Ni-Catalyzed Reductive Cyanation of Alkenyl Tosylates and Triflates

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Supporting Info: Experimental data

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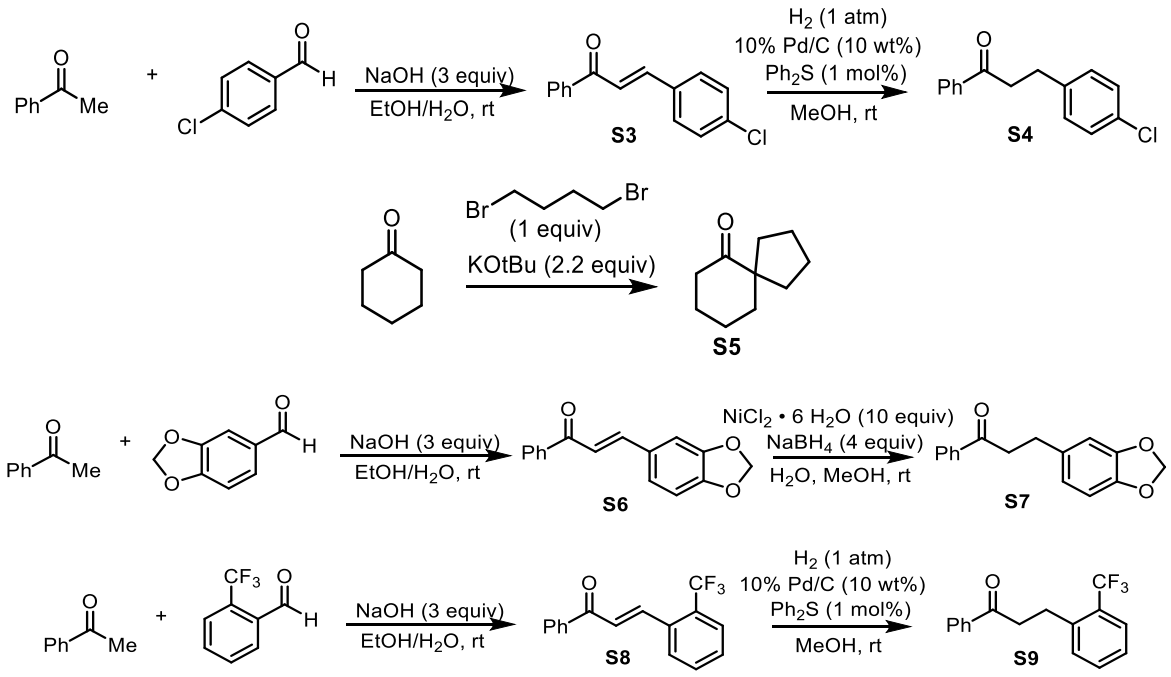
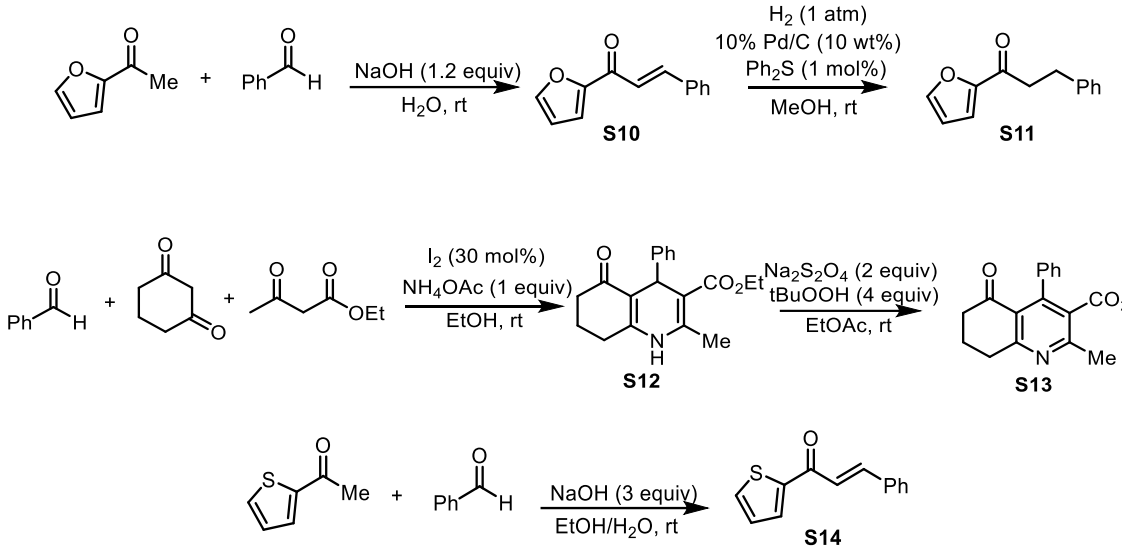
A. General Information

Unless otherwise noted, all reactions were set up on the benchtop and run under an atmosphere of Ar or N_2 using flame-dried glassware and anhydrous solvents. CH_2Cl_2, Et_2O, MeCN, PhMe, and THF were purchased as HPLC-grade (inhibitor-free) from Caledon or Sigma–Aldrich and were dried using a PureSolv MD 5 solvent purification system and used without further manipulation. DMA and DMF were purchased from Acros as Extra Dry over molecular sieves and were used as received. DMA was sparged with Ar for at least 30 min before use. DMSO was purchased as reagent-grade and was dried over 3Å molecular sieves for 3 days. Zn(0) dust was activated with HCl before use.[1] LiBr, $MgBr_2$, and $ZnBr_2$ were purchased as anhydrous reagents and were stored in a glovebox. All other commercial reagents and starting materials were used as received. Compounds were purified by flash column chromatography using SiliCycle SilicaFlash P60 silica gel. GC-MS data was obtained on a Shimadzu GCMS-QP2010 SE. ^{1}H and ^{13}C NMR spectra were recorded on Varian MercuryPlus 400 MHz, Agilent DD2 500MHz, or Bruker Avance III 400MHz spectrometers. TLC samples were run on EMD Millipore TLC Silica gel 60 F254plates and were visualized by UV or by staining with standard $KMnO_4$. IR spectra were obtained on a Perkin-Elmer Spectrum 100 instrument equipped with a single-bounce diamond/ZnSe ATR accessory as solids or thin films. Melting points were obtained on a Fisher-Johns Melting Point Apparatus. High-resolution mass spectra (HRMS) were recorded on a JEOL AccuTOF JMS-T1000LV mass spectrometer equipped with a Direct Analysis in Real Time (DART) ion source.

Compounds 2-methyl-2-phenyl malononitrile[1], Pybox (2,6-bis(4,5-dihydrooxazol-2-yl)pyridine)[2] **S3**[3], **S4**[4], **S5**[5], **S6**[3], **S7**[6], **S8**[3], **S9**[4], **S10**[7], **S11**[4], **S12**[8], **S13**[9] and **S14**[3] were synthesized according to a literature procedures.

Schemes associated with the Synthesis of SI Compounds



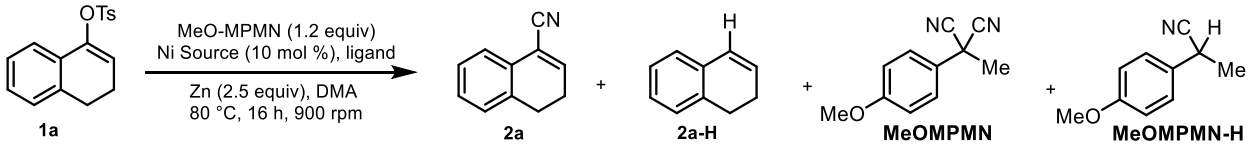


B. Optimization Details

Caution: Depending on the reductant, ligand, and nickel catalyst used, decyanation of excess MPMN was sometimes observed, suggesting formation of cyanide salts *in situ* may be possible. As a precaution, all reactions were handled under basic conditions and were disposed of appropriately.

General Procedure for Optimization Trials: To a flame-dried 8-mL culture tube equipped with a stir bar was added Zn(0) dust (13.0 mg, 0.200 mmol, 2.00 equiv), Ni source (0.010 mmol, 10 mol %), 2-(4-methoxyphenyl)-2-methylmalononitrile (22.3 mg, 0.120 mmol, 1.20 equiv), ligand (if appropriate) and **1a** (30.0 mg, 0.100 mmol, 1.00 equiv). The reaction vial was then capped with a septum and sealed with parafilm and electrical tape, then evacuated and refilled with nitrogen (3x) using standard Schlenk technique. Argon-sparged DMA (0.50 mL, at least 30 min sparge time) was then added to the reaction container, which was then heated at 80 °C for 16h while stirring at 900 rpm. After the indicated reaction time, the vial was cooled to room temperature, then quenched with saturated sodium bicarbonate solution. Dodecane (1.00 equiv, 22.7 μL) was then added to the reaction mixture, which was then analyzed by GCMS.

Table S1: *Optimization of the reductive cyanation of alkenyl tosylates*



Entry	Ni Source	Ligand (mol%)	1a Remaining[a]	2a[a]	2a-H	MeOMPMN[a]	MeOMPMN-H
1	$NiBr_2bpy{\cdot}xH_2O$	NA	0%	30%	0%	0%	74%
2	$NiBr_2{\cdot}DME$	**1** (12)	0%	9%	16%	0%	0%
3	$NiBr_2{\cdot}DME$	**2** (15)	0%	26%	27%	6%	108%
4	$NiBr_2{\cdot}DME$	**3** (12)	0%	13%	20%	0%	18%
5	$NiBr_2{\cdot}DME$	**4** (12)	18%	7%	12%	0%	35%
6	$NiBr_2{\cdot}DME$	**5** (12)	43%	9%	12%	35%	13%
7	$NiBr_2Py_4$	**3** (12)	73%	32%	8%	41%	31%
8	$NiBr_2{\cdot}Py_4$	**6**(12)	43%	60%	0%	42%	64%
9	$NiBr_2{\cdot}Py_4$	**7** (12)	27%	24%	27%	58%	24%
10	$NiBr_2{\cdot}Py_4$	**8** (12)	0%	80%	0%	0%	80%

[a] Calibrated against dodecane as an internal standard on GC-MS.

Ligand Structures

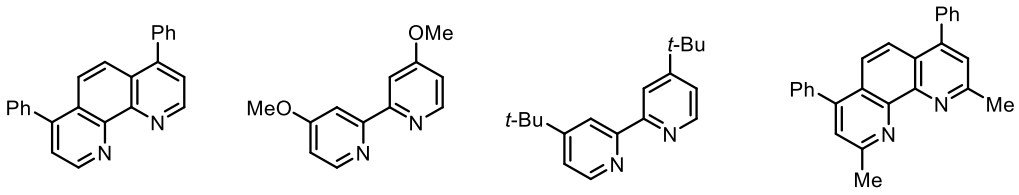
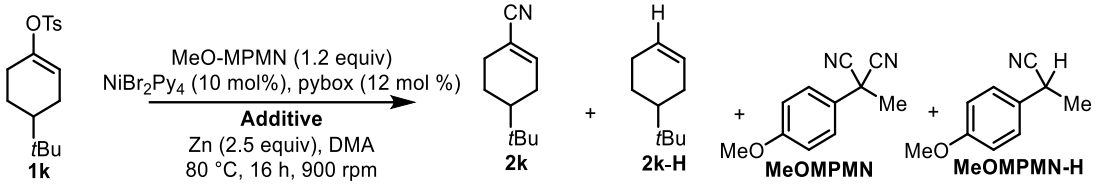


Table S2: Optimization of bromide salt additive for reticent alkenyl tosylates

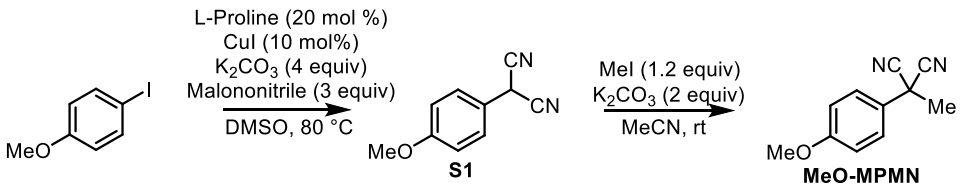


Entry	Additive (equivalents)	**1k** Remaining[a]	**2k**[a]	**2k-H**	**MeOMPMN**[a]	**MeOMPMN-H**
1	None	100%	0%	0%	98%	0%
2	NaBr	0%	67%	5%	0%	100%
3	TBABr	0%	73%	5%	0%	100%
4	$ZnBr_2$	100%	0%	0%	53%	35%
5	LiBr	0%	73%	4%	0%	100%
6	KBr	70%	30%	12%	66%	33%
7	CsBr	90%	9%	0%	66%	36%
8	$MgBr_2$	85%	14%	0%	40%	63%

[a] Calibrated against dodecane as an internal standard on GC-MS.

C. Preparation of Starting Materials

a. Miscellaneous Starting Material Synthesis

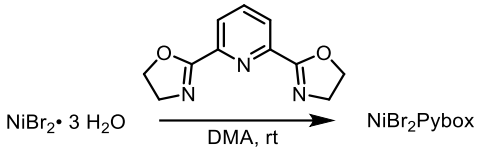


2-(4-methoxyphenyl)malononitrile (S1): 4-iodoanisole (2.3 g, 10 mmol, 1.0 equiv), L-proline (230 mg, 2.0 mmol, 20 mol %), CuI (190 mg, 1.0 mmol, 10 mol %), K_2CO_3 (5.5 g, 40 mmol, 4.0 equiv) were added to a flame-dried flask. The flask was charged with DMSO (0.20 M vs iodoarene, 50 mL) and back-filled with nitrogen. Malononitrile (2.0 g, 30 mmol, 3.0 equivalents) was quickly added, then the flask was evacuated and back-filled with nitrogen three times while the mixture was stirring. The flask was heated at 80 °C for 18 hours. After the reaction was judged to have reached completion by TLC, the flask was cooled to room temperature, then to 0°C with an ice bath, and carefully brought to a pH of ~ 3-4 by slow addition of 1.0 M HCl (reaction bubbles vigorously). The mixture was then extracted with ethyl acetate (3x 250 mL). The organic fractions were washed with brine, dried over $MgSO_4$, and then purified by column chromatography (0-15% EtOAc/Hexanes) to yield **S1** as a pink solid (92%, 1.6 g).

Analytical Data: **^{1}H NMR** (400Hz, $CDCl_3$) δ 7.45 – 7.36 (m, 2H), 7.03 – 6.94 (m, 2H), 5.00 (s, 1H), 3.84 (s, 3H) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$) δ 161.1, 128.7, 118.0, 115.5, 112.2, 55.6, 27.6 ppm.

(4`methoxy)-2-methyl-2-phenylmalononitrile (MeO-MPMN): **S1** (1.6 g, 8.4 mmol, 1.0 equiv,) and K_2CO_3 (2.3 g, 17 mmol, 2.0 equiv,) were dissolved in MeCN (1.0 M vs **S1**, 8.4 mL), followed by MeI (640 μL, 10 mmol , 1.2 equiv,). The reaction was stirred until the starting material was judged to have reached completion by TLC (~3h), then filtered through a pad of celite. The pad of celite was then washed with EtOAc (10 mL). The organic layer was concentrated under reduced pressure and purified by column chromatography (0-10% EtOAc/Hexanes) to give **MeO-MPMN** as an off-white solid (89%, 1.4 g).

Analytical Data: **^{1}H NMR** (400Hz, $CDCl_3$) δ 7.52–7.46 (m, 2H), 7.02–6.95 (m, 2H), 3.84 (s, 3H), 2.09 (s, 3H) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$) δ 160.8 126.8, 124.9, 116.0, 115.2, 55.6, 35.9, 29.4 ppm. **HRMS** m/z (DART): calcd for $C_{11}H_{14}N_3O$ ($M + NH_4^+$): 204.11314; found 204.11362. **IR (neat):** 1608, 1511, 1257, 1184, 1028 cm^{-1}. **M.P.:** 40 °C–41 °C.



NiBr$_2$Pybox: To a flame-dried scintillation vial was added nickel dibromide trihydrate (1.0 equiv, 2.0 mmol) in dimethylacetamide (1.0 M relative to Ni, 2.0 mL). 1,3-bis(4,5-dihydrooxazol-2-yl)benzene (Pybox, 2.0 mmol) was then added and stirred until the resulting precipitate was a consistent color. Diethyl ether (2.0 mL) was then added, and the mixture shaken. Once the precipitate had settled, the supernatant was taken off with a pipette. This addition and removal of diethyl ether was repeated three additional times. The solid precipitate was then collected by vacuum filtration and washed with diethyl ether until it was a consistent color, then dried under vacuum overnight to give a green solid (870 mg, 2.0 mmol, 99%).

b. Alkenyl Tosylate Synthesis

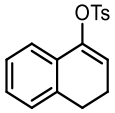
General Procedure A for the Synthesis of Alkenyl Tosylates – Deprotonation and Trapping:

A solution of hexamethyldisilazane (HMDS – 1.3 equiv) in THF (2.3 mmol HMDS/mL THF) was cooled to -78 °C. A solution of n-butyl lithium (1.2 equiv as a solution in hexanes) was then added over 5 minutes to the solution containing HMDS. This mixture was then stirred for 30 minutes at -78 °C. A solution of ketone in THF (1.0 equiv, 2.0 mmol ketone/mL THF) was then added dropwise to the solution containing LiHMDS over 5-10 minutes. The flask was

stirred for 1–1.5 hours at -78 °C. After the allotted time, a solution of Ts_2O in THF (1.4 equivalents, 0.70 mmol Ts_2O/ml THF) was added to the solution containing the enolate. The reaction was left to stir overnight allowing to warm to room temperature over this time, then quenched with saturated $NH_4Cl_{(aq)}$. The reaction was extracted with ethyl acetate (3x), dried over $MgSO_4$, and purified by column chromatography.

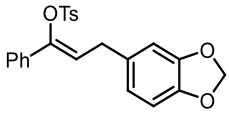
General Procedure B for the Synthesis of Alkenyl Tosylates – 1,4-Conjugate Addition and Trapping:

Copper(I) iodide (1.1 equivalents) was added to a flame-dried flask, that was then placed in a cooling bath at -10 °C. Et_2O was added (3.0 mL / mmol copper), followed by the dropwise addition of MeLi (2.1 equiv, as a solution in Et_2O). The clear heterogenous solution of copper iodide slowly became opaque and yellow, then completely clear and homogenous as the addition of MeLi progressed. The reaction mixture was then left to stir at -10 °C for 30 minutes, after which time it was cooled to -20 °C. A solution of the enone or enal in Et_2O was prepared (1.0 equivalent, 3.0 mL / mmol substrate), then added dropwise to the reaction over 5-10 minutes, which was maintained at -20 °C for the entire addition. The reaction was left to stir at -20 °C until complete conversion of the starting material was observed by TLC (30 min – 2 h). Then, a solution of Ts_2O in THF (1.3 equivalents, 3.0 mL/ mmol Ts_2O) was added while maintaining the reaction at -20 °C. After the complete consumption of the intermediate as judged by TLC, the reaction was quenched with saturated aqueous NH_4Cl, extracted with ethyl acetate (3x), dried over $MgSO_4$ then purified by column chromatography (hexanes:ethyl acetate).



3,4-dihydronaphthalen-1-yl 4-methylbenzenesulfonate (1a): Prepared by General Procedure A for the Synthesis of Alkenyl Tosylates on a 10 mmol scale from α-tetralone with the following modification: after workup and removal of solvent, hexanes were added to the crude product residue, which was then sonicated to triturate **1a** as a white solid (2.7 g, 88%).

Analytical Data:[10] **^{1}H NMR** (400Hz, $CDCl_3$) δ 7.88–7.80 (m, 2H), 7.29 (d, *J* = 8.1 Hz, 2H), 7.22 (dd, *J* = 7.2, 1.8 Hz, 1H), 7.17–7.05 (m, 3H), 5.73 (t, *J* = 4.8 Hz, 1H), 2.76 (t, *J* = 8.1 Hz, 2H), 2.42 (s, 3H), 2.37 (td, *J* = 8.0, 4.8 Hz, 2H) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$) δ 145.7, 145.2, 136.2, 133.4, 130.0, 129.8, 128.5, 128.4, 127.4, 126.5, 122.0, 117.1, 27.3, 22.4, 21.8 ppm.

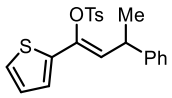


3-(benzo[d][1,3]dioxol-5-yl)-1-phenylprop-1-en-1-yl 4-methylbenzenesulfonate (1b): Prepared by General Procedure A for the Synthesis of Alkenyl Tosylates on a 2.5 mmol scale from **S7**. Purified by column chromatography (0-10% hexanes/ethyl acetate) to give **1b** as white solid (630 mg, 63%, >20:1 Z/E).

Analytical Data: **^{1}H NMR** (400Hz, $CDCl_3$) δ 7.69 (d, *J* = 8.1 Hz, 2H), 7.28 (dd, *J* = 7.6, 1.8 Hz, 2H), 7.22–7.13 (m, 5H), 6.72 (d, *J* = 7.9 Hz, 1H), 6.68 (d, *J* = 1.6 Hz, 1H), 6.64 (dd, *J* =

7.9, 1.7 Hz, 1H), 5.92 (s, 2H), 5.81 (t, *J* = 7.4 Hz, 1H), 3.46 (d, *J* = 7.4 Hz, 2H), 2.39 (s, 3H) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$) δ 147.7, 146.5, 146.1, 145.0, 134.5, 133.7, 133.1, 129.5, 128.4, 128.3, 128.1, 125.8, 121.4, 121.3, 109.1, 108.2, 100.9, 32.5, 21.6 ppm. **IR (neat):** 1598, 1503, 1488, 1443, 1371, 1244, 1175, 1037, 928 cm^{-1}. **HRMS** m/z (DART): calcd for $C_{23}H_{24}NO_5S$ ($M + NH_4^+$) 426.13697; found 426.13677. **M.P.:** 112 °C–113 °C.

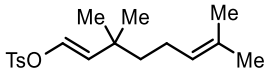
Stereochemistry of **1b** was determined by way of a NOESY spectrum. See section **G-1** for analysis.



3-phenyl-1-(thiophen-2-yl)but-1-en-1-yl 4-methylbenzenesulfonate (1c): Prepared by General Procedure B for the Synthesis of Alkenyl Tosylates on a 5.0 mmol scale from **S14** with the following modification: the temperature of the reaction was held between -5 °C and -15 °C for the duration of the reaction. Purified by column chromatography (0-10% hexanes/ethyl acetate) to give **1c** as a thick, clear oil (1.3 g, 66%, 7.7:1 Z/E).

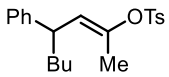
Analytical Data: **^{1}H NMR** (400Hz, $CDCl_3$) δ 7.79–7.75 (m, 2H), 7.34–7.16 (m, 7H), 7.11 (dd, *J* = 5.1, 1.3 Hz, 1H), 6.87 (dd, *J* = 3.7, 1.3 Hz, 1H), 6.80 (dd, *J* = 5.1, 3.7 Hz, 1H) 5.81 (d, *J* = 10.3 Hz, 1H), 4.01 (dq, *J* = 10.3, 7.0 Hz, 1H), 2.42 (s, 3H), 1.41 (d, *J* = 7.0 Hz, 3H) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$) δ 145.2, 144.5, 139.8, 137.9, 134.0, 129.7, 128.6, 128.3, 127.2, 127.1, 126.5, 126.4, 125.9, 125.6, 36.8, 21.8, 21.2 ppm. **IR (neat):** 1653, 1598, 1493, 1452, 1366, 1189, 1174, 1234, 1016 cm^{-1}. **HRMS** m/z (DART): calcd for $C_{21}H_{24}NO_3S_2$ ($M + NH_4^+$) 402.11921; found 402.11954.

Stereochemistry of **1c** was determined by way of a NOESY spectrum. See section **G-1** for analysis.



(E)-3,3,7-trimethylocta-1,6-dien-1-yl 4-methylbenzenesulfonate (1d): Prepared by General Procedure B for the Synthesis of Alkenyl Tosylates on a 5.0 mmol scale from citral. Purified by column chromatography (0-10% hexanes/ethyl acetate) to give **1d** as a clear solid (1.1 g, 68%, >20:1 E/Z).

Analytical Data: **^{1}H NMR** (400Hz, $CDCl_3$) δ 7.80–7.74 (m, 2H), 7.36–7.30 (m, 2H), 6.26 (d, *J* = 12.2 Hz, 1H), 5.31 (d, *J* = 12.2 Hz, 1H), 5.00–4.93 (m, 1H), 2.44 (s, 3H), 1.73 – 1.67 (m, 2H), 1.65 (d, *J* = 1.3 Hz, 3H), 1.52 (d, *J* = 1.4 Hz, 3H), 1.22–1.15 (m, 2H), 0.94 (s, 6H) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$) δ 145.2, 134.5, 132.7, 131.7, 131.5, 129.9, 128.3, 124.5, 43.0, 34.5, 27.1, 25.8, 23.3, 21.8, 17.7 ppm. **IR (neat):** 2964, 2920, 1658, 1598, 1453, 1373, 1178, 1097 cm^{-1}. **HRMS** m/z (DART): calcd for $C_{18}H_{27}O_3S$ ($M + H^+$) 323.16754; found 323.16854. **M. P.:** 25 °C–26 °C.

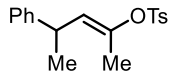


4-phenyloct-2-en-2-yl 4-methylbenzenesulfonate (1e): Prepared by General Procedure B for the Synthesis of Alkenyl Tosylates on a 4 mmol scale from 4-phenyl-3-buten-2-one with the

following modification: n-butyl lithium in hexanes was used instead of MeLi in Et_2O. Purified by column chromatography (0-5% hexanes/ethyl acetate) to give **1e** as a clear oil (1.1 g, 75%, 11:1 E/Z) containing 0.070 equiv of 4-phenyloctan-2-one.

Analytical Data: **^{1}H NMR** (400Hz, $CDCl_3$) δ 7.71–7.66 (m, 2H), 7.31–7.24 (m, 2H), 7.23–7.16 (m, 3H), 7.02–6.98 (m, 2H), 5.12 (dq, *J* = 10.4, 1.1 Hz, 1H), 3.21 (ddd, *J* = 10.4, 8.6, 6.2 Hz, 1H), 2.42 (s, 3H), 1.88 (d, *J* = 1.1 Hz, 3H), 1.66–1.54 (m, 2H), 1.52–1.44 (m, 1H), 1.29–1.22 (m, 1H), 1.31–1.05 (m, 2H), 0.86 (t, *J* = 7.3 Hz, 3H) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$) δ 145.2, 144.8, 144.0, 132.9, 129.6, 128.5, 127.5, 127.1, 126.3, 125.2, 43.4, 36.4, 29.5, 22.5, 21.7, 16.4, 14.0 ppm. **IR (neat):** 2957, 2929, 2860, 1494, 1453, 1365, 1177 cm^{-1}. **HRMS** m/z (DART): calcd for $C_{21}H_{30}NO_3S$ 376.19409 (M + NH_4^+); found 376.19461.

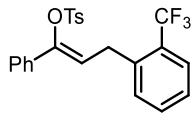
Stereochemistry of **1e** was determined by way of a NOESY spectrum. See section **G-1** for analysis.



(**E)-4-phenylpent-2-en-2-yl 4-methylbenzenesulfonate (1f):** Prepared by General Procedure B for the Synthesis of Alkenyl Tosylates on a 5.0 mmol scale from 4-phenyl-3-buten-2-one. Purified by column chromatography (0-5% hexanes/ethyl acetate) to give **1f** as a white solid (950 mg, 60%, 7.5:1 E/Z).

Analytical Data: **^{1}H NMR** (400Hz, $CDCl_3$) δ 7.77–7.70 (m, 2H), 7.32–7.23 (m, 5H), 7.11–7.05 (m, 2H), 5.16 (dq, *J* = 10.1, 1.1 Hz, 1H), 3.49 (dq, *J* = 10.2, 7.0 Hz, 1H), 2.46 (s, 3H), 1.96 (d, *J* = 1.1 Hz, 3H), 1.28 (d, *J* = 7.0 Hz, 3H) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$) δ 144.9, 144.9, 144.8, 129.9, 129.7, 128.6, 128.0, 126.8, 126.5, 126.2, 37.4, 22.0, 21.8, 16.4 ppm. **IR (neat):** 2968, 1598, 1494, 1451, 1363, 1177 cm^{-1}. **HRMS** m/z (DART): calcd for $C_{18}H_{24}NO_3S$ (M + NH_4^+): 334.14714; found 334.14788. **M.P.:** 48 °C – 49 °C.

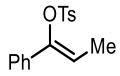
Stereochemistry of **1f** was determined by way of a NOESY spectrum. See section **G-1** for analysis.



1-phenyl-3-(2-(trifluoromethyl)phenyl)prop-1-en-1-yl 4-methylbenzenesulfonate (1g): Prepared by General Procedure A for the Synthesis of Alkenyl Tosylates on a 3.2 mmol scale from **S9**. Purified by column chromatography (0-10% hexanes/ethyl acetate) to give **1g** as a clear, thick oil (1.1 g, 75%, >20:1 Z/E).

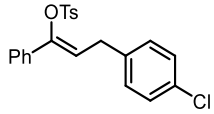
Analytical Data: **^{1}H NMR** (400Hz, $CDCl_3$) δ 7.74 – 7.68 (m, 2H), 7.61 (dd, *J* = 7.8, 1.3 Hz, 1H), 7.46 (td, *J* = 7.5, 1.3 Hz, 1H), 7.40–7.34 (m, 3H), 7.33–7.27 (m, 1H), 7.25–7.18 (m, 5H), 5.79 (t, *J* = 7.3 Hz, 1H), 3.60 (d, *J* = 7.3 Hz, 2H), 2.39 (s, 3H) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$) δ 147.4, 145.4, 138.1 (q, *J* = 1.6 Hz), 134.6, 133.6, 132.1 (q, *J* = 1.3 Hz), 131.3, 129.8, 128.8, 128.6, 128.4 (d, *J* = 3.8 Hz), 126.6, 126.0, 126.0 (q, *J* = 5.7 Hz), 125.6, 123.4, 119.9, 29.3 (q, *J* = 2.1 Hz), 21.7 ppm. **^{19}F NMR** (377 MHz, $CDCl_3$) δ -59.96 ppm. **IR (neat):** 1600, 1494, 1450, 1372, 1312, 1176, 1158, 1114, 1061, 1036 cm^{-1}. **HRMS** m/z (DART): calcd for $C_{23}H_{23}NO_3F_3S$ (M + NH_4^+) 450.13453; found 450.13508.

Stereochemistry of **1g** could not be unambiguously determined. Stereochemistry proposed to be in-line with other substrates of this class.



(Z)-1-phenylprop-1-en-1-yl 4-methylbenzenesulfonate (1h): Prepared by General Procedure A for the Synthesis of Alkenyl Tosylates on a 10 mmol scale from propiophenone. Purified by column chromatography (0-10% hexanes/ethyl acetate) to give **1h** as a white solid (2.4 g, 83%, >20:1 Z/E).

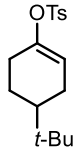
Analytical data: [10] **^{1}H NMR** (400Hz, $CDCl_3$) δ 7.64–7.58 (m, 2H), 7.22–7.18 (m, 2H), 7.15–7.09 (m, 5H), 5.73 (d, *J* = 7.0 Hz, 1H), 2.32 (s, 3H), 1.66 (d, *J* = 7.0 Hz, 3H) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$) δ 147.5, 145.0, 135.0, 134.0, 129.6, 128.4, 128.2, 125.7, 117.4, 21.7, 12.3 ppm.



3-(4-chlorophenyl)-1-phenylprop-1-en-1-yl 4-methylbenzenesulfonate (1i): Prepared by General Procedure A for the Synthesis of Alkenyl Tosylates on a 2.0 mmol scale from **S4**. Purified by column chromatography (0-10% hexanes/ethyl acetate) to give **1i** as a white solid (500 mg, 63%, >20:1 Z/E).

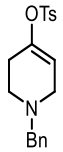
Analytical Data: **^{1}H NMR** (400Hz, $CDCl_3$) δ 7.75–7.70 (m, 2H), 7.36–7.16 (m, 11H), 5.87 (td, *J* = 7.4, 0.8 Hz, 1H), 3.60 (d, *J* = 7.4 Hz, 2H), 2.41 (s, 3H) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$) δ 147.2, 145.2, 138.0, 134.5, 133.8, 132.8, 130.0, 129.7, 128.8, 128.7, 128.4, 128.3, 126.0, 120.7, 32.3, 21.7. **IR (neat):** 1678, 1597, 1491, 1447, 1407, 1368, 1174, 1090, 1015 cm^{-1}. **HRMS** m/z (DART): calcd for $C_{22}H_{20}O_3SCl$ ($M + H^+$) 399.08162; found 399.08157. **M.P.:** 59 °C–60 °C.

Stereochemistry of **1i** was determined by way of a NOESY spectrum. See section **G-1** for analysis.



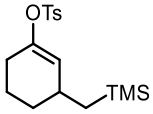
4-(tert-butyl)cyclohex-1-en-1-yl 4-methylbenzenesulfonate (1j): Prepared by General Procedure A for the Synthesis of Alkenyl Tosylates on a 5.0 mmol scale from 4-tert-butylcyclohexanone. Purified by column chromatography (0-5% hexanes/ethyl acetate) to give **1j** as a white solid (1.3 g, 81%).

Analytical Data:[11] **^{1}H NMR** (400Hz, $CDCl_3$) δ 7.82–7.77 (m, 2H), 7.36–7.31 (m, 2H), 5.32 (ddt, *J* = 5.5, 2.7, 1.3 Hz, 1H), 2.45 (s, 3H), 2.12 (dtd, *J* = 8.2, 3.0, 1.5 Hz, 2H), 2.07–1.98 (m, 1H), 1.86 – 1.74 (m, 2H), 1.23–1.17 (m, 2H), 0.84 (s, 9H) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$) δ 148.3, 144.9, 133.9, 129.8, 128.4, 117.2, 43.3, 32.2, 28.8, 27.4, 25.4, 24.2, 21.8 ppm.



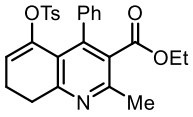
1-benzyl-1,2,3,6-tetrahydropyridin-4-yl 4-methylbenzenesulfonate (1k): Prepared by General Procedure A for the Synthesis of Alkenyl Tosylates on a 5.0 mmol scale from 1-benzylpiperidin-4-one. Purified by column chromatography 0-10% hexanes/ethyl acetate) to give **1k** as an orange oil (1.4 g, 80%).

Analytical Data: **^{1}H NMR** (400Hz, $CDCl_3$) δ 7.84–7.79 (m, 2H), 7.36–7.32 (m, 2H), 7.31–7.22 (m, 5H), 5.31 (tt, *J* = 3.6, 1.4 Hz, 1H), 3.56 (s, 2H), 2.98 (dt, *J* = 3.6, 2.8 Hz, 2H), 2.59 (t, *J* = 5.7 Hz, 1H), 2.45 (s, 3H), 2.22 (ttd, *J* = 5.7, 2.8, 1.4 Hz, 1H) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$) δ 146.5, 145.2, 138.1, 133.6, 129.8, 129.1, 128.5, 128.4, 127.4, 114.9, 61.5, 50.9, 49.4, 28.4, 21.8 ppm. **IR (neat):** 1690, 1597, 1453, 1362, 1177 cm^{-1}. **HRMS** m/z (DART): calcd for $C_{19}H_{22}NO_3S$ ($M + H^+$) 344.13149; found 344.13272.



3-((trimethylsilyl)methyl)cyclohex-1-en-1-yl 4-methylbenzenesulfonate (1l): Prepared by General Procedure B for the Synthesis of Alkenyl Tosylates on a 5.0 mmol scale from 2-cyclohexen-1-one. (Trimethylsilyl)methyllithium in pentane was used instead of MeLi in Et_2O. Purified by column chromatography (0-5% hexanes/ethyl acetate) to give **1l** as a clear oil (820 mg, 49%).

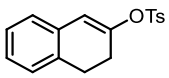
Analytical Data: **^{1}H NMR** (400Hz, $CDCl_3$) δ 7.82–7.77 (m, 2H), 7.33 (dt, *J* = 7.9, 0.8 Hz, 2H), 5.14 (dt, *J* = 3.2, 1.6 Hz, 1H), 2.45 (s, 3H), 2.23 (ddq, *J* = 10.5, 5.5, 2.5 Hz, 1H), 2.07 (dddt, *J* = 8.3, 5.2, 3.0, 1.8 Hz, 2H), 1.80–1.64 (m, 2H), 1.55–1.45 (m, 1H), 1.12–1.00 (m, 1H), 0.49 (d, *J* = 7.4 Hz, 2H), -0.06 (s, 9H) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$) δ 147.7, 145.0, 133.7, 129.7, 128.5, 124.3, 31.7, 31.5, 27.7, 24.3, 21.8, 21.7 ppm. **IR (neat):** 2942, 2902, 2870, 1676, 1599, 1366, 1248, 1177 cm^{-1}. **HRMS** m/z (DART): calcd for $C_{17}H_{27}O_3SiS$ ($M + H^+$): 339.14447; found 339.14438.



ethyl 2-methyl-4-phenyl-5-(tosyloxy)-7,8-dihydroquinoline-3-carboxylate (1m): Prepared by General Procedure A for the Synthesis of Alkenyl Tosylates on a 2.0 mmol scale from **S13**. Purified by column chromatography (0-10% hexanes/ethyl acetate) to give **1m** as a white solid (330 mg, 35%).

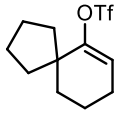
Analytical Data: **^{1}H NMR** (400Hz, $CDCl_3$) δ 7.48–7.44 (m, 2H), 7.29–7.24 (m, 3H), 7.22–7.18 (m, 2H), 7.15–7.11 (m, 2H), 5.73 (t, *J* = 5.2 Hz, 1H), 3.93 (q, *J* = 7.1 Hz, 2H), 2.96 (dd, *J* = 8.8, 6.8 Hz, 2H), 2.52 (s, 3H), 2.41 (s, 3H), 2.40–2.33 (m, 2H), 0.90 (t, *J* = 7.1 Hz, 3H) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$) δ 168.2, 159.3, 153.1, 145.1, 144.3, 137.3, 132.5, 129.6, 129.4, 128.6, 128.5, 128.0, 127.8, 122.4, 121.1, 61.4, 31.7, 22.6, 21.8, 21.2, 13.7 ppm. **IR**

(neat): 1724, 1641, 1599, 1550, 1373, 1259, 1211, 1176, 1075 cm^{-1}. **HRMS** m/z (DART): calcd for $C_{26}H_{26}NO_5S$ ($M + H^+$) 464.15262; found 464.15296. **M.P.:** 123 °C–124 °C.



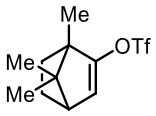
3,4-dihydronaphthalen-2-yl 4-methylbenzenesulfonate (1n): Prepared by General Procedure A for the Synthesis of Alkenyl Tosylates on a 4.0 mmol scale from ß-tetralone. Purified by column chromatography (0-10% hexanes/ethyl acetate) to give **1n** as a white solid (960 mg, 80%).

Analytical Data:[12] **^{1}H NMR** (400Hz, $CDCl_3$) δ 7.87–7.81 (m, 2H), 7.35 (d, *J* = 8.1 Hz, 2H), 7.15–7.09 (m, 2H), 7.07 (d, *J* = 4.1 Hz, 1H), 6.92 (dd, *J* = 5.3, 3.5 Hz, 1H), 6.11 (d, *J* = 1.5 Hz, 1H), 2.88 (t, *J* = 8.3 Hz, 2H), 2.47–2.41 (m, 5H) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$) δ 149.9, 145.4, 133.2, 132.5, 129.9, 128.6, 128.6, 127.7, 127.5, 126.8, 126.8, 117.5, 28.7, 26.7, 21.9 ppm.



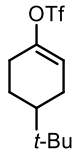
spiro[4.5]dec-6-en-6-yl trifluoromethanesulfonate (1o): S5 (760 mg, 5.0 mmol, 1.0 equiv) was dissolved in DCM (20 mL, 0.25 M). 2-chloropyridine (570 µL, 6.0 mmol, 1.2 equiv) was then added to the solution, which was then cooled to 0 °C. A solution of Tf_2O (1.0 mL, 6.0 mmol, 1.2 equiv) in DCM (3.0 mL, 2.0 M relative to Tf_2O) was then added dropwise over 5 minutes. The reaction was allowed to warm to room temperature and stirred overnight. The reaction was cooled to 0 °C, quenched with saturated $NaHCO_{3\,(aq)}$, then extracted with ethyl acetate, dried over $MgSO_4$ and purified by column chromatography (0-2% hexanes/ethyl acetate). **1o** was isolated as a clear oil (760 mg, 54%).

