## Electronic Supplementary Information

# Azido-Type-Selective Triazole Formation by Iridium-Catalyzed Cycloaddition with Thioalkyne

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**Contents**



## General Remarks

All reactions were performed with dry glassware under argon atmosphere, unless otherwise noted. Analytical thin-layer chromatography (TLC) was performed on precoated (0.25 mm) silica-gel plates (Merck Chemicals, Silica Gel 60 F254, Cat. No. 1.05715). Column chromatography was conducted using silica-gel (Kanto Chemical Co., Inc., Silica Gel 60N, spherical neutral, particle size 40–50 μm, Cat. No. 37563-85 or particle size 63–210 μm, Cat. No. 37565-85), Florisil (Kanto Chemical Co., Inc., particle size 75–150 μm, Cat. No. 16231-08), and Biotage ZIP sphere cartridge [silica] 30 g (Cat. No. 445-3000-FZ-20), 80 g (Cat. No. 445-8000-JZ-20), 120 g (Cat. No. 445-120G-UZ-20) 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 B-5F, Cat. No. 230-00043). Melting points (Mp) were measured on a YANACO MP-J3 instrument or an OptiMelt MPA100 (Stanford Research Systems) and are uncorrected. $^{1}$H and $^{13}$C NMR spectra were obtained with a Bruker AVANCE 500 spectrometer at 500 or 126 MHz, respectively. All NMR measurements were carried out at 25 °C. $CDCl_3$ (Kanto Chemical Co., Inc., Cat. No. 07663-23) 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 in $CDCl_3$) or the solvent peak (δ 77.0 for $^{13}$C NMR in $CDCl_3$) as an internal reference with coupling constants (*J*) in hertz (Hz). The abbreviations s, d, t, sept, m, and br signify singlet, doublet, triplet, 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. High-performance liquid chromatography (HPLC) was performed on a Shimadzu Prominence HPLC system (CBM-20A lite, LC-20AD × 2, DGU-20A3R, SUS316L, and CTO-20A) equipped with a Shimadzu SPD-20A UV/Vis detector.

Unless otherwise noted, materials obtained from commercial suppliers were used without further purification. Tetrakis(acetonitrile)copper(I) tetrafluoroborate ($(MeCN)_4CuBF_4$) (Cat. No.

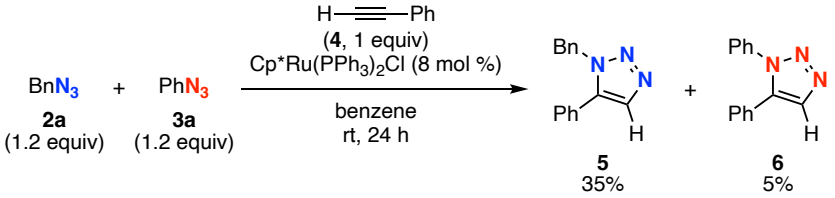
T2666), tris[(1-benzyl-1*H*-1,2,3-triazol-4-yl)methyl]amine (TBTA) (Cat. No. T2993), diethyl azodicarboxylate (DEAD) (40% in toluene, ca. 2.2 M) (Cat. No. A0705), phthalimide (Cat. No. P0402), 1-heptyne (Cat. No. H0048), propargyl alcohol (Cat. No. P0536), *N*-chlorosuccinimide (NCS) (Cat. No. C0291), 3-azidopropylamine (Cat. No. A2738), and (1*R*,8*S*,9*s*)-bicyclo[6.1.0]non-4-yn-9-ylmethanol (**25**) (Cat. No. B5467) were purchased from Tokyo Chemical Industry Co., Ltd. Benzyl azide (**2a**) (Cat. No. 355-40762), bis(1,5-cyclooctadiene)diiridium(I) dichloride ($[Ir(cod)Cl]_2$) (Cat. No. 047-31443), bis(2-methoxyethyl) azodicarboxylate (DMEAD) (Cat. No. 024-16693), triphenylphosphine ($PPh_3$) (Cat. No. 204-03061), hydrazine monohydrate ($N_2H_4 \cdot H_2O$) (Cat. No. 085-00891), 4-(dimethylamino)pyridine (DMAP) (Cat. No. 042-19212), and triethylamine ($Et_3N$) (Cat. No. 202-02646) were purchased from FUJIFILM Wako Pure Chemical Corporation. Pentamethylcyclopentadienylbis(triphenylphosphine)ruthenium(II) chloride ($Cp^*Ru(PPh_3)_2Cl$) (Cat. No. 673293), chloro(pentamethylcyclopentadienyl)(cyclooctadiene)-ruthenium(II) ($Cp^*Ru(cod)Cl$) (Cat. No. 667234), chlorodicarbonylrhodium(I) dimer ($[Rh(CO)_2Cl]_2$) (Cat. No. 209031), and 1-azidoadamantane (**2g**) (Cat. No. 276219) were purchased from Sigma-Aldrich Japan. Phenylacetylene (**4**) (Cat. No. 32228-32) and *n*-butyllithium (*n*-BuLi) (2.6 M, *n*-hexane solution, Cat. No. 04935-05) were purchased from Kanto Chemical Co., Inc. 1-(3-Dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (EDC·HCl) (Cat. No. A00007) and diphenylphosphoryl azide (DPPA) (Cat. No. A00009) were purchased from WATANABE Chemical Ind., Ltd.

3′,4-Diazido-5′-azidomethyl-3,5-diisopropyl-1,1′-biphenyl (**1**),[S1] 3-phenylpropyl azide (**2b**),[S2] 2-azido-4-phenylbutane (**2c**),[S3] 2-azido-2-methyl-4-phenylbutane (**2d**),[S4] cyclohexyl azide (**2e**),[S5] 2-azidoadamantane (**2f**),[S6] 1-(azidomethyl)adamantane (**2h**),[S7] phenyl azide (**3a**),[S8] 2-azidoanisole (**3b**),[S9] methyl 2-azidobenzoate (**3c**),[S10] 2-isopropylphenyl azide (**3d**),[S9] 2,6-diisopropylphenyl azide (**3e**),[S11] phenylethynyl *p*-tolyl sulfide (**9a**),[S12] benzyl phenylethynyl sulfide (**9b**),[S12] methyl phenylethynyl sulfide (**9c**),[S13] 3-azido-5-(azidomethyl)benzyl alcohol,[S14] 1-azido-4-(azidomethyl)-benzene (**16a**),[S15] 1-azido-3-(azidomethyl)benzene (**16b**),[S14] 1-azido-2-(azidomethyl)benzene (**16c**),[S16] 3-azido-5-(azidomethyl)phenol (**16d**),[S14] 3-azido-5-(azidomethyl)benzaldehyde (**16e**),[S14] methyl 3-azido-5-(azidomethyl)benzoate (**16f**),[S14] 1-azido-3-azidomethyl-5-bromobenzene (**16g**),[S14] 1-azido-3-azidomethyl-5-iodobenzene (**16h**),[S14] 3-azido-5-(azidomethyl)phenylacetylene (**16j**),[S17] 4-(azidomethyl)benzyl alcohol,[S18] 3-azido-1-adamantanecarboxylic acid (**S2**),[S19] 1,4-diazido-2,6-diisopropylbenzene (**18**),[S20] *S*-(4-tolyl) 4-toluenethiosulfonate,[S21] *S*-benzyl 4-toluenethio-sulfonate,[S22] and 5,6-didehydro-11,12-dihydrodibenzo[*a*,*e*]cyclooctene (**22**)[S23] were prepared according to the reported methods.

**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.**

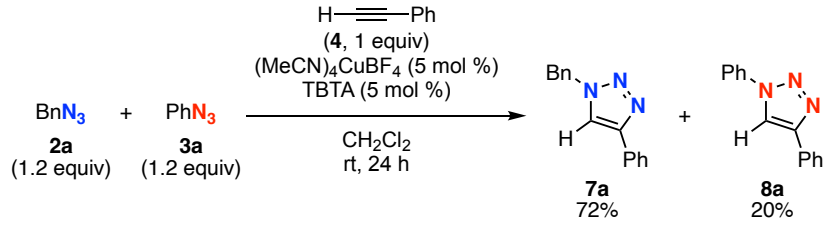
## Experimental Procedures

*A procedure for the competitive experiment using a ruthenium catalyst with terminal alkyne*



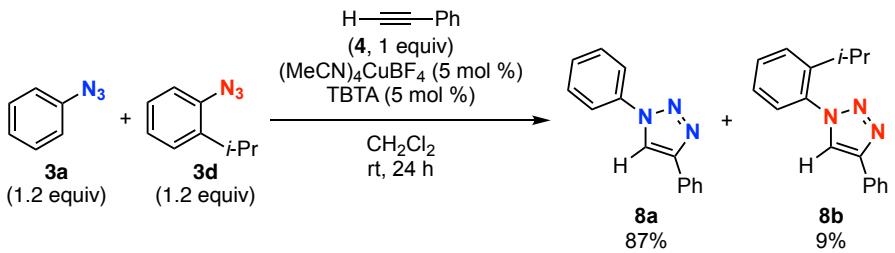

To a solution of phenylacetylene (**4**) (10.1 mg, 98.9 μmol) in benzene (1.0 mL) was added pentamethylcyclopentadienylbis(triphenylphosphine)ruthenium(II) chloride ($Cp^*Ru(PPh_3)_2Cl$) (6.4 mg, 8.0 μmol, 8 mol %) at room temperature. After stirring for 5 min at the same temperature, to the solution was added a mixture of benzyl azide (**2a**) (16.0 mg, 120 μmol, 1.21 equiv) and phenyl azide (**3a**) (14.3 mg, 120 μmol, 1.21 equiv) dissolved in benzene (1.0 mL) at room temperature. After stirring for 24 h at the same temperature, the mixture was concentrated under reduced pressure. To the residue was added 1,1,2,2-tetrachloroethane (14.2 mg, 84.7 μmol) as an internal standard, dissolved in $CDCl_3$, and $^1H$ NMR analysis (400 MHz) was performed. Yields of triazoles **5** and **6** were determined to be 35% and 5.4%, respectively, by comparing the relative values of integration for the peaks observed at 5.55 ppm (s, 2H) for **5** and 7,87 ppm (s, 1H) for **6** with that of 1,1,2,2-tetrachloroethane observed at 5.95 ppm (s, 2H).

*A typical procedure for the competitive experiment using a copper catalyst with terminal alkyne*




To a mixture of benzyl azide (**2a**) (16.0 mg, 120 μmol, 1.20 equiv), phenyl azide (**3a**) (14.3 mg, 120 μmol, 1.20 equiv), tris[(1-benzyl-1*H*-1,2,3-triazol-4-yl)methyl]amine (TBTA) (2.65 mg 4.99 μmol, 5 mol %), and tetrakis(acetonitrile)copper(I) tetrafluoroborate ($(MeCN)_4CuBF_4$) (1.57 mg, 4.99 μmol, 5 mol %) dissolved in $CH_2Cl_2$ (1.0 mL) was added phenylacetylene (**4**) (11.0 μL, 100 μmol) at room temperature. After stirring for 24 h at the same temperature, the mixture was concentrated under reduced pressure. To the residue was added 1,1,2,2-tetrachloroethane (14.4 mg, 85.8 μmol) as an internal standard, dissolved in $CDCl_3$, and $^1H$ NMR analysis (400 MHz) was performed. Yields of triazoles **7a** and **8a** were determined to be 72% and 20%, respectively, by comparing the relative values of integration for the peaks observed at 5.57 ppm (s, 2H) for **7a** and 8.20 ppm (s, 1H) for **8a** with that of 1,1,2,2-tetrachloroethane observed at 5.95 ppm (s, 2H).

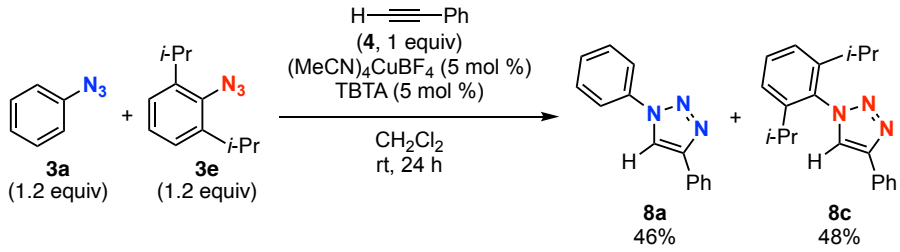
Fig . 4, Competitive reaction between **3a** and **3d** under Condition B




Yields of triazoles **8a** and **8b** were determined to be 87% and 8.6%, respectively, by comparing the relative values of integration for the peaks observed at 8.20 ppm (s, 1H) for **8a** and 2.82 ppm

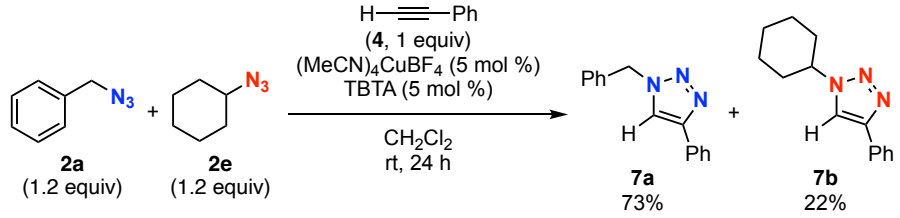
(sept, 1H, $J$ = 6.9 Hz) for **8b** with that of 1,1,2,2-tetrachloroethane observed at 5.95 ppm (s, 2H).

Fig . 4, Competitive reaction between **3a** and **3e** under Condition B



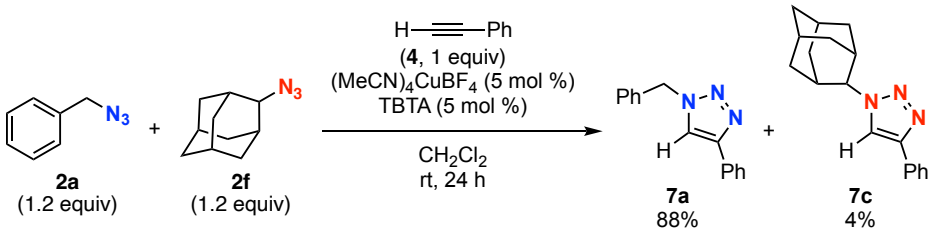

Yields of triazoles **8a** and **8c** were determined to be 46% and 48%, respectively, by comparing the relative values of integration for the peaks observed at 8.20 ppm (s, 1H) for **8a** and 7.87 ppm (s, 1H) for **8c** with that of 1,1,2,2-tetrachloroethane observed at 5.95 ppm (s, 2H).

Table 2, Entry 3, Condition B



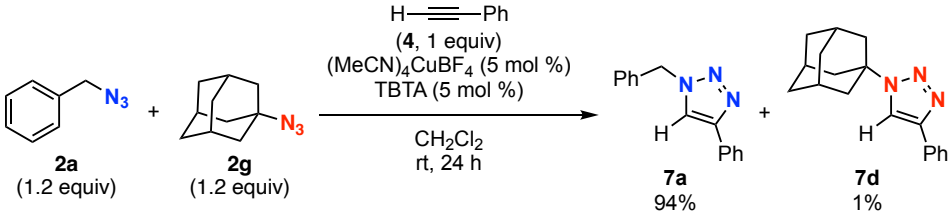

Yields of triazoles **7a** and **7b** were determined to be 73% and 22%, respectively, by comparing the relative values of integration for the peaks observed at 5.57 ppm (s, 2H) for **7a** and 4.41–4.62 ppm (br s, 1H) for **7b** with that of 1,1,2,2-tetrachloroethane observed at 5.95 ppm (s, 2H).

Table 2, Entry 4, Condition B



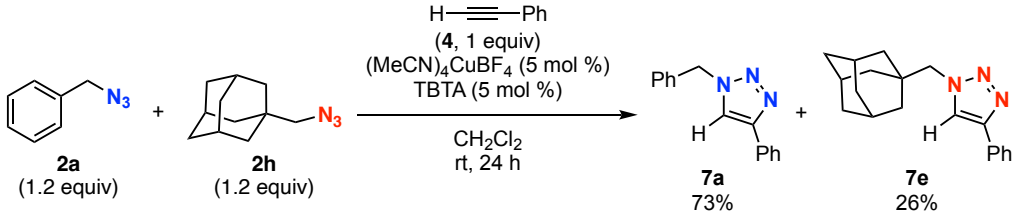

Yields of triazoles **7a** and **7c** were determined to be 88% and 3.5%, respectively, by comparing the relative values of integration for the peaks observed at 5.57 ppm (s, 2H) for **7a** and 4.51–4.56 ppm (br, 1H) for **7c** with that of 1,1,2,2-tetrachloroethane observed at 5.95 ppm (s, 2H).

Table 2, Entry 5, Condition B



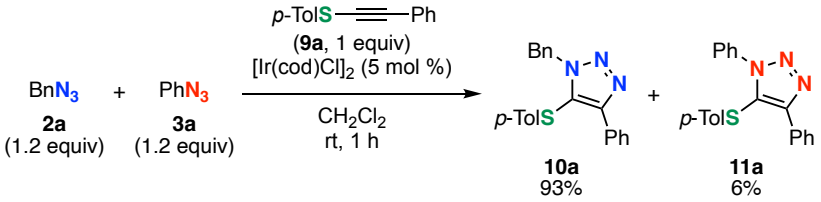

Yields of triazoles **7a** and **7d** were determined to be 94% and 1.4%, respectively, by comparing the relative values of integration for the peaks observed at 5.57 ppm (s, 2H) for **7a** and 7.83 ppm (s, 1H) for **7d** with that of 1,1,2,2-tetrachloroethane observed at 5.95 ppm (s, 2H).

Table 2, Entry 6, Condition B



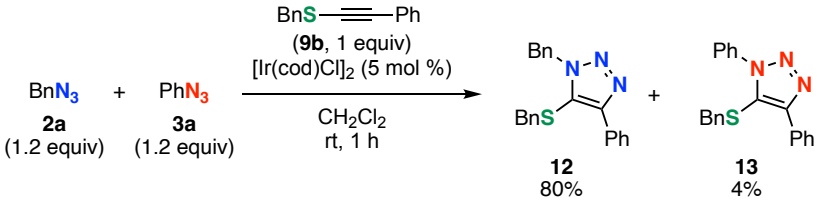

Yields of triazoles **7a** and **7e** were determined to be 73% and 26%, respectively, by comparing the relative values of integration for the peaks observed at 5.57 ppm (s, 2H) for **7a** and 4.06 ppm (s, 2H) for **7e** with that of 1,1,2,2-tetrachloroethane observed at 5.95 ppm (s, 2H).

*A typical procedure for the competitive experiment using an iridium catalyst with thioalkyne*



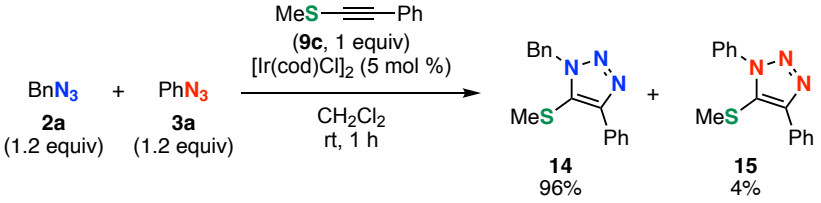

To a mixture of benzyl azide (**2a**) (16.0 mg, 120 μmol, 1.20 equiv), phenyl azide (**3a**) (14.3 mg, 120 μmol, 1.20 equiv), and bis(1,5-cyclooctadiene)diiridium(I) dichloride ([Ir(cod)Cl]$_2$) (3.41 mg, 5.08 μmol, 5 mol %) dissolved in $CH_2Cl_2$ (1.0 mL) was added phenylethynyl *p*-tolyl sulfide (**9a**) (22.4 mg, 100 μmol) at room temperature. After stirring for 1 h at the same temperature, the mixture was concentrated under reduced pressure. To the residue was added 1,1,2,2-tetrachloroethane (13.7 mg, 81.7 μmol) as an internal standard, dissolved in $CDCl_3$, and $^1$H NMR analysis (400 MHz) was performed. Yields of triazoles **10a** and **11a** were determined to be 93% and 6.4%, respectively, by comparing the relative values of integration for the peaks observed at 5.56 ppm (s, 2H) for **10a** and 8.14–8.20 ppm (m, 2H) for **11a** with that of 1,1,2,2-tetrachloroethane observed at 5.95 ppm (s, 2H).

Table 1, Entry 8



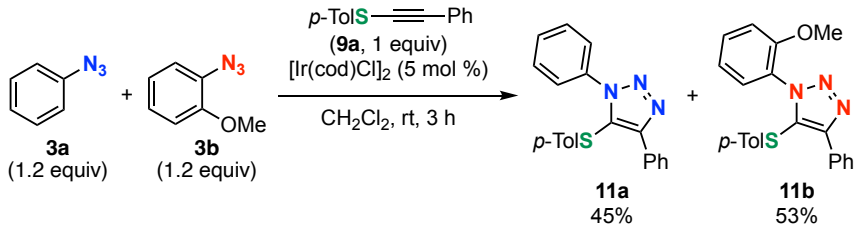

Yields of triazoles **12** and **13** were determined to be 80% and 4.4%, respectively, by comparing the relative values of integration for the peaks observed at 3.55 ppm (s, 2H) for **12** and 3.62 ppm (s, 2H) for **13** with that of 1,1,2,2-tetrachloroethane observed at 5.95 ppm (s, 2H).

Table 1, Entry 9



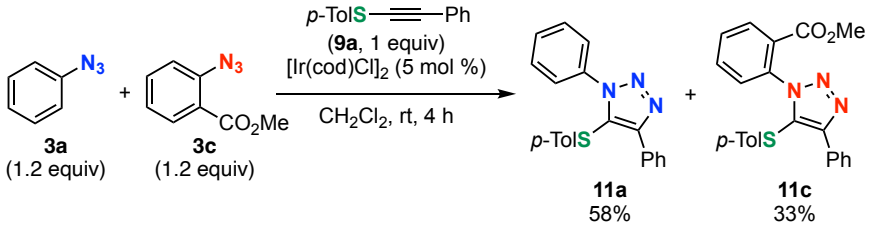

Yields of triazoles **14** and **15** were determined to be 96% and 4.1%, respectively, by comparing the relative values of integration for the peaks observed at 5.70 ppm (s, 2H) for **14** and 2.07 ppm (s, 3H) for **15** with that of 1,1,2,2-tetrachloroethane observed at 5.95 ppm (s, 2H).

Fig . 4, Competitive reaction between **3a** and **3b** under Condition A



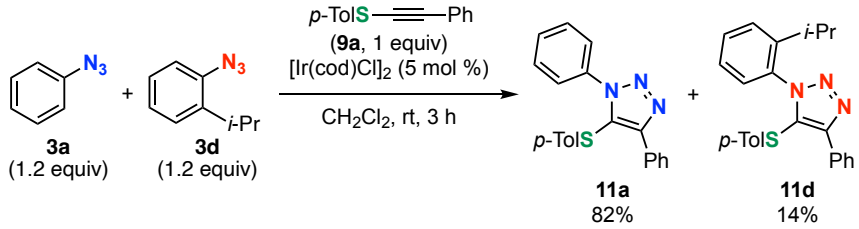

Yields of triazoles **11a** and **11b** were determined to be 45% and 53%, respectively, by comparing the relative values of integration for the peaks observed at 2.24 ppm (s, 3H) for **11a** and 2.23 ppm (s, 3H) for **11b** with that of 1,1,2,2-tetrachloroethane observed at 5.95 ppm (s, 2H).

Fig . 4, Competitive reaction between **3a** and **3c** under Condition A



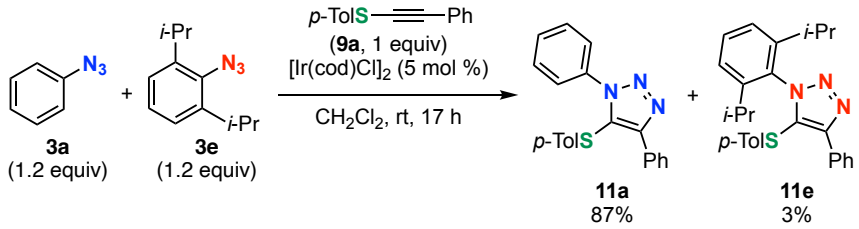

Yields of triazoles **11a** and **11c** were determined to be 58% and 33%, respectively, by comparing the relative values of integration for the peaks observed at 2.24 ppm (s, 3H) for **11a** and 2.22 ppm (s, 3H) for **11c** with that of 1,1,2,2-tetrachloroethane observed at 5.95 ppm (s, 2H).

Fig . 4, Competitive reaction between **3a** and **3d** under Condition A



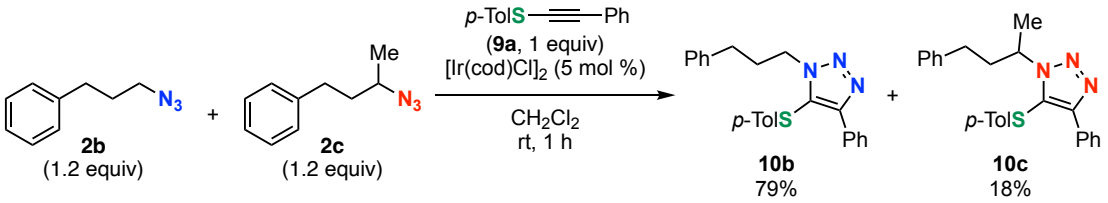

Yields of triazoles **11a** and **11d** were determined to be 82% and 14%, respectively, by comparing the relative values of integration for the peaks observed at 8.14–8.20 ppm (m, 2H) for **11a** and 8.24–8.30 ppm (m, 2H) for **11d** with that of 1,1,2,2-tetrachloroethane observed at 5.95 ppm (s, 2H).

Fig . 4, Competitive reaction between **3a** and **3e** under Condition A



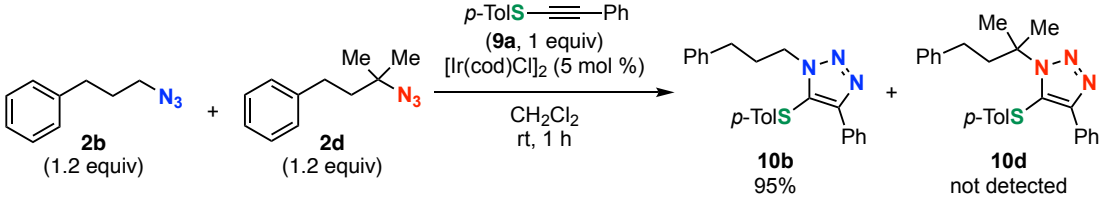

Yields of triazoles **11a** and **11e** were determined to be 87% and 2.5%, respectively, by comparing the relative values of integration for the peaks observed at 8.14–8.20 ppm (m, 2H) for **11a** and 8.32–8.38 ppm (m, 2H) for **11e** with that of 1,1,2,2-tetrachloroethane observed at 5.95 ppm (s, 2H).

Table 2, Entry 1, Condition A



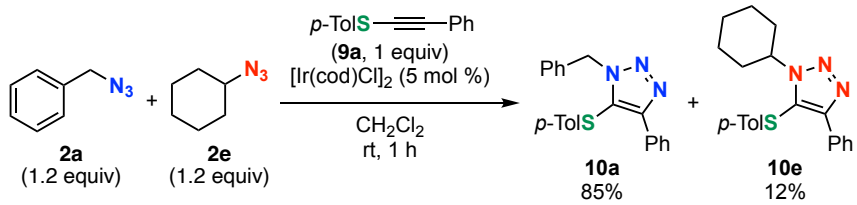

Yields of triazoles **10b** and **10c** were determined to be 79% and 18%, respectively, by comparing the relative values of integration for the peaks observed at 4.37 ppm (t, 2H, $J$ = 7.4 Hz) for **10b** and 4.75–4.90 ppm (m, 1H) for **10c** with that of 1,1,2,2-tetrachloroethane observed at 5.95 ppm (s, 2H).

Table 2, Entry2, Condition A



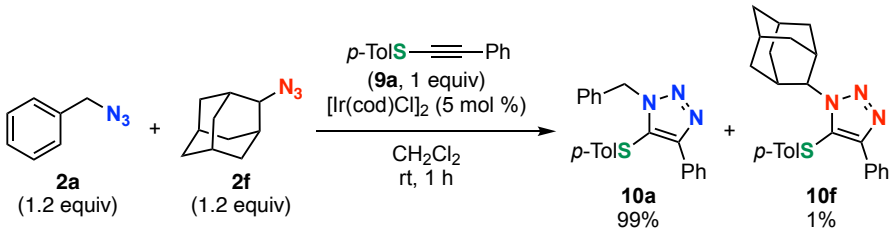

Yields of triazoles **10b** and **10d** were determined to be 95% and 0%, respectively, by comparing the relative values of integration for the peaks observed at 4.37 ppm (t, 2H, $J$ = 7.4 Hz) for **10b** with that of 1,1,2,2-tetrachloroethane observed at 5.95 ppm (s, 2H).

Table 2, Entry 3, Condition A



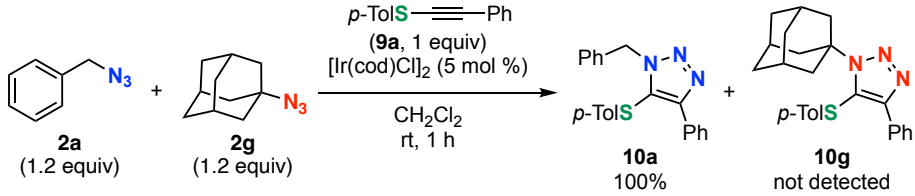

Yields of triazoles **10a** and **10e** were determined to be 85% and 12%, respectively, by comparing the relative values of integration for the peaks observed at 5.56 ppm (s, 2H) for **10a** and 4.54 ppm (tt, 1H, $J$ = 11.8, 3.6 Hz) for **10e** with that of 1,1,2,2-tetrachloroethane observed at 5.95 ppm (s, 2H).

Table 2, Entry 4, Condition A



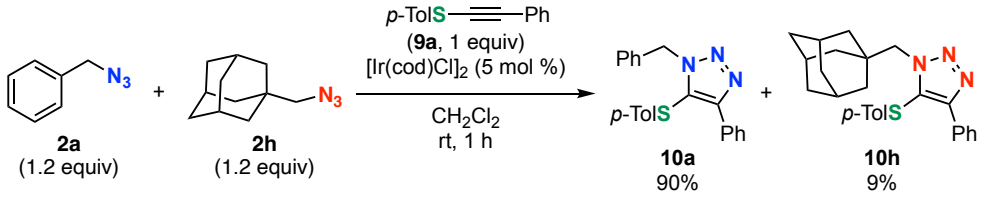

Yields of triazoles **10a** and **10f** were determined to be 99% and 0.7%, respectively, by comparing the relative values of integration for the peaks observed at 5.56 ppm (s, 2H) for **10a** and 4.79–4.87 ppm (br, 1H) for **10f** with that of 1,1,2,2-tetrachloroethane observed at 5.95 ppm (s, 2H).

Table 2, Entry 5, Condition A



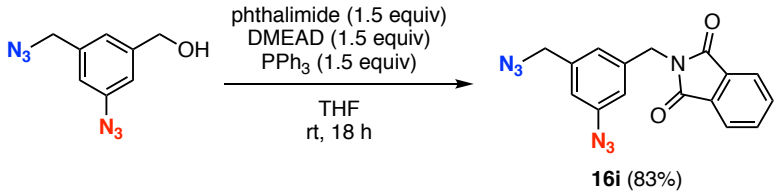

Yields of triazoles **10a** and **10g** were determined to be 100% and 0%, respectively, by comparing the relative values of integration for the peaks observed at 5.56 ppm (s, 2H) for **10a** with that of 1,1,2,2-tetrachloroethane observed at 5.95 ppm (s, 2H).

Table 2, Entry 6, Condition A



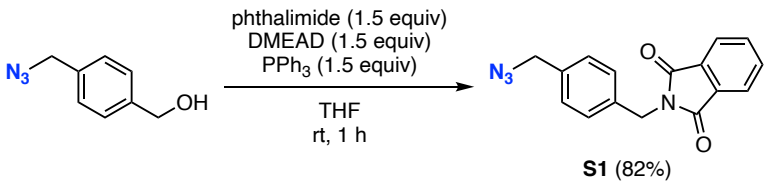

Yields of triazoles **10a** and **10h** were determined to be 90% and 9.0%, respectively, by comparing the relative values of integration for the peaks observed at 5.56 ppm (s, 2H) for **10a** and 4.10 ppm (s, 2H) for **10h** with that of 1,1,2,2-tetrachloroethane observed at 5.95 ppm (s, 2H).

*Synthesis of 2-(3-azido-5-(azidomethyl)benzyl)phthalimide (**16i**)*




To a solution of 3-azido-5-(azidomethyl)benzyl alcohol (613 mg, 3.00 mmol) in THF (15.0 mL) were added phthalimide (666 mg, 4.53 mmol, 1.51 equiv), bis(2-methoxyethyl) azodicarboxylate (DMEAD) (1.06 g, 4.52 mmol, 1.51 equiv), and triphenylphosphine ($PPh_3$) (1.18 g, 4.50 mmol, 1.50 equiv) 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 = 83/17 to 62/38) to afford 2-(3-azido-5-(azidomethyl)benzyl)phthalimide (**16i**) (833 mg, 2.50 mmol, 83%) as a pale yellow solid.

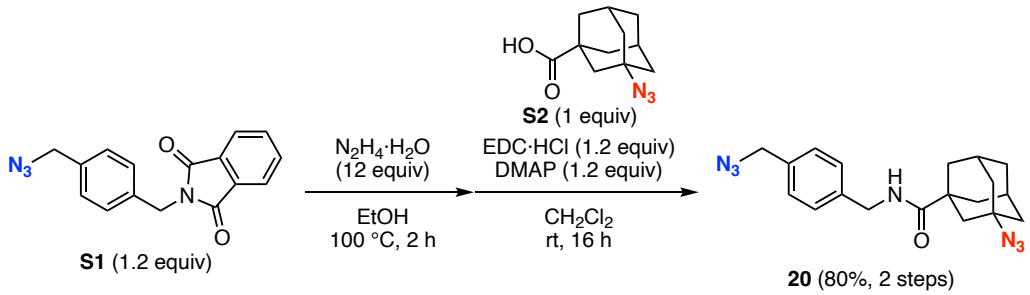
*Synthesis of 2-(4-(azidomethyl)benzyl)phthalimide (**S1**)*




To a mixture of 4-(azidomethyl)benzyl alcohol (1.63 g, 9.99 mmol), phthalimide (2.21 g, 15.0 mmol, 1.50 equiv), and bis(2-methoxyethyl) azodicarboxylate (DMEAD) (3.51 g, 15.0 mmol, 1.50 equiv) dissolved in THF (100 mL) was added triphenylphosphine ($PPh_3$) (3.93 g, 15.0 mmol, 1.50 equiv) at room temperature. After stirring for 1 h at the same temperature, the mixture was concentrated under reduced pressure. The residue was purified by flash column chromatography (Biotage ZIP-sphere cartridge 120 g, *n*-hexane/EtOAc = 86/14) to give 2-(4-

(azidomethyl)benzyl)phthalimide (**S1**) (2.38 g, 8.14 mmol, 82%) as a pale yellow solid.

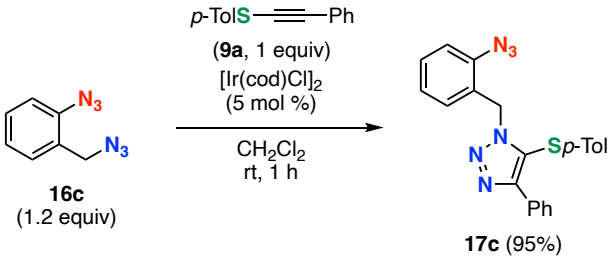
*Synthesis of 3-azido-N-(4-(azidomethyl)benzyl)-1-adamantanamide (**20**)*




To a solution of 2-(4-(azidomethyl)benzyl)phthalimide (**S1**) (1.05 g, 3.59 mmol, 1.20 equiv) in EtOH (320 mL) was added hydrazine monohydrate ($N_2H_4 \cdot H_2O$) (1.80 g, 36.0 mmol, 12.0 equiv) at room temperature. After stirring with heating at 100 °C for 2 h, the mixture was cooled to room temperature and water (100 mL) was added. The mixture was extracted with EtOAc (50 mL × 3), and the combined organic extract was washed with brine (50 mL × 3), dried ($Na_2SO_4$), and after filtration, the filtrate was concentrated under reduced pressure.

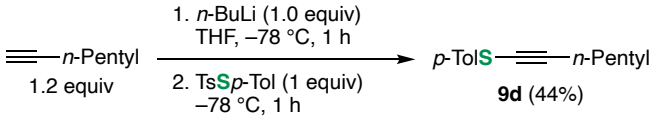
To a solution of the residue dissolved in $CH_2Cl_2$ (30 mL) were added 3-azido-1-adamantanecarboxylic acid (**S2**) (664 mg, 3.00 mmol), 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (EDC·HCl) (690 mg, 3.60 mmol, 1.20 equiv), and 4-(dimethylamino)pyridine (DMAP) (440 mg, 3.60 mmol, 1.20 equiv) at room temperature. After stirring for 16 h at the same temperature, to the mixture was added brine (30 mL). The mixture was extracted with $CH_2Cl_2$ (5 mL × 3), and the combined extract was 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, *n*-hexane/EtOAc = 75/25) to give 3-azido-*N*-(4-(azidomethyl)-benzyl)-1-adamantanamide (**20**) (879 mg, 2.40 mmol, 80% in two steps) as a pale yellow solid.

*A typical procedure for the azido-type-selective iridium-catalyzed triazole formation*



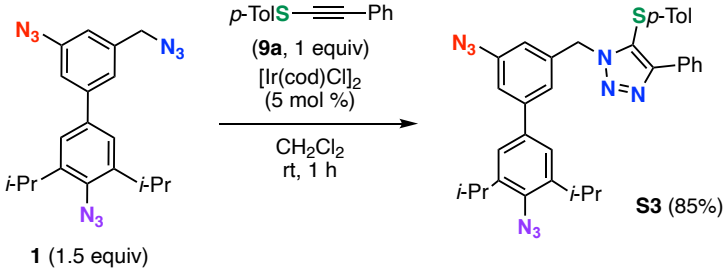

To a mixture of 1-azido-2-(azidomethyl)benzene (**16c**) (42.2 mg, 243 μmol, 1.21 equiv) and bis(1,5-cyclooctadiene)diiridium(I) dichloride ($[Ir(cod)Cl]_2$) (6.7 mg, 10 μmol, 5 mol %) dissolved in $CH_2Cl_2$ (1.0 mL) was added phenylethynyl *p*-tolyl sulfide (**9a**) (44.9 mg, 200 μmol) at room temperature. After stirring for 1 h at the same temperature, the mixture was concentrated under reduced pressure. The residue was purified by preparative TLC (*n*-hexane/EtOAc = 4/1) to give 1-(2-azidobenzyl)-4-phenyl-5-(*p*-tolylthio)-1*H*-1,2,3-triazole (**17c**) (75.6 mg, 190 μmol, 95%) as a brown solid.

*Synthesis of 1-heptyn-1-yl p-tolyl sulfide (**9d**)*



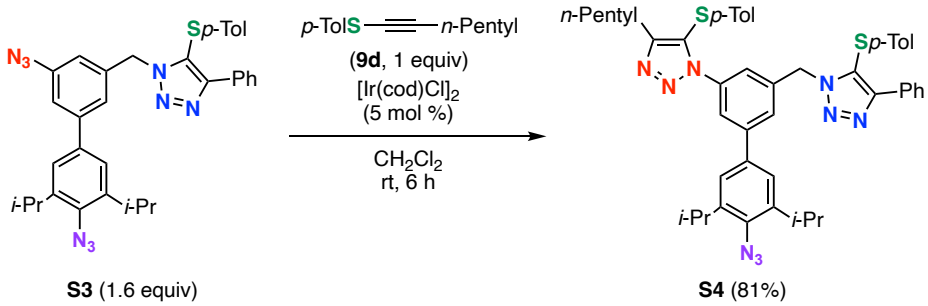

To a solution of 1-heptyne (135 mg, 1.40 mmol, 1.18 equiv) in THF (1.0 mL) was added *n*-BuLi (2.6 M in hexane, 462 µL, 1.20 mmol, 1.01 equiv) at −78 °C. After stirred for 1 h at the same temperature, to the mixture was added a solution of *S*-(4-tolyl) 4-toluenethiosulfonate (TS*p*-Tol) (330 mg, 1.19 mmol) dissolved in THF (20 mL). After stirring for 1 h at the same temperature, to the mixture was added $NaHCO_3$ (40 mL). The mixture was extracted with EtOAc (20 mL × 3), and the combined organic extract was washed with brine (20 mL), dried ($Na_2SO_4$), and after filtration, the filtrate was concentrated under reduced pressure. The residue was purified by column chromatography (silica-gel 10 g, *n*-hexane/EtOAc = 99/1) to give 1-heptyn-1-yl *p*-toly sulfide (**9d**) (115 mg, 527 µmol, 44%) as a colorless oil.

*Synthesis of mono(triazole) **S3***



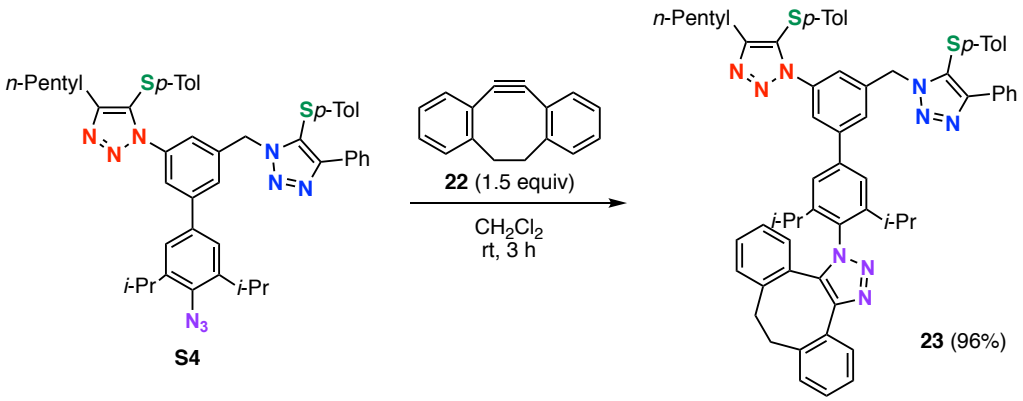

To a mixture of 3′,4-diazido-5′-azidomethyl-3,5-diisopropyl-1,1′-biphenyl (**1**) (113 mg, 300 µmol, 1.50 equiv) and bis(1,5-cyclooctadiene)diiridium(I) dichloride ($[Ir(cod)Cl]_2$) (6.7 mg, 10 µmol, 5 mol %) dissolved in $CH_2Cl_2$ (1.0 mL) was added phenylethynyl *p*-tolyl sulfide (**9a**) (44.8 mg, 200 µmol) at room temperature. After stirring for 1 h at the same temperature, the mixture was concentrated under reduced pressure. The residue was purified by preparative TLC (*n*-hexane/EtOAc = 4/1) to give mono(triazole) **S3** (101 mg, 169 µmol, 85%) as a brown oil.

*Synthesis of bis(triazole) **S4***



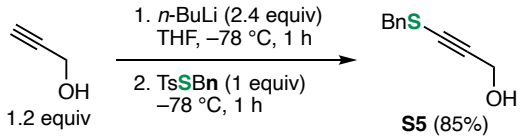

To a mixture of mono(triazole) **S3** (35.9 mg, 59.9 µmol, 1.61 equiv) and bis(1,5-cyclooctadiene)diiridium(I) dichloride ($[Ir(cod)Cl]_2$) (1.34 mg, 2.00 µmol, 5 mol %) dissolved in $CH_2Cl_2$ (1.0 mL) was added a 1-heptyn-1-yl *p*-toly sulfide (**9d**) (8.14 mg, 37.3 µmol) at room temperature. After stirring for 6 h at the same temperature, to the mixture was concentrated under reduced pressure. The residue was purified by preparative TLC (*n*-hexane/EtOAc = 4/1) to give bis(triazole) **S4** (24.6 mg, 30.1 µmol, 81%) as a brown oil.

*Synthesis of tris(triazole)* ***23***



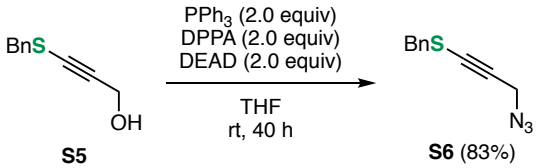

To a solution of bis(triazole) **S4** (11.0 mg, 13.5 μmol) in $CH_2Cl_2$ (1.0 mL) was added 5,6-didehydro-11,12-dihydrodibenzo[*a,e*]cyclooctene (**22**) (4.18 mg, 20.5 μmol, 1.52 equiv) at room temperature. After stirring for 3 h at the same temperature, the mixture was concentrated under reduced pressure. The residue was purified by preparative TLC (*n*-hexane/EtOAc = 1/2) to give tris(triazole) (**23**) (13.2 mg, 12.9 μmol, 96%) as a colorless oil.

*Synthesis of 3-benzylthio-2-propyn-1-ol (**S5**)*



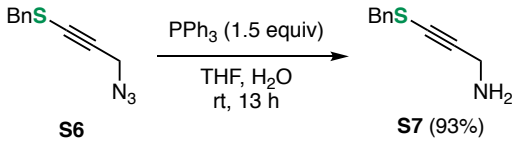

To a solution of propargyl alcohol (1.37 g, 24.4 mmol, 1.22 equiv) in THF (20.0 mL) was added *n*-BuLi (2.6 M in hexane, 18.8 mL, 48.8 mmol, 2.44 equiv) at −78 °C. After stirred for 1 h at the same temperature, to the mixture was added *S*-benzyl 4-toluenethiosulfonate (5.56 g, 20.0 mmol) dissolved in THF (20 mL). After stirring for 1 h at the same temperature, to the mixture was added $NaHCO_3$ (40 mL). The mixture was extracted with EtOAc (20 mL ×3) and the combined organic extract was washed with brine (20 mL), dried ($Na_2SO_4$), and after filtration, the filtrate was concentrated under reduced pressure. The residue was purified by column chromatography (Florisil, 150 g, *n*-hexane/EtOAc = 8/1) to give 3-benzylthio-2-propyn-1-ol (**S5**) (3.04 g, 17.1 mmol, 85%) as pale yellow oil.

*Synthesis of 3-benzylthio-2-propyn-1-yl azide (**S6**)*




To a mixture of 3-benzylthio-2-propyn-1-ol (**S5**) (540 mg, 3.03 mmol), triphenylphosphine ($PPh_3$) (1.57 g, 5.99 mmol, 1.98 equiv), and diethyl azodicarboxylate (DEAD) (2.2 M in toluene, 2.73 mL, 6.01 mmol, 1.98 equiv) dissolved in THF (30.0 mL) was added diphenylphosphoryl azide (DPPA) (1.66 g, 6.05 mmol, 2.00 equiv) at room temperature. After stirring for 40 h at the same temperature, to the mixture was added water (30 mL). 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 flash column chromatography (silica-gel 120 g, *n*-hexane/EtOAc = 8/1) to give 3-benzylthio-2-propyn-1-yl azide (**S6**) (513 mg, 2.52 mmol, 83%) as a colorless oil.

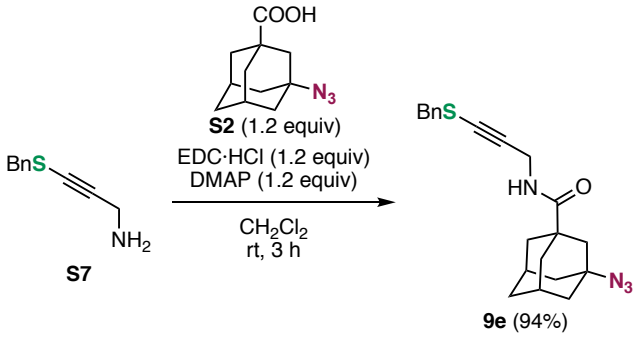
*Synthesis of 3-benzylthio-2-propyn-1-ylamine (**S7**)*




**S6** **S7** (93%)

To a solution of 3-benzylthio-2-propyn-1-yl azide (**S6**) (204 mg, 1.00 mmol) in THF (3.0 mL) were added $H_2O$ (0.30 mL) and triphenylphosphine ($PPh_3$) (393 mg, 1.50 mmol, 1.50 equiv) at room temperature. After stirring for 13 h at the same temperature, the mixture was concentrated under reduced pressure. The residue was purified by flash column chromatography (silica-gel 9 g, EtOAc) to give 3-benzylthio-2-propyn-1-ylamine (**S7**) (166 mg, 933 μmol, 93%) as a colorless oil.

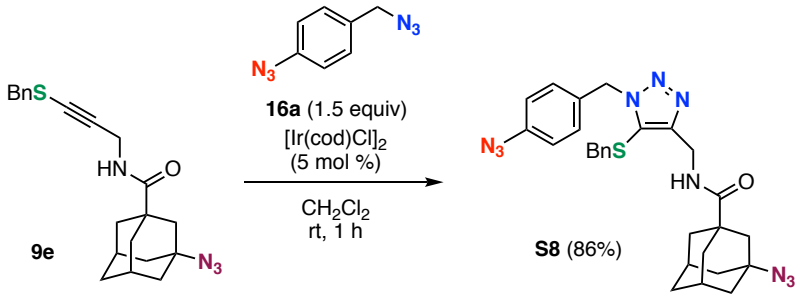
*Synthesis of 3-azido-N-(3-benzylthio-2-propyn-1-yl)-1-adamantanamide (**9e**)*




**S7** **9e** (94%)

To a mixture of 3-benzylthio-2-propyn-1-ylamine (**S7**) (166 mg, 933 μmol), 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (EDC·HCl) (215 mg, 1.12 mmol, 1.20 equiv), and 4-(dimethylamino)pyridine (DMAP) (138 mg, 1.13 mmol, 1.21 equiv) dissolved in $CH_2Cl_2$ (20 mL) was added 3-azido-1-adamantanecarboxylic acid (**S2**) (247 mg, 1.12 mmol, 1.20 equiv) at room temperature. After stirring for 3 h at the same temperature, the mixture was concentrated under reduced pressure. The residue was purified by flash column chromatography (silica-gel 16 g, *n*-hexane/EtOAc = 1/1) to give 3-azido-*N*-(3-benzylthio-2-propyn-1-yl)-1-adamantanamide (**9e**) (334 mg, 877 μmol, 94%) as a colorless solid.

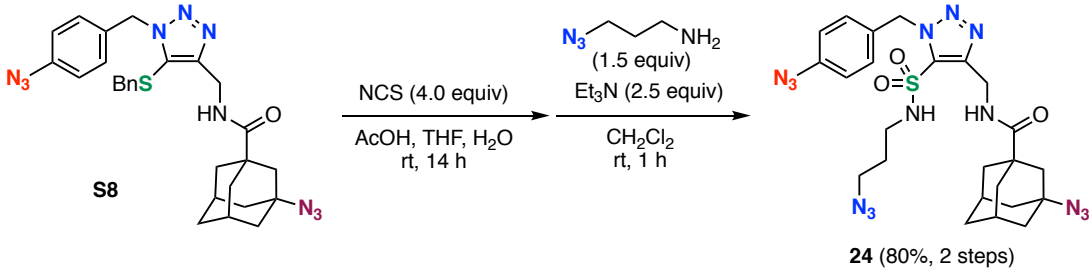
*Synthesis of 3-azido-N-((1-(4-azidobenzyl)-5-benzylthio-1H-1,2,3-triazol-4-yl)methyl)-1-adamantanamide (**S8**)*




**9e** **S8** (86%)

To a mixture of 1-azido-4-(azidomethyl)benzene (**16a**) (105 mg, 600 μmol, 1.50 equiv) and 3-azido-*N*-(3-benzylthio-2-propyn-1-yl)-1-adamantanamide (**9e**) (152 mg, 400 μmol) dissolved in $CH_2Cl_2$ (4.0 mL) was added bis(1,5-cyclooctadiene)diiridium(I) dichloride ($[Ir(cod)Cl]_2$) (13.4 mg, 19.9 μmol, 5 mol %) at room temperature. After stirring for 1 h at the same temperature, the mixture was concentrated under reduced pressure. The residue was purified by flash column chromatography (silica-gel 10 g, *n*-hexane/EtOAc = 3/2) to give 3-azido-*N*-((1-(4-azidobenzyl)-5-benzylthio-1*H*-1,2,3-triazol-4-yl)methyl)-1-adamantanamide (**S8**) (190 mg, 344 μmol, 86%) as a colorless solid.

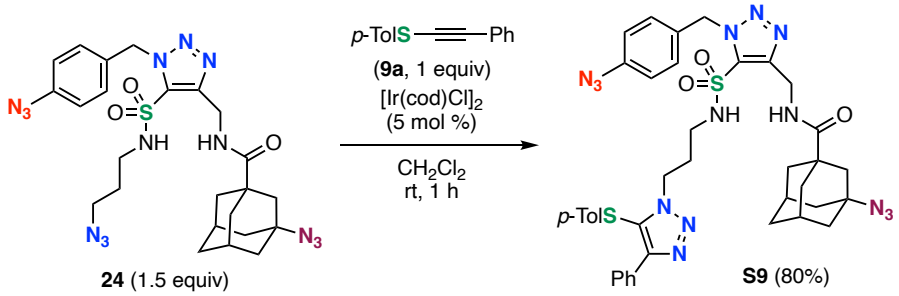
*Synthesis of 3-azido-N-((1-(4-azidobenzyl)-5-(N-(3-azidopropyl)sulfamoyl)-1H-1,2,3-triazol-4-yl)methyl)-1-adamantanamide (**24**)*




To a solution of 3-azido-*N*-((1-(4-azidobenzyl)-5-benzylthio-1*H*-1,2,3-triazol-4-yl)methyl)-1-adamantanamide (**S8**) (139 mg, 250 μmol) in THF (1.0 mL) were added AcOH (5.0 mL), $H_2O$ (1.0 mL), and *N*-chlorosuccinimide (NCS) (134 mg, 1.00 mmol, 4.00 equiv) at room temperature. After stirring for 14 h at the same temperature, to the mixture was added water (20 mL). The mixture was extracted with EtOAc (20 mL × 3) and the combined organic extract was washed with brine (20 mL), dried ($Na_2SO_4$), and after filtration, the filtrate was concentrated under reduced pressure.

