SUPPORTING INFORMATION

Silver Effect in Regiodivergent Gold-Catalyzed Hydroaminations

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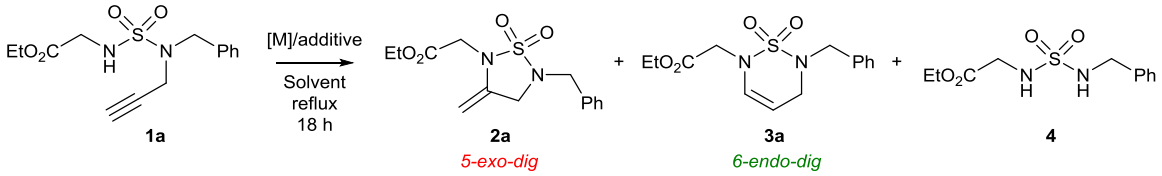
1. General Considerations.

^{1}H NMR spectra were recorded on a Bruker AV300 or AV400 spectrometer at 300 MHz or 400 MHz respectively. ^{13}C NMR spectra were recorded using the same spectrometers at 75 MHz or 100 MHz respectively. Chemical shifts (δ in ppm) were referenced to tetramethylsilane (TMS) or to residual solvent peaks ($CDCl_3$ at δ_H 7.26 ppm and δ_C at 77.0 ppm and CD_3CN at δ_H 2.130 , 1.940 ppm and δ_C at 116.3, 1.3 ppm). ^{31}P NMR spectra were recorded on a Bruker AV300 spectrometer at 121 MHz. *J* values are given in Hz and b, s, d, t, q, quin, sext, sept, m, are abbreviations corresponding to. broad, singlet, doublet, triplet, quartet, quintet, sextuplet, septuplet, multiplet respectively or a combination of these. Mass spectra were obtained from the EPSRC UK National Mass Spectrometry Facility at Swansea University. Infrared spectra were obtained on Perkin-Elmer Spectrum 100 FT-IR Universal ATR Sampling Accessory, deposited neat to a diamond/ZnSe plate.

Column chromatography was carried out using Matrix silica gel 60 from fluorochem or neutral alumina Brockmann I 50-200 µm 60 from Acros Organics and TLC performed using Merck silica gel 60 F254 pre-coated sheets and visualised by UV (254 nm). Anhydrous solvents obtained from a solvent purification system (SPS) and stored under an argon atmosphere until use.

2. *Optimization of the Reaction Conditions.*

Table S1 Screening of the catalyst.

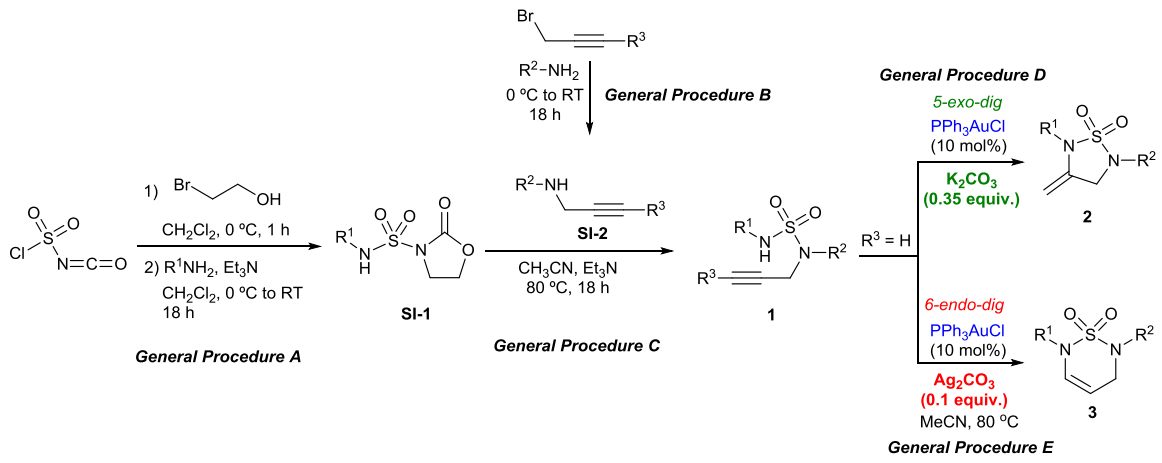


Entry	[M] (10 mol%)	Additive	Solvent/C (M)	Ratio **2a**:**3a**:**4**[a]	Conv. (%)[a]
1	$InBr_3$	---	$CHCl_3$/C = 0.1 M	N.d.	0
2	$InBr_3$	---	Tol./C = 0.1 M	N.d.	C.m.
3	$InBr_3$	-----	CH_3CN/C = 0.2 M	0:0:100	5
4	$InBr_3$	Et_3N	CH_3CN/C = 0.2 M	N.d.	0
5	PPh_3AuNTf_2	---	$CHCl_3$/C = 0.1 M	N.d.	C.m.
6	PPh_3AuNTf_2	---	Tol./C = 0.1 M	N.d.	0
7	PPh_3AuNTf_2	-----	CH_3CN/C = 0.2 M	N.d.	0
8	PPh_3AuNTf_2	Et_3N	CH_3CN/C = 0.2 M	N.d.	0
9	PPh_3AuCl	---	Tol./C = 0.1 M	N.d.	0
10	PPh_3AuCl	-----	CH_3CN/C = 0.2 M	N.d.	0
11	PPh_3AuCl	Et_3N	CH_3CN/C = 0.2 M	N.d.	0
12	PPh_3AuCl	$Ag(OCOCF_3)$ (10 mol%)	$CHCl_3$/C = 0.1 M	0:0:100	5
13	PPh_3AuCl	$Ag(OCOCF_3)$ (10 mol%)	Tol./C = 0.1 M	N.d.	C.m.
14	PPh_3AuCl	$Ag(OCOCF_3)$ (10 mol%)	CH_3CN/C = 0.2 M	N.d.	0
15	PPh_3AuCl	$Ag(OCOCF_3)$ (10 mol%)/Et_3N	CH_3CN/C = 0.2 M	0:0:100	100
16	-----	$Ag(OCOCF_3)$ (10 mol%)/Et_3N	CH_3CN/C = 0.2 M	N.d.	0
17	-----	Ag $OCOCF_3$) (10 mol%)	Tol./C = 0.1 M	N.d.	0
18	---	$Ag(OCOCF_3)$ (10 mol%)	$CHCl_3$/C = 0.1 M	N.d.	0
19	---	$Ag(OCOCF_3)$ (10 mol%)	CH_3CN/C = 0.2 M	N.d.	0
20	PPh_3AuCl	$AgSbF_6$ (10 mol%)	CH_3CN/C = 0.2 M	0:25:75	100
21	-----	$AgSbF_6$ (10 mol%)	CH_3CN/C = 0.2 M	0:0:100	100
22	PPh_3AuCl	$AgPF_6$ (10 mol%)	CH_3CN/C = 0.2 M	0:33:67	100
23	PPh_3AuCl	$AgPF_6$ (20 mol%)	CH_3CN/C = 0.2 M	0:100:0	65
24	-----	$AgPF_6$ (10 mol%)	CH_3CN/C = 0.2 M	0:0:100	100
25	-----	Ag(OAc) (10 mol%)	CH_3CN/C = 0.2 M	0:100:0	17
26	-----	Ag(OAc) (10 mol%)/Et_3N	CH_3CN/C = 0.2 M	N.d.	0
27	PPh_3AuCl	Ag(OTf) (10 mol%)	Tol./C = 0.1 M	N.d.	0
28	PPh_3AuCl	Ag(OTf) (10 mol%)	$CHCl_3$/C = 0.1 M	0:100:0	5
29	PPh_3AuCl	Ag(OTf) (10 mol%)/Et_3N	CH_3CN/C = 0.2 M	0:0:100	100
30	PPh_3AuCl	Ag(OTf) (10 mol%)	CH_3CN/C = 0.2 M	0:75:25	70
31	PPh_3AuCl	Ag(OTf) (20 mol%)	CH_3CN/C = 0.2 M	0:100:0	70
32	-----	Ag(OTf) (10 mol%)	Tol./C = 0.1 M	N.d.	0
33	-----	Ag(OTf) (10 mol%)	$CHCl_3$/C = 0.1 M	N.d.	0
34	-----	Ag(OTf) (10 mol%)	CH_3CN/C = 0.2 M	0:0:100	50
35	-----	Ag(OTf) (10 mol%)/Et_3N	CH_3CN/C = 0.2 M	0:100:0	12
36	PPh_3AuCl	$AgNTf_2$ (10 mol%)	CH_3CN/C = 0.2 M	0:0:100	43
37	-----	$AgNTf_2$ (10 mol%)	CH_3CN/C = 0.2 M	0:0:100	60
38	PPh_3AuCl	Ag(*p*-TsO) (10 mol%)	CH_3CN/C = 0.2 M	0:30:70	100
39	-----	Ag(*p*-TsO) (10 mol%)	CH_3CN/C = 0.2 M	0:0:100	68
40	PPh_3AuCl	$AgBF_4$ (10 mol%)	CH_3CN/C = 0.2 M	0:0:100	100
41	-----	$AgBF_4$ (10 mol%)	CH_3CN/C = 0.2 M	0:0:100	100
42	**PPh_3AuCl**	**Ag_2CO_3 (10 mol%)**	**CH_3CN/C = 0.2 M**	**0:100:0**	**100**
43	PPh_3AuCl	Ag_2CO_3 (5 mol%)	CH_3CN/C = 0.2 M	0:0:100	100
44	PPh_3AuCl (5 mol%)	Ag_2CO_3 (5 mol%)	CH_3CN/C = 0.2 M	0:22:78	65
45	-----	Ag_2CO_3 (10 mol%)	CH_3CN/C = 0.2 M	N.d.	0

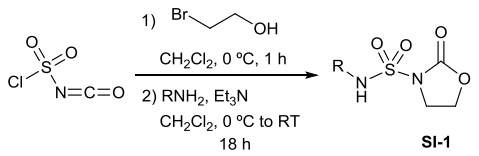
46	PPh_3AuCl	K_2CO_3 (10mol%)	CH_3CN/C = 0.2 M	N.d.	C.m.
47	PPh_3AuCl	K_2CO_3 (20 mol%)	CH_3CN/C = 0.2 M	100:0:0	65
48	**PPh_3AuCl**	**K_2CO_3 (35 mol%)**	**CH_3CN/C = 0.2 M**	**100:0:0**	**100**
49	PPh_3AuCl	Na_2CO_3 (35 mol%)	CH_3CN/C = 0.2 M	100:0:0	100
50	PPh_3AuCl	Cs_2CO_3 (35 mol%)	CH_3CN/C = 0.2 M	100:0:0	23
51	-----	K_2CO_3 (20 mol%)	CH_3CN/C = 0.2 M	N.d.	0
52	-----	K_2CO_3 (35 mol%)	CH_3CN/C = 0.2 M	N.d.	0
53	PPh_3AuCl (2 mol%)	$Cu(OTf)_2$ (10 mol%)	CH_3CN/C = 0.2 M	0:0:100	100
54	PPh_3AuCl (5 mol%)	$Cu(OTf)_2$ (10 mol%)	CH_3CN/C = 0.2 M	0:0:100	100
55	PPh_3AuCl (5 mol%)	$Cu(OTf)_2$ (20 mol%)	CH_3CN/C = 0.2 M	0:0:100	100
56	PPh_3AuCl	$Cu(OTf)_2$ (10 mol%)	CH_3CN/C = 0.2 M	0:0:100	100
57	-----	$Cu(OTf)_2$ (10 mol%)	CH_3CN/C = 0.2 M	N.d.	0

[a] Determined by ^1H NMR analysis. N.d. = not determined; C.m. = Complex mixture.

3. *Synthesis and Characterization of Compounds.*

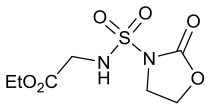


General Procedure A. **General procedure for the synthesis of the *N*-substituted-2-oxooxazolidine-3-sulfonamides SI-1.**



Following the general procedure described by Borghese *et al.*,[1] a solution of 2-bromoethan-1-ol (14.13 mmol, 1 equiv.) in dry CH_2Cl_2 (17.66 mL) was added dropwise to a solution of chlorosulfonyl isocyanate (14.13 mmol, 1 equiv.) in dry CH_2Cl_2 (88 mL) at 0 °C. The mixture was stirred for 1 hour at 0 °C and then a solution of triethylamine (31.1 mmol, 2.2 equiv.) and the corresponding amine (15.54 mmol, 1.1 equiv.) in dry CH_2Cl_2 (35.3 mL) was added dropwise. The mixture was stirred for 1 hour at 0 °C, then it was allowed to warm up at 25 °C and stirred overnight. The reaction was quenched by the addition of an aqueous solution of HCl 10%. The layers were separated and the aqueous phase was extracted with CH_2Cl_2 (2x), the combined organic phases were dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. Unless otherwise stated, the crude product was purified by flash column chromatography using the eluent indicated in each case.

Ethyl ((2-oxooxazolidin-3-yl)sulfonyl)glycinate. (SI-1a).

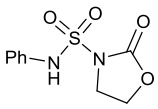


SI-1a

Following the general procedure A, the reaction of chlorosulfonyl isocyanate (2.46 mL, 28.3 mmol) in CH_2Cl_2 (177 mL) with 2-bromoethan-1-ol (2.00 mL, 28.3 mmol) in CH_2Cl_2 (35.3 mL) and subsequent reaction with ethyl glycinate (2.91 g, 28.3 mmol) and triethylamine (8.67 mL, 62.2 mmol) in CH_2Cl_2 (70.7 mL) provided ethyl ((2-oxooxazolidin-3-yl)sulfonyl)glycinate (**SI-1a**) as a white solid (6.06 g, 85% yield) after purification by flash column chromatography using petroleum ether/EtOAc (2:1 to

1:5) as eluent. **M. p.:** 151-154 °C. **^{1}H NMR (300 MHz, $CDCl_3$):** δ = 5.73 (s, 1H, NH), 4.51 – 4.38 (m, 2H, CH_2), 4.24 (q, *J* = 7.1 Hz, 2H, $OC\underline{H}_2CH_3$), 4.11 – 4.00 (m, 4H, 2xCH_2), 1.30 (t, *J* = 7.1 Hz, 3H, $OCH_2C\underline{H}_3$). **^{13}C NMR (75 MHz, CD_3CN)**: δ = 170.2, 154.2, 63.7, 62.4, 46.2, 45.7, 14.3. **IR (cm^{-1}):** 3321, 3274, 1737, 1446, 1415, 1377, 1331, 1246, 1212, 1144, 1086, 1059, 1009, 925, 898, 879, 836, 768, 728, 691, 666, 623, 580. **HRMS (ESI - ion trap) m/z:** $[M+H]^+$ **Calcd for** $C_7H_{13}N_2O_6S$ 253.0489; **Found:** 253.0483 (δ ppm = -2.3).

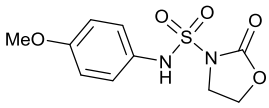
2-Oxo-*N*-phenyloxazolidine-3-sulfonamide. (SI-1e). [1]



SI-1e

Following the general procedure A, the reaction of chlorosulfonyl isocyanate (0.92 mL, 10.60 mmol) in CH_2Cl_2 (66.2 mL) with 2-bromoethan-1-ol (0.75 mL, 10.60 mmol) in CH_2Cl_2 (13.2 mL) and subsequent reaction with aniline (1.06 mL, 11.66 mmol) and triethylamine (3.25 mL, 23.32 mmol) in CH_2Cl_2 (26.5 mL) provided 2-oxo-*N*-phenyloxazolidine-3-sulfonamide (**SI-1e**) as a white solid (2.31 g, 90% yield) without further purification. **M. p.:** 132-135°C. **^{1}H NMR (300 MHz, $CDCl_3$):** δ = 7.52 (bs, 1H, NH), 7.44 – 7.27 (m, 5H, Ar-H), 4.33 – 4.22 (m, 2H, OCH_2), 3.88 – 3.78 (m, 2H, NCH_2). **^{13}C NMR (75 MHz, $CDCl_3$)**: δ = 153.2, 135.1, 129.7, 127.0, 123.1, 62.8, 46.3. **IR (cm^{-1}):** 3234, 1745, 1490, 1423, 1398, 1355, 1215, 1179, 1145, 1055, 1021, 960, 939, 914, 762, 693, 645, 604, 574, 536, 478, 405. **HRMS (ESI - ion trap) m/z:** $[M+H]^+$ **Calcd for** $C_9H_{11}N_2O_4S$ 243.0434; **Found:** 243.0427 (δ ppm = -2.9).

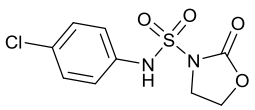
***N*-(4-Methoxyphenyl)-2-oxooxazolidine-3-sulfonamide. (SI-1f).**



SI-1f

Following the general procedure A, the reaction of chlorosulfonyl isocyanate (0.65 mL, 7.07 mmol) in CH_2Cl_2 (44.2 mL) with 2-bromoethan-1-ol (0.50 mL, 7.07 mmol) in CH_2Cl_2 (8.83 mL) and subsequent reaction with 4-methoxylaniline (957 mg, 7.77 mmol) and triethylamine (2.17 mL, 15.54 mmol) in CH_2Cl_2 (17.7 mL) provided *N*-(4-methoxyphenyl)-2-oxooxazolidine-3-sulfonamide (**SI-1f**) as a white solid (1.66 g, 86% yield) after recrystallization from CH_2Cl_2/petroleum ether. **M. p.:** 158-162 °C. **^{1}H NMR (300 MHz, $CDCl_3$):** δ = 7.24 (d, *J* = 9.0 Hz, 2H, Ar-H), 6.89 (d, *J* = 9.0 Hz, 2H, Ar-H), 4.34 – 4.24 (m, 2H, OCH_2), 3.81 (s, 3H, OCH_3), 3.80 – 3.72 (m, 2H, NCH_2).**^{13}C NMR (75 MHz, $CDCl_3$)**: δ = 158.9, 153.4, 127.4, 126.0, 114.8, 62.8, 55.5, 46.2. **IR (cm^{-1}):** 3283, 1750, 1607, 1509, 1444, 1400, 1355, 1301, 1147, 1029, 929, 817, 763, 596, 570. **HRMS (ESI - ion trap) m/z:** $[M+NH_4]^+$ **Calcd for** $C_{10}H_{16}N_3O_5S$ 290.0805; **Found:** 290.0805 (δ ppm = -0.1).

***N*-(4-Chlorophenyl)-2-oxooxazolidine-3-sulfonamide. (SI-1g).** [1]

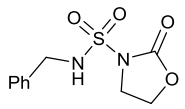


SI-1g

Following the general procedure A, the reaction of chlorosulfonyl isocyanate (0.92 mL, 10.60 mmol) in CH_2Cl_2 (66.2 mL) with 2-bromoethan-1-ol (0.75 mL, 10.60 mmol) in CH_2Cl_2 (13.25 mL) and subsequent reaction with 4-chloroaniline (1.49 g, 11.66 mmol) and triethylamine (3.25 mL,

23.32 mmol) in CH_2Cl_2 (26.5 mL) provided *N*-(4-chlorophenyl)-2-oxooxazolidine-3-sulfonamide (**SI-1g**) as a pale violet solid (2.31 g, 79% yield) after purification by flash column chromatography using petroleum ether/EtOAc (10:1) as eluent. **M. p.:** 146-148 °C. **^{1}H NMR (300 MHz, $CDCl_3$):** δ = 7.54 (bs, 1H, NH), 7.35 (d, *J* = 9.0 Hz, 2H, Ar-H), 7.26 (d, *J* = 9.0 Hz, 2H, Ar-H), 4.45 – 4.14 (m, 2H, OCH_2), 3.94 – 3.76 (m, 2H, NCH_2).**^{13}C NMR (75 MHz, $CDCl_3$)**: δ = 153.2, 133.6, 132.8, 129.9, 124.6, 62.8, 46.1. **IR (cm^{-1}):** 3201, 1740, 1482, 1396, 1369, 1188, 1145, 1090, 1055, 1014, 965, 932, 813, 748, 705, 627, 578. **HRMS (ESI - ion trap) m/z:** $[M+H]^+$ **Calcd for** $C_9H_{10}ClN_2O_4S$ 277.0044; **Found:** 277.0049 (δ ppm = 1.7).

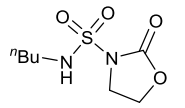
***N*-Benzyl-2-oxooxazolidine-3-sulfonamide. (SI-1h).**



SI-1h

Following the general procedure A, the reaction of chlorosulfonyl isocyanate (0.92 mL, 10.60 mmol) in CH_2Cl_2 (66.2 mL) with 2-bromoethan-1-ol (0.75 mL, 10.60 mmol) in CH_2Cl_2 (13.25 mL) and subsequent reaction with benzyl amine (1.27 mL, 11.66 mmol) and triethylamine (3.25 mL, 23.32 mmol) in CH_2Cl_2 (26.5 mL) provided *N*-benzyl-2-oxooxazolidine-3-sulfonamide (**SI-1h**) as a pale yellow solid (6.06 g, 85% yield). The crude was used in the next step without further purification. **M. p.:** 106-110 °C. **^{1}H NMR (300 MHz, $CDCl_3$):** δ = 7.41 – 7.29 (m, 5H, Ar-H), 5.91 (bs, 1H, NH), 4.31 (d, *J* = 6.2 Hz, 2H, $NHC\underline{H}_2$), 4.17 (dd, *J* = 8.8, 7.0 Hz, 2H, OCH_2), 3.79 (dd, *J* = 8.9, 6.9 Hz, 2H, NCH_2). **^{13}C NMR (75 MHz, $CDCl_3$)**: δ = 153.2, 135.4, 128.9, 128.4, 128.2, 62.5, 48.1, 44.8. **IR (cm^{-1}):** 3245, 1749, 1475, 1402, 1362, 1224, 1153, 1053, 963, 925, 844, 746, 704, 617. **HRMS (ESI - ion trap) m/z:** $[M+NH_4]^+$ **Calcd for** $C_{10}H_{16}N_3O_4S$ 274.0860; **Found:** 274.0859 (δ ppm = 1.1).

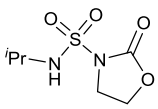
***N*-Butyl-2-oxooxazolidine-3-sulfonamide. (SI-1i).**



SI-1i

Following the general procedure A, the reaction of chlorosulfonyl isocyanate (0.92 mL, 10.60 mmol) in CH_2Cl_2 (66.2 mL) with 2-bromoethan-1-ol (0.75 mL, 10.60 mmol) in CH_2Cl_2 (13.25 mL) and subsequent reaction with *n*-butyl amine (853 mg, 11.66 mmol) and triethylamine (3.25 mL, 23.32 mmol) in CH_2Cl_2 (26.5 mL) provided *N*-butyl-2-oxooxazolidine-3-sulfonamide (**SI-1i**) as a white solid (2.07 g, 88% yield). The crude was used in the next step without further purification. **M. p.:** 107-110 °C. **^{1}H NMR (300 MHz, $CDCl_3$):** δ = 5.32 (t, *J* = 5.4 Hz, 1H, NH), 4.50 – 4.39 (m, 2H, OCH_2), 4.12 – 4.01 (m, 2H, NCH_2), 3.11 (td, *J* = 7.1, 6.2 Hz, 2H, $NHC\underline{H}_2$), 1.66 – 1.50 (m, 2H, CH_2), 1.47 – 1.32 (m, 2H, CH_3), 0.94 (t, *J* = 7.3 Hz, 3H, $CH_2C\underline{H}_3$). **^{13}C NMR (75 MHz, $CDCl_3$)**: δ = 153.6, 62.7, 45.4, 43.7, 31.2, 19.6, 13.5. **IR (cm^{-1}):** 3286, 2960, 1749, 1434, 1393, 1347, 1218, 1147, 1075, 1023, 969, 763, 608, 560, 502. **HRMS (ESI - ion trap) m/z:** $[M+H]^+$ **Calcd for** $C_7H_{15}N_2O_4S$ 223.0747; **Found:** 223.0747 (δ ppm = -0.0).

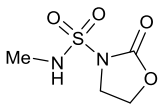
***N*-Isopropyl-2-oxooxazolidine-3-sulfonamide. (SI-1j).** [1]



SI-1j

Following the general procedure A, the reaction of chlorosulfonyl isocyanate (0.92 mL, 10.60 mmol) in CH_2Cl_2 (66.2 mL) with 2-bromoethan-1-ol (0.75 mL, 10.60 mmol) in CH_2Cl_2 (13.25 mL) and subsequent reaction with isopropyl amine (689 mg, 11.66 mmol) and triethylamine (3.25 mL, 23.32 mmol) in CH_2Cl_2 (26.5 mL) provided *N*-isopropyl-2-oxooxazolidine-3-sulfonamide (**SI-1j**) as a white solid (1.74 g, 79% yield) after recrystallization from CH_2Cl_2/petroleum ether. **M. p.:** 120-122 °C. **^{1}H NMR (300 MHz, $CDCl_3$):** δ = 5.20 (bs, 1H, NH), 4.49 – 4.38 (m, 2H, OCH_2), 4.12 – 4.01 (m, 2H, NCH_2), 3.74 – 3.53 (sept, *J* = 6.5 Hz, 1H, CH), 1.26 (d, *J* = 6.5 Hz, 6H, CH_3). **^{13}C NMR (75 MHz, $CDCl_3$)**: δ = 153.6, 62.6, 47.6, 45.3, 23.1. **IR (cm^{-1}):** 3293, 1750, 1475, 1422, 1387, 1344, 1215, 1138, 1118, 1050, 1003, 902, 762, 617, 557, 511, 445. **HRMS (ESI - ion trap) m/z:** $[M+H]^+$ **Calcd for** $C_6H_{13}N_2O_4S$ 209.0591 ; **Found:** 209.0591 (δ ppm = -0.3).

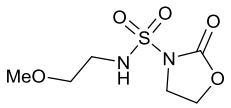
***N*-Methyl-2-oxooxazolidine-3-sulfonamide. (SI-1k).** [1]



SI-1k

Following the general procedure A, the reaction of chlorosulfonyl isocyanate (2.46 mL, 28.3 mmol) in CH_2Cl_2 (177 mL) with 2-bromoethan-1-ol (2.00 mL, 28,3 mmol) in CH_2Cl_2 (35.3 mL) and subsequent reaction with methylamine (7.77 mL, 15.54 mmol, C = 2 M in THF) and triethylamine (8.67 mL, 62.2 mmol) in CH_2Cl_2 (70.7 mL) provided *N*-methyl-2-oxooxazolidine-3-sulfonamide (**SI-1k**) as a white solid (2.02 g, 79% yield) after purification by flash column chromatography using as eluent petroleum ether/EtOAc (2:1).**M. p.:** 115-117 °C. **^{1}H NMR (300 MHz, $CDCl_3$):** δ = 5.30 (bs, 1H, NH), 4.53 – 4.39 (m, 2H, OCH_2), 4.15 – 3.98 (m, 2H, NCH_2), 2.82 (d, *J* = 4.7 Hz, 3H, CH_3). **^{13}C NMR (75 MHz, $CDCl_3$)**: δ = 153.4, 62.6, 45.1, 30.0. **IR (cm^{-1}):** 3330, 1754, 1477, 1396, 1355, 1218, 1153, 1076, 1029, 966, 849 755, 611. **HRMS (ESI - ion trap) m/z:** $[M+H]^+$ **Calcd for** $C_4H_9N_2O_4S$ 181.0278; **Found:** 181.0278 (δ ppm = 0.3).

***N*-(2-Methoxyethyl)-2-oxooxazolidine-3-sulfonamide. (SI-1l).**

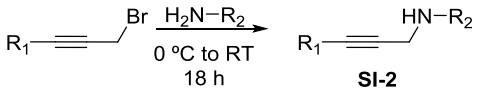


SI-1l

Following the general procedure A, the reaction of chlorosulfonyl isocyanate (1.23 mL, 14.13 mmol) in CH_2Cl_2 (88 mL) with 2-bromoethan-1-ol (1.00 mL, 14.13 mmol) in CH_2Cl_2 (17.66 mL) and subsequent reaction with 2-methoxyethan-1-amine (1.35 mL, 15.54 mmol) and triethylamine (4.33 mL, 31.1 mmol) in CH_2Cl_2 (26.5 mL) provided *N*-(2-methoxyethyl)-2-oxooxazolidine-3-sulfonamide (**SI-1l**) as a white solid (2.31 g, 79% yield) after recrystallization from petroleum ether/ CH_2Cl_2. **M. p.:** 104-107 °C. **^{1}H NMR (300 MHz, $CDCl_3$):** δ = 5.77 (t, *J* = 5.3 Hz, 1H, NH), 4.47 – 4.35 (m, 2H, OCH_2), 4.11 – 4.00 (m, 2H, NCH_2), 3.55 – 3.45 (m, 2H, OCH_2), 3.40 – 3.28 (m, 5H, OCH_3+NCH_2). **^{13}C NMR (75 MHz, $CDCl_3$)**: δ = 153.5, 70.6, 62.6, 58.9, 45.4, 43.9. **IR (cm^{-1}):** 3282,

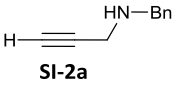
1747, 1473, 1440, 1393, 1350, 1220, 1150, 1076, 1023, 967, 895, 832, 763, 607, 554, 511. **HRMS (ASAP+ - TOF) m/z:** $[M+H]^+$ **Calcd for** $C_6H_{13}N_2O_5S$ 225.0545; **Found:** 225.0549 (δ ppm = 0.4).

General procedure B. General procedure for the synthesis of propargyl amines.



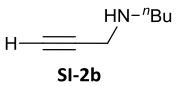
Following the general procedure described by Nevado *et al.,*[2] the propargyl bromide (1 equiv.) was added very slowly dropwise to the corresponding neat amine (6 equiv.) at 0 °C. The mixture was allowed to warm to room temperature and stirred overnight. Then, a mixture of a solution 1 M of NaOH (4 mL/mmol) and Et_2O (4 mL/mmol) was added and stirred for 5 min. The mixture was transferred to a separating funnel, the layers were separated, and the organic phase was extracted with Et_2O (3x). The organic phases were combined and dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The crude was then purified by flash column chromatography unless otherwise stated.

***N*-Benzylprop-2-yn-1-amine. (SI-2a).**[3]



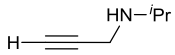
Following the general procedure B, the reaction of 3-bromoprop-1-yne (3.75 mL, 33.6 mmol) and benzyl amine (22.0 mL, 202 mmol) provided *N*-benzylprop-2-yn-1-amine **SI-2a** (3.62 g, 74% yield) as a yellow oil after purification by flash chromatography using petroleum ether/EtOAc 15:1 as eluent. **^{1}H-NMR (300 MHz, $CDCl_3$):** δ = 7.39 – 7.22 (m, 5H, Ar-H), 3.89 (s, 2H, CH_2), 3.44 (d, *J* = 2.4 Hz, 2H, NCH_2), 2.26 (t, *J* = 2.4 Hz, 1H, CH). 1.45 (bs, 1H, NH). **^{13}C-NMR (75 MHz, $CDCl_3$)**: δ = 139.4, 128.5, 128.4, 127.2, 82.1, 71.5, 52.3, 37.4. **IR (cm^{-1}):** 3290, 1494, 1453, 1329, 1103, 1028, 906, 734, 697, 635. **HRMS (ESI - ion trap) m/z:** $[M+H]^+$ **Calcd for** $C_{10}H_{12}N$ 146.0964, **found** 146.0961. (δ ppm = -2.2).

***N*-(Prop-2-yn-1-yl)butan-1-amine. (SI-2b).**



Following the general procedure B, the reaction of 3-bromoprop-1-yne (4.49 mL, 40.3 mmol) and *n*-butyl amine (23.93 mL, 242 mmol) provided *N*-(prop-2-yn-1-yl)butan-1-amine **SI-2b** (2.98 g, 64% yield) as yellow oil after purification by distillation. **B.p.:** 142 °C. **^{1}H-NMR (300 MHz, $CDCl_3$):** δ = 3.42 (d, *J* = 2.4 Hz, 2H, NCH_2), 2.73 – 2.63 (m, 2H, NCH_2), 2.20 (t, *J* = 2.4 Hz, 1H, CH), 1.55 – 1.41 (m, 2H, CH_2), 1.41 – 1.28 (m, 2H, CH_2), 1.12 (bs, 1H, NH), 0.92 (t, *J* = 7.2 Hz, 3H, $CH_2C\underline{H}_3$). **^{13}C-NMR (75 MHz, $CDCl_3$)**: δ = 82.4, 71.1, 48.4, 38.2, 32.0, 20.4, 14.0. **IR (cm^{-1}):** 3303, 2957, 2928, 1456, 1328, 1114, 905, 733, 624. **HRMS (EI – TOF+) m/z:** $[M]^+$ **Calcd for** $C_7H_{13}N$ 111.1048, **found** 111.1050. (δ ppm = 0.2).

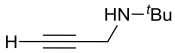
***N*-Isopropylprop-2-yn-1-amine. (SI-2c).**[4]



SI-2c

Following the general procedure B, the reaction of 3-bromoprop-1-yne (4.49 mL, 40.3 mmol) and isopropyl amine (19.8 mL, 242 mmol) provided *N*-isopropylprop-2-yn-1-amine **SI-2c** (2.56 g, 65% yield) as a colourless oil after purification by distillation. **B.p.:** 91 °C. **^{1}H-NMR (300 MHz, $CDCl_3$):** δ = 4.76 (d, *J* = 1.0 Hz, 1H,), 3.41 (d, *J* = 2.4 Hz, 2H, $NC\underline{H}_2$), 3.01 (sept, *J* = 6.2 Hz, 1H, CH), 2.18 (t, *J* = 2.4 Hz, 1H, CH), 2.06 (bs, 1H, NH), 1.04 (d, *J* = 6.2 Hz, 6H, CH_3). **^{13}C-NMR (75 MHz, $CDCl_3$)**: δ = 82.3, 71.1, 46.9, 35.6, 22.4. **IR (cm^{-1}):** 3303, 2957, 2928, 1456, 1328, 1114, 905, 733, 624. **HRMS (EI – TOF+) m/z:** $[M]^+$ **Calcd for** $C_6H_{11}N$ 97.0891, **found** 97.0895. (δ ppm = 0.4).

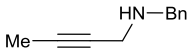
***N*-(*tert*-Butyl)prop-2-yn-1-amine. (SI-2d).**



SI-2d

Following the general procedure B, the reaction of 3-bromoprop-1-yne (1.87 mL, 16.8 mmol) and *tert*-butyl amine (10.6 mL, 101 mmol) provided *N*-(*tert*-butyl)prop-2-yn-1-amine **SI-2d** (1.3 g, 69% yield) as a colourless oil after purification by distillation. **B.p.:** 92 °C. **^{1}H-NMR (300 MHz, $CDCl_3$):** δ = 3.37 (d, *J* = 2.5 Hz, 2H, NCH_2), 2.17 (t, *J* = 2.5 Hz, 1H, CH), 1.11 (s, 10H, NH+CH_3).**^{13}C-NMR (75 MHz, $CDCl_3$)**: δ = 83.6, 70.6, 50.8, 32.4, 28.9. **IR (cm^{-1}):** 3285, 1457, 1367, 1328, 1303, 1139, 1057, 1012, 949, 892, 765, 733, 697, 673, 648, 623. **HRMS (ESI - ion trap) m/z:** $[M+H]^+$ **Calcd for** $C_7H_{14}N$ 112.1121, **found** 112.1122. (δ ppm = 1.1).

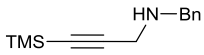
***N*-Benzylbut-2-yn-1-amine. (SI-2e).**[5]



SI-2e

Following the general procedure B, the reaction of 1-bromobut-2-yne (0.59 mL, 6.77 mmol) and benzyl amine (4.44 ml, 40.6 mmol) provided *N*-benzylbut-2-yn-1-amine (674 mg, 62% yield) **SI-2e** as a yellow oil after purification by flash column chromatography using petroleum ether/EtOAc 10:1 as eluent. **^{1}H-NMR (300 MHz, $CDCl_3$):** δ = 7.37 – 7.22 (m, 5H, Ar-H), 3.86 (s, 2H, NCH_2), 3.38 (q, *J* = 2.4 Hz, 2H, NCH_2), 1.84 (t, *J* = 2.4 Hz, 3H, CH_3). 1.41 (bs, 1H, NH). **^{13}C-NMR (75 MHz, $CDCl_3$)**: δ = 139.7, 128.4, 128.4, 127.1, 79.2, 77.2, 52.6, 37.9, 3.5. **IR (cm^{-1}):** 2918, 1495, 1452, 1331, 1128, 1098, 1028, 734, 696, 586, 466. **HRMS (ESI - ion trap) m/z:** $[M+H]^+$ **Calcd for** $C_{11}H_{14}N$ 160.1121, **found** 160.1118. (δ ppm = -1.7).

***N*-Benzyl-3-(trimethylsilyl)prop-2-yn-1-amine. (SI-2f)**

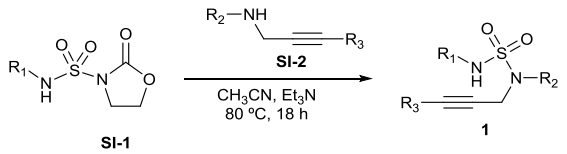


SI-2f

Following the general procedure B, the reaction of (3-bromoprop-1-yn-1-yl)trimethylsilane (2.09 mL, 10.46 mmol) and benzyl amine (6.86 mL, 62.8 mmol) provided *N*-benzyl-3-(trimethylsilyl)prop-2-yn-1-amine **SI-2f** (1.3 g, 57% yield) as yellow oil after purification by flash chromatography using petroleum ether/EtOAc 7:1 as eluent. **^{1}H-NMR (300 MHz, $CDCl_3$):** δ = 7.39 – 7.21 (m, 5H, Ar-H), 3.87 (s, 2H, CH_2), 3.44 (s, 2H, CH_2), 0.19 (s, 9H, CH_3). **^{13}C-NMR (75 MHz, $CDCl_3$)**: δ = 139.6, 128.5 (2x), 127.2, 104.4, 88.2,

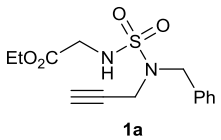
52.5, 38.5, 0.1. **IR (cm^{-1}):** 2959, 2168, 1453, 1249, 1106, 987, 837,758,732, 696, 647, 572, 443. **HRMS (ESI - ion trap) m/z:** $[M+H]^+$ **Calcd for** $C_{13}H_{20}NSi$ 218.1360, **found** 218.1357. (δ ppm = -1.2).

General Procedure C. General procedure for the synthesis of the N-alkynyl sulfamides derivatives.



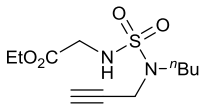
Following the general procedure described by Borghese *et al.*,[1] a mixture of the corresponding *N*-substituted-2-oxooxazolidine-3-sulfonamide **SI-1** (3.69 mmol), the corresponding propargylamine **SI-2** (4.06 mmol, 1.1 equiv.) and triethylamine (8.13 mmol, 2.2 equiv.) in acetonitrile (4.5 mL, C = 0.81 M) was heated to reflux and stirred overnight. The solvent was removed under reduced pressure, and the residue dissolved in EtOAc. The resulting solution was transferred to a separating funnel and washed with aqueous HCl 10%. The layers were separated and the organic phase was collected, dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The crude product was purified by flash column chromatography on silica gel using the eluent indicated in each case.

Ethyl (*N*-benzyl-*N*-(prop-2-yn-1-yl)sulfamoyl)glycinate. (1a).



Following the general procedure C, the reaction of ethyl ((2-oxooxazolidin-3-yl)sulfonyl)glycinate **SI-1a** (932 mg, 3.69 mmol), *N*-benzylprop-2-yn-1-amine **SI-2a** (590 mg, 4.06 mmol) and triethylamine (1.1 mL, 8.13 mmol) in CH_3CN (4.5 mL) provided ethyl (*N*-benzyl-*N*-(prop-2-yn-1-yl)sulfamoyl)glycinate (**1a**) (817 mg, 71% yield) as a white solid after purification by flash column chromatography using a mixture of petroleum ether/EtOAc (3:1 to 1:1) as eluent. **M. p.:** 58-60 °C. **^{1}H NMR (300 MHz, $CDCl_3$):** δ = 7.41 – 7.27 (m, 5H, Ar-H), 5.02 (bs, 1H, NH), 4.46 (s, 2H, NCH_2), 4.24 (q, *J* = 7.1 Hz, 2H, $OC\underline{H}_2CH_3$), 3.90 (d, *J* = 5.4 Hz, 2H, $NHC\underline{H}_2$), 3.87 (d, *J* = 2.4 Hz, 2H, NCH_2), 2.38 (t, *J* = 2.4 Hz, 1H, CH), 1.30 (t, *J* = 7.1 Hz, 3H, $OCH_2C\underline{H}_3$). **^{13}C NMR (75 MHz, $CDCl_3$)**: δ = 169.2, 135.0, 128.8, 128.7, 128.2, 74.0, 62.0, 50.5, 44.4, 36.2, 14.2. **IR (cm^{-1}):** 3321, 3274, 2992, 1736, 1495, 1446, 1415, 1377, 1331, 1246, 1212, 1143, 1086, 1059, 1009, 925, 898, 879, 836, 768, 728, 691, 666, 623, 580. **HRMS (ESI - ion trap) m/z:** $[M+H]^+$ **Calcd for** $C_{14}H_{19}N_2O_4S$ 311.1060; **Found:** 311.1060 (δ ppm = -0.0).

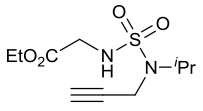
Ethyl (*N*-butyl-*N*-(prop-2-yn-1-yl)sulfamoyl)glycinate. (1b).



1b

Following the general procedure C, the reaction of ethyl ((2-oxooxazolidin-3-yl)sulfonyl)glycinate **SI-1a** (1.49 g, 5.91 mmol), *N*-(prop-2-yn-1-yl)butan-1-amine **SI-2b** (722 mg, 6.50 mmol) and triethylamine (1.81 mL, 13.0 mmol) in CH_3CN (7.3 mL) provided ethyl (*N*-butyl-*N*-(prop-2-yn-1-yl)sulfamoyl)glycinate (**1b**) (1.09 g, 67% yield) as a yellow oil after purification by flash column chromatography using a mixture of petroleum ether/EtOAc (5:1) as eluent. **^{1}H NMR (300 MHz, $CDCl_3$):** δ = 4.85 (t, *J* = 5.4 Hz, 1H, NH), 4.24 (q, *J* = 7.1 Hz, 2H, $OC\underline{H}_2CH_3$), 4.03 (d, *J* = 2.5 Hz, 2H, $NHC\underline{H}_2$), 3.84 (d, *J* = 5.4 Hz, 2H, CH_2), 3.35 – 3.24 (m, 2H, NCH_2), 2.32 (t, *J* = 2.5 Hz, 1H, CH_2), 1.65 – 1.48 (m, 2H, CH_2), 1.44 – 1.23 (m, 5H, CH_2+$OCH_2C\underline{H}_3$), 0.94 (t, *J* = 7.3 Hz, 3H, CH_3). **^{13}C NMR (75 MHz, $CDCl_3$)**: δ = 169.3, 78.0, 73.5, 61.9, 47.0, 44.3, 36.71, 3.6, 19.8, 14.1, 13.7. **IR (cm^{-1}):** 3278, 2960, 1739, 1419, 1372, 1344, 1207, 1151, 1124, 1037, 902, 848, 599. **HRMS (ASAP+ - TOF) m/z:** $[M+H]^+$ **Calcd for** $C_{11}H_{21}N_2O_4S$ 277.1262; **Found:** 277.1255 (δ ppm = -0.7).

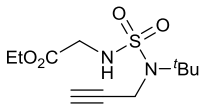
Ethyl (*N*-isopropyl-*N*-(prop-2-yn-1-yl)sulfamoyl)glycinate. (1c).



1c

Following the general procedure C, the reaction of ethyl ((2-oxooxazolidin-3-yl)sulfonyl)glycinate **SI-1a** (1.28 g, 5.07 mmol), *N*-isopropylprop-2-yn-1-amine **SI-2c** (542 mg, 5.58 mmol) and triethylamine (1.56 mL, 11.16 mmol) in CH_3CN (6.3 mL) provided ethyl (*N*-isopropyl-*N*-(prop-2-yn-1-yl)sulfamoyl)glycinate (**1c**) (809 mg , 61% yield) as a yellow oil after purification by flash column chromatography using a mixture of petroleum ether/EtOAc (7:3) as eluent. **^{1}H NMR (300 MHz, $CDCl_3$):** δ = 4.88 (bs, 1H, NH), 4.24 (q, *J* = 7.1 Hz, 2H, $OC\underline{H}_2CH_3$), 4.09 (sept, *J* = 6.8 Hz, 1H, CH), 3.95 (d, *J* = 2.5 Hz, 2H, $NHC\underline{H}_2$), 3.84 (d, *J* = 5.3 Hz, 2H, NCH_2), 2.28 (t, *J* = 2.5 Hz, 1H, CH), 1.33 – 1.24 (m, 9H, CH_3+$OCH_2C\underline{H}_3$). **^{13}C NMR (75 MHz, $CDCl_3$)**: δ = 169.3, 80.9, 72.1, 61.9, 50.5, 44.1, 32.1, 20.9, 14.1. **IR (cm^{-1}):** 3278, 2979, 1738, 1393, 1370, 1330, 1200, 1146, 1074, 1034, 907, 855, 731, 596. **HRMS (ESI - ion trap) m/z:** $[M+H]^+$ **Calcd for** $C_{10}H_{19}N_2O_4S$ 263.1060; **Found:** 263.1062 (δ ppm = 0.7).

Ethyl (*N*-(*tert*-butyl)-*N*-(prop-2-yn-1-yl)sulfamoyl)glycinate. (1d).

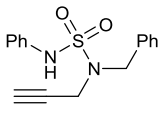


1d

Following the general procedure C, the reaction of ethyl ((2-oxooxazolidin-3-yl)sulfonyl)glycinate **SI-1a** (1.00 g, 3.96 mmol), *N*-(*tert*-butyl)prop-2-yn-1-amine **SI-2d** (485 mg, 4.36 mmol) and triethylamine (1.22 mL, 8.72 mmol) in CH_3CN (4.9 mL) provided ethyl (*N*-(*tert*-butyl)-*N*-(prop-2-yn-1-yl)sulfamoyl)glycinate (**1d**) (768 mg , 70% yield) as a white solid after purification by flash column chromatography using a mixture of petroleum ether/EtOAc (3:1) as eluent. **M.p.:** 70-72 °C. **^{1}H NMR (300 MHz, $CDCl_3$):** δ = 4.83 (bs, 1H, NH), 4.24 (q, *J* = 7.1 Hz, 2H, $OC\underline{H}_2CH_3$), 4.08 (d, *J* = 2.4 Hz, 2H, CH_2), 3.86 (d, *J* = 5.3 Hz, 2H, NCH_2), 2.30 (t, *J* = 2.4 Hz, 1H, CH), 1.51 (s, 9H, CH_3), 1.30 (t, *J*

= 7.2 Hz, 3H, $OCH_2C\underline{H}_3$). **^{13}C NMR (75 MHz, $CDCl_3$)**: δ = 169.4, 81.8, 72.0, 61.9, 59.9, 44.1, 36.04, 29.4, 14.2. **IR (cm^{-1}):** 3303, 3259, 2974, 1723, 1474, 1455, 1394, 1344, 1241, 1148, 1098, 1052, 1015, 925, 866, 808, 711, 692, 565. **HRMS (ASAP+ - TOF) m/z:** $[M+H]^+$ **Calcd for** $C_{11}H_{21}N_2O_4S$ 277.1222; **Found:** 277.1218 (δ ppm = -0.4).

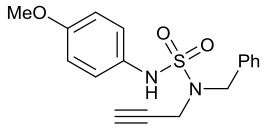
***N*-Benzyl-*N*-(prop-2-yn-1-yl)-*N'*-phenyl sulfuric diamide. (1e).**



1e

Following the general procedure C, the reaction of 2-oxo-*N*-phenyloxazolidine-3-sulfonamide **SI-1e** (2.31 g, 9.54 mmol), *N*-benzylprop-2-yn-1-amine **SI-2a** (1.52 g, 10.49 mmol) and triethylamine (2.92 mL, 20.98 mmol) in CH_3CN (11.8 mL) provided **1e** (2.05 g, 71.6 % yield) as a white solid after purification by flash column chromatography using a mixture of petroleum ether/EtOAc (7:1) as eluent. **M.p.:** 69-72 °C. **^{1}H NMR (300 MHz, $CDCl_3$):** δ = 7.42 – 7.13 (m, 10H, Ar-H), 6.45 (bs, 1H, NH), 4.39 (s, 2H, NCH_2), 3.90 (d, *J* = 2.4 Hz, 2H, CH_2), 2.35 (t, *J* = 2.4 Hz , 1H, CH). **^{13}C NMR (75 MHz, $CDCl_3$)**: δ = 137.1, 134.9, 129.4, 128.8, 128.8, 128.3, 125.0, 120.9, 77.5, 74.0, 50.9, 36.3. **IR (cm^{-1}):** 3271, 1601, 1484, 1457, 1419, 1332, 1316, 1227, 1130, 1055, 1029, 927, 896, 824, 774, 754, 736, 671, 606, 520. **HRMS (ESI - ion trap) m/z:** $[M+H]^+$ **Calcd for** $C_{16}H_{17}N_2O_4S$ 301.1005; **Found:** 301.1007 (δ ppm = 0.6).

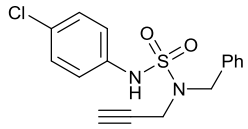
***N*-Benzyl-*N*-(prop-2-yn-1-yl)-*N'*-(*p*-methoxyphenyl)sulfuric diamide. (1f).**



1f

Following the general procedure C, the reaction of *N*-(4-methoxyphenyl)-2-oxooxazolidine-3-sulfonamide **SI-1f** (950 mg, 3.49 mmol), *N*-benzylprop-2-yn-1-amine **SI-2a** (557 mg, 3.84 mmol) and triethylamine (1.07 mL, 7.68 mmol) in CH_3CN (4.3 mL) provided **1f** (893 mg, 77% yield) as a white solid after purification by flash column chromatography using a mixture of petroleum ether/EtOAc (7:1) as eluent. **M.p.:** 102-105 °C. **^{1}H NMR (300 MHz, $CDCl_3$):** δ = 7.34 – 7.19 (m, 7H, Ar-H), 6.86 (d, *J* = 8.9 Hz, 2H, Ar-H), 6.27 (bs, 1H, NH), 4.36 (s, 2H, CH_2), 3.89 (d, *J* = 2.5 Hz, 2H, CH_2), 3.81 (s, 3H, OCH_3), 2.37 (t, *J* = 2.5 Hz, 1H, CH).**^{13}C NMR (75 MHz, $CDCl_3$)**: δ = 157.8, 135.0, 129.4, 128.7 (2x), 128.2, 125.0, 114.5, 77.9, 74.2, 55.5, 51.0, 36.3. **IR (cm^{-1}):** 3268, 1509, 1442, 1338, 1320, 1304, 1280, 1251, 1137, 1088, 1063, 1030, 950, 907, 894, 857, 809, 762, 737, 699, 680, 635. **HRMS (ESI - ion trap) m/z:** $[M+H]^+$ **Calcd for** $C_{17}H_{19}N_2O_3S$ 331.1111; **Found:** 331.1119 (δ ppm = 2.4).

***N*-Benzyl-*N*-(prop-2-yn-1-yl)-*N'*-(*p*-chlorophenyl)sulfuric diamide. (1g).**

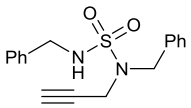


1g

Following the general procedure C, the reaction of *N*-(4-chlorophenyl)-2-oxooxazolidine-3-sulfonamide **SI-1g** (1.5 g, 5.42 mmol), *N*-benzylprop-2-yn-1-amine **SI-2a** (1.17 g, 5.96 mmol) and triethylamine (1.66 mL, 11.93 mmol) in CH_3CN (6.7 mL) provided **1g** (896 mg, 49% yield) as a white solid after purification by flash column chromatography using a mixture of petroleum ether/EtOAc

(4:1) as eluent. **M.p.:** 88-91 °C. **^{1}H NMR (300 MHz, $CDCl_3$):** δ = 7.34 – 7.22 (m, 7H, Ar-H), 7.20 – 7.14 (m, 2H, Ar-H), 6.43 (bs, 1H, NH), 4.38 (s, 2H, CH_2), 3.90 (d, *J* = 2.4 Hz, 2H, CH_2), 2.36 (t, *J* = 2.4 Hz, 1H, CH). **^{13}C NMR (75 MHz, $CDCl_3$)**: δ = 135.7, 134.7, 130.6, 129.5, 128.9, 128.8, 128.5, 122.6, 77.6, 74.5, 51.1, 36.5. **IR (cm^{-1}):** 3237, 1491, 1465, 1433, 1394, 1326, 1295, 1277, 1233, 1152, 1133, 1083, 1064, 1011, 915, 893, 844, 816, 753, 698, 658, 596, 508, 439. **HRMS (ESI - ion trap) m/z:** $[M+H]^+$ **Calcd for** $C_{16}H_{16}ClN_2O_2S$ 335.0616; **Found:** 335.0619 (δ ppm = 1.0).

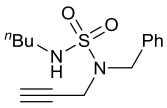
***N*-Benzyl-*N*-(prop-2-yn-1-yl)-*N'*-(benzyl)sulfuric diamide. (1h).**



1h

Following the general procedure C, the reaction of *N*-benzyl-2-oxooxazolidine-3-sulfonamide **SI-1h** (1.2 g, 4.68 mmol), *N*-benzylprop-2-yn-1-amine **SI-2a** (748 mg, 5.15 mmol) and triethylamine (1.44 mL, 10.30 mmol)) in CH_3CN (5.8 mL) provided **1h** (1.09 g, 74% yield) as a white solid after purification by flash column chromatography using a mixture of petroleum ether/EtOAc (6:1) as eluent. **M.p.:** 68-70 °C. **^{1}H NMR (300 MHz, $CDCl_3$):** δ = 7.42 – 7.28 (m, 10H, Ar-H), 4.52 (s, 2H, CH_2), 4.46 (t, *J* = 5.6 Hz, 1H, NH), 4.32 (d, *J* = 5.6 Hz, 2H, CH_2), 3.91 (d, *J* = 2.4 Hz, 2H, CH_2), 2.38 (t, *J* = 2.4 Hz, 1H, CH). **^{13}C NMR (75 MHz, $CDCl_3$)**: δ = 136.6, 135.2, 128.8, 128.8, 128.7 (2x), 128.2, 128.1, 78.0, 74.0, 50.7, 47.5, 36.2. **IR (cm^{-1}):** 3282, 1422, 1346, 1326, 1148, 1089, 1063, 1049, 1025, 923, 895, 821, 768, 751, 732, 696, 667, 651, 607, 577. **HRMS (ASAP+ - TOF) m/z:** $[M+H]^+$ **Calcd for** $C_{17}H_{19}N_2O_2S$ 315.1167; **Found:** 315.1165 (δ ppm = -0.2).

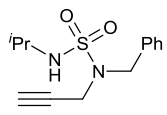
***N*-Benzyl-*N*-(prop-2-yn-1-yl)-*N'*-(butyl)sulfuric diamide. (1i).**



1i

Following the general procedure C, the reaction of *N*-butyl-2-oxooxazolidine-3-sulfonamide **SI-1i** (1.32 g, 5.94 mmol), *N*-benzylprop-2-yn-1-amine **SI-2a** (949 mg, 6.53 mmol) and triethylamine (1.82 mL, 13.07 mmol) in CH_3CN (7.3 mL) provided **1i** (1.46 mg, 88% yield) as a colourless oil after purification by flash column chromatography using a mixture of petroleum ether/EtOAc (7:1) as eluent. **^{1}H NMR (300 MHz, $CDCl_3$):** δ = 7.43 – 7.27 (m, 5H, Ar-H), 4.48 (s, 2H, CH_2), 4.16 (t, *J* = 6.3 Hz, 1H, NH), 3.88 (d, *J* = 2.4 Hz, 2H, CH_2), 3.14 (td, *J* = 7.1, 6.3 Hz, 2H, CH_2), 2.37 (t, *J* = 2.4 Hz, 1H, CH), 1.67 – 1.49 (m, 2H, CH_2), 1.49 – 1.30 (m, 2H, CH_2), 0.94 (t, *J* = 7.3 Hz, 3H, CH_3). **^{13}C NMR (75 MHz, $CDCl_3$)**: δ = 135.4, 128.7, 128.7, 128.1, 78.0, 73.7, 50.7, 43.2, 36.2, 31.81 19.9, 13.7. **IR (cm^{-1}):** 2959, 2873, 1495, 1455, 1424, 1323, 1148, 1084, 1059, 894, 766, 733, 698, 596. **HRMS (ESI - ion trap) m/z:** $[M+H]^+$ **Calcd for** $C_{14}H_{21}N_2O_2S$ 281.1318; **Found:** 281.1317 (δ ppm = -0.4).

***N*-Benzyl-*N*-(prop-2-yn-1-yl)-*N'*-(isopropyl)sulfuric diamide. (1j).**

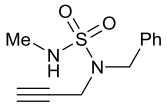


1j

Following the general procedure C, the reaction of *N*-isopropyl-2-oxooxazolidine-3-sulfonamide **SI-1j** (1.74 g, 8.36 mmol), *N*-benzylprop-2-yn-1-amine **SI-2a** (1.33 g, 9.19 mmol) and triethylamine (2.56 mL, 18.38 mmol) in CH_3CN (10.30 mL) provided **1j** (1.69 g, 72% yield) as a white solid after purification by flash

column chromatography using a mixture of petroleum ether/EtOAc (6:1) as eluent. **M.p.:** 62-65 °C. **^{1}H NMR (300 MHz, $CDCl_3$):** δ = 7.45 – 7.27 (m, 5H, Ar-H), 4.45 (s, 2H, CH_2), 4.03 (d, *J* = 8.0 Hz, 1H, NH), 3.87 (d, *J* = 2.4 Hz, 2H, CH_2), 3.66 (dsept, *J* = 8.0, 6.5 Hz, 1H, NCH), 2.37 (t, *J* = 2.4 Hz, 1H, CH), 1.26 (d, *J* = 6.5 Hz, 6H, CH_3). **^{13}C NMR (75 MHz, $CDCl_3$)**: δ = 135.4, 128.7, 128.7, 128.1, 77.9, 73.8, 50.4, 46.4, 36.1, 24.0. **IR (cm^{-1}):** 3285, 2975, 1457, 1421, 1383, 1367, 1328, 1302, 1240, 1207, 1139, 1057, 1012, 949, 927, 892, 834, 764, 734, 697, 673, 648, 623, 589. **HRMS (ESI - ion trap) m/z:** $[M+H]^+$ **Calcd for** $C_{13}H_{19}N_2O_2S$ 267.1162; **Found:** 267.1163 (δ ppm = 0.5).

