Supporting Information

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1.1 General information.

NMR Spectroscopy: Proton (^{1}H) and carbon (^{13}C) NMR spectra were recorded on a Bruker DPX400 (400 MHz), Bruker AVN400 (400 MHz) or Bruker AVC500 (500 MHz) spectrometer. Proton and carbon chemical shifts (δ_H, δ_C) are quoted in ppm. ^{1}H NMR spectra were recorded using an internal deuterium lock for the residual protons in $CDCl_3$ (δ 7.26) and C_6D_6 (δ 7.16). ^{13}C NMR Spectra were recorded using an internal deuterium lock using solvents $CDCl_3$ (δ 77.0) and C_6D_6 (δ 128.06). Assignments were determined either on the basis of unambiguous chemical shift or coupling patterns, COSY and/or HSQC experiments. Peak multiplicities are defined as: s = singlet, d = doublet, t = triplet, q = quartet, quin = quintet, sxt = sextet, spt = septet, m = multiplet, app. = apparent, br. = broad; and coupling constants (*J*) are reported to the nearest 0.1 Hz.

Infrared Spectroscopy: Infrared spectra were recorded on a Bruker Tensor 27 FT-IR spectrometer with the sample being prepared as a thin film on a diamond ATR module. Absorption maxima (ν_{max}) are quoted in wavenumbers (cm^{-1}).

Mass Spectroscopy: Low resolution mass spectra were recorded on a Micromass LCT Premier Open Access using electrospray ionisation (ESI). Accurate mass (HRMS) data was determined under conditions of ESI on a Bruker MicroTOF. High resolution values are calculated to 4 decimal places from the molecular formula, and all values are within a tolerance of 5 ppm.

Melting Points: Melting points were obtained using a Griffin melting point apparatus and are uncorrected.

Reagents, solvents and techniques: All reagents, obtained from Acros, Aldrich, Fluka, Lancaster, Strem and Fluorochem fine chemicals suppliers, were used directly as supplied. Solvents were either used as commercially supplied, or as purified by standard techniques. Anhydrous THF was obtained from solvent dispenser units having been passed through an activated alumina column under argon. Unless otherwise stated, non-aqueous reactions were performed in oven dried apparatus under argon atmospheres at room temperature.

Reactions were monitored by thin layer chromatography on pre-coated aluminium-backed plates (Merck Kieselgel 60 with fluorescent indicator UV254). Spots were visualised by quenching of UV fluorescence or by staining with potassium permanganate or vanillin, and retention factors are reported with the solvent system in parentheses. Flash column chromatography was performed on silica gel obtained from Macherey Nagel (MN 60, 230–400 mesh) under positive nitrogen pressure, using the solvent system quoted in parentheses.

1.2 Experimental Procedures

1.2a: General procedure for the Cs_2CO_3 promoted synthesis of 1,2-dichloroenamides.

To a stirring suspension of amide (1.0 eq.), powdered Cs_2CO_3 (1.5 eq.) and DMF (0.75 mL $mmol^{-1}$ of amide substrate), at 50 °C, was added trichloroethylene (1.1 eq.) dropwise over 10 minutes. The resulting mixture was stirred at 50 ºC until reaction completion, as analysed by TLC (~1–2 h). Upon cooling to room temperature, the mixture was partitioned between EtOAc and H_2O (roughly 2:1 of EtOAc:H_2O), the organic layer was separated and further washed with water (×3). The organic layer was then dried (Na_2SO_4), filtered and concentrated *in vacuo*. Purification was then performed as described for each compound. Note: The use of an inert atmosphere or rigorously dried solvent is not necessary for this transformation.

1.2b: General procedure for the NaH promoted synthesis of 1,2-dichloroenamides.

To a stirring suspension of NaH (2.1 eq.) in anhydrous DMF (0.75 mL $mmol^{-1}$ of amide substrate), at 0 °C under an argon atmosphere, was added a solution of amide (1.0 eq.) in anhydrous DMF (0.75 mL $mmol^{-1}$ of amide substrate) dropwise over 5 minutes, and H_2 gas was evolved. The mixture was allowed to warm to room temperature and stirred for a further 2 hours. Trichloroethylene (1.0 eq.) was then added dropwise over 30 minutes at room temperature, with further evolution of H_2 observed. The mixture was then stirred at room temperature until reaction completion, as analysed by TLC (overnight). The reaction mixture was quenched with EtOAc, and washed with aqueous saturated $NaHCO_3$ (×3). The organic layer was then dried (Na_2SO_4), and concentrated *in vacuo*. Purification was then performed as described for each compound.

1.2c: General procedure for the phase-transfer catalysed synthesis of 1,2-dichloroenamides.

To a stirring mixture of amide (1.0 eq.), tetrabutylammonium hydrogensulfate (TBAHS) (0.2 eq.), toluene (3 mL $mmol^{-1}$ of amide substrate) and CH_2Cl_2 (2.5 mL $mmol^{-1}$ of amide substrate), at room temperature under argon, was added 25% w/v aqueous NaOH (3 mL $mmol^{-1}$ of amide substrate). The solution was then stirred vigorously for 15 minutes, followed by the dropwise addition of trichloroethylene (3.0 eq.) over 30 minutes. The reaction was then stirred until reaction completion, as analysed by TLC (overnight). The aqueous layer was then extracted with Et_2O (×3), organic extracts combined, dried (Na_2SO_4) and concentrated *in vacuo*. Purification was then performed as described for each compound.

1.2d: General procedure for the synthesis of ynamides using phenyllithium.

To an oven dried, argon flushed flask was added 1,2-dichloroenamide (1.0 eq.) and anhydrous THF (10 mL $mmol^{-1}$ of enamide substrate), and cooled to –78 °C whilst stirring. A solution of phenyllithium (2.0 M solution in dibutyl ether, 2.2 eq.) was then added dropwise over 10 minutes, and left to stir at –78 °C for 1 hour. After complete conversion to the lithiated ynamide (confirmed by TLC), the electrophile (1.2 eq.) was added at –78 °C and the stirring mixture was allowed to warm to room temperature. Upon reaction completion, as analysed by TLC (~1 h), the reaction mixture was quenched with water, followed by extraction with Et_2O (×2). The organic extracts were combined and dried (Na_2SO_4), filtered and concentrated *in vacuo*. Purification was then performed as described for each compound.

1.2e: General procedure for the synthesis of ynamides using *n*-butyllithium.

To an oven dried, argon flushed flask was added 1,2-dichloroenamide (1.0 eq.) and anhydrous THF (4 mL $mmol^{-1}$ of enamide substrate), and cooled to –78 °C whilst stirring. A solution of *n*-butyllithium (2.5 M solution in hexanes, 1.2 eq.) was then added dropwise over 10 minutes, such that the reaction does not exceed –70 °C, and the resulting mixture was then stirred at –78 °C for 5 minutes, followed by warming to –41 °C for 30 minutes. Upon cooling to –78 °C, another portion of *n*-butyllithium (2.5 M solution in hexanes, 1.0 eq.) was added dropwise over 10 minutes, and stirred for a further 10 minutes. Next, the electrophile (1.2 eq.) was added at –78 °C and the stirring mixture was allowed to warm to room temperature. Upon reaction completion, as analysed by TLC (~ 1 h), the reaction mixture was quenched with water, followed by extraction with Et_2O (×2). The organic extracts were combined and dried (Na_2SO_4), filtered and concentrated *in vacuo*. Purification was then performed as described for each compound.

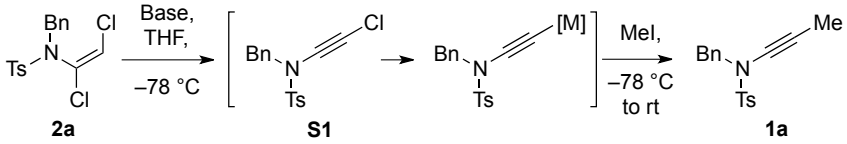
1.3 Optimisation of ynamide synthesis and preparation of chloroynamide S1

Conditions to convert dichloroenamide **2a** into ynamide **1a** are shown in Table S1.

For the purposes of the optimisation, the *in situ* generated ynamide anion was trapped with iodomethane to give methyl ynamide **1a**. *n*-BuLi served as a suitable base (Entry 1), however careful control of reaction temperature and slow addition of this base was required. We believe this prevents deprotonation at other sites which occurs when the rate of *n*-BuLi addition exceeds that of chloroynamide formation, thus resulting in an excess of base accumulating in the reaction.

Phenyllithium proved efficient and procedurally robust (Entry 2), and was our preferred base for the conversion. Treatment of **2a** with 1.2 equivalents of phenyllithium afforded only the intermediate chloroynamide **S1** (Entry 3), which was formed as the exclusive product using LiHMDS (Entry 5). Weaker bases were ineffective, with starting material returned in these cases (Entries 6, 7).

Table S1. Optimization of ynamide synthesis.



2a **S1** **1a**

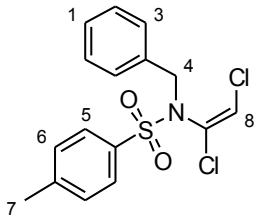
Entry	Base (2.2 equiv.)	Yield [%]
1	*n*-BuLi	83[a]
2	PhLi	85[a]
3	PhLi[b]	62[c]
4	$LiN(i\text{-}Pr)_2$	dec.
5	$LiN(SiMe_3)_2$	74[c]
6	*i*-PrMgCl	n.r.[d]
7	*t*-BuOK[e]	n.r.[e]

[a] Isolated yield of **1a**. [b] 1.2 equiv. of base. [c] Isolated yield of **S1**. [d] No reaction after reflux for 24 h. [e] No reaction with up to 5.0 equiv. *t*-BuOK at reflux for 24 h.

1.4 Experimental Procedures and Characterisation Data.

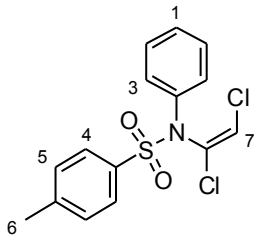
1.4a Dichloroenamides:

(*E*)-*N*-Benzyl-*N*-(1,2-dichlorovinyl)-4-methylbenzenesulfonamide, 2a



Synthesised from *N*-benzyl tosylamide (4.10 g, 15.7 mmol, 1.0 eq.) with Cs_2CO_3 (7.67 g, 23.5 mmol, 1.5 eq.), DMF (11.8 mL) and trichloroethylene (1.55 mL, 17.3 mmol, 1.1 eq.), taking approximately 1.5 hours following general procedure **1.2a**. Recrystallisation from Et_2O afforded **2a** (5.32 g, 14.9 mmol, 95%) as colourless crystals. Crystals suitable for X-ray diffraction were grown by slow evaporation of a solution of **2a** in CH_2Cl_2; **m.p.** 136–137 °C; $\mathbf{R_f}$ 0.53 (20% EtOAc/40-60 petroleum ether); **IR** (thin film, ν_{max} / cm^{-1}) 3088, 3033, 2925, 1597, 1496, 1456, 1402, 1167, 1122, 1090, 948, 818, 704, 659, 608; **^{1}H NMR** (400 MHz, $CDCl_3$) δ_H 7.86 (2H, d, *J* = 8.0 Hz, *H*5), 7.36 (2H, d, *J* = 8.0 Hz, *H*6), 7.35–7.28 (5H, m, *H*1, *H*2, *H*3), 6.27 (1H, s, *H*8), 5.05–3.70 (2H, br. s*, *H*4), 2.47 (3H, s, *H*7); **^{13}C NMR** (101 MHz, $CDCl_3$) δ_c 144.7, 135.1, 133.3, 129.8, 129.39, 129.35, 128.4, 128.3, 121.7, 51.8, 21.7;** **HRMS** (ES+) calc. for $C_{16}H_{15}{}^{35}Cl_2NNaO_2S$ $[M+Na]^+$ 378.0093, found 378.0110. *Peak spanning 5.05–3.70 ppm is unresolved due to rotameric forms of this molecule. ** Note: a single ^{13}C resonance is obscured due to signal overlap.

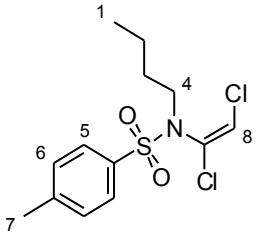
(*E*)-*N*-(1,2-Dichlorovinyl)-4-methyl-*N*-phenylbenzenesulfonamide, 2b



Synthesised from *N*-tosyl aniline (200 mg, 809 µmol, 1.0 eq.) with Cs_2CO_3 (395 mg, 1.21 mmol, 1.5 eq.), DMF (0.6 mL) and trichloroethylene (80 µL, 890 µmol, 1.1 eq.), taking approximately 2 hours following general procedure **1.2a**. Column chromatography (10% EtOAc/40-60 petroleum ether) afforded **2b** (255 mg, 745 µmol, 92%) as colourless crystals; **m.p**. 115 °C; $\mathbf{R_f}$ 0.52 (20% EtOAc/40-60 petroleum ether); **IR** (thin film, ν_{max} / cm^{-1}) 3087, 2315, 1720, 1596, 1490, 1365, 1283, 1169, 1090, 948, 813, 695, 662; **^{1}H NMR** (400 MHz, $CDCl_3$) δ_H 7.65 (2H, d, *J* = 8.4 Hz, *H*4), 7.39–7.30 (5H, m, *H*1*, H*2*, H*3), 7.24 (2H, d, *J* = 8.4 Hz, *H*5), 6.45 (1H, s, *H*7), 2.42 (3H, s, *H*6); **^{13}C NMR** (101 MHz, $CDCl_3$) δ_c 144.6, 137.7, 135.6, 130.7, 129.43, 129.35, 129.1, 128.7, 128.6, 120.5, 21.7; **MS** (ESI+) *m/z* 359.0 (61, $[\{^{35}Cl_2\}M+NH_4]^+$), 361.1 (41, $[\{^{35}Cl^{37}Cl\}M+NH_4]^+$), 363.1 (7, $[\{^{37}Cl_2\}M+NH_4]^+$), 364.0 (100, $[\{^{35}Cl_2\}M+Na]^+$), 366.0 (67,

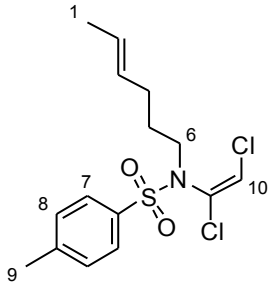
[{$^{35}Cl^{37}Cl$}M+Na]$^+$), 368.1 (11, [{$^{37}Cl_2$}M+Na]$^+$), 380.0 (57, [{$^{35}Cl_2$}M+K]$^+$), 382.0 (38, [{$^{35}Cl^{37}Cl$}M+K]$^+$), 384.0 (6, [{$^{37}Cl_2$}M+K]$^+$). Data are consistent with literature values.[1]

(*E*)-*N*-(*n*-Butyl)-*N*-(1,2-dichlorovinyl)-4-methylbenzenesulfonamide, 2c



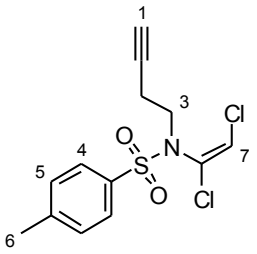
Synthesised from *N*-(*n*-butyl)tosylamide (100 mg, 440 µmol, 1.0 eq.) with Cs_2CO_3 (215 mg, 660 µmol, 1.5 eq.), DMF (0.3 mL) and trichloroethylene (43 µL, 484 µmol, 1.1 eq.), taking approximately 1 hour following general procedure **1.2a**. Column chromatography (10% Et_2O/40-60 petroleum ether) afforded **2c** (112 mg, 347 µmol, 79%) as colourless crystals; **m.p.** 45–46 °C; $\mathbf{R_f}$ 0.60 (20% EtOAc/40-60 petroleum ether); **IR** (thin film, ν_{max} / cm^{-1}) 3089, 2962, 2934, 2874, 1738, 1598, 1459, 1362, 1168, 1090, 1027, 816, 673; **^{1}H NMR** (400 MHz, $CDCl_3$) δ_H 7.79 (2H, d, *J* = 8.3 Hz, *H*5), 7.32 (2H, d, *J* = 8.3 Hz, *H*6), 6.49 (1H, s, *H*8), 3.48–2.93 (2H, br. app. s, *H*4), 2.44 (3H, s, *H*7), 1.50 (2H, quin, *J* = 7.3 Hz, *H*3), 1.36 (2H, sxt, *J* = 7.3 Hz, *H*2), 0.89 (3H, t, *J* = 7.3 Hz, *H*1); **^{13}C NMR** (101 MHz, $CDCl_3$) δ_c 144.5, 135.1, 129.7, 129.6, 128.3, 121.3, 47.6, 29.5, 21.6, 19.8, 13.6; **HRMS** (ES+) calc. for $C_{13}H_{17}{}^{35}Cl_2NNaO_2S$ $[M+Na]^+$ 344.0249, found 344.0263.

***N*-((*E*)-1,2-Dichlorovinyl)-*N*-((*E*)-hex-4-en-1-yl)-4-methylbenzenesulfonamide, 2d**



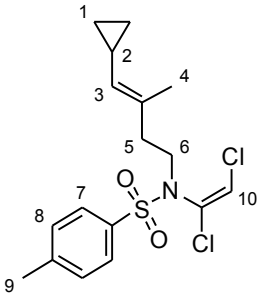
Synthesised from (*E*)-*N*-(hex-4-en-1-yl)tosylamide (100 mg, 395 µmol, 1.0 eq.) with Cs_2CO_3 (193 mg, 592 µmol, 1.5 eq.), DMF (0.3 mL) and trichloroethylene (39 µL, 434 µmol, 1.1 eq.), taking approximately 1 hour following general procedure **1.2a**. Column chromatography (5% EtOAc/40-60 petroleum ether) afforded **2d** (128 mg, 367 µmol, 93%) as a pale yellow oil; $\mathbf{R_f}$ 0.46 (10% EtOAc/40-60 petroleum ether); **IR** (thin film, ν_{max} / cm^{-1}) 2923, 1598, 1441, 1361, 1166, 1090, 967, 805, 707; **^{1}H NMR** (400 MHz, $CDCl_3$) δ_H 7.78 (2H, d, *J* = 8.2 Hz, *H*7), 7.31 (2H, d, *J* = 8.2 Hz, *H*8), 6.48 (1H, s, *H*10), 5.51–5.25 (2H, m, *H*2, *H*3), 3.50–2.93 (2H, br. app. s, *H*6), 2.42 (3H, s, *H*9), 2.07–1.96 (2H, m, *H*5), 1.61 (3H, dd, *J* = 6.0, 1.1 Hz, *H*1), 1.60–1.52 (2H, m, *H*4); **^{13}C NMR** (101 MHz, $CDCl_3$) δ_c 144.4, 135.1, 129.7, 129.6, 129.5, 128.3, 126.0, 121.2, 47.3, 29.3, 27.3, 21.5, 17.8; **HRMS** (ES+) calc. for $C_{15}H_{19}{}^{35}Cl_2NNaO_2S$ $[M+Na]^+$ 370.0406, found 370.0419.

(*E*)-*N*-(But-3-yn-1-yl)-*N*-(1,2-dichlorovinyl)-4-methylbenzenesulfonamide, 2e



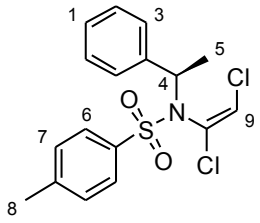
Synthesised from *N*-(but-3-yn-1-yl) tosylamide (51 mg, 227 µmol, 1.0 eq.) with Cs_2CO_3 (111 mg, 341 µmol, 1.5 eq.), DMF (0.1 mL) and trichloroethylene (23 µL, 250 µmol, 1.1 eq.), taking approximately 1 hour following general procedure **1.2a**. Column chromatography (10% EtOAc/40-60 petroleum ether) afforded **2e** (66 mg, 208 µmol, 92%) as colourless crystals; **m.p.** 90 °C; $\mathbf{R_f}$ 0.43 (20% EtOAc/40-60 petroleum ether); **IR** (thin film, ν_{max} / cm^{-1}) 3296, 3080, 2915, 1597, 1362, 1167, 1091, 979, 816, 709; **^{1}H NMR** (400 MHz, $CDCl_3$) δ_H 7.80 (2H, d, *J* = 8.2 Hz, *H*4), 7.33 (2H, d, *J* = 8.2 Hz, *H*5), 6.51 (1H, s, *H*7), 3.42 (2H, br. app. s, *H*3), 2.48 (2H, td, *J* = 7.8, 2.6 Hz, *H*2), 2.44 (3H, s, *H*6), 1.98 (1H, t, *J* = 2.6 Hz, *H*1); **^{13}C NMR** (101 MHz, $CDCl_3$) δ_c 144.8, 135.0, 129.7, 129.2, 128.3, 122.0, 79.8, 70.5, 46.7, 21.6, 18.4; **HRMS** (ES+) calc. for $C_{13}H_{13}{}^{35}Cl_2NNaO_2S$ $[M+Na]^+$ 339.9936, found 339.9925.

***N*-((*E*)-4-Cyclopropyl-3-methylbut-3-en-1-yl)-*N*-((*E*)-1,2-dichlorovinyl)-4-methylbenzenesulfonamide, 2f**



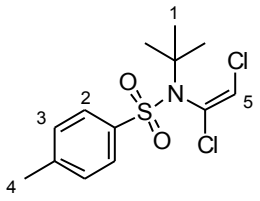
Synthesised from *N*-((*E*)-4-cyclopropyl-3-methylbut-3-en-1-yl)tosylamide (50 mg, 179 µmol, 1.0 eq.) with Cs_2CO_3 (88 mg, 268 µmol, 1.5 eq.), DMF (0.1 mL) and trichloroethylene (18 µL, 197 µmol, 1.1 eq.), taking approximately 1 hour following general procedure **1.2a**. Column chromatography (2% EtOAc/40-60 petroleum ether) afforded **2f** (53 mg, 141 µmol, 79%) as a colourless oil; $\mathbf{R_f}$ 0.65 (20% EtOAc/40-60 petroleum ether); **IR** (thin film, ν_{max} / cm^{-1}) 2924, 1598, 1362, 1166, 1091, 957, 806, 661; **^{1}H NMR** (400 MHz, $CDCl_3$) δ_H 7.79 (2H, d, *J* = 8.3 Hz, *H*7), 7.31 (2H, d, *J* = 8.2 Hz, *H*8), 6.48 (1H, s, *H*10), 4.57 (1H, dd, *J* = 9.4, 1.1 Hz, *H*3), 3.29 (2H, br. app. s, *H6*), 2.43 (3H, s, *H*9), 2.19 (2H, t, *J* = 7.8 Hz, *H*5), 1.70 (3H, d, *J* = 1.1 Hz, *H*4), 1.46-1.34 (1H, m, *H*2), 0.72–0.64 (2H, m, *H*1), 0.29–0.23 (2H, m, *H*1); **^{13}C NMR** (101 MHz, $CDCl_3$)* δ_c 144.5, 135.2, 131.6, 129.6, 129.1, 128.3, 121.3, 46.7, 37.5, 21.6, 16.2, 10.0, 6.6; **HRMS** (ES+) calc. for $C_{17}H_{21}{}^{35}Cl_2NNaO_2S$ $[M+Na]^+$ 396.0562, found 396.0565. * Note: a single ^{13}C resonance is obscured due to signal overlap.

(*R*,*E*)-*N*-(1,2-Dichlorovinyl)-4-methyl-*N*-(1-phenylethyl)benzenesulfonamide, 2g



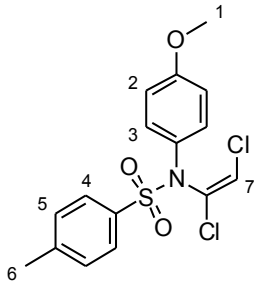
Synthesised from (*R*)-*N*-(1-phenylethyl)tosylamide (100 mg, 363 μmol, 1.0 eq.) with K_2CO_3 (151 mg, 1.09 mmol, 3.0 eq.), anhydrous DMF (0.3 mL) and trichloroethylene (0.10 mL, 1.09 mmol, 3.0 eq.) following general procedure **1.2a**. Column chromatography (5% EtOAc/40-60 petroleum ether) afforded **2g** (97 mg, 262 μmol, 72%) as a colourless oil; $\mathbf{R_f}$ 0.71 (20% EtOAc/40-60 petroleum ether); $[\boldsymbol{\alpha}]_{\boldsymbol{D}}^{\mathbf{20}}$ +3.7 (c 1.0, $CHCl_3$); **IR** (thin film, ν_{max} / cm^{-1}) 3081, 2971, 1598, 1495, 1455, 1354, 1306, 1164, 1139, 1090, 1049, 971, 808, 766, 699; **^{1}H NMR** (400 MHz, $CDCl_3$)* δ_H 7.72 and 7.62 (2H, d (×2), *J* = 8.1 Hz, *H*6), 7.35–7.06 (7H, m, *H*1, *H*2, *H*3, *H*7), 6.56 and 6.39 (1H, s (×2), *H*9), 5.18–5.05 (*H*4), 2.40 and 2.38 (3H, s (×2), *H*8), 1.62 and 1.48 (3H, d (×2), *J* = 7.1 Hz, *H*5); **^{13}C NMR** (101 MHz, $CDCl_3$)* δ_c 144.1, 143.9, 138.4, 138.2, 136.8, 129.4, 129.2, 128.5, 128.4, 128.2, 128.11, 128.06, 123.2, 60.5, 59.7, 21.5, 20.5, 18.6; **HRMS** (ES+) calc. for $C_{17}H_{17}{}^{35}Cl_2NNaO_2S$ $[M+Na]^+$ 392.0249, found 392.0236. *Note that the NMR spectra show highly rotameric behaviour.

(*E*)-*N*-(*tert*-Butyl)-*N*-(1,2-dichlorovinyl)-4-methylbenzenesulfonamide, 2h



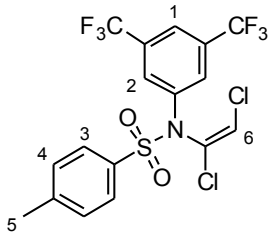
Synthesised from *t*-butyltosylamide (100 mg, 440 μmol, 1.0 eq.) with Cs_2CO_3 (215 mg, 660 μmol, 1.5 eq.), DMF (0.3 mL) and trichloroethylene (43 μL, 484 μmol, 1.1 eq.), taking approximately 1–2 hours following general procedure **1.2a**. Column chromatography (5% EtOAc/40-60 petroleum ether) afforded **2h** (119 mg, 369 μmol, 84%) as colourless crystals; **m.p.** 92–93 °C; $\mathbf{R_f}$ 0.75 (20% EtOAc/40-60 petroleum ether); **IR** (thin film, ν_{max} / cm^{-1}) 3087, 2984, 1598, 1351, 1159, 1107, 1089, 951, 812, 787, 706, 670; **^{1}H NMR** (400 MHz, $CDCl_3$) δ_H 7.84 (2H, d, *J* = 8.2 Hz, *H*2), 7.26 (2H, d, *J* = 8.2 Hz, *H*3), 6.39 (1H, s, *H*5), 2.41 (3H, s, *H*4), 1.52 (9H, s, *H*1); **^{13}C NMR** (101 MHz, $CDCl_3$) δ_c 143.9, 138.0, 131.5, 129.2, 128.5, 121.6, 64.3, 29.8, 21.5; **HRMS** (ES+) calc. for $C_{13}H_{17}{}^{35}Cl_2NNaO_2S$ $[M+Na]^+$ 344.0249, found 344.0243.

(*E*)-*N*-(1,2-Dichlorovinyl)-*N*-(4-methoxyphenyl)-4-methylbenzenesulfonamide, 2i



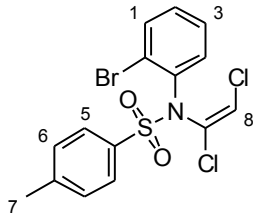
Synthesised from *N*-(4-methoxyphenyl)tosylamide (200 mg, 721 μmol, 1.0 eq.) with Cs_2CO_3 (352 mg, 1.08 mmol, 1.5 eq.), DMF (0.5 mL) and trichloroethylene (71 μL, 793 μmol, 1.1 eq.), taking approximately 1–2 hours following general procedure **1.2a**. Column chromatography (20% Et_2O/ 40-60 petroleum ether) afforded **2i** (251 mg, 674 μmol, 94%) as a beige solid. **m.p.** 134 °C; $\mathbf{R_f}$ 0.28 (20% EtOAc/40-60 petroleum ether); **IR** (thin film, ν_{max} / cm^{-1}) 2989, 1599, 1505, 1360, 1252.8, 1165, 1088, 1030, 811, 667; **^{1}H NMR** (400 MHz, $CDCl_3$) δ_H 7.63 (2H, d, *J* = 8.3 Hz, *H*4), 7.27–7.21 (4H, m, *H*5, *H*2), 6.85-6.79 (2H, m, *H*3), 6.40 (1H, s, *H*7), 3.79 (3H, s, *H*1), 2.42 (3H, s, *H*6); **^{13}C NMR** (101 MHz, $CDCl_3$) δ_c 160.0, 144.4, 135.5, 130.9, 130.6, 130.0, 129.3, 128.6, 119.8, 114.4, 55.4, 21.6; **HRMS** (ES+) calc. for $C_{16}H_{15}{}^{35}Cl_2NNaO_3S$ $[M+Na]^+$ 394.0042, found 394.0039.

(*E*)-*N*-(3,5-Bis(trifluoromethyl)phenyl)-*N*-(1,2-dichlorovinyl)-4-methylbenzenesulfonamide, 2j



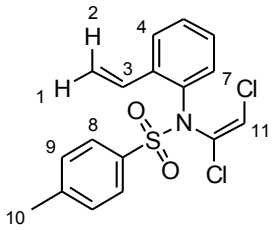
Synthesised from *N*-(3,5-bis(trifluoromethyl)phenyl)tosylamide (100 mg, 261 μmol, 1.0 eq.) with Cs_2CO_3 (171 mg, 523 μmol, 2.0 eq.), DMF (0.2 mL) and trichloroethylene (82 μL, 913 μmol, 3.5 eq.) following general procedure **1.2a** at 60 °C. The trichloroethylene was added in 3 equal portions (27 μL, 1.17 eq.), one portion every 1.5 hours; the reaction reached completion after approximately 5–6 hours. Column chromatography (10% Et_2O/40-60 petroleum ether) afforded **2j** (110 mg, 230 μmol, 88%) as yellow crystals; **m.p.** 86–87°C; $\mathbf{R_f}$ 0.65 (20% EtOAc/40-60 petroleum ether); **IR** (thin film, ν_{max} / cm^{-1}) 3092, 1598, 1463, 1368, 1276, 1169, 1133, 1088, 980, 814, 701, 663; **^{1}H NMR** (400 MHz, $CDCl_3$) δ_H 7.85 (1H, s, *H*1), 7.79 (2H, s, *H*2), 7.67 (2H, d, *J* = 8.4 Hz, *H*3), 7.31 (2H, d, *J* = 8.4 Hz, *H*4), 6.58 (1H, s, *H*6), 2.45 (3H, s, *H*5); **^{13}C NMR** (101 MHz, $CDCl_3$) δ_c 145.8, 139.3, 134.5, 133.0 (2C, q, *J* = 34.3 Hz), 129.8, 129.3, 128.6, 127.7 (2C, q, *J* = 3.2 Hz), 122.5 (2C, q, *J* = 273 Hz), 122.4, 122.2 (1C, spt, *J* = 3.6 Hz), 21.6; **^{19}F NMR** (376 MHz, $CDCl_3$) δ_F –63.1; **HRMS** (ES+) calc. for $C_{17}H_{11}{}^{35}Cl_2F_6NNaO_2S$ $[M+Na]^+$ 499.9684, found 499.9691.

(*E*)-*N*-(2-Bromophenyl)-*N*-(1,2-dichlorovinyl)-4-methylbenzenesulfonamide, 2k



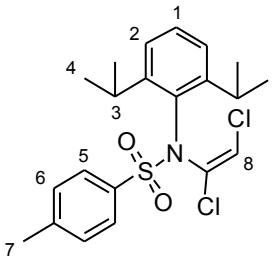
Synthesised from (2-bromophenyl)tosylamide (100 mg, 307 μmol, 1.0 eq.) with Cs_2CO_3 (150 mg, 460 μmol, 1.5 eq.), DMF (0.3 mL) and trichloroethylene (30 μL, 337 μmol, 1.1 eq.), taking approximately 1–2 hours following general procedure **1.2a**. Column chromatography (10% Et_2O/40-60 petroleum ether) afforded **2k** (93 mg, 221 μmol, 72%) as colourless crystals; **m.p.** 133–135 °C; $\mathbf{R_f}$ 0.37 (10% EtOAc/40-60 petroleum ether); **IR** (thin film, ν_{max} / cm^{-1}) 3075, 2922, 1597, 1470, 1369, 1289, 1227, 1169, 1088, 1048, 930, 813, 757, 707; **^{1}H NMR** (400 MHz, $CDCl_3$) δ_H 7.67 (2H, d, *J* = 8.3 Hz, *H*5), 7.62–7.55 (2H, m, *H*1), 7.34–7.20 (3H, m, *H*2, *H*3, *H*4) 7.26 (2H, d, *J* = 8.3 Hz, *H*6), 6.42 (1H, s, *H*8), 2.43 (3H, s, *H*7); **^{13}C NMR** (101 MHz, $CDCl_3$) δ_c 144.9, 135.7, 135.3, 134.2, 133.9, 130.7, 129.4, 129.3, 128.9, 127.5, 124.9, 119.4, 21.7; **HRMS** (ES+) calc. for $C_{15}H_{12}{}^{79}Br^{35}Cl_2NNaO_2S$ $[M+Na]^+$ 441.9041, found 441.9057.

(*E*)-*N*-(1,2-Dichlorovinyl)-*4*-methyl-N-(2-vinylphenyl)benzenesulfonamide, 2l



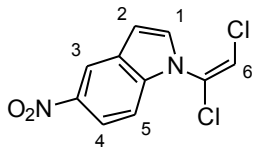
Synthesised from *N*-(2-vinylphenyl)tosylamide (145 mg, 530 μmol, 1.0 eq.) with K_2CO_3 (220 mg, 1.59 mmol, 3.0 eq.), anhydrous DMF (0.4 mL) and trichloroethylene (0.14 mL, 1.59 mmol, 3.0 eq.) following general procedure **1.2a**. Column chromatography (5% EtOAc/40-60 petroleum ether) afforded **2l** (161 mg, 437 μmol, 82%) as a pale grey solid; **m.p.** 102–104 °C; $\mathbf{R_f}$ 0.52 (20% EtOAc/40-60 petroleum ether); **IR** (thin film, ν_{max} / cm^{-1}) 3086, 1597, 1482, 1449, 1366, 1286, 1168, 1111, 1076, 928, 814, 772, 705, 675, 666; **^{1}H NMR** (400 MHz, $CDCl_3$) δ_H 7.66–7.59 (3H, m, *H*4, *H*8), 7.39–7.14 (6H, m, *H*3, *H*5, *H*6, *H*7, *H*9), 6.40 (1H, s, *H*11), 5.65 (1H, dd, *J* = 17.6, 1.2 Hz, *H*2), 5.24 (1H, dd, *J* = 11.0, 1.2 Hz, *H*1), 2.42 (3H, s, *H*10); **^{13}C NMR** (101 MHz, $CDCl_3$) δ_c 144.8, 138.6, 135.3, 134.6, 133.1, 131.2, 130.7, 129.7, 129.4, 128.9, 127.9, 126.4, 119.4, 116.0, 21.6; **HRMS** (ES+) calc. for $C_{17}H_{15}{}^{35}Cl_2NNaO_2S$ $[M+Na]^+$ 390.0093, found 390.0082.

(*E*)-*N*-(1,2-Dichlorovinyl)-*N*-(2,6-diisopropylphenyl)-4-methylbenzenesulfonamide, 2m



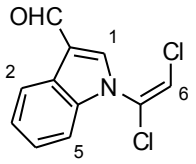
Synthesised from *N*-(2,6-diisopropylphenyl)tosylamide (100 mg, 302 µmol, 1.0 eq.) with Cs_2CO_3 (147 mg, 453 µmol, 1.5 eq.), DMF (0.2 mL) and trichloroethylene (30 µL, 332 µmol, 1.1 eq.), taking approximately 1 hour following general procedure **1.2a**. Column chromatography (20% Et_2O/40-60 petroleum ether) afforded **2m** (128 mg, 300 µmol, 99%) as pale yellow crystals; **m.p.** 140 °C; $\mathbf{R_f}$ 0.63 (20% EtOAc/40-60 petroleum ether); **IR** (thin film, ν_{max} / cm^{-1}) 2973, 1598, 1466, 1359, 1168, 1075, 932, 809, 666; **^{1}H NMR** (400 MHz, $CDCl_3$) δ_H 7.67–7.62 (2H, m, *H*5), 7.43–7.37 (1H, m, *H*1), 7.27–7.21 (4H, m, *H*2, *H*6), 6.19 (1H, s, *H*8), 3.37 (2H, spt, *J* = 6.6 Hz, *H*3), 2.41 (3H, s, *H*7), 1.17 (6H, d, *J* = 6.6 Hz, *H*4), 1.12 (6H, d, *J* = 6.6 Hz, *H*4); **^{13}C NMR** (101 MHz, $CDCl_3$) δ_c 150.6, 144.4, 136.9, 132.0, 131.7, 130.1, 129.1, 128.9, 125.3, 113.3, 28.9, 25.2, 24.0, 21.6; **HRMS** (ES+) calc. for $C_{21}H_{25}{}^{35}Cl_2NNaO_2S$ $[M+Na]^+$ 448.0875, found 448.0881.

(*E*)-*N*-(1,2-Dichlorovinyl)-5-nitro-1*H*-indole, 2n



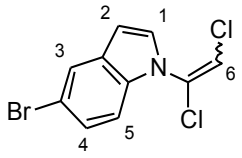
Synthesised from 5-nitroindole (100 mg, 617 µmol, 1.0 eq.) with Cs_2CO_3 (301 mg, 925 µmol, 1.5 eq.), DMF (0.5 mL) and trichloroethylene (61 µL, 678 µmol, 1.1 eq.), taking approximately 2–3 hours following general procedure **1.2a**. Column chromatography (10% EtOAc/40-60 petroleum ether) afforded **2n** (125 mg, 486 µmol, 79%) as yellow crystals; **m.p.** 74–75 °C; $\mathbf{R_f}$ 0.56 (20% EtOAc/40-60 petroleum ether); **IR** (thin film, ν_{max} / cm^{-1}) 3092, 1624, 1512, 1456, 1341, 1316, 1193, 1070, 898, 826, 740, 710; **^{1}H NMR** (400 MHz, $CDCl_3$) δ_H 8.57 (1H, d, *J* = 2.2 Hz, *H*3), 8.19 (1H, dd, *J* = 9.0, 2.2 Hz, *H*4), 7.39 (1H, d, *J* = 9.0 Hz, *H*5), 7.33 (1H, d, *J* = 3.5 Hz, *H*1), 6.83 (1H, dd, *J* = 3.5, 0.7 Hz, *H*2), 6.65 (1H, s, *H*6); **^{13}C NMR** (101 MHz, $CDCl_3$) δ_c 143.1, 137.8, 130.0, 128.2, 126.6, 118.6, 118.0, 115.6, 111.4, 107.4; **HRMS** (ES+) calc. for $C_{10}H_6{}^{35}Cl_2N_2NaO_2$ $[M+Na]^+$ 278.9699, found 278.9697.

(*E*)-*N*-(1,2-Dichlorovinyl)-1*H*-indole-3-carbaldehyde, 2o



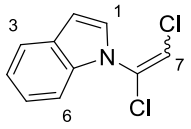
Synthesised from 1*H*-indole-3-carbaldehyde (100 mg, 689 μmol, 1.0 eq.) with Cs_2CO_3 (337 mg, 1.03 mmol, 1.5 eq.), DMF (0.5 mL) and trichloroethylene (68 μL, 758 μmol, 1.1 eq.), taking approximately 1–2 hours following general procedure **1.2a**. Column chromatography (10% Et_2O/40-60 petroleum ether) afforded **2o** (130 mg, 541 μmol, 79%) as a pale yellow solid; **m.p.** 85 °C; $\mathbf{R_f}$ 0.37 (20% EtOAc/40-60 petroleum ether); **IR** (thin film, ν_{max} / cm^{-1}) 3078, 1664, 1537, 1453, 1167, 1047, 827, 746; **^{1}H NMR** (400 MHz, $CDCl_3$) δ_H 10.10 (1H, s, C*H*O), 8.38–8.32 (1H, m, *H*2), 7.80 (1H, s, *H*1), 7.46–7.35 (3H, m, *H*3, *H*4, *H*5) 6.70 (1H, s, *H*6); **^{13}C NMR** (101 MHz, $CDCl_3$) δ_c 184.9, 137.3, 136.0, 126.4, 125.2, 124.8, 124.1, 122.4, 121.2, 116.5, 111.5; **HRMS** (ES+) calc. for $C_{11}H_7{}^{35}Cl_2NNaO$ $[M+Na]^+$ 261.9797, found 261.9804.

(*E*)-5-Bromo-1-(1,2-dichlorovinyl)-1*H*-indole, 2p



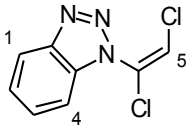
Synthesised from 5-bromoindole (100 mg, 510 μmol, 1.0 eq.) with Cs_2CO_3 (249 mg, 765 μmol, 1.5 eq.), DMF (0.4 mL) and trichloroethylene (50 μL, 561 μmol, 1.1 eq.), taking approximately 2–3 hours following the general procedure. Column chromatography (10% Et_2O/40-60 petroleum ether) afforded **2p** (101 mg, 347 μmol, 68%) as a colourless oil (yellows on standing); $\mathbf{R_f}$ 0.68 (20% EtOAc/40-60 petroleum ether); **IR** (thin film, ν_{max} / cm^{-1}) 3089, 1623, 1446, 1365, 1189, 1054, 876, 823, 714; **^{1}H NMR** (400 MHz, $CDCl_3$)* δ_H 7.78 (1H, d, *J* = 1.5 Hz, (*Z*)-*H*3), 7.66 (1H, d, *J* = 1.7 Hz, (*E*)-*H*3), 7.33 (1H, dd, *J* = 8.5, 2.0 Hz, (*Z*)-*H*4), 7.29 (1H, dd, *J* = 8.7, 1.7 Hz, (*E*)-*H*4), 7.13 (1H, d, *J* = 8.7 Hz, (*E*)/(*Z*)-*H*5), 7.06 (1H, d, *J* = 3.4 Hz, (*E*)/(*Z*)-*H*1), 6.50 (1H, dd, *J* = 3.4, 0.7 Hz, (*E*)/(*Z*)-*H*2), 6.46 (1H, s, (*Z*)-*H*6), 6.43 (1H, s, (*E*)-*H*6); **^{13}C NMR** (101 MHz, $CDCl_3$)* δ_c 133.8, 133.0, 131.6, 130.4, 128.1, 127.5, 127.3, 126.5, 126.0, 123.8, 123.1, 116.0, 115.4, 114.9, 114.2, 113.1, 112.9, 105.4, 100.7; **HRMS** (FI+) calc. for $C_{10}H_6{}^{79}Br\,{}^{35}Cl_2N$ $[M]^+$ 288.9061, found 288.9059. *Note: the spectra show a mixture of inseparable (*E*)/(*Z*) isomers (94:6 (*E*):(*Z*)).

(*E*)-1-(1,2-Dichlorovinyl)-1*H*-indole, 2q



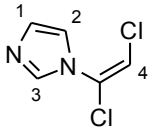
Synthesised from 1*H*-indole (100 mg, 854 μmol, 1.0 eq.), with NaH (68 mg (60% in mineral oil), 1.71 mmol, 2.0 eq.), anhydrous DMF (2 × 0.6 mL) and trichloroethylene (77 μL, 854 μmol, 1.0 eq.) following general procedure **1.2c**. Column chromatography (40-60 petroleum ether) afforded **2q** (146 mg, 688 μmol 80%) as a colourless oil; $\mathbf{R_f}$ 0.73 (20% EtOAc/40-60 petroleum ether); **IR** (thin film, ν_{max} / cm^{-1}) 3088, 1739, 1622, 1452, 1326, 1209, 1190, 886, 820, 739, ; **^{1}H NMR** (400 MHz, $CDCl_3$)* δ_H 7.55 (1H, d, *J* = 7.8 Hz, *H*3), 7.32–7.26 (1H, m, *H*6), 7.21 (1H, td, *J* = 7.6, 1.1 Hz, *H*5), 7.17–7.10 (1H, m, *H*4), 7.06 (1H, d, *J* = 3.4 Hz, *H*1) 6.58 (1H, dd, *J* = 3.4, 0.7 Hz, *H*2), 6.40 (1H, s, *H*7); **^{13}C NMR** (101 MHz, $CDCl_3$)* δ_c 135.1, 128.7, 128.0, 126.9, 123.1, 121.5, 121.3, 113.6, 111.5, 106.0; **HRMS** (FI+) calc. for $C_{10}H_7{}^{35}Cl_2N$ $[M]^+$ 210.9956, found 210.9954. *Note: the spectra show a mixture of inseparable (*E*)/(*Z*) isomers (93:7 (*E*):(*Z*)), data above is for (*E*)-isomer only.

(*E*)-1-(1,2-Dichlorovinyl)-1*H*-benzo[*d*][1,2,3]triazole, 2r



Synthesised from 1*H*-benzotriazole (100 mg, 839 μmol, 1.0 eq.) with Cs_2CO_3 (410 mg, 1.26 mmol, 1.5 eq.), DMF (0.6 mL) and trichloroethylene (83 μL, 923 μmol, 1.1 eq.), taking less than 1 hour following the general procedure. Column chromatography (10% Et_2O/40-60 petroleum ether) afforded **2r** (144 mg, 673 μmol, 80%) as a colourless oil; $\mathbf{R_f}$ 0.41 (20% EtOAc/40-60 petroleum ether); **IR** (thin film, ν_{max} / cm^{-1}) 3086, 1624, 1451, 1382, 1289, 1155, 1032, 938, 834, 743; **^{1}H NMR** (400 MHz, $CDCl_3$) δ_H 8.10 (1H, d, *J* = 8.3 Hz, *H*1), 7.58 (1H, ddd, *J* = 8.3, 6.9, 1.2 Hz, *H*3), 7.52 (1H, d, *J* = 8.3 Hz, *H*4), 7.43 (1H, ddd, *J* = 8.3, 6.9, 1.2 Hz, *H*2), 6.81 (1H, s, *H*5); **^{13}C NMR** (101 MHz, $CDCl_3$) δ_c 145.1, 131.8, 129.0, 124.9, 124.4, 120.4, 117.9, 110.2; **HRMS** (ES+) calc. for $C_8H_5{}^{35}Cl_2N_3Na$ $[M+Na]^+$ 235.9753, found 235.9755.

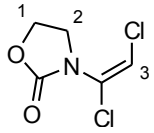
(*E*)-*N*-(1,2-Dichlorovinyl)-1*H*-imidazole, 2s



Synthesised from imidazole (100 mg, 1.47 mmol, 1.0 eq.) with Cs_2CO_3 (718 mg, 2.21 mmol, 1.5 eq.), DMF (1 mL) and trichloroethylene (0.15 mL, 1.62 mmol, 1.1 eq.), taking less than 1 hour following the general procedure. Column chromatography (30% EtOAc/40-60 petroleum ether) afforded **2s** (198 mg, 1.21 mmol,

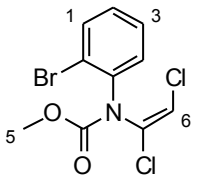
83%) as a pale yellow oil; **R_f** 0.15 (20% EtOAc/40-60 petroleum ether); **IR** (thin film, ν_{max} / cm^{-1}) 3093, 1626, 1516, 1477, 1371, 1304, 1204, 1103, 1073, 1030, 898, 830, 730, 652, 631; **^{1}H NMR** (400 MHz, $CDCl_3$) δ_H 7.71 (1H, app. s, *H*3), 7.09 (1H, dd, *J* = 1.6, 1.4 Hz, *H*2), 7.04–7.01 (1H, m, *H*1), 6.28 (1H, s, *H*4); **^{13}C NMR** (101 MHz, $CDCl_3$) δ_c 136.9, 129.5, 124.9, 118.5, 111.1; **MS** (ESI^+) *m/z* 163.0 (100, $[\{^{35}Cl_2\}M+H]^+$), 185.0 (75, $[\{^{35}Cl_2\}M+Na]^+$), 187.0 (50, $[\{^{35}Cl^{37}Cl\}M+Na]^+$), 189.0 (8, $[\{^{37}Cl_2\}M+Na]^+$). Data are consistent with literature values.[2]

(*E*)-3-(1,2-Dichlorovinyl)oxazolidin-2-one, 2t



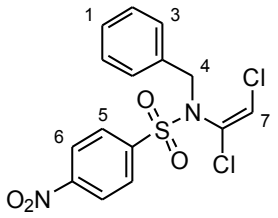
Synthesised from 2-oxazolidinone (100 mg, 1.15 mmol, 1.0 eq.) with Cs_2CO_3 (561 mg, 1.72 mmol, 1.5 eq.), DMF (1 mL) and trichloroethylene (0.11 mL, 1.26 mmol, 1.1 eq.), taking approximately 1–2 hours following the general procedure. Column chromatography (25% EtOAc/40-60 petroleum ether) afforded **2t** (179 mg, 0.98 mmol, 85%) as colourless crystals. Crystals suitable for X-ray diffraction were grown by vapour diffusion of pentane into a concentrated solution of **2t** in benzene; **R_f** 0.10 (10% EtOAc/40-60 petroleum ether); **IR** (thin film, ν_{max} / cm^{-1}) 3094, 1757, 1622, 1480, 1395, 1312, 1221, 1100, 1033, 895, 820, 756; **^{1}H NMR** (400 MHz, $CDCl_3$) δ_H 6.34 (1H, s, *H*3), 4.54–4.43 (2H, m, *H*1), 3.88–3.78 (2H, m, *H*2); **^{13}C NMR** (101 MHz, $CDCl_3$) δ_c 153.7, 127.0, 116.8, 62.8, 44.0; **HRMS** (ES+) calc. for $C_5H_5{}^{35}Cl_2NNaO_2$ $[M+Na]^+$ 203.9590, found 203.9591.

(*E*)-Methyl (2-bromophenyl)(1,2-dichlorovinyl)carbamate, 2u



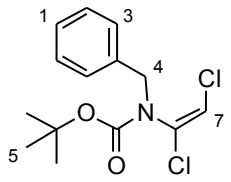
Synthesised from methyl (2-bromophenyl)carbamate (100 mg, 435 µmol, 1.0 eq.) with Cs_2CO_3 (212 mg, 652 µmol, 1.5 eq.), DMF (0.3 mL) and trichloroethylene (43 µL, 478 µmol, 1.1 eq.), taking approximately 1–2 hours following the general procedure. Column chromatography (10% EtOAc/40-60 petroleum ether) afforded **2u** (123 mg, 378 µmol, 87%) as a low melting solid; **R_f** 0.31 (10% EtOAc/40-60 petroleum ether); **IR** (thin film, ν_{max} / cm^{-1}) 3074, 2949, 1740, 1475, 1439, 1309, 1264, 1157, 1070, 1019, 527, 757; **^{1}H NMR** (400 MHz, $CDCl_3$)* δ_H 7.66 (1H, dd, *J* = 8.1, 1.2 Hz, *H*1), 7.45–7.32 (2H, m, *H*2, *H*3), 7.27–7.19 (1H, m, H*4*), 6.33 (1H, br. s, *H*6), 3.82 and 3.80 (3H, br. s and s, *H*5); **^{13}C NMR** (101 MHz, $CDCl_3$)* δ_c 152.0, 137.3, 133.8, 131.1, 129.8, 128.8, 128.5, 123.5, 155.7, 54.1; **HRMS** (ES+) calc. for $C_{10}H_8{}^{79}Br^{35}Cl_2NNaO_2$ $[M+Na]^+$ 345.9008, found 345.9017. *Note that the spectra show a rotameric nature.

(*E*)-*N*-Benzyl-*N*-(1,2-dichlorovinyl)-4-nitrobenzenesulfonamide, 2v



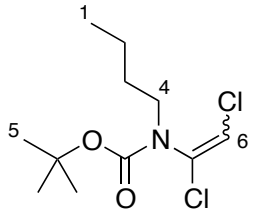
Synthesised from *N*-benzyl nosylamide (200 mg, 684 μmol, 1.0 eq.) with Cs_2CO_3 (445 mg, 1.37 mmol, 2.0 eq.), DMF (0.6 mL) and trichloroethylene (0.19 mL, 2.05 mmol, 3.0 eq.) following the general procedure. The trichloroethylene was added in 3 equal portions (63 μL, 1.0 eq.), one portion every 1.5 hours; and reaction completion occurred after approximately 5–6 hours. Column chromatography (10% EtOAc/40-60 petroleum ether) afforded **2v** (235 mg, 607 μmol, 89%) as yellow crystals; **m.p.** 163–164 °C; $\mathbf{R_f}$ 0.57 (20% EtOAc/40-60 petroleum ether); **IR** (thin film, ν_{max} / cm^{-1}) 3105, 1607, 1531, 1402, 1350, 1172, 1089, 1028, 855, 802, 738; **^{1}H NMR** (400 MHz, $CDCl_3$) δ_H 8.44–8.35 (2H, m, *H*6), 8.17–8.07 (2H, m, *H*5), 7.36–7.27 (5H, m, *H*1, *H*2, *H*3), 6.34 (1H, s, *H*7), 5.28–3.70 (2H, br. m, *H*4); **^{13}C NMR** (101 MHz, $CDCl_3$) δ_c 150.6, 144.0, 132.5, 129.6, 129.5, 128.8, 128.5, 124.3, 122.6, 52.5; **HRMS** (EI+) calc. for $C_{15}H_{12}{}^{35}Cl_2NO_2S$ $[M]^+$ 385.9895, found 385.9908. Note: a single ^{13}C resonance is obscured due to signal overlap.

(*E*)-*tert*-Butyl benzyl(1,2-dichlorovinyl)carbamate, 2w



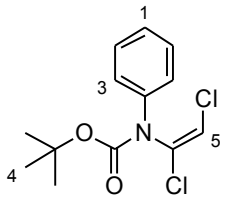
Synthesised from *t*-butyl benzylcarbamate (100 mg, 482 μmol, 1.0 eq.) with NaH (41 mg (60% in mineral oil), 1.01 mmol, 2.1 eq.), anhydrous DMF (2 × 0.3 mL), and trichloroethylene (43 μL, 482 μmol, 1.0 eq.) following general procedure **1.2b**. Column chromatography (40-60 petroleum ether → 5% Et_2O/40-60 petroleum ether) afforded **2w** (97 mg, 321 μmol, 67%) as a colourless oil; $\mathbf{R_f}$ 0.72 (20% EtOAc/40-60 petroleum ether); **IR** (thin film, ν_{max} / cm^{-1}) 2924, 2854, 1722, 1629, 1456, 1368, 1315, 1239, 1155, 930, 859, 825, 740, 699; **^{1}H NMR** (400 MHz, $CDCl_3$) δ_H 7.42–7.25 (5H, m, *H*1, *H*2, *H*3), 6.08 (1H, br. s, *H*7), 4.96–4.31 (2H, br. m, *H*4), 1.50 (9H, s, *H*5); **^{13}C NMR** (101 MHz, $CDCl_3$) δ_c 152.2, 135.9, 131.7, 128.9, 128.2, 127.7, 115.3, 82.1, 49.8, 28.0; **HRMS** (ES+) calc. for $C_{14}H_{17}{}^{35}Cl_2NNaO_2$ $[M+Na]^+$ 324.0529, found 324.0524.

(*E*)-*tert*-Butyl butyl(1,2-dichlorovinyl)carbamate, 2x



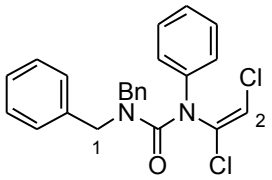
Synthesised from *t*-butyl butylcarbamate (100 mg, 577 μmol, 1.0 eq.) with NaH (49 mg (60% in mineral oil), 1.21 mmol, 2.1 eq.), anhydrous DMF (2 × 0.4 mL), and trichloroethylene (49 μL, 577 μmol, 1.0 eq.) following general procedure **1.2b**. Column chromatography (40-60 petroleum ether) afforded **2x** (90 mg, 335 μmol, 58%) as a colourless oil; $\mathbf{R_f}$ 0.80 (20% EtOAc/40-60 petroleum ether); **IR** (thin film, ν_{max} / cm^{-1}) 2962, 1719, 1457, 1368, 1302, 1254, 1148, 1087, 916, 823; **^{1}H NMR** (400 MHz, $CDCl_3$)* δ_H 6.16 (1H, br. s, *H*6), 3.64–3.16 (2H, br. m, *H*4), 1.68–1.47 (2H, br. m, *H*3), 1.46 (9H, s, H5), 1.39–1.25 (2H, br. m, *H*2), 0.91 (3H, t, *J* = 7.3 Hz, *H*1); **^{13}C NMR** (101 MHz, $CDCl_3$)* δ_c 152.2, 132.2, 114.7, 81.6, 45.3, 29.9, 28.0, 20.0, 13.7; **HRMS** (FI+) calc. for $C_{11}H_{19}{}^{35}Cl_2NO_2$ $[M]^+$ 267.0793, found 267.0789. * Note: the spectra show a mixture of inseparable (*E*)/(*Z*) isomers (88:12 (*E*):(*Z*)), data above for (*E*) isomer only.