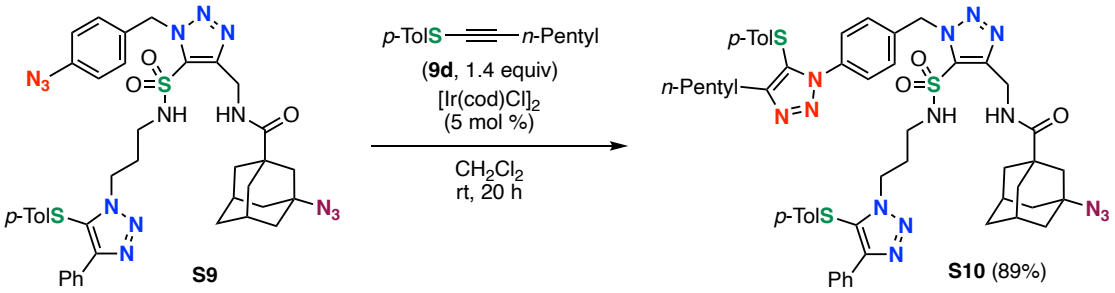
To a solution of the residue dissolved in $CH_2Cl_2$ (5.0 mL) were added triethylamine ($Et_3N$) (87.1 μL, 625 μmol, 2.50 equiv) and 3-azidopropylamine (36.8 μL, 375 μmol, 1.50 equiv) at room temperature. After stirring for 1 h at the same temperature, to the mixture was added water (20 mL). The mixture was extracted with EtOAc (20 mL × 3) and the combined organic extract was washed with brine (20 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 12 g, *n*-hexane/EtOAc = 3/2) to give 3-azido-*N*-((1-(4-azidobenzyl)-5-(*N*-(3-azidopropyl)sulfamoyl)-1*H*-1,2,3-triazol-4-yl)methyl)-1-adamantanamide (**24**) (119 mg, 200 μmol, 80% in two steps) as a colorless oil.

*Synthesis of bis(triazole) **S9***



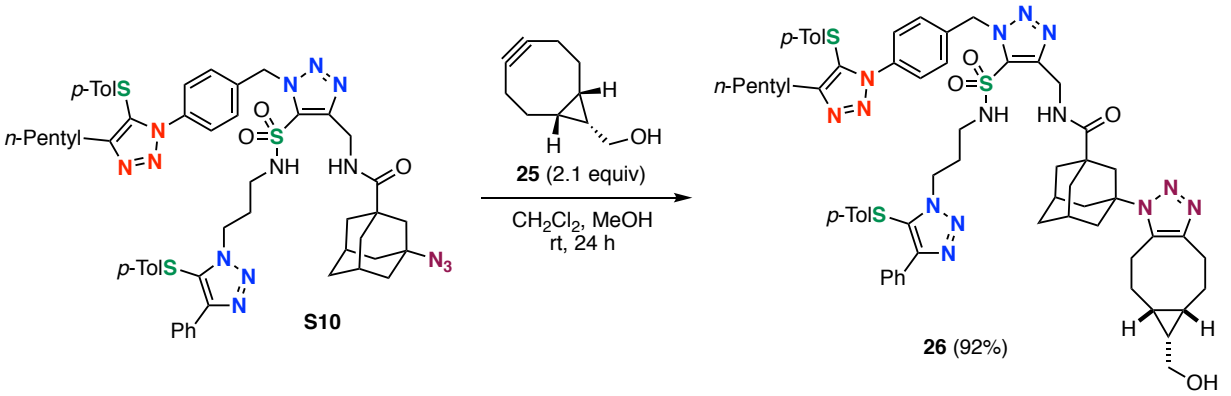

To a mixture of triazide **24** (72.3 mg, 122 μmol, 1.50 equiv) and phenylethynyl *p*-tolyl sulfide (**9a**) (18.2 mg, 81.1 μmol) dissolved in $CH_2Cl_2$ (1.0 mL) was added bis(1,5-cyclooctadiene)diiridium(I) dichloride ($[Ir(cod)Cl]_2$) (2.72 mg, 4.06 μmol, 5 mol %) at room temperature. After stirring for 1 h at the same temperature, the mixture was concentrated under reduced pressure. The residue was purified by preparative TLC (*n*-hexane/EtOAc = 1/1) to give bis(triazole) **S9** (52.4 mg, 64.0 μmol, 80%) as a pale yellow oil.

*Synthesis of tris(triazole)* ***S10***




To a mixture of bis(triazole) **S9** (28.7 mg, 35.0 mmol) and 1-heptyn-1-yl *p*-toly sulfide (**9d**) (10.8 mg, 49.4 mmol, 1.41 equiv) dissolved in $CH_2Cl_2$ (0.50 mL) was added bis(1,5-cyclooctadiene)diiridium(I) dichloride ([Ir(cod)Cl]$_2$) (1.18 mg, 1.76 μmol, 5 mol %) at room temperature. After stirring for 20 h at the same temperature, the mixture was concentrated under reduced pressure. The residue was purified by preparative TLC (*n*-hexane/EtOAc = 4/5) to give tris(triazole) **S10** (32.3 mg, 30.9 μmol, 89%) as a colorless solid.

*Synthesis of tetrakis(triazole)* ***26***

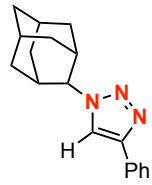



To a solution of tris(triazole) **S10** (10.7 mg, 10.3 μmol) in $CH_2Cl_2$ (0.50 mL) and MeOH (0.50 mL) was added (1*R*,8*S*,9*s*)-bicyclo[6.1.0]non-4-yn-9-ylmethanol (**25**) (3.20 mg, 21.3 μmol, 2.07 equiv) at the room temperature. After stirring for 24 h at the same temperature, the mixture was concentrated under reduced pressure. The residue was purified by preparative TLC ($CH_2Cl_2$/MeOH = 20/1) to give tetrakis(triazole) **26** (11.2 mg, 9.39 μmol, 92%) as a colorless solid.

**Characterization Data of New Compounds**

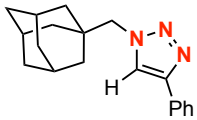
5-Phenyl-1-phenylmethyl-1*H*-1,2,3-triazole (**5**),[S24] 1,5-diphenyl-1*H*-1,2,3-triazole (**6**),[S25] 4-phenyl-1-phenylmethyl-1*H*-1,2,3-triazole (**7a**),[S26] 1-cyclohexyl-4-phenyl-1*H*-1,2,3-triazole (**7b**),[S27] 1-(1-adamantyl)-4-phenyl-1*H*-1,2,3-triazole (**7d**),[S28] 1,4-diphenyl-1*H*-1,2,3-triazole (**8a**),[S29] 1-(2-isopropylphenyl)-4-phenyl-1*H*-1,2,3-triazole (**8b**),[S30] and 1-(2,6-diisopropylphenyl)-4-phenyl-1*H*-1,2,3-triazole (**8c**)[S31] were identical in spectra data with those reported.

1-(2-Adamantyl)-4-phenyl-1*H*-1,2,3-triazole (**7c**)



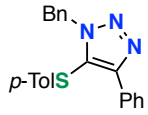
Colorless solid; Mp 163–164 °C; TLC $R_f$ 0.72 (*n*-hexane/EtOAc = 4/1); $^1$H NMR ($CDCl_3$, 500 MHz): δ 1.67–1.73 (m, 2H), 1.80–1.84 (br, 2H), 1.85–1.89 (m, 1H), 1.90–1.95 (m, 2H), 1.96–2.01 (m, 2H), 2.02–2.11 (m, 3H), 2.76–2.82 (br, 2H), 4.51–4.56 (br, 1H), 7.29–7.35 (m, 1H), 7.39–7.45 (m, 2H), 7.83–7.88 (m, 3H); $^{13}$C NMR ($CDCl_3$, 126 MHz): δ 26.9 (1C), 27.2 (1C), 31.3 (2C), 31.6 (2C), 37.1 (2C), 37.3 (1C), 64.7 (1C), 118.2 (1C), 125.6 (2C), 127.9 (1C), 128.8 (2C), 131.0 (1C), 147.0 (1C); IR (KBr, cm$^{-1}$) 762, 1072, 1229, 1366, 1450, 2853, 2916, 3132; HRMS (ESI$^+$) *m/z* 280.1808 ([M+H]$^+$, $C_{18}H_{22}N_3^+$ requires 280.1808).

1-(1-Adamantylmethyl)-4-phenyl-1*H*-1,2,3-triazole (**7e**)



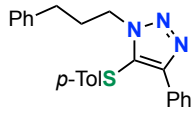
Colorless solid; Mp 171–173 °C; TLC $R_f$ 0.48 ($CH_2CH_2$/EtOAc = 30/1); $^1$H NMR ($CDCl_3$, 500 MHz) δ 1.50–1.62 (m, 9H), 1.67–1.75 (m, 3H), 1.95–2.04 (br, 3H), 4.06 (s, 2H), 7.29–7.35 (m, 1H), 7.38–7.45 (m, 2H), 7.67 (s, 1H), 7.82–7.88 (m, 2H); $^{13}$C NMR ($CDCl_3$, 126 MHz) δ 28.1 (3C), 34.2 (1C), 36.5 (3C), 40.3 (3C), 62.3 (1C), 120.9 (1C), 125.7 (2C), 128.0 (1C), 128.8 (2C), 130.8 (1C), 147.1 (1C); IR (KBr, cm$^{-1}$) 764, 1076, 1225, 1350, 1452, 1483, 2847, 2903; HRMS (ESI$^+$) *m/z* 294.1965 ([M+H]$^+$, $C_{19}H_{24}N_3^+$ requires 294.1965).

1-Benzyl-4-phenyl-5-(*p*-tolylthio)-1*H*-1,2,3-triazole (**10a**)



Pale yellow solid; Mp 105–107 °C; TLC $R_f$ 0.52 (*n*-hexane/EtOAc = 4/1); $^1$H NMR ($CDCl_3$, 500 MHz) δ 2.24 (s, 3H), 5.56 (s, 2H), 6.76–6.82 (m, 2H), 6.92–6.97 (m, 2H), 7.19–7.24 (m, 5H), 7.31–7.36 (m, 1H), 7.37–7.42 (m, 2H), 8.06–8.11 (m, 2H); $^{13}$C NMR ($CDCl_3$, 126 MHz) δ 20.9 (1C), 52.3 (1C), 123.1 (1C), 126.9 (2C), 127.1 (2C), 128.0 (2C), 128.2 (1C), 128.56 (2C), 128.65 (1C), 128.67 (2C), 129.9 (1C), 130.21 (1C), 130.23 (2C), 134.6 (1C), 136.8 (1C), 150.5 (1C); IR (KBr, cm$^{-1}$) 1219, 1342, 1433, 1491, 1605, 2920, 3032, 3062; HRMS (ESI$^+$) *m/z* 358.1366 ([M+H]$^+$, $C_{22}H_{20}N_3S^+$ requires 358.1372).

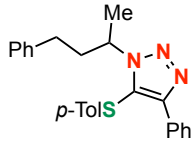
4-Phenyl-1-(3-phenylpropyl)-5-(*p*-tolylthio)-1*H*-1,2,3-triazole (**10b**)



Colorless solid; Mp 77–79 °C; TLC $R_f$ 0.65 (*n*-hexane/EtOAc = 4/1); $^1$H NMR ($CDCl_3$, 500 MHz) δ 2.13 (tt, 2H, *J* = 7.4, 7.4 Hz), 2.26 (s, 3H), 2.62 (t, 2H, *J* = 7.4 Hz), 4.37 (t, 2H, *J* = 7.4 Hz), 6.83–6.91 (m, 2H), 6.98–7.05 (m, 2H), 7.06–7.12 (m, 2H), 7.14–7.21 (m, 1H), 7.22–7.29 (m, 2H), 7.32–

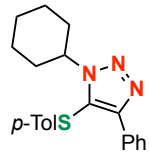
7.37 (m, 1H), 7.38–7.45 (m, 2H), 8.07–8.15 (m, 2H); $^{13}$C NMR ($CDCl_3$, 126 MHz) δ 20.9 (1C), 31.2 (1C), 32.6 (1C), 48.0 (1C), 123.0 (1C), 126.2 (1C), 127.1 (2C), 127.2 (2C), 128.4 (2C), 128.5 (2C), 128.58 (2C), 128.60 (1C), 130.2 (1C), 130.3 (1C), 130.4 (2C), 137.1 (1C), 140.4 (1C), 150.3 (1C); IR (KBr, $cm^{-1}$) 1015, 1082, 1211, 1344, 1450, 1491, 2922, 3026; HRMS ($ESI^+$) *m/z* 386.1686 ($[M+H]^+$, $C_{24}H_{24}N_3S^+$ requires 385.1685).

4-Phenyl-1-(4-phenyl-2-butanyl)-5-(*p*-tolylthio)-1*H*-1,2,3-triazole (**10c**)



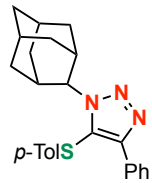

Colorless oil; TLC $R_f$ 0.54 (*n*-hexane/EtOAc = 4/1); $^1$H NMR ($CDCl_3$, 500 MHz) δ 1.47 (d, 3H, $J$ = 6.8 Hz), 2.08–2.18 (m, 1H), 2.26 (s, 3H), 2.35–2.48 (m, 3H), 4.75–4.90 (m, 1H), 6.84–6.94 (m, 2H), 6.95–7.08 (m, 4H), 7.12–7.18 (m, 1H), 7.19–7.27 (m, 2H), 7.32–7.38 (m, 1H), 7.39–7.46 (m, 2H), 8.10–8.18 (m, 2H); $^{13}$C NMR ($CDCl_3$, 126 MHz): δ 20.9 (1C), 21.3 (1C), 32.3 (1C), 37.9 (1C), 54.8 (1C), 122.7 (1C), 126.0 (1C), 127.1 (2C), 127.2 (2C), 128.3 (2C), 128.4 (2C), 128.6 (2C+1C, two signals overlapped), 130.3 (2C), 130.39 (1C), 130.44 (1C), 136.9 (1C), 140.7 (1C), 150.1 (1C); IR (KBr, $cm^{-1}$) 986, 1332, 1228, 1475, 1490, 1602, 2927, 3026; HRMS ($ESI^+$) *m/z* 400.1842 ($[M+H]^+$, $C_{25}H_{26}N_3S^+$ requires 400.1842).

1-Cyclohexyl-4-phenyl-5-(*p*-tolylthio)-1*H*-1,2,3-triazole (**10e**)



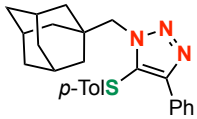

Colorless solid; Mp 82–84 °C; TLC $R_f$ 0.55 (*n*-hexane/EtOAc = 4/1); $^1$H NMR ($CDCl_3$, 500 MHz) δ 1.24–1.39 (m, 3H), 1.69–1.74 (br, 1H), 1.80–1.92 (m, 4H), 1.97–2.10 (m, 2H), 2.27 (s, 3H), 4.54 (tt, 1H, $J$ = 11.8, 3.6 Hz), 6.90–6.95 (m, 2H), 7.00–7.07 (m, 2H), 7.31–7.36 (m, 1H), 7.37–7.43 (m, 2H), 8.05–8.12 (m, 2H); $^{13}$C NMR ($CDCl_3$, 126 MHz) δ 21.0 (1C), 25.0 (1C), 25.6 (2C), 33.1 (2C), 58.3 (1C), 122.1 (1C), 127.0 (2C), 127.2 (2C), 128.45 (1C), 128.51 (2C), 130.3 (2C), 130.5 (1C), 130.7 (1C), 136.9 (1C), 149.8 (1C); IR (KBr, $cm^{-1}$) 1263, 1327, 1341, 1447, 1476, 1491, 2857, 2934; HRMS ($ESI^+$) *m/z* 350.1686 ($[M+H]^+$, $C_{21}H_{24}N_3S^+$ requires 350.1685).

1-(2-Adamantyl)-4-phenyl-5-(*p*-tolylthio)-1*H*-1,2,3-triazole (**10f**)



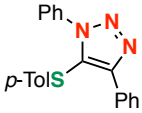

Colorless solid; Mp 143–144 °C; TLC $R_f$ 0.21 (*n*-hexane/EtOAc = 8/1); $^1$H NMR ($CDCl_3$, 500 MHz) δ 1.57–1.64 (m, 2H), 1.76–1.87 (m, 4H), 1.88–2.02 (m, 4H), 2.11–2.19 (br, 2H), 2.27 (s, 3H), 2.58–2.69 (m, 2H), 4.79–4.87 (br, 1H), 6.87–6.95 (m, 2H), 6.99–7.06 (m, 2H), 7.31–7.37 (m, 1H), 7.38–7.44 (m, 2H), 8.07–8.14 (m, 2H); $^{13}$C NMR ($CDCl_3$, 126 MHz) δ 21.0 (1C), 27.1 (1C), 27.5 (1C), 31.3 (2C), 33.1 (2C), 37.8 (1C), 38.6 (2C), 63.6 (1C), 123.1 (1C), 127.1 (2C), 127.2 (2C), 128.4 (1C), 128.5 (2C), 130.3 (2C), 130.5 (1C), 130.7 (1C), 136.9 (1C), 149.5 (1C); IR (KBr, $cm^{-1}$) 694, 804, 1332, 1452, 1491, 2852, 2909, 3047; HRMS ($ESI^+$) *m/z* 402.2004 ($[M+H]^+$, $C_{25}H_{28}N_3S^+$ requires 402.1998).

1-(1-Adamantylmethyl)-4-phenyl-5-(*p*-tolylthio)-1*H*-1,2,3-triazole (**10h**)



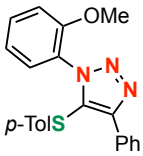

Colorless solid; Mp 116–118 °C; TLC $R_f$ 0.45 (*n*-hexane/EtOAc = 8/1); $^1$H NMR ($CDCl_3$, 500 MHz) δ 1.55–1.63 (m, 9H), 1.65–1.73 (m, 3H), 1.94–2.02 (br, 3H), 2.26 (s, 3H), 4.10 (s, 2H), 6.81–6.88 (m, 2H), 6.98–7.05 (m, 2H), 7.29–7.36 (m, 1H), 7.37–7.42 (m, 2H), 8.08–8.14 (m, 2H); $^{13}$C NMR ($CDCl_3$, 126 MHz) δ 20.9 (1C), 28.2 (3C), 35.2 (1C), 36.6 (3C), 40.5 (3C), 59.1 (1C), 124.0 (1C), 126.6 (2C), 127.0 (2C), 128.4 (1C), 128.5 (2C), 130.3 (2C), 130.40 (1C), 130.42 (1C), 136.7 (1C), 149.4 (1C); IR (KBr, cm$^{-1}$) 1082, 1342, 1448, 1491, 1738, 2847, 2903, 3030; HRMS (ESI$^+$) *m/z* 416.2154 ([M+H]$^+$, $C_{26}H_{30}N_3S^+$ requires 416.2155).

1,4-Diphenyl-5-(*p*-tolylthio)-1*H*-1,2,3-triazole (**11a**)



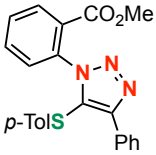

Colorless solid; Mp 149–150 °C; TLC $R_f$ 0.44 (*n*-hexane/EtOAc = 4/1); $^1$H NMR ($CDCl_3$, 500 MHz) δ 2.24 (s, 3H), 6.79–6.84 (m, 2H), 6.93−6.98 (m, 2H), 7.36–7.41 (m, 1H), 7.42–7.51 (m, 7H), 8.14–8.20 (m, 2H); $^{13}$C NMR ($CDCl_3$, 126 MHz) δ 20.9 (1C), 124.6 (1C), 125.8 (2C), 127.3 (2C), 127.9 (2C), 128.6 (2C), 128.7 (1C), 129.0 (2C), 129.7 (1C), 130.07 (1C), 130.14 (2C), 130.2 (1C), 136.1 (1C), 137.1 (1C), 150.4 (1C); IR (KBr, cm$^{-1}$) 1267, 1366, 1473, 1653, 3246; HRMS (ESI$^+$) *m/z* 344.1216 ([M+H]$^+$, $C_{21}H_{18}N_3S^+$ requires 344.1216).

1-(2-Methoxyphenyl)-4-phenyl-5-(*p*-tolylthio)-1*H*-1,2,3-triazole (**11b**)



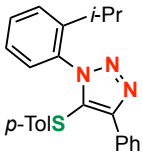

Colorless solid; Mp 121–122 °C; TLC $R_f$ 0.58 (*n*-hexane/EtOAc = 2/1); $^1$H NMR ($CDCl_3$, 500 MHz) δ 2.23 (s, 3H), 3.61 (s, 3H), 6.78–6.84 (m, 2H), 6.89–6.94 (m, 2H), 6.95–7.03 (m, 2H), 7.19–7.23 (m, 1H), 7.33–7.39 (m, 1H), 7.40–7.49 (m, 3H), 8.17–8.23 (m, 2H); $^{13}$C NMR ($CDCl_3$, 126 MHz) δ 20.9 (1C), 55.5 (1C), 111.8 (1C), 120.4 (1C), 124.8 (1C), 126.6 (1C), 127.1 (2C), 128.4 (2C), 128.47 (1C), 128.51 (2C), 128.8 (1C), 129.8 (2C), 130.0 (1C), 130.3 (1C), 131.7 (1C), 136.8 (1C), 148.9 (1C), 154.6 (1C); IR (KBr, cm$^{-1}$) 1257, 1283, 1467, 1506, 1603, 2924, 3051; HRMS (ESI$^+$) *m/z* 374.1322 ([M+H]$^+$, $C_{22}H_{20}N_3OS^+$ requires 374.1322).

Methyl 2-(4-phenyl-5-(*p*-tolylthio)-1*H*-1,2,3-triazol-1-yl)benzoate (**11c**)



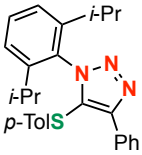

Colorless solid; Mp 116 °C (decomp.); TLC $R_f$ 0.35 (*n*-hexane/EtOAc = 3/1); $^1$H NMR ($CDCl_3$, 500 MHz) δ 2.22 (s, 3H), 3.62 (s, 3H), 6.77–6.83 (m, 2H), 6.87–6.93 (m, 2H), 7.18–7.23 (m, 1H), 7.36–7.42 (m, 1H), 7.43–7.49 (m, 2H), 7.52–7.62 (m, 2H), 8.07-8.12 (m, 1H), 8.19–8.25 (m, 2H); $^{13}$C NMR ($CDCl_3$, 126 MHz) δ 20.9 (1C), 52.4 (1C), 126.3 (1C), 127.2 (2C), 128.3 (1C), 128.59 (2C), 128.62 (1C), 128.85 (1C), 128.90 (2C), 129.3 (2C), 129.9 (1C), 130.2 (1C), 130.3 (1C), 131.5 (1C), 132.6 (1C), 135.3 (1C), 137.3 (1C), 149.1 (1C), 164.7 (1C); IR (KBr, cm$^{-1}$) 1090, 1271, 1294, 1433, 1492, 1601, 1728; HRMS (ESI$^+$) *m/z* 402.1277 ([M+H]$^+$, $C_{23}H_{20}N_3O_2S^+$ requires 402.1271).

1-(2-Isopropylphenyl)-4-phenyl-5-(*p*-tolylthio)-1*H*-1,2,3-triazole (**11d**)



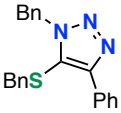

Colorless solid; Mp 119–121 °C; TLC $R_f$ 0.41 (*n*-hexane/EtOAc = 4/1); $^1$H NMR ($CDCl_3$, 500 MHz) δ 0.93–1.23 (br, 6H), 2.24 (s, 3H), 2.38 (sept, 1H, $J$ = 6.9 Hz), 6.76–6.83 (m, 2H), 6.90–6.98 (m, 3H), 7.14–7.20 (m, 1H), 7.36–7.50 (m, 5H), 8.24–8.30 (m, 2H); $^{13}$C NMR ($CDCl_3$, 126 MHz) δ 21.0 (1C), 28.3 (2C+1C, two signals overlapped), 126.0 (1C), 126.2 (1C), 126.6 (1C), 127.1 (2C), 127.8 (1C), 128.65 (2C+2C, two signals overlapped), 128.71 (1C), 129.6 (1C), 130.0 (2C), 130.2 (1C), 130.7 (1C), 133.7 (1C), 137.3 (1C), 146.3 (1C), 149.2 (1C); IR (KBr, cm$^{-1}$) 1107, 1232, 1385, 1492, 1605, 2868, 2965, 3034 HRMS (ESI$^+$) *m/z* 386.1685 ([M+H]$^+$, $C_{24}H_{24}N_3S^+$ requires 386.1685).

1-(2,6-Diisopropylphenyl)-4-phenyl-5-(*p*-tolylthio)-1*H*-1,2,3-triazole (**11e**)



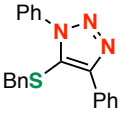

Colorless solid; Mp 105–107 °C; TLC $R_f$ 0.37 (*n*-hexane/EtOAc = 8/1); $^1$H NMR ($CDCl_3$, 500 MHz) δ 0.88 (d, 6H, $J$ = 6.9 Hz), 1.08 (d, 6H, $J$ = 6.9 Hz), 2.04 (sept, 2H, $J$ = 6.9 Hz), 2.21 (s, 3H), 6.82–6.87 (m, 2H), 6.90–6.95 (m, 2H), 7.21–7.27 (m, 2H), 7.35–7.40 (m, 1H), 7.41–7.51 (m, 3H), 8.32–8.38 (m, 2H); $^{13}$C NMR ($CDCl_3$, 126 MHz) δ 20.9 (1C), 22.3 (2C), 25.4 (2C), 28.8 (2C), 123.7 (2C), 125.9 (1C), 126.8 (2C), 128.0 (2C), 128.66 (2C), 128.70 (1C), 130.0 (2C), 130.2 (1C), 130.9 (1C+1C, two signals overlapped), 131.7 (1C), 137.1 (1C), 146.7 (2C), 149.0 (1C); IR (KBr, cm$^{-1}$) 761, 804, 1263, 1447, 1470, 2927, 2964, 3051; HRMS (ESI$^+$) *m/z* 428.2160 ([M+H]$^+$, $C_{27}H_{30}N_3S^+$ requires 428.2155).

1-Benzyl-5-benzylthio-4-phenyl-1*H*-1,2,3-triazole (**12**)



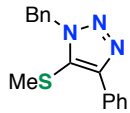

Brown solid; Mp 78–80 °C; TLC $R_f$ 0.54 (*n*-hexane/EtOAc = 4/1); $^1$H NMR ($CDCl_3$, 500 MHz) δ 3.55 (s, 2H), 5.24 (s, 2H), 6.82−6.88 (m, 2H), 7.13–7.19 (m, 3H), 7.22–7.26 (m, 2H), 7.27–7.37 (m, 4H), 7.40–7.46 (m, 2H), 8.11–8.16 (m, 2H); $^{13}$C NMR ($CDCl_3$, 126 MHz) δ 40.1 (1C), 51.6 (1C), 124.5 (1C), 126.8 (2C), 127.81 (1C), 127.83 (2C), 128.3 (1C), 128.4 (1C), 128.6 (2C), 128.68 (2C), 128.74 (2C), 128.8 (2C), 130.6 (1C), 135.3 (1C), 136.0 (1C), 149.5 (1C); IR (KBr, cm$^{-1}$) 696, 1072, 1221, 1344, 1454, 1495, 1604, 3030; HRMS (ESI$^+$) *m/z* 358.1373 ([M+H]$^+$, $C_{22}H_{20}N_3S^+$ requires 358.1372).

5-Benzylthio-1,4-diphenyl-1*H*-1,2,3-triazole (**13**)



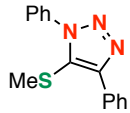

Brown solid; Mp 104–106 °C; TLC $R_f$ 0.50 (*n*-hexane/EtOAc = 4/1); $^1$H NMR ($CDCl_3$, 500 MHz) δ 3.62 (s, 2H), 6.72–6.77 (m, 2H), 7.05−7.10 (m, 2H), 7.11–7.16 (m, 1H), 7.27–7.32 (m, 2H), 7.39–7.44 (m, 1H), 7.45–7.52 (m, 5H), 8.12–8.18 (m, 2H); $^{13}$C NMR ($CDCl_3$, 126 MHz) δ 39.5 (1C), 125.4 (1C), 125.9 (2C), 127.2 (2C), 127.6 (1C), 128.5 (2C), 128.6 (1C), 128.65 (2C), 128.70 (2C), 128.9 (2C), 129.5 (1C), 130.5 (1C), 135.7 (1C), 136.0 (1C), 149.7 (1C); IR (KBr, cm$^{-1}$) 1070, 1233, 1389, 1497, 1597, 1882, 1951, 3028; HRMS (ESI$^+$) *m/z* 344.1210 ([M+H]$^+$, $C_{21}H_{18}N_3S^+$ requires 344.1216).

1-Benzyl-5-methylthio-4-phenyl-1*H*-1,2,3-triazole (**14**)



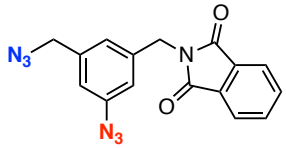
Brown oil; TLC $R_f$ 0.36 (*n*-hexane/EtOAc = 4/1); $^1$H NMR ($CDCl_3$, 500 MHz) δ 1.94 (s, 3H), 5.70 (s, 2H), 7.28−7.39 (m, 6H), 7.42–7.48 (m, 2H), 8.14–8.20 (m, 2H); $^{13}$C NMR ($CDCl_3$, 126 MHz) δ 18.5 (1C), 52.1 (1C), 126.6 (1C), 126.7 (2C), 127.8 (2C), 128.3 (1C), 128.4 (1C), 128.6 (2C), 128.9 (2C), 130.6 (1C), 135.4 (1C), 148.7 (1C); IR (KBr, $cm^{-1}$) 989, 1223, 1344, 1431, 1496, 1605, 2924, 3032; HRMS (ESI$^+$) *m/z* 282.1061 ([M+H]$^+$, $C_{16}H_{16}N_3S^+$ requires 282.1059).

5-Methylthio-1,4-diphenyl-1*H*-1,2,3-triazole (**15**)



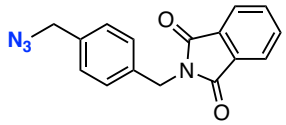
Colorless solid; Mp 112–114 °C; TLC $R_f$ 0.38 (*n*-hexane/EtOAc = 4/1); $^1$H NMR ($CDCl_3$, 500 MHz) δ 2.07 (s, 3H), 7.38–7.44 (m, 1H), 7.47–7.52 (m, 2H), 7.54–7.61 (m, 3H), 7.63–7.68 (m, 2H), 8.14−8.20 (m, 2H); $^{13}$C NMR ($CDCl_3$, 126 MHz) δ 18.4 (1C), 125.6 (2C), 127.3 (2C), 127.7 (1C), 128.5 (1C), 128.6 (2C), 129.3 (2C), 129.7 (1C), 130.5 (1C), 136.3 (1C), 148.6 (1C); IR (KBr, $cm^{-1}$) 764, 986, 1236, 1388, 1475, 1499, 1597, 3064; HRMS (ESI$^+$) *m/z* 290.0725 ([M+Na]$^+$, $C_{15}H_{13}N_3NaS^+$ requires 290.0722).

2-(3-Azido-5-(azidomethyl)benzyl)phthalimide (**16i**)



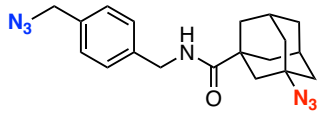
Pale yellow solid; Mp 92–94 °C; TLC $R_f$ 0.26 (*n*-hexane/EtOAc = 4/1); $^1$H NMR ($CDCl_3$, 500 MHz) δ 4.32 (s, 2H), 4.83 (s, 2H), 6.90 (s, 1H), 7.06 (s, 1H), 7.13 (s, 1H), 7.70–7.76 (m, 2H), 7.84–7.90 (m, 2H); $^{13}$C NMR ($CDCl_3$, 126 MHz) δ 41.0 (1C), 54.1 (1C), 117.9 (1C), 119.0 (1C), 123.5 (2C), 124.6 (1C), 131.9 (2C), 134.2 (2C), 138.0 (1C), 138.9 (1C), 141.1 (1C), 167.9 (2C); IR (KBr, $cm^{-1}$) 1231, 1265, 1392, 1466, 1597, 1714, 1771, 2110; HRMS (ESI$^+$) *m/z* 356.0866 ([M+Na]$^+$, $C_{16}H_{11}N_7NaO_2^+$ requires 356.0866).

2-(4-(Azidomethyl)benzyl)phthalimide (**S1**)



Pale yellow solid; Mp 99–101 °C; TLC $R_f$ 0.48 (*n*-hexane/EtOAc = 3/1); $^1$H NMR ($CDCl_3$, 500 MHz) δ 4.30 (s, 2H), 4.85 (s, 2H), 7.24–7.30 (m, 2H), 7.43–7.49 (m, 2H), 7.67–7.74 (m, 2H), 7.82–7.88 (m, 2H); $^{13}$C NMR ($CDCl_3$, 126 MHz) δ 41.2 (1C), 54.4 (1C), 123.4 (2C), 128.5 (2C), 129.1 (2C), 132.1 (1C), 134.0 (2C), 135.0 (2C), 136.5 (1C), 168.0 (2C); IR (KBr, $cm^{-1}$) 1086, 1346, 1394, 1468, 1717, 1769, 2100, 2253; HRMS (ESI$^+$) *m/z* 315.0851 ([M+Na]$^+$, $C_{16}H_{12}N_4NaO_2^+$ requires 315.0852).

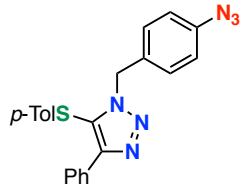
3-Azido-*N*-(4-(azidomethyl)benzyl)-1-adamantanamide (**20**)



Pale yellow solid; Mp 61–63 °C; TLC $R_f$ 0.37 (*n*-hexane/EtOAc = 1/1); $^1$H NMR ($CDCl_3$, 500 MHz) δ 1.63–1.68 (m, 2H), 1.75–1.86 (m, 8H), 1.89–1.94 (br, 2H), 2.28–2.34 (m, 2H), 4.33 (s, 2H), 4.45 (d, 2H, *J* = 5.7 Hz), 5.82–5.92 (br, 1H), 7.24–7.32 (m, 4H); $^{13}$C NMR ($CDCl_3$, 126 MHz) δ

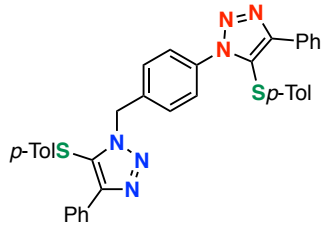
29.5 (2C), 34.9 (1C), 38.0 (2C+1C, two signals overlapped), 40.5 (2C), 43.12 (1C), 43.14 (1C), 54.4 (1C), 59.0 (1C), 128.2 (2C), 128.7 (2C), 134.7 (1C), 138.5 (1C), 175.8 (1C); IR (KBr, $cm^{-1}$) 1246, 1514, 1655, 1794, 2093, 2253, 2928, 3458; HRMS ($ESI^+$) *m/z* 388.1857 ($[M+Na]^+$, $C_{19}H_{23}N_7NaO^+$ requires 388.1856).

1-(4-Azidobenzyl)-4-phenyl-5-(*p*-tolylthio)-1*H*-1,2,3-triazole (**17a**)



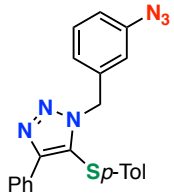

Purified by preparative TLC (*n*-hexane/EtOAc = 4/1); yield: 84% (66.9 mg, 168 µmol) from **9a** (44.7 mg, 199 µmol); pale brown solid; Mp 85–87 °C; TLC $R_f$ 0.57 (*n*-hexane/EtOAc = 2/1); $^1H$ NMR ($CDCl_3$, 500 MHz) δ 2.25 (s, 3H), 5.53 (s, 2H), 6.71–6.77 (m, 2H), 6.80–6.86 (m, 2H), 6.90–6.96 (m, 2H), 7.15–7.21 (m, 2H), 7.31–7.42 (m, 3H), 8.05–8.13 (m, 2H); $^{13}C$ NMR ($CDCl_3$, 126 MHz) δ 20.9 (1C), 51.7 (1C), 119.2 (2C), 122.8 (1C), 126.7 (2C), 127.0 (2C), 128.6 (2C), 128.7 (1C), 129.7 (2C), 129.8 (1C), 130.1 (1C), 130.2 (2C), 131.1 (1C), 136.8 (1C), 140.1 (1C), 150.8 (1C); IR (KBr, $cm^{-1}$) 1281, 1342, 1506, 1607, 2112, 2409, 2920, 3032; HRMS ($ESI^+$) *m/z* 399.1379 ($[M+H]^+$, $C_{22}H_{19}N_6S^+$ requires 399.1386).

4-Phenyl-1-(4-(4-phenyl-5-(*p*-tolylthio)-1*H*-1,2,3-triazol-1-yl)benzyl)-5-(*p*-tolylthio)-1*H*-1,2,3-triazole




Purified by preparative TLC (*n*-hexane/EtOAc = 4/1); yield: 5% (6.0 mg, 9.6 µmol) from **9a** (44.7 mg, 199 µmol); brown solid; Mp 63–65 °C; TLC $R_f$ 0.58 (*n*-hexane/EtOAc = 1/1); $^1H$ NMR ($CDCl_3$, 500 MHz) δ 2.21 (s, 3H), 2.22 (s, 3H), 5.62 (s, 2H), 6.73–6.83 (m, 4H), 6.89–6.99 (m, 4H), 7.22–7.32 (m, 4H), 7.33–7.48 (m, 6H), 8.07–8.19 (m, 4H); $^{13}C$ NMR ($CDCl_3$, 126 MHz) δ 20.9 (2C), 51.6 (1C), 123.2 (1C), 124.4 (1C), 125.8 (2C), 126.9 (2C), 127.0 (2C), 127.3 (2C), 127.8 (2C), 128.5 (2C), 128.6 (4C), 128.8 (2C), 129.5 (1C), 129.9 (1C), 130.0 (2C), 130.2 (2C), 130.4 (2C), 135.8 (1C), 136.1 (1C), 137.17 (1C), 137.21 (1C), 150.5 (1C), 150.7 (1C); IR (KBr, $cm^{-1}$) 986, 1230, 1263, 1246, 1446, 1491, 1514, 3049; HRMS ($ESI^+$) *m/z* 623.2046 ($[M+H]^+$, $C_{37}H_{31}N_6S_2^+$ requires 623.2046).

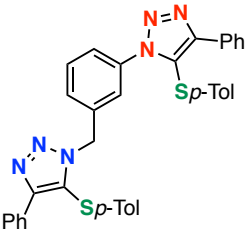
1-(3-Azidobenzyl)-4-phenyl-5-(*p*-tolylthio)-1*H*-1,2,3-triazole (**17b**)




Purified by preparative TLC (*n*-hexane/EtOAc = 4/1); yield: 86% (68.2 mg, 171 µmol) from **9a** (44.8 mg, 200 µmol); brown solid; Mp 82–83 °C; TLC $R_f$ 0.52 (*n*-hexane/EtOAc = 4/1); $^1H$ NMR ($CDCl_3$, 500 MHz) δ 2.23 (s, 3H), 5.54 (s, 2H), 6.71−6.79 (m, 3H), 6.81–6.87 (m, 1H), 6.89–6.94 (m, 2H), 6.97–7.02 (m, 1H), 7.15–7.21 (m, 1H), 7.32–7.36 (m, 1H), 7.37–7.43 (m, 2H), 8.06–8.13 (m, 2H); $^{13}C$ NMR ($CDCl_3$, 126 MHz) δ 20.9 (1C), 51.8 (1C), 118.6 (1C), 118.7 (1C), 123.0 (1C), 124.5 (1C), 126.7 (2C), 127.0 (2C), 128.6 (2C), 128.7 (1C), 129.6 (1C), 130.05 (1C), 130.07 (1C), 130.2 (2C), 136.4 (1C), 136.8 (1C), 140.3 (1C), 150.8 (1C); IR (KBr, $cm^{-1}$) 1082, 1219, 1294, 1449,

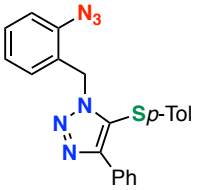
1589, 1606, 2113, 3032; HRMS (ESI$^+$) *m/z* 399.1387 ([M+H]$^+$, $C_{22}H_{19}N_6S^+$ requires 399.1386).

4-Phenyl-1-(3-(4-phenyl-5-(*p*-tolylthio)-1*H*-1,2,3-triazol-1-yl)benzyl)-5-(*p*-tolylthio)-1*H*-1,2,3-triazole



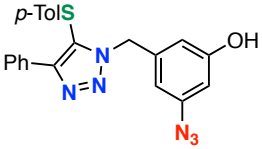

Purified by preparative TLC (*n*-hexane/EtOAc = 4/1); yield: 4% (5.1 mg, 8.2 μmol) from **9a** (44.8 mg, 200 μmol); brown solid; Mp 61–63 °C; TLC $R_f$ 0.55 (*n*-hexane/EtOAc = 1/1); $^1$H NMR ($CDCl_3$, 500 MHz) δ 2.18 (s, 3H), 2.20 (s, 3H), 5.57 (s, 2H), 6.71–6.79 (m, 4H), 6.86–6.94 (m, 4H), 7.26–7.31 (m, 2H), 7.32–7.48 (m, 8H), 8.07–8.12 (m, 2H), 8.13–8.18 (m, 2H); $^{13}$C NMR ($CDCl_3$, 126 MHz) δ 20.9 (2C), 51.5 (1C), 123.2 (1C), 124.4 (1C), 125.2 (1C), 125.3 (1C), 126.9 (2C), 127.0 (2C), 127.4 (2C), 127.8 (2C), 128.6 (4C), 128.77 (1C), 128.81 (1C), 129.1 (1C), 129.4 (1C), 129.5 (1C), 129.9 (2C), 130.0 (1C), 130.2 (2C), 130.3 (2C), 135.8 (1C), 136.3 (1C), 137.1 (1C), 137.2 (1C), 150.5 (1C), 150.6 (1C); IR (KBr, cm$^{-1}$) 988, 1082, 1227, 1344, 1398, 1447, 1491, 1593; HRMS (ESI$^+$) *m/z* 645.1858 ([M+Na]$^+$, $C_{37}H_{30}N_6NaS_2^+$ requires 645.1866).

1-(2-Azidobenzyl)-4-phenyl-5-(*p*-tolylthio)-1*H*-1,2,3-triazole (**17c**)



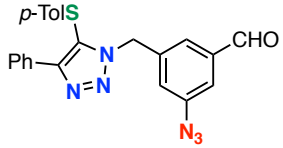

Brown solid; Mp 104–106 °C; TLC $R_f$ 0.68 (*n*-hexane/EtOAc = 4/1); $^1$H NMR ($CDCl_3$, 500 MHz) δ 2.23 (s, 3H), 5.56 (s, 2H), 6.78–6.83 (m, 2H), 6.90–6.99 (m, 4H), 7.00–7.05 (m, 1H), 7.23–7.29 (m, 1H), 7.33–7.38 (m, 1H), 7.39–7.44 (m, 2H), 8.09–8.15 (m, 2H); $^{13}$C NMR ($CDCl_3$, 126 MHz) δ 20.9 (1C), 47.1 (1C), 118.0 (1C), 123.4 (1C), 124.9 (1C), 125.9 (1C), 127.01 (2C), 127.04 (2C), 128.6 (2C), 128.7 (1C), 129.30 (1C), 129.34 (1C), 129.7 (1C), 130.0 (2C), 130.2 (1C), 136.7 (1C), 137.5 (1C), 150.5 (1C); IR (KBr, cm$^{-1}$) 1083, 1220, 1285, 1452, 1491, 1585, 2123, 3051; HRMS (ESI$^+$) *m/z* 399.1388 ([M+H]$^+$, $C_{22}H_{19}N_6S^+$ requires 399.1386).

3-Azido-5-((4-phenyl-5-(*p*-tolylthio)-1*H*-1,2,3-triazol-1-yl)methyl)phenol (**17d**)



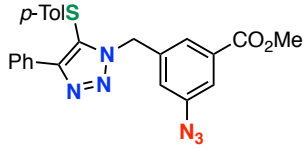

Purified by preparative TLC (*n*-hexane/EtOAc = 4/1); yield: 77% (63.9 mg, 154 μmol) from **9a** (44.7 mg, 199 μmol); colorless solid; Mp 137–138 °C; TLC $R_f$ 0.26 (*n*-hexane/EtOAc = 4/1); $^1$H NMR ($CDCl_3$, 500 MHz) δ 2.24 (s, 3H), 5.52 (s, 2H), 6.29 (s, 1H), 6.44 (s, 1H), 6.65–6.73 (m, 2H), 6.88–6.96 (m, 2H), 7.08 (s, 1H), 7.30–7.42 (m, 3H), 7.88–7.96 (m, 2H), 9.84–9.98 (br s, 1H); $^{13}$C NMR ($CDCl_3$, 126 MHz) δ 20.9 (1C), 52.6 (1C), 106.8 (1C), 111.0 (1C), 111.9 (1C), 123.8 (1C), 126.4 (2C), 127.3 (2C), 128.8 (2C), 129.0 (1C), 129.2 (1C), 129.3 (1C), 130.2 (2C), 136.2 (1C), 136.9 (1C), 141.2 (1C), 151.0 (1C), 159.0 (1C); IR (KBr, cm$^{-1}$) 1003, 1252, 1331, 1465, 1490, 1599, 2106, 3404; HRMS (ESI$^+$) *m/z* 415.1348 ([M+H]$^+$, $C_{22}H_{19}N_6OS^+$ requires 415.1336).

3-Azido-5-((4-phenyl-5-(*p*-tolylthio)-1*H*-1,2,3-triazol-1-yl)methyl)benzaldehyde (**17e**)



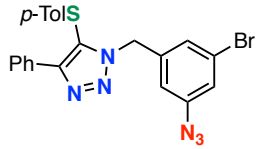
Purified by preparative TLC (*n*-hexane/EtOAc = 4/1); yield: 86% (73.1 mg, 171 μmol) from **9a** (44.8 mg, 200 μmol); brown oil; TLC $R_f$ 0.38 (*n*-hexane/EtOAc = 4/1); $^1$H NMR ($CDCl_3$, 500 MHz) δ 2.21 (s, 3H), 5.63 (s, 2H), 6.67−6.74 (m, 2H), 6.84–6.91 (m, 2H), 7.00 (s, 1H), 7.31–7.45 (m, 5H), 8.07–8.14 (m, 2H), 9.76 (s, 1H); $^{13}$C NMR ($CDCl_3$, 126 MHz) δ 20.8 (1C), 51.3 (1C), 118.1 (1C), 123.0 (1C), 124.2 (1C), 126.4 (1C), 126.7 (2C), 127.0 (2C), 128.7 (2C), 128.9 (1C), 129.5 (1C), 129.8 (1C), 130.2 (2C), 137.0 (1C), 137.3 (1C), 137.9 (1C), 141.8 (1C), 151.1 (1C), 190.3 (1C); IR (KBr, cm$^{-1}$) 1226, 1265, 1307, 1491, 1597, 1701, 2112, 3053; HRMS (ESI$^+$) *m/z* 427.1337 ([M+H]$^+$, $C_{23}H_{19}N_6OS^+$ requires 427.1336).

Methyl 3-azido-5-(4-phenyl-5-(*p*-tolylthio)-1*H*-1,2,3-triazol-1-yl)benzoate (**17f**)



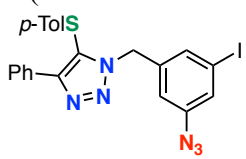
Purified by preparative TLC (*n*-hexane/EtOAc = 2/1); yield: 81% (73.9 mg, 162 μmol) from **9a** (44.8 mg, 200 μmol); pale yellow solid; Mp 68–70 °C; TLC $R_f$ 0.59 (*n*-hexane/EtOAc = 2/1); $^1$H NMR ($CDCl_3$, 500 MHz) δ 2.22 (s, 3H), 3.89 (s, 3H), 5.59 (s, 2H), 6.67–6.74 (m, 2H), 6.85–6.92 (m, 3H), 7.34–7.44 (m, 3H), 7.50 (s, 1H), 7.62 (s, 1H), 8.07–8.14 (m, 2H); $^{13}$C NMR ($CDCl_3$, 126 MHz) δ 20.8 (1C), 51.5 (1C), 52.4 (1C), 119.5 (1C), 122.8 (1C), 122.9 (1C), 125.6 (1C), 126.6 (2C), 127.0 (2C), 128.6 (2C), 128.8 (1C), 129.4 (1C), 129.9 (1C), 130.1 (2C), 132.2 (1C), 136.6 (1C), 136.8 (1C), 141.0 (1C), 151.0 (1C), 165.5 (1C); IR (KBr, cm$^{-1}$) 1202, 1263, 1315, 1597, 1724, 2112, 2359, 2949; HRMS (ESI$^+$) *m/z* 457.1441 ([M+H]$^+$, $C_{24}H_{21}N_6O_2S^+$ requires 457.1441).

1-(3-Azido-5-bromophenyl)-4-phenyl-5-(*p*-tolylthio)-1*H*-1,2,3-triazole (**17g**)



Purified by preparative TLC (*n*-hexane/EtOAc = 8/1); yield: 78% (531 mg, 1.11 mmol) from **9a** (325 mg, 1.45 mmol); brown oil; TLC $R_f$ 0.38 (*n*-hexane/EtOAc = 4/1); $^1$H NMR ($CDCl_3$, 500 MHz) δ 2.25 (s, 3H), 5.51 (s, 2H), 6.68 (s, 1H), 6.72–6.78 (m, 2H), 6.90–6.96 (m, 3H), 7.00 (s, 1H), 7.34–7.46 (m, 3H), 8.09–8.15 (m, 2H); $^{13}$C NMR ($CDCl_3$, 126 MHz) δ 20.9 (1C), 51.2 (1C), 117.5 (1C), 121.6 (1C), 123.1 (1C), 123.4 (1C), 126.8 (2C), 127.0 (2C), 127.4 (1C), 128.6 (2C), 128.9 (1C), 129.4 (1C), 129.9 (1C), 130.2 (2C), 137.0 (1C), 137.8 (1C), 141.7 (1C), 151.0 (1C); IR (KBr, cm$^{-1}$) 1204, 1294, 1344, 1449, 1576, 1601, 2106, 3051; HRMS (ESI$^+$) *m/z* 477.0492 ([M+H]$^+$, $C_{22}H_{18}{}^{79}BrN_6S^+$ requires 477.0492).

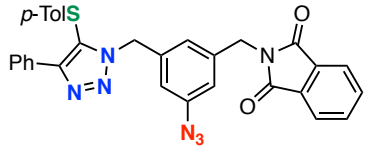
1-(3-Azido-5-iodobenzyl)-4-phenyl-5-(*p*-tolylthio)-1*H*-1,2,3-triazole (**17h**)



Purified by preparative TLC (*n*-hexane/EtOAc = 4/1); yield: 81% (85.0 mg, 162 μmol) from **9a** (44.7 mg, 199 μmol); brown oil; TLC $R_f$ 0.35 (*n*-hexane/EtOAc = 4/1); $^1$H NMR ($CDCl_3$, 500 MHz) δ 2.25 (s, 3H), 5.48 (s, 2H), 6.67−6.76 (m, 3H), 6.90–6.96 (m, 2H), 7.13 (s, 1H), 7.19 (s, 1H), 7.33–7.47 (m, 3H), 8.08–8.16 (m, 2H); $^{13}$C NMR ($CDCl_3$, 126 MHz) δ 21.0 (1C), 51.0 (1C), 94.8 (1C), 118.3 (1C), 123.0 (1C), 126.7 (2C), 127.0 (2C), 127.5 (1C), 128.6 (2C), 128.9 (1C), 129.4

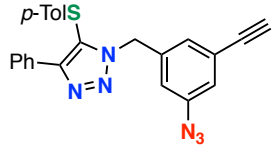
(1C), 129.9 (1C), 130.2 (2C), 133.3 (1C), 136.9 (1C), 137.7 (1C), 141.4 (1C), 151.0 (1C); IR (KBr, $cm^{-1}$) 1202, 1294, 1344, 1449, 1490, 1568, 1595, 2116; HRMS ($ESI^+$) *m/z* 525.0352 ($[M+H]^+$, $C_{22}H_{18}IN_6S^+$ requires 525.0353).

2-(3-Azido-5-((4-phenyl-5-(*p*-tolylthio)-1*H*-1,2,3-triazol-1-yl)methyl)benzyl)phthalimide (**17i**)



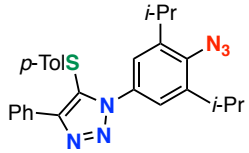

Purified by preparative TLC (*n*-hexane/EtOAc = 2/1); yield: 84% (94.0 mg, 169 µmol) from **9a** (44.8 mg, 200 µmol); pale yellow solid; Mp 68–71 °C; TLC $R_f$ 0.32 (*n*-hexane/EtOAc = 4/1); $^1H$ NMR ($CDCl_3$, 500 MHz) δ 2.22 (s, 3H), 4.68 (s, 2H), 5.52 (s, 2H), 6.64 (s, 1H), 6.68–6.74 (m, 2H), 6.84–6.92 (m, 3H), 7.06 (s, 1H), 7.33–7.43 (m, 3H), 7.70–7.76 (m, 2H), 7.83–7.89 (m, 2H), 8.06–8.12 (m, 2H); $^{13}C$ NMR ($CDCl_3$, 126 MHz) δ 20.8 (1C), 40.8 (1C), 51.7 (1C), 118.0 (1C), 118.6 (1C), 123.0 (1C), 123.5 (2C), 124.7 (1C), 126.7 (2C), 127.0 (2C), 128.6 (2C), 128.7 (1C), 129.6 (1C), 130.0 (1C), 130.1 (2C), 131.9 (2C), 134.2 (2C), 136.7 (1C), 136.8 (1C), 138.6 (1C), 140.9 (1C), 150.9 (1C), 167.8 (2C); IR (KBr, $cm^{-1}$) 1101, 1265, 1392, 1465, 1598, 1714, 1771, 2110; HRMS ($ESI^+$) *m/z* 558.1696 ($[M+H]^+$, $C_{31}H_{24}N_7O_2S^+$ requires 558.1707).

