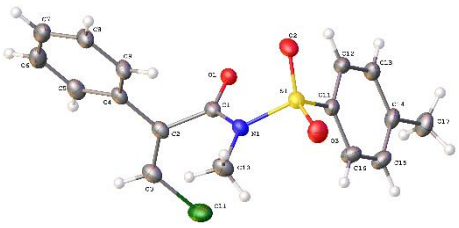
R_f = 0.51 (eluent = 20% EtOAc in hexanes); **ν_{max} / cm^{-1}** (thin film), 1731, 1597, 1495, 1435, 1336, 1255, 1208, 1176, 908, 692 ; *data for vinyl chloride **(27)*** **^{1}H NMR (500 MHz, $CDCl_3$)** δ_H: 3.89 (3H, s), 6.64 (1H, s), 7.30-7.44 (5H, m); **^{13}C NMR (126 MHz, $CDCl_3$)** δ_C: 52.6, 122.0, 127.0, 128.9, 129.0, 134.4, 137.7, 166.5; **HRMS (ASAP +)** [$C_{10}H_9ClO_2$] requires $[M+H]^+$ 197.0369, found 197.0369 (+ 0.0 ppm); *data for dichlorinated ester **(28)*** **^{1}H NMR (500 MHz, $CDCl_3$)** δ_H: 3.85 (3H, s), 4.17 (1H, d, *J* 11.8 Hz), 4.33 (1H, d, *J* 11.8 Hz), 7.30-7.43 (3H, m), 7.49-7.54 (2H, m); **^{13}C NMR (126 MHz, $CDCl_3$)** δ_C: 51.8, 54.0, 73.5, 126.6, 128.8, 129.4, 136.5, 168.9; **HRMS (ASAP +)** [$C_{10}H_{10}Cl_2O_2$] requires $[M-Cl]^+$ 197.0369, found 197.0369 (+ 0.0 ppm).


7.52
7.52
7.52
7.51
7.51
7.51
7.41
7.41
7.40
7.40
7.39
7.38
7.38
7.37
7.37
7.36
7.36
7.35
7.33
7.33
7.33
7.32
7.32
7.32
7.31
7.29
6.69
4.34
4.31
4.18
4.16
3.89
3.85
3.79
1.87
6.20
2.15
1.00
0.91
0.93
3.04
2.57
f1 (ppm)


168.86
166.49
137.65
136.52
134.29
129.36
129.02
128.92
128.81
126.95
126.55
122.00
77.41
77.16
76.91
73.49
54.05
52.62
51.75
f1 (ppm)

3.3 Xray Crystallography Data Evidencing Z Selectivity

(1)



Experimental. Single colourless block crystals of **2021ncs0078z** were supplied.. A suitable cut fragment with dimensions 0.25 × 0.22 × 0.18 mm^3 was selected and mounted on a MITIGEN holder in perfluoroether oil on a Rigaku FRE+ equipped with VHF Varimax confocal mirrors and an AFC12 goniometer and HyPix 6000 detector diffractometer. The crystal was kept at a steady T = 100(2) K during data collection. The structure was solved with the ShelXT 2018/2 (Sheldrick, 2015) solution program using dual methods and by using Olex2 (Dolomanov et al., 2009) as the graphical interface. The model was refined with ShelXL 2018/3 (Sheldrick, 2015) using full matrix least squares minimisation on $\boldsymbol{F^2}$.

Crystal Data. $C_{17}H_{16}ClNO_3S$, M_r = 349.82, triclinic, P-1 (No. 2), a = 8.7344(4) Å, b = 8.9409(4) Å, c = 10.7084(3) Å, α = 80.648(3)°, β = 88.789(3)°, γ = 84.471(4)°, V = 821.29(6) Å^3, T = 100(2) K, Z = 2, Z' = 1, μ(Mo K$_\alpha$) = 0.373, 24406 reflections measured, 5152 unique (R_{int} = 0.0763) which were used in all calculations. The final wR_2 was 0.1443 (all data) and R_1 was 0.0522 (I≥2 σ(I)).

Crystal Data and Experimental

Compound	**2021ncs0078z**
Formula	$C_{17}H_{16}ClNO_3S$
$D_{calc.}$/ g cm^{-3}	1.415
μ/mm^{-1}	0.373
Formula Weight	349.82
Colour	colourless
Shape	block (cut fragment)
Size/mm^3	0.25×0.22×0.18
T/K	100(2)
Crystal System	triclinic
Space Group	P-1
a/Å	8.7344(4)
b/Å	8.9409(4)
c/Å	10.7084(3)
α/°	80.648(3)
β/°	88.789(3)
γ/°	84.471(4)
V/Å^3	821.29(6)
Z	2
Z'	1
Wavelength/Å	0.71075
Radiation type	Mo K$_\alpha$
Θ_{min}/°	1.927
Θ_{max}/°	32.615
Measured Refl's.	24406
Indep't Refl's	5152
Refl's I≥2 σ(I)	4065
R_{int}	0.0763
Parameters	210
Restraints	0
Largest Peak	0.685
Deepest Hole	-0.598
GooF	1.036
wR_2 (all data)	0.1443
wR_2	0.1333
R_1 (all data)	0.0687
R_1	0.0522

Structure Quality Indicators

Reflections:	d min (Mo) 2θ=65.2° 0.66	I/σ(I) 21.0	Rint 7.63%	CAP 57.3° 86% to 65.2° 100
Refinement:	Shift 0.000	Max Peak 0.7	Min Peak -0.6	GooF 1.036

A colourless cut fragment of a block-shaped crystal with dimensions 0.25 × 0.22 × 0.18 mm^3 was mounted on a MITIGEN holder in perfluoroether oil. Data were collected using a Rigaku FRE+ equipped with VHF Varimax confocal mirrors and an AFC12 goniometer and HyPix 6000 detector diffractometer equipped with an Oxford Cryosystems low-temperature device operating at T = 100(2) K.

Data were measured using profile data from ω-scans using Mo K_α radiation. The diffraction pattern was indexed and the total number of runs and images was based on the strategy calculation from the program CrysAlisPro (Rigaku, V1.171.41.103a, 2021). The maximum resolution that was achieved was Θ = 32.615° (0.66 Å).

The diffraction pattern was indexed and the total number of runs and images was based on the strategy calculation from the program CrysAlisPro (Rigaku, V1.171.41.103a, 2021). The unit cell was refined using CrysAlisPro (Rigaku, V1.171.41.103a, 2021) on 10857 reflections, 44% of the observed reflections.

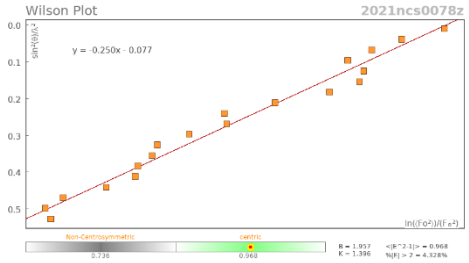
Data reduction, scaling and absorption corrections were performed using CrysAlisPro (Rigaku, V1.171.41.103a, 2021). The final completeness is 100.00 % out to 32.615° in Θ. A multi-scan absorption correction was performed using CrysAlisPro (Rigaku, V1.171.41.103a, 2021). Empirical absorption correction using spherical harmonics as implemented in SCALE3 ABSPACK scaling algorithm.. The absorption coefficient μ of this material is 0.373 mm^{-1} at this wavelength (λ = 0.71075Å) and the minimum and maximum transmissions are 0.680 and 1.000.

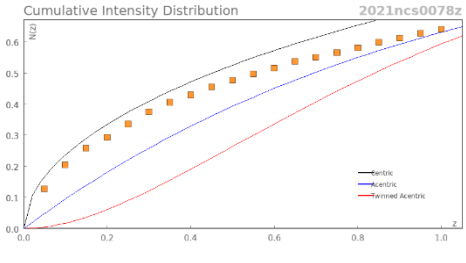
The structure was solved and the space group *P*-1 (# 2) determined by the ShelXT 2018/2 (Sheldrick, 2015) structure solution program using dual methods and refined by full matrix least squares minimisation on F^2 using ShelXL 2018/3 (Sheldrick, 2015). All non-hydrogen atoms were refined anisotropically. Hydrogen atom positions were calculated geometrically and refined using the riding model.

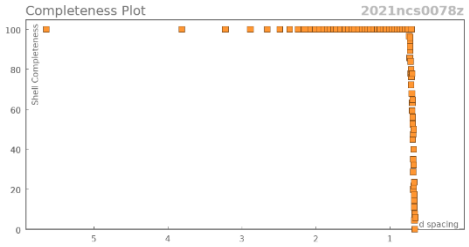
_exptl_absorpt_process_details: CrysAlisPro 1.171.41.103a (Rigaku, V1.171.41.103a, 2021) using spherical harmonics as implemented in SCALE3 ABSPACK scaling algorithm.

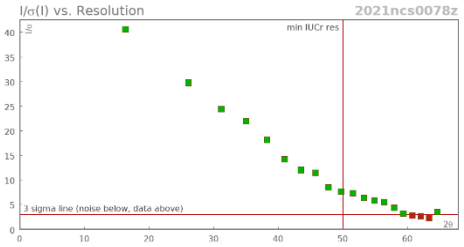
There is a single molecule in the asymmetric unit, which is represented by the reported sum formula. In other words: Z is 2 and Z' is 1.