Analytical Data:[13] **^{1}H NMR** (400Hz, $CDCl_3$) δ 5.70 (t, *J* = 4.1 Hz, 1H), 2.17 (td, *J* = 5.7, 4.1 Hz, 2H), 1.92–1.81 (m, 2H), 1.72–1.56 (m, 9H), 1.53–1.45 (m, 2H) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$) δ 155.0, 118.5 (d, *J* = 319.2 Hz), 116.3, 45.9, 37.5, 36.8, 25.4, 24.7, 19.6 ppm. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -74.9 ppm.



1,7,7-trimethylbicyclo[2.2.1]hept-2-en-2-yl 4-methylbenzenesulfonate (1p): Prepared by General Procedure A for the Synthesis of Alkenyl Tosylates on a 5.0 mmol scale with the following modification: the enolate was quenched with $PhNTf_2$ instead of Ts_2O. Purified by column chromatography (0-2% hexanes/ethyl acetate) to give **1p** as a clear oil (1.0 g, 72%).

Analytical Data:[17] **^{1}H NMR** (400Hz, $CDCl_3$) δ 5.67 (d, *J* = 3.8 Hz, 1H), 2.45 (t, *J* = 3.7 Hz, 1H), 1.93 (ddt, *J* = 12.2, 8.6, 3.7 Hz, 1H), 1.65 (ddd, *J* = 12.2, 8.5, 3.6 Hz, 1H), 1.33 (ddd, *J* = 12.4, 9.1, 3.6 Hz, 1H), 1.15 (ddd, *J* = 12.5, 9.1, 3.6 Hz, 1H), 1.03 (s, 3H), 0.92 (s, 3H), 0.79 (s, 3H) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$) δ 155.4, 117.8, 57.1, 54.0, 50.3, 31.0, 25.5, 19.9, 19.1, 9.6 ppm. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -73.7 ppm.



4-(tert-butyl)cyclohex-1-en-1-yl trifluoromethanesulfonate (**1j-OTf):** Prepared by General Procedure A for the Synthesis of Alkenyl Tosylates on a 4.0 mmol scale with the following modification: the enolate was quenched with $PhNTf_2$ instead of Ts_2O. Purified by column chromatography (0-1% hexanes/ethyl acetate) to give **1j-OTf** as a clear oil (770 mg, 67%).

Analytical Data:[18] **^{1}H NMR** (400 MHz, $CDCl_3$) δ 5.74 (dt, *J* = 5.2, 2.3 Hz, 1H), 2.48 – 2.27 (m, 2H), 2.27 – 2.14 (m, 1H), 2.02 – 1.87 (m, 2H), 1.45 – 1.26 (m, 2H), 0.89 (s, 9H) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$) δ149.4, 118.6, 43.1, 32.2, 28.7, 27.3, 25.5, 24.2 ppm. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -74.04 ppm.

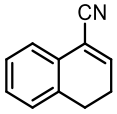
D. Procedures for the Synthesis of Alkenyl Nitriles

General Alkenyl Nitrile Synthesis A:

A flame-dried reaction tube was charged with Zn (2.5 equiv), 2-(4-methoxyphenyl)-2-methylmalononitrile (1.2 equiv), $NiBr_2$PyBOX (10 mol%) and substrate (1.0 equiv) if it was solid. The flask was sealed, back-filled 3x with nitrogen and charged with argon-sparged DMA (0.20 M vs substrate). If the substrate was an oil, it was added by dissolving it in DMA and adding it as part of the initial DMA charge. This flask was then added to a pre-heated oil bath (80 °C) and stirred (900 RPM) for 18 hours. After the allotted time, the flask was allowed to cool to room temperature, then quenched with saturated $NaHCO_{3\,(aq)}$. This was then extracted with either Et_2O or EtOAc, washed 3x with brine, then dried over $MgSO_4$. The residue was concentrated and purified by column chromatography (EtOAc / Hexanes).

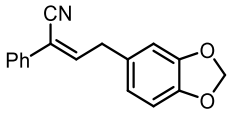
General Alkenyl Nitrile Synthesis B:

A flame-dried reaction tube was charged with Zn (2.5 equiv), 2-(4-methoxyphenyl)-2-methylmalononitrile (1.2 equiv), $NiBr_2PyBOX$ (10 mol%), tetrabutylammonium bromide (1.7 equiv) and substrate (1.0 equiv) if it was solid. The flask was sealed, back-filled 3x with nitrogen and charged with DMA (0.20 M vs substrate). If the substrate was an oil, it was added by dissolving it in DMA and adding it as part of the initial DMA charge. This flask was then added to a pre-heated oil bath (80 °C) and stirred (900 RPM) for 18 hours. After the allotted time, the flask was allowed to cool to room temperature, then quenched with saturated $NaHCO_{3\,(aq)}$. This was then extracted with either Et_2O or EtOAc, washed 3x with brine, then dried over $MgSO_4$. The residue was concentrated and purified by column chromatography (EtOAc / Hexanes).



3,4-dihydronaphthalene-1-carbonitrile (2a): Prepared by General Alkenyl Nitrile Synthesis A on a 0.40 mmol scale from **1a**. Purified by column chromatography (0-10% hexanes/ethyl acetate) to give **2a** as a clear oil (47 mg, 76%).

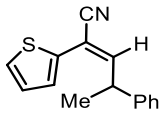
Analytical Data:[14] **^{1}H NMR** (400Hz, $CDCl_3$) δ 7.46 (dd, *J* = 7.1, 1.9 Hz, 1H), 7.32–7.23 (m, 2H), 7.18–7.13 (m, 1H), 6.89 (t, *J* = 4.8 Hz, 1H), 2.89–2.83 (m, 2H), 2.50 (ddd, *J* = 8.9, 7.8, 4.8 Hz, 2H) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$) δ 143.9, 134.3, 129.3, 128.9, 128.1, 127.4, 124.9, 117.2, 114.6, 26.2, 23.9 ppm.



4-(benzo[d][1,3]dioxol-5-yl)-2-phenylbut-2-enenitrile (2b): Prepared by General Alkenyl Nitrile Synthesis A on a 0.40 mmol scale from **1b**. Purified by column chromatography (0-10% hexanes/ethyl acetate) to give **2b** as a white solid (69 mg, 65%, >20:1 Z/E).

Analytical Data: **^{1}H NMR** (400Hz, $CDCl_3$) δ 7.58–7.52 (m, 2H), 7.43–7.33 (m, 3H), 6.88 (t, *J* = 7.9 Hz, 1H), 6.80–6.70 (m, 3H), 5.95 (s, 2H), 3.82 (d, *J* = 7.8 Hz, 2H) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$) δ 148.2, 146.8, 144.7, 133.1, 131.1, 129.3, 129.1, 125.9, 121.7, 116.7, 116.3, 109.2, 108.8, 101.2, 38.1 ppm. **IR (neat):** 1608, 1502, 1487, 1442, 1243, 1036, 925 cm^{-1}. **HRMS** m/z (DART): calcd for $C_{17}H_{14}NO_2$ ($M + H^+$) 264.10191; found 264.10200. **M.P.:** 55–56 °C.

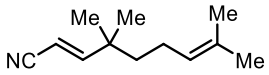
Stereochemistry of **2b** was determined by way of a NOESY spectrum. See section **G-1** for analysis.



4-phenyl-2-(thiophen-2-yl)pent-2-enenitrile (2c): Prepared by General Alkenyl Nitrile Synthesis B on a 0.40 mmol scale from **1c**. Purified by column chromatography (0-10% hexanes/ethyl acetate) to give **2c** as a clear oil (62 mg, 65%, 5:1 Z/E).

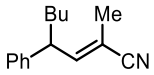
Analytical Data: **^{1}H NMR** (400Hz, $CDCl_3$) δ 7.39–7.30 (m, 3H), 7.29–7.22 (m, 2H), 7.01 (dd, *J* = 5.1, 3.7 Hz, 1H), 6.67 (d, *J* = 10.3 Hz, 1H), 4.16 (dq, *J* = 10.3, 6.9 Hz, 1H), 1.54 (d, *J* = 7.0 Hz, 3H) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$) δ 148.3, 142.8, 137.6, 129.1, 127.9, 127.3, 127.1, 126.9, 126.0, 115.7, 109.0, 42.3, 20.9 ppm. **IR (neat):** 2224, 1601, 1493, 1451, 1235, 1015 cm^{-1}. **HRMS** m/z (DART): calcd for $C_{15}H_{17}N_2S$ ($M + NH_4^+$) 257.11070; found 257.11157.

Stereochemistry of **2c** was determined by way of derivatization using a DIBAL-H reduction and a subsequent a NOESY spectrum of the resulting aldehyde containing product **2c-a**. A toluene solution of **2c** (~0.075 mmol, ~0.2 M) was cooled to -78 °C and DIBAL-H (~1.5 equivalents, 1.0 M in hexanes) was added dropwise. The reaction was allowed to stir for 4h at this temperature, then quenched with 1 M H_2SO_4 at that temperature. The reaction mixture was allowed to warm and stir overnight, then diluted with EtOAc and separated from the aqueous material. Organic solvent was removed under reduced pressure and the aldehyde **2c-a** isolated as a clear oil.



(E)-4,4,8-trimethylnona-2,7-dienenitrile (2d): Prepared by General Procedure B on a 0.40 mmol scale from **1d**. Purified by column chromatography (0-10% hexanes/ethyl acetate) to give **2d** as a clear oil (55 mg, 78%, >20:1 E/Z).

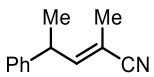
Analytical Data: **^{1}H NMR** (400Hz, $CDCl_3$) δ 6.68 (d, *J* = 16.7 Hz, 1H), 5.22 (d, *J* = 16.7 Hz, 1H), 5.08–5.00 (m, 1H), 1.92–1.82 (m, 2H), 1.68 (d, *J* = 1.3 Hz, 3H), 1.58 (s, 3H), 1.40–1.33 (m, 2H), 1.05 (s, 6H) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$) δ 164.9, 132.2, 124.0, 118.1, 96.7, 42.1, 38.2, 25.9, 25.8, 23.4, 17.8 ppm. **IR (neat):** 2966, 2921, 2870, 2223, 1628, 1456, 1100 cm^{-1}. **HRMS** m/z (DART): calcd for $C_{12}H_{20}N$ ($M + H^+$) 178.15903; found 178.15789.



2-methyl-4-phenyloct-2-enenitrile (2e): Prepared by General Alkenyl Nitrile Synthesis B on a 0.40 mmol scale from **1e**. Purified by column chromatography (0-10% hexanes/ethyl acetate) to give **2e** as a clear oil (47 mg, 55%, >20:1 E/Z).

Analytical Data: **^{1}H NMR** (400Hz, $CDCl_3$) δ 7.28–7.22 (m, 2H), 7.20–7.13 (m, 1H), 7.11–7.05 (m, 2H), 6.40 (dq, *J* = 10.1, 1.6 Hz, 1H), 3.48 (ddd, *J* = 10.1, 8.0, 6.8 Hz, 1H), 1.84 (d, J = 1.6 Hz, 3H), 1.75–1.55 (m, 2H), 1.30–1.05 (m, 4H), 0.80 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 151.6, 142.4, 129.0, 127.4, 127.0, 120.7, 108.9, 45.0, 36.0, 29.7, 22.7, 15.3, 14.1 ppm. **IR (neat):** 2958, 2930, 2860, 2217, 1495, 1453 cm^{-1}. **HRMS** m/z (DART): calcd for $C_{15}H_{20}N$ ($M + H^+$) 214.15903; found 214.15880.

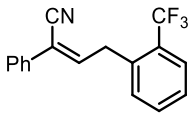
Stereochemistry of **2e** was determined by way of a NOESY spectrum. See section **G-1** for analysis.



(E/Z)-2-methyl-4-phenylpent-2-enenitrile (2f): Prepared by General Alkenyl Nitrile Synthesis B on a 0.40 mmol scale from **1f**. Purified by column chromatography (0-10% hexanes/ethyl acetate) to give **2f** as a clear oil (50 mg, 73%, 10:1 E/Z).

Analytical Data: **^{1}H NMR** (400Hz, $CDCl_3$) δ 7.36–7.29 (m, 2H), 7.28–7.21 (m, 1H), 7.21–7.16 (m, 2H), 6.46 (dq, *J* = 9.8, 1.6 Hz, 1H), 3.82–3.72 (m, 1H), 1.93 (d, *J* = 1.6 Hz, 3H), 1.39 (d, *J* = 7.0 Hz, 3H) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$) δ 152.2, 143.2, 129.0, 127.1, 127.0, 120.6, 108.4, 38.7, 21.2, 15.1 ppm. **IR (neat):** 2971, 2257, 2218, 1494, 1452 cm^{-1}. **HRMS** m/z (DART): calcd for $C_{12}H_{14}N$ ($M + H^+$) 172.11208; found 172.11140.

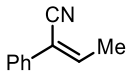
Stereochemistry of **2f** was determined by way of derivatization using a DIBAL-H reduction and a subsequent a NOESY spectrum of the resulting aldehyde containing product **2f-a**. A toluene solution of **2f** (~0.075 mmol, ~0.20 M) was cooled to -78 °C and DIBAL-H (~1.5 equivalents, 1.0 M in hexanes) was added dropwise. The reaction was allowed to stir for 4h at this temperature, then quenched with 1 M H_2SO_4 at that temperature. The reaction mixture was allowed to warm and stir overnight, then diluted with EtOAc and separated from the aqueous material. Organic solvent was removed under reduced pressure and the aldehyde **2f-a** isolated as a clear oil.



2-phenyl-4-(2-(trifluoromethyl)phenyl)but-2-enenitrile (2g): Prepared by General Alkenyl Nitrile Synthesis A on a 0.40 mmol scale from **1g**. Purified by column chromatography (0-10% hexanes/ethyl acetate) to give **2g** as a clear oil (89 mg, 77%, >20:1 Z/E).

Analytical Data: **^{1}H NMR** (400Hz, $CDCl_3$) δ 7.69 (dd, *J* = 7.9, 1.4 Hz, 1H), 7.57–7.50 (m, 3H), 7.44 (d, *J* = 7.7 Hz, 1H), 7.43–7.35 (m, 4H), 6.87 (t, *J* = 7.7 Hz, 1H), 4.10 (d, *J* = 7.7 Hz, 2H) ppm.**^{13}C NMR** (126 MHz, $CDCl_3$) δ 143.4, 136.1 (d, *J* = 1.7 Hz), 132.9, 132.6, 131.7, 129.5, 129.2, 128.6, 127.5, 126.5 (q, *J* = 5.7 Hz), 126.0, 123.2, 117.0, 116.7, 35.3 (d, *J* = 1.9 Hz) ppm. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -59.6 ppm. **IR (neat):** 2222, 1608, 1496, 1450, 1310, 1158, 1112, 1061, 1035 cm^{-1}. **HRMS** m/z (DART): calcd for $C_{17}H_{16}N_2F_3$ ($M + NH_4^+$) 305.12601; found 305.12649.

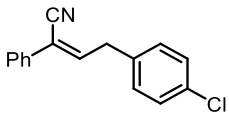
Stereochemistry of **2g** was determined by way of a NOESY spectrum. See section **G-1** for analysis.



Major Isomer

(Z/E)-2-phenylbut-2-enenitrile (2h): Prepared by General Alkenyl Nitrile Synthesis A on a 0.40 mmol scale from **1h**. Purified by column chromatography (0-10% hexanes/ethyl acetate) to give **2h** as a clear oil (34 mg, 60%, 8:1 Z/E).

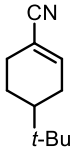
Analytical Data:[15] **^{1}H NMR** (400Hz, $CDCl_3$) δ 7.54 – 7.49 (m, 2H), 7.43–7.31 (m, 3H), 6.89 (q, *J* = 7.1 Hz, 1H), 2.22 (d, *J* = 7.1 Hz, 3H), 1.97 (d, *J* = 7.4 Hz, 1H) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$) δ 142.0, 133.5, 129.1, 129.0, 128.9, 125.7, 117.3, 18.0 ppm.



4-(4-chlorophenyl)-2-phenylbut-2-enenitrile (2i): Prepared by General Alkenyl Nitrile Synthesis A on a 0.40 mmol scale from **1i**. Purified by column chromatography (0-10% hexanes/ethyl acetate) to give **2i** as a white solid (44 mg, 43%, >20:1 Z/E).

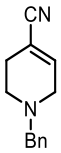
Analytical Data: **^{1}H NMR** (400Hz, $CDCl_3$) δ 7.58–7.52 (m, 2H), 7.44–7.36 (m, 3H), 7.34–7.29 (m, 2H), 7.23–7.18 (m, 2H), 6.88 (t, *J* = 7.9 Hz, 1H), 3.88 (d, *J* = 7.8 Hz, 2H) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$) δ 143.8, 136.0, 133.1, 132.9, 130.1, 129.4, 129.2, 129.2, 125.9, 116.9, 116.6, 37.7 ppm. **IR (neat):** 2220, 1597, 1492, 1448, 1408, 1091, 1015 cm^{-1}. **HRMS** m/z (DART): calcd for $C_{16}H_{16}N_2Cl$ ($M + NH_4^+$) 271.09965; found 271.10039. **M.P.:** 47 °C–48°C.

Stereochemistry of **2i** was determined by way of a NOESY spectrum. See section **G-1** for detailed analysis.



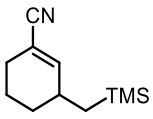
4-(tert-butyl)cyclohex-1-ene-1-carbonitrile (2j): Prepared by General Alkenyl Nitrile Synthesis B on a 0.40 mmol scale from **1j**. Purified by column chromatography (0-10% hexanes/ethyl acetate) to give **2j** as a clear oil (47 mg, 72%).

Analytical Data:[16] **^{1}H NMR** (400Hz, $CDCl_3$) δ 6.67–6.60 (m, 1H), 2.38–2.15 (m, 3H), 1.98–1.85 (m, 2H), 1.33–1.11 (m, 2H), 0.88 (s, 9H) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$) δ 145.8, 119.9, 112.3, 42.7, 32.2, 28.2, 27.7, 27.1, 23.2 ppm.



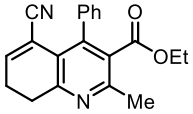
1-benzyl-1,2,3,6-tetrahydropyridine-4-carbonitrile (2k): Prepared by General Alkenyl Nitrile Synthesis B on a 0.40 mmol scale from **1k**. Purified by column chromatography (0-10% hexanes/ethyl acetate) to give **2k** as a white solid (56 mg, 70%).

Analytical Data: **^{1}H NMR** (400Hz, $CDCl_3$) δ 7.36–7.27 (m, 5H), 6.55 (tt, *J* = 3.6, 1.8 Hz, 1H), 3.60 (s, 2H), 3.12 (dt, *J* = 3.7, 3.0 Hz, 2H), 2.62 (t, *J* = 5.6 Hz, 2H), 2.36 (ttd, *J* = 5.7, 2.9, 1.7 Hz, 2H) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$) δ 142.5, 137.5, 129.1, 128.6, 127.6, 118.9, 110.9, 62.4, 52.6, 48.5, 27.8 ppm. **IR (neat):** 2917, 2804, 2216, 1646, 1454 cm^{-1}. **HRMS** m/z (DART): calcd for $C_{13}H_{15}N_2$ ($M + H^+$) 199.12297; found 199.12263. **M.P.:** 33–34 °C.



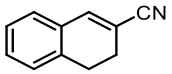
3-((trimethylsilyl)methyl)cyclohex-1-ene-1-carbonitrile (2l): Prepared by General Alkenyl Nitrile Synthesis B on a 0.40 mmol scale from **1l**. Purified by column chromatography (0-10% hexanes/ethyl acetate) to give **2l** as a clear oil (50 mg, 65%).

Analytical Data: **^{1}H NMR** (400Hz, $CDCl_3$) δ 6.46 (dtd, *J* = 2.8, 1.9, 0.7 Hz, 1H), 2.38–2.26 (m, 1H), 2.20–2.13 (m, 2H), 1.89–1.74 (m, 2H), 1.63–1.49 (m, 1H) 1.28–1.17 (m, 1H), 0.71 (dd, *J* = 14.7, 6.5 Hz, 1H), 0.59 (dd, *J* = 14.7, 8.4 Hz, 1H), 0.04 (s, 9H) ppm.**^{13}C NMR** (126 MHz, $CDCl_3$) δ 151.9, 120.0, 111.1, 32.7, 30.7, 26.6, 23.5, 20.6, -0.6 ppm. **IR (neat):** 2943, 2901, 2873, 2215, 1631, 1248 cm^{-1}. **HRMS** m/z (DART): calcd for $C_{11}H_{20}NSi$ ($M + H^+$) 194.13595; found 194.13539.



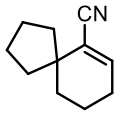
ethyl 5-cyano-2-methyl-4-phenyl-7,8-dihydroquinoline-3-carboxylate (2m): Prepared by General Alkenyl Nitrile Synthesis A on a 0.40 mmol scale from **1m**. Purified by column chromatography (0-10% hexanes/ethyl acetate) to give **2m** as a white solid (98 mg, 77%).

Analytical Data: **^{1}H NMR** (400Hz, $CDCl_3$) δ 7.43–7.32 (m, 3H), 7.21–7.16 (m, 2H), 6.92 (t, *J* = 5.1 Hz, 1H), 3.93 (q, *J* = 7.1 Hz, 2H), 2.99 (t, *J* = 8.1 Hz, 2H), 2.51 (s, 3H), 0.86 (t, *J* = 7.1 Hz, 3H) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$) δ 167.8, 157.3, 154.0, 148.4, 144.3, 135.2, 129.6, 129.5, 129.3, 128.5, 120.9, 115.7, 112.5, 61.6, 30.4, 23.3, 22.6, 13.7 ppm. **IR (neat):** 2222, 1721, 1550, 1264, 1215, 1179, 1082 cm^{-1}. **HRMS** m/z (DART): calcd for $C_{20}H_{19}N_2O_2$ ($M + H^+$) 319.14410; found 319.14474. **M.P.:** 113 °C–114°C



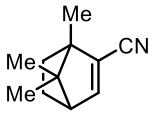
3,4-dihydronaphthalene-2-carbonitrile (2n): Prepared by General Alkenyl Nitrile Synthesis A on a 0.40 mmol scale from **1n**. Purified by column chromatography (0-10% hexanes/ethyl acetate) to give **2n** as a clear oil (62 mg, 76%).

Analytical Data:[14] **^{1}H NMR** (400Hz, $CDCl_3$) δ 7.24–7.13 (m, 2H), 7.12–7.05 (m, 3H), 2.83 (t, *J* = 8.3 Hz, 2H), 2.47 (ddd, *J* = 9.6, 7.4, 1.6 Hz, 2H) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$) δ 141.8, 135.5, 131.3, 130.4, 128.1, 127.3, 119.8, 109.8, 26.8, 24.8 ppm.



spiro[4.5]dec-6-ene-6-carbonitrile (2o): Prepared by General Alkenyl Nitrile Synthesis A on a 0.40 mmol scale from **1o** with the following modification: the reaction was performed at 100 °C for the noted duration. Purified by column chromatography (0-10% hexanes/ethyl acetate) to give **2o** as a clear oil (33 mg, 51%).

Analytical Data: **^{1}H NMR** (400Hz, $CDCl_3$) δ 6.55 (t, *J* = 4.1 Hz, 1H), 2.13 (td, *J* = 6.1, 4.0 Hz, 2H), 1.87–1.73 (m, 3H), 1.70–1.58 (m, 3H), 1.58–1.49 (m, 4H) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$) δ 144.4, 122.6, 119.1, 43.9, 39.0, 34.7, 26.1, 24.9, 19.2 ppm. **IR (neat):** 2941, 2867, 2209, 1626, 1447, 1424, 945 cm^{-1}. **HRMS** m/z (DART): calcd for $C_{11}H_{19}N_2$ ($M + NH_4^+$) 179.15428; found 179.15361.



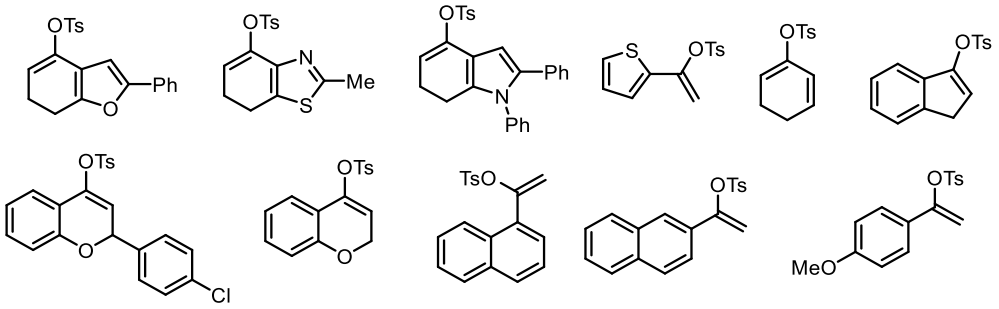
1,7,7-trimethylbicyclo[2.2.1]hept-2-ene-2-carbonitrile (2p): Prepared by General Alkenyl Nitrile Synthesis A on a 0.40 mmol scale from **1p** with the following modification: the reaction was performed at 100 °C for the noted duration. Purified by column chromatography (0-10% hexanes/ethyl acetate) to give **2p** as a white solid (32 mg, 50%).

Analytical Data:[16] **^{1}H NMR** (400Hz, $CDCl_3$) δ 6.87 (d, *J* = 3.4 Hz, 1H), 2.52 (t, *J* = 3.7 Hz, 1H), 1.96 (ddt, *J* = 12.5, 8.8, 3.8 Hz, 1H), 1.68 (ddd, *J* = 12.1, 8.7, 3.5 Hz, 1H), 1.18 (s, 3H), 1.14 (dd, *J* = 12.3, 3.4 Hz, 1H), 1.03 (ddd, *J* = 12.6, 9.2, 3.6 Hz, 1H), 0.82 (d, *J* = 9.8 Hz, 6H) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$) δ 151.7, 122.4, 116.4, 57.9, 56.0, 53.0, 30.9, 23.9, 19.3, 19.2, 11.6 ppm.

E. Unstable/Unsuccessful Alkenyl Tosylate Substrates

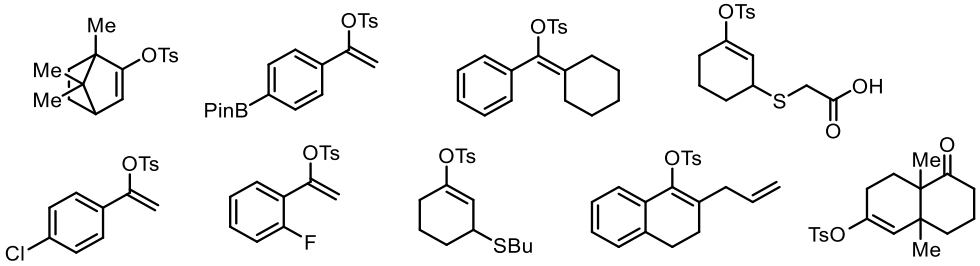
A. Unstable Alkenyl Tosylates

The following alkenyl tosylates were found to decompose to some extent on concentration at ambient temperature following synthesis, before or during purification using the appropriate **General Alkenyl Nitrile** synthesis.



B. Unsuccessful Substrate attempts

The following alkenyl tosylates did not give any product after being subject to both **General Alkenyl Nitrile Synthesis A** and **General Alkenyl Nitrile Synthesis B:**



F. References:

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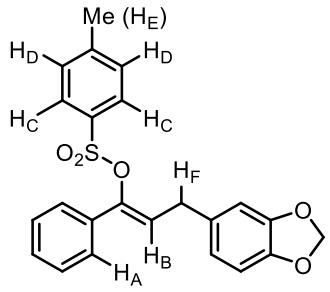
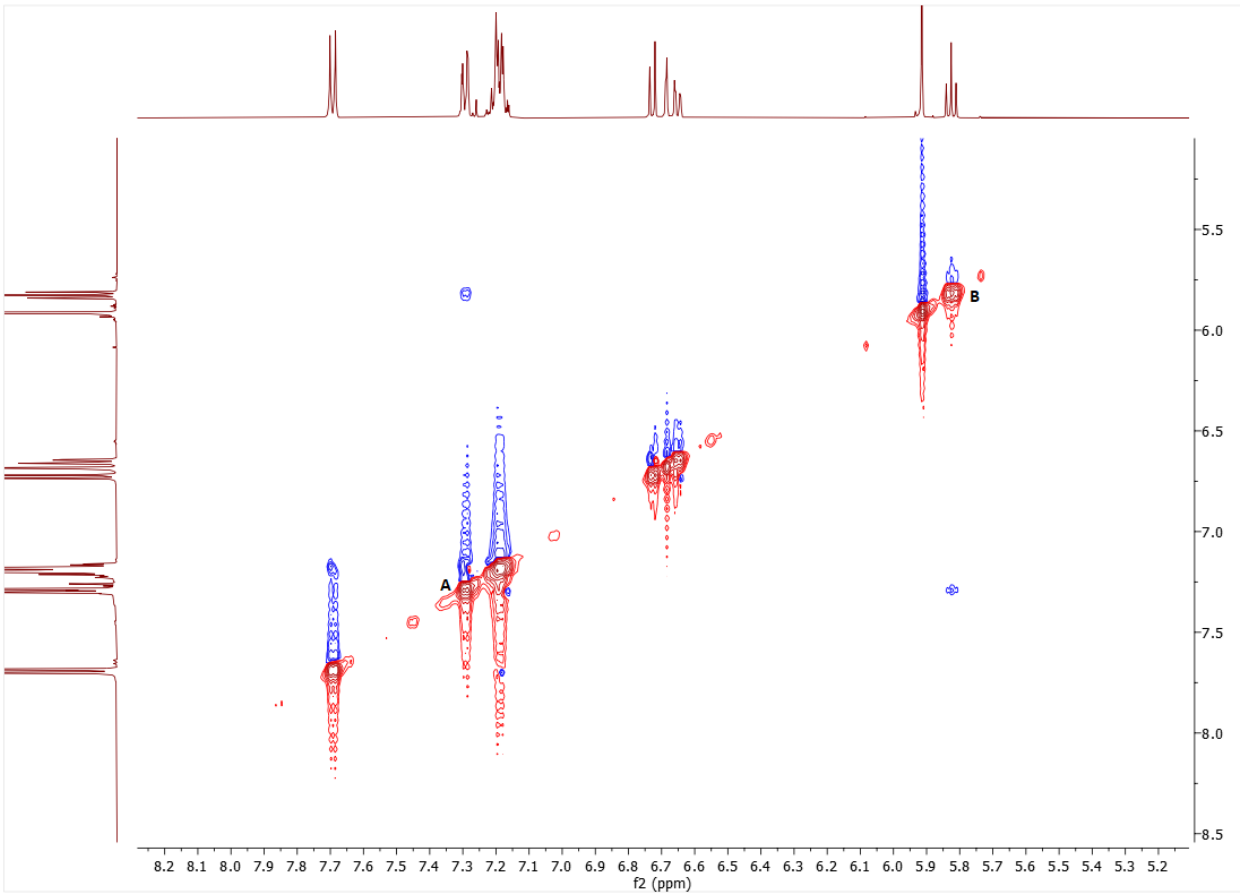
G. ^{1}H and ^{13}C NMR Spectra:

G-1: NOESY stereochemical determinations

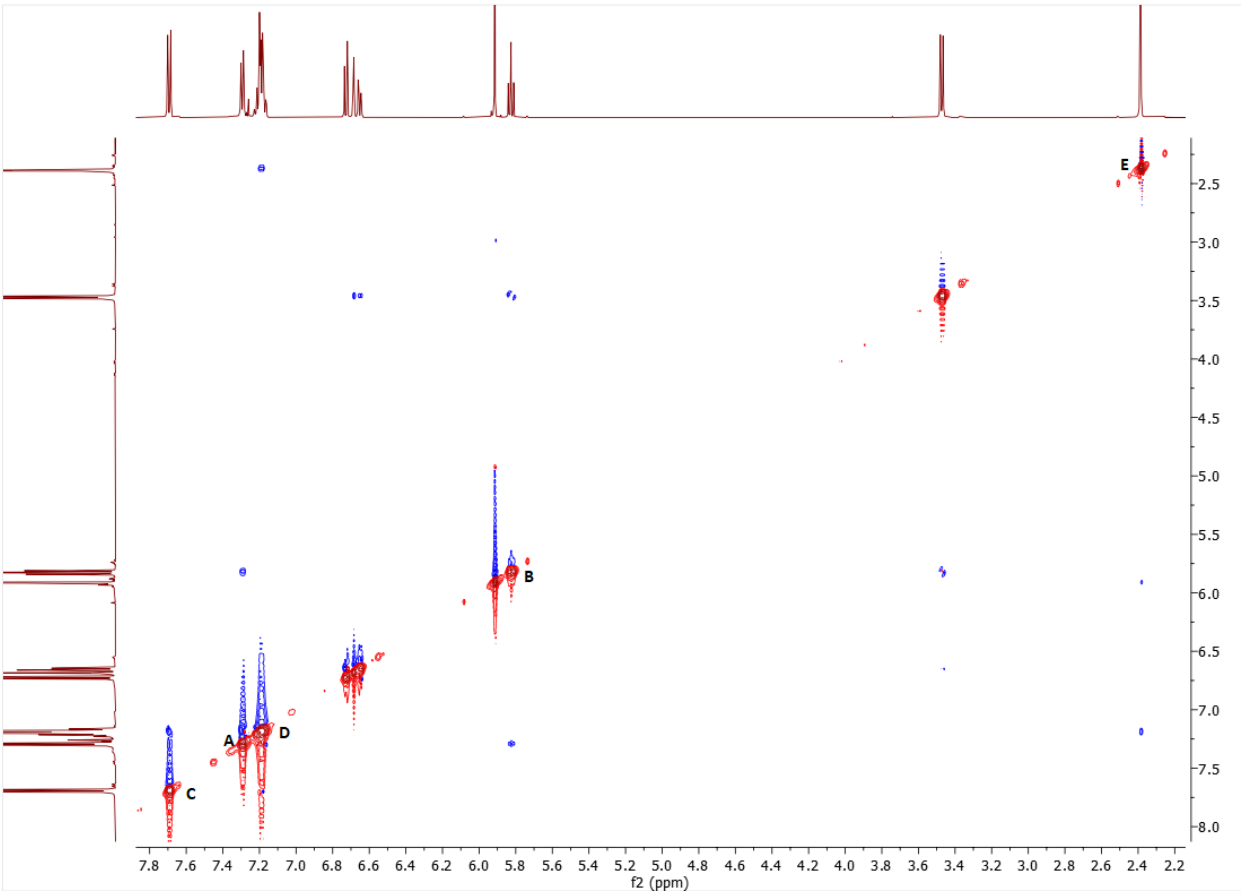


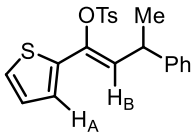
1b

For compound **1b**, nOe correlation between vinyl H_B and aryl H_A observed, which confirms Z stereochemistry (See spectrum below).



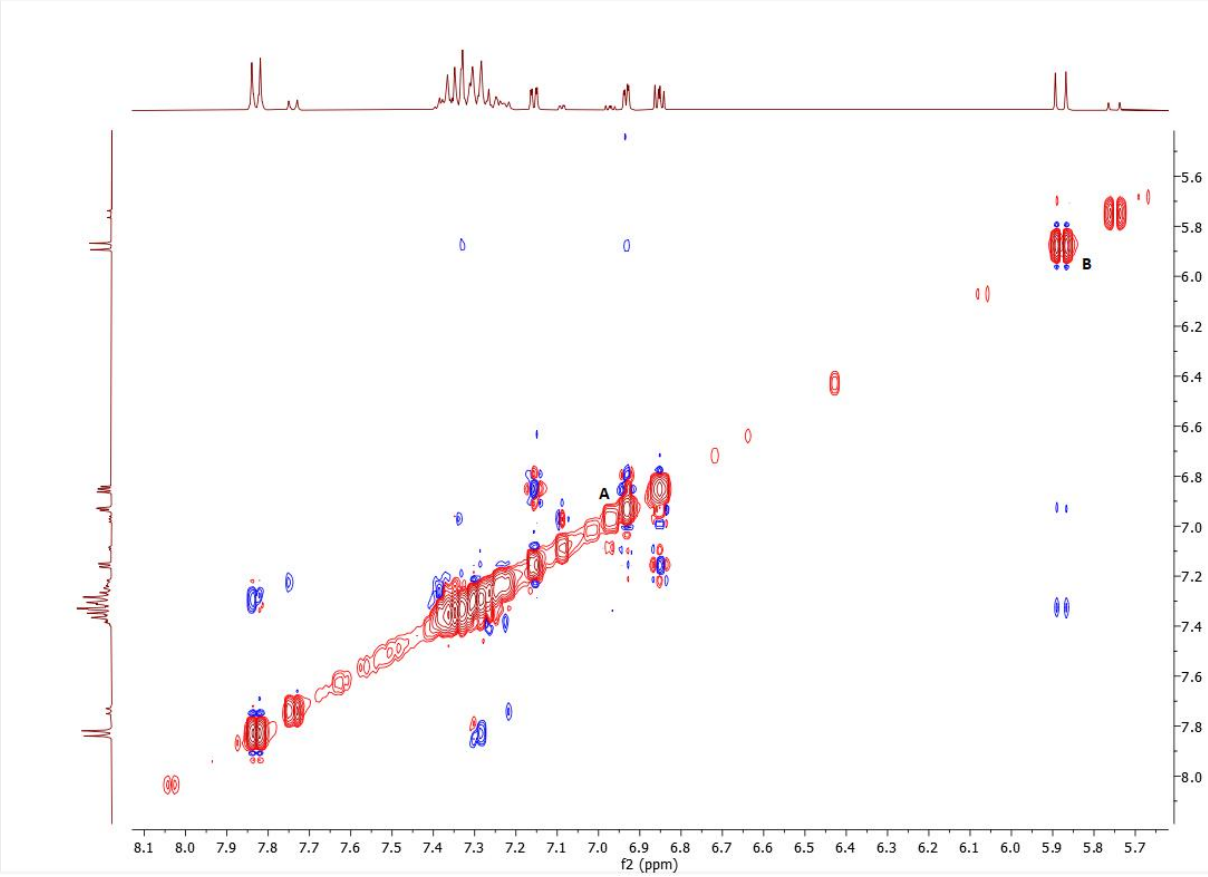
For compound **1b**, nOe correlation between methyl H_E and tosyl H_D confirms that the diagnostic signal mentioned above is not between vinyl H_B and a tosyl hydrogen (See spectrum below).

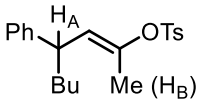




1c

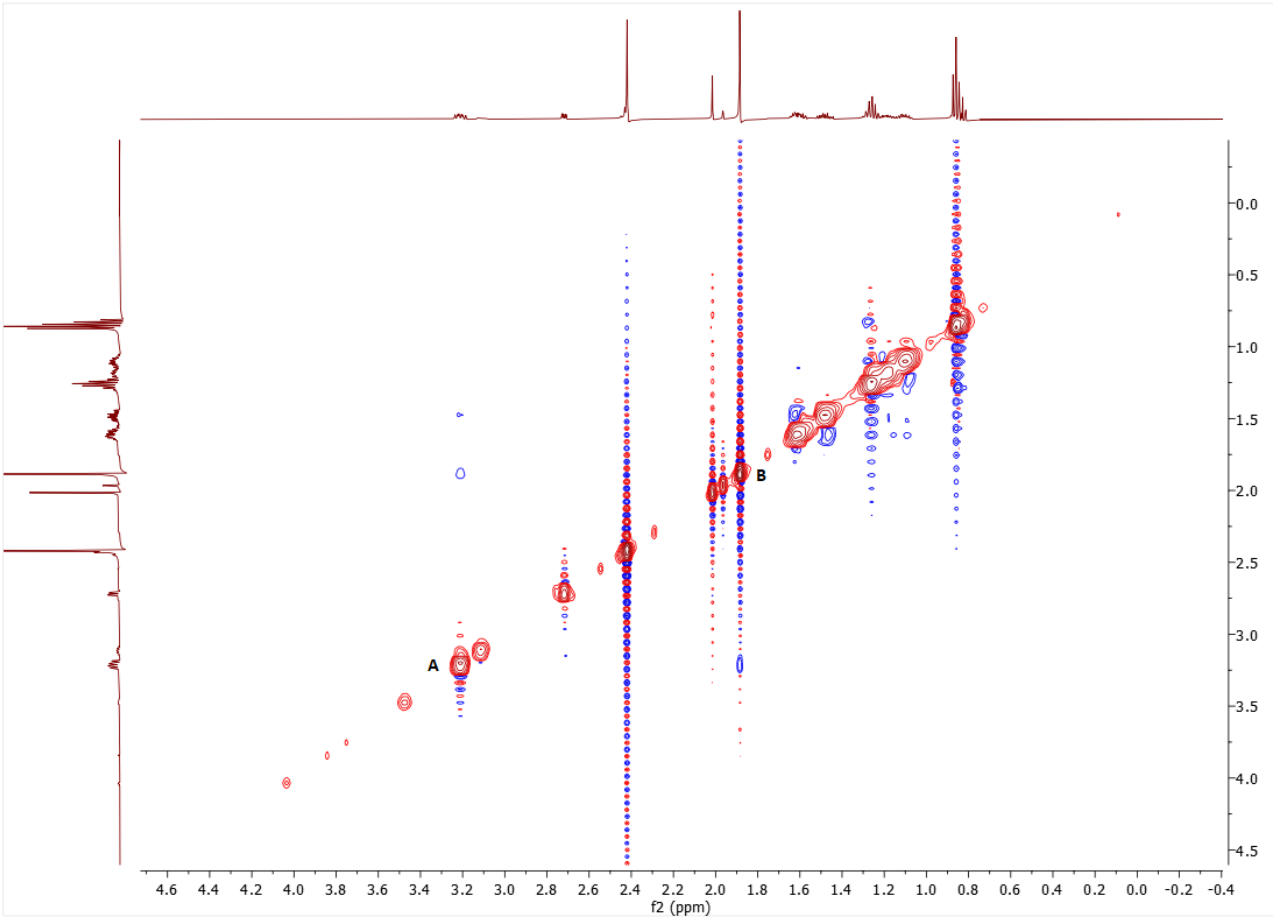
For compound **1c**, nOe correllation between H_A of the thiophene ring and alkene proton H_B is observed, indicating Z stereochemistry of the alkene (See spectrum below).

