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Synthesis and Reactivity of 1-Sulfonylcyclooctatriazoles

Supporting Information

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CAUTION

NITROGEN-RICH COMPOUNDS, SUCH AS AZIDES AND TRIAZOLES, CAN DECOMPOSE VIOLENTLY WITH THE LOSS OF NITROGEN GAS.

Although no problems were encountered in the course of this study, appropriate precautions should be taken.

General Experimental Considerations

NMR spectra were recorded on 400 and 500 MHz Bruker spectrometers. Chemical shifts are given in ppm and the spectra are calibrated to the residual ^{1}H and ^{13}C signals of the solvents. ^{13}C NMR spectra were collected with complete proton decoupling and assignments were made using COSY, HSQC, HMBC and NOESY experiments. Samples were melted directly from the procedures described.

High-resolution mass spectra were obtained on Agilent 6546 LC/Q-TOF and Bruker microTOFq instruments by Analytical Services at the University of Glasgow School of Chemistry.

IR spectra were recorded using spectrometers fitted with an ATR device.

CH_2Cl_2, THF and toluene were purified on a PureSolv PM500 and other reagents were used as received.

Reactions were monitored by thin layer chromatography (TLC) using Merck TLC silica gel 60 F254 aluminum-foil baked plates. Compounds were visualized by UV light at nm or by staining with potassium permanganate.

Column chromatography was performed using a Teledyne ISCO Combiflash Rf+ System using Redisep Rf silica cartridges.

Enantiomeric excess was determined by integration of HPLC traces using chiral stationary phase Daicel Chiralpak AD-H column (0.46 ⌀ × 25 cm) using a Shimadzu Prominence System (LC20AD) with Oven (CTO20AC, 25 °C) and diode array detector (SPDM20A).

Experimental Protocols and Compound Data

*1,2-Dibromocyclooctane (**S1**)*

cis-Cyclooctene (50.8 mL, 390 mmol, 1.0 equiv.) was dissolved in dichloromethane (200 mL) and cooled to −40 °C (acetone, dry ice). A solution of bromine (20.0 mL, 390 mmol, 1.0 equiv.) in dichloromethane (40 mL) was added dropwise until a persistent yellow colour was observed. The reaction was quenched by the addition of saturated aqueous sodium thiosulfate (80 mL) and the aqueous phase extracted with dichloromethane (3 × 80 mL). The combined organic layers were dried ($MgSO_4$), filtered and concentrated *in vacuo* to give the title compound (97.2 g, 92%) as a colourless oil. The crude product was used without further purification. ^{1}H NMR (500 MHz, 25.0 °C, $CDCl_3$) δ 4.61–4.56 (2 H, m, CH), 2.45–2.38 (2 H, m, CH_2), 2.13–2.06 (2 H, m, CH_2), 1.90–1.81 (2 H, m, CH_2), 1.72–1.65 (2 H, m, CH_2), 1.64–1.55 (2 H, m, CH_2) and 1.51–1.41 (2 H, m, CH_2). Recorded data consistent with previous values.[1]

*(E)-1-Bromocyclooctene (**S2**)*

In a flame-dried flask under argon, KO*t*Bu (59.5 g, 531 mmol, 1.5 equiv.) was suspended in THF (200 mL) and the suspension was cooled to 0 °C (ice bath). A solution of 1,2-dibromocyclooctane **S1** (95.2 g, 353 mmol, 1.0 equiv.) in THF (40 mL) was added dropwise over 30 min. Then the reaction mixture was stirred at ambient temperature for 1 h and the reaction was quenched by the addition of ice-cold saturated aqueous ammonium chloride (160 mL). The THF was removed *in vacuo* and the aqueous phase extracted with dichloromethane (3 × 80 mL). The combined organic layers were dried ($MgSO_4$), filtered and concentrated *in vacuo*. The residue was purified by Kugelrohr bulb to bulb distillation (110 °C, 15.0 mbar) to afford the title compound (48.6 g, 73%) as an orange oil. ^{1}H NMR (500 MHz, 25.0 °C, $CDCl_3$) δ 6.03 (1 H, t, J = 8.5 Hz, =CH), 2.64–2.59 (2 H, m, CH_2), 2.12–2.07 (2 H, m, CH_2), 1.66–1.61 (2 H, m, CH_2) and 1.58–1.47 (6 H, m, CH_2); ^{13}C{^{1}H} NMR (126 MHz, 25.0 °C, $CDCl_3$) δ 131.7 (=CH), 124.8 (=C), 35.1 (CH_2), 29.8 (CH_2), 28.6 (CH_2), 27.5 (CH_2), 26.4 (CH_2) and 25.5 (CH_2). Recorded data consistent with previous values.[1]

*Cyclooctyne (**18**)*

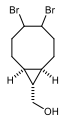
In a flame-dried flask under argon, a solution of diisopropylamine (26.8 mL, 191 mmol, 1.0 equiv.) in THF (90 mL) was cooled to −25 °C (dry ice, acetone) and *n*BuLi (2.5 M solution in hexanes, 76.4 mL, 191 mmol, 1.0 equiv.) was added dropwise. 1-Bromocyclooct-1-ene **S2** (36.1 g, 191 mmol, 1.0 equiv.) was added in one portion and a dark orange colour was immediately observed. The reaction was allowed to warm up to 15 °C over 45 min and stirred at this temperature for a further 3 h by which point the reaction mixture had turned pale yellow. The reaction was quenched by the addition of ice-cold HCl (2 M aq., 95.0 mL) and the aqueous phase was extracted with pentane (5 × 20 mL). The combined organic layers were washed with water and brine; dried ($MgSO_4$) and carefully concentrated *in vacuo* (0 °C, ice bath, ~100 mbar). The residue was purified by distillation (Vigreux column) to afford the title compound (6.31 g, 31%) as a colourless oil. b.pt. 56 °C, 18 mbar; ν_{max}(film) 2928 cm^{-1}; ^{1}H NMR (500 MHz, −3.3 °C, $CDCl_3$) δ 2.19–2.14 (4 H, m, 2 × CH_2), 1.89–1.83 (4 H, m, 2 × CH_2) and 1.65–1.60 (4 H, m, 2 × CH_2); ^{13}C{^{1}H} NMR (126 MHz, 25.0 °C, $CDCl_3$) δ 94.7 (2 × C≡C), 34.7 (2 × CH_2), 29.8 (2 × CH_2) and 21.0 (2 × CH_2). Recorded data consistent with previous values.[1]

Ethyl (1R,8S*,9r*,Z)-bicyclo[6.1.0]non-4-ene-9-carboxylate (**S3**)*

In a flame-dried flask, cyclooctadiene (55.4 mL, 452 mmol, 8.0 equiv.) and $Rh_2(OAc)_4$ (1.00 g, 4 mol %) were dissolved in dichloromethane (40 mL). A solution of ethyl diazoacetate (85 wt% in dichloromethane, 7.58 g, 56.5 mmol, 1.0 equiv.) in dichloromethane (20 mL) was added dropwise over 6 h. The reaction mixture was concentrated *in vacuo* and filtered through a short pad of silica (eluting with hexane followed by 20% EtOAc in hexane). The filtrate was concentrated *in vacuo* and the residue was purified by flash column chromatography (SiO_2, gradient from 1 to 3% EtOAc in petroleum ether) to give the (1*R**,8*S**,9*s**,*Z*)-diastereomer (3.74 g, 34%) as a colourless oil (data not presented) followed by the (1*R**,8*S**,9*r**,*Z*)-diastereomer (4.08 g, 37%) as a colourless oil. ν_{max}(film) 2980, 2933, 1721, 1307, 1184 and 1153 cm^{-1}; ^1H NMR (400 MHz, 24.9 °C, $CDCl_3$) δ 5.68–5.59 (2.0 H, m, =CH), 4.10 (2 H, q, J = 7.1 Hz, Et CH_2), 2.35–2.25 (2 H, m, CH_2), 2.24–2.15 (2 H, m, CH_2), 2.13–2.04 (2 H, m, CH_2), 1.60–1.52 (2 H, m, cyclopropane CH), 1.53–1.42 (2 H, m, CH_2), 1.25 (3 H, t, J = 7.1 Hz, Et CH_3) and 1.18 (1 H, t, J = 4.5 Hz, cyclopropane CH); $^{13}C\{^1H\}$ NMR (101 MHz, 24.9 °C, $CDCl_3$) δ 174.4 (C=O), 129.9 (2 × =CH), 60.2 (Et CH_2), 28.3 (2 × CH_2), 27.9 (cyclopropane CH), 27.7 (2 × cyclopropane CH), 26.6 (2 × CH_2) and 14.3 (Et CH_3); HRMS (ESI-TOF) *m*/*z*: $[M+Na]^+$ Calcd for $C_{12}H_{18}NaO_2^+$ 217.1199; Found 217.1200. Recorded data consistent with previous values.[2]

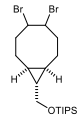
(1R,8S*,9r*,Z)-Bicyclo[6.1.0]non-4-en-9-ylmethanol (**S4**)*

In a flame-dried flask under argon, $LiAlH_4$ (1.48 g, 38.9 mmol, 1.0 equiv.) was suspended in diethyl ether (200 mL) and cooled to 0 °C (ice bath). A solution of ester **S3** (7.64 g, 38.9 mmol, 1.0 equiv.) in diethyl ether (20 mL) was added dropwise over 10 min. The reaction mixture was stirred for 15 min and then the reaction was quenched by the addition of water (1.5 mL), 1 M aqueous NaOH (1.5 mL) and water (4.5 mL). $MgSO_4$ was added and the reaction allowed to stir for 15 min before being filtrated and concentrated *in vacuo* to afford the title compound (5.92 g, >98%) as a colourless oil. The crude product was used without further purification. ν_{max}(film) 3304, 2992, 2913, 2859 and 1026 cm^{-1}; ^1H NMR (400 MHz, 24.9 °C, $CDCl_3$) δ 5.99–5.68 (2 H, m, =CH), 3.47 (2 H, d, J = 7.0 Hz, CH_2OH), 2.34–2.24 (2 H, m, CH_2), 2.21–2.12 (2 H, m, CH_2), 2.11–2.02 (2 H, m, CH_2), 1.48–1.34 (2 H, m, CH_2), 1.28 (1 H, br s, OH), 0.83–0.73 (2 H, m, cyclopropane CH) and 0.69–0.63 (1 H, m, cyclopropane CH); $^{13}C\{^1H\}$ NMR (101 MHz, 24.9 °C, $CDCl_3$) δ 130.2 (2 × =CH), 67.3 (CH_2OH), 29.0 (2 × CH_2), 28.9 (cyclopropane CH), 27.1 (2 × CH_2) and 22.1 (2 × cyclopropane CH); HRMS (ESI-TOF) *m*/*z*: $[M+Na]^+$ Calcd for $C_{10}H_{16}NaO^+$ 175.1093; Found 175.1098. Recorded data consistent with previous values.[2]



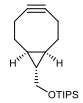
(1R,8S*,9r*)-4,5-Dibromobicyclo[6.1.0]non-9-ylmethanol (**S5**)*

A solution of alkene **S4** (5.92 g, 38.0 mmol, 1.0 equiv.) in dichloromethane (200 mL) was cooled to −40 °C. A solution of bromine (1.95 mL, 38.0 mmol, 1.0 equiv.) in dichloromethane (4 mL) was added dropwise until a yellow colour persisted. The reaction was quenched by the addition of saturated aqueous sodium thiosulfate (8.0 mL) and the aqueous phase extracted with dichloromethane (3 × 8.0 mL). The combined organic layers were dried ($MgSO_4$) filtered and concentrated *in vacuo* to give the title compound (11.5 g, 97%) as a colourless oil. The crude product was used without further purification. ν_{max}(film) 3337, 2990, 2920, 2862, 1427 and 1026 cm^{-1}; ^1H NMR (400 MHz, 25.0 °C, $CDCl_3$) δ 4.87–4.76 (2 H, m, CHBr), 3.45 (2 H, dd, J = 7.1, 1.2 Hz, CH_2), 2.66–2.57 (1 H, m, CH_2), 2.56–2.50 (1 H, m, CH_2), 2.24–2.14 (1 H, m, CH_2), 2.06–1.95 (3 H, m, CH_2), 1.43–1.26 (2 H, m, CH_2), 0.90–0.76 (2 H, m, cyclopropane CH) and 0.65–0.57 (1 H, m, cyclopropane CH); $^{13}C\{^1H\}$ NMR (101 MHz, 25.0 °C, $CDCl_3$) δ 66.6 (CH_2OH), 56.2 (CHBr), 53.2 (CHBr), 34.9 (CH_2), 34.8 (CH_2), 28.2 (cyclopropane CH), 24.4 (CH_2), 23.6 (CH_2), 22.5 (cyclopropane CH) and 19.8 (cyclopropane CH). Recorded data consistent with previous values.[2]



(1R,8S*,9r*)-4,5-Dibromobicyclo[6.1.0]non-9-ylmethoxytriisopropylsilane (**S6**)*

Alcohol **S5** (3.00 g, 9.61 mmol, 1.0 equiv.), imidazole (1.31 g, 19.2 mmol, 2.0 equiv.) and *N*,*N*-dimethyl-4-aminopyridine (1.17 g, 9.61 mmol, 1.0 equiv.) were dissolved in dichloromethane (40 mL) and cooled to 0 °C (ice bath). Triisopropylsilylchloride (2.69 mL, 12.58 mmol, 1.3 equiv.) was added dropwise and the reaction allowed to warm to ambient temperature overnight. Saturated aqueous sodium bicarbonate (20 mL) was added and the aqueous phase extracted with dichloromethane (3 × 10 mL). The combined organic layers were washed with brine, dried ($MgSO_4$), filtered and concentrated *in vacuo*. The residue was purified by flash column chromatography (SiO_2, gradient from 2 to 10% EtOAc in petroleum ether) to afford the title compound (4.29 g, 95%) as a colourless oil. ν_{max}(film) 2940, 2862, 1462, 1103 and 1065 cm^{-1}; ^1H NMR (400 MHz, 25.0 °C, $CDCl_3$) δ 4.85–4.76 (2 H, m, CHBr), 3.66–3.59 (2 H, m, CH_2OTIPS), 2.71–2.63 (1 H, m, CH_2), 2.62–2.55 (1 H, m, CH_2), 2.29–2.19 (2 H, m, CH_2), 2.12–2.00 (2 H, m, CH_2), 1.49–1.29 (2 H, m, CH_2), 1.09–1.01 (21 H, m, 3 × *i*Pr), 0.96–0.81 (2 H, m, 2 × cyclopropane CH) and 0.58 (1 H, td, J = 6.1, 4.6 Hz, cyclopropane CH); $^{13}C\{^1H\}$ NMR (101 MHz, 25.0 °C, $CDCl_3$) δ 66.1 (CH_2OH), 56.6 (CHBr), 53.5 (CHBr), 35.1 (2 × CH_2), 28.2 (cyclopropane CH), 24.5 (CH_2), 23.8 (CH_2), 22.0 (cyclopropane CH), 19.2 (cyclopropane CH), 18.0 (6 × *i*Pr) and 12.1 (3 × *i*Pr).

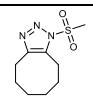


(1R,8S*,9r*)-Bicyclo[6.1.0]non-4-yn-9-ylmethoxytriisopropylsilane (**19**)*

In a flame-dried flask under argon, a solution of dibromobicycle **S6** (4.00 g, 8.54 mmol, 1.0 equiv.) in THF (100 mL) was cooled to 0 °C (ice bath). KO*t*Bu (2.30 g, 20.5 mmol, 2.4 equiv.) was added in one portion and the reaction vigorously stirred for 1 h. The reaction was heated under reflux for a further 2 h before being cooled to ambient temperature. The reaction was quenched by the addition of saturated aqueous ammonium chloride (50 mL). THF was removed *in vacuo* and the aqueous phase was extracted with diethyl ether (3 × 15 mL). The combined organic layers were washed with brine, dried ($MgSO_4$), filtered and concentrated *in vacuo*. The residue was purified by flash column chromatography (SiO_2, gradient from 2 to 10% EtOAc in petroleum ether) to give the title compound (1.89 g, 72%) as a yellow oil. ν_{max}(film) 2940, 2864, 1462, 1445, 1098 and 1067 cm^{-1}; ^1H NMR (400 MHz, 27.0 °C, $CDCl_3$) δ 3.65 (2 H, d, J = 6.0 Hz, CH_2OTIPS), 2.43–2.36 (2 H, m, CH_2), 2.33–2.23 (2 H, m, CH_2), 2.17–2.09 (2 H, m, CH_2), 1.44–1.31 (2 H, m, CH_2), 1.07–1.04 (21 H, m, 3 × *i*Pr), 0.74–0.66 (2 H, m, cyclopropane CH) and 0.62–0.55 (1 H, m, cyclopropane CH); $^{13}C\{^1H\}$ NMR (101 MHz, 27.0 °C, $CDCl_3$) δ 98.9 (2 × C≡C), 66.6 (CH_2OTIPS), 33.6 (2 × CH_2), 27.5 (cyclopropane CH), 22.1 (2 × cyclopropane CH), 21.6 (2 × CH_2), 18.0 (6 × *i*Pr) and 12.1 (3 × *i*Pr); HRMS (ESI-TOF) *m*/*z*: $[M+Na]^+$ Calcd for $C_{19}H_{34}NaOSi^+$ 329.2271; Found 329.2263.

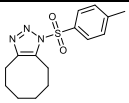
General Procedure 1

Cyclic alkyne (1.0 equiv.) was dissolved in CH_2Cl_2 (0.4 M In a flame-dried vial under argon). Methanesulfonyl azide (1.0 equiv.) was added in one portion and the reaction stirred for 20 min. The reaction mixture was concentrated *in vacuo* to afford the triazole. Where required, purification was by flash column chromatography (silica gel, gradient of 10−30% EtOAc in petroleum ether).



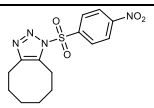
*1-Methanesulfonyl-4,5,6,7,8,9-hexahydrocycloocta[d][1,2,3]triazole (**20a**)*

Cyclooctyne **18** (324 mg, 3.0 mmol, 0.94 equiv.) and methanesulfonyl azide (386 mg, 3.2 mmol, 1.0 equiv.) were mixed in CH_2Cl_2 (7.5 mL) according to General Procedure 1 to give the title compound **20a** (725 mg, >98%) as a white solid. m.pt. 50–52 °C; ν_{max}(film) cm^{-1}; ^1H NMR (500 MHz, 25.0 °C, $CDCl_3$) δ 3.52 (3 H, s, CH_3), 3.11–3.07 (2 H, m, α–CH_2), 2.94–2.89 (2 H, m, α'–CH_2), 1.89–1.83 (2 H, m, β–CH_2), 1.79–1.73 (2 H, m, β'–CH_2) and 1.52–1.40 (4 H, m, γ–CH_2); $^{13}C\{^1H\}$ NMR (126 MHz, 25.0 °C, $CDCl_3$) δ 146.0 (triazole), 135.7 (triazole), 42.9 (CH_3), 28.8 (β'–CH_2), 26.9 (β–CH_2), 25.7 (α'–CH_2), 24.9 (α–CH_2), 24.6 (γ'–CH_2) and 21.7 (γ–CH_2); HRMS (ESI-TOF) *m/z*: $[M+Na]^+$ Calcd for $C_9H_{15}N_3NaO_2S^+$ 252.0777; Found 252.0769.



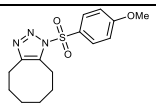
*1-(4-Tolyl)sulfonyl-4,5,6,7,8,9-hexahydrocycloocta[d][1,2,3]triazole (**20b**)*

Cyclooctyne **18** (988 mg, 9.1 mmol, 1.7 equiv.) and 4-toluenesulfonyl azide (1.03 g, 5.2 mmol, 1.0 equiv.) were mixed in CH_2Cl_2 (5.0 mL) according to General Procedure 1 to give the title compound **20b** (1.56 g, 98%) as a white solid. m.pt. 159–161 °C; ν_{max}(film) 2928, 2857, 1387 and 1194 cm^{-1}; ^1H NMR (500 MHz, 25.0 °C, $CDCl_3$) δ 7.93 (2 H, d, *J* = 8.5 Hz, ArH), 7.36 (2 H, d, *J* = 8.5 Hz, ArH), 3.07–3.03 (2 H, m, α–CH_2), 2.86–2.81 (2 H, m, α'–CH_2), 2.44 (3 H, s, CH_3), 1.84–1.78 (2 H, m, β–CH_2), 1.72–1.67 (2 H, m, β'–CH_2) and 1.44–1.36 (4 H, m, γ–CH_2); $^{13}C\{^1H\}$ NMR (126 MHz, 25.0 °C, $CDCl_3$) δ 146.6 (Ar), 146.0 (triazole), 135.3 (triazole), 134.2 (Ar), 130.3 (2 × ArH), 128.3 (2 × ArH), 28.8 (β'–CH_2), 27.0 (β–CH_2), 25.7 (γ'–CH_2), 24.9 (γ–CH_2), 24.6 (α'–CH_2), 21.9 (α–CH_2) and 21.8 (CH_3); HRMS (ESI-TOF) *m/z*: $[M+Na]^+$ Calcd for $C_{15}H_{19}N_3NaO_2S^+$ 328.1090; Found 328.1090.



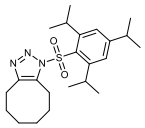
*1-(4-Nitrobenzene)sulfonyl-4,5,6,7,8,9-hexahydrocycloocta[d][1,2,3]triazole (**20c**)*

Cyclooctyne **18** (324 mg, 3.0 mmol, 1.0 equiv.) and 4-nitrobenzenesulfonyl azide (685 mg, 3.0 mmol, 1.0 equiv.) were mixed in CH_2Cl_2 (7.5 mL) according to General Procedure 1 to give the title compound **20c** (1.00 g, >98%) as a white solid. m.pt. 121–122 °C; ν_{max}(film) 3107, 2930, 2857, 1533, 1393, 1348, 1192 and 1173 cm^{-1}; ^1H NMR (500 MHz, 25.0 °C, $CDCl_3$) δ 8.41 (2 H, d, *J* = 8.9 Hz, ArH), 8.27 (2 H, d, *J* = 8.9 Hz, ArH), 3.10–3.05 (2 H, m, α–CH_2), 2.87–2.83 (2 H, m, α'–CH_2), 1.88–1.82 (2 H, m, β–CH_2), 1.75–1.68 (2 H, m, β'–CH_2) and 1.46–1.37 (4 H, m, γ–CH_2); $^{13}C\{^1H\}$ NMR (126 MHz, 25.0 °C, $CDCl_3$) δ 151.4 (Ar), 146.4 (triazole), 142.5 (Ar), 136.0 (triazole), 129.8 (2 × ArH), 124.8 (2 × ArH), 28.7 (β'–CH_2), 27.1 (β–CH_2), 25.6 (α'–CH_2), 24.9 (α–CH_2), 24.6 (γ'–CH_2) and 22.0 (γ–CH_2); HRMS (ESI-TOF) *m/z*: $[M+Na]^+$ Calcd for $C_{14}H_{16}N_4NaO_4S^+$ 359.0784; Found 359.0775.



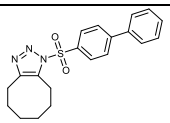
*1-(4-Methoxybenzene)sulfonyl-4,5,6,7,8,9-hexahydrocycloocta[d][1,2,3]triazole (**20d**)*

Cyclooctyne **18** (324 mg, 3.0 mmol, 1.0 equiv.) and 4-methoxybenzenesulfonyl azide (640 mg, 3.0 mmol, 1.0 equiv.) were mixed in CH_2Cl_2 (7.5 mL) according to General Procedure 1 to give the title compound **20d** (961 mg, >98%) as a white solid. m.pt. 113–114 °C; ν_{max}(film) 2928, 2855, 1593, 1576, 1497, 1385, 1265, 1196, 1163 and 1090 cm^{-1}; ^1H NMR (500 MHz, 25.0 °C, $CDCl_3$) δ 7.99 (2 H, d, *J* = 9.0 Hz, SO_2Ar), 7.01 (2 H, d, *J* = 9.0 Hz, SO_2Ar), 3.88 (3 H, s, CH_3), 3.06 (2 H, br t, *J* = 6.3 Hz, α–CH_2), 2.84 (2 H, br t, *J* = 6.4 Hz, α'–CH_2), 1.84–1.78 (2 H, m, β–CH_2), 1.72–1.66 (2 H, m, β'–CH_2) and 1.44–1.35 (4 H, m, γ–CH_2); $^{13}C\{^1H\}$ NMR (126 MHz, 25.0 °C, $CDCl_3$) δ 164.9 (SO_2Ar), 145.9 (triazole), 135.2 (triazole), 130.8 (2 × SO_2Ar), 128.2 (SO_2Ar), 114.9 (2 × SO_2Ar), 55.9 (OMe), 28.8 (β'–CH_2), 27.0 (β–CH_2), 25.7 (γ'–CH_2), 24.9 (γ–CH_2), 24.6 (α'–CH_2) and 21.9 (α–CH_2); HRMS (ESI-TOF) *m/z*: $[M+Na]^+$ Calcd for $C_{15}H_{19}N_3NaO_3S^+$ 344.1039; Found 344.1039.



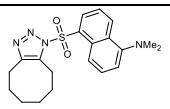
*1-(2,4,6-Triisopropylbenzene)sulfonyl-4,5,6,7,8,9-hexahydrocycloocta[d][1,2,3]triazole (**20e**)*

Cyclooctyne **18** (216 mg, 2.0 mmol, 1.0 equiv.) and 2,4,6-triisopropylbenzenesulfonyl azide (619 mg, 2.0 mmol, 1.0 equiv.) were mixed in CH_2Cl_2 (5.0 mL) according to General Procedure 1 to give the title compound **20e** (743 mg, 89%) as a white solid. m.pt. 89–92 °C; ν_{max}(film) cm^{-1}; ^{1}H NMR (500 MHz, 25.0 °C, $CDCl_3$) δ 7.22 (2 H, s, ArH), 4.02 (2 H, sept., J = 6.7 Hz, *i*Pr), 3.07–3.03 (2 H, m, α–CH_2), 2.94 (1 H, sept., J = 6.9 Hz, *i*Pr), 2.90–2.86 (2 H, m, α′–CH_2), 1.76–1.70 (4 H, m, β–CH_2), 1.49–1.39 (4 H, m, γ–CH_2), 1.26 (6 H, d, J = 6.9 Hz, *i*Pr) and 1.18 (12 H, d, J = 6.9 Hz, *i*Pr); ^{13}C{^{1}H} NMR (126 MHz, 25.0 °C, $CDCl_3$) δ 155.9 (Ar), 152.7 (2 × Ar), 145.8 (triazole), 134.5 (triazole), 129.8 (Ar), 124.3 (2 × ArH), 34.4 (*i*Pr), 29.8 (2 × *i*Pr), 28.7 (β′–CH_2), 26.5 (β–CH_2), 25.7 (α–CH_2), 25.0 (α′–CH_2), 24.6 (γ′–CH_2), 24.4 (4 × *i*Pr), 23.4 (2 × *i*Pr) and 21.7 (γ–CH_2); HRMS (ESI-TOF) *m/z*: [M+Na]$^+$ Calcd for $C_{23}H_{35}N_3NaO_2S^+$ 440.2342; Found 440.2332. Recorded data consistent with previous values.[3]



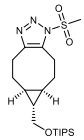
*1-(4-Biphenyl)sulfonyl-4,5,6,7,8,9-hexahydrocycloocta[d][1,2,3]triazole (**20f**)*

Cyclooctyne **18** (324 mg, 3.0 mmol, 1.0 equiv.) and 4-phenylbenzenesulfonyl azide (779 mg, 3.0 mmol, 1.0 equiv.) were mixed in CH_2Cl_2 (7.5 mL) according to General Procedure 1 to give the title compound **20f** (798 mg, 72%) as a white solid. m.pt. 109–113 °C; ν_{max}(film) 3067, 2928, 2857, 1591, 1389 and 1171 cm^{-1}; ^{1}H NMR (500 MHz, 25.1 °C, $CDCl_3$) δ 8.12 (2 H, d, J = 8.6 Hz, ArH), 7.76 (2 H, d, J = 8.6 Hz, ArH), 7.60–7.56 (2 H, m, ArH), 7.51–7.41 (3 H, m, ArH), 3.10 (2 H, br t, J = 6.3 Hz, α–CH_2), 2.86 (2 H, br t, J = 6.4 Hz, α′–CH_2), 1.87–1.81 (2 H, m, β–CH_2), 1.75–1.68 (2 H, m, β′–CH_2) and 1.46–1.37 (4 H, m, γ–CH_2); ^{13}C{^{1}H} NMR (126 MHz, 25.0 °C, $CDCl_3$) δ 148.2 (Ar), 146.1 (triazole), 138.5 (Ar), 135.5 (Ar), 135.5 (triazole), 129.2 (2 × ArH), 129.1 (Ar), 128.8 (2 × ArH), 128.2 (2 × ArH), 127.4 (2 × ArH), 28.8 (β′–CH_2), 27.1 (β–CH_2), 25.7 (γ′–CH_2), 25.0 (γ–CH_2), 24.6 (α′–CH_2) and 22.0 (α–CH_2); HRMS (ESI-TOF) *m/z*: [M+Na]$^+$ Calcd for $C_{20}H_{21}N_3NaO_2S^+$ 390.1247; Found 390.1235.



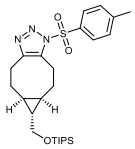
*1-(5-Dimethylaminonaphth-1-yl)sulfonyl-4,5,6,7,8,9-hexahydrocycloocta[d][1,2,3]triazole (**20g**)*

Cyclooctyne **18** (324 mg, 3.0 mmol, 1.0 equiv.) and 4-biphenylsulfonyl azide (829 mg, 3.0 mmol, 1.0 equiv.) were mixed in CH_2Cl_2 (7.5 mL) according to General Procedure 1 to give the title compound **20g** (1.08 g, 94%) as a yellow solid. m.pt. 116–118 °C; ν_{max}(film) 2928, 2857, 2791, 1568, 1454, 1381, 1202, 1186, 1171 and 1153 cm^{-1}; ^{1}H NMR (500 MHz, 25.1 °C, $CDCl_3$) δ 8.68 (1 H, dt, J = 8.5, 1.0 Hz, Dansyl Ar), 8.51 (1 H, dd, J = 7.5, 1.3 Hz, Dansyl Ar), 8.40 (1 H, d, J = 8.7 Hz, Dansyl Ar), 7.61 (1 H, dd, J = 8.5, 7.5 Hz, Dansyl Ar), 7.55 (1 H, dd, J = 8.7, 7.6 Hz, Dansyl Ar), 7.17 (1 H, dd, J = 7.6, 1.0 Hz, Dansyl Ar), 2.95 (2 H, br t, J = 6.3 Hz, α–CH_2), 2.85 (6 H, s, NMe_2), 2.80 (2 H, br t, J = 6.4 Hz, α′–CH_2), 1.70–1.62 (4 H, m, β–CH_2) and 1.37–1.30 (4 H, m, γ–CH_2); ^{13}C{^{1}H} NMR (126 MHz, 25.0 °C, $CDCl_3$) δ 152.0 (Dansyl Ar), 146.0 (triazole), 135.0 (triazole), 133.5 (Dansyl Ar), 132.1 (Dansyl Ar), 131.3 (Dansyl Ar), 129.8 (Dansyl Ar), 129.8 (Dansyl Ar), 129.6 (Dansyl Ar), 122.9 (Dansyl Ar), 118.3 (Dansyl Ar), 116.0 (Dansyl Ar), 45.4 (2 × CH_3), 28.5 (β′–CH_2), 26.6 (β–CH_2), 25.6 (γ′–CH_2), 24.9 (γ–CH_2), 24.5 (α′–CH_2) and 22.0 (α–CH_2); HRMS (ESI-TOF) *m/z*: [M+Na]$^+$ Calcd for $C_{20}H_{24}N_4NaO_2S^+$ 407.1512; Found 407.1512.



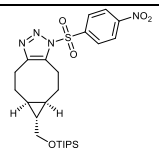
*(5a**S***,6**S***,6a**R***)-1-Methanesulfonyl-6-triisopropylsilyloxymethyl-1,4,5,5a,6,6a,7,8-octahydrocyclopropa[5,6]cycloocta[1,2-d][1,2,3]triazole (**21a**)*

Bicyclononyne **19** (50 mg, 0.16 mmol, 1.0 equiv.) and methanesulfonyl azide (20 mg, 0.16 mmol, 1.0 equiv.) were mixed in CH_2Cl_2 (410 µL) according to General Procedure 1 to give the title compound **21a** (69 mg, >98%) as a colourless oil. ν_{max}(film) 2941, 2864, 1379, 1193, 1179, 1103 and 1066 cm^{-1}; ^{1}H NMR (400 MHz, 20.7 °C, $CDCl_3$) δ 3.65–3.56 (2 H, m, CH_2OTIPS), 3.55 (3 H, s, CH_3), 3.32 (1 H, ddd, J = 16.7, 7.1, 3.6 Hz, CH_2), 3.08–2.99 (2 H, m, CH_2), 2.92 (1 H, ddd, J = 15.9, 9.2, 4.2 Hz, CH_2), 2.50–2.41 (1 H, m, CH_2), 2.40–2.32 (1 H, m, CH_2), 1.56–1.42 (2 H, m, CH_2), 1.08–1.01 (21 H, m, 3 × *i*Pr), 0.81–0.74 (2 H, m, cyclopropane CH) and 0.71–0.64 (1 H, m, cyclopropane CH); ^{13}C{^{1}H} NMR (101 MHz, 21.4 °C, $CDCl_3$) δ 146.1 (triazole), 136.0 (triazole), 65.9 (CH_2OTIPS), 42.9 (CH_3), 28.1 (cyclopropane CH), 27.2 (CH_2), 26.6 (CH_2), 25.1 (CH_2), 22.8 (CH_2), 21.3 (cyclopropane CH), 20.6 (cyclopropane CH), 18.0 (6 × *i*Pr) and 12.0 (3 × *i*Pr); HRMS (ESI-TOF) *m/z*: [M+Na]$^+$ Calcd for $C_{20}H_{37}N_3NaO_3SSi^+$ 450.2217; Found 450.2206.



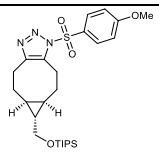
(5aS,6S*,6aR*)-1-(4-Tolyl)sulfonyl-6-triisopropylsilyloxymethyl-1,4,5,5a,6,6a,7,8-octahydrocyclopropa[5,6]cycloocta[1,2-d][1,2,3]triazole (**21b**)*

Bicyclononyne **19** (50 mg, 0.16 mmol, 1.0 equiv.) and 4-toluenesulfonyl azide (32 mg, 0.16 mmol, 1.0 equiv.) were mixed in CH_2Cl_2 (410 µL) according to General Procedure 1 to give the title compound **21b** (81 mg, >98%) as a colourless oil. ν_{max}(film) 2941, 2864, 1389, 1196, 1177, 1092 and 1065 cm^{-1}; ^1H NMR (400 MHz, 25.5 °C, $CDCl_3$) δ 7.92 (2 H, d, J = 8.2 Hz, Ts Ar), 7.36 (2 H, d, J = 8.2 Hz, Ts Ar), 3.59 (1 H, dd, J = 10.5, 5.5 Hz, CH_AOTIPS), 3.53 (1 H, dd, J = 10.5, 5.7 Hz, CH_BOTIPS), 3.30 (1 H, dd, J = 7.2, 3.7 Hz, CH_A), 3.03–2.92 (2 H, m, CH_2), 2.85 (1 H, ddd, J = 15.8, 9.2, 4.2 Hz, CH_B), 2.44 (3 H, s, CH_3), 2.43–2.27 (2 H, m, CH_2), 1.48–1.30 (2 H, m, CH_2), 1.10–0.98 (21 H, m, 3 × *i*Pr) and 0.77–0.59 (3 H, m, cyclopropane CH); $^{13}C\{^1H\}$ NMR (101 MHz, 24.8 °C, $CDCl_3$) δ 146.6 (Ts Ar), 146.2 (triazole), 135.8 (triazole), 134.2 (Ts Ar), 130.3 (2 × Ts Ar), 128.4 (2 × Ts Ar), 65.9 (CH_2OTIPS), 28.2 (cyclopropane CH), 27.3 (CH_2), 26.8 (CH_2), 25.1 (CH_2), 22.7 (CH_2), 21.8 (CH_3), 21.4 (cyclopropane CH), 20.7 (cyclopropane CH), 18.0 (6 × *i*Pr) and 12.0 (3 × *i*Pr); HRMS (ESI-TOF) *m*/*z*: $[M+Na]^+$ Calcd for $C_{26}H_{41}N_3NaO_3SSi^+$ 526.2530; Found 526.2526.