Data Plots: Diffraction Data

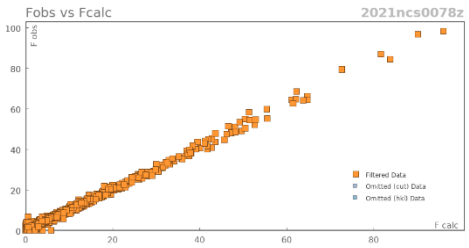


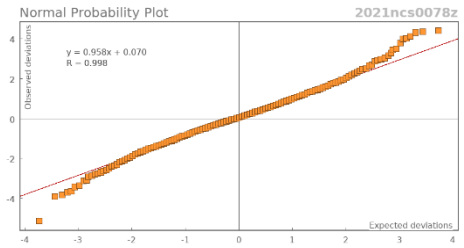






Data Plots: Refinement and Data





Reflection Statistics

Total reflections (after filtering)	24406	Unique reflections	5152
Completeness	0.86	Mean I/σ	13.06
hkl_{max} collected	(13, 12, 16)	hkl_{min} collected	(-12, -13, -16)
hkl_{max} used	(12, 13, 16)	hkl_{min} used	(-13, -12, 0)
Lim d_{max} collected	100.0	Lim d_{min} collected	0.36
d_{max} used	10.57	d_{min} used	0.66
Friedel pairs	4347	Friedel pairs merged	1
Inconsistent equivalents	36	R_{int}	0.0763
R_{sigma}	0.0475	Intensity transformed	0
Omitted reflections	0	Omitted by user (OMIT hkl)	0
Multiplicity	(2379, 3031, 1942, 1134, 587, 330, 81, 14, 1)	Maximum multiplicity	12
Removed systematic absences	0	Filtered off (Shel/OMIT)	0

Table 1: Fractional Atomic Coordinates (×10⁴) and Equivalent Isotropic Displacement Parameters (Å²×10³) for **2021ncs0078z**. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij}.

Atom	x	y	z	U_{eq}
Cl1	3346.4(6)	4008.2(6)	7342.7(5)	35.83(14)
S1	1991.2(5)	9378.4(5)	6616.9(4)	22.46(12)
O1	4095.3(14)	7606.9(14)	5242.1(11)	22.7(2)
O2	2137.4(16)	10454.7(14)	5491.7(12)	29.4(3)
O3	733.8(16)	9615.4(16)	7463.8(13)	31.6(3)
N1	1761.1(16)	7659.2(16)	6213.2(13)	21.5(3)
C1	2913.1(19)	7016.4(18)	5510.4(15)	19.9(3)
C2	2654.2(18)	5555.5(19)	5040.6(16)	21.8(3)
C3	2884(2)	4208(2)	5763.1(18)	27.0(4)
C4	2272.9(19)	5736.8(19)	3683.2(16)	21.8(3)
C5	2916(2)	4720(2)	2912.4(18)	27.6(4)
C6	2501(2)	4911(2)	1648.1(19)	32.1(4)
C7	1445(2)	6097(2)	1143.2(18)	32.0(4)
C8	820(2)	7126(2)	1896.4(17)	29.0(4)
C9	1235(2)	6951.5(19)	3158.2(17)	24.7(3)
C10	307(2)	6994(2)	6578.5(19)	28.2(4)
C11	3709(2)	9134.6(19)	7475.6(15)	21.9(3)
C12	4997(2)	9778(2)	6942.2(16)	25.2(3)
C13	6321(2)	9635(2)	7661.0(16)	27.3(4)

Atom	x	y	z	U_{eq}
C14	6363(2)	8864(2)	8901.4(16)	26.5(4)
C15	5052(2)	8232(2)	9409.9(17)	29.9(4)
C16	3716(2)	8356(2)	8705.9(16)	27.6(4)
C17	7815(2)	8704(3)	9663.1(19)	35.3(4)

Table 2: Anisotropic Displacement Parameters (×10⁴) for **2021ncs0078z**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2} \times U_{11} + ... + 2hka^* \times b^* \times U_{12}]$

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Cl1	35.9(3)	33.4(3)	33.9(2)	9.81(19)	-10.44(19)	-5.15(19)
S1	24.0(2)	19.3(2)	23.6(2)	-2.28(15)	-3.30(15)	-0.88(15)
O1	23.6(6)	23.3(6)	22.2(5)	-3.3(5)	-0.8(4)	-7.0(5)
O2	37.6(7)	20.0(6)	29.0(6)	1.8(5)	-9.2(5)	-3.0(5)
O3	26.1(6)	33.5(7)	35.6(7)	-10.1(6)	1.2(5)	2.4(5)
N1	21.1(7)	18.5(6)	25.2(7)	-2.8(5)	-1.4(5)	-3.8(5)
C1	21.2(7)	18.0(7)	19.8(7)	0.1(6)	-5.1(5)	-1.8(6)
C2	17.1(7)	20.0(7)	28.4(8)	-2.9(6)	-3.1(6)	-2.7(6)
C3	23.0(8)	22.5(8)	34.5(9)	-0.9(7)	-5.1(7)	-2.8(6)
C4	19.7(7)	18.8(7)	27.6(8)	-3.8(6)	-2.5(6)	-5.4(6)
C5	21.8(8)	24.7(8)	37.7(9)	-8.0(7)	0.7(7)	-3.9(7)
C6	32.0(9)	33.8(10)	34.4(9)	-14.3(8)	7.5(7)	-9.8(8)
C7	37.3(10)	35.7(10)	25.6(8)	-7.0(7)	-0.6(7)	-14.0(8)
C8	35.9(10)	23.7(8)	28.2(8)	-3.1(7)	-8.9(7)	-6.0(7)
C9	28.3(8)	19.0(7)	27.5(8)	-5.7(6)	-6.5(6)	-1.0(6)
C10	20.3(8)	27.4(9)	36.1(9)	-1.7(7)	0.8(7)	-5.3(7)
C11	26.1(8)	21.2(7)	19.0(7)	-4.1(6)	-1.9(6)	-3.6(6)
C12	31.4(9)	25.6(8)	19.6(7)	-2.8(6)	-1.6(6)	-8.5(7)
C13	28.8(9)	31.7(9)	23.9(8)	-6.7(7)	-0.5(6)	-12.0(7)
C14	30.3(9)	29.6(9)	21.4(7)	-9.1(7)	-4.3(6)	-2.4(7)
C15	32.1(9)	37.5(10)	18.8(7)	-0.9(7)	-1.6(6)	-2.7(8)
C16	26.3(8)	33.7(9)	21.6(7)	0.6(7)	1.2(6)	-4.9(7)
C17	32.7(10)	47.4(12)	28.2(9)	-11.5(8)	-8.3(7)	-4.4(9)

Table 3: Bond Lengths in Å for **2021ncs0078z**.

Atom	Atom	Length/Å
Cl1	C3	1.7241(19)
S1	O2	1.4263(13)
S1	O3	1.4314(14)
S1	N1	1.6939(14)
S1	C11	1.7537(17)
O1	C1	1.213(2)
N1	C1	1.381(2)
N1	C10	1.472(2)
C1	C2	1.512(2)
C2	C3	1.322(2)
C2	C4	1.478(2)
C4	C5	1.396(2)

Atom	Atom	Length/Å
C4	C9	1.397(2)
C5	C6	1.388(3)
C6	C7	1.384(3)
C7	C8	1.386(3)
C8	C9	1.387(2)
C11	C12	1.383(2)
C11	C16	1.386(2)
C12	C13	1.386(2)
C13	C14	1.393(2)
C14	C15	1.388(3)
C14	C17	1.505(3)
C15	C16	1.388(3)

Table 4: Bond Angles in ° for **2021ncs0078z**.

Atom	Atom	Atom	Angle/°
O2	S1	O3	119.25(9)

Atom	Atom	Atom	Angle/°
O2	S1	N1	108.94(8)

Atom	Atom	Atom	Angle/°
O2	S1	C11	109.59(8)
O3	S1	N1	103.69(8)
O3	S1	C11	108.58(8)
N1	S1	C11	105.90(8)
C1	N1	S1	117.81(11)
C1	N1	C10	124.56(14)
C10	N1	S1	117.55(12)
O1	C1	N1	121.93(15)
O1	C1	C2	119.83(15)
N1	C1	C2	118.23(14)
C3	C2	C1	122.32(15)
C3	C2	C4	122.57(16)
C4	C2	C1	114.85(14)
C2	C3	Cl1	122.20(15)
C5	C4	C2	121.72(15)
C5	C4	C9	119.08(16)
C9	C4	C2	119.19(15)
C6	C5	C4	119.92(17)
C7	C6	C5	120.60(17)
C6	C7	C8	119.84(17)
C7	C8	C9	120.01(18)
C8	C9	C4	120.52(16)
C12	C11	S1	119.84(13)
C12	C11	C16	121.52(16)
C16	C11	S1	118.56(13)
C11	C12	C13	118.85(16)
C12	C13	C14	121.05(17)
C13	C14	C17	120.35(17)
C15	C14	C13	118.72(16)
C15	C14	C17	120.92(17)
C16	C15	C14	121.21(16)
C11	C16	C15	118.65(17)

Table 5: Torsion Angles in ° for **2021ncs0078z**.

Atom	Atom	Atom	Atom	Angle/°
S1	N1	C1	O1	4.0(2)
S1	N1	C1	C2	-174.36(11)
S1	C11	C12	C13	176.83(14)
S1	C11	C16	C15	-176.62(15)
O1	C1	C2	C3	99.6(2)
O1	C1	C2	C4	-74.75(19)
O2	S1	N1	C1	59.59(14)
O2	S1	N1	C10	-117.18(13)
O2	S1	C11	C12	-8.64(17)
O2	S1	C11	C16	168.25(14)
O3	S1	N1	C1	-172.43(12)
O3	S1	N1	C10	10.79(14)
O3	S1	C11	C12	-140.46(14)
O3	S1	C11	C16	36.43(17)
N1	S1	C11	C12	108.73(15)
N1	S1	C11	C16	-74.38(15)
N1	C1	C2	C3	-82.0(2)
N1	C1	C2	C4	103.64(17)
C1	C2	C3	Cl1	5.5(3)
C1	C2	C4	C5	137.75(16)
C1	C2	C4	C9	-42.6(2)
C2	C4	C5	C6	178.55(16)
C2	C4	C9	C8	-178.10(16)
C3	C2	C4	C5	-36.6(3)
C3	C2	C4	C9	143.02(18)
C4	C2	C3	Cl1	179.38(13)
C4	C5	C6	C7	-0.4(3)
C5	C4	C9	C8	1.5(3)
C5	C6	C7	C8	1.5(3)
C6	C7	C8	C9	-1.0(3)
C7	C8	C9	C4	-0.5(3)
C9	C4	C5	C6	-1.1(3)

Atom	Atom	Atom	Atom	Angle/°
C10	N1	C1	O1	-179.48(15)
C10	N1	C1	C2	2.2(2)
C11	S1	N1	C1	-58.21(14)
C11	S1	N1	C10	125.02(13)
C11	C12	C13	C14	-0.3(3)
C12	C11	C16	C15	0.2(3)
C12	C13	C14	C15	0.2(3)
C12	C13	C14	C17	179.27(17)
C13	C14	C15	C16	0.0(3)
C14	C15	C16	C11	-0.3(3)
C16	C11	C12	C13	0.0(3)
C17	C14	C15	C16	-179.01(18)

Table 6: Hydrogen Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for **2021ncs0078z**. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij}.