***N*-Benzyl-*N*-(prop-2-yn-1-yl)-*N'*-(methyl)sulfuric diamide. (1k).**

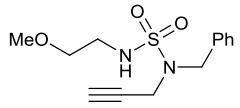


1k

Following the general procedure C, the reaction of *N*-methyl-2-oxooxazolidine-3-sulfonamide **SI-1k** (510 mg, 2.83 mmol), *N*-benzylprop-2-yn-1-amine **SI-2a** (611 mg, 3.11 mmol) and triethylamine (0.87 mL, 6.23 mmol) in CH_3CN (4.3 mL) provided **1k** (426 mg, 63% yield) as a yellow oil after purification by flash column chromatography using a mixture of petroleum ether/EtOAc (3:1) as eluent. **^{1}H NMR (300 MHz, $CDCl_3$):** δ = 7.43 – 7.27 (m, 5H, Ar-H), 4.50 (s, 2H, CH_2), 4.20 (t, *J* = 5.1 Hz, 1H, NH), 3.88 (d, *J* = 2.4 Hz, 2H, CH_2), 2.81 (d, *J* = 5.1 Hz, 3H, NCH_3), 2.38 (t, *J* = 2.5 Hz, 1H, CH). **^{13}C NMR (75 MHz, $CDCl_3$)**: δ = 135.4, 128.8, 128.7, 128.2, 77.9, 73.7, 50.7, 36.1, 29.5. **IR (cm^{-1}):** 3308, 1750, 1455, 1325, 1207, 1147, 1049, 894, 842, 771, 698, 531, 474. **HRMS (ESI - ion trap) m/z:** $[M+H]^+$ **Calcd for** $C_{11}H_{15}N_2O_2S$ 239.0849; **Found:** 239.0851 (δ ppm = 0.9).

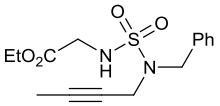
***N*-Benzyl-*N*-(prop-2-yn-1-yl)-*N'*-(2-methoxyethyl)sulfuric diamide. (1l).**

Following the general procedure C, the reaction of *N*-(2-methoxyethyl)-2-oxooxazolidine-3-sulfonamide (**SI-1l**) (800 mg, 3.57 mmol), *N*-benzylprop-2-yn-1-amine **SI-2a** (570 mg, 3.92 mmol) and triethylamine (1.09 mL, 7.85 mmol) in CH_3CN (4.3 mL) provided **1l** (842 mg, 84% yield) as a yellow oil after purification by flash column chromatography using a mixture of petroleum ether/EtOAc (5:1) as eluent. **^{1}H NMR (300 MHz, $CDCl_3$):** δ = 7.42 – 7.27 (m, 5H, Ar-H), 4.76 (bs, 1H, NH), 4.47 (s, 2H, CH_2), 3.87 (d, *J* = 2.5 Hz, 2H, CH_2), 3.53 (t, *J* = 5.1 Hz, 2H, CH_2), 3.37 (s, 3H, CH_3), 3.31 (q, *J* = 5.8 Hz, 2H, CH_2), 2.38 (t, *J* = 2.4 Hz, 1H, CH). **^{13}C NMR (75 MHz, $CDCl_3$)**: δ = 135.3, 128.8, 128.7, 128.1, 77.8, 73.9, 70.9, 58.9, 50.6, 43.1, 36.1. **IR (cm^{-1}):** 3279, 1455, 1323, 1148, 1083, 1028, 894, 731, 698, 594, 537. **HRMS (ESI - ion trap) m/z:** $[M+H]^+$ **Calcd for** $C_{13}H_{19}N_2O_3S$ 283.1111; **Found:** 283.1108 (δ ppm = -1.0).



1l

Ethyl (*N*-benzyl-*N*-(but-2-yn-1-yl)sulfamoyl)glycinate. (1m).

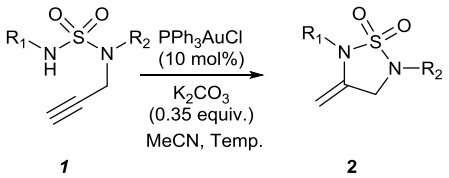


1m

Following the general procedure C, the reaction of ethyl ((2-oxooxazolidin-3-yl)sulfonyl)glycinate **SI-1a** (600 mg, 2.38 mmol), *N*-benzylbut-2-yn-1-amine **SI-2e** (417 mg, 2.62 mmol) and triethylamine (0.73 mL, 5.23 mmol) in CH_3CN (2.9 mL) provided **1m** (436 mg, 56,5% yield) as a white solid after

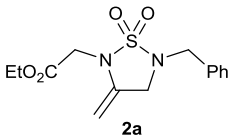
purification by flash column chromatography using a mixture of petroleum ether/EtOAc (5:1) as eluent. **M.p.:** 63-65 °C. **^{1}H NMR (300 MHz, $CDCl_3$):** δ = 7.41 – 7.27 (m, 5H, Ar-H), 4.98 (t, *J* = 5.4 Hz, 1H, NH), 4.44 (s, 2H), 4.25 (q, *J* = 7.1 Hz, 2H, $OC\underline{H}_2CH_3$), 3.91 (d, *J* = 5.4 Hz, 2H, CH_2), 3.82 (q, *J* = 2.3 Hz, 2H, CH_2), 1.87 (t, *J* = 2.4 Hz, 3H, CH_3), 1.30 (t, *J* = 7.1 Hz, 3H, $OCH_2C\underline{H}_3$). **^{13}C NMR (75 MHz, $CDCl_3$)**: δ = 169.3, 135.5, 128.7, 128.7, 128.1, 82.0, 72.9, 61.9, 50.6, 44.4, 36.8, 14.1, 3.5. **IR (cm^{-1}):** 3310, 1751, 1455, 1375, 1339, 1204, 1159, 1147, 1048, 1009, 924, 895, 841, 772, 699, 611, 530, 474. **HRMS (ESI - ion trap) m/z:** $[M+H]^+$ **Calcd for** $C_{15}H_{21}N_2O_4S$ 325.1217; **Found:** 325.1218 (δ ppm = 0.4).

General Procedure D. General procedure for the synthesis of the 5-exo-dig products.



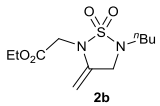
A suspension of K_2CO_3 (0.053 mmol, 0.35 equiv.) and PPh_3AuCl (0.015 mmol, 0.1 equiv.) in CH_3CN (0.76 mL, C = 0.2 M) was stirred for 15 min at room temperature, then the corresponding sulfamide **1** (0.15 mmol, 1 equiv.) was added and stirred at the temperature and time indicated in each case. The solution was concentrated under reduced pressure and the crude product was purified by flash column chromatography using the conditions indicated in each case.

Ethyl 2-(5-benzyl-3-methylene-1,1-dioxido-1,2,5-thiadiazolidin-2-yl)acetate. (2a)



Following the general procedure D, the reaction of the sulfamide **1a** (50 mg, 0.16 mmol) in the presence of K_2CO_3 (7.8 mg, 0.056 mmol) and PPh_3AuCl (8.0 mg, 0.016 mmol) in CH_3CN (0.8 mL) afforded ethyl 2-(5-benzyl-3-methylene-1,1-dioxido-1,2,5-thiadiazolidin-2-yl)acetate (**2a**) (43 mg, 86% yield) as colourless oil after purification by flash column chromatography in neutral alumina using a mixture of petroleum ether/EtOAc (7:1) as eluent. **Reaction time:** 8 h. **Temp.:** 80 °C. **^{1}H NMR (300 MHz, $CDCl_3$):** δ = 7.45 – 7.28 (m, 5H, Ar-H), 4.36 (q, *J* = 7.2 Hz, 2H, $OC\underline{H}_2CH_3$), 4.24 (s, 2H, NCH_2), 4.16 (s, 2H, NCH_2), 4.05 (dd, *J* = 3.2, 1.6 Hz, 1H, =C$\underline{H}$H), 4.01 – 3.97 (m, 1H, =CH$\underline{H}$), 3.84 (t, *J* = 1.6 Hz, 2H, =CCH_2N), 1.30 (t, *J* = 7.2 Hz, 3H, $OCH_2C\underline{H}_3$). **^{13}C NMR (75 MHz, $CDCl_3$)**: δ = 166.8, 137.5, 134.2, 129.0, 128.9, 128.5, 83.0, 62.0, 52.0, 50.2, 43.7, 14.2. **IR (cm^{-1}):** 2982, 1755, 1673, 1497, 1455, 1319, 1202, 1156, 1062, 1025, 938, 877, 790, 732, 698, 621, 595. **HRMS (ESI - ion trap) m/z:** $[M+H]^+$ **Calcd for** $C_{14}H_{19}N_2O_4S$ 311.1060; **Found:** 311.1061 (δ ppm = 0.3).

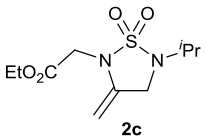
Ethyl 2-(5-butyl-3-methylene-1,1-dioxido-1,2,5-thiadiazolidin-2-yl)acetate. (2b).



2b

Following the general procedure D, the reaction of sulfamide **1b** (50 mg, 0.18 mmol) in the presence of K_2CO_3 (8.75 mg, 0.063 mmol) and PPh_3AuCl (13.43 mg, 0.027 mmol) in CH_3CN (0.9 mL) afforded ethyl 2-(5-butyl-3-methylene-1,1-dioxido-1,2,5-thiadiazolidin-2-yl)acetate (**2b**) (43 mg, 86% yield) as a colourless oil after purification by flash column chromatography in neutral alumina using a mixture of petroleum ether/EtOAc (5:1) as eluent. **Reaction time:** 7 h. **Temp.:** 80 °C. **^{1}H NMR (300 MHz, CD_3CN):** δ = 4.23 – 4.15 (q, *J* = 7.3 Hz, 2H, $OC\underline{H}_2CH_3$), 4.15 – 4.13 (m, 1H, =C<u>H</u>H), 4.12 (s, 2H, NCH_2), 4.03 (dd, *J* = 2.9, 1.8 Hz, 1H, =CH<u>H</u>), 3.98 (t, *J* = 1.8 Hz, 2H, =CCH_2N), 3.01 (t, *J* = 7.2 Hz, 2H, NCH_2), 1.66 – 1.52 (m, 2H, CH_2), 1.47 – 1.29 (m, 2H, CH_2), 1.24 (t, *J* = 7.1 Hz, 3H, $CH_2C\underline{H}_3$), 0.93 (t, *J* = 7.3 Hz, 3H, $OCH_2C\underline{H}_3$). **^{13}C NMR (75 MHz, CD_3CN)**: δ = 167.9, 138.8, 83.0, 62.4, 51.4, 48.3, 44.2, 30.0, 20.5, 14.4, 13.8. **IR (cm^{-1}):** 2960, 1757, 1673, 1317, 1200, 1156, 1064, 1023, 940, 873, 778, 717, 583. **HRMS (ESI - ion trap) m/z:** $[M+H]^+$ **Calcd for** $C_{11}H_{21}N_2O_4S$ 277.1217; **Found:** 277.1216 (δ ppm = - 0.2).

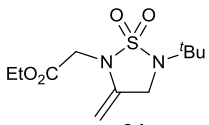
Ethyl 2-(5-isopropyl-3-methylene-1,1-dioxido-1,2,5-thiadiazolidin-2-yl)acetate. (2c).



2c

Following the general procedure D, the reaction of sulfamide **1c** (50 mg, 0.16 mmol) in the presence of K_2CO_3 (9.22 mg, 0.067 mmol) and PPh_3AuCl (9.43 mg, 0.019 mmol) in CH_3CN (0.95 mL) afforded ethyl 2-(5-isopropyl-3-methylene-1,1-dioxido-1,2,5-thiadiazolidin-2-yl)acetate (**2c**) (44 mg, 88% yield) as yellow oil after purification by flash column chromatography in silica gel using a mixture of petroleum ether/EtOAc/Et_3N (10:1:0.1) as eluent. **Reaction time:** 8 h. **Temp.:** 80 °C. **^{1}H NMR (300 MHz, $CDCl_3$):** δ = 4.23 (q, *J* = 7.1 Hz, 2H, $OC\underline{H}_2CH_3$), 4.14 – 4.04 (m, 3H, =C<u>H</u>H+NCH_2), 3.98 (t, *J* = 1.8 Hz, 2H, =CCH_2N), 3.95 (dd, *J* = 3.1, 1.8 Hz, 1H, =CH<u>H</u>), 3.74 (sept, *J* = 6.6 Hz, 1H, NC<u>H</u>), 1.29 (d, *J* = 6.6 Hz, 6H, CH_3), 1.28 (t, *J* = 7.1 Hz, 3H, $OCH_2C\underline{H}_3$). **^{13}C NMR (75 MHz, $CDCl_3$)**: δ = 166.8, 137.6, 81.9, 61.8, 49.4, 46.1, 43.5, 20.2, 14.1. **IR (cm^{-1}):** 1310, 1182, 1153, 1063, 1023, 942, 863, 806, 764, 718, 599. **HRMS (ESI - ion trap) m/z:** $[M+H]^+$ **Calcd for** $C_{13}H_{19}N_2O_4S$ 263,1066; **Found:** 263.1062 (δ ppm = 0.8).

Ethyl 2-(5-(*tert*-butyl)-3-methylene-1,1-dioxido-1,2,5-thiadiazolidin-2-yl)acetate. (2d).

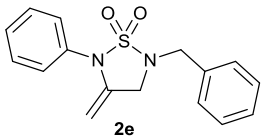


2d

Following the general procedure D, the reaction of sulfamide **1c** (50 mg, 0.18 mmol) in the presence of K_2CO_3 (8.75 mg, 0.063 mmol) and PPh_3AuCl (8.95 mg, 0.018 mmol) in CH_3CN (0.9 mL) afforded ethyl 2-(5-(*tert*-butyl)-3-methylene-1,1-dioxido-1,2,5-thiadiazolidin-2-yl)acetate (**2d**) (41 mg, 82% yield) as yellow oil after purification by flash column chromatography in silica gel using a mixture of petroleum ether/EtOAc/Et_3N (8:1:0.1) as eluent. **Reaction time:** 8 h. **Temp.:** 60 °C. **^{1}H NMR (300 MHz, CD_3CN):** δ = 4.18 (q, *J* = 7.1 Hz, 2H, $OC\underline{H}_2CH_3$), 4.10 (d, *J* = 2.2 Hz, 3H, =C<u>H</u>H+=CCH_2N),

4.07 (s, 2H, NCH_2), 3.98 (q, *J* = 2.2 Hz, 1H, =CH<u>H</u>), 1.39 (s, 9H, CH_3), 1.24 (t, *J* = 7.1 Hz, 3H, $OCH_2C\underline{H}_3$). **^{13}C NMR (75 MHz, CD_3CN)**: δ = 167.9, 137.9, 82.0, 62.4, 57.6, 46.6, 43.9, 27.4, 14.4. **IR (cm^{-1}):** 1757, 1310, 1193, 1152, 1028, 596, 582. **HRMS (ESI - ion trap) m/z:** $[M+H]^+$ **Calcd for** $C_{11}H_{21}N_2O_4S$ 277.1217; **Found:** 277.1212 (δ ppm = -1.6).

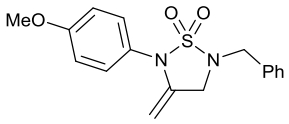
5-Benzyl-3-methylene-2-phenyl-1,2,5-thiadiazolidine 1,1-dioxide. (2e).



2e

Following the general procedure D, the reaction of sulfamide **1e** (50 mg, 0.17 mmol) in the presence of K_2CO_3 (8.05 mg, 0.058 mmol) and PPh_3AuCl (8.23 mg, 0.017 mmol) in CH_3CN (0.83 mL) afforded 5-benzyl-3-methylene-2-phenyl-1,2,5-thiadiazolidine 1,1-dioxide (**2e**) (43 mg, 86% yield) as a white solid after purification by flash column chromatography in neutral alumina using a mixture of petroleum ether/EtOAc (7:1) as eluent. **Reaction time:** 4 d. **Temp.:** 25 °C. **M. p.:** 83-85 °C. **^{1}H NMR (300 MHz, $CDCl_3$):** δ = 7.47 – 7.23 (m, 10H, Ar-H), 4.24 (s, 2H, NCH_2), 3.93 (t, *J* = 2.0 Hz, 1H, =C<u>H</u>H), 3.88 (m, 3H, =CCH_2N+=CH<u>H</u>).**^{13}C NMR (75 MHz, $CDCl_3$)**: δ = 139.4, 134.4, 133.1, 130.1, 129.4, 129.2, 129.0, 129.0, 128.5, 84.0, 52.2, 50.1. **IR (cm^{-1}):** 3030, 1671, 1621, 1490, 1456, 1320, 1167, 1121, 1041, 949, 909, 811, 779, 767, 737, 692, 566. **HRMS (ESI - ion trap) m/z:** $[M+H]^+$ **Calcd for** $C_{16}H_{17}N_2O_2S$ 301.1005; **Found:** 301.1007 (δ ppm = 0.6).

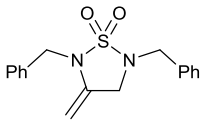
5-Benzyl-2-(4-methoxyphenyl)-3-methylene-1,2,5-thiadiazolidine 1,1-dioxide (2f).



2f

Following the general procedure D, the reaction of sulfamide **1f** (50 mg, 0.15 mmol) in the presence of K_2CO_3 (7.32 mg, 0.053 mmol) and PPh_3AuCl (7.49 mg, 0.015 mmol) in CH_3CN (0.76 mL) afforded 5-benzyl-2-(4-methoxyphenyl)-3-methylene-1,2,5-thiadiazolidine 1,1-dioxide (**2f**) (45 mg, 90% yield) as a pale yellow solid after purification by flash column chromatography in neutral alumina using a mixture of petroleum ether/EtOAc (10:1) as eluent. **Reaction time:** 18 h. **Temp.:** 60 °C. **M. p.:** 99-102 °C. **^{1}H NMR (300 MHz, $CDCl_3$):** δ = 7.51 – 7.29 (m, 7H, Ar-H), 7.05 – 6.96 (m, 2H, Ar-H), 4.31 (s, 2H, NCH_2), 3.97 (q, *J* = 1.8 Hz, 1H, =C<u>H</u>H), 3.92 (t, *J* = 1.8 Hz, 2H, =CCH_2N), 3.90 (q, *J* = 2.0 Hz, 1H, =CH<u>H</u>), 3.84 (s, 3H, OCH_3).**^{13}C NMR (75 MHz, $CDCl_3$)**: δ = 160.3, 139.6, 134.4, 130.8, 128.9, 128.9, 128.4, 124.9, 115.2, 83.5, 55.5, 52.0, 49.9. **IR (cm^{-1}):** 2936, 2837, 1896, 1684, 1646, 1606, 1509, 1458, 1441, 1369, 1330, 1299, 1218, 1155, 954, 944, 852, 829, 801, 773, 733, 700, 661, 581. **HRMS (ESI - ion trap) m/z:** $[M+H]^+$ **Calcd for** $C_{17}H_{19}N_2O_3S$ 331.1111; **Found:** 331.1110 (δ ppm = -0.3).

2,5-Dibenzyl-3-methylene-1,2,5-thiadiazolidine 1,1-dioxide. (2h).

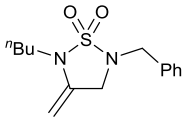


2h

Following the general procedure D, the reaction of sulfamide **1h** (50 mg, 0.16 mmol) in the presence of K_2CO_3 (7.69 mg, 0.056 mmol) and PPh_3AuCl (7.87 mg, 0.016 mmol) in CH_3CN (0.79 mL) afforded 2,5-dibenzyl-3-methylene-1,2,5-thiadiazolidine 1,1-dioxide (**2h**) (43 mg, 86% yield) as a

colourless oil after purification by flash column chromatography in neutral alumina using a mixture of petroleum ether/EtOAc (11:1) as eluent. **Reaction time:** 7 h. **Temp.:** 80 °C. **^{1}H NMR (300 MHz, $CDCl_3$):** δ = 7.45 – 7.27 (m, 10H, Ar-H), 4.64 (s, 2H, NCH_2), 4.27 (s, 2H, NCH_2), 3.95 (t, *J* = 2.2 Hz, 1H, =C<u>H</u>H), 3.94 – 3.90 (m, 1H, =CH<u>H</u>), 3.81 (t, *J* = 1.7 Hz, 2H, =CCH_2N). **^{13}C NMR (75 MHz, $CDCl_3$)**: δ = 137.1, 135.0, 134.3, 129.0, 128.9, 128.8, 128.2, 127.9, 127.4, 83.6, 51.7, 50.2, 46.8. **IR (cm^{-1}):** 3031, 1670, 1496, 1454, 1308, 1167, 1112, 1028, 940, 908, 864, 789, 715, 695, 609, 565. **HRMS (ASAP+ - TOF) m/z:** $[M+H]^+$ **Calcd for** $C_{17}H_{19}N_2O_2S$ 315.1167; **Found:** 315.1171 (δ ppm = 1.3).

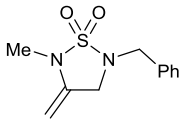
5-Benzyl-2-butyl-3-methylene-1,2,5-thiadiazolidine 1,1-dioxide. (2i).



2i

Following the general procedure D, the reaction of sulfamide **1i** (50 mg, 0.16 mmol) in the presence of K_2CO_3 (8.63 mg, 0.062 mmol) and PPh_3AuCl (13.23 mg, 0.027 mmol) in CH_3CN (0.89 mL) afforded 5-benzyl-2-butyl-3-methylene-1,2,5-thiadiazolidine 1,1-dioxide (**2i**) (43 mg, 86% yield) as a yellow solid after purification by flash column chromatography in silica gel using a mixture of petroleum ether/EtOAc/Et_3N (7:1:0.1) as eluent. **Reaction time:** 18 h. **Temp.:** 80 °C. **^{1}H NMR (300 MHz, $CDCl_3$):** δ = 7.42 – 7.27 (m, 5H, Ar-H), 4.20 (s, 2H, NCH_2), 4.09 – 4.04 (m, 1H, =CH<u>H</u>), 3.96 (dt, *J* = 2.6, 1.7 Hz, 1H, =C<u>H</u>H), 3.75 (t, *J* = 1.7 Hz, 2H, =CCH_2N), 3.49 – 3.39 (m, 2H, NCH_2), 1.78 – 1.65 (m, 2H, CH_2), 1.50 – 1.35 (m, 2H, CH_2), 0.97 (t, *J* = 7.3 Hz, 3H, CH_3). **^{13}C NMR (75 MHz, $CDCl_3$)**: δ = 137.4, 134.3, 128.8, 128.8, 128.3, 81.7, 51.5, 50.2, 42.8, 29.0, 20.2, 13.6. **IR (cm^{-1}):** 2959, 2872, 1667, 1496, 1455, 1312, 1171, 1118, 1027, 1012, 886, 783, 732, 697, 619, 592. **HRMS (**ASAP+ - TOF**) m/z:** $[M+H]^+$ **Calcd for** $C_{14}H_{21}N_2O_2S$ 281.1327; **Found:** 281.1324 (δ ppm = 1.1).

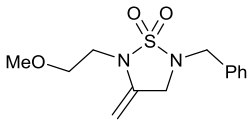
5-Benzyl-2-methyl-3-methylene-1,2,5-thiadiazolidine 1,1-dioxide. (2k).



2k

Following the general procedure D, the reaction of sulfamide **1k** (50 mg, 0.21 mmol) in the presence of K_2CO_3 (10.15 mg, 0.073 mmol) and PPh_3AuCl (10.38 mg, 0.021 mmol) in CH_3CN (1.05 mL) afforded 5-benzyl-2-methyl-3-methylene-1,2,5-thiadiazolidine 1,1-dioxide (**2k**) (41 mg, 82% yield) as a colourless oil after purification by flash column chromatography in silica gel using a mixture of petroleum ether/EtOAc/Et_3N (4:1:0.1) as eluent. **Reaction time:** 2 d. **Temp.:** 80 °C. **^{1}H NMR (300 MHz, CD_3CN):** δ = 7.47 – 7.24 (m, 5H, Ar-H), 4.21 (s, 2H, CH_2), 4.15 – 4.13 (m, 1H, =C<u>H</u>H), 4.13 – 4.09 (m, 1H, =CH<u>H</u>), 3.87 (t, *J* = 1.8 Hz, 2H, =CCH_2N), 2.90 (s, 3H, NCH_3). **^{13}C NMR (101 MHz, CD_3CN)**: δ = 139.8, 136.2, 129.7 (2x), 129.1, 83.3, 52.3, 51.1, 28.6. **IR (cm^{-1}):** 2924, 1671, 1455, 1309, 1209, 1160, 964, 879, 783, 735, 696, 618, 565, 527, 462, 417. **HRMS (ESI - ion trap) m/z:** $[M+H]^+$ **Calcd for** $C_{11}H_{15}N_2O_2S$ 239.0849; **Found:** 239.0848 (δ ppm = -0.3).

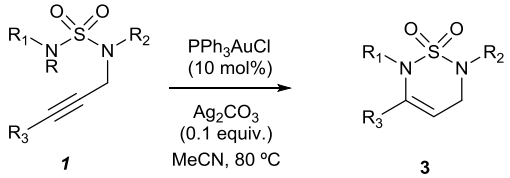
5-Benzyl-2-(2-methoxyethyl)-3-methylene-1,2,5-thiadiazolidine 1,1-dioxide. (2l).



2l

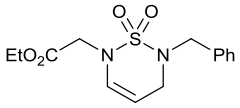
Following the general procedure D, the reaction of sulfamide **1l** (50 mg, 0.18 mmol) in the presence of K_2CO_3 (8.57 mg, 0.062 mmol) and PPh_3AuCl (13.14 mg, 0.027 mmol) in CH_3CN (0.88 mL) afforded 5-benzyl-2-(2-methoxyethyl)-3-methylene-1,2,5-thiadiazolidine 1,1-dioxide (**2l**) (36 mg, 72% yield) as a colourless oil after purification by flash column chromatography in silica gel using a mixture of petroleum ether/EtOAc/Et_3N (7:1:0.1) as eluent. **Reaction time:** 18 h. **Temp.:** 80 °C. **^{1}H NMR (300 MHz, CD_3CN):** δ = 7.38 (s, 5H, Ar-H), 4.25 – 4.21 (m, 1H, =C<u>H</u>H), 4.17 (s, 2H, CH_2), 4.07 (dd, *J* = 2.5, 1.7 Hz, 1H, =CH<u>H</u>), 3.83 (t, *J* = 1.8 Hz, 2H, =CCH_2N), 3.57 (s, 4H, 2xCH_2), 3.32 (s, 3H, OCH_3). **^{13}C NMR (101 MHz, CD_3CN)**: δ = 137.7, 134.8, 128.5, 128.4, 127.8, 81.9, 68.6, 57.8, 51.0, 50.0, 42.5. **IR (cm^{-1}):** 2927, 1669, 1497, 1455, 1311, 1253, 1202, 1168, 1110, 1028, 975, 895, 809, 781, 735, 696, 618, 580, 523, 462, 428. **HRMS (ESI - ion trap) m/z:** $[M+H]^+$ **Calcd for** $C_{13}H_{19}N_2O_3S$ 283.1116; **Found:** 283.1105 (δ ppm = -4.3).

General Procedure E. General procedure for the synthesis of the 6-endo-dig products.



A suspension of Ag_2CO_3 (0.015 mmol, 0.1 equiv.) and PPh_3AuCl (0.015 mmol, 0.1 equiv.) in CH_3CN (0.76 mL, C = 0.2 M) was stirred for 15 min at room temperature, then the corresponding sulfamide **1** (0.15 mmol, 1 equiv.) was added, heated to 80 °C and stirred for the time indicated in each case. The solution was filtered through a short pad of neutral alumina, concentrated under reduced pressure and then the crude product was purified by flash column chromatography with the eluents indicated in each case.

Ethyl 2-(6-benzyl-1,1-dioxido-5,6-dihydro-2*H*-1,2,6-thiadiazin-2-yl)acetate. (3a)

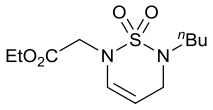


3a

Following the general procedure E, the reaction of the sulfamide **1a** (50 mg, 0.16 mmol) in the presence of Ag_2CO_3 (4.4 mg, 0.016 mmol) and PPh_3AuCl (8.0 mg, 0.016 mmol) in CH_3CN (0.8 mL) provided ethyl 2-(6-benzyl-1,1-dioxido-5,6-dihydro-2*H*-1,2,6-thiadiazin-2-yl)acetate (**3a**) (42 mg, 84% yield) as a colourless oil after purification by flash column chromatography in silica gel using a mixture of petroleum ether/EtOAc/Et_3N (7:1:0.1) as eluent. **Reaction time:** 5 h. **Temp.:** 80 °C. **^{1}H NMR (300 MHz, $CDCl_3$):** δ = 7.40 – 7.27 (m, 5H, Ar-H), 6.01 (dt, *J* = 8.4, 1.5 Hz, 1H, N<u>H</u>C=), 4.77 (dt, *J* = 8.4, 3.3 Hz, 1H, =C<u>H</u>CH_2), 4.30 – 4.21 (m, 4H, 2xCH_2), 4.20 (s, 2H, CH_2), 3.90

(dd, *J* = 3.3, 1.5 Hz, 2H, =CHC$\underline{H}_2$), 1.31 (t, *J* = 7.2 Hz, 3H, CH_3).**^{13}C NMR (75 MHz, $CDCl_3$)**: δ = 168.7, 135.2, 130.4, 128.8, 128.7, 128.0, 98.8, 61.8, 52.8, 48.9, 48.4, 14.2. **IR (cm^{-1}):** 1749, 1645, 1389, 1350, 1320, 1197, 1168, 1107, 1075, 973, 938, 895, 821, 774, 751, 697, 608. **HRMS (ESI - ion trap) m/z:** $[M+H]^+$ **Calcd for** $C_{14}H_{19}N_2O_4S$ 311.1060; **Found:** 311.1059 (δ ppm = -0.3).

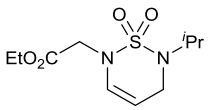
Ethyl 2-(6-butyl-1,1-dioxido-5,6-dihydro-2*H*-1,2,6-thiadiazin-2-yl)acetate. (3b).



3b

Following the general procedure E, the reaction of the sulfamide **1b** (50 mg, 0.18 mmol) in the presence of Ag_2CO_3 (4.99 mg, 0.018 mmol) and PPh_3AuCl (8.95 mg, 0.018 mmol) in CH_3CN (0.9 mL) provided **3b** (29 mg, 58% yield) as a yellow oil after purification by flash column chromatography in neutral alumina using a mixture of petroleum ether/EtOAc (7:1) as eluent. **Reaction time:** 18 h. **Temp.:** 80 °C. **^{1}H NMR (300 MHz, $CDCl_3$):** δ = 5.94 (dt, *J* = 8.4, 1.5 Hz, 1H, N$\underline{H}$C=), 4.77 (dt, *J* = 8.4, 3.3 Hz, 1H, =C$\underline{H}$$CH_2$), 4.22 (q, *J* = 7.1 Hz, 2H, OC$\underline{H}_2$$CH_3$), 4.13 (s, 2H, CH_2), 4.04 (dd, *J* = 3.3, 1.5 Hz, 2H, =CHC$\underline{H}_2$), 3.05 (t, *J* = 7.0 Hz, 2H, NC$\underline{H}_2$$CH_2$), 1.60 – 1.48 (m, 2H, CH_2), 1.45 – 1.32 (m, 2H, CH_2), 1.29 (t, *J* = 7.1 Hz, 3H, $OCH_2C\underline{H}_3$), 0.92 (t, *J* = 7.3 Hz, 3H, CH_3).**^{13}C NMR (75 MHz, $CDCl_3$)**: δ = 168.7, 130.4, 99.0, 61.6, 49.6, 48.8, 29.9, 19.8, 14.1, 13.7. **IR (cm^{-1}):** 2932, 1751, 1645, 1352, 1193, 1170, 1090, 1025, 958, 904, 867, 829, 760, 705, 567. **HRMS (ESI - ion trap) m/z:** $[M+H]^+$ **Calcd for** $C_{11}H_{21}N_2O_4S$ 277,1222; **Found:** 277.1290.

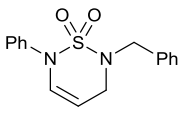
Ethyl 2-(6-isopropyl-1,1-dioxido-5,6-dihydro-2*H*-1,2,6-thiadiazin-2-yl)acetate. (3c).



3c

Following the general procedure E, the reaction of the sulfamide **1c** (50 mg, 0.19 mmol) in the presence of Ag_2CO_3 (5.26 mg, 0.019 mmol) and PPh_3AuCl (9.43 mg, 0.019 mmol) in CH_3CN (0.95 mL) provided ethyl 2-(6-isopropyl-1,1-dioxido-5,6-dihydro-2*H*-1,2,6-thiadiazin-2-yl)acetate (**3c**) (37 mg, 74% yield) as a yellow oil after purification by flash column chromatography in neutral alumina using as eluent a mixture of petroleum ether/EtOAc (7:1). **Reaction time:** 18 h. **Temp.:** 80 °C. **^{1}H-NMR (300 MHz, $CDCl_3$):** δ = 5.88 (dt, *J* = 8.4, 1.6 Hz, 1H, N$\underline{H}$C=), 4.91 (dt, *J* = 8.5, 3.3 Hz, 1H, =C$\underline{H}$$CH_2$), 4.22 (q, *J* = 7.2 Hz, 2H, OC$\underline{H}_2$$CH_3$), 4.15 – 4.04 (m, 3H, NCH, CH_2), 4.00 (dd, *J* = 3.3, 1.7 Hz, 2H, =CHC$\underline{H}_2$), 1.29 (t, *J* = 7.2 Hz, 3H, $OCH_2C\underline{H}_3$), 1.21 (d, *J* = 6.8 Hz, 6H, CH_3).**^{13}C-NMR (75 MHz, $CDCl_3$)**: δ = 168.5, 130.9, 102.7, 61.6, 51.0, 48.6, 43.4, 20.0, 14.1. **IR (cm^{-1}):** 2980, 1752, 1650, 1463, 1389, 1344, 1188, 1142, 1095, 1061, 1024, 946, 918, 860, 826, 745, 703, 571. **HRMS (ESI - ion trap) m/z:** $[M+H]^+$ **Calcd for** $C_{10}H_{19}N_2O_4S$ 263.1060, **found** 263.1062 (δ ppm = 0.7).

2-Benzyl-6-phenyl-3,6-dihydro-2*H*-1,2,6-thiadiazine 1,1-dioxide. (3e).

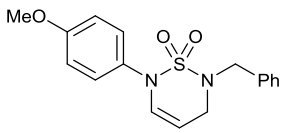


3e

Following the general procedure E, the reaction of the sulfamide **1e** (50 mg, 0.17 mmol) in the presence of Ag_2CO_3 (4.59 mg, 0.017 mmol) and PPh_3AuCl (8.23 mg, 0.017 mmol) in CH_3CN (0.83 mL) provided 2-benzyl-6-phenyl-3,6-dihydro-2*H*-1,2,6-thiadiazine 1,1-dioxide (**3e**) (37 mg, 74% yield) as a brown oil after purification

by flash column chromatography in neutral alumina using a mixture of petroleum ether/EtOAc (7:1) as eluent. **Reaction time:** 7 h. **Temp.:** 80 °C. **^{1}H-NMR (300 MHz, $CDCl_3$):** δ = 7.47 – 7.28 (m, 10H, Ar-H), 6.31 (dt, *J* = 8.4, 1.6 Hz, 1H, N<u>H</u>C=), 4.92 (dt, *J* = 8.4, 3.3 Hz, 1H, =C<u>H</u>CH_2), 4.25 (s, 2H, NCH_2), 3.97 (dd, *J* = 3.3, 1.6 Hz, 2H, =CHC<u>H</u>$_2$). **^{13}C-NMR (75 MHz, $CDCl_3$)**: δ = 139.5, 134.9, 131.2, 129.4, 128.8 (2x), 128.2, 127.4, 126.1, 99.9, 52.5, 48.2. **IR (cm^{-1}):** 2926, 1643, 1592, 1491, 1454, 1357, 1330, 1261, 1170, 1113, 1071, 1027, 892, 804, 730, 692, 564. **HRMS (ESI - ion trap) m/z:** $[M+H]^+$ **Calcd for** $C_{16}H_{17}N_2O_2S$ 301.1005, **found** 301.1006 (δ ppm = 0.2).

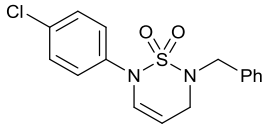
2-Benzyl-6-(4-methoxyphenyl)-3,6-dihydro-2*H*-1,2,6-thiadiazine 1,1-dioxide. (3f).



3f

Following the general procedure E, the reaction of the sulfamide **1f** (50 mg, 0.15 mmol) in the presence of Ag_2CO_3 (4.17 mg, 0.015 mmol) and PPh_3AuCl (7.49 mg, 0.015 mmol) in CH_3CN (0.76 mL) provided 2-benzyl-6-(4-methoxyphenyl)-3,6-dihydro-2*H*-1,2,6-thiadiazine 1,1-dioxide (**3f**) (39 mg, 78% yield) as a brown oil after purification by flash column chromatography in neutral alumina using a mixture of petroleum ether/EtOAc (7:1) as eluent. **Reaction time:** 18 h. **Temp.:** 80 °C. **^{1}H-NMR (300 MHz, $CDCl_3$):** δ = 7.41 – 7.33 (m, 5H, Ar-H), 7.33 – 7.29 (m, 2H, Ar-H), 6.97 – 6.90 (m, 2H, Ar-H), 6.22 (dt, *J* = 8.3, 1.5 Hz, 1H, NCH=), 4.87 (dt, *J* = 8.4, 3.3 Hz, 1H, =C<u>H</u>CH_2), 4.26 (s, 2H, CH_2), 3.95 (dd, *J* = 3.3, 1.6 Hz, 2H, =CHC<u>H</u>$_2$), 3.83 (s, 3H, CH_3). **^{13}C-NMR (75 MHz, $CDCl_3$)**: δ = 159.1, 135.0, 132.1, 131.9, 128.8, 128.8, 128.3, 128.2, 114.6, 99.3, 55.6, 52.5, 48.2. **IR (cm^{-1}):** 2956, 2933, 646, 1581, 1505, 1457, 1443, 1381, 1365, 1350, 1329, 1297, 1245, 1230, 1180, 1166, 1103, 1073, 1042, 1023, 975, 953, 924, 824, 786, 728, 697, 636, 560. **HRMS (ESI - ion trap) m/z:** $[M+H]^+$ **Calcd for** $C_{17}H_{19}N_2O_3S$ 331.1111, **found** 331.1116. (δ ppm = 1.5).

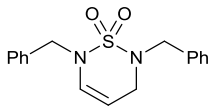
2-Benzyl-6-(4-chlorophenyl)-3,6-dihydro-2*H*-1,2,6-thiadiazine 1,1-dioxide. (3g).



3g

Following the general procedure E, the reaction of the sulfamide **1g** (50 mg, 0.15 mmol) in the presence of Ag_2CO_3 (4.12 mg, 0.015 mmol) and PPh_3AuCl (7.39 mg, 0.015 mmol) in CH_3CN (0.75 mL) provided 2-benzyl-6-(4-chlorophenyl)-3,6-dihydro-2*H*-1,2,6-thiadiazine 1,1-dioxide (**3g**) (41 mg, 82% yield) as a yellow oil after purification by flash column chromatography in neutral alumina using a mixture of petroleum ether/EtOAc (7:1) as eluent. **Reaction time:** 7 h. **Temp.:** 80 °C. **^{1}H-NMR (300 MHz, $CDCl_3$):** δ = 7.46 – 7.27 (m, 9H, Ar-H), 6.25 (dt, *J* = 8.4, 1.6 Hz, 1H, N<u>H</u>C=), 4.95 (dt, *J* = 8.4, 3.3 Hz, 1H, =C<u>H</u>CH_2), 4.23 (s, 2H, NCH_2), 3.97 (dd, *J* = 3.3, 1.6 Hz, 2H, =CHC<u>H</u>$_2$). **^{13}C-NMR (75 MHz, $CDCl_3$)**: δ = 138.0, 134.7, 133.2, 130.8, 129.5, 128.8, 128.8, 128.3, 127.3, 100.6, 52.6, 48.2. **IR (cm^{-1}):** 2924,1643, 1486, 1358, 1265, 1169, 1087, 1013, 893, 833, 769, 736, 695, 595, 554. **HRMS (ESI - ion trap) m/z:** $[M+H]^+$ **Calcd for** $C_{16}H_{16}ClN_2O_2S$ 335.0616, **found** 335.0618. (δ ppm = 0.7).

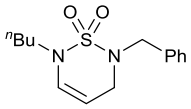
2,6-Dibenzyl-3,6-dihydro-2*H*-1,2,6-thiadiazine 1,1-dioxide. (3h).



3h

Following the general procedure E, the reaction of the sulfamide **1h** (50 mg, 0.16 mmol) in the presence of Ag_2CO_3 (4.39 mg, 0.016 mmol) and PPh_3AuCl (7.87 mg, 0.016 mmol) in CH_3CN (0.79 mL) provided 2,6-dibenzyl-3,6-dihydro-2*H*-1,2,6-thiadiazine 1,1-dioxide (**3h**) (32 mg, 64% yield) as a yellow oil after purification by flash column chromatography in neutral alumina using a mixture of petroleum ether/EtOAc (5:1) as eluent. **Reaction time:** 7 h. **Temp.:** 80 °C. **^{1}H-NMR (300 MHz, CD_3CN):** δ = 7.48 – 7.26 (m, 10H, Ar-H), 6.14 (dt, *J* = 8.4, 1.6 Hz, 1H, N<u>H</u>C=), 4.78 (d, *J* = 8.4 Hz, 1H, =C<u>H</u>CH$_2$), 4.62 (s, 2H, NCH$_2$), 4.01 (s, 2H, NCH$_2$), 3.82 (dd, *J* = 3.3, 1.6 Hz, 2H, =CHC<u>H$_2$</u>). **^{13}C-NMR (75 MHz, CD_3CN)**: δ = 137.9, 136.7, 130.9, 129.6, 129.6, 129.5, 129.3, 128.9, 128.8, 100.3, 53.1, 52.7, 49.8. **IR (cm^{-1}):** 1642, 1495, 1454, 1348, 1208, 1167, 1070, 1027, 975, 893, 821, 772, 732, 696, 606, 592. **HRMS (ESI - ion trap) m/z:** $[M+H]^+$ **Calcd for** $C_{17}H_{19}N_2O_2S$ 315.1162, **found** 315.1162. (δ ppm = 0.1).

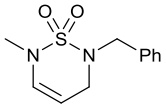
2-Benzyl-6-butyl-3,6-dihydro-2*H*-1,2,6-thiadiazine 1,1-dioxide. (3i).



3i

Following the general procedure E, the reaction of the sulfamide **1i** (50 mg, 0.18 mmol) in the presence of Ag_2CO_3 (4.92 mg, 0.018 mmol) and PPh_3AuCl (8.82 mg, 0.018 mmol) in CH_3CN (0.89 mL) provided 2-benzyl-6-butyl-3,6-dihydro-2*H*-1,2,6-thiadiazine 1,1-dioxide (**3i**) (42 mg, 84% yield) as a colourless oil after purification by flash column chromatography in neutral alumina using a mixture of petroleum ether/EtOAc (7:1) as eluent. **Reaction time:** 7 h. **Temp.:** 80 °C. **^{1}H-NMR (300 MHz, CD_3CN):** δ = 7.35 (s, 5H, Ar-H), 6.03 (dt, *J* = 8.4, 1.5 Hz, 1H, N<u>H</u>C=), 4.71 (dt, *J* = 8.4, 3.3 Hz, 1H, =C<u>H</u>CH$_2$), 4.09 (s, 2H, NCH$_2$), 3.84 (dd, *J* = 3.3, 1.5 Hz, 2H, =CHC<u>H$_2$</u>), 3.58 – 3.37 (m, 2H, NCH$_2$), 1.82 – 1.59 (m, 2H, CH$_2$), 1.56 – 1.34 (m, 2H, CH$_2$), 0.98 (t, *J* = 7.3 Hz, 3H, CH$_3$). **^{13}C-NMR (75 MHz, CD_3CN)**: δ = 135.2, 130.5, 128.7, 128.7, 128.0, 98.2, 52.3, 49.1, 48.2, 31.7, 19.7, 13.7. **IR (cm^{-1}):** 2930, 1642, 1496, 1455, 1348, 1213, 1169, 1067, 1026, 895, 821, 771, 731, 697, 606. **HRMS (ESI - ion trap) m/z:** $[M+H]^+$ **Calcd for** $C_{14}H_{21}N_2O_2S$ 281.1318, **found** 281.1316. (δ ppm = -0.8).

2-Benzyl-6-methyl-3,6-dihydro-2*H*-1,2,6-thiadiazine 1,1-dioxide. (3k).

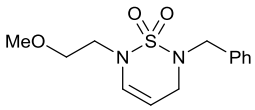


3k

Following the general procedure E, the reaction of the sulfamide **1k** (50 mg, 0.21 mmol) in the presence of Ag_2CO_3 (5.79 mg, 0.021 mmol) and PPh_3AuCl (10.38 mg, 0.021 mmol) in CH_3CN (1.05 mL) provided 2-benzyl-6-methyl-3,6-dihydro-2*H*-1,2,6-thiadiazine 1,1-dioxide (**3k**) (5.5 mg, 11% yield) as a colourless oil after purification by flash column chromatography in neutral alumina using a mixture of petroleum ether/EtOAc (4:1) as eluent. **Reaction time:** 18 h. **Temp.:** 80 °C. **^{1}H-NMR (300 MHz, CD_3CN):** δ =

7.46 – 7.23 (m, 5H, Ar-H), 6.05 (dt, *J* = 8.4, 1.6 Hz, 1H, N<u>H</u>C=), 4.80 (dt, *J* = 8.4, 3.3 Hz, 1H, =C<u>H</u>CH_2), 4.10 (s, 2H, CH_2), 3.80 (dd, *J* = 3.3, 1.6 Hz, 2H, =CHC<u>H_2</u>), 3.07 (s, 3H, CH_3). **^{13}C-NMR (101 MHz, CD_3CN)**: δ = 135.6, 131.8, 128.4, 128.3, 127.6, 99.2, 52.0, 48.5, 35.1. **IR (cm^{-1}):** 2925, 1645, 1496, 1455, 1382, 1347, 1273, 1156, 1096, 1062, 1029, 1001, 947, 895, 857, 818, 774, 734, 697, 674, 607, 545, 529, 500, 465. **HRMS (ESI - ion trap) m/z:** $[M+H]^+$ **Calcd for** $C_{11}H_{15}N_2O_2S$ 239.0849, **found** 239.0842. (δ ppm = -2.8).

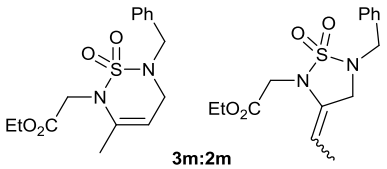
2-Benzyl-6-(2-methoxyethyl)-3,6-dihydro-2*H*-1,2,6-thiadiazine 1,1-dioxide. (3l).



3l

Following the general procedure E, the reaction of the sulfamide **1l** (50 mg, 0.18 mmol) in the presence of Ag_2CO_3 (4.88 mg, 0.018 mmol) and PPh_3AuCl (8.76 mg, 0.018 mmol) in CH_3CN (0.88 mL) provided 2-benzyl-6-(2-methoxyethyl)-3,6-dihydro-2*H*-1,2,6-thiadiazine 1,1-dioxide (**3l**) (39 mg, 78% yield) as a colourless oil after purification by flash column chromatography in silica gel using a mixture of petroleum ether/EtOAc/Et_3N (6:1:0.1) as eluent. **Reaction time:** 18 h. **Temp.:** 80 °C. **^{1}H-NMR (300 MHz, CD_3CN):** δ = 7.41 – 7.27 (m, 5H, Ar-H), 6.14 (dt, *J* = 8.4, 1.5 Hz, 1H, N<u>H</u>C=), 4.66 (dt, *J* = 8.4, 3.3 Hz, 1H, =C<u>H</u>CH_2), 4.09 (s, 2H, CH_2), 3.84 (dd, *J* = 3.3, 1.6 Hz, 2H, =CHC<u>H_2</u>), 3.65 -3.62 (m, 4H, 2xCH_2), 3.40 (s, 3H, OCH_3). **^{13}C-NMR (101 MHz, CD_3CN)**: δ = 135.1, 131.6, 128.8, 128.7, 128.1, 97.5, 71.9, 59.0, 52.2, 48.8, 48.2. **IR (cm^{-1}):** 2926, 1642, 1455, 1348, 1168, 1113, 894, 771, 733, 696, 606, 542, 493. **HRMS (ESI - ion trap) m/z:** $[M+H]^+$ **Calcd for** $C_{13}H_{19}N_2O_3S$ 283.111, **found** 283.1109. (δ ppm = -0.7).

Ethyl 2-(6-benzyl-3-methyl-1,1-dioxido-5,6-dihydro-2*H*-1,2,6-thiadiazin-2-yl)acetate and ethyl 2-(5-benzyl-3-ethylidene-1,1-dioxido-1,2,5-thiadiazolidin-2-yl)acetate mixture 90:10 (3m:2m).

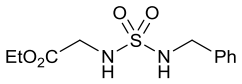


3m:2m
90:10

Following the general procedure E, the reaction of the sulfamide **1m** (50 mg, 0.15 mmol) in the presence of Ag_2CO_3 (4.25 mg, 0.015 mmol) and PPh_3AuCl (7.63 mg, 0.015 mmol) in CH_3CN (0.77 mL) provided a mixture of ethyl 2-(6-benzyl-3-methyl-1,1-dioxido-5,6-dihydro-2*H*-1,2,6-thiadiazin-2-yl)acetate (**3m**) and ethyl 2-(5-benzyl-3-ethylidene-1,1-dioxido-1,2,5-thiadiazolidin-2-yl)acetate (**2m**) (90:10), which was inseparable by flash column chromatography (38 mg, 76% yield). **Reaction time:** 18 h. **Temp.:** 80 °C. **^{1}H-NMR (300 MHz, CD_3CN):** δ =7.98 – 7.47 (m, 0.5H, Ar-H (**2m**)), 7.49 – 6.87 (m, 4.5H, Ar-H (**3m**)), 4.74 (qt, *J* = 7.3, 1.7 Hz, 0.1H, =C<u>H</u>CH_3 (**2m**)), 4.72 – 4.67 (m, 0.9H, =C<u>H</u>CH_2 (**3m**)), 4.35 (s, 1.8H, CH_2 (**3m**)), 4.26 (s, 0.2H (**2m**)), 4.21 (q, *J* = 7.3 Hz, 2.2H, OC<u>H_2</u>CH_3(**3m**)+OC<u>H_2</u>CH_3 (**2m**)+CH_2 (**2m**)), 4.14 (s, 1.8H, CH_2 (**3m**)), 3.78 (t, *J* = 1.8 Hz, 0.2H, =CCH_2N (**2m**)), 3.74 (dd, *J* = 3.4, 1.8 Hz, 1.8H, =CCH_2N (**3m**)), 1.89 (td, *J* = 1.8, 1.2 Hz, 2.7H, CH_3 (**3m**)), 1.62 (dt, *J* = 7.3, 1.8 Hz, 0.3H, CH_3 (**2m**)), 1.26 (t, *J* = 7.1 Hz, 3H, OCH_2C<u>H_3</u>(**3m**)+OCH_2C<u>H_3</u> (**2m**)). **^{13}C-NMR (75 MHz, CD_3CN)**: δ = 170.5, 137.09, 133.2,

129.6, 129.5, 128.8, 98.8, 62.4, 53.4, 49.1, 46.9, 20.0, 14.4. (only the signals for the major product are shown).

Ethyl (*N*-benzylsulfamoyl)glycinate. (4).



4

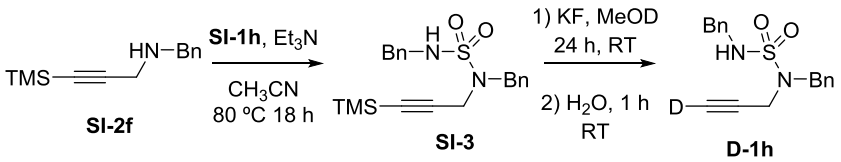
A solution of ethyl (*N*-benzyl-*N*-(prop-2-yn-1-yl)sulfamoyl)glycinate, **1a**, (25 mg, 0.081 mmol) and $AgSbF_6$ (2.77 mg, 8.05 µmol) in CH_3CN (0.4 mL) was stirred for 18 h at 80 °C. The solution was filtered through a short pad of silica and concentrated. The crude product was chromatographed on silica gel using petroleum Ether/EtOAc (5:1) as eluent to provide ethyl (*N*-benzylsulfamoyl)glycinate (18 mg, 82% yield) as yellow oil. **^{1}H-NMR (300 MHz, $CDCl_3$):** δ = 7.34 (m, 5H, Ar-H), 4.84 (bs, 1H, NH), 4.57 (bs, 1H, NH), 4.29 – 4.15 (m, $OC\underline{H}_2CH_3$+CH_2), 3.80 (d, *J* = 4.6 Hz, 2H, CH_2), 1.28 (t, *J* = 7.2 Hz, 3H, $OCH_2C\underline{H}_3$). **^{13}C-NMR (101 MHz, $CDCl_3$)**: δ = 169.6, 136.5, 128.8, 128.1, 62.0, 47.4, 44.5, 14.2. **HRMS (ESI - ion trap) m/z:** $[M+H]^+$ **Calcd for** $C_{11}H_{17}N_2O_4S$ 273.0904, **found** 273.0907. (δ ppm = 1.3).

(3-(Benzyl(*N*-benzylsulfamoyl)amino)prop-1-yn-1-yl)((2-biphenyl)di-*tert*-butylphosphine)gold. (5).

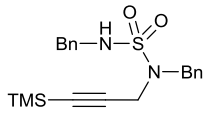
N-Benzyl-*N*-(prop-2-yn-1-yl)-*N*'-(benzyl)sulfuric diamide (**1h**) (43.5 mg, 0.14 mmol, 1.47 equiv.) was dissolved in CH_2Cl_2 (8.8 mL) and triethylamine (4.4 mL) and stirred for 5 min. Then, JohnPhosAuCl (50 mg, 0,09 mmol, 1 equiv.) was added and the resulting solution was stirred overnight. Next, the solvent was removed under reduced pressure and the residue washed with pentane. The crude product was purified by flash column chromatography using petroleum ether/EtOAc/Et_3N (4:1:0.1) as eluent to provide **5** (63 mg, 83% yield) as a white solid. **M.p.:** 148-152 °C. **^{1}H-NMR (300 MHz, $CDCl_3$):** δ = 7.89 – 7.78 (m, 1H, Ar-H), 7.55 – 7.39 (m, 6H, Ar-H), 7.39 – 7.17 (m, 10H, Ar-H), 7.04 (dd, *J* = 8.1, 1.3 Hz, 2H, Ar-H), 5.26 (t, *J* = 6.7 Hz, 1H, NH), 4.57 (s, 2H, CH_2), 4.45 (d, *J* = 6.7 Hz, 2H, CH_2), 3.91 (d, *J* = 1.5 Hz, 2H, CH_2), 1.39 (s, 9H, CH_3), 1.34 (s, 9H, CH_3). **^{13}C-NMR (75 MHz, $CDCl_3$)**: δ = 150.1 (d, ^2J (^{13}C-^{31}P) = 15.1 Hz), 142.4 (d, ^3J (^{13}C-^{31}P) = 5.9 Hz), 137.9, 136.6, 134.3 (d, ^4J (^{13}C-^{31}P) = 1.1 Hz), 133.1 (d, ^3J (^{13}C-^{31}P) = 7.3 Hz), 130.3 (d, ^3J (^{13}C-^{31}P) = 7.3 Hz), 129.7, 129.2, 128.9, 128.7, 128.53, 128.49, 128.2, 128.1, 127.7, 127.4, 127.0 (d, ^1J (^{13}C-^{31}P) = 40.3 Hz), 126.7, (d, ^3J (^{13}C-^{31}P) = 2.5 Hz), 94.4 (d, ^2J (^{13}C-^{31}P) = 22.9 Hz), 51.0, 47.3, 38.1 (d, ^4J (^{13}C-^{31}P) = 2.3 Hz), 37.4 (d, ^1J (^{13}C-^{31}P) = 22.6 Hz), 31.0 (d, ^2J (^{13}C-^{31}P) = 7.0 Hz). **^{31}P-NMR (121 MHz, $CDCl_3$):** δ = 63.86. **IR (cm^{-1}):** 3254, 2944, 1495, 1454, 1350, 1158, 1111, 1070, 1028, 979, 912, 892, 808, 778, 748, 733, 696, 613, 525 477, 418.

HRMS (ESI - ion trap) m/z: $[M+H]^+$ **Calcd for** $C_{37}H_{45}AUN_2O_2PS$ 809.2599, **found** 809.2590. (δ ppm = -1.2).

