Electronic Supplementary Material (ESI) for ChemComm.

SUPPORTING INFORMATION

A Gold-Catalysed Fully Intermolecular Oxidation and Sulfur-Ylide Formation Sequence on Ynamides

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General Experimental

All reactions were carried out under Ar in flame-dried glassware unless otherwise mentioned. The solvents used were purified using a Pure Solv-MD Solvent Purification System (alumina columns) from Innovative Technology and were transferred under Ar. Asynt DrySyn heating blocks on stirrer hotplates were employed with temperature control *via* external probe. Flash chromatography: Fluorochem silica gel 60 (43-63 μm). Thin layer chromatography (TLC): Macherey Nagel silica gel $60F_{254}$ analytical plates (plastic support) which were developed using standard visualizing agents: UV fluorescence (254 and 366 nm), phosphomolybdic acid /Δ, and potassium permanganate /Δ. IR: Perkin-Elmer Spectrum 100 FTIR spectrometer, only selected absorbencies (υ_{max}) are reported in cm^{-1}. MS and HRMS (EI): VG ProSpec or VG-ZabSpec at 70 eV. High resolution EI spectra were measured using perfluorokerosene (PFK) as an internal calibrant. MS and HRMS (ES): Micromass LCT using a methanol mobile phase. HRMS was obtained using a lock-mass to adjust the calibrated mass scale. MS data are reported as *m/z* (relative intensity). Commercially available compounds were purchased from Aldrich, Fluka, Acros, Strem, Alfa Aesar and used without further purification. NMR: Spectra were recorded on Bruker AVIII300 (^1H = 300 MHz, ^{13}C = 75.5 MHz), Bruker AVIII400 (^1H = 400 MHz, ^{13}C = 101 MHz) in the solvents indicated; $CDCl_3$ was purchased from Aldrich (no TMS) and Cambridge Isotope Laboratory (0.05% v/v TMS); Chemical shifts (δ) are given in ppm relative to TMS. In the absence of TMS, solvent signals were used as references and the chemical shifts converted to the TMS scale ($CDCl_3$: $\delta_C \equiv$ 77.0 ppm; residual $CHCl_3$ in $CDCl_3$: $\delta_H \equiv$ 7.26 ppm). Coupling constants (*J*) are reported in Hz. Multiplicity is denoted in ^1H NMR by: s (singlet), d (doublet), t (triplet), q (quadruplet), m (multiplet). 1D ^{13}C NMR spectra were recorded using the JMOD or PENDANT pulse sequences from the Bruker standard pulse program library. JMOD were combined with DEPT 135 to assign quaternary carbons.

Starting Materials

The following compounds were prepared following literature procedures:

_N_-Phenylmethanesulfonamide (A)

(51% yield).[1] Spectroscopic data were identical to those reported in literature.[2]

_N_-Phenyl-4-methylbenzenesulfonamide (B)

(97% yield).[3] Spectroscopic data were identical to those reported in literature.[2]

_N_-Benzylmethanesulfonamide (C)

(88% yield).[1] Spectroscopic data were identical to those reported in literature.[2]

_N_-Benzyl-4-methylbenzenesulfonamide (D)

(83% yield).[1] Spectroscopic data were identical to those reported in literature.[2]

1-Ethynyl-4-fluorobenzene (E)

(44% yield over 2 steps).[4] Spectroscopic data were identical to those reported in literature.[5]

Methyl-4-ethynylbenzoate (F)

(88% yield over 2 steps).[6] Spectroscopic data were identical to those reported in literature.[6]

1-Ethynyl-4-methoxybenzene (G)

(96% yield over 2 steps).[7] Spectroscopic data were identical to those reported in literature.[7]

(_E_)-But-1-en-3-yn-1-ylbenzene (H)

(34% yield over 2 steps).[8] Spectroscopic data were identical to those reported in literature.[9]

Allyl(phenyl)sulfide (2a)

(Quant. yield).[10] Spectroscopic data were identical to those reported in literature.[11]

Allyl(_p_-tolyl)sulfide (2b)

(Quant. yield).[10] Spectroscopic data were identical to those reported in literature.[12]

Allyl(_p_-bromophenyl)sulfide (2c)

(Quant. yield).[10] Spectroscopic data were identical to those reported in literature.[13]

Allyl(benzyl)sulfide (2d)

(97% yield). Spectroscopic data were identical to those reported in literature.[14]

Allyl(_n_-butyl)sulfide (2e)

(76% yield).[13] Spectroscopic data were identical to those reported in literature.[15]

Cinnamyl(phenyl)sulfide (2g)

(71% yield).[13] Spectroscopic data were identical to those reported in literature.[16]

2-Vinyltetrahydrothiophene (2h)

(70% yield over 2 steps).[17] Spectroscopic data were identical to those reported in literature.[16]

Methyl picolinate (I)

(97% yield).[18] Spectroscopic data were identical to those reported in literature.[19]

2-(Methoxycarbonyl)pyridine-1-oxide (3)

(97% yield).[20] Spectroscopic data were identical to those reported in literature.[21]

(*E*)-*N*-Phenyl-*N*-tosylhex-2-enamide (6)

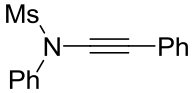
Spectroscopic data were identical to those reported in literature.[22]

Formation of Ynamides

General procedure 1 (GP1)

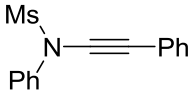
Following the method of Stahl,[23] $CuCl_2$ (0.2 eq), amide (5 eq) and Na_2CO_3 (2 eq) were added to a flame-dried 500 mL three-necked round-bottomed flask. The flask was purged with oxygen for 15 min and a solution of freshly distillated pyridine (2 eq) in dry toluene (0.2 M) was added. A balloon filled with oxygen was connected to the flask and the stirred mixture was heated at 70 °C. After 15 min, a solution of alkyne (1.0 eq) in dry toluene (0.2 M) was added by syringe pump over 4 h. The mixture was allowed to stir at 70 °C for another 4 h and was then cooled to rt. The reaction mixture was concentrated under reduced pressure and the residue was purified by flash chromatography to afford the desired product.

N-Phenyl-N-(phenylethynyl)methanesulfonamide (1a)



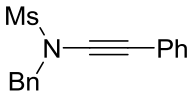
Following **GP1** using amide **A** (855 mg, 5 mmol) and phenylacetylene (0.11 mL, 1 mmol). After purification by flash chromatography [hexane:EtOAc (4:1)] *ynamide* **1a** was isolated as a white solid (238.5 mg, 88%). Spectroscopic data were identical to those reported in literature.[24]

N-Methyl-N-(phenylethynyl)methanesulfonamide (1b)



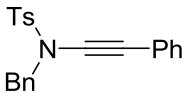
Following **GP1** using amide **A** (855 mg, 5 mmol) and phenylacetylene (0.11 mL, 1 mmol). After purification by flash chromatography [hexane:EtOAc (4:1)] *ynamide* **1a** was isolated as a white solid (238.5 mg, 88%). Spectroscopic data were identical to those reported in literature.[24,25]

N-Benzyl-N-phenylethynyl-methanesulfonamide (1c)



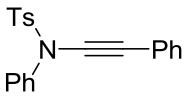
Following **GP1** using amide **C** (1.9 g, 10 mmol) and phenylacetylene (0.22 mL, 2 mmol). After purification by flash chromatography [hexane:EtOAc (4:1)] *ynamide* **1c** was isolated as a white solid (291 mg, 51%). Spectroscopic data were identical to those reported in literature.[24]

N-Benzyl-4-methyl-N-phenylethynyl-benzenesulfonamide (1d)



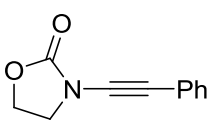
Following **GP1** using amide **D** (2.6 g, 10 mmol) and phenylacetylene (0.22 mL, 2 mmol). After purification by flash chromatography [hexane:EtOAc (4:1)] *ynamide* **1d** was isolated as a white solid (317.7 mg, 44%). Spectroscopic data were identical to those reported in literature.[24]

4-Methyl-N-phenyl-N-(phenylethynyl)benzenesulfonamide (1e)



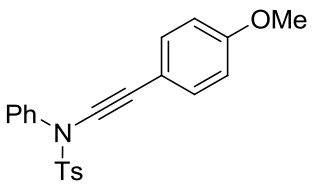
Following **GP1** using amide **B** (4.9 g, 20 mmol) and phenylacetylene (0.44 mL, 4 mmol). After purification by flash chromatography [hexane:EtOAc (4:1)] *ynamide* **1e** was isolated as a white solid (1.1 g, 82%). Spectroscopic data were identical to those reported in literature.[24]

3-(Phenylethynyl)oxazolidin-2-one (1f)



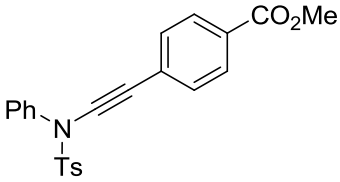
Following **GP1** using oxazolidinone (435 mg, 5 mmol) and phenylacetylene (0.11 mL, 1 mmol). After purification by flash chromatography [hexane:EtOAc (4:1)] *ynamide* **1f** was isolated as a white solid (153.3 mg, 82%). Spectroscopic data were identical to those reported in literature.[24]

N-((4-Methoxyphenyl)ethynyl)-4-methyl-N-phenylbenzenesulfonamide (1g)



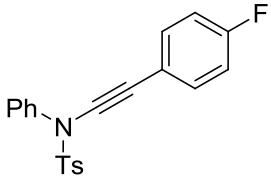
Following **GP1** using amide **B** (1.8 g, 7.5mmol) and alkyne **G** (200.0 mg, 1.5 mmol). After purification by flash chromatography [hexane:EtOAc (9:1)] *ynamide* **1g** was isolated as a colourless solid (463.7 mg, 82%); mp: 100-102 ºC; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.62 (d, *J* = 8.3 Hz, 2H), 7.38-7.25 (m, 9H), 6.84 (d, *J* = 8.9 Hz, 2H), 3.81 (s, 3H), 2.45 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 159.8, 145.0, 139.3, 133.6 (2C), 133.2, 129.6 (2C), 129.2 (2C), 128.4 (2C), 128.2, 126.3 (2C), 114.7, 114.1 (2C), 81.7, 70.4, 55.4, 21.8; IR (neat): ν = 3065, 2936, 2838, 2241, 1370, 1172; HR-MS (ES-TOF): *m/z*: calcd for $C_{22}H_{19}NO_3NaS$: 400.0983, found 400.0985 [*M*+*Na*].[26]

Methyl 4-((4-methyl-N-phenylphenylsulfonamido)ethynyl)benzoate (1h)



Following **GP1** using amide **B** (2.96 g, 12.0 mmol) and alkyne **F** (384.3 mg, 2.4 mmol). After purification by flash chromatography [hexane:EtOAc (4:1)] *ynamide* **1h** was isolated as a colourless solid (418.0 mg, 43%); mp: 96-98 ºC; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.96 (d, *J* = 8.5 Hz, 2H), 7.62 (d, *J* = 8.4 Hz, 2H), 7.42 (d, *J* = 8.5 Hz, 2H), 7.38-7.34 (m, 3H), 7.33-7.27 (m, 4H), 3.92 (s, 3H), 2.44 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 166.7, 145.4, 138.8, 133.2, 130.9 (2C), 129.8 (2C), 129.6 (2C), 129.4 (2C), 129.1, 128.6, 128.4 (2C), 127.8, 126.5 (2C), 86.3, 70.5, 52.3, 21.9; IR (neat): ν = 3071, 2923, 2853, 2234, 1717, 1371, 1170; HR-MS (ES-TOF): *m/z*: calcd for $C_{23}H_{19}NO_4NaS$: 428.0932, found 428.0927 [*M*+*Na*].

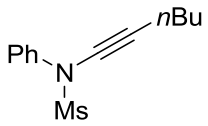
N-((4-Fluorophenyl)ethynyl)-4-methyl-N-phenylbenzenesulfonamide (1i)



Following **GP1** using amide **B** (547.4 g, 2.2 mmol) and alkyne **E** (53.2 mg, 0.44 mmol). After purification by flash chromatography [hexane:EtOAc (4:1)] *ynamide* **1i** was isolated as a colourless solid (58.5 mg, 18%); mp: 80-82 ºC; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.61 (d, *J* = 8.3 Hz, 2H), 7.41-7.27 (m, 9H), 7.00 (t, *J* = 8.8 Hz, 2H), 2.46 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 162.7 (d,

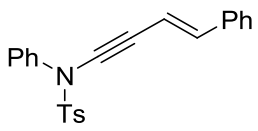
J = 249.7 Hz, 1C), 145.3, 139.2, 133.9, 133.8, 133.4, 129.8 (2C), 129.4 (2C), 128.6 (3C), 126.5 (2C), 118.9, 115.8 (d, *J* = 22.1 Hz, 2C), 82.3, 69.7, 22.0; IR (neat): ν = 3057, 2982, 2243, 1680, 1374, 1174; HR-MS (ES-TOF): *m/z*: calcd for $C_{21}H_{16}NO_2NaSF$: 388.0783, found 388.0776 [*M*+*Na*].

N-(Hex-1-ynyl)-N-phenylmethanesulfonamide (1j)



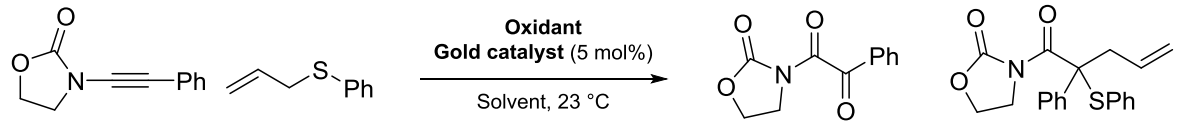
Following **GP1** using amide **A** (855 mg, 5.0 mmol) and hexyne (0.11 mL, 1.0 mmol). After purification by flash chromatography [hexane:EtOAc (4:1)] *ynamide* **1j** was isolated as a colourless solid (188.5 mg, 75%). Spectroscopic data were identical to those reported in literature.[22]

(E)-4-methyl-N-phenyl-N-(4-phenylbut-3-en-1-ynyl)benzenesulfonamide (1k)

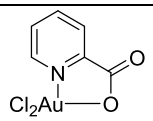
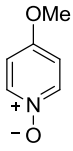
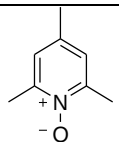
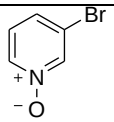
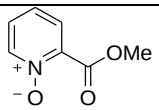
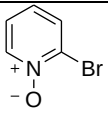


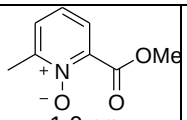
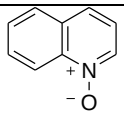
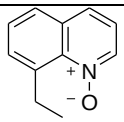
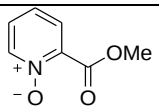
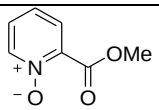
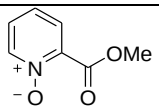
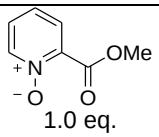
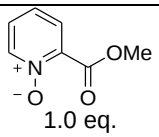
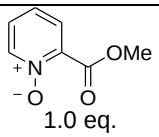
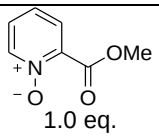
Following **GP1** using amide **B** (1.7 g, 7.0 mmol) and alkyne **H** (175.4 mg, 1.4 mmol). After purification by flash chromatography [hexane:EtOAc (4:1)] *ynamide* **1k** was isolated as a yellow solid (386.3 mg, 75%); mp: 105-107 ºC; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.61 (d, *J* = 8.3 Hz, 2H), 7.42-7.25 (m, 12H), 6.86 (d, *J* = 16.2 Hz, 1H), 6.27 (d, *J* = 16.2 Hz, 1H), 2.45 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 145.1, 140.1, 139.1, 136.5, 133.3, 129.7 (2C), 129.3 (2C), 128.9 (2C), 128.6, 128.4 (3C), 126.4 (2C), 126.3 (2C), 107.5, 85.1, 70.3, 21.8; IR (neat): ν = 3067, 2970, 2847, 2249, 1607, 1368, 1172; HR-MS (ES-TOF): *m/z*: calcd for $C_{23}H_{19}NO_2NaS$: 396.1034, found 396.1043 [*M*+*Na*].

