Supplementary Information

Modular Synthesis of Bis- and Tris-1,2,3-triazoles by Permutable Sequential Azide–Aryne and Azide–Alkyne Cycloadditions

Suguru Yoshida, Takako Nonaka, Takamoto Morita, and Takamitsu Hosoya*

Laboratory of Chemical Bioscience, Institute of Biomaterials and Bioengineering, Tokyo Medical and Dental University, 2-3-10 Kanda-Surugadai, Chiyoda-ku, Tokyo 101-0062, Japan

Contents

General Remarks

All reactions were performed with dry glassware under atmosphere of argon otherwise noted. ^{1}H and ^{13}C NMR spectra were obtained with a Bruker AVANCE 500 spectrometer at 500 or 126 MHz, respectively. ^{19}F NMR spectrum was obtained with a Bruker AVANCE 400 spectrometer at 376 MHz. $CDCl_3$ (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 and ^{13}C NMR in $CDCl_3$) as an internal reference, or α,α,α-trifluorotoluene (δ –63.0 ppm for ^{19}F NMR) as an external standard with coupling constants (*J*) in hertz (Hz). The abbreviations s, d, t, q, m, and br signify singlet, doublet, triplet, quartet, 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}. 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), 80 g (Cat. No. 445-8000-JZ-20), or 120 g (Cat. No. 445-120G-UZ-20) with medium pressure liquid chromatography (Yamazen, W-Prep 2XY A-type) or silica-gel (Kanto Chemical Co., Inc., Silica Gel 60N, spherical neutral, particle size 40–50 μm, Cat. No. 37563-85). A recycling preparative HPLC system (Japan Analytical Industry Co., Ltd., LC-9210) was used for the purification of azide **2d**. Melting points (Mp) were measured with an Opti Melt MPA100 (Stanford Research Systems) and are uncorrected. High-resolution mass spectra (HRMS) were measured on a Bruker micrOTOF mass spectrometer under positive electrospray ionization (ESI^+) conditions. Electron ionization mass spectra (EI-MS) were measured on a Shimadzu GCMS-QP2010 SE gas chromatograph mass spectrometer with a direct injection probe. Elemental analyses were carried out at the Center for Advanced Material Analysis (Ookayama) of Tokyo Institute of Technology.

N-Ethyldiisopropylamine (Cat. No. 053-05355), sodium azide (Cat. No. 197-11091), benzyl azide (**2a**) (Cat. No. 327-79632), methyl 3-amino-4-methyl-2-thiophenecarboxylate (Cat. No. 329-39191), 4-(dimethylamino)pyridine (DMAP) (Cat. No. 042-19212), 1,2-dimethoxyethane (DME) (Cat. No.

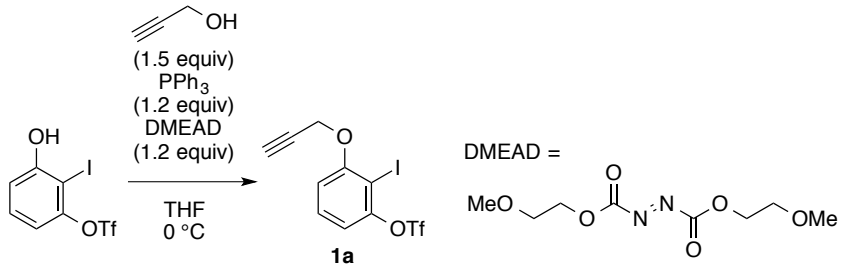
046-21785), cesium carbonate (Cat. No. 036-06541), bis(2-methoxyethyl) azodicarboxylate (DMEAD) (Cat. No. 024-16693), ethyl azidoacetate (**2o**) (Cat. No. 326-44312), benzene (Cat. No. 023-16945), silver nitrate (Cat. No. 196-00831), sodium nitrite (Cat. No. 196-02575), triethylamine (Cat. No. 202-02646), acetic acid (Cat. No. 017-00256), concentrated sulfuric acid (Cat. No. 192-04696), *tert*-butyl alcohol (Cat. No. 028-03386), *N*,*N*-dimethylformamide (DMF) (Cat. No. 045-02911), dichloromethane (Cat. No. 204-08745), acetonitrile (Cat. No. 014-00381), methanol (Cat. No. 131-01826), and ethanol (Cat. No. 057-00451) were purchased from Wako Pure Chemical Industries Ltd. 2-Methylthio-5-trifluoromethylaniline (Cat. No. A1666), trimethylsilylmethyl azide (**2b**) (Cat. No. T1184), azidomethyl phenyl sulfide (**2k**) (Cat. No. A1341), 4-ethynylaniline (Cat. No. E0505), 2-azido-1,3-dimethylimidazolinium hexafluorophosphate (ADMP) (Cat. No. A2457), dimethyl(phenyl)silylmethyl chloride (Cat. No. C1419), trimethylsilylacetylene (Cat. No. T1239), tetrakis(acetonitrile)copper(I) tetrafluoroborate (Cat. No. T2666), 2,6-lutidine (Cat. No. L0067), trimethylsilylmethyl chloride (Cat. No. C0862), 1-adamantanecarboxylic acid (Cat. No. A0742), and 4-iodoaniline (Cat. No. I0048) were purchased from Tokyo Chemical Industry Co., Ltd. 2-Bromo-6-chloro-4-fluoroaniline (Cat. No. 569283), 1,4-benzodioxan-6-amine (Cat. No. 193232), 4-((5,6-dimethoxypyrimidin-4-yl)aminosulfonyl)aniline (sulfadoxine) (Cat. No. S7821), ethyl 3-aminobenzo[*b*]furan-2-carboxylate (Cat. No. 642363), (trimethylsilyl)methyllithium (1.0 M, pentane solution, Cat. No. 297054), methylmagnesium bromide (3.0 M, diethyl ether solution, Cat. No. 189898), isopropylmagnesium chloride lithium chloride complex (1.3 M, THF solution, Cat. No. 656984), 2-bromoresorcinol (Cat. No. 750778), propargyl alcohol (Cat. No. P50803), 4-ethynylbenzyl alcohol (Cat. No. 519235), pentamethylcyclopentadienylbis(triphenylphosphine)ruthenium(II) chloride (Cp*RuCl(PPh_3)$_2$) (Cat. No. 673293), bis(triphenylphosphine)palladium(II) dichloride (Cat. No. 412740), copper(I) iodide (Cat. No. 215554), *n*-butylmagnesium chloride (2.0 M, THF solution, Cat. No. 291005), bromobenzene (Cat. No. 16350), were purchased from Sigma–Aldrich Japan. Triphenylphosphine (Cat. No. 40950-25), *n*-butyllithium (1.6 M, hexane solution, Cat. No. 04937-05), magnesium (turnings, Cat. No. 26000-25), and anhydrous tetrahydrofuran (THF) (Cat. No. 41001-84) were purchased from Kanto Chemical Co. Inc. Trifluoromethanesulfonic anhydride was kindly provided from Central Grass Co., Ltd.,

tert-Butyl azidoacetate (**2c**),[S1] 4-methoxyphenyl azide (**2e**),[S2] 4-trifluoromethylphenyl azide (**2f**),[S3] 2,6-diisopropylphenyl azide (**2g**),[S4] 4-benzoylphenyl azide (**2m**),[S5] 4-toluenesulfonyl azide (**2n**),[S6] 3-hydroxy-2-iodophenyl triflate,[S7] and tris[(1-benzyl-1*H*-1,2,3-triazol-4-yl)methyl]amine (TBTA)[S8] were prepared according to the reported methods. Phenylmagnesium bromide (1.05 M, THF solution) and (trimethylsilyl)methylmagnesium chloride (1.23 M, THF solution) were prepared from bromobenzene and trimethylsilylmethyl chloride, respectively, with magnesium in the conventional way. Grignard reagents and organolithium reagents were used after titrimetric determination of the concentration by the 1,10-phenanthroline method.[S9] All other chemical reagents used were commercial grade and used as received.

CAUTION! **Azido-containing compounds are presumed to be potentially explosive. Although we have never experienced such an explosion with azido compounds used in this study, all manipulations should be carefully carried out behind a safety shield in a hood.**

Experimental Section

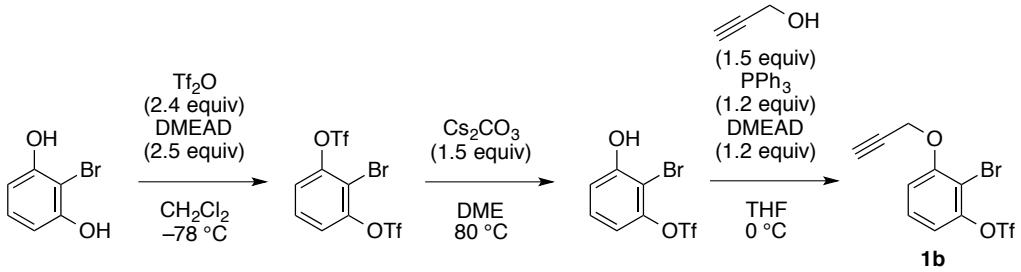
*Preparation of ortho-iodoaryl triflate bearing a terminal alkyne **1a***



Under an argon atmosphere, to a solution of 3-hydroxy-2-iodophenyl triflate (6.18 g, 15.0 mmol) and propargyl alcohol (1.30 mL, 22.0 mmol, 1.47 equiv) in THF (50 mL) was added triphenylphosphine (4.72 g, 18.0 mmol, 1.20 equiv) and DMEAD[S10] (4.22 g, 18.0 mmol, 1.20 equiv) at 0 °C. After stirring for 20 min at the same temperature, to the mixture was added water (20 mL). The mixture was extracted with EtOAc (30 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 flash column chromatography (Biotage® ZIP-sphere cartridge 80 g, *n*-hexane/EtOAc = 12/1 to 7/3) to afford 2-iodo-3-(propargyloxy)phenyl triflate (**1a**) (5.60 g, 13.8 mmol, 92.0%) as a pale pink oil. Further purification by crystallization from hexane afforded **1a** (3.03 g, 7.46 mmol, 49.8%) as a colorless solid.

According to the procedure above, another *ortho*-iodoaryl triflate bearing a terminal alkyne **1c** was prepared from 3-hydroxy-2-iodophenyl triflate (1.71 g, 4.15 mmol) and 4-ethynylbenzyl alcohol (822 mg, 6.22 mmol) quantitatively (2.00 g, 4.15 mmol).

*Preparation of ortho-bromoaryl triflate bearing a terminal alkyne **1b***



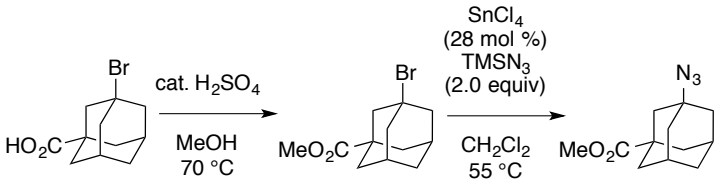
Under an argon atmosphere, to a suspension of 2-bromoresorcinol (4.86 g, 25.7 mmol) in dichloromethane (41 mL) was added *N*-ethyldiisopropylamine (11.0 mL, 63.8 mmol, 2.48 equiv) and trifluoromethanesulfonic anhydride (10.2 mL, 60.9 mmol, 2.37 equiv) at –78 °C. After stirring for 20 min at the same temperature, to the mixture was added water (20 mL). The mixture was extracted with EtOAc (30 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 flash column chromatography (Biotage® ZIP-sphere cartridge 80 g, *n*-hexane only to *n*-hexane/EtOAc = 4/1) to afford 2,6-bis(triflyloxy)-1-bromobenzene (12.8 g, 91% purity containing EtOAc, ca. quant.) as a pale yellow oil.

Under an argon atmosphere, to a suspension of 2,6-bis(triflyloxy)-1-bromobenzene (11.0 g, 91% purity containing EtOAc, ca. 22 mmol) in DME (50 mL) was added cesium carbonate (11.9 g, 36.5 mmol, 1.50 equiv) at room temperature, and the mixture was heated at 80 °C with stirring for 3 h. After cooling to room temperature, to the mixture was added saturated aqueous ammonium chloride (20 mL). The mixture was extracted with EtOAc (30 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 flash column chromatography (Biotage® ZIP-sphere cartridge 80 g, *n*-hexane/EtOAc = 6/1 to 3/1) to afford 2-bromo-3-hydroxyphenyl triflate (8.70 g, 81% purity containing EtOAc, ca. quant.) as a brown oil.

According to the synthetic procedure for **1a**, *ortho*-bromoaryl triflate bearing a terminal alkyne **1b** was prepared from 2-bromo-3-hydroxyphenyl triflate (8.00 g, 81% purity containing EtOAc, ca. 20 mmol) and propargyl alcohol (1.90 mL, 32.2 mmol) in ca. 93% yield (6.64 g, 18.5 mmol).

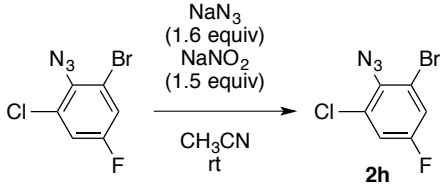
*Preparation of methyl 3-azido-1-adamantanecarboxylate (**2d**)*



3-Bromo-1-adamantanecarboxylic acid was prepared from 1-adamantanecarboxylic acid according to the reported procedure.[S11] To a solution of 3-bromo-1-adamantanecarboxylic acid (2.59 g, 10.0 mmol) in methanol (40 mL) was added three drops of concentrated sulfuric acid at room temperature, and the mixture was heated at 70 °C with stirring for 24 h. After cooling to room temperature, to the mixture was added aqueous potassium hydroxide (1 M, 10 mL). The mixture was extracted with dichloromethane (20 mL × 3), and the combined organic extract was washed with brine (10 mL), dried (Na_2SO_4), and after filtration through a short pad of silica gel, the filtrate was concentrated under reduced pressure to afford a crude product containing methyl 3-bromo-1-adamantanecarboxylate (ca. 10 mmol) as a pale yellow oil. This product was used in the next procedure without further purification.

To a solution of the crude product of methyl 3-bromo-1-adamantanecarboxylate (ca. 10 mmol) in dichloromethane (25 mL) was added trimethylsilyl azide (2.60 mL, 19.9 mmol, 1.99 equiv) and tin(IV) chloride (1.0 M in dichloromethane, 2.80 mL, 2.80 mmol, 28 mol %) at room temperature. After stirring for 6 h at 55 °C, the mixture was cooled to room temperature and then ice (10 g) was added. The mixture was filtered through a short pad of Celite and the filtrate was extracted with EtOAc (20 mL × 3). 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 flash column chromatography (Silica gel 60 g, *n*-hexane/EtOAc = 10/1) and fractions (20 mL each) were separately concentrated under reduced pressure. Fractions that contained methyl 3-azido-1-adamantanecarboxylate (**2d**), as judged from ^{1}H NMR analyses, were collected. To remove a small amount of impurity, further purification was carried out by a recycling preparative HPLC system (JAI, LC-9210) equipped with a refractive index detector and JAIGEL-1H and 2H columns (GPC) using $CHCl_3$ as an eluent provided methyl 3-azido-1-adamantanecarboxylate (**2d**) (1.48 g, 6.29 mmol, 62.9% from 3-bromo-1-adamantanecarboxylic acid) as a colorless oil.

*Preparation of azide **2h** from the corresponding aniline by Sandmeyer-type reaction*

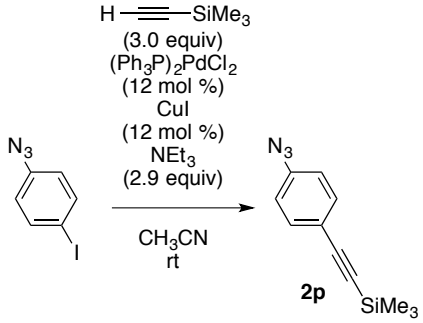


To a solution of 2-bromo-6-chloro-4-fluoroaniline (2.24 g, 10.0 mmol) in acetic acid (22.5 mL) and water (2.5 mL) was added sodium azide (1.04 g, 16.0 mmol, 1.60 equiv) and sodium nitrite (1.04 g, 15.0 mmol, 1.50 equiv) at 0 °C under air. After stirring for 2.5 h at the same temperature, to the

mixture was added saturated aqueous sodium bicarbonate (100 mL). The mixture was extracted with EtOAc (20 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 flash column chromatography (Biotage® ZIP-sphere cartridge 45 g, *n*-hexane only to *n*-hexane/EtOAc = 3/1) to afford 2-azido-1-bromo-3-chloro-5-fluorobenzene (**2h**) (814 mg, 3.24 mmol, 32.5%) as a colorless solid.

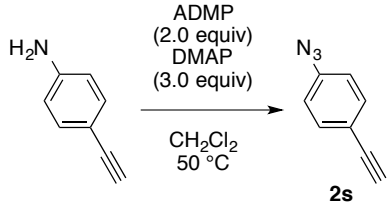
Similarly, azides **2i**, **2j**, **2l**, **2q**, **2r**, **2t**, and 4-iodophenyl azide were prepared from the corresponding anilines.

*Preparation of azide **2p** by Sonogashira coupling*



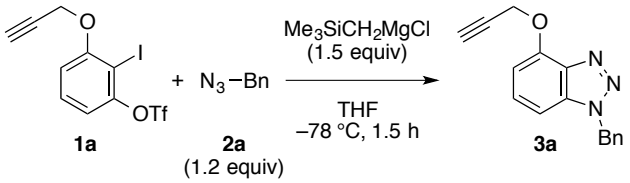
Under an argon atmosphere, to a solution of triethylamine (59.0 mL, 42.6 mmol, 2.94 equiv) in acetonitrile (90 mL) was added trimethylsilylacetylene (1.44 g, 14.8 mmol, 1.02 equiv), 4-iodophenyl azide (3.54 g, 14.5 mmol), copper(I) iodide (34.4 mg, 0.181 mmol, 12 mol %), and bis(triphenylphosphine)palladium(II) dichloride (122 mg, 0.174 mmol, 12 mol %) at room temperature. After stirring for 24 h at the same temperature, to the mixture was added an additional amount of trimethylsilylacetylene (2.85 g, 29.0 mmol, 2.00 equiv) and stirred for 24 h at the same temperature. After concentration of the reaction mixture under reduced pressure, the residue was purified by flash column chromatography (Biotage® ZIP-sphere cartridge 80 g, *n*-hexane only to *n*-hexane/EtOAc = 12/1) to afford 4-(trimethylsilylethynyl)phenyl azide (**2s**) (722 mg, 3.36 mmol, 23.1%) as a pale yellow solid.

*Preparation of azide **2s** from the corresponding aniline by diazo-transfer method using ADMP*



Under an argon atmosphere, to a solution of 4-ethynylaniline (234 mg, 2.00 mmol) and DMAP (733 mg, 6.01 mmol, 3.00 equiv) in dichloromethane (4 mL) was added ADMP (1.14 g, 4.00 mmol, 2.00 equiv) at room temperature, and the mixture was heated at 50 °C with stirring for 16 h. After cooling to room temperature, to the mixture was added saturated aqueous sodium bicarbonate (40 mL). The mixture was extracted with dichloromethane (30 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 flash column chromatography (Biotage® ZIP-sphere cartridge 45 g, *n*-hexane only to *n*-hexane/EtOAc = 10/1) to afford 4-ethynylphenyl azide (**2s**) (196 mg, 1.37 mmol, 68.5%) as a brown oil.

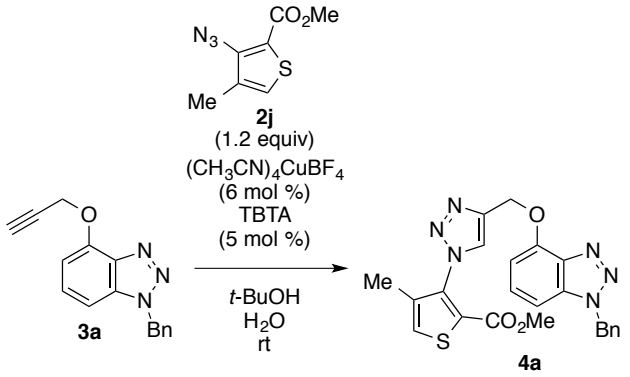
A typical procedure for azide–aryne cycloaddition using (trimethylsilyl)methylmagnesium chloride (Table 1, entry 7)



Under an argon atmosphere, to a solution of 2-iodo-3-(propargyloxy)phenyl triflate (**1a**) (207 mg, 0.509 mmol) and benzyl azide (**2a**) (80.8 mg, 0.608 mmol, 1.19 equiv) in THF (2.5 mL) was added a solution of (trimethylsilyl)methylmagnesium chloride (1.23 M in THF, 0.600 mL, 0.738 mmol, 1.45 equiv) at –78 °C. After stirring the mixture for 1.5 h at the same temperature, to the mixture was added saturated aqueous ammonium chloride (20 mL). The mixture was extracted with EtOAc (20 mL × 3), and the combined organic extract was washed with brine (5 mL), dried (Na_2SO_4), and after filtration, the filtrate was concentrated under reduced pressure. The residue was purified by flash column chromatography (Biotage® ZIP-sphere cartridge 10 g, *n*-hexane/EtOAc = 4/1 to 3/2) to afford 1-benzyl-4-propargyloxy-1*H*-benzo[*d*][1,2,3]triazole (**3a**) (125 mg, 0.476 mmol, 93.2%) as a colorless solid.

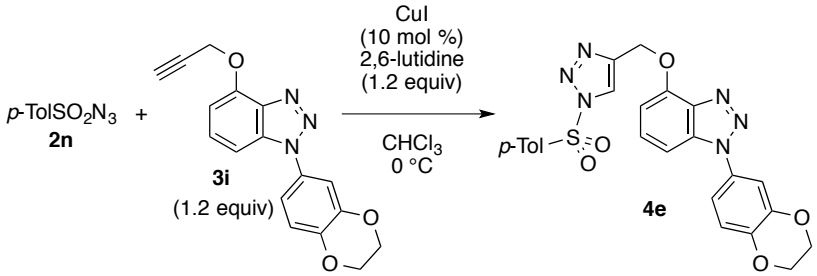
The reaction could be uneventfully performed at gram scale. For instance, the reaction using 2-iodo-3-(propargyloxy)phenyl triflate (**1a**) (1.01 g, 2.50 mmol), benzyl azide (**2a**) (400 mg, 3.00 mmol, 1.20 equiv), (trimethylsilyl)methylmagnesium chloride (1.23 M in THF, 3.05 mL,3.75 mmol, 1.50 equiv), and THF (12.5 mL) afforded 1-benzyl-4-propargyloxy-1*H*-benzo[*d*][1,2,3]triazole (**3a**) in 87.3% yield (575 mg, 2.18 mmol).

A typical synthetic procedure for bistriazoles by copper-catalyzed azide–alkyne cycloaddition (condition A) (Table 3, entry 1)



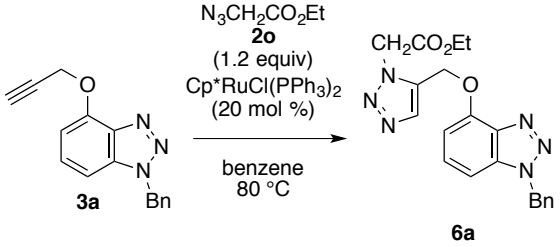
Under an argon atmosphere, to a solution of 1-benzyl-4-propargyloxy-1*H*-benzo[*d*][1,2,3]triazole (**3a**) (151 mg, 0.574 mmol) and methyl 3-azido-4-methyl-2-thiophenecarboxylate (**2j**) (113 mg, 0.574 mmol, 1.00 equiv) in *tert*-butyl alcohol (0.6 mL) and water (0.6 mL) was added tetrakis(acetonitrile)copper(I) tetrafluoroborate (10.2 mg, 32.8 μmol, 5.7 mol %) and TBTA (14.9 mg, 28.1 μmol, 4.9 mol %) at room temperature. After stirring for 64 h at the same temperature, to the mixture was water (20 mL). The mixture was extracted with EtOAc (20 mL × 3), and the combined organic extract was washed with brine (5 mL), dried (Na_2SO_4), and after filtration, the filtrate was concentrated under reduced pressure. The residue was purified by flash column chromatography (Biotage® ZIP-sphere cartridge 10 g, *n*-hexane/EtOAc = 3/2 to 2/3) to afford 1-benzyl-4-(1-(2-methoxycarbonyl-4-methylthiophen-3-yl)-1*H*-1,2,3-triazol-4-yl)methoxy-1*H*-benzo[*d*][1,2,3]triazole (**4a**) (212 mg, 0.461 mmol, 80.3%) as a colorless solid.

Synthesis of bistriazole ***4e*** *by copper-catalyzed cycloaddition of alkyne* ***3i*** *with sulfonylazide* ***2n*** (condition B) (Table 3, entry 5)



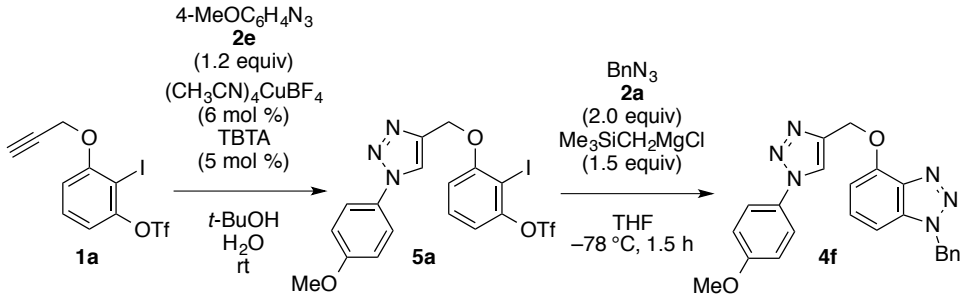
Under an argon atmosphere, to a solution of 1-(3,4-ethylenedioxyphenyl)-4-propargyloxy-1*H*-benzo[*d*][1,2,3]triazole (**3i**) (92.6 mg, 0.302 mmol, 1.21 equiv), 4-toluenesulfonyl azide (**2n**) (49.2 mg, 0.250 mmol), and copper(I) iodide (4.8 mg, 25 μmol, 10 mol %) in chloroform (2.5 mL) was added 2,6-lutidine (35 μL, 0.30 mmol, 1.2 equiv) at 0 °C. After stirring for 21 h at the same temperature, to the mixture was added dichloromethane (20 mL) and saturated aqueous ammonium chloride (20 mL). The mixture was extracted with dichloromethane (10 mL × 3), and the combined organic extract was washed with brine (5 mL), dried (Na_2SO_4), and after filtration, the filtrate was concentrated under reduced pressure. The residue was purified by flash column chromatography (Biotage® ZIP-sphere cartridge 10 g, *n*-hexane/EtOAc = 3/2 to 2/3) to afford 1-(3,4-ethylenedioxyphenyl)-4-(1-(4-toluene-sulfonyl)-1*H*-1,2,3-triazol-4-yl)methoxy-1*H*-benzo[*d*][1,2,3]triazole (**4e**) (105 mg, 0.208 mmol, 83.3%) as a colorless solid.

Synthesis of bistriazole ***6a*** *by ruthenium-catalyzed azide–alkyne cycloaddition* (condition C) (Table 3, entry 6)



Under an argon atmosphere, to a solution of 1-benzyl-4-propargyloxy-1*H*-benzo[*d*][1,2,3]triazole (**3a**) (158 mg, 0.601 mmol, 1.20 equiv) and ethyl azidoacetate (**2o**) (64.8 mg, 0.502 mmol) in benzene (3.3 mL) was added $Cp^*RuCl(PPh_3)_2$ (81.9 mg, 0.103 mmol, 20 mol %) at room temperature, and the mixure was heated at 80 °C with stirring for 4 h. After cooling to room temperature, the mixure was concentrated under reduced pressure. The residue was purified by flash column chromatography (Biotage® ZIP-sphere cartridge 30 g, *n*-hexane/EtOAc = 1/1 to 3/1) to afford 1-benzyl-4-(1-(ethoxycarbonyl)methyl-1*H*-1,2,3-triazol-5-yl)methoxy-1*H*-benzo[*d*][1,2,3]triazole (**6a**) (137 mg, 0.349 mmol, 69.8%) as a pale brown solid.

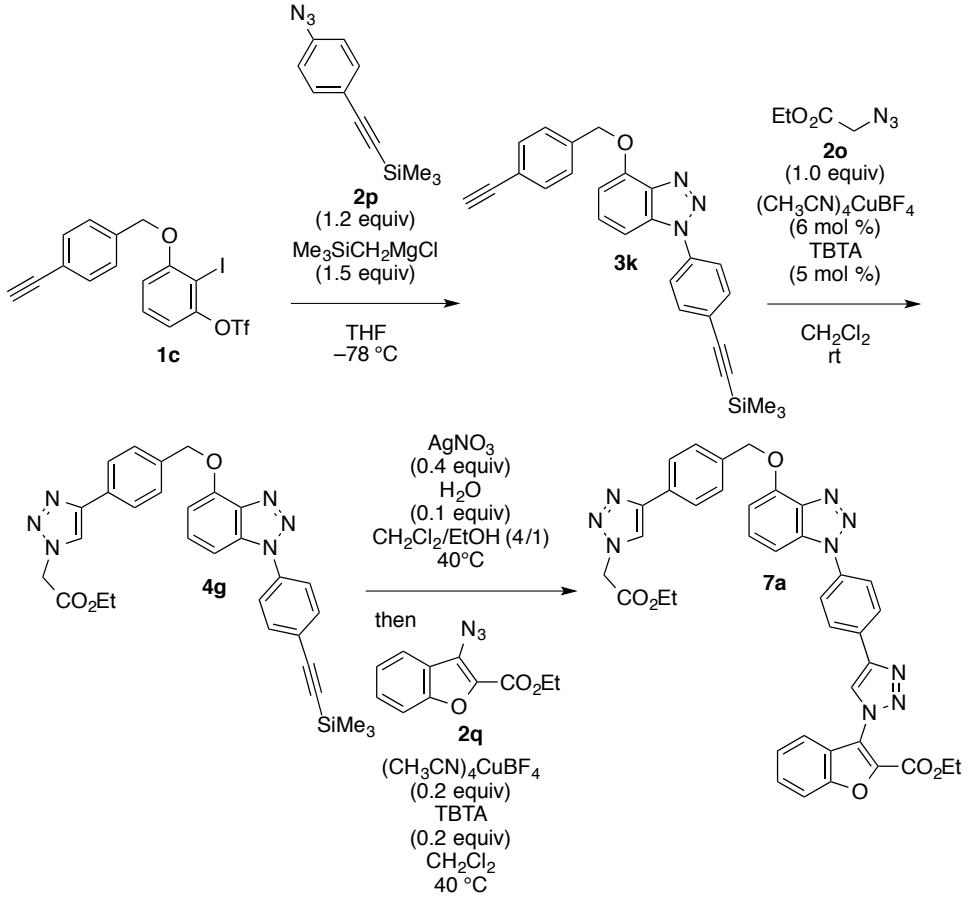
Bistriazole synthesis by sequential azide–alkyne and azide–aryne cycloadditions (Scheme 2)



Under an argon atmosphere, to a solution of 2-iodo-3-(propargyloxy)phenyl triflate (**1a**) (813 mg, 2.00 mmol) and 4-methoxyphenyl azide (**2e**) (298 mg, 2.00 mmol, 1.00 equiv) in dichloromethane (4.0 mL) was added tetrakis(acetonitrile)copper(I) tetrafluoroborate (35.3 mg, 0.112 mmol, 5.6 mol %) and TBTA (54.0 mg, 0.102 mmol, 5.1 mol %) at room temperature. After stirring for 18 h at the same temperature, the mixture was concentrated under reduced pressure. The residue was purified by flash column chromatography (Biotage® ZIP-sphere cartridge 80 g, *n*-hexane/EtOAc = 3/1 to 1/1) to afford 2-iodo-3-((1-(4-methoxyphenyl)-1*H*-1,2,3-triazol-4-yl)methoxy)phenyl triflate (**5a**) (1.09 g, 0.461 mmol, 98.5%) as a colorless solid.

