Supporting Information

Generation of cycloheptynes and cyclooctynes via a sulfoxide–magnesium exchange reaction of readily synthesized 2-sulfinylcycloalkenyl triflates

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Contents

General Remarks

All reactions were performed in a dry glassware under atmosphere of argon otherwise noted. Analytical thin-layer chromatography (TLC) was performed on precoated (0.25 mm) silica-gel plates (Merck Chemicals, Silica Gel 60 F_{254}, Cat. No. 1.05715). Column chromatography was conducted using Biotage® ZIP sphere cartridge [silica] 5 g (Cat. No. 445-0500-DZ-20), 10 g (Cat. No. 445-1000-FZ-20), 30 g (Cat. No. 445-3000-FZ-20), 45 g (Cat. No. 445-4500-SZ-20), 80 g (Cat. No. 445-8000-JZ-20), or 120 g (Cat. No. 445-120G-UZ-20) or Biotage® SNAP Ultra 25 g (Cat. No. FSUL-0442-0025) or 340 g (Cat. No. FSUL-0442-0340) with medium pressure liquid chromatography (Yamazen, W-Prep 2XY A-type). Preparative thin-layer chromatography (PTLC) was performed on silica-gel (Wako Pure Chemical Industries Ltd., Wakogel B5-F, Cat. No. 230-00043). Recycling preparative HPLC was conducted using JAIGEL-1H and -2H columns (600 mm × 20 ϕ, Japan Analytical Industry Co., Ltd.) with a recycling preparative HPLC (LC-9210 NEXT, Japan Analytical Industry Co., Ltd., eluent: $CHCl_3$). Melting points (Mp) were measured on an Opti Melt MPA100 (Stanford Research Systems), and are uncorrected. ^{1}H NMR spectra were obtained with a Bruker AVANCE 400 spectrometer or a Bruker AVANCE 500 spectrometer at 400 or 500 MHz, respectively. ^{13}C NMR spectra were obtained with a Bruker AVANCE 500 spectrometer at 126 MHz. ^{19}F NMR spectra were obtained with a Bruker AVANCE 400 spectrometer at 376 MHz. All NMR measurements were carried out at 23 ºC unless otherwise noted. $CDCl_3$ (Acros Organics, Cat. No. 368651000) was used as a solvent for obtaining NMR spectra. Chemical shifts (δ) are given in parts per million (ppm) downfield from $(CH_3)_4Si$ (δ 0.00 for ^{1}H NMR and ^{13}C NMR in $CDCl_3$) as an internal reference, or α,α,α-trifluorotoluene (δ –63.0 ppm for ^{19}F NMR in $CDCl_3$) as an external standard with coupling constants (*J*) in hertz (Hz). The abbreviations s, d, t, q, sept, m, and br signify singlet, doublet,

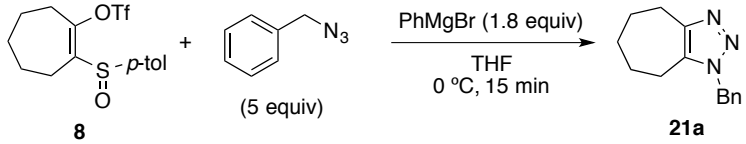
triplet, quartet, septet, multiplet, and broad, respectively. IR spectra were measured by diffuse reflectance method on a Shimadzu IRPrestige-21 spectrometer attached with DRS-8000A with the absorption band given in cm^{-1}. High-resolution mass spectra (HRMS) were measured on a Bruker micrOTOF mass spectrometer under positive electrospray ionization (ESI^+) conditions or a JEOL JMS-700 mass spectrometer under positive fast atom bombardment (FAB^+) conditions. Elemental analyses were carried out at the Elemental Analysis Center of Kyushu University.

Cyclohexanone (Cat. No. C0489), cycloheptanone (Cat. No. C0466), cyclooctanone (Cat. No. C0504), 1-benzosuberone (Cat. No. T1347), potassium bis(trimethylsilyl)amide (KHMDS) (*ca.* 0.5 M, toluene solution, Cat. No. H0893), 4-azidobenzoic acid (Cat. No. A0930), tetrakis(acetonitrile)copper(I) tetrafluoroborate (Cat. No. T2666), 1,1,2,2-tetrachloroethane (Cat. No. T0063), *N*-*tert*-butyl-α-phenylnitrone (Cat. No. B1701), furan (Cat. No. F0074), and 1,3-diphenylisobenzofuran (Cat. No. D1520) were purchased from Tokyo Chemical Industry Co., Ltd. Bis(triphenylphosphine)palladium(II) dichloride (Cat. No. 412740), ethylmagnesium bromide (1.0 M, THF solution, Cat. No. 364673), isopropylmagnesium chloride (2.0 M, diethyl ether solution, Cat. No. 224383), (trimethylsilyl)diazomethane (2.0 M, diethyl ether solution, Cat. No. 527254), and (*S*)-2-(azidomethyl)-1-(*tert*-butoxycarbonyl)pyrrolidine (Cat. No. 669881) were purchased from Sigma–Aldrich Japan. 2,2′-Azobisisobutyronitrile (AIBN) (Cat. No. 019-04932), *N*-bromosuccinimide (NBS) (Cat. No. 025-07235), 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) (Cat. No. 043-16383), *N*-hydroxysuccinimide (Cat. No. 089-04032), dimethylamine (50%, aqueous solution, Cat. No. 048-17151), benzyl azide (Cat. No. 327-79632), 2-furanboronic acid (Cat. No. 320-73441), potassium carbonate (Cat. No. 165-03505), isopropylmagnesium chloride lithium chloride complex (*ca.* 14%, THF solution, Cat. No. 095-06431), and tetraphenylcyclopentadienone (tetracyclone) (Cat. No. 326-46632) were purchased from Wako Pure Chemical Industries Ltd. Lithium diisopropylamide (1.09 M, THF/*n*-hexane solution, Cat. No. 24159-25), bis(trifluoromethanesulfonyl)aniline (Cat. No. 32515-32), *m*-chloroperbenzoic acid (*m*CPBA) (>65.0%, Cat. No. 07938-02), *n*-butyllithium (1.6 M, *n*-hexane solution, Cat. No. 04937-05), methylmagnesium bromide (*ca.* 1 M, THF solution, Cat. No. 25856-25), *tert*-butylmagnesium chloride (0.8–1.1 M, THF solution, Cat. No. 04942-25), tetrahydrofuran (THF) (Cat. No. 31001-84), and magnesium (Cat. No. 19108-1A) were purchased from Kanto Chemical Co. Inc. 1-Ethyl-3-(3-dimethylaminopropyl)carbodiimide hydrochloride (EDCI·HCl) (Cat. No. 344-03633) was purchased from Dojindo Laboratories. Palladium (10%) on carbon (Cat. No. 8.07104.0010) was purchased from Merck Millipore. Phenylmagnesium bromide was purchased from Sigma–Aldrich Japan (1.0 M, THF solution, Cat. No. 331376) or prepared from bromobenzene and magnesium in the conventional way (1.07 M, THF solution). (Trimethylsilylmethyl)magnesium chloride (0.968 M, THF solution) was prepared from trimethylsilylmethyl chloride and magnesium. *n*-Butyllithium, (trimethylsilylmethyl)magnesium chloride, methylmagnesium bromide, ethylmagnesium bromide, isopropylmagnesium chloride, isopropylmagnesium chloride lithium chloride complex, *tert*-butylmagnesium chloride, and phenylmagnesium bromide were used after titrimetric determination of the concentration by the 1,10-phenanthroline method.[S1] *S*-*p*-Tolyl *p*-toluenethiosulfonate,[S2] 5,6,7,8-tetrahydro-4*H*-cyclohepta[*b*]thiophen-4-one,[S3] dibenzo[*a*,*e*]-

cycloocten-5(6*H*)-one,[S4] *N*-methyl-α-(4-chlorophenyl)nitrone,[S5] 2-(4-tolylsulfinyl)phenyl triflate,[S6] 2,6-diisopropylphenyl azide,[S7] 2-azido-1-bromo-3-chloro-5-fluorobenzene,[S8] 5-fluoro-2-piperidinophenyl azide,[S8] *N*-*tert*-butyl-α-(3-iodo-4,5-dimethoxy-phenyl)nitrone,[S9] 4-iodophenyl azide,[S8] 4-ethynylphenyl azide,[S8] and tris[(1-benzyl-1*H*-1,2,3-triazol-4-yl)methyl]amine (TBTA)[S10] were prepared according to the reported methods. All other chemical reagents used were commercial grade and used as received.

Experimental Procedures

A typical procedure for the cycloadditions between 1,3-dipoles and cycloalkynes generated from 2-sulfinylcycloalkenyl triflates



To a mixture of 2-(4-tolylsulfinyl)cyclohept-1-en-1-yl triflate (**8**) (76.6 mg, 0.200 mmol) and benzyl azide (132 mg, 0.991 mmol) dissolved in THF (3.0 mL) was added phenylmagnesium bromide (1.13 M, THF solution, 0.309 mL, 0.350 mmol) at 0 ºC. After stirring for 15 min at the same temperature, to the mixture was added water. The mixture was diluted with brine (10 mL) and extracted with EtOAc (15 mL × 3), and the combined organic extract was washed with brine (10 mL), dried (Na_2SO_4), and after filtration, the filtrate was concentrated under reduced pressure. The residue was purified by preparative TLC (*n*-hexane/EtOAc = 1/1) to give 1-benzyl-1,4,5,6,7,8-hexahydrocyclohepta[*d*][1,2,3]triazole (**21a**) (41.2 mg, 0.181 mmol, 90.5%) as a colorless oil.

Reactions under reduced amount of benzyl azide

The reactions were performed according to the procedure mentioned above using indicated amount of benzyl azide (1.18, 2.46, 3.70 and 4.95 equiv). After the aqueous work up, to the crude mixture was added 1,1,2,2-tetrachloroethane (30.1 mg, 0.179 mmol, 31.4 mg, 0.187 mmol, 30.5 mg, 0.182 mmol, and 33.9 mg, 0.202 mmol, respectively) as an internal standard and the mixture was dissolved in $CDCl_3$. The yields of **21a** were determined by ^{1}H NMR analysis (400 MHz) to be 73.4%, 94.1%, 99.3% and quant., respectively, by comparing the relative values of integration for the peaks observed at 5.47 ppm with that of 1,1,2,2-tetrachloroethane observed at 5.94 ppm.

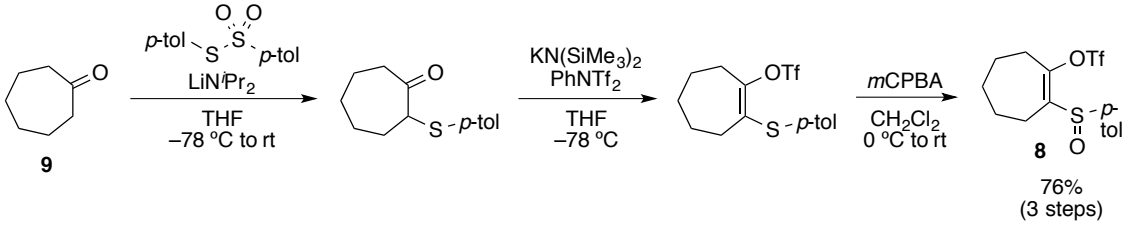
Table S1

Entry	Benzyl azide (equiv)	Yield (%)
1	1.18	73.4
2	2.46	94.1
3	3.70	99.3
4	4.95	quant.

Preparation of cycloalkyne precursors

A typical procedure for the synthesis of 2-sulfinylcycloalkenyl triflates

2-(4-Tolylsulfinyl)cyclohept-1-en-1-yl triflate (**8**)

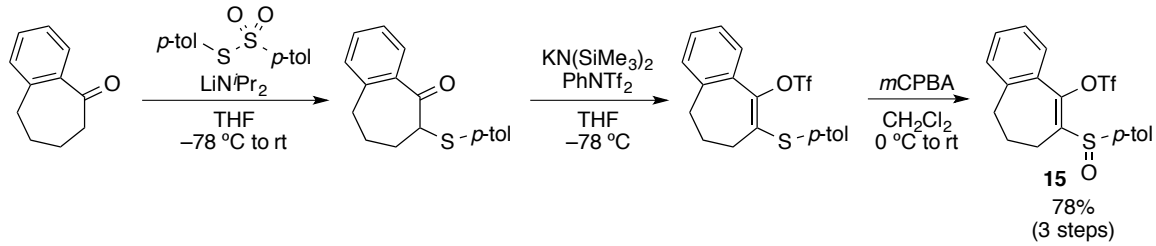


To a solution of cycloheptanone (**9**) (2.26 g, 20.1 mmol) in THF (40 mL) was added lithium diisopropylamide (1.09 M, THF/*n*-hexane solution, 18.5 mL, 20.2 mmol) at –78 ºC. After stirring for 30 min at –78 ºC, the mixture was transferred into a solution of *S*-*p*-tolyl *p*-toluenethiosulfonate (6.46 g, 23.2 mmol) in THF (40 mL) at –78 ºC. After gradually warming to room temperature, the mixture was stirred for 14 h, and to this was added an aqueous saturated solution of ammonium chloride. The mixture was extracted with EtOAc (100 mL × 3), and the combined organic extract was washed with brine (50 mL), dried (Na_2SO_4), and after filtration, the filtrate was concentrated under reduced pressure. The residue was purified by column chromatography (silica-gel 120 g, *n*-hexane/EtOAc = 100/0 to 84/16) to give 2-(4-tolylthio)cycloheptanone (4.7 g, *ca.* 80% purity judged from ^{1}H NMR analysis, *ca.* 15 mmol, *ca.* 77%).

To a solution of the mixture containing 2-(4-tolylthio)cycloheptanone prepared as above in THF (90 mL) was added potassium bis(trimethylsilyl)amide (11% in toluene, *ca.* 0.5 M, 40.2 mL, 20 mmol) at –78 ºC. After stirring for 30 min at the same temperature, to this was added a solution of bis(trifluoromethanesulfonyl)aniline (7.24 g, 20.3 mmol) in THF (90 mL) at the same temperature. After stirring for 1 h at the same temperature, to this was added an aqueous saturated solution of ammonium chloride. The mixture was diluted with water and extracted with EtOAc (100 mL × 3), and the combined organic extract was washed with brine (100 mL), dried (Na_2SO_4), and after filtration, the filtrate was concentrated under reduced pressure. The residue was purified by column chromatography (silica-gel 340 g, *n*-hexane/EtOAc = 100/0 to 80/20) to give a mixture containing 2-(4-tolylthio)cyclohept-1-en-1-yl triflate (9.8 g, *ca.* 60% purity judged from ^{1}H NMR analysis, *ca.* 14 mmol, *ca.* 93%).

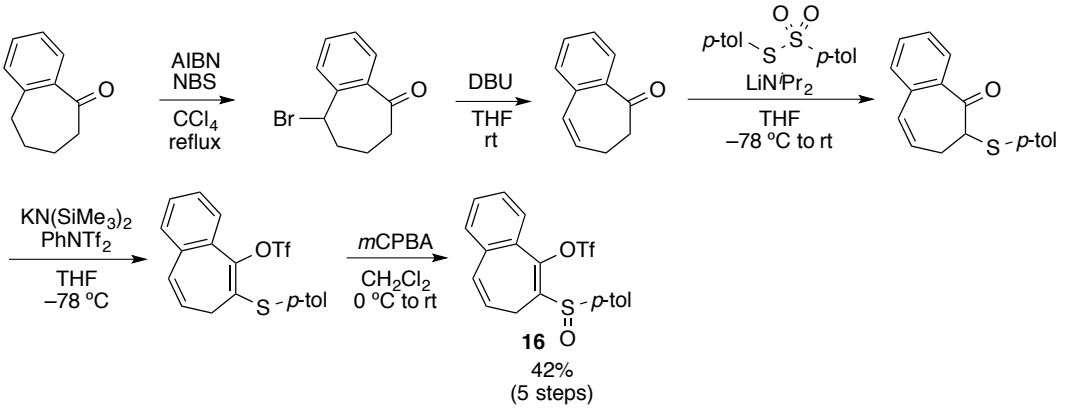
To a solution of the mixture containing 2-(4-tolylthio)cyclohept-1-en-1-yl triflate prepared as above in dichloromethane (200 mL) was slowly added *m*CPBA (>65%, 5.34 g, >20 mmol) at 0 ºC. After gradually warming to room temperature, the mixture was stirred for 16 h, and to this was added an aqueous saturated solution of sodium thiosulfate and an aqueous saturated solution of potassium carbonate. The mixture was extracted with dichloromethane (100 mL × 3), and the combined organic extract was washed with brine (100 mL), dried (Na_2SO_4), and after filtration, the filtrate was concentrated under reduced pressure. The residue was purified by column chromatography (silica-gel 165 g, *n*-hexane/EtOAc = 83/17 to 62/38) to give 2-(4-tolylsulfinyl)cyclohept-1-en-1-yl triflate (**8**) (5.84 g, 15.3 mmol, 76.0% in 3 steps from **9**) as a colorless solid. Analytically pure sample was obtained by purification with recycling preparative HPLC.

8-(4-Tolylsulfinyl)-6,7-dihydro-5*H*-benzocyclohepten-9-yl triflate (**15**)



According to the procedure for preparing **8** from **9**, 8-(4-tolylsulfinyl)-6,7-dihydro-5*H*-benzocyclohepten-9-yl triflate (**15**) was prepared from 1-benzosuberone (14.9 mmol) in 78% yield (3 steps). Analytically pure sample was obtained by recrystallized from toluene.

6-(4-Tolylsulfinyl)-7*H*-benzocyclohepten-5-yl triflate (**16**)



A mixture of 1-benzosuberone (6.41 g, 40.0 mmol), *N*-bromosuccinimide (7.89 g, 44.3 mmol) and 2,2′-azobisisobutyronitrile (65.5 mg, 0.399 mmol) in tetrachloromethane (120 mL) was refluxed (oil bath temperature 100 °C) with stirring for 2 h. After cooling to room temperature, the mixture was filtrated and the filtrate was concentrated under reduced pressure. The residue was purified by column chromatography (silica-gel 200 g, *n*-hexane/EtOAc = 94/6 to 73/27) to give 9-bromo-6,7,8,9-tetrahydro-5*H*-benzocyclohepten-5-one (7.7 g, 97% purity judged from ^{1}H NMR analysis, 31 mmol, 77%).

To a solution of the mixture containing 9-bromo-6,7,8,9-tetrahydro-5*H*-benzocyclohepten-5-one prepared as above in THF (200 mL) was added 1,8-diazabicyclo[5.4.0]undec-7-ene (14.6 g, 96.1 mmol) at room temperature, and the mixture was stirred for 19 h at the same temperature. To this was added an aqueous saturated solution of ammonium chloride. The mixture was extracted with EtOAc (100 mL × 3), and the combined organic extract was washed with an aqueous saturated solution of ammonium chloride (50 mL × 3) and brine (50 mL), dried (Na_2SO_4), and after filtration, the filtrate was concentrated under reduced pressure. The residue was purified by column chromatography (silica-gel 120 g, *n*-hexane/EtOAc = 100/0 to 86/14) to give 6,7-dihydro-5*H*-benzocyclohepten-5-one (3.9 g, 97% purity judged from ^{1}H NMR analysis, 24 mmol, 78%).

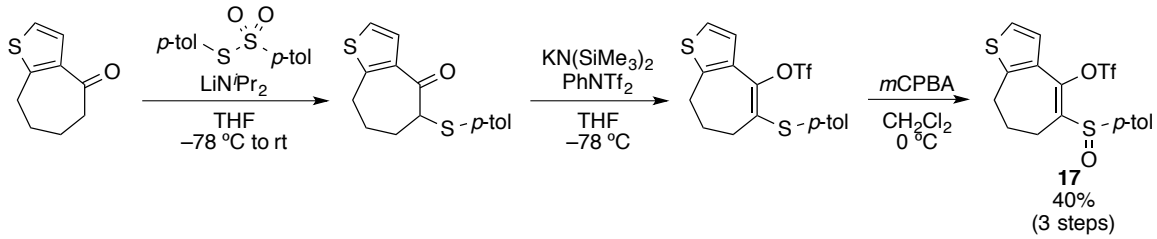
To a solution of the mixture containing 6,7-dihydro-5*H*-benzocyclohepten-5-one prepared as above in THF (40 mL) was added lithium diisopropylamide (1.09 M, THF/*n*-hexane solution, 22.8 mL, 24.9 mmol) at –78 ºC. After stirring for 30 min at the same temperature,

the mixture was transferred into a solution of *S*-*p*-tolyl *p*-toluenethiosulfonate (7.58 g, 27.2 mmol) in THF (40 mL) at –78 ºC. After gradually warming to room temperature, the mixture was stirred for 18 h, and to this was added an aqueous saturated solution of ammonium chloride. The mixture was extracted with EtOAc (100 mL × 3), and the combined organic extract was washed with brine (100 mL), dried (Na_2SO_4), and after filtration, the filtrate was concentrated under reduced pressure. The residue was purified by column chromatography (silica-gel 200 g, *n*-hexane/EtOAc = 100/0 to 84/16) to give 6-(4-tolylthio)-6,7-dihydro-5*H*-benzocyclohepten-5-one (6.6 g, 94% purity judged from ^{1}H NMR analysis, 24 mmol, 98%).

To a solution of the mixture containing 6-(4-tolylthio)-6,7-dihydro-5*H*-benzocyclohepten-5-one prepared as above in THF (120 mL) was added potassium bis(trimethylsilyl)amide (11% in toluene, *ca.* 0.5 M, 49.6 mL, *ca.* 25 mmol) at –78 ºC. After stirring for 30 min at the same temperature, to this was added a solution of bis(trifluoromethanesulfonyl)aniline (8.89 g, 24.9 mmol) in THF (120 mL) at the same temperature. After stirring for 1 h at the same temperature, to the mixture was added an aqueous saturated solution of ammonium chloride. The mixture was diluted with water and extracted with EtOAc (100 mL × 3), and the combined organic extract was washed with brine (100 mL), dried (Na_2SO_4), and after filtration, the filtrate was concentrated under reduced pressure. The residue was purified by column chromatography (silica-gel 340 g, *n*-hexane/EtOAc = 100/0 to 87/13) to give 6-(4-tolylthio)-7*H*-benzocyclohepten-5-yl triflate (9.2 g, *ca.* 80% purity judged from ^{1}H NMR analysis, *ca.* 22 mmol, *ca.* 95%).

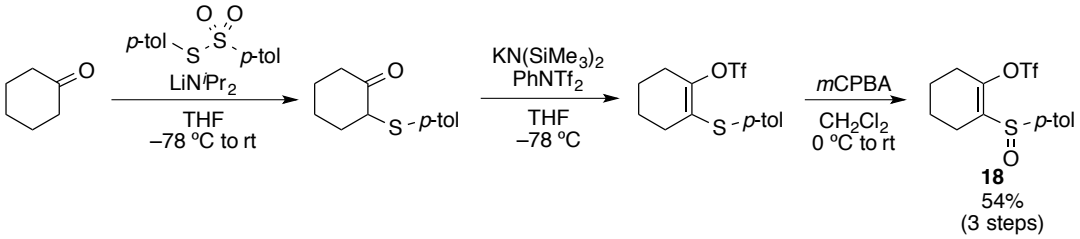
To a solution of the mixture containing 6-(4-tolylthio)-7*H*-benzocyclohepten-5-yl triflate prepared as above in dichloromethane (250 mL) was slowly added *m*CPBA (*ca.* 65%, 6.61 g, *ca.* 25 mmol) at 0 ºC. After gradually warming to room temperature, the mixture was stirred for 14 h, and to this was added an aqueous saturated solution of sodium thiosulfate and an aqueous saturated solution of potassium carbonate. The mixture was extracted with dichloromethane (50 mL × 3), and the combined organic extract was washed with brine (100 mL), dried (Na_2SO_4), and after filtration, the filtrate was concentrated under reduced pressure. The residue was purified by column chromatography (silica-gel 200 g, *n*-hexane/EtOAc = 90/10 to 69/31) to give 6-(4-tolylsulfinyl)-7*H*-benzocyclohepten-5-yl triflate (**16**) (7.21 g, 16.8 mmol, 42.1% in 5 steps from 1-benzosuberone; 67.8% in 3 steps from 6,7-dihydro-5*H*-benzocyclohepten-5-one) as a colorless solid. Analytically pure sample was obtained by purification with recycling preparative HPLC and column chromatography (*n*-hexane/EtOAc = 90/10 to 69/31).

5-(4-Tolylsulfinyl)-7,8-dihydro-6*H*-cyclohepta[*b*]thiophen-4-yl triflate (**17**)



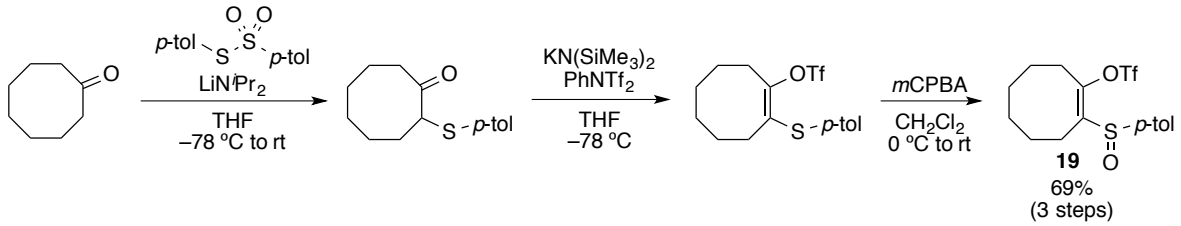
According to the procedure for preparing **8** from **9**, 5-(4-tolylsulfinyl)-7,8-dihydro-6*H*-cyclohepta[*b*]thiophen-4-yl triflate (**17**) was prepared from 5,6,7,8-tetrahydro-4*H*-cyclohepta[*b*]thiophen-4-one (0.755 mmol) in 40% yield (3 steps).

2-(4-Tolylsulfinyl)cyclohex-1-en-1-yl triflate (**18**)



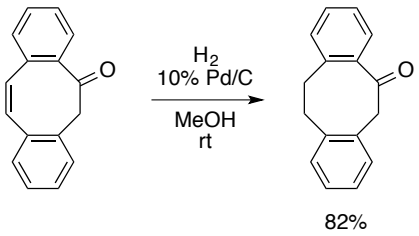
According to the procedure for preparing **8** from **9**, 2-(4-tolylsulfinyl)cyclohex-1-en-1-yl triflate (**18**) was prepared from cyclohexanone (17.0 mmol) in 54% yield (3 steps).

2-(4-Tolylsulfinyl)cyclooct-1-en-1-yl triflate (**19**)



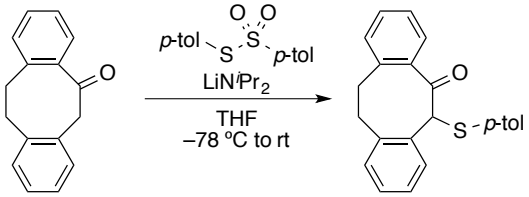
According to the procedure for preparing **8** from **9**, 2-(4-tolylsulfinyl)cyclooct-1-en-1-yl triflate (**19**) was prepared from cyclooctanone (8.89 mmol) in 69% yield (3 steps).

11,12-Dihydrodibenzo[*a*,*e*]cycloocten-5(6*H*)-one



A mixture of dibenzo[*a*,*e*]cycloocten-5(6*H*)-one (3.46 g, 15.7 mmol) and palladium (10%) on carbon (344 mg) in methanol (300 mL) was stirred under hydrogen atmosphere at room temperature for 2 h. The mixture was filtrated and the filtrate was concentrated under reduced pressure. The residue was purified by column chromatography (silica-gel 80 g, *n*-hexane/EtOAc = 99/1 to 78/22) to give 11,12-dihydrodibenzo[*a*,*e*]cycloocten-5(6*H*)-one (2.84 g, 12.8 mmol, 81.5%) as a colorless solid.

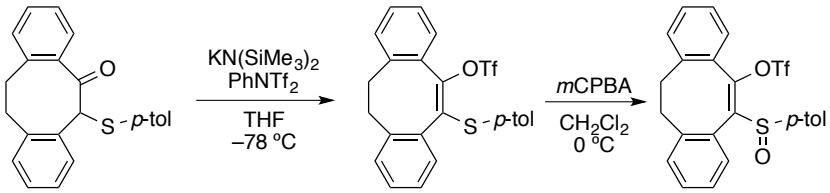
6-(4-Tolylthio)-11,12-dihydrodibenzo[*a*,*e*]cycloocten-5(6*H*)-one



34%

To a solution of 11,12-dihydrodibenzo[*a*,*e*]cycloocten-5(6*H*)-one (1.78 g, 8.00 mmol) in THF (16 mL) was added lithium diisopropylamide (1.09 M, THF/*n*-hexane solution, 7.34 mL, 8.00 mmol) at –78 ºC. After stirring for 30 min at the same temperature, the mixture was transferred into a solution of *S*-*p*-tolyl *p*-toluenethiosulfonate (2.58 g, 9.19 mmol) in THF (16 mL) at –78 ºC. After gradually warming to room temperature, the mixture was stirred for 23 h, and to this was added an aqueous saturated solution of ammonium chloride. The mixture was extracted with EtOAc (50 mL × 3), and the combined organic extract was washed with brine (30 mL), dried (Na_2SO_4), and after filtration, the filtrate was concentrated under reduced pressure. The residue was purified by column chromatography (silica-gel 80 g, *n*-hexane/EtOAc = 100/0 to 83/17) and recycling preparative HPLC to give 6-(4-tolylthio)-11,12-dihydrodibenzo[*a*,*e*]cycloocten-5(6*H*)-one (924 mg, 2.68 mmol, 33.5%) as a pale-yellow amorphous.

