Supplementary Information

Further enhancement of the clickability of doubly sterically-hindered aryl azides by *para*-amino substitution

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Contents

General Remarks

All reactions were performed in dry glasswares under atmosphere of argon, unless otherwise noted. Analytical thin-layer chromatography (TLC) was performed on precoated (0.25 mm) silica-gel plates (Merck Chemicals, Silica Gel 60 F_{254}, Cat. No. 1.05715). Column chromatography was conducted using 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). Preparative TLC 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, and are uncorrected. ^{1}H and ^{13}C NMR spectra were obtained with a Bruker AVANCE 500 spectrometer at 500 or 126 MHz, respectively. ^{19}F NMR spectra were obtained with a Bruker AVANCE 400 spectrometer at 376 MHz. All NMR measurements were carried out at 23 ºC. $CDCl_3$ (Acros Organics, Cat. No. 368651000), CD_3OD (Kanto Chemical Co., Inc., Cat. No. 25221-33), or DMSO-d_6 (CIL, Cat. No. DLM-10) was used as a solvent for obtaining NMR spectra. Chemical shifts (δ) are given in parts per million (ppm) downfield from $(CH_3)_4Si$ (δ 0.00 for ^{1}H NMR and ^{13}C NMR in $CDCl_3$) as an internal reference, or α,α,α-trifluorotoluene (δ –63.0 ppm for ^{19}F NMR in $CDCl_3$) as an external standard with coupling constants (J) in hertz (Hz). The abbreviations s, d, t, q, sept, m, and br signify singlet, doublet, triplet, quartet, septet, multiplet, and broad, respectively. The absorbance spectra (UV) were measured with a JASCO V-650 spectrophotometer at 25 °C (temperature controlled by an air-cool type Peltier thermostatted cell holder) using a quartz cuvette (10 mm light path). 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. Elemental analyses were carried out at A Rabbit Science Japan Co., Ltd.

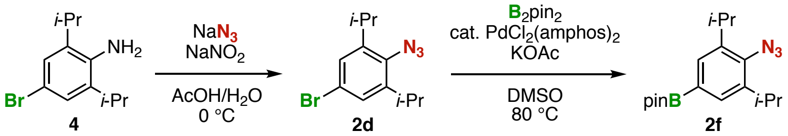
All chemical reagents used were commercial grade and used as received, unless otherwise noted.

sym-Dibenzo-1,5-cyclooctadiene-3,7-diyne (Sondheimer diyne, **1**),[S1] phenyl azide (**2a**),[S2] 4-methoxyphenyl azide (**2b**),[S3] 2,6-diisopropylphenyl azide (**2c**),[S4] 4-morpholinophenyl azide (**2q**),[S5] 4-bromo-2,6-diisopropylaniline (**4**),[S6] 1,4-diazido-2,6-diisopropylbenzene (**5**),[S7] *sym*-dibenzo-1,5-cyclooctadiene-3-yne (**7**),[S8] succinimidyl 4-azidobenzoate (**S3**),[S9] (1α,8α,9α)-bicyclo[6.1.0]non-4-yn-9-ylmethanol (**S7**),[S10] 5-acetyl-5*H*,6*H*-11,12-didehydrodibenzo[*b*,*f*]azocin (**S9**),[S11] tris[(1-benzyl-1*H*-1,2,3-triazol-4-yl)methyl]amine (TBTA),[S12] and 4-iodo-2,6-diisopropylaniline,[S13] were prepared according to the reported method. 4-Azidoaniline (**2r**) was prepared from commercially available 4-azidoaniline hydrochloride (**2s**) by treatment with aqueous $NaHCO_3$.