Atom	x	y	z	U_{eq}
H3	2791.97	3319.55	5399.82	32
H5	3636.88	3898.15	3252.67	33
H6	2946.26	4221.08	1124.89	39
H7	1148.46	6206.01	282.21	38
H8	107.29	7950.8	1548.26	35
H9	809.97	7663.79	3669.62	30
H10A	248.83	6739.72	7502.57	42
H10B	265.51	6069.24	6204.16	42
H10C	-560.38	7731.61	6272.08	42
H12	4975.41	10309.27	6097.96	30
H13	7212.24	10069.57	7301.89	33
H15	5068.49	7704.19	10255.21	36
H16	2824.61	7916.16	9059.87	33
H17A	8411.78	7739.21	9577.52	53
H17B	7551.91	8715.57	10555.77	53
H17C	8427.87	9551.49	9351.97	53

Citations

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O.V. Dolomanov and L.J. Bourhis and R.J. Gildea and J.A.K. Howard and H. Puschmann, Olex2: A complete structure solution, refinement and analysis program, *J. Appl. Cryst.*, (2009), **42**, 339-341.

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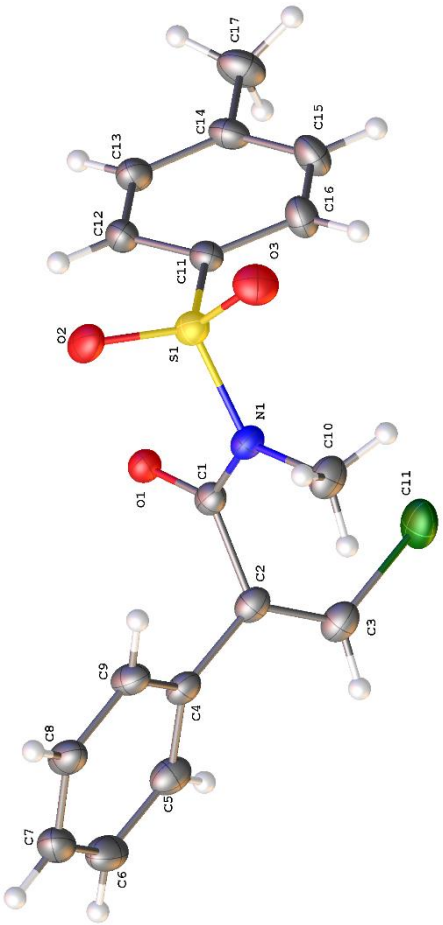
Sheldrick, G.M., ShelXT-Integrated space-group and crystal-structure determination, *Acta Cryst.*, (2015), **A71**, 3-8.



4. Electrochemical Flow Scale Up

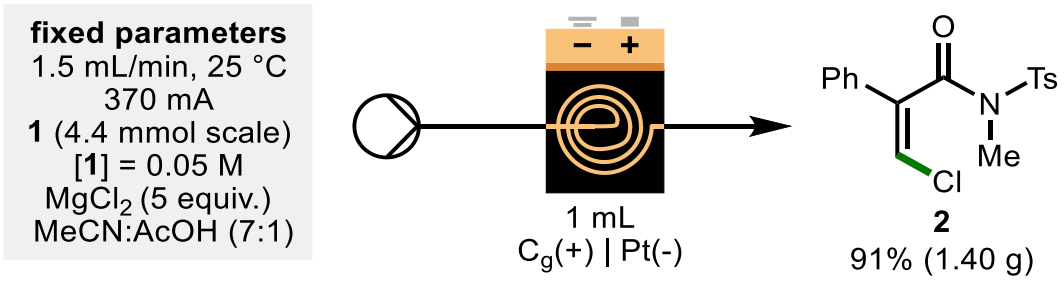
4.1 General Information

The flow set-up used PFA tubing with a 0.79 ± 0.1 mm internal diameter and 1.58±0.1 mm outer diameter supplied by Polyflon. All flow fittings and connections were purchased from Kinesis (Gripper fitting nuts, part number: 002103; Adapters, part number: P-618; Omnilok type-p fitting ferrule, part number: 008FT16; Y-Connector, part number: P-512; Threaded union, part number: P-623; 40 psi Back pressure regulator (used as check valve for DCM pump; part number: P-785). The syringe pumps used was the the Chemyx Fusion 100 syringe pump.

The power supply used was a Voltcraft LRP-1205 that supplied DC to the electrochemical system. The electrochemical flow cell was purchased from Cambridge Reactor Design, the Ammonite 8 (part number: 74660). The electrochemical flow cell consists of 1 carbon/PVDF electrode and one platinum electrode that are fixed either side of a FFKM gasket with a channel groove length of 1000 mm and an internal volume of 2.5 mL, of which 1 mL is exposed to the electrodes. The inlet and outlet fittings of the ammonite 8 cell were modified from 1/16” ID to accommodate 1/32” ID PFA tubing using Swagelok reducers, nuts and ferrules. The ammonite reactor was cell was dismantled for electrode cleaning every 3 passes. The graphite electrode was cleaned with acetone, water, acetone rinses and then the surface regenerated by rubbing with silica gel and cotton wool to remove surface contaminants. The platinum electrode was cleaned with acetone, water acetone rinses, left to dry and then burned with a blow torch.

The electrochemical flow system was used only in single pass electrolysis. Recirculating flow was not examined.

4.2 Gram Scale Flow Experimental



A 250 mL round-bottom flask was flame dried and charged with N-methyl-N-tosylphenacrylamide (1.50 g, 4.75 mmol, 1 equiv.) and $MgCl_2$ (2.26 g, 23.8 mmol, 5 equiv.) and sealed with a Suba-seal and parafilm. The reagent flask was evacuated on a Schlenk line and back filled with nitrogen gas for three cycles. Dry MeCN (83 mL) and glacial acetic acid (12 mL) were then added. After deoxygenating, (bubbling with nitrogen for 10 min) the mixture was drawn up into two 60 mL syringes and loaded onto a syringe pump.

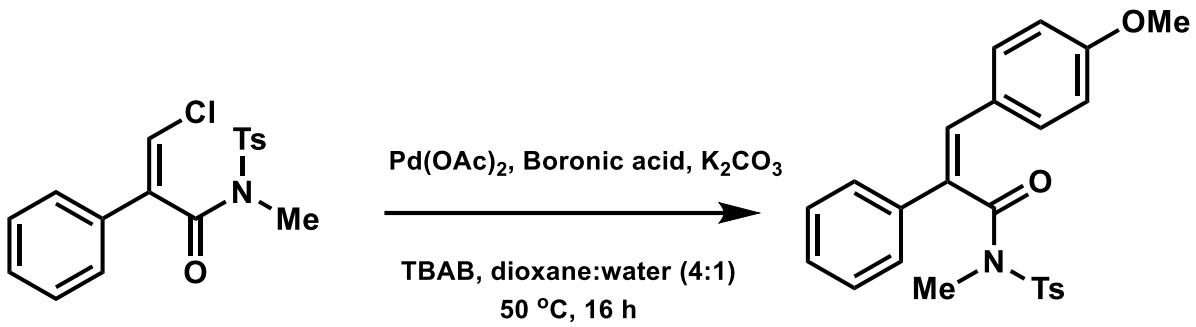
The ammonite electrochemical flow reactor set up with a graphite anode and platinum cathode, was flushed with nitrogen gas for 5 min by connecting the inlet tubing directly to a dry nitrogen line. The reagent solution in 2 x 60 mL syringes were then connected to the flow set up via a T-piece. The syringe pumps were set to 0.75 mL/min, giving a combined total flow rate of 1.5 mL/min at the mixing-tee. The electrochemical set up was primed by pulling through 2 mL of reaction mixture to fill the volume of the flow reactor and tubing. The power supply was set (370 mA, constant current) and attached to the ammonite flow reactor. The power supply was switched on and syringe pumping was initiated, and the outlet of the flow system was set to waste for the first 3 mL (representing 1 whole flow path volume, inclusive of tubing, connectors and reactor) of reaction mixture to allow the flow system to be filled. The outlet stream of the flow system was then collected for 88 mL (representing 4.42 mmol of material processed) at an operating potential of 2.2-2.4 V. Mesitylene (1.47 mmol, 206 µL) was added to the product mixture, stirred for 5 min and then the ^{1}H NMR spectrum was recorded to give a crude reaction yield of 98%.

The reaction mixture was then washed with a saturated solution of $NaHCO_3$ (3 x 100 mL) until off-gassing subsided. The organics were then dried over $MgSO_4$ and concentrated *in vacuo* to afford the crude product as a colourless oil. The crude residue was purified by flash column chromatography (eluent = 10 to 20% EtOAc in hexanes, silica gel) to yield pure product (1.40 g, 91% yield).