(5aS,6S*,6aR*)-1-(4-Nitrobenzene)sulfonyl-6-triisopropylsilyloxymethyl-1,4,5,5a,6,6a,7,8-octahydrocyclopropa[5,6]cycloocta[1,2-d][1,2,3]triazole (**21c**)*

Bicyclononyne **19** (50 mg, 0.16 mmol, 1.0 equiv.) and 4-nitrobenzenesulfonyl azide (37 mg, 0.16 mmol, 1.0 equiv.) were mixed in CH_2Cl_2 (410 µL) according to General Procedure 1 to give the title compound **21c** (84 mg, 96%) as a white waxy solid. m.pt. 136 °C dec. ν_{max}(film) 2941, 2864, 1537, 1406, 1349, 1198, 1184, 1090 and 1067 cm^{-1}; ^1H NMR (400 MHz, 27.0 °C, $CDCl_3$) δ 8.41 (2 H, d, J = 9.1 Hz, Ns Ar), 8.26 (2 H, d, J = 9.1 Hz, Ns Ar), 3.62 (1 H, dd, J = 10.6, 5.5 Hz, CH_AOTIPS), 3.55 (1 H, dd, J = 10.6, 5.8 Hz, CH_BOTIPS), 3.30 (1 H, ddd, J = 16.7, 7.1, 3.7 Hz, CH_A), 3.07–2.94 (2 H, m, CH_2), 2.93–2.82 (1 H, m, CH_B), 2.50–2.40 (1 H, m, CH_2), 2.39–2.28 (1 H, m, CH_2), 1.52–1.37 (2 H, m, CH_2), 1.07–0.98 (21 H, m, 3 × *i*Pr) and 0.79–0.61 (3 H, m, cyclopropane CH); $^{13}C\{^1H\}$ NMR (101 MHz, 27.0 °C, $CDCl_3$) δ 151.4 (Ns Ar), 146.5 (triazole), 142.5 (Ns Ar), 136.4 (triazole), 129.9 (2 × Ns Ar), 124.8 (2 × Ns Ar), 65.7 (CH_2OTIPS), 28.2 (cyclopropane CH), 27.1 (CH_2), 26.7 (CH_2), 25.1 (CH_2), 22.9 (CH_2), 21.2 (cyclopropane CH), 20.5 (cyclopropane CH), 18.0 (6 × *i*Pr) and 12.0 (3 × *i*Pr); HRMS (ESI-TOF) *m*/*z*: $[M+Na]^+$ Calcd for $C_{25}H_{38}N_4NaO_5SSi^+$ 557.2224; Found 557.2204.

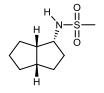


(5aS,6S*,6aR*)-1-(4-Methoxybenzene)sulfonyl-6-triisopropylsilyloxymethyl-1,4,5,5a,6,6a,7,8-octahydrocyclopropa[5,6]cycloocta[1,2-d][1,2,3]triazole (**21d**)*

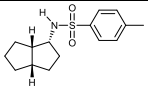
Bicyclononyne **19** (50 mg, 0.16 mmol, 1.0 equiv.) and 4-methoxybenzenesulfonyl azide (35 mg, 0.16 mmol, 1.0 equiv.) were mixed in CH_2Cl_2 (410 µL) according to General Procedure 1 to give the title compound **21d** (84 mg, >98%) as a colourless oil. ν_{max}(film) 2941, 2864, 1593, 1578, 1389, 1267, 1198, 1169, 1094, 1065 and 1020 cm^{-1}; ^1H NMR (400 MHz, 20.8 °C, $CDCl_3$) δ 7.98 (2 H, d, J = 9.0 Hz, SO_2Ar), 7.01 (2 H, d, J = 9.0 Hz, SO_2Ar), 3.80 (3 H, s, OMe), 3.59 (1 H, dd, J = 10.5, 5.6 Hz, CH_AOTIPS), 3.53 (1 H, dd, J = 10.5, 5.9 Hz, CH_BOTIPS), 3.29 (1 H, ddd, J = 16.5, 7.2, 3.6 Hz, CH_A), 3.03–2.92 (2 H, m, CH_2), 2.84 (1 H, ddd, J = 15.9, 9.2, 4.1 Hz, CH_B), 2.46–2.36 (1 H, m, CH_2), 2.37–2.36 (1 H, m, CH_2), 1.47–1.30 (2 H, m, CH_2), 1.09–0.98 (21 H, m, 3 × *i*Pr) and 0.77–0.59 (3 H, m, cyclopropane CH); $^{13}C\{^1H\}$ NMR (101 MHz, 21.4 °C, $CDCl_3$) δ 164.9 (SO_2Ar), 146.2 (triazole), 135.6 (triazole), 130.9 (2 × SO_2Ar), 128.1 (SO_2Ar), 114.9 (2 × SO_2Ar), 65.9 (CH_2OTIPS), 55.9 (OMe), 28.2 (cyclopropane CH), 27.3 (CH_2), 26.8 (CH_2), 25.1 (CH_2), 22.7 (CH_2), 21.4 (cyclopropane CH), 20.8 (cyclopropane CH), 18.0 (6 × *i*Pr) and 12.0 (3 × *i*Pr); HRMS (ESI-TOF) *m*/*z*: $[M+Na]^+$ Calcd for $C_{26}H_{41}N_3NaO_4SSi^+$ 542.2479; Found 542.2470.

General Procedure 2

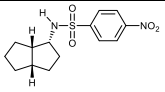
Sulfonyl triazole (1.0 equiv.) was dissolved in PhMe (0.04 M) in a flame dried vial under argon. $Rh_2(OAc)_4$ (5 mol%) was added and the vial sealed with a Teflon cap and heated to 50 °C (aluminium block) until complete conversion of starting material was observed by TLC (0.5 – 2 h). The reaction mixture was cooled to ambient temperature and diluted with THF (0.5 reaction volumes). $LiAlH_4$ (1.5 equiv.) was added in one portion and the reaction stirred at this temperature for 15 min. The reaction was quenched by consecutive addition of water, 1 M aqueous NaOH, a further portion of water and stirred for 5 min. Anhydrous $MgSO_4$ was added and the reaction mixture filtered, concentrated *in vacuo* and purified by flash column chromatography (silica gel, gradient 5–30% EtOAc in petroleum ether) to afford the sulfonamide.



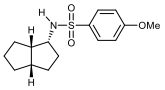
(1R,3aS*,6aS*)-1-Methanesulfonylaminooctahydropentalene (**22a**)*. Triazole **20a** (46 mg, 0.20 mmol, 1.0 equiv.) was treated was treated according to General Procedure 2 with $Rh_2(OAc)_4$ (4 mg, 10 µmol, 5.0 mol %) in PhMe (10 mL) at 50 °C then $LiAlH_4$ (15 mg, 0.40 mmol, 2.0 equiv.) and THF (5.0 mL) to give the title compound **22a** (18 mg, 44%) as a colourless wax. m.pt. 64–67 °C; ν_{max}(film) 3275, 2945, 2864, 1312, 1153 and 1132 cm^{-1}; ^1H NMR (500 MHz, 25.0 °C, $CDCl_3$) δ 4.28 (1 H, d, J = 8.3 Hz, NH), 3.73–3.61 (1 H, m, CH), 2.91 (3 H, s, CH_3), 2.56–2.46 (1 H, m, CH), 2.44–2.34 (1 H, m, CH), 1.95–1.85 (1 H, m, CH_2), 1.85–1.78 (1 H, m, CH_2), 1.68–1.54 (2 H, m, CH_2), 1.44–1.15 (5 H, m, CH_2) and 1.11–1.00 (1 H, m, CH_2); $^{13}C\{^1H\}$ NMR (126 MHz, 25.0 °C, $CDCl_3$) δ 57.3 (CH), 45.9 (CH), 41.4 (CH), 41.4 (Ms CH_3), 35.6 (CH_2), 31.0 (CH_2), 29.5 (CH_2), 28.2 (CH_2) and 27.4 (CH_2); HRMS (ESI-TOF) *m/z*: $[M+Na]^+$ Calcd for $C_9H_{17}NNaO_2S^+$ 226.0872; Found 226.0872.



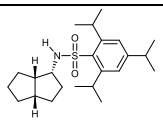
(1R,3aS*,6aS*)-1-(4-Tolyl)sulfonylaminooctahydropentalene (**22b**)*. Triazole **20b** (61 mg, 0.20 mmol, 1.0 equiv.) was treated was treated according to General Procedure 2 with $Rh_2(OAc)_4$ (4 mg, 10 µmol, 5.0 mol %) in PhMe (10 mL) at 50 °C then $LiAlH_4$ (15 mg, 0.40 mmol, 2.0 equiv.) and THF (5.0 mL) to give the title compound **22b** (34 mg, 61%) as a colourless oil. ν_{max}(film) 3277, 2943, 2862, 1319, 1306, 1288, 1157 and 1094 cm^{-1}; ^1H NMR (400 MHz, 24.9 °C, $CDCl_3$) δ 7.77 (2 H, d, J = 7.9 Hz, ArH), 7.29 (2 H, d, J = 7.9 Hz, ArH), 4.52 (1 H, d, J = 8.2 Hz, NH), 3.59–3.50 (1 H, m, CH), 2.43 (3 H, s, CH_3), 2.37–2.28 (2 H, m, CH), 1.90–1.82 (1 H, m, CH_2), 1.66–1.39 (4 H, m, CH_2), 1.31–1.14 (4 H, m, CH_2) and 1.08–1.00 (1 H, m, CH_2); $^{13}C\{^1H\}$ NMR (101 MHz, 25.0 °C, $CDCl_3$) δ 143.2 (Ar), 138.0 (Ar), 129.6 (2 × ArH), 127.1 (2 × ArH), 57.1 (CH), 45.5 (CH), 41.3 (CH), 35.5 (CH_2), 30.6 (CH_2), 29.4 (CH_2), 28.1 (CH_2), 27.3 (CH_2) and 21.5 (CH_2); HRMS (ESI-TOF) *m/z*: $[M+Na]^+$ Calcd for $C_{15}H_{21}NNaO_2S^+$ 302.1185; Found 302.1180. Recorded data consistent with previous values.[4]



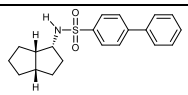
(1R,3aS*,6aS*)-1-(4-Nitrobenzene)sulfonylaminooctahydropentalene (**22c**)*. Triazole **20c** (67 mg, 0.20 mmol, 1.0 equiv.) was treated was treated according to General Procedure 2 with $Rh_2(OAc)_4$ (4 mg, 10 µmol, 5.0 mol %) in PhMe (10 mL) at 50 °C then $LiAlH_4$ (15 mg, 0.40 mmol, 2.0 equiv.) and THF (5.0 mL) to give the title compound **22c** (5 mg, 8%) as a yellow oil. ν_{max}(film) 3277, 2947, 2866, 1530, 1348, 1312, 1163 and 1094 cm^{-1}; ^1H NMR (500 MHz, 25.0 °C, $CDCl_3$) δ 8.29 (2 H, d, J = 8.9 Hz, Ns Ar), 8.01 (2 H, d, J = 8.9 Hz, Ns Ar), 4.64 (1 H, d, J = 8.4 Hz, NH), 3.61–3.52 (1 H, m, CH), 2.36–2.24 (2 H, m, CH), 1.87–1.78 (1 H, m, CH_2), 1.64–1.58 (1 H, m, CH_2), 1.56–1.46 (2 H, m, CH_2), 1.41–1.33 (1 H, m, CH_2), 1.33–1.12 (3 H, m, CH_2) and 1.10–0.96 (2 H, m, CH_2); $^{13}C\{^1H\}$ NMR (126 MHz, 25.0 °C, $CDCl_3$) δ 150.0 (Ns Ar), 147.0 (Ns Ar), 128.3 (2 × Ns Ar), 124.4 (2 × Ns Ar), 57.4 (CH), 45.6 (CH), 41.3 (CH), 35.5 (CH_2), 30.7 (CH_2), 29.3 (CH_2), 28.1 (CH_2) and 27.3 (CH_2); HRMS (ESI-TOF) *m/z*: $[M+Na]^+$ Calcd for $C_{14}H_{18}N_2NaO_4S^+$ 333.0879; Found 333.0879.



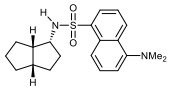
(1R,3aS*,6aS*)-1-(4-Methoxybenzene)sulfonylaminooctahydropentalene* ***(22d)***. Triazole **20d** (64 mg, 0.20 mmol, 1.0 equiv.) was treated was treated according to General Procedure 2 with $Rh_2(OAc)_4$ (4 mg, 10 µmol, 5.0 mol %) in PhMe (10 mL) at 50 °C then $LiAlH_4$ (15 mg, 0.40 mmol, 2.0 equiv.) and THF (5.0 mL) to give the title compound **22d** (45 mg, 77%) as a colourless oil. ν_{max}(film) 3257, 2945, 2864, 1597, 1499, 1302, 1258, 1153 and 1096 cm^{-1}; ^1H NMR (500 MHz, 25.0 °C, $CDCl_3$) δ 7.82 (2 H, d, J = 8.9 Hz, ArH), 6.96 (2 H, d, J = 8.9 Hz, ArH), 4.52 (1 H, d, J = 8.3 Hz, NH), 3.87 (3 H, s, CH_3), 3.57–3.47 (1 H, m, CH), 2.38–2.27 (2 H, m, 2 × CH), 1.90–1.82 (1 H, m, CH_2), 1.65–1.59 (1 H, m, CH_2), 1.59–1.48 (2 H, m, CH_2), 1.47–1.40 (1 H, m, CH_2), 1.58–1.11 (4 H, m, CH_2) and 1.08–1.00 (1 H, m, CH_2); $^{13}C\{^1H\}$ NMR (126 MHz, 25.0 °C, $CDCl_3$) δ 162.7 (Ar), 132.6 (Ar), 129.2 (2 × ArH), 114.1 (2 × Ar), 57.1 (CH), 55.6 (CH), 45.5 (CH_3), 41.3 (CH), 35.5 (CH_2), 30.6 (CH_2), 29.4 (CH_2), 28.1 (CH_2) and 27.3 (CH_2); HRMS (ESI-TOF) *m/z*: $[M+Na]^+$ Calcd for $C_{15}H_{21}NNaO_3S^+$ 318.1134; Found 318.1134.



(1R,3aS*,6aS*)-1-(2,4,6-Triisopropylbenzene)sulfonylaminooctahydropentalene (**22e**)* Triazole **20e** (84 mg, 0.20 mmol, 1.0 equiv.) was treated was treated according to General Procedure 2 with $Rh_2(OAc)_4$ (4 mg, 10 µmol, 5.0 mol %) in PhMe (10 mL) at 50 °C then $LiAlH_4$ (15 mg, 0.40 mmol, 2.0 equiv.) and THF (5.0 mL) to give the title compound **22e** (28 mg, 36%) as a colourless oil. ν_{max}(film) 3271, 2953, 2866 and 1152 cm^{-1}; ^1H NMR (500 MHz, 24.9 °C, $CDCl_3$) δ 7.15 (2 H, s, ArH), 4.36 (1 H, d, J = 8.1 Hz, NH), 4.18 (2 H, sept., J = 6.7 Hz, *i*Pr), 3.60–3.50 (1 H, m, CH), 2.88 (1 H, sept., J = 6.7 Hz, *i*Pr), 2.53–2.45 (1 H, m, CH), 2.42–2.32 (1 H, m, CH), 1.94–1.86 (1 H, m, CH_2), 1.68–1.49 (4 H, m, CH_2), 1.36–1.30 (2 H, m, CH_2), 1.27 (6 H, d, J = 6.7 Hz, 2 × *i*Pr), 1.25 (12 H, d, J = 6.7 Hz, 4 × *i*Pr) and 1.11–1.03 (3 H, m, CH_2); $^{13}C\{^1H\}$ NMR (126 MHz, 25.0 °C, $CDCl_3$) δ 152.5 (Ar), 150.2 (2 × Ar), 133.1 (Ar), 123.7 (2 × ArH), 56.7 (CH), 46.1 (CH), 41.1 (CH), 35.6 (CH_2), 34.1 (*i*Pr), 30.6 (CH_2), 29.6 (2 × *i*Pr), 29.5 (CH_2), 28.2 (CH_2), 27.4 (CH_2), 24.9 (2 × *i*Pr), 24.8 (2 × *i*Pr) and 23.6 (2 × *i*Pr); HRMS (ESI-TOF) *m/z*: $[M+Na]^+$ Calcd for $C_{23}H_{37}NNaO_2S^+$ 414.2437; Found 414.2425.



(1R,3aS*,6aS*)-1-(4-Biphenyl)sulfonylaminooctahydropentalene (**22f**)* Triazole **20f** (74 mg, 0.20 mmol, 1.0 equiv.) was treated was treated according to General Procedure 2 with $Rh_2(OAc)_4$ (4 mg, 10 µmol, 5.0 mol %) in PhMe (10 mL) at 50 °C then $LiAlH_4$ (15 mg, 0.40 mmol, 2.0 equiv.) and THF (5.0 mL) to give the title compound **22f** (38 mg, 55%) as a colourless wax. m.pt. 146–149 °C; ν_{max}(film) 3277, 2947, 2864, 1321, 1159 and 1098 cm^{-1}; ^1H NMR (500 MHz, 25.0 °C, $CDCl_3$) δ 7.95 (2 H, d, J = 8.4 Hz, ArH), 7.65–7.60 (2 H, m, ArH), 7.51–7.46 (2 H, m, ArH), 7.42 (2 H, d, J = 8.4 Hz, ArH), 7.43–7.39 (1 H, m, ArH), 4.57 (1 H, d, J = 8.3 Hz, NH), 3.65–3.58 (1 H, m, CH), 2.41–2.31 (2 H, m, 2 × CH), 1.92–1.85 (1 H, m, CH_2), 1.72–1.65 (1 H, m, CH_2), 1.62–1.44 (3 H, m, CH_2), 1.38–1.14 (4 H, m, CH_2) and 1.11–0.98 (1 H, m, CH_2); $^{13}C\{^1H\}$ NMR (126 MHz, 25.0 °C, $CDCl_3$) δ 145.4 (Ar), 139.5 (Ar), 139.3 (Ar), 129.0 (2 × ArH), 128.4 (Ar), 127.6 (2 × ArH), 127.6 (2 × ArH), 127.3 (2 × ArH), 57.2 (CH), 45.6 (CH), 41.3 (CH), 35.5 (CH_2), 30.7 (CH_2), 29.4 (CH_2), 28.1 (CH_2) and 27.3 (CH_2); HRMS (ESI-TOF) *m/z*: $[M+Na]^+$ Calcd for $C_{20}H_{23}NNaO_2S^+$ 364.1342; Found 364.1342.



(1R,3aS*,6aS*)-1-(5-Dimethylaminonaphth-1-yl)sulfonylaminooctahydropentalene (**22g**)*

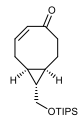
Triazole **20g** (77 mg, 0.20 mmol, 1.0 equiv.) was treated was treated according to General Procedure 2 with $Rh_2(OAc)_4$ (4 mg, 10 µmol, 5.0 mol %) in PhMe (10 mL) at 50 °C then $LiAlH_4$ (15 mg, 0.40 mmol, 2.0 equiv.) and THF (5.0 mL) to give the title compound **22g** (54 mg, 76%) as a yellow oil. ν_{max}(film) 3288, 2943, 2864, 2787, 1452, 1310, 1159 and 1144 cm^{-1}; ^1H NMR (500 MHz, 25.0 °C, $CDCl_3$) δ 8.53 (1 H, d, *J* = 8.5 Hz, Dansyl Ar), 8.32–8.24 (2 H, m, Dansyl Ar), 7.56 (1 H, dd, *J* = 8.6, 7.5 Hz, Dansyl Ar), 7.52 (1 H, dd, *J* = 8.5, 7.3 Hz, Dansyl Ar), 7.18 (1 H, d, *J* = 7.5 Hz, Dansyl Ar), 4.68 (1 H, d, *J* = 8.3 Hz, NH), 3.55–3.47 (1 H, m, CH), 2.89 (6 H, s, CH_3), 2.31–2.23 (1 H, m, CH), 2.22–2.13 (1 H, m, CH), 1.84–1.75 (1 H, m, CH_2), 1.54–1.41 (4 H, m, CH_2), 1.30–1.04 (4 H, m, CH_2) and 1.02–0.96 (1 H, m, CH_2); $^{13}C\{^1H\}$ NMR (126 MHz, 25.0 °C, $CDCl_3$) δ 152.0 (Dansyl Ar), 135.6 (Dansyl Ar), 130.3 (Dansyl Ar), 129.8 (Dansyl Ar), 129.7 (Dansyl Ar), 129.4 (Dansyl Ar), 128.2 (Dansyl Ar), 123.2 (Dansyl Ar), 118.8 (Dansyl Ar), 115.1 (Dansyl Ar), 57.3 (CH), 45.5 (2 × CH_3), 45.4 (CH), 41.1 (CH), 35.5 (CH_2), 30.5 (CH_2), 29.3 (CH_2), 27.9 (CH_2) and 27.2 (CH_2); HRMS (ESI-TOF) *m/z*: $[M+Na]^+$ Calcd for $C_{20}H_{26}N_2NaO_2S^+$ 381.1607; Found 381.1601.

*(3aS,6aS)-1-Oxohexahydropentalene (**23**)*

In a flame-dried flask under argon, triazole **20c** (750 mg, 2.23 mmol, 1.0 equiv.) was dissolved in C_6F_6 (55.8 mL). Rh_2(*S*-NTTL)$_4$ (162 mg, 5 mol %) was added and the reaction heated to 50 °C (oil bath) for 1 h. The reaction was cooled to ambient temperature and basic alumina (22.3 g, pH 9.5, Brockmann activity III, *i.e.* 6 wt % H_2O) was added and the mixture vigorously stirred for 15 min. Filtration through celite and concentration *in vacuo* afforded a residue that was purified by flash column chromatography (silica, gradient from 2–10% ethyl acetate in petrol) to give the title compound (238 mg, 1.92 mmol, 86%) as a volatile colourless oil. $\alpha_D^{23.5}$ +159 (c 1.1, EtOH), Lit. $\alpha_D^{23.0}$ +116 (c 1.3, EtOH); ν_{max}(film) 2951, 2870 and 1732 cm^{-1}; ^1H NMR (500 MHz, 25.0 °C, $CDCl_3$) δ 2.81–2.73 (1 H, m, CH), 2.54 (1 H, td, *J* = 9.4, 4.4 Hz, CH), 2.29–2.24 (2 H, m, CH_2), 2.16–2.07 (1 H, m, CH_2), 1.90–1.76 (3 H, m, CH_2), 1.64–1.49 (3 H, m, CH_2) and 1.45–1.38 (1 H, m, CH_2); $^{13}C\{^1H\}$ NMR (101 MHz, 25.0 °C, $CDCl_3$) δ 223.5 (C=O), 52.0 (CH), 40.9 (CH), 37.9 (CH_2), 33.4 (CH_2), 29.8 (CH_2), 26.3 (CH_2) and 26.1 (CH_2); HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcd for $C_8H_{13}O^+$ 125.0961; Found 125.0961. Recorded data consistent with previous values.[5]

*(1R,3aS,6aS)-1-Hydroxy-1-phenyloctahydropentalene (**24**)*

In a flame-dried flask under argon, triazole **20c** (168 mg, 0.50 mmol, 1.0 equiv.) was dissolved in C_6F_6 (25.0 mL). Rh_2(*S*-NTTL)$_4$ (72 mg, 0.05 mmol, 5 mol %) was added and the reaction heated to 50 °C (oil bath) for 1 h. The reaction was cooled to ambient temperature and basic alumina (2.5 g, pH 9.5, Brockmann activity III, *i.e.* 6 wt % H_2O) was added and the mixture vigorously stirred for 30 min and filtered through a short pad of Celite, cooled to 0 °C and diluted with diethyl ether (12.5 mL). PhMgBr (3.0 M solution in diethyl ether, 0.5 mL, 1.5 mmol, 3.0 equiv.) was added dropwise and the reaction allowed to warm to rt overnight (ca. 16 h). The reaction was quenched by the addition of saturated aqueous ammonium chloride (30.0 mL) and the aqueous phase extracted with diethyl ether (3 × 40 mL). The combined organics were washed with brine, dried $MgSO_4$, filtered and concentrated *in vacuo*. The residue was purified by flash column chromatography (silica, gel, 5–30% ethyl acetate in petrol) to afford the title compound (79.0 mg, 78%) as a colourless oil. $\alpha_D^{22.6}$ +56.7 (c 1.0, $CHCl_3$); ν_{max}(film) 3458, 2943, 2862, 1445 and 1034 cm^{-1}; ^1H NMR (400 MHz, 25.6 °C, $CDCl_3$) δ 7.52–7.47 (2 H, m, ArH), 7.37–7.32 (2 H, m, ArH), 7.25–7.21 (1 H, m, ArH), 2.76–2.58 (2 H, m, 2 × CH), 2.14–1.90 (3 H, m, CH_2), 1.86–1.68 (3 H, m, CH_2), 1.64–1.48 (3 H, m, CH_2) and 1.47–1.38 (1 H, m, CH_2); $^{13}C\{^1H\}$ NMR (101 MHz, 25.0 °C, $CDCl_3$) δ 147.7 (Ar), 128.2 (2 × ArH), 126.7 (ArH), 125.2 (2 × ArH), 83.1 (C–OH), 54.5 (CH), 44.6 (CH), 43.6 (CH_2), 34.0 (CH_2), 30.9 (CH_2), 28.0 (CH_2) and 26.5 (CH_2); HRMS (ESI-TOF) *m/z*: $[M+Na]^+$ Calcd for $C_{14}H_{18}NaO^+$ 225.1250; Found 225.1254.

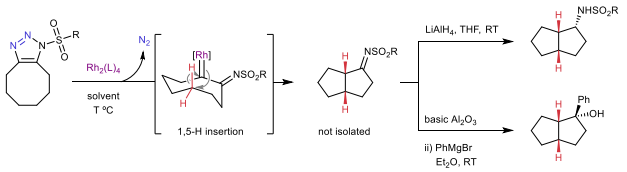


(1R,8S*,9r*)-5-Oxo-bicyclo[6.1.0]non-3-en-9-ylmethoxytriisopropylsilane (**25**)*

In a flame-dried vial under argon, triazole **21** (0.40 mmol, 1.0 equiv.) was dissolved in PhMe (20.0 mL). $Rh_2(OAc)_4$ (8.8 mg, 5 mol %) was added and the vial sealed with a Teflon cap. The reaction was heated to 120 °C (aluminium block) for 15 min after which time the reaction was cooled to ambient temperature. Basic alumina (4.20 g, pH 9.5, Brockmann activity III, *i.e.* 6 wt % H_2O) was added and the mixture vigorously stirred for 15 min. Filtration through Celite and concentration *in vacuo* afforded a residue that was purified by flash column chromatography (silica gel, gradient from 5 to 30% ethyl acetate in petrol) to afford the title compound as a colourless oil. ν_{max}(film) 2941, 2864, 1686, 1462, 1105, 1083, 1065 and 1013 cm^{-1}; ^1H NMR (400 MHz, 27.0 °C, $CDCl_3$) δ 5.99 (1 H, ddd, *J* = 12.9, 7.1, 4.1 Hz, =CH), 5.83 (1 H, dd, *J* = 12.9, 2.9 Hz, =CH), 9.95–0.88 (1 H, m, cyclopropane CH), 3.64–3.48 (2 H, m, CH_2OTIPS), 2.80–2.65 (2 H, m, CH_2), 2.54 (1 H, ddd, *J* = 13.5, 11.4, 5.3 Hz, CH_2), 2.19–2.11 (1 H, m, CH_2), 1.93 (1 H, dddd, *J* = 17.8, 10.6, 4.1, 3.0 Hz, CH_2), 1.63 (1 H, dddd, *J* = 14.4, 11.5, 10.2, 5.2 Hz, CH_2), 1.11–0.96 (21 H, m, 3 × *i*Pr) and 0.87–0.75 (2 H, m, cyclopropane CH); $^{13}C\{^1H\}$ NMR (101 MHz, 27.0 °C, $CDCl_3$) δ 209.2 (C=O), 135.5 (=CH), 130.3 (=CH), 65.7 (CH_2OTIPS), 45.3 (CH_2), 30.3 (CH_2), 29.1 (cyclopropane CH), 22.6 (CH_2), 20.9 (cyclopropane CH), 20.0 (cyclopropane CH), 17.9 (6 × *i*Pr) and 12.0 (3 × *i*Pr); HRMS (ESI-TOF) *m*/*z*: $[M+Na]^+$ Calcd for $C_{19}H_{34}NaO_2Si^+$ 345.2220; Found 345.2221.

21a (128 mg) gave enone **25** (61 mg) in 63% yield.
21b (151 mg) gave enone **25** (53 mg) in 55% yield.
21c (160 mg) gave enone **25** (54 mg) in 56% yield.
21d (156 mg) gave enone **25** (54 mg) in 56% yield.

Optimisation and *ee* Data



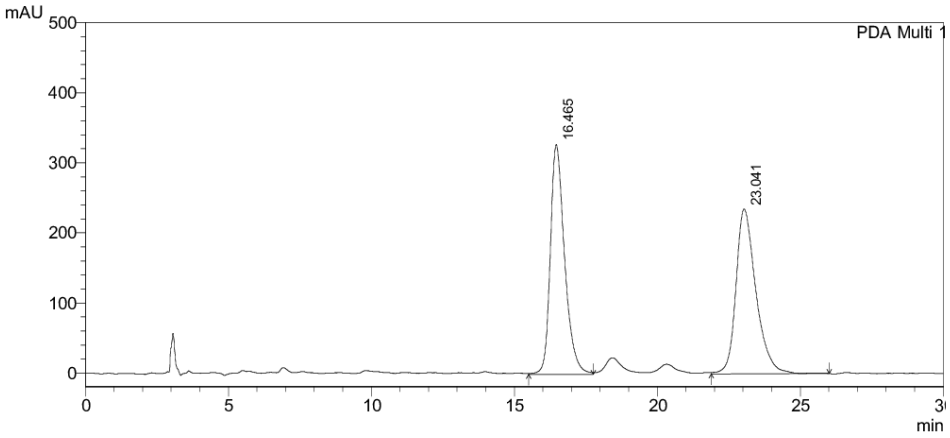
Entry	R	Catalyst[a]	Solvent[b]	T[c]	Workup	Yield[d]	ee[e]
1	*p*Tol	$Rh_2(OAc)_4$	CH_2Cl_2	90	$LiAlH_4$	61%	0%
2	*p*Tol	Rh_2(*S*-DOSP)$_4$	CH_2Cl_2	90	$LiAlH_4$	-	−8%[f]
3	*p*Tol	Rh_2(*S*-PTAD)$_4$	CH_2Cl_2	90	$LiAlH_4$	-	−8%[f]
4	*p*Tol	Rh_2(*S*-NTTL)$_4$	CH_2Cl_2	90	$LiAlH_4$	29%	18%
5	*p*Tol	Rh_2(*S*-NTTL)$_4$	CH_2Cl_2	20	$LiAlH_4$	N.R.[g]	
6	*p*Tol	Rh_2(*S*-NTTL)$_4$	PhMe	20	$LiAlH_4$	N.R.[g]	
7	*p*Tol	Rh_2(*S*-NTTL)$_4$	PhMe	50	$LiAlH_4$	43%	68%
8	*p*Tol	Rh_2(*S*-NTTL)$_4$	PhMe[h]	50	$LiAlH_4$	-	69%
9	*p*Tol	Rh_2(*S*-*t*PTTL)$_4$	PhMe	50	$LiAlH_4$	-	23%
10	*p*Tol	Rh_2(*S*-NTTL)$_4$	CH_2Cl_2	50	$LiAlH_4$	36%	29%
11	*p*Tol	Rh_2(*S*-NTTL)$_4$	C_6H_6	50	$LiAlH_4$	72%	56%
12	*p*Tol	Rh_2(*S*-NTTL)$_4$	PhCl	50	$LiAlH_4$	43%	31%
13	*p*Tol	Rh_2(*S*-NTTL)$_4$	*t*BuOMe	50	$LiAlH_4$	-	46%
14	*p*Tol	Rh_2(*S*-NTTL)$_4$	cyclohexane	50	$LiAlH_4$	-	71%
15	*p*Tol	Rh_2(*S*-NTTL)$_4$	C_6F_6	50	$LiAlH_4$	72%	93%
16	*p*Tol	Rh_2(*S*-NTTL)$_4$	nC_7F_{16}	50	$LiAlH_4$	insol.[i]	
17	$pNO_2C_6H_4$	$Rh_2(OAc)_4$	PhMe	50	$LiAlH_4$	8%	0%
18	$pNO_2C_6H_4$	Rh_2(*S*-NTTL)$_4$	PhMe	50	$LiAlH_4$	-	58%
19	$pNO_2C_6H_4$	Rh_2(*S*-*t*PTTL)$_4$	PhMe	50	$LiAlH_4$	-	47%
20	$pMeOC_6H_4$	$Rh_2(OAc)_4$	PhMe	50	$LiAlH_4$	77%	0%
21	$pMeOC_6H_4$	Rh_2(*S*-NTTL)$_4$	PhMe	50	$LiAlH_4$	36%	24%
22	$pPhC_6H_4$	$Rh_2(OAc)_4$	PhMe	50	$LiAlH_4$	55%	10%
23	$pPhC_6H_4$	Rh_2(*S*-NTTL)$_4$	PhMe	50	$LiAlH_4$	53%	35%
24	*p*Tol	$Rh_2(OAc)_4$	CH_2Cl_2	90	Hydrolysis/Grignard	-	1%
25	Me	Rh_2(*S*-NTTL)$_4$	PhMe	50	Hydrolysis/Grignard	80%	32%
26	2,4,6-(*i*Pr)$_3C_6H_2$	Rh_2(*S*-NTTL)$_4$	PhMe	50	Hydrolysis/Grignard	64%	12%
27	Dansyl[j]	Rh_2(*S*-NTTL)$_4$	PhMe	50	Hydrolysis/Grignard	17%	9%
28	$pNO_2C_6H_4$	Rh_2(*S*-NTTL)$_4$	PhMe	50	Hydrolysis/Grignard	57%	69%
29	$pNO_2C_6H_4$	Rh_2(*S*-NTTL)$_4$	C_6F_6	50	Hydrolysis/Grignard	78%	94%

[a] 5 mol % catalyst employed; [b] 0.02 M concentration of 1-ST; [c] sealed vial in aluminium heating block; [d] isolated yield following column chromatography; where no yield is reported, ee was determined on crude reaction mixture; [e] determined by chiral solid phase HPLC; [f] opposite selectivity observed to Rh_2(*S*-NTTL)$_4$; [g] no consumption of starting material detected; [h] syringe pump addition of triazole to solution of catalyst; [i] total insolubility of reagents and catalyst; [j] Dansyl, R = 5-dimethylaminonaphthalen-1-yl. DOSP = *N*-(4-*n*-dodecylbenzenesulfonyl)prolinate; PTAD = 2-adamantyl-2-(1,3-dioxoisoindolin-2-yl)ethanoate; NTTL = 2-(1,3-dioxobenzo[*de*]isoquinolin-2-yl)-3,3-dimethyl-butanoate; *t*PTTL = 3,3-dimethyl-2-(5-*tert*-butyl-1,3-dioxoisoindolin-2-yl)butanoate.

