Synthesis

Reviews and Full Papers in Chemical Synthesis

Supporting Information

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Thieme

Cascade Radical Cyclization to Vinylogous Carbonates/Carbamates for the Synthesis of Oxa- and Aza-Angular Triquinanes: Diastereoselectivity Depends on the Ring Size of Radical Precursor

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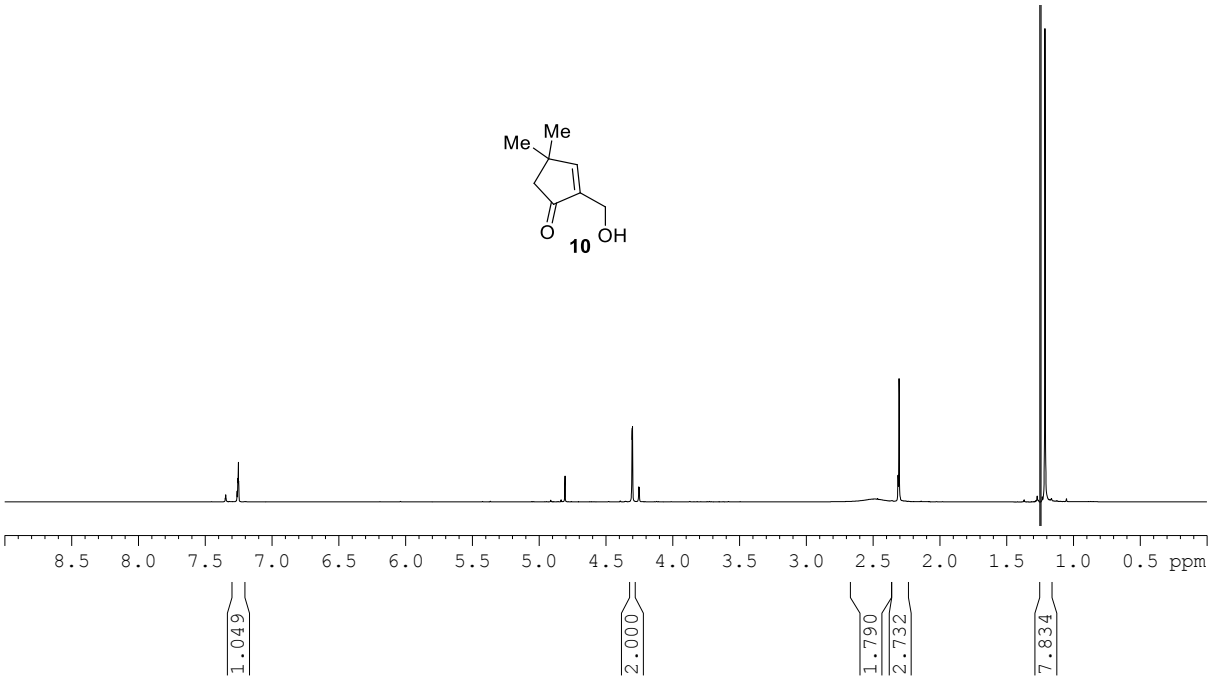
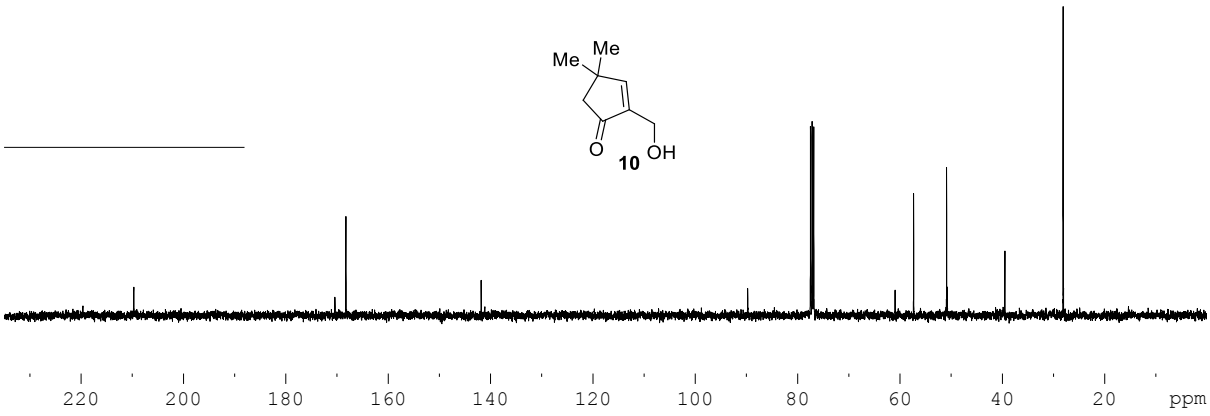
Representative Experimental Procedure and Spectra

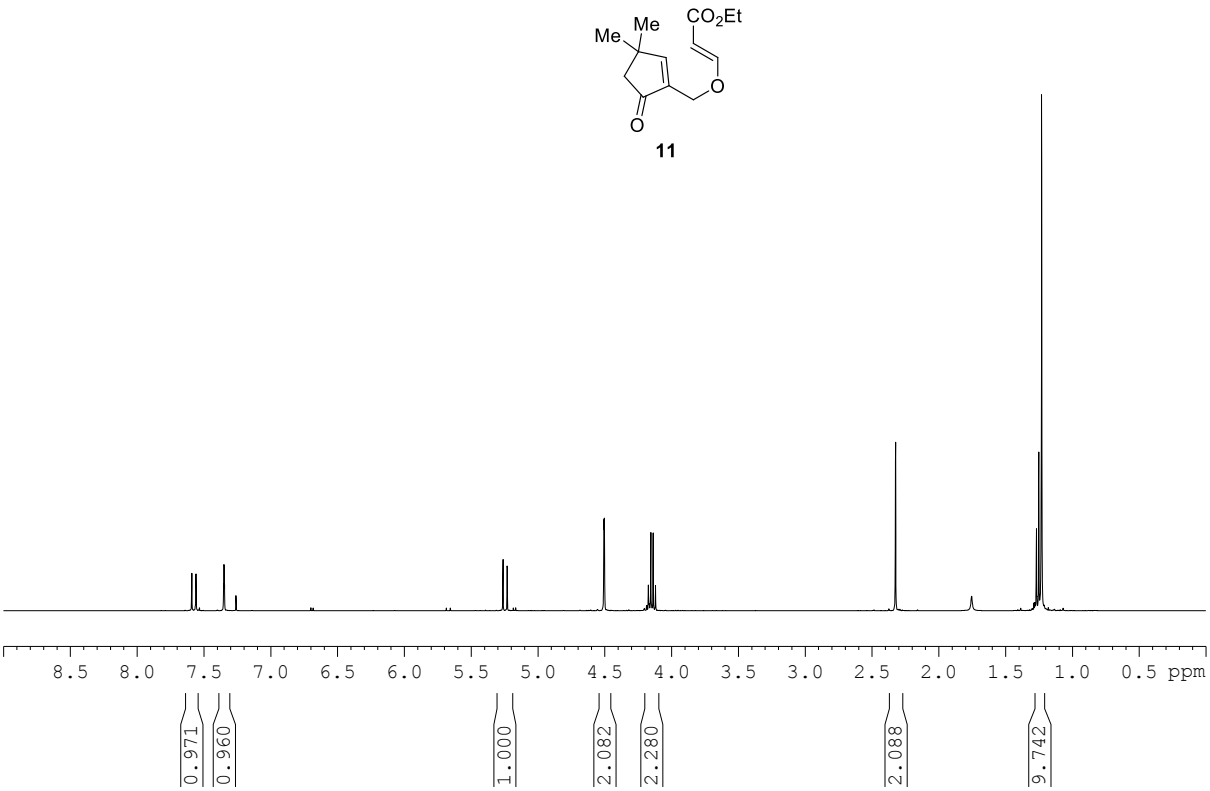
General: Melting points are recorded using sigma melting point apparatus in capillary tubes and are uncorrected. IR spectra were recorded on Nicolet 6700 spectrophotometer and JASCO FT-IR-4100 spectrophotometer. 1H (400 MHz) and 13C (100 MHz) spectra were recorded on Bruker Avance 400 spectrophotometer. 1H (500 MHz) and 13C (125 MHz) spectra were recorded on Bruker Avance 500 spectrophotometer. The chemical shifts (ppm) and coupling constants (Hz) are reported in the standard fashion with reference to chloroform . In the 13C NMR spectra, the nature of the carbons (C, CH, CH2 or CH3) was determined by recording the DEPT-135 experiment and is given in parentheses. CHN analysis was carried out using Elemental analyzer VSM-VT. High resolution mass measurements were carried out using Micromass Q-ToF instrument using direct inlet mode. Analytical thin-layer chromatography (TLC) was performed on glass plates (7.5 x 2.5 and 7.5 x 5.0 cm) coated with Merck silica gel G containing 13% calcium sulfate as binder or on pre-coated 0.2 mm thick Merck 60 F245 silica plates and various combinations of ethyl acetate and hexane were used as eluent. Visualization of spots was accomplished by exposure to iodine vapour and UV light. All compounds were purified using silica gel [Acme's silica gel (100-200 mesh)] column chromatography. All small-scale dry reactions were carried out using standard syringe septum technique. Dry THF was obtained by distillation over sodium-benzophenone ketyl. Dry dichloromethane and dry DMF was prepared by distilling over calcium hydride. AIBN obtained from spectrochem was recrystallized from ether and stored at 0-5 ^{o}C in the dark. All the commercial reagents were used as such without further purification.