(*E*)-*tert*-Butyl (1,2-dichlorovinyl)(phenyl)carbamate, 2y



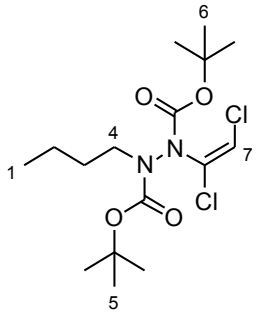
Synthesised from *t*-butyl phenylcarbamate (100 mg, 517 μmol, 1.0 eq.) with TBAHS (35 mg, 104 μmol, 0.2 eq.), toluene (1.5 mL), CH_2Cl_2 (1 mL), trichloroethylene (140 μL, 1.55 mmol, 3.0 eq.) and 25% w/v aqueous NaOH (1.5 mL) following general procedure **1.2c**. Column chromatography (5% Et_2O/40-60 petroleum ether) afforded **2y** (142 mg, 493 μmol, 95%) as a pale yellow oil; $\mathbf{R_f}$ 0.67 (20% EtOAc/40-60 petroleum ether); **IR** (thin film, ν_{max} / cm^{-1}) 3081, 2928, 1730, 1598, 1495, 1369, 1315, 1154, 1014, 900, 826, 756, 693; **^{1}H NMR** (400 MHz, $CDCl_3$) δ_H 7.41–7.34 (4H, m, *H*2*, H*3), 7.41–7.31–7.24 (1H, m, *H*1), 6.31 (1H, s, *H*5), 1.52 (9H, s, *H*4); **^{13}C NMR** (101 MHz, $CDCl_3$) δ_c 151.3, 138.5, 132.0, 128.9, 127.0, 125.7, 115.9, 82.8, 28.0; **MS** (ESI+) *m/z* 232.0 (100, $[\{^{35}Cl_2\}M\text{-}t\text{Bu}+2H]^+$), 234.1 (69, $[\{^{35}Cl^{37}Cl\}M\text{-}t\text{Bu}+2H]^+$), 236.0 (15, $[\{^{37}Cl_2\}M\text{-}t\text{Bu}+2H]^+$), 310.1 (26, $[\{^{35}Cl_2\}M+Na]^+$), 234.1 (19, $[\{^{35}Cl^{37}Cl\}M+Na]^+$). Data are consistent with literature values.[2]

(*E*)-1,1-Dibenzyl-3-(1,2-dichlorovinyl)-3-phenylurea, 2z



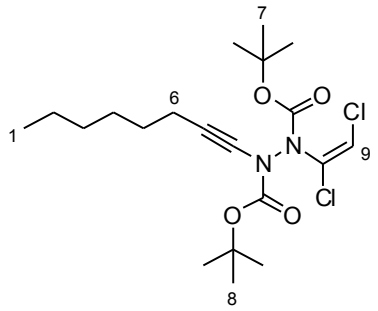
Synthesised from *N*,*N*-dibenzyl-*N*'-phenylurea (500 mg, 1.58 mmol, 1.0 eq.) with TBAHS (107 mg, 316 μmol, 0.2 eq.), toluene (5 mL), CH_2Cl_2 (4 mL), trichloroethylene (0.40 mL, 4.74 mmol, 3.0 eq.) and 25% w/v aqueous NaOH (5 mL) following general procedure **1.2c**. Column chromatography (5% Et_2O/40-60 petroleum ether) afforded **2z** (572 mg, 1.39 mmol, 88%) as colourless needles; **m.p.** 105–107 °C; $\mathbf{R_f}$ 0.65 (20% EtOAc/40-60 petroleum ether); **IR** (thin film, ν_{max} / cm^{-1}) 2909, 1669, 1595, 1494, 1455, 1404, 1227, 1142, 1079, 908, 814, 731, 694; ^{1}**H NMR** (400 MHz, $CDCl_3$) δ_H 7.34–7.03 (15H, m, Ph*H* (×3)), 6.25 (1H, s, *H*2), 4.35 (1H, s, *H*1); ^{13}**C NMR** (101 MHz, $CDCl_3$) δ_c 157.9, 140.7, 136.1, 133.6, 129.5, 128.5, 128.4, 127.6, 126.2, 124.1, 113.9, 50.4; **HRMS** (ES+) calc. for $C_{23}H_{20}{}^{35}Cl_2N_2NaO$ $[M+Na]^+$ 433.0845, found 433.0842.

(*E*)-Di-*tert*-butyl 1-butyl-2-(1,2-dichlorovinyl)hydrazine-1,2-dicarboxylate, 2aa



Synthesised from di-*t*-butyl 1-butylhydrazine-1,2-dicarboxylate[3] (150 mg, 520 μmol, 1.0 eq.) with TBAHS (35 mg, 104 μmol, 0.2 eq.), toluene (1.5 mL), trichloroethylene (0.14 mL, 1.56 mmol, 3.0 eq.) and 25% w/v aqueous NaOH (1.5 mL) following general procedure **1.2c**. Column chromatography (40-60 petroleum ether → 5% Et_2O/40-60 petroleum ether) afforded **2aa** (151 mg, 394 μmol, 76%) as pale yellow oil; $\mathbf{R_f}$ 0.79 (20% EtOAc/40-60 petroleum ether); **IR** (thin film, ν_{max} / cm^{-1}) 2978, 1744, 1716, 1456, 1393, 1368, 1298, 1255, 1147, 831; ^{1}**H NMR** (400 MHz, $CDCl_3$)* δ_H 6.32–6.05 (1H, m, *H*7), 3.63–3.15 (2H, br. m, *H*4), 1.70–1.53 (2H, br. m, *H*3), 1.52–1.37 (18H, br. m, *H*5, *H*6), 1.36–1.19 (2H, br. m, *H*2), 0.99–0.80 (3H, br. m, *H*1); ^{13}**C NMR** (101 MHz, $CDCl_3$)* δ_c 154.2, 154.0, 150.2, 150.0, 130.5, 129.6, 115.8, 115.3, 114.5, 114.0, 83.1, 83.0, 81.5, 81.3, 50.5, 49.9, 49.0, 48.6, 30.1, 29.9, 29.7, 28.1, 28.0, 27.8, 19.9, 19.8, 13.7; **HRMS** (ES+) calc. for $C_{16}H_{28}{}^{35}Cl_2N_2NaO_4$ $[M+Na]^+$ 405.1318, found 405.1312. *Note that the spectra show a highly rotameric nature.

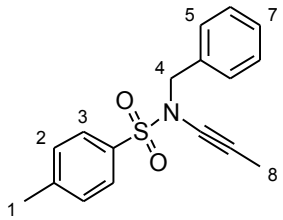
(*E*)-Di-*tert*-butyl 1-(1,2-dichlorovinyl)-2-(oct-1-yn-1-yl)hydrazine-1,2-dicarboxylate, 2bb



Synthesised from di-*t*-butyl 1-(oct-1-yn-1-yl)hydrazine-1,2-dicarboxylate[4] (100 mg, 294 µmol, 1.0 eq.) with TBAHS (20 mg, 58.7 µmol, 0.2 eq.), toluene (0.9 mL) trichloroethylene (79 µL, 882 µmol, 3.0 eq.) and 25% w/v aqueous NaOH (0.9 mL) following general procedure **1.2c**. Column chromatography (5% EtOAc/40-60 petroleum ether) afforded **2bb** (105 mg, 241 µmol, 82%) as a pale yellow oil; $\mathbf{R_f}$ 0.63 (20% EtOAc/40-60 petroleum ether); **IR** (thin film, ν_{max} / cm^{-1}) 2932, 1752, 1458, 1370, 1321, 1253, 1151, 853; **^{1}H NMR** (400 MHz, $CDCl_3$)* δ_H 6.30 and 6.23 (1H, br. m, *H*9), 2.28 (2H, br. t, *J* = 6.4 Hz, *H*6), 1.58–1.17 (26H, br. m, *H*2, *H*3, *H*4, *H*5, *H*7, *H*8), 0.85 (3H, br. t, *J* = 6.7 Hz, *H*1); **^{13}C NMR** (101 MHz, $CDCl_3$)* δ_c 152.0, 148.9, 138.9, 128.9, 128.4, 117.4, 116.8, 84.1, 83.8, 72.5, 71.6, 31.3, 28.4, 27.9, 28.0, 27.8, 22.5, 18.4, 14.0; **HRMS** (ES+) calc. for $C_{20}H_{32}{}^{35}Cl_2N_2NaO_4$ $[M+Na]^+$ 457.1631, found 457.1627. *Note that the spectra show a highly rotameric nature.

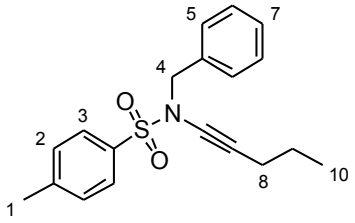
1.4b Ynamides:

***N*-Benzyl-4-methyl-*N*-(prop-1-yn-1-yl)benzenesulfonamide, 1a**



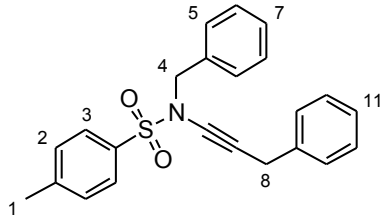
Synthesised from (*E*)-*N*-benzyl-*N*-(1,2-dichlorovinyl)tosylamide **2a** (100 mg, 281 µmol, 1.0 eq.) in anhydrous THF (2.8 mL) with phenyllithium (0.31 mL of a 2.0 M solution in dibutyl ether, 618 µmol, 2.2 eq.) and methyl iodide (21 µL, 337 µmol, 1.2 eq.) following general procedure **1.2d**. Column chromatography (5% EtOAc/40-60 petroleum ether) afforded **1a** (71 mg, 237 µmol, 85%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ_H 7.65 (2H, d, *J* = 8.3 Hz, *H*3), 7.27–7.18 (7H, m, *H*2, *H*5, *H*6, *H*7), 4.34 (2H, s, *H*4), 2.34 (3H, s, *H*1), 1.71 (3H, s, *H*8); **^{13}C NMR** (101 MHz, $CDCl_3$) δ_c 144.5, 134.9, 134.8, 129.7, 128.7, 128.3, 128.2, 127.7, 72.3, 66.3, 55.6, 21.7, 3.4; **MS** (ESI+) *m/z* 300.1 (100, $[M+H]^+$). Data are consistent with literature values.[4]

***N*-Benzyl-4-methyl-*N*-(pent-1-yn-1-yl)benzenesulfonamide, 1b**



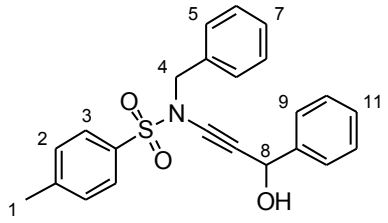
Synthesised from (*E*)-*N*-benzyl-*N*-(1,2-dichlorovinyl)tosylamide **2a** (100 mg, 281 μmol, 1.0 eq.) in anhydrous THF (2.8 mL) with phenyllithium (0.31 mL of a 2.0 M solution in dibutyl ether, 618 μmol, 2.2 eq.) and 1-iodopropane (33 μL, 337 μmol, 1.2 eq.) following general procedure **1.2d**. Column chromatography (10% EtOAc/40-60 petroleum ether) afforded **1b** (73 mg, 223 μmol, 79%) as a pale yellow oil; $\mathbf{R_f}$ 0.46 (10% EtOAc/40-60 petroleum ether); **IR** (thin film, ν_{max} / cm^{-1}) 2963, 2936, 2271, 1597, 1496, 1456, 1362, 1168, 1091, 1025, 814, 701, 654; **^{1}H NMR** (400 MHz, $CDCl_3$) δ_H 7.75 (2H, d, *J* = 8.3 Hz, *H*3), 7.34–7.24 (7H, m, *H*2, *H*5, *H*6, *H*7), 4.44 (2H, s, *H*4), 2.44 (3H, s, *H*1), 2.14 (2H, t, *J* = 7.1 Hz, *H*8), 1.40 (2H, sxt, *J* = 7.1 Hz, *H*9), 0.83 (3H, t, *J* = 7.1 Hz, *H*10); **^{13}C NMR** (101 MHz, $CDCl_3$) δ_c 144.2, 134.8, 134.7, 129.5, 128.7, 128.3, 128.0, 127.6, 73.4, 70.7, 55.5, 22.2, 21.6, 20.3, 13.2; **HRMS** (ES+) calc. for $C_{19}H_{21}NNaO_2S$ $[M+Na]^+$ 350.1185, found 350.1190.

***N*-Benzyl-4-methyl-*N*-(3-phenylprop-1-yn-1-yl)benzenesulfonamide, 1c**



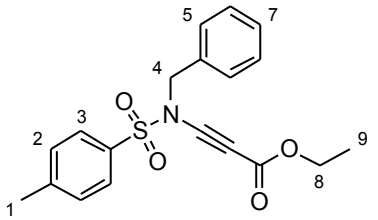
Synthesised from (*E*)-*N*-benzyl-*N*-(1,2-dichlorovinyl)tosylamide **2a** (100 mg, 281 μmol, 1.0 eq.) in anhydrous THF (2.8 mL) with phenyllithium (0.31 mL of a 2.0 M solution in dibutyl ether, 618 μmol, 2.2 eq.) and benzyl bromide (40 μL, 337 μmol, 1.2 eq.) following general procedure **1.2d**. Column chromatography (10% Et_2O /40-60 petroleum ether) afforded **1c** (80 mg, 213 μmol, 76%) as a colourless oil; $\mathbf{R_f}$ 0.47 (20% EtOAc/40-60 petroleum ether); **IR** (thin film, ν_{max} / cm^{-1}) 3031, 2932, 2255, 1597, 1495, 1454, 1362, 1168, 968; **^{1}H NMR** (400 MHz, $CDCl_3$) δ_H 7.72 (2H, d, *J* = 8.3 Hz, *H*3), 7.31–7.17 (10H, m, Ph*H* (×2), *H*2), 7.11-7.03 (2H, m, Ph*H*), 4.47 (2H, s, *H*4), 3.57 (2H, s, *H*8), 2.41 (3H, s, *H*1); **^{13}C NMR** (101 MHz, $CDCl_3$) δ_c 144.4, 136.7, 134.6, 134.6, 129.6, 128.7, 128.4, 128.3, 128.1, 127.7, 127.7, 126.4, 75.5, 66.5, 55.4, 24.7, 21.6; **HRMS** (ES+) calc. for $C_{23}H_{21}NNaO_2S$ $[M+Na]^+$ 398.1185, found 398.1190.

***N*-Benzyl-*N*-(3-hydroxy-3-phenylprop-1-yn-1-yl)-4-methylbenzenesulfonamide, 1d**



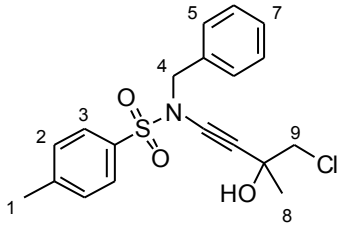
Synthesised from (*E*)-*N*-benzyl-*N*-(1,2-dichlorovinyl)tosylamide **2a** (100 mg, 281 μmol, 1.0 eq.) in anhydrous THF (2.8 mL) with phenyllithium (0.31 mL of a 2.0 M solution in dibutyl ether, 618 μmol, 2.2 eq.) and benzaldehyde (34 μL, 337 μmol, 1.2 eq.) following general procedure **1.2d**. Column chromatography (20% EtOAc/40-60 petroleum ether) afforded **1d** (86 mg, 220 μmol, 78%) as a colourless oil; **^{1}H NMR** (400 MHz, $CDCl_3$) δ_H 7.69 (2H, d, J = 8.3 Hz, *H*3), 7.31–7.22 (12H, Ph*H* (×2), *H*2), 5.44 (1H, d, J = 5.4 Hz, *H*8), 4.52 (1H, AB d, J_{AB} = 13.8 Hz, $H4_A$), 4.44 (2H, AB d, J_{BA} = 13.8 Hz, $H4_B$), 2.41 (3H, s, *H*1), 2.35 (1H, d, J = 5.4 Hz, O*H*); **^{13}C NMR** (101 MHz, $CDCl_3$) δ_c 144.7, 140.5, 134.4, 134.2, 129.7, 128.8, 128.5, 128.4, 128.3, 128.1, 127.7, 126.6, 80.2, 71.6, 64.6, 55.3, 21.6; **MS** (ESI^+) *m/z* 378.1 (63, $[M+H]^+$), 400.1 (100, $[M+Na]^+$). Data are consistent with literature values.[5]

Ethyl 3-(*N*-benzyl-4-methylphenylsulfonamido)propiolate, 1e



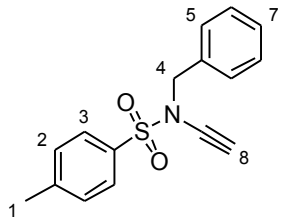
Synthesised from (*E*)-*N*-benzyl-*N*-(1,2-dichlorovinyl)tosylamide **2a** (100 mg, 281 μmol, 1.0 eq.) in anhydrous THF (2.8 mL) with phenyllithium (0.31 mL of a 2.0 M solution in dibutyl ether, 618 μmol, 2.2 eq.) and ethyl chloroformate (32 μL, 337 μmol, 1.2 eq.) following general procedure **1.2d**. Column chromatography (10% EtOAc/40-60 petroleum ether) afforded **1e** (84 mg, 235 μmol, 84%) as a colourless oil; **^{1}H NMR** (400 MHz, $CDCl_3$) δ_H 7.71 (2H, d, J = 8.4 Hz, *H*3), 7.37–7.22 (7H, m, *H*2, *H*5, *H*6, *H*7), 4.62 (2H, s, *H*4), 4.18 (2H, q, J = 7.2 Hz, *H*8), 2.44 (3H, s, *H*1), 1.28 (3H, t, J = 7.2 Hz, *H*9); **^{13}C NMR** (101 MHz, $CDCl_3$) δ_c 154.0, 145.4, 134.3, 133.5, 129.9, 128.64, 128.60, 127.8, 82.7, 68.1, 61.5, 55.5, 21.7, 14.1;* **MS** (ES^+) *m/z* 358.1 (78, $[M+H]^+$), 380.1 (100, $[M+Na]^+$). Data are consistent with literature values.[6] * Note: a single ^{13}C resonance is obscured due to signal overlap.

***N*-Benzyl-*N*-(4-chloro-3-hydroxy-3-methylbut-1-yn-1-yl)-4-methylbenzenesulfonamide, 1f**



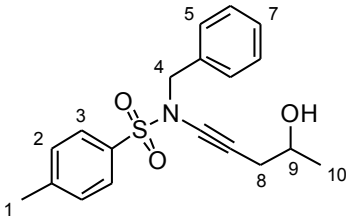
Synthesised from (*E*)-*N*-benzyl-*N*-(1,2-dichlorovinyl)tosylamide **2a** (100 mg, 281 μmol, 1.0 eq.) in anhydrous THF (2.8 mL) with phenyllithium (0.31 mL of a 2.0 M solution in dibutyl ether, 618 μmol, 2.2 eq.) and chloroacetone (27 μL, 337 μmol, 1.2 eq.) following general procedure **1.2d**. Column chromatography (4% EtOAc/10% CH_2Cl_2/40-60 petroleum ether) afforded **1f** (78 mg, 205 μmol, 73%) as a colourless oil; $\mathbf{R_f}$ 0.24 (20% EtOAc/40-60 petroleum ether); **IR** (thin film, ν_{max} / cm^{-1}) 3502, 2932, 2247, 1597, 1496, 1364, 1168, 1090, 1022, 738, 700, 666; **^{1}H NMR** (400 MHz, $CDCl_3$) δ_H 7.75 (2H, d, J = 8.6 Hz, *H*3), 7.30 (2H, d, J = 8.7 Hz, *H*2), 7.31–7.22 (5H, m, *H*5, *H*6, *H*7), 4.47 (1H, AB d, J_{AB} = 13.9 Hz, $H4_A$), 4.43 (1H, AB d, J_{BA} = 13.9 Hz, $H4_B$), 3.51 (1H, AB d, J_{AB} = 10.3 Hz, $H9_A$Cl), 3.45 (1H, AB d, J_{BA} = 10.3 Hz, $H9_B$), 2.77 (1H, s, O*H*), 2.43 (3H, s, *H*1), 1.42 (3H, s, *H*8); **^{13}C NMR** (101 MHz, $CDCl_3$) δ_c 144.8, 134.3, 134.0, 129.7, 129.0, 128.4, 128.4, 127.7, 78.1, 72.4, 67.8, 55.3, 54.0, 26.8, 21.6; **HRMS** (ES+) calc. for $C_{19}H_{20}{}^{35}ClNNaO_3S$ $[M+Na]^+$ 400.0745, found 400.0748.

***N*-Benzyl-*N*-ethynyl-4-methylbenzenesulfonamide, 1g**



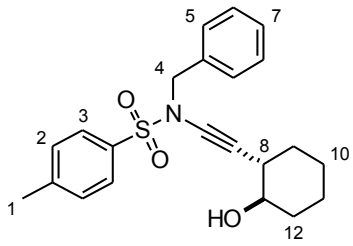
Synthesised from (*E*)-*N*-benzyl-*N*-(1,2-dichlorovinyl)tosylamide **2a** (100 mg, 281 μmol, 1.0 eq.) in anhydrous THF (2.8 mL) with phenyllithium (0.31 mL of a 2.0 M solution in dibutyl ether, 618 μmol, 2.2 eq.). Water and Et_2O (2 mL each) was added and the reaction worked up following general procedure **1.2d**. Column chromatography (10% EtOAc/40-60 petroleum ether) afforded **1g** (73 mg, 256 μmol, 91%) as colourless crystals; **m.p.** 99–101 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ_H 7.77 (2H, d, J = 8.3 Hz, *H*3), 7.36–7.26 (7H, m, *H*2, *H*5, *H*6, *H*7), 4.50 (2H, s, *H*4), 2.70 (1H, s, *H*8), 2.44 (3H, s, *H*1); **^{13}C NMR** (101 MHz, $CDCl_3$) δ_c 144.8, 134.6, 134.3, 129.8, 128.7, 128.5, 128.4, 127.7, 76.2, 59.7, 55.2, 21.7; **MS** (ESI+) *m/z* 286.1 (100, $[M+H]^+$), 318.1 (86, $[M+MeOH+H]^+$). Data are consistent with literature values.[7] Note that this compound is sensitive to moisture.

***N*-benzyl-*N*-(4-hydroxypent-1-yn-1-yl)-4-methylbenzenesulfonamide, 1h**



Synthesised from (*E*)-*N*-benzyl-*N*-(1,2-dichlorovinyl)tosylamide **2a** (100 mg, 281 µmol, 1.0 eq.) in anhydrous THF (2.8 mL) with phenyllithium (0.31 mL of a 2.0 M solution in dibutyl ether, 618 µmol, 2.2 eq.), followed by propylene oxide (23 µL, 337 µmol, 1.2 eq.) and $BF_3{\cdot}Et_2O$ (18 µL, 377 µmol, 1.2 eq), according to procedure **1.2d**. Column chromatography (20% EtOAc/40-60 petroleum ether → 50% EtOAc/40-60 petroleum ether) afforded **1h** (79 mg, 229 µmol, 82%) as a colourless oil; $\mathbf{R_f}$ 0.37 (50% EtOAc/40-60 petroleum ether); **IR** (thin film, ν_{max} / cm^{-1}) 3397, 2925, 2253, 1597, 1496, 1360, 1168, 1089, 814, 709, 656; **^{1}H NMR** (400 MHz, $CDCl_3$) δ_H 7.74 (2H, d, *J* = 8.3 Hz, *H*3), 7.35–7.20 (7H, m, *H*2, *H*5, *H*6, *H*7), 4.43 (2H, s, *H*4), 3.73 (1H, ABX ddq, J_{XA} = 5.1, J_{XB} = 6.4 Hz, J_{XCH3} = 6.4 Hz, *H*9), 2.42 (3H, s, *H*1), 2.34 (1H, ABX dd, J_{AB} = 16.5 Hz, J_{AX} = 5.1 Hz, $H8_A$), 2.25 (1H, ABX dd, J_{BA} = 16.5 Hz, J_{BX} = 6.4 Hz, $H8_B$), 1.90 (1H, br. s, O*H*), 1.06 (3H, d, *J* = 6.4 Hz, *H*10); **^{13}C NMR** (101 MHz, $CDCl_3$)* δ_c 144.6, 134.4, 129.7, 128.6, 128.4, 128.2, 127.5, 75.4, 67.5, 66.3, 55.2, 28.9, 21.9, 21.5; **HRMS** (ES+) calc. for $C_{19}H_{21}NNaO_3S$ $[M+Na]^+$ 366.1134, found 366.1139. *Note: a single ^{13}C resonance is obscured due to signal overlap.

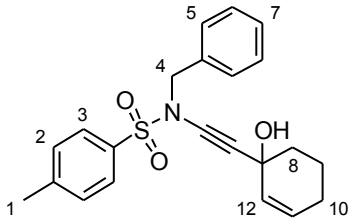
***N*-Benzyl-*N*-(((1*S**,2*R**)-2-hydroxycyclohexyl)ethynyl)-4-methylbenzenesulfonamide, 1i**



Synthesised from (*E*)-*N*-benzyl-*N*-(1,2-dichlorovinyl)tosylamide **2a** (100 mg, 281 µmol, 1.0 eq.) in anhydrous THF (2.8 mL) with phenyllithium (0.31 mL of a 2.0 M solution in dibutyl ether, 618 µmol, 2.2 eq.), followed by cyclohexene oxide (34 µL, 37 µmol, 1.2 eq.), and $BF_3{\cdot}Et_2O$ (18 µL, 377 µmol, 1.2 eq), according to procedure **1.2d**. Column chromatography (10% EtOAc/40-60 petroleum ether → 30% EtOAc/40-60 petroleum ether) afforded **1i** (68 mg, 179 µmol, 64%) as a pale yellow oil; $\mathbf{R_f}$ 0.58 (50% EtOAc/40-60 petroleum ether); **IR** (thin film, ν_{max} / cm^{-1}) 3449, 2930, 2858, 2249, 1597, 1496, 1364, 1169, 1090, 814, 712, 655; **^{1}H NMR** (400 MHz, C_6D_6) δ_H 7.85 (2H, d, *J* = 8.3 Hz, *H*3), 7.21–7.15 (2H, m, *H*6), 7.10–6.99 (3H, m, *H*5, *H*7), 6.82 (2H, d, *J* = 8.3 Hz, H*2*), 4.32 (2H, s, *H*4), 3.22 (1H, dt, *J* = 9.2, 3.9 Hz, *H*13), 2.13 (1H, ddd, *J* = 11.2, 9.2, 3.7 Hz, *H*8), 2.10 (1H, br. s, O*H*), 1.88 (3H, s, *H*1), 1.92–1.82 (1H, m, *H*12), 1.72–1.63 (1H, m, *H*9), 1.45–1.33 (1H, m, *H*11), 1.32–1.22 (1H, m, *H*10), 1.18–1.08 (2H, m, *H*9,

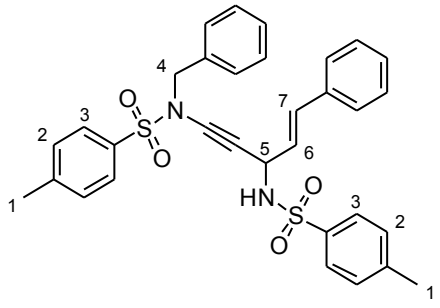
*H*12), 1.04–0.89 (1H, m, *H*11), 0.89–0.74 (1H, m, *H*10); **^{13}C NMR** (101 MHz, C_6D_6) δ_c 144.3, 135.6, 135.3, 129.8, 129.2, 128.8, 128.5, 128.1, 76.2, 73.7, 73.0, 55.5, 39.1, 33.3, 30.9, 24.8, 24.2, 21.2; **HRMS** (ES+) calc. for $C_{22}H_{25}NNaO_3S$ $[M+Na]^+$ 406.1447, found 406.1453.

_N_-Benzyl-_N_-((1-hydroxycyclohex-2-en-1-yl)ethynyl)-4-methylbenzenesulfonamide, 1j



Synthesised from (*E*)-*N*-benzyl-*N*-(1,2-dichlorovinyl)tosylamide **2a** (100 mg, 281 μmol, 1.0 eq.) in anhydrous THF (2.8 mL) with phenyllithium (0.31 mL of a 2.0 M solution in dibutyl ether, 618 μmol, 2.2 eq.) and 2-cyclohexen-1-one (33 μL, 337 μmol, 1.2 eq.). Column chromatography (4% EtOAc/10% CH_2Cl_2/40-60 petroleum ether) afforded **1j** (89 mg, 233 μmol, 83%) as a colourless oil; $\mathbf{R_f}$ 0.24 (20% EtOAc/40-60 petroleum ether); **IR** (thin film, ν_{max} / cm^{-1}) 3494, 2933, 2241, 1597, 1496, 1363, 1168, 1089, 736, 697, 662; **^{1}H NMR** (400 MHz, $CDCl_3$) δ_H 7.75–7.69 (2H, m, *H*3), 7.31–7.21 (7H, m, *H*2, *H*5, *H*6, *H*7), 5.71 (1H, dt, J = 10.0, 3.7 Hz, *H*11), 5.58 (1H, br. dt, J = 10.0, 2.2 Hz, *H*12), 4.46 (1H, AB d, J_{AB} = 13.7 Hz, *H*4$_A$), 4.42 (1H, AB d, J_{BA} = 13.7 Hz, *H*4$_B$Ph), 2.42 (3H, s, *H*1), 2.32 (1H, s, O*H*), 2.03–1.87 (2H, m, *H*10), 1.87–1.72 (2H, m, *H*8), 1.70–1.59 (1H, m, *H*9), 1.56–1.44 (1H, m, *H*9); **^{13}C NMR** (101 MHz, $CDCl_3$) δ_c 144.5, 134.4, 134.2, 130.3, 129.6, 128.9, 128.8, 128.3, 128.2, 127.7, 77.6, 74.8, 65.3, 55.3, 37.7, 24.5, 21.6, 19.0; **HRMS** (ES+) calc. for $C_{22}H_{23}NNaO_3S$ $[M+Na]^+$ 404.1291, found 400.1298.

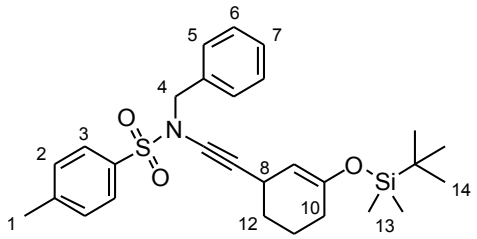
(*E*)-*N*-Benzyl-4-methyl-*N*-(3-(4-methylphenylsulfonamido)-5-phenylpent-4-en-1-yn-1-yl)benzenesulfonamide, 1k



Synthesised from (*E*)-*N*-benzyl-*N*-(1,2-dichlorovinyl)tosylamide **2a** (100 mg, 281 μmol, 1.0 eq.) in anhydrous THF (2.8 mL) with phenyllithium (0.31 mL of a 2.0 M solution in dibutyl ether, 618 μmol, 2.2 eq.) and a solution of (*E*)-cinnamylidenetosylamide (96 mg, 337 μmol, 1.2 eq.) in anhydrous THF (2 mL), following general procedure **1.2d**. Column chromatography (20% EtOAc/40-60 petroleum ether) afforded **1k** (133 mg, 233 μmol, 83%) as a yellow foam; $\mathbf{R_f}$ 0.10 (20% EtOAc/40-60 petroleum ether); **IR** (thin film, ν_{max} / cm^{-1}) 3279, 2925, 2251, 1597, 1495, 1365, 1164, 1091, 1027, 814, 6695, 667; **^{1}H NMR** (400 MHz,

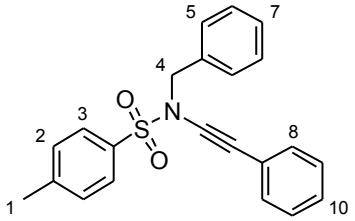
$CDCl_3$) δ_H 7.69 (2H, d, J = 8.3 Hz, H3), 7.62 (2H, d, J = 8.3 Hz, H3), 7.29–7.09 (14H, m, PhH (×2), H2 (×2)), 6.51 (1H, dd, J = 15.9, 1.5 Hz, H7), 5.92 (1H, dd, J = 15.9, 5.4 Hz, H6), 5.00 (1H, d, J = 8.8 Hz, NH), 4.90 (1H, ddd, J = 8.8, 5.4, 1.5 Hz, H5), 4.30 (1H, AB d, J_{AB} = 14.2 Hz, $H4_A$), 4.23 (1H, AB d, J_{BA} = 14.2 Hz, $H4_B$), 2.35 (3H, s, H1), 2.28 (3H, s, H1); **^{13}C NMR** (101 MHz, $CDCl_3$) δ_c 144.7, 143.4, 137.5, 135.6, 134.4, 134.1, 132.5, 129.7, 129.5, 128.5, 128.5, 128.4, 128.3, 128.0, 127.5, 127.2, 126.7, 125.3, 80.0, 67.3, 55.1, 47.4, 21.5, 21.4; **HRMS** (ES+) calc. for $C_{32}H_{30}N_2NaO_4S_2$ $[M+Na]^+$ 593.1539, found 593.1551.

***N*-Benzyl-*N*-((3-((*tert*-butyldimethylsilyl)oxy)cyclohex-2-en-1-yl)ethynyl)-4-methylbenzenesulfonamide, 1l[8]**



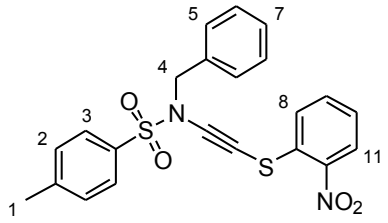
Synthesised from (*E*)-*N*-benzyl-*N*-(1,2-dichlorovinyl)tosylamide **2a** (100 mg, 281 μmol, 1.0 eq.) in anhydrous THF (2.8 mL) with phenyllithium (0.31 mL of a 2.0 M solution in dibutyl ether, 618 μmol, 2.2 eq.). Upon conversion to the alkynyllithium (as confirmed by TLC), a zinc(II) chloride solution (281 μL of a 1.0 M solution in Et_2O, 281 μmol, 1.0 eq.) was added, and the reaction warmed to room temperature and stirred for 10 minutes. The reaction was then cooled to –40 °C and 2-cyclohexen-1-one (28 μL, 281 μmol, 1.0 eq.), followed by *t*-butyldimethylsilyl triflate (64.5 μL, 281 μmol, 1.0 eq.), was added and the reaction mixture was stirred at –40 °C until reaction completion (3 hours, as analysed by TLC). Work-up as described by general procedure **1.2d**. Column chromatography (2% EtOAc/1% Et_3N/40-60 petroleum ether) afforded **1l** (73 mg, 148 μmol, 53%) as a colourless oil; $\mathbf{R_f}$ 0.24 (20% EtOAc/40-60 petroleum ether); **IR** (thin film, ν_{max} / cm^{-1}) 2929, 2858, 2248, 1664, 1598, 1456, 1366, 1170, 839, 780; **^{1}H NMR** (400 MHz, $CDCl_3$) δ_H 7.73 (2H, d, J = 8.3 Hz, H3), 7.31–7.26 (7H, m, H2, H5, H6, H7), 4.73–4.69 (1H, m, H9), 4.43 (2H, s, H4), 3.17–3.10 (1H, m, H8), 2.44 (3H, s, H1), 1.97–1.90 (2H, m, H10), 1.72–1.59 (2H, m, H11, H12), 1.58–1.49 (1H, m, H11), 1.49–1.39 (1H, m, H12), 0.92 (9H, s, H14), 0.11 (6H, s, H13); **^{13}C NMR** (101 MHz, $CDCl_3$) δ_c 151.4, 144.2, 134.7, 134.6, 129.4, 128.8, 128.3, 128.0, 127.7, 105.0, 74.1, 73.3, 55.6, 29.5, 29.1, 26.5, 25.6, 21.6, 20.7, 18.0, -4.5, -4.5; **HRMS** (ES+) calc. for $C_{28}H_{37}NNaO_3SSi$ $[M+Na]^+$ 518.2156, found 518.2154.

***N*-Benzyl-4-methyl-*N*-(phenylethynyl)benzenesulfonamide, 1m**[9]



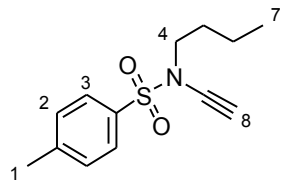
Synthesised from (*E*)-*N*-benzyl-*N*-(1,2-dichlorovinyl)tosylamide **2a** (100 mg, 281 μmol, 1.0 eq.) in anhydrous THF (2.8 mL) with phenyllithium (0.31 mL of a 2.0 M solution in dibutyl ether, 618 μmol, 2.2 eq.). Upon conversion to the alkynyllithium (as confirmed by TLC), a zinc(II) chloride solution (281 μL of a 1.0 M solution in Et_2O, 281 μmol, 1.0 eq.) was added, and the reaction warmed to room temperature and stirred for 10 minutes. The mixture was transferred to a solution of tris(dibenzylideneacetone)dipalladium(0) (7.7 mg, 8.42 μmol, 0.03 eq.), triphenylphosphine (4.4 mg, 16.8 μmol, 0.06 eq.) and iodobenzene (38 μL, 337 μmol, 1.2 eq.) in anhydrous THF (2 ml), and stirred at room temperature until reaction completion (5 hours, as analysed by TLC). Work-up as described by general procedure **1.2d**. Column chromatography (10% Et_2O/40-60 petroleum ether) afforded **1m** (51 mg, 141 μmol, 50%) as colourless crystals; **^{1}H NMR** (400 MHz, $CDCl_3$) δ_H 7.78 (2H, d, *J* = 8.3 Hz, *H*3), 7.34–7.26 (7H, m, *H*2, *H*5, *H*6, *H*7), 7.21 (5H, app. s, *H*8, *H*9, *H*10), 4.56 (2H, s, *H*4), 2.41 (3H, s, *H*1); **^{13}C NMR** (101 MHz, $CDCl_3$) δ_c 144.6, 134.6, 134.4, 131.0, 129.7, 128.9, 128.5, 128.3, 128.1, 127.7, 127.6, 122.7, 82.6, 71.3, 55.6, 21.6. Data are consistent with literature values.[10]

***N*-Benzyl-4-methyl-*N*-(((2-nitrophenyl)thio)ethynyl)benzenesulfonamide, 1n**



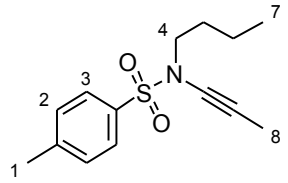
Synthesised from (*E*)-*N*-benzyl-*N*-(1,2-dichlorovinyl)tosylamide **2a** (100 mg, 281 μmol, 1.0 eq.) in anhydrous THF (2.8 mL) with phenyllithium (0.31 mL of a 2.0 M solution in dibutyl ether, 618 μmol, 2.2 eq.) and a solution of 1,2-bis(2-nitrophenyl)disulfide (104 mg, 337 μmol, 1.2 eq.) in anhydrous THF (2 mL), following general procedure **1.2d**. Column chromatography (4% EtOAc/10% CH_2Cl_2/40-60 petroleum ether) afforded **1n** (100 mg, 227 μmol, 81%) of **1n** as yellow crystals; **m.p.** 96 °C, **R_f** 0.24 (20% EtOAc/40-60 petroleum ether); **IR** (thin film, ν_{max} / cm^{-1}) 3092, 2923, 2158, 1592, 1517, 1337, 1169, 734; **^{1}H NMR** (400 MHz, $CDCl_3$) δ_H 8.24 (1H, dd, *J* = 8.2, 1.3 Hz, *H*11), 7.75 (2H, d, *J* = 8.3 Hz, *H*3), 7.62 (1H, dd, *J* = 8.2, 1.3 Hz, *H*8), 7.48–7.41 (1H, m, *H*9), 7.36–7.29 (8H, m, *H*10, *H*2, *H*5, *H*6, *H*7), 4.67 (2H, s, *H*4), 2.45 (3H, s, *H*1); **^{13}C NMR** (101 MHz, $CDCl_3$) δ_c 145.1, 144.5, 135.6, 134.6, 134.3, 134.0, 129.8, 128.9, 128.6, 128.5, 128.5, 127.8, 126.4, 125.8, 95.7, 61.6, 55.8, 21.7; **HRMS** (ES+) calc. for $C_{22}H_{18}N_2NaO_4S_2$ $[M+Na]^+$ 461.0600, found 461.0622.

***N*-Butyl-*N*-ethynyl-4-methylbenzenesulfonamide, 1o**



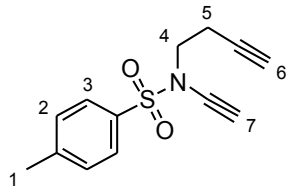
Synthesised from (*E*)-*N*-butyl-*N*-(1,2-dichlorovinyl) tosylamide **2c** (100 mg, 310 μmol, 1.0 eq.) in anhydrous THF (3.1 mL) with phenyllithium (0.34 mL of a 2.0 M solution in dibutyl ether, 683 μmol, 2.2 eq.). Water and Et_2O (2 mL each) was added and the reaction worked up following general procedure **1.2d**. Column chromatography (5% EtOAc/40-60 petroleum ether) afforded **1o** (68 mg, 270 μmol, 87%) as colourless crystals; **^{1}H NMR** (400 MHz, $CDCl_3$) δ_H 7.79 (2H, d, J = 8.2 Hz, *H*3), 7.34 (2H, d, J = 8.2 Hz, *H*2), 3.29 (2H, t, J = 7.3 Hz, *H*4), 2.72 (1H, s, *H*8), 2.44 (3H, s, *H*1), 1.61 (2H, quin, J = 7.3 Hz, *H*5), 1.33 (2H, sxt, J = 7.3 Hz, *H*6), 0.89 (3H, t, J = 7.3 Hz, *H*7); **^{13}C NMR** (101 MHz, $CDCl_3$) δ_c 144.6, 134.5, 129.7, 127.6, 76.0, 58.9, 50.9, 29.6, 21.6, 19.3, 13.5; **MS** (ESI+) *m/z* 252.1 (100, $[M+H]^+$), 274.1 (53, $[M+Na]^+$). Data are consistent with literature values.[11] Note that this compound is sensitive to moisture.

***N*-Butyl-4-methyl-*N*-(prop-1-yn-1-yl)benzenesulfonamide, 1p**



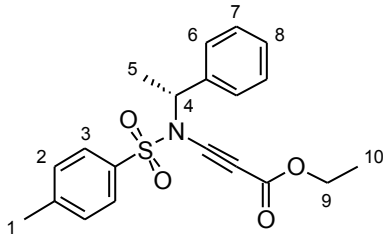
Synthesised from (*E*)-*N*-butyl-*N*-(1,2-dichlorovinyl) tosylamide **2c** (100 mg, 310 μmol, 1.0 eq.) in anhydrous THF (3.1 mL) with phenyllithium (0.34 mL of a 2.0 M solution in dibutyl ether, 683 μmol, 2.2 eq.) and methyl iodide (23 μL, 372 μmol, 1.2 eq.), following general procedure **1.2d**. Column chromatography (10% CH_2Cl_2/2% EtOAc/40-60 petroleum ether) afforded **1p** (69 mg, 259 μmol, 83%) as a colourless oil; $\mathbf{R_f}$ 0.54 (20% EtOAc/40-60 petroleum ether); **IR** (thin film, ν_{max} / cm^{-1}) 2960, 2253, 1597, 1360, 1170, 1091, 1041, 854, 814, 707; **^{1}H NMR** (400 MHz, $CDCl_3$) δ_H 7.76 (2H, d, J = 8.2 Hz, *H*3), 7.32 (2H, d, J = 8.2 Hz, *H*2), 3.22 (2H, t, J = 7.2 Hz, *H*4), 2.43 (3H, s, *H*1), 1.88 (3H, s, *H*8), 1.58 (2H, quin, J = 7.2 Hz, *H*5), 1.32 (2H, sxt, J = 7.2 Hz, *H*6), 0.89 (3H, t, J = 7.2 Hz, *H*7); **^{13}C NMR** (101 MHz, $CDCl_3$) δ_c 144.1, 134.6, 129.5, 127.4, 71.9, 65.4, 51.1, 29.7, 21.5, 19.4, 13.5, 3.2; **HRMS** (ES+) calc. for $C_{14}H_{19}NNaO_2S$ $[M+Na]^+$ 288.1029, found 288.1030.

***N*-(But-3-yn-1-yl)-*N*-ethynyl-4-methylbenzenesulfonamide, 1q**



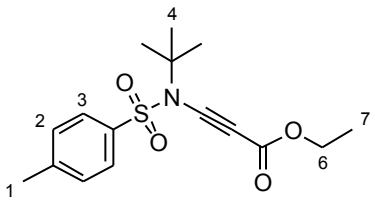
Synthesised from (*E*)-*N*-(but-3-yn-1-yl)-*N*-(1,2-dichlorovinyl) tosylamide **2e** (50 mg, 157 µmol, 1.0 eq.) in anhydrous THF (1.6 mL) with phenyllithium (0.25 mL of a 2.0 M solution in dibutyl ether, 503 µmol, 3.2 eq.). Water and Et_2O (1 mL each) was added and the reaction worked up following general procedure **1.2d**. Column chromatography (10% Et_2O/40-60 petroleum ether) afforded **1q** (31 mg, 126 µmol, 80%) as colourless crystals; **^{1}H NMR** (400 MHz, $CDCl_3$) δ_H 7.80 (2H, d, *J* = 8.3 Hz, *H*3), 7.35 (2H, d, *J* = 8.3 Hz, *H*2), 3.49 (2H, t, *J* = 7.6 Hz, *H*4), 2.78 (1H, s, *H*7), 2.53 (2H, td, *J* = 7.6, 2.7 Hz, *H*5), 2.45 (3H, s, *H*1), 1.97 (1H, t, *J* = 2.7 Hz, *H*6); **^{13}C NMR** (101 MHz, $CDCl_3$) δ_c 145.0, 134.4, 129.8, 127.6, 79.5, 75.3, 70.6, 59.7, 49.7, 21.6, 18.2; **MS** (ESI^+) *m/z* 248.1 (14, $[M+H]^+$), 270.1 (100, $[M+Na]^+$), 280.1 (72, $[M+MeOH+H]^+$). **HRMS** (ES+) calc. for $C_{13}H_{13}NNaO_2S$ $[M+Na]^+$ 270.0559, found 270.0563. Data are consistent with literature values.[12] Note that this compound is sensitive to moisture.

(*R*)-Ethyl 3-(4-methyl-*N*-(1-phenylethyl)phenylsulfonamido)propiolate, 1r



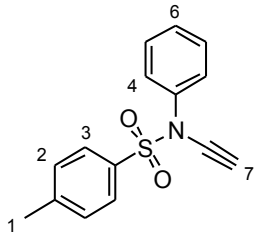
Synthesised from (*R*,*E*)-*N*-(1,2-Dichlorovinyl)-*N*-(1-phenylethyl)tosylamide **2g** (50 mg, 135 µmol, 1.0 eq.) in anhydrous THF (0.5 mL) with *n*-butyllithium (65 µL and 54 µL of a 2.5 M solution in hexanes, 297 µmol, 2.2 eq.) and ethyl chloroformate (16 µL, 162 µmol, 1.2 eq.), following general procedure **1.2e**. Column chromatography (10% EtOAc/40-60 petroleum ether) afforded **1r** (42 mg, 113 µmol, 83%) as a colourless oil; $\mathbf{R_f}$ 0.40 (20% EtOAc/40-60 petroleum ether); $[\boldsymbol{\alpha}]_{\boldsymbol{D}}^{\mathbf{20}}$ +79.6 (c 0.5, $CHCl_3$); **IR** (thin film, ν_{max} / cm^{-1}) 2975, 2212, 1702, 1597, 1455, 1373, 1306, 1170, 1148, 1090, 1020, 951, 888, 814, 775, 742, 718, 700; **^{1}H NMR** (400 MHz, $CDCl_3$) δ_H 7.60 (2H, d, *J* = 8.3 Hz, *H*3), 7.27–7.18 (7H, m, *H*2, *H*6, *H*7, *H*8), 5.16 (1H, q, *J* = 7.1 Hz, *H*4), 4.22 (2H, q, *J* = 7.1 Hz, *H*9), 2.40 (3H, s, *H*1), 1.59 (3H, d, *J* = 7.1 Hz, *H*5), 1.3 (3H, t, *J* = 7.1 Hz, *H*10); **^{13}C NMR** (101 MHz, $CDCl_3$) δ_c 154.2, 145.1, 138.9, 134.6, 129.7, 128.5, 128.3, 127.7, 126.7, 81.0, 70.7, 61.4, 59.6, 21.6, 20.0, 14.2; **HRMS** (ES+) calc. for $C_{20}H_{21}NNaO_4S$ $[M+Na]^+$ 394.1083, found 394.075.

Ethyl 3-(*N*-(*tert*-butyl)-4-methylphenylsulfonamido)propiolate, 1s



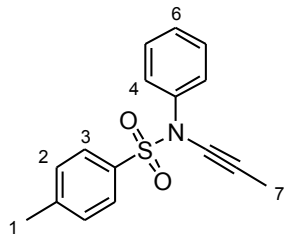
Synthesised from (*E*)-*N*-(*t*-butyl)-*N*-(1,2-dichlorovinyl) tosylamide **2h** (100 mg, 310 μmol, 1.0 eq.) in anhydrous THF (3.1 mL) with phenyllithium (0.34 mL of a 2.0 M solution in dibutyl ether, 683 μmol, 2.2 eq.) and ethyl chloroformate (35 μL, 372 μmol, 1.2 eq.) following general procedure **1.2d**. Column chromatography (10% EtOAc/40-60 petroleum ether) afforded **1s** (81 mg, 251 μmol, 81%) as a colourless oil; $\mathbf{R_f}$ 0.46 (20% EtOAc/40-60 petroleum ether); **IR** (thin film, ν_{max} / cm^{-1}) 2983, 2208, 1701, 1597, 1364, 1251, 1143, 1089, 1040, 922, 885, 813, 743, 705; **^{1}H NMR** (400 MHz, $CDCl_3$) δ_H 7.85 (2H, d, *J* = 8.6 Hz, *H*3), 7.34 (2H, d, *J* = 8.6 Hz, *H*2), 4.21 (2H, d, *J* = 7.1 Hz, *H*6), 2.45 (3H, s, *H*1), 1.48 (9H, s, *H*4), 1.29 (3H, t, *J* = 7.1 Hz, *H*7); **^{13}C NMR** (101 MHz, $CDCl_3$) δ_c 154.5, 145.0, 136.4, 129.7, 127.9, 83.5, 70.4, 65.6, 61.3, 29.3, 21.6, 14.2; **HRMS** (ES+) calc. for $C_{16}H_{21}NNaO_4S$ $[M+Na]^+$ 346.1083, found 346.1079.

***N*-Ethynyl-4-methyl-*N*-phenylbenzenesulfonamide, 1t**



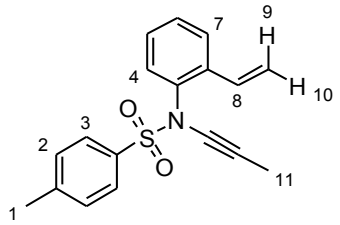
Synthesised from (*E*)-*N*-phenyl-*N*-(1,2-dichlorovinyl)tosylamide **2b** (100 mg, 292 μmol, 1.0 eq.) in anhydrous THF (2.9 mL) with phenyllithium (0.32 mL of a 2.0 M solution in dibutyl ether, 643 μmol, 2.2 eq.). Water and Et_2O (2 mL each) was added and the reaction worked up following general procedure **1.2d**. Column chromatography (10% Et_2O/40-60 petroleum ether) afforded **1t** (70 mg, 258 μmol, 88%) as a colourless solid; **^{1}H NMR** (400 MHz, $CDCl_3$) δ_H 7.58 (2H, d, *J* = 8.3 Hz, *H*3), 7.36–7.23 (7H, m, *H*2, *H*4, *H*5, *H*6), 2.83 (1H, s, *H*7), 2.44 (3H, s, *H*1); **^{13}C NMR** (101 MHz, $CDCl_3$) δ_c 145.1, 138.2, 132.7, 129.5, 129.1, 128.4, 128.2, 126.3, 76.4, 58.9, 21.7; **MS** (ESI^+) *m/z* 310.0 (100, $[M+K]^+$). Data consistent with literature values.[12]

4-Methyl-*N*-phenyl-*N*-(prop-1-yn-1-yl)benzenesulfonamide, 1u



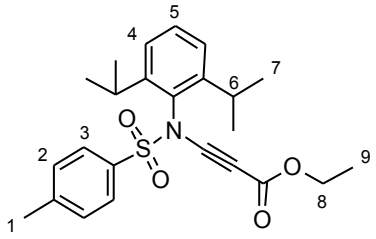
Synthesised from (*E*)-*N*-phenyl-*N*-(1,2-dichlorovinyl)tosylamide **2b** (100 mg, 292 µmol, 1.0 eq.) in anhydrous THF (2.9 mL) with phenyllithium (0.32 mL of a 2.0 M solution in dibutyl ether, 643 µmol, 2.2 eq.) and methyl iodide (22 µL, 351 µmol, 1.2 eq.), following general procedure **1.2d**. Column chromatography (10% Et_2O/40-60 petroleum ether) afforded **1u** (68 mg, 239 µmol, 82%) as colourless crystals; **^{1}H NMR** (400 MHz, $CDCl_3$) δ_H 7.54 (2H, d, *J* = 8.3 Hz, *H*3), 7.32–7.21 (7H, m, *H*2, *H*4, *H*5, *H*6), 2.41 (3H, s, *H*1), 1.91 (3H, s, *H*7); **^{13}C NMR** (101 MHz, $CDCl_3$) δ_c 144.6, 139.2, 133.0, 129.3, 128.9, 128.1, 127.9, 126.1, 72.7, 65.6, 21.6, 3.25; **MS** (ESI^+) *m/z* 308.1 (100, $[M+Na]^+$). Data consistent with literature values.[13]

4-Methyl-N-(prop-1-yn-1-yl)-N-(2-vinylphenyl)benzenesulfonamide, 1v



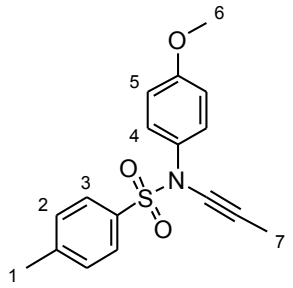
Synthesised from (*E*)-*N*-(1,2-dichlorovinyl)-*N*-(2-vinylphenyl) tosylamide **2l** (100 mg, 272 µmol, 1.0 eq.) in anhydrous THF (1 mL) with *n*-butyllithium (127 µL and 106 µL of a 2.5 M solution in hexanes, 580 µmol, 2.2 eq.) and methyl iodide (20 µL, 316 µmol, 1.2 eq.), following general procedure **1.2e**. Column chromatography (10% Et_2O/40-60 petroleum ether) afforded **1v** (59 mg, 188 µmol, 69%) as a pale yellow oil; $\mathbf{R_f}$ 0.45 (20% EtOAc/40-60 petroleum ether); **IR** (thin film, ν_{max} / cm^{-1}) 2919, 2258, 1597, 1483, 1451, 1368, 1308, 1171, 1090, 927, 814, 770, 705, 677, 645; **^{1}H NMR** (400 MHz, $CDCl_3$) δ_H 7.68 (2H, d, *J* = 8.3 Hz, *H*3), 7.64 (1H, dd, *J* = 7.8, 1.3 Hz, *H*7), 7.35–7.31 (3H, m, *H*2, *H*5), 7.18 (1H, td, *J* = 7.8, 1.2 Hz, *H*6), 6.96 (1H, dd, *J* = 17.6, 11.0 Hz, *H*8), 6.89 (1H, dd, *J* = 7.8, 1.2 Hz, *H*4), 5.74 (1H, dd, *J* = 17.6, 1.0 Hz, *H*9), 5.28 (1H, dd, *J* = 11.0, 1.0 Hz, *H*10), 2.47 (3H, s, *H*1), 1.88 (3H, s, *H*11); **^{13}C NMR** (101 MHz, $CDCl_3$) δ_c 144.7, 136.8, 136.5, 133.9, 131.7, 129.5, 129.2, 128.4, 128.34, 128.26, 126.2, 116.2, 73.3, 64.8, 21.7, 3.3; **HRMS** (ES+) calc. for $C_{18}H_{17}NNaO_2S$ $[M+Na]^+$ 334.0872, found 334.0858.

Ethyl 3-(*N*-(2,6-diisopropylphenyl)-4-methylphenylsulfonamido)propiolate, 1w



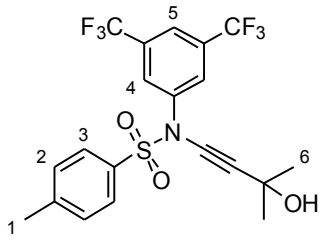
Synthesised from (*E*)-*N*-(1,2-dichlorovinyl)-*N*-(2,6-diisopropylphenyl)tosylamide **2m** (50 mg, 117 μmol, 1.0 eq.) in anhydrous THF (1.2 mL) with phenyllithium (0.13 mL of a 2.0 M solution in dibutyl ether, 258 μmol, 2.2 eq.), and ethyl chloroformate (13 μL, 141 μmol, 1.2 eq.), following general procedure **1.2d**. Column chromatography (5% EtOAc/40-60 petroleum ether) afforded **1w** (42 mg, 99 μmol, 85%) as colourless crystals; **m.p.** 113–114 °C; $\mathbf{R_f}$ 0.56 (20% EtOAc/40-60 petroleum ether); **IR** (thin film, ν_{max} / cm^{-1}) 2969, 2214, 1704, 1596, 1466, 1372, 1172, 1129, 1086, 913, 806, 727, 664; **^{1}H NMR** (400 MHz, $CDCl_3$) δ_H 7.89 (2H, d, *J* = 8.5 Hz, *H*3), 7.41 (2H, d, *J* = 8.5 Hz, *H*2), 7.37 (1H, d, *J* = 7.8 Hz, *H*5), 7.19 (2H, d, *J* = 7.6 Hz, *H*4), 4.20 (2H, q, *J* = 7.3 Hz, *H*8), 2.92 (2H, spt, *J* = 6.8 Hz, *H*6), 2.50 (3H, s, *H*1), 1.28 (3H, t, *J* = 7.3 Hz, *H*9), 1.16 (6H, d, *J* = 6.8 Hz, *H*7), 1.12 (6H, d, *J* = 6.8 Hz, *H*7); **^{13}C NMR** (101 MHz, $CDCl_3$) δ_c 154.2, 148.1, 145.8, 134.1, 132.1, 130.5, 129.9, 128.6, 124.8, 83.5, 66.8, 61.4, 29.1, 25.0, 23.1, 21.8, 14.1; **HRMS** (ES+) calc. for $C_{24}H_{30}NO_4S$ $[M+H]^+$ 428.1890, found 428.1881.

