Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Supporting Information

Synthesis of 2-amidoindenone derivatives through an ynamide carbosilylation / Houben-Hoesch cyclization 2-step sequence.

Pierre Hansjacob, Célia Schwoerer, Frédéric R. Leroux and Morgan Donnard

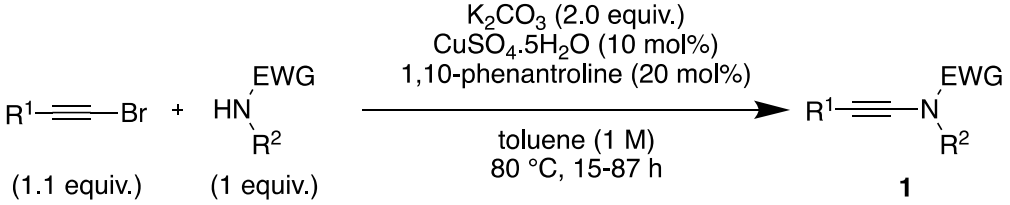
University of Strasbourg, University of Haute-Alsace, CNRS, UMR 7042-LIMA, ECPM, 67000 Strasbourg, France
E-mail: donnard@unistra.fr

1. General Information

Commercially available starting materials were purchased from standard suppliers (Sigma-Aldrich, Fluorochem, ABCR, TCI, Strem, Thermo Fisher Scientific or Apollo scientific) and used without further purification unless otherwise stated. When required, solvents were dried following standard procedures: toluene and xylene were dried by distillation over CaH_2. Anhydrous solvents like DMF and THF were purchased from Thermo Fisher Scientific and Sigma Aldrich respectively and used as such. Air- and moisture-sensitive materials were stored and handled under argon atmosphere. Air- and moisture-sensitive reactions were carried out under argon atmosphere in flame-dried glassware.
Reactions were monitored using thin-layer chromatography (TLC) with precoated silica on aluminium foils (0.25 mm thickness, Merck silica-gel (60-F_{254}). Chromatograms were either visualized by fluorescence quenching with UV light at 254 nm or by staining using potassium permanganate or ninhydrine. Flash column chromatography was performed on VWR silica gel (40 – 63 µm) using indicated solvents (v/v). ^{1}H NMR (400 or 500 MHz), ^{29}Si NMR (80 or 99 MHz) and ^{13}C NMR (101 or 126 MHz) spectra were recorded on Bruker Avance III HD 400 and 500 MHz instruments respectively in $CDCl_3$ or CD_2Cl_2. All chemical shifts (δ) are reported in parts per million (ppm) and are referenced to residual solvent peaks in ^{1}H and ^{13}C NMR experiments: δ(^{1}H) 7.26, δ(^{13}C) 77.16 for $CDCl_3$ and δ (^{1}H) 5.32, δ (^{13}C) 53.84 for CD_2Cl_2. ^{29}Si NMR spectra were referenced using the unified scale (derived from the ^{1}H NMR spectrum) in agreement with IUPAC recommendations, and values were expressed against TMS. Multiplicities are abbreviated as br s (broad singlet), s (singlet), d (doublet), t (triplet), q (quartet), pentet (p), m (multiplet), td (triplet of doublets), dd (doublet of doublets), ddd (doublet of doublets of doublets). Coupling constants were quoted in Hz (J). Spectra were processed with the program MestReNova (Version 14.2, Mestrelab). Infra-red spectra were recorded using a Perkin Elmer UATR Two spectrometer (ATR). Wavenumbers (ν) are reported in cm^{-1}. High-resolution mass spectra (HRMS) were recorded with a Brucker MicroTOF mass analyzer under ESI in positive ionization mode detection by the analytical facility at the Université de Strasbourg. Melting points were recorded on a Büchi Melting Point M-560.

2. Syntheses of ynamides

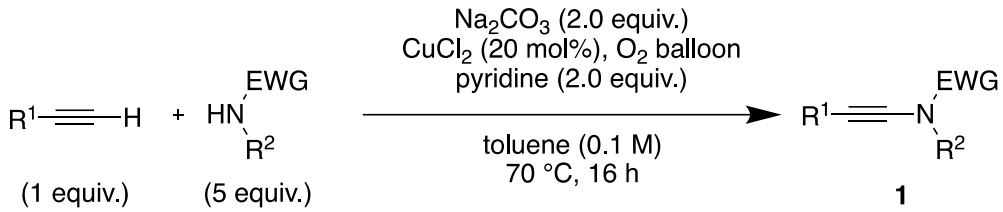
a. General Procedure ***GP1***



Procedure developed by Hsung.[1]

A flame-dried sealed tube was charged with the alkynyl bromide (1.1 equiv.), the nitrogen nucleophile (1.0 equiv.), K_2CO_3 (2.0 equiv.), $CuSO_4{\cdot}5H_2O$ (10 mol%) and 1,10-phenantroline (20 mol%) under argon. Dry toluene (1 M) was finally added to the sealed tube and the reaction mixture was heated at 80 °C for 63 – 87 h. After reaction completion, the crude mixture was diluted in EA and filtered on Celite® pad. The solvent was then removed under reduced pressure and the crude product was purified by flash chromatography.

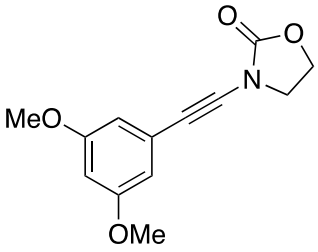
b. General Procedure ***GP2***



Procedure developed by Stahl.[2]

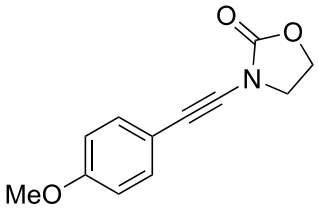
To a flame-dried 250 mL three-neck round-bottomed flask were added $CuCl_2$ (20 mol%), 2-oxazolidinone (5.0 equiv.) and Na_2CO_3 (2.0 equiv.). The reaction flask was flushed with oxygen. A solution of pyridine (2.0 equiv.) in dry toluene (0.1 M) was added. The reaction was finally heated at 70 °C under oxygen. After 15 minutes, a solution of the alkyne (1.0 equiv.) in dry toluene (0.1 M) was added over 4 hours. After the addition, the mixture was allowed to stir at 70 °C for additional 12 hours. After reaction completion, the crude mixture was concentrated under reduced pressure and was purified by flash chromatography.

3-((3,5-Dimethoxyphenyl)ethynyl)oxazolidin-2-one [**CAS Number:** 1638645-71-2] (**1a**): Prepared following **GP1** starting from 1-(bromoethynyl)-3,5-dimethoxybenzene (1.1 equiv., 2.9 g, 11.9 mmol) and *N*-methylcarbamate (1.0 equiv., 1.2 g, 10.8 mmol). Reaction time: 66 h. Purification by flash column chromatography over silica gel (gradient from pentane/EA = 100:0 to 2:1) afforded the title compound (2.4 g, 9.5 mmol, 88%) as a pale-yellow solid. **TLC**: R*f* (pentane/EA = 2:1) = 0.23. **^{1}H NMR** (400 MHz, $CDCl_3$): *δ* (ppm) 6.59 (d, *J* = 2.3 Hz, C**H**$_{ortho}$, 2H), 6.42 (t, *J* = 2.3 Hz, C**H**$_{para}$, 1H), 4.54 – 4.45 (m, O-C**H**$_2$-, 2H), 4.07 – 3.97 (m, N-C**H**$_2$-, 2H), 3.77 (s, -OC**H**$_3$, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$): *δ* (ppm) 160.6 (2**C**$_q$), 155.9 (**C**$_q$), 123.6 (**C**$_q$), 109.3 (2**C**H$_{ortho}$), 101.8 (**C**H$_{para}$), 78.7 (**C**$_{alkyne}$), 71.5 (**C**$_{alkyne}$), 63.2 (O-**C**H$_2$-), 55.6 (-O**C**H$_3$), 47.2 (N-**C**H$_2$-). *Characterization data are consistent with those of the literature.*[3]

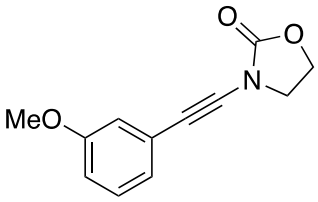


3-((4-Methoxyphenyl)ethynyl)oxazolidin-2-one [**CAS Number**: 1007597-79-6] (**1b**):

Prepared following **GP1** from 1-(bromoethynyl)-4-methoxybenzene (1.0 equiv., 2.1 g, 10.1 mmol) and 2-oxazolidinone (1.0 equiv., 879 mg, 10.1 mmol). Reaction time: 15 h. Purification by flash column chromatography over silica gel (gradient from pentane to pentane/EA = 2:1) afforded the title compound (750 g, 3.7 mmol, 31%) as a colorless solid. **TLC**: R*f* (pentane/EA = 70:30) = 0.25. **^{1}H NMR** (400 MHz, $CDCl_3$): *δ* (ppm) 7.38 (d, *J* = 8.8 Hz, C**H**$_{arom.}$, 2H), 6.82 (d, *J* = 8.8 Hz, C**H**$_{arom.}$, 2H), 4.48 – 4.43 (m, O-C**H**$_2$, 2H), 4.00 – 3.94 (m, N-C**H**$_2$, 2H), 3.79 (s, -OC**H**$_3$, 3H). *Characterization data are consistent with those of the literature.*[4]

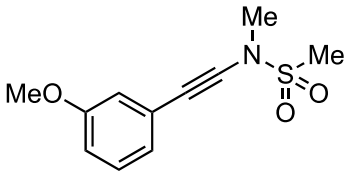


3-((3-Methoxyphenyl)ethynyl)oxazolidin-2-one [**CAS Number**: 1375467-22-3] (**1c**):



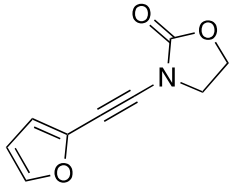
Prepared following **GP1** starting from 1-(bromoethynyl)-3-methoxybenzene (1.1 equiv., 3.5 g, 16.6 mmol) and 2-oxazolidinone (1.0 equiv., 1.3 g, 15.1 mmol). Reaction time: 63 h. Purification by flash column chromatography over silica gel (gradient from pentane/EA = 100:0 to 50:50) afforded the title compound (2.8 g, 12.9 mmol, 85%) as a colorless solid. **TLC**: R*f* (pentane/EA = 50:50) = 0.41. **^{1}H NMR** (500 MHz, $CDCl_3$): *δ* (ppm) 7.19 (t, *J* = 7.9 Hz, C**H**$_{arom.}$, 1H), 7.03 – 7.00 (m, C**H**$_{arom.}$, 1H), 6.97 – 6.94 (m, C**H**$_{arom.}$, 1H), 6.86 – 6.83 (m, C**H**$_{arom.}$, 1H), 4.45 (ddd, *J* = 8.0, 6.9, 2.1 Hz, O-C**H**$_2$, 2H), 3.97 (td, *J* = 8.0, 6.9, 2.1 Hz, N-C**H**$_2$, 2H), 3.77 – 3.77 (m, -OC**H**$_3$, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$): *δ* (ppm) 159.4 (**C**$_q$), 156.0 (**C**$_q$), 129.4 (**C**H$_{arom.}$), 124.0 (**C**H$_{arom.}$), 123.2 (**C**$_q$), 116.3 (**C**H$_{arom.}$), 114.8 (**C**H$_{arom.}$), 78.9 (**C**$_{alkyne}$), 71.2 (**C**$_{alkyne}$), 63.2 (O-**C**H$_2$), 55.3 (-O**C**H$_3$), 47.1 (N-**C**H$_2$). *Characterization data are consistent with those of the literature.*[4]

N-[2-(3-Methoxyphenyl)ethynyl]-N-methylmethanesulfonamide [**CAS Number:**1402850-57-0] (**1d**):



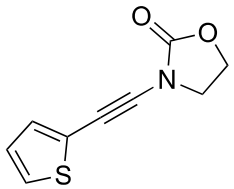
Prepared following **GP1** starting from 1-(bromoethynyl)-3,5-dimethoxybenzene (1.1 equiv., 1.2 g, 5.5 mmol) and N-methylmethanesulfonamide (1.0 equiv., 543 mg, 5 mmol). Reaction time: 85 h. Purification by flash chromatography over silica gel (gradient from cyclohexane/EA = 70:30 to 65:35) afforded the title compound (1.0 g, 4.3 mmol, 78%) as a dark orange solid. **TLC**: R*f* (pentane/EA = 75:25) = 0.24. **^{1}H NMR** (400 MHz, $CDCl_3$): *δ* (ppm) 7.20 (t, *J* = 8.1 Hz, C**H**$_{arom.}$, 1H), 6.99 (dt, *J* = 8.1, 1.2 Hz, C**H**$_{arom.}$, 1H), 6.93 (dd, *J* = 2.6, 1.2 Hz, C**H**$_{arom.}$, 1H), 6.85 (ddd, *J* = 8.0, 2.6, 1.2 Hz, C**H**$_{arom.}$, 1H), 3.78 (s, -OC**H**$_3$, 3H), 3.29 (s, -C**H**$_3$, 3H), 3.11 (s, -C**H**$_3$, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): *δ* (ppm) 159.4 (**C**$_q$), 129.5 (**C**H$_{arom.}$), 124.1 (**C**$_q$), 123.5 (**C**H$_{arom.}$), 116.4 (**C**H$_{arom.}$), 114.7 (**C**H$_{arom.}$), 83.0 (**C**$_{alkyne}$), 69.5 (**C**$_{alkyne}$), 55.4 (-O**C**H$_3$), 39.3 (-**C**H$_3$), 36.9 (-**C**H$_3$). *Characterization data are consistent with those of the literature.*[6]

3-(Furan-2-ylethynyl)oxazolidin-2-one [**CAS Numbe**r: 1221282-95-6] (**1e**):



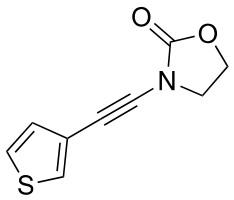
Prepared following **GP2** from 2-ethynylfuran (1.0 equiv. 9.2 mmol, 850 mg) and 2-oxazolidinone (5.0 equiv., 4.0 g, 46 mmol). Purification by flash column chromatography over silica gel (pentane/EA = 70:30) afforded the title compound (650 mg, 3.7 mmol, 40%) as a pale-yellow solid. **TLC**: R*f* (pentane/EA = 70:30) = 0.28. **^{1}H NMR** (500 MHz, $CDCl_3$): *δ* (ppm) 7.39 (dd, *J* = 1.9, 0.8 Hz, C**H**$_{arom.}$, 1H), 6.63 (dd, *J* = 3.4, 0.8 Hz, C**H**$_{arom.}$, 1H), 6.38 (dd, *J* = 3.4, 1.9 Hz, C**H**$_{arom.}$, 1H), 4.50 – 4.45 (m, O-C**H**$_2$, 2H), 4.01 – 3.96 (m, N-C**H**$_2$, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$): *δ* (ppm) 155.8 (**C**$_q$), 144.3 (**C**H$_{arom.}$), 136.2 (**C**$_q$), 117.3 (**C**H$_{arom.}$), 111.2 (**C**H$_{arom.}$), 83.1 (**C**$_{alkyne}$), 63.4 (**C**$_{alkyne}$), 62.1 (O-**C**H$_2$), 46.9 (N-**C**H$_2$). *Characterization data are consistent with those of the literature.*[4]

3-(Thiophen-2-ylethynyl)oxazolidin-2-one [**CAS Numbe**r: 1821029-54-2] (**1f**):



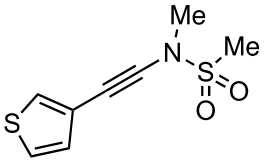
Prepared following **GP2** from 2-ethynylthiophene (1.0 equiv., 9.3 mmol, 1.0 g) and 2-oxazolidinone (5.0 equiv., 46.5 mmol, 4.0 g). Purification by flash column chromatography over silica gel (gradient from DCM to DCM/MeOH= 99:1) afforded the title compound (1.1 g, 5.4 mmol, 59%) as a pale-yellow solid. **TLC**: R*f* (DCM) = 0.33. **^{1}H NMR** (500 MHz, $CDCl_3$): *δ* (ppm) 7.28 (dd, *J* = 5.2, 1.2 Hz, C**H**$_{arom.}$, 1H), 7.23 (dd, *J* = 3.6, 1.2 Hz, C**H**$_{arom.}$, 1H), 6.97 (dd, *J* = 5.2, 3.6 Hz, C**H**$_{arom.}$, 1H), 4.50 – 4.45 (m, O-C**H**$_2$, 2H), 4.01 – 3.96 (m, N-C**H**$_2$, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$): *δ* (ppm) 155.9 (**C**$_q$), 133.3 (**C**H$_{arom.}$), 128.1 (**C**H$_{arom.}$), 127.1 (**C**H$_{arom.}$), 122.1 (**C**$_q$), 82.5 (**C**$_{alkyne}$), 64.8 (**C**$_{alkyne}$), 63.3 (O-**C**H$_2$), 47.1 (N-**C**H$_2$). *Characterization data are consistent with those of the literature.*[4]

3-(Thiophen-3-ylethynyl)oxazolidin-2-one [**CAS Number**: 1375467-24-5] (**1g**):



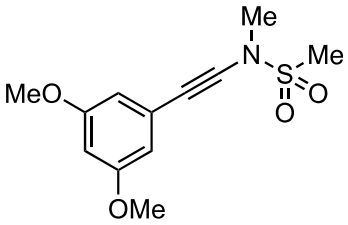
Prepared following **GP2** from 3-ethynylthiophene (1.1 equiv., 9.25 mmol, 1.0 g) and 2-oxazolidinone (5.0 equiv., 4.0 g, 46.3 mmol). Purification by flash column chromatography over silica gel (gradient from DCM to DCM/MeOH = 99:1) afforded the title compound (1.3 g, 6.9 mmol, 74%) as a colorless solid. **TLC**: R*f* (DCM) = 0.35. **^{1}H NMR** (500 MHz, $CDCl_3$): *δ* (ppm) 7.46 (dd, *J* = 3.0, 1.2 Hz, C**H**$_{arom.}$, 1H), 7.26 (dd, *J* = 5.0, 3.0 Hz, C**H**$_{arom.}$, 1H), 7.11 (dd, *J* = 5.0, 1.2 Hz, C**H**$_{arom.}$, 1H), 4.50 – 4.45 (m, O-C**H**$_2$, 2H), 4.01 – 3.96 (m, N-C**H**$_2$, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$): *δ* (ppm) 156.1 (**C**$_q$), 130.2 (**C**H$_{arom.}$), 129.3 (**C**H$_{arom.}$), 125.4 (**C**H$_{arom.}$), 121.0 (**C**$_q$), 78.5 (**C**$_{alkyne}$), 66.5 (**C**$_{alkyne}$), 63.2 (O-**C**H$_2$), 47.1 (N-**C**H$_2$). *Characterization data are consistent with those of the literature.*[4]

N-Methyl-N-(thiophen-3-ylethynyl)methanesulfonamide [**CAS Number**: 1333483-21-8] (**1h**):



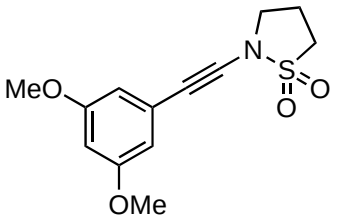
Prepared following **GP1** starting from 3-(2-bromoethynyl)thiophene (1.1 equiv., 0.94 g, 5.0 mmol) and N-methylmethanesulfonamide (1.0 equiv., 0.5 g, 4.6 mmol). Reaction time: 87 h. Purification by flash chromatography over silica gel (cyclohexane/EA = 80:20) gave the title compound (975 mg, 4.5 mmol, 90%) as a pale-pink solid. **TLC:** R*f* (pentane/EA = 70:30) = 0.5. **^{1}H NMR** (400 MHz, $CDCl_3$): *δ* (ppm) 7.44 (dd, *J* = 3.0, 1.2 Hz, C**H**$_{arom.}$, 1H), 7.27 (dd, *J* = 5.0, 3.0 Hz, C**H**$_{arom.}$, 1H), 7.10 (dd, *J* = 5.0, 1.2 Hz, C**H**$_{arom.}$, 1H), 3.28 (s, -C**H**$_3$, 3H), 3.11 (s, -C**H**$_3$, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): *δ* (ppm) 130.3 (**C**H$_{arom.}$), 129.3 (**C**H$_{arom.}$), 125.4 (**C**H$_{arom.}$), 121.2 (**C**$_q$), 82.5 (**C**$_{alkyne}$), 64.6 (**C**$_{alkyne}$), 39.3 (-**C**H$_3$), 36.9 (-**C**H$_3$). *Characterization data are consistent with the literature.*[5]

N-((3,5-Dimethoxyphenyl)ethynyl)-N-methylmethanesulfonamide
[**CAS Number**: 1357012-01-1] (**1i**):



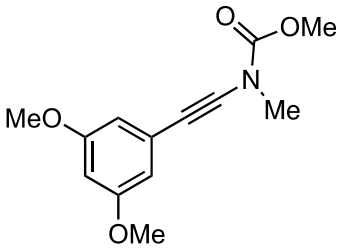
Prepared following **GP1** starting from 1-(2-bromoethynyl)-3,5-dimethoxybenzene (1.1 equiv., 788 mg, 3.3 mmol) and N-methylmethanesulfonamide (1.0 equiv., 324 mg, 3.0 mmol). Reaction time: 63 h. Purification by flash chromatography over silica gel (cyclohexane/EA = 70/30) gave the title compound (667 mg, 2.5 mmol, 93%) as a pale-yellow oil. **TLC:** R*f* (pentane/EA = 70:30) = 0.36. **^{1}H NMR** (400 MHz, $CDCl_3$): *δ* (ppm) 6.55 (d, *J* = 2.3 Hz, C**H**$_{ortho}$, 2H), 6.42 (t, *J* = 2.3 Hz, C**H**$_{para}$, 1H), 3.77 (s, -OC**H**$_3$, 6H), 3.30 (s, -C**H**$_3$, 3H), 3.12 (s, -C**H**$_3$, 3H). *Characterization data are consistent with the literature.*[5]

2-((3,5-Dimethoxyphenyl)ethynyl)isothiazolidine 1,1-dioxide (**1j**):



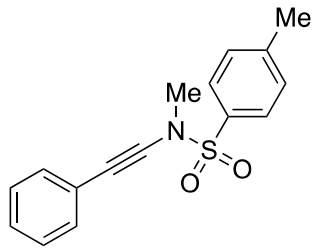
Prepared following **GP1** starting from 1-(2-bromoethynyl)-3,5-dimethoxybenzene (1.1 equiv., 444 mg, 1.8 mmol) and isothiazolidine 1,1-dioxide (1.0 equiv., 203 mg, 1.7 mmol). Reaction time: 87 h. Purification by flash chromatography over silica gel (gradient from cyclohexane/EA = 60:40 to 50:50) gave the title compound (356 mg, 1.3 mmol, 69%) as a pale-yellow solid. **TLC:** R*f* (cyclohexane/EA = 60:40) = 0.21. **^{1}H NMR** (400 MHz, $CDCl_3$): *δ* (ppm) 6.57 (d, *J* = 2.3 Hz, C**H**$_{ortho}$, 2H), 6.41 (t, *J* = 2.3 Hz, C**H**$_{para}$, 1H), 3.80 (t, *J* = 7.1 Hz, -C**H**$_2$-, 2H), 3.78 (s, -OC**H**$_3$, 6H), 3.27 (t, *J* = 7.1 Hz, -C**H**$_2$-, 2H), 2.50 (p, *J* = 7.1 Hz, C-C**H**$_2$-C, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$): *δ* (ppm) 160.6 (2**C**$_q$), 124.0 (**C**$_q$), 109.4 (2**C**H$_{ortho}$), 101.7 (**C**H$_{para}$), 78.5 (**C**$_{alkyne}$), 71.8 (**C**$_{alkyne}$), 55.6 (-O**C**H$_3$), 49.9 (-**C**H$_2$-), 46.3 (-**C**H$_2$-), 19.5 (C-**C**H$_2$-C). **HRMS** (ESI positive): calculated for $C_{13}H_{15}KNO_4S$: 320.0353, found: 320.0346. **Mp**: 107 °C.

Methyl N-[2-(3,5-dimethoxyphenyl)ethynyl]-N-methylcarbamate
[**CAS Number**: 2413990-50-6] (**1k**):

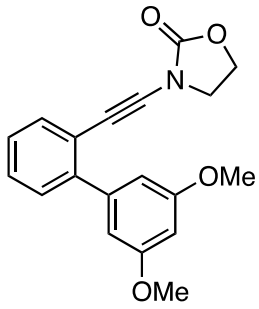


Prepared following **GP1** starting from 1-(2-bromoethynyl)-3,5-dimethoxybenzene (1.1 equiv., 988 mg, 4.1 mmol) and methyl *N*-methylcarbamate (1.0 equiv., 406 mg, 4.6 mmol). Reaction time: 63 h. Purification by flash chromatography over silica gel (cyclohexane/EA = 70:30) gave the title compound (301 mg, 1.2 mmol, 29%) as a beige solid. **TLC**: R*f* (cyclohexane/EA = 70:30) = 0.36. **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 6.55 (d, *J* = 2.3 Hz, C**H**$_{ortho}$, 2H), 6.40 (t, *J* = 2.3 Hz, C**H**$_{para}$, 1H), 3.84 (s, -C**H**$_3$, 3H), 3.77 (s, -OC**H**$_3$, 6H), 3.26 (s, -C**H**$_3$, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$): δ (ppm) 160.6 (2**C**$_q$), 156.0 (-**C**(O)OCH$_3$), 124.6 (**C**$_q$), 109.1 (2**C**H$_{ortho}$), 101.2 (**C**H$_{para}$), 55.5 (-O**C**H$_3$), 54.3 (-C(O)O**C**H$_3$), 38.1 (-C(O)N**C**H$_3$). *Characterization data are consistent with the literature.*[3]

N,4-Dimethyl-*N*-(phenylethynyl)benzenesulfonamide [**CAS Number:** 1005500-77-5] (**1l**): Prepared following **GP1** from 1-(bromoethynyl)benzene (1.2 equiv., 1.5 g, 8.4 mmol). Reaction time: 86 h. Purification by flash column chromatography over silica gel (gradient from pentane/EA = 100:0 to 90:10) afforded the title compound (1.46 g, 5.1 mmol, 73%) as a colorless solid. **TLC:** R*f* (pentane/EA 95:5) = 0.30. **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 7.84 (d, *J* = 8.4 Hz, C**H**$_{arom.}$, 2H), 7.40 – 7.34 (m, C**H**$_{arom.}$, 3H), 7.31 – 7.27 (m, C**H**$_{arom.}$, 4H), 3.16 (s, -C**H**$_3$, 3H), 2.46 (s, C**H**$_3$, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ (ppm) 144.9 (**C**$_{q\ arom.}$), 133.4 (**C**$_{q\ arom.}$), 131.6 (**C**H$_{arom.}$), 130.0 (**C**H$_{arom.}$), 128.4 (**C**H$_{arom.}$), 128.0 (**C**H$_{arom.}$), 128.0 (**C**H$_{arom.}$), 122.9 (**C**$_{q\ arom.}$), 84.1 (**C**$_{alkyne}$), 69.2 (**C**$_{alkyne}$), 39.5 (-**C**H$_3$), 21.8 (-**C**H$_3$). *Characterization data are consistent with those of the literature.*[2]



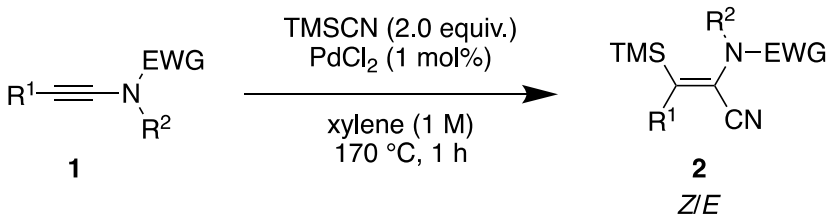
3-((3',5'-Dimethoxy-[1,1'-biphenyl]-2-yl)ethynyl)oxazolidin-2-one (**1m**):



Prepared following **GP2** starting from 2-(bromoethynyl)-3',5'-dimethoxy-1,1'-biphenyl (1.0 equiv., 2.0 g, 8.3 mmol) and oxazolidinone (5.0 equiv., 3.6 g, 42 mmol). Purification by flash column chromatography over silica gel (pentane/EA = 2:1) gave the title compound (2.2 g, 6.8 mmol, 82%) as a pale-orange oil. **TLC**: R*f* (cyclohexane/EA = 2:1) = 0.25. **^{1}H NMR** (500 MHz, $CDCl_3$): δ (ppm) 7.55 (ddd, J = 7.7, 1.4, 0.6 Hz, C**H**$_{arom.}$, 1H), 7.38 (ddd, J = 7.7, 1.8, 0.6 Hz, C**H**$_{arom.}$, 1H), 7.35 (td, J = 7.7, 1.4 Hz, C**H**$_{arom.}$, 1H), 7.29 (td, J = 7.7, 1.8 Hz, C**H**$_{arom.}$, 1H), 6.72 (d, J = 2.3 Hz, C**H**$_{ortho}$, 2H), 6.48 (t, J = 2.3 Hz, C**H**$_{para}$, 1H), 4.44 – 4.38 (m, O-C**H**$_2$, 2H), 3.84 (s, -OC**H**$_3$, 6H), 3.85 – 3.81 (m, N-C**H**$_2$, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$): δ (ppm) 160.5 (2**C**$_{q\ arom.}$), 155.7 (N-**C**(O)-O), 143.7 (**C**$_{q\ arom.}$), 142.6 (**C**$_{q\ arom.}$), 133.0 (**C**H$_{arom.}$), 129.4 (**C**H$_{arom.}$), 128.4 (**C**H$_{arom.}$), 127.4 (**C**H$_{arom.}$), 120.7 (**C**$_{q\ arom.}$), 107.5 (2**C**H$_{ortho}$), 100.0 (CH$_{para}$), 82.0 (**C**$_{alkyne}$), 71.2 (**C**$_{alkyne}$), 63.1 (O-**C**H$_2$), 55.6 (-O**C**H$_3$), 46.9 (N-**C**H$_2$). **HRMS** (ESI positive): calculated for $C_{19}H_{17}NNaO_4$: 346.1050, found: 346.1049.

3. Syntheses of β-silyl-α-cyanoenamide derivatives

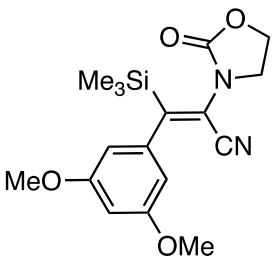
*a. General Procedure **GP3***



Procedure developed by Donnard.[4]

A flame-dried sealed tube was charged with ynamide **1a**-**m** (1.0 equiv.) and palladium chloride (1 mol%) under argon. Freshly distilled xylene (1 M) was then added, followed by TMSCN (2.0 equiv.). The mixture was stirred at 170 °C for 1 h. After reaction completion the solvent was evaporated, and the crude product was directly purified by flash chromatography.

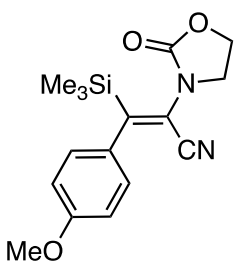
3-(3,5-Dimethoxyphenyl)-2-(2-oxooxazolidin-3-yl)-3-(trimethylsilyl)acrylonitrile (**2a**):



Z/*E* 90:10

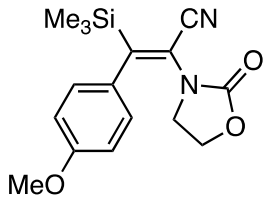
Prepared following **GP3** starting from **1a** (1.0 equiv., 124 mg, 0.5 mmol). Reaction time: 10 min. Purification by flash chromatography over silica gel (cyclohexane/EA = 2:1) gave an inseparable mixture of *Z*/*E* isomers (155 mg, 0.45 mmol, 90%) as a light brown oil. **TLC:** R*f* (pentane/EA = 75:25) = 0.17. **^{1}H NMR** (500 MHz, $CDCl_3$): δ (ppm) 6.40 (t, *J* = 2.2 Hz, C**H**$_{ortho}$, 1H, *Z*-isomer), 6.34 (t, *J* = 2.2 Hz, C**H**$_{ortho}$, 1H, *E*-isomer), 6.21 (d, *J* = 2.2 Hz, C**H**$_{para}$, 2H, *Z*-isomer), 6.07 (d, *J* = 2.2 Hz, C**H**$_{para}$, 2H, *E*-isomer), 4.47 – 4.42 (m, O-C**H**$_2$, 2H, *Z*-isomer), 4.16 – 4.10 (m, O-C**H**$_2$, 2H, *E*-isomer), 3.85 – 3.79 (m, N-C**H**$_2$, 2H, *Z*-isomer), 3.77 (s, -OC**H**$_3$, 6H, *Z*-isomer), 3.74 (s, -OC**H**$_3$, 6H, *E*-isomer), 3.34 – 3.28 (m, N-C**H**$_2$, 2H, *E*-isomer), 0.27 (s, -Si(C**H**$_3$)$_3$, 9H, *E*-isomer), 0.15 (s, -Si(C**H**$_3$)$_3$, 9H, *Z*-isomer). **^{13}C NMR** (126 MHz, $CDCl_3$): δ (ppm) 166.7 (**C**$_q$, *Z*-isomer), 162.3 (**C**$_q$, *E*-isomer), 161.0 (2**C**$_q$, *E*-isomer), 160.9 (2**C**$_q$, *Z*-isomer), 156.6 (**C**$_q$, *Z*-isomer), 155.7 (**C**$_q$, *E*-isomer), 140.4 (**C**$_q$, *Z*-isomer), 140.0 (**C**$_q$, *E*-isomer), 116.8 (**C**$_q$, *Z*-isomer), 115.4 (**C**$_q$, *E*-isomer), 115.0 (**C**$_q$, *E*-isomer), 113.0 (**C**$_q$, *Z*-isomer), 104.8 (2**C**H$_{ortho}$, *Z*-isomer), 103.8 (2**C**H$_{ortho}$, *E*-isomer), 99.9 (**C**H$_{para}$, *Z*-isomer), 99.2 (**C**H$_{para}$, *E*-isomer), 62.8 (O-**C**H$_2$, *E*-isomer), 62.4 (O-**C**H$_2$, *Z*-isomer), 55.6 (-O**C**H$_3$, *E*-isomer), 55.5 (-O**C**H$_3$, *Z*-isomer), 45.9 (N-**C**H$_2$, *Z*-isomer), 45.6 (N-**C**H$_2$, *E*-isomer), -1.16 (-Si(**C**H$_3$)$_3$, *E*-isomer), -1.24 (-Si(**C**H$_3$)$_3$, *Z*-isomer). **^{29}Si NMR** (99 MHz, $CDCl_3$): δ (ppm) -1.42 (*E*-isomer), -1.75 (*Z*-isomer). **HRMS** (ESI positive): calculated for $C_{17}H_{23}KN_2O_4Si$: 347.1422, found: 347.1419.

3-(4-Methoxyphenyl)-2-(2-oxooxazolidin-3-yl)-3-(trimethylsilyl)acrylonitrile (**2b**):
Prepared following **GP3** starting from **1b** (1.0 equiv., 109 mg, 0.5 mmol). Reaction time: 10 min. Purification by flash column chromatography over silica gel (pentane/EA = 85:15) afforded the title compound (148 mg, 0.47 mmol, 94%).
(*Z*)-3-(4-Methoxyphenyl)-2-(2-oxooxazolidin-3-yl)-3-(trimethylsilyl)acrylonitrile



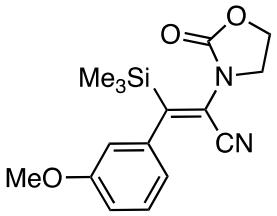
[**CAS Number**: 2763576-69-6] (**2b**$_Z$) (136 mg, 0.43 mmol) was isolated as a pale-yellow oil. **TLC**: R*f* (pentane/EA = 75:25) = 0.26. **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 7.07 – 7.02 (m, C**H**$_{arom.}$, 2H), 6.94 – 6.89 (m, C**H**$_{arom.}$, 2H), 4.54 – 4.35 (m, O-C**H**$_2$, 2H), 3.84 – 3.80 (m, N-C**H**$_2$, 2H), 3.80 (s, -OC**H**$_3$, 3H), 0.14 (s, -Si(C**H**$_3$)$_3$, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ (ppm) 167.0 (**C**$_q$), 159.6 (**C**$_q$), 156.7 (**C**$_q$), 130.6 (**C**$_q$), 128.2 (**C**H$_{arom.}$), 116.8 (**C**$_q$), 114.2 (**C**H$_{arom.}$), 113.5 (**C**$_q$), 62.4 (O-**C**H$_2$), 55.3 (-O**C**H$_3$), 45.9 (N-**C**H$_2$), -1.1 (-Si(**C**H$_3$)$_3$). **^{29}Si NMR** (80 MHz, $CDCl_3$): δ (ppm) -1.78. *Characterization data are consistent with the literature.*[4]

(*E*)-3-(4-Methoxyphenyl)-2-(2-oxooxazolidin-3-yl)-3-(trimethylsilyl)acrylonitrile



[**CAS Number**: 2763576-70-9] (**2b*E***) (12 mg, 0.04 mmol) was isolated as a pale-yellow oil. **TLC**: R*f* (pentane/EA = 75:25) = 0.23. **^{1}H NMR** (500 MHz, $CDCl_3$): δ (ppm) 7.07 –7.04 (m, C**H**$_{arom.}$, 2H), 6.94 – 6.90 (m, C**H**$_{arom.}$, 2H), 4.50 – 4.43 (m, O-C**H**$_2$, 2H), 3.86 – 3.82 (m, N-C**H**$_2$, 2H), 3.82 – 3.80 (m, -OC**H**$_3$, 3H), 0.20 – 0.12 (m, -Si(C**H**$_3$)$_3$, 9H). **^{13}C NMR** (126 MHz, $CDCl_3$): δ (ppm) 167.0 (**C**$_q$), 159.6 (**C**$_q$), 156.7 (**C**$_q$), 130.7 (**C**$_q$), 128.3 (2**C**H$_{arom.}$), 116.9 (**C**$_q$), 114.2 (2**C**H$_{arom.}$), 113.5 (**C**$_q$), 62.4 (O-**C**H$_2$), 55.3 (-O**C**H$_3$), 46.0 (N-**C**H$_2$), -1.1 (-Si(**C**H$_3$)$_3$). **^{29}Si NMR** (99, MHz, $CDCl_3$): δ (ppm) -1.77. *Characterization data are consistent with the literature.*[4]

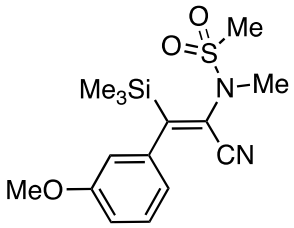
3-(3-Methoxyphenyl)-2-(2-oxooxazolidin-3-yl)-3-(trimethylsilyl)acrylonitrile [**CAS Number**: 2763576-77-6 (*Z*) ; 2763576-78-7 (*E*)] (**2c**):



Z/*E* 91:9

Prepared following **GP3** starting from **1c** (1.0 equiv., 109 mg, 0.5 mmol). Reaction time: 15 min. Purification by flash column chromatography over silica gel (pentane/EA = 75:25) afforded an inseparable mixture of *Z*/*E* isomers (124 mg, 0.39 mmol, 78%) as a colorless solid. **TLC**: R*f* (pentane/EA = 75:25) = 0.28. **^{1}H NMR** (500 MHz, $CDCl_3$): δ (ppm) 7.29 (t, *J* = 7.9 Hz, 1H, C**H**$_{arom.}$, *Z*-isomer), 7.25 (t, *J* = 7.9 Hz, C**H**$_{arom.}$, 1H, *E*-isomer), 6.86 (dd, *J* = 7.9, 2.2 Hz, C**H**$_{arom.}$, 1H, *Z*-isomer), 6.80 (dd, *J* = 7.9, 2.2 Hz, C**H**$_{arom.}$, 1H, *E*-isomer), 6.67 (dt, *J* = 7.9, 2.2 Hz, C**H**$_{arom.}$, 1H, *Z*-isomer), 6.62 (t, *J* = 2.2 Hz, C**H**$_{arom.}$, 1H, *Z*-isomer), 6.51 (dd, *J* = 7.9, 2.2 Hz, C**H**$_{arom.}$, 1H, *E*-isomer), 6.48 (t, *J* = 2.2 Hz, C**H**$_{arom.}$, 1H, *E*-isomer), 4.47 – 4.40 (m, O-C**H**$_2$, 2H, *Z*-isomer), 4.12 – 4.08 (m, O-C**H**$_2$, 2H, *E*-isomer), 3.85 – 3.80 (m, N-C**H**$_2$, 2H, *Z*-isomer), 3.79 (s, -OC**H**$_3$, 3H, *Z*-isomer), 3.76 (s, -OC**H**$_3$, 3H, *E*-isomer), 3.29 – 3.22 (m, N-C**H**$_2$, 2H, *E*-isomer), 0.27 (s, -Si(C**H**$_3$)$_3$, 9H, *E*-isomer), 0.15 (s, -Si(C**H**$_3$)$_3$, 9H, *Z*-isomer). **^{13}C NMR** (126 MHz, $CDCl_3$): δ (ppm) 166.7 (**C**$_q$, *Z*-isomer), 162.3 (**C**$_q$, *E*-isomer), 159.7 (**C**$_q$, *E*-isomer), 159.6 (**C**$_q$, *Z*-isomer), 156.6 (**C**$_q$, *Z*-isomer), 155.6 (**C**$_q$, *E*-isomer), 139.9 (**C**$_q$, *Z*-isomer), 139.4 (**C**$_q$, *E*-isomer), 129.90 (**C**H$_{arom.}$, *E*-isomer), 129.87 (**C**H$_{arom.}$, *Z*-isomer), 119.0 (**C**H$_{arom.}$, *Z*-isomer), 118.0 (**C**H$_{arom.}$, *E*-isomer), 116.9 (**C**$_q$, *Z*-isomer), 115.5 (**C**$_q$, *E*-isomer), 115.0 (**C**$_q$, *E*-isomer), 113.6 (**C**H$_{arom.}$, *Z*-isomer), 113.1 (**C**$_q$, *Z*-isomer), 113.0 (**C**H$_{arom.}$, *E*-isomer), 112.3 (**C**H$_{arom.}$, *Z*-isomer), 111.5 (**C**H$_{arom.}$, *E*-isomer), 62.7 (O-**C**H$_2$, *E*-isomer), 62.4 (O-**C**H$_2$, *Z*-isomer), 55.4 (-O**C**H$_3$, *Z*-isomer + *E*-isomer), 45.9 (N-**C**H$_2$, *Z*-isomer), 45.6 (N-**C**H$_2$, *E*-isomer), -1.1 (-Si(**C**H$_3$)$_3$, *E*-isomer), -1.3 (-Si(**C**H$_3$)$_3$, *Z*-isomer). **^{29}Si NMR** (99 MHz, $CDCl_3$): δ (ppm) -1.40 (*E*-isomer), -1.70 (*Z*-isomer).
Characterization data are consistent with the literature.[4]

N-(1-Cyano-2-(3-methoxyphenyl)-2-(trimethylsilyl)vinyl)-N-methylmethanesulfonamide (**2d**):



Z/*E* 85:15

Prepared following **GP3** starting from **1d** (1.0 equiv., 100 mg, 0.42 mmol). Purification by flash chromatography over silica gel (cyclohexane/EA = 80:20) gave an inseparable mixture of *Z*/*E* isomers (77 mg, 0.23 mmol, 54%) as a beige solid. **TLC:** R*f* (pentane/EA = 75:25) = 0.34. **^{1}H NMR** (500 MHz, $CDCl_3$): δ (ppm) 7.32 (t, *J* = 8.0 Hz, C**H**$_{arom.}$, 1H, *Z*-isomer), 7.27 (m, C**H**$_{arom.}$, 1H, *E*-isomer), 7.09 (ddd, *J* = 7.7, 1.8, 0.9 Hz, C**H**$_{arom.}$, 1H, *E*-isomer), 7.04 (t, *J* = 2.3 Hz, C**H**$_{arom.}$, 1H, *E*-isomer), 6.88 (ddd, *J* = 8.4, 2.6, 0.9 Hz, C**H**$_{arom.}$, 1H, *Z*-isomer), 6.81 (ddd, *J* = 8.4, 2.6, 0.9 Hz, C**H**$_{arom.}$, 1H, *E*-isomer), 6.64 (ddd, *J* = 7.6, 1.6, 0.9 Hz, C**H**$_{arom.}$, 1H, *Z*-isomer), 6.58 (dd, *J* = 2.6, 1.6 Hz, C**H**$_{arom.}$, 1H, *Z*-isomer), 3.82 (s, -OC**H**$_3$, 3H, *Z*-isomer), 3.80 (s, -OC**H**$_3$, 3H, *E*-isomer), 3.15 (s, -C**H**$_3$, 3H, *Z*-isomer), 3.02 (s, -C**H**$_3$, 3H, *Z*-isomer), 2.82 (s, -C**H**$_3$, 3H, *E*-isomer), 2.78 (s, -C**H**$_3$, 3H, *E*-isomer), 0.28 (s, -Si(C**H**$_3$)$_3$, 9H, *E*-isomer), 0.22 (s, -Si(C**H**$_3$)$_3$, 9H, *Z*-isomer). **^{13}C NMR** (126 MHz, $CDCl_3$): δ (ppm) 171.2 (**C**$_q$, *Z*-isomer), 166.5 (**C**$_q$, *E*-isomer), 159.8 (**C**$_q$, *Z*-isomer), 159.7 (**C**$_q$, *E*-isomer), 140.0 (**C**$_q$, *Z*-isomer), 139.4 (**C**$_q$, *E*-isomer), 130.0 (**C**H$_{arom.}$, *Z*-isomer), 129.6 (**C**H$_{arom.}$, *E*-isomer), 120.3 (**C**H$_{arom.}$, *E*-isomer), 119.9 (**C**$_q$, *Z*-isomer), 118.8 (**C**H$_{arom.}$, *Z*-isomer), 118.3 (**C**$_q$, *E*-isomer), 114.9 (**C**$_q$, *E*-isomer), 113.6 (**C**H$_{arom.}$, *Z*-isomer), 113.5 (**C**$_q$, *Z*-isomer), 113.3 (**C**H$_{arom.}$, *E*-isomer), 113.2 (**C**H$_{arom.}$, *E*-isomer), 112.3 (**C**H$_{arom.}$, *Z*-isomer), 55.5 (-O**C**H$_3$, *E*-isomer), 55.4 (-O**C**H$_3$, *Z*-isomer), 37.8 (-**C**H$_3$, *E*-isomer), 37.2 (-**C**H$_3$, *Z*-isomer), 36.7 (-**C**H$_3$, *E*-

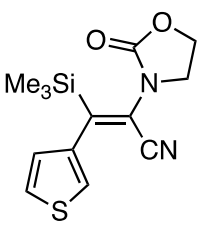
isomer), 35.8 (-**C**H_3, *Z*-isomer), -0.7 (-Si(**C**H_3)$_3$, *Z*-isomer), -1.1 (-Si(**C**H_3)$_3$, *E*-isomer). **^{29}Si NMR** (99 MHz, $CDCl_3$): *δ* (ppm) -1.02 (*Z*-isomer), -1.24 (*E*-isomer). **HRMS** (ESI positive): calculated for $C_{15}H_{22}N_2NaO_3SSi$: 361.1013, found: 361.1007.