6-(4-Tolylsulfinyl)-11,12-dihydrodibenzo[*a*,*e*]cycloocten-5-yl triflate (**20**)



20
58%
(2 steps)

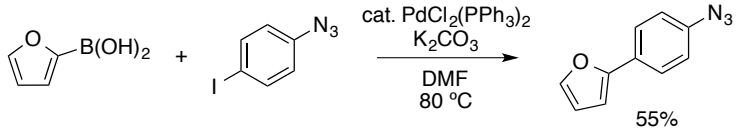
To a solution of 6-(4-tolylthio)-11,12-dihydrodibenzo[*a*,*e*]cycloocten-5(6*H*)-one (924 mg, 2.68 mmol) in THF (13 mL) was added potassium bis(trimethylsilyl)amide (11% in toluene, *ca.* 0.5 M, 6.97 mL, *ca.* 4 mmol) at –78 ºC. After stirring for 30 min at the same temperature, to this was added a solution of bis(trifluoromethanesulfonyl)aniline (1.25 g, 3.50 mmol) in THF (13 mL) at the same temperature. After stirring for 1 h at the same temperature, to this was added an aqueous saturated solution of ammonium chloride. The mixture was extracted with EtOAc (30 mL × 3), and the combined organic extract was washed with brine (30 mL), dried (Na_2SO_4), and after filtration, the filtrate was concentrated under reduced pressure. The residue was purified by column chromatography (silica-gel 80 g, *n*-hexane/EtOAc = 100/0 to 80/20) gave 6-(4-tolylthio)-11,12-dihydrodibenzo[*a*,*e*]cycloocten-5-yl triflate (1.2 g, *ca.* 70% purity judged from ^{1}H NMR analysis, *ca.* 1.6 mmol, *ca.* 61%).

To a solution of the mixture containing 6-(4-tolylthio)-11,12-dihydrodibenzo[*a*,*e*]cycloocten-5-yl triflate prepared as above in dichloromethane (25 mL) was slowly added *m*CPBA (*ca.* 65%, 714 mg, *ca.* 2.7 mmol) at 0 ºC. After stirring for 20 min at the same temperature, to the mixture was added an aqueous saturated solution of sodium thiosulfate and an aqueous

saturated solution of potassium carbonate. The mixture was extracted with dichloromethane (30 mL × 3), and the combined organic extract was washed with brine (30 mL), dried (Na_2SO_4), and after filtration, the filtrate was concentrated under reduced pressure. The residue was purified by column chromatography (silica-gel 50 g, *n*-hexane/EtOAc = 97/3 to 76/24) to give 6-(4-tolylsulfinyl)-11,12-dihydrodibenzo[*a*,*e*]cycloocten-5-yl triflate (**20**) (762 mg, 1.55 mmol, 57.7% in 2 steps from 6-(4-tolylthio)-11,12-dihydrodibenzo[*a*,*e*]cycloocten-5(6*H*)-one) as a colorless solid, which was a mixture of diastereomers (major/minor = 84/16 judged from ^{1}H NMR analysis).

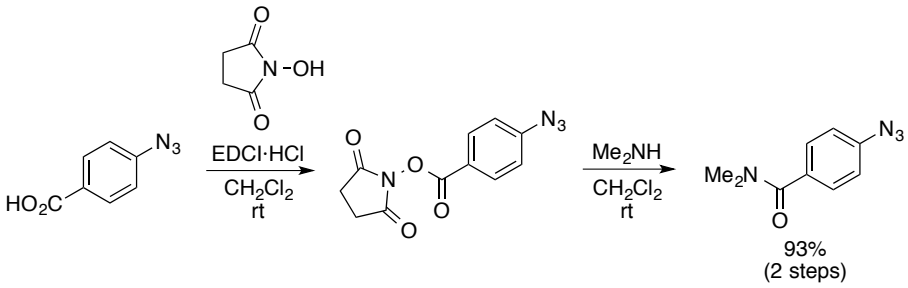
Preparation of ynophiles

4-(2-Furyl)phenyl azide



A mixture of 2-furanboronic acid (315 mg, 2.81 mmol), 4-iodophenyl azide (823 mg, 3.36 mmol), bis(triphenylphosphine)palladium(II) dichloride (101 mg, 0.413 mmol), and potassium carbonate (768 mg, 5.56 mmol) in DMF (6 mL) was heated at 80 ºC (oil bath temperature) with stirring for 90 min. After cooling to room temperature, the mixture was filtrated and the filtrate was concentrated under reduced pressure. The residue was purified by column chromatography (twice, silica-gel 30 g and 25 g, *n*-hexane/EtOAc = 100/0 to 91/9) to give 4-(2-furyl)phenyl azide (288 mg, 1.55 mmol, 55.2%) as a yellow solid.

4-Azido-*N*,*N*-dimethylbenzamide

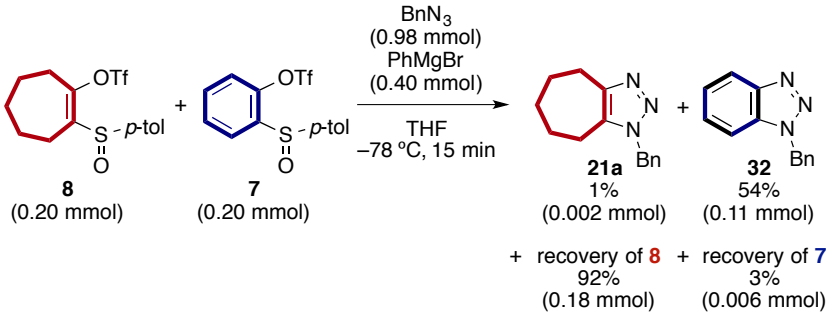


To a mixture of 4-azidobenzoic acid (4.09 g, 25.1 mmol) and *N*-hydroxysuccinimide (3.46 g, 30.0 mmol) in dichloromethane (100 mL) was added 1-ethyl-3-(3-dimethylaminopropyl)-carbodiimide hydrochloride (5.66 g, 29.5 mmol) at room temperature. After stirring for 4 h at the same temperature, to the mixture was added dichloromethane. The organic layer was washed with water (50 mL × 3) and brine (50 mL), dried (Na_2SO_4), and after filtration, the filtrate was concentrated under reduced pressure. The residue containing *N*-(4-azidobenzoyl-oxy)succinimide was used in the next step without further purification.

To a solution of crude *N*-(4-azidobenzoyloxy)succinimide prepared as above in dichloromethane (100 mL) was added dimethylamine (50% in water, 4.50 mL, 43 mmol) at room temperature. After stirring for 18 h at the same temperature, to the mixture was added an aqueous saturated solution of ammonium chloride. The organic extract was washed with brine (30 mL), dried (Na_2SO_4), and after filtration, the filtrate was concentrated under

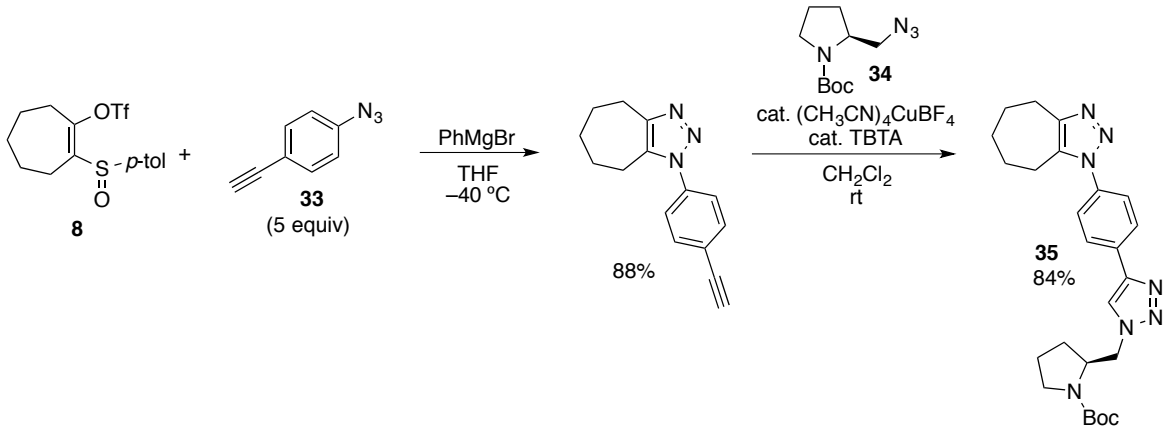
reduced pressure. The residue was purified by column chromatography (silica-gel 80 g, *n*-hexane/EtOAc = 42/58 to 21/79) to give 4-azido-*N*,*N*-dimethylbenzamide (4.43 g, 23.3 mmol, 92.9% in 2 steps from 4-azidobenzoic acid) as a brown solid.

A procedure for the competitive generation of cycloheptyne and benzyne from each precursor



To a mixture of 2-(4-tolylsulfinyl)cyclohept-1-en-1-yl triflate (**8**) (75.5 mg, 0.197 mmol), 2-(4-tolylsulfinyl)phenyl triflate (**7**) (72.5 mg, 0.199 mmol), and benzyl azide (131 mg, 0.982 mmol) dissolved in THF (3.0 mL) was slowly added phenylmagnesium bromide (0.922 M, THF solution, 0.434 mL, 0.400 mmol) at –78 ºC. After stirring for 15 min at the same temperature, to the mixture was added water. The mixture was diluted with brine (10 mL) and extracted with EtOAc (10 mL × 3), and the combined organic extract was washed with brine (10 mL), dried (Na_2SO_4), and after filtration, the filtrate was concentrated under reduced pressure. To the residue was added 1,1,2,2-tetrachloroethane (12.7 mg, 75.7 μmol) as an internal standard and the mixture was dissolved in $CDCl_3$. The yields of **21a** and 1-benzyl-1*H*-benzo[*d*][1,2,3]triazole (**32**),[S11] and recovered **8** and **7** were determined by ^{1}H NMR analysis (400 MHz) to be 1.1%, 53.7%, 91.9%, and 3.0%, respectively, by comparing the relative values of integration for the peaks observed at 5.47 ppm (for **21a**), 5.83 ppm (for **32**), 2.69–2.75 ppm (for **8**), and 8.06 ppm (for **7**) with that of 1,1,2,2-tetrachloroethane observed at 5.94 ppm.

A procedure for the sequential cycloaddition reation



1-(4-Ethynylphenyl)-1,4,5,6,7,8-hexahydrocyclohepta[*d*][1,2,3]triazole

To a mixture of 2-(4-tolylsulfinyl)cyclohept-1-en-1-yl triflate (**8**) (76.6 mg, 0.200 mmol) and 4-ethynylphenyl azide (**33**) (143 mg, 0.996 mmol) dissolved in THF (3.0 mL) was added phenylmagnesium bromide (0.922 M, THF solution, 0.651 mL, 0.600 mmol) at –40 ºC. After stirring for 15 min at the same temperature, to the mixture was added water. The mixture was diluted with brine (10 mL) and extracted with EtOAc (10 mL × 3), and the combined organic extract was washed with brine (10 mL), dried (Na_2SO_4), and after filtration, the filtrate was concentrated under reduced pressure. The residue was purified by column chromatography (silica-gel 5 g, *n*-hexane/EtOAc = 68/32 to 47/53) and preparative TLC (*n*-hexane/EtOAc = 5/1) to give 1-(4-ethynylphenyl)-1,4,5,6,7,8-hexahydrocyclohepta[*d*][1,2,3]triazole (42.0 mg, 0.177 mmol, 88.4%) as a pale-yellow solid.

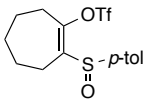
(*S*)-1-(4-(1-((1-(*tert*-Butoxycarbonyl)pyrrolidin-2-yl)methyl)-1*H*-1,2,3-triazol-4-yl)phenyl)-1,4,5,6,7,8-hexahydrocyclohepta[*d*][1,2,3]triazole (**35**)

To a mixture of 1-(4-ethynylphenyl)-1,4,5,6,7,8-hexahydrocyclohepta[*d*][1,2,3]triazole (25.5 mg, 0.108 mmol) and (*S*)-2-(azidomethyl)-1-(*tert*-butoxycarbonyl)pyrrolidine (**34**) (24.8 mg, 0.110 mmol) in dichloromethane (1.0 mL) was added TBTA (2.9 mg, 5.5 μmol) and tetrakis(acetonitrile)copper(I) tetrafluoroborate (1.7 mg, 5.4 μmol) at room temperature. After stirring for 49 h at the same temperature, the mixture was concentrated under reduced pressure. The residue was purified by preparative TLC (twice, dichloromethane/methanol = 10/1 and *n*-hexane/EtOAc = 1/3) to give (*S*)-1-(4-(1-((1-(*tert*-butoxycarbonyl)pyrrolidin-2-yl)methyl)-1*H*-1,2,3-triazol-4-yl)phenyl)-1,4,5,6,7,8-hexahydrocyclohepta[*d*][1,2,3]triazole (**35**) (42.0 mg, 90.6 μmol, 84.3%) as a colorless solid.

Characterization Data of New Compounds

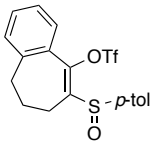
11,12-Dihydrodibenzo[*a*,*e*]cycloocten-5(6*H*)-one,[S12] 6,7,8,9-tetrahydro-1,2,3,4-tetraphenyl-5*H*-benzocycloheptene (**26**),[S13] and 1-benzyl-4,5,6,7-tetrahydro-1*H*-benzotriazole (**30**)[S14] were identical in the spectrum data with those reported in the literatures.

2-(4-Tolylsulfinyl)cyclohept-1-en-1-yl triflate (**8**)



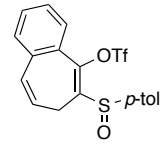
Colorless solid; Mp 52–53 ºC; TLC R_f 0.20 (*n*-hexane/EtOAc = 5/1); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.19–1.28 (m, 1H, aliphatic), 1.45–1.54 (m, 1H, aliphatic), 1.56–1.78 (m, 4H, aliphatic), 2.06–2.13 (m, 1H, aliphatic), 2.36–2.46 (m, 1H, aliphatic), 2.41 (s, 3H, CH_3), 2.58–2.66 (m, 1H, aliphatic), 2.69–2.77 (m, 1H, aliphatic), 7.29–7.33 (AA'BB', 2H, aromatic), 7.49–7.52 (AA'BB', 2H, aromatic); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 20.8 (1C), 21.4 (1C), 23.8 (1C), 26.0 (1C), 30.3 (1C), 34.0 (1C), 118.4 (q, 1C, $J^1_{C–F}$ = 321 Hz), 124.2 (2C), 130.0 (2C), 138.4 (1C), 140.8 (1C), 141.5 (1C), 152.6 (1C); ^{19}F NMR ($CDCl_3$, 376 MHz) δ –73.9 (s); IR (KBr, cm^{-1}) 811, 857, 992, 1058, 1084, 1139, 1213, 1247, 1419, 2931; Anal. calcd. for $C_{15}H_{17}F_3O_4S_2$: C, 47.11; H, 4.48%; N, 0.00; Found: C, 46.92; H, 4.48%; N, 0.00.

8-(4-Tolylsulfinyl)-6,7-dihydro-5*H*-benzocyclohepten-9-yl triflate (**15**)



Colorless solid; Mp 124–126 ºC; TLC R_f 0.25 (*n*-hexane/EtOAc = 5/1); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.36–1.46 (m, 1H, aliphatic), 1.99–2.22 (m, 3H, aliphatic), 2.43 (s, 3H, CH_3), 2.50–2.66 (m, 2H, aliphatic), 7.24 (dd, 1H, *J* = 7.5, 1.6 Hz, aromatic), 7.31–7.41 (m, 4H, aromatic), 7.51 (dd, 1H, *J* = 7.2, 1.2 Hz, aromatic), 7.67–7.71 (AA'BB', 2H, aromatic); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 20.0 (1C), 21.5 (1C), 31.5 (1C), 35.6 (1C), 118.4 (q, 1C, $J^1_{C–F}$ = 322 Hz), 124.2 (2C), 126.8 (1C), 127.3 (1C), 129.6 (1C), 130.1 (2C), 131.3 (1C), 131.4 (1C), 138.9 (1C), 139.6 (1C), 141.7 (1C), 141.8 (1C), 145.7 (1C); ^{19}F NMR ($CDCl_3$, 376 MHz) δ –73.2 (s); IR (KBr, cm^{-1}) 845, 964, 1010, 1056, 1083, 1137, 1211, 1216, 1419; HRMS (ESI^+) m/z 453.0392 ($[M+Na]^+$, $C_{19}H_{17}F_3NaO_4S_2^+$ requires 453.0413).

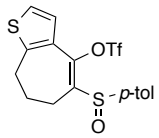
6-(4-Tolylsulfinyl)-7*H*-benzocyclohepten-5-yl triflate (**16**)



Colorless solid; Mp 117–118 ºC (decomp.); TLC R_f 0.30 (*n*-hexane/EtOAc = 5/1); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.43 (s, 3H, CH_3), 2.54–2.64 (m, 2H, CH_2), 5.50–5.55 (m, 1H, CH), 6.59 (d, 1H, *J* = 10.0 Hz, CH), 7.32–7.36 (m, 3H, aromatic), 7.40 (ddd, 1H, *J* = 7.7, 7.7, 1.3 Hz, aromatic), 7.47 (ddd, 1H, *J* = 7.7, 7.7, 1.3 Hz, aromatic), 7.63–7.67 (AA'BB', 2H, aromatic), 7.80 (d, 1H, *J* = 7.7 Hz, aromatic); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 19.2 (1C), 21.4 (1C), 118.3 (q, 1C, $J^1_{C–F}$ = 322 Hz), 124.6 (2C), 126.9 (1C), 127.7 (1C), 129.2 (1C), 129.7

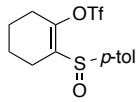
(1C), 130.0 (2C), 130.4 (1C), 130.5 (1C), 132.0 (1C), 137.1 (1C), 139.49 (1C), 139.57 (1C), 141.8 (1C), 144.5 (1C); ^{19}F NMR ($CDCl_3$, 376 MHz) δ –73.0 (s); IR (KBr, cm^{-1}) 823, 848, 982, 1023, 1055, 1082, 1137, 1219, 1236, 1423; HRMS (ESI^+) m/z 451.0266 ($[M+Na]^+$, $C_{19}H_{15}F_3NaO_4S_2^+$ requires 451.0256).

5-(4-Tolylsulfinyl)-7,8-dihydro-6*H*-cyclohepta[*b*]thiophen-4-yl triflate (**17**)



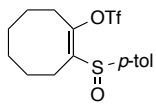
Colorless solid; Mp 88–91 ºC; TLC R_f 0.38 (*n*-hexane/EtOAc = 3/1); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.57–1.68 (m, 1H, aliphatic), 2.11–2.35 (m, 3H, aliphatic), 2.42 (s, 3H, CH_3), 2.70–2.79 (m, 1H, aliphatic), 2.85–2.92 (m, 1H, aliphatic), 7.14–7.17 (m, 2H, aromatic), 7.31–7.36 (AA'BB', 2H, aromatic), 7.63–7.67 (AA'BB', 2H, aromatic); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 21.1 (1C), 21.4 (1C), 26.9 (1C), 34.3 (1C), 118.4 (q, 1C, $J^1_{C–F}$ = 321 Hz), 123.3 (1C), 124.3 (2C), 126.3 (1C), 129.6 (1C), 130.1 (2C), 139.1 (1C), 139.9 (1C), 141.7 (1C), 143.5 (1C), 148.3 (1C); ^{19}F NMR ($CDCl_3$, 376 MHz) δ –73.1 (s); IR (KBr, cm^{-1}) 811, 845, 887, 1026, 1053, 1083, 1137, 1219, 1243, 1421; HRMS (ESI^+) m/z 458.9966 ($[M+Na]^+$, $C_{17}H_{15}F_3NaO_4S_3^+$ requires 458.9977).

2-(4-Tolylsulfinyl)cyclohex-1-en-1-yl triflate (**18**)



Colorless solid; Mp 76–78 ºC; TLC R_f 0.65 (*n*-hexane/EtOAc = 1/1); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.53–1.77 (m, 4H, aliphatic), 1.81–1.91 (m, 1H, aliphatic), 2.42 (s, 3H, CH_3), 2.43–2.68 (m, 3H, aliphatic), 7.31–7.34 (AA'BB', 2H, aromatic), 7.50–7.54 (AA'BB', 2H, aromatic); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 18.5 (1C), 21.1 (1C), 21.4 (1C), 22.4 (1C), 28.7 (1C), 118.3 (q, 1C, $J^1_{C–F}$ = 321 Hz), 124.3 (2C), 130.0 (2C), 136.6 (1C), 138.1 (1C), 141.6 (1C), 149.4 (1C); ^{19}F NMR ($CDCl_3$, 376 MHz) δ –74.0 (s); IR (KBr, cm^{-1}) 846, 881, 883, 1035, 1056, 1084, 1138, 1213, 1218, 1240, 1244, 1418; HRMS (ESI^+) m/z 369.0442 ($[M+H]^+$, $C_{14}H_{16}F_3O_4S_2^+$ requires 369.0437).

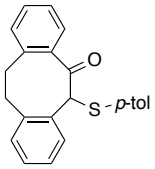
2-(4-Tolylsulfinyl)cyclooct-1-en-1-yl triflate (**19**)



Colorless oil; TLC R_f 0.12 (*n*-hexane/EtOAc = 10/1); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 0.76–0.87 (m, 1H, aliphatic), 1.30–1.43 (m, 3H, aliphatic), 1.50–1.64 (m, 2H, aliphatic), 1.78–1.86 (m, 2H, aliphatic), 2.14–2.22 (m, 1H, aliphatic), 2.41 (s, 3H, CH_3), 2.51–2.71 (m, 3H, aliphatic), 7.30–7.34 (AA'BB', 2H, aromatic), 7.55–7.58 (AA'BB', 2H, aromatic); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 21.4 (1C), 22.2 (1C), 25.6 (1C), 25.7 (1C), 27.3 (1C), 30.7 (1C), 30.8 (1C), 118.4 (q, 1C, $J^1_{C–F}$ = 321 Hz), 124.2 (2C), 130.0 (2C), 138.4 (1C), 138.5 (1C), 141.6 (1C), 150.9 (1C); ^{19}F NMR ($CDCl_3$, 376 MHz) δ –74.0 (s); IR (KBr, cm^{-1}) 855, 933, 1039,

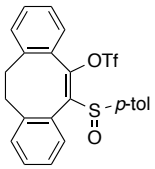
1054, 1083, 1137, 1211, 1243, 1404, 1417; HRMS (ESI^+) m/z 419.0557 ($[M+Na]^+$, $C_{16}H_{19}F_3NaO_4S_2^+$ requires 419.0569).

6-(4-Tolylthio)-11,12-dihydrodibenzo[*a*,*e*]cycloocten-5(6*H*)-one



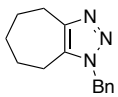
Colorless solid; Mp 96–98 ºC; TLC R_f 0.48 (*n*-hexane/EtOAc = 4/1); ^1H NMR ($CDCl_3$, 500 MHz) δ 2.28 (s, 3H, CH_3), 3.09–3.20 (m, 3H, aliphatic), 3.24–3.33 (m, 1H, aliphatic), 5.49 (s, 1H, CH), 6.90–7.12 (m, 8H, aromatic), 7.14–7.24 (m, 4H, aromatic); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 21.1 (1C), 31.0 (1C), 35.3 (1C), 66.1 (1C), 126.1 (1C), 126.2 (1C), 126.5 (1C), 128.3 (1C), 129.6 (1C+1C, two signals overlapped), 129.7 (1C), 129.8 (1C), 130.1 (2C), 130.3 (1C), 133.7 (2C), 135.5 (1C), 136.2 (1C), 137.9 (1C), 138.7 (1C), 139.1 (1C), 203.6 (1C); IR (KBr, cm^{-1}) 804, 809, 1004, 1242, 1445, 1487, 1666, 1671, 1692, 1696; HRMS (ESI^+) m/z 367.1118 ($[M+Na]^+$, $C_{23}H_{20}NaOS^+$ requires 367.1127).

6-(4-Tolylsulfinyl)-11,12-dihydrodibenzo[*a*,*e*]cycloocten-5-yl triflate (**20**)



Colorless solid; Mp 143–144 ºC (decomp.); TLC R_f 0.52, 0.37 (*n*-hexane/EtOAc = 3/1); ^1H NMR ($CDCl_3$, 500 MHz) δ 2.18–2.27 (m, 1H, aliphatic), 2.27–2.35 (m, 1H, aliphatic), 2.33 (s, 3H, CH_3), 2.71–2.80 (m, 1H, aliphatic), 3.24–3.32 (m, 1H, aliphatic), 6.88 (dd, 1H, J = 7.5, 1.3 Hz, aromatic), 6.96 (d, 1H, J = 7.4 Hz, aromatic), 7.07–7.10 (AA'BB', 2H, aromatic), 7.10–7.20 (m, 4H, aromatic), 7.23–7.27 (AA'BB', 2H, aromatic), 7.36 (dd, 1H, J = 7.5, 1.5 Hz, aromatic), 7.50 (dd, 1H, J = 7.4, 1.5 Hz, aromatic); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 21.5 (1C), 31.2 (1C), 34.5 (1C), 118.2 (q, 1C, J^1_{C-F} = 321 Hz), 125.0 (2C), 125.4 (1C), 126.2 (1C), 127.6 (1C), 128.6 (1C), 128.9 (1C), 129.4 (2C), 129.7 (1C), 129.9 (1C), 130.6 (1C), 130.9 (1C), 131.1 (1C), 137.5 (1C), 137.9 (1C), 139.3 (1C), 140.3 (1C), 142.2 (1C), 147.3(1C); ^{19}F NMR ($CDCl_3$, 376 MHz) δ –73.7 (s); IR (KBr, cm^{-1}) 809, 833, 917, 922, 1058, 1083, 1136, 1211, 1418; HRMS (ESI^+) m/z 515.0540 ($[M+Na]^+$, $C_{24}H_{19}F_3NaO_4S_2^+$ requires 515.0575).

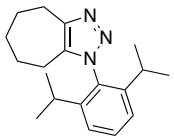
1-Benzyl-1,4,5,6,7,8-hexahydrocyclohepta[*d*][1,2,3]triazole (**21a**)



Colorless oil; TLC R_f 0.35 (*n*-hexane/EtOAc = 1/1); ^1H NMR ($CDCl_3$, 500 MHz) δ 1.56–1.63 (m, 2H, aliphatic), 1.66–1.84 (m, 4H, aliphatic), 2.52–2.57 (m, 2H, aliphatic), 2.85–2.90 (m, 2H, aliphatic), 5.47 (s, 2H, CH_2), 7.09–7.13 (m, 2H, aromatic), 7.27–7.35 (m, 3H, aromatic); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 24.2 (1C), 26.8 (1C), 27.20 (1C), 27.23 (1C), 30.7 (1C), 51.8 (1C), 126.8 (2C), 128.1 (1C), 128.9 (2C), 135.0 (1C), 135.5 (1C), 147.7 (1C); IR (KBr, cm^{-1})

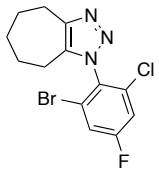
1211, 1306, 1443, 1453, 1495, 2847, 2887, 2916, 2920; HRMS (ESI^+) m/z 250.1311 ($[M+Na]^+$, $C_{14}H_{17}N_3Na^+$ requires 250.1315).

1-(2,6-Diisopropylphenyl)-1,4,5,6,7,8-hexahydrocyclohepta[*d*][1,2,3]triazole (**21b**)



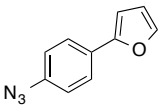
Yellow solid; Mp 90–92 ºC; TLC R_f 0.32 (*n*-hexane/EtOAc = 5/1); ^1H NMR ($CDCl_3$, 500 MHz) δ 1.11 (d, 6H, J = 6.9 Hz, CH_3×2), 1.13 (d, 6H, J = 6.9 Hz, CH_3×2), 1.59–1.66 (m, 2H, aliphatic), 1.76–1.91 (m, 4H, aliphatic), 2.17 (sept, 2H, J = 6.9 Hz, CH×2), 2.39–2.43 (m, 2H, aliphatic), 2.98–3.03 (m, 2H, aliphatic), 7.28 (d, 2H, J = 7.8 Hz, aromatic), 7.47 (t, 1H, J = 7.8 Hz, aromatic); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 23.4 (2C), 24.3 (1C), 24.5 (2C), 27.1 (1C), 27.4 (1C), 27.5 (1C), 28.2 (2C), 31.0 (1C), 123.8 (2C), 130.6 (1C), 131.9 (1C), 137.2 (1C), 146.5 (1C), 146.6 (2C); IR (KBr, cm^{-1}) 807, 1002, 1364, 1446, 1461, 1478, 2852, 2869, 2926, 2964; HRMS (ESI^+) m/z 298.2281 ($[M+H]^+$, $C_{19}H_{28}N_3^+$ requires 298.2278).

1-(2-Bromo-6-chloro-4-fluorophenyl)-1,4,5,6,7,8-hexahydrocyclohepta[*d*][1,2,3]triazole (**21c**)



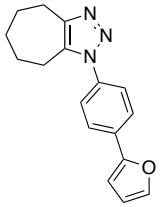
Pale yellow solid; Mp 138–140 ºC; TLC R_f 0.39 (*n*-hexane/EtOAc = 3/1); ^1H NMR ($CDCl_3$, 500 MHz) δ 1.68–1.92 (m, 6H, aliphatic), 2.42–2.48 (m, 2H, aliphatic), 2.96–3.02 (m, 2H, aliphatic), 7.32 (dd, 1H, J_{H-F} = 7.8, J = 2.7 Hz, aromatic), 7.44 (dd, 1H, J_{H-F} = 7.4, J = 2.7 Hz, aromatic); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 23.9 (1C), 26.8 (1C), 27.2 (1C), 27.3 (1C), 30.8 (1C), 117.1 (d, 1C, J^2_{C-F} = 25.6 Hz), 119.6 (d, 1C, J^2_{C-F} = 25.5 Hz), 124.8 (d, 1C, J^3_{C-F} = 11.3 Hz), 130.6 (d, 1C, J^4_{C-F} = 4.16 Hz), 135.5 (d, 1C, J^3_{C-F} = 11.7 Hz), 136.9 (1C), 146.8 (1C), 162.4 (d, 1C, J^1_{C-F} = 259 Hz); ^{19}F NMR ($CDCl_3$, 376 MHz) δ –106.0 (dd, J_{F-H} = 7.1, 7.1 Hz); IR (KBr, cm^{-1}) 858, 935, 1064, 1243, 1398, 1447, 1500, 1576, 1592, 2927; HRMS (ESI^+) m/z 343.9964 ($[M+H]^+$, $C_{13}H_{13}BrClFN_3^+$ requires 343.9960).