Under an argon atmosphere, to a solution of 2-iodo-3-((1-(4-methoxyphenyl)-1*H*-1,2,3-triazol-4-yl)methoxy)phenyl triflate (**5a**) (100 mg, 0.180 mmol) and benzyl azide (**2a**) (53.7 mg, 0.360 mmol, 2.00 equiv) in THF (0.9 mL) was added a solution of (trimethylsilyl)methylmagnesium chloride (1.23 M in THF, 0.220 mL, 0.271 mmol, 1.51 equiv) at –78 °C. After stirring for 1.5 h at the same temperature, to the mixture was added saturated aqueous ammonium chloride (20 mL). The mixture was extracted with EtOAc (20 mL × 3), and the combined organic extract was washed with brine (5 mL), dried (Na_2SO_4), and after filtration, the filtrate was concentrated under reduced pressure. The residue was purified by flash column chromatography (Biotage® ZIP-sphere cartridge 5 g, *n*-hexane/EtOAc = 3/2 to 1/12) to afford 1-benzyl-4-(1-(4-methoxyphenyl)-1*H*-1,2,3-triazol-4-yl)methoxy-1*H*-benzo[*d*][1,2,3]triazole (**4f**) (61.2 mg, 0.149 mmol, 82.4%) as a colorless solid.

Synthesis of tristriazole ***7a*** *by three sequential cycloadditions* (Scheme 3)



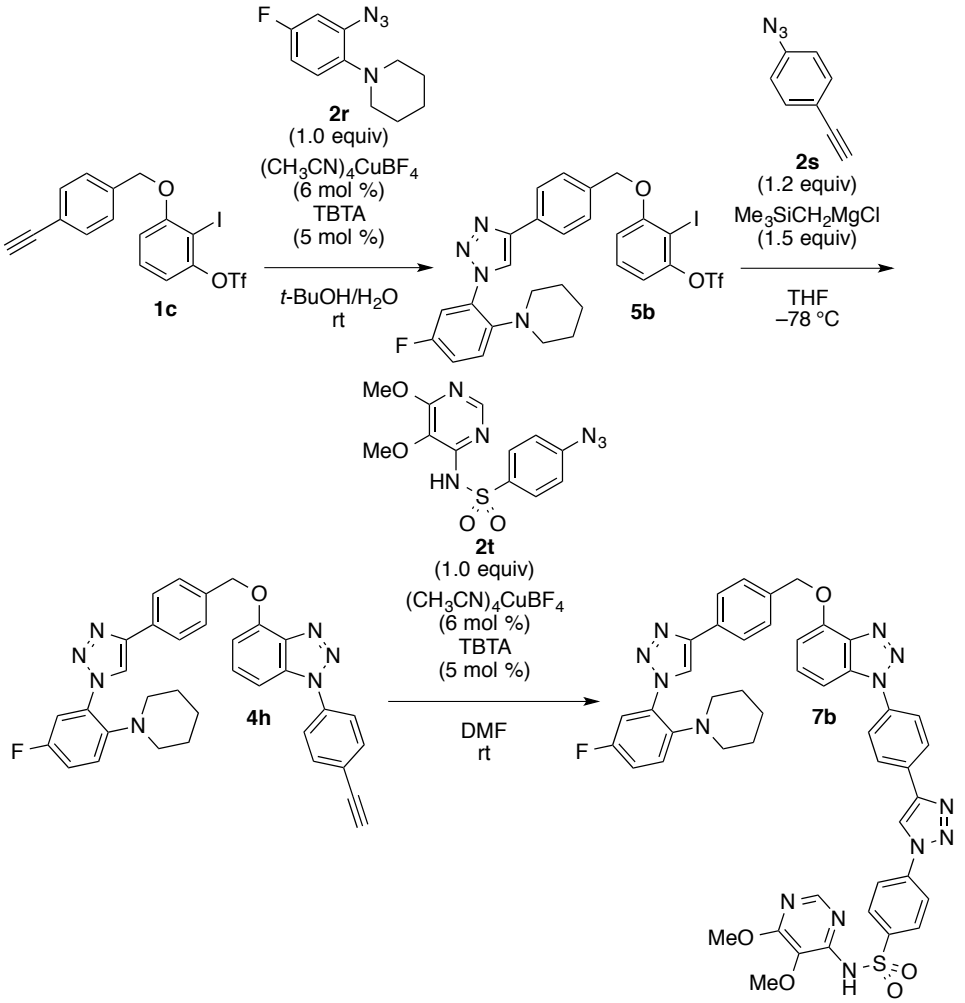
Under an argon atmosphere, to a solution of 3-(4-ethynylbenzyl)oxy-2-iodophenyl triflate (**1c**) (2.41 g, 5.00 mmol) and 4-(trimethylsilylethynyl)phenyl azide (1.29 g, 6.00 mmol, 1.20 equiv) in THF (10 mL) was added a solution of (trimethylsilyl)methylmagnesium chloride (1.23 M in THF, 6.10 mL, 7.50 mmol, 1.50 equiv) at –78 °C. After stirring the mixture for 1.5 h at the same temperature, to the mixture was added saturated aqueous ammonium chloride (30 mL). The mixture was extracted with EtOAc (30 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 flash column chromatography (Biotage® ZIP-sphere cartridge 120 g, CH_2Cl_2 only) to afford 4-(4-ethynylbenzyl)oxy-1-(4-(trimethylsilylethynyl)phenyl)-1*H*-benzo[*d*][1,2,3]triazole (**3k**) (1.66 g, 0.713 mmol, 78.8%) as a colorless solid.

Under an argon atmosphere, to a solution of 4-(4-ethynylbenzyl)oxy-1-(4-(trimethylsilylethynyl)-phenyl)-1*H*-benzo[*d*][1,2,3]triazole (**3k**) (1.47 g, 3.48 mmol) and ethyl azidoacetate (**2o**) (450 mg, 3.48 mmol, 1.00 equiv) in dichloromethane (19 mL) was added tetrakis(acetonitrile)copper(I) tetrafluoroborate (65.0 mg, 0.206 mmol, 5.9 mol %) and TBTA (92.3 mg, 0.174 mmol, 5.0 mol %) at room temperature. After stirring for 24 h at the same temperature, to the mixture was water (20 mL). The mixture was extracted with EtOAc (20 mL × 3), and the combined organic extract was washed with brine (5 mL), dried (Na_2SO_4), and after filtration, the filtrate was concentrated under reduced pressure. The residue was purified by flash column chromatography (Biotage® ZIP-sphere cartridge 80 g, CH_2Cl_2 only to CH_2Cl_2/MeOH = 32/1) to afford 4-(4-(1-(ethoxycarbonyl)methyl-1*H*-1,2,3-triazol-4-yl)benzyl)oxy-1-(4-(trimethylsilylethynyl)phenyl)-1*H*-benzo[*d*][1,2,3]triazole (**4g**) (1.92 g, 3.48 mmol, quant.) as a colorless solid.

Under an argon atmosphere, to a solution of 4-(4-(1-(ethoxycarbonyl)methyl-1*H*-1,2,3-triazol-

4-yl)benzyl)oxy-1-(4-(trimethylsilylethynyl)phenyl)-1*H*-benzo[*d*][1,2,3]triazole (**4g**) (54.7 mg, 99.3 μmol) in dichloromethane (0.64 mL) and ethanol (0.16 mL) was added water (0.2 μL, 11 μmol, 0.11 equiv) and silver(I) nitrate (6.0 mg, 35 μmol, 0.36 equiv) at room temperature. After stirring for 24 h at 40 °C, disappearance of **4g** was checked by TLC monitoring and then to the mixture was added a solution of ethyl 3-azidobenzo[*b*]furan-2-carboxylate (**2q**) (34.7 mg, 149 μmol, 1.50 equiv) in dichloromethane (2.0 mL), tetrakis(acetonitrile)copper(I) tetrafluoroborate (6.7 mg, 21 μmol, 0.21 equiv) and TBTA (10.6 mg, 20.0 μmol, 0.20 equiv) at room temperature. After stirring for 24 h at 40 °C, the mixture was concentrated under reduced pressure. The residue was purified by flash column chromatography (Biotage® ZIP-sphere cartridge 5 g, CH_2Cl_2 only to CH_2Cl_2/MeOH = 16/1) to afford 1-(4-(1-(2-(ethoxycarbonyl)benzo[*b*]furan-3-yl)-1*H*-1,2,3-triazol-4-yl)phenyl)-4-(4-(1-(ethoxycarbony l)methyl-1*H*-1,2,3-triazol-4-yl)benzyl)oxy-1*H*-benzo[*d*][1,2,3]triazole (**7a**) (62.2 mg, 87.6 μmol, 88.3%) as a colorless solid.

Synthesis of tristriazole ***7b*** *by three sequential cycloadditions* (Scheme 3)



Under an argon atmosphere, to a solution of 3-(4-ethynylbenzyl)oxy-2-iodophenyl triflate (**1c**) (482 mg, 1.00 mmol) and 5-fluoro-2-piperidinophenyl azide (**2r**) (221 mg, 1.00 mmol, 1.00 equiv) in *tert*-butyl alcohol (1.0 mL) and water (1.0 mL) was added tetrakis(acetonitrile)copper(I) tetrafluoroborate (19.6 mg, 63.0 μmol, 6.3 mol %) and TBTA (26.7 mg, 50.3 μmol, 5.0 mol %) at room temperature. After stirring for 23 h at the same temperature, the mixture was concentrated under reduced pressure. The residue was purified by flash column chromatography (Biotage® ZIP-sphere

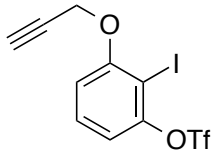
cartridge 45 g, *n*-hexane/EtOAc = 6/1 to 2/1) to afford 3-(4-(1-(5-fluoro-2-piperidinophenyl)-1*H*-1,2,3-triazol-4-yl)benzyl)oxy-2-iodophenyl triflate (**5b**) (670 mg, 0.954 mmol, 95.4%).

Under an argon atmosphere, to a solution of 3-(4-(1-(5-fluoro-2-piperidinophenyl)-1*H*-1,2,3-triazol-4-yl)benzyl)oxy-2-iodophenyl triflate (**5b**) (351 mg, 0.500 mmol) and 4-ethynylphenyl azide (**2s**) (85.8 mg, 0.600 mmol, 1.20 equiv) in THF (2.5 mL) was added a solution of (trimethylsilyl)methylmagnesium chloride (1.23 M in THF, 0.610 mL, 0.750 mmol, 1.50 equiv) at –78 °C. After stirring for 1.5 h at the same temperature, to the mixture was added saturated aqueous ammonium chloride (20 mL). The mixture was extracted with EtOAc (20 mL × 3), and the combined organic extract was washed with brine (5 mL), dried (Na_2SO_4), and after filtration, the filtrate was concentrated under reduced pressure. The residue was purified by flash column chromatography (Biotage® ZIP-sphere cartridge 30 g, CH_2Cl_2 only to CH_2Cl_2/MeOH = 24/1; then Biotage® ZIP-sphere cartridge 30 g, CH_2Cl_2 only to CH_2Cl_2/MeOH = 99/1) to afford 1-(4-ethynylphenyl)-4-(4-(1-(5-fluoro-2-piperidinophenyl)-1*H*-1,2,3-triazol-4-yl)benzyl)oxy-1*H*-benzo[*d*][1,2,3]triazole (**4h**) (190 mg, 0.333 mmol, 66.6%) as a colorless solid.

Under an argon atmosphere, to a solution of 1-(4-ethynylphenyl)-4-(4-(1-(5-fluoro-2-piperidinophenyl)-1*H*-1,2,3-triazol-4-yl)benzyl)oxy-1*H*-benzo[*d*][1,2,3]triazole (**4h**) (42.1 mg, 73.9 μmol) and 4-((5,6-dimethoxypyrimidin-4-yl)aminosulfonyl)phenyl azide (**2t**) (25.2 mg, 75.0 μmol, 1.01 equiv) in DMF (0.2 mL) was added tetrakis(acetonitrile)copper(I) tetrafluoroborate (1.4 mg, 4.5 μmol, 6.1 mol %) and TBTA (2.0 mg, 3.8 μmol, 5.1 mol %) at room temperature. After stirring for 17 h at the same temperature, the mixture was concentrated under reduced pressure. The residue was purified by flash column chromatography (Biotage® ZIP-sphere cartridge 10 g, CH_2Cl_2 only to CH_2Cl_2/MeOH = 24/1; then Biotage® ZIP-sphere cartridge 10 g, *n*-hexane/EtOAc = 4/1 to 1/1, then CH_2Cl_2 only to CH_2Cl_2/MeOH = 16/1) to afford 1-(4-(1-(4-((5,6-dimethoxypyrimidin-4-yl)aminosulfonyl)phenyl)-1*H*-1,2,3-triazol-4-yl)phenyl)-4-(4-(1-(5-fluoro-2-piperidinophenyl)-1*H*-1,2,3-triazol-4-yl)benzyl)oxy-1*H*-benzo[*d*][1,2,3]triazole (**7b**) (52.7 mg, 58.2 μmol, 78.7%) as a brown solid.

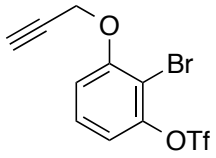
Analytical data of compounds

2-Iodo-3-(propargyloxy)phenyl trifluoromethanesulfonate (**1a**)



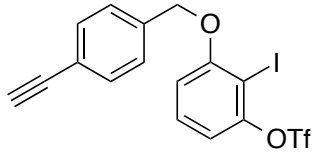
Colorless solid; Mp 35–36 °C; TLC R_f 0.39 (*n*-hexane/EtOAc = 4/1); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.58 (t, 1H, *J* = 2.0 Hz), 4.82 (d, 2H, *J* = 2.0 Hz), 6.999 (d, 1H, *J* = 8.5 Hz), 7.007 (d, 1H, *J* = 8.5 Hz), 7.40 (dd, 1H, *J* = 8.5, 8.5 Hz); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 57.4 (1C), 76.9 (1C), 77.2 (1C), 83.4 (1C), 111.9 (1C), 115.0 (1C), 118.7 (q, 1C, $J^1_{C–F}$ = 321 Hz), 130.2 (1C), 151.3 (1C), 158.5 (1C); ^{19}F NMR ($CDCl_3$, 376 MHz) δ –73.4 (s); IR (KBr, cm^{-1}) 600, 823, 948, 1053, 1140, 1215, 1425, 1460, 1588, 3298; Anal. calcd. for $C_{10}H_6F_3IO_4S$: C, 29.57; H, 1.49; S, 7.90%. Found: C, 29.59; H, 1.51; S, 7.86%.

2-Bromo-3-(propargyloxy)phenyl trifluoromethanesulfonate (**1b**)



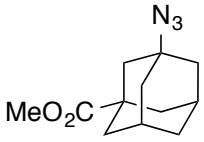
Colorless solid; Mp 37–38 °C; TLC R_f 0.35 (*n*-hexane/EtOAc = 4/1); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.59 (t, 1H, *J* = 2.5 Hz), 4.83 (d, 2H, *J* = 2.5 Hz), 7.04 (d, 1H, *J* = 8.0 Hz), 7.09 (d, 1H, *J* = 8.0 Hz), 7.37 (dd, 1H, *J* = 8.0, 8.0 Hz); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 57.3 (1C), 76.9 (1C), 77.1 (1C), 107.2 (1C), 113.0 (1C), 115.5 (1C), 118.6 (q, 1C, $J^1_{C–F}$ = 320 Hz), 128.6 (1C), 148.1 (1C), 155.9 (1C); ^{19}F NMR ($CDCl_3$, 376 MHz) δ –73.6 (s); IR (KBr, cm^{-1}) 824, 913, 1038, 1060, 1141, 1220, 1427, 1467, 3297; HRMS (ESI^+) *m*/*z* 380.9021 ($[M+Na]^+$, $C_{10}H_6BrF_3NaO_4S^+$ requires 380.9014).

3-(4-Ethynylbenzyl)oxy-2-iodophenyl trifluoromethanesulfonate (**1c**)



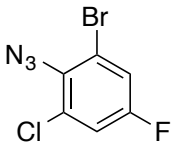
Colorless solid; Mp 97–98 °C; TLC R_f 0.51 (*n*-hexane/EtOAc = 4/1); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 3.10 (s, 1H), 5.18 (s, 2H), 6.82 (dd, 1H, *J* = 1.0, 8.5 Hz), 6.98 (dd, 1H, *J* = 1.0, 8.5 Hz), 7.36 (dd, 1H, *J* = 8.5, 8.5 Hz), 7.44–7.47 (AA'BB', 2H), 7.52–7.55 (AA'BB', 2H); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 71.1 (1C), 77.7 (1C), 83.2 (1C), 83.5 (1C), 111.6 (1C), 114.6 (1C), 118.7 (q, 1C, $J^1_{C–F}$ = 321 Hz), 122.0 (1C), 126.9 (2C), 130.4 (1C), 132.5 (2C), 136.4 (1C), 151.4 (1C), 159.2 (1C); ^{19}F NMR ($CDCl_3$, 376 MHz) δ –73.4 (s); IR (KBr, cm^{-1}) 599, 832, 1062, 1140, 1217, 1274, 1425, 1450, 1588, 3294; HRMS (ESI^+) *m*/*z* 504.9188 ($[M+Na]^+$, $C_{16}H_{10}F_3INaO_4S^+$ requires 504.9189).

Methyl 3-azido-1-adamantanecarboxylate (**2d**)



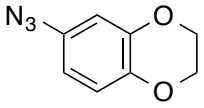
Colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.60–1.68 (br, 2H), 1.72–1.87 (m, 8H), 1.90–1.95 (br, 2H), 2.21–2.30 (br, 2H), 3.68 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 29.3, 34.8, 37.5, 40.6, 42.6, 43.0, 51.9, 58.8, 176.5 (three pairs of equivalent carbons were not identified); IR (KBr, cm^{-1}) 1090, 1247, 1454, 1729, 2089, 2859, 2933; HRMS (ESI^+) *m*/*z* 258.1206 ($[M+Na]^+$, $C_{12}H_{17}N_3NaO_2^+$ requires 258.1213).

2-Azido-1-bromo-3-chloro-5-fluorobenzene (**2h**)



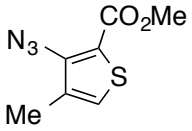
Colorless solid; Mp 35–36 °C; TLC R_f 0.56 (*n*-hexane); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.14 (dd, 1H, J = 3.0, 7.5 Hz), 7.26 (dd, 1H, J = 3.0, 7.5 Hz); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 117.3 (d, 1C, $J^2_{C–F}$ = 26.5 Hz), 118.7 (d, 1C, $J^3_{C–F}$ = 10.1 Hz), 119.7 (d, 1C, $J^2_{C–F}$ = 25.2 Hz), 130.5 (d, 1C, $J^3_{C–F}$ = 10.1 Hz), 132.3 (d, 1C, $J^4_{C–F}$ = 5.0 Hz), 159.1 (d, 1C, $J^1_{C–F}$ = 253 Hz); ^{19}F NMR ($CDCl_3$, 376 MHz) δ –113.3 (dd, $J_{H–F}$ = 7.5, 7.5 Hz); IR (KBr, cm^{-1}) 859, 938, 1230, 1454, 1570, 2139, 3084; Anal. calcd. for $C_6H_2BrClFN_3$: C, 28.77; H, 0.80; N, 16.78%. Found: C, 28.65; H, 0.95; N, 16.61%.

3,4-Ethylenedioxyphenyl azide (**2i**)



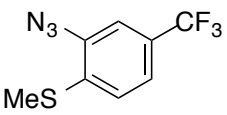
Brown oil; TLC R_f 0.37 (*n*-hexane/EtOAc = 10/1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.22–4.27 (m, 4H), 6.52 (dd, 1H, J = 2.5, 8.5 Hz), 6.56 (d, 1H, J = 2.5 Hz), 6.83 (d, 1H, J = 8.5 Hz); ^{13}C NMR (126 MHz, $CDCl_3$) δ 64.2 (1C), 64.4 (1C), 107.9 (1C), 112.0 (1C), 118.1 (1C), 133.1 (1C), 141.0 (1C), 144.2 (1C); IR (KBr, cm^{-1}) 914, 1068, 1234, 1246, 1502, 2114; HRMS (ESI$^+$) m/z 150.0543 ([M+H–N_2]$^+$, $C_8H_8NO_2^+$ requires 150.0550).

Methyl 3-azido-4-methyl-2-thiophenecarboxylate (**2j**)



Colorless solid; Mp 59–60 °C; TLC R_f 0.36 (*n*-hexane/EtOAc = 9/1); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.13 (d, 3H, J = 1.0 Hz), 3.90 (s, 3H), 7.09 (q, 1H, J = 1.0 Hz); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 13.7 (1C), 52.1 (1C), 118.4 (1C), 126.6 (1C), 134.0 (1C), 141.5 (1C), 161.8 (1C); IR (KBr, cm^{-1}) 786, 1125, 1224, 1315, 1386, 1460, 1704, 2133, 2955, 3103; Anal. calcd. for $C_7H_7N_3O_2S$: C, 42.63; H, 3.58; N, 21.31; S, 16.26%. Found: C, 42.68; H, 3.72; N, 21.32; S, 16.30%.

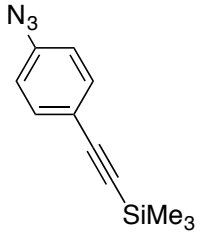
3-Azido-4-(methylthio)benzotrifluoride (**2l**)



Colorless solid; Mp 42–43 °C; TLC R_f 0.24 (*n*-hexane); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.48 (s, 3H), 7.21 (d, 1H, J = 8.0 Hz), 7.30 (d, 1H, J = 0.5 Hz), 7.36 (dd, 1H, J = 0.5, 8.0 Hz); ^{13}C NMR ($CDCl_3$,

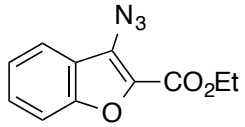
126 MHz) δ 14.6 (1C), 114.6 (q, 1C, $J^3_{C–F}$ = 3.8 Hz), 122.0 (q, 1C, $J^3_{C–F}$ = 3.8 Hz), 123.7 (q, 1C, $J^1_{C–F}$ = 272 Hz), 125.4 (1C), 127.8 (q, 1C, $J^2_{C–F}$ = 34.0 Hz), 135.3 (1C), 137.3 (1C); ^{19}F NMR ($CDCl_3$, 376 MHz) δ –62.7 (s); IR (KBr, cm^{-1}) 1088, 1125, 1154, 1269, 1286, 1331, 2114, 2927; Anal. calcd. for $C_8H_6F_3N_3S$: C, 41.20; H, 2.59; N, 18.02; S, 13.75%. Found: C, 41.25; H, 2.85; N, 18.03; S, 13.45%.

4-(Trimethylsilylethynyl)phenyl azide (**2p**)



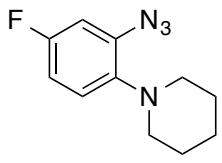
Pale yellow solid; Mp 32–33 °C; TLC R_f 0.51 (*n*-hexane/EtOAc = 10/1); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 0.25 (s, 9H), 6.93–6.97 (AA'BB', 2H), 7.43–7.46 (AA'BB', 2H); ^{13}C NMR ($CDCl_3$, 126 MHz) δ –0.07 (3C), 94.5 (1C), 104.3 (1C), 118.9 (2C), 119.7 (1C), 133.5 (2C), 140.1 (1C); IR (KBr, cm^{-1}) 840, 1251, 1297, 1502, 2112, 2960; EI-MS *m*/*z* 215 (25%) [M^+], 187 (100%), 172 (72%), 157 (23%), 145 (55%), 44 (92%); HRMS (ESI^+) *m*/*z* 453.1651 ([2M+Na]$^+$, $C_{22}H_{26}N_6NaSi_2^+$ requires 453.1650).

Ethyl 3-azidobenzo[*b*]furan-2-carboxylate (**2q**)



Colorless solid; Mp 54–55 °C; TLC R_f 0.32 (*n*-hexane/EtOAc = 9/1); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.46 (t, 3H, *J* = 7.5 Hz), 4.49 (q, 2H, *J* = 7.5 Hz), 7.32 (dd, 1H, *J* = 8.0, 8.0 Hz), 7.48–7.54 (m, 2H), 7.73 (d, 1H, *J* = 8.0 Hz); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 14.4 (1C), 61.7 (1C), 112.7 (1C), 120.4 (1C), 123.2 (1C), 123.8 (1C), 128.4 (1C), 129.0 (1C), 134.0 (1C), 153.4 (1C), 159.2 (1C); IR (KBr, cm^{-1}) 748, 1145, 1224, 1301, 1413, 1709, 2128, 2985; Anal. calcd. for $C_{11}H_9N_3O_3$: C, 57.14; H, 3.92; N, 18.17%. Found: C, 57.25; H, 4.13; N, 18.13%.

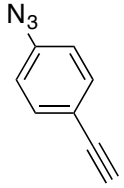
5-Fluoro-2-piperidinophenyl azide (**2r**)



Brown oil; TLC R_f 0.32 (*n*-hexane/EtOAc = 10/1); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.52–1.59 (m, 2H), 1.71–1.78 (m, 4H), 2.86–2.90 (m, 4H), 6.73–6.81 (m, 2H), 6.98 (dd, 1H, *J* = 5.5, 9.0 Hz); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 24.1 (1C), 25.8 (2C), 53.5 (2C), 107.4 (d, 1C, $J^2_{C–F}$ = 25.2 Hz), 111.7 (d, 1C, $J^2_{C–F}$ = 21.4 Hz), 121.2 (d, 1C, $J^3_{C–F}$ = 8.8 Hz), 134.8 (d, 1C, $J^3_{C–F}$ = 10.1 Hz), 142.4 (d, 1C, $J^4_{C–F}$ = 2.5 Hz), 158.8 (d, 1C, $J^1_{C–F}$ = 244 Hz); ^{19}F NMR ($CDCl_3$, 376 MHz) δ –119.0 (ddd, $J_{H–F}$ = 5.5, 8.2, 8.2

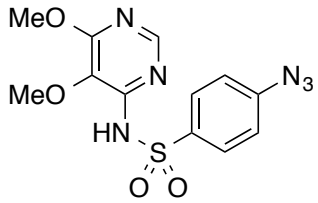
Hz); IR (KBr, cm^{-1}) 913, 1191, 1296, 1498, 1594, 2116, 2940; HRMS (ESI^+) *m*/*z* 221.1202 ($[M+H]^+$, $C_{11}H_{14}FN_4^+$ requires 221.1197).

4-Ethynylphenyl azide (**2s**)



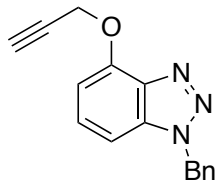
Brown oil; TLC R_f 0.58 (*n*-hexane/EtOAc = 10/1); ^1H NMR ($CDCl_3$, 500 MHz) δ 3.08 (s, 1H), 6.95–6.99 (AA'BB', 2H), 7.45–7.50 (AA'BB', 2H); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 77.5 (1C), 82.9 (1C), 118.6 (1C), 119.0 (2C), 133.6 (2C), 140.6 (1C); IR (KBr, cm^{-1}) 835, 1219, 1276, 1296, 1502, 1601, 2102, 3298; EI-MS *m*/*z* 143 (45%) [M^+], 115 (100%), 88 (62%), 62 (56%); HRMS (ESI^+) *m*/*z* 309.0849 ($[2M+Na]^+$, $C_{16}H_{10}N_6Na^+$ requires 309.0859).

4-((5,6-Dimethoxypyrimidin-4-yl)aminosulfonyl)phenyl azide (**2t**)



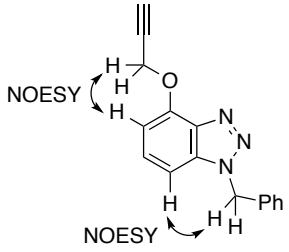
Colorless solid; Mp 134 °C (decomp.); TLC R_f 0.34 (*n*-hexane/EtOAc = 3/2); ^1H NMR ($CDCl_3$, 500 MHz) δ 3.87 (s, 3H), 3.99 (s, 3H), 7.11–7.14 (AA'BB', 2H), 7.89 (br s, 1H), 8.13–8.16 (AA'BB', 2H), 8.16 (s, 1H); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 54.2 (1C), 60.6 (1C), 119.0 (2C), 126.5 (1C), 130.5 (2C), 135.4 (1C), 145.5 (1C), 149.6 (1C), 151.0 (1C), 160.9 (1C); IR (KBr, cm^{-1}) 560, 1082, 1167, 1286, 1304, 1338, 1411, 1449, 1485, 1582, 2128, 3221; Anal. calcd. for $C_{12}H_{12}N_6O_4S$: C, 42.85; H, 3.60; N, 24.99; S, 9.53%. Found: C, 43.03; H, 3.76; N, 25.01; S, 9.45%.

1-Benzyl-4-propargyloxy-1*H*-benzo[*d*][1,2,3]triazole (**3a**)

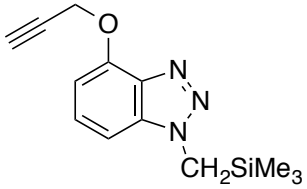


Colorless solid; Mp 97–99 °C; TLC R_f 0.26 (*n*-hexane/EtOAc = 4/1); ^1H NMR ($CDCl_3$, 500 MHz) δ 2.54 (t, 1H, *J* = 2.5 Hz), 5.13 (d, 2H, *J* = 2.5 Hz), 5.81 (s, 2H), 6.84 (d, 1H, *J* = 8.0 Hz), 6.95 (d, 1H, *J* = 8.0 Hz), 7.24–7.35 (m, 6H**)**; ^{13}C NMR ($CDCl_3$, 126 MHz) δ 52.3 (1C), 57.1 (1C), 76.2 (1C), 78.1 (1C), 102.8 (1C), 105.9 (1C), 127.6 (2C), 128.4 (2C), 129.0 (1C+1C, two signals overlapped), 134.7 (1C), 134.9 (1C), 138.3 (1C), 149.4 (1C); IR (KBr, cm^{-1}) 734, 1062, 1283, 1511, 1600, 3288; Anal. calcd. for $C_{16}H_{13}N_3O$: C, 72.99; H, 4.98; N, 15.96%. Found: C, 72.86; H, 5.28; N, 15.68%.