Synthesis of *N*-benzyl-*N*-(prop-2-yn-1-yl-3*d*-)-*N'*-(benzyl)sulfuric diamide (**D-1h**).



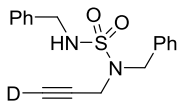
***N*-Benzyl-*N*-(prop-2-yn-1-yl-3-trimethylsilyl-)-*N'*-(benzyl)sulfuric diamide. (SI-3).**



SI-3

Following the general procedure B, the *N*-benzyl-2-oxooxazolidine-3-sulfonamide **SI-1h** (1.5 g, 5.85 mmol), *N*-benzyl-3-(trimethylsilyl)prop-2-yn-1-amine **SI-2f** (1.20 mL, 6,44 mmol) and triethylamine (1.79 mL, 12.88 mmol) in CH_3CN (7.2 mL) provided **SI-3** (1.73 g, 76% yield) as a pale orange solid after purification by flash column chromatography using a mixture of petroleum ether/EtOAc (5:1) as eluent. **M.p.:** 57-60 °C. **^{1}H NMR (300 MHz, $CDCl_3$):** δ = 7.45 – 7.28 (m, 10H, Ar-H), 4.51 (m, 3H, NH+CH_2), 4.33 (d, *J* = 6.2 Hz, 2H, CH_2), 3.92 (s, 2H, CH_2), 0.14 (s, 9H, CH_3). **^{13}C NMR (75 MHz, $CDCl_3$)**: δ = 136.90, 135.52, 128.94, 128.89, 128.86 (2x), 128.24, 128.15, 99.79, 91.49, 50.94, 47.58, 37.52, -0.11. **IR (cm^{-1}):** 3259, 1495, 1457, 1333, 1254, 1144, 1086, 1064, 1028, 1000, 942, 918, 887, 838, 761, 734, 696, 645, 614, 594, 549, 526, 459. **HRMS (ESI – ion trap) m/z:** $[M+H]^+$ **Calcd for** $C_{20}H_{27}N_2O_2SSi$ 387.1557; **Found:** 387.1554 (δ ppm = -0.8).

***N*-Benzyl-*N*-(prop-2-yn-1-yl-3*d*-)-*N'*-(benzyl)sulfuric diamide. (D-1h).**

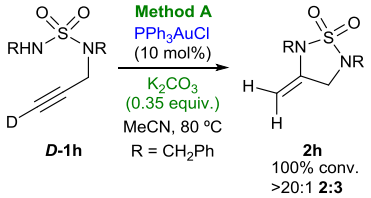


D-1h

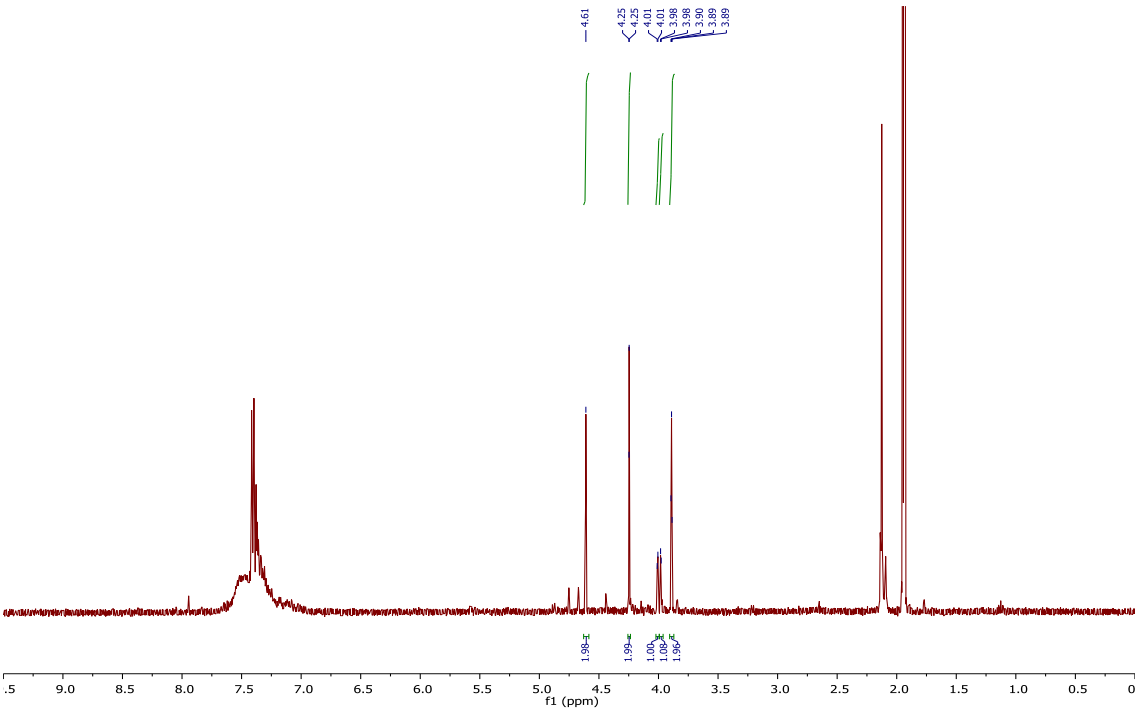
A solution of potassium fluoride (94 mg, 1.617 mmol) in MeOD (1.997 mL) was added dropwise to a solution of *N*-benzyl-*N*-(prop-2-yn-1-yl-3-trimethylsilyl-)-*N'*-(benzyl)sulfuric diamide (**SI-3**) (250 mg, 0,647 mmol) in MeOD (1.5 mL) and stirred at 25 °C for 18 h. Afterwards, an additional portion of KF (18.79, 0.323 mmol) dissolved in the minimum amount of MeOD was added and stirred for 3 h. The solution was filtered through a short pad of silica and concentrated. The residue was dissolved in CH_2Cl_2, water was added and then the mixture was stirred for 1 hour. Next, the phases were separated, and the organic phase was dried over anhydrous Na_2SO_4, filtered and concentrated. The crude was purified by flash column chromatography using petroleum ether/EtOAc 5:1 as eluent to provide **D-1h** as a white solid (183 mg, 90% yield, 95%-d). **M.p.:** 67-69 °C. **^{1}H-NMR (300 MHz, $CDCl_3$):** δ = 7.45 – 7.31 (m, 10H, Ar-H), 4.52 (s, 2H, CH_2), 4.45 (t, *J* = 6.1 Hz, 1H, NH), 4.32 (d, *J* = 6.1 Hz, 2H, CH_2), 3.91 (s, 2H, CH_2), 2.38 (t, *J* = 2.4 Hz, 0.05H, CH). **^{13}C-NMR (101 MHz, $CDCl_3$)**: δ = 136.6, 135.2, 128.8, 128.8, 128.7 (2x), 128.2, 128.1, 50.7, 47.5, 36.2. ($\underline{C}_{sp}$-D and $\underline{C}_{sp}$ C_{sp}-D were not detected due to the multiplicity leading to low intensity signals.) **IR (cm^{-}**

[1]): 3275, 2584, 1456, 1422, 1326, 1148, 1089, 1063, 892, 821, 768, 731, 696, 607, 576, 545, 523, 505, 456. **HRMS (ESI - ion trap) m/z:** $[M+H]^+$ **Calcd for** $C_{17}H_{18}DN_2O_2S$ 316.1230, **found** 316.1226. (δ ppm = -1.2).

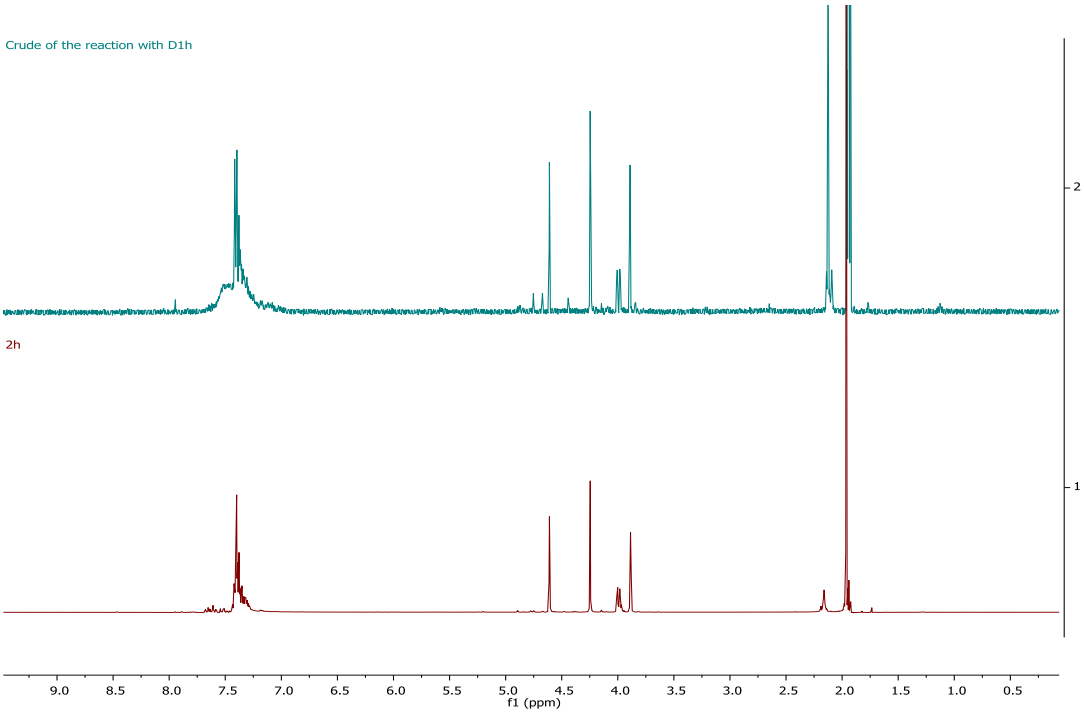
4. ^{1}H NMR Spectra of the Crude of the Reactions with D-1h.

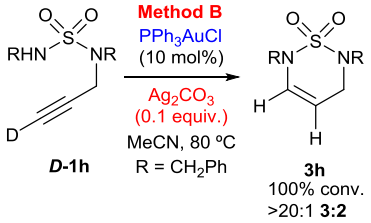


^{1}H NMR, 300 MHz, CD_3CN, Crude of the reaction with **D-1h**

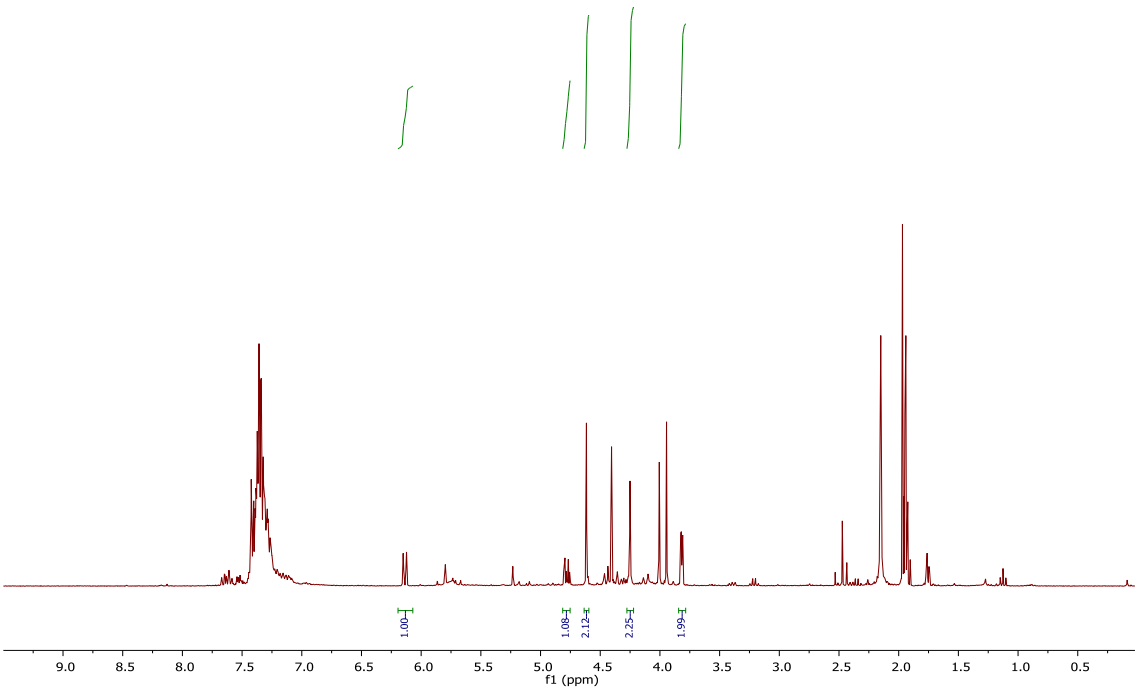


^{1}H NMR, 300 MHz, CD_3CN, Crude of the reaction with **D-1h** vs **2h**

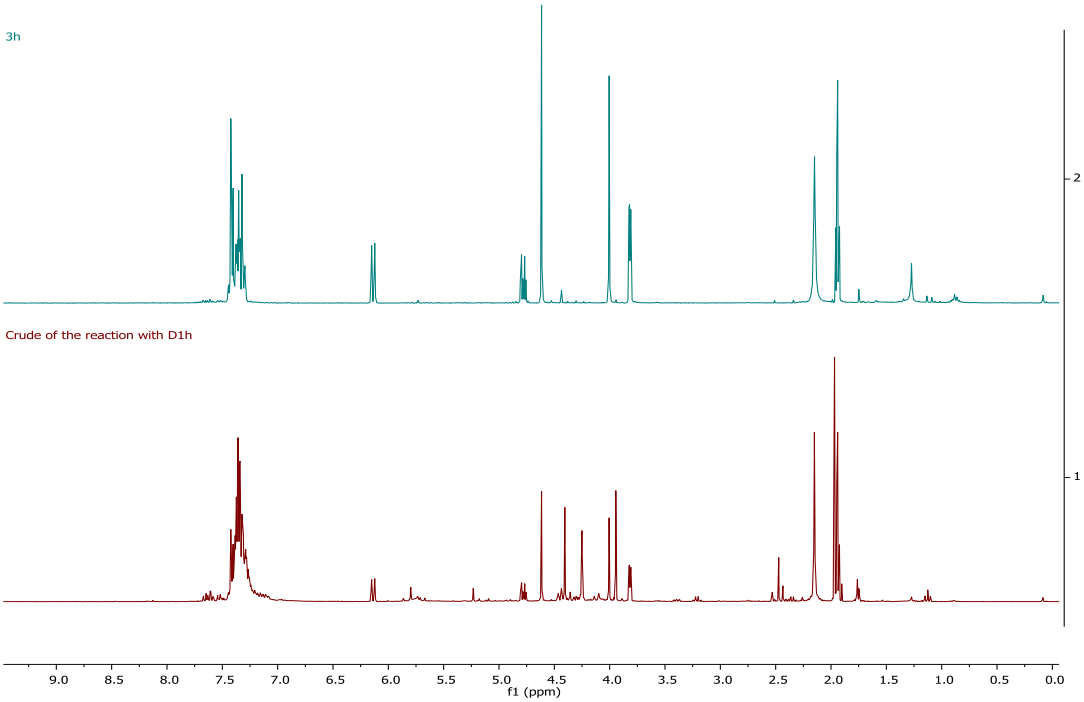




^{1}H NMR, 300 MHz, CD_3CN. Crude of the reaction with **D-1h**

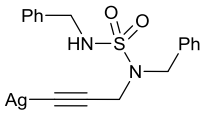


^{1}H NMR, 300 MHz, CD_3CN, **3h** vs Crude of the reaction with **D-1h**



5. *Sylver Acetylide Control Experiments.*

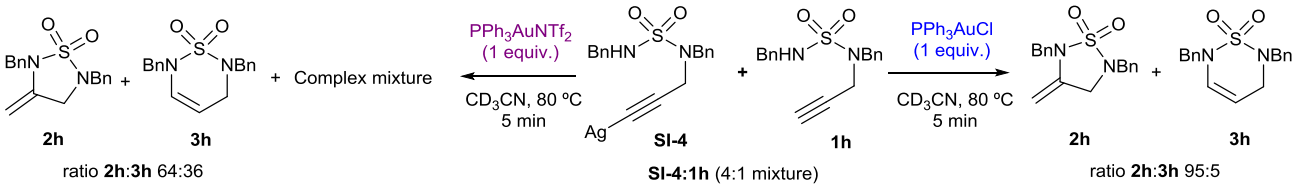
Preparation of (3-(benzyl(*N*-benzylsulfamoyl)amino)prop-1-yn-1-yl)silver. (SI-4).



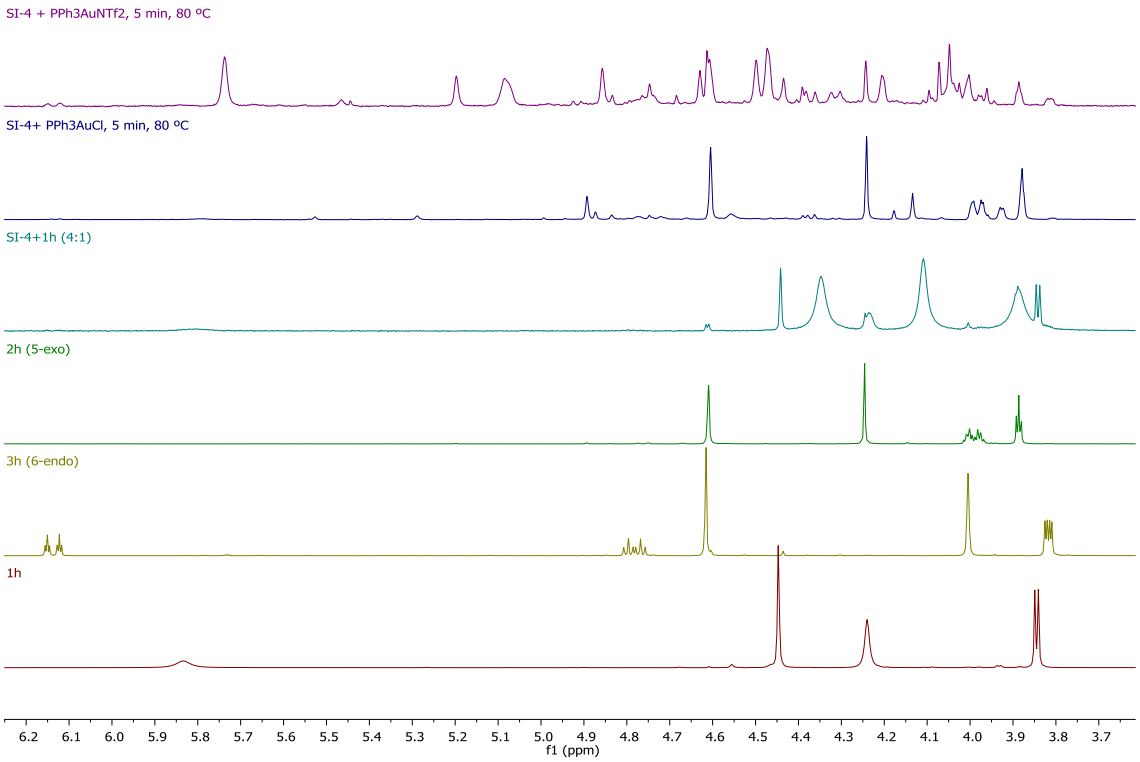
SI-4

Following the general procedure for the synthesis of silver acetylides described by Scheiber,[6] a solution of silver nitrate (130 mg, 0.76 mmol) in EtOH/$NH_{3(aq)}$ (1.06 mL/10.6 mL) was added to a solution of **1h** (200 mg, 0.64 mmol) in EtOH (2.0 mL). Upon completion of the addition, the formation of a sticky solid is observed. The solid was collected by filtration and washed with cold water and then with EtOH. After drying under high vacuum, the initially formed white sticky solid turned to an orange powder, which was determined to be a 4:1 mixture of **SI-4**:**1h** by ^{1}H NMR analysis. **SI-4** is highly unstable in solution (silver mirror observed within minutes), so this 4:1 mixture was used immediately in the control experiments shown below. **HRMS (ESI - ion trap) m/z:** $[M+H]^+$ **Calcd for** $C_{17}H_{18}AgN_2O_4S$ 421.0134; **Found:** 421.0127 (δ ppm = -1.6).

Control experiments with silver acetylide:



^{1}H NMR, 300 MHz, CD_3CN.

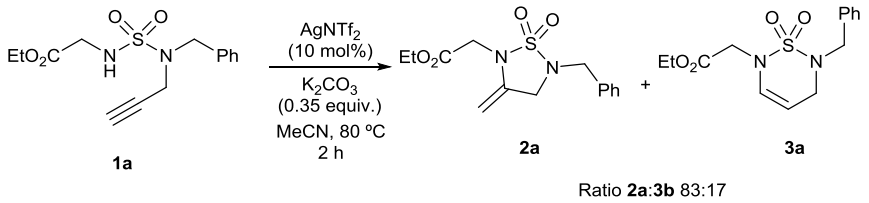


The 4:1 mixture of **SI-4:1h** produces **2h** as the major product, therefore **SI-4** was discounted as a possible intermediate towards **3h**.

Silver reactions (without gold):

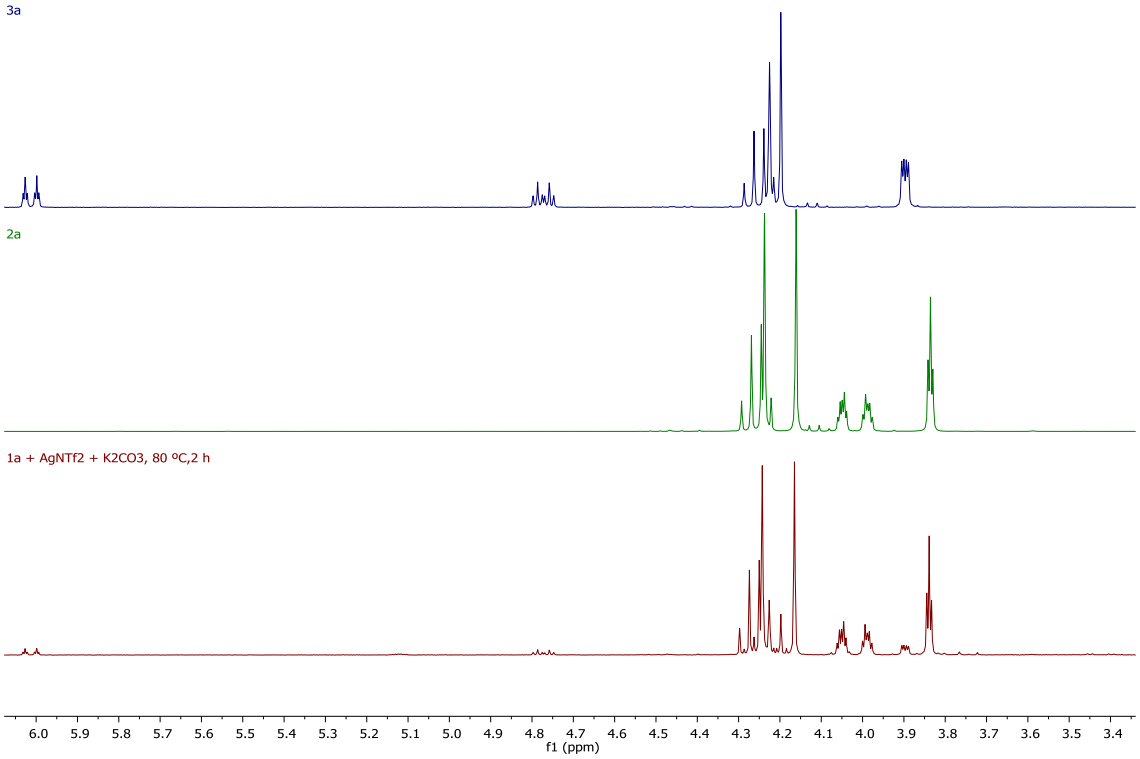
When only Ag_2CO_3 is used (without gold), no reaction is observed (Entry 8, Table 1 of article).

When a more cationic $AgNTf_2$ is used in the absence of gold, **2a** is once again the major product:



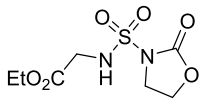
Ratio **2a**:**3b** 83:17

^{1}H NMR, 300 MHz, CD_3CN.



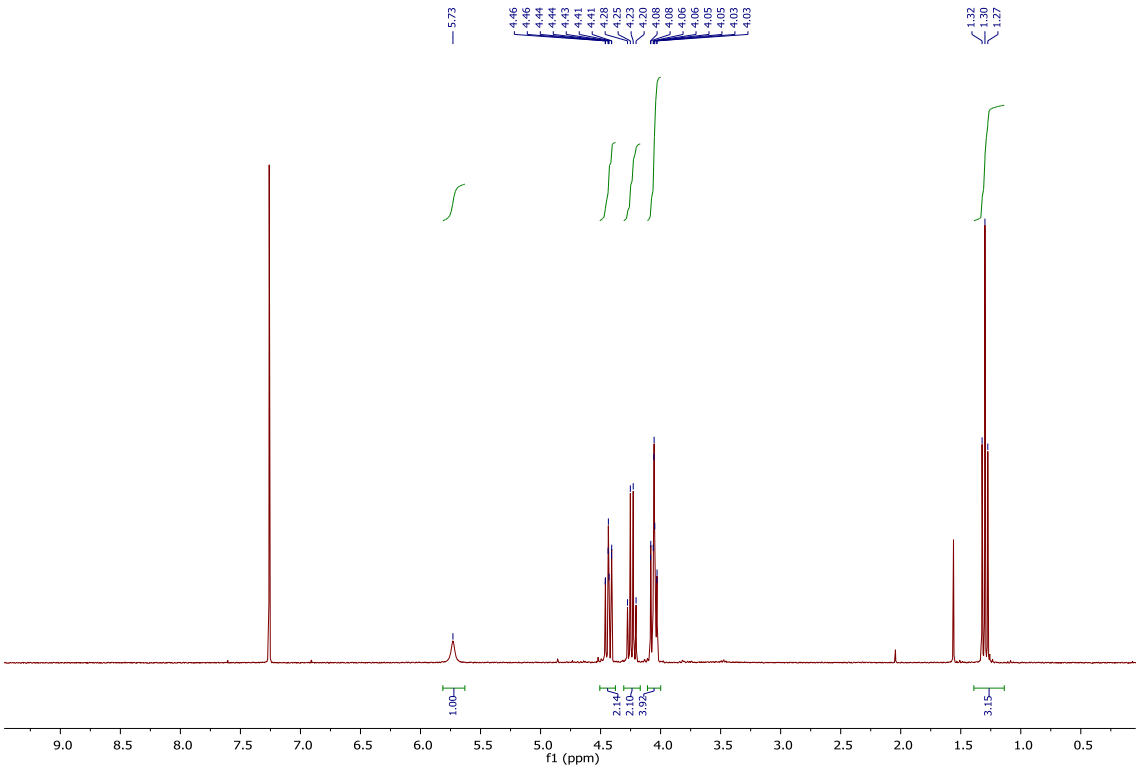
The combined results on pages SI-30-31 seem to indicate that the silver acetylides **SI-4** favour the formation of the 5-exo product **2** rather than **3.** Therefore, they are consistent with the hypothesis of the gold acetylide **E** as the intermediate rather than the corresponding silver acetylide **SI-4**.