3-(Furan-2-yl)-2-(2-oxooxazolidin-3-yl)-3-(trimethylsilyl)acrylonitrile (**2e**):
Prepared following **GP3** starting from **1e** (1.0 equiv., 44 mg, 0.25 mmol). Reaction time: 10 min. Purification by flash column chromatography over silica gel (pentane/EA = 75:25) afforded the title compound (30 mg, 0.11 mmol, 43%).
(*Z*)-3-(Furan-2-yl)-2-(2-oxooxazolidin-3-yl)-3-(trimethylsilyl)acrylonitrile [**CAS Number**: 2763576-94-7] (**2e$_Z$**) (22 mg, 0.08 mmol) was isolated as a pale-yellow oil. **TLC:** R*f* (pentane/EA = 75:25) = 0.28. **^{1}H NMR** (500 MHz, $CDCl_3$): *δ* (ppm) 7.55 (dd, *J* = 1.8, 0.6 Hz, C**H**$_{arom.}$, 1H), 7.05 (dd, *J* = 3.6, 0.6 Hz, C**H**$_{arom.}$, 1H), 6.52 (dd, *J* = 3.6, 1.8 Hz, C**H**$_{arom.}$, 1H), 4.52 – 4.42 (m, O-C**H**$_2$, 2H), 3.88 – 3.82 (m, N-C**H**$_2$, 2H), 0.30 (s, -Si(C**H**$_3$)$_3$, 9H). **^{13}C NMR** (126 MHz, $CDCl_3$): *δ* (ppm) 156.8 (**C**$_q$), 151.3 (**C**$_q$), 150.3(**C**$_q$), 144.3 (**C**H$_{arom.}$), 114.8 (**C**$_q$), 113.5 (**C**H$_{arom.}$), 112.2 (**C**H$_{arom.}$), 110.8 (**C**$_q$), 62.3 (O-**C**H$_2$), 45.9 (N-**C**H$_2$), 0.2 (-Si(**C**H_3)$_3$). **^{29}Si NMR** (99 MHz, $CDCl_3$): *δ* (ppm) 1.29. *Characterization data are consistent with the literature.*[4]

(*E*)-3-(Furan-2-yl)-2-(2-oxooxazolidin-3-yl)-3-(trimethylsilyl)acrylonitrile [**CAS Number**: 2763576-95-8] (**2e$_E$**) (8 mg, 0.03 mmol) was isolated as a pale-yellow oil. **TLC:** R*f* (pentane/EA = 75:25) = 0.16. **^{1}H NMR** (500 MHz, $CDCl_3$): *δ* (ppm) 7.52 (dd, *J* = 1.8, 0.7 Hz, C**H**$_{arom.}$, 1H), 6.59 (dd, *J* = 3.6, 0.7 Hz, C**H**$_{arom.}$, 1H), 6.49 (dd, *J* = 3.6, 1.8 Hz, C**H**$_{arom.}$, 1H), 4.47 – 4.39 (m, O-**C**H$_2$, 2H), 3.74 – 3.67 (m, N-**C**H$_2$, 2H), 0.42 (s, -Si(C**H**$_3$)$_3$, 9H). **^{13}C NMR** (126 MHz, $CDCl_3$): *δ* (ppm) 155.4 (**C**$_q$), 150.5 (**C**$_q$), 146.3 (**C**$_q$), 144.2 (**C**H$_{arom.}$), 115.9 (**C**$_q$), 114.4 (**C**H$_{arom.}$), 112.4 (**C**H$_{arom.}$), 112.0 (**C**$_q$), 62.8 (O-**C**H$_2$), 45.0 (N-**C**H$_2$), 0.3 (-Si(**C**H_3)$_3$). **^{29}Si NMR** (99 MHz, $CDCl_3$): *δ* (ppm) 0.75. *Characterization data are consistent with the literature.*[4]

2-(2-Oxooxazolidin-3-yl)-3-(thiophen-2-yl)-3-(trimethylsilyl)acrylonitrile
[**CAS Number**: 2763576-92-5 (*Z*) ; 2763576-93-6 (*E*)] (**2f**):
Prepared following **GP3** starting from **1f** (1.0 equiv., 97 mg, 0.5mmol). Reaction time: 10 min. Purification by flash column chromatography over silica gel (pentane/EA = 3:1) gave an inseparable mixture of *Z*/*E* isomers (60 mg, 0.21 mmol, 41%) as a pale-orange oil. **TLC:** R*f* (pentane/EA = 75:25) = 0.30. **^{1}H NMR** (500 MHz, $CDCl_3$): *δ* (ppm) 7.40 (dd, *J* = 5.2, 1.2 Hz, C**H**$_{arom.}$, 1H, *Z*-isomer), 7.39 (dd, *J* = 5.2, 1.2 Hz, 1H, C**H**$_{arom.}$, *E*-isomer), 7.07 (dd, *J* = 5.2, 3.6 Hz, 1H, C**H**$_{arom.}$, *Z*-isomer), 7.05 (dd, *J* = 5.2, 3.6 Hz, C**H**$_{arom.}$, 1H, *E*-isomer), 7.02 (dd, *J* = 3.6, 1.2 Hz, C**H**$_{arom.}$, 1H, *Z*-isomer), 6.91 (dd, *J* = 3.6, 1.2 Hz, C**H**$_{arom.}$, 1H, *E*- isomer), 4.49 – 4.45 (m, 2H, O-C**H**$_2$, *Z*-isomer), 4.31 – 4.26 (m, O-C**H**$_2$, 2H, *E*-isomer), 3.90 – 3.81 (m, N-C**H**$_2$, 2H, *Z*- isomer), 3.49 – 3.43 (m, N-C**H**$_2$, 2H, *E*-isomer), 0.37 (s, -Si(C**H**$_3$)$_3$, 9H, *E*-isomer), 0.22 (s, -Si(C**H**$_3$)$_3$, 9H, *Z*-isomer). **^{13}C NMR** (126 MHz, $CDCl_3$): *δ* (ppm) 158.7 (**C**$_q$, *Z*-isomer), 156.5 (**C**$_q$, *Z*-isomer), 155.4 (**C**$_q$, *E*-isomer), 153.6 (**C**$_q$, *E*- isomer), 138.5 (**C**$_q$, *Z*-isomer), 137.6 (**C**$_q$, *E*-isomer), 127.8 (**C**H$_{arom.}$, *E*-isomer), 127.7 (**C**H$_{arom.}$, *E*-isomer), 127.62 (**C**H$_{arom.}$, *Z*-isomer), 127.56 (**C**H$_{arom.}$, *E*-isomer), 127.4 (**C**H$_{arom.}$, *Z*-isomer), 127.3 (**C**H$_{arom.}$, *Z*-isomer), 117.3 (**C**$_q$, *Z*-isomer), 115.5 (**C**$_q$, *E*-isomer), 115.1 (**C**$_q$, *E*-isomer), 113.4 (**C**$_q$, *Z*-isomer), 62.9 (O-**C**H$_2$, *E*-isomer), 62.4 (O-**C**H$_2$, *Z*-isomer), 45.9 (N-**C**H$_2$, *Z*-isomer), 45.2 (N-**C**H$_2$, *E*-isomer), -0.3 (-Si(**C**H_3)$_3$, *E*-isomer), -1.0 (-Si(**C**H_3)$_3$, *Z*-isomer). **^{29}Si NMR** (99 MHz, $CDCl_3$): *δ* (ppm) 0.14 (*E*--isomer), -0.32 (*Z*-isomer). *Characterization data are consistent with the literature.*[4]

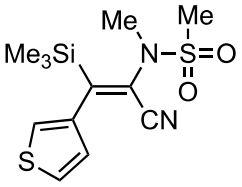
2-(2-Oxooxazolidin-3-yl)-3-(thiophen-3-yl)-3-(trimethylsilyl)acrylonitrile [**CAS Number**: 2763576-90-3 (*Z*) ; 2763576-91-4 (*E*)] (**2g**):



Z/*E* 89:11

Prepared following **GP3** starting from **1g** (1.0 equiv., 97 mg, 0.5 mmol). Reaction time: 10 min. Purification by flash column chromatography over silica gel (pentane/EA = 75:25) gave an inseparable mixture of *Z*/*E* isomers (95 mg, 0.32 mmol, 65%) as a pale orange oil. **TLC:** R*f* (pentane/EA = 75:25) = 0.26. **^{1}H NMR** (500 MHz, $CDCl_3$): *δ* (ppm) 7.38 (dd, *J* = 5.0, 2.9 Hz, C**H**$_{arom.}$, 1H, *Z*-isomer), 7.36 (dd, *J* = 5.0, 2.9 Hz, C**H**$_{arom.}$, 1H, *E*-isomer), 7.18 (dd, *J* = 3.0, 1.3 Hz, C**H**$_{arom.}$, 1H, *Z*-isomer), 6.97 (dd, *J* = 3.0, 1.3 Hz, C**H**$_{arom.}$, 1H, *E*-isomer), 6.94 (dd, *J* = 5.0, 1.3 Hz, C**H**$_{arom.}$, 1H, *Z*-isomer), 6.79 (dd, *J* = 5.0, 1.3 Hz, C**H**$_{arom.}$, 1H, *E*- isomer), 4.48 – 4.41 (m, O-C**H**$_2$, 2H, *Z*-isomer), 4.19 – 4.12 (m, O-C**H**$_2$, 2H, *E*-isomer), 3.85 – 3.79 (m, N-C**H**$_2$, 2H, *Z*-isomer), 3.30 – 3.24 (m, N-C**H**$_2$, 2H, *E*-isomer), 0.28 (s, -Si(C**H**$_3$)$_3$, 9H, *E*-isomer), 0.16 (s, -Si(C**H**$_3$)$_3$, 9H, *Z*-isomer). **^{13}C NMR** (126 MHz, $CDCl_3$): *δ* (ppm) 162.0 (**C**$_q$, *Z*-isomer), 157.2 (**C**$_q$, *E*-isomer), 156.6 (**C**$_q$, *Z*-isomer), 155.6 (**C**$_q$, *E*- isomer), 138.0 (**C**$_q$, -*Z*-isomer), 137.3 (**C**$_q$, *E*-isomer), 126.9 (**C**H$_{arom.}$, *Z*-isomer), 126.7 (**C**H$_{arom.}$, *E*-isomer), 126.6 (**C**H$_{arom.}$, *Z*- isomer), 126.4 (**C**H$_{arom.}$, *E*-isomer), 122.9 (**C**H$_{arom.}$, *Z*-isomer), 121.3 (**C**H$_{arom.}$, *E*-isomer), 116.5 (**C**$_q$, *Z*-isomer), 115.7 (**C**$_q$, *E*- isomer), 115.0 (**C**$_q$, E-isomer), 113.5 (**C**$_q$, *Z*-isomer), 62.8 (O-**C**H$_2$, *E*-isomer), 62.4 (O-**C**H$_2$, *Z*-isomer), 45.9 (N-**C**H$_2$, *Z*-isomer), 45.3 (N-**C**H$_2$, *E*-isomer), -1.0 (-Si(**C**H$_3$)$_3$, *E*-isomer), -1.1 (-Si(**C**H$_3$)$_3$, *Z*-isomer). **^{29}Si NMR** (99 MHz, $CDCl_3$): *δ* (ppm) -1.21 (*E*- isomer), -1.38 (*Z*-isomer). *Characterization data are consistent with the literature.*[4]

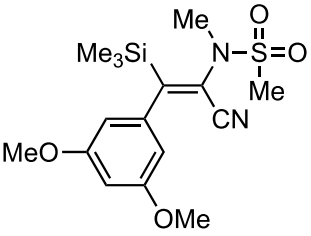
N-(1-Cyano-2-(thiophen-3-yl)-2-(trimethylsilyl)vinyl)-N-methylmethanesulfonamide (**2h**):



Z/*E* 90:10

Prepared following **GP3** starting from **1h** (1.0 equiv., 100 mg, 0.46 mmol). Purification by flash chromatography over silica gel (cyclohexane/EA = 90:10) gave an inseparable mixture of *Z*/*E* isomers (97 mg, 0.31 mmol, 66%) as a pale-yellow solid. **TLC:** R*f* (pentane/EA = 70:30) = 0.63. **^{1}H NMR** (400 MHz, $CDCl_3$): *δ* (ppm) 7.41 (dd, *J* = 5.0, 3.0 Hz, C**H**$_{arom.}$, 1H, *Z*-isomer), 7.36 (dd, *J* = 5.0, 3.0 Hz, C**H**$_{arom.}$, 1H, *E*-isomer), 7.16 (dd, *J* = 3.0, 1.3 Hz, C**H**$_{arom.}$, 1H, *Z*-isomer), 7.09 (dd, *J* = 3.0, 1.3 Hz, C**H**$_{arom.}$, 1H, *E*-isomer), 6.93 (dd, *J* = 5.0, 1.3 Hz, C**H**$_{arom.}$, 1H, *Z*-isomer), 6.89 (dd, *J* = 5.0, 1.3 Hz, C**H**$_{arom.}$, 1H, *E*-isomer), 3.14 (s, -C**H**$_3$, 3H, *Z*-isomer), 3.02 (s, -C**H**$_3$, 3H, *Z*-isomer), 2.87 (s, -C**H**$_3$, 3H, *E*-isomer), 2.80 (s, -C**H**$_3$, 3H, *E*-isomer), 0,30 (s, -Si(C**H**$_3$)$_3$, 9H, *E*-isomer), 0,23 (s, -Si(C**H**$_3$)$_3$, 9H, *Z*-isomer). **^{13}C NMR** (101 MHz, $CDCl_3$): *δ* (ppm) 166.6 (**C**$_q$, *Z*-isomer), 138.1 (**C**$_q$, *Z*-isomer), 126.9 (C**H**$_{arom.}$, *Z*-isomer), 126.8 (C**H**$_{arom.}$, *Z*-isomer), 126.4 (C**H**$_{arom.}$, *E*-isomer), 126.2 (C**H**$_{arom.}$, *E*-isomer), 122.85 (C**H**$_{arom.}$, *Z*-isomer), 122.02 (C**H**$_{arom.}$, *E*-isomer), 119.44 (**C**$_q$, *Z*-isomer), 113.89 (**C**$_q$, *Z*-isomer), 37.76 (-**C**H$_3$, *E*-isomer), 37.23 (-**C**H$_3$, *Z*-isomer), 36.47 (-**C**H$_3$, *E*-isomer), 35.83 (-**C**H$_3$, *Z*-isomer), -0.59 (-Si(**C**H$_3$)$_3$, *Z*-isomer), -0.92 (-Si(**C**H$_3$)$_3$, *E*-isomer). *E*-isomer could not be completely characterized due to low signals. **^{29}Si NMR** (80 MHz, $CDCl_3$): *δ* (ppm) -0.68, -0.95. **HRMS** (ESI positive): calculated for $C_{12}H_{18}KN_2O_2S_2Si$: 353.0211, found: 353.0203.

N-(1-Cyano-2-(3,5-dimethoxyphenyl)-2-(trimethylsilyl)vinyl)-N-methylmethanesulfonamide (**2i**):

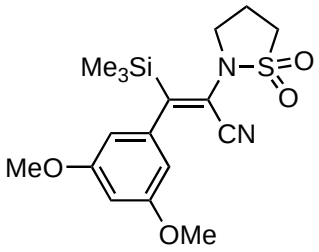


Z/*E* 89:11

Prepared following **GP3** starting from **1i** (1.0 equiv., 100 mg, 0.4 mmol). **TLC:** R*f* (pentane/EA = 80:20) = 0.27. Purification by flash chromatography over silica gel (cyclohexane/EA = 80:20) gave an inseparable mixture of *Z*/*E* isomers (79 mg, 0.21 mmol, 58%) as a pale-yellow solid. **^{1}H NMR** (500 MHz, $CDCl_3$): *δ* (ppm) 6.41 (t, *J* = 2.3 Hz, C**H**$_{para}$, 1H, *Z*-isomer), 6.37 (t, *J* = 2.3 Hz, C**H**$_{para}$, 1H, *E*-isomer), 6.17 (d, *J* = 2.3 Hz, C**H**$_{ortho}$, 2H, *Z*-isomer), 6.17 (d, *J* = 2.3 Hz, C**H**$_{ortho}$, 2H, *E*-isomer), 3.79 (s, -OC**H**$_3$, 6H, *Z*-isomer), 3.77 (s, -OC**H**$_3$, 6H, *E*-isomer), 3.14 (s, -C**H**$_3$, 3H, *Z*-isomer), 3.02 (s, -C**H**$_3$, 3H, *Z*-isomer), 2.88 (s, -C**H**$_3$, 3H, *E*-isomer), 2.78 (s, -C**H**$_3$, 3H, *E*-isomer), 0.29 (s, -Si(C**H**$_3$)$_3$, 9H, *E*-isomer), 0.22 (s, -Si(C**H**$_3$)$_3$, 9H, *Z*-isomer). **^{13}C NMR** (126 MHz, $CDCl_3$): *δ* (ppm) 171.1 (**C**$_q$, *Z*-isomer), 166.3 (**C**$_q$, *E*-isomer), 161.0 (2**C**$_q$, *Z*-isomer), 160.8 (2**C**$_q$, *E*-isomer), 140.5 (**C**$_q$, *Z*-isomer), 139.8 (**C**$_q$, *E*-isomer), 119.8 (**C**$_q$, *Z*-isomer), 118.3 (**C**$_q$, *E*-isomer), 113.4 (**C**$_q$, *Z*-isomer), 112.2 (**C**$_q$, *E*-isomer), 104.6 (2**C**H$_{ortho}$, *Z*-isomer), 104.2 (2**C**H$_{ortho}$, *E*-isomer), 99.8 (**C**H$_{para}$, *Z*-

isomer), 99.4 (**C**H$_{para}$, *E*-isomer), 55.6 (-O**C**H$_3$, *E*-isomer), 55.5 (-O**C**H$_3$, *Z*-isomer), 37.8 (-**C**H$_3$, *E*-isomer), 37.2 (-**C**H$_3$, *Z*-isomer), 36.7 (-**C**H$_3$, *E*-isomer), 35.8 (-**C**H$_3$, *Z*-isomer), -0.7 (-Si(**C**H$_3$)$_3$, *Z*-isomer), -1.1 (-Si(**C**H$_3$)$_3$, *E*-isomer). **^{29}Si NMR** (80 MHz, CDCl$_3$): δ (ppm) -1.08 (*Z*-isomer), -1.27 (*E*-isomer). **HRMS** (ESI positive): calculated for $C_{16}H_{24}KN_2O_4SSi$: 407.0858, found: 407.0855.

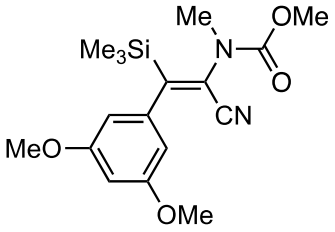
3-(3,5-Dimethoxyphenyl)-2-(1,1-dioxidoisothiazolidin-2-yl)-3-(trimethylsilyl)acrylonitrile (**2j**):



Z/E = 93/7

Prepared following **GP3** starting from **1j** (1.0 equiv., 100 mg, 0.4 mmol). **TLC:** R*f* (pentane/EA = 60:40) = 0.4. Purification by flash chromatography over silica gel (cyclohexane/EA = 70:30) gave an inseparable mixture of *Z*/*E* isomers (98 mg, 0.26 mmol, 72%) as a white solid. **^{1}H NMR** (400 MHz, CDCl$_3$): δ (ppm) 6.41 (t, *J* = 2.3 Hz, C**H**$_{para}$, 1H, *Z*-isomer), 6.35 (t, *J* = 2.3 Hz, C**H**$_{para}$, 1H, *E*-isomer), 6.19 (d, *J* = 2.3 Hz, C**H**$_{ortho}$, 2H, *Z*-isomer), 6.11 (d, *J* = 2.3 Hz, C**H**$_{ortho}$, 2H, *E*-isomer), 3.79 (s, -OC**H**$_3$, 6H, *Z*-isomer), 3.78 (s, -OC**H**$_3$, 6H, *E*-isomer), 3.62 (t, J = 6.8 Hz, -C**H**$_2$-, 2H, *Z*-isomer), 3.36 (t, J = 6.8 Hz, -C**H**$_2$-, 2H, *E*-isomer), 3.20 (t, *J* = 7.4 Hz, -C**H**$_2$-, 2H, *Z*-isomer), 3.03 (t, *J* = 7.4 Hz, -C**H**$_2$-, 2H, *E*-isomer), 2.52 (p, *J* = 7.2 Hz, C-C**H**$_2$-C, 2H, *Z*-isomer), 2.32 (p, *J* = 7.2 Hz, C-C**H**$_2$-C, 2H, *E*-isomer), 0.28 (s, -Si(C**H**$_3$)$_3$, 9H, *E*-isomer), 0.22 (s, -Si(C**H**$_3$)$_3$, 9H, *Z*-isomer). **^{13}C NMR** (101 MHz, CDCl$_3$): δ (ppm) 170.7 (**C**$_q$, *Z*-isomer), 167.9 (**C**$_q$, *E*-isomer), 161.0 (2**C**$_q$, *Z*-isomer), 160.5 (2**C**$_q$, *E*-isomer), 140.6 (**C**$_q$, *Z*-isomer), 140.0 (**C**$_q$, *E*-isomer), 119.2 (**C**$_q$, *Z*-isomer), 116.3 (**C**$_q$, *E*-isomer), 115.6 (**C**$_q$, *E*-isomer), 113.7 (**C**$_q$, *Z*-isomer), 104.7 (2**C**H$_{ortho}$, *Z*-isomer), 104.4 (2**C**H$_{ortho}$, *E*-isomer), 99.9 (**C**H$_{para}$, *Z*-isomer), 99.3 (**C**H$_{para}$, *E*-isomer), 55.5 (-O**C**H$_3$, *Z*-isomer + *E*-isomer), 48.7 (-**C**H$_2$-, *Z*-isomer), 48.0 (-**C**H$_2$-, *E*-isomer), 46.6 (-**C**H$_2$-, *E*-isomer), 46.5 (-**C**H$_2$-, *Z*-isomer), 19.7 (C-**C**H$_2$-C, *Z*-isomer), 19.5 (C-**C**H$_2$-C, *E*-isomer), -0.6 (-Si(**C**H$_3$)$_3$, *Z*-isomer), -1.1 (-Si(**C**H$_3$)$_3$, *E*-isomer). **^{29}Si NMR** (80 MHz, CDCl$_3$): δ (ppm) -1.15 (*Z*-isomer), -1.55 (*E*-isomer). **HRMS** (ESI positive): calculated for $C_{17}H_{24}KN_2O_4SSi$: 419.0858, found: 419.0855.

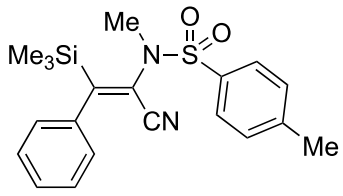
Methyl [1-cyano-2-(3,5-dimethoxyphenyl)-2-(trimethylsilyl)vinyl](methyl)carbamate (**2k**):



Z/*E* 88:12

Prepared following **GP3** from **1k** (1.0 equiv., 125 mg, 0.5 mmol). Reaction time: 10 min. Purification by flash column chromatography over silica gel (pentane/EA = 88:12) gave an inseparable mixture of *Z*/*E* isomers (164 mg, 0.47 mmol, 94%) as a pale-yellow oil. **TLC**: R*f* (pentane/EA = 90:10) = 0.15. **^{1}H NMR** (500 MHz, CDCl$_3$): δ (ppm) 6.40 (t, *J* = 2.3 Hz, C**H**$_{para}$, 1H, *Z*-isomer), 6.33 (t, *J* = 2.3 Hz, C**H**$_{para}$, 1H, *E*-isomer), 6.18 (br s, C**H**$_{ortho}$, 2H, *Z*-isomer), 5.98 (br s, C**H**$_{ortho}$, 2H, *E*-isomer), 3.79 (s, -O**C**H$_3$, 6H, *Z*-isomer), 3.79 (s, -**C**H$_3$, 3H, *Z*-isomer), 3.74 (s, -O**C**H$_3$, 6H, *E*-isomer), 3.72 (br s, -**C**H$_3$, 3H, *E*-isomer), 3.12 (s, -**C**H$_3$, 3H, *Z*-isomer), 2.74 (br s, -**C**H$_3$, 3H, *E*-isomer), 0.27 (s, -Si(C**H**$_3$)$_3$, 9H, *E*-isomer), 0.11 (s, -Si(C**H**$_3$)$_3$, 9H, *Z*-isomer). **^{13}C NMR** (126 MHz, CDCl$_3$): δ (ppm) 164.1 (**C**$_q$, *Z*-isomer), 161.4 (**C**$_q$, *E*-isomer), 161.0 (2**C**$_q$, *Z*-isomer + *E*-isomer), 155.8 (**C**$_q$, *Z*-isomer), 155.0 (**C**$_q$, *E*-isomer), 140.7 (**C**$_q$, *Z*-isomer), 140.1 (**C**$_q$, *E*-isomer), 122.0 (**C**$_q$, *Z*-isomer), 114.5 (**C**$_q$, *Z*-isomer), 105.0 (2**C**H$_{ortho}$, *Z*-isomer), 104.0 (2**C**H$_{ortho}$, *E*-isomer), 99.5 (**C**H$_{para}$, *Z*-isomer), 98.8 (**C**H$_{para}$, *E*-isomer), 55.5 (-O**C**H$_3$, *Z*-isomer), 55.4 (-O**C**H$_3$, *E*-isomer), 53.6 (-**C**H$_3$, *Z*-isomer), 53.5 (-**C**H$_3$, *E*-isomer) 36.5 (-**C**H$_3$, *Z*-isomer), 36.0 (-**C**H$_3$, *E*-isomer) -1.1 (-Si(**C**H$_3$)$_3$, *E*-isomer), -1.2 (-Si(**C**H$_3$)$_3$, *Z*-isomer). **^{29}Si NMR** (99 MHz, CDCl$_3$): δ (ppm) -1.95 (*E*-isomer), -2.68 (*Z*-isomer). *Note: a few carbon atoms of E-compound could not be identified.*

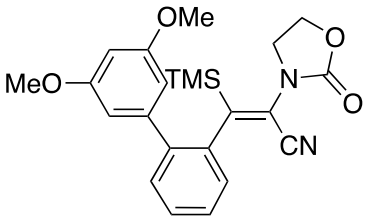
N-(1-Cyano-2-phenyl-2-(trimethylsilyl)vinyl)-*N*,4-dimethylbenzenesulfonamide (**2l**):



Z/E 86:14

Prepared following **GP3** from **1l** (1.0 equiv., 143 mg, 0.5 mmol). Purification by flash column chromatography over basified silica gel (pentane/EA = 90:10) afforded an inseparable mixture of *Z*/*E* isomers (95 mg, 0.25 mmol, 49%) as a yellow oil. **TLC:** R*f* (pentane/EA 8:1) = 0.38. **^{1}H NMR** (400 MHz, $CDCl_3$): *δ* (ppm) 7.78 – 7.74 (m, C**H**$_{arom.}$, 2H, *Z*-isomer), 7.64 – 7.59 (m, C**H**$_{arom.}$, 2H, *E*-isomer), 7.44 – 7.29 (m, C**H**$_{arom.}$, 5H, *Z*-isomer), 7.42 – 7.25 (m, C**H**$_{arom.}$, 5H, *E*-isomer) 7.12 – 7.07 (m, C**H**$_{arom.}$, 2H, *Z*-isomer), 7.05 – 7.00 (m, C**H**$_{arom.}$, 2H, *Z*-isomer), 3.00 (s, -C**H**$_3$, 3H, *Z*-isomer), 2.67 (s, -C**H**$_3$, 3H, *E*-isomer), 2.42 (s, -C**H**$_3$, 3H, *E*-isomer), 2.41 (s, -C**H**$_3$, 3H, *Z*-isomer), 0.29 (s, -Si(C**H**$_3$)$_3$, 9H, *Z*-isomer), 0.29 (s, -Si(C**H**$_3$)$_3$, 9H, *E*-isomer). **^{13}C NMR** (101 MHz, $CDCl_3$): *δ* (ppm) 170.5 (**C**$_q$, *Z*-isomer), 167.4 (**C**$_q$, *E*-isomer), 144.8 (**C**$_q$, *Z*-isomer), 144.3 (**C**$_q$, *E*-isomer), 138.9 (**C**$_q$, *Z*-isomer), 138.3 (**C**$_q$, *E*-isomer), 134.3 (**C**$_q$, *E*-isomer), 132.8 (**C**$_q$, *Z*-isomer), 129.9 (2C**H**$_{arom}$, *Z*-isomer), 129.7 (2C**H**$_{arom}$, *E*-isomer), 128.7 (2C**H**$_{arom}$, *Z*-isomer), 128.5 (2C**H**$_{arom}$, *Z*-isomer), 128.3 (2C**H**$_{arom}$, *E*-isomer), 128.2 (2C**H**$_{arom}$, *E*-isomer), 127.9 (C**H**$_{arom}$, *Z*-isomer), 127.3 (C**H**$_{arom}$, *E*-isomer), 126.4 (2**C**H$_{arom}$, *Z*-isomer), 126.1 (2C**H**$_{arom}$, *E*-isomer), 120.4 (**C**$_q$, *Z*-isomer), 118.4 (**C**$_q$, *E*-isomer), 115.2 (**C**$_q$, *E*-isomer), 112.2 (**C**$_q$, *Z*-isomer), 36.8 (-**C**H$_3$, *Z*-isomer), 36.6 (-**C**H$_3$, *E*-isomer), 21.7 (-**C**H$_3$, *Z*-isomer), 21.6 (-**C**H$_3$, *E*-isomer), -0.8 (-Si(**C**H$_3$)$_3$, *Z*-isomer), -1.2 (-Si(**C**H$_3$)$_3$, *E*-isomer). **^{29}Si NMR** (80 MHz, $CDCl_3$): *δ* (ppm) -1.00 (*Z*-isomer), -1.32 (*E*-isomer). *Characterization data are consistent with the literature.*[4]

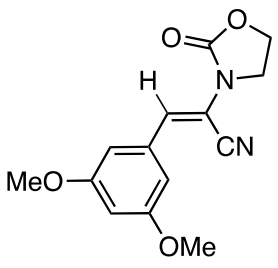
3-(3',5'-Dimethoxy-[1,1'-biphenyl]-2-yl)-2-(2-oxooxazolidin-3-yl)-3-(trimethylsilyl)acrylonitrile (**2m**):



Prepared following **GP3** starting from 3-((3',5'- dimethoxy-[1,1'-biphenyl]-2-yl)ethynyl)oxazolidin-2-one (1.0 equiv., 75 mg, 0.25 mmol). Purification by flash column chromatography over silica gel (pentane/EA = 2:1) afforded the title compound (28 mg, 0.07 mmol, 27%) as a brown oil. **TLC**: R*f* (pentane/EA = 2:1) = 0.49. **^{1}H NMR** (400 MHz, $CDCl_3$): *δ* (ppm) 7.49 –7.10 (m, **C**H$_{arom.}$, 4H), 6.52 – 6.50 (m, **C**H$_{ortho}$, 2H), 6.47 – 6.43 (m, C**H**$_{para}$, 1H), 4.50 – 4.38 (m, O-C**H**$_2$, 2H), 3.82 (s, -OC**H**$_3$, 6H), 3.80 – 3.62 (m, N-C**H**$_2$, 2H), -0.12 (s, -Si(C**H**$_3$)$_3$, 9H). **^{13}C NMR** (126 MHz, $CDCl_3$): *δ* (ppm) 171.4 (**C**$_q$, *Z*-isomer), 160.6 (2**C**$_q$, *Z*-isomer), 157.0 (**C**$_q$, *Z*-isomer), 142.6 (**C**$_q$, *Z*-isomer), 139.2 (**C**$_q$, *Z*-isomer), 137.51 (**C**$_q$, *Z*-isomer), 130.3 (**C**H$_{arom.}$, *Z*-isomer), 128.6 (**C**H$_{arom.}$, *Z*-isomer), 128.1 (**C**H$_{arom.}$, *Z*-isomer), 127.6 (**C**H$_{arom.}$, *Z*-isomer), 118.6 (**C**$_q$, *Z*-isomer), 113.8 (**C**$_q$, *Z*-isomer), 108.7 (2**C**H$_{ortho}$, *Z*-isomer), 99.8 (**C**H$_{para}$, *Z*-isomer), 62.7 (O-**C**H$_2$, *Z*-isomer), 55.6 (-O**C**H$_3$, *Z*-isomer), 46.7 (N-**C**H$_2$, *Z*-isomer), -1.0 (-Si(**C**H$_3$)$_3$, *Z*-isomer). **^{29}Si NMR** (80 MHz, $CDCl_3$): *δ* (ppm) -1.19. *Note: Traces of beta-isomer couldn't be removed from desired alpha compounds; E compound was not clearly identified.*

4. Synthesis of trisubstituted α-cyanoenamide derivatives

(*E*)-3-(3,5-Dimethoxyphenyl)-2-(2-oxooxazolidin-3-yl)acrylonitrile (**2a'$_E$**):

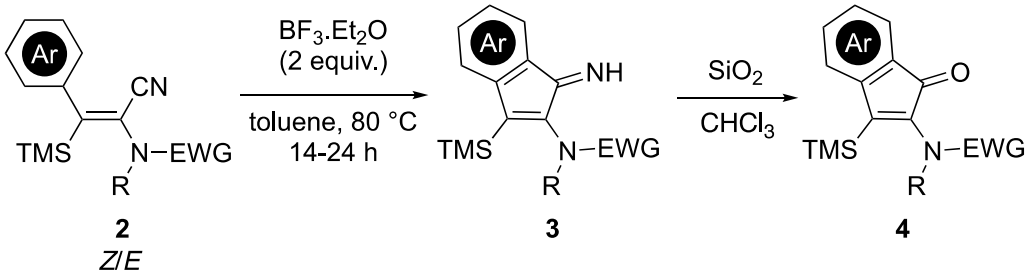


A flame-dried microwave vial was charged with **1a** (1 equiv., 55 mg, 0.22 mmol) and zinc bromide (30 mol%, 16 mg, 0.07 mmol) under argon. Freshly distilled xylene (0.2 mL) was added, followed by TMSCN (2 equiv., 55 µL, 0.44 mmol). The mixture was then heated at 130 °C for 13 h. After reaction completion, the crude mixture was diluted with DCM, insoluble salts were filtrated over a Celite® pad and the solvent was removed under reduced pressure. Purification by flash column chromatography over silica gel (pentane/EA = 50:50) afforded the title compound (43 mg, 0.16 mmol, 70%) as a pale orange solid. **TLC**: R*f*: 0.32 (pentane/EA 50:50). **^{1}H NMR** (500 MHz, CDCl3): *δ* (ppm) 7.35 (s, C**H**$_{alkene}$, 1H), 6.84 (d, *J* = 2.2 Hz, **C**H$_{ortho}$, 2H), 6.50 (t, *J* = 2.2 Hz, **C**H$_{para}$, 1H), 4.51 – 4.45 (m, O-C**H**$_2$, 2H), 4.03 – 3.96 (m, N-C**H**$_2$, 2H), 3.81 (s, -OC**H**$_3$, 6H). **^{13}C NMR** (126 MHz, CDCl3): *δ* (ppm) 161.06 (**C**q, arom.), 154.94 (N-**C**(O)-O), 135.55 (**C**H$_{alkene}$), 133.31 (**C**q, arom.), 113.98 (**C**N), 108.38 (**C**q), 106.71 (2**C**Harom.),

103.11 (**C**$H_{arom.}$), 61.99 (O-**C**H_2), 55.62 (2 -O**C**H_3), 45.66 (N-**C**H_2). **IR**: *ν* (cm^{-1}) 2927, 2226, 1752, 1588, 1456, 1401, 1348, 1315, 1252, 1224, 1205, 1152, 1122, 1061, 1043. **HRMS** (ESI positive): calculated for $C_{14}H_{14}O_4N_2Na$: 297.0846, found: 297.0839. **Mp:** 95-96 °C

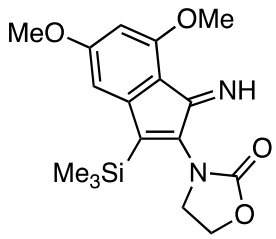
5. Syntheses of 3-silyl-2-aminoindenones

*a. General Procedure **GP4***



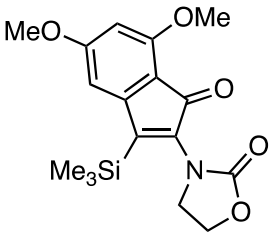
A solution of $BF_3{\cdot}Et_2O$ (1.0 equiv., 46 % BF_3 in Et_2O) in freshly distilled toluene (0.7 M) was added in a flame-dried sealed tube charged with the desired *Z*-silylcyanated product (1.0 equiv.) under argon. The resulting mixture was then heated at 80 °C. After 5 h, another equivalent of $BF_3{\cdot}Et_2O$ (1.0 equiv., 46 % BF_3 in Et_2O) was added to the reaction mixture and the latter was heated at 80 °C until full conversion of starting material. After reaction completion, the reaction mixture was quenched with water and was extracted with DCM. The combined organic layers were washed with brine, dried over $MgSO_4$ and the solvent was removed under reduced pressure. The crude was then either directly purified by flash chromatography or stirred overnight in a mixture of silica gel and chloroform before chromatography to insure complete hydrolysis to desired indenone.

3-[5/7-Dimethoxy-1-oxo-3-(trimethylsilyl)-1H-inden-2-yl]-1,3-oxazolidin-2-one (**4a**):



Prepared following **GP4** starting from **2a** (1.0 equiv., 36 mg, 0.104 mmol) Reaction time: 24 h. After trituration in a pentane/EtO_2 (3:1) mixture, the intermediate indenimine **3a** (33 mg, 0.095 mmol, 92%) could be isolated as a yellow solid. **TLC:** R*f* (DCM/MeOH = 98:2) = 0.2. **^{1}H NMR** (400 MHz, $CDCl_3$): *δ* (ppm) 10.52 (br s, 1H), 6.50 (d, *J* = 1.9 Hz, C**H**$_{arom.}$, 1H), 6.26 (d, *J* = 1.9 Hz, C**H**$_{arom.}$, 1H), 4.47 (t, *J* = 8.0 Hz, O-C**H**$_2$, 2H), 4.13 (br s, N-C**H**$_2$, 2H), 3.91 (s, -OC**H**$_3$, 3H), 3.84 (s, -OC**H**$_3$, 3H), 0.35 (s, -Si(C**H**$_3$)$_3$, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$): *δ* (ppm) 171.6 (**C**=N), 164.3 (**C**$_q$), 158.2 (**C**$_q$), 157.4 (N-**C**(O)-O), 148.2 (**C**$_q$), 147.4 (**C**$_q$), 145.1 (**C**$_q$), 107.7 (**C**$_q$), 104.3 (**C**H$_{arom.}$), 95.8 (**C**H$_{arom.}$), 62.7 (O-**C**H$_2$), 55.7 (-O**C**H$_3$), 55.6 (-O**C**H$_3$), 47.8 (N-**C**H$_2$), -0.6 (-Si(**C**H$_3$)$_3$). **^{29}Si NMR** (80 MHz, $CDCl_3$): *δ* (ppm) -7.92. **HRMS** (ESI positive): calculated for $C_{17}H_{23}N_2O_4Si$: 347.1422, found: 347.1419. **IR:** ν (cm^{-1}) 3272, 2955, 2927, 2844, 1755, 1598, 1478, 1411, 1267, 1202, 1095, 1041, 844. **Mp:** dec. 173 °C.

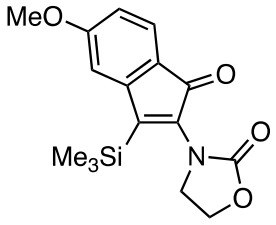
After hydrolysis the title compound (33 mg, 0.095 mmol, 91%) was obtained as a yellow solid. **TLC:**



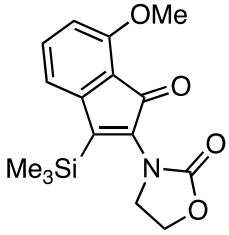
R*f*(DCM/MeOH = 98:2) = 0,4. **^{1}H NMR** (400 MHz, $CDCl_3$): *δ* (ppm) 6.42 (d, *J* = 1.9 Hz, C**H**$_{arom.}$, 1H), 6.15 (d, *J* = 1.9 Hz, C**H**$_{arom.}$, 1H), 4.43 (t, *J* = 8 Hz, O-C**H**$_2$, 2H), 4.07 (t, *J* = 8 Hz, N-C**H**$_2$, 2H), 3.92 (s, -OC**H**$_3$, 3H), 3.85 (s, -OC**H**$_3$, 3H), 0.33 (s, -Si(C**H**$_3$)$_3$, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$): *δ* (ppm) 190.5 (**C**=O), 167.4 (**C**$_q$), 159.0 (**C**$_q$), 156.8 (N-**C**(O)-O), 150.6 (**C**$_q$), 149.9 (**C**$_q$), 142.0 (**C**$_q$), 107.4 (**C**$_q$), 107.1 (**C**H$_{arom.}$), 95.9 (**C**H$_{arom.}$), 62.9 (O-**C**H$_2$), 56.2 (-O**C**H$_3$), 55.9 (-O**C**H$_3$), 46.1 (N-**C**H$_2$), -0.6 (-Si(**C**H$_3$)$_3$). **^{29}Si NMR** (80 MHz, $CDCl_3$): *δ* (ppm) -7.32. **HRMS** (ESI positive): calculated for $C_{17}H_{21}KNO_5Si$: 386.0821, found: 386.0815. **IR:** ν (cm^{-1}) 2952, 2921, 2851, 1743, 1695, 1599, 1471, 1411, 1203, 1153, 1090, 1032, 845. **Mp:** 148 – 154 °C.

3-(5/7-Methoxy-1-oxo-3-(trimethylsilyl)-1H-inden-2-yl)oxazolidin-2-one (**4c**):
Prepared following **GP4** starting from **2c** (1.0 equiv., 36 mg, 0.12 mmol). Reaction time: 18 h. Purification by preparative TLC (pentane/EA = 40:60) afforded the title compound (10 mg, 0.032 mmol, 27%).