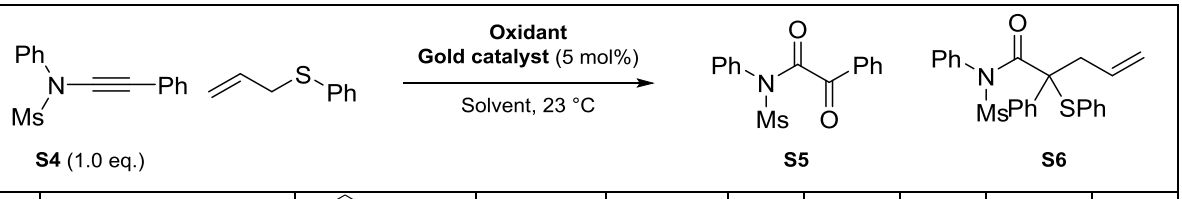
Study of Reaction Parameters



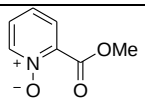
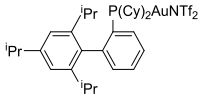
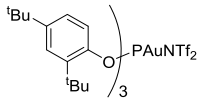
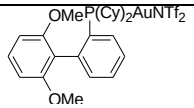
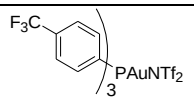
S1 (1.0 eq.) **S2** **S3**

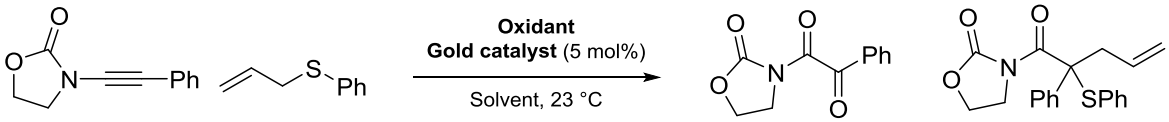
#	**Catalyst** (5 mol%)	**Oxidant**	**Solvent**	**Sulfide**	**T ºC**	**Time**	**S2**	**S3**	**S1**
1	$AuClPPh_3$ $AgOTf$	 1.0 eq.	CH_2Cl_2	1.0 eq.	23	22h	17%	10%	49%
2	$AuClPPh_3$ $AgSbF_6$	 1.0 eq.	CH_2Cl_2	1.0 eq.	23	22h	30%	28%	36%
3	$AuPPh_3NTf_2$	 1.0 eq.	CH_2Cl_2	1.0 eq.	23	22h	23%	24%	47%
4	IPrAuCl AgOTf	 1.0 eq.	CH_2Cl_2	1.0 eq.	23	22h	25%	-	38%
5		 1.0 eq.	CH_2Cl_2	1.0 eq.	23	24h	54%	-	-
6	$AuPPh_3NTf_2$	 1.0 eq.	CH_2Cl_2	1.0 eq.	23	17h	27%	20%	36%
7	$AuPPh_3NTf_2$	 1.0 eq.	CH_2Cl_2	1.0 eq.	23	24h	18%	38%	41%
8	$AuPPh_3NTf_2$	 1.0 eq.	CH_2Cl_2	1.0 eq.	23	24h	25%	36%	37%
9	$AuPPh_3NTf_2$	 1.0 eq.	CH_2Cl_2	1.0 eq.	23	24h	22%	39%	38%
10	$AuPPh_3NTf_2$	 1.0 eq.	CH_2Cl_2	1.0 eq.	23	24h	29%	35%	33%

11	$AuPPh_3NTf_2$	 1.0 eq.	CH_2Cl_2	1.0 eq.	23	24h	32%	14%	42%
12	$AuPPh_3NTf_2$	 1.0 eq.	CH_2Cl_2	1.0 eq.	23	24h	29%	15%	55%
13	$AuPPh_3NTf_2$	 1.0 eq.	CH_2Cl_2	1.0 eq.	23	24h	17%	24%	32%
14	$AuPPh_3NTf_2$	 1.0 eq.	THF	1.0 eq.	23	24h	30%	6%	46%
15	$AuPPh_3NTf_2$	 1.0 eq.	$PhCH_3$	1.0 eq.	23	24h	24%	10%	53%
16	$AuPPh_3NTf_2$	 1.0 eq.	CH_3CN	1.0 eq.	23	24h	31%	41%	25%
17	$AuPPh_3NTf_2$	 1.0 eq.	CH_3NO_2	1.0 eq.	23	24h	22%	40%	31%
18	$AuPPh_3NTf_2$	 1.0 eq.	DCE	1.0 eq.	70	24h	27%	35%	29%
19	$AuPPh_3NTf_2$	 1.0 eq.	CH_2Cl_2	2 eq.	23	24h	18%	49%	24%
20	$AuPPh_3NTf_2$	 1.0 eq.	CH_2Cl_2	1.2 eq.	23	24h	23%	46%	28%

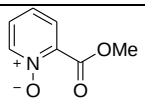
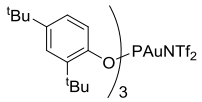
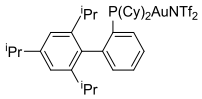
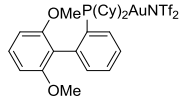
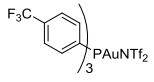
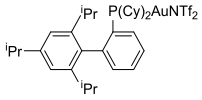


S4 (1.0 eq.) **S5** **S6**

#	Catalyst (5 mol%)		Solvent	Sulfide	T ºC	Time	S5	S6	S4
21		1.0 eq.	CH_2Cl_2	1.2 eq.	23	24h	N/D	37%	33%
22		1.0 eq.	CH_2Cl_2	1.2 eq.	23	24h	N/D	62%	12%
23	$AuPPh_3NTf_2$	1.0 eq.	CH_2Cl_2	1.2 eq.	23	24h	N/D	53%	32%
24	$IPrAuNTf_2$	1.0 eq.	CH_2Cl_2	1.2 eq.	23	24h	N/D	traces	54%
25		1.0 eq.	CH_2Cl_2	1.2 eq.	23	24h	N/D	49%	31%
26		1.0 eq.	CH_2Cl_2	1.2 eq.	23	24h	N/D	53%	37%



S1 (1.0 eq.) **S2** **S3**

#	Catalyst (5 mol%)		Solvent	Sulfide	T ºC	Time	S2	S3	S1
27	$AuPPh_3NTf_2$	1.0 eq.	CH_2Cl_2	1.2 eq.	23	24h	23%	44%	27%
28		1.0 eq.	CH_2Cl_2	1.2 eq.	23	24h	14%	20%	59%
29		1.0 eq.	CH_2Cl_2	1.2 eq.	23	24h	17%	58%	24%
30		1.0 eq.	CH_2Cl_2	1.2 eq.	23	24h	23%	48%	26%
31		1.0 eq.	CH_2Cl_2	1.2 eq.	23	24h	28%	19%	51%
32	$IPrAuNTf_2$	1.0 eq.	CH_2Cl_2	1.2 eq.	23	24h	49%	-	50%
33		1.2 eq.	CH_2Cl_2	1.2 eq.	23	24h	22%	59%	16%

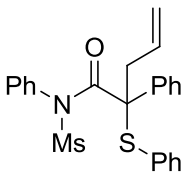
Yields determined from ^{1}H NMR spectra against the addition of a known quantity of internal standard. Overlap of resonances and co-elution prevented accurate calculation of **S5** yield.

Products of the Catalysis Reaction

General procedure 2 (GP2)

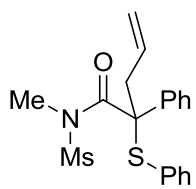
A solution of allyl sulfide **2** (1.2 eq) in CH_2Cl_2 (0.1 M) was added to a mixture of gold catalyst (5 mol% unless indicated in the main paper) and the corresponding ynamide **1** (1.0 eq). Pyridine *N*-oxide **3** (1.3 eq) was then added and the reaction mixture was stirred at room temperature until complete consumption of the starting material was observed (monitored by TLC). The mixture was filtered through a pad of silica and the filtrate was concentrated under reduced pressure. The residue was purified by column chromatography.

N-(Methylsulfonyl)-N,2-diphenyl-2-(phenylthio)pent-4-enamide (4aa)



Following **GP2** using *ynamide* **1a** (54.2 mg, 0.2 mmol) and *allyl sulfide* **2a** (36.0 mg, 0.24 mmol) for 2 h. After purification by chromatography [hexane:EtOAc (4:1)] thioether **4aa** was isolated as a colourless solid (62.4 mg, 71%); mp: 132-134 ºC; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.35-7.27 (m, 1H), 7.24-7.07 (m, 8H), 6.97 (t, *J* = 8.0 Hz, 2H), 6.89 (d, *J* = 7.2 Hz, 2H), 6.72 (d, *J* = 7.5 Hz, 2H), 5.80-5.99 (m, 1H), 5.14 (dd, *J* = 10.4, 1.6 Hz, 1H), 5.01 (dd, *J* = 17.2, 1.6 Hz, 1H), 3.50 (s, 3H), 2.61 (ddt, *J* = 15.8, 5.9, 1.7 Hz, 1H), 2.48 (ddd, *J* = 15.8, 7.1, 1.2 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 173.1, 138.8, 137.3 (2C), 133.5, 132.8, 132.0, 130.0, 129.7, 129.4, 128.8 (3C), 128.4 (2C), 128.0 (2C), 127.8, 127.2 (2C), 118.9, 66.2, 42.5, 39.4; IR (neat): ν = 3059, 2927, 1681, 1355, 1158; HR-MS (ES-TOF): *m/z*: calcd for $C_{24}H_{23}NO_3NaS_2$: 460.1017, found 460.1021 [*M*+*Na*].

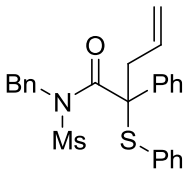
N-Methyl-2-phenyl-2-(phenylthio)-N-tosylpent-4-enamide (4ba)



Following **GP2** using *ynamide* **1b** (81.0 mg, 0.2 mmol) and *allyl sulfide* **2a** (39.4 mg, 0.24 mmol) for 6 h. After purification by chromatography [hexane:EtOAc (17:3)] thioether **4ba** was isolated as a colourless solid (57.3 mg, 76%); mp: 95-97 ºC; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.56-7.19 (m, 10H), 5.72 (ddt,

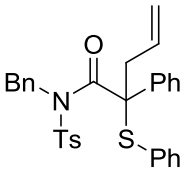
J = 17.2, 10.3, 6.9 Hz, 1H), 4.98 (dd, *J* = 10.3, 1.9 Hz, 1H), 4.80 (dd, *J* = 17.2, 1.9 Hz, 1H), 3.27 (s, 3H), 3.03 (s, 3H), 2.76 (d, *J* = 6.9 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 172.3, 137.8, 137.2 (2C), 132.7, 130.3, 129.3 (2C), 129.2, 129.1 (2C), 128.2, 126.4 (2C), 119.2, 64.0, 44.2, 42.3, 34.1; IR (neat): ν = 2947, 2869, 1700, 1679, 1360, 1168; HR-MS (ES-TOF): *m/z*: calcd for $C_{19}H_{21}NO_3NaS_2$: 398.0861, found 398.0870 [*M+Na*].

N-Benzyl-N-(methylsulfonyl)-2-phenyl-2-(phenylthio)pent-4-enamide (4ca)



Following **GP2** using *ynamide* **1c** (57.0 mg, 0.2 mmol) and *allyl sulfide* **2a** (36.0 mg, 0.24 mmol) for 5 h. After purification by chromatography [toluene:EtOAc (16:1)] thioether **4ca** was isolated as a colourless solid (52.6 mg, 58%); mp: 127-129 ºC; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.54-7.47 (m, 2H), 7.46-7.31 (m, 5H), 7.30-7.22 (m, 2H), 7.21-7.11 (m, 4H), 7.10-7.01 (m, 2H), 5.67 (ddt, *J* = 17.1, 10.3, 6.8 Hz, 1H), 4.96 (dd, *J* = 10.3, 1.9 Hz, 1H), 4.85 (d, *J* = 16.8 Hz, 1H), 4.75 (d, *J* = 17.1 Hz, 1H), 4.74 (d, *J* = 16.8 Hz, 1H), 3.19 (s, 3H), 2.85-2.69 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 173.8, 137.4, 136.8 (2C), 136.2, 132.4, 130.1, 129.5, 129.3 (2C), 129.0 (2C), 128.3, 128.2 (2C), 127.3, 127.1 (2C), 127.0 (2C), 119.2, 63.9, 51.0, 43.7, 43.2; IR (neat): ν = 3055, 3037, 2985, 1677, 1339, 1159; HR-MS (ES-TOF): *m/z*: calcd for $C_{25}H_{25}NO_3NaS_2$: 474.1174, found 474.1165 [*M+Na*].

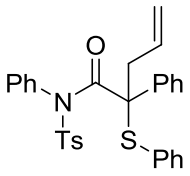
N-Benzyl-2-phenyl-2-(phenylthio)-N-tosylpent-4-enamide (4da)



Following **GP2** using *ynamide* **1d** (72.2 mg, 0.2 mmol) and *allyl sulfide* **2a** (36.0 mg, 0.24 mmol) for 5 h. After purification by chromatography [toluene:EtOAc (49:1)] thioether **4da** was isolated as a colourless solid (64.2 mg, 61%); mp: 134-136 ºC; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.76 (d, *J* = 8.4 Hz, 2H), 7.34-7.27 (m, 3H), 7.22-7.12 (m, 10H), 7.12-7.03 (m, 4H), 5.52 (ddt, *J* = 17.1, 10.3, 6.8 Hz, 1H), 5.00 (d, *J* = 17.1 Hz, 1H), 4.85 (dd, *J* = 10.3, 1.8 Hz, 1H), 4.72 (d, *J* = 17.1 Hz, 1H), 4.57 (dd, *J* = 17.1, 1.8 Hz, 1H), 2.59-2.44 (m, *2*H), 2.50 (s, 3H);^{13}C NMR (101 MHz, $CDCl_3$): δ = 172.1, 144.7, 137.5, 136.7, 136.6 (2C), 136.5, 132.2, 129.8 (2C), 129.6 (2C), 129.3 (2C),

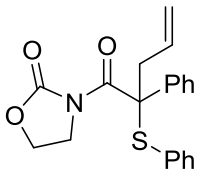
129.1 (2C), 129.0 (2C), 128.1, 128.0 (2C), 127.2 (2C), 127.0, 126.8 (2C), 118.9, 63.3, 52.0, 42.8, 21.8; IR (neat): ν = 3060, 3025, 2926, 2847, 1679, 1354, 1167; HR-MS (ES-TOF): *m/z*: calcd for $C_{31}H_{29}NO_3NaS_2$: 550.1487, found 550.1480 [*M+Na*].

N,2-Diphenyl-2-(phenylthio)-N-tosylpent-4-enamide (4ea)



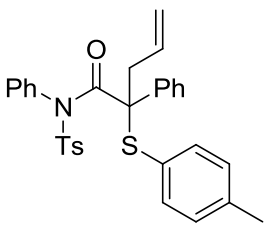
Following **GP2** using *ynamide* **1e** (69.4 mg, 0.2 mmol) and *allyl sulfide* **2a** (36.0 mg, 0.24 mmol) for 2 h. After purification by chromatography [hexane:EtOAc (4:1)] thioether **4ea** was isolated as a colourless solid (78.6 mg, 77%); mp: 137-139 ºC; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.98 (d, *J* = 8.2 Hz, 2H), 7.40 (d, *J* = 8.2 Hz, 2H), 7.29-7.22 (m, 2H), 7.21-7.13 (m, 2H), 7.10-6.94 (m, 9H), 6.78 (d, *J* = 7.5 Hz, 2H), 5.68-5.55 (m, 1H), 4.97 (d, *J* = 10.3 Hz, 1H), 4.83 (d, *J* = 17.1 Hz, 1H), 2.53 (s, 3H), 2.50 (dd, *J* = 15.8, 6.2 Hz, 1H), 2.37 (dd, *J* = 15.8, 6.8 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 171.3, 144.9, 138.8, 137.1 (2C), 136.6, 134.3, 132.6 (2C), 130.0 (3C), 129.5, 129.4 (3C), 129.2, 128.7 (2C), 128.4 (2C), 127.8 (2C), 127.6, 127.1 (2C), 118.6, 65.2, 40.1, 21.9; IR (neat): ν = 2970, 2922, 2854, 1683, 1359, 1164; HR-MS (ES-TOF): *m/z*: calcd for $C_{30}H_{27}NO_3NaS_2$: 536.1330, found 536.1332 [*M+Na*].

3-(2-Phenyl-2-(phenylthio)pent-4-enoyl)oxazolidin-2-one (4fa)



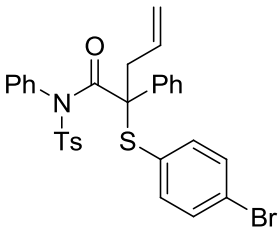
Following **GP2** using *ynamide* **1f** (18.7 mg, 0.1 mmol) and *allyl sulfide* **2a** (30.0 mg, 0.2 mmol), and **Au-II** (7 mol%) for 24 h. After purification by chromatography [hexane:EtOAc (17:3)] thioether **4fa** was isolated as a yellow oil (22.5 mg, 64%); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.39-7.21 (m, 6H), 7.20-7.12 (m, 4H), 6.06-5.78 (m, 1H), 5.05 (d, *J* = 10.2 Hz, 1H), 4.94 (d, *J* = 17.1 Hz, 1H), 4.39-4.15 (m, 3H), 3.87-3.67 (m, 1H), 3.10 (dd, *J* = 14.9, 8.2 Hz, 1H), 2.74 (ddt, *J* = 14.9, 5.7, 1.5 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 171.0, 151.5, 138.8, 137.6 (2C), 133.4, 130.1, 129.8, 128.9 (2C), 128.3 (2C), 127.6, 126.9 (2C), 118.8, 66.7, 62.1, 44.8, 40.0; IR (neat): ν = 3065, 2923, 2850, 1787, 1678, 1383, 1180; HR-MS (ES-TOF): *m/z*: calcd for $C_{20}H_{19}NO_3NaS$: 376.0983 found 376.0989 [*M+Na*].