6. *NMR Spectra*

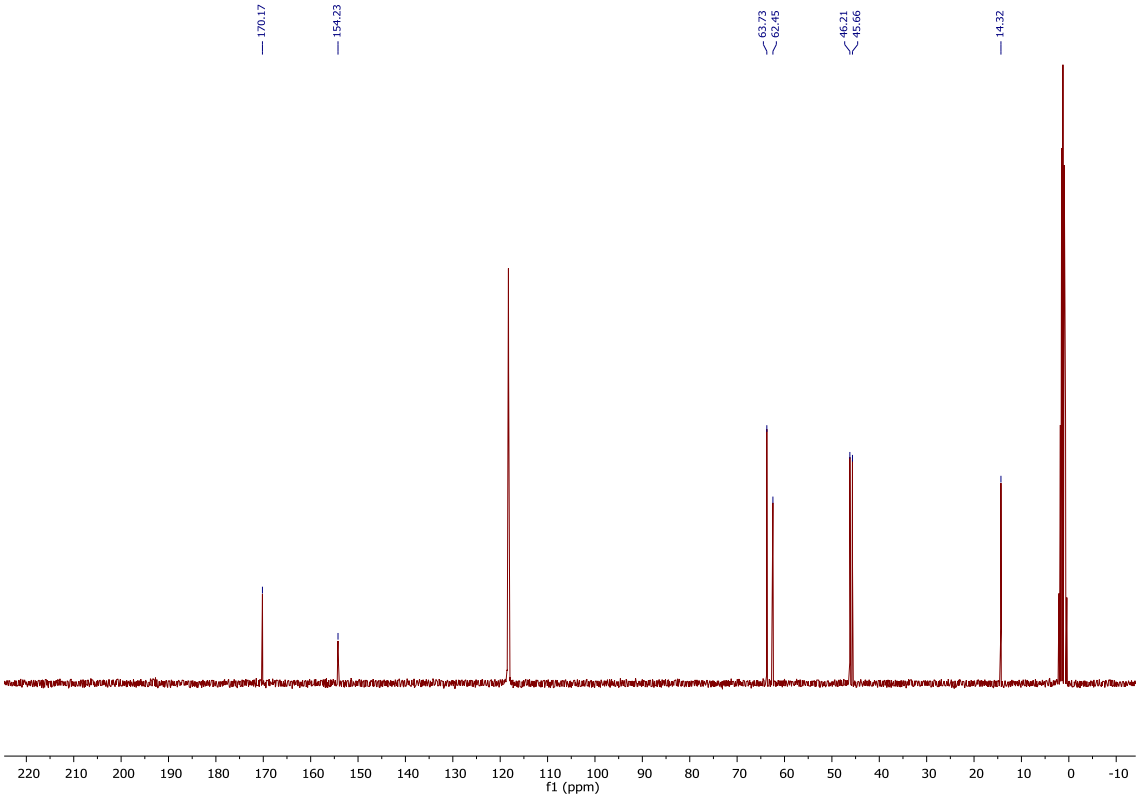


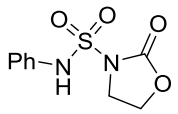
SI-1a

300 MHz, ^{1}H NMR, $CDCl_3$



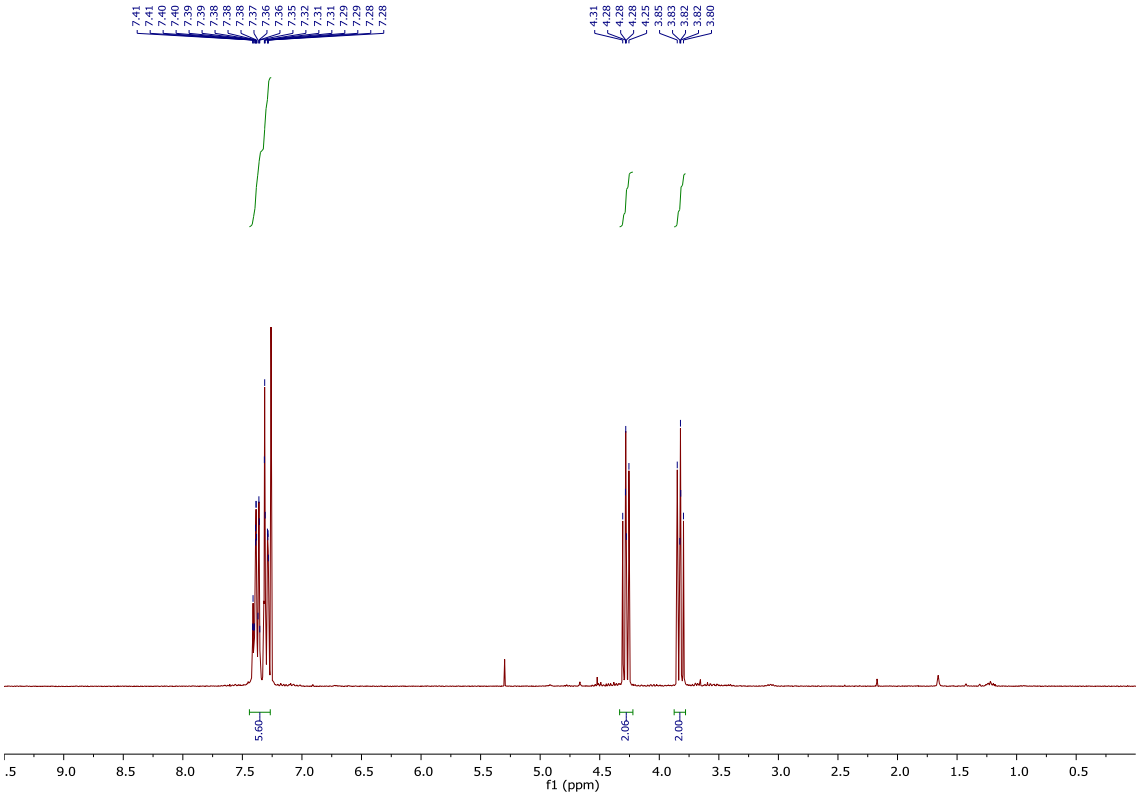
75 MHz, ^{13}C NMR, CD_3CN



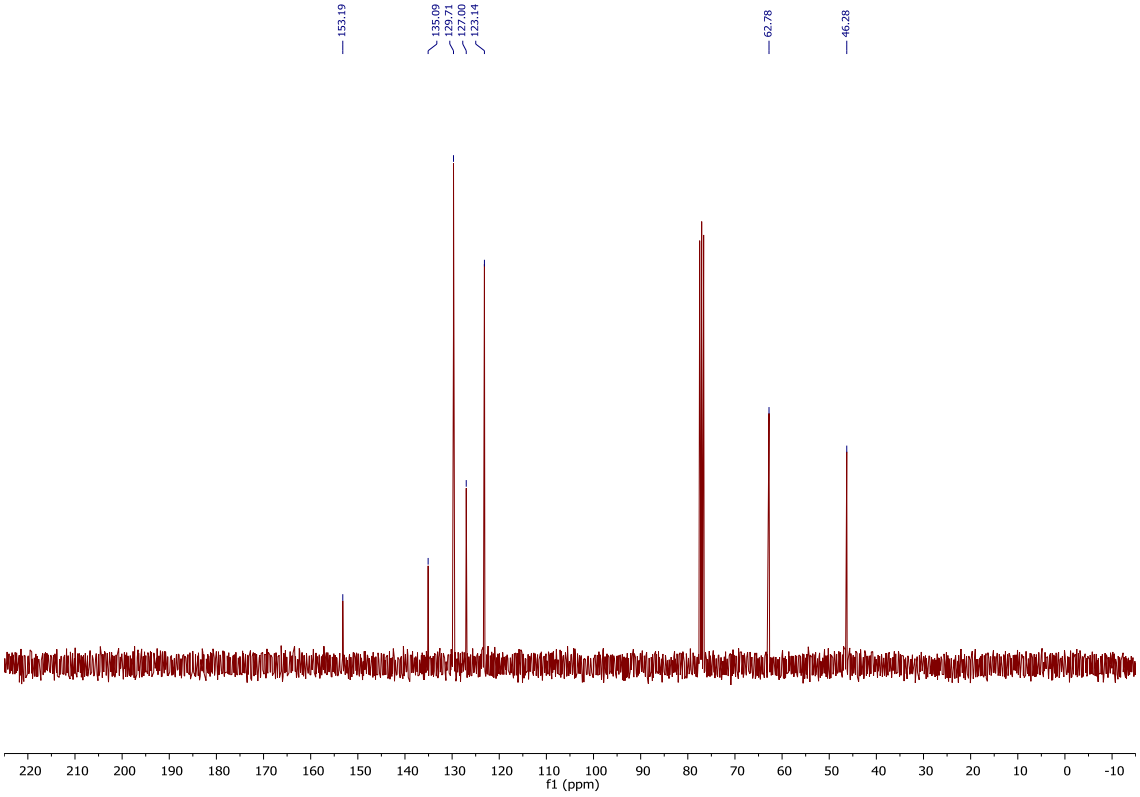


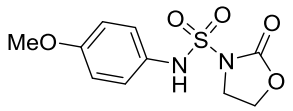
SI-1e

300 MHz, ^{1}H NMR, $CDCl_3$



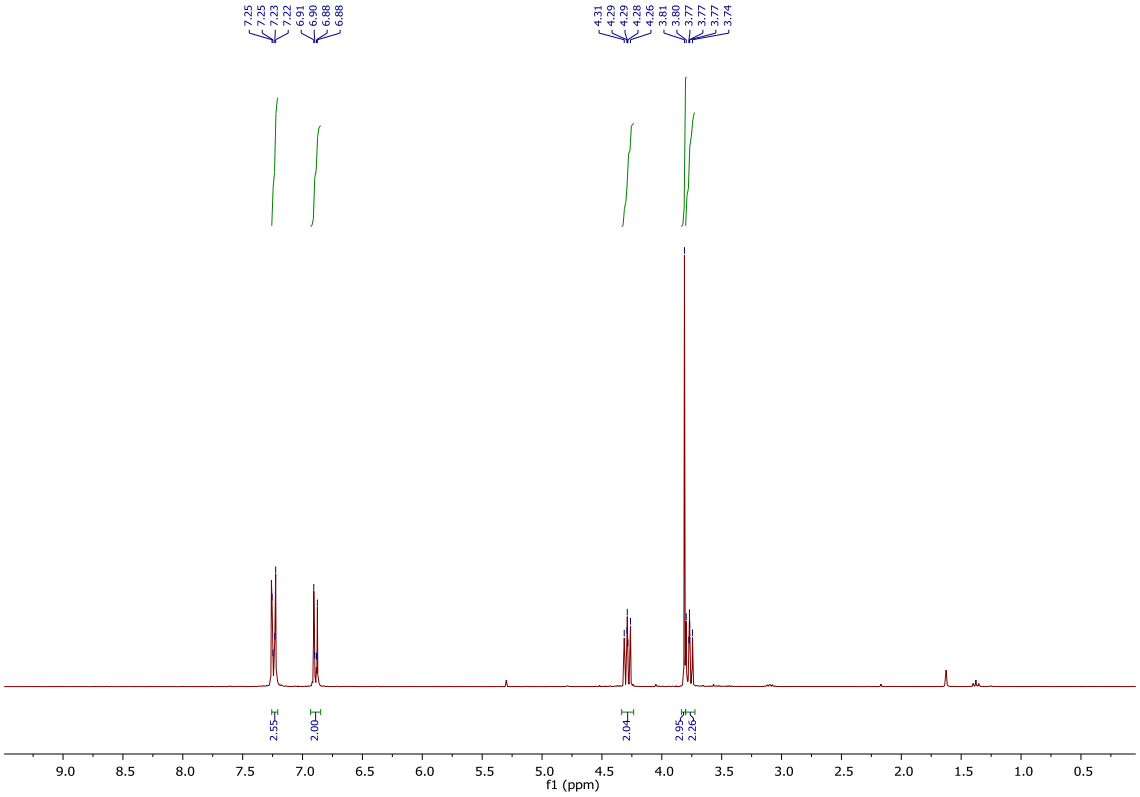
75 MHz, ^{13}C NMR, $CDCl_3$



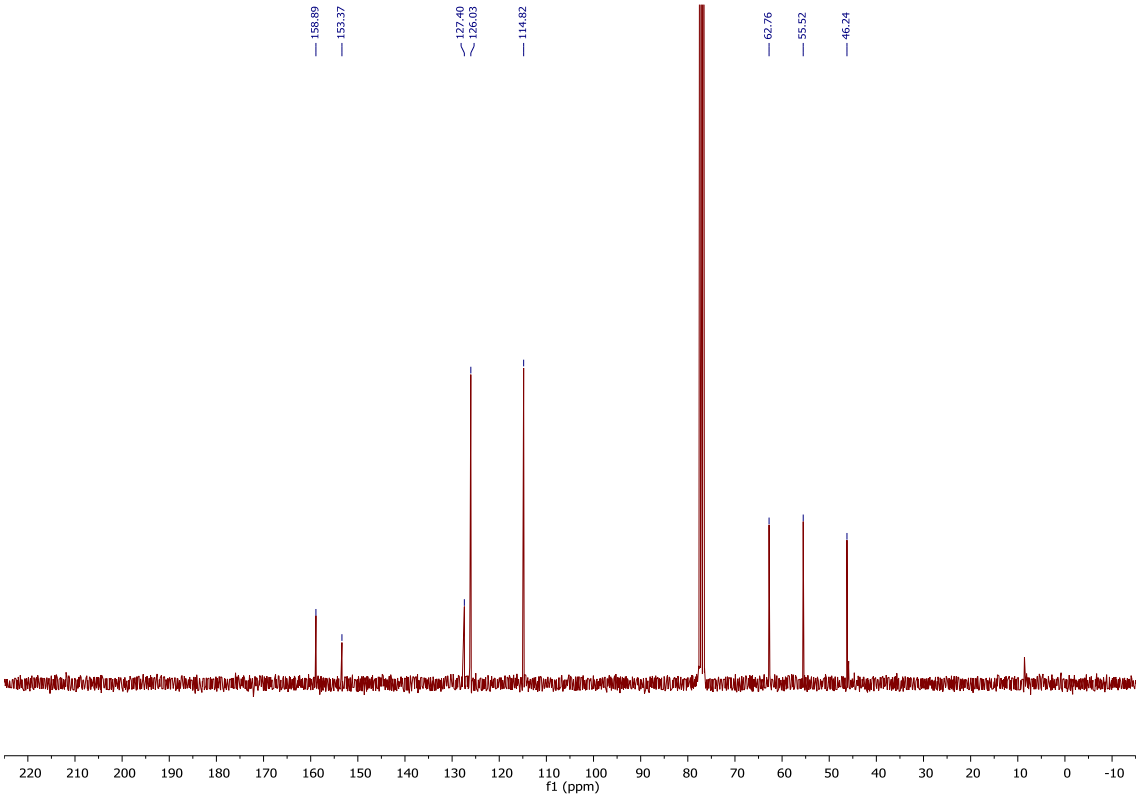


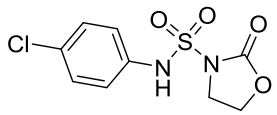
SI-1f

300 MHz, ^{1}H NMR, $CDCl_3$



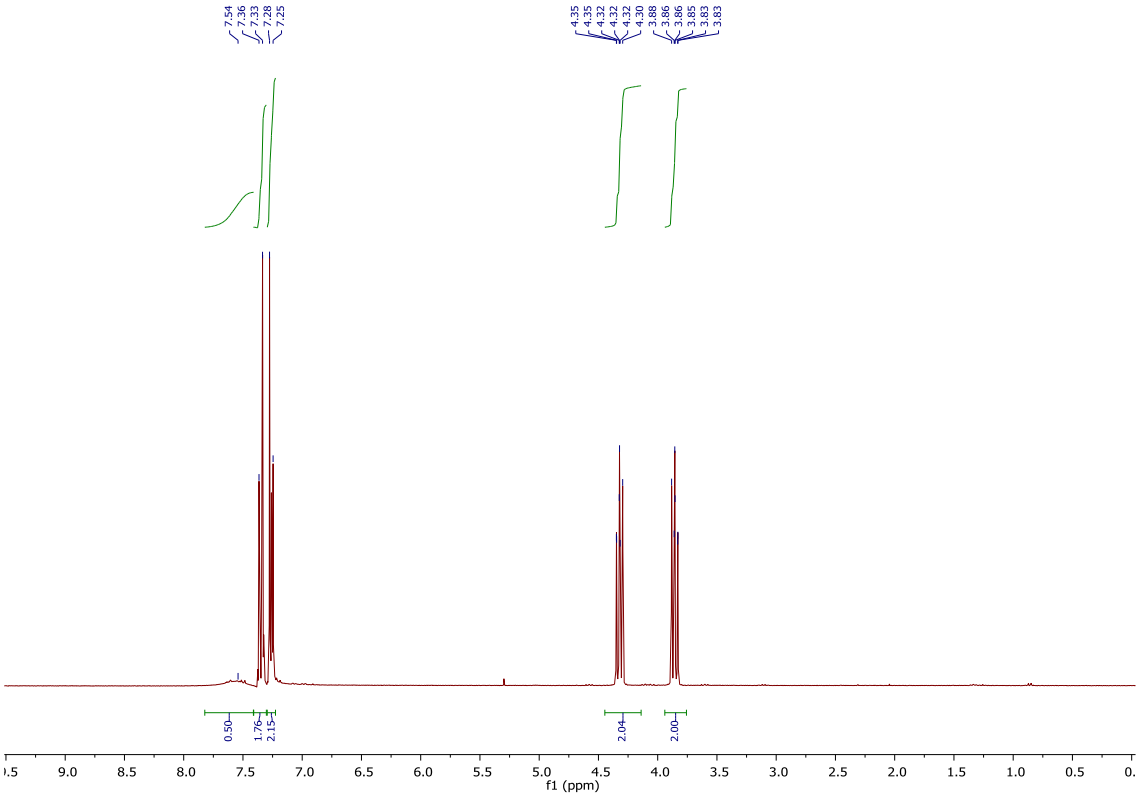
75 MHz, ^{13}C NMR, $CDCl_3$



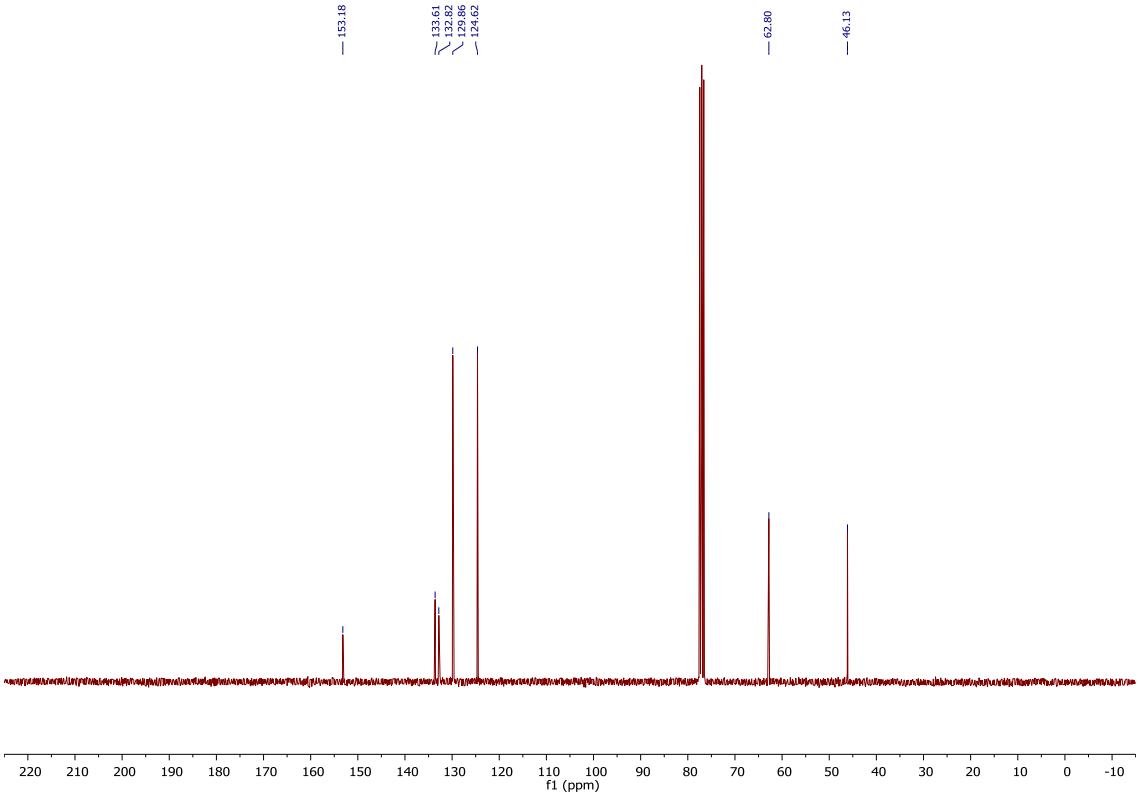


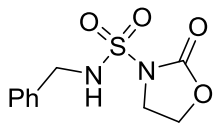
SI-1g

300 MHz, ^{1}H NMR, $CDCl_3$



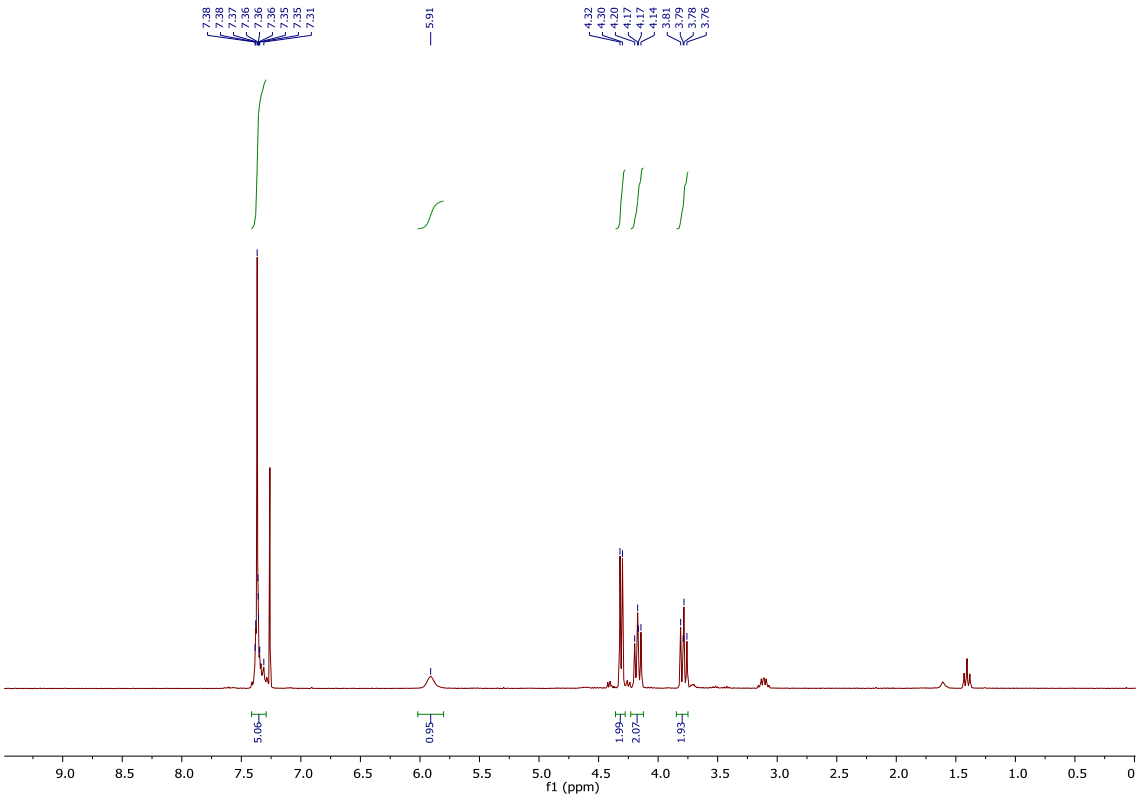
75 MHz, ^{13}C NMR, $CDCl_3$



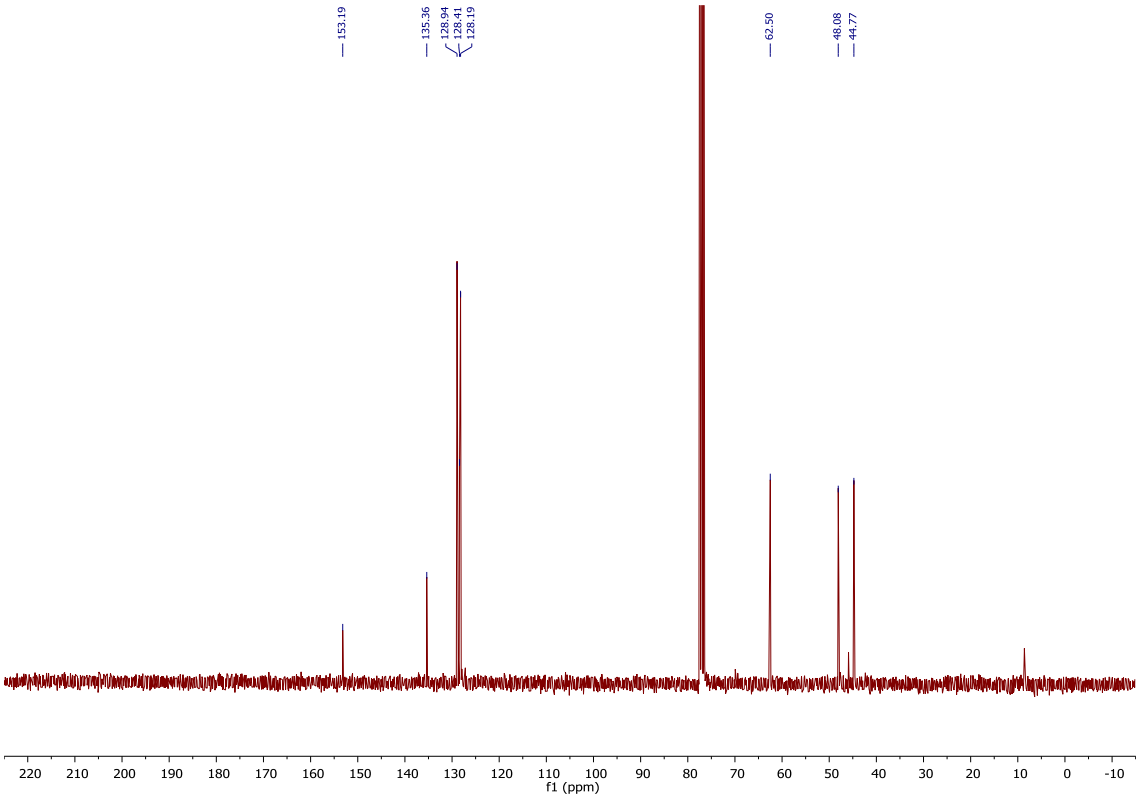


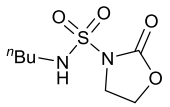
SI-1h

300 MHz, ^{1}H NMR, $CDCl_3$



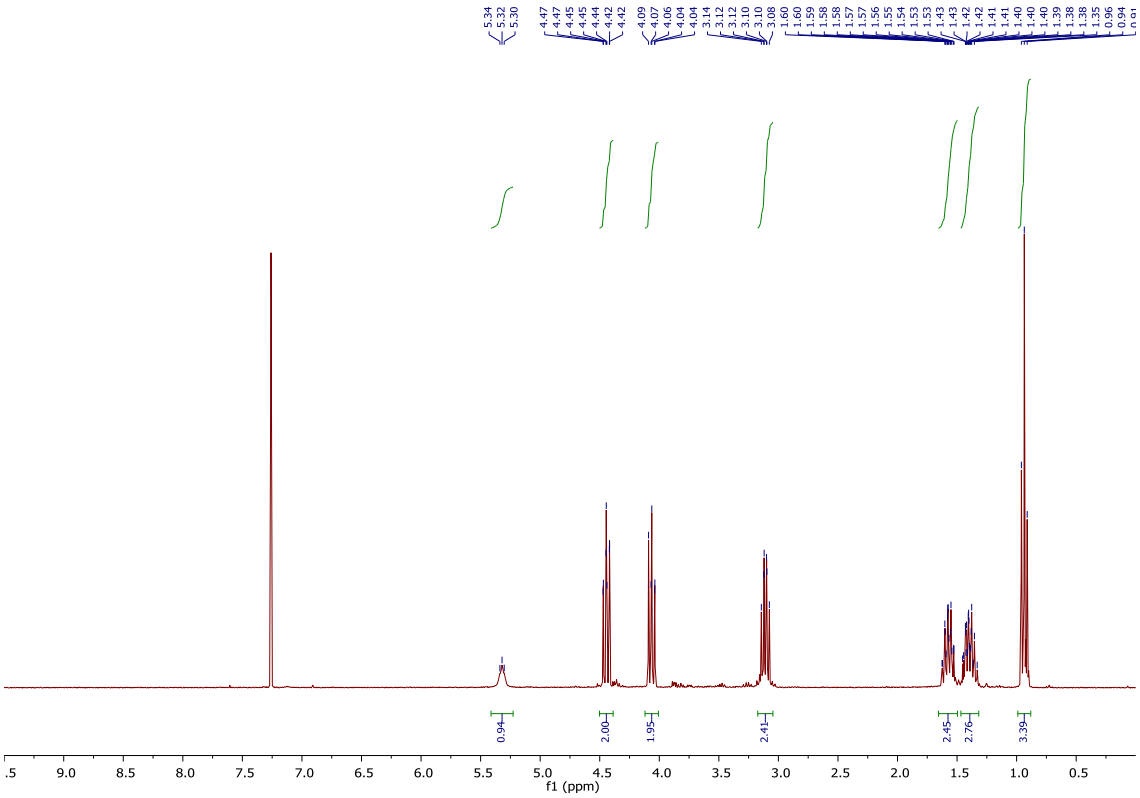
75 MHz, ^{13}C NMR, $CDCl_3$



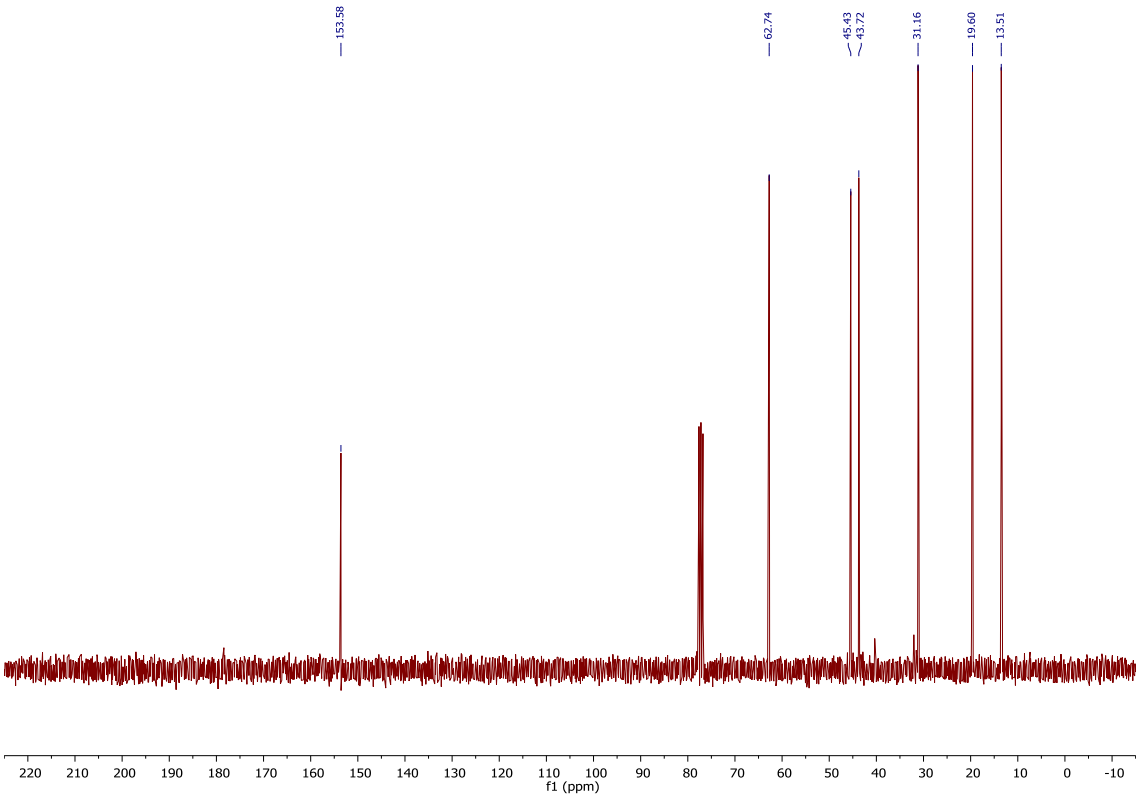


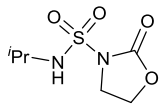
SI-1i

300 MHz, ^{1}H NMR, $CDCl_3$



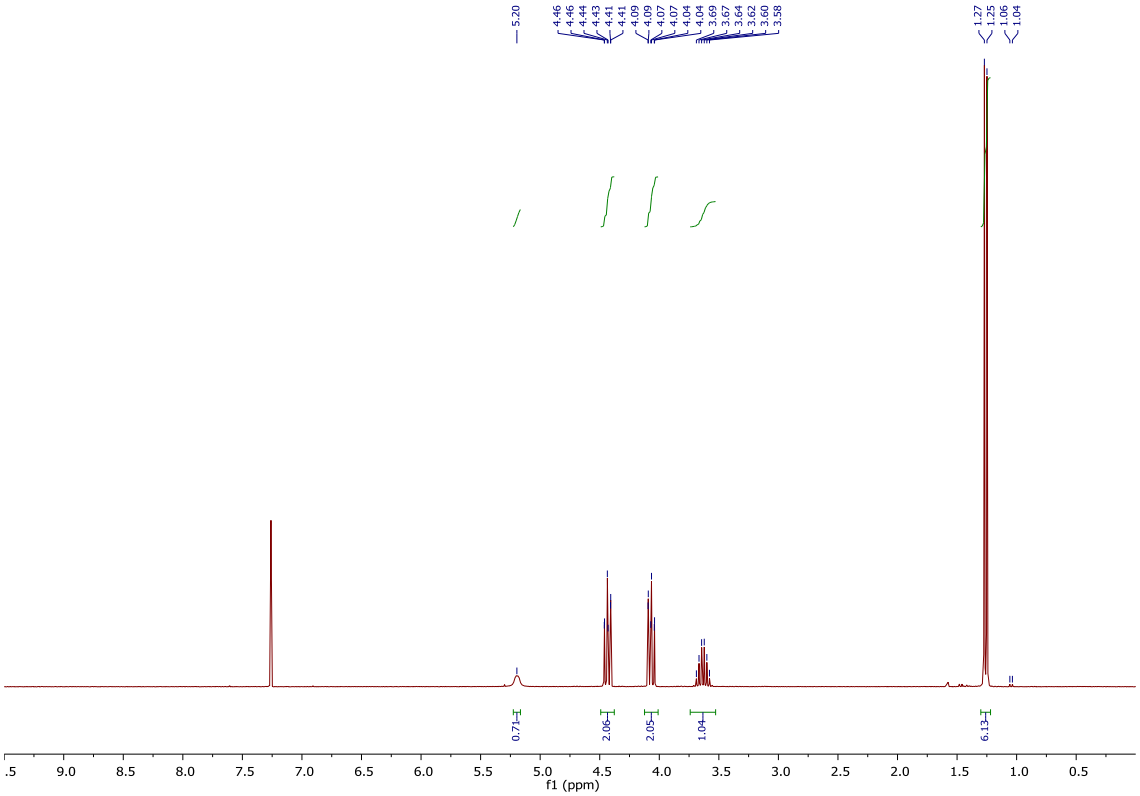
75 MHz, ^{13}C NMR, $CDCl_3$



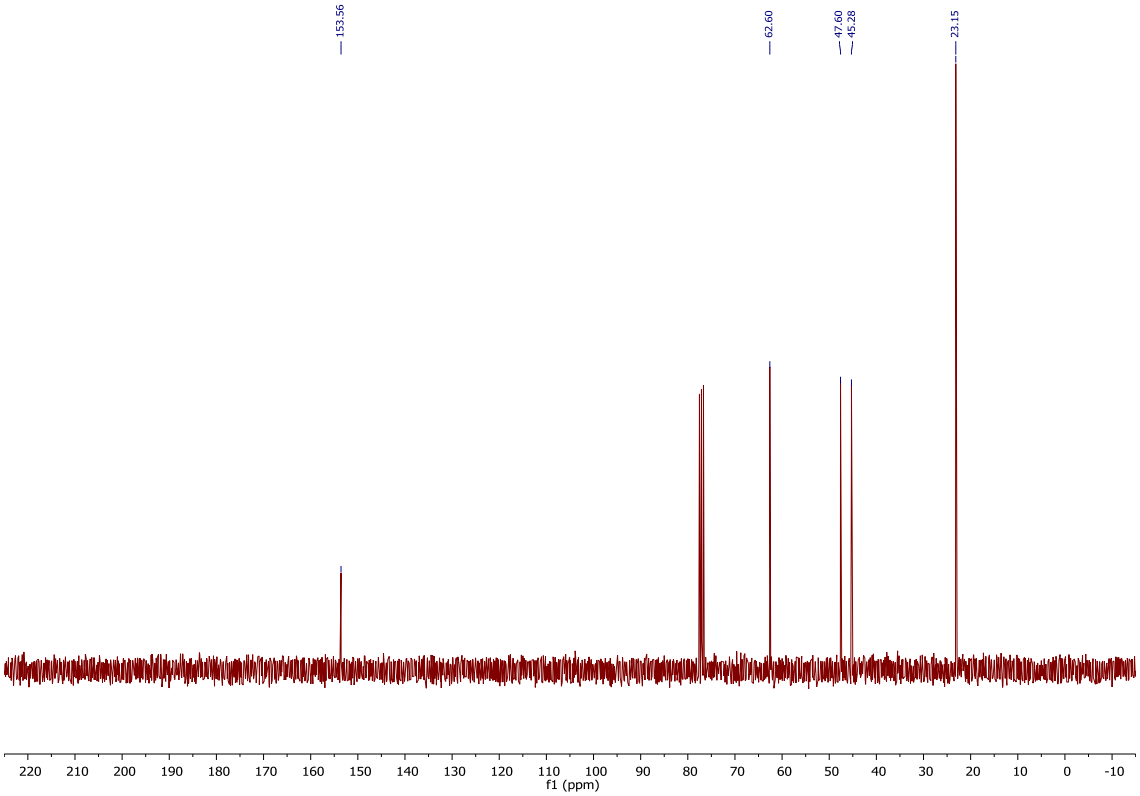


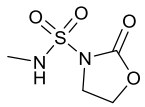
SI-1j

300 MHz, ^{1}H NMR, $CDCl_3$



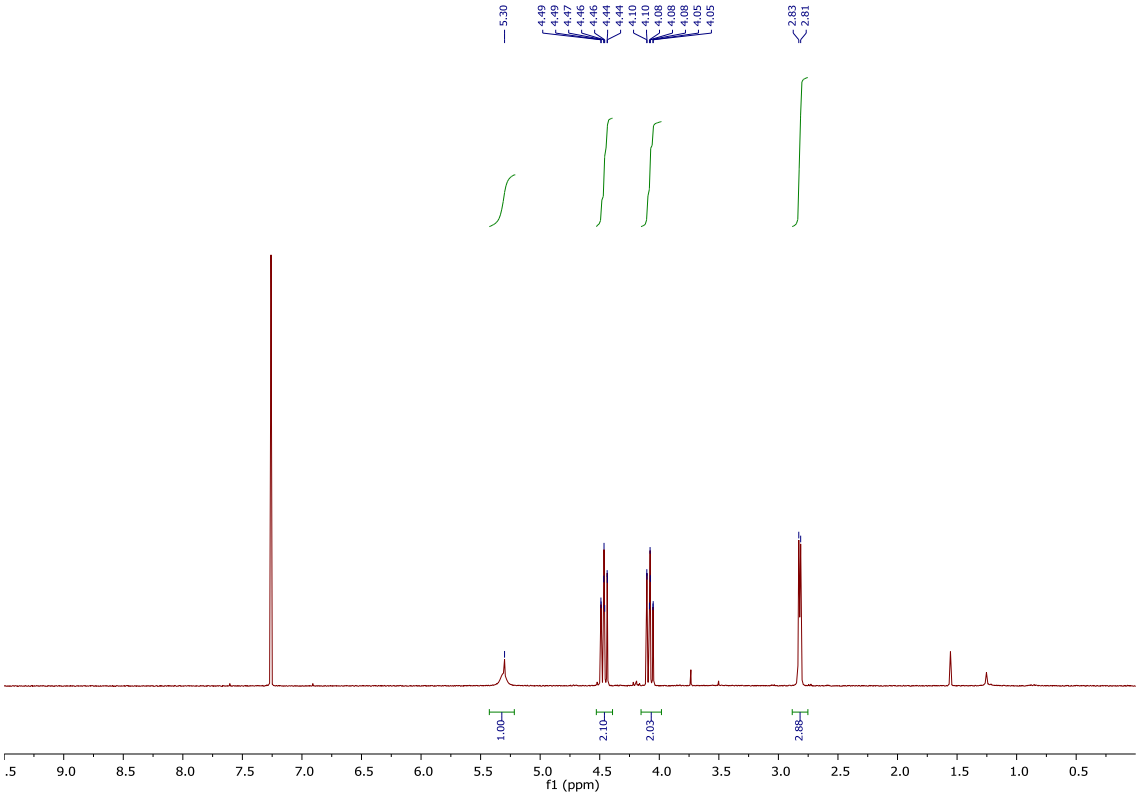
75 MHz, ^{13}C NMR, $CDCl_3$



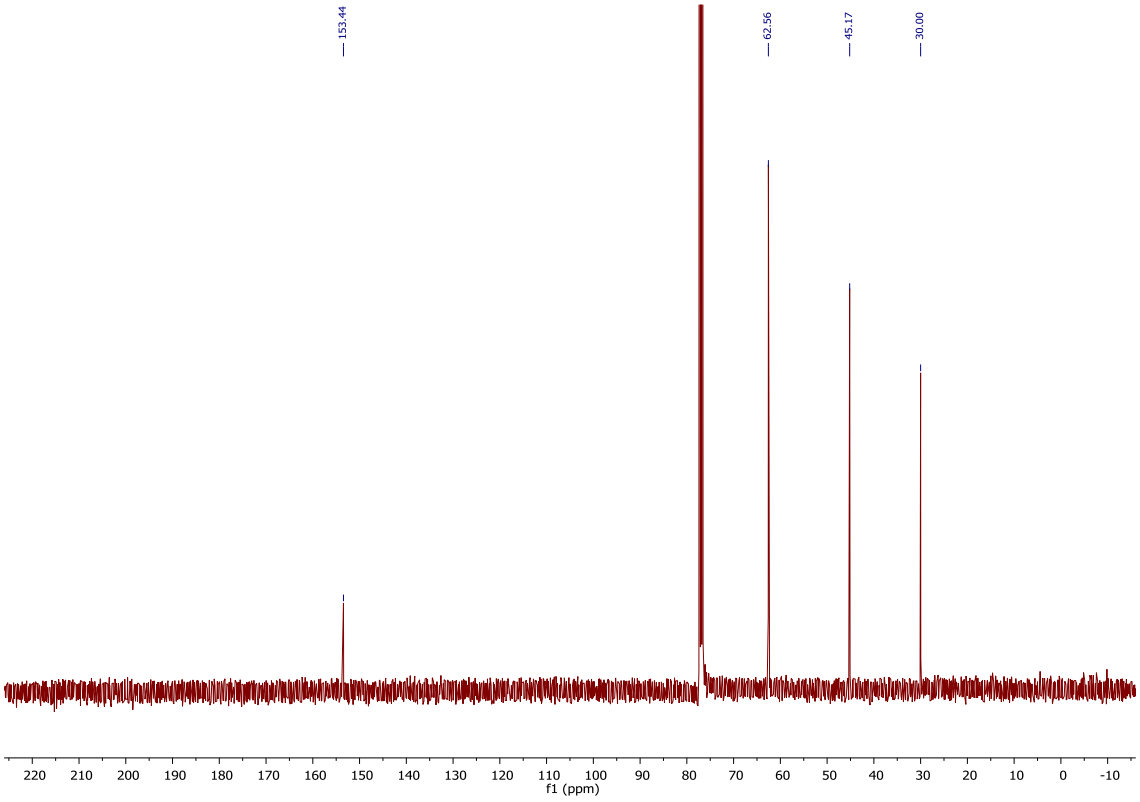


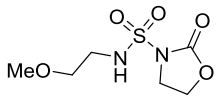
SI-1k

300 MHz, ^{1}H NMR, $CDCl_3$



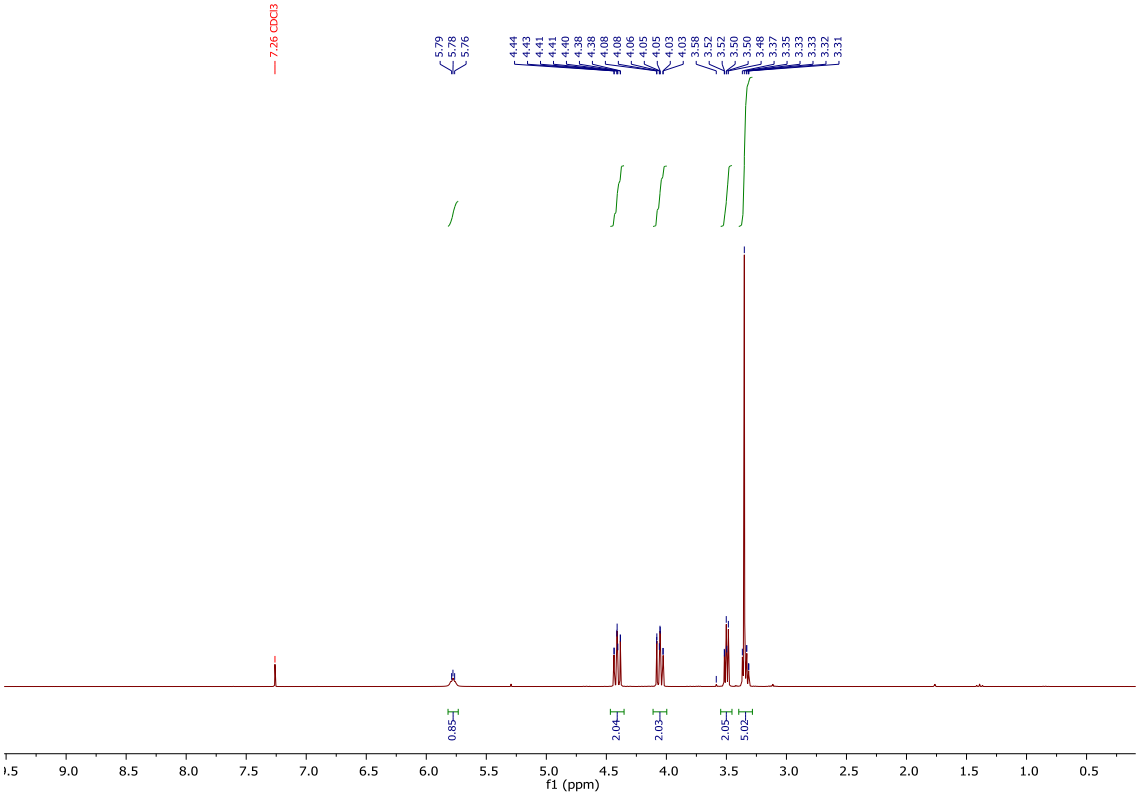
75 MHz, ^{13}C NMR, $CDCl_3$



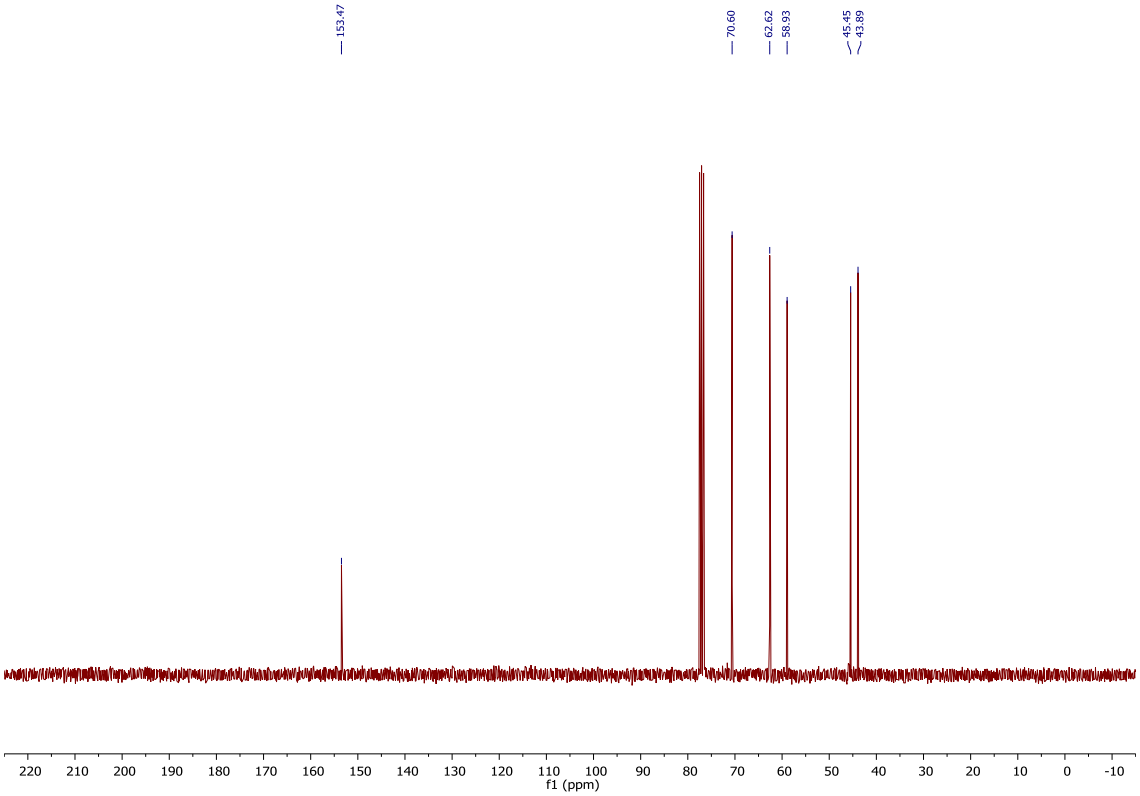


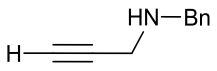
SI-1l

300 MHz, ^{1}H NMR, $CDCl_3$



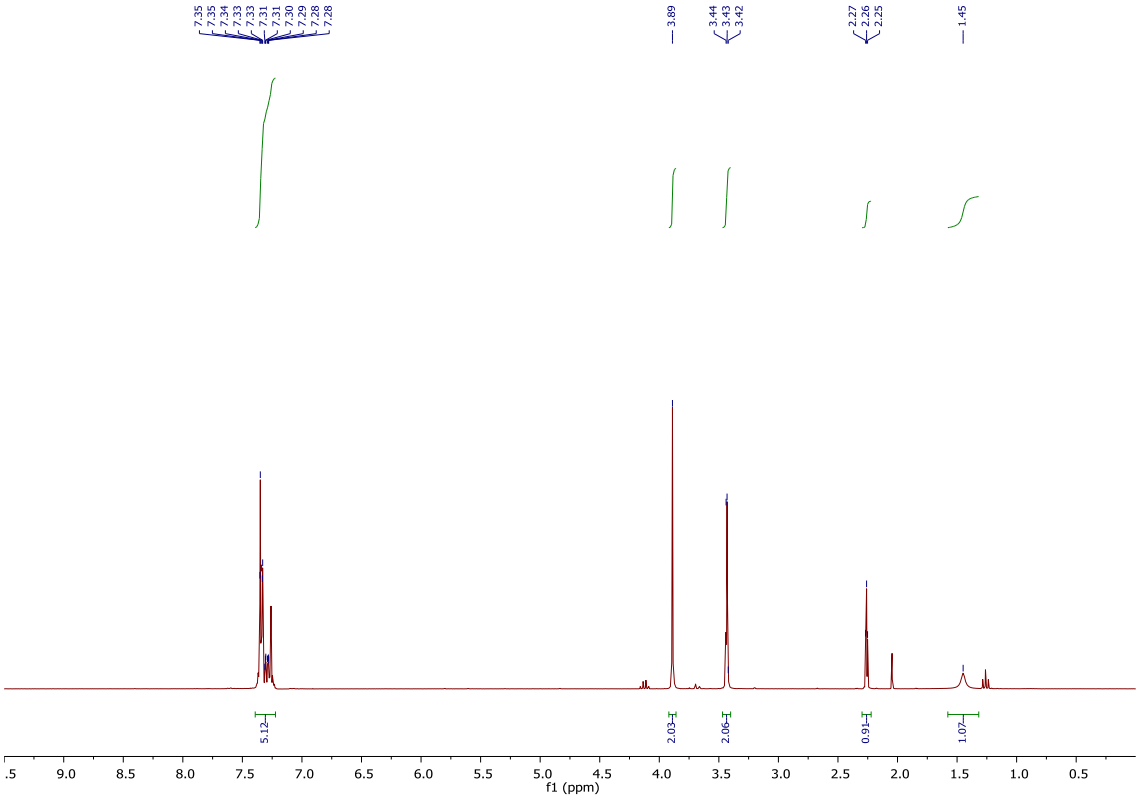
75 MHz, ^{13}C NMR, $CDCl_3$



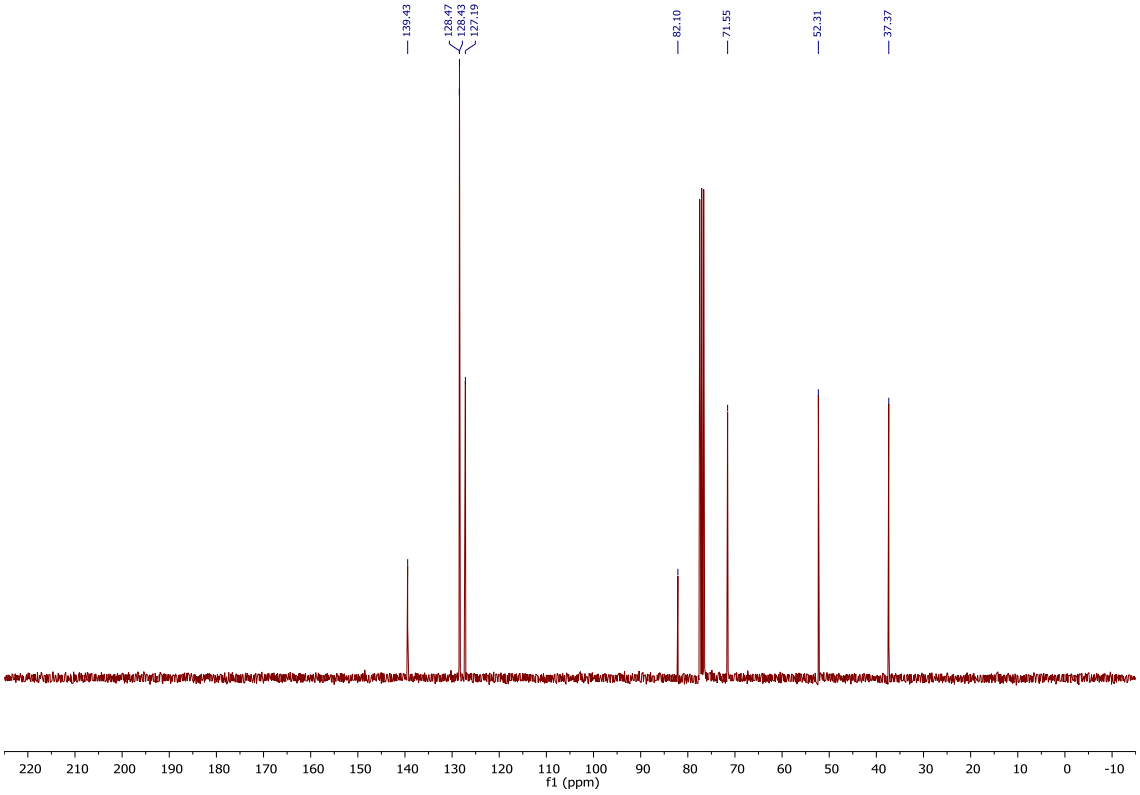


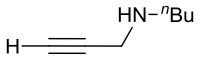
SI-2a

300 MHz, ^{1}H NMR, $CDCl_3$



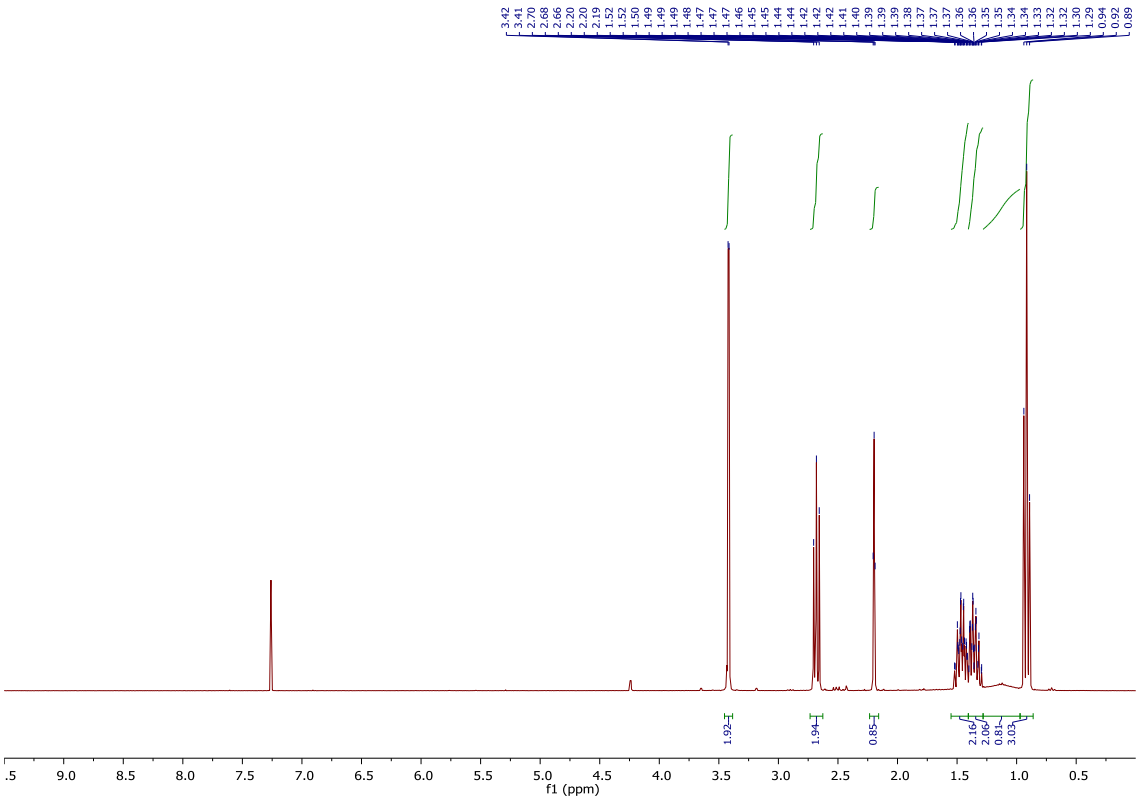
75 MHz, ^{13}C NMR, $CDCl_3$



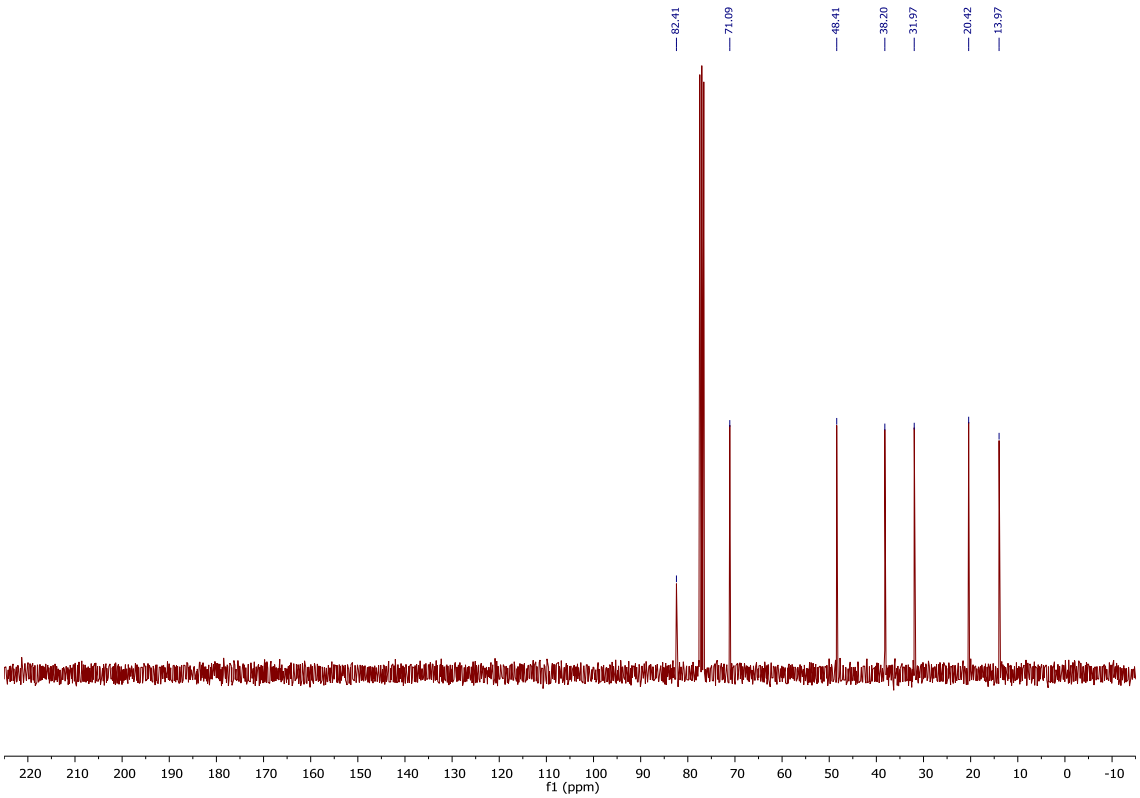


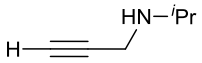
SI-2b

300 MHz, ^{1}H NMR, $CDCl_3$



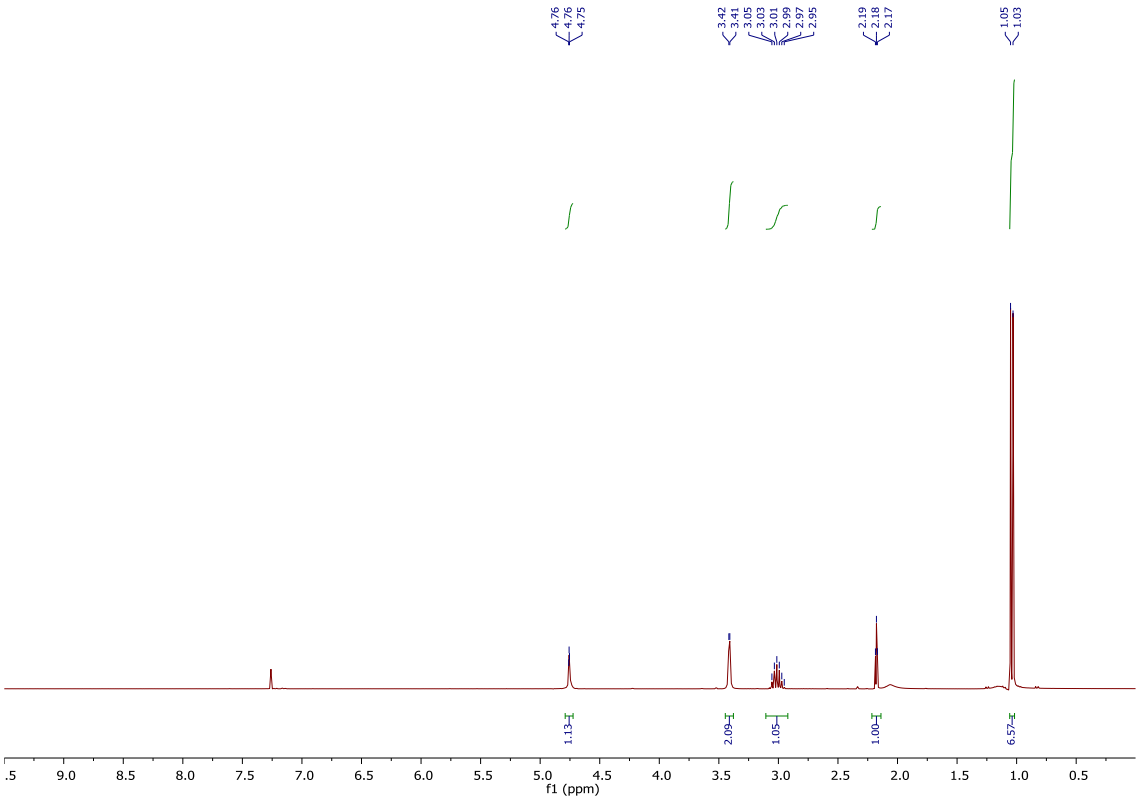
75 MHz, ^{13}C NMR, $CDCl_3$



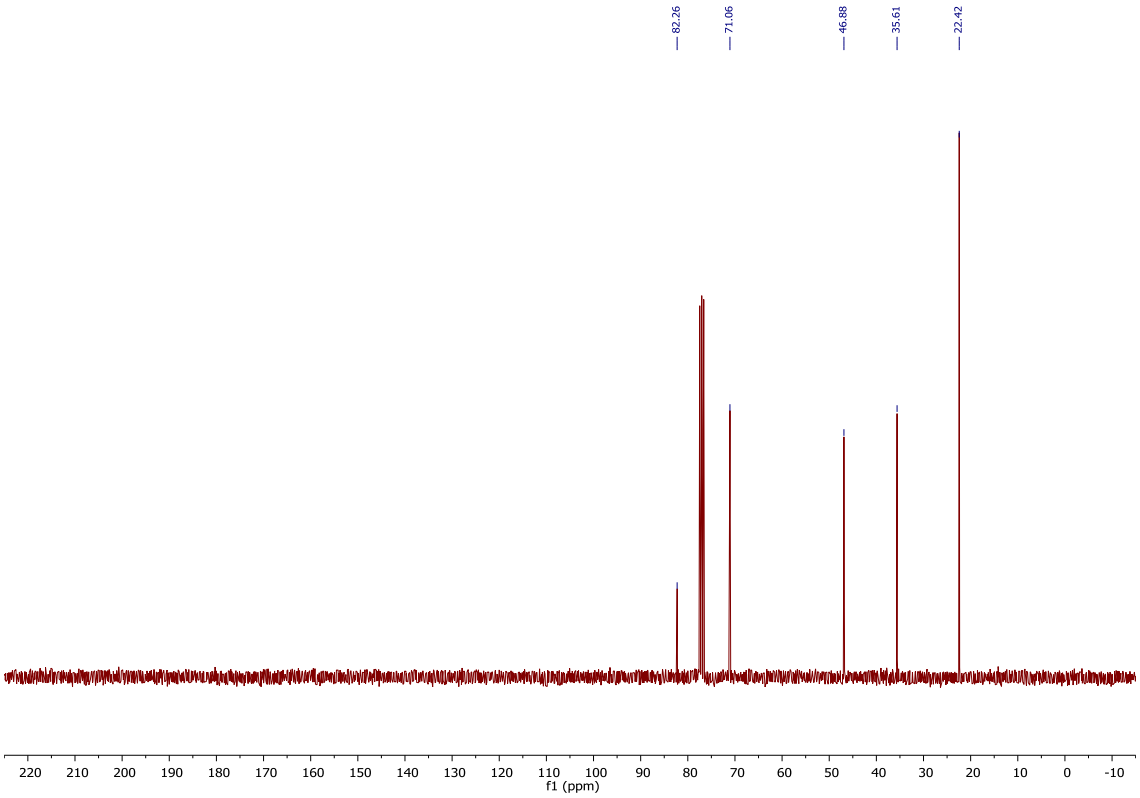


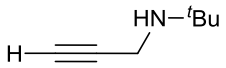
SI-2c

300 MHz, ^{1}H NMR, $CDCl_3$



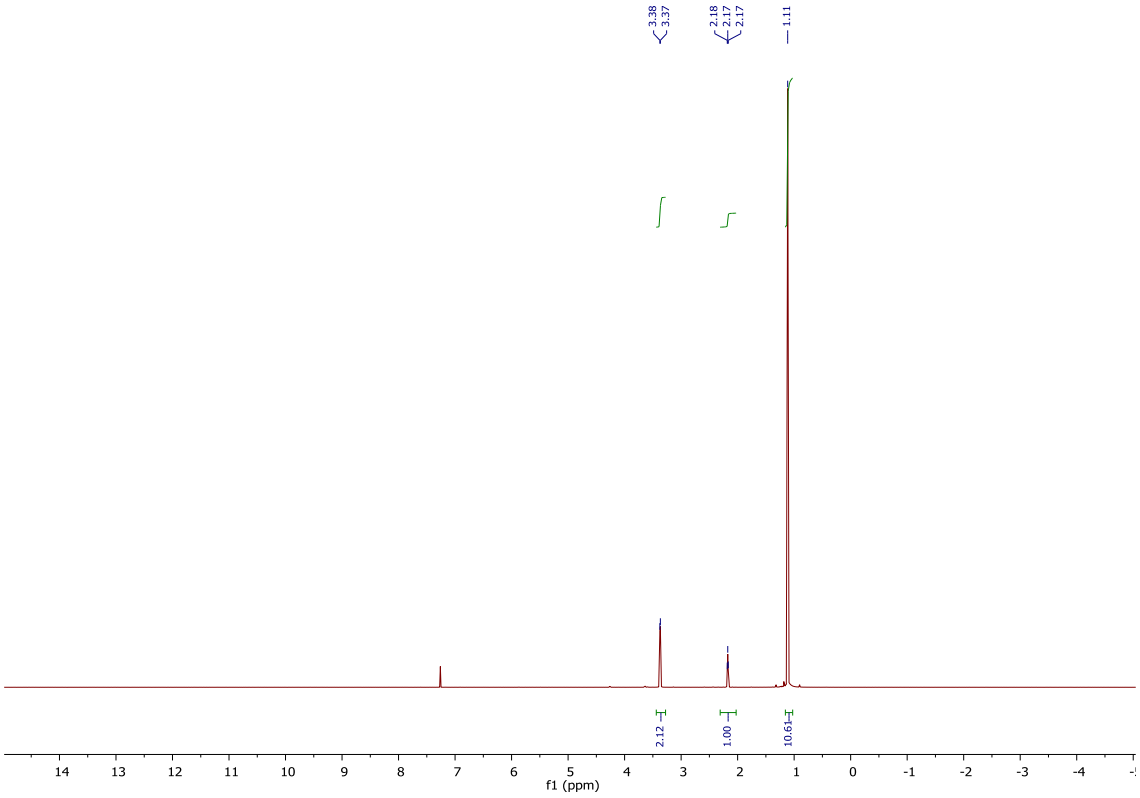
75 MHz, ^{13}C NMR, $CDCl_3$



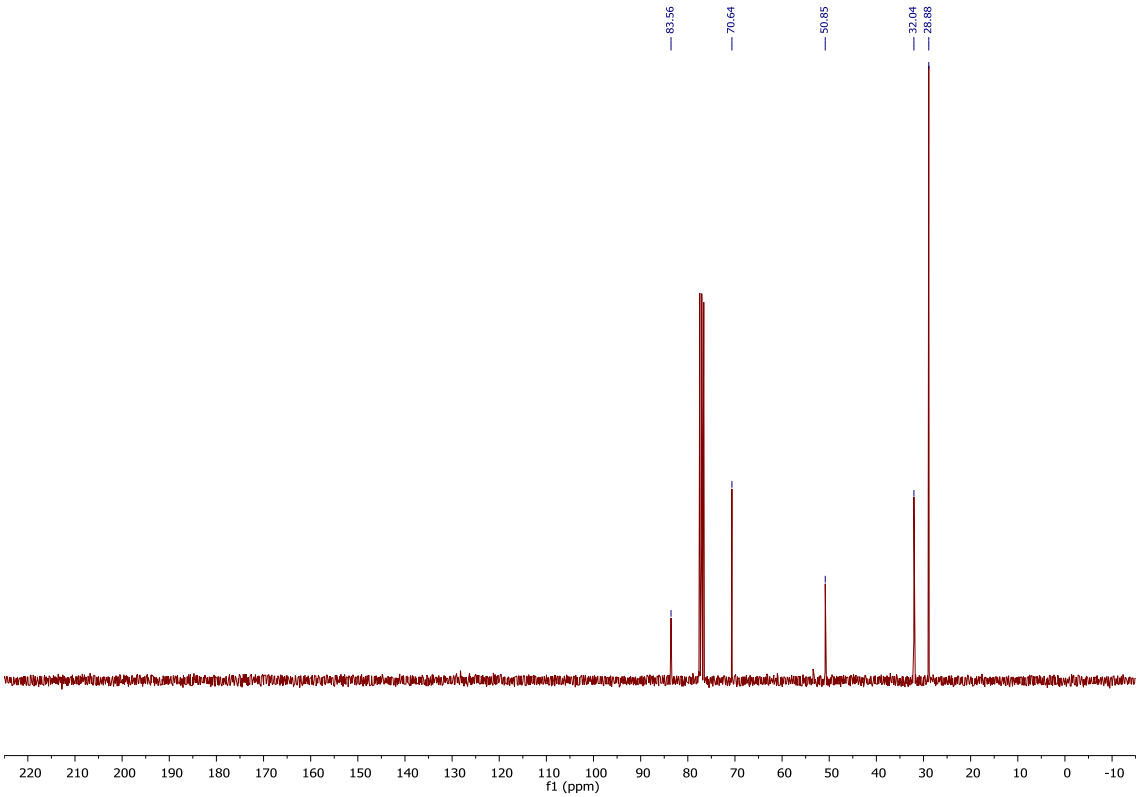