4-(2-Furyl)phenyl azide



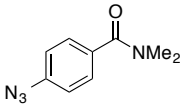
Yellow solid; Mp 57–59 ºC; TLC R_f 0.40 (*n*-hexane/EtOAc = 50/1); ^1H NMR ($CDCl_3$, 500 MHz) δ 6.47 (dd, 1H, J = 3.3, 1.7 Hz), 6.61 (dd, 1H, J = 3.3, 0.4 Hz), 7.02–7.05 (AA'BB', 2H), 7.45 (dd, 1H, J = 1.7, 0.4 Hz), 7.63–7.67 (AA'BB', 2H); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 104.9 (1C), 111.7 (1C), 119.3 (2C), 125.2 (2C), 127.9 (1C), 138.8 (1C), 142.1 (1C), 153.2 (1C); IR (KBr, cm^{-1}) 801, 834, 904, 1008, 1016, 1282, 1298, 1483, 1511, 2092, 2129; HRMS (ESI^+) m/z 158.0599 ($[M+H-N_2]^+$, $C_{10}H_8NO^+$ requires 158.0600).

1-(4-(2-Furyl)phenyl)-1,4,5,6,7,8-hexahydrocyclohepta[*d*][1,2,3]triazole (**21d**)



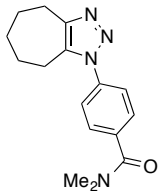
Brown solid; Mp 136–139 ºC (decomp.); TLC R_f 0.12 (*n*-hexane/EtOAc = 3/1); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.67–1.73 (m, 2H, aliphatic), 1.73–1.80 (m, 2H, aliphatic), 1.85–1.92 (m, 2H, aliphatic), 2.73–2.77 (m, 2H, aliphatic), 2.94–3.00 (m, 2H, aliphatic), 6.51 (dd, 1H, *J* = 3.4, 1.8 Hz, aromatic), 6.74 (dd, 1H, *J* = 3.4, 0.5 Hz, aromatic), 7.40–7.45 (AA'BB', 2H, aromatic), 7.52 (dd, 1H, *J* = 1.8, 0.5 Hz, aromatic), 7.79–7.83 (AA'BB', 2H, aromatic); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 24.8 (1C), 27.0 (1C+1C, two signals overlapped), 27.2 (1C), 30.9 (1C), 106.4 (1C), 112.0 (1C), 124.5 (2C), 125.6 (2C), 131.6 (1C), 135.2 (1C), 135.6 (1C), 142.9 (1C), 147.4 (1C), 152.6 (1C); IR (KBr, cm^{-1}) 835, 845, 855, 905, 1001, 1011, 1083, 1220, 1484, 1519, 2925; HRMS (ESI^+) m/z 280.1457 ($[M+H]^+$, $C_{17}H_{18}N_3O^+$ requires 280.1444).

4-Azido-*N*,*N*-dimethylbenzamide



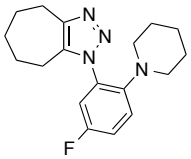
Brown solid; Mp 41–43 ºC; TLC R_f 0.38 (*n*-hexane/EtOAc = 1/2); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 3.00 (s, 3H, CH_3), 3.10 (s, 3H, CH_3), 7.03–7.07 (AA'BB', 2H, aromatic), 7.42–7.46 (AA'BB', 2H, aromatic); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 35.5 (1C), 39.6 (1C), 118.9 (2C), 129.0 (2C), 132.7 (1C), 141.4 (1C), 170.7 (1C); IR (KBr, cm^{-1}) 1281, 1289, 1392, 1601, 1625, 1632, 1641, 2089, 2093, 2127; HRMS (ESI^+) m/z 213.0749 ($[M+Na]^+$, $C_9H_{10}N_4NaO^+$ requires 213.0747).

1-(4-(*N*,*N*-Dimethylcarbamoyl)phenyl)-1,4,5,6,7,8-hexahydrocyclohepta[*d*][1,2,3]triazole (**21e**)



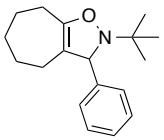
Colorless solid; Mp 173–175 ºC; TLC R_f 0.31 (EtOAc); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.67–1.73 (m, 2H, aliphatic), 1.74–1.81 (m, 2H, aliphatic), 1.85–1.92 (m, 2H, aliphatic), 2.72–2.77 (m, 2H, aliphatic), 2.95–3.00 (m, 2H, aliphatic), 3.02 (s, 3H, CH_3), 3.15 (s, 3H, CH_3), 7.45–7.49 (AA'BB', 2H, aromatic), 7.57–7.61 (AA'BB', 2H, aromatic); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 24.7 (1C), 26.98 (1C), 26.99 (1C), 27.2 (1C), 30.8 (1C), 35.4 (1C), 39.6 (1C), 125.4 (2C), 128.2 (2C), 135.7 (1C), 137.2 (1C), 137.3 (1C), 147.6 (1C), 170.3 (1C); IR (KBr, cm^{-1}) 855, 1004, 1082, 1397, 1409, 1497, 1606, 1627, 2926; HRMS (ESI^+) m/z 285.1716 ($[M+H]^+$, $C_{16}H_{21}N_4O^+$ requires 285.1710).

1-(5-Fluoro-2-piperidinophenyl)-1,4,5,6,7,8-hexahydrocyclohepta[*d*][1,2,3]triazole (**21f**)



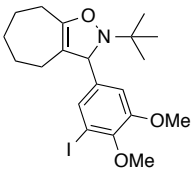
Colorless solid; Mp 93–95 ºC; TLC R_f 0.43 (*n*-hexane/EtOAc = 3/1); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.35–1.48 (m, 6H, aliphatic), 1.53–1.66 (m, 1H, aliphatic), 1.68–1.94 (m, 5H, aliphatic), 2.36–2.44 (m, 1H, aliphatic), 2.52–2.75 (m, 5H, aliphatic), 2.88–3.03 (m, 2H, aliphatic), 7.05–7.17 (m, 3H, aromatic); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 23.9, 24.8, 26.3, 26.9, 27.32, 27.34, 31.1, 52.6, 116.2 (d, $J^2_{C–F}$ = 24.7 Hz), 117.2 (d, $J^2_{C–F}$ = 21.9 Hz), 120.7 (d, $J^3_{C–F}$ = 8.3 Hz), 131.0 (d, $J^3_{C–F}$ = 10.1 Hz), 137.1, 145.7 (d, $J^4_{C–F}$ = 2.7 Hz), 146.8, 157.9 (d, $J^1_{C–F}$ = 244.2 Hz); ^{19}F NMR ($CDCl_3$, 376 MHz) δ –120.2 (ddd, $J_{F–H}$ = 7.9, 7.9, 5.6 Hz); IR (KBr, cm^{-1}) 891, 1196, 1215, 1221, 1237, 1444, 1452, 1505, 2851, 2932; HRMS (ESI^+) m/z 315.1985 ($[M+H]^+$, $C_{18}H_{24}FN_4^+$ requires 315.1980).

2-(*tert*-Butyl)-3-phenyl-3,4,5,6,7,8-hexahydro-2*H*-cyclohepta[*d*]isoxazole (**22a**)



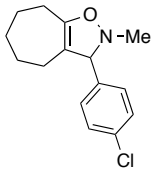
Colorless oil; TLC R_f 0.52 (*n*-hexane/EtOAc = 10/1); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.10 (s, 9H, CH_3×3), 1.37–1.71 (m, 7H, aliphatic), 1.83–1.90 (m, 1H, aliphatic), 2.23–2.37 (m, 2H, aliphatic), 4.83 (s, 1H, CH), 7.21–7.25 (m, 1H, aromatic), 7.28–7.35 (m, 4H, aromatic); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 24.2 (1C), 24.9 (3C), 25.9 (1C), 26.3 (1C), 28.5 (1C), 29.7 (1C), 60.1 (1C), 73.4 (1C), 108.8 (1C), 127.0 (1C), 127.8 (2C), 128.3 (2C), 144.1 (1C), 150.2 (1C); IR (KBr, cm^{-1}) 1207, 1222, 1363, 1389, 1453, 1713, 2854, 2926, 2971; HRMS (ESI^+) m/z 272.2013 ($[M+H]^+$, $C_{18}H_{26}NO^+$ requires 272.2009).

2-(*tert*-Butyl)-3-(3-iodo-4,5-dimethoxyphenyl)-3,4,5,6,7,8-hexahydro-2*H*-cyclohepta[*d*]isoxazole (**22b**)



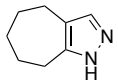
Pale-yellow oil; TLC R_f 0.38 (*n*-hexane/EtOAc = 10/1); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.10 (s, 9H, CH_3×3), 1.38–1.49 (m, 1H, aliphatic), 1.52–1.73 (m, 6H, aliphatic), 1.83–1.92 (m, 1H, aliphatic), 2.22–2.38 (m, 2H, aliphatic), 3.81 (s, 3H, CH_3), 3.85 (s, 3H, CH_3), 4.74 (s, 1H, CH), 6.93 (d, 1H, *J* = 1.8 Hz, aromatic), 7.23 (d, 1H, *J* = 1.8 Hz, aromatic); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 24.1 (1C), 24.9 (3C), 25.8 (1C), 26.3 (1C), 28.6 (1C), 29.7 (1C), 56.0 (1C), 60.1 (1C), 60.3 (1C), 72.6 (1C), 92.0 (1C), 108.5 (1C), 112.2 (1C), 129.3 (1C), 142.1 (1C), 147.9 (1C), 150.7 (1C), 152.8 (1C); IR (KBr, cm^{-1}) 1002, 1043, 1229, 1268, 1401, 1453, 1463, 1478, 1553, 1561, 2929, 2969; HRMS (ESI^+) m/z 458.1188 ($[M+H]^+$, $C_{20}H_{29}INO_3^+$ requires 458.1187).

2-Methyl-3-(4-chlorophenyl)-3,4,5,6,7,8-hexahydro-2*H*-cyclohepta[*d*]isoxazole (**22c**)



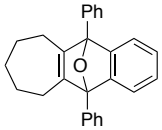
Colorless oil; TLC R_f 0.38 (*n*-hexane/EtOAc = 10/1); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.41–1.51 (m, 1H, aliphatic), 1.55–1.77 (m, 6H, aliphatic), 1.89–1.97 (m, 1H, aliphatic), 2.23–2.36 (m, 2H, aliphatic), 2.81 (s, 3H, CH_3), 4.40 (s, 1H, CH), 7.22–7.25 (AA'BB', 2H, aromatic), 7.28–7.32 (AA'BB', 2H, aromatic); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 24.3 (1C), 26.1 (1C), 26.3 (1C), 28.4 (1C), 29.6 (1C), 47.0 (1C), 81.1 (1C), 108.0 (1C), 128.6 (2C), 128.9 (2C), 133.4 (1C), 140.2 (1C), 149.9 (1C); IR (KBr, cm^{-1}) 819, 1015, 1059, 1089, 1446, 1490, 1705, 2850, 2872, 2921; HRMS (ESI^+) m/z 286.0969 ($[M+Na]^+$, $C_{15}H_{18}ClNNaO^+$ requires 286.0969).

1,4,5,6,7,8-Hexahydrocyclohepta[*c*]pyrazole (**23**)



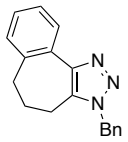
Colorless solid; Mp 64–66 ºC; TLC R_f 0.24 (*n*-hexane/EtOAc = 1/1); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.60–1.71 (m, 4H, aliphatic), 1.80–1.86 (m, 2H, aliphatic), 2.54–2.58 (m, 2H, aliphatic), 2.74–2.79 (m, 2H, aliphatic), 7.26 (s, 1H, CH), 8.33 (br s, 1H, NH); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 25.4 (1C), 27.7 (1C), 28.4 (1C), 29.3 (1C), 32.2 (1C), 120.1 (1C), 132.7 (1C), 148.7 (1C); IR (KBr, cm^{-1}) 964, 1444, 2807, 2847, 2920, 2999, 3073, 3100, 3151, 3193; HRMS (ESI^+) m/z 137.1078 ($[M+Na]^+$, $C_8H_{12}N_2Na^+$ requires 137.1073).

5,11-Epoxy-6,7,8,9,10,11-hexahydro-5,11-diphenyl-5*H*-cyclohepta[*b*]naphthalene (**25b**)



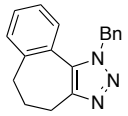
Colorless solid; Mp 150–151 ºC (lit.[S15] 167–168 °C); TLC R_f 0.54 (*n*-hexane/EtOAc = 10/1); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.20–1.33 (m, 1H, aliphatic), 1.37–1.49 (m, 2H, aliphatic), 1.57–1.69 (m, 2H, aliphatic), 1.73–1.82 (m, 1H, aliphatic), 1.90–2.01 (m, 2H, aliphatic), 2.44–2.56 (m, 2H, aliphatic), 6.98–7.04 (m, 2H, aromatic), 7.35–7.44 (m, 4H, aromatic), 7.50 (dd, 4H, J = 8.0, 8.0 Hz, aromatic), 7.76 (dd, 4H, J = 8.0, 1.5 Hz, aromatic); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 27.6 (2C), 27.9 (2C), 29.5 (1C), 93.3 (2C), 119.4 (2C), 124.6 (2C), 127.5 (4C), 127.8 (2C), 128.3 (4C), 135.5 (2C), 151.1 (2C), 151.4 (2C); IR (KBr, cm^{-1}) 912, 999, 1218, 1307, 1451, 2853, 2923; HRMS (ESI^+) m/z 387.1717 ($[M+Na]^+$, $C_{27}H_{24}NaO^+$ requires 387.1719).

3-Benzyl-3,4,5,6-tetrahydrobenzo[3,4]cyclohepta[1,2-*d*][1,2,3]triazole (**27**)



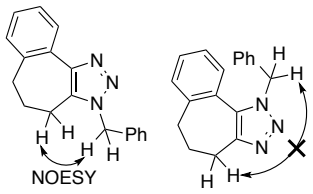
Colorless solid; Mp 95–96 ºC; TLC R_f 0.25 (toluene/EtOAc = 20/1); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.97–2.03 (m, 2H, aliphatic), 2.72–2.76 (m, 2H, aliphatic), 2.80–2.84 (m, 2H, aliphatic), 5.51 (s, 2H, CH_2), 7.10 (dd, 1H, J = 7.5, 0.5 Hz, aromatic), 7.17–7.21 (m, 3H, aromatic), 7.28–7.37 (m, 4H, aromatic), 8.38 (dd, 1H, J = 7.8, 1.2 Hz); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 23.4 (1C), 25.5 (1C), 35.0 (1C), 52.0 (1C), 126.7 (1C), 127.0 (1C), 127.2 (2C), 127.5 (1C), 128.3 (1C), 129.0 (2C), 129.4 (1C), 129.9 (1C), 133.3 (1C), 134.7 (1C), 139.5 (1C), 144.0 (1C); IR (KBr, cm^{-1}) 1007, 1250, 1355, 1426, 1445, 1452, 1495, 2927; HRMS (ESI$^+$) m/z 298.1304 ([M+Na]$^+$, $C_{18}H_{17}N_3Na^+$ requires 298.1315).

1-Benzyl-1,4,5,6-tetrahydrobenzo[3,4]cyclohepta[1,2-*d*][1,2,3]triazole (**27'**)



Colorless oil; TLC R_f 0.18 (toluene/EtOAc = 20/1); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.16–2.24 (m, 2H, aliphatic), 2.56–2.60 (m, 2H, aliphatic), 2.93–2.98 (m, 2H, aliphatic), 5.66 (s, 2H, CH_2), 7.13–7.35 (m, 9H, aromatic); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 23.3 (1C), 29.7 (1C), 32.8 (1C), 52.1 (1C), 126.5 (1C), 126.66 (1C), 126.71 (2C), 127.3 (1C), 128.0 (1C), 128.89 (1C), 128.91 (2C), 130.0 (1C), 133.1 (1C), 136.0 (1C), 142.4 (1C), 146.0 (1C); IR (KBr, cm^{-1}) 1012, 1127, 1205, 1307, 1432, 1451, 1495, 2850, 2856, 2904, 2934; HRMS (ESI$^+$) m/z 298.1319 ([M+Na]$^+$, $C_{18}H_{17}N_3Na^+$ requires 298.1315).

Regiochemistries of the isomers **27** and **27'** were determined by the NOESY experiments.

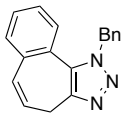


3-Benzyl-3,4-dihydrobenzo[3,4]cyclohepta[1,2-*d*][1,2,3]triazole (**28**)

Pale yellow oil; TLC R_f 0.33 (*n*-hexane/EtOAc = 3/1), 0.25 (toluene/AcOEt = 20/1); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 3.37 (dd, 2H, J = 5.8, 1.5 Hz, CH_2), 5.54 (s, 2H, CH_2), 5.61 (dt, 1H, J = 11.8, 5.8 Hz, CH), 6.47 (d, 1H, J = 11.8 Hz, CH), 7.15–7.19 (m, 3H, aromatic), 7.24–7.37 (m, 5H, aromatic), 8.30 (dd, 1H, J = 7.9, 1.0 Hz, aromatic); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 23.4 (1C), 51.8 (1C), 123.8 (1C), 126.9 (1C+2C, two signals overlapped), 127.6 (1C), 127.9 (1C), 128.4 (1C), 129.1 (2C), 129.2 (1C), 131.4 (1C), 131.7 (1C), 132.6 (1C), 132.8

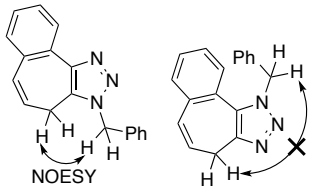
(1C), 134.9 (1C), 144.1 (1C); IR (KBr, cm^{-1}) 1009, 1242, 1356, 1362, 1436, 1452, 1495, 1563, 1596, 3022; HRMS (ESI^+) m/z 274.1346 ($[M+H]^+$, $C_{18}H_{16}N_3^+$ requires 274.1339).

1-Benzyl-1,4-dihydrobenzo[3,4]cyclohepta[1,2-*d*][1,2,3]triazole (**28'**)

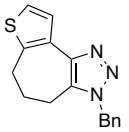


Colorless oil; TLC R_f 0.33 (*n*-hexane/EtOAc = 3/1), 0.18 (toluene/AcOEt = 20/1); ^1H NMR ($CDCl_3$, 500 MHz) δ 3.42 (dd, 2H, *J* = 6.3, 0.8 Hz, CH_2), 5.66 (s, 2H, CH_2), 6.16 (dt, 1H, *J* = 11.0, 6.3 Hz, CH), 6.55 (d, 1H, *J* = 11.0 Hz, CH), 7.18–7.21 (m, 2H, aromatic), 7.22–7.38 (m, 7H, aromatic); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 24.6, 52.5, 124.3, 126.6, 126.8, 127.5, 128.1, 128.3, 129.0, 130.2, 131.1, 131.8, 132.3, 135.85, 135.88, 146.8; IR (KBr, cm^{-1}) 840, 844, 1212, 1299, 1434, 1453, 1495, 1596, 1620, 1634; HRMS (ESI^+) m/z 274.1347 ($[M+H]^+$, $C_{18}H_{16}N_3^+$ requires 274.1339).

Regiochemistries of the isomers **28** and **28'** were determined by the NOESY experiments.

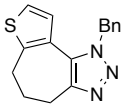


3-Benzyl-3,4,5,6-tetrahydrothieno[3',2':3,4]cyclohepta[1,2-*d*][1,2,3]triazole (**29**)



Pale yellow oil; TLC R_f 0.54 (toluene/EtOAc = 3/1); ^1H NMR ($CDCl_3$, 500 MHz) δ 2.03–2.08 (m, 2H, aliphatic), 2.76–2.80 (m, 2H, aliphatic), 3.02–3.05 (m, 2H, aliphatic), 5.50 (s, 2H, CH_2), 7.08 (d, 1H, *J* = 5.3 Hz, aromatic), 7.15–7.18 (m, 2H, aromatic), 7.28–7.36 (m, 3H, aromatic), 7.76 (d, 1H, *J* = 5.3 Hz, aromatic); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 22.4 (1C), 25.2 (1C), 29.2 (1C), 51.9 (1C), 122.2 (1C), 126.9 (1C), 127.1 (2C), 128.3 (1C), 129.0 (2C), 129.1 (1C), 132.2 (1C), 134.8 (1C), 137.4 (1C), 141.9 (1C); IR (KBr, cm^{-1}) 884, 1252, 1322, 1436, 1455, 1497, 2929; HRMS (ESI^+) m/z 282.1060 ($[M+H]^+$, $C_{16}H_{16}N_3S^+$ requires 282.1059).

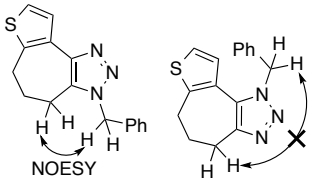
1-Benzyl-1,4,5,6-tetrahydrothieno[3',2':3,4]cyclohepta[1,2-*d*][1,2,3]triazole (**29'**)



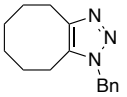
Pale yellow oil; TLC R_f 0.39 (toluene/EtOAc = 3/1); ^1H NMR ($CDCl_3$, 500 MHz) δ 2.08–2.14 (m, 2H, aliphatic), 2.96–3.02 (m, 2H, aliphatic), 3.21–3.25 (m, 2H, aliphatic), 5.74 (s, 2H, CH_2), 6.96 (d, 1H, *J* = 5.4 Hz, aromatic), 7.02 (d, 1H, *J* = 5.4 Hz, aromatic), 7.10–7.13 (m, 2H, aromatic), 7.27–7.38 (m, 3H, aromatic); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 25.2 (1C), 27.0 (1C), 28.6 (1C), 52.6 (1C), 122.8 (1C), 123.2 (1C), 125.9 (1C), 126.1 (2C), 128.0 (1C), 129.1 (2C), 129.8 (1C), 135.9 (1C), 144.0 (1C), 144.9 (1C); IR (KBr, cm^{-1}) 864, 889, 1134,

1232, 1301, 1311, 1437, 1454, 1497, 2934; HRMS (ESI^+) m/z 282.1062 ($[M+H]^+$, $C_{16}H_{16}N_3S^+$ requires 282.1059).

Regiochemistries of the isomers **29** and **29'** were determined by the NOESY experiments.

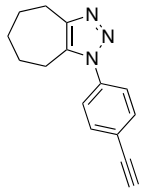


1-Benzyl-4,5,6,7,8,9-hexahydro-1*H*-cycloocta[*d*][1,2,3]triazole (**31**)



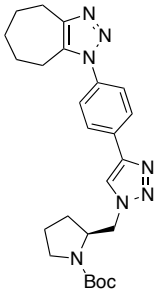
Colorless oil; TLC R_f 0.41 (*n*-hexane/EtOAc = 1/1); ^1H NMR ($CDCl_3$, 500 MHz) δ 1.33–1.43 (m, 4H, aliphatic), 1.47–1.55 (m, 2H, aliphatic), 1.69–1.77 (m, 2H, aliphatic), 2.59–2.64 (m, 2H, aliphatic), 2.87–2.93 (m, 2H, aliphatic), 5.46 (s, 2H, CH_2), 7.12–7.16 (m, 2H, aromatic), 7.27–7.35 (m, 3H, aromatic); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 21.7 (1C), 24.6 (1C), 24.8 (1C), 25.86 (1C), 25.90 (1C), 28.2 (1C), 51.8 (1C), 127.0 (2C), 128.1 (1C), 128.9 (2C), 133.2 (1C), 135.5 (1C), 145.3 (1C); IR (KBr, cm^{-1}) 1433, 1440, 1453, 1495, 2848, 2897, 2911, 2918, 2924; HRMS (ESI^+) m/z 264.1460 ($[M+Na]^+$, $C_{15}H_{19}N_3Na^+$ requires 264.1471).

1-(4-Ethynylphenyl)-1,4,5,6,7,8-hexahydrocyclohepta[*d*][1,2,3]triazole



Pale yellow solid; Mp 128–129 ºC; TLC R_f 0.46 (*n*-hexane/EtOAc = 1/1); ^1H NMR ($CDCl_3$, 500 MHz) δ 1.67–1.73 (m, 2H, aliphatic), 1.73–1.80 (m, 2H, aliphatic), 1.85–1.91 (m, 2H, aliphatic), 2.72–2.77 (m, 2H, aliphatic), 2.94–2.99 (m, 2H, aliphatic), 3.19 (s, 1H, CH), 7.37–7.41 (AA'BB', 2H, aromatic), 7.62–7.66 (AA'BB', 2H, aromatic); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 24.8 (1C), 27.00 (1C), 27.02 (1C), 27.2 (1C), 30.8 (1C), 79.1 (1C), 82.3 (1C), 123.2 (1C), 125.1 (2C), 133.1 (2C), 135.6 (1C), 136.5 (1C), 147.7 (1C); IR (KBr, cm^{-1}) 843, 848, 1002, 1245, 1442, 1507, 2846, 2916, 2920, 3280; HRMS (ESI^+) m/z 238.1348 ($[M+H]^+$, $C_{15}H_{16}N_3^+$ requires 238.1339).

(*S*)-1-(4-(1-((1-(*tert*-Butoxycarbonyl)pyrrolidin-2-yl)methyl)-1*H*-1,2,3-triazol-4-yl)phenyl)-1,4,5,6,7,8-hexahydrocyclohepta[*d*][1,2,3]triazole (**35**)

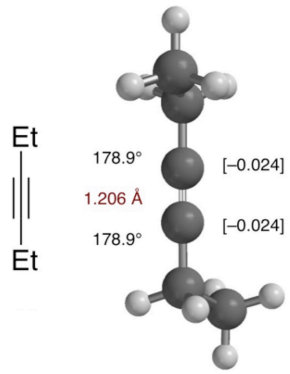


Colorless solid; Mp 168–170 ºC; TLC R_f 0.22 (*n*-hexane/EtOAc = 1/3); ^{1}H NMR ($CDCl_3$, 500 MHz, 60 ºC) δ 1.51 (s, 9H, CH_3×3), 1.52–2.05 (m, 10H, aliphatic), 2.73–2.79 (m, 2H, aliphatic), 2.94–3.00 (m, 2H, aliphatic), 3.15–3.24 (m, 1H, CH_2), 3.31–3.43 (m, 1H, CH_2), 4.13–4.22 (m, 1H, CH), 4.50–4.78 (m, 2H, CH_2), 7.44–7.49 (AA'BB', 2H, aromatic), 7.80 (br s, 1H, CH), 7.94–7.99 (AA'BB', 2H, aromatic); ^{13}C NMR ($CDCl_3$, 126 MHz, 60 ºC) δ 23.3 (1C), 24.9 (1C), 27.1 (1C), 27.16 (1C), 27.22 (1C), 28.6 (3C), 28.8 (1C), 30.9 (1C), 47.1 (1C), 52.1 (1C), 57.4 (1C), 80.3 (1C), 120.9 (1C), 125.8 (2C), 126.6 (2C), 131.8 (1C), 135.6 (1C), 136.4 (1C), 146.7 (1C), 147.5 (1C), 154.7 (1C); IR (KBr, cm^{-1}) 1109, 1115, 1163, 1364, 1393, 1456, 1501, 1682, 2916, 2922; HRMS (ESI^+) m/z 464.2776 ($[M+H]^+$, $C_{25}H_{34}N_7O_2^+$ requires 464.2768).

Computational Methods

The optimized structures of cycloalkynes, benzyne, methyl azide, and furan (Fig. 2) were computed in Spartan '14[S16] using density functional theory (B3LYP/6-311+G(d,p)).