5. Post Functionalisation Derivatisations

5.1 Palladium Catalysed Suzuki Coupling

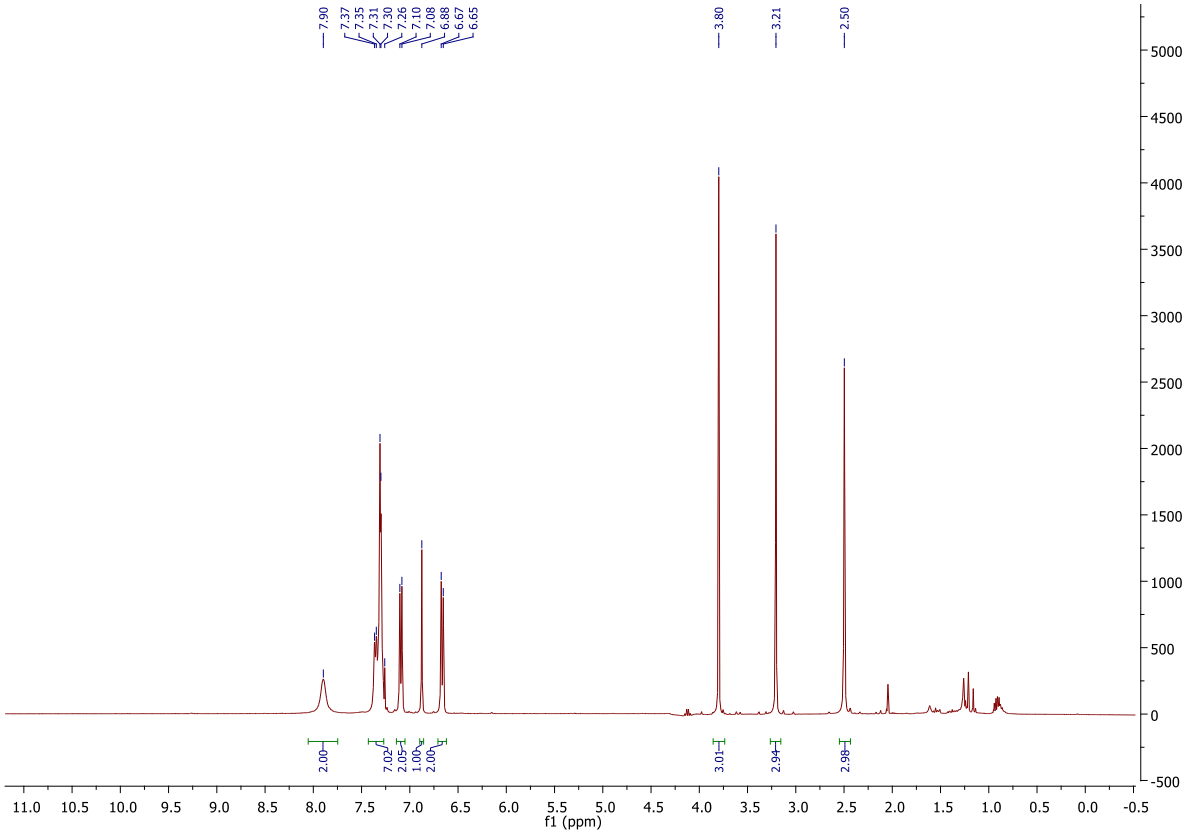
(31)



(2) **(31)**

To a 5 mL microwave vial was added (Z)-3-chloro-N-methyl-2-phenyl-N-tosylacrylamide (70.0 mg, 0.20 mmol), 4-methoxyphenylboronic acid (33.4 mg, 0.22 mmol, 1.1 equiv.), tetrabutylammonium bromide (64.5 mg, 0.20 mmol, 1 equiv.), palladium acetate (2.3 mg, 0.01 mmol, 0.05 equiv.) and potassium carbonate (70.0 mg, 0.50 mmol, 2.5 equiv.). The vial was sealed and evacuated and backfilled with nitrogen (X 3). Degassed dioxane: water (4:1, 2 mL) was added and the mixture was heated at 50 °C for 16 h. The reaction mixture was diluted with ethyl acetate (5 mL) and water (5 mL) and partitioned. The aqueous was extracted with ethyl acetate (2 x 10 mL), organics combined and dried over $MgSO_4$. The organics were concentrated *in vacuo* affording crude product as a yellow oil. The crude residue was purified by flash column chromatography to yield pure product **(31)** (eluent = 10-30% EtOAc in hexanes) as a yellow oil (41.8 mg, 49% yield).

R_f = 0.22 (eluent = 20% EtOAc in hexanes); **ν_{max} / cm^{-1}** (thin film) 2945, 1686, 1604, 1595, 1510, 1460, 1446, 1356, 1304, 1250, 1169, 1078, 1030, 949; **^{1}H NMR (400 MHz, $CDCl_3$)** δ_H: 2.42 (3H, s), 3.13 (3H, s), 3.72 (3H, s), 6.58 (2H, d, *J* 8.5 Hz), 6.80 (1H, s), 7.01 (2H, d, *J* 8.5 Hz), 7.12-7.37 (7H, m), 7.80-7.95 (2H, m);); **^{13}C NMR (101 MHz, $CDCl_3$)** δ_C: 21.7, 33.6, 55.3, 114.3, 125.6, 127.4, 128.5, 128.7, 129.0, 129.2, 129.5, 129.9, 133.3, 135.6, 135.8, 145.0, 160.0, 170.4; **HRMS (ES+)** [$C_{24}H_{23}NO_4$] requires $[M+H]^+$ 422.1426, found 422.1427 (+ 0.2 ppm).


7.90
7.37
7.35
7.31
7.30
7.26
7.10
7.08
6.88
6.67
6.65
3.80
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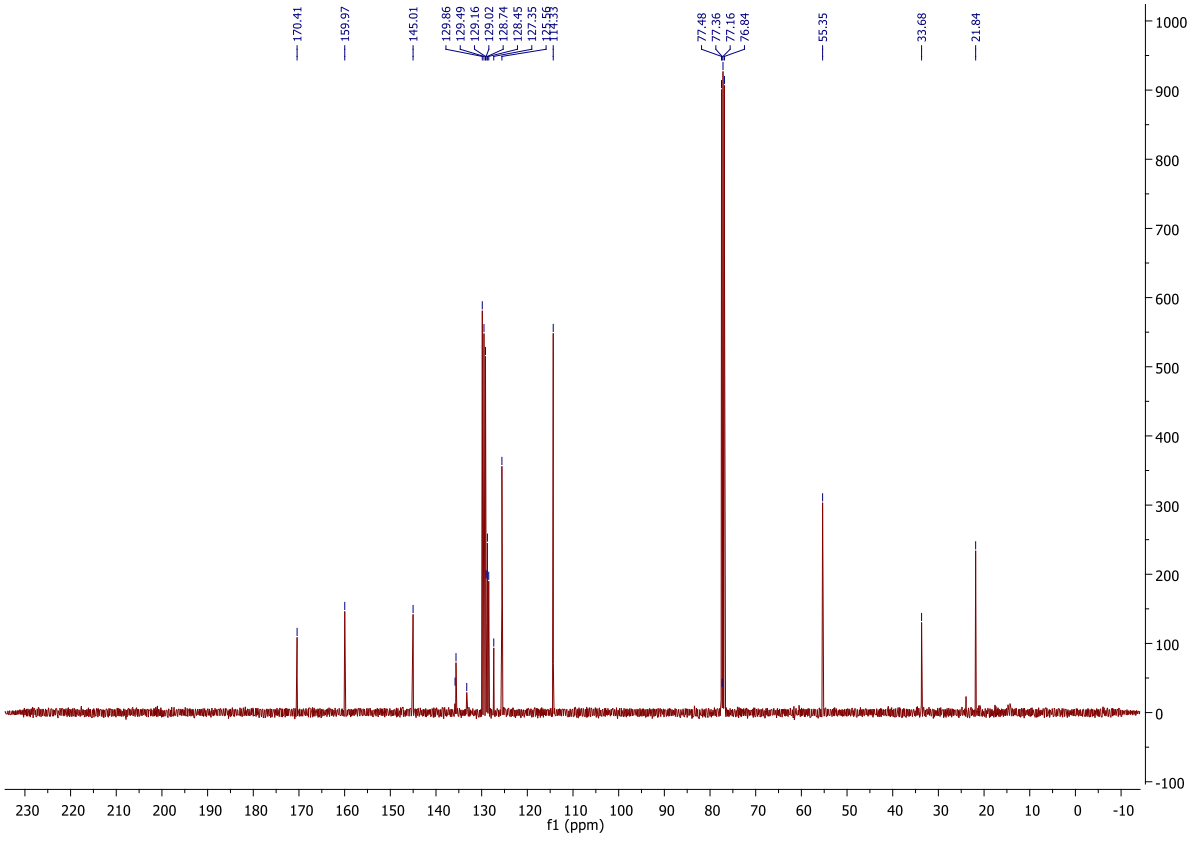
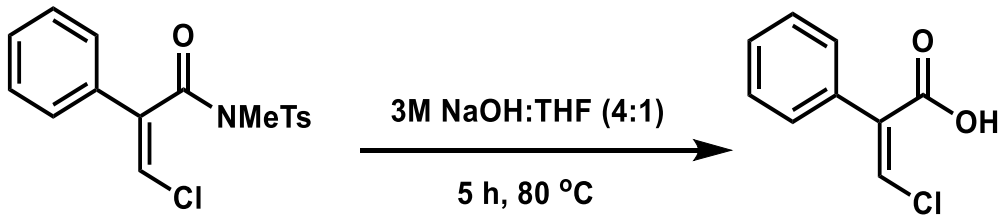
2.00
7.02
2.05
1.00
2.06
3.01
2.94
2.98
f1 (ppm)


170.41
159.97
145.01
129.86
129.49
129.16
129.02
128.74
128.45
127.35
114.53
77.48
77.36
77.16
76.84
55.35
33.68
21.84
f1 (ppm)