Regiochemistry of benzotriazole **3a** was determined by NOESY experiment.

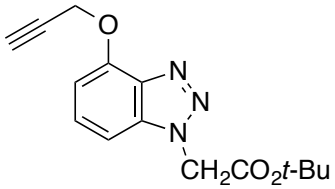


4-Propargyloxy-1-(trimethylsilyl)methyl-1*H*-benzo[*d*][1,2,3]triazole (**3b**)



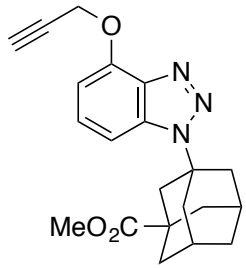
Colorless solid; Mp 86–88 °C; TLC R_f 0.39 (*n*-hexane/EtOAc = 4/1); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 0.19 (s, 9H), 2.54 (t, 1H, *J* = 2.5 Hz), 4.01 (s, 2H), 5.17 (d, 2H, *J* = 2.5 Hz), 6.85 (dd, 1H, *J* = 1.0, 8.0 Hz), 7.08 (dd, 1H, *J* = 1.0, 8.0 Hz), 7.37 (dd, 1H, *J* = 8.0, 8.0 Hz); ^{13}C NMR ($CDCl_3$, 126 MHz) δ –1.9 (3C), 39.1 (1C), 57.3 (1C), 76.0 (1C), 78.3 (1C), 102.7 (1C), 105.9 (1C), 127.7 (1C), 135.9 (1C), 137.7 (1C), 149.2 (1C); IR (KBr, cm^{-1}) 742, 856, 1061, 1252, 1510, 1599, 2956, 3290; Anal. calcd. for $C_{13}H_{17}N_3OSi$: C, 60.20; H, 6.61; N, 16.20%. Found: C, 60.29; H, 6.88; N, 16.05%.

1-(*tert*-Butoxycarbonyl)methyl-4-propargyloxy-1*H*-benzo[*d*][1,2,3]triazole (**3c**)



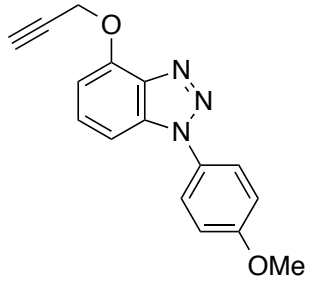
Colorless solid; Mp 120–121 °C; TLC R_f 0.20 (*n*-hexane/EtOAc = 4/1); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.45 (s, 9H), 2.54 (t, 1H, *J* = 2.5 Hz), 5.15 (d, 2H, *J* = 2.5 Hz), 5.29 (s, 2H), 6.89 (d, 1H, *J* = 8.0 Hz), 7.06 (d, 1H, *J* = 8.0 Hz), 7.43 (dd, 1H, *J* = 8.0, 8.0 Hz); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 27.9 (3C), 49.9 (1C), 57.3 (1C), 76.2 (1C), 78.1 (1C), 83.7 (1C), 102.3 (1C), 106.2 (1C), 128.9 (1C), 135.5 (1C), 138.0 (1C), 149.5 (1C), 165.2 (1C); IR (KBr, cm^{-1}) 743, 1067, 1157, 1238, 1269, 1369, 1513, 1604, 1745, 2982; Anal. calcd. for $C_{15}H_{17}N_3O_3$: C, 62.71; H, 5.96; N, 14.63%. Found: C, 62.44; H, 6.26; N, 14.40%.

1-(3-(Methoxycarbonyl)adamantan-1-yl)-4-propargyloxy-1*H*-benzo[*d*][1,2,3]triazole (**3d**)



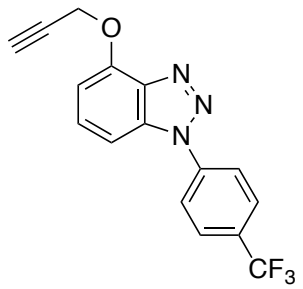
Colorless solid; Mp 148–149 °C; TLC R_f = 0.24 (*n*-hexane/EtOAc = 1/1); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.78–1.85 (m, 2H), 1.98–2.03 (br, 4H), 2.43–2.50 (m, 6H), 2.54 (t, 1H, *J* = 2.0 Hz), 2.58–2.63 (br, 2H), 3.69 (s, 3H), 5.10 (s, 2H), 6.83 (d, 1H, *J* = 8.0 Hz), 7.32 (dd, 1H, *J* = 8.0, 8.0 Hz), 7.37 (d, 1H, *J* = 8.0 Hz); ^{13}C NMR (126 MHz, $CDCl_3$) δ 29.1, 34.9, 37.6, 40.9, 42.7, 42.8, 51.9, 56.9, 61.3, 76.0 (1C), 78.1 (1C), 105.2 (1C), 105.3 (1C), 127.2 (1C), 133.5 (1C), 138.9 (1C), 149.4 (1C), 176.2 (1C) (three pairs of equivalent carbons were not identified); IR (KBr, cm^{-1}) 913, 1093, 1203, 1243, 1502, 1591, 1726, 2910; HRMS (ESI^+) *m*/*z* 388.1618 ($[M+Na]^+$, $C_{21}H_{23}N_3NaO_3^+$ requires 388.1632).

1-(4-Methoxyphenyl)-4-propargyloxy-1*H*-benzo[*d*][1,2,3]triazole (**3e**)



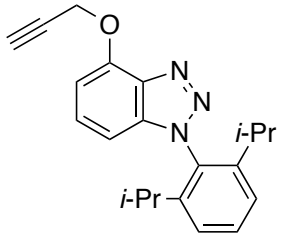
Colorless solid; Mp 128–129 °C; TLC R_f 0.20 (*n*-hexane/EtOAc = 4/1); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.56 (t, 1H, *J* = 2.5 Hz), 3.91 (s, 3H), 5.18 (d, 2H, *J* = 2.5 Hz), 6.93 (d, 1H, *J* = 8.0 Hz), 7.09–7.13 (AA'BB', 2H), 7.27 (d, 1H, *J* = 8.0 Hz), 7.44 (dd, 1H, *J* = 8.0, 8.0 Hz), 7.63–7.68 (AA'BB', 2H); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 55.7 (1C), 57.2 (1C), 76.2 (1C), 78.1 (1C), 103.3 (1C), 106.3 (1C), 114.9 (2C), 124.7 (2C), 129.0 (1C), 129.9 (1C), 134.8 (1C), 138.3 (1C), 149.4 (1C), 159.9 (1C); IR (KBr, cm^{-1}) 742, 829, 1000, 1099, 1258, 1285, 1519, 1603, 3227; Anal. calcd. for $C_{16}H_{13}N_3O_2$: C, 68.81; H, 4.69; N, 15.05%. Found: C, 68.76; H, 4.95; N, 14.98%.

4-Propargyloxy-1-(4-(trifluoromethyl)phenyl)-1*H*-benzo[*d*][1,2,3]triazole (**3f**)



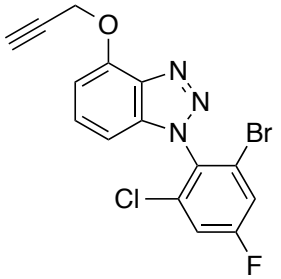
Colorless solid; Mp 118–119 °C; TLC R_f 0.21 (*n*-hexane/EtOAc = 4/1); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.58 (s, 1H), 5.17 (s, 2H), 6.98 (d, 1H, J = 8.0 Hz), 7.37 (d, 1H, J = 8.0 Hz), 7.52 (dd, 1H, J = 8.0, 8.0 Hz), 7.86–7.90 (AA'BB', 2H), 7.95–7.99 (AA'BB', 2H); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 57.3 (1C), 76.5 (1C), 77.8 (1C), 103.1 (1C), 106.9 (1C), 122.7 (2C), 123.7 (q, 1C, $J^1_{C–F}$ = 273 Hz), 127.1 (q, 2C, $J^3_{C–F}$ = 3.8 Hz), 130.0 (1C), 130.5 (q, 1C, $J^2_{C–F}$ = 34.0 Hz), 134.0 (1C), 138.6 (1C), 139.8 (1C), 149.7 (1C); ^{19}F NMR ($CDCl_3$, 376 MHz) δ –62.8 (s); IR (KBr, cm^{-1}) 691, 753, 786, 840, 1004, 1056, 1120, 1332, 1502, 1603, 3097, 3279; Anal. calcd. for $C_{16}H_{10}F_3N_3O$: C, 60.57; H, 3.18; N, 13.24%. Found: C, 60.65; H, 3.47; N, 12.96%.

1-(2,6-Diisopropylphenyl)-4-propargyloxy-1*H*-benzo[*d*][1,2,3]triazole (**3g**)



Colorless solid; Mp 109–110 °C; TLC R_f 0.50 (*n*-hexane/EtOAc = 4/1); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.01 (d, 6H, J = 7.0 Hz), 1.10 (d, 6H, J = 7.0 Hz), 2.07 (qq, 2H, J = 7.0, 7.0 Hz), 2.61 (t, 1H, J = 2.5 Hz), 5.20 (d, 2H, J = 2.5 Hz), 6.80 (dd, 1H, J = 0.5, 8.0 Hz), 6.93 (d, 1H, J = 0.5, 8.0 Hz), 7.34–7.40 (m, 3H), 7.56 (dd, 1H, J = 8.0, 8.0 Hz); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 23.7 (2C), 24.3 (2C), 28.5 (2C), 57.2 (1C), 76.3 (1C), 78.1 (1C), 102.9 (1C), 105.8 (1C), 124.1 (1C), 129.0 (2C), 131.0 (1C), 131.3 (1C), 137.3 (1C), 137.4 (1C), 147.3 (2C), 149.4 (1C); IR (KBr, cm^{-1}) 745, 766, 1002, 1084, 1283, 1386, 1505, 1599, 2929, 2967; Anal. calcd. for $C_{21}H_{23}N_3O$: C, 75.65; H, 6.95; N, 12.60%. Found: C, 75.53; H, 7.25; N, 12.43%.

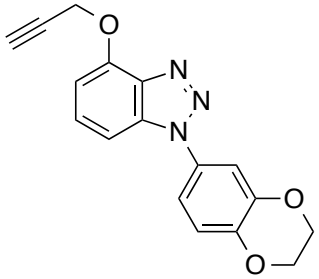
1-(2-Bromo-6-chloro-4-fluorophenyl)-4-propargyloxy-1*H*-benzo[*d*][1,2,3]triazole (**3h**)



Colorless solid; Mp 140–142 °C; TLC R_f 0.38 (*n*-hexane/EtOAc = 4/1); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.60 (t, 1H, J = 2.5 Hz), 5.19 (d, 2H, J = 2.5 Hz), 6.85 (d, 1H, J = 8.0 Hz), 6.97 (d, 1H, J = 8.0 Hz), 7.39 (dd, 1H, J = 2.5, 7.5 Hz), 7.46 (dd, 1H, J = 8.0 Hz), 7.52 (dd, 1H, J = 2.5, 7.5 Hz); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 57.4 (1C), 76.4 (1C), 77.9 (1C), 102.3 (1C), 106.5 (1C), 117.4 (d, 1C, $J^2_{C–F}$ = 26.5 Hz), 119.9 (d, 1C, $J^2_{C–F}$ = 25.2 Hz), 124.9 (d, 1C, $J^3_{C–F}$ = 12.6 Hz), 129.8 (1C), 130.1 (d, 1C, $J^4_{C–F}$ = 3.8 Hz), 135.6 (1C), 135.9 (d, 1C, $J^3_{C–F}$ = 12.6 Hz), 137.3 (1C), 149.7 (1C), 162.7 (d, 1C, $J^1_{C–F}$ = 258 Hz); ^{19}F NMR ($CDCl_3$, 376 MHz) δ –105.5 (dd, $J_{H–F}$ = 7.5, 7.5 Hz); IR (KBr, cm^{-1}) 783, 935, 1067,

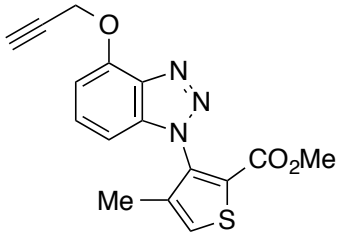
1231, 1290, 1394, 1509, 1575, 1591, 3086, 3295; Anal. calcd. for $C_{15}H_8BrClFN_3O$: C, 47.34; H, 2.12; N, 11.04%. Found: C, 47.58; H, 2.36; N, 10.78%.

1-(3,4-Ethylenedioxyphenyl)-4-propargyloxy-1*H*-benzo[*d*][1,2,3]triazole (**3i**)



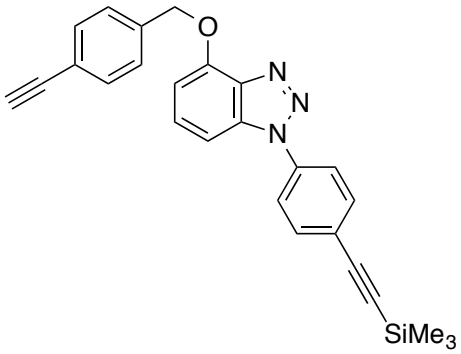
Colorless solid; Mp 156 °C (decomp.); TLC R_f 0.51 (*n*-hexane/EtOAc = 3/2); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.57 (t, 1H, *J* = 2.0 Hz), 4.35 (s, 4H), 5.16 (d, 2H, *J* = 2.0 Hz), 6.92 (d, 1H, *J* = 8.0 Hz), 7.06 (d, 1H, *J* = 8.0 Hz), 7.23 (dd, 1H, *J* = 2.5, 8.5 Hz), 7.28 (d, 1H, *J* = 2.5 Hz), 7.30 (d, 1H, *J* = 8.5 Hz), 7.45 (dd, 1H, *J* = 8.0, 8.0 Hz); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 57.1 (1C), 64.4 (1C+1C, two signals overlapped), 76.3 (1C), 78.0 (1C), 103.4 (1C), 106.1 (1C), 112.6 (1C), 116.4 (1C), 118.1 (1C), 129.1 (1C), 130.3 (1C), 134.5 (1C), 138.2 (1C), 144.0 (1C), 144.1 (1C), 149.3 (1C); IR (KBr, cm^{-1}) 742, 898, 1064, 1219, 1286, 1313, 1514, 3284; Anal. calcd. for $C_{17}H_{13}N_3O_3$: C, 66.44; H, 4.26; N, 13.67%. Found: C, 66.40; H, 4.56; N, 13.39%.

1-(2-Methoxycarbonyl-4-methylthiophen-3-yl)-4-propargyloxy-1*H*-benzo[*d*][1,2,3]triazole (**3j**)



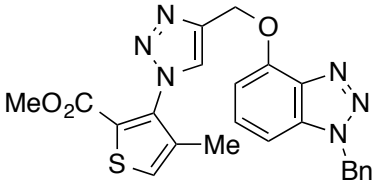
Colorless solid; Mp 145 °C (decomp.); TLC R_f 0.21 (*n*-hexane/EtOAc = 4/1); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.00 (d, 3H, *J* = 0.5 Hz), 2.58 (dd, 1H, *J* = 2.5, 2.5 Hz), 3.60 (s, 3H), 5.18 (d, 1H, *J* = 2.5 Hz), 5.19 (d, 1H, *J* = 2.5 Hz), 6.87 (d, 1H, *J* = 8.0 Hz), 6.93 (d, 1H, *J* = 8.0 Hz), 7.40 (q 1H, *J* = 0.5 Hz), 7.42 (dd, 1H, *J* = 8.0, 8.0 Hz); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 13.5 (1C), 52.3 (1C), 57.3 (1C), 76.3 (1C), 78.1 (1C), 102.9 (1C), 106.2 (1C), 127.2 (1C), 128.8 (1C), 129.2 (1C), 136.2 (1C), 136.3 (1C), 137.18 (1C), 137.22 (1C), 149.5 (1C), 160.3 (1C); IR (KBr, cm^{-1}) 1037, 1246, 1271, 1287, 1508, 1722, 2953, 3289; Anal. calcd. for $C_{16}H_{13}N_3O_3S$: C, 58.70; H, 4.00; N, 12.84; S, 9.80%. Found: C, 58.61; H, 4.12; N, 12.60; S, 9.51%.

4-(4-Ethynylbenzyl)oxy-1-(4-(trimethylsilyl)ethynylphenyl)-1*H*-benzo[*d*][1,2,3]triazole (**3k**)



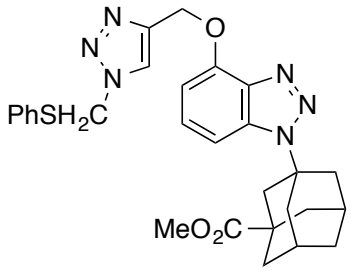
Colorless solid; Mp 198–199 °C; TLC R_f 0.39 (*n*-hexane/EtOAc = 4/1); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 0.29 (s, 9H), 3.08 (s, 1H), 5.56 (s, 2H), 6.79 (d, 1H, *J* = 8.0 Hz), 7.29 (d, 1H, *J* = 8.0 Hz), 7.41 (dd, 1H, *J* = 8.0, 8.0 Hz), 7.47–7.54 (m, 4H), 7.67–7.70 (AA'BB', 2H), 7.73–7.76 (AA'BB', 2H); ^{13}C NMR ($CDCl_3$, 126 MHz) δ –0.1 (3C), 70.9 (1C), 77.5 (1C), 83.4 (1C), 96.4 (1C), 102.8 (1C), 103.7 (1C), 106.6 (1C), 121.8 (1C), 122.5 (2C), 123.6 (1C), 127.3 (2C), 129.6 (1C), 132.4 (2C), 133.4 (2C), 134.2 (1C), 136.7 (1C), 137.2 (1C), 138.6 (1C), 150.6 (1C); IR (KBr, cm^{-1}) 842, 1059, 1272, 1381, 1513, 1600, 2156, 2957, 3274; HRMS (ESI^+) *m*/*z* 444.1480 ($[M+Na]^+$, $C_{26}H_{23}N_3NaOSi^+$ requires 444.1503).

1-Benzyl-4-(1-(2-methoxycarbonyl-4-methylthiophen-3-yl)-1*H*-1,2,3-triazol-4-yl)methoxy-1*H*-benzo[*d*][1,2,3]triazole (**4a**)



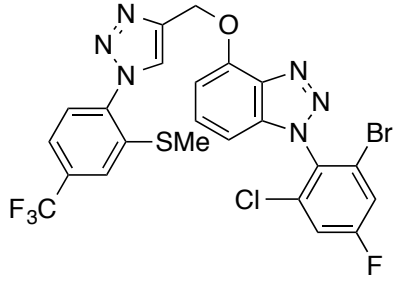
Colorless solid; Mp 56–57 °C; TLC R_f 0.40 (*n*-hexane/EtOAc = 1/1); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.05 (d, 3H, *J* = 1.0 Hz), 3.61 (s, 3H), 5.74 (s, 2H), 5.82 (s, 2H), 6.93 (d, 1H, *J* = 7.0 Hz), 6.94 (d, 1H, *J* = 7.5 Hz), 7.23–7.26 (m, 2H), 7.28–7.35 (m, 5H), 7.99 (s, 1H); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 13.6 (1C), 52.29 (1C), 52.32 (1C), 63.3 (1C), 102.4 (1C), 105.9 (1C), 126.2 (1C), 127.1 (1C), 127.5 (2C), 127.6 (1C), 128.5 (1C), 128.7 (1C), 129.0 (2C), 134.7 (1C), 134.9 (1C), 136.6 (1C), 137.3 (1C), 138.4 (1C), 143.1 (1C), 150.2 (1C), 160.3 (1C); IR (KBr, cm^{-1}) 730, 784, 1042, 1198, 1249, 1438, 1510, 1600, 1713, 2952; Anal. calcd. for $C_{23}H_{20}N_6O_3S$: C, 59.99; H, 4.38; N, 18.25; S, 6.96%. Found: C, 59.96; H, 4.66; N, 18.00; S, 6.68%.

1-(3-(Methoxycarbonyl)adamantan-1-yl)-4-(1-(phenylthio)methyl-1*H*-1,2,3-triazol-4-yl)methoxy-1*H*-benzo[*d*][1,2,3]triazole (**4b**)



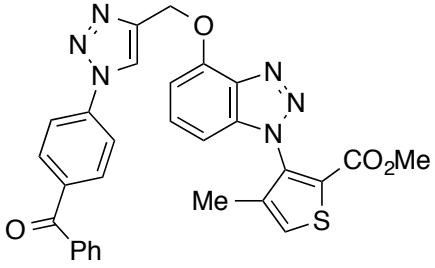
Colorless solid; Mp 66–67 °C; TLC R_f = 0.26 (*n*-hexane/EtOAc = 3/1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.82–1.84 (m, 2H), 1.97–2.04 (br, 4H), 2.45–2.50 (m, 6H), 2.54–2.63 (br, 2H), 3.70 (s, 3H), 5.58 (s, 2H), 5.59 (s, 2H), 6.82 (d, 1H, J = 8.0 Hz), 7.19–7.36 (m, 7H), 7.73 (s, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 29.2, 35.0, 37.7, 41.0, 42.8, 42.9, 52.0, 54.0, 61.4, 63.0, 104.9 (1C), 105.1 (1C), 122.8 (1C), 127.5 (1C), 128.8 (2C), 129.4 (1C), 131.6 (1C), 132.5 (2C), 133.5 (1C), 139.0 (1C), 144.4 (1C), 150.1 (1C), 176.3 (1C) (three pairs of equivalent carbons were not identified); IR (KBr, cm^{-1}) 990, 1044, 1093, 1165, 1232, 1261, 1502, 1591, 1725, 2859, 2911, 2942; HRMS (ESI$^+$) *m*/*z* 553.1988 ([M+Na]$^+$, $C_{28}H_{30}N_6NaO_3S^+$ requires 553.1992).

1-(2-Bromo-6-chloro-4-fluorophenyl)-4-(1-(2-methylthio-4-(trifluoromethyl)phenyl)-1*H*-1,2,3-triazol-4-yl)methoxy-1*H*-benzo[*d*][1,2,3]triazole (**4c**)



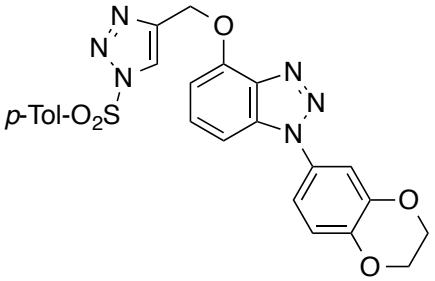
Colorless solid; Mp 77–79 °C; TLC R_f 0.24 (*n*-hexane/EtOAc = 7/3); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.46 (s, 3H), 5.81 (s, 2H), 6.84 (d, 1H, J = 8.0 Hz), 7.05 (d, 1H, J = 8.0 Hz), 7.39 (dd, 1H, J = 2.5, 7.5 Hz), 7.46–7.50 (m, 2H), 7.52 (dd, 1H, J = 2.5, 7.5 Hz), 7.71 (s, 1H), 7.72 (d, 1H, J = 8.5 Hz), 8.22 (s, 1H); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 15.3 (1C), 63.4 (1C), 102.1 (1C), 106.6 (1C), 117.4 (d, 1C, $J^2_{C–F}$ = 25.2 Hz), 119.9 (d, 1C, $J^2_{C–F}$ = 25.2 Hz), 123.3 (q, 1C, $J^1_{C–F}$ = 272 Hz), 123.7 (q, 1C, $J^3_{C–F}$ = 3.8 Hz), 124.9 (d, 1C, $J^3_{C–F}$ = 11.2 Hz), 125.2 (1C), 126.4 (1C), 126.9 (q, 1C, $J^3_{C–F}$ = 3.8 Hz), 127.8 (q, 1C, $J^2_{C–F}$ = 34.0 Hz), 130.05 (d, 1C, $J^4_{C–F}$ = 3.8 Hz), 130.11 (1C), 134.6 (1C), 135.6 (1C), 135.9 (d, 1C, $J^3_{C–F}$ = 11.6 Hz), 137.3 (1C), 140.9 (1C), 143.8 (1C), 150.4 (1C), 162.7 (d, 1C, $J^1_{C–F}$ = 260 Hz); ^{19}F NMR ($CDCl_3$, 376 MHz) δ –105.4 (dd, 1F, $J_{H–F}$ = 7.5, 7.5 Hz), –62.7 (s, 3F); IR (KBr, cm^{-1}) 1066, 1128, 1220, 1329, 1509, 1591; HRMS (ESI$^+$) *m*/*z* 634.9638 ([M+Na]$^+$, $C_{23}H_{14}BrClF_4N_6NaOS^+$ requires 634.9650).

1-(2-Methoxycarbonyl-4-methylthiophen-3-yl)-4-(1-(4-benzoylphenyl)-1*H*-1,2,3-triazol-4-yl)methoxy-1*H*-benzo[*d*][1,2,3]triazole (**4d**)



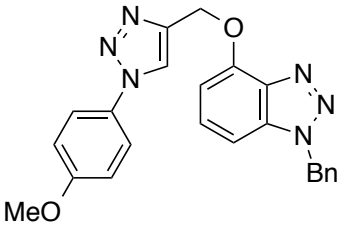
Colorless solid; Mp 80–82 °C; TLC R_f 0.23 (*n*-hexane/EtOAc = 3/2); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.01 (s, 3H), 3.61 (s, 3H), 5.76 (d, 1H, *J* = 12.5 Hz), 5.83 (d, 1H, *J* = 12.5 Hz), 6.87 (d, 1H, *J* = 8.0 Hz), 6.99 (d, 1H, *J* = 8.0 Hz), 7.41 (s, 1H), 7.42 (dd, 1H, *J* = 8.0, 8.0 Hz), 7.52 (t, 1H, *J* = 7.5 Hz), 7.63 (dd, 1H, *J* = 7.5, 7.5 Hz), 7.82 (d, 1H, *J* = 7.5 Hz), 7.92–7.95 (AA'BB', 2H), 7.98–8.00 (AA'BB', 2H), 8.38 (s, 1H); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 13.5 (1C), 52.3 (1C), 63.3 (1C), 102.8 (1C), 106.1 (1C), 120.0 (2C), 121.5 (1C), 127.2 (1C), 128.5 (2C), 128.7 (1C), 129.5 (1C), 130.0 (2C), 131.8 (2C), 132.9 (1C), 136.2 (1C), 136.4 (1C), 137.0 (1C), 137.1 (1C), 137.2 (1C), 137.6 (1C), 139.5 (1C), 145.0 (1C), 150.0 (1C), 160.2 (1C), 195.2 (1C); IR (KBr, cm^{-1}) 1045, 1218, 1254, 1439, 1509, 1603, 1659, 1722; HRMS (ESI^+) *m*/*z* 573.1309 ($[M+Na]^+$, $C_{29}H_{22}N_6NaO_4S^+$ requires 573.1315).

1-(3,4-Ethylenedioxyphenyl)-4-(1-(4-toluenesulfonyl)-1*H*-1,2,3-triazol-4-yl)methoxy-1*H*-benzo[*d*][1,2,3]triazole (**4e**)



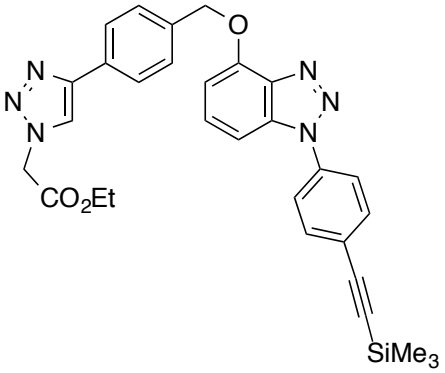
Colorless solid; Mp 68–69 °C; TLC R_f 0.20 (*n*-hexane/EtOAc = 3/2); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.46 (s, 3H), 4.34–4.37 (m, 4H), 5.66 (s, 2H), 6.87 (d, 1H, *J* = 8.0 Hz), 7.06 (d, 1H, *J* = 8.5 Hz), 7.22 (dd, 1H, *J* = 2.5, 9.0 Hz), 7.26–7.30 (m, 2H), 7.38–7.44 (m, 3H), 8.00–8.04 (AA'BB', 2H), 8.35 (s, 1H); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 21.9 (1C), 62.8 (1C), 64.4 (1C+1C, two signals overlapped), 103.4 (1C), 106.1 (1C), 112.7 (1C), 116.4 (1C), 118.2 (1C), 123.2 (1C), 128.9 (2C), 129.2 (1C), 130.2 (1C), 130.5 (2C), 134.6 (1C), 138.0 (1C), 132.8 (1C), 143.5 (1C), 144.1 (1C), 144.2 (1C), 147.5, (1C) 149.8 (1C); IR (KBr, cm^{-1}) 900, 1064, 1195, 1284, 1394, 1513, 1593, 2932; HRMS (ESI^+) *m*/*z* 527.1110 ($[M+Na]^+$, $C_{24}H_{20}N_6NaO_5S^+$ requires 527.1108).

1-Benzyl-4-(1-(4-methoxyphenyl)-1*H*-1,2,3-triazol-4-yl)methoxy-1*H*-benzo[*d*][1,2,3]triazole (**4f**)



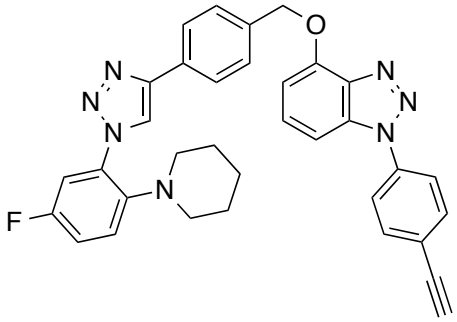
Colorless solid; Mp 137–138 °C; TLC R_f 0.48 (*n*-hexane/EtOAc = 1/1); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 3.86 (s, 3H), 5.68 (s, 2H), 5.81 (s, 2H), 6.91 (d, 1H, *J* = 7.5 Hz), 6.94 (d, 1H, *J* = 8.0 Hz), 6.99–7.02 (AA'BB', 2H), 7.23–7.34 (m, 6H), 7.61–7.64 (AA'BB', 2H), 8.12 (s, 1H); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 52.3 (1C), 55.6 (1C), 63.2 (1C), 102.4 (1C), 105.5 (1C), 114.8 (2C), 121.7 (1C), 122.2 (2C), 127.5 (2C), 128.4 (1C), 128.7 (1C), 129.0 (2C), 130.4 (1C), 134.7 (1C), 134.9 (1C), 138.3 (1C), 144.2 (1C), 150.1 (1C), 159.9 (1C); IR (KBr, cm^{-1}) 832, 1045, 1060, 1251, 1511, 1600; HRMS (ESI^+) *m*/*z* 435.1536 ($[M+Na]^+$, $C_{23}H_{20}N_6NaO_2^+$ requires 435.1540).