***N*-(4-Methoxyphenyl)-4-methyl-*N*-(prop-1-yn-1-yl)benzenesulfonamide, 1x**



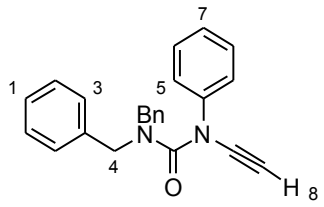
Synthesised from (*E*)-*N*-(4-methoxyphenyl)-*N*-(1,2-dichlorovinyl)tosylamide **2i** (50 mg, 134 μmol, 1.0 eq.) in anhydrous THF (1.2 mL) with phenyllithium (0.15 mL of a 2.0 M solution in dibutyl ether, 298 μmol, 2.2 eq.), and methyl iodide (10 μL, 161 μmol, 1.2 eq.), following general procedure **1.2d**. Column chromatography (5% Et_2O/40-60 petroleum ether) afforded **1x** (30 mg, 94 μmol, 70%) as a colourless oil; $\mathbf{R_f}$ 0.44 (20% EtOAc/40-60 petroleum ether); **IR** (thin film, ν_{max} / cm^{-1}) 2919, 2256, 1597, 1505, 1366, 1251, 1170, 1090, 1031, 669; **^{1}H NMR** (400 MHz, $CDCl_3$) δ_H 7.56 (2H, d, *J* = 8.3 Hz, *H*3), 7.27 (2H, d, *J* = 8.3 Hz, *H*2), 7.14–7.07 (2H, m, *H*4), 6.84–6.77 (2H, m, *H*5), 3.79 (3H, s, *H*6), 2.44 (3H, s, *H*1), 1.91 (3H, *H*7); **^{13}C NMR** (101 MHz, $CDCl_3$) δ_c 159.3, 144.5, 133.1, 131.9, 129.3, 128.2, 127.9, 114.1, 73.2, 65.0, 55.4, 21.7, 3.3; **HRMS** (ES+) calc. for $C_{17}H_{17}NNaO_3S$ $[M+Na]^+$ 338.0821, found 338.0821.

***N*-(3,5-Bis(trifluoromethyl)phenyl)-*N*-(3-hydroxy-3-methylbut-1-yn-1-yl)-4-methylbenzenesulfonamide, 1y**



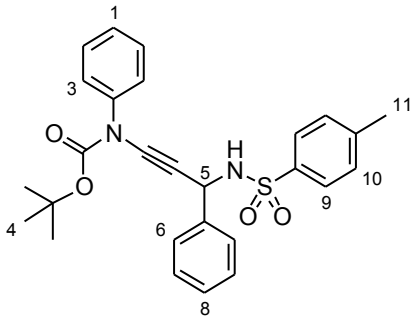
Synthesised from (*E*)-*N*-(3,5-bis(trifluoromethyl)phenyl)-*N*-(1,2-dichlorovinyl)tosylamide (39 mg, 82 μmol, 1.0 eq.) in anhydrous THF (1.0 mL) with phenyllithium (90 μL of a 2.0 M solution in dibutyl ether, 179 μmol, 2.2 eq.) and acetone (7 μL, 98 μmol, 1.2 eq.), following general procedure **1.2d**. Column chromatography (10% Et_2O → 50% Et_2O/40-60 petroleum ether) afforded **1y** (30 mg, 64 μmol, 78%) as a yellow oil; $\mathbf{R_f}$ 0.34 (20% EtOAc/40-60 petroleum ether); **IR** (thin film, ν_{max} / cm^{-1}) 3406, 2938, 2266, 1371, 1279, 1176, 1138, 963, 900; **^{1}H NMR** (500 MHz, $CDCl_3$) δ_H 7.80 (1H, s, *H*5), 7.74 (2H, s, *H*4), 7.58 (2H, d, *J* = 8.2 Hz, *H*3), 7.33 (2H, d, *J* = 8.2 Hz, *H*2), 2.46 (3H, s, *H*1), 2.07 (1H, br. s, O*H*), 1.55 (6H, s, H6); **^{13}C NMR** (126 MHz, $CDCl_3$) δ_c 146.1, 140.5, 132.6 (2C, q, *J* = 34.3 Hz), 132.1, 129.8, 128.2, 125.4 (2C, q, *J* = 2.9 Hz), 122.6 (2C, q, *J* = 273 Hz), 121.4 (1C, spt, *J* = 3.8 Hz), 77.3, 74.8, 65.4, 31.3, 21.7; **^{19}F NMR** (376 MHz, $CDCl_3$) δ_F -63.0; **HRMS** (ES+) calc. for $C_{20}H_{18}F_6NO_3S$ $[M+H]^+$ 466.0906, found 466.0902.

1,1-Dibenzyl-3-ethynyl-3-phenylurea, 1z



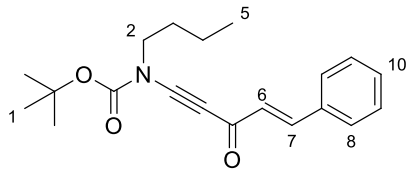
Synthesised from (*E*)-1,1-dibenzyl-3-(1,2-dichlorovinyl)-3-phenylurea **2z** (100 mg, 243 μmol, 1.0 eq.) in anhydrous THF (2.4 mL) with phenyllithium (0.26 mL of a 2.0 M solution in dibutyl ether, 535 μmol, 2.2 eq.). Water and Et_2O (2 mL each) was added and the reaction worked up following general procedure **1.2d**. Column chromatography (5% Et_2O) afforded **1z** (75 mg, 221 μmol, 91%) as a pale yellow oil; $\mathbf{R_f}$ 0.55 (20% EtOAc/40-60 petroleum ether); **IR** (thin film, ν_{max} / cm^{-1}) 3300, 3030, 2924, 2133, 1683, 1596, 1495, 1406, 1262, 1222, 752, 692; **^{1}H NMR** (400 MHz, $CDCl_3$) δ_H 7.37–725 (10H, m, *H*1, *H*2, *H*3), 7.25–7.20 (4H, m, *H*5, *H*6), 7.13 (1H, tt, *J* = 7.0, 1.5 Hz, *H*7), 4.59 (4H, s, *H*4), 3.02 (1H, s, *H*8); **^{13}C NMR** (101 MHz, $CDCl_3$) δ_c 158.0, 140.6, 136.4, 129.0, 128.6, 128.0, 127.6, 125.2, 121.5, 77.3, 60.2, 50.8; **HRMS** (ES+) calc. for $C_{23}H_{20}N_2NaO$ $[M+Na]^+$ 363.1468, found 363.1463.

***tert*-Butyl (3-(4-methylphenylsulfonamido)-3-phenylprop-1-yn-1-yl)(phenyl)carbamate, 1aa**



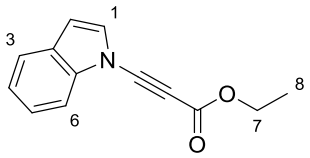
Synthesised from (*E*)-*t*-Butyl (1,2-dichlorovinyl)(phenyl)carbamate **2y** (100 mg, 347 µmol, 1.0 eq.) in anhydrous THF (3.5 mL) with phenyllithium (0.38 mL of a 2.0 M solution in dibutyl ether, 763 µmol, 2.2 eq.) and a solution of *N*-benzylidenetosylamide (108 mg, 416 µmol, 1.2 eq.) in anhydrous THF (2 mL), following general procedure **1.2d**. Column chromatography (10% Et_2O → 25% Et_2O/40-60 petroleum ether), followed by low temperature recrystallisation from benzene/pentane (2:1) afforded **1aa** (117 mg, 245 µmol, 71%) as colourless crystals; **m.p.** 156–157 °C; $\mathbf{R_f}$ 0.30 (20% EtOAc/40-60 petroleum ether); **IR** (thin film, ν_{max} / cm^{-1}) 3270, 2979, 2255, 1714, 1598, 1494, 1319, 1158, 910, 729, 699, 665; **^{1}H NMR** (500 MHz, $CDCl_3$)* δ_H 7.94–6.45 (14H, br. m, Ph*H* (×2), *H*9, *H*10), 6.14–5.37 (1H, br. m, *H*5), 5.14 (1H, d, *J* = 7.7 Hz, N*H*), 2.40 (3H, s, *H*11), 1.57–0.73 (9H, br. m, *H*4); **^{13}C NMR** (126 MHz, $CDCl_3$)* δ_c 152.8, 143.1, 137.6, 136.8, 129.5, 129.3, 128.9, 128.7, 128.3, 127.9, 127.4, 127.1, 125.2, 124.2, 82.2, 81.8, 57.9, 27.6, 21.5; **HRMS** (ES+) calc. for $C_{27}H_{29}N_2O_4S$ $[M+H]^+$ 477.1843, found 477.1838. * Note that the spectra show a highly rotameric nature.

(*E*)-*tert*-butyl butyl(3-oxo-5-phenylpent-4-en-1-yn-1-yl)carbamate, 1bb



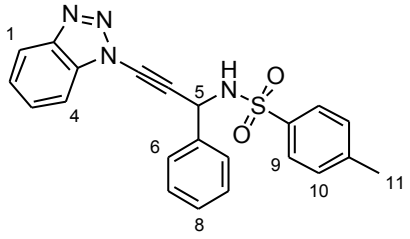
Synthesised from (*E*)-*t*-Butyl (1,2-dichlorovinyl)(butyl)carbamate **2x** (50 mg, 186 µmol, 1.0 eq.) in anhydrous THF (1.9 mL) with phenyllithium (0.25 mL of a 1.6 M solution in dibutyl ether, 409 µmol, 2.2 eq.) and a solution of cinnamoyl chloride (37 mg, 223 µmol, 1.2 eq.) in anhydrous THF (1 mL), following general procedure **1.2d**. Column chromatography (20% Et_2O/40-60 petroleum ether) afforded **1bb** (50 mg, 152 µmol, 82%) as a yellow oil; $\mathbf{R_f}$ 0.45 (20% EtOAc/40-60 petroleum ether); **IR** (thin film, ν_{max} / cm^{-1}) 2961, 2204, 1733, 1631, 1286, 1146, 762; **^{1}H NMR** (400 MHz, $CDCl_3$) δ_H 7.77 (1H, br. d, *J* = 15.9 Hz, *H*7), 7.57–7.49 (2H, br. m, *H*9), 7.43–7.36 (3H, br. m, *H*8, *H*10), 6.75 (1H, d, *J* = 15.9 Hz, *H*6), 3.56 (2H, t, *J* = 7.3 Hz, *H*2), 1.72 (2H, qu, *J* = 7.3 Hz, *H*3), 1.58 (9H, s, *H*1), 1.39 (2H, sxt, *J* = 7.3 Hz, *H*4), 0.96 (3H, t, *J* = 7.3 Hz, *H*5); **^{13}C NMR** (101 MHz, $CDCl_3$)* δ_c 177.7, 153.0, 146.2, 134.5, 130.7, 129.0, 128.8, 128.3, 84.0, 49.9, 30.2, 28.1, 19.6, 13.7; **HRMS** (ES+) calc. for $C_{20}H_{26}NO_3$ $[M+H]^+$ 328.1907, found 328.1902. * Note, alkyne carbons are not visible due to slow relaxation on NMR timescale.

Ethyl 3-(1*H*-indol-1-yl)propiolate 1cc



Synthesised from (*E*)-1-(1,2-dichlorovinyl)-1*H*-indole (50 mg, 236 μmol, 1.0 eq.) in anhydrous THF (2.4 mL) with phenyllithium (0.32 mL of a 1.6 M solution in dibutyl ether, 519 μmol, 2.2 eq.) and ethyl chloroformate (27 μL, 283 μmol, 1.2 eq.), following general procedure **1.2d**. Column chromatography (toluene) yielded **1cc** (34 mg, 158 μmol, 67%) as a pale yellow oil; $\mathbf{R_f}$ 0.30 (20% EtOAc/40-60 petroleum ether); **IR** (thin film, ν_{max} / cm^{-1}) 2922, 2233, 1705, 1531, 1465, 1245, 1187, 741; **^{1}H NMR** (400 MHz, C_6D_6) δ_H 7.49–7.39 (1H, m, *H*3), 7.29–7.23 (1H, m, *H*6), 7.04–6.98 (2H, m, *H*4, *H*5), 6.44 (1H, d, *J* = 3.4 Hz, *H*1), 6.06 (1H, dd, *J* = 3.4, 0.9 Hz, *H*2), 4.02 (2H, q, *J* = 7.1 Hz, *H*7), 0.96 (3H, t, *J* = 7.1 Hz, *H*8); **^{13}C NMR** (101 MHz, C_6D_6) δ_c 154.2, 138.5, 128.6, 128.6, 124.9, 123.6, 121.6, 111.9, 108.3, 79.3, 67.6, 61.6, 14.1; **HRMS** (ES+) calc. for $C_{13}H_{12}NO_2$ $[M+H]^+$ 214.0863, found 214.0863.

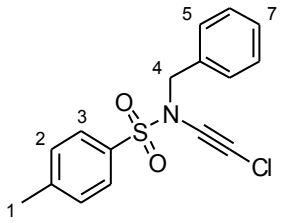
***N*-(3-(1*H*-benzo[*d*][1,2,3]triazol-1-yl)-1-phenylprop-2-yn-1-yl)-4-methylbenzenesulfonamide, 1dd**



Synthesised from (*E*)-1-(1,2-dichlorovinyl)-1*H*-benzotriazole **2r** (50 mg, 234 μmol, 1.0 eq.) in anhydrous THF (2.3 mL) with phenyllithium (0.32 mL of a 1.6 M solution in dibutyl ether, 514 μmol, 2.2 eq.) and a solution of *N*-benzylidenetosylamide (72.7 mg, 281 μmol, 1.2 eq.) in anhydrous THF (1 mL), following general procedure **1.2d**. Column chromatography (20% Et_2O → 50% Et_2O/40-60 petroleum ether) afforded **1dd** (81 mg, 200 μmol, 86%) as colourless crystals; **m.p.** 150 °C; $\mathbf{R_f}$ 0.30 (20% EtOAc/40-60 petroleum ether); **IR** (thin film, ν_{max} / cm^{-1}) 3277, 3016, 2225, 1599, 1495, 1454, 1325, 1159, 699, 671; **^{1}H NMR** (400 MHz, $CDCl_3$) δ_H 7.57 (2H, d, *J* = 8.3 Hz, *H*9), 7.21–7.11 (9H, m, *H*1, *H*2, *H*3, *H*4, *H*6, *H*7, *H*8), 7.1 (2H, d, *J* = 8.3 Hz, *H*10), 5.82 (1H, d, *J* = 7.8 Hz, N*H*), 5.59 (1H, d, *J* = 7.8 Hz, *H*5), 2.36 (3H, s, *H*11); **^{13}C NMR** (101 MHz, $CDCl_3$) δ_c 142.0, 140.5, 137.3, 129.2, 128.4, 127.3, 127.3, 127.0, 61.2, 21.4. Note, as observed by Katritzky[14] in other benzotriazole systems, the carbons for the benzotriazole ring and the alkyne are not visible due to slow relaxation on NMR timescale. We were also unable to gain an accurate mass (FI+), due to decomposition upon ionisation; however, an unidentified peak was observed at 337.1132 (desired molecular ion at 402.1151).

1.4c Chloroynamide S1

***N*-Benzyl-*N*-(chloroethynyl)-4-methylbenzenesulfonamide, S1**



To a a stirred solution of (*E*)-*N*-benzyl-*N*-(1,2-dichlorovinyl)tosylamide **2a** (400 mg, 1.12 mmol, 1.0 equiv) in anhydrous THF (1.1 mL) at 0 °C was added a solution of LiHMDS (1.35 mL, 1.0 M solution in THF, 1.2 equiv.) dropwise. The reaction was stirred at 0 °C until completion (~5 mins as analysed by TLC). The mixture was warmed to room temperature and quenched with water, followed by extraction with Et_2O (×2). The organic extracts were combined and dried ($MgSO_4$), filtered and concentrated *in vacuo*. Column chromatography (10% Et_2O/40-60 petroleum ether) afforded **S1** (304 mg, 0.95 mmol, 85%) as a colourless oil; $\mathbf{R_f}$ 0.52 (20% Et_2O/40-60 petroleum ether); **IR** (thin film, ν_{max} / cm^{-1}) 2925, 2242, 1597, 1496, 1456, 1365, 1169, 1090, 1022, 813, 779, 745, 698, 663; **^{1}H NMR** (400 MHz, $CDCl_3$) δ_H 7.73 (2H, d, J = 8.3 Hz, *H*3), 7.34–7.22 (7H, m, *H*2, *H*5, *H*6, *H*7), 4.46 (2H, s, *H*4), 2.44 (3H, s, *H*1); **^{13}C NMR** (101 MHz, $CDCl_3$) δ_c 144.8, 134.4, 134.1, 129.8, 128.5, 128.5, 128.3, 127.5, 63.1, 55.2, 52.7, 21.6; **HRMS** (ES+) calc. for $C_{16}H_{14}{}^{35}ClNNaO_2S$ $[M+Na]^+$ 342.0326, found 342.0321. Note that this compound is slightly moisture sensitive and polymerisation begins upon concentration *in vacuo* above 20 °C.

1.5 References

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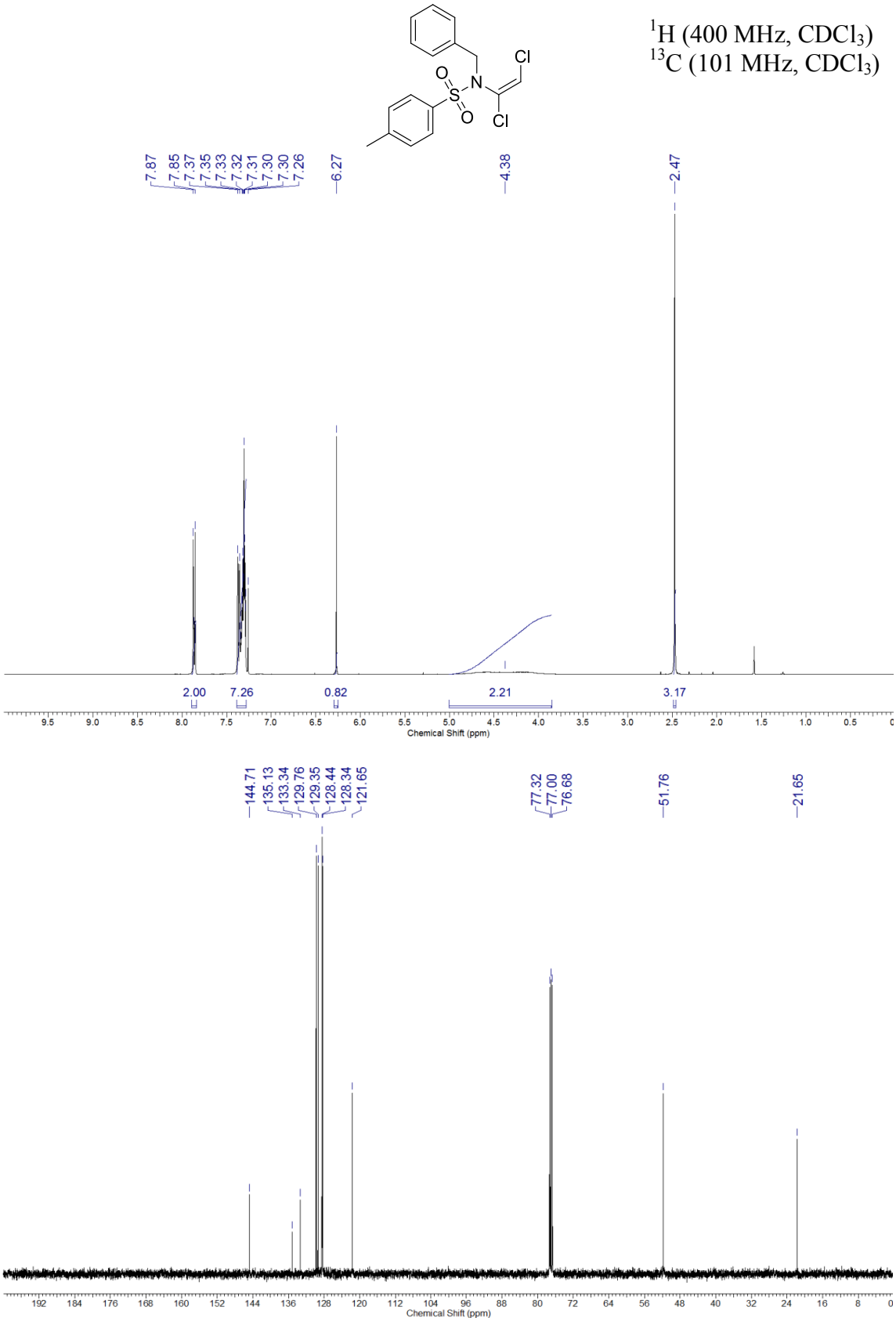
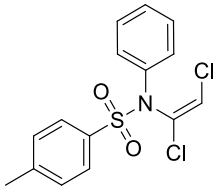
2.1 NMR Spectra.

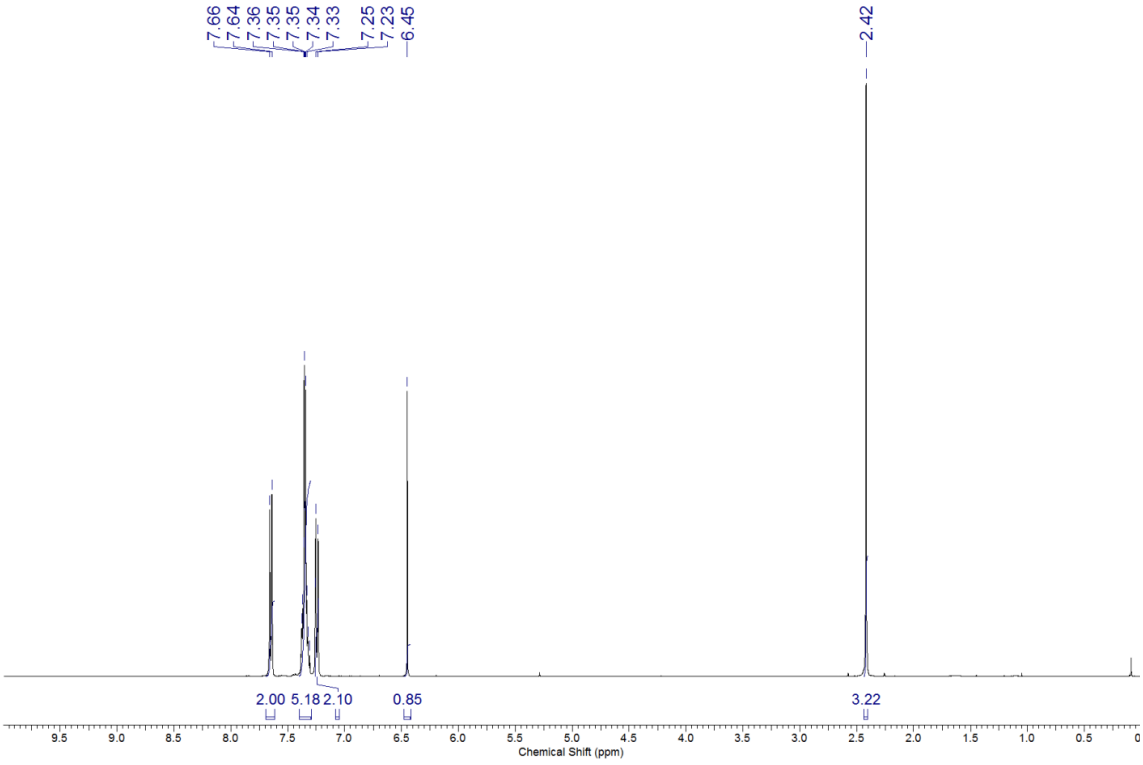
2.1a Dichloroenamides: (*E*)-*N*-Benzyl-*N*-(1,2-dichlorovinyl)-4-methylbenzenesulfonamide, 2a

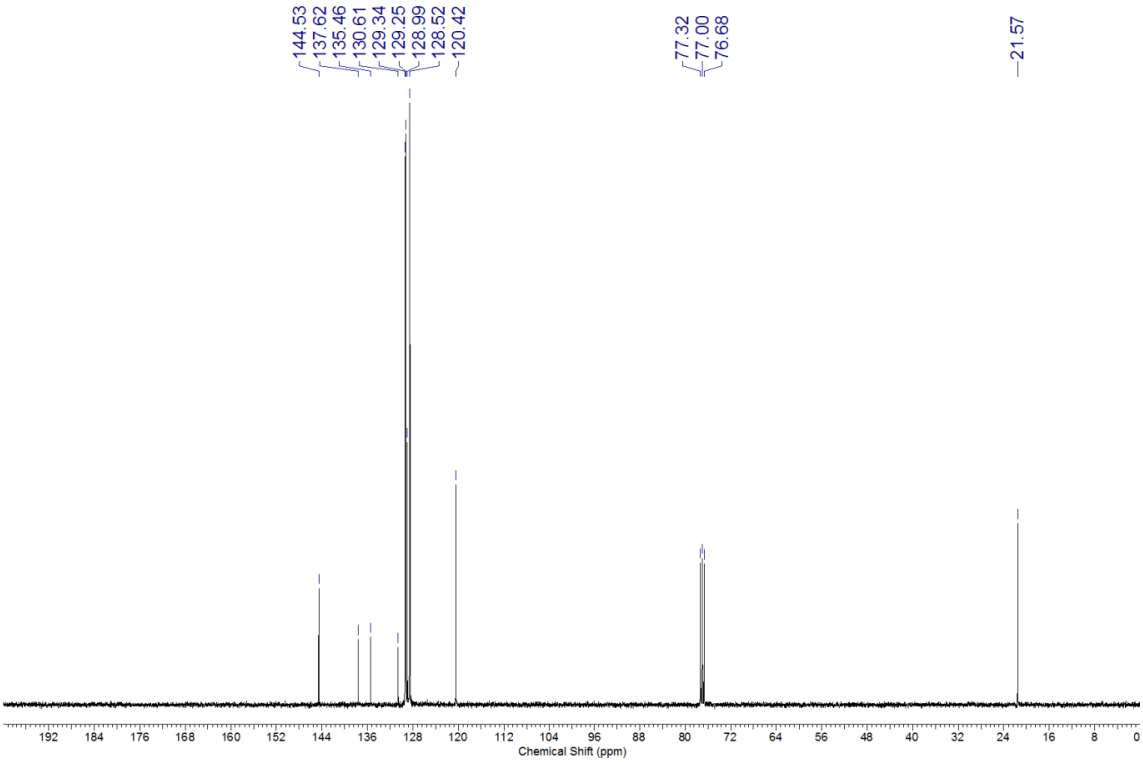


(*E*)-*N*-(1,2-Dichlorovinyl)-4-methyl-*N*-phenylbenzenesulfonamide, 2b

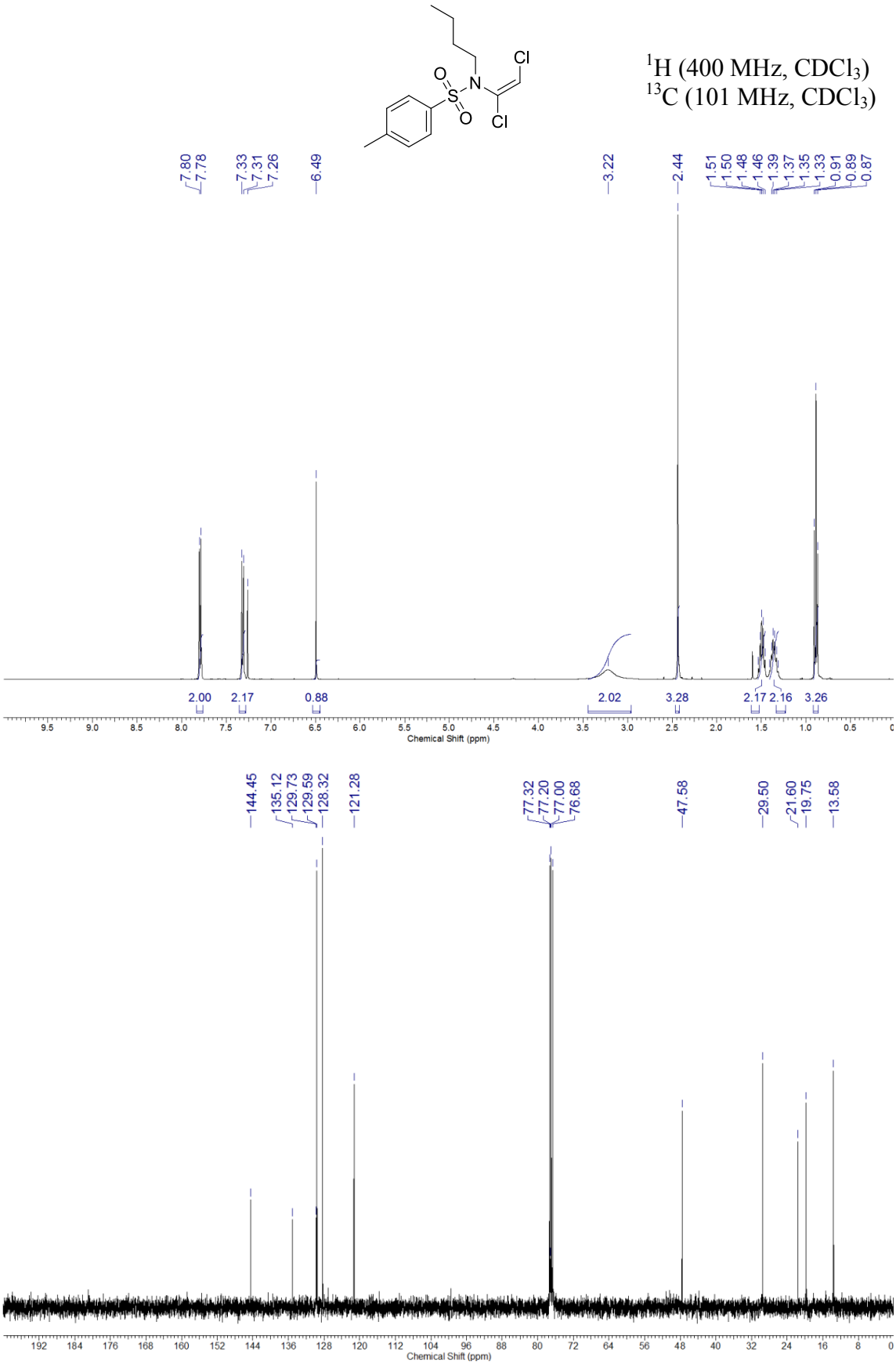


^{1}H (400 MHz, $CDCl_3$)
^{13}C (101 MHz, $CDCl_3$)

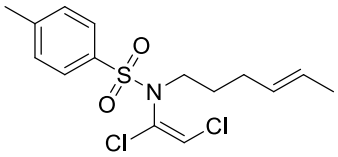




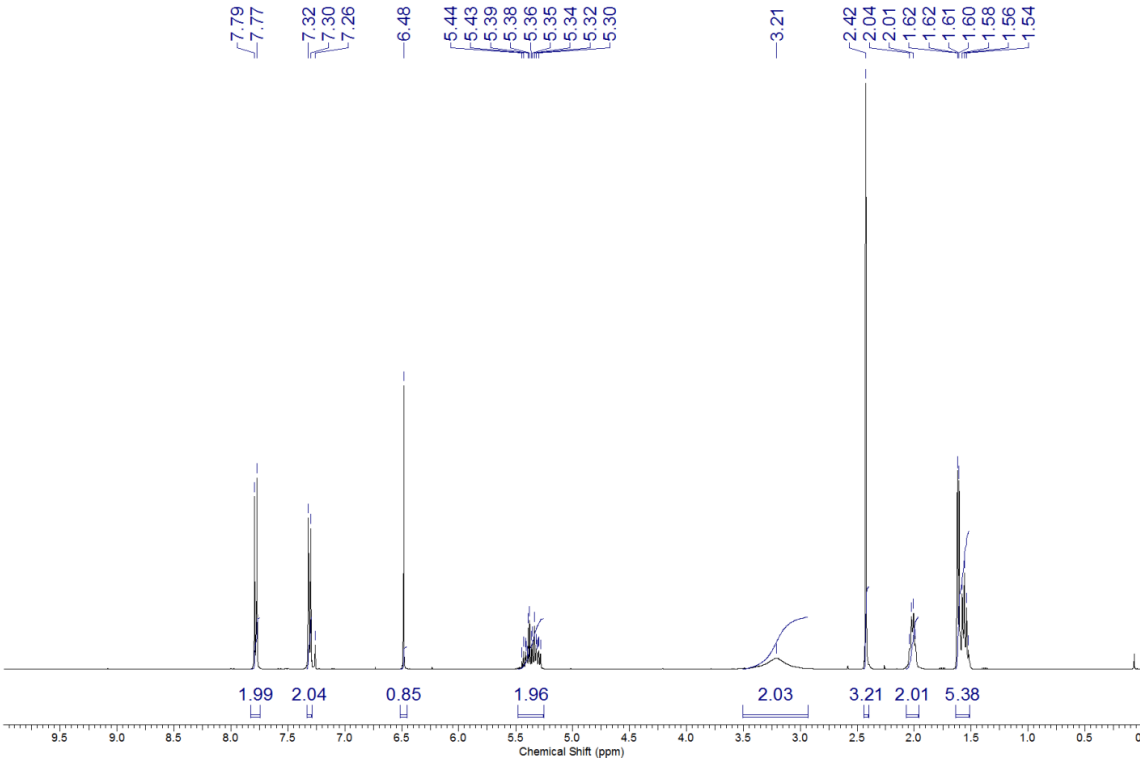
(*E*)-*N*-(*n*-Butyl)-*N*-(1,2-dichlorovinyl)-4-methylbenzenesulfonamide, 2c

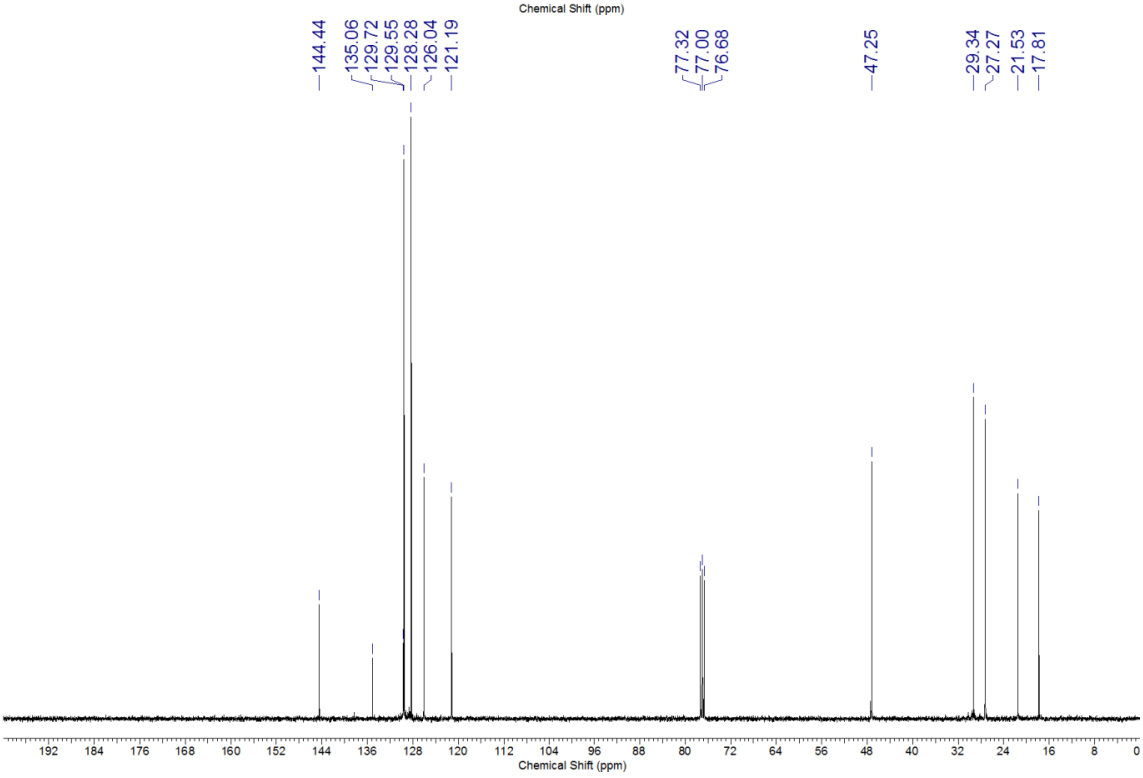


***N*-((*E*)-1,2-Dichlorovinyl)-*N*-((*E*)-hex-4-en-1-yl)-4-methylbenzenesulfonamide, 2d**

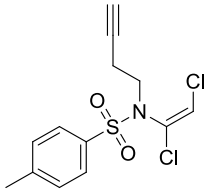


^{1}H (400 MHz, $CDCl_3$)
^{13}C (101 MHz, $CDCl_3$)

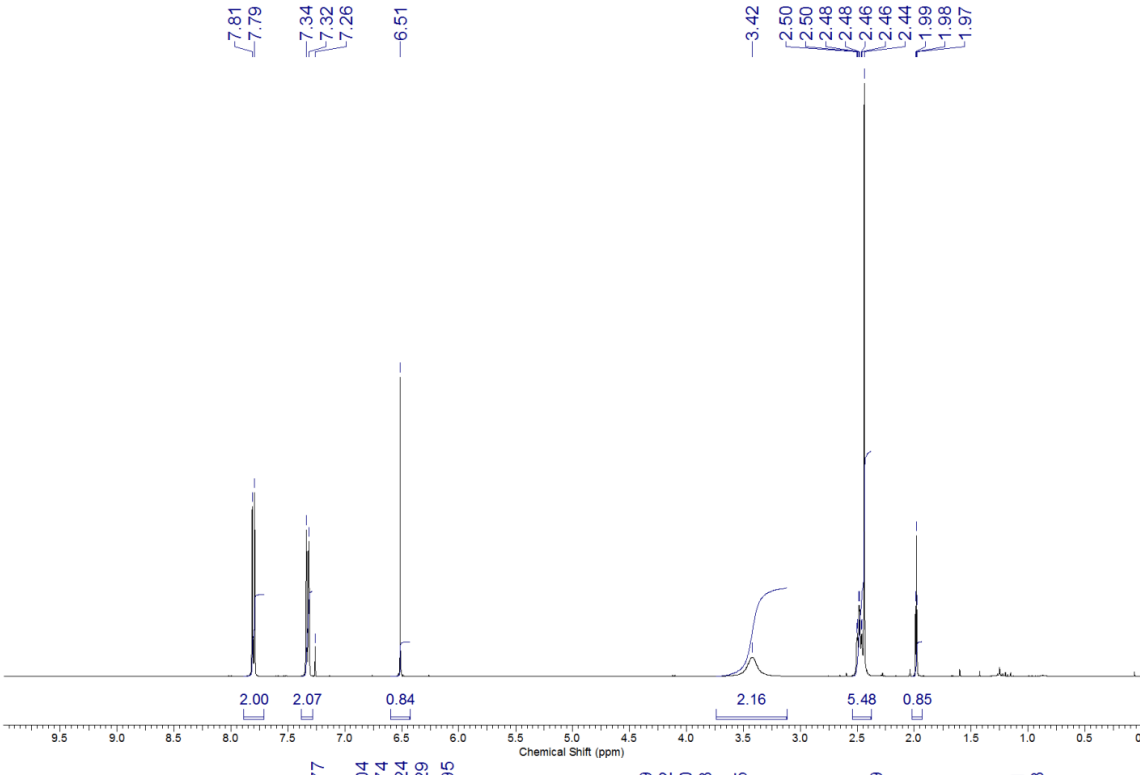


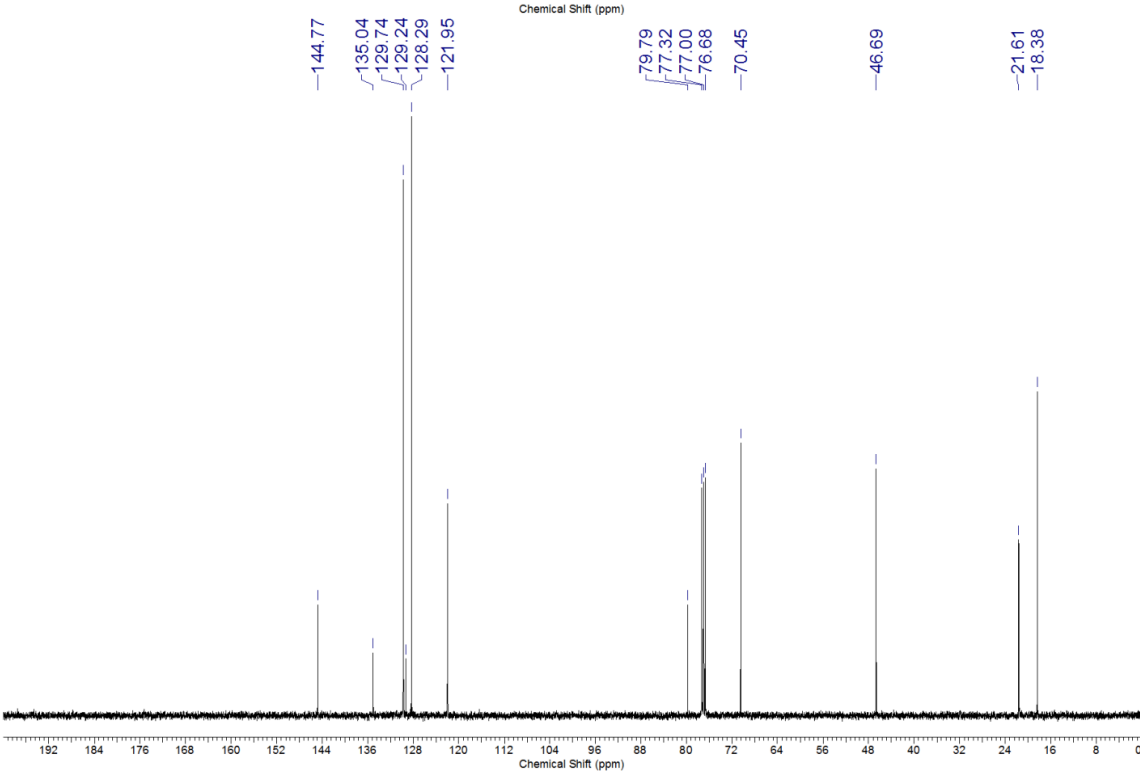


(*E*)-*N*-(But-3-yn-1-yl)-*N*-(1,2-dichlorovinyl)-4-methylbenzenesulfonamide, 2e

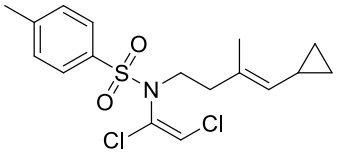


^{1}H (400 MHz, $CDCl_3$)
^{13}C (101 MHz, $CDCl_3$)

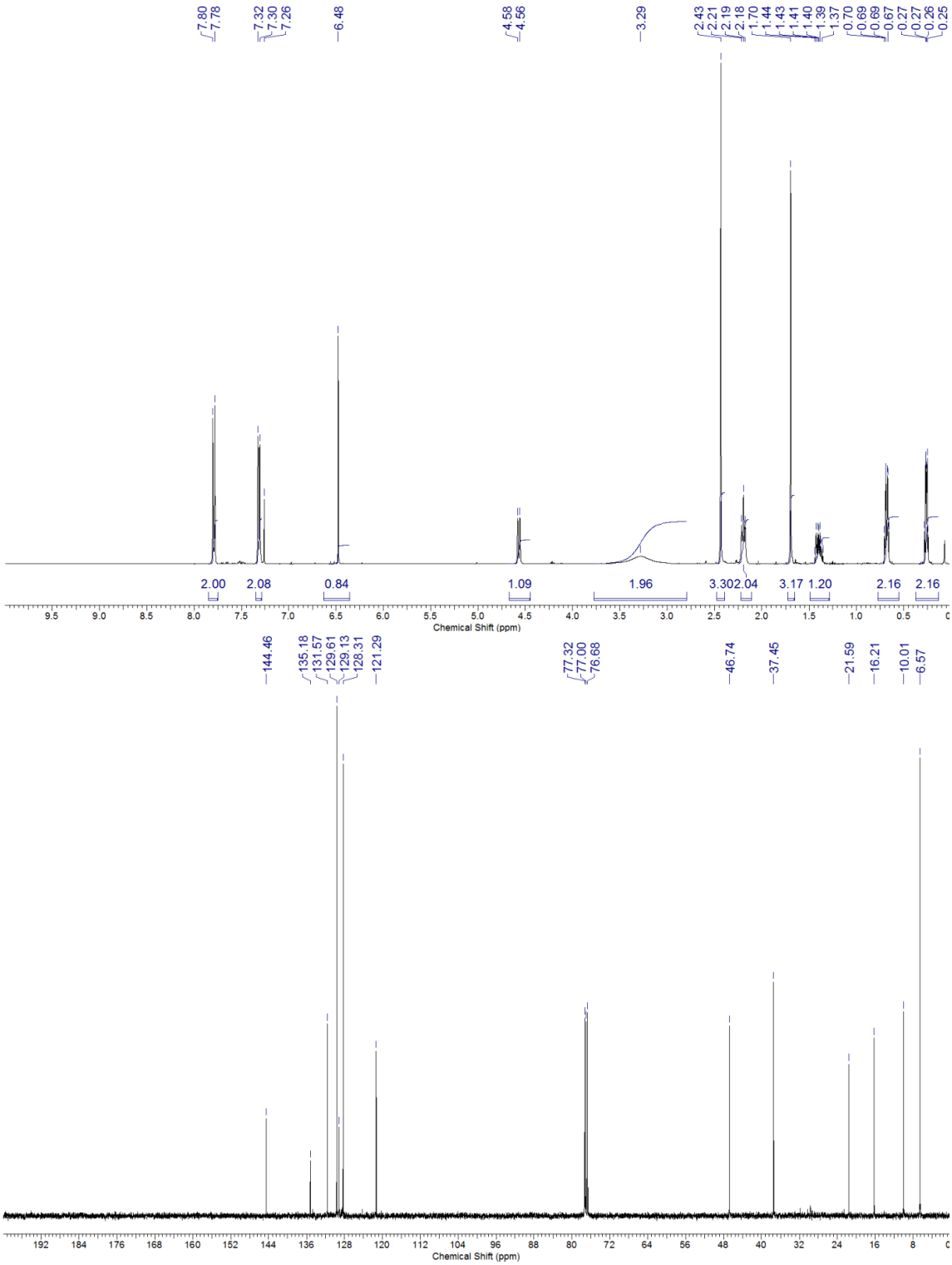




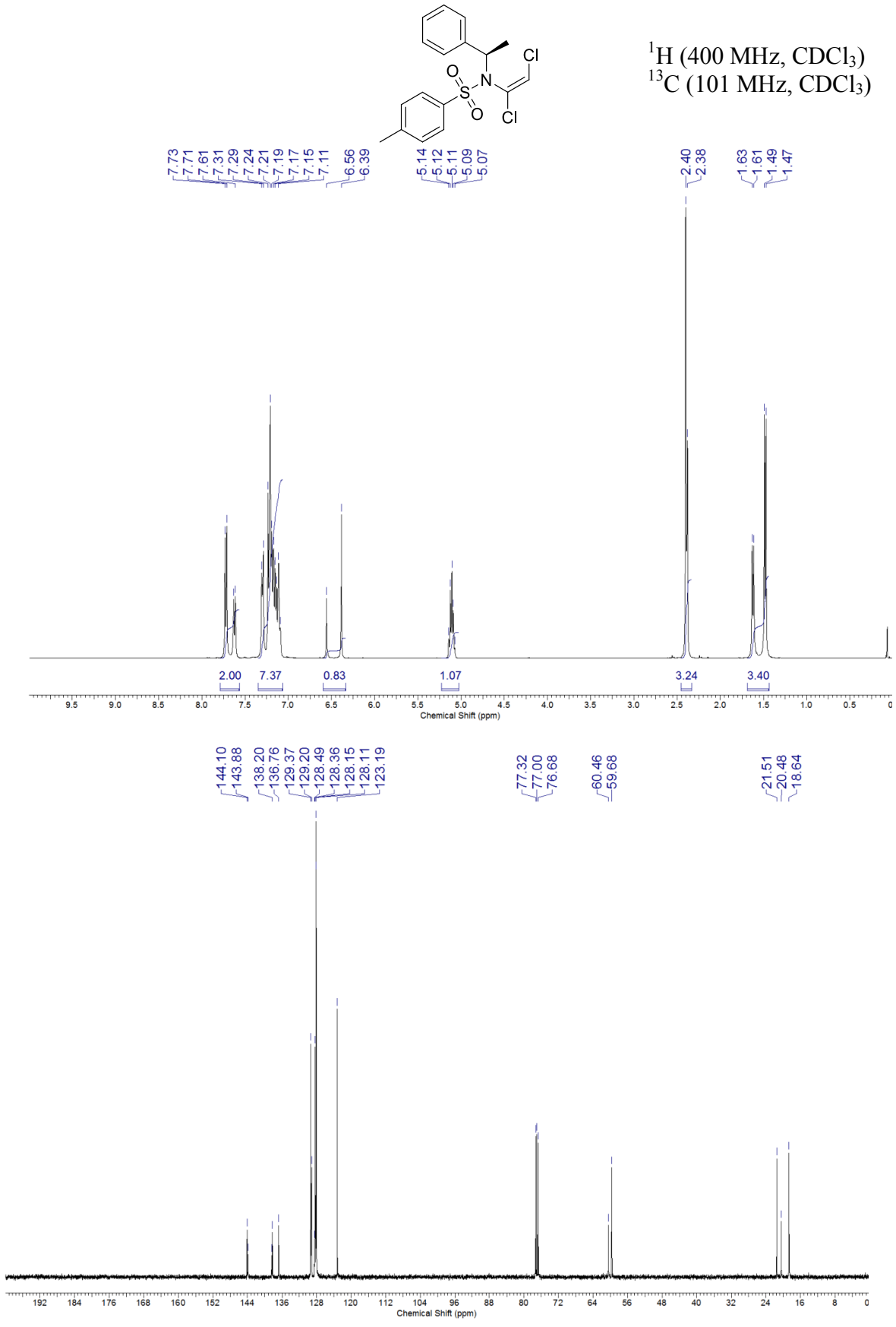
***N*-((*E*)-4-Cyclopropyl-3-methylbut-3-en-1-yl)-*N*-((*E*)-1,2-dichlorovinyl)-4-methylbenzenesulfonamide, 2f**



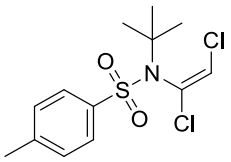
^{1}H (400 MHz, $CDCl_3$)
^{13}C (101 MHz, $CDCl_3$)



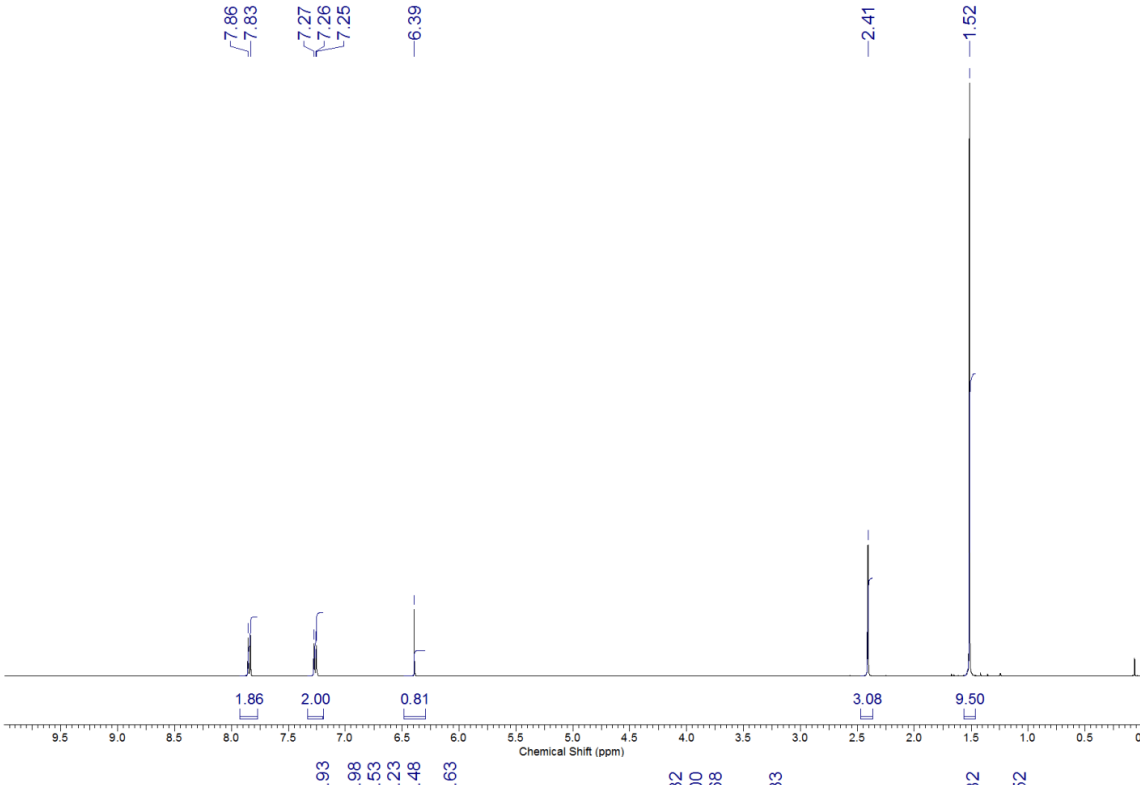
(*R*,*E*)-*N*-(1,2-Dichlorovinyl)-4-methyl-*N*-(1-phenylethyl)benzenesulfonamide, 2g

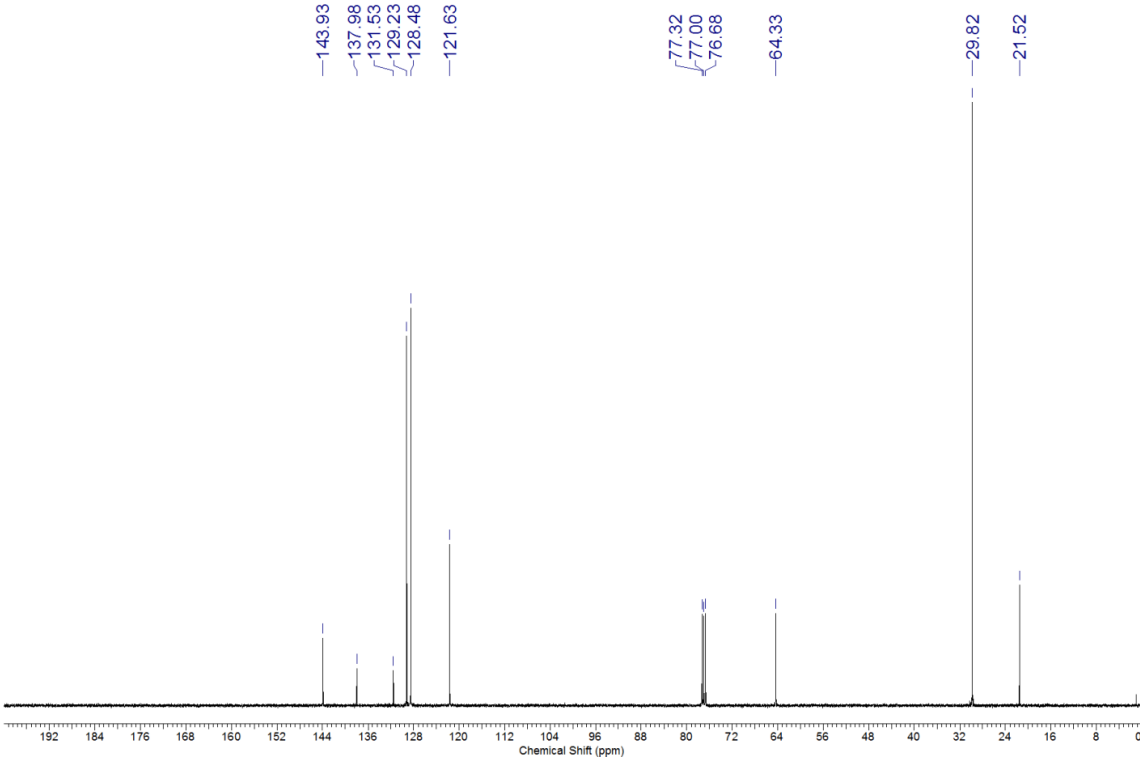


(*E*)-*N*-(*tert*-Butyl)-*N*-(1,2-dichlorovinyl)-4-methylbenzenesulfonamide, 2h

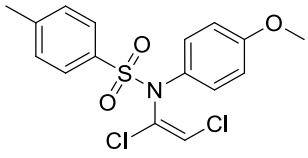


^{1}H (400 MHz, $CDCl_3$)
^{13}C (101 MHz, $CDCl_3$)