5.2 Amide Hydrolysis

5.2.1 Carboxylic acid

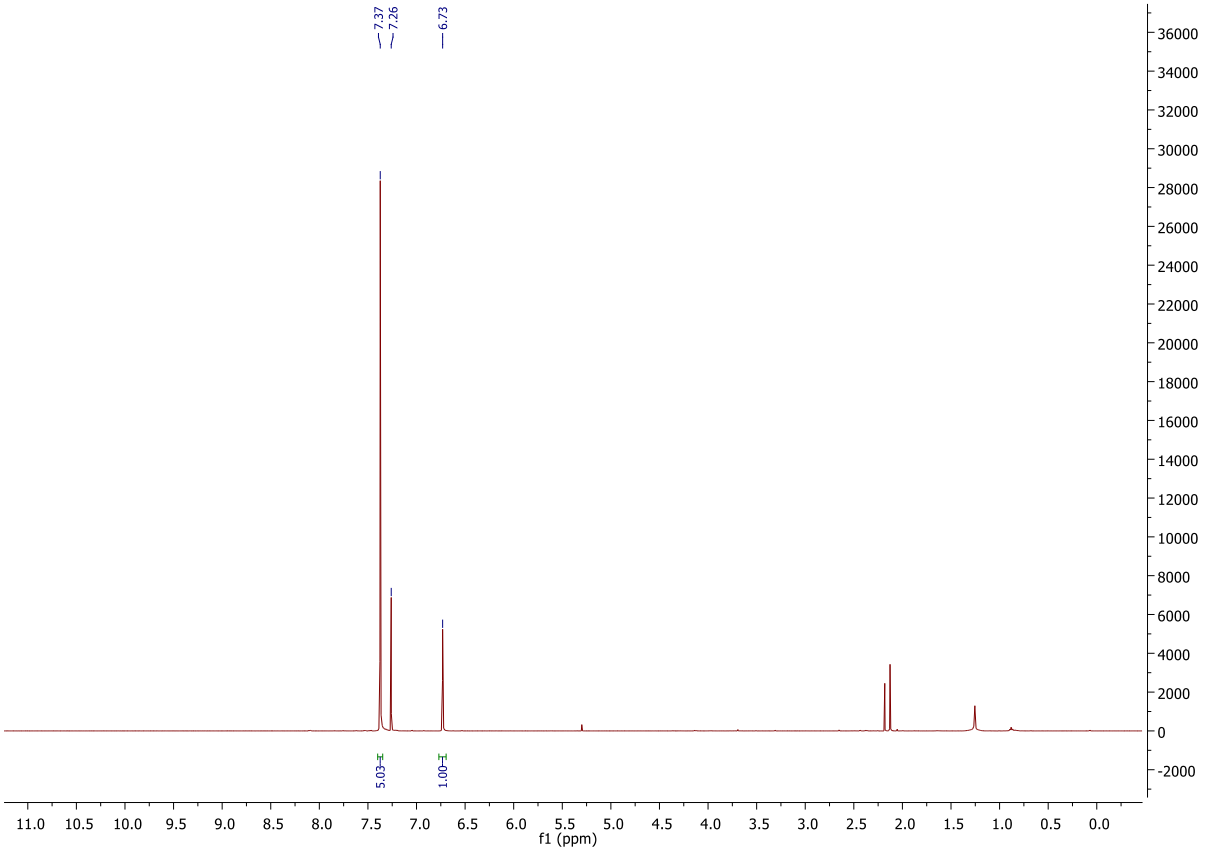
(32)

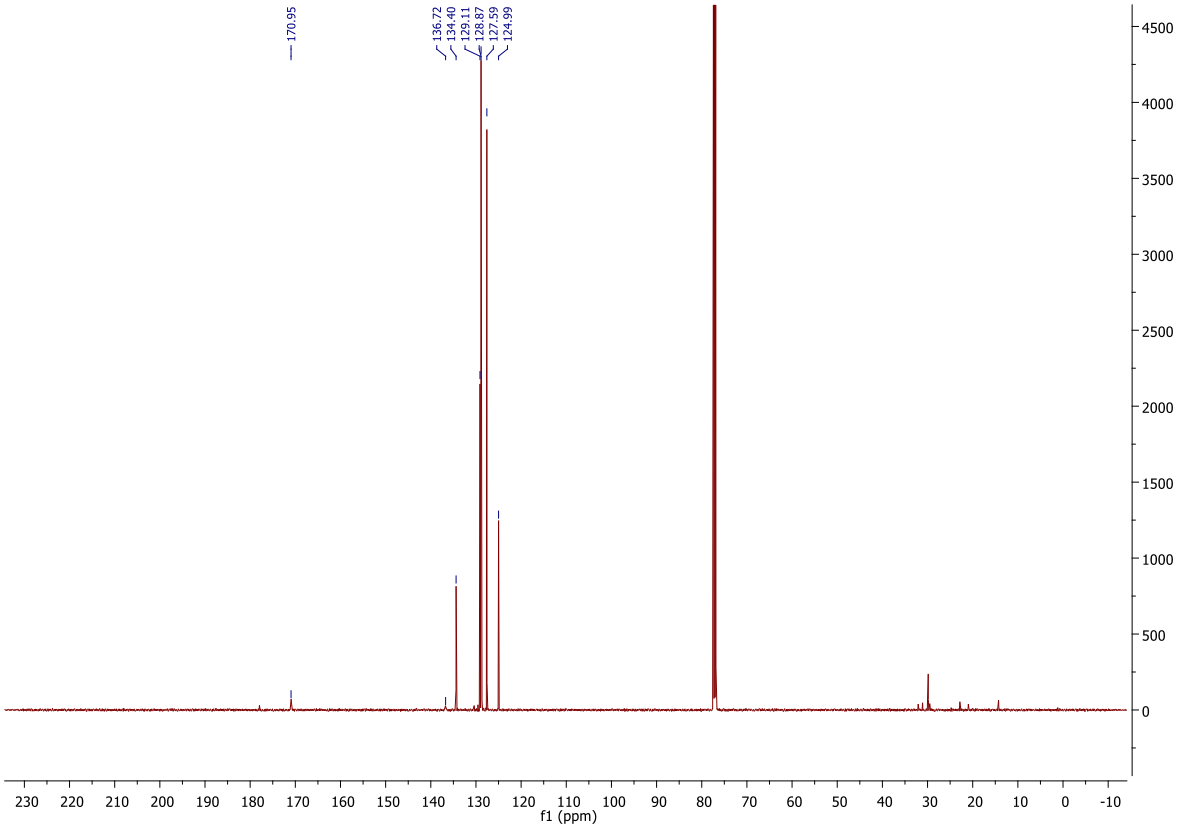


(32)

To a 5 mL microwave vial was added (Z)-3-chloro-N-methyl-2-phenyl-N-tosylacrylamide (35.0 mg, 0.10 mmol), 3M NaOH solution (2.60 mL) and THF (0.60 mL). The vial was sealed and heated to 80 °C for 5 h. The reaction was cooled to room temperature, diluted with 1M NaOH (3.0 mL) and transferred to a separating funnel. The aqueous reaction mixture was washed with EtOAc (4 x 10 mL) before being acidified to pH 1 with 2M HCl. The acidic aqueous was extracted with CH_2Cl_2 (3 x 20 mL), organics combined, dried over $MgSO_4$, and concentrated *in vacuo* to give crude carboxylic acid **(32)** as a pale orange oil (13.1 mg, 72% yield).

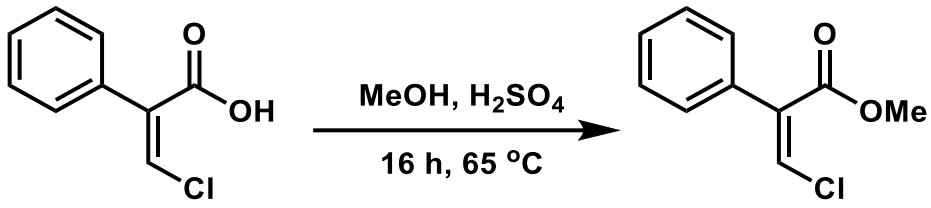
R_f = 0.07 (eluent = 100% CH_2Cl_2); **ν_{max} / cm^{-1}** (thin film) 2849-3077 (br), 1685, 1598, 1496, 1415, 1219, 1078, 988, 688; **^{1}H NMR (500 MHz, $CDCl_3$)** δ_H: 6.73 (1H, s), 7.37 (5H, m); **^{13}C NMR (126 MHz, $CDCl_3$)** δ_C: 125.0, 127.6, 128.9, 129.1, 134.4, 136.7, 171.0; **HRMS (FTMS)** [$C_9H_7ClO_2$] requires $[M]^+$ 182.0135, found 182.0129 (- 0.8 ppm).





*Quaternary centres difficult to determine even at 1024 scans.