Entry 1 R = *p*Tol, $Rh_2(OAc)_4$, 90 °C, CH_2Cl_2, $LiAlH_4$ workup
AD-H, 7% *i*PrOH in hexane, 1 cm^3 min^{-1}

PDA Ch1 204nm 1nm

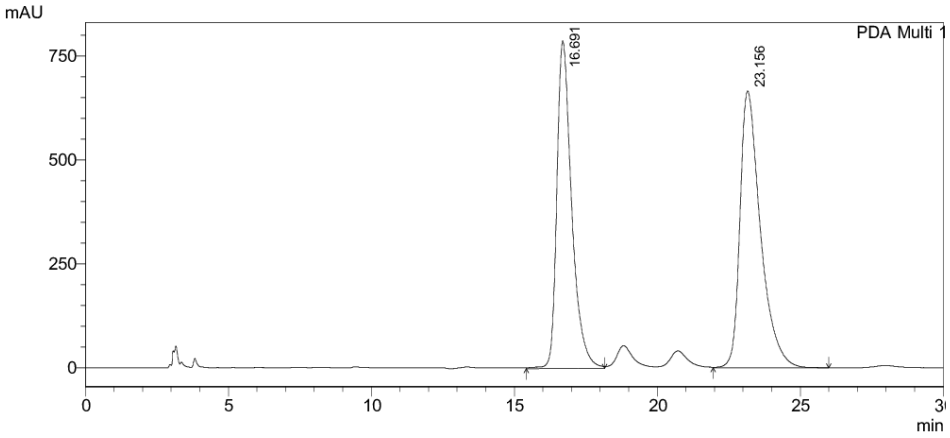
Peak#	Ret. Time	Height	Area	Area %
1	16.47	328290	11409010	49.944
2	23.04	235032	11434799	50.056
Total		563322	22843810	100.000



Entry 2 R = *p*Tol, Rh_2(*S*-DOSP)$_4$, 90 °C, CH_2Cl_2, $LiAlH_4$ workup
AD-H, 7% *i*PrOH in hexane, 1 cm^3 min^{-1}

PDA Ch1 204nm 4nm

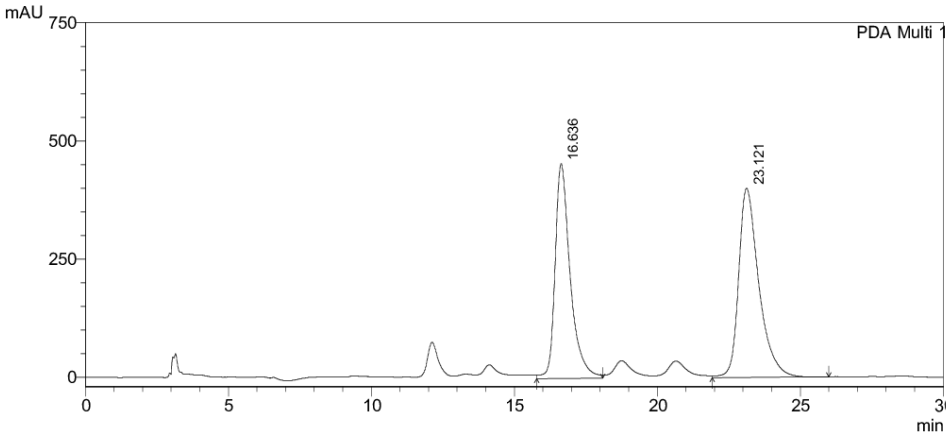
Peak#	Ret. Time	Height	Area	Area %
1	16.69	788109	28417142	46.030
2	23.16	666393	33318880	53.970
Total		1454502	61736021	100.000



Entry 3 R = *p*Tol, Rh_2(*S*-PTAD)$_4$, 90 °C, CH_2Cl_2, $LiAlH_4$ workup
AD-H, 7% *i*PrOH in hexane, 1 cm^3 min^{-1}

PDA Ch1 204nm 4nm

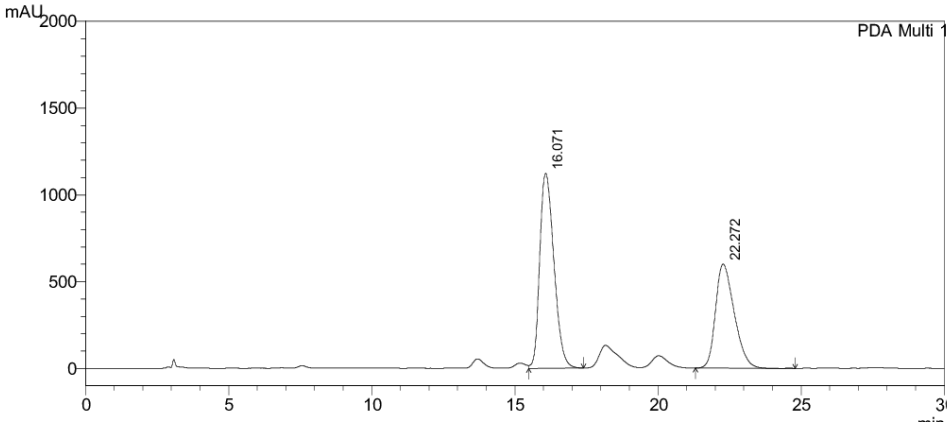
Peak#	Ret. Time	Height	Area	Area %
1	16.64	454609	16748482	46.089
2	23.12	399983	19591168	53.911
Total		854592	36339650	100.000



Entry 4 R = *p*Tol, Rh_2(*S*-NTTL)$_4$, 90 °C, CH_2Cl_2, $LiAlH_4$ workup
AD-H, 7% *i*PrOH in hexane, 1 cm^3 min^{-1}

PDA Ch1 204nm 1nm

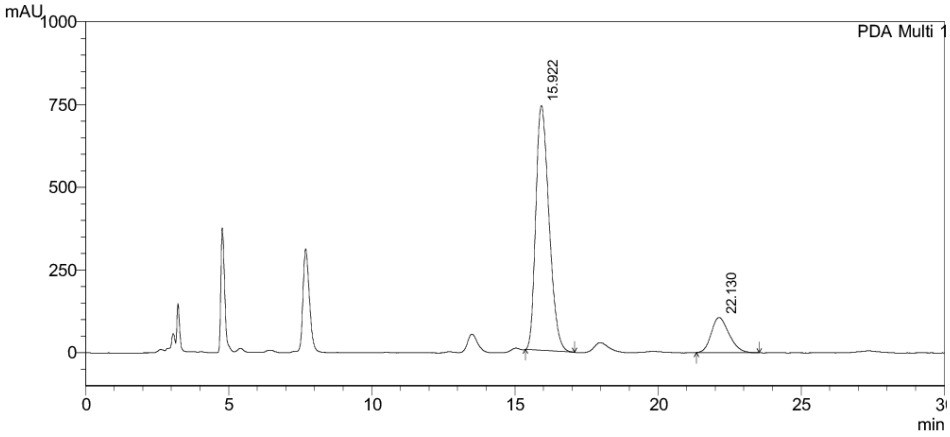
Peak#	Ret. Time	Height	Area	Area %
1	16.07	1124451	38842213	58.805
2	22.27	600179	27209965	41.195
Total		1724630	66052177	100.000



Entry 7 R = *p*Tol, Rh_2(*S*-NTTL)$_4$, 50 °C, PhMe, $LiAlH_4$ workup
AD-H, 7% *i*PrOH in hexane, 1 cm^3 min^{-1}

PDA Ch1 204nm 1nm

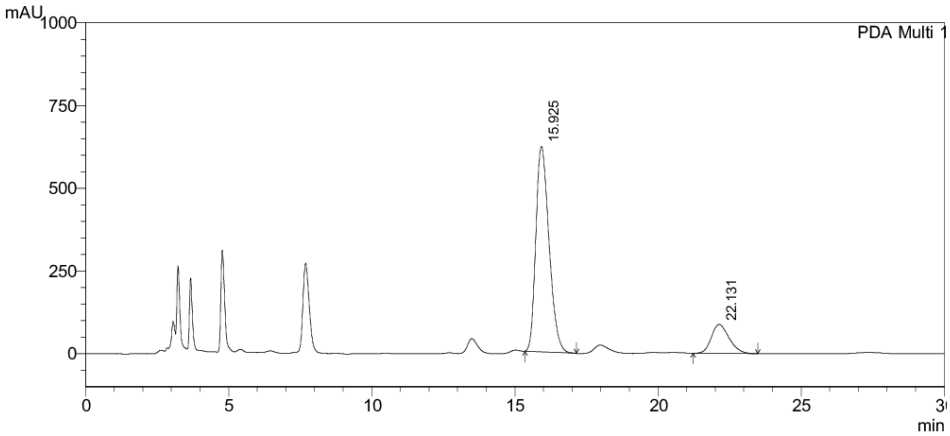
Peak#	Ret. Time	Height	Area	Area %
1	15.92	740105	23811827	83.932
2	22.13	105852	4558450	16.068
Total		845956	28370277	100.000



Entry 8 R = *p*Tol, Rh_2(*S*-NTTL)$_4$, 50 °C, PhMe, syringe pump, $LiAlH_4$ workup
AD-H, 7% *i*PrOH in hexane, 1 cm^3 min^{-1}

PDA Ch1 204nm 1nm

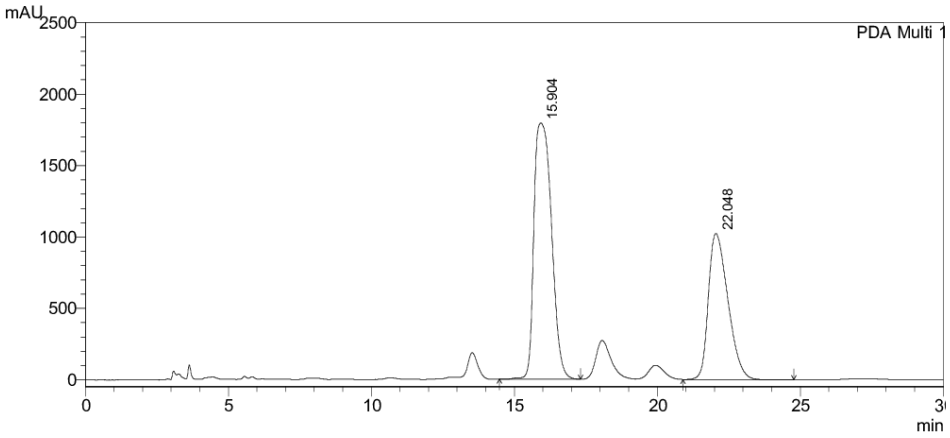
Peak#	Ret. Time	Height	Area	Area %
1	15.92	620753	19883161	84.265
2	22.13	87025	3712702	15.735
Total		707778	23595863	100.000



Entry 9 R = *p*Tol, Rh_2(*S*- *t*PTTL)$_4$, 50 °C, PhMe, $LiAlH_4$ workup
AD-H, 7% *i*PrOH in hexane, 1 cm^3 min^{-1}

PDA Ch1 204nm 1nm

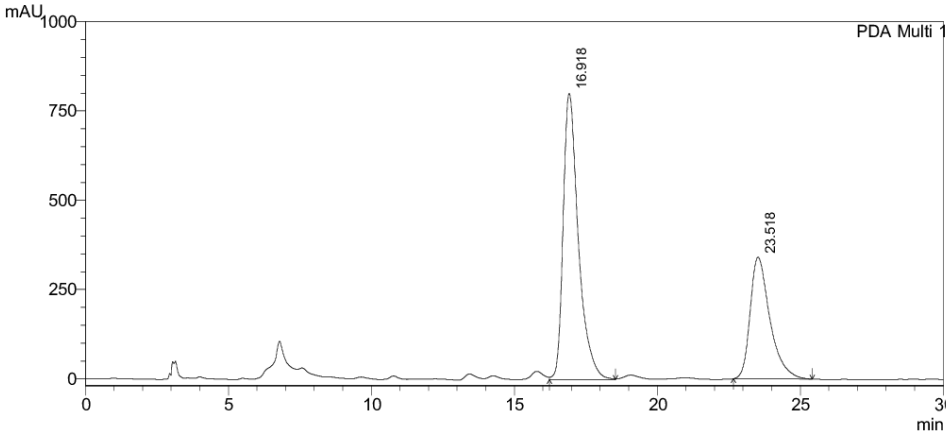
Peak#	Ret. Time	Height	Area	Area %
1	15.90	1792874	76941999	61.364
2	22.05	1022704	48443898	38.636
Total		2815578	125385897	100.000



Entry 10 R = *p*Tol, Rh_2(*S*-NTTL)$_4$, 50 °C, CH_2Cl_2, $LiAlH_4$ workup
AD-H, 7% *i*PrOH in hexane, 1 cm^3 min^{-1}

PDA Ch1 204nm 4nm

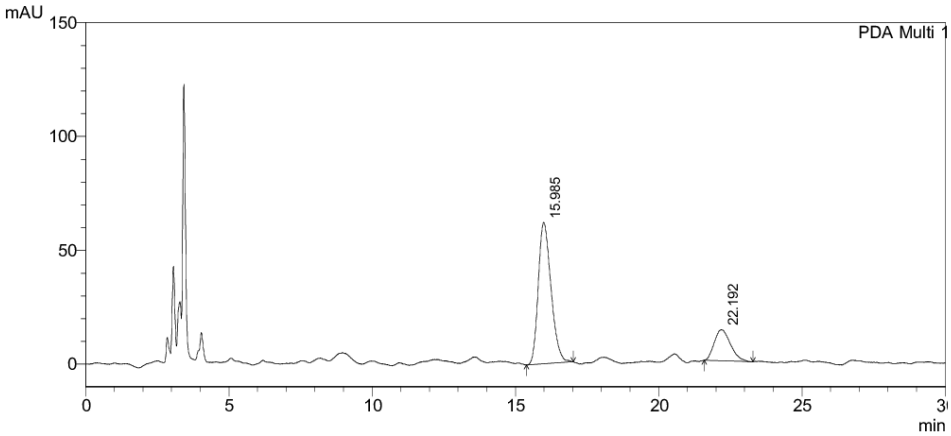
Peak#	Ret. Time	Height	Area	Area %
1	16.92	801589	29700606	64.505
2	23.52	340451	16343243	35.495
Total		1142040	46043849	100.000



Entry 11 R = *p*Tol, Rh_2(*S*-NTTL)$_4$, 50 °C, C_6H_6, $LiAlH_4$ workup
AD-H, 7% *i*PrOH in hexane, 1 cm^3 min^{-1}

PDA Ch1 204nm 1nm

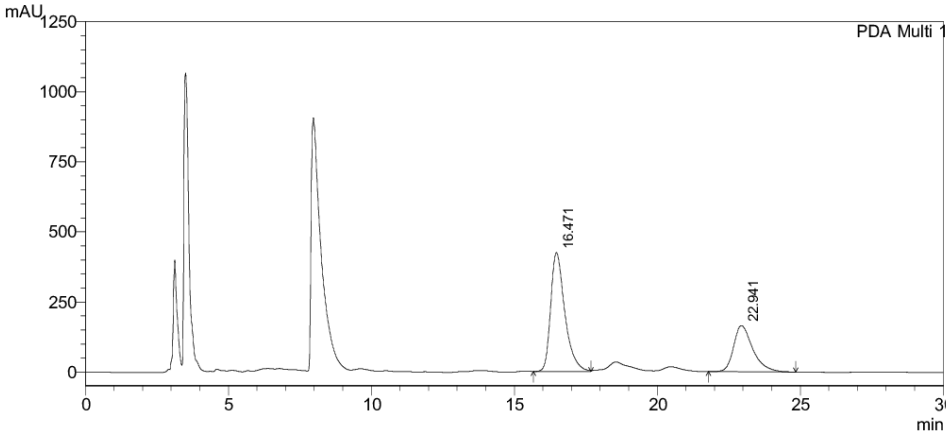
Peak#	Ret. Time	Height	Area	Area %
1	15.99	62129	1922935	78.178
2	22.19	13757	536742	21.822
Total		75885	2459676	100.000



Entry 12 R = *p*Tol, Rh_2(*S*-NTTL)$_4$, 50 °C, C_6H_6, $LiAlH_4$ workup
AD-H, 7% *i*PrOH in hexane, 1 cm^3 min^{-1}

PDA Ch1 204nm 4nm

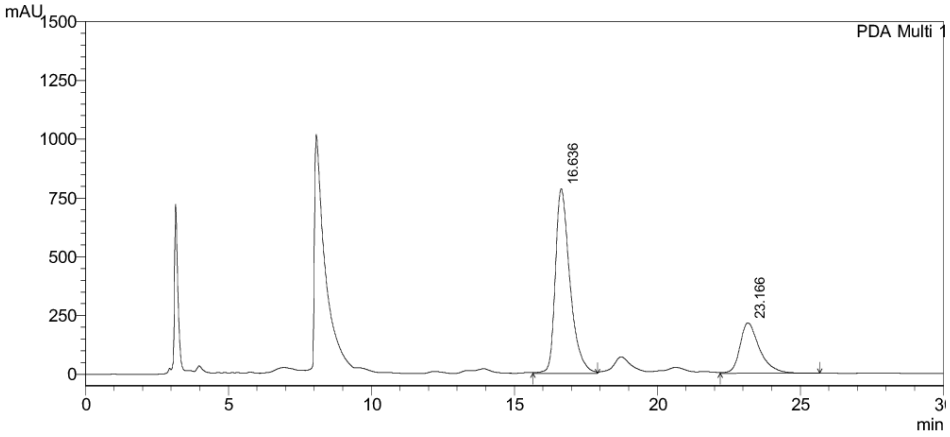
Peak#	Ret. Time	Height	Area	Area %
1	16.47	424241	14600490	65.499
2	22.94	165095	7690543	34.501
Total		589336	22291033	100.000



Entry 13 R = *p*Tol, Rh_2(*S*-NTTL)$_4$, 50 °C, *t*BuOMe, $LiAlH_4$ workup
AD-H, 7% *i*PrOH in hexane, 1 cm^3 min^{-1}

PDA Ch1 204nm 4nm

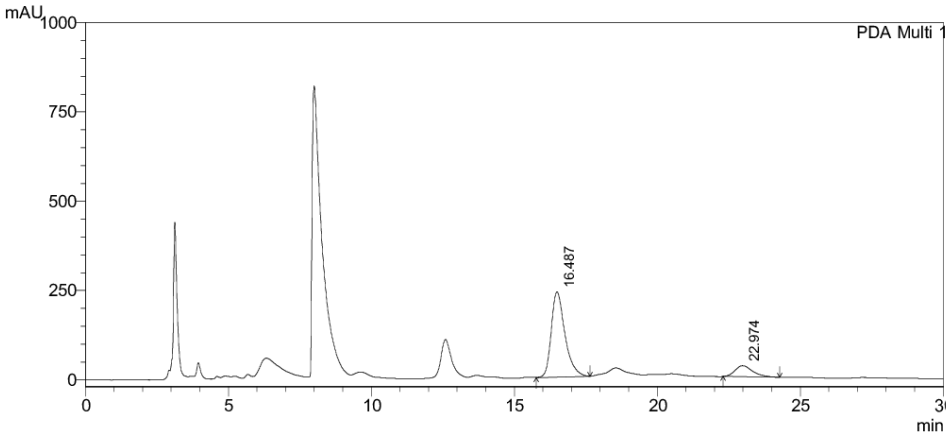
Peak#	Ret. Time	Height	Area	Area %
1	16.64	786182	27837788	73.225
2	23.17	214192	10178796	26.775
Total		1000374	38016583	100.000



Entry 14 R = *p*Tol, Rh_2(*S*-NTTL)$_4$, 50 °C, *cy*Hex, $LiAlH_4$ workup
AD-H, 7% *i*PrOH in hexane, 1 cm^3 min^{-1}

PDA Ch1 204nm 4nm

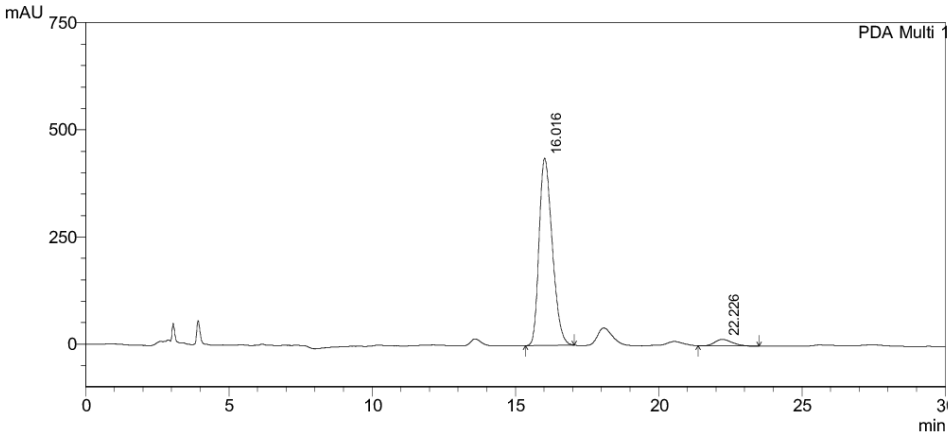
Peak#	Ret. Time	Height	Area	Area %
1	16.49	239196	7946477	85.527
2	22.97	30976	1344678	14.473
Total		270171	9291155	100.000



Entry 15 R = *p*Tol, Rh_2(*S*-NTTL)$_4$, 50 °C, C_6F_6, $LiAlH_4$ workup
AD-H, 7% *i*PrOH in hexane, 1 cm^3 min^{-1}

PDA Ch1 204nm 1nm

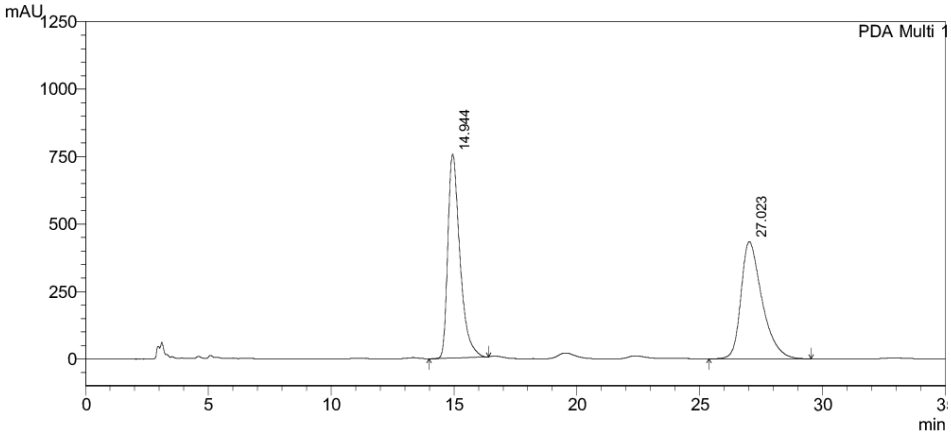
Peak#	Ret. Time	Height	Area	Area %
1	16.02	436885	13975150	95.689
2	22.23	15206	629616	4.311
Total		452091	14604766	100.000



Entry 17 R = *p*$NO_2C_6H_4$, $Rh_2(OAc)_4$, 50 °C, PhMe, $LiAlH_4$ workup
AD-H, 15% *i*PrOH in hexane, 1 cm^3 min^{-1}

PDA Ch1 204nm 1nm

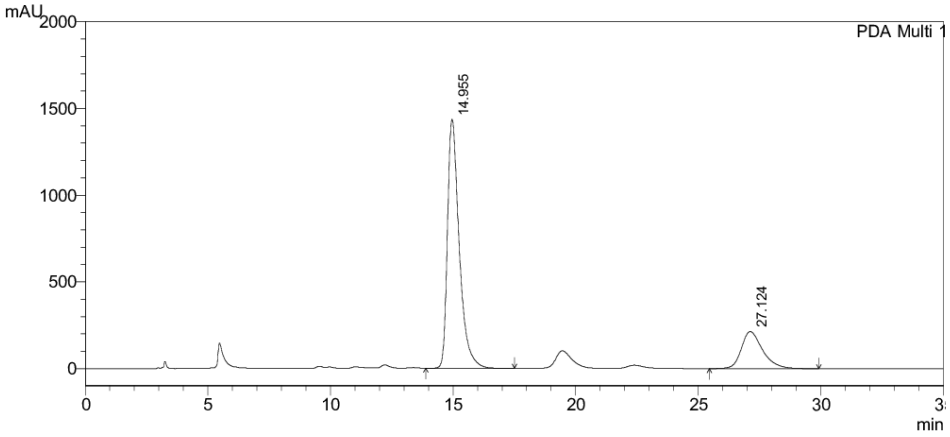
Peak#	Ret. Time	Height	Area	Area %
1	14.94	755750	25843143	49.950
2	27.02	433979	25894635	50.050
Total		1189729	51737778	100.000



Entry 18 R = *p*$NO_2C_6H_4$, Rh_2(*S*-NTTL)$_4$, 50 °C, PhMe, $LiAlH_4$ workup
AD-H, 15% *i*PrOH in hexane, 1 cm^3 min^{-1}

PDA Ch1 268nm 4nm

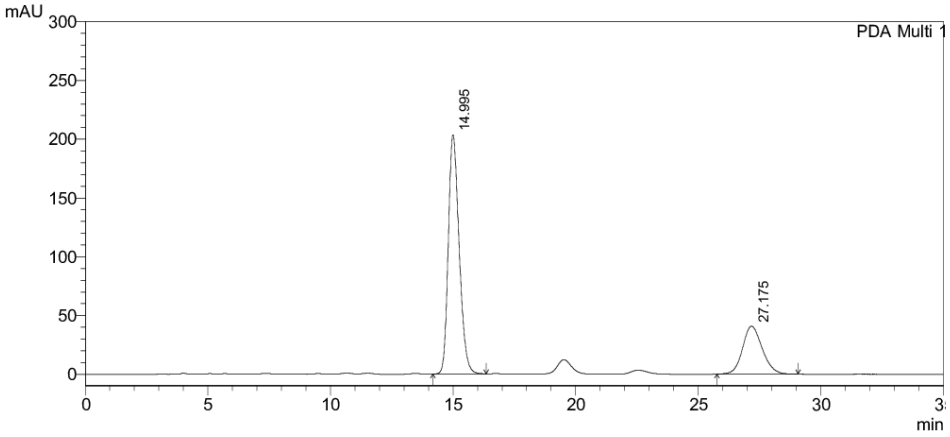
Peak#	Ret. Time	Height	Area	Area %
1	14.96	1436823	48007626	78.907
2	27.12	213350	12832865	21.093
Total		1650173	60840490	100.000



Entry 19 R = *p*$NO_2C_6H_4$, Rh_2(*S*-*t*PTTL)$_4$, 50 °C, PhMe, $LiAlH_4$ workup
AD-H, 15% *i*PrOH in hexane, 1 cm^3 min^{-1}

PDA Ch1 268nm 4nm

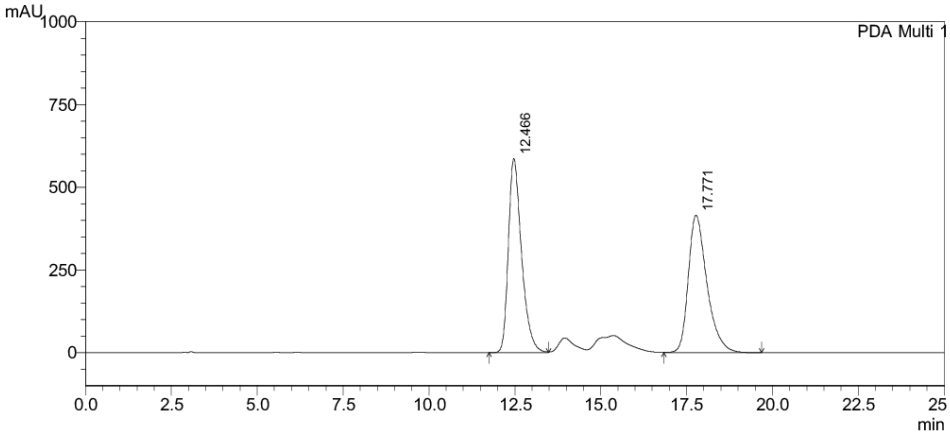
Peak#	Ret. Time	Height	Area	Area %
1	14.99	203636	6271089	73.431
2	27.17	40759	2269075	26.569
Total		244395	8540164	100.000



Entry 20 R = *p*MeOC$_6$H$_4$, Rh$_2$(OAc)$_4$, 50 °C, PhMe, LiAlH$_4$ workup
AD-H, 15% *i*PrOH in hexane, 1 cm^3 min^{-1}

PDA Ch1 238nm 4nm

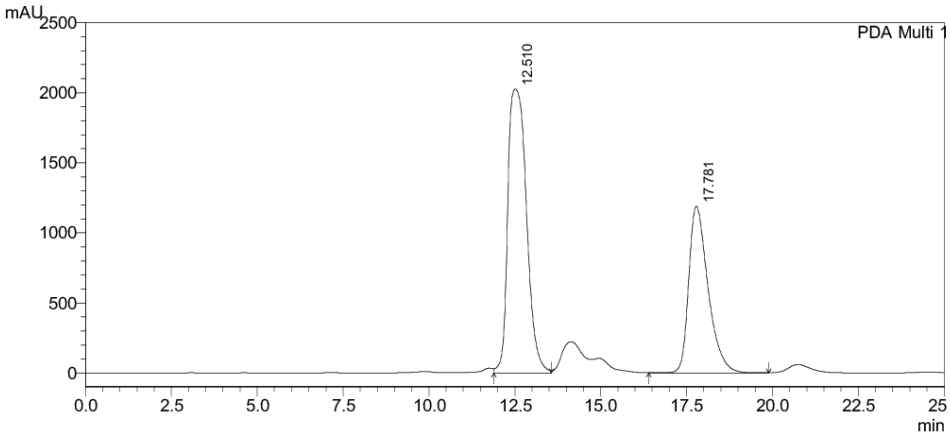
Peak#	Ret. Time	Height	Area	Area %
1	12.47	585829	15659518	49.962
2	17.77	415360	15683564	50.038
Total		1001190	31343082	100.000



Entry 21 R = *p*MeOC$_6$H$_4$, Rh$_2$(*S*-NTTL)$_4$, 50 °C, PhMe, LiAlH$_4$ workup
AD-H, 15% *i*PrOH in hexane, 1 cm^3 min^{-1}

PDA Ch1 238nm 4nm

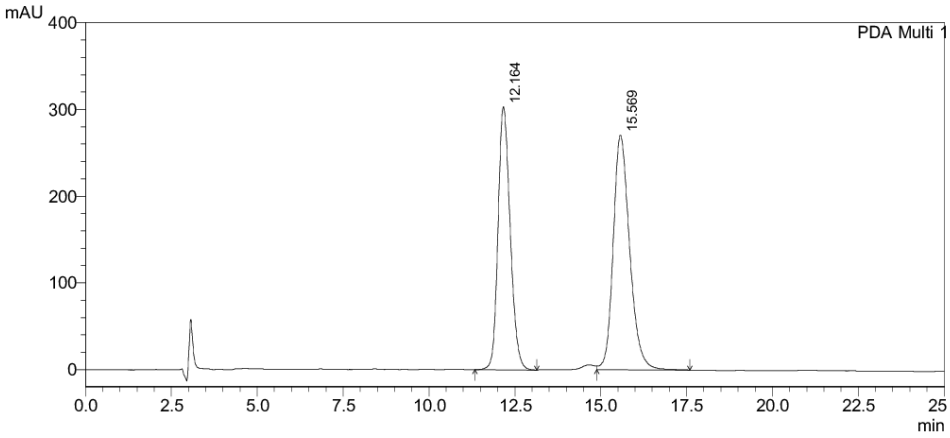
Peak#	Ret. Time	Height	Area	Area %
1	12.51	2027105	76618292	62.133
2	17.78	1188906	46694981	37.867
Total		3216011	123313273	100.000



Entry 22 R = *p*PhC_6H_4, $Rh_2(OAc)_4$, 50 °C, PhMe, $LiAlH_4$ workup
AD-H, 15% *i*PrOH in hexane, 1 cm^3 min^{-1}

PDA Ch1 209nm 4nm

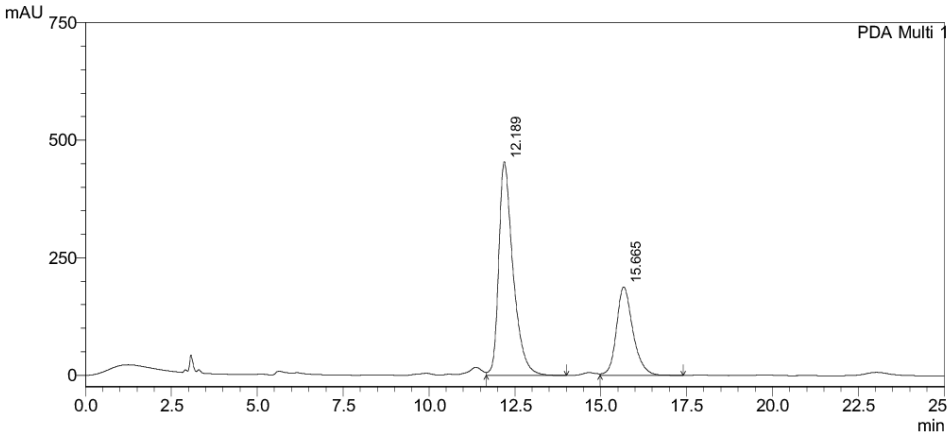
Peak#	Ret. Time	Height	Area	Area %
1	12.16	303388	7462161	45.244
2	15.57	270643	9030949	54.756
Total		574031	16493110	100.000



Entry 23 R = *p*PhC_6H_4, Rh_2(*S*-NTTL)$_4$, 50 °C, PhMe, $LiAlH_4$ workup
AD-H, 15% *i*PrOH in hexane, 1 cm^3 min^{-1}

PDA Ch1 209nm 4nm

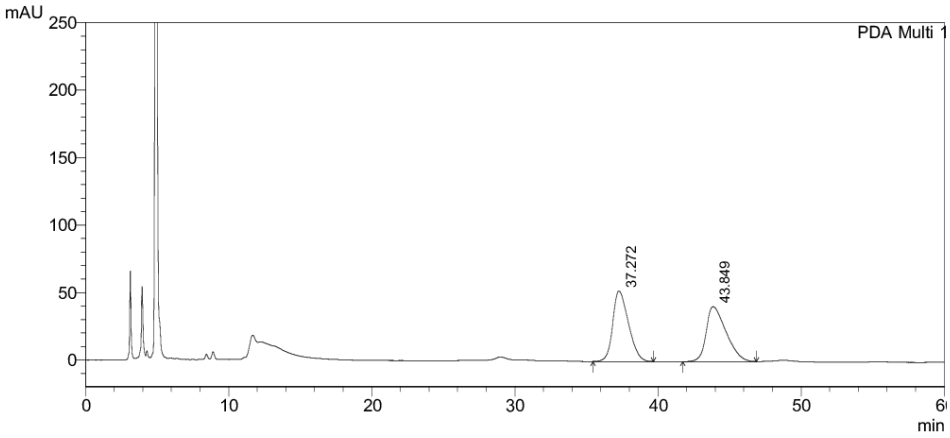
Peak#	Ret. Time	Height	Area	Area %
1	12.19	454658	13176524	67.655
2	15.67	188482	6299615	32.345
Total		643140	19476139	100.000