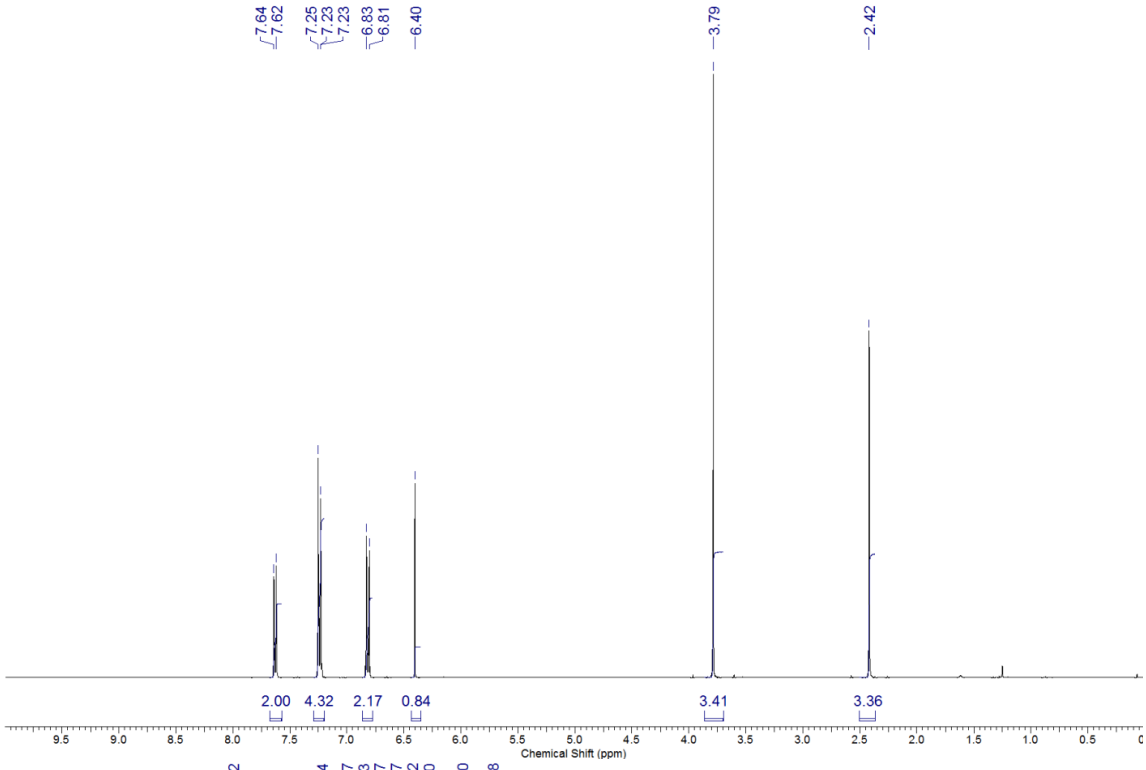


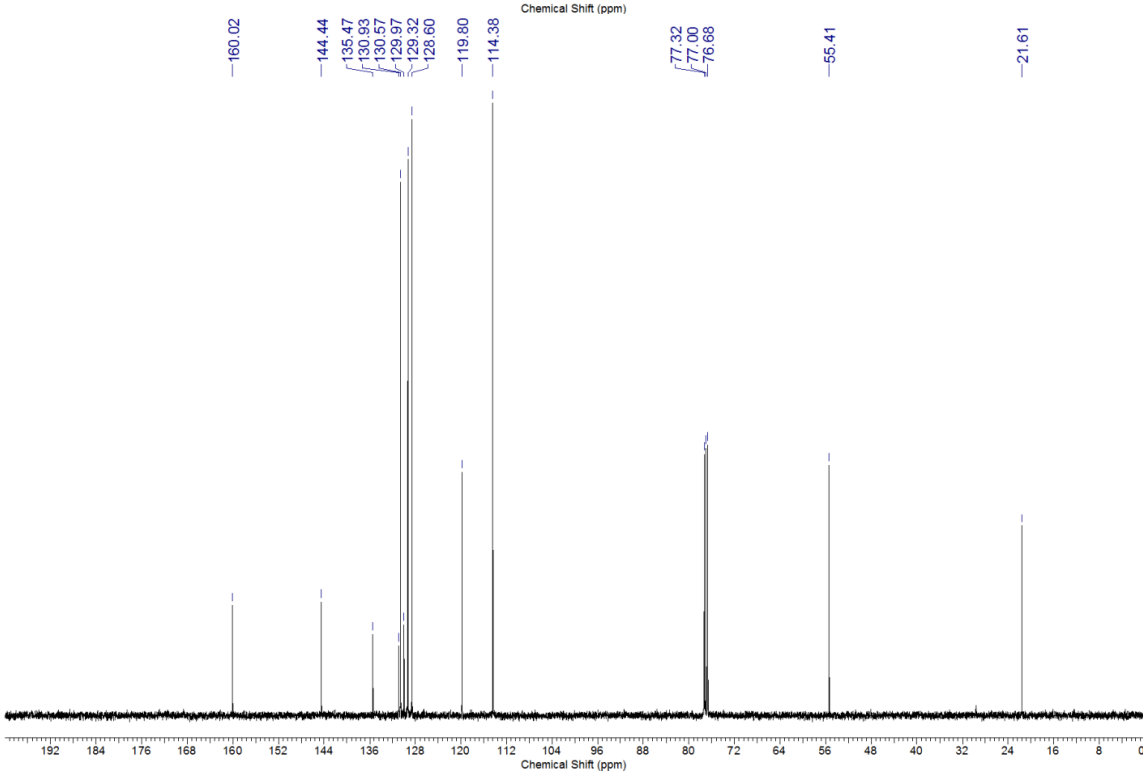


(*E*)-*N*-(1,2-Dichlorovinyl)-*N*-(4-methoxyphenyl)-4-methylbenzenesulfonamide, 2i

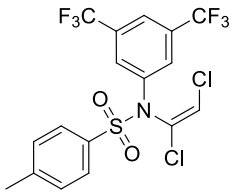


^{1}H (400 MHz, $CDCl_3$)
^{13}C (101 MHz, $CDCl_3$)

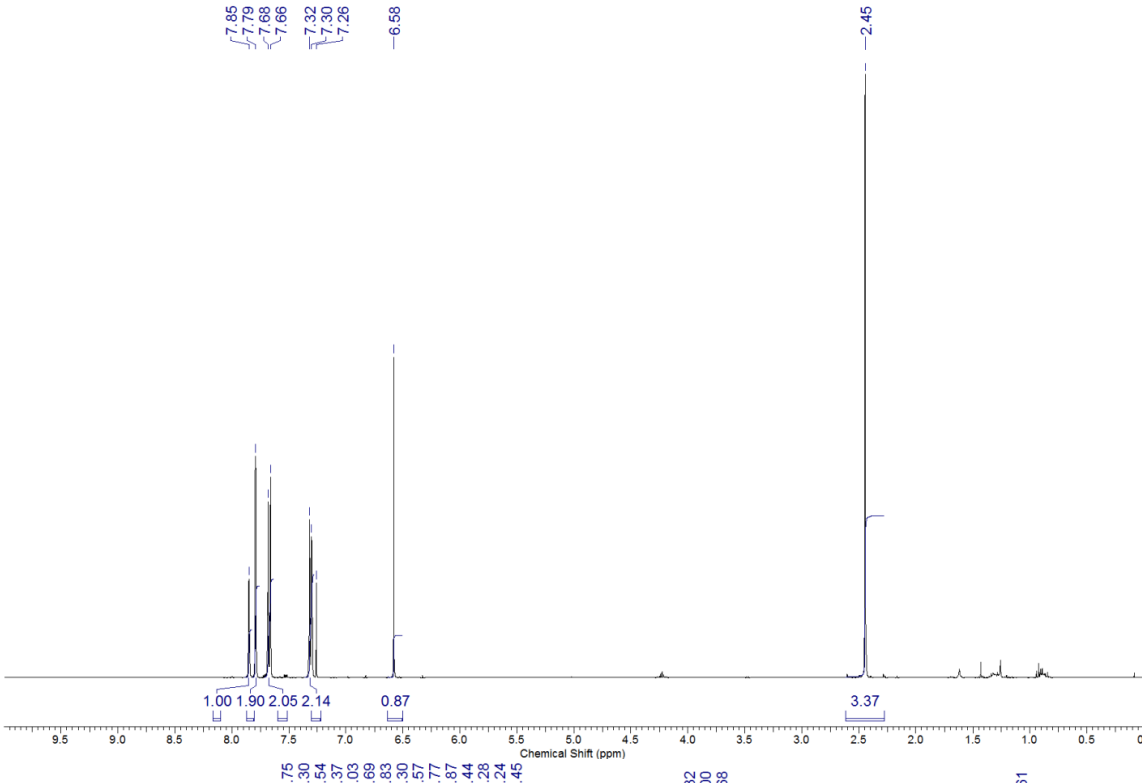


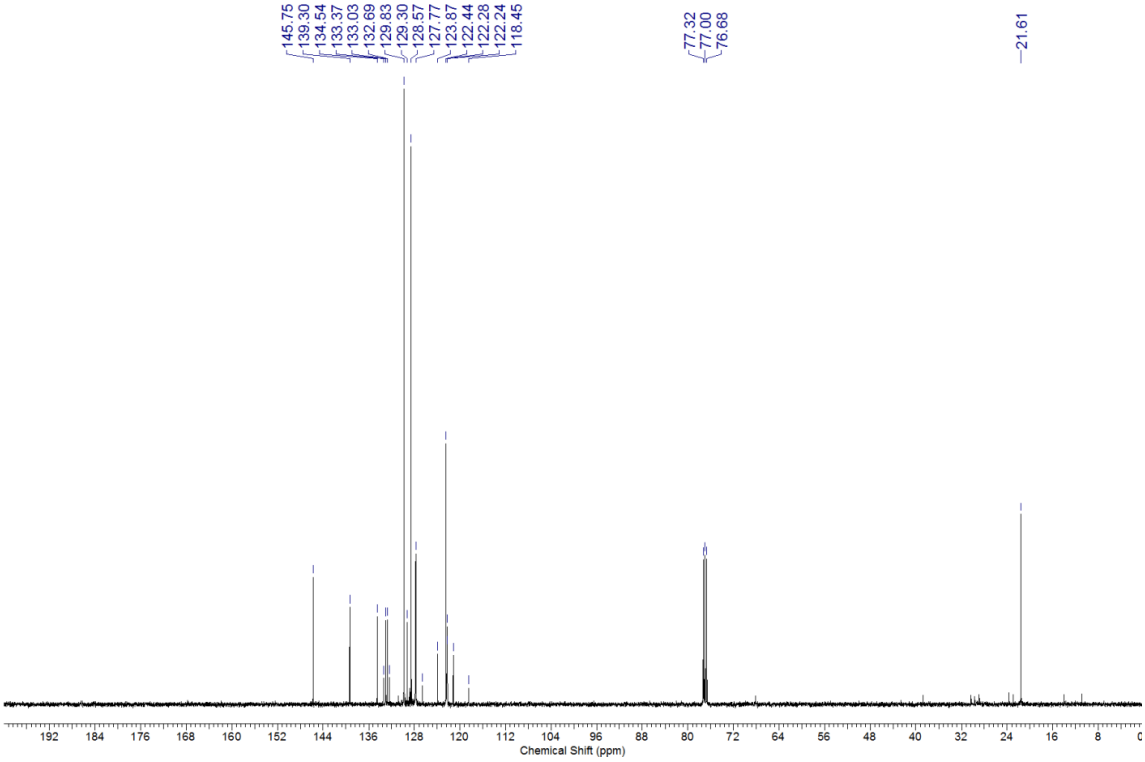


(*E*)-*N*-(3,5-Bis(trifluoromethyl)phenyl)-*N*-(1,2-dichlorovinyl)-4-methylbenzenesulfonamide, 2j

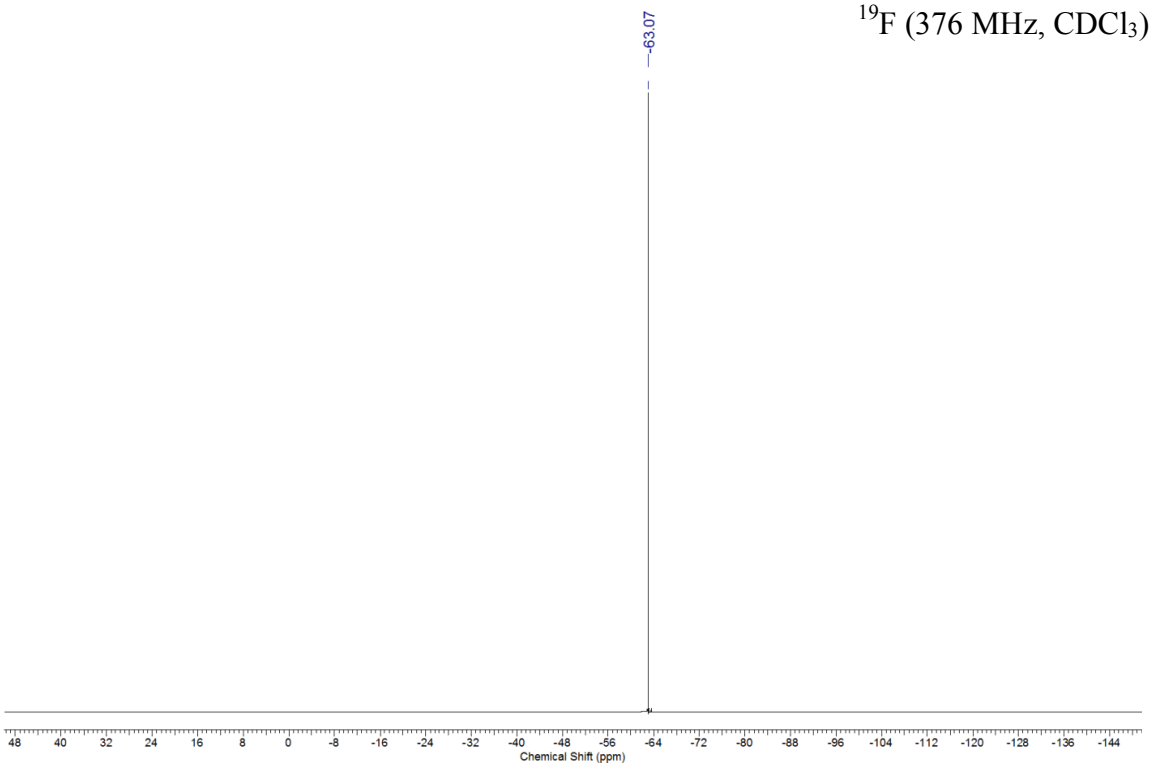


^{1}H (400 MHz, $CDCl_3$)
^{13}C (101 MHz, $CDCl_3$)

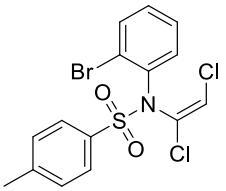




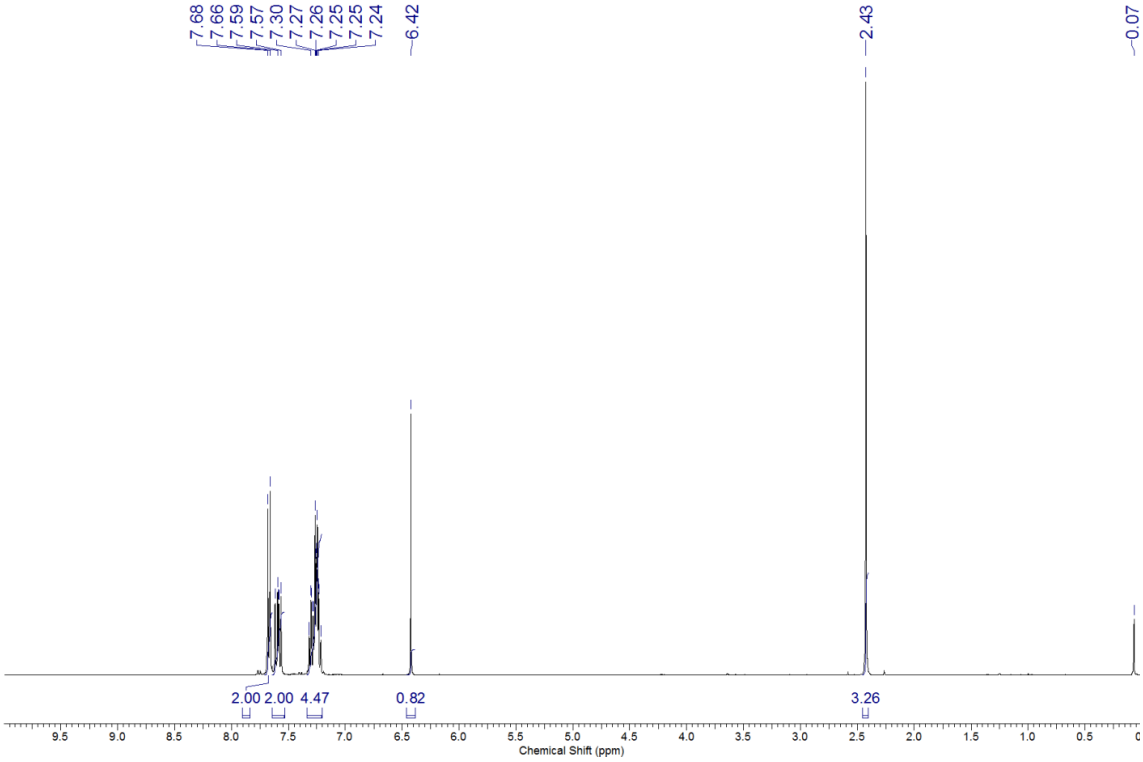
^{19}F (376 MHz, $CDCl_3$)

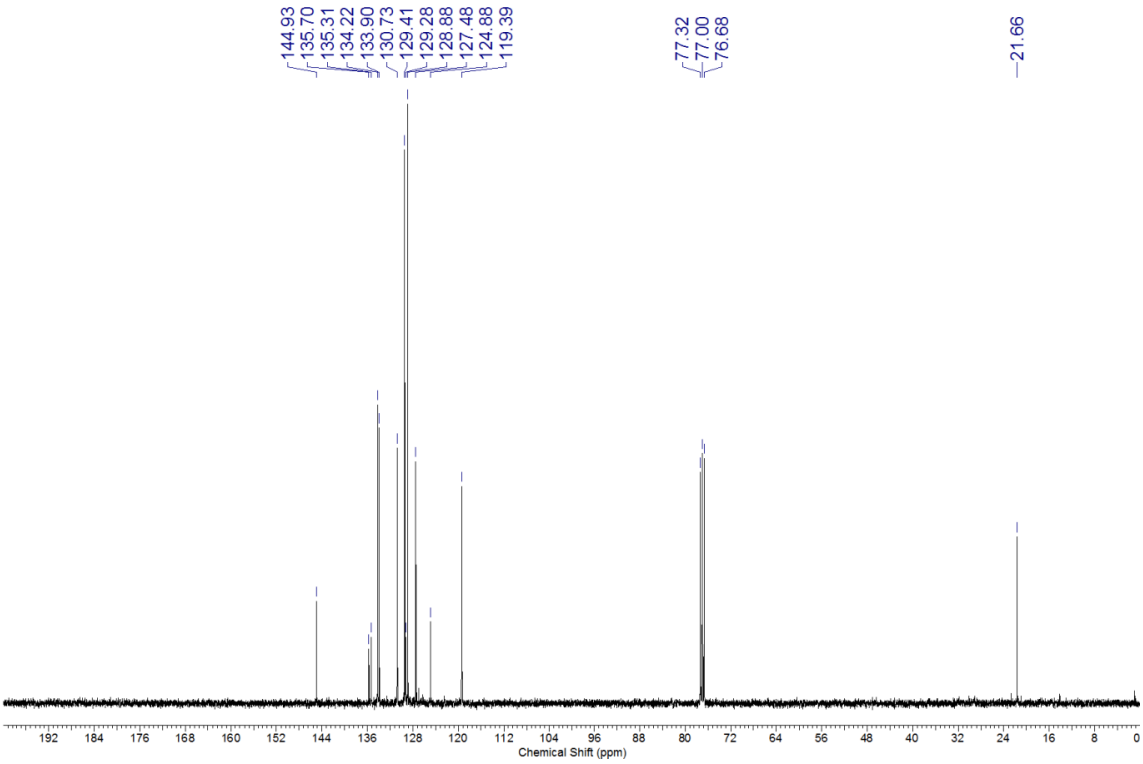


(*E*)-*N*-(2-Bromophenyl)-*N*-(1,2-dichlorovinyl)-4-methylbenzenesulfonamide, 2k

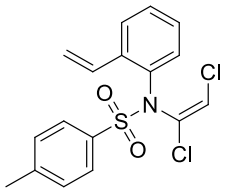


^{1}H (400 MHz, $CDCl_3$)
^{13}C (101 MHz, $CDCl_3$)

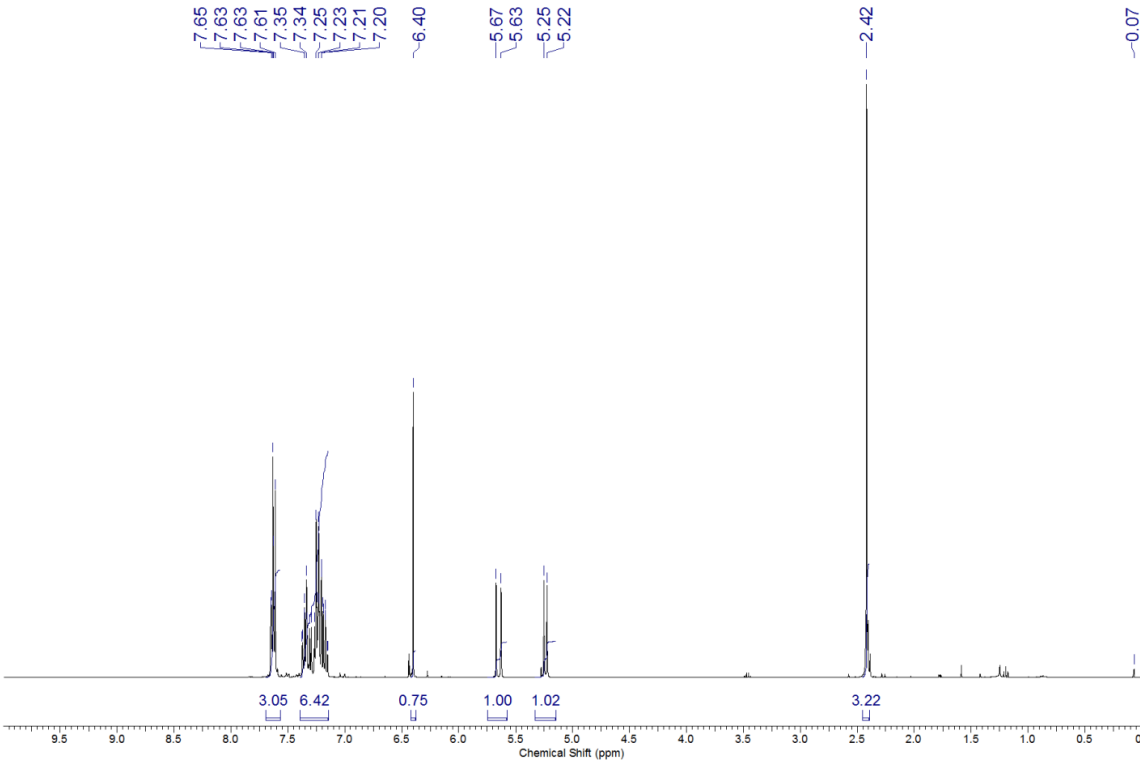


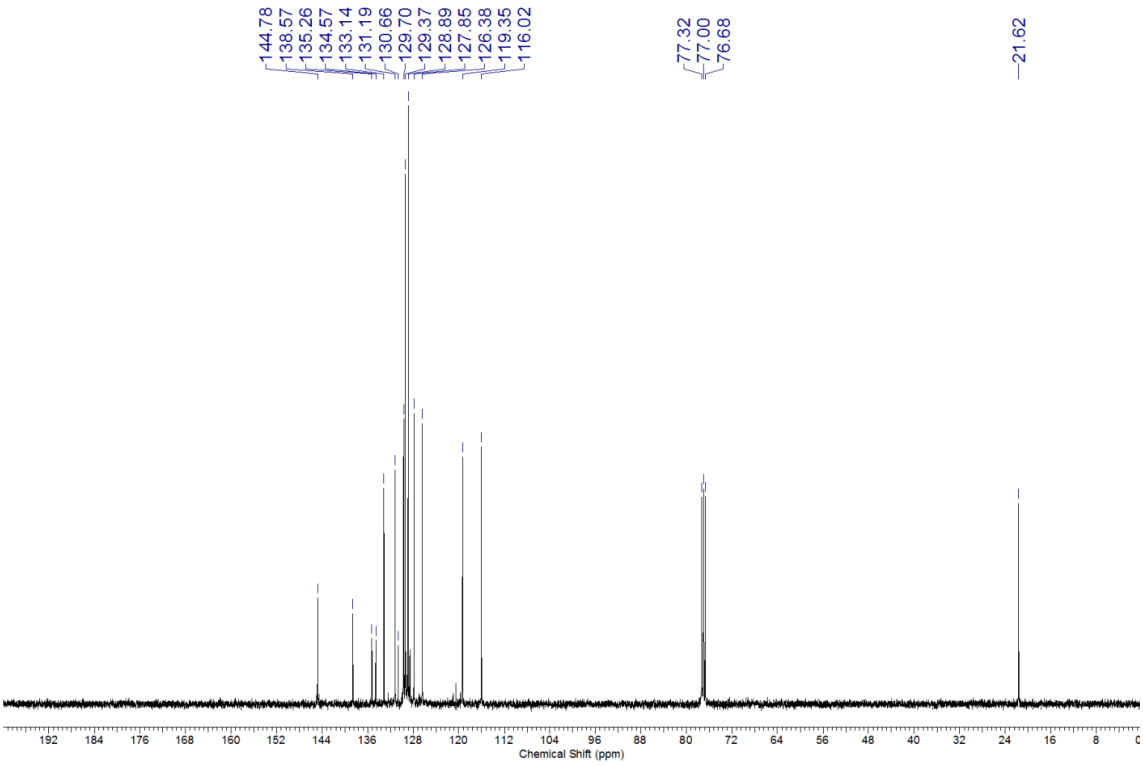


(*E*)-*N*-(1,2-Dichlorovinyl)-*4*-methyl-N-(2-vinylphenyl)benzenesulfonamide, 2l

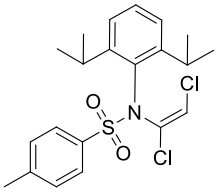


^{1}H (400 MHz, $CDCl_3$)
^{13}C (101 MHz, $CDCl_3$)

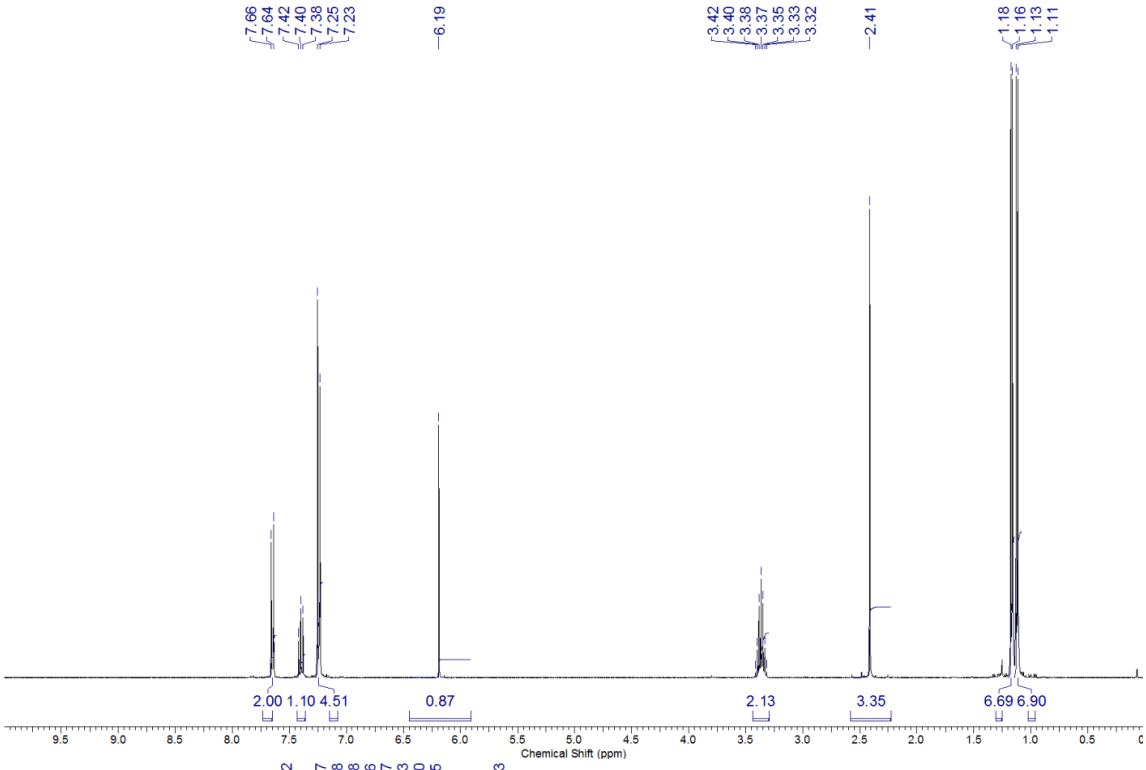


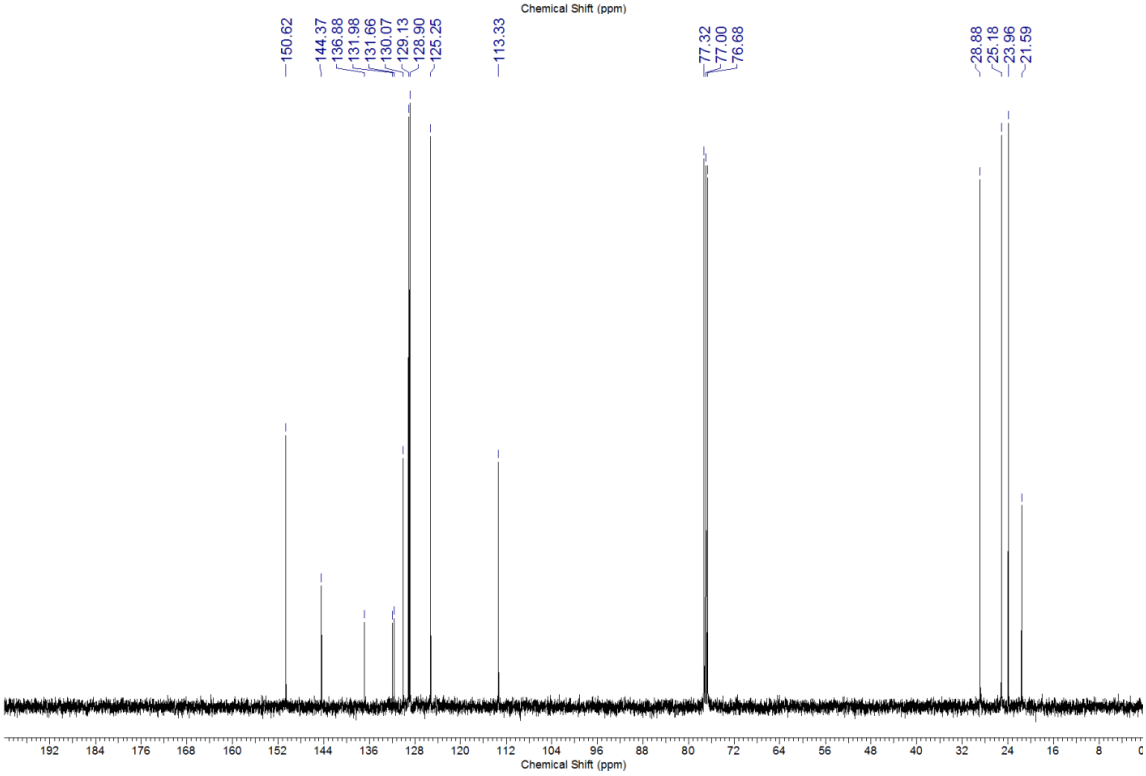


(*E*)-*N*-(1,2-Dichlorovinyl)-*N*-(2,6-diisopropylphenyl)-4-methylbenzenesulfonamide, 2m

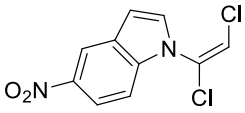


^{1}H (400 MHz, $CDCl_3$)
^{13}C (101 MHz, $CDCl_3$)

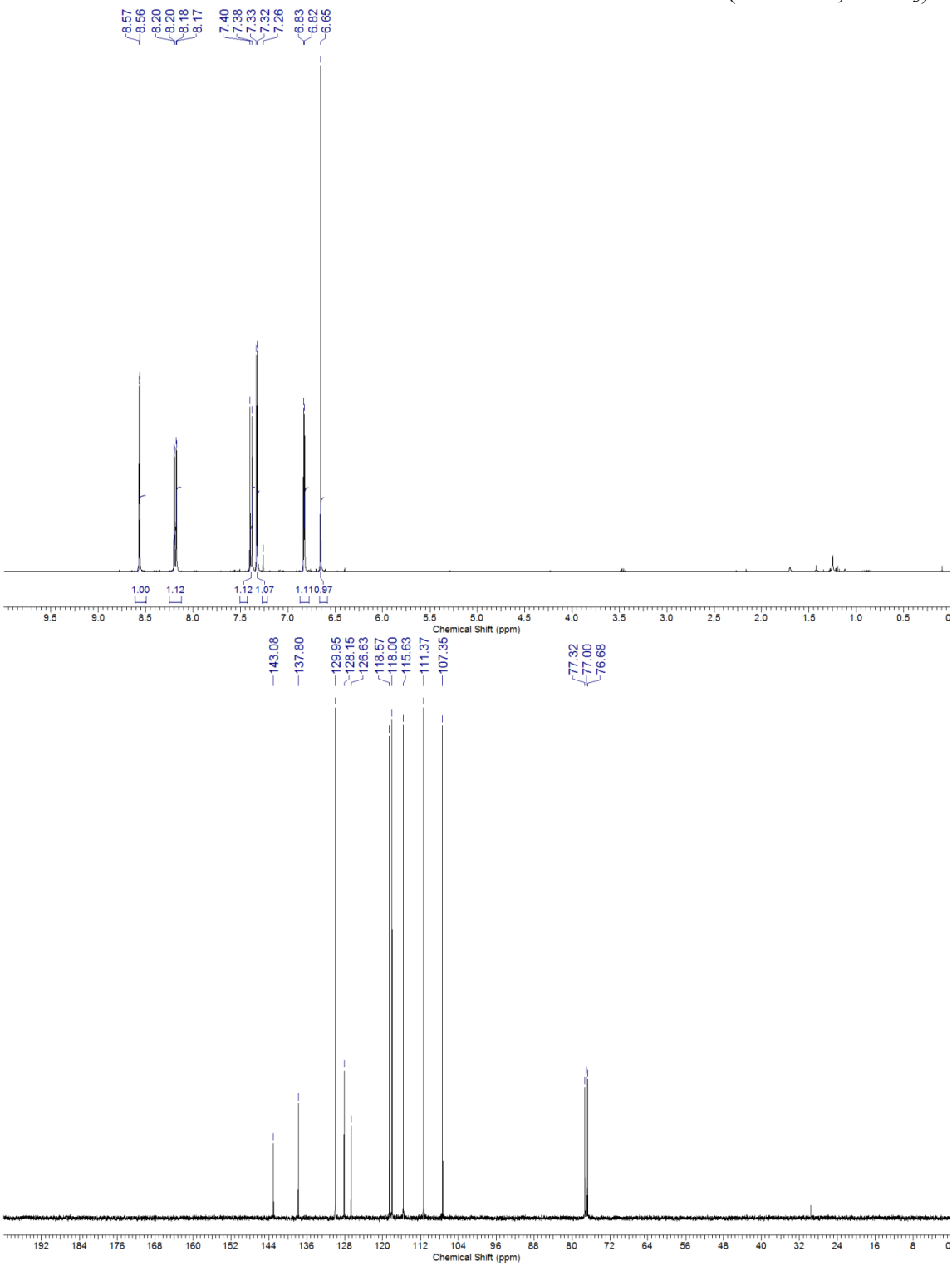




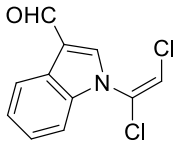
(*E*)-*N*-(1,2-Dichlorovinyl)-5-nitro-1*H*-indole, 2n



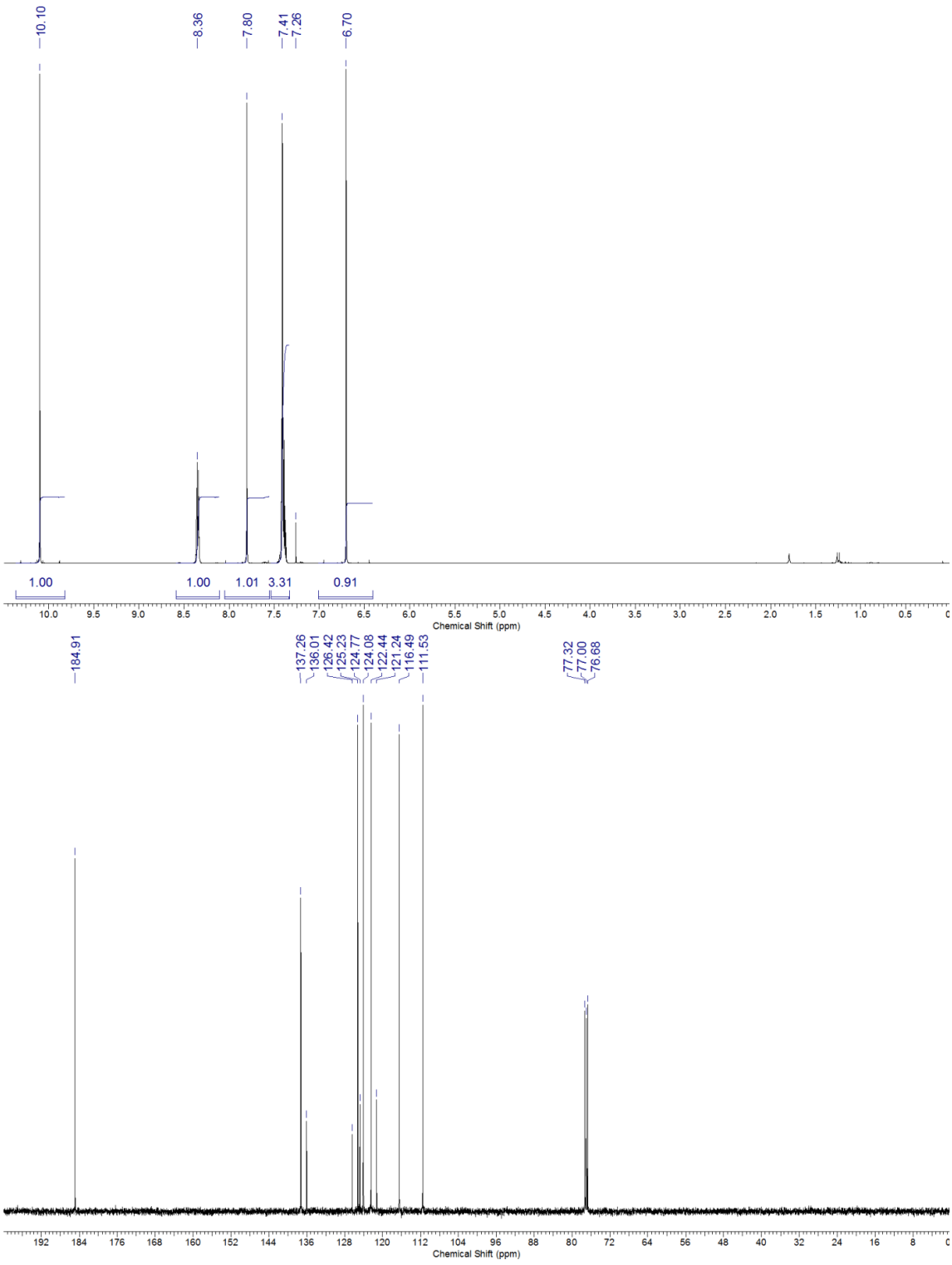
^{1}H (400 MHz, $CDCl_3$)
^{13}C (101 MHz, $CDCl_3$)



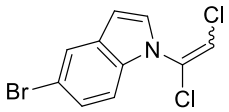
(*E*)-*N*-(1,2-Dichlorovinyl)-1*H*-indole-3-carbaldehyde, 2o



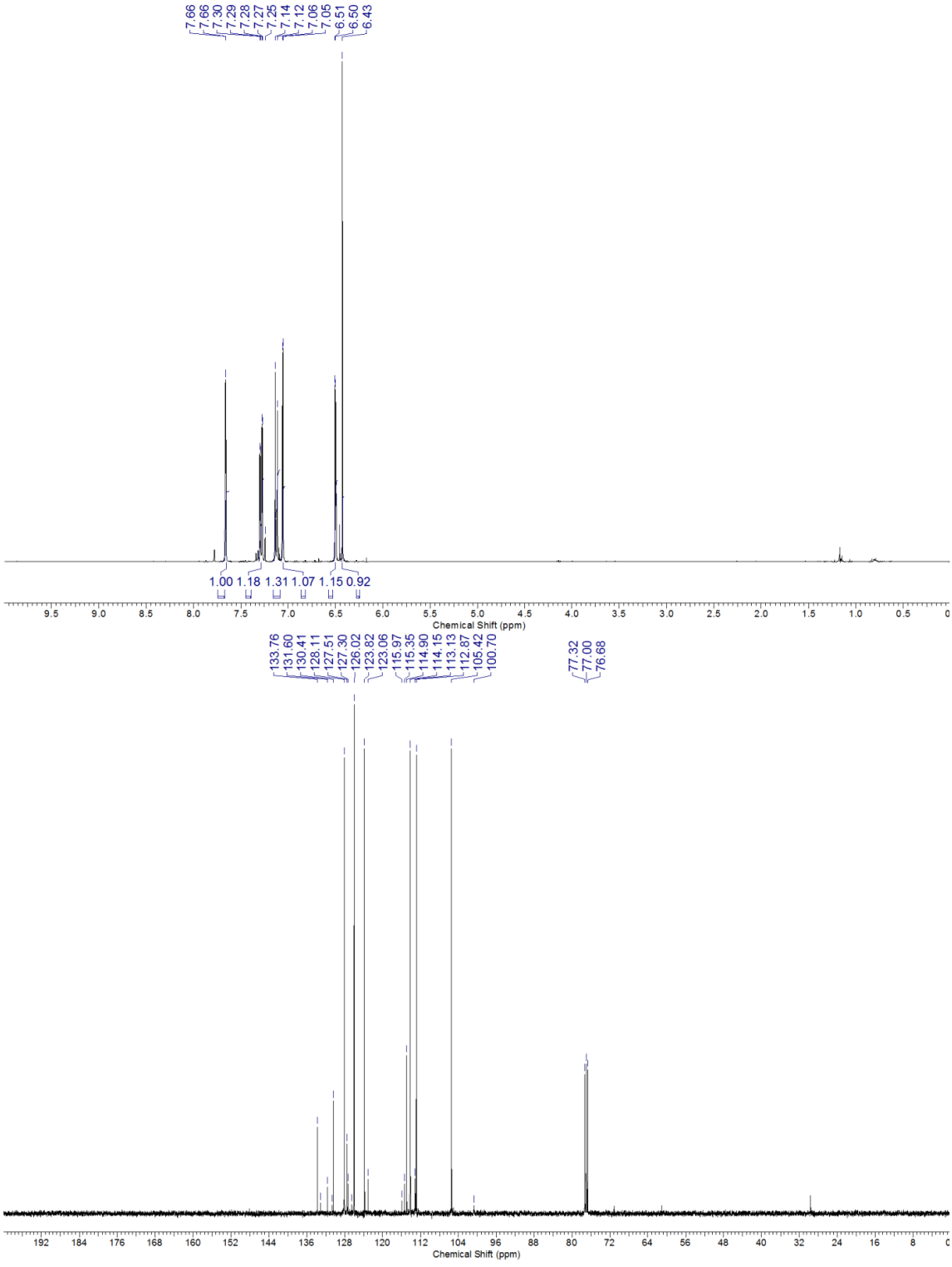
^{1}H (400 MHz, $CDCl_3$)
^{13}C (101 MHz, $CDCl_3$)



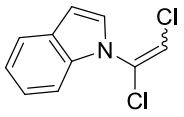
(*E*)-5-Bromo-1-(1,2-dichlorovinyl)-1*H*-indole, 2p



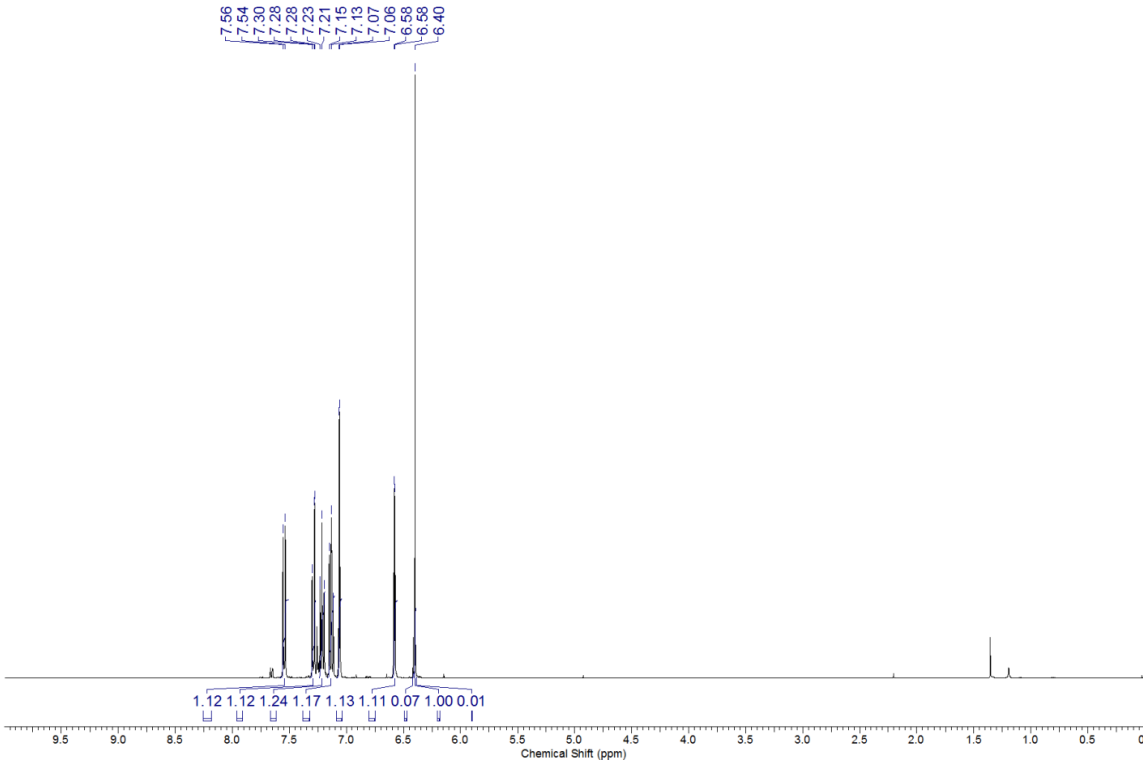
^{1}H (400 MHz, $CDCl_3$)
^{13}C (101 MHz, $CDCl_3$)

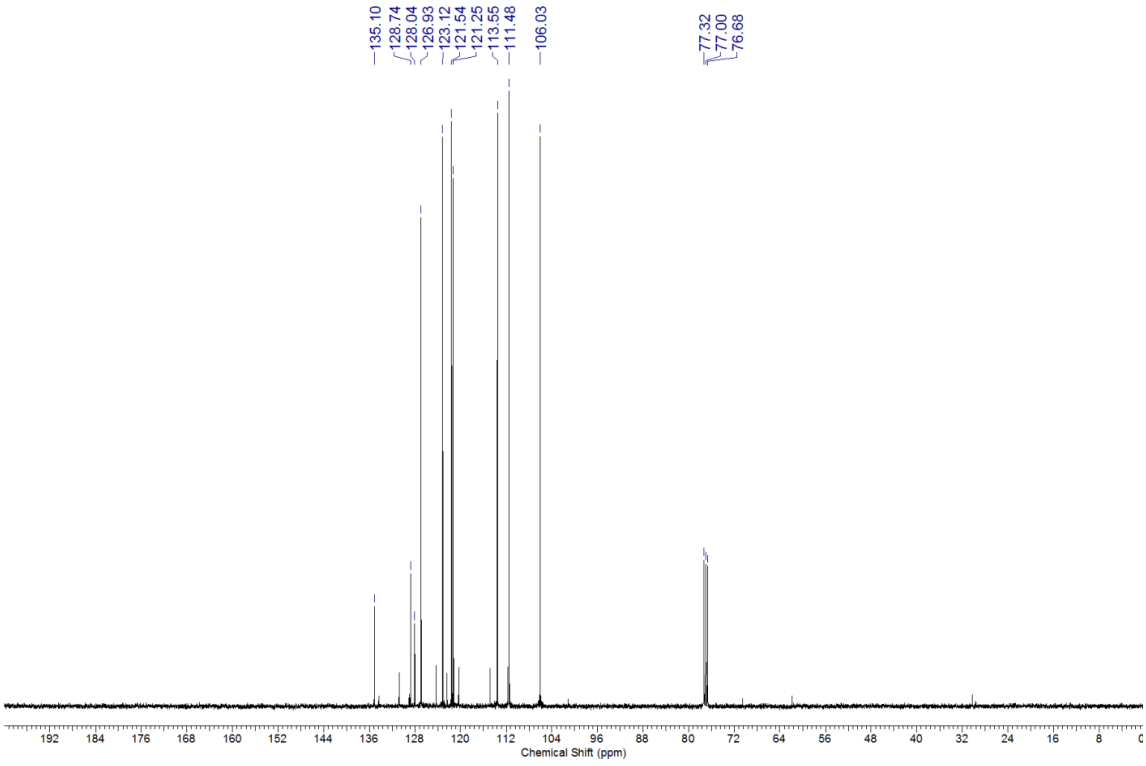


(*E*)-1-(1,2-Dichlorovinyl)-1*H*-indole, 2q

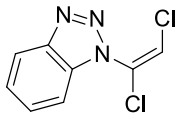


^{1}H (400 MHz, $CDCl_3$)
^{13}C (101 MHz, $CDCl_3$)

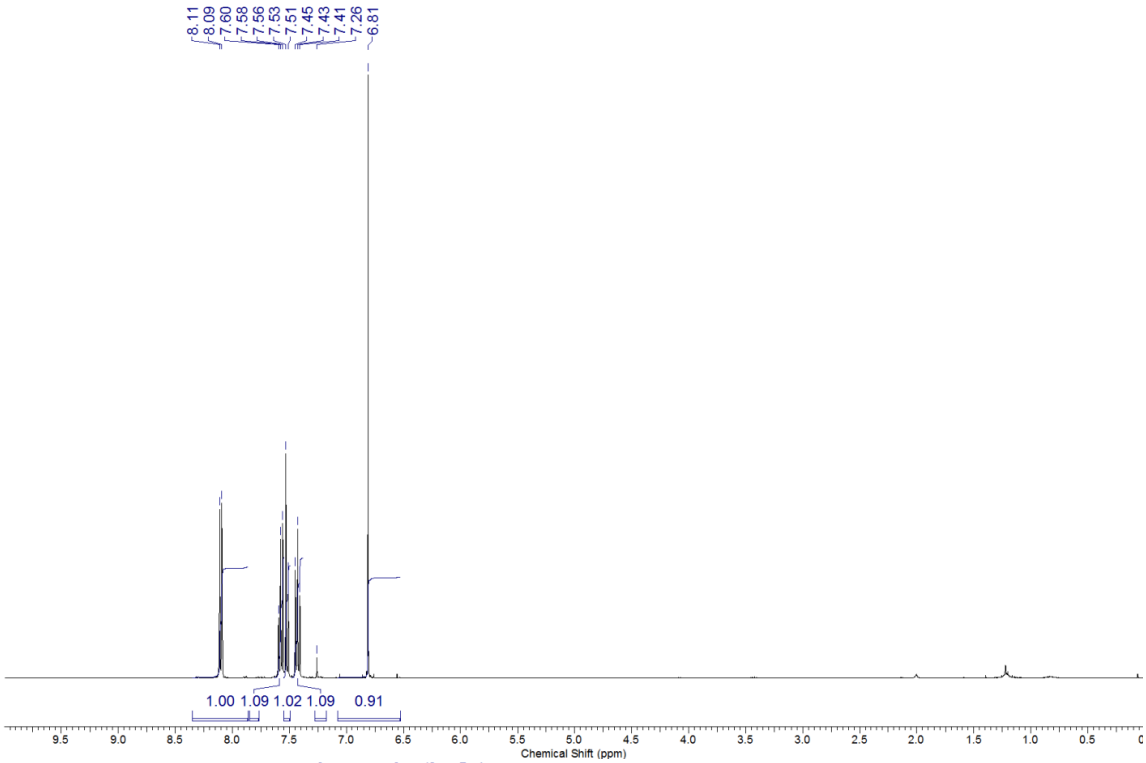


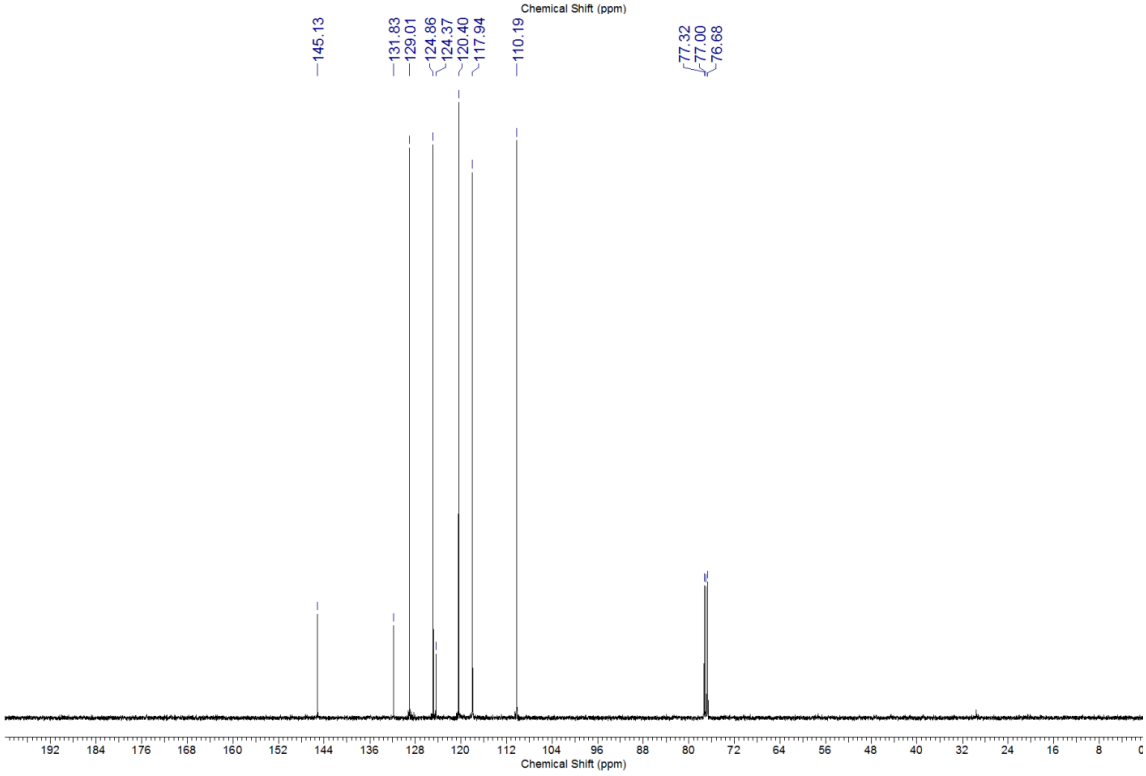


(*E*)-1-(1,2-Dichlorovinyl)-1*H*-benzo[*d*][1,2,3]triazole, 2r

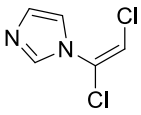


^{1}H (400 MHz, $CDCl_3$)
^{13}C (101 MHz, $CDCl_3$)