4-(4-(1-(Ethoxycarbonyl)methyl-1*H*-1,2,3-triazol-4-yl)benzyl)oxy-1-(4-(trimethylsilylethynyl)phenyl)-1*H*-benzo[*d*][1,2,3]triazole (**4g**)



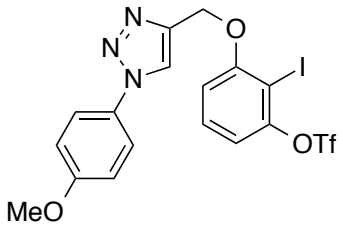
Colorless solid; Mp 210 °C (decomp.); TLC R_f 0.39 (CH_2Cl_2/MeOH = 19/1); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 0.29 (s, 9H), 1.32 (t, 3H, J = 7.5 Hz), 4.29 (q, 2H, *J* = 7.5 Hz), 5.21 (s, 2H), 5.58 (s, 2H), 6.82 (d, 1H, *J* = 8.0 Hz), 7.28 (d, 1H, *J* = 8.0 Hz), 7.42 (dd, 1H, *J* = 8.0, 8.0 Hz), 7.62 (d, 2H, *J* = 8.5 Hz), 7.67–7.70 (AA'BB', 2H), 7.74–7.77 (AA'BB', 2H), 7.88 (d, 2H, *J* = 8.5 Hz), 7.92 (s, 1H); ^{13}C NMR ($CDCl_3$, 126 MHz) δ –0.1 (3C), 14.1 (1C), 51.0 (1C), 62.5 (1C), 71.1 (1C), 96.3 (1C), 102.6 (1C), 103.7 (1C), 106.5 (1C), 121.0 (1C), 122.4 (2C), 123.5 (1C), 126.1 (2C), 127.9 (2C), 129.6 (1C), 130.2 (1C), 133.4 (2C), 134.1 (1C), 136.5 (1C), 136.7 (1C), 138.6 (1C), 147.9 (1C), 150.8 (1C), 166.2 (1C); IR (KBr, cm^{-1}) 840; 1050, 1214, 1278, 1379, 1514, 1600, 1750, 2157, 2957; HRMS (ESI^+) *m*/*z* 573.2035 ($[M+Na]^+$, $C_{30}H_{30}N_6NaO_3Si^+$ requires 573.2041).

1-(4-Ethynylphenyl)-4-(4-(1-(5-fluoro-2-piperidinophenyl)-1*H*-1,2,3-triazol-4-yl)benzyl)oxy-1*H*-benzo[*d*] [1,2,3]triazole (**4h**)



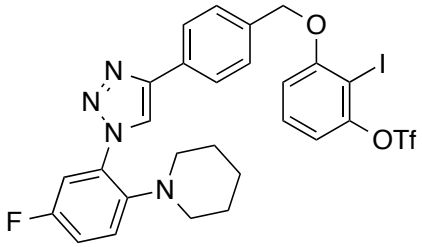
Colorless solid; Mp 238 °C (decomp.); TLC R_f 0.35 (CH_2Cl_2/MeOH = 97/3); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.49–1.58 (br, 6H), 2.68–2.71 (m, 4H), 3.20 (s, 1H), 5.61 (s, 2H), 6.86 (d, 1H, J = 8.0 Hz), 7.09–7.18 (m, 2H), 7.31 (d, 1H, J = 8.0 Hz), 7.44 (dd, 1H, J = 8.0, 8.0 Hz), 7.50 (dd, 1H, J = 3.0, 8.5 Hz), 7.67 (d, 2H, J = 8.0 Hz), 7.72 (d, 2H, J = 8.5 Hz), 7.79 (d, 2H, J = 8.5 Hz), 7.94 (d, 2H, J = 8.0 Hz), 8.74 (s, 1H); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 23.8 (1C), 26.4 (2C), 52.9 (2C) 71.1 (1C), 78.9 (1C), 82.4 (1C), 102.6 (1C), 106.5 (1C), 113.3 (d, 1C, $J^2_{C–F}$ = 26.5 Hz), 116.3 (d, 1C, $J^2_{C–F}$ = 21.4 Hz), 121.1 (1C), 121.4 (d, 1C, $J^3_{C–F}$ = 8.8 Hz), 122.5 (2C), 126.0 (2C), 128.1 (2C), 129.68 (1C), 129.72 (1C), 130.4 (1C), 131.5 (d, 1C, $J^3_{C–F}$ = 10.1 Hz), 133.6 (2C), 134.2 (1C), 136.5 (1C), 137.1 (1C), 138.6 (1C), 142.8 (d, 1C, $J^4_{C–F}$ = 2.5 Hz), 147.1 (1C), 150.8 (1C), 158.4 (d, 1C, $J^1_{C–F}$ = 244 Hz); ^{19}F NMR ($CDCl_3$, 376 MHz) δ –118.8 (ddd, $J_{H–F}$ = 5.6, 8.0, 8.0 Hz); IR (KBr, cm^{-1}) 842, 1035, 1270, 1388, 1513, 1602, 2939, 3212; HRMS (ESI$^+$) *m*/*z* 592.2232 ([M+Na]$^+$, $C_{34}H_{28}FN_7NaO^+$ requires 592.2232).

2-Iodo-3-((1-(4-methoxyphenyl)-1*H*-1,2,3-triazol-4-yl)methoxy)phenyl trifluoromethanesulfonate (**5a**)



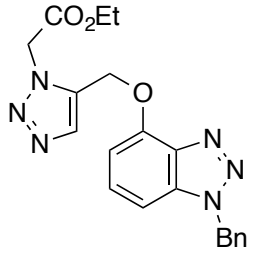
Colorless solid; Mp 133–134 °C; TLC R_f 0.19 (*n*-hexane/EtOAc = 7/3); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 3.87 (s, 3H), 5.41 (s, 2H), 6.99 (d, 1H, J = 8.5 Hz), 7.01–7.05 (AA'BB', 2H), 7.08 (d, 1H, J = 8.5 Hz), 7.40 (dd, 1H, J = 8.5, 8.5 Hz), 7.63–7.67 (AA'BB', 2H), 8.08 (s, 1H); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 55.7 (1C), 64.1 (1C), 83.4 (1C), 111.9 (1C), 114.8 (2C+1C, two signals overlapped), 118.7 (q, 1C, $J^1_{C–F}$ = 321 Hz), 121.4 (1C), 122.3 (2C), 130.3 (1C), 130.6 (1C), 143.8 (1C), 151.3 (1C), 159.0 (1C), 160.0 (1C); ^{19}F NMR ($CDCl_3$, 376 MHz) δ –73.4 (s); IR (KBr, cm^{-1}) 831, 1041, 1139, 1219, 1257, 1423, 1455, 1519, 1587; Anal. calcd. for $C_{17}H_{13}F_3IN_3O_5S$: C, 36.77; H, 2.36; N, 7.57; S, 5.77%. Found: C, 36.97; H, 2.64; N, 7.43; S, 5.53%.

3-(4-(1-(5-Fluoro-2-piperidinophenyl)-1*H*-1,2,3-triazol-4-yl)benzyl)oxy-2-iodophenyl triflate (**5b**)



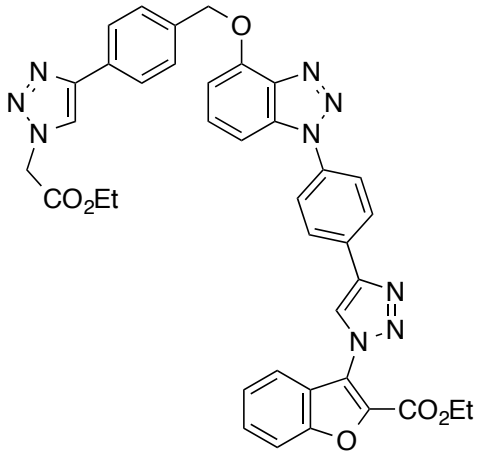
Colorless solid; Mp 127–129 °C; TLC R_f 0.36 (*n*-hexane/EtOAc = 7/3); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.50–1.62 (br, 6H), 2.69–2.73 (m, 4H), 5.24 (s, 2H), 6.89 (d, 1H, J = 8.0 Hz), 6.99 (d, 1H, J = 8.0 Hz), 7.09–7.19 (m, 2H), 7.37 (dd, 1H, J = 8.0, 8.0 Hz), 7.51 (dd, 1H, J = 2.5, 8.5 Hz), 7.60 (d, 2H, J = 8.5 Hz), 7.96 (d, 2H, J = 8.5 Hz), 8.75 (s, 1H); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 23.8 (1C), 26.4 (2C), 53.0 (2C), 71.3 (1C), 83.5 (1C), 111.7 (1C), 113.4 (d, 1C, $J^2_{C–F}$ = 26.5 Hz), 114.5 (1C), 116.3 (d, 1C, $J^2_{C–F}$ = 21.4 Hz), 118.7 (q, 1C, $J^1_{C–F}$ = 321 Hz), 121.1 (1C), 121.5 (d, 1C, $J^3_{C–F}$ = 8.8 Hz), 126.0 (2C), 127.7 (2C), 130.4 (1C), 130.5 (1C), 131.5 (d, 1C, $J^3_{C–F}$ = 10.0 Hz), 135.7 (1C), 142.8 (d, 1C, $J^4_{C–F}$ = 2.5 Hz), 147.0 (1C), 151.4 (1C), 158.4 (d, 1C, $J^1_{C–F}$ = 244 Hz), 159.4 (1C); ^{19}F NMR ($CDCl_3$, 376 MHz) δ –118.5 (ddd, 1F, $J_{H–F}$ = 6.4, 8.0, 8.0 Hz), –73.2 (s, 3F); IR (KBr, cm^{-1}) 827, 1139, 1273, 1424, 1452, 1497, 1507, 1587, 2939; HRMS (ESI$^+$) *m*/*z* 725.0284 ([M+Na]$^+$, $C_{27}H_{23}F_4IN_4NaO_4S^+$ requires 725.0313).

1-Benzyl-4-(1-(ethoxycarbonyl)methyl-1*H*-1,2,3-triazol-5-yl)methoxy-1*H*-benzo[*d*][1,2,3]triazole (**6a**)



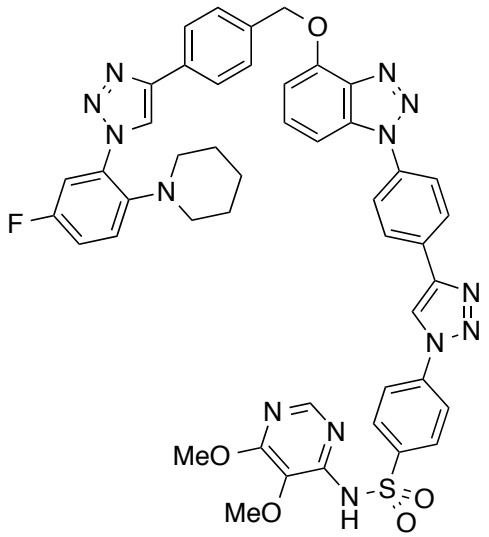
Pale yellow solid; Mp 135 °C (decomp.); TLC R_f 0.18 (*n*-hexane/EtOAc = 1/1); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.19 (t, 3H, J = 7.5 Hz), 4.18 (q, 2H, J = 7.5 Hz), 5.44 (s, 2H), 5.75 (s, 2H), 5.81 (s, 2H), 6.76 (d, 1H, J = 7.5 Hz), 7.00 (d, 1H, J = 7.5 Hz), 7.24–7.36 (m, 6H), 7.79 (s, 1H); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 13.9 (1C), 50.1 (1C), 52.3 (1C), 60.8 (1C), 62.3 (1C), 103.5 (1C), 107.2 (1C), 127.6 (2C), 128.5 (1C), 128.6 (2C), 129.0 (1C), 133.1 (1C), 134.4 (1C), 133.5 (1C), 135.1 (1C), 138.2 (1C), 149.0 (1C), 166.5 (1C); IR (KBr, cm^{-1}) 1061, 1219, 1247, 1511, 1748; HRMS (ESI$^+$) *m*/*z* 415.1470 ([M+Na]$^+$, $C_{20}H_{20}N_6NaO_3^+$ requires 415.1489).

1-(4-(1-(2-(Ethoxycarbonyl)benzo[*b*]furan-3-yl)-1*H*-1,2,3-triazol-4-yl)phenyl)-4-(4-(1-(ethoxycarbony l)methyl-1*H*-1,2,3-triazol-4-yl)benzyl)oxy-1*H*-benzo[*d*][1,2,3]triazole (**7a**)



Colorless solid; Mp 232 °C (decomp.); TLC R_f 0.48 (CH_2Cl_2/MeOH = 16/1); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.32 (t, 3H, *J* = 7.0 Hz), 1.45 (t, 3H, *J* = 7.0 Hz), 4.30 (q, 2H, *J* = 7.0 Hz), 4.51 (q, 2H, *J* = 7.0 Hz), 5.22 (s, 2H), 5.61 (s, 2H), 6.84 (d, 1H, *J* = 7.5 Hz), 7.36 (d, 1H, *J* = 8.5 Hz), 7.44 (d, 1H, *J* = 8.0 Hz), 7.47 (dd, 1H, *J* = 7.5, 7.5 Hz), 7.60–7.69 (m, 4H), 7.87–7.90 (AA'BB', 2H), 7.91–7.94 (AA'BB', 2H), 7.94 (s, 1H), 8.18–8.23 (m, 3H), 8.97 (s, 1H); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 14.1 (1C), 14.2 (1C), 51.0 (1C), 62.4 (1C), 62.5 (1C), 71.1 (1C), 102.8 (1C), 106.5 (1C), 112.5 (1C), 121.0 (1C), 122.6 (1C), 123.1 (1C), 123.36 (2C), 123.43 (1C), 125.2 (1C), 125.7 (1C), 126.1 (2C), 127.3 (2C), 128.0 (2C), 129.58 (1C), 129.60 (1C), 130.2 (1C), 130.5 (1C), 134.35 (1C), 134.44 (1C), 136.6 (1C), 136.9 (1C), 138.6 (1C), 145.9 (1C), 148.0 (1C), 150.8 (1C), 153.6 (1C), 158.7 (1C), 166.2 (1C); IR (KBr, cm^{-1}) 913, 1025, 1226, 1258, 1379, 1508, 1712, 1748, 2987; HRMS (ESI^+) *m*/*z* 710.2447 ($[M+H]^+$, $C_{38}H_{32}N_9O_6^+$ requires 710.2470).

1-(4-(1-(4-((5,6-Dimethoxypyrimidine-4-yl)aminosulfonyl)phenyl)-1*H*-1,2,3-triazol-4-yl)phenyl)-4-(4 -(1-(5-fluoro-2-piperidinophenyl)-1*H*-1,2,3-triazol-4-yl)benzyl)oxy-1*H*-benzo[*d*][1,2,3]triazole (**7b**)



Brown solid; Mp 230 °C (decomp.); TLC R_f 0.31 (CH_2Cl_2/MeOH = 24/1); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.50–1.61 (m, 6H), 2.68–2.72 (m, 4H), 3.91 (s, 3H), 4.00 (s, 3H), 5.61 (s, 2H), 6.87 (d, 1H, J = 7.5 Hz), 7.08–7.19 (m, 2H), 7.36 (d, 1H, J = 8.0 Hz), 7.44–7.52 (m, 2H), 7.68 (d, 2H, J = 8.0 Hz), 7.78–7.96 (m, 5H), 8.01–8.05 (AA'BB', 2H), 8.14–8.17 (AA'BB', 2H), 8.19 (s, 1H), 8.38–8.41 (m, 3H), 8.75 (s, 1H); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 23.8 (1C), 26.4 (2C), 53.0 (2C), 54.3 (1C), 60.7 (1C), 71.1 (1C), 102.7 (1C), 106.5 (1C), 113.3 (d, 1C, $J^2_{C–F}$ = 26.5 Hz), 116.3 (d, 1C, $J^2_{C–F}$ = 21.4 Hz), 117.7 (1C), 120.1 (2C), 121.2 (1C), 121.4 (d, 1C, $J^3_{C–F}$ = 8.8 Hz), 123.3 (2C), 126.0 (2C), 126.6 (1C), 127.3 (2C), 128.2 (2C), 129.7 (1C), 130.0 (1C), 130.4 (1C), 130.6 (2C), 131.5 (d, 1C, $J^3_{C–F}$ = 10.1 Hz), 134.3 (1C), 136.5 (1C), 137.2 (1C), 138.7 (1C), 139.6 (1C), 140.1 (1C), 142.8 (d, 1C, $J^4_{C–F}$ = 2.5 Hz), 147.1 (1C), 147.8 (1C), 149.3 (1C), 150.8 (1C), 151.0 (1C), 158.4 (d, 1C, $J^1_{C–F}$ = 244 Hz), 160.9 (1C); ^{19}F NMR ($CDCl_3$, 376 MHz) δ –118.8 (ddd, $J_{H–F}$ = 5.6, 8.0, 8.0 Hz); IR (KBr, cm^{-1}) 1094, 1164, 1338, 1505, 1587, 2938, 3151; HRMS (ESI$^+$) m/z 928.2847 ([M+Na]$^+$, $C_{46}H_{40}FN_{13}NaO_5S^+$ requires 928.2872).

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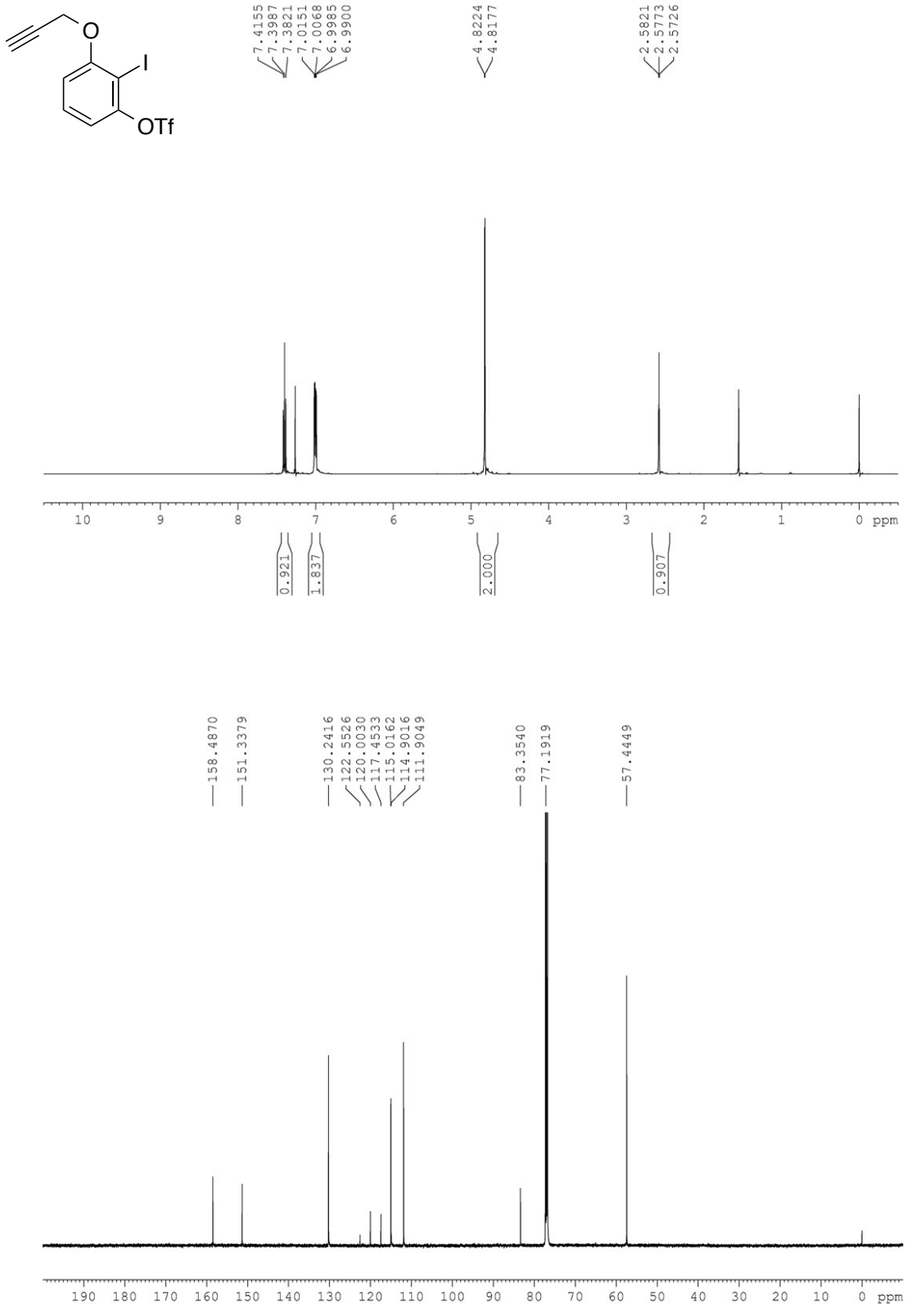
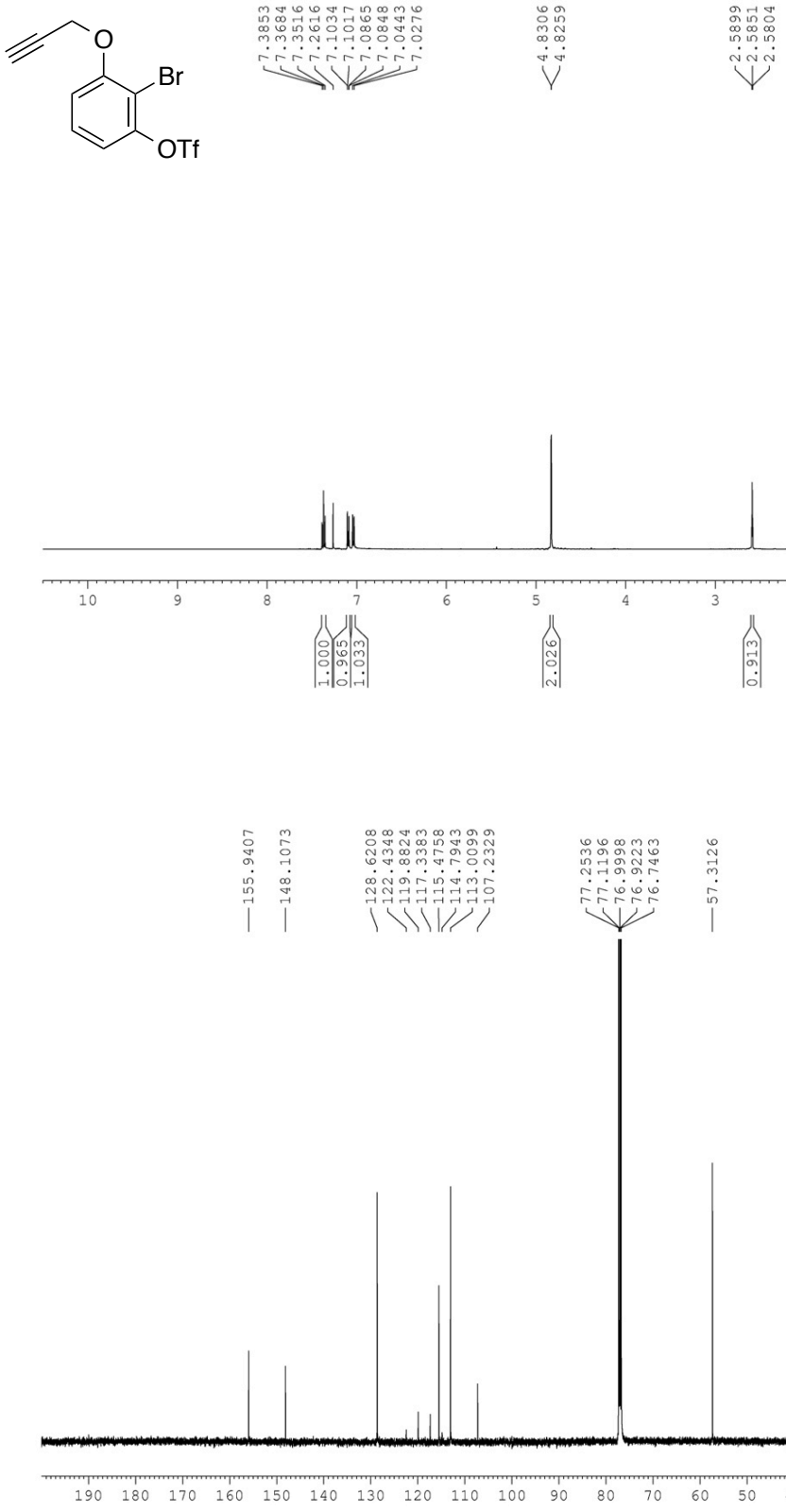
^{1}H and ^{13}C NMR Spectra of Compounds

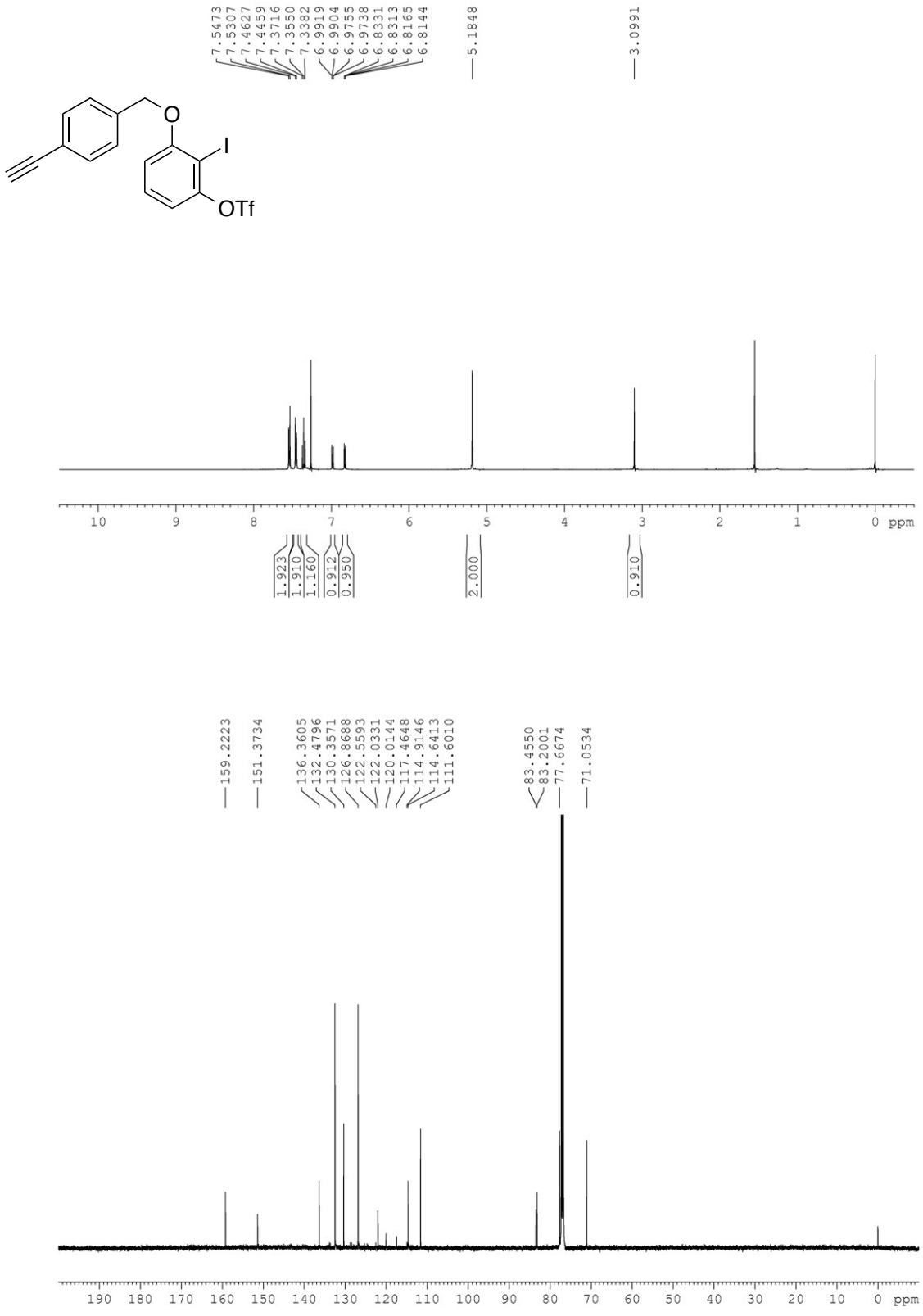
^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of **1a** ($CDCl_3$)



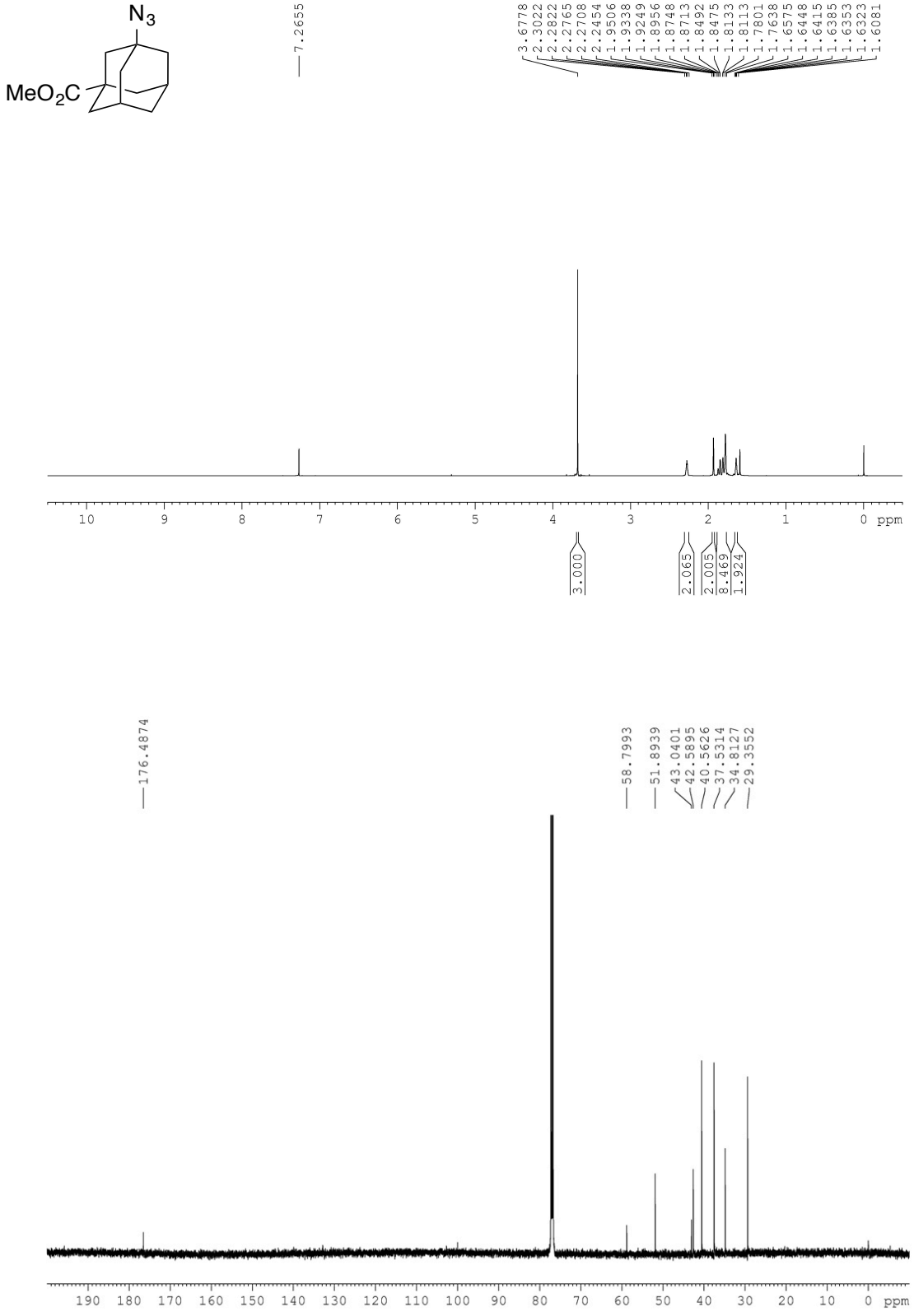
^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of **1b** ($CDCl_3$)