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

*Preparation of azides **2d–f***

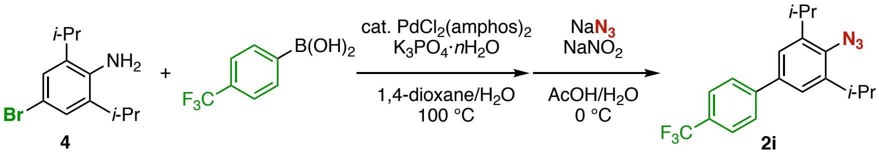


To a mixture of 4-bromo-2,6-diisopropylaniline (**4**) (2.56 g, 9.99 mmol) and sodium azide (1.06 g, 16.3 mmol) dissolved in acetic acid (21.4 mL) and water (2.4 mL) was slowly added sodium nitrite (1.06 g, 15.4 mmol) at 0 °C. After stirring for 1 h at the same temperature, to the mixture was added a saturated aqueous solution of $NaHCO_3$ until the mixture became pH 10. The mixture was extracted with EtOAc (20 mL × 3), and the combined organic extract was washed with brine (10 mL), dried (Na_2SO_4), and after filtration, the filtrate was concentrated under reduced pressure. The residue was purified by column chromatography (silica-gel 30 g, *n*-hexane only) to give 4-bromo-2,6-diisopropyl phenyl azide (**2d**) (2.59 g, 9.18 mmol, 91.9%) as a brown oil.

According to this procedure, azide 4-iodo-2,6-diisopropyl phenyl azide (**2e**) was also prepared from 4-iodo-2,6-diisopropylaniline.

To a solution of 4-bromo-2,6-diisopropyl phenyl azide (**2d**) (1.02 g, 3.61 mmol) dissolved in dimethyl sulfoxide (10 mL) were added bis(pinacolato)diboron (1.37 g, 5.39 mmol), bis(di-*tert*-butyl(4-(dimethylamino)phenyl)phosphine)dichloropalladium(II) ($PdCl_2(amphos)_2$) (176 mg, 0.249 mmol), and potassium acetate (720 mg, 7.34 mmol) at room temperature. After stirring for 1 h at 80 °C, to this was added water (40 mL). The mixture was extracted with EtOAc (40 mL × 3), and the combined organic extract was washed with water (30 mL × 2) and brine (50 mL), dried (Na_2SO_4), and after filtration, the filtrate was concentrated under reduced pressure. The residue was purified by column chromatography (silica-gel 40 g, *n*-hexane/EtOAc = 20/1) to give 2,6-diisopropyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl azide (**2f**) (877 mg, 2.66 mmol, 73.7%) as a pale brown oil.

*A typical procedure for preparation of 4-aryl-2,6-diisopropylphenyl azides **2g–k** (Scheme 1, upper)*

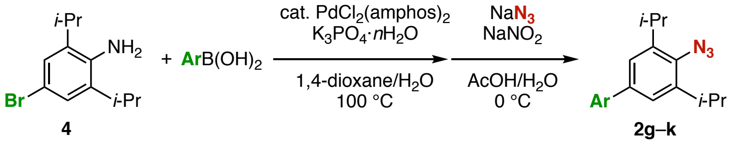


To a solution of 4-bromo-2,6-diisopropylaniline (**4**) (515 mg, 2.01 mmol) dissolved in 1,4-dioxane (20 mL) and water (2 mL) were added 4-(trifluoromethyl)phenylboronic acid (570 mg, 3.00 mmol), bis(di-*tert*-butyl(4-(dimethylamino)phenyl)phosphine)dichloropalladium(II) ($PdCl_2(amphos)_2$) (93.2 mg, 0.132 mmol), and tripotassium phosphate *n*-hydrate (852 mg, ca. 4.0 mmol) at room temperature. After stirring for 2 h at 100 °C, to this was added an aqueous saturated solution of NH_4Cl (20 mL). The mixture was extracted with EtOAc (20 mL × 3), and the combined organic extract was washed with brine (50 mL), dried (Na_2SO_4), and after filtration, the filtrate was concentrated under reduced pressure. The residue was purified by column chromatography (silica-gel 30 g, *n*-hexane/EtOAc = 10/1) to give 2,6-diisopropyl-4-(4-(trifluoromethyl)phenyl)aniline (604 mg, 1.88 mmol, 93.5%) as a pale brown solid.

To a mixture of 2,6-diisopropyl-4-(4-(trifluoromethyl)phenyl)aniline (560 mg, 1.74 mmol) and sodium azide (200 mg, 3.08 mmol) dissolved in acetic acid (4.3 mL) and water (0.5 mL) was slowly added sodium nitrite (177 mg, 2.57 mmol) at 0 °C. After stirring for 24 h at the same temperature, to the mixture was added a saturated aqueous solution of $NaHCO_3$ until the mixture became pH 10. The mixture was extracted with EtOAc (20 mL × 3), and the combined organic extract was washed with brine (10 mL), dried (Na_2SO_4), and after filtration, the filtrate was concentrated under reduced pressure. The residue was purified by column chromatography (silica-gel 30 g, *n*-hexane only) to give 2,6-diisopropyl-4-(4-(trifluoromethyl)phenyl)phenyl azide (**2i**) (493 mg, 1.42 mmol, 81.4%) as a pale brown solid.