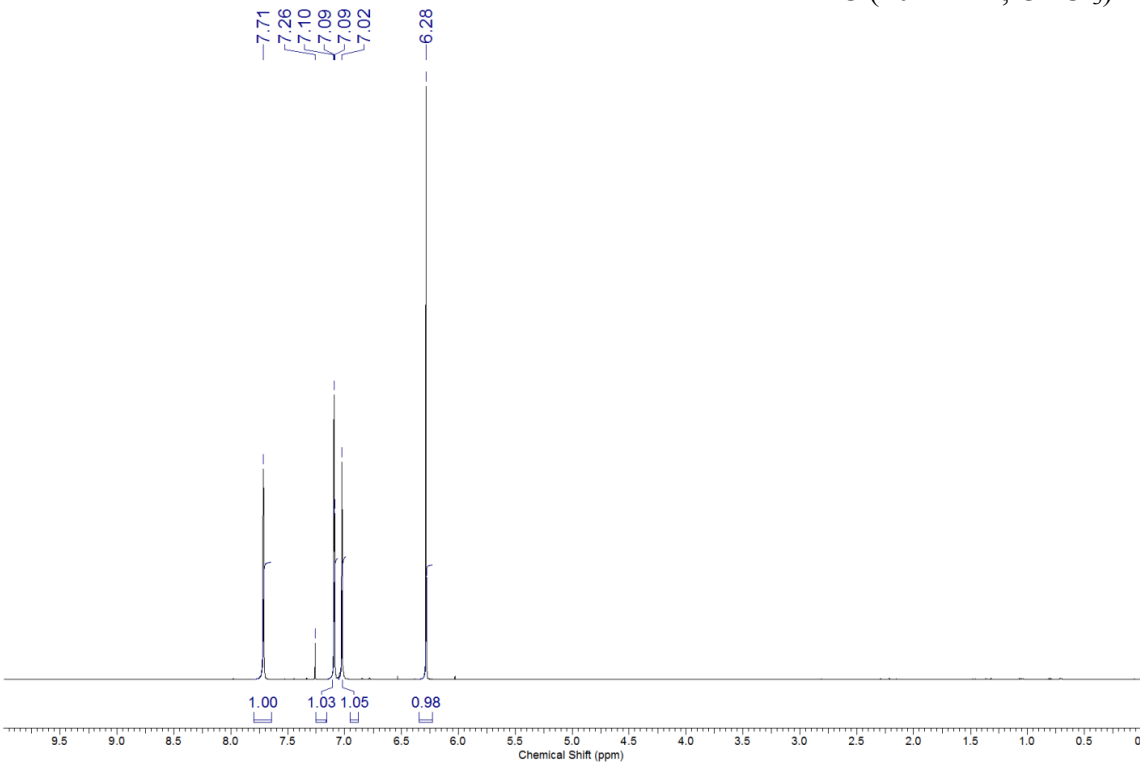


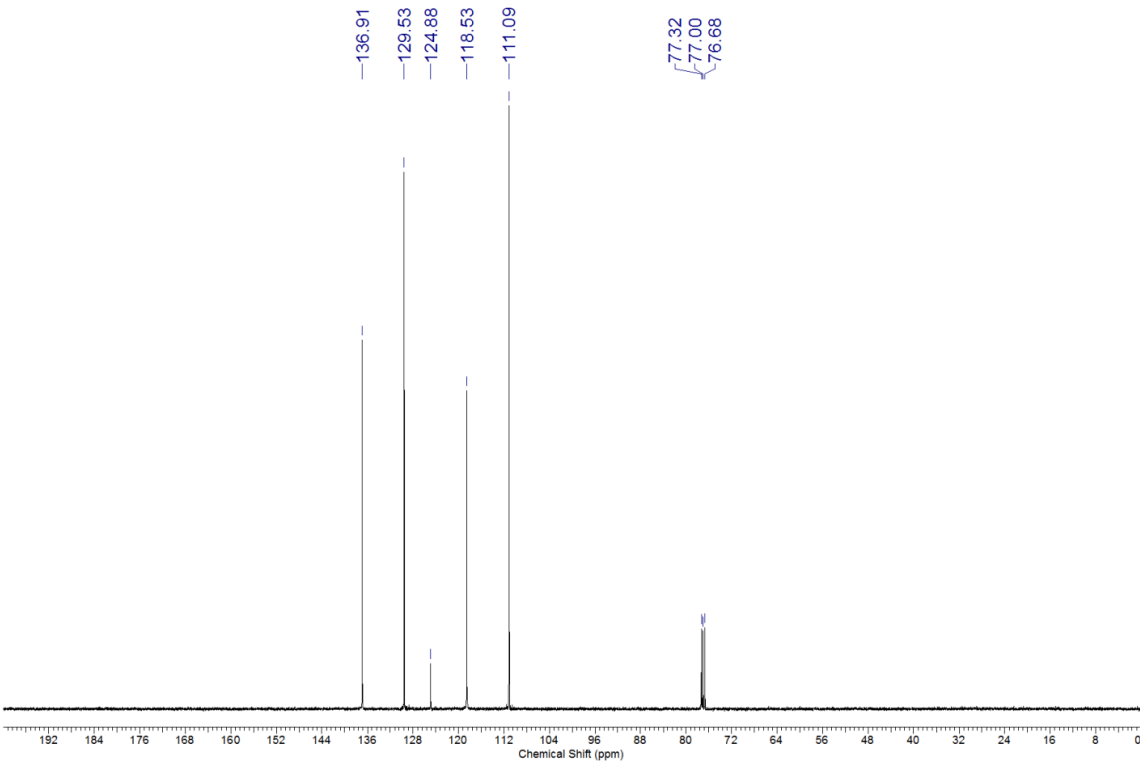


(*E*)-*N*-(1,2-Dichlorovinyl)-1*H*-imidazole, 2s

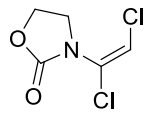


^{1}H (400 MHz, $CDCl_3$)
^{13}C (101 MHz, $CDCl_3$)

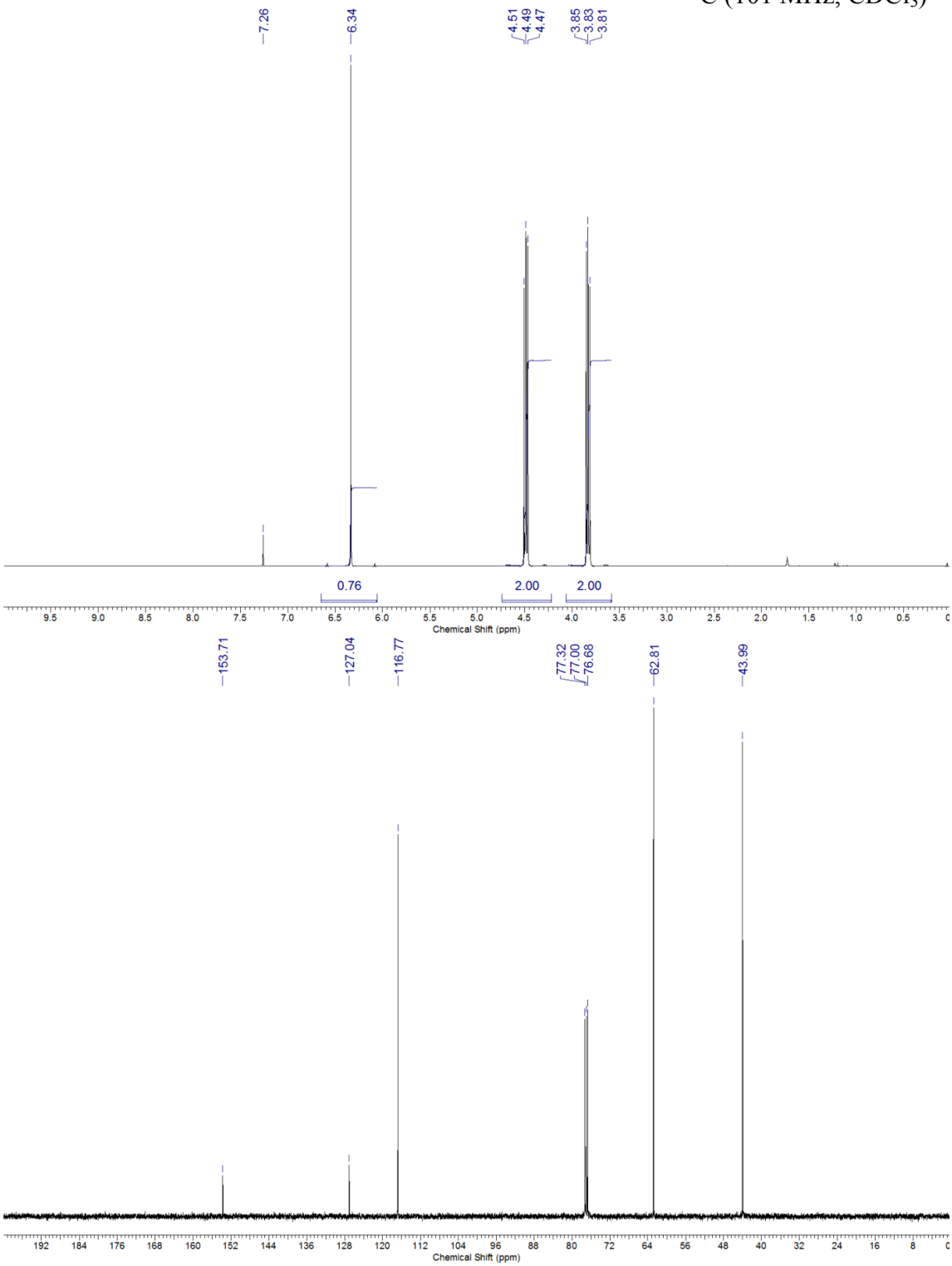




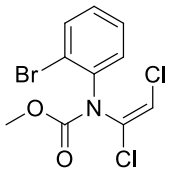
(*E*)-3-(1,2-Dichlorovinyl)oxazolidin-2-one, 2t



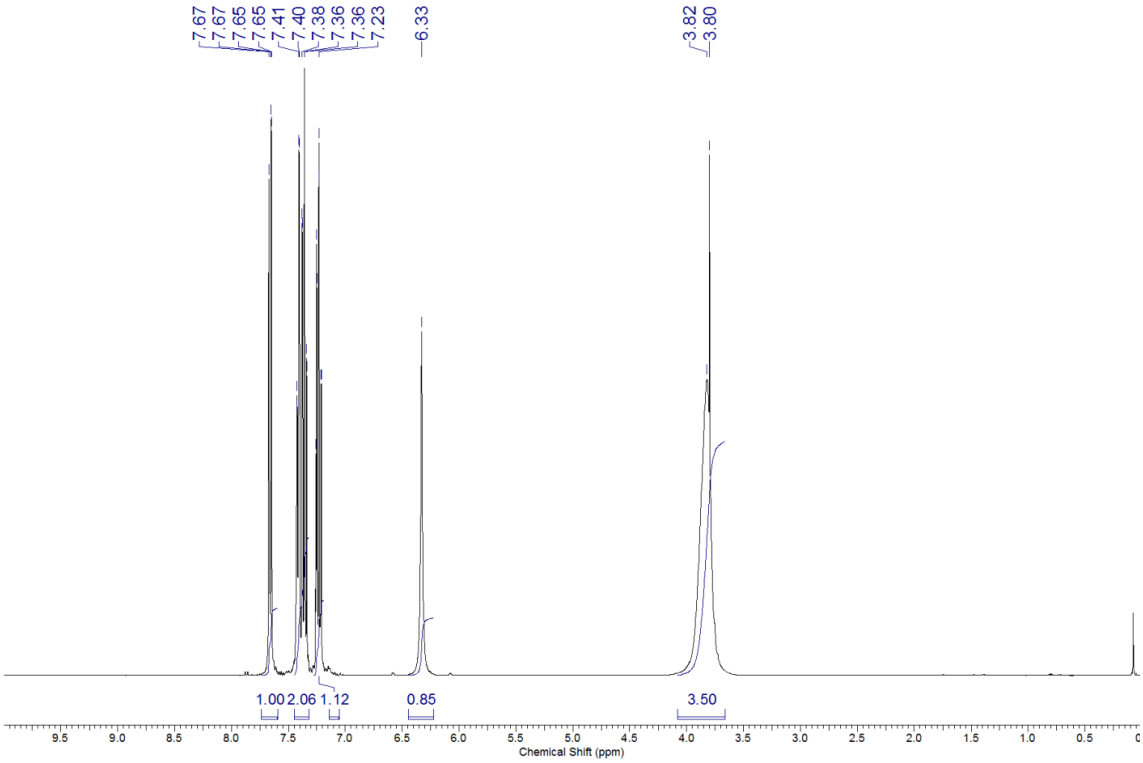
^{1}H (400 MHz, $CDCl_3$)
^{13}C (101 MHz, $CDCl_3$)

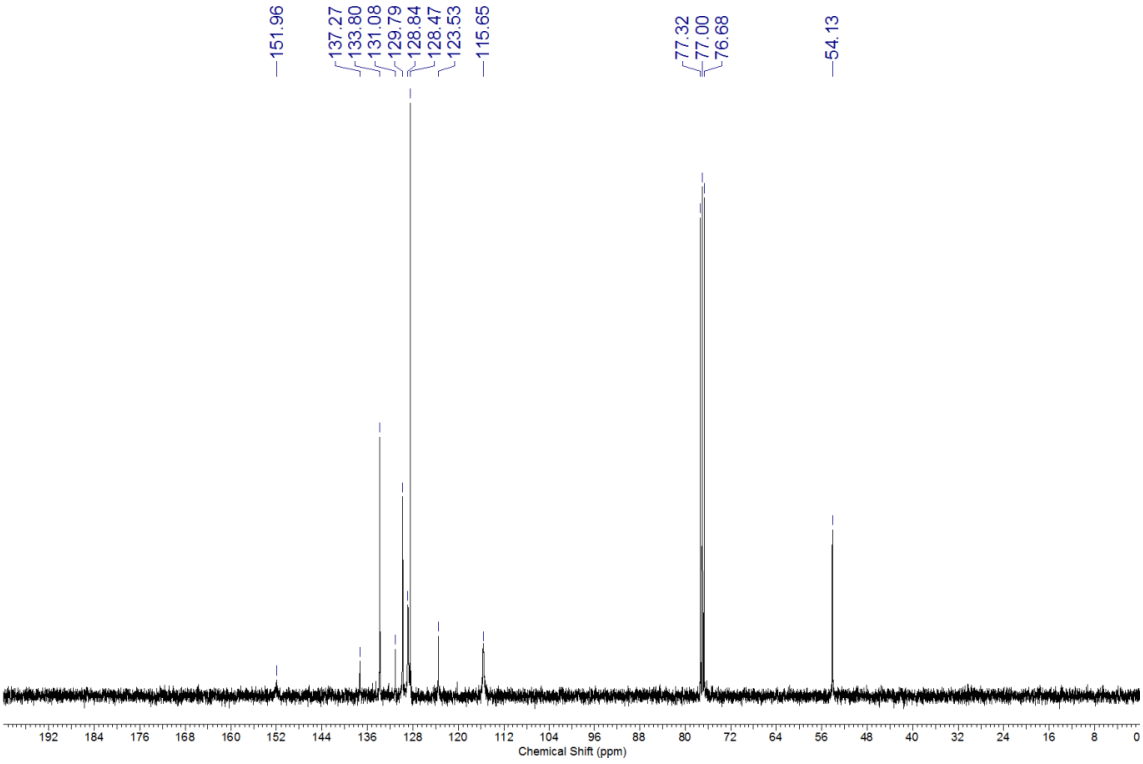


(*E*)-Methyl (2-bromophenyl)(1,2-dichlorovinyl)carbamate, 2u

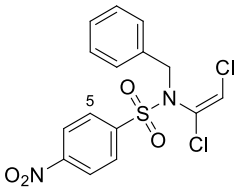


^{1}H (400 MHz, $CDCl_3$)
^{13}C (101 MHz, $CDCl_3$)

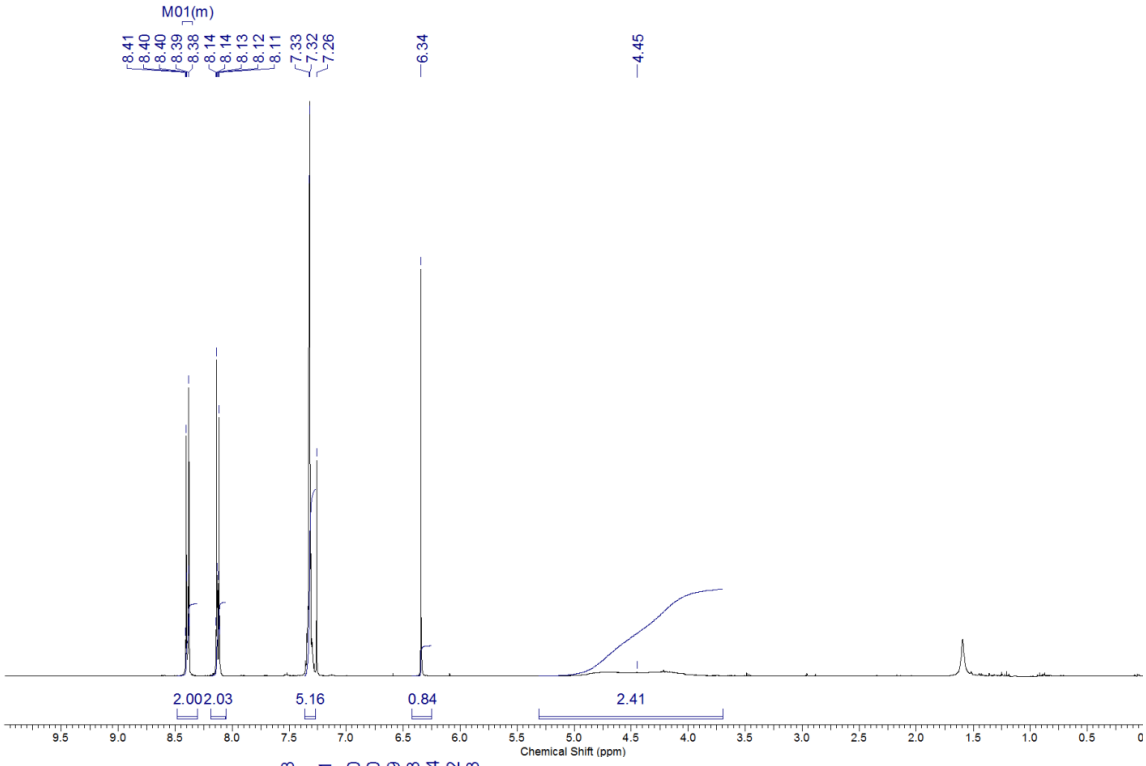


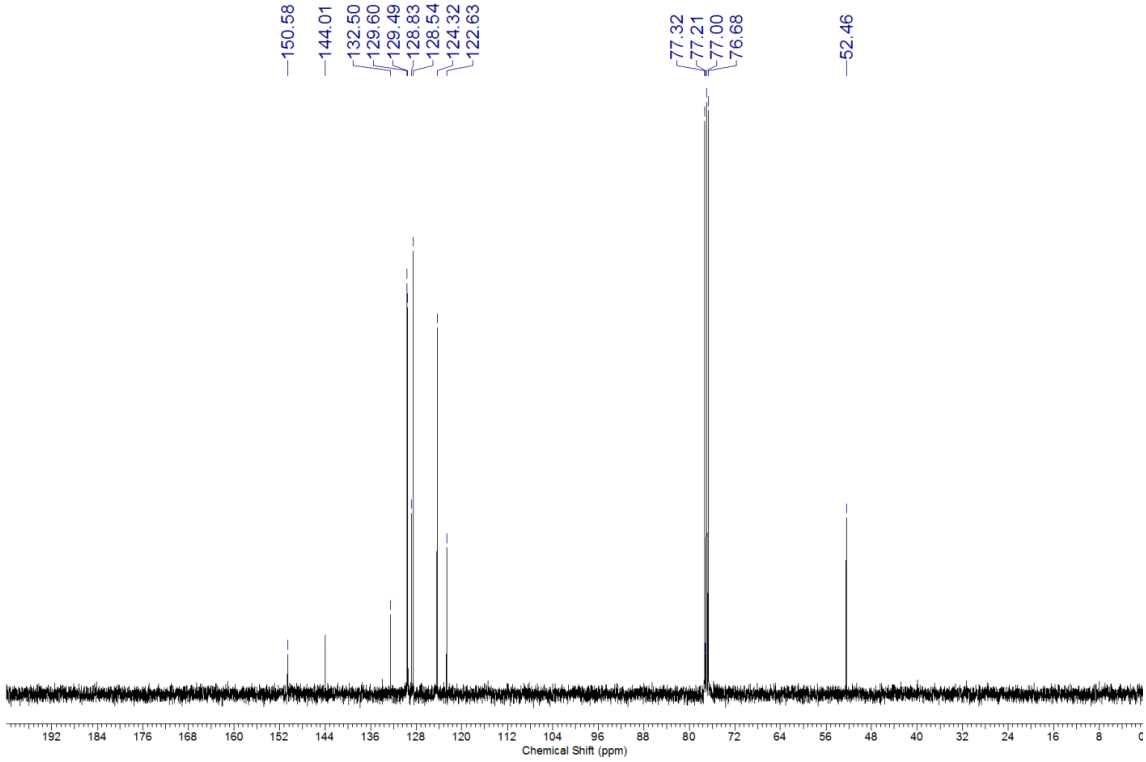


(*E*)-*N*-Benzyl-*N*-(1,2-dichlorovinyl)-4-nitrobenzenesulfonamide, 2v

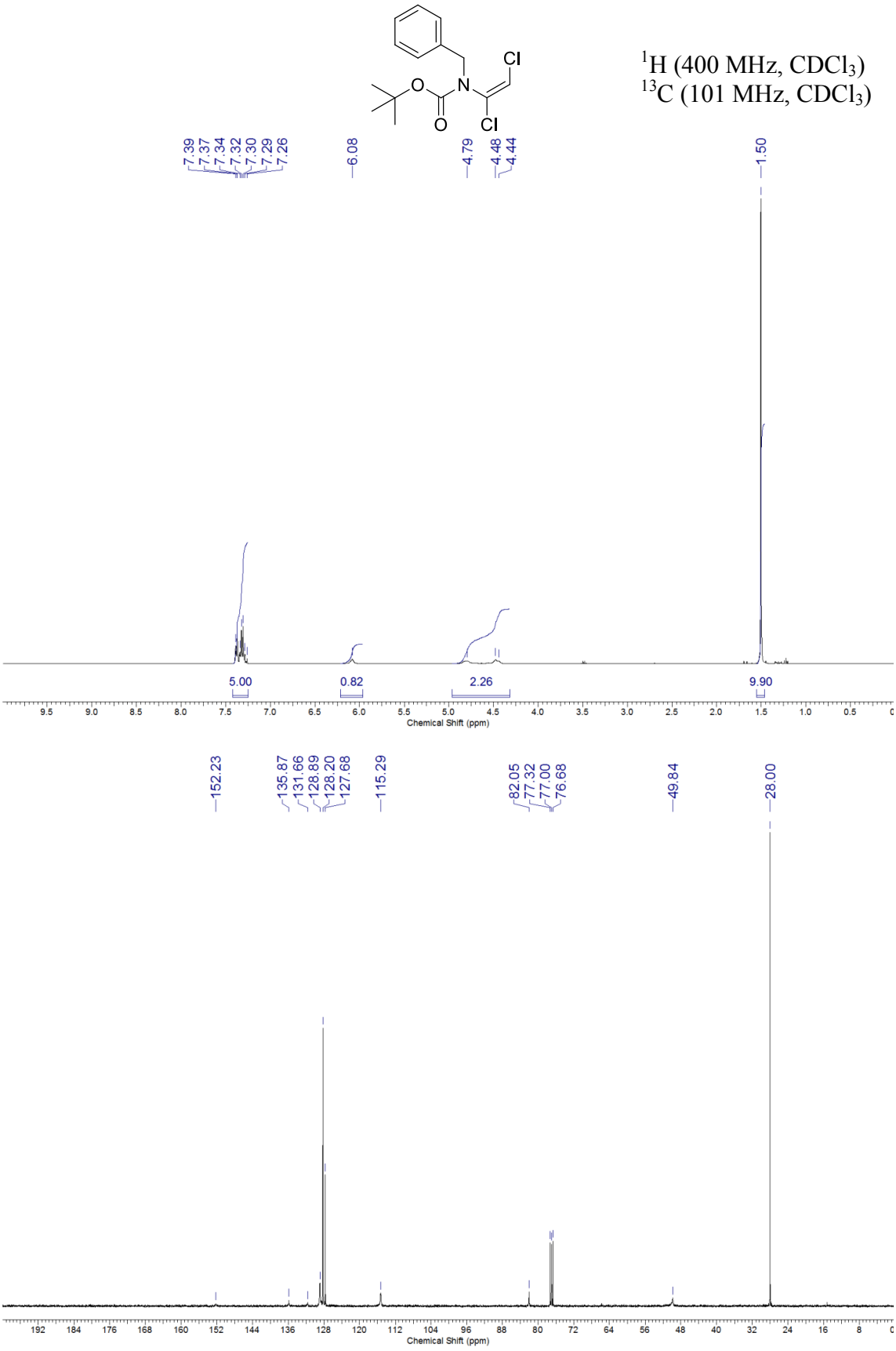


^{1}H (400 MHz, $CDCl_3$)
^{13}C (101 MHz, $CDCl_3$)

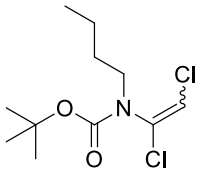




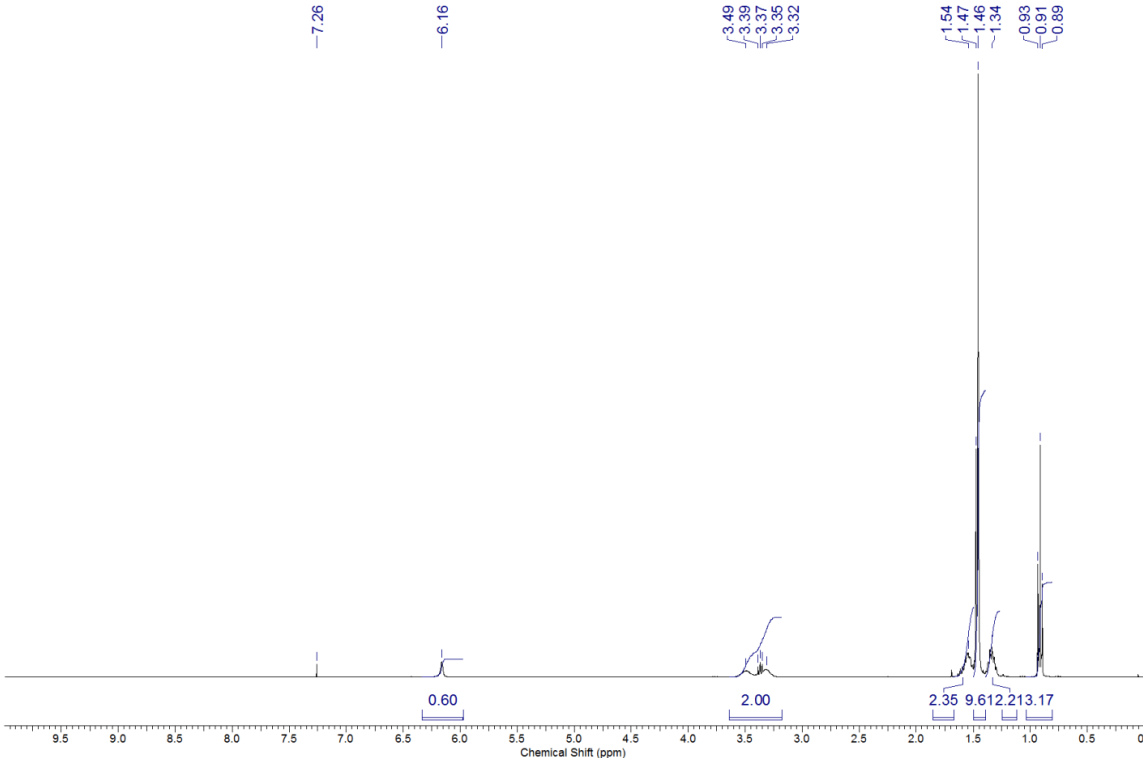
(*E*)-*tert*-Butyl benzyl(1,2-dichlorovinyl)carbamate, 2w

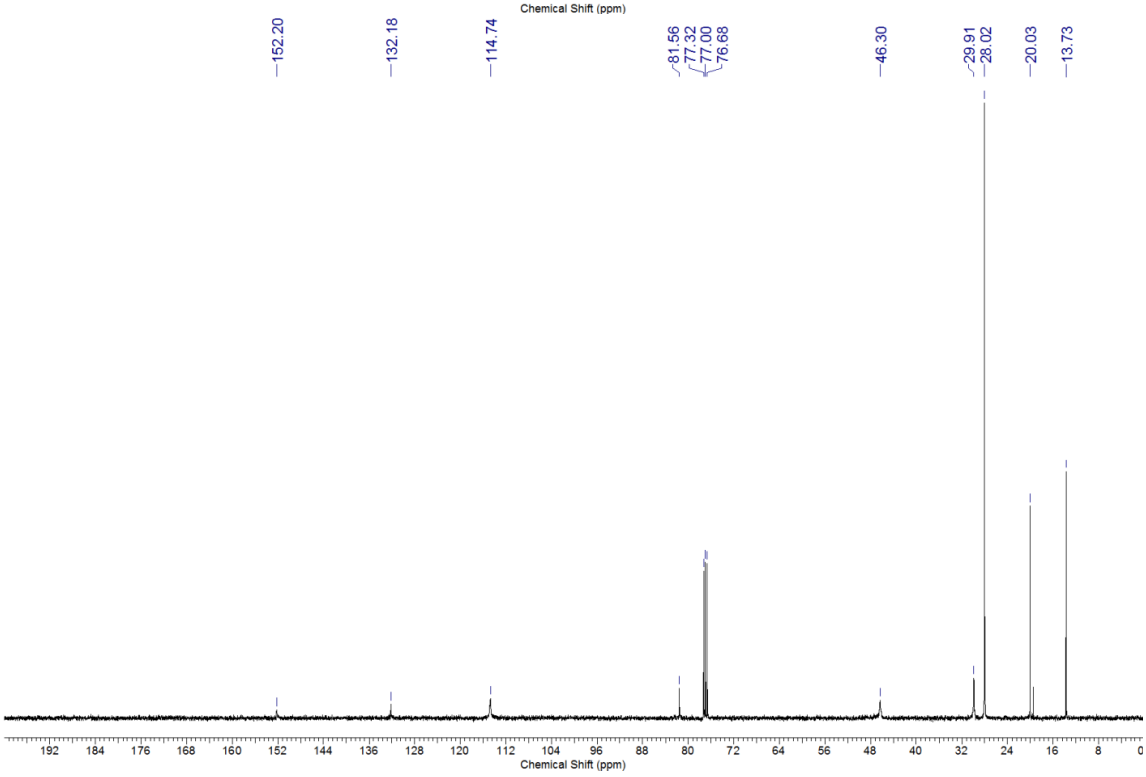


(*E*)-*tert*-Butyl butyl(1,2-dichlorovinyl)carbamate, 2x

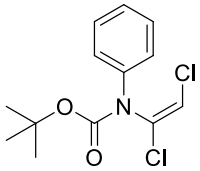


^{1}H (400 MHz, $CDCl_3$)
^{13}C (101 MHz, $CDCl_3$)

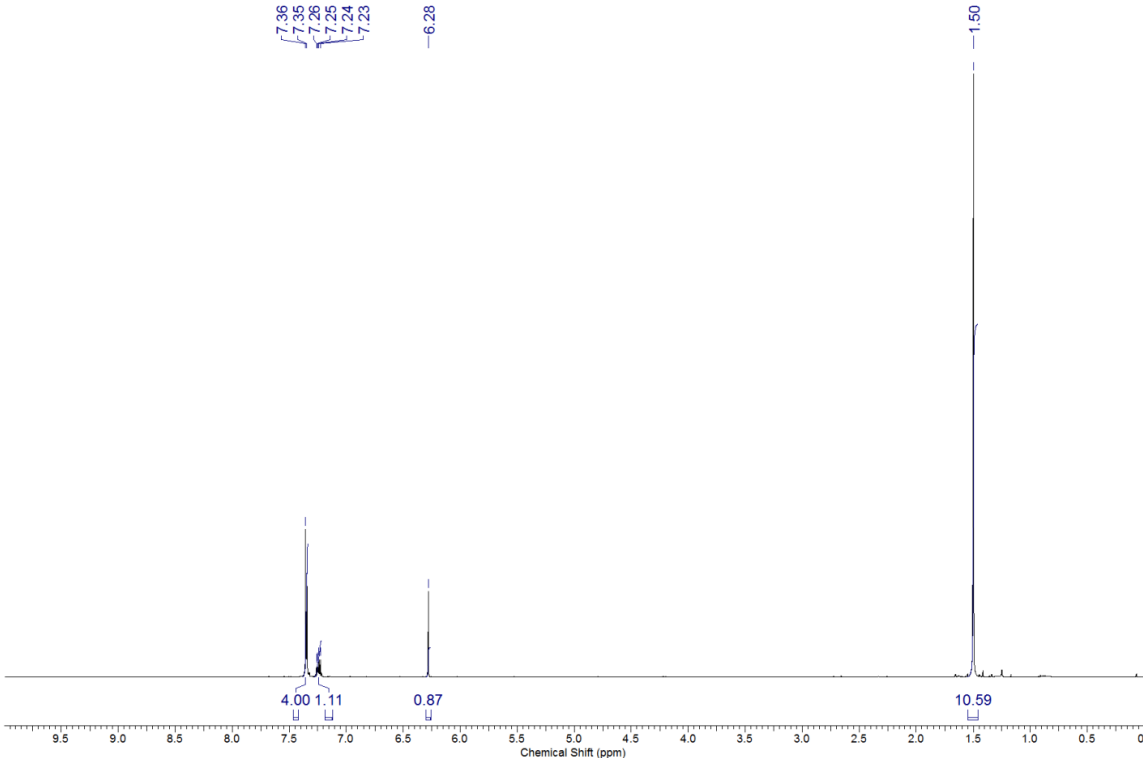


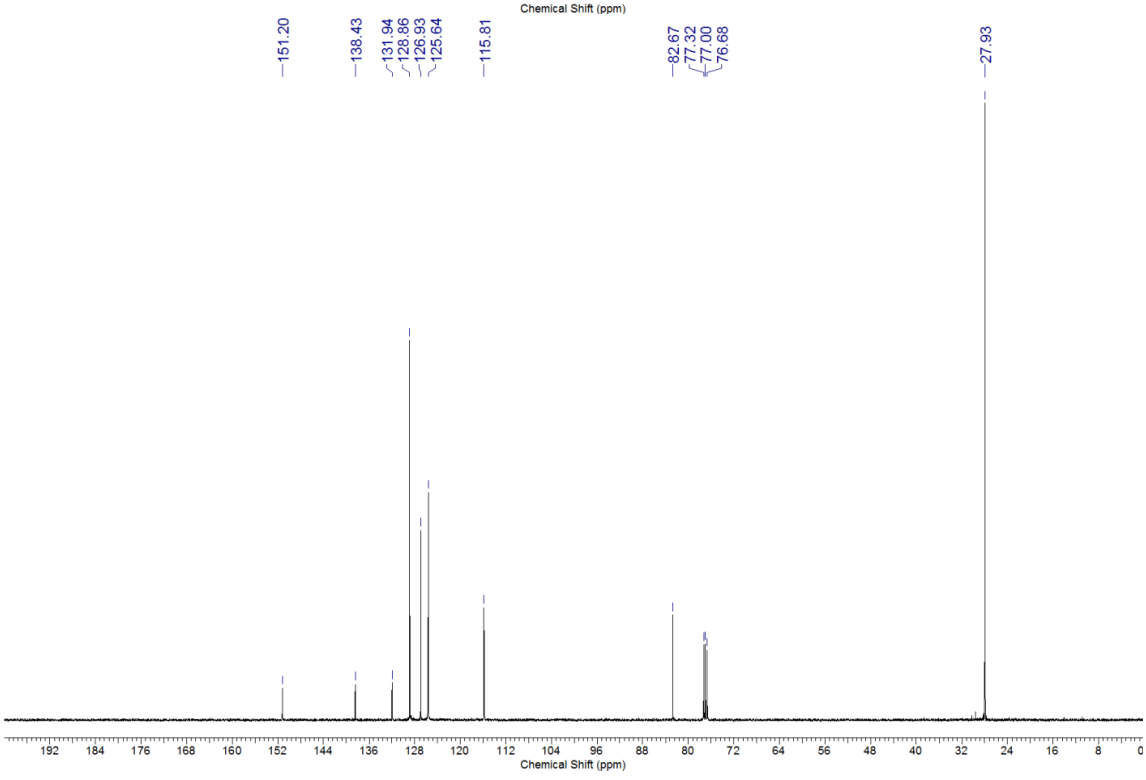


(*E*)-*tert*-Butyl (1,2-dichlorovinyl)(phenyl)carbamate, 2y

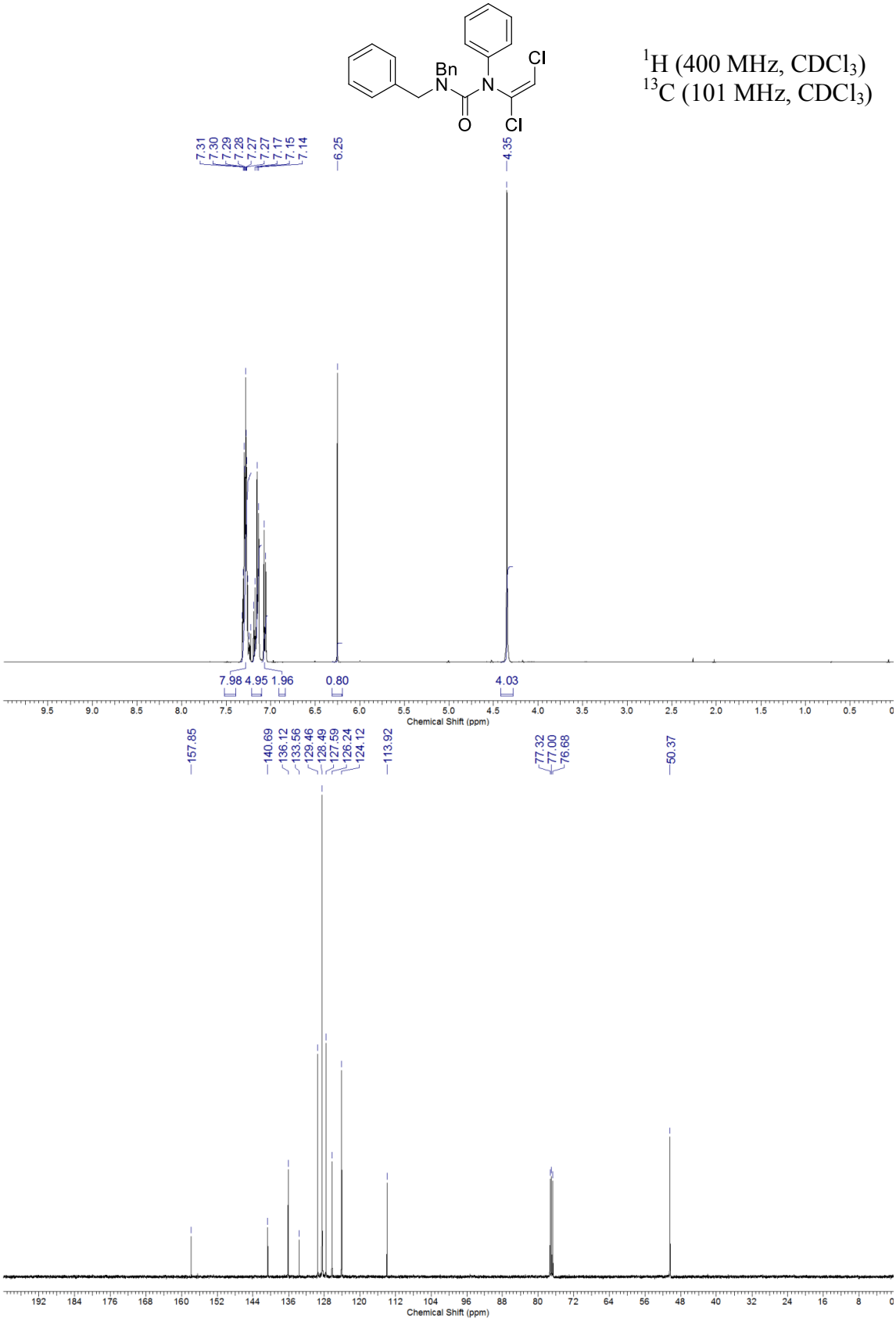


^{1}H (400 MHz, $CDCl_3$)
^{13}C (101 MHz, $CDCl_3$)

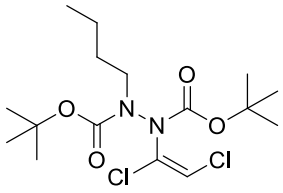




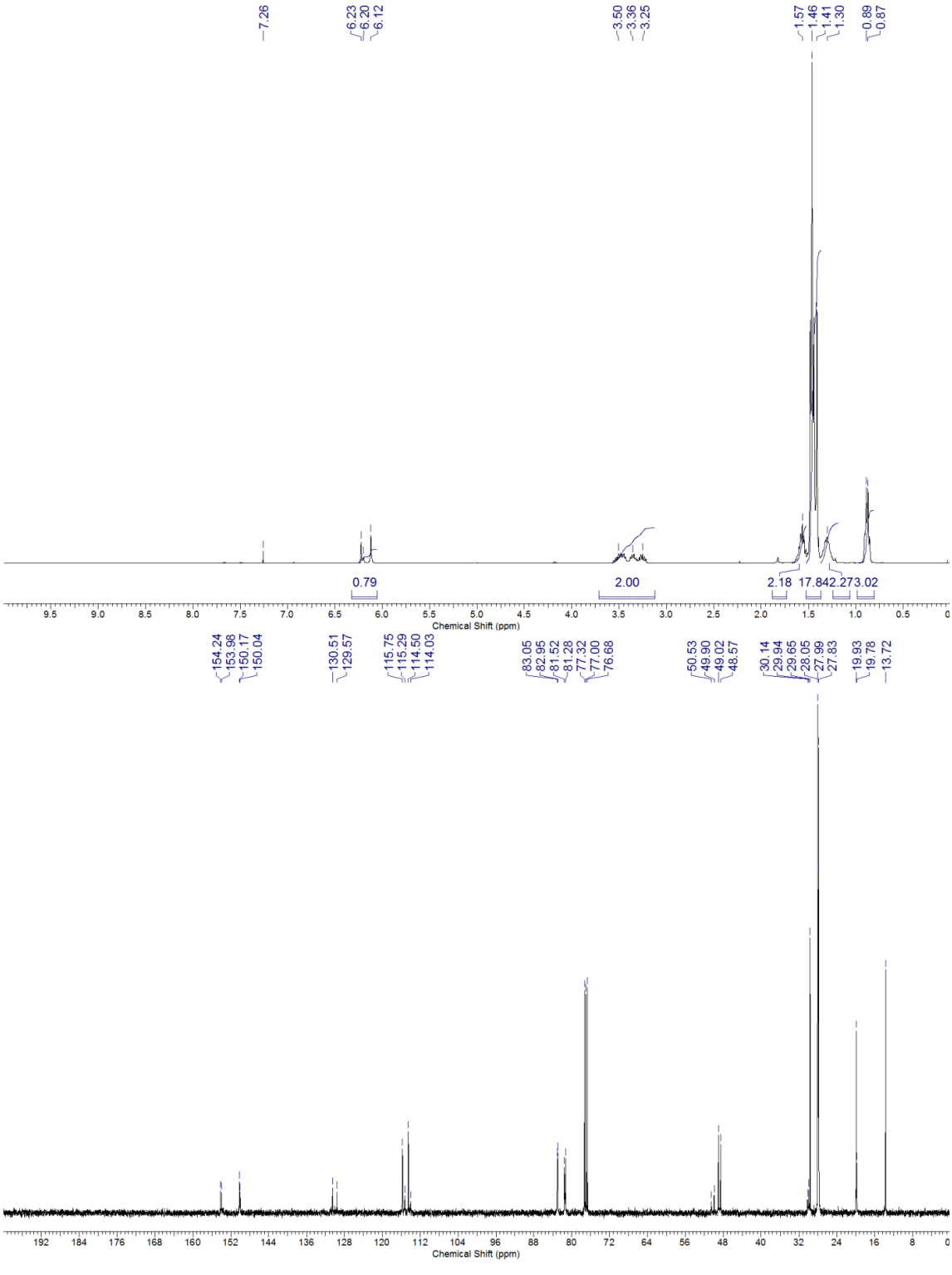
(*E*)-1,1-Dibenzyl-3-(1,2-dichlorovinyl)-3-phenylurea, 2z



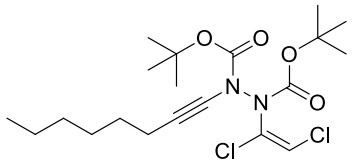
(*E*)-Di-*tert*-butyl 1-butyl-2-(1,2-dichlorovinyl)hydrazine-1,2-dicarboxylate, 2aa



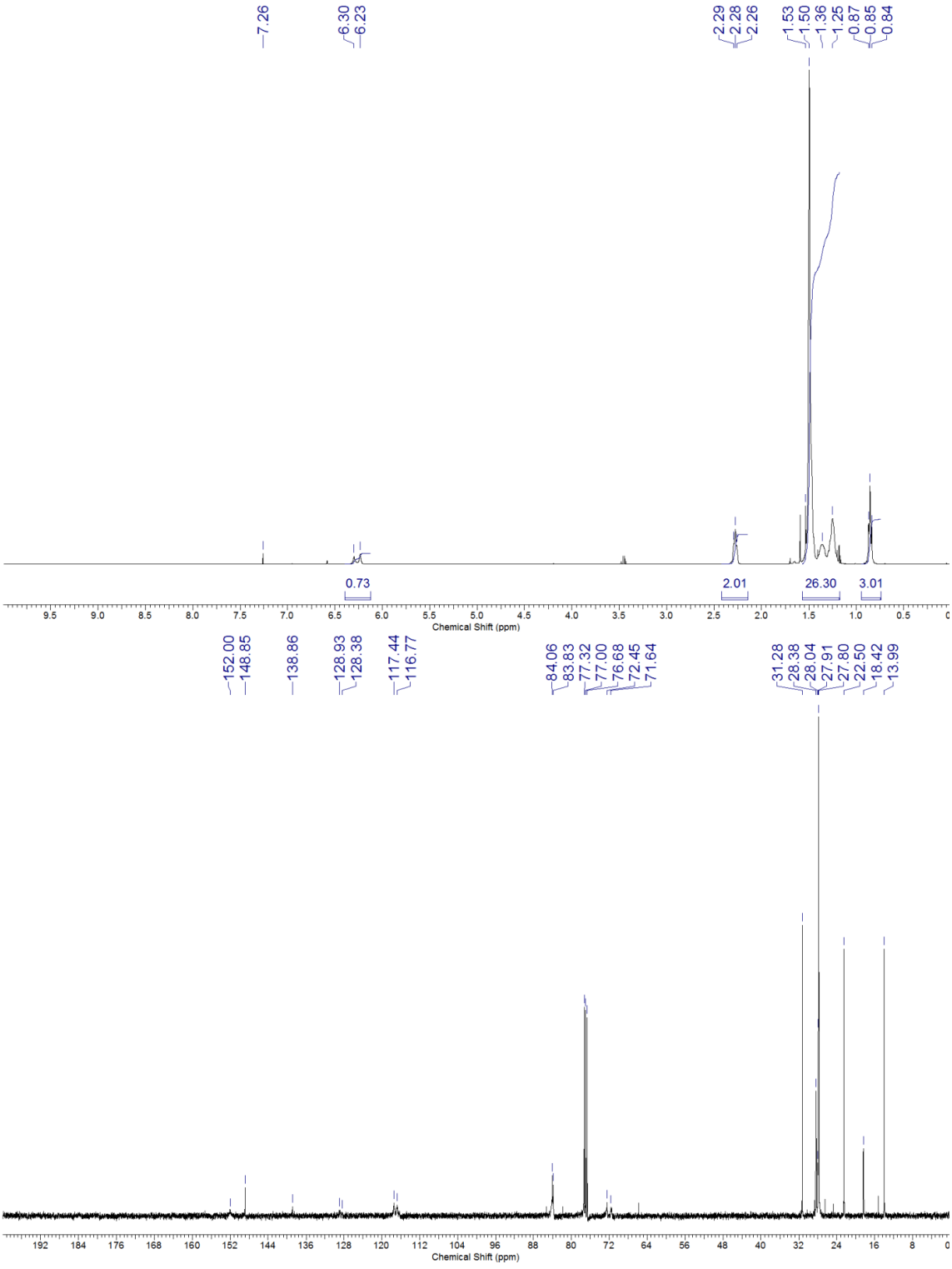
^{1}H (400 MHz, $CDCl_3$)
^{13}C (101 MHz, $CDCl_3$)



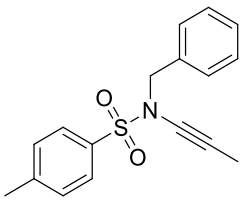
(*E*)-Di-*tert*-butyl 1-(1,2-dichlorovinyl)-2-(oct-1-yn-1-yl)hydrazine-1,2-dicarboxylate, 2bb



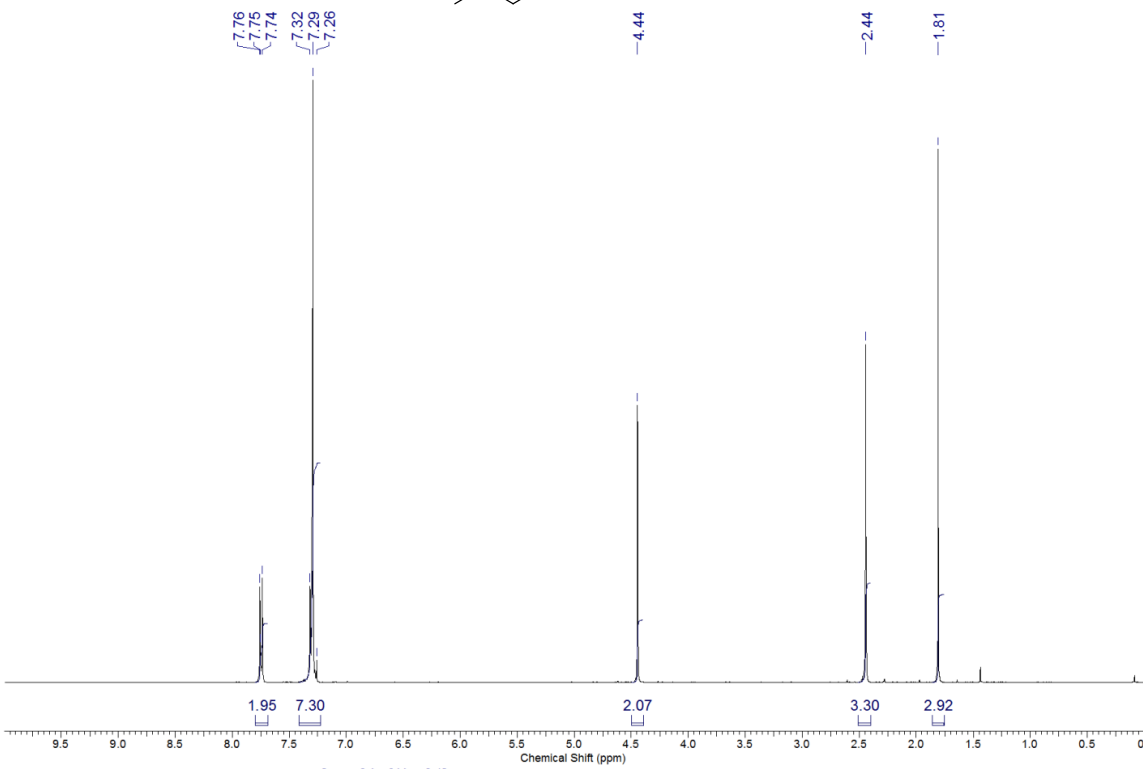
^{1}H (400 MHz, $CDCl_3$)
^{13}C (101 MHz, $CDCl_3$)

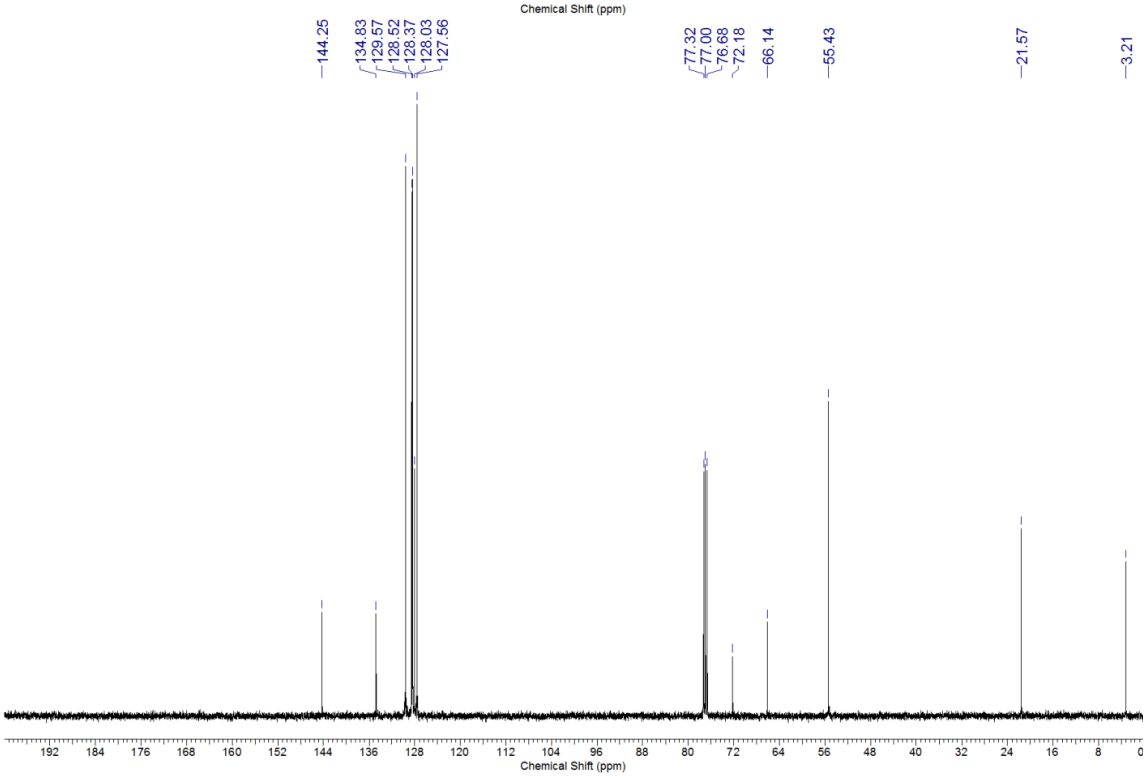


2.1b Ynamides: *N*-Benzyl-4-methyl-*N*-(prop-1-yn-1-yl)benzenesulfonamide, 1a

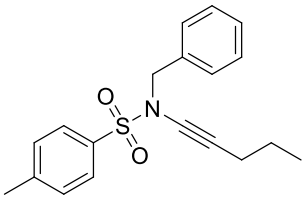


^{1}H (400 MHz, $CDCl_3$)
^{13}C (101 MHz, $CDCl_3$)