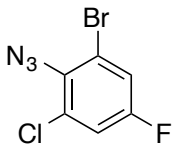
^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of **1c** ($CDCl_3$)

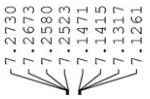


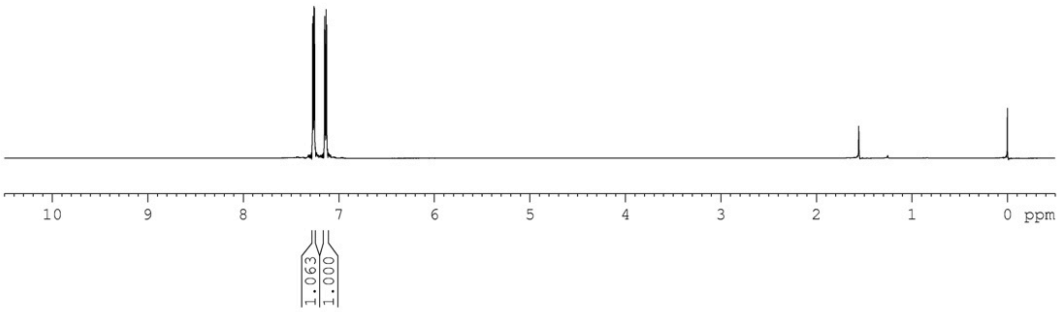
^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of **2d** ($CDCl_3$)

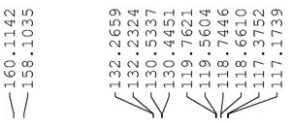


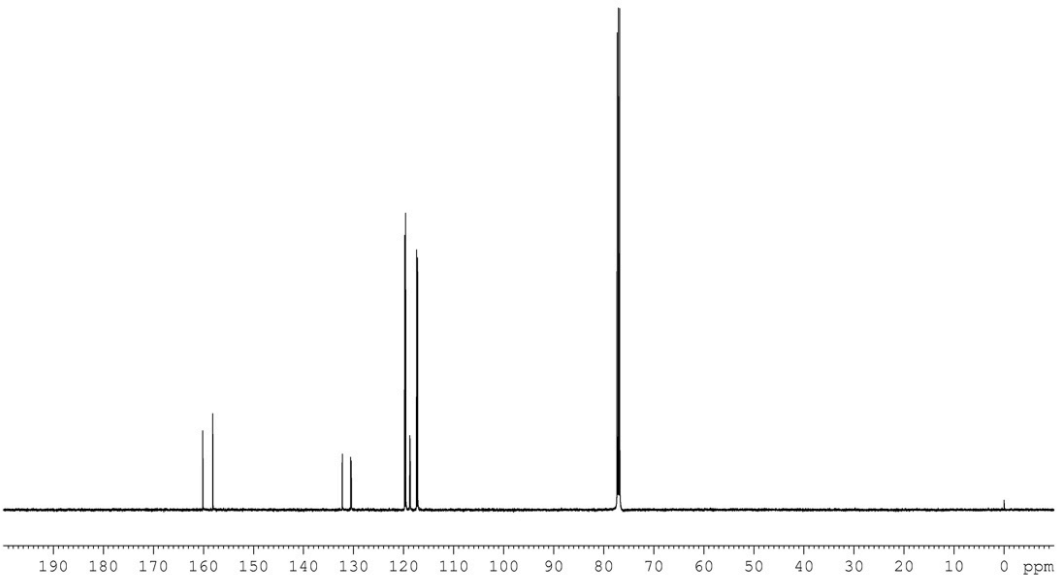
^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of **2h** ($CDCl_3$)



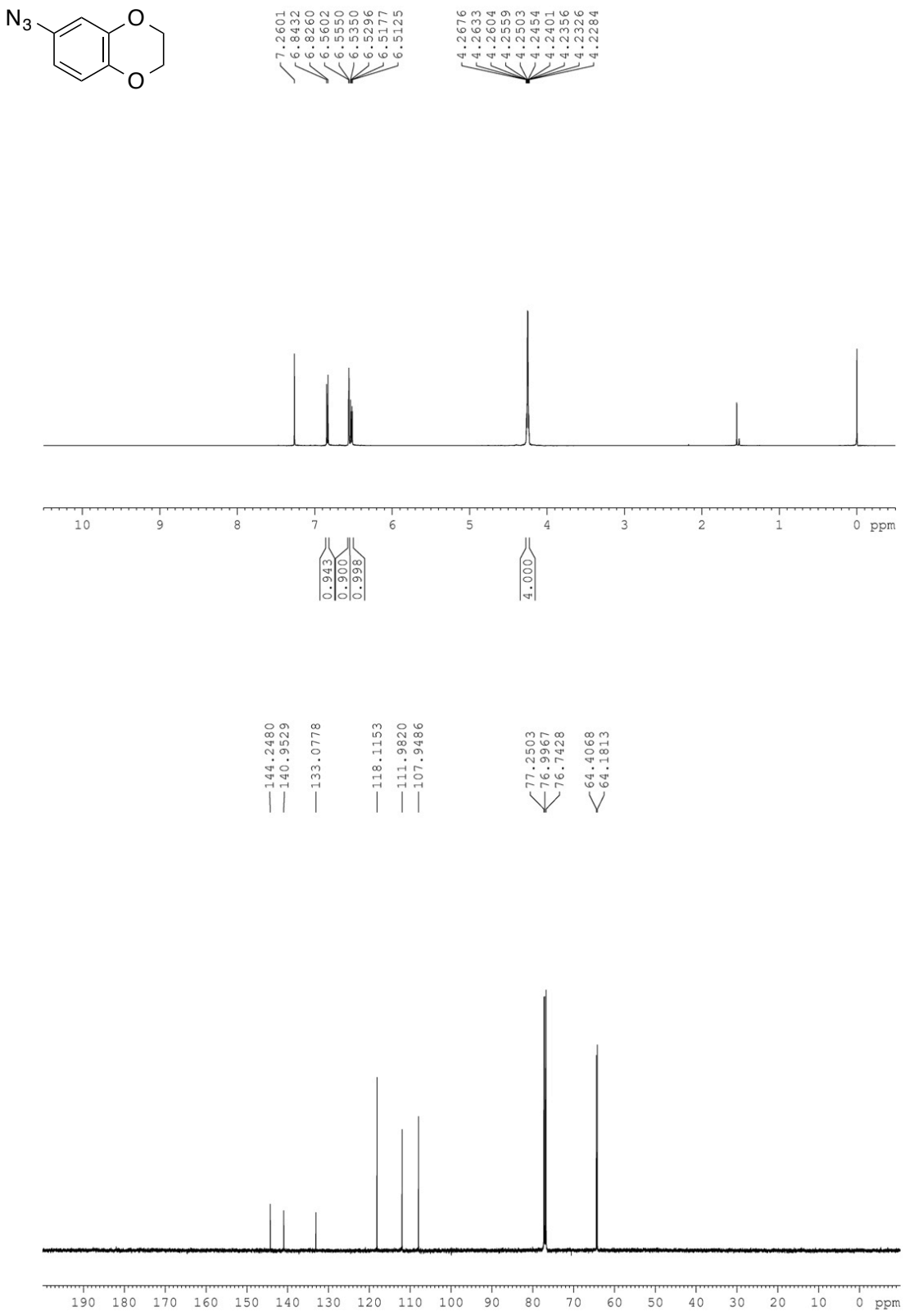




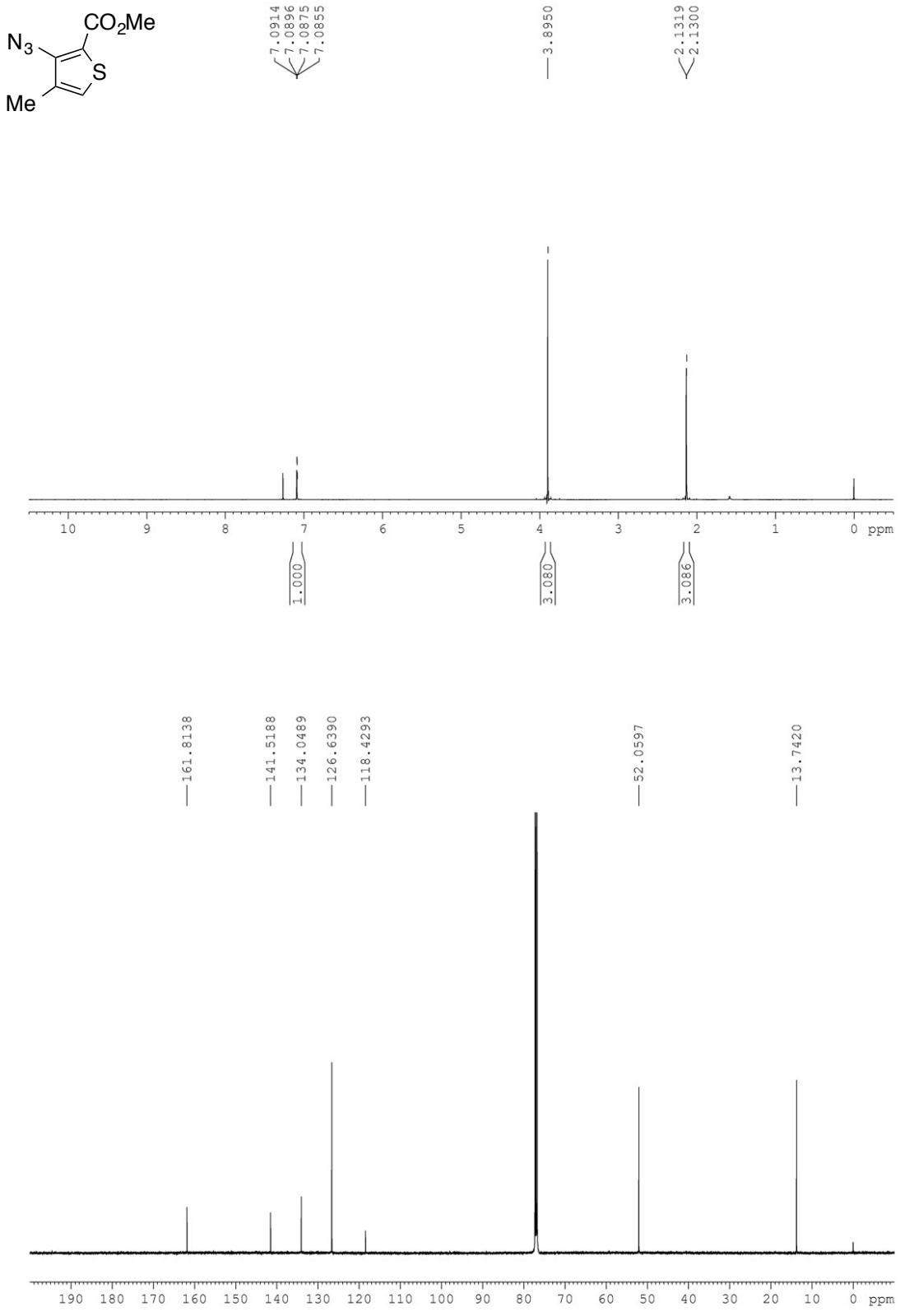




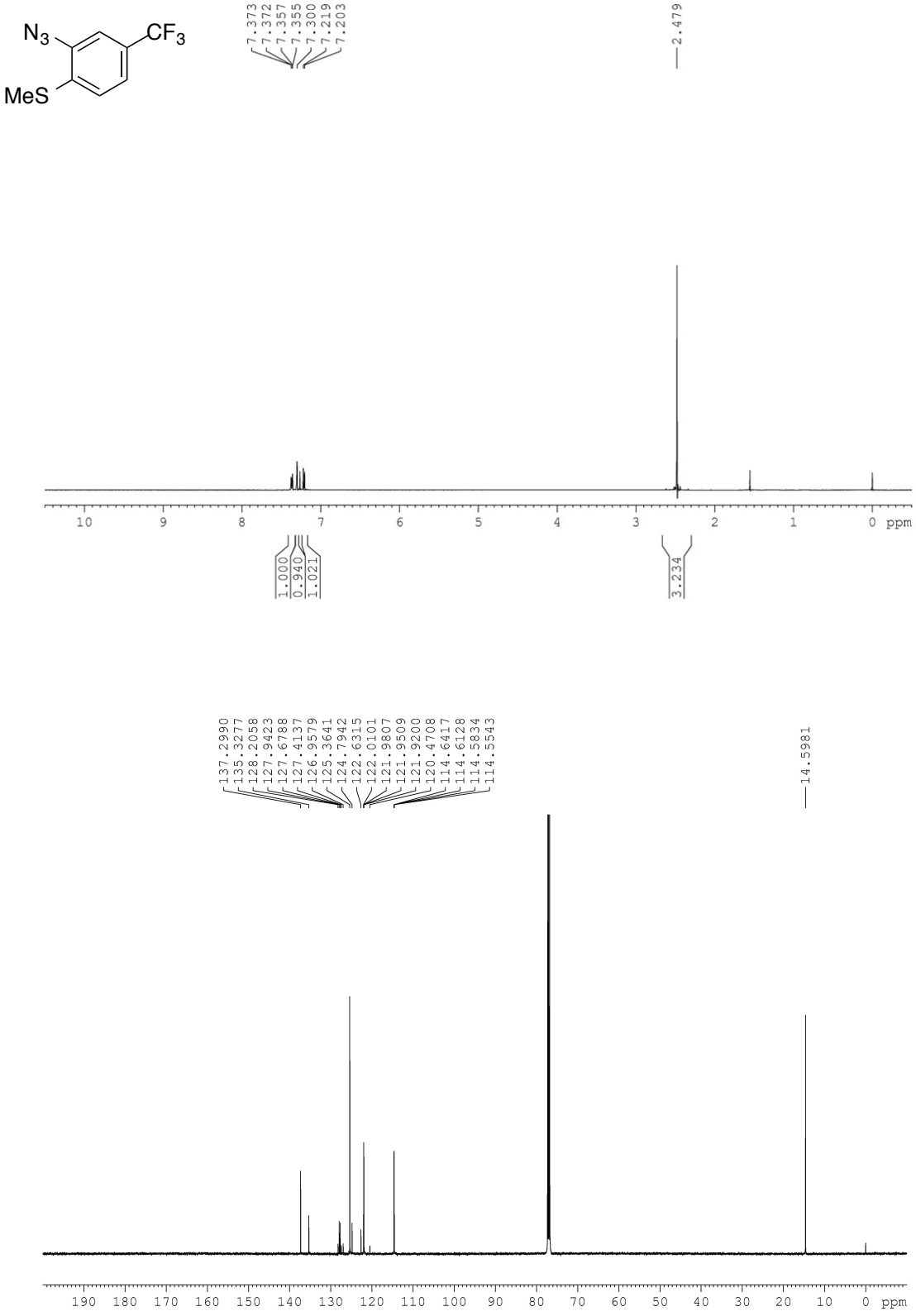
^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of **2i** ($CDCl_3$)



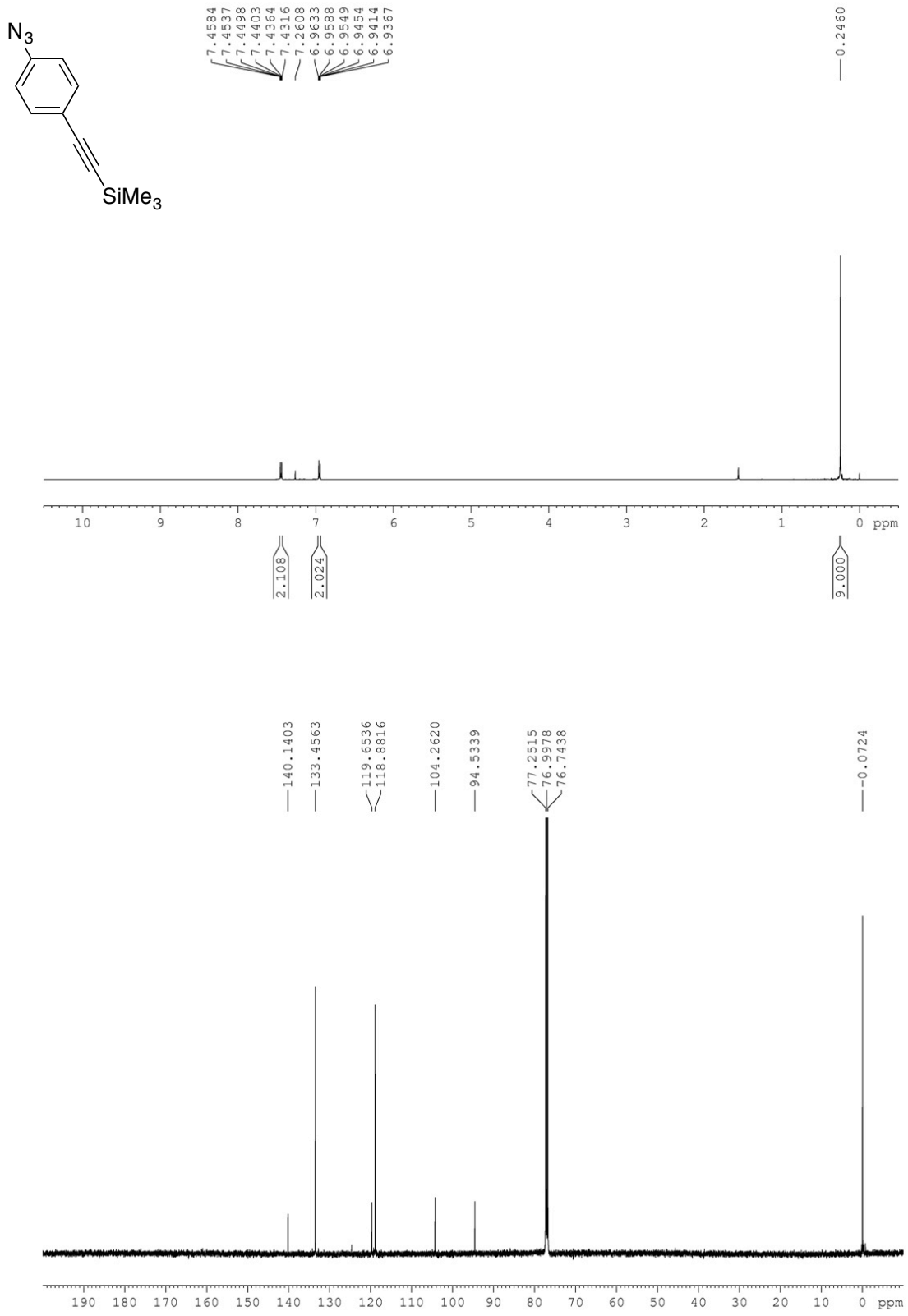
^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of **2j** ($CDCl_3$)



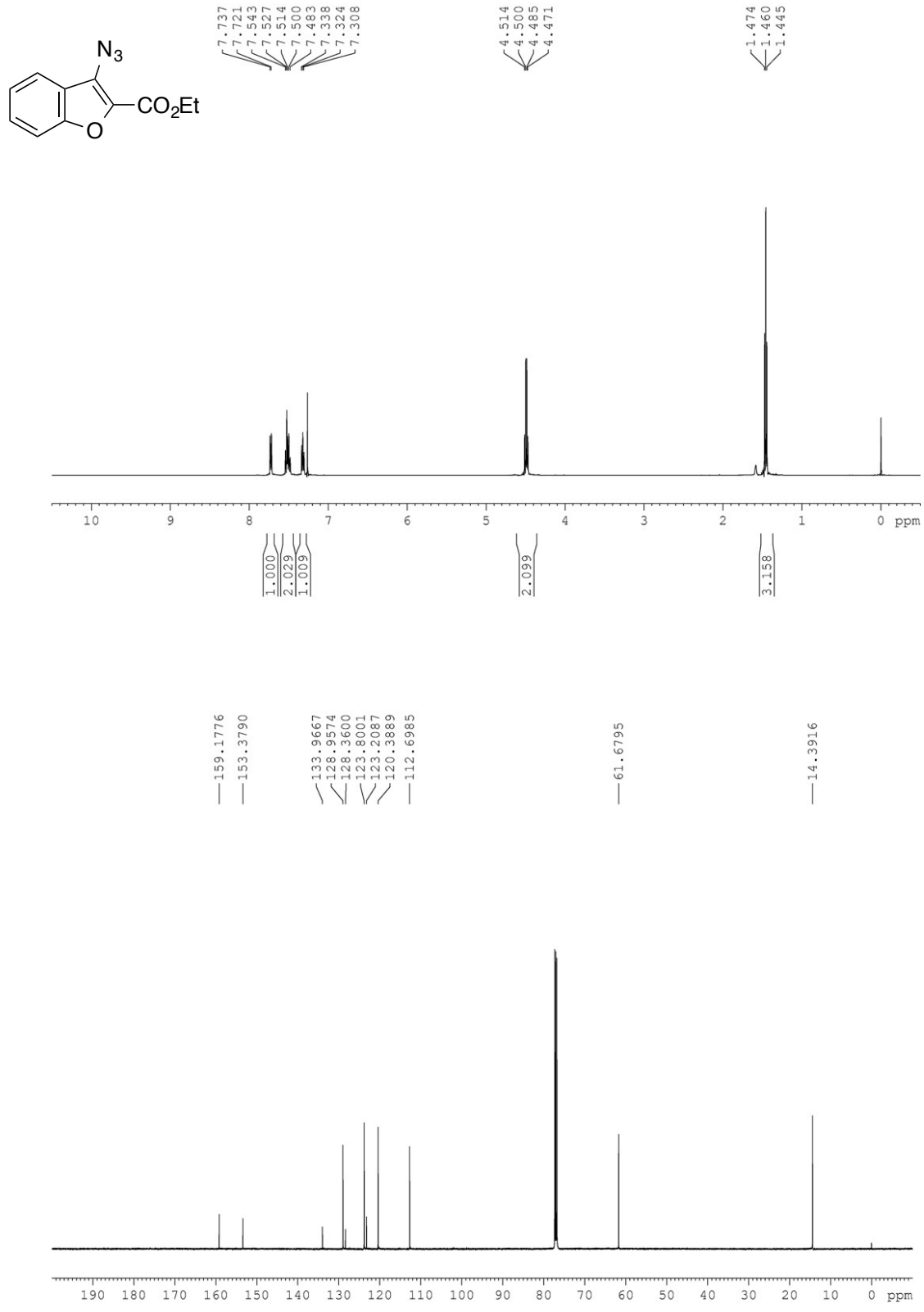
^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of **2l** ($CDCl_3$)



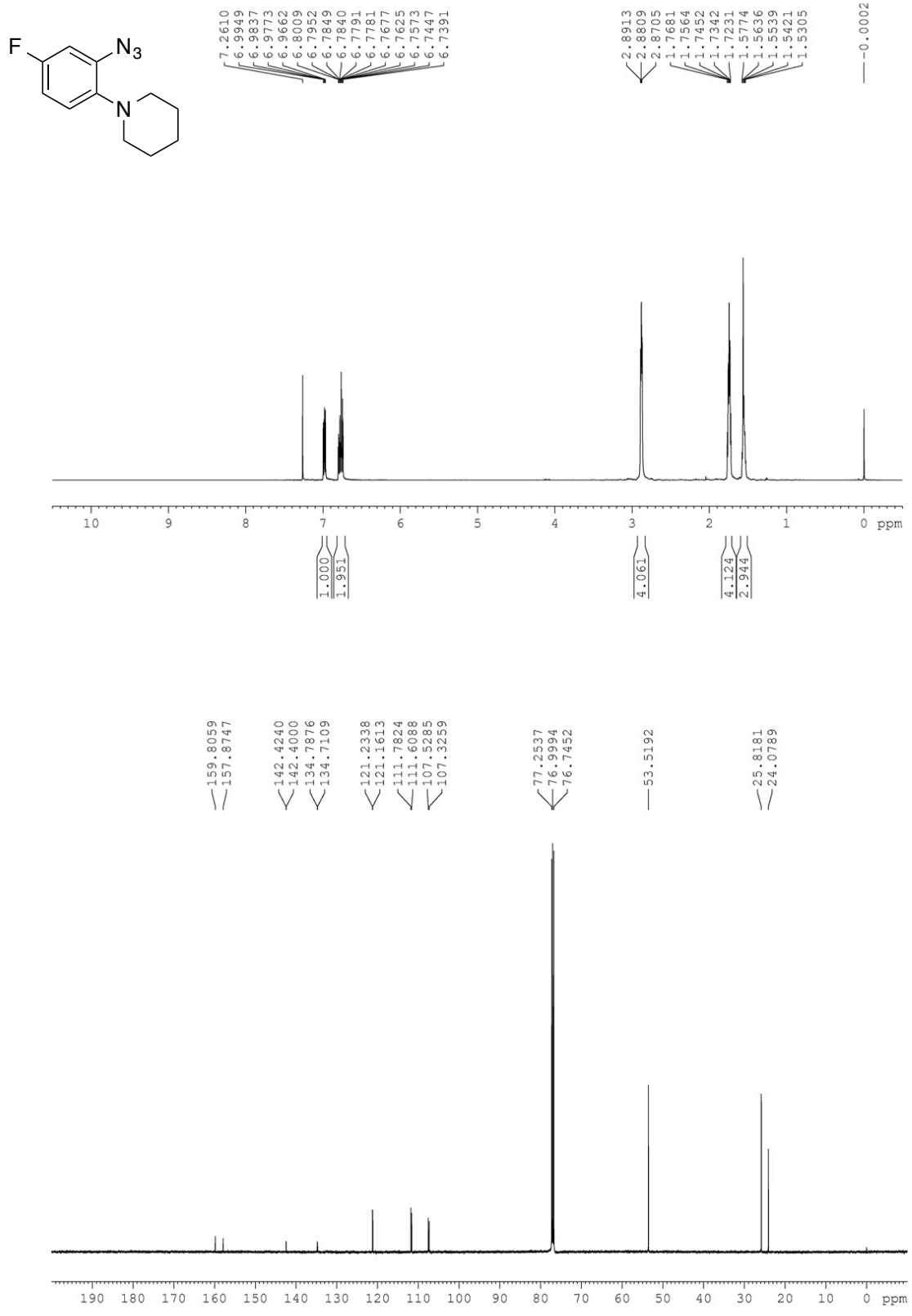
^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of **2p** ($CDCl_3$)



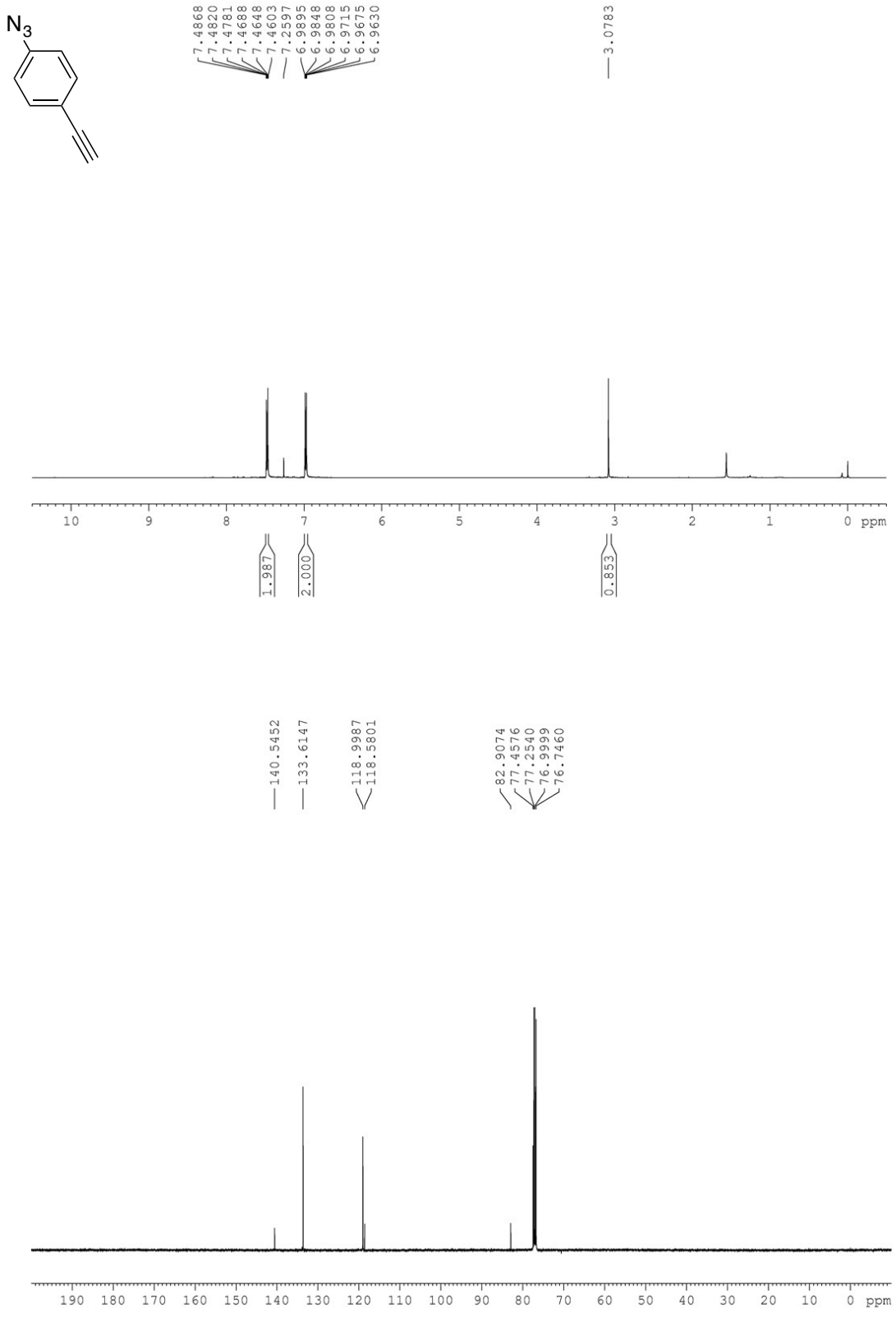
^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of **2q** ($CDCl_3$)