3-[5-Methoxy-1-oxo-3-(trimethylsilyl)-1H-inden-2-yl]-1,3-oxazolidin-2-one (**4c**[5]) (7 mg, 0.022 mmol, 19%) was isolated as a bright yellow orange oil. **TLC:** R*f* (pentane/EA = 40:60) = 0.54. **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 7.36 (d, *J* = 8.0 Hz, C**H**$_{arom.}$, 1H), 6.74 (d, *J* = 2.2 Hz, C**H**$_{arom.}$, 1H), 6.56 (dd, *J* = 8.0 and 2.2 Hz, C**H**$_{arom.}$, 1H), 4.45 (t, *J* = 8.0 Hz, O-C**H**$_2$, 2H), 4.07 (t, *J* = 8.0 Hz, N-C**H**$_2$, 2H), 3.85 (s, -OC**H**$_3$, 3H), 0.36 (s, -Si(C**H**$_3$)$_3$, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ (ppm) 193.1 (**C**=O), 165.4 (**C**$_q$), 156.8 (N-**C**(O)-O), 153.2 (**C**$_q$), 149.0 (**C**$_q$), 141.7 (**C**$_q$), 125.2 (**C**H$_{arom.}$), 121.5 (**C**$_q$), 113.5 (**C**H$_{arom.}$), 109.3 (**C**H$_{arom.}$), 62.9 (O-**C**H$_2$), 55.9 (-O**C**H$_3$), 46.1 (N-**C**H$_2$), -0.8 (-Si(**C**H$_3$)$_3$). **^{29}Si NMR** (80 MHz, $CDCl_3$) δ (ppm) -6.94. **HRMS** (ESI positive): calculated for $C_{16}H_{19}NNaO_4Si$: 340.0976, found: = 340.0973. **IR**: ν (cm^{-1}) 3063, 2956, 2915, 2844, 1753, 1706, 1593, 1472, 1406, 1222, 1093, 1029, 841, 720.

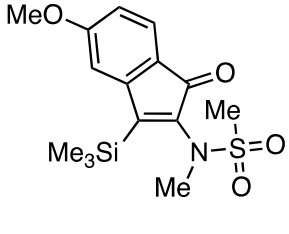


3-[7-Methoxy-1-oxo-3-(trimethylsilyl)-1H-inden-2-yl]-1,3-oxazolidin-2-one (**4c**[7]) (3 mg, 0.01 mmol, 8%) was isolated as a bright yellow-orange oil. **TLC:** R*f* (pentane/EA = 40:60) = 0.4. **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 7.33 (dd, *J* = 8.6 and 7.2 Hz, C**H**$_{arom.}$, 1H), 6.81 (d, *J* = 7.2 Hz, C**H**$_{arom.}$, 1H), 6.80 (d, *J* = 8.0 Hz, C**H**$_{arom.}$, 1H), 4.45 (t, *J* = 8.0 Hz, O-C**H**$_2$, 2H), 4.06 (t, *J* = 8.0 Hz, N-C**H**$_2$, 2H), 3.93 (s, -OC**H**$_3$, 3H), 0.35 (s, -Si(C**H**$_3$)$_3$, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ (ppm) 192.4 (**C**=O), 157.0 (**C**$_q$), 156.9 (**C**$_q$), 152.9 (**C**$_q$), 148.7 (**C**$_q$), 140.5 (**C**$_q$), 136.9 (**C**H$_{arom.}$), 117.3 (**C**H$_{arom.}$), 114.1 (**C**H$_{arom.}$), 113.7 (**C**$_q$), 62.9 (O-**C**H$_2$), 56.1 (-O**C**H$_3$), 46.1 (N-**C**H$_2$), -0.7 (-Si(**C**H$_3$)$_3$). **^{29}Si NMR** (80 MHz, $CDCl_3$): δ (ppm) -6.98. **HRMS** (ESI positive): calculated for $C_{16}H_{20}NO_4Si$: 318.1156, found: 318.1168. **IR**: ν (cm^{-1}) 2952, 2924, 2853, 1753, 1702, 1592, 1476, 1409, 1278, 1247, 1217, 1177, 1082, 1038, 843, 718.

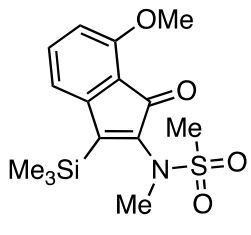


N-(5/7-Methoxy-1-oxo-3-(trimethylsilyl)-1H-inden-2-yl)-N-methylmethanesulfonamide (**4d**)
Prepared following **GP4** starting from **2d** (1.0 equiv., 29 mg, 0.085 mmol). Reaction time: 18 h. Purification by preparative TLC (pentane/EA = 50:50) afforded the title compound (20 mg, 0.059 mmol, 69%).

N-[5-Methoxy-1-oxo-3-(trimethylsilyl)-1H-inden-2-yl]-N-methylmethanesulfonamide (**4d**[5]) (17 mg, 0.050 mmol, 59%) was isolated as a bright yellow solid. **TLC:** R*f* (pentane/EA = 40:60) = 0.61. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.35 (d, *J* = 8.0 Hz, C**H**$_{arom.}$, 1H), 6.77 (d, *J* = 2.2 Hz, C**H**$_{arom.}$, 1H), 6.60 (dd, *J* = 8.0, 2.2 Hz, C**H**$_{arom.}$, 1H), 3.85 (s, -OC**H**$_3$, 3H), 3.20 (s, -C**H**$_3$, 3H), 3.02 (s, -C**H**$_3$, 3H), 0.42 (s, -Si(C**H**$_3$)$_3$, 9H). **^{13}C NMR** (126 MHz, $CDCl_3$): δ 193.9 (**C**=O), 165.43 (**C**$_q$), 160.69 (**C**$_q$), 148.42 (**C**$_q$), 145.46 (**C**$_q$), 125.16 (**C**H$_{arom.}$), 121.49 (**C**$_q$), 113.97 (**C**H$_{arom.}$), 109.87 (**C**H$_{arom.}$), 55.89 (-O**C**H$_3$), 38.29 (-**C**H$_3$), 37.72 (-**C**H$_3$), -0.50 (-Si(**C**H$_3$)$_3$). **^{29}Si NMR** (99 MHz, $CDCl_3$): δ -6.46. **HRMS** (ESI positive): calculated for $C_{15}H_{21}NNaO_4SSi$: 362.0853, found: = 362.0845. **IR:** ν (cm^{-1}) 3016, 2955, 2930, 2897, 2851, 1705, 1601, 1476, 1334, 1242, 1142, 1063, 965, 936, 847. **Mp:** 133 °C.

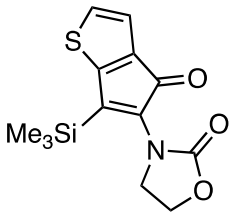


N-[7-Methoxy-1-oxo-3-(trimethylsilyl)-1H-inden-2-yl]-N-methylmethanesulfonamide (**4d**[7]) (3 mg, 0.0088 mmol, 10%) was isolated as a bright yellow solid. **TLC:** R*f* (pentane/EA = 40:60) = 0.53. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.36 (dd, *J* = 8.6 and 7.3 Hz, C**H**$_{arom.}$, 1H), 6.84 (m, C**H**$_{arom.}$, 2H), 3.95 (s, -OC**H**$_3$, 3H), 3.20 (s, -C**H**$_3$, 3H), 3.04 (s, -C**H**$_3$, 3H), 0.41 (s, -Si(C**H**$_3$)$_3$, 9H). **^{13}C NMR** (126 MHz, $CDCl_3$): δ 193.3 (**C**=O), 160.3 (**C**$_q$), 156.8 (**C**$_q$), 148.1 (**C**$_q$), 144.3 (**C**$_q$), 137.1 (**C**H$_{arom.}$), 117.8 (**C**H$_{arom.}$), 114.5 (**C**H$_{arom.}$), 113.7 (**C**$_q$), 56.1 (-O**C**H$_3$), 38.3 (-**C**H$_3$), 37.8 (-**C**H$_3$), -0.4 (-Si(**C**H$_3$)$_3$). **^{29}Si NMR** (99 MHz, $CDCl_3$): δ -6.49. **HRMS** (ESI positive): calculated for $C_{15}H_{21}KNO_4SSi$:



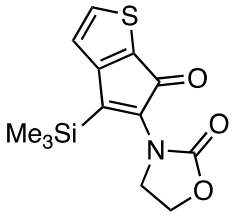
378.0592, found: = 378.0596. **IR:** ν (cm^{-1}) 2958, 2922, 2852, 1698, 1591, 1473, 1337, 1272, 1139, 1073, 1028, 940, 862. **Mp:** 141-148 °C.

3-(4-Oxo-6-(trimethylsilyl)-4H-cyclopenta[b]thiophen-5-yl)oxazolidin-2-one (**4f**):



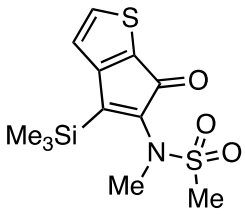
Prepared following **GP4** from **2f** (1.0 equiv., 40 mg, 0.137 mmol). Reaction time: 14 h. **TLC:** R*f* (pentane/EA = 5:1) = 0.33. Purification by flash chromatography over silica gel (pentane/EA = 5:1) afforded the title compound (30 mg, 0.10 mmol, 75%) as a bright red solid. **^{1}H NMR** (500 MHz, $CDCl_3$): *δ* (ppm) 7.09 (d, *J* = 4.9 Hz, C**H**$_{arom.}$, 1H), 6.96 (d, *J* = 4.9 Hz, C**H**$_{arom.}$, 1H), 4.47 – 4.41 (m, O-C**H**$_2$, 2H), 4.03 – 3.98 (m, N-C**H**$_2$, 2H), 0.33 (s, -Si(C**H**$_3$)$_3$, 9H). **^{13}C NMR** (126 MHz, $CDCl_3$): *δ* (ppm) 188.8 (**C**=O), 160.5 (**C**$_q$), 156.8 (N-**C**(O)-O), 146.0 (**C**$_q$), 137.2 (**C**$_q$), 133.0 (**C**$_q$), 128.0 (**C**H$_{arom.}$), 121.2 (**C**H$_{arom.}$), 62.8 (O-**C**H$_2$), 46.5 (N-**C**H$_2$), -1.3 (-Si(**C**H$_3$)$_3$). **^{29}Si NMR** (99 MHz, $CDCl_3$): *δ* (ppm) -5.90. **IR:** ν (cm^{-1}) 2955, 2923, 2853, 1749, 1695, 1478, 1391, 1203, 1117, 1035, 756, 706. **HRMS** (ESI positive): calculated for $C_{13}H_{16}NNaO_3SSi$: 316.0434, found: 316.0433. **Mp:** dec. 130 °C

3-(6-Oxo-4-(trimethylsilyl)-6H-cyclopenta[b]thiophen-5-yl)oxazolidin-2-one (**4g**):



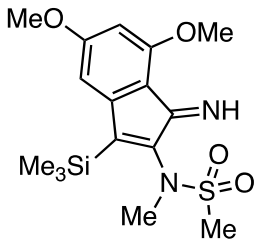
Prepared following **GP4** from **2g** (1.0 equiv., 39 mg, 0.13 mmol). Reaction time: 17 h. **TLC:** R*f* (pentane/EA = 5:1) = 0.26. Purification by flash chromatography over silica gel (pentane/EA = 5:1) afforded the title compound (24 mg, 0.08 mmol, 62%) as a bright red solid. **^{1}H NMR** (500 MHz, $CDCl_3$): *δ* (ppm) 7.67 (d, *J* = 4.6 Hz, C**H**$_{arom.}$, 1H), 6.90 (d, *J* = 4.6 Hz, C**H**$_{arom.}$, 1H), 4.47 – 4.40 (m, O-C**H**$_2$, 2H), 4.02 – 3.97 (m, N-C**H**$_2$, 2H), 0.31 (s, -Si(C**H**$_3$)$_3$, 9H). **^{13}C NMR** (126 MHz, $CDCl_3$): *δ* (ppm) 186.5 (**C**=O), 159.9 (**C**$_q$), 156.8 (N-**C**(O)-O), 147.6 (**C**$_q$), 139.5 (**C**$_q$), 137.9 (**C**H$_{arom.}$), 127.1 (**C**$_q$), 123.3 (**C**H$_{arom.}$), 62.7 (O-**C**H$_2$), 46.6 (N-**C**H$_2$), -1.3 (-Si(**C**H$_3$)$_3$). **^{29}Si NMR** (99 MHz, $CDCl_3$): *δ* (ppm) -6.76. **IR:** ν (cm^{-1}) 3106, 3096, 2958, 2923, 2853, 1753, 1738, 1705, 1584, 1478, 1404, 1245, 1210, 1135, 1085, 1042, 1029, 837, 764. **HRMS** (ESI positive): calculated for $C_{13}H_{16}NO_3SSi$: 294.0615, found: 294.0622. **Mp:** 105 °C

N-Methyl-N-(6-oxo-4-(trimethylsilyl)-6H-cyclopenta[b]thiophen-5-yl)methanesulfonamide (**4h**):



Prepared following **GP4** starting from **2h** (1.0 equiv., 45 mg, 0.14 mmol). Reaction time: 17 h. Purification by flash chromatography over silica gel (gradient from pentane/EA/toluene = 85:10:5 to 75:20:5) afforded the title compound (24 mg, 0.076, 53%) as a bright red solid. **TLC:** R*f* (pentane/EA = 70:30) = 0.67. **^{1}H NMR** (500 MHz, $CDCl_3$): *δ* (ppm) 7.70 (d, *J* = 4.6 Hz, C**H**$_{arom.}$, 1H), 6.93 (d, *J* = 4.6 Hz, C**H**$_{arom.}$, 1H), 3.19 (s, -C**H**$_3$, 3H), 3,03 (s, -C**H**$_3$, 3H), 0.37 (s, -Si(C**H**$_3$)$_3$, 9H). **^{13}C NMR** (126 MHz, $CDCl_3$): *δ* (ppm) 187.4 (**C**=O), 159.3 (**C**$_q$), 154.2 (**C**$_q$), 143.0 (**C**$_q$), 137.9 (**C**H$_{arom.}$), 127.3 (**C**$_q$), 123.6 (**C**H$_{arom.}$), 38.2 (-**C**H$_3$), 38.0 (-**C**H$_3$), -1.1 (-Si(**C**H$_3$)$_3$). **^{29}Si NMR** (80 MHz, $CDCl_3$): *δ* (ppm) -6.21. **HRMS** (ESI positive): calculated for $C_{12}H_{17}NNaO_3S_2Si$: 338.0311 found: 338.0306. **IR:** ν (cm^{-1}) 3115, 2924, 2852, 1709, 1571, 1434, 1329, 1242, 1144, 972, 841, 765. **Mp**: 139 °C.

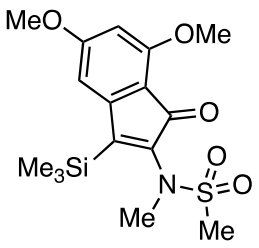
N-(1-Oxo-5,7-dimethoxy-3-(trimethylsilyl)-1*H*-inden-2-yl)-*N*-methylmethanesulfonamide (**4i**):



Prepared following **GP4** starting from **2i** (1.0 equiv., 35 mg, 0.094 mmol). Reaction time: 18 h. After purification by flash chromatography over silica gel (pentane/EA = 65:35 to 60:40) the intermediate indenimine **3i** (28 mg, 0.076 mmol, 80%) could be isolated. **TLC:** R*f* (pentane/EA = 65:35) = 0.32. **^{1}H NMR** (400 MHz, $CDCl_3$): *δ* (ppm) 10.59 (br s, N-**H**, 1H), 6.52 (d, *J* = 1,9 Hz, C**H**$_{arom.}$, 1H), 6.28 (d, *J* = 1.9 Hz, C**H**$_{arom.}$, 1H), 3.91 (s, -OC**H**$_3$, 3H), 3.84 (s, -OC**H**$_3$, 3H), 3.32 (s, -C**H**$_3$, 3H), 3,12 (s, -C**H**$_3$, 3H), 0.40 (s, -Si(C**H**$_3$)$_3$, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$): *δ* (ppm) 171.7 (**C**=N), 164.3 (**C**$_q$), 158.2 (**C**$_q$), 153.2 (**C**$_q$), 148.5 (**C**$_q$), 147.2 (**C**$_q$), 107.6 (**C**$_q$), 104.4 (**C**H$_{arom.}$), 96.2 (**C**H$_{arom.}$), 55.8 (-O**C**H$_3$), 55.5 (-O**C**H$_3$), 38.8 (-**C**H$_3$), 38.6 (-**C**H$_3$), -0.2 (-Si(**C**H$_3$)$_3$). **^{29}Si NMR** (80 MHz, $CDCl_3$): *δ* (ppm) -7.63. **HRMS** (ESI positive): calculated for $C_{16}H_{25}N_2O_4SSi$:

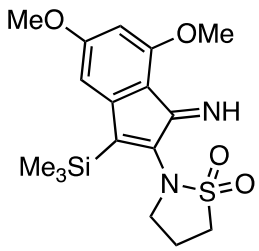
369.1299 found: 369.1292. **IR** ν (cm^{-1}): 3271, 2924, 2853, 2184, 1596, 1466, 1416, 1333, 1250, 1143, 1121, 917, 840. **Mp**: dec. 143 °C.

After hydrolysis the title compound (27 mg, 0.073 mmol, 77%) was eventually obtained as a yellow solid. **TLC:** R*f* (pentane/EA = 60:40) = 0.17. **^{1}H NMR** (400 MHz, $CDCl_3$): *δ* (ppm) 6.46 (d, *J* = 1.9 Hz, C**H**$_{arom.}$, 1H), 6.19 (d, *J* = 1.9 Hz, C**H**$_{arom.}$, 1H), 3.93 (s, -OC**H**$_3$, 3H), 3,86 (s, -OC**H**$_3$, 3H), 3.19 (s, -C**H**$_3$, 3H), 3,03 (s, -C**H**$_3$, 3H), 0.40 (s, -Si(C**H**$_3$)$_3$, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$): *δ* (ppm) 191.4 (**C**=O), 167.5 (**C**$_q$), 158.9 (**C**$_q$), 157.4 (**C**$_q$), 150.0 (**C**$_q$), 145.8 (**C**$_q$), 107.5 (**C**H$_{arom.}$), 107.4 (**C**$_q$), 96.2 (**C**H$_{arom.}$), 56.1 (-O**C**H$_3$), 55.9 (-O**C**H$_3$), 38.3 (-**C**H$_3$), 37.8 (-**C**H$_3$), -0.3 (-Si(**C**H$_3$)$_3$). **^{29}Si NMR** (80 MHz, $CDCl_3$): *δ* (ppm) -6.81. **HRMS** (ESI positive): calculated for $C_{16}H_{23}KNO_5SSi$: 408.0698, found: 408.0680. **IR:** ν (cm^{-1}) 3115, 3007, 2955, 2928, 2847, 1682, 1601, 1574, 1472, 1429, 1339, 1308, 1209, 1139, 970, 930, 844. **Mp:** 161 °C.

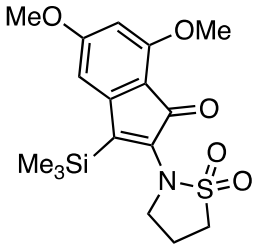


2-(1-Oxo-5,7-dimethoxy-3-(trimethylsilyl)-1H-inden-2-yl)isothiazolidine 1,1-dioxide (**4j**):

Prepared following **GP4** starting from **2j** (1.0 equiv., 27 mg, 0.070 mmol). Reaction time: 18 h. After purification by flash chromatography over silica gel (gradient from cyclohexane/EA = 50:50 to 40:60) the intermediate indenimine **3j** (25 mg, 0.065 mmol, 93%) could be isolated. **TLC:** R*f* (pentane/EA = 60:40) = 0.17. **^{1}H NMR** (400 MHz, $CDCl_3$): *δ* (ppm) 6.52 (d, *J* = 1.9 Hz, C**H**$_{arom.}$, 1H), 6.27 (d, *J* = 1.9 Hz, C**H**$_{arom.}$, 1H), 3,93 – 3.76 (m, -C**H**$_2$-, 2H), 3.88 (s, -OC**H**$_3$, 3H), 3.83 (s, -OC**H**$_3$, 3H), 3.40 (br s, -C**H**$_2$-, 2H), 2.51 (p, *J* = 7.3 Hz, C-C**H**$_2$-C, 2H), 0.41 (s, -Si(C**H**$_3$)$_3$, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$): *δ* (ppm) 171.5 (**C**=N), 164.2 (**C**$_q$), 158.3 (**C**$_q$), 154.0 (**C**$_q$), 147.3 (**C**$_q$), 147.0 (**C**$_q$), 107.9 (**C**$_q$), 104.2 (**C**H$_{arom.}$), 96.3 (**C**H$_{arom.}$), 55.8 (-O**C**H$_3$), 55.5 (-O**C**H$_3$), 49.6 (-**C**H$_2$-), 46.4 (-**C**H$_2$-), 20.3 (C-**C**H$_2$-C), 0.0 (-Si(**C**H$_3$)$_3$). **^{29}Si NMR** (80 MHz, $CDCl_3$): *δ* (ppm) -7.42. **HRMS** (ESI positive): calculated for $C_{17}H_{25}N_2O_4SSi$: 381.1299 found: 381.1290. **IR:** ν (cm^{-1}) 3255, 2951, 2851, 1624, 1596, 1467, 1308, 1257, 1228, 1143, 842. **Mp:** dec. 135 °C.

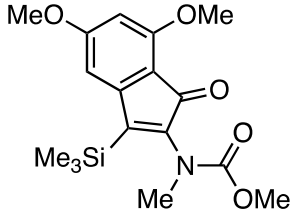


After hydrolysis the title compound (25 mg, 0.065 mmol, 93%) was eventually obtained as a yellow solid. **TLC:** R*f* (pentane/EA = 60:40) = 0.17. **^{1}H NMR** (400 MHz, $CDCl_3$): *δ* (ppm) 6.44 (d, *J* = 1,9 Hz, C**H**$_{arom.}$, 1H), 6.18 (d, *J* = 1.9 Hz, C**H**$_{arom.}$, 1H), 3.91 (s, -OC**H**$_3$, 3H), 3.85 (s, -OC**H**$_3$, 3H), 3.64 (t, *J* = 7.4 Hz, -C**H**$_2$-, 2H), 3.40 (t, *J* = 7.4 Hz, -C**H**$_2$-, 2H), 2.51 (p, *J* = 7.4 Hz, C-C**H**$_2$-C, 2H), 0.40 (s, -Si(C**H**$_3$)$_3$, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$): *δ* (ppm) 191.3 (**C**=O), 167.5 (**C**$_q$), 158.9 (**C**$_q$), 157.3 (**C**$_q$), 150.0 (**C**$_q$), 145.5 (**C**$_q$), 107.5 (**C**$_q$), 107.2 (**C**H$_{arom.}$), 96.2 (**C**H$_{arom.}$), 56.1 (-O**C**H$_3$), 55.9 (-O**C**H$_3$), 48.7 (-**C**H$_2$-), 46.3 (-**C**H$_2$-), 20.6 (C-**C**H$_2$-C), -0.0 (-Si(**C**H$_3$)$_3$). **^{29}Si NMR** (80 MHz, $CDCl_3$): *δ* (ppm) -6.73. **HRMS** (ESI positive): calculated for $C_{17}H_{24}NO_5SSi$: 382.1139 found: 382.1166. **IR:** ν (cm^{-1}) 3017, 2952, 2930, 2854, 1692, 1596, 1464, 1434, 1384, 1295, 1137, 844. **Mp:** 170-176 °C.



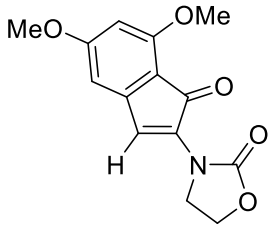
Methyl (5,7-dimethoxy-1-oxo-3-(trimethylsilyl)-1H-inden-2-yl)(methyl)carbamate (**4k**):

Prepared following **GP4** starting from **2k** (1.0 equiv., 40 mg, 0.103 mmol). Reaction time: 18 h. Purification by flash chromatography over silica gel (gradient from pentane/EA = 60:40 to 40:60) gave the title compound (29 mg, 0.083 mmol, 80%). **TLC:** R*f* (pentane/EA = 60:40) = 0.26. **^{1}H NMR** (400 MHz, $CDCl_3$): *δ* (ppm) 6.42 (d, *J* = 1.9 Hz, C**H**$_{arom.}$, 1H), 6.18 (d, *J* = 1.9 Hz, C**H**$_{arom.}$, 1H), 3.93 (s, -OC**H**$_3$, 3H), 3.86 (s, -OC**H**$_3$, 3H), 3.63 (s, -C**H**$_3$, 3H), 3.08 (s, -C**H**$_3$, 3H), 0.30 (s, -Si(C**H**$_3$)$_3$, 9H). **^{13}C NMR** (126 MHz, $CDCl_3$): *δ* (ppm) 190.4 (**C**=O), 167.2 (**C**$_q$), 158.8 (**C**$_q$), 156.3 (**C**$_q$), 150.5 (**C**$_q$), 149.2 (**C**$_q$), 148.1 (**C**$_q$), 107.4 (**C**$_q$), 106.8 (**C**H$_{arom.}$), 95.9 (**C**H$_{arom.}$), 56.2 (-O**C**H$_3$), 55.9 (-O**C**H$_3$), 53.1 (-**C**H$_3$), 37.3 (-**C**H$_3$), -0.7 (-Si(**C**H$_3$)$_3$). **^{29}Si NMR** (99 MHz, $CDCl_3$): *δ* (ppm) -7.90. **HRMS** (ESI positive) calculated for $C_{17}H_{24}NO_5Si$: 350.1418, found: 350.1417. **IR:** ν (cm^{-1}) 2956, 2930, 2854, 1710, 1697, 1598, 1434, 1303, 1201, 1157, 1133, 841. **Mp:** 111 °C.



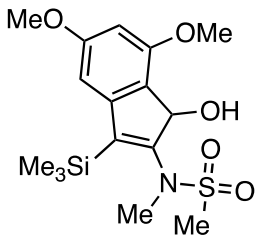
6. Post-functionalization of 3-silyl-2-aminoindenone derivatives

3-(5,7-Dimethoxy-1-oxo-1H-inden-2-yl)oxazolidin-2-one (**4a'**):



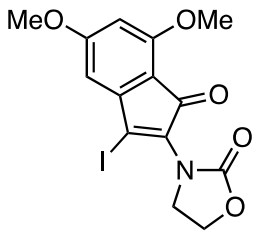
A flame-dried Schlenk tube was charged with **4a** (1.0 equiv., 50 mg, 0.12 mmol) and dissolved in anhydrous THF (0.9 mL). Then, TBAF (1.5 equiv., 78 µL, 1 M solution in THF, 0,078 mmol) was added under argon as well as 3 droplets of glacial acetic acid and the reaction mixture was stirred for 1 h. After reaction completion, the reaction mixture was quenched with water. The resulting mixture was extracted three times with DCM and the combined organic layer was washed with brine, dried over MgSO4 and the solvent was removed under vacuum. Purification by flash chromatography over silica gel (DCM/MeOH = 100:1) afforded the title compound (8 mg, 0.029 mmol, 59%) as an orange solid. **TLC**: R*f* (pentane/EA = 50:50) = 0.17. **^{1}H NMR** (400 MHz, CD_2Cl_2): *δ* (ppm) 7.28 (s, C**H**, 1H), 6.23 (d, *J* = 1.8 Hz, C**H**$_{arom.}$, 1H), 6.08 (d, *J* = 1.8 Hz, C**H**$_{arom.}$, 1H), 4.43 – 4.37 (m, O-C**H**$_2$, 2H), 4.33 – 4.25 (m, N-C**H**$_2$, 2H), 3.89 (s, -OC**H**$_3$, 3H), 3.84 (s, -OC**H**$_3$, 3H). **^{13}C NMR** (101 MHz, CD_2Cl_2): *δ* (ppm) 189.0 (**C**$_q$), 168.3 (**C**$_{q,\ arom.}$), 159.6 (**C**$_{q,\ arom.}$), 156.3 (N-**C**(O)-O), 149.5 (**C**$_{q,\ arom.}$), 134.1 (**C**$_q$), 122.1 (C5, CH), 105.8 (**C**$_{q,\ arom.}$), 104.4 (**C**H$_{arom.}$), 95.6 (**C**H$_{arom.}$), 63.7 (O-**C**H$_2$), 56.2 (-O**C**H$_3$), 56.2 (-O**C**H$_3$), 44.1 (N-**C**H$_2$). **HRMS** (ESI positive) calculated for $C_{14}H_{12}INNaO_5$: 423.9652 found: 423.9641. **IR ν** (cm^{-1}) 2953, 2924, 2853, 1756, 1699, 1588, 1461, 1397, 1210, 1154, 1095. **Mp:** 209-214 °C.

3-(1-Hydroxy-5,7-dimethoxy-3-(trimethylsilyl)-1H-inden-2-yl)oxazolidin-2-one (**6i**):



To a stirred solution of **4i** (1.0 equiv., 38 mg, 0.103 mmol) in a mixture of anhydrous THF (1.1 mL) and freshly distilled MeOH (0.11 mL) was added $NaBH_4$ (6.0 equiv., 23 mg, 0.62 mmol) in one portion at 0 °C under an inert atmosphere. After reaction completion, the reaction medium was quenched with water and extracted thrice with EA. The combined organic layers were then washed with brine, dried over $MgSO_4$ and the solvent was finally removed under reduced pressure. Purification by flash column chromatography on silica gel (gradient from pentane/EA = 60:40 to 40:60) gave the title compound (19 mg, 0.051 mmol, 50%) as a pale-yellow solid. **TLC**: R*f* (pentane/EA = 60:40) = 0.21. **^{1}H NMR** (500 MHz, $CDCl_3$): *δ* (ppm) 6.57 (d, *J* = 1.9 Hz, C**H**$_{arom.}$, 1H), 6.31 (d, *J* = 1.9 Hz, C**H**$_{arom.}$, 1H), 5.41 (d, *J* = 4.0 Hz, C**H**-OH, 1H), 3.86 (s, -OC**H**$_3$, 3H), 3.82 (s, -OC**H**$_3$, 3H), 3.26 (s, -C**H**$_3$, 3H), 3.13 (s, -C**H**$_3$, 3H), 2.50 (d, *J* = 4.0 Hz, CH-O**H**, 1H), 0.37 (s, -Si(C**H**$_3$)$_3$, 9H). **^{13}C NMR** (126 MHz, $CDCl_3$): *δ* (ppm) 162.3 (**C**$_q$), 156.3 (**C**$_q$), 155.8 (**C**$_q$), 146.8 (**C**$_q$), 141.5 (**C**$_q$), 121.2 (**C**$_q$), 102.9 (**C**H$_{arom.}$), 96.1 (**C**H$_{arom.}$), 74.4 (**C**H-OH), 56.0 (-O**C**H$_3$), 55.8 (-O**C**H$_3$), 39.0 (-**C**H$_3$), 38.3 (-**C**H$_3$), 0.0 (-Si(**C**H$_3$)$_3$). **^{29}Si NMR** (99 MHz, $CDCl_3$): *δ* (ppm) -8.64. **HRMS** (ESI positive) calculated for $C_{16}H_{25}NNaO_5SSi$: 394.1115, found: 394.1109. **IR:** ν (cm^{-1}) 3474, 3001, 2973, 2952, 2890, 2847, 1613, 1590, 1467, 1321, 1148, 1113, 844, 813. **Mp:** 175 °C.

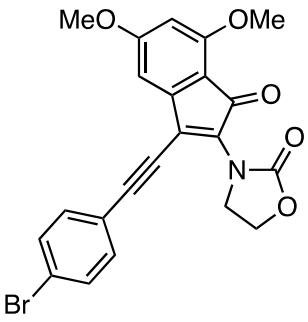
3-(3-Iodo-5,7-dimethoxy-1-oxo-1H-inden-2-yl)oxazolidin-2-one (**8a**):



In a flame-dried Schlenk tube, **4a** (1.0 equiv., 50 mg, 0.14 mmol) was dissolved in freshly distilled DCM (0.25 mL) under argon. Then NIS (2.0 equiv., 65 mg, 0.29 mmol) was added at 0 °C and the mixture was stirred at r.t. for 72 h. At the end of the reaction, the reaction medium was quenched with sat. $Na_2S_2O_3$ solution and the aqueous layer was extracted thrice with DCM. The combined organic layers were then washed with brine, dried over $MgSO_4$ and the solvent was finally removed under reduced pressure. Purification by chromatography on silica gel column (DCM/EA = 90:10) gave 3-(3-iodo-5,7-dimethoxy-1-oxo-1H-inden-2-yl)-1,3-oxazolidin-2-one (40 mg, 0.10 mmol, 69%) as a bright yellow-orange solid. **^{1}H NMR** (400 MHz, $CDCl_3$): *δ* (ppm) 6.34 (d, *J* = 1,9 Hz, C**H**$_{arom.}$, 1H), 6.25 (d, *J* = 1.9 Hz, C**H**$_{arom.}$, 1H), 4.54-4.48 (m, O-C**H**$_2$, 2H), 4,18 – 4.11 (m, N-C**H**$_2$, 2H), 3.93 (s, -OC**H**$_3$, 3H), 3,89 (s, -OC**H**$_3$, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): *δ* (ppm) 186.4 (**C**=O), 167.0 (**C**$_q$), 158.5 (**C**$_q$), 154.2 (N-**C**(O)-O), 147.4 (**C**$_q$), 140.3 (**C**$_q$), 110.3 (**C**$_q$), 107.5 (**C**$_q$), 107.1 (**C**H$_{arom.}$), 97.9 (**C**H$_{arom.}$), 63.3 (O-**C**H$_2$), 56.4 (-O**C**H$_3$), 56.2 (-O**C**H$_3$), 45.5 (N-**C**H$_2$). **HRMS** (ESI

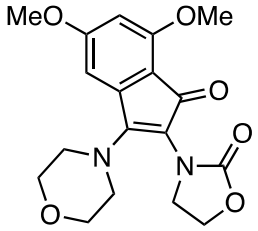
positive): calculated for $C_{14}H_{12}INNaO_5$: 423.9652 found: 423.9641. **IR**: ν (cm^{-1}) 3106, 3004, 2980, 2949, 2912, 2851, 1738, 1699, 1587, 1471, 1381, 1311, 1208, 1186, 1155, 1100, 1027, 1008, 834. **Mp:** dec. 215 °C.

3-(3-((4-Bromophenyl)ethynyl)-5,7-dimethoxy-1-oxo-1H)-inden-2-yl)oxazolidin-2-one (**9**):



In a flame-dried sealed tube were added **8a** (1.0 equiv., 50 mg, 0.12 mmol), 1-bromo-4-ethynylbenzene (1.5 equiv., 34 mg, 0.19 mmol), cesium carbonate (2.0 equiv., 81 mg, 0.25 mmol), copper iodide (10 mol%, 2.4 mg, 0.012 mmol) and dichlorobis(triphenylphosphine)palladium (5 mol%, 4.4 mg, 0.006 mmol). Anhydrous DMF (2.6 mL) was then added under argon and the mixture was heated at 70 °C for 8 h. After reaction completion, the reaction medium was diluted with DCM, washed thrice with water and the organic layer was dried over $MgSO_4$. The solvent was finally removed under reduced pressure. Purification by chromatography on C18-reverse phase silica gel (gradient from MeCN/H_2O = 70:30 to 90:10) gave the title compound (29 mg, 0.063 mmol, 51%) as a dark orange-red solid. **TLC**: Normal phase: R*f* (DCM/MeOH 98:2) = 0.41. Reverse phase: R*f* (MeCN/water = 70:30) = 0.33. **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm) 7.53 – 7.47 (m, C**H**$_{arom.}$, 2H), 7.46 – 7.40 (m, C**H**$_{arom.}$, 2H), 6.53 (d, *J* = 2.0 Hz, C**H**$_{arom.}$, 1H), 6.18 (d, *J* = 2.0 Hz, C**H**$_{arom.}$, 1H), 4.52 – 4.44 (m, O-C**H**$_2$, 2H), 4,34 – 4.27 (m, N-C**H**$_2$, 2H), 3.93 (s, -OC**H**$_3$, 3H), 3,90 (s, -OC**H**$_3$, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ (ppm) 188.8 (**C**=O), 167.7 (**C**$_q$), 158.8 (**C**$_q$), 154.3 (N-**C**(O)-O), 146.7 (**C**$_q$), 135.0 (**C**$_q$), 133.5 (2**C**H$_{arom.}$), 131.9 (2**C**H$_{arom.}$), 124.2 (**C**$_q$), 123.9 (**C**$_q$), 121.4 (**C**$_q$), 107.7 (**C**$_q$), 106.3 (**C**$_q$), 103.3 (**C**H$_{arom.}$), 96.8 (**C**H$_{arom.}$), 82.8 (**C**$_{alkyne}$), 63.3 (O-**C**H$_2$), 56.2 (-O**C**H$_3$), 56.1 (-O**C**H$_3$), 45.3 (N-**C**H$_2$). **HRMS** (ESI positive) calculated for $C_{22}H_{17}BrNO_5$: 454.0285 found: 454.0300. **IR**: *ν* (cm^{-1}) 2955, 2919, 2841, 2190, 1741, 1704, 1585, 1476, 1403, 1378, 1312, 1204, 1156, 1096, 1026, 1008, 820, 757, 513. **Mp**: 188 °C.

3-(5,7-Dimethoxy-3-morpholino-1-oxo-1H-inden-2-yl)oxazolidin-2-one (**10**):



In a flame-dried sealed tube was added a solution of palladium diacetate (1.4 mg, 0.0062 mmol, 5 mol%) and (rac)-BINAP (4 mg, 0.0062 mmol, 5 mol%) in freshly distilled toluene (1.25 mL) to a mixture of **8a** (1.0 equiv., 50 mg, 0.12 mmol) cesium carbonate (5.00 equiv., 203 mg, 0.62 mmol) and morpholine (1.2 equiv., 13 mg , 0.15 mmol) under argon. The resulting mixture was heated to 120 °C for 16 h. At the end of the reaction, the reaction medium was diluted with DCM and filtered on a Celite® pad. The solvent was removed under reduced pressure and the crude product was purified by flash chromatography on silica gel (DCM/MeOH = 98:2) to give the title compound (41 mg, 0.11 mmol, 91%) as a bright orange solid. **TLC**: R*f* (DCM/MeOH = 98:2) = 0.16. **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 6.44 (d, *J* = 1.8 Hz, C**H**$_{arom.}$, 1H), 6.29 (d, *J* = 1.8 Hz, C**H**$_{arom.}$, 1H), 4.62 – 4.20 (m, O-C**H**$_2$, 2H), 3.91 (s, -OC**H**$_3$, 3H), 3.84 (s, -OC**H**$_3$, 3H), 3.87 – 3.78 (m, -C**H**$_2$-, 4H), 3.74 – 3.34 (m, -C**H**$_2$-, 5H). **^{13}C NMR** (101 MHz, CD_2Cl_2): δ (ppm) 188.4 (**C**=O), 165.0 (**C**$_q$), 158.3 (**C**$_q$), 157.9 (**C**$_q$), 157.1 (**C**$_q$), 142.1 (**C**$_q$), 109.7 (**C**$_q$), 109.6 (**C**$_q$), 104.9 (**C**H$_{arom.}$), 97.6 (**C**H$_{arom.}$), 66.9 (2O-**C**H$_2$), 62.8 (O-**C**H$_3$), 56.4 (-O**C**H$_2$), 55.9 (-O**C**H$_3$), 49.6 (2N-**C**H$_2$), 46.4 (N-**C**H$_2$). **HRMS** (ESI positive): calculated for $C_{18}H_{21}N_2O_6$: 361.1394 found: 361.1401. **IR**: ν (cm^{-1}) 2977, 2900, 2855, 2231, 1738, 1681, 1597, 1440, 1399, 1209, 1156, 1083, 1020, 942, 836. **Mp:** 225-229 °C.

7. References

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2 T. Hamada, X. Ye and S. S. Stahl, *J. Am. Chem. Soc.*, 2008, **130**, 833–835.

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5 R. B. Dateer, B. S. Shaibu and R.-S. Liu, *Angew. Chem. Int. Ed.*, 2012, **51**, 113–117.