Entry 24 R = *p*Tol, $Rh_2(OAc)_4$, 90 °C, CH_2Cl_2, hydrolysis/Grignard workup
AD-H, 0.25% *i*PrOH in hexane, 1 cm^3 min^{-1}

PDA Ch1 204nm 4nm

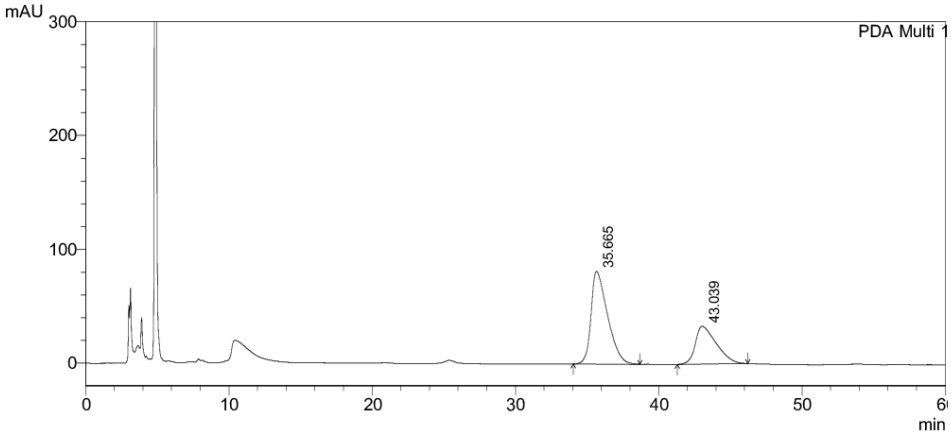
Peak#	Ret. Time	Height	Area	Area %
1	37.27	52211	3989917	50.305
2	43.85	40812	3941578	49.695
Total		93022	7931495	100.000



Entry 25 R = Me, Rh_2(*S*-NTTL)$_4$, 50 °C, PhMe, hydrolysis/Grignard workup
AD-H, 0.25% *i*PrOH in hexane, 1 cm^3 min^{-1}

PDA Ch1 204nm 4nm

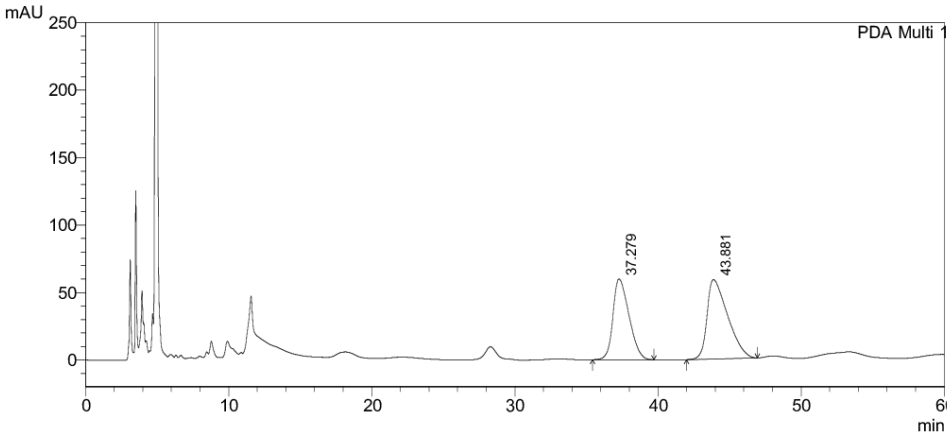
Peak#	Ret. Time	Height	Area	Area %
1	35.66	81513	6546925	65.913
2	43.04	33231	3385724	34.087
Total		114744	9932648	100.000



Entry 26 R = 2,4,6-(*i*Pr)$_3C_6H_2$, Rh_2(*S*-NTTL)$_4$, 50 °C, PhMe, hydrolysis/Grignard workup
AD-H, 0.25% *i*PrOH in hexane, 1 cm^3 min^{-1}

PDA Ch1 204nm 4nm

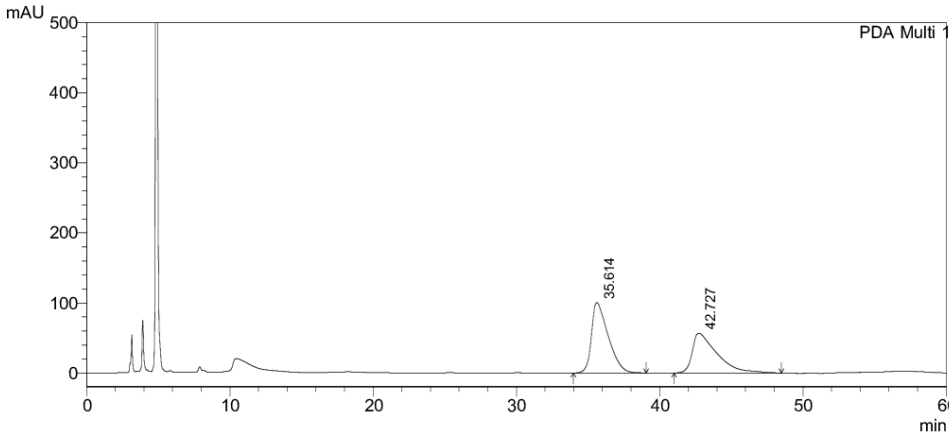
Peak#	Ret. Time	Height	Area	Area %
1	37.28	59780	4656926	44.181
2	43.88	58876	5883700	55.819
Total		118656	10540626	100.000



Entry 27 R = 5-dimethylaminonaphthalen-1-yl, Rh_2(*S*-NTTL)$_4$, 50 °C, PhMe, hydrolysis/Grignard workup
AD-H, 0.25% *i*PrOH in hexane, 1 cm^3 min^{-1}

PDA Ch1 204nm 4nm

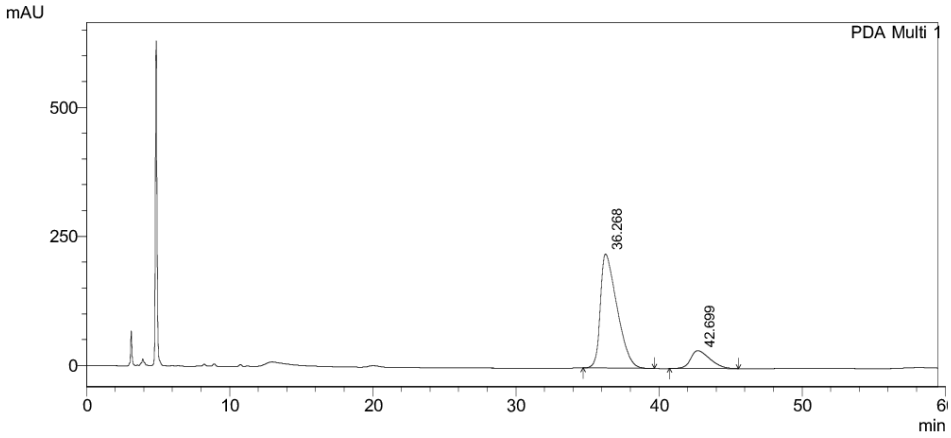
Peak#	Ret. Time	Height	Area	Area %
1	35.61	100471	8131938	54.496
2	42.73	56826	6790281	45.504
Total		157297	14922219	100.000



Entry 28 R = *p*$NO_2C_6H_4$, Rh_2(*S*-NTTL)$_4$, 50 °C, PhMe, hydrolysis/Grignard workup
AD-H, 0.25% *i*PrOH in hexane, 1 cm^3 min^{-1}

PDA Ch1 204nm 4nm

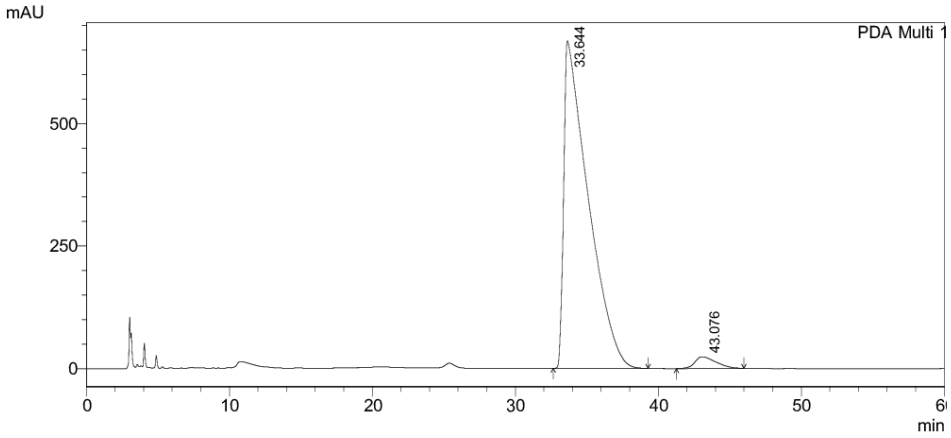
Peak#	Ret. Time	Height	Area	Area %
1	36.27	220744	17845494	84.621
2	42.70	34549	3243124	15.379
Total		255293	21088617	100.000



Entry 29 R = *p*$NO_2C_6H_4$, Rh_2(*S*-NTTL)$_4$, 50 °C, C_6F_6, hydrolysis/Grignard workup
AD-H, 0.25% *i*PrOH in hexane, 1 cm^3 min^{-1}

PDA Ch1 204nm 4nm

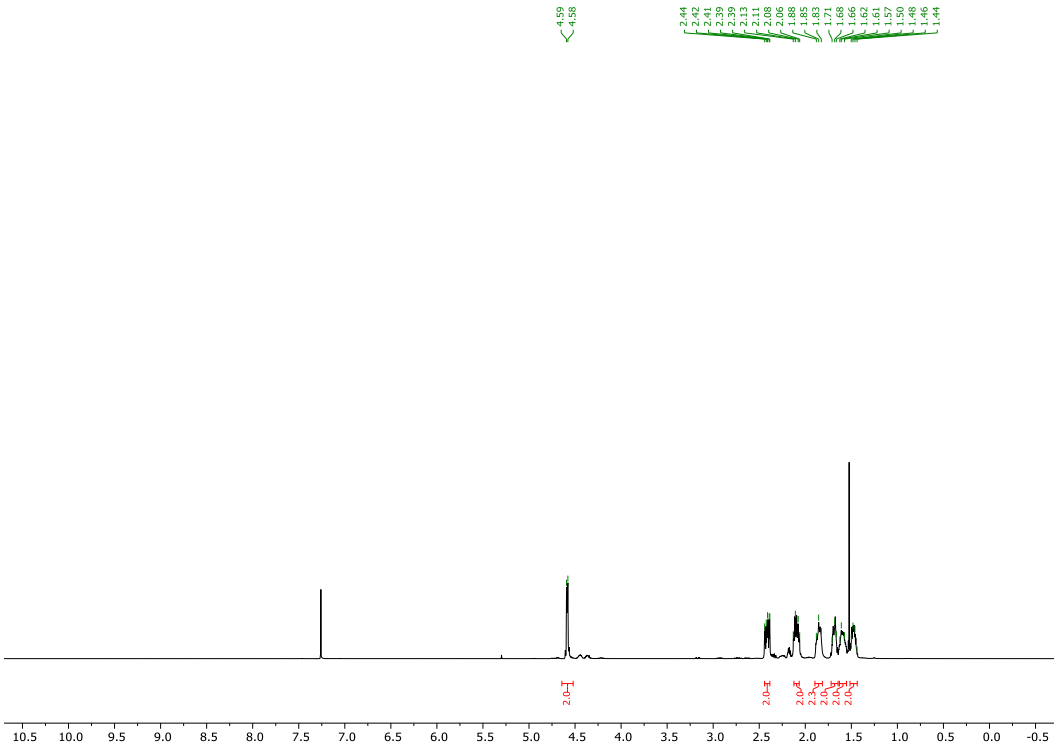
Peak#	Ret. Time	Height	Area	Area %
1	33.64	667819	79116805	97.010
2	43.08	23833	2438555	2.990
Total		691652	81555360	100.000