3-Hexyne

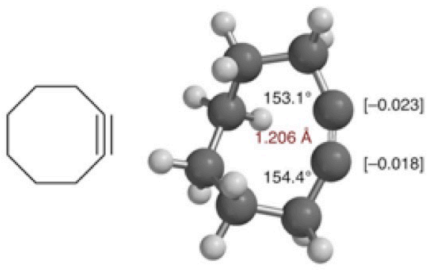


LUMO 0.0 eV
HOMO –6.9 eV

Cartesian Coordinates (Angstroms)

	Atom		X	Y	Z
1	H	H1	–2.7220248	–0.7667846	1.2947561
2	C	C1	–2.9524395	–0.4318857	0.2809385
3	H	H2	–2.9094977	–1.3011553	–0.3790919
4	H	H4	–3.9740376	–0.0424188	0.2707235
5	C	C2	–1.9597043	0.6520398	–0.1764694
6	H	H5	–2.0463312	1.5265288	0.4787549
7	H	H6	–2.2326377	0.9973616	–1.1803719
8	C	C3	–0.5695695	0.1974666	–0.1852641
9	C	C4	0.5695695	–0.1974666	–0.1852641
10	C	C5	1.9597043	–0.6520398	–0.1764694
11	H	H3	2.2326377	–0.9973616	–1.1803719
12	H	H7	2.0463312	–1.5265288	0.4787549
13	C	C6	2.9524395	0.4318857	0.2809385
14	H	H8	3.9740376	0.0424188	0.2707235
15	H	H9	2.7220248	0.7667846	1.2947561
16	H	H10	2.9094977	1.3011553	–0.3790919

Cyclooctyne (**13**)

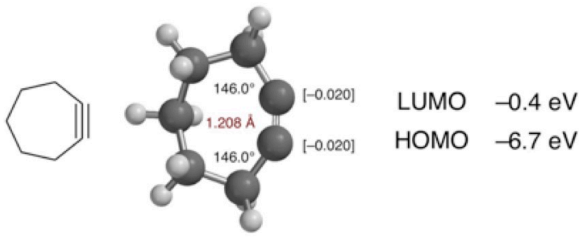


LUMO 0.0 eV
HOMO –6.8 eV

Cartesian Coordinates (Angstroms)

	Atom		X	Y	Z
1	C	C1	0.4170969	−1.5518774	0.2102533
2	C	C2	−0.7789185	−1.4735465	0.0750881
3	C	C3	1.7826071	−1.0305790	0.1907328
4	H	H1	2.1640942	−0.8949335	1.2097649
5	H	H4	2.4798646	−1.7035025	−0.3185865
6	C	C4	−2.0262627	−0.7290464	−0.0902356
7	H	H2	−2.6224328	−0.7620216	0.8288405
8	H	H5	−2.6572765	−1.1290124	−0.8896862
9	C	C5	1.7203466	0.3255957	−0.5629992
10	H	H7	1.3225835	0.1228713	−1.5622255
11	H	H8	2.7444783	0.6903670	−0.7088929
12	C	C6	0.9211649	1.4782790	0.0936361
13	H	H3	1.4904466	1.8335852	0.9617382
14	H	H10	0.9422912	2.3065668	−0.6255216
15	C	C7	−0.5467307	1.3062855	0.5785486
16	H	H11	−0.8670355	2.3075094	0.8875607
17	H	H12	−0.5543607	0.7034277	1.4909110
18	C	C8	−1.6071782	0.7392881	−0.4048060
19	H	H13	−2.5063115	1.3640825	−0.3835876
20	H	H14	−1.2290937	0.7746657	−1.4316237

Cycloheptyne (**3**)

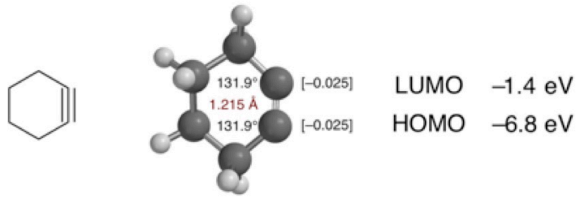


Cartesian Coordinates (Angstroms)

	Atom		X	Y	Z
1	C	C1	−0.0023823	−1.3977733	0.6039014
2	C	C2	−0.0023823	−1.3977733	−0.6039014
3	C	C3	−0.0485301	−0.5783477	1.8192174
4	H	H1	−1.0446288	−0.6279257	2.2737281
5	H	H4	0.6651414	−0.8872321	2.5884357
6	C	C4	0.2612130	0.8700894	1.3341412
7	H	H5	1.3461396	0.9701784	1.2211487
8	H	H6	−0.0376747	1.5684025	2.1242169
9	C	C5	−0.4145932	1.3054947	0.0000000
10	H	H3	−1.4659621	0.9922678	0.0000000
11	H	H8	−0.4280423	2.4002969	0.0000000
12	C	C6	0.2612130	0.8700894	−1.3341412
13	H	H9	1.3461396	0.9701784	−1.2211487

14	H	H10	−0.0376747	1.5684025	−2.1242169
15	C	C7	−0.0485301	−0.5783477	−1.8192174
16	H	H7	−1.0446288	−0.6279257	−2.2737281
17	H	H12	0.6651414	−0.8872321	−2.5884357

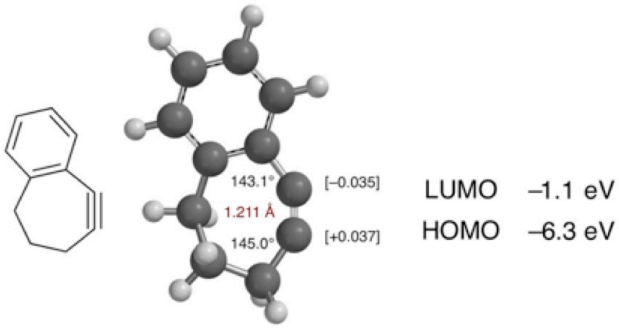
Cyclohexyne (**1**)



Cartesian Coordinates (Angstroms)

Atom			X	Y	Z
1	C	C1	0.6067344	−0.0258114	1.2988828
2	C	C2	−0.6067344	0.0258114	1.2988828
3	C	C3	1.5904050	−0.1142125	0.2006802
4	H	H1	2.4439349	0.5620711	0.2935570
5	H	H4	1.9900439	−1.1294501	0.1115664
6	C	C4	−1.5904050	0.1142125	0.2006802
7	H	H2	−1.9900439	1.1294501	0.1115664
8	H	H5	−2.4439349	−0.5620711	0.2935570
9	C	C5	−0.7216105	−0.2780425	−1.0557521
10	H	H7	−1.2350357	0.0688125	−1.9591122
11	H	H8	−0.6847500	−1.3712670	−1.1088770
12	C	C6	0.7216105	0.2780425	−1.0557521
13	H	H9	1.2350357	−0.0688125	−1.9591122
14	H	H10	0.6847500	1.3712670	−1.1088770

Benzo-fused cycloheptyne **10**

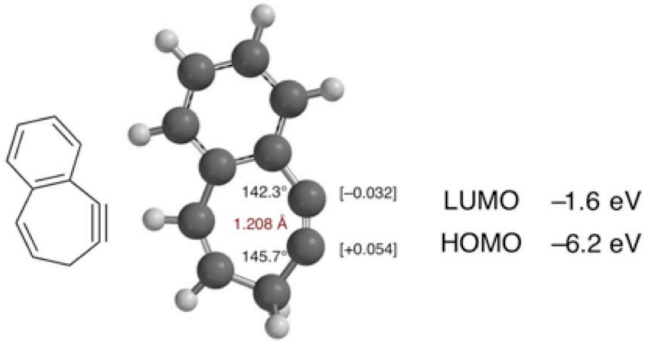


Cartesian Coordinates (Angstroms)

Atom			X	Y	Z
1	C	C1	−0.7760307	−1.4950497	−0.1562337
2	C	C2	−1.9740846	−1.3214586	−0.1111163
3	C	C3	0.4819276	−0.8126286	−0.1071188
4	C	C4	2.7469913	0.7931780	0.1167290
5	C	C5	0.3341799	0.6023557	−0.1558078
6	C	C6	1.7423701	−1.3953730	0.0399640
7	C	C7	2.8753205	−0.5928061	0.1493412

8	C	C8	1.4875169	1.3777263	−0.0352728
9	H	H6	1.8252831	−2.4752923	0.0746925
10	H	H5	3.8524776	−1.0479646	0.2642398
11	H	H3	1.4030035	2.4596505	−0.0683830
12	H	H4	3.6249867	1.4232058	0.2057295
13	C	C9	−1.0160037	1.2760409	−0.4169491
14	H	H7	−1.2963933	1.0649633	−1.4575685
15	H	H8	−0.8464459	2.3549576	−0.3655124
16	C	C10	−2.2529834	0.9562482	0.4812609
17	H	H1	−1.9344468	0.8643934	1.5233704
18	H	H10	−2.9383253	1.8090933	0.4308923
19	C	C11	−3.0368929	−0.3324618	0.0870507
20	H	H9	−3.6160847	−0.1793245	−0.8299025
21	H	H11	−3.7479217	−0.6083100	0.8713577

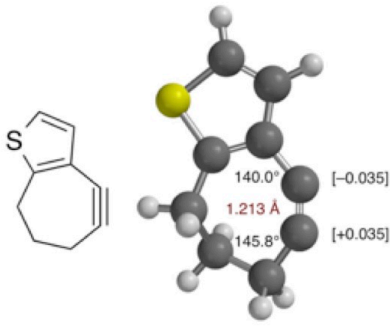
Benzo-fused cycloheptyne **11**



Cartesian Coordinates (Angstroms)

Atom			X	Y	Z
1	H	H1	−1.7756262	−2.4703721	0.0000000
2	C	C1	−1.6952140	−1.3897977	0.0000000
3	C	C4	−1.4474529	1.3817990	0.0000000
4	C	C2	−0.4304455	−0.8049456	0.0000000
5	C	C6	−2.8380651	−0.5921577	0.0000000
6	C	C5	−2.7117302	0.7945201	0.0000000
7	C	C3	−0.2756805	0.6123842	0.0000000
8	H	H6	−3.8198231	−1.0516864	0.0000000
9	H	H5	−3.5955725	1.4222392	0.0000000
10	H	H4	−1.3643879	2.4639458	0.0000000
11	C	C7	0.8258778	−1.4860776	0.0000000
12	C	C8	2.0186682	−1.2925315	0.0000000
13	C	C9	3.0775976	−0.2862147	0.0000000
14	H	H2	3.7340907	−0.3550980	−0.8762679
15	H	H7	3.7340907	−0.3550980	0.8762679
16	C	C10	2.3345208	1.0477505	0.0000000
17	H	H9	3.0044209	1.9066774	0.0000000
18	C	C11	1.0164898	1.3511326	0.0000000
19	H	H8	0.8354115	2.4242232	0.0000000

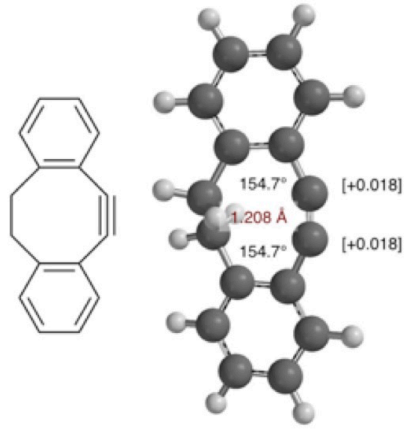
Thieno-fused cycloheptyne **12**



Cartesian Coordinates (Angstroms)

Atom		X	Y	Z
1	C C1	2.6619757	−0.5183648	−0.1479229
2	H H2	3.7289679	−0.6195888	−0.2727558
3	C C2	1.7168912	−1.5000270	−0.0898413
4	H H4	1.9386374	−2.5559677	−0.1651468
5	C C3	0.3995210	−0.9754589	0.0746500
6	C C4	0.3531736	0.4081958	0.1389670
7	S S1	1.9571296	1.0637895	−0.0077768
8	C C5	−0.8950741	−1.5820785	0.1244677
9	C C6	−2.0669691	−1.2699910	0.1329623
10	C C7	−0.8653084	1.2774743	0.3873893
11	H H1	−1.1379973	1.1782006	1.4467310
12	H H6	−0.5752192	2.3228146	0.2500488
13	C C8	−2.1518781	1.0344467	−0.4675661
14	H H7	−1.8684802	0.9035116	−1.5151143
15	H H8	−2.7630431	1.9410121	−0.4098035
16	C C9	−3.0323405	−0.1801011	−0.0368669
17	H H5	−3.5689114	0.0302128	0.8941114
18	H H9	−3.7879761	−0.3853996	−0.8010758

Dibenzo-fused cyclooctyne **14**

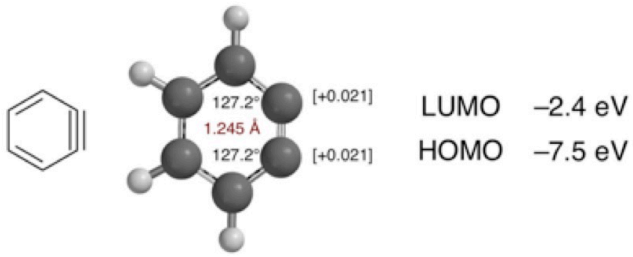


Cartesian Coordinates (Angstroms)

Atom		X	Y	Z
1	H H1	3.1094207	-0.3669340	2.5203857
2	C C1	3.1086447	-0.1943833	1.4506241
3	C C4	3.0678358	0.2354755	-1.3040823

4	C	C2	1.8914866	0.0237480	0.7942212
5	C	C6	4.2993898	-0.1968537	0.7316242
6	C	C5	4.2787065	0.0128032	-0.6461568
7	C	C3	1.8583528	0.2572867	-0.6104133
8	H	H6	5.2398056	-0.3653975	1.2438306
9	H	H5	5.2045581	0.0090617	-1.2103467
10	H	H4	3.0656794	0.4078823	-2.3756843
11	C	C7	0.6065082	-0.0063708	1.3997192
12	C	C8	-0.6065082	0.0063708	1.3997192
13	C	C9	-1.8914866	-0.0237480	0.7942212
14	C	C10	-4.2787065	-0.0128032	-0.6461568
15	C	C11	-3.1086447	0.1943833	1.4506241
16	C	C12	-1.8583528	-0.2572867	-0.6104133
17	C	C13	-3.0678358	-0.2354755	-1.3040823
18	C	C14	-4.2993898	0.1968537	0.7316242
19	H	H2	-3.1094207	0.3669340	2.5203857
20	H	H8	-3.0656794	-0.4078823	-2.3756843
21	H	H9	-5.2398056	0.3653975	1.2438306
22	H	H10	-5.2045581	-0.0090617	-1.2103467
23	C	C15	0.5484558	0.5678511	-1.3111643
24	H	H3	0.1190592	1.4657075	-0.8561587
25	H	H12	0.7729233	0.8284571	-2.3482579
26	C	C16	-0.5484558	-0.5678511	-1.3111643
27	H	H13	-0.1190592	-1.4657075	-0.8561587
28	H	H14	-0.7729233	-0.8284571	-2.3482579

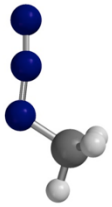
Benzyne (**6**)



Cartesian Coordinates (Angstroms)

Atom			X	Y	Z
1	H	H1	2.5411488	0.0000000	−0.1362158
2	C	C1	1.4589926	0.0000000	−0.1339193
3	C	C4	−1.4589926	0.0000000	−0.1339193
4	C	C2	0.6222873	0.0000000	−1.2345866
5	C	C6	0.7025569	0.0000000	1.0568152
6	C	C5	−0.7025569	0.0000000	1.0568152
7	C	C3	−0.6222873	0.0000000	−1.2345866
8	H	H6	1.2282992	0.0000000	2.0063597
9	H	H5	−1.2282992	0.0000000	2.0063597
10	H	H4	−2.5411488	0.0000000	−0.1362158

Methyl azide

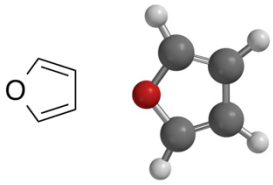
MeN_3 

LUMO –1.2 eV
HOMO –7.3 eV

Cartesian Coordinates (Angstroms)

	Atom		X	Y	Z
1	H	H1	2.4363908	–0.3460108	–0.0106113
2	C	C1	1.5482572	0.2816851	0.0000100
3	H	H2	1.5669052	0.9073577	0.8983468
4	H	H4	1.5563473	0.9225937	–0.8877672
5	N	N1	0.3891638	–0.6286121	–0.0001507
6	N	N2	–0.7178604	–0.0957999	0.0002738
7	N	N3	–1.7926158	0.2709761	–0.0001272

Furan

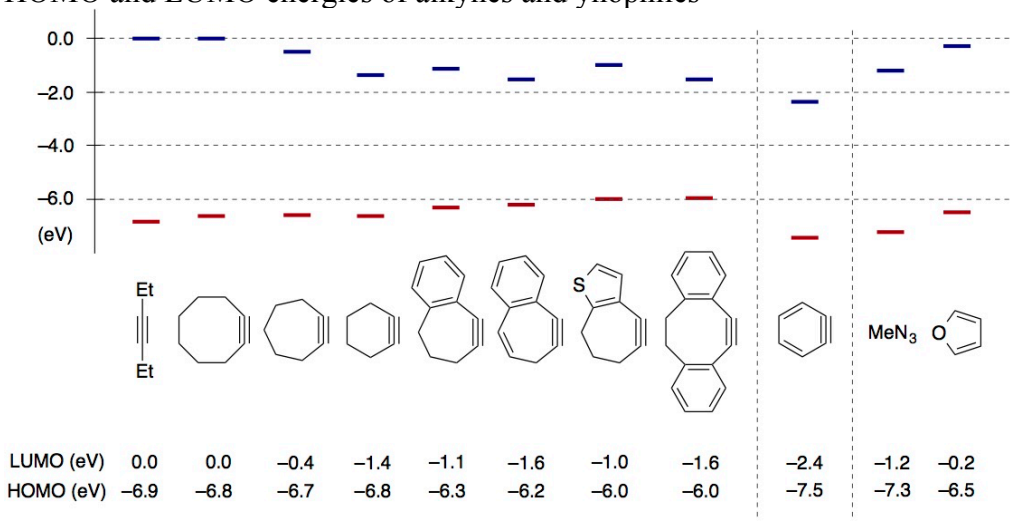


LUMO –0.2 eV
HOMO –6.5 eV

Cartesian Coordinates (Angstroms)

	Atom		X	Y	Z
1	C	C1	1.0952698	0.0000000	-0.3469016
2	H	H2	2.0498500	0.0000000	-0.8449795
3	C	C2	0.7176721	0.0000000	0.9577108
4	H	H4	1.3732770	0.0000000	1.8139158
5	C	C3	-0.7176721	0.0000000	0.9577108
6	H	H5	-1.3732770	0.0000000	1.8139158
7	C	C4	-1.0952698	0.0000000	-0.3469016
8	H	H6	-2.0498500	0.0000000	-0.8449795
9	O	O1	0.0000000	0.0000000	-1.1584479

HOMO and LUMO energies of alkynes and ynophiles



LUMO (eV)	0.0	0.0	–0.4	–1.4	–1.1	–1.6	–1.0	–1.6	–2.4	–1.2	–0.2
HOMO (eV)	–6.9	–6.8	–6.7	–6.8	–6.3	–6.2	–6.0	–6.0	–7.5	–7.3	–6.5

References for Supporting Information

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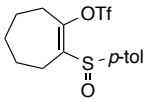
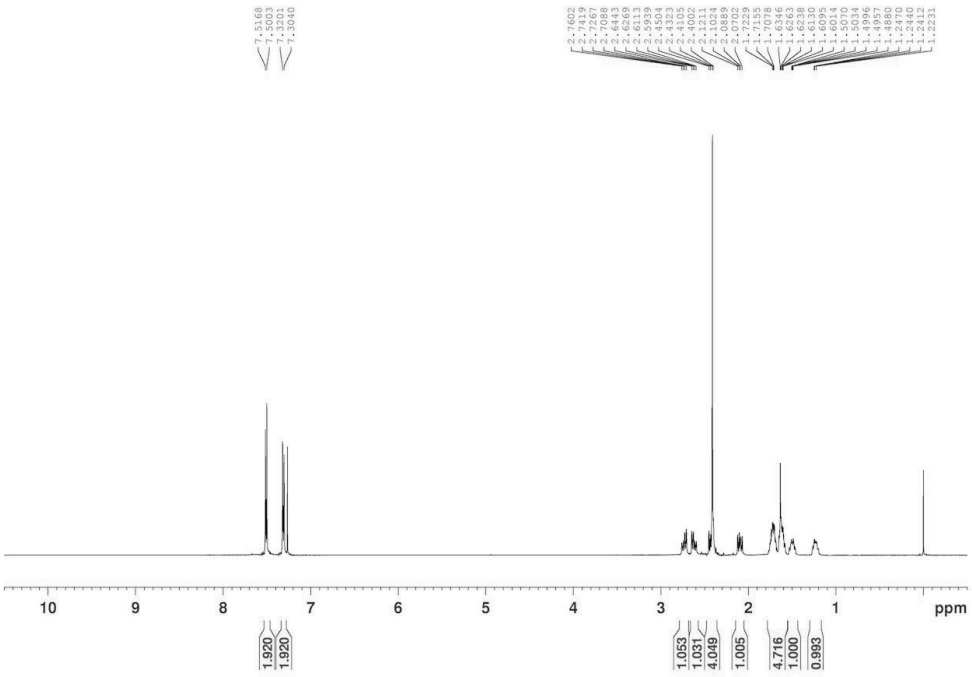
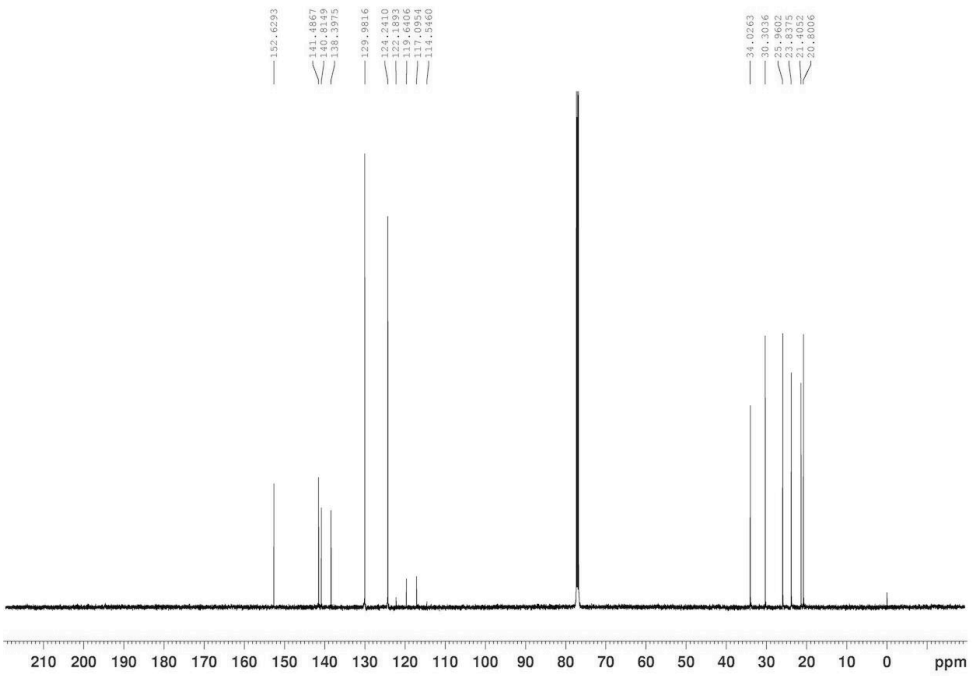
^{1}H and ^{13}C NMR Spectra of Compounds

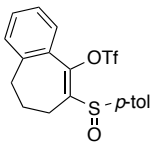
^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of **8** ($CDCl_3$)

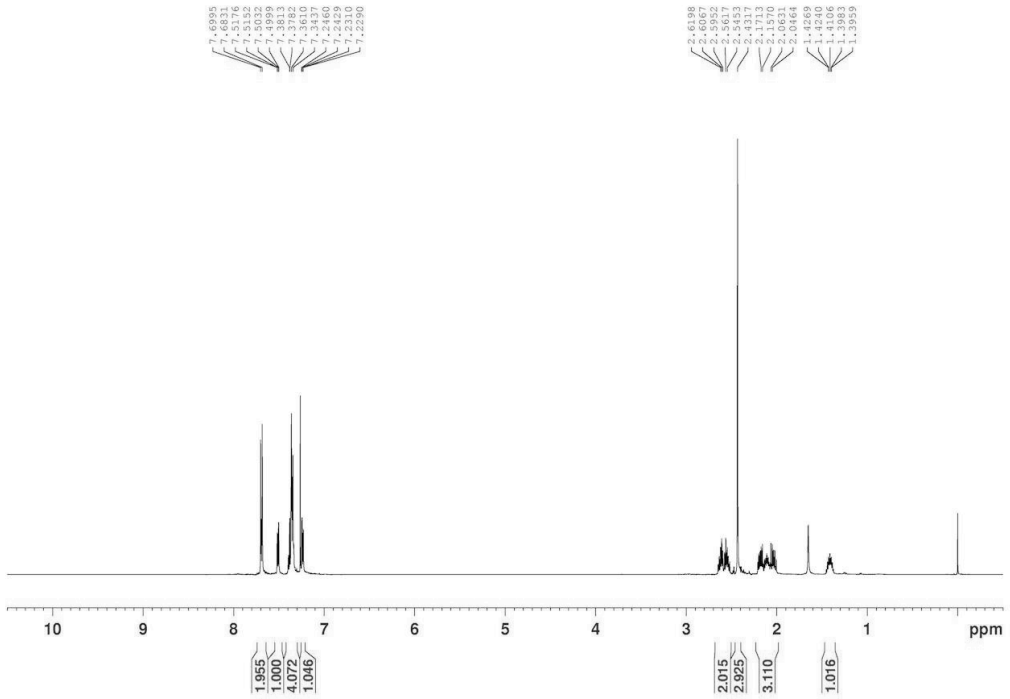


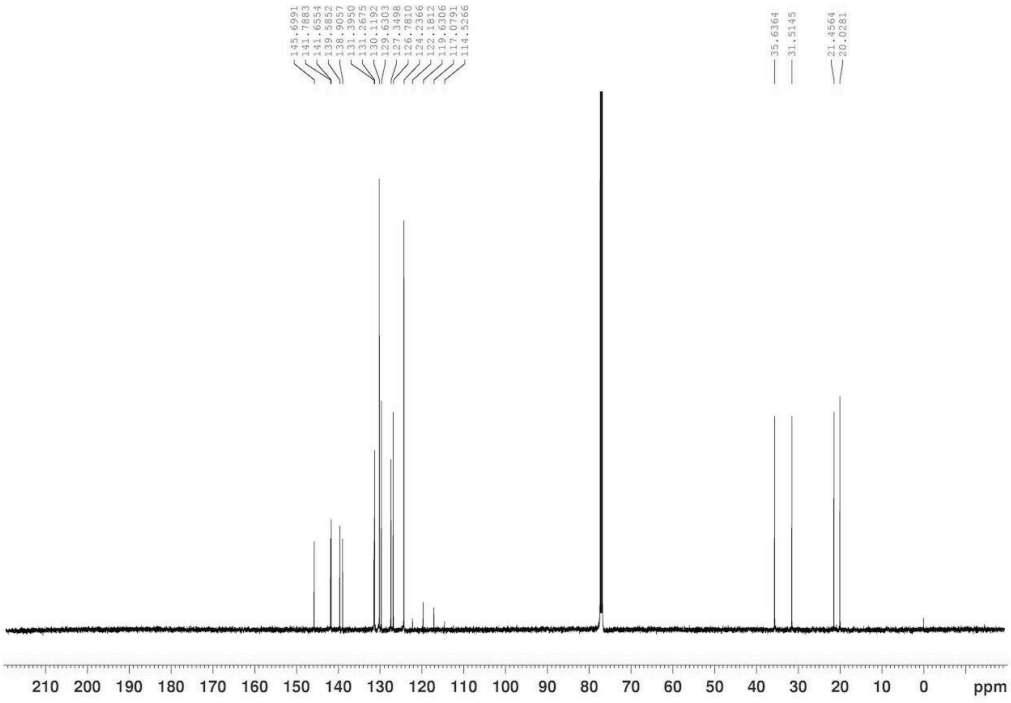




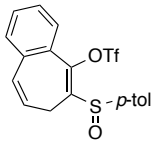
^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of **15** ($CDCl_3$)

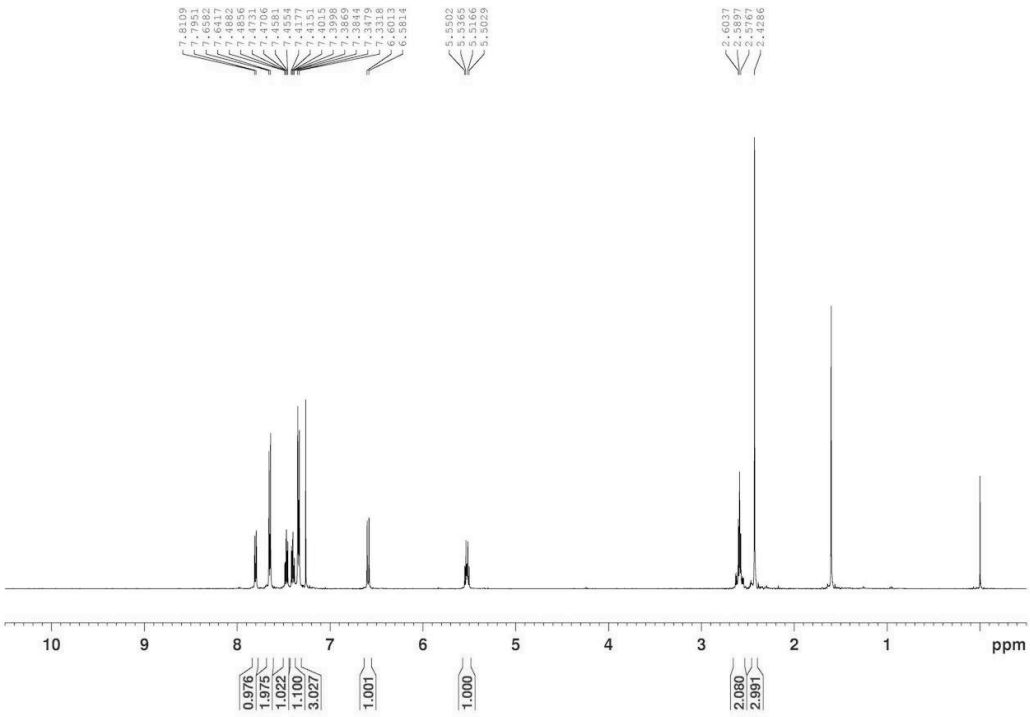


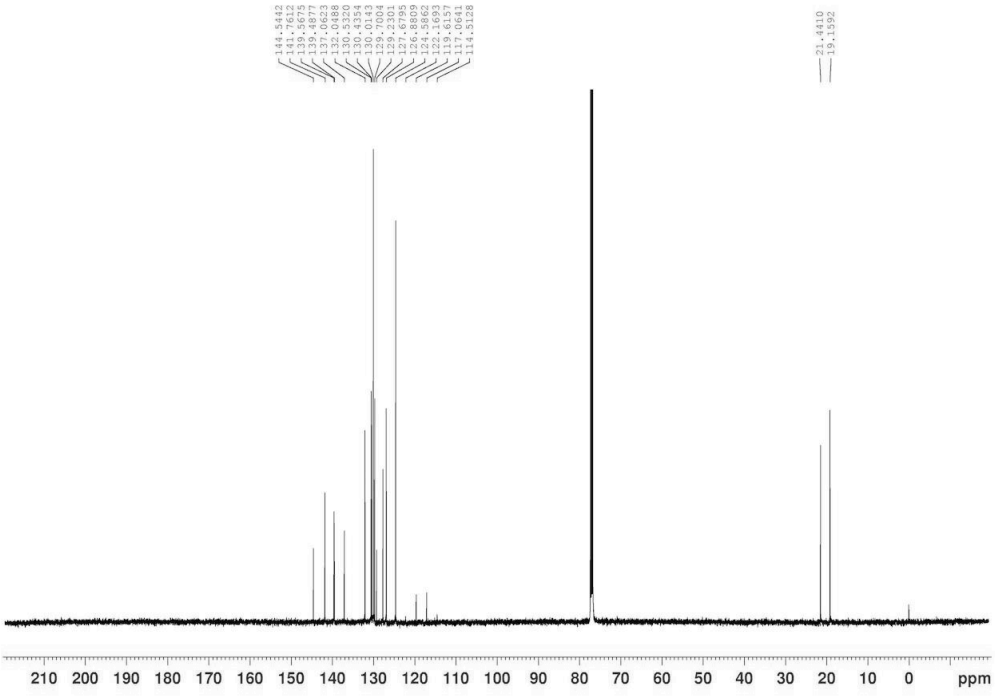




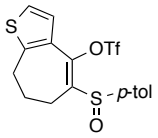
^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of **16** ($CDCl_3$)