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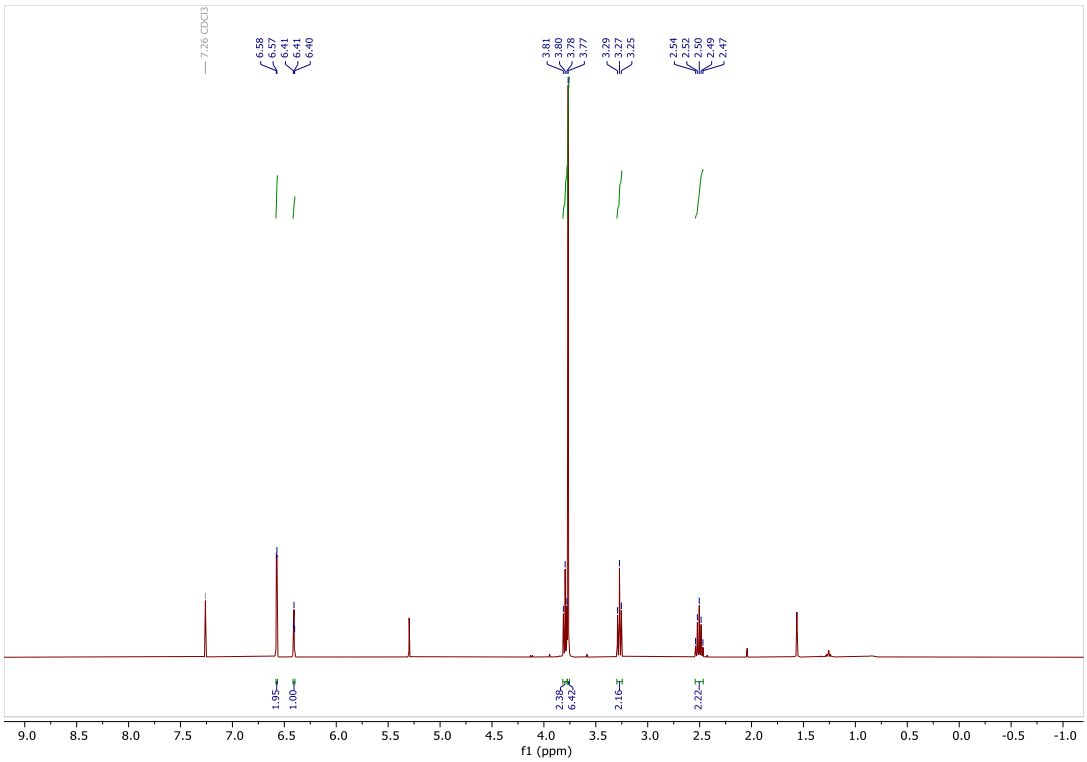
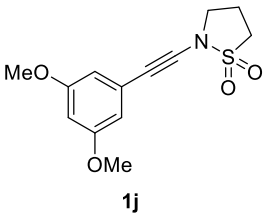
NMR Spectra

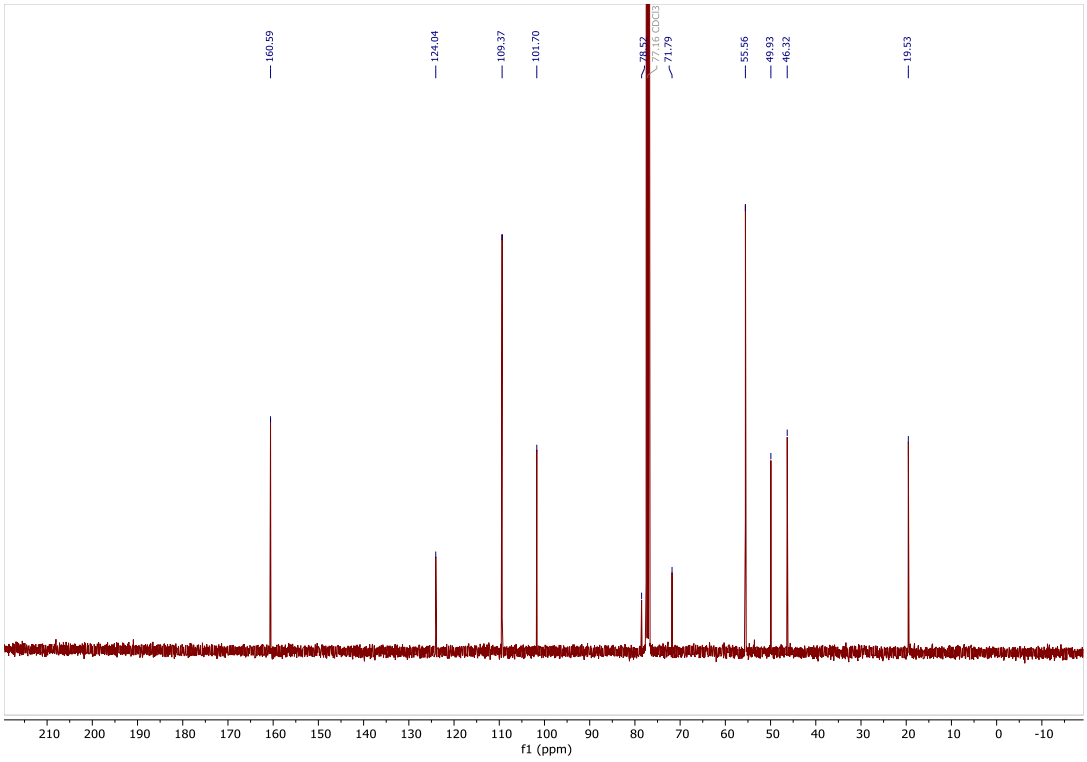
^{1}H NMR of compound **1j** (400 MHz, $CDCl_3$)

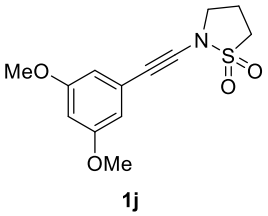




1j

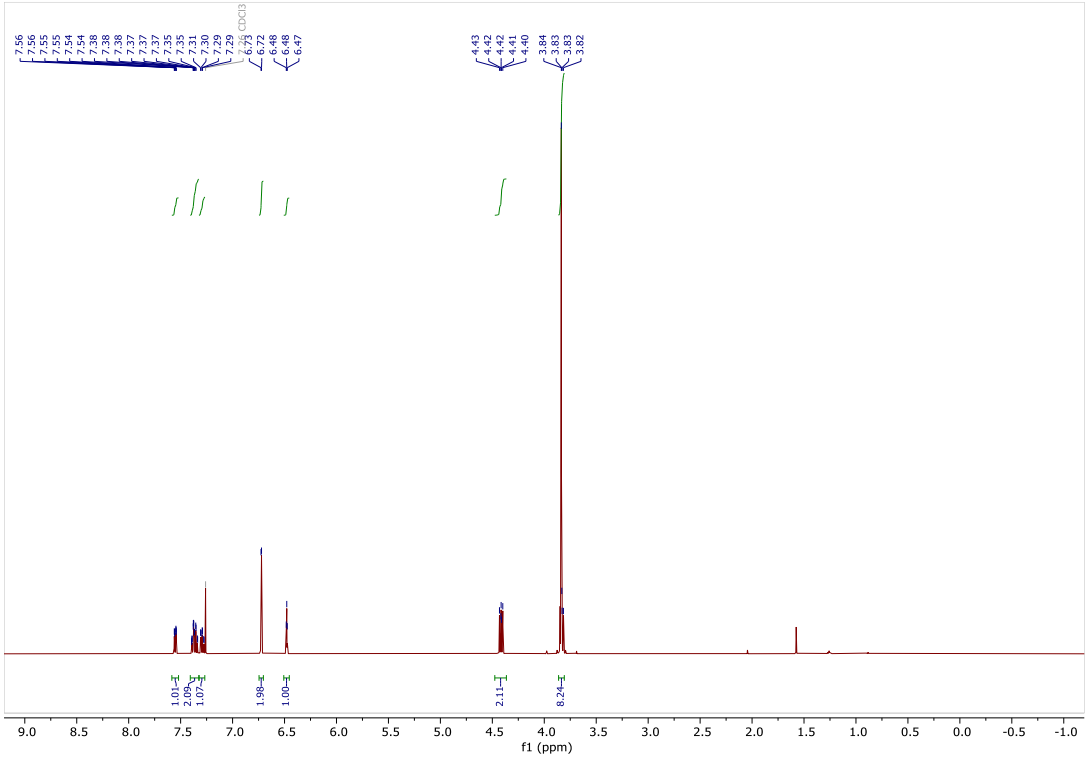
^{13}C NMR of compound **1j** (101 MHz, $CDCl_3$)

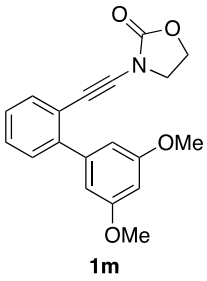




1j

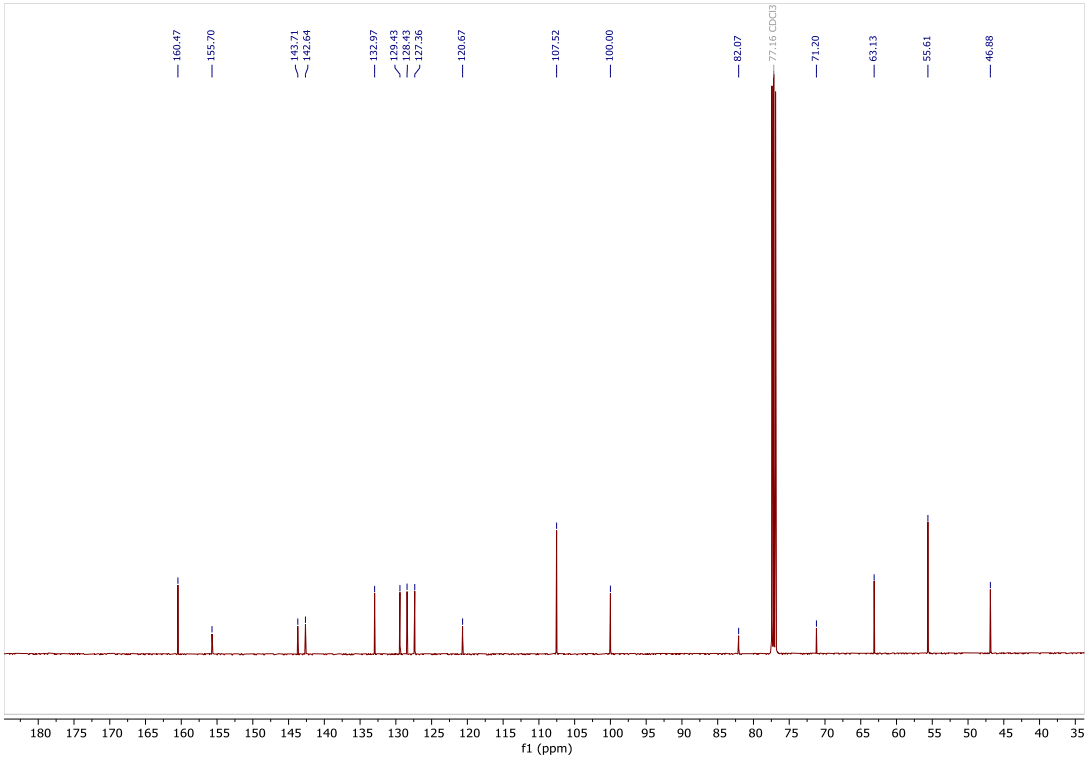
^{1}H NMR of compound **1m** (500 MHz, $CDCl_3$)

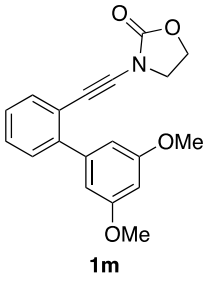




1m

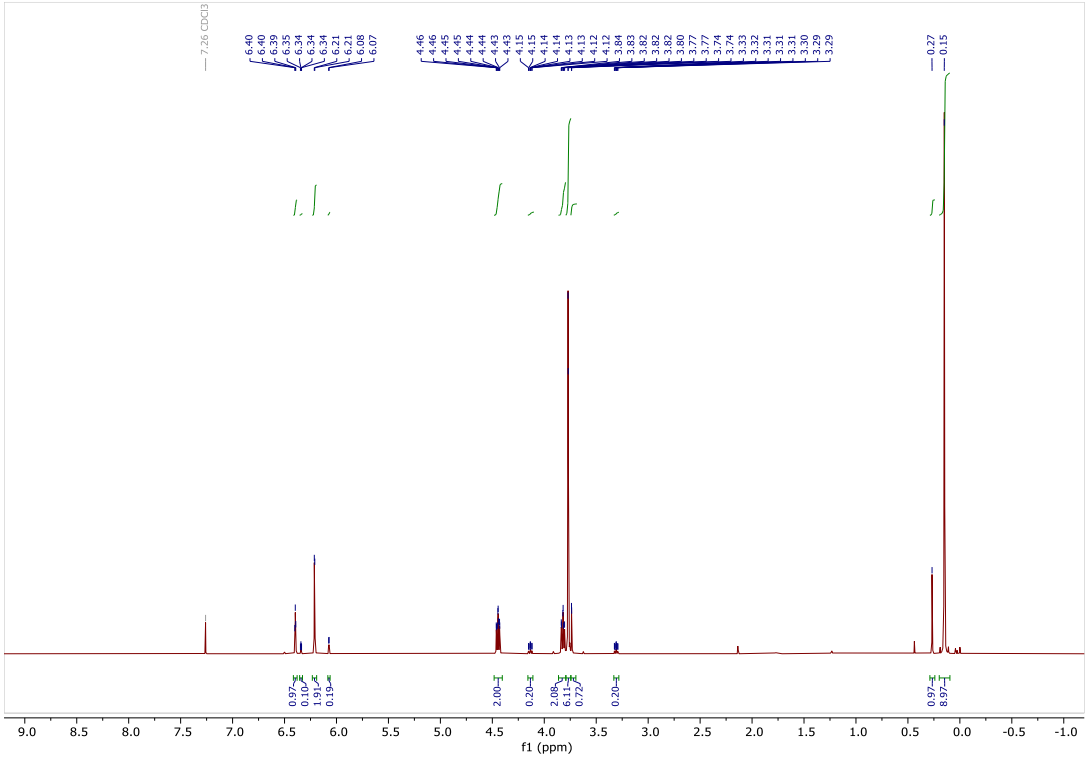
^{13}C NMR of compound **1m** (126 MHz, $CDCl_3$)

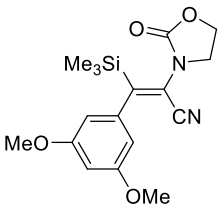




1m

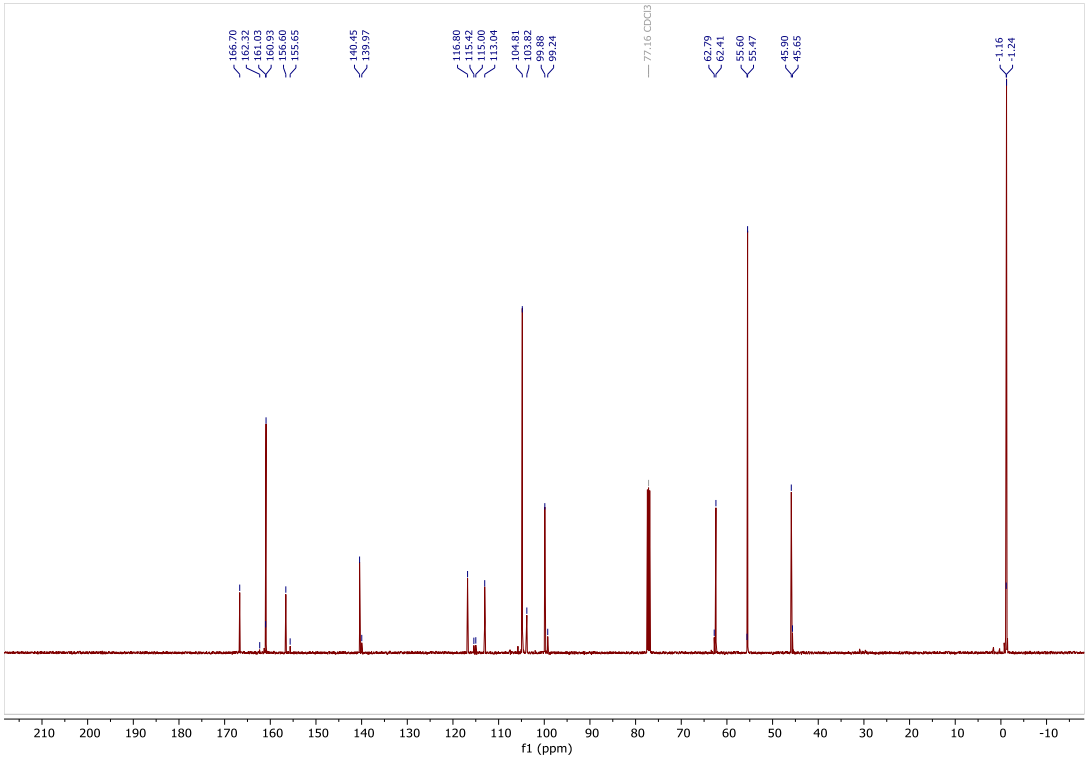
^{1}H NMR of compound **2a** (500 MHz, $CDCl_3$)

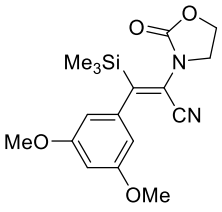




2a
Z/*E* 90:10

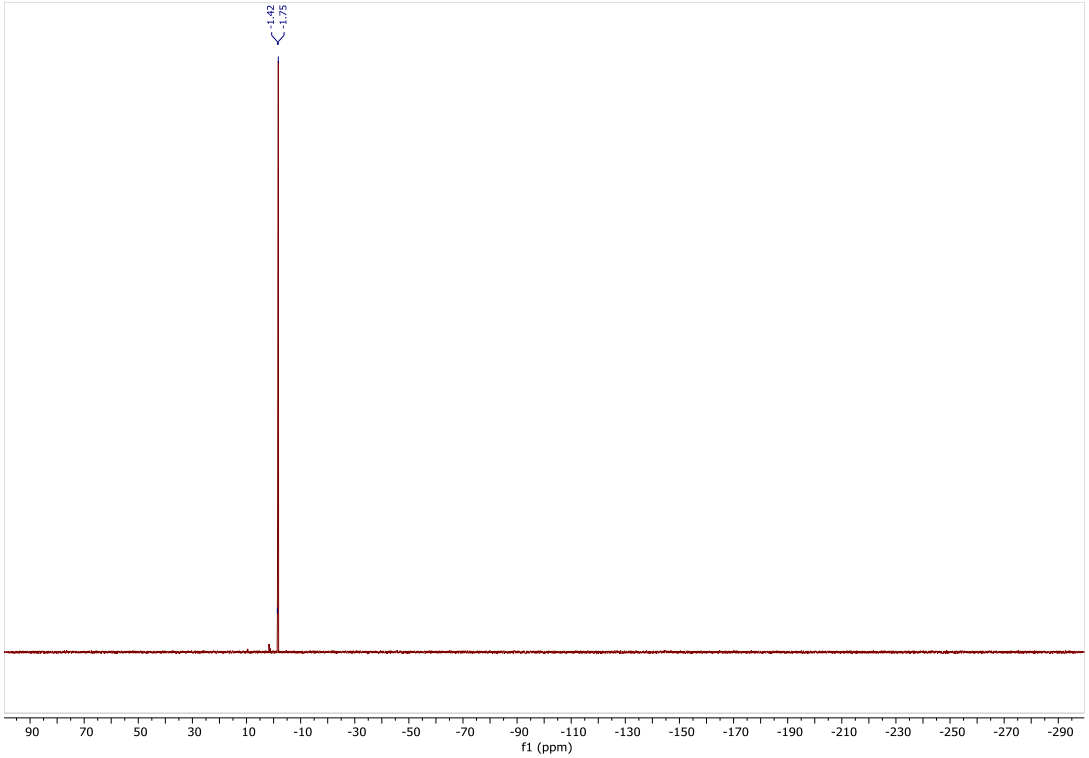
^{13}C NMR of compound **2a** (126 MHz, $CDCl_3$)

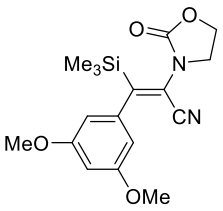




2a
Z/*E* 90:10

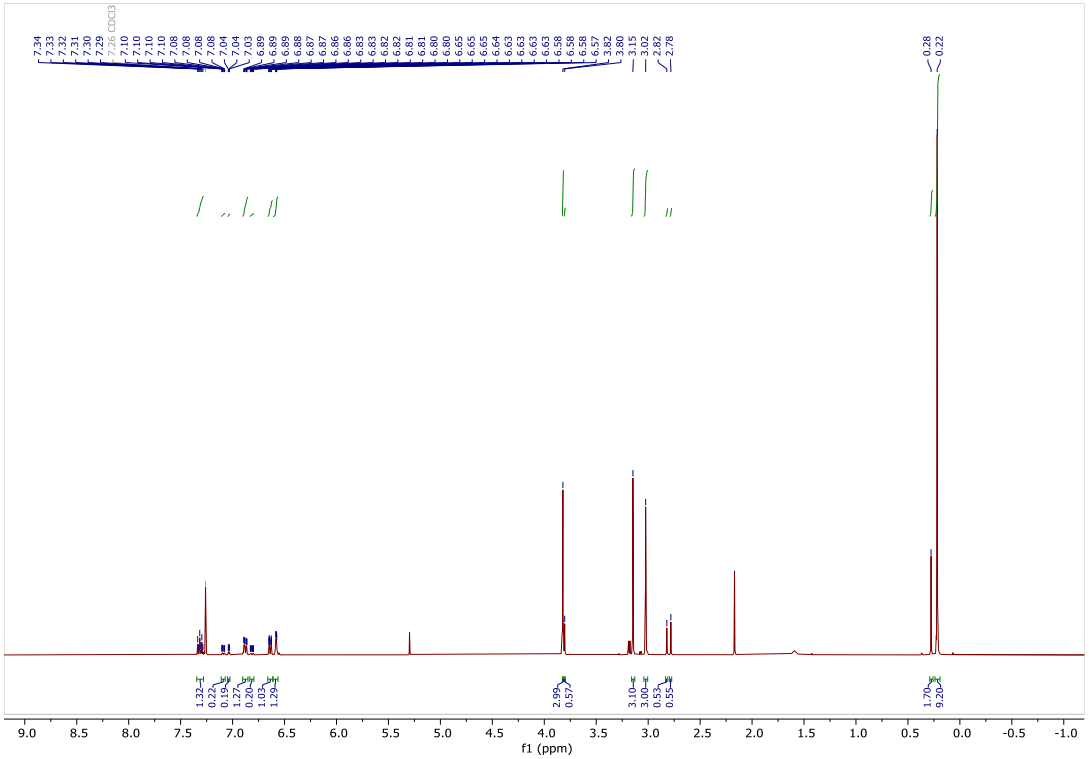
^{29}Si NMR of compound **2a** (99 MHz, $CDCl_3$)

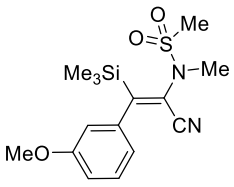




2a
Z/E 90:10

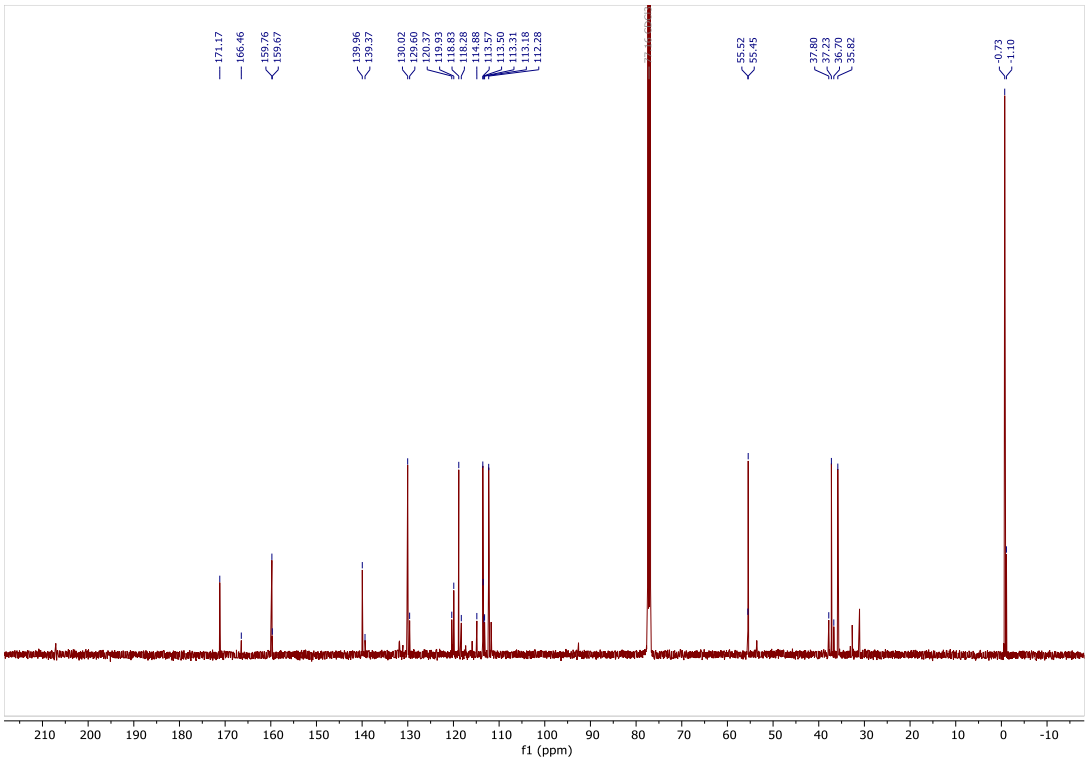
^{1}H NMR of compound **2d** (500 MHz, $CDCl_3$)

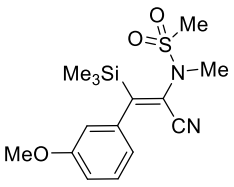




2d
Z/E 85:15

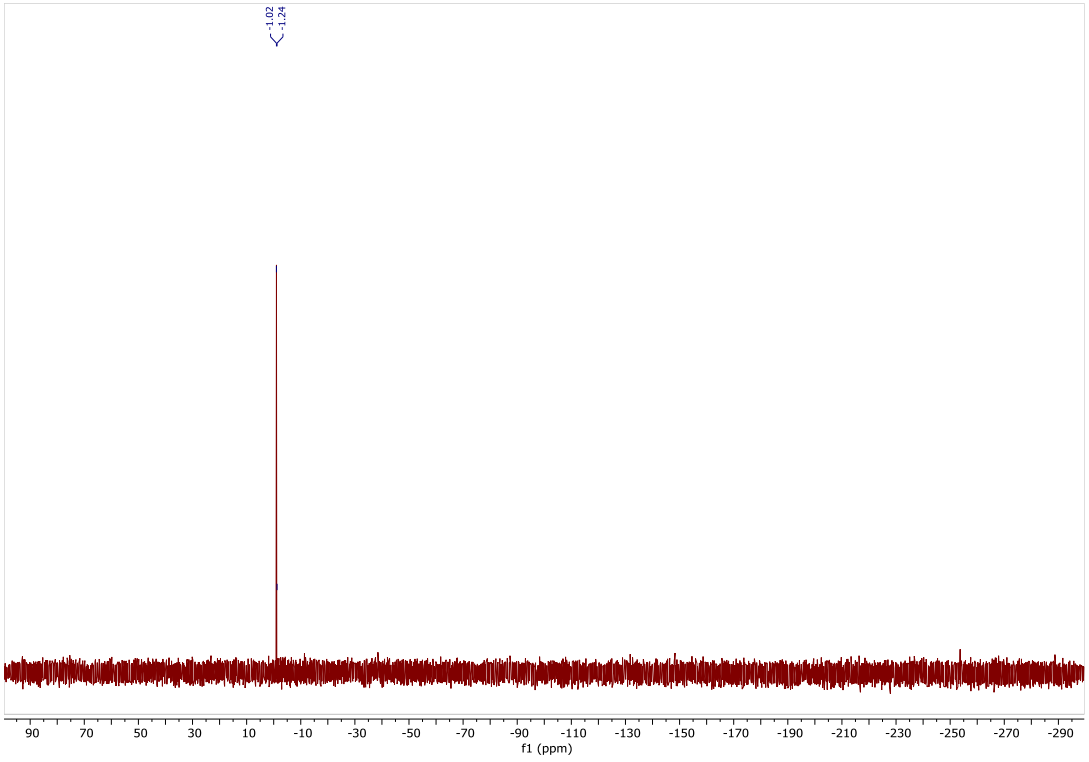
^{13}C NMR of compound **2d** (126 MHz, $CDCl_3$)

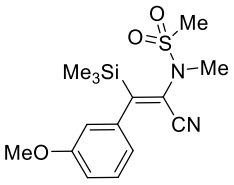




2d
Z/E 85:15

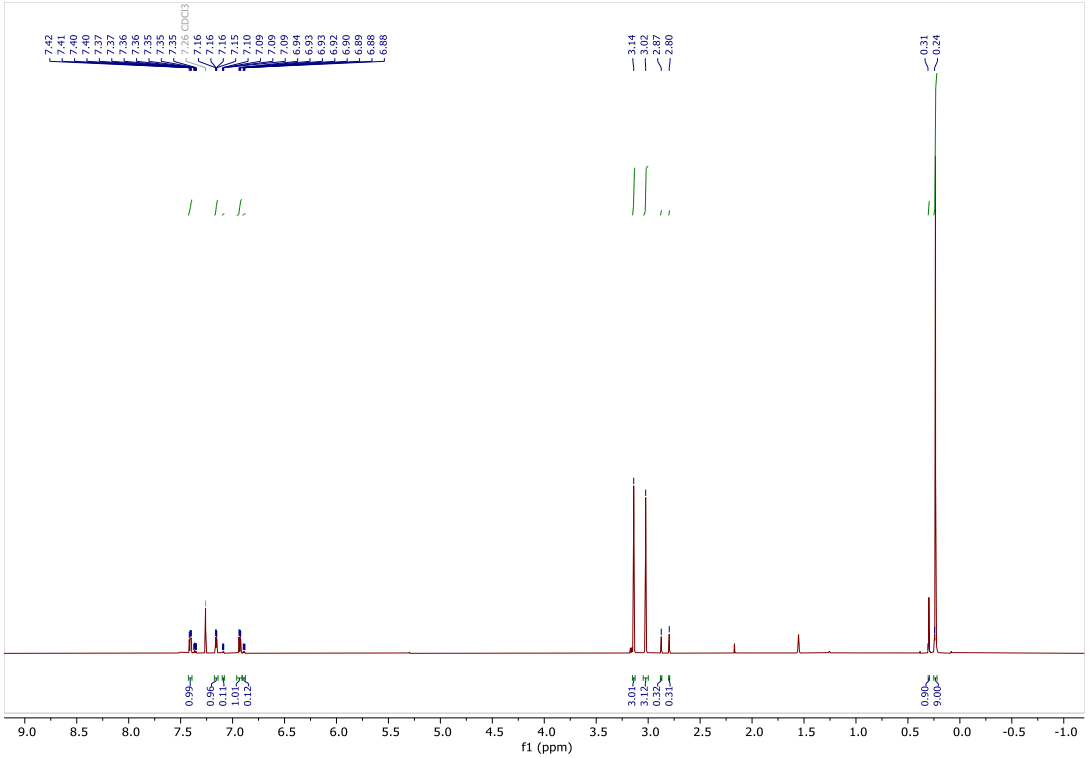
^{29}Si NMR of compound **2d** (99 MHz, $CDCl_3$)

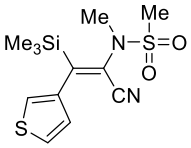




2d
Z/E 85:15

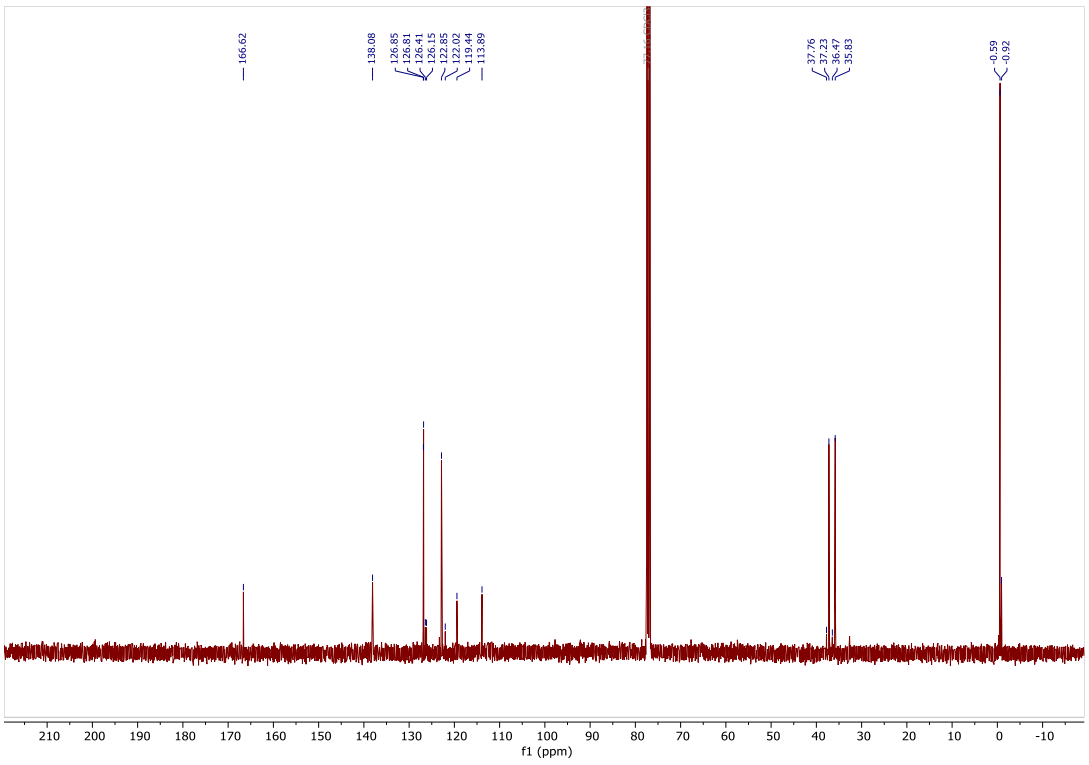
^{1}H NMR of compound **2h** (400 MHz, $CDCl_3$)

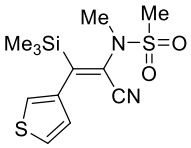




2h
Z/*E* 90:10

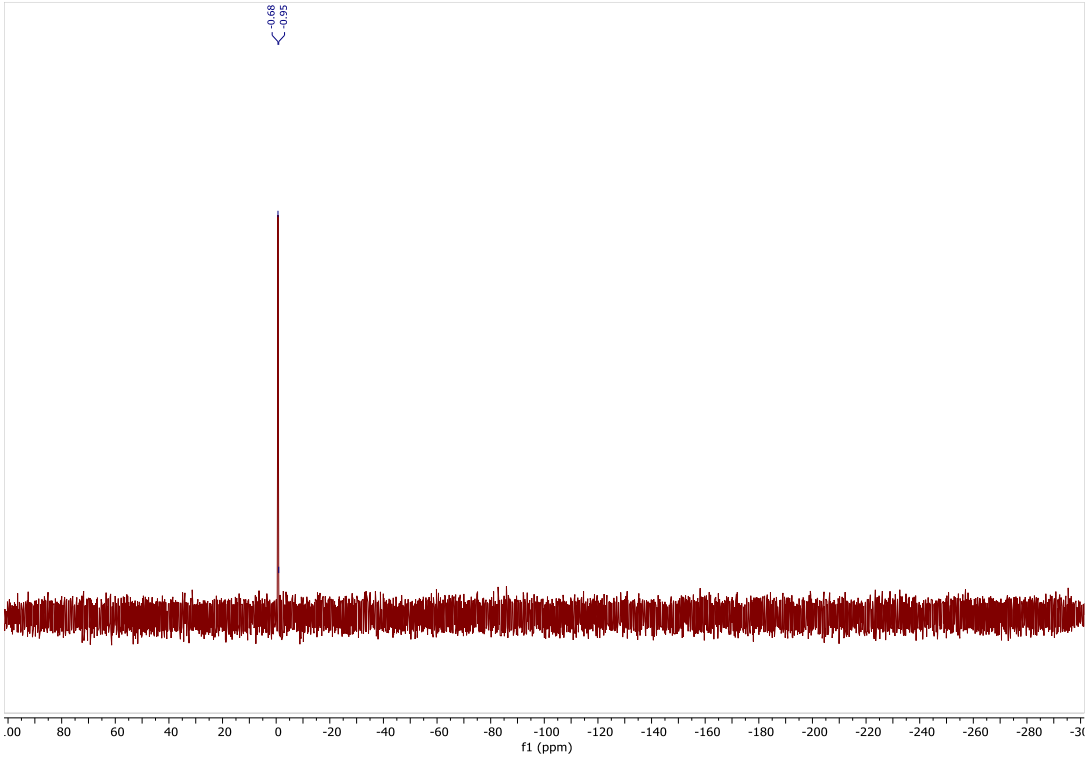
^{13}C NMR of compound **2h** (101 MHz, $CDCl_3$)

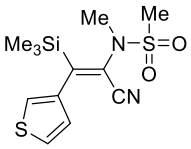




2h
Z/*E* 90:10

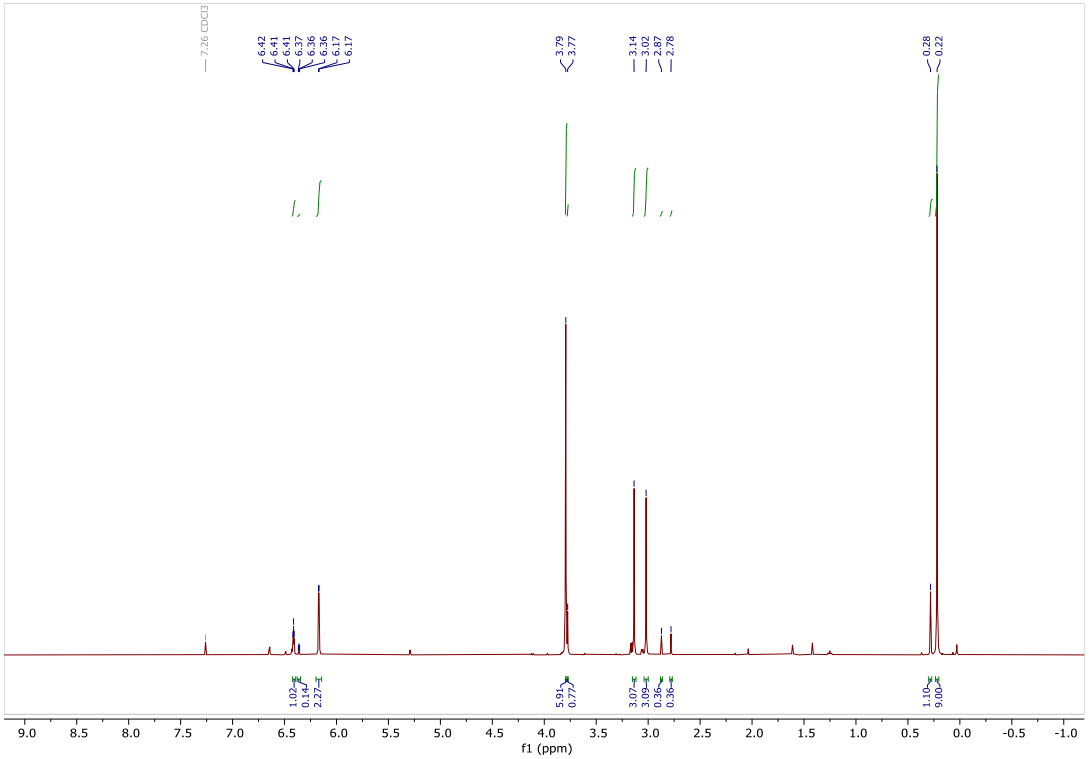
^{29}Si NMR of compound **2h** (80 MHz, $CDCl_3$)

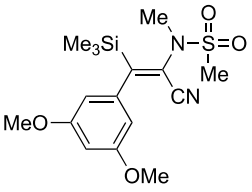




2h
Z/*E* 90:10

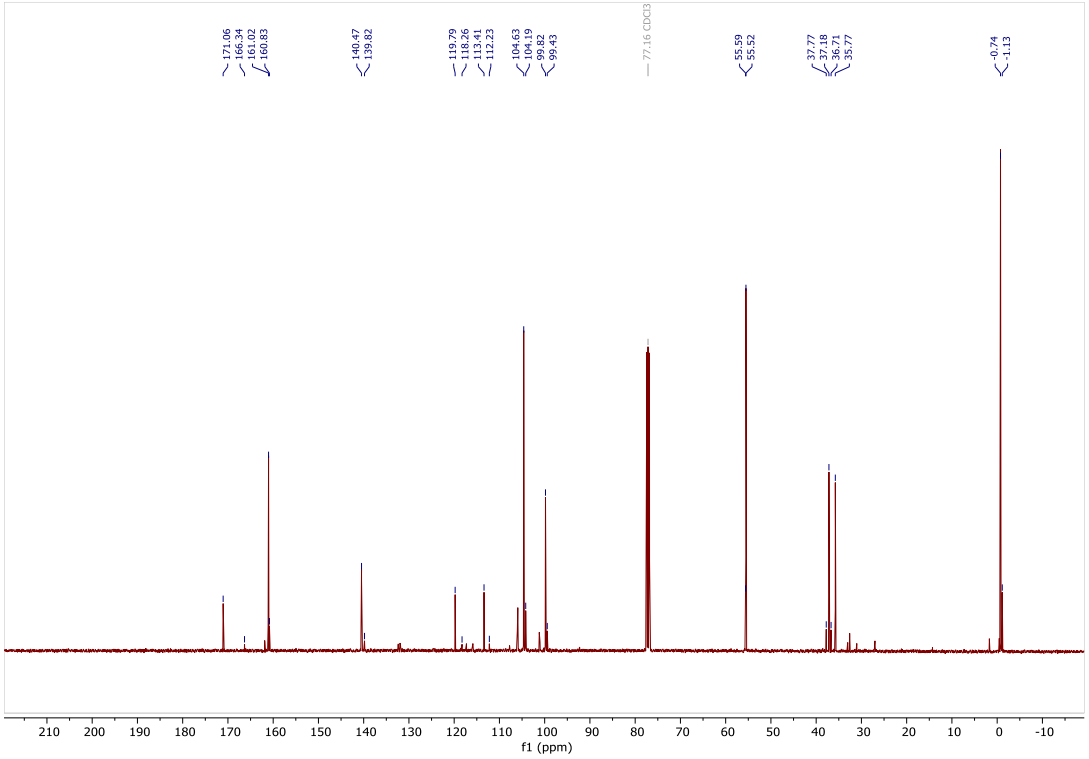
^{1}H NMR of compound **2i** (500 MHz, $CDCl_3$)

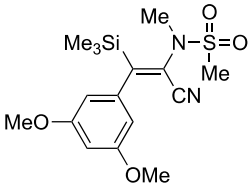




2i
Z/*E* 89:11

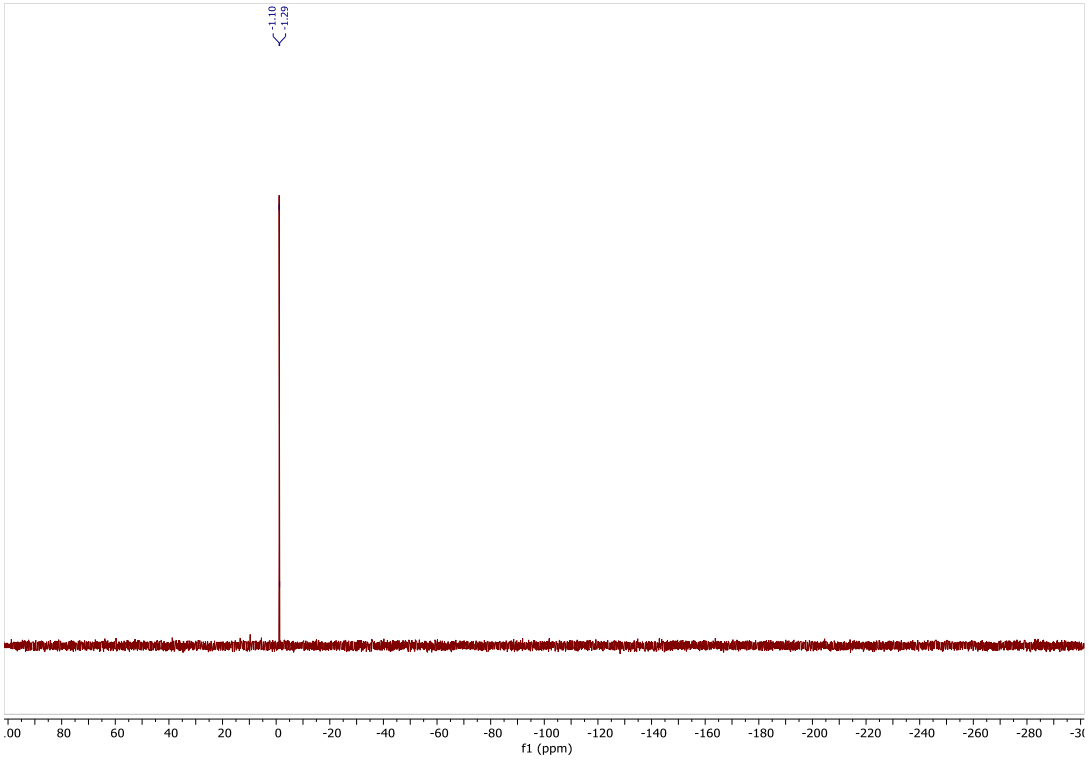
^{13}C NMR of compound **2i** (126 MHz, $CDCl_3$)

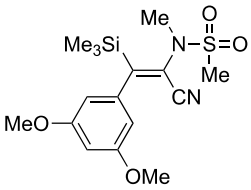




2i
Z/*E* 89:11

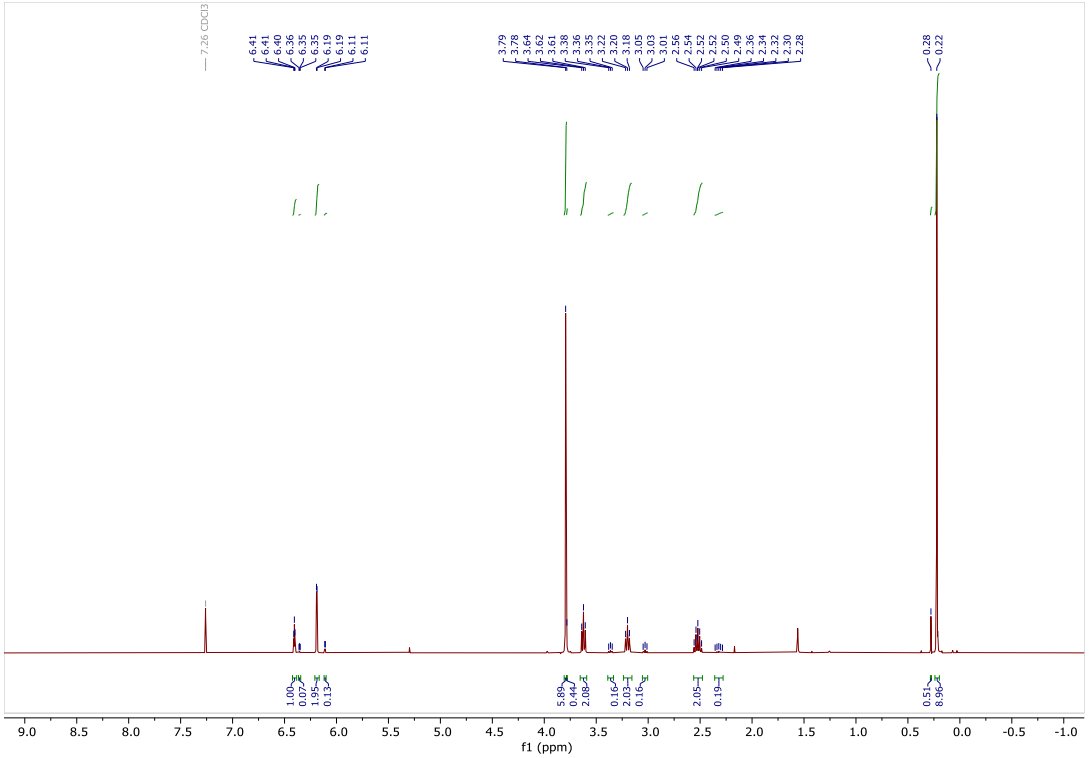
^{29}Si NMR of compound **2i** (80 MHz, $CDCl_3$)