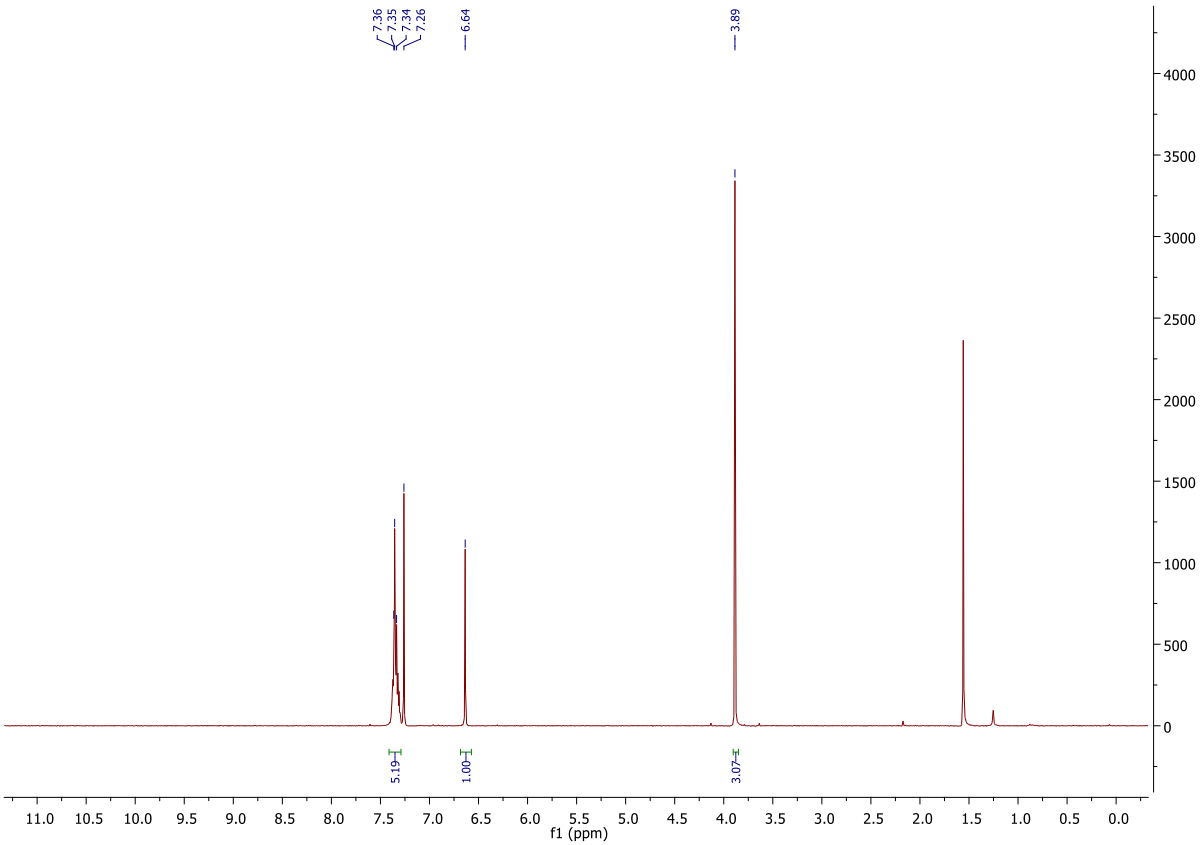
5.2.2 Methyl ester



(32)

To a 5 mL microwave vial was added carboxylic acid (13.0 mg, 0.071 mmol), MeOH (1.0 mL) and 1 drop of conc. H_2SO_4. The vial was sealed and heated to 65 °C for 16 h. The mixture was allowed to cool and then concentrated *in vacuo*. The residue was taken up in EtOAc (10 mL), washed with saturated sodium bicarbonate solution (10 mL), organics dried over $MgSO_4$, filtered and concentrated yielding crude ester. The residue was purified by preparative TLC (eluent = 10% EtOAc in hexanes) to yield pure product as a thin film residue (12.1 mg, 85% yield).

R_f = 0.48 (eluent = 20% EtOAc in hexanes); **ν_{max} / cm^{-1}**(thin film) 2953, 1732, 1597, 1495, 1435, 1336, 1255, 1208, 1176, 908, 692; **^{1}H NMR (300 MHz, $CDCl_3$)** δ_H: 3.89 (3H, s), 6.64 (1H, s), 7.29-7.42 (5H, m); **^{13}C NMR (126 MHz, $CDCl_3$)** δ_C: 52.6, 122.0, 127.0, 128.9, 129.0, 134.4, 137.7, 166.5; **HRMS (FTMS)** [$C_{10}H_9ClO_2$] requires $[M+H]^+$ 197.0364, found 197.0366 (+ 1.2 ppm).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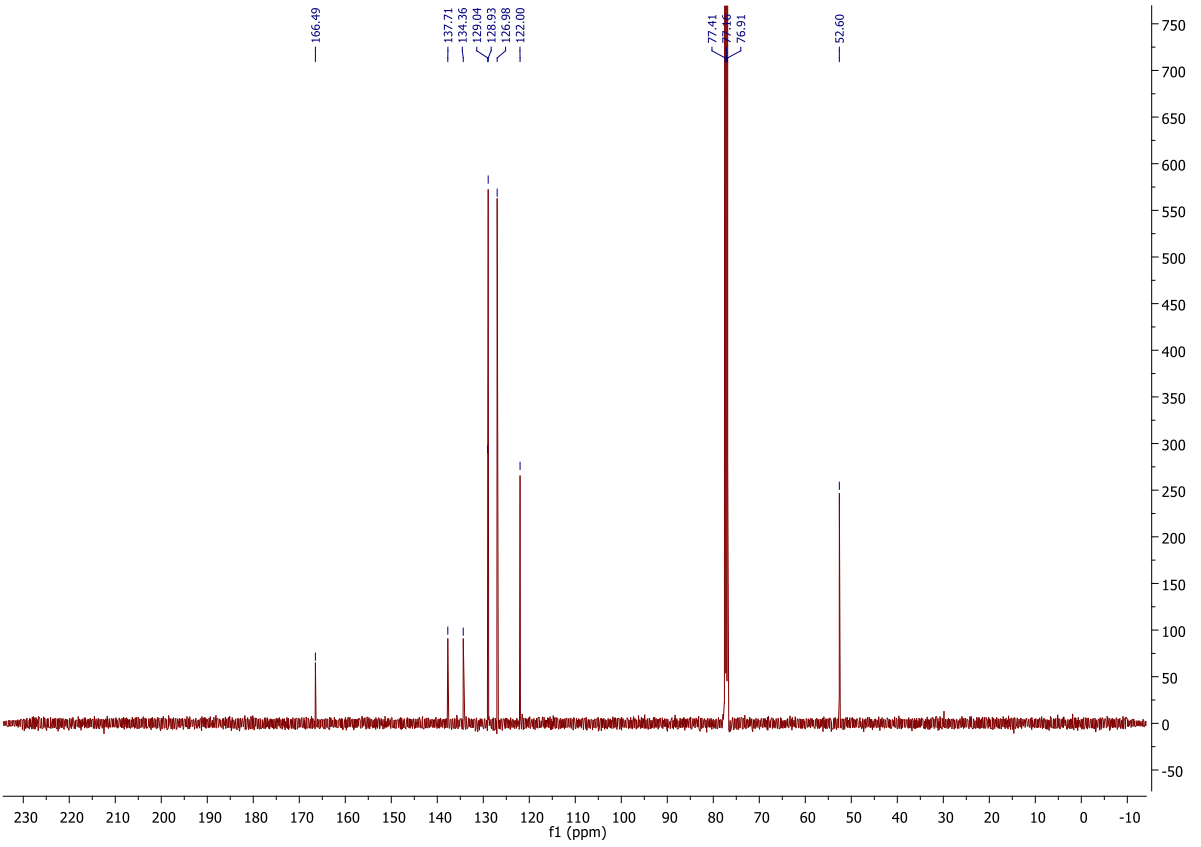
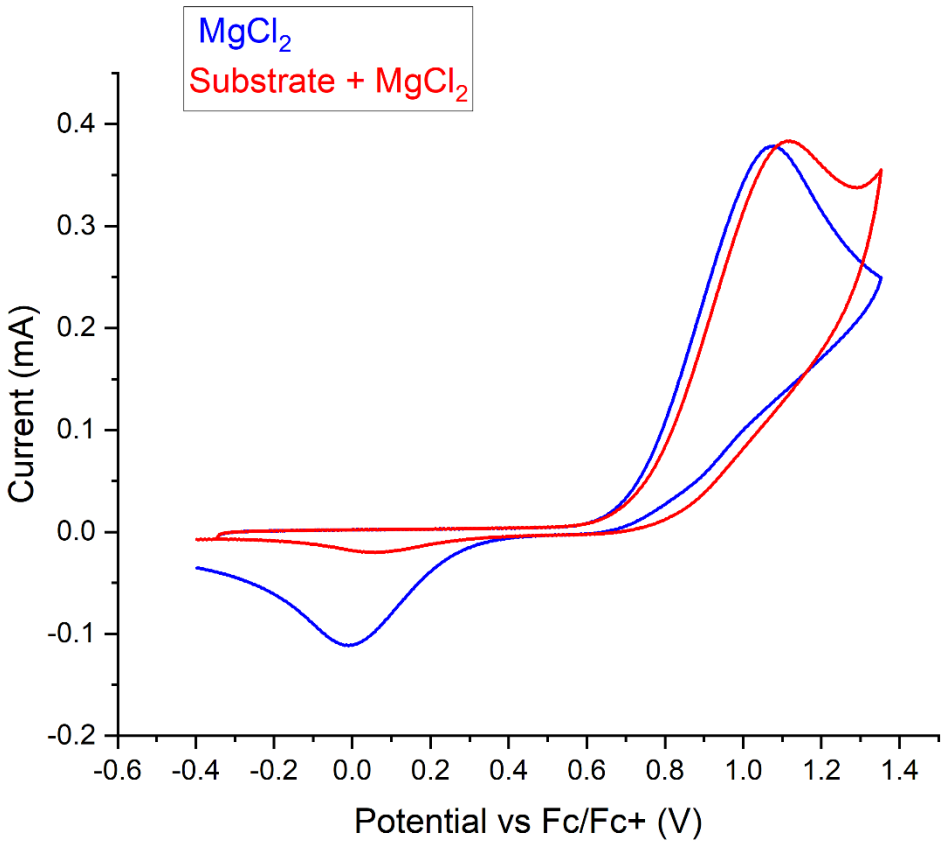
7.34
7.26
6.64
3.89
5.19
1.00
3.07
f1 (ppm)


166.49
137.71
134.36
129.04
128.93
126.98
122.00
77.41
77.16
76.91
52.60
f1 (ppm)