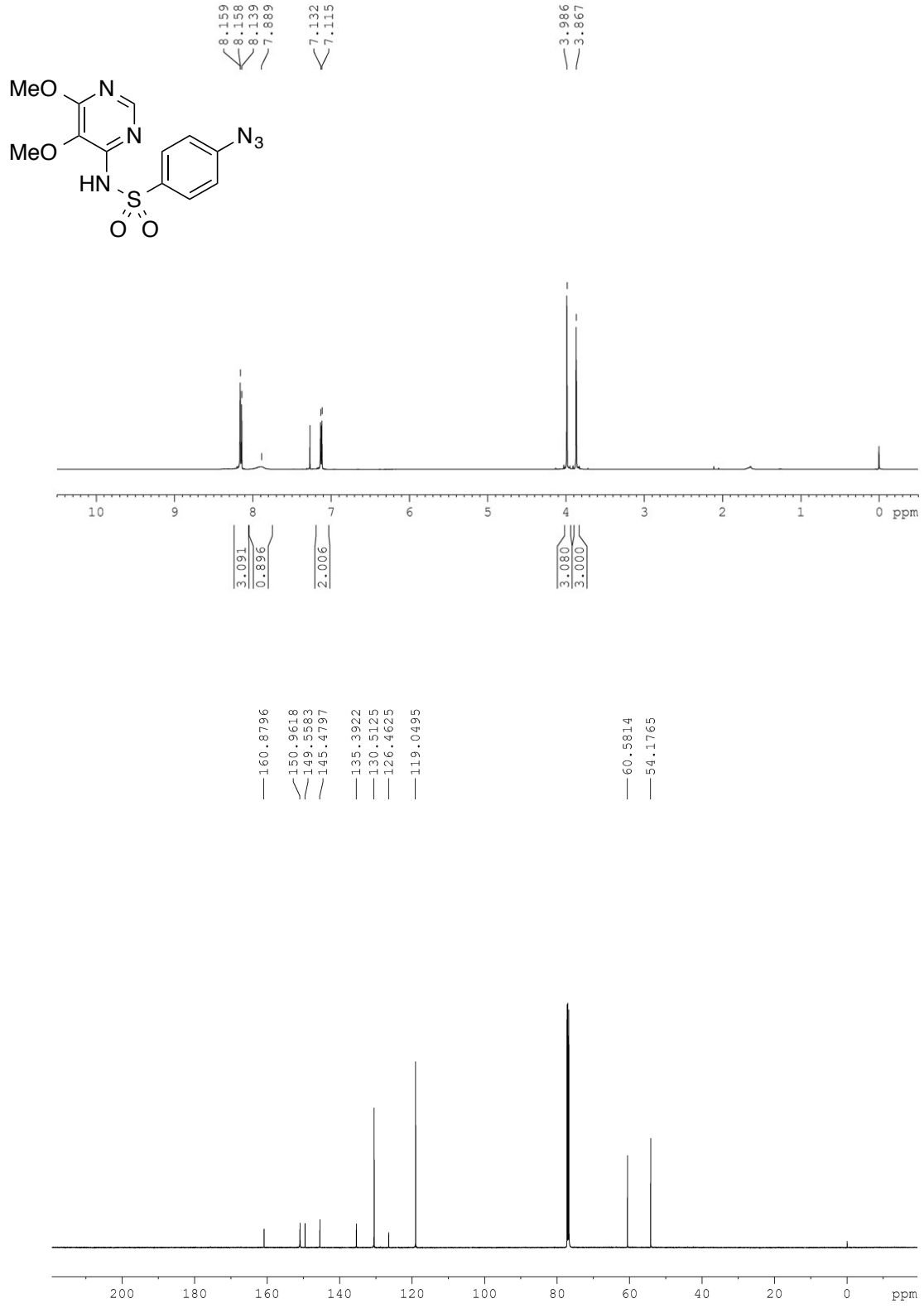
^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of **2r** ($CDCl_3$)



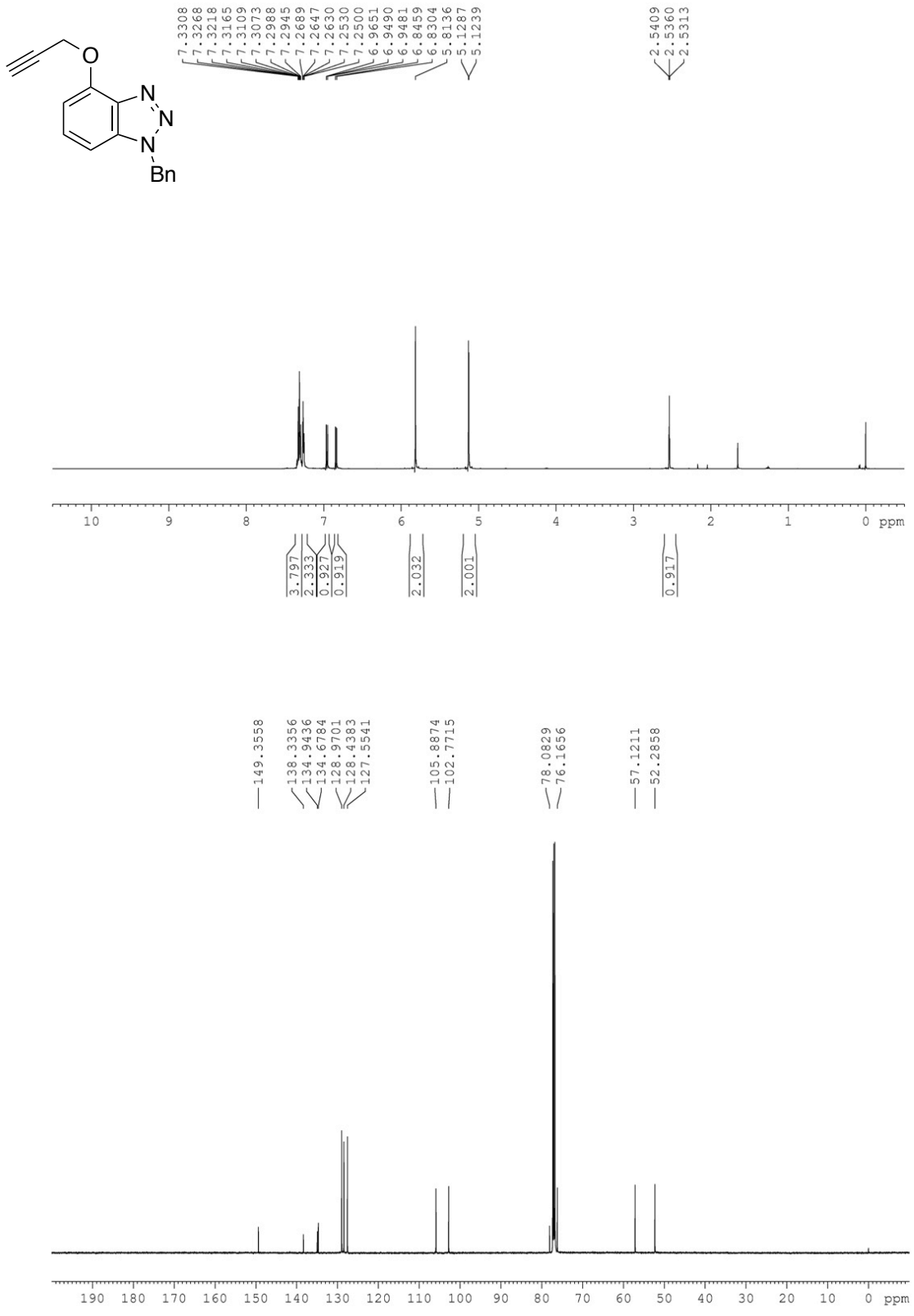
^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of **2s** ($CDCl_3$)



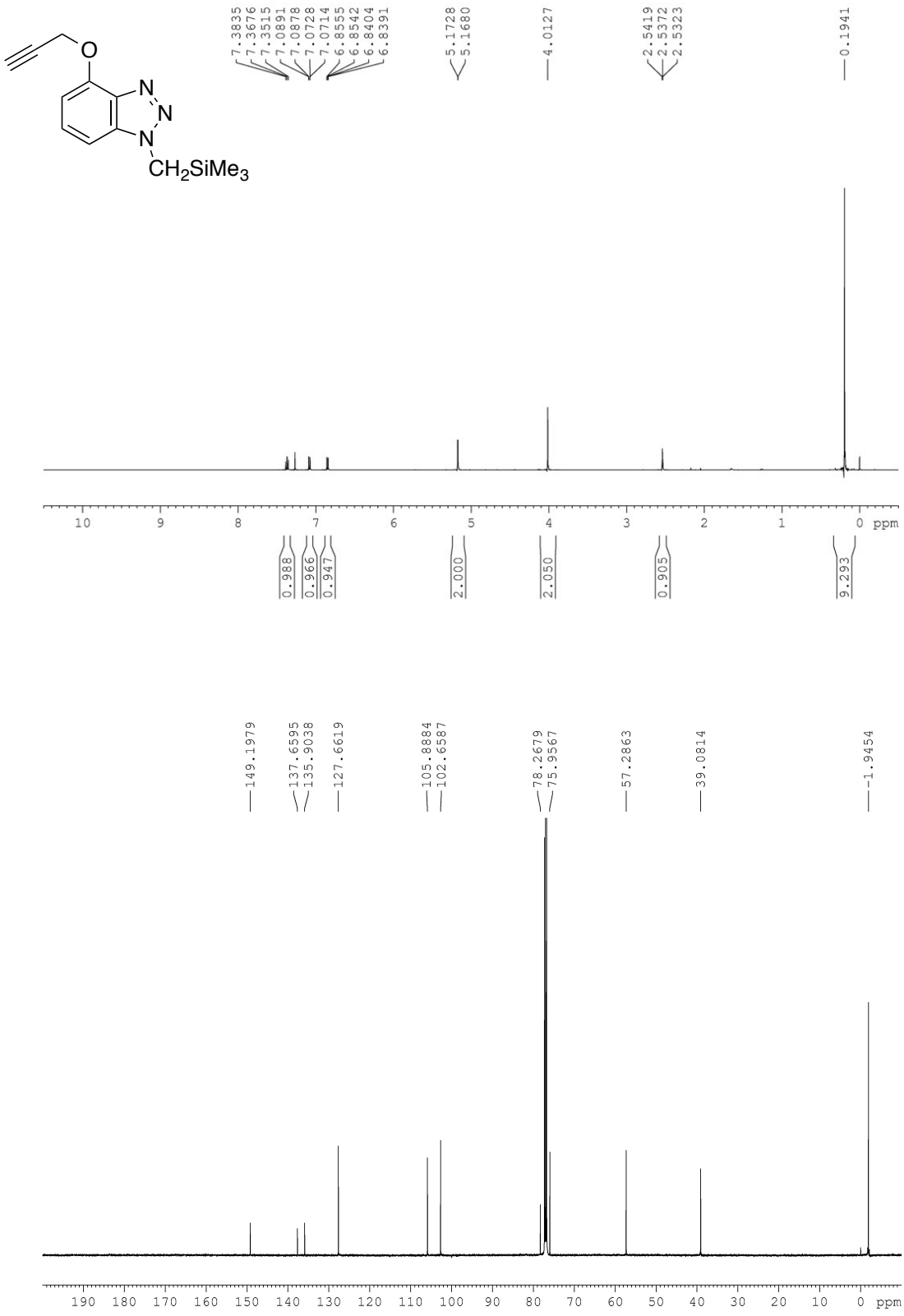
^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of **2t** ($CDCl_3$)



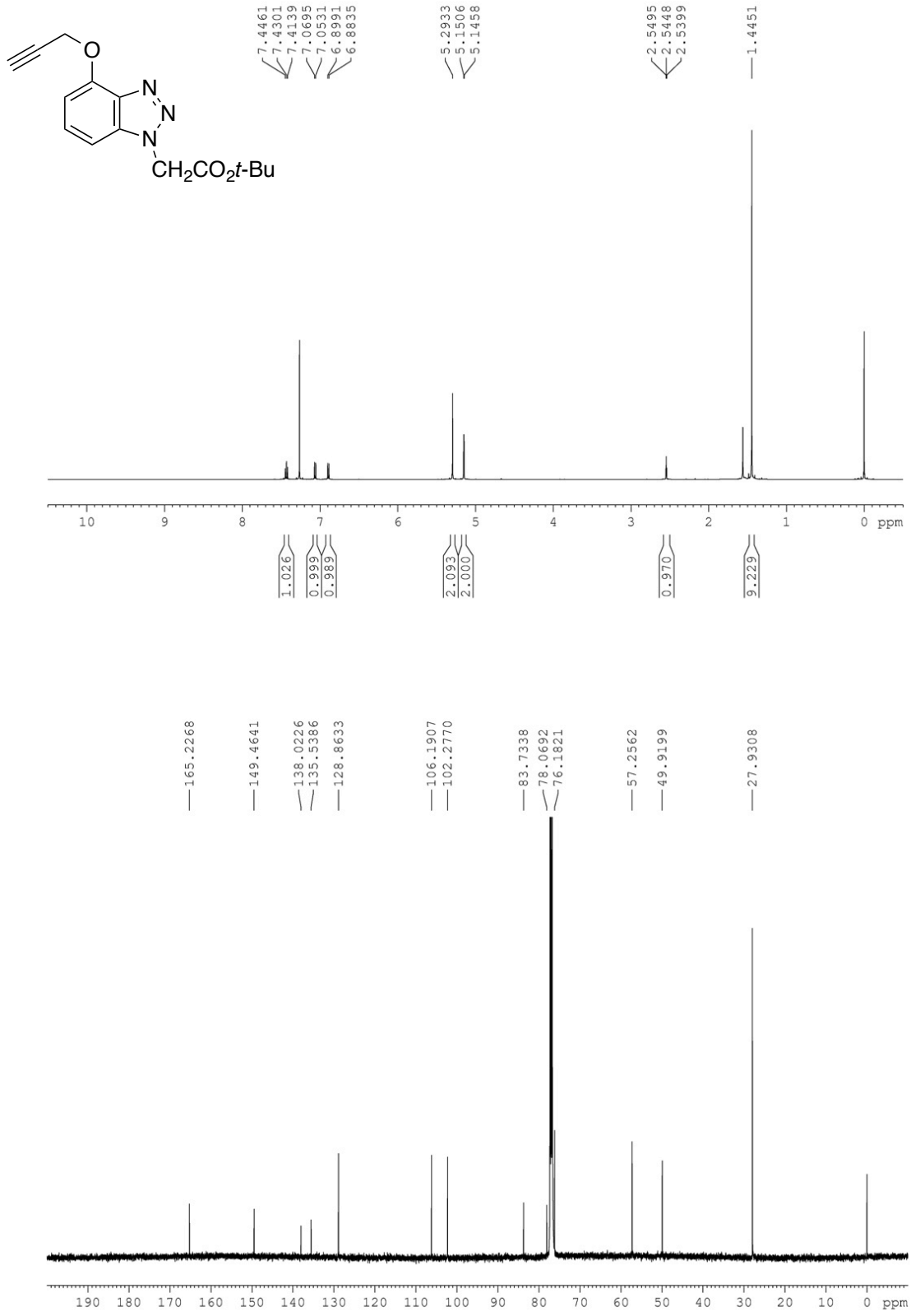
^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of **3a** ($CDCl_3$)



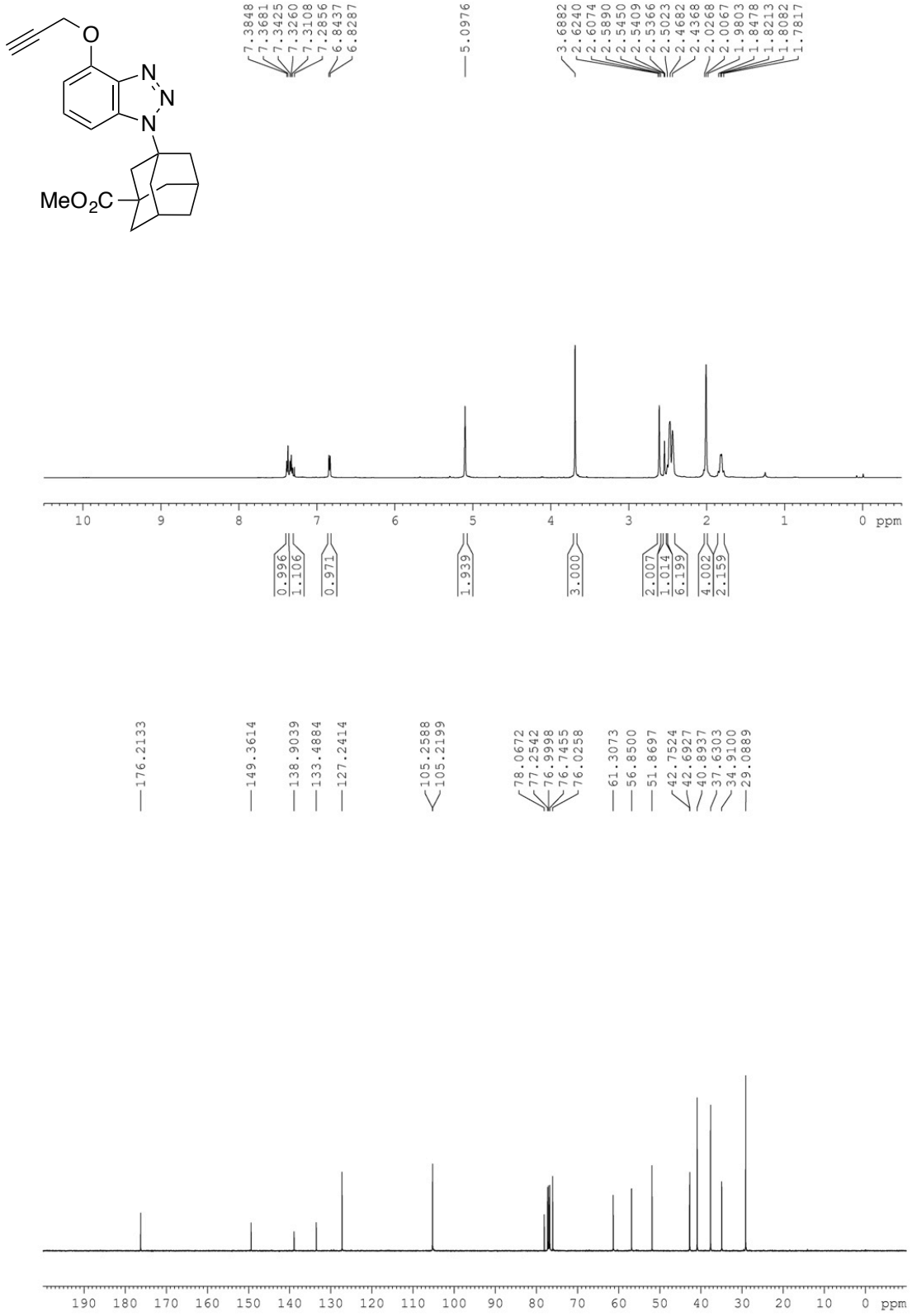
^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of **3b** ($CDCl_3$)



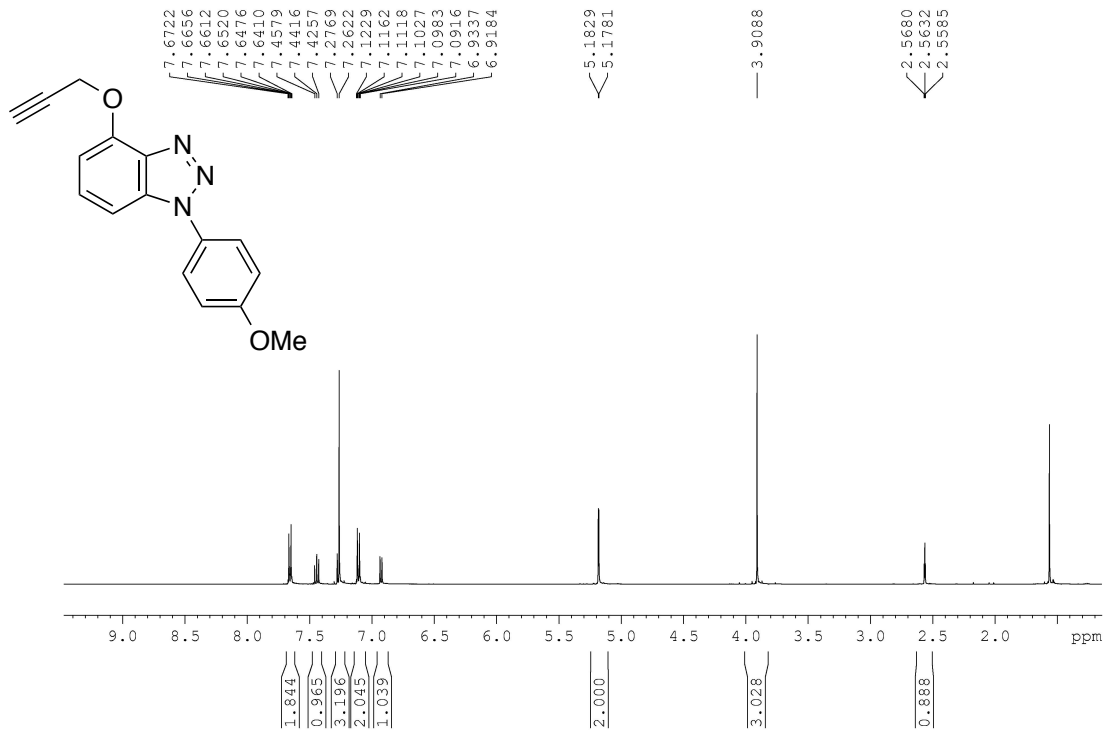
^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of **3c** ($CDCl_3$)

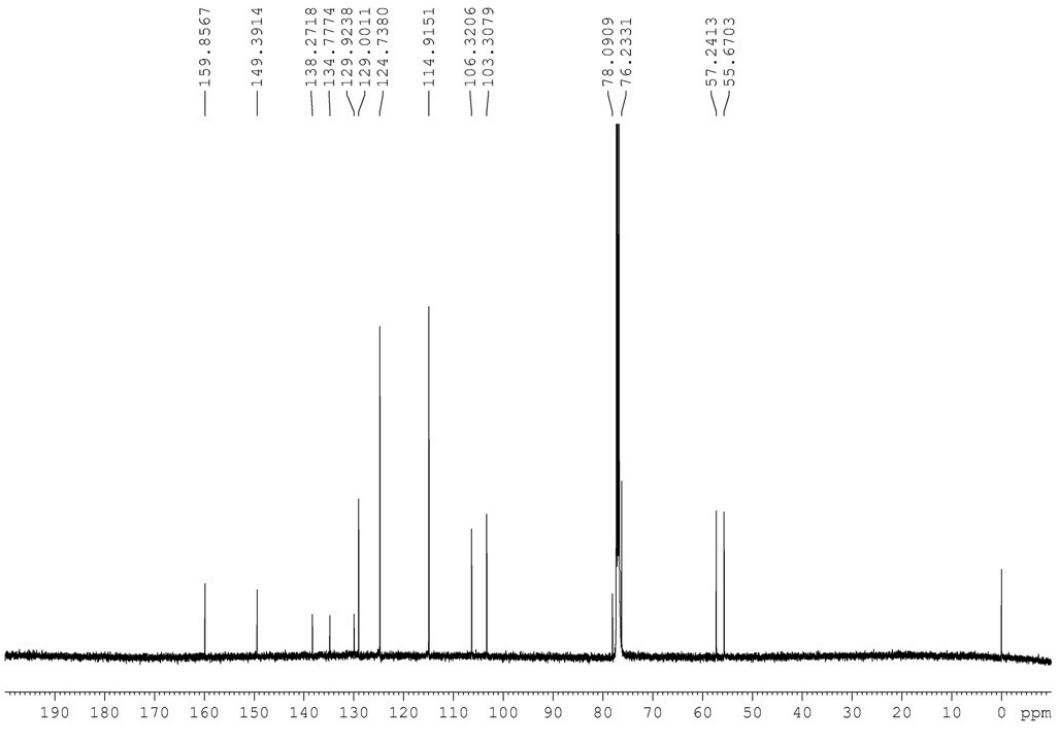


^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of **3d** ($CDCl_3$)

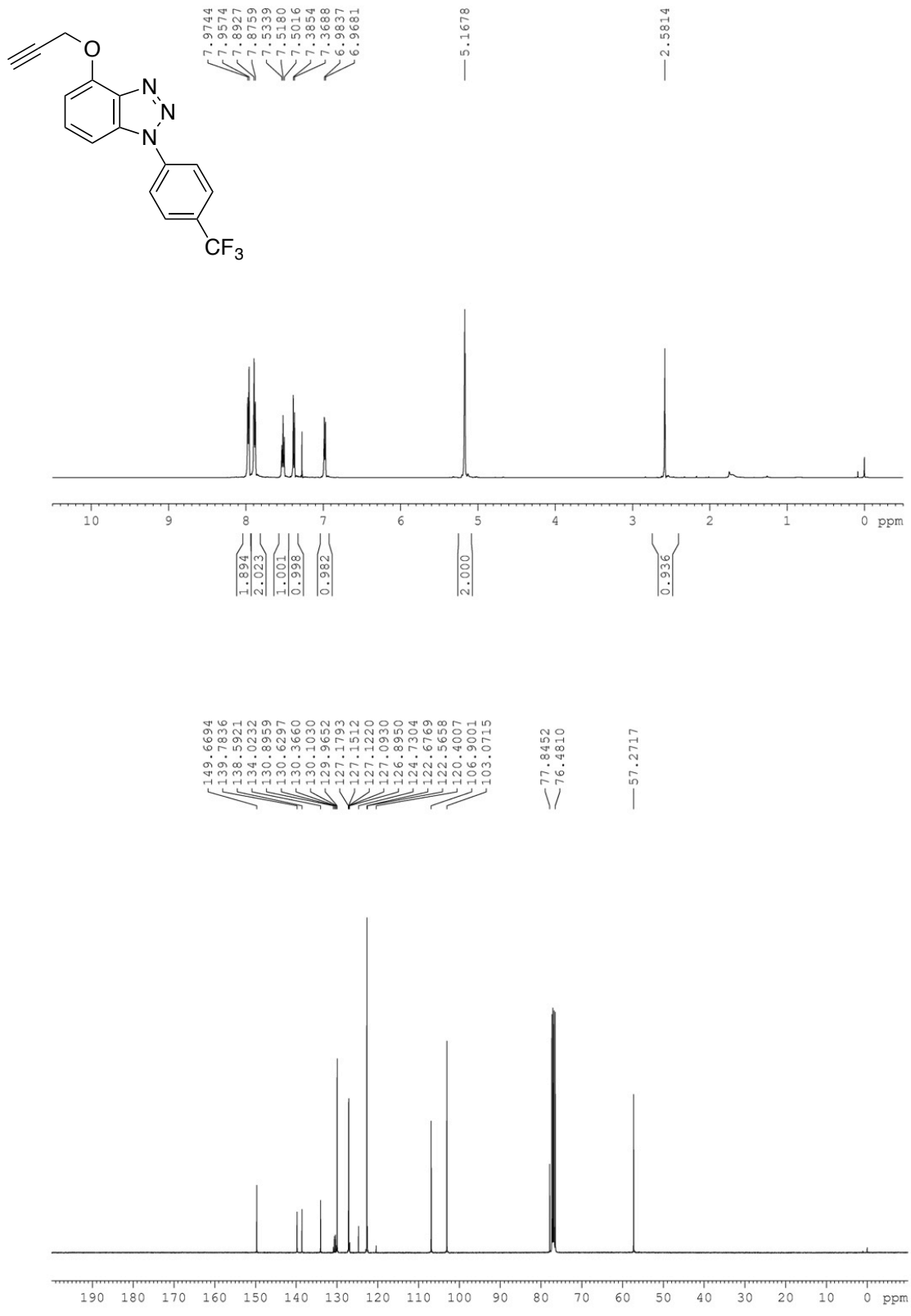


^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of **3e** ($CDCl_3$)