N,2-Diphenyl-2-(p-tolylthio)-N-tosylpent-4-enamide (4eb)



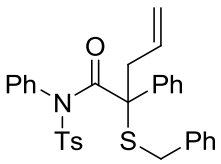
Following **GP2** using *ynamide* **1e** (69.4 mg, 0.2 mmol) and *allyl sulfide* **2b** (39.4 mg, 0.24 mmol) for 1 h. After purification by chromatography [hexane:EtOAc (17:3)] thioether **4eb** was isolated as a colourless solid (78.4 mg, 74%); mp: 163-165 ºC; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.98 (d, *J* = 8.2 Hz, 2H), 7.40 (d, *J* = 8.2 Hz, 2H), 7.22-7.12 (m, 2H), 7.11-7.03 (m, 2H), 6.95 (br s, 2H), 6.90-6.84 (m, 5H), 6.78 (d, *J* = 7.4 Hz, 2H), 6.61 (br s, 1H), 5.60 (ddt, *J* = 17.1, 10.4, 6.5 Hz, 1H), 4.95 (dd, *J* = 10.4, 1.8 Hz, 1H), 4.82 (dd, *J* = 17.1, 1.8 Hz, 1H), 2.53 (s, 3H), 2.51 (dd, *J* = 15.8, 6.2 Hz, 1H), 2.37 (dd, *J* = 15.8, 6.8 Hz, 1H), 2.27 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 171.3, 144.8, 139.7, 138.8, 137.1 (2C), 136.6 (2C), 134.3, 132.7, 130.0 (2C), 129.5 (2C), 129.4 (2C), 129.1 (2C), 128.3 (2C), 127.7 (2C), 127.5, 127.1 (2C), 126.2, 118.5, 64.9, 40.2, 21.9, 21.4; IR (neat): ν = 3066, 3022, 2979, 2927, 1683, 1359, 1164; HR-MS (ES-TOF): *m/z*: calcd for $C_{31}H_{29}NO_3NaS_2$: 550.1487, found 550.1479 [*M+Na*].

2-(4-Bromophenylthio)-N,2-diphenyl-N-tosylpent-4-enamide (4ec)



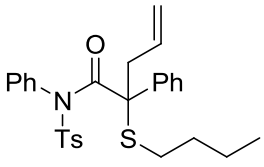
Following **GP2** using *ynamide* **1e** (69.4 mg, 0.2 mmol) and *allyl sulfide* **2c** (55.0 mg, 0.24 mmol) for 4 h. After purification by chromatography [hexane:EtOAc (17:3)] thioether **4ec** was isolated as a colourless solid (66.4 mg, 56%); mp: 154-156 ºC; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.96 (d, *J* = 8.4 Hz, 2H), 7.40 (d, *J* = 8.0 Hz, 2H), 7.23-7.13 (m, 4H), 7.08 (app. t, *J* = 7.5 Hz, 2H), 6.99 (app. t, *J* = 7.8 Hz, 2H), 6.81-6.70 (m, 6H), 5.62 (ddt, *J* = 17.0, 10.4, 6.4 Hz, 1H), 5.01 (dd, *J* = 10.4, 1.6 Hz, 1H), 4.88 (dd, *J* = 17.0, 1.6 Hz, 1H), 2.53 (s, 3H), 2.47 (dd, *J* = 15.9, 6.1 Hz, 1H), 2.36 (dd, *J* = 15.9, 6.8 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 171.0, 145.0, 138.6, 138.5 (2C), 136.4, 134.0, 132.3 (2C), 131.8 (2C), 129.9 (2C), 129.4 (2C), 129.3, 129.2, 128.4 (2C), 127.9 (2C), 127.8 (2C), 127.1 (2C), 124.3, 118.9, 65.8, 39.6, 21.9; IR (neat): ν = 3061, 2923, 2853, 1681, 1359, 1164; HR-MS (ES-TOF): *m/z*: calcd for $C_{30}H_{26}NO_3NaS_2Br$: 614.0435, found 614.0427 [*M+Na*].

2-(Benzylthio)-N,2-diphenyl-N-tosylpent-4-enamide (4ed)



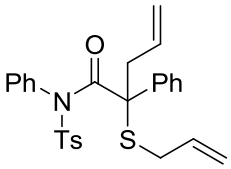
Following **GP2** using *ynamide* **1e** (69.4 mg, 0.2 mmol) and *allyl sulfide* **2d** (39.4 mg, 0.24 mmol) for 24 h. After purification by chromatography [hexane:EtOAc (17:3)] thioether **4ed** was isolated as a colourless solid (57.4 mg, 55%); mp: 124-126 ºC; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.95 (d, *J* = 8.2 Hz, 2H), 7.38 (d, *J* = 8.2 Hz, 2H), 7.32-7.23 (m, 4H), 7.18-7.00 (m, 6H), 6.98-6.84 (m, 3H), 6.82 (dd, *J* = 8.2, 1.2 Hz, 2H), 5.49-5.22 (m, 1H), 4.89 (d, *J* = 16.6 Hz, 1H), 4.82 (dd, *J* = 10.7, 1.5 Hz, 1H), 3.55 (d, *J* = 11.1 Hz, 1H), 3.44 (d, *J* = 11.1 Hz, 1H), 3.03 (dd, *J* = 15.3, 7.7 Hz, 1H), 2.77 (dd, *J* = 15.3, 5.9 Hz, 1H), 2.48 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 171.6, 144.9, 138.3, 136.8, 136.3, 134.5, 132.5 (3C), 129.8 (2C), 129.6 (2C), 129.5 (2C), 129.1, 128.8 (2C), 128.5 (2C), 127.8 (2C), 127.6, 127.5, 126.9 (2C), 118.4, 62.7, 42.1, 33.8, 21.9; IR (neat): ν = 3063, 3028, 2920, 1677, 1359, 1164; HR-MS (ES-TOF): *m/z*: calcd for $C_{31}H_{29}NO_3NaS_2$: 550.1487, found 550.1488 [*M*+*Na*].

2-(Butylthio)-N,2-diphenyl-N-tosylpent-4-enamide (4ee)



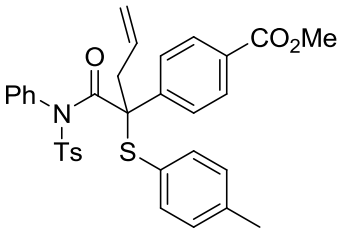
Following **GP2** using *ynamide* **1e** (69.4 mg, 0.2 mmol) and *allyl sulfide* **2e** (31.3 mg, 0.24 mmol) for 4.5 h. After purification by chromatography [hexane:EtOAc (17:3)] thioether **4ee** was isolated as a yellow oil (60.1 mg, 61%); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.94 (d, *J* = 8.2 Hz, 2H), 7.34 (d, *J* = 8.2 Hz, 2H), 7.42-7.17 (m, 5H), 6.97 (br s, 3H), 6.83 (dd, *J* = 8.2, 1.4 Hz, 2H), 5.43-5.21 (m, 1H), 4.85 (d, *J* = 15.9 Hz, 1H), 4.84 (dd, *J* = 11.9, 1.8 Hz, 1H), 2.95 (dd, *J* = 15.3, 7.5 Hz, 1H), 2.74 (dd, *J* = 15.3, 6.1 Hz, 1H), 2.49 (s, 3H), 2.33 (dt, *J* = 11.0, 7.3 Hz, 1H), 2.22 (dt, *J* = 11.0, 7.3 Hz, 1H), 1.53-1.41 (m, 2H), 1.36-1.24 (m, 2H), 0.88 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 171.7, 138.4, 136.8, 134.4, 132.6, 132.4 (3C), 129.7 (2C), 129.3 (2C), 128.9, 128.3 (2C), 127.6 (2C), 127.3, 126.8 (2C), 118.1, 61.4, 42.2, 30.6, 28.2, 22.4, 21.8, 13.8; IR (neat): ν = 3069, 2958, 2930, 2872, 1678, 1360, 1165; HR-MS (ES-TOF): *m/z*: calcd for $C_{28}H_{31}NO_3NaS_2$: 516.1643, found 516.1635 [*M*+*Na*].

2-(Allylthio)-N,2-diphenyl-N-tosylpent-4-enamide (4ef)



Following **GP2** using *ynamide* **1e** (69.4 mg, 0.2 mmol) and *allyl sulfide* **2f** (27.4 mg, 0.24 mmol) for 6 h. After purification by chromatography [hexane:EtOAc (17:3)] thioether **4ef** was isolated as a yellow oil (64.8 mg, 68%); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.92 (d, *J* = 8.2 Hz, 2H), 7.36 (d, *J* = 8.2 Hz, 2H), 7.21-7.01 (m, 5H), 7.01-6.87 (m, 3H), 6.81 (dd, *J* = 8.2, 1.2 Hz, 2H), 5.66 (ddt, *J* = 17.0, 9.9, 7.1 Hz, 1H), 5.45-5.27 (m, 1H), 5.10 (dd, *J* = 17.0, 1.3 Hz, 1H), 5.03 (d, *J* = 9.9 Hz, 1H), 4.85-4.81 (m, 2H), 2.98 (dd, *J* = 12.1, 7.2 Hz, 1H), 2.92 (dd, *J* = 15.3, 7.5 Hz, 1H), 2.89 (dd, *J*-= 12.1, 7.5 Hz, 1H), 2.75 (dd, *J* = 15.3, 6.1 Hz, 1H), 2.48 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 171.6, 144.8, 138.2, 136.6, 134.3, 132.7, 132.4 (3C), 129.6 (2C), 129.3 (2C), 129.0, 128.4 (2C), 127.7 (2C), 127.4, 126.8 (2C), 118.6, 118.3, 62.2, 42.0, 32.1, 21.8; IR (neat): ν = 3070, 2924, 2860, 1678, 1359, 1164; HR-MS (ES-TOF): *m/z*: calcd for $C_{27}H_{27}NO_3NaS_2$: 500.1330, found 500.1327 [*M+Na*].

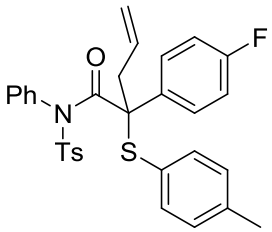
Methyl-4-(1-(4-methyl-N-phenylphenylsulfonamido)-1-oxo-2-(p-tolylthio)pent-4-en-2-yl)benzoate (4hb)



Following **GP2** using *ynamide* **1h** (81.0 mg, 0.2 mmol) and *allyl sulfide* **2b** (39.4 mg, 0.24 mmol) for 9 h. After purification by chromatography [hexane:EtOAc (17:3)] thioether **4hb** was isolated as a colourless solid (70.8 mg, 61%); mp: 193-195 ºC; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.96 (d, *J* = 8.4 Hz, 2H), 7.73 (d, *J* = 8.5 Hz, 2H), 7.40 (d, *J* = 8.5 Hz, 2H), 7.18 (t, *J* = 7.4 Hz, 1H), 7.08-6.92 (m, 3H), 6.91-6.79 (m, 7H), 5.61 (ddt, *J* = 17.1, 10.4, 6.5 Hz, 1H), 4.96 (dd, *J* = 10.4, 1.6 Hz, 1H), 4.83 (dd, *J* = 17.1, 1.6 Hz, 1H), 3.94 (s, 3H), 2.53 (s, 3H), 2.48 (dd, *J* = 15.8, 6.6 Hz, 1H), 2.39 (dd, *J* = 15.8, 6.6 Hz, 1H), 2.27 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 170.6, 166.7, 145.0, 144.1, 140,1, 137.1 (2C), 136.4, 134.0, 132.7 (2C), 132.2, 130.0 (2C), 129.7 (2C), 129.5 (2C), 129.4 (3C), 129.1, 127.9 (2C), 127.2 (2C), 125.8, 118.0, 65.0, 52.4, 40.0, 21.9, 21.4; IR (neat): ν = 3075, 2985,

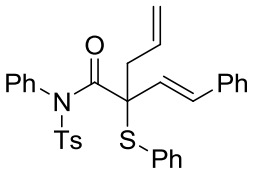
2953, 1720, 1684, 1361, 1164; HR-MS (ES-TOF): *m/z*: calcd for $C_{33}H_{31}NO_5NaS_2$: 608.1541, found 608.1543 [*M+Na*].

2-(4-Fluorophenyl)-N-phenyl-2-(p-tolylthio)-N-tosylpent-4-enamide (4ib)



Following **GP2** using *ynamide* **1i** (47.0 mg, 0.13 mmol) and *allyl sulfide* **2b** (25.3 mg, 0.15 mmol) for 9 h. After purification by chromatography [hexane:EtOAc (17:3)] thioether **4ib** was isolated as a colourless solid (40.4 mg, 57%); mp: 174-176 ºC; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.96 (d, *J* = 8.3 Hz, 2H), 7.40 (d, *J* = 8.3 Hz, 2H), 7.21 (t, *J* = 7.2 Hz, 1H), 7.05 (brd, 2H), 7.00-6.73 (m, 10H), 5.60 (ddt, *J* = 17.1, 10.4, 6.5 Hz, 1H), 4.96 (dd, *J* = 10.4, 1.7 Hz, 1H), 4.83 (dd, *J* = 17.1, 1.7 Hz, 1H), 2.53 (s, 3H), 2.46 (dd, *J* = 15.7, 6.3 Hz, 1H), 2.36 (dd, *J* = 15.7, 6.7 Hz, 1H), 2.28 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 171.1, 162.1 (d, *J* = 248.0 Hz, 1C), 144.9, 139.9, 137.1 (2C), 136.5, 134.8, 134.4, 132.4 (2C), 130.0 (2C), 129.6 (2C), 129.4 (2C), 129.3, 129.2, 128.8 (d, *J* = 8.1 Hz, 2C), 127.9 (2C), 126.1, 118.8, 115.2 (d, *J* = 21.5 Hz, 2C), 64.4, 40.2, 21.9, 21.4; ^{19}F-NMR (282 MHz, $CDCl_3$): δ = -114.3 (ddd, *J* = 13.6, 7.6, 6.6 Hz, 1F); IR (neat): ν = 3072, 2985, 2927, 1683, 1360, 1165; HR-MS (ES-TOF): *m/z*: calcd for $C_{31}H_{28}NO_3NaS_2F$: 568.1392, found 568.1378 [*M+Na*].

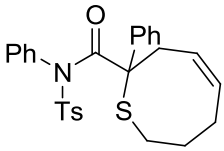
(E)-N-Phenyl-2-(phenylthio)-2-styryl-N-tosylpent-4-enamide (4ka)



Following **GP2** using *ynamide* **1k** (74.6 mg, 0.2 mmol) and *allyl sulfide* **2a** (36.0 mg, 0.24 mmol) for 3 h. After purification by chromatography [hexane:EtOAc (17:3)] thioether **4ka** was isolated as a colourless solid (56.7 mg, 53%); mp: 129-131 ºC; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.95 (d, *J* = 8.3 Hz, 2H), 7.37 (d, *J* = 8.3 Hz, 2H), 7.34-7.27 (m, 3H), 7.25-7.19 (m, 3H), 7.19-7.10 (m, 7H), 6.97 (dd, *J* = 7.4, 2.0 Hz, 2H), 5.85 (d, *J* = 16.2 Hz, 1H), 5.80-5.73 (m, 1H), 5.69 (d, *J* = 16.2 Hz, 1H), 5.06 (dd, *J* = 10.4, 1.4 Hz, 1H), 4.96 (dd, *J* = 17.2, 1.5 Hz, 1H), 2.51 (s, 3H), 2.47 (dd, *J* = 15.2, 6.0 Hz, 1H), 2.30 (dd, *J* = 15.2, 7.4 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 170.4, 144.9, 137.7 (2C), 136.3, 136.2, 135.2, 133.0, 132.6 (2C), 130.3, 130.1 (2C), 129.9, 129.8,

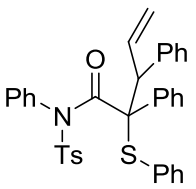
129.7, 129.4 (2C), 128.7 (2C), 128.5 (2C), 128.4 (2C), 127.9, 127.3, 126.6 (2C),118.9, 62.3, 40.5, 21.9; IR (neat): ν = 3059, 2923, 2852, 1686, 1362, 1166; HR-MS (ES-TOF): *m/z*: calcd for $C_{32}H_{29}NO_3NaS_2$: 562.1487, found 562.1481 [*M+Na*].

(Z)-N,2-Diphenyl-N-tosyl-3,6,7,8-tetrahydro-2H-thiocine-2-carboxamide (4eg)



Following **GP2** using *ynamide* **1e** (69.4 mg, 0.2 mmol) and *allyl sulfide* **2g** (27.4 mg, 0.24 mmol) for 8 h. After purification by chromatography [hexane:EtOAc (17:3)] product **4eg** was isolated as a colourless solid (69.5 mg, 65%); mp: 174-176 ºC; ^{1}H NMR (300 MHz, $CDCl_3$): δ =7.88 (d, *J* = 8.2 Hz, 2H), 7.34 (d, *J* = 8.2 Hz, 2H), 7.20-7.06 (m, 2H), 6.92-6.87 (m, 5H), 6.71 (br s, 1H), 5.73 (dd, *J* = 18.4, 8.2 Hz, 1H), 5.52-5.42 (br s, 1H), 3.17 (br s, 1H), 2.72 (br s, 3H), 2.47 (s, 3H), 2.22 (br s, 2H), 1.86 (br s, 1H), 1.59 (br s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 172.4, 144.5, 138.8, 136.6, 134.7, 132.9, 132.4 (2C), 124.4 (2C), 129.3 (2C), 128.9, 128.4 (2C), 127.6 (2C), 127.5, 126.8 (2C), 126.5, 63.9, 38.9, 30.9, 29.5, 25.8, 21.8; IR (neat): ν = 2923, 2853, 1677, 1360, 1164; HR-MS (ES-TOF): *m/z*: calcd for $C_{27}H_{27}NO_3NaS_2$: 500.1330, found 500.1335 [*M+Na*].