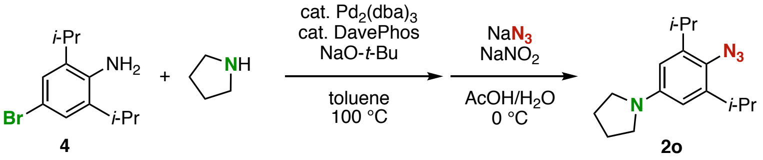
According to this procedure, azides **2g**, **2h**, **2j**, and **2k** were also prepared. The results are summarized in Table S1.

Table S1. Preparation of 4-aryl-2,6-diisopropylphenyl azides **2g–k**



Entry	Ar	Yield of cross-coupling product (%)	2	Yield of azide **2** (%)
1	Ph	quant	**2g**	quant
2	2,6-$Me_2C_6H_3$	86	**2h**	97
3	4-$F_3CC_6H_4$	93	**2i**	81
4	4-$MeOC_6H_4$	quant	**2j**	74
5	4-$Me_2NC_6H_4$	—	**2k**	73 (2 steps from **4**)

*A typical procedure for preparation of 4-amino-2,6-diisopropylphenyl azides **2l–o** (Scheme 1, lower)*

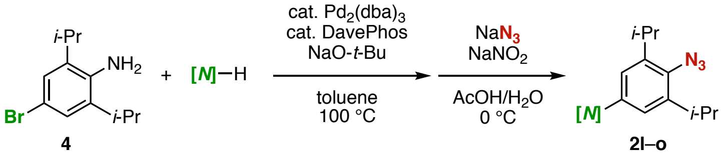


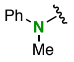
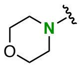
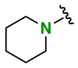
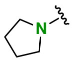
To a solution of 4-bromo-2,6-diisopropylaniline (**4**) (790 mg, 3.08 mmol) and pyrrolidine (376 µL, 4.50 mmol) dissolved in toluene (80 mL) were added sodium *tert*-butoxide (465 mg, 4.84 mmol), tris(dibenzylideneacetone)dipalladium(0) ($Pd_2(dba)_3$) (71.3 mg, 77.9 µmol), and 2-dicyclohexylphosphino-2'-(dimethylamino)biphenyl (DavePhos) (88.0 mg, 0.224 mmol) at room temperature. After stirring for 12 h at 100 °C, to this was added an aqueous saturated solution of NH_4Cl (20 mL). The mixture was extracted with EtOAc (40 mL × 3), and the combined organic extract was washed with brine (30 mL), dried (Na_2SO_4), and after filtration, the filtrate was concentrated under reduced pressure. The residue was purified by column chromatography (silica-gel 20 g, *n*-hexane/EtOAc = 10/1) to give 2,6-diisopropyl-4-pyrrolidinoaniline (579 mg, 2.35 mmol, 76.2%) as a brown solid.

To a mixture of 2,6-diisopropyl-4-pyrrolidinoaniline (449 mg, 1.82 mmol) and sodium azide (191 mg, 2.94 mmol) dissolved in acetic acid (3.9 mL) and water (0.4 mL) was slowly added sodium nitrite (189 mg, 2.74 mmol) at 0 °C. After stirring for 24 h at the same temperature, to the mixture was added a saturated aqueous solution of $NaHCO_3$ until the mixture became pH 10. The mixture was extracted with EtOAc (20 mL × 3), and the combined organic extract was washed with brine (10 mL), dried (Na_2SO_4), and after filtration, the filtrate was concentrated under reduced pressure. The residue was purified by column chromatography (silica-gel 30 g, *n*-hexane/EtOAc = 5/1) to give 2,6-diisopropyl-4-pyrrolidinophenyl azide (**2o**) (340 mg, 1.25 mmol, 68.5%) as a brown oil.

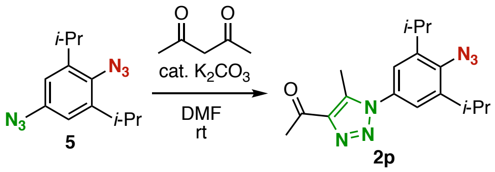
According to this procedure, azides **2l–n** were also prepared. The results are summarized in Table S2.