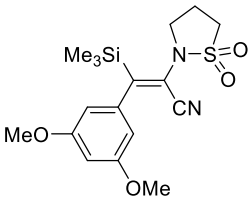




2i
Z/*E* 89:11

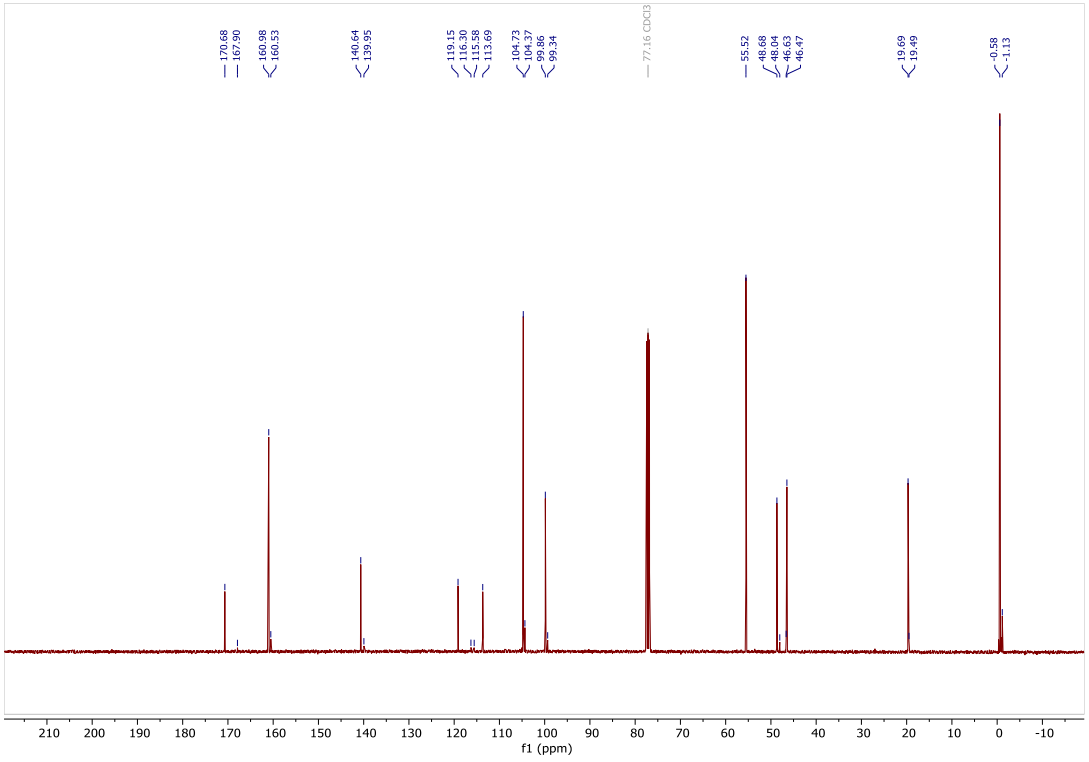
^{1}H NMR of compound **2j** (400 MHz, $CDCl_3$)

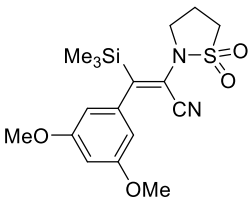




2j
Z/E = 93:7

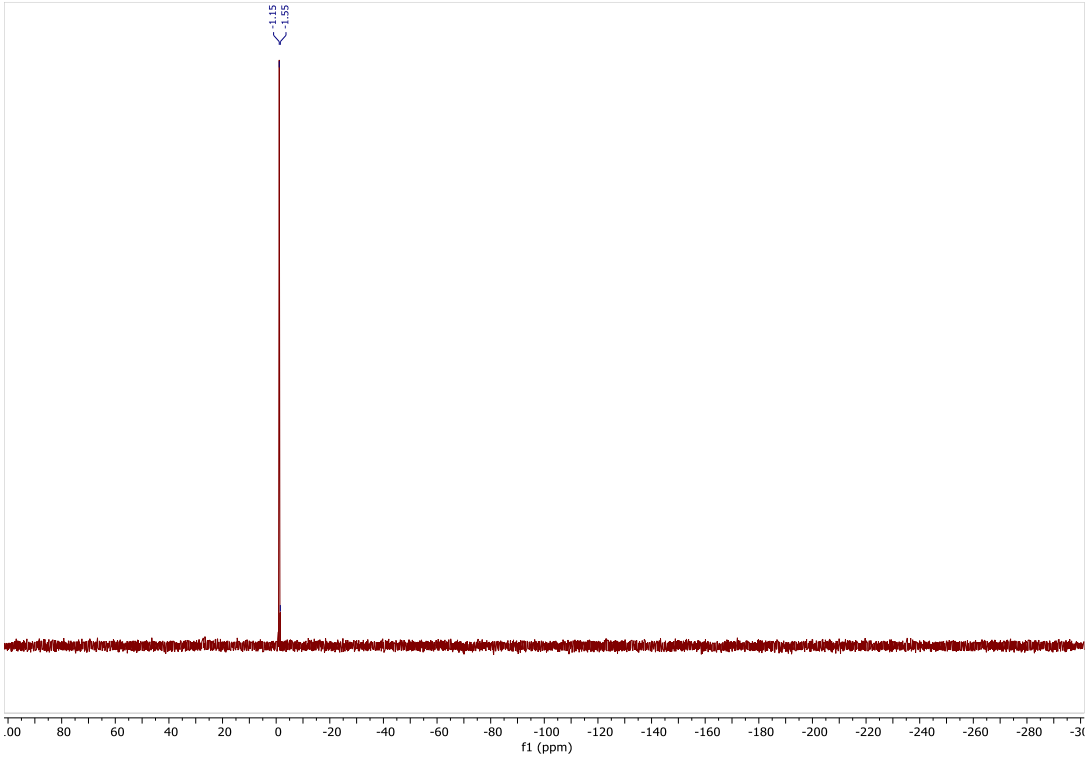
^{13}C NMR of compound **2j** (101 MHz, $CDCl_3$)

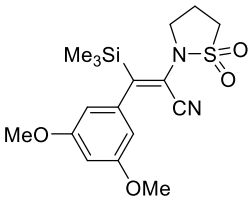




2j
Z/E = 93:7

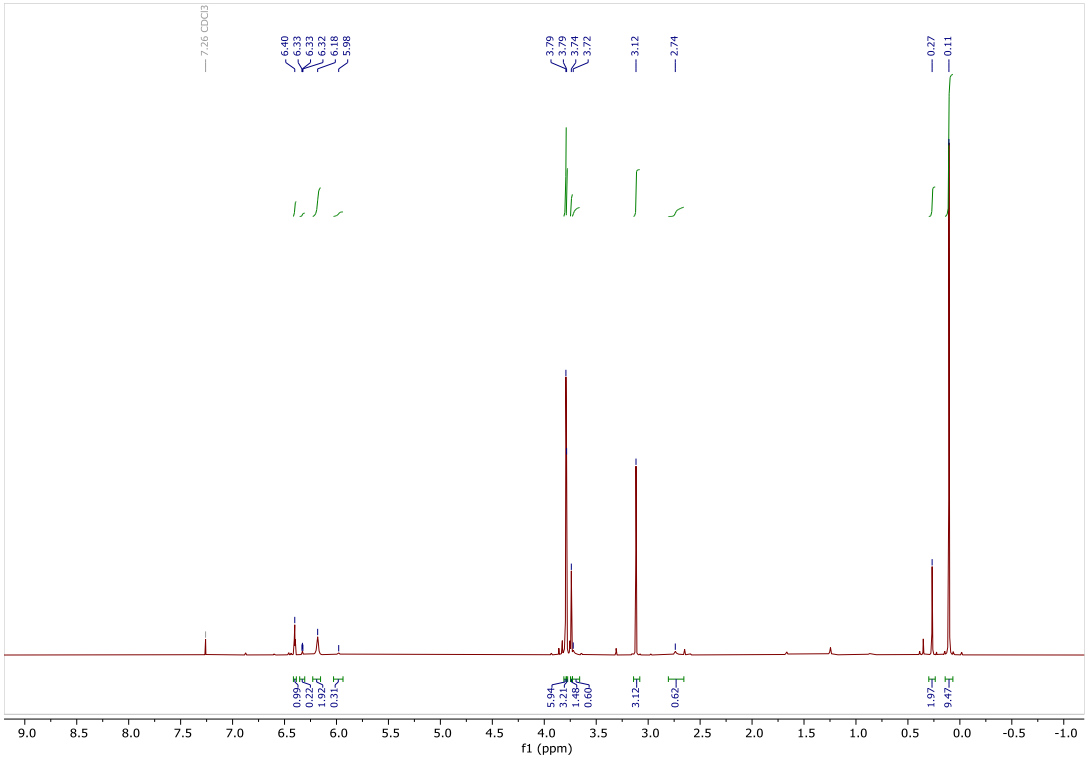
^{29}Si NMR of compound **2j** (80 MHz, $CDCl_3$)

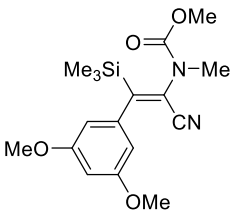




2j
Z/E = 93:7

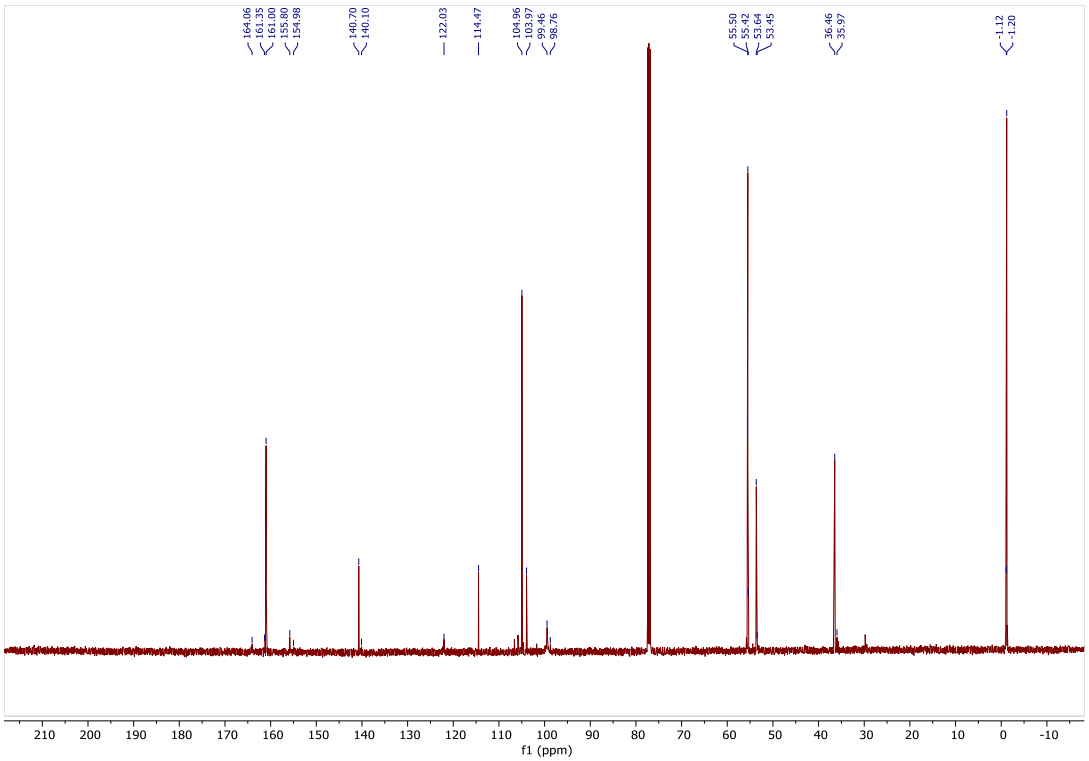
^{1}H NMR of compound **2k** (500 MHz, $CDCl_3$)

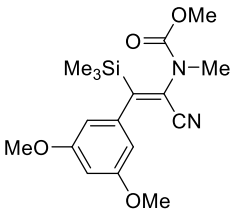




2k
Z/E 88:12

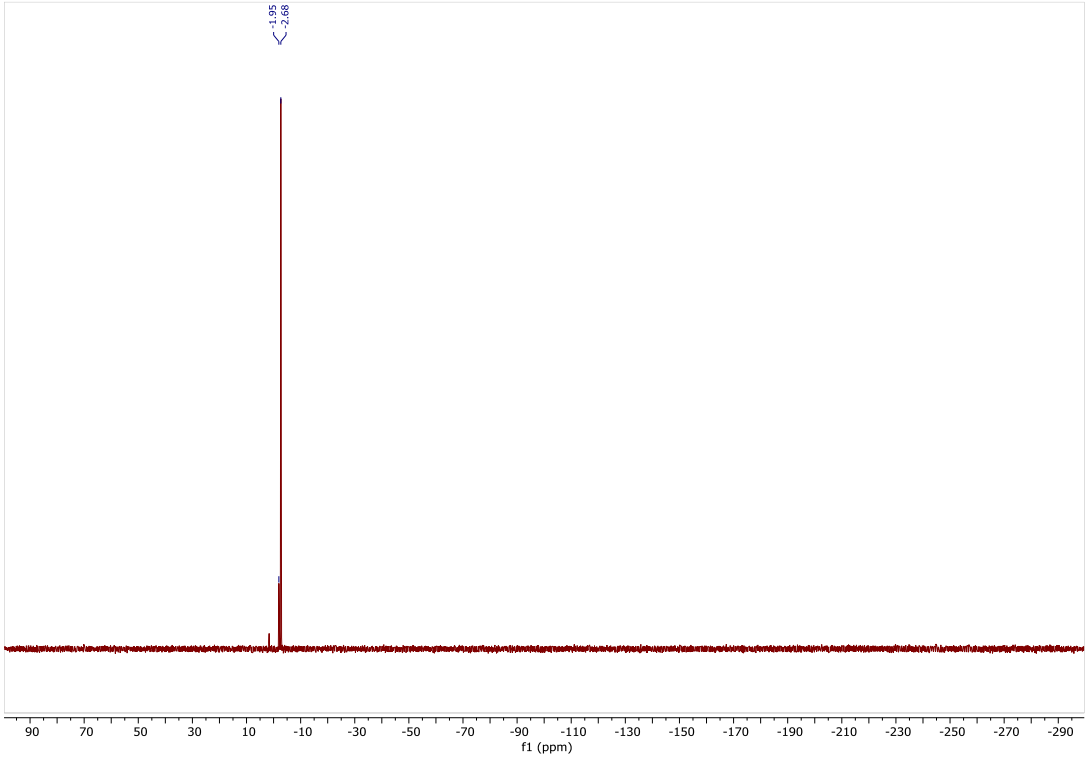
^{13}C NMR of compound **2k** (500 MHz, $CDCl_3$)

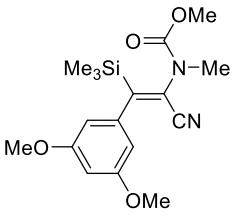




2k
Z/E 88:12

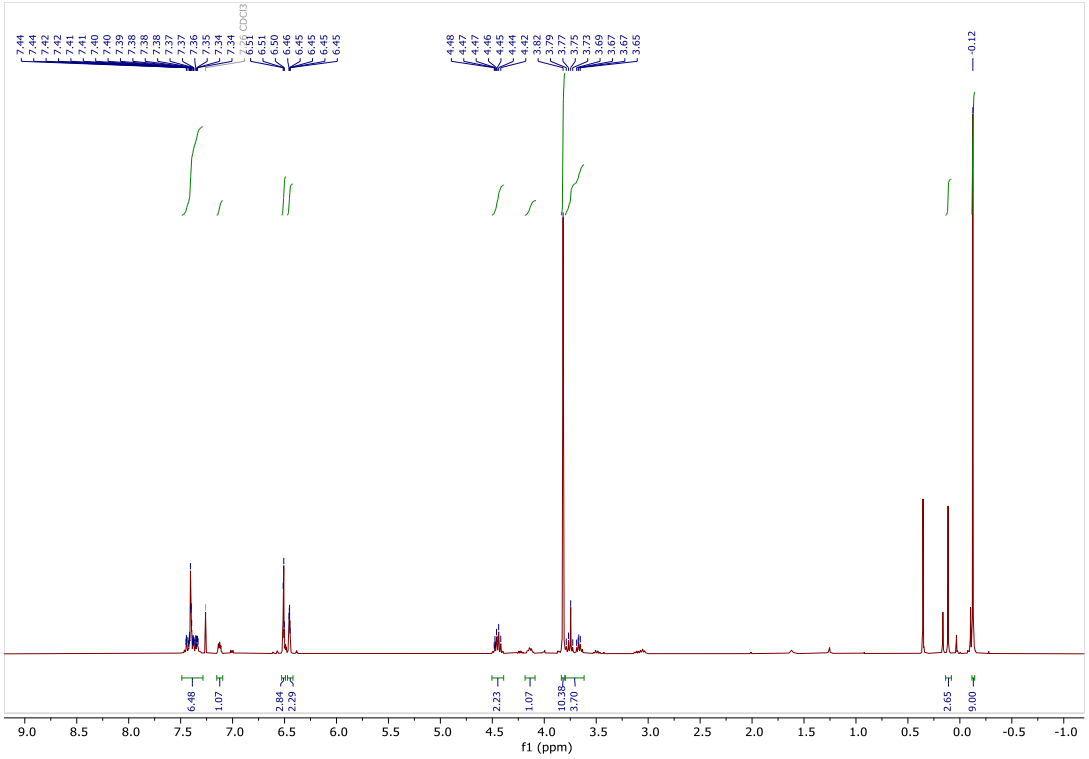
^{29}Si NMR of compound **2k** (99 MHz, $CDCl_3$)

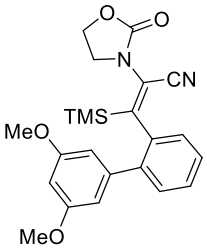




2k
Z/E 88:12

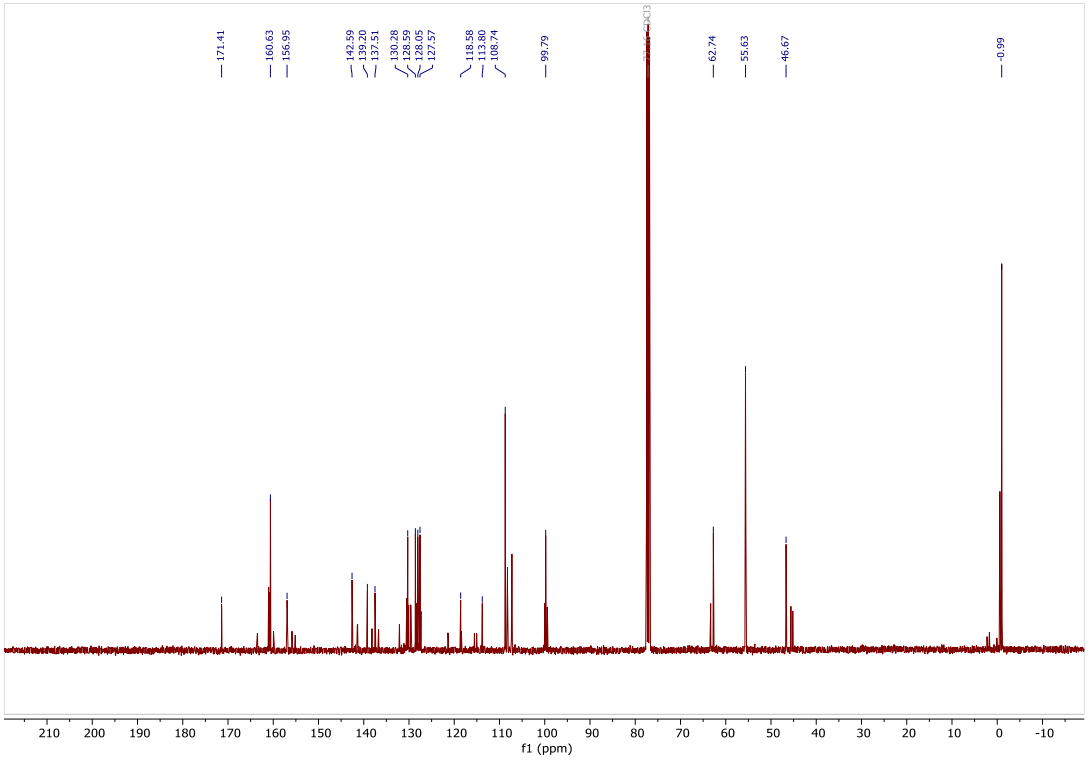
^{1}H NMR of compound **2m** (400 MHz, $CDCl_3$)

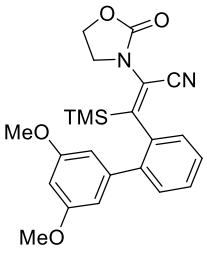




2m

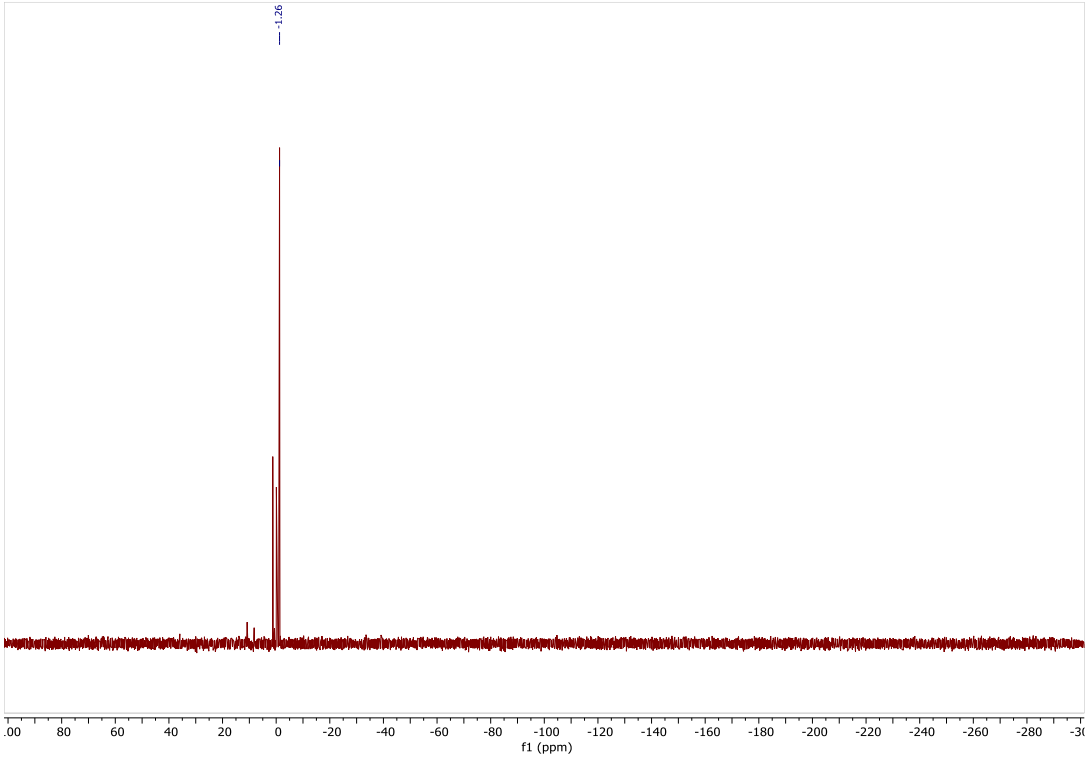
^{13}C NMR of compound **2m** (126 MHz, $CDCl_3$)

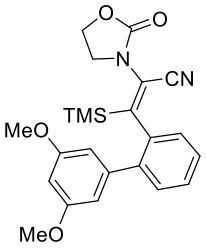




2m

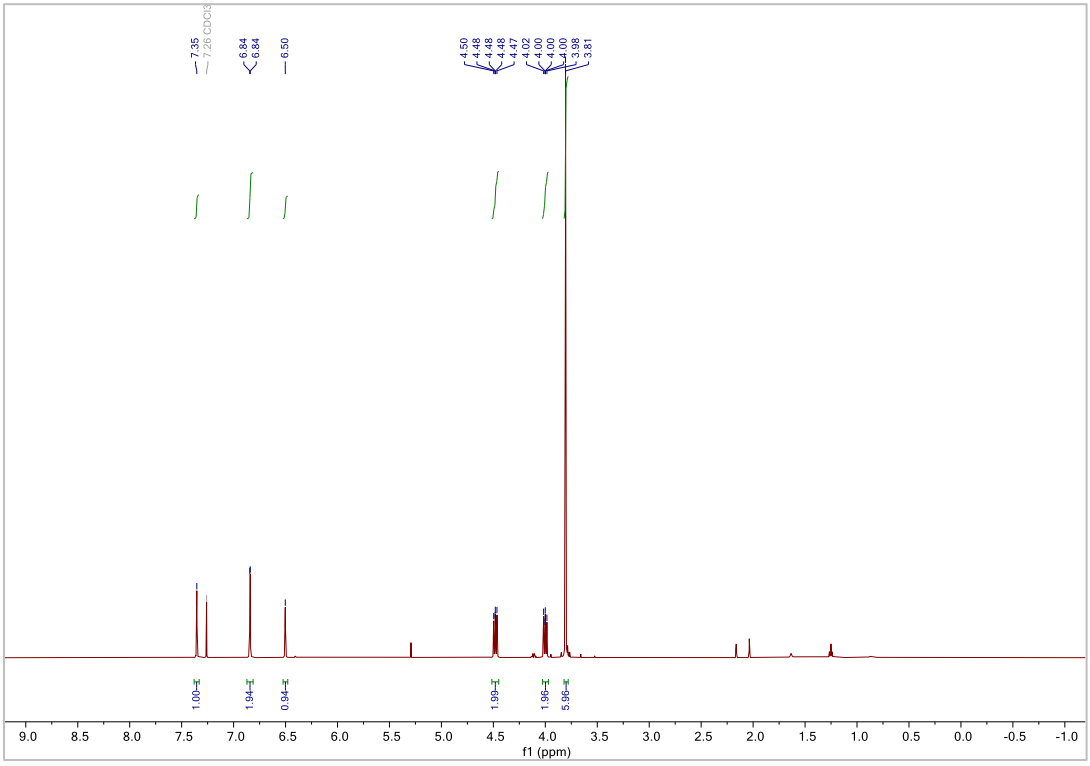
^{29}Si NMR of compound **2m** (80 MHz, $CDCl_3$)

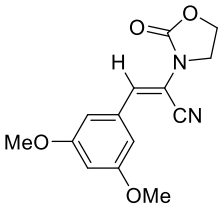




2m

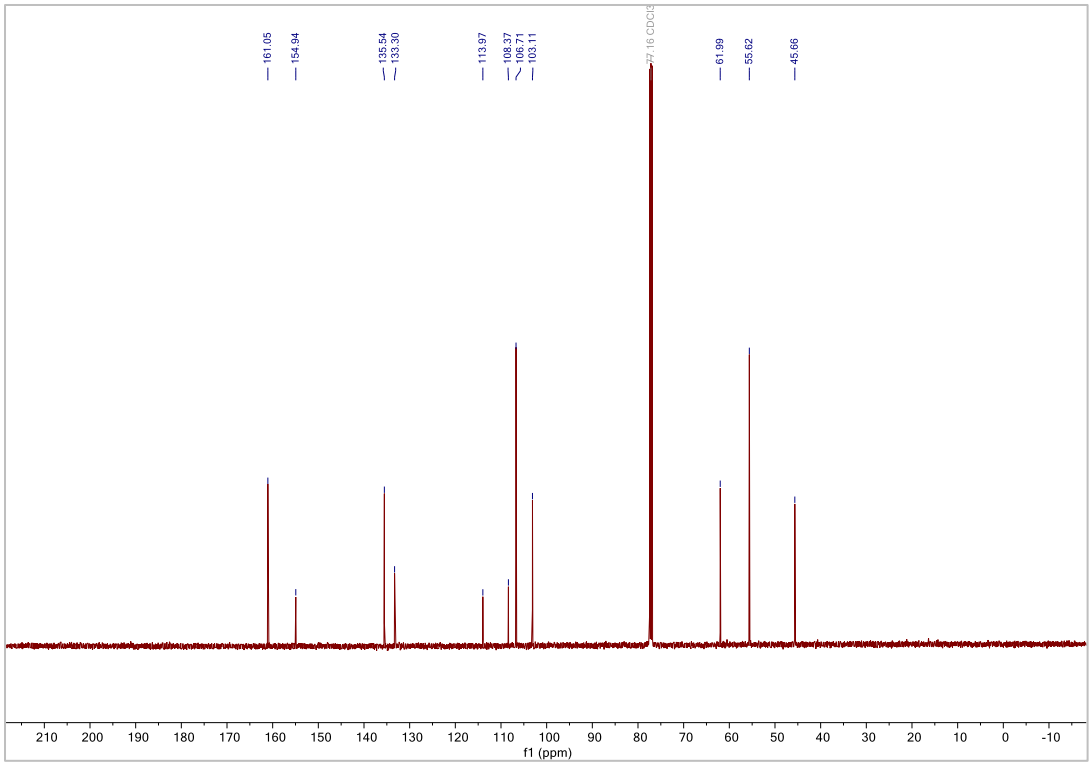
^{1}H NMR of compound **2a'$_E$** (500 MHz, $CDCl_3$)

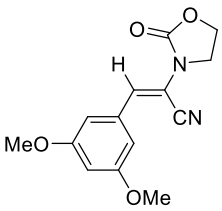




2a'$_E$

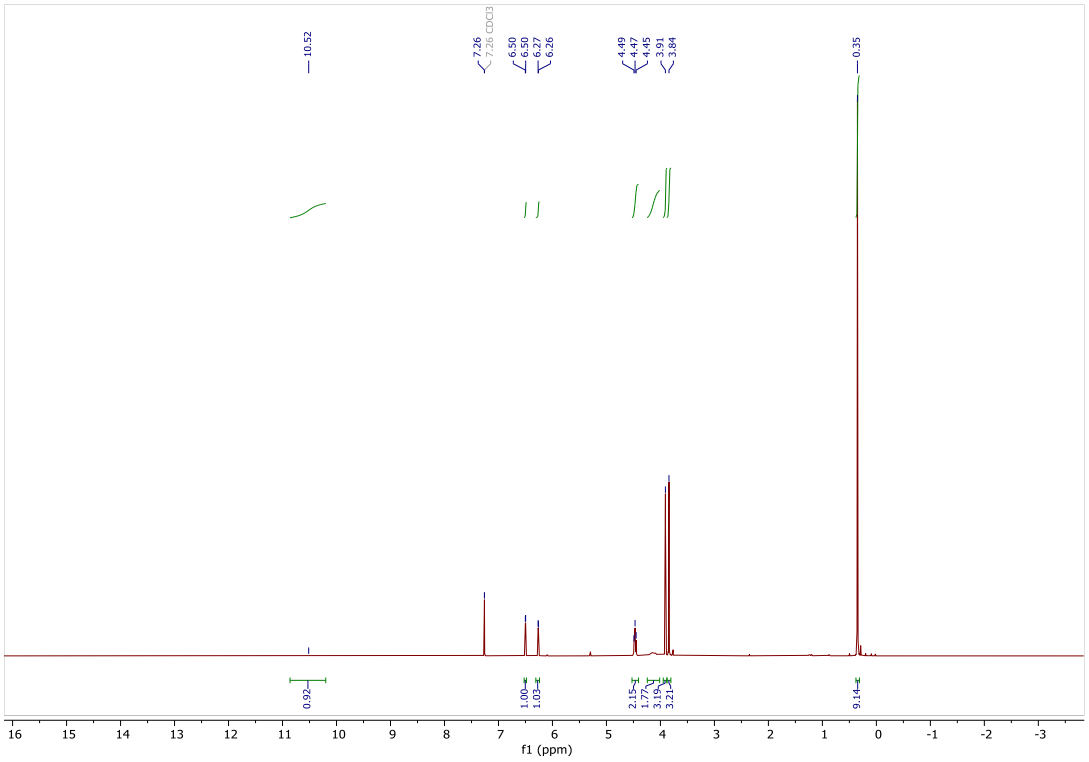
^{13}C NMR of compound **2a'$_E$** (126 MHz, $CDCl_3$)

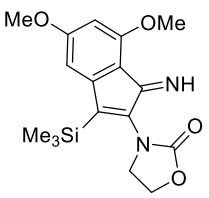




2a'$_E$

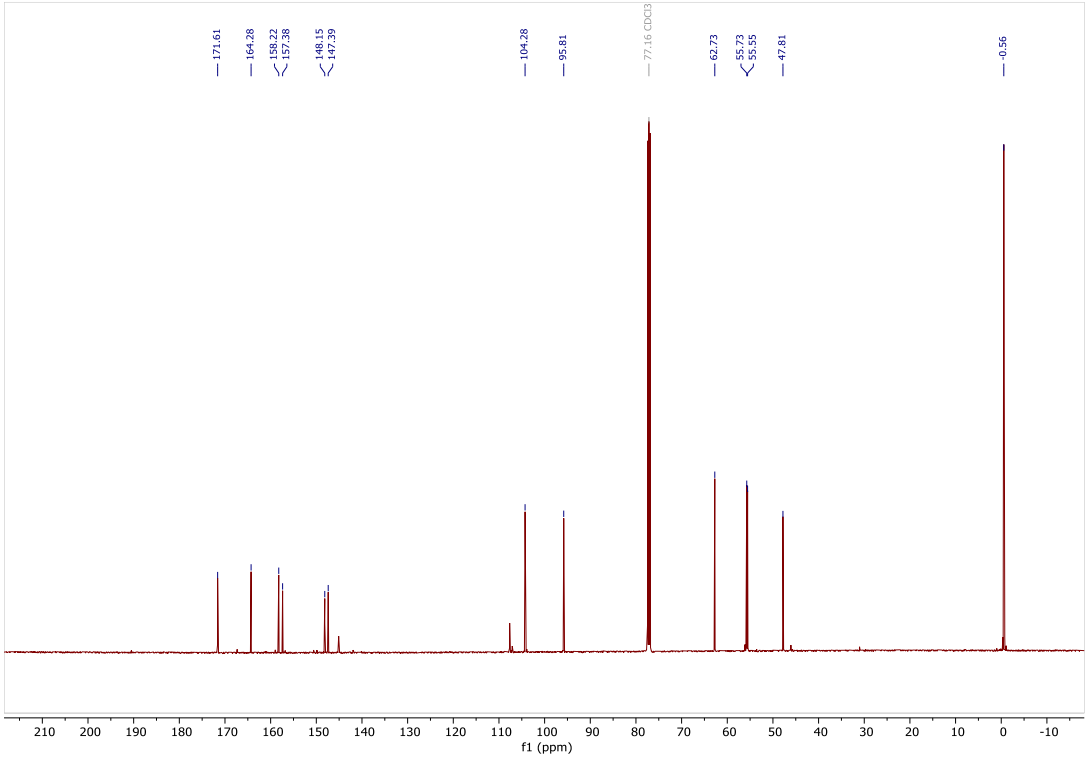
^{1}H NMR of compound **3a** (400 MHz, $CDCl_3$)

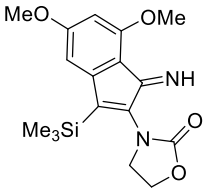




3a

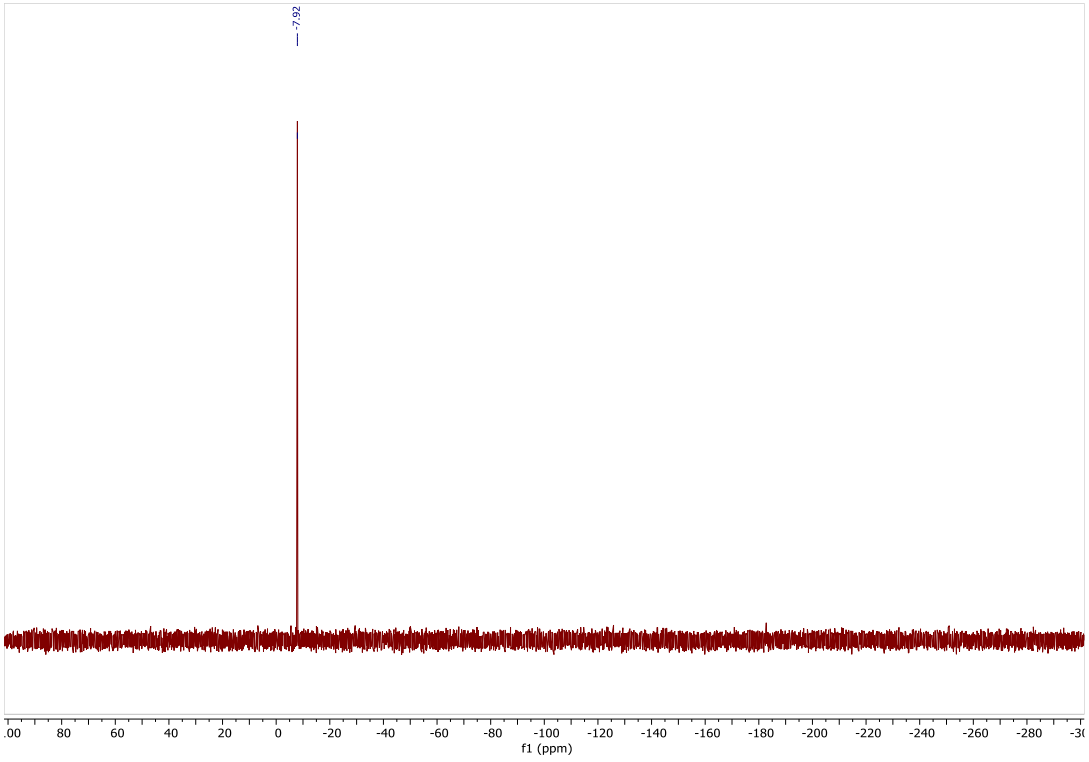
^{13}C NMR of compound **3a** (101 MHz, $CDCl_3$)

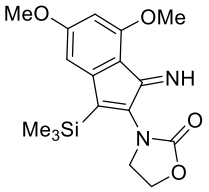




3a

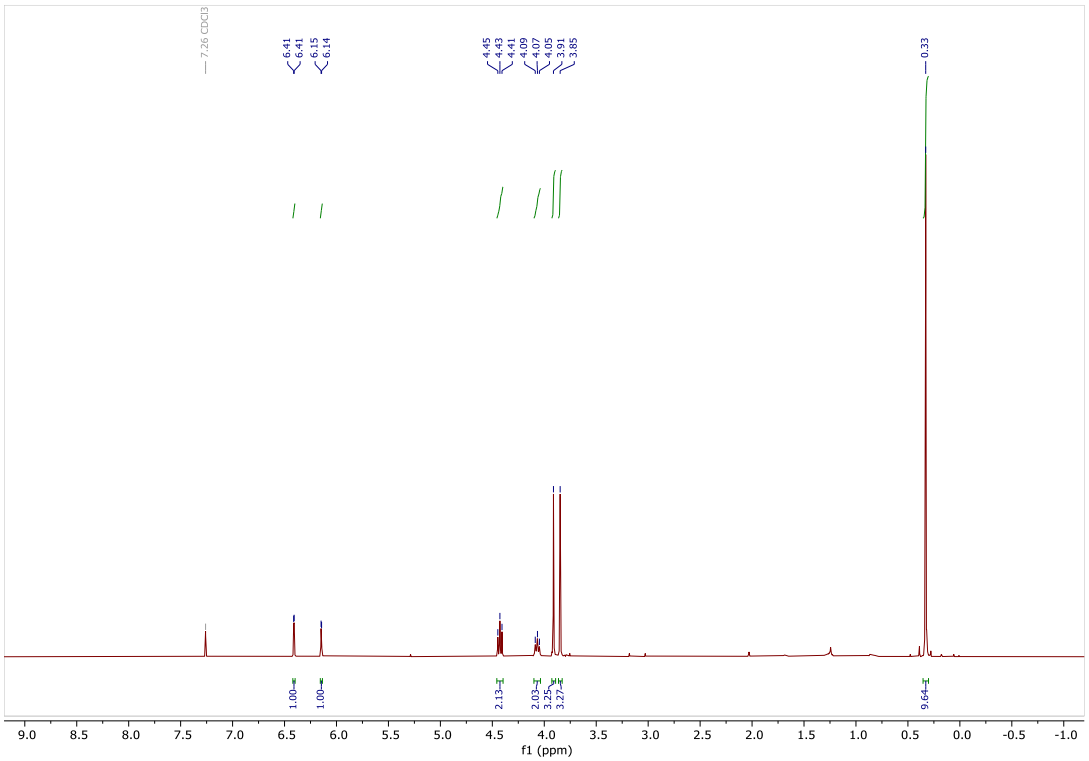
^{29}Si NMR of compound **3a** (80 MHz, $CDCl_3$)

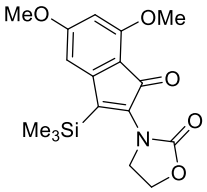




3a

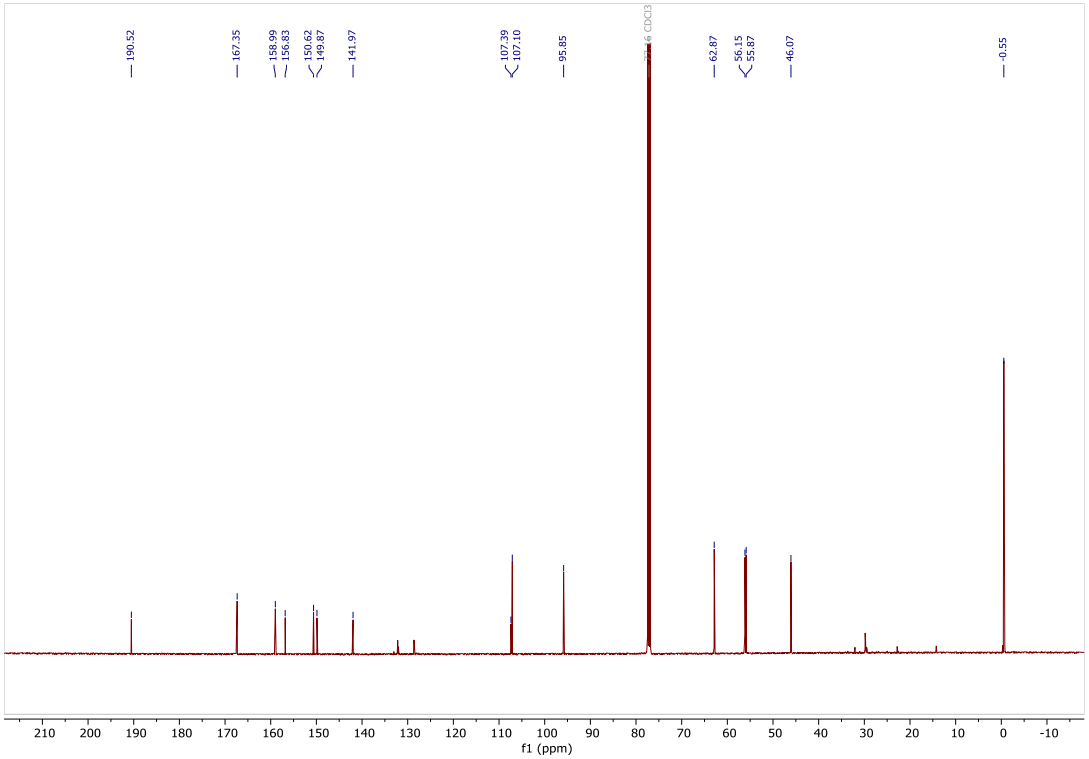
^{1}H NMR of compound **4a** (400 MHz, $CDCl_3$)

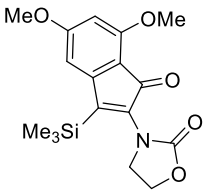




4a

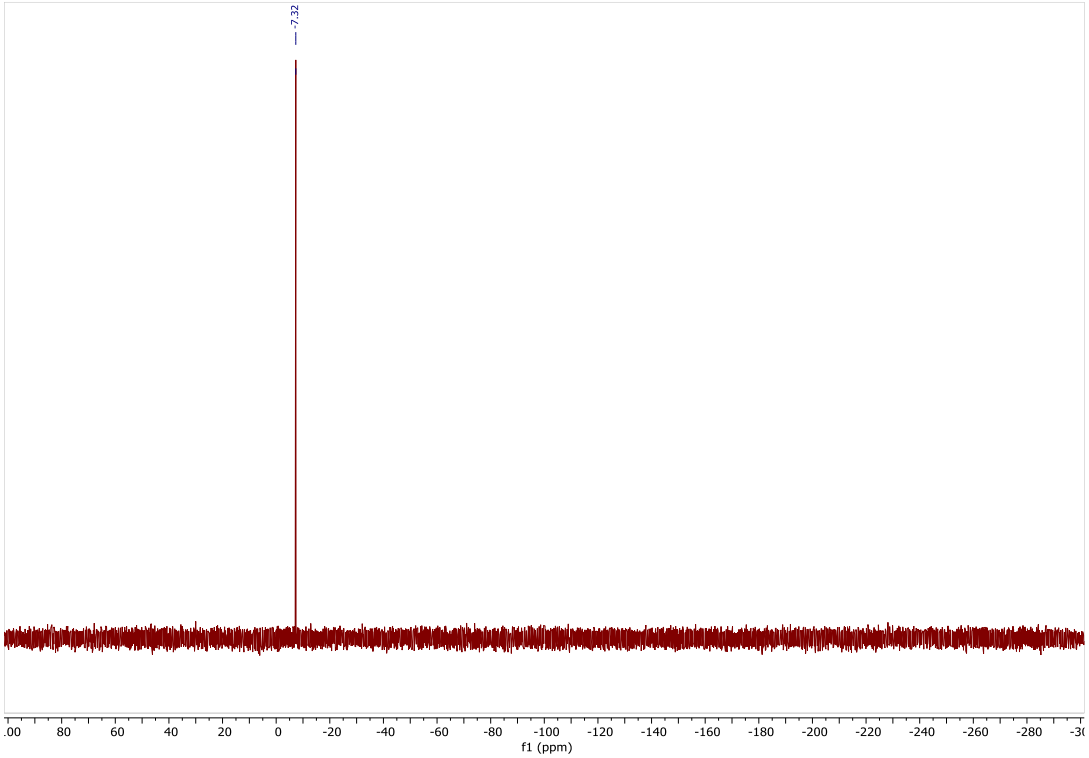
^{13}C NMR of compound **4a** (101 MHz, $CDCl_3$)