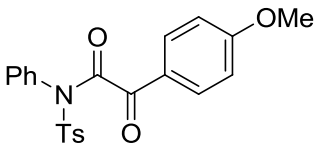
N,2,3-Triphenyl-2-(phenylthio)-N-tosylpent-4-enamide (4eh)



Following **GP2** using *ynamide* **1e** (69.4 mg, 0.2 mmol) and *allyl sulfide* **2h** (54.2 mg, 0.24 mmol) for 24 h. After purification by chromatography [hexane:EtOAc (17:3)] thioether **4eh** was isolated as a colourless solid (70.7 mg, 60%) and a 10.1:1 mixture of two diastereoisomers; mp: 170-172 ºC; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.01 (d, *J* = 8.3 Hz, 2H), 7.62-7.32 (m, 4H), 7.31-7.14 (m, 6H), 7.13-6.99 (m, 5H), 6.95 (t, *J* = 7.4 Hz, 2H), 6.84-6.52 (m, 5H), 5.93 (dt, *J* = 17.1, 9.9 Hz, 1H), 4.99 (d, *J* = 10.3 Hz, 1H), 4.60 (d, *J* = 17.1 Hz, 1H), 4.15 (d, *J* = 9.4 Hz, 1H), 2.56 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 170.1, 144.6, 141.3, 137.2, 136.8, 136.1 (2C), 134.7, 133.6, 133.4 (2C), 132.0 (2C), 130.2 (3C), 130.0, 129.4, 129.2 (2C), 128.7 (4C), 128.2, 127.2 (4C), 126.8 (2C), 126.3, 117.2, 66.1, 53.7, 21.9; IR (neat): ν = 3060, 3034, 2964, 2925, 2853,

1686, 1360, 1162; HR-MS (ES-TOF): *m/z*: calcd for $C_{36}H_{31}NO_3NaS_2$: 612.1643, found 612.1632 [*M*+*Na*].

2-(4-Methoxyphenyl)-2-oxo-N-phenyl-N-tosylacetamide (5)



Following **GP2** using *ynamide* **1g** (75.4 mg, 0.2 mmol) and *allyl sulfide* **1b** (39.4 mg, 0.24 mmol) for 24 h. After purification by chromatography [hexane:EtOAc (17:3)] keto imide **5** was isolated as a colourless solid (44.2 mg, 54%); mp: 148-150 ºC; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.88 (d, *J* = 8.9 Hz, 2H), 7.79 (d, *J* = 8.4 Hz, 2H), 7.49-7.29 (m, 5H), 7.13 (d, *J* = 6.8 Hz, 2H), 6.98 (d, *J* = 8.9 Hz, 2H), 3.89 (s, 3H), 2.47 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): 186.5, 167.1, 165.0, 146.0, 134.6, 133.9, 132.3 (2C), 130.9 (2C), 130.4, 130.0 (2C), 129.6 (2C), 129.3 (2C), 126.0, 114.6 (2C), 55.9, 22.0; IR (neat): ν = 3980, 2945, 2845, 1692, 1669, 1368, 1169; HR-MS (ES-TOF): *m/z*: calcd for $C_{22}H_{19}NO_5NaS$: 432.0882, found 432.0879 [*M*+*Na*].

Crystal structure of 4eh

Crystal Data for 4eh: $C_{36}H_{31}NO_3S_2$, *M* = 589.74, Monoclinic, *a* = 16.0175(3), *b* = 9.6290(2), *c* = 19.5279(5) Å, β = 98.570(1), *U*= 2978.2(1) Å^3, T = 120(2) K, space group $P2_1/c$, *Z* = 4, 34108 reflections measured, 6813 unique (R_{int} = 0.0607) which were used in all calculations. The final *R*1 was 0.0458 ($I>2\sigma(I)$) and *wR*(F_2) was 0.1150 (all data).

The dataset was measured on a Bruker KappaCCD diffractometer at the window of a Bruker FR591 rotating anode ($\lambda_{Mo\text{-}K\alpha}$ = 0.71073 Å). The data collection was driven by COLLECT[27] and processed by DENZO.[28] An absorption correction was applied using SADABS.[29] The structure was solved using ShelXS-97[30] and refined by a full-matrix least-squares procedure on F^2 in ShelXL-97.[30] All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were added at calculated positions and refined by use of a riding model with isotropic displacement parameters based on the equivalent isotropic displacement parameter (U_{eq}) of the parent atom. Figures were produced using OLEX2.[31] The CIF has been deposited with the CCDC and has been given the deposition number 984457.

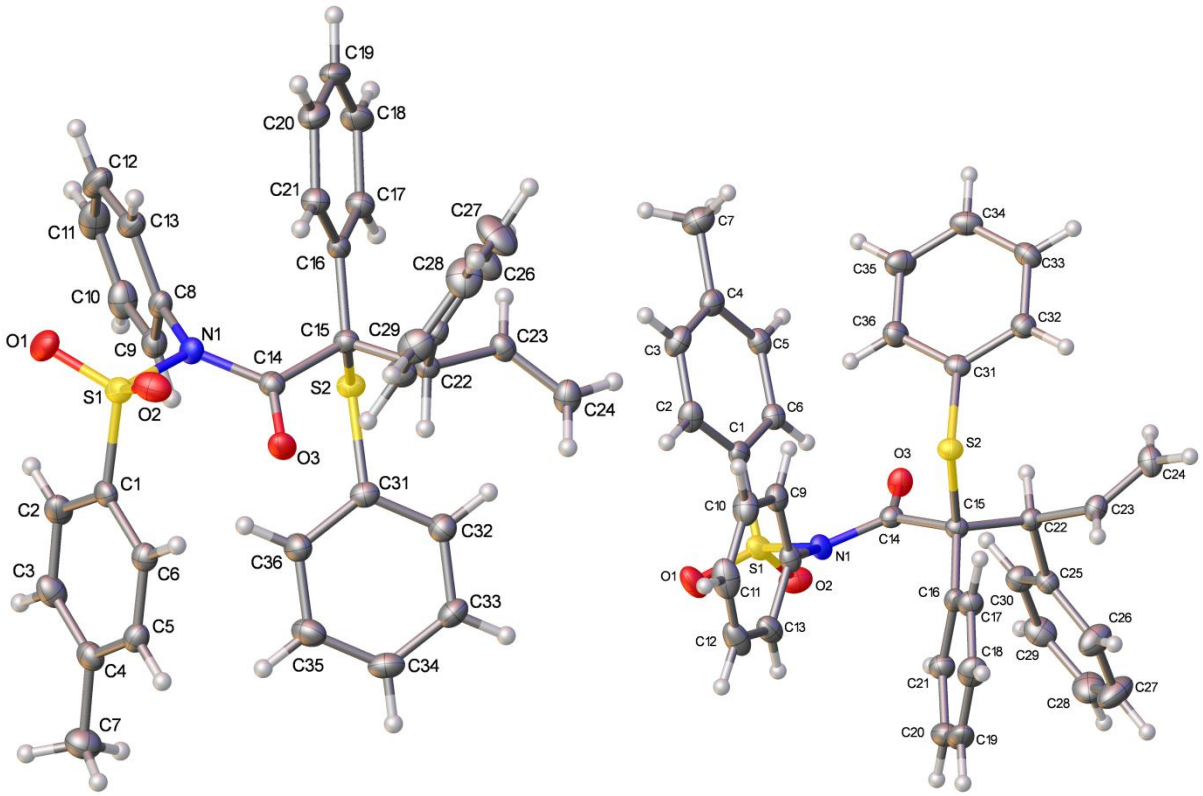


Figure S1 Alternative views of the crystal structure of MDS_242 with ellipsoids drawn at the 50% probability level.

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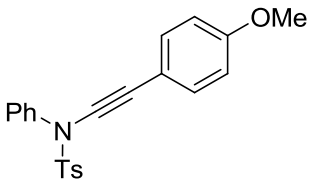
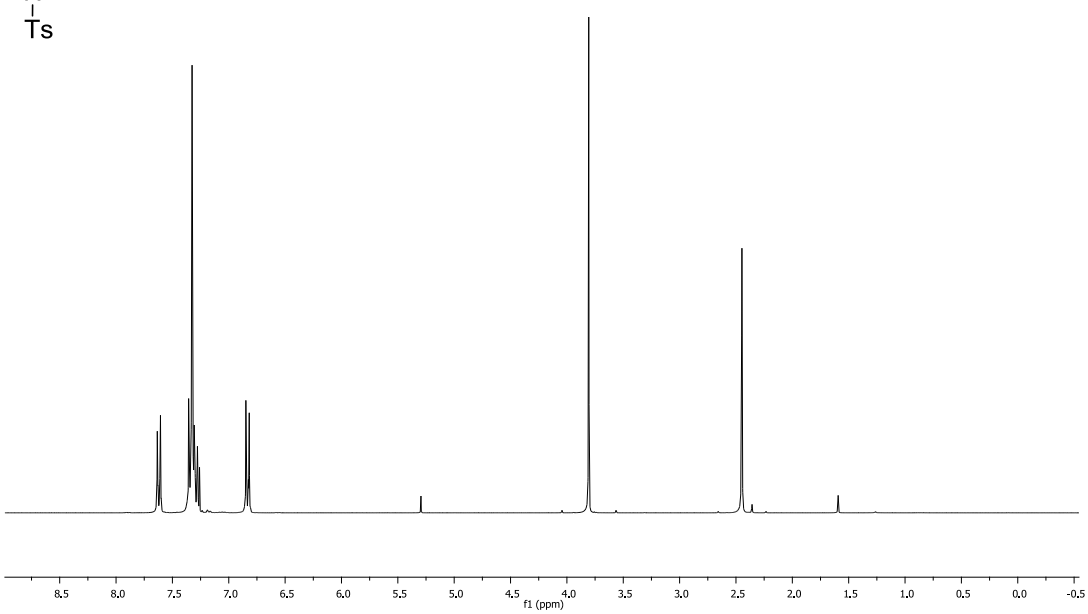
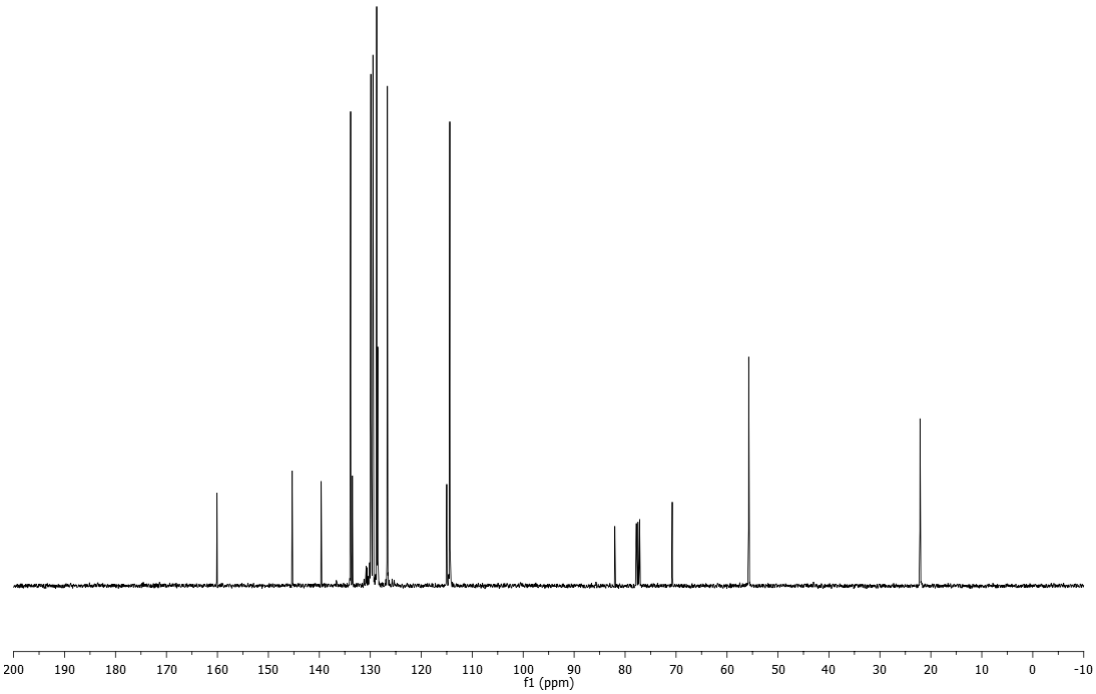
^{1}H and ^{13}C NMR Spectra of New Substrates