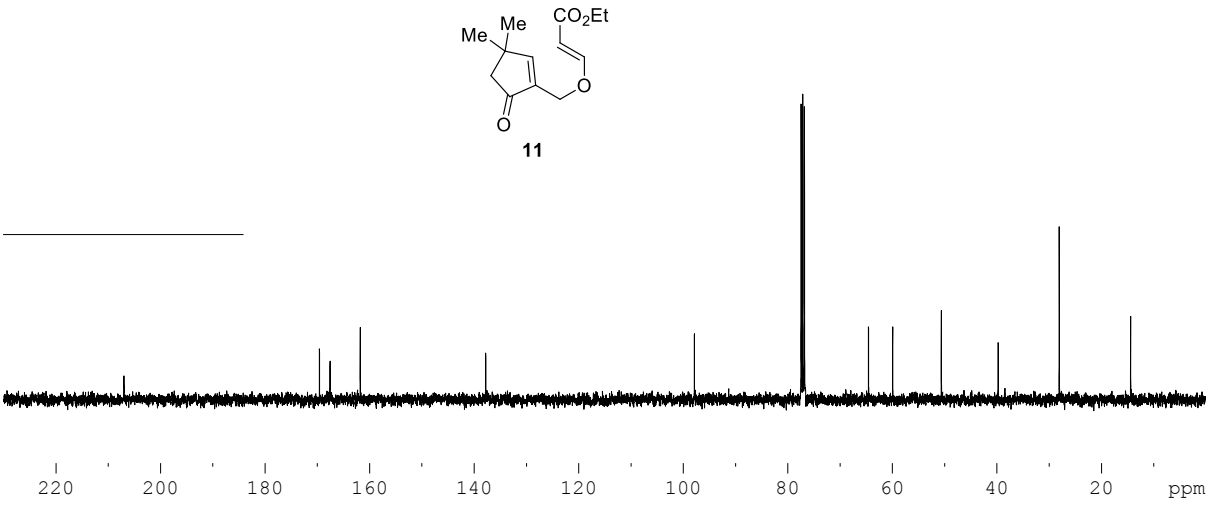
^{1}H NMR spectrum of alcohol 10



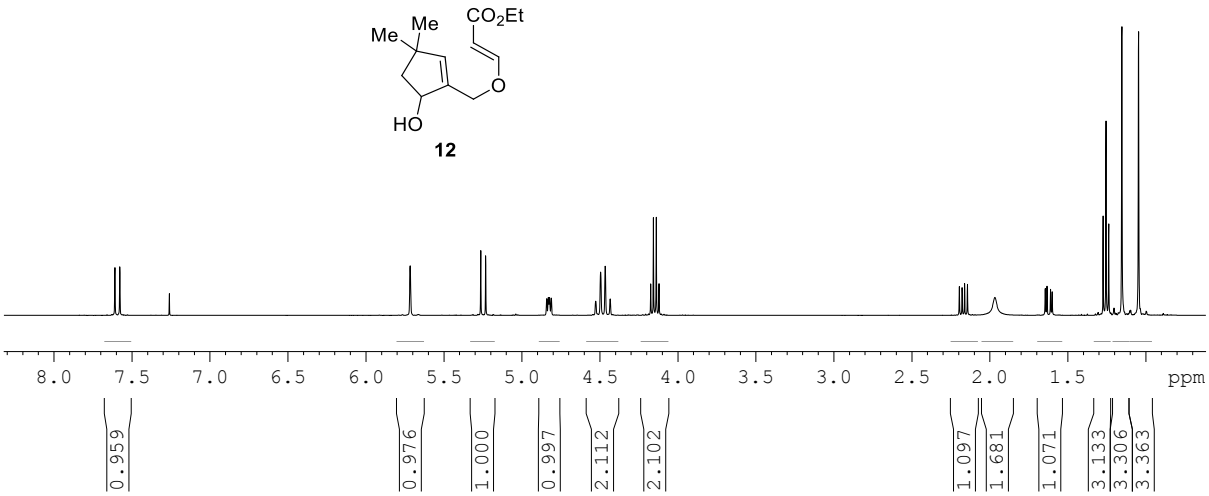
^{13}C NMR spectrum of vinylogous carbonate 10



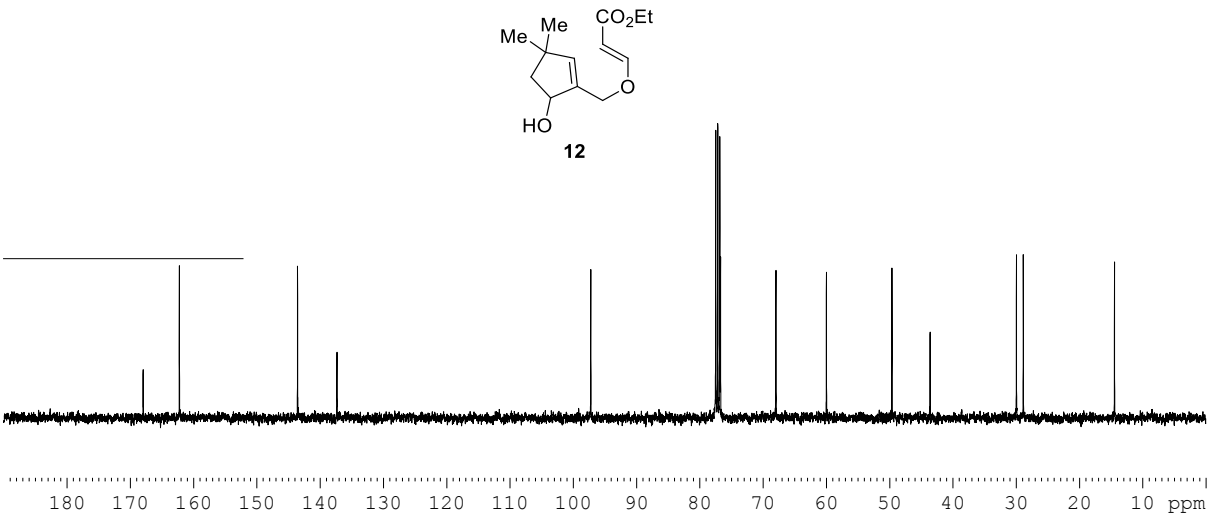
^{1}H NMR spectrum of vinylogous carbonate 11



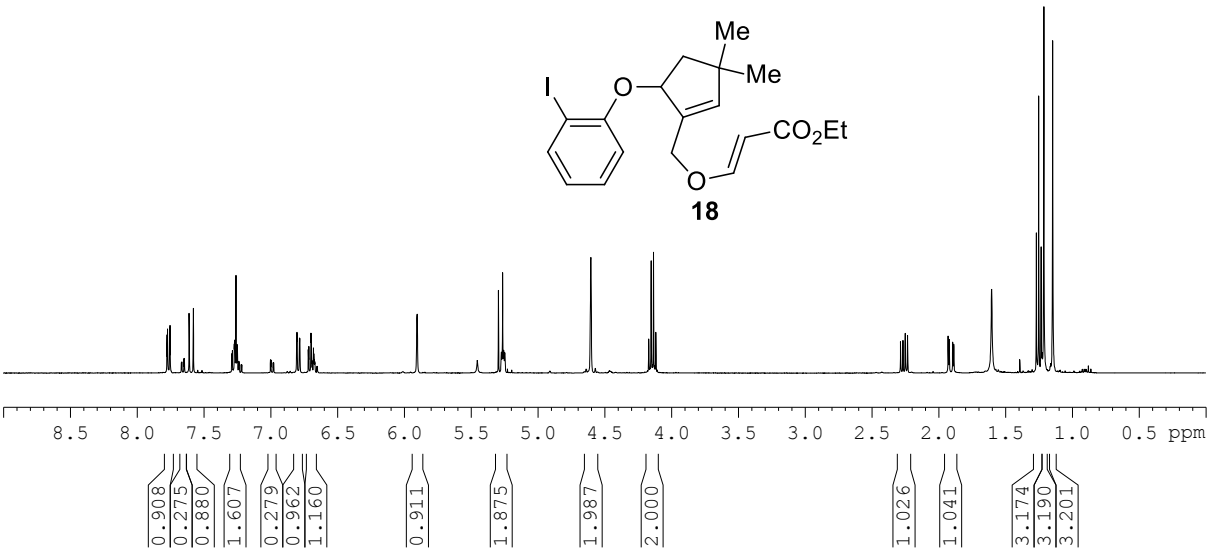
^{13}C NMR spectrum of vinylogous carbonate 11