Table S2. Preparation of 4-amino-2,6-diisopropylphenyl azides **2l–o**



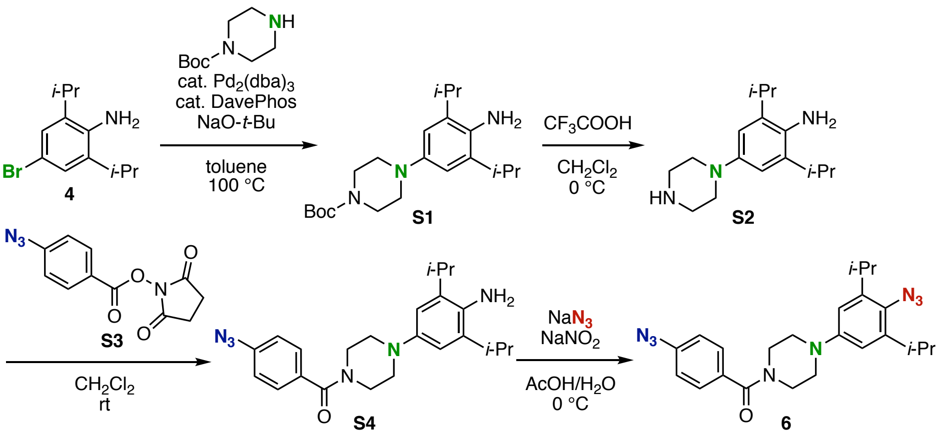
Entry	[*N*]–	Yield of aminated product (%)	**2**	Yield of azide **2** (%)
1		93	**2l**	47
2		72	**2m**	29
3		63	**2n**	45
4		76	**2o**	68

*Preparation of azide **2p** from diazide **5** (Scheme 2)*



To a solution of 1,4-diazido-2,6-diisopropylbenzene (**5**) (588 mg, 2.41 mmol) and acetylacetone (205 µL, 2.00 mmol) dissolved in *N*,*N*-dimethylformamide (DMF) (24 mL) was added potassium carbonate (5.5 mg, 40 µmol) at room temperature. After stirring for 25 h at the same temperature, to this was added water (50 mL). The mixture was extracted with EtOAc (50 mL × 3), and the combined organic extract was washed with water (50 mL) and brine (30 mL), dried (Na_2SO_4), and after filtration, the filtrate was concentrated under reduced pressure. The residue was purified by column chromatography twice (1st: silica-gel 30 g, *n*-hexane only to *n*-hexane/EtOAc = 20/1, then EtOAc only; 2nd: silica-gel 20 g, *n*-hexane/EtOAc = 30/1 to 10/1) to give 4-(4-acetyl-5-methyl-1*H*-1,2,3-triazol-1-yl)-2,6-diisopropylphenyl azide (**2p**) (405 mg, 1.24 mmol, 62.1%) as a yellow solid.