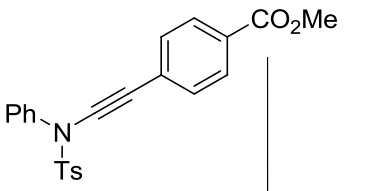
Compound 1g

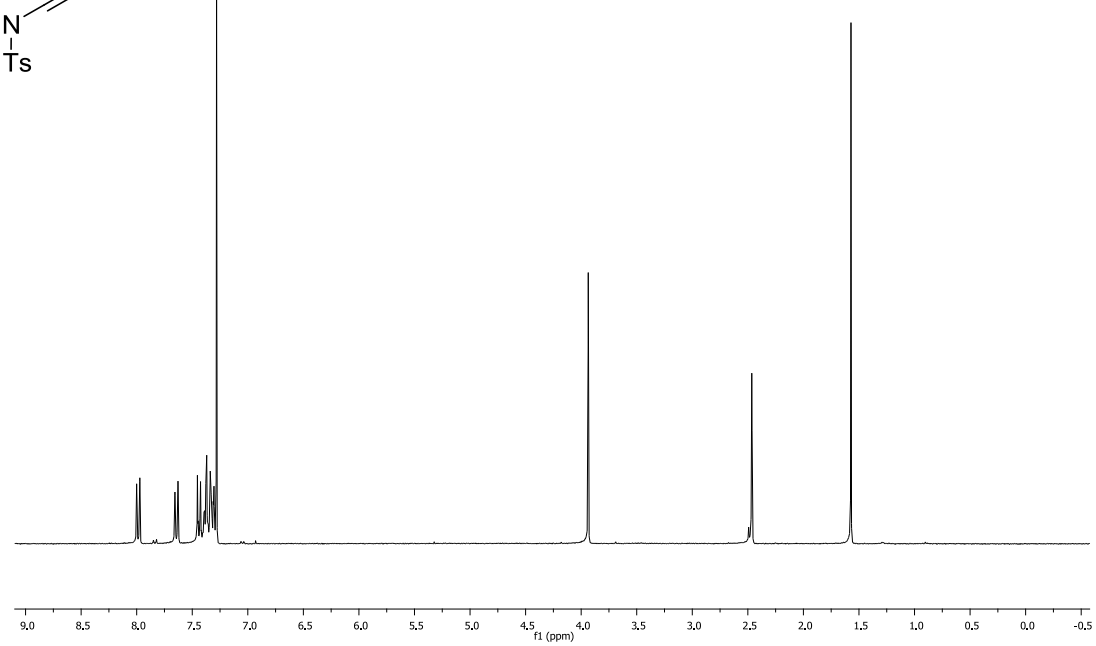


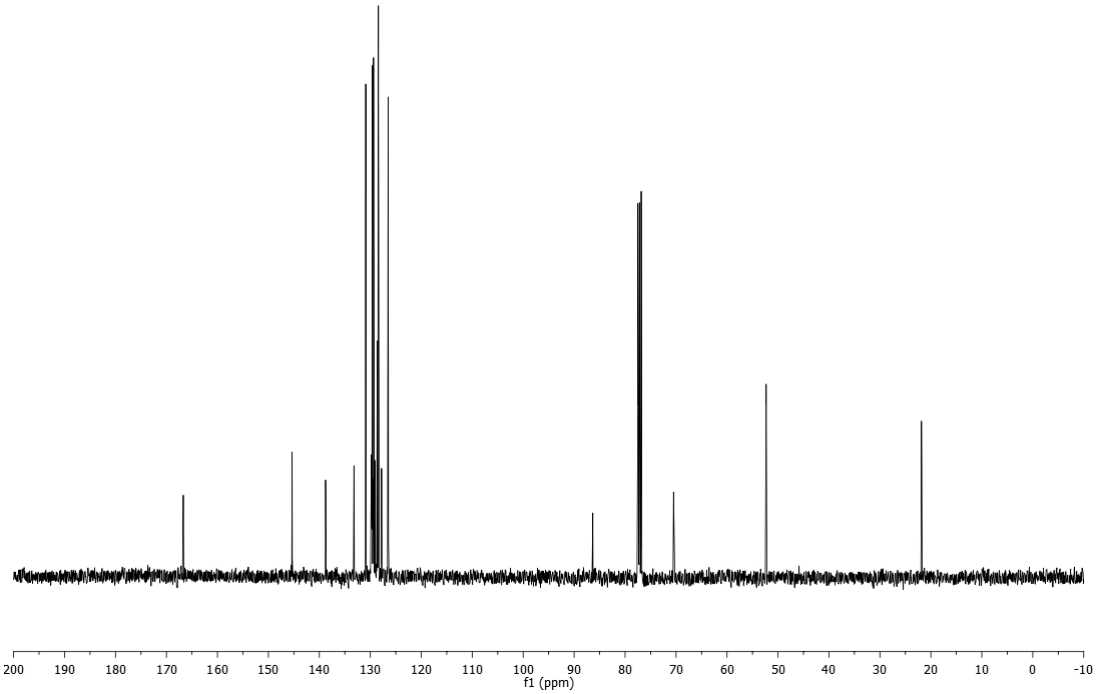




Compound 1h


CO2Me
Ph
N
Ts


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
-0.5
f1 (ppm)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190
180
170
160
150
140
130
120
110
100
90
80
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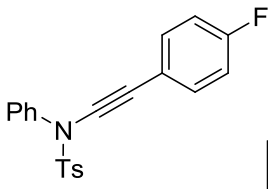
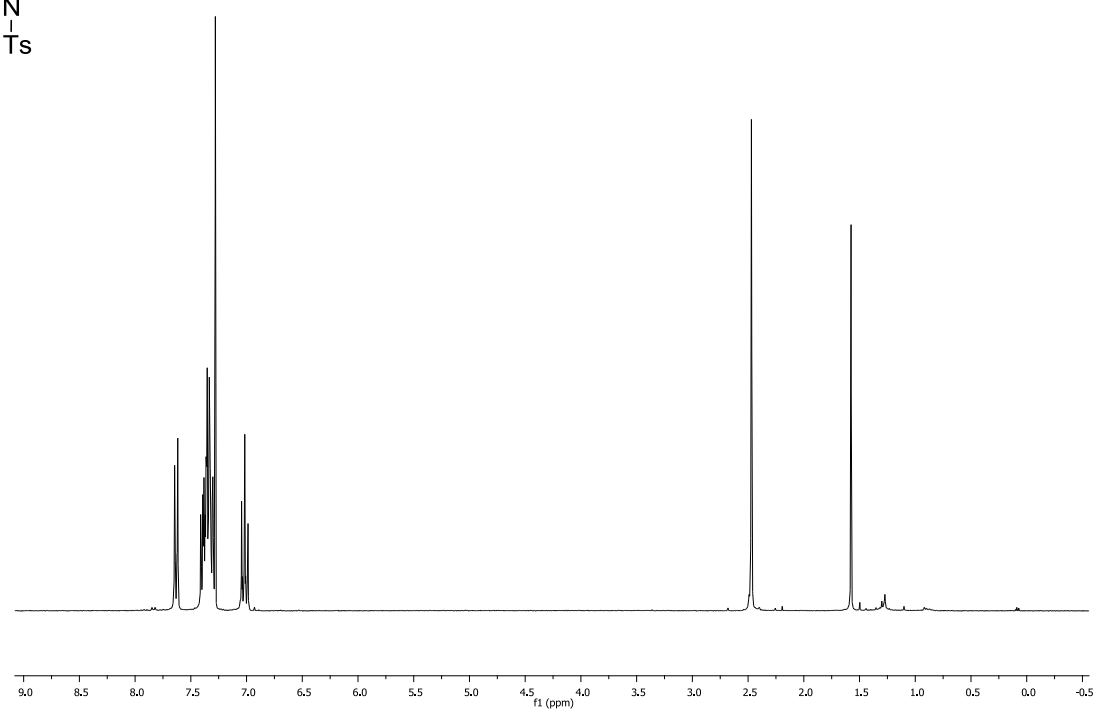
60
50
40
30
20
10
0
-10
f1 (ppm)

Compound 1i


F
Ph
N
Ts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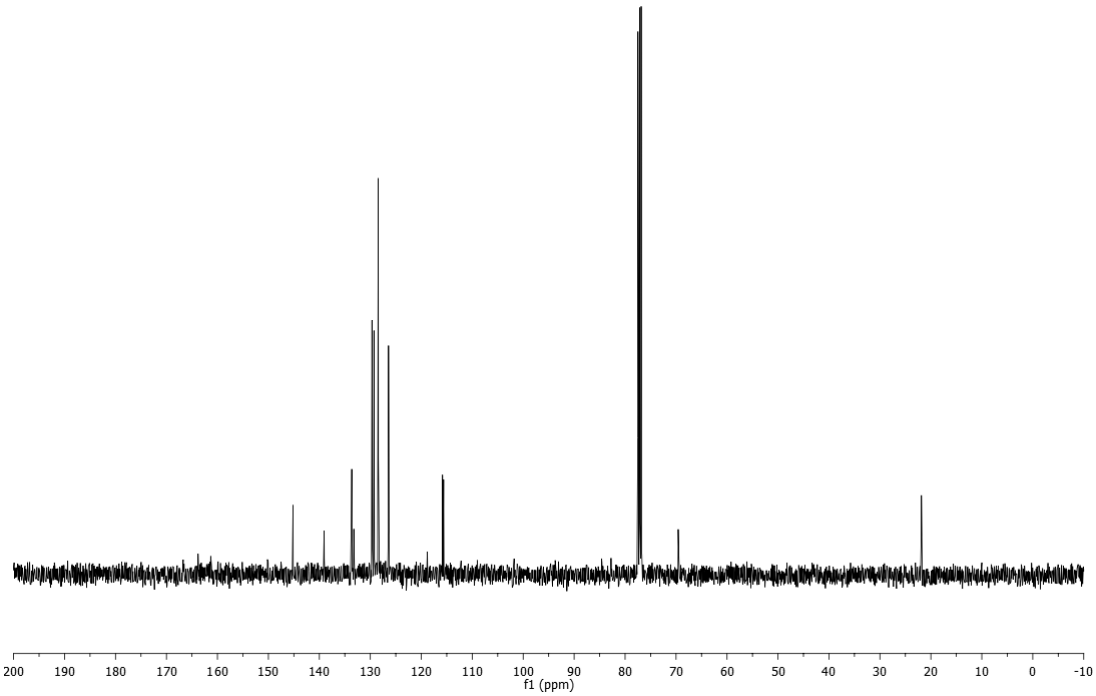
f1 (ppm)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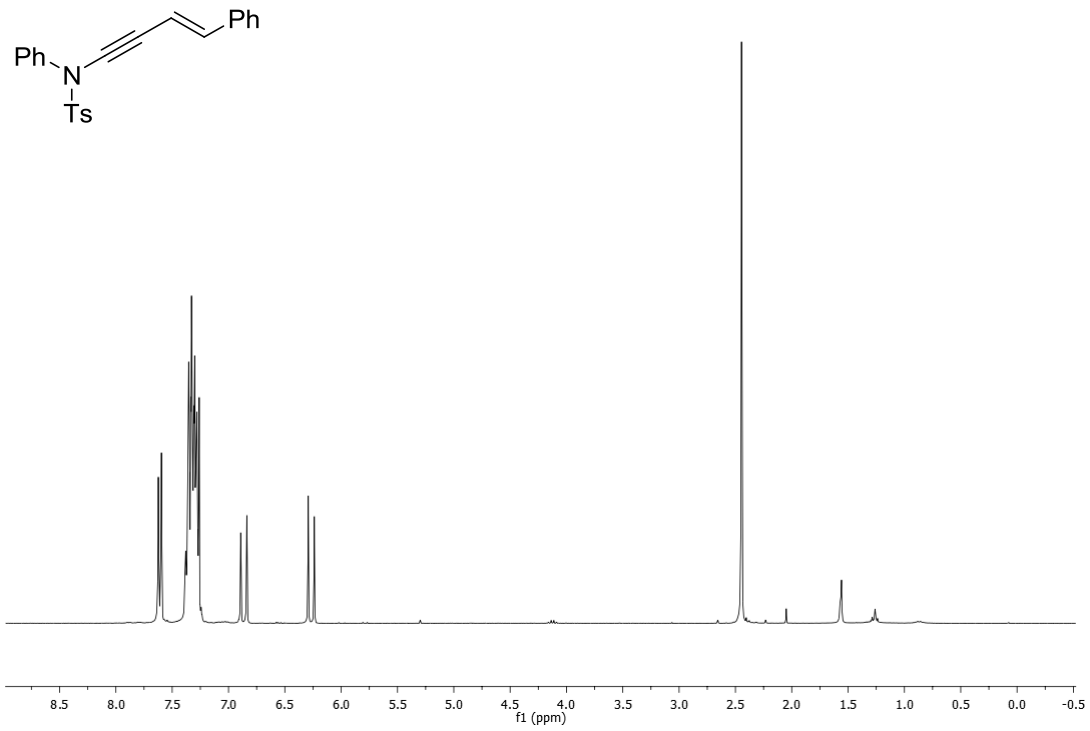
f1 (ppm)

Compound 1k


Ph
Ph
N
Ts
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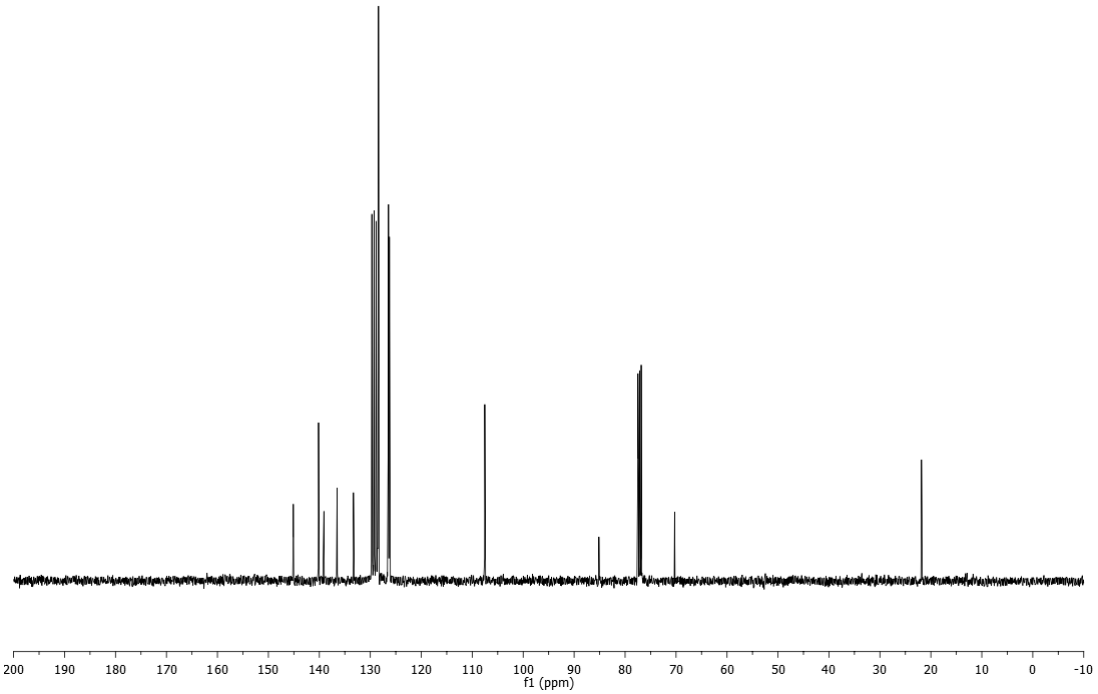
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)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160
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120
110
100
90
80
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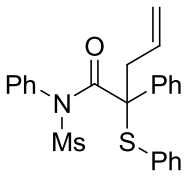
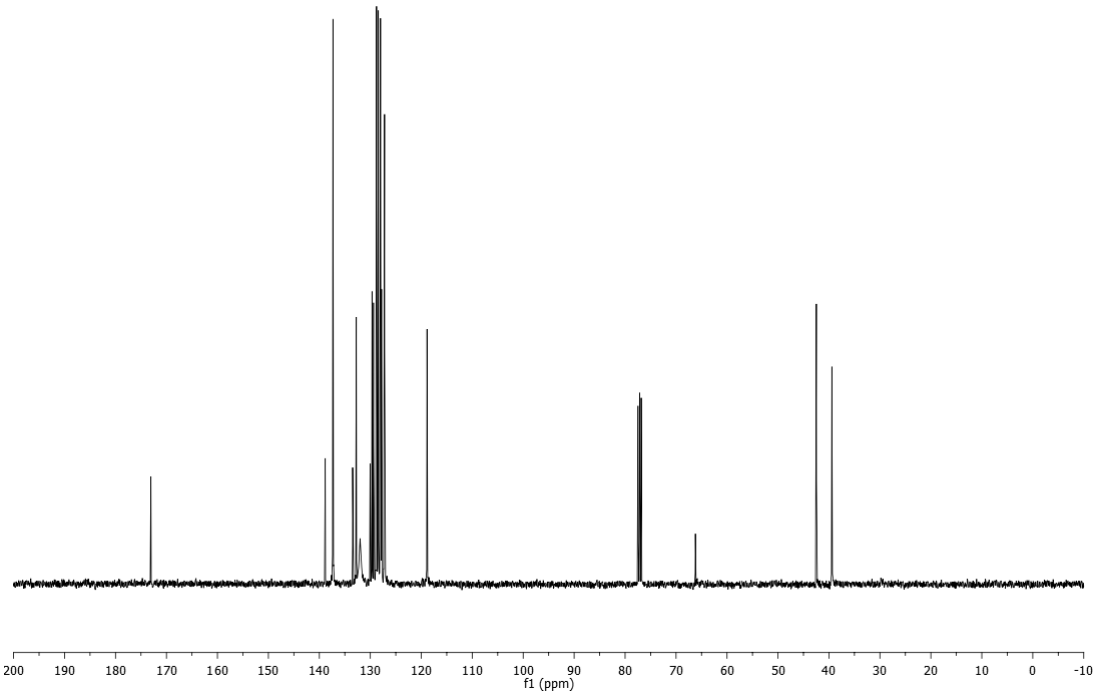
30
20
10
0
-10
f1 (ppm)

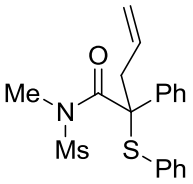
^{1}H and ^{13}C NMR Spectra of Catalysis Products

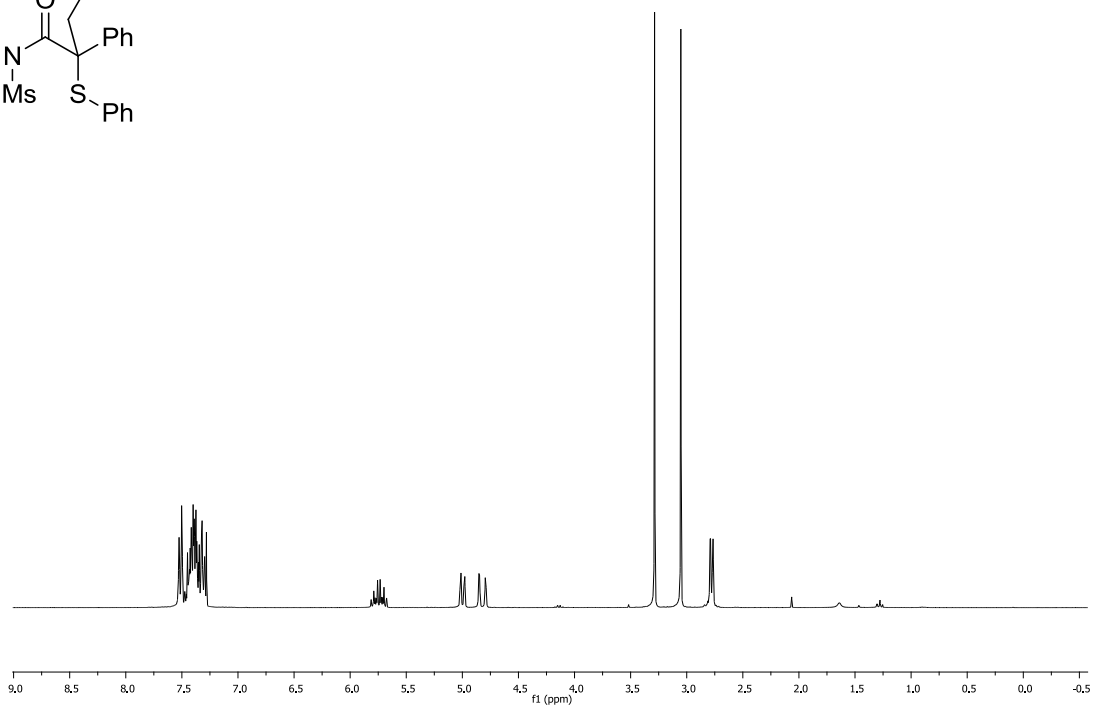
Compound 4aa

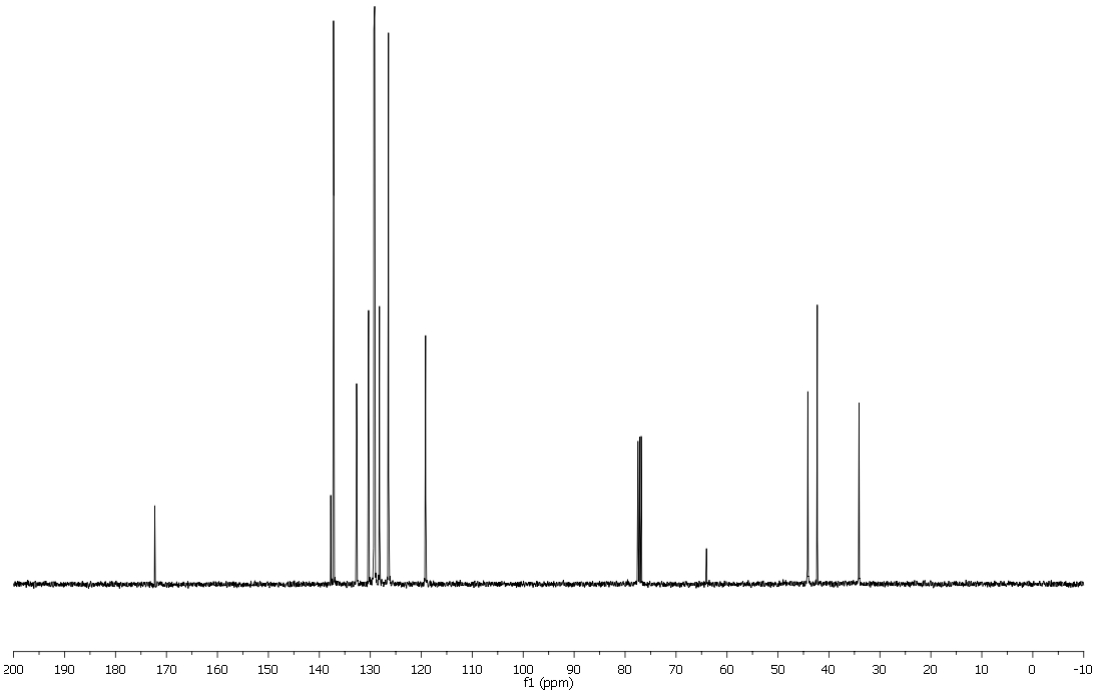




Compound 4ba







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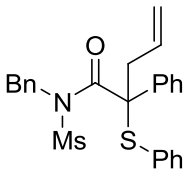