NMR Spectra

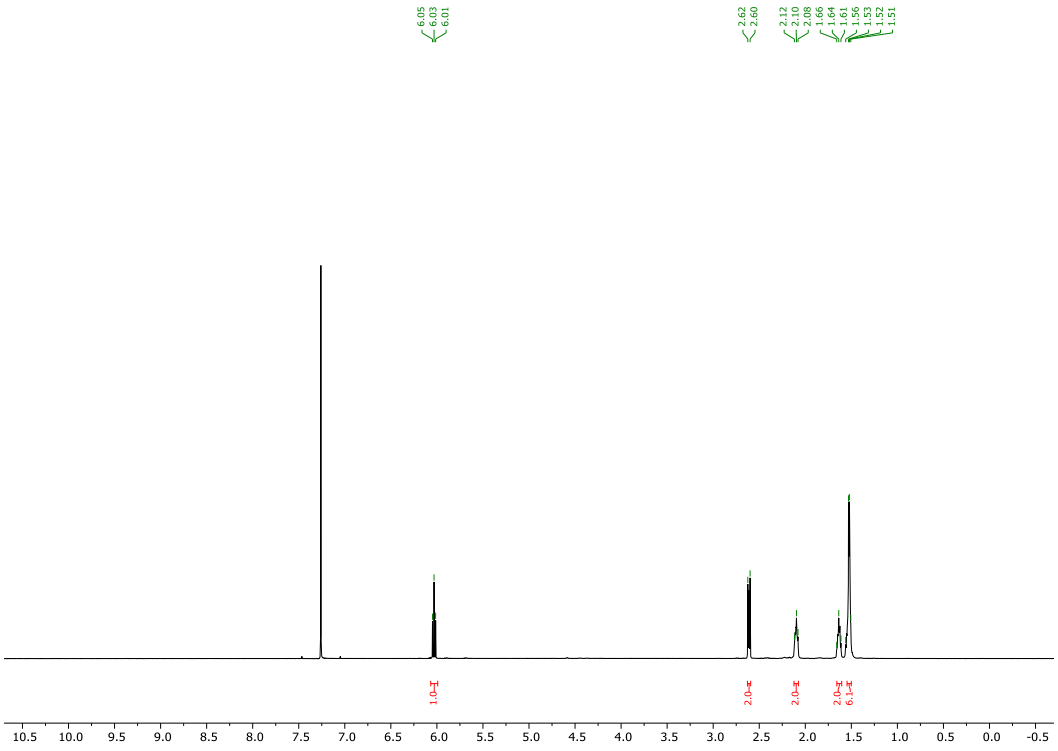
S1

^{1}H, $CDCl_3$, 500 MHz

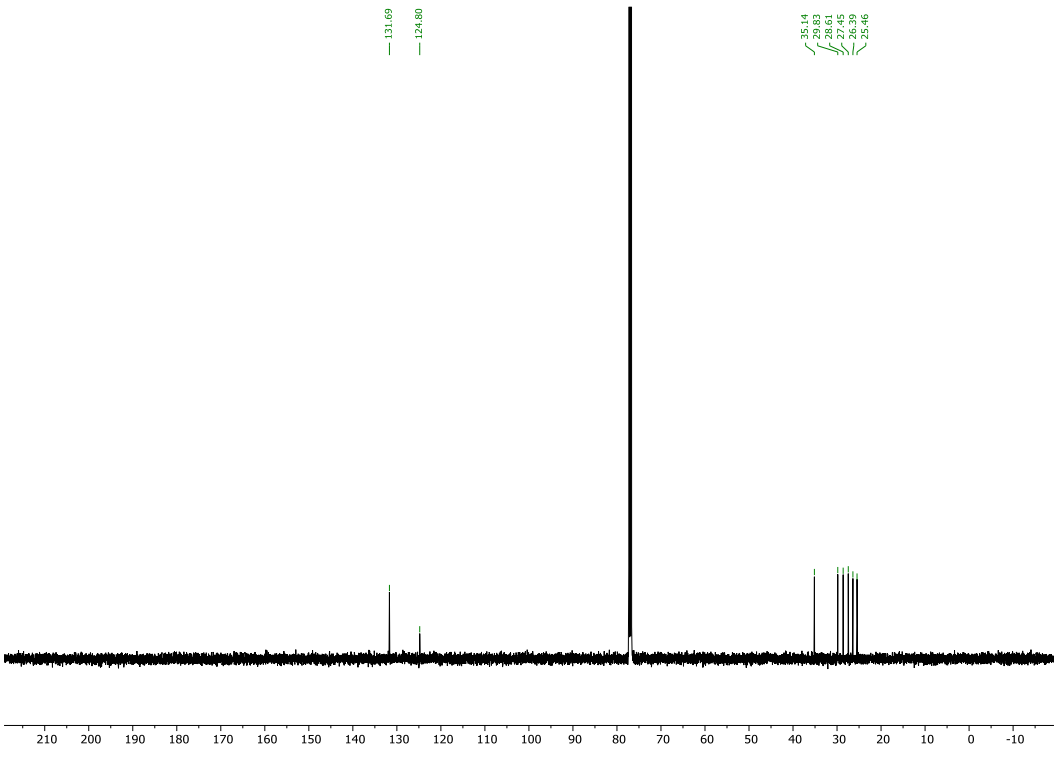


S2

^{1}H, $CDCl_3$, 500 MHz

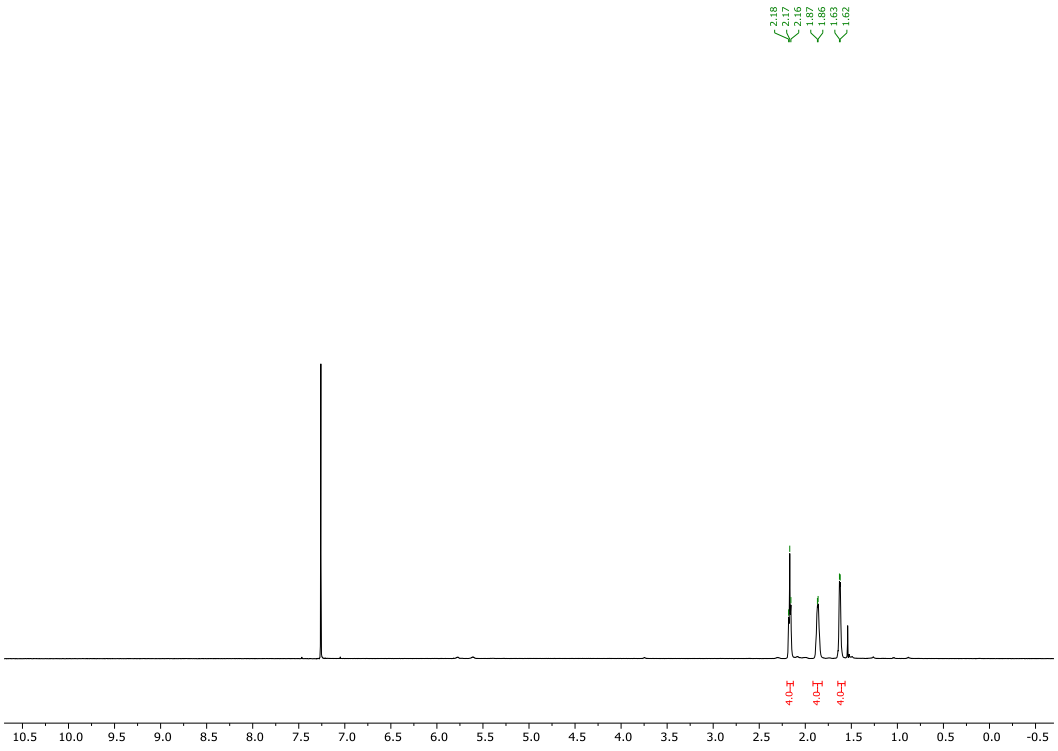


^{13}C{^{1}H}, $CDCl_3$, 126 MHz

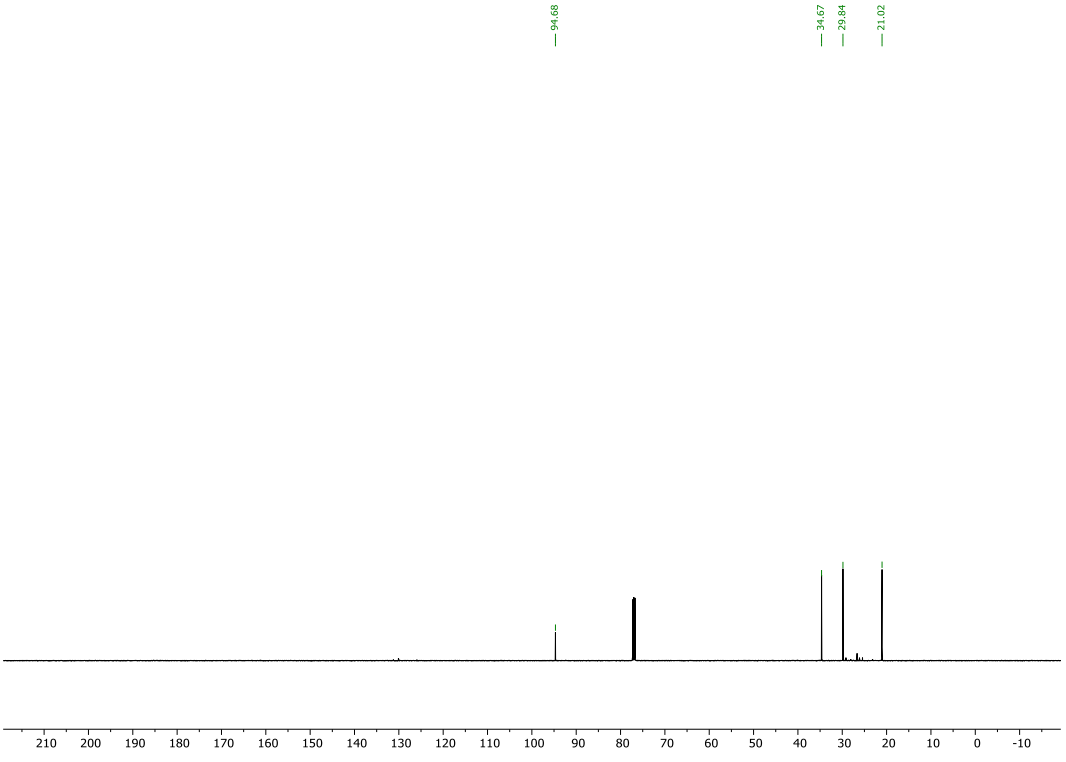


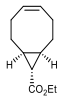
18

^{1}H, $CDCl_3$, 500 MHz



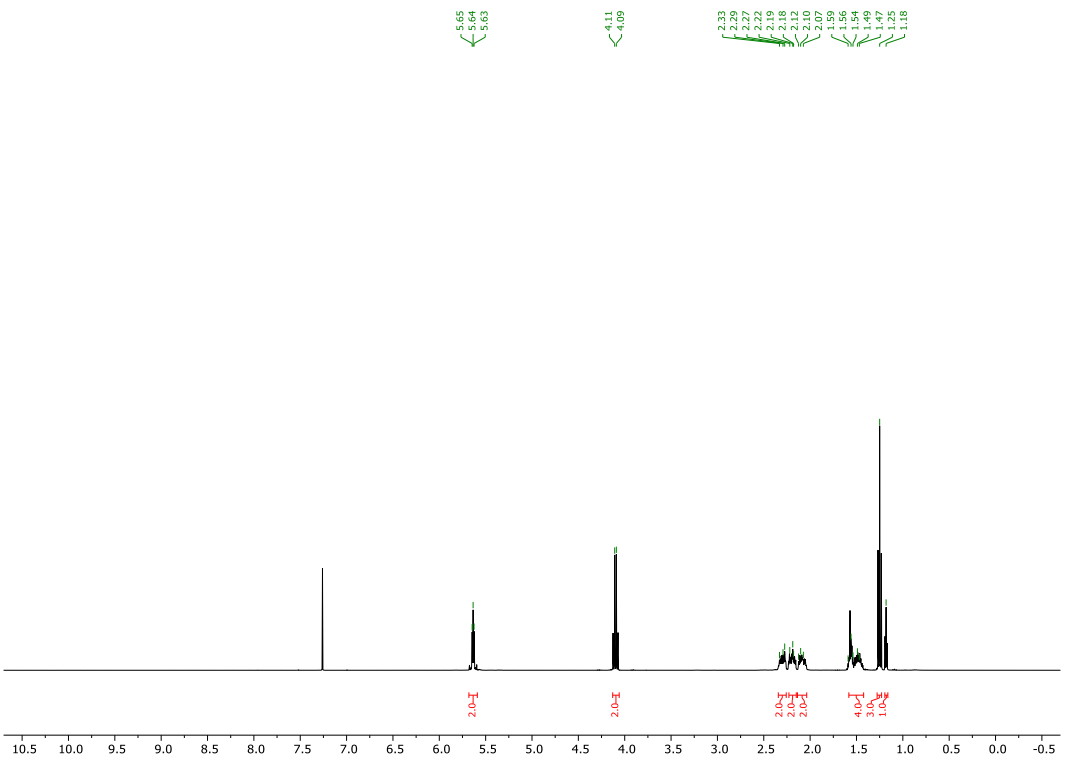
^{13}C{^{1}H}, $CDCl_3$, 126 MHz



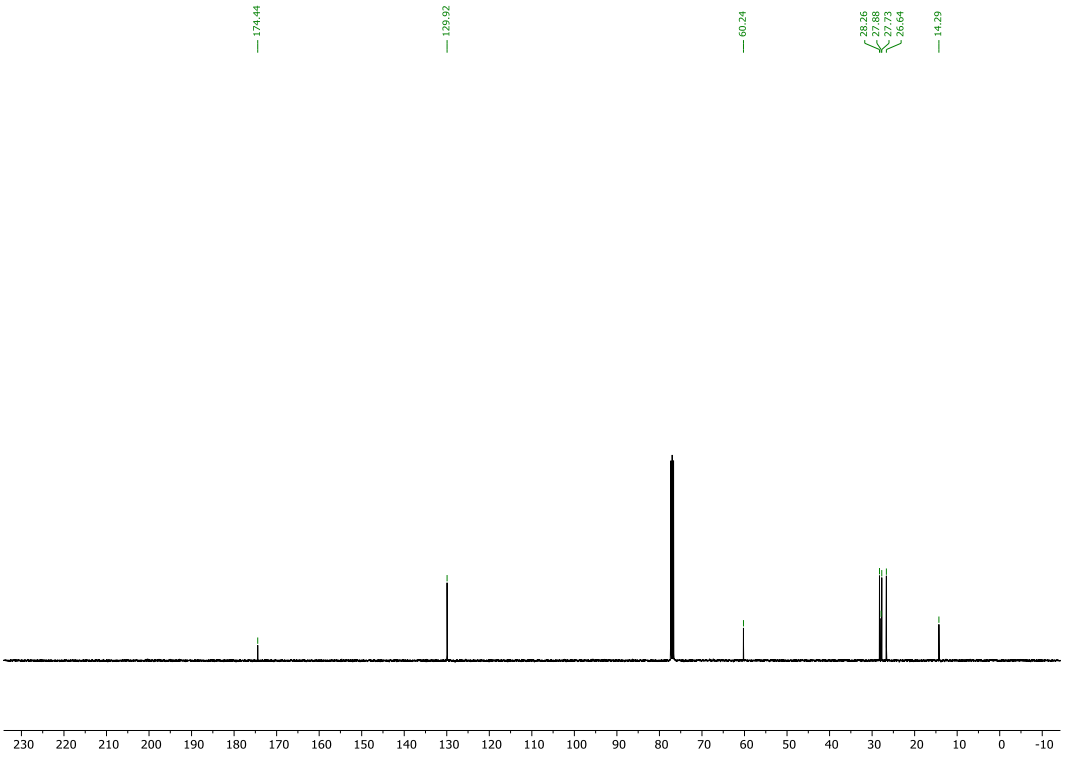


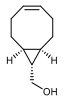
S3

^{1}H, $CDCl_3$, 400 MHz



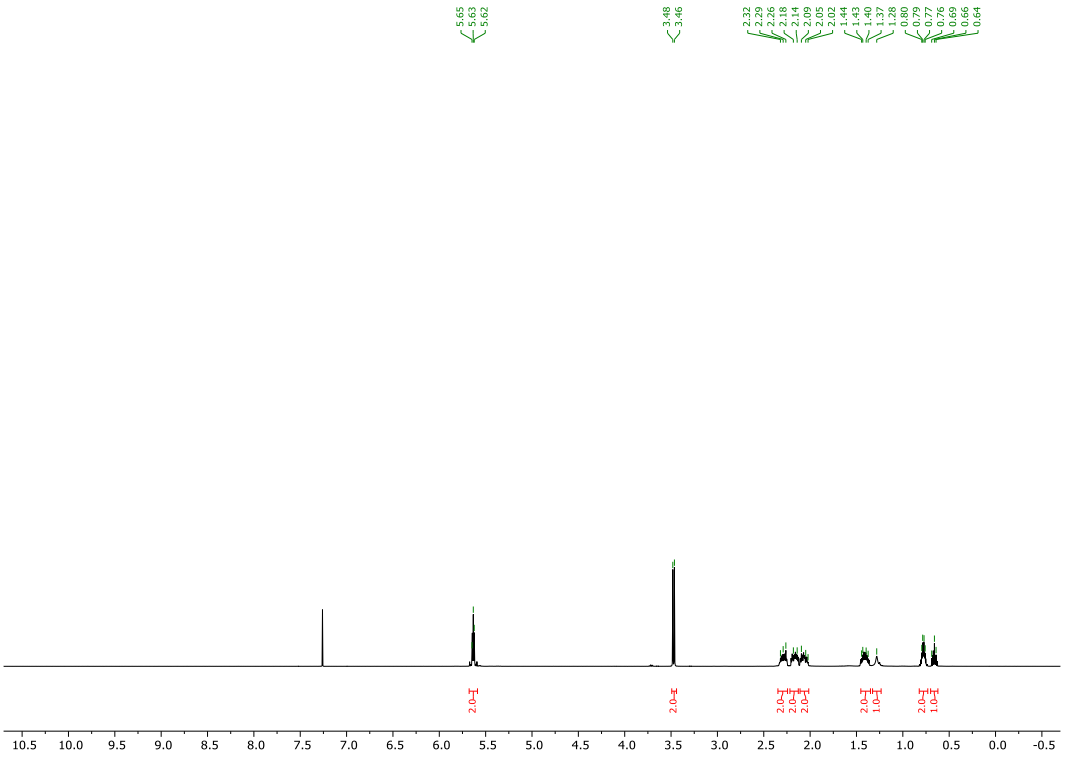
^{13}C{^{1}H}, $CDCl_3$, 101 MHz



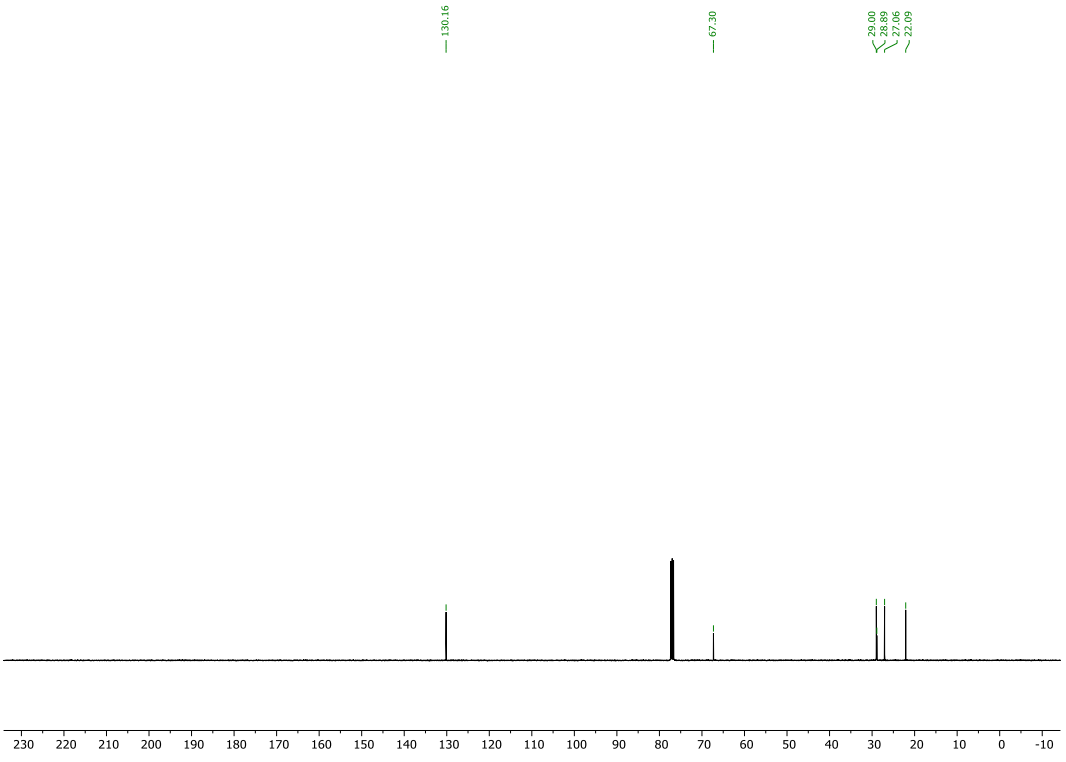


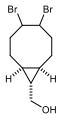
S4

^{1}H, $CDCl_3$, 400 MHz



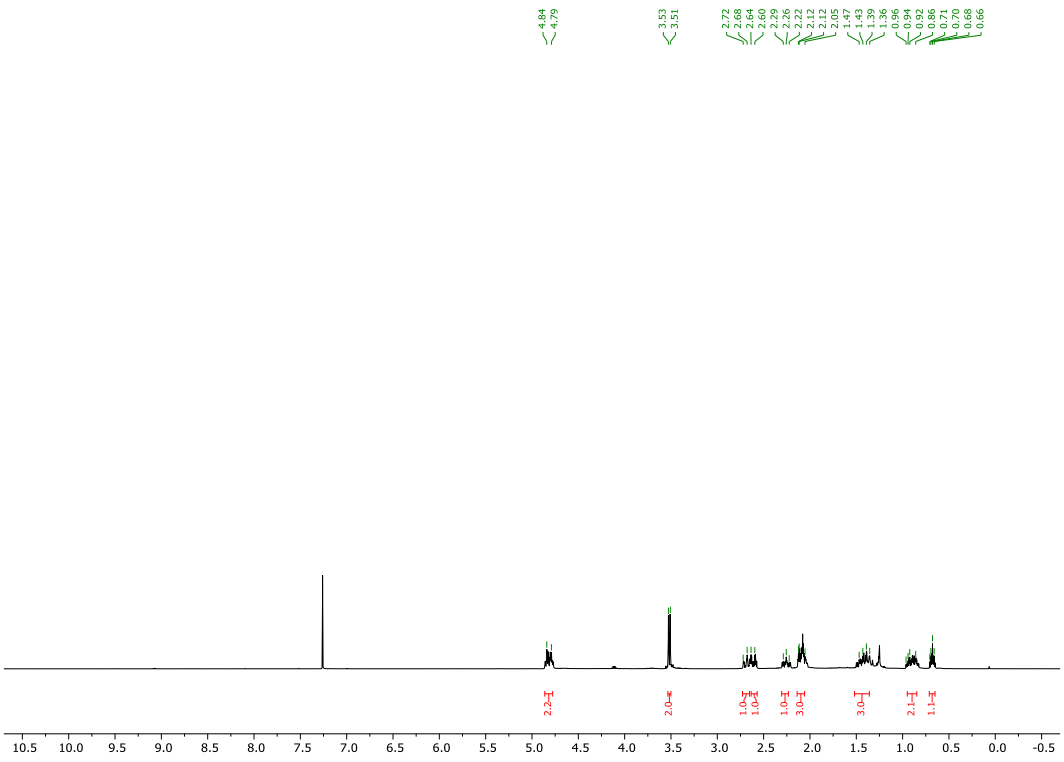
^{13}C{^{1}H}, $CDCl_3$, 101 MHz



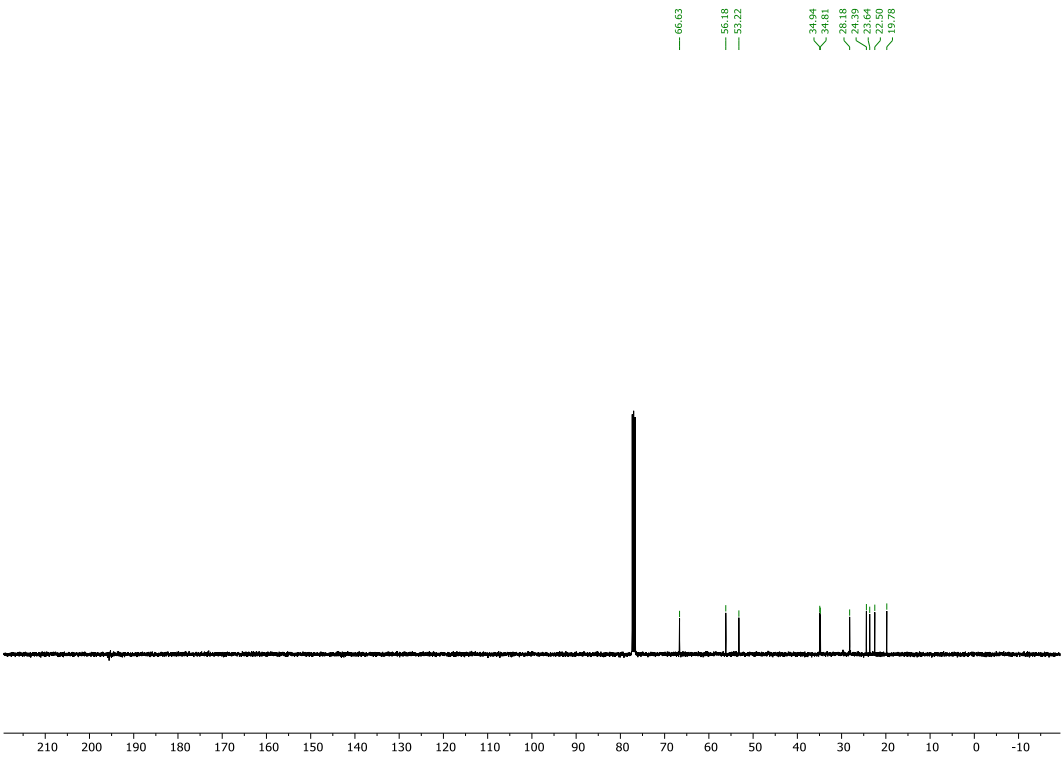


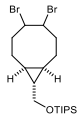
S5

^{1}H, $CDCl_3$, 400 MHz



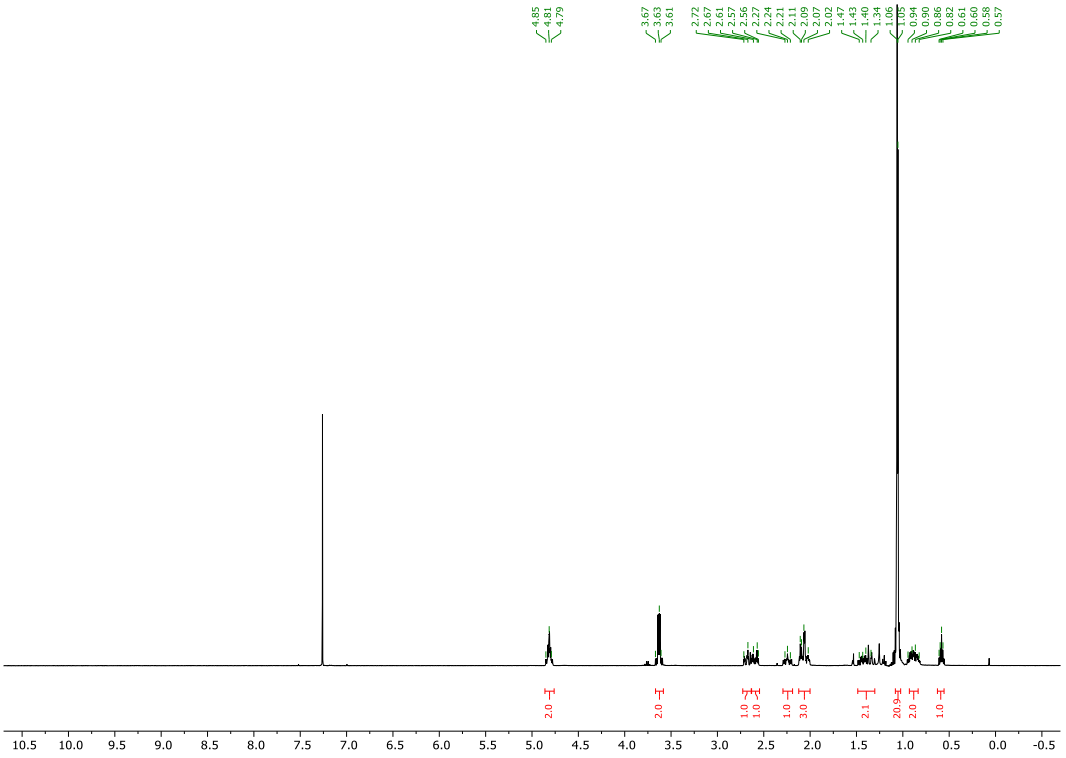
^{13}C{^{1}H}, $CDCl_3$, 101 MHz



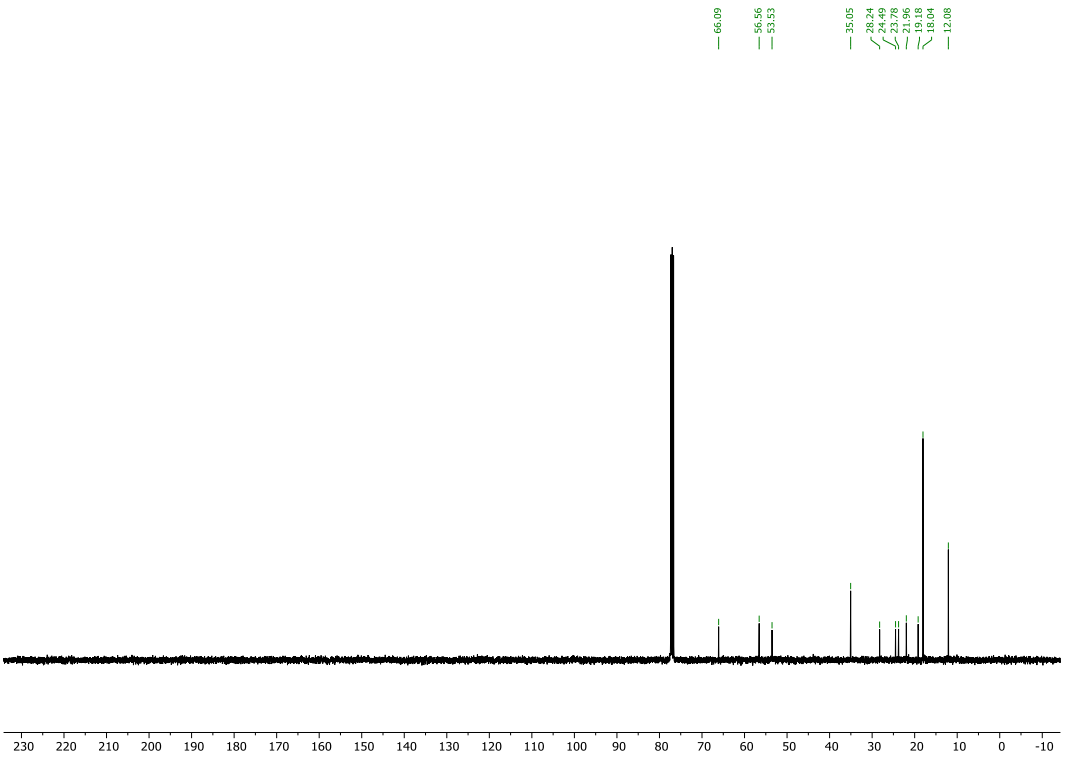


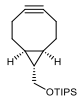
S6

^{1}H, $CDCl_3$, 400 MHz



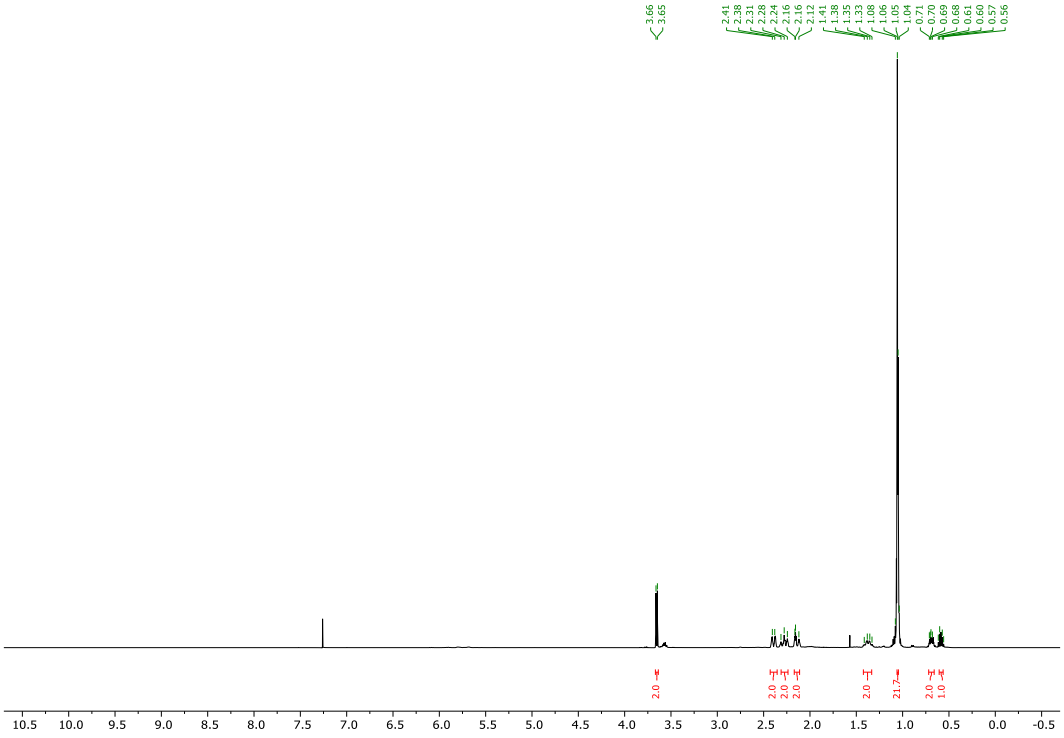
^{13}C{^{1}H}, $CDCl_3$, 101 MHz



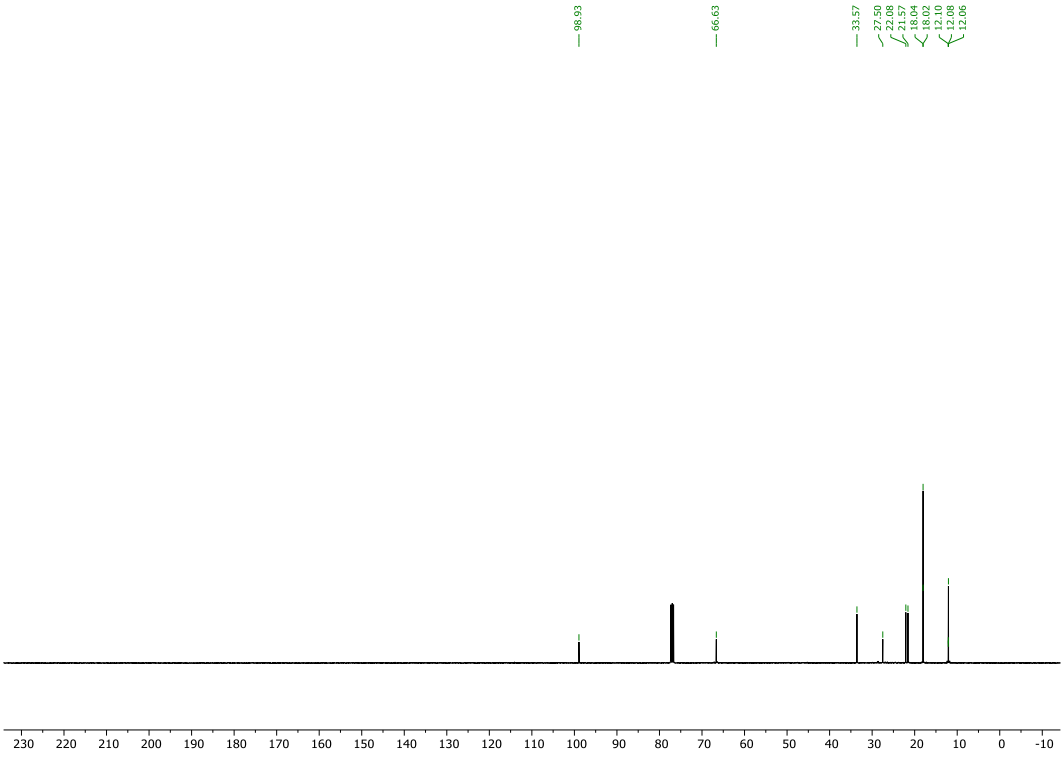


19

^{1}H, $CDCl_3$, 400 MHz

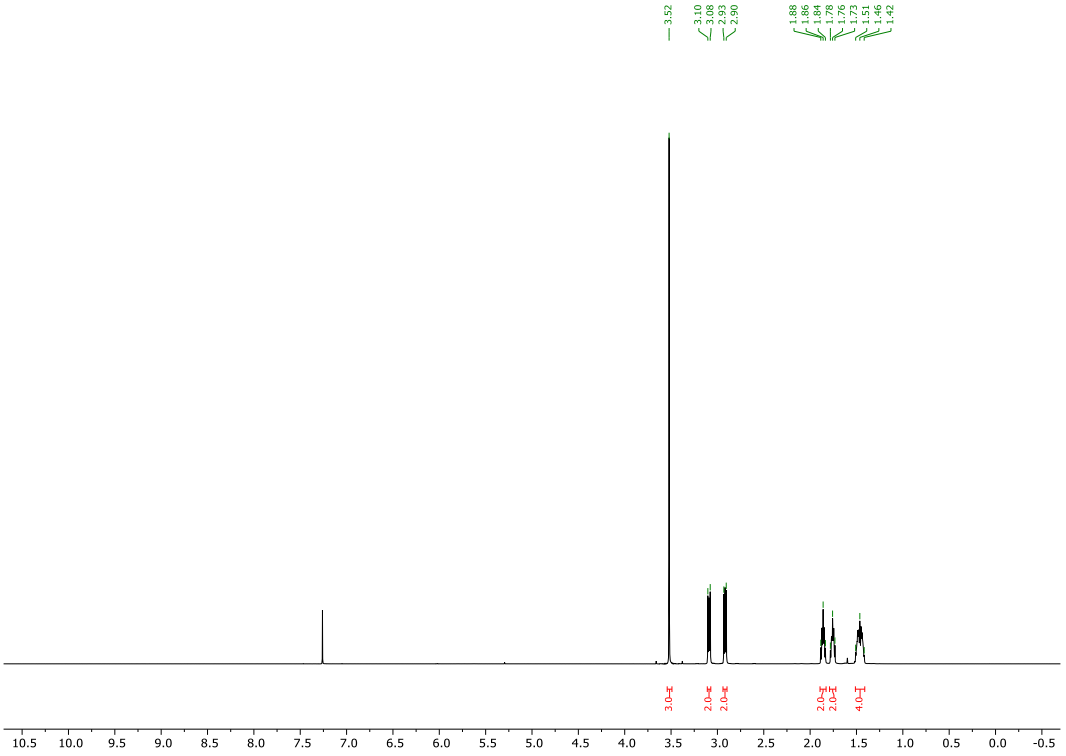


^{13}C{^{1}H}, $CDCl_3$, 101 MHz

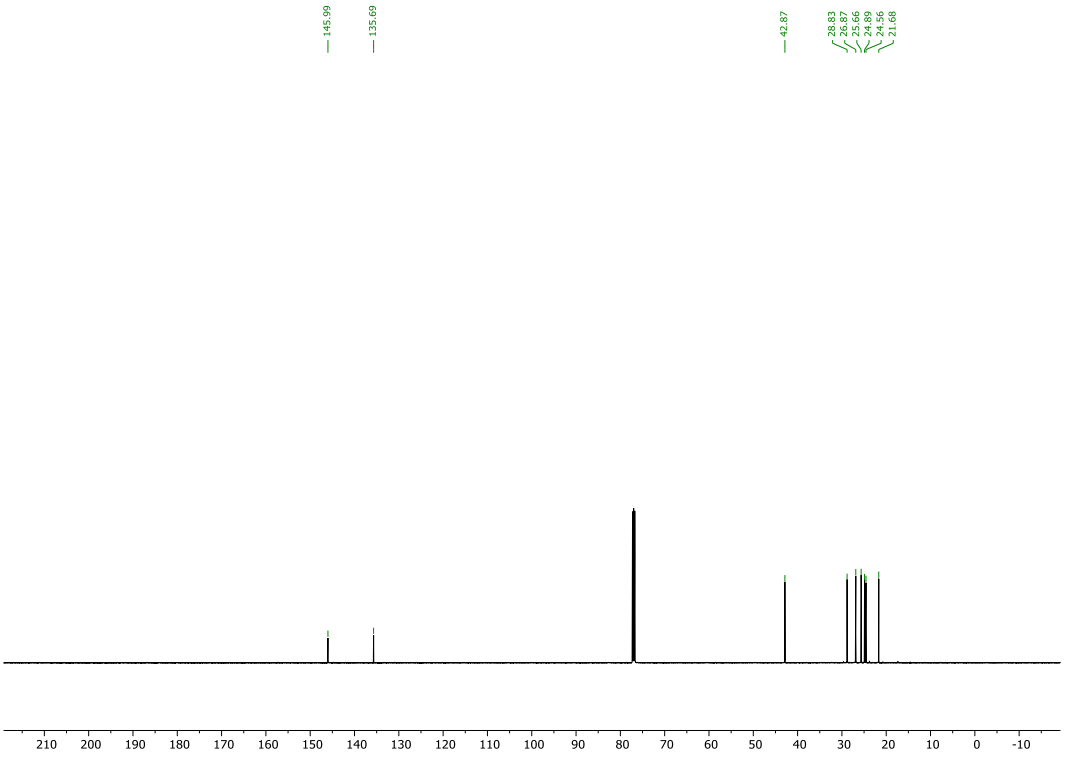


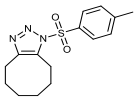
20a

^{1}H, $CDCl_3$, 500 MHz



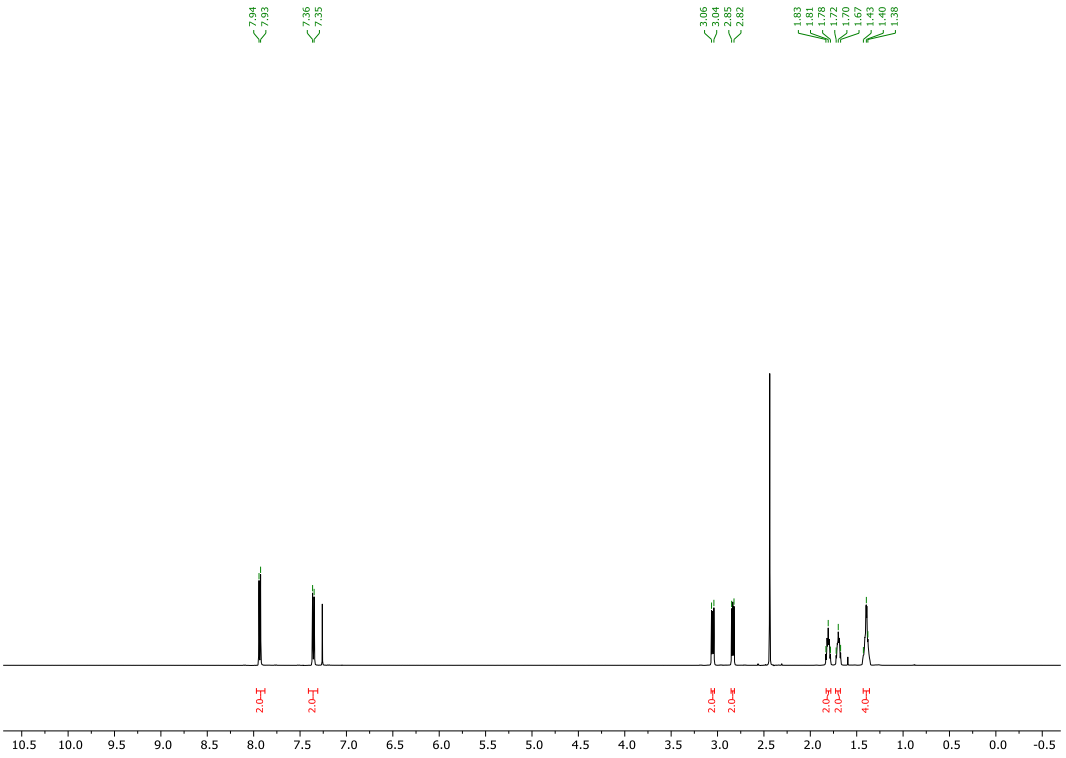
^{13}C{^{1}H}, $CDCl_3$, 126 MHz



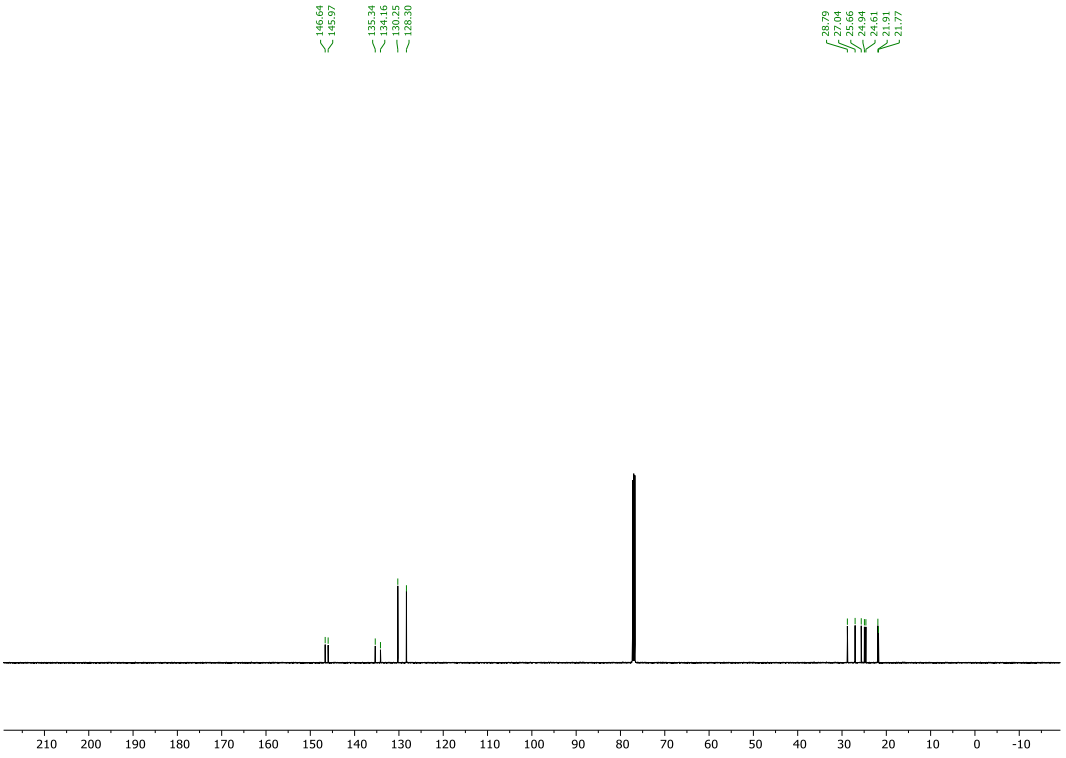


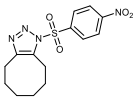
20b

^{1}H, $CDCl_3$, 500 MHz



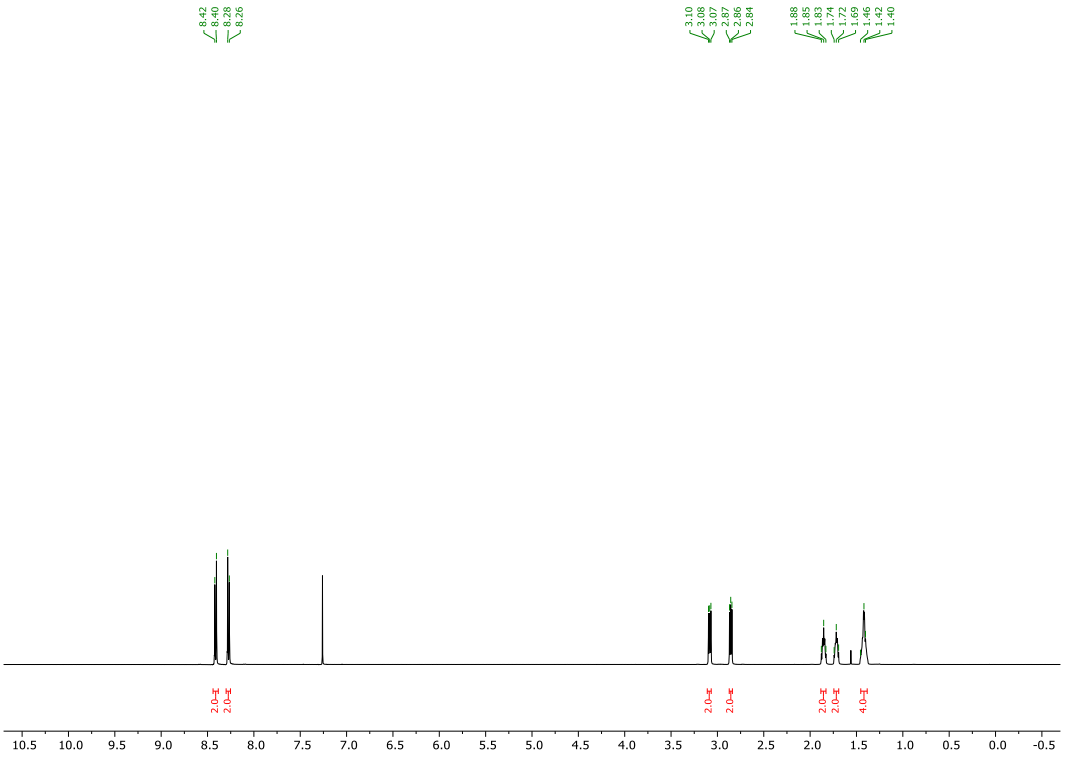
^{13}C{^{1}H}, $CDCl_3$, 126 MHz



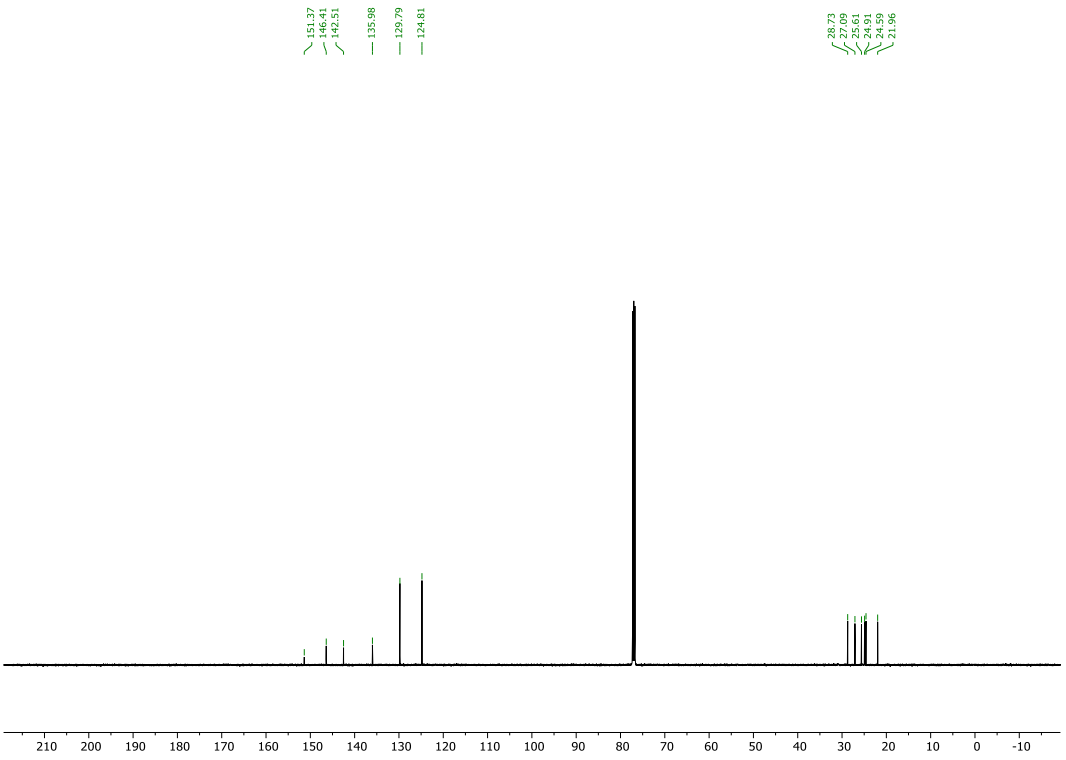


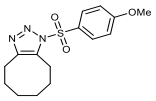
20c

^{1}H, $CDCl_3$, 500 MHz



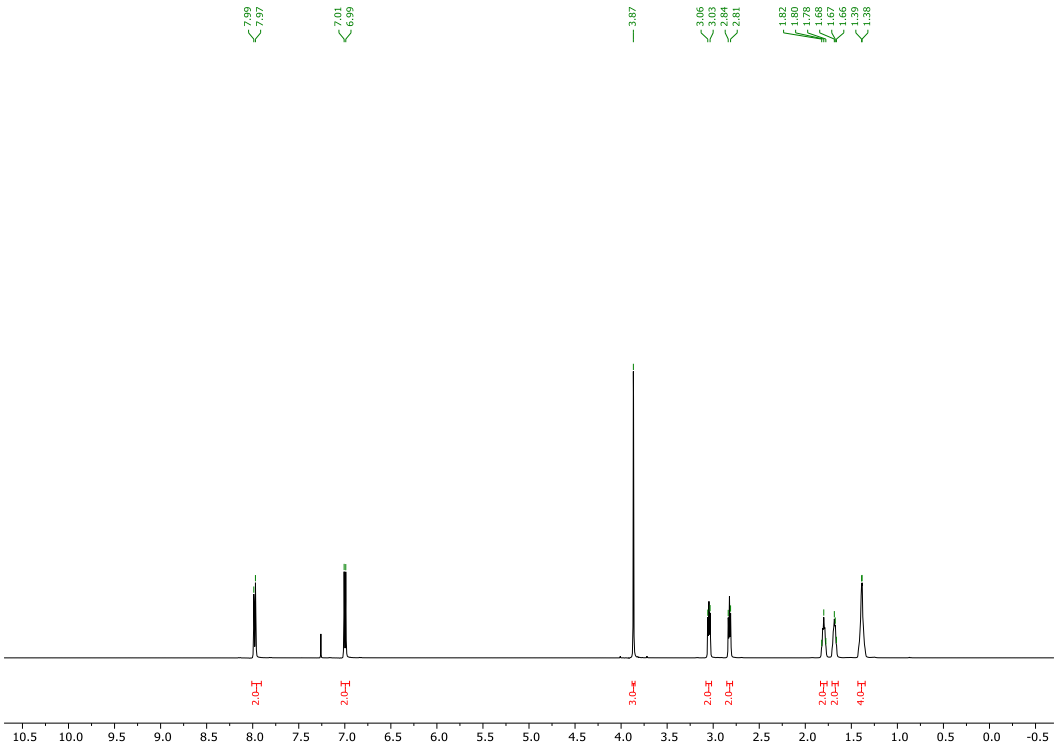
^{13}C{^{1}H}, $CDCl_3$, 126 MHz



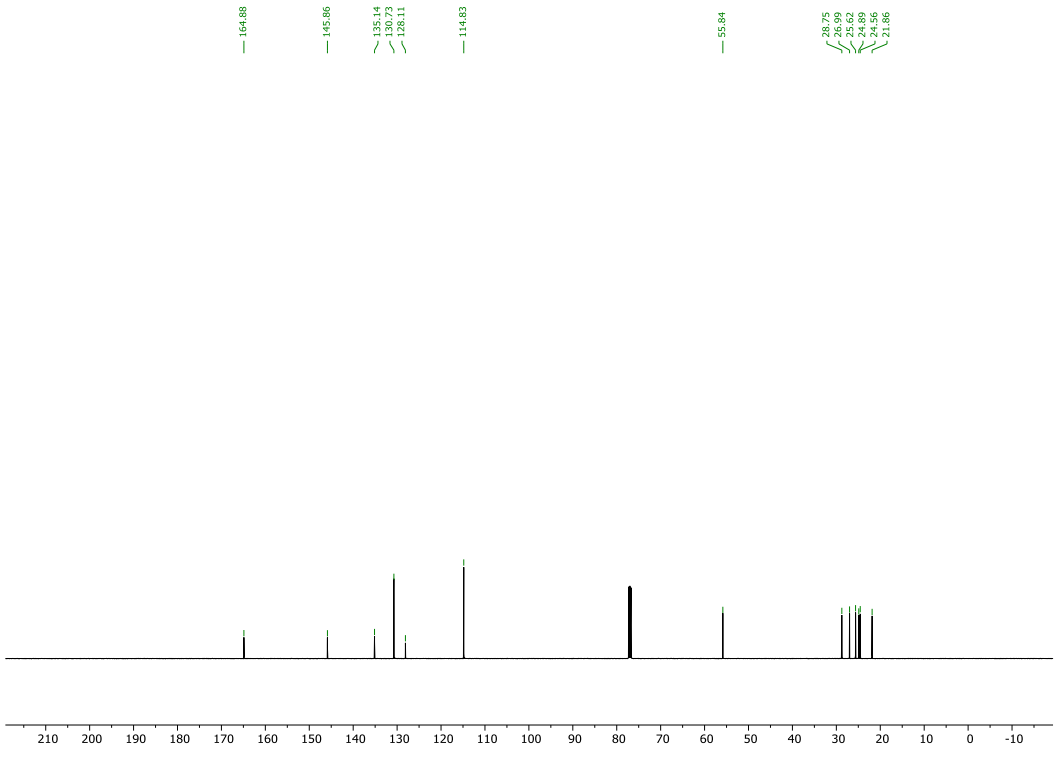


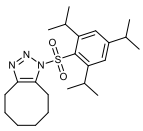
20d

^{1}H, $CDCl_3$, 500 MHz



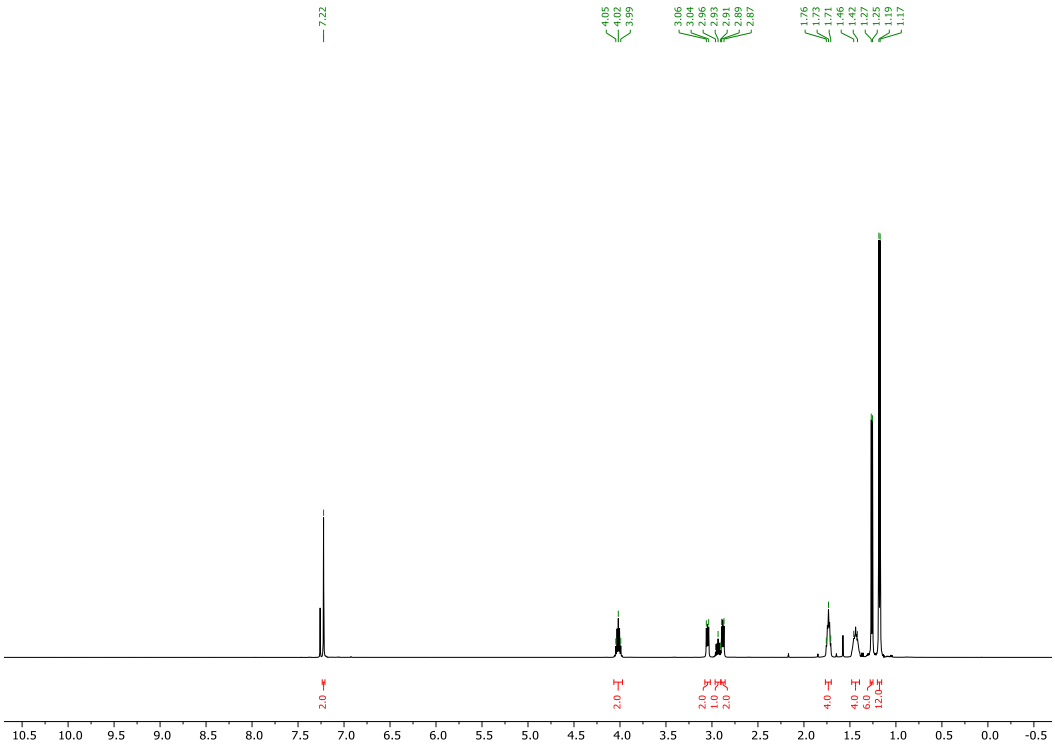
^{13}C{^{1}H}, $CDCl_3$, 126 MHz



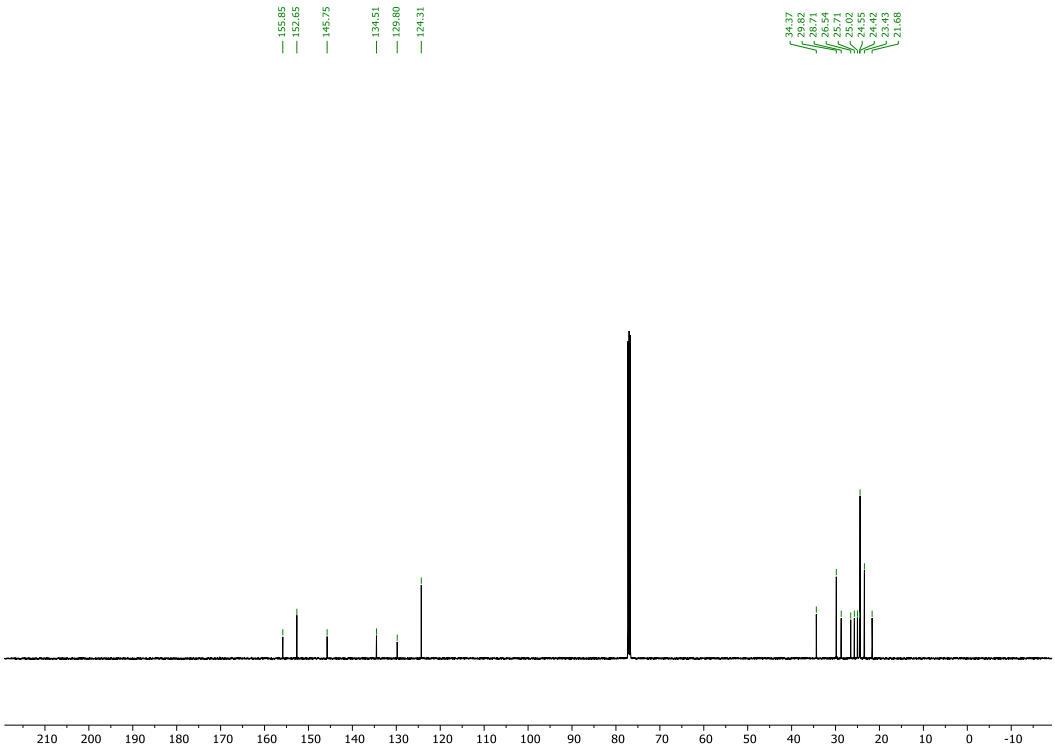


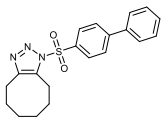
20e

^{1}H, $CDCl_3$, 500 MHz



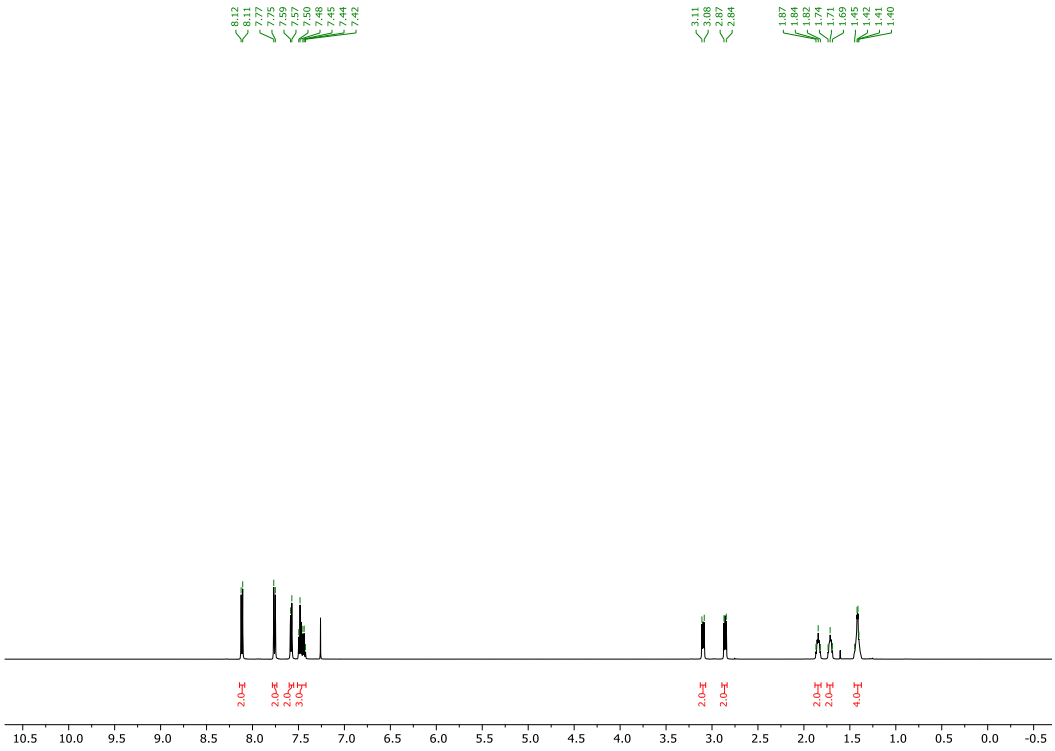
^{13}C{^{1}H}, $CDCl_3$, 126 MHz



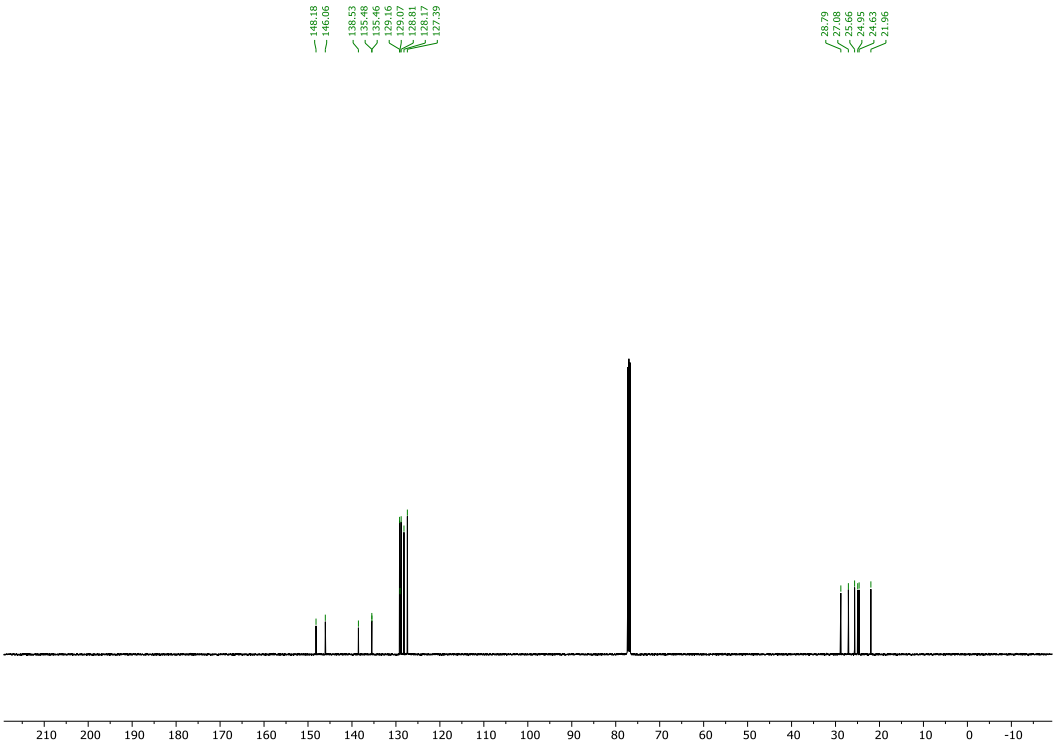


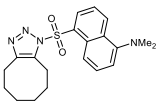
20f

^{1}H, $CDCl_3$, 500 MHz



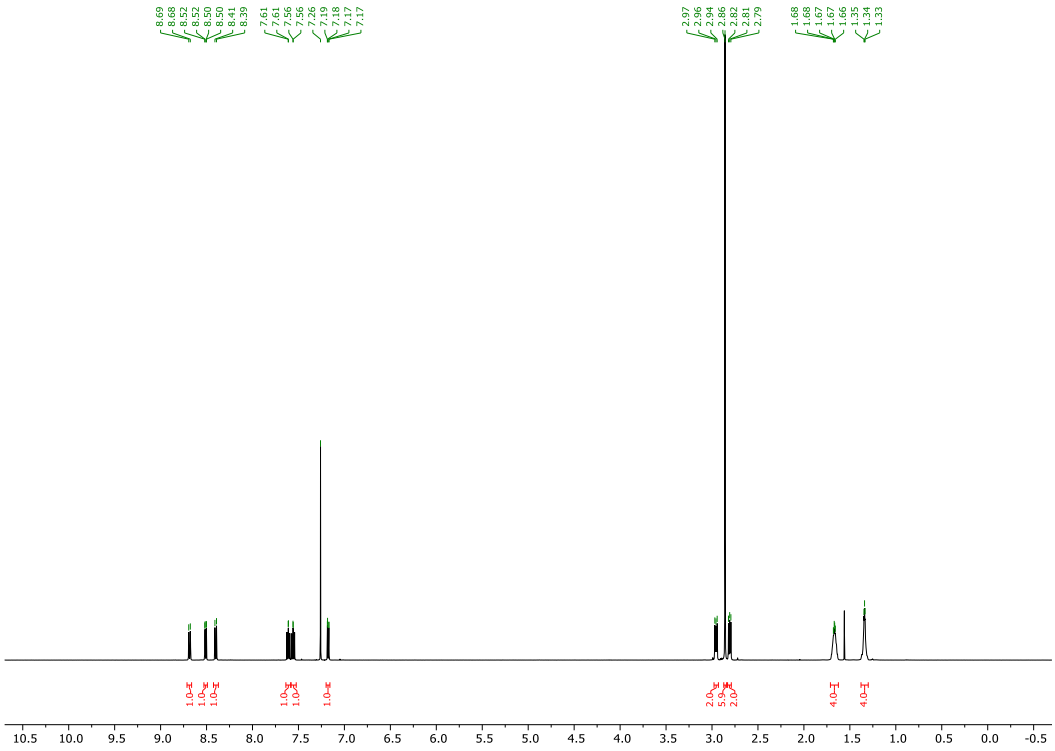
^{13}C{^{1}H}, $CDCl_3$, 126 MHz



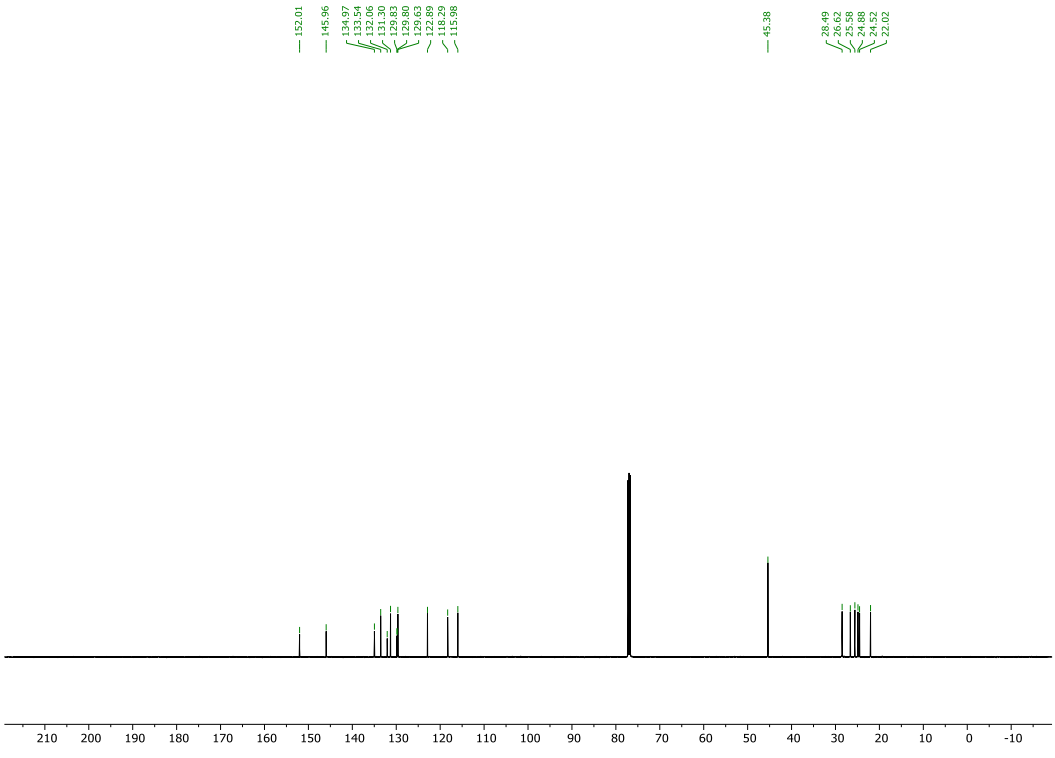


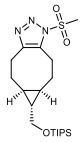
20g

^{1}H, $CDCl_3$, 500 MHz



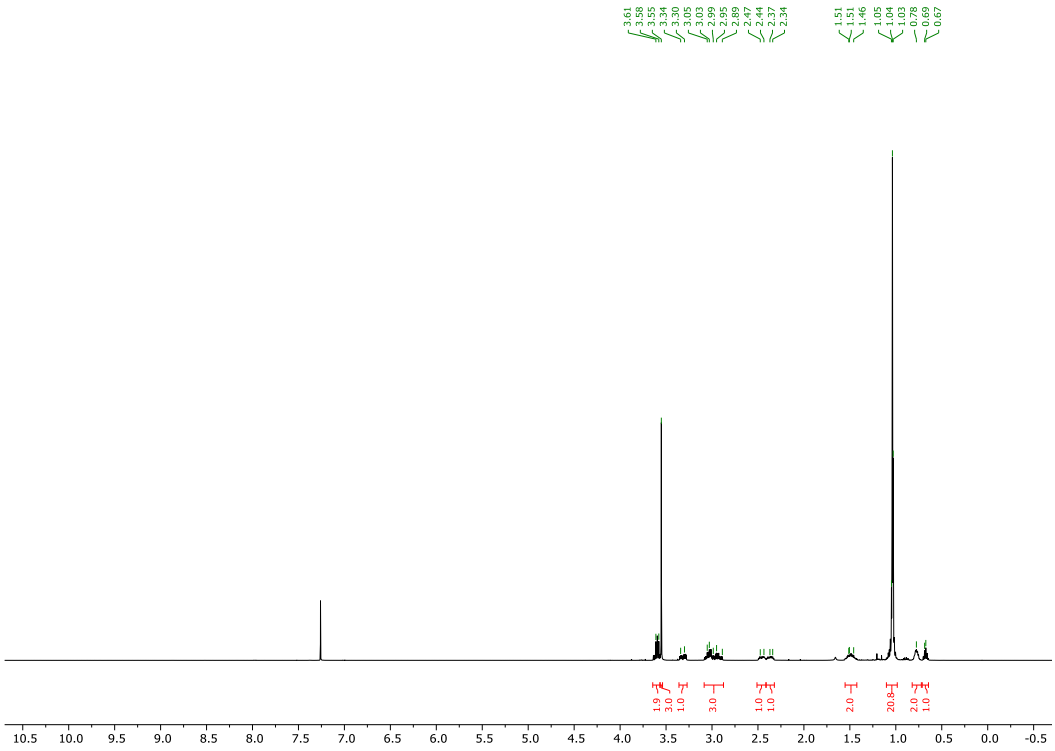
^{13}C{^{1}H}, $CDCl_3$, 126 MHz



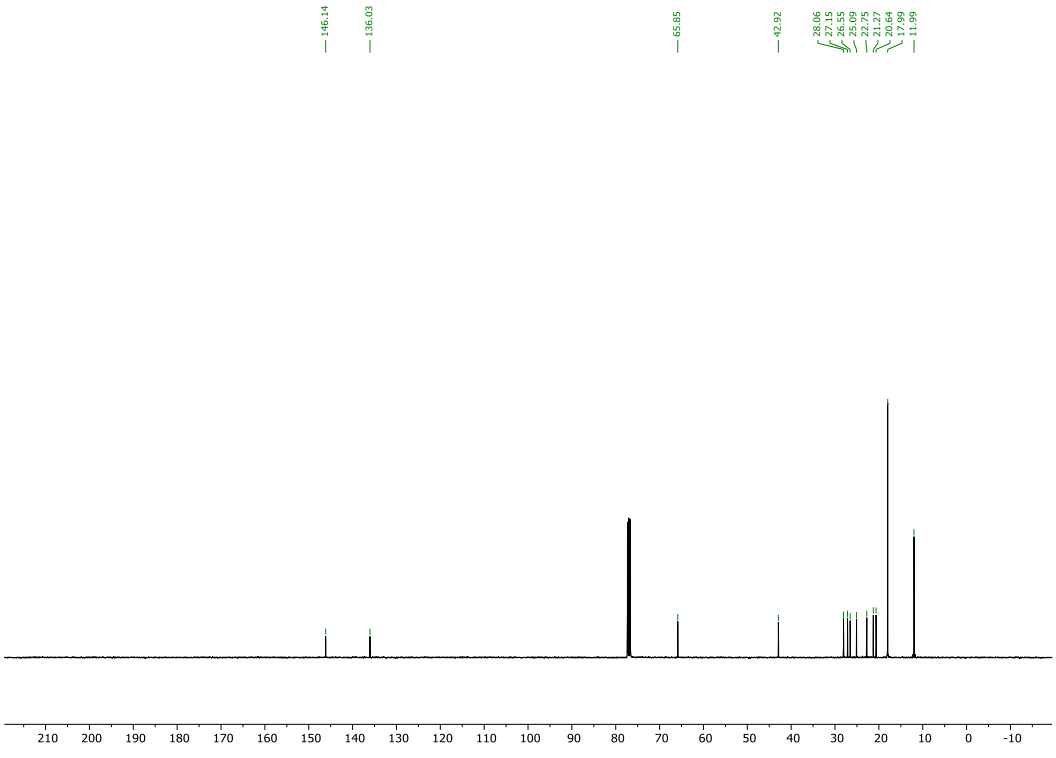


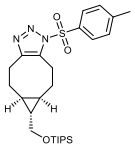
21a

^{1}H, $CDCl_3$, 400 MHz



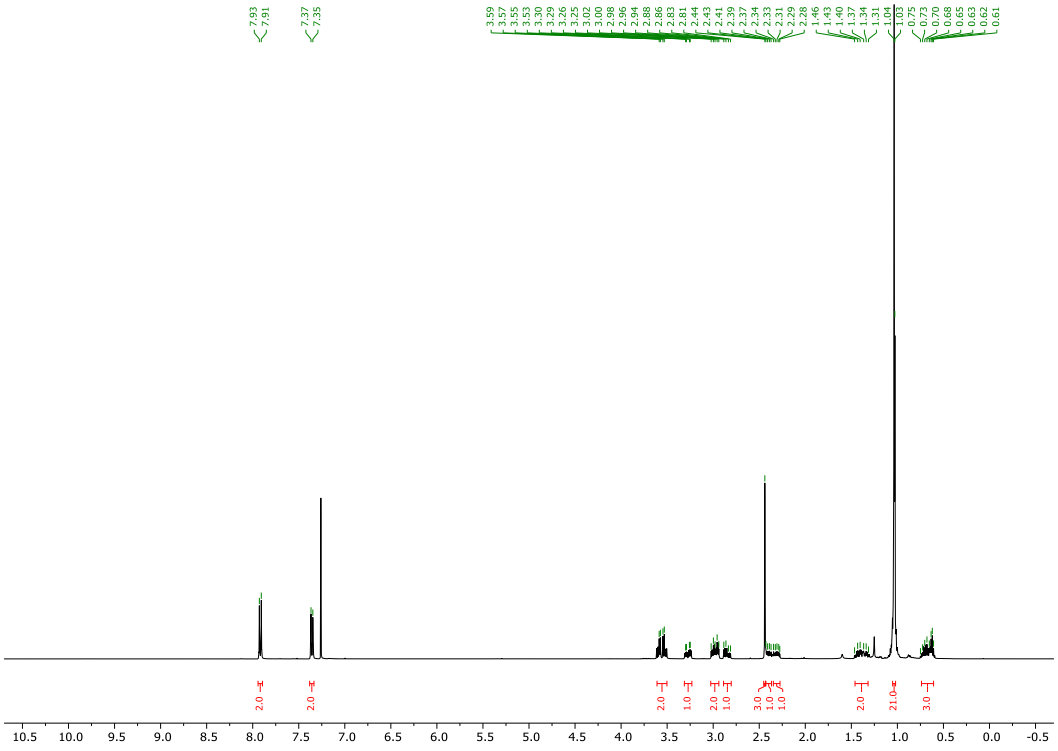
^{13}C{^{1}H}, $CDCl_3$, 101 MHz



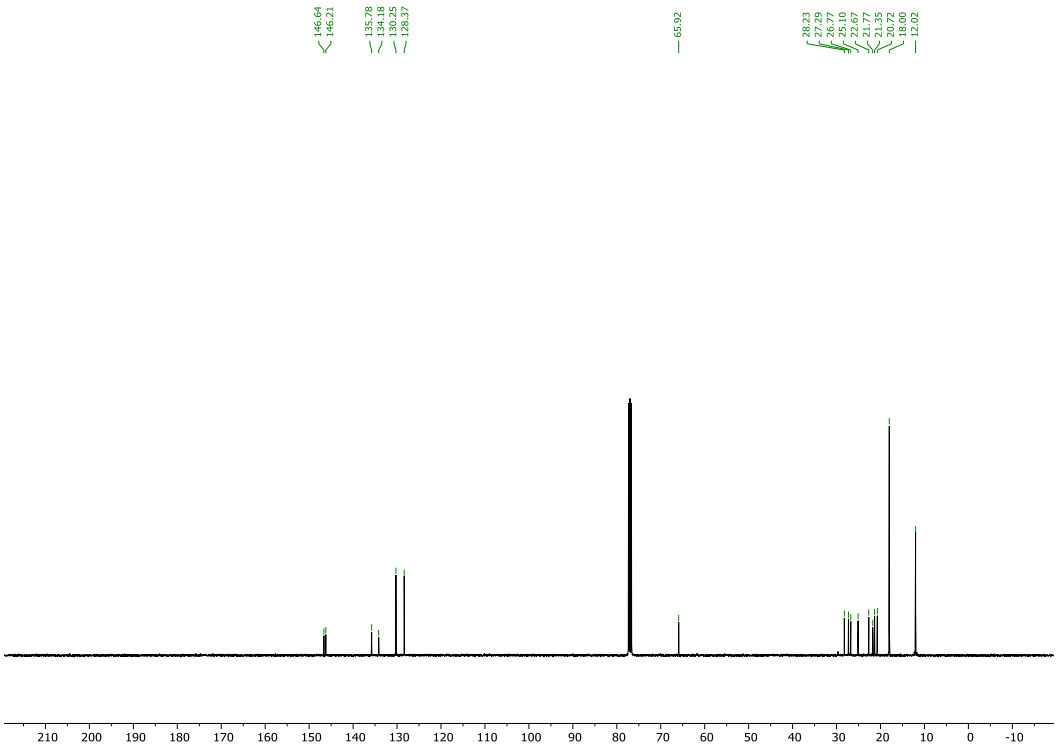


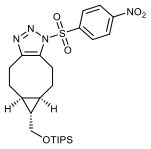
21b

^{1}H, $CDCl_3$, 400 MHz



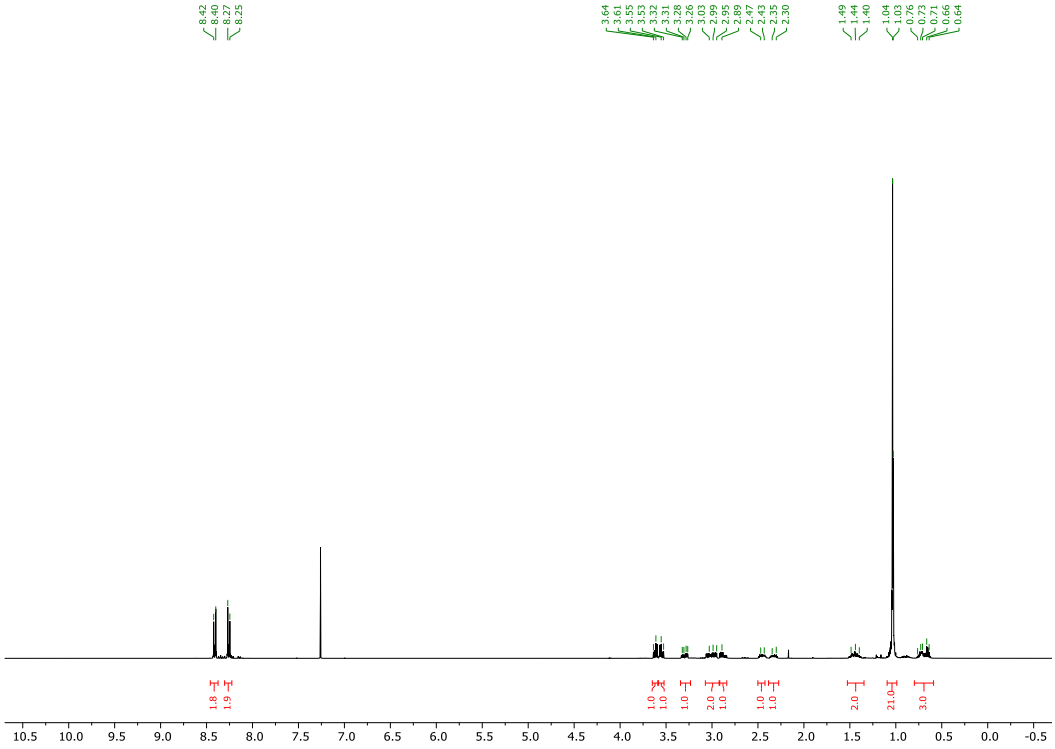
^{13}C{^{1}H}, $CDCl_3$, 101 MHz



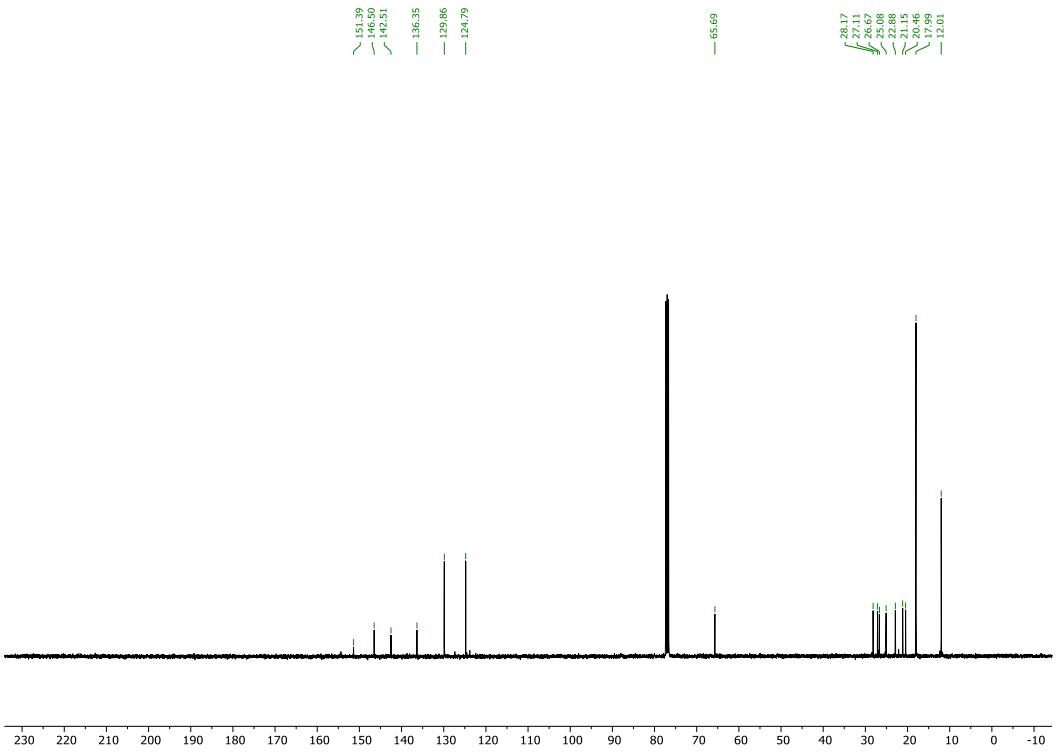


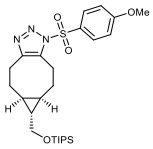
21c

^{1}H, $CDCl_3$, 400 MHz



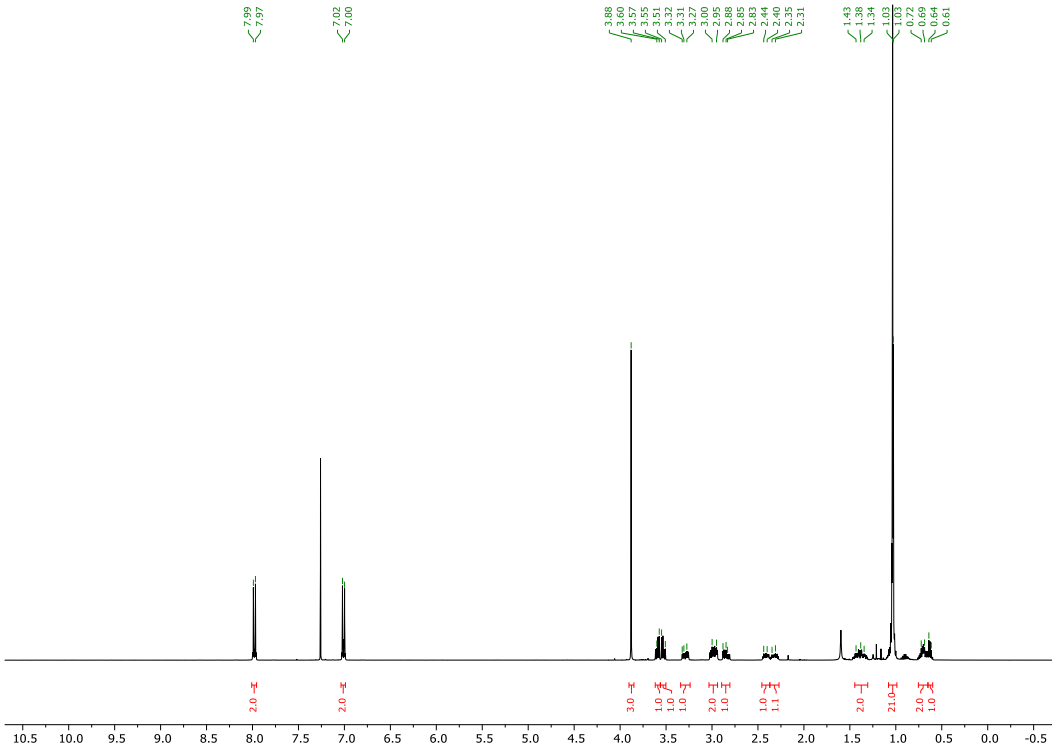
^{13}C{^{1}H}, $CDCl_3$, 101 MHz



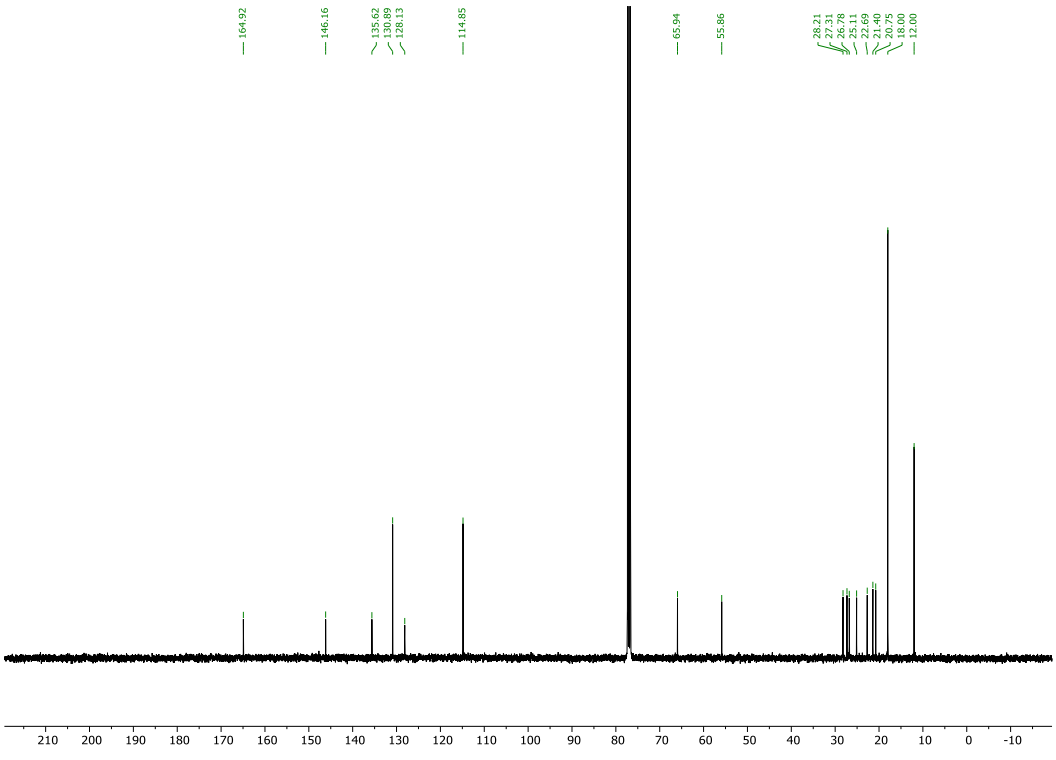


21d

^{1}H, $CDCl_3$, 400 MHz

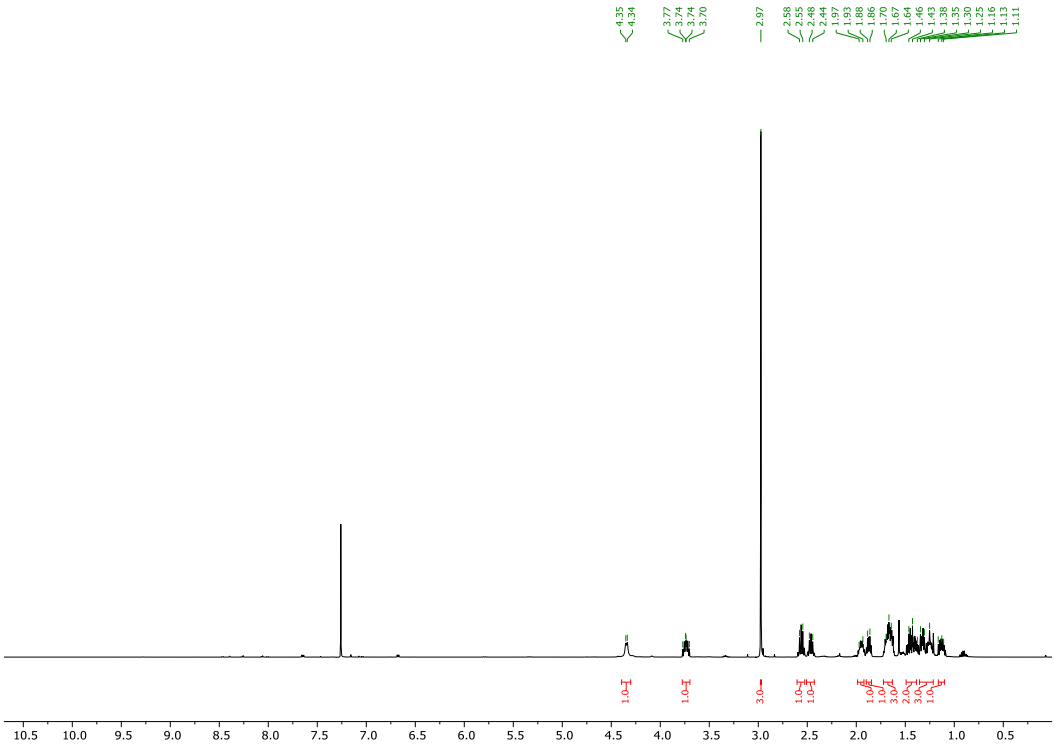


^{13}C{^{1}H}, $CDCl_3$, 101 MHz

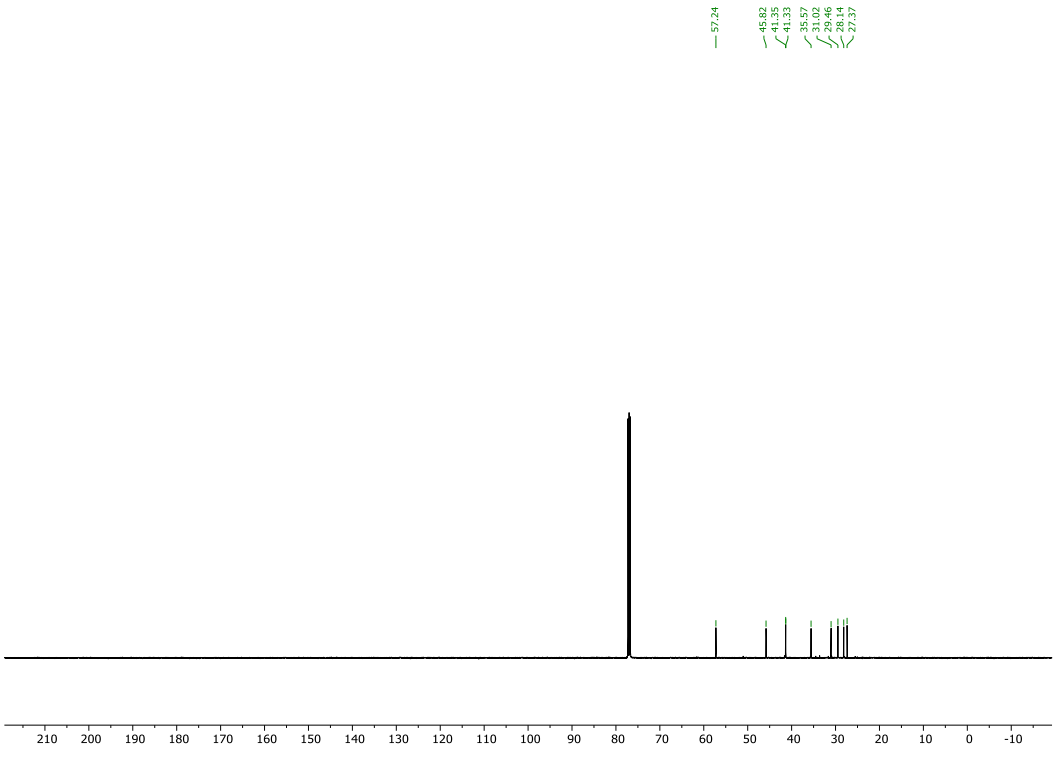


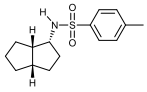
22a

^{1}H, $CDCl_3$, 500 MHz



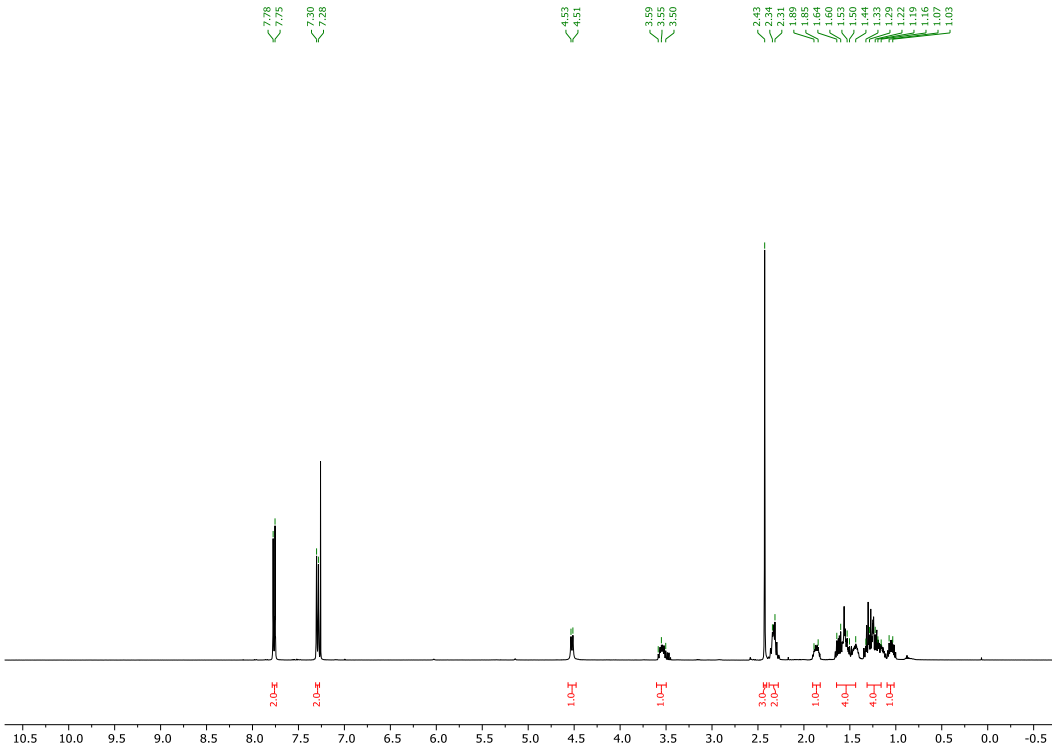
^{13}C{^{1}H}, $CDCl_3$, 126 MHz



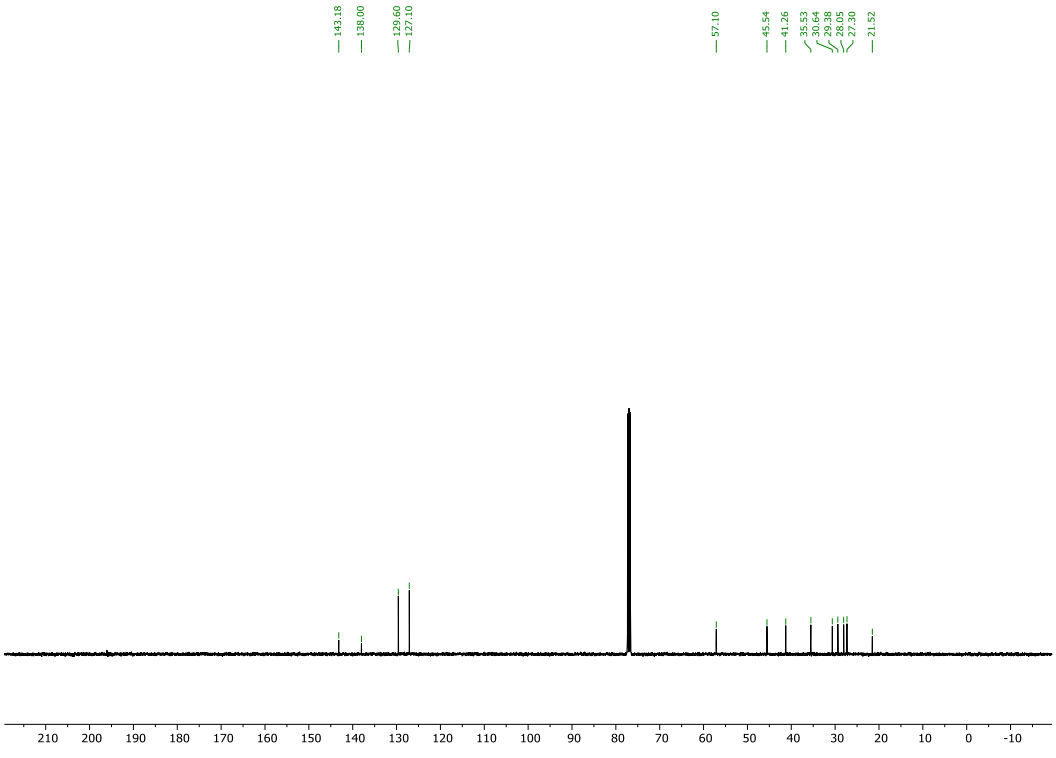


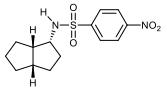
22b

^{1}H, $CDCl_3$, 400 MHz



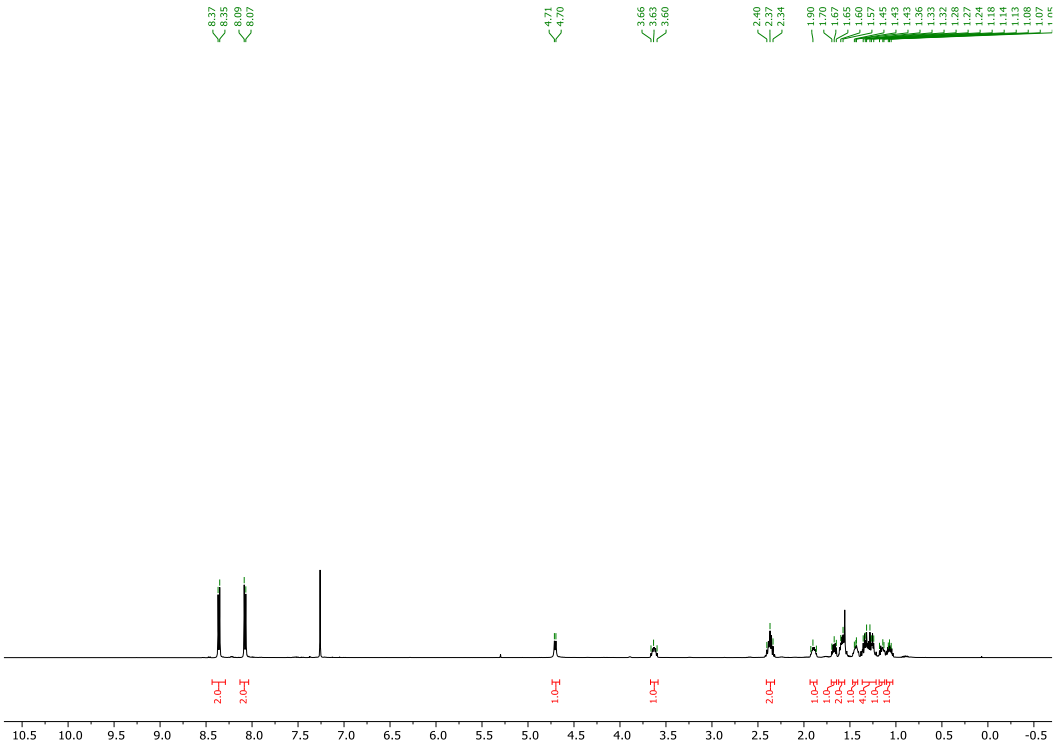
^{13}C{^{1}H}, $CDCl_3$, 101 MHz



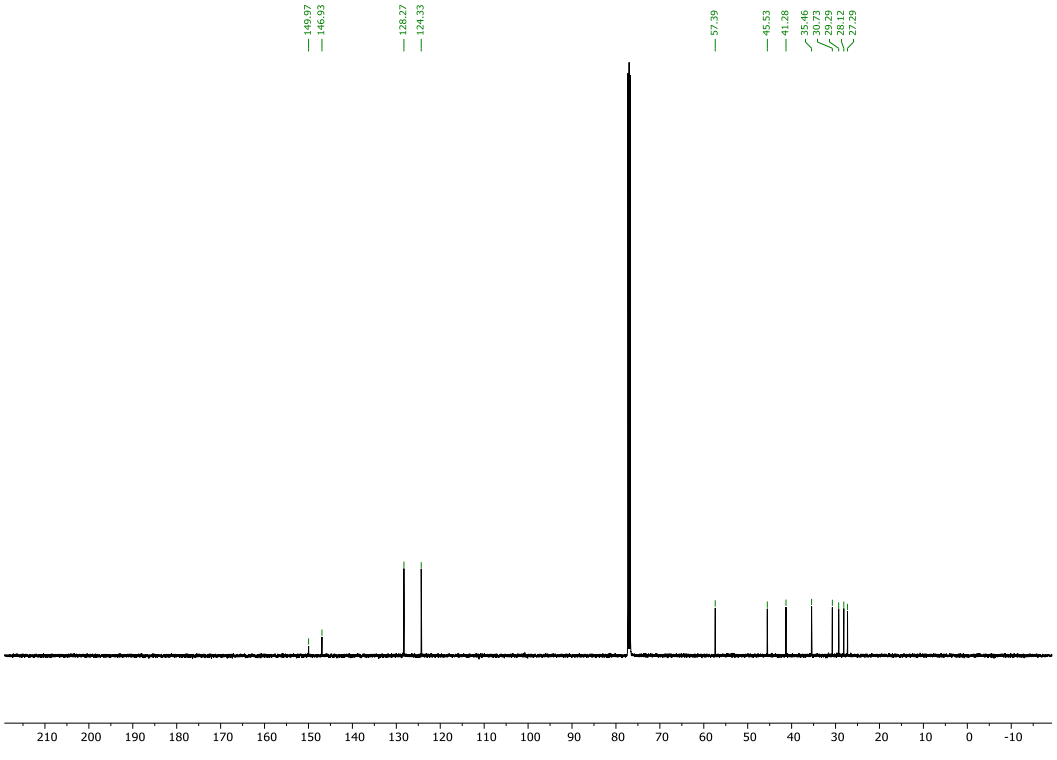


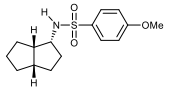
22c

^{1}H, $CDCl_3$, 500 MHz



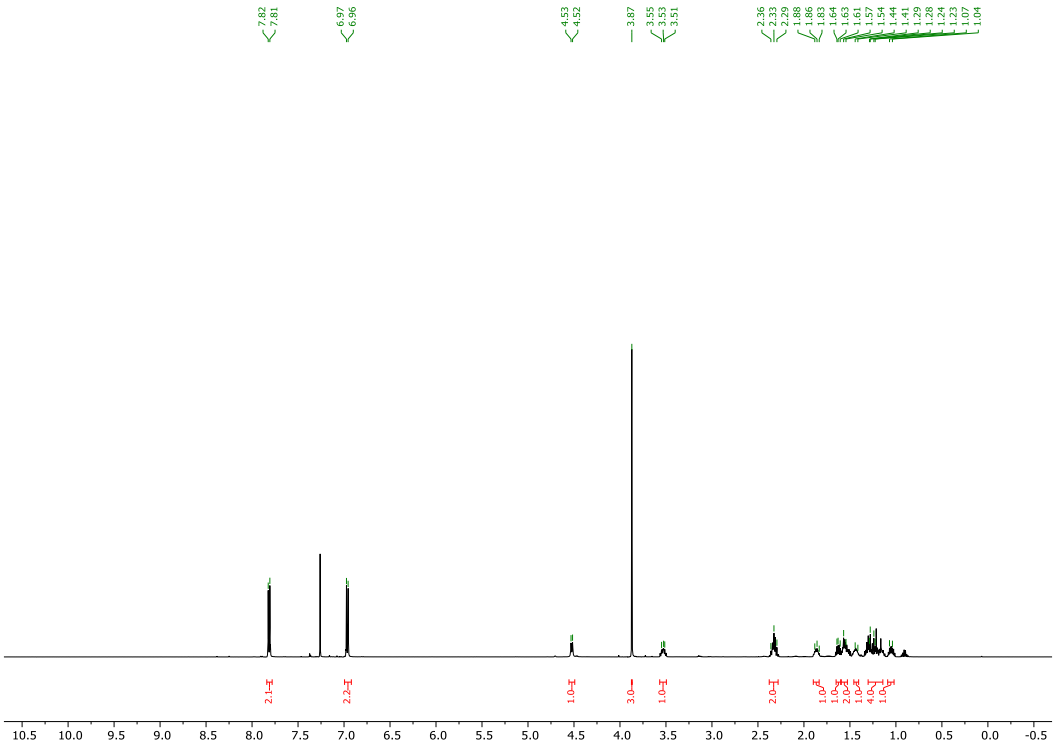
^{13}C{^{1}H}, $CDCl_3$, 126 MHz



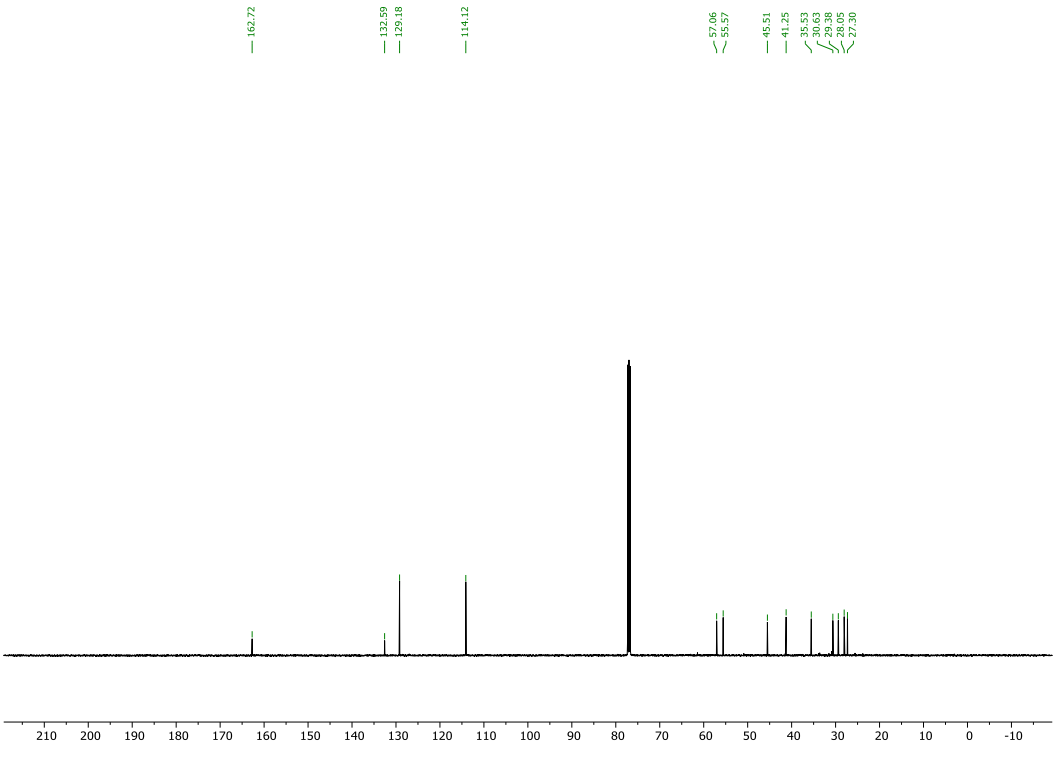


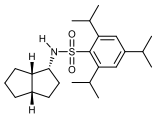
22d

^{1}H, $CDCl_3$, 500 MHz



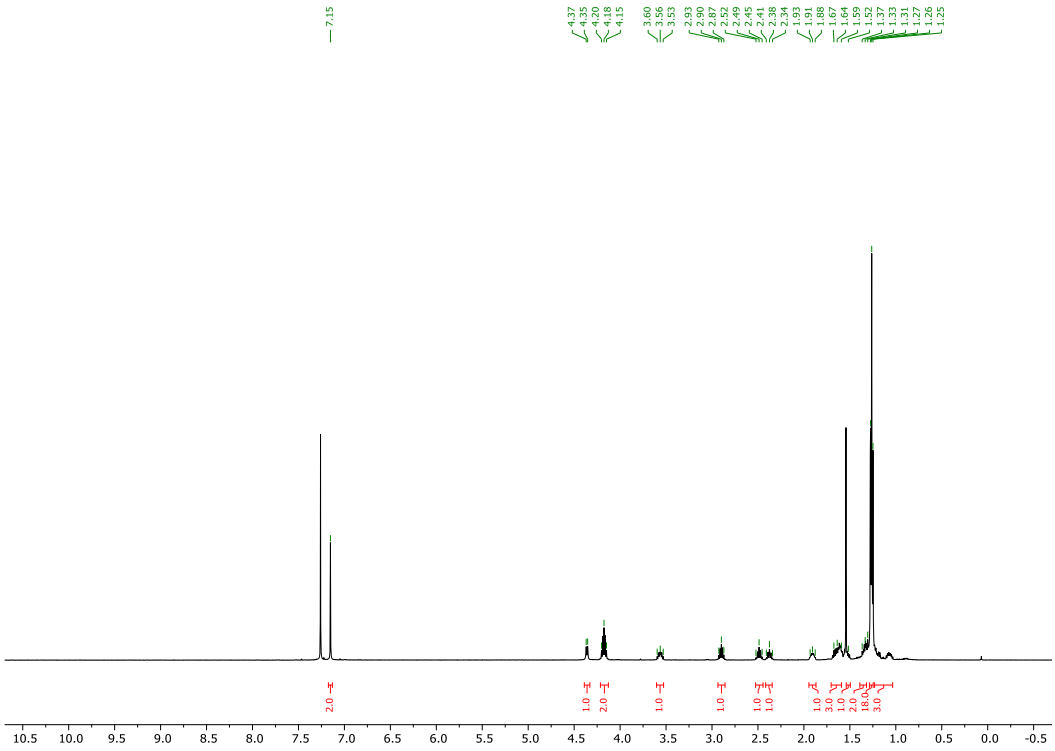
^{13}C{^{1}H}, $CDCl_3$, 126 MHz



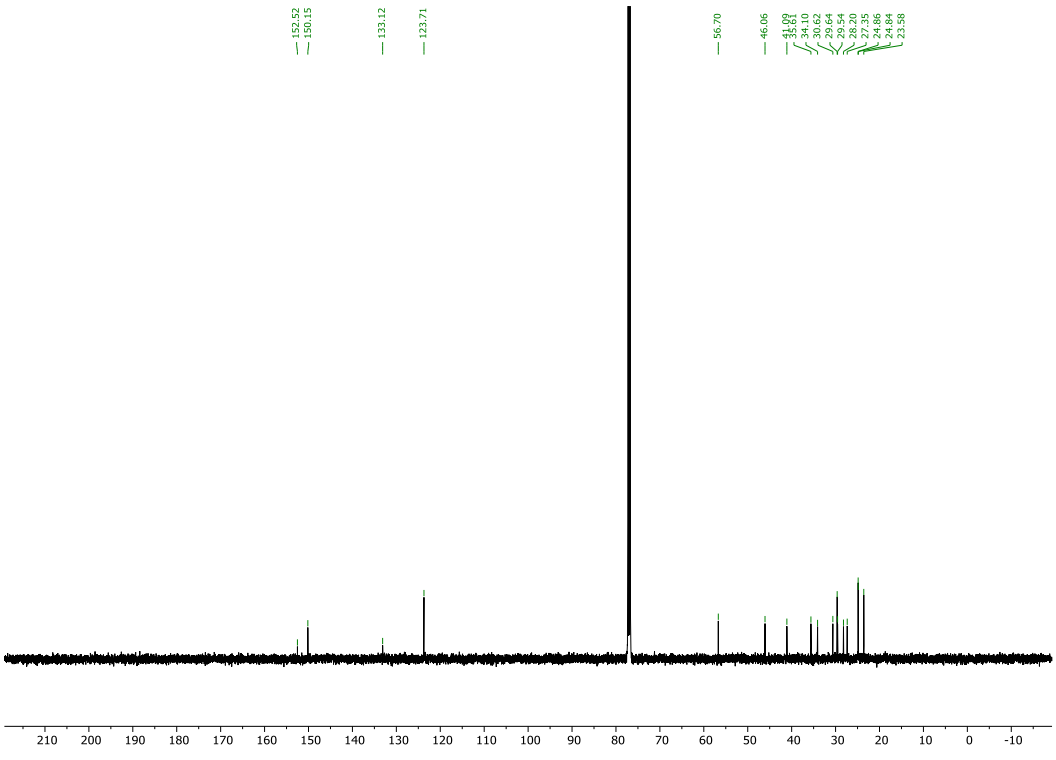


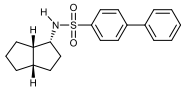
22e

^{1}H, $CDCl_3$, 500 MHz



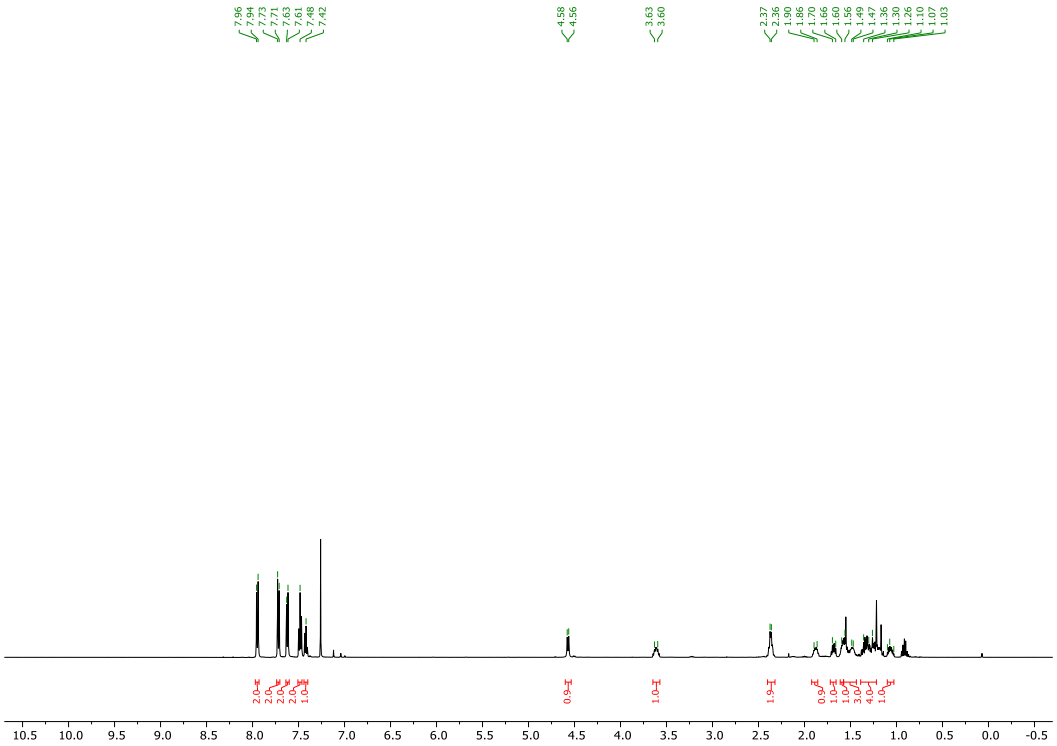
^{13}C{^{1}H}, $CDCl_3$, 126 MHz



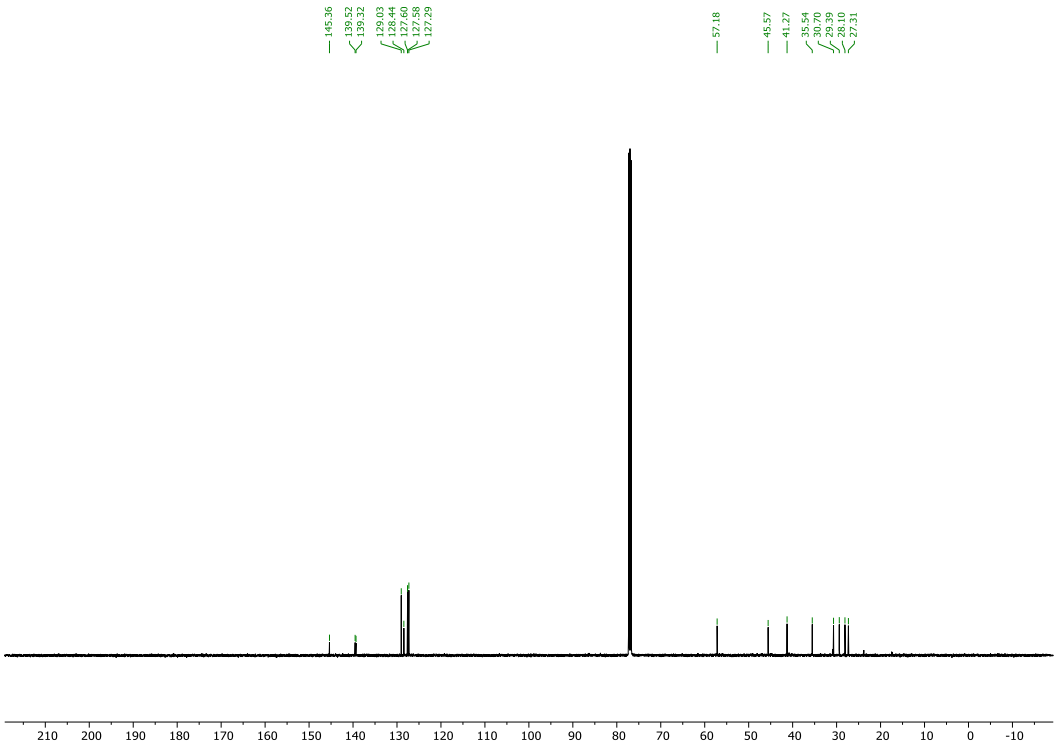


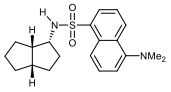
22f

^{1}H, $CDCl_3$, 500 MHz



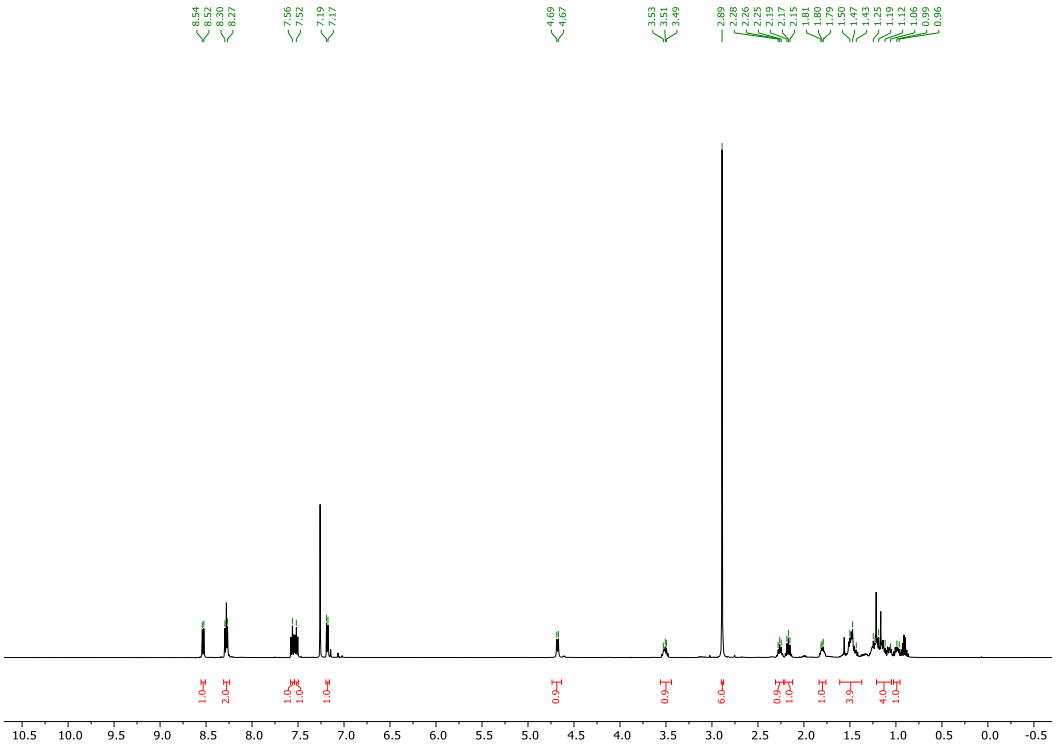
^{13}C{^{1}H}, $CDCl_3$, 126 MHz



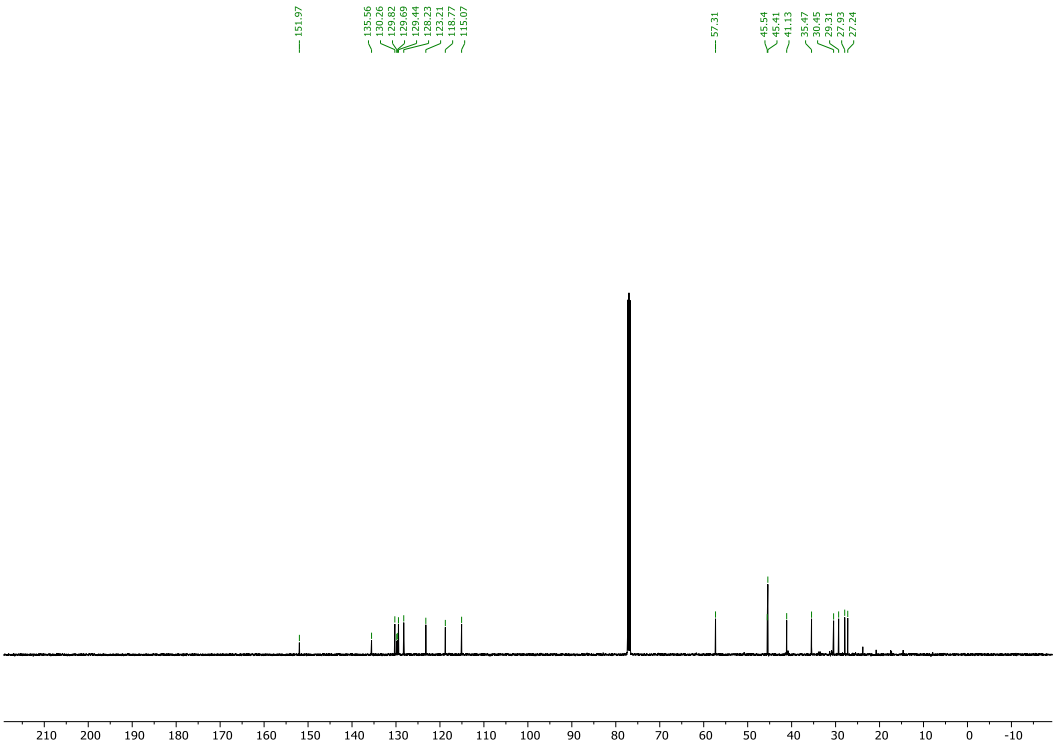


22g

^{1}H, $CDCl_3$, 500 MHz

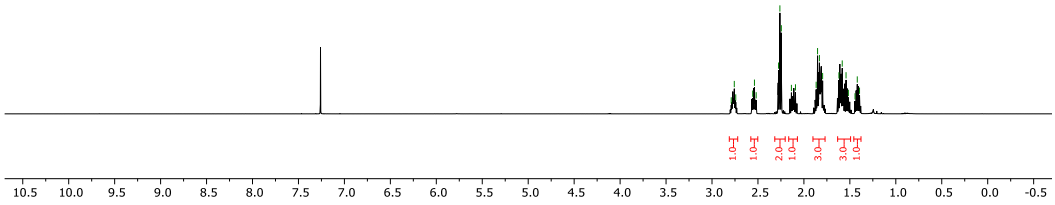


^{13}C{^{1}H}, $CDCl_3$, 126 MHz

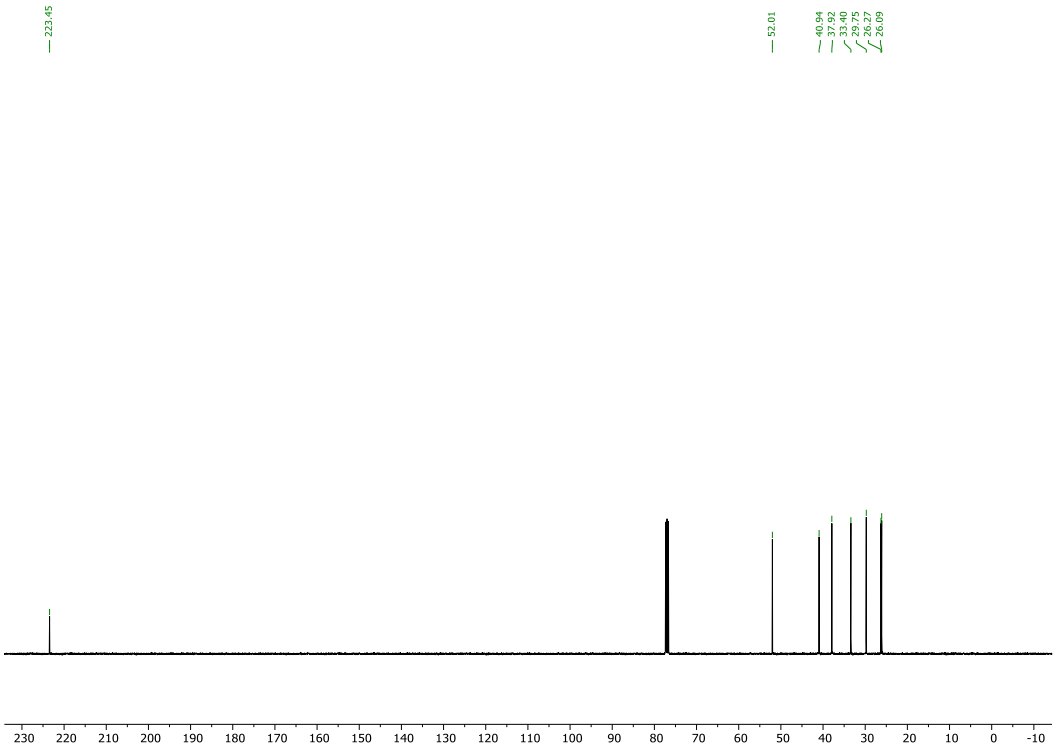


23

^{1}H, $CDCl_3$, 500 MHz

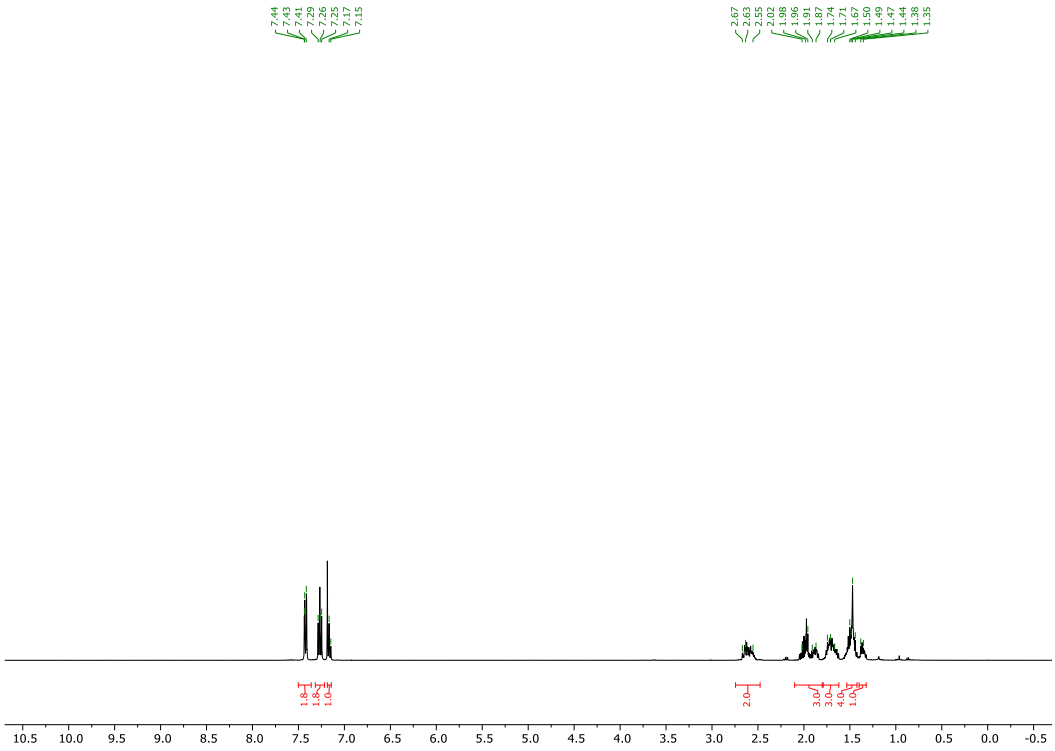


^{13}C{^{1}H}, $CDCl_3$, 101 MHz

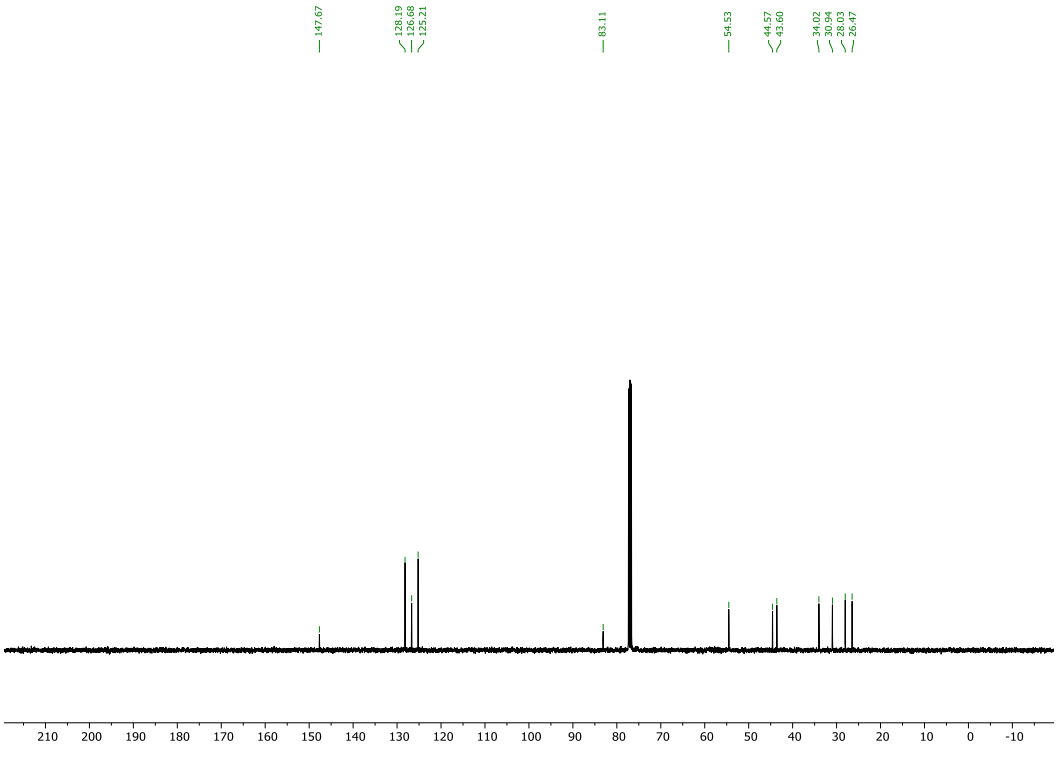


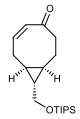
24

^{1}H, $CDCl_3$, 400 MHz



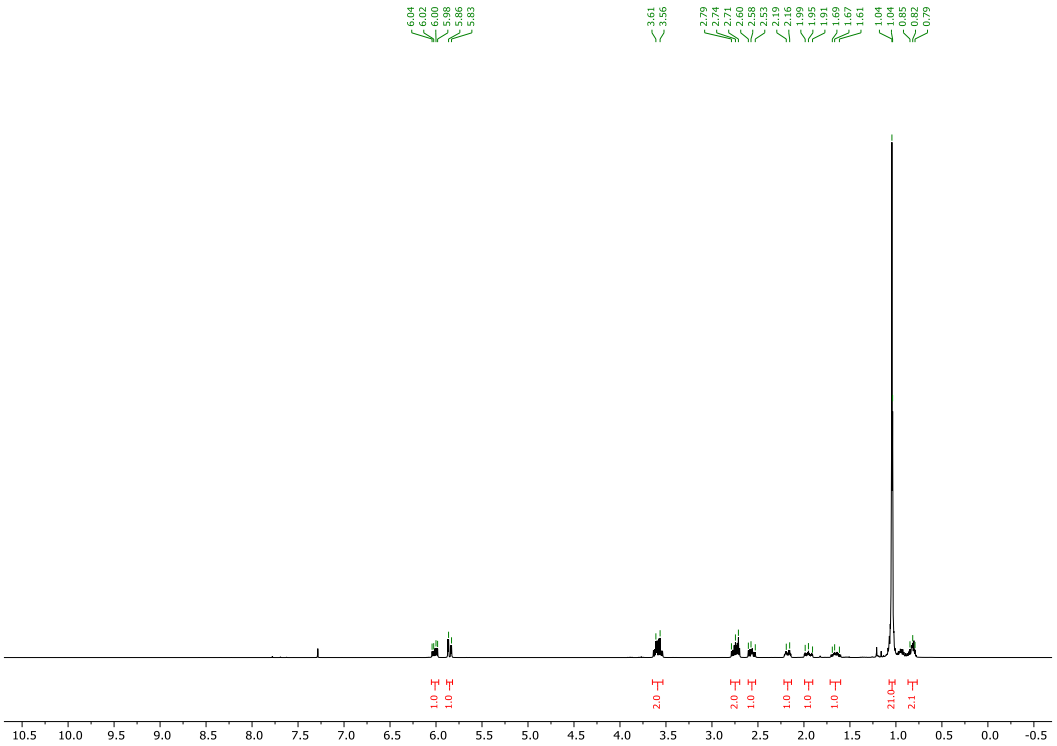