1-(3-Azido-5-ethynylbenzyl)-4-phenyl-5-(*p*-tolylthio)-1*H*-1,2,3-triazole (**17j**)



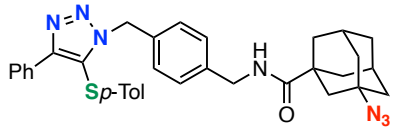

Purified by preparative TLC (*n*-hexane/EtOAc = 4/1); yield: 81% (68.1 mg, 161 µmol) from **9a** (44.7 mg, 199 µmol); pale yellow solid; Mp 75–77 °C; TLC $R_f$ 0.59 (*n*-hexane/EtOAc = 4/1); $^1H$ NMR ($CDCl_3$, 500 MHz) δ 2.24 (s, 3H), 3.08 (s, 1H), 5.51 (s, 2H), 6.69−6.77 (m, 3H), 6.89–6.95 (m, 3H), 7.02 (s, 1H), 7.33–7.45 (m, 3H), 8.08–8.15 (m, 2H); $^{13}C$ NMR ($CDCl_3$, 126 MHz) δ 20.9 (1C), 51.4 (1C), 78.7 (1C), 81.9 (1C), 119.2 (1C), 121.9 (1C), 123.1 (1C), 124.1 (1C), 126.8 (2C), 127.0 (2C), 128.0 (1C), 128.6 (2C), 128.8 (1C), 129.4 (1C), 130.0 (1C), 130.2 (2C), 136.5 (1C), 137.0 (1C), 140.6 (1C), 150.9 (1C); IR (KBr, $cm^{-1}$) 1265, 1307, 1449, 1491, 1587, 2110, 3051, 3292; HRMS ($ESI^+$) *m/z* 423.1390 ($[M+H]^+$, $C_{24}H_{19}N_6S^+$ requires 423.1386).

1-(4-Azido-3,5-diisopropylphenyl)-4-phenyl-5-(*p*-tolylthio)-1*H*-1,2,3-triazole (**19**)



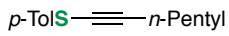

Purified by preparative TLC (*n*-hexane/EtOAc = 4/1); yield: 81% (38.2 mg, 81.5 µmol) from **9a** (22.5 mg, 100 µmol); colorless solid; Mp 95–96 °C; TLC $R_f$ 0.65 (*n*-hexane/EtOAc = 4/1); $^1H$ NMR ($CDCl_3$, 500 MHz) δ 1.16 (d, 12H, $J$ = 6.9 Hz), 2.24 (s, 3H), 3.34 (sept, 2H, $J$ = 6.9 Hz), 6.79–6.85 (m, 2H), 6.95–7.01 (m, 2H), 7.15 (s, 2H), 7.36–7.42 (m, 1H), 7.43–7.49 (m, 2H), 8.12–8.18 (m, 2H); $^{13}C$ NMR ($CDCl_3$, 126 MHz) δ 20.9 (1C), 23.1 (4C), 28.8 (2C), 121.5 (2C), 124.2 (1C), 127.4 (2C), 127.6 (2C), 128.6 (2C), 128.8 (1C), 130.0 (1C), 130.2 (2C), 130.4 (1C), 134.4 (1C), 136.3 (1C), 137.0 (1C), 144.2 (2C), 150.8 (1C); IR (KBr, $cm^{-1}$) 748, 1263, 1447, 1462, 1491, 2113, 2967, 3051; HRMS ($ESI^+$) *m/z* 469.2162 ($[M+H]^+$, $C_{27}H_{29}N_6S^+$ requires 469.2169).

3-Azido-*N*-(4-((4-phenyl-5-(*p*-tolylthio)-1*H*-1,2,3-triazol-1-yl)methyl)benzyl)-1-adamantanamide (**21**)



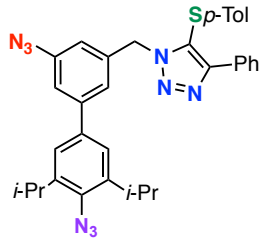
Purified by preparative TLC (*n*-hexane/EtOAc = 2/1); yield: 89% (61.3 mg, 88.7 μmol) from **9a** (22.5 mg, 100 μmol); colorless solid; Mp 49–51 °C; TLC $R_f$ 0.31 (*n*-hexane/EtOAc = 2/1); $^1$H NMR ($CDCl_3$, 500 MHz) δ 1.60–1.66 (br, 2H), 1.72–1.84 (m, 8H), 1.86–1.93 (br, 2H), 2.24–2.33 (m, 5H), 4.37 (d, 2H, $J$ = 5.6 Hz), 5.53 (s, 2H), 5.86–5.94 (br, 1H), 6.77–6.85 (m, 2H), 6.94–7.01 (m, 2H), 7.08–7.15 (m, 2H), 7.16–7.23 (m, 2H), 7.31–7.43 (m, 3H), 8.04–8.11 (m, 2H); $^{13}$C NMR ($CDCl_3$, 126 MHz) δ 20.9 (1C), 29.5 (2C), 34.8 (1C), 38.0 (2C), 40.5 (2C), 43.0 (1C), 43.1 (2C), 51.8 (1C), 59.0 (1C), 123.0 (1C), 126.9 (2C), 127.0 (2C), 127.9 (2C), 128.5 (2C), 128.6 (2C), 128.7 (1C), 129.8 (1C), 130.1 (1C), 130.3 (2C), 133.9 (1C), 136.9 (1C), 138.5 (1C), 150.5 (1C), 175.8 (1C); IR (KBr, cm$^{-1}$) 1015, 1261, 1448, 1518, 1643, 2089, 2922, 3340; HRMS (ESI$^+$) *m/z* 590.2696 ([M+H]$^+$, $C_{34}H_{36}N_7OS^+$ requires 590.2697).

1-Heptyn-1-yl *p*-tolyl sulfide (**9d**)



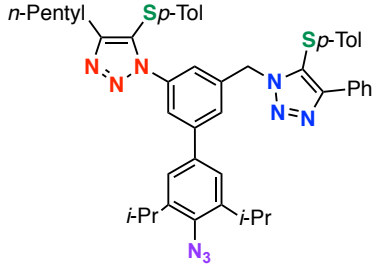
Colorless oil; TLC $R_f$ 0.78 (*n*-hexane/EtOAc = 4/1); $^1$H NMR ($CDCl_3$, 500 MHz) δ 0.91 (t, 3H, $J$ = 7.3 Hz), 1.29–1.45 (m, 4H), 1.59 (tt, 2H, $J$ = 7.3, 7.3 Hz), 2.32 (s, 3H), 2.42 (t, 2H, $J$ = 7.3 Hz), 7.10–7.15 (m, 2H), 7.27–7.32 (m, 2H); $^{13}$C NMR ($CDCl_3$, 126 MHz) δ 14.0 (1C), 20.3 (1C), 20.9 (1C), 22.2 (1C), 28.4 (1C), 31.1 (1C), 65.1 (1C), 99.4 (1C), 126.1 (2C), 129.8 (2C), 130.1 (1C), 136.0 (1C); IR (KBr, cm$^{-1}$) 1016, 1084, 1456, 1491, 2859, 2930, 2955, 3021; HRMS (ESI$^+$) *m/z* 219.1202 ([M+H]$^+$, $C_{14}H_{19}S$ requires 219.1202).

1-((4′,5-Diazido-3′,5′-diisopropyl-1,1′-biphenyl-3-yl)methyl)-4-phenyl-5-(*p*-tolylthio)-1*H*-1,2,3-triazole (**S3**)



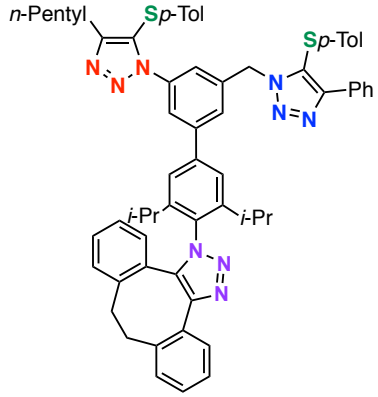
Brown oil; TLC $R_f$ 0.42 (*n*-hexane/EtOAc = 4/1); $^1$H NMR ($CDCl_3$, 500 MHz) δ 1.31 (d, 12H, $J$ = 6.9 Hz), 2.21 (s, 3H), 3.40 (sept, 2H, $J$ = 6.9 Hz), 5.62 (s, 2H), 6.72–6.79 (m, 3H), 6.87–6.93 (m, 2H), 6.97 (s, 1H), 7.15–7.21 (m, 3H), 7.31–7.43 (m, 3H), 8.06–8.13 (m, 2H); $^{13}$C NMR ($CDCl_3$, 126 MHz) δ 20.9 (1C), 23.5 (4C), 29.0 (2C), 51.9 (1C), 117.4 (1C+1C, two signals overlapped), 122.8 (2C), 122.9 (1C), 123.5 (1C), 126.7 (2C), 127.1 (2C), 128.6 (2C), 128.8 (1C), 129.7 (1C), 130.0 (1C), 130.2 (2C), 135.4 (1C), 136.8 (1C+1C, two signals overlapped), 138.1 (1C), 140.8 (1C), 143.5 (1C), 143.7 (2C), 150.9 (1C); IR (KBr, cm$^{-1}$) 1265, 1292, 1402, 1441, 1491, 1595, 2110, 2965; HRMS (ESI$^+$) *m/z* 600.2638 ([M+H]$^+$, $C_{34}H_{34}N_9S^+$ requires 600.2652).

1-(4′-Azido-3′,5′-diisopropyl-5-((4-phenyl-5-(*p*-tolylthio)-1*H*-1,2,3-triazol-1-yl)methyl)-1,1′-biphenyl-3-yl)-4-pentyl-5-(*p*-tolylthio)-1*H*-1,2,3-triazole (**S4**)



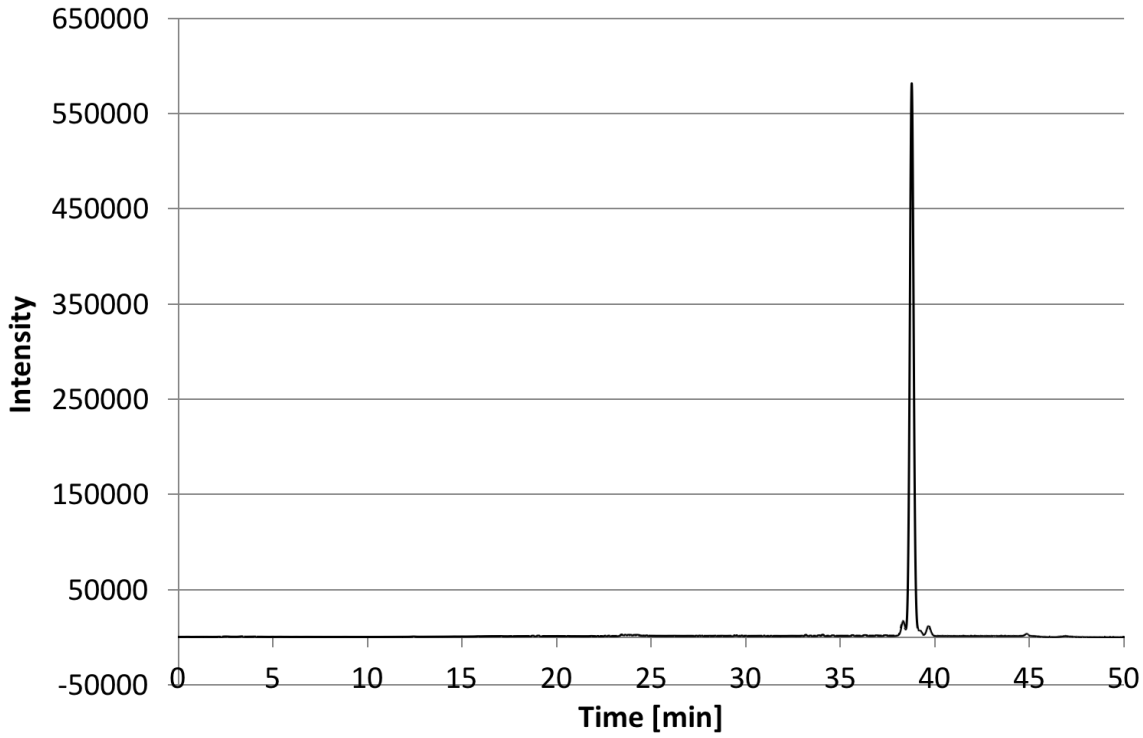

Brown oil; TLC $R_f$ 0.40 (*n*-hexane/EtOAc = 3/1); $^1$H NMR ($CDCl_3$, 500 MHz) δ 0.85–0.91 (m, 3H), 1.27 (d, 12H, *J* = 6.9 Hz), 1.30–1.39 (m, 4H), 1.69–1.78 (m, 2H), 2.15 (s, 3H), 2.17 (s, 3H), 2.77 (t, 2H, *J* = 7.9 Hz), 3.37 (sept, 2H, *J* = 6.9 Hz), 5.64 (s, 2H), 6.72–6.81 (m, 4H), 6.83–6.89 (m, 2H), 6.91–6.97 (m, 2H), 7.13 (s, 2H), 7.33–7.45 (m, 5H), 7.53 (s, 1H), 8.06–8.11 (m, 2H); $^{13}$C NMR ($CDCl_3$, 126 MHz) δ 14.0 (1C), 20.86 (1C), 20.88 (1C), 22.4 (1C), 23.4 (4C), 25.4 (1C), 28.7 (1C), 28.9 (2C), 31.5 (1C), 51.6 (1C), 122.7 (2C), 123.1 (1C), 123.3 (1C), 123.4 (1C), 125.0 (1C), 126.8 (2C), 127.0 (2C), 127.4 (1C), 127.6 (2C), 128.6 (2C), 128.8 (1C), 129.5 (1C), 130.0 (1C), 130.1 (2C), 130.26 (2C), 130.33 (1C), 135.4 (1C), 136.2 (1C), 136.9 (1C), 137.03 (1C), 137.04 (1C), 137.4 (1C), 142.6 (1C), 143.7 (2C), 150.7 (1C), 153.6 (1C); IR (KBr, $cm^{-1}$) 1310, 1460, 1491, 1597, 2120, 2868, 2928, 2961; HRMS ($ESI^+$) *m/z* 818.3782 ($[M+H]^+$, $C_{48}H_{52}N_9S_2^+$ requires 818.3782).

1-(3,5-Diisopropyl-3′-(4-pentyl-5-(*p*-tolylthio)-1*H*-1,2,3-triazol-1-yl)-5′-((4-phenyl-5-(*p*-tolylthio)-1*H*-1,2,3-triazol-1-yl)methyl)-1,1′-biphenyl-4-yl)-8,9-dihydro-1*H*-dibenzo[3,4:7,8]cycloocta[1,2-*d*][1,2,3]triazole (**23**)

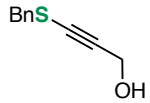



Colorless oil; TLC $R_f$ 0.25 (*n*-hexane/EtOAc = 3/1); HPLC analysis: R*t* = 38.8 min [column: Shiseido CAPCELL PAK MG II (4.6 mm i.d. × 250 mm); mobile phase: $CH_3CN$:$H_2O$ = 40:60 (0−5 min), linear gradient from 40:60 to 99:1 (5−25 min), 99:1 (25−50 min); flow rate: 1.00 mL/min; detection: UV at 254 nm]; $^1$H NMR ($CDCl_3$, 500 MHz) δ 0.80–1.39 (m, 19H), 1.69–1.78 (m, 2H), 2.14 (s, 3H), 2.17 (s, 3H), 2.32–2.52 (br, 2H), 2.77 (t, 2H, *J* = 7.7 Hz), 3.06–3.24 (br, 2H), 3.30–3.50 (br, 2H), 5.65 (s, 2H), 6.67–6.72 (m, 1H), 6.73–6.81 (m, 4H), 6.82–6.87 (m, 2H), 6.91–6.99 (m, 3H), 7.17–7.29 (m, 6H), 7.30–7.45 (m, 5H), 7.50 (s, 1H), 7.57 (s, 1H), 7.66–7.72 (m, 1H), 8.05–8.11 (m, 2H); $^{13}$C NMR ($CDCl_3$, 126 MHz) δ 14.0, 20.9, 22.4, 22.5, 25.4, 28.8, 28.9, 31.5, 32.7, 36.9, 51.6, 122.6, 123.2, 123.6, 123.8, 125.0, 125.8, 126.0, 126.2, 126.8, 127.1, 127.5, 127.7, 128.1, 128.6, 128.7, 128.8, 129.4, 129.5, 129.6, 129.88, 129.95, 130.2, 130.26, 130.28, 130.9, 132.0, 132.6, 135.0, 136.3, 137.0, 137.10, 137.12, 137.4, 141.0, 141.4, 142.1, 146.2, 150.8, 153.7; IR (KBr, $cm^{-1}$) 737, 1215, 1265, 1465, 1491, 1599, 2961, 3443 ; HRMS ($ESI^+$) *m/z* 1022.4722 ($[M+H]^+$, $C_{64}H_{64}N_9S_2^+$ requires 1022.4721).

HPLC chart:

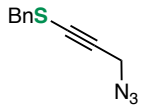



3-Benzylthio-2-propyn-1-ol (**S5**)



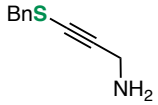

Pale yellow oil; TLC $R_f$ 0.25 (*n*-hexane/EtOAc = 3/1); $^1$H NMR ($CDCl_3$, 500 MHz) δ 1.52–1.60 (br, 1H), 3.94 (s, 2H), 4.31 (d, 2H, $J$ = 5.8 Hz), 7.27–7.40 (m, 5H); $^{13}$C NMR ($CDCl_3$, 126 MHz) δ 40.1 (1C), 51.9 (1C), 76.5 (1C), 93.9 (1C), 127.8 (1C), 128.6 (2C), 129.0 (2C), 136.4 (1C); IR (KBr, $cm^{-1}$) 993, 1063, 1238, 1454, 1495, 1600, 2181, 3317; HRMS (ESI$^+$) *m/z* 201.0343 ([M+Na]$^+$, $C_{10}H_{10}NaOS^+$ requires 201.0345).

3-Benzylthio-2-propyn-1-yl azide (**S6**)



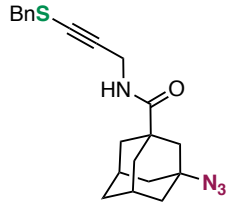

Colorless oil; TLC $R_f$ 0.72 (*n*-hexane/EtOAc = 8/1); $^1$H NMR ($CDCl_3$, 500 MHz) δ 3.96 (s, 2H), 3.98 (s, 2H), 7.27–7.39 (m, 5H), $^{13}$C NMR ($CDCl_3$, 126 MHz) δ 40.1 (1C), 41.1 (1C), 78.3 (1C), 87.4 (1C), 127.9 (1C), 128.6 (2C), 129.0 (2C), 136.2 (1C); IR (KBr, $cm^{-1}$) 1069, 1240, 1333, 1454, 1495, 2120, 2185, 2359; HRMS (ESI$^+$) *m/z* 204.0589 ([M+H]$^+$, $C_{10}H_{10}N_3S^+$ requires 204.0590).

3-Benzylthio-2-propyn-1-ylamine (**S7**)



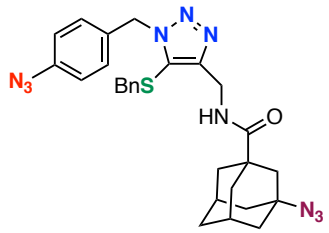

Colorless oil; TLC $R_f$ 0.14 (EtOAc); $^1$H NMR ($CDCl_3$, 500 MHz) δ 1.38–1.52 (br s, 2H), 3.48 (s, 2H), 3.92 (s, 2H), 7.27–7.37 (m, 5H); $^{13}$C NMR ($CDCl_3$, 126 MHz) δ 32.7 (1C), 40.1 (1C), 71.6 (1C), 96.3 (1C), 127.7 (1C), 128.5 (2C), 129.0 (2C), 136.7 (1C); IR (KBr, $cm^{-1}$) 912, 1452, 1495, 1601, 2178, 2920, 3028, 3366; HRMS (ESI$^+$) *m/z* 178.0680 ([M+H]$^+$, $C_{10}H_{12}NS^+$ requires 178.0685).

3-Azido-*N*-(3-benzylthio-2-propyn-1-yl)-1-adamantanamide (**9e**)



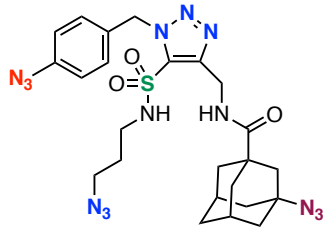
Colorless solid; Mp 66–68 °C; TLC $R_f$ 0.35 (*n*-hexane/EtOAc = 1/1); $^1$H NMR ($CDCl_3$, 500 MHz) δ 1.60–1.66 (br, 2H), 1.71–1.82 (m, 8H), 1.83–1.89 (br, 2H), 2.26–2.33 (m, 2H), 3.91 (s, 2H), 4.10 (d, 2H, *J* = 5.0 Hz), 5.70–5.78 (br, 1H), 7.26–7.38 (m, 5H); $^{13}$C NMR ($CDCl_3$, 126 MHz) δ 29.5 (2C), 30.7 (1C), 34.8 (1C), 37.8 (2C), 39.9 (1C), 40.5 (2C), 42.9 (1C), 43.0 (1C), 59.0 (1C), 73.7 (1C), 91.0 (1C), 127.8 (1C), 128.6 (2C), 129.1 (2C), 136.5 (1C), 175.4 (1C); IR (KBr, cm$^{-1}$) 1259, 1344, 1452, 1518, 1639, 2089, 2855, 2924; HRMS (ESI$^+$) *m/z* 403.1561 ([M+Na]$^+$, $C_{21}H_{24}N_4NaOS^+$ requires 403.1563).

3-Azido-*N*-(1-(4-azidobenzyl)-5-benzylthio-1*H*-1,2,3-triazol-4-ylmethyl)-1-adamantanamide (**S8**)



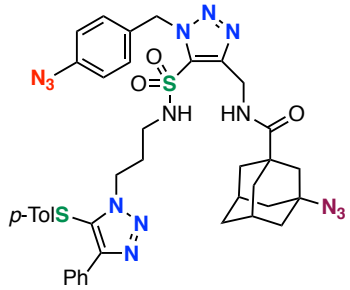
Colorless solid; Mp 120–121 °C; TLC $R_f$ 0.20 (*n*-hexane/EtOAc = 1/1); $^1$H NMR ($CDCl_3$, 500 MHz): δ 1.59–1.66 (m, 2H) 1.73–1.82 (m, 8H), 1.86–1.92 (br, 2H), 2.26–2.33 (m, 2H), 3.63 (s, 2H), 4.20 (d, 2H, *J* = 5.2 Hz), 5.13 (s, 2H), 6.23–6.33 (br, 1H), 6.84–6.91 (AA'BB', 2H), 6.95–7.02 (AA'BB', 2H), 7.19–7.31 (m, 5H); $^{13}$C NMR ($CDCl_3$, 126 MHz) δ 29.5 (2C), 34.5 (1C), 34.9 (1C), 37.8 (2C), 40.4 (1C), 40.5 (2C), 43.0 (1C), 43.1 (1C), 51.1 (1C), 59.0 (1C), 119.4 (2C), 125.4 (1C), 128.0 (1C), 128.8 (2C), 128.9 (2C), 129.7 (2C), 131.4 (1C), 136.5 (1C), 140.4 (1C), 149.3 (1C), 175.8 (1C); IR (KBr, cm$^{-1}$) 1244, 1279, 1508, 1655, 2089, 2112, 2855, 2924; HRMS (ESI$^+$) *m/z* 577.2220 ([M+Na]$^+$, $C_{28}H_{30}N_{10}NaOS^+$ requires 577.2217).

3-Azido-*N*-(1-(4-azidobenzyl)-5-(*N*-(3-azidopropylsulfamoyl)-1*H*-1,2,3-triazol-4-ylmethyl)-1-adamantanamide (**24**)



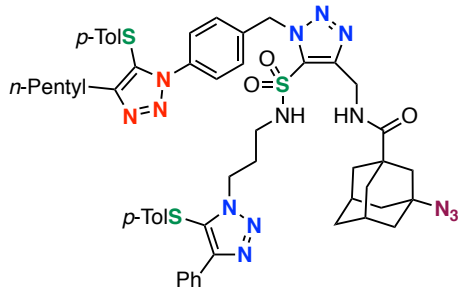
Colorless oil; TLC $R_f$ 0.50 (n-hexane/EtOAc = 1/1); $^1$H NMR ($CDCl_3$, 500 MHz) δ 1.57–1.68 (m, 5H), 1.71–1.83 (m, 9H), 2.25–2.33 (m, 2H), 2.52–2.60 (m, 2H), 3.29 (t, 2H, *J* = 6.4 Hz), 4.65 (d, 2H, *J* = 6.4 Hz), 5.80 (s, 2H), 6.76 (br t, 1H, *J* = 6.4 Hz), 6.98–7.04 (m, 2H), 7.33–7.43 (m, 3H); $^{13}$C NMR ($CDCl_3$, 126 MHz) δ 28.7 (1C), 29.4 (2C), 34.1 (1C), 34.7 (1C), 37.6 (2C), 40.1 (1C), 40.4 (2C), 42.7 (1C), 43.1 (1C), 48.2 (1C), 53.2 (1C), 58.7 (1C), 119.4 (2C), 130.1 (2C), 131.1 (1C), 133.0 (1C), 140.8 (1C), 145.2 (1C), 177.4 (1C); IR (KBr, cm$^{-1}$) 1180, 1281, 1344, 1508, 1638, 2090, 2112, 2926; HRMS (ESI$^+$) *m/z* 617.2238 ([M+Na]$^+$, $C_{24}H_{30}N_{14}NaO_3S^+$ requires 617.2238).

3-Azido-*N*-(1-(4-azidobenzyl)-5-(*N*-(3-(4-phenyl-5-(*p*-tolylthio)-1*H*-1,2,3-triazol-1-yl)propyl)sulfamoyl)-1*H*-1,2,3-triazol-4-ylmethyl)-1-adamantanamide (**S9**)



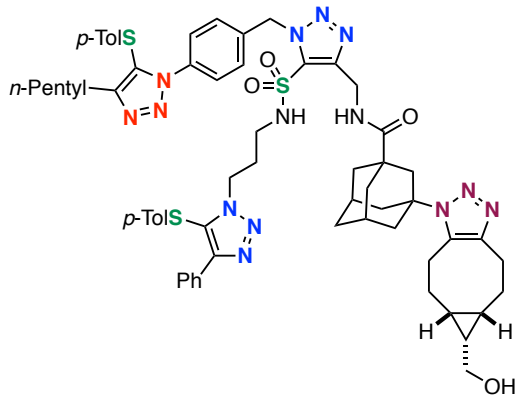
Pale yellow oil; TLC $R_f$ 0.25 (*n*-hexane/EtOAc = 3/1); $^1$H NMR ($CDCl_3$, 500 MHz) δ 1.53–1.59 (m, 2H), 1.65–1.77 (m, 8H), 1.78–1.82 (br, 2H), 1.96 (tt, 2H, $J$ = 6.8, 6.8 Hz), 2.19–2.25 (m, 2H), 2.28 (s, 3H), 2.57–2.74 (m, 2H), 4.35 (t, 2H, $J$ = 6.8 Hz), 4.64 (d, 2H, $J$ = 6.3 Hz), 5.75 (s, 2H), 6.89 (br t, 1H, $J$ = 6.3 Hz), 6.92–6.99 (m, 4H), 7.03–7.09 (m, 2H), 7.32–7.38 (m, 3H), 7.39–7.47 (m, 3H), 8.06–8.12 (m, 2H); $^{13}$C NMR ($CDCl_3$, 126 MHz) δ 21.0 (1C), 29.3 (2C), 29.4 (1C), 34.2 (1C), 34.6 (1C), 37.6 (2C), 40.0 (1C), 40.4 (2C), 42.7 (1C), 43.1 (1C), 45.2 (1C), 53.2 (1C), 58.8 (1C), 119.4 (2C), 123.3 (1C), 127.0 (2C), 127.2 (2C), 128.6 (2C), 128.7 (1C), 129.8 (1C), 130.0 (2C), 130.1 (1C), 130.5 (2C), 131.0 (1C), 132.9 (1C), 137.3 (1C), 140.7 (1C), 145.3 (1C), 150.2 (1C), 177.4 (1C); IR (KBr, cm$^{-1}$) 1180, 1279, 1344, 1508, 1637, 2088, 2112, 2924; HRMS (ESI$^+$) *m/z* 841.2897 ([M+Na]$^+$, $C_{39}H_{42}N_{14}NaO_3S_2^+$ requires 841.2898).

3-Azido-*N*-(1-(4-(4-pentyl-5-(*p*-tolylthio)-1*H*-1,2,3-triazol-1-yl)benzyl)-5-(*N*-(3-(4-phenyl-5-(*p*-tolylthio)-1*H*-1,2,3-triazol-1-yl)propyl)sulfamoyl)-1*H*-1,2,3-triazol-4-ylmethyl)-1-adamantanamide (**S10**)



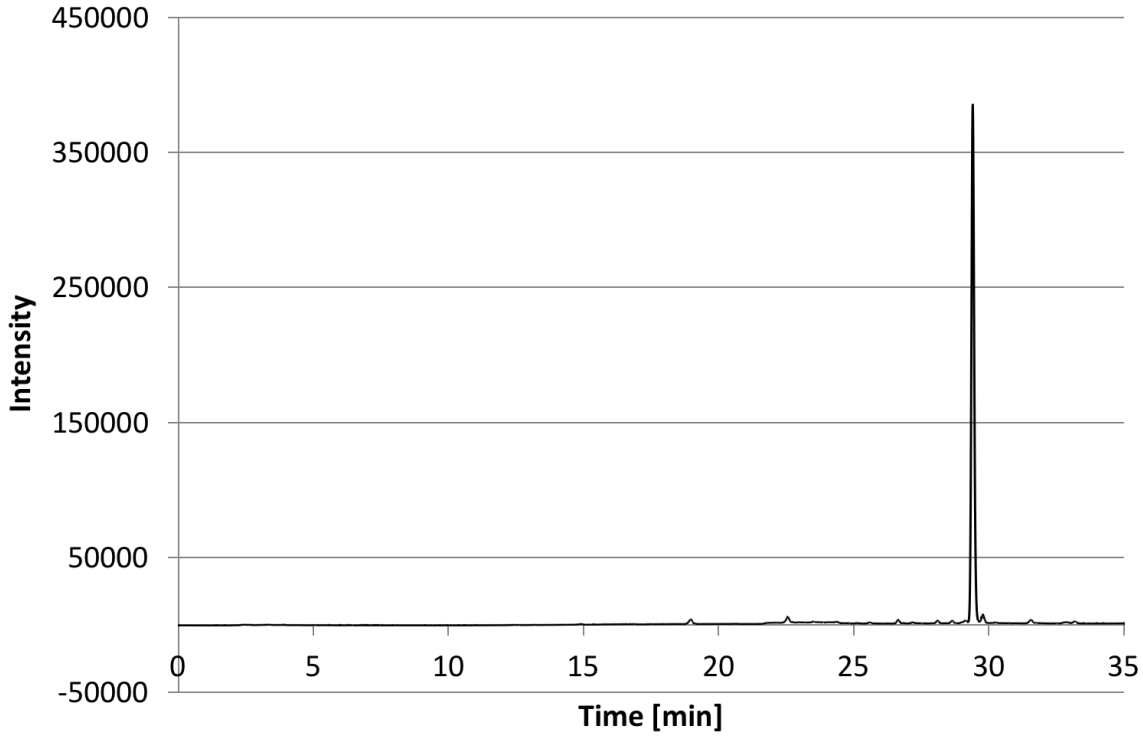
Colorless solid; Mp 65–67 °C; TLC $R_f$ 0.31 (*n*-hexane/EtOAc = 4/5); $^1$H NMR ($CDCl_3$, 500 MHz) δ 0.82–0.89 (m, 3H), 1.26–1.36 (m, 4H), 1.53–1.60 (m, 2H), 1.67–1.82 (m, 12H), 1.91–2.00 (m, 2H), 2.20–2.30 (m, 8H), 2.61–2.68 (m, 2H), 2.69–2.75 (m, 2H), 4.35 (t, 2H, $J$ = 6.7 Hz), 4.66 (d, 2H, $J$ = 6.2 Hz), 5.83 (s, 2H), 6.63 (br t, 1H, $J$ = 6.2 Hz), 6.76–6.82 (m, 2H), 6.89–6.94 (m, 2H), 6.95–7.00 (m, 2H), 7.02–7.08 (m, 2H), 7.32–7.48 (m, 8H), 8.04–8.10 (m, 2H); $^{13}$C NMR ($CDCl_3$, 126 MHz) δ 13.9 (1C), 20.91 (1C), 20.95 (1C), 22.3 (1C), 25.3 (1C), 28.7 (1C), 29.3 (2C), 29.4 (1C), 31.5 (1C), 34.2 (1C), 34.6 (1C), 37.6 (2C), 40.1 (1C), 40.4 (2C), 42.7 (1C), 43.1 (1C), 45.3 (1C), 53.1 (1C), 58.7 (1C), 123.3 (1C), 125.0 (1C), 125.6 (2C), 127.0 (2C), 127.2 (2C), 127.7 (2C), 128.6 (2C), 128.7 (1C), 129.1 (2C), 129.8 (1C), 130.1 (1C), 130.2 (2C), 130.4 (1C), 130.5 (2C), 133.1 (1C), 135.7 (1C), 136.6 (1C), 137.1 (1C), 137.2 (1C), 145.2 (1C), 150.1 (1C), 153.6 (1C), 177.4 (1C); IR (KBr, cm$^{-1}$) 1180, 1344, 1449, 1516, 1638, 2089, 2857, 2924, 3350; HRMS (ESI$^+$) *m/z* 1059.4029 ([M+Na]$^+$, $C_{53}H_{60}N_{14}NaO_3S_3^+$ requires 1059.4027).

3-((5a*S*,6*R*,6a*R*)-6-(Hydroxymethyl)-5,5a,6,6a,7,8-hexahydrocyclopropa[5,6]cycloocta[1,2-*d*][1,2,3]triazol-1-yl)-*N*-(1-(4-(4-pentyl-5-(*p*-tolylthio)-1*H*-1,2,3-triazol-1-yl)benzyl)-5-(*N*-(3-(4-phenyl-5-(*p*-tolylthio)-1*H*-1,2,3-triazol-1-yl)propyl)sulfamoyl)-1*H*-1,2,3-triazol-4-ylmethyl)-1-adamantanamide (**26**)




Colorless solid; Mp 170–173 °C; TLC $R_f$ 0.24 ($CH_2Cl_2$/MeOH = 20/1); HPLC analysis: R*t* = 29.4 min [column: Shiseido CAPCELL PAK MG II (4.6 mm i.d. × 250 mm); mobile phase: $CH_3CN$:$H_2O$ = 40:60 (0−5 min), linear gradient from 40:60 to 99:1 (5−25 min), 99:1 (25−35 min); flow rate: 1.00 mL/min; detection: UV at 254 nm]; $^1$H NMR ($CDCl_3$, 500 MHz) δ 0.79–1.01 (m, 5H), 1.10–1.19 (m, 1H), 1.22–1.36 (m, 5H), 1.38–1.53 (m, 2H), 1.59–1.75 (m, 6H), 1.76–1.89 (m, 4H), 1.91–2.00 (m, 2H), 2.16–2.41 (m, 16H), 2.62–2.68 (m, 2H), 2.69–2.75 (m, 2H), 2.76–2.90 (m, 2H), 2.94–3.03 (m, 1H), 3.09–3.19 (m, 1H), 3.56–3.66 (m, 1H), 3.67–3.78 (m, 1H), 4.31–4.39 (m, 2H), 4.64–4.72 (br, 2H), 5.83 (s, 2H), 6.74–6.82 (m, 2H), 6.87–6.93 (m, 2H), 6.94–7.00 (m, 2H), 7.01–7.07 (m, 2H), 7.32–7.47 (m, 7H), 8.03–8.09 (m, 2H); $^{13}$C NMR ($CDCl_3$, 126 MHz) δ 13.9, 19.3, 19.8, 20.91, 20.95, 21.6, 22.3, 23.3, 23.5, 24.0, 25.28, 25.33, 28.7, 29.3, 29.5, 31.5, 34.3, 34.8, 37.6, 37.7, 40.1, 40.9, 41.0, 42.9, 43.0, 45.3, 53.1, 59.7, 61.1, 123.3, 125.0, 125.6, 127.0, 127.2, 127.8, 128.6, 128.7, 129.1, 129.8, 130.0, 130.2, 130.3, 130.5, 133.0, 133.5, 135.7, 136.6, 137.1, 137.2, 145.2, 147.1, 150.1, 153.6, 177.3; IR (KBr, cm$^{-1}$) 738, 1119, 1179, 1261, 1346, 1449, 1632, 2922, 3398; HRMS (ESI$^+$) *m/z* 1187.5253 ([M+H]$^+$, $C_{63}H_{75}N_{14}O_4S_3^+$ requires 1187.5252).

HPLC chart:



## Computational Details

*General Methods*

All calculations were performed at RIKEN on Hokusai Big Waterfall (BW) using Gaussian 16 (revision C.01) program package.[S32] We employed the same theory and basis sets for the calculation as that used in the previous report for theoretical studies on the iridium-catalyzed cycloaddition reaction of methyl azide and thioalkynes.[S33] Namely, geometry optimization and trasition state (TS) calculations were carried out using the M06 level of density functional theory (DFT)[S34] in the gas phase. The effective core potentials (ECPs) of Hay and Wadt with double-ζ valence basis sets (LanL2DZ)[S35] were employed to describe Ir. The 6-31G(d) basis set was used for N, Cl, and S as well as the C atoms in the alkynes and double bonds of 1,5-cyclooctadiene (cod). The 6-31G basis set was used for all other atoms. Harmonic frequency calculations were conducted at the same level of theory on the optimized geometries to check all the stationary points as either minima or first-order saddle points and to provide relative free energies (298.15 K, 1 atm, gas phase). Intrinsic reaction coordinate (IRC) calculations[S36] were carried out to confirm the transition states connecting the correct reactants and products on the potential energy surface. The zero-point energy (ZPE) and thermal energy corrections were calculated using vibrational frequencies. Computed structures are illustrated using CYL-view.[S37]

*Energy profiles*

Jia, Sun, and Lin have precisely investigated the iridium-catalyzed cycloaddition reaction of methyl azide and thioalkynes and indicated several possible mechanisms.[S33] Since they fixed methyl azide as a substrate in the study, we conducted DFT calculation to elucidate the substituent effects of organic azides by calculating activation energies of the reactions of **2a** or **3a** with **9a** (Table 1, entry 9). According to the literature, we focused on five possible pathways A-1, A-2, B-1, B-2, and B-3 (Figs. S1 and S2) and drew their energy profiles (Figs. S3–S7). In these figures, ligand L–L and R indicate 1,5-cyclooctadiene and the substituent of the azides (R = Bn for **2a** or Ph for **3a**), respectively. Fig. 2 in the main text was prepared based on pathway A-1 (Fig. S3).

Overall, pathways A-1 and B-1 show the lowest activation energies (15.1 kcal/mol for **2a**, 19.1 kcal/mol for **3a**) and are responsible for the reactions. These mechanisms are almost similar, except the direction of thioalkyne **9a**. Through the mechanisms, the free energy levels of all the intermediates and transition states with **3a** are higher than that for the corresponding states with **2a**. The larger energies would be needed for more resonance-stablized aromatic azido group to be twisted out of the aromatic plane in the reaction intermediate and transition state structures, as discussed in the main text.

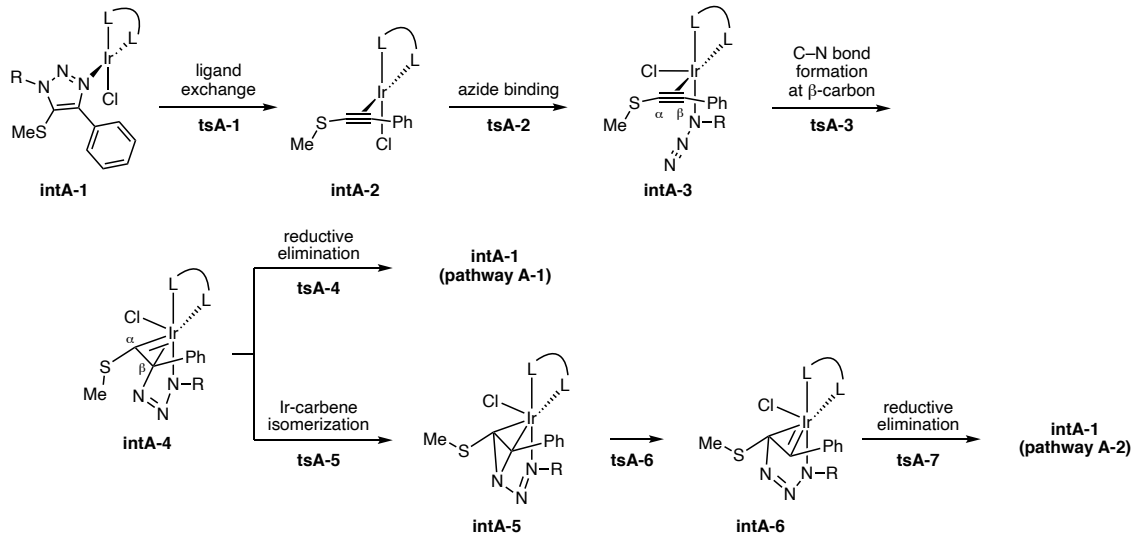



**Fig. S1** Schematic summary of reaction pathways A-1 and A-2.

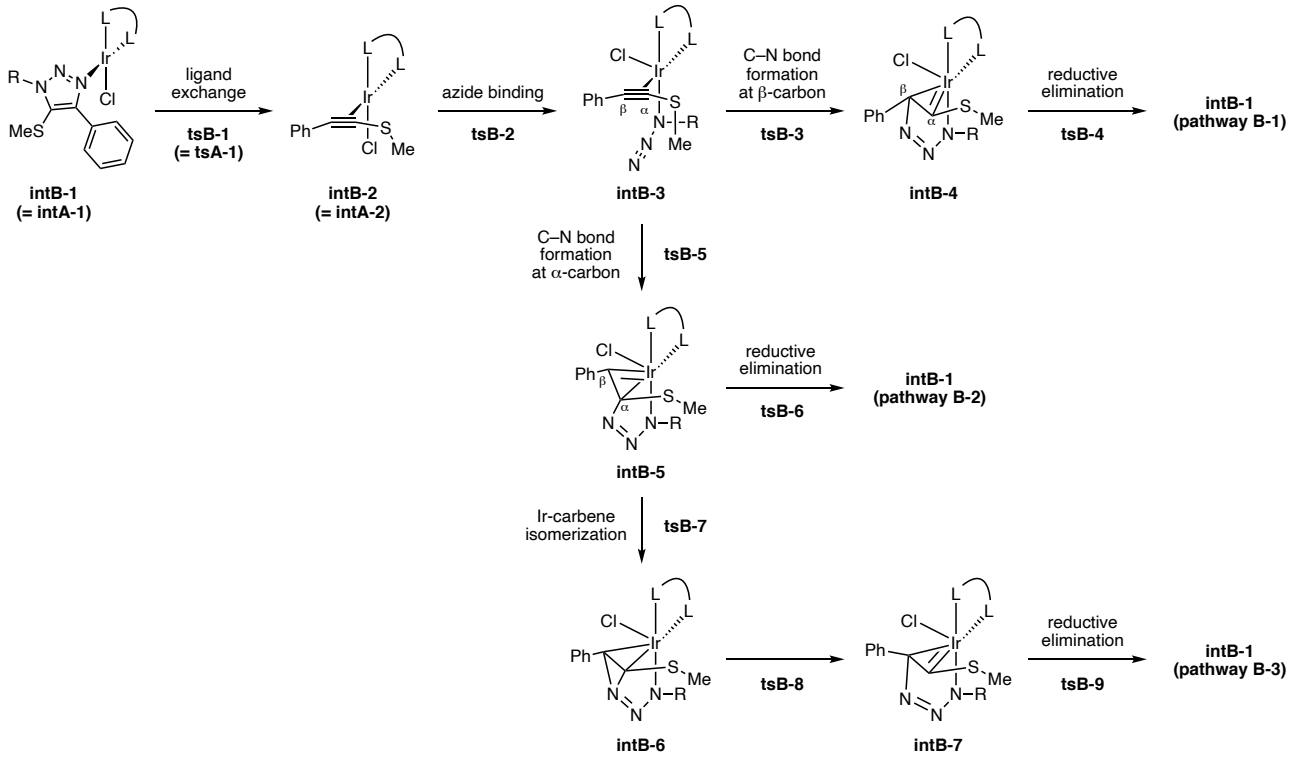



**Fig. S2** Schematic summary of reaction pathways B-1, B-2, and B-3.

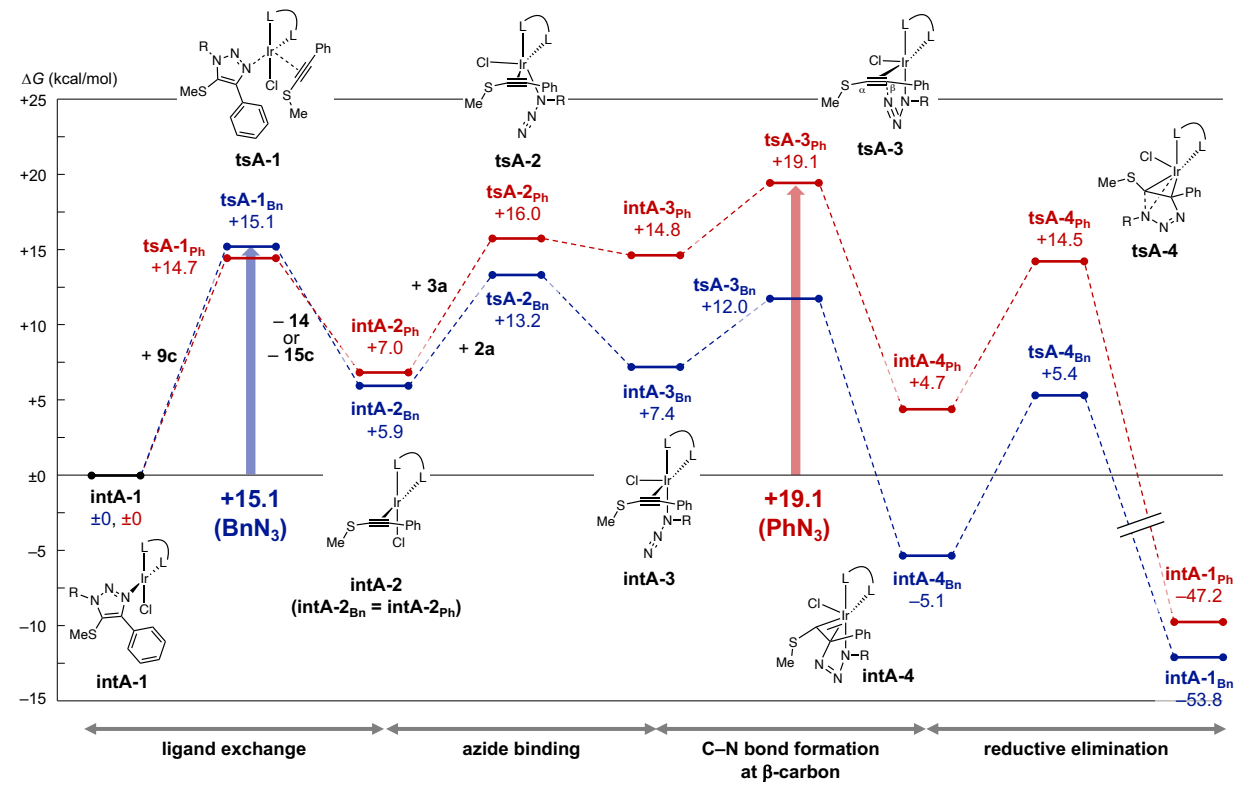



**Fig. S3** Energy profile for pathway A-1.

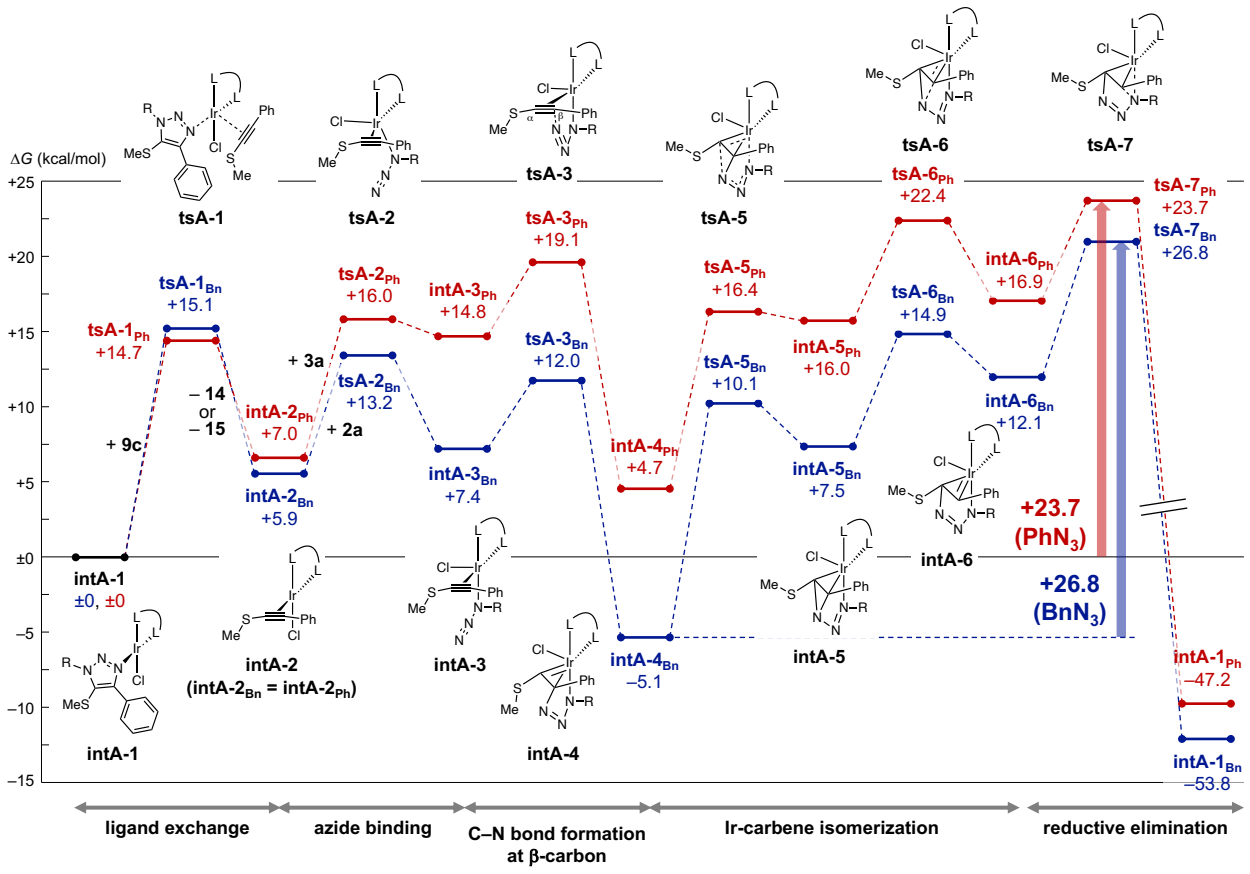



**Fig. S4** Energy profile for pathway A-2.

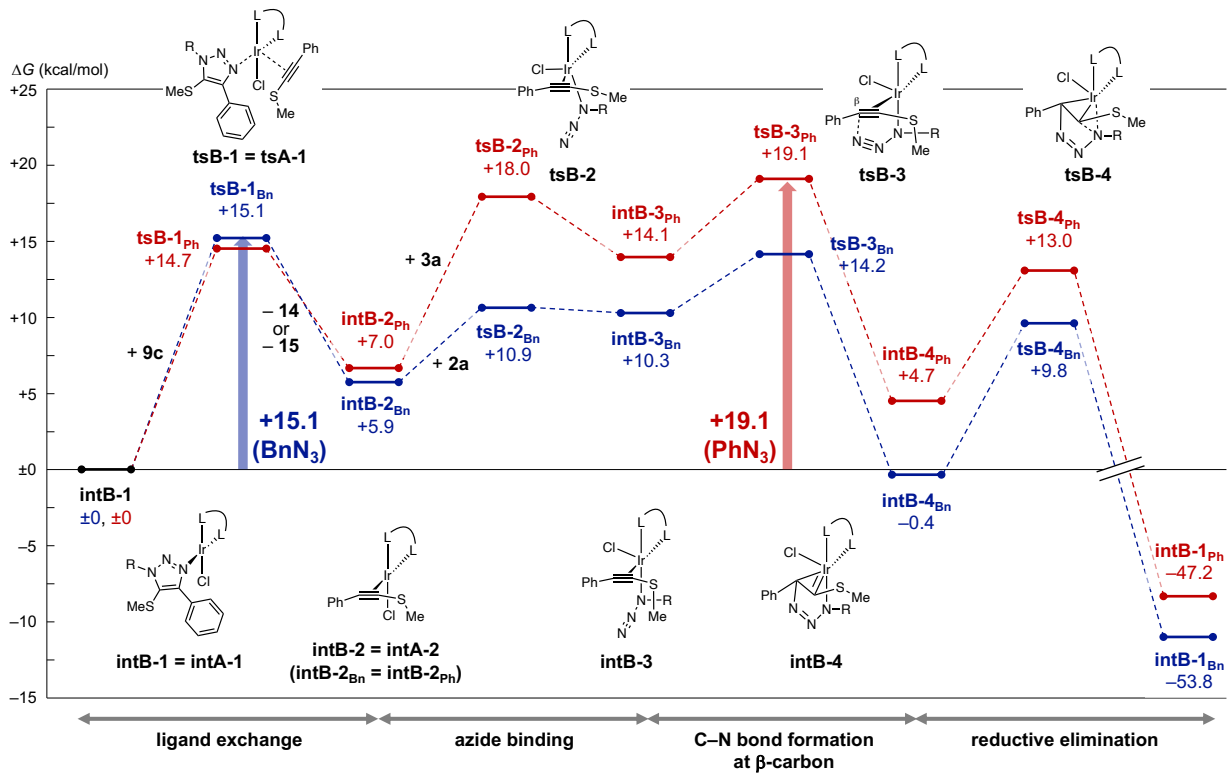



**Fig. S5** Energy profile for pathway B-1.

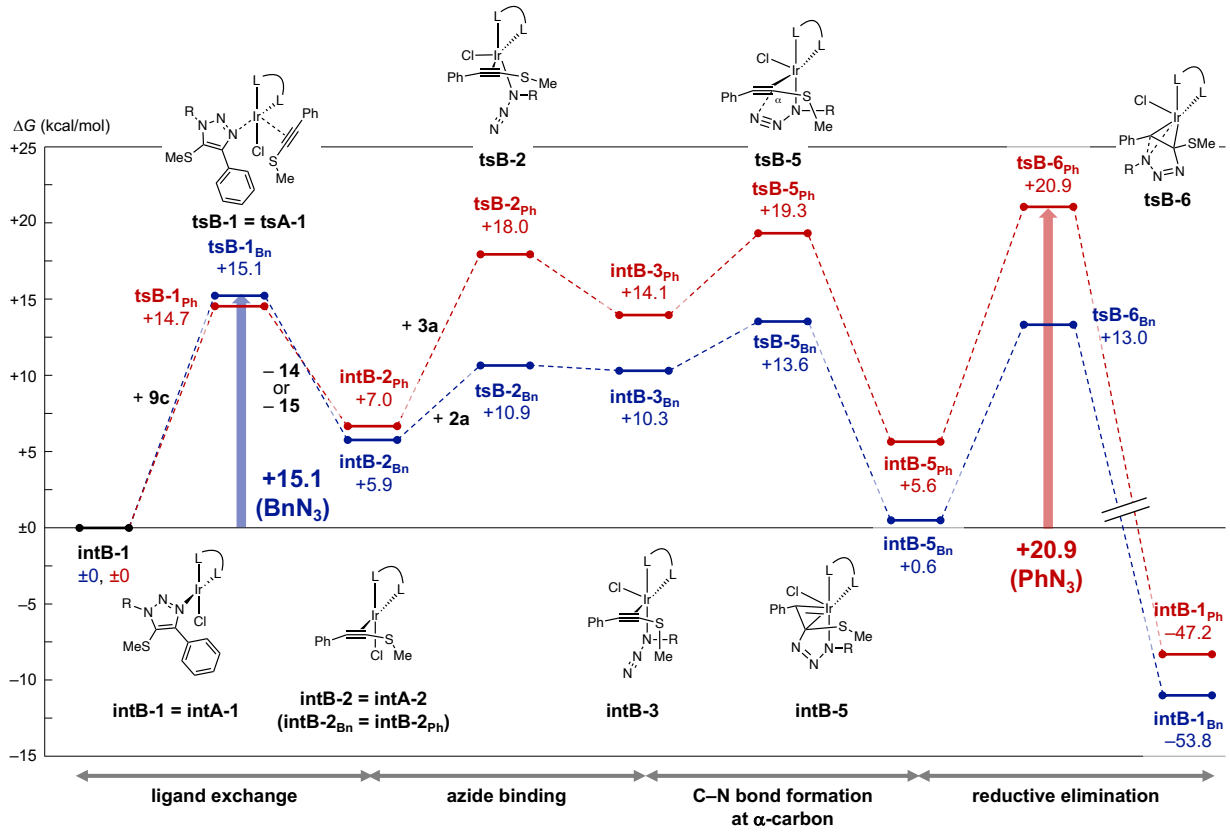



**Fig. S6** Energy profile for pathway B-2.

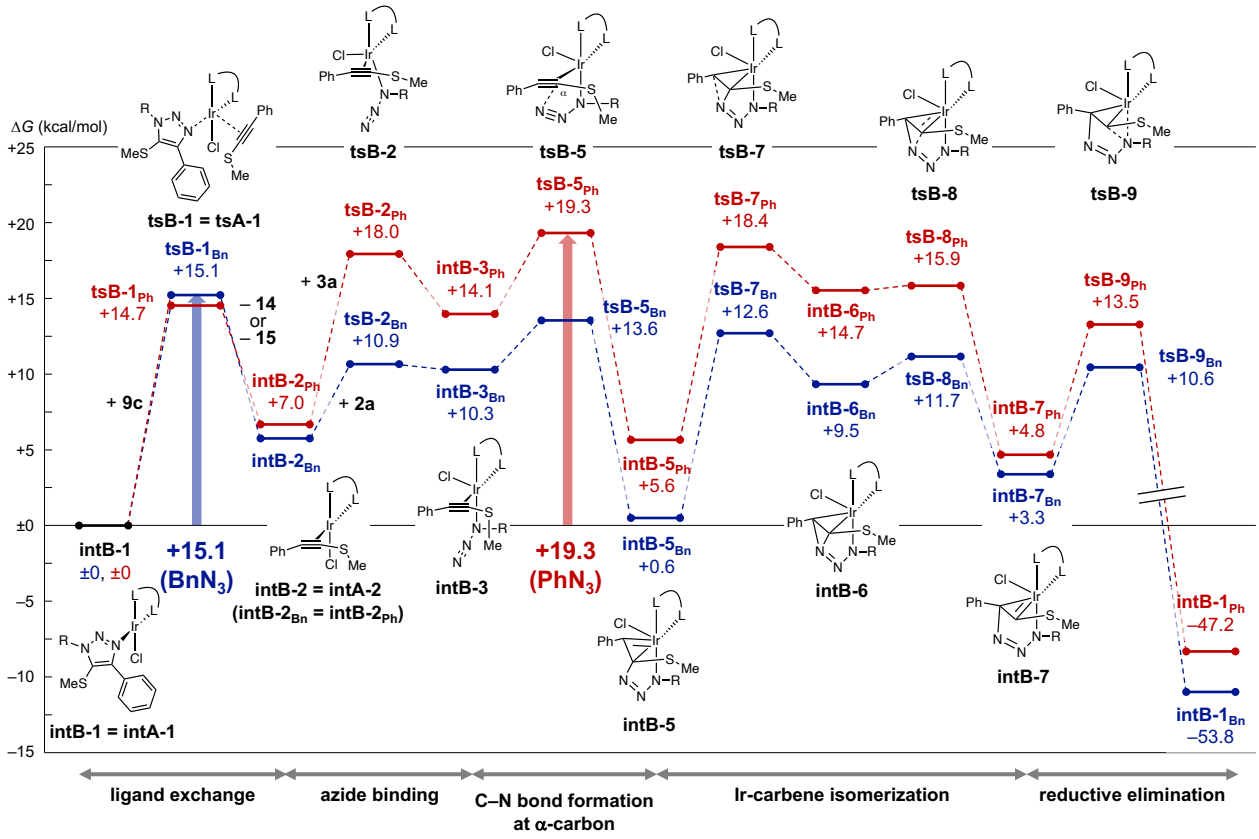



**Fig. S7** Energy profile for pathway B-3.

**Table S1. Calculated energies of the optimized structures (in Hartree).** *ZPVE*: zero-point vibrational energy, *TCH*: thermal correction to enthalpy, *TCG*: thermal correction to Gibbs free energy, *E*: Sum of electronic and thermal energies, *H*: Sum of electronic and thermal enthalpies, *G*: Sum of electronic and thermal Gibbs free energies.