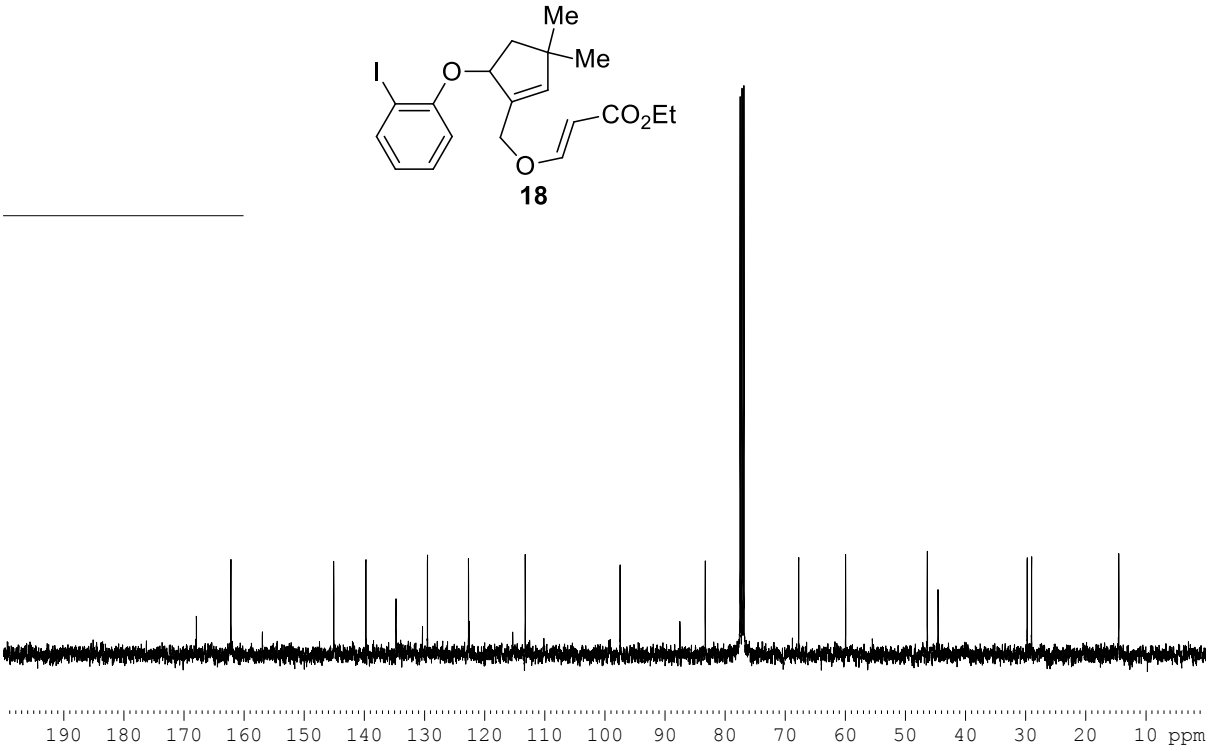
^{1}H NMR spectrum of alcohol 12



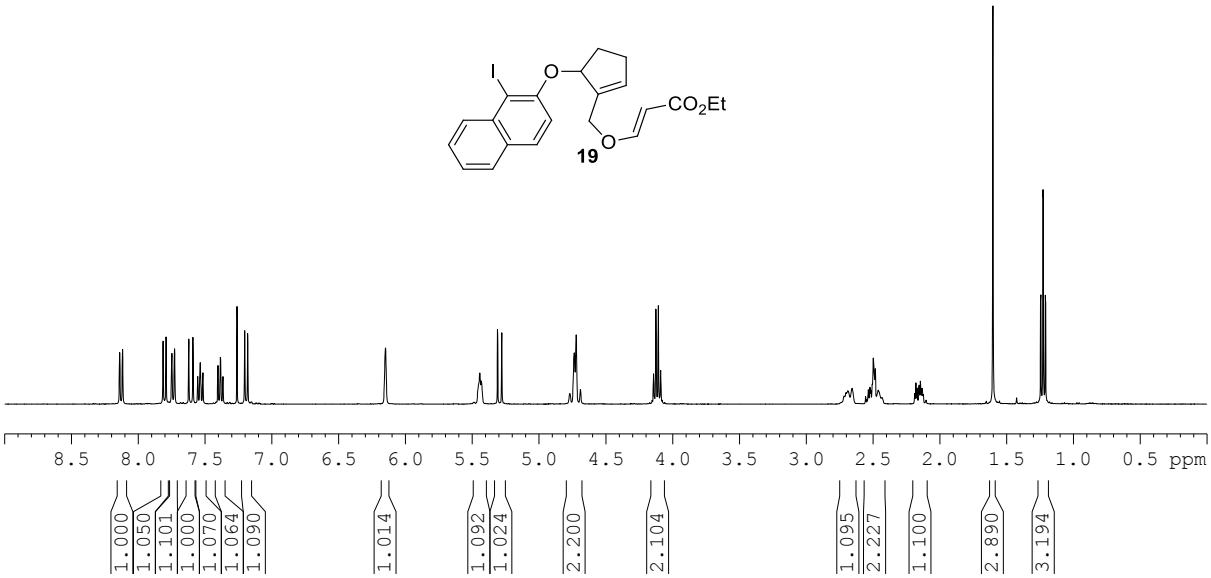
^{13}C NMR spectrum of alcohol 12



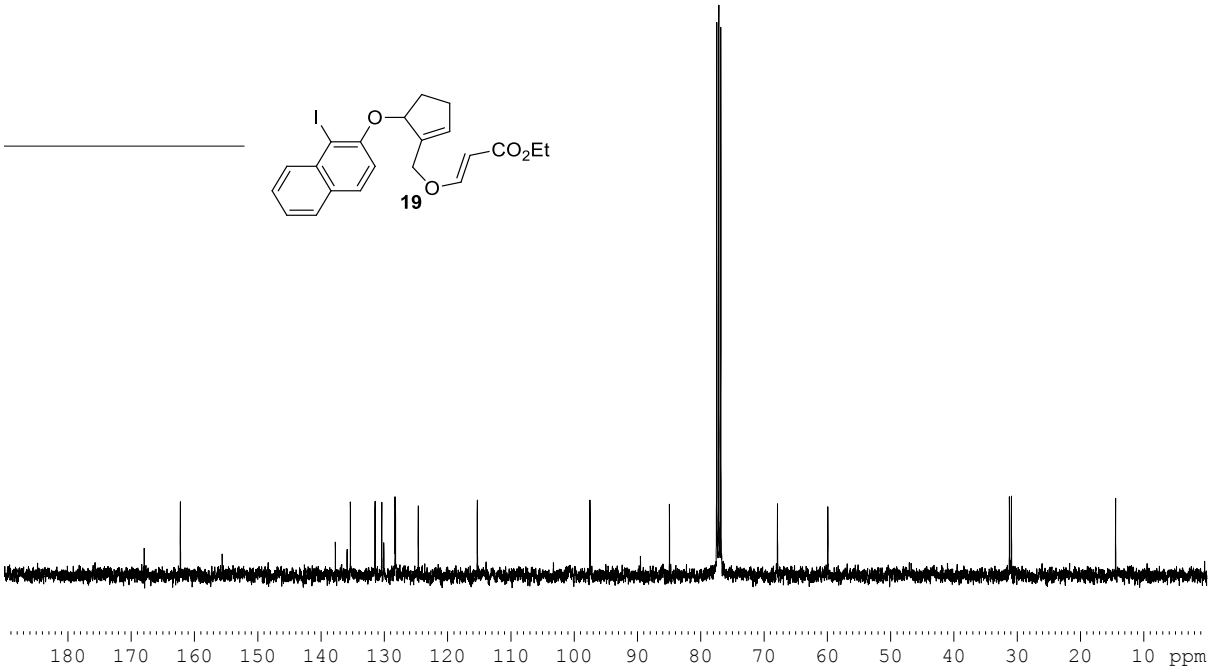
^{1}H NMR spectrum of iodide 18



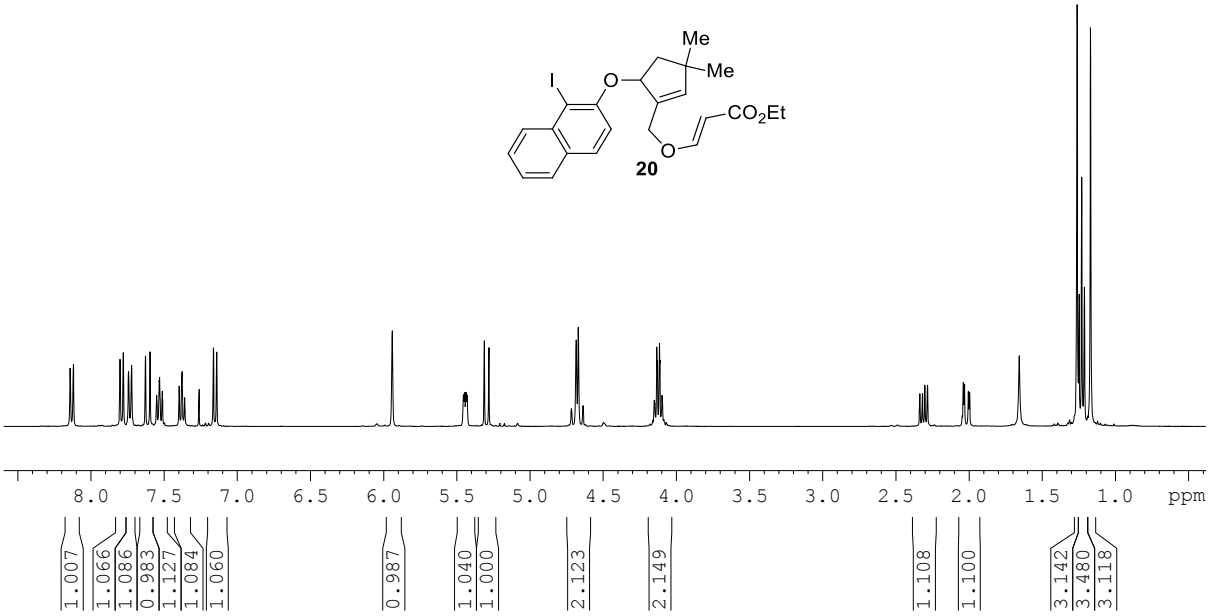
^{13}C NMR spectrum of iodide 18



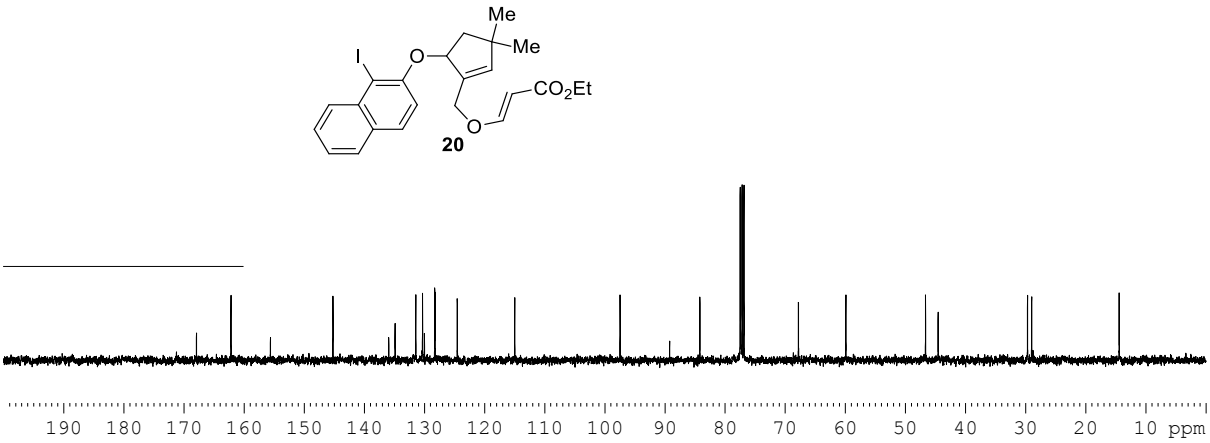
^{1}H NMR spectrum of iodide 19



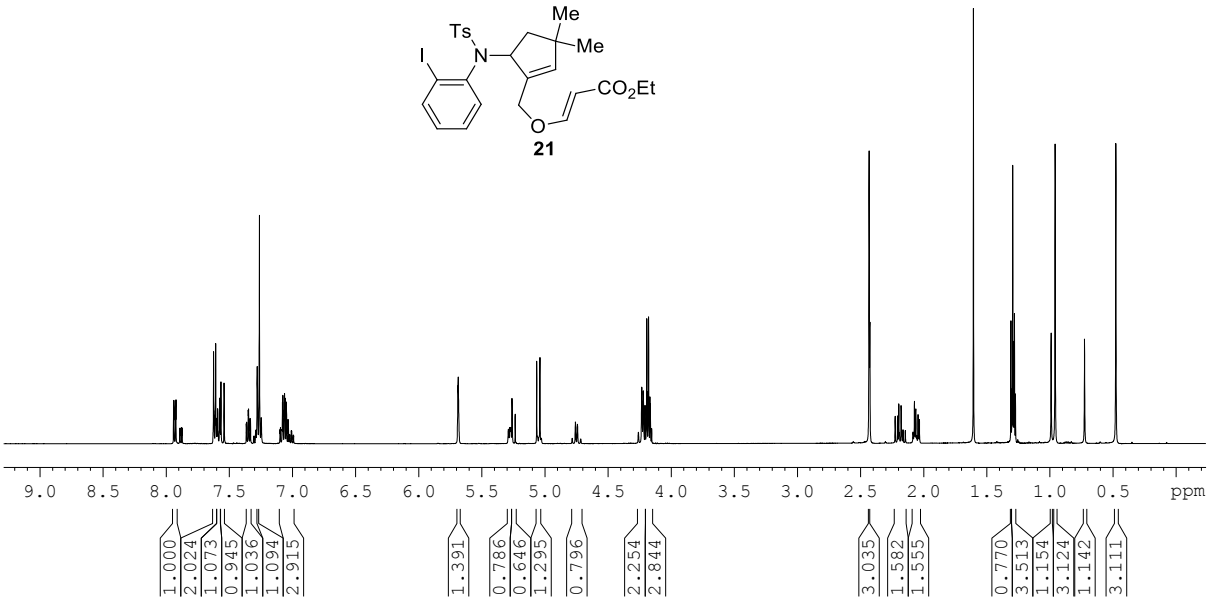
^{13}C NMR spectrum of iodide 19



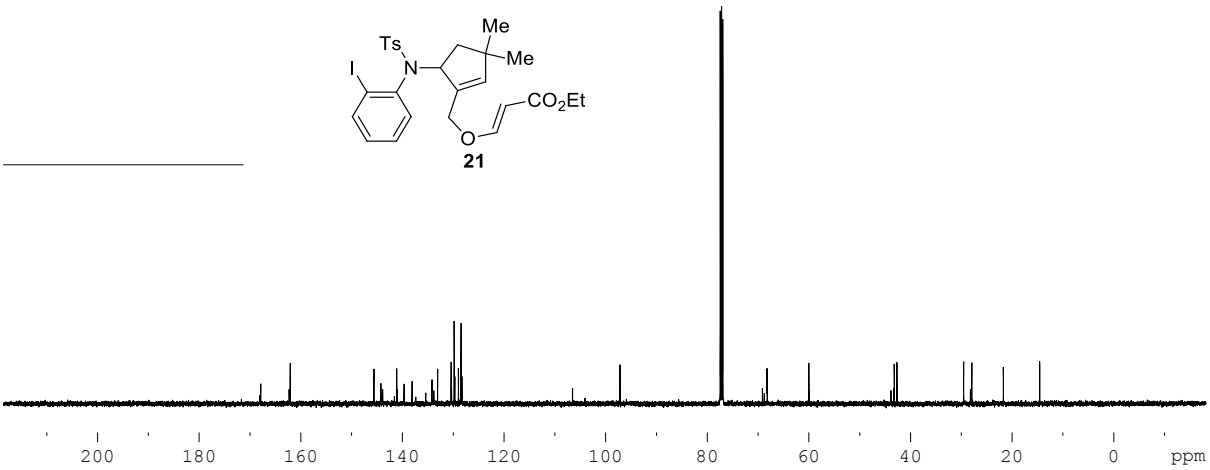
^{1}H NMR spectrum of iodide 20



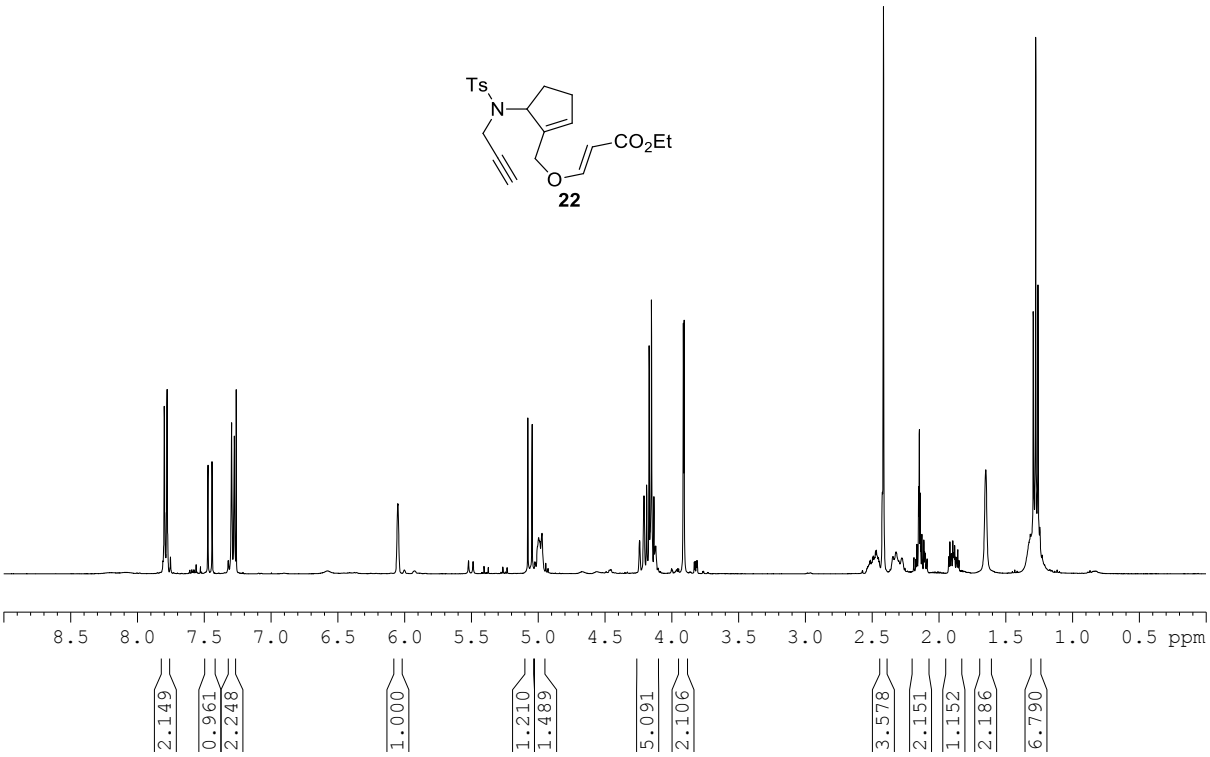
^{13}C NMR spectrum of iodide 20



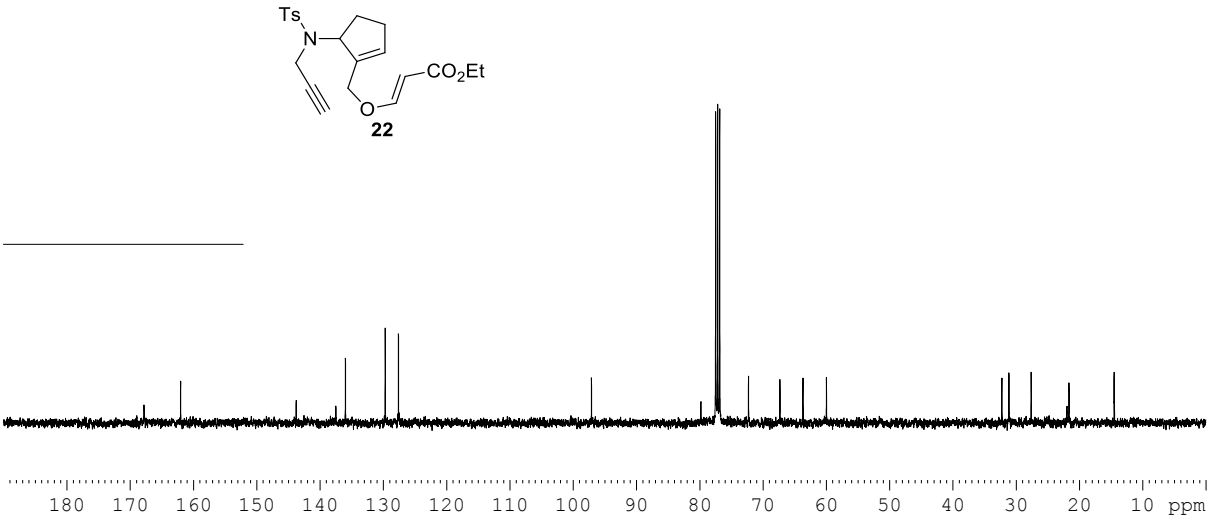