^{13}C{^{1}H}, $CDCl_3$, 101 MHz



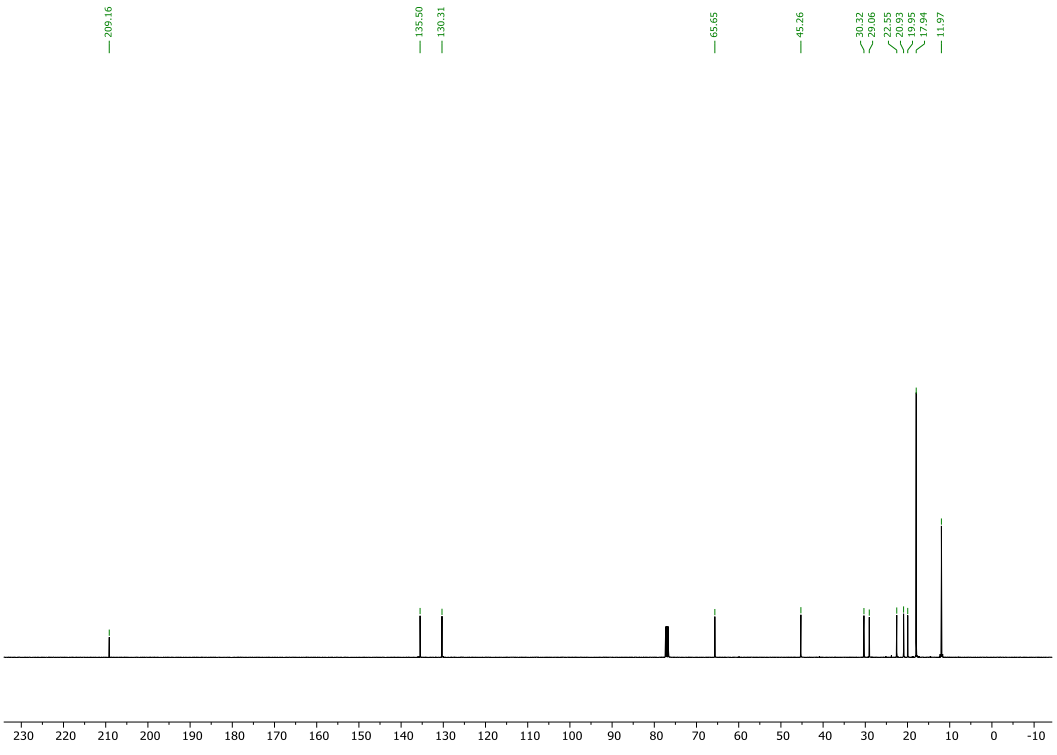


25

^{1}H, $CDCl_3$, 400 MHz



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



Optimised Structures and Thermochemical Analyses

Calculations were performed on the PSI4 program.[6]

Geometry optimisation and thermochemistry analysis was performed using B3LYP/6-31G(d).

Molecular orbitals were calculated using HF/6-311++G(2d,p) at B3LYP/6-31G(d) geometry.

Ground state structures were optimised and found to have zero imaginary frequencies by vibrational analysis:

- **GS1**: Methanesulfonyl azide
- **GS2**: Cyclooctyne in a chair conformation
- **GS3**: Bicyclononyne
- **GS4**: Acetylene

Geometries were inspired by previous work by the groups of Zeng[7] and Houk.[8]

Transition structures were optimised and found to have exactly one imaginary frequency by vibrational analysis:

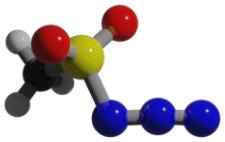
- **TS1**: MsN_3 + Cyclooctyne
- **TS2**: MsN_3 + BCN
- **TS3**: MsN_3 + Acetylene

Geometries were inspired by previous work by groups of Houk[8] and Bickelhaupt *et al*.[9]

Distortion interaction analysis was performed following the work in this area by Houk *et al*.[8]

Cycloaddition between MsN_3 and cyclooctyne in its twist boat geometry was found to be a less favourable pathway than ring flip[10] to the cyclooctyne chair conformation and then cycloaddition so was not considered.

GS1



B3LYP/6-31G(D) optimised cartesian coordinates in Å

C	-1.608519319467	1.457500593759	-0.063963233043
H	-2.591326236454	1.284233387220	0.380714572510
H	-1.703330072376	1.703787214968	-1.122526158519
H	-1.066467955548	2.232920246299	0.478506732644
N	0.730021096991	0.400535623236	-0.835722057356
N	1.790949197114	0.048652886187	-0.287660921488
N	2.807257072661	-0.226759045565	0.137837070379
O	-1.393245800251	-1.114220638337	-0.699273589930
O	-0.315596877748	-0.322374532977	1.469000339776
S	-0.706036913645	-0.090337630567	0.078877676271

N1-N2 distance : 1.245 Å
N2-N3 distance : 1.136 Å
Azide N-N-N angle : 174.96°

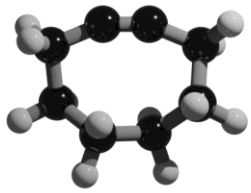
B3LYP/6-31G(D) frequency analysis

Number of imaginary frequencies: 0

E0 : -752.66557042 Ha
ZPE: -752.60487666 Ha
H : -752.59652407 Ha
S : 0.13770244 mHa/K
G : -752.63758005 Ha
evaluated at 298.15 K

HOMO-1	HOMO	LUMO	LUMO+1		
-12.434656	-11.815705	0.902765	1.685338	eV	HF/6-311++G(2D,P)

GS2



B3LYP/6-31G(D) optimised cartesian coordinates in Å

C	-1.950674577258	-0.872434863451	-0.132659300671
C	-1.854882674202	0.620417969012	0.290791614893
C	-0.698207387431	1.429617578033	-0.353182137875
C	-0.604210769791	-1.431719108537	-0.035598782290
C	0.604281019996	-1.431678020515	0.035652352377
C	0.698135403896	1.429670144360	0.353127403667
C	1.854853651130	0.620505769309	-0.290812981004
C	1.950717841297	-0.872327732409	0.132691459716
H	-2.810441636177	1.102275105372	0.042928450235
H	-2.681695085584	-1.395968343418	0.496870195418
H	-2.319706995271	-0.946365782036	-1.165443627177
H	-1.758620098866	0.666886709905	1.383247961761
H	-1.037120632674	2.472810040819	-0.389173207832
H	-0.580908227713	1.124072540978	-1.401817423593
H	0.580853087312	1.124162616689	1.401775545124
H	1.036992982379	2.472882213043	0.389074632411
H	1.758592832225	0.666931041743	-1.383271340529
H	2.319755234564	-0.946203531625	1.165477957667
H	2.681762036372	-1.395848927384	-0.496820741601
H	2.810387577134	1.102419277917	-0.042963050523

Alkyne C-C distance : 1.211 Å
Alkyne bond angles : 157.48°, 157.48°

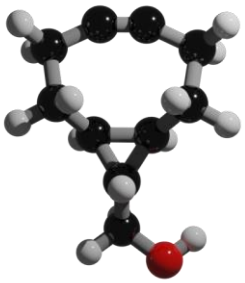
B3LYP/6-31G(D) frequency analysis

Number of imaginary frequencies: 0

E0 : -312.00018962 Ha
ZPE: -311.81936907 Ha
H : -311.81059064 Ha
S : 0.13622001 mHa/K
G : -311.85120464 Ha
evaluated at 298.15 K

HOMO-1	HOMO	LUMO	LUMO+1		
-9.745517	-9.619991	1.166634	1.320705	eV	HF/6-311++G(2D,P)

GS3



B3LYP/6-31G(D) optimised cartesian coordinates in Å

C	-1.535097805949	0.216503152613	0.780603654246
C	-1.495090093543	1.592247350513	1.512416110485
C	-0.583177128793	2.434719011952	0.735956935942
C	-0.169263588230	-0.441440948246	0.623624893310
C	0.109186941333	-1.468694381617	-0.458871679429
C	0.244048846417	2.653339920087	-0.121852450203
C	0.767282996305	0.828386259312	-1.611291291532
C	0.785648802185	-2.780881364275	-0.134939498689
C	0.872157587237	-0.163406806813	-0.458921400949
C	1.140428599355	2.290573658533	-1.221560587898
H	-2.508430457570	2.008394816913	1.578569841869
H	-2.195452973410	-0.464822382033	1.337290223612
H	-1.998249942838	0.367435601721	-0.201268965622
H	-1.140115995246	1.466284535412	2.544651523560
H	-0.667538343066	-1.554610854643	-1.219833441177
H	-0.586794161487	-3.376231200620	1.101739405570
H	-0.251051046393	0.834619363749	-2.016709540497
H	0.291822242378	-0.667666194936	1.588307389820
H	1.033395614403	2.947897589999	-2.093820310176
H	1.236828759874	-3.216391703341	-1.033506361872
H	1.428297890856	0.493937387495	-2.423986640385
H	1.601612453019	-2.605739035855	0.587565164217
H	1.892651806174	-0.241947999357	-0.078830560910
H	2.193451540313	2.347571154581	-0.913147757673
O	-0.122946256015	-3.767565082668	0.344530139492