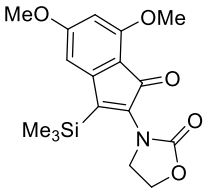




4a

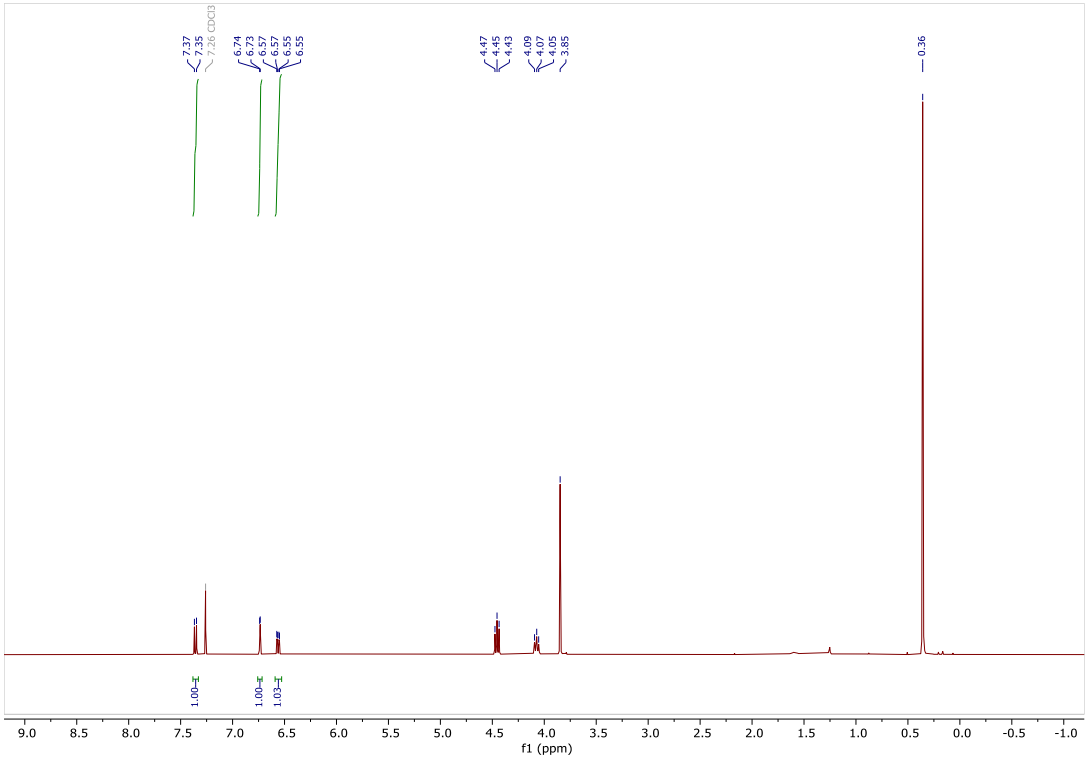
^{29}Si NMR of compound **4a** (80 MHz, $CDCl_3$)

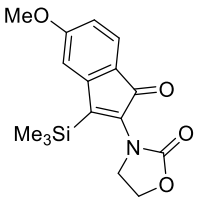




4a

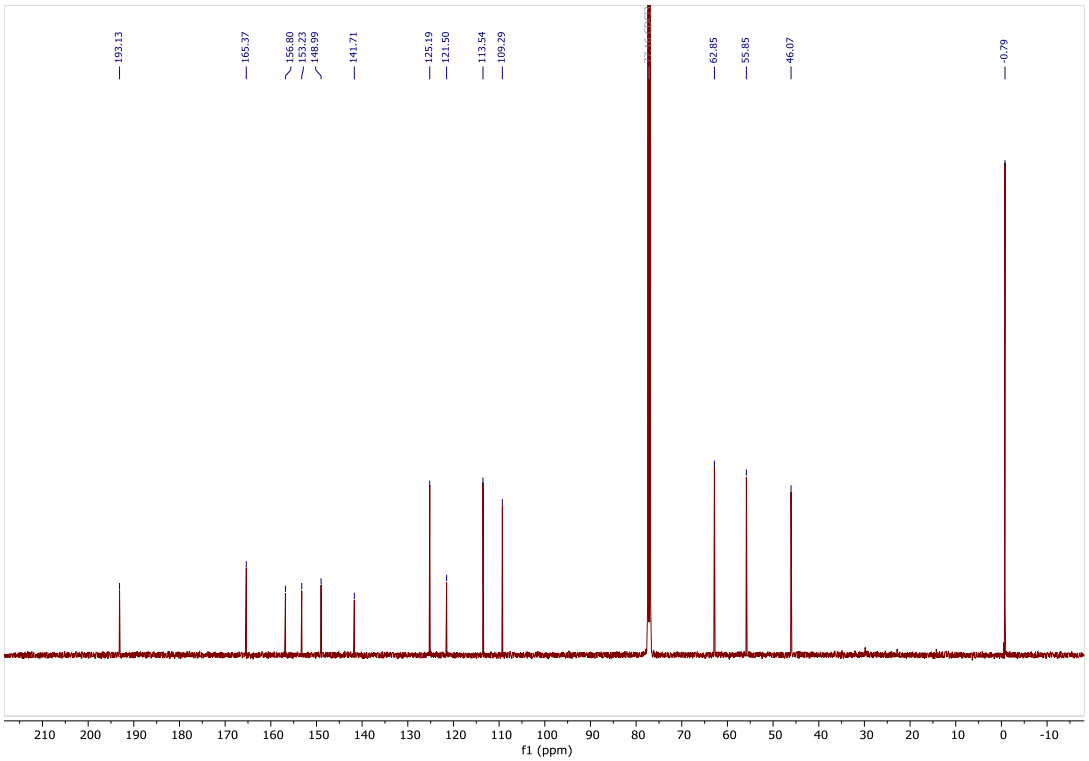
^{1}H NMR of compound **4c**[5] (400 MHz, $CDCl_3$)

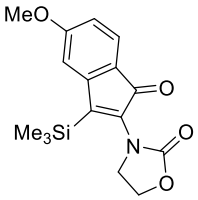




4c[5]

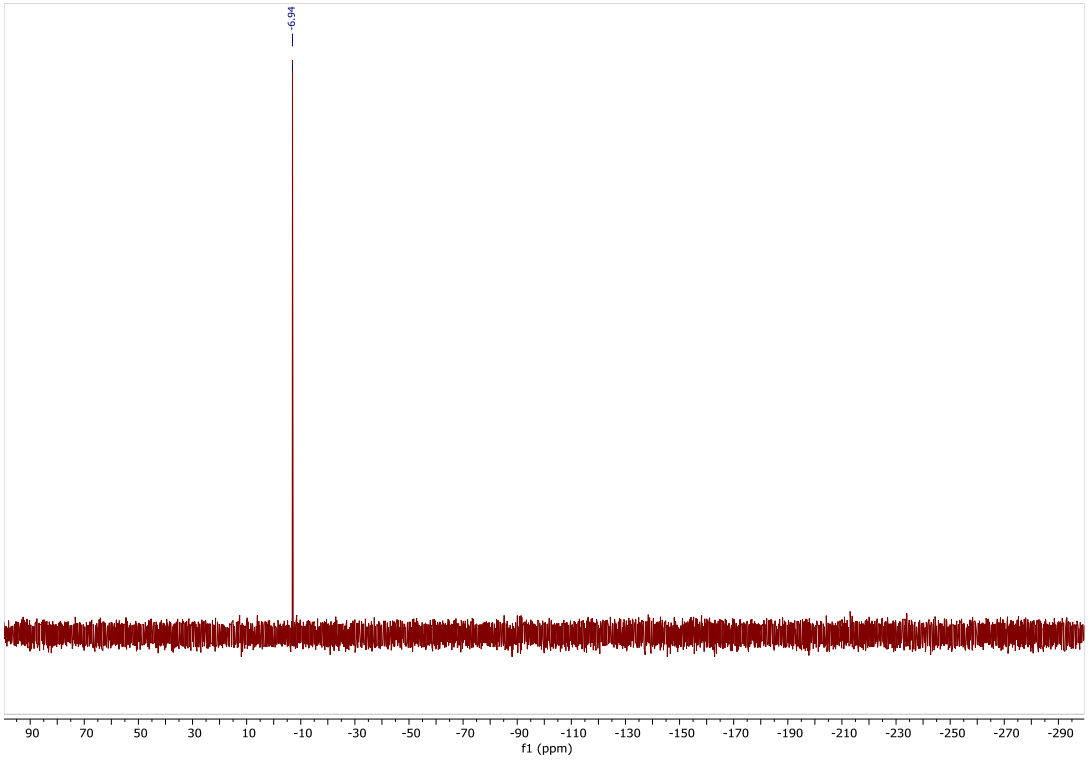
^{13}C NMR of compound **4c^5** (101 MHz, $CDCl_3$)

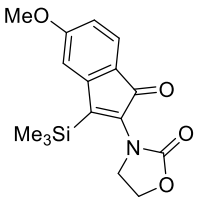




4c^5

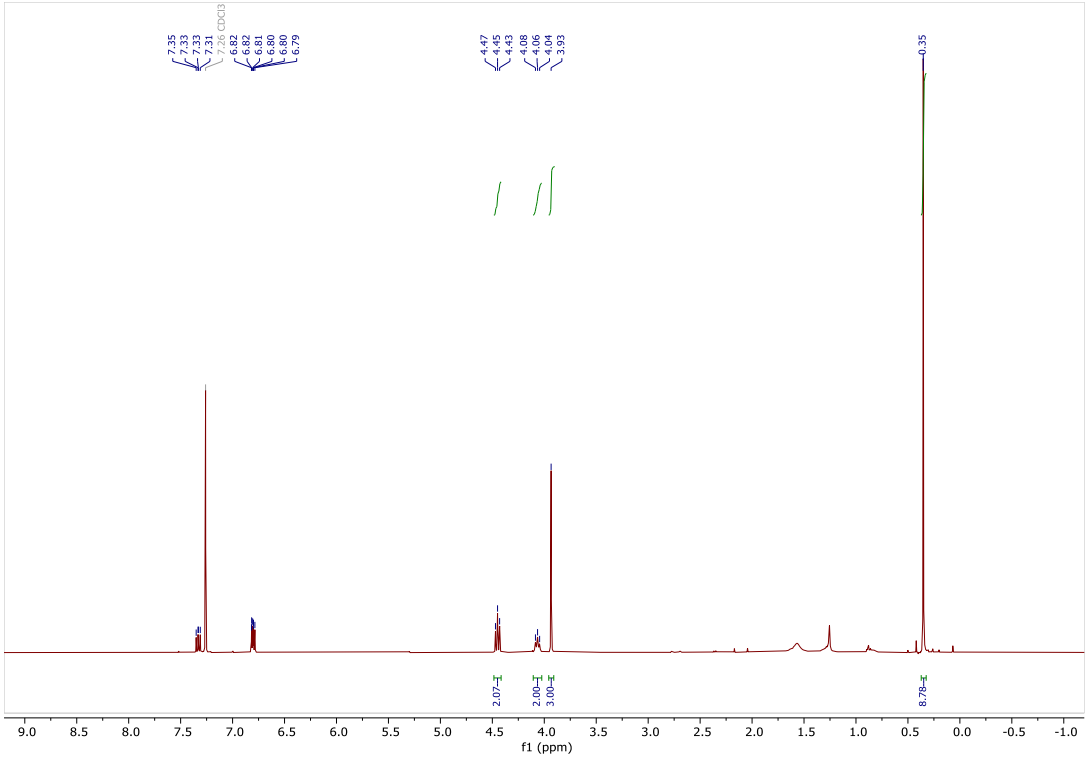
^{29}Si NMR of compound **4c^5** (80 MHz, $CDCl_3$)

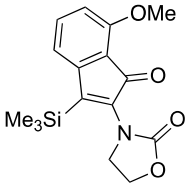




4c^5

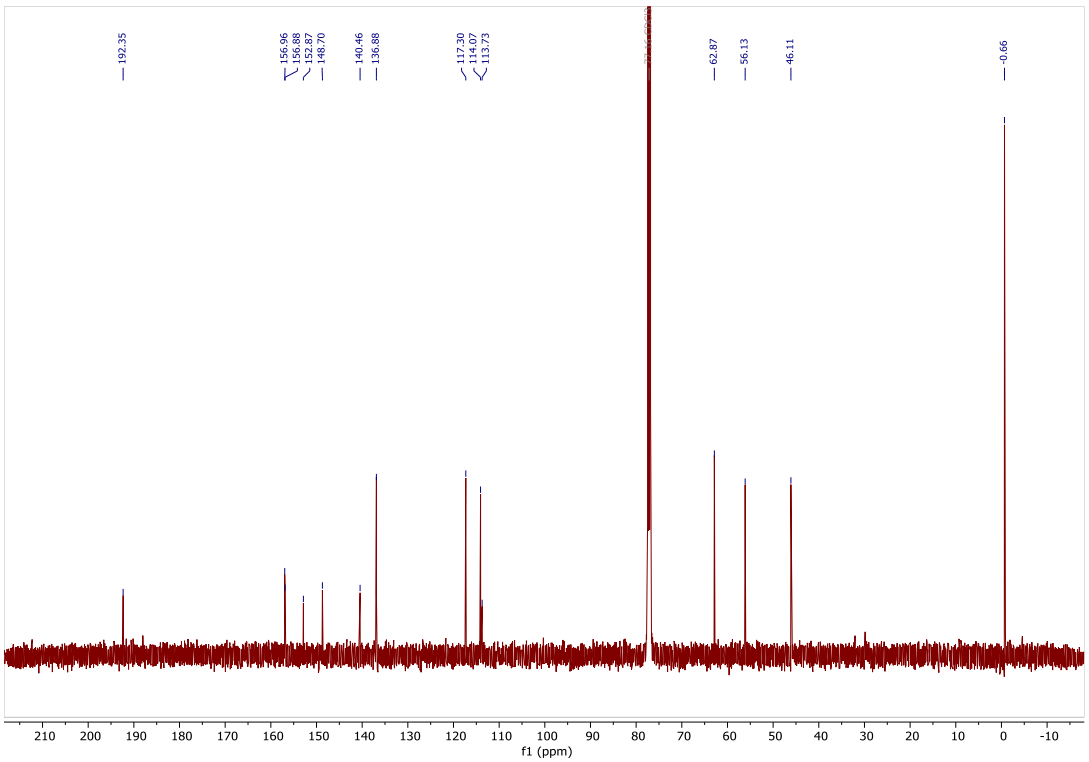
^{1}H NMR of compound **4c**^{7} (400 MHz, $CDCl_3$)

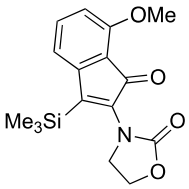




4c^{7}

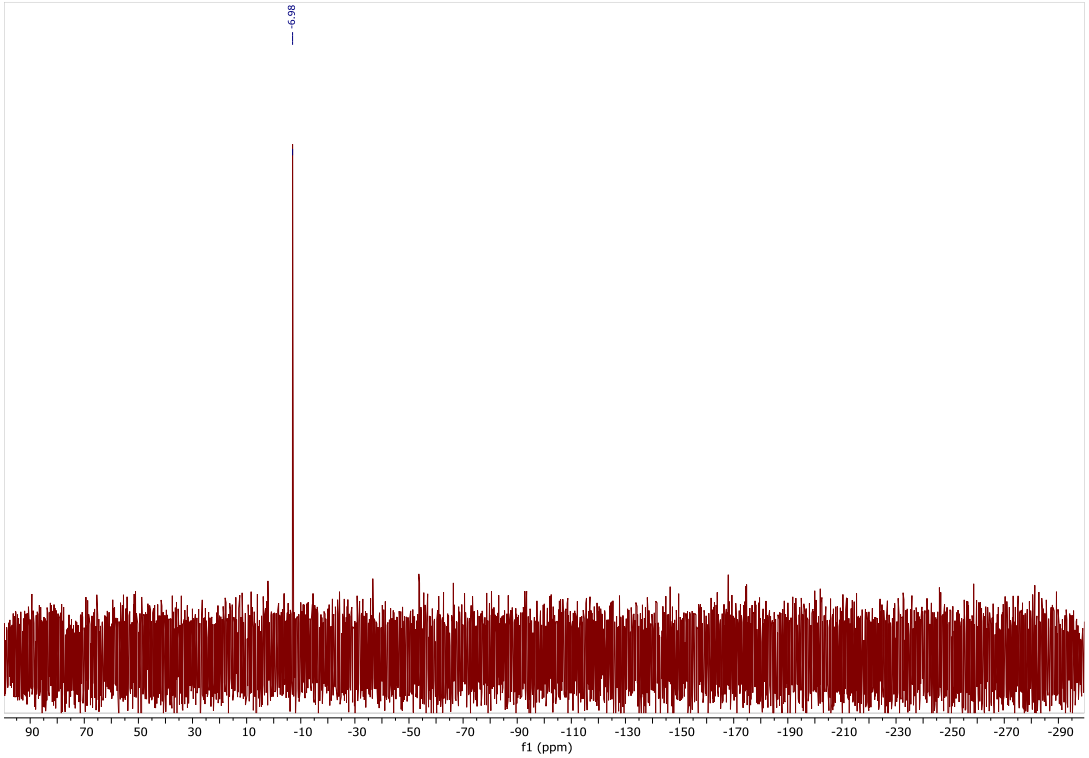
^{13}C NMR of compound **4c**^{7} (101 MHz, $CDCl_3$)

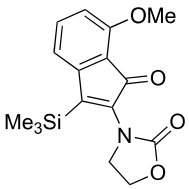




4c^{7}

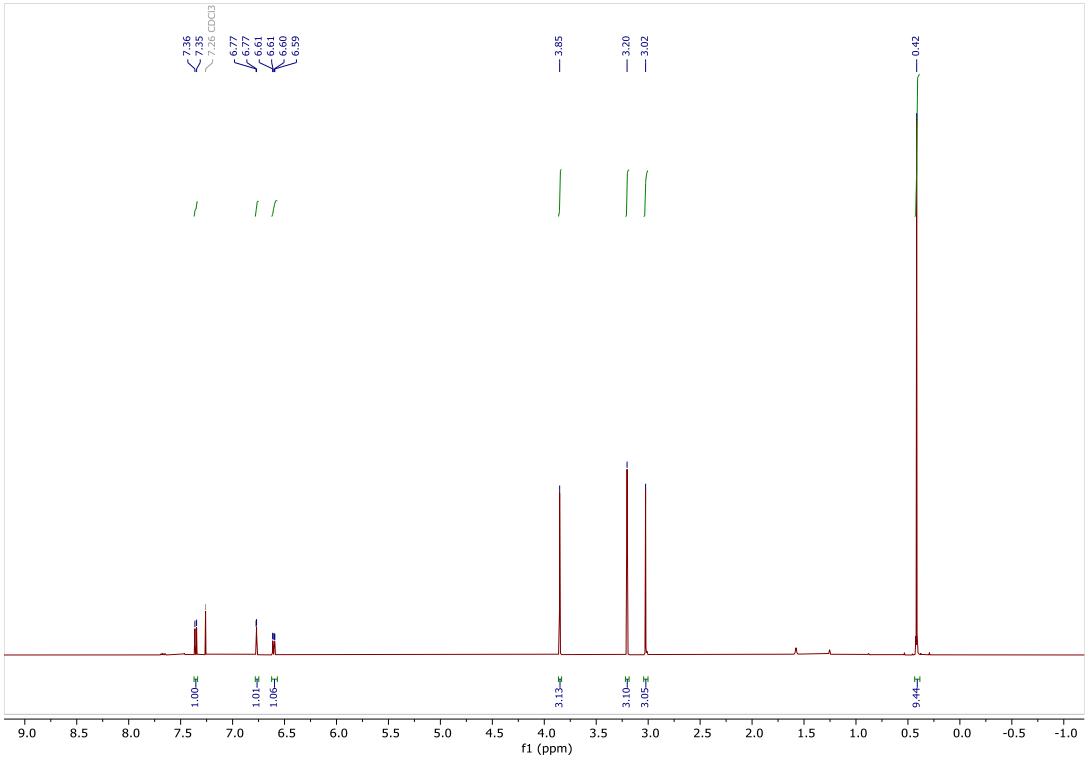
^{29}Si NMR of compound **4c**[7] (80 MHz, $CDCl_3$)

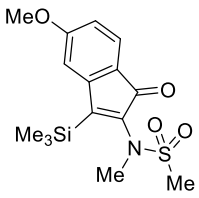




4c[7]

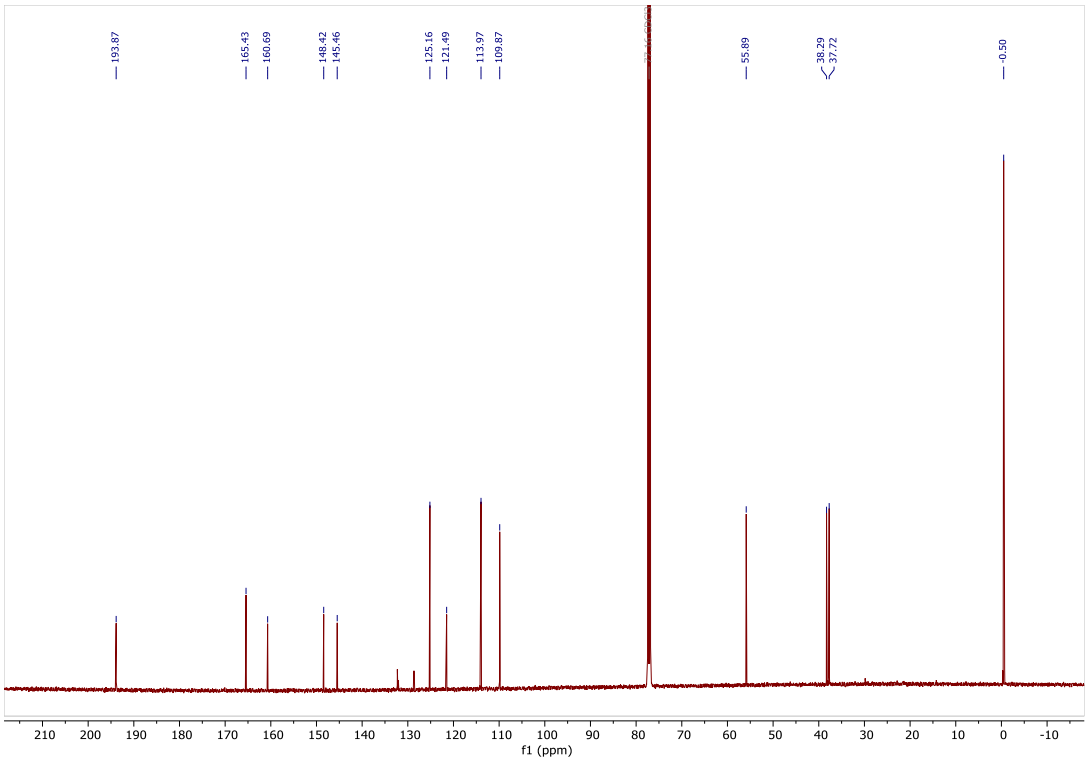
^{1}H NMR of compound **4d**[5] (500 MHz, $CDCl_3$)

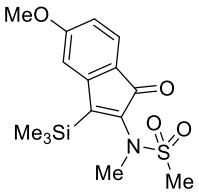




4d[5]

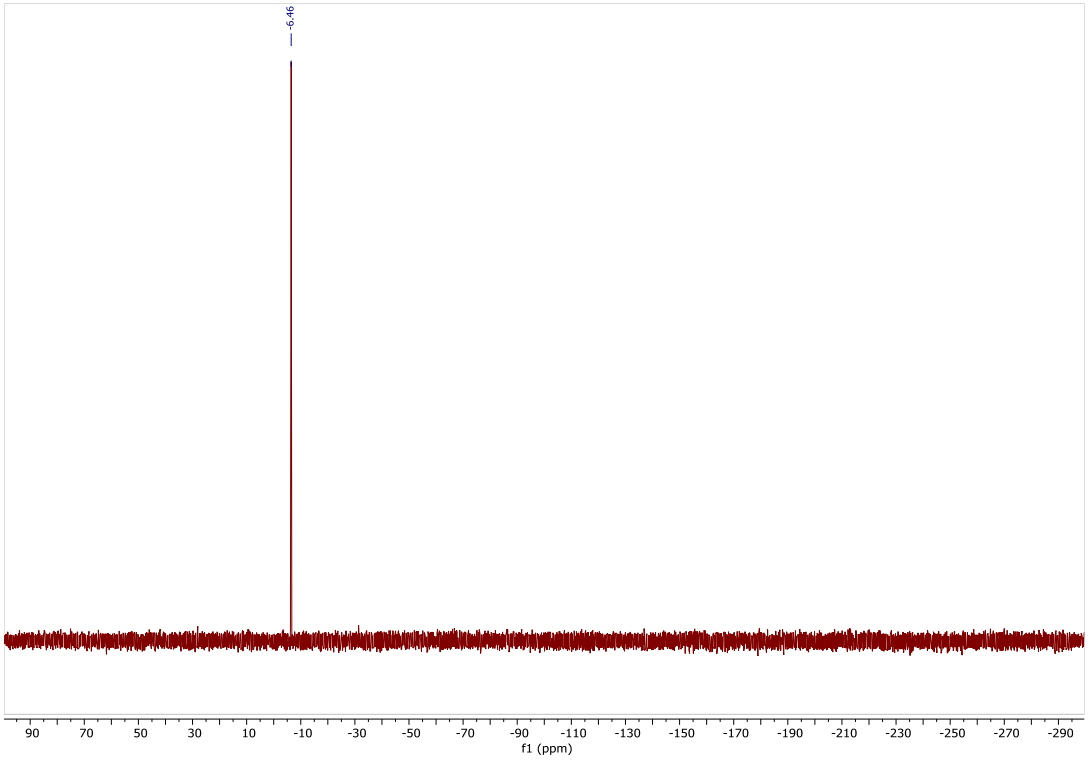
^{13}C NMR of compound **4d^5** (126 MHz, $CDCl_3$)

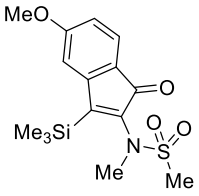




4d^5

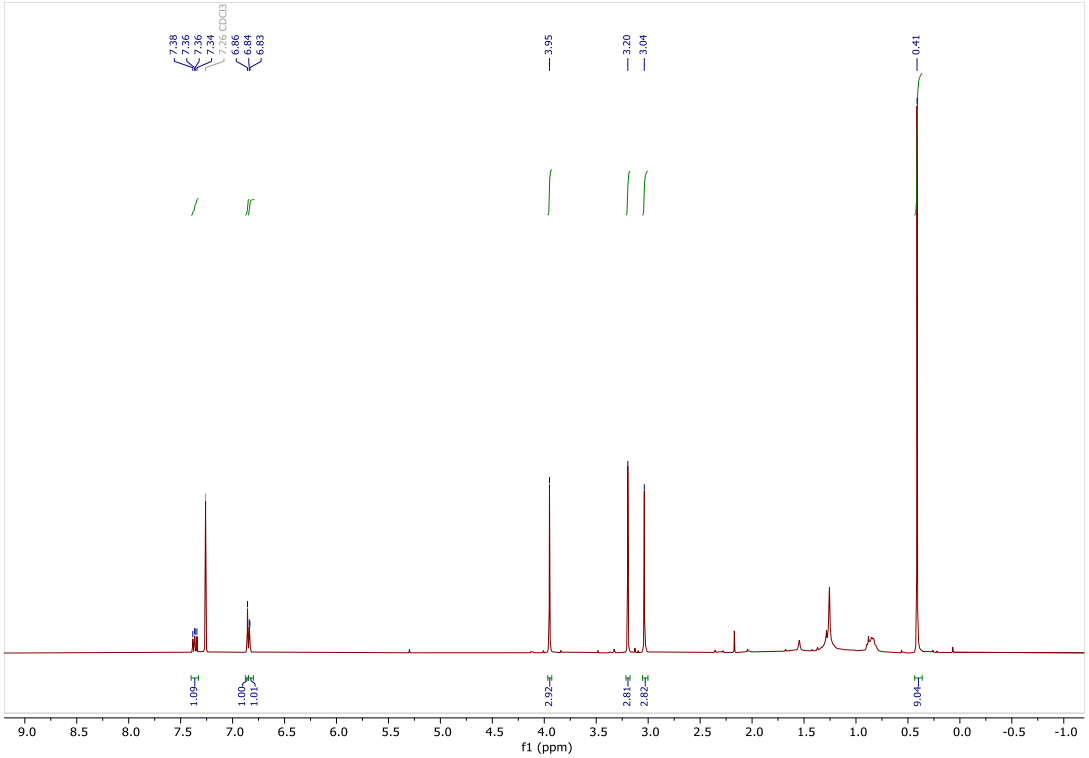
^{29}Si NMR of compound **4d^5** (99 MHz, $CDCl_3$)

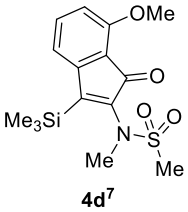




4d^5

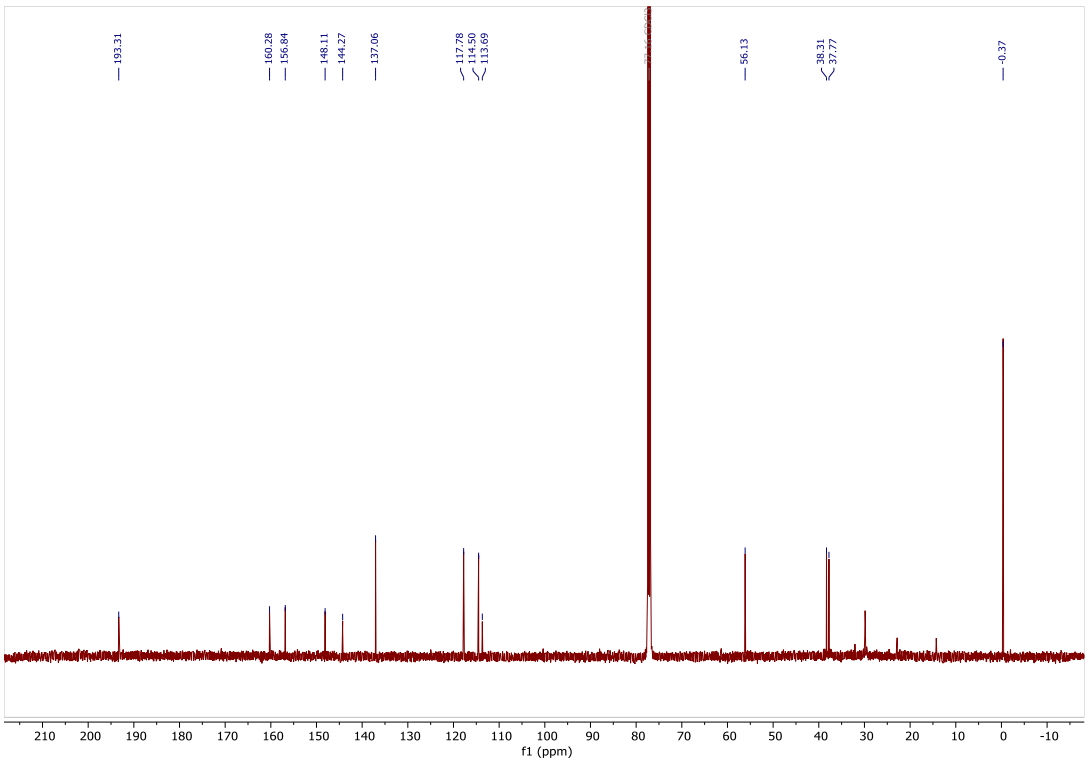
^{1}H NMR of compound **4d**[7] (400 MHz, $CDCl_3$)

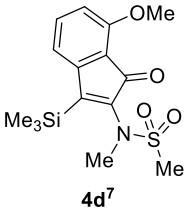




4d[7]

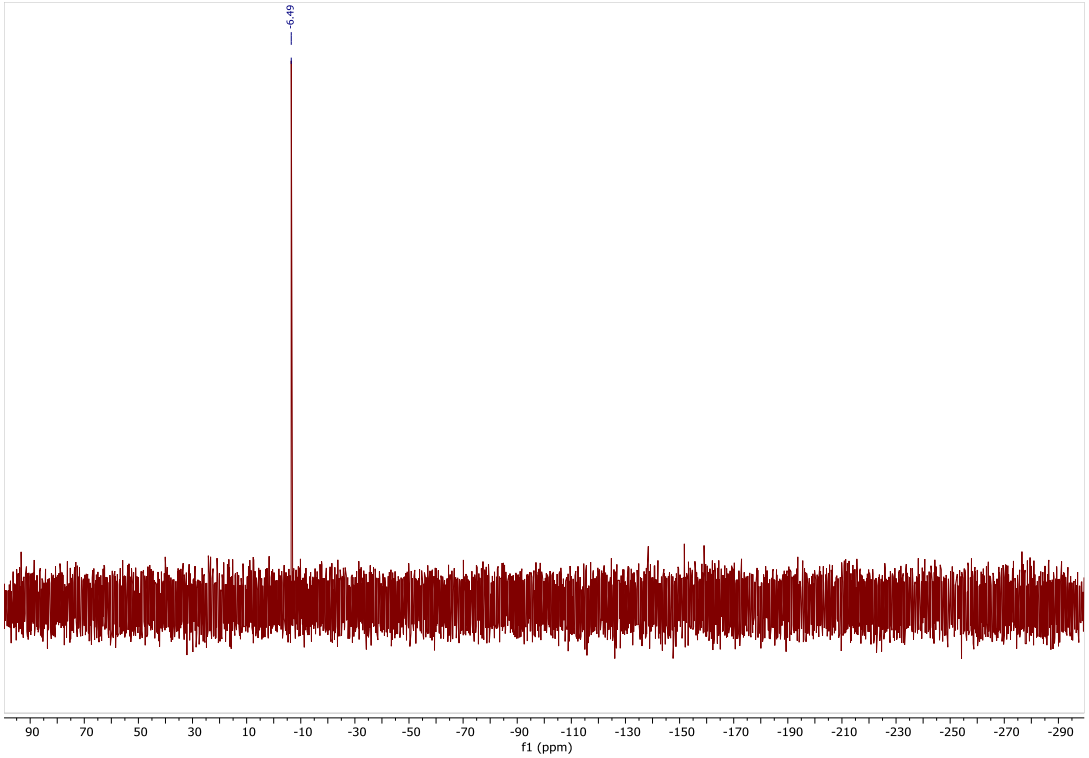
^{13}C NMR of compound **4d**[7] (126 MHz, $CDCl_3$)

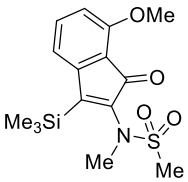




4d[7]

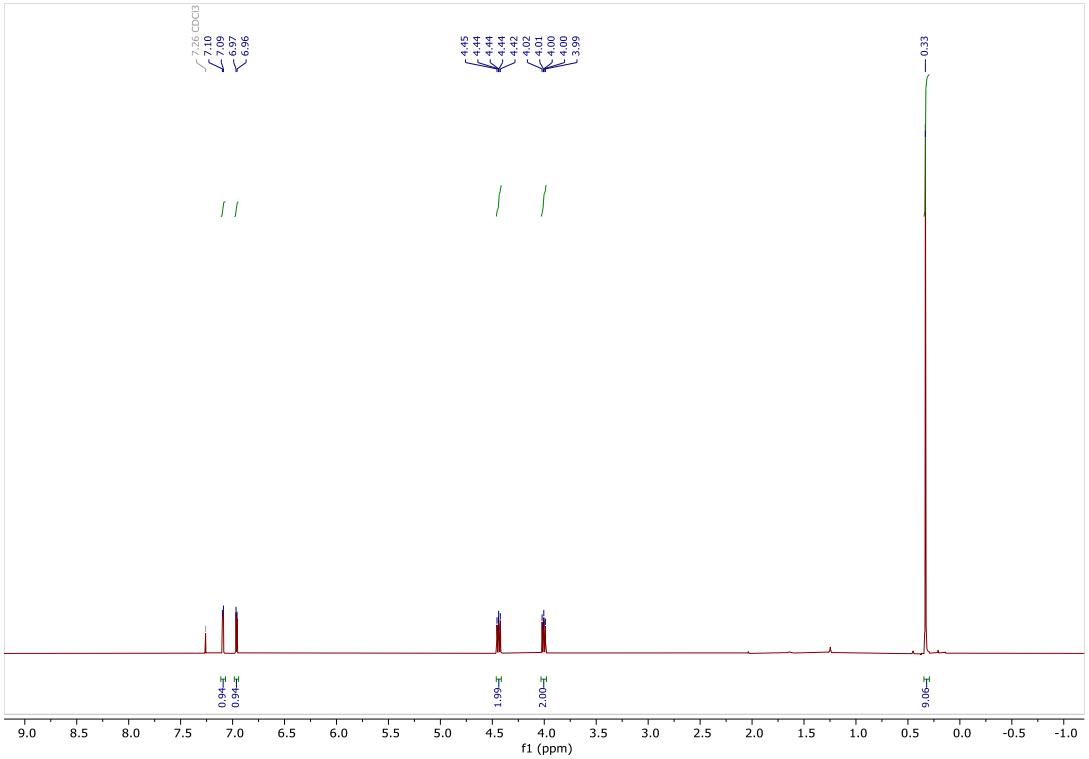
^{29}Si NMR of compound **4d**[7] (99 MHz, $CDCl_3$)

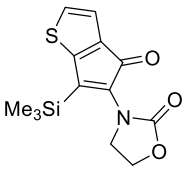




4d[7]

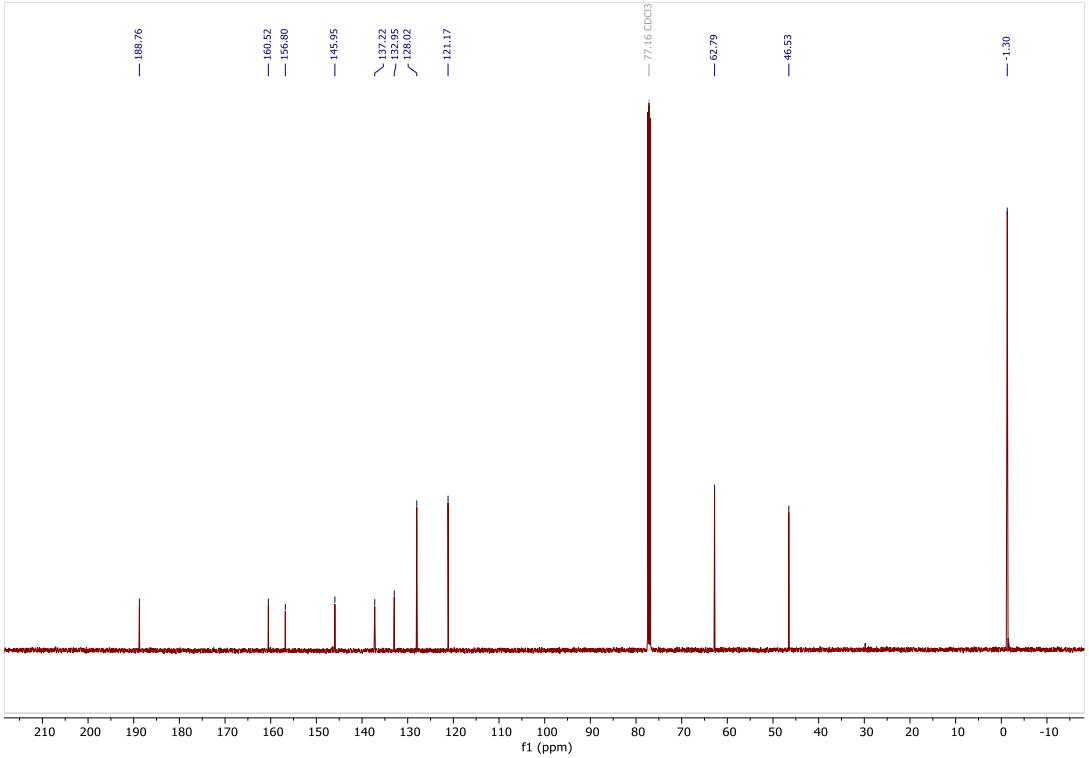
^{1}H NMR of compound **4f** (500 MHz, $CDCl_3$)

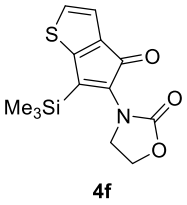




4f

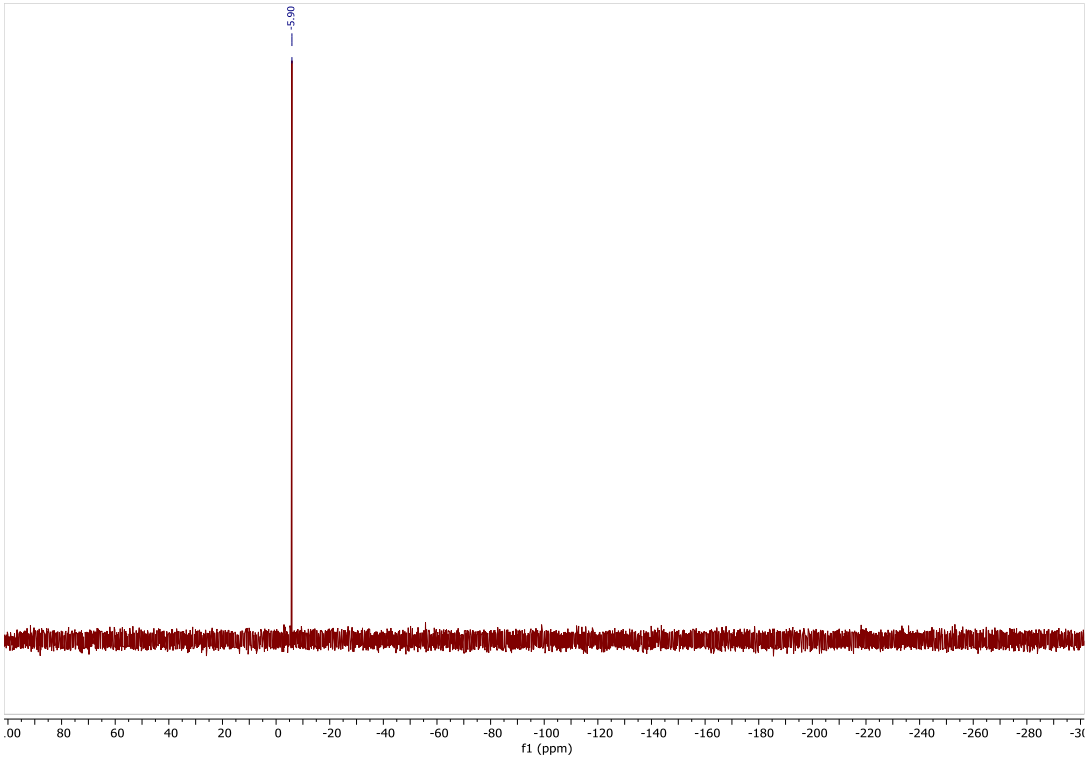
^{13}C NMR of compound **4f** (126 MHz, $CDCl_3$)

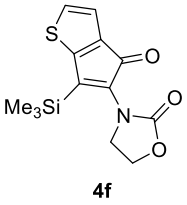




4f

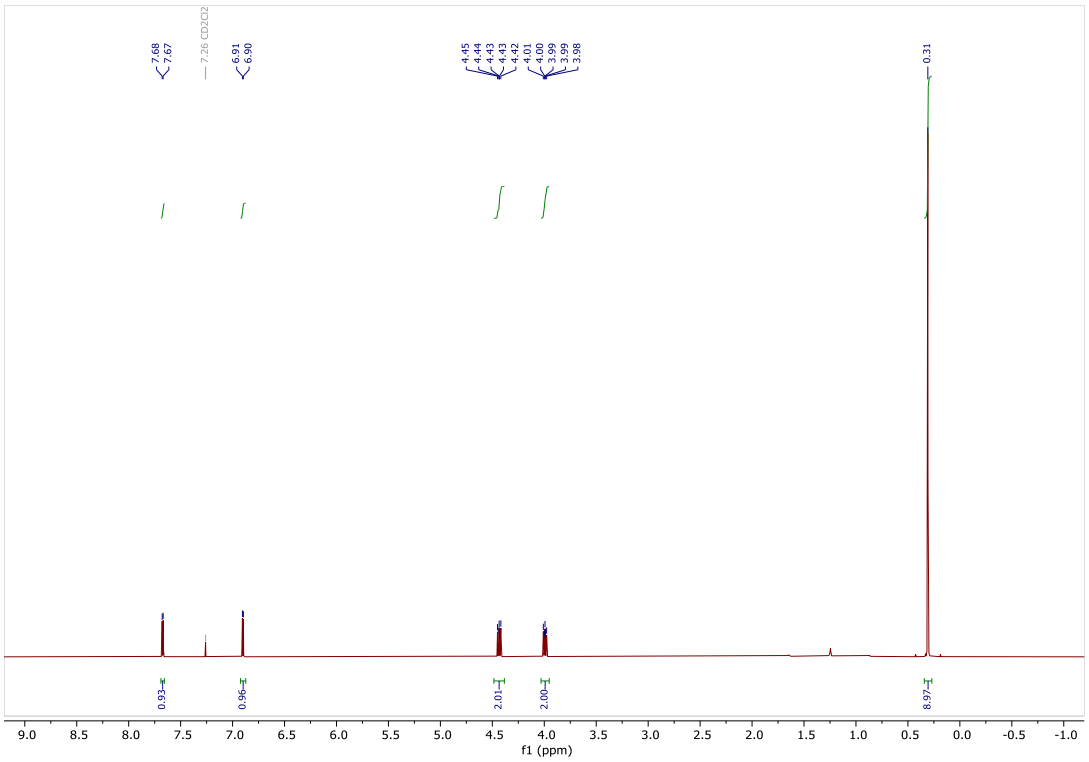
^{29}Si NMR of compound **4f** (99 MHz, $CDCl_3$)