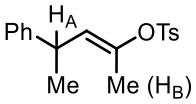




1e

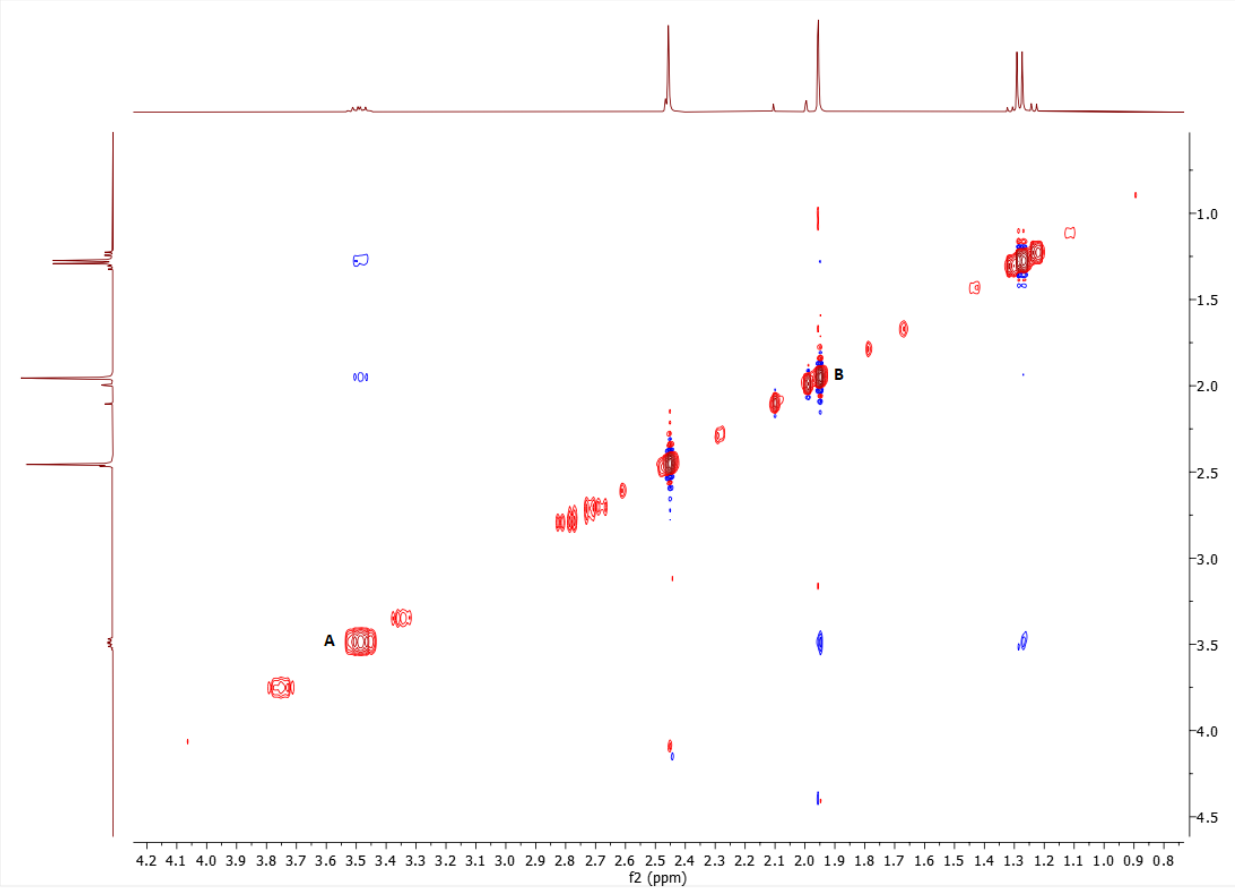
For compound **1e**, nOe between allylic methyl protons and benzylic protons observed. Confirms E geometry around alkene (See spectrum below).

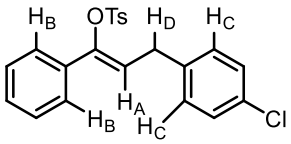




1f

For compound **1f**, nOe between benzylic H_A and allylic H_B observed. Confirms E geometry around alkene (See spectrum below).

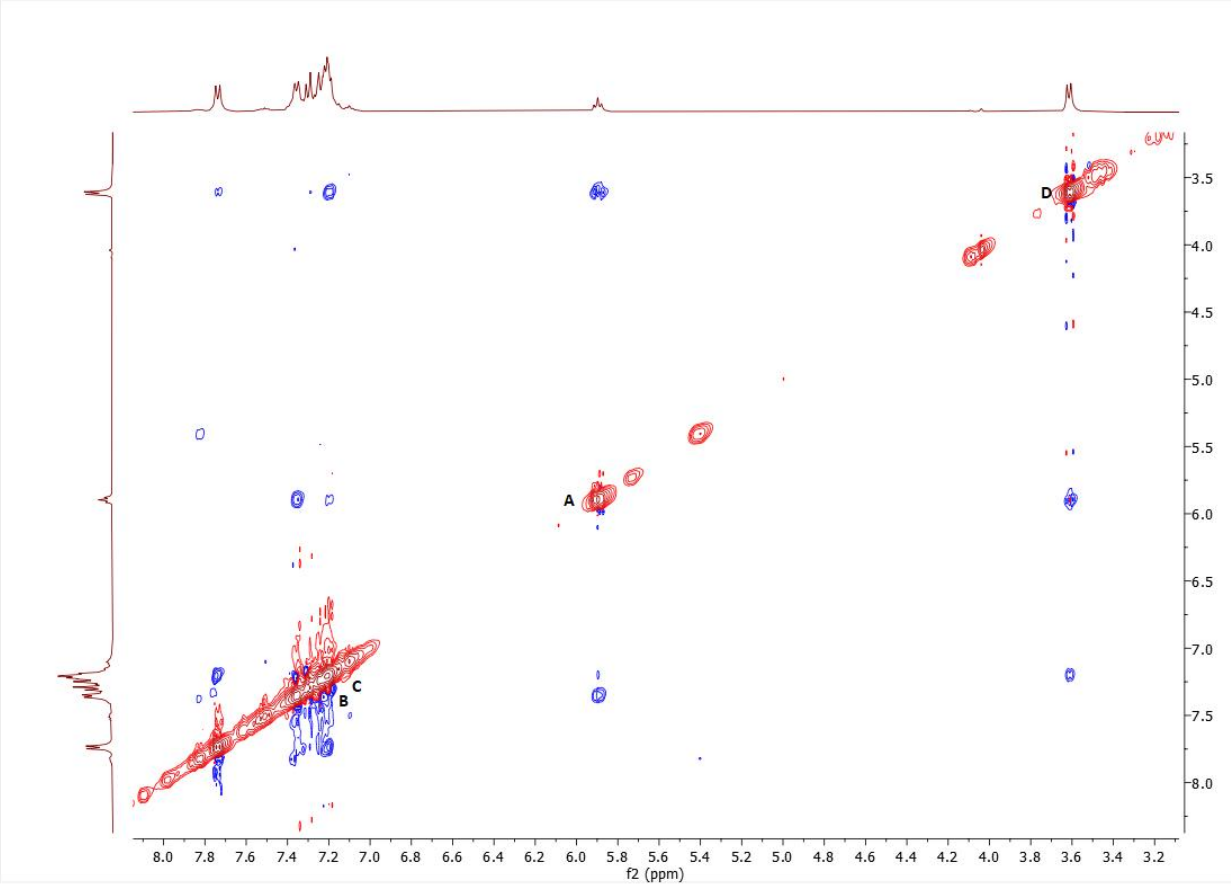


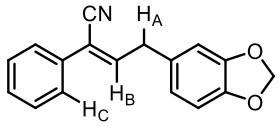


1i

For compound **1i**, nOe observed between vinyl H_A and aryl H_B, which confirms Z geometry. This diagnostic nOe is not due to an nOe between vinyl H_A and aryl H_C interaction, as the

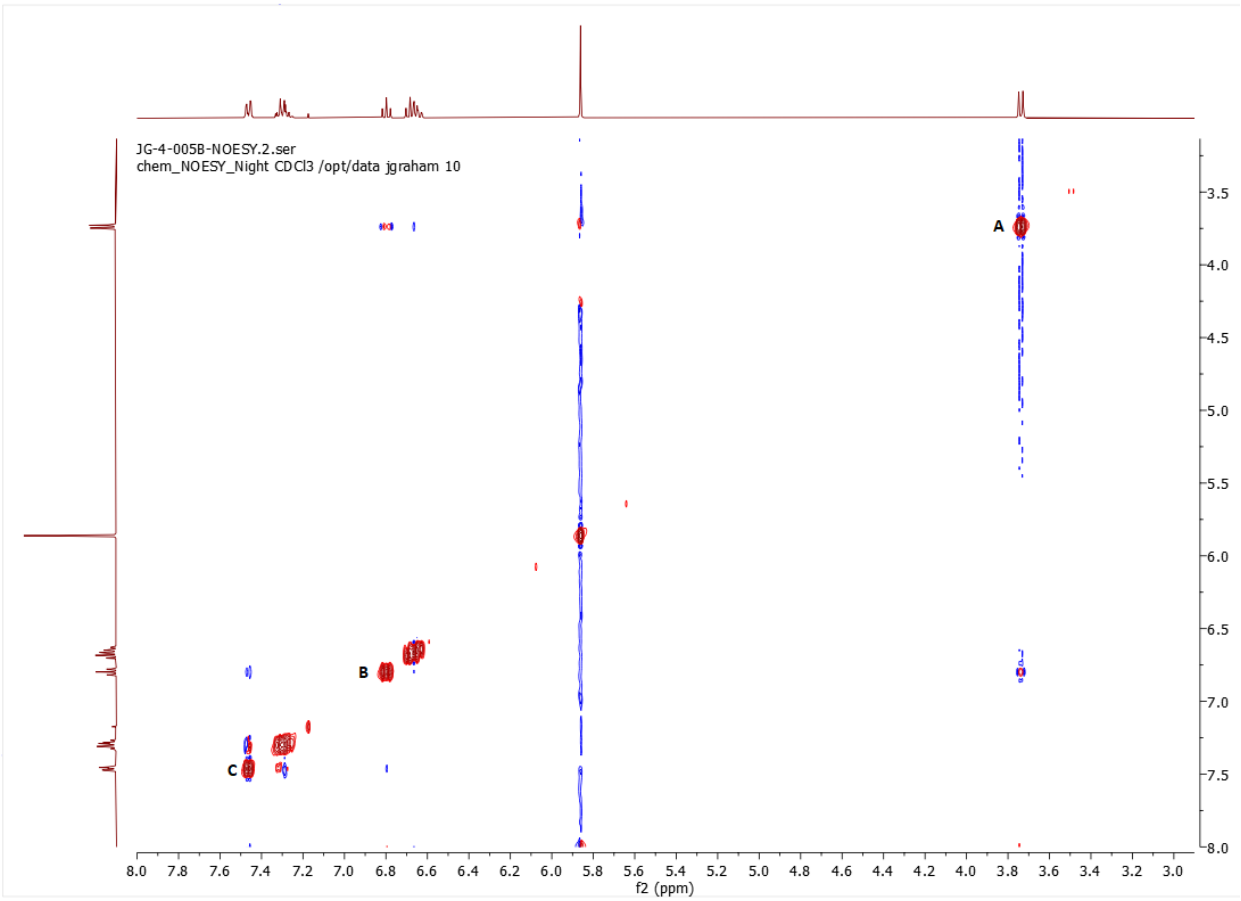
benzylic H_D and aryl H_C nOe confirms that H_C and H_B do not overlap (See spectrum below).

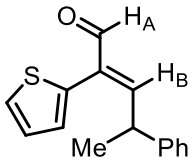




2b

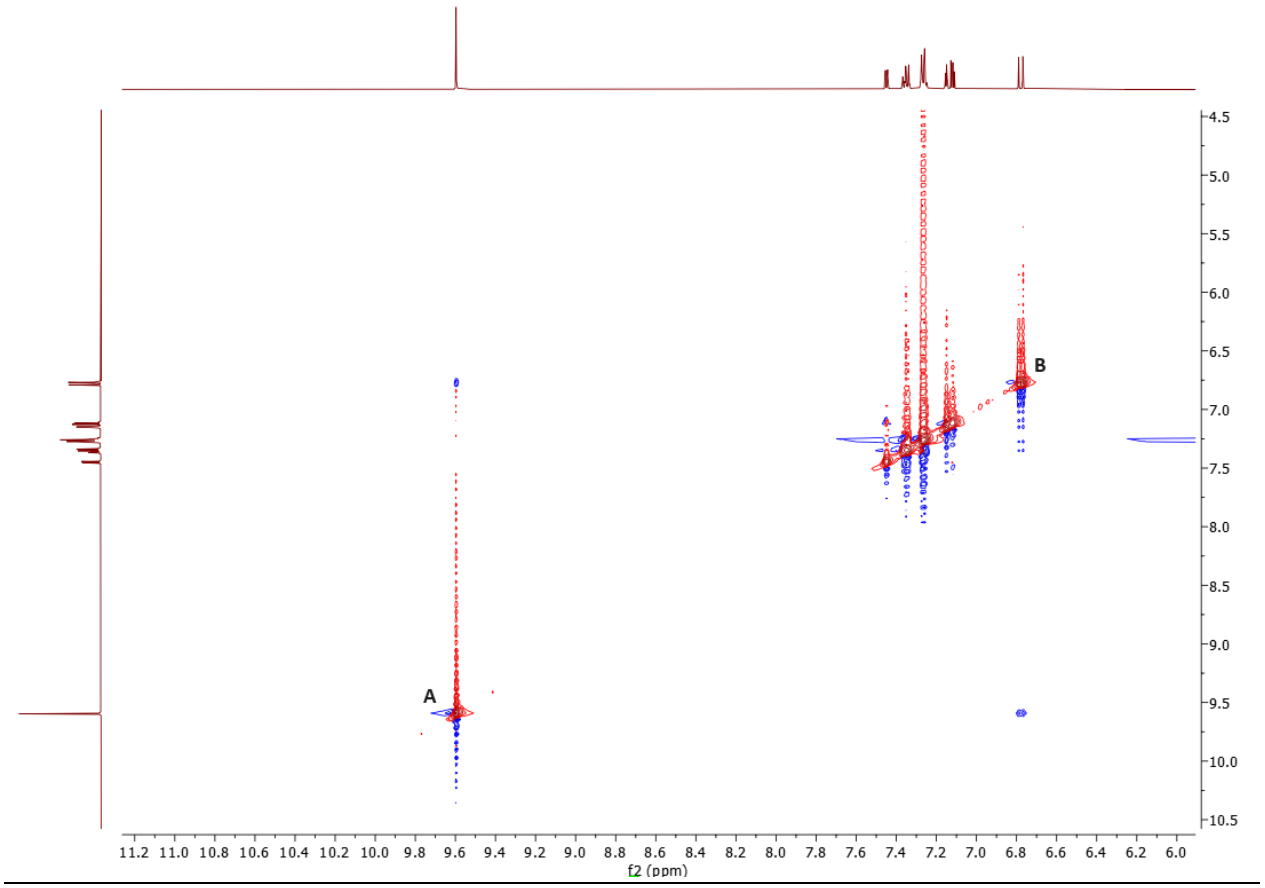
For compound **2b**, nOe observed between vinyl H_B and H_C confirms Z geometry of alkene. nOe observed with H_A confirms identity of H_B (See spectrum below).

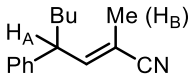




2c-a

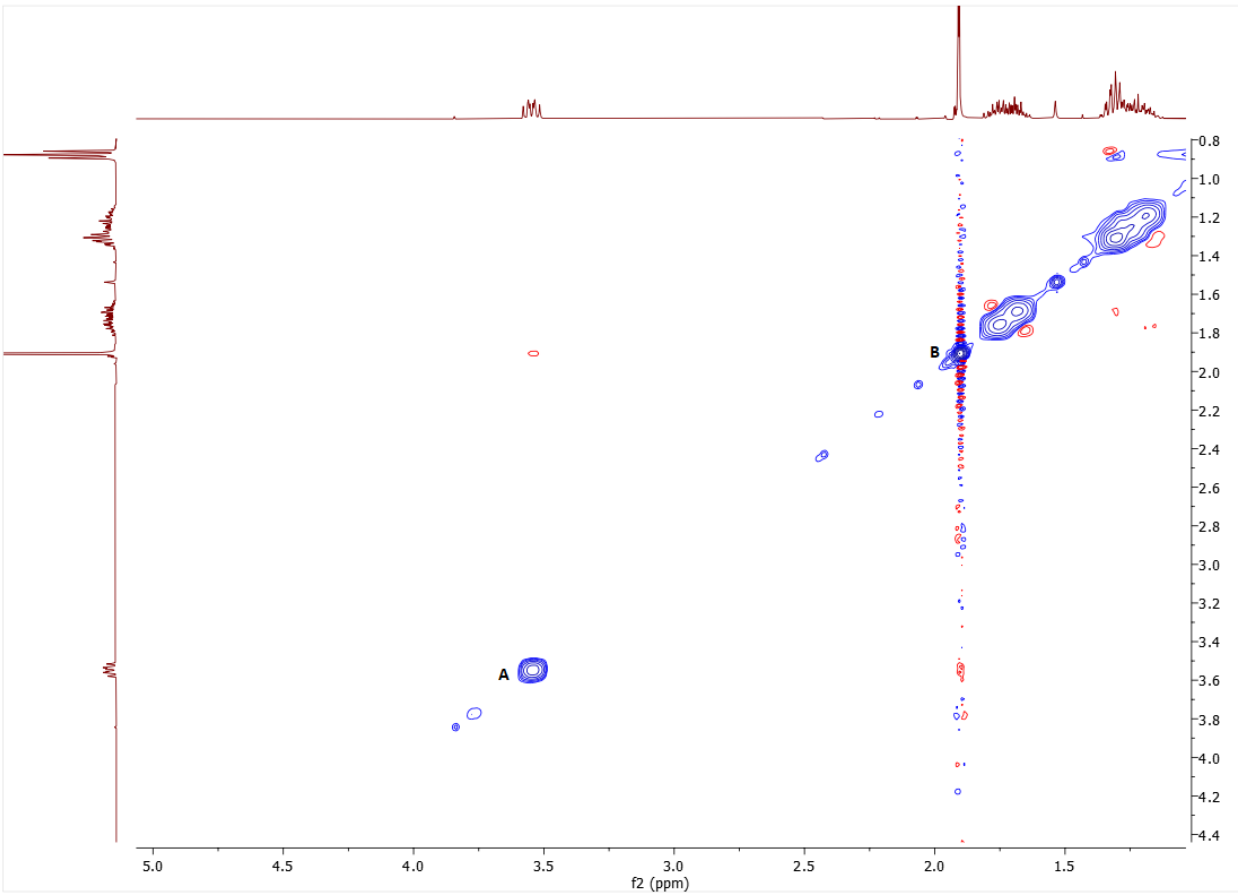
For compound **2c-a**, nOe observed between aldehyde proton H_A and alkene proton H_B confirms Z geometry around alkene (See spectrum below).

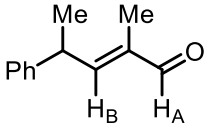




2e

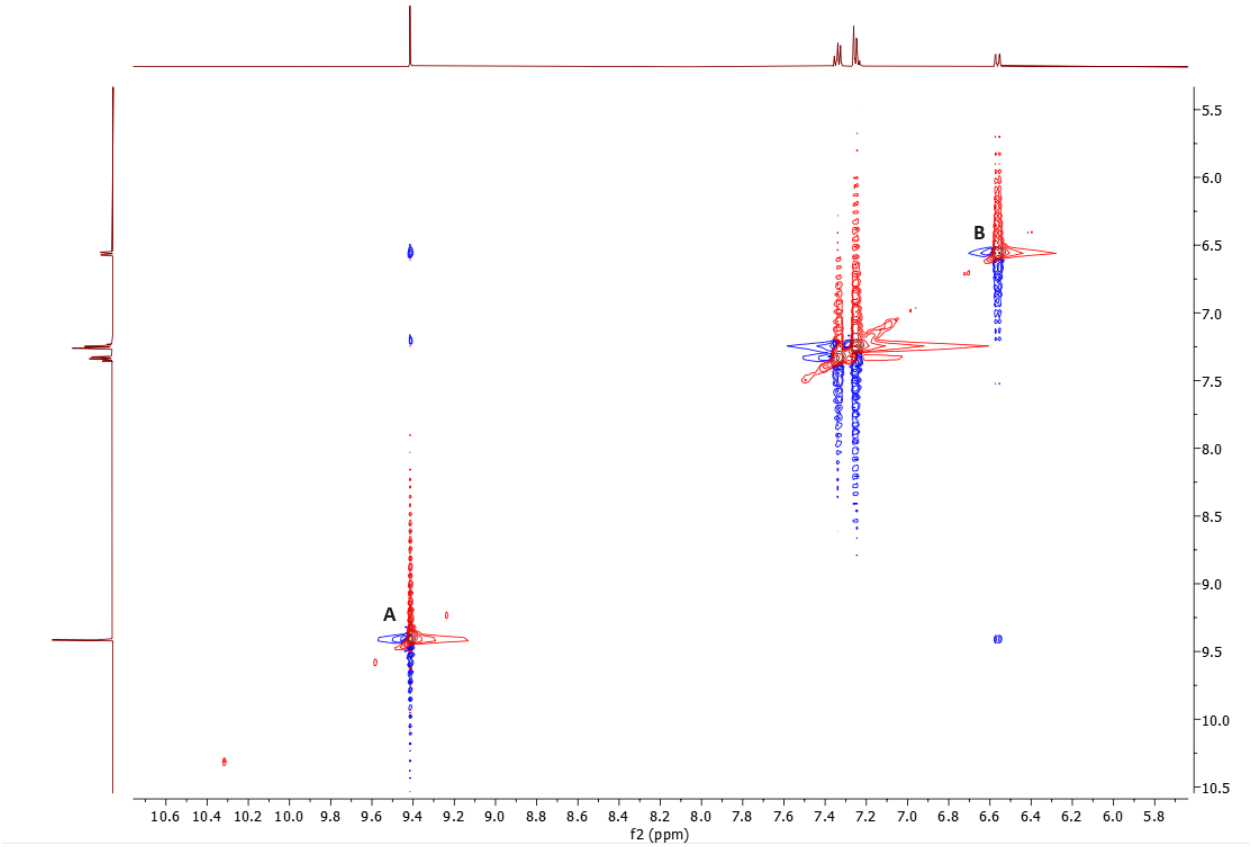
For compound **2e**, nOe between benzylic H_A and methyl H_B confirms the E geometry of the alkene (See spectrum below).

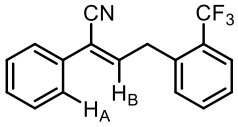




2f-a

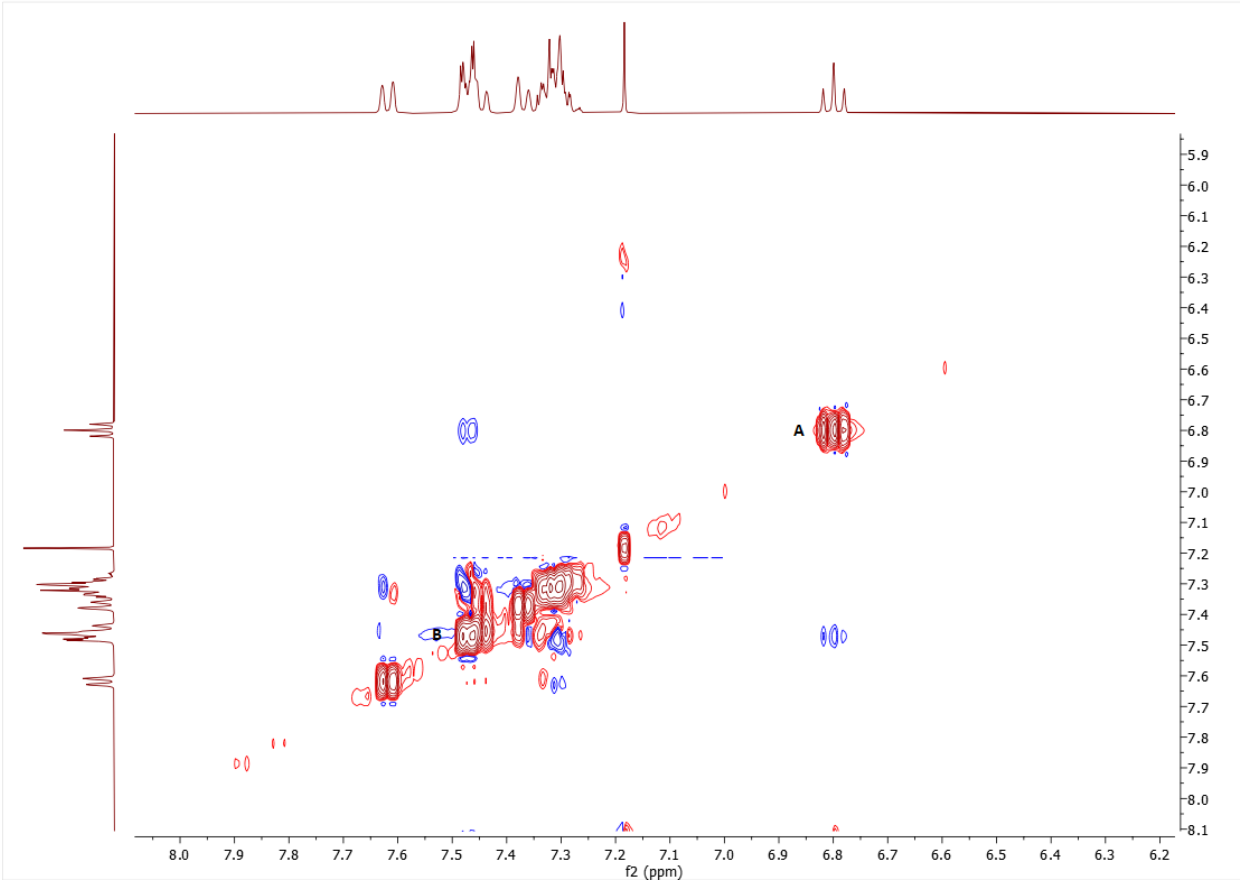
For compound **2f-a**, nOe between aldehyde H_A and alkene H_B confirms E geometry around the alkene (See spectrum below).

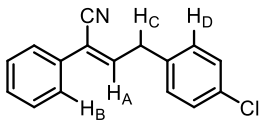




2g

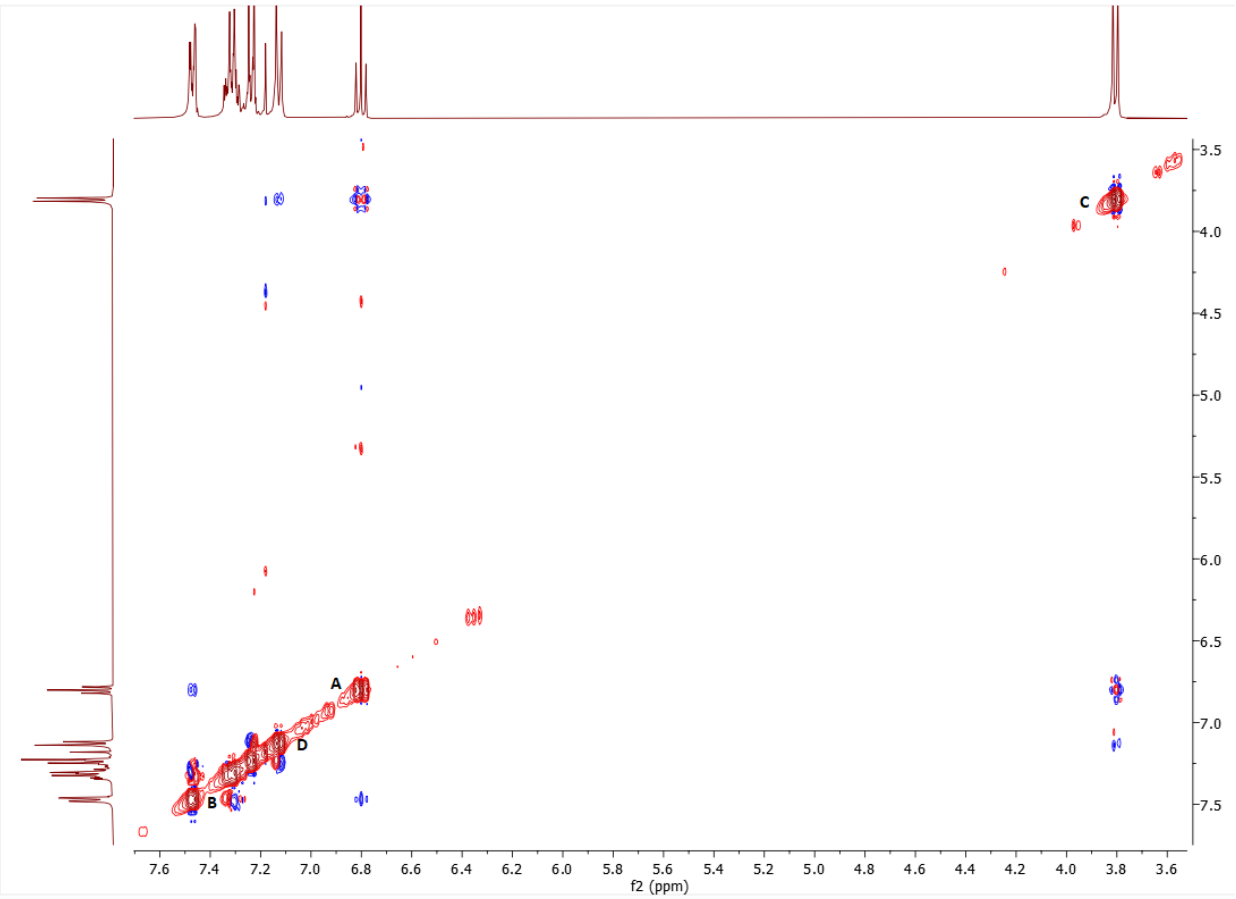
For compound **2g**, nOe between vinyl H_A and H_B confirms Z geometry of the alkene (See spectrum below).



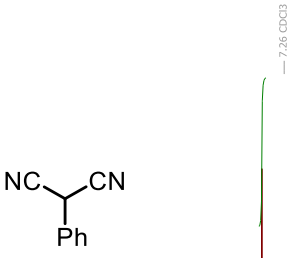


2i

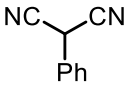
For compound **2i**, nOe between vinyl H_A and phenyl H_B confirms the Z stereochemistry around the alkene. nOe between H_C and H_D confirms that designation of H_B (See spectrum below).


A
B
C
D
7.6
7.4
7.2
7.0
6.8
6.6
6.4
6.2
6.0
5.8
5.6
5.4
5.2
5.0
4.8
4.6
4.4
4.2
4.0
3.8
3.6
f2 (ppm)
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5