| Structure | Imaginary frequency ($cm^{-1}$) | *ZPVE* | *TCH* | *TCG* | *E* | *H* | *G* |
|---|---|---|---|---|---|---|---|
| **2a** | | 0.133617 | 0.142901 | 0.098680 | -434.633532 | -434.632588 | -434.676808 |
| **3a** | | 0.104921 | 0.112760 | 0.073023 | -395.398054 | -395.397110 | -395.436846 |
| **9a** | | 0.140683 | 0.151433 | 0.103490 | -745.381204 | -745.380260 | -745.428202 |
| **14** | | 0.281050 | 0.299106 | 0.233490 | -1180.126022 | -1180.125077 | -1180.190693 |
| **15** | | 0.252088 | 0.268799 | 0.207500 | -1140.879976 | -1140.879032 | -1140.940331 |
| **intA-1$_{Bn}$** | | 0.467259 | 0.496791 | 0.403186 | -2056.626827 | -2056.625883 | -2056.719488 |
| **intA-2$_{Bn}$** | | 0.326423 | 0.348550 | 0.273289 | -1621.873282 | -1621.872338 | -1621.947599 |
| **intA-3$_{Bn}$** | | 0.462304 | 0.493554 | 0.398560 | -2056.528040 | -2056.527096 | -2056.622090 |
| **intA-4$_{Bn}$** | | 0.464711 | 0.494210 | 0.405026 | -2056.553760 | -2056.552816 | -2056.642000 |
| **intA-5$_{Bn}$** | | 0.464898 | 0.494140 | 0.405914 | -2056.534631 | -2056.533686 | -2056.621912 |
| **intA-6$_{Bn}$** | | 0.464159 | 0.493974 | 0.403827 | -2056.525319 | -2056.524375 | -2056.614522 |
| **tsA-1$_{Bn}$** | -72.88 | 0.609775 | 0.649371 | 0.536065 | -2802.011262 | -2802.010318 | -2802.123625 |
| **tsA-2$_{Bn}$** | -29.63 | 0.461825 | 0.492717 | 0.397782 | -2056.518775 | -2056.517831 | -2056.612766 |
| **tsA-3$_{Bn}$** | -175.72 | 0.462303 | 0.492293 | 0.401543 | -2056.524891 | -2056.523947 | -2056.614697 |
| **tsA-4$_{Bn}$** | -378.48 | 0.463908 | 0.492835 | 0.404786 | -2056.538095 | -2056.537151 | -2056.625199 |
| **tsA-5$_{Bn}$** | -375.15 | 0.463803 | 0.492846 | 0.404328 | -2056.530082 | -2056.529138 | -2056.617656 |
| **tsA-6$_{Bn}$** | -296.57 | 0.463585 | 0.492663 | 0.404721 | -2056.523087 | -2056.522143 | -2056.610084 |
| **tsA-7$_{Bn}$** | -195.23 | 0.463840 | 0.492641 | 0.405963 | -2056.513578 | -2056.512634 | -2056.599312 |
| **intA-1$_{Ph}$** | | 0.438267 | 0.466536 | 0.376997 | -2017.382235 | -2017.381291 | -2017.470830 |
| **intA-2$_{Ph}$** | = **intA-2$_{Bn}$** | | | | | | |
| **intA-3$_{Ph}$** | | 0.434003 | 0.463806 | 0.372435 | -2017.281543 | -2017.280599 | -2017.371970 |
| **intA-4$_{Ph}$** | | 0.435328 | 0.463733 | 0.376802 | -2017.302132 | -2017.301188 | -2017.388118 |
| **intA-5$_{Ph}$** | | 0.435449 | 0.463630 | 0.377672 | -2017.285014 | -2017.284070 | -2017.370028 |
| **intA-6$_{Ph}$** | | 0.434459 | 0.463391 | 0.374257 | -2017.280392 | -2017.279448 | -2017.368582 |
| **tsA-1$_{Ph}$** | -65.49 | 0.580746 | 0.619010 | 0.509603 | -2762.767142 | -2762.766198 | -2762.875606 |
| **tsA-2$_{Ph}$** | -45.51 | 0.432669 | 0.462228 | 0.370180 | -2017.278951 | -2017.278007 | -2017.370056 |
| **tsA-3$_{Ph}$** | -120.35 | 0.433656 | 0.462216 | 0.375255 | -2017.279032 | -2017.278088 | -2017.365048 |
| **tsA-4$_{Ph}$** | -305.83 | 0.435068 | 0.462723 | 0.378133 | -2017.288808 | -2017.287864 | -2017.372455 |
| **tsA-5$_{Ph}$** | -321.78 | 0.434888 | 0.462604 | 0.377924 | -2017.285720 | -2017.284776 | -2017.369456 |
| **tsA-6$_{Ph}$** | -327.62 | 0.433926 | 0.462037 | 0.375907 | -2017.274613 | -2017.273668 | -2017.359798 |
| **tsA-7$_{Ph}$** | -152.94 | 0.434510 | 0.462351 | 0.376726 | -2017.273115 | -2017.272171 | -2017.357796 |

## Table S1 (continued).

| Structure | Imaginary frequency ($cm^{-1}$) | *ZPVE* | *TCH* | *TCG* | *E* | *H* | *G* |
|---|---|---|---|---|---|---|---|
| **intB-1$_{Bn}$** | = **intA-1$_{Bn}$** | | | | | | |
| **intB-2$_{Bn}$** | = **intA-2$_{Bn}$** | | | | | | |
| **intB-3$_{Bn}$** | | 0.463300 | 0.494235 | 0.399981 | -2056.524110 | -2056.523166 | -2056.617420 |
| **intB-4$_{Bn}$** | | 0.464346 | 0.493944 | 0.404450 | -2056.545814 | -2056.544870 | -2056.634364 |
| **intB-5$_{Bn}$** | | 0.464816 | 0.494434 | 0.404720 | -2056.544054 | -2056.543109 | -2056.632824 |
| **intB-6$_{Bn}$** | | 0.464507 | 0.493995 | 0.404158 | -2056.529832 | -2056.528887 | -2056.618724 |
| **intB-7$_{Bn}$** | | 0.464095 | 0.493918 | 0.403080 | -2056.538641 | -2056.537696 | -2056.628535 |
| **tsB-1$_{Bn}$** | = **tsA-1$_{Bn}$** | | | | | | |
| **tsB-2$_{Bn}$** | -48.46 | 0.462490 | 0.492845 | 0.401561 | -2056.526132 | -2056.525188 | -2056.616473 |
| **tsB-3$_{Bn}$** | -111.85 | 0.462595 | 0.492436 | 0.402127 | -2056.521782 | -2056.520838 | -2056.611146 |
| **tsB-4$_{Bn}$** | -162.99 | 0.463476 | 0.492499 | 0.404896 | -2056.531578 | -2056.530634 | -2056.618237 |
| **tsB-5$_{Bn}$** | -222.77 | 0.463004 | 0.492722 | 0.402684 | -2056.523024 | -2056.522080 | -2056.612117 |
| **tsB-6$_{Bn}$** | -325.28 | 0.464104 | 0.493028 | 0.405559 | -2056.526544 | -2056.525600 | -2056.613069 |
| **tsB-7$_{Bn}$** | -396.79 | 0.464002 | 0.492987 | 0.404546 | -2056.526259 | -2056.525315 | -2056.613756 |
| **tsB-8$_{Bn}$** | -457.95 | 0.463114 | 0.492442 | 0.403092 | -2056.526766 | -2056.525822 | -2056.615172 |
| **tsB-9$_{Bn}$** | -214.11 | 0.463779 | 0.492576 | 0.405491 | -2056.530757 | -2056.529813 | -2056.616898 |
| **intB-1$_{Ph}$** | = **intA-1$_{Ph}$** | | | | | | |
| **intB-2$_{Ph}$** | = **intA-2$_{Bn}$** | | | | | | |
| **intB-3$_{Ph}$** | | 0.433985 | 0.463701 | 0.373596 | -2017.283999 | -2017.283054 | -2017.373159 |
| **intB-4$_{Ph}$** | | 0.435292 | 0.463728 | 0.376877 | -2017.302097 | -2017.301153 | -2017.388005 |
| **intB-5$_{Ph}$** | | 0.435526 | 0.463892 | 0.377501 | -2017.301161 | -2017.300217 | -2017.386608 |
| **intB-6$_{Ph}$** | | 0.435981 | 0.463982 | 0.378788 | -2017.287880 | -2017.286936 | -2017.372129 |
| **intB-7$_{Ph}$** | | 0.435356 | 0.463761 | 0.377005 | -2017.302099 | -2017.301155 | -2017.387910 |
| **tsB-1$_{Ph}$** | = **tsA-1$_{Ph}$** | | | | | | |
| **tsB-2$_{Ph}$** | -57.91 | 0.433287 | 0.462566 | 0.372058 | -2017.277252 | -2017.276308 | -2017.366815 |
| **tsB-3$_{Ph}$** | -120.35 | 0.433657 | 0.462217 | 0.375257 | -2017.279031 | -2017.278087 | -2017.365047 |
| **tsB-4$_{Ph}$** | -160.36 | 0.434256 | 0.462192 | 0.375850 | -2017.289383 | -2017.288438 | -2017.374781 |
| **tsB-5$_{Ph}$** | -132.45 | 0.433620 | 0.462216 | 0.375351 | -2017.278897 | -2017.277953 | -2017.364817 |
| **tsB-6$_{Ph}$** | -292.00 | 0.434499 | 0.462372 | 0.376913 | -2017.277668 | -2017.276724 | -2017.362183 |
| **tsB-7$_{Ph}$** | -392.07 | 0.434865 | 0.462620 | 0.377524 | -2017.282019 | -2017.281074 | -2017.366170 |
| **tsB-8$_{Ph}$** | -449.37 | 0.434799 | 0.462588 | 0.377861 | -2017.286404 | -2017.285460 | -2017.370187 |
| **tsB-9$_{Ph}$** | -157.77 | 0.434335 | 0.462185 | 0.376673 | -2017.289475 | -2017.288531 | -2017.374043 |

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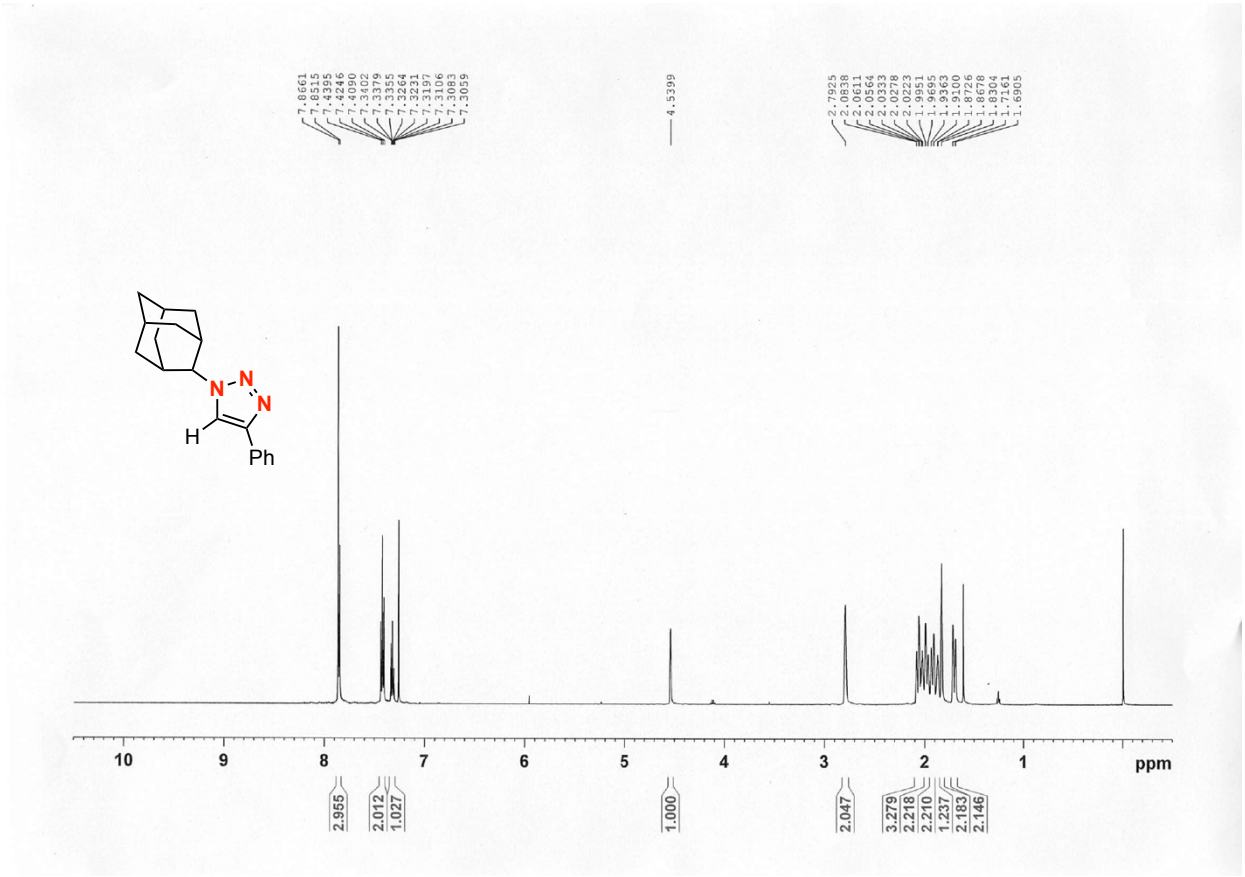
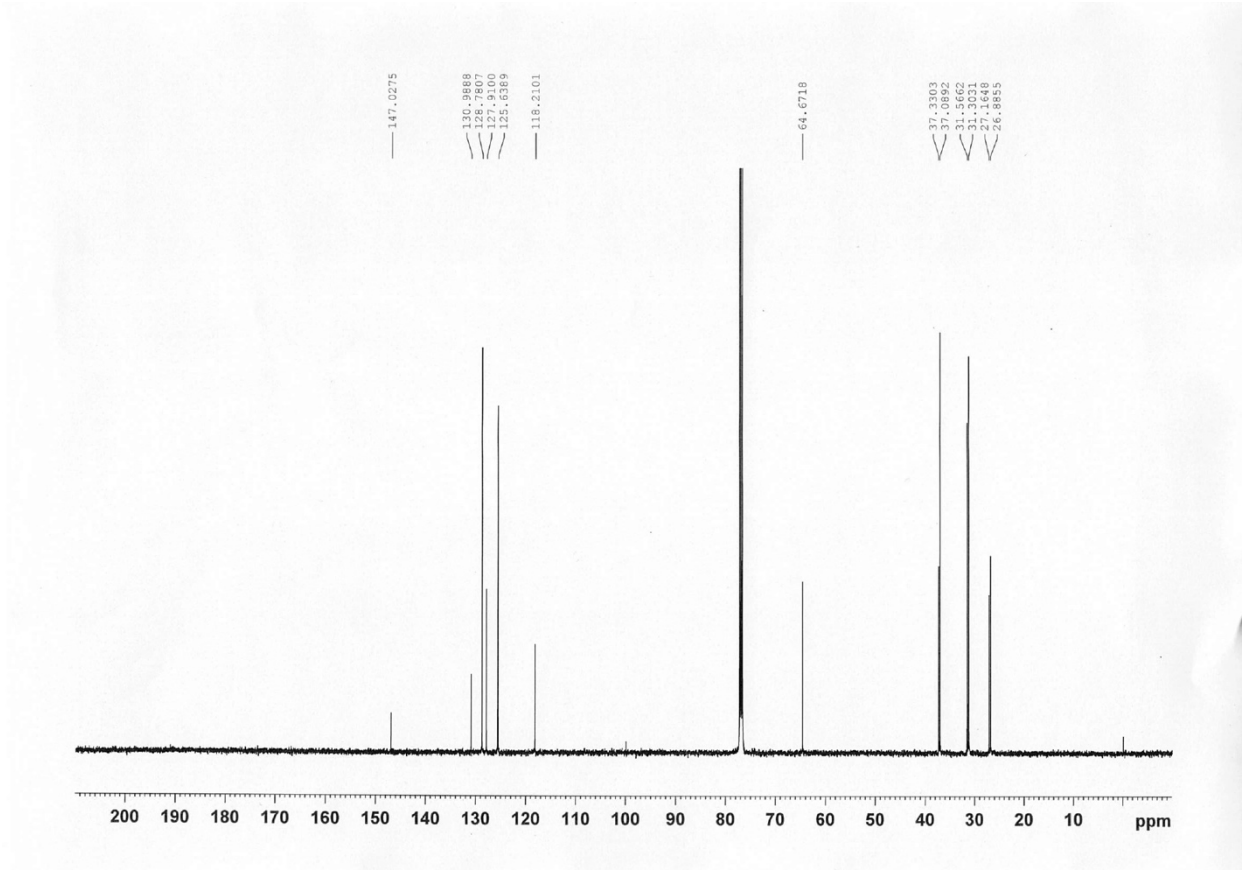
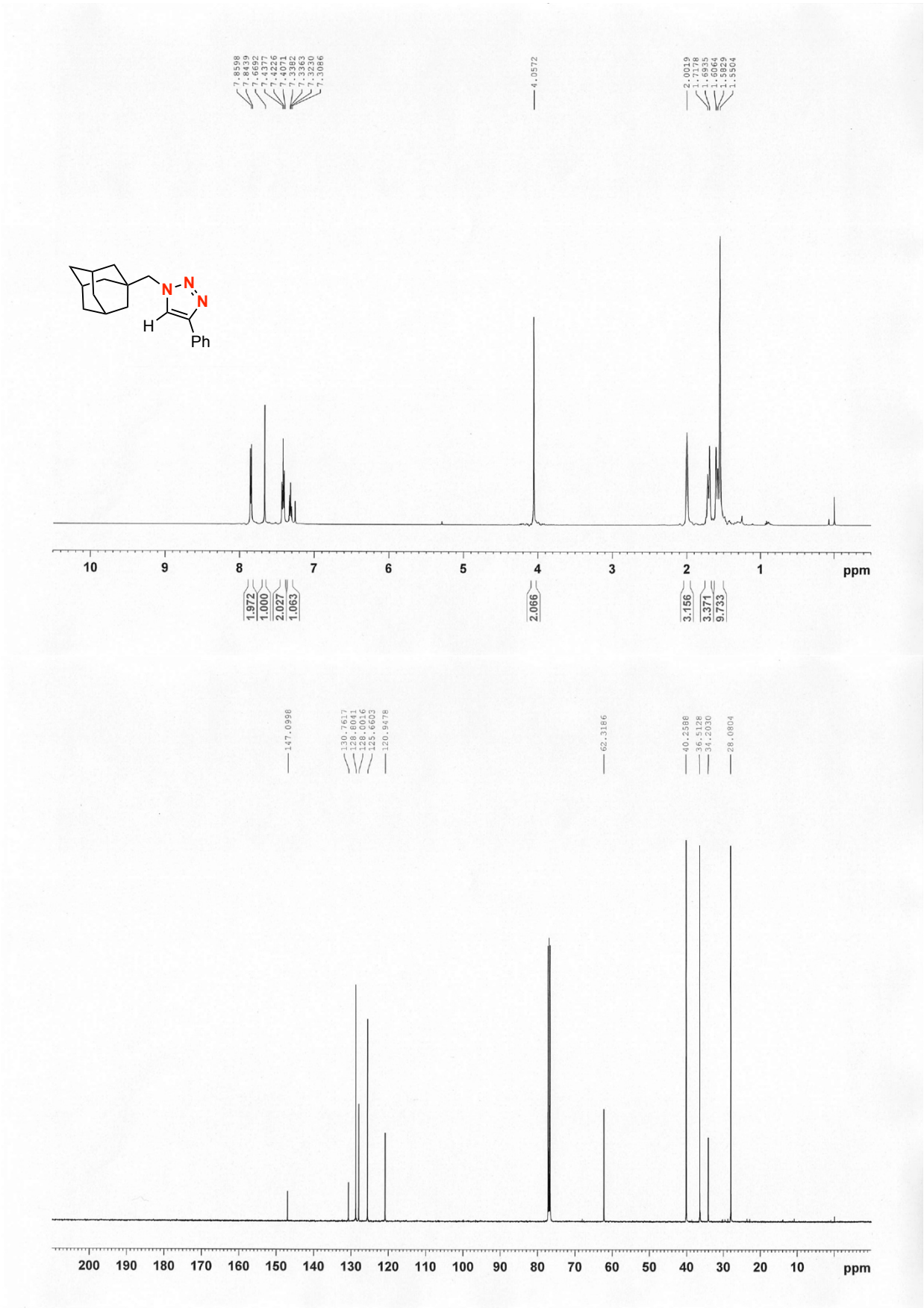
**NMR Spectra of New Compounds**

$^{1}$H NMR (500 MHz) and $^{13}$C NMR (126 MHz) spectra of 1-(2-adamantyl)-4-phenyl-1*H*-1,2,3-triazole (**7c**) ($CDCl_3$)

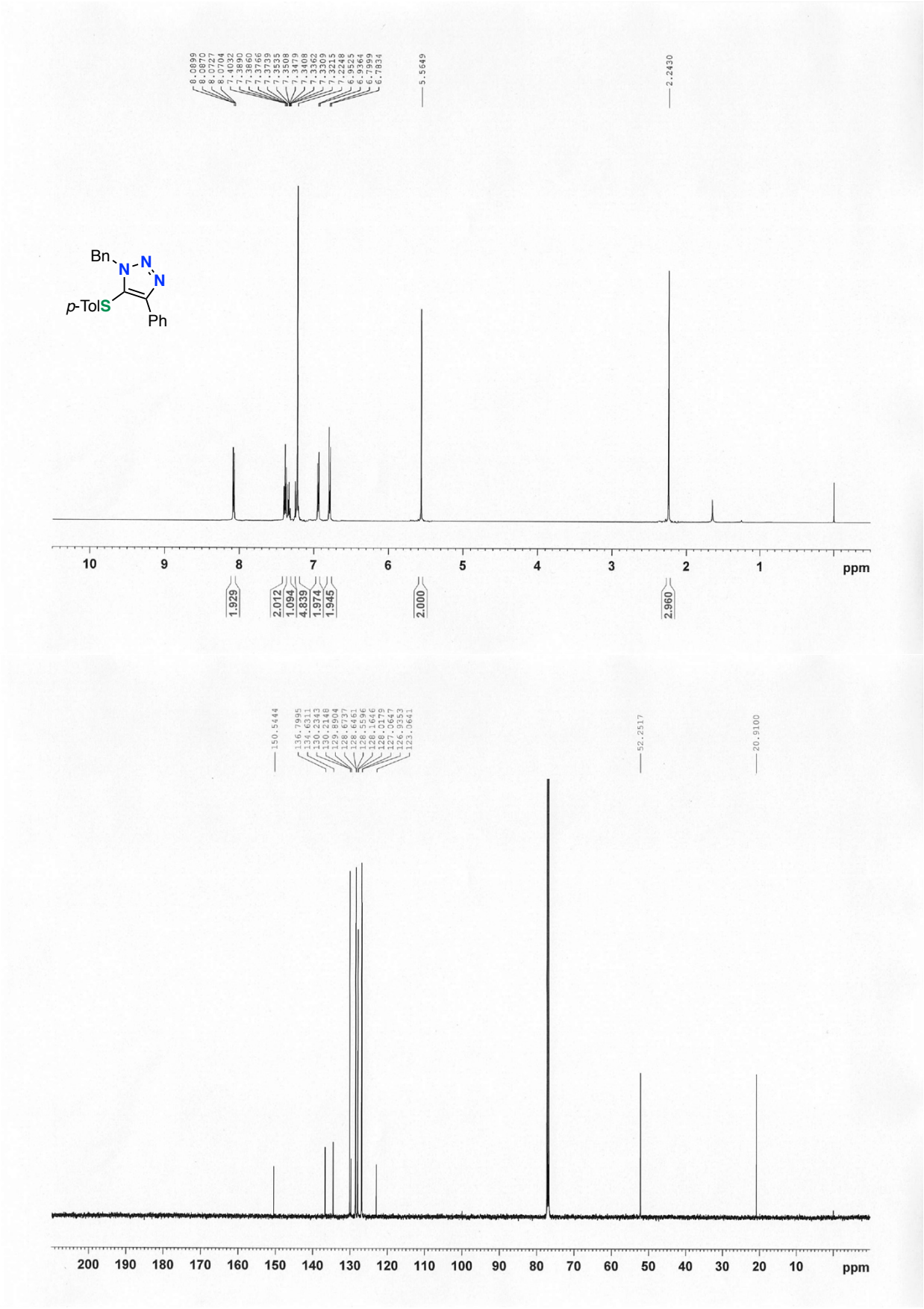


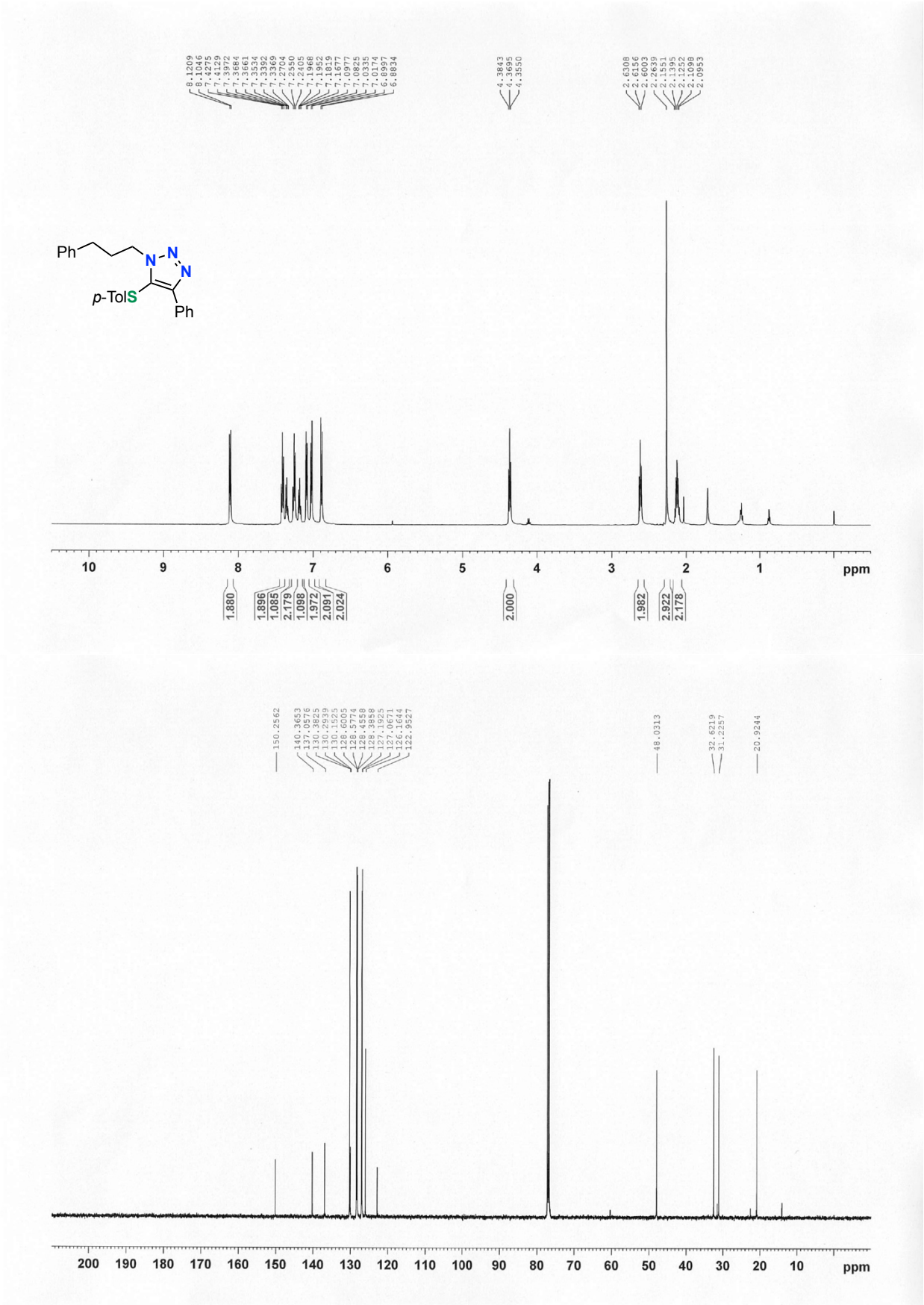
$^{1}$H NMR (500 MHz) and $^{13}$C NMR (126 MHz) spectra of 1-(1-adamantylmethyl)-4-phenyl-1*H*-1,2,3-triazole (**7e**) ($CDCl_3$)



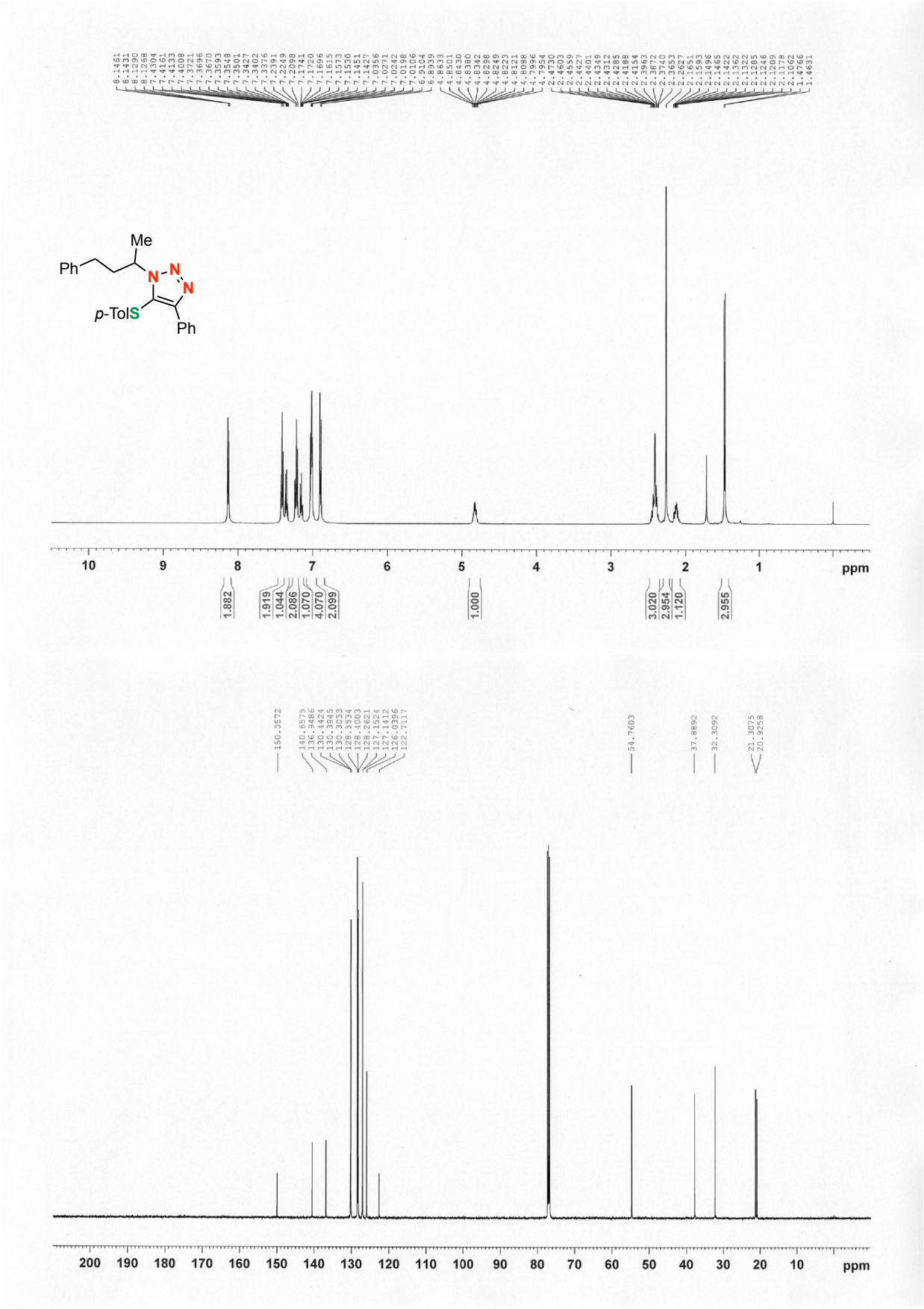
$^{1}$H NMR (500 MHz) and $^{13}$C NMR (126 MHz) spectra of 1-benzyl-4-phenyl-5-(*p*-tolylthio)-1*H*-1,2,3-triazole (**10a**) ($CDCl_3$)



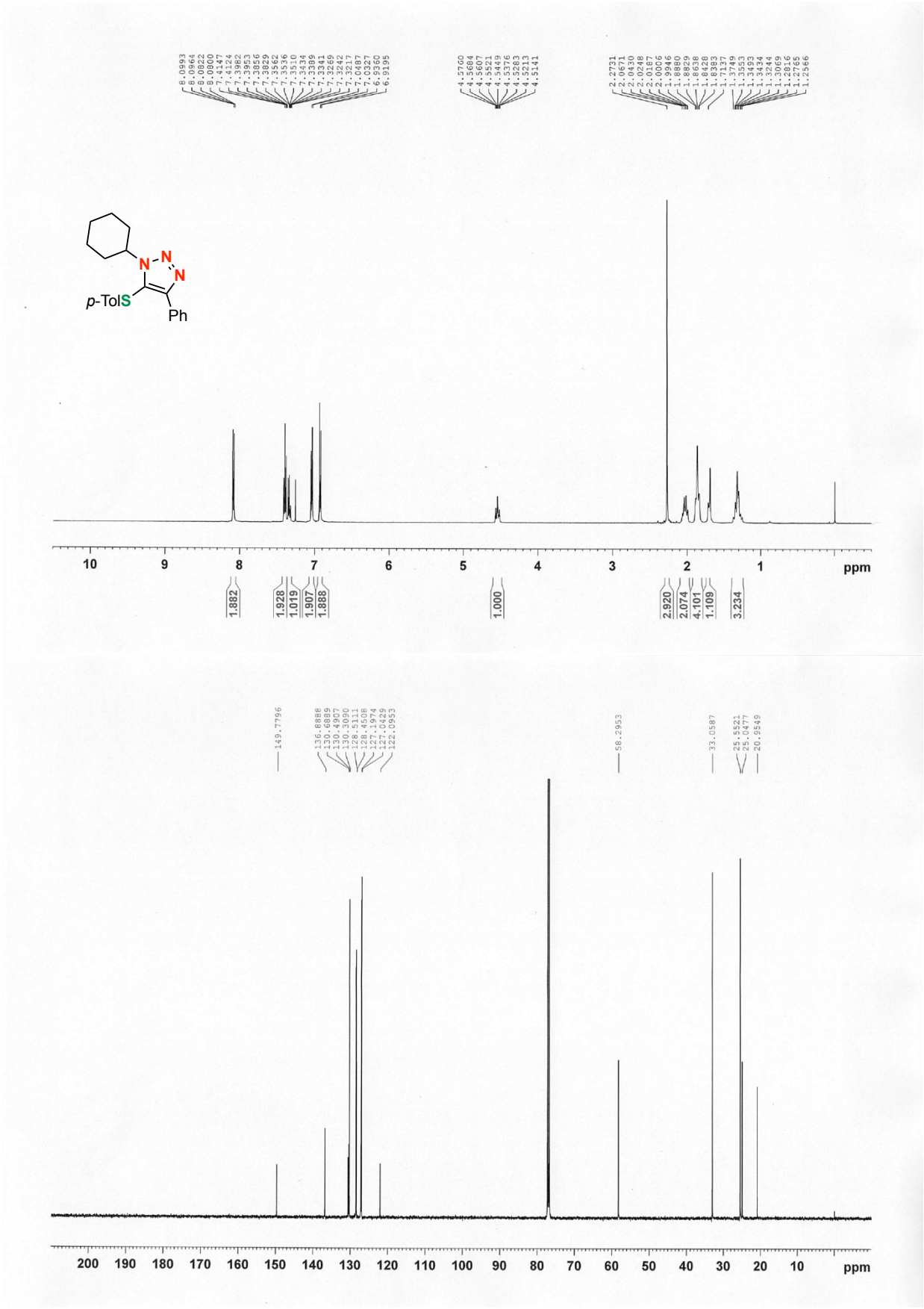
$^{1}$H NMR (500 MHz) and $^{13}$C NMR (126 MHz) spectra of 4-phenyl-1-(3-phenylpropyl)-5-(*p*-tolylthio)-1*H*-1,2,3-triazole (**10b**) ($CDCl_3$)



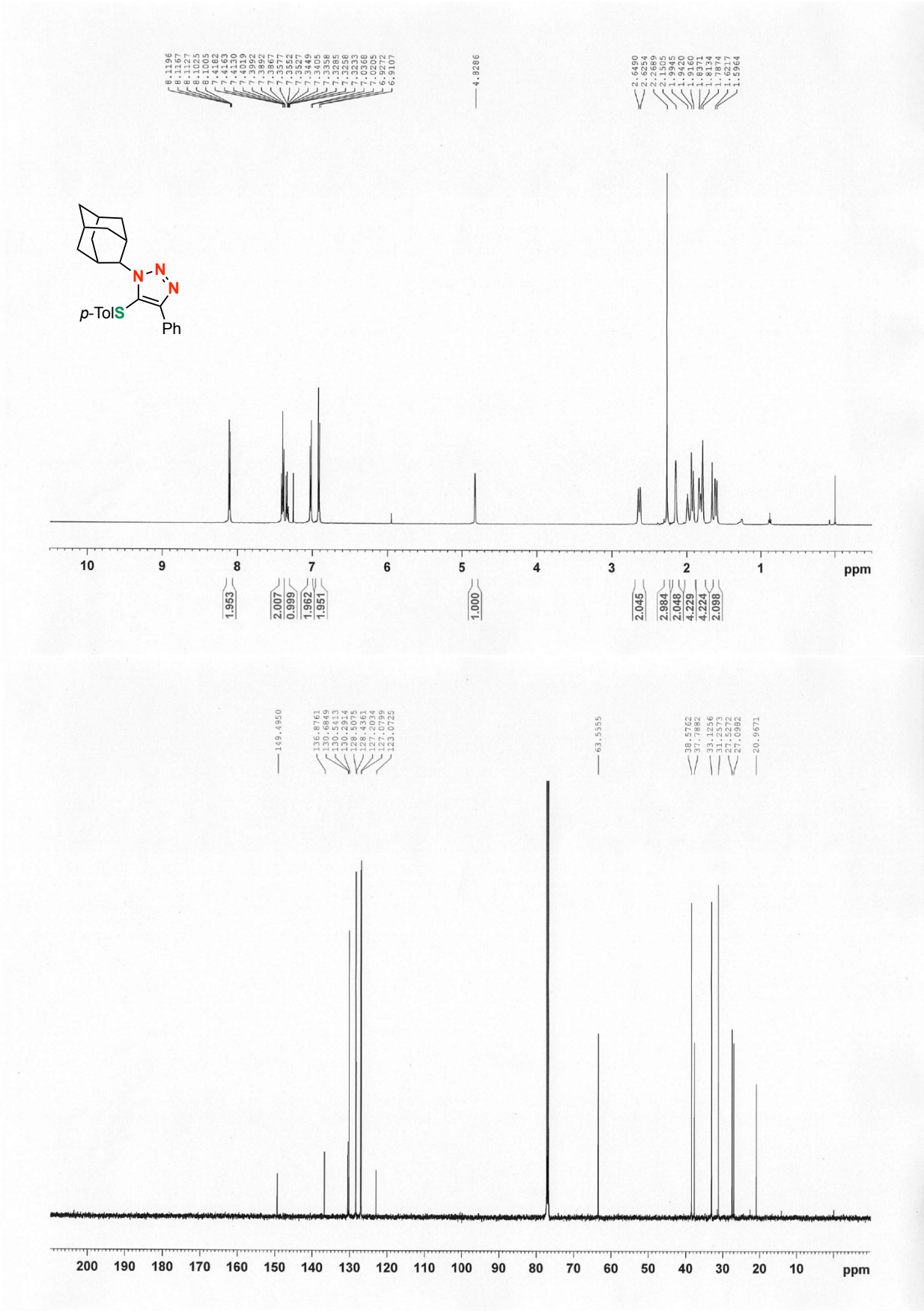
$^{1}$H NMR (500 MHz) and $^{13}$C NMR (126 MHz) spectra of 4-phenyl-1-(4-phenyl-2-butanyl)-5-(*p*-tolylthio)-1*H*-1,2,3-triazole (**10c**) ($CDCl_3$)



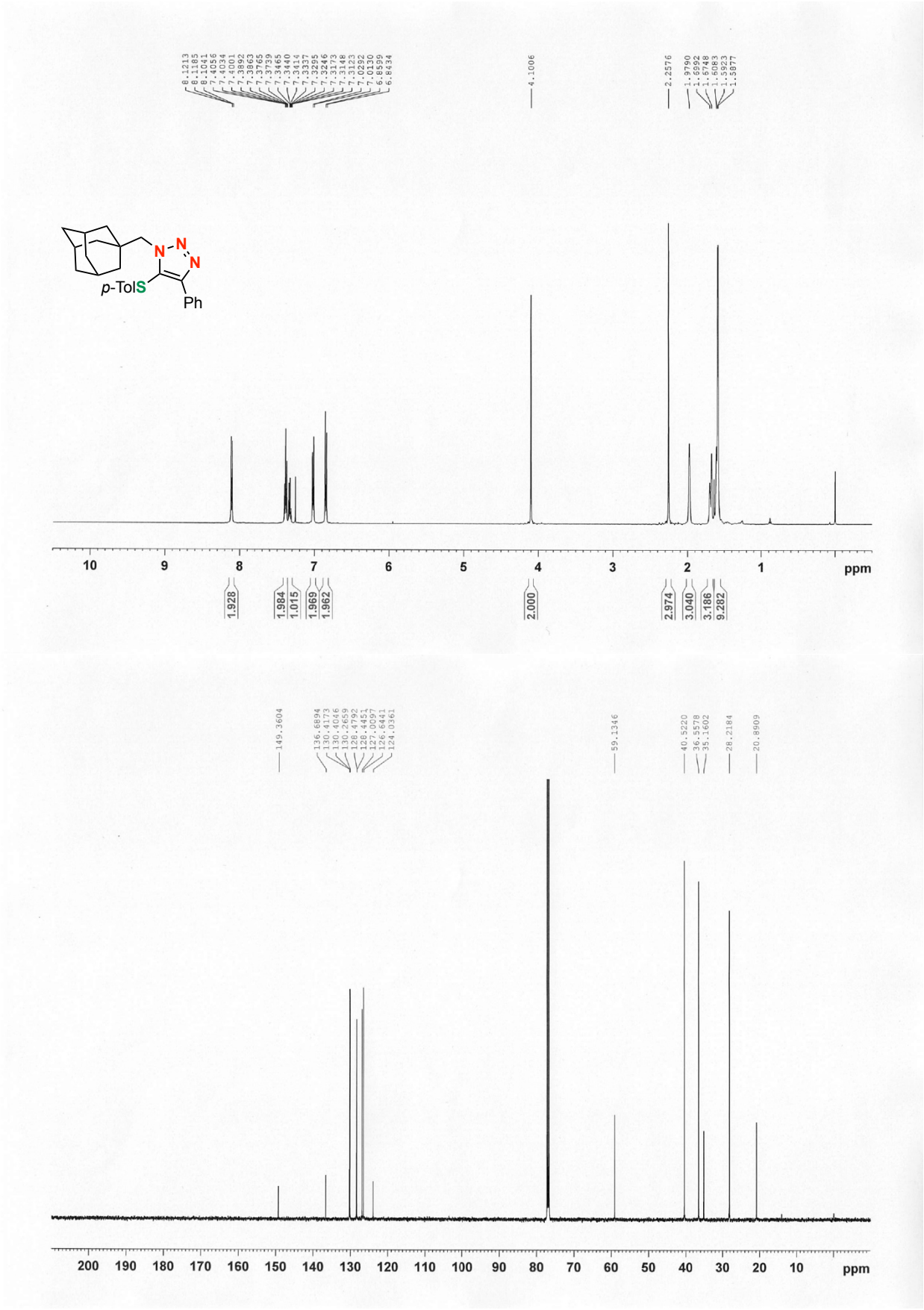
$^{1}$H NMR (500 MHz) and $^{13}$C NMR (126 MHz) spectra of 1-cyclohexyl-4-phenyl-5-(*p*-tolylthio)-1*H*-1,2,3-triazole (**10e**) ($CDCl_3$)



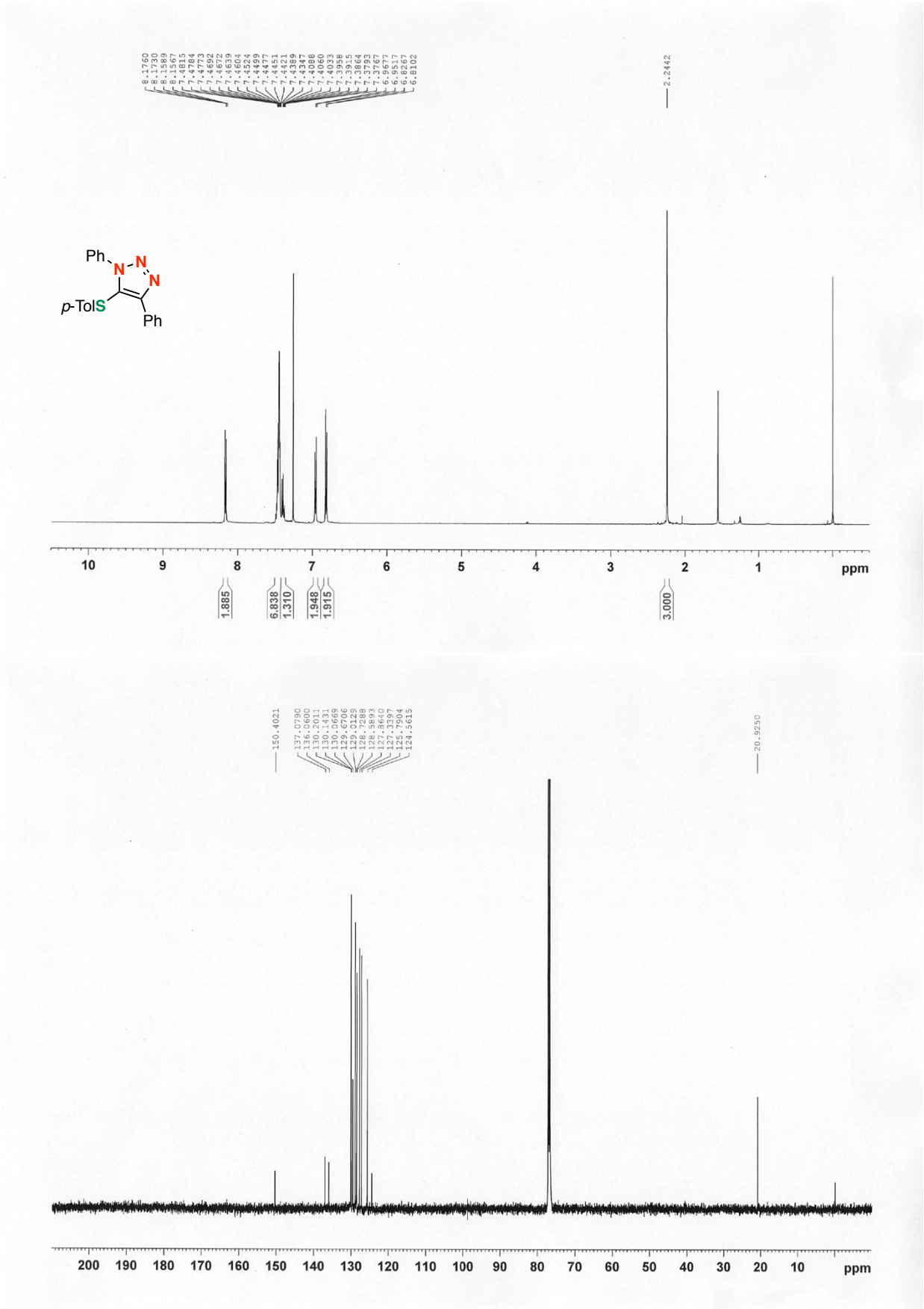
$^{1}$H NMR (500 MHz) and $^{13}$C NMR (126 MHz) spectra of 1-(2-adamantyl)-4-phenyl-5-(*p*-tolylthio)-1*H*-1,2,3-triazole (**10f**) ($CDCl_3$)