^{1}H NMR spectrum of iodide 21



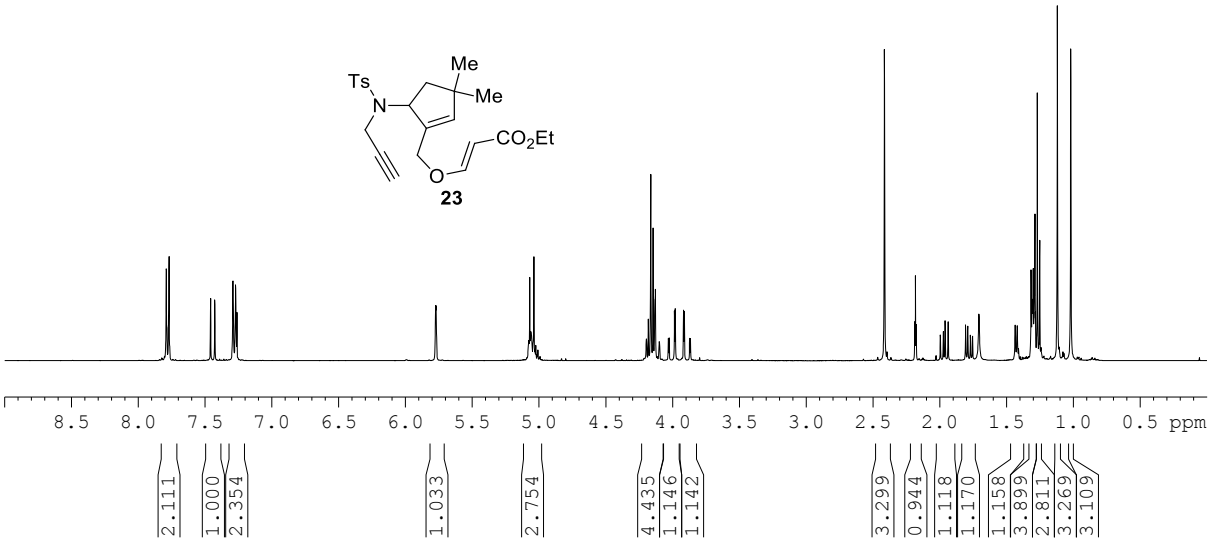
^{13}C NMR spectrum of iodide 21



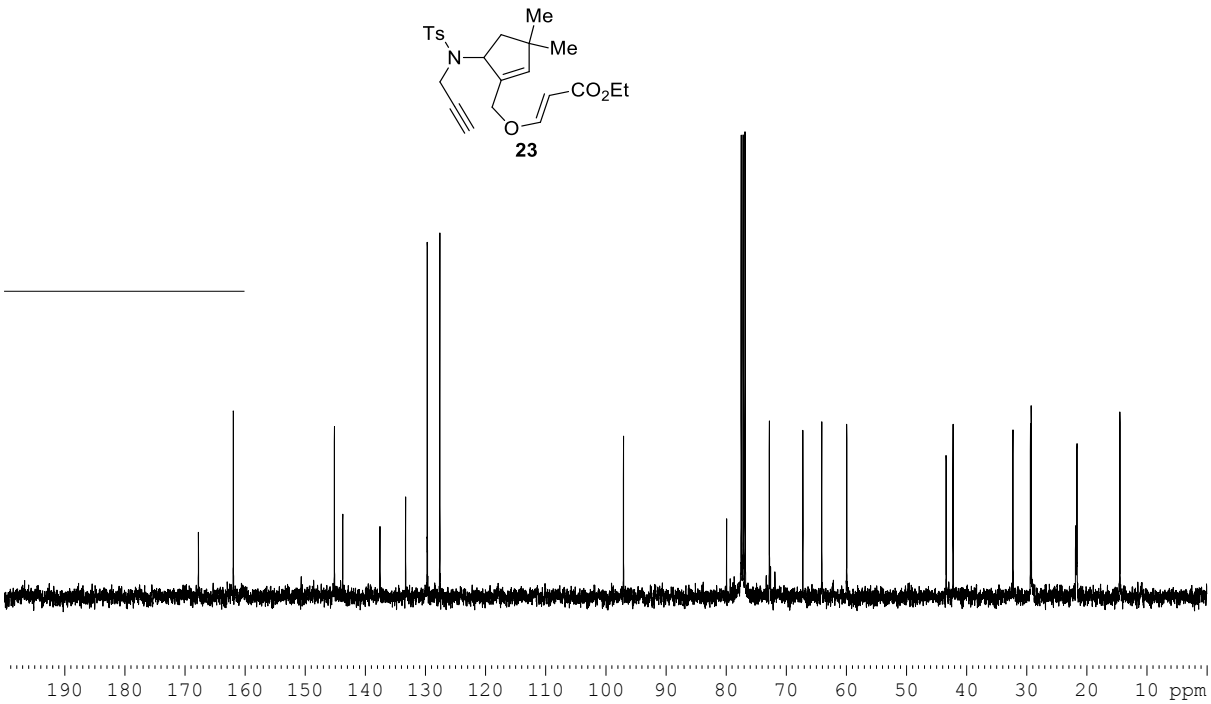
^{1}H NMR spectrum of alkyne 22



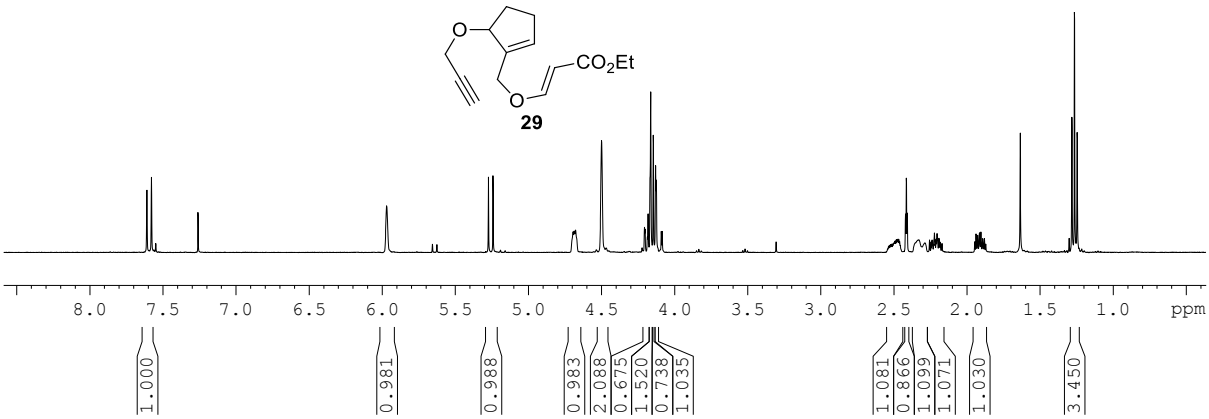
^{13}C NMR spectrum of alkyne 22



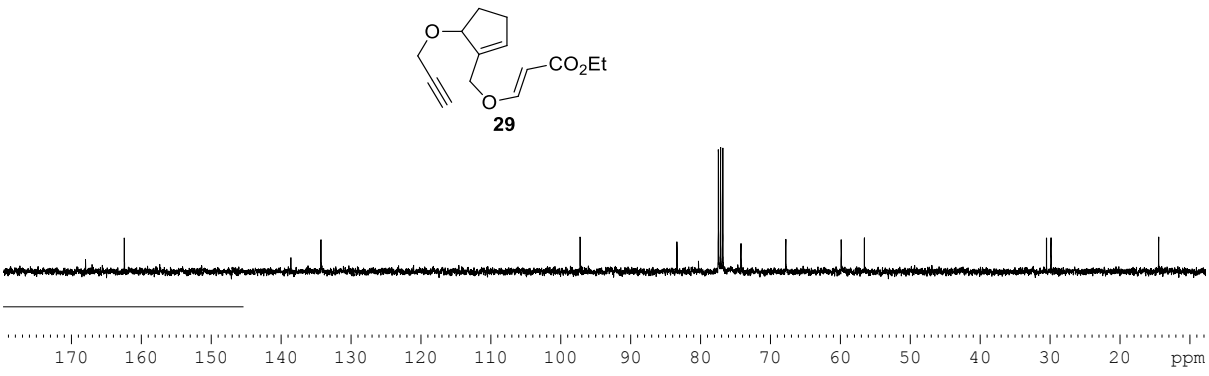
^{1}H NMR spectrum of alkyne 23



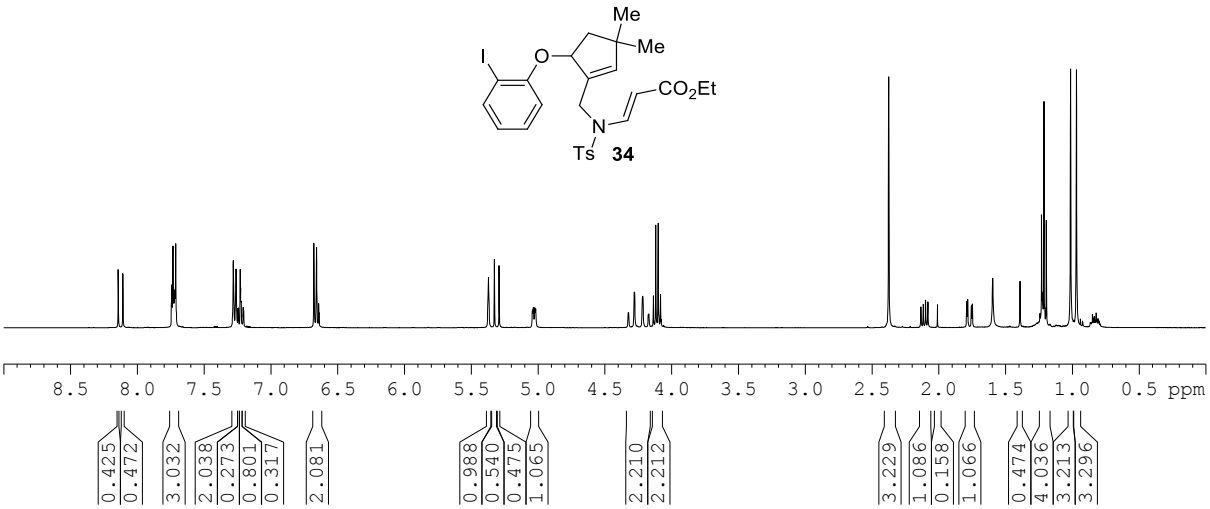
^{13}C NMR spectrum of alkyne 23



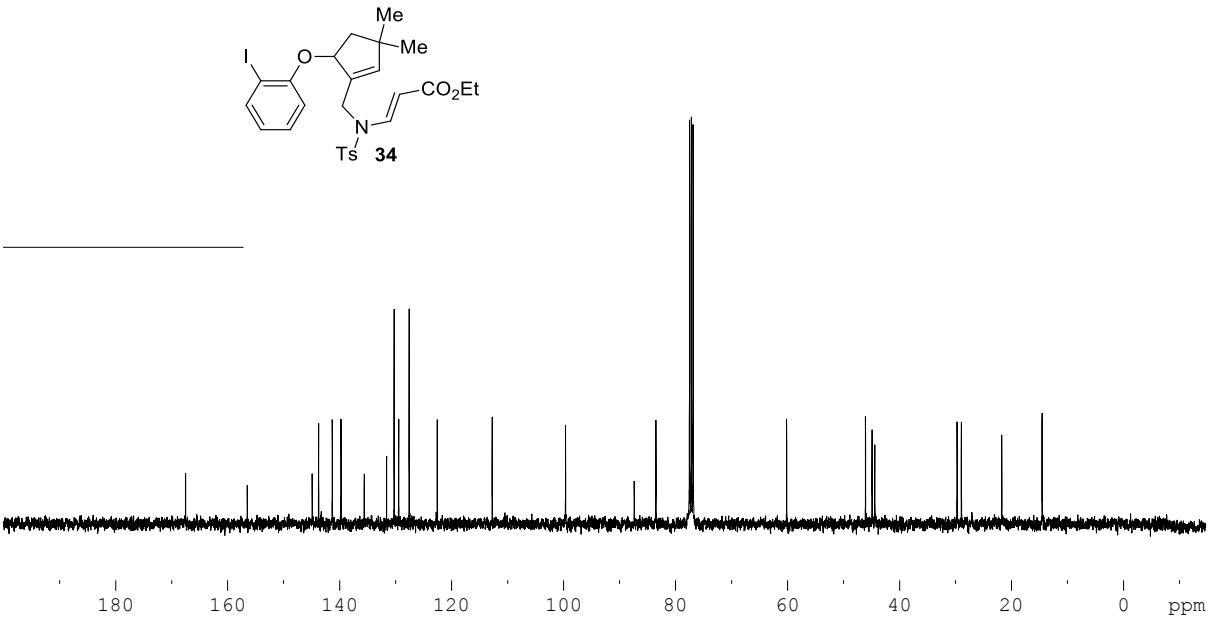
^{1}H NMR spectrum of alkyne 29



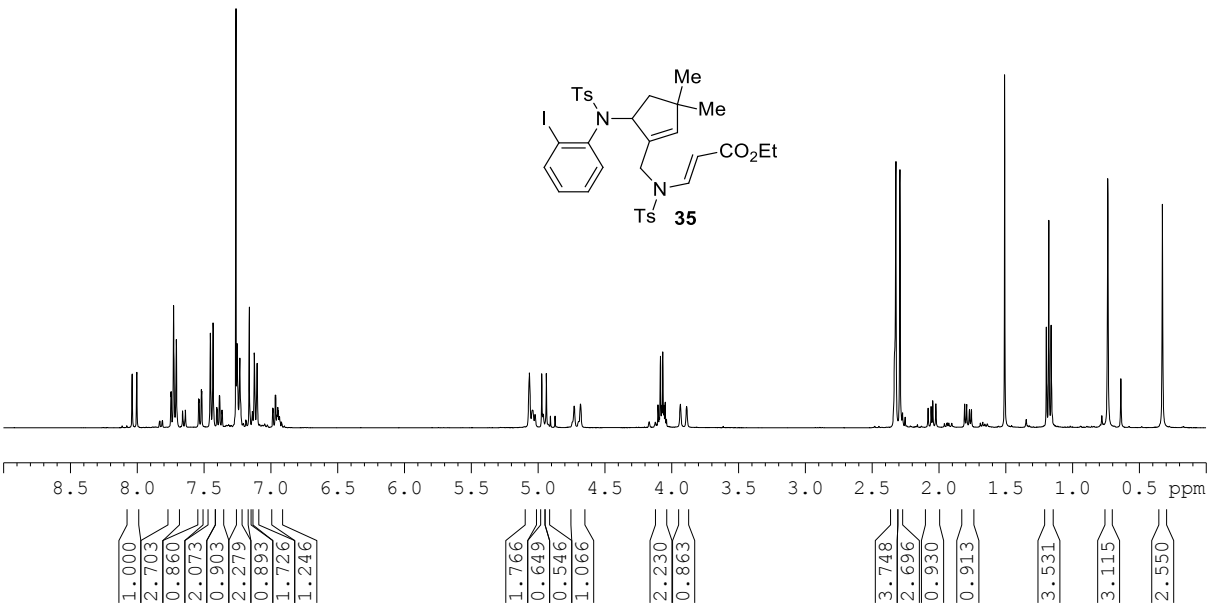
^{13}C NMR spectrum of iodide 29



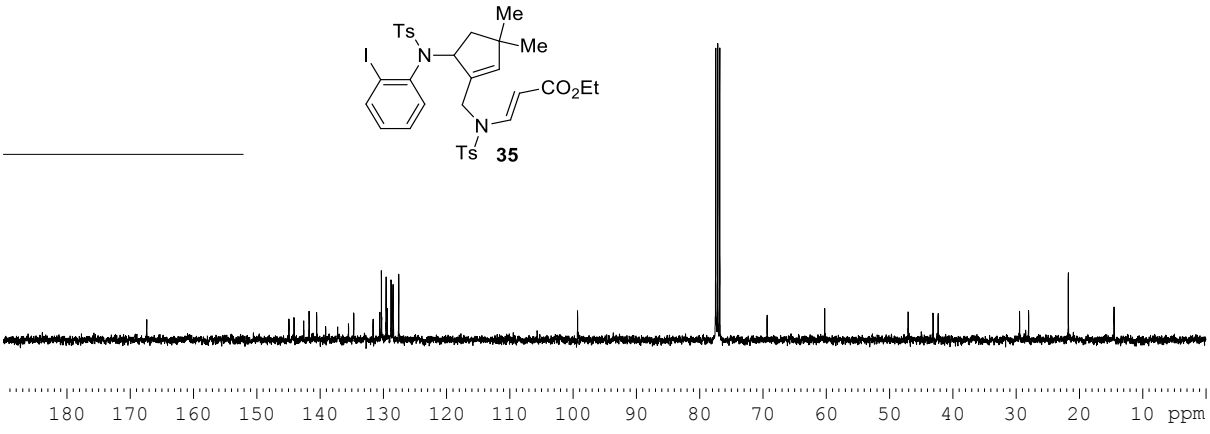
^{1}H NMR spectrum of iodide 34