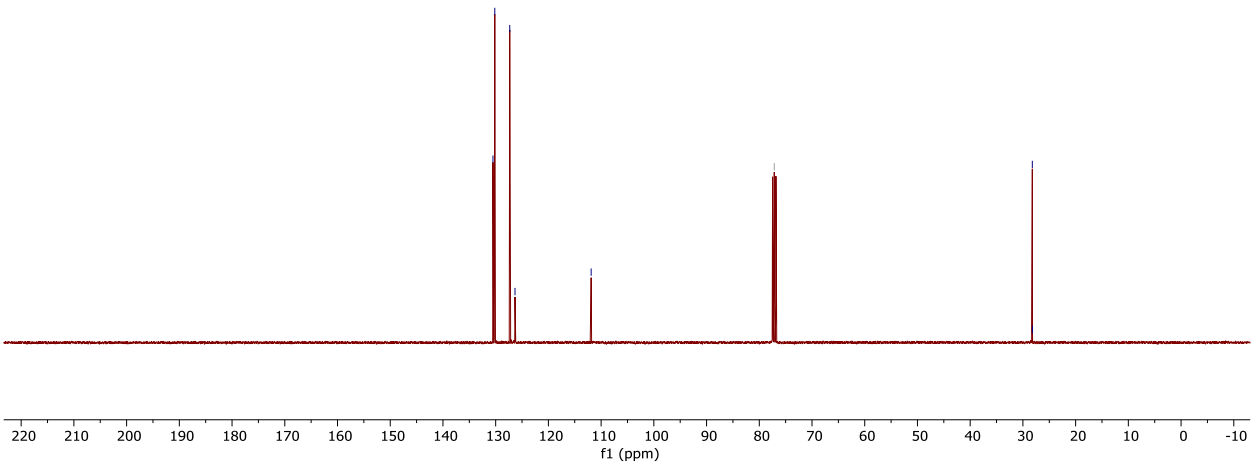
G-2: NMR Spectra

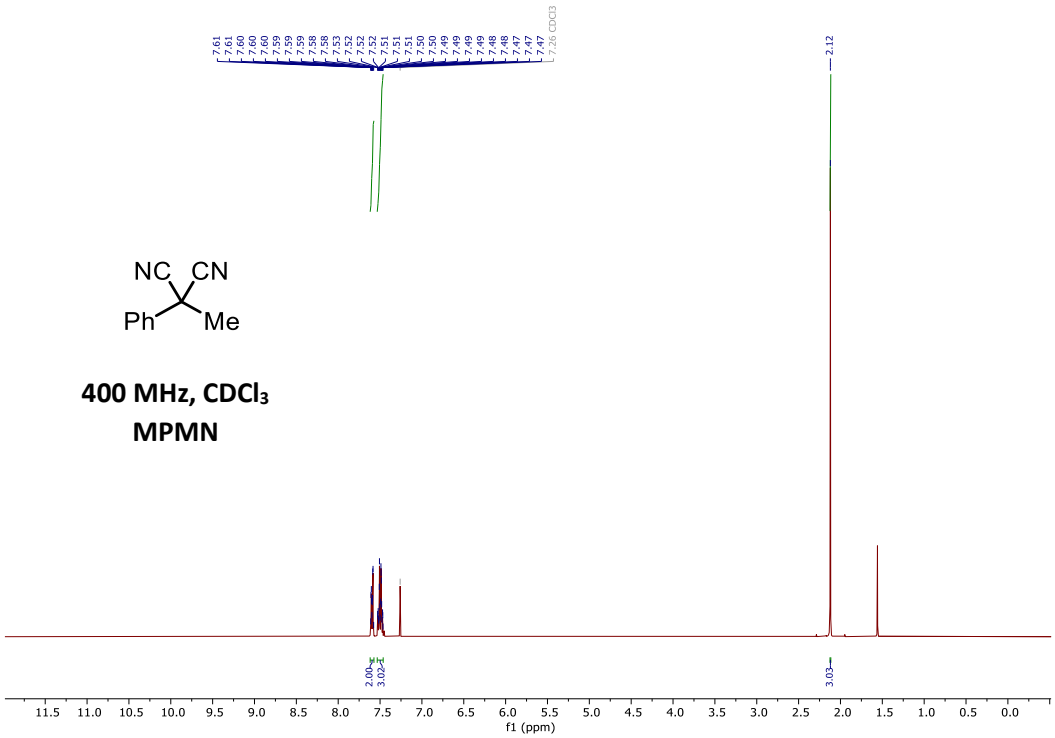


400 MHz, $CDCl_3$, phenylmalononitrile

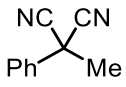


100 MHz, $CDCl_3$, phenylmalononitrile

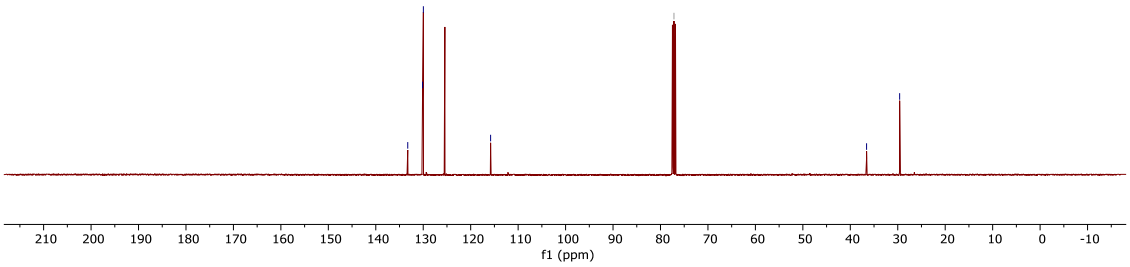


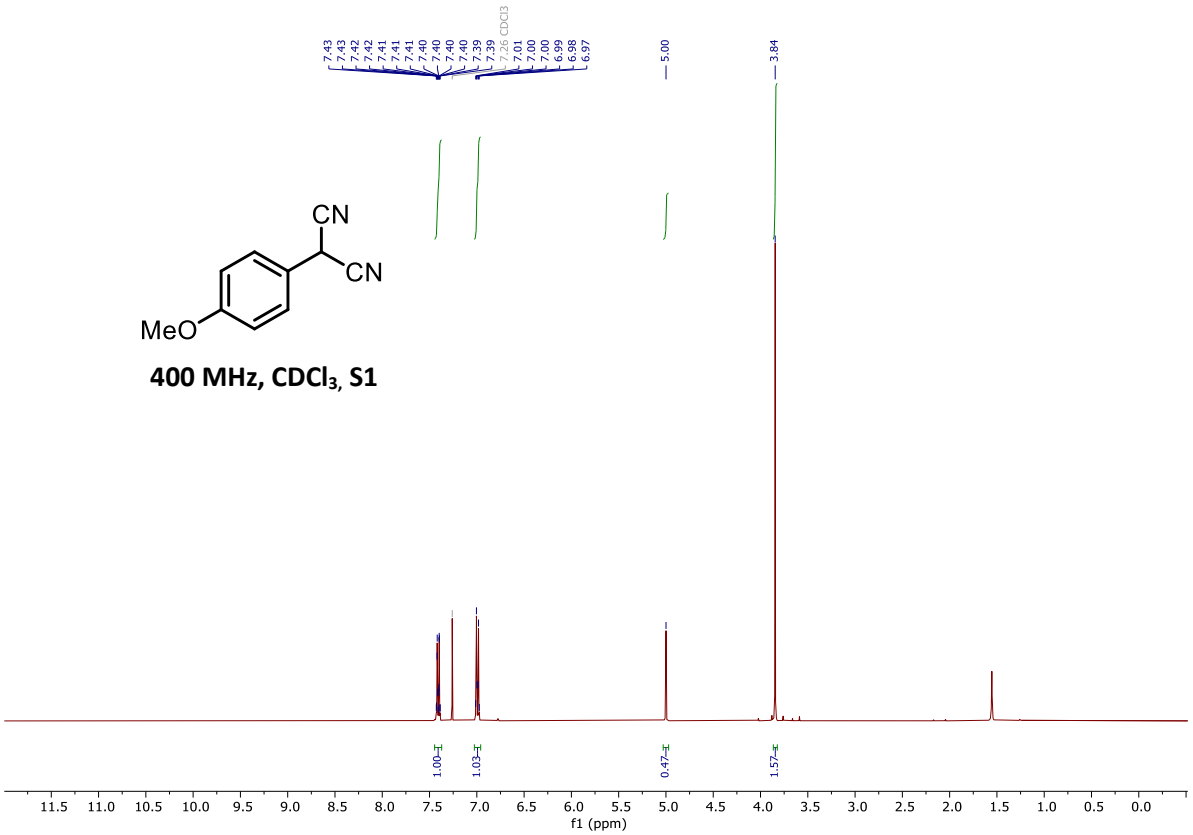


400 MHz, $CDCl_3$
MPMN

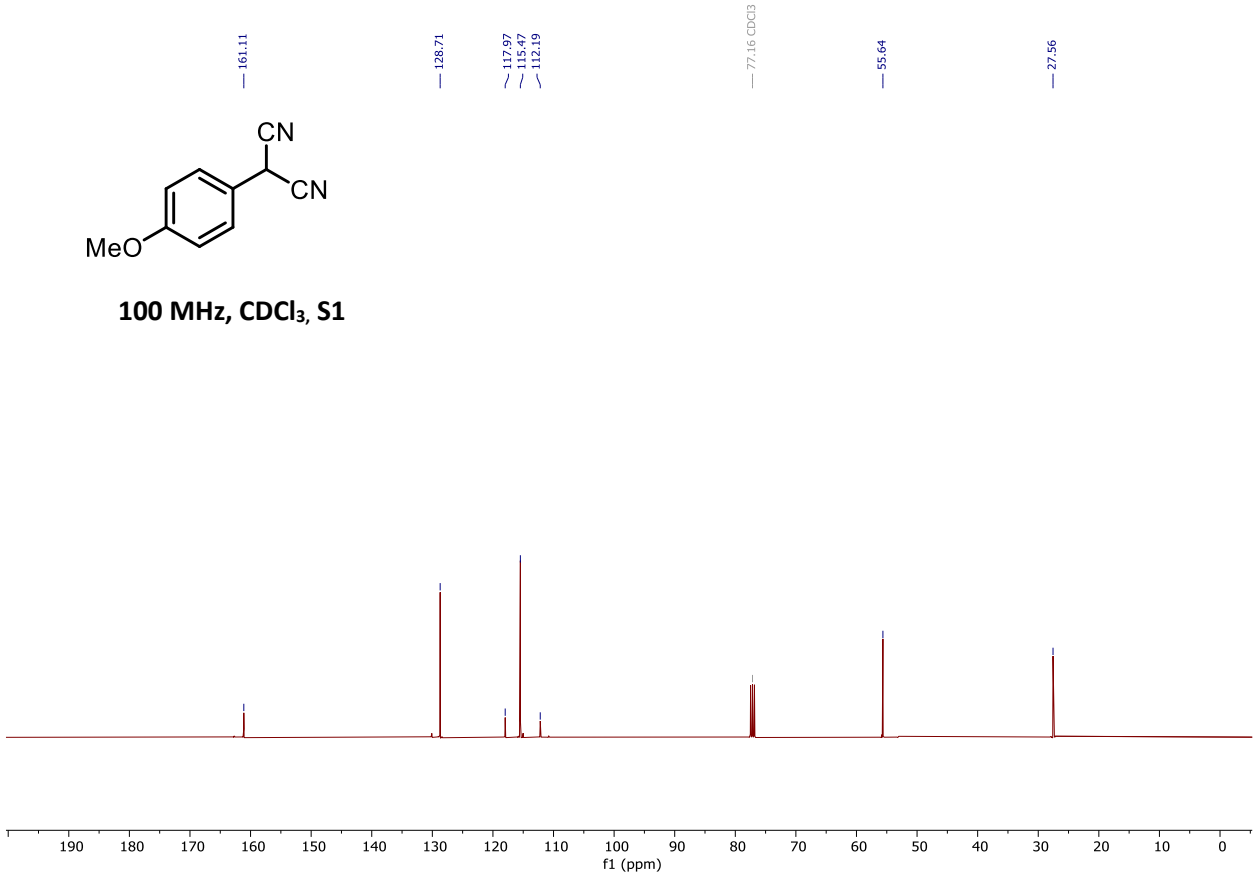


100 MHz, $CDCl_3$
MPMN

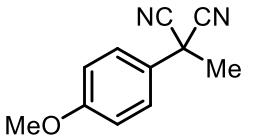




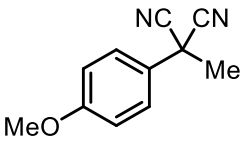
400 MHz, $CDCl_3$, S1



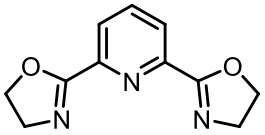
100 MHz, $CDCl_3$, S1



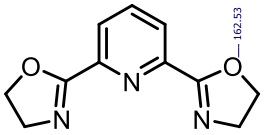
400 MHz, $CDCl_3$
MeOMPMN



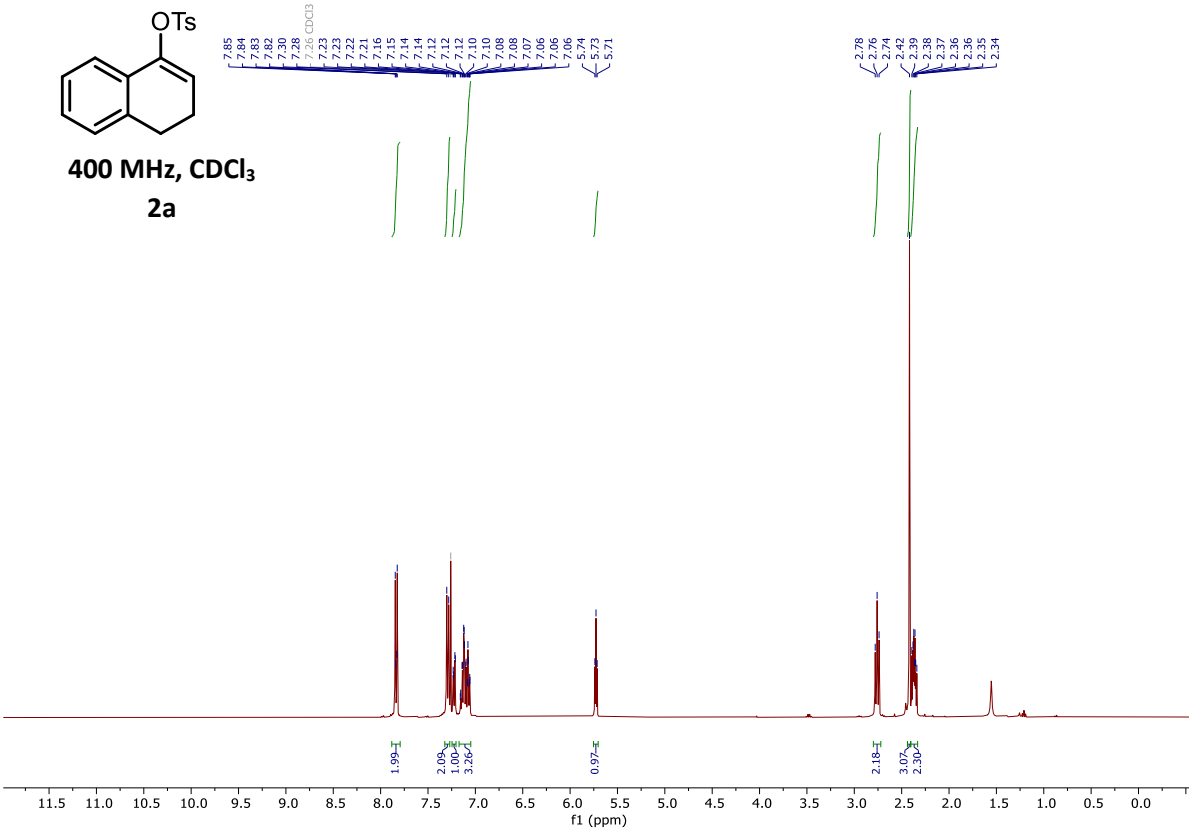
100 MHz, $CDCl_3$
MeOMPMN

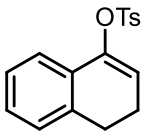


400 MHz, DMSO-d$_6$
Pybox



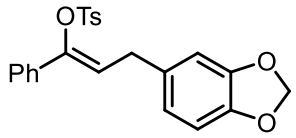
100 MHz, DMSO-d$_6$
Pybox


OTs
400 MHz, CDCl3
2a
7.85
7.84
7.83
7.82
7.30
7.28
7.26 CDCl3
7.23
7.23
7.22
7.21
7.16
7.15
7.14
7.14
7.12
7.12
7.12
7.10
7.08
7.08
7.07
7.06
7.06
7.06
5.74
5.73
5.71
2.78
2.76
2.74
2.42
2.39
2.38
2.37
2.36
2.36
2.35
2.34
1.99
2.09
1.08
3.26
0.97
2.18
3.07
2.30
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)



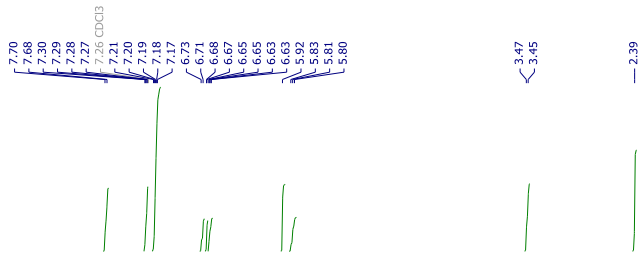
100 MHz, $CDCl_3$

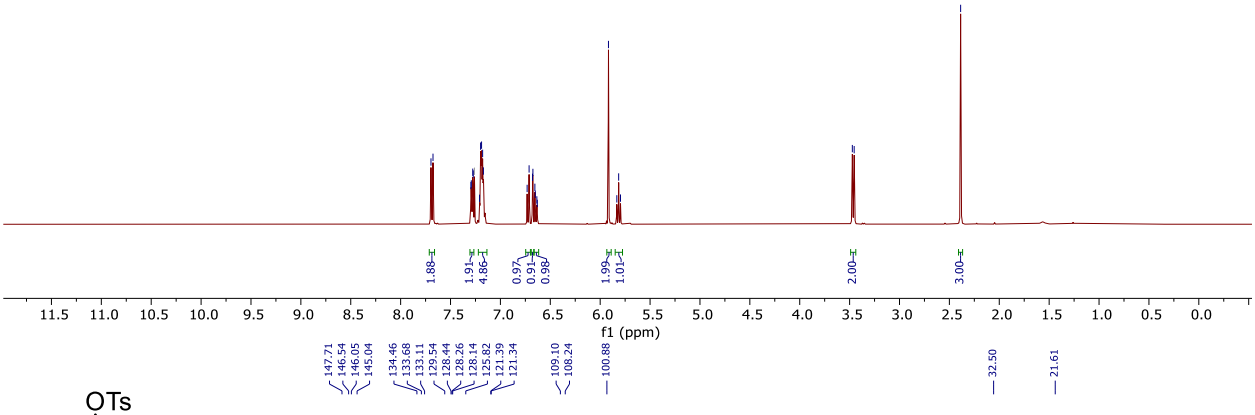
1a

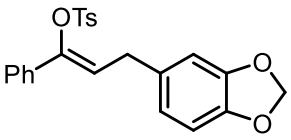


400 MHz, $CDCl_3$

1b

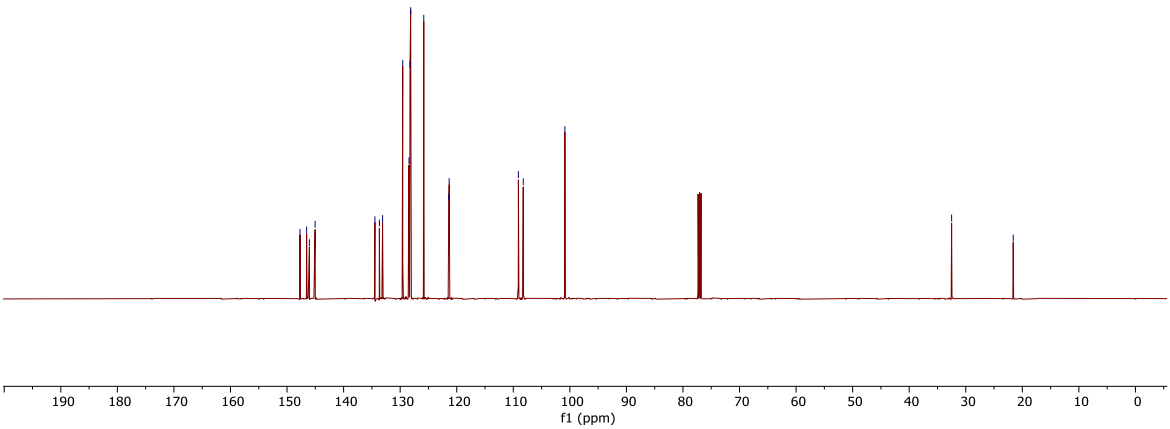


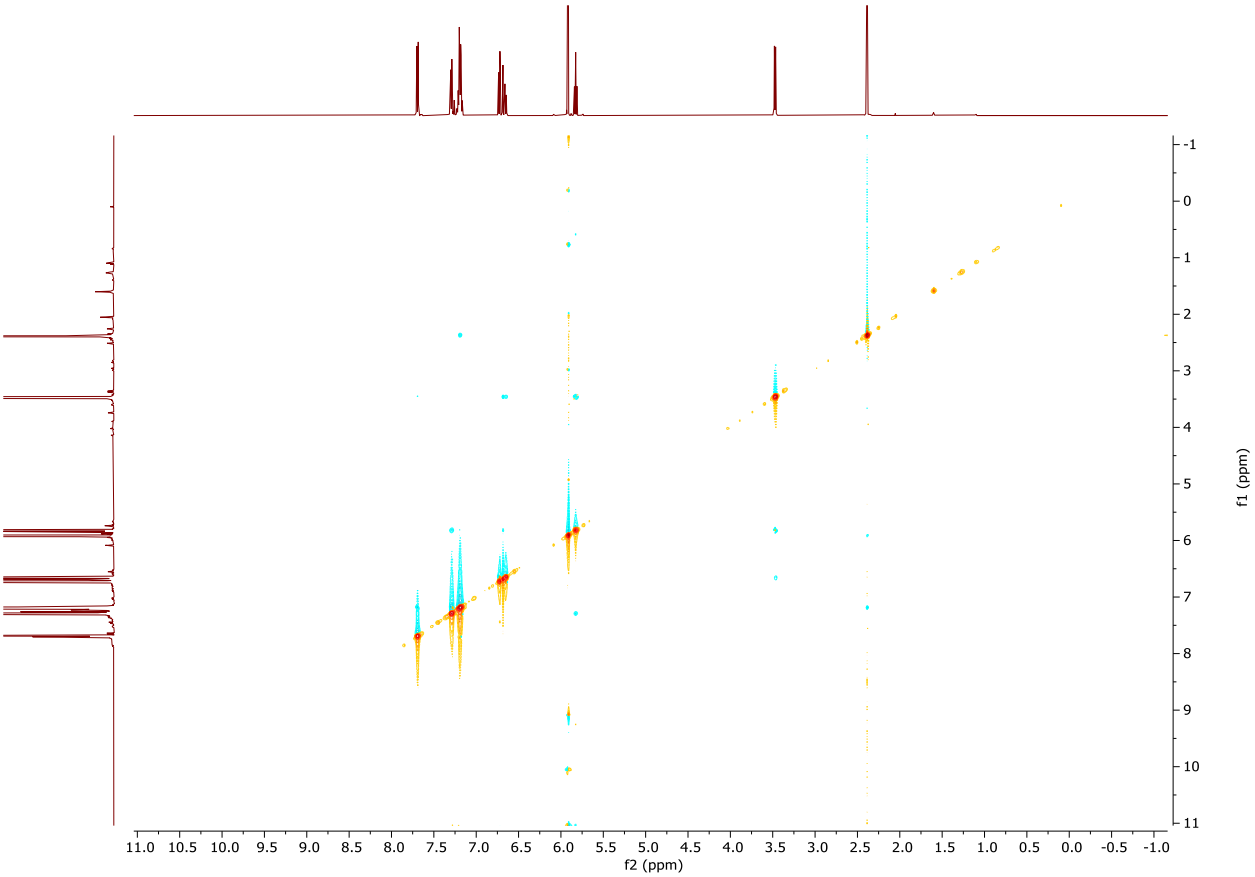


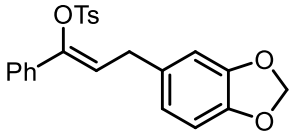


100 MHz, $CDCl_3$

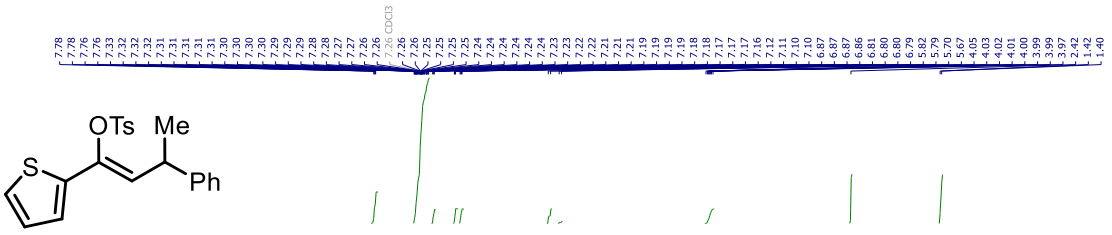
1b





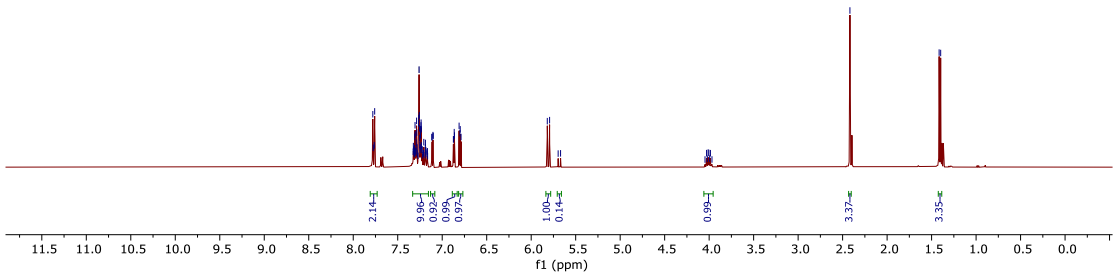


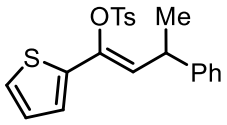
500 MHz, $CDCl_3$
1b – NOESY



400 MHz, $CDCl_3$

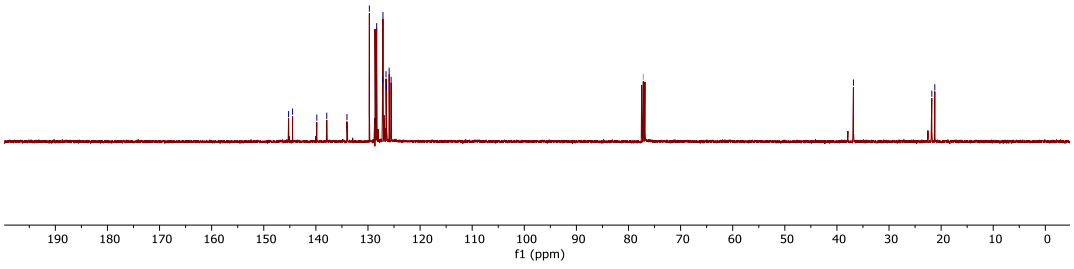
1c

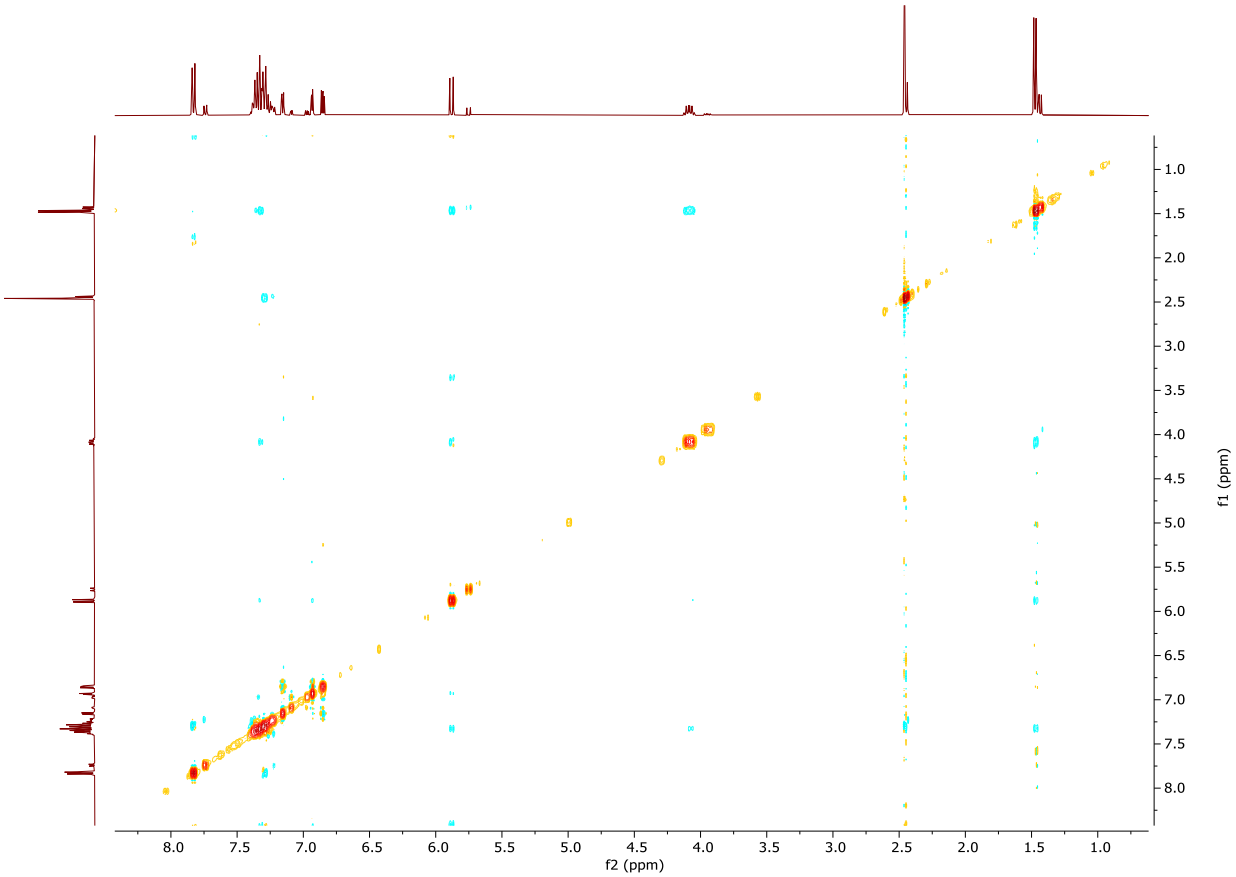


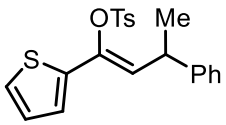


100 MHz, $CDCl_3$

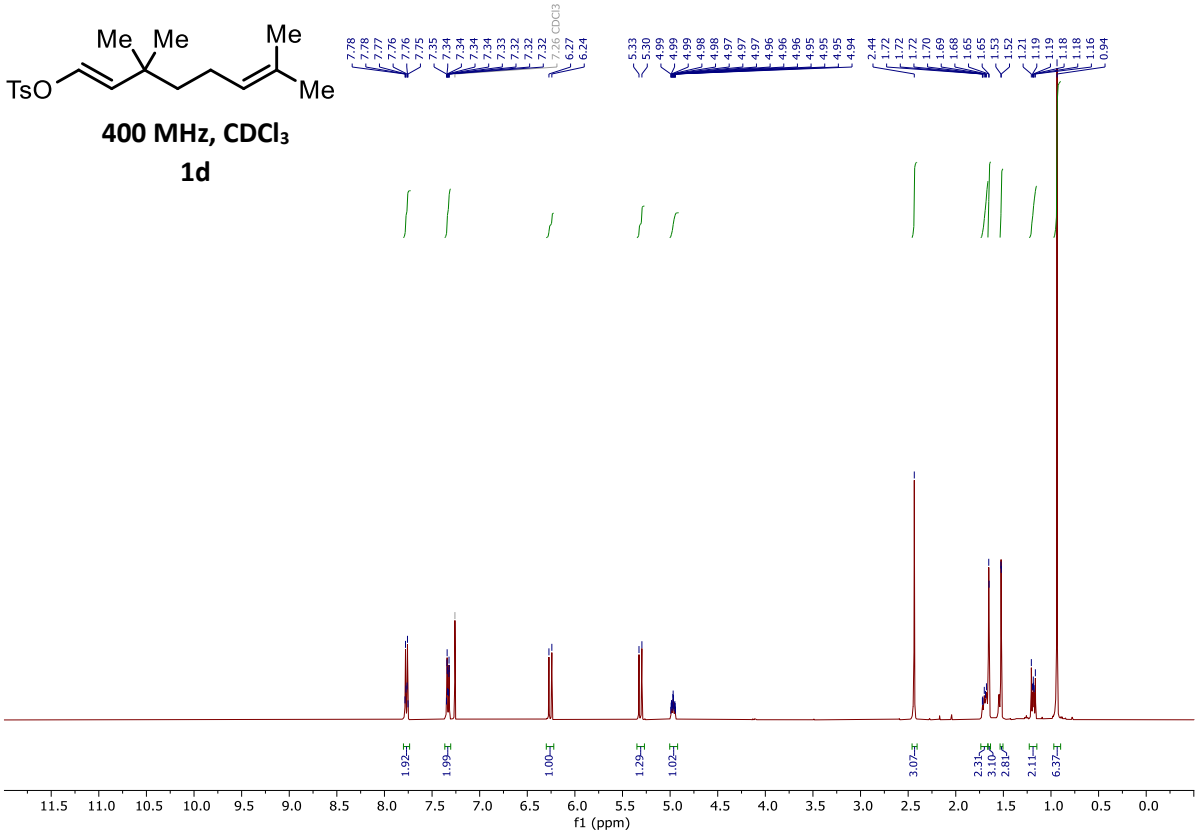
1c

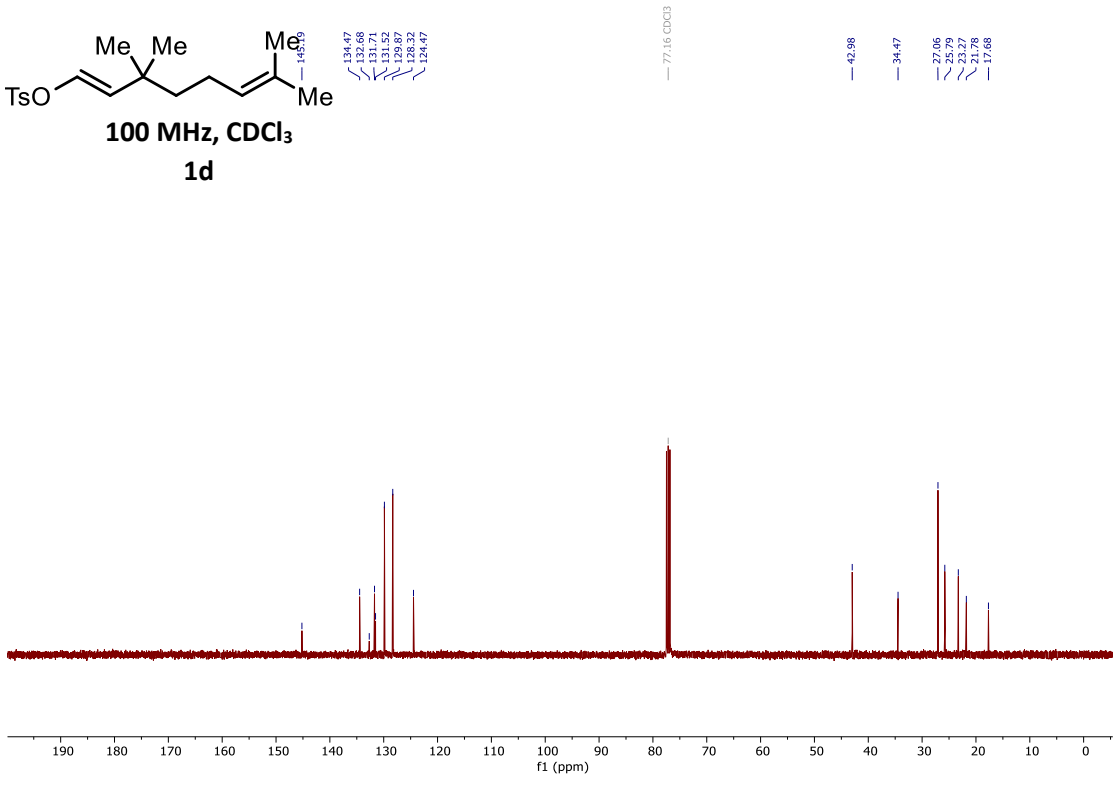


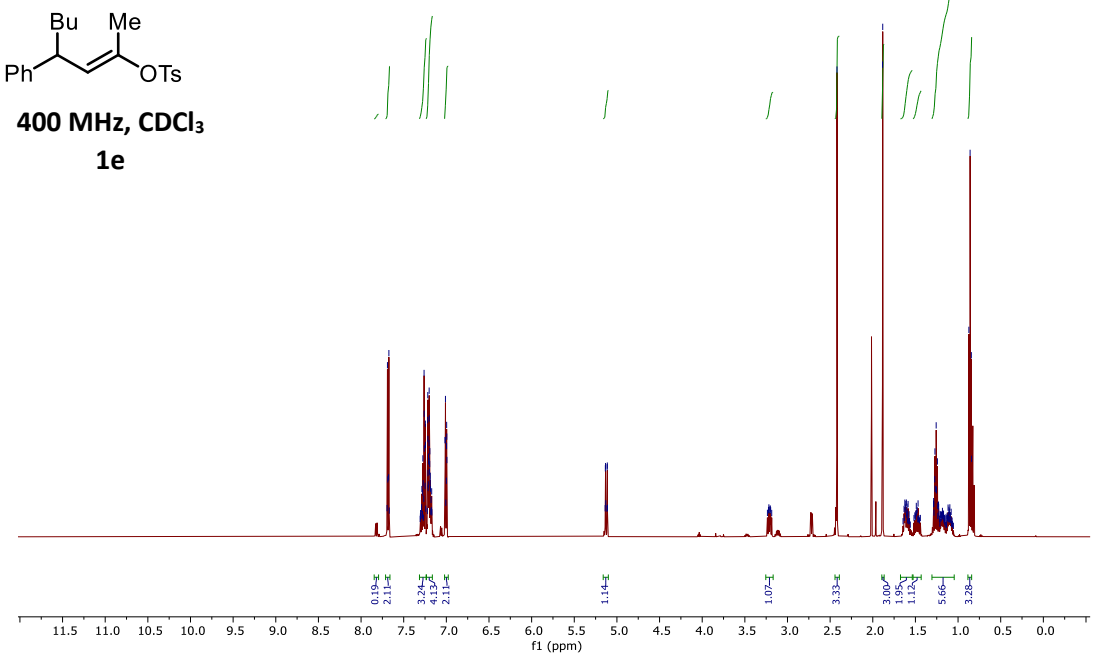




500 MHz, $CDCl_3$
1c – NOESY

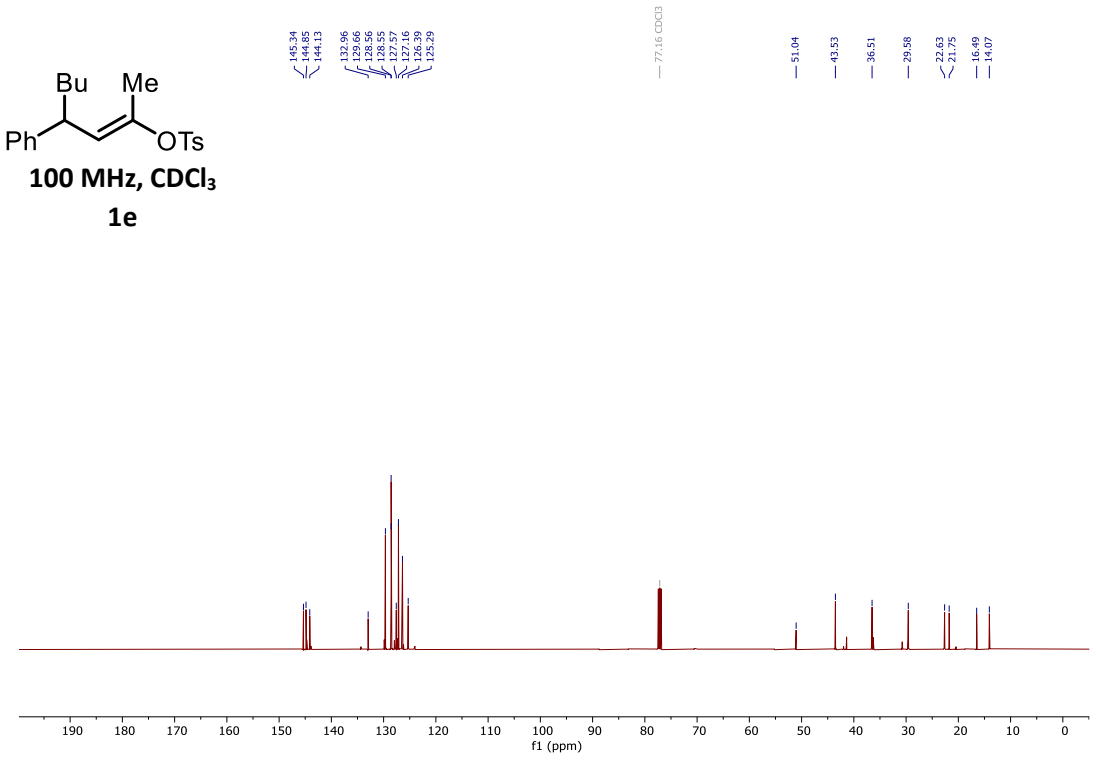

Me Me
Me
TsO
Me
400 MHz, CDCl3
1d
f1 (ppm)


Me Me
Me
TsO
Me
100 MHz, CDCl3
1d
f1 (ppm)