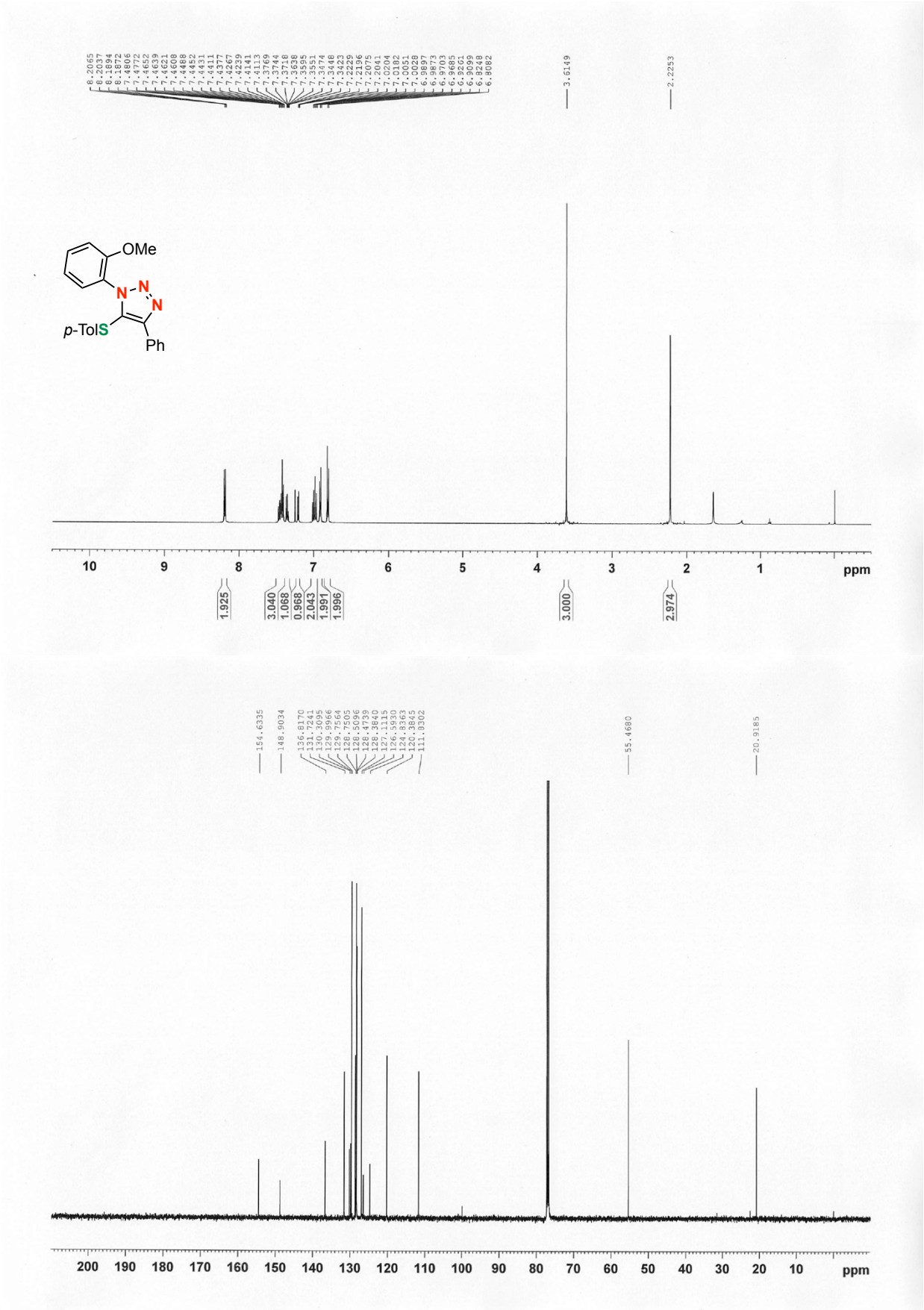
$^{1}$H NMR (500 MHz) and $^{13}$C NMR (126 MHz) spectra of 1-(1-adamantylmethyl)-4-phenyl-5-(*p*-tolylthio)-1*H*-1,2,3-triazole (**10h**) ($CDCl_3$)



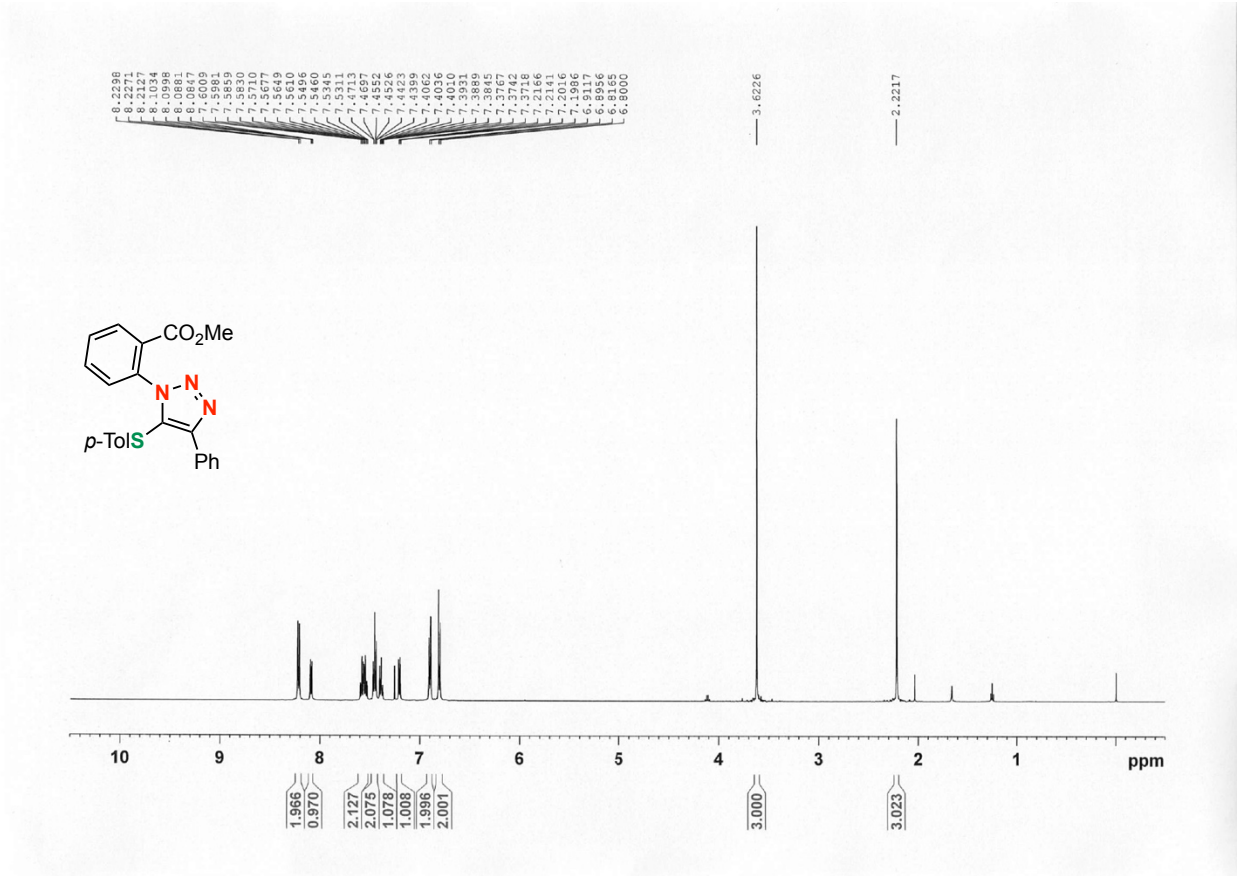
$^{1}$H NMR (500 MHz) and $^{13}$C NMR (126 MHz) spectra of 1,4-diphenyl-5-(*p*-tolylthio)-1*H*-1,2,3-triazole (**11a**) ($CDCl_3$)

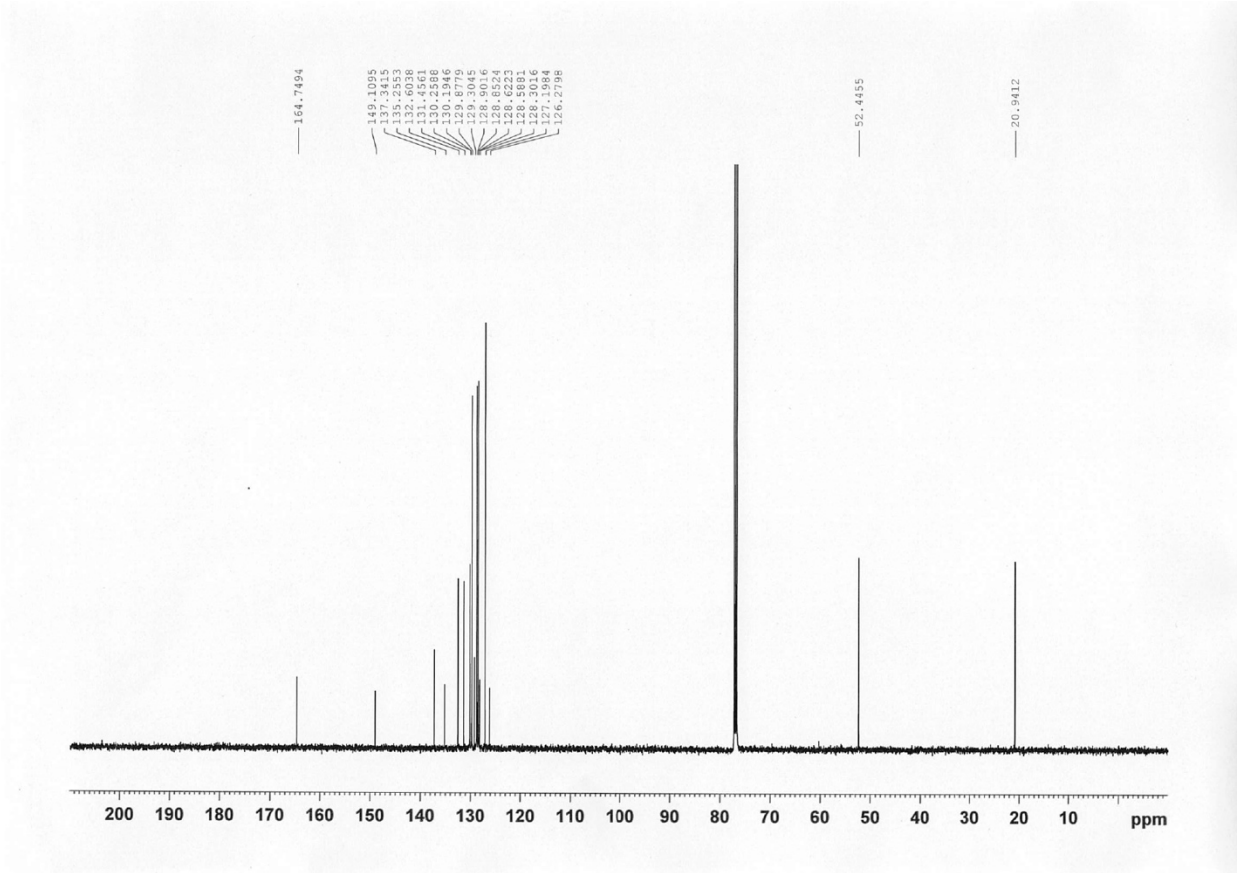


$^{1}$H NMR (500 MHz) and $^{13}$C NMR (126 MHz) spectra of 1-(2-methoxyphenyl)-4-phenyl-5-(*p*-tolylthio)-1*H*-1,2,3-triazole (**11b**) ($CDCl_3$)

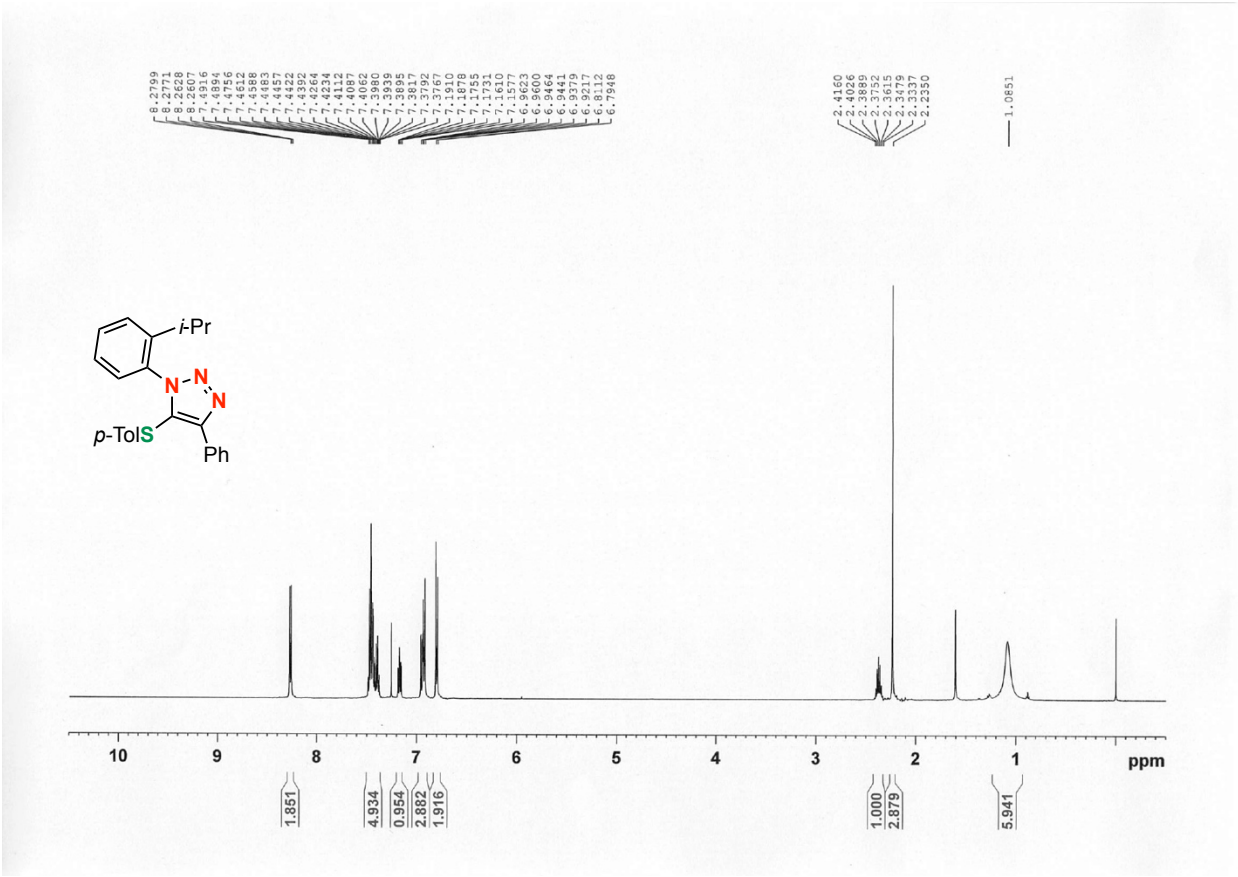


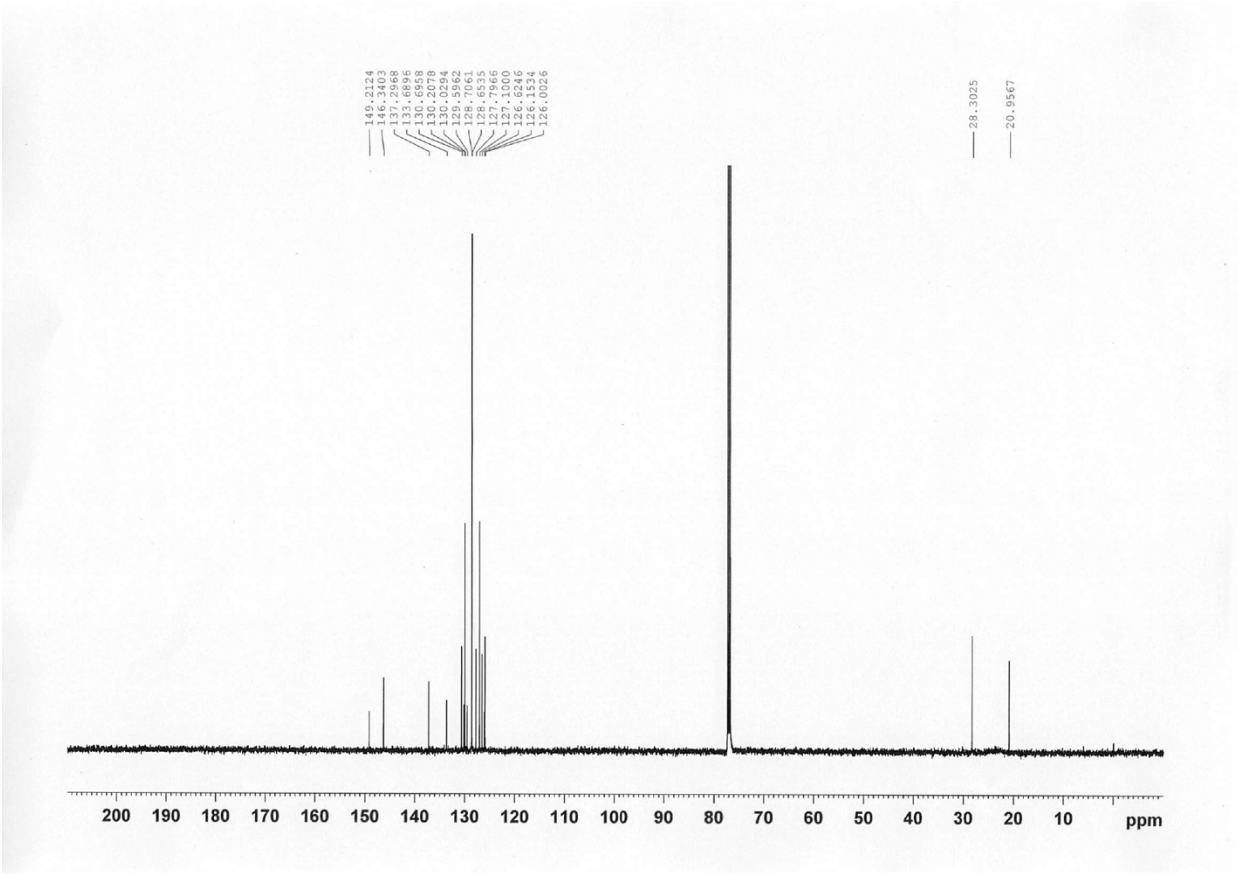
$^{1}$H NMR (500 MHz) and $^{13}$C NMR (126 MHz) spectra of methyl 2-(4-phenyl-5-(*p*-tolylthio)-1*H*-1,2,3-triazol-1-yl)benzoate (**11c**) ($CDCl_3$)



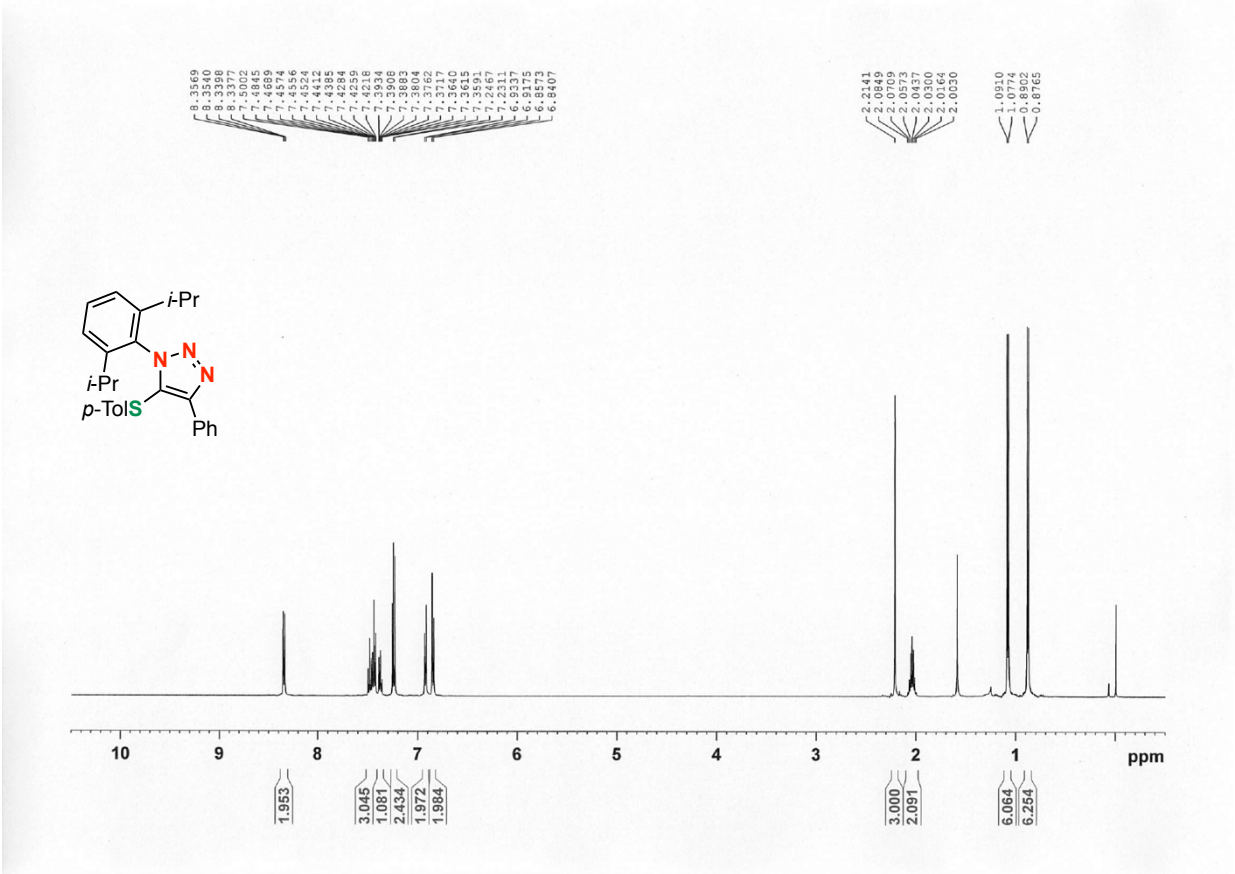



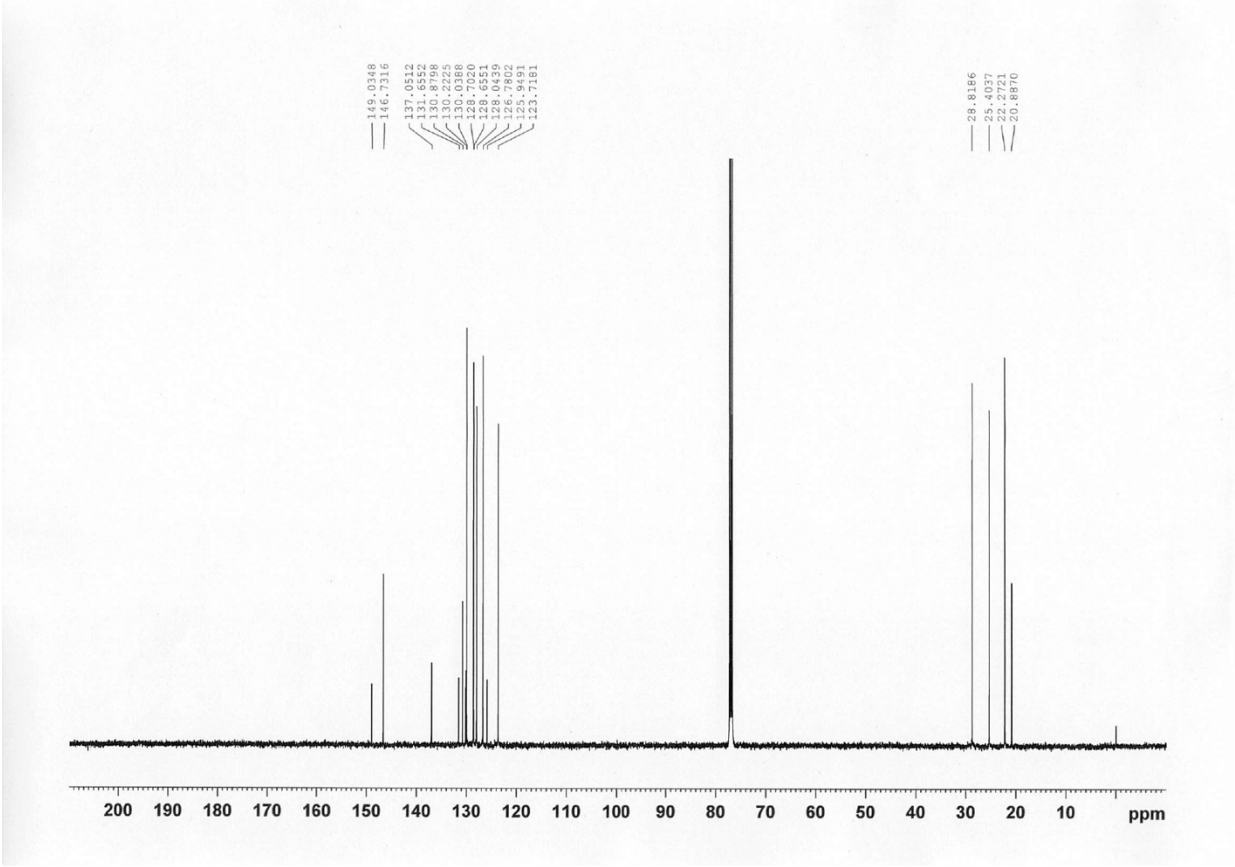
$^{1}$H NMR (500 MHz) and $^{13}$C NMR (126 MHz) spectra of 1-(2-isopropylphenyl)-4-phenyl-5-(*p*-tolylthio)-1*H*-1,2,3-triazole (**11d**) ($CDCl_3$)



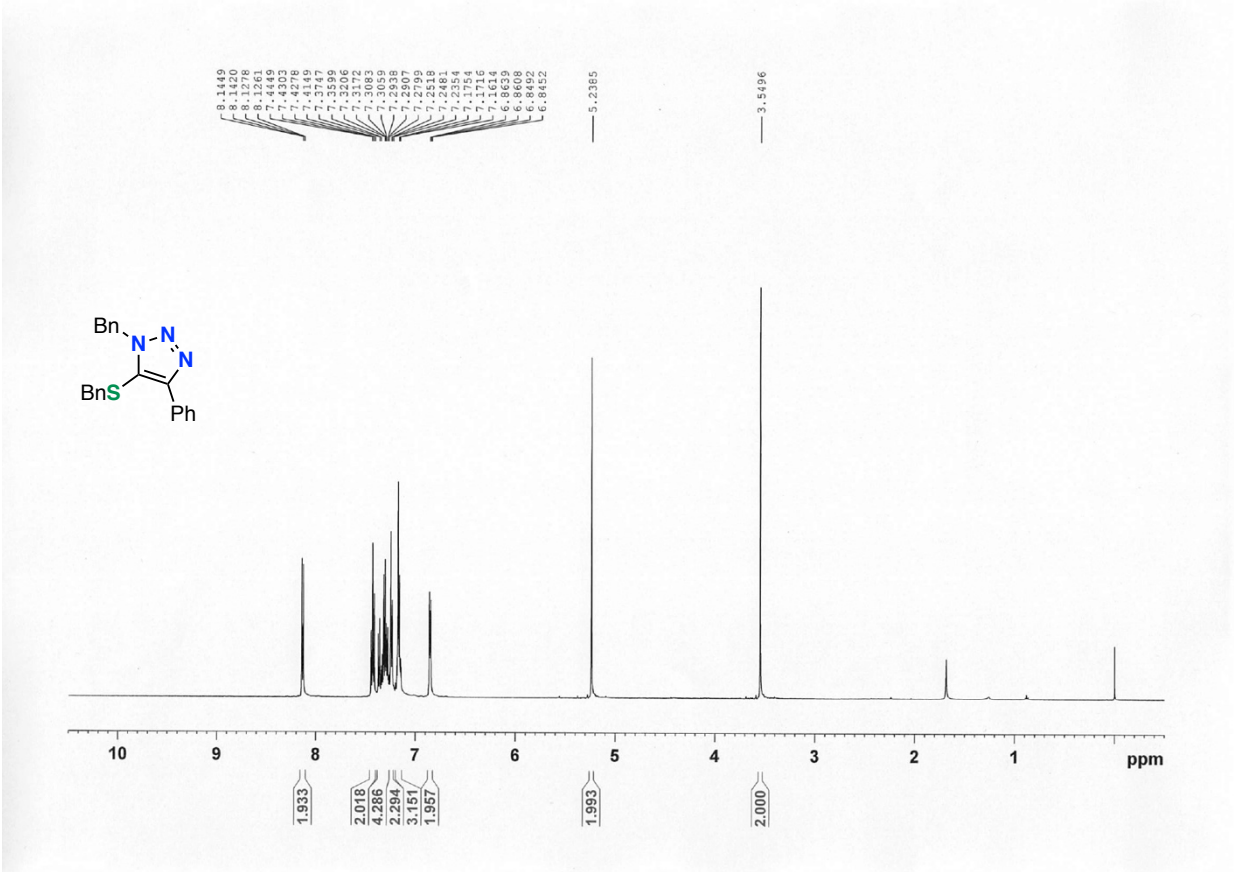



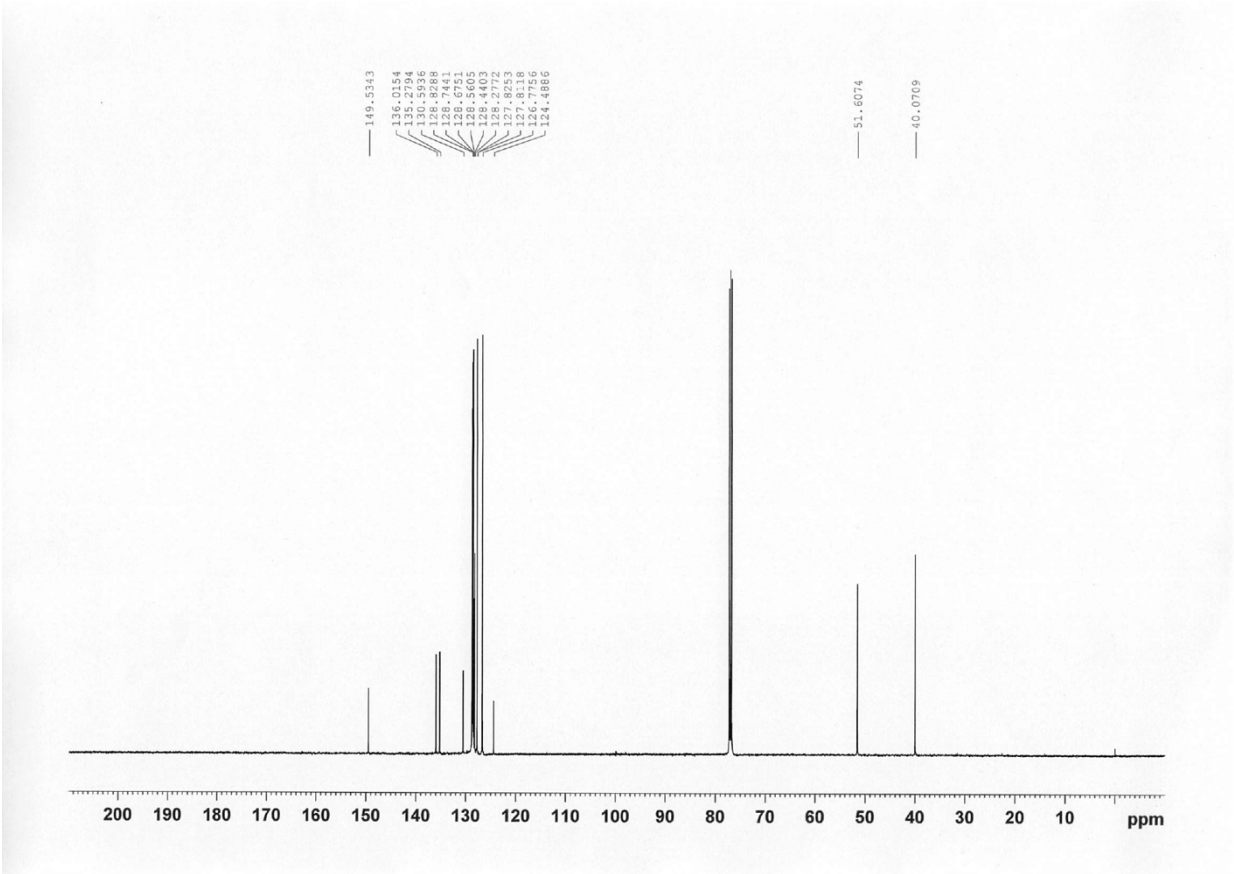
$^{1}$H NMR (500 MHz) and $^{13}$C NMR (126 MHz) spectra of 1-(2,6-diisopropylphenyl)-4-phenyl-5-(*p*-tolylthio)-1*H*-1,2,3-triazole (**11e**) ($CDCl_3$)



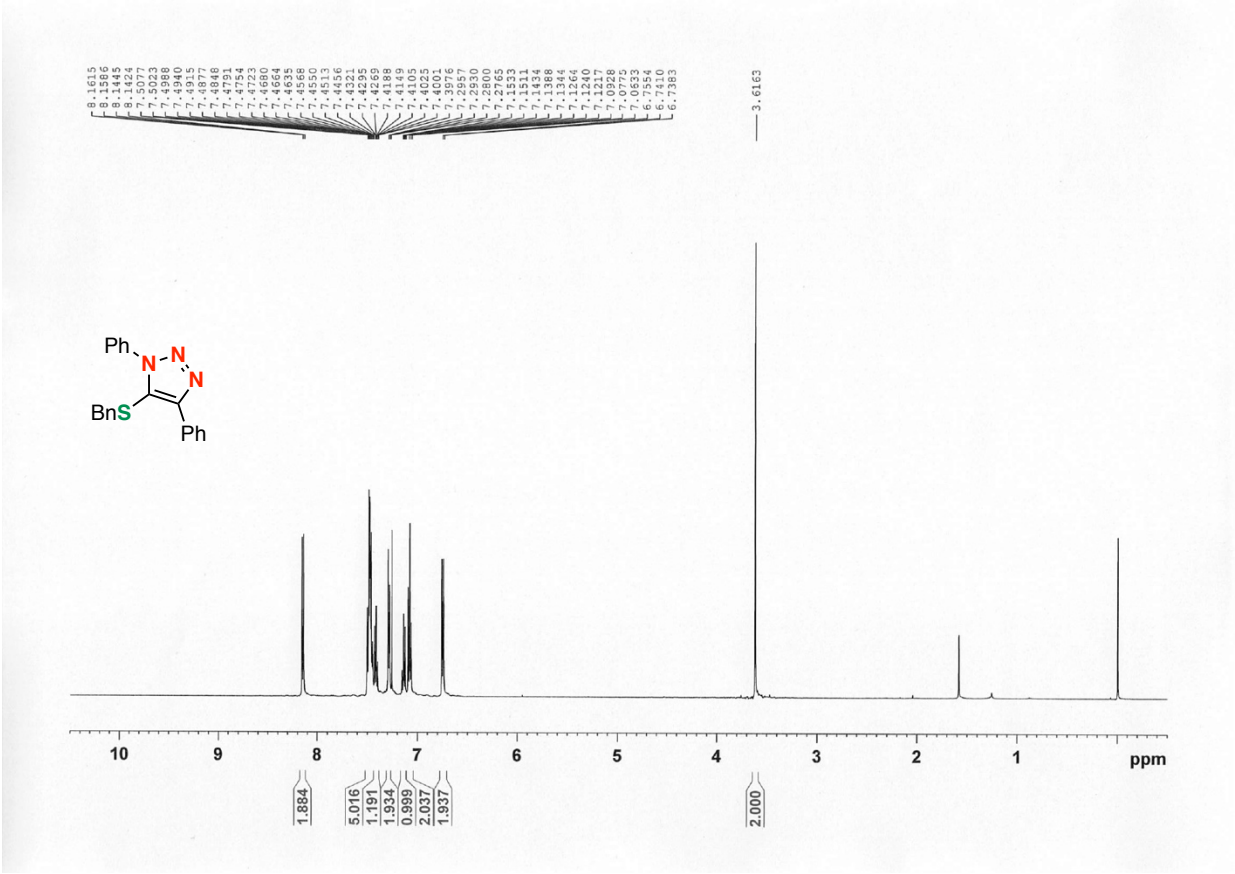



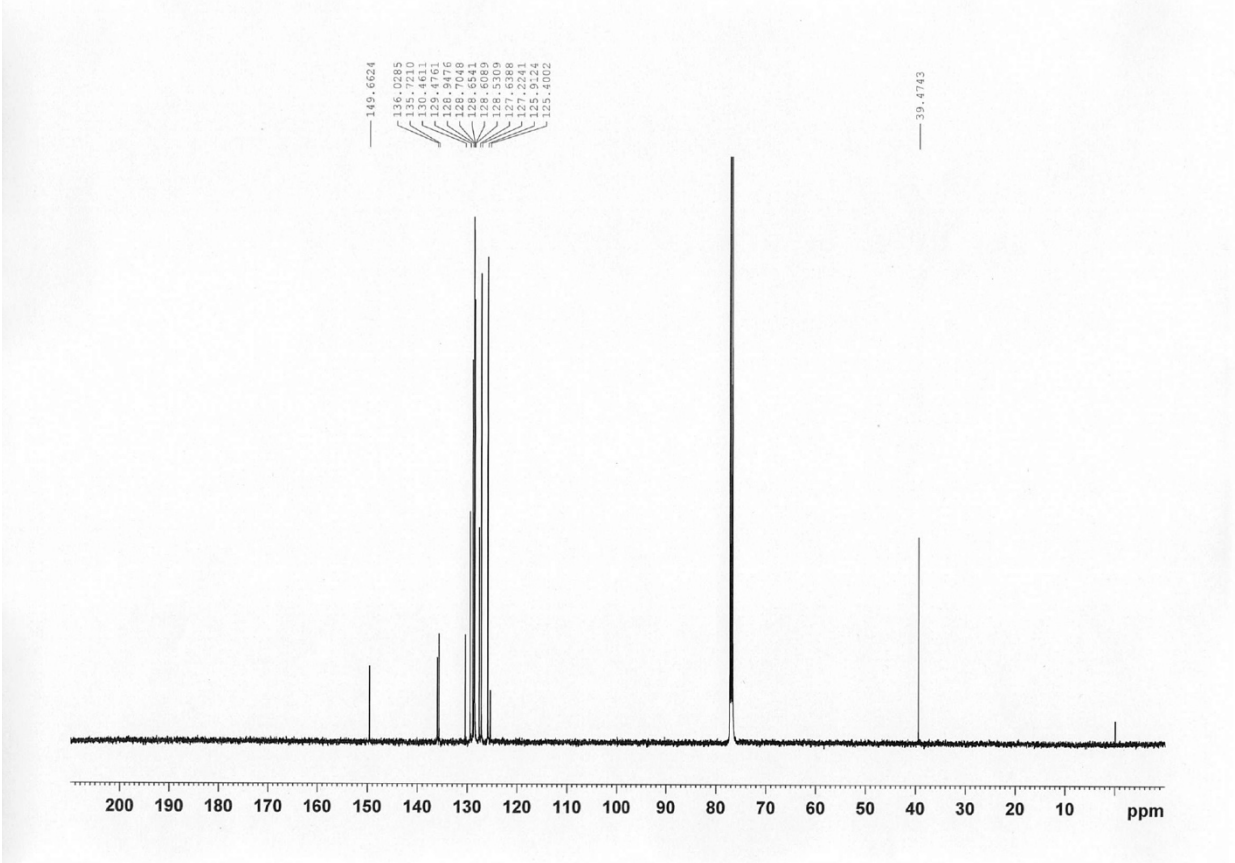
$^{1}$H NMR (500 MHz) and $^{13}$C NMR (126 MHz) spectra of 1-benzyl-5-benzylthio-4-phenyl-1*H*-1,2,3-triazole (**12**) ($CDCl_3$)



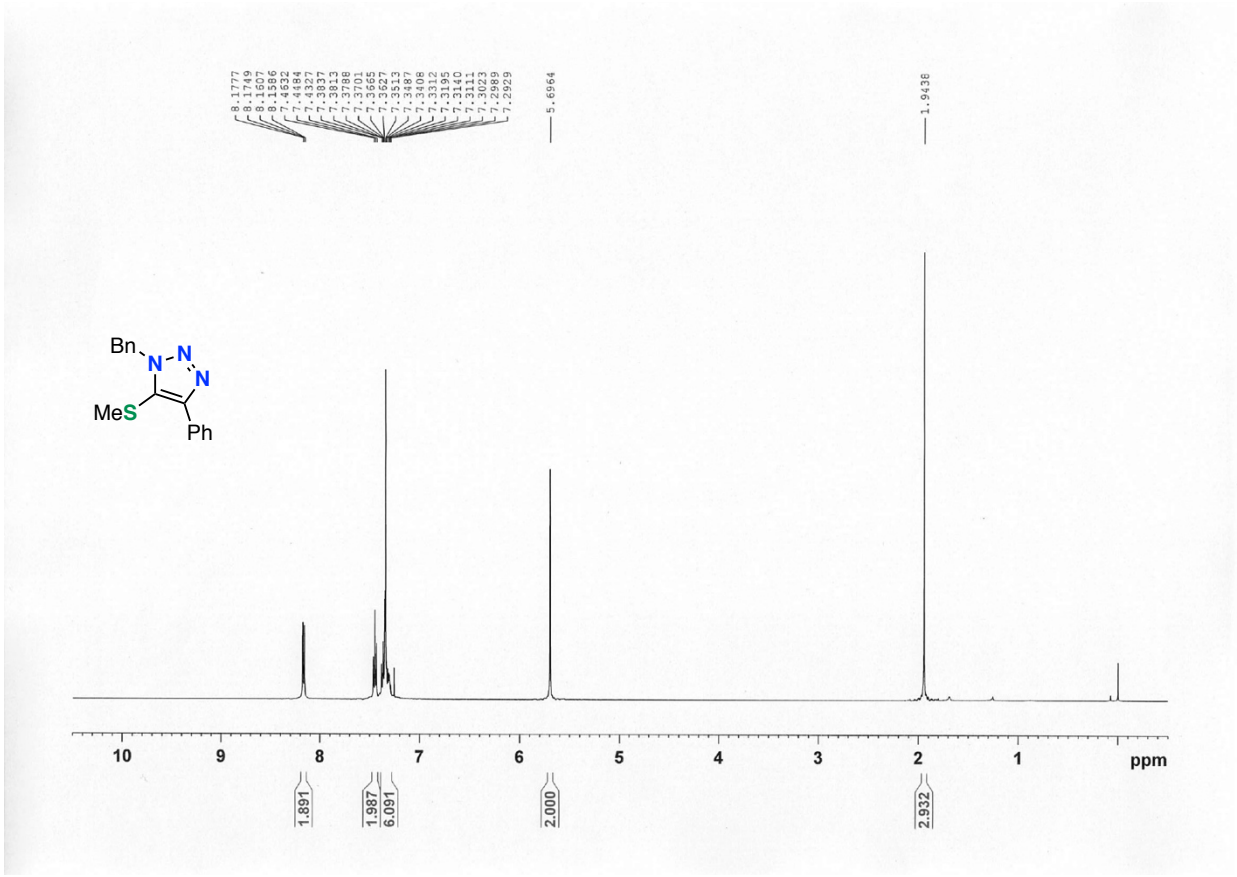



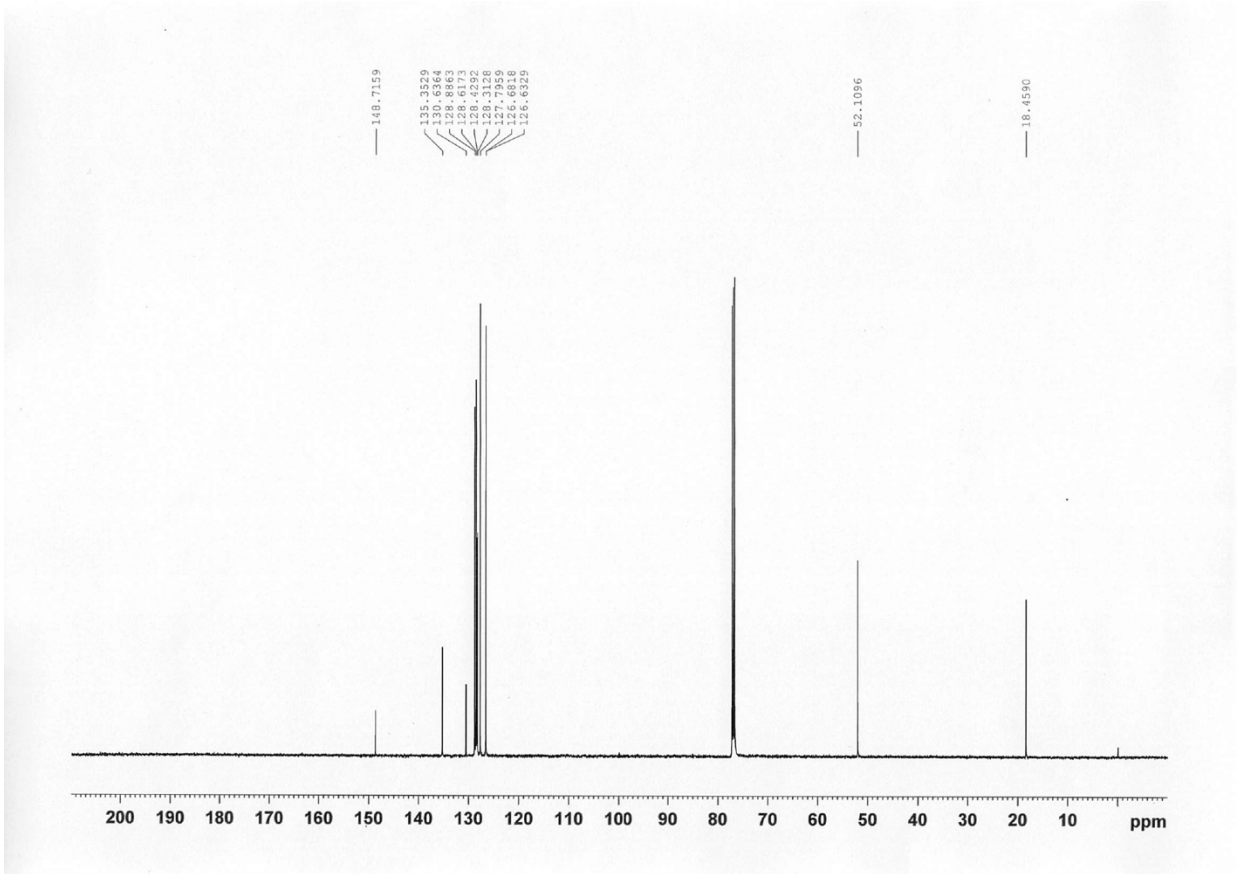
$^{1}$H NMR (500 MHz) and $^{13}$C NMR (126 MHz) spectra of 5-benzylthio-1,4-diphenyl-1*H*-1,2,3-triazole (**13**) ($CDCl_3$)



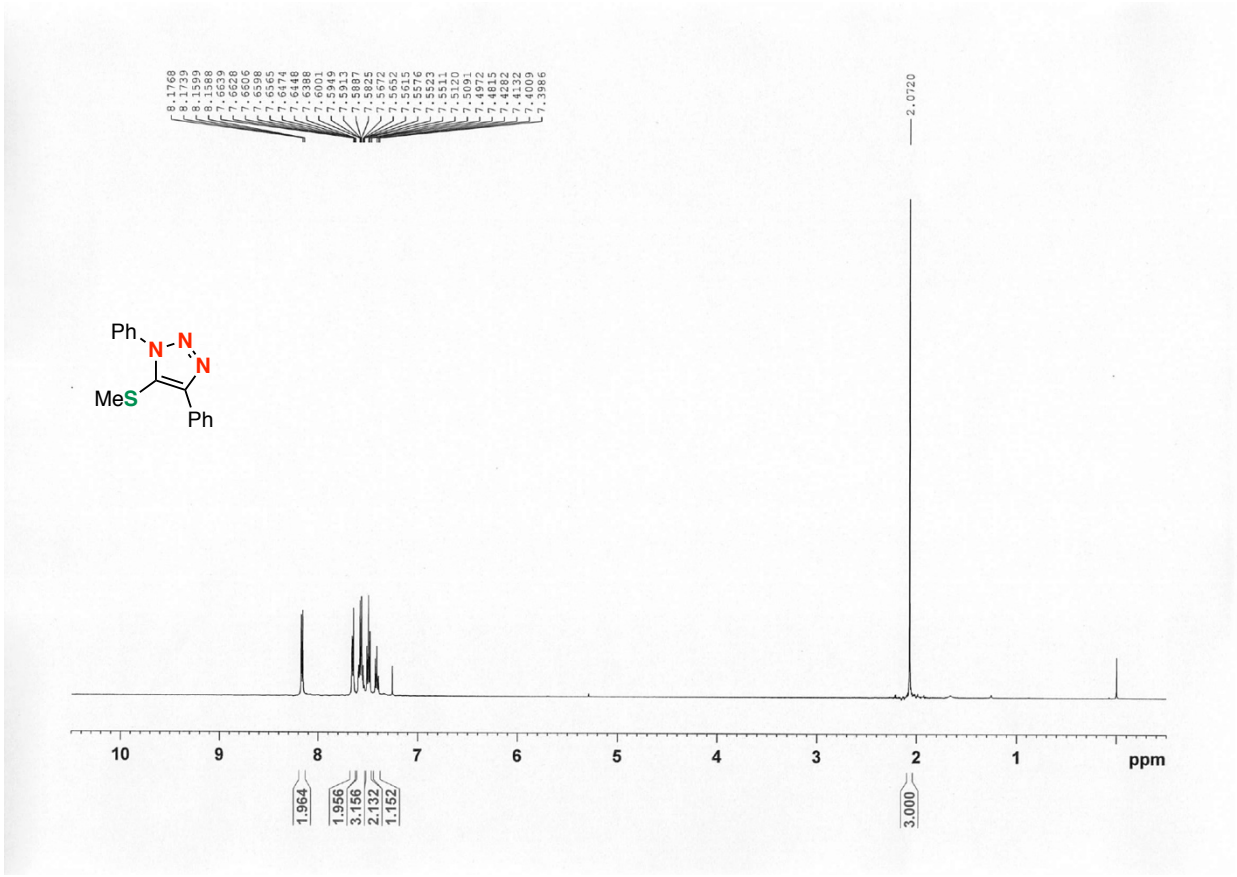



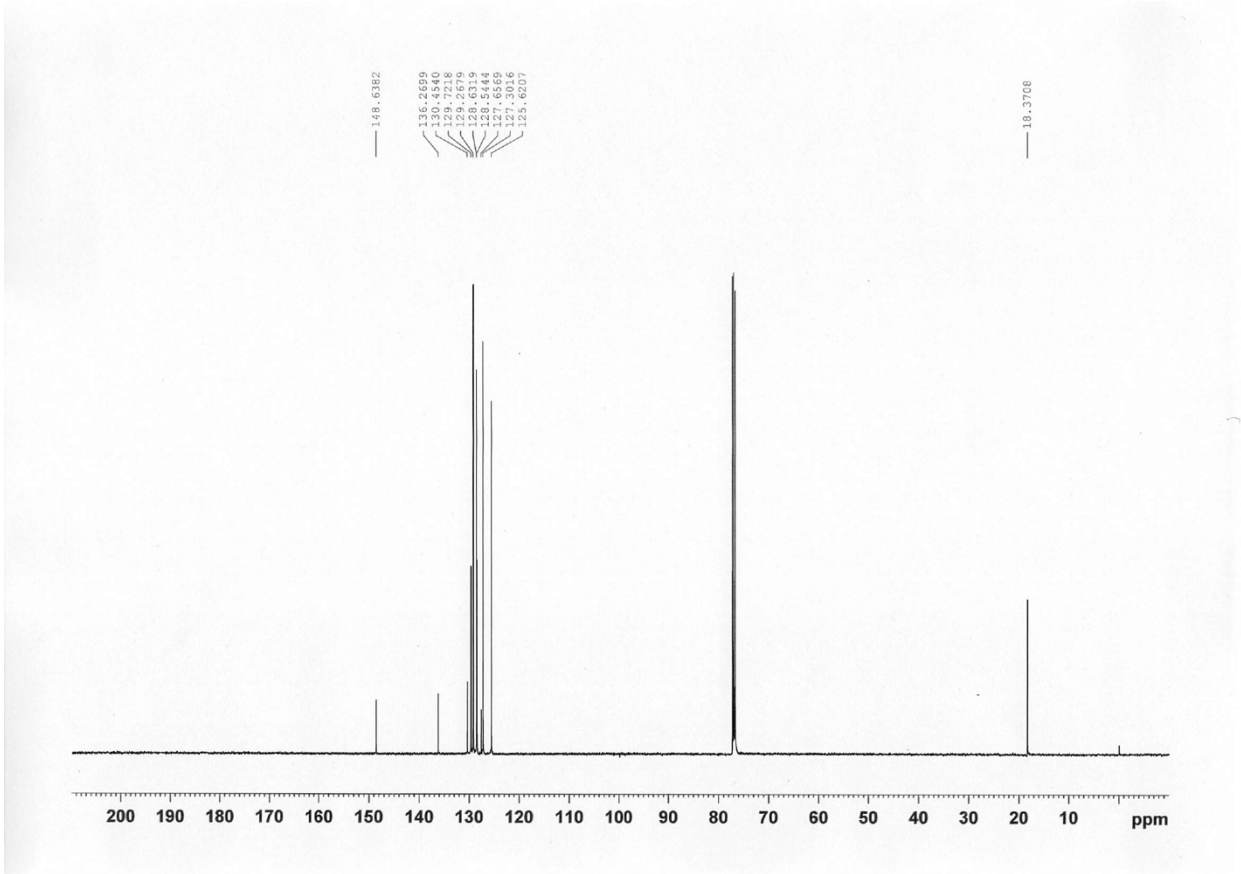
$^{1}$H NMR (500 MHz) and $^{13}$C NMR (126 MHz) spectra of 1-benzyl-5-methylthio-4-phenyl-1*H*-1,2,3-triazole (**14**) ($CDCl_3$)