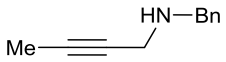
SI-2d

300 MHz, ^{1}H NMR, $CDCl_3$



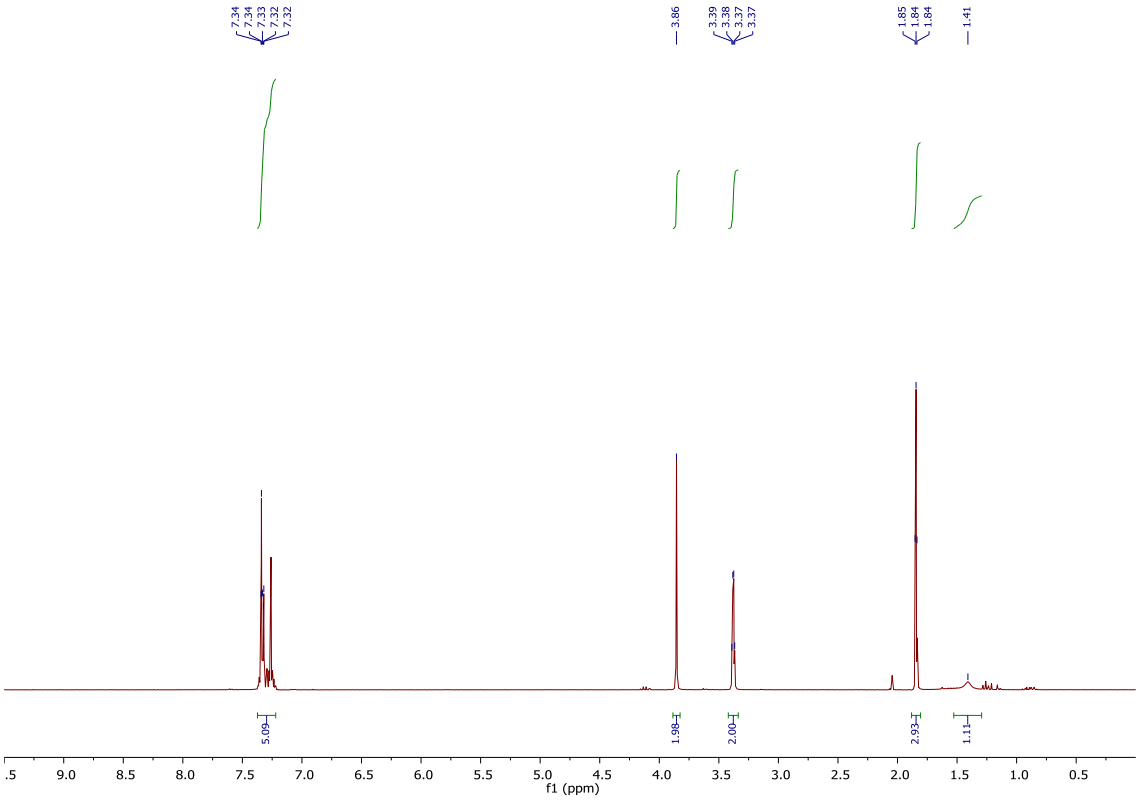
75 MHz, ^{13}C NMR, $CDCl_3$



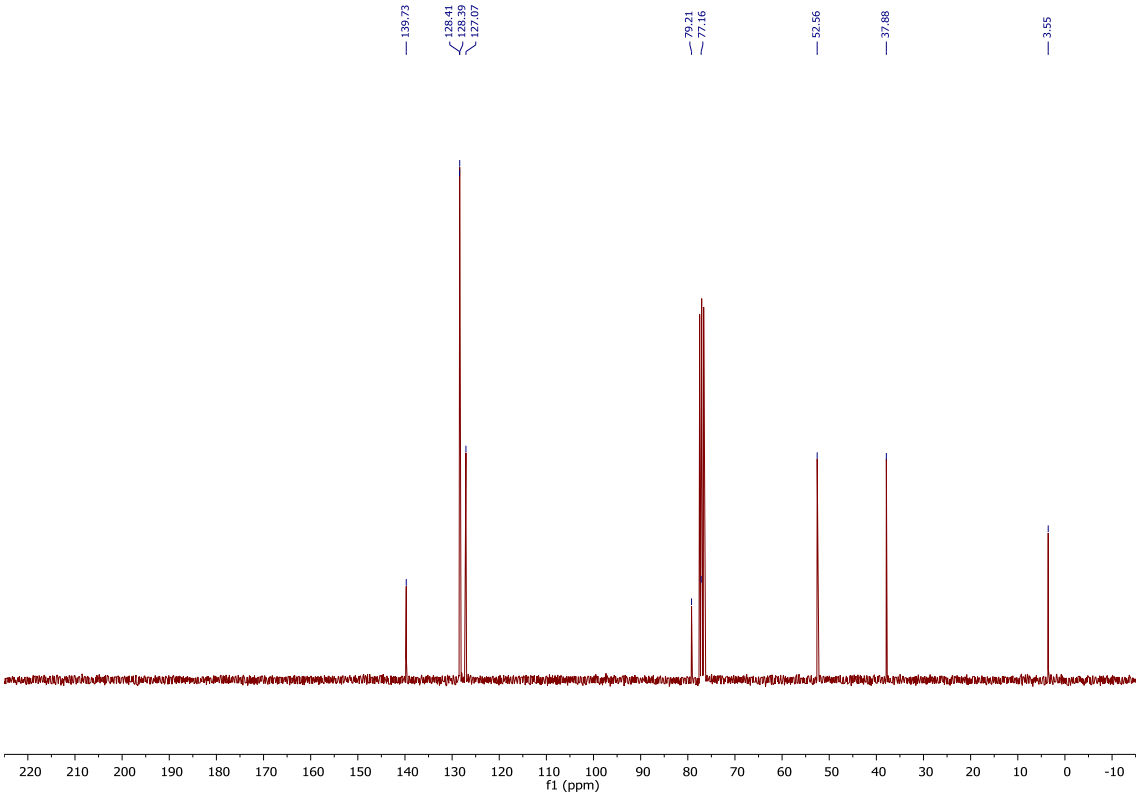


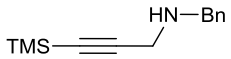
SI-2e

300 MHz, ^{1}H NMR, $CDCl_3$



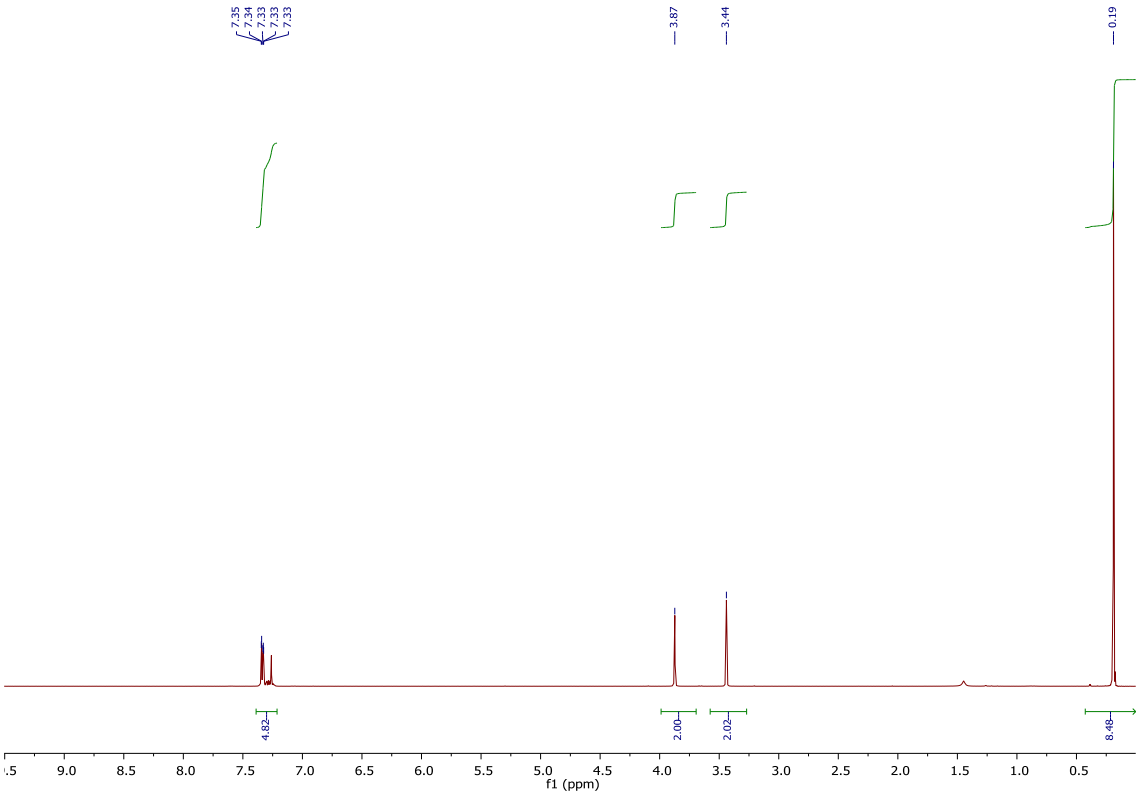
75 MHz, ^{13}C NMR, $CDCl_3$



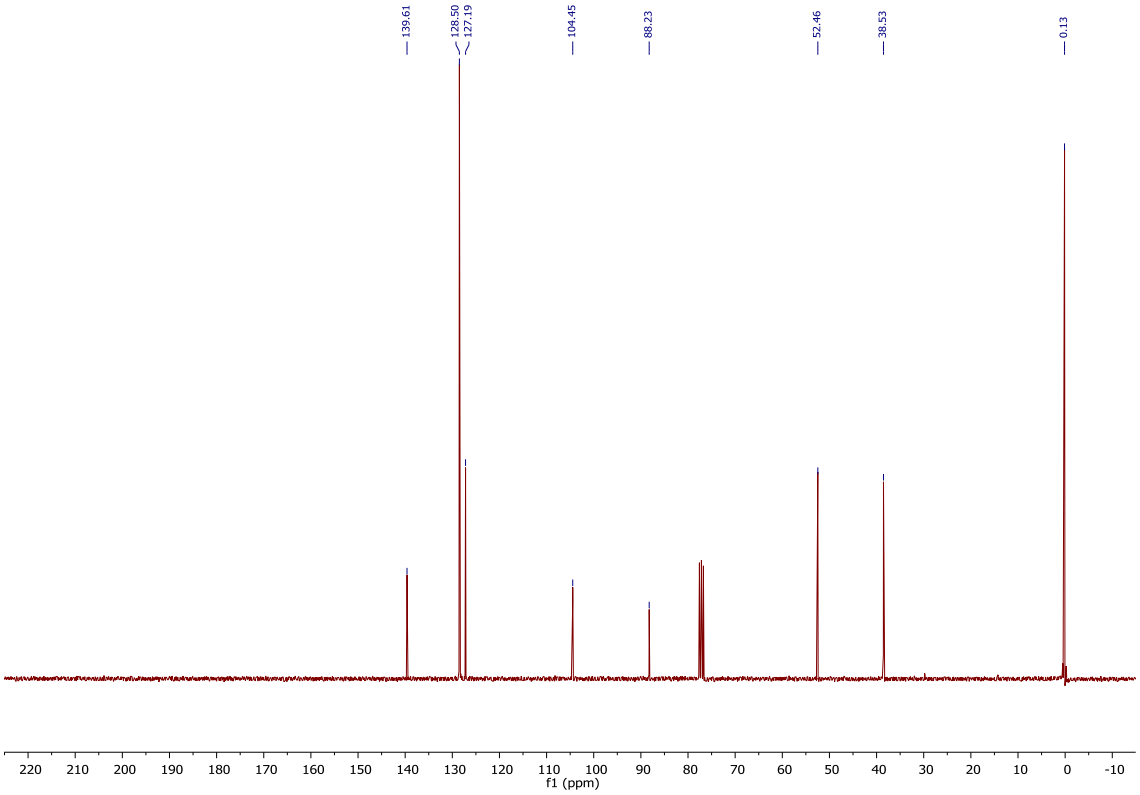


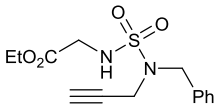
SI-2f

300 MHz, ^{1}H NMR, $CDCl_3$



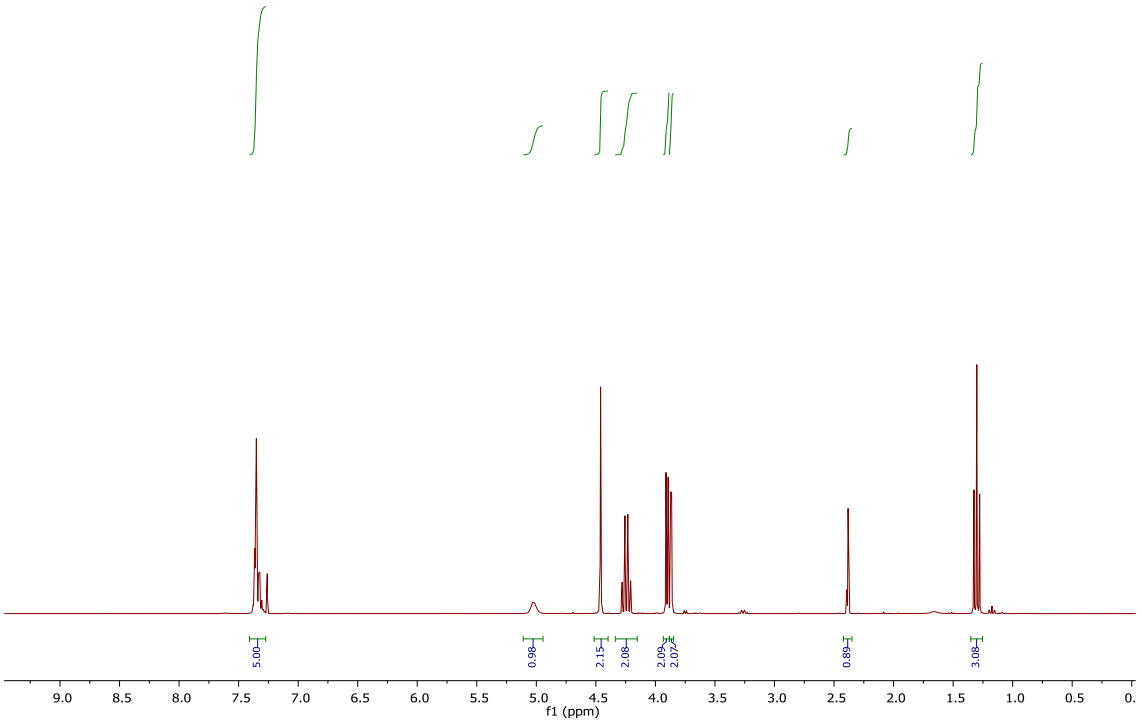
75 MHz, ^{13}C NMR, $CDCl_3$



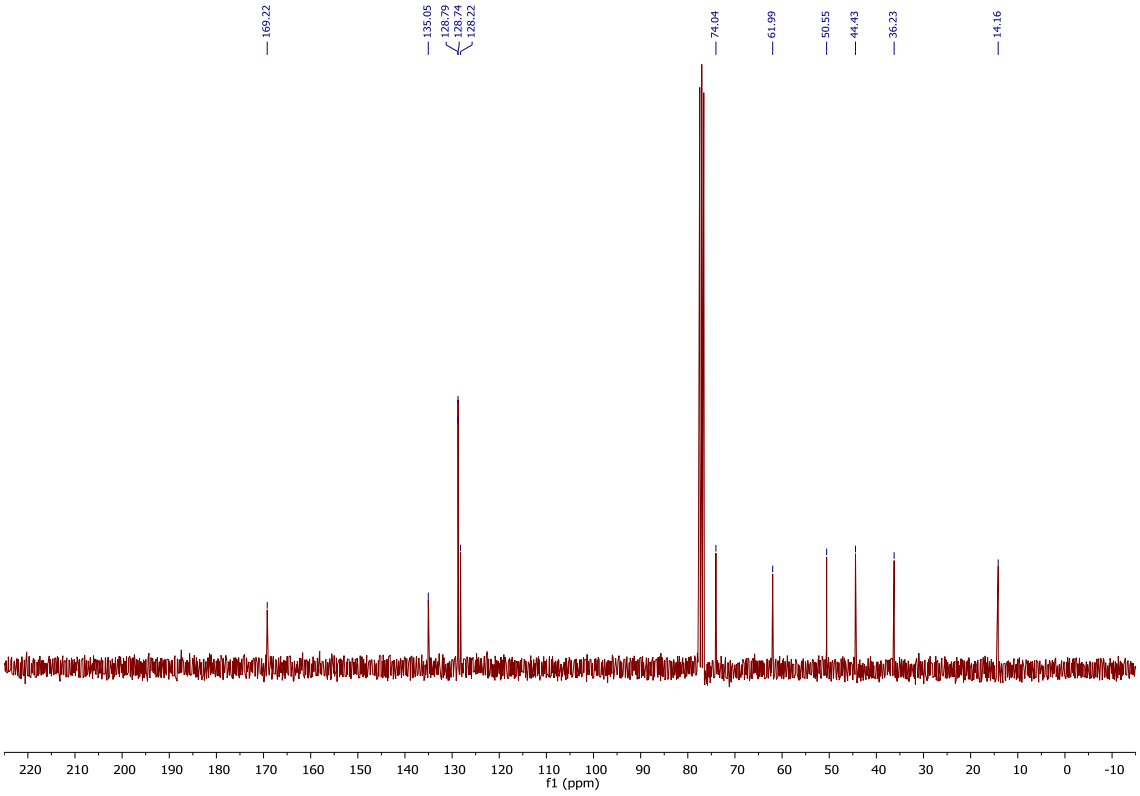


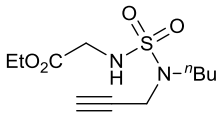
1a

300 MHz, ^{1}H NMR, $CDCl_3$



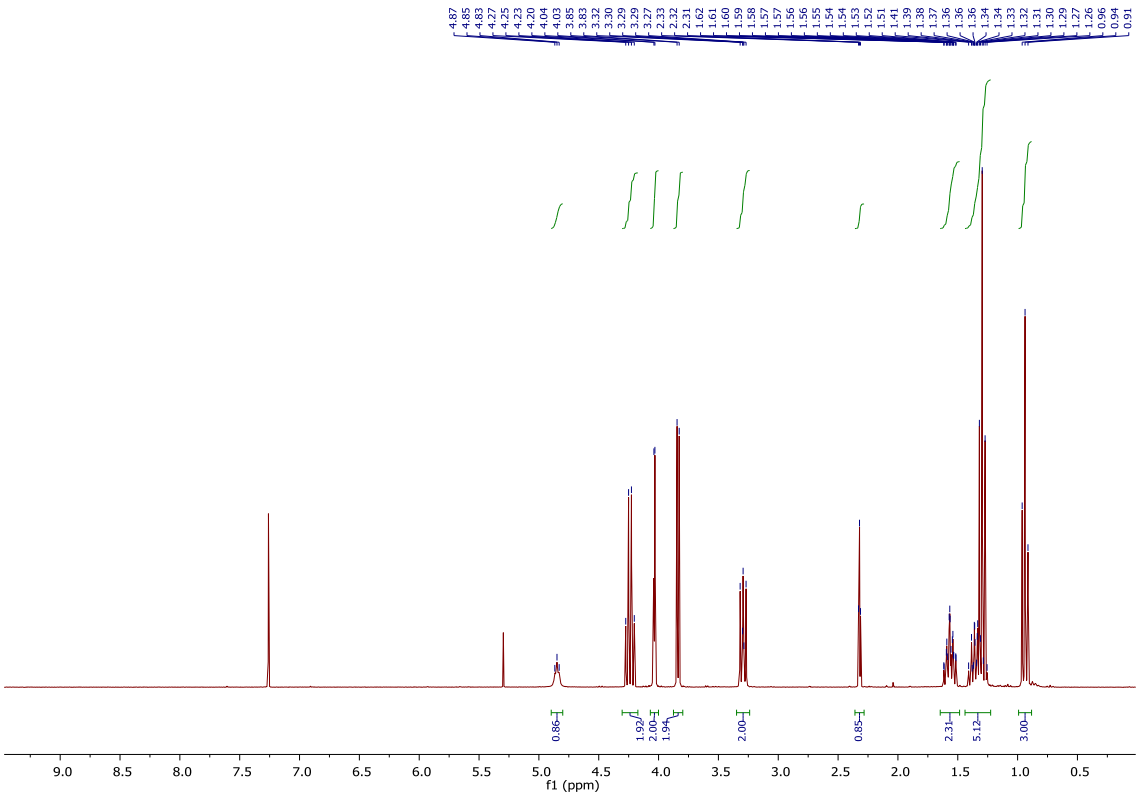
75 MHz, ^{13}C NMR, $CDCl_3$



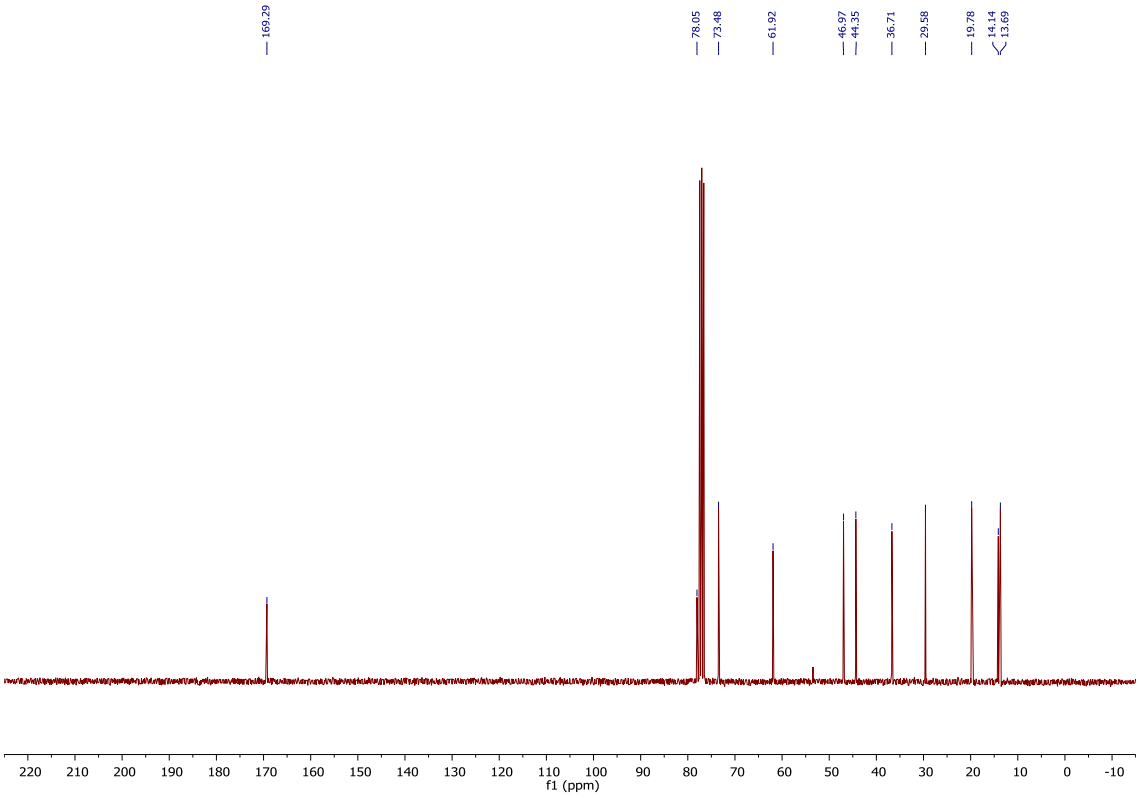


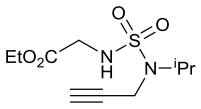
1b

300 MHz, ^{1}H NMR, $CDCl_3$



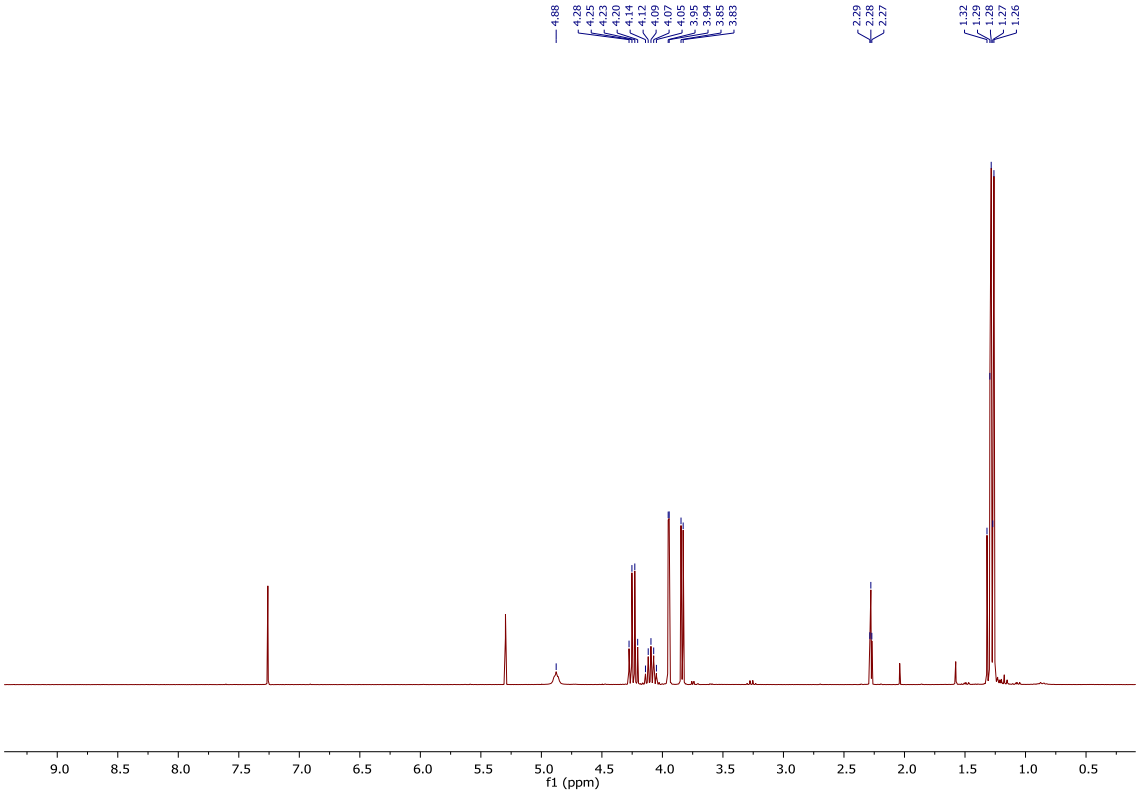
75 MHz, ^{13}C NMR, $CDCl_3$



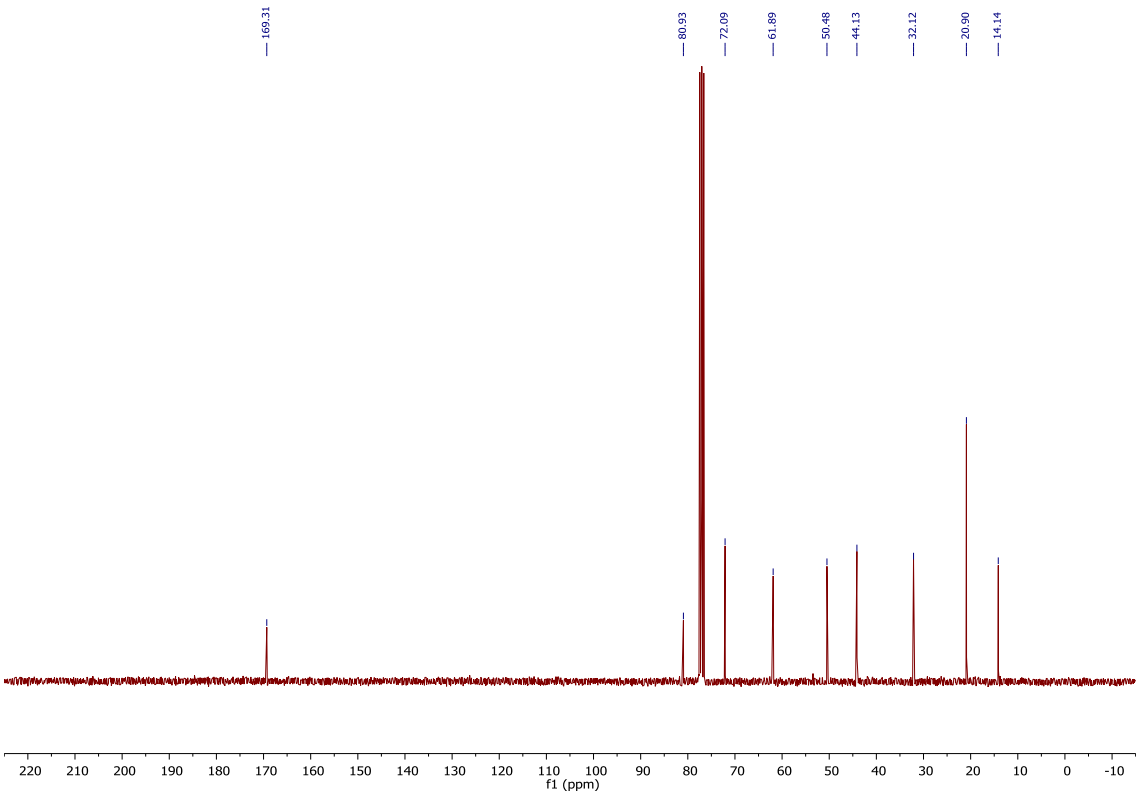


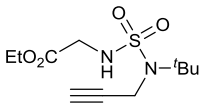
1c

300 MHz, ^{1}H NMR, $CDCl_3$



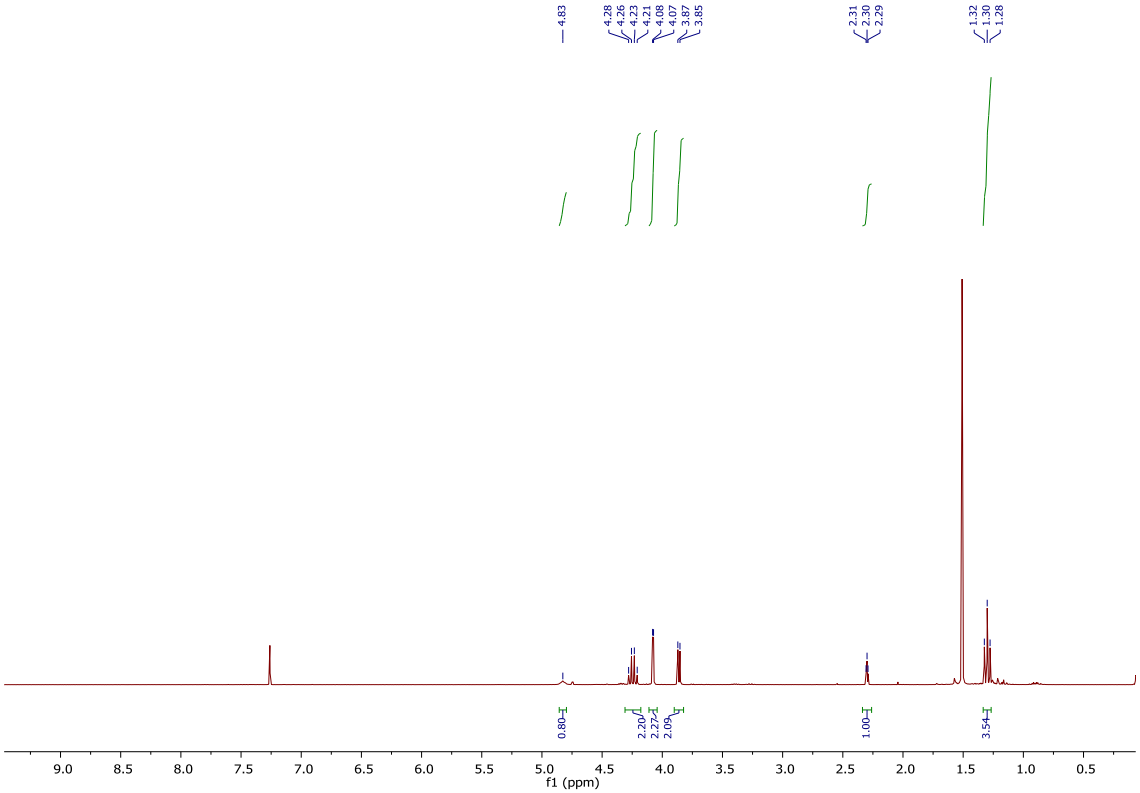
75 MHz, ^{13}C NMR, $CDCl_3$



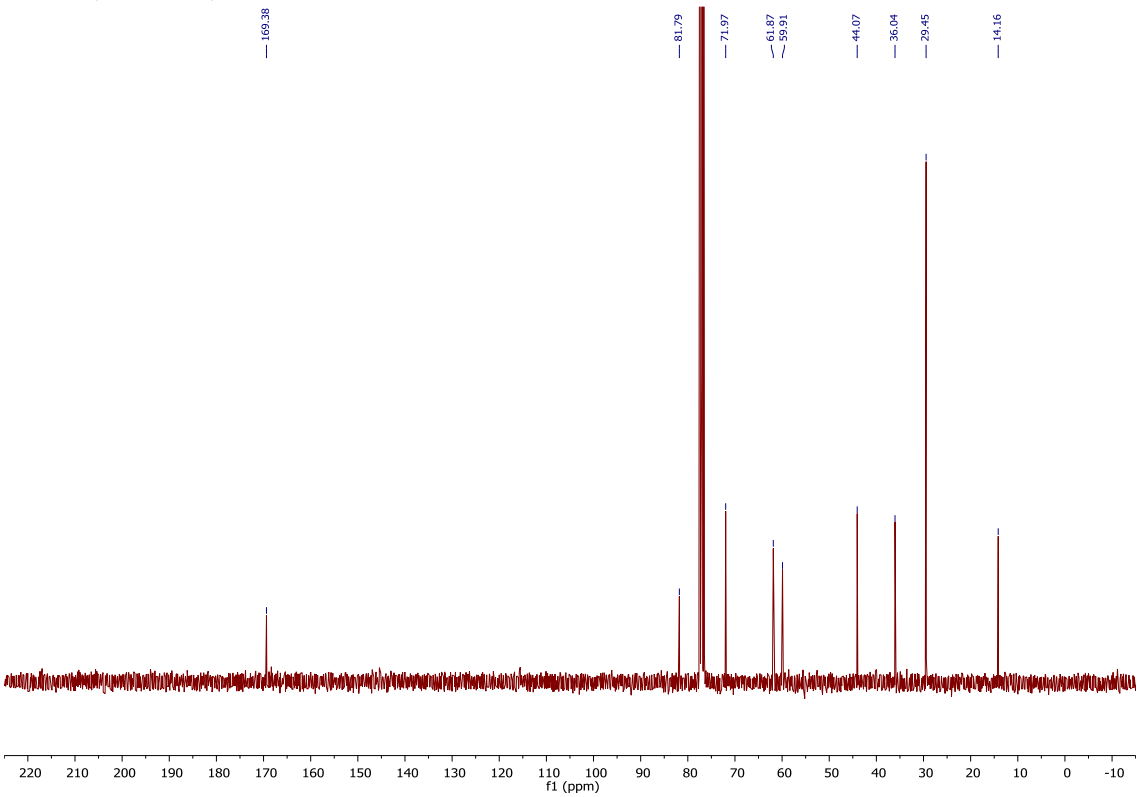


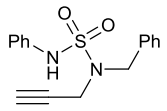
1d

300 MHz, ^{1}H NMR, $CDCl_3$



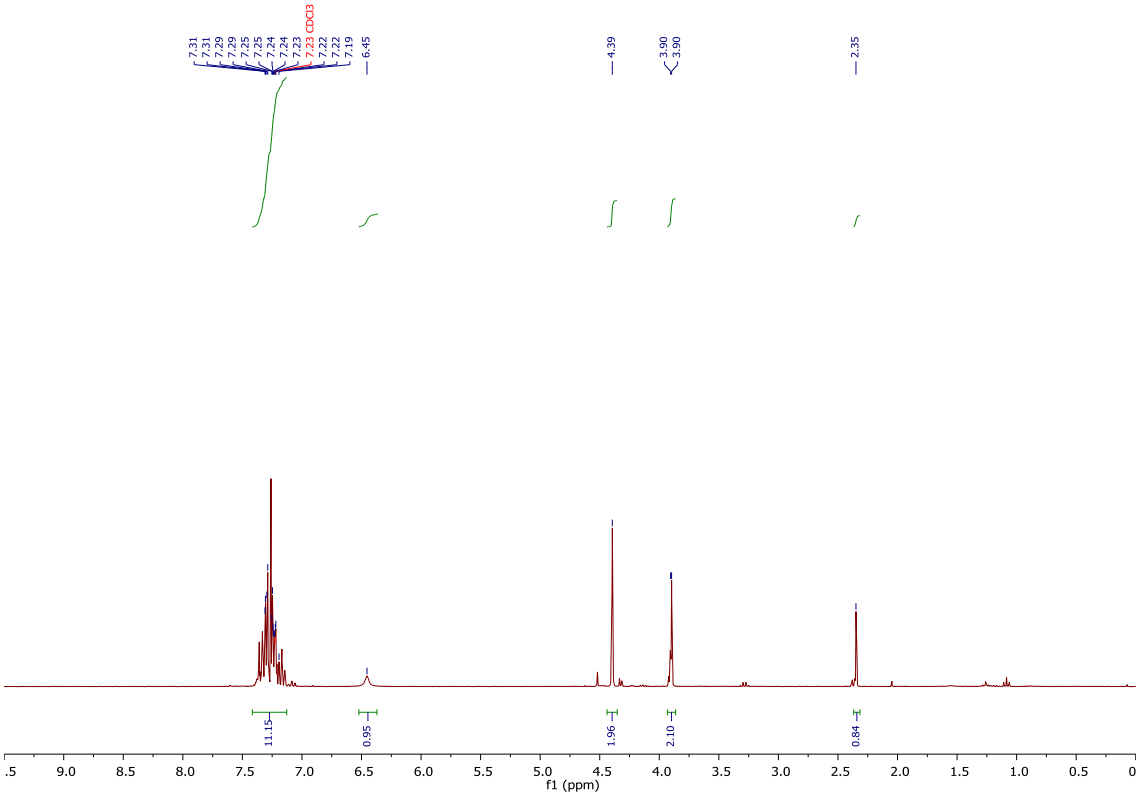
75 MHz, ^{13}C NMR, $CDCl_3$



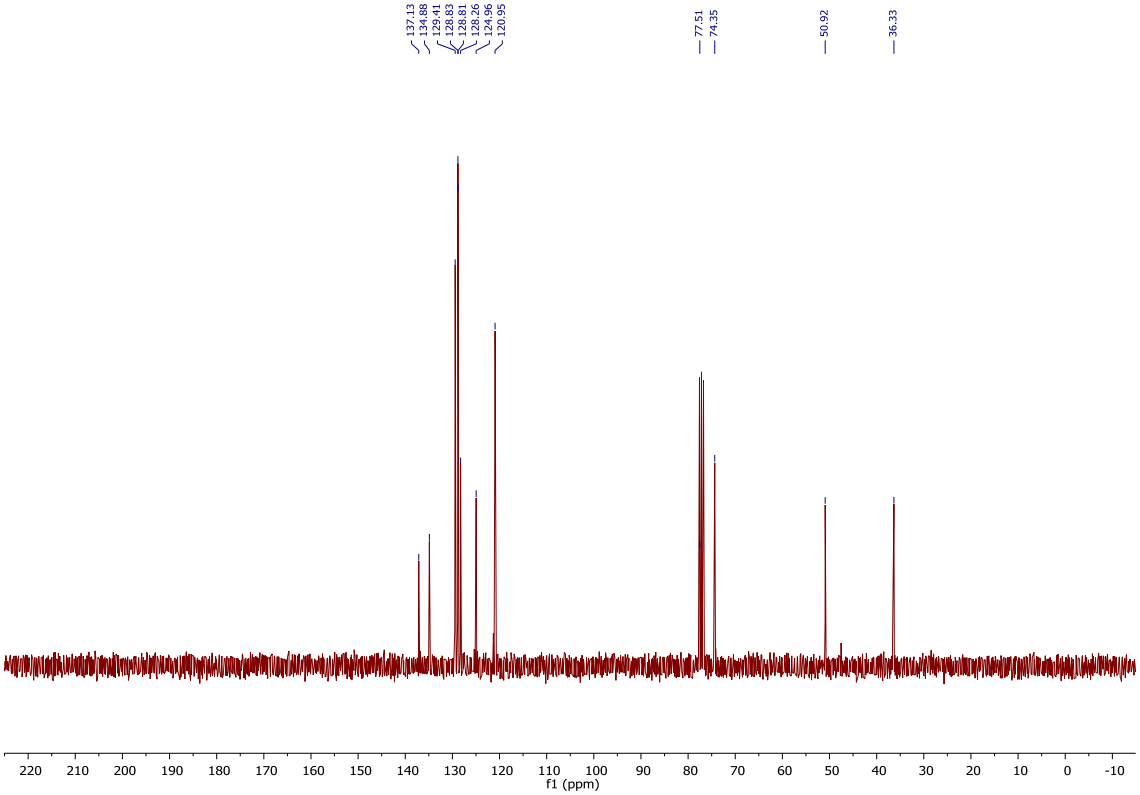


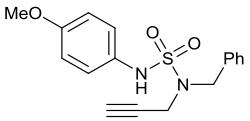
1e

300 MHz, ^{1}H NMR, $CDCl_3$



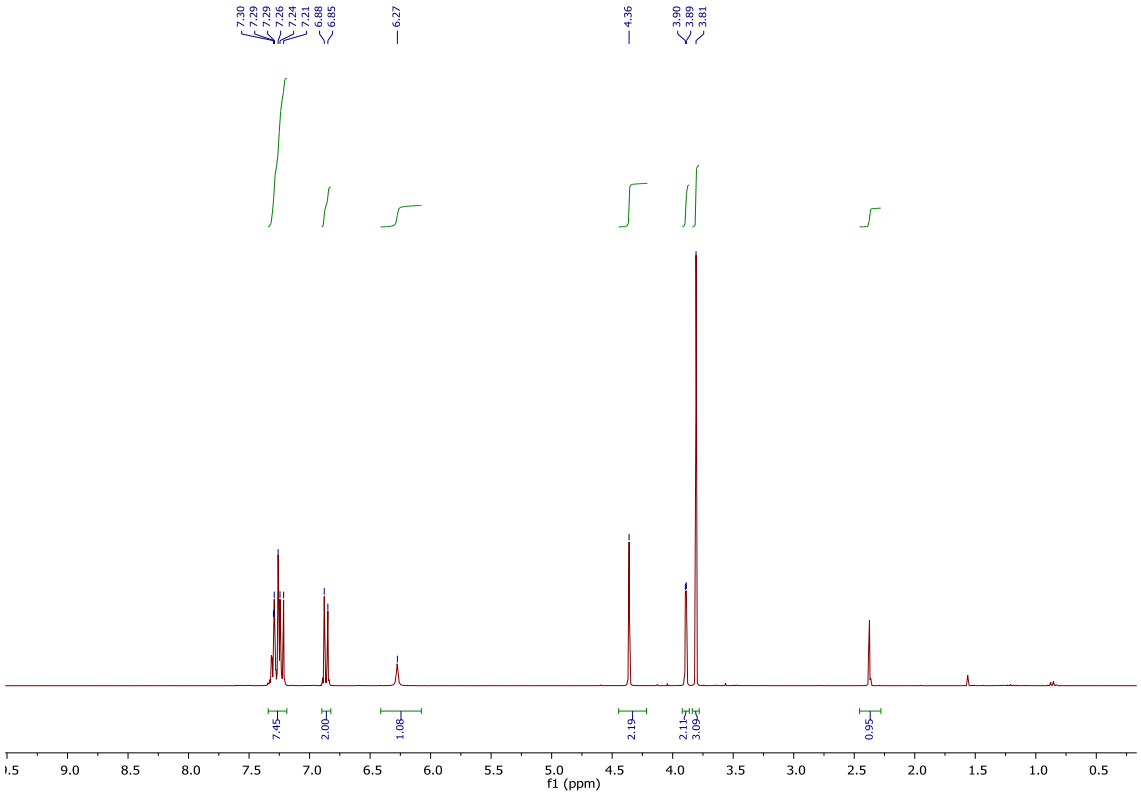
75 MHz, ^{13}C NMR, $CDCl_3$



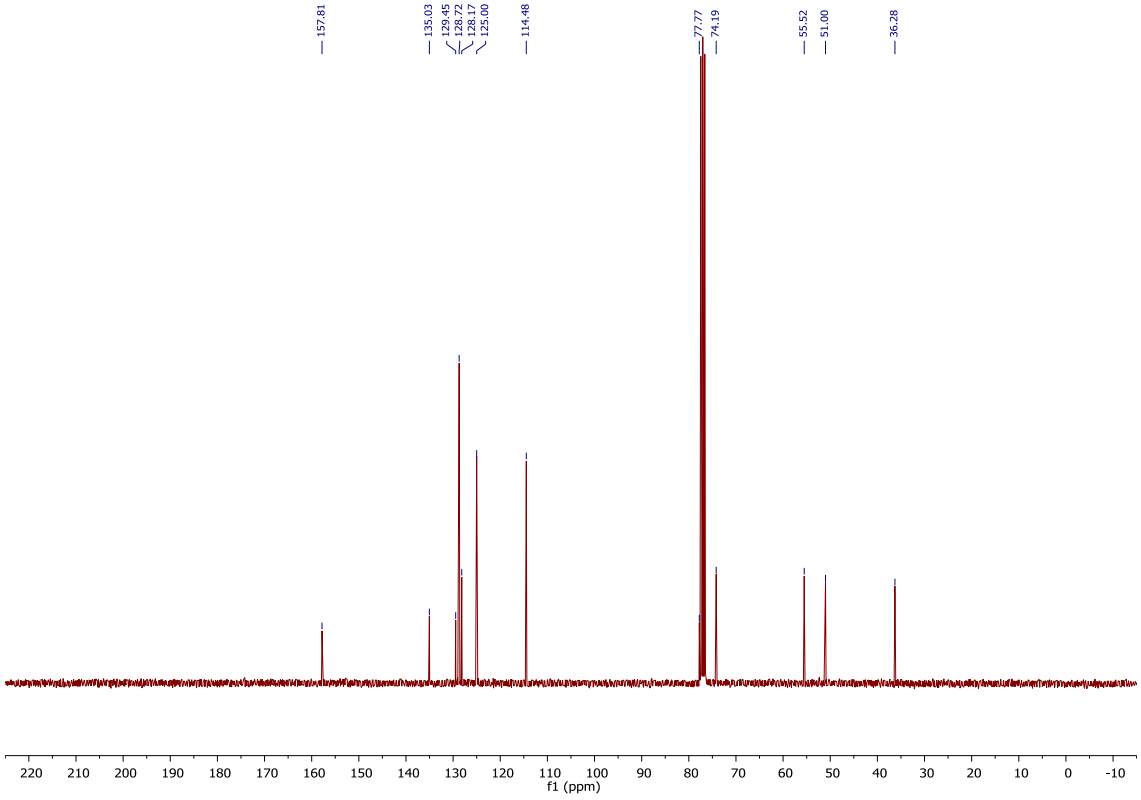


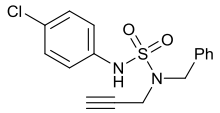
1f

300 MHz, ^{1}H NMR, $CDCl_3$



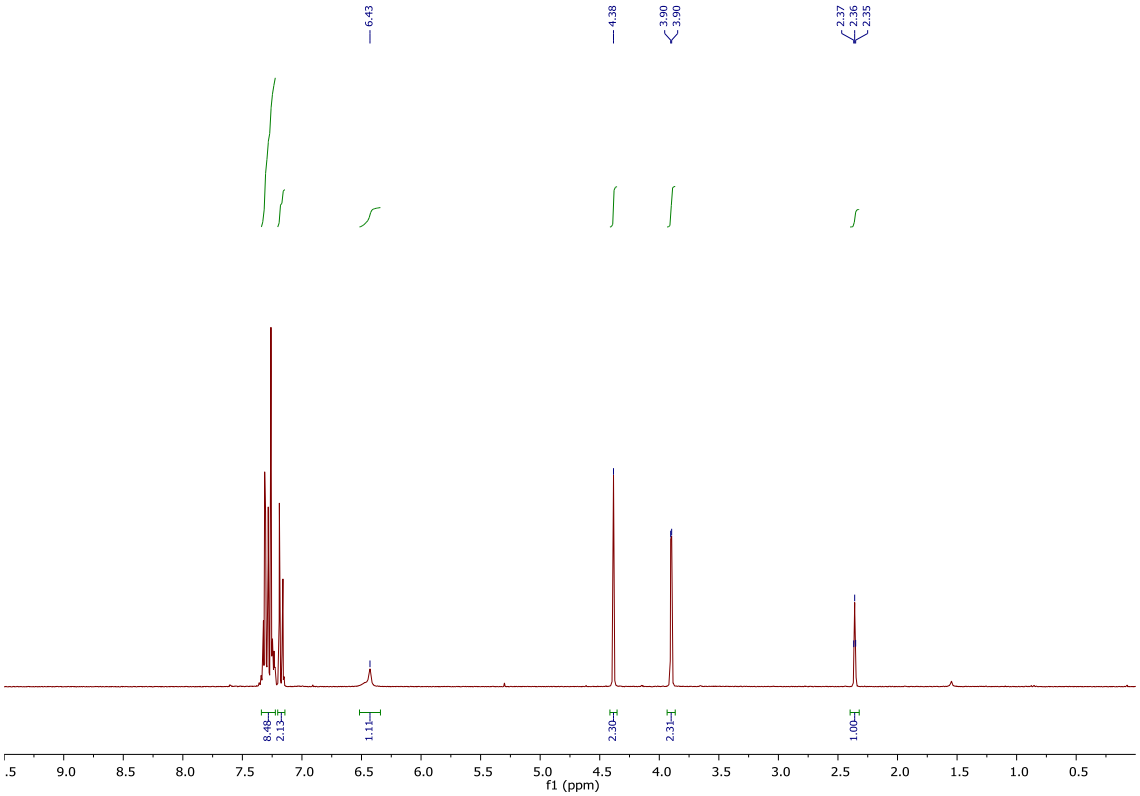
75 MHz, ^{13}C NMR, $CDCl_3$



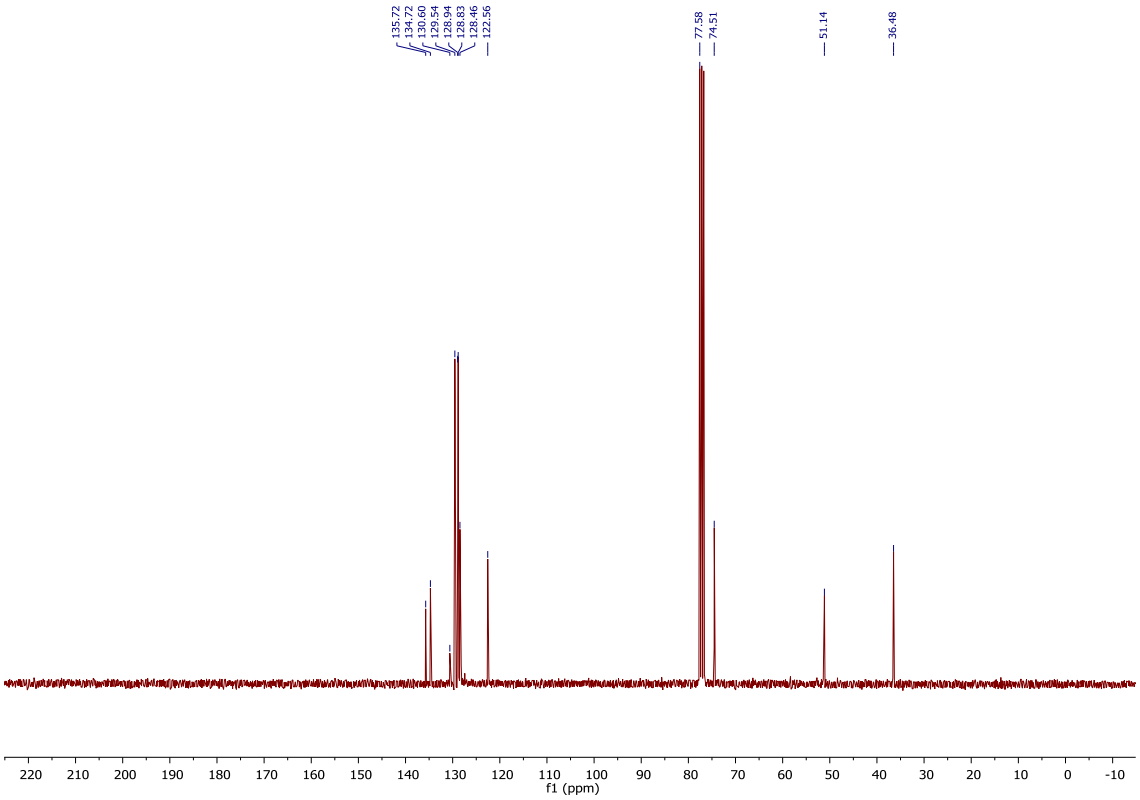


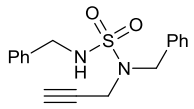
1g

300 MHz, ^{1}H NMR, $CDCl_3$



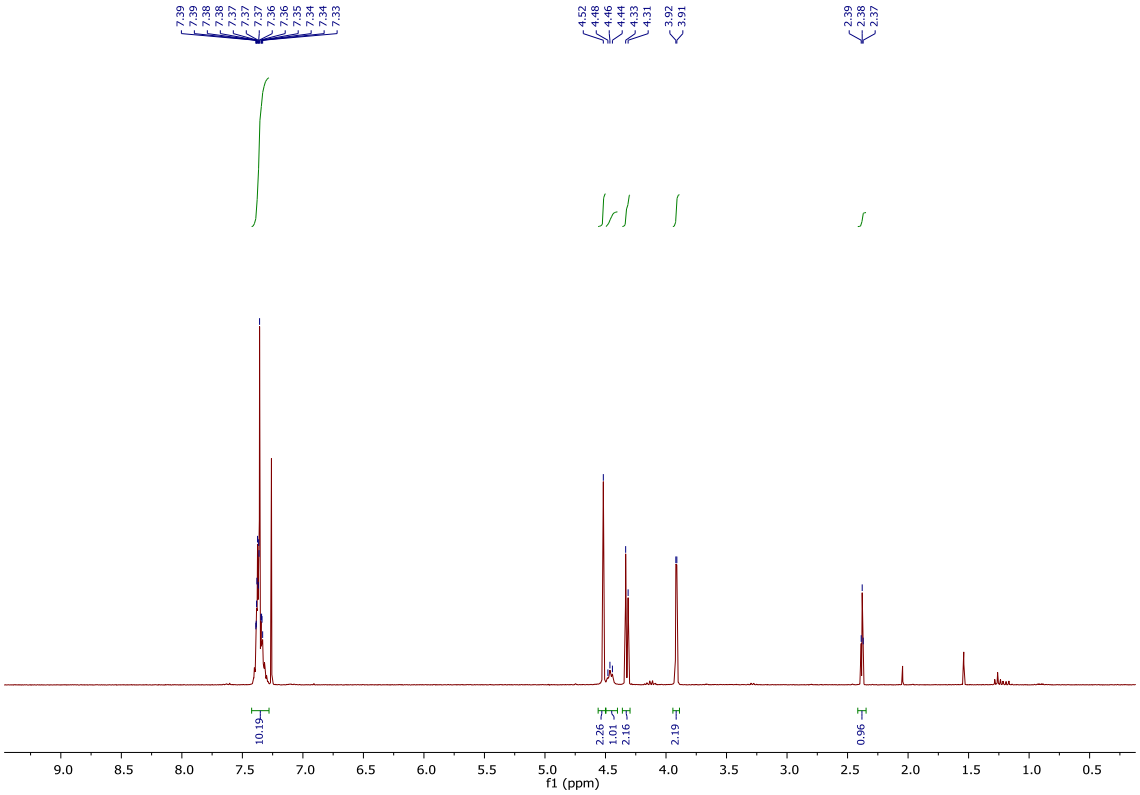
75 MHz, ^{13}C NMR, $CDCl_3$



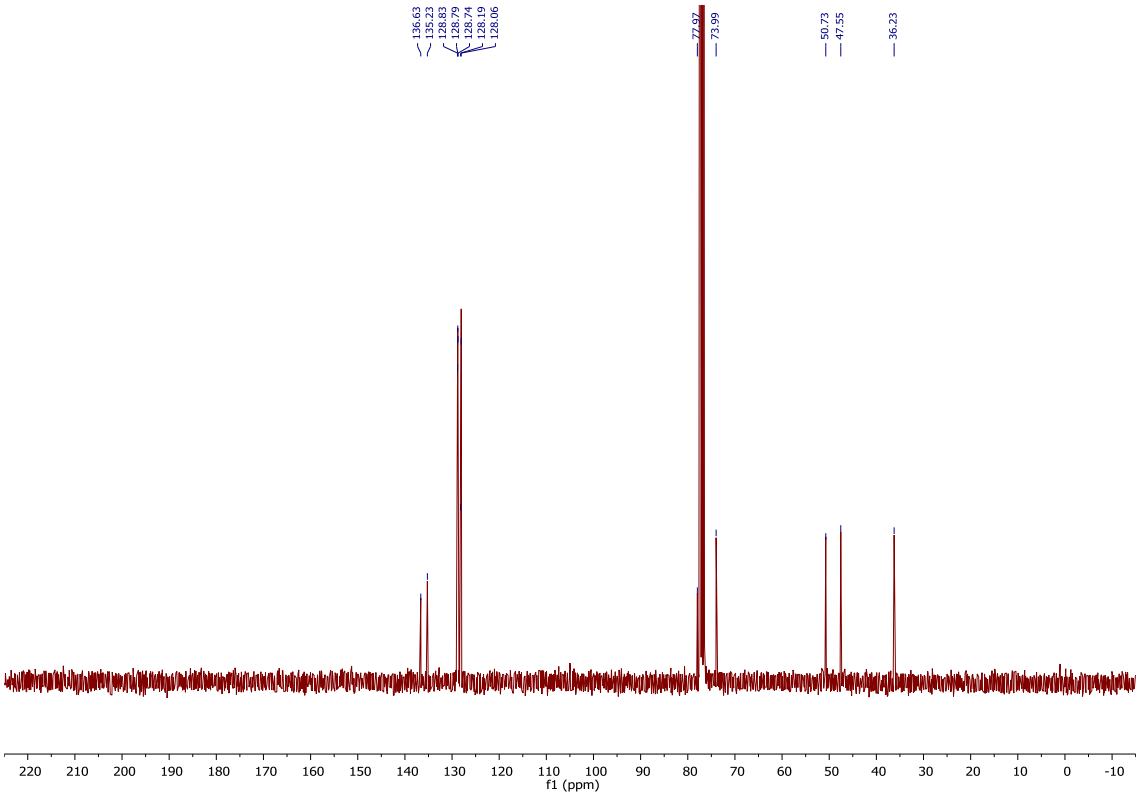


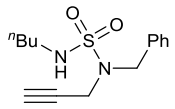
1h

300 MHz, ^{1}H NMR, $CDCl_3$



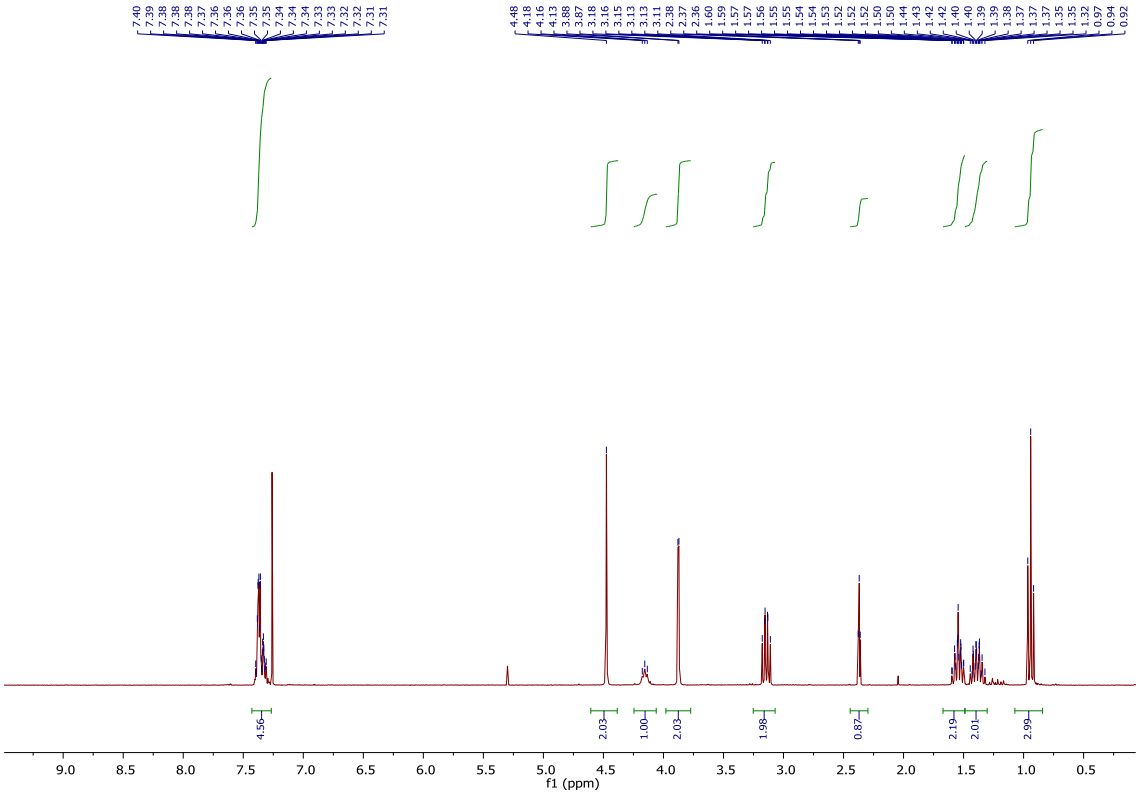
75 MHz, ^{13}C NMR, $CDCl_3$



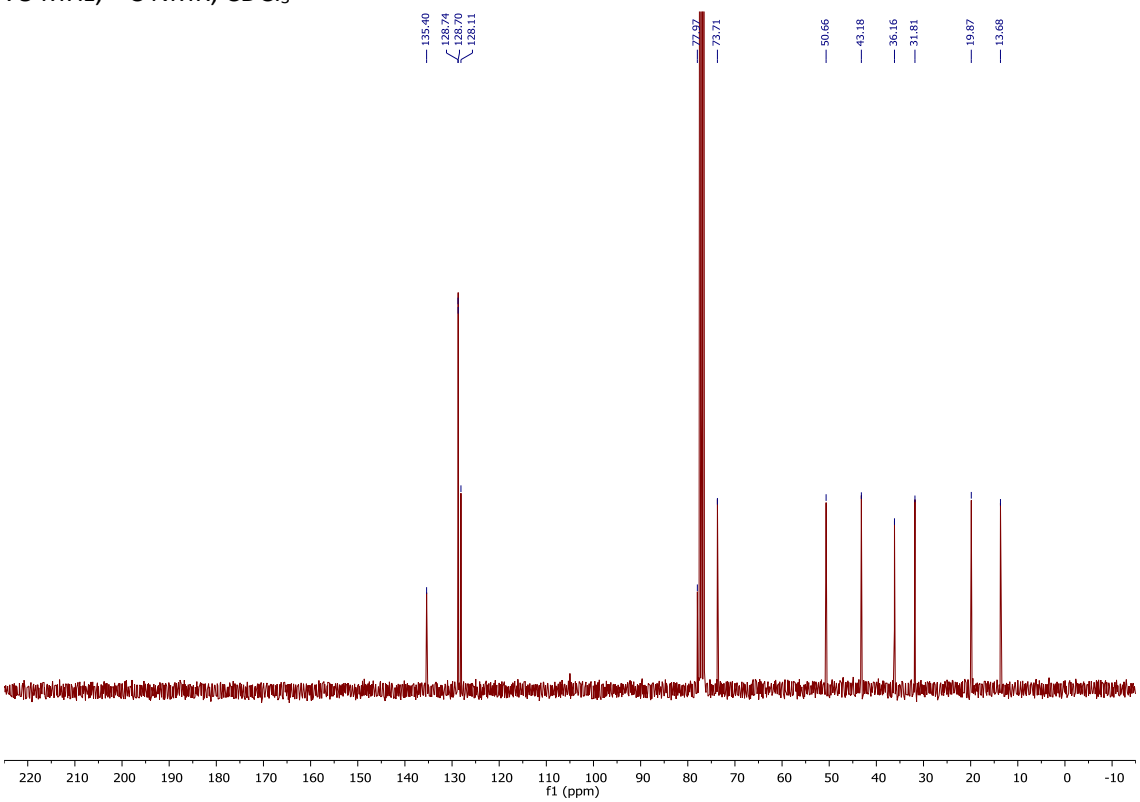


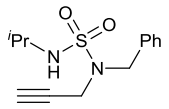
1i

300 MHz, ^{1}H NMR, $CDCl_3$



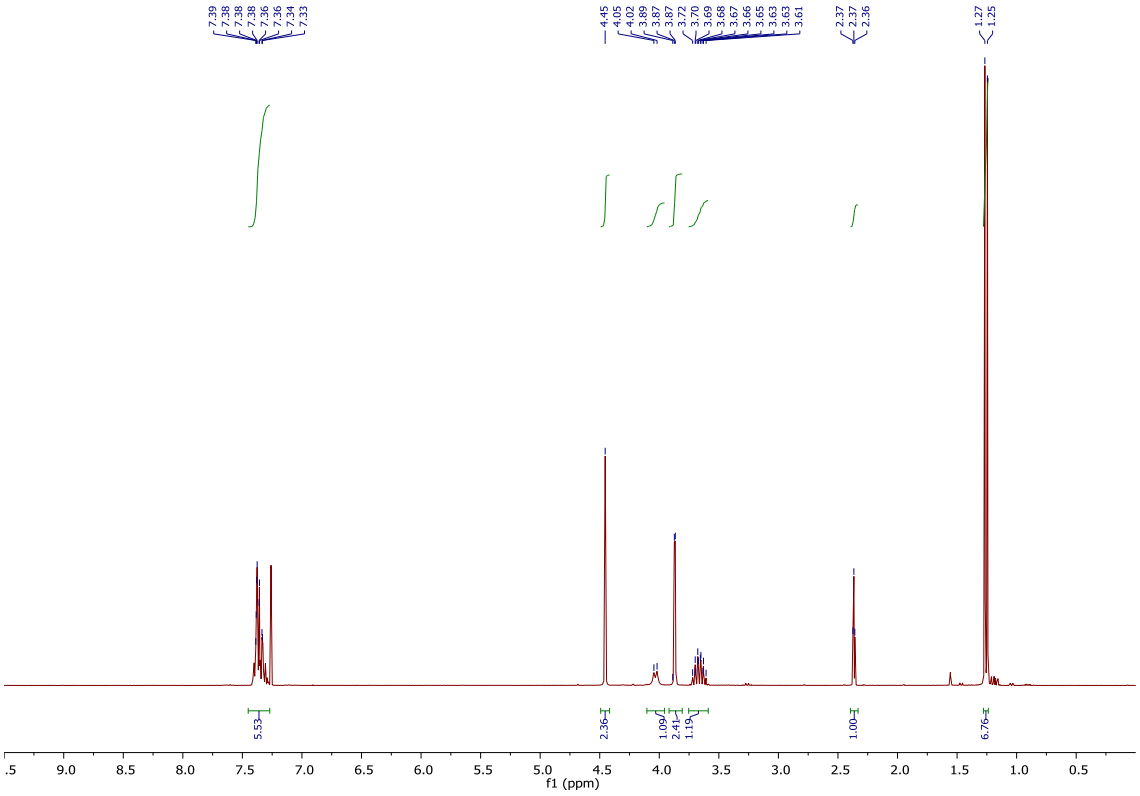
75 MHz, ^{13}C NMR, $CDCl_3$



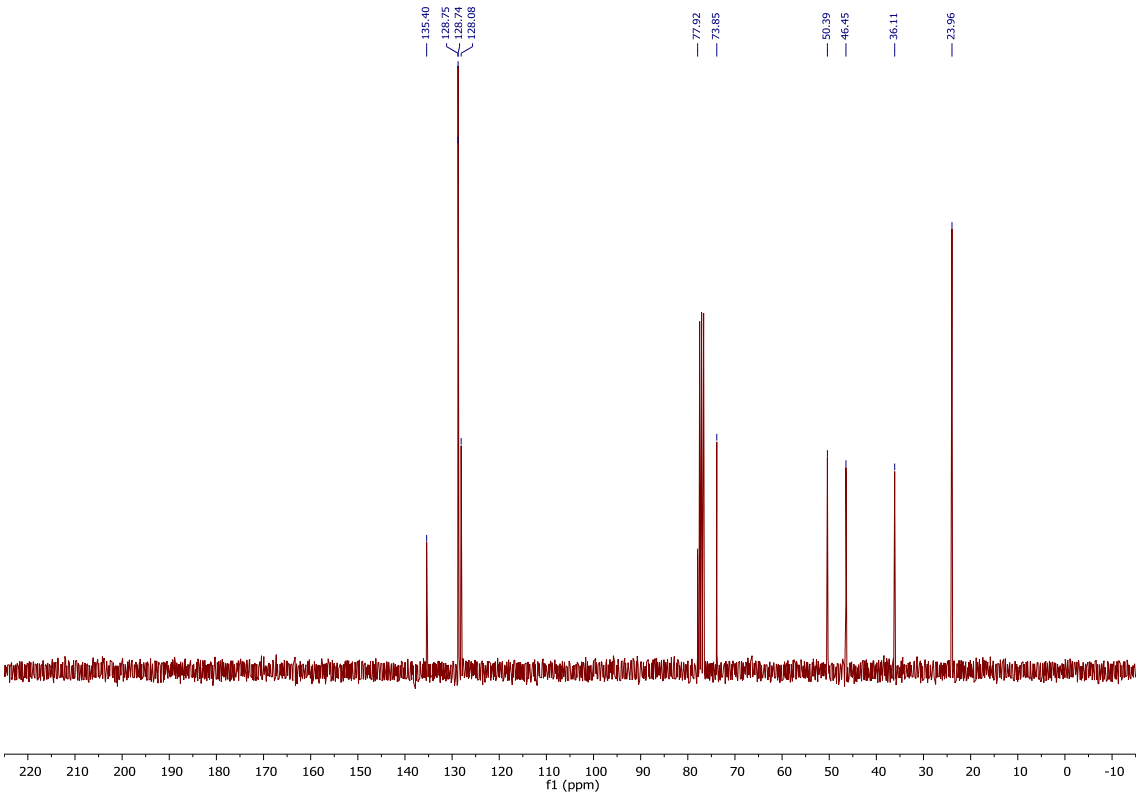


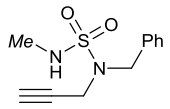
1j