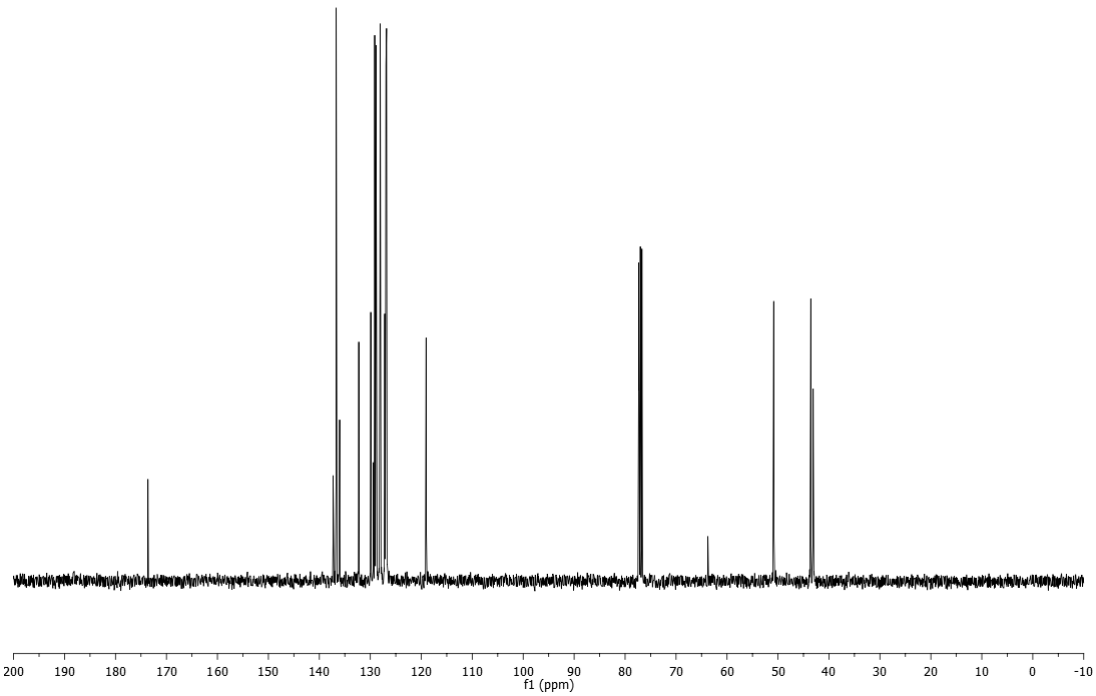

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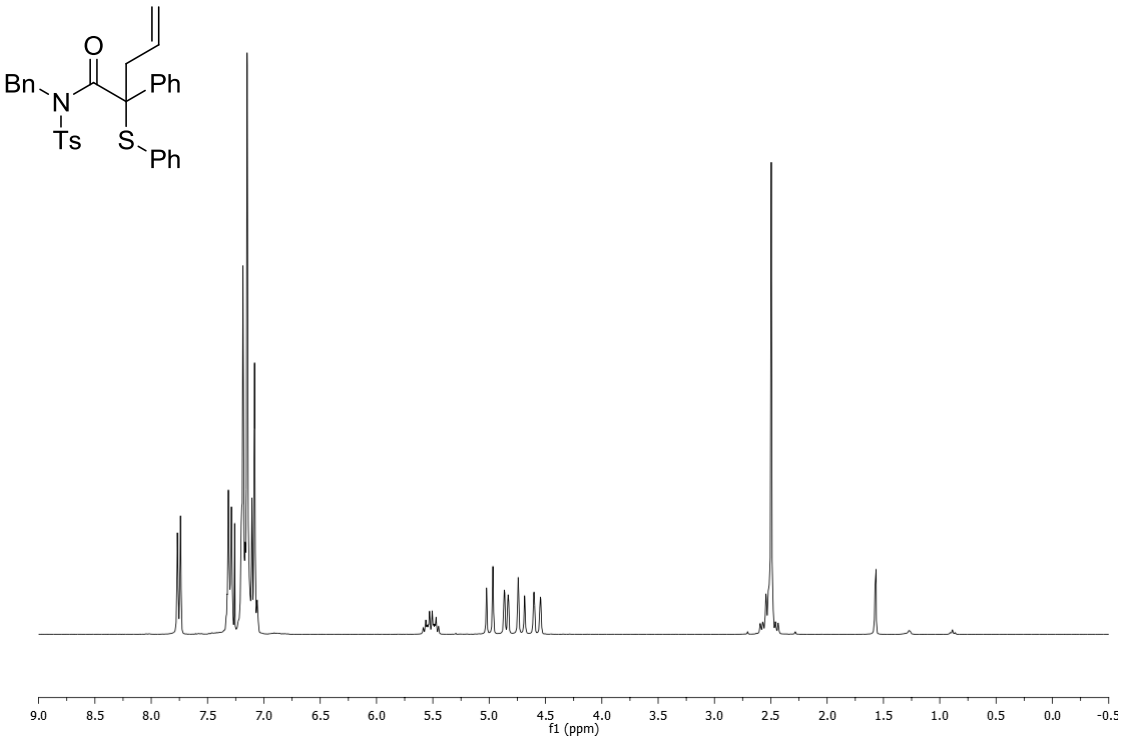

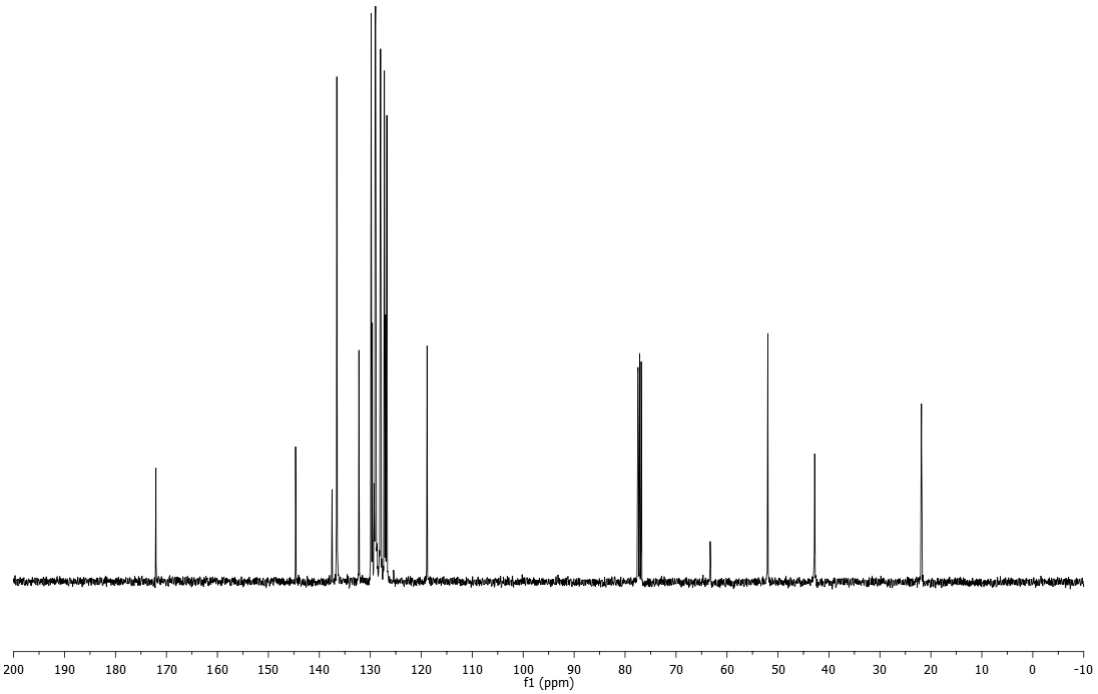

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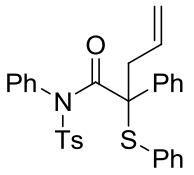
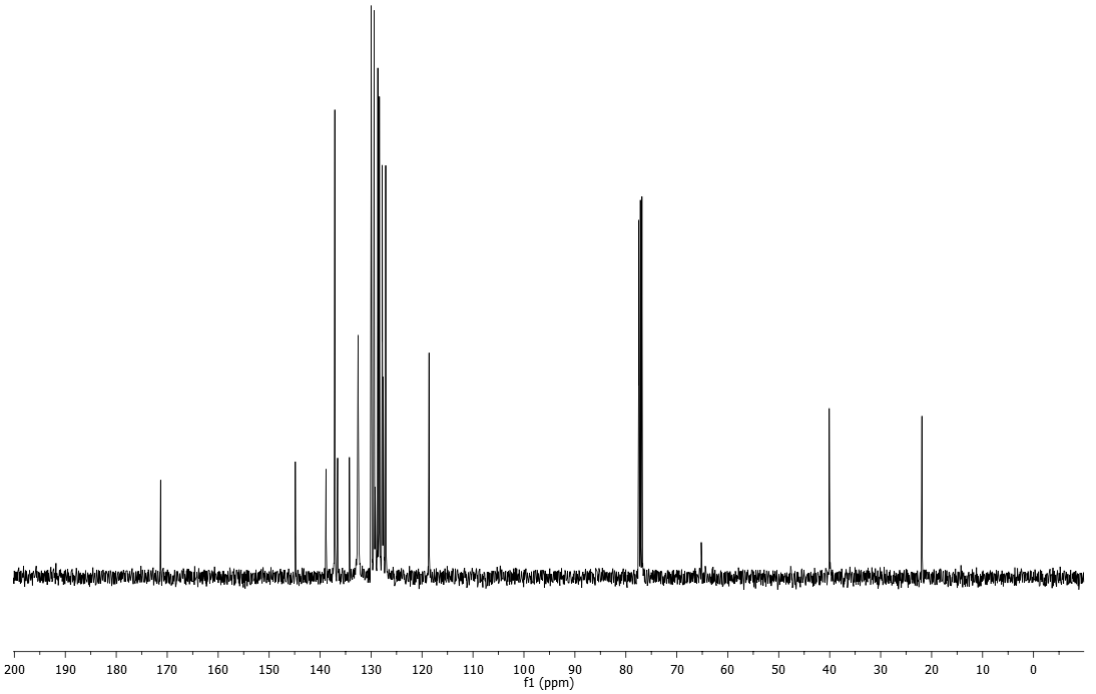
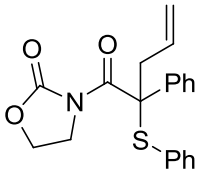
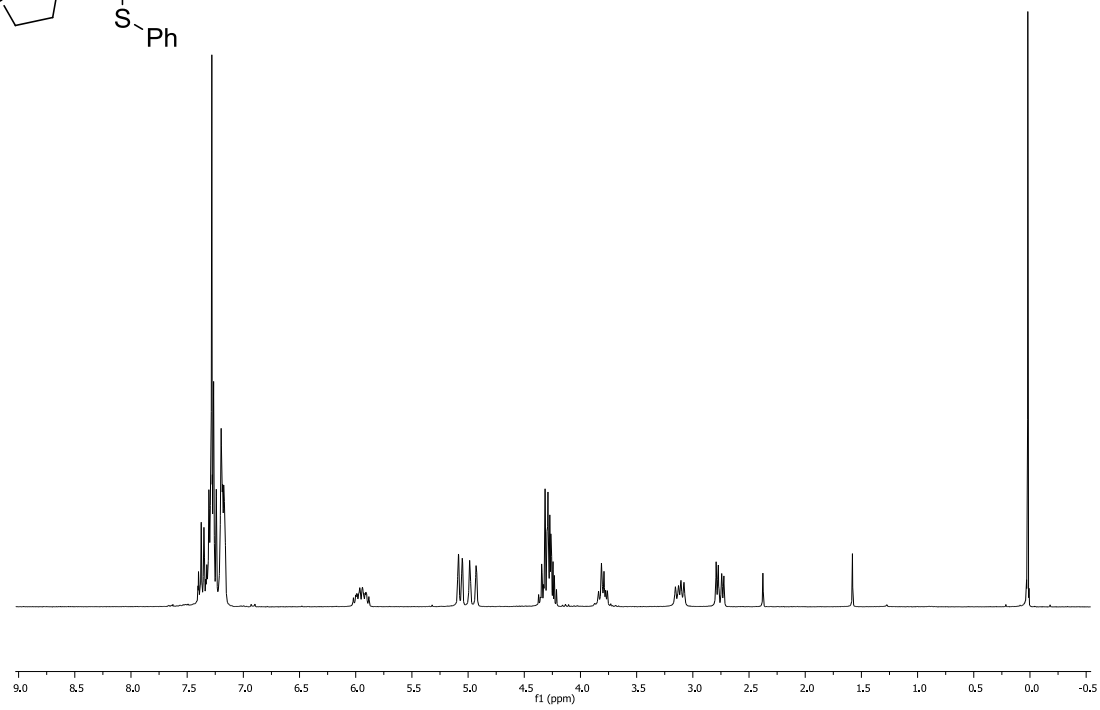
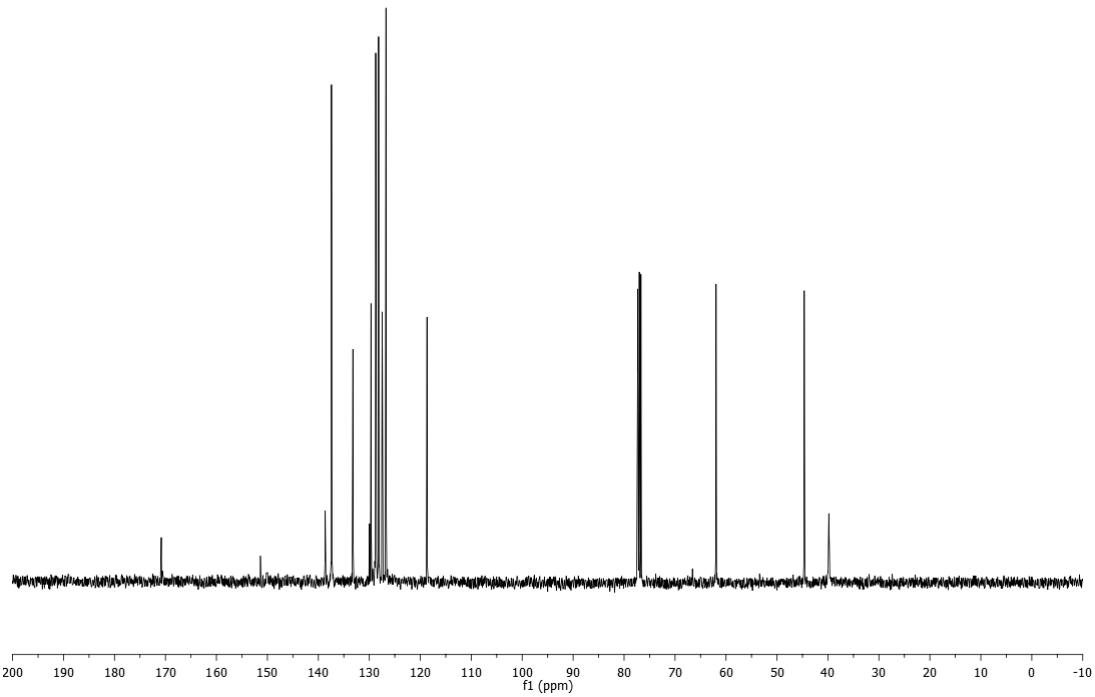