Alkyne C-C distance : 1.212 Å
Alkyne bond angles : 154.75°, 154.81°

B3LYP/6-31G(D) frequency analysis

Number of imaginary frequencies: 0

E0 : -464.59664904 Ha
ZPE: -464.37720029 Ha
H : -464.36559127 Ha
S : 0.15892050 mHa/K
G : -464.41297342 Ha
evaluated at 298.15 K

HOMO-1	HOMO	LUMO	LUMO+1		
-9.829246	-9.688074	1.037652	1.160974	eV	HF/6-311++G(2D,P)

GS4

B3LYP/6-31G(D) optimised cartesian coordinates in Å

C	-0.000000010212	0.000000044425	-0.602484980775
C	-0.000000010212	0.000000044425	0.602484961555
H	-0.000009075862	0.000000896472	-1.669106428570
H	0.000009319050	-0.000001954388	1.669106657424

Alkyne C-C distance : 1.205 Å
Alkyne bond angles : 180.00°, 180.00°

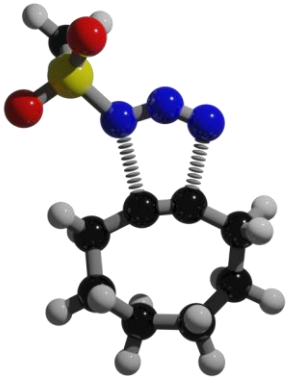
B3LYP/6-31G(D) frequency analysis

Number of imaginary frequencies: 0

E0 : -77.32563186 Ha
ZPE: -77.30021899 Ha
H : -77.29654192 Ha
S : 0.07809315 mHa/K
G : -77.31982539 Ha
evaluated at 298.15 K

HOMO-1	HOMO	LUMO	LUMO+1		
-11.168183	-11.168183	1.141436	1.277385	eV	HF/6-311++G(2D,P)

TS1



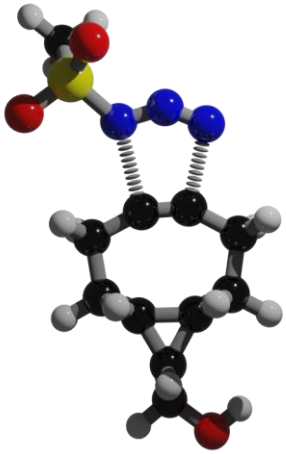
B3LYP/6-31G(D) optimised cartesian coordinates in Å

C	-3.148356606691	2.579235149662	-0.629254936799
C	-3.027257989458	1.046133973733	-0.481679825435
C	-2.489050159376	3.431648407520	0.483020338988
C	-1.612112977838	0.657849554129	-0.330011101966
C	-1.001734129975	3.866989184529	0.309246065630
C	-0.456104384370	0.974430838826	-0.040441426088
C	0.090117519094	3.083299470390	1.076267803709
C	0.659987310033	1.826462452254	0.370388697199
C	2.676426564695	-2.785659093179	-1.312864560995
H	-4.220091931329	2.816298001876	-0.665577489478
H	-3.588451562976	0.706613721437	0.400176913716
H	-3.486082475129	0.548420341769	-1.344059877114
H	-3.079243116013	4.353741915128	0.553211334665
H	-2.736038842590	2.874177337299	-1.603212644586
H	-2.615515008982	2.931194267156	1.453487257949
H	-0.934373145855	4.905502230570	0.656457264528
H	-0.749004009673	3.900597074728	-0.760118784000
H	-0.300024319340	2.788748259424	2.058998297846
H	0.938486660294	3.752844146722	1.269023735382
H	1.242813376475	2.123138717616	-0.512461867438
H	1.350608128839	1.297673465552	1.035015464400
H	1.958406934123	-3.439511933723	-1.811274383124
H	2.957848476371	-1.946364012920	-1.950348244872
H	3.560306365280	-3.352539616321	-1.010371192347
N	-1.597783731448	-1.491540562685	-0.772255161078
N	-0.475011006244	-1.752813705039	-0.628079762228
N	0.635833790780	-1.164113703577	-0.412163200442
O	1.413984488191	-3.262291132365	0.975516552379
O	2.833894298629	-1.148992777790	0.777690933893
S	1.928267026432	-2.137016393881	0.195501909826

N1-N2 distance	:	1.276 Å
N2-N3 distance	:	1.162 Å
Alkyne C-C distance	:	1.233 Å
N1-C distance	:	2.430 Å
N3-C distance	:	2.194 Å
Azide N-N-N angle	:	139.36°
Alkyne bond angles	:	158.54°, 148.86°

```
B3LYP/6-31G(D) frequency analysis

  Number of imaginary frequencies: 1

   E0 :   -1064.65235543 Ha
   ZPE:   -1064.41014712 Ha
   H  :   -1064.39312311 Ha
   S  :       0.21064736 mHa/K
   G  :   -1064.45592762 Ha
  evaluated at 298.15 K

  Difference from GS1 and GS2 ground states
  ΔE0 :       0.01340461 Ha          8.411 kcal/mol
  ΔH  :       0.01399160 Ha          8.780 kcal/mol
  ΔS  :      -0.06327509 mHa/K      -39.705 cal/mol/K
  ΔG  :       0.03285707 Ha         20.618 kcal/mol
  evaluated at 298.15 K

Azide at transition state geometry

   E0 :    -752.63732419 Ha   B3LYP/6-31G(D)
   E0 :    -749.98581599 Ha   HF/6-311++G(2D,P)

  ΔEdist from GS1 ground state   17.72458 kcal/mol    B3LYP/6-31G(D)

      HOMO-1         HOMO         LUMO       LUMO+1
  -12.326763   -12.053560     0.085689     0.906194  eV   HF/6-311++G(2D,P)

Alkyne at transition state geometry

   E0 :    -311.99750562 Ha   B3LYP/6-31G(D)
   E0 :    -309.84573460 Ha   HF/6-311++G(2D,P)

  ΔEdist from GS2 ground state    1.68432 kcal/mol    B3LYP/6-31G(D)

      HOMO-1         HOMO         LUMO       LUMO+1
   -9.627120    -9.532969     1.156756     1.320542  eV   HF/6-311++G(2D,P)

HF/6-311++G(2D,P) Ground State HOMO - LUMO gaps (at distorted geometry)
  HOMO Alkyne GS2 - LUMO Azide GS1 :   10.523 eV  (   9.619 eV)
  HOMO Azide GS1 - LUMO Alkyne GS2 :   12.982 eV  (  13.210 eV)

B3LYP/6-31G(D) distortion-interaction analysis
  ΣΔEdist:                  19.40890 kcal/mol
  Eint = ΣΔE0 - ΣΔEdist:   -10.99737 kcal/mol
```

TS2



B3LYP/6-31G(D) optimised cartesian coordinates in Å

C	-2.022111563594	-2.228277861997	1.049130742828
C	-1.863024780567	-0.831017202717	1.702547399656
C	-0.888715754848	-0.044649410523	0.920549895337
C	-0.729858535861	-3.028789117841	0.975109882452
C	-0.548308879960	-4.162192829496	-0.017848473608
C	-0.047813329422	-0.025935040922	0.020202148841
C	0.018251375085	-5.494268991846	0.417814424645
C	0.270916674810	-2.016368222835	-1.337058971375
C	0.323857708171	-2.933122371726	-0.123538420297
C	0.782926283316	-0.576353711387	-1.054069694270
C	2.309181097022	4.461929033121	-0.161109890160
H	-2.834210168754	-0.323899505614	1.748397590242
H	-2.762637747934	-2.801209320932	1.625769053271
H	-2.446362162882	-2.096667663941	0.046835060133