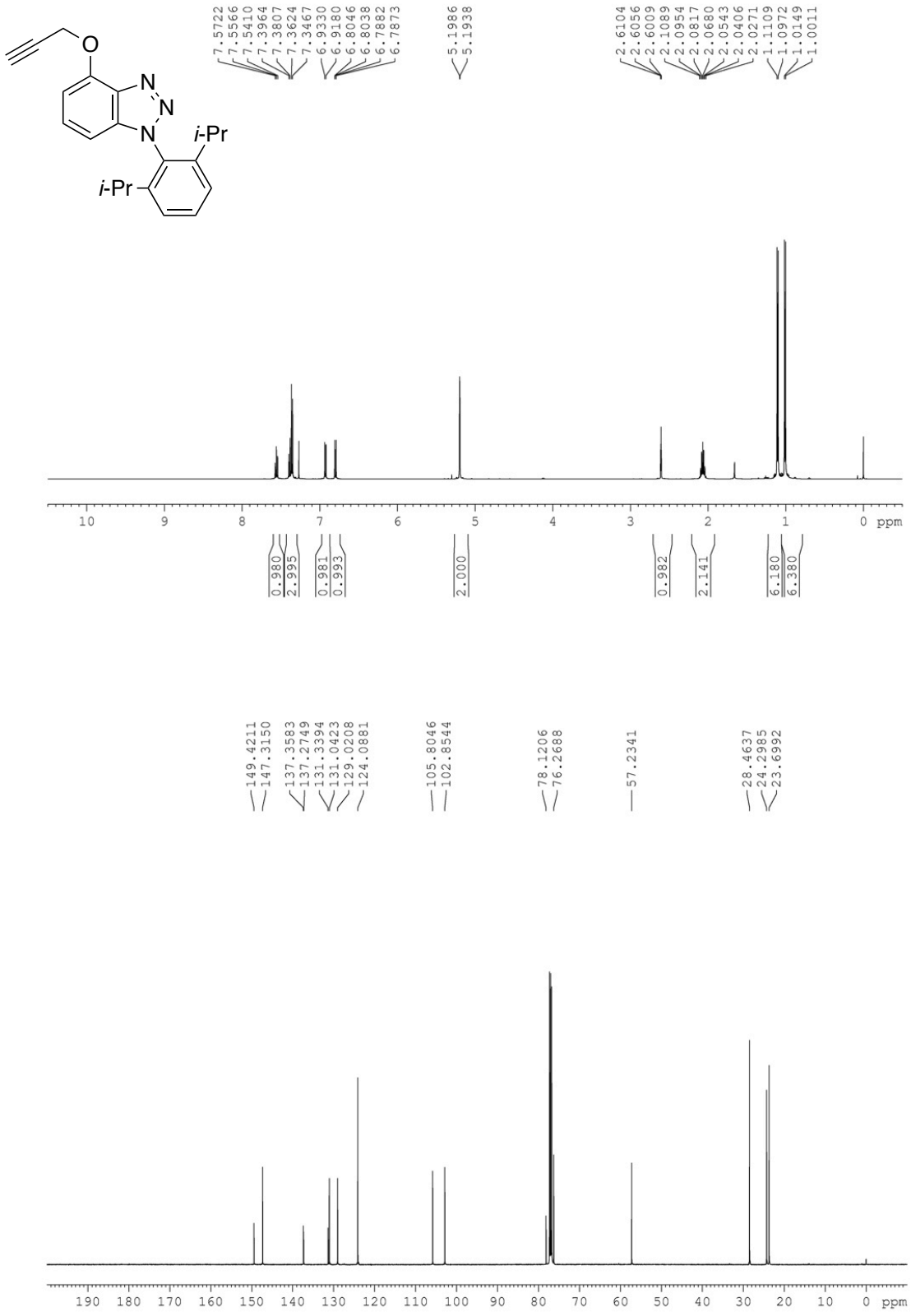




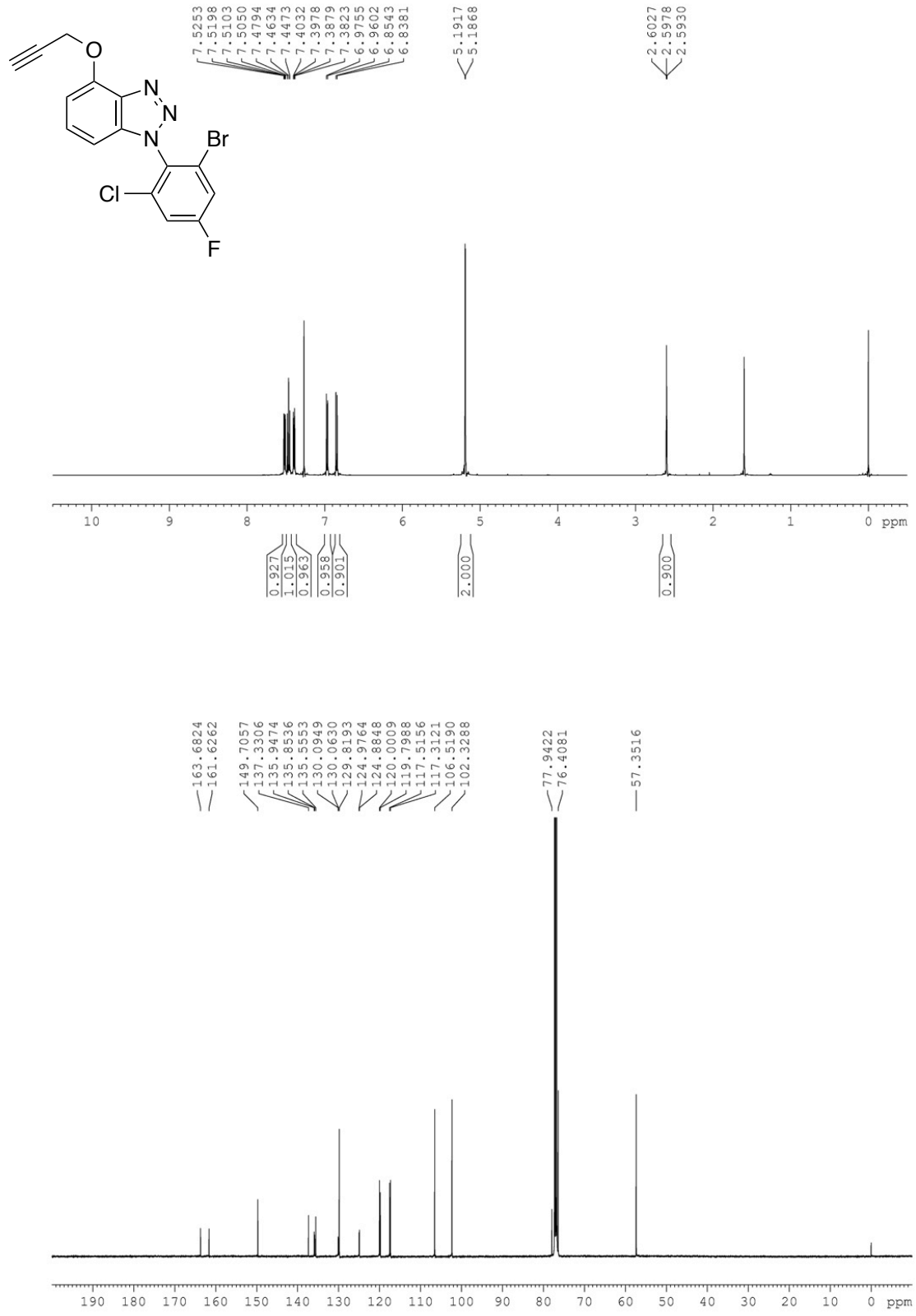
^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of **3f** ($CDCl_3$)



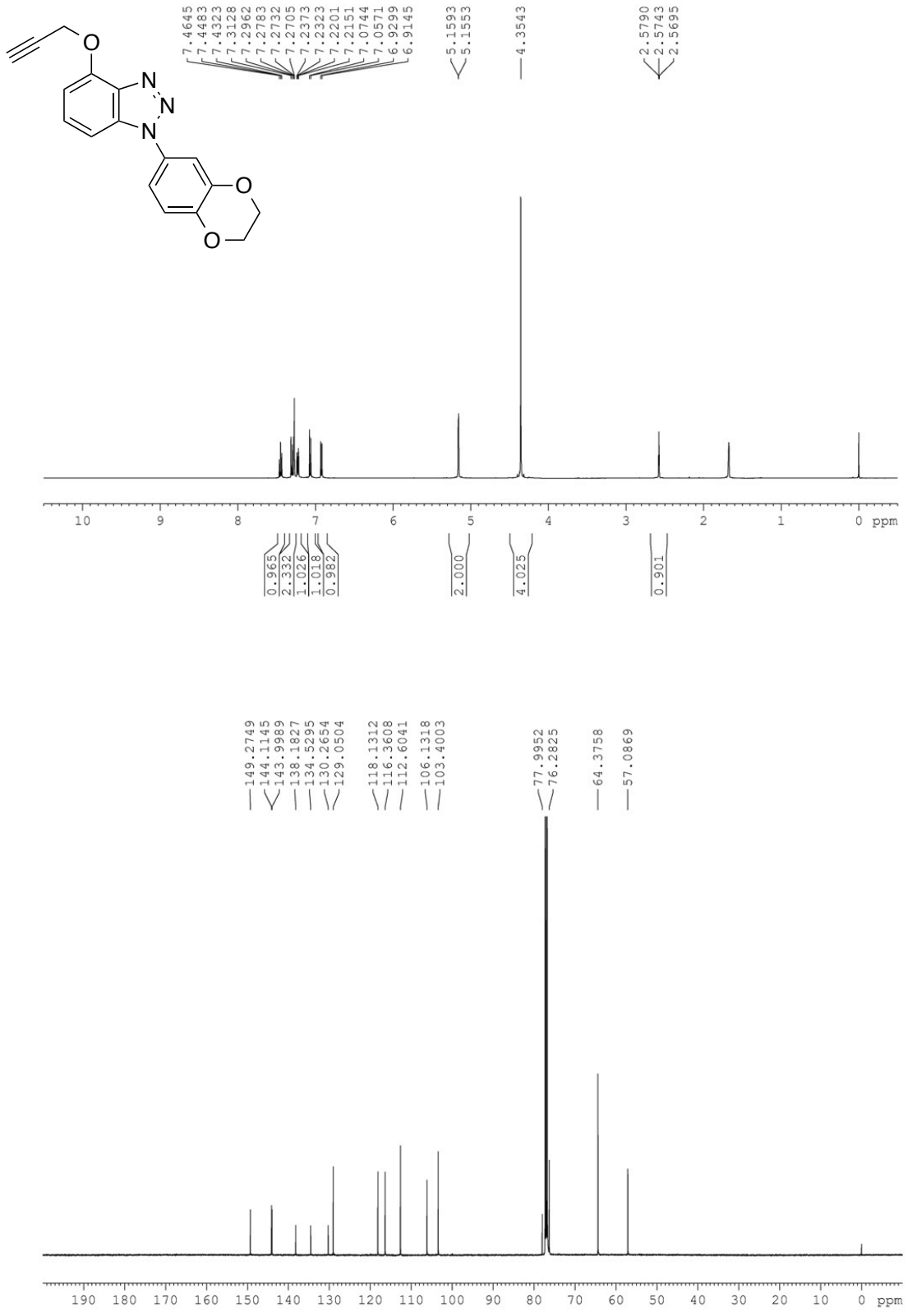
^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of **3g** ($CDCl_3$)



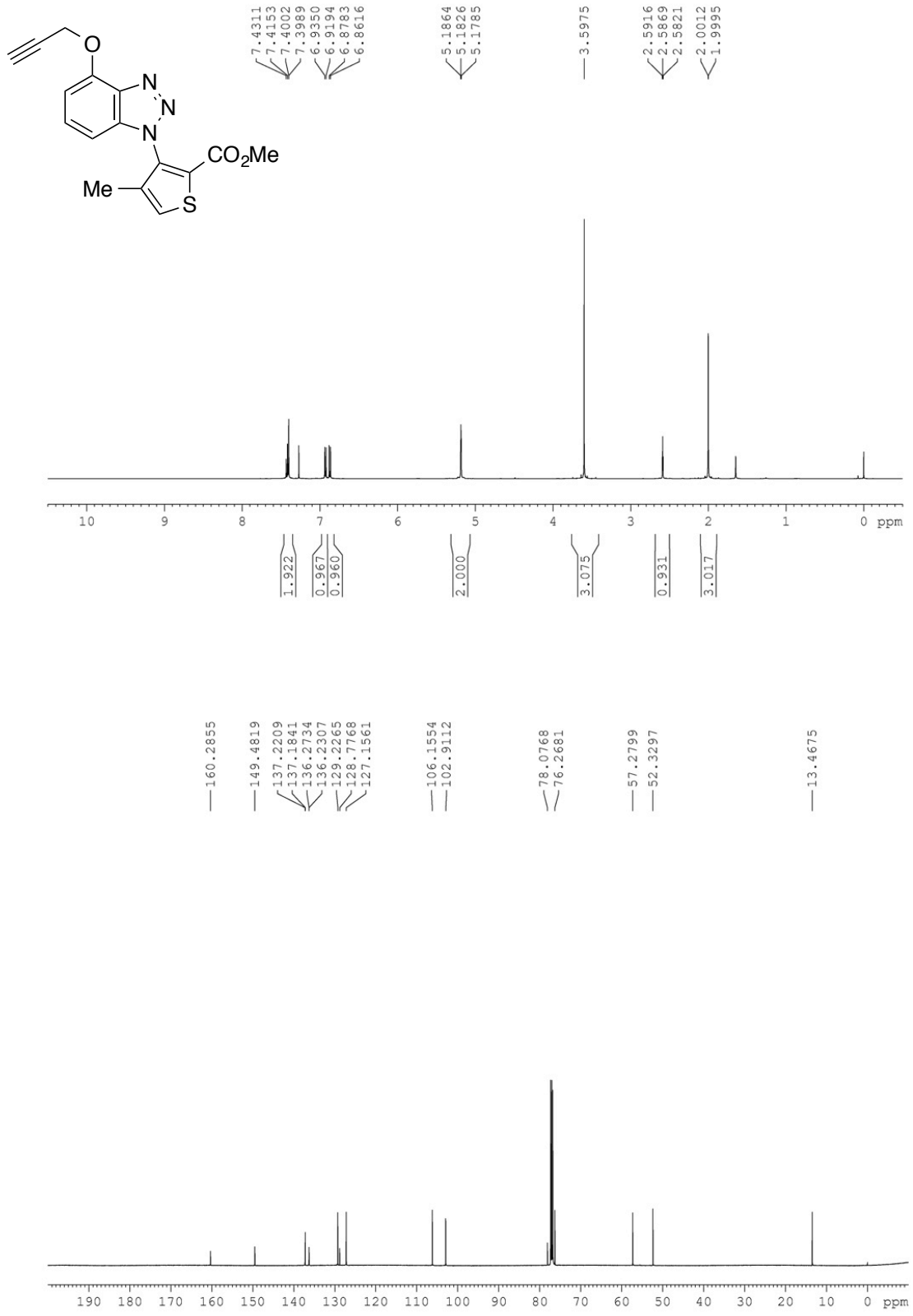
^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of **3h** ($CDCl_3$)



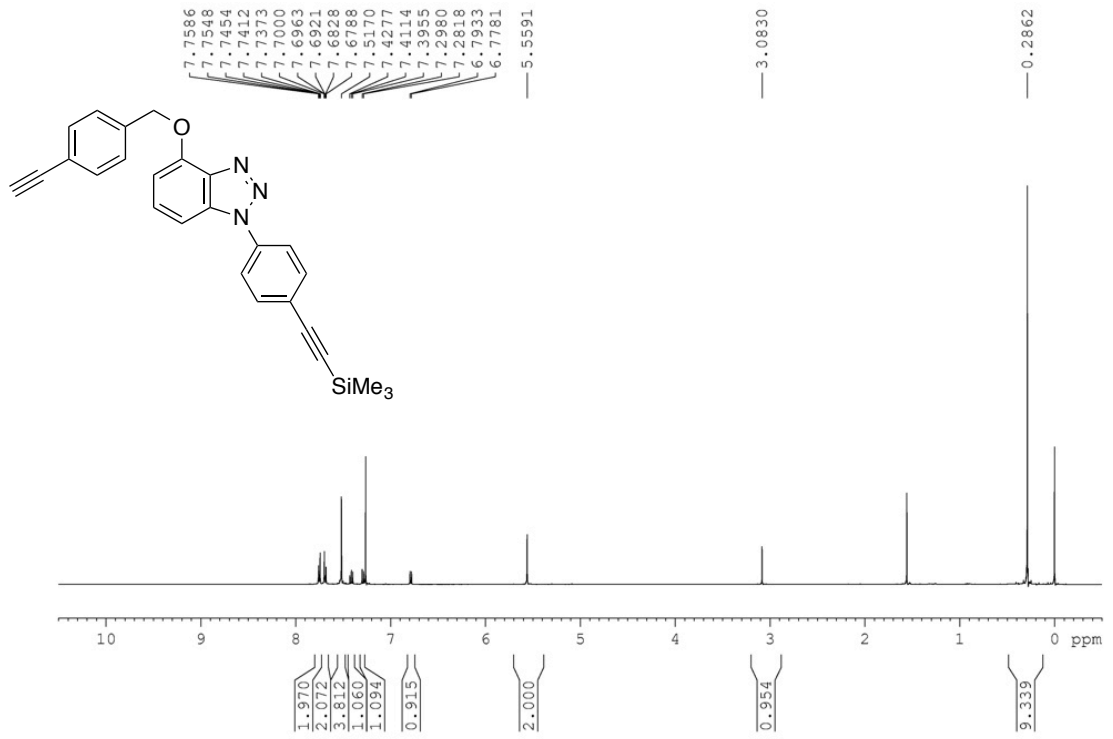
^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of **3i** ($CDCl_3$)

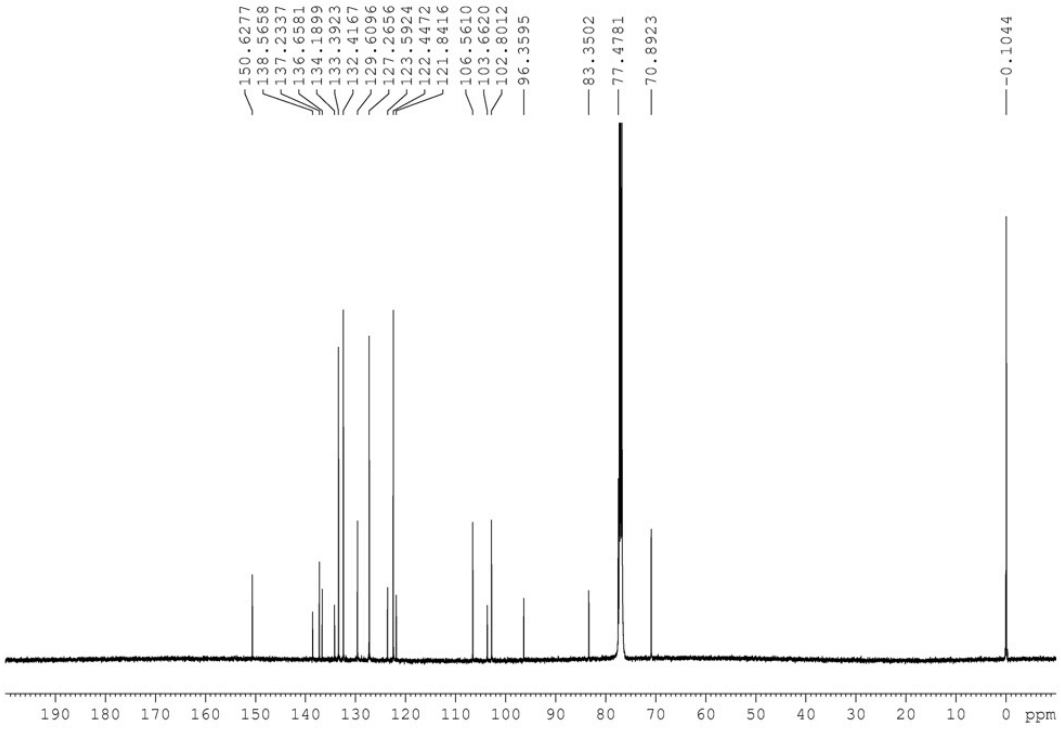


^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of **3j** ($CDCl_3$)

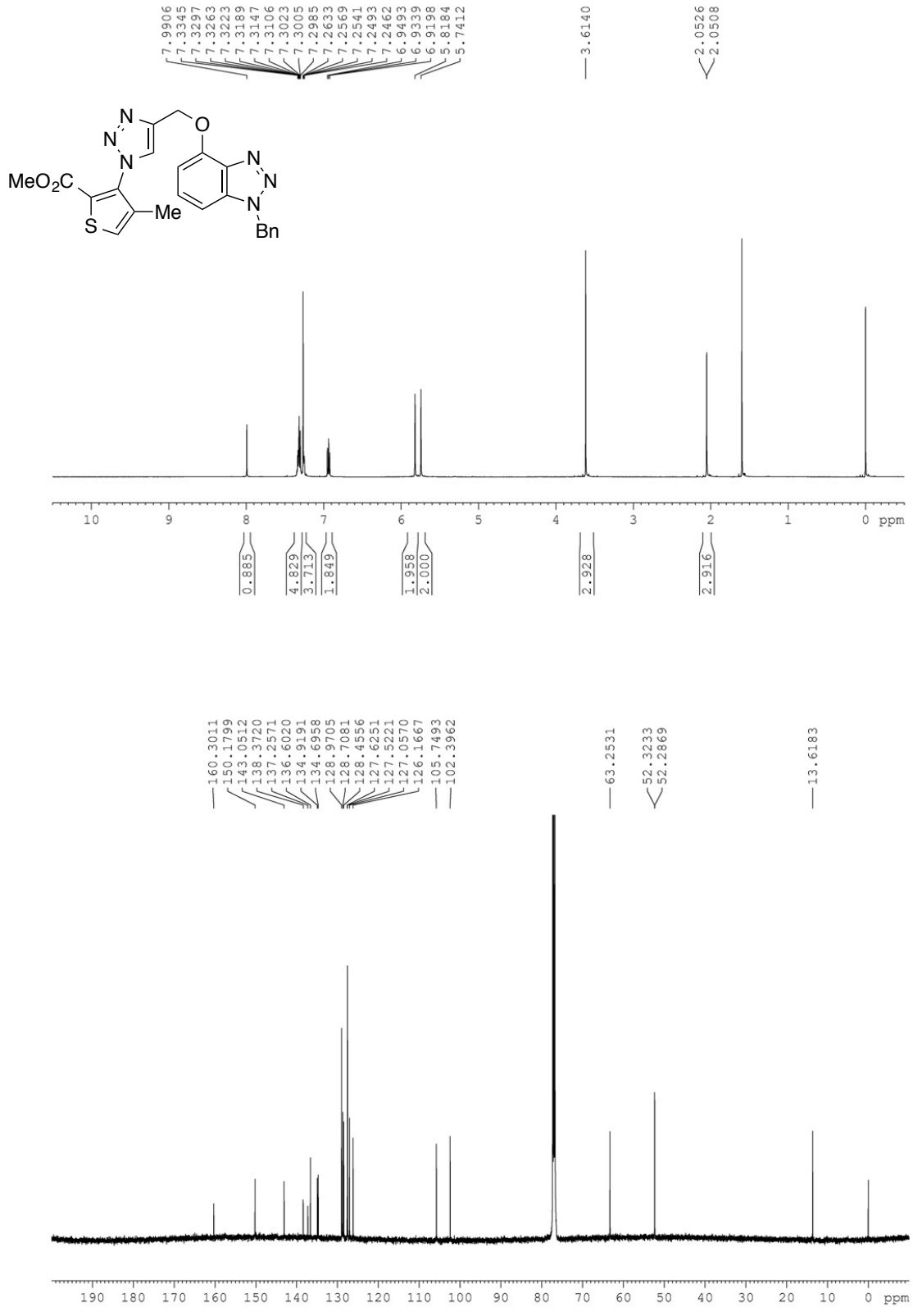


^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of **3k** ($CDCl_3$)



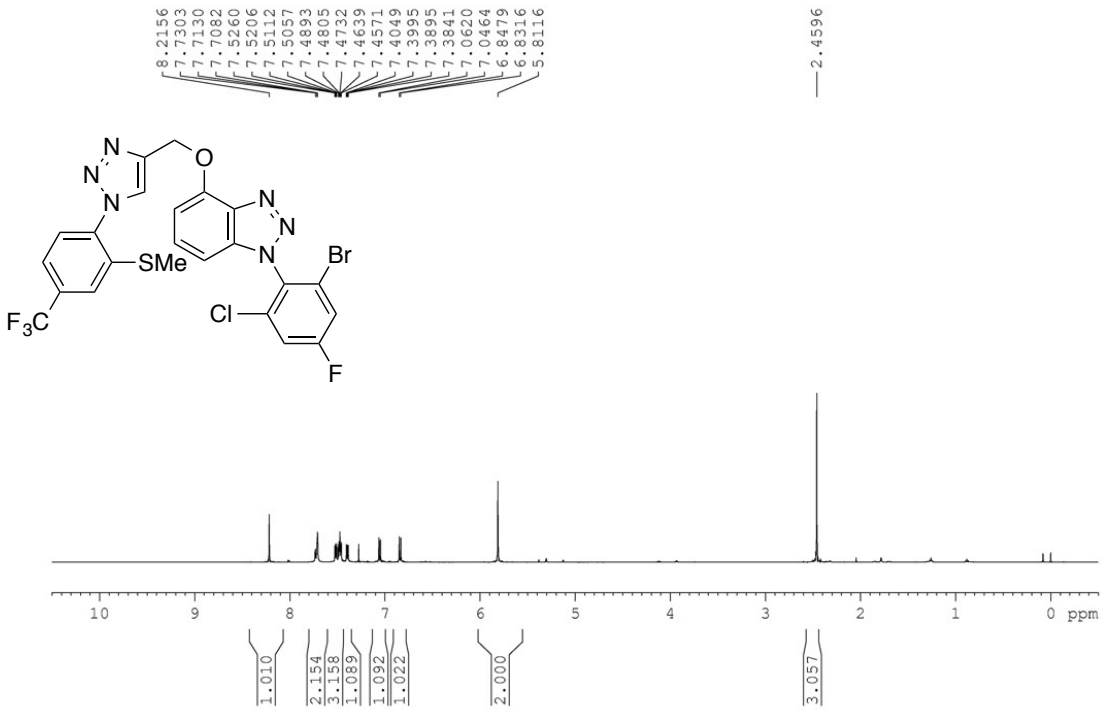


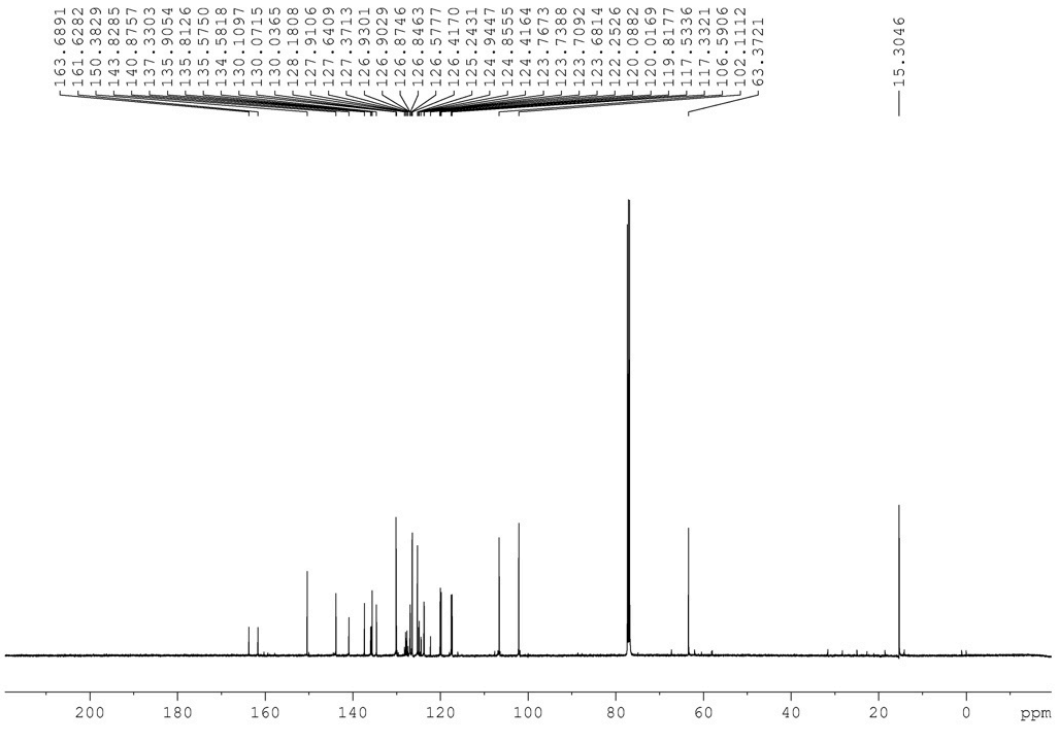
^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of **4a** ($CDCl_3$)



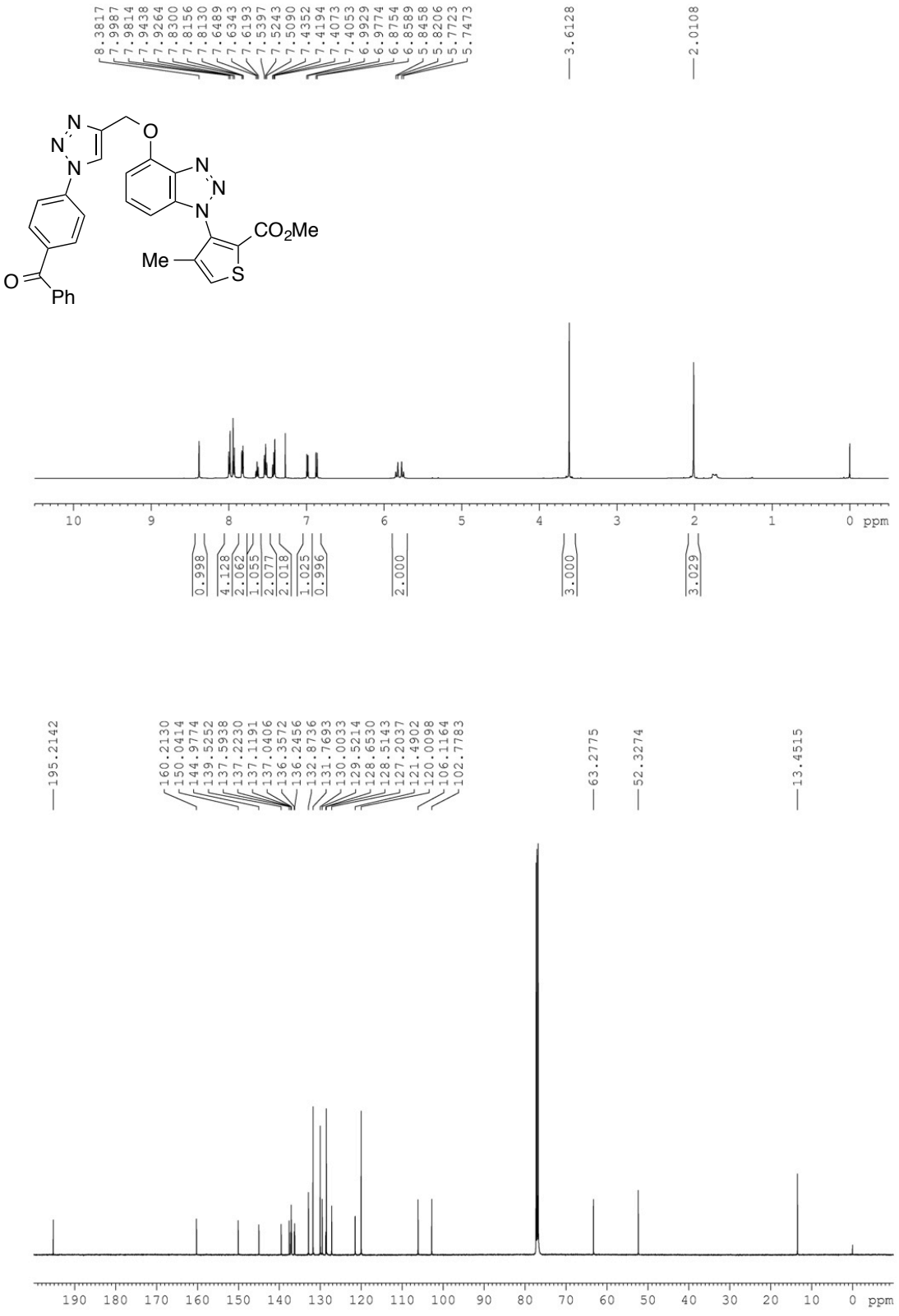
^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of **4b** ($CDCl_3$)

^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of **4c** ($CDCl_3$)