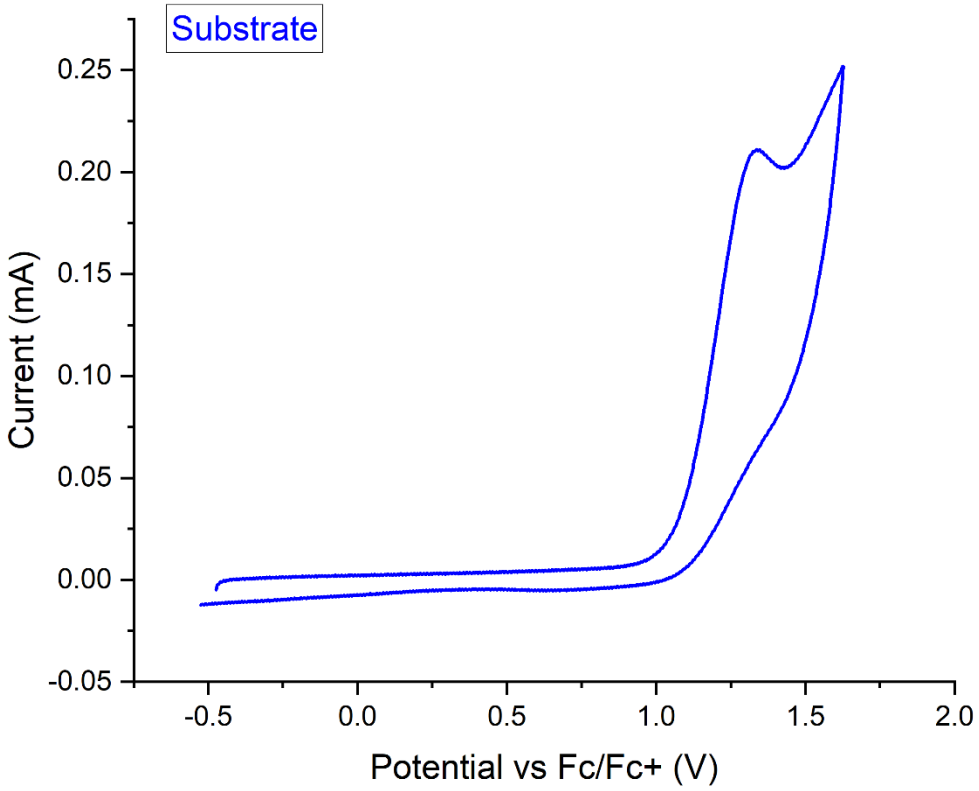
6. Mechanistic Studies

6.1 Cyclic Voltammetry Studies

General Information: Cyclic Voltammetry (CV) experiments were conducted with in a 10 mL glass vial fitted with a glassy carbon working electrode (3 mm dia., BASi), a Ag/AgCl reference electrode and a platinum wire counter electrode. The solution of interest was purged with N_2 for 5 minutes before data collection. After data collection, ferrocene (5 mM) was added, and an additional scan was run. The parent data was referenced relative to the $Fc^{+/0}$ couple that was recorded.



Cyclic Voltammogram of $MgCl_2$ and the parent substrate mixture in MeCN/AcOH. (a – blue line) $MgCl_2$ (8.0 mM); (b – red line) parent substrate (4.0 mM) in MeCN with AcOH and $LiClO_4$ (0.1 M). **Scan rate: 100 mV/s.**

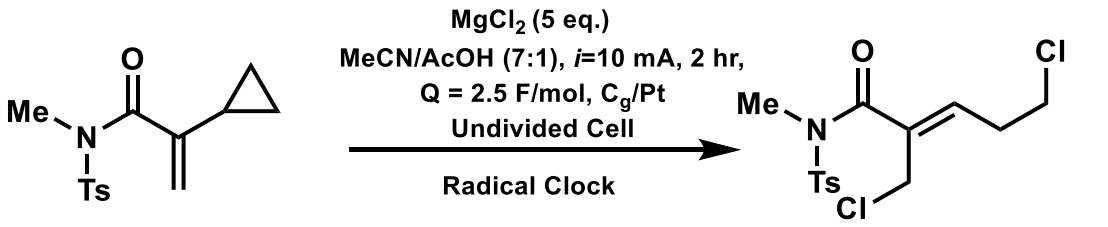


Cyclic voltammogram of parent substrate (a – blue line) (4.0 mM); (b – red line) 1 in MeCN with AcOH and $LiClO_4$ (0.1 M). **Scan rate: 100 mV/s.**

6.2 Experimental Evidence

6.2.1 Radical Clock Experiment

(34)

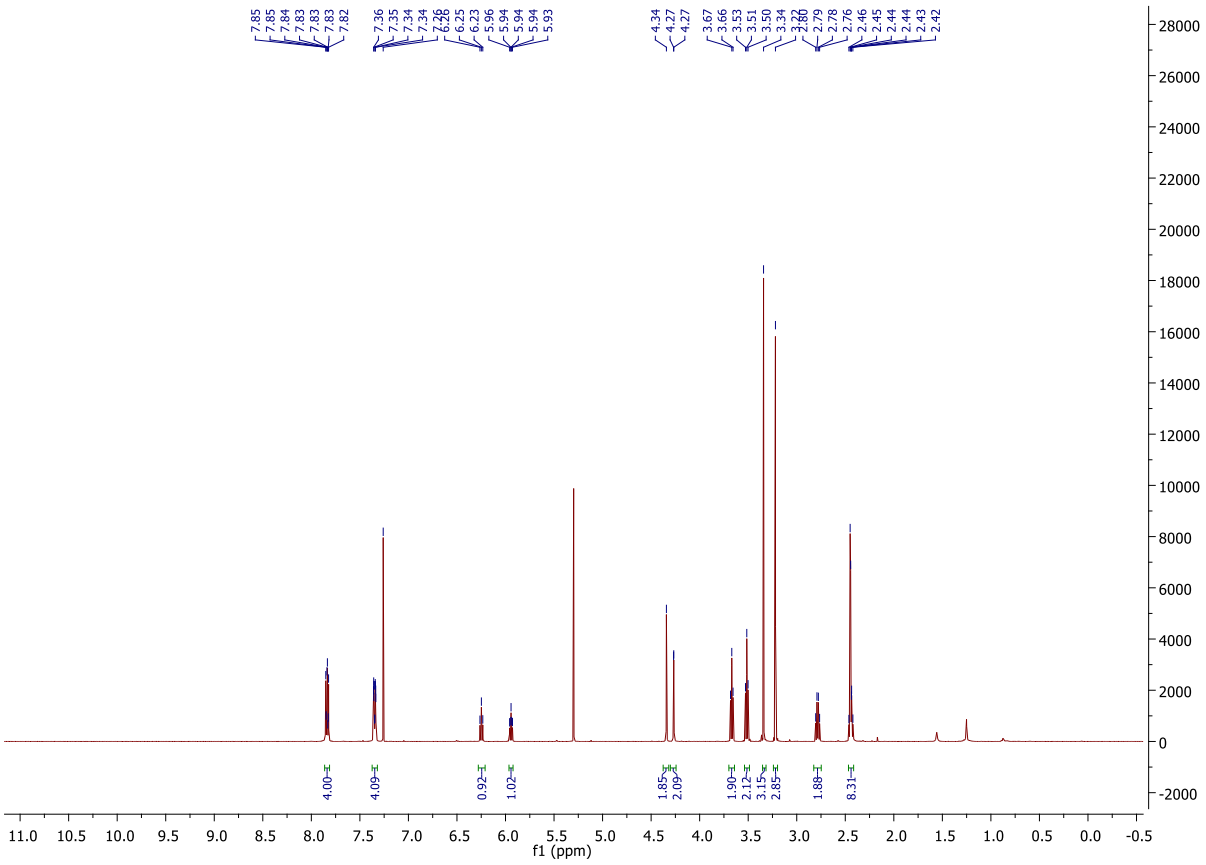


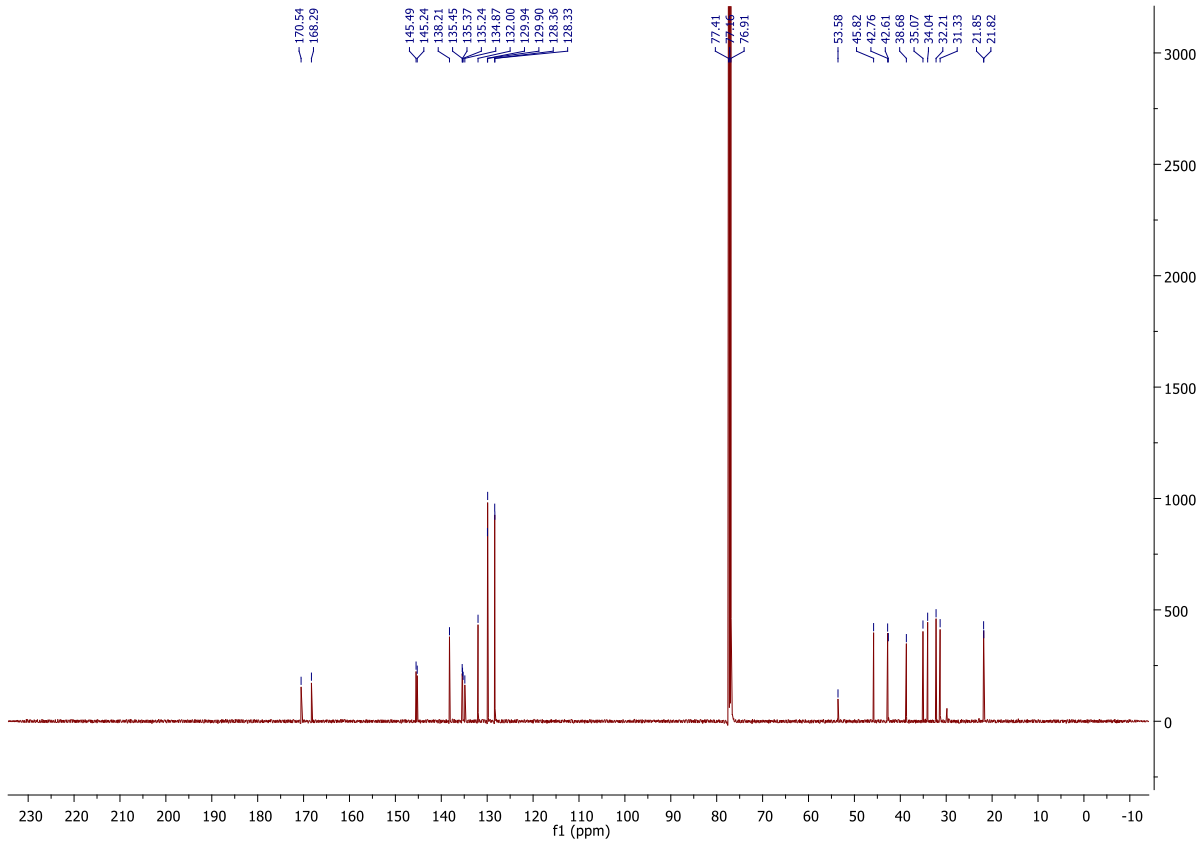
44 % conversion by NMR
Mixture of E:Z stereoisomers