Preparation of diazide ***6***



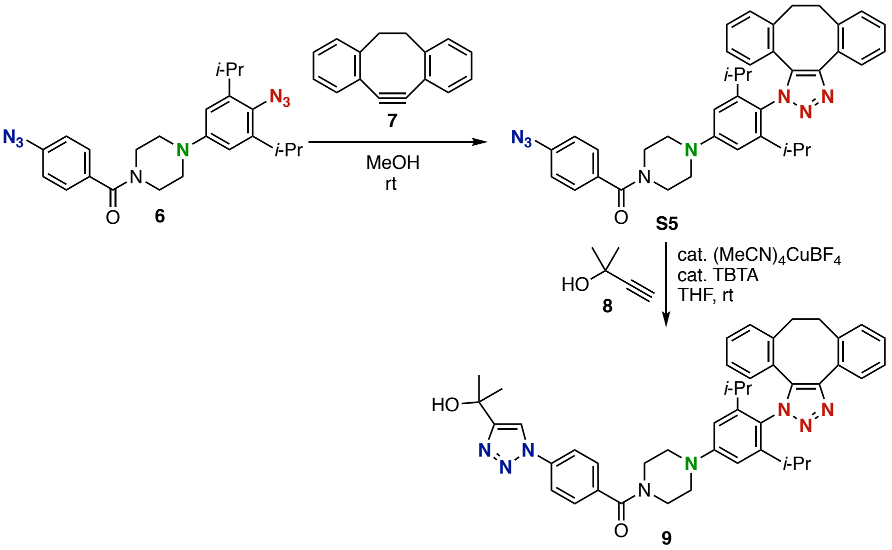
To a solution of 4-bromo-2,6-diisopropylaniline (**4**) (2.91 g, 11.4 mmol) and 1-(*tert*-butoxycarbonyl)piperazine (3.17 g, 17.0 mmol) dissolved in toluene (150 mL) were added sodium *tert*-butoxide (1.75 g, 18.2 mmol), tris(dibenzylideneacetone)dipalladium(0) ($Pd_2(dba)_3$) (261 mg, 0.285 mmol), and 2-dicyclohexylphosphino-2'-(dimethylamino)biphenyl (DavePhos) (336 mg, 0.854 mmol) at room temperature. After stirring for 12 h at 100 °C, to this was added an aqueous saturated solution of NH_4Cl (100 mL). The mixture was extracted with EtOAc (200 mL × 3), and the combined organic extract was washed with brine (50 mL), dried (Na_2SO_4), and after filtration, the filtrate was concentrated under reduced pressure. The residue was purified by column chromatography (silica-gel 80 g, *n*-hexane/EtOAc = 5/1 to EtOAc only) to give 4-(4-(*tert*-butoxycarbonyl)piperazino)-2,6-diisopropylaniline (**S1**) (2.89 g, <8.0 mmol, <70%) as a pale brown solid, which contained a small amount of a side-product. This product was used for the next step without further purification.

To a solution of **S1** (1.34 g, <3.7 mmol) dissolved in dichloromethane (12 mL) was slowly added trifluoroacetic acid (3.50 mL, 45.7 mmol) at 0 °C. After stirring for 24 h at the same temperature, to the mixture was added a saturated aqueous solution of $NaHCO_3$ (20 mL). The mixture was extracted with EtOAc (20 mL × 3), and the combined organic extract was washed with water (10 mL) and brine (10 mL), dried (Na_2SO_4), and after filtration, the filtrate was concentrated under reduced pressure. The residue containing 2,6-diisopropyl-4-piperazinoaniline (**S2**) was used for the next step without purification.

To a solution of crude **S2** dissolved in dichloromethane (15 mL) was added succinimidyl 4-azidobenzoate (**S3**) (1.94 g, 7.46 mmol) at room temperature. After stirring for 20 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 water (10 mL) and brine (10 mL), dried (Na_2SO_4), and after filtration, the filtrate was concentrated under reduced pressure. The residue was purified by column chromatography (silica-gel 20 g, dichloromethane/MeOH = 50/1) to give 4-(4-(4-azidobenzoyl)piperazino)-2,6-diisopropylaniline (**S4**) (<3.7 mmol), which contained a small amount of impurity. This product was used for the next step without further purification.

To a mixture of **S4** (<3.7 mmol) and sodium azide (385 mg, 5.92 mmol) dissolved in acetic acid (7.66 mL) and water (0.85 mL) was slowly added sodium nitrite (385 mg, 5.58 mmol) at 0 °C. After stirring for 1 h at the same temperature, to the mixture was added a saturated aqueous solution of $NaHCO_3$ until the mixture became pH 10. The mixture was extracted with EtOAc (20 mL × 3), and the combined organic extract was washed with brine (10 mL), dried (Na_2SO_4), and after filtration, the filtrate was concentrated under reduced pressure. The residue was purified by column chromatography (silica-gel 30 g, *n*-hexane/EtOAc = 5/1) to give 1-(4-azidobenzoyl)-4-(4-azido-3,5-diisopropylphenyl)-piperazine (**6**) (418 mg, 0.966 mmol, 18.3% from **4**) as a brown solid.