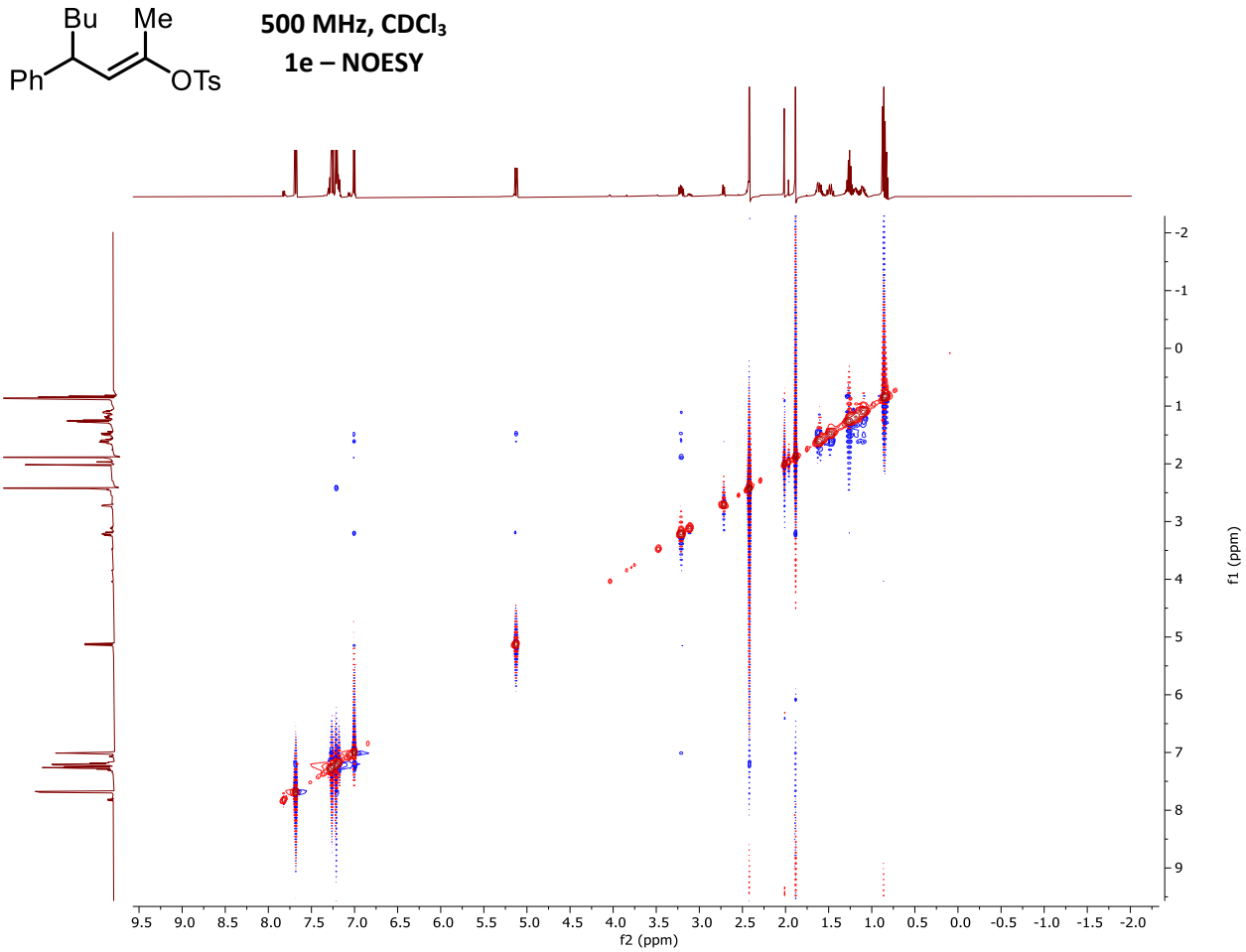
400 MHz, $CDCl_3$

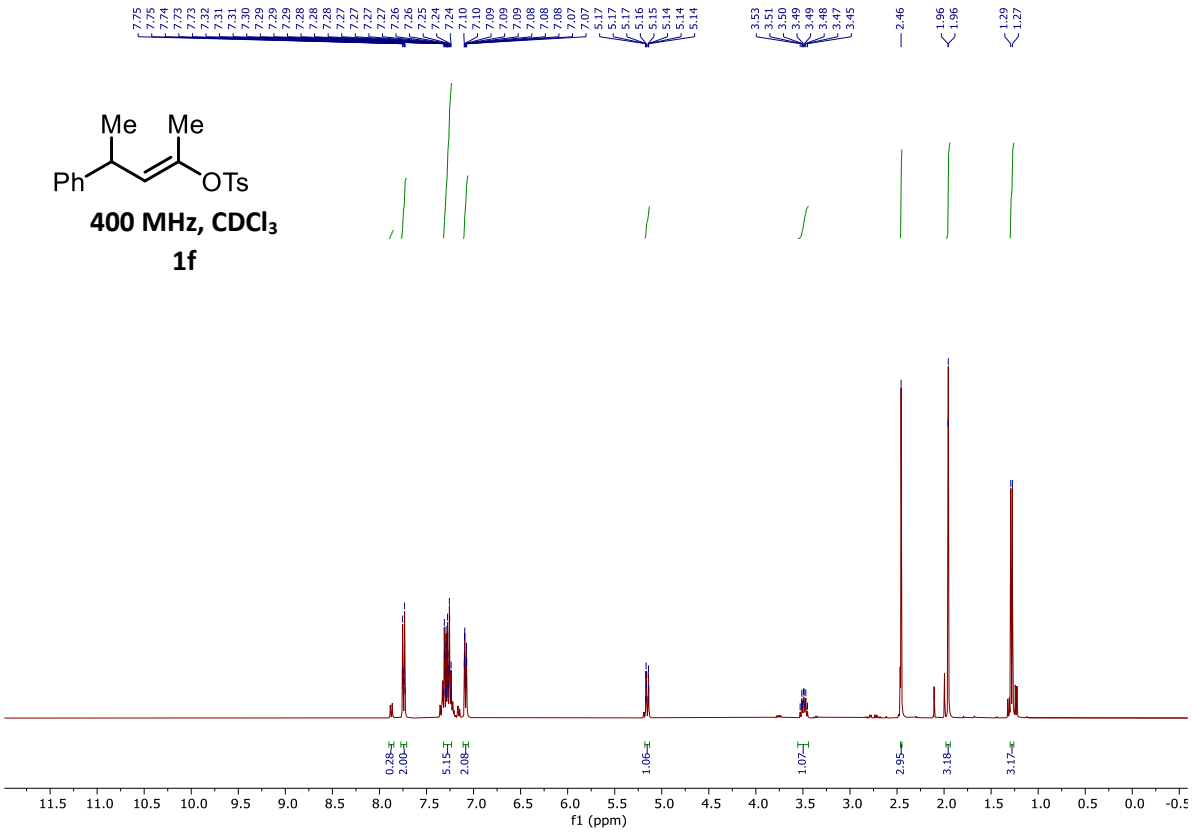
1e

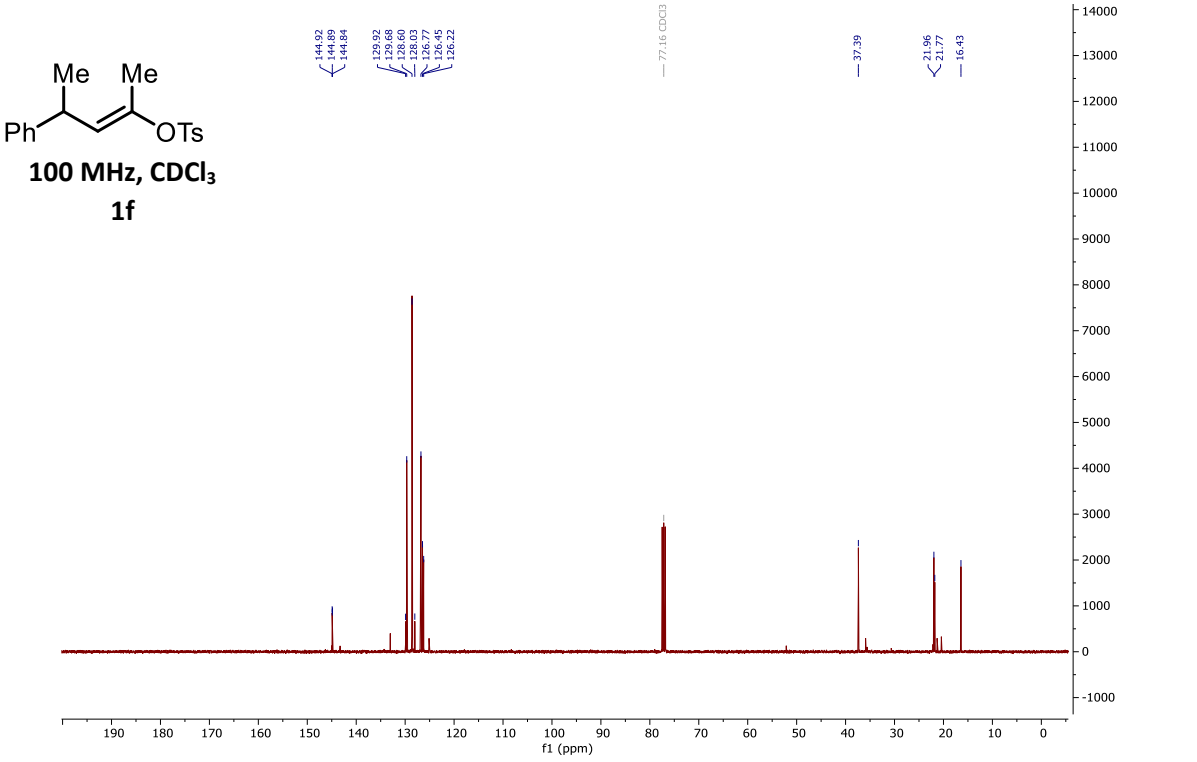


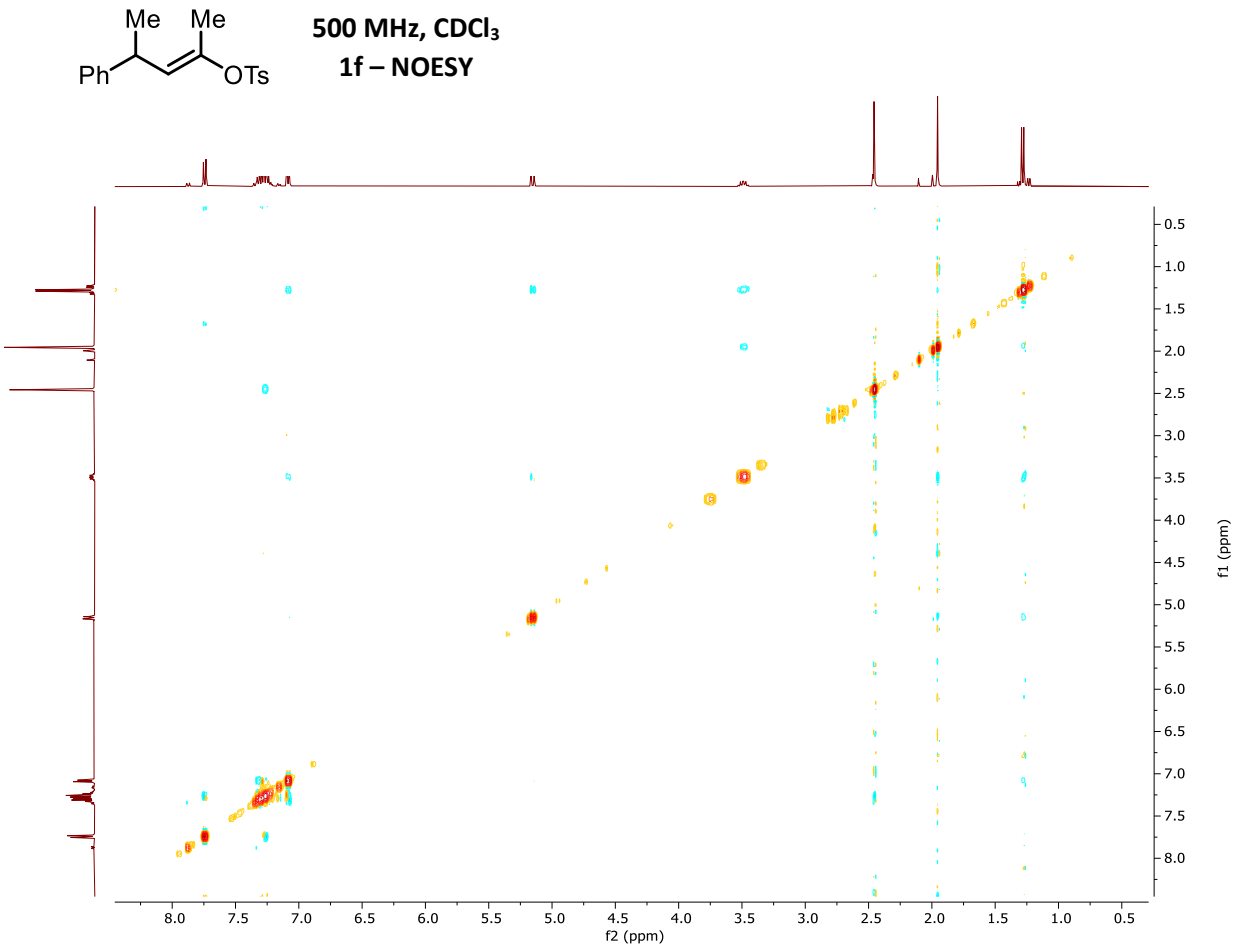
100 MHz, $CDCl_3$

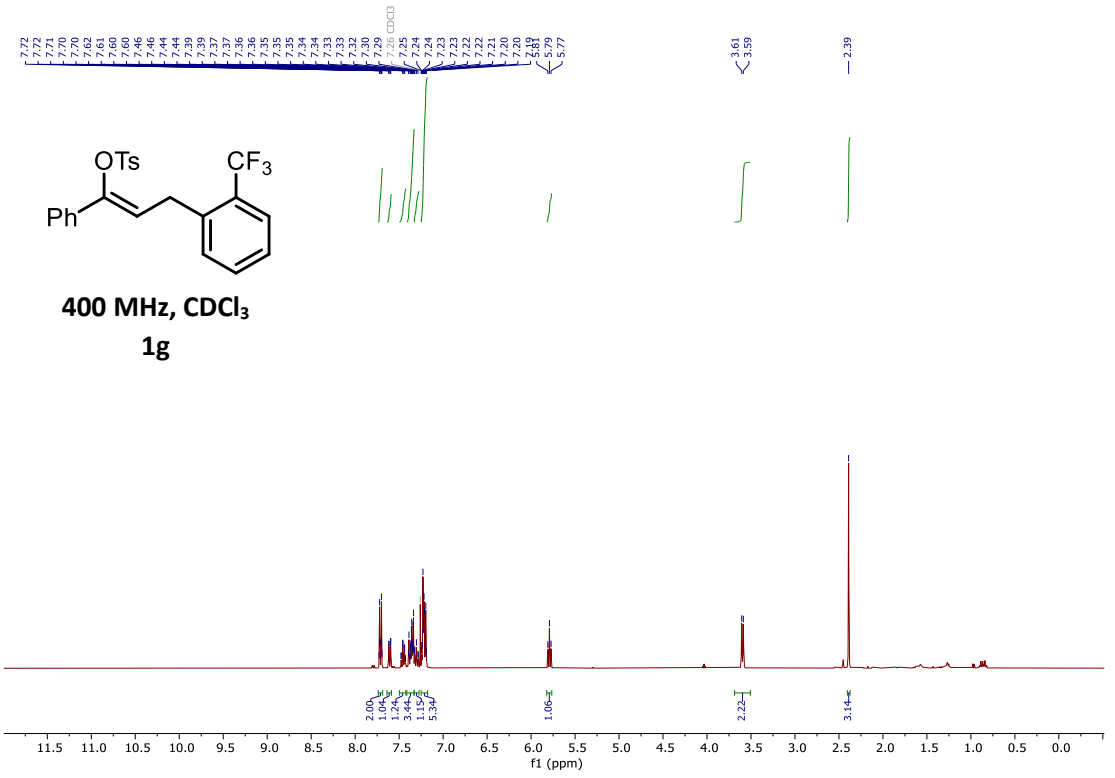
1e


Bu
Me
Ph
OTs
500 MHz, CDCl3
1e – NOESY
f2 (ppm)
f1 (ppm)


Me
Me
Ph
OTs
400 MHz, CDCl3
1f
f1 (ppm)

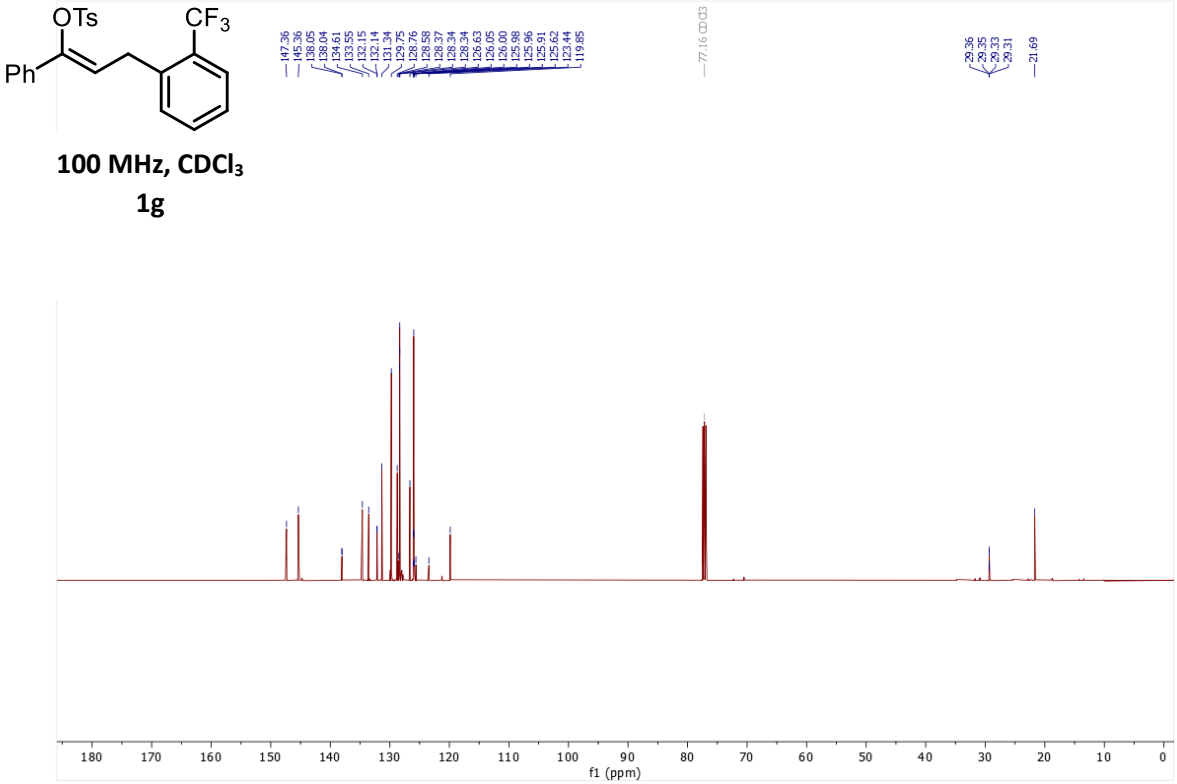

Me
Me
Ph
OTs
100 MHz, CDCl3
1f
f1 (ppm)


Me
Me
Ph
OTs
500 MHz, CDCl3
1f – NOESY
f2 (ppm)
f1 (ppm)