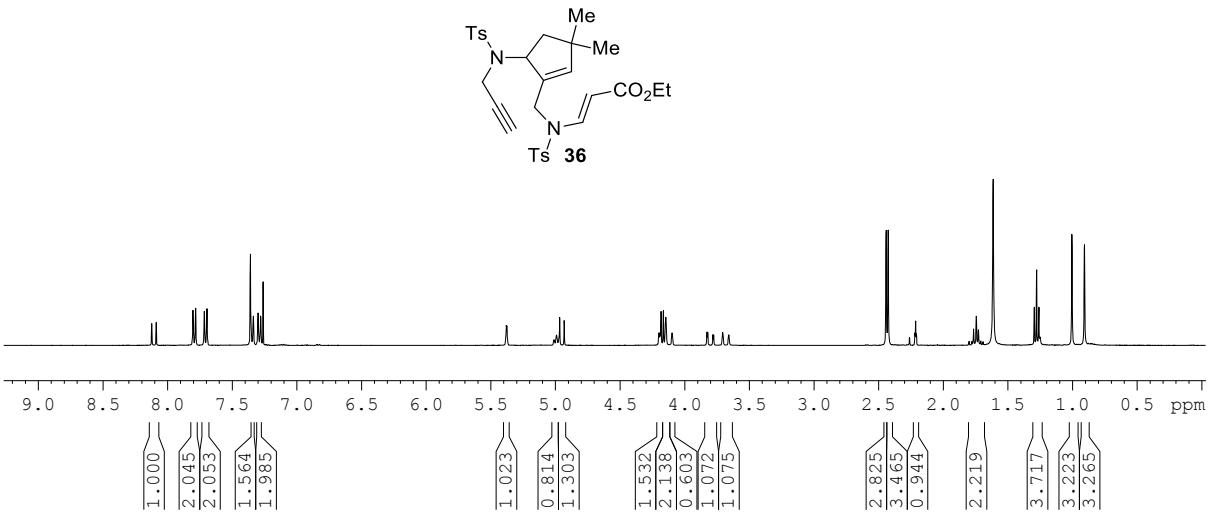
^{13}C NMR spectrum of iodide 34



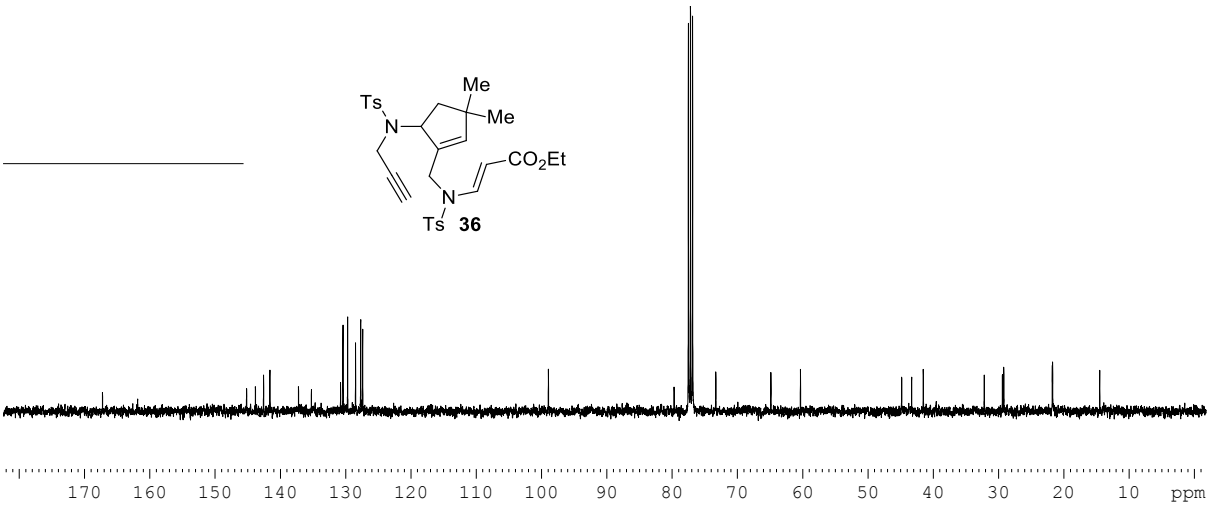
^{1}H NMR spectrum of iodide 35



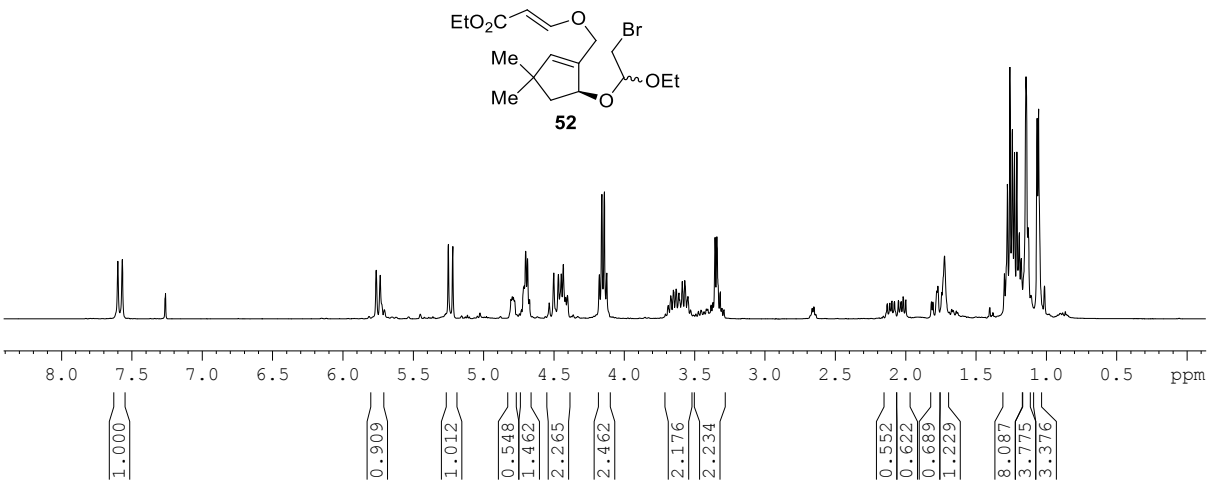
^{13}C NMR spectrum of iodide 35



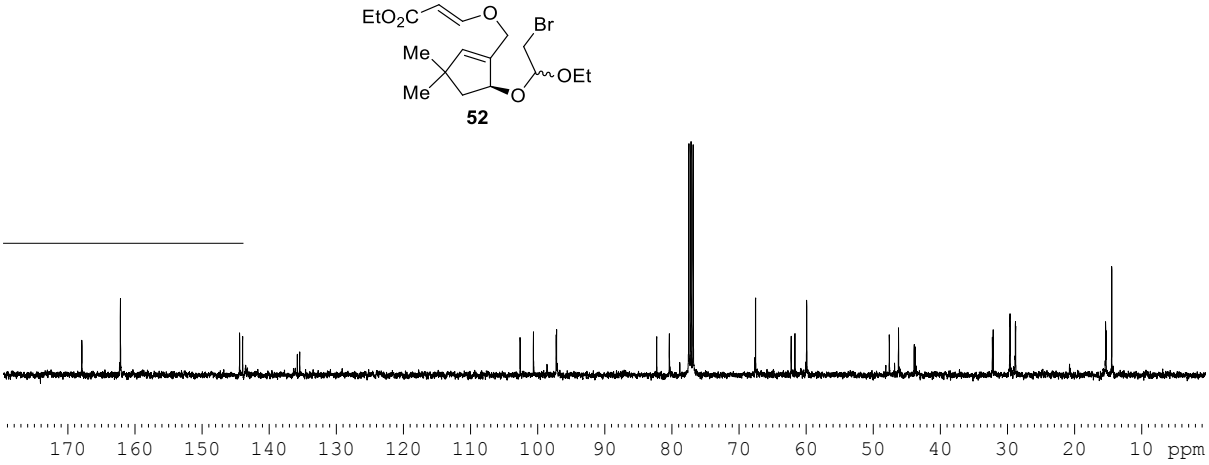
^{1}H NMR spectrum of alkyne 36



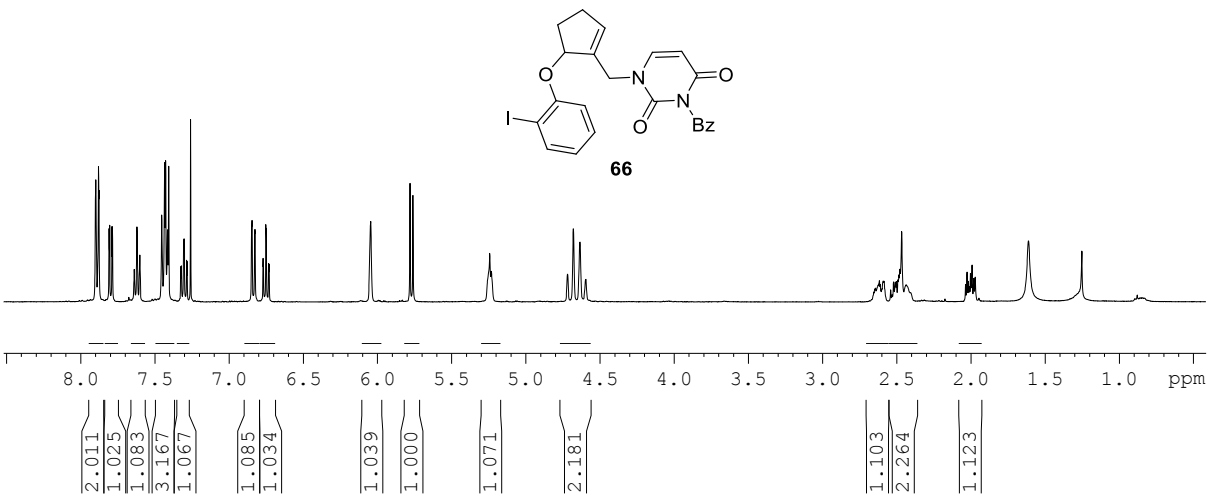
^{13}C NMR spectrum of alkyne 36



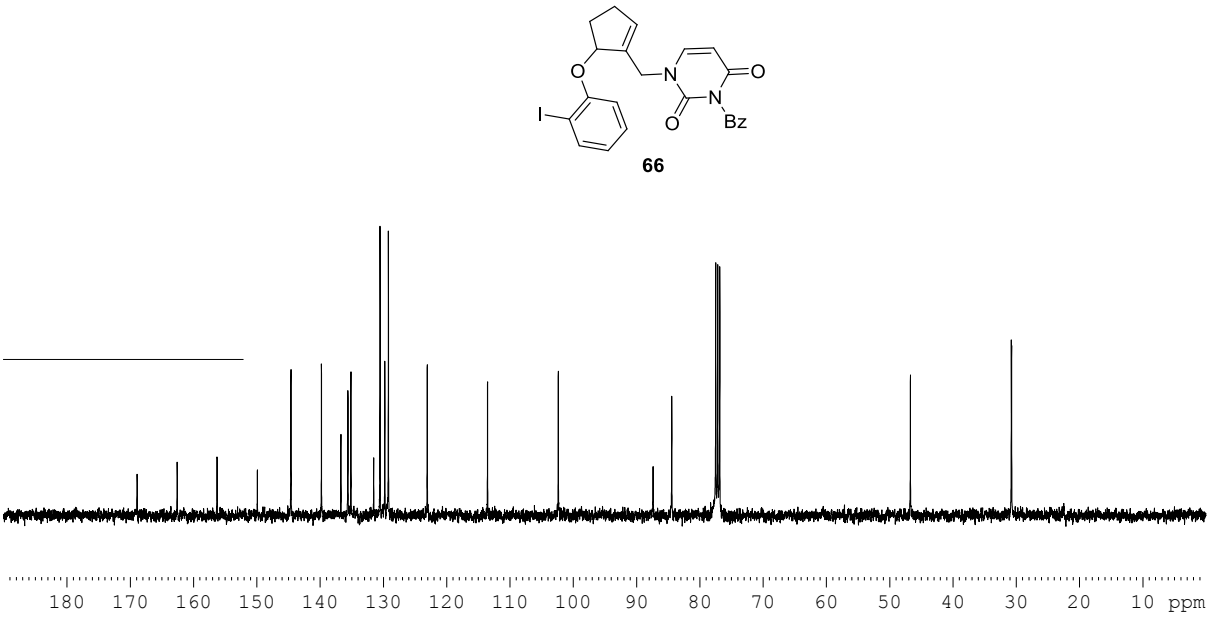
^{1}H NMR spectrum of cyclic acetal 52



^{13}C NMR spectrum of cyclic acetal 52



^{1}H NMR spectrum of iodide 66



^{13}C NMR spectrum of iodide 66

General instructions for crystal data and structure refinement

Single crystal was grown in suitable solvent systems for their structural studies by slow evaporation of the solvents. Crystals of suitable size were tested for single crytallinity using Leica DM-EP polarizing microscope. X-ray data collection was performed with Bruker AXS (Kappa Apex 2) CCD Diffractometer equipped with graphite monochromated Mo (Kα) (λ = 0.7107 Å) radiation. Crystal fixed at the tip of the glass fibre was mounted on the goniometer head and was optically centered. The automatic cell determination routine, with 32 frames (frame width 0.5°) at three different orientaions of the detector was employed to collect reflections and the program APEX- SAINT was used for finding the unit cell parameters. Four–fold redundancy per reflection was utilized for achieving good absorption correction using multi-scan procedure. Besides absorption, Lorentz polarization and decay correction were applied during data reduction. The program SADABS was used for absorption correction using multi-scan procedure.

The structure was solved using SHELXS-97 and refined by full-matrix least square techniques using SHELXL-97. All hydrogens were fixed at chemically meaningful positions and riding model refinement was applied.

Molecular graphics were drawn using ORTEP32.