300 MHz, ^{1}H NMR, $CDCl_3$



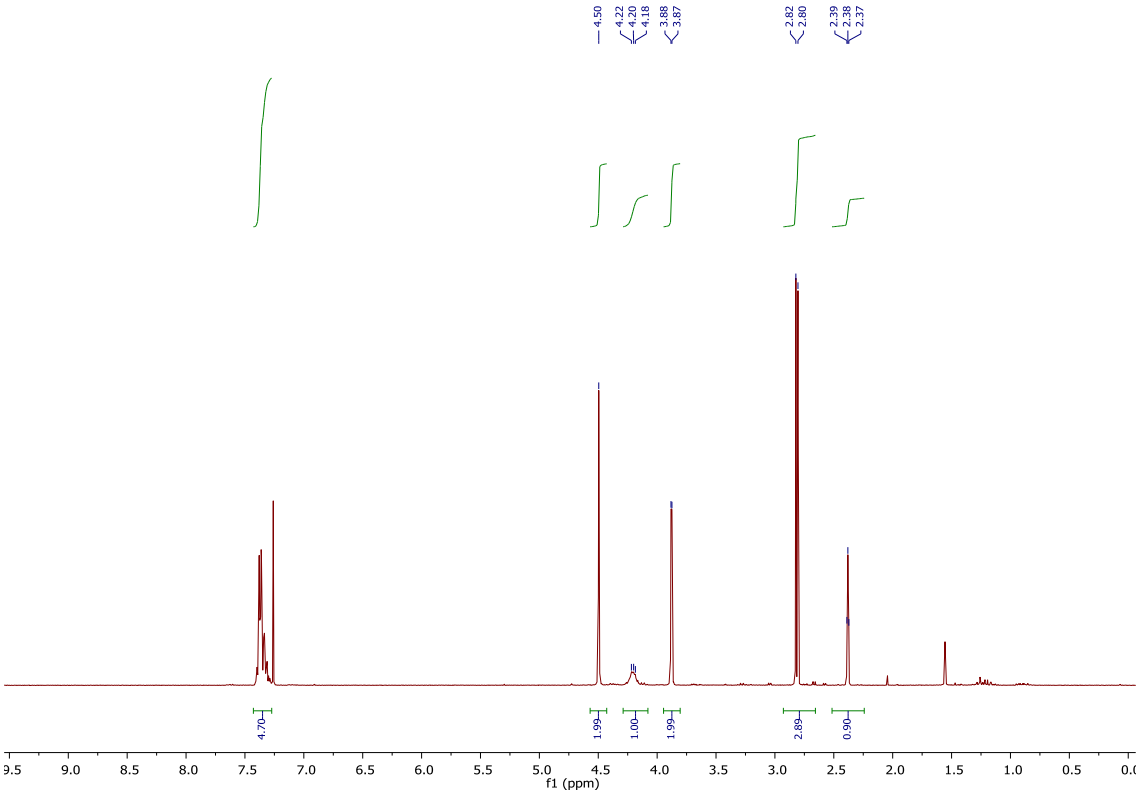
75 MHz, ^{13}C NMR, $CDCl_3$



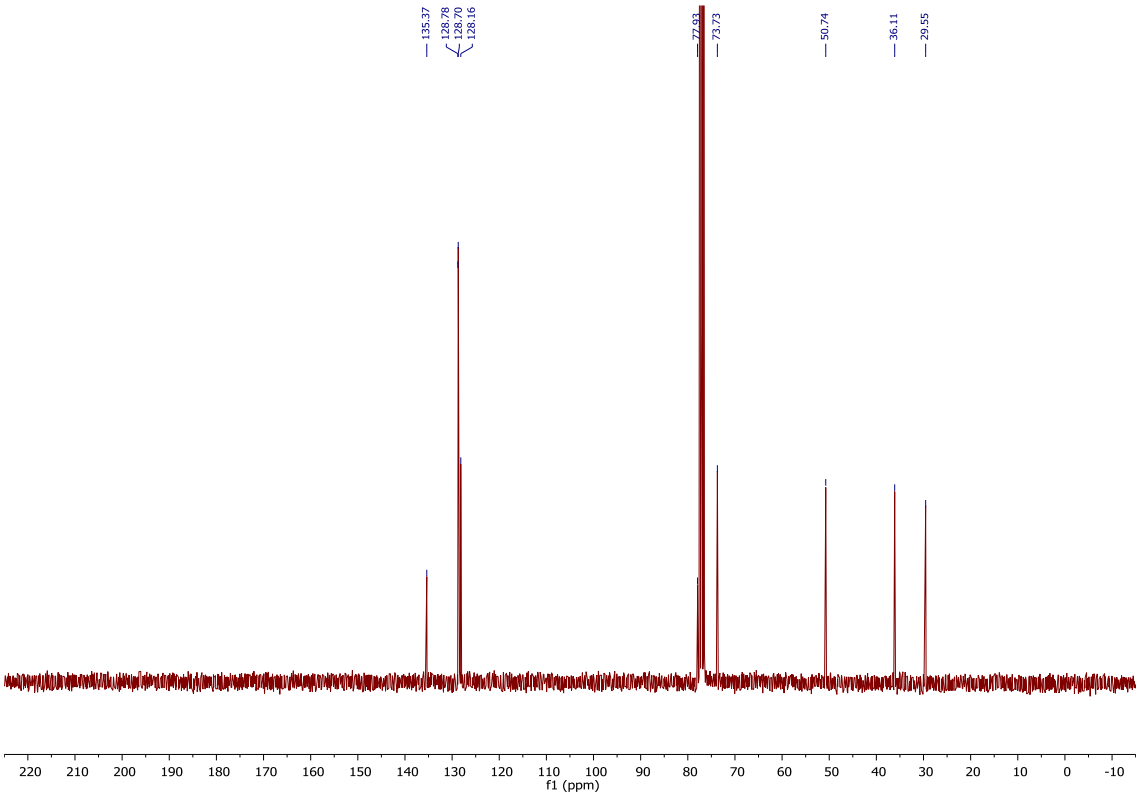


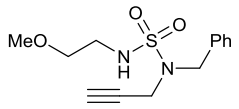
1k

300 MHz, ^{1}H NMR, $CDCl_3$



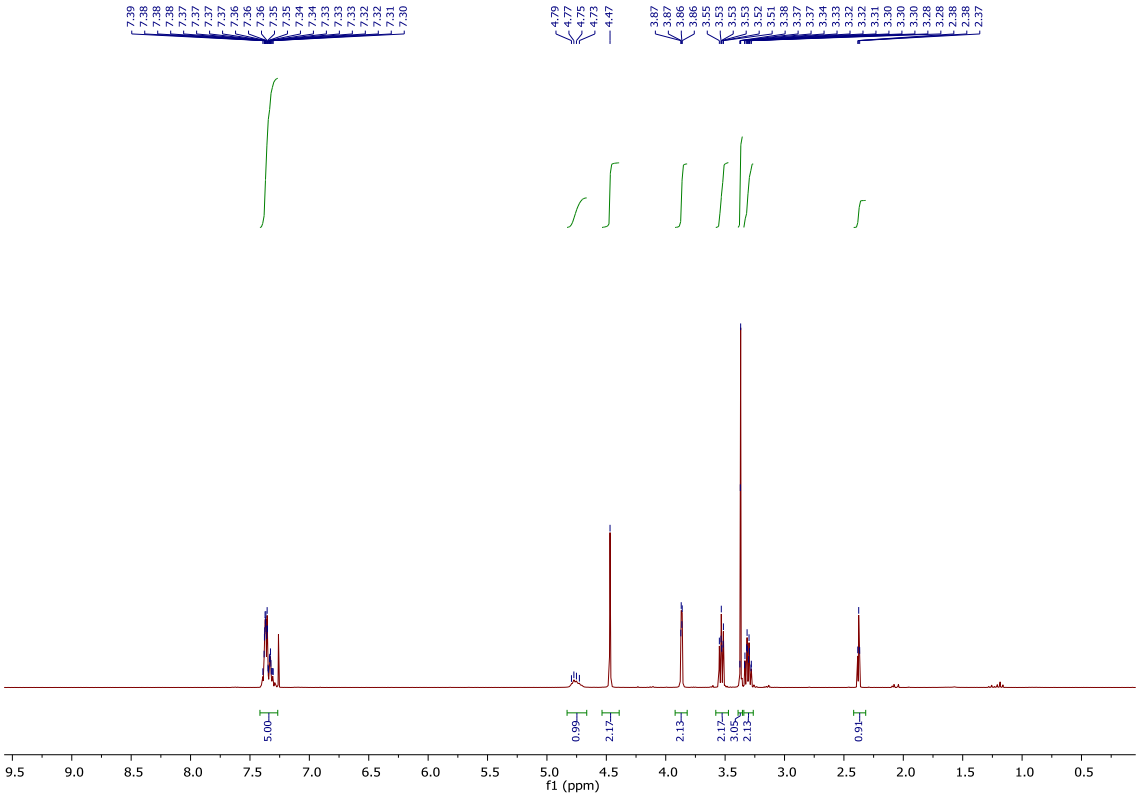
75 MHz, ^{13}C NMR, $CDCl_3$



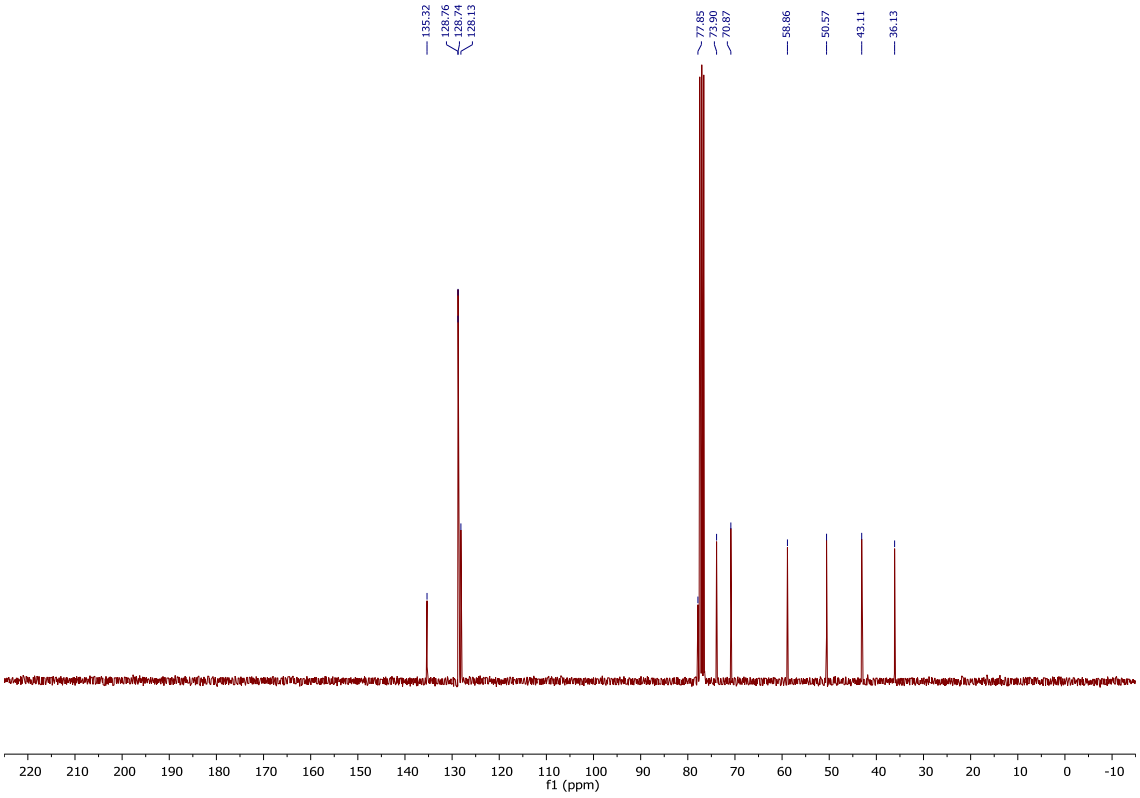


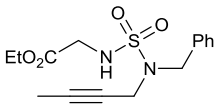
1l

300 MHz, ^{1}H NMR, $CDCl_3$



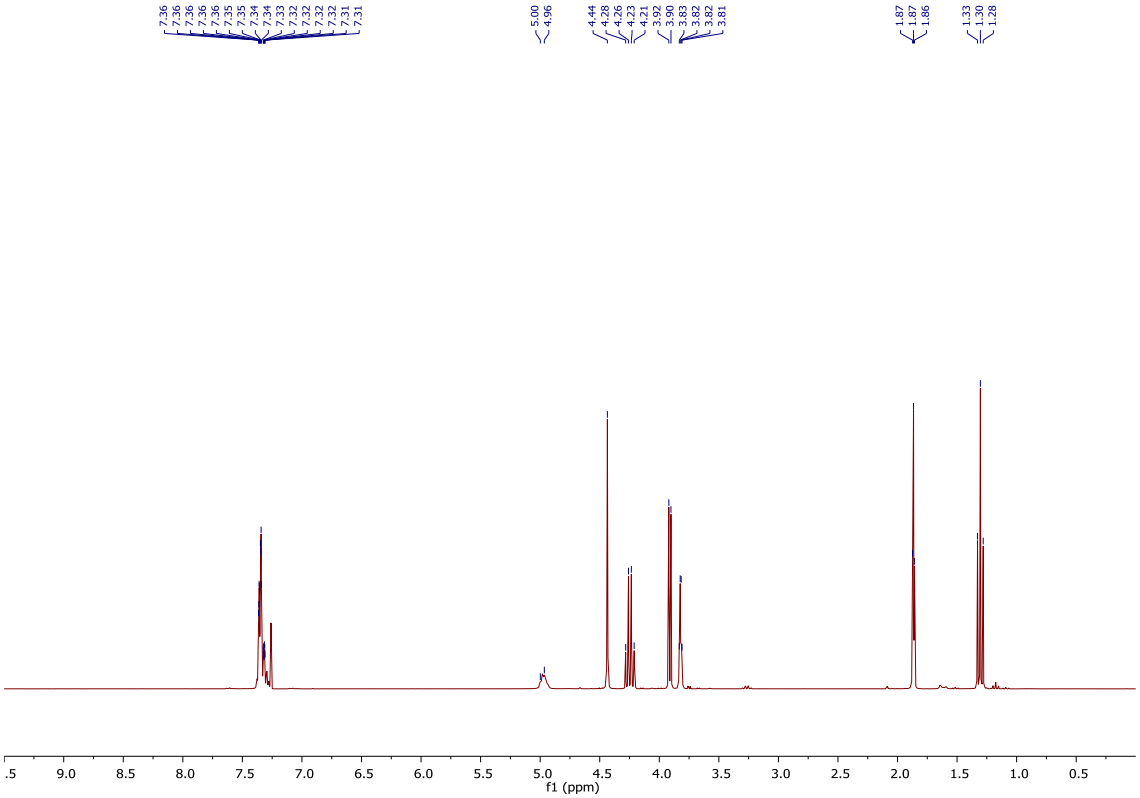
75 MHz, ^{13}C NMR, $CDCl_3$



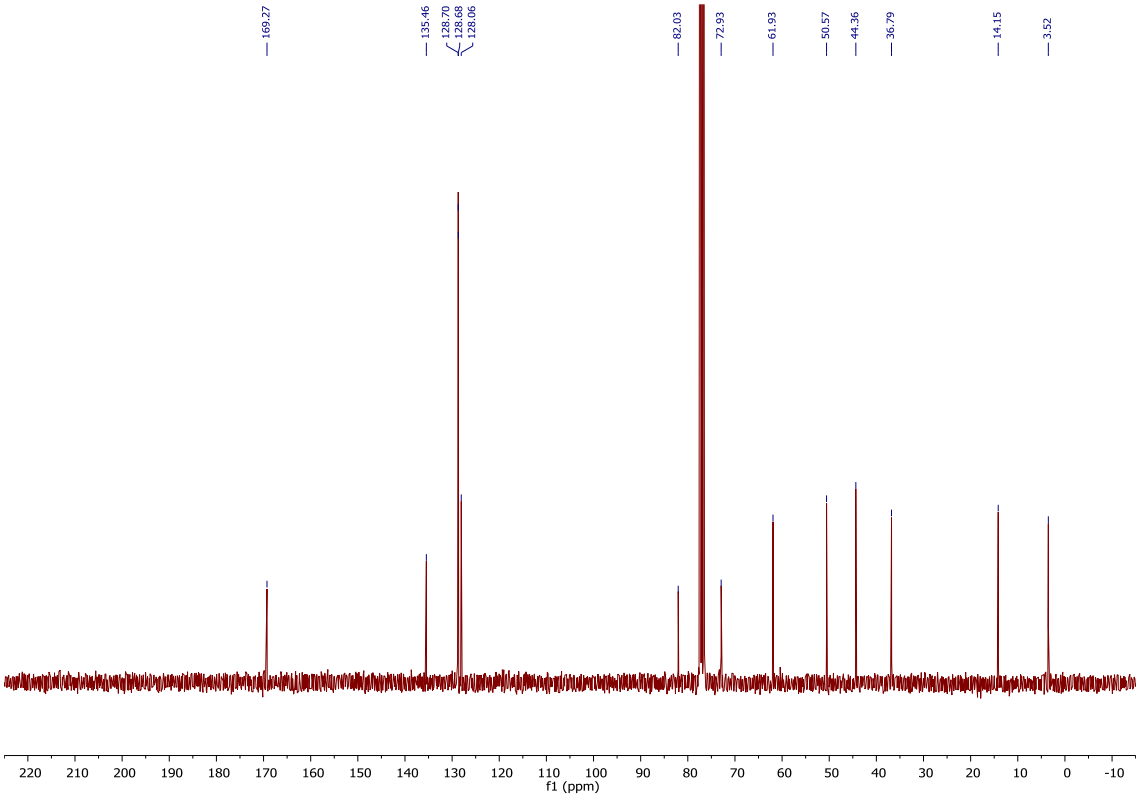


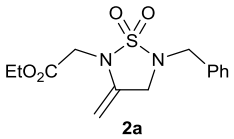
1m

300 MHz, ^{1}H NMR, $CDCl_3$



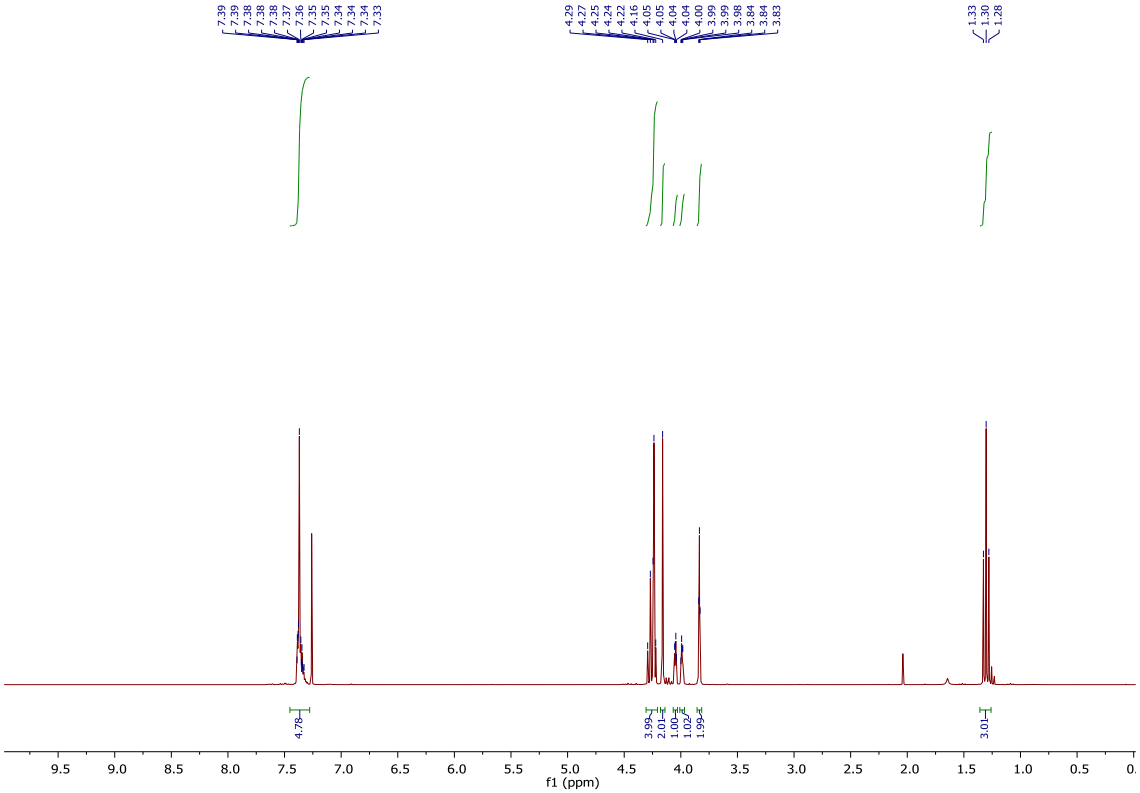
75 MHz, ^{13}C NMR, $CDCl_3$



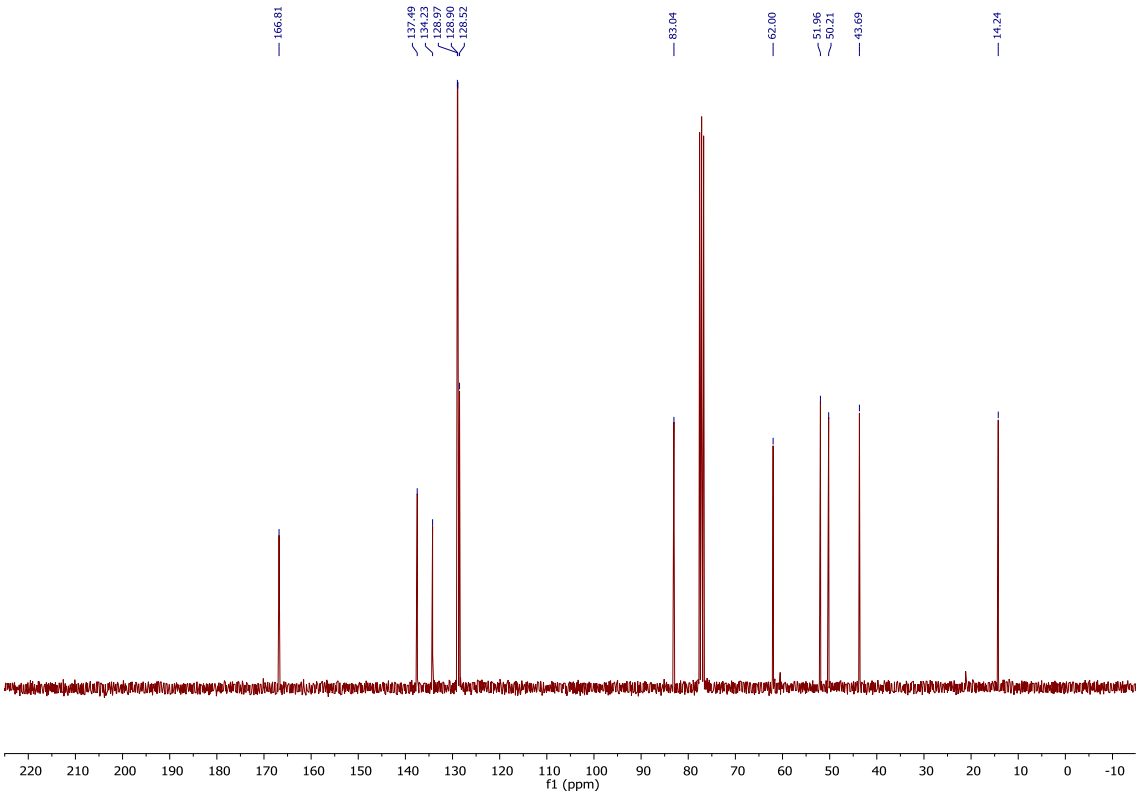


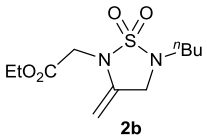
2a

300 MHz, ^{1}H NMR, $CDCl_3$



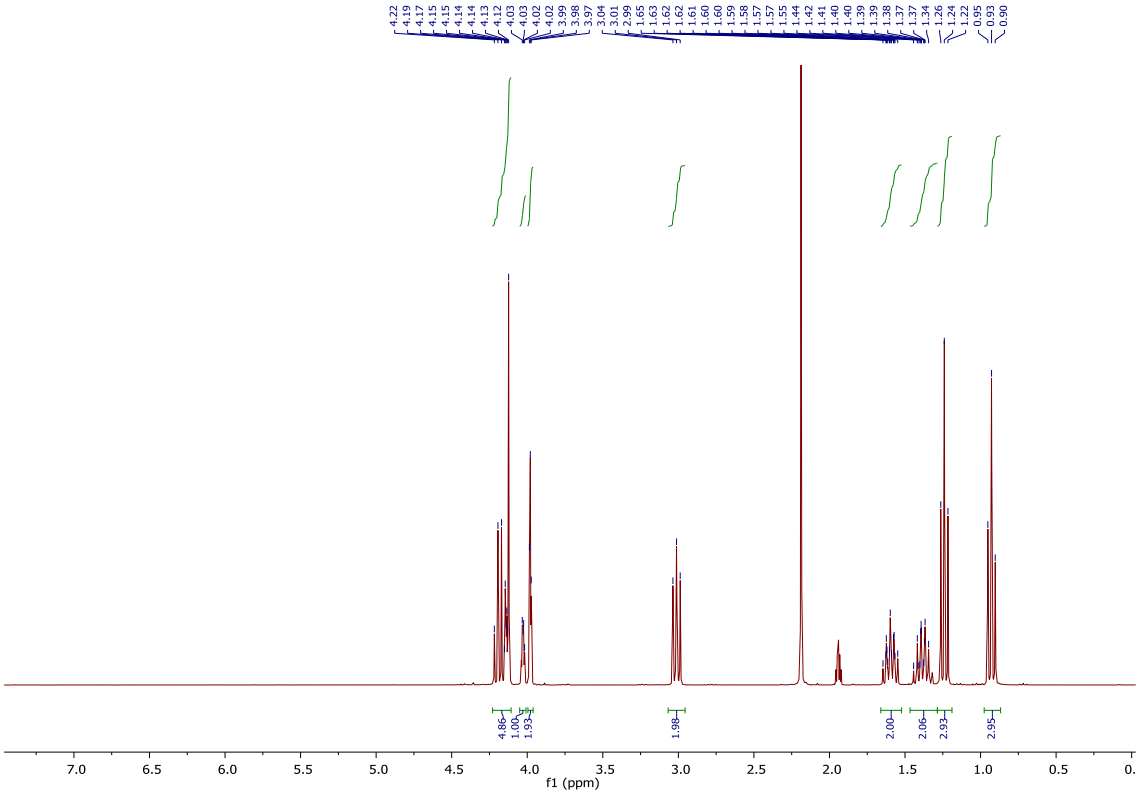
75 MHz, ^{13}C NMR, $CDCl_3$



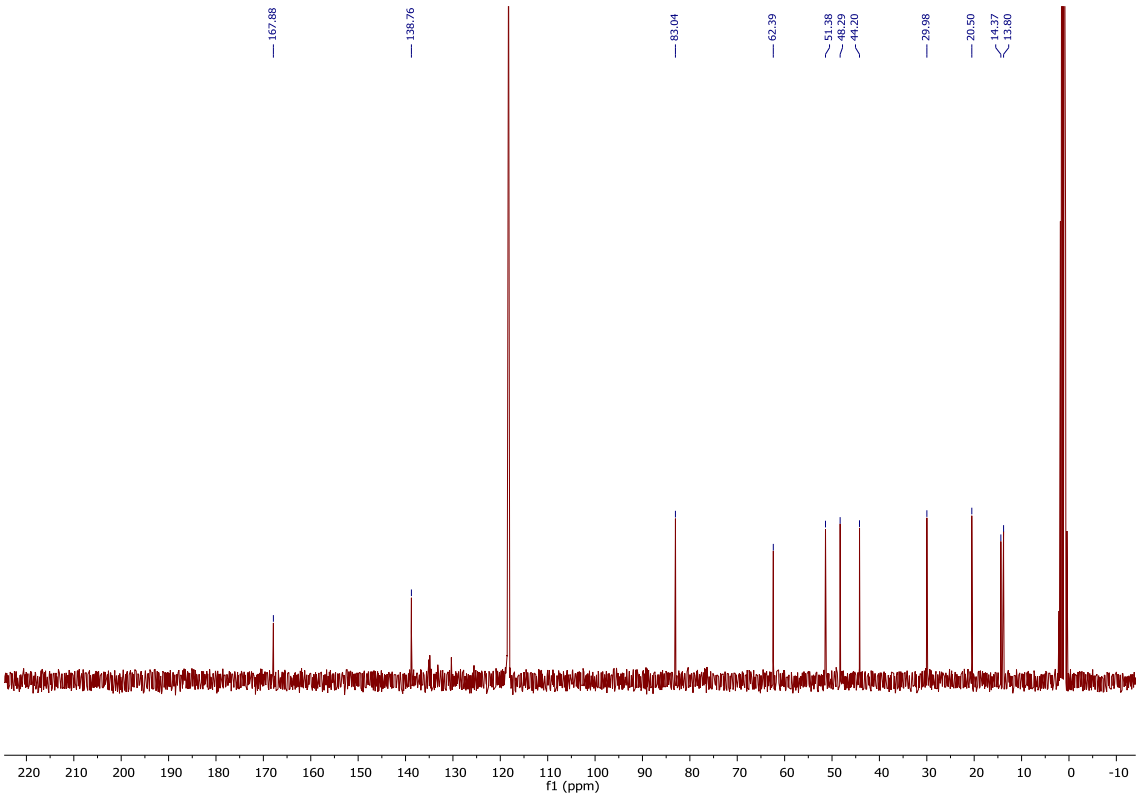


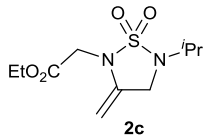
2b

300 MHz, ^{1}H NMR, CD_3CN



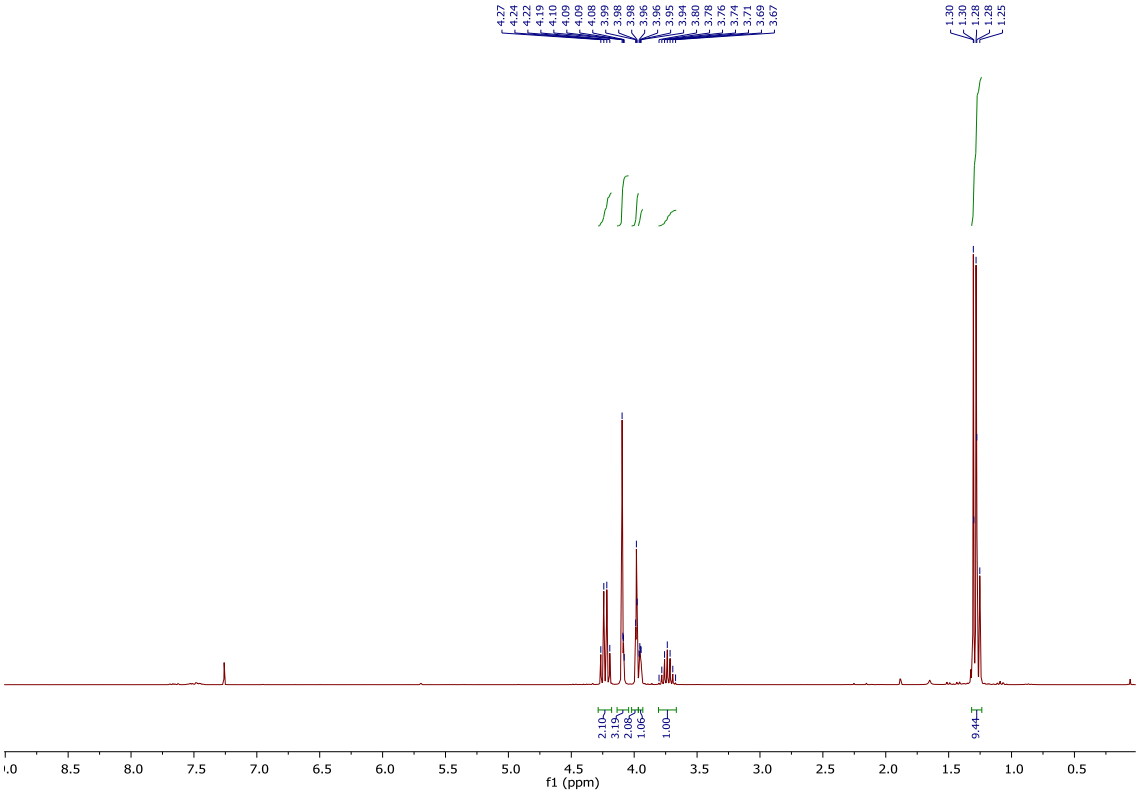
75 MHz, ^{13}C NMR, CD_3CN



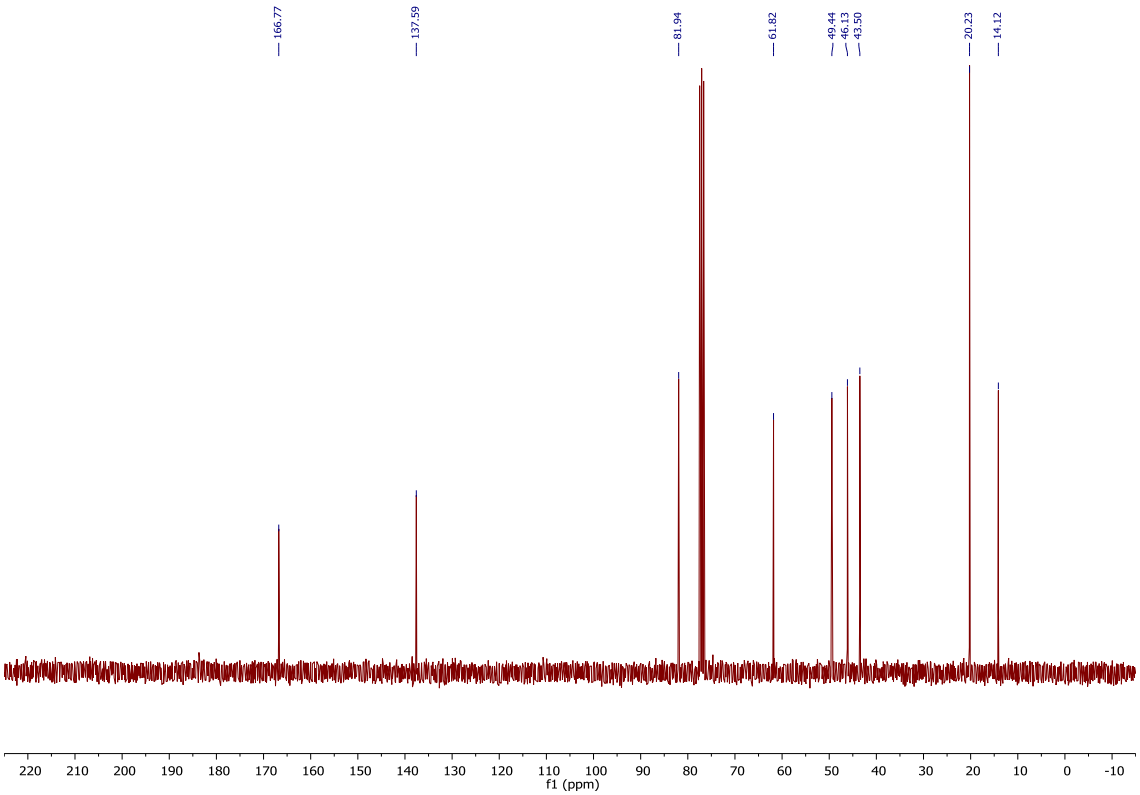


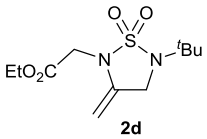
2c

300 MHz, ^{1}H NMR, $CDCl_3$



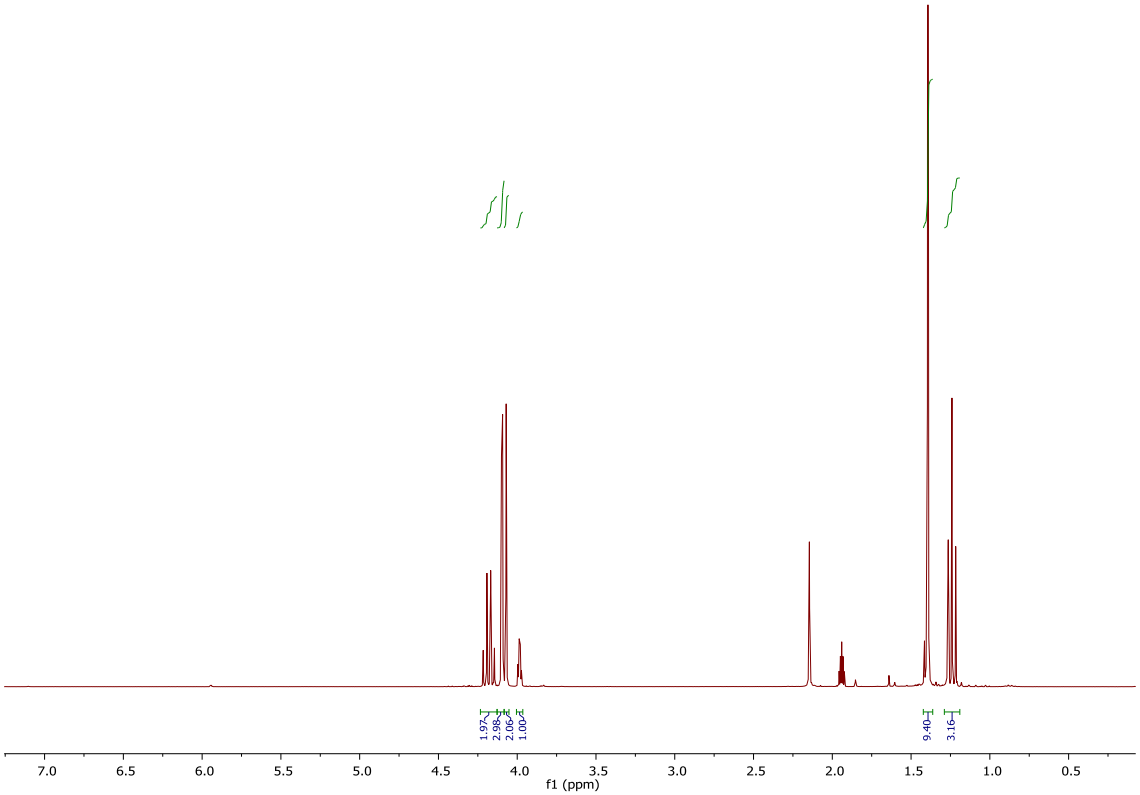
75 MHz, ^{13}C NMR, $CDCl_3$



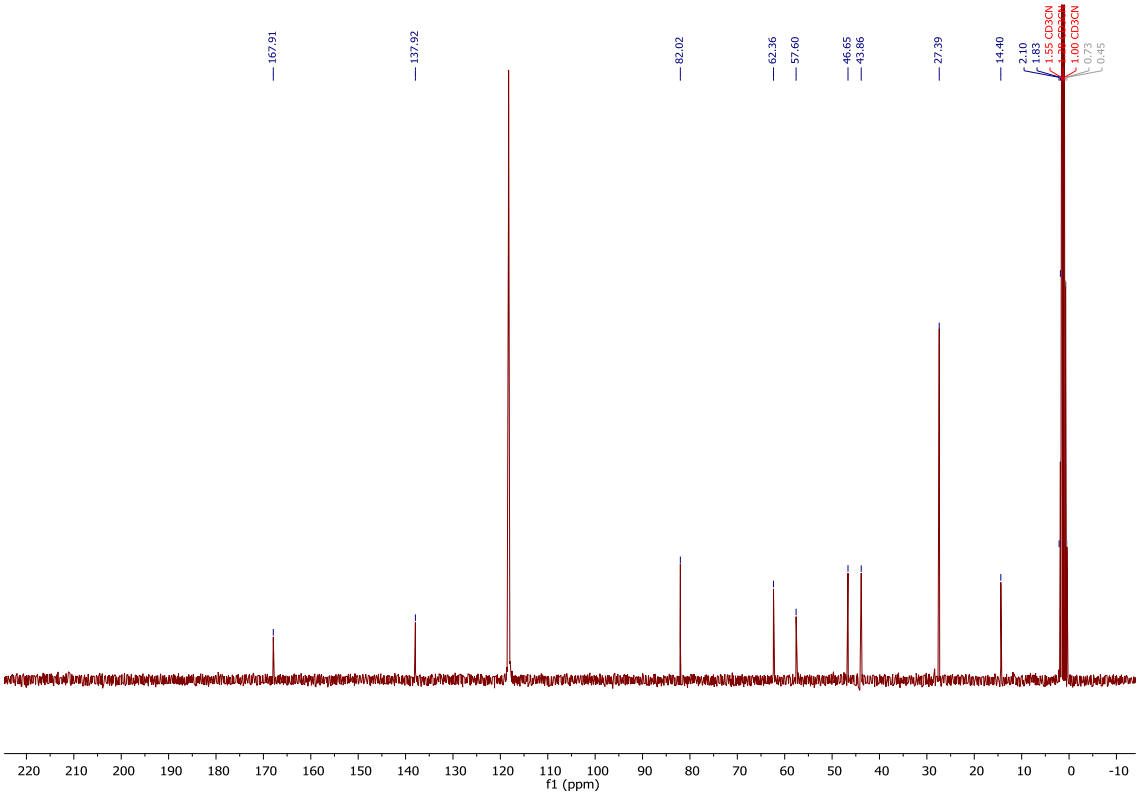


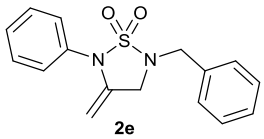
2d

300 MHz, ^{1}H NMR, CD_3CN



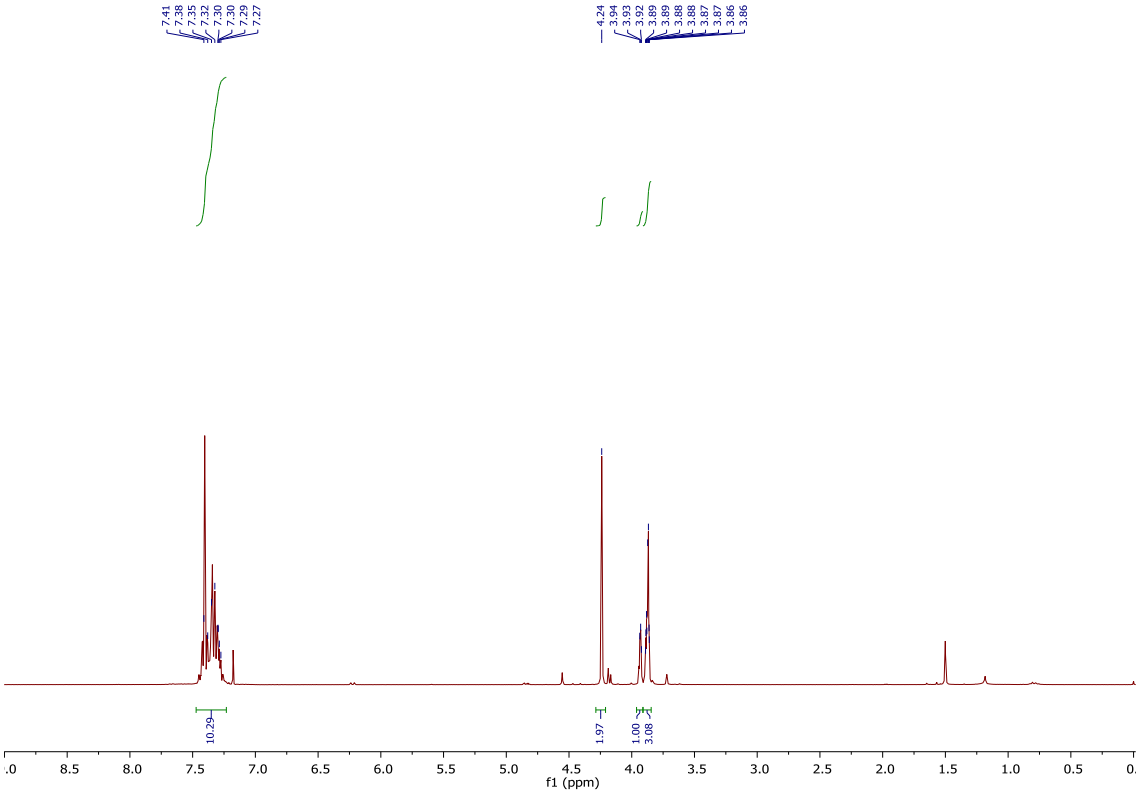
101 MHz, ^{13}C NMR, CD_3CN



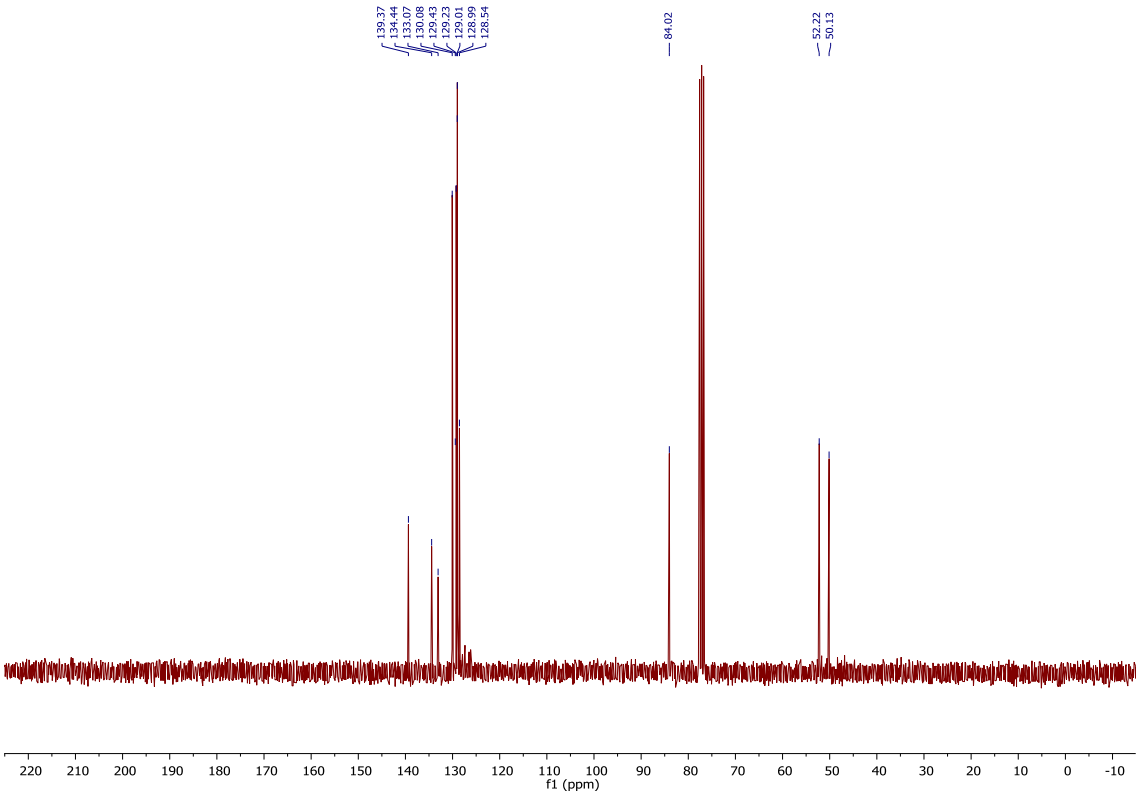


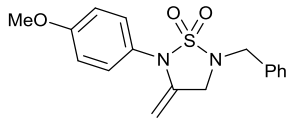
2e

300 MHz, ^{1}H NMR, $CDCl_3$



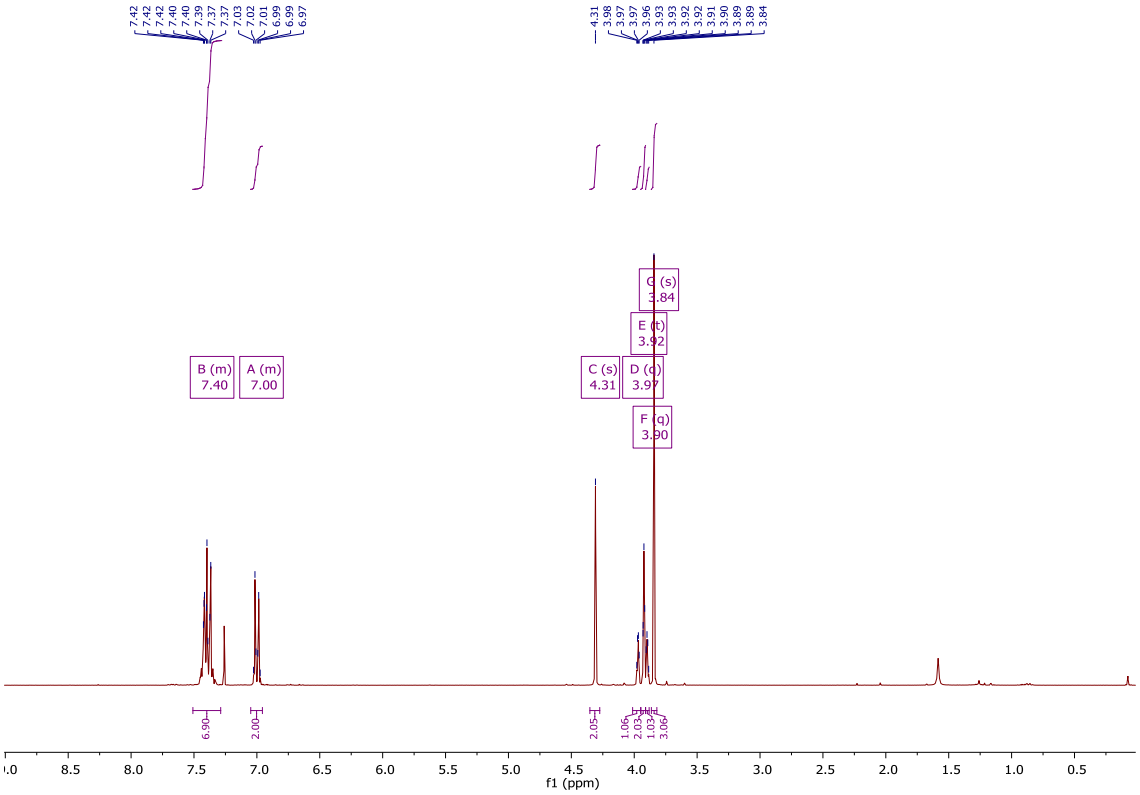
75 MHz, ^{13}C NMR, $CDCl_3$



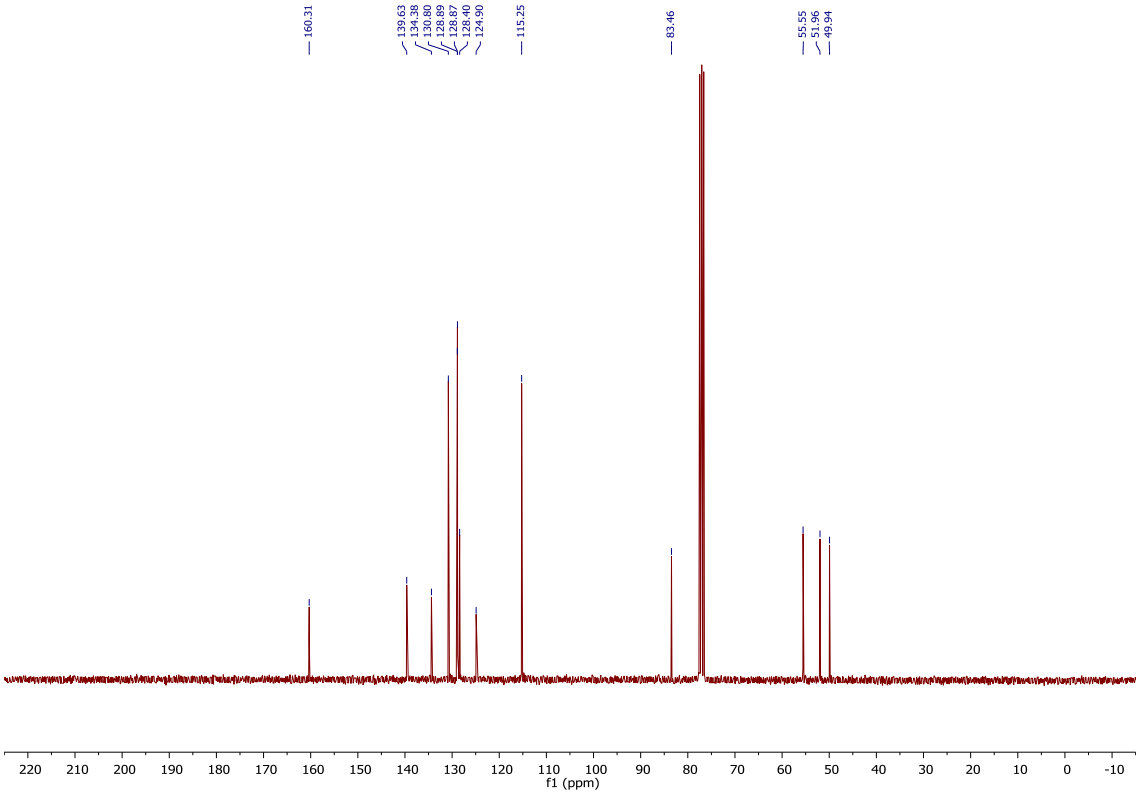


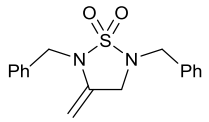
2f

300 MHz, ^{1}H NMR, $CDCl_3$



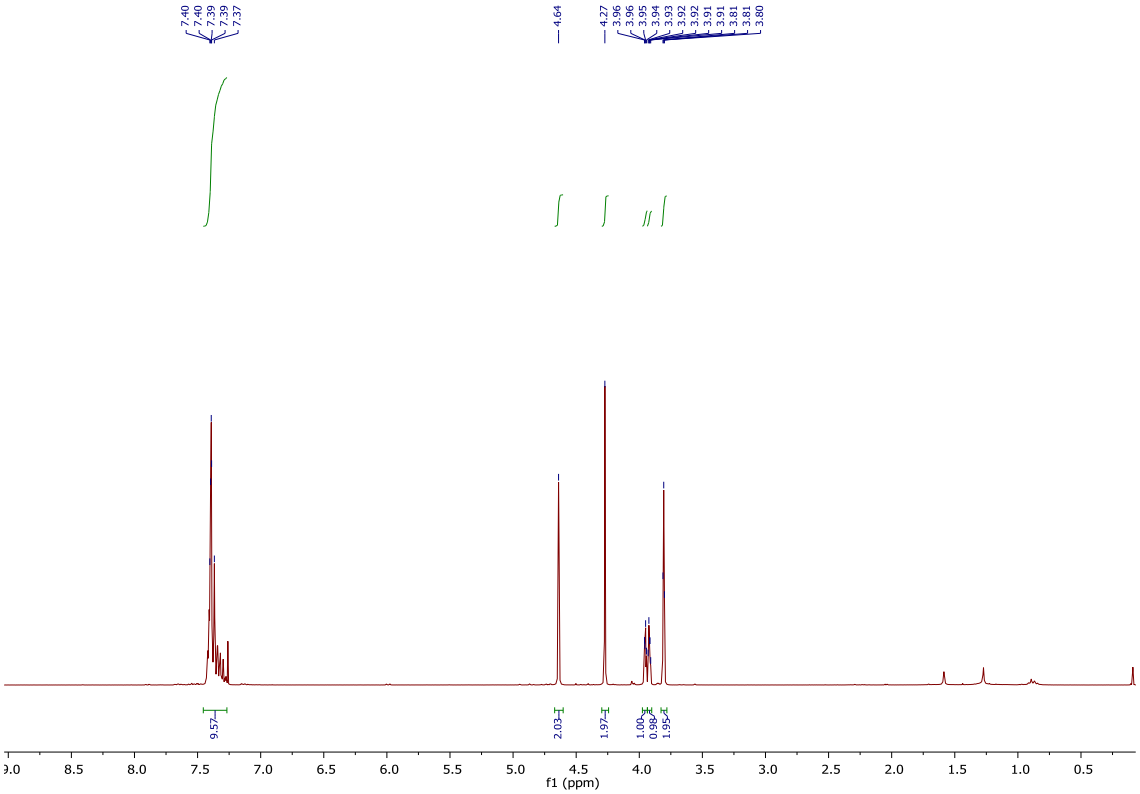
75 MHz, ^{13}C NMR, $CDCl_3$



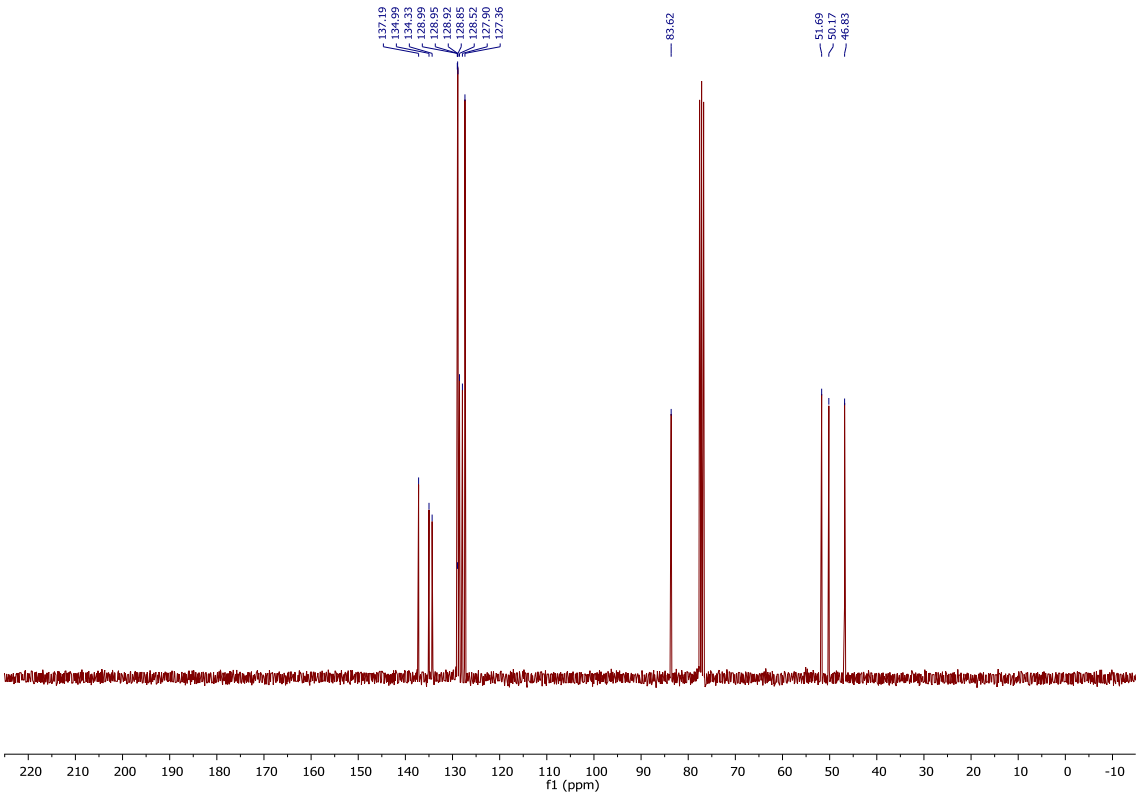


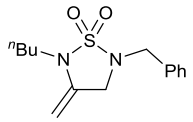
2h

300 MHz, ^{1}H NMR, $CDCl_3$



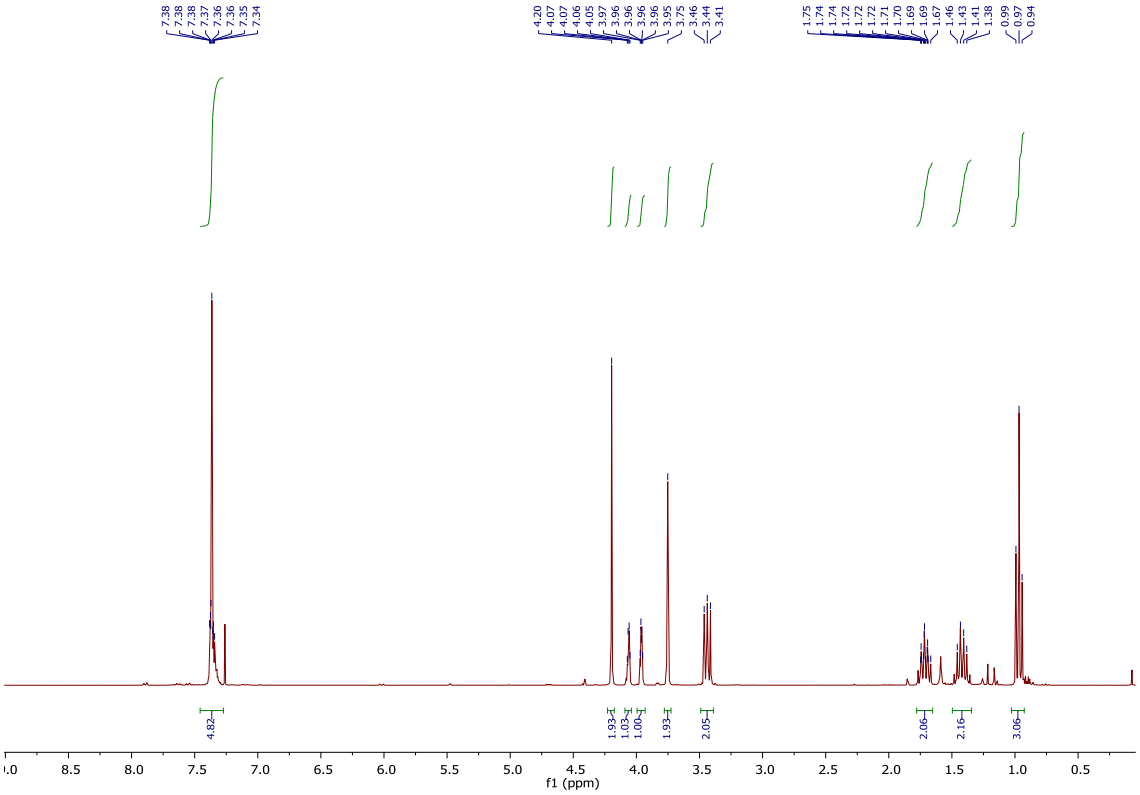
75 MHz, ^{13}C NMR, $CDCl_3$



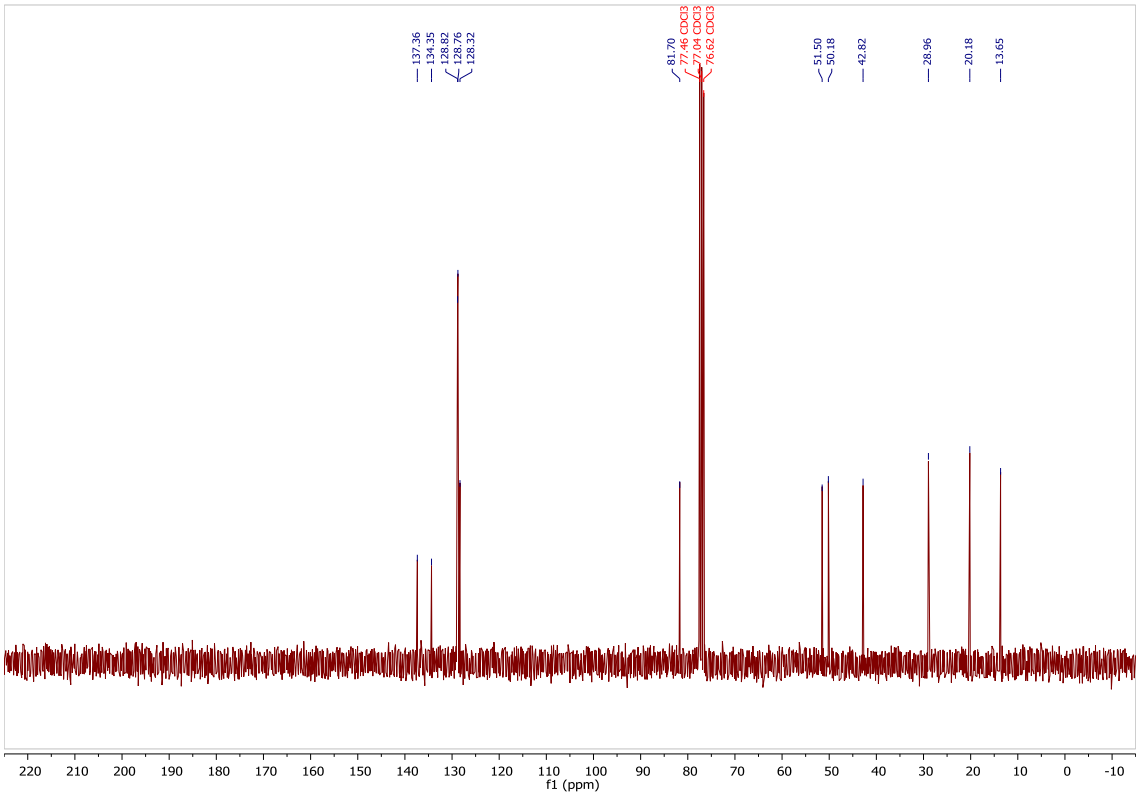


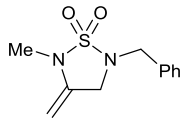
2i

300 MHz, ^{1}H NMR, $CDCl_3$



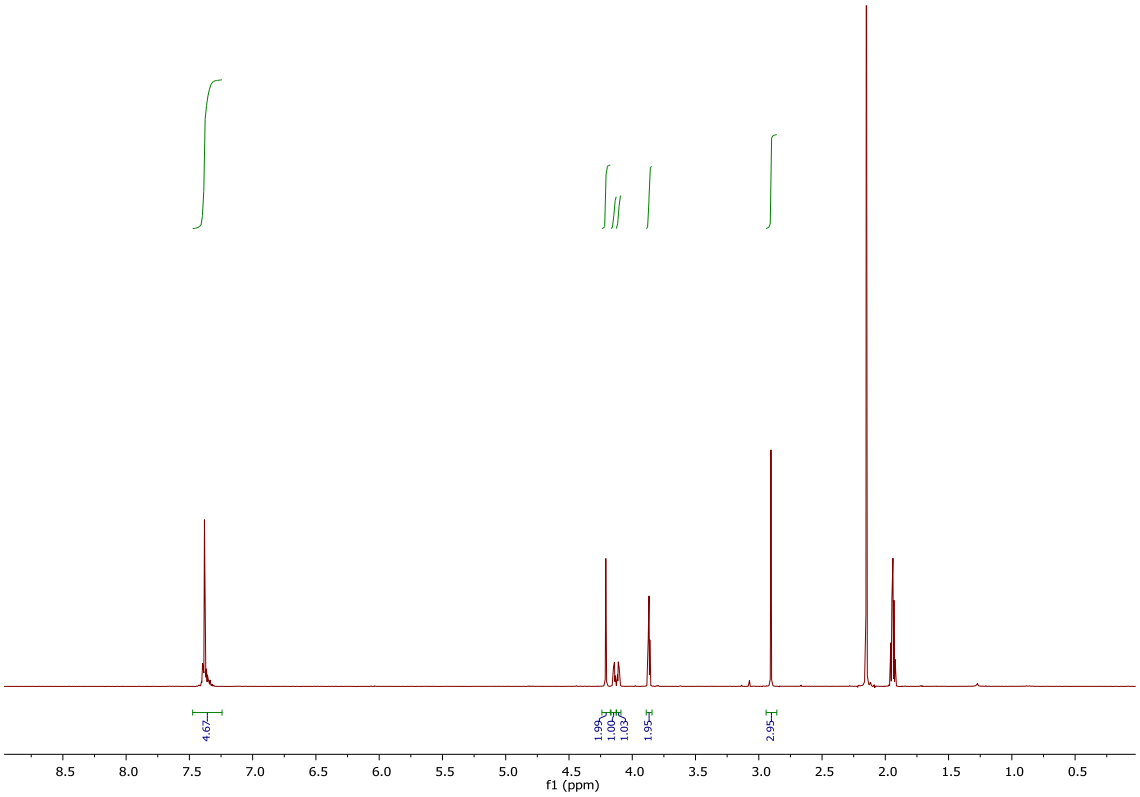
75 MHz, ^{13}C NMR, $CDCl_3$



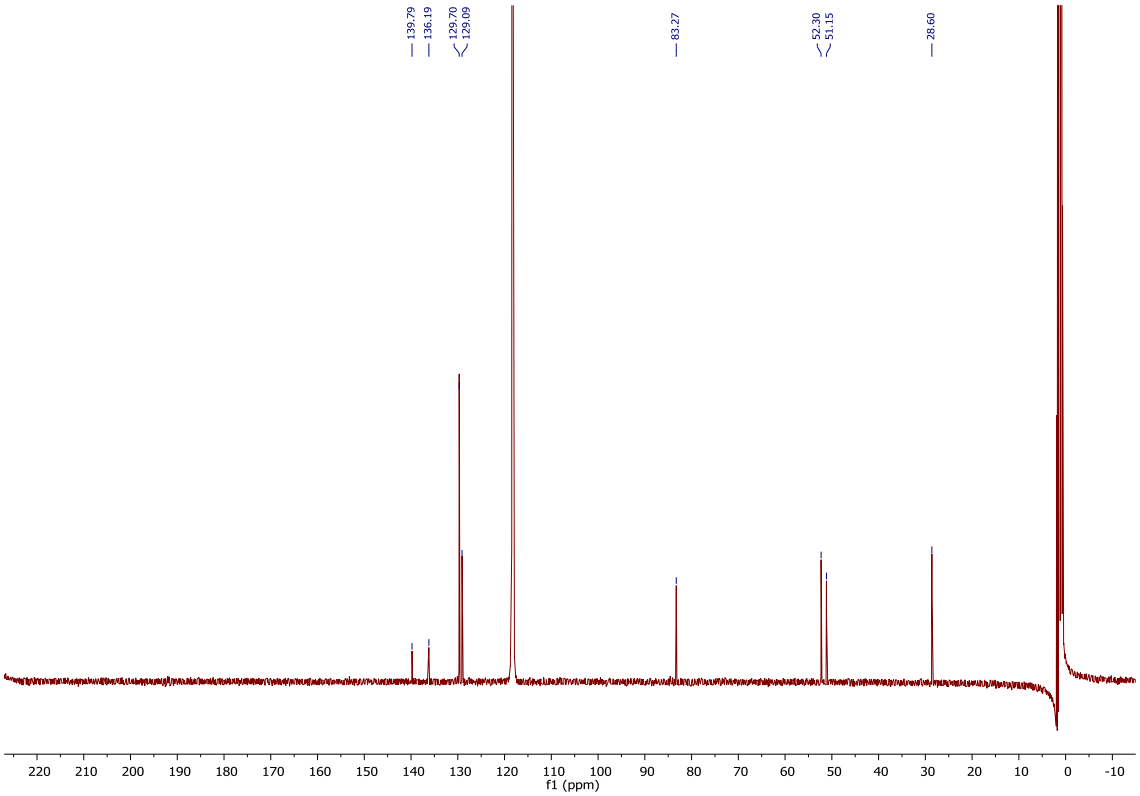


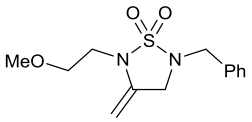
2k

300 MHz, ^{1}H NMR, CD_3CN



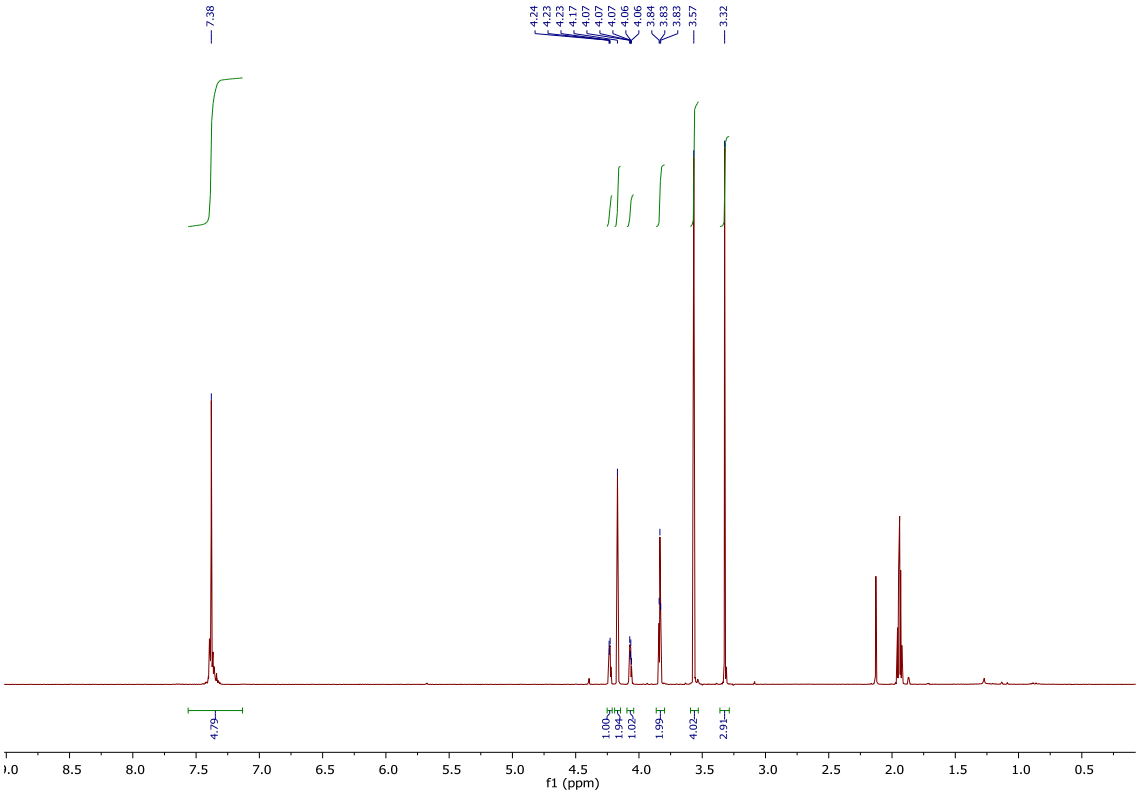
101 MHz, ^{13}C NMR, CD_3CN