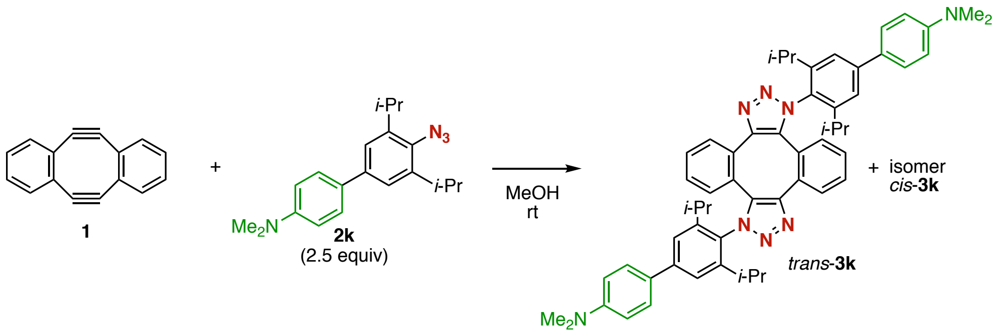
*Azido-type-selective double-click reaction of diazide **6** (Scheme 3)*



To a solution of 1-(4-azidobenzoyl)-4-(4-azido-3,5-diisopropylphenyl)piperazine (**6**) (44.2 mg, 0.102 mol) dissolved in MeOH (8.5 mL) was added *sym*-dibenzo-1,5-cyclooctadiene-3-yne (**7**) (13.9 mg, 68.0 μmol) at room temperature. After stirring for 4 min at the same temperature, the mixture was concentrated under reduced pressure. The residue was purified by column chromatography (silica-gel 5 g, *n*-hexane/EtOAc = 5/1 to EtOAc only) to give 1-(4-azidobenzoyl)-4-(4-(8,9-dihydro-1*H*-dibenzo-[3,4:7,8]cycloocta[1,2-*d*][1,2,3]triazol-1-yl)-3,5-diisopropylphenyl)piperazine (**S5**) (43.8 mg, 99% purity containing EtOAc, 68.2 μmol, quant.) as a yellow solid.

To a solution of **S5** (41.4 mg, 65.0 μmol) dissolved in THF (8.0 mL) were added tetrakis(acetonitrile)copper(I) tetrafluoroborate (1.0 mg, 3.2 μmol), tris[(1-benzyl-1*H*-1,2,3-triazol-4-yl)methyl]-amine (TBTA) (1.7 mg, 3.2 μmol), and 2-methyl-3-butyn-2-ol (**8**) (7.0 mg, 83 μmol) at room temperature. After stirring for 14 h at the same temperature, the mixture was filtered and the filtrate was concentrated under reduced pressure. The residue was purified by column chromatography (silica-gel 5 g, *n*-hexane/EtOAc = 5/1 to EtOAc only) to give 4-(4-(8,9-dihydro-1*H*-dibenzo-[3,4:7,8]cycloocta[1,2-*d*][1,2,3]triazol-1-yl)-3,5-diisopropylphenyl)-1-(4-(4-(2-hydroxypropan-2-yl)-1*H*-1,2,3-triazol-1-yl)benzoyl)piperazine (**9**) (41.3 mg, 57.3 μmol, 88.1%) as a pale yellow solid.

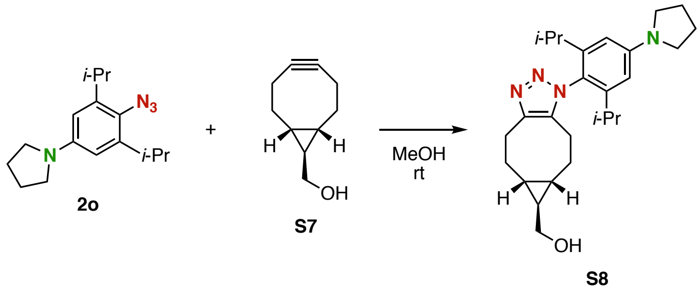
*A typical procedure for the double-click reaction of Sondheimer diyne (**1**) with azides **2** to prepare authentic samples of bistriazoles **3** for kinetic studies*



To a solution of 4-(4-(dimethylamino)phenyl)-2,6-diisopropylphenyl azide (**2k**) (40.1 mg, 0.124 mmol) in MeOH (6.3 mL) was added *sym*-dibenzo-1,5-cyclooctadiene-3,7-diyne (**1**) (10.0 mg, 49.9 μmol) at room temperature. After stirring for 5 min at the same temperature, the mixture was concentrated under reduced pressure. The residue was purified by preparative TLC (*n*-hexane/EtOAc = 5/1) to give a regioisomeric mixture of *trans*-**3k** and *cis*-**3k** (37.0 mg, 43.8 μmol, 87.7%, *trans*/*cis* = 96/4) as an orange solid. The ratio was determined based on the ^{1}H NMR analysis. Further purification by preparative TLC (*n*-hexane/EtOAc = 5/1) afforded pure *trans*-**3k** (35.6 mg, 42.1 μmol, 84.3%) as an orange solid.