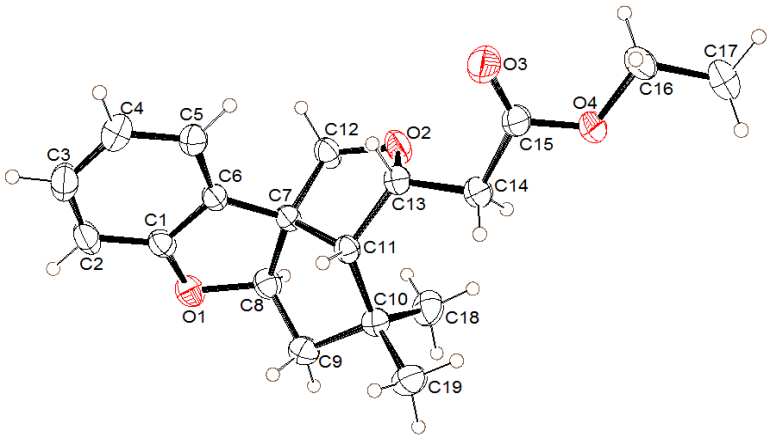


Fig. 1: ORTEP picture of triquinane 38

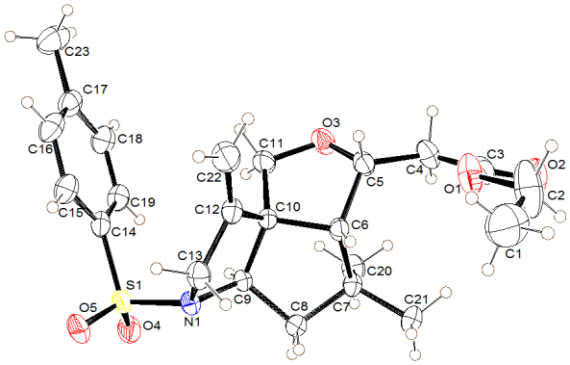


Fig. 2: ORTEP picture of triquinane 49

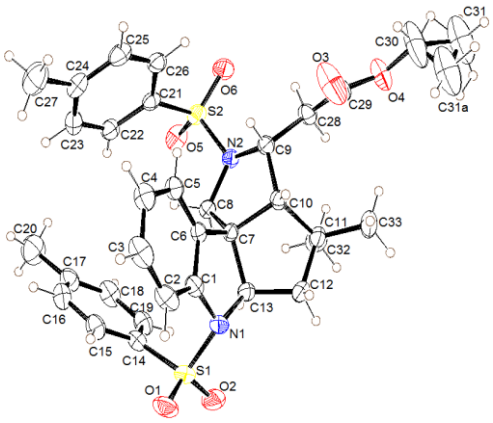


Fig. 3: ORTEP picture of triquinane 46

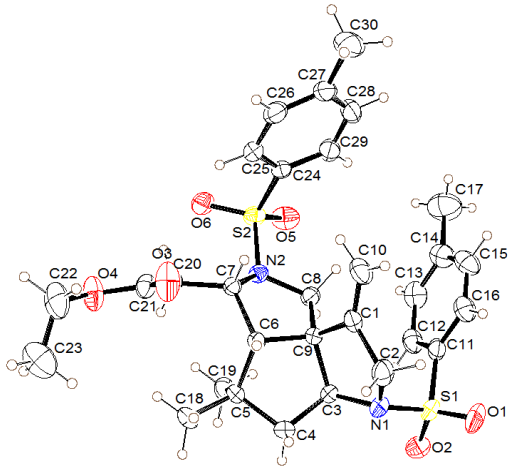


Fig. 4: ORTEP picture of triquinane 51

Crystal data and structure refinement for 38.

CCDC 900731

Suitable solvent	Acetonitrile
Identification code	**38**
Empirical formula	C19 H24 O4
Formula weight	316.38
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system, space group	Monoclinic, P21/n
Unit cell dimensions	a = 10.086(5) Å, α = 90(5) °.
	b = 13.642(5) Å, β = 108.816(5) °.
	c = 12.796(5) Å, γ = 90(5) °.
Volume	1666.6(12) $Å^3$
Z, Calculated density	4, 1.261 Mg/m^3
Absorption coefficient	0.087 mm^{-1}
F(000)	680
Crystal size	0.35 x 0.30 x 0.25 mm
Theta range for data collection	2.25 to 24.75°
Limiting indices	$-10 \leq h \leq 11$, $-16 \leq k \leq 16$, $-15 \leq l \leq 15$
Reflections collected / unique	15940 / 2834 [R(int) = 0.0326]
Completeness to theta = 24.75	99.80 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9785 and 0.9001
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2834 / 0 / 212
Goodness-of-fit on F^2	1.016
Final R indices [I>2sigma(I)]	R1 = 0.0375, wR2 = 0.0980
R indices (all data)	R1 = 0.0541, wR2 = 0.1091
Absolute structure parameter	0.019(2)
Largest diff. peak and hole	0.175 and -0.127 $e.A^{-3}$

Crystal data and structure refinement for 41.

CCDC 900733

Suitable solvent	Acetonitrile
Identification code	**41**
Empirical formula	C26 H31 N O5 S
Formula weight	469.58
Temperature	298(2) K
Wavelength	0.71073 Å
Crystal system, space group	Monoclinic, P21/n
Unit cell dimensions	a = 9.4749(3) Å, α = 90 °.
	b = 20.5466(5) Å, β = 104.2950(10) °.
	c = 12.8261(4) Å, γ = 90 °.
Volume	2419.63(12) $Å^3$
Z, Calculated density	4, 1.289 Mg/m^3
Absorption coefficient	0.171 mm^{-1}
F(000)	1000
Crystal size	0.42 x 0.35 x 0.20 mm
Theta range for data collection	1.91 to 28.53°
Limiting indices	$-12 \leq h \leq 12$, $-27 \leq k \leq 22$, $-17 \leq l \leq 16$
Reflections collected / unique	18295 / 10798 [R(int) = 0.0182]
Completeness to theta = 25.00	99.7 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9667 and 0.9318
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	10798 / 1 / 603
Goodness-of-fit on F^2	0.976
Final R indices [I>2sigma(I)]	R1 = 0.0433, wR2 = 0.1233
R indices (all data)	R1 = 0.0560, wR2 = 0.1354
Absolute structure parameter	0.00(5)
Largest diff. peak and hole	0.328 and -0.341 $e.A^{-3}$

Crystal data and structure refinement for 46

CCDC 900732	
Suitable solvent	Acetonitrile
Identification code	**46**
Empirical formula	C33 H38 N2 O6 S2
Formula weight	622.77
Temperature	298(2) K
Wavelength	0.71073 Å
Crystal system, space group	Monoclinic, P21/n
Unit cell dimensions	a = 9.8485(3) Å, α = 90 °.
	b = 16.1832(7) Å, β = 103.2770(10) °.
	c = 20.6665(8) Å, γ = 90 °.
Volume	3205.8(2) $Å^3$
Z, Calculated density	4, 1.290 Mg/m^3
Absorption coefficient	0.212 mm^{-1}
F(000)	1320
Crystal size	0.35 x 0.32 x 0.22 mm
Theta range for data collection	2.13 to 24.25°
Limiting indices	$-10 \leq h \leq 11$, $-14 \leq k \leq 18$, $-22 \leq l \leq 23$
Reflections collected / unique	16538 / 4958 [R(int) = 0.0363]
Completeness to theta = 24.25	95.60 %
Absorption correction	None <41 Multi-scan
Max. and min. transmission	0.9548 and 0.9294
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4958 / 1 / 399
Goodness-of-fit on F^2	1.021
Final R indices [I>2sigma(I)]	R1 = 0.0431, wR2 = 0.0970
R indices (all data)	R1 = 0.0709, wR2 = 0.1110
Largest diff. peak and hole	0.210 and -0.236 $e.A^{-3}$

Crystal data and structure refinement for 49.

CCDC 900733	
Suitable solvent	Acetonitrile
Identification code	**49**
Empirical formula	C23 H31 N O5 S
Formula weight	433.55
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system, space group	Monoclinic, P21/n
Unit cell dimensions	a = 11.4677(4) Å, α = 90°.
	b = 14.2273(4) Å, β = 92.9960(10) °.
	c = 13.5877(4) Å, γ = 90°.
Volume	2213.86(12) $Å^3$
Z, Calculated density	4, 1.301 Mg/m^3
Absorption coefficient	0.180 mm^{-1}
F(000)	928
Crystal size	0.30 x 0.25 x 0.20 mm
Theta range for data collection	2.07 to 31.14°
Limiting indices	$-16 \leq h \leq 8$, $-20 \leq k \leq 20$, $-19 \leq l \leq 19$
Reflections collected / unique	30796 / 7152 [R(int) = 0.0342]
Completeness to theta = 25.00	100.0 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9648 and 0.8879
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	7152 / 0 / 275
Goodness-of-fit on F^2	1.014
Final R indices [I>2sigma(I)]	R1 = 0.0501, wR2 = 0.1340
R indices (all data)	R1 = 0.0894, wR2 = 0.1582
Largest diff. peak and hole	0.272 and -0.388 $e.A^{-3}$

Crystal data and structure refinement for 51

CCDC 900730	
Suitable solvent	Ethyl Acetate
Identification code	**51**
Empirical formula	C30 H38 N2 O6 S2
Formula weight	586.74
Temperature	298(2) K
Wavelength	0.71073 Å
Crystal system, space group	Monoclinic, P21/c
Unit cell dimensions	a = 10.2052(6) Å, α = 90°.
	b = 18.7686(9) Å, β = 101.595(2) °.
	c = 16.2613(7) Å, γ = 90°.
Volume	3051.1(3) $Å^3$
Z, Calculated density	4, 1.277 Mg/m^3
Absorption coefficient	0.219 mm^{-1}
F(000)	1248
Crystal size	0.45 x 0.35 x 0.15 mm
Theta range for data collection	2.17 to 32.82°
Limiting indices	$-15 \leq h \leq 14$, $-27 \leq k \leq 24$, $-21 \leq l \leq 24$
Reflections collected / unique	29123 / 10672 [R(int) = 0.0278]
Completeness to theta = 25.00	99.9 %
Absorption correction	Multi-scan
Max. and min. transmission	0.9680 and 0.9081
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	10672 / 0 / 374
Goodness-of-fit on F^2	1.008
Final R indices [I>2sigma(I)]	R1 = 0.0561, wR2 = 0.1350
R indices (all data)	R1 = 0.1252, wR2 = 0.1701
Largest diff. peak and hole	0.333 and -0.443 $e.A^{-3}$