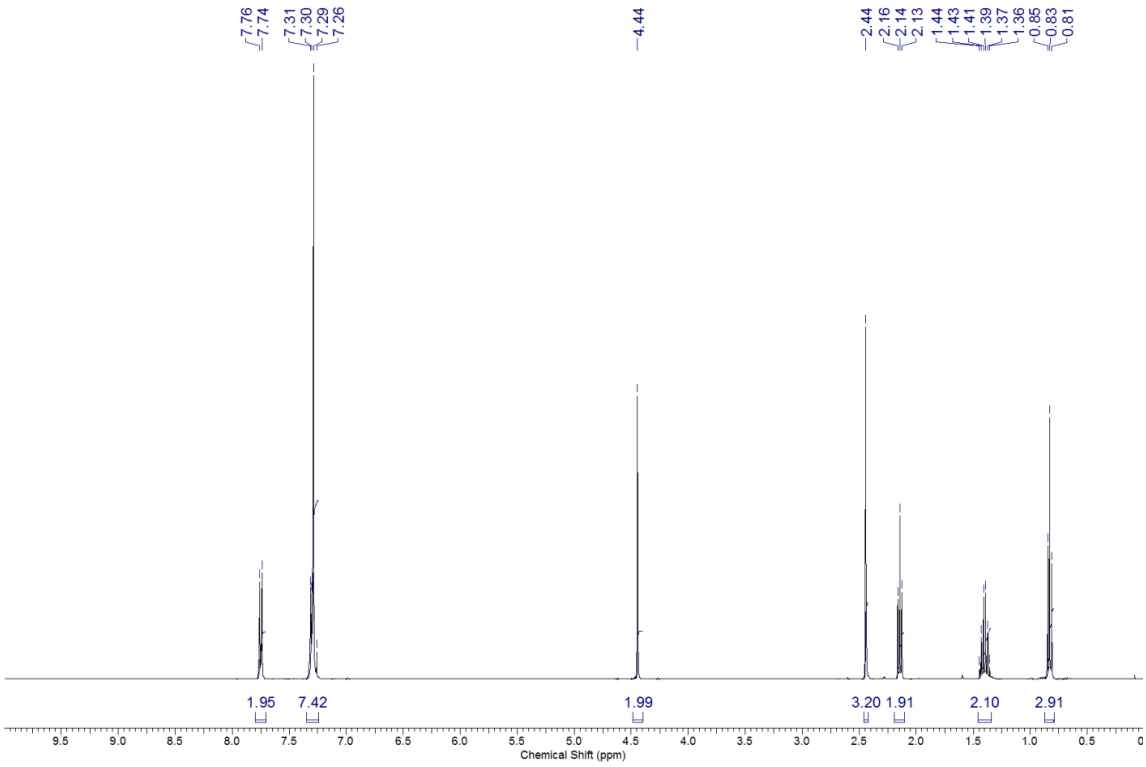


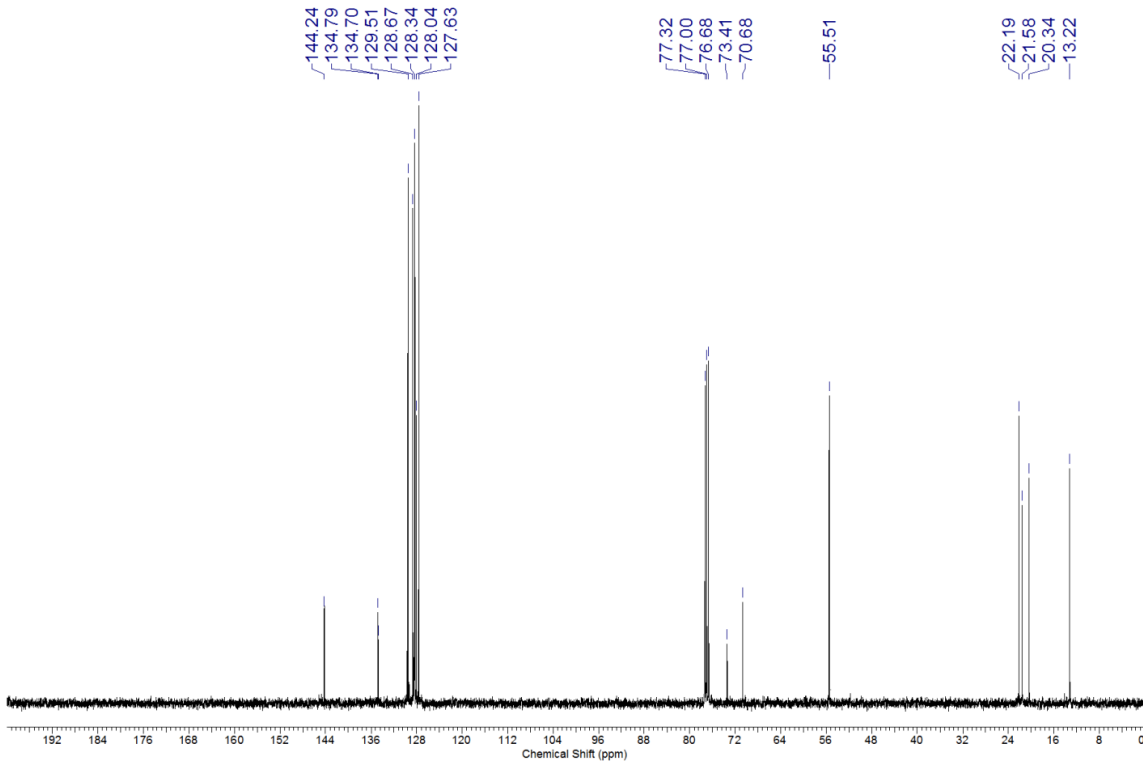


_N_-Benzyl-4-methyl-_N_-(pent-1-yn-1-yl)benzenesulfonamide, 1b

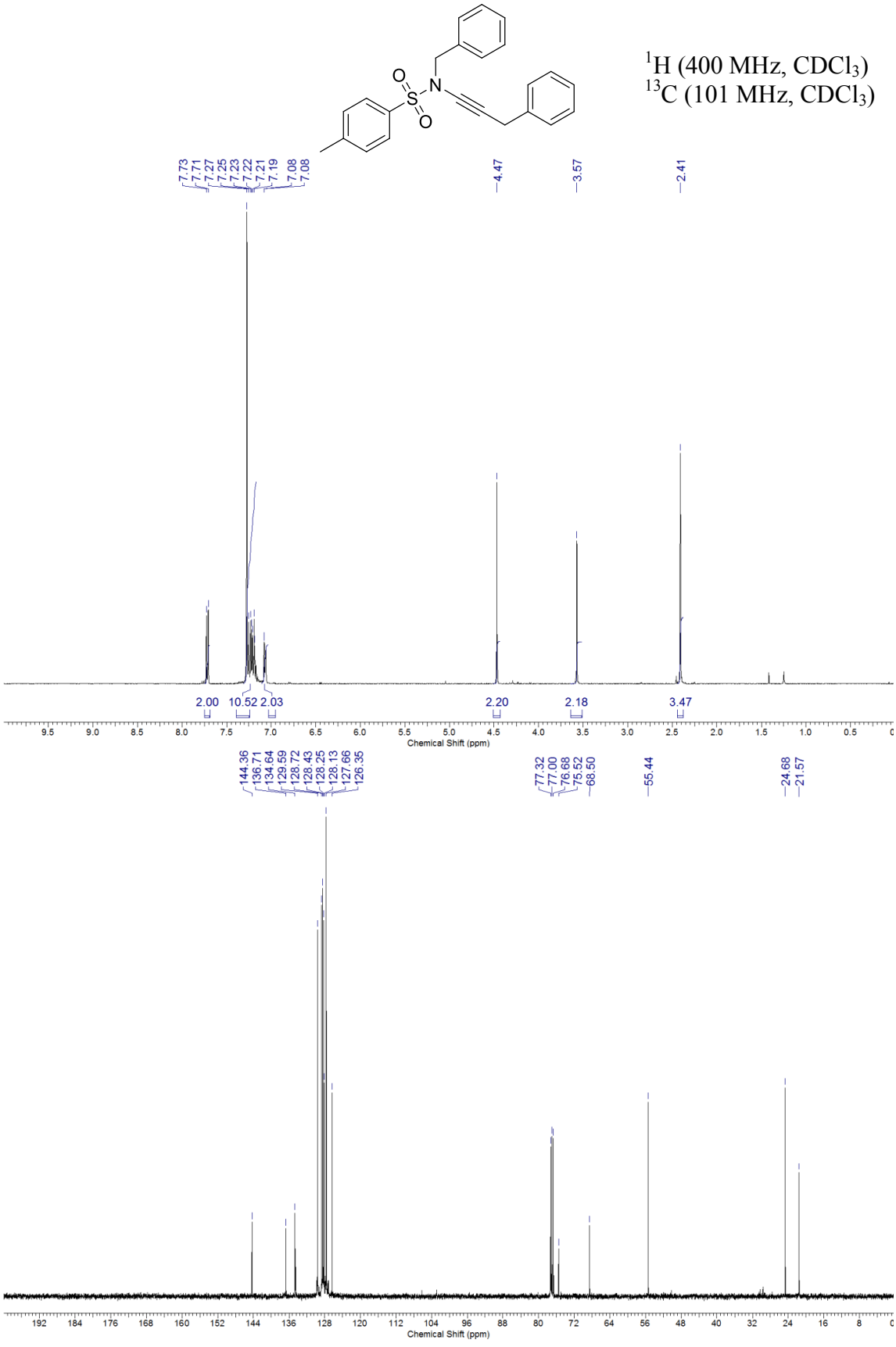


^{1}H (400 MHz, $CDCl_3$)
^{13}C (101 MHz, $CDCl_3$)

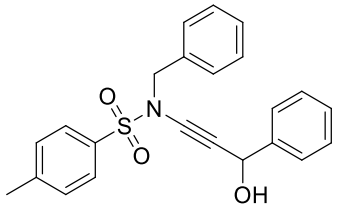




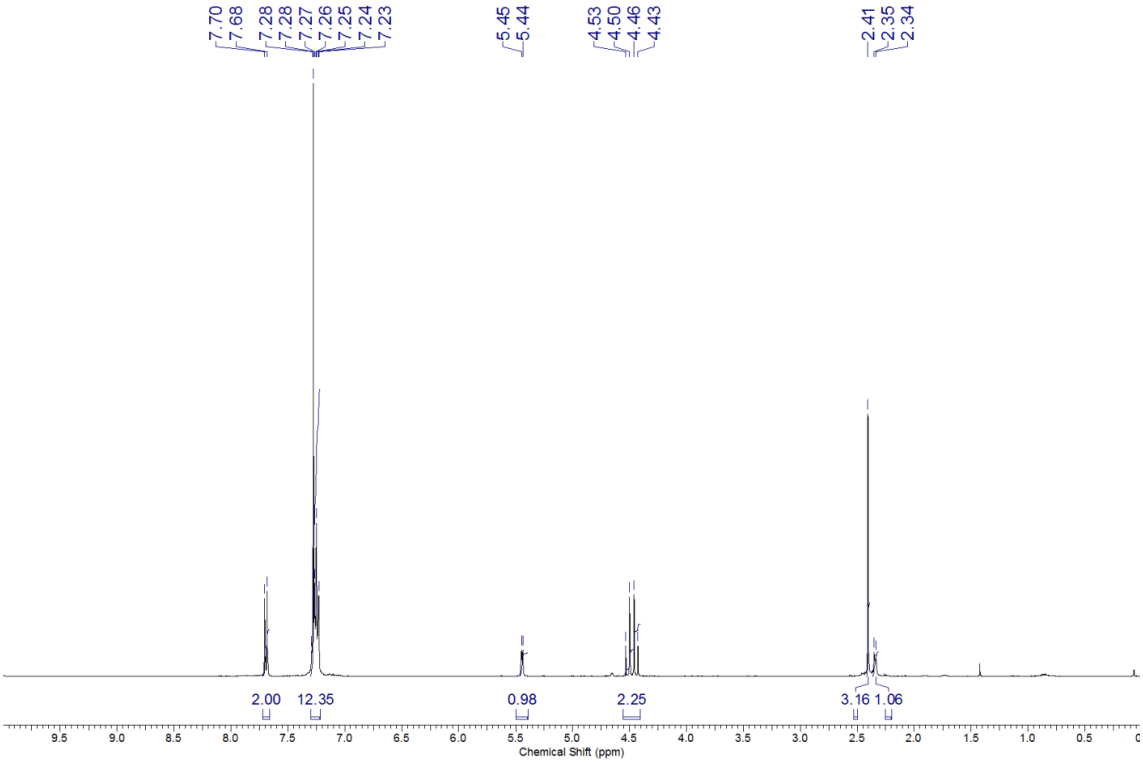
***N*-Benzyl-4-methyl-*N*-(3-phenylprop-1-yn-1-yl)benzenesulfonamide, 1c**

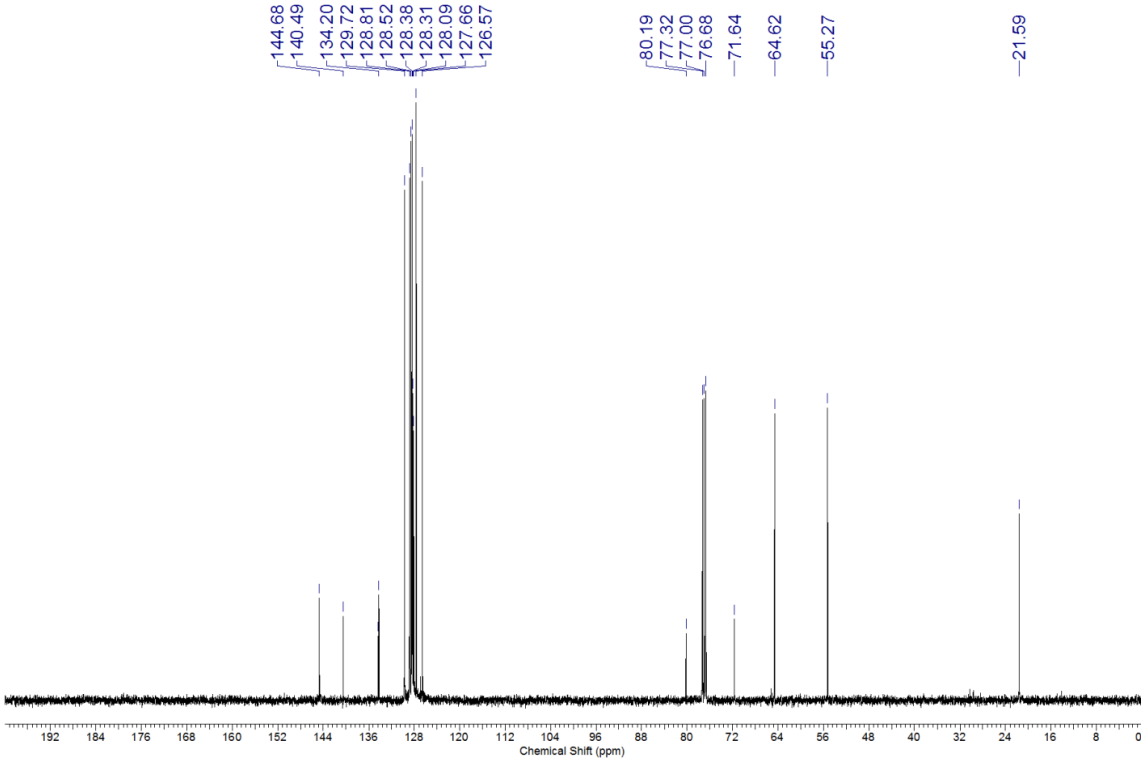


_N_-Benzyl-_N_-(3-hydroxy-3-phenylprop-1-yn-1-yl)-4-methylbenzenesulfonamide, 1d

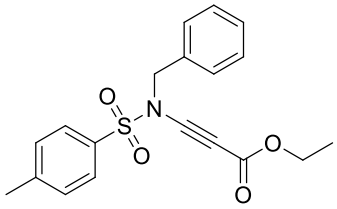


^{1}H (400 MHz, $CDCl_3$)
^{13}C (101 MHz, $CDCl_3$)

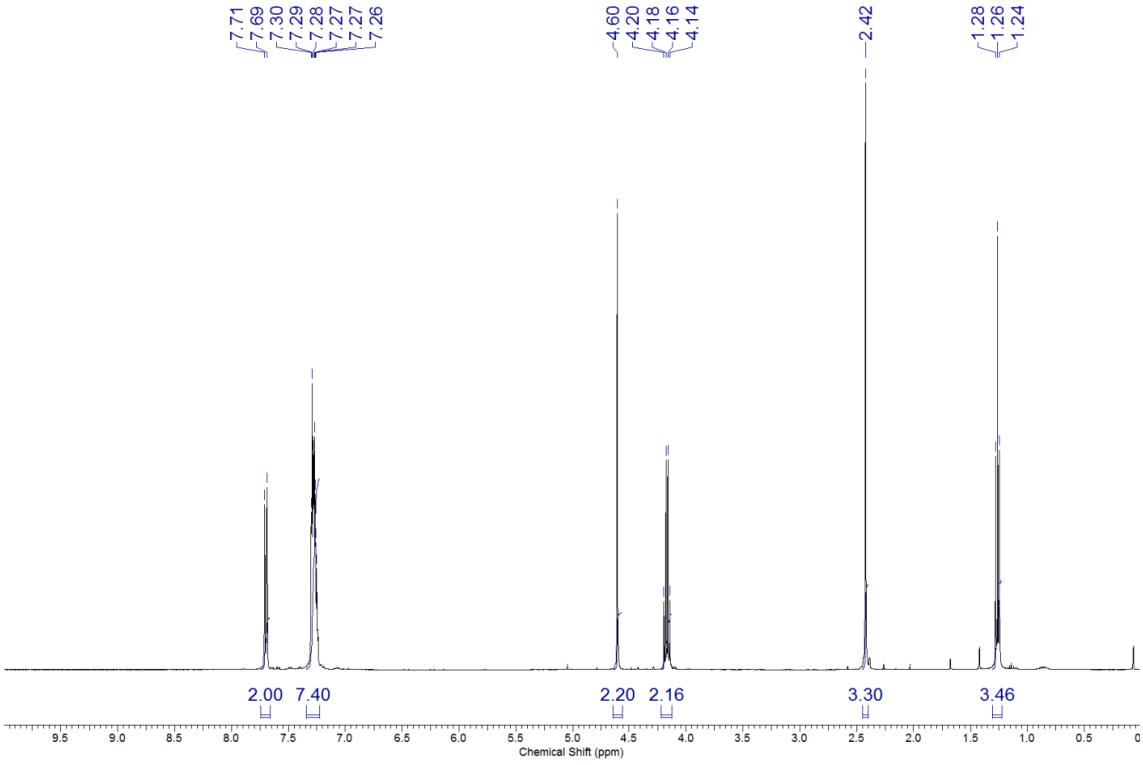


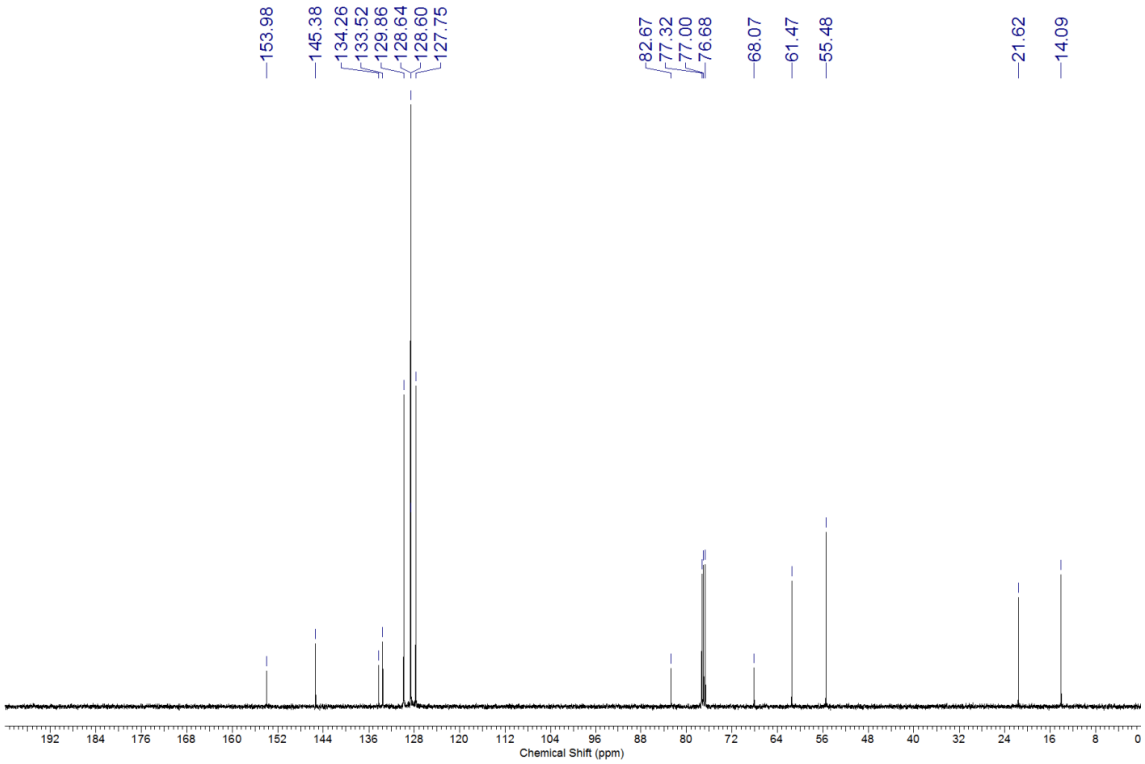


Ethyl 3-(*N*-benzyl-4-methylphenylsulfonamido)propiolate, 1e

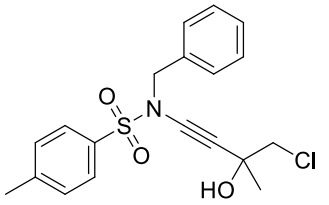


^{1}H (400 MHz, $CDCl_3$)
^{13}C (101 MHz, $CDCl_3$)

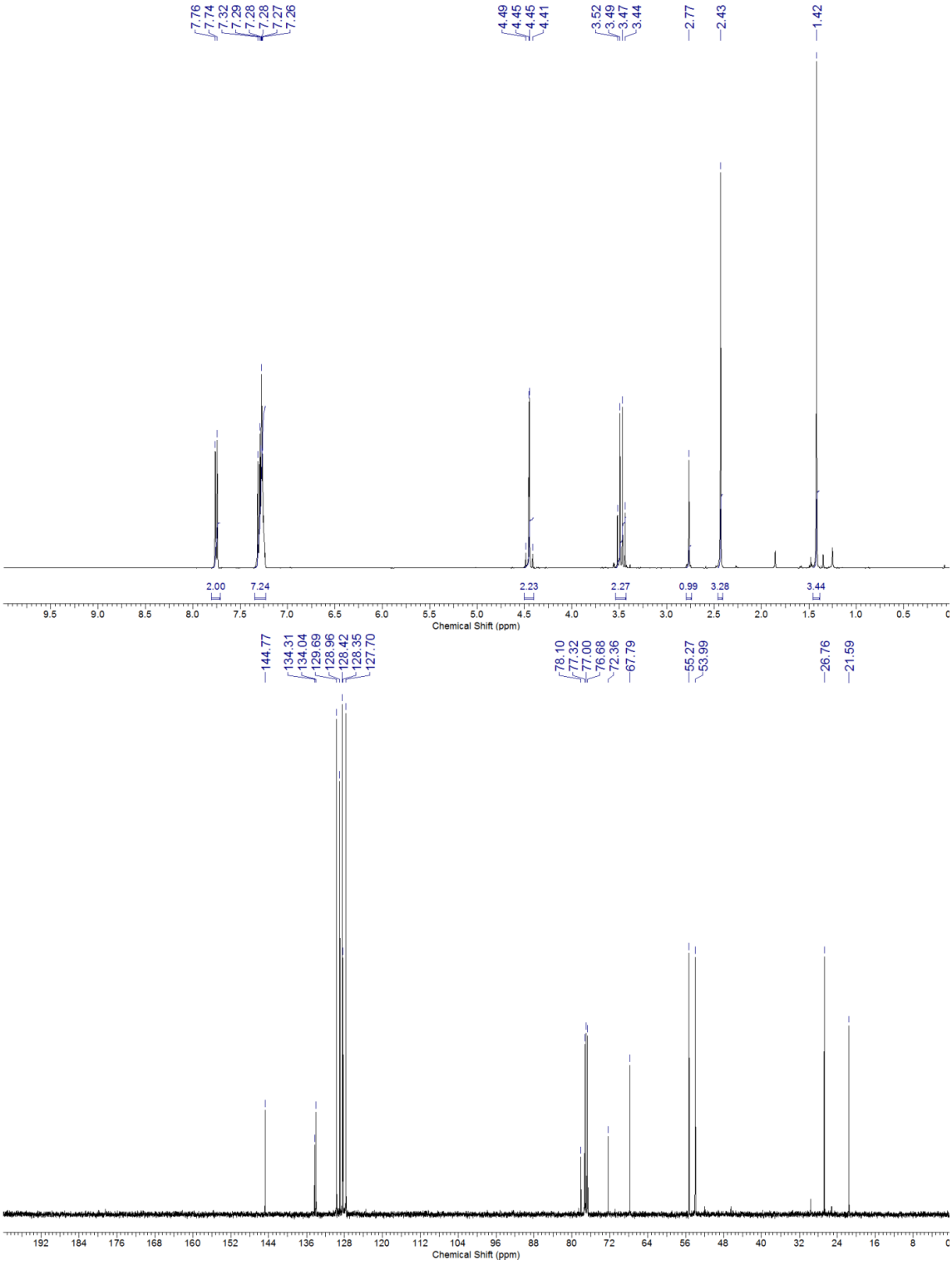




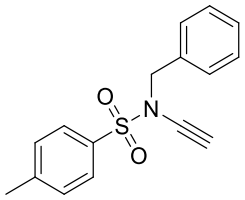
***N*-Benzyl-*N*-(4-chloro-3-hydroxy-3-methylbut-1-yn-1-yl)-4-methylbenzenesulfonamide, 1f**



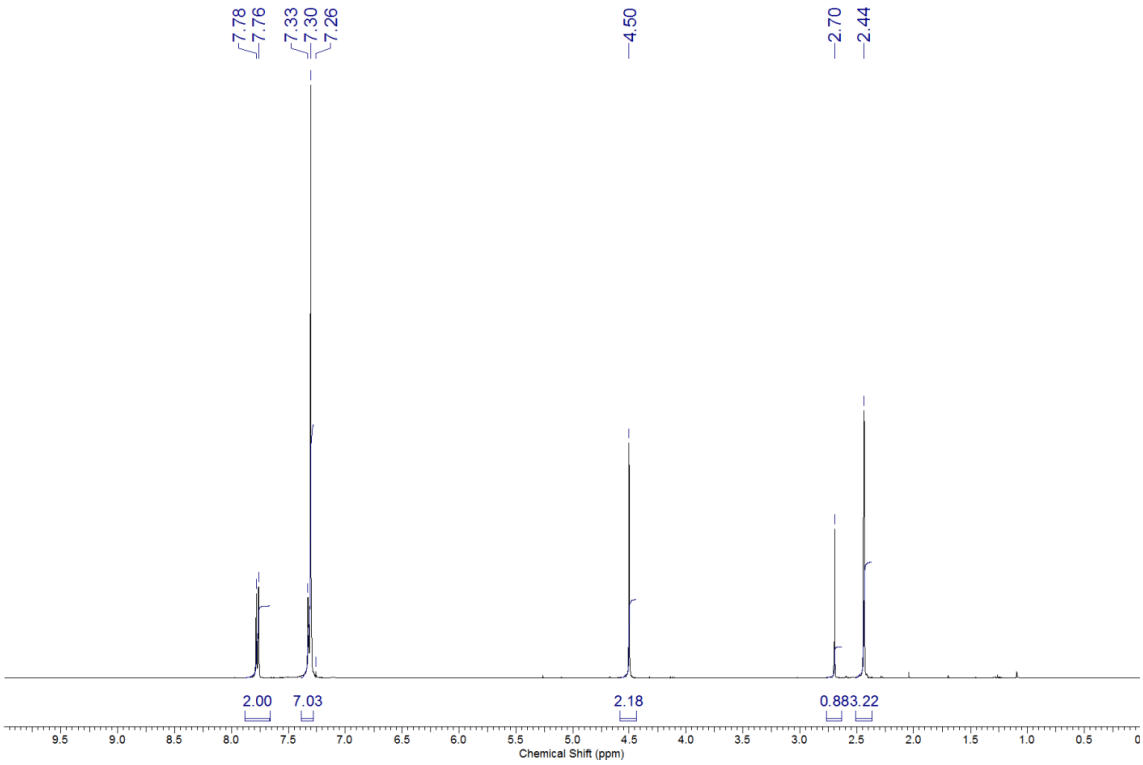
^{1}H (400 MHz, $CDCl_3$)
^{13}C (101 MHz, $CDCl_3$)

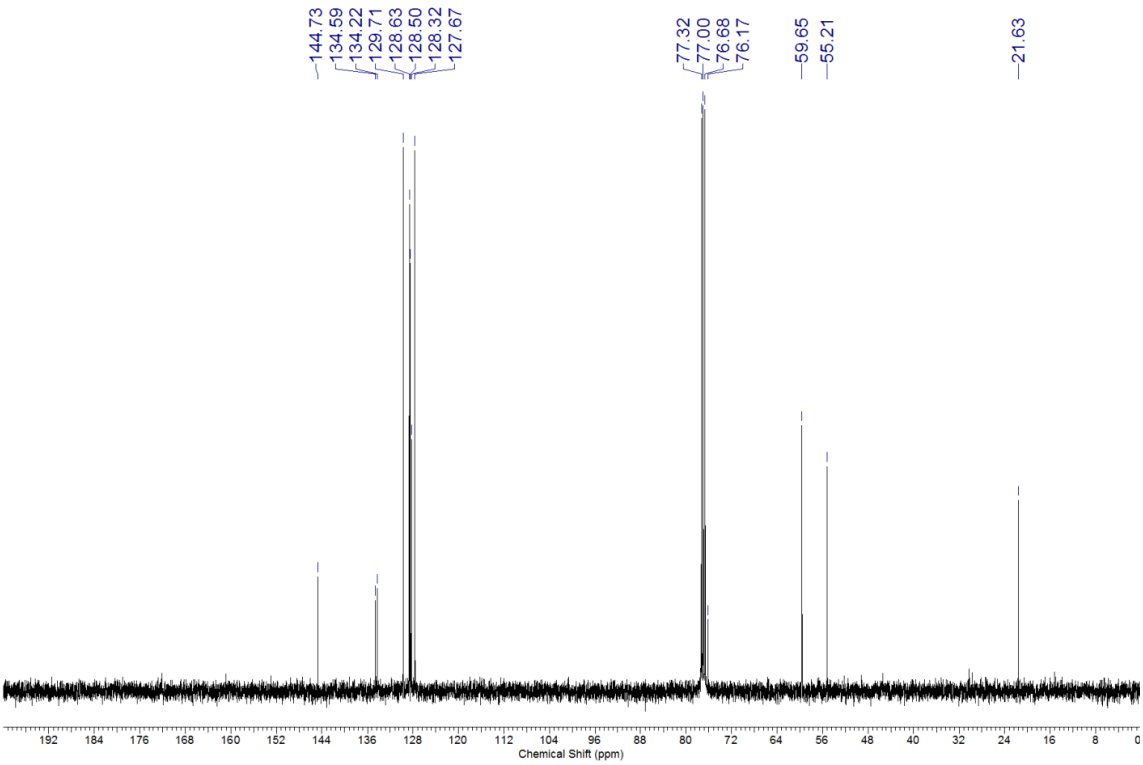


***N*-Benzyl-*N*-ethynyl-4-methylbenzenesulfonamide, 1g**

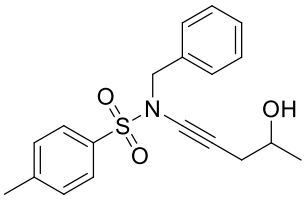


^{1}H (400 MHz, $CDCl_3$)
^{13}C (101 MHz, $CDCl_3$)

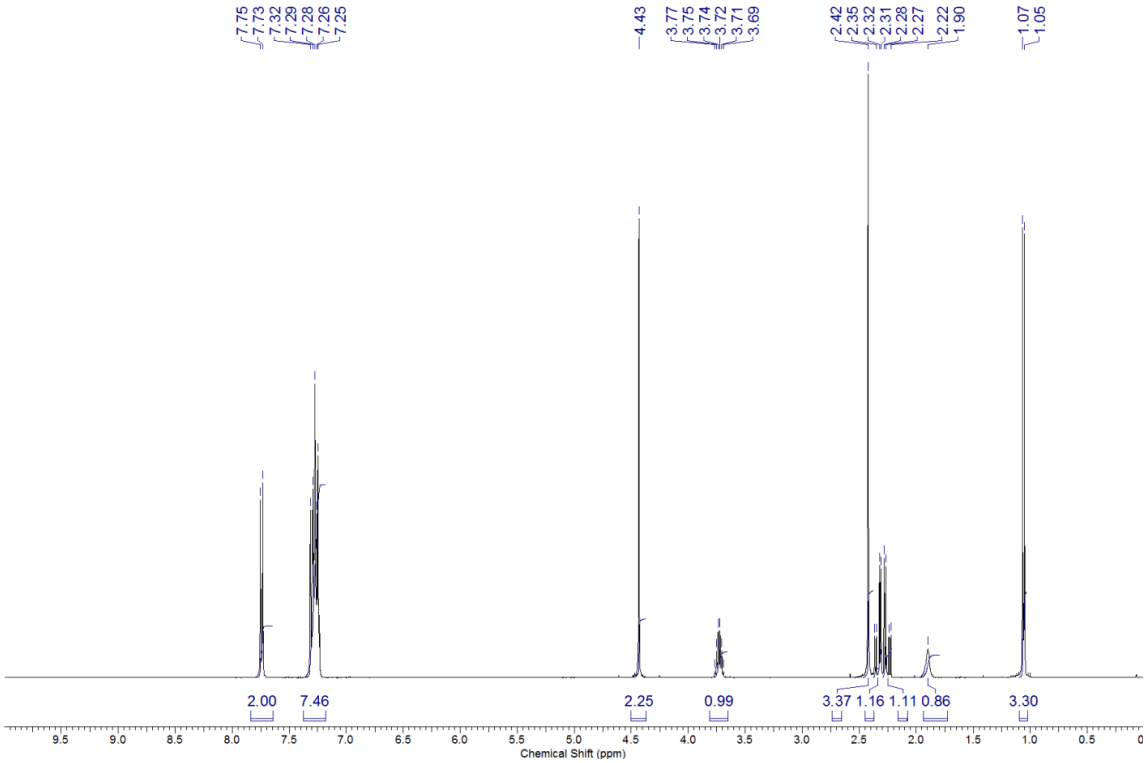


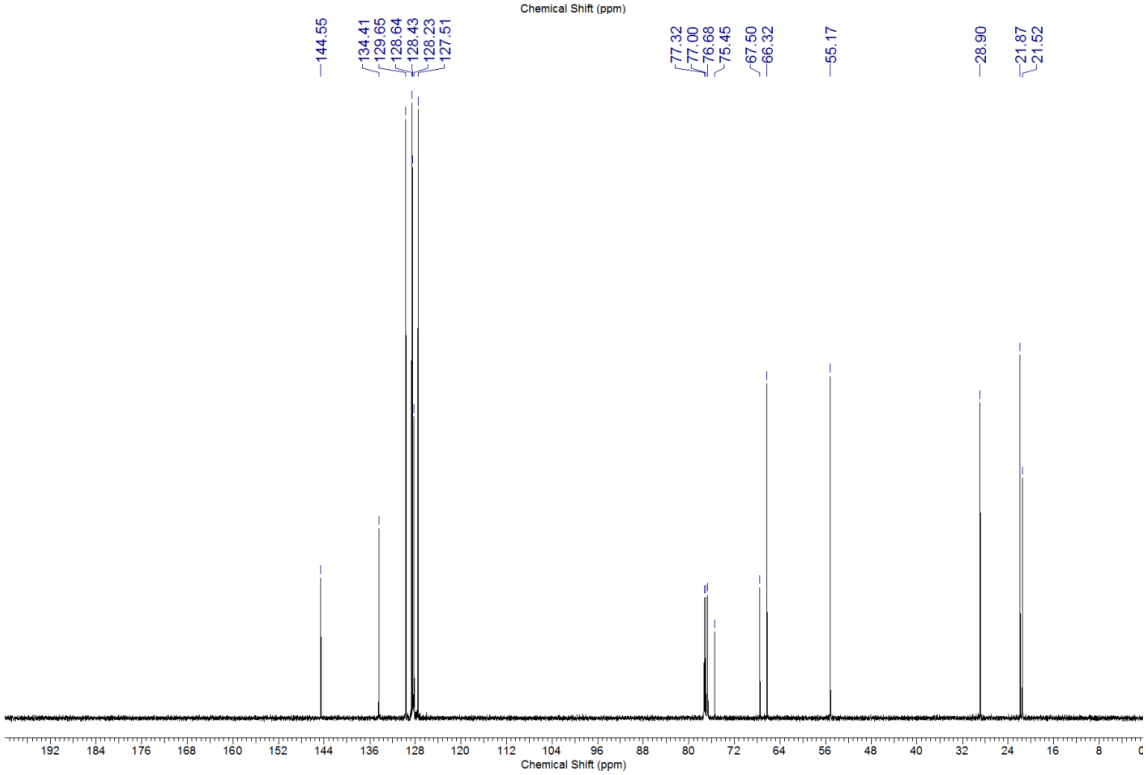


***N*-benzyl-*N*-(4-hydroxypent-1-yn-1-yl)-4-methylbenzenesulfonamide, 1h**

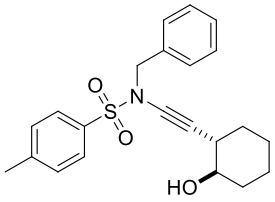


^{1}H (400 MHz, $CDCl_3$)
^{13}C (101 MHz, $CDCl_3$)

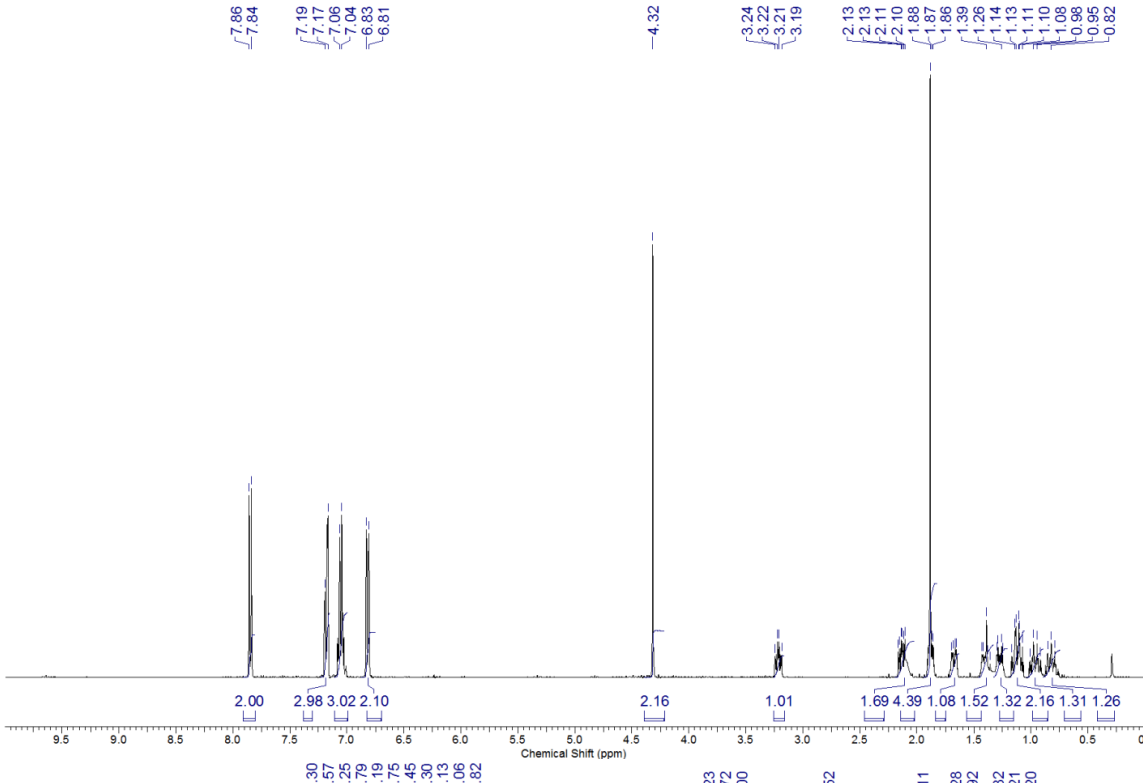


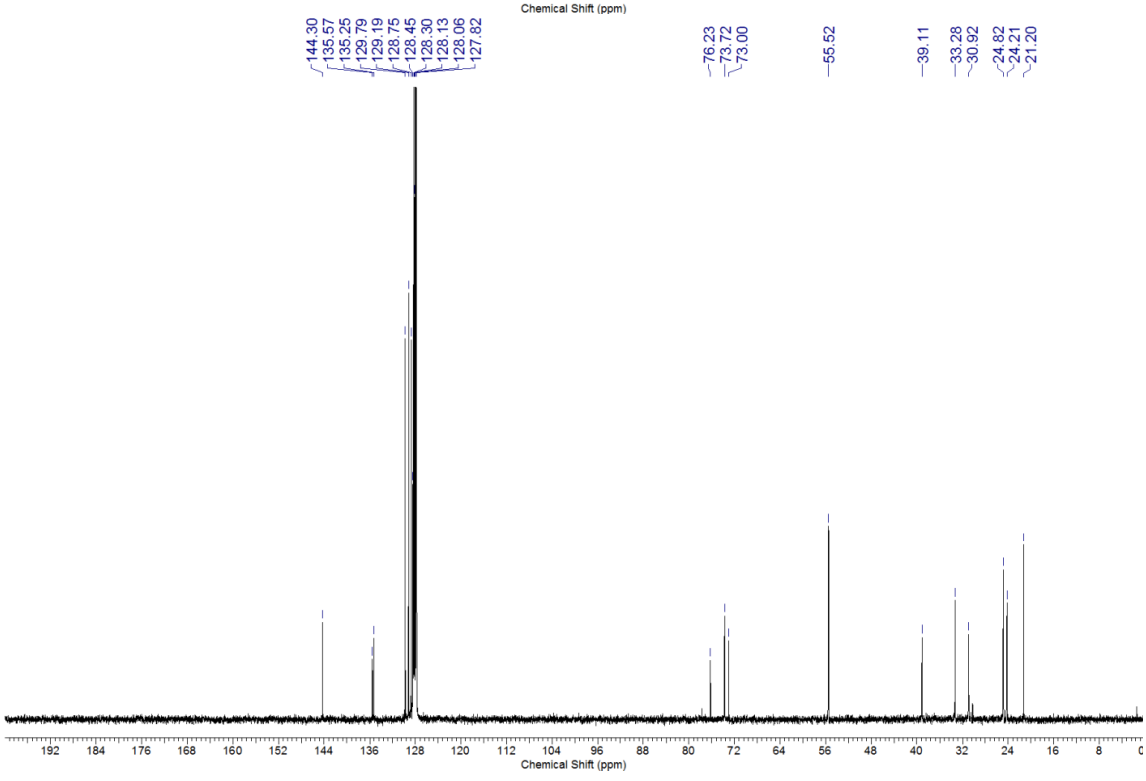


***N*-Benzyl-*N*-(((1*S**,2*R**)-2-hydroxycyclohexyl)ethynyl)-4-methylbenzenesulfonamide, 1i**

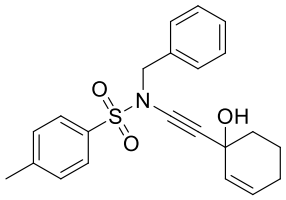


^{1}H (400 MHz, C_6D_6)
^{13}C (101 MHz, C_6D_6)

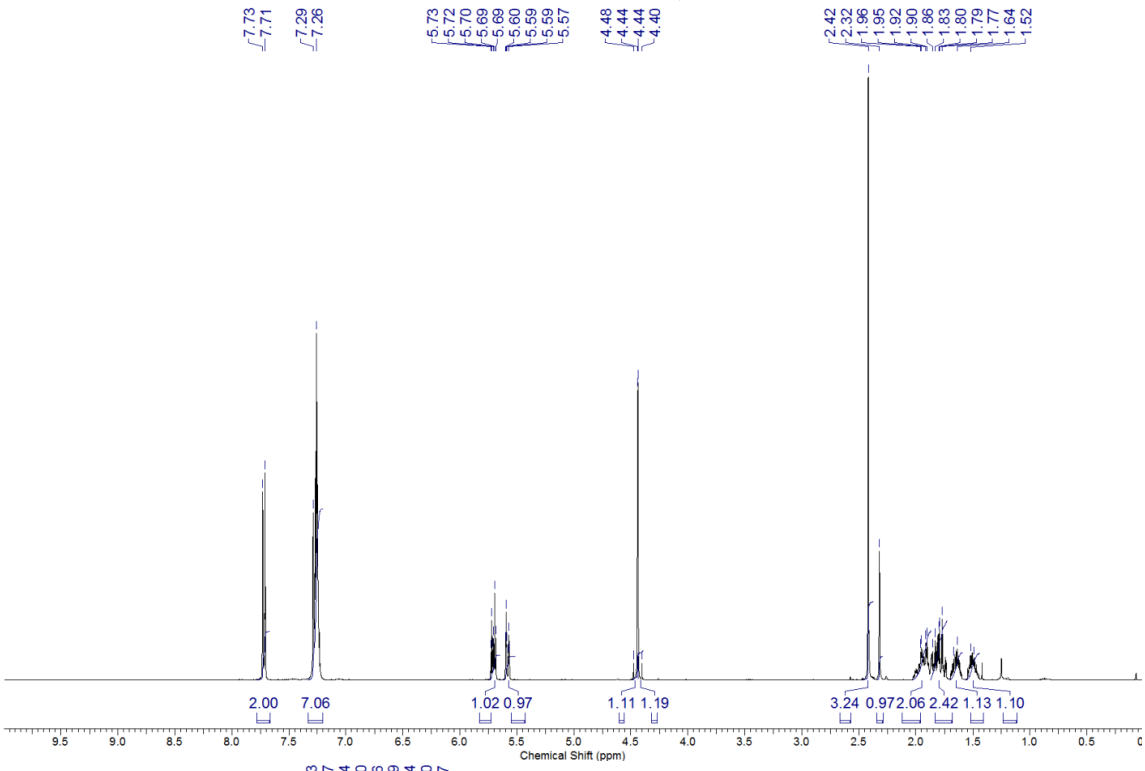


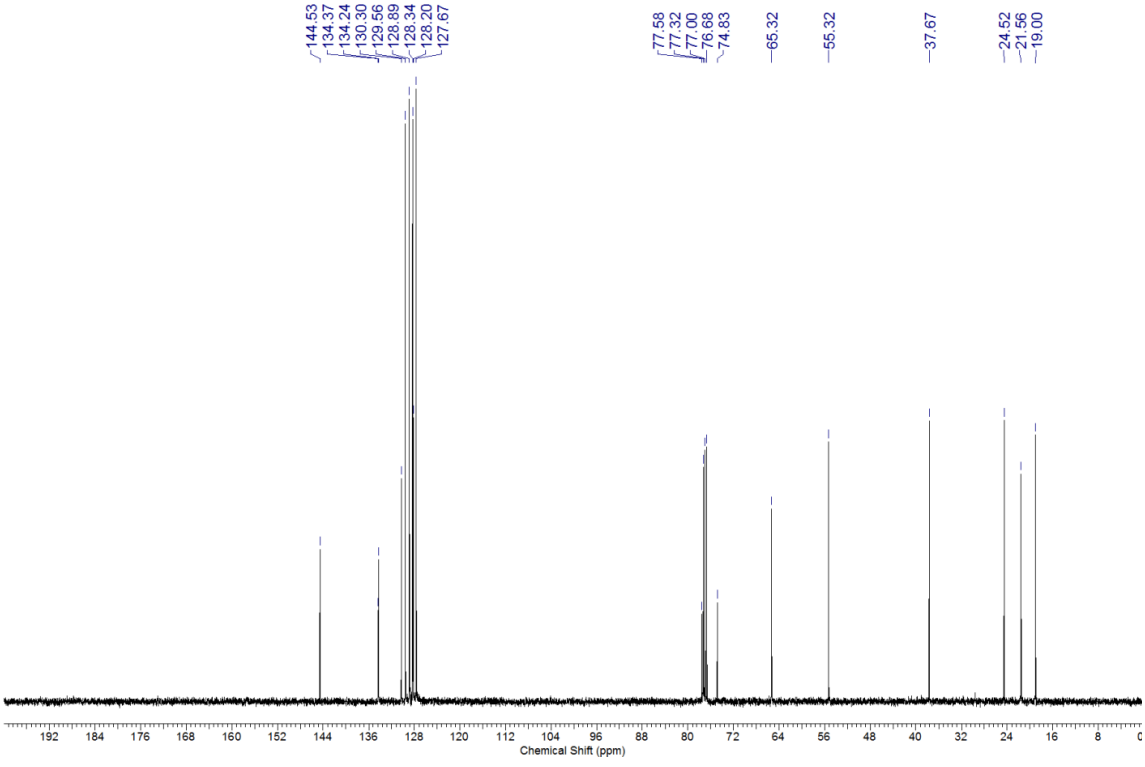


***N*-Benzyl-*N*-((1-hydroxycyclohex-2-en-1-yl)ethynyl)-4-methylbenzenesulfonamide, 1j**

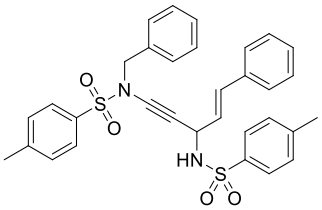


^{1}H (400 MHz, $CDCl_3$)
^{13}C (101 MHz, $CDCl_3$)

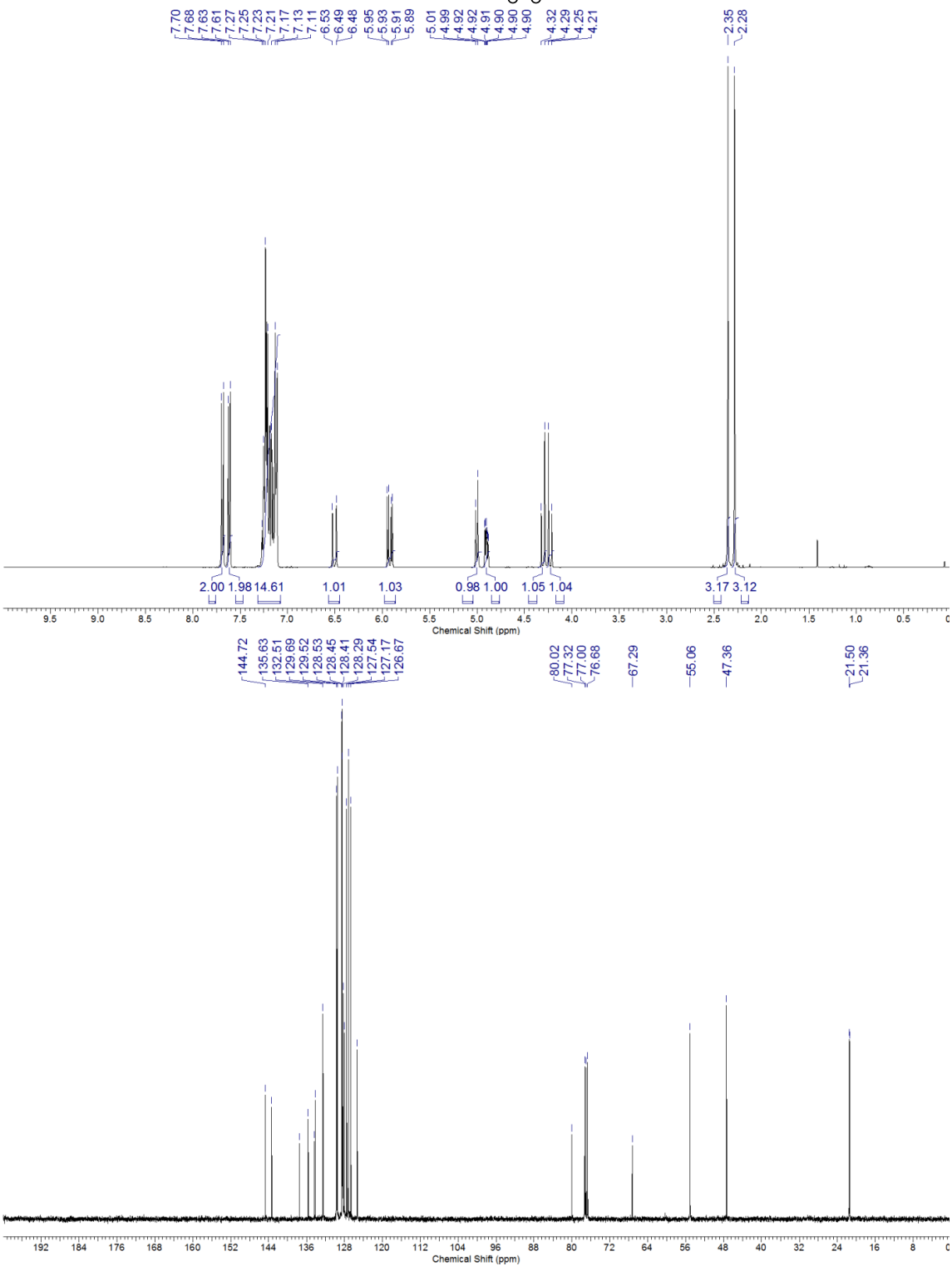




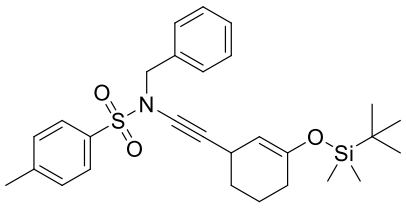
(*E*)-*N*-Benzyl-4-methyl-*N*-(3-(4-methylphenylsulfonamido)-5-phenylpent-4-en-1-yn-1-yl)benzenesulfonamide, 1k



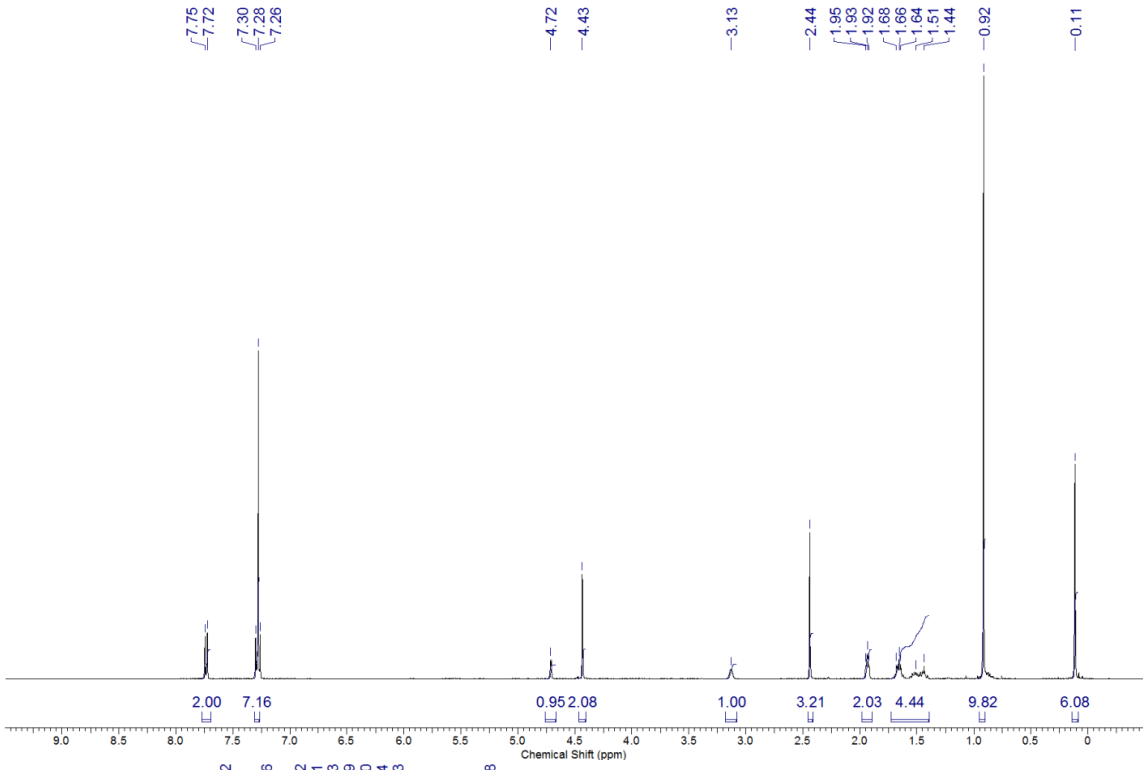
^{1}H (400 MHz, $CDCl_3$)
^{13}C (101 MHz, $CDCl_3$)

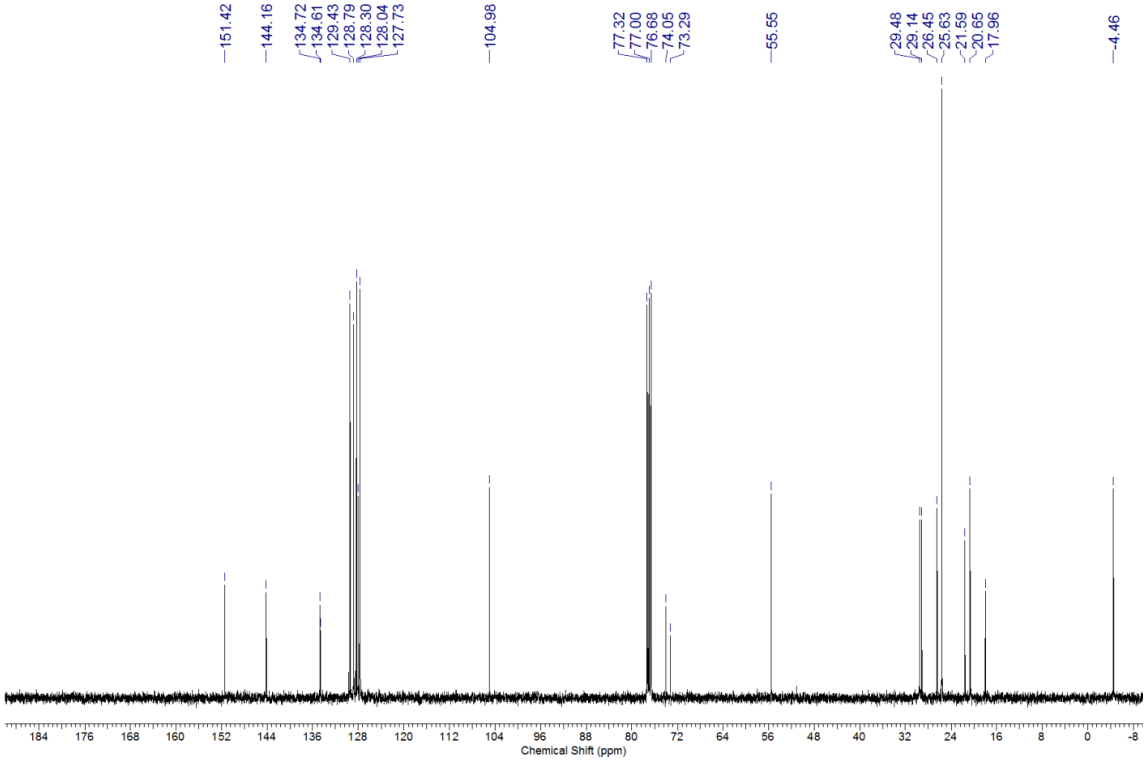


***N*-Benzyl-*N*-((3-((*tert*-butyldimethylsilyl)oxy)cyclohex-2-en-1-yl)ethynyl)-4-methylbenzenesulfonamide, 1l**

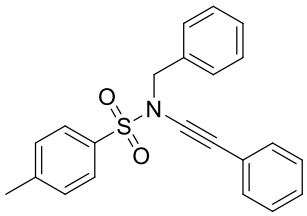


^{1}H (400 MHz, $CDCl_3$)
^{13}C (101 MHz, $CDCl_3$)