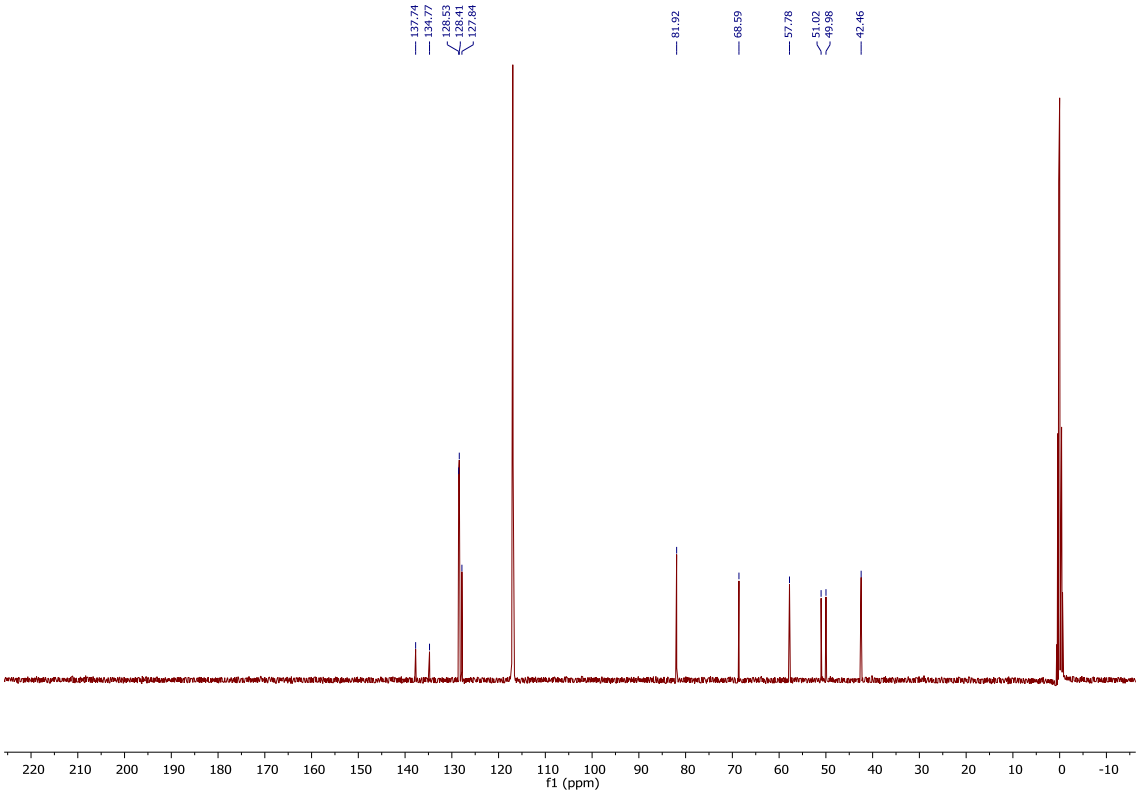


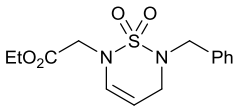
2l

300 MHz, ^{1}H NMR, CD_3CN



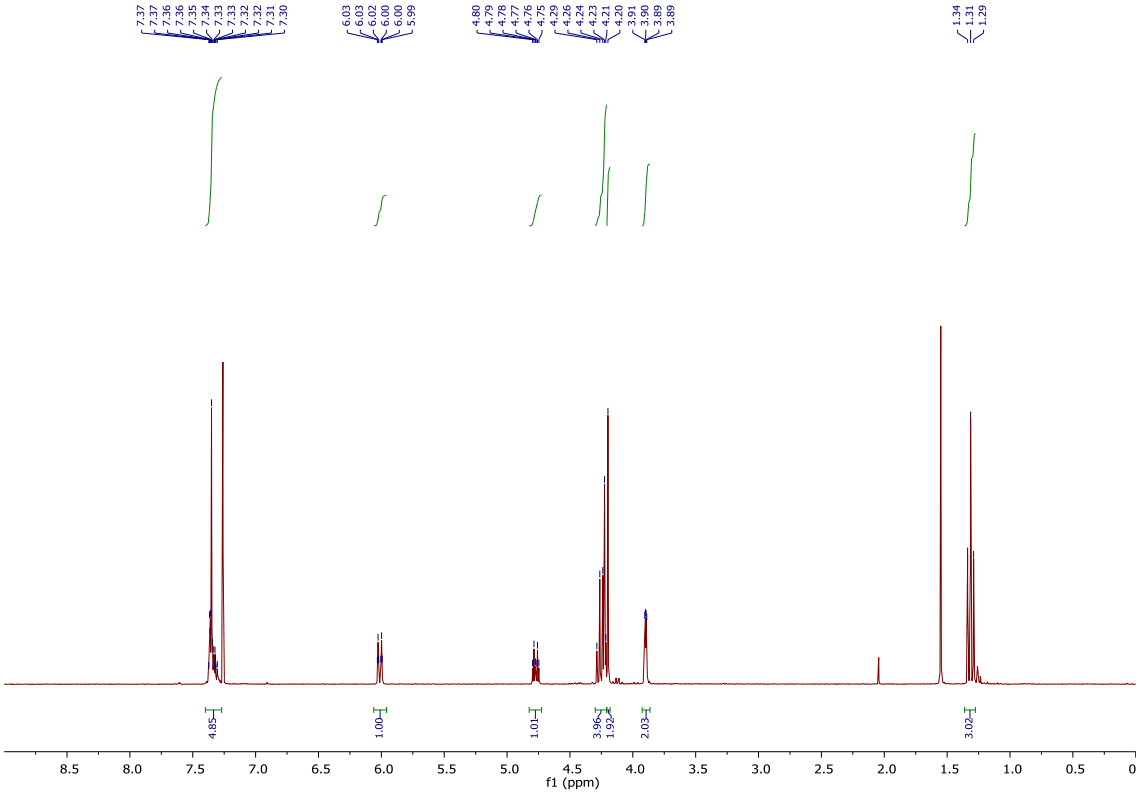
101 MHz, ^{13}C NMR, CD_3CN



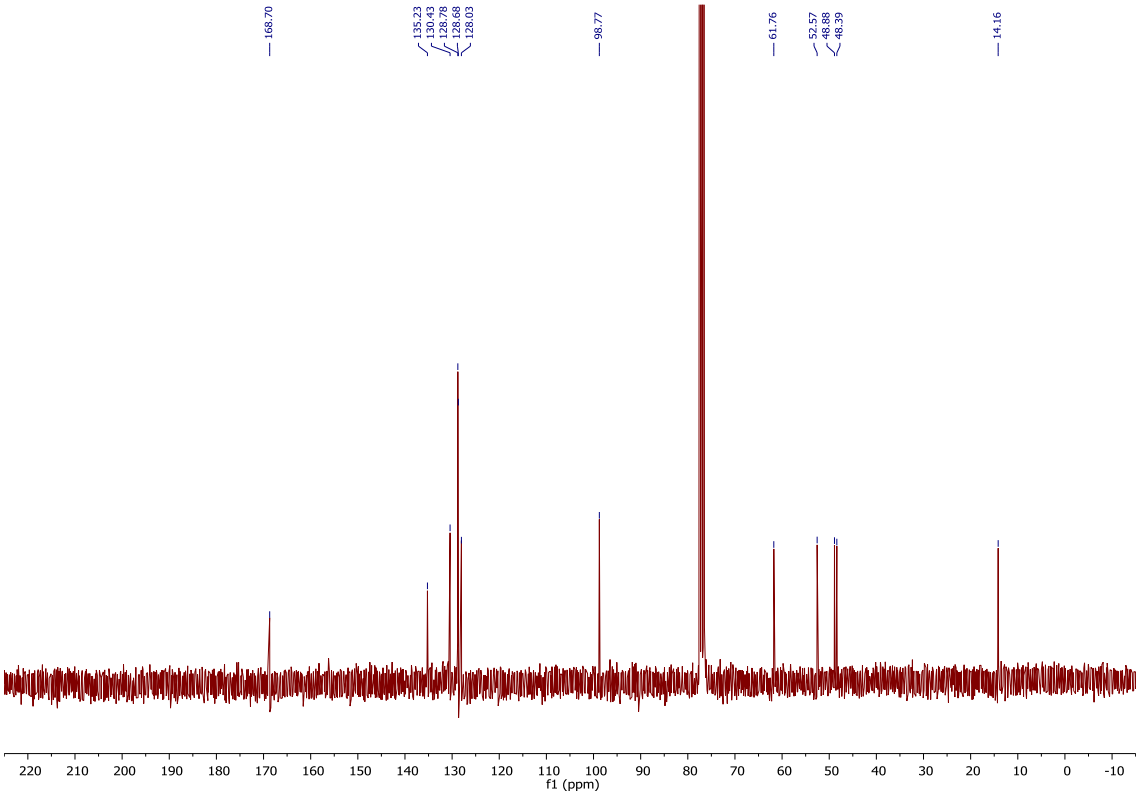


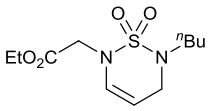
3a

300 MHz, ^{1}H NMR, $CDCl_3$



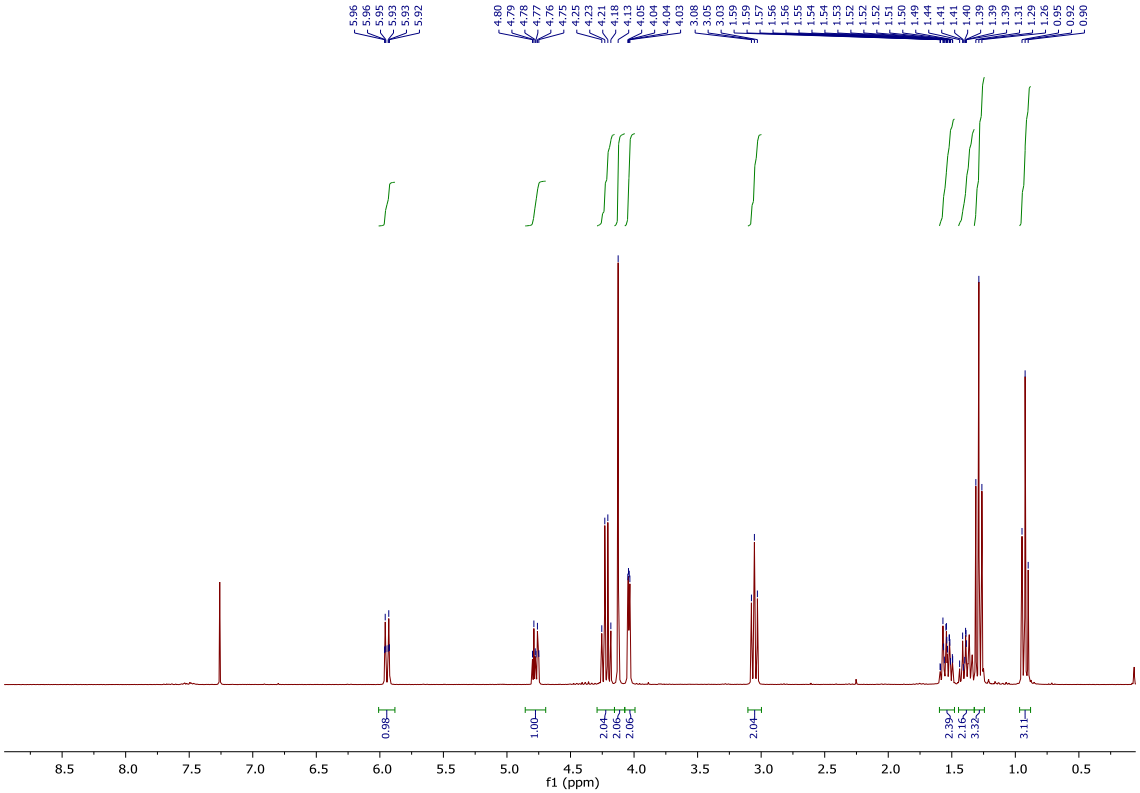
75 MHz, ^{13}C NMR, $CDCl_3$



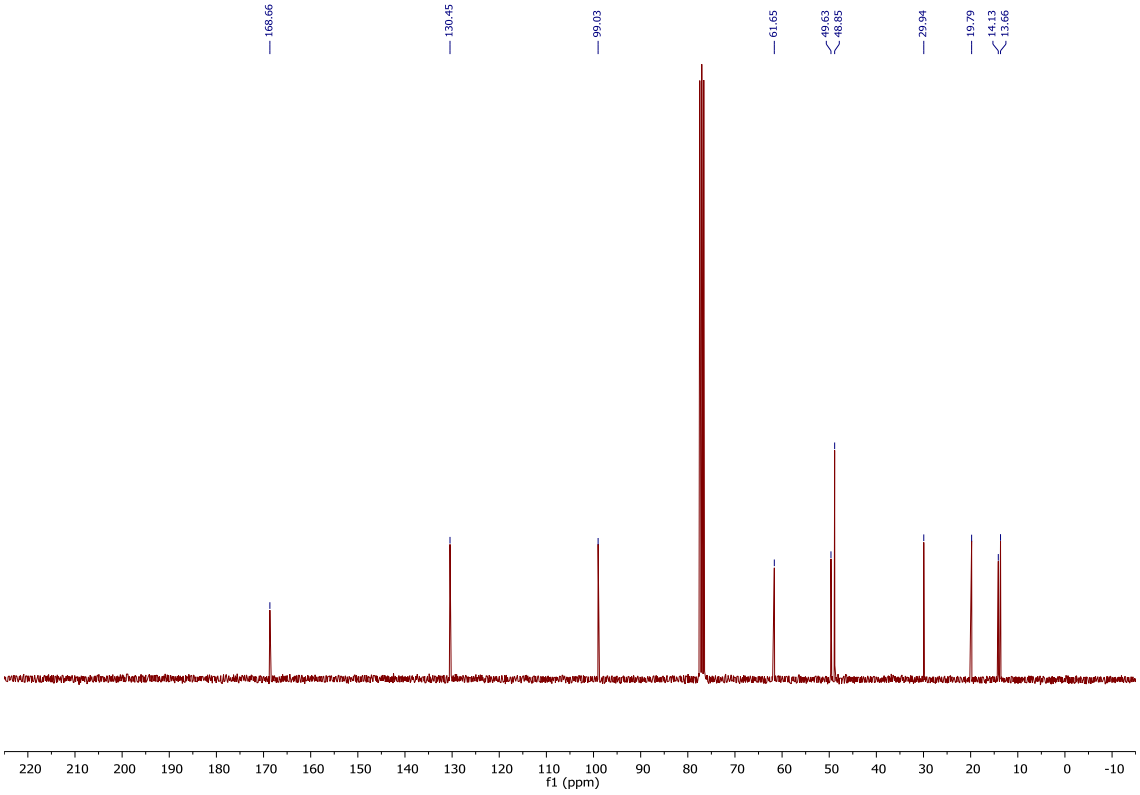


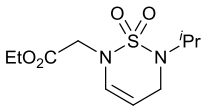
3b

300 MHz, ^{1}H NMR, $CDCl_3$



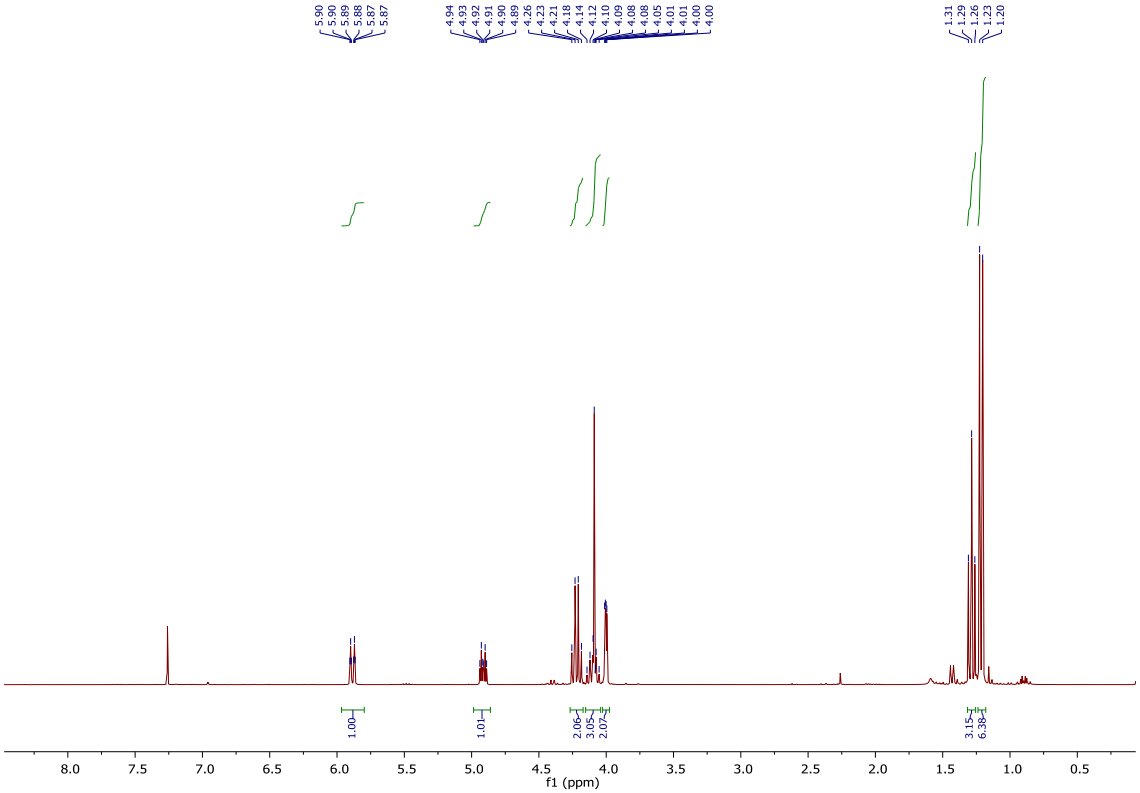
75 MHz, ^{13}C NMR, $CDCl_3$



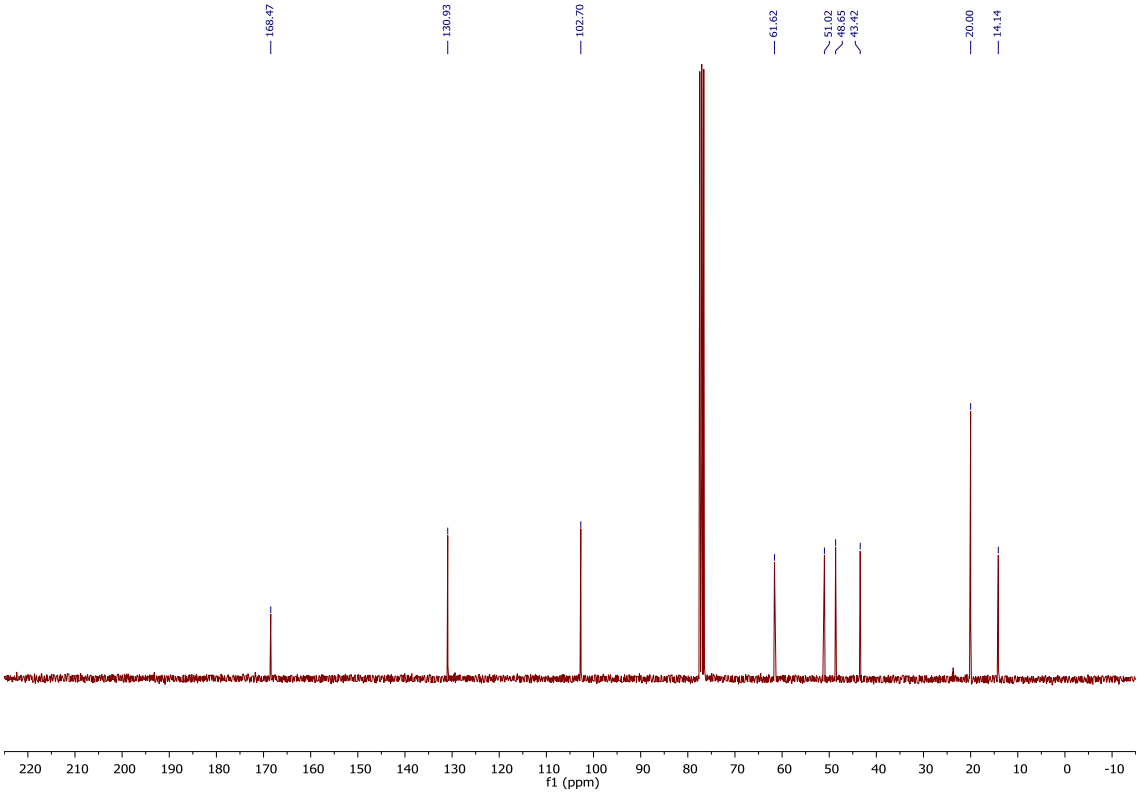


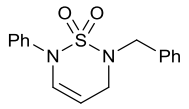
3c

300 MHz, ^{1}H NMR, $CDCl_3$



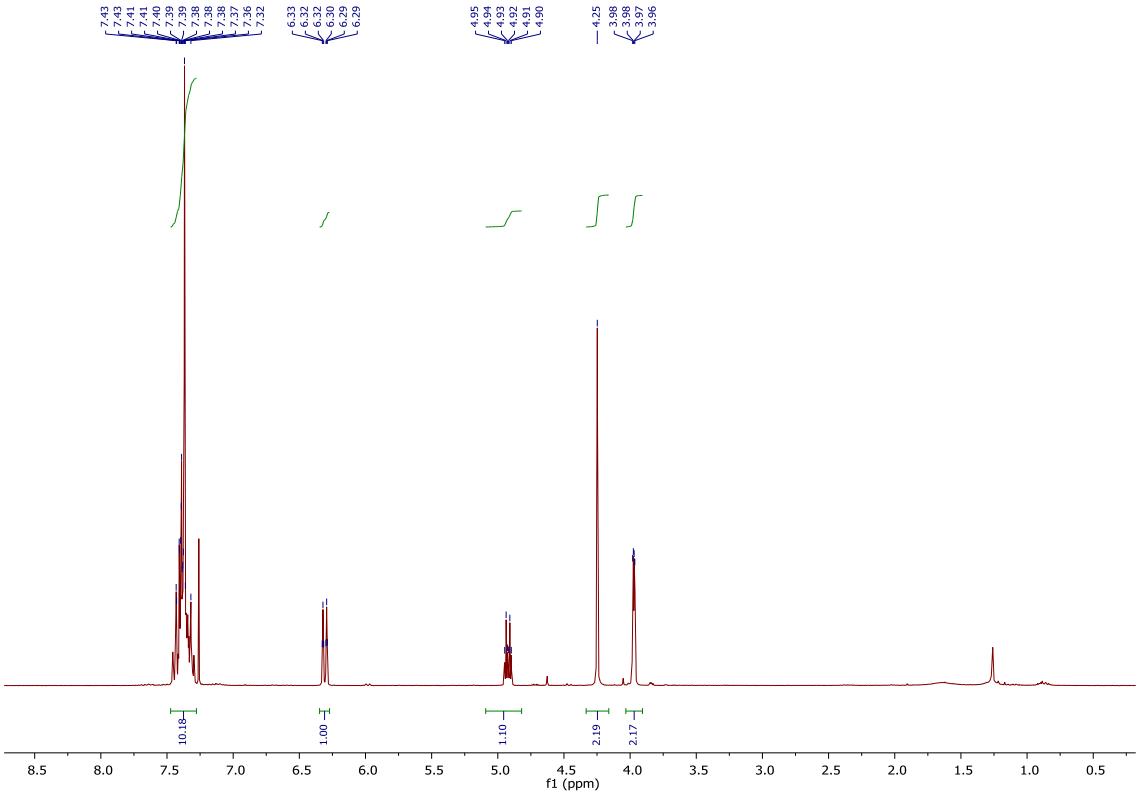
75 MHz, ^{13}C NMR, $CDCl_3$



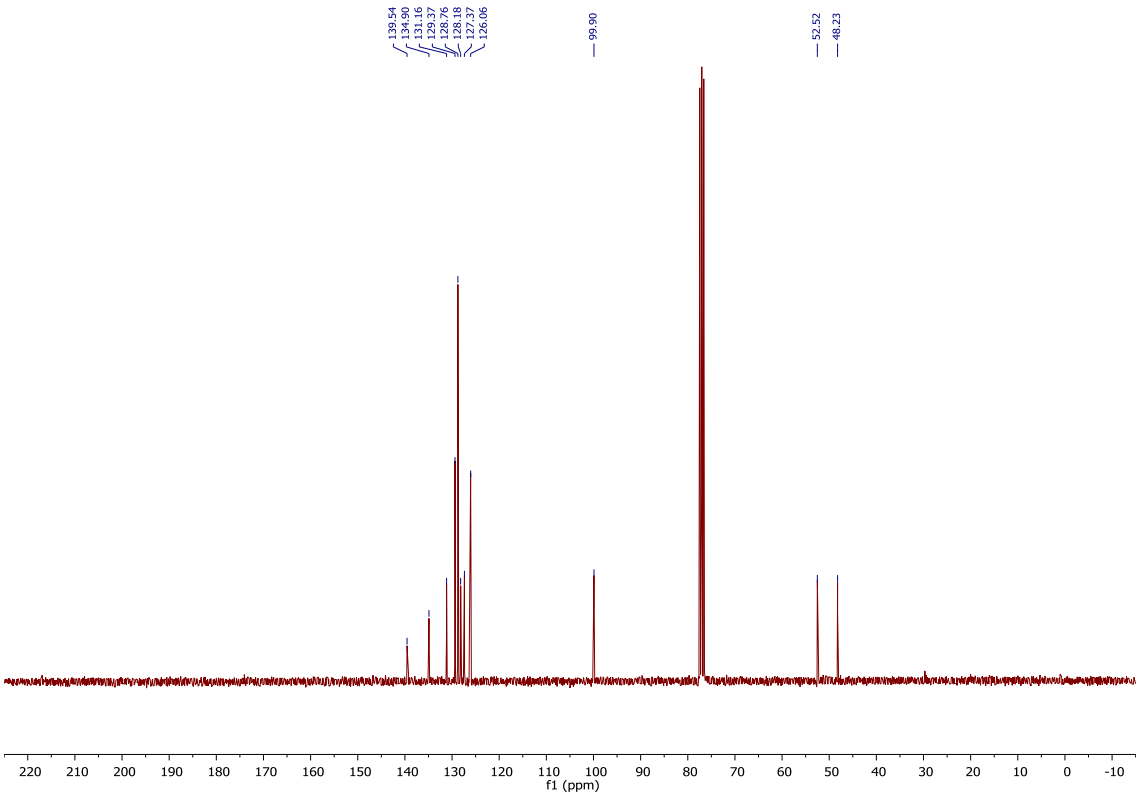


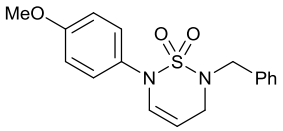
3e

300 MHz, ^{1}H NMR, $CDCl_3$



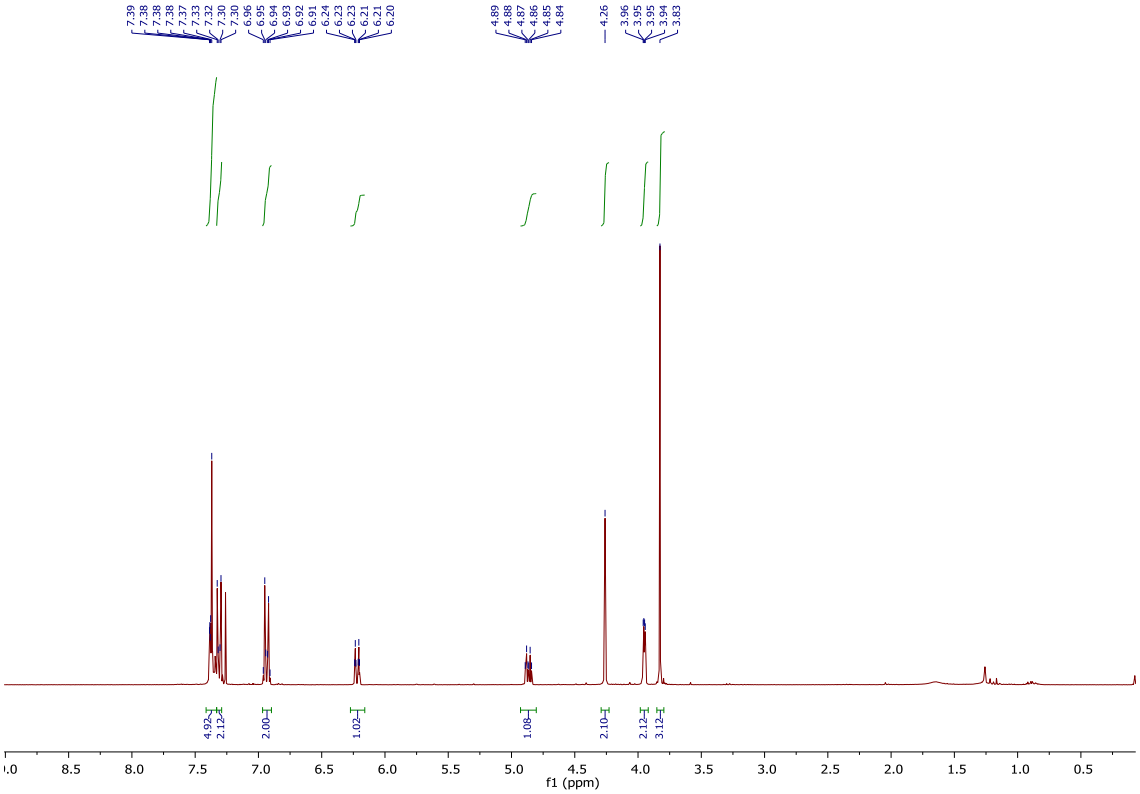
75 MHz, ^{13}C NMR, $CDCl_3$



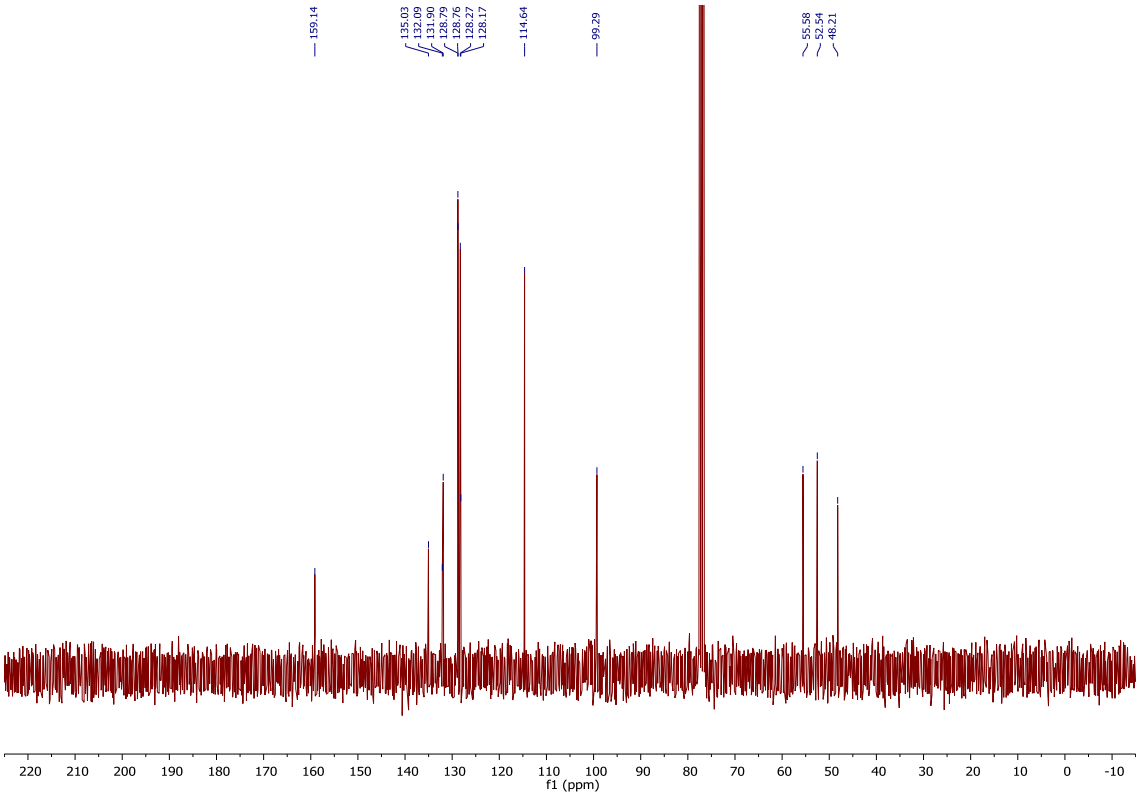


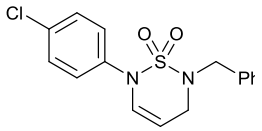
3f

300 MHz, ^{1}H NMR, $CDCl_3$



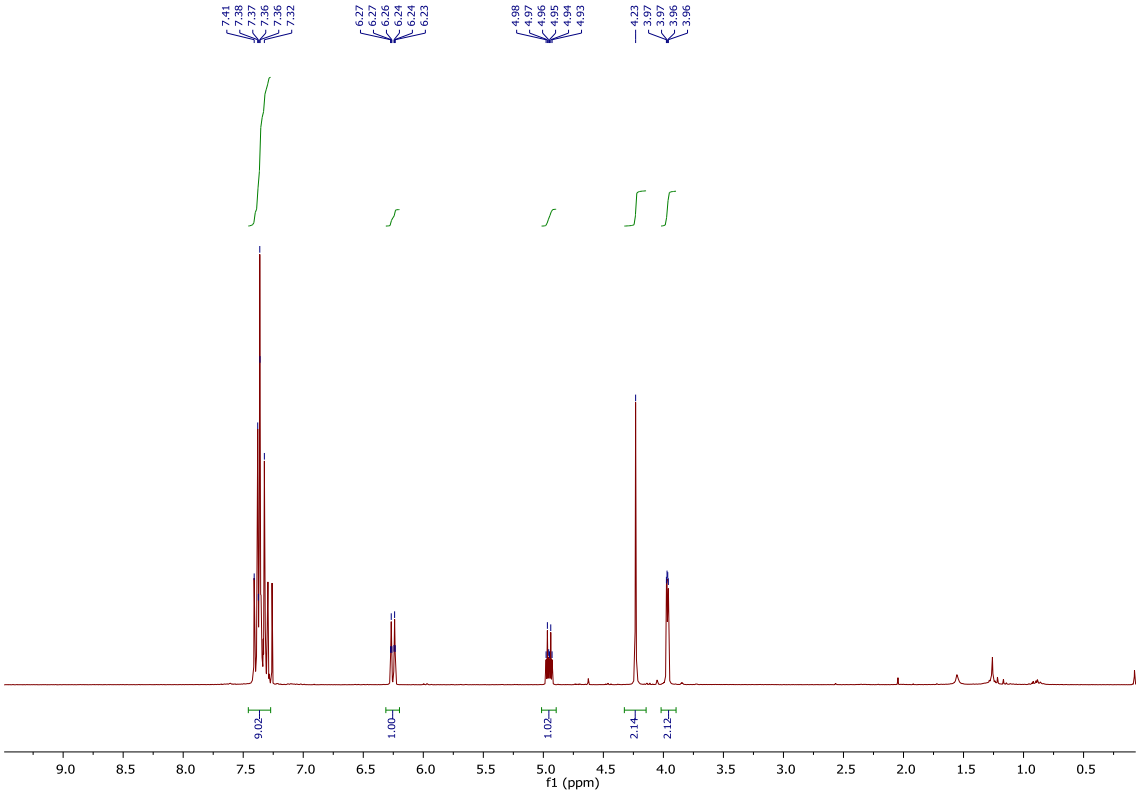
75 MHz, ^{13}C NMR, $CDCl_3$



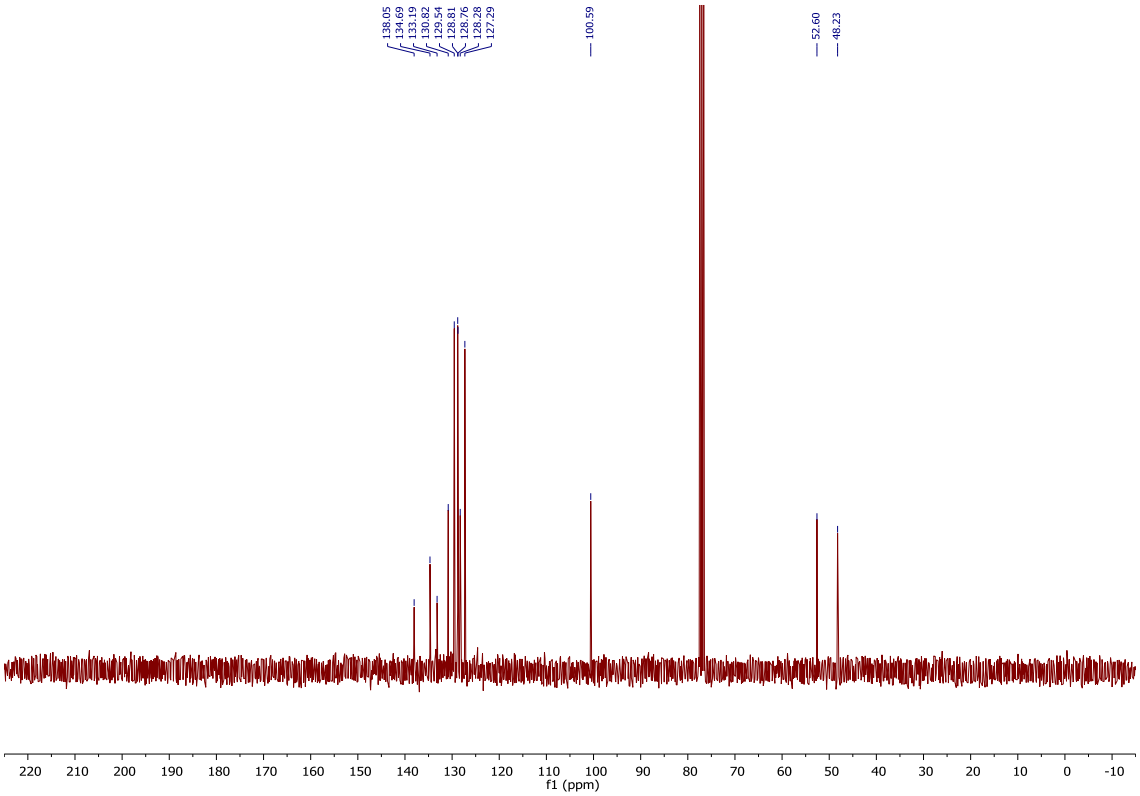


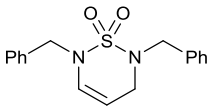
3g

300 MHz, ^{1}H NMR, $CDCl_3$



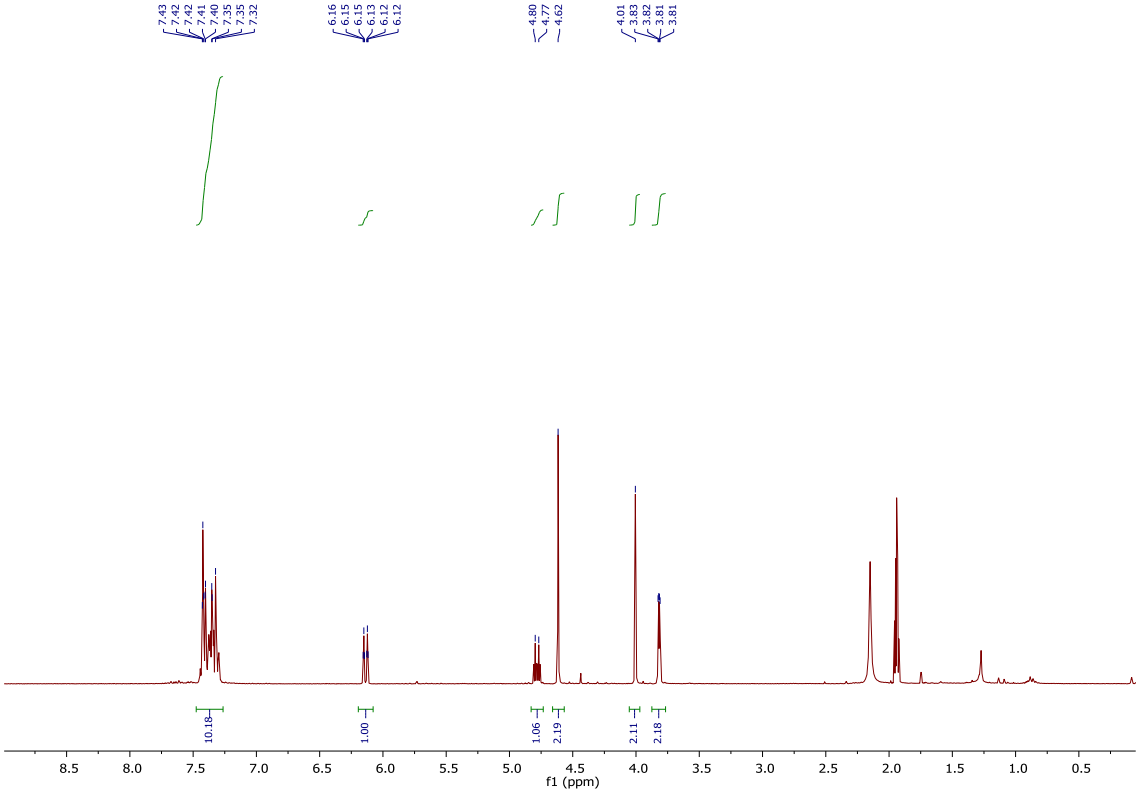
75 MHz, ^{13}C NMR, $CDCl_3$



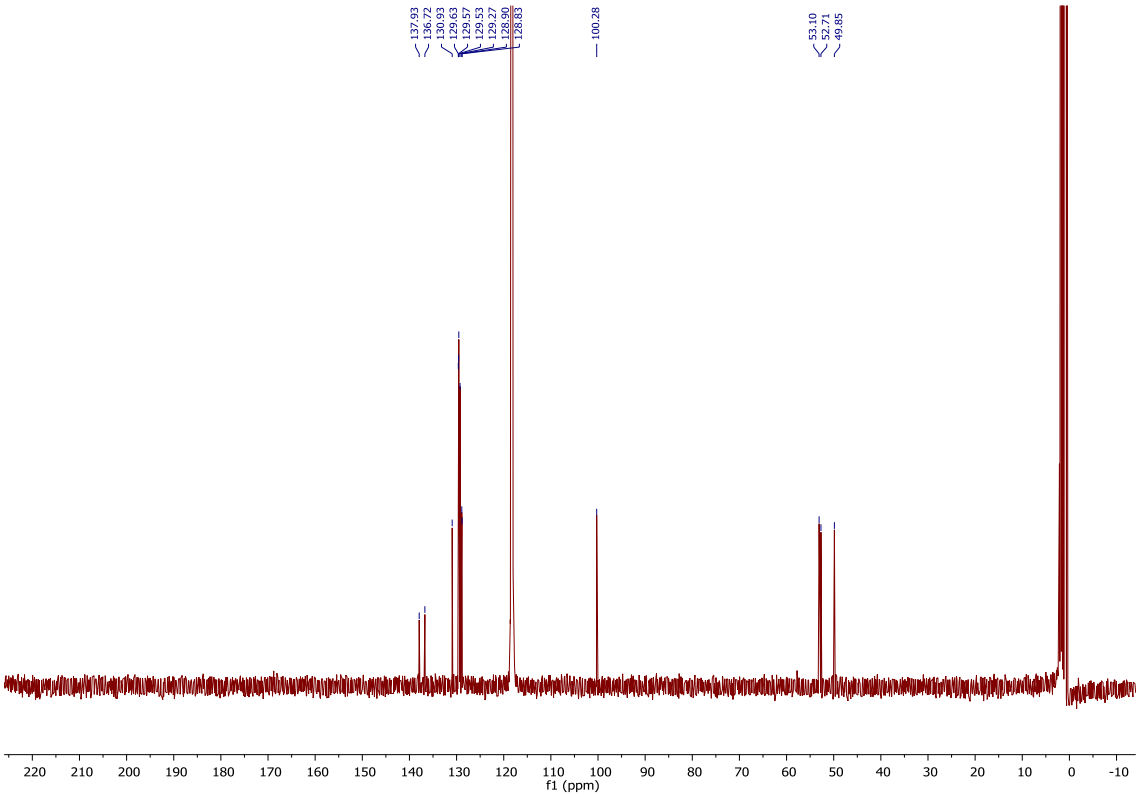


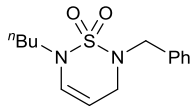
3h

300 MHz, ^{1}H NMR, CD_3CN



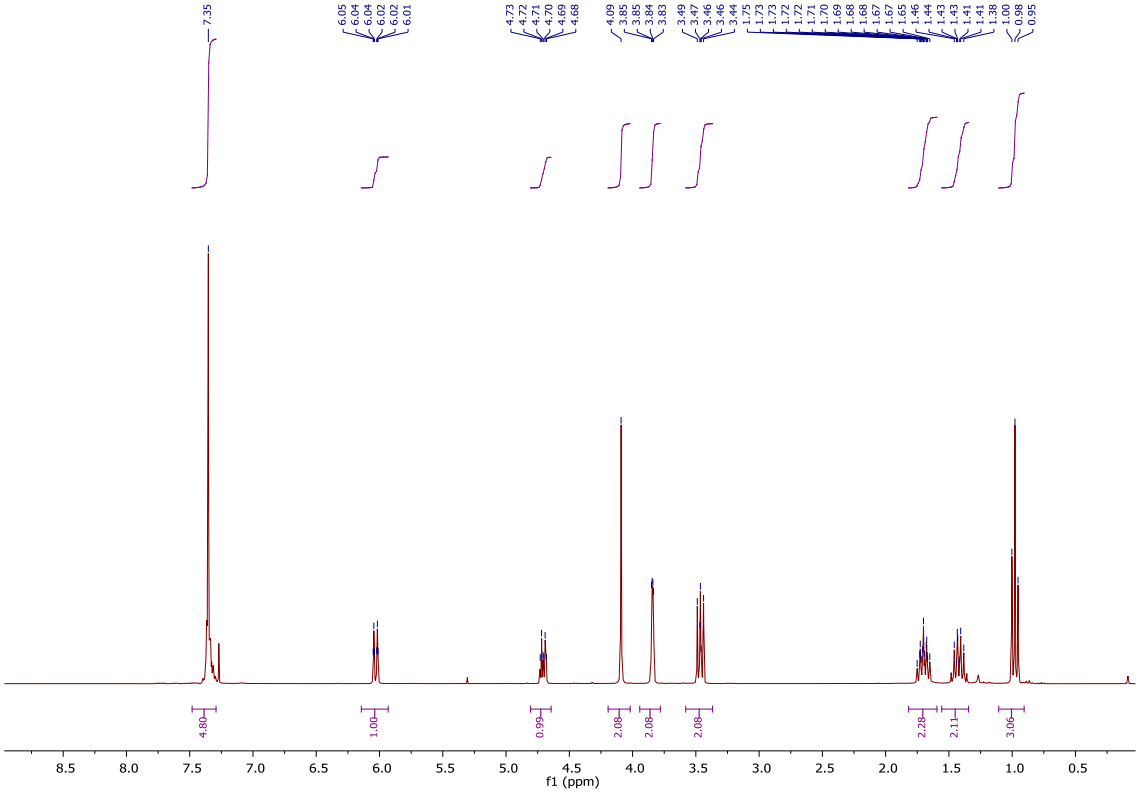
75 MHz, ^{13}C NMR, CD_3CN



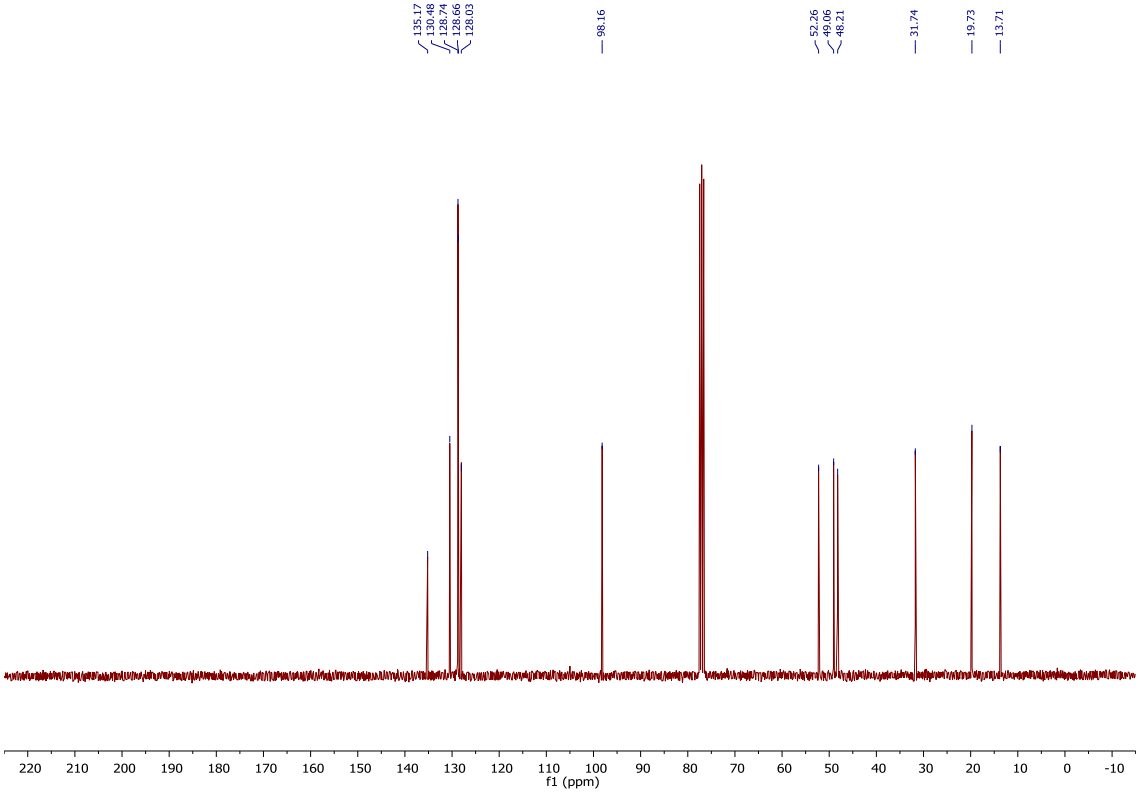


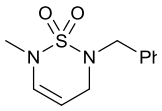
3i

300 MHz, ^{1}H NMR, $CDCl_3$



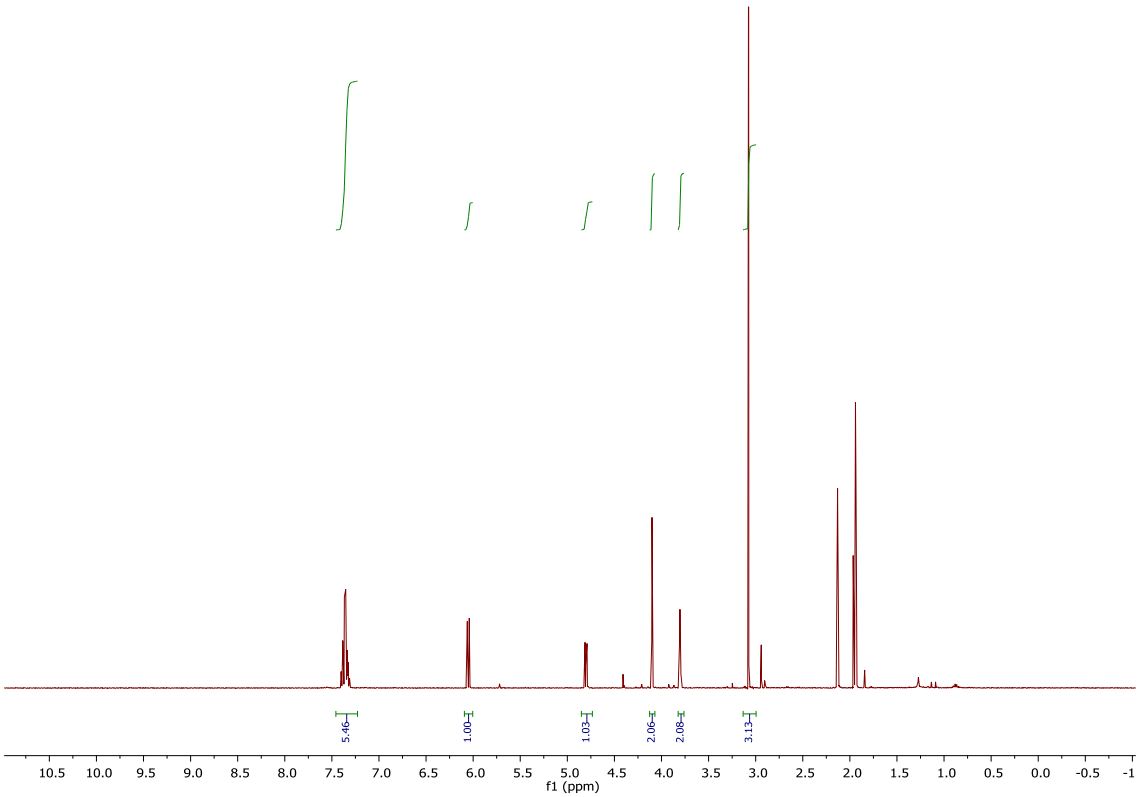
75 MHz, ^{13}C NMR, $CDCl_3$



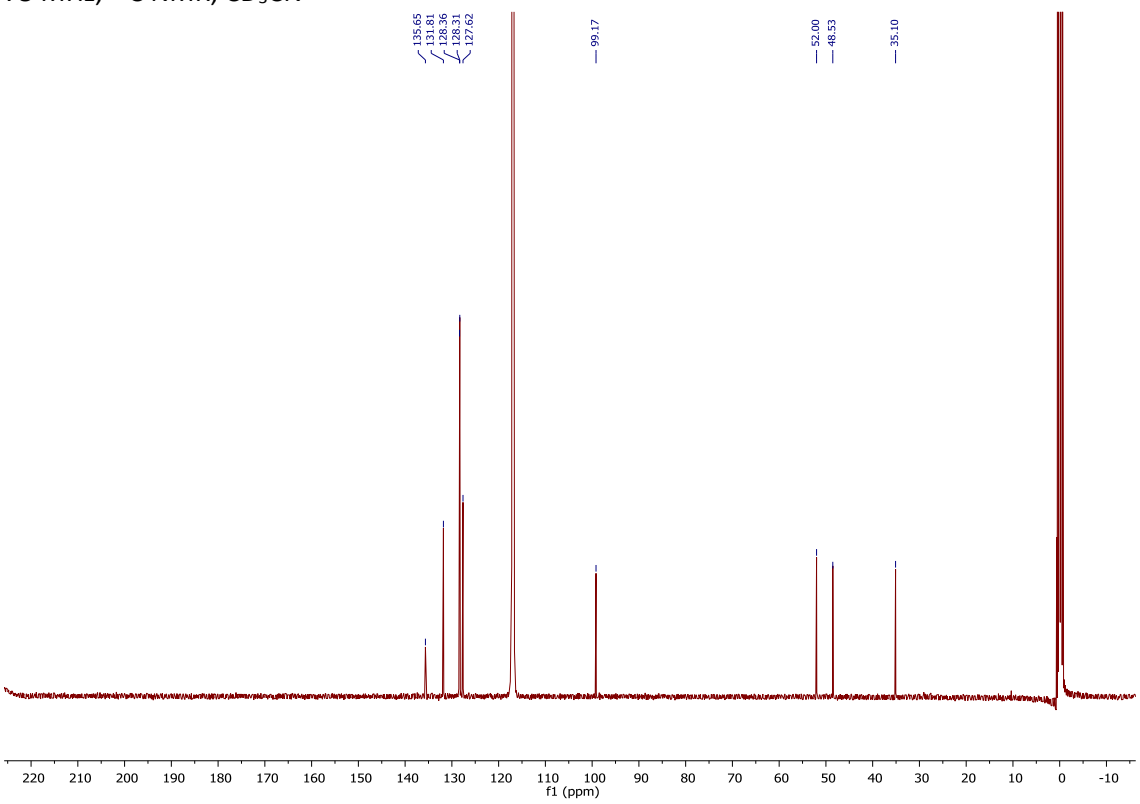


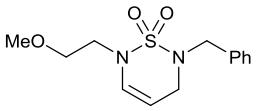
3k

300 MHz, ^{1}H NMR, CD_3CN



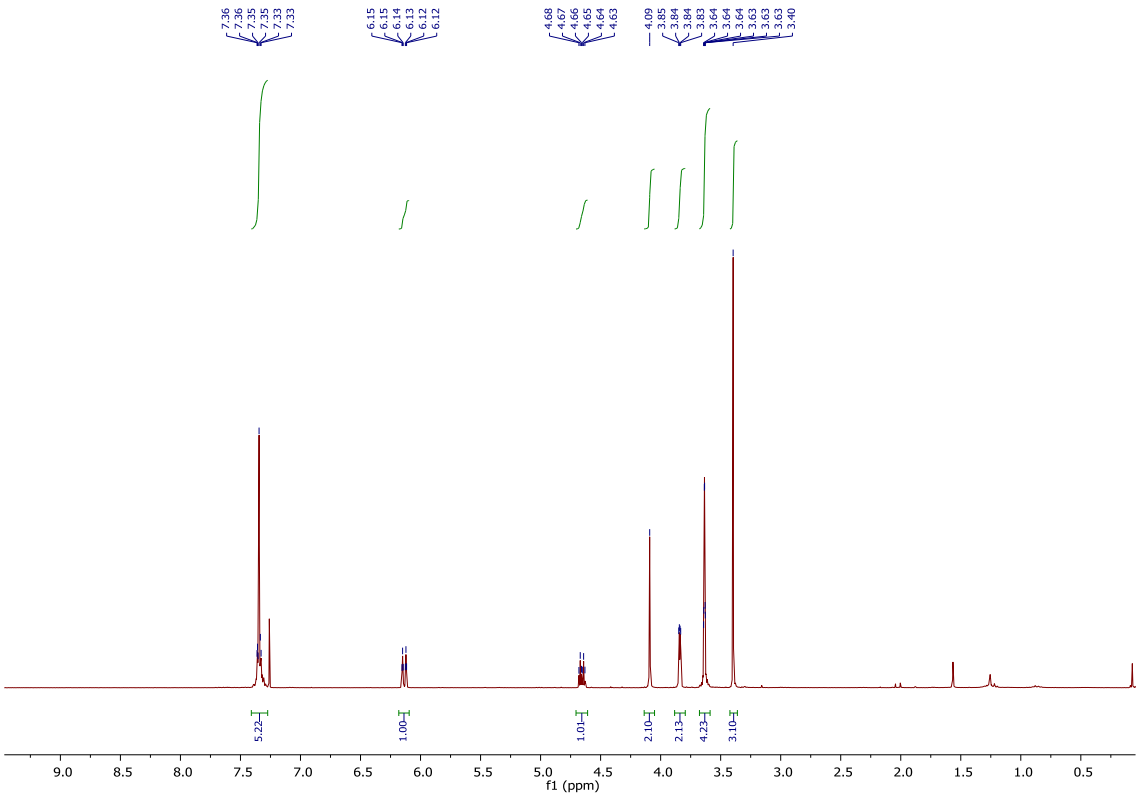
75 MHz, ^{13}C NMR, CD_3CN



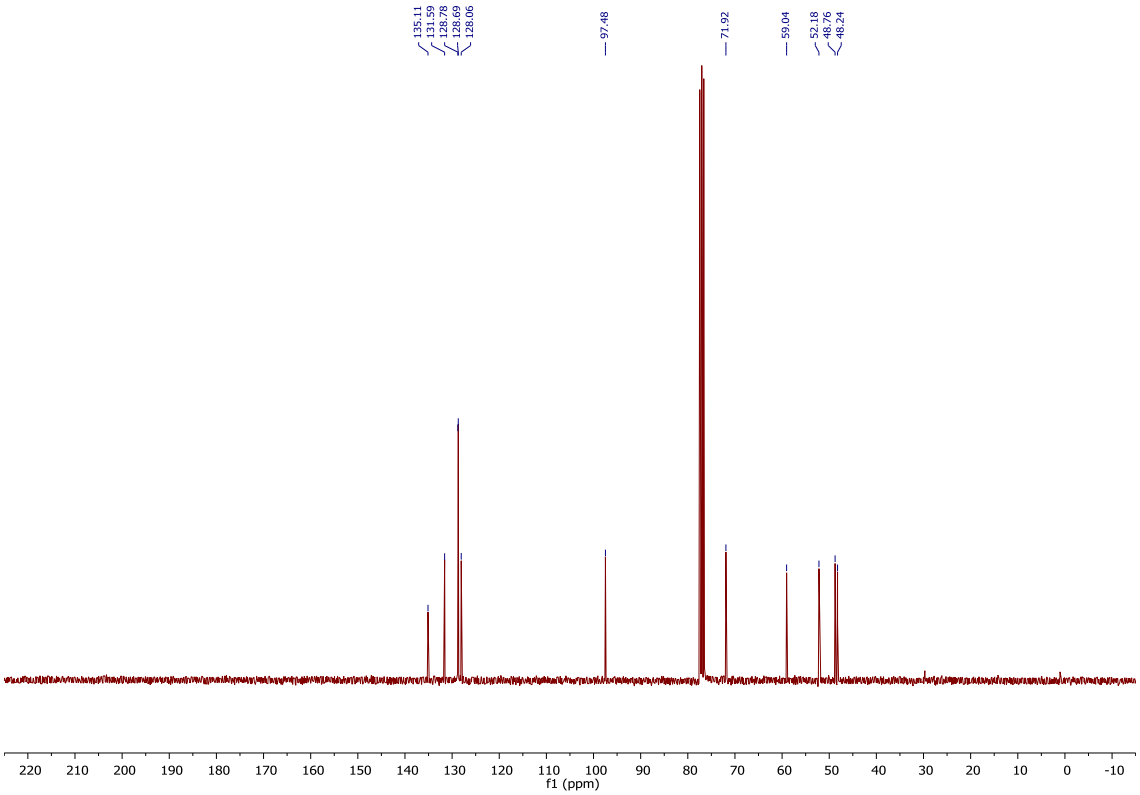


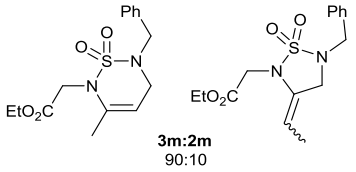
3l

300 MHz, ^{1}H NMR, CD_3CN

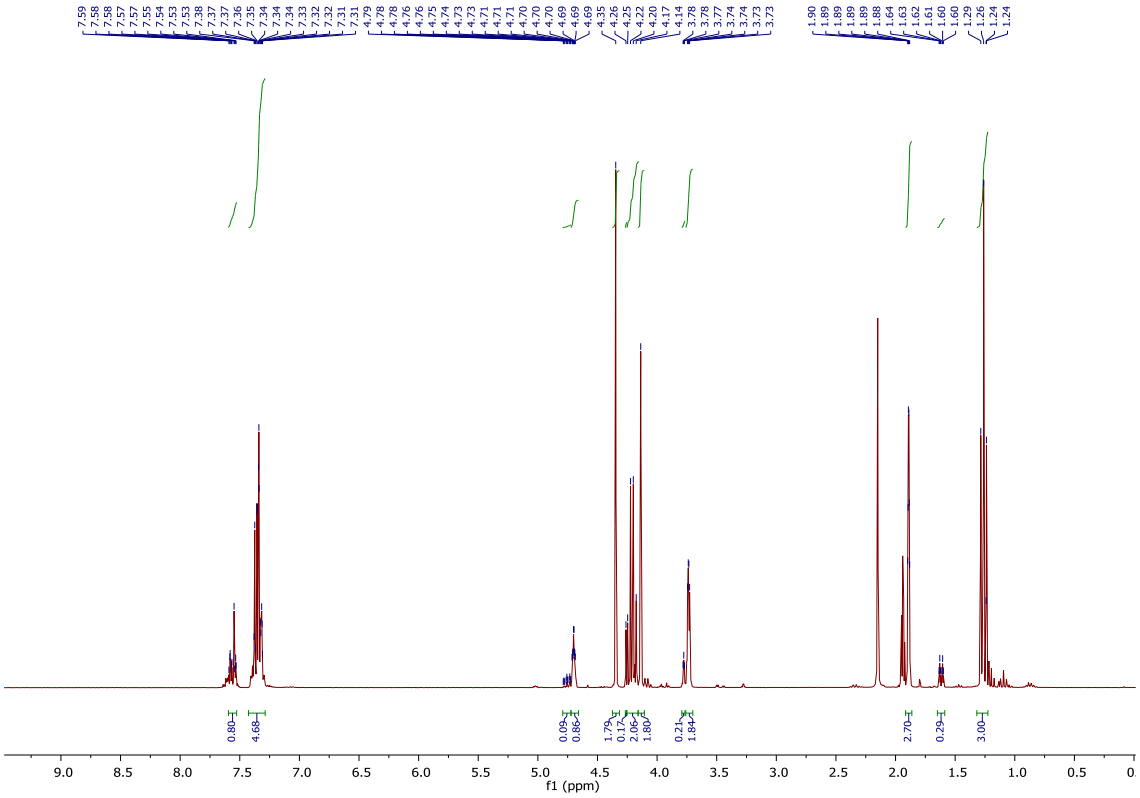


101 MHz, ^{13}C NMR, CD_3CN

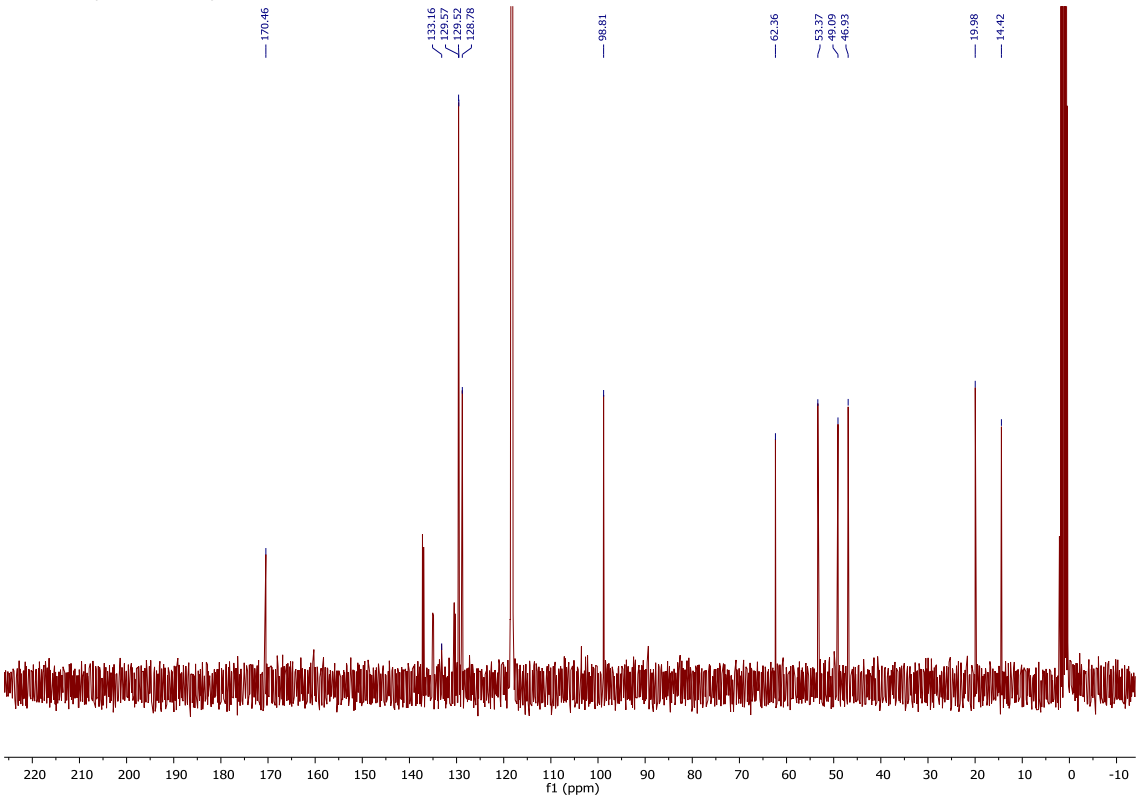


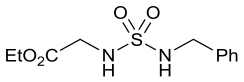


300 MHz, ^{1}H NMR, CD_3CN



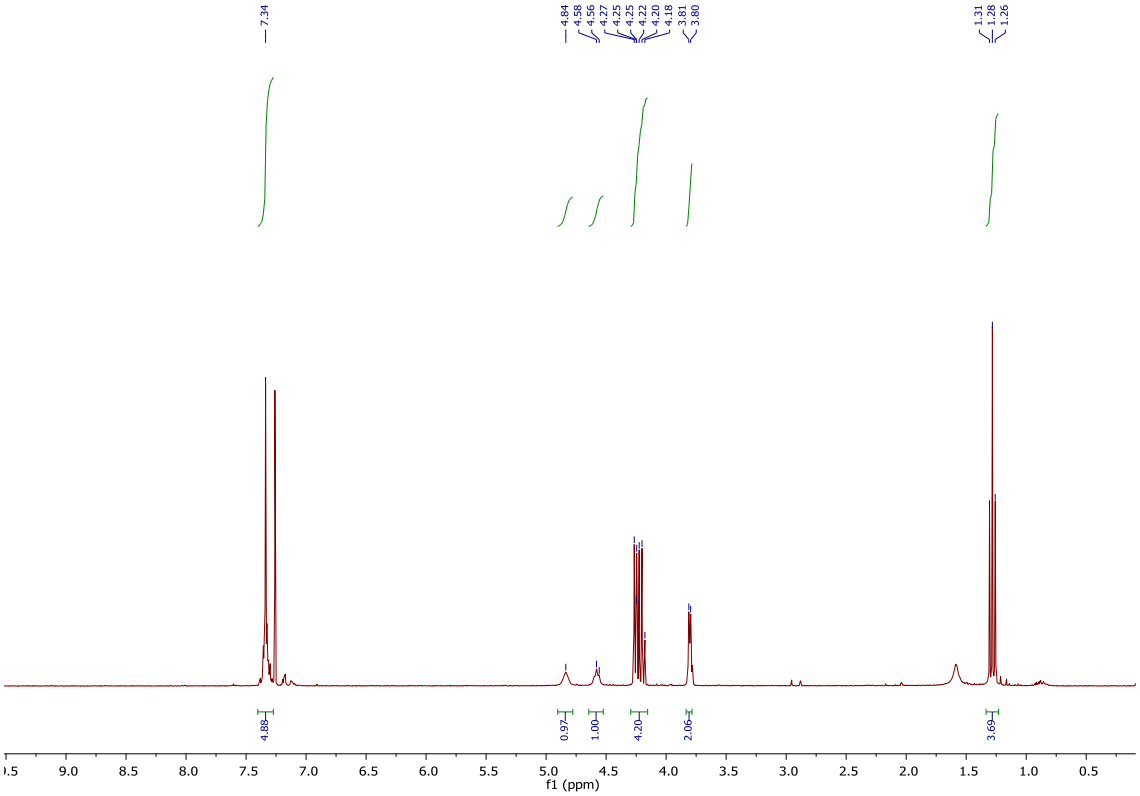
75 MHz, ^{13}C NMR, CD_3CN



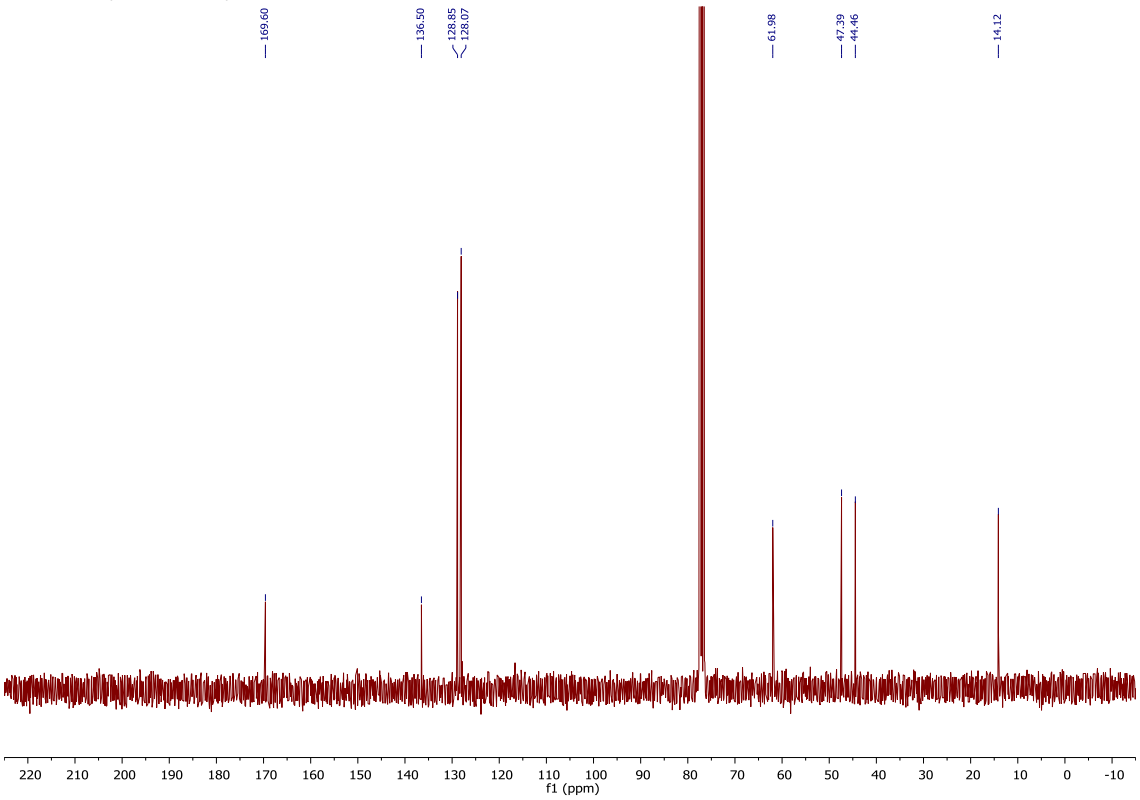


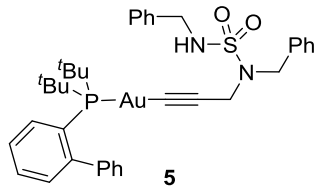
4