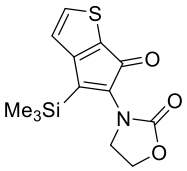




4f

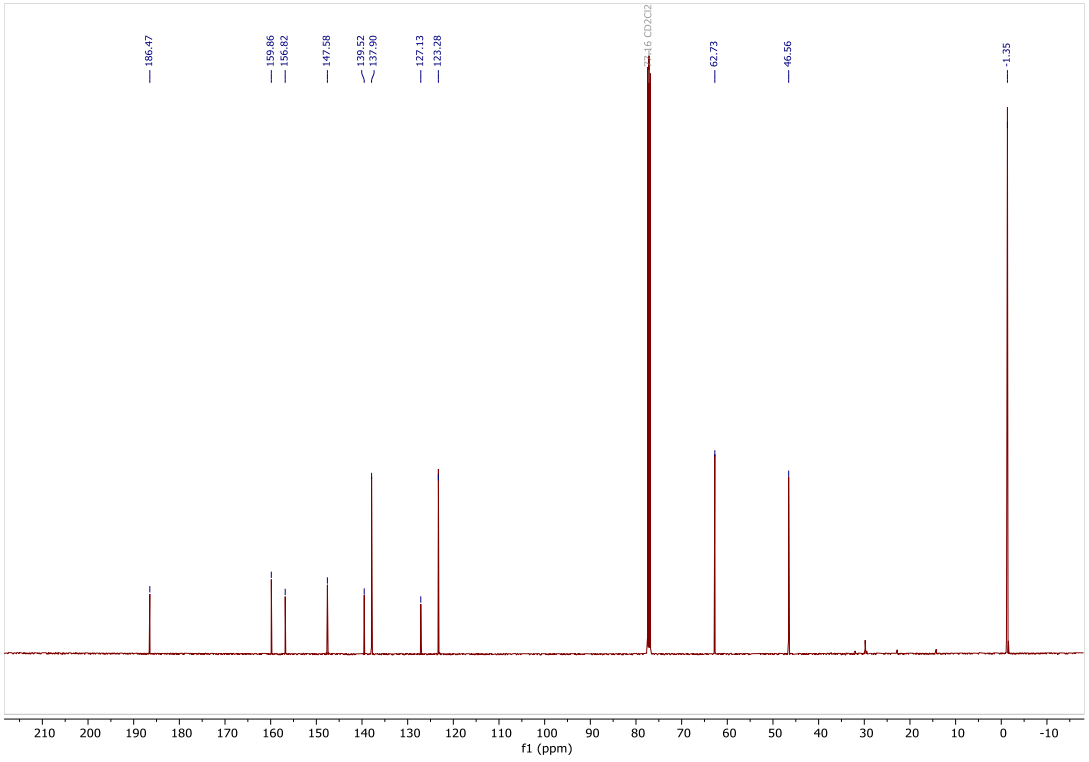
^{1}H NMR of compound **4g** (500 MHz, $CDCl_3$)

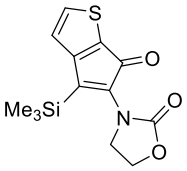




4g

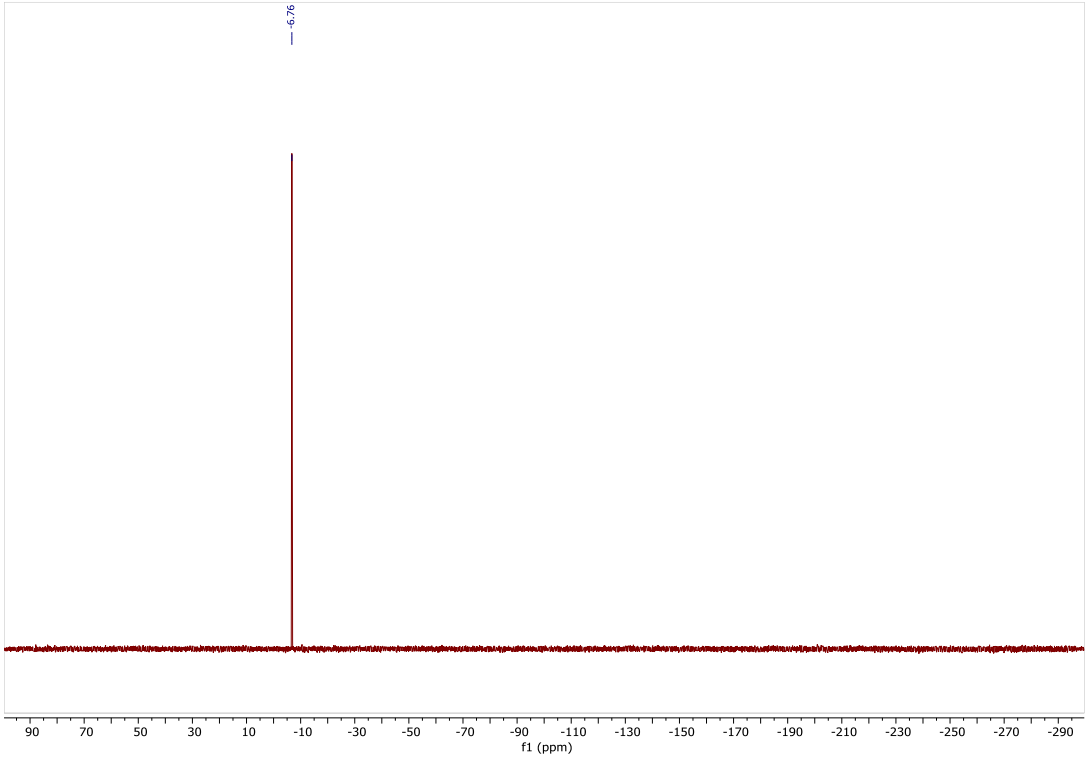
^{13}C NMR of compound **4g** (126 MHz, $CDCl_3$)

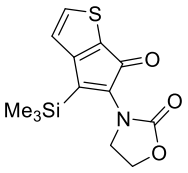




4g

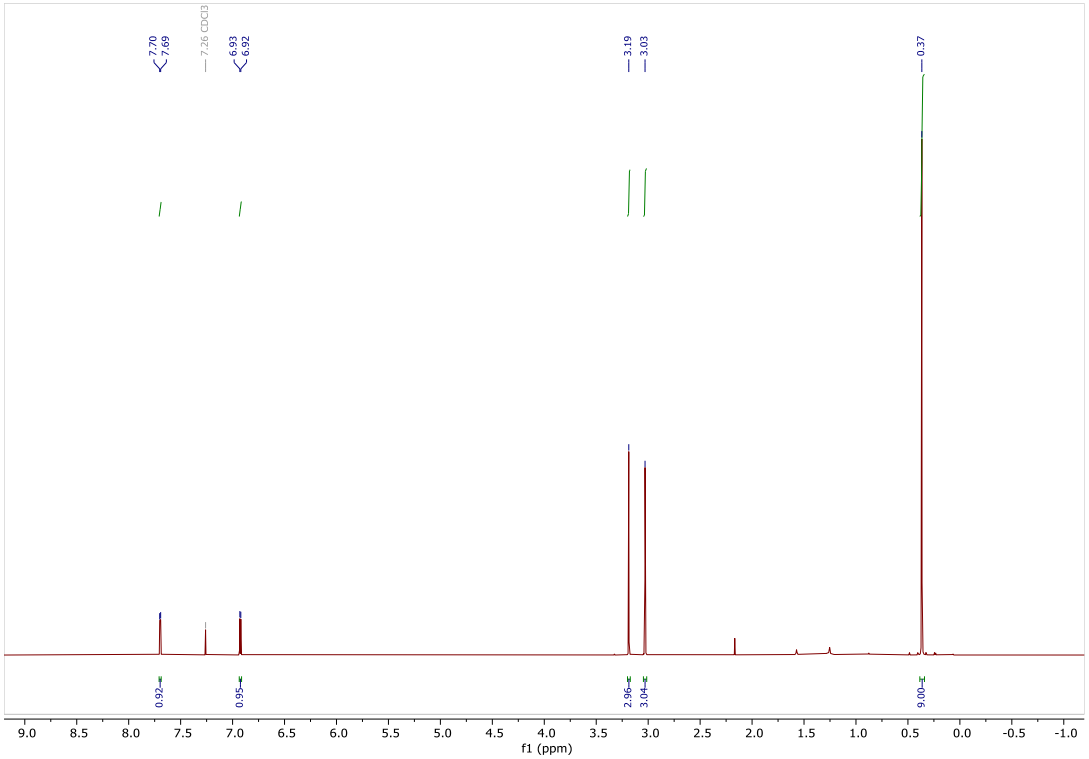
^{29}Si NMR of compound **4g** (99 MHz, $CDCl_3$)

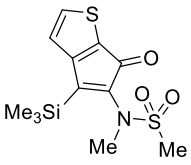




4g

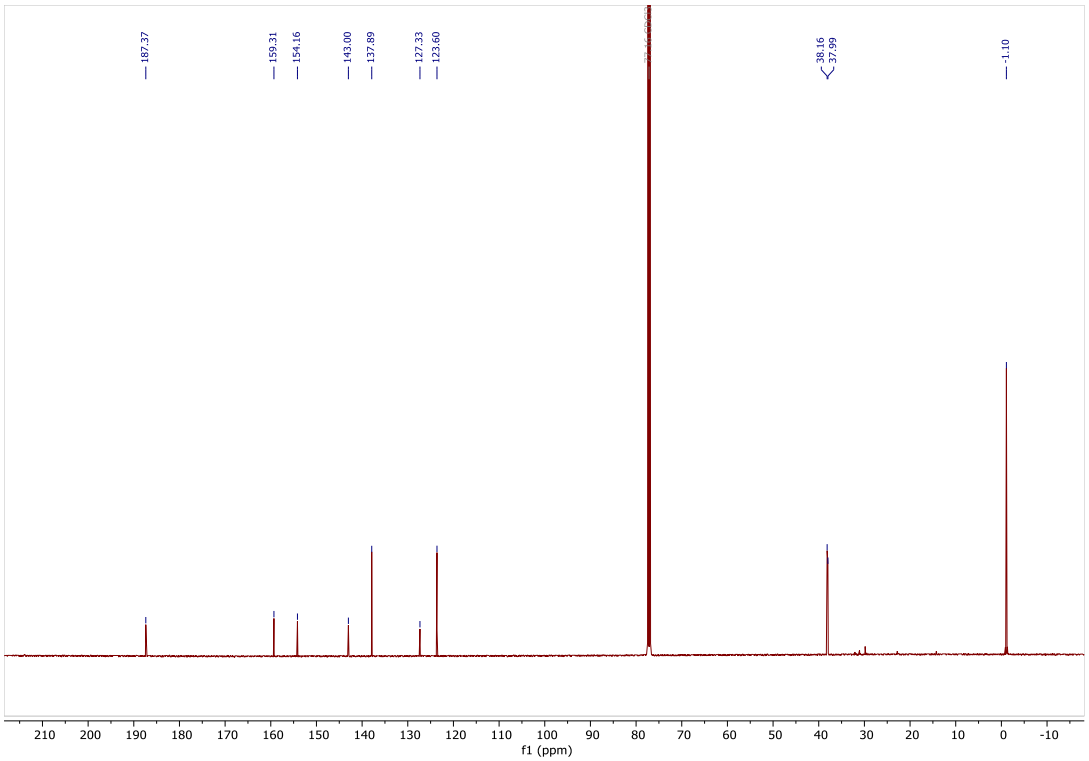
^{1}H NMR of compound **4h** (500 MHz, $CDCl_3$)

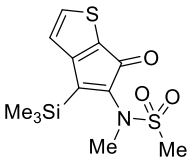




4h

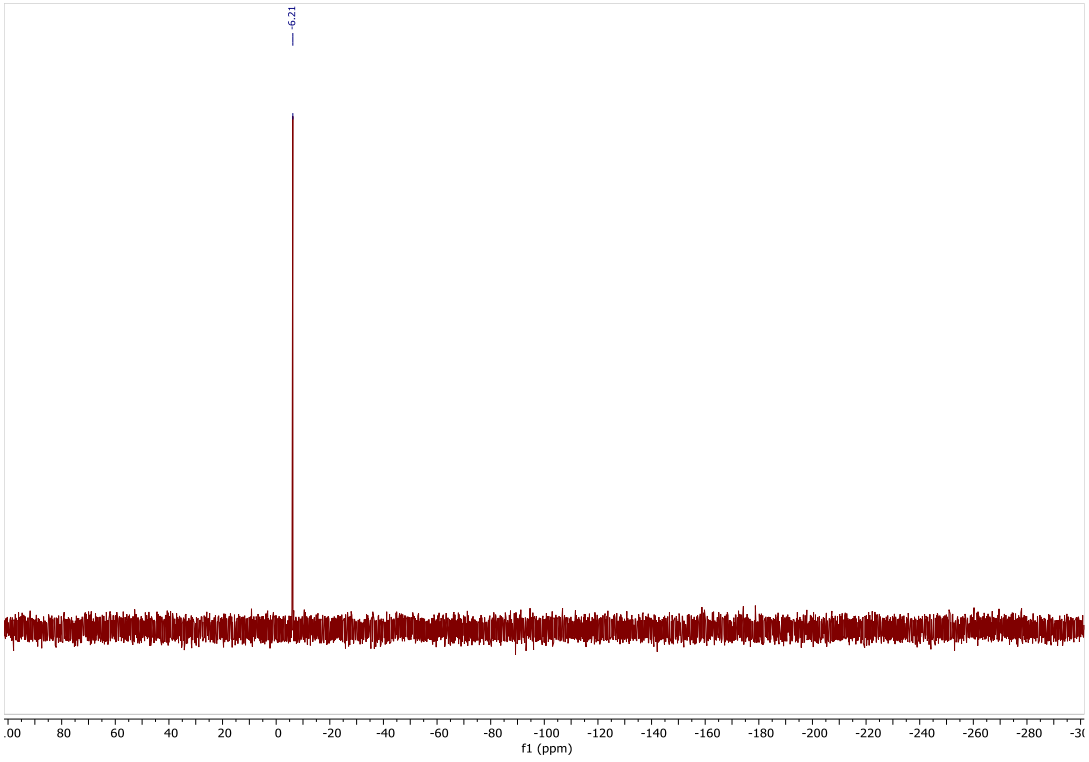
^{13}C NMR of compound **4h** (126 MHz, $CDCl_3$)

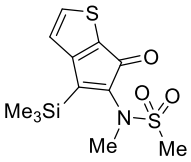




4h

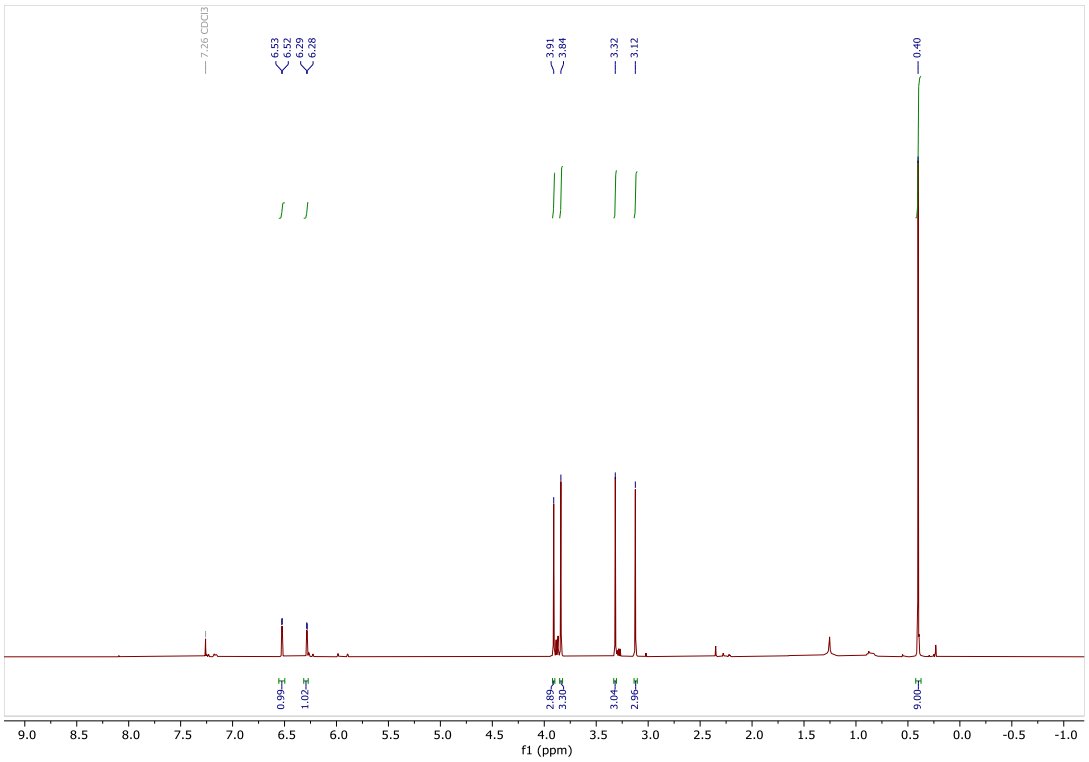
^{29}Si NMR of compound **4h** (99 MHz, $CDCl_3$)

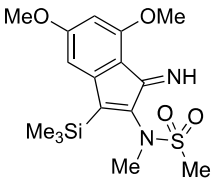




4h

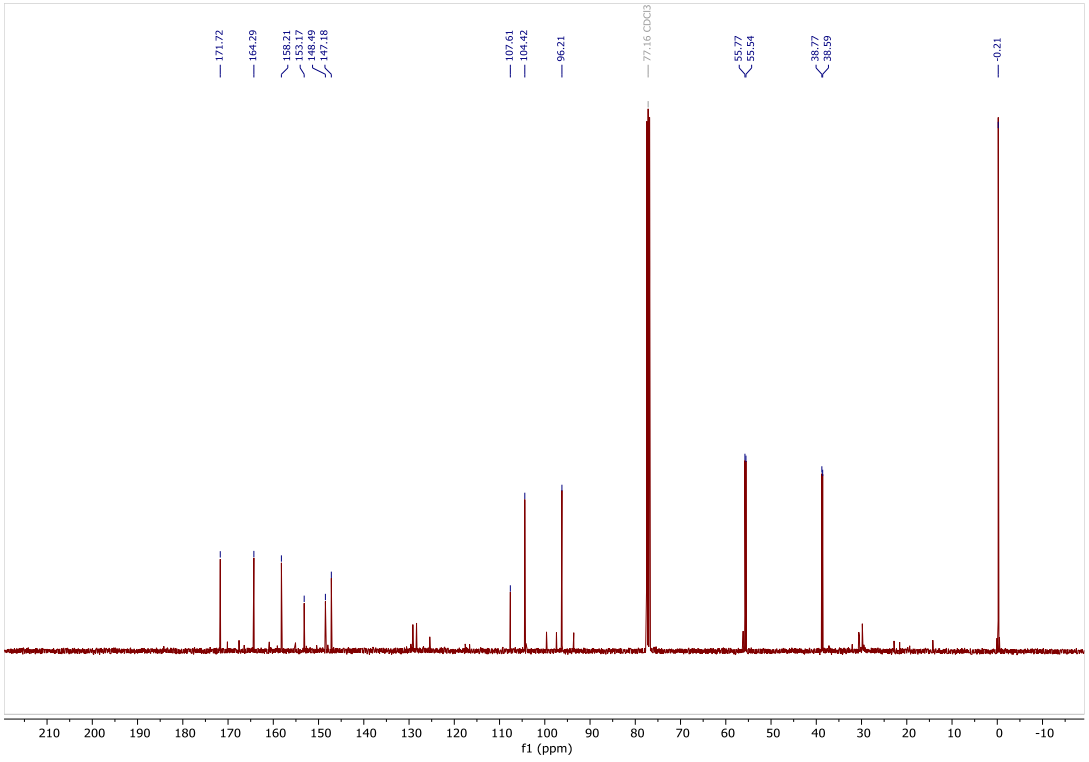
^{1}H NMR of compound **3i** (400 MHz, $CDCl_3$)

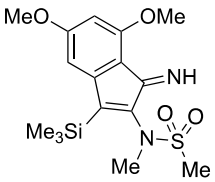




3i

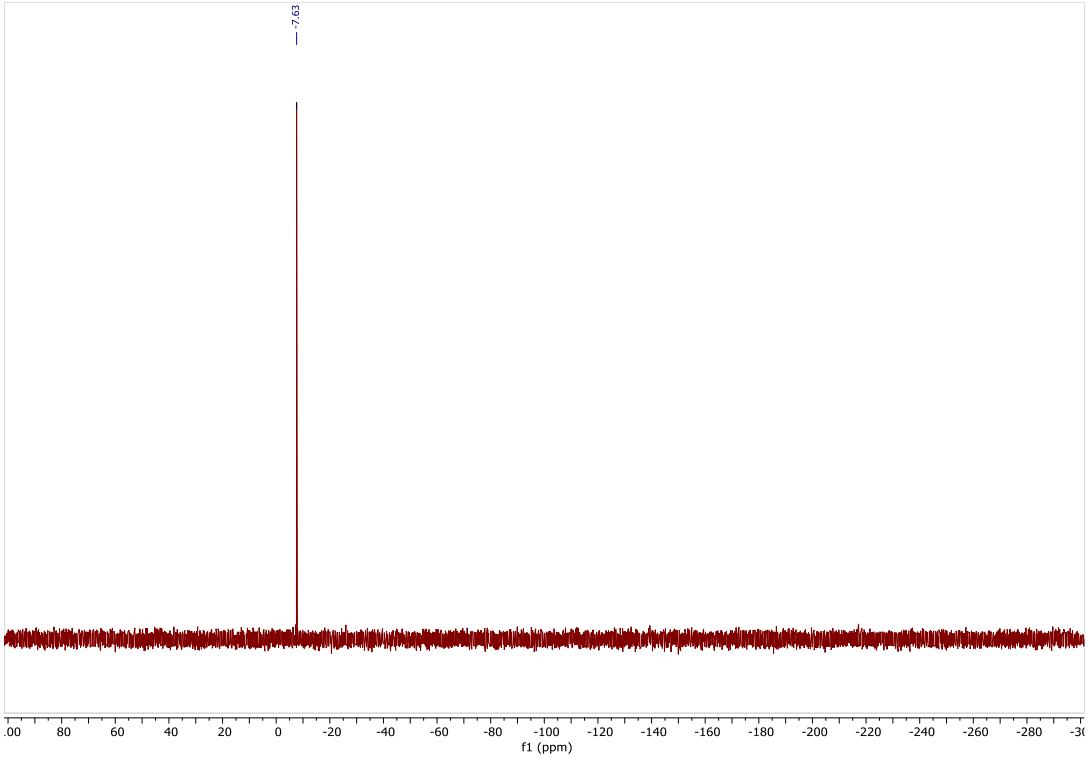
^{13}C NMR of compound **3i** (101 MHz, $CDCl_3$)

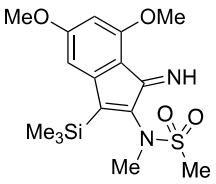




3i

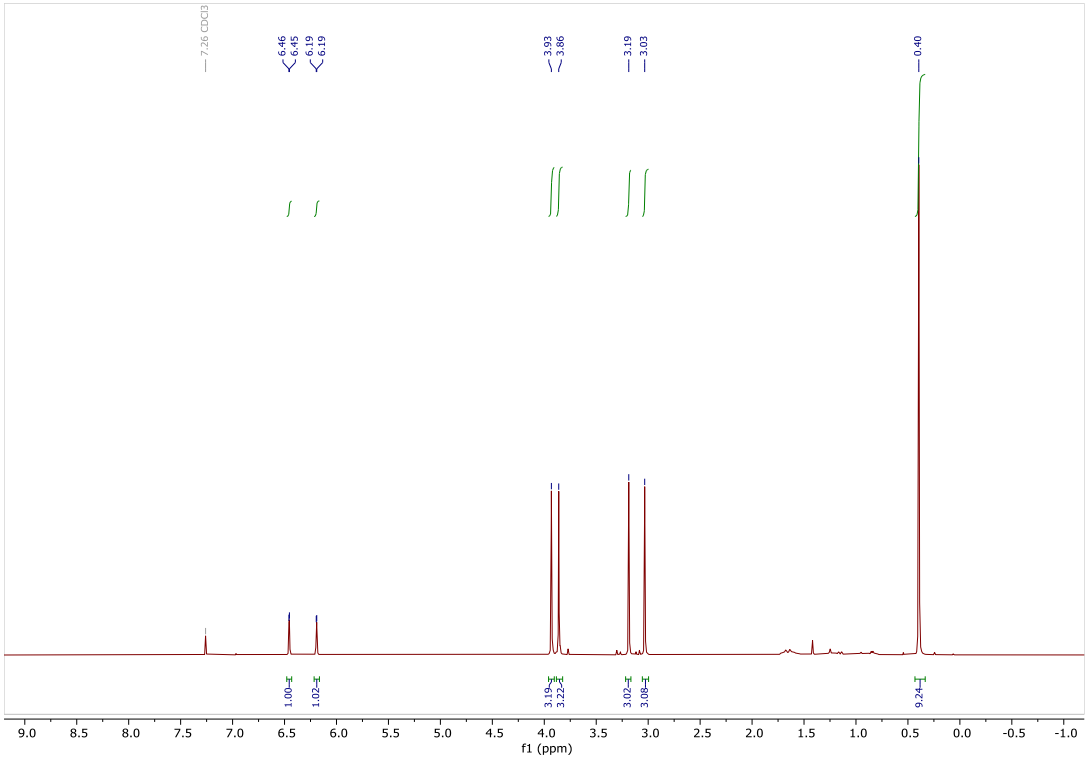
^{29}Si NMR of compound **3i** (80 MHz, $CDCl_3$)

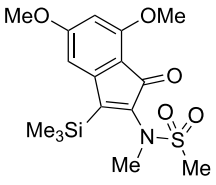




3i

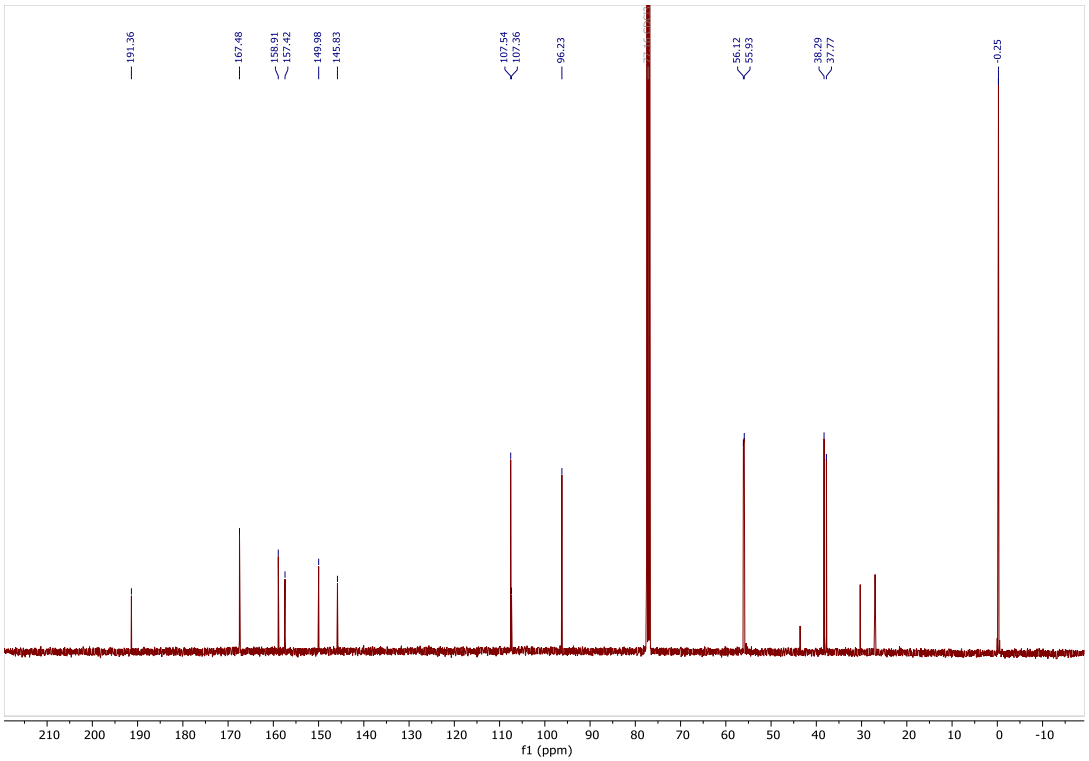
^{1}H NMR of compound **4i** (400 MHz, $CDCl_3$)

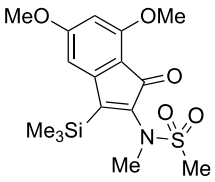




4i

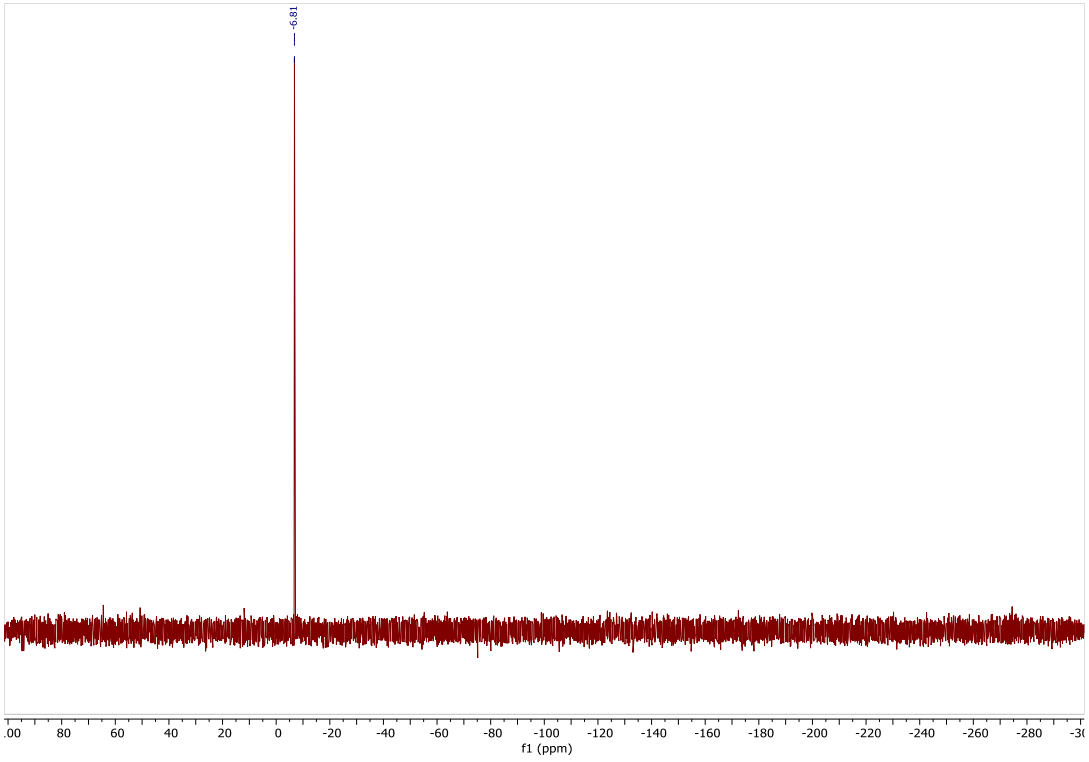
^{13}C NMR of compound **4i** (101 MHz, $CDCl_3$)

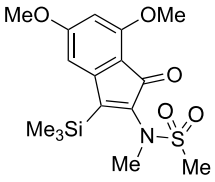




4i

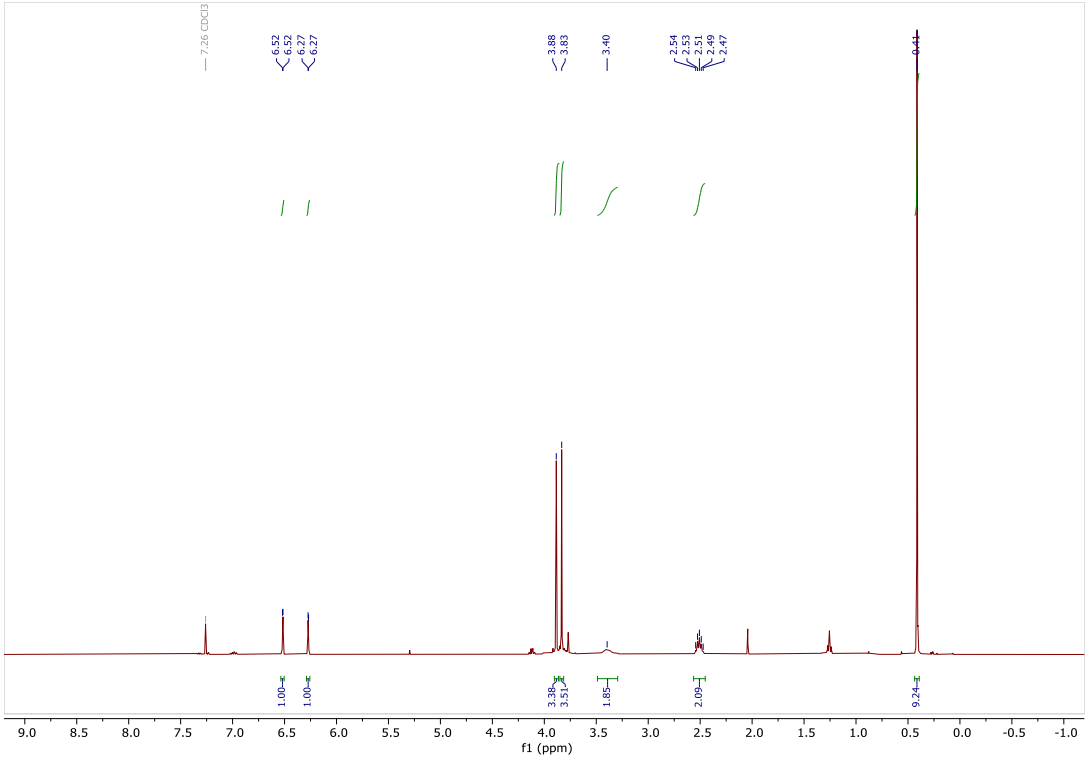
^{29}Si NMR of compound **4i** (80 MHz, $CDCl_3$)

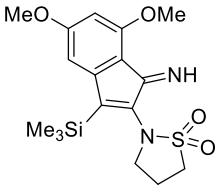




4i

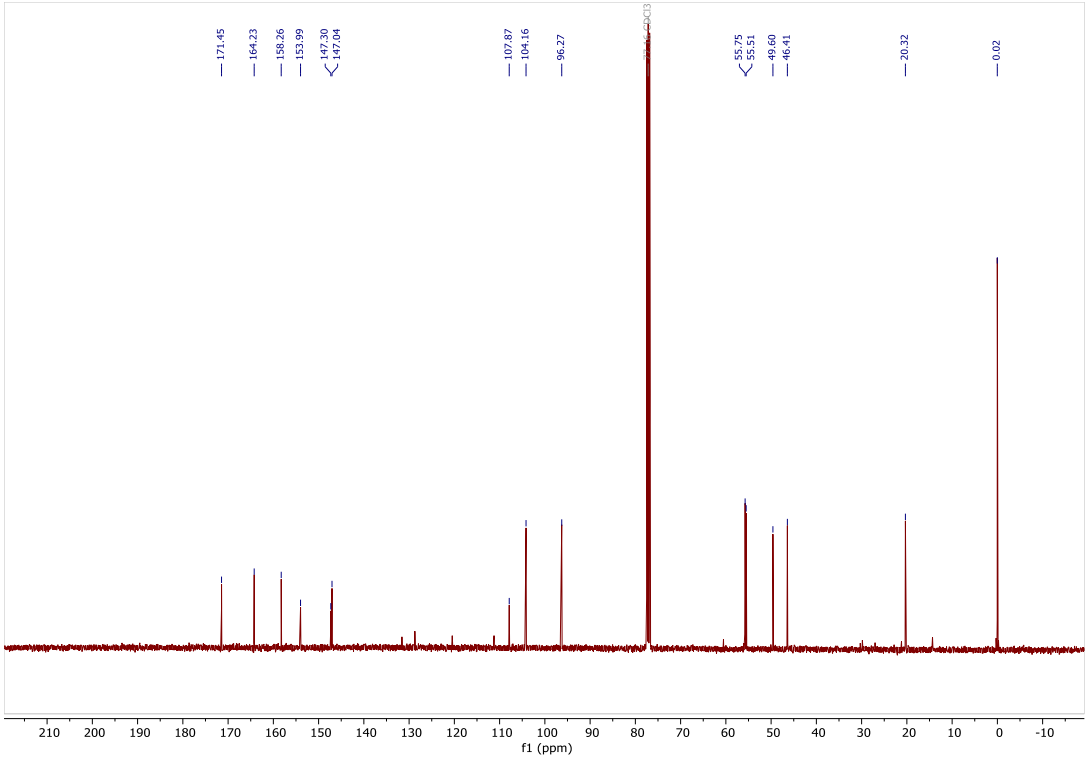
^{1}H NMR of compound **3j** (400 MHz, $CDCl_3$)

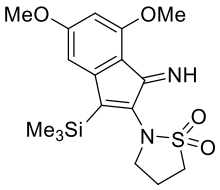




3j

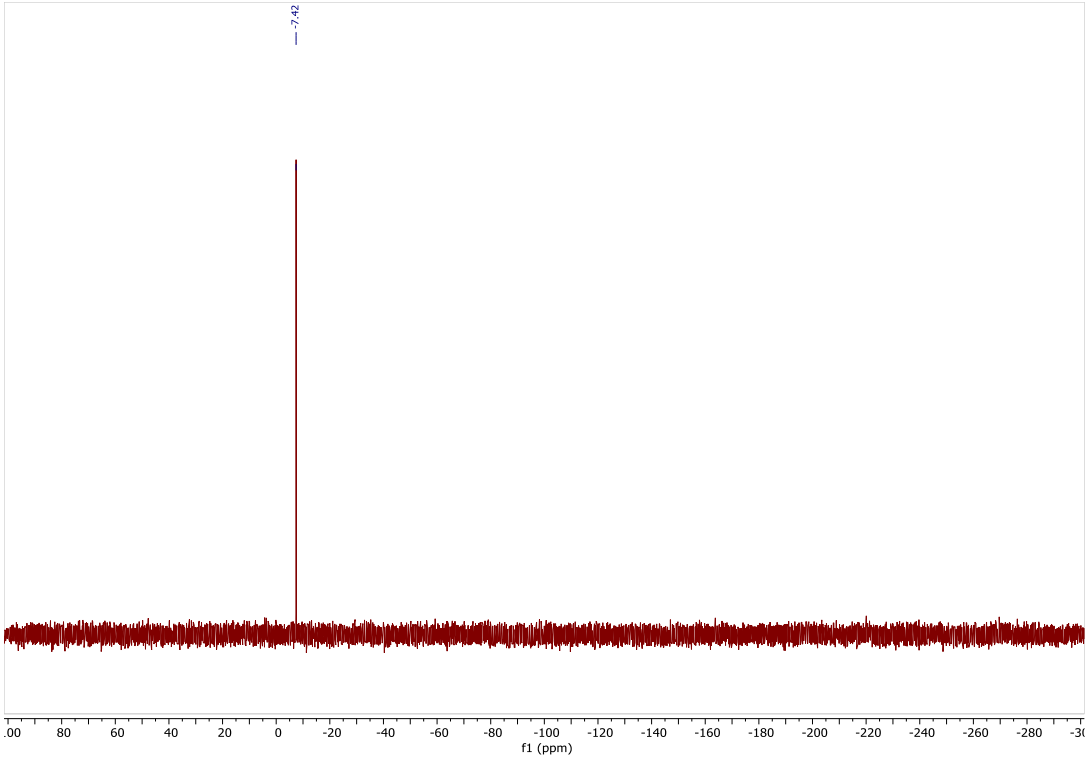
^{13}C NMR of compound **3j** (101 MHz, $CDCl_3$)

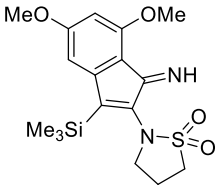




3j

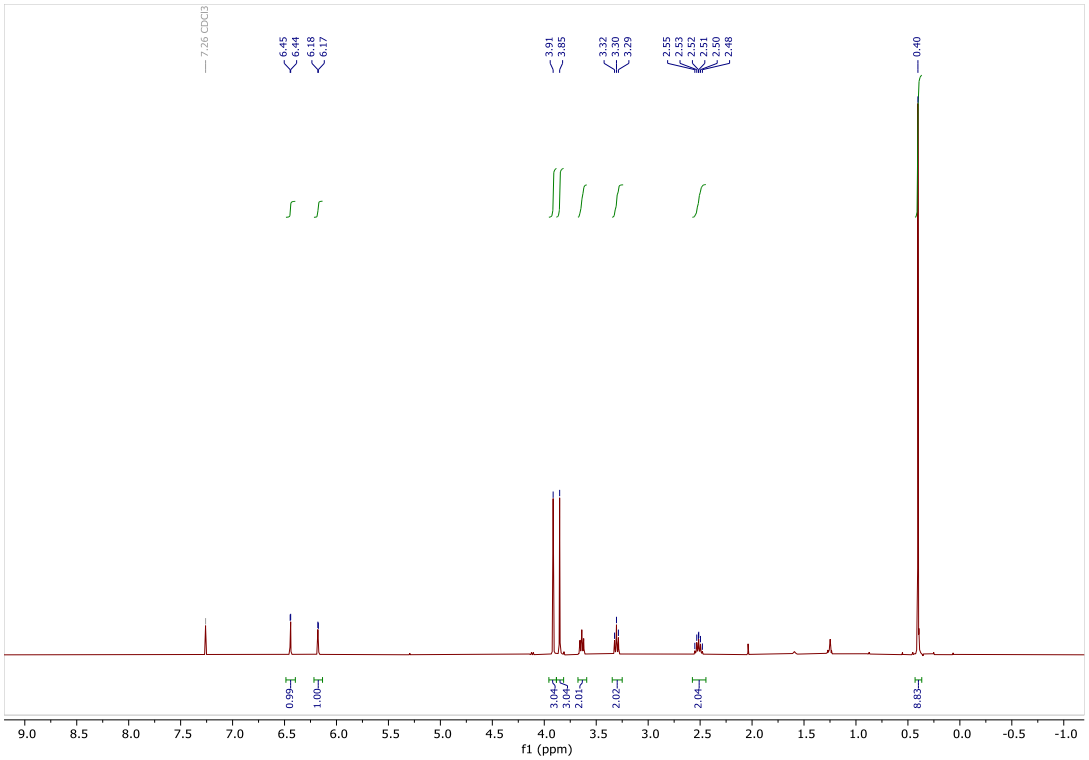
^{29}Si NMR of compound **3j** (80 MHz, $CDCl_3$)