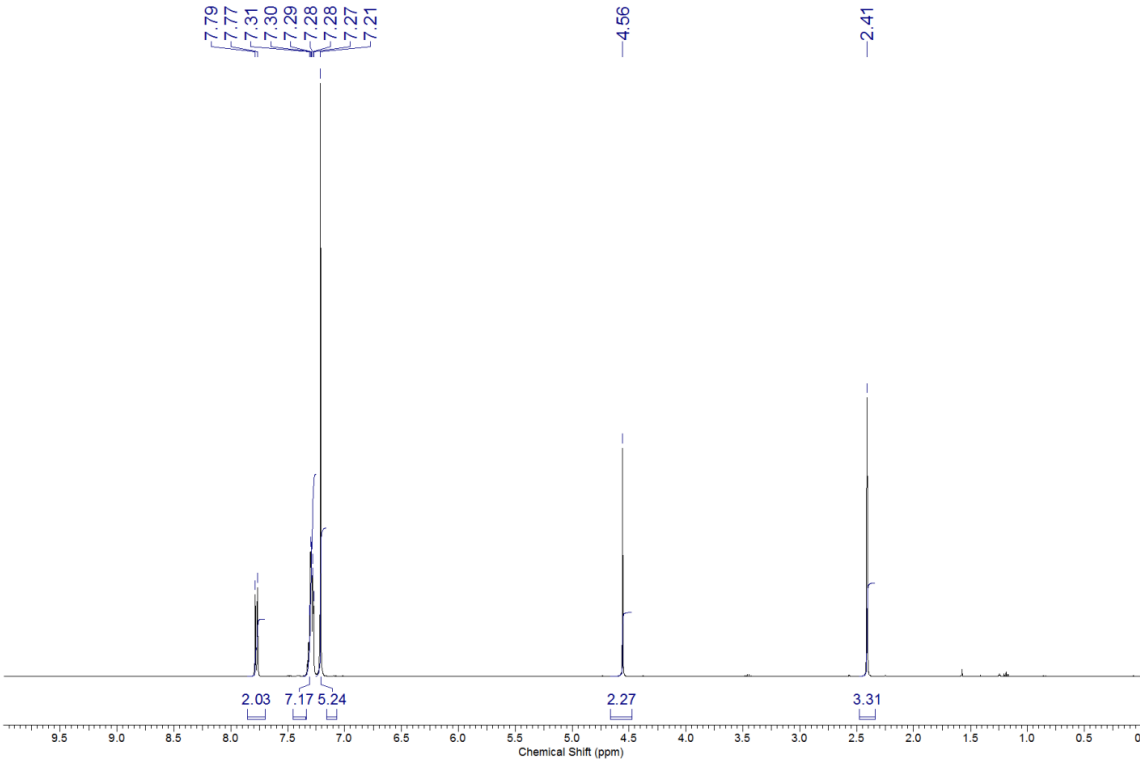


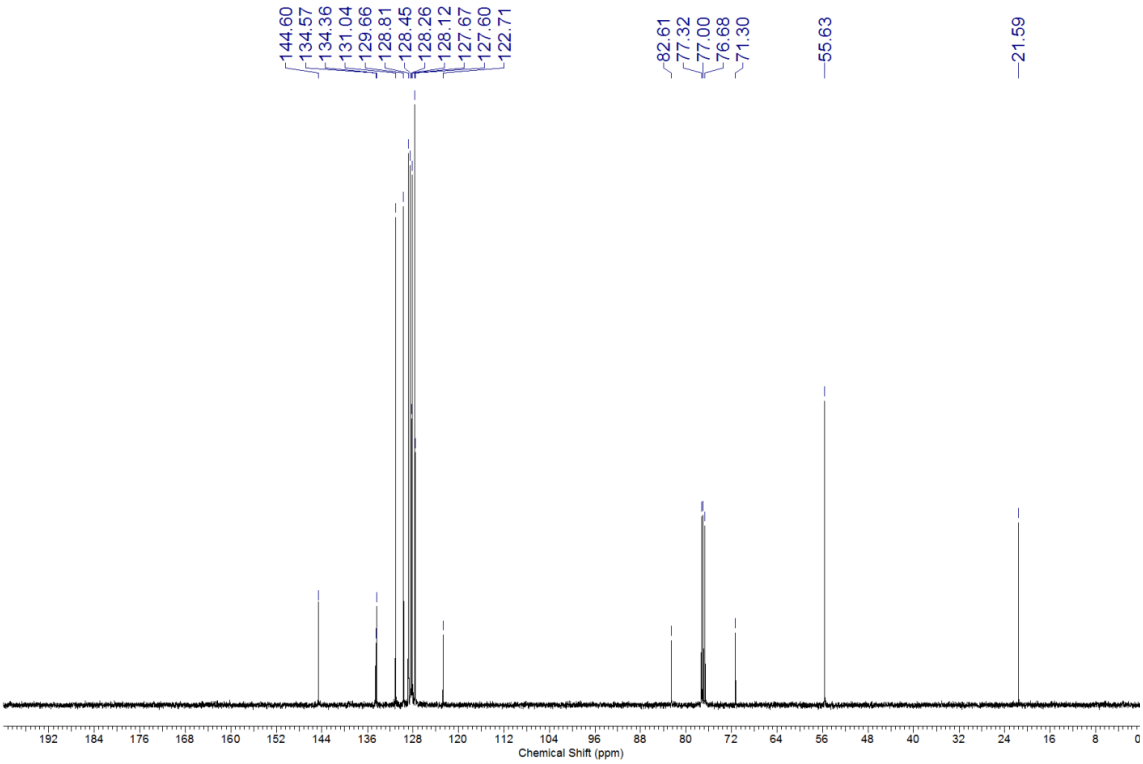


***N*-Benzyl-4-methyl-*N*-(phenylethynyl)benzenesulfonamide, 1m**

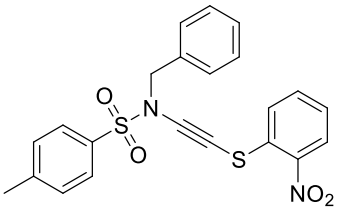


^{1}H (400 MHz, $CDCl_3$)
^{13}C (101 MHz, $CDCl_3$)

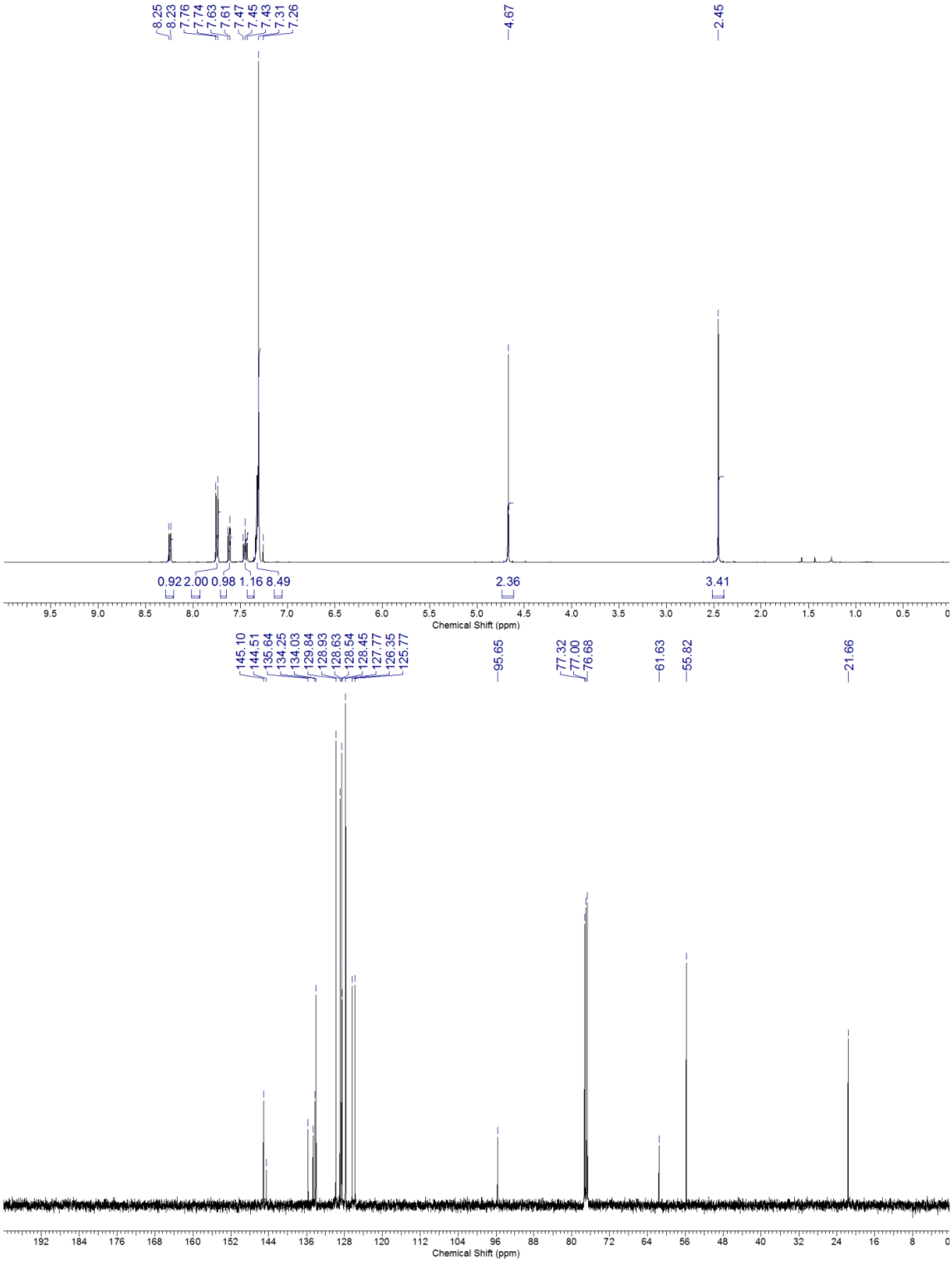




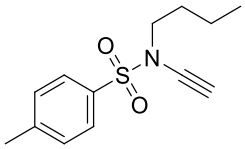
***N*-Benzyl-4-methyl-*N*-(((2-nitrophenyl)thio)ethynyl)benzenesulfonamide, 1n**



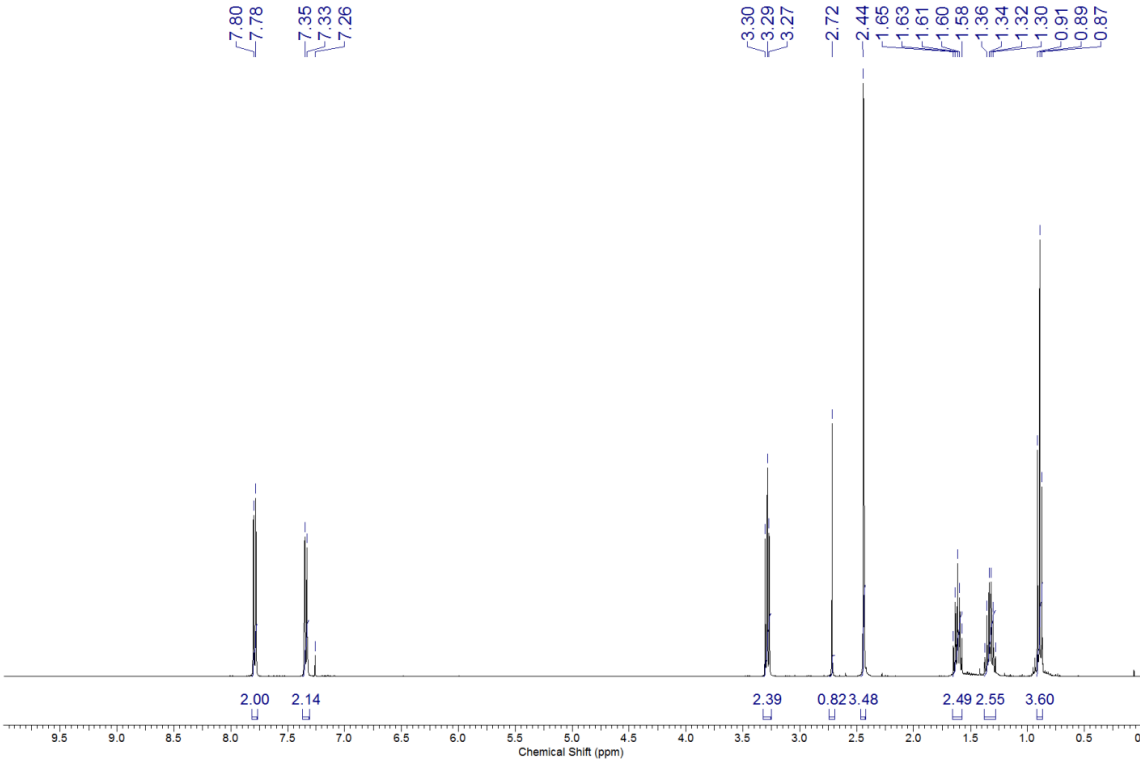
^{1}H (400 MHz, $CDCl_3$)
^{13}C (101 MHz, $CDCl_3$)

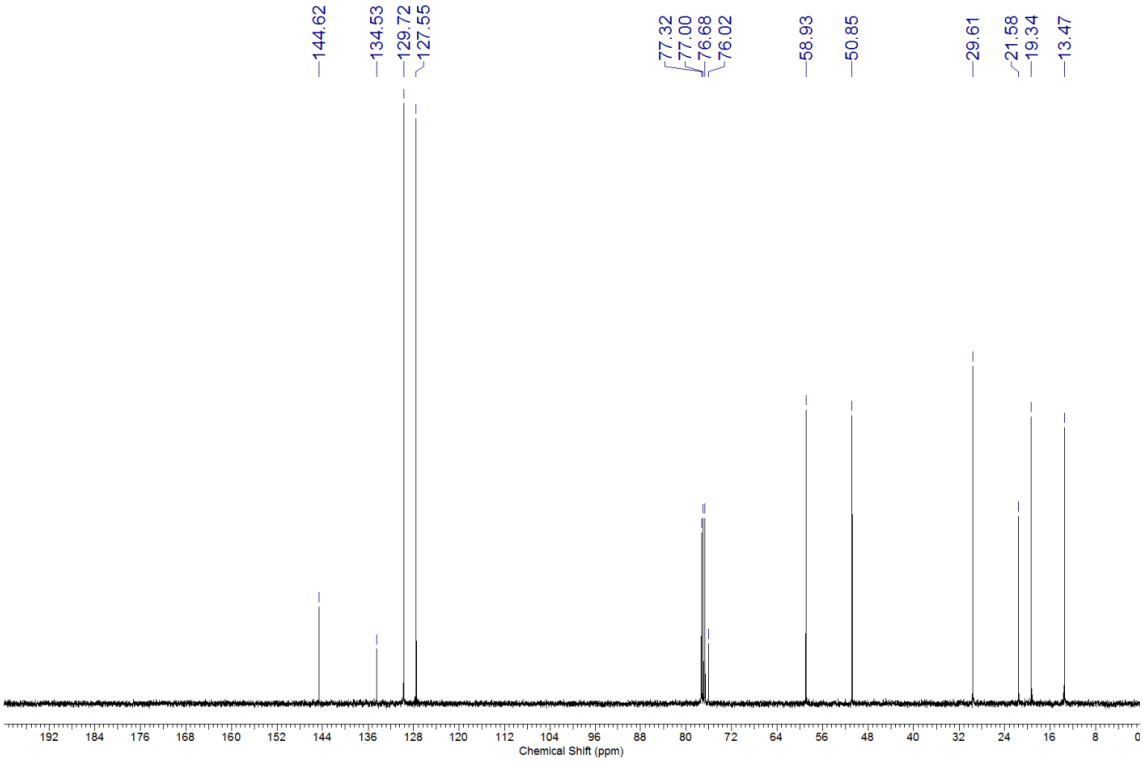


***N*-Butyl-*N*-ethynyl-4-methylbenzenesulfonamide, 1o**

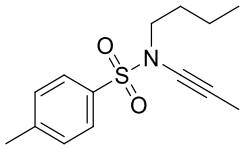


^{1}H (400 MHz, $CDCl_3$)
^{13}C (101 MHz, $CDCl_3$)

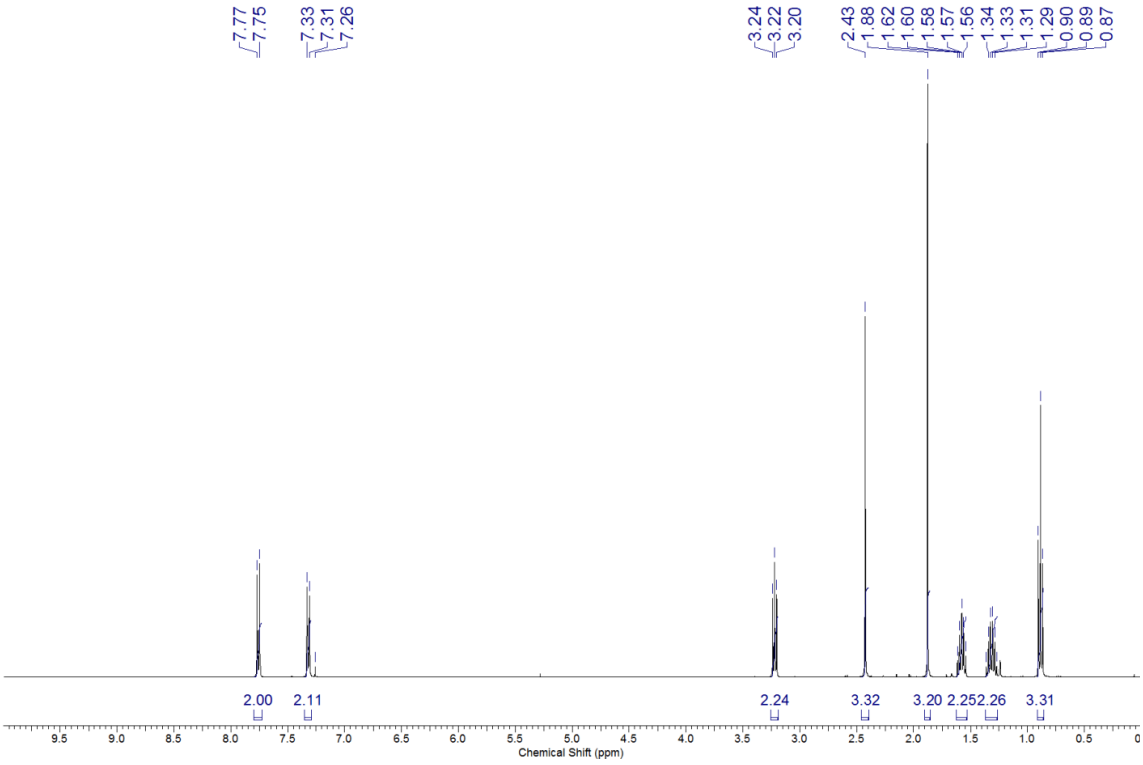


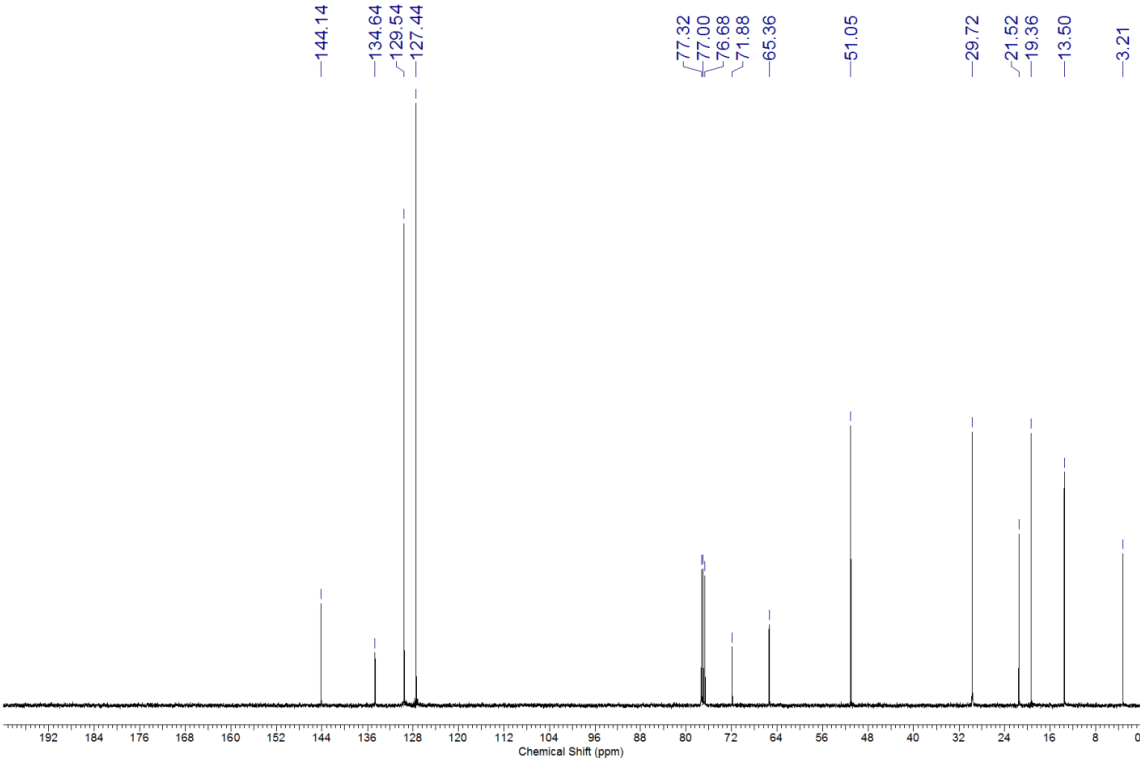


***N*-Butyl-4-methyl-*N*-(prop-1-yn-1-yl)benzenesulfonamide, 1p**

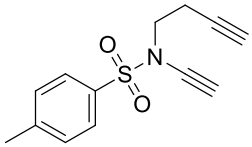


^{1}H (400 MHz, $CDCl_3$)
^{13}C (101 MHz, $CDCl_3$)

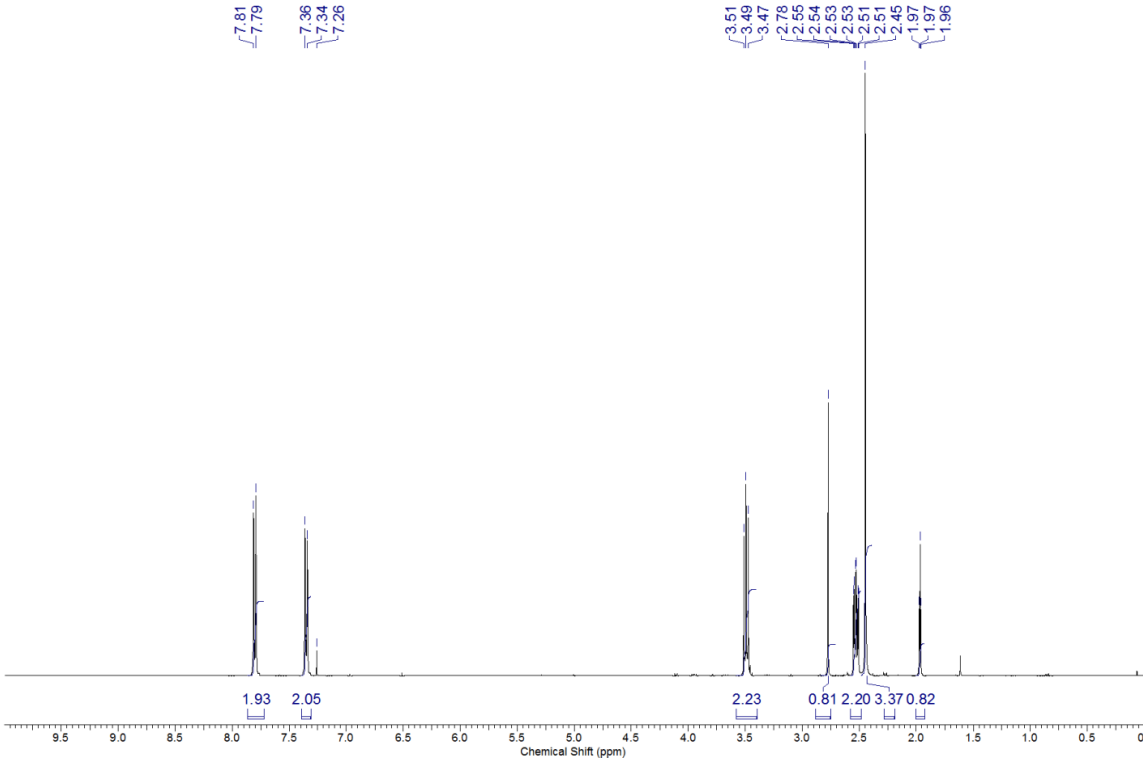


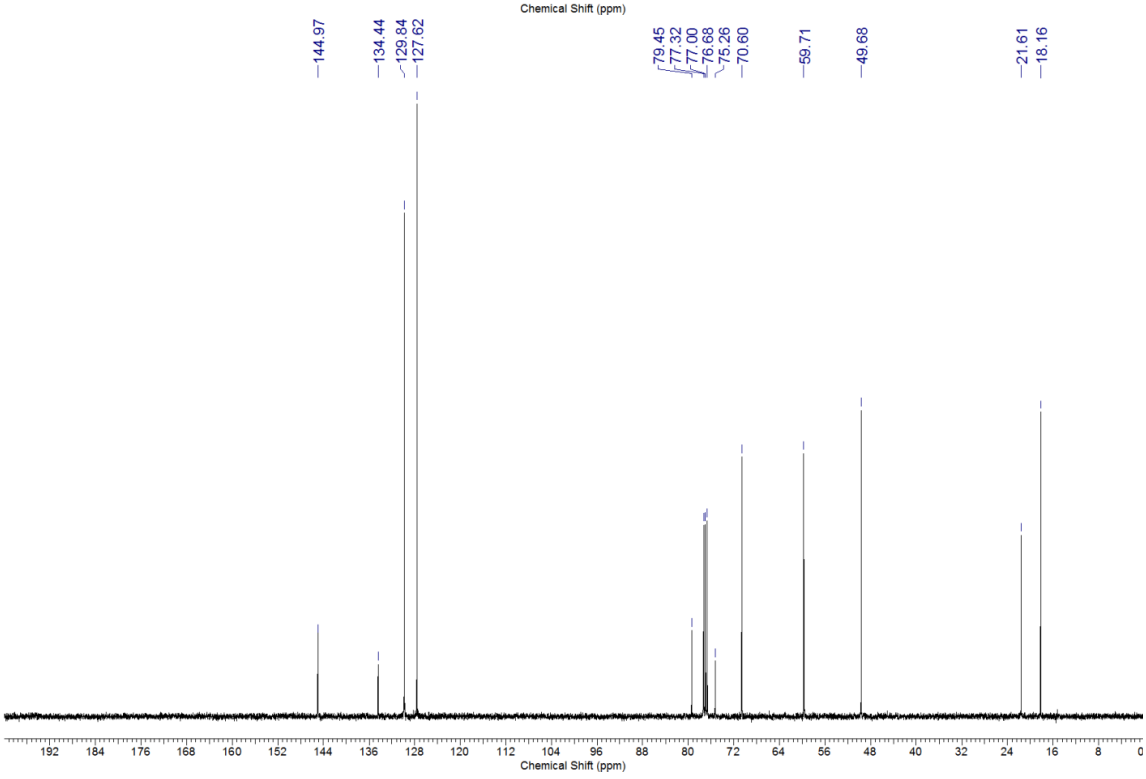


***N*-(But-3-yn-1-yl)-*N*-ethynyl-4-methylbenzenesulfonamide, 1q**

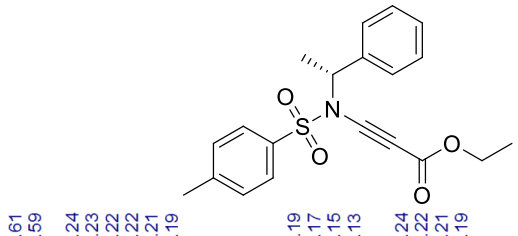


^{1}H (400 MHz, $CDCl_3$)
^{13}C (101 MHz, $CDCl_3$)

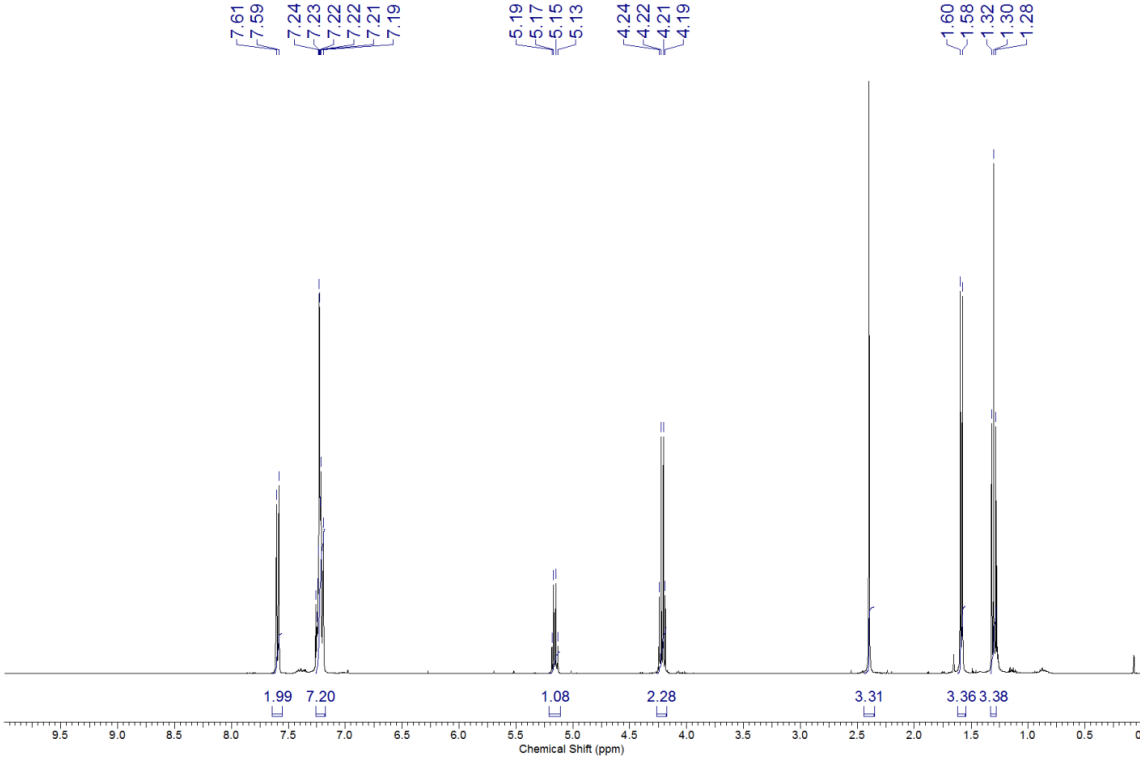


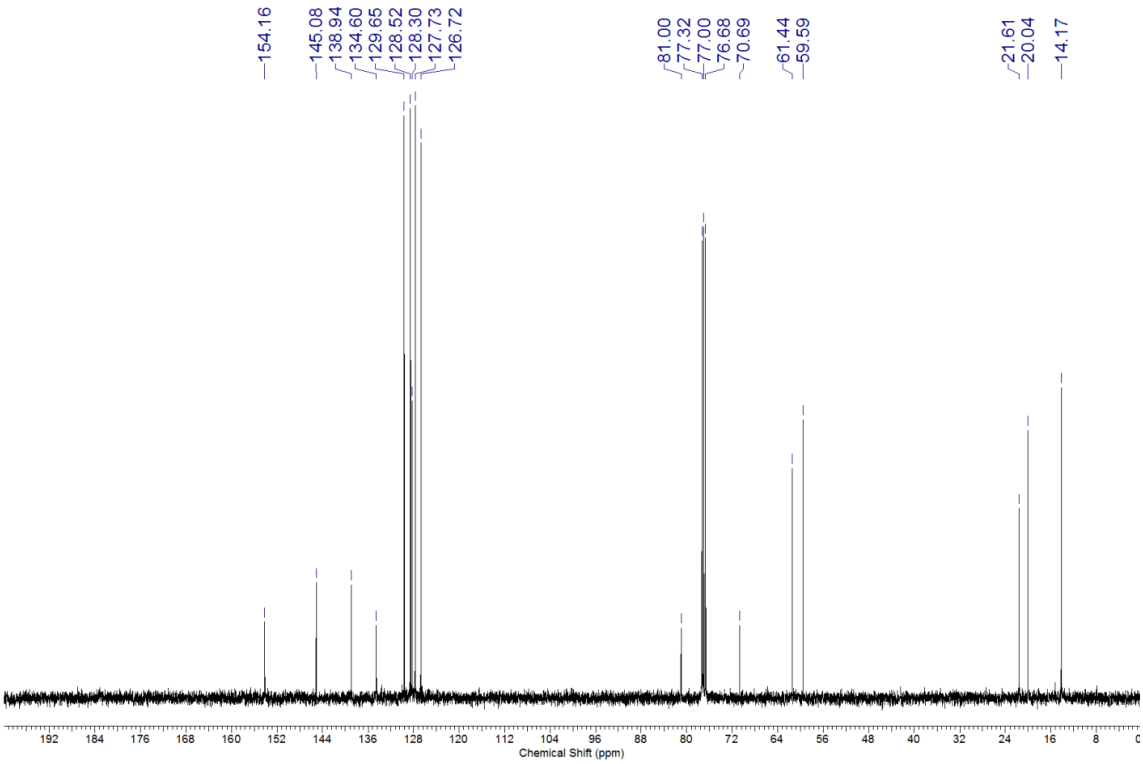


(*R*)-Ethyl 3-(4-methyl-*N*-(1-phenylethyl)phenylsulfonamido)propiolate, 1r

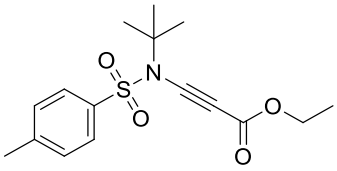


^{1}H (400 MHz, $CDCl_3$)
^{13}C (101 MHz, $CDCl_3$)

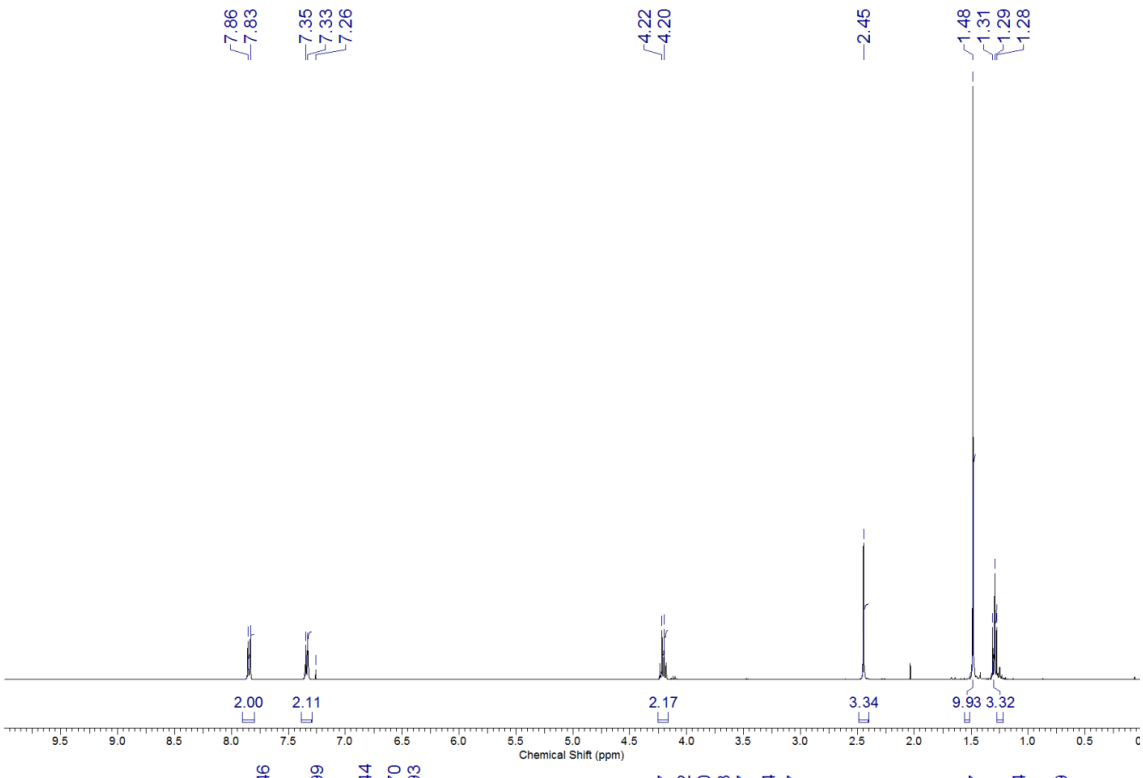


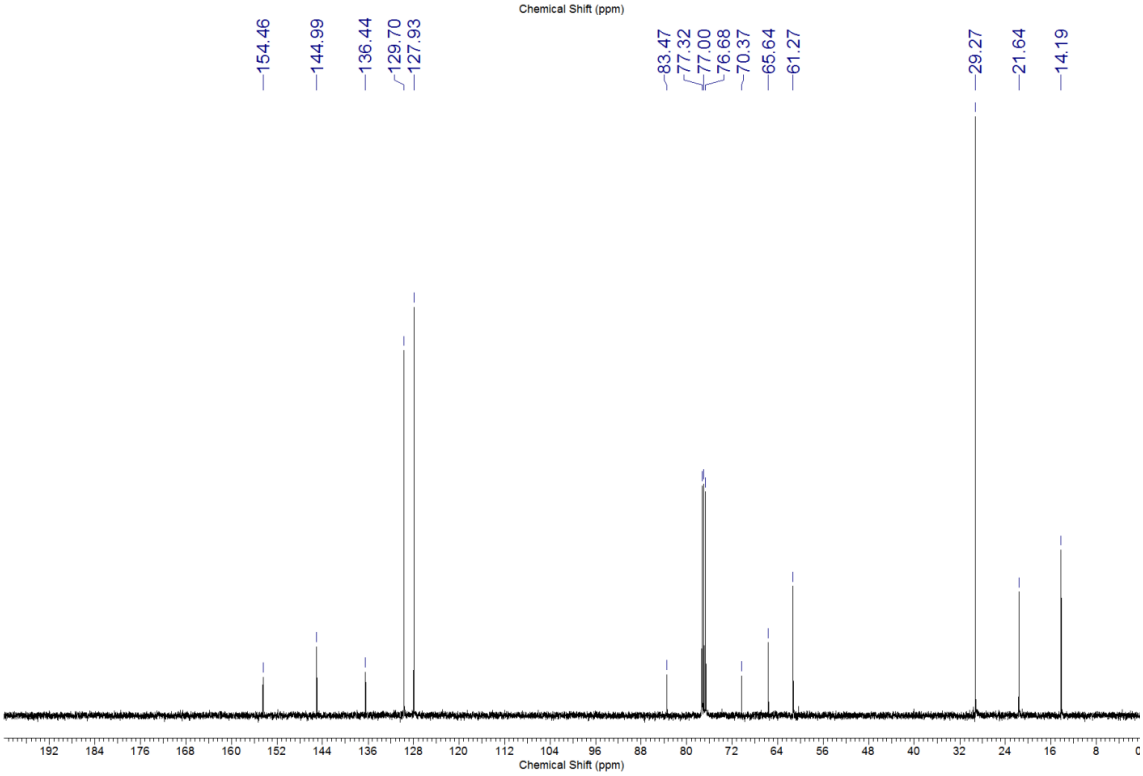


Ethyl 3-(*N*-(*tert*-butyl)-4-methylphenylsulfonamido)propiolate, 1s

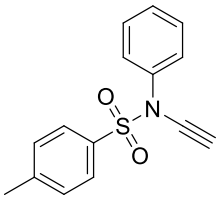


^{1}H (400 MHz, $CDCl_3$)
^{13}C (101 MHz, $CDCl_3$)

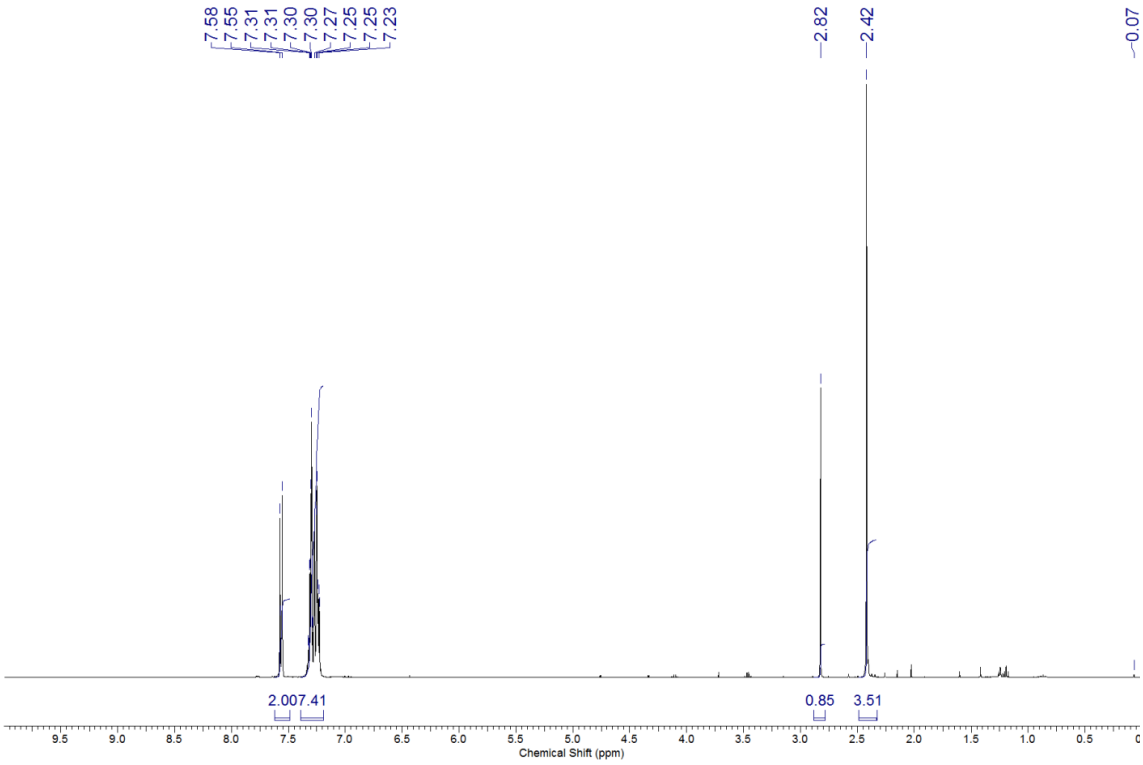


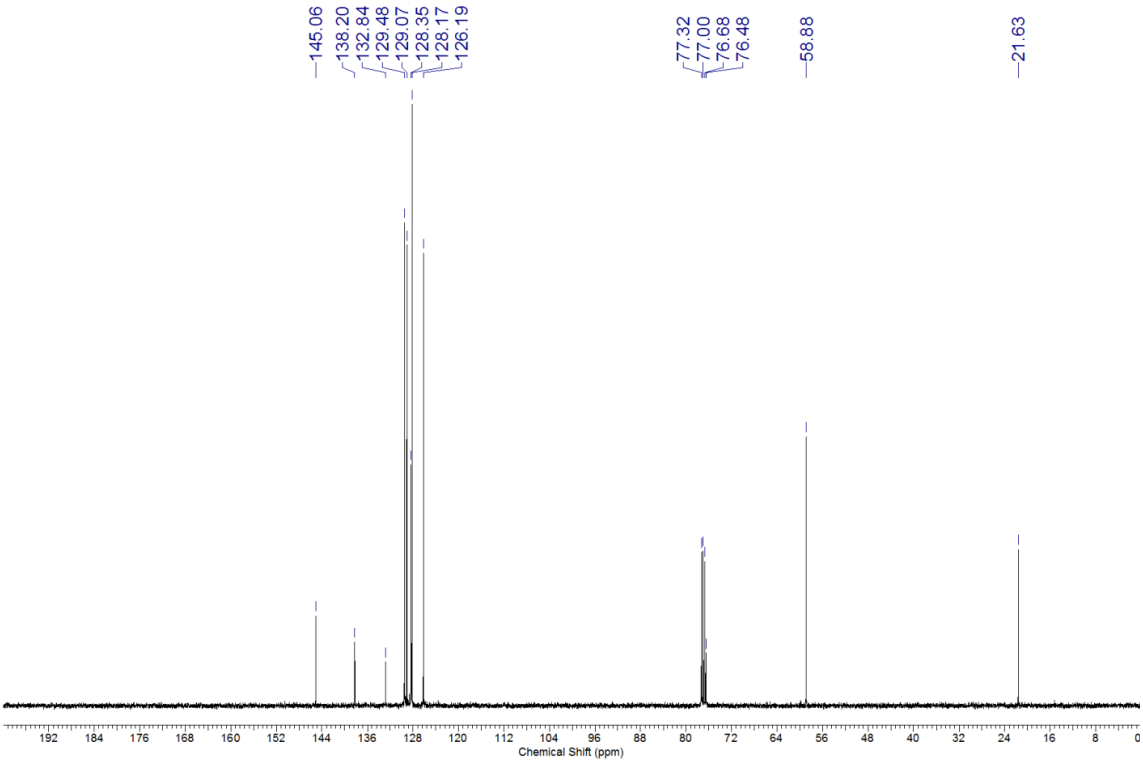


_N_-Ethynyl-4-methyl-_N_-phenylbenzenesulfonamide, 1t

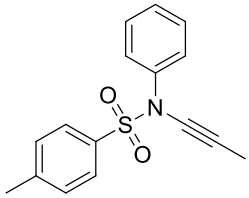


^{1}H (400 MHz, $CDCl_3$)
^{13}C (101 MHz, $CDCl_3$)

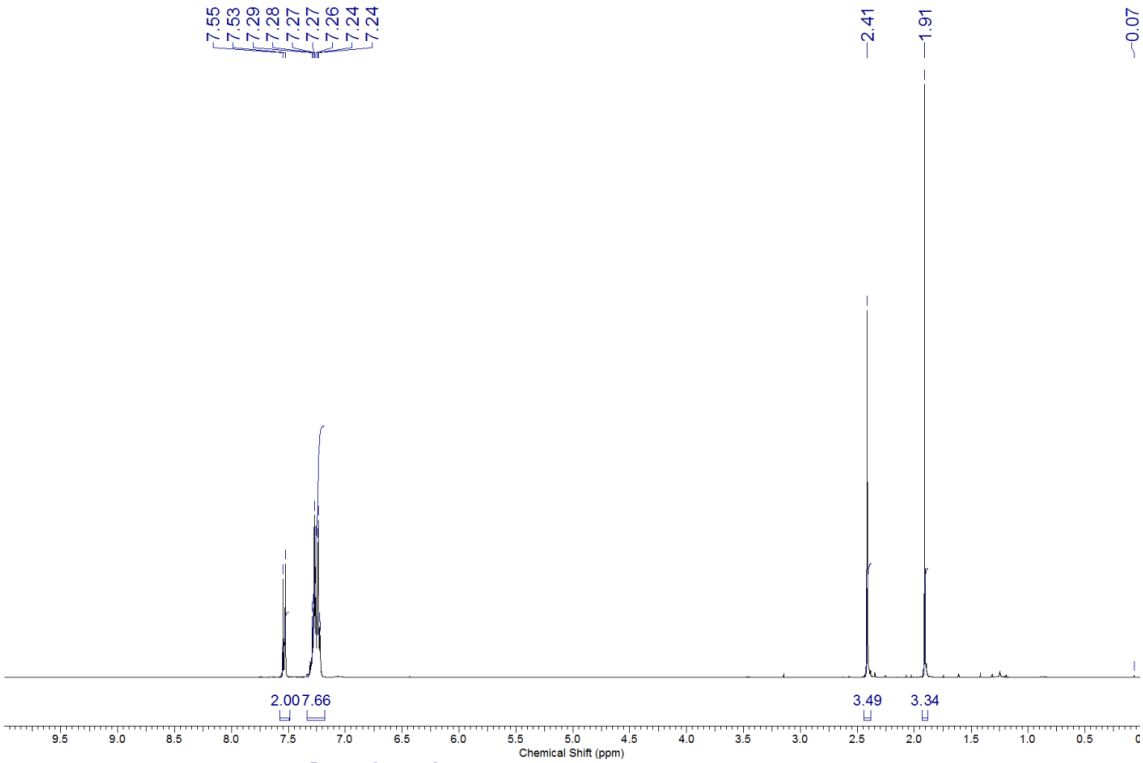


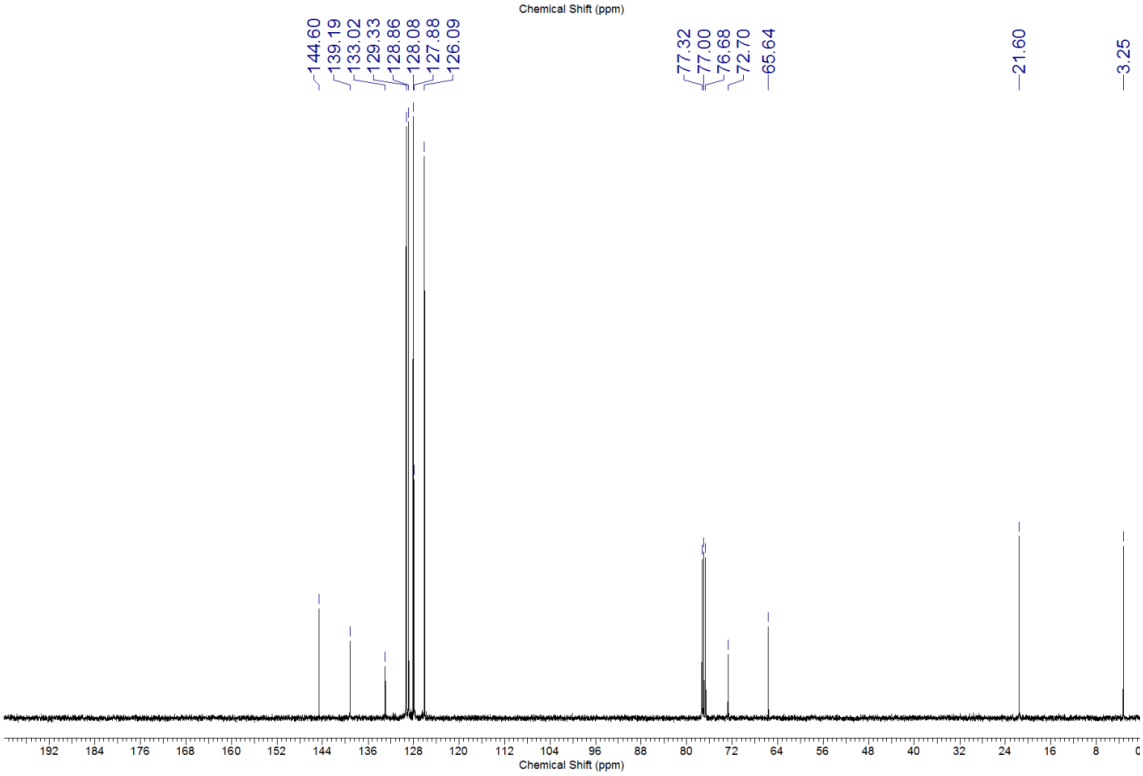


4-Methyl-*N*-phenyl-*N*-(prop-1-yn-1-yl)benzenesulfonamide, 1u

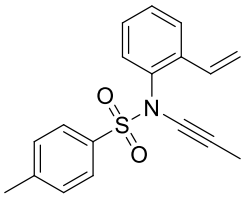


^{1}H (400 MHz, $CDCl_3$)
^{13}C (101 MHz, $CDCl_3$)

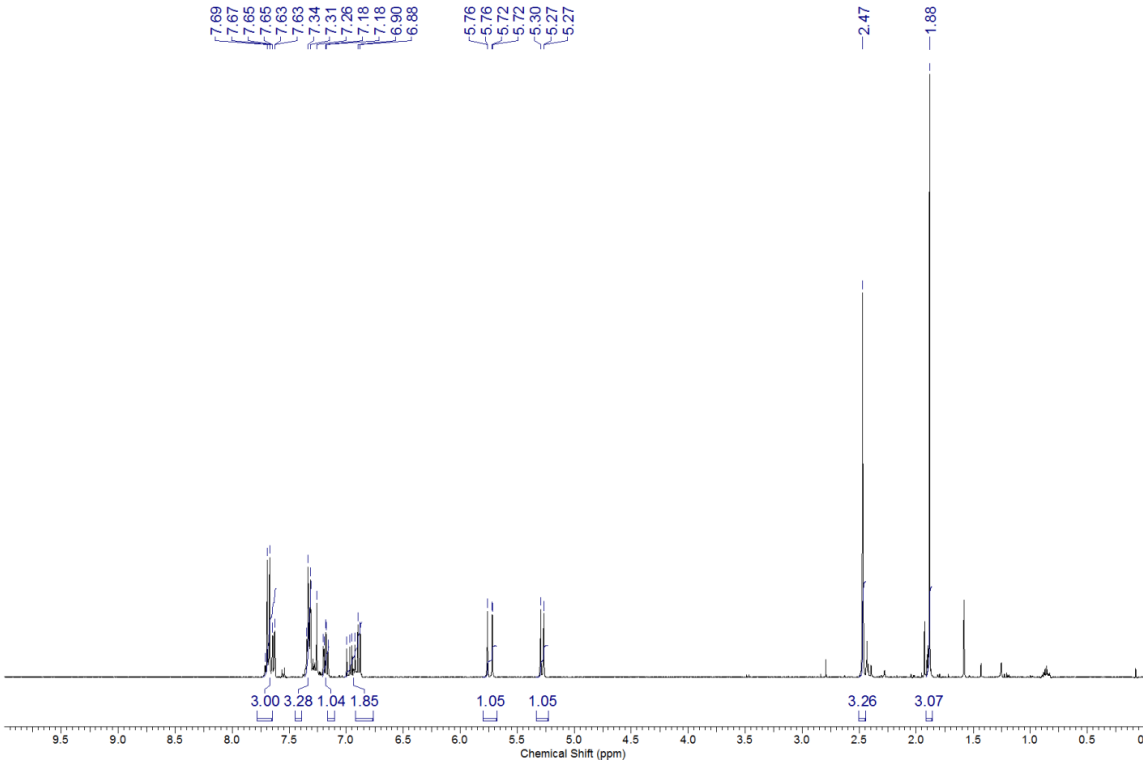


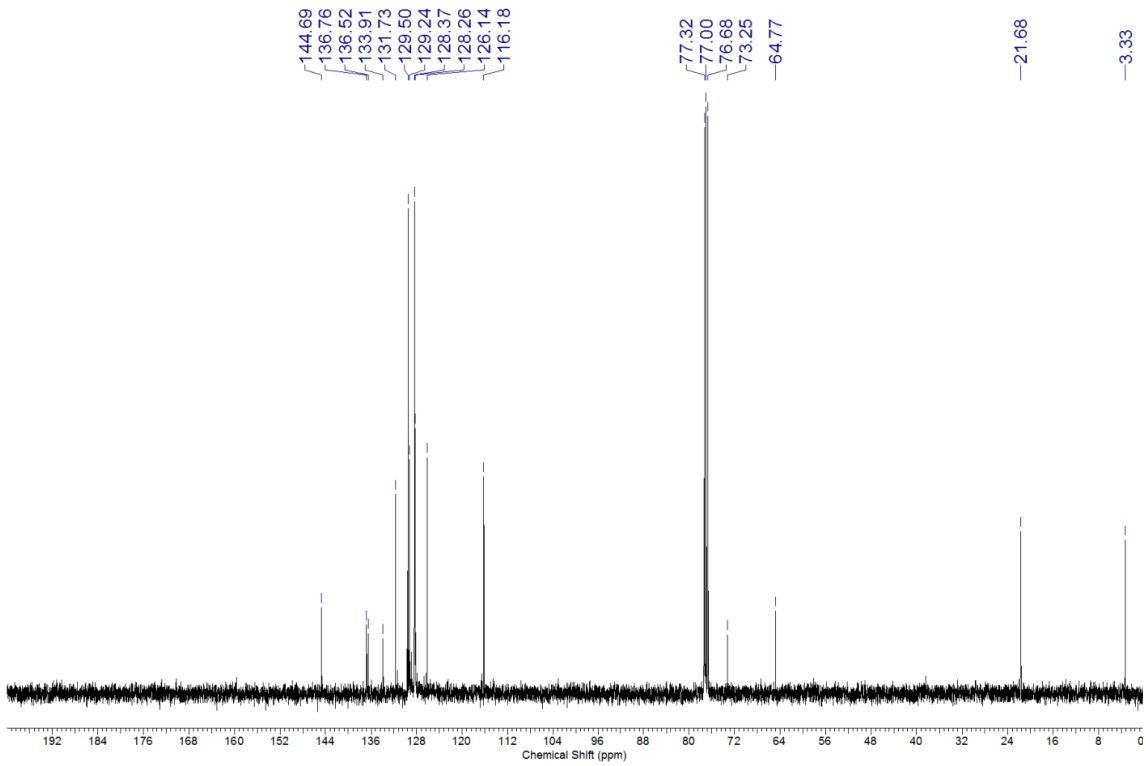


4-Methyl-*N*-(prop-1-yn-1-yl)-*N*-(2-vinylphenyl)benzenesulfonamide, 1v

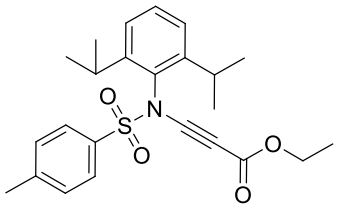


^{1}H (400 MHz, $CDCl_3$)
^{13}C (101 MHz, $CDCl_3$)