Compound 4fa







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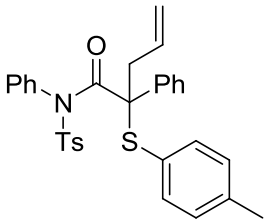

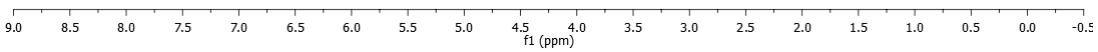

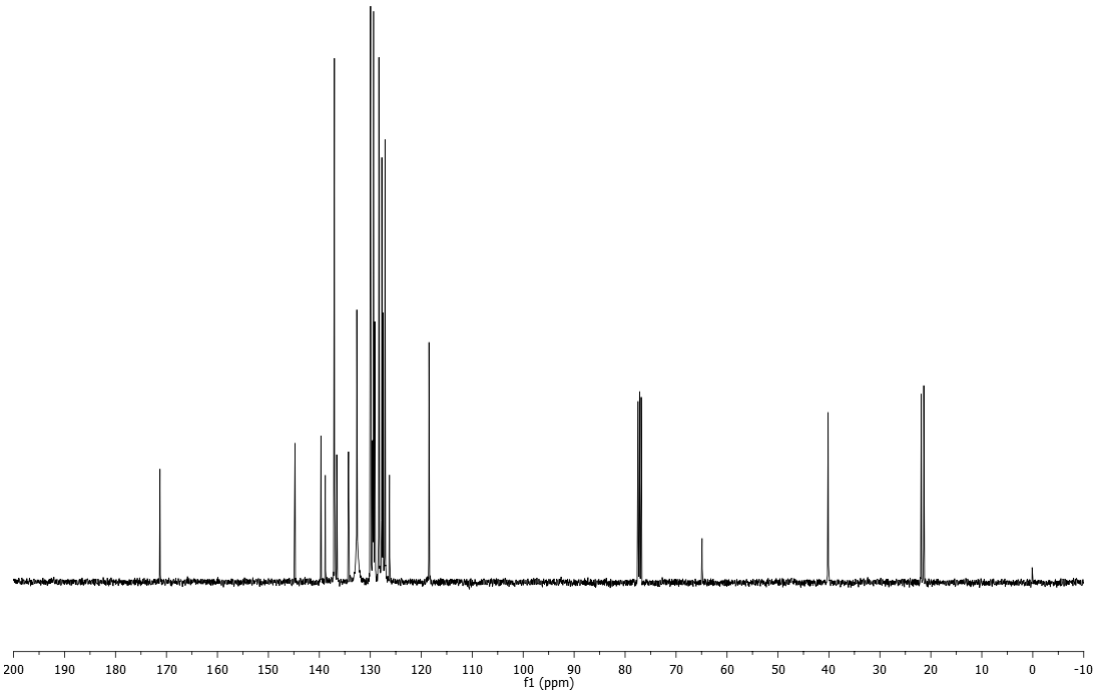

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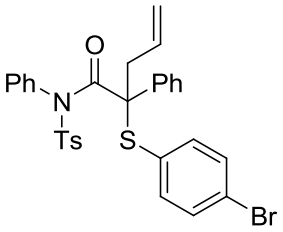
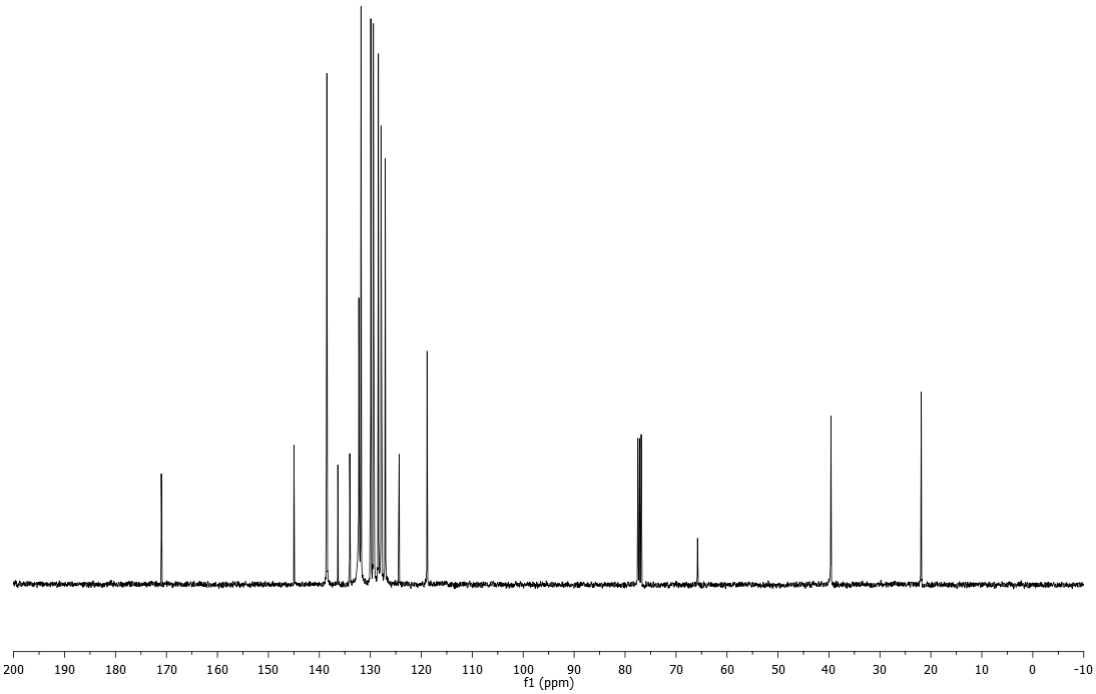
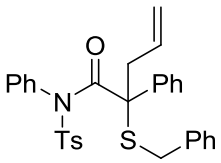
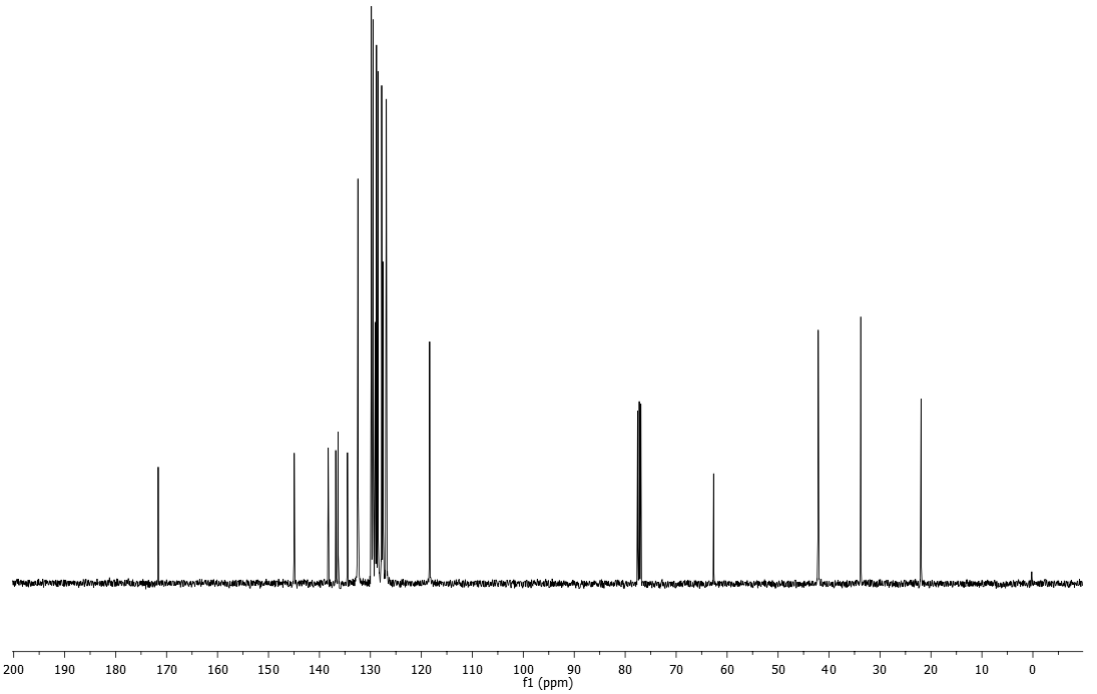




Compound 4ed





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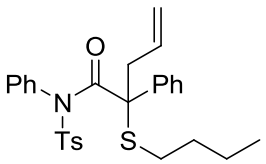

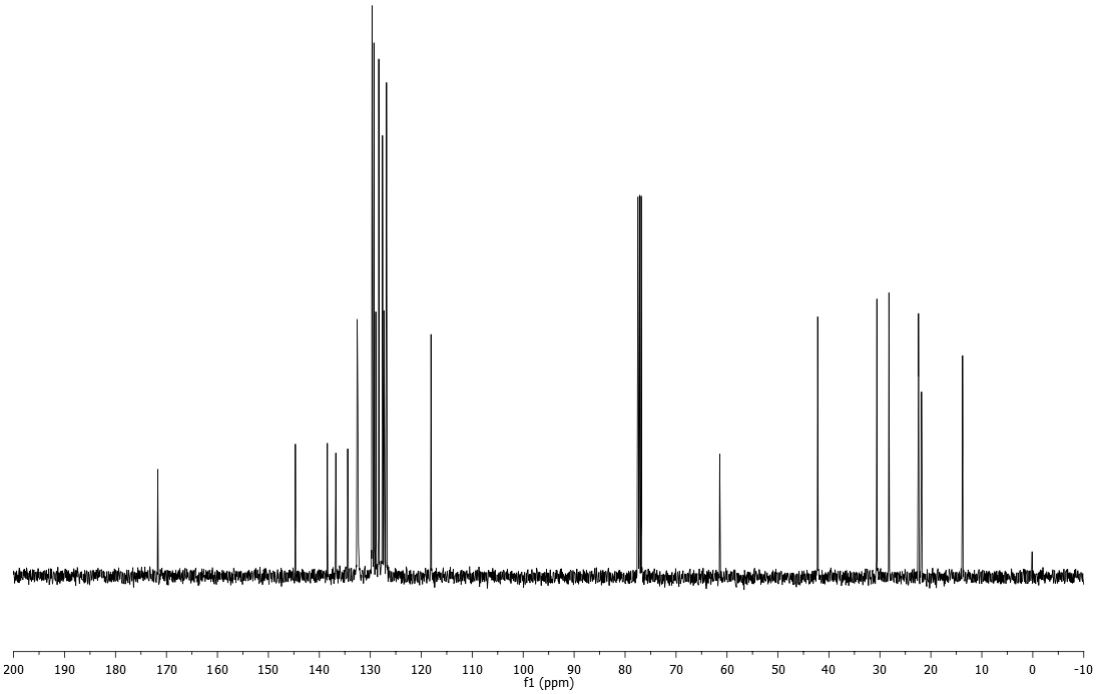

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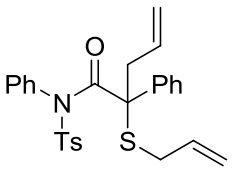

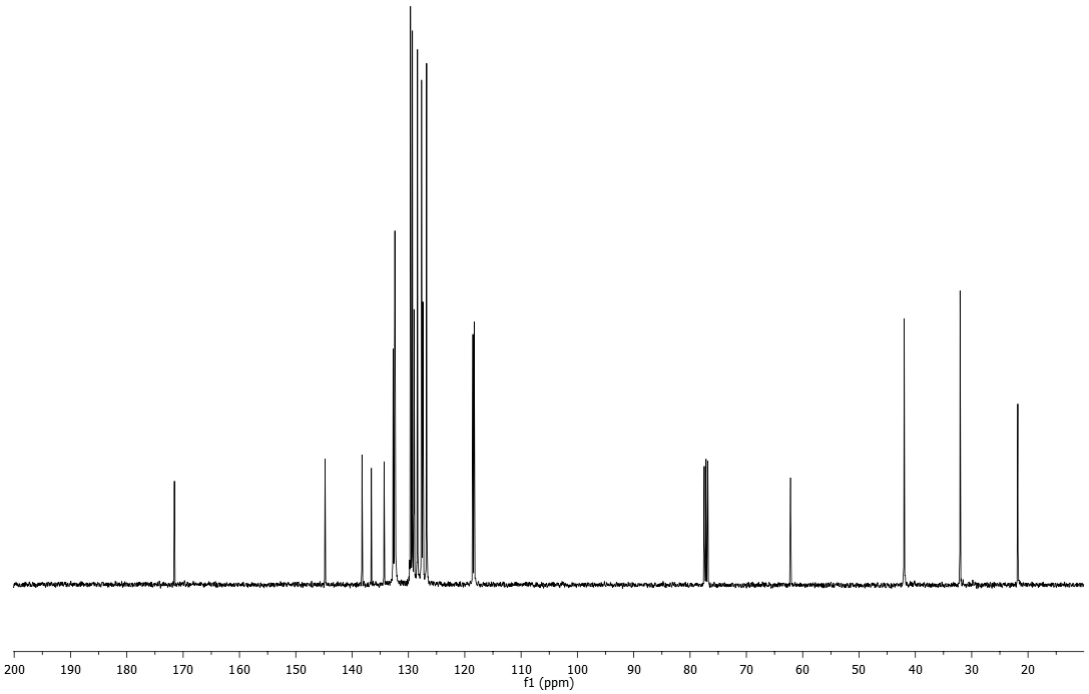

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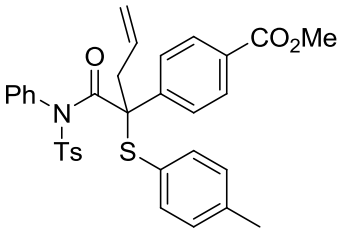
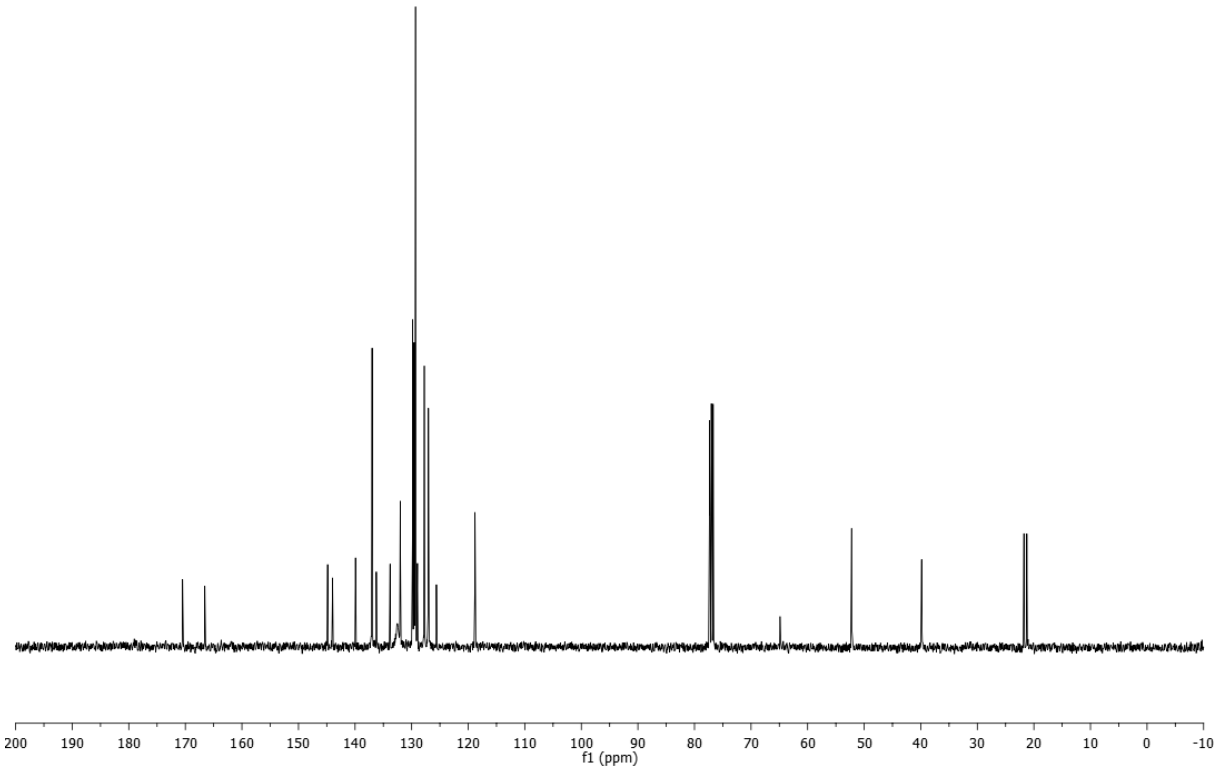
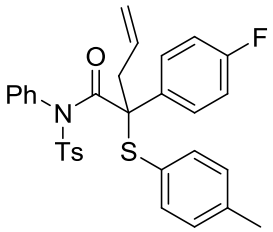
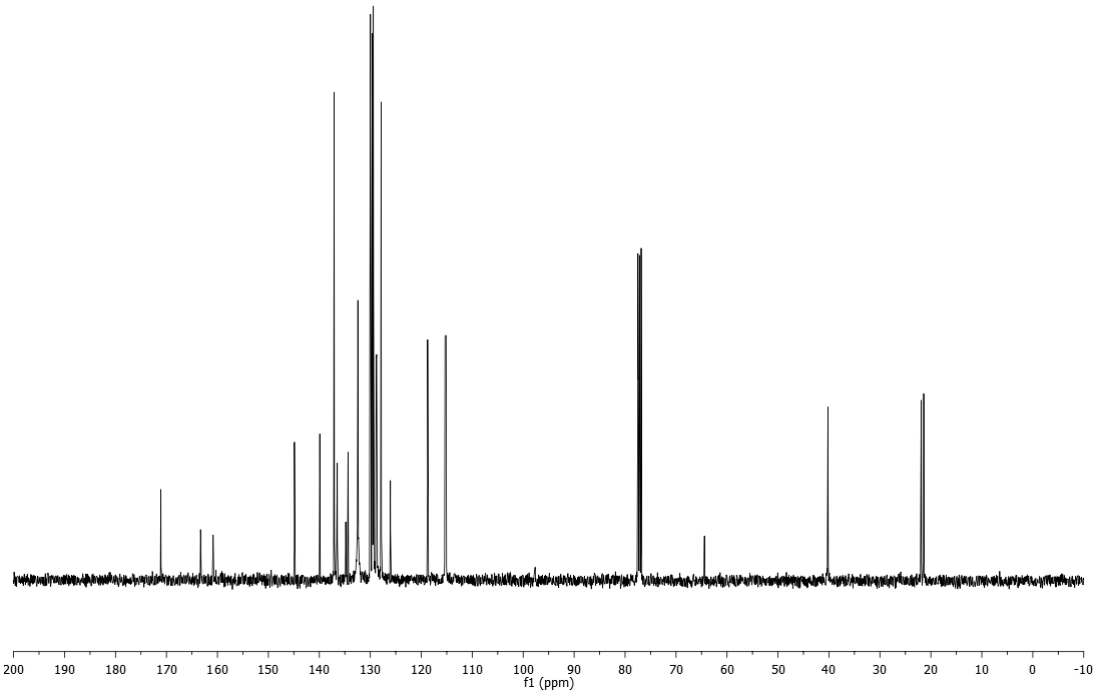