300 MHz, ^{1}H NMR, $CDCl_3$



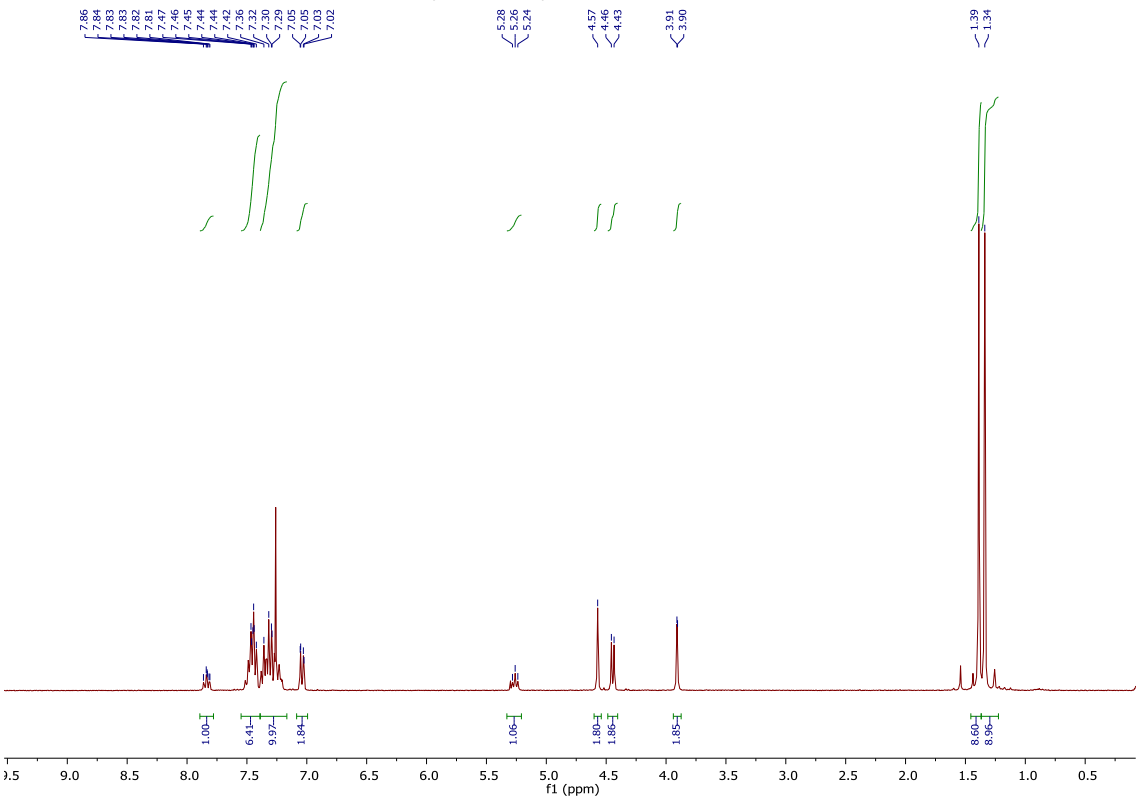
101 MHz, ^{13}C NMR, $CDCl_3$



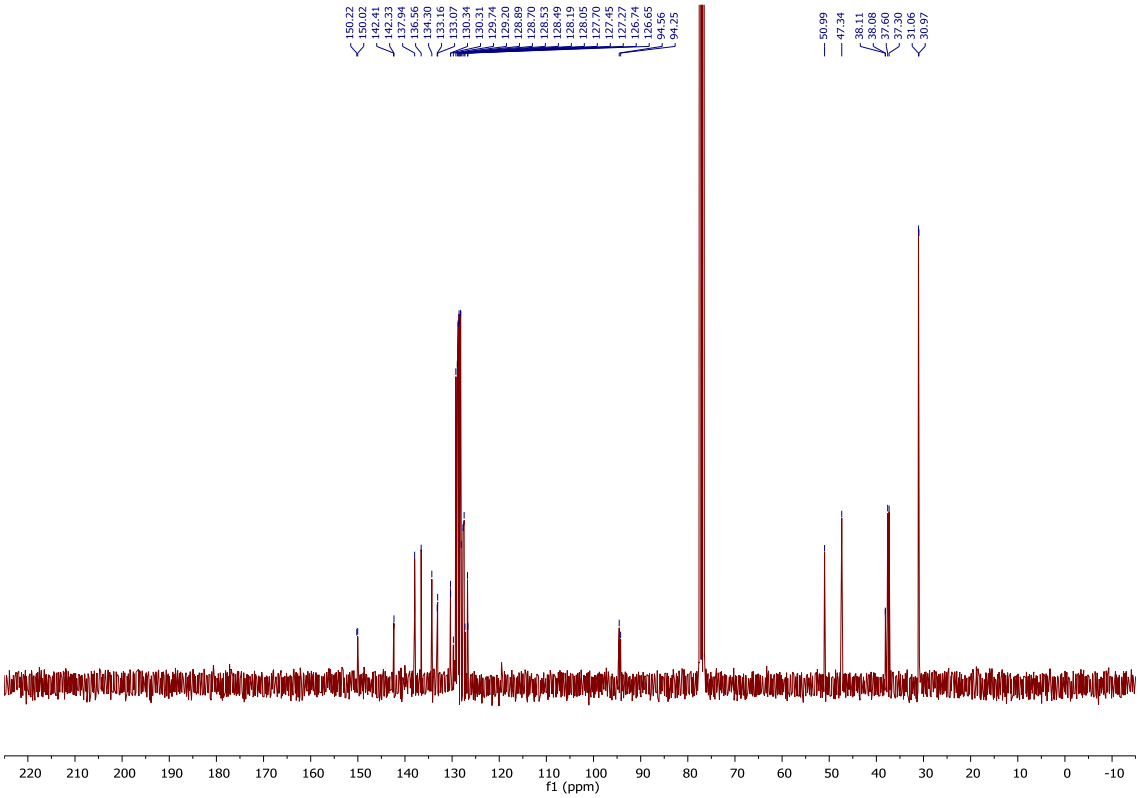


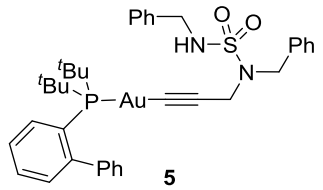
5

300 MHz, ^{1}H NMR, $CDCl_3$



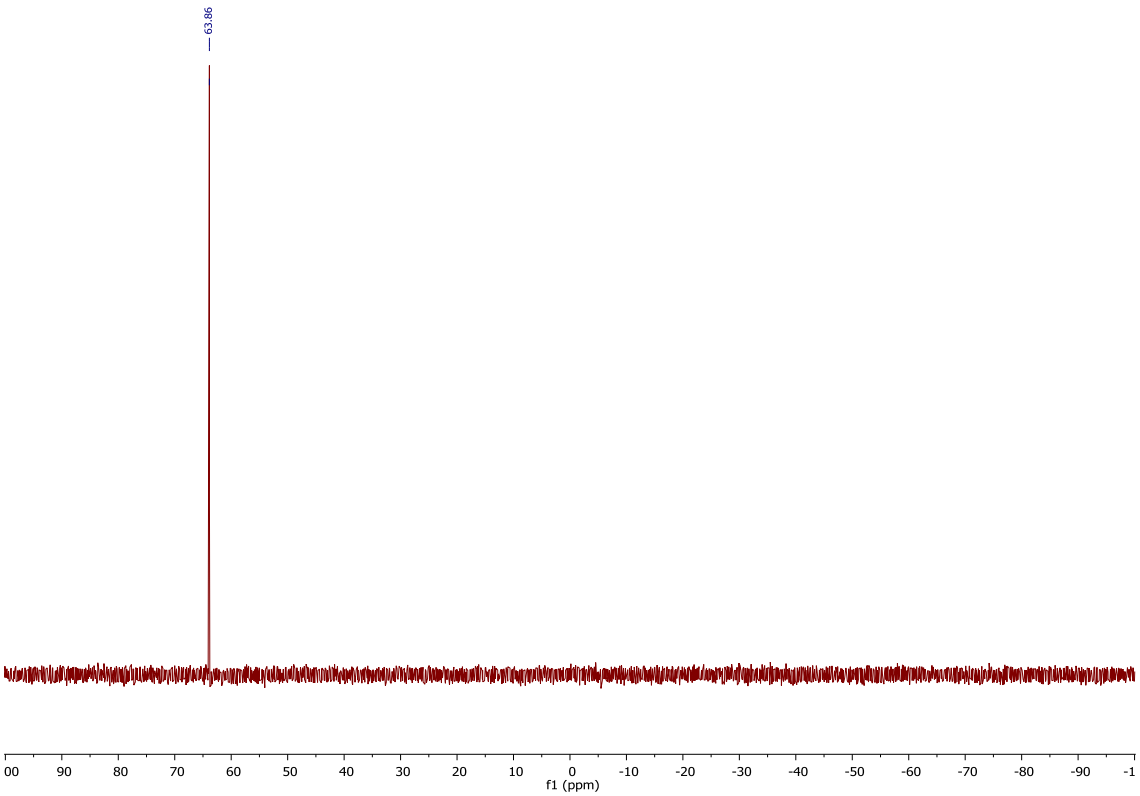
75 MHz, ^{13}C NMR, $CDCl_3$

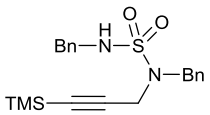




5

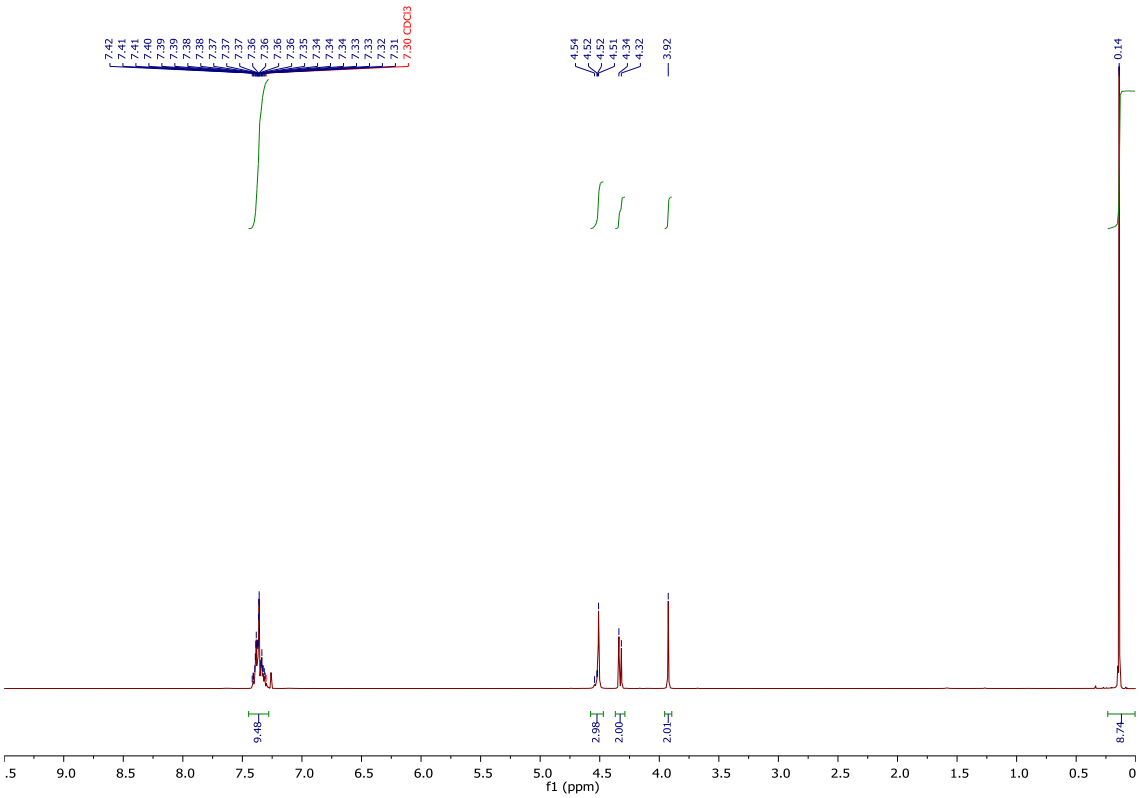
121 MHz, ^{31}P NMR, $CDCl_3$



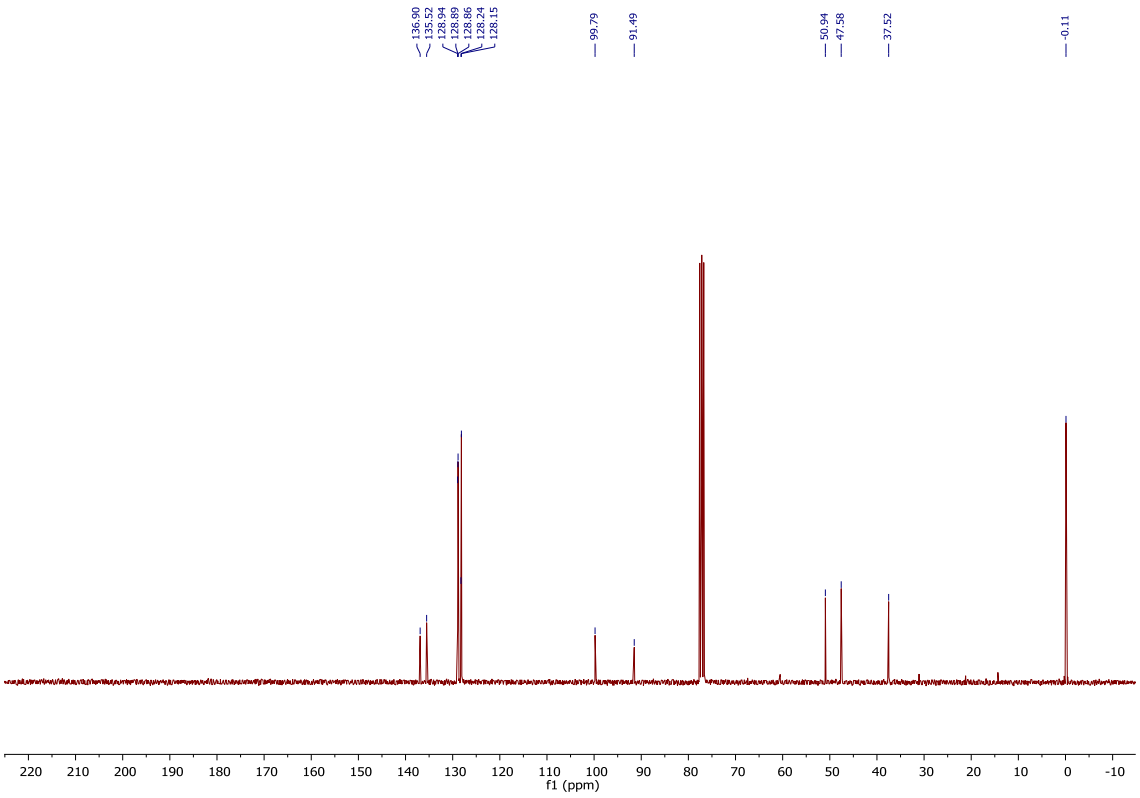


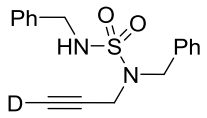
SI-3

300 MHz, ^{1}H NMR, $CDCl_3$



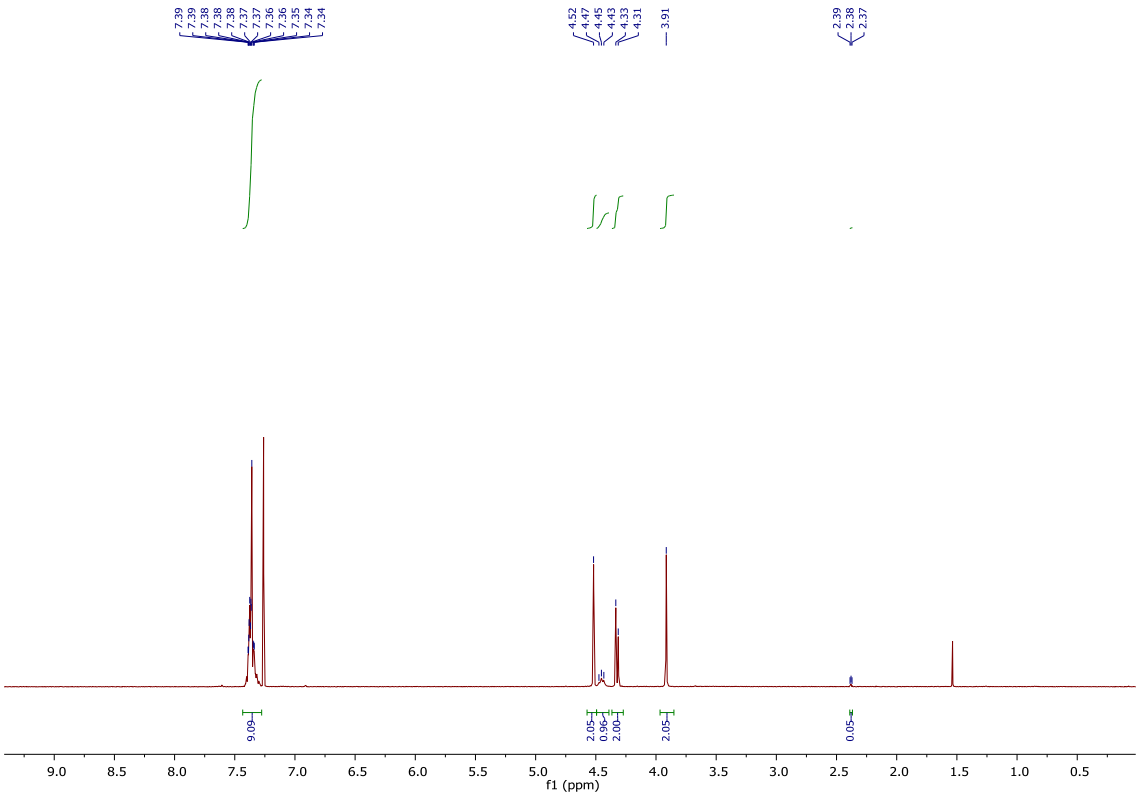
75 MHz, ^{13}C NMR, $CDCl_3$



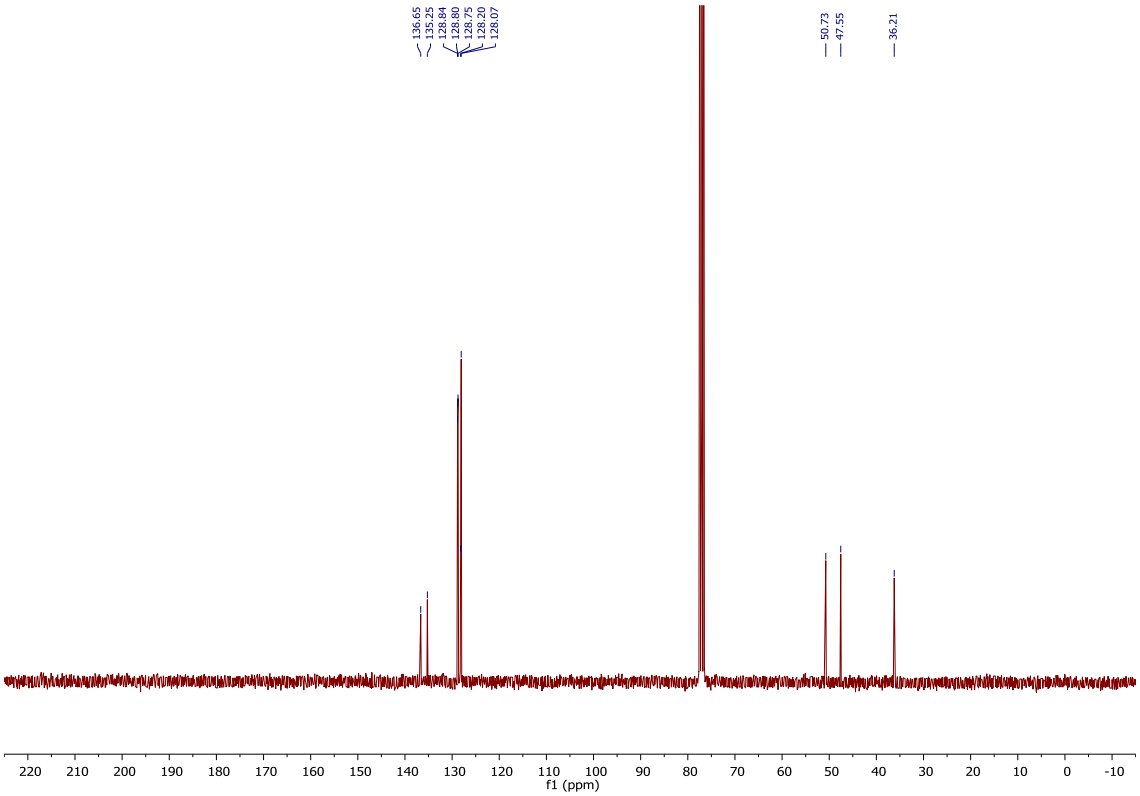


D-2h

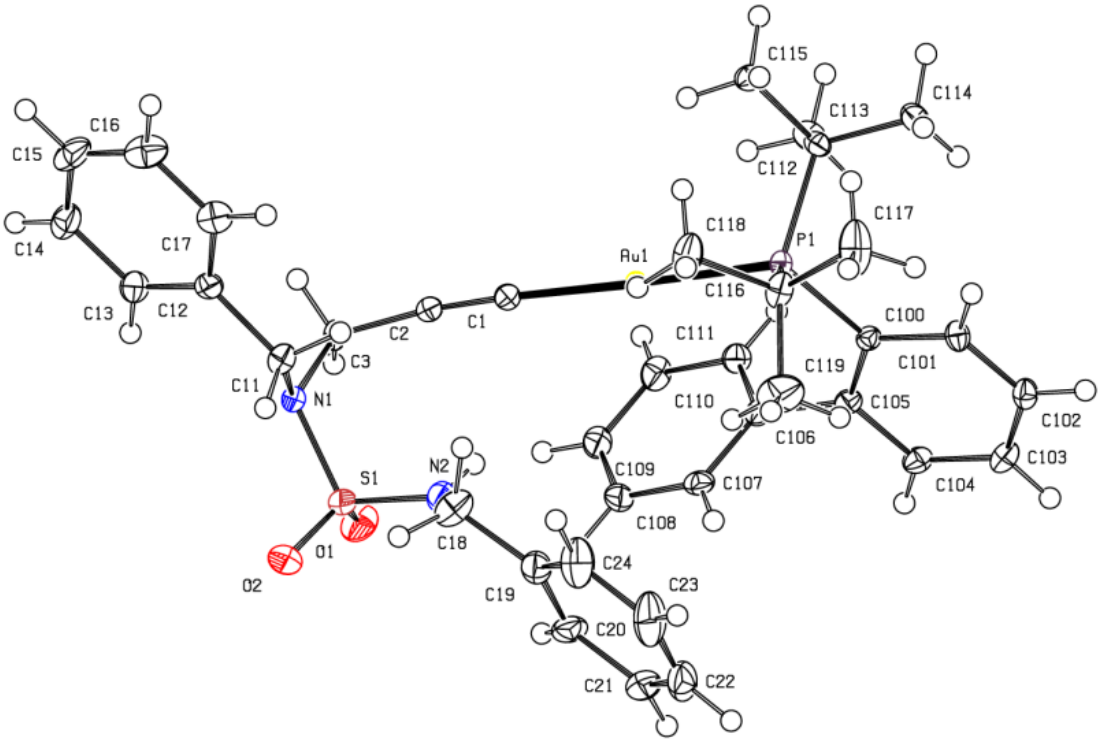
300 MHz, ^{1}H NMR, $CDCl_3$



101 MHz, ^{13}C NMR, $CDCl_3$



7. *X-ray Structure of* (3-(Benzyl(*N*-benzylsulfamoyl)amino)prop-1-yn-1-yl)((2-biphenyl)di-*tert*-butylphosphine)gold. *5.*



Single crystals of $C_{37}H_{44}AuN_2O_2PS$ (**5**) were grown from CH_2Cl_2/petroleum ether. A suitable crystal was selected and mounted on a 'Bruker APEX-II CCD' diffractometer. The crystal was kept at 100.0 K during data collection. Using Olex2,[7] the structure was solved with the XT[8] structure solution program using Intrinsic Phasing and refined with the XL[9] refinement package using Least Squares minimisation.

Crystallographic data have been deposited at the Cambridge Crystallographic Data Centre and assigned to the following deposition number: CCDC 1832068.

Table S2 Crystal data and structure refinement for 5.

Identification code	**5**
Empirical formula	$C_{37}H_{44}AuN_2O_2PS$
Formula weight	808.74
Temperature/K	100.0
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a/Å	11.084(11)

b/Å	15.090(15)
c/Å	20.90(2)
α/°	90
β/°	90
γ/°	90
Volume/$Å^3$	3496(6)
Z	4
ρ_{calc}g/cm^3	1.537
μ/mm^{-1}	4.348
F(000)	1624.0
Crystal size/mm^3	0.5 × 0.46 × 0.32
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.742 to 63.878
Index ranges	-16 ≤ h ≤ 16, -22 ≤ k ≤ 22, -30 ≤ l ≤ 28
Reflections collected	41893
Independent reflections	11946 [R_{int} = 0.0418, R_{sigma} = 0.0623]
Data/restraints/parameters	11946/0/406
Goodness-of-fit on F^2	0.811
Final R indexes [I>=2σ (I)]	R_1 = 0.0259, wR_2 = 0.0448
Final R indexes [all data]	R_1 = 0.0320, wR_2 = 0.0464
Largest diff. peak/hole / e $Å^{-3}$	1.27/-1.63
Flack parameter	0.007(3)

8. References

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