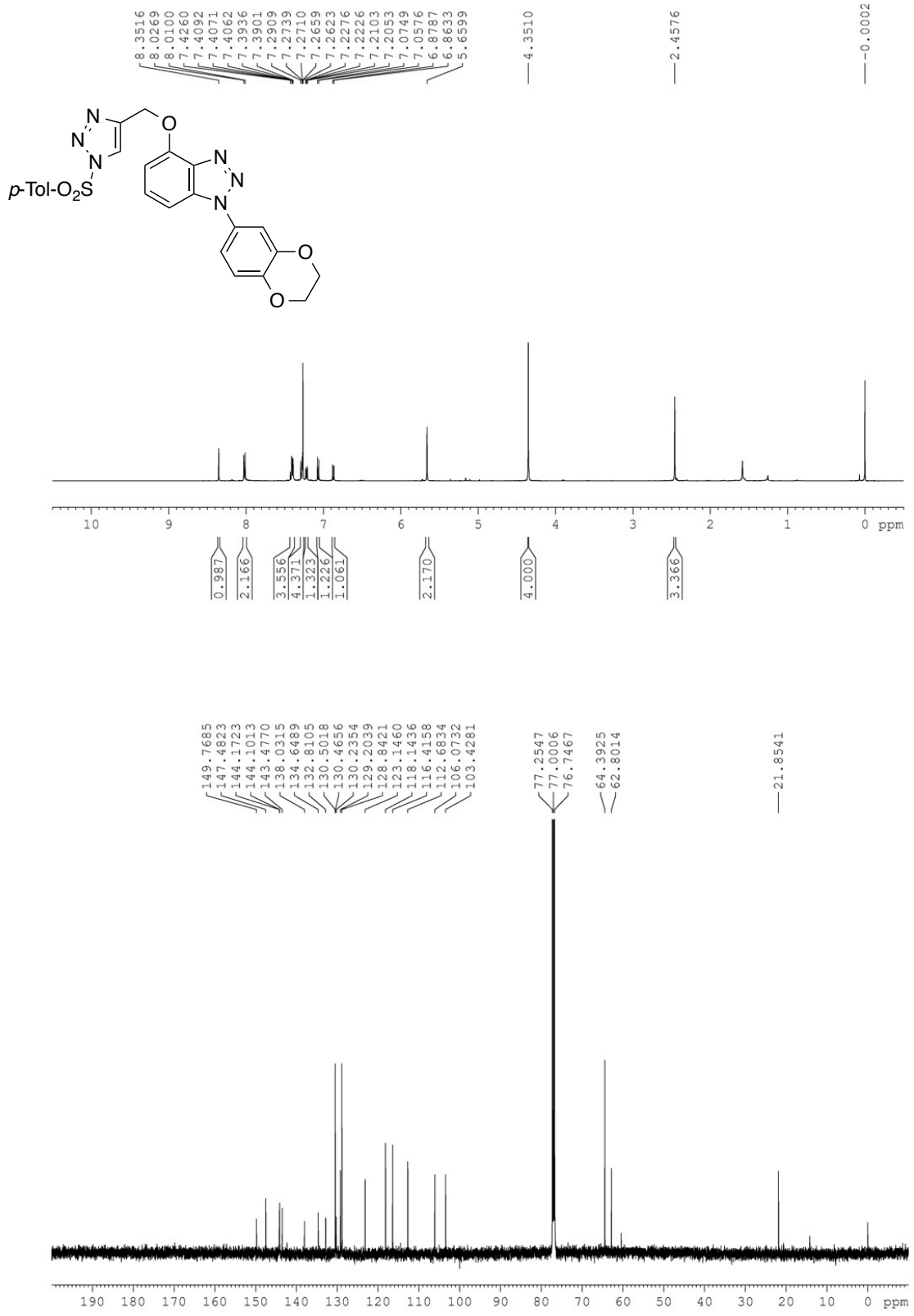




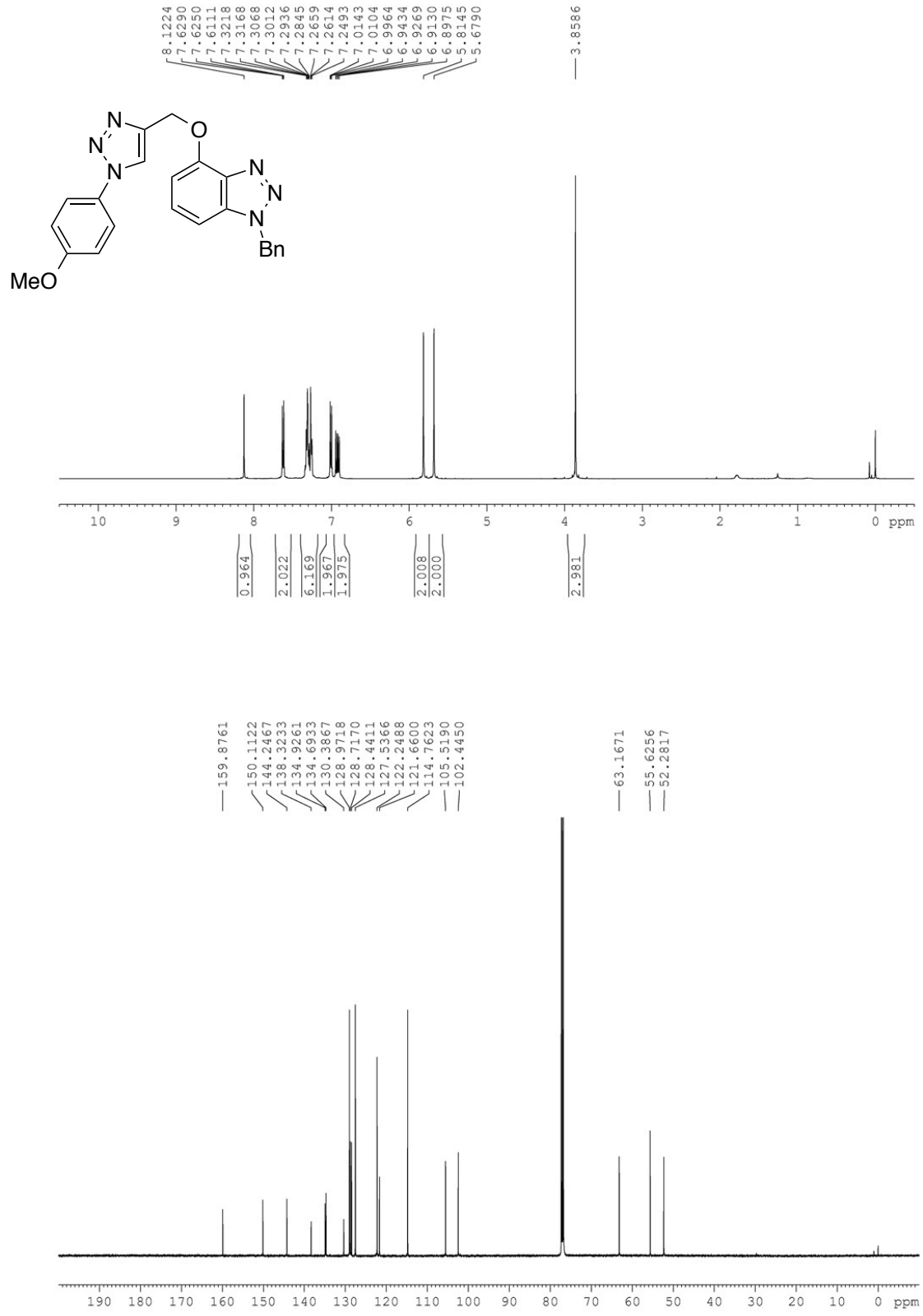
^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of **4d** ($CDCl_3$)



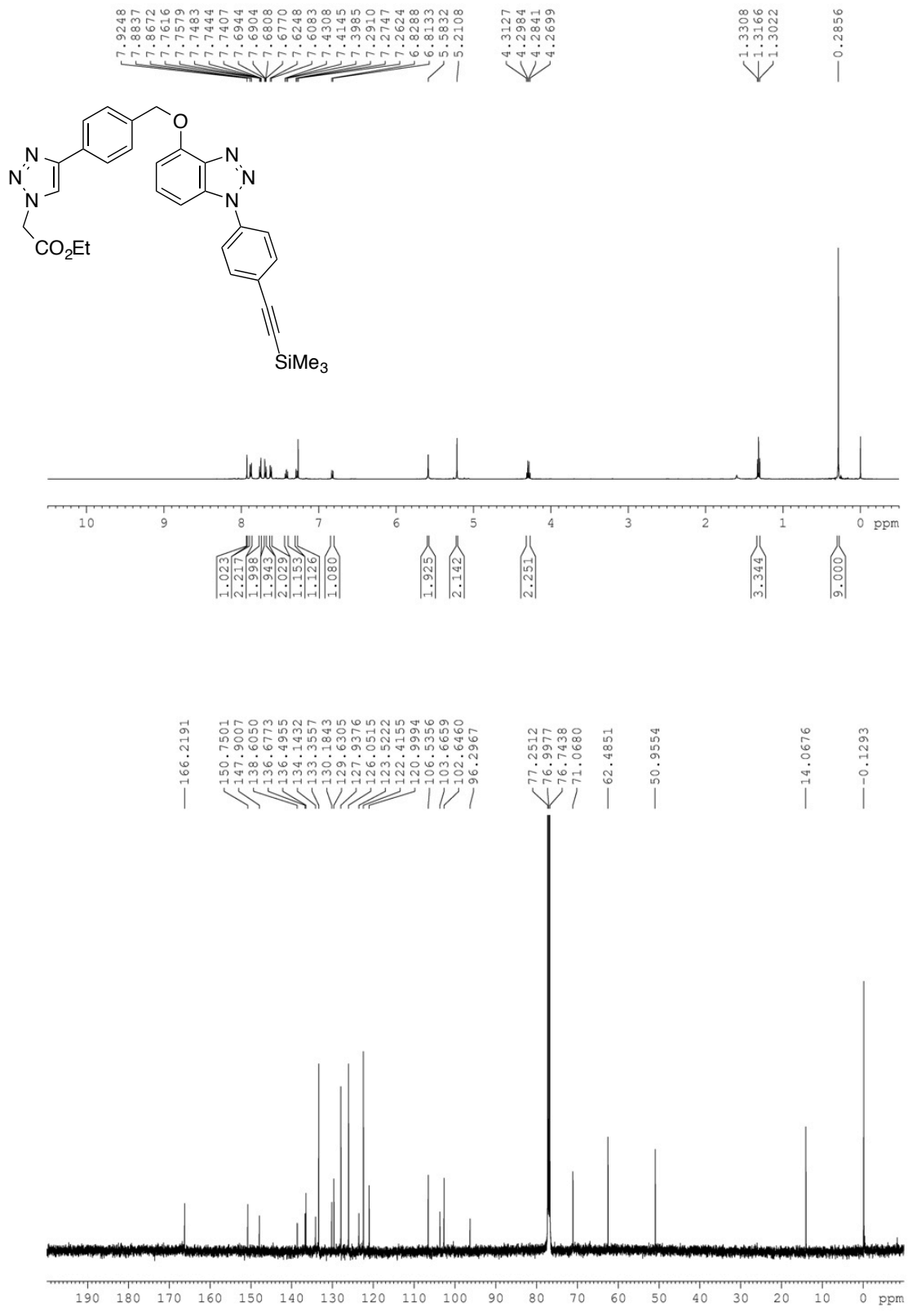
^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of **4e** ($CDCl_3$)



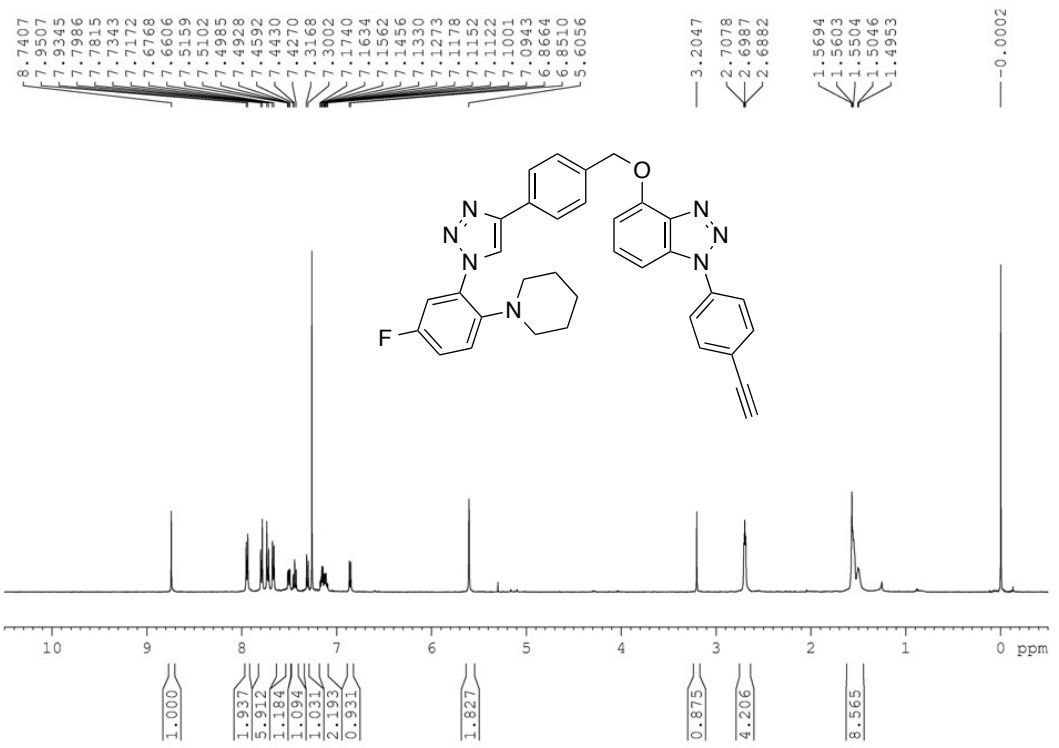
^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of **4f** ($CDCl_3$)

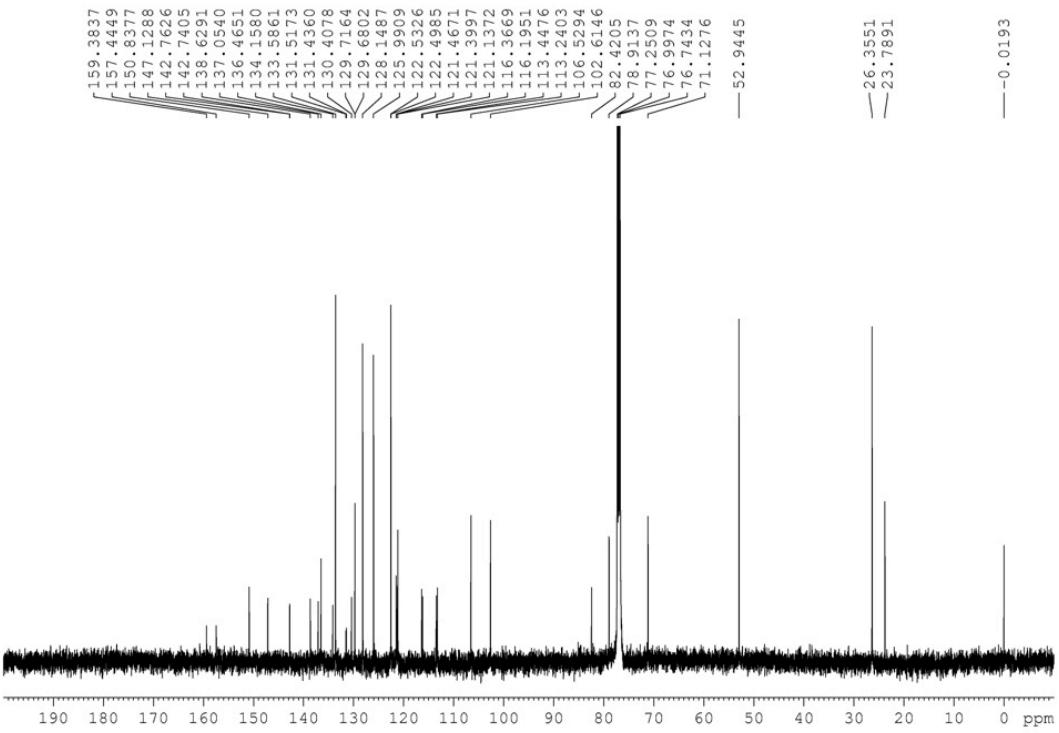


^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of **4g** ($CDCl_3$)

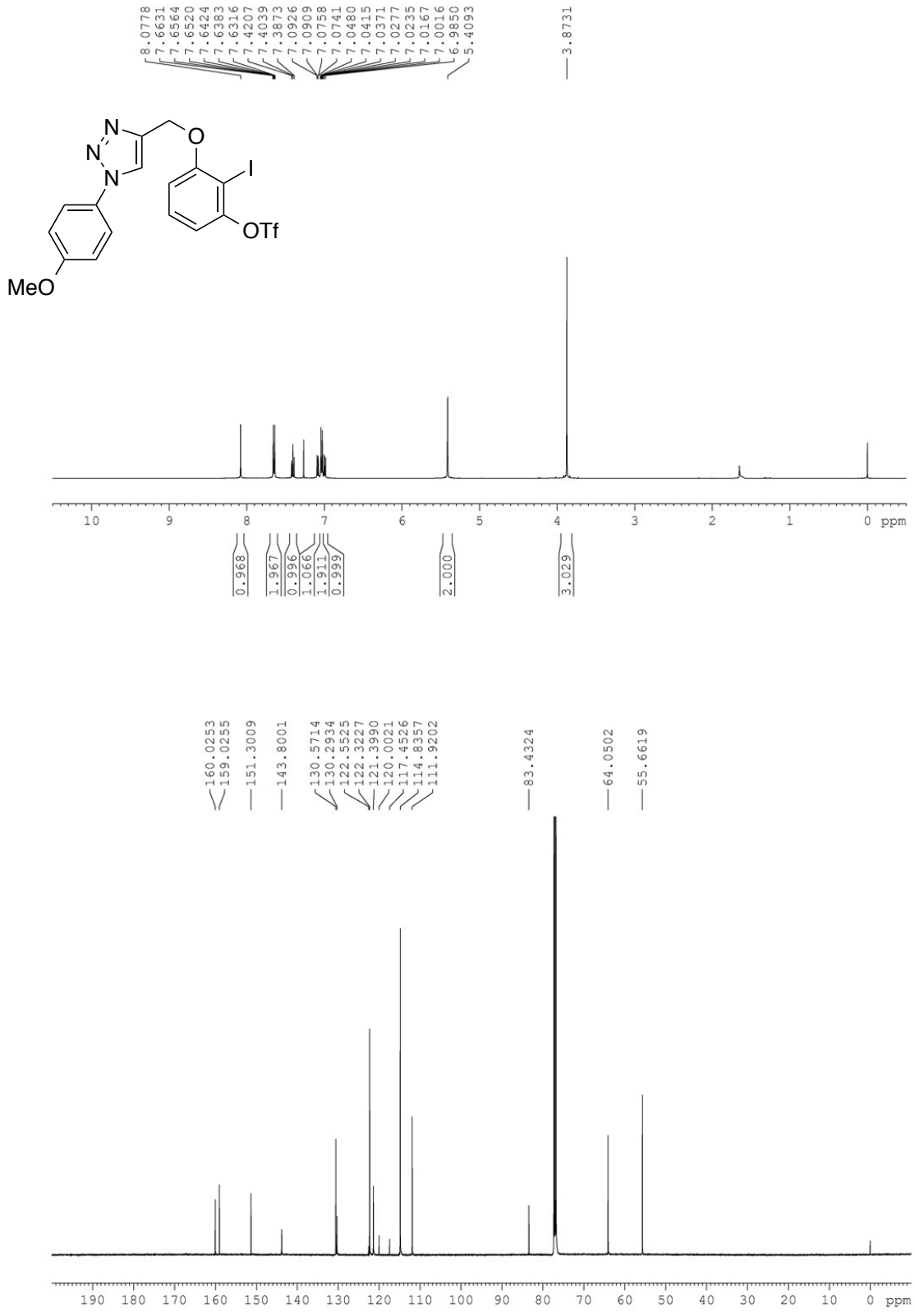


^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of **4h** ($CDCl_3$)

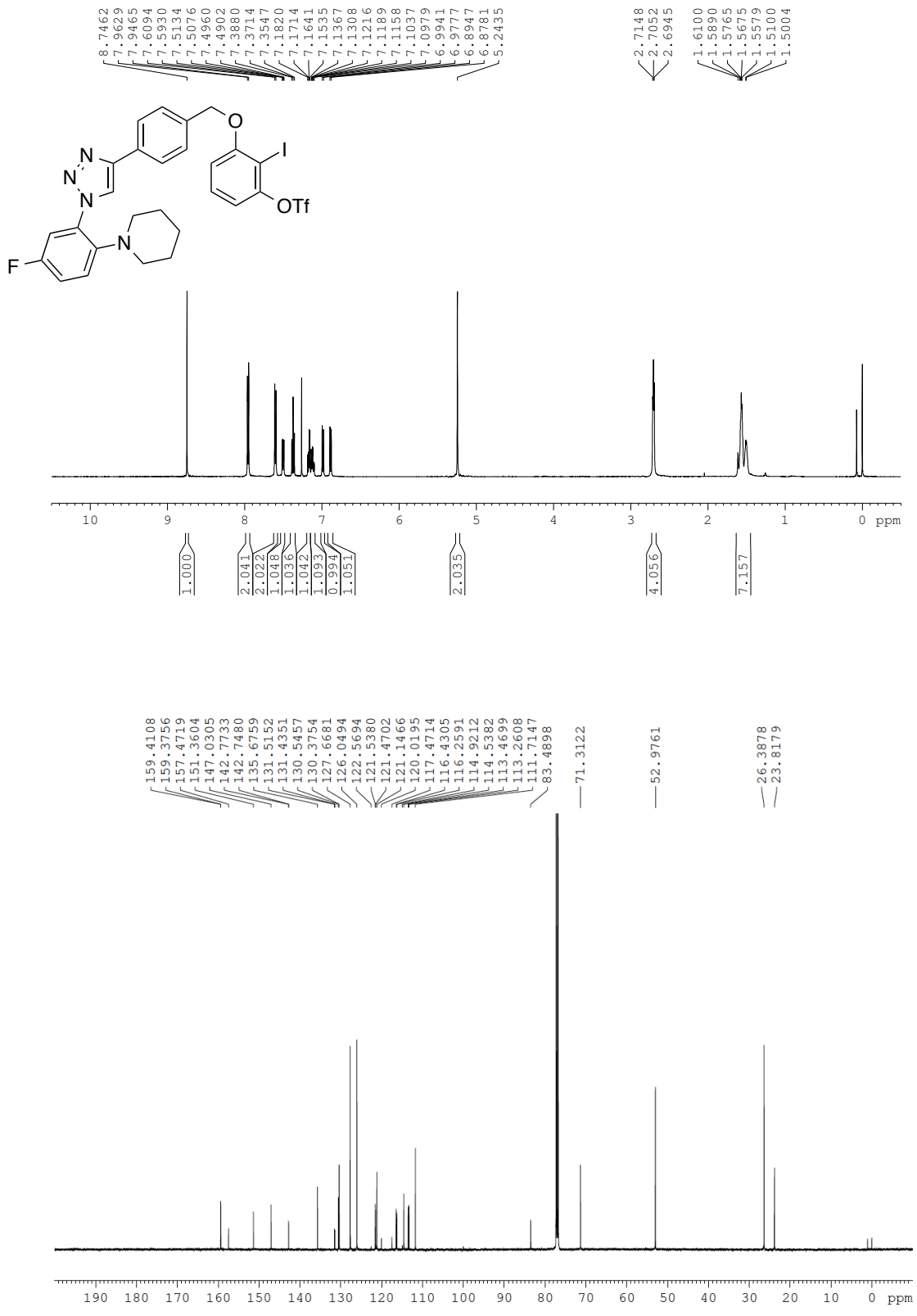




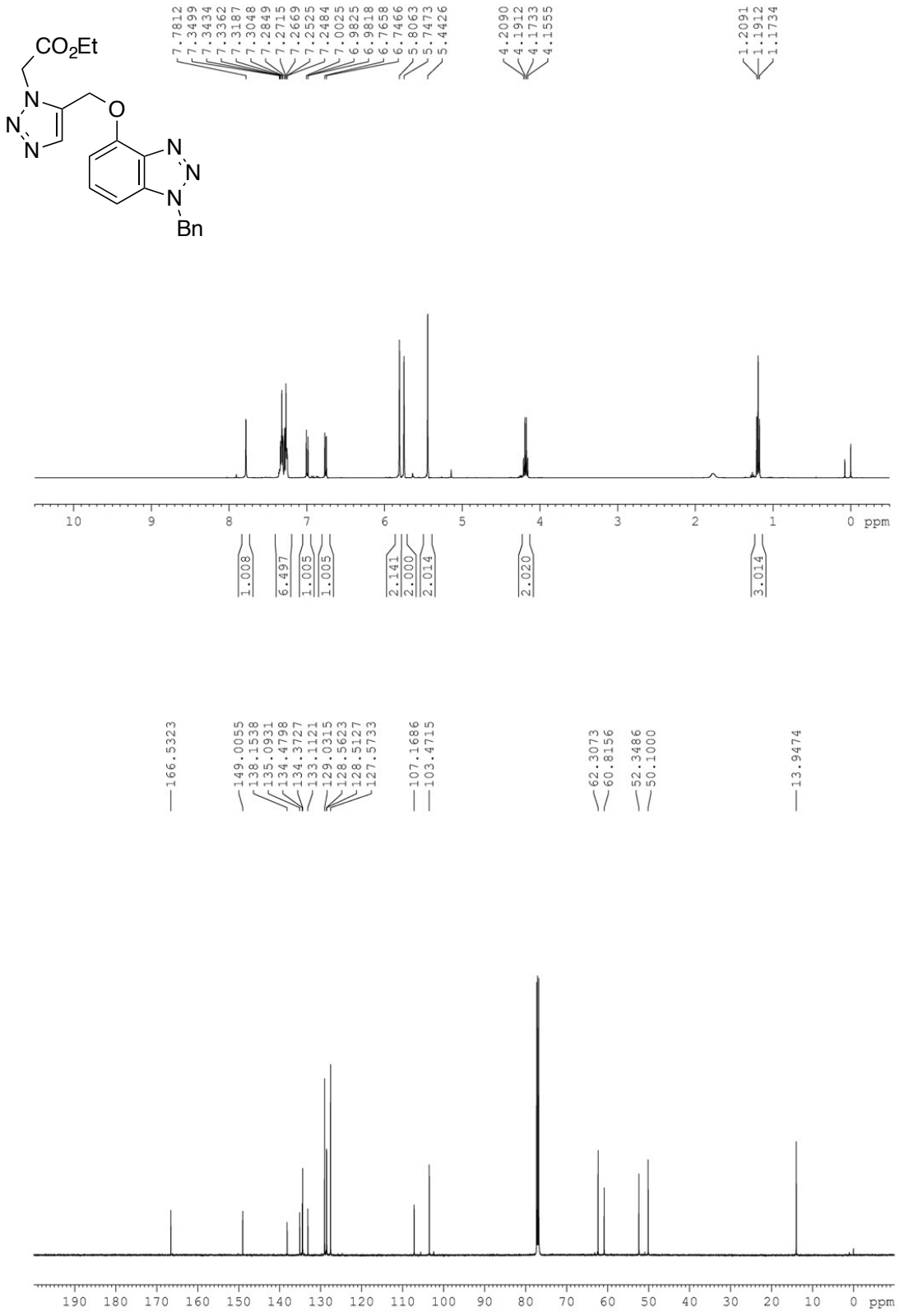
^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of **5a** ($CDCl_3$)



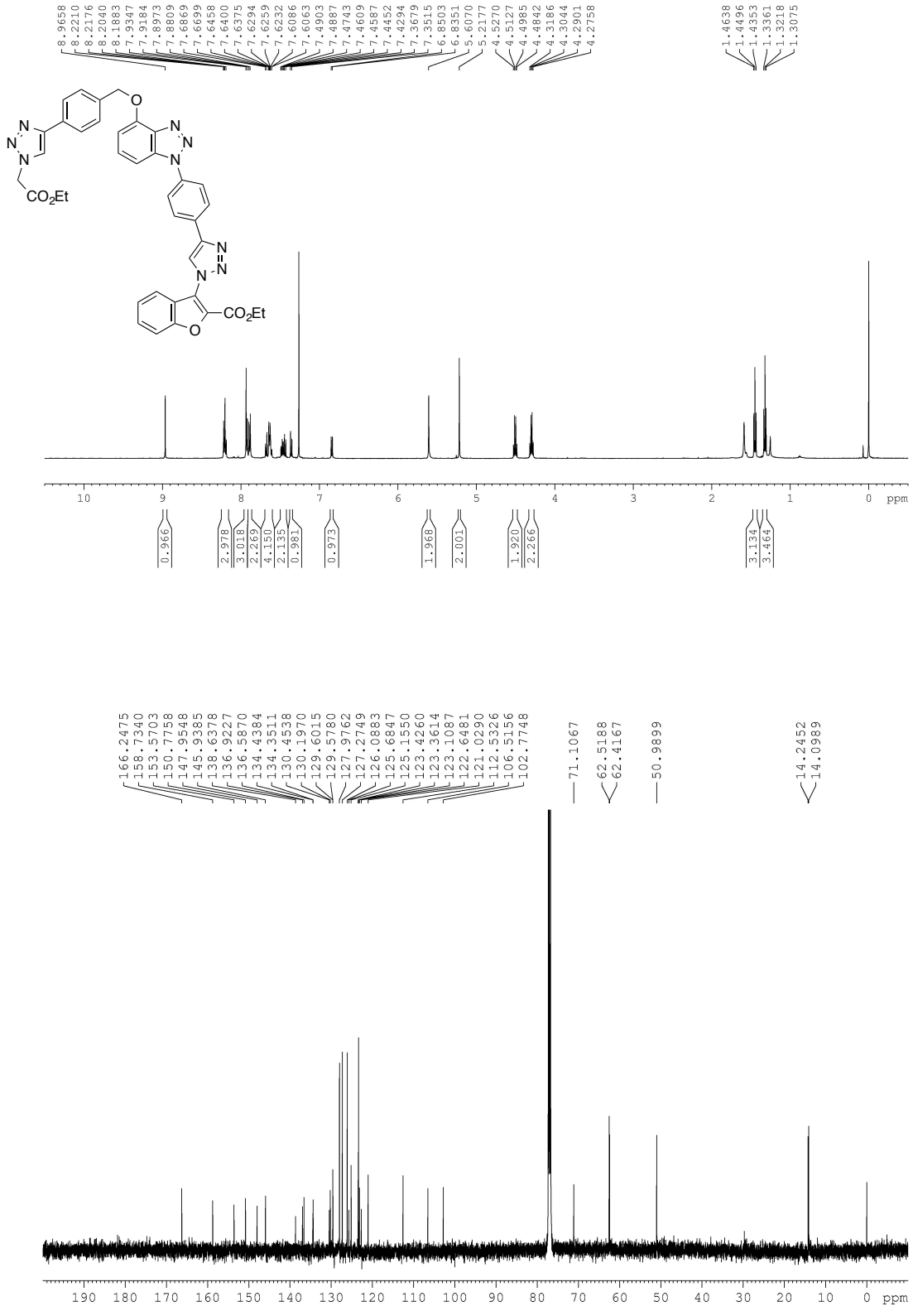
^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of **5b** ($CDCl_3$)



^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of **6a** ($CDCl_3$)



^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of **7a** ($CDCl_3$)



^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of **7b** ($CDCl_3$)