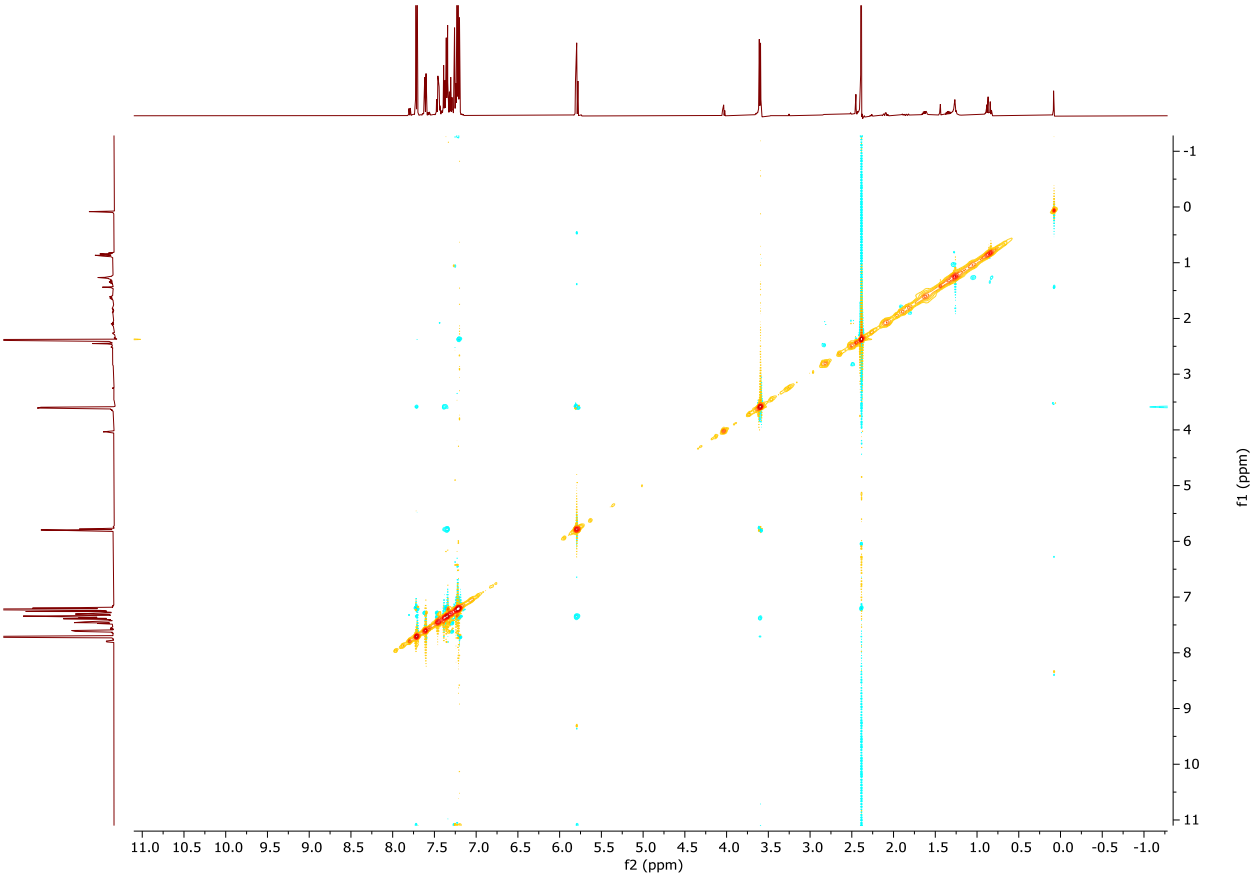
400 MHz, $CDCl_3$

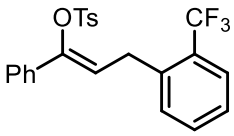
1g



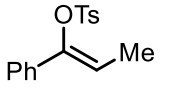
100 MHz, $CDCl_3$

1g





500 MHz, $CDCl_3$
1g – NOESY

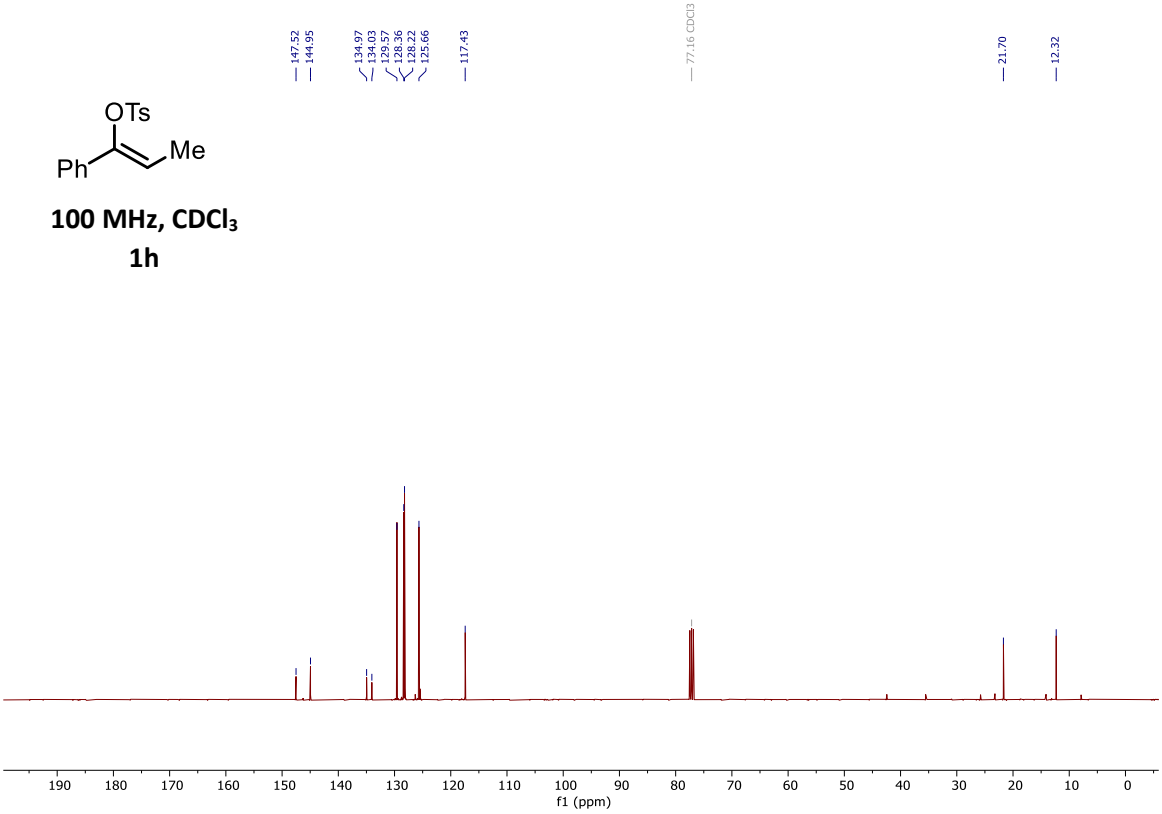


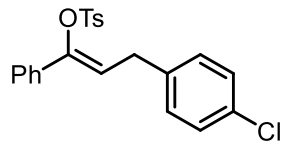
400 MHz, $CDCl_3$

1h

100 MHz, $CDCl_3$

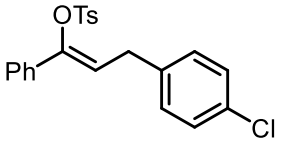
1h





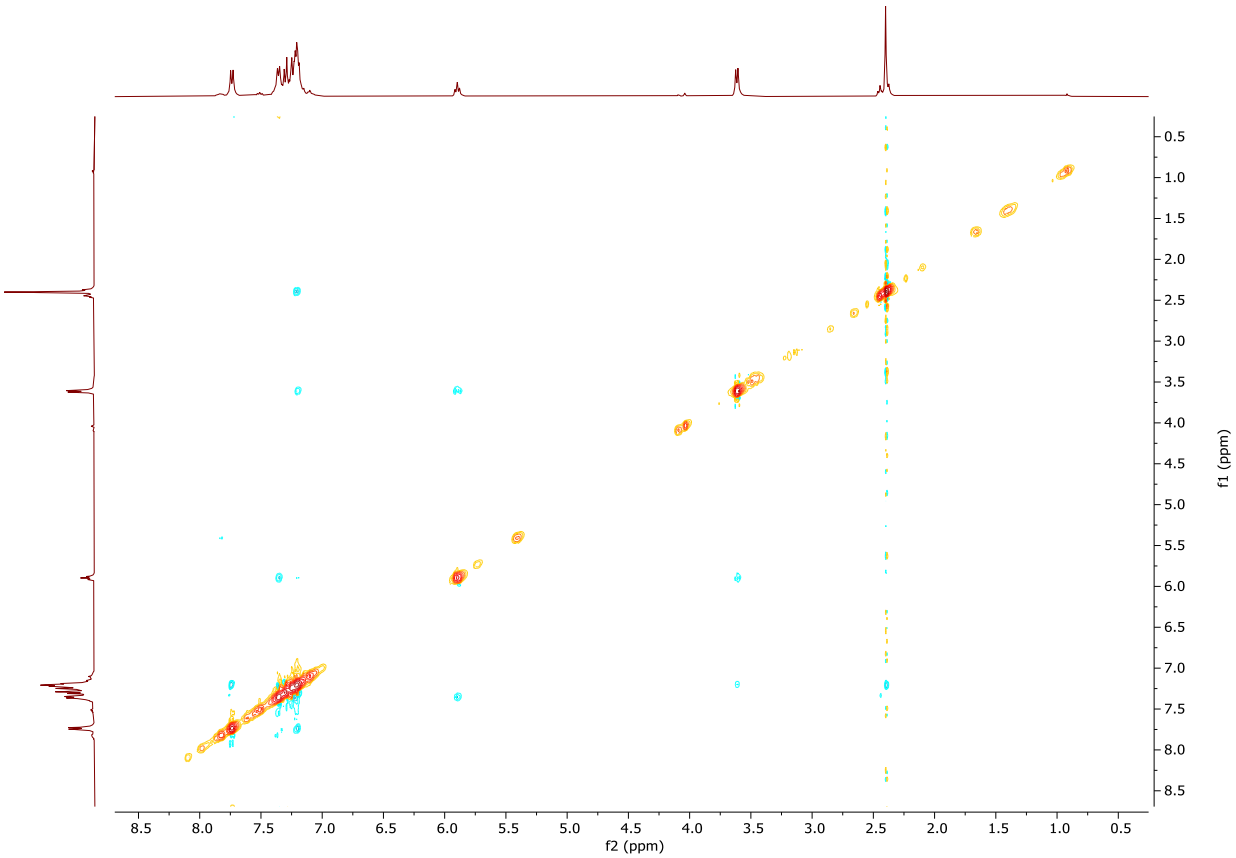
400 MHz, $CDCl_3$

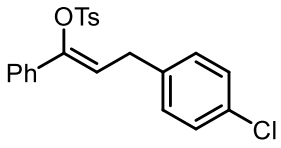
1i



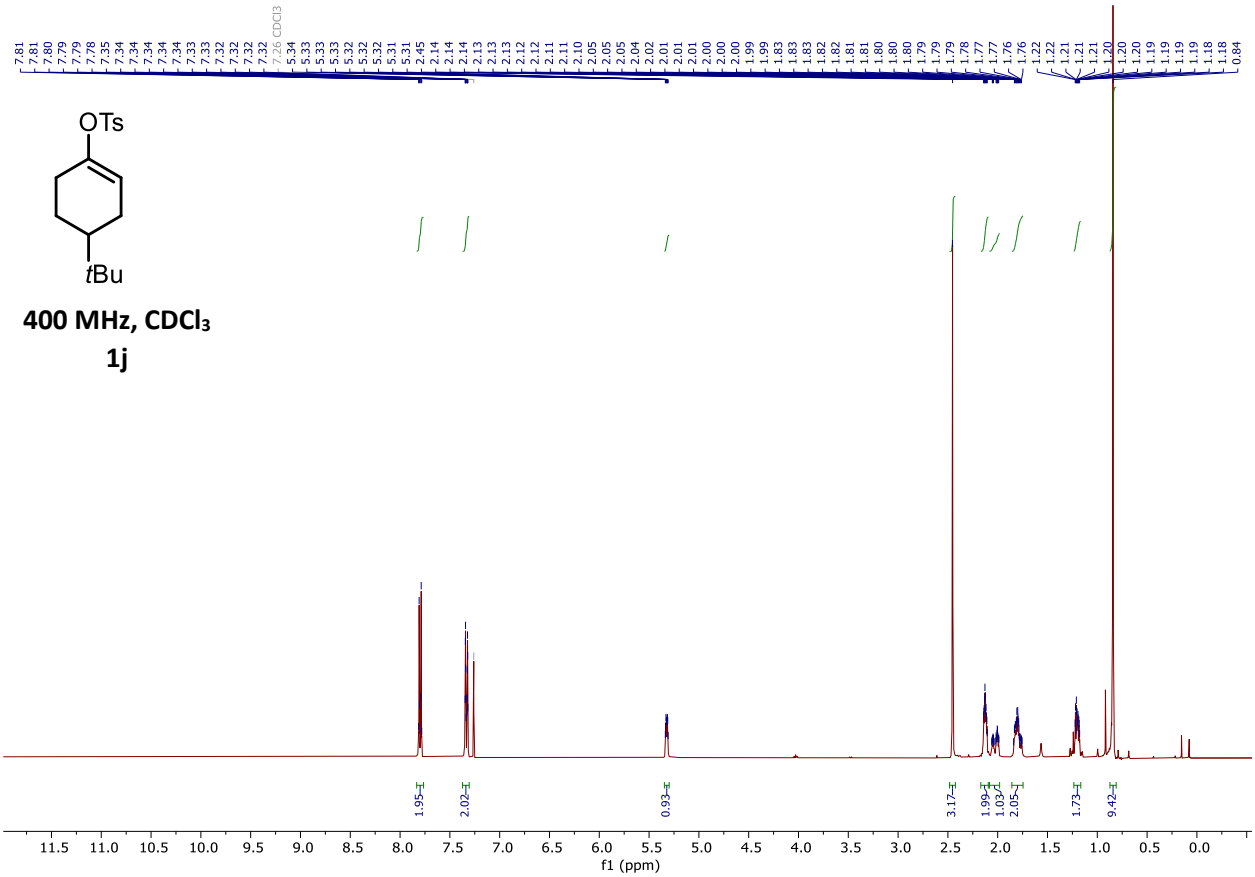
100 MHz, $CDCl_3$

1i



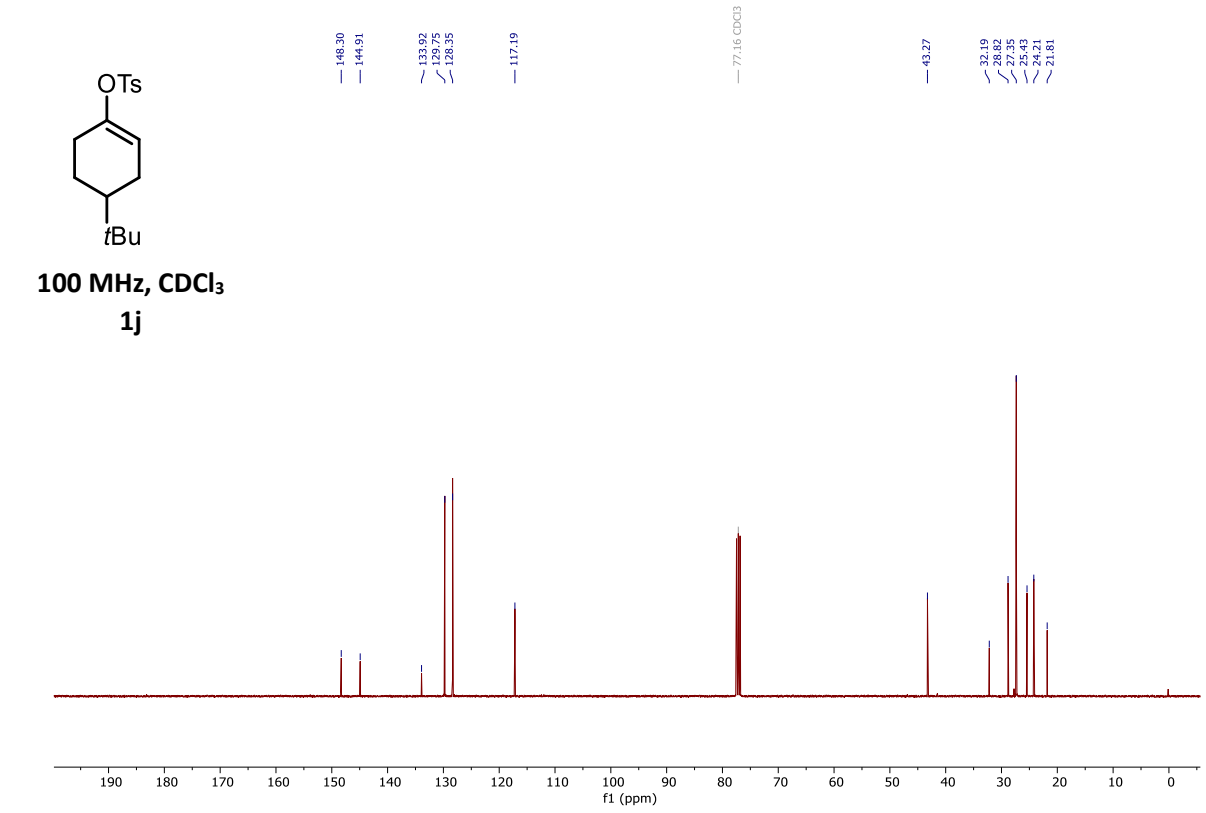


500 MHz, $CDCl_3$
1i – NOESY



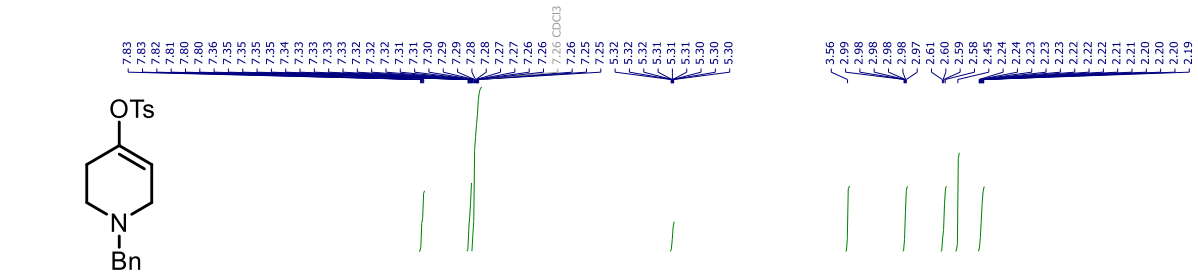
400 MHz, $CDCl_3$

1j



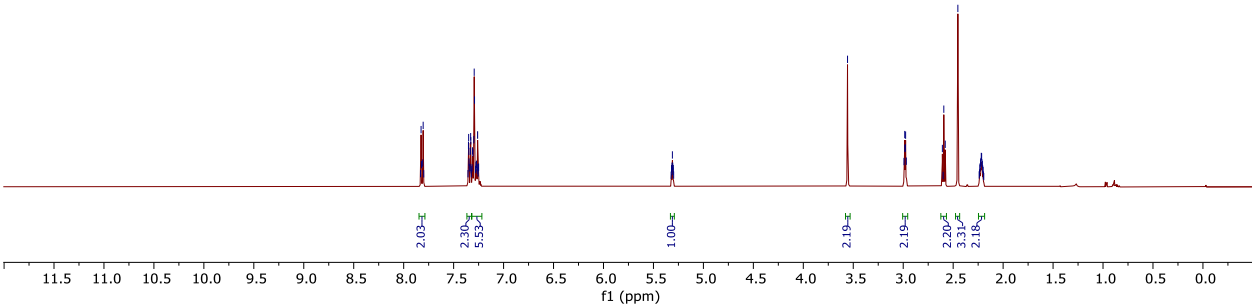
100 MHz, $CDCl_3$

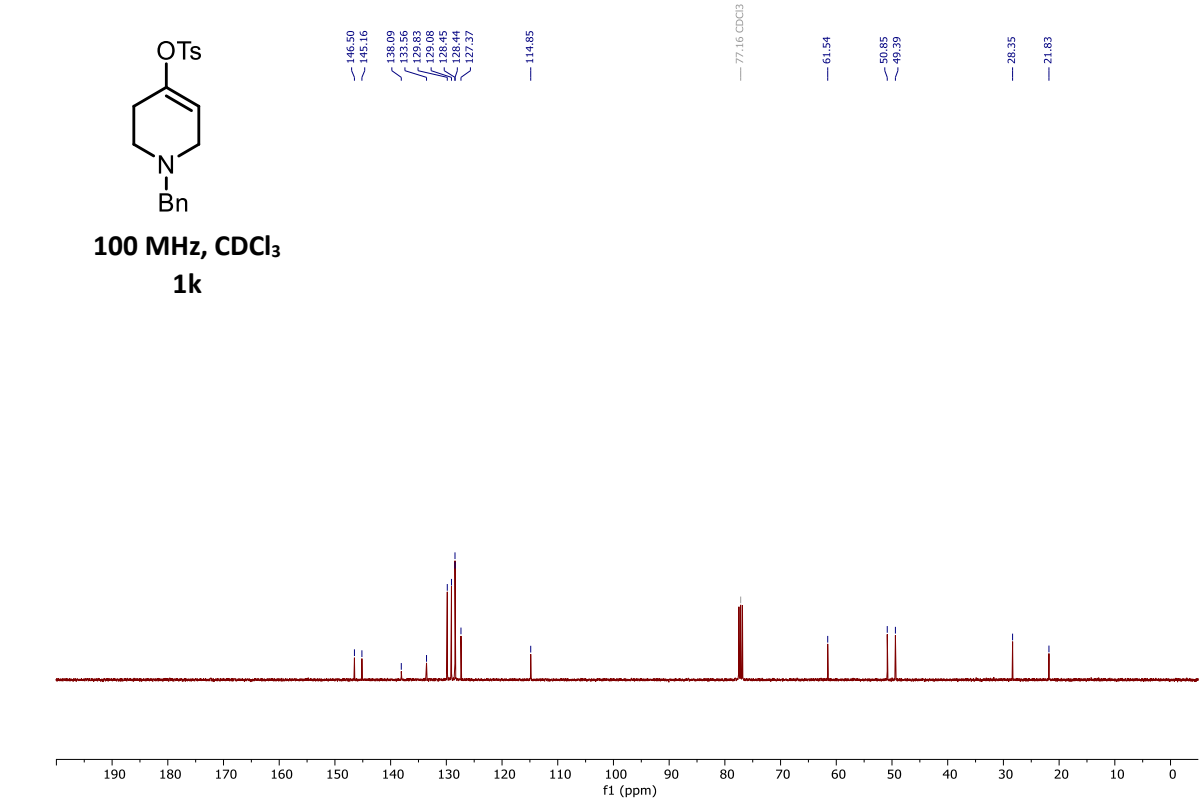
1j



400 MHz, $CDCl_3$

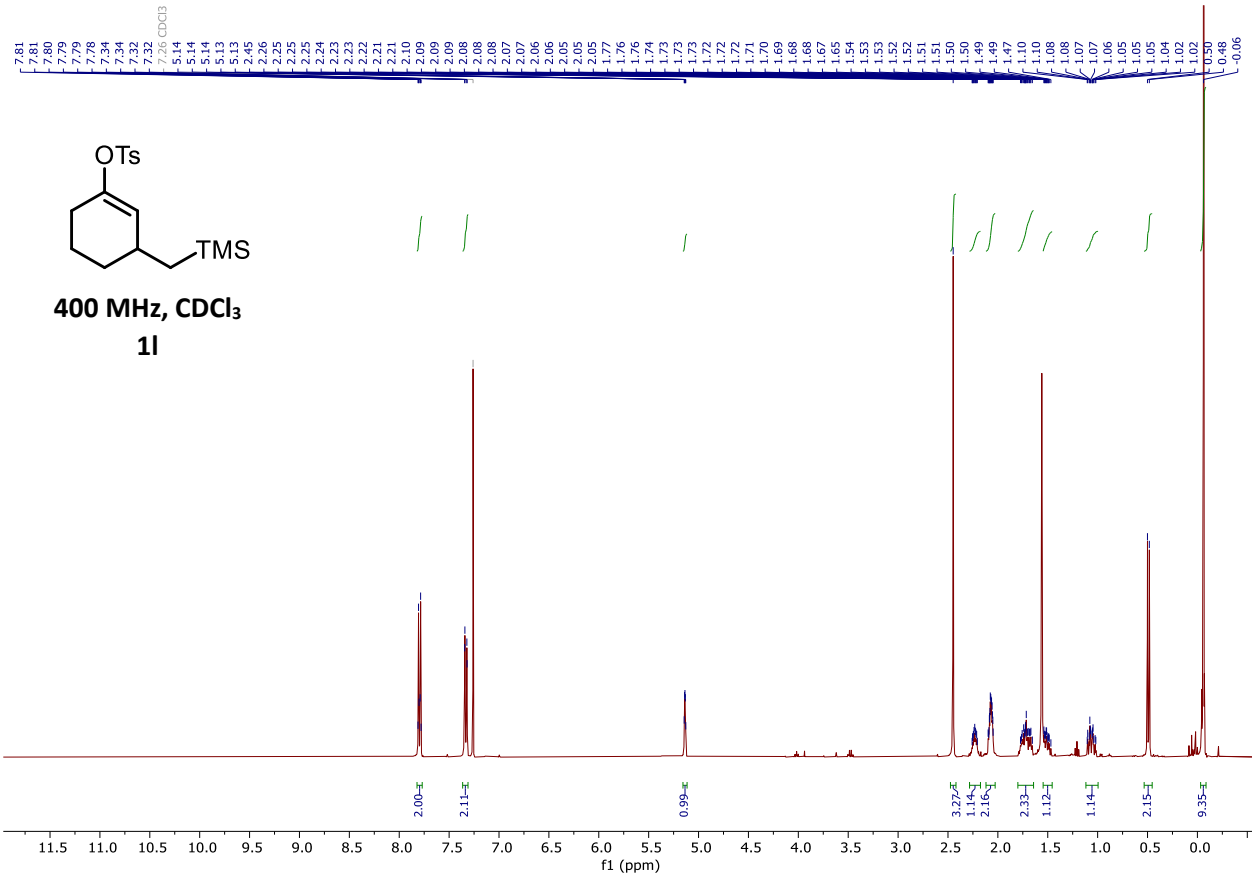
1k

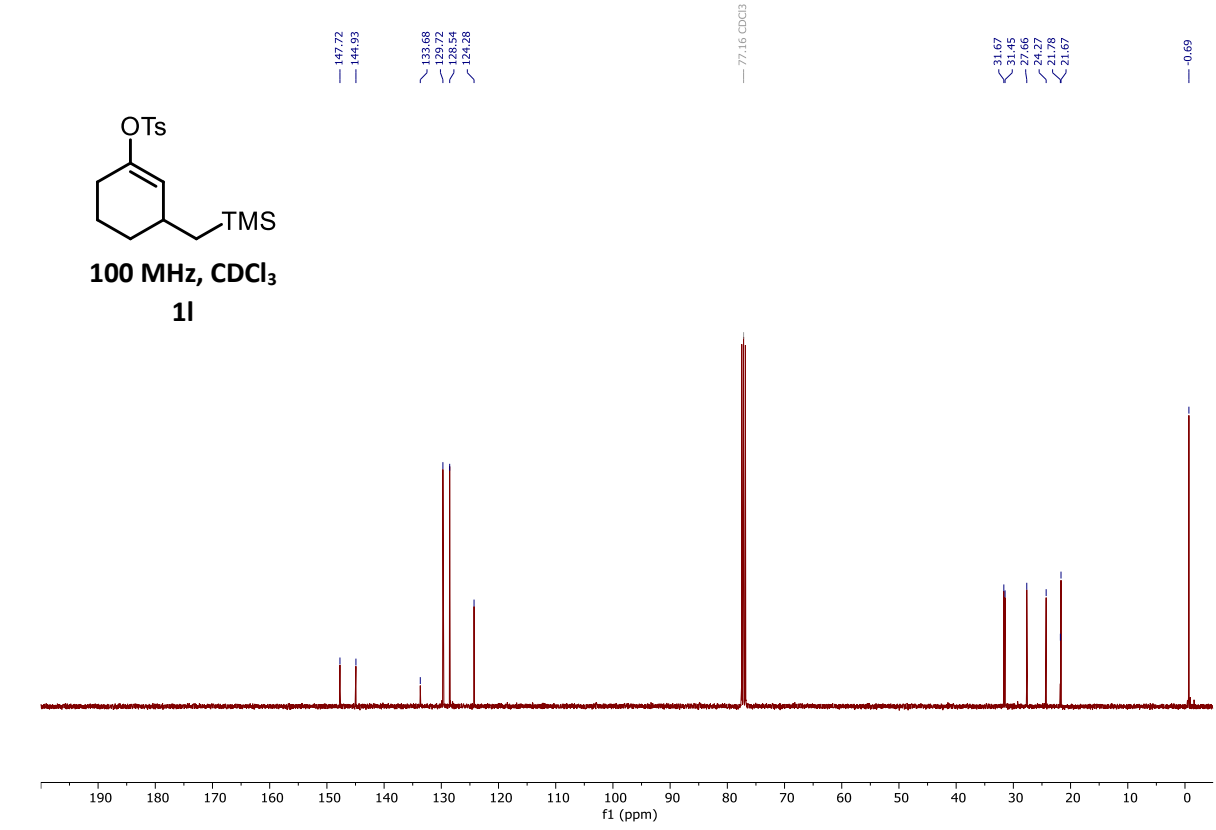


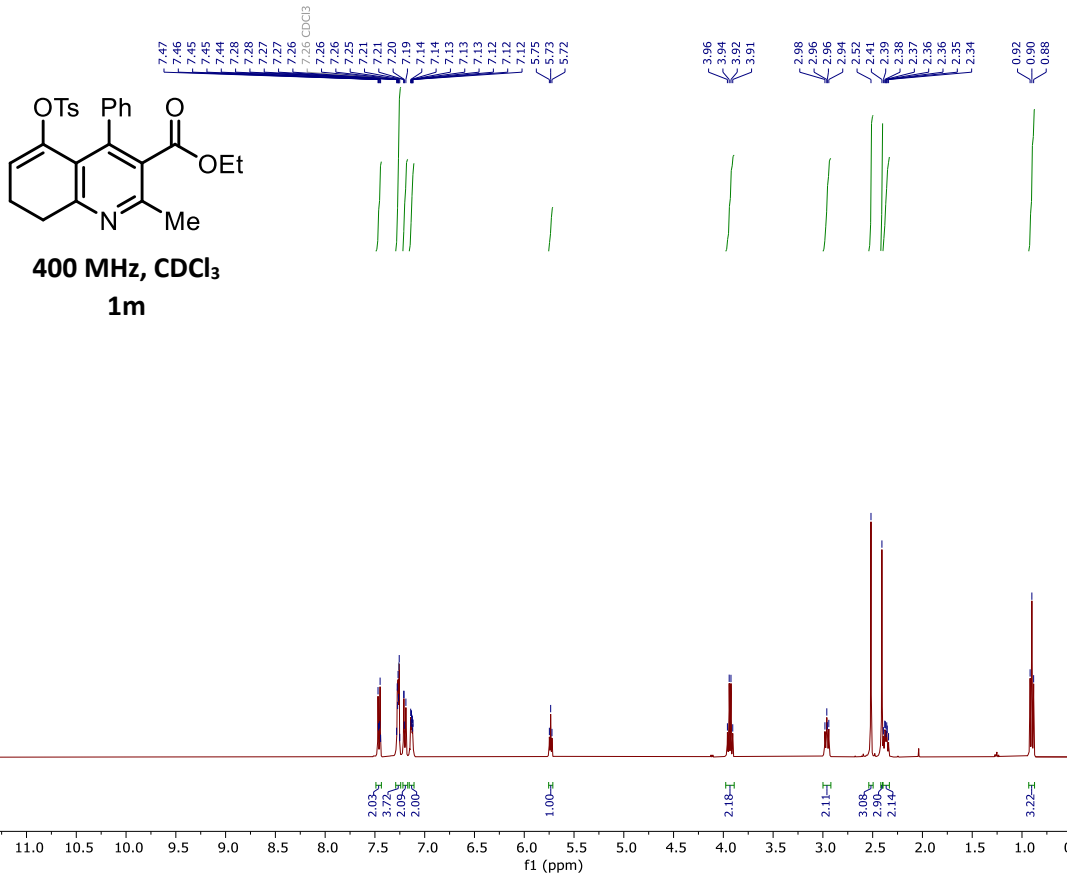


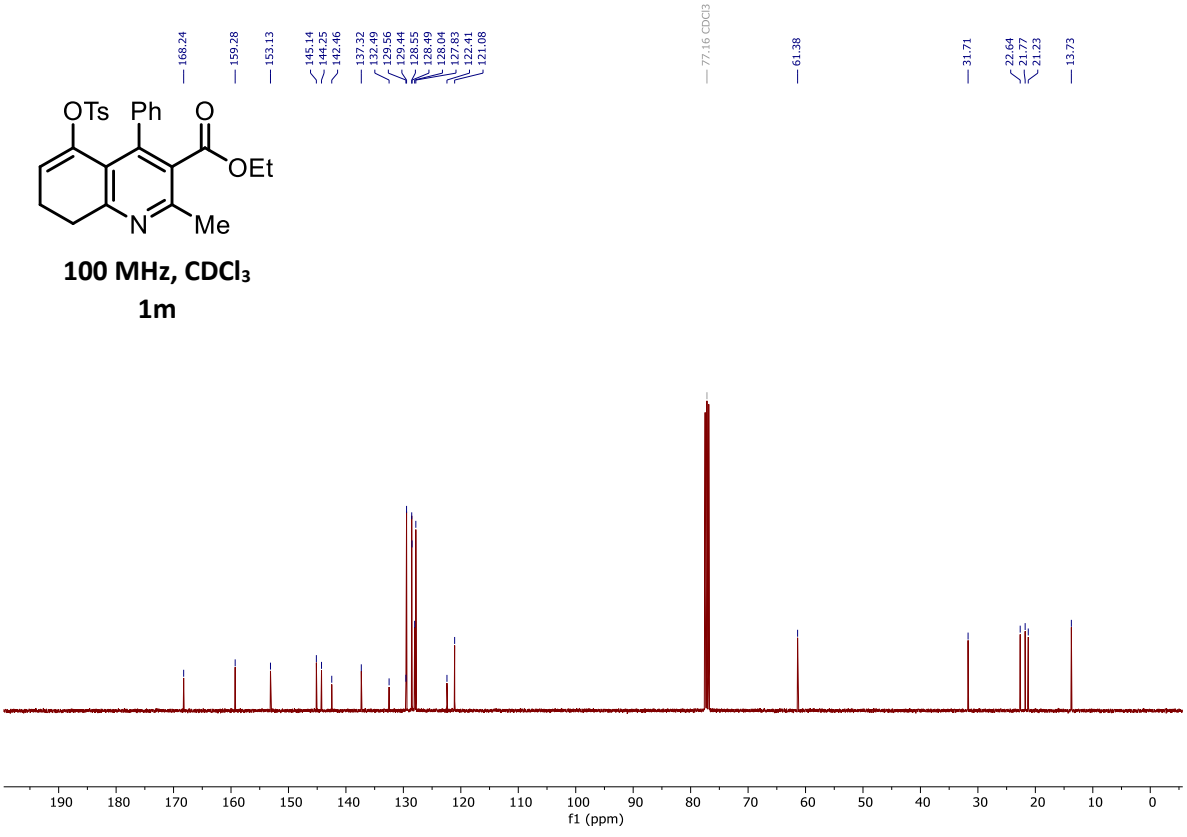
100 MHz, $CDCl_3$

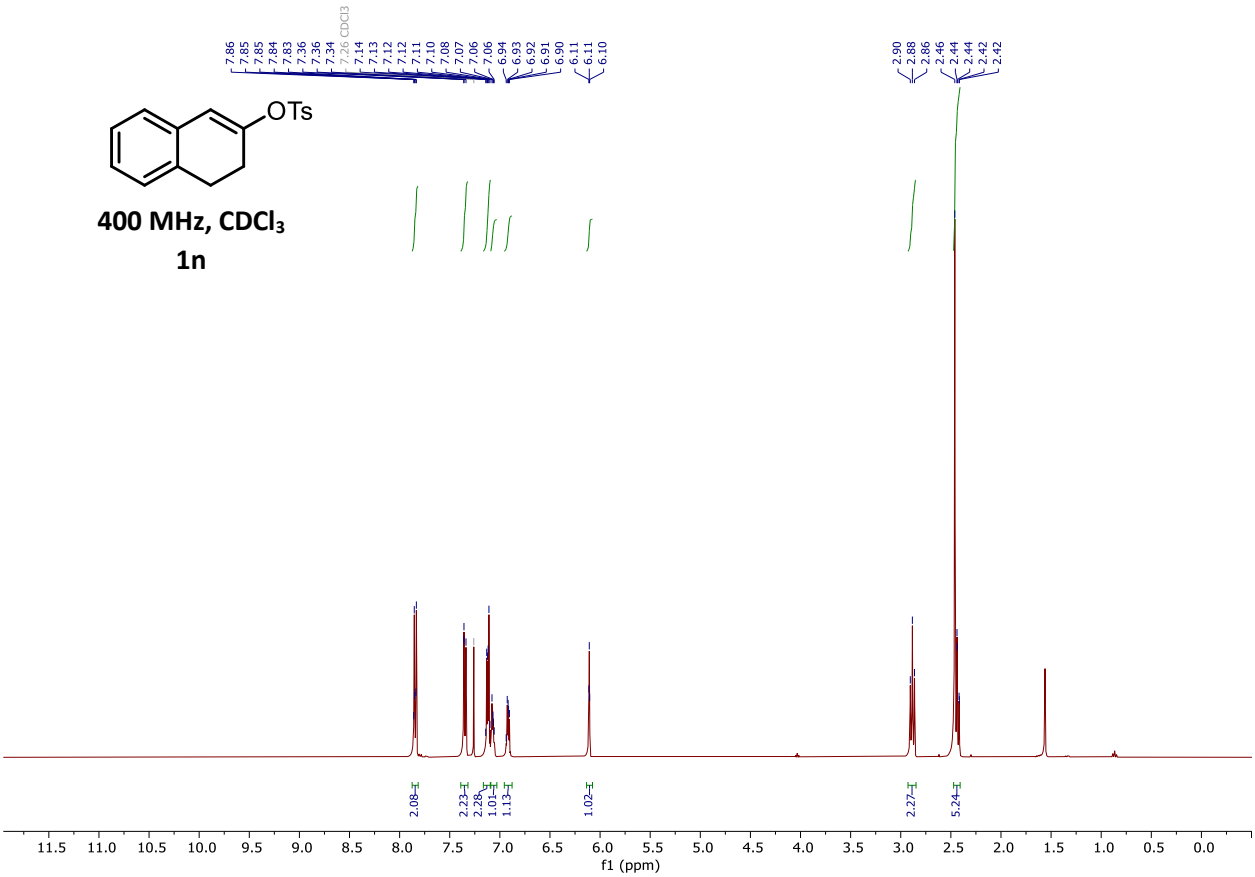
1k

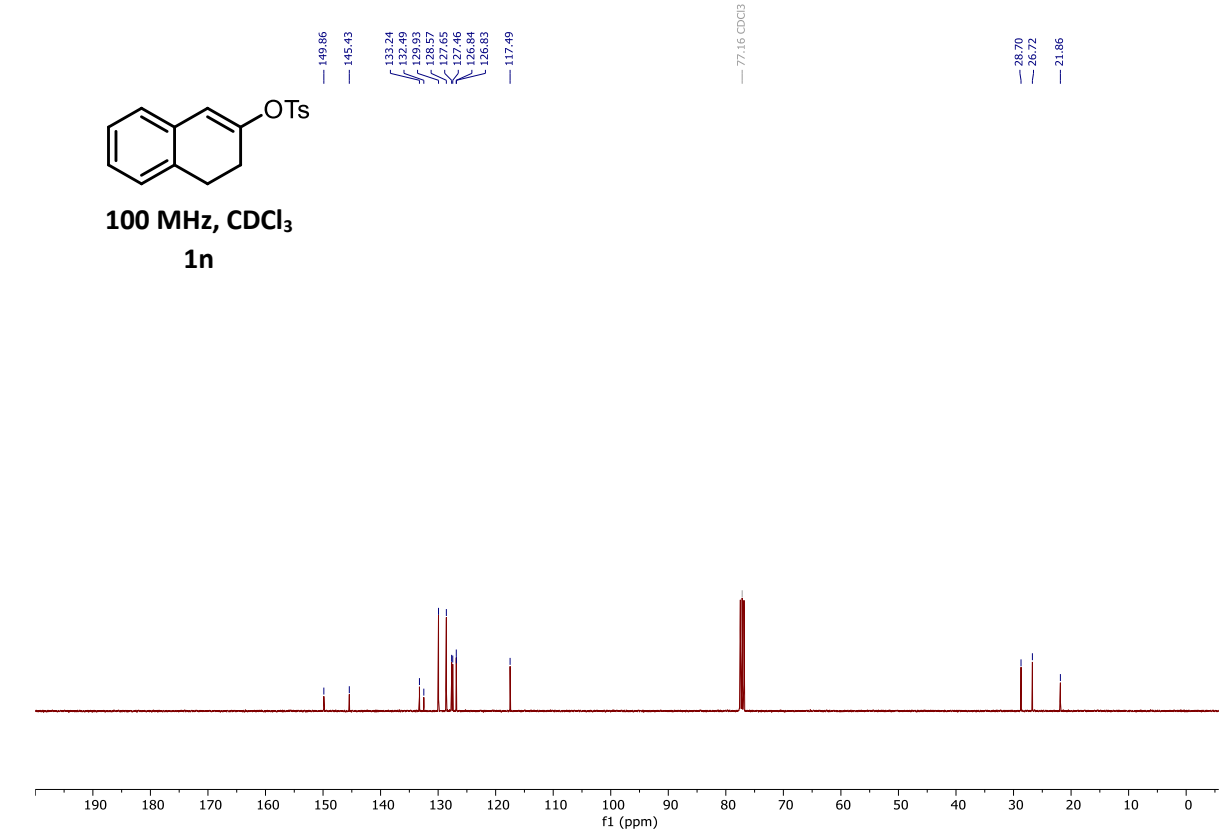

OTs
TMS
400 MHz, CDCl3
1l
f1 (ppm)

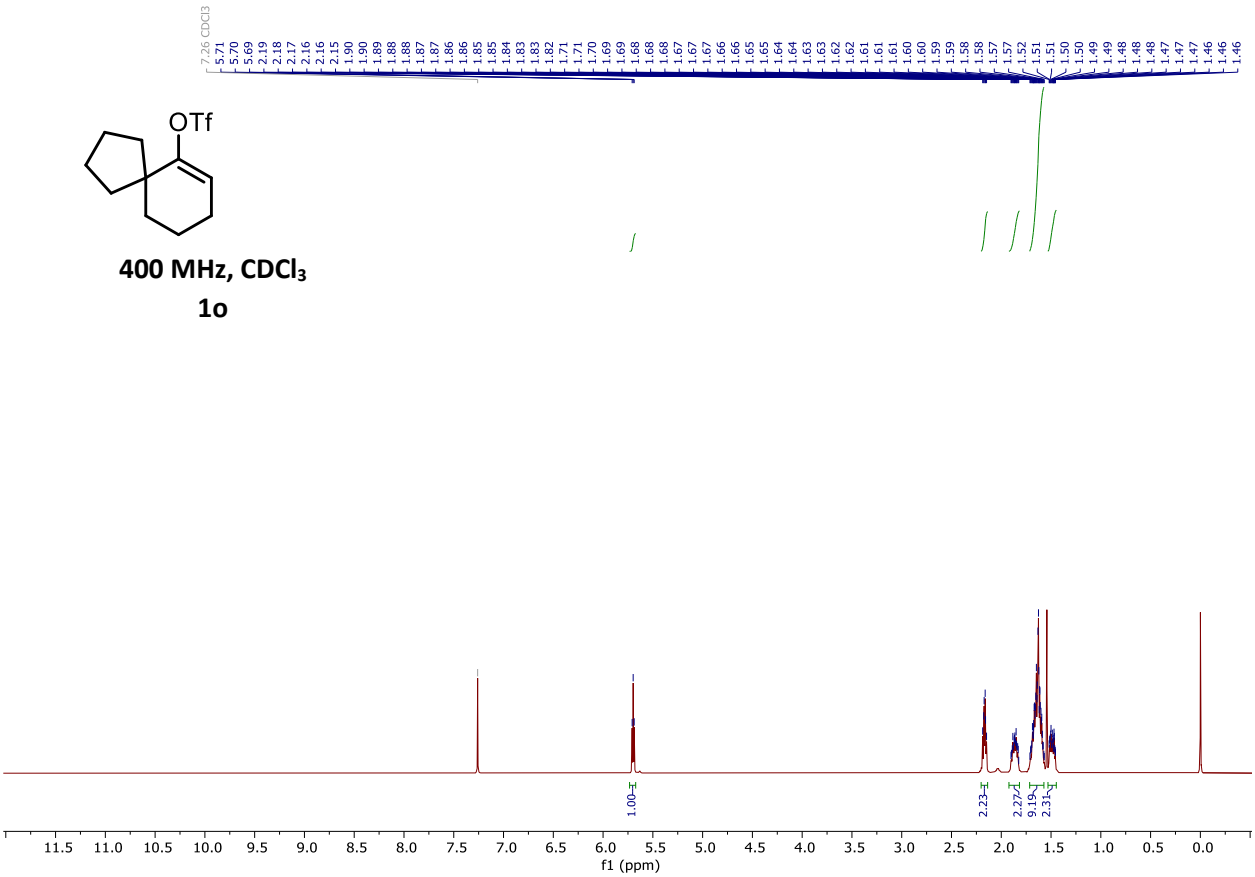

OTs
TMS
100 MHz, CDCl3
1l
f1 (ppm)


OTs Ph O
OEt
N Me
400 MHz, CDCl3
1m
f1 (ppm)


OTs Ph O
OEt
N Me
100 MHz, CDCl3
1m
f1 (ppm)

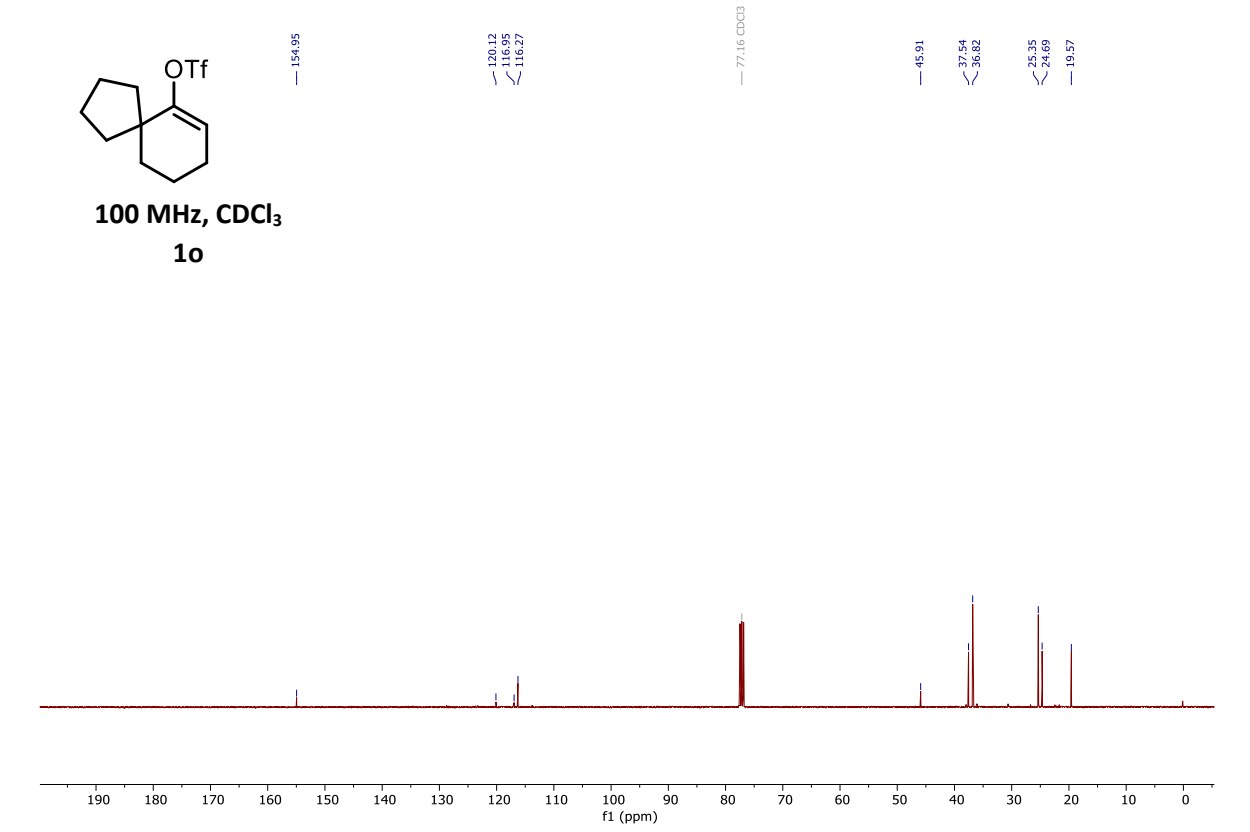

OTs
400 MHz, CDCl3
1n
f1 (ppm)


OTs
100 MHz, CDCl3
1n
f1 (ppm)