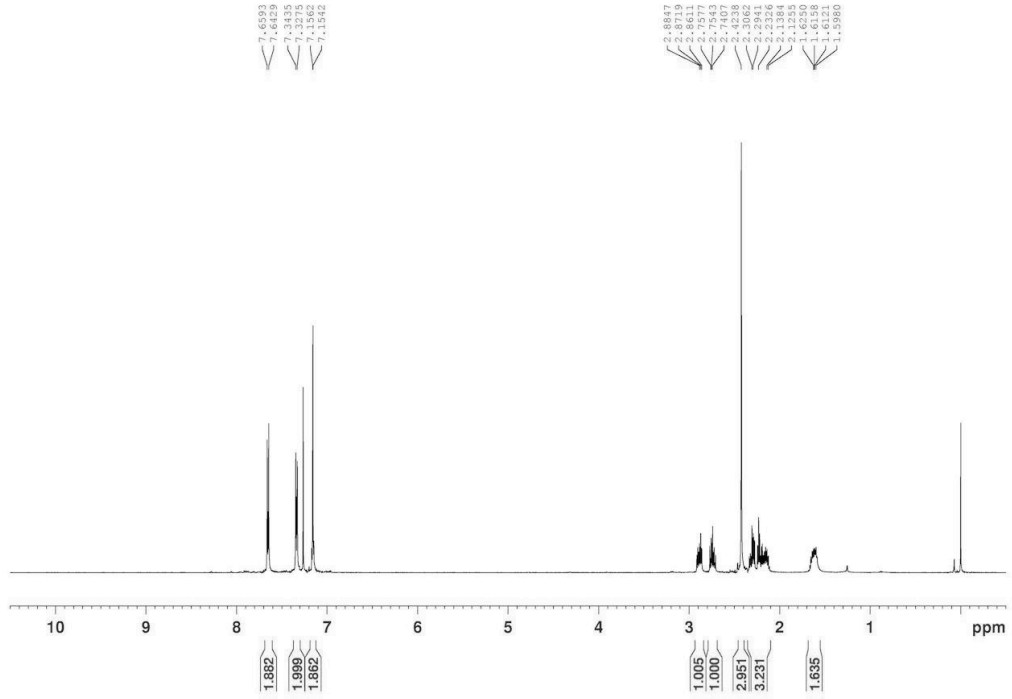


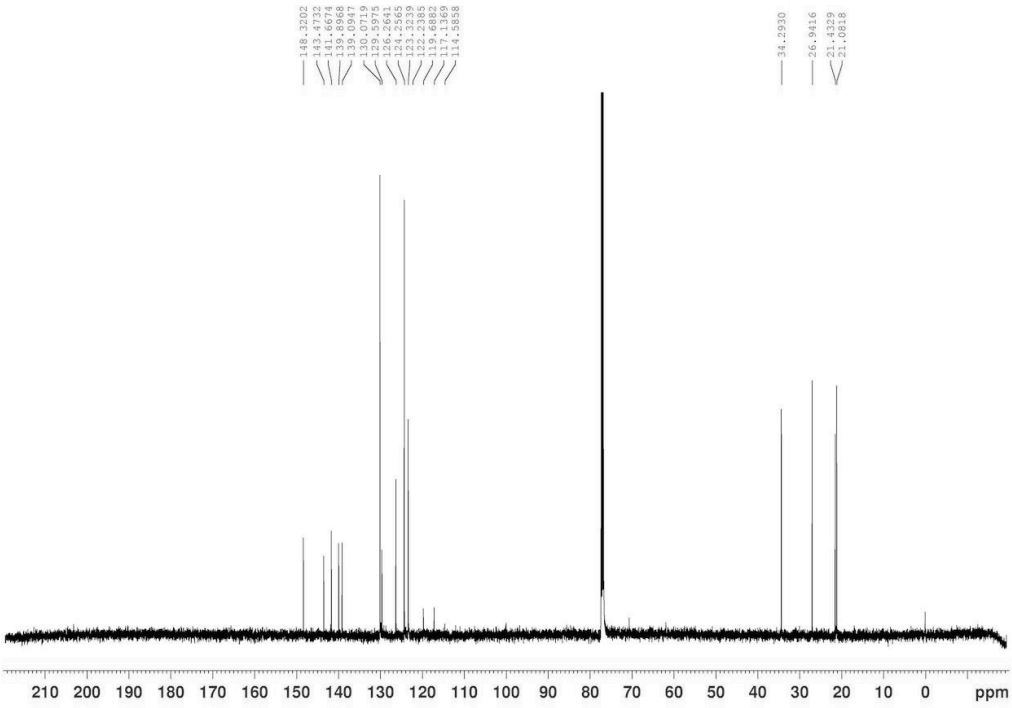




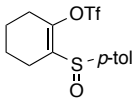
^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of **17** ($CDCl_3$)

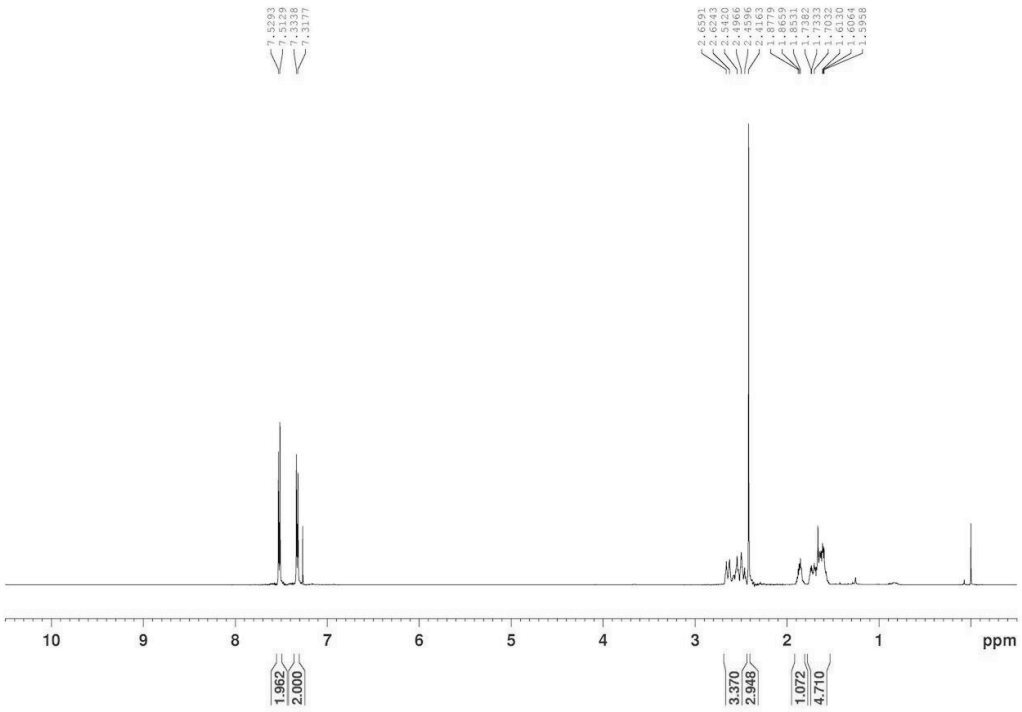


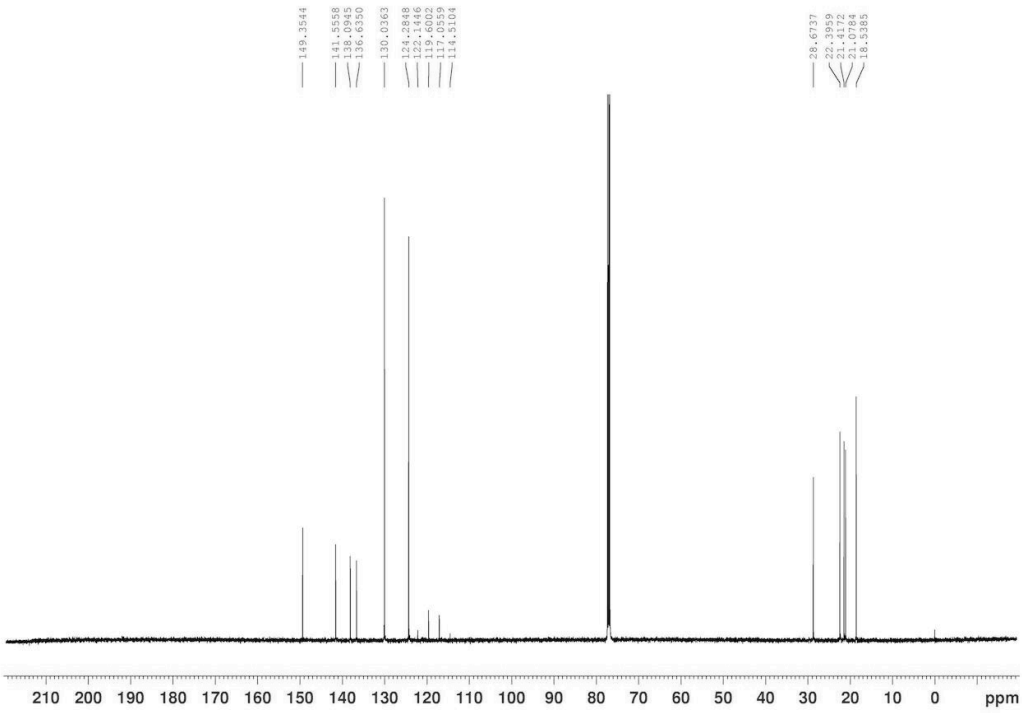




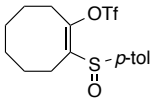
^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of **18** ($CDCl_3$)

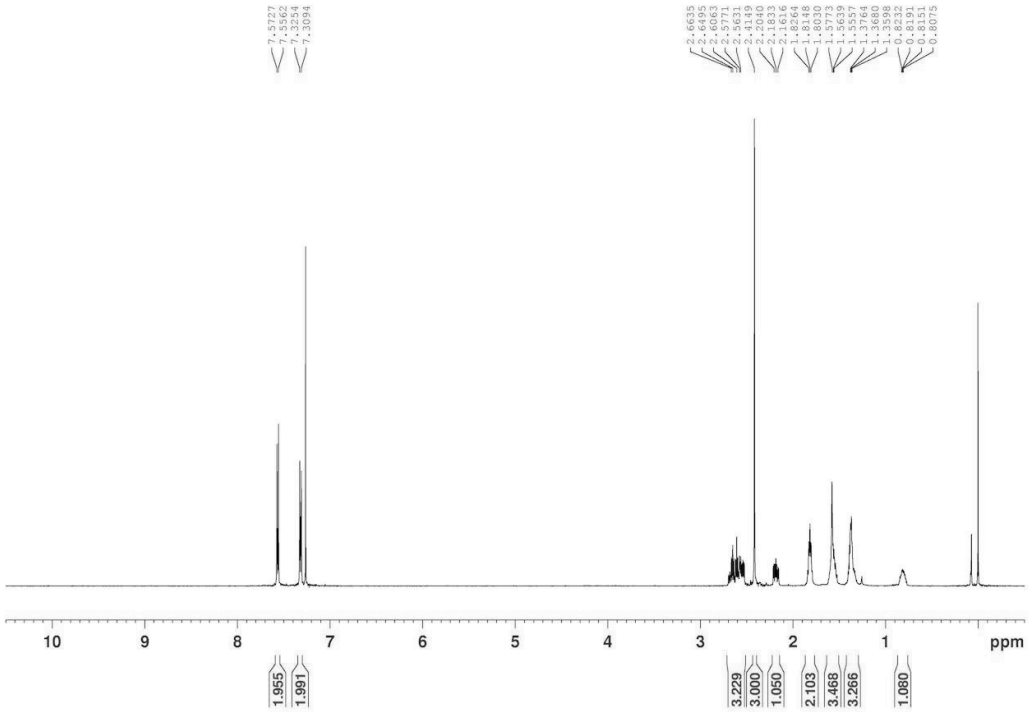


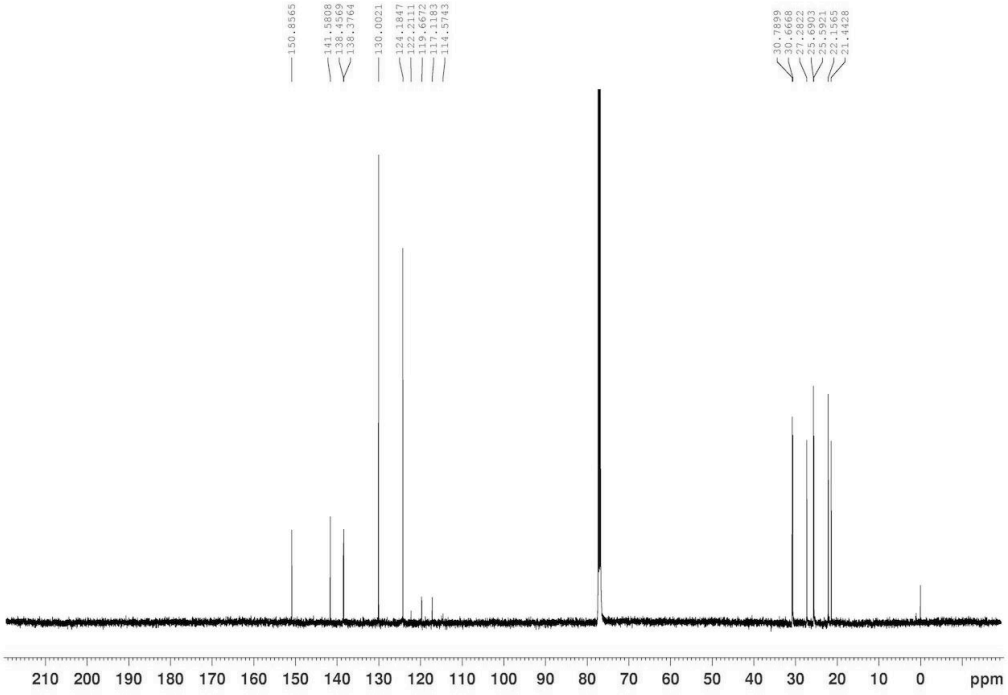




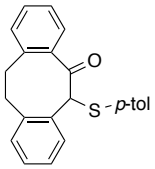
^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of **19** ($CDCl_3$)

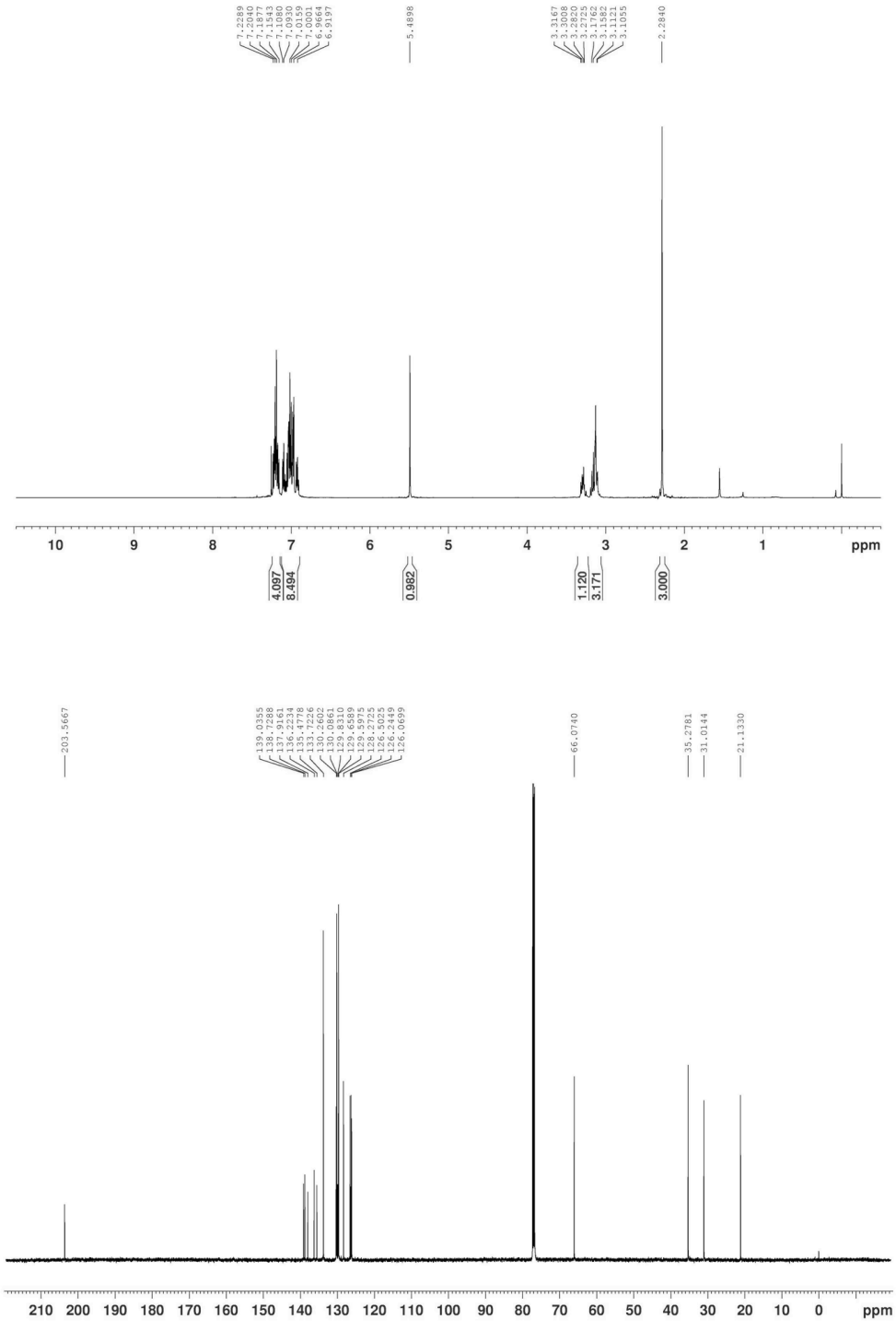




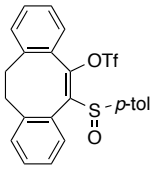


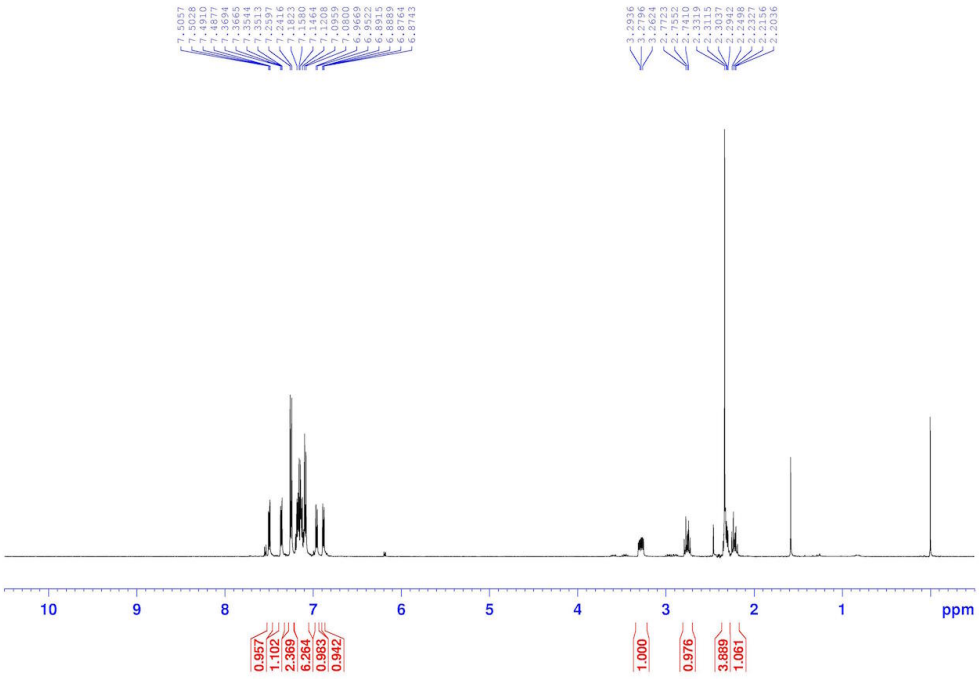
^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of
6-(4-tolylthio)-11,12-dihydrodibenzo[*a*,*e*]cyclooctan-5(6*H*)-one ($CDCl_3$)

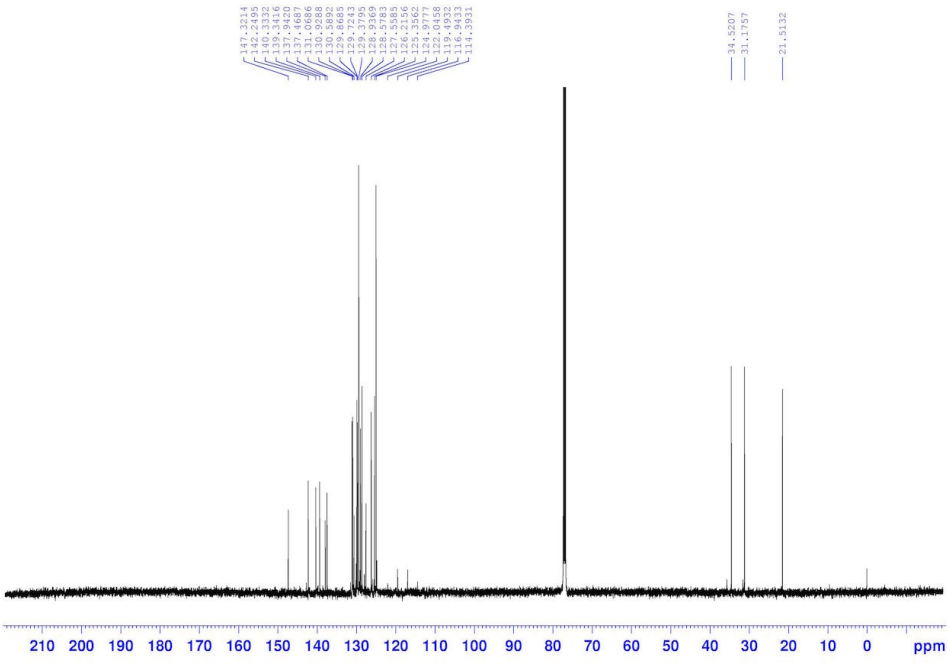




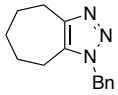
^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of **20** ($CDCl_3$)
(a mixture of diastereomers (major/minor = 84/16 judged from ^{1}H NMR analysis))

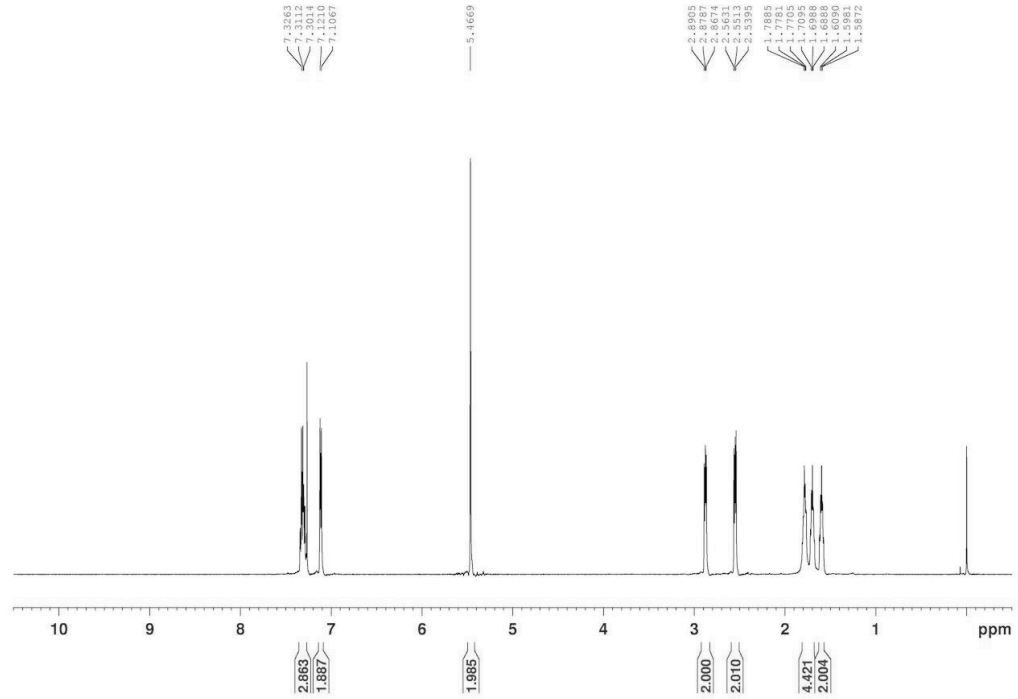


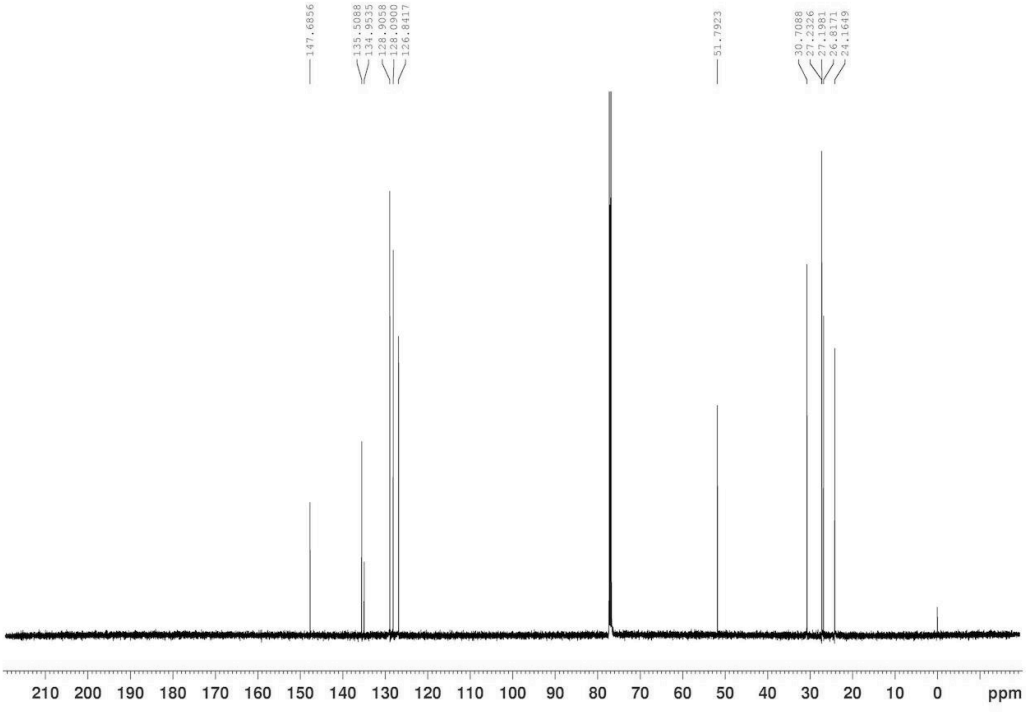




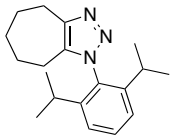
^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of **21a** ($CDCl_3$)