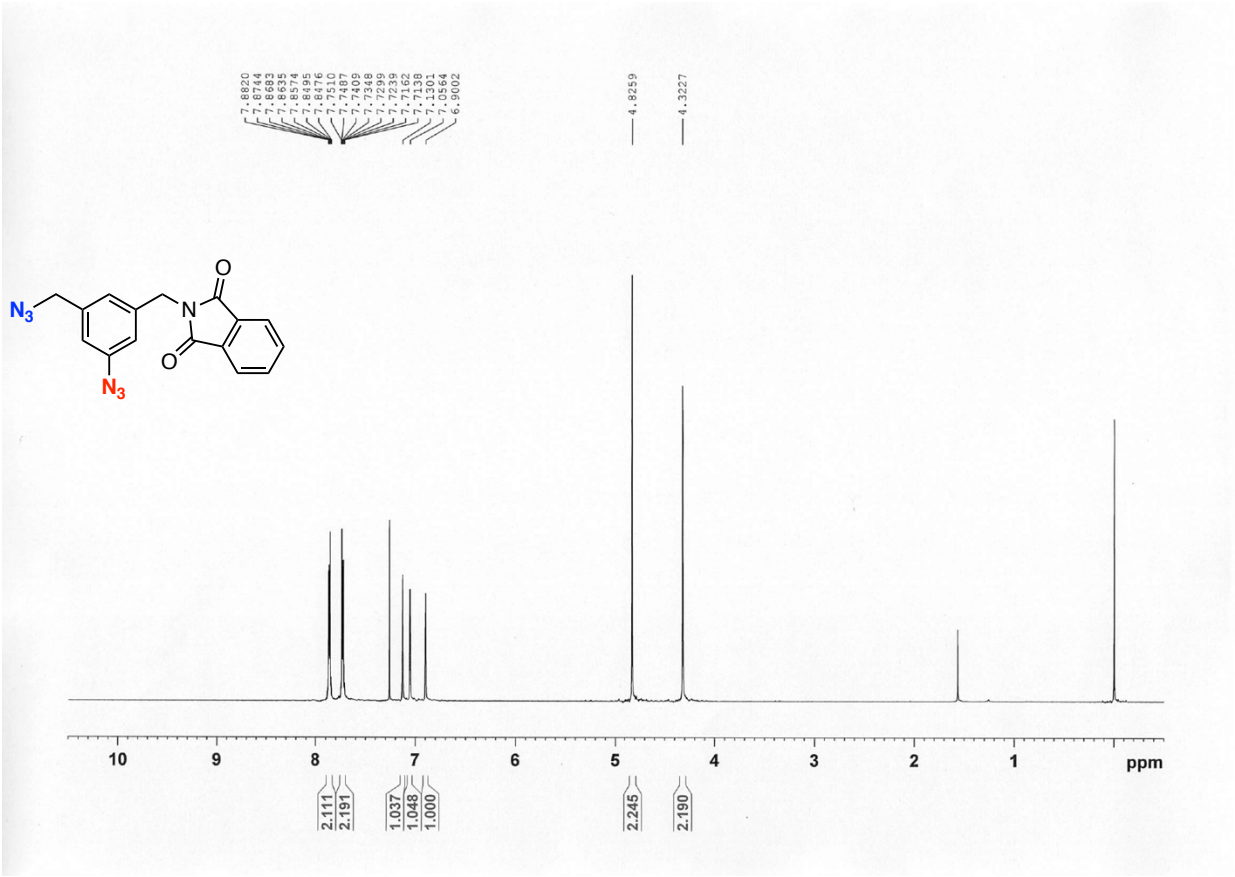



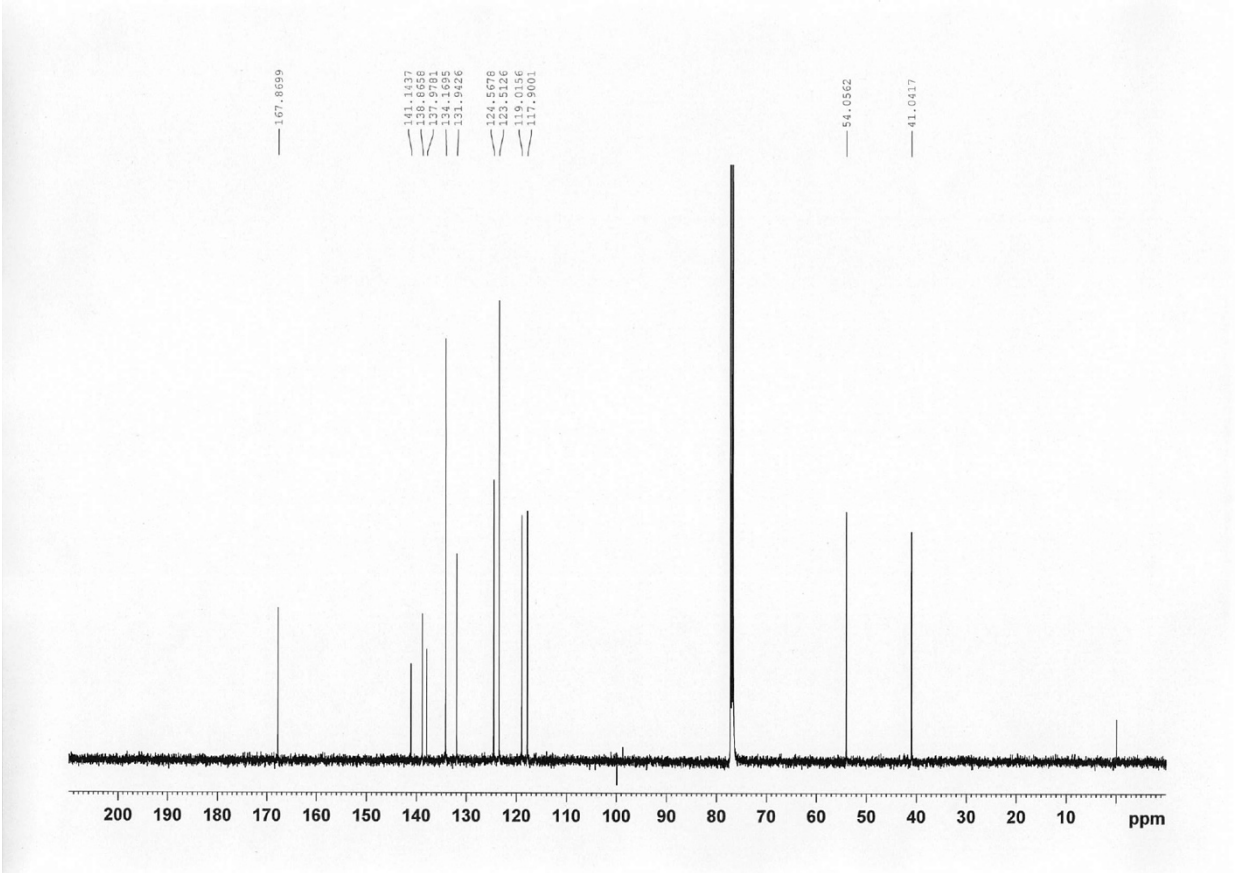
$^{1}$H NMR (500 MHz) and $^{13}$C NMR (126 MHz) spectra of 5-methylthio-1,4-diphenyl-1*H*-1,2,3-triazole (**15**) ($CDCl_3$)



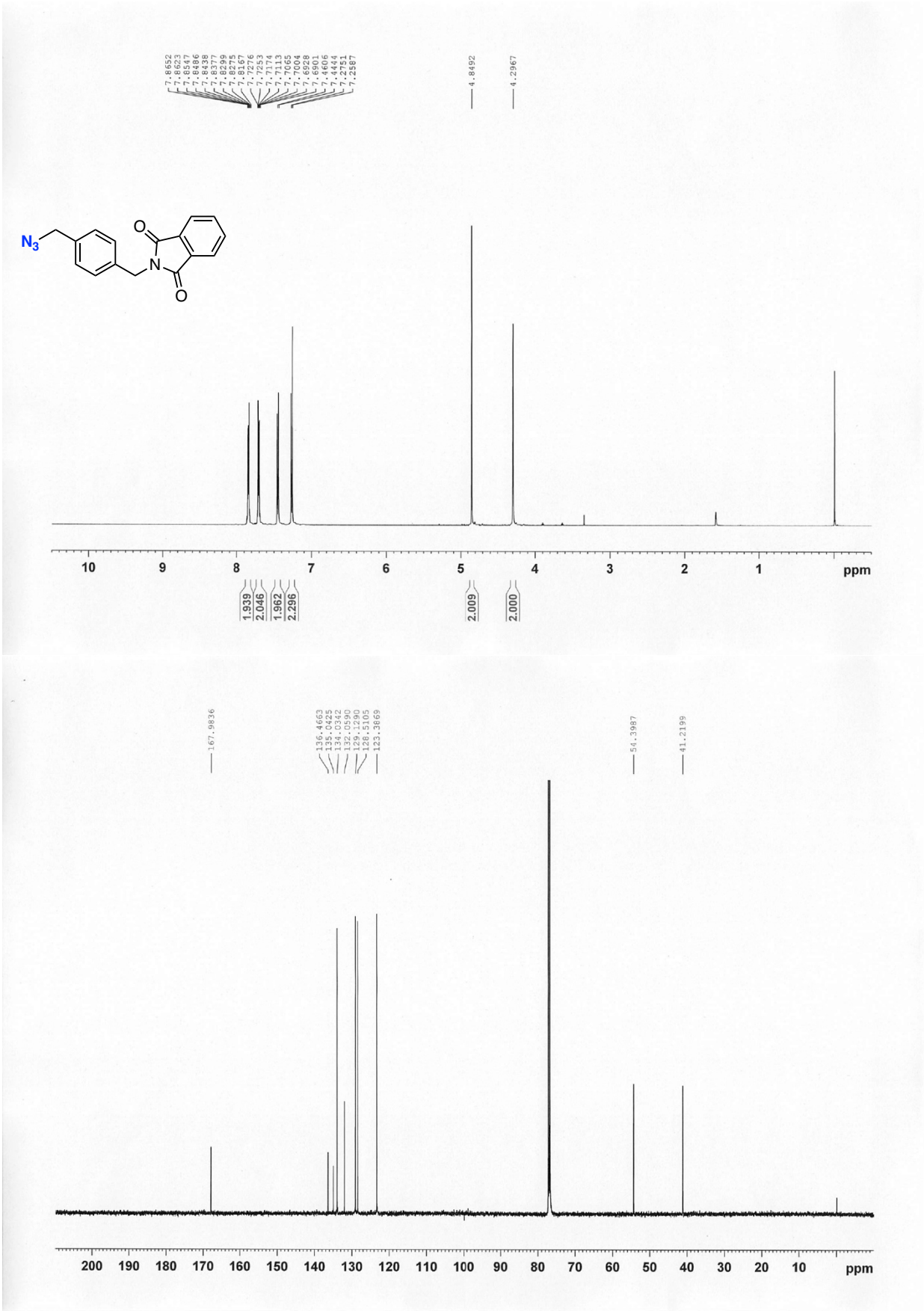



$^{1}$H NMR (500 MHz) and $^{13}$C NMR (126 MHz) spectra of 2-(3-azido-5-(azidomethyl)benzyl)phthalimide (**16i**) ($CDCl_3$)

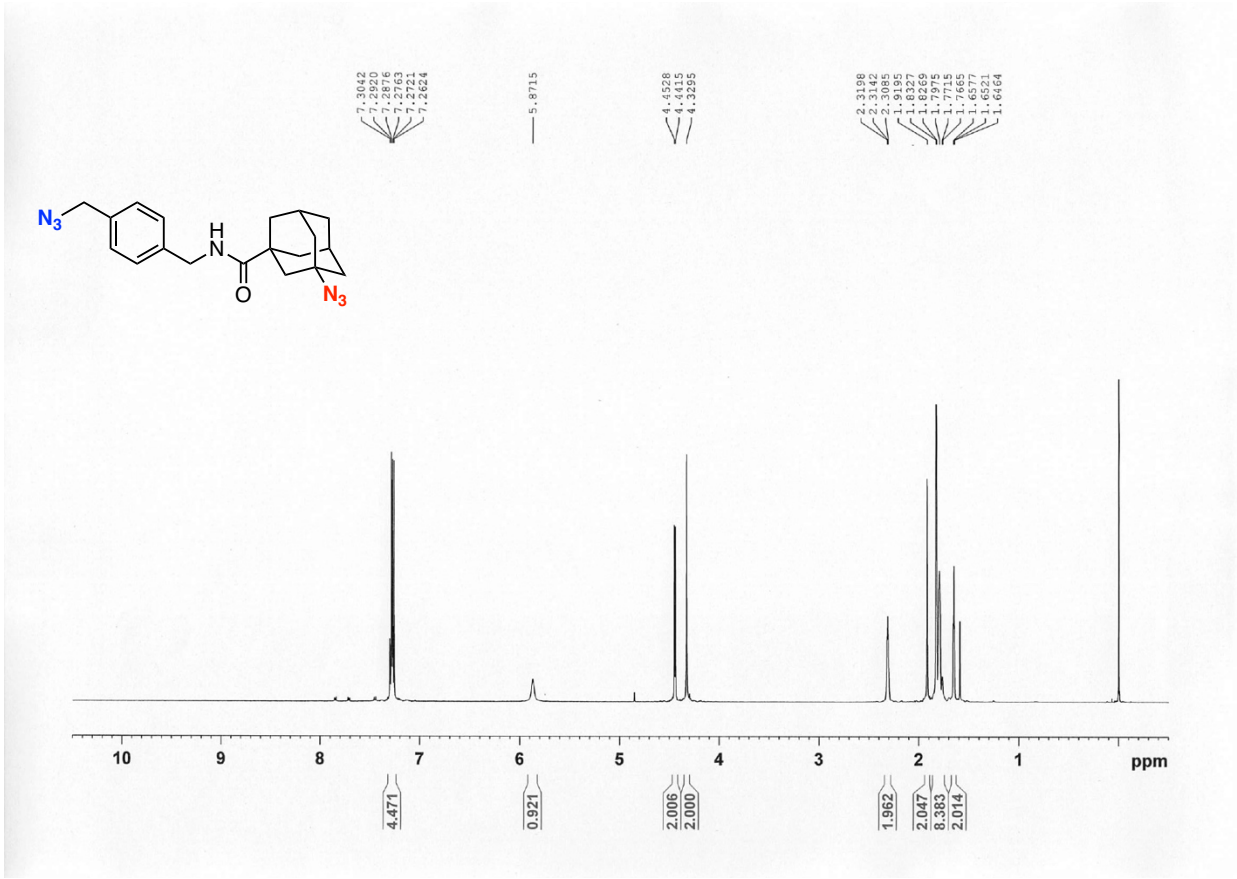


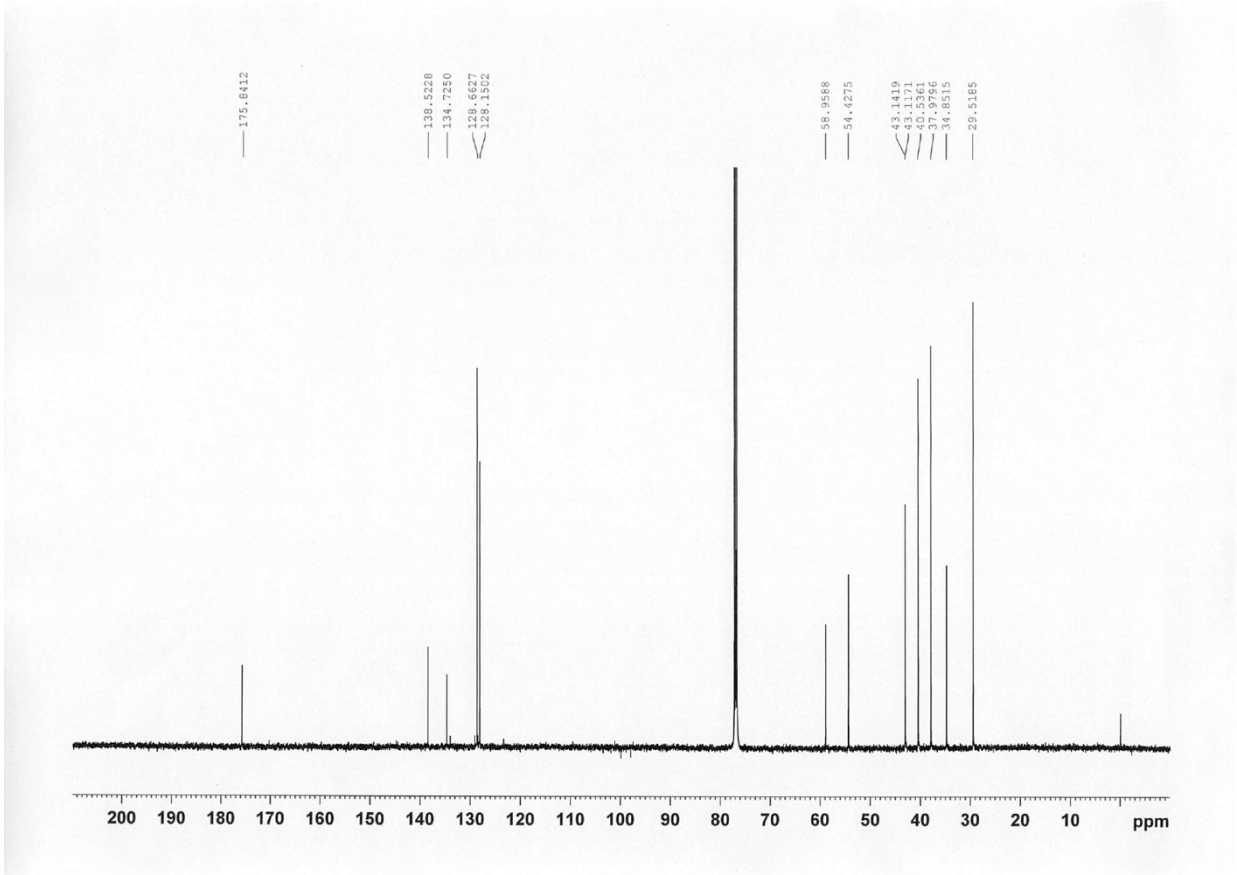



$^{1}$H NMR (500 MHz) and $^{13}$C NMR (126 MHz) spectra of 2-(4-(azidomethyl)benzyl)phthalimide (**S1**) ($CDCl_3$)

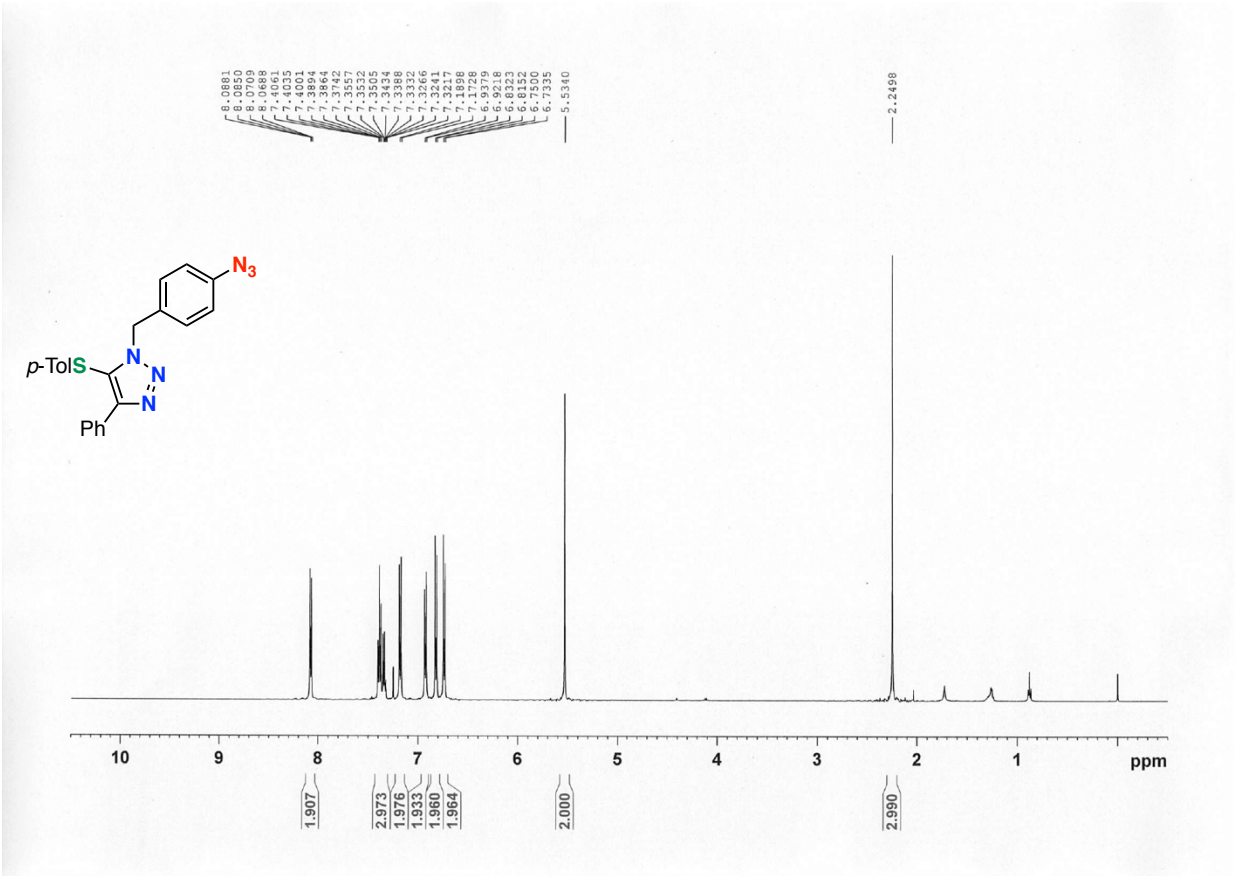


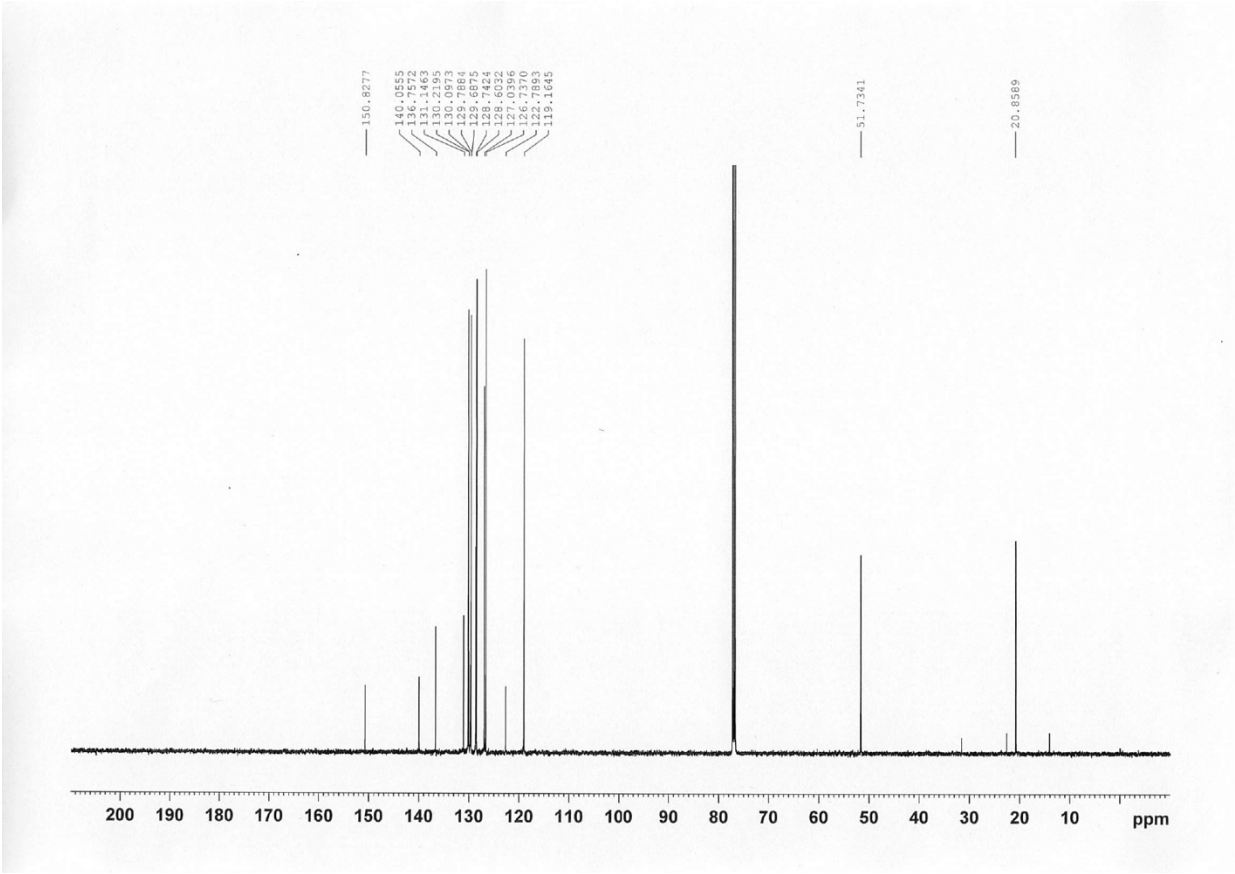
$^{1}$H NMR (500 MHz) and $^{13}$C NMR (126 MHz) spectra of 3-azido-*N*-(4-(azidomethyl)benzyl)-1-adamantanamide (**20**) ($CDCl_3$)



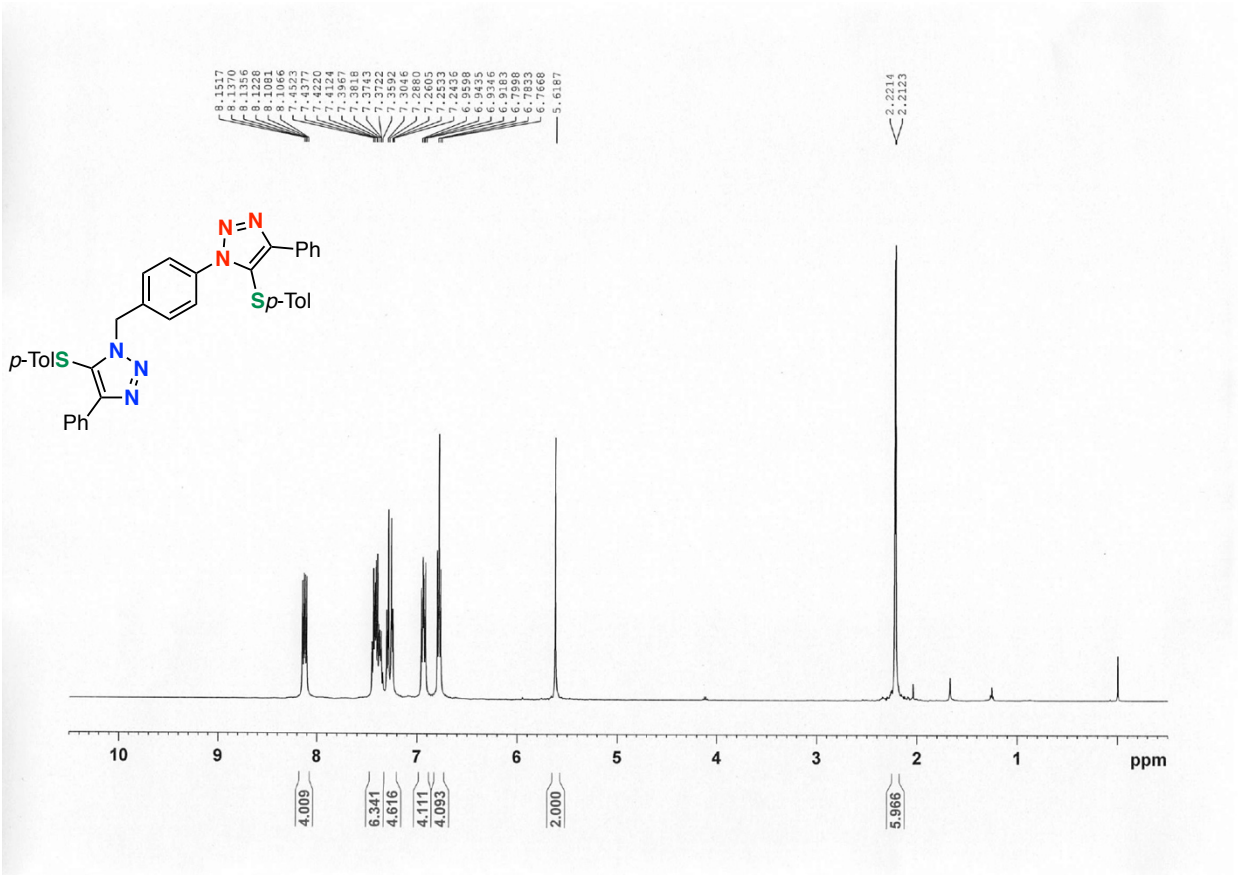



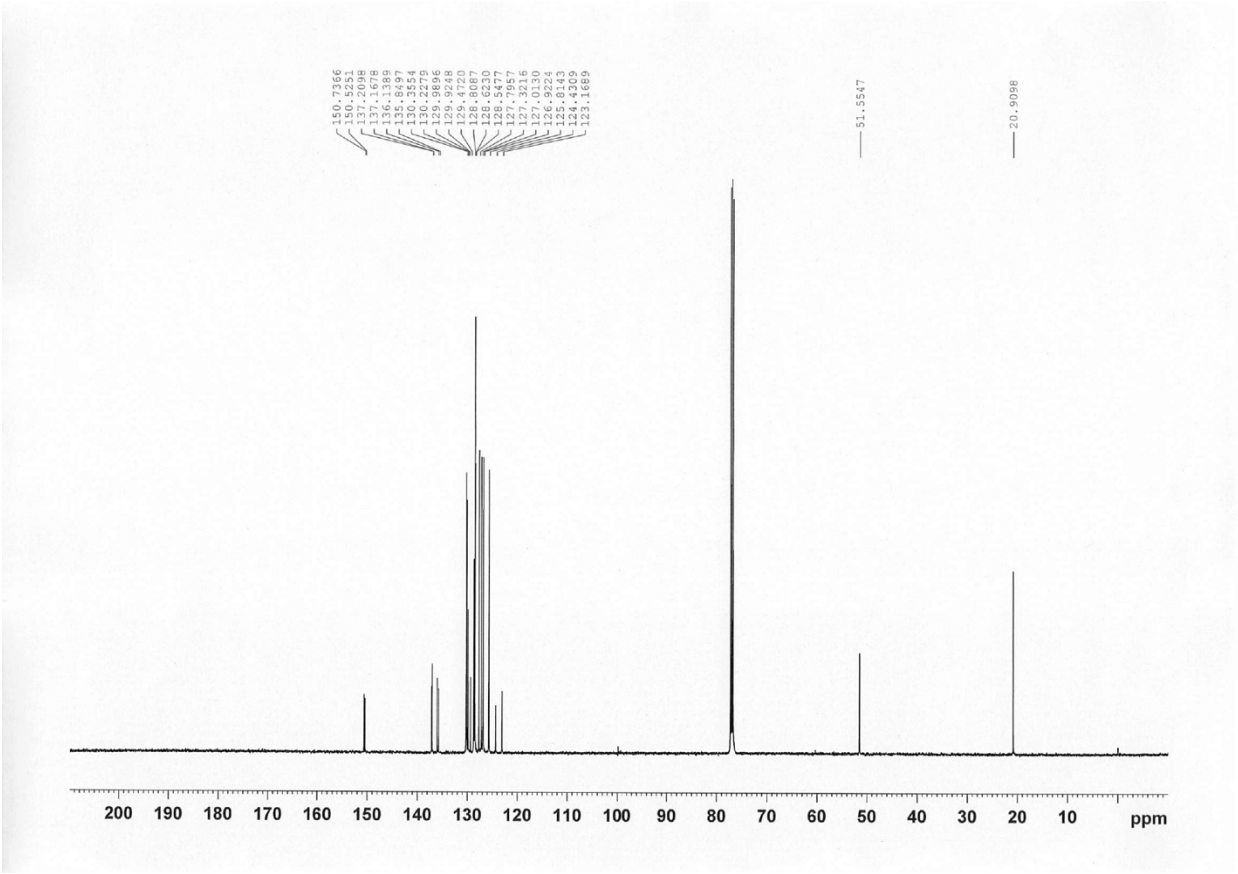
$^{1}$H NMR (500 MHz) and $^{13}$C NMR (126 MHz) spectra of 1-(4-azidobenzyl)-4-phenyl-5-(*p*-tolylthio)-1*H*-1,2,3-triazole (**17a**) ($CDCl_3$)



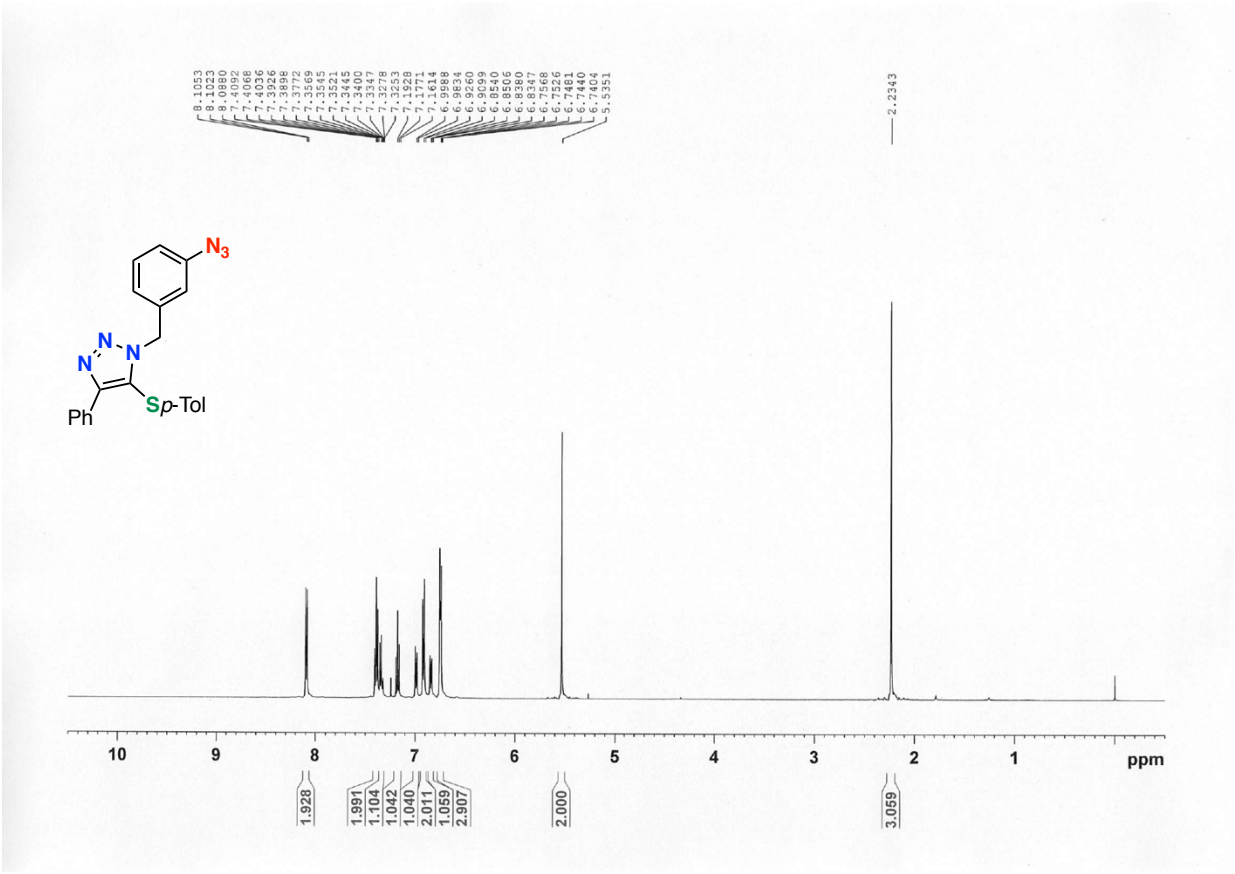



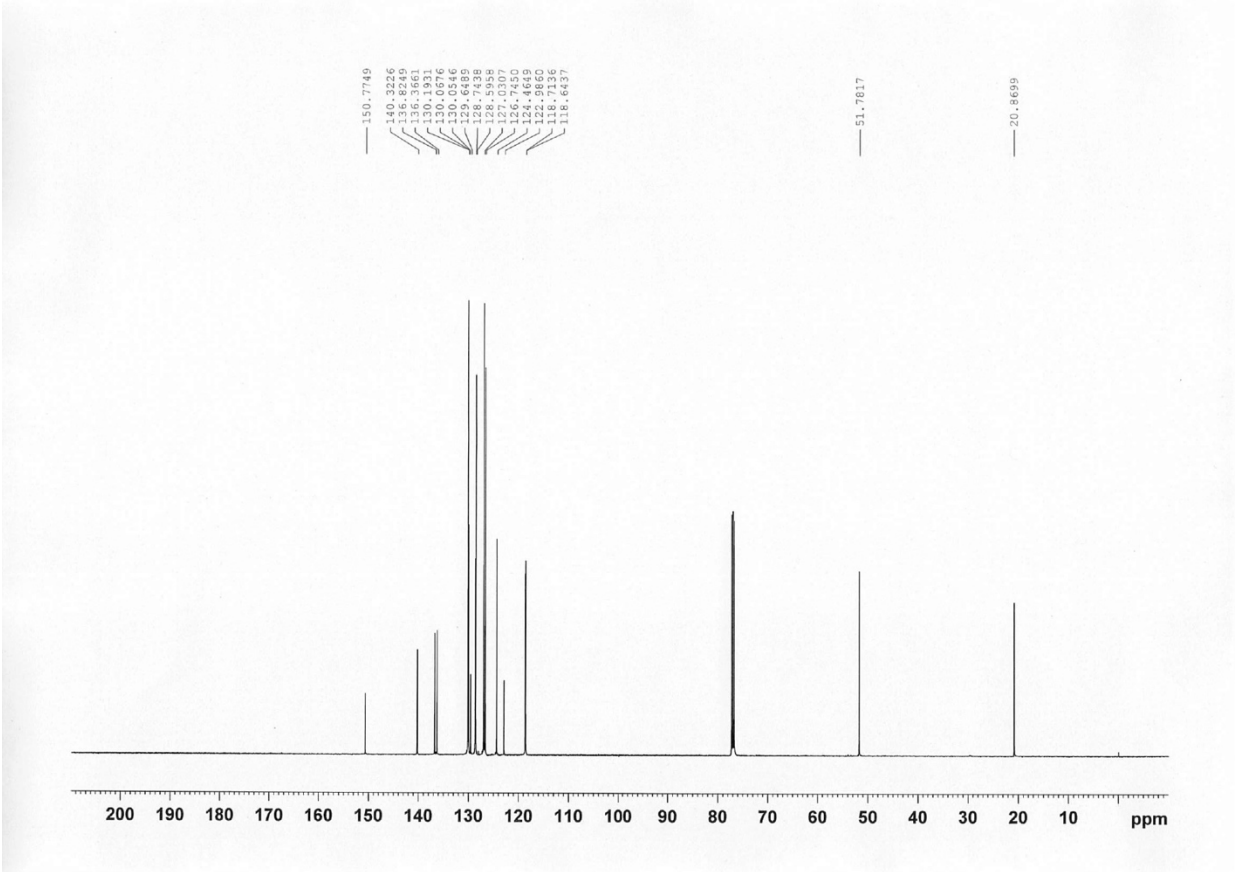
$^{1}$H NMR (500 MHz) and $^{13}$C NMR (126 MHz) spectra of 4-phenyl-1-(4-(4-phenyl-5-(*p*-tolylthio)-1*H*-1,2,3-triazol-1-yl)benzyl)-5-(*p*-tolylthio)-1*H*-1,2,3-triazole ($CDCl_3$)



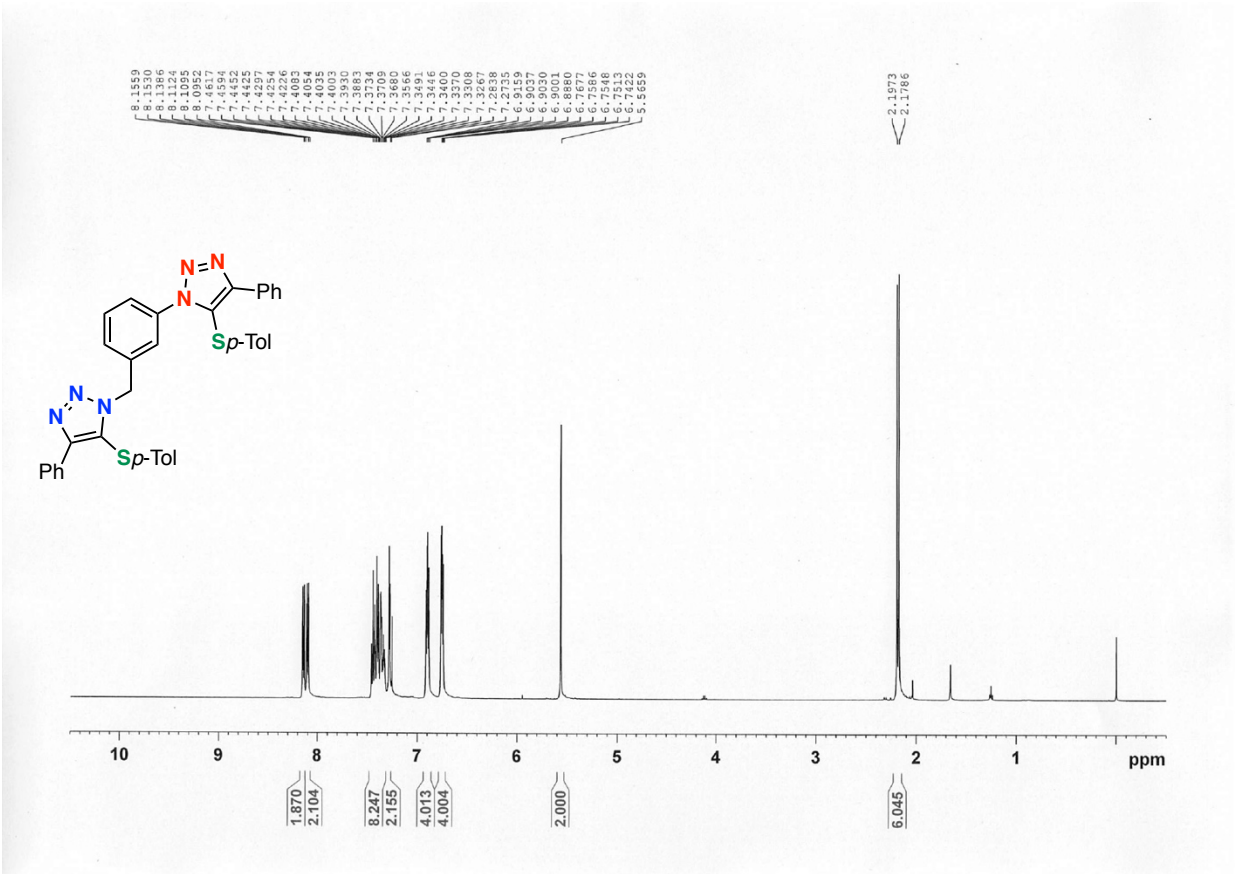



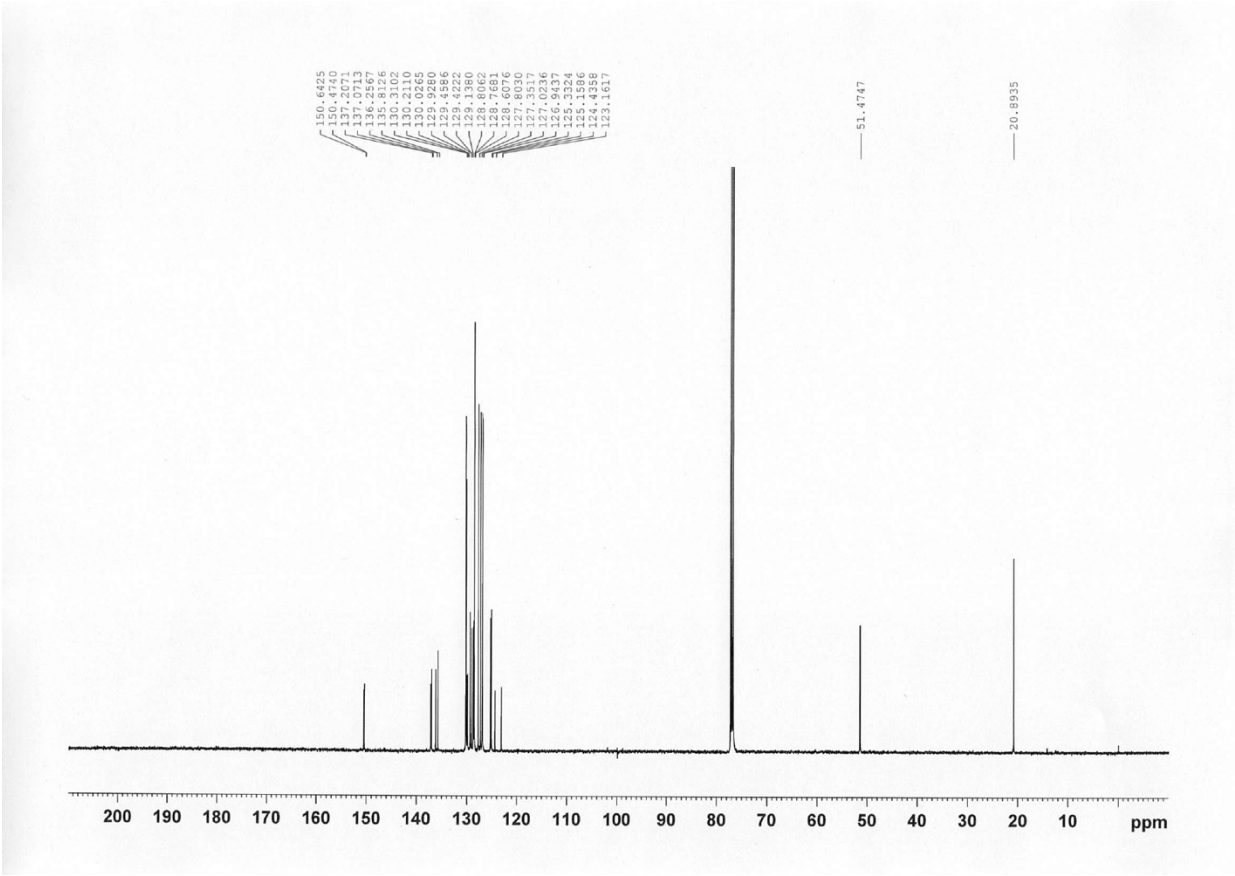
$^{1}$H NMR (500 MHz) and $^{13}$C NMR (126 MHz) spectra of 1-(3-azidobenzyl)-4-phenyl-5-(*p*-tolylthio)-1*H*-1,2,3-triazole (**17b**) ($CDCl_3$)



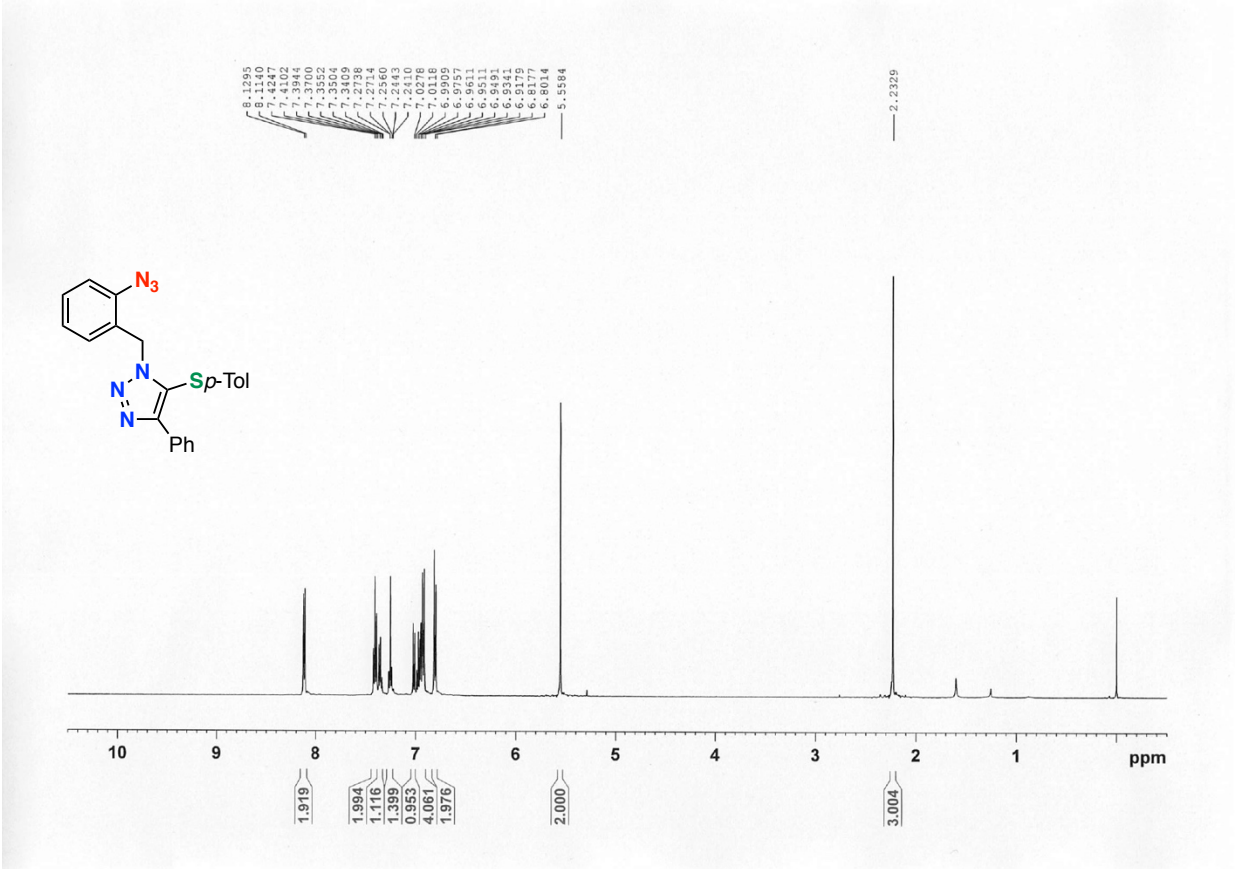



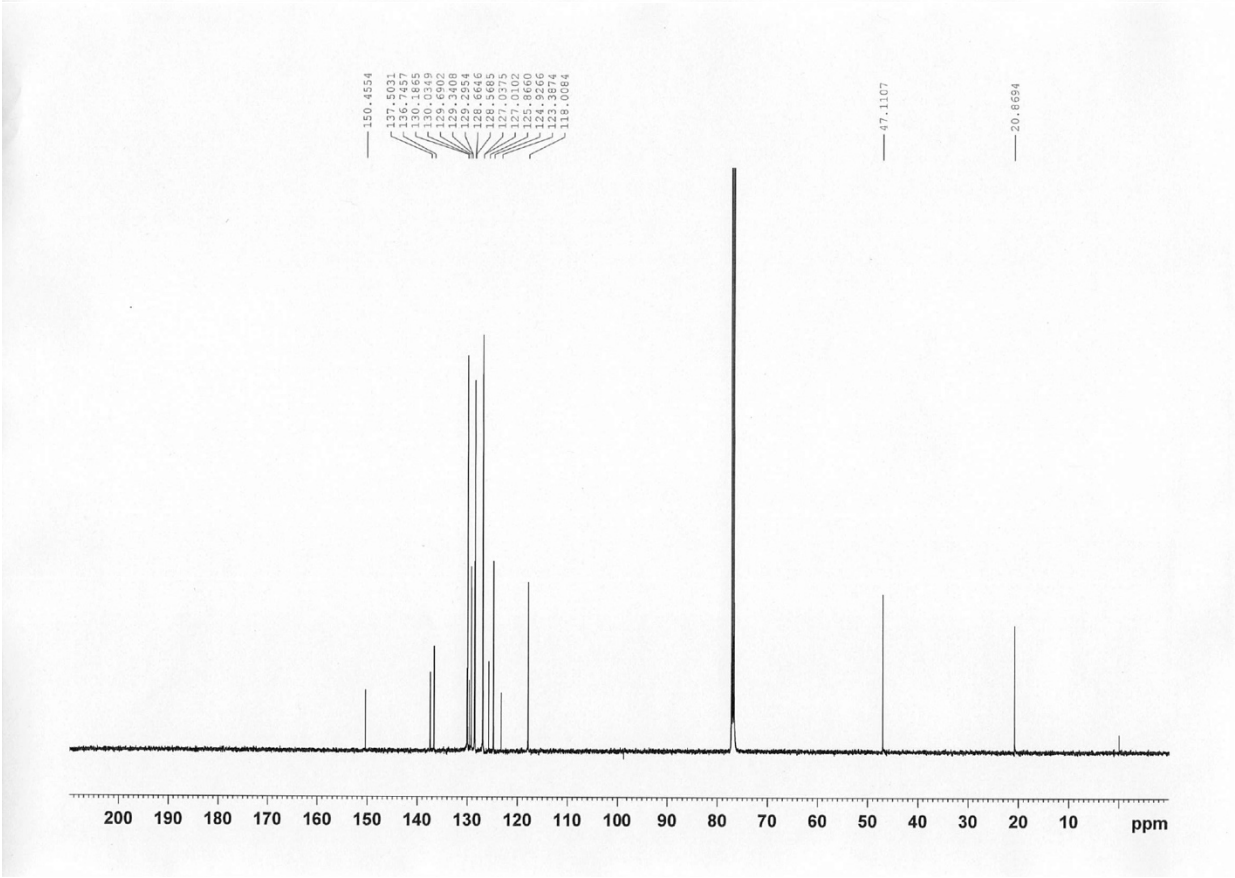
$^{1}$H NMR (500 MHz) and $^{13}$C NMR (126 MHz) spectra of 4-phenyl-1-(3-(4-phenyl-5-(*p*-tolylthio)-1*H*-1,2,3-triazol-1-yl)benzyl)-5-(*p*-tolylthio)-1*H*-1,2,3-triazole ($CDCl_3$)