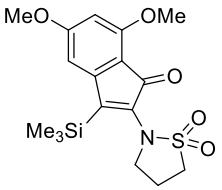




3j

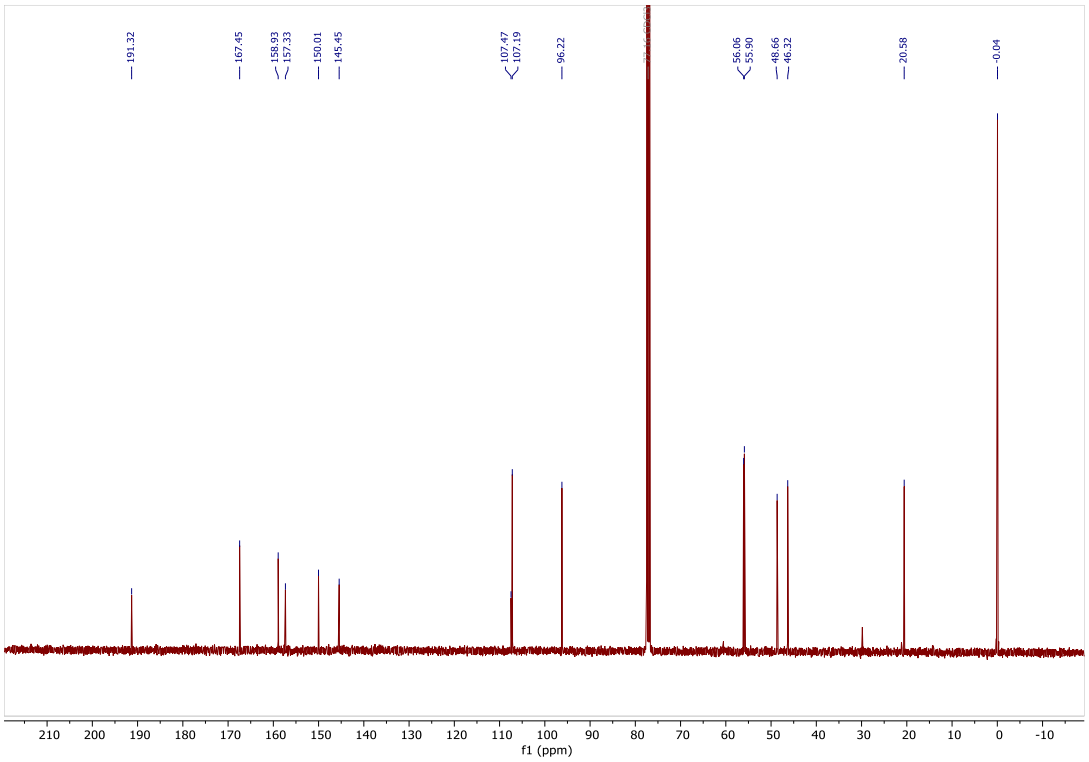
^{1}H NMR of compound **4j** (400 MHz, $CDCl_3$)

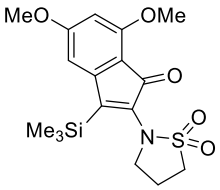




4j

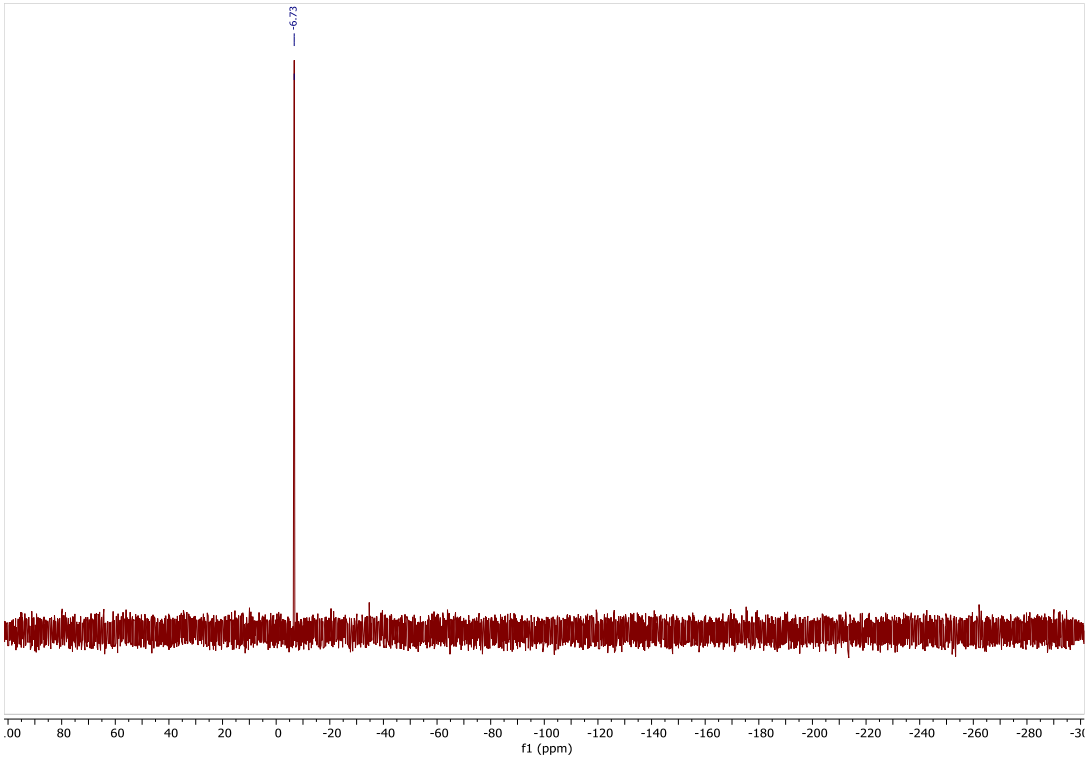
^{13}C NMR of compound **4j** (101 MHz, $CDCl_3$)

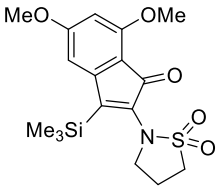




4j

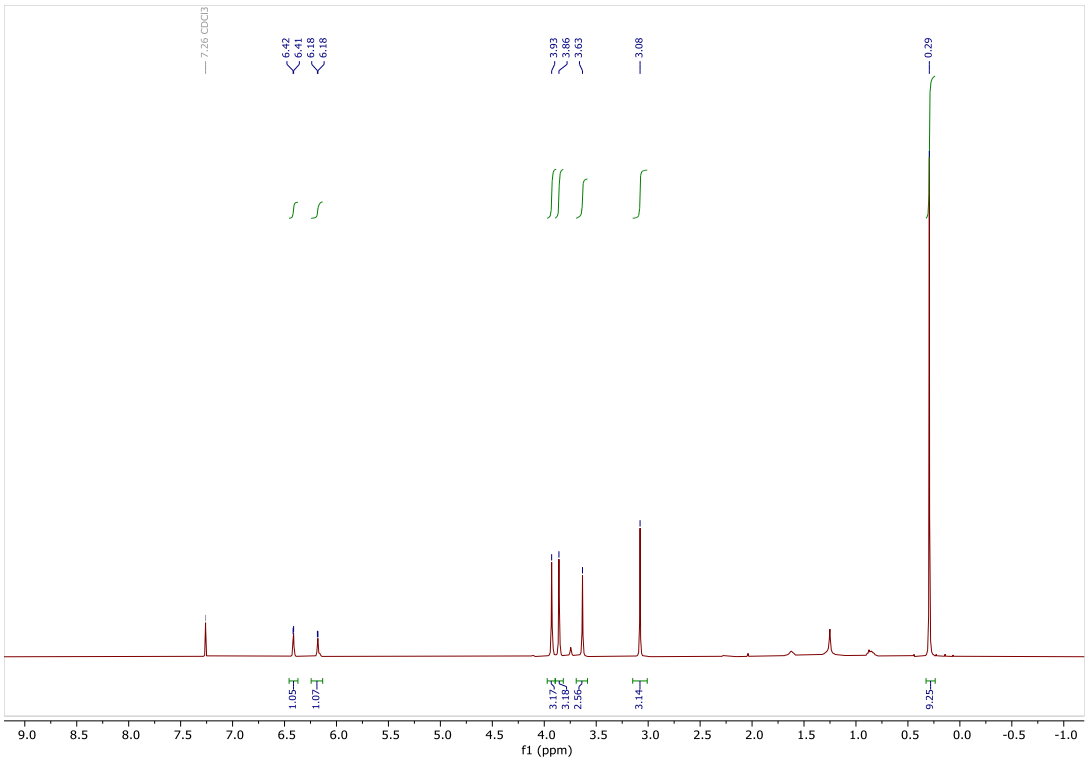
^{29}Si NMR of compound **4j** (80 MHz, $CDCl_3$)

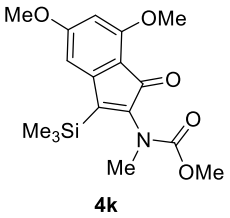




4j

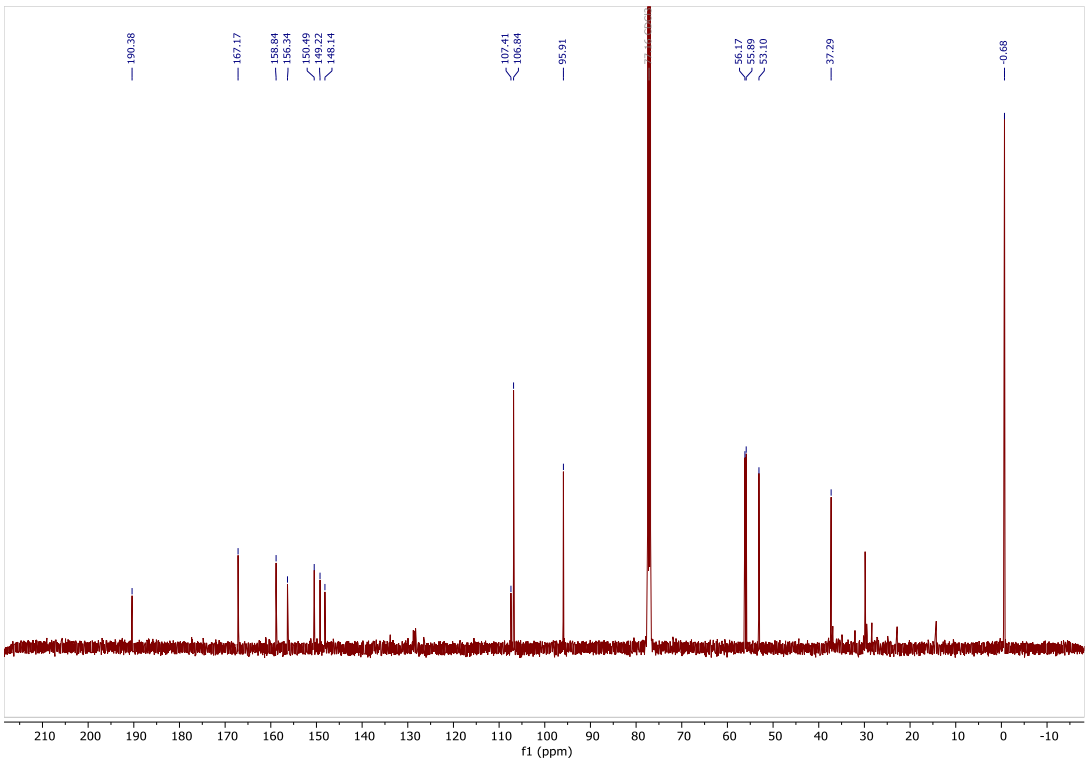
^{1}H NMR of compound **4k** (400 MHz, $CDCl_3$)

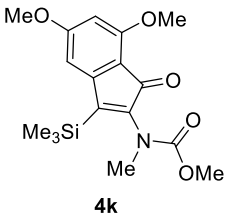




4k

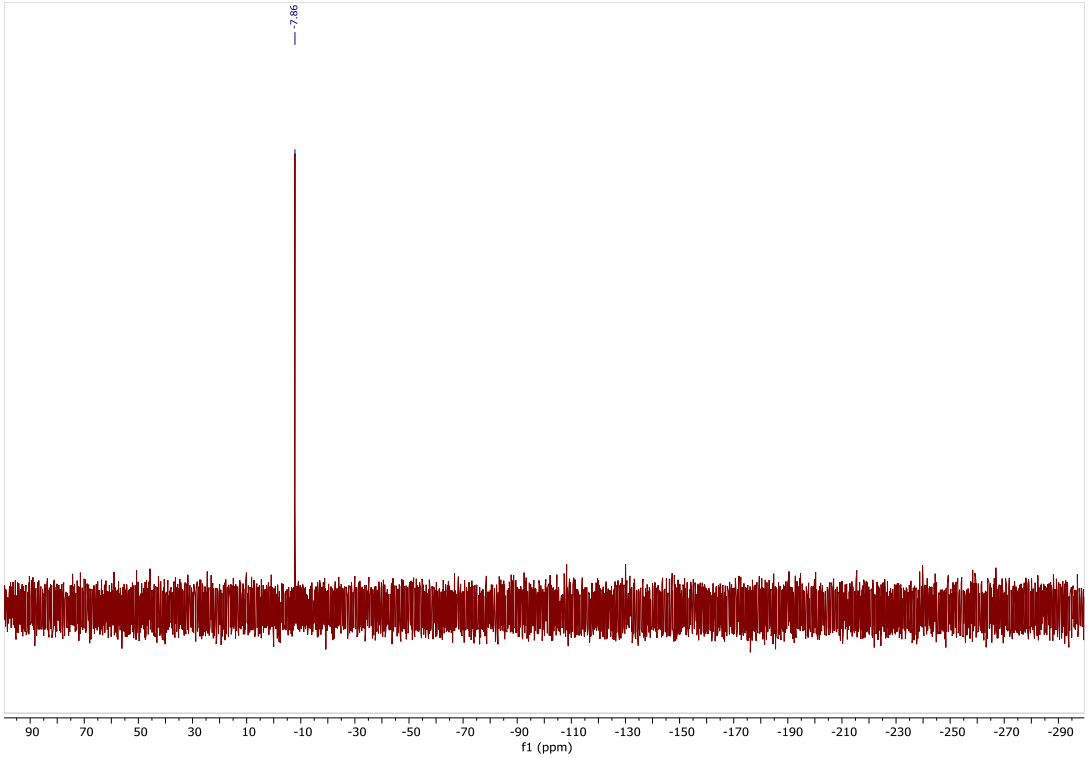
^{13}C NMR of compound **4k** (126 MHz, $CDCl_3$)

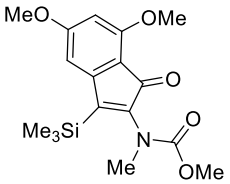




4k

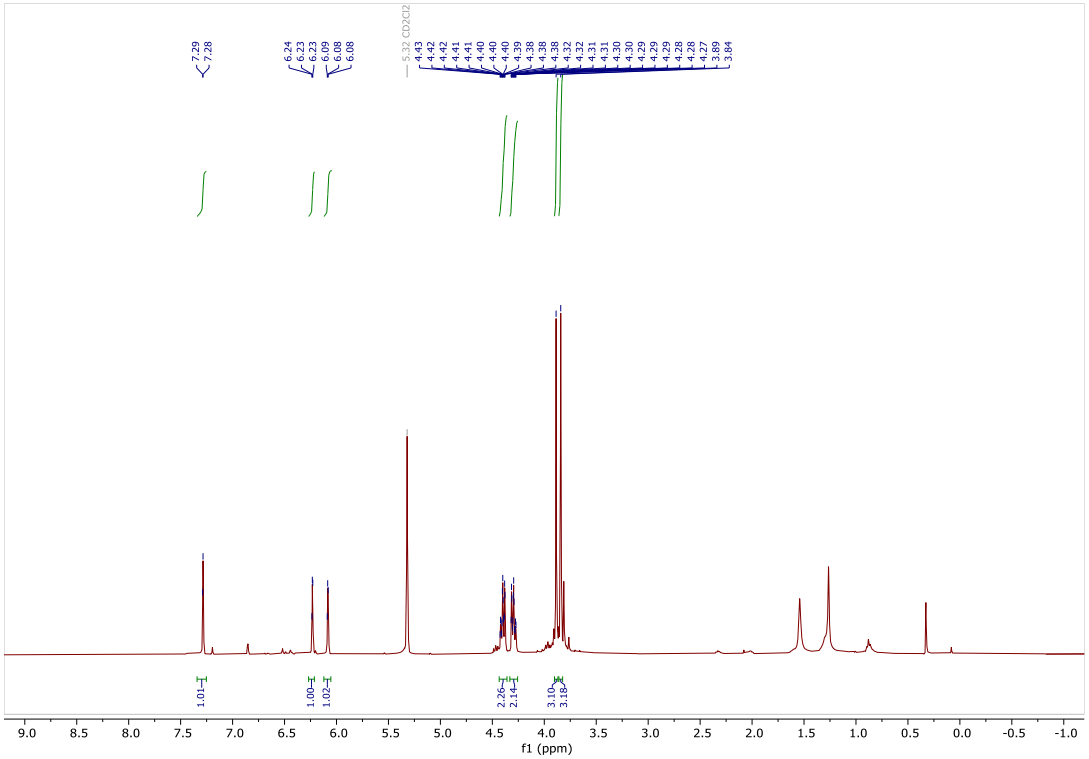
^{29}Si NMR of compound **4k** (99 MHz, $CDCl_3$)

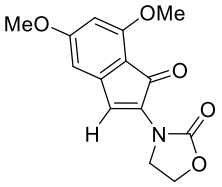




4k

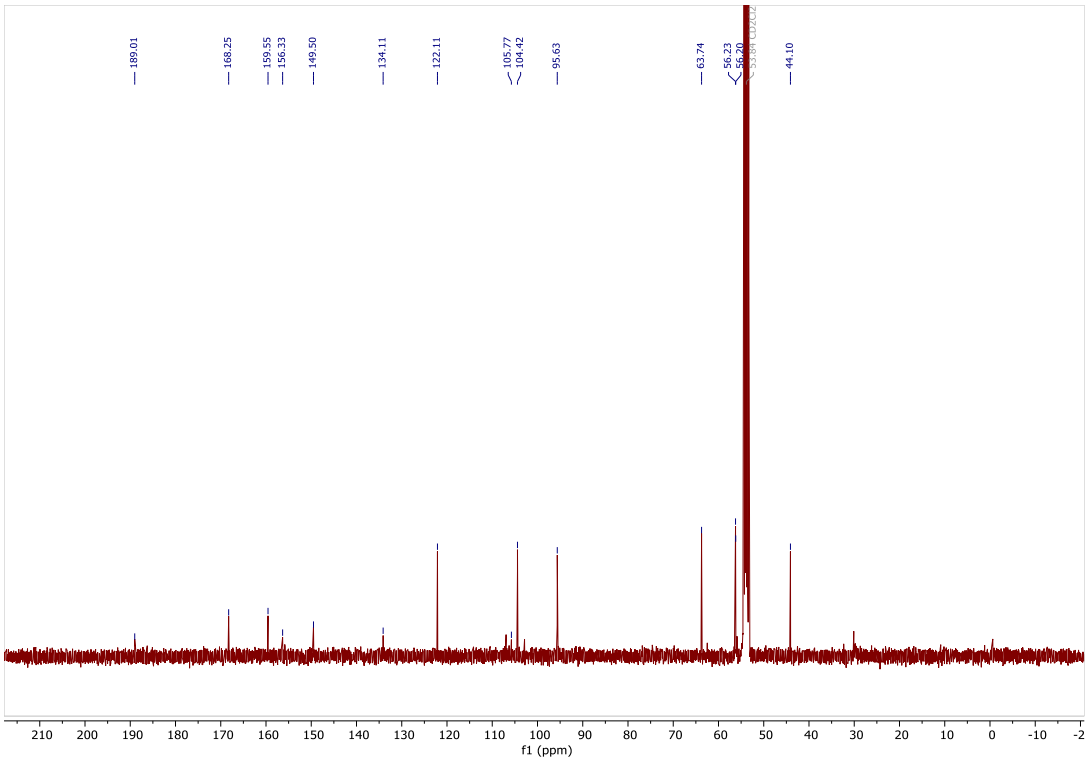
^{1}H NMR of compound **4a'** (400 MHz, CD_2Cl_2)

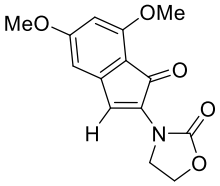




4a'

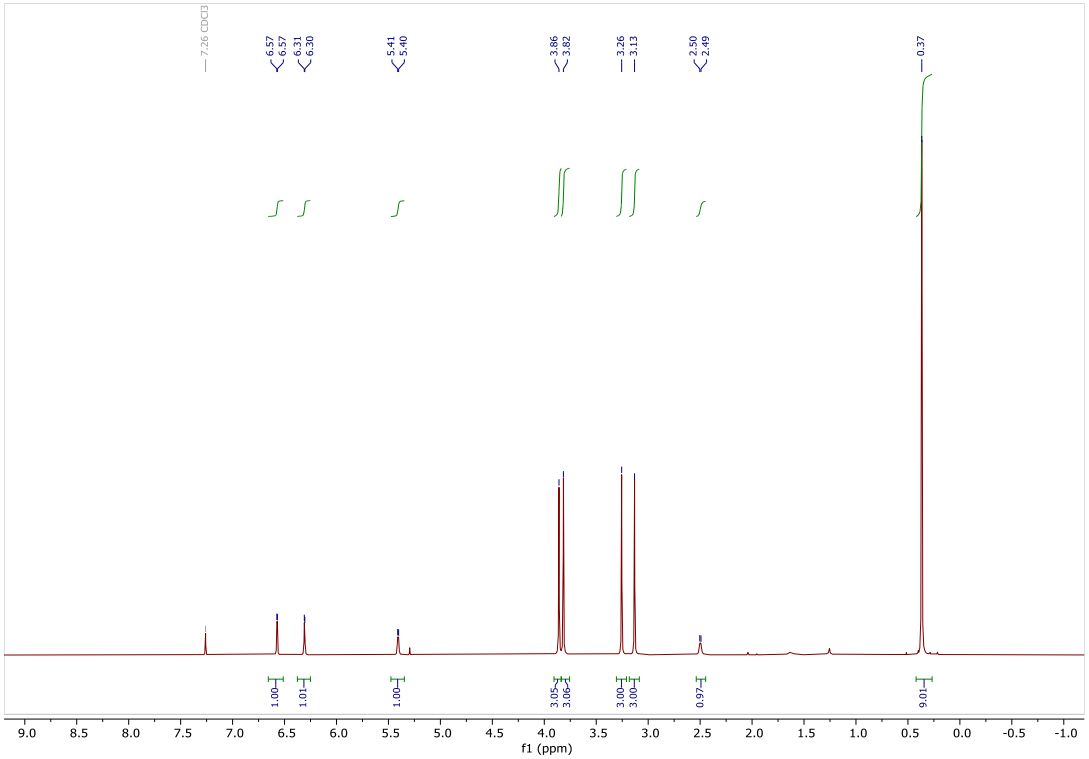
^{13}C NMR of compound **4a'** (101 MHz, $CDCl_3$)

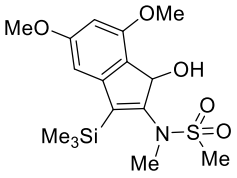




4a'

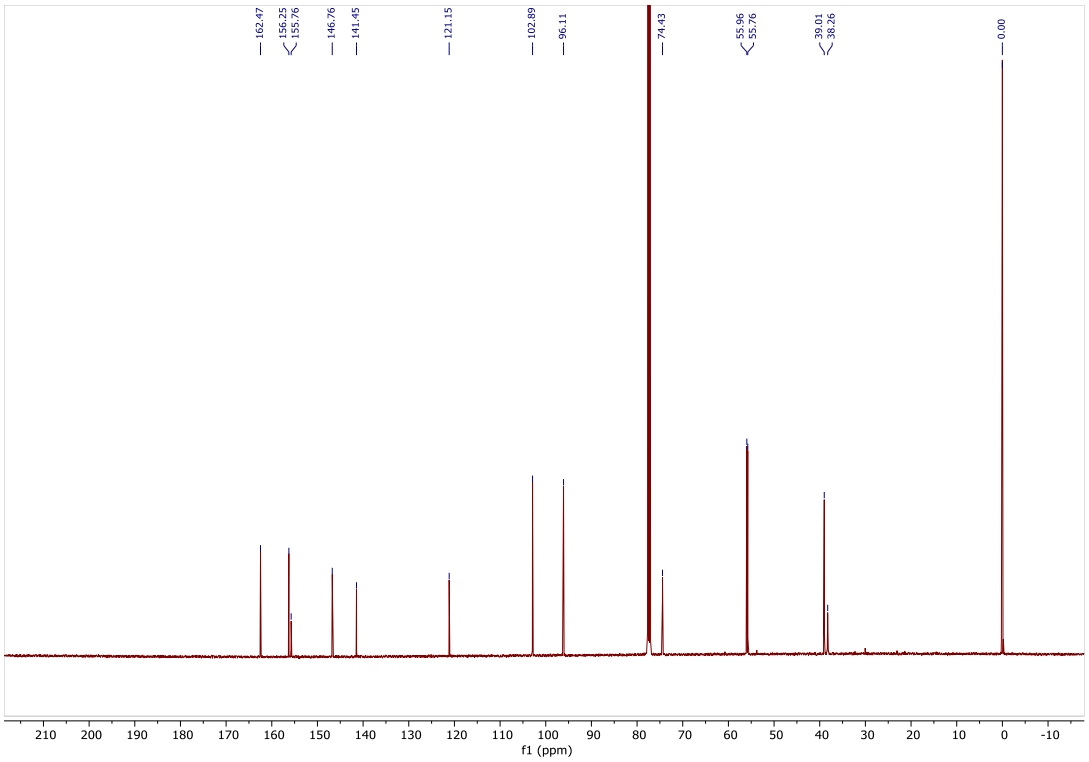
^{1}H NMR of compound **6i** (400 MHz, $CDCl_3$)

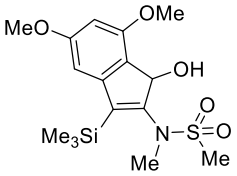




6i

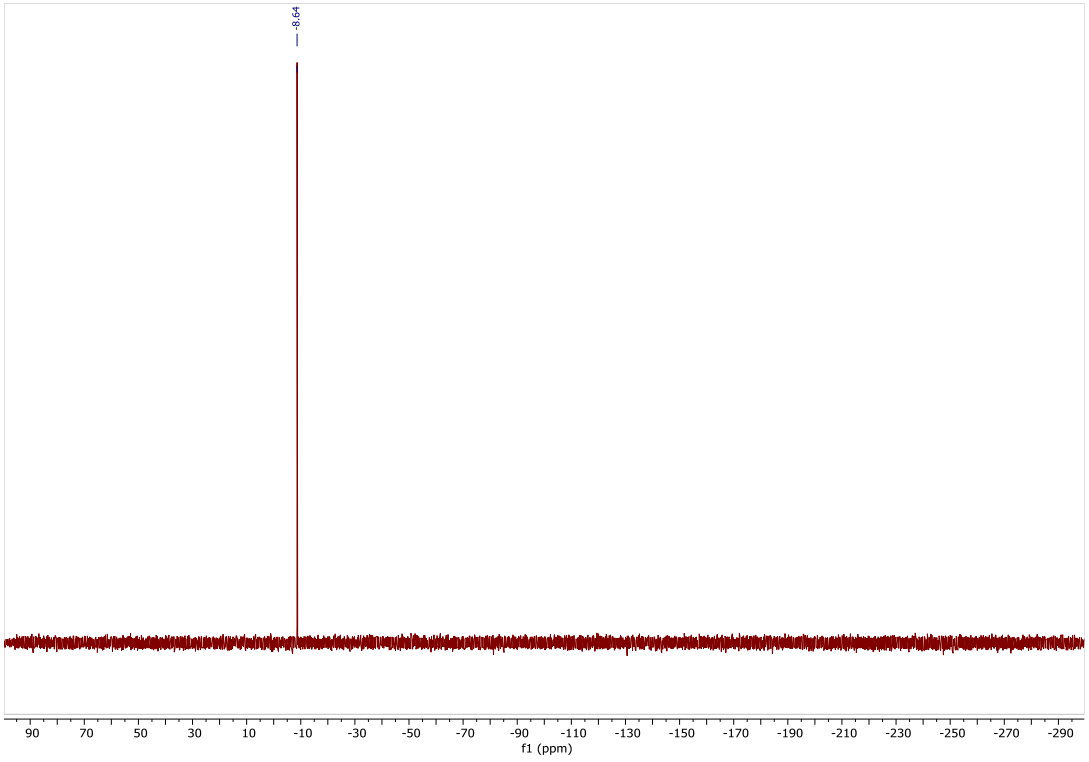
^{13}C NMR of compound **6i** (126 MHz, $CDCl_3$)

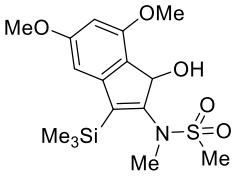




6i

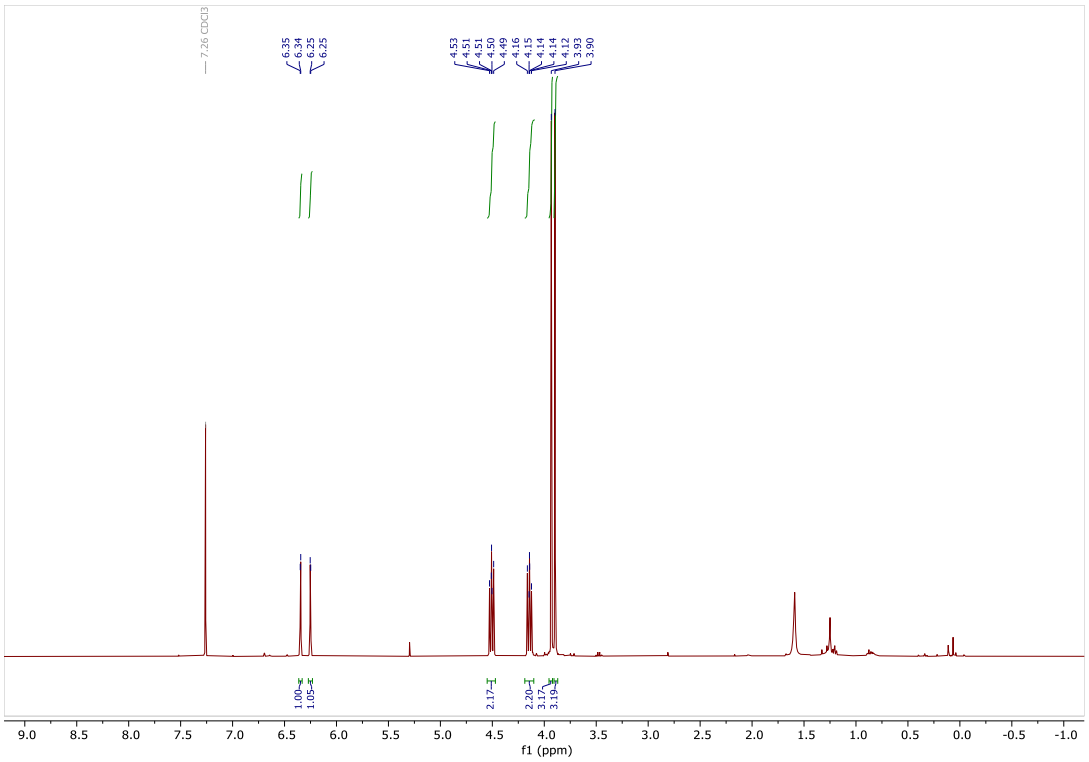
^{29}Si NMR of compound **6i** (99 MHz, $CDCl_3$)

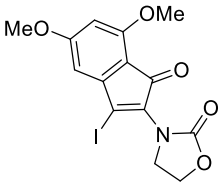




6i

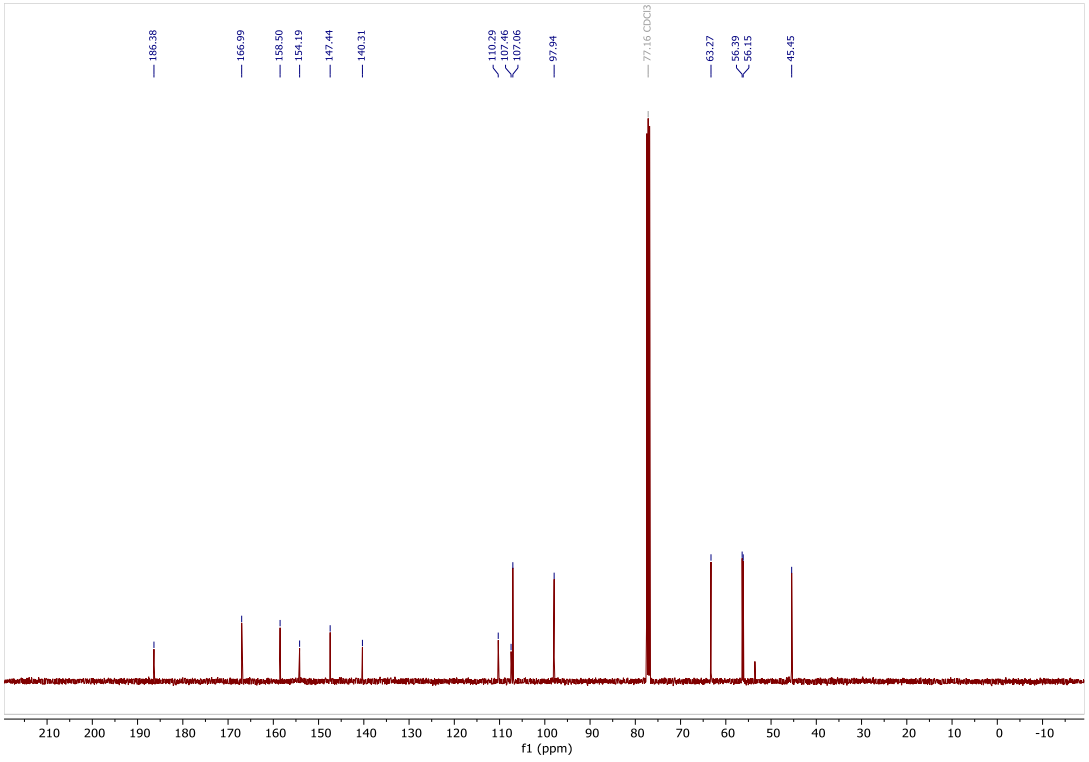
^{1}H NMR of compound **8a** (400 MHz, $CDCl_3$)

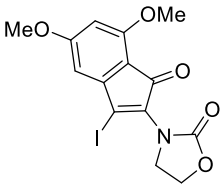




8a

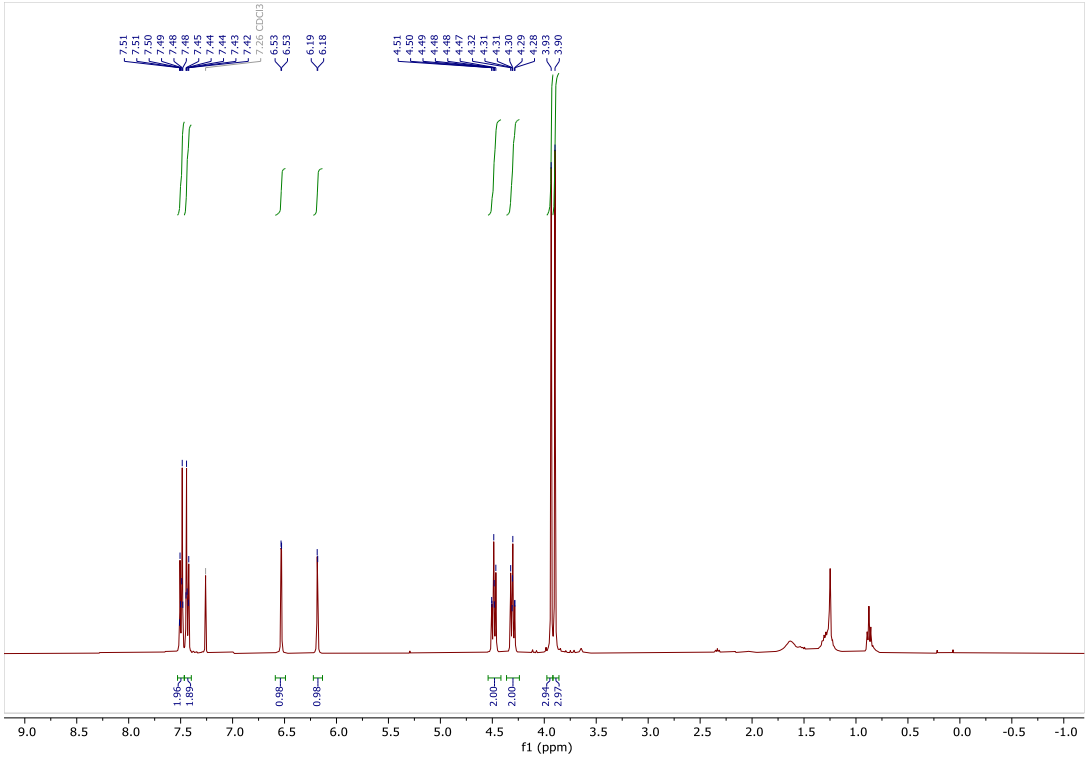
^{13}C NMR of compound **8a** (101 MHz, $CDCl_3$)

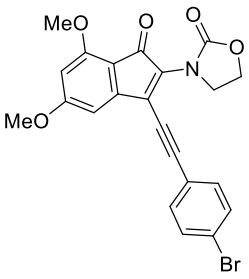




8a

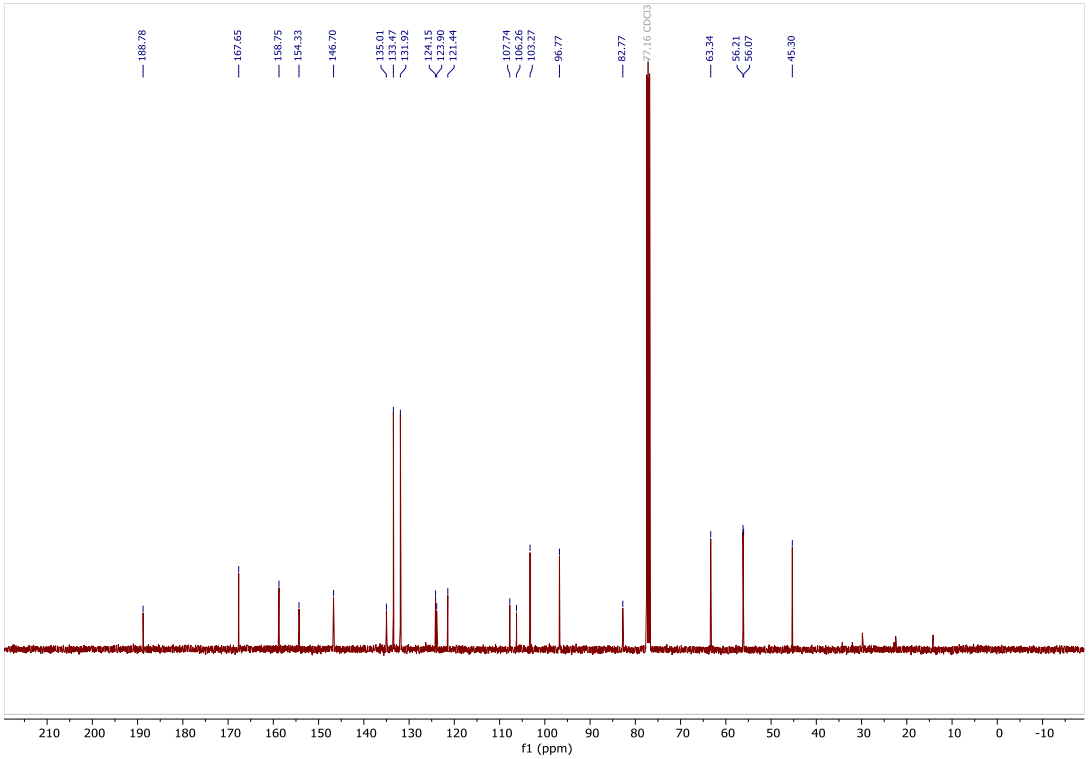
^{1}H NMR of compound **9** (400 MHz, $CDCl_3$)

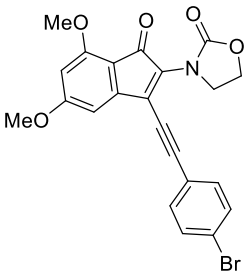




9

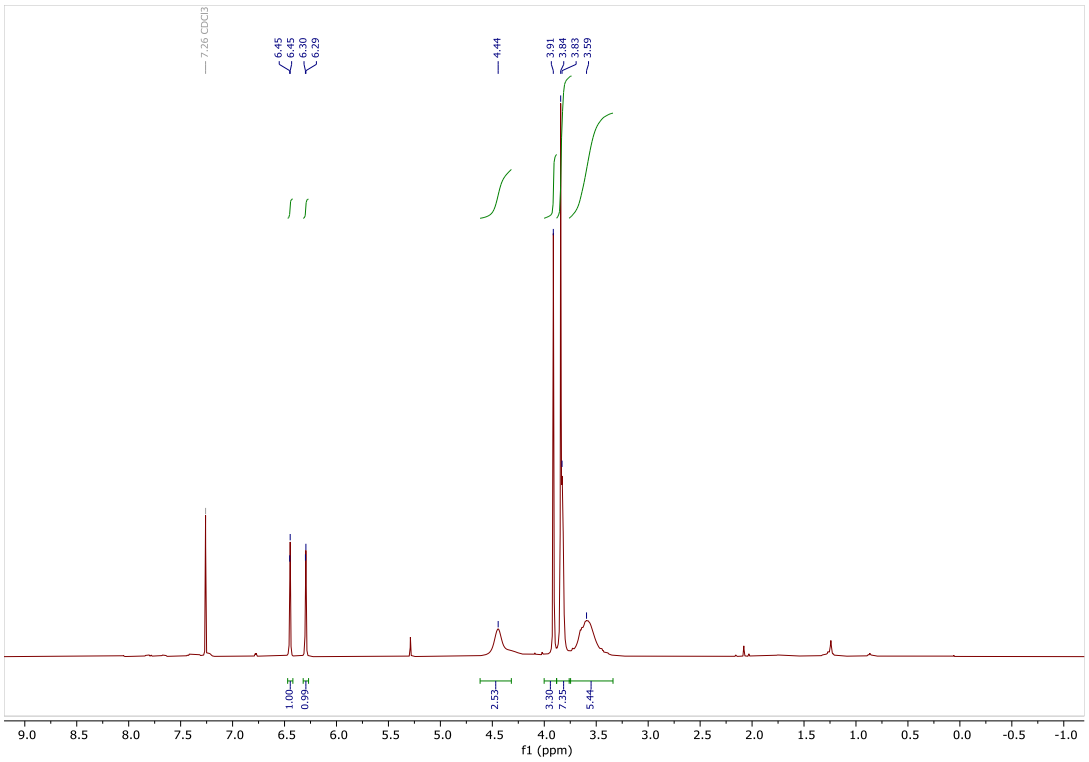
^{13}C NMR of compound **9** (101 MHz, $CDCl_3$)

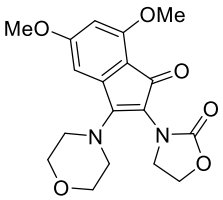




9

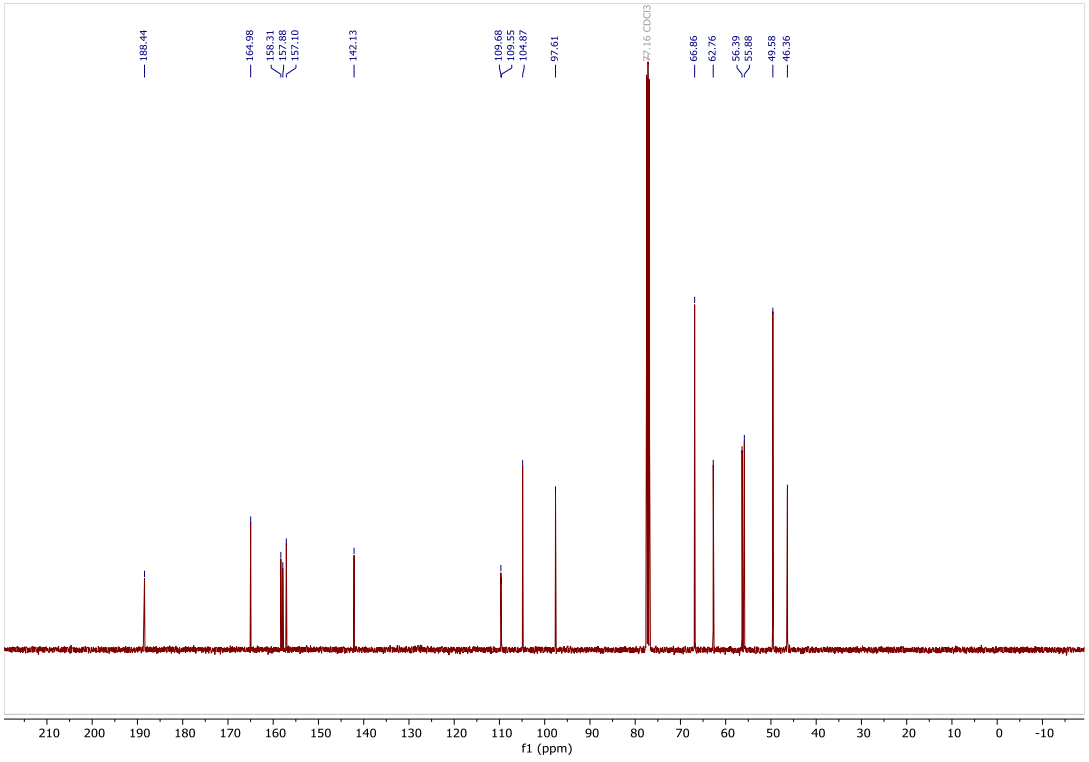
^{1}H NMR of compound **10** (400 MHz, $CDCl_3$)

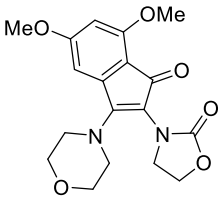




10

^{13}C NMR of compound **10** (101 MHz, $CDCl_3$)





10