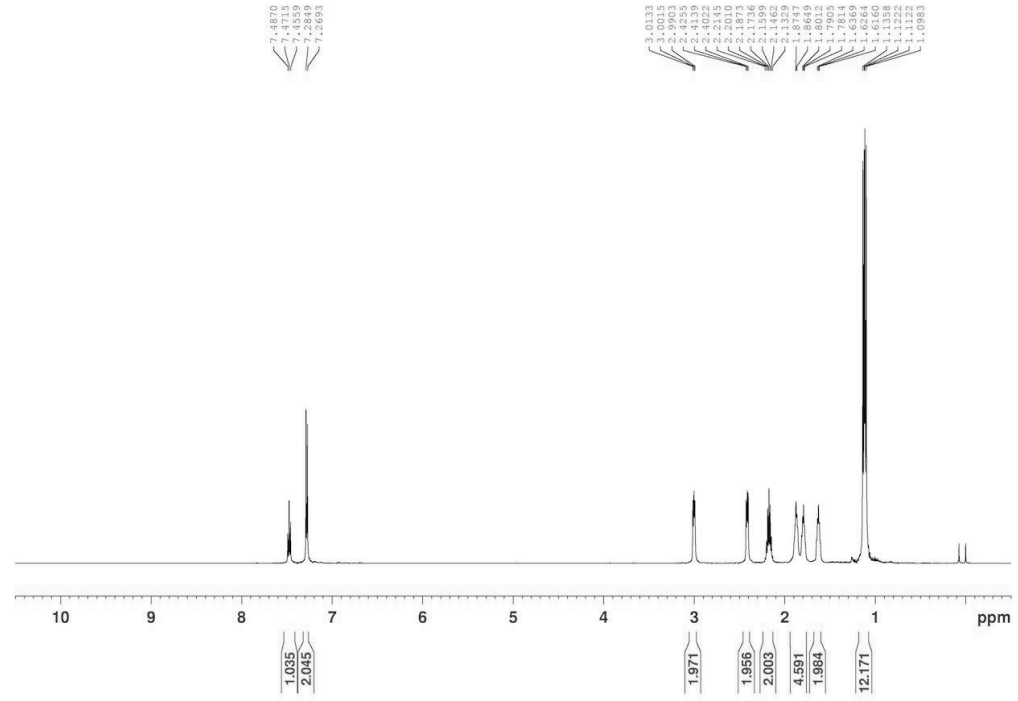


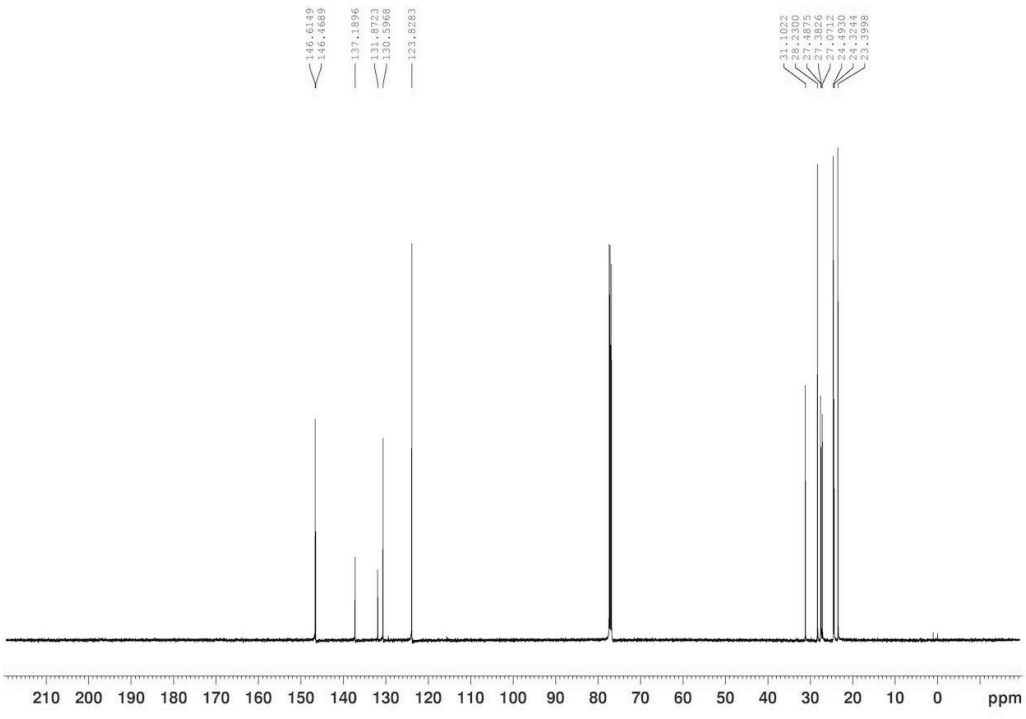




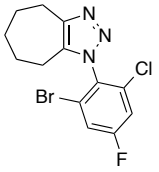
^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of **21b** ($CDCl_3$)

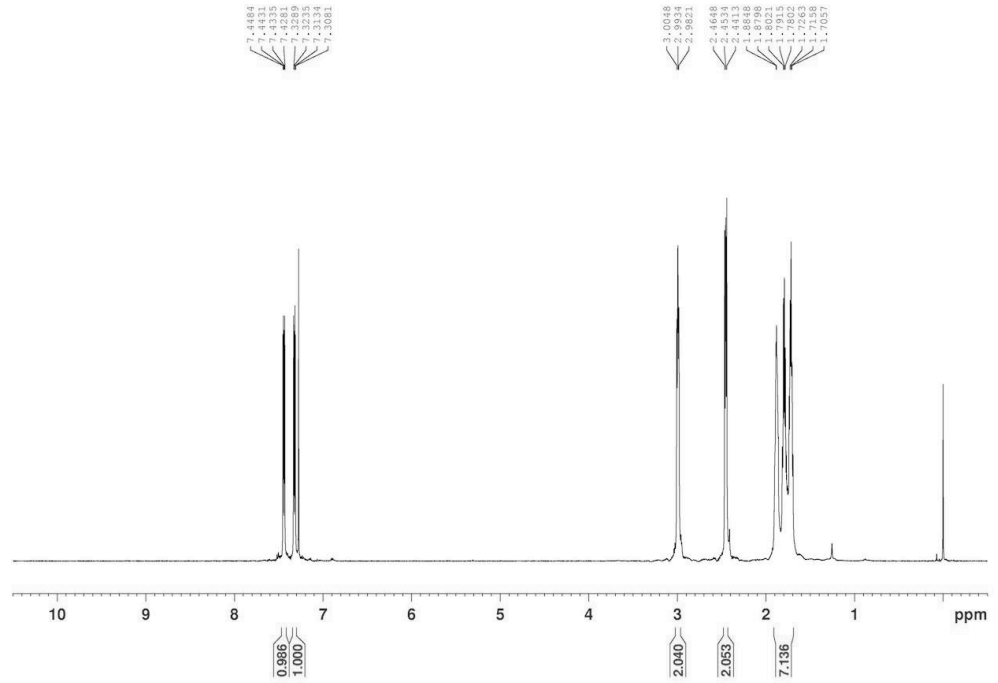


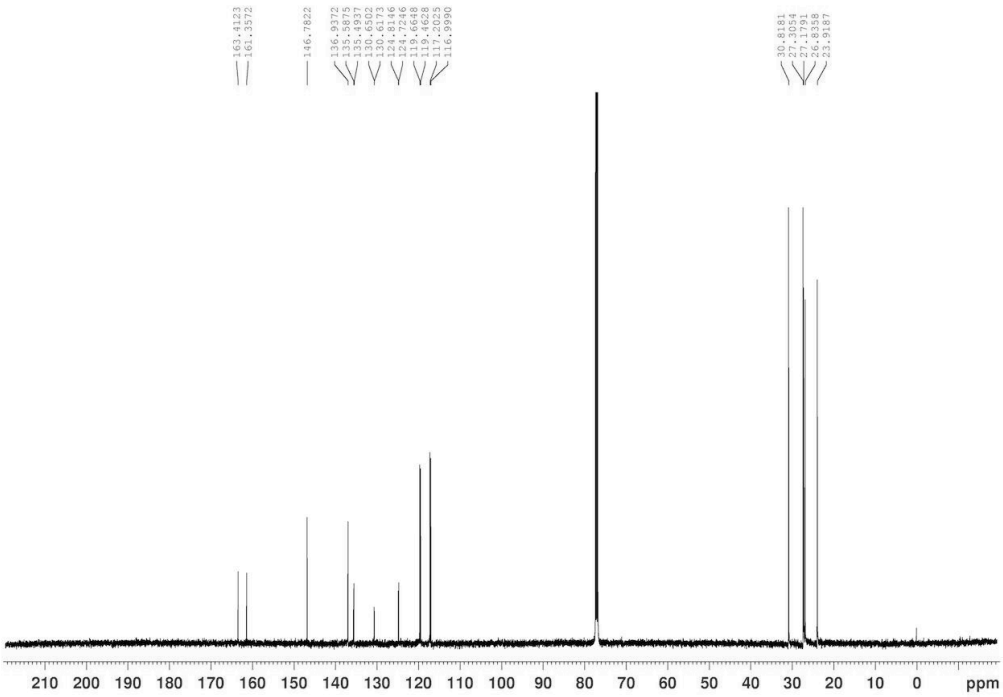




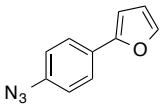
^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of **21c** ($CDCl_3$)

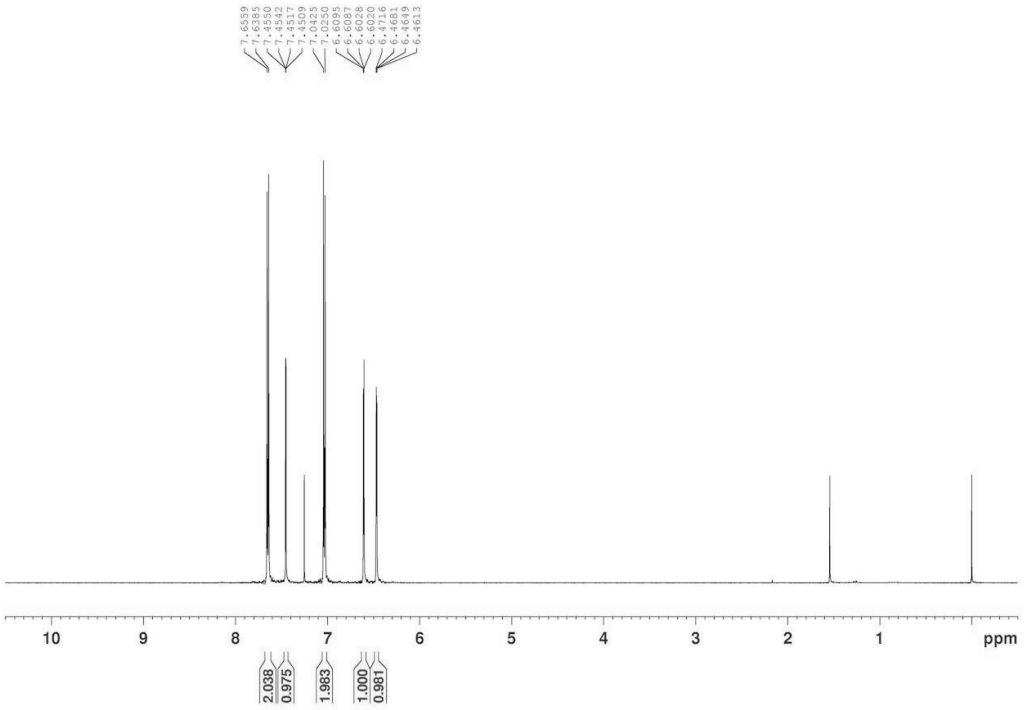


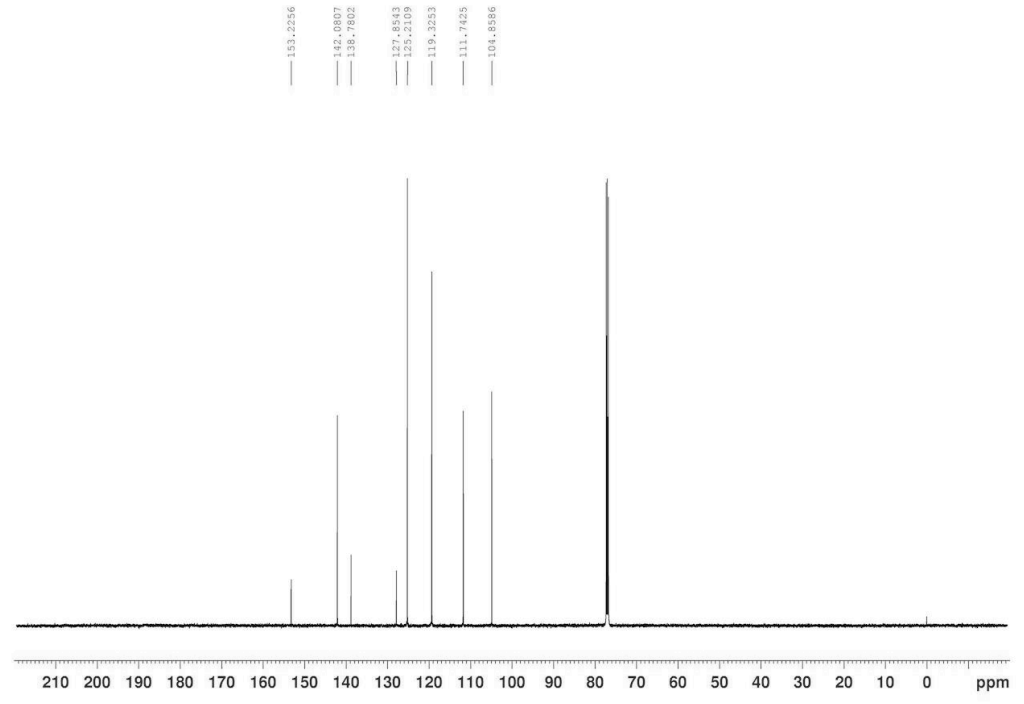




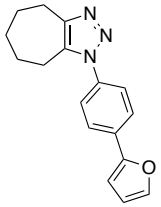
^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of
4-(2-furyl)phenyl azide ($CDCl_3$)

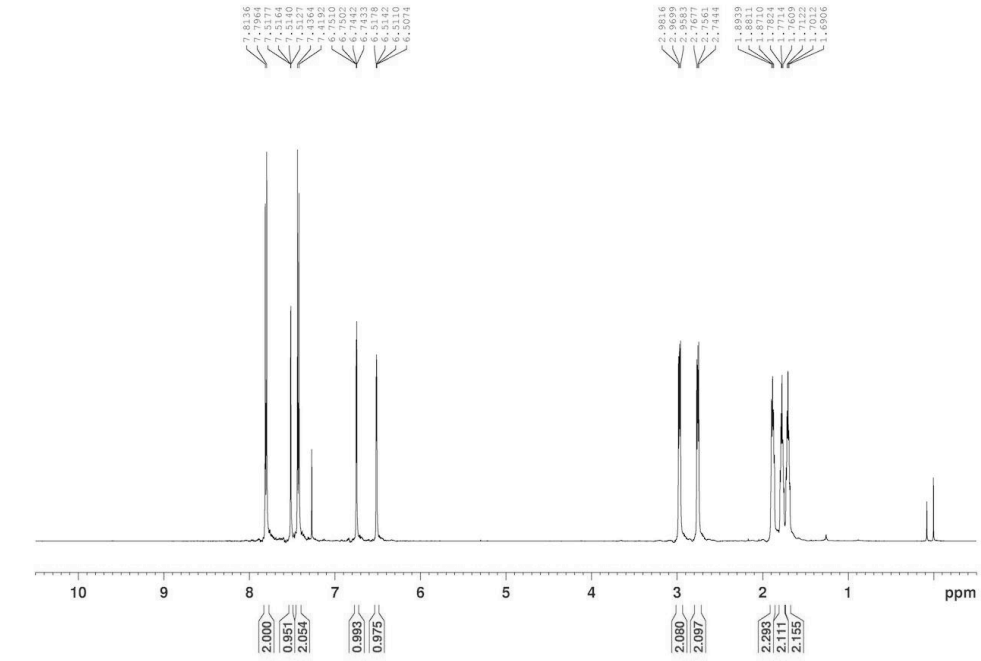


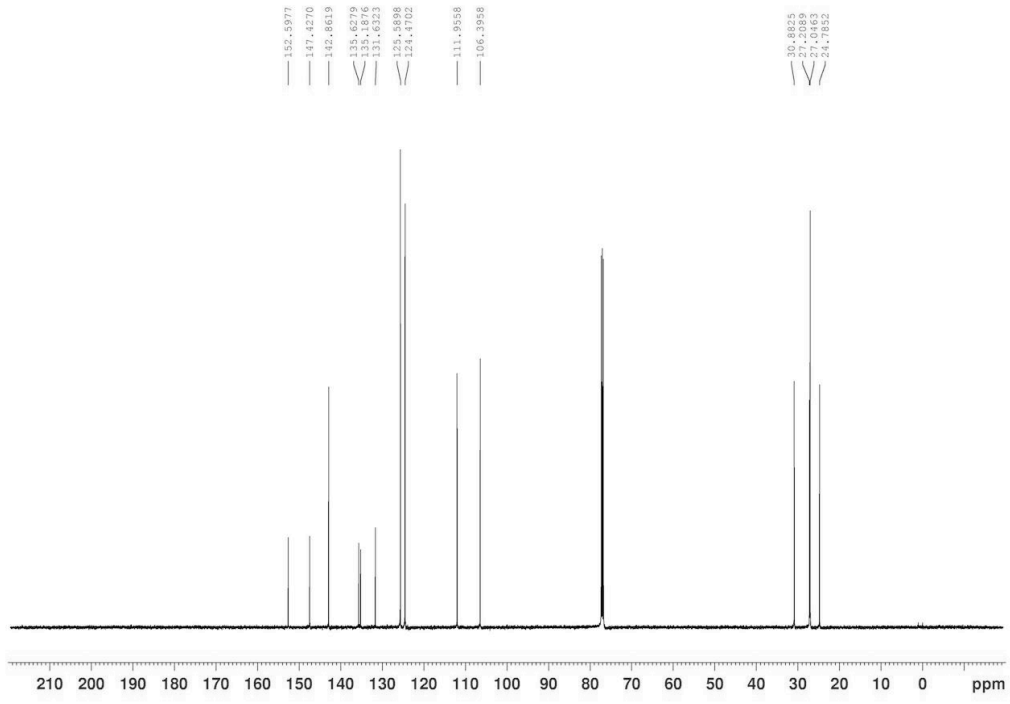




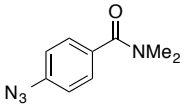
^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of **21d** ($CDCl_3$)

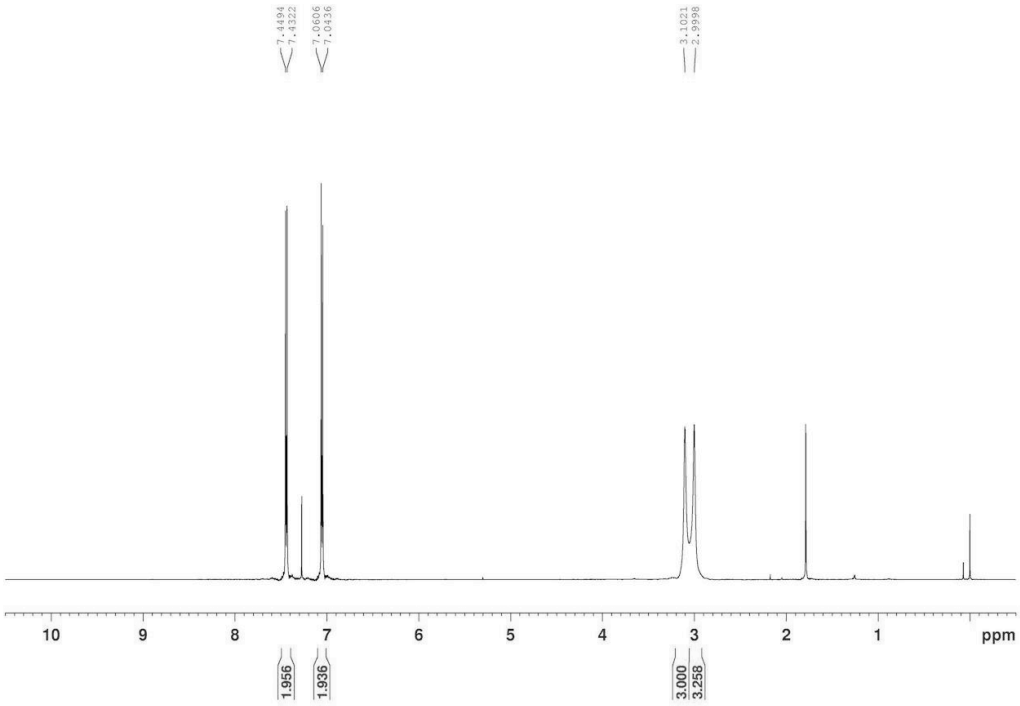


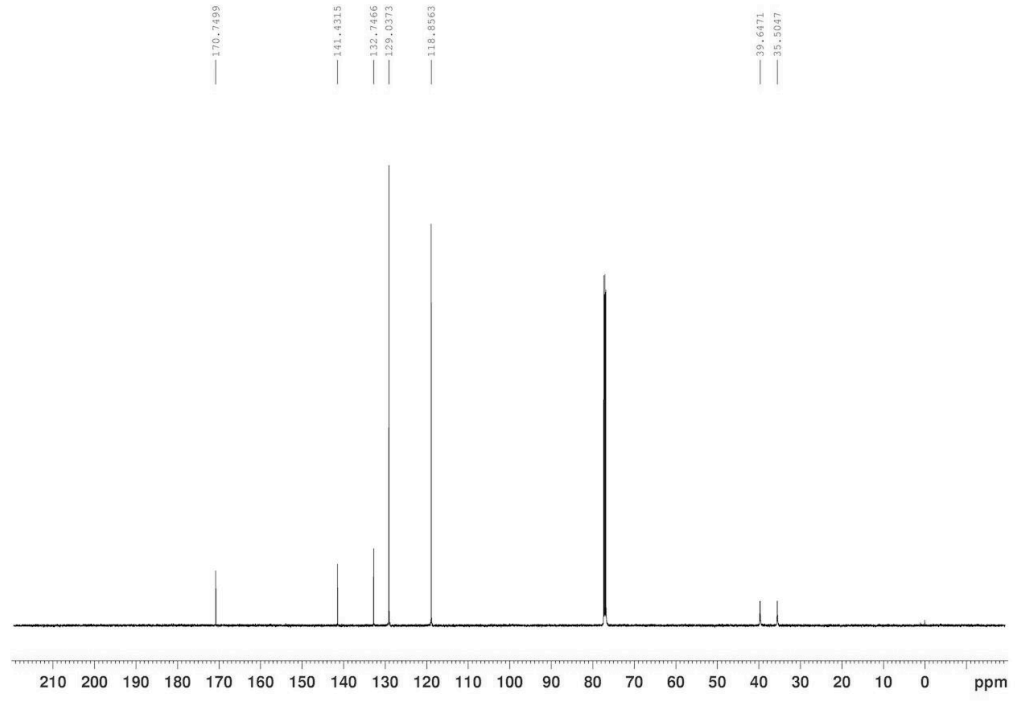




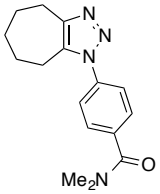
^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of
4-azido-*N*,*N*-dimethylbenzamide ($CDCl_3$)

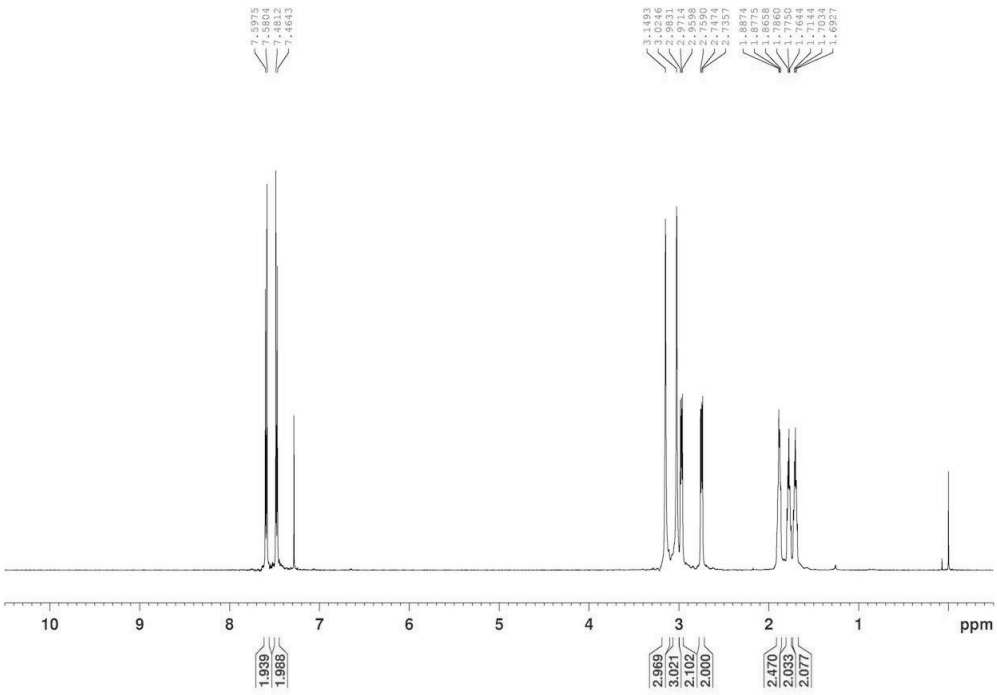


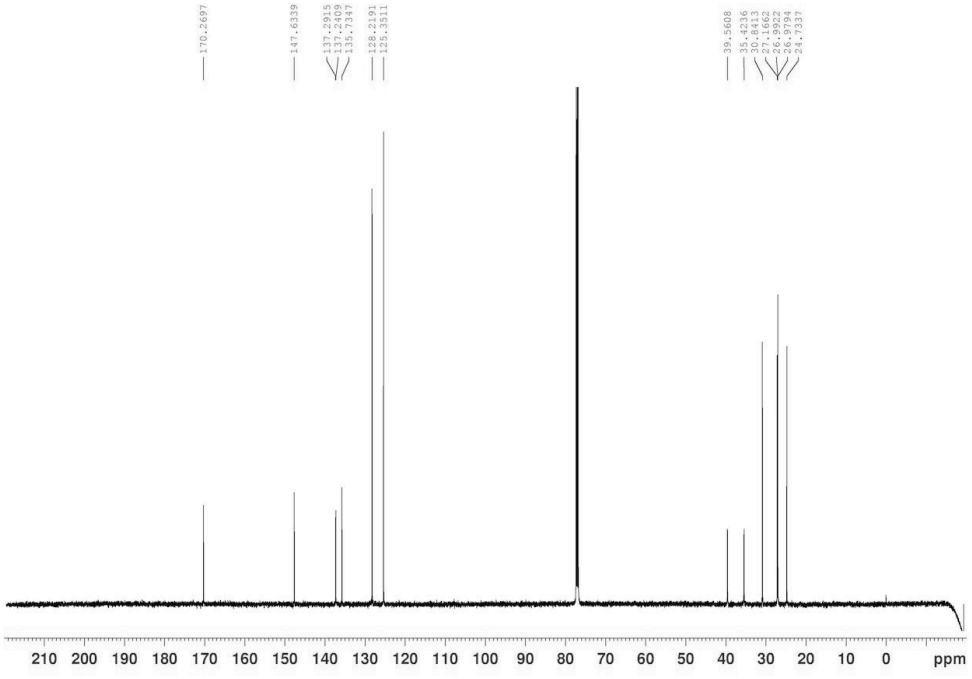




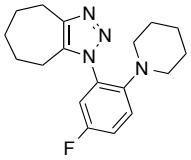
^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of **21e** ($CDCl_3$)

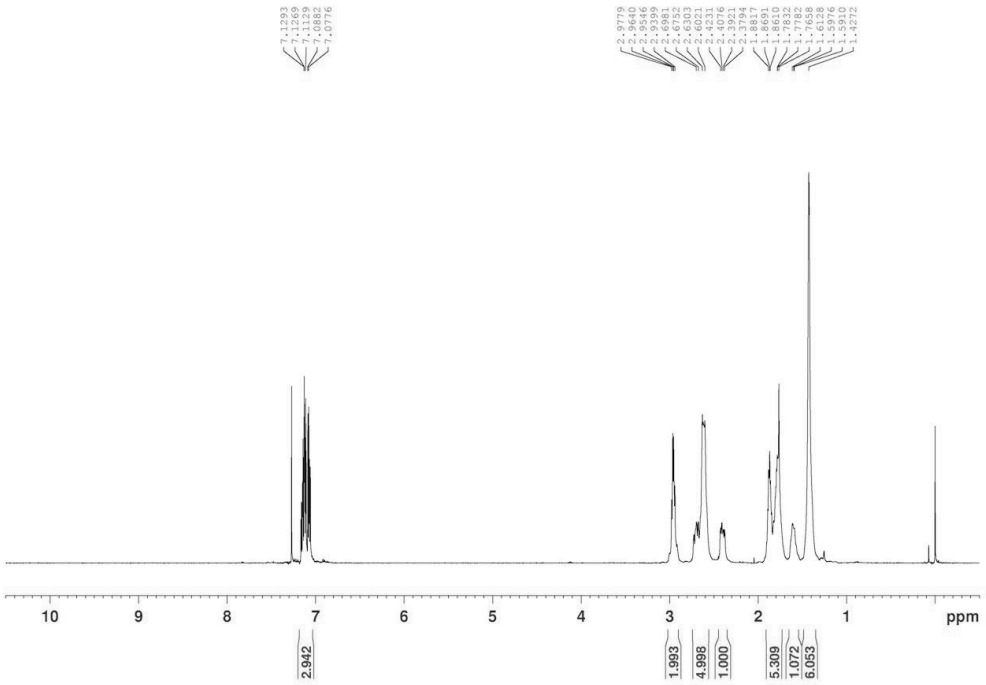


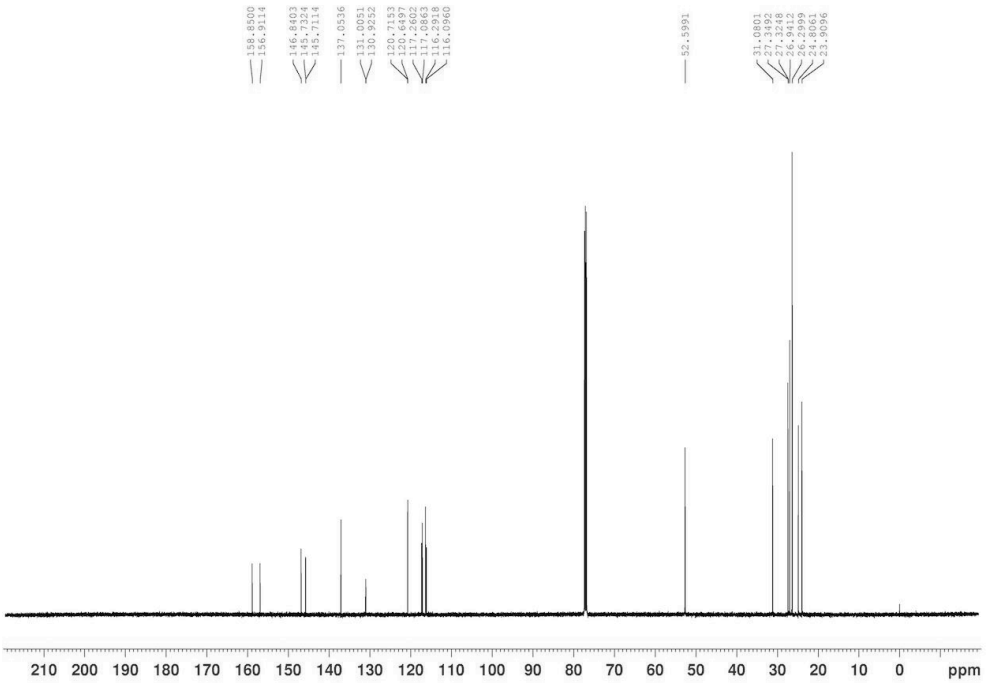




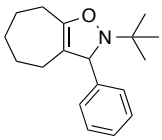
^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of **21f** ($CDCl_3$)