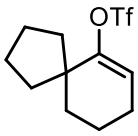
400 MHz, $CDCl_3$

1o



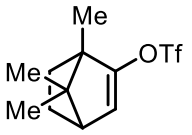
100 MHz, $CDCl_3$

1o



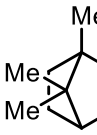
376 MHz, $CDCl_3$

1o



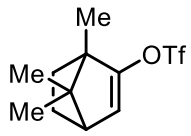
400 MHz, $CDCl_3$

1p



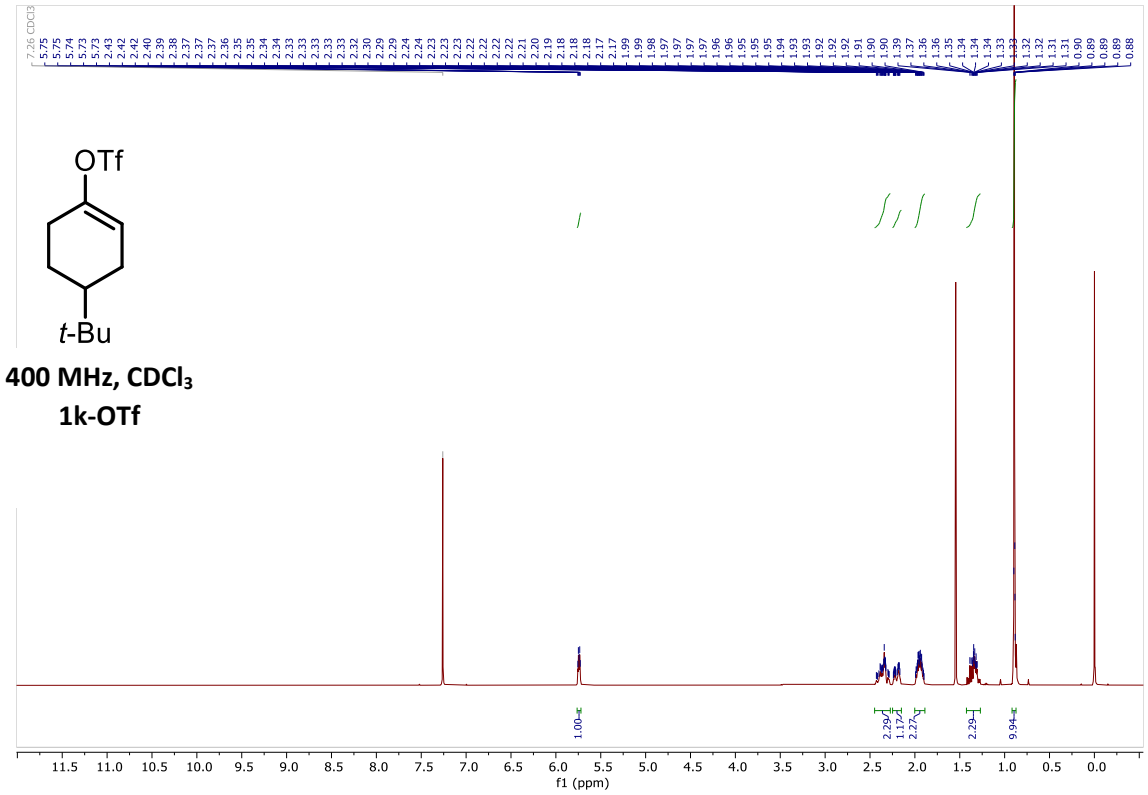
100 MHz, $CDCl_3$

1p

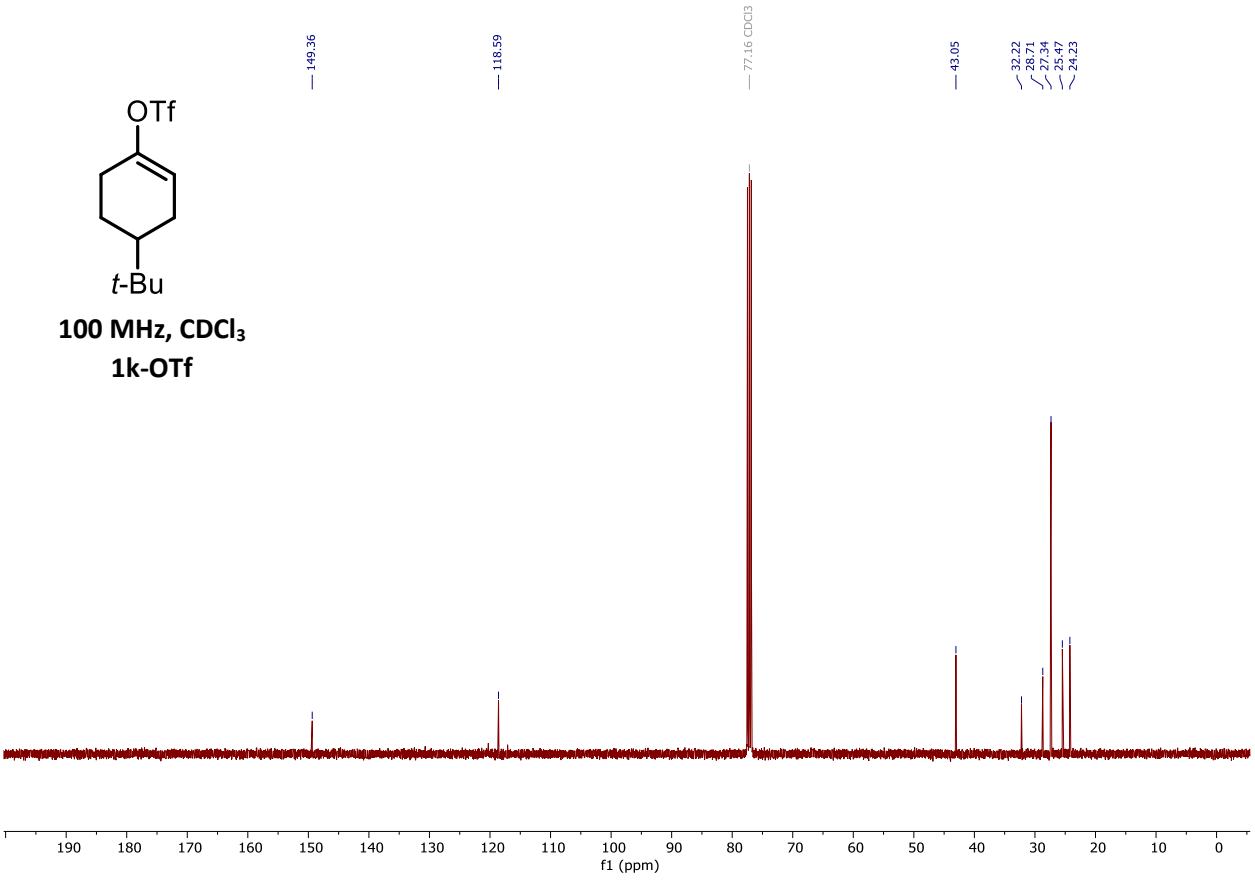


376 MHz, $CDCl_3$

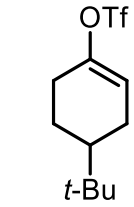
1p



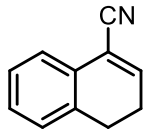
400 MHz, $CDCl_3$
1k-OTf



100 MHz, $CDCl_3$
1k-OTf

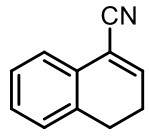


376 MHz, $CDCl_3$
1k-OTf



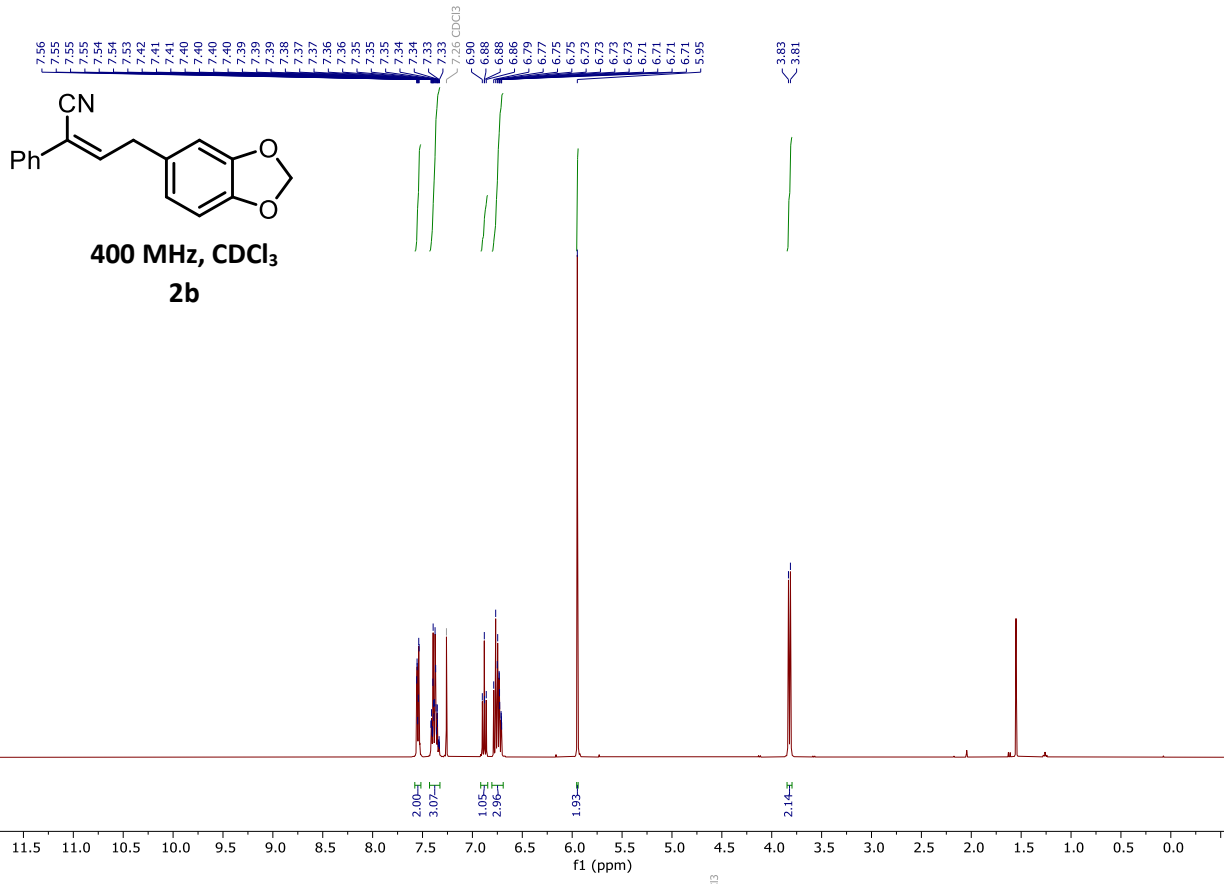
400 MHz, $CDCl_3$

2a



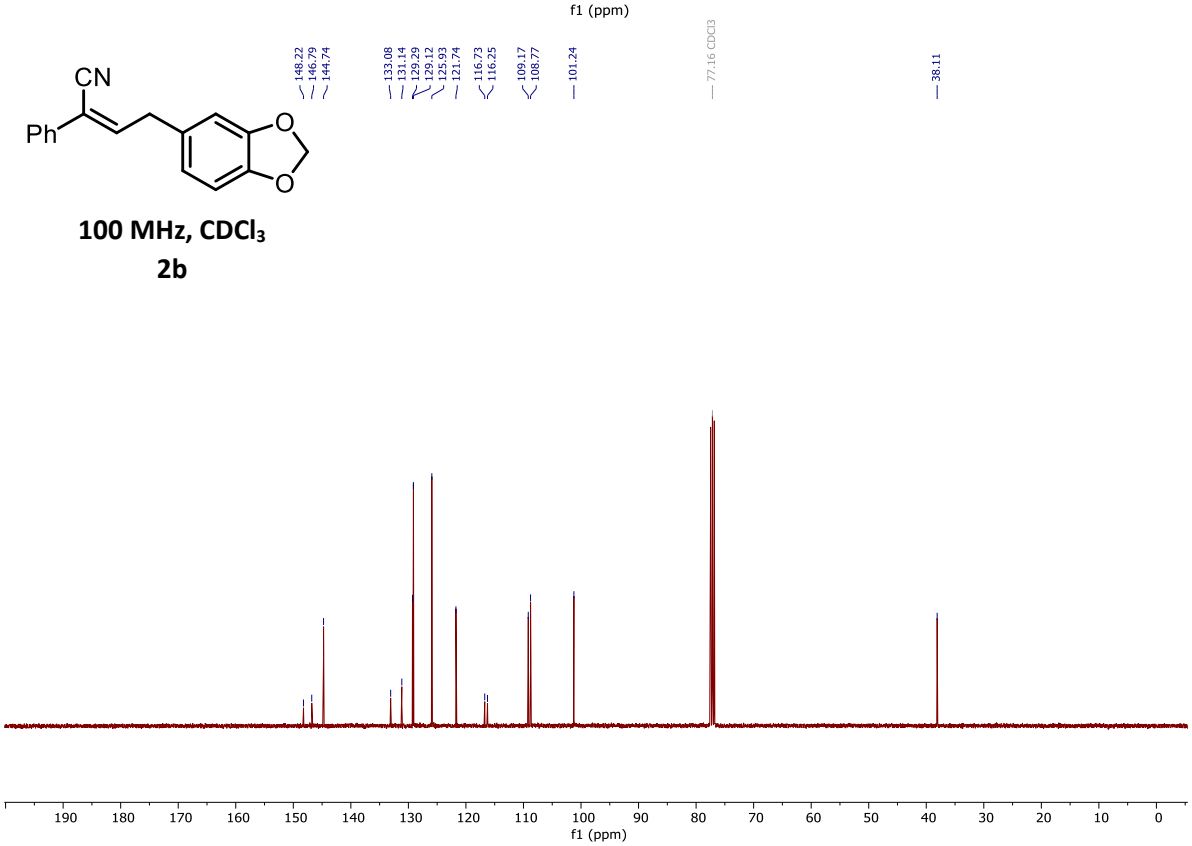
100 MHz, $CDCl_3$

2a



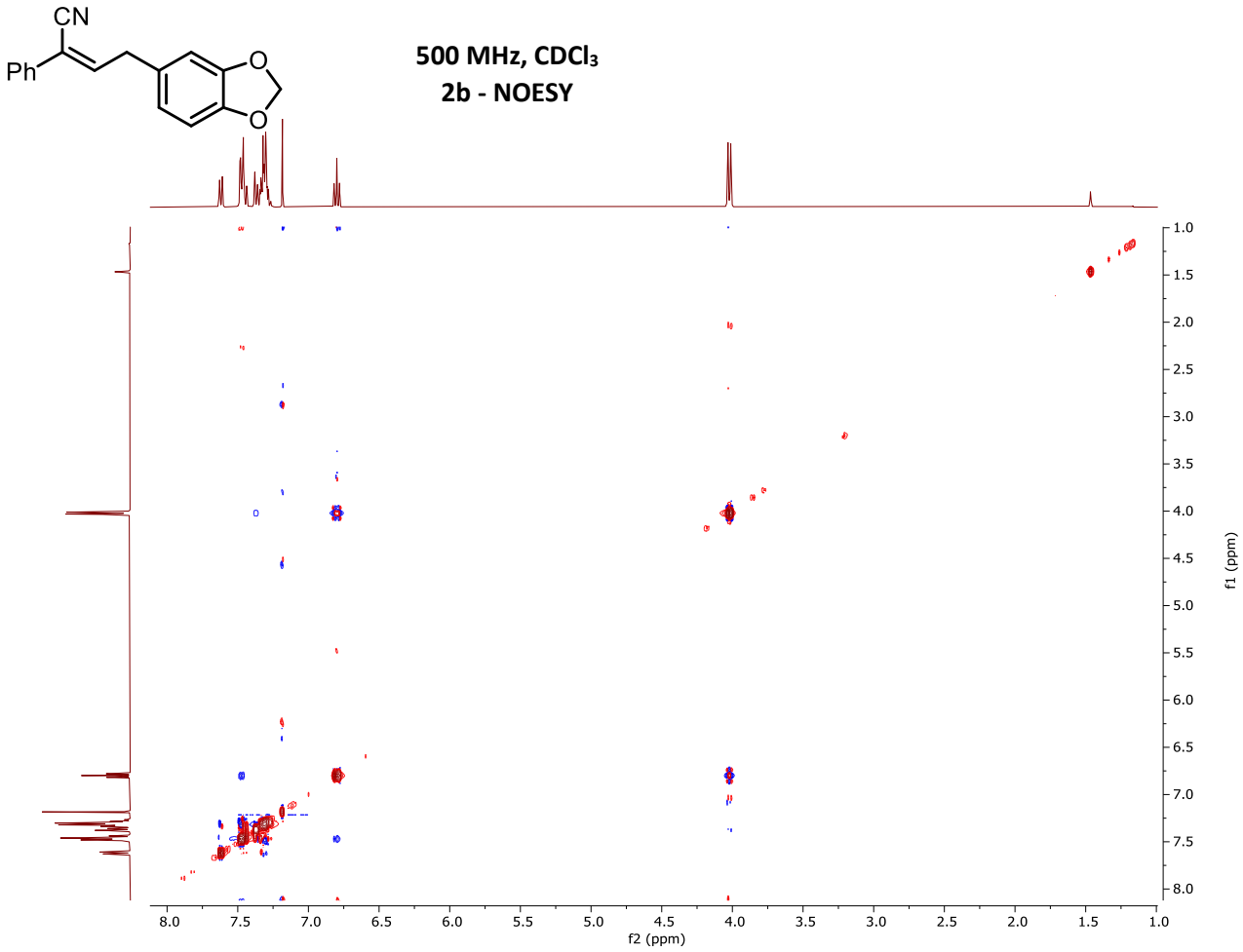
400 MHz, $CDCl_3$

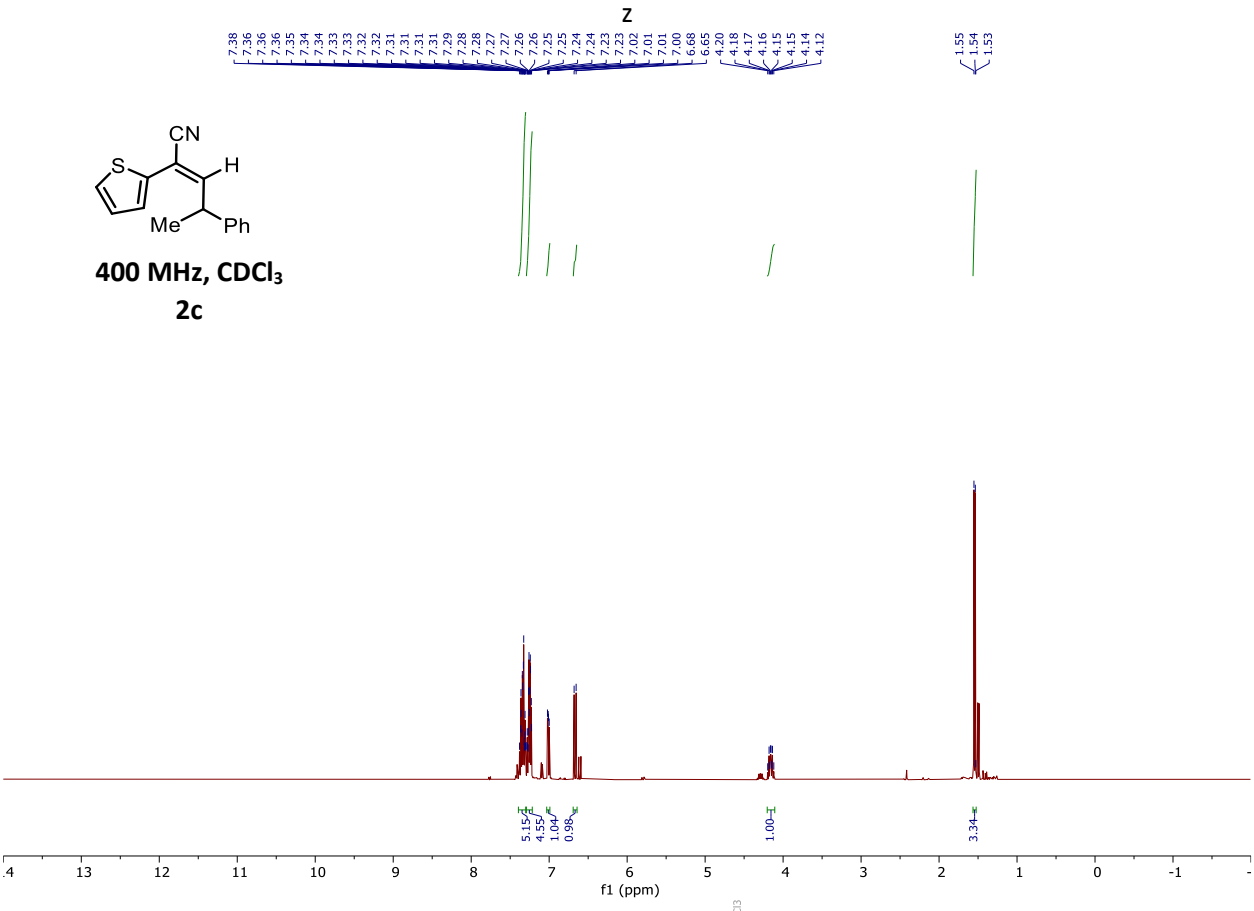
2b



100 MHz, $CDCl_3$

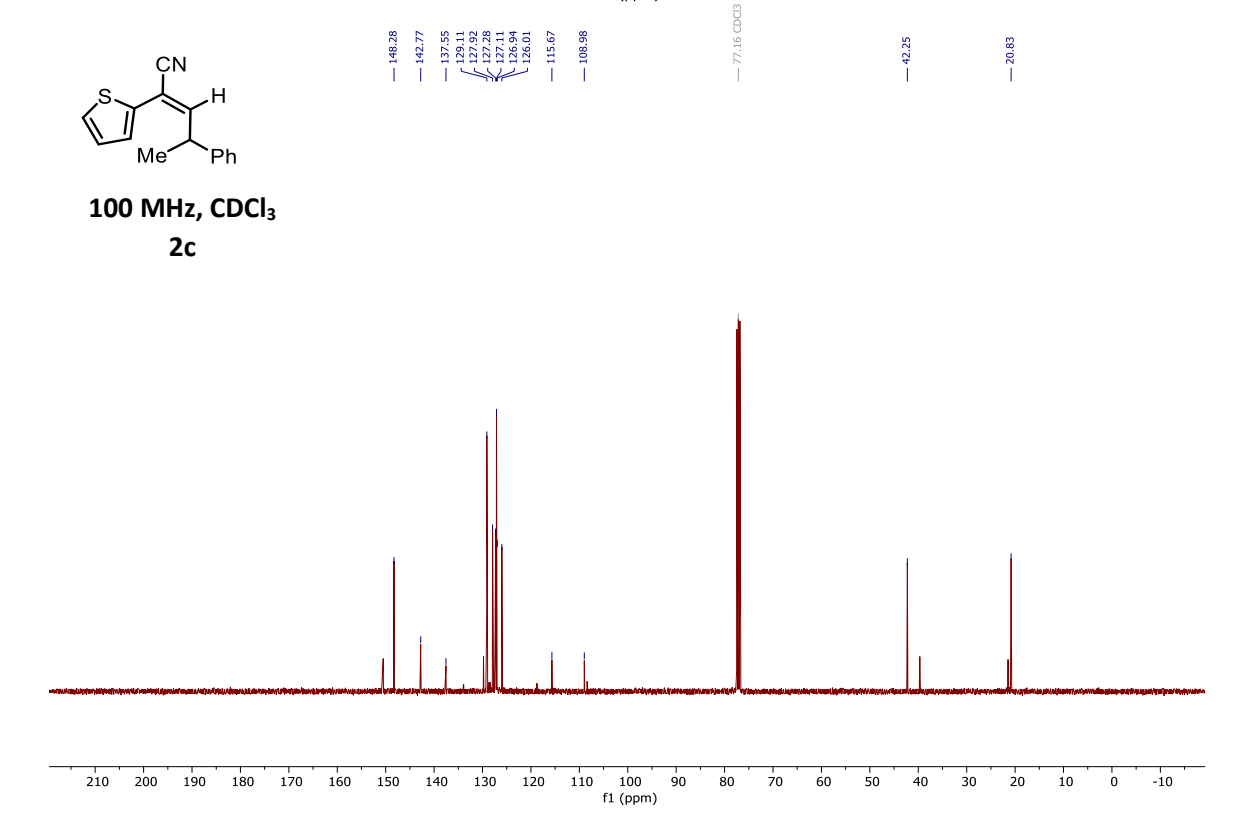
2b


CN
Ph
O
O
500 MHz, CDCl3
2b - NOESY
f1 (ppm)
f2 (ppm)
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0



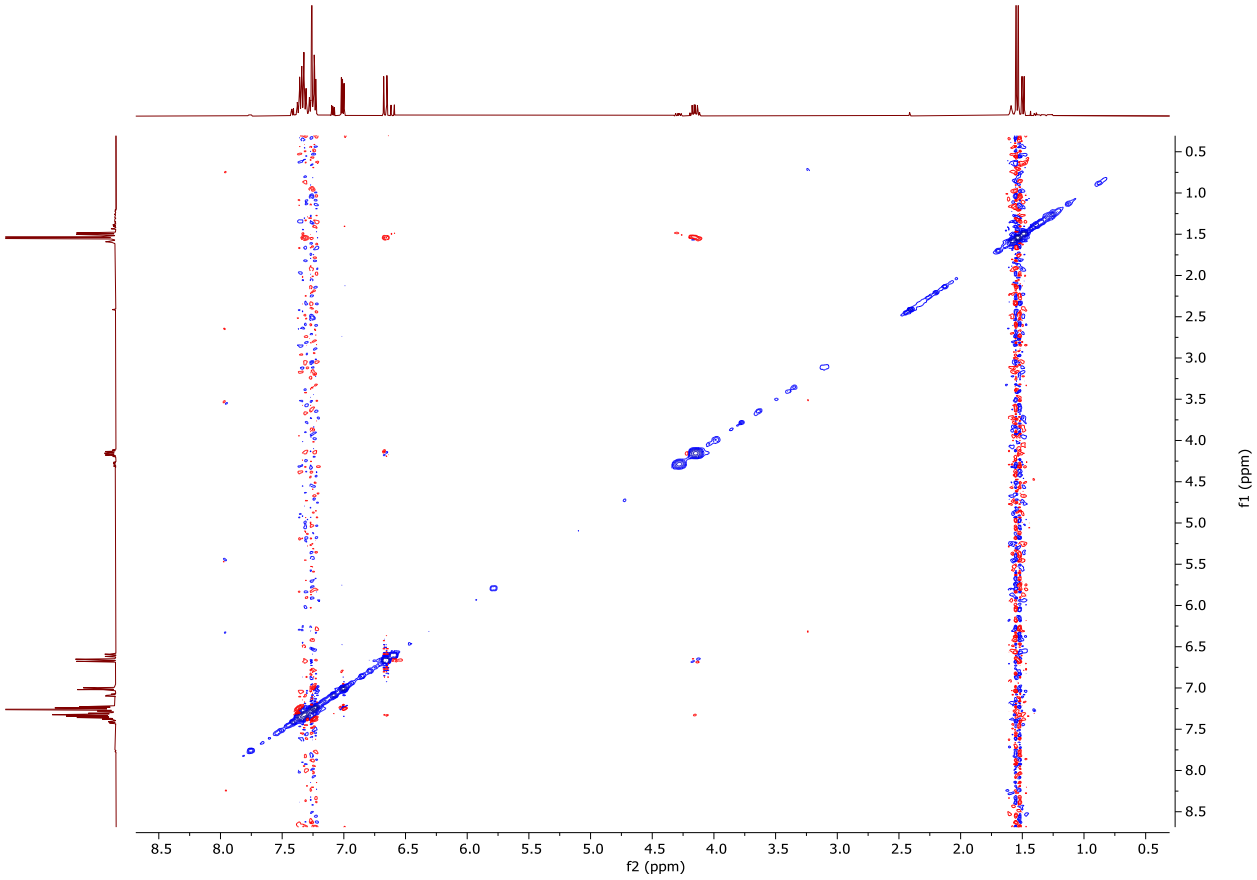
400 MHz, $CDCl_3$

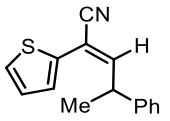
2c



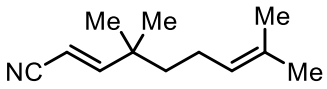
100 MHz, $CDCl_3$

2c



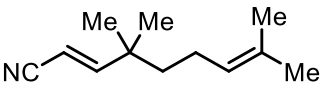


500 MHz, $CDCl_3$
2c – NOESY



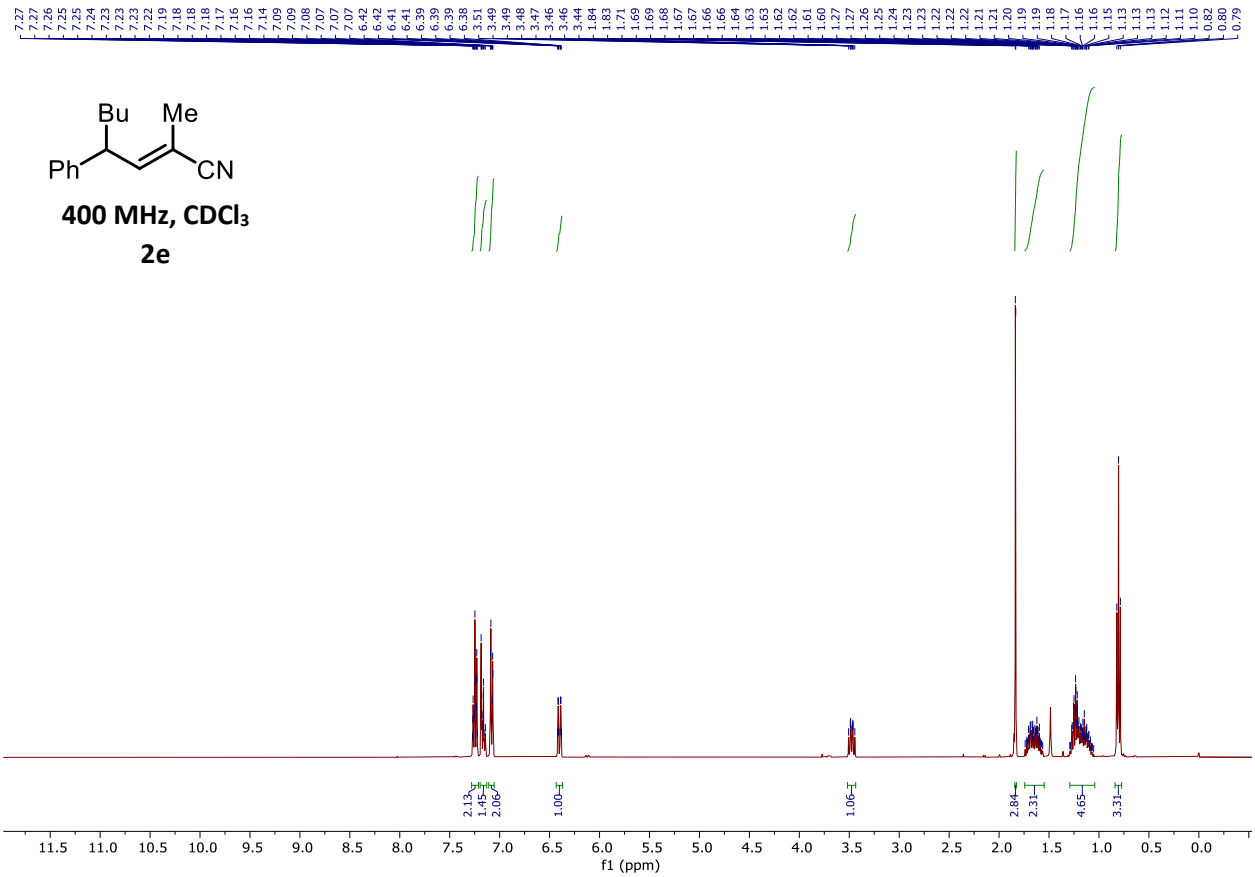
400 MHz, $CDCl_3$

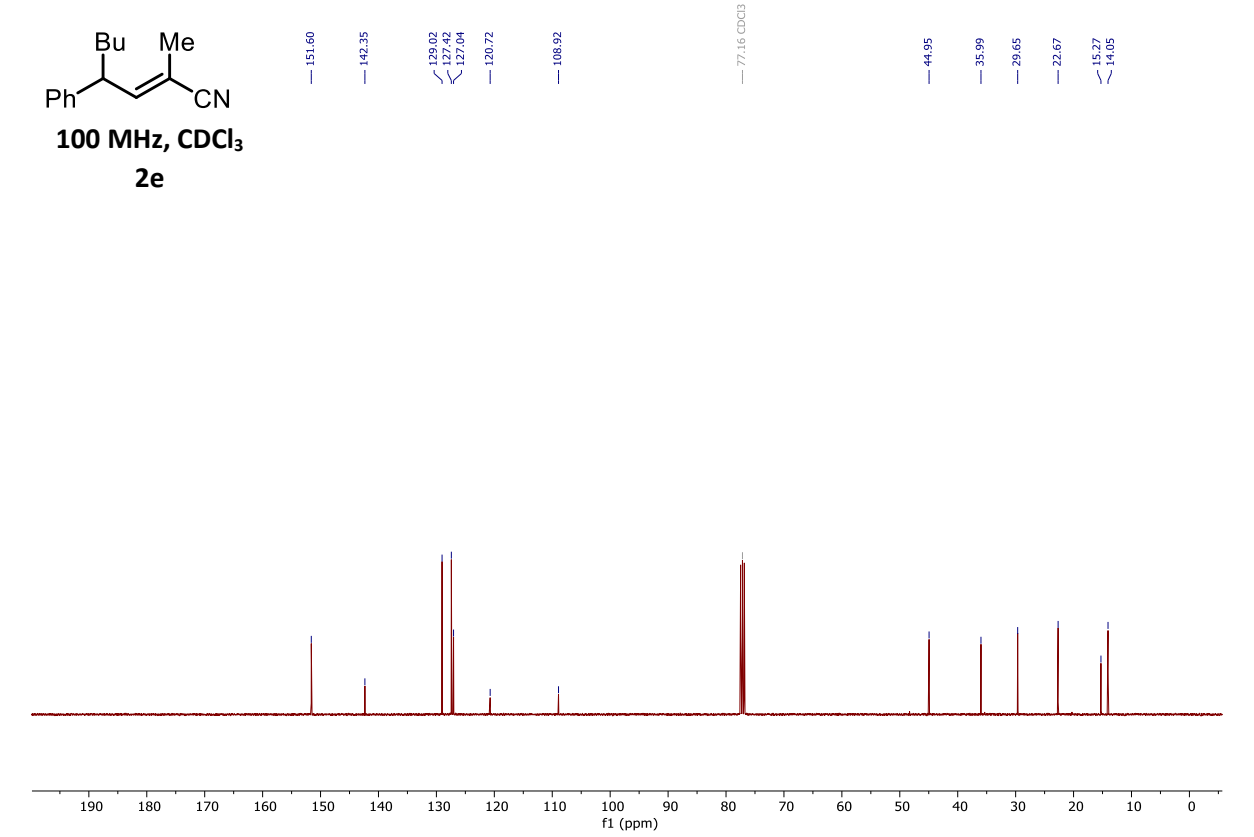
2d



100 MHz, $CDCl_3$

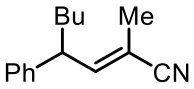
2d

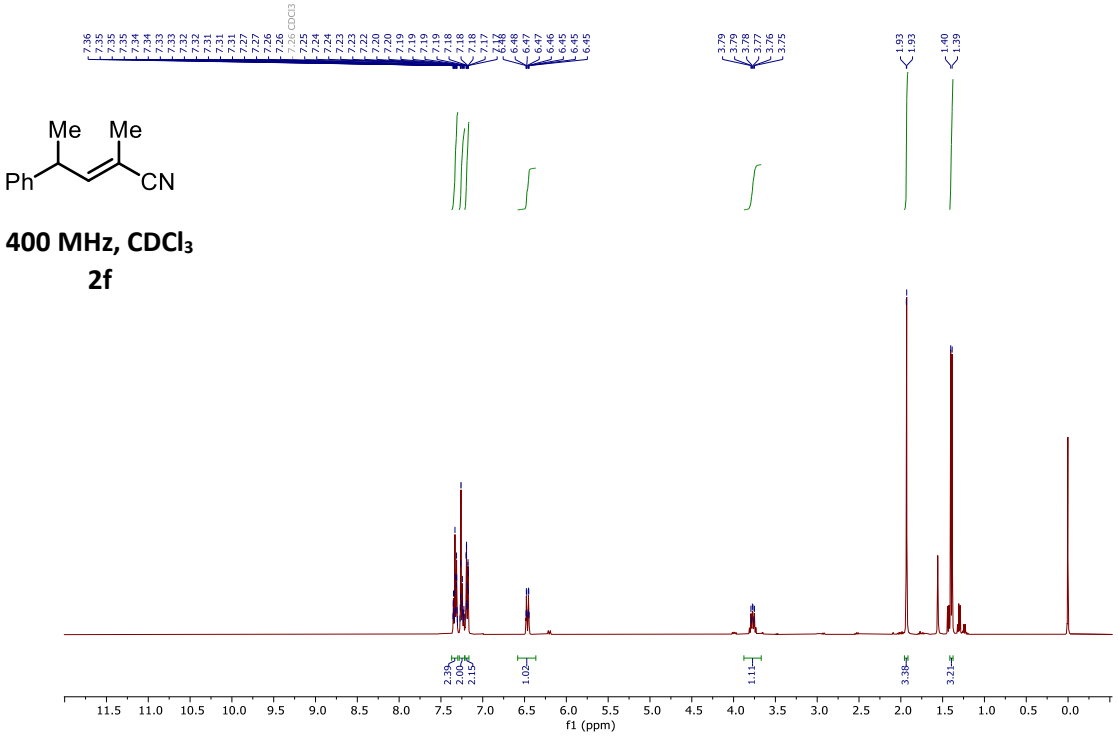

Bu
Me
Ph
CN
400 MHz, CDCl3
2e
f1 (ppm)


Bu
Me
Ph
CN
100 MHz, CDCl3
2e
f1 (ppm)

500 MHz, $CDCl_3$

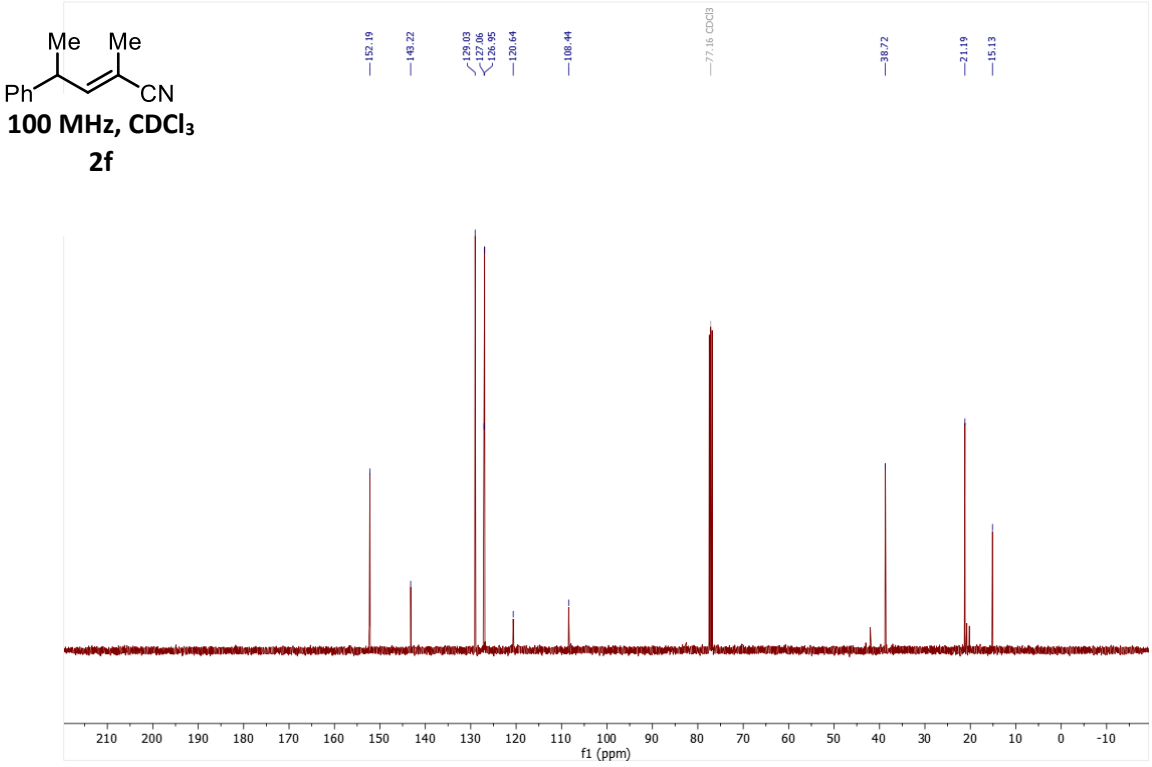
2e – NOESY





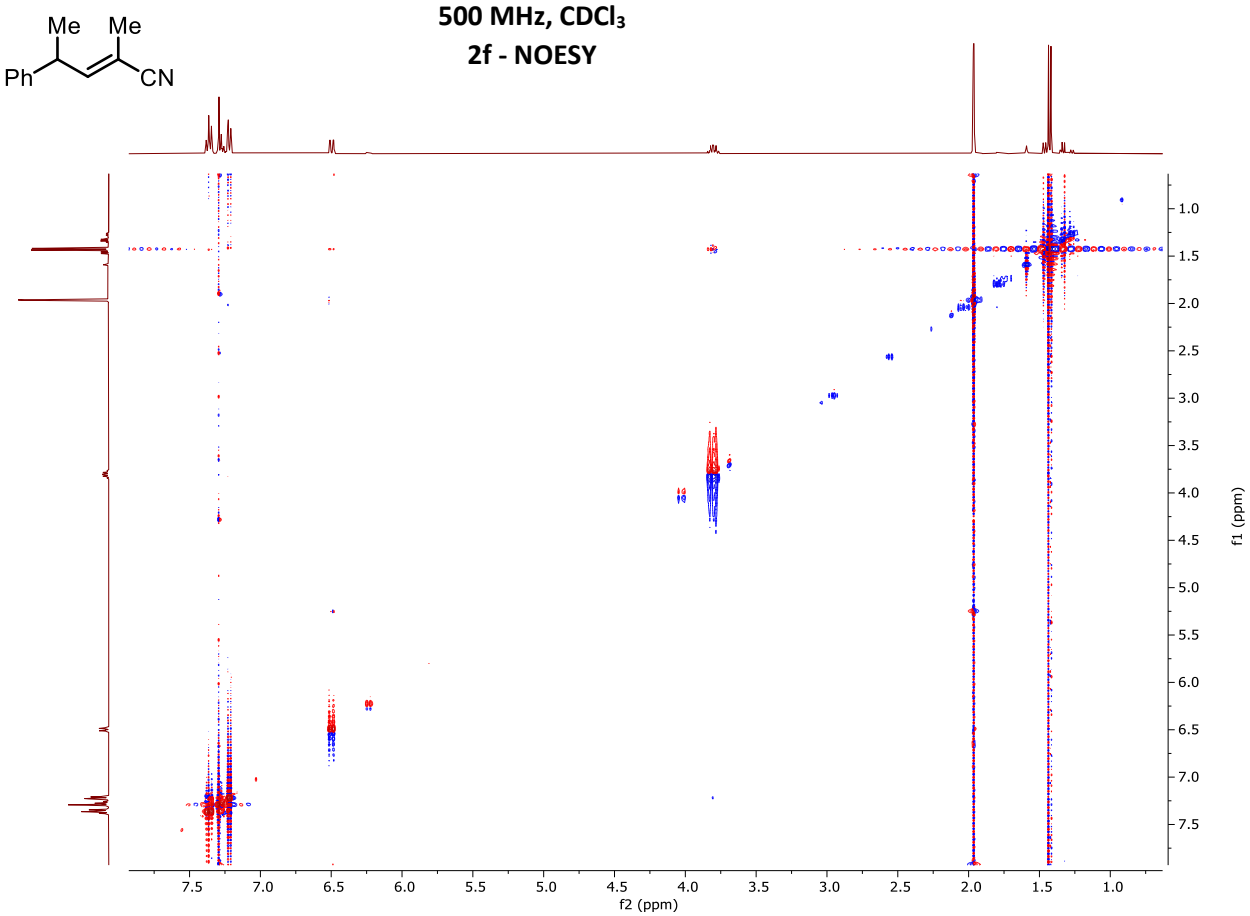
400 MHz, $CDCl_3$

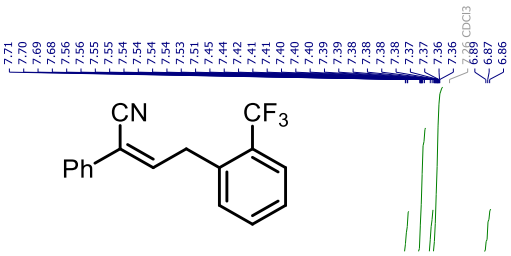
2f



100 MHz, $CDCl_3$

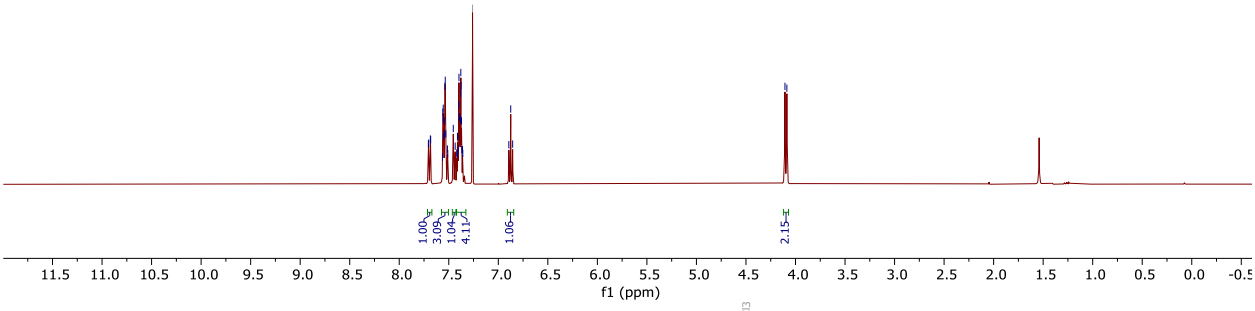
2f

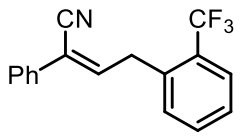

Me
Me
Ph
CN
500 MHz, CDCl3
2f - NOESY
f2 (ppm)
f1 (ppm)