H	-1.520135497527	-0.931254426770	2.741462610835
H	-1.389401031039	-5.873394989862	1.700454769105
H	-1.333532581728	-4.246437551285	-0.769959117561
H	-0.752163591247	-1.952605016436	-1.725336548514
H	-0.296280414780	-3.214107534550	1.960820222318
H	0.428639919463	-6.038461120230	-0.439977352555
H	0.731312578252	0.037098107593	-1.959809669835
H	0.848595471205	-5.327560801211	1.125795029127
H	0.882514510313	-2.451504551281	-2.139471111355
H	1.340176527489	-3.065954784983	0.251849783126
H	1.838237383231	-0.598143932850	-0.752046370862
H	1.900548499608	4.918040850202	0.742426510414
H	2.672043653627	5.232679328916	-0.845512232073
H	3.104054900337	3.753611999897	0.076410261754
N	-1.064671444746	2.064228680929	1.663523682143
N	-0.299392369364	2.584669593412	0.966069336147
N	0.596342690262	2.318612671573	0.100836437261
O	-0.967096032873	-6.358644108786	0.973967617369
O	-0.140032167486	4.491087457093	-1.192869344461
O	1.570693274951	2.849880538736	-2.143154323102
S	0.990162593876	3.579531286392	-1.018666878886

N1-N2 distance	:	1.273 Å
N2-N3 distance	:	1.159 Å
Alkyne C-C distance	:	1.232 Å
N1-C distance	:	2.433 Å
N3-C distance	:	2.243 Å
Azide N-N-N angle	:	141.22°
Alkyne bond angles	:	156.48°, 147.74°

B3LYP/6-31G(D) frequency analysis

  Number of imaginary frequencies: 1

   E0 :   -1217.25087376 Ha
   ZPE: -1216.97011412 Ha
   H :   -1216.95018599 Ha
   S :   0.23423057 mHa/K
   G :   -1217.02002183 Ha
  evaluated at 298.15 K

  Difference from GS1 and GS3 ground states
  ΔE0 :   0.01134570 Ha   7.119 kcal/mol
  ΔH :   0.01192935 Ha   7.486 kcal/mol
  ΔS :   -0.06239237 mHa/K   -39.151 cal/mol/K
  ΔG :   0.03053164 Ha   19.159 kcal/mol
  evaluated at 298.15 K

Azide at transition state geometry

   E0 :   -752.64006601 Ha   B3LYP/6-31G(D)
   E0 :   -749.98880533 Ha   HF/6-311++G(2D,P)

  ΔEdist from GS1 ground state   16.00408 kcal/mol   B3LYP/6-31G(D)

      HOMO-1   HOMO   LUMO   LUMO+1
  -12.342436   -12.024988   0.217392   0.907391 eV   HF/6-311++G(2D,P)

Alkyne at transition state geometry

   E0 :   -464.59474472 Ha   B3LYP/6-31G(D)
   E0 :   -461.56849346 Ha   HF/6-311++G(2D,P)

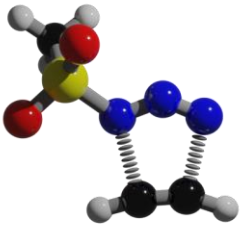
  ΔEdist from GS3 ground state   1.19496 kcal/mol   B3LYP/6-31G(D)

      HOMO-1   HOMO   LUMO   LUMO+1
   -9.728482   -9.614358   1.033489   1.151913 eV   HF/6-311++G(2D,P)

HF/6-311++G(2D,P) Ground State HOMO - LUMO gaps (at distorted geometry)
  HOMO Alkyne GS3 - LUMO Azide GS1 :   10.591 eV (9.832 eV)
  HOMO Azide GS1 - LUMO Alkyne GS3 :   12.853 eV (13.058 eV)

B3LYP/6-31G(D) distortion-interaction analysis
  ΣΔEdist: 17.19904 kcal/mol
  Eint = ΣΔE0 - ΣΔEdist: -10.07959 kcal/mol

TS3



B3LYP/6-31G(D) optimised cartesian coordinates in Å

C	-2.739635483330	0.775690313641	1.293251677467
C	-1.845072207042	1.538666465355	0.923791422009
C	1.409303265664	-0.516354327130	-2.056292985287
H	-3.652576283571	0.476594525023	1.761638671629
H	-1.179930526456	2.342842462708	0.698867336253
H	0.912993045703	0.211438887901	-2.699568394561
H	0.980392971178	-1.512717313123	-2.177247268723
H	2.483652133035	-0.537796547430	-2.255314883106
N	-2.172692392396	-1.179621990615	0.666267398821
N	-1.159427975084	-0.937588718638	0.140207201235
N	-0.516342897870	0.115053009108	-0.189188468793
O	1.627225503708	1.392971381461	-0.211176310430
O	1.737206309212	-1.050994529889	0.525481693670
S	1.208567381609	0.000075350137	-0.340672719257

N1-N2 distance : 1.277 Å
N2-N3 distance : 1.167 Å
Alkyne C-C distance : 1.232 Å
N1-C distance : 2.243 Å
N3-C distance : 2.130 Å
Azide N-N-N angle : 136.43°
Alkyne bond angles : 169.03°, 157.61°

B3LYP/6-31G(D) frequency analysis

Number of imaginary frequencies: 1

E0 : -829.96554018 Ha
ZPE: -829.87630716 Ha
H : -829.86552540 Ha
S : 0.15716510 mHa/K
G : -829.91238418 Ha
evaluated at 298.15 K

Difference from GS1 and GS4 ground states

ΔE0 :	0.02566210 Ha	16.103 kcal/mol
ΔH :	0.02754059 Ha	17.282 kcal/mol
ΔS :	-0.05863049 mHa/K	-36.791 cal/mol/K
ΔG :	0.04502126 Ha	28.251 kcal/mol

evaluated at 298.15 K

Azide at transition state geometry

```
   E0 :    -752.63114165 Ha   B3LYP/6-31G(D)
   E0 :    -749.97767517 Ha   HF/6-311++G(2D,P)

  ΔEdist from GS1 ground state   21.60414 kcal/mol    B3LYP/6-31G(D)

      HOMO-1         HOMO         LUMO       LUMO+1
  -12.268068   -11.929204    -0.049389     0.907418  eV   HF/6-311++G(2D,P)
```

Alkyne at transition state geometry

```
   E0 :     -77.31705545 Ha   B3LYP/6-31G(D)
   E0 :     -76.80371615 Ha   HF/6-311++G(2D,P)

  ΔEdist from GS4 ground state    5.38172 kcal/mol    B3LYP/6-31G(D)

      HOMO-1         HOMO         LUMO       LUMO+1
  -11.026657   -11.008153     1.179913     1.367672  eV   HF/6-311++G(2D,P)

HF/6-311++G(2D,P) Ground State HOMO - LUMO gaps (at distorted geometry)
  HOMO Alkyne GS4 - LUMO Azide GS1 :   12.071 eV  (  10.959 eV)
  HOMO Azide GS1 - LUMO Alkyne GS4 :   12.957 eV  (  13.109 eV)

B3LYP/6-31G(D) distortion-interaction analysis
  ΣΔEdist:                  26.98587 kcal/mol
  Eint = ΣΔE0 - ΣΔEdist:   -10.88284 kcal/mol
```

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