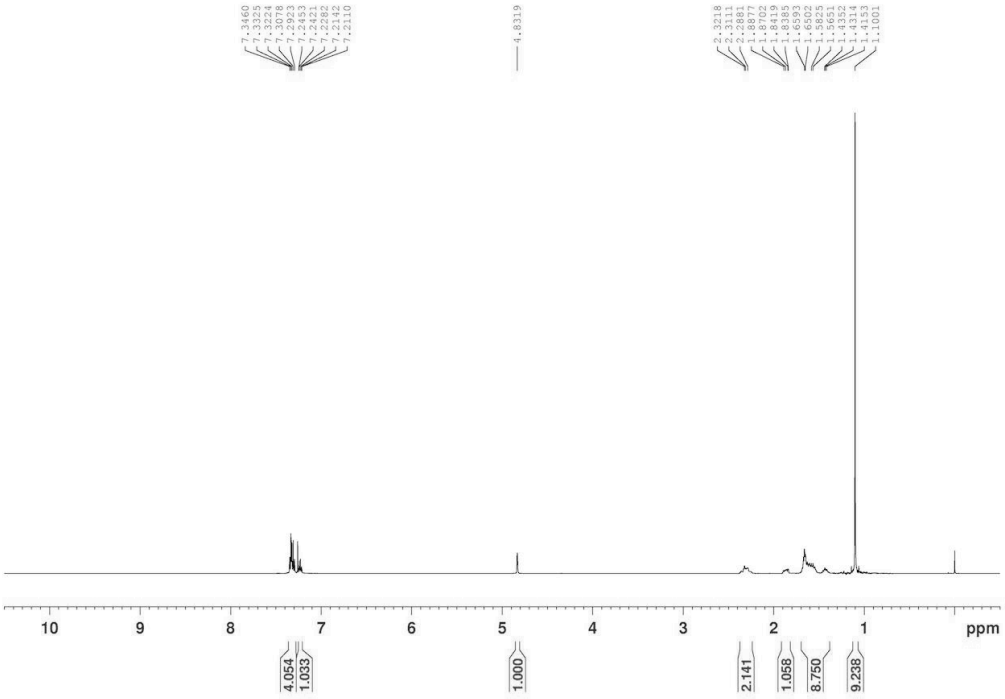


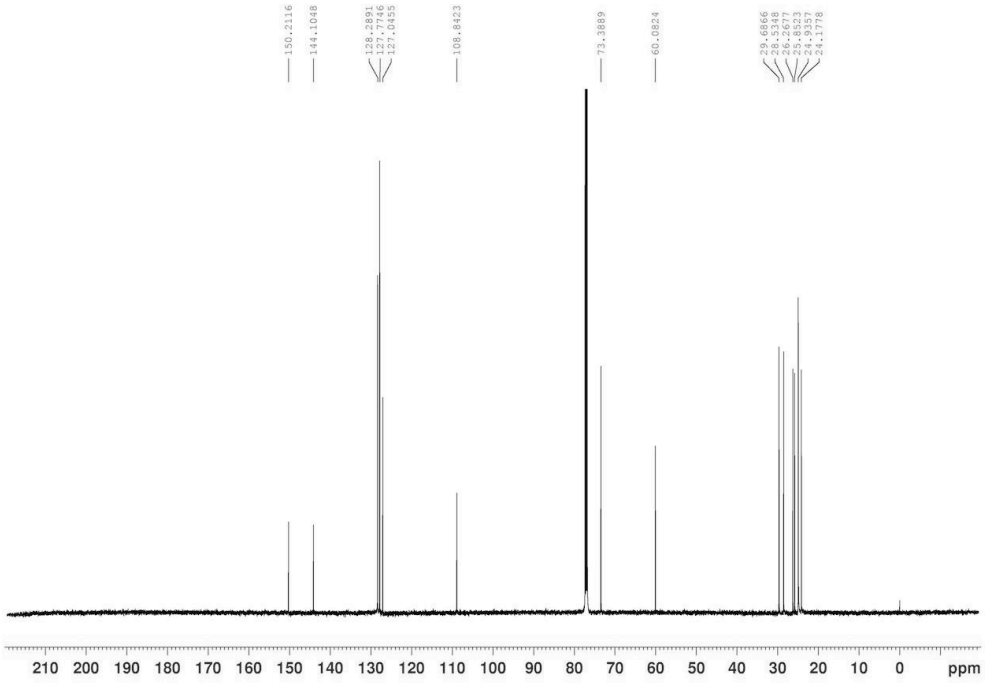




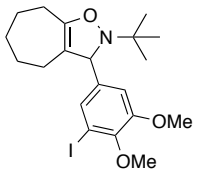
^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of **22a** ($CDCl_3$)

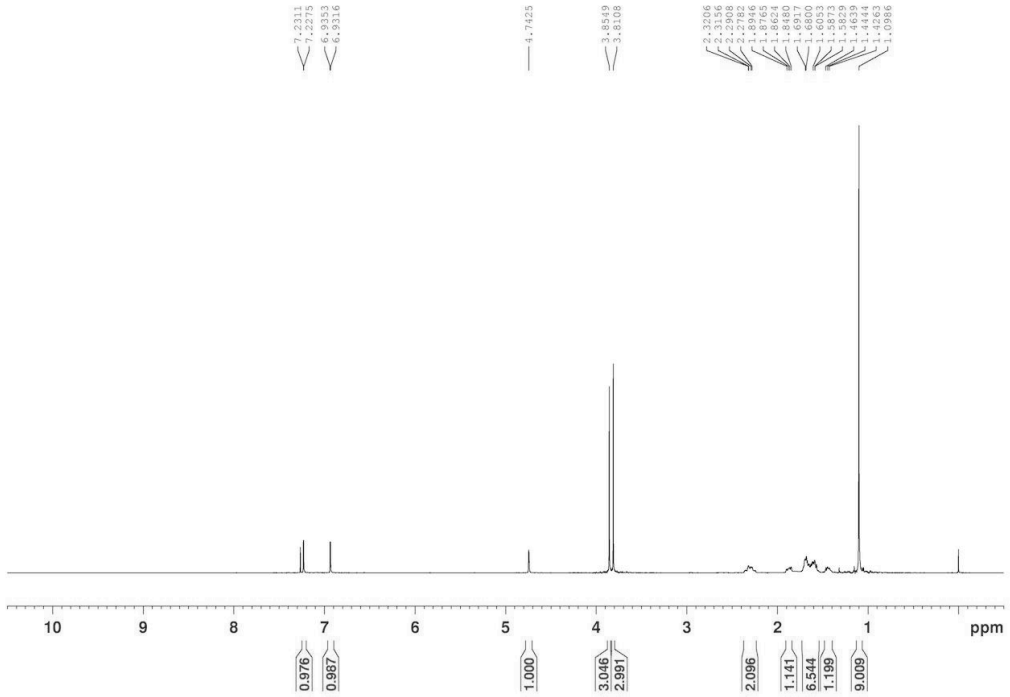


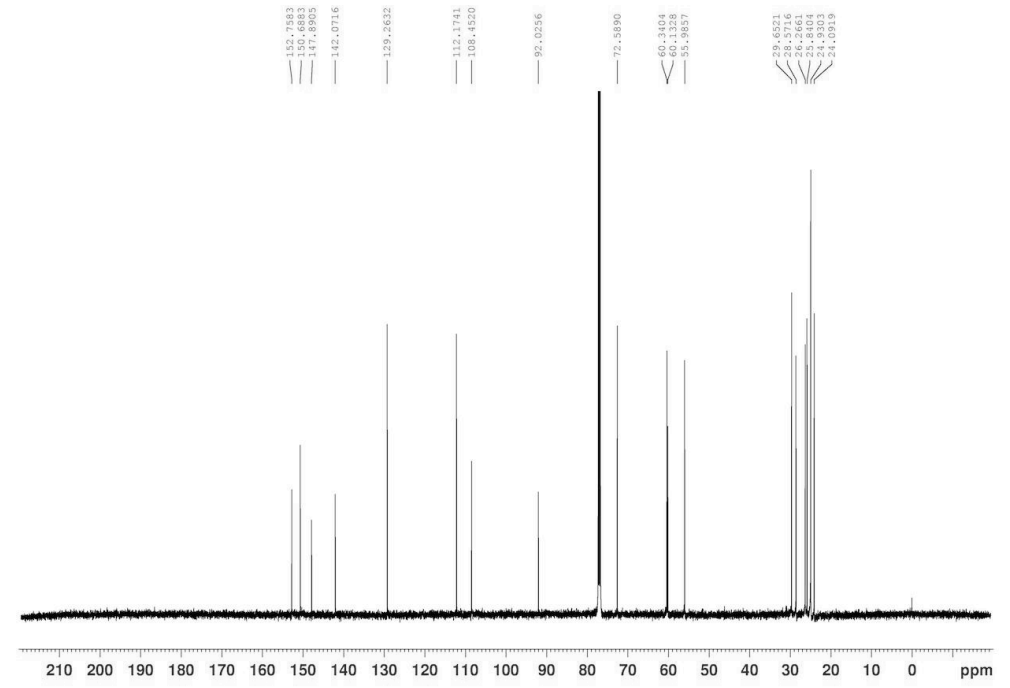




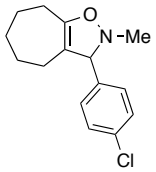
^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of **22b** ($CDCl_3$)

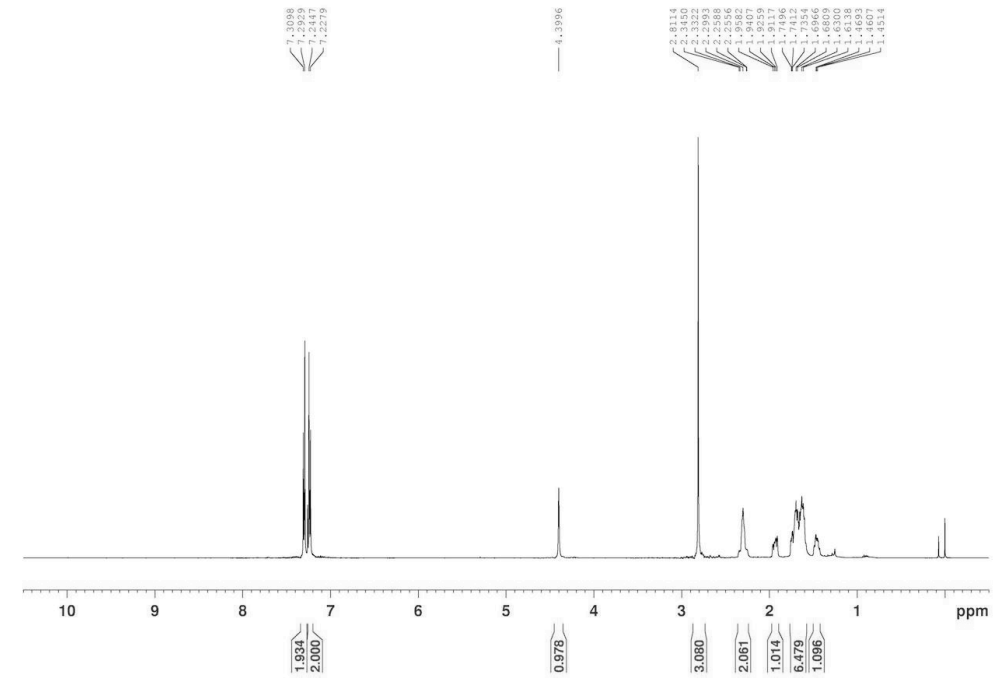


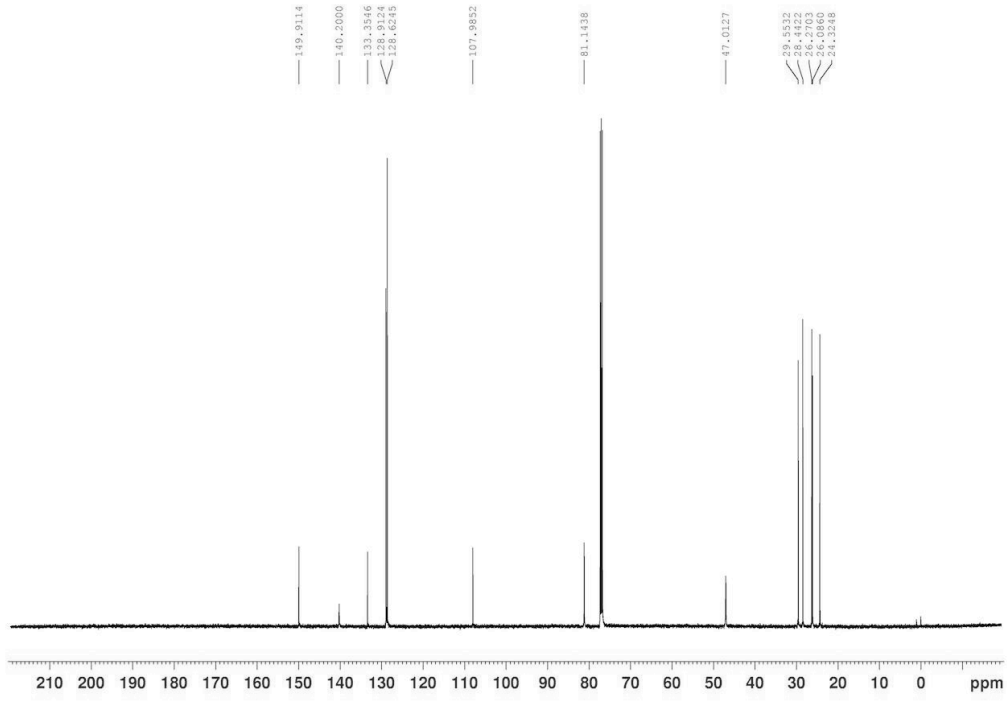




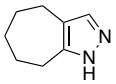
^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of **22c** ($CDCl_3$)

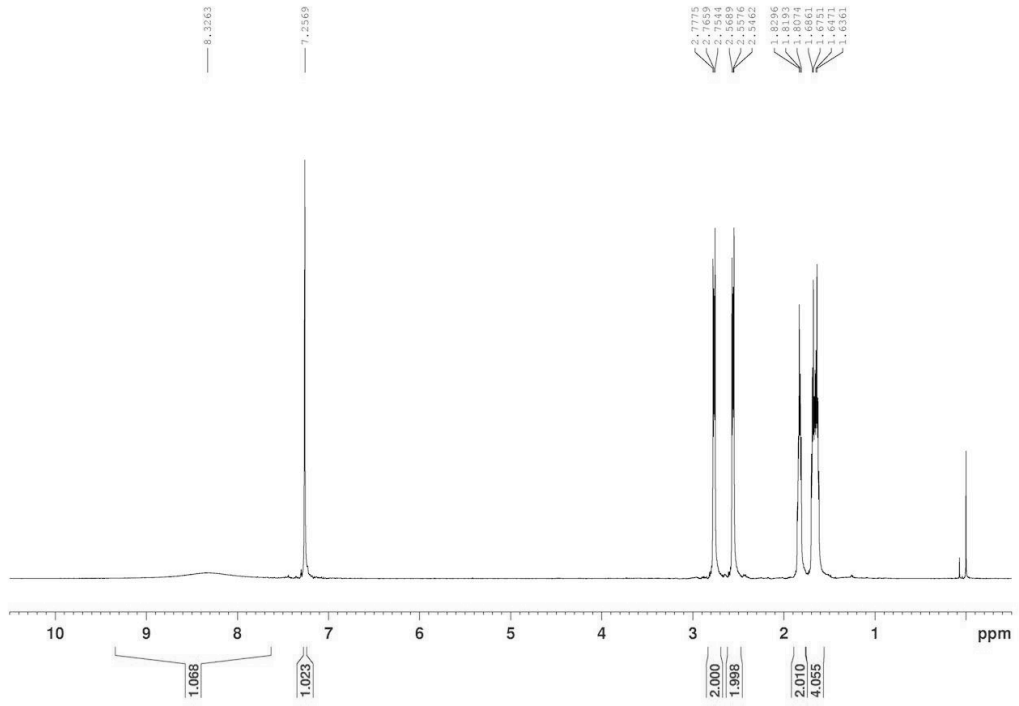


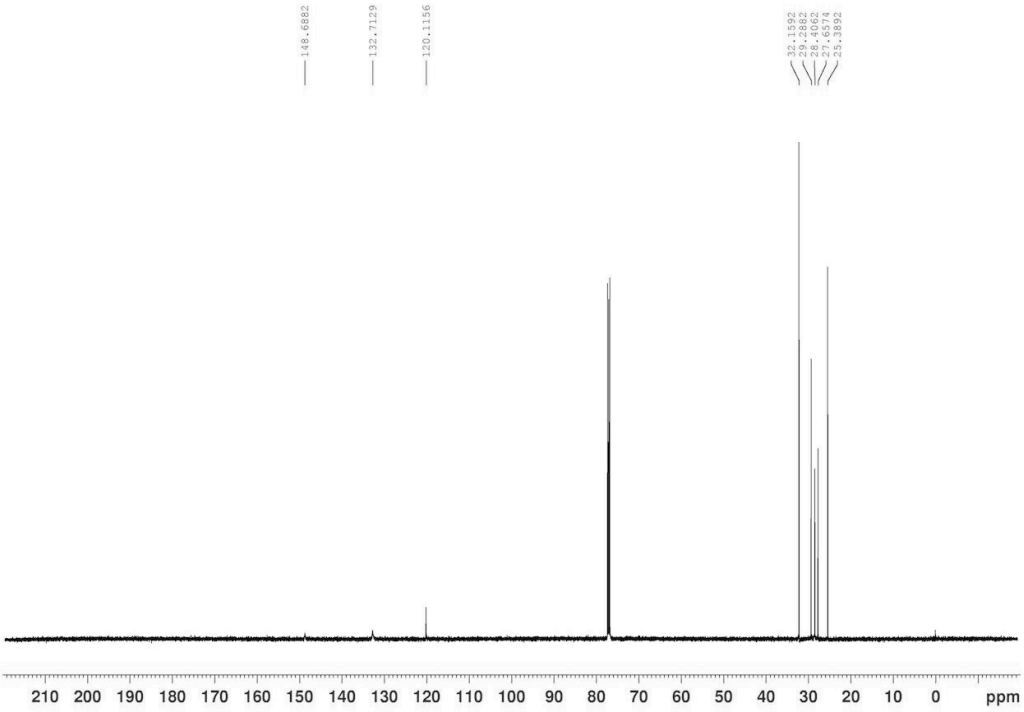




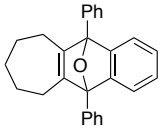
^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of **23** ($CDCl_3$)

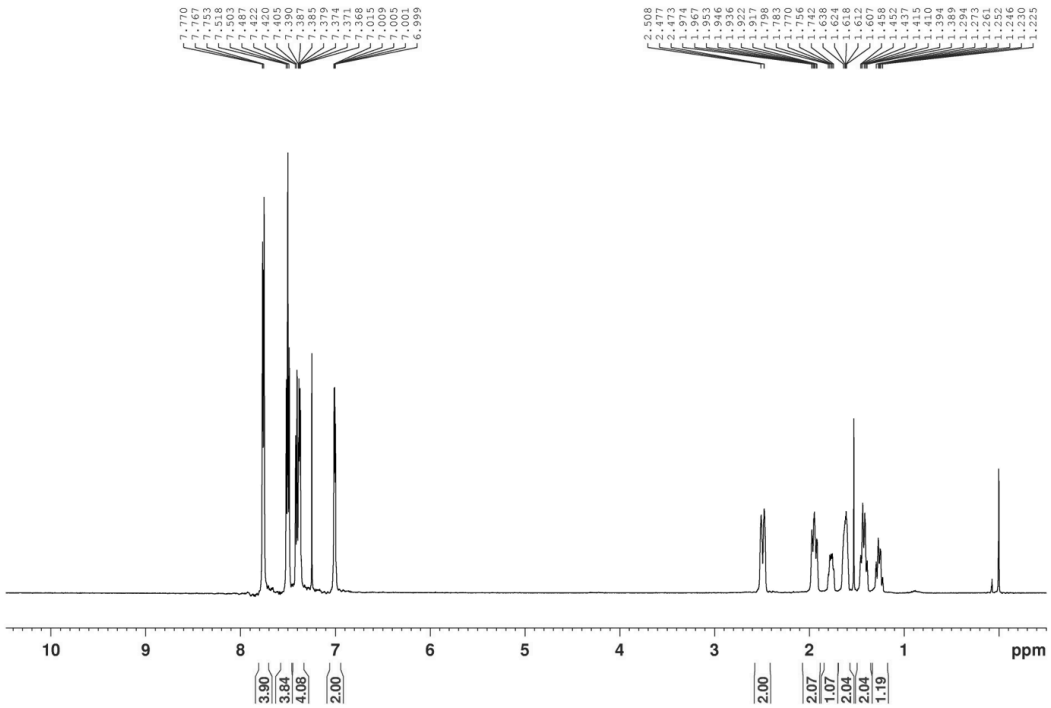


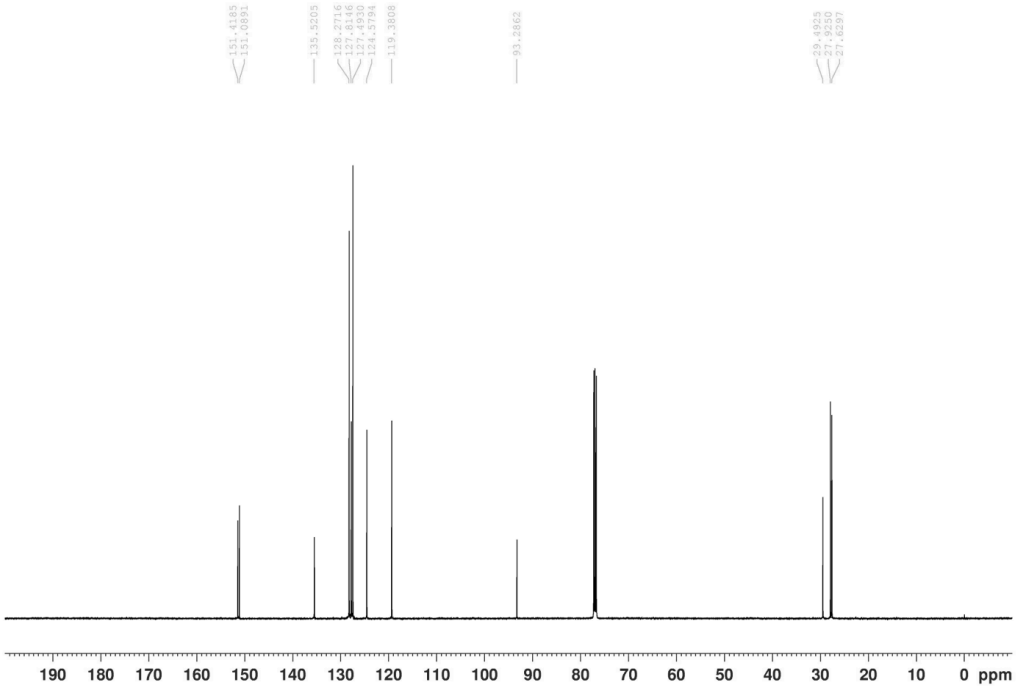




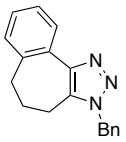
^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of **25b** ($CDCl_3$)

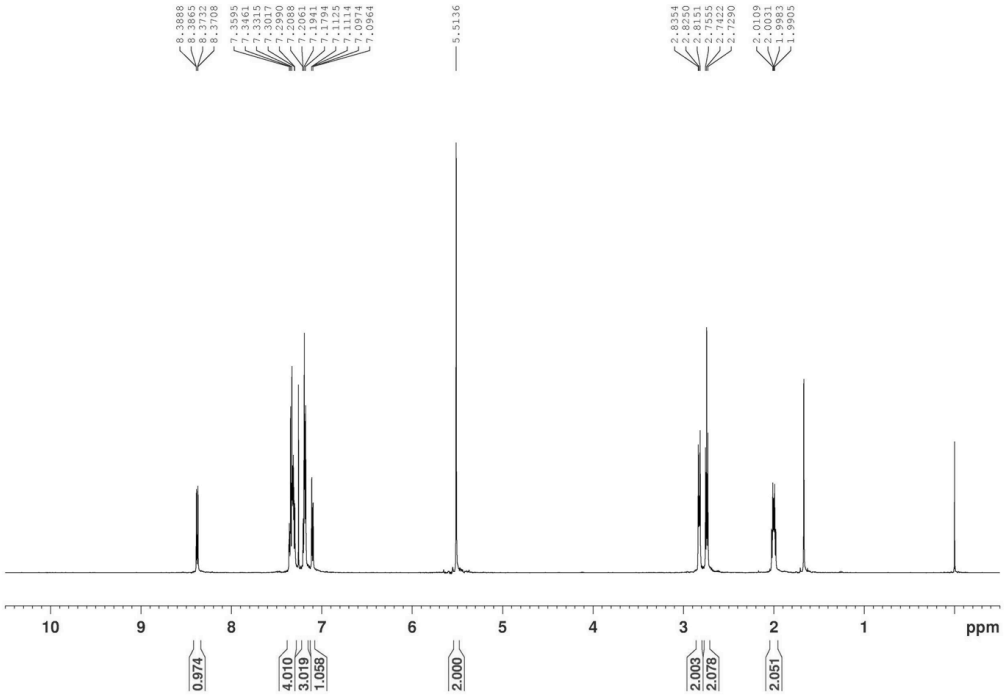


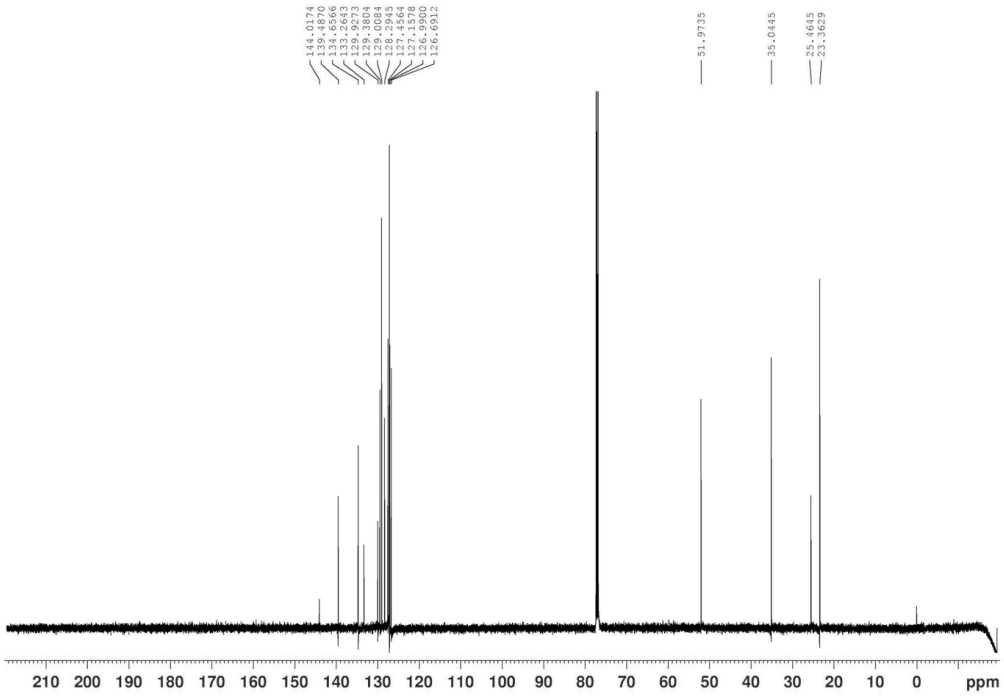




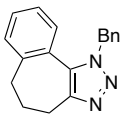
^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of **27** ($CDCl_3$)