400 MHz, $CDCl_3$

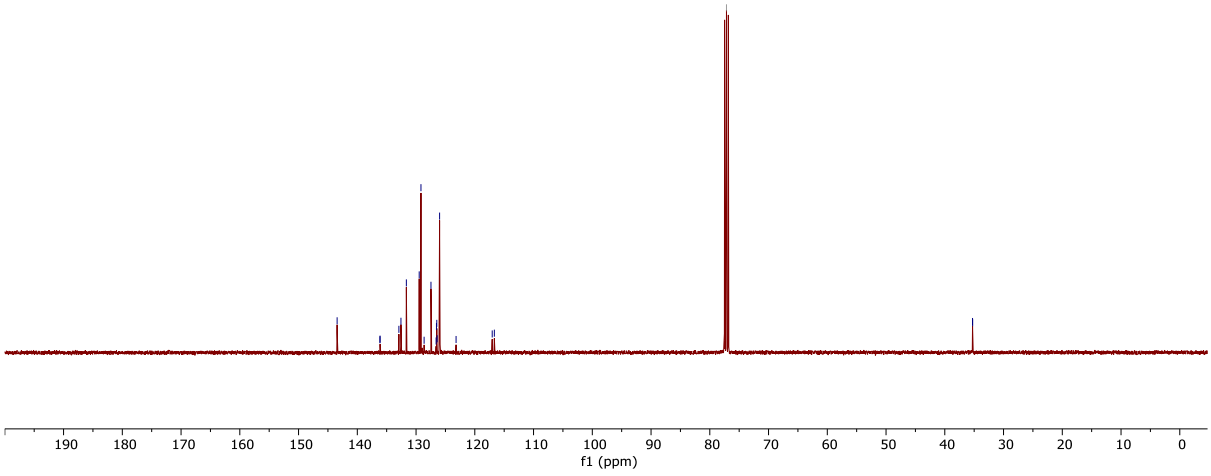
2g

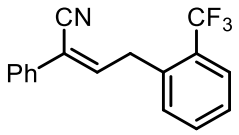




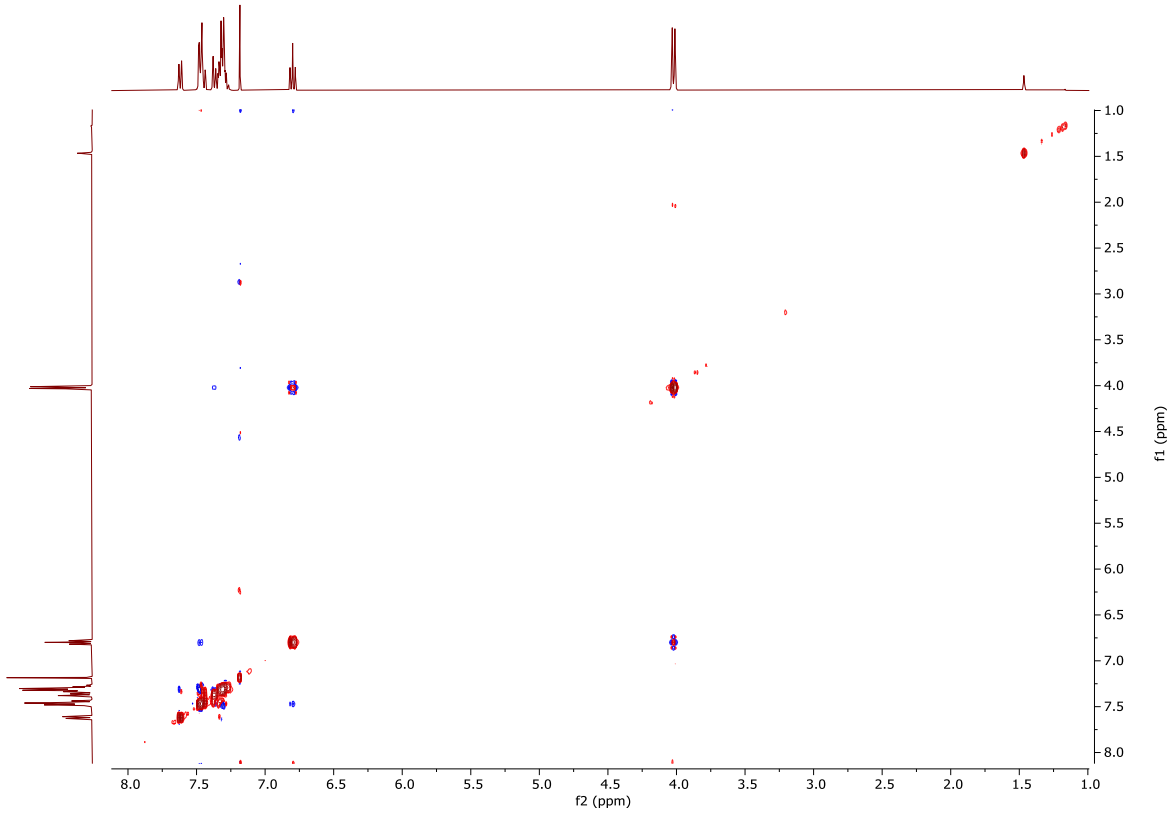
100 MHz, $CDCl_3$

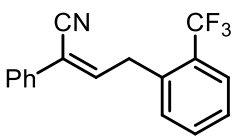
2g



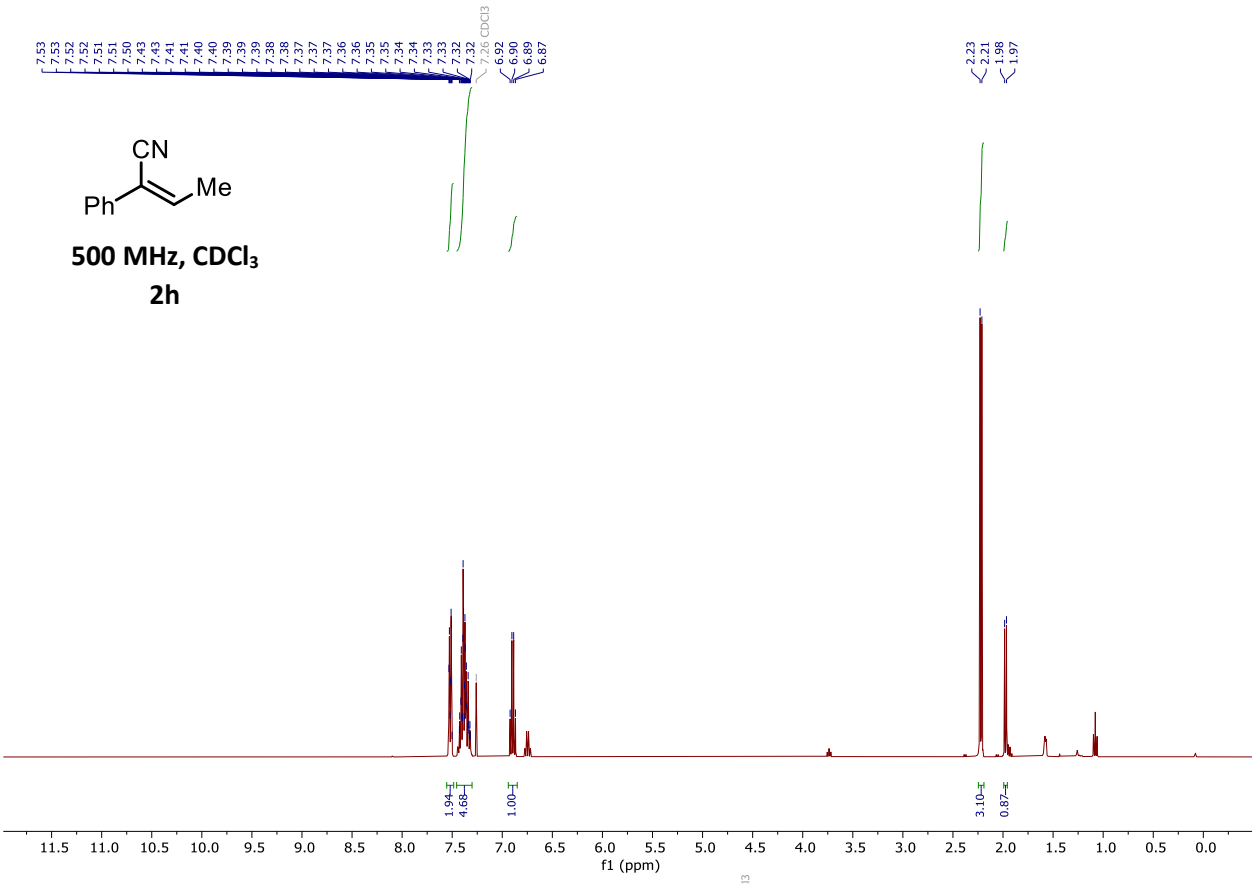


376 MHz, $CDCl_3$
2g

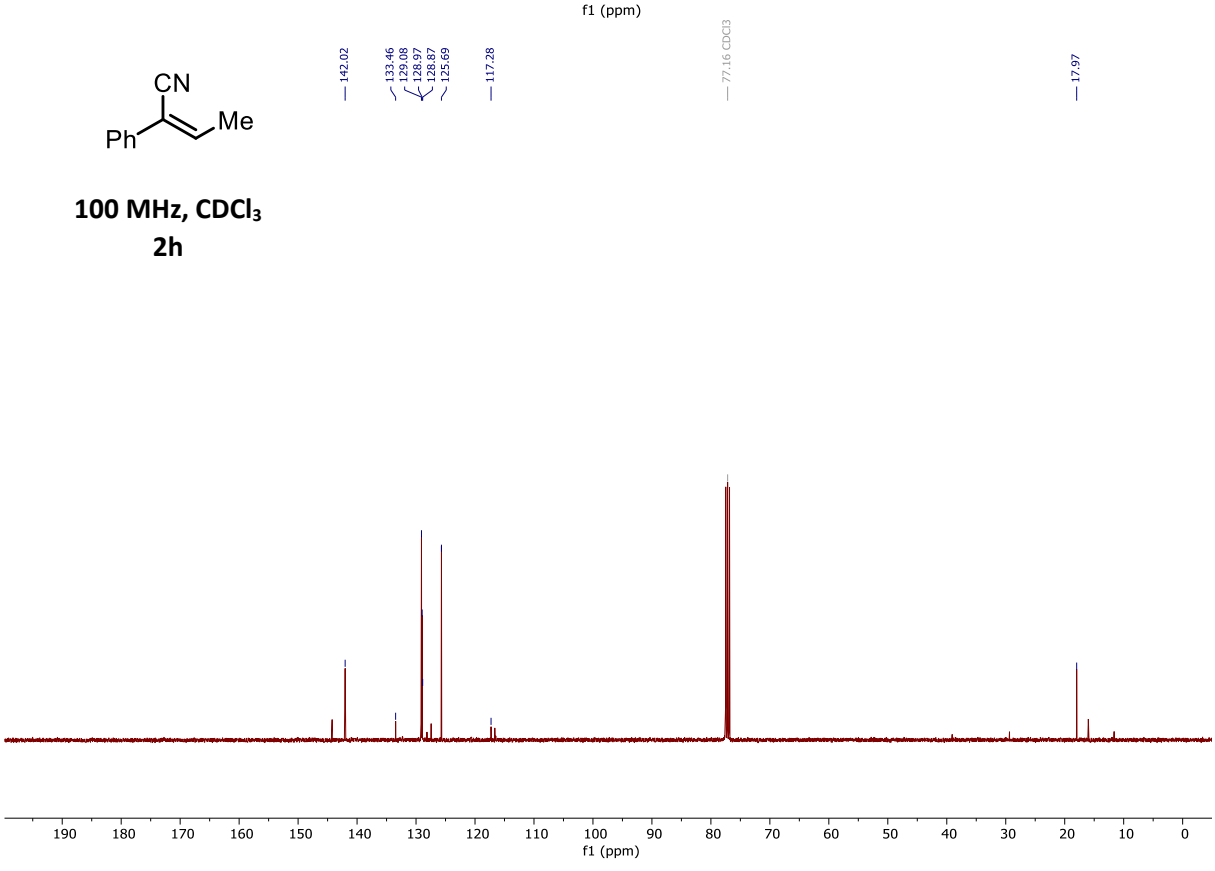




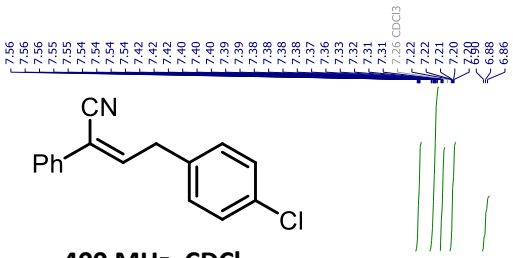
500 MHz, $CDCl_3$
2g - NOESY



500 MHz, $CDCl_3$
2h

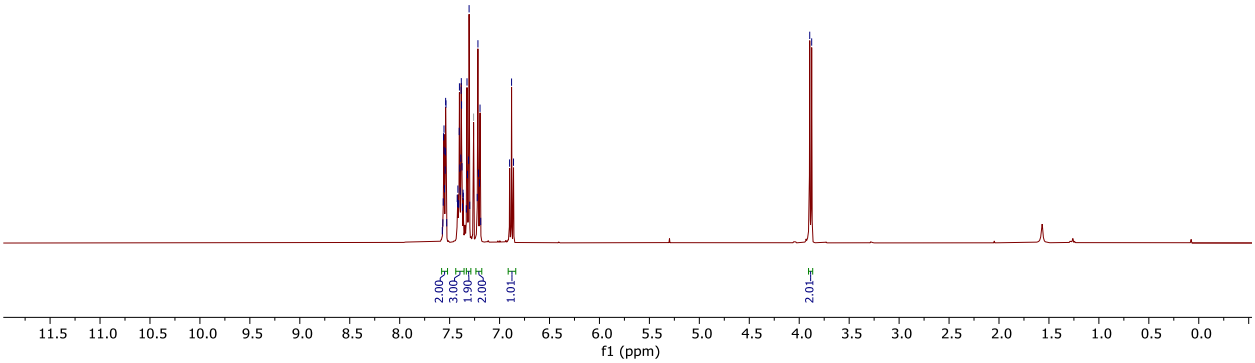


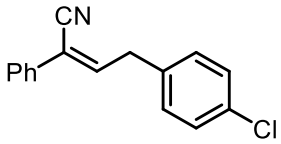
100 MHz, $CDCl_3$
2h



400 MHz, $CDCl_3$

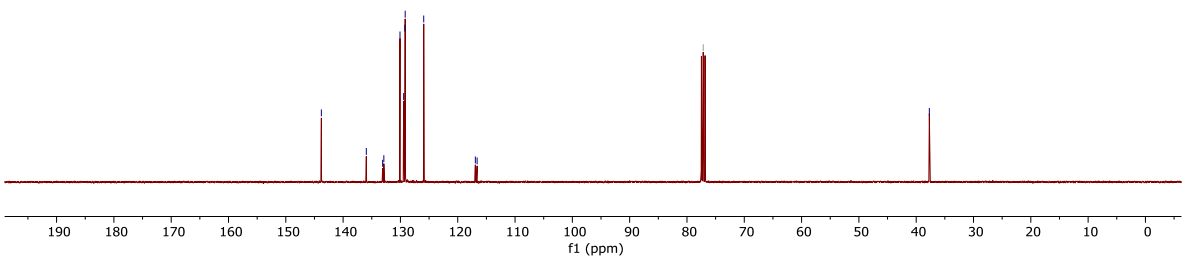
2i

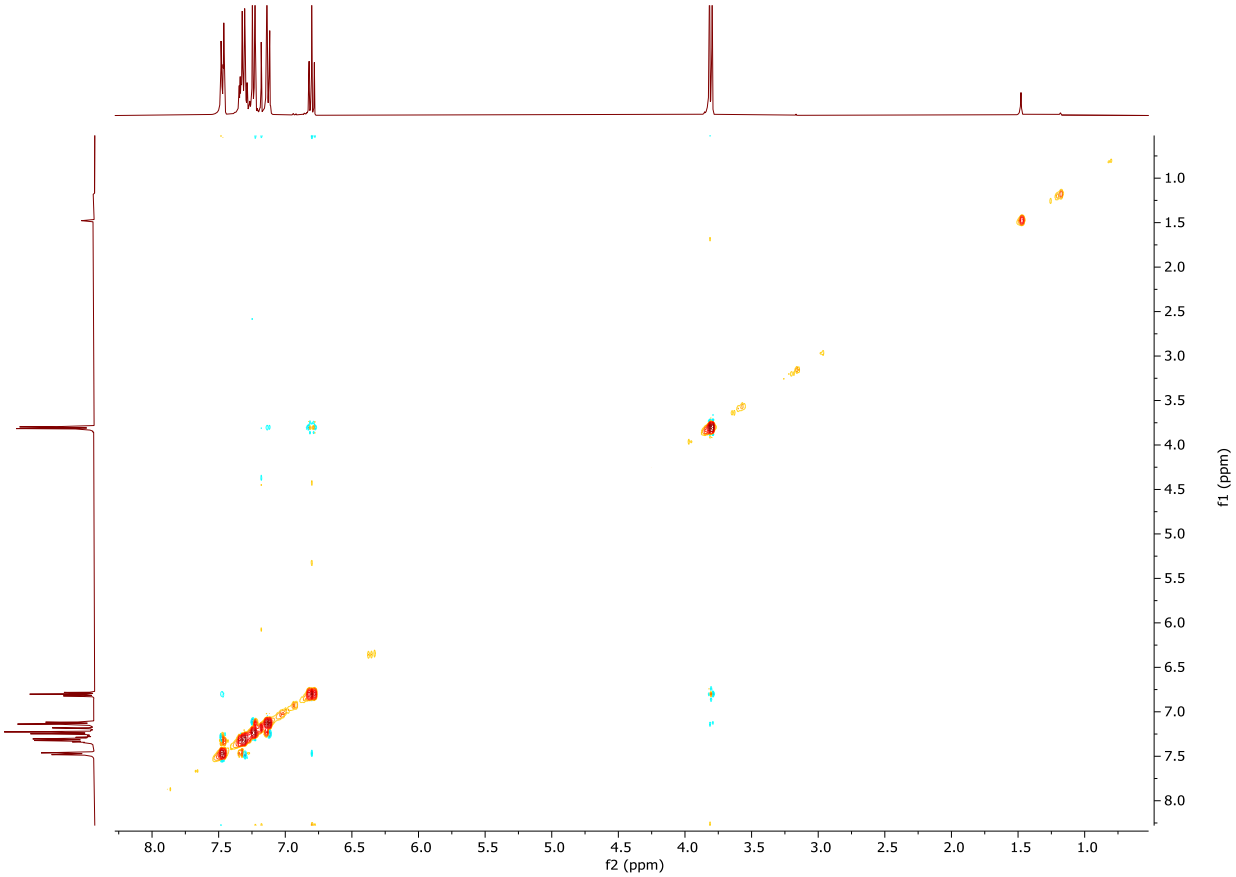


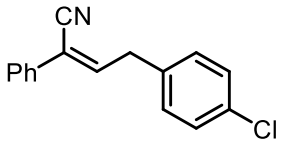


100 MHz, $CDCl_3$

2i

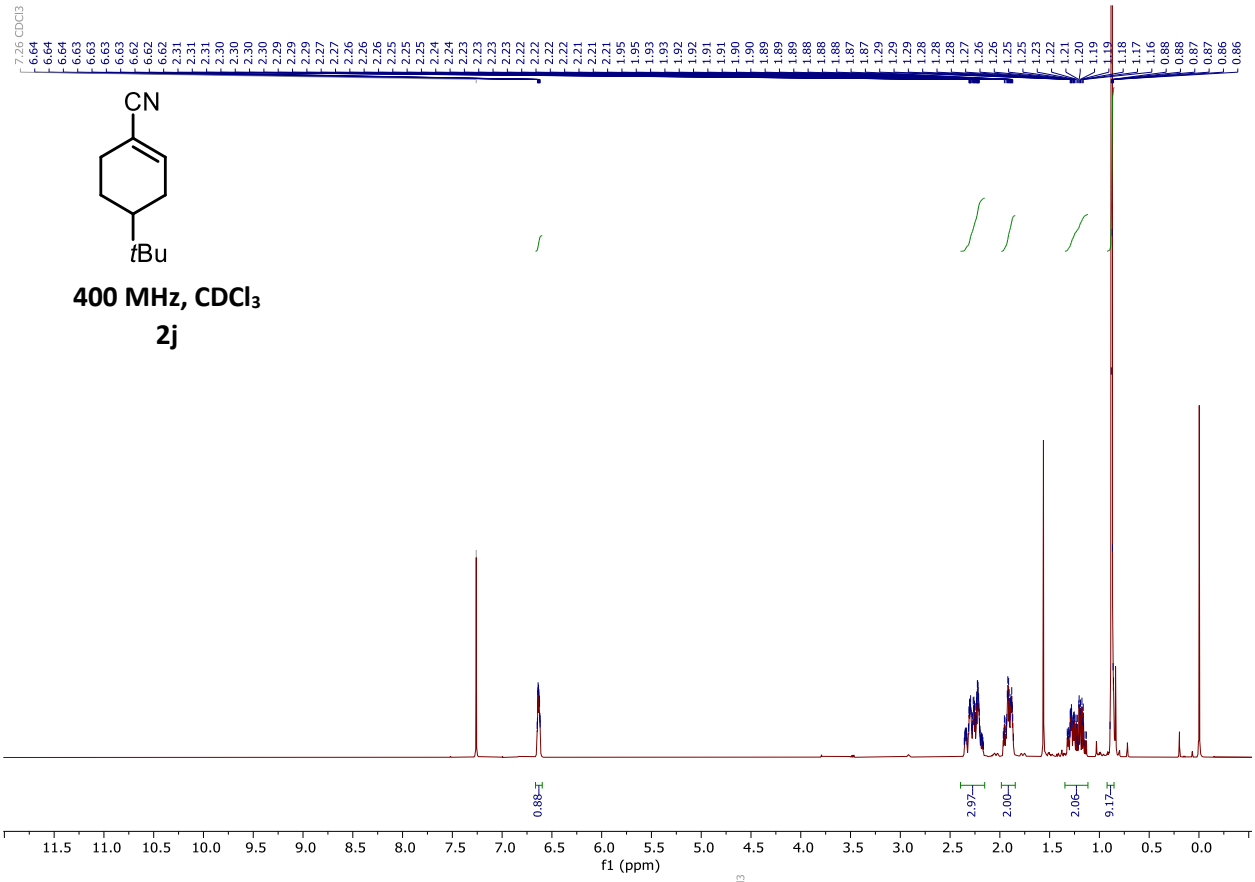






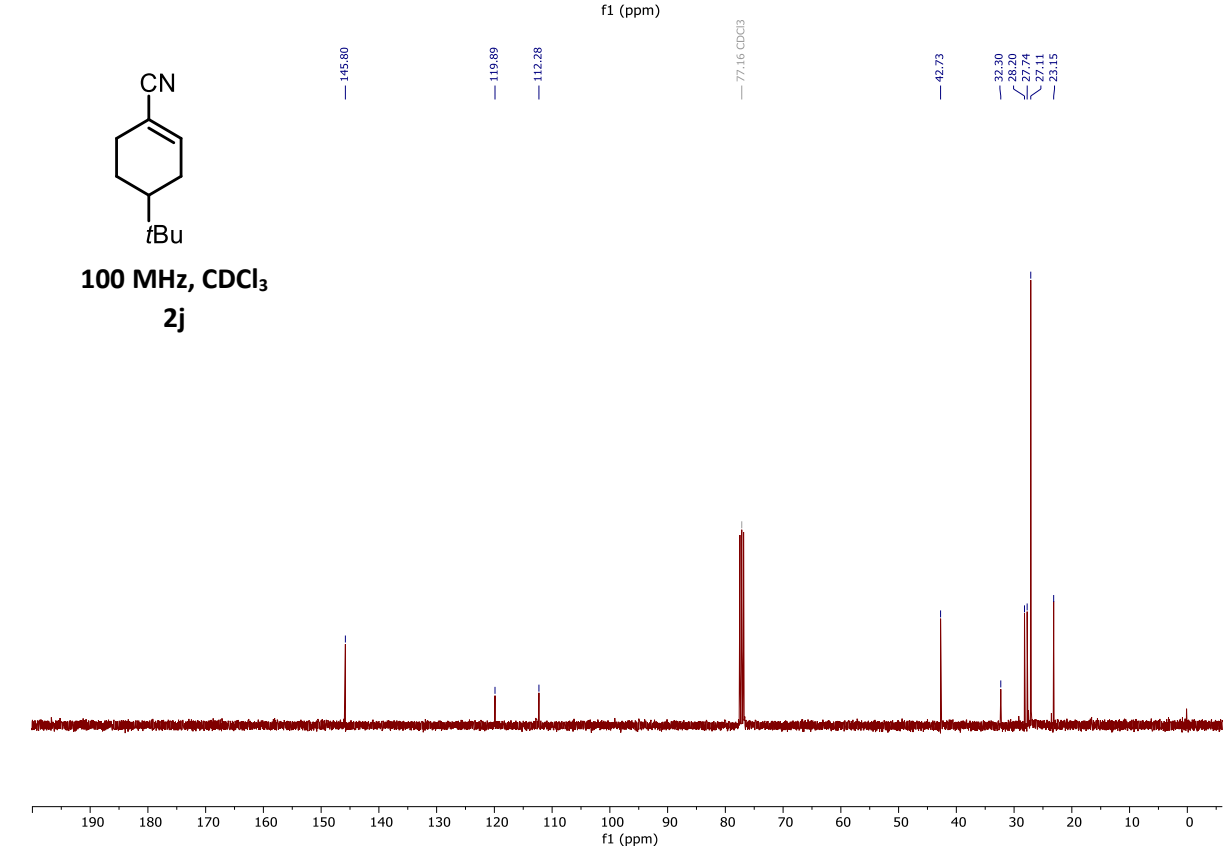
500 MHz, $CDCl_3$

2i - NOESY



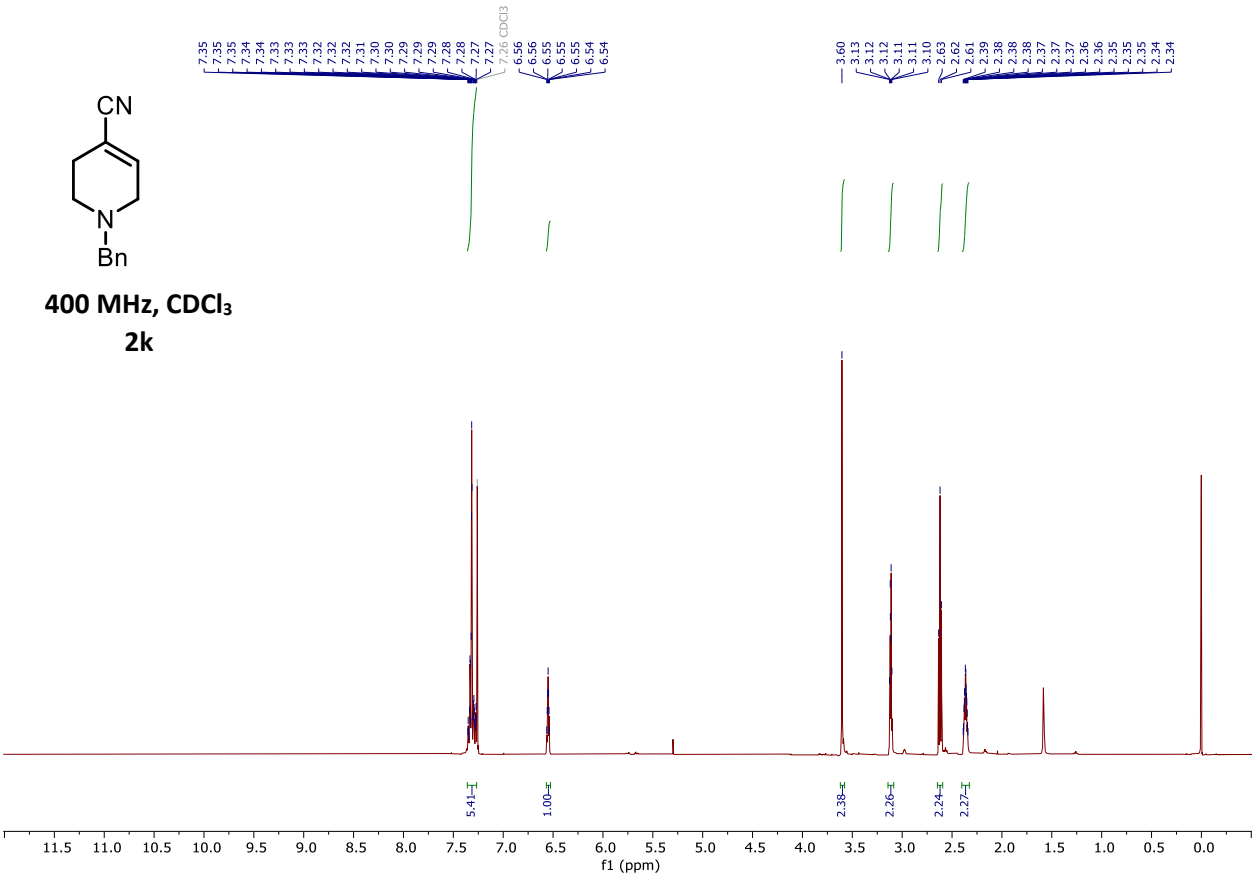
400 MHz, $CDCl_3$

2j



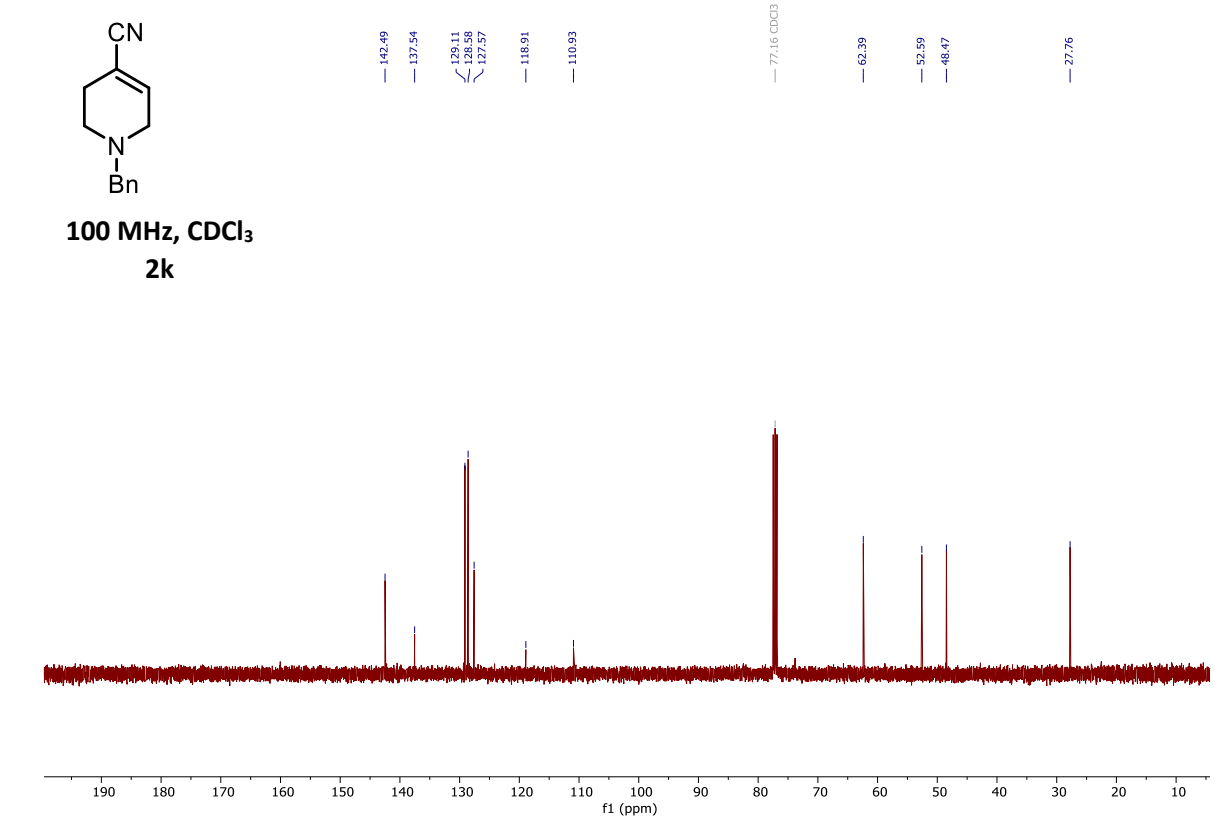
100 MHz, $CDCl_3$

2j



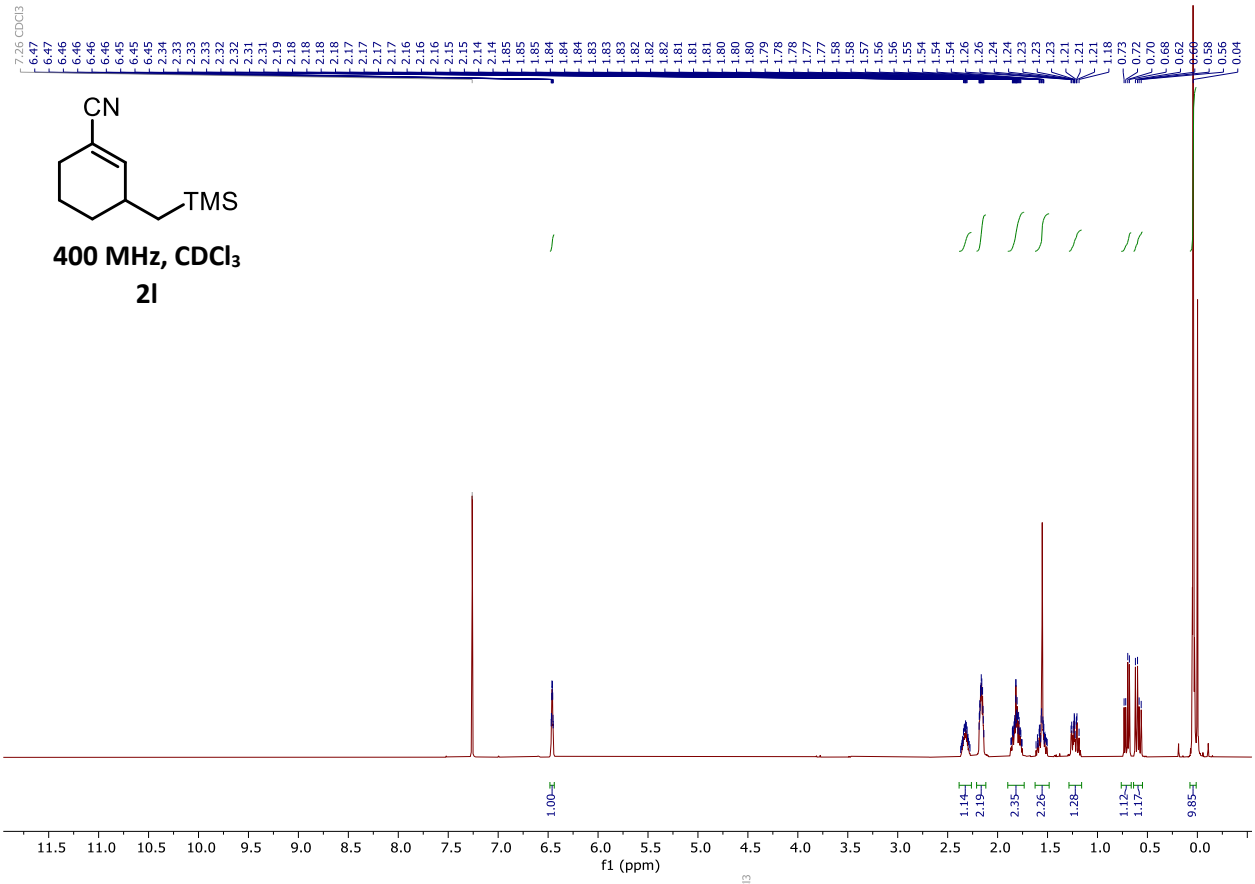
400 MHz, $CDCl_3$

2k



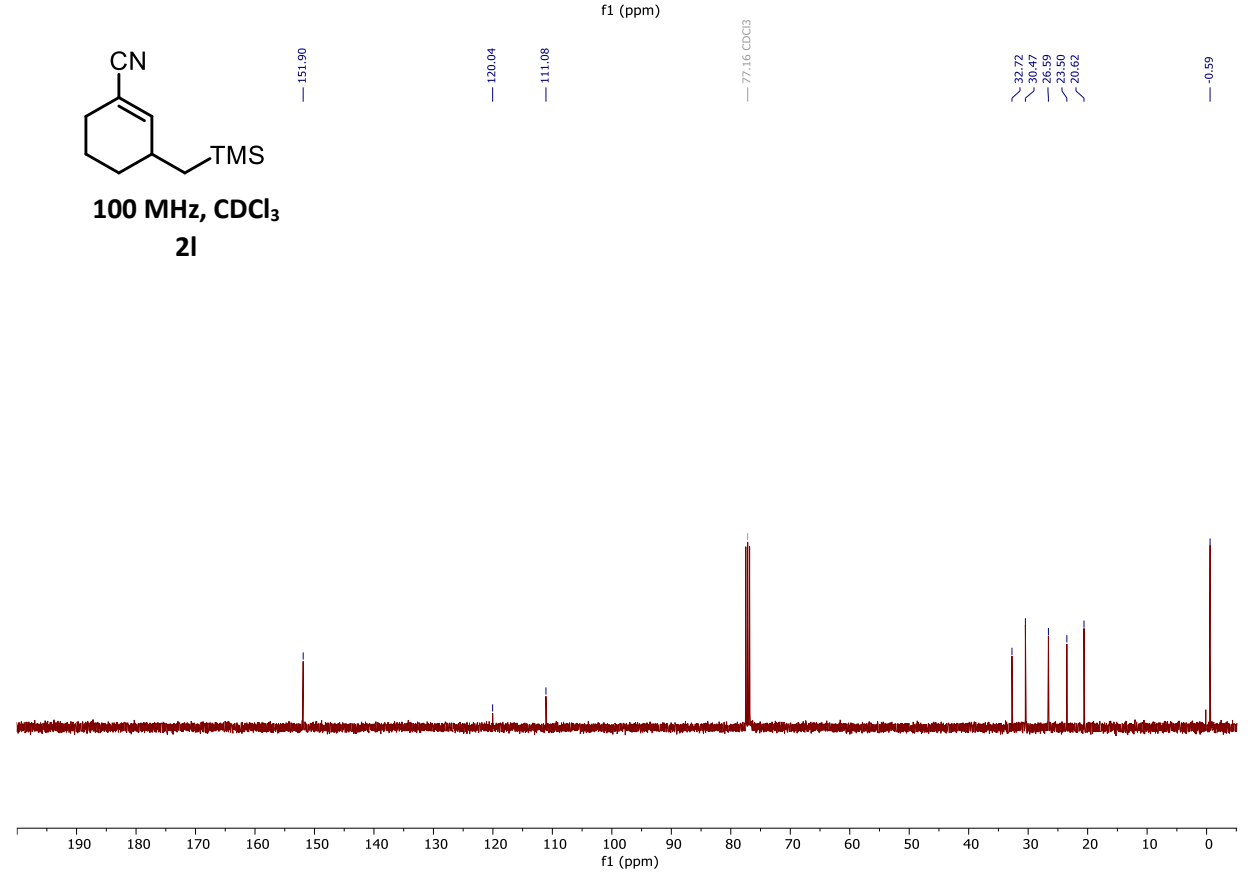
100 MHz, $CDCl_3$

2k



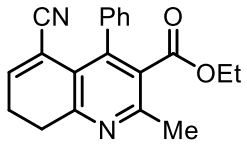
400 MHz, $CDCl_3$

2l



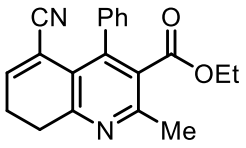
100 MHz, $CDCl_3$

2l



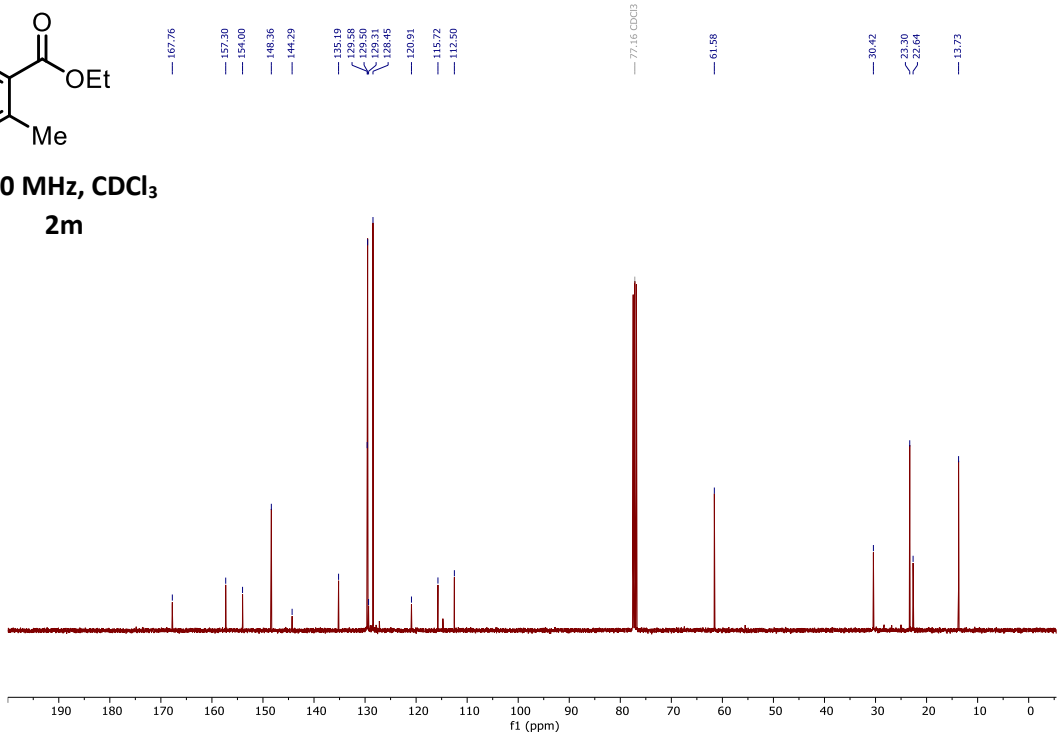
400 MHz, $CDCl_3$

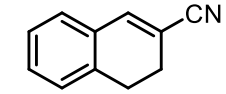
2m



100 MHz, $CDCl_3$

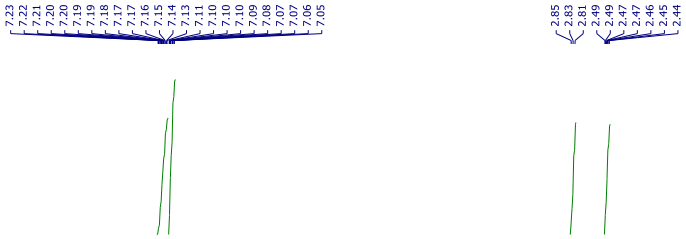
2m

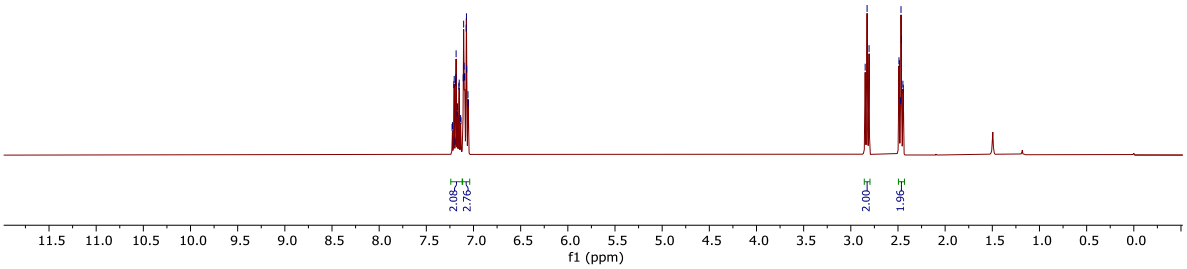


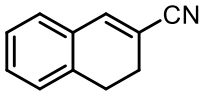


400 MHz, $CDCl_3$

2n

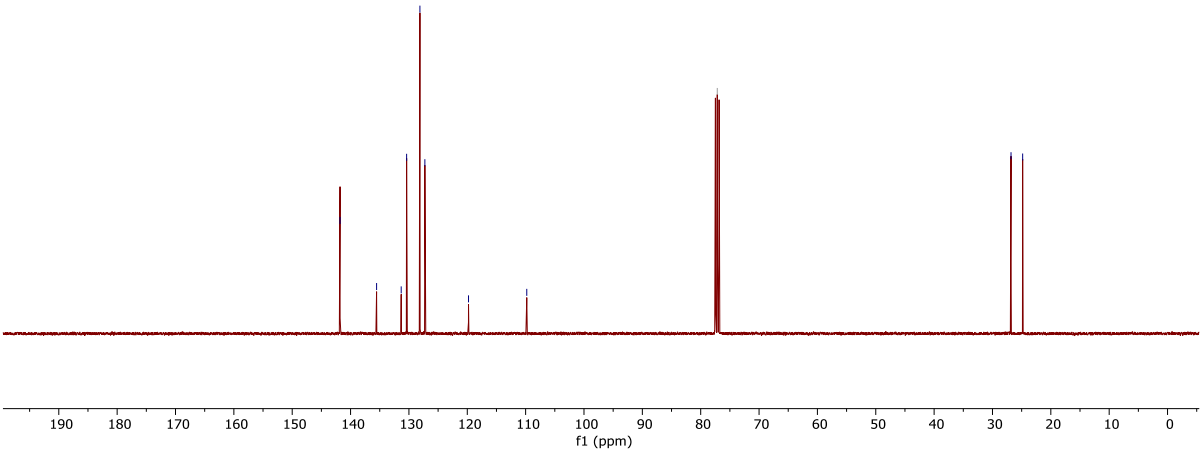


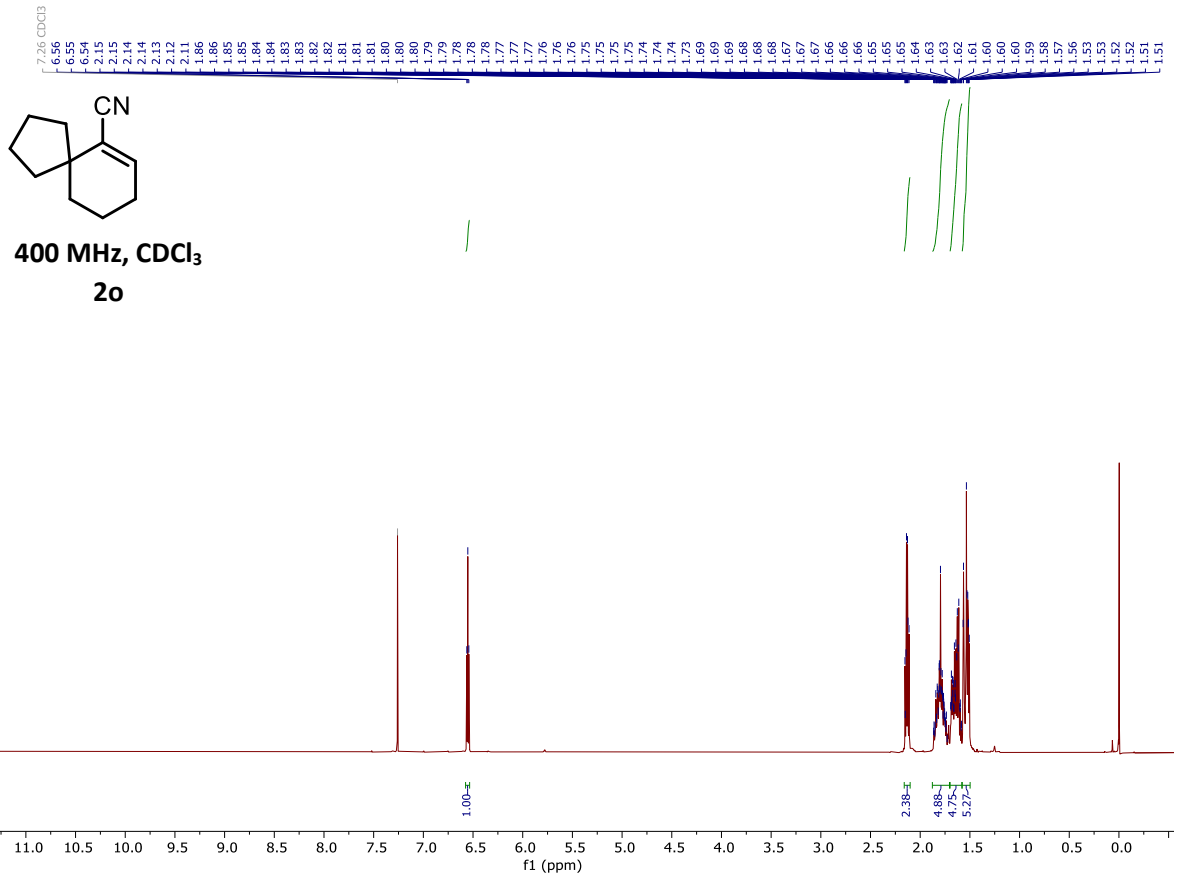


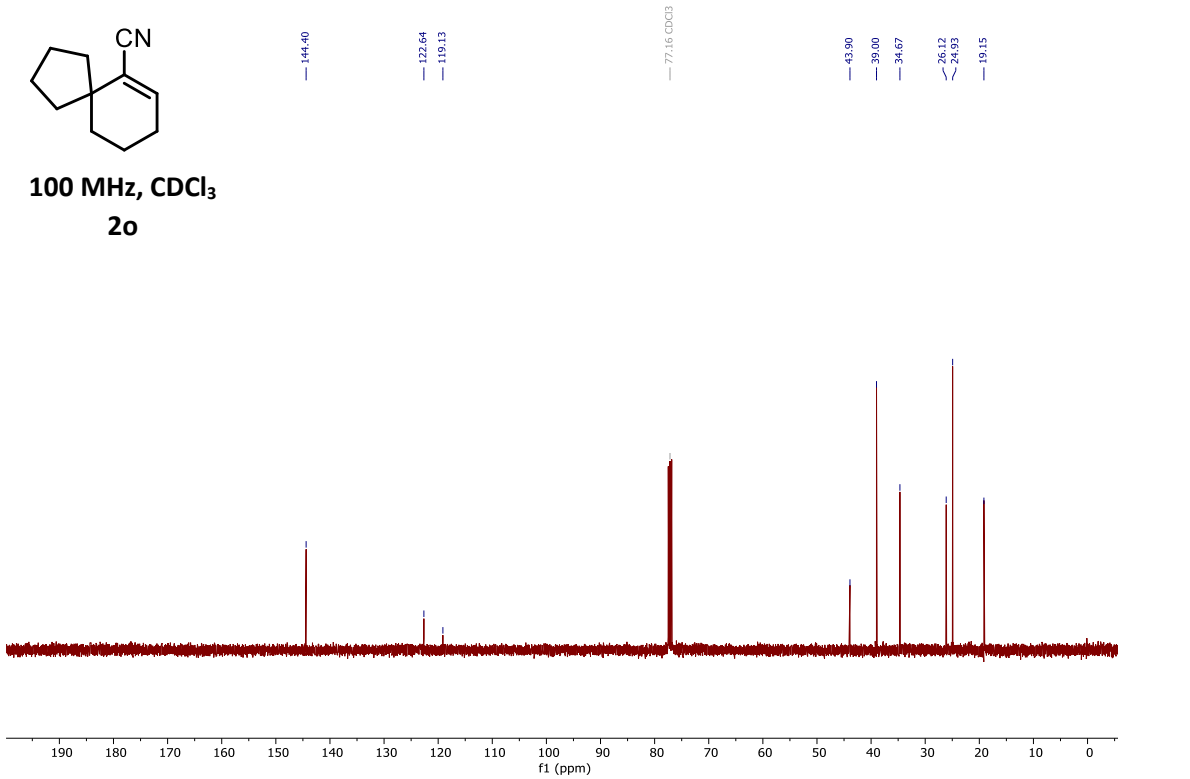


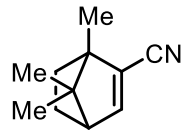
100 MHz, $CDCl_3$

2n



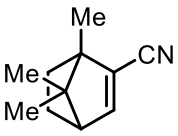

CN
400 MHz, CDCl3
2o
7.26 CDCl3
1.00
2.38
4.88
4.75
5.27
f1 (ppm)


CN
100 MHz, CDCl3
2o
144.40
122.64
119.13
77.16 CDCl3
43.90
39.00
34.67
26.12
24.93
19.15
f1 (ppm)



400 MHz, $CDCl_3$

2p



100 MHz, $CDCl_3$

2p