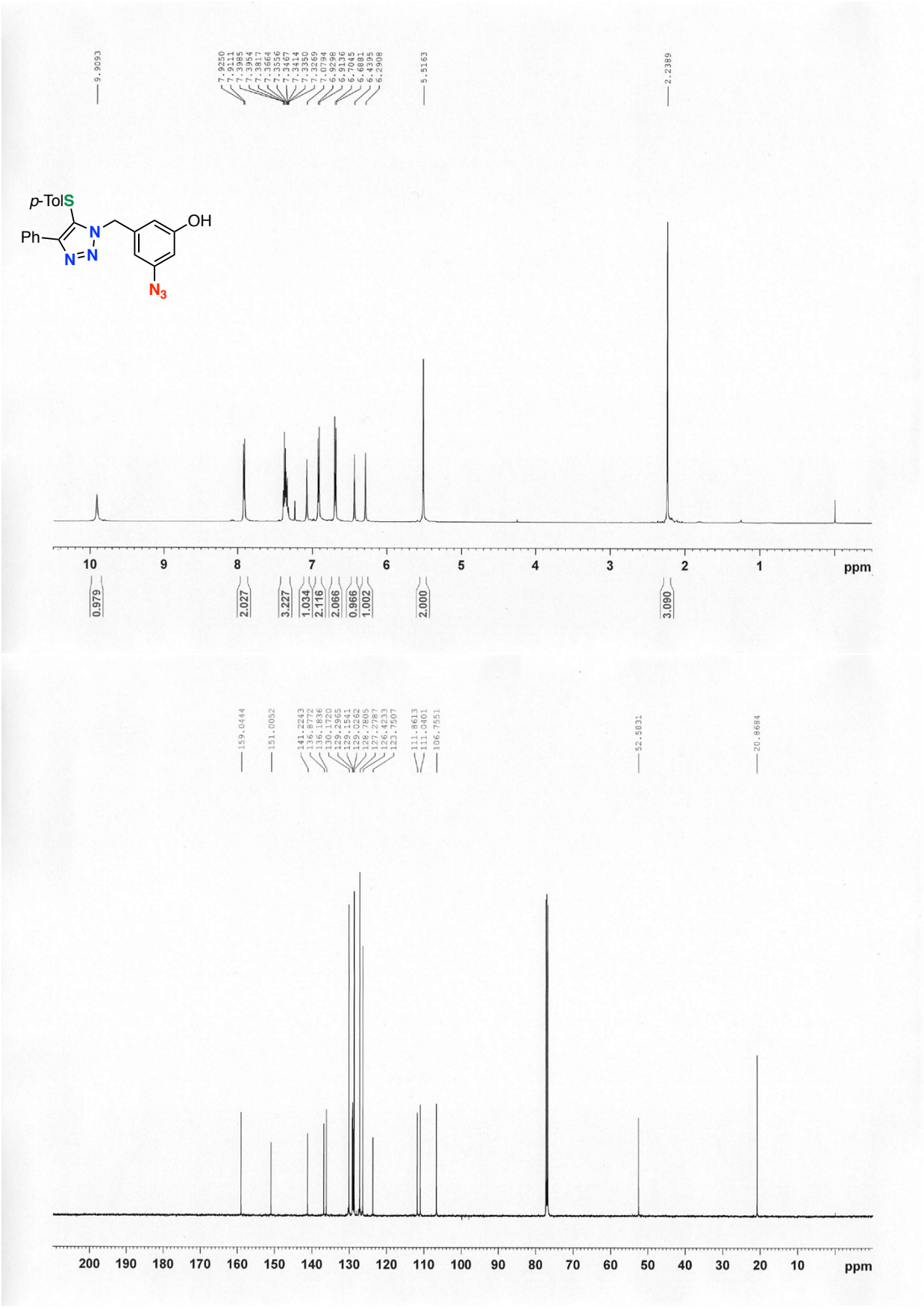



$^{1}$H NMR (500 MHz) and $^{13}$C NMR (126 MHz) spectra of 1-(2-azidobenzyl)-4-phenyl-5-(*p*-tolylthio)-1*H*-1,2,3-triazole (**17c**) ($CDCl_3$)

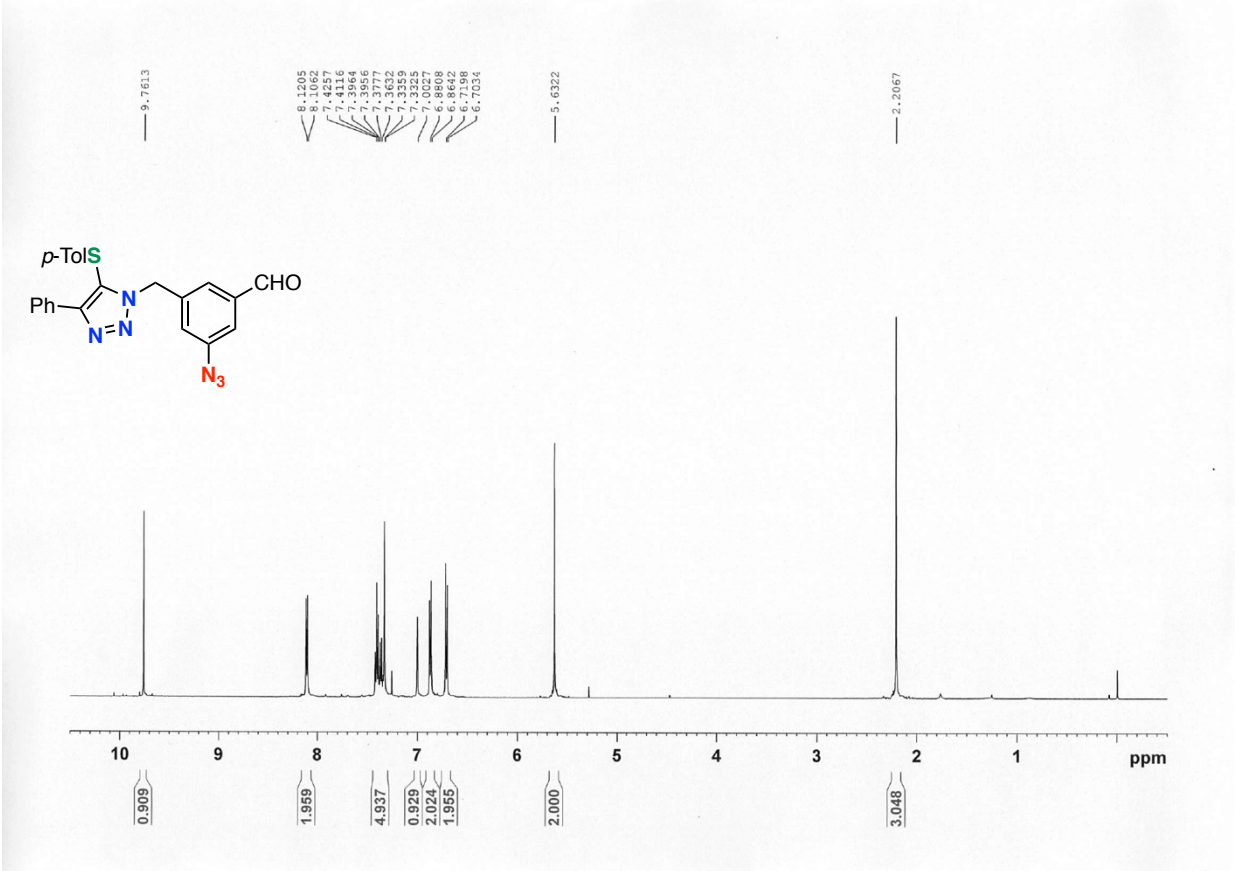


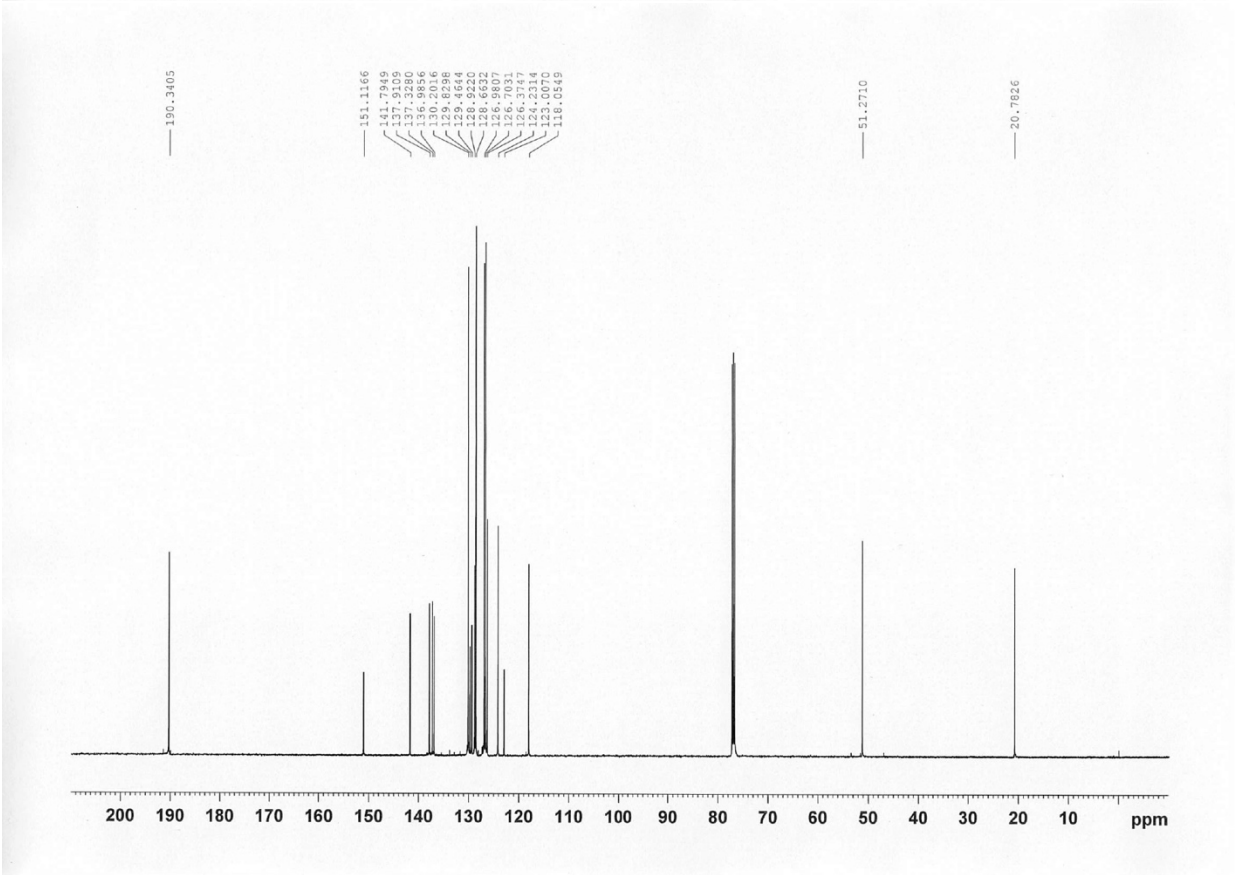



$^{1}$H NMR (500 MHz) and $^{13}$C NMR (126 MHz) spectra of 3-azido-5-((4-phenyl-5-(*p*-tolylthio)-1*H*-1,2,3-triazol-1-yl)methyl)phenol (**17d**) ($CDCl_3$)

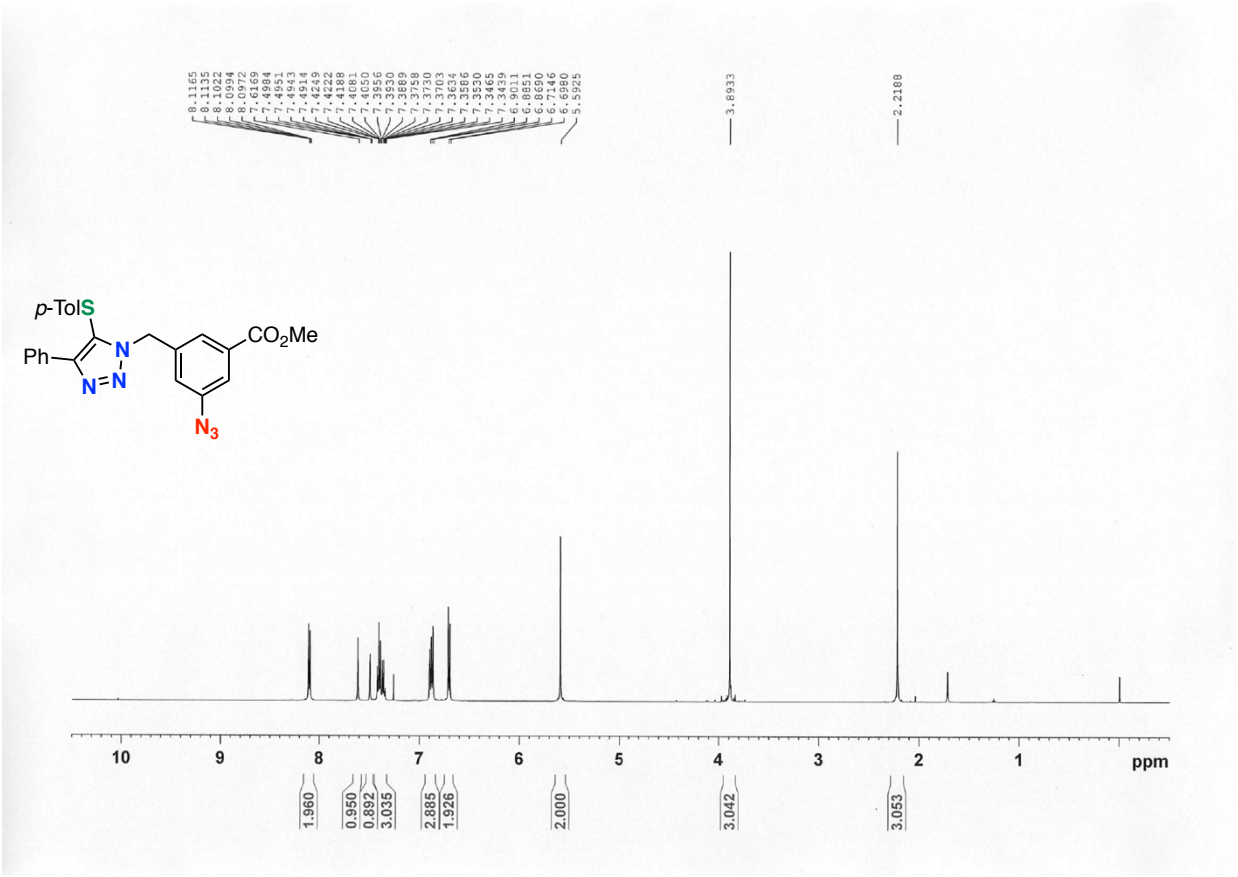


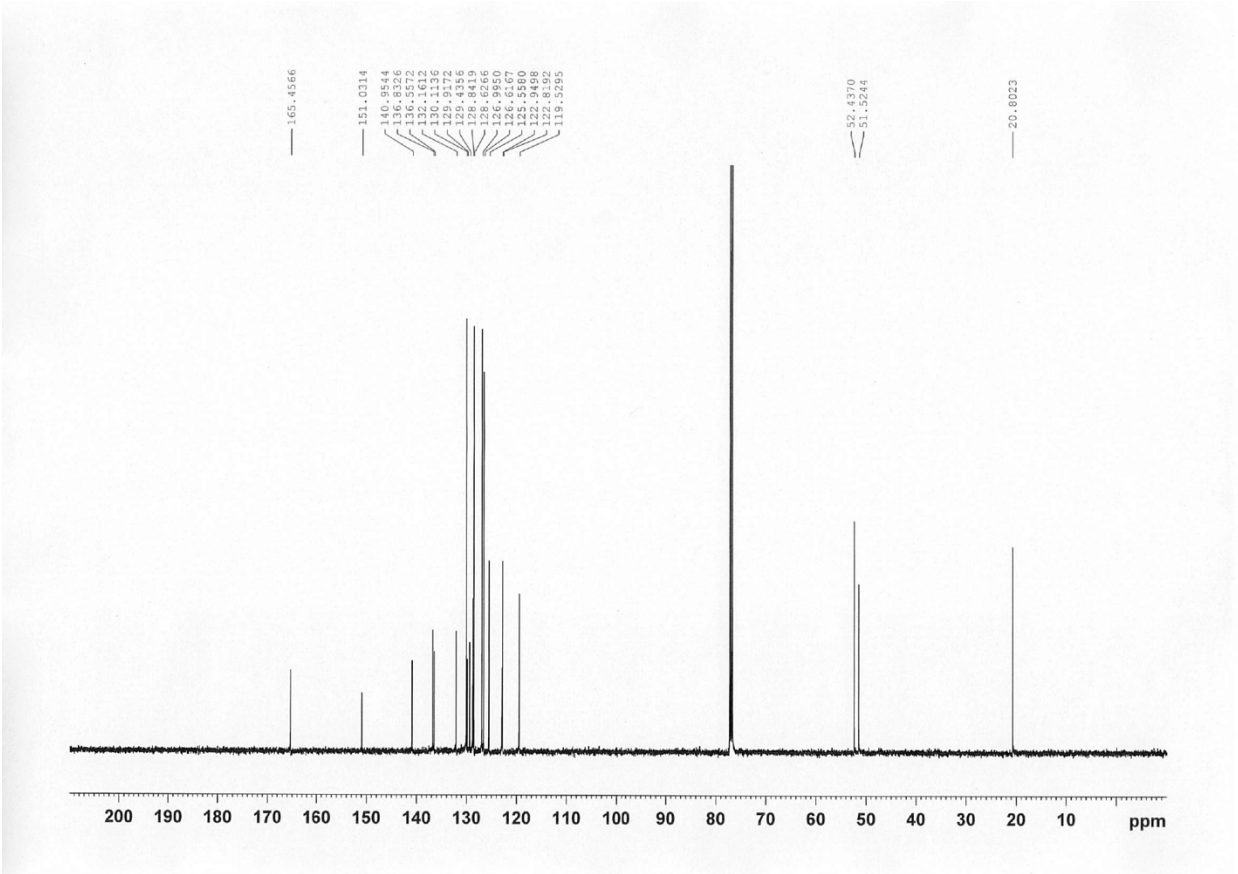
$^{1}$H NMR (500 MHz) and $^{13}$C NMR (126 MHz) spectra of 3-azido-5-((4-phenyl-5-(*p*-tolylthio)-1*H*-1,2,3-triazol-1-yl)methyl)benzaldehyde (**17e**) ($CDCl_3$)



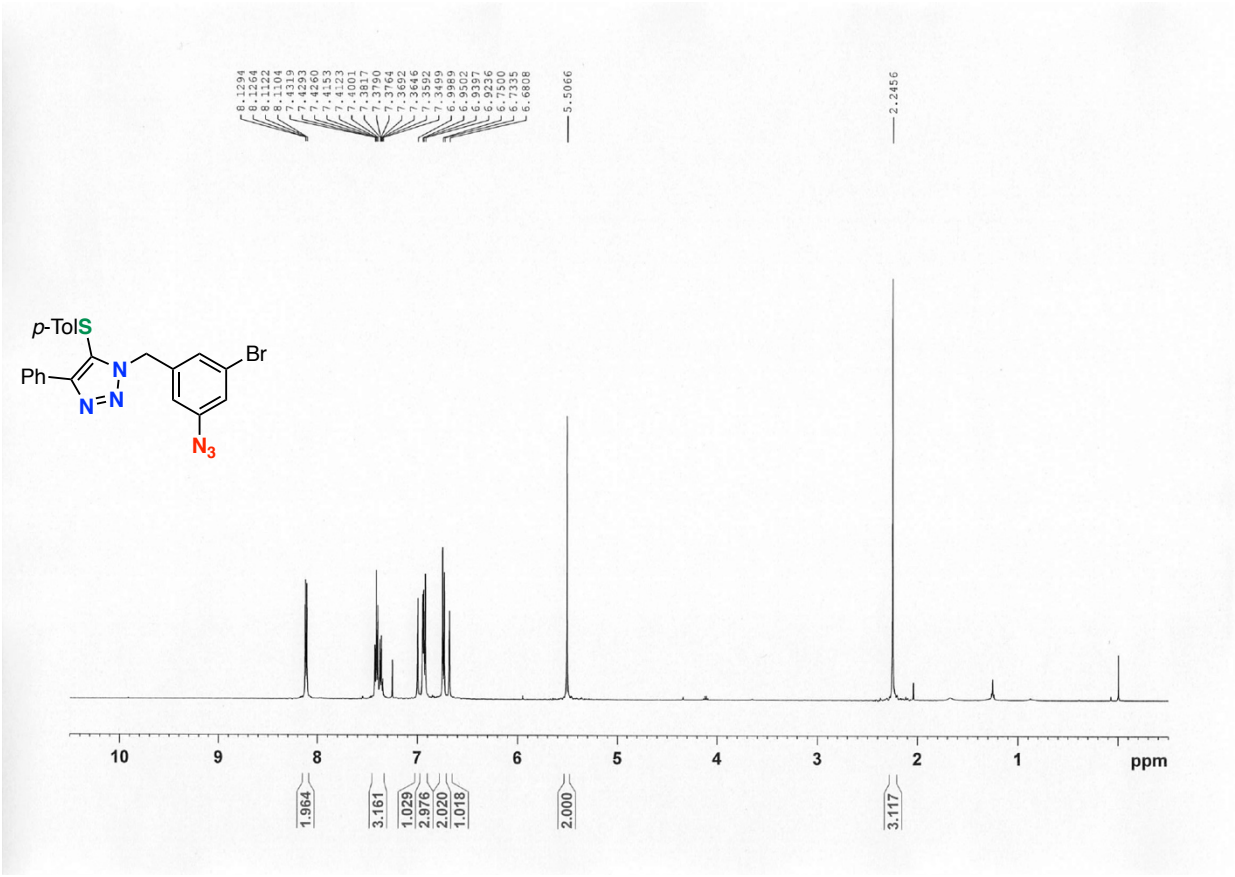



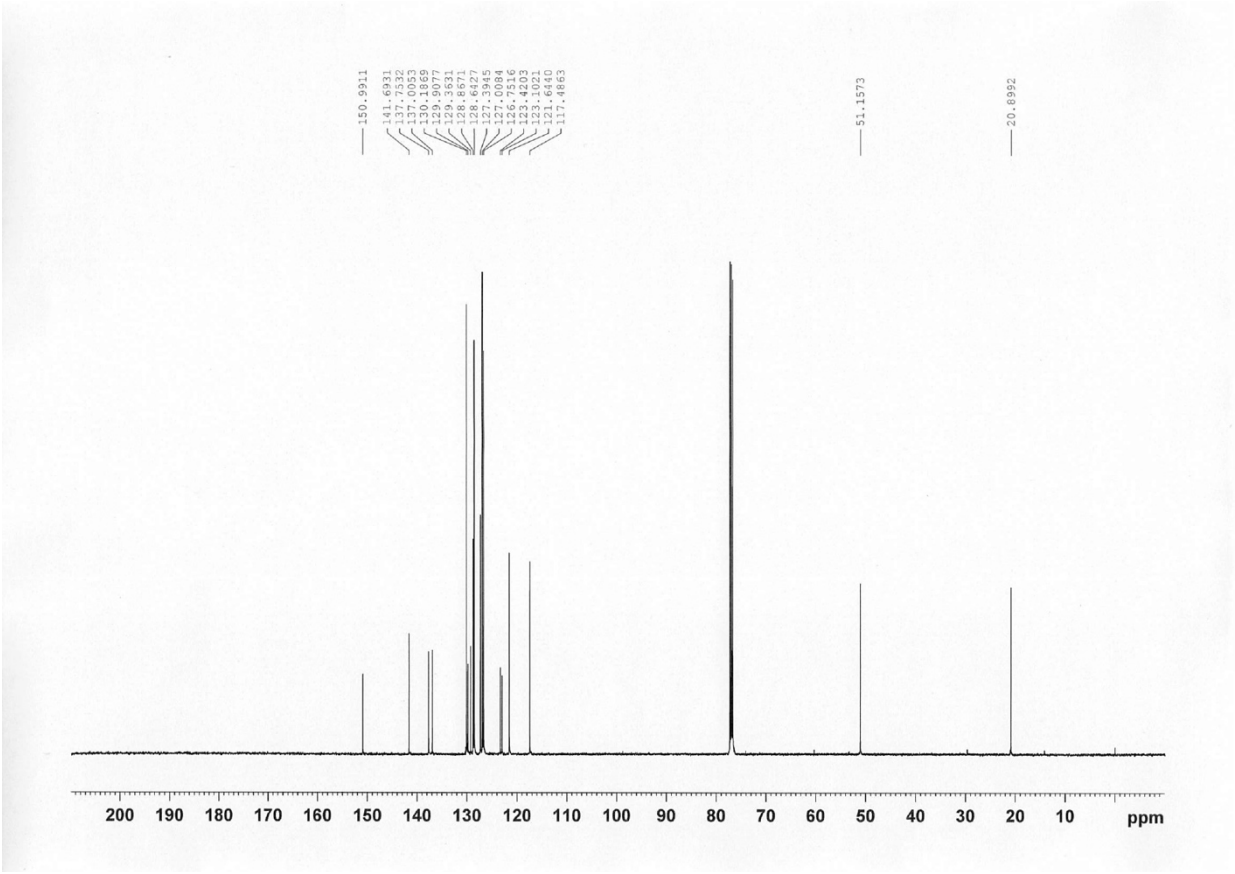
$^{1}$H NMR (500 MHz) and $^{13}$C NMR (126 MHz) spectra of methyl 3-azido-5-(4-phenyl-5-(*p*-tolylthio)-1*H*-1,2,3-triazol-1-yl)benzoate (**17f**) ($CDCl_3$)



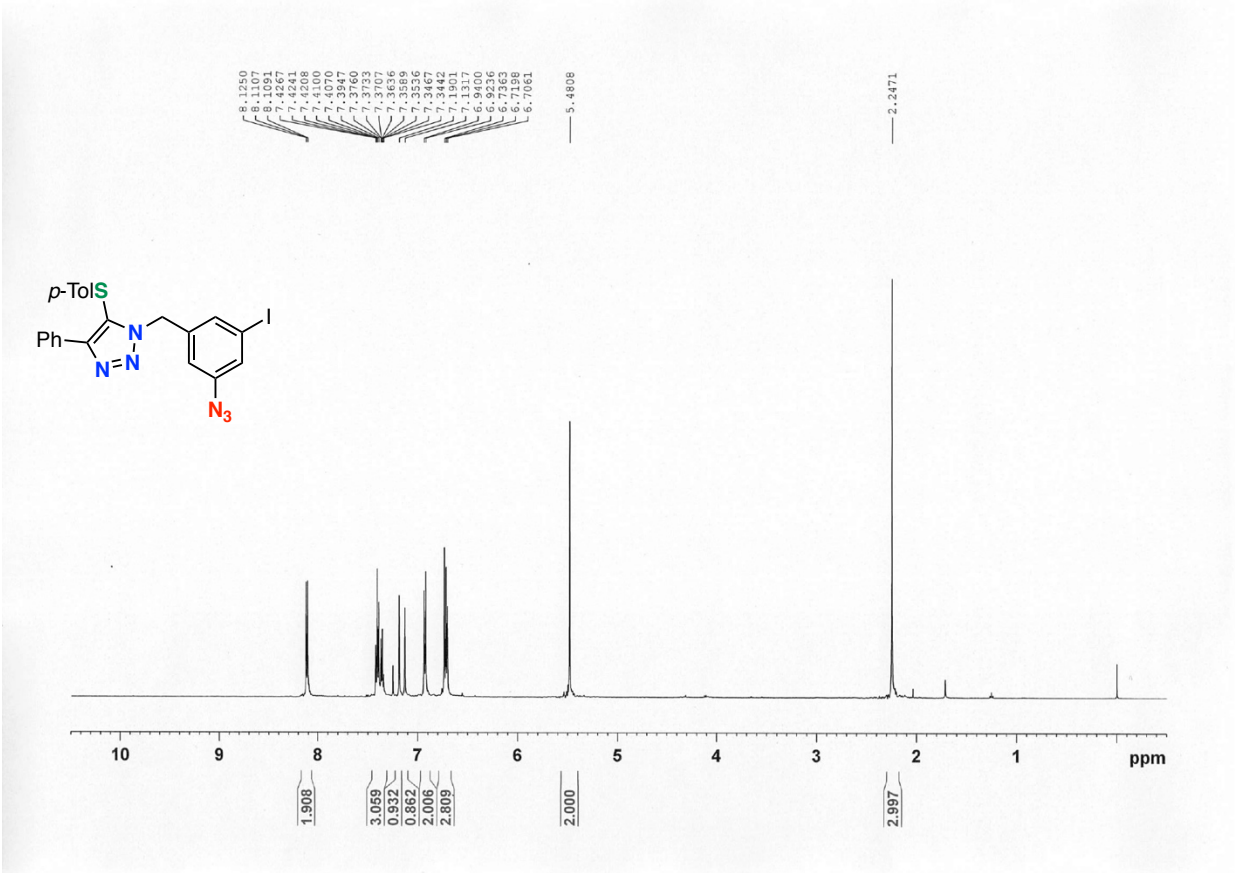



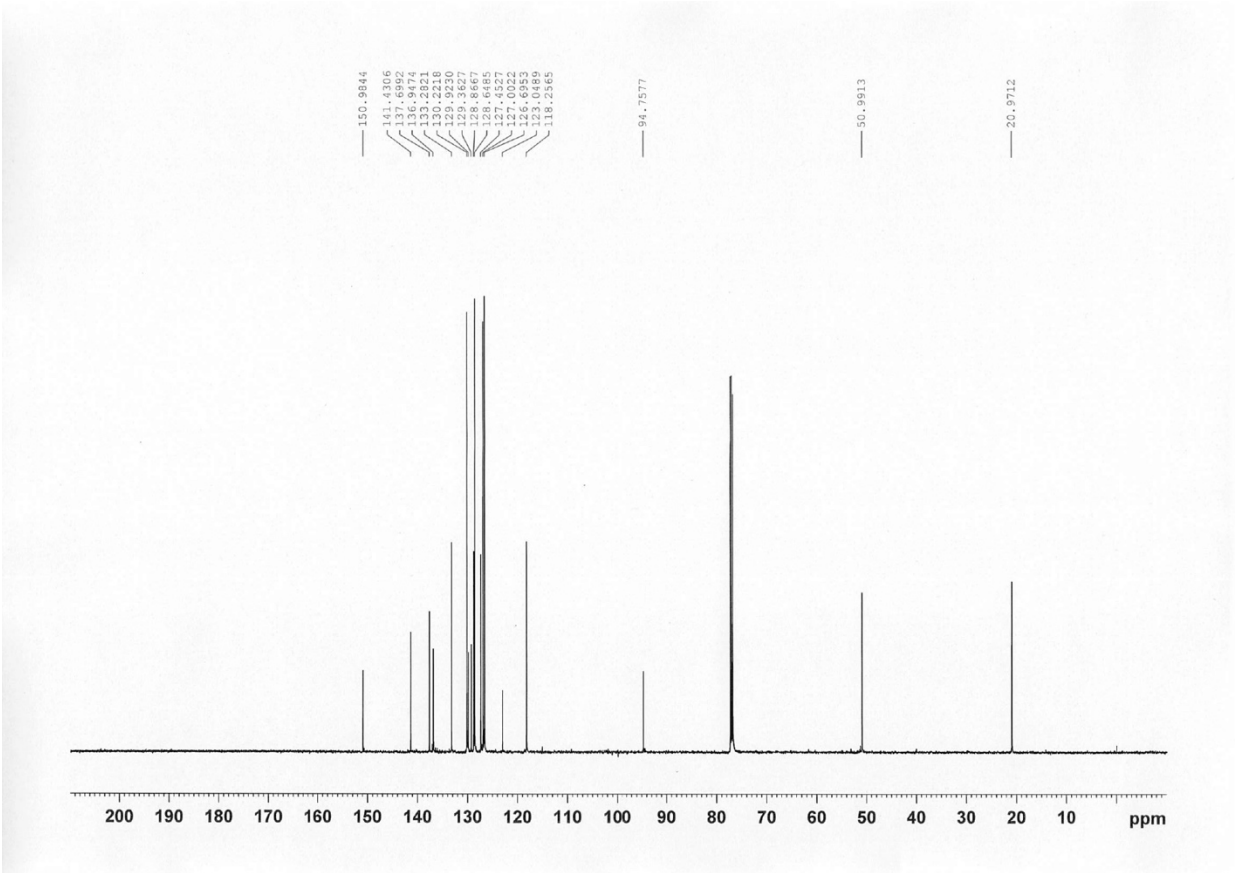
$^{1}$H NMR (500 MHz) and $^{13}$C NMR (126 MHz) spectra of 1-(3-azido-5-bromophenyl)-4-phenyl-5-(*p*-tolylthio)-1*H*-1,2,3-triazole (**17g**) ($CDCl_3$)



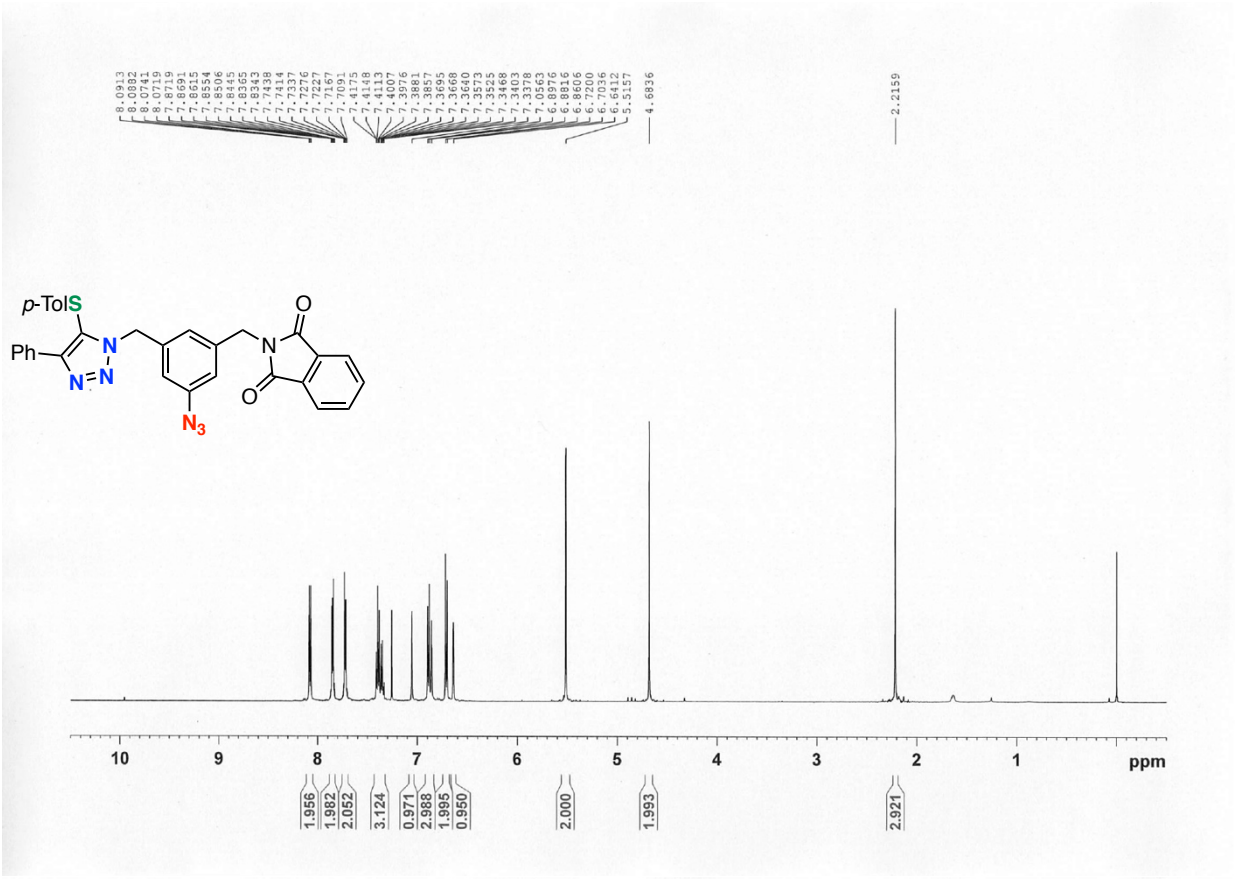



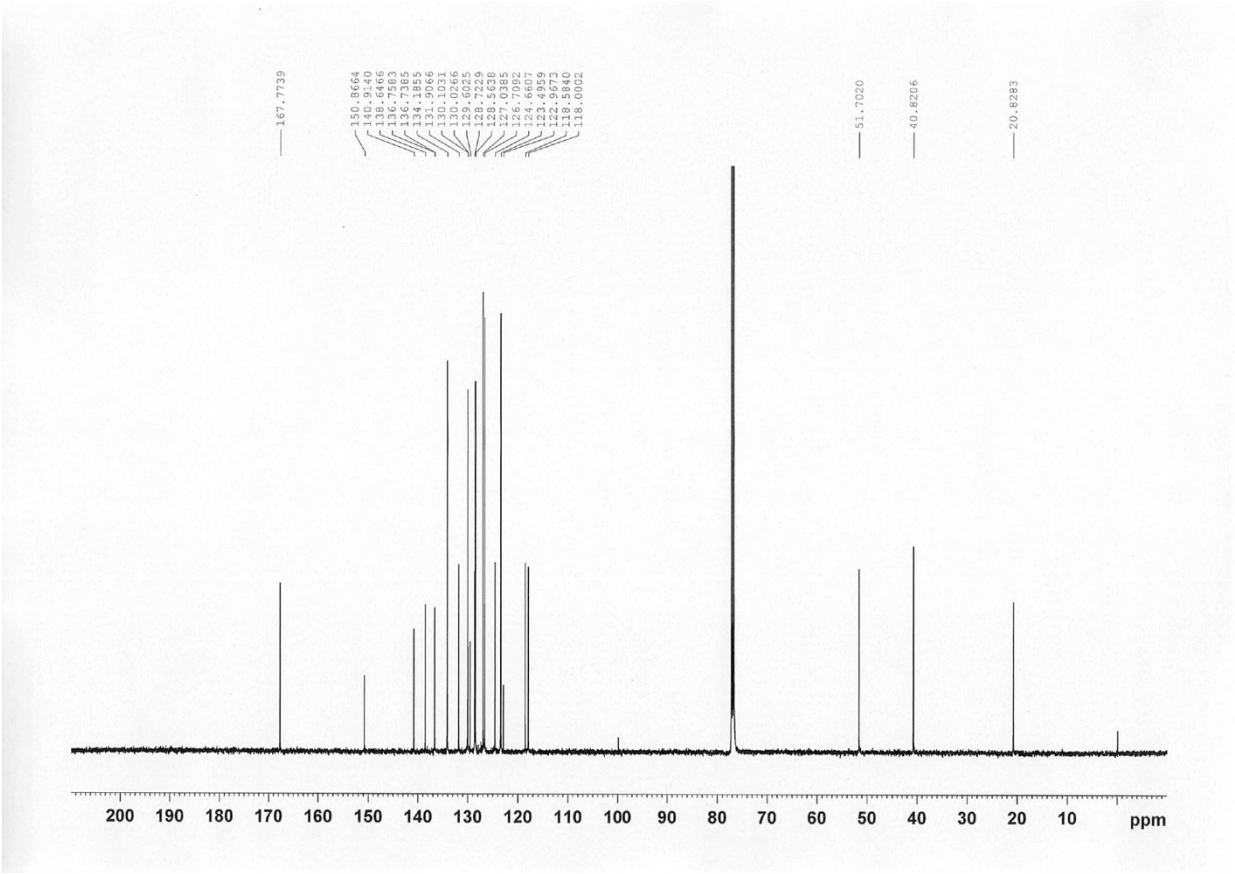
$^{1}$H NMR (500 MHz) and $^{13}$C NMR (126 MHz) spectra of 1-(3-azido-5-iodobenzyl)-4-phenyl-5-(*p*-tolylthio)-1*H*-1,2,3-triazole (**17h**) ($CDCl_3$)



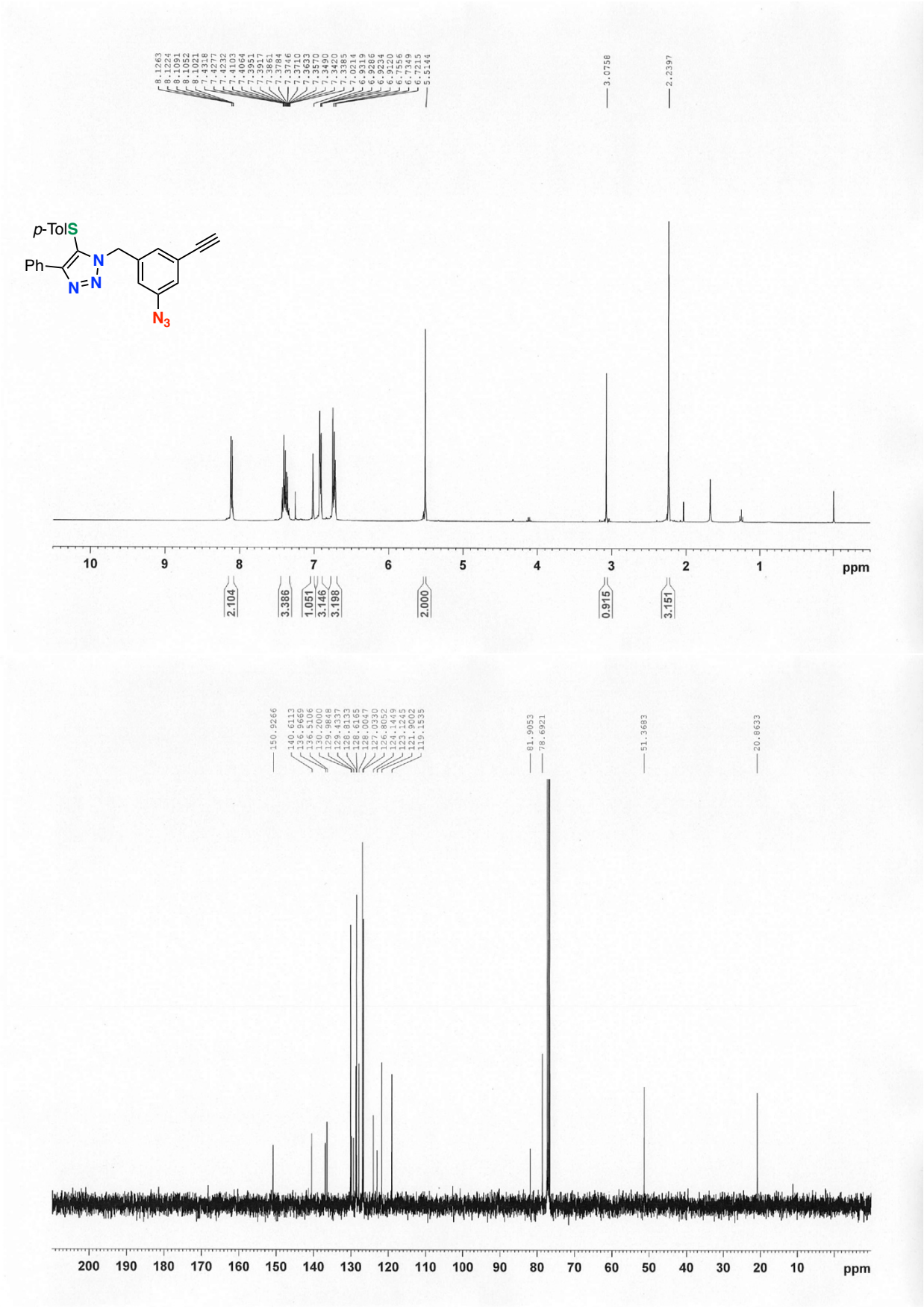



$^{1}$H NMR (500 MHz) and $^{13}$C NMR (126 MHz) spectra of 2-(3-azido-5-((4-phenyl-5-(*p*-tolylthio)-1*H*-1,2,3-triazol-1-yl)methyl)benzyl)phthalimide (**17i**) ($CDCl_3$)

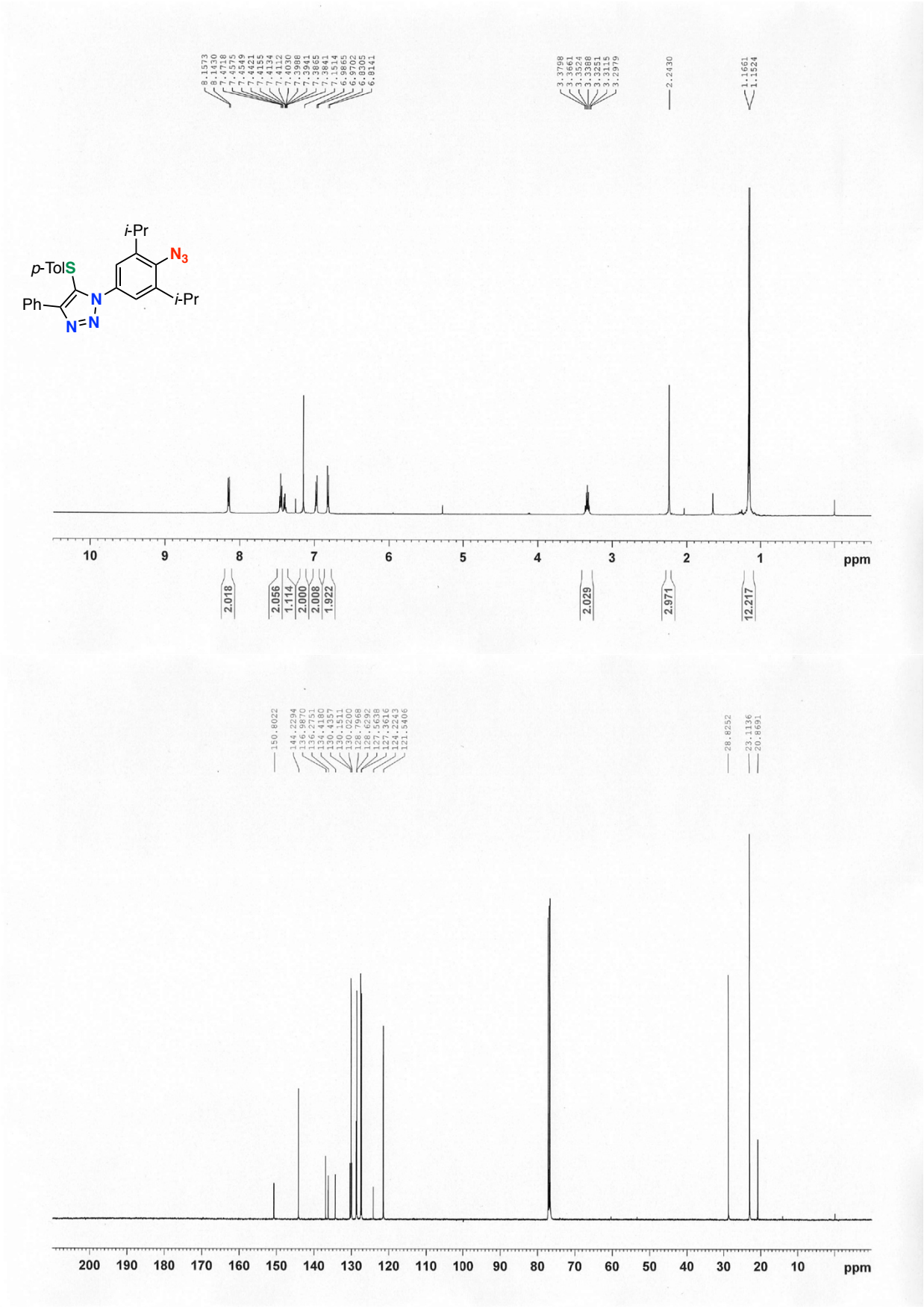


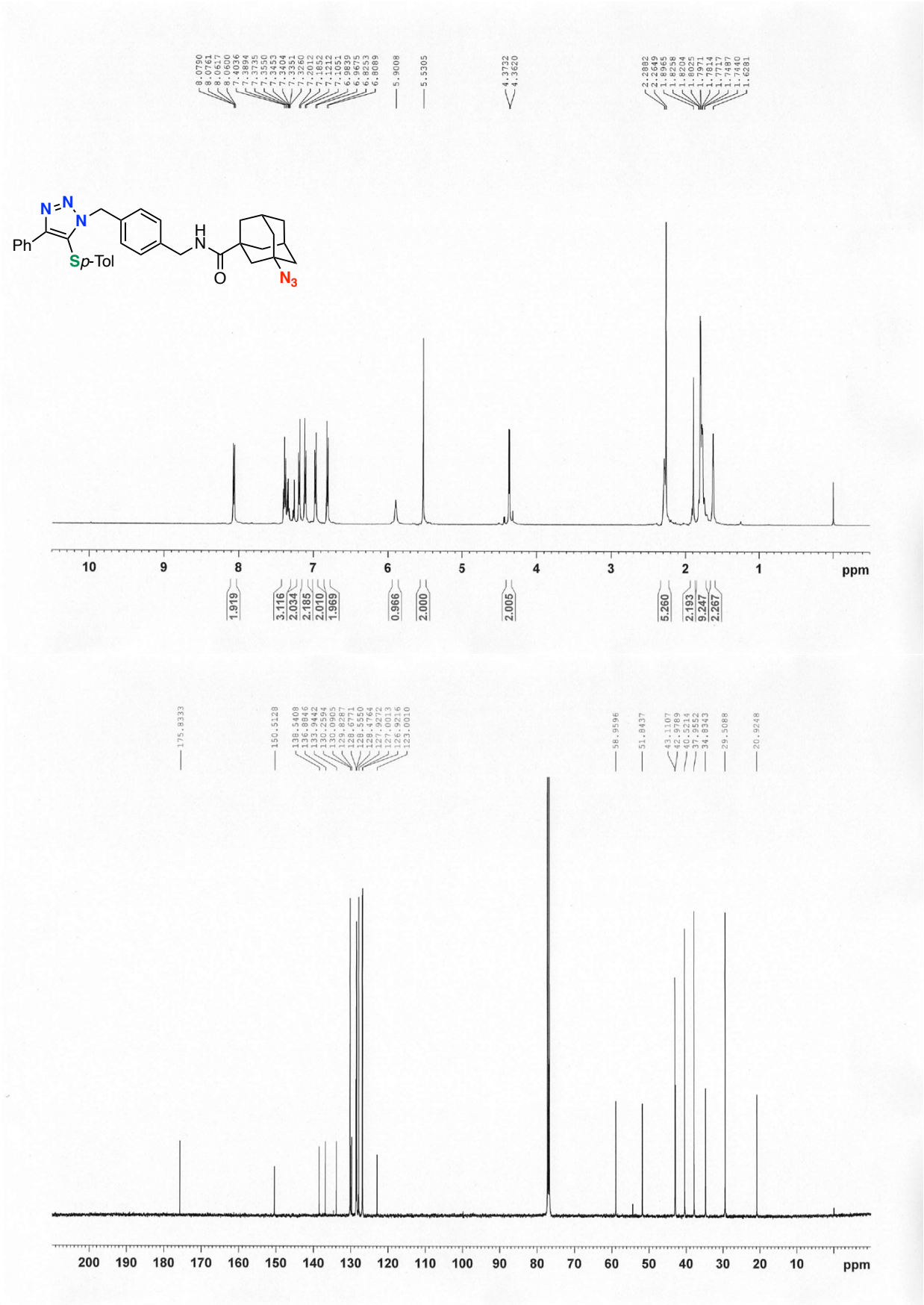
$^{1}$H NMR (500 MHz) and $^{13}$C NMR (126 MHz) spectra of 1-(3-azido-5-ethynylbenzyl)-4-phenyl-5-(*p*-tolylthio)-1*H*-1,2,3-triazole (**17j**) ($CDCl_3$)



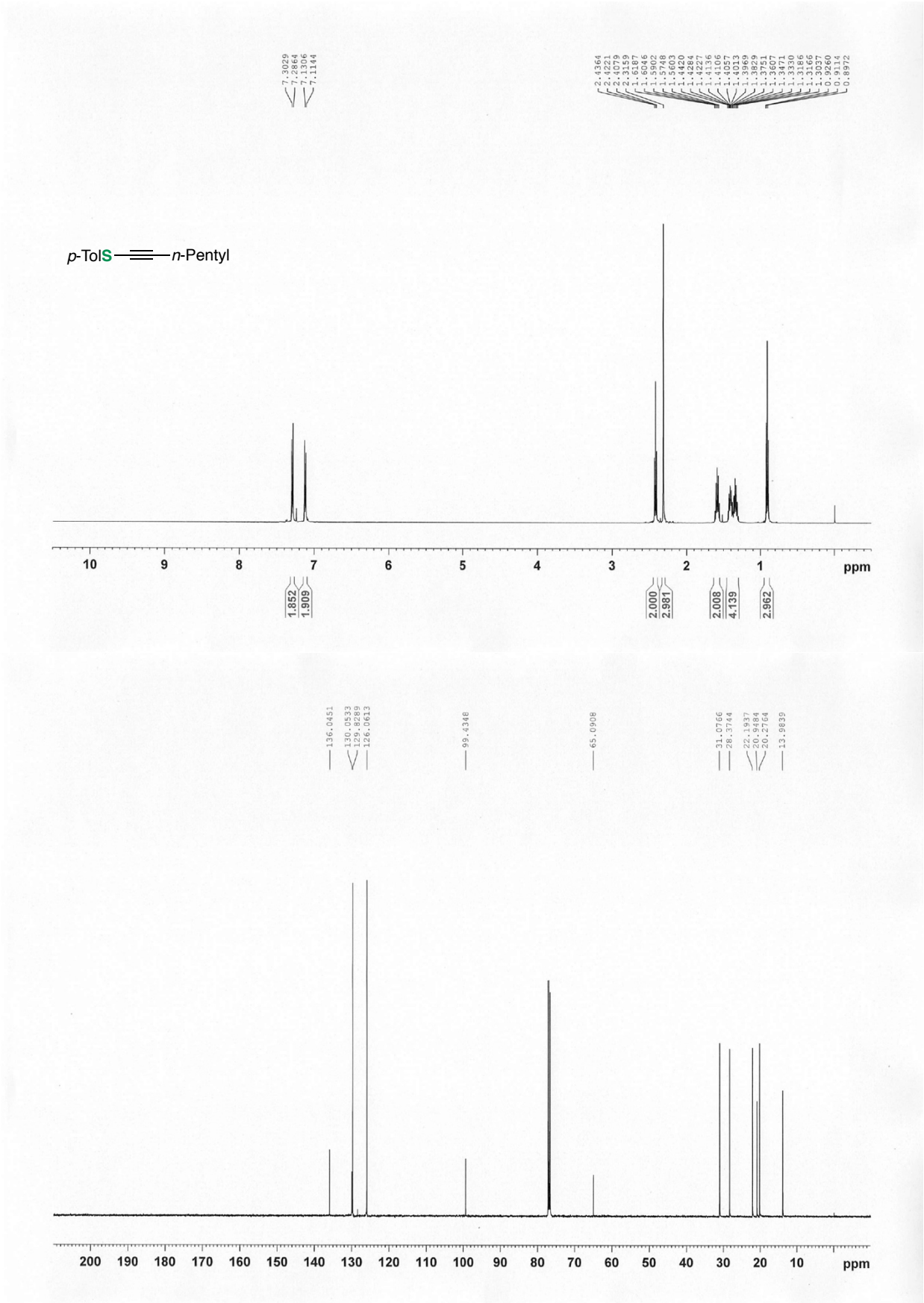
$^{1}$H NMR (500 MHz) and $^{13}$C NMR (126 MHz) spectra of 1-(4-azido-3,5-diisopropylphenyl)-4-phenyl-5-(*p*-tolylthio)-1*H*-1,2,3-triazole (**19**) ($CDCl_3$)