Compound 4ib





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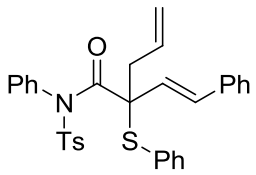
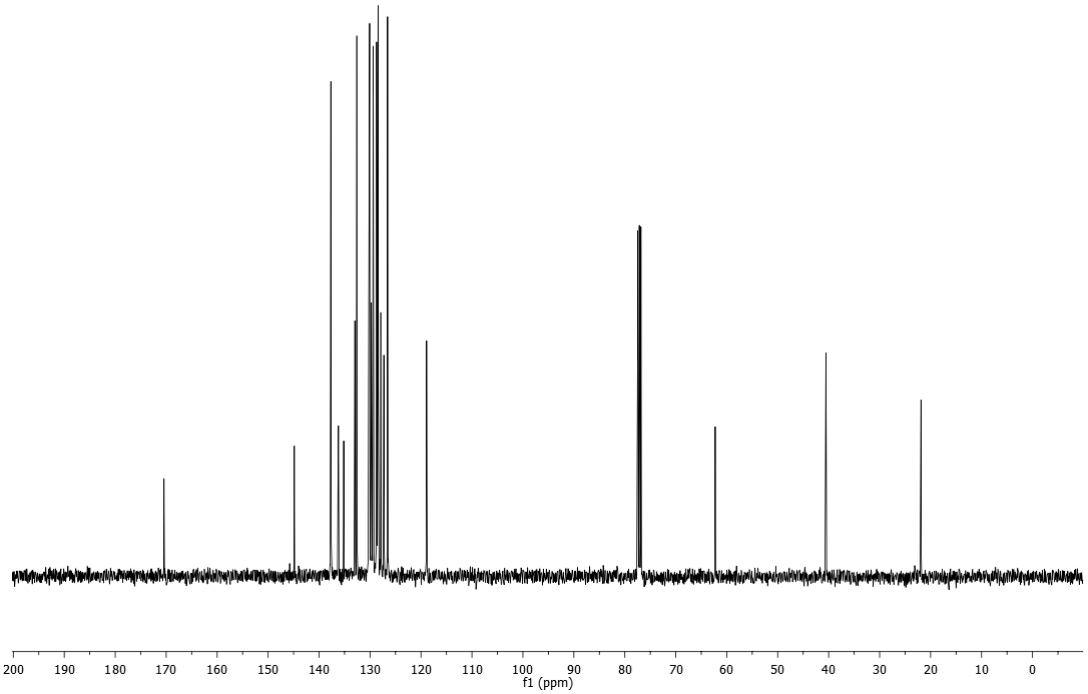
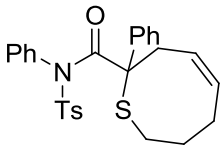
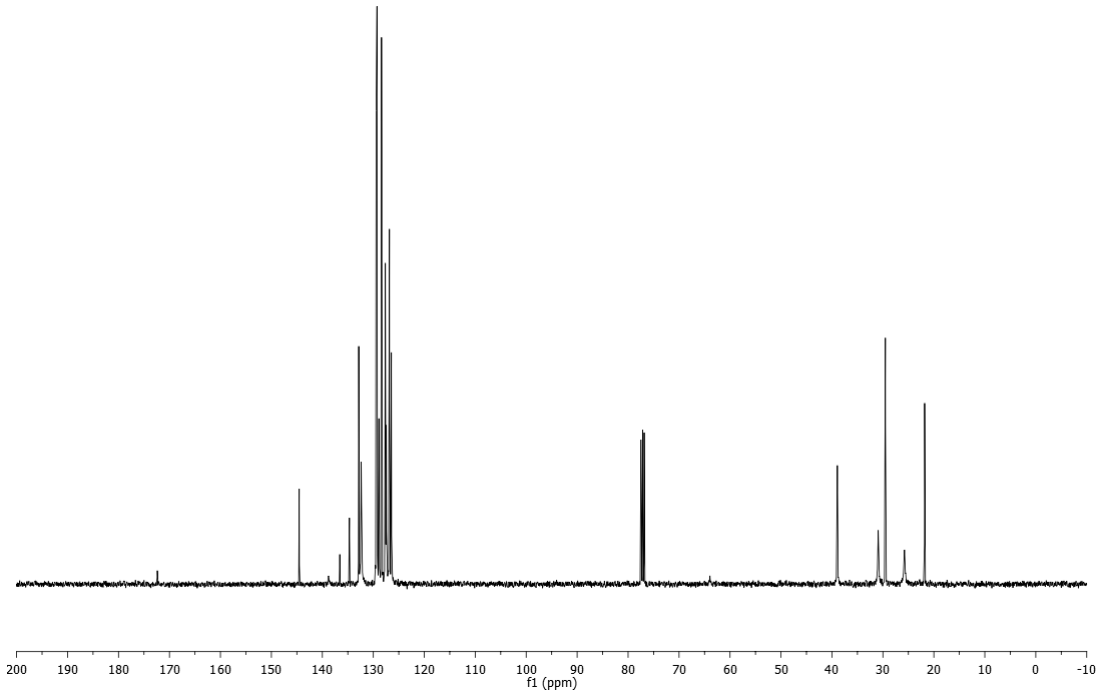




Compound 4eg





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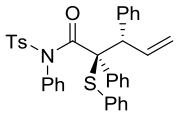
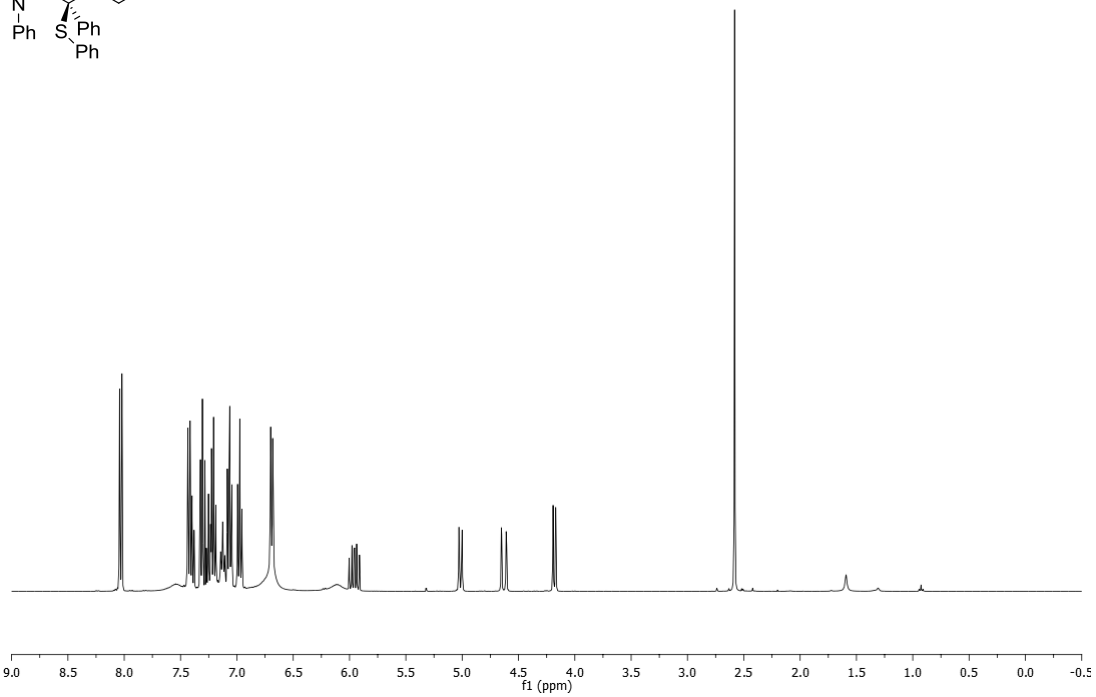
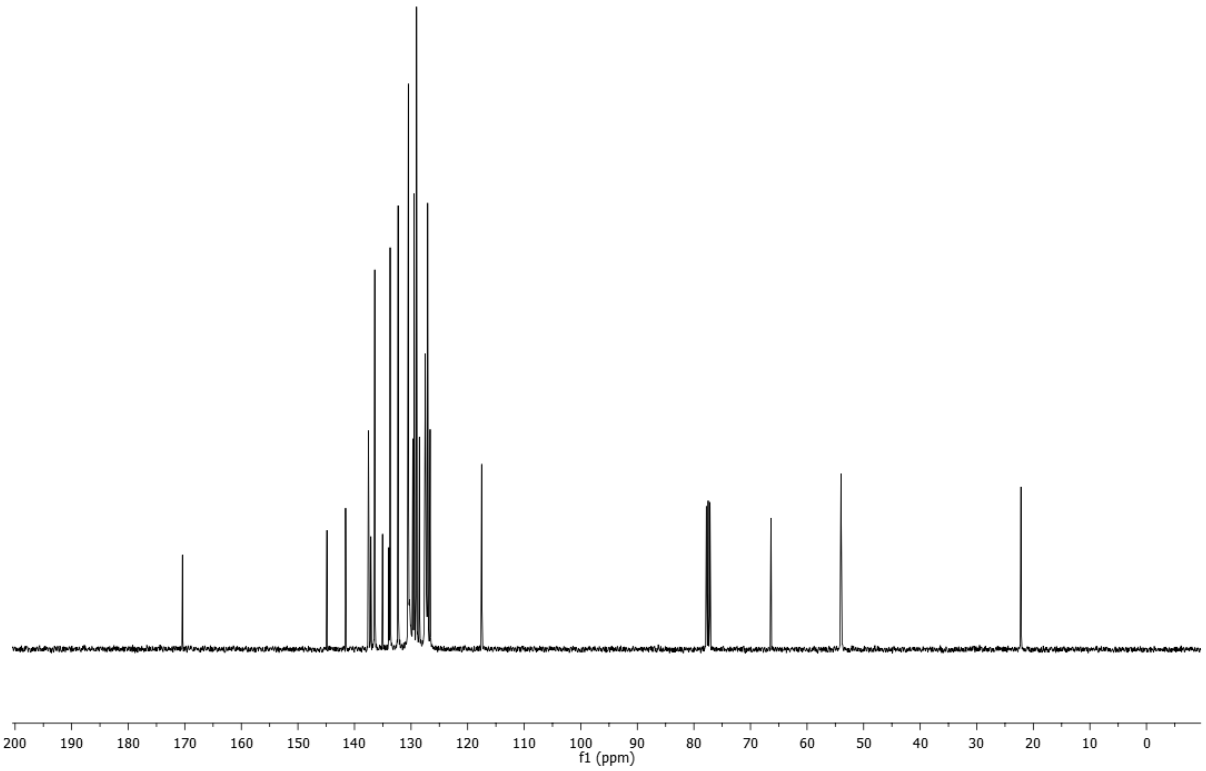
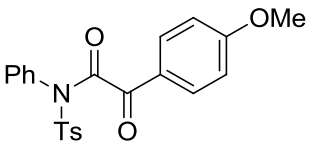






Compound 5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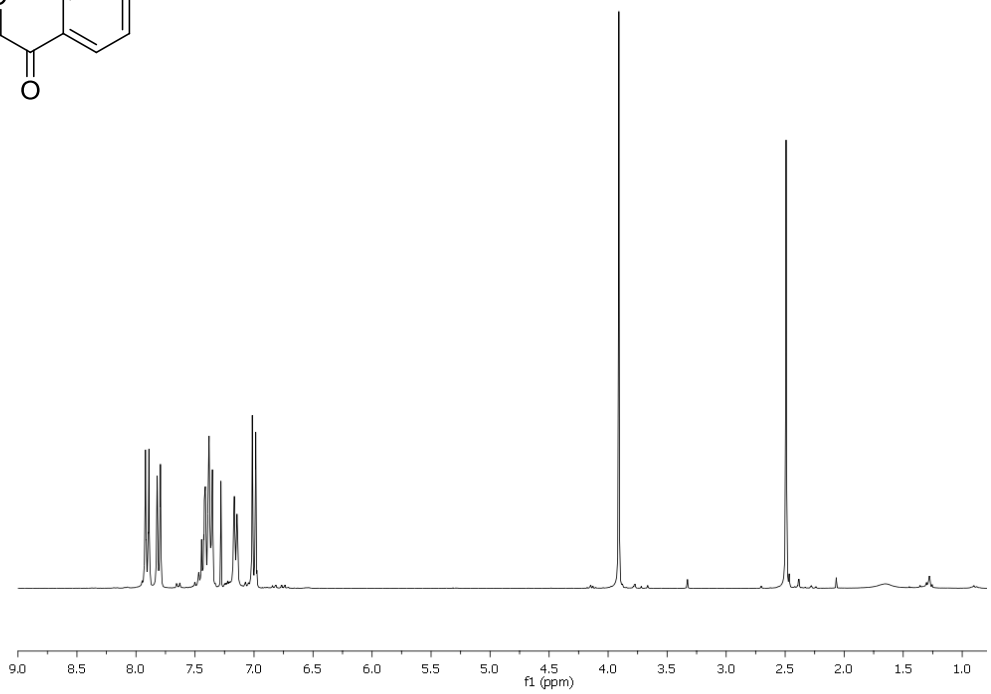
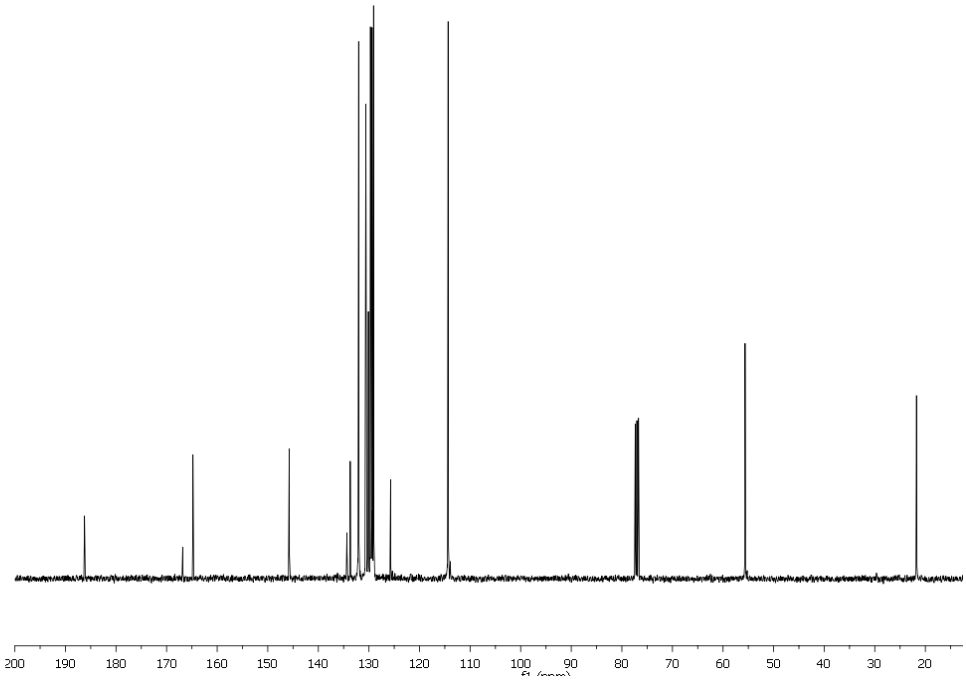
Ph
N
Ts
O


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
f1 (ppm)


200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20