(33) **(34)**

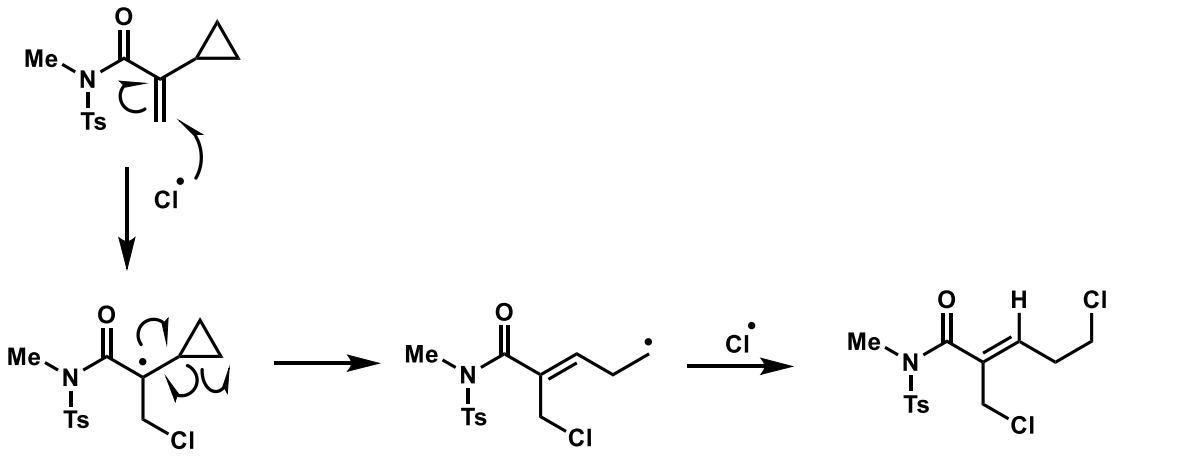
Prepared according to General Procedure G using 2-cyclopropyl-N-methyl-N-tosylacrylamide (84.0 mg, 0.30 mmol, 1 equiv.), magnesium chloride (143 mg, 1.50 mmol, 5 equiv.), acetonitrile (5.25 mL) and acetic acid (0.75 mL). Purification by flash column chromatography (eluent = 5 to 15% EtOAc in hexanes, silica gel) to afford product **(34)** as a 1:1 mixture of E/Z stereoisomers as a colourless oil (21.1 mg, 20% yield).

R_f = 0.27 (eluent = 15% EtOAc in hexanes); **ν_{max} / cm^{-1}** (thin film) 1685, 1355, 1168, 545; **^{1}H NMR (500 MHz, $CDCl_3$)** δ_H: 2.33-2.53 (8H, m), 2.78 (2H, m), 3.22 (3H, s), 3.34 (3H, s), 3.51 (2H, t, *J* 6.5 Hz), 3.67 (2H, t, *J* 6.4 Hz), 4.27 (2H, s), 4.34 (2H, s), 5.94 (1H, t, *J* 7.3, 1.1 Hz), 6.25 (1H, t, *J* 7.3 Hz), 7.33-7.36 (4H, m), 7.75-7.93 (4H, m); **^{13}C NMR (126 MHz, $CDCl_3$)** δ_C: 21.8, 21.9, 31.3, 32.2, 34.0, 35.1, 38.7, 42.6, 42.8, 45.8, 53.6, 128.3, 128.4, 129.9, 129.9, 132.0, 134.9, 135.2, 135.4, 135.4, 138.2, 145.2, 145.5, 168.3, 170.5; **HRMS** (ES^+) [$C_{14}H_{17}Cl_2NO_3S$] requires $[M+H]^+$ 350.0385, found 350.0384.

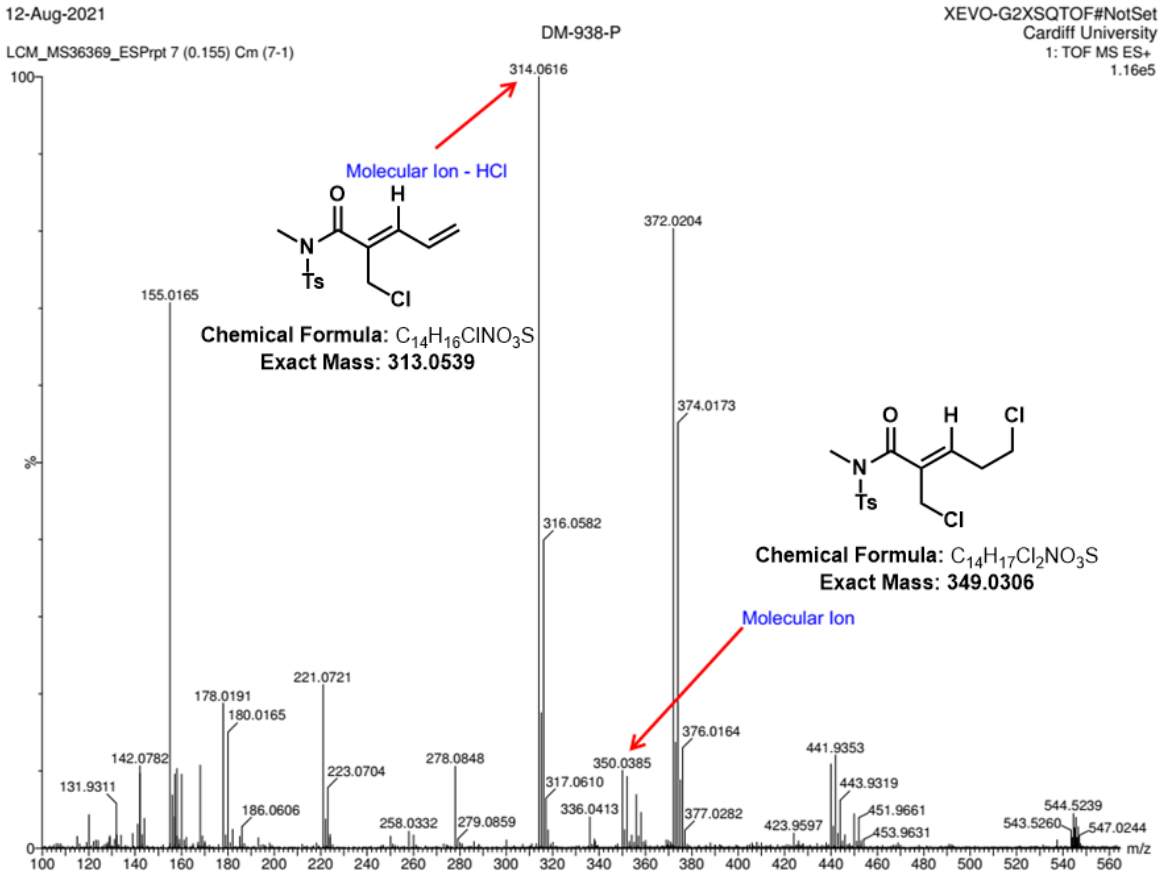



170.54
168.29
145.49
145.24
138.21
135.45
135.37
135.24
134.87
132.00
129.94
129.90
128.36
128.33
77.41
77.16
76.91
53.58
45.82
42.76
42.61
38.68
35.07
34.04
32.21
31.33
21.85
21.82
3000
2500
2000
1500
1000
500
0
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

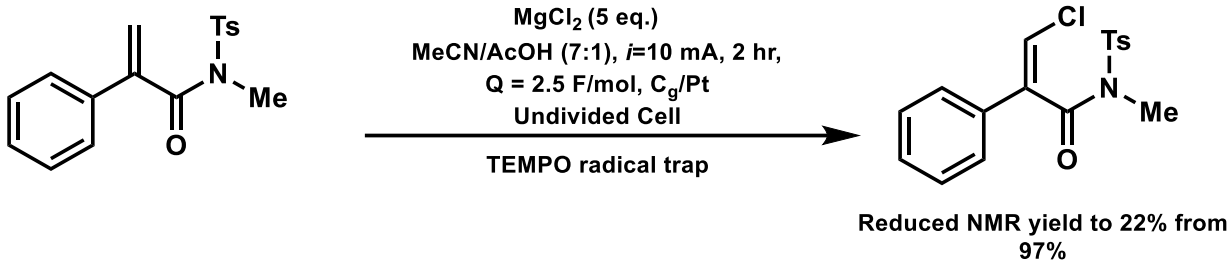
Proposed Mechanism:



Mass Spectrometry:



6.2.2 Tempo Trapping Experiment



Reduced NMR yield to 22% from 97%

7. References

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