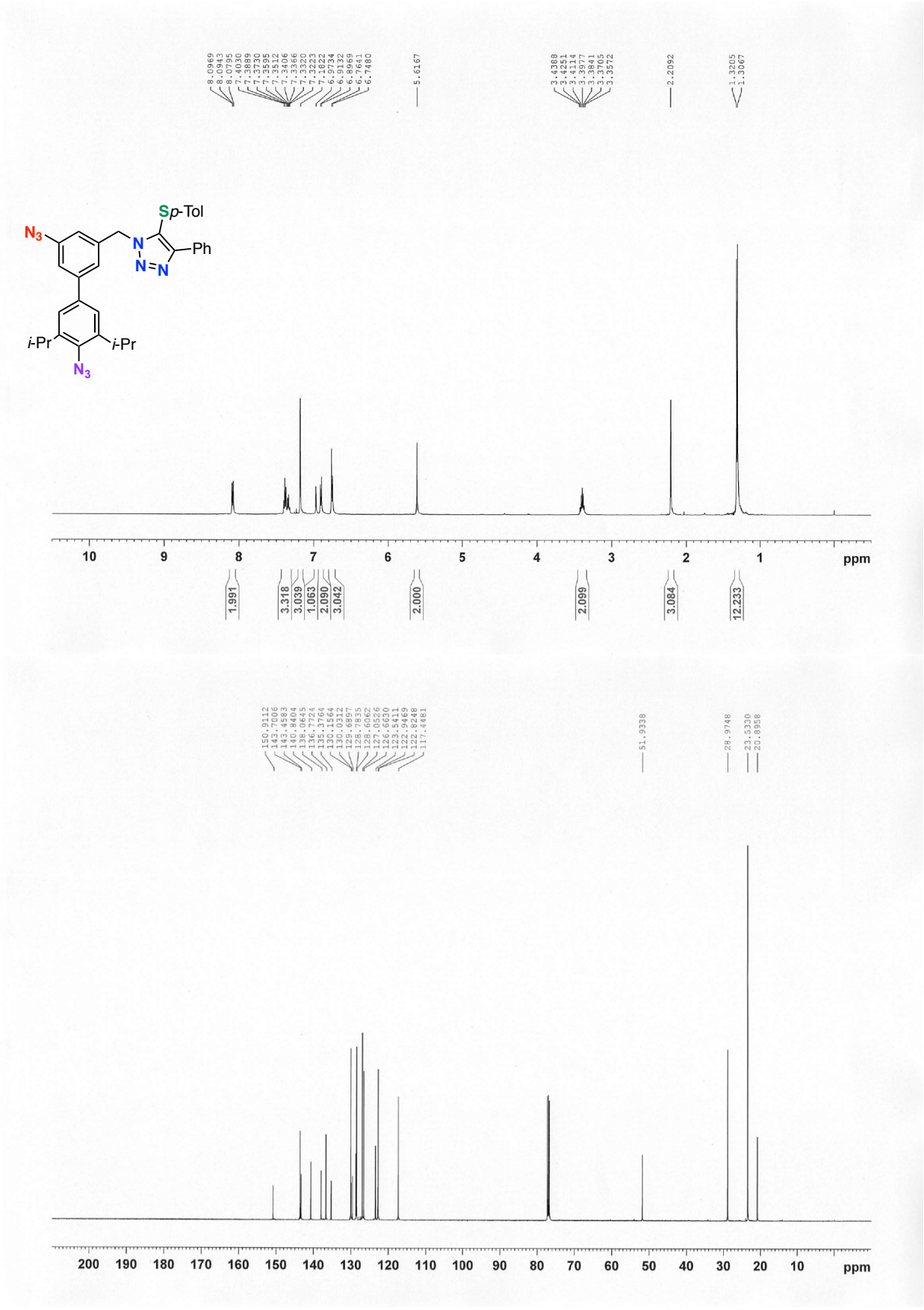
$^{1}$H NMR (500 MHz) and $^{13}$C NMR (126 MHz) spectra of 3-azido-*N*-(4-((4-phenyl-5-(*p*-tolylthio)-1*H*-1,2,3-triazol-1-yl)methyl)benzyl)-1-adamantanamide (**21**) ($CDCl_3$)



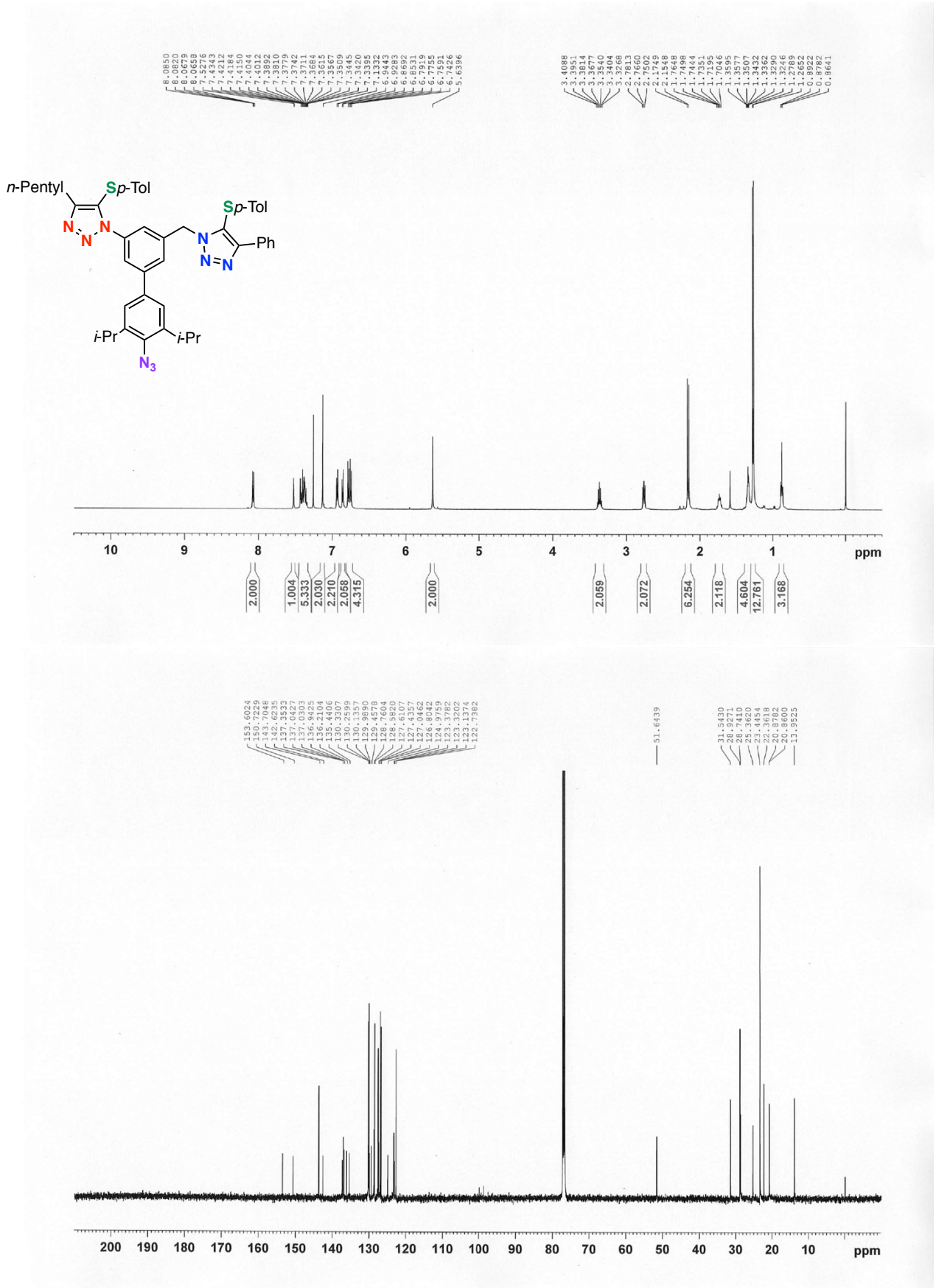
$^{1}$H NMR (500 MHz) and $^{13}$C NMR (126 MHz) spectra of 1-heptyn-1-yl *p*-tolyl sulfide (**9d**) ($CDCl_3$)



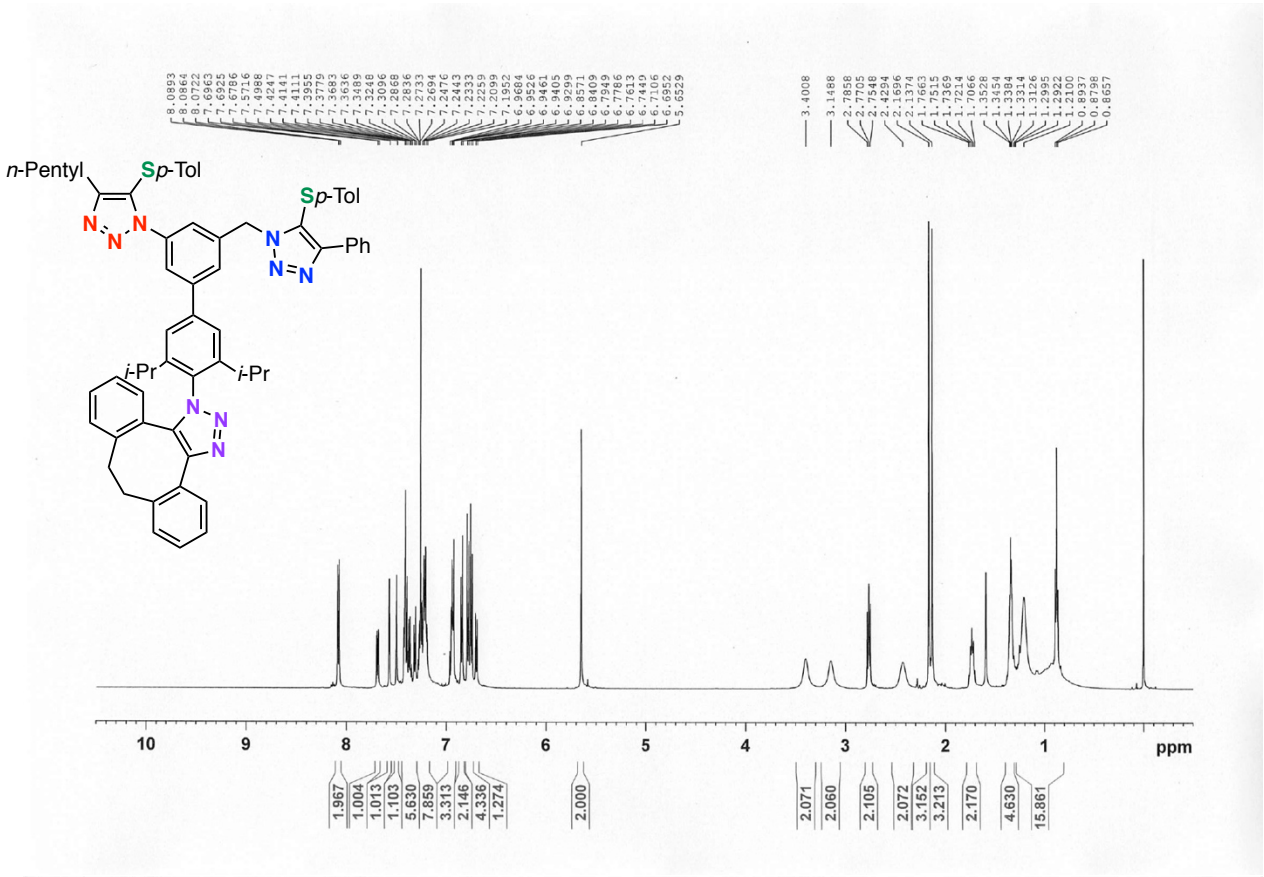
$^{1}$H NMR (500 MHz) and $^{13}$C NMR (126 MHz) spectra of 1-((4′,5-diazido-3′,5′-diisopropyl-1,1′-biphenyl-3-yl)methyl)-4-phenyl-5-(*p*-tolylthio)-1*H*-1,2,3-triazole (**S3**) ($CDCl_3$)

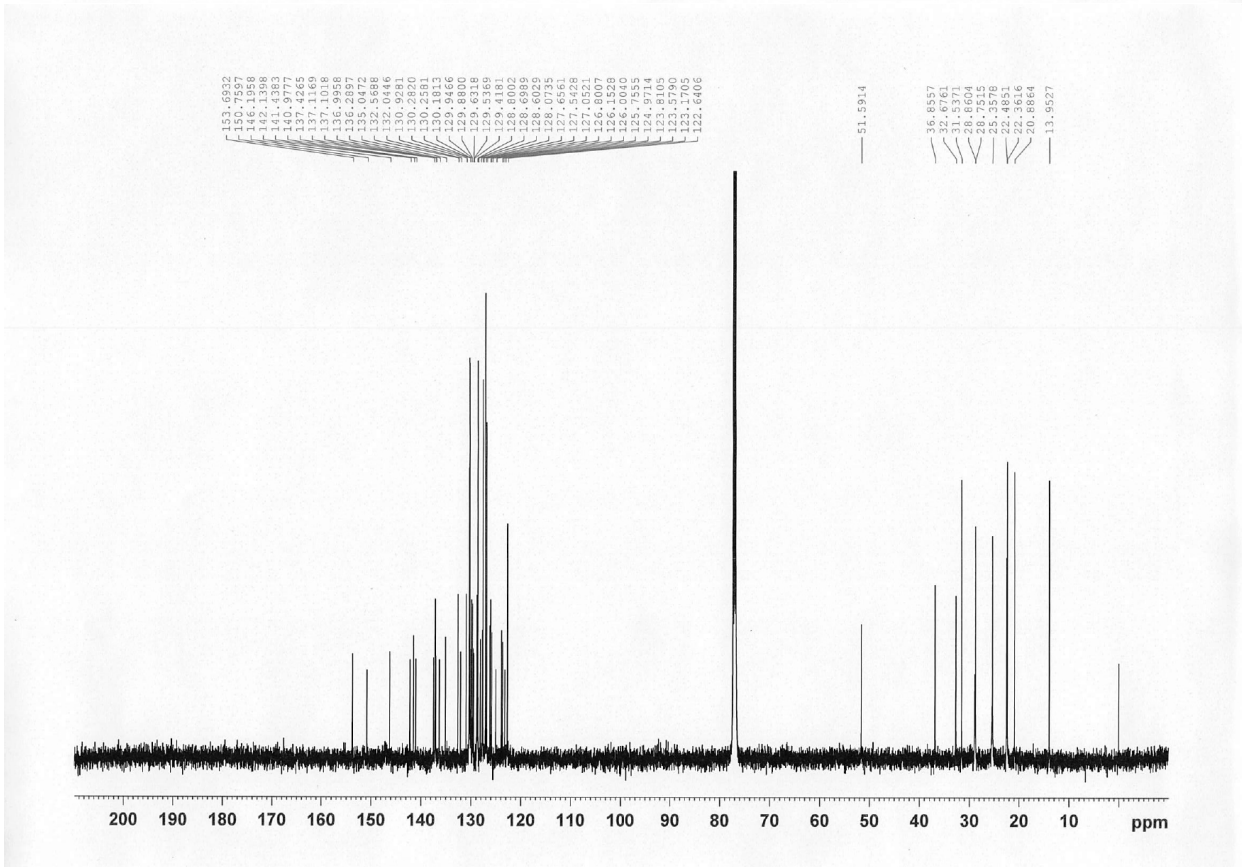


$^{1}$H NMR (500 MHz) and $^{13}$C NMR (126 MHz) spectra of 1-(4′-azido-3′,5′-diisopropyl-5-((4-phenyl-5-(*p*-tolylthio)-1*H*-1,2,3-triazol-1-yl)methyl)-1,1′-biphenyl-3-yl)-4-pentyl-5-(*p*-tolylthio)-1*H*-1,2,3-triazole (**S4**) ($CDCl_3$)

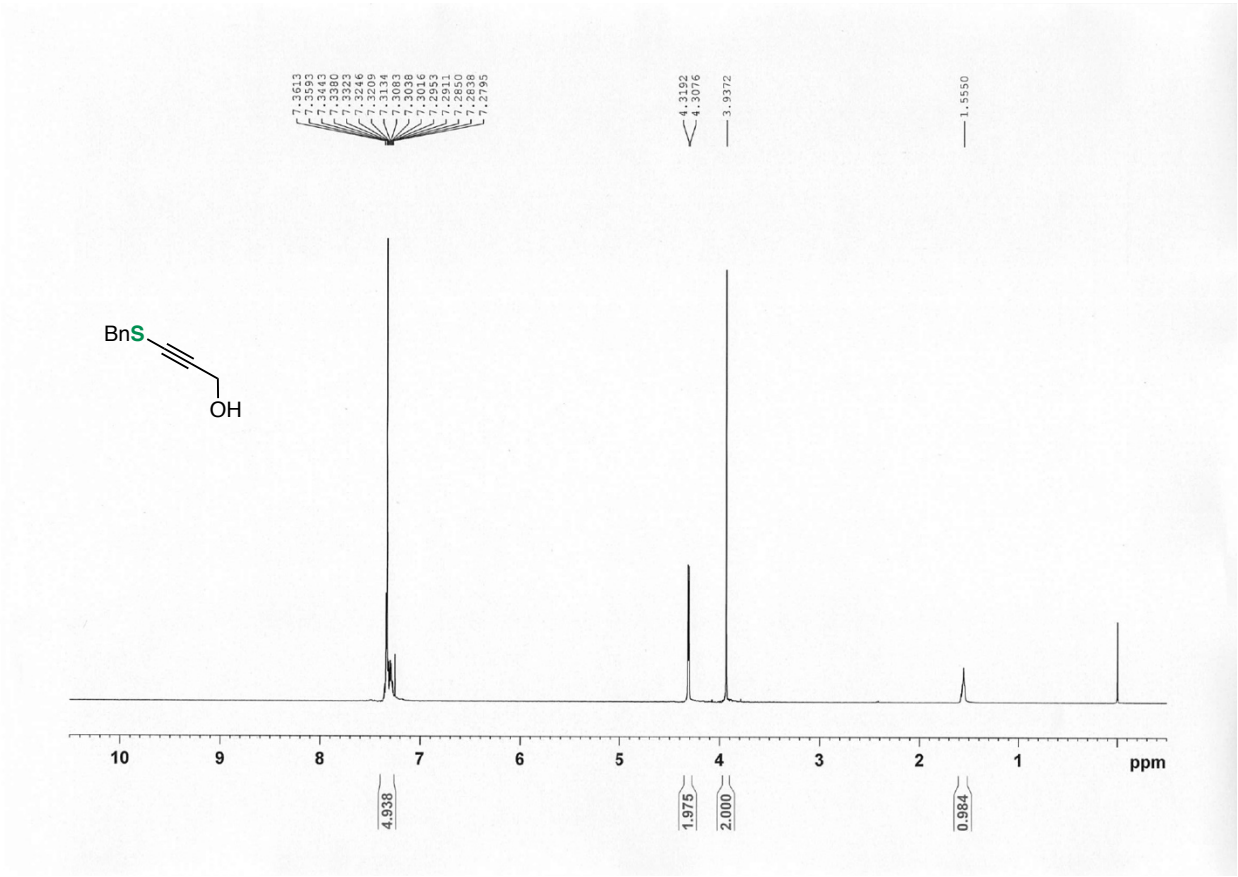


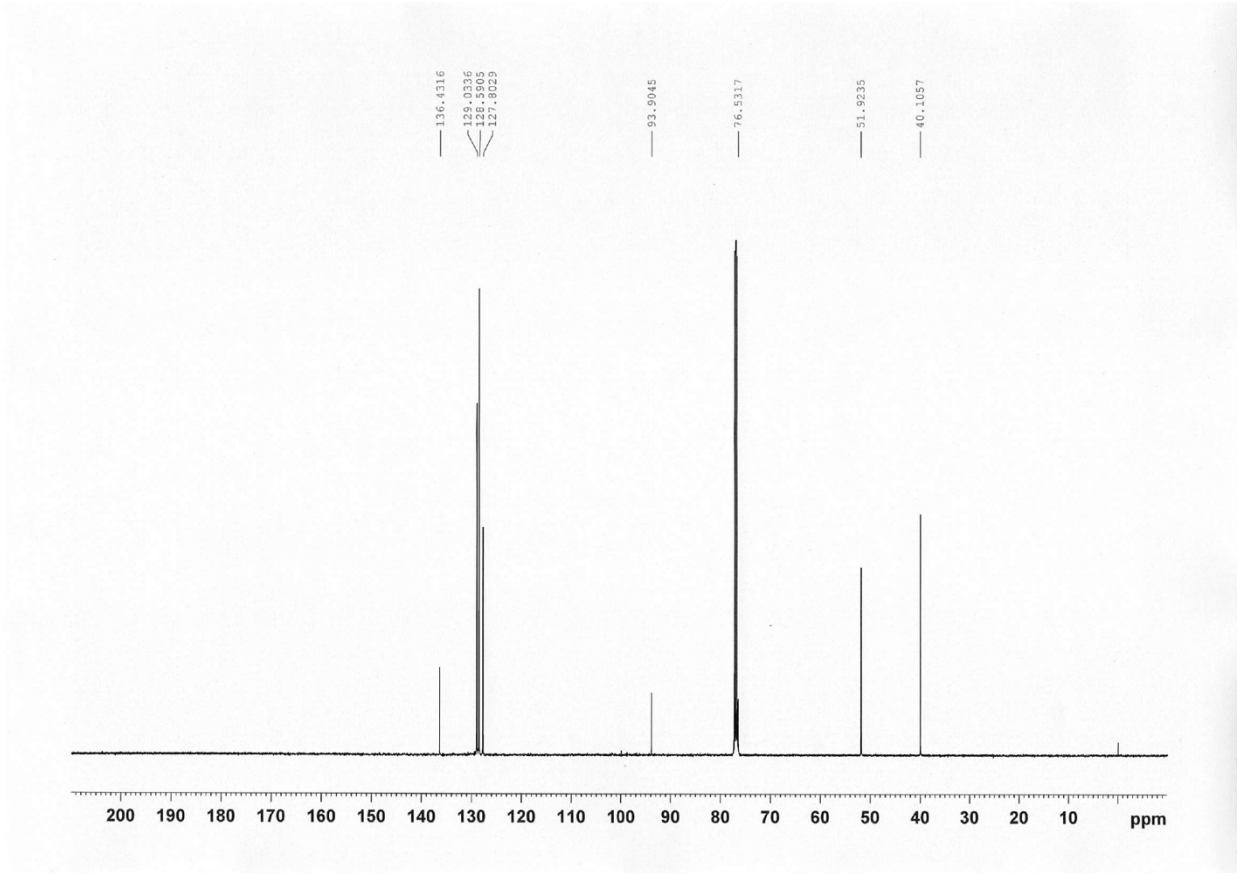
$^{1}$H NMR (500 MHz) and $^{13}$C NMR (126 MHz) spectra of 1-(3,5-diisopropyl-3′-(4-pentyl-5-(*p*-tolylthio)-1*H*-1,2,3-triazol-1-yl)-5′-((4-phenyl-5-(*p*-tolylthio)-1*H*-1,2,3-triazol-1-yl)methyl)-1,1′-biphenyl-4-yl)-8,9-dihydro-1*H*-dibenzo[3,4:7,8]cycloocta[1,2-*d*][1,2,3]triazole (**23**) ($CDCl_3$)



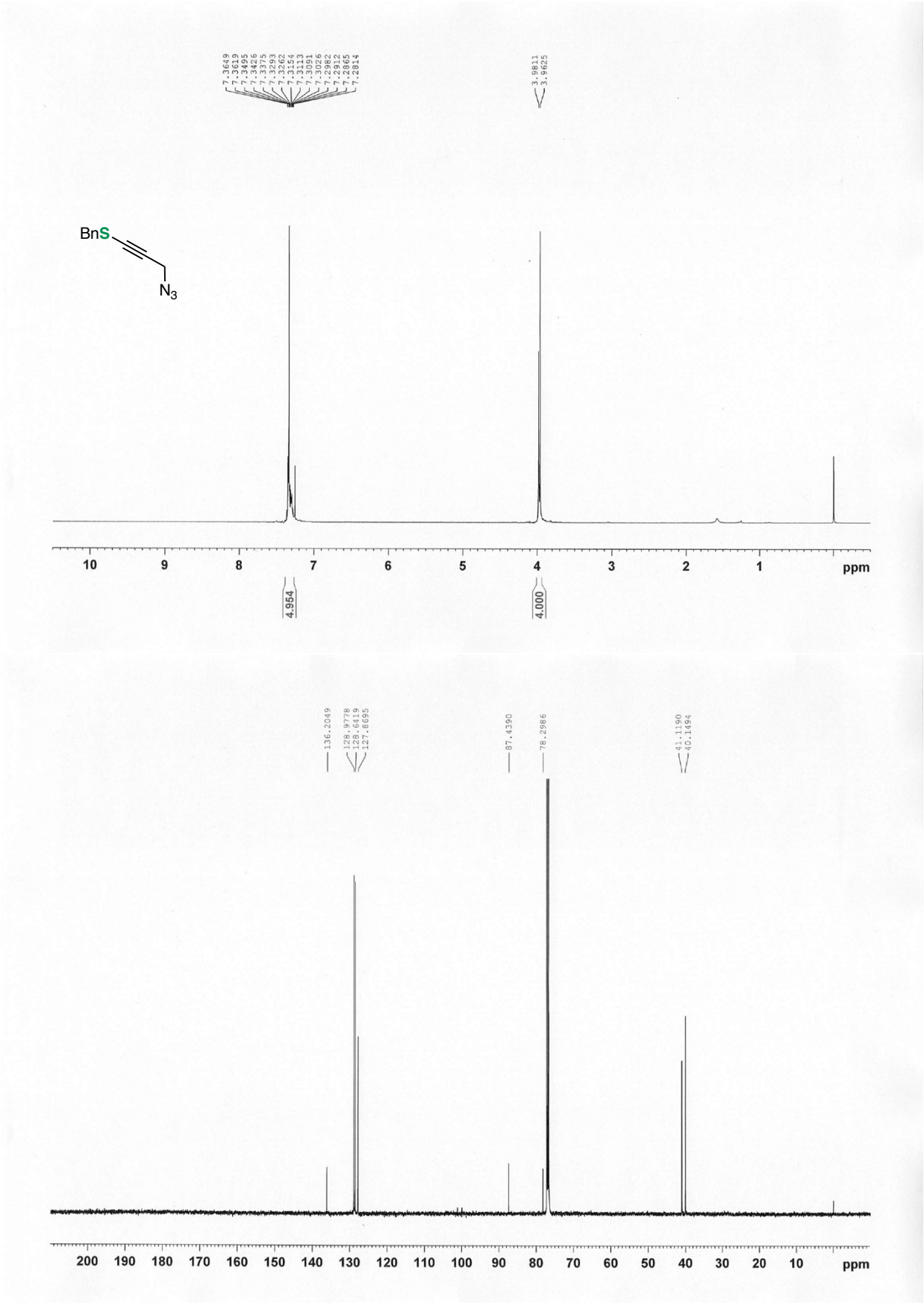



$^{1}$H NMR (500 MHz) and $^{13}$C NMR (126 MHz) spectra of 3-benzylthio-2-propyn-1-ol (**S5**) ($CDCl_3$)

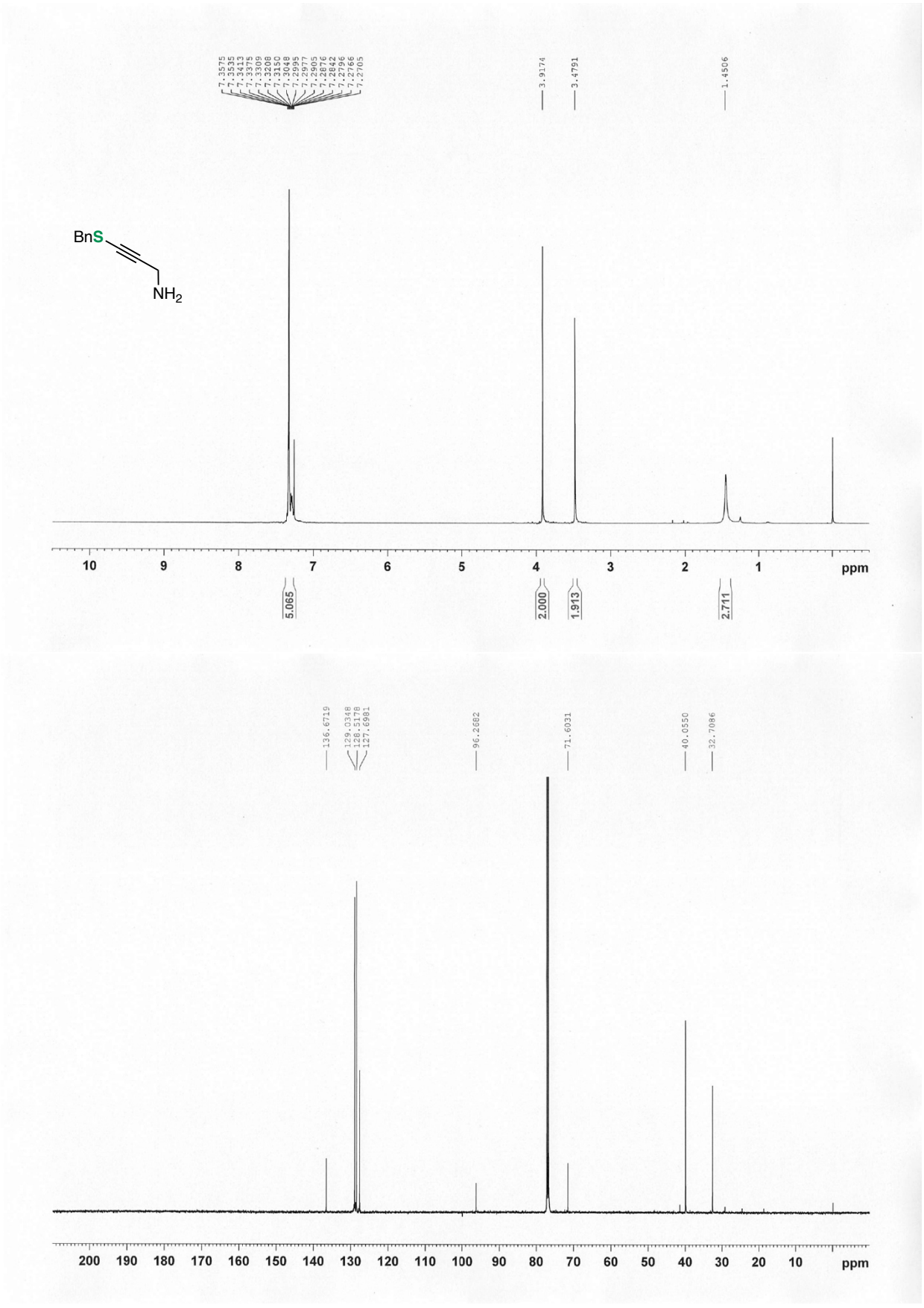


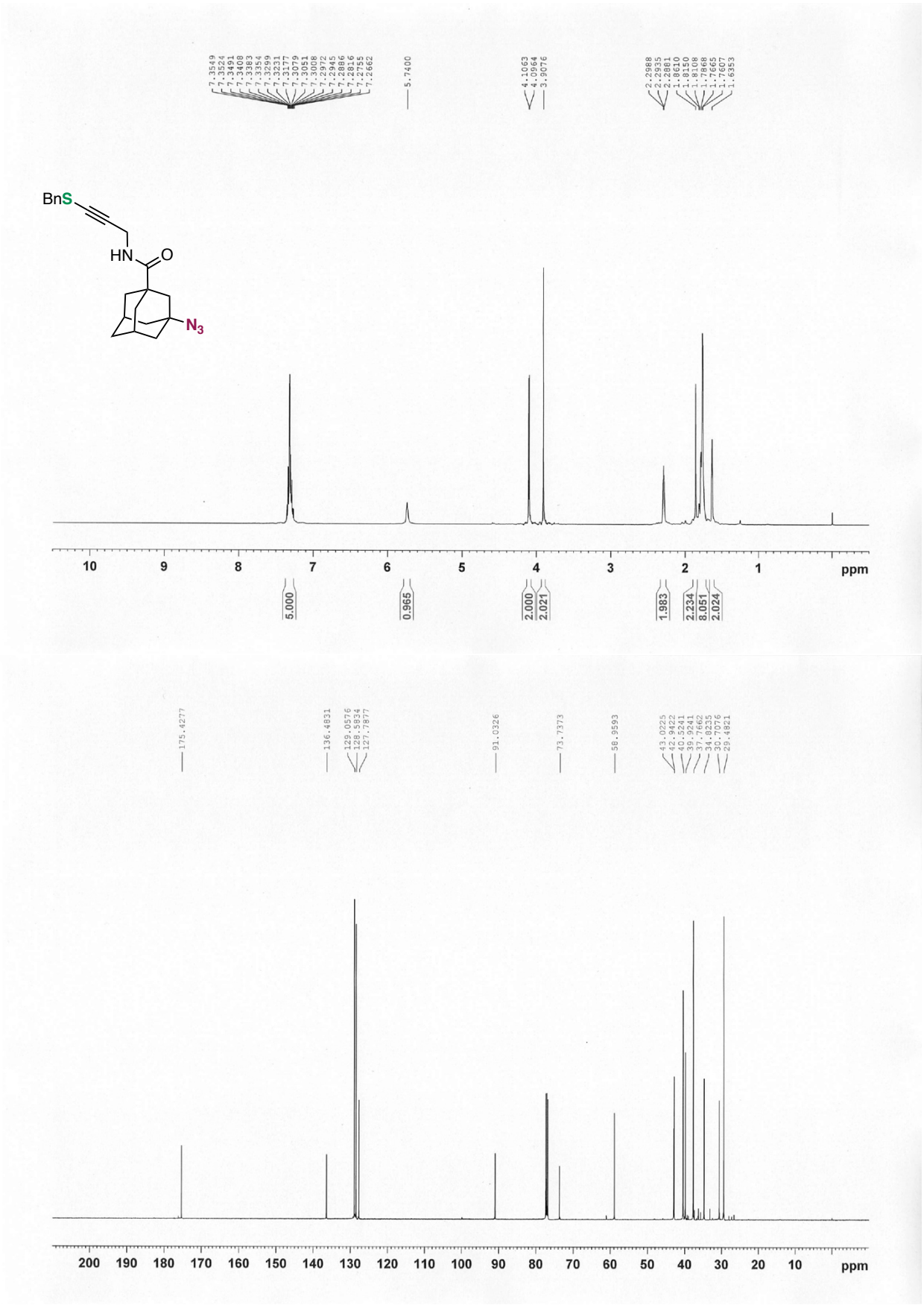
$^{1}$H NMR (500 MHz) and $^{13}$C NMR (126 MHz) spectra of 3-benzylthio-2-propyn-1-yl azide (**S6**) ($CDCl_3$)



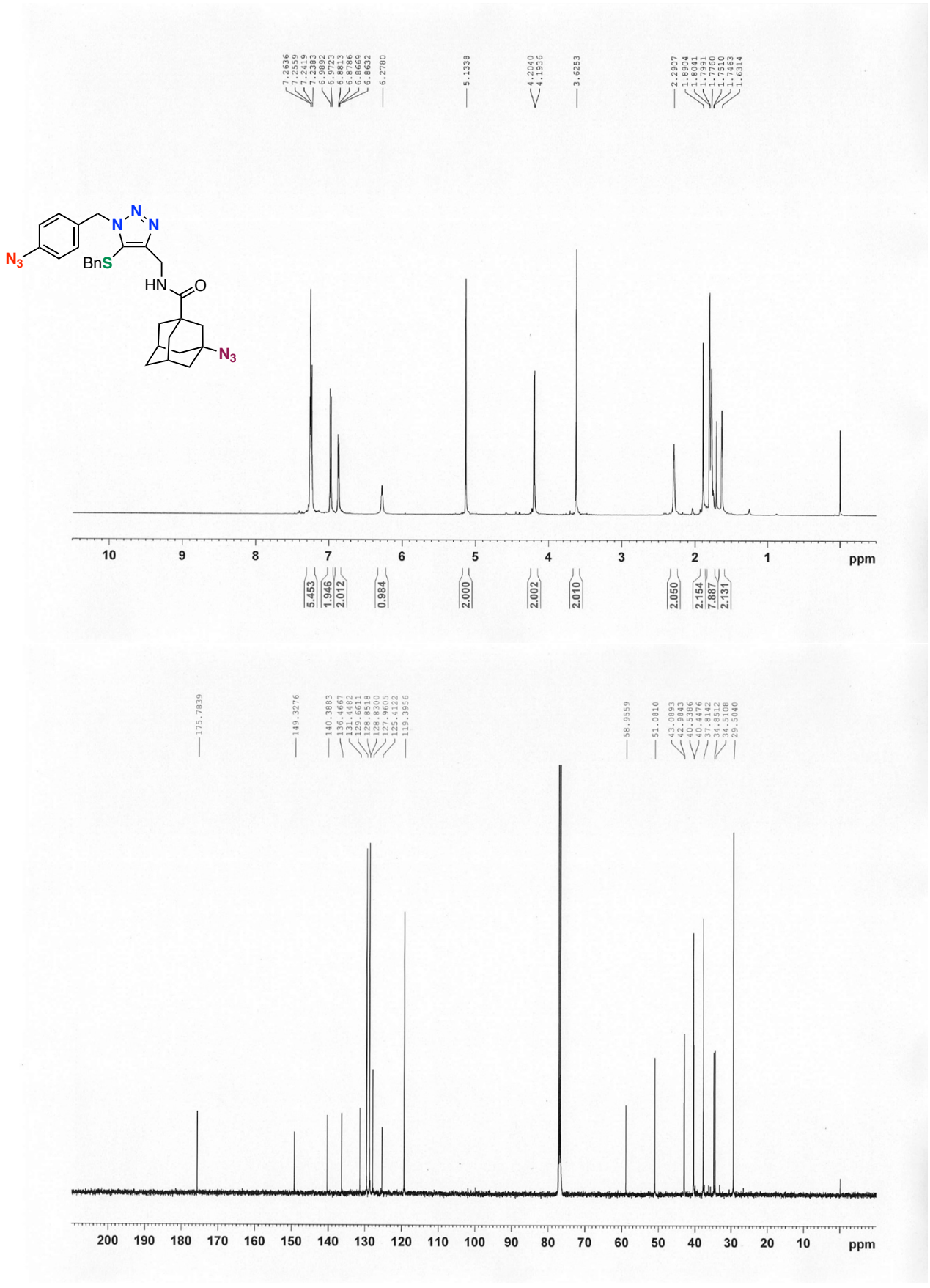
$^{1}H$ NMR (500 MHz) and $^{13}C$ NMR (126 MHz) spectra of 3-benzylthio-2-propyn-1-ylamine (**S7**) ($CDCl_3$)



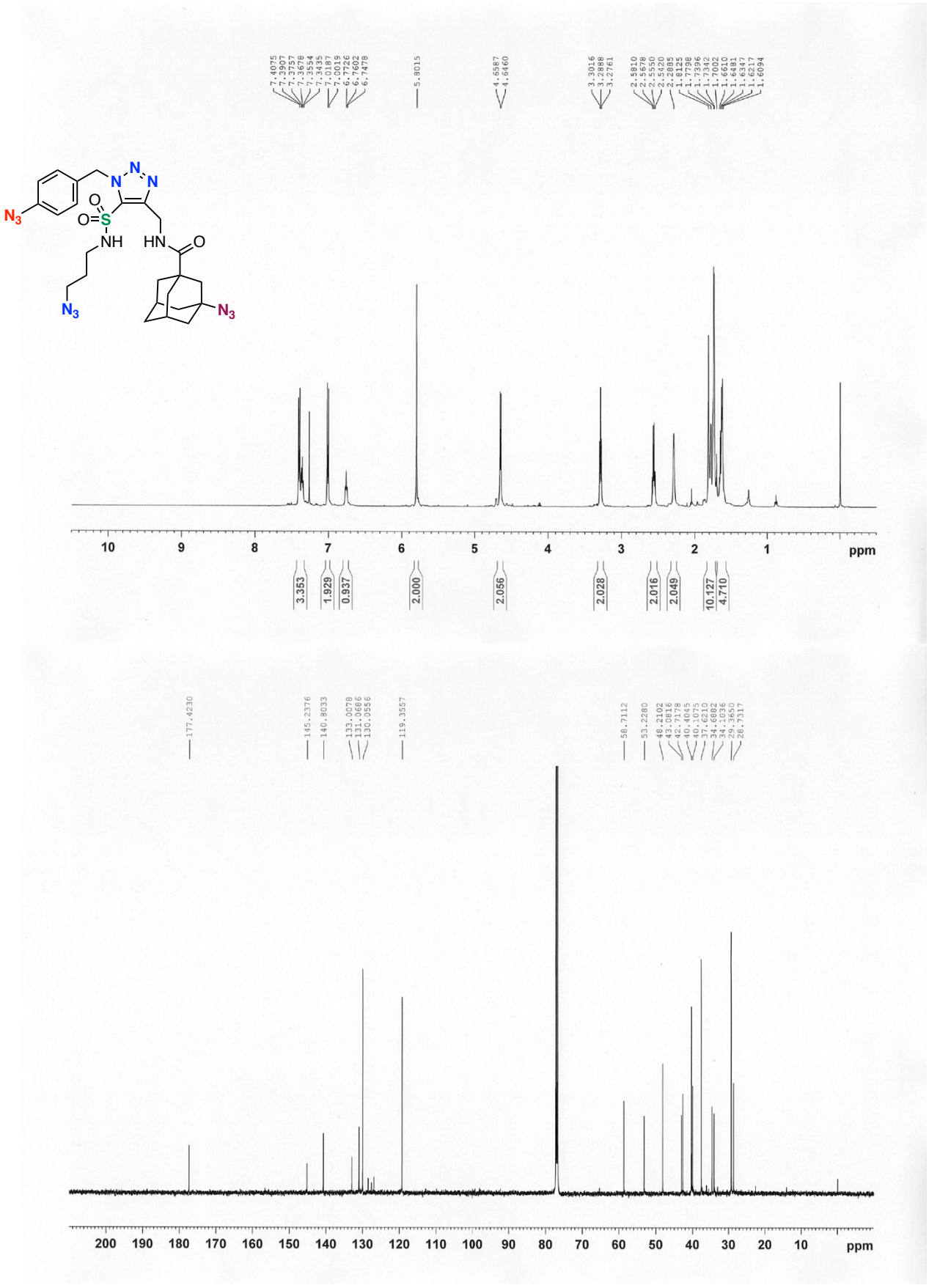
$^{1}$H NMR (500 MHz) and $^{13}$C NMR (126 MHz) spectra of 3-azido-*N*-(3-benzylthio-2-propyn-1-yl)-1-adamantanamide (**9e**) ($CDCl_3$)



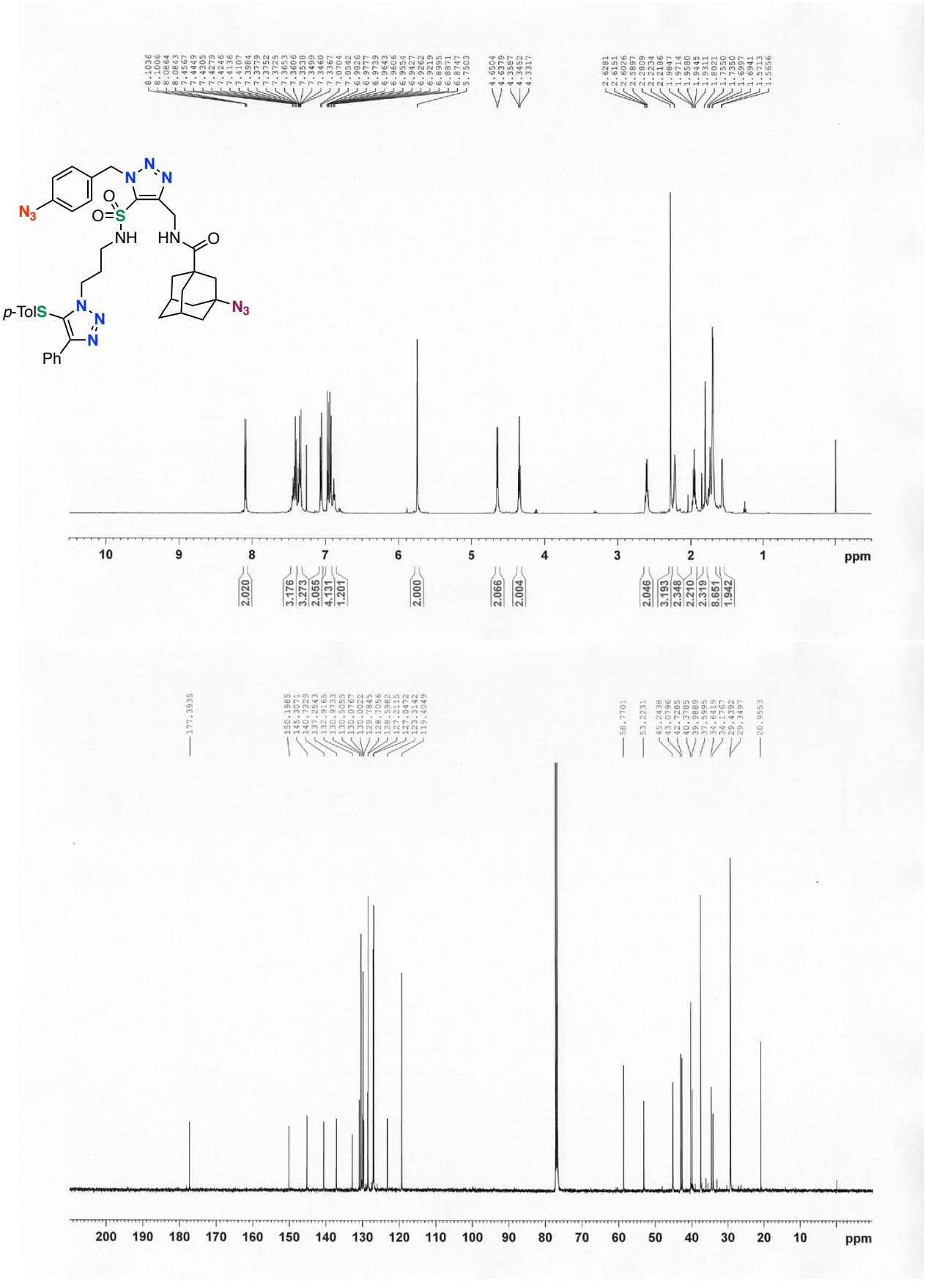
$^{1}$H NMR (500 MHz) and $^{13}$C NMR (126 MHz) spectra of 3-azido-*N*-(1-(4-azidobenzyl)-5-benzylthio-1*H*-1,2,3-triazol-4-ylmethyl)-1-adamantanamide (**S8**) ($CDCl_3$)



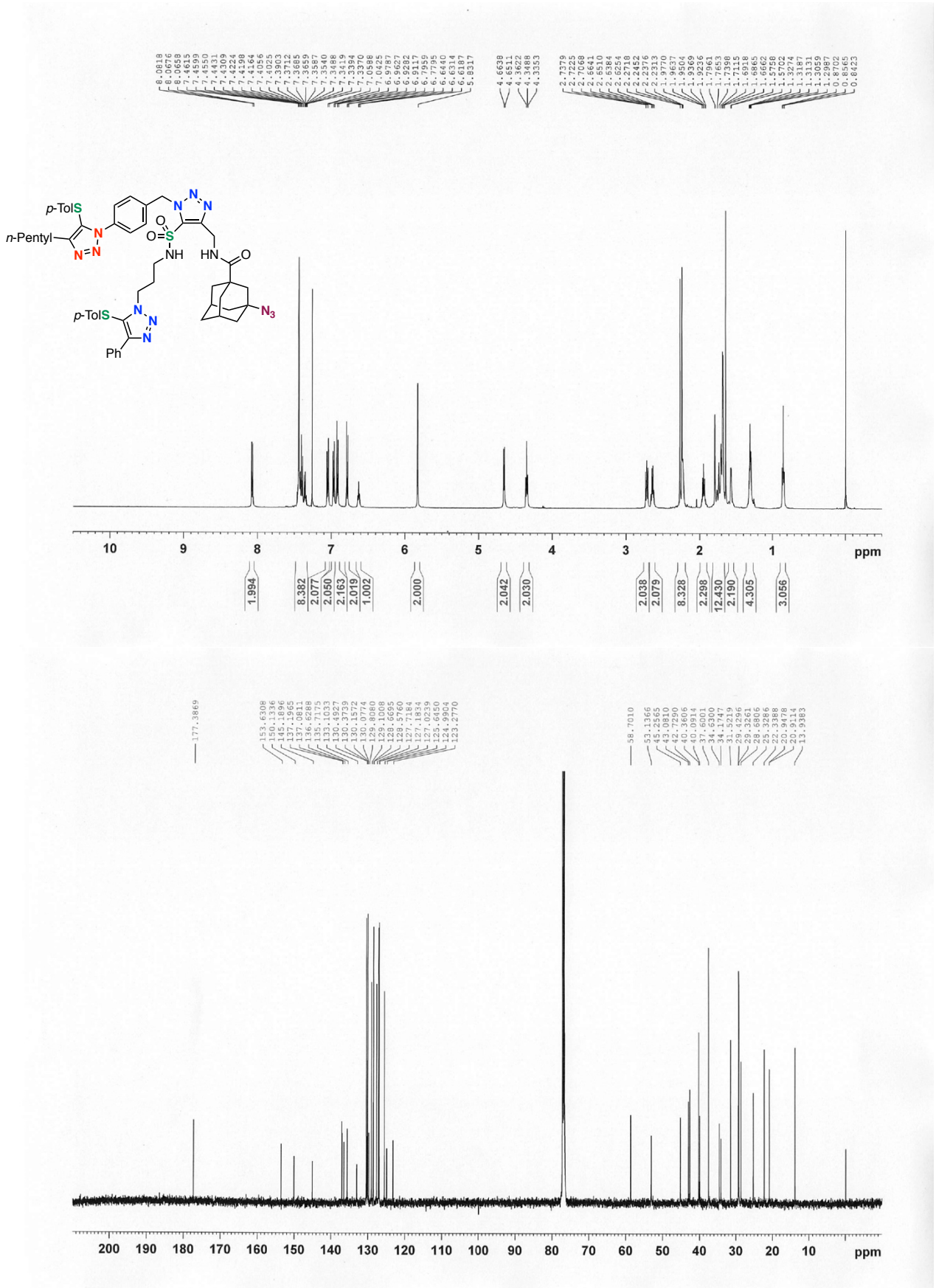
$^{1}$H NMR (500 MHz) and $^{13}$C NMR (126 MHz) spectra of 3-azido-*N*-(1-(4-azidobenzyl)-5-(*N*-(3-azidopropylsulfamoyl)-1*H*-1,2,3-triazol-4-ylmethyl)-1-adamantanamide (**24**) ($CDCl_3$)



$^{1}$H NMR (500 MHz) and $^{13}$C NMR (126 MHz) spectra of 3-azido-*N*-(1-(4-azidobenzyl)-5-(*N*-(3-(4-phenyl-5-(*p*-tolylthio)-1*H*-1,2,3-triazol-1-yl)propyl)sulfamoyl)-1*H*-1,2,3-triazol-4-ylmethyl)-1-adamantanamide (**S9**) ($CDCl_3$)



$^{1}$H NMR (500 MHz) and $^{13}$C NMR (126 MHz) spectra of 3-azido-*N*-(1-(4-(4-pentyl-5-(*p*-tolylthio)-1*H*-1,2,3-triazol-1-yl)benzyl)-5-(*N*-(3-(4-phenyl-5-(*p*-tolylthio)-1*H*-1,2,3-triazol-1-yl)propyl)sulfamoyl)-1*H*-1,2,3-triazol-4-ylmethyl)-1-adamantanamide (**S10**) ($CDCl_3$)



$^{1}$H NMR (500 MHz) and $^{13}$C NMR (126 MHz) spectra of 3-((5a*S*,6*R*,6a*R*)-6-(hydroxymethyl)-5,5a,6,6a,7,8-hexahydrocyclopropa[5,6]cycloocta[1,2-*d*][1,2,3]triazol-1-yl)-*N*-(1-(4-(4-pentyl-5-(*p*-tolylthio)-1*H*-1,2,3-triazol-1-yl)benzyl)-5-(*N*-(3-(4-phenyl-5-(*p*-tolylthio)-1*H*-1,2,3-triazol-1-yl)propyl)sulfamoyl)-1*H*-1,2,3-triazol-4-ylmethyl)-1-adamantanamide (**26**) ($CDCl_3$)