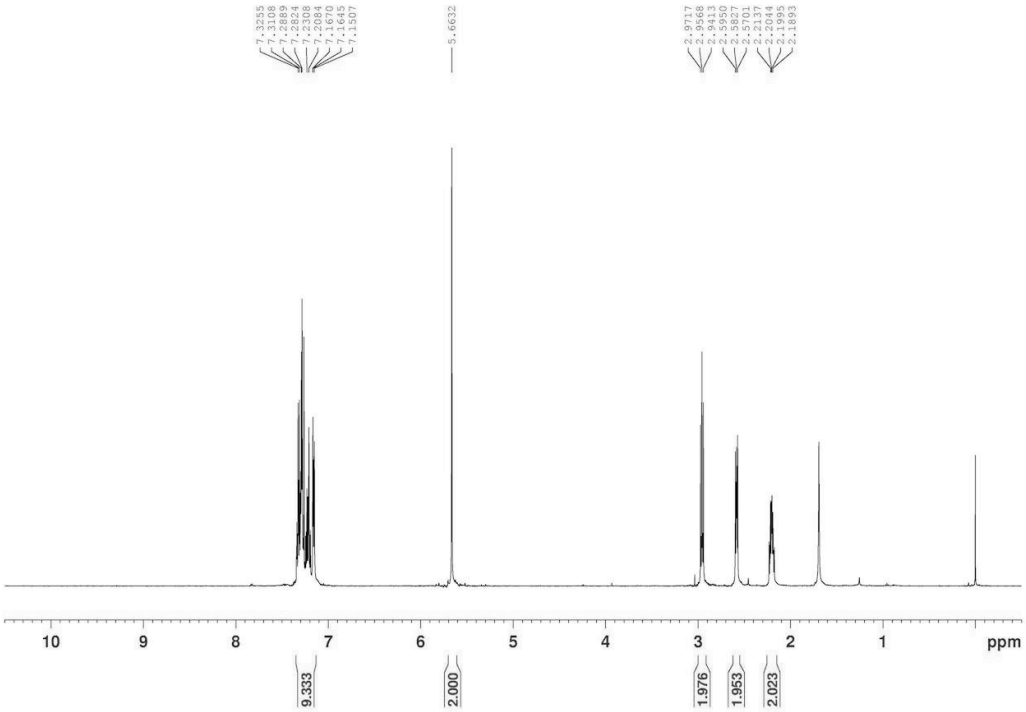


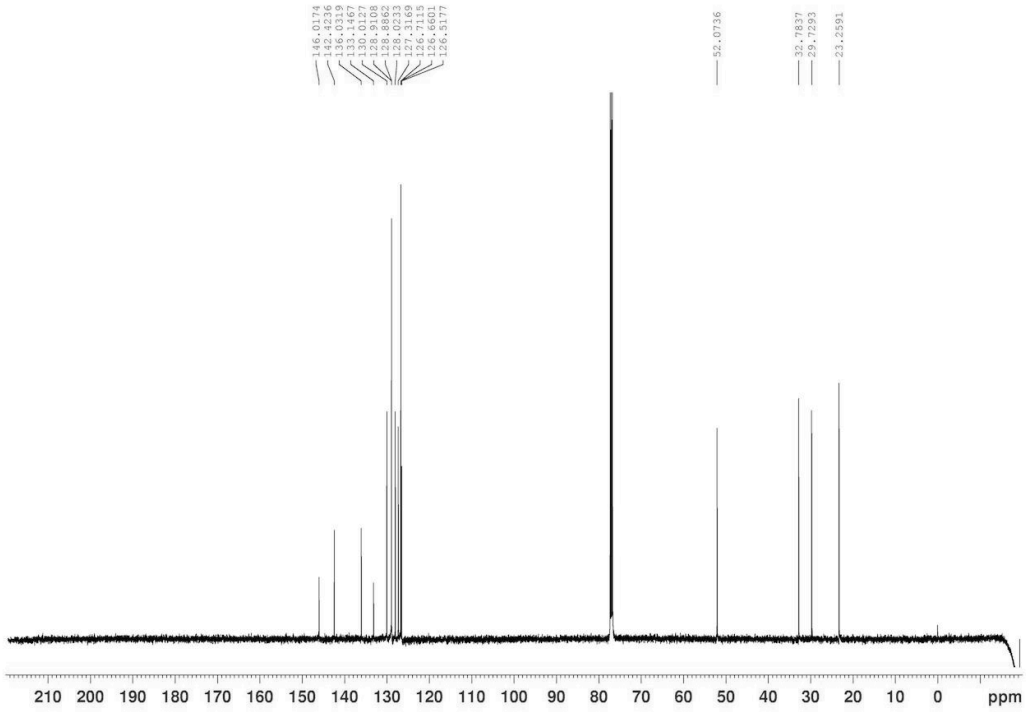




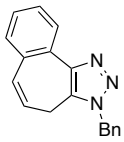
^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of **27'** ($CDCl_3$)

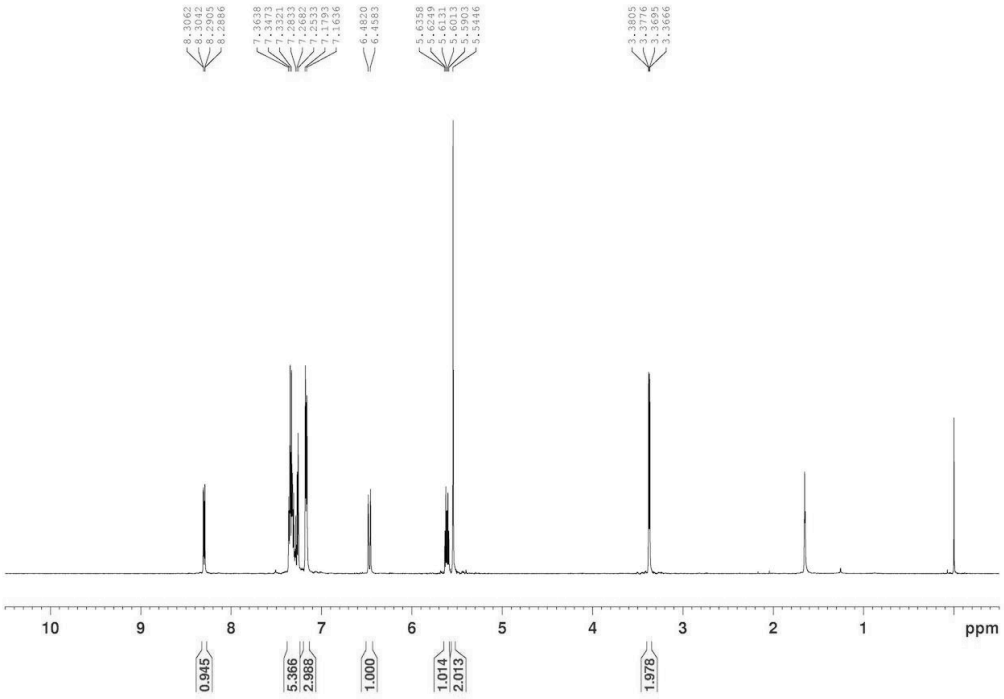


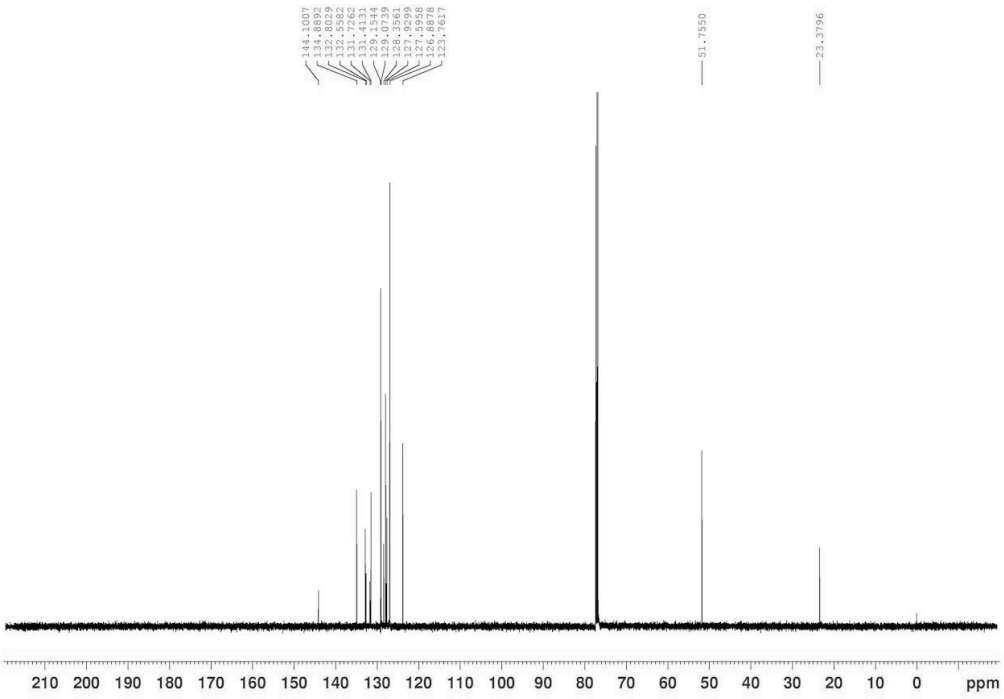




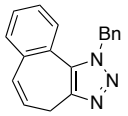
^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of **28** ($CDCl_3$)

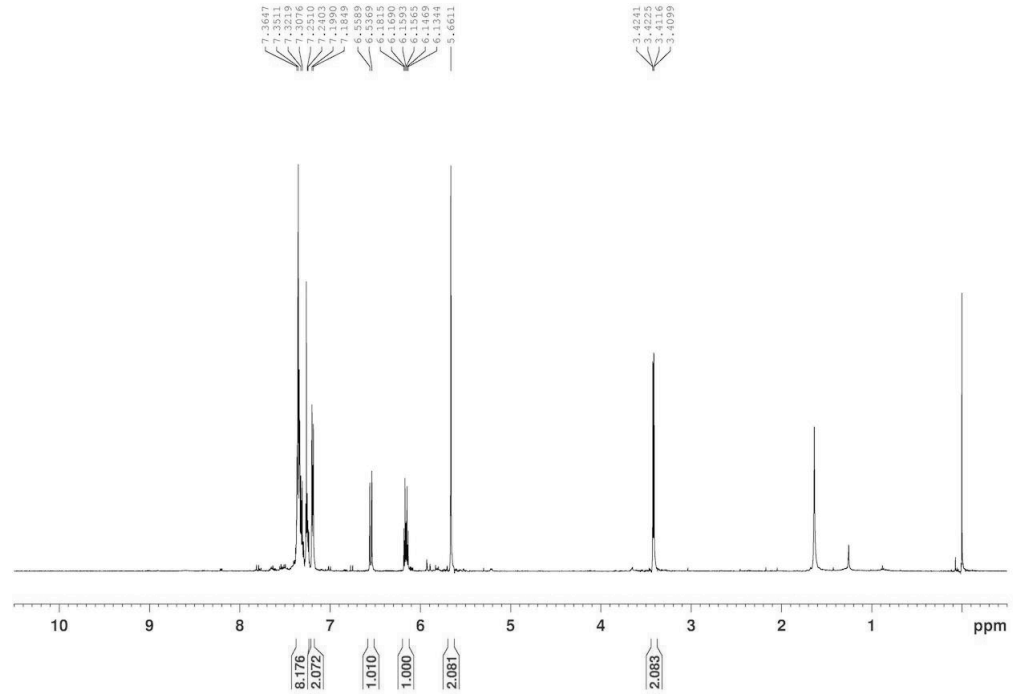


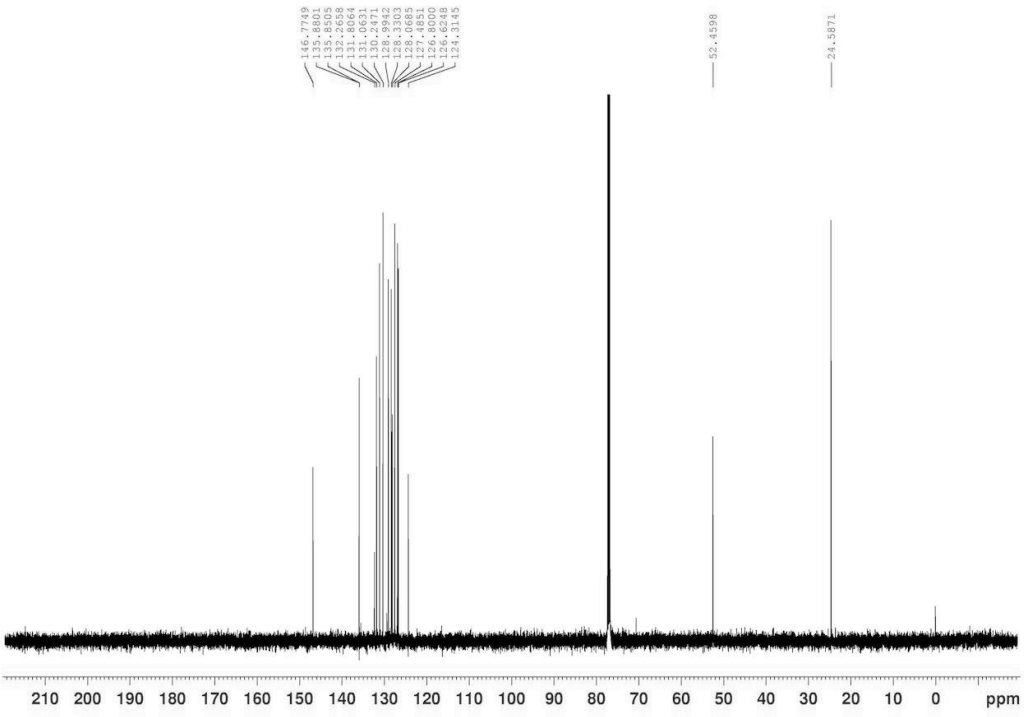




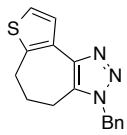
^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of **28'** ($CDCl_3$)

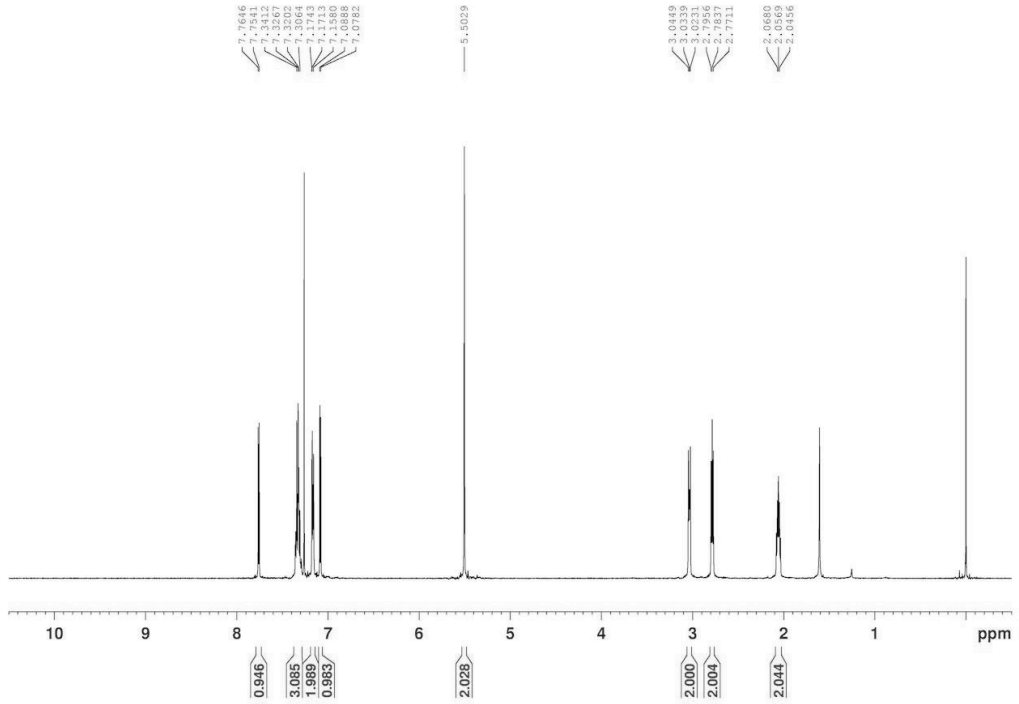


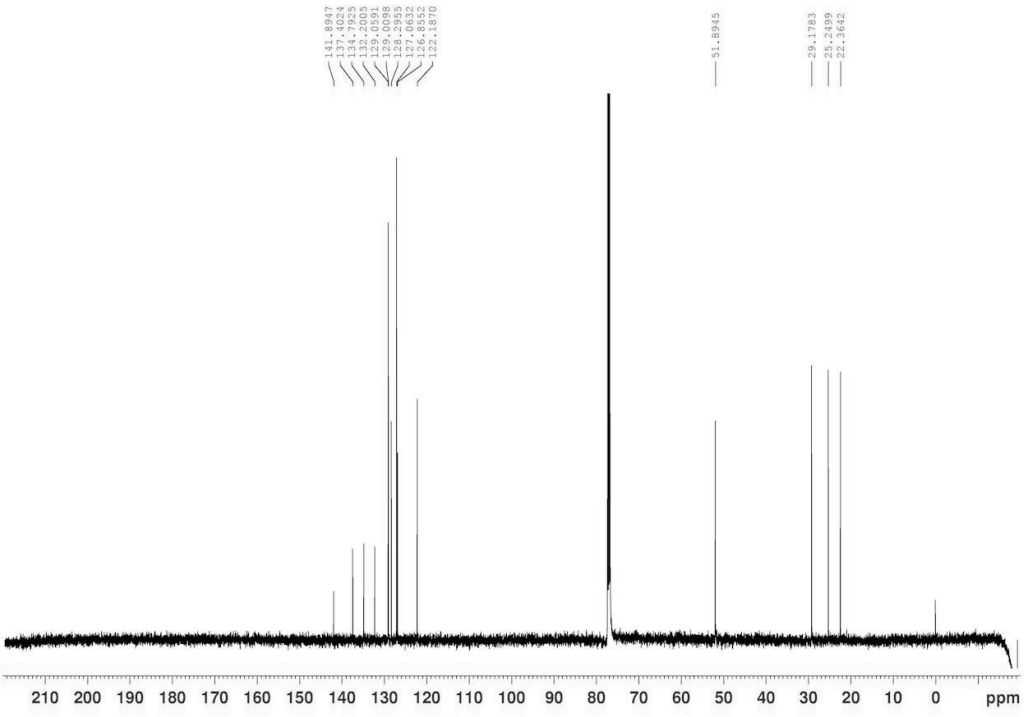




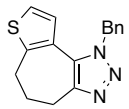
^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of **29** ($CDCl_3$)

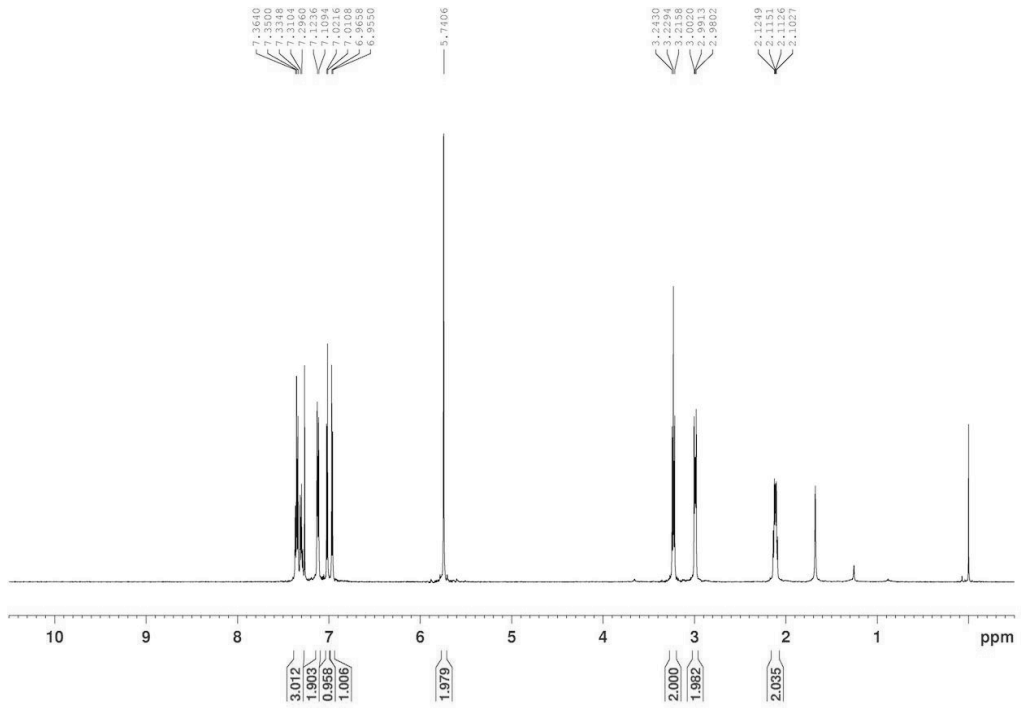


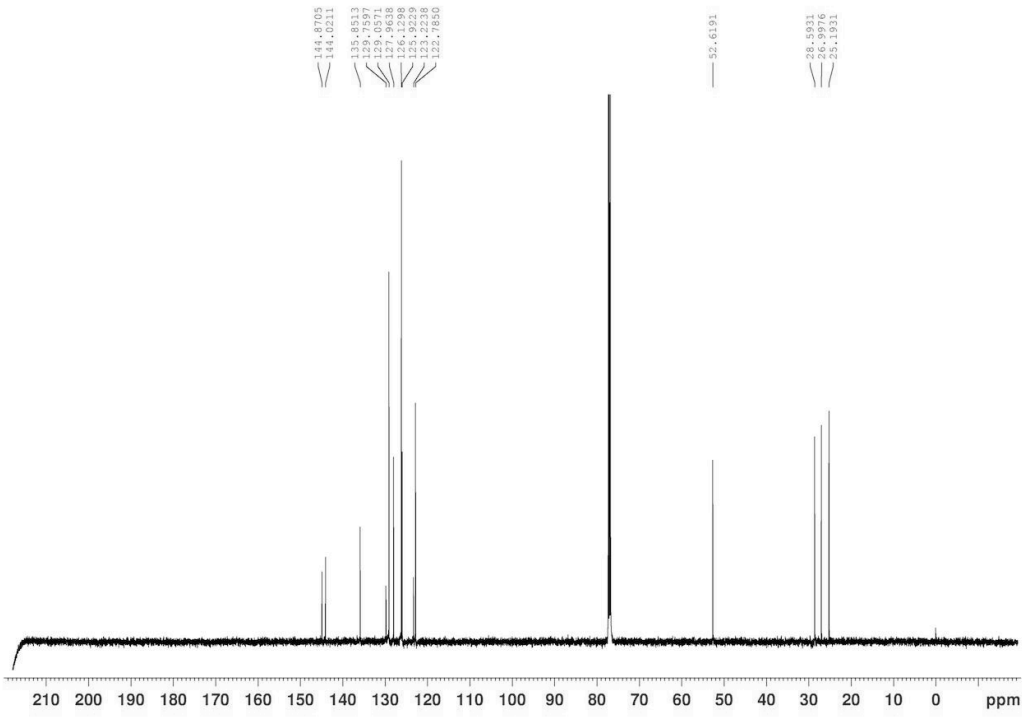




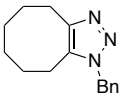
^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of **29'** ($CDCl_3$)

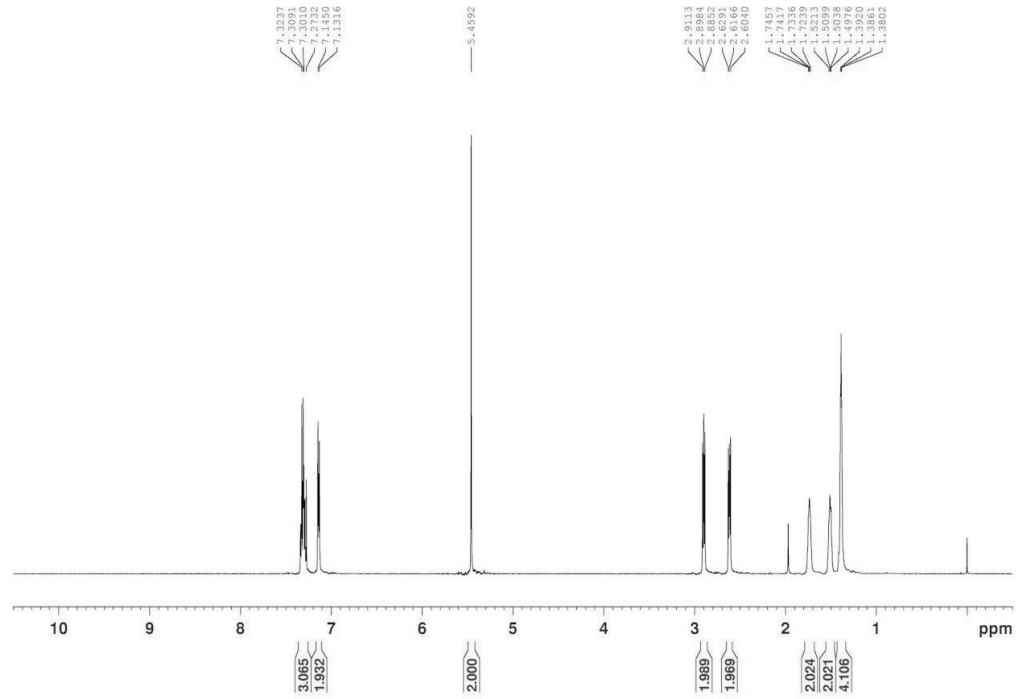


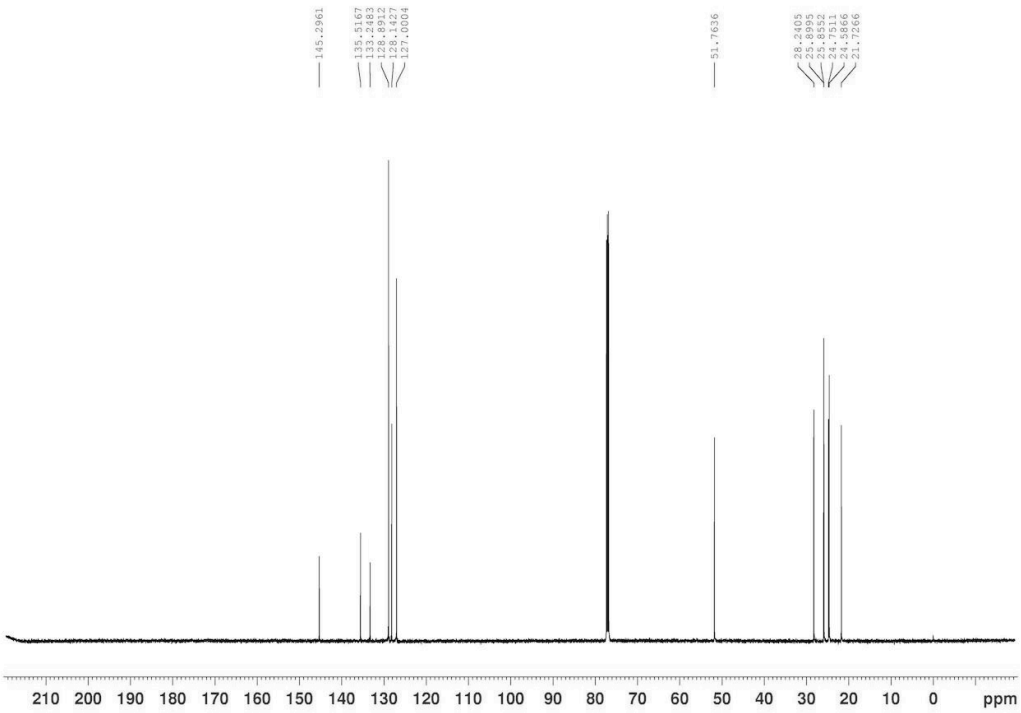




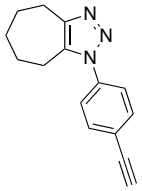
^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of **31** ($CDCl_3$)

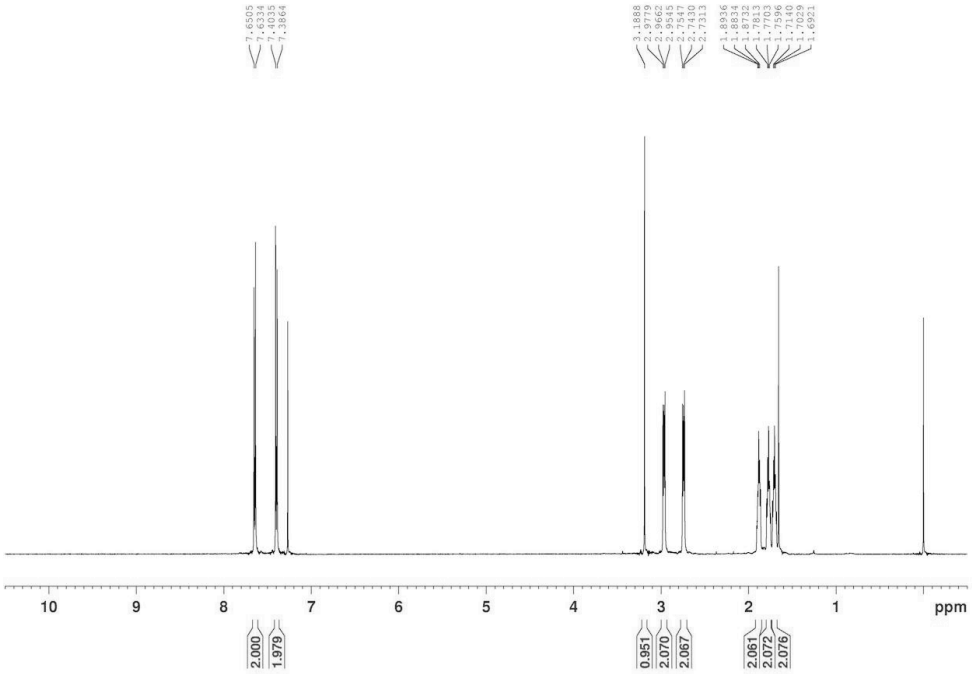


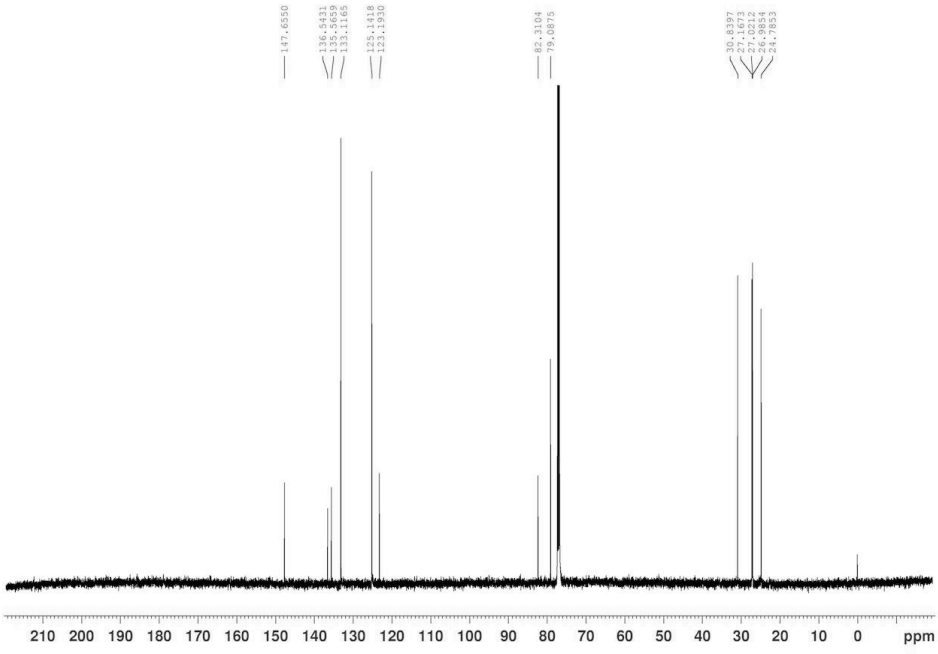




^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of
1-(4-ethynylphenyl)-1,4,5,6,7,8-hexahydrocyclohepta[*d*][1,2,3]triazole ($CDCl_3$)







^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of **35** ($CDCl_3$, 60 ºC)