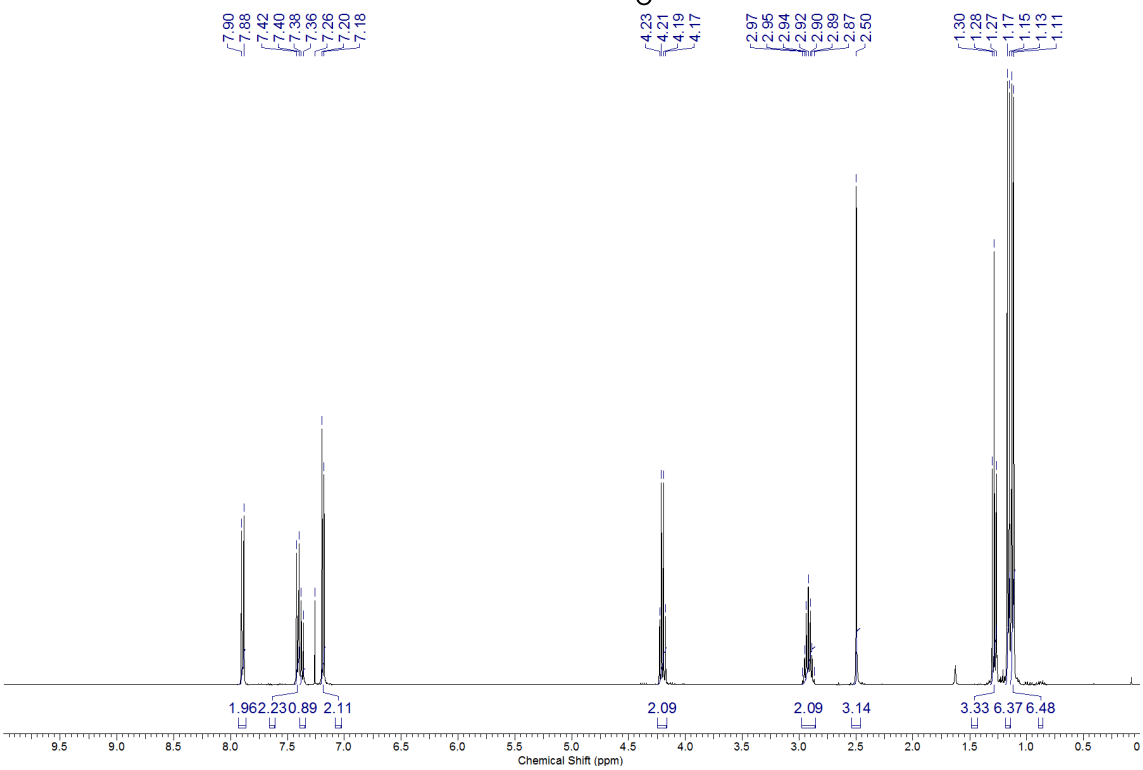


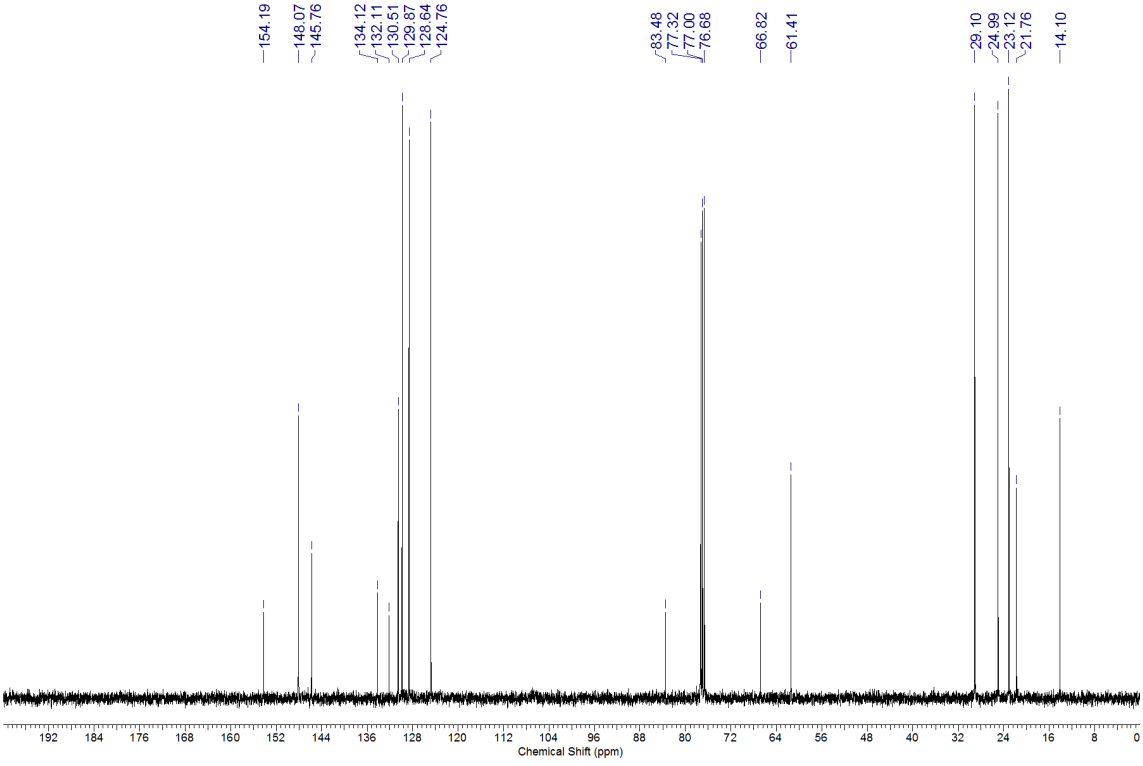


Ethyl 3-(*N*-(2,6-diisopropylphenyl)-4-methylphenylsulfonamido)propiolate, 1w

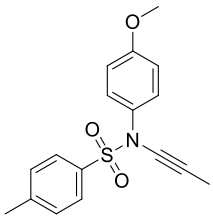


^{1}H (400 MHz, $CDCl_3$)
^{13}C (101 MHz, $CDCl_3$)

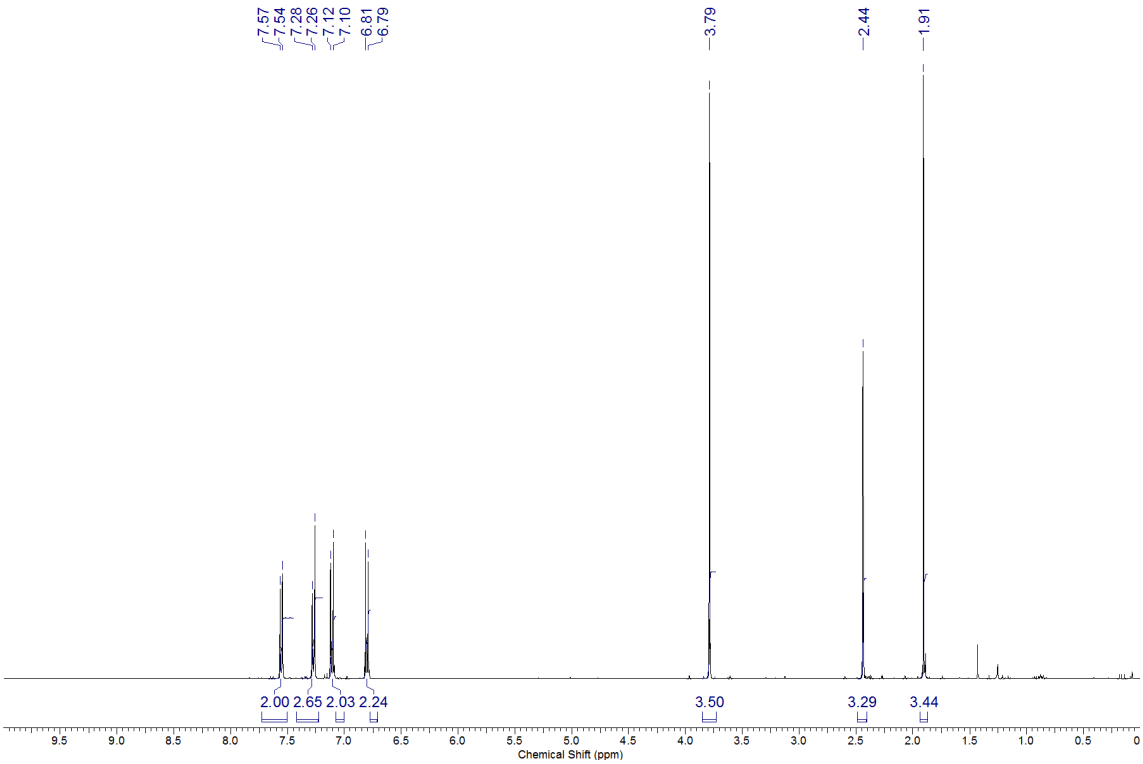


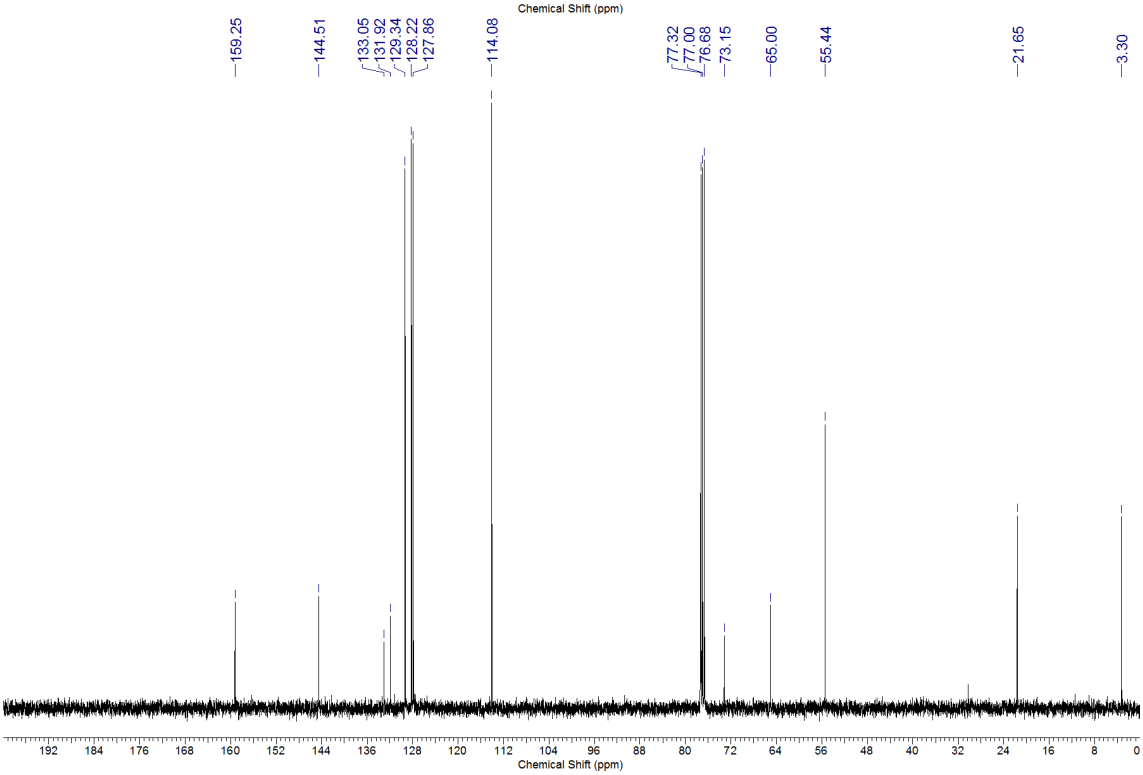


_N_-(4-Methoxyphenyl)-4-methyl-_N_-(prop-1-yn-1-yl)benzenesulfonamide, 1x

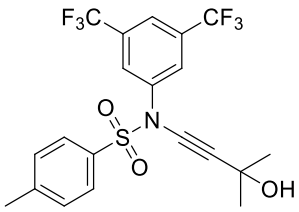


^{1}H (400 MHz, $CDCl_3$)
^{13}C (101 MHz, $CDCl_3$)

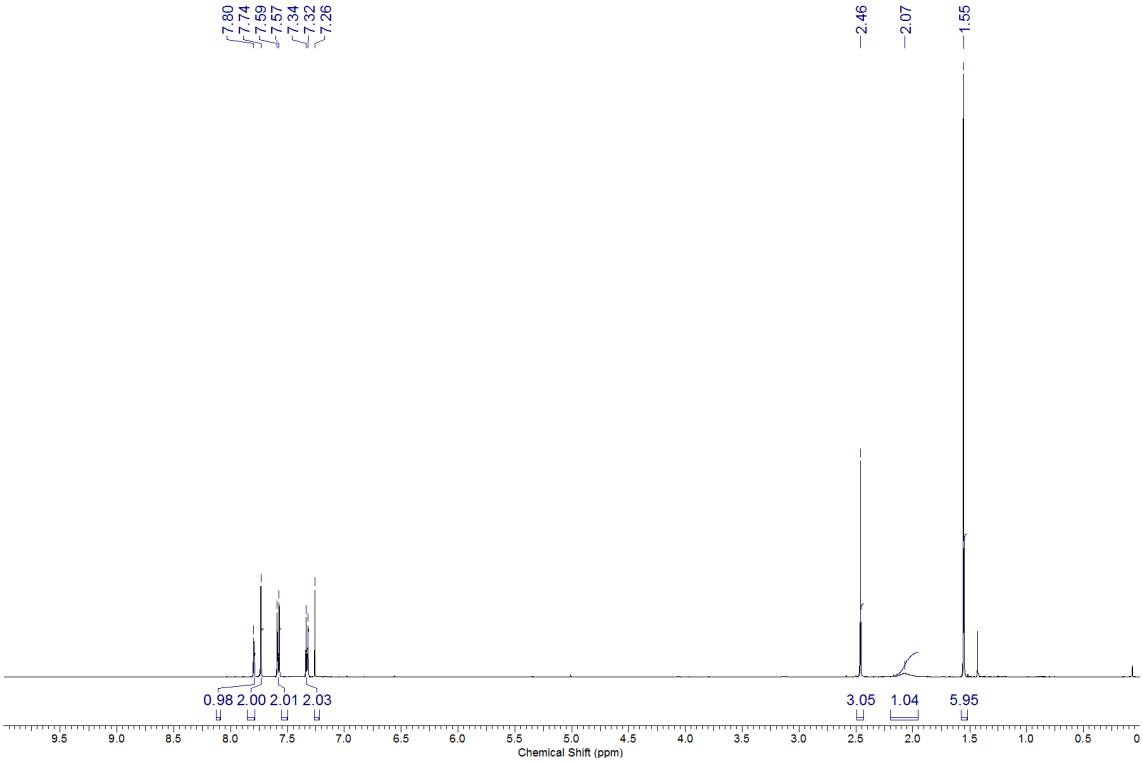


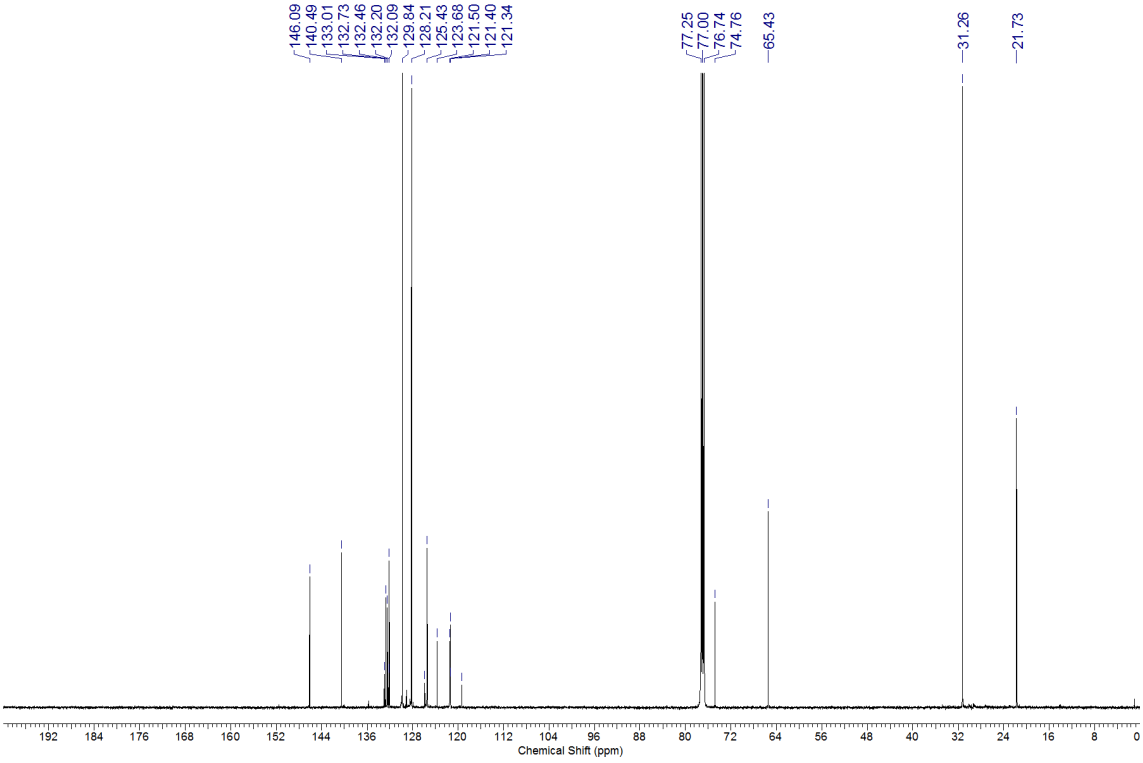


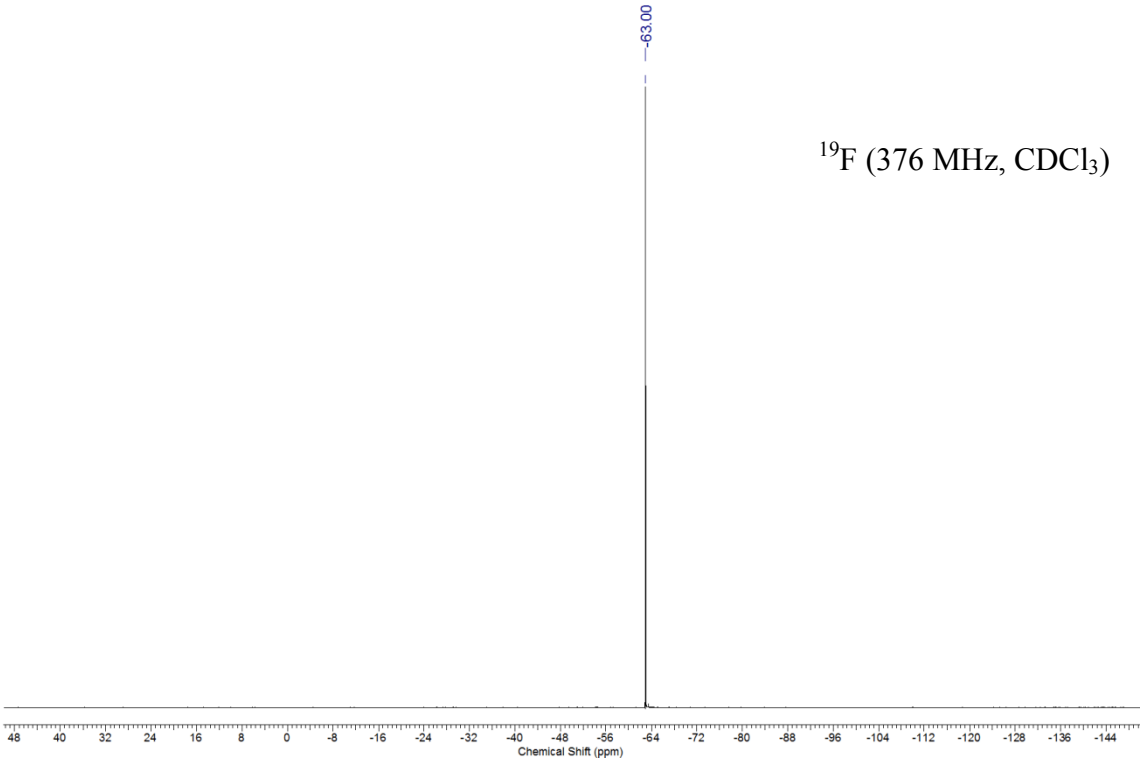
***N*-(3,5-Bis(trifluoromethyl)phenyl)-*N*-(3-hydroxy-3-methylbut-1-yn-1-yl)-4-methylbenzenesulfonamide, 1y**



^{1}H (500 MHz, $CDCl_3$)
^{13}C (126 MHz, $CDCl_3$)

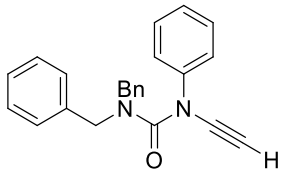




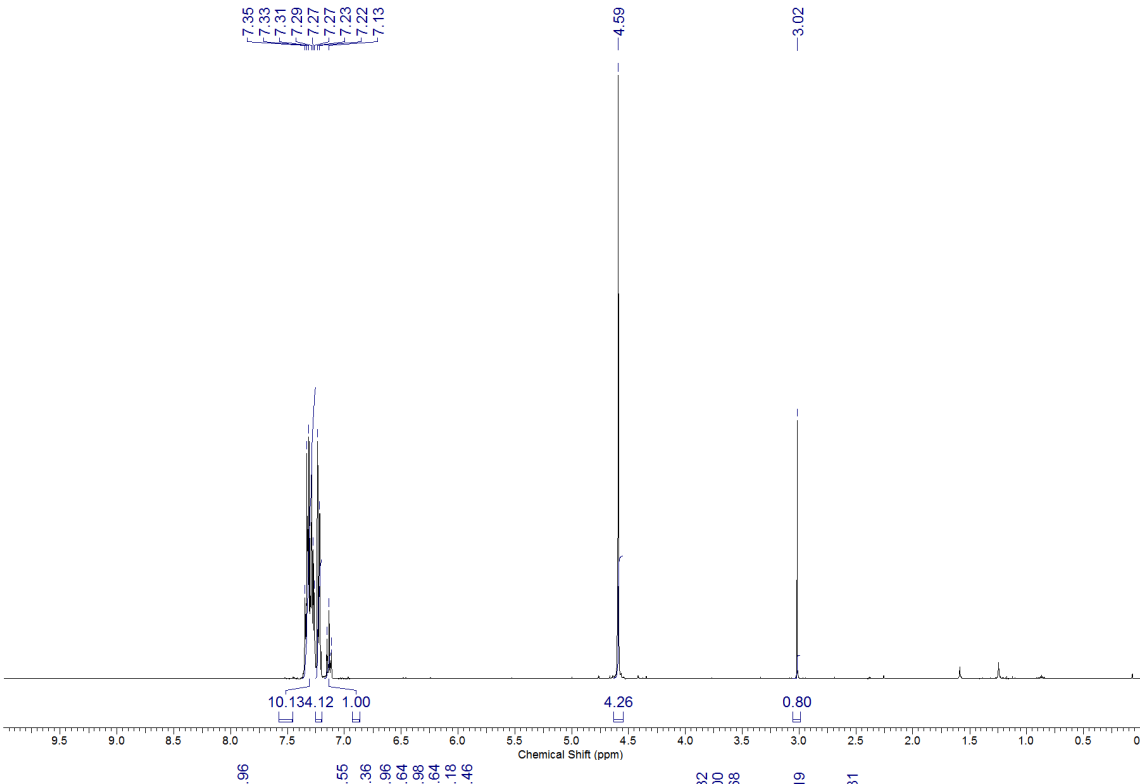


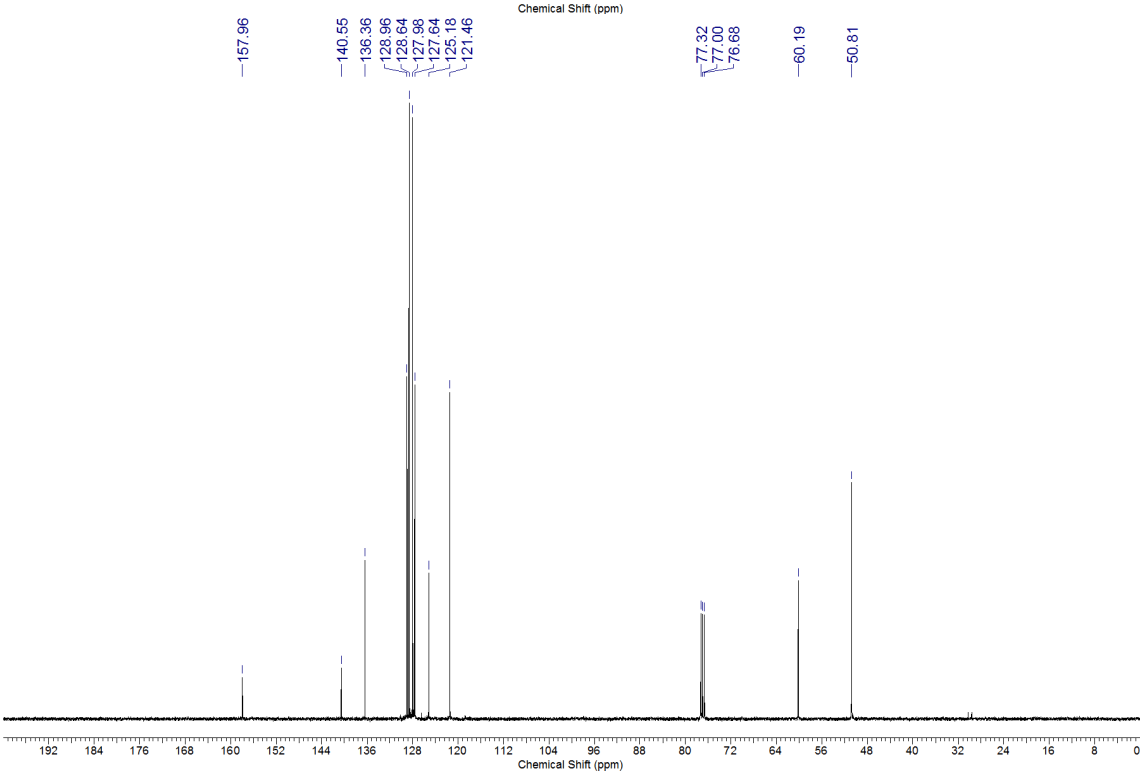
^{19}F (376 MHz, $CDCl_3$)

1,1-Dibenzyl-3-ethynyl-3-phenylurea, 1z

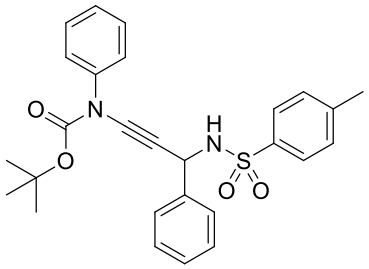


^{1}H (400 MHz, $CDCl_3$)
^{13}C (101 MHz, $CDCl_3$)

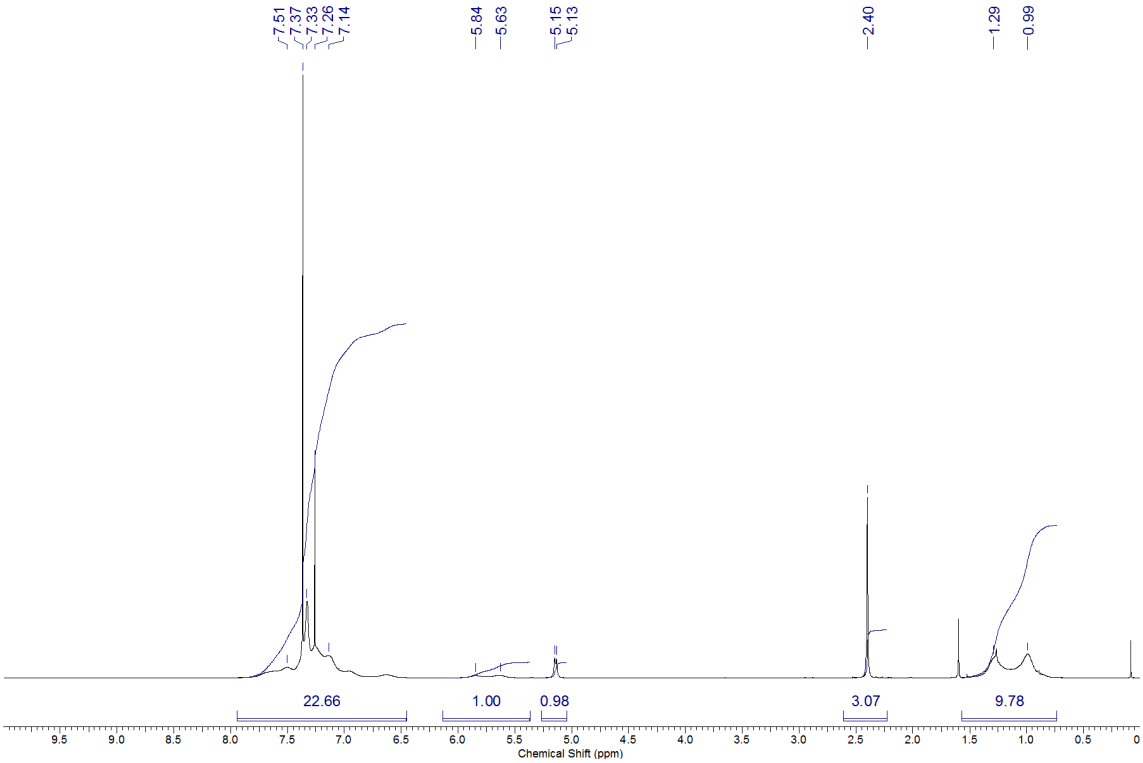


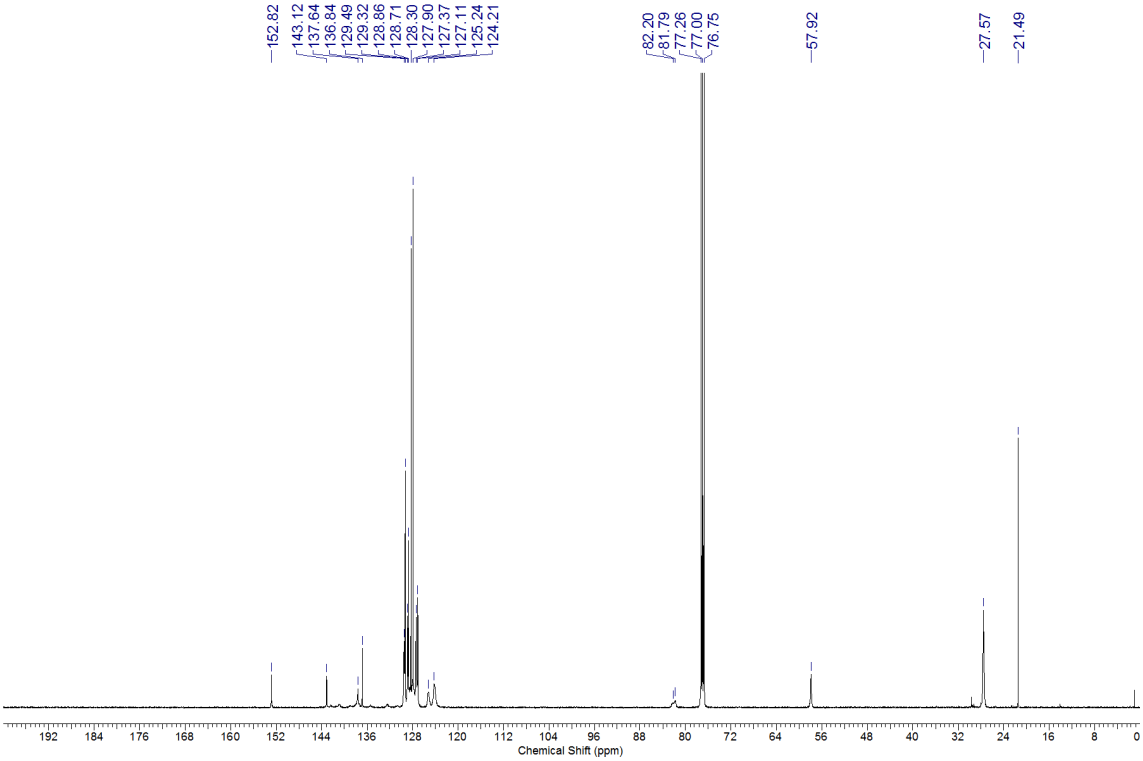


***tert*-Butyl (3-(4-methylphenylsulfonamido)-3-phenylprop-1-yn-1-yl)(phenyl)carbamate, 1aa**

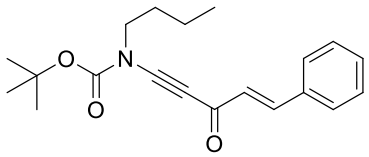


^{1}H (500 MHz, $CDCl_3$)
^{13}C (126 MHz, $CDCl_3$)

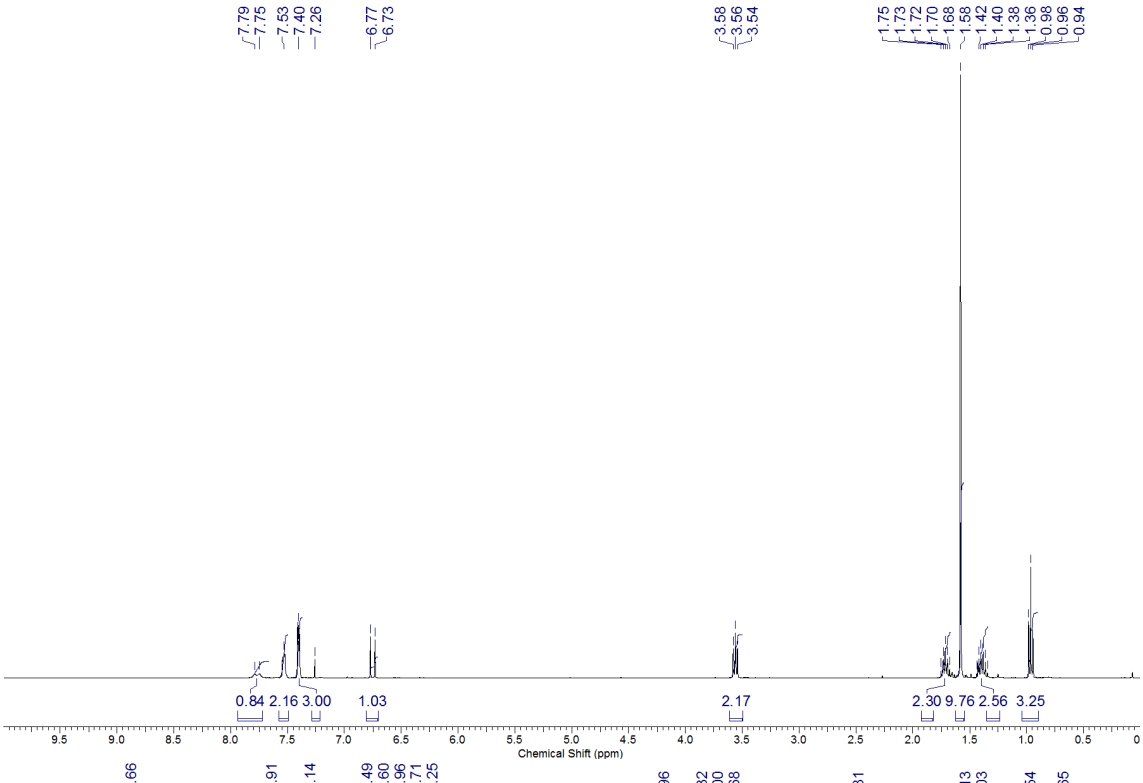


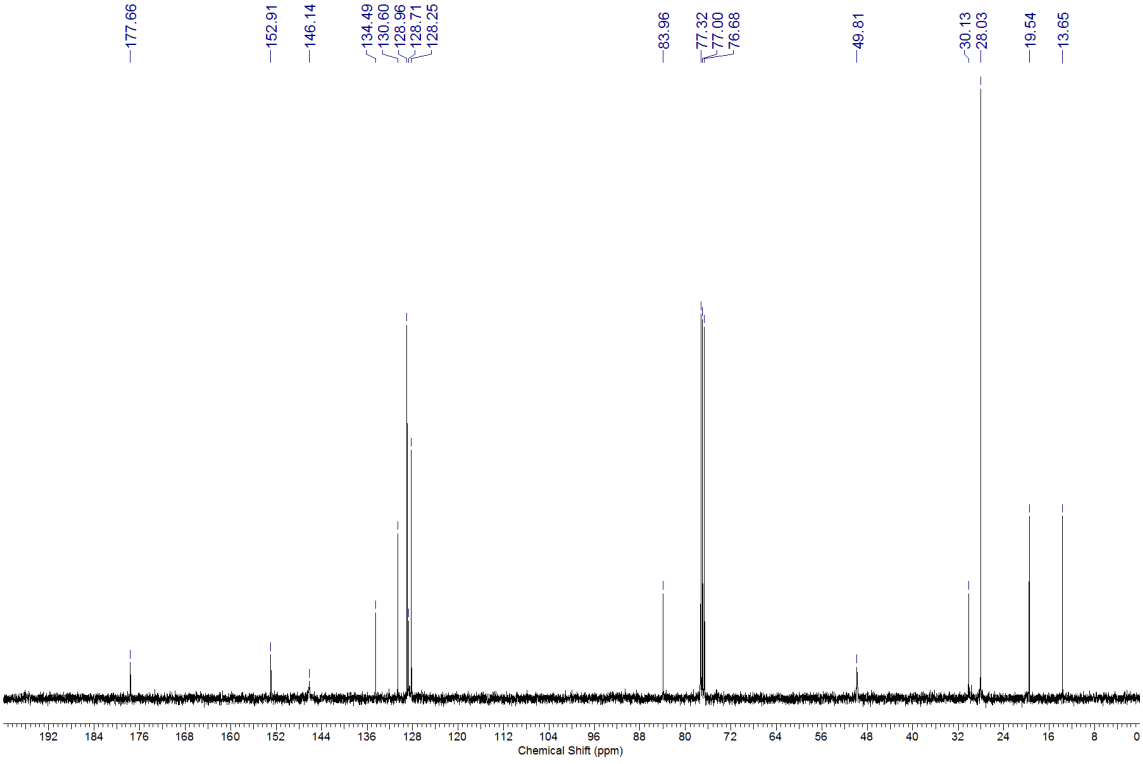


(*E*)-*tert*-butyl butyl(3-oxo-5-phenylpent-4-en-1-yn-1-yl)carbamate, 1bb

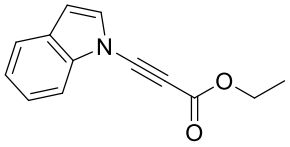


^{1}H (400 MHz, $CDCl_3$)
^{13}C (101 MHz, $CDCl_3$)

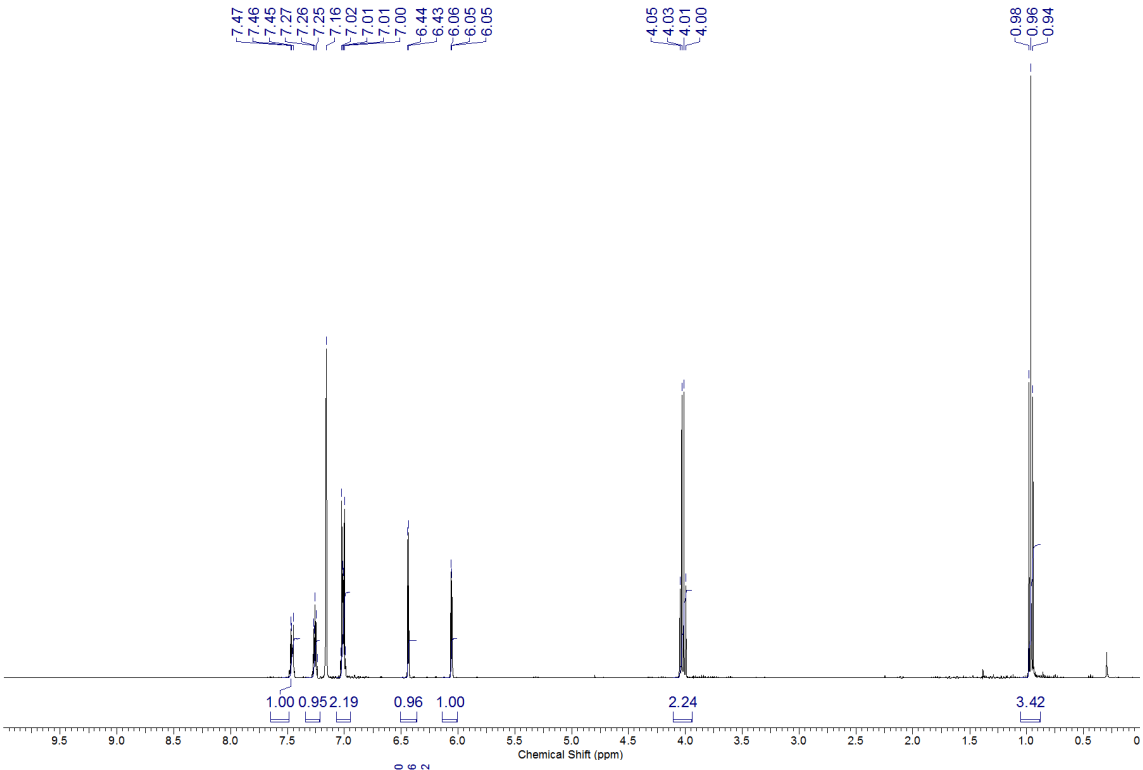


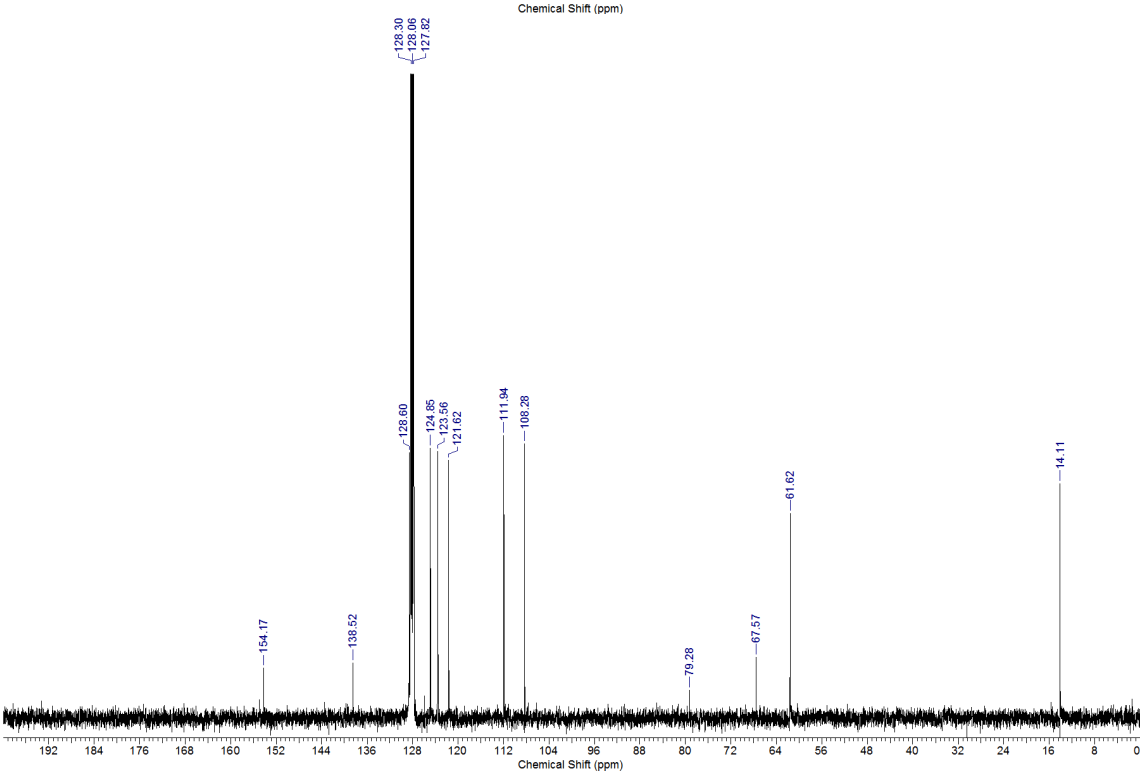


Ethyl 3-(1*H*-indol-1-yl)propiolate 1cc

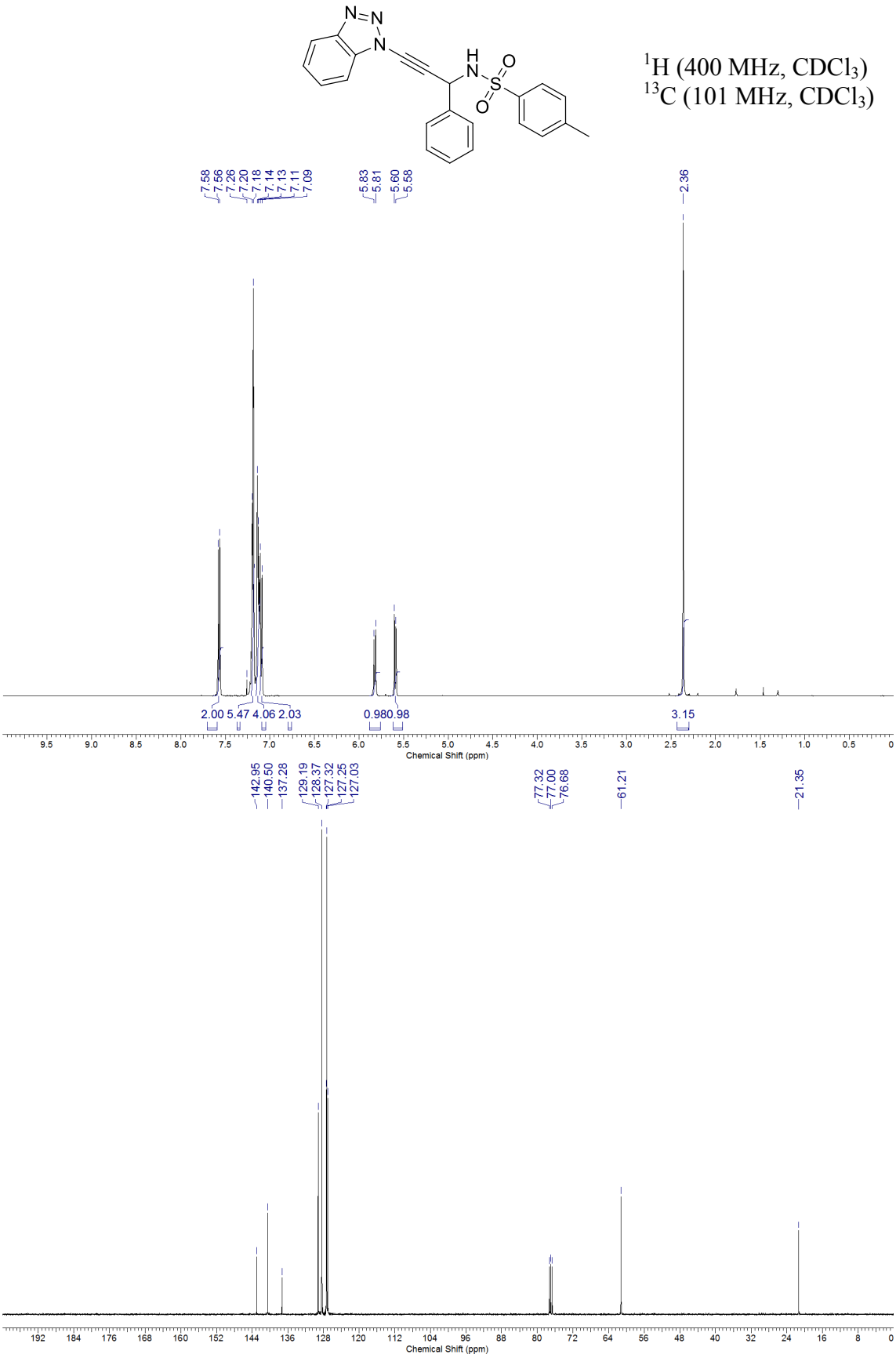


^{1}H (400 MHz, C_6D_6)
^{13}C (101 MHz, C_6D_6)

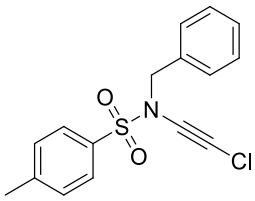




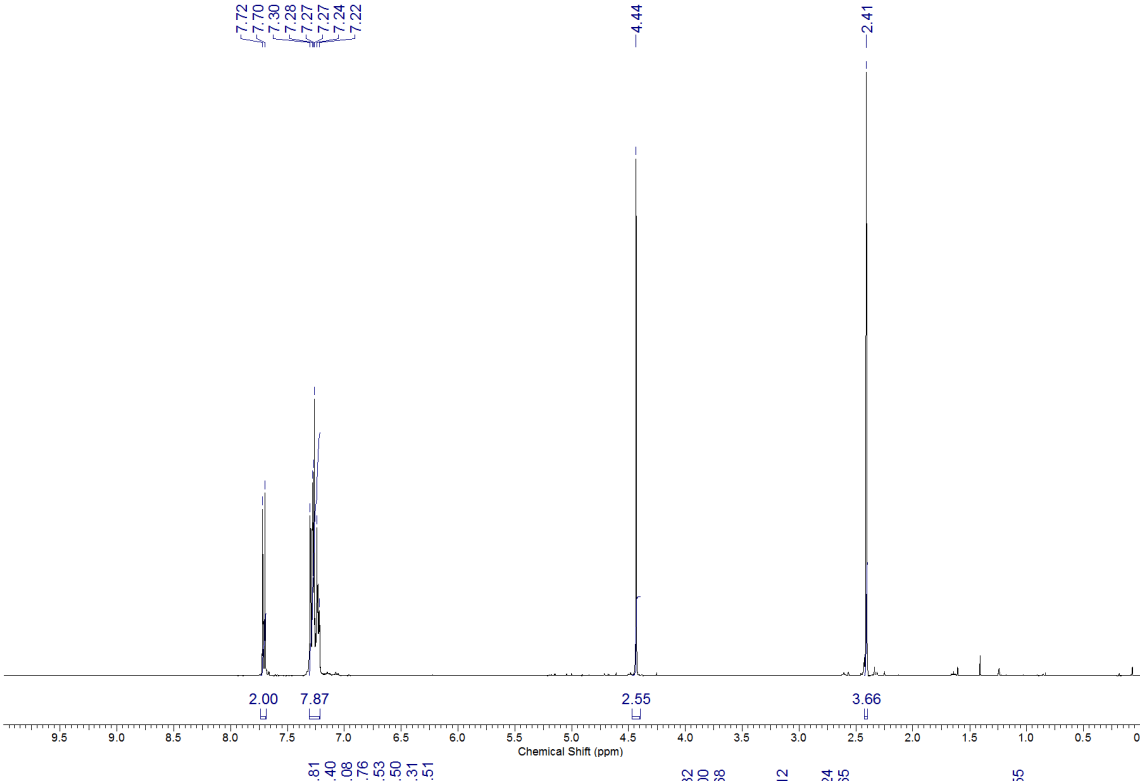
***N*-(3-(1*H*-benzo[*d*][1,2,3]triazol-1-yl)-1-phenylprop-2-yn-1-yl)-4-methylbenzenesulfonamide, 1dd**

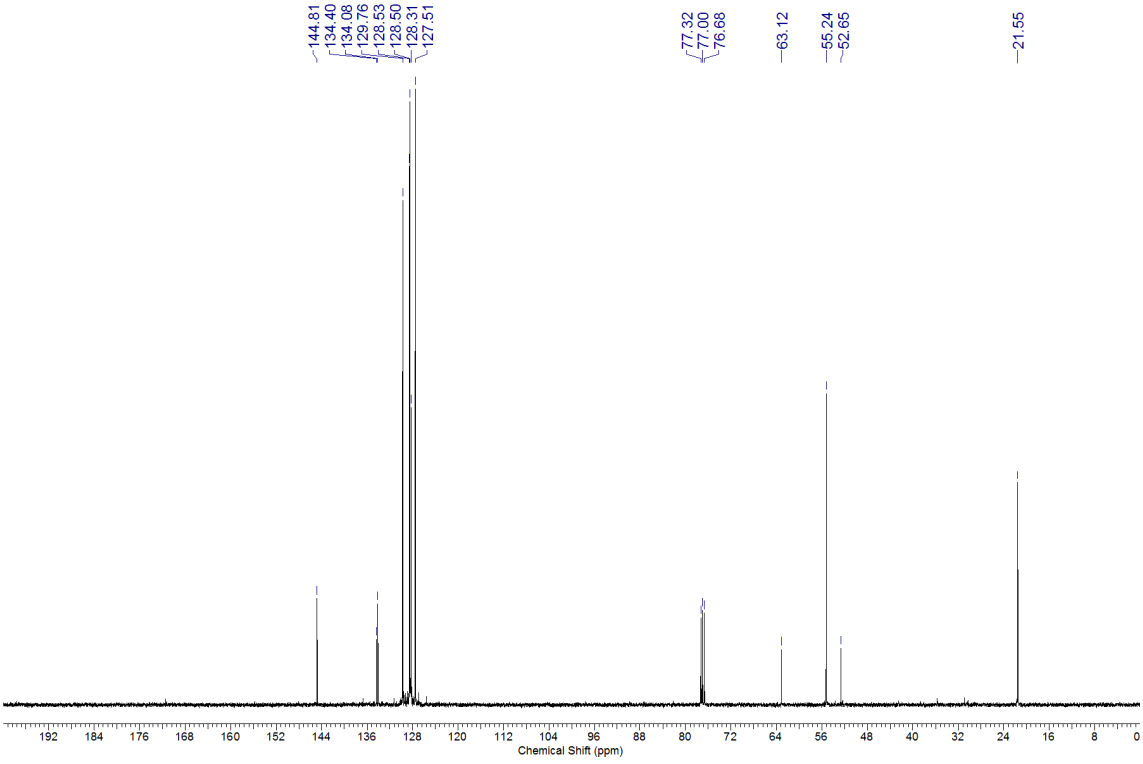


2.1c Chloroynamides: *N*-Benzyl-*N*-(chloroethynyl)-4-methylbenzenesulfonamide, S1



^{1}H (400 MHz, $CDCl_3$)
^{13}C (101 MHz, $CDCl_3$)





3.1 X-ray crystallographic information

Single crystal X-ray diffraction data were obtained for compounds **2a** and **2t**. In each case, a typical crystal was mounted using the oil drop technique, in perfluoropolyether oil at 150(2) K using a Cryostream N_2 open-flow cooling device.[1] Diffraction data were collected using graphite monochromatic Mo-K_α radiation (λ = 0.71073 Å) on a Nonius Kappa CCD diffractometer. For all data collections, series of ω-scans were performed in such a way as to collect a complete data set to a maximum resolution of 0.77 Å. Data reduction including unit cell refinement and inter-frame scaling was carried out using DENZO-SMN/SCALEPACK.[2] Intensity data were processed and corrected for absorption effects by the multi-scan method, based on repeat measurements of identical and Laue equivalent reflections. Structure solution was carried out with direct methods using the program SIR92[3] within the CRYSTALS software suite.[4] Coordinates and anisotropic displacement parameters of all non-hydrogen atoms were refined freely. Hydrogen atoms were generally visible in the difference map and refined with soft restraints prior to inclusion in the final refinement using a riding model.[5] A summary of the X-ray crystallographic data is provided below (Table SI1) and ORTEP depictions of the single crystal X-ray structures follow (Fig. SI1–SI2.) Crystallographic data (excluding structure factors) for all the structures have been deposited with the Cambridge Crystallographic Data Centre (CCDC 1022574 and 1022575).

Table SI1 Summary of the X-ray crystallographic data for compounds **2a**, **2t**.

	2a	**2t**
CCDC number	1022574	1022575
Chemical Formula	$C_{16}H_{15}Cl_2NO_2S$	$C_5H_5Cl_2NO_2$
FW	356.27	182.01
Crystal system	Triclinic	Orthorhombic
Space group	P-1	P 21 c n
Crystal colour	Colourless	Colourless
Crystal size (mm)	0.17 × 0.23 × 0.29	0.08 × 0.16 × 0.16
a (Å)	8.2507(2)	5.8979(2)
b (Å)	9.1868(2)	10.4250(3)
c (Å)	10.7811(3)	11.8622(3)
α (°)	92.8871(10)	90
β (°)	100.0815(10)	90
γ (°)	91.7403(10)	90
V (Å^3)	802.90(3)	725.64(4)
Z	2	4
D_{calcd} (g/cm^3)	1.474	1.666
μ (mm^{-1})	0.540	0.828
F (000)	368	368
Reflections collected	13254	9210
Unique reflections (R_{int})	3627 (0.024)	909 (0.018)
R_1 $(I>2\sigma(I))$	0.0342	0.0305
wR'_2 $(I>2\sigma(I))$	0.0784	0.0563

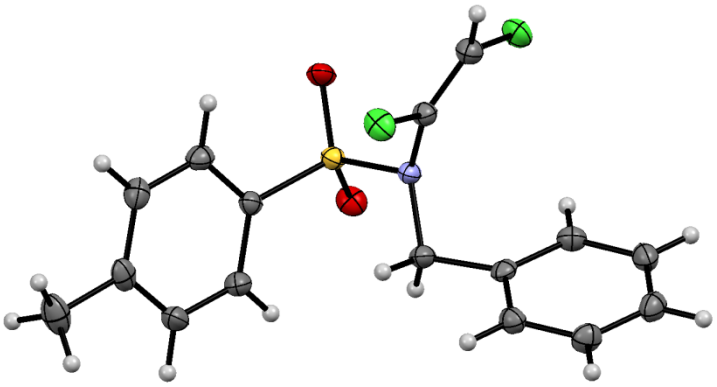


Fig. SI1 ORTEP representation of the X-ray crystal structure of **2a** with thermal ellipsoids at 50% probability.

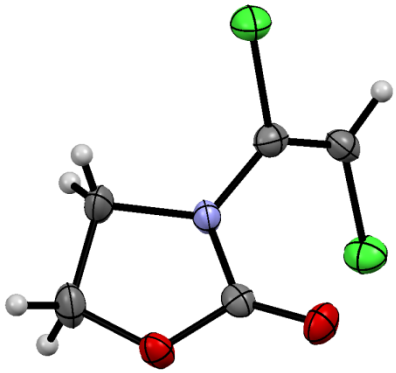


Fig. SI2 ORTEP representation of the X-ray crystal structure of **2t** with thermal ellipsoids at 50% probability.

1. Cosier, J.; Glazer, A. M., *J Appl Crystallography* **1986,** *19*, 105-107.
2. Otwinowski, Z.; Minor, W., *Macromol Crystallography Part A* **1997,** *276*, 307-326.
3. Altomare, A.; Cascarano, G.; Giacovazzo, C.; Guagliardi, A.,. *J Appl Crystallography* **1994,** *27*, 1045-1050.
4. Watkin, D.; Cooper, R.; Prout, C. K., *Zeitschrift Fur Kristallographie* **2002,** *217* (7-8), 429-430.
5. Cooper, R. I.; Thompson, A. L.; Watkin, D. J., *J Appl Crystallography* **2010,** *43*, 1100-1107.