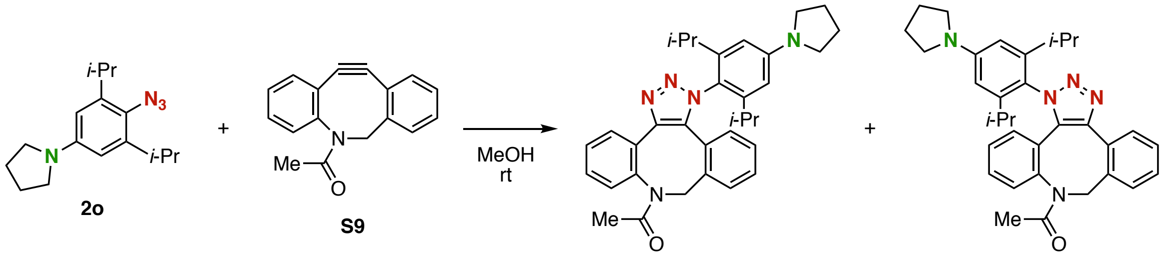
According to this procedure, cycloadducts **3d–j** and **3l–p** were prepared.

*The SPAAC reaction of azide **2o** with BCN derivative **S7** to prepare the authentic sample of triazole **S8** for kinetic studies*



A solution of 2,6-diisopropyl-4-pyrrolidinophenyl azide (**2o**) in MeOH (10.0 mM, 1.50 mL, 15.0 μmol) and a solution of (1α,8α,9α)-bicyclo[6.1.0]non-4-yn-9-ylmethanol (**S7**) (10.0 mM, 1.50 mL, 15.0 μmol) were mixed up at room temperature. After stirring for 2 h at the same temperature, the mixture was concentrated under reduced pressure. The residue was purified by preparative TLC (*n*-hexane/EtOAc = 1/4) to give (5a*S*,6*S*,6a*R*)-1-(2,6-diisopropyl-4-pyrrolidinophenyl)-6-(hydroxymethyl)-1,4,5,5a,6,6a,7,8-octahydrocyclopropa[5,6]cycloocta[1,2-*d*][1,2,3]triazole (**S8**) (5.8 mg, 14 μmol, 91%) as a colorless oil.

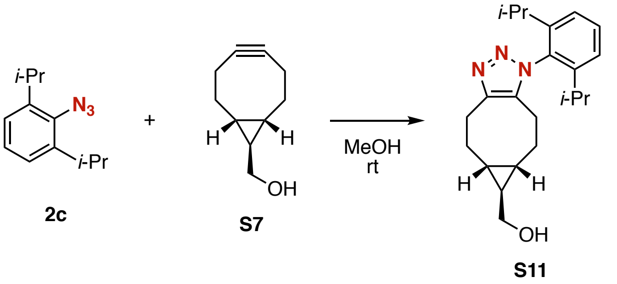
*The SPAAC reaction of azide **2o** with DIBAC derivative **S9** to prepare the authentic samples of triazoles **S10** and **S10’** for a competition experiment*



major isomer **S10** + minor isomer **S10’**

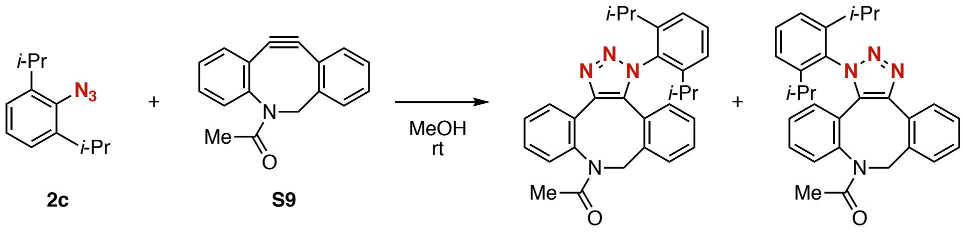
8-Acetyl-1-(2,6-diisopropyl-4-pyrrolidinophenyl)-8,9-dihydro-1*H*-dibenzo[*b*,*f*][1,2,3]triazolo[4,5-*d*]azocine and 8-acetyl-3-(2,6-diisopropyl-4-pyrrolidinophenyl)-8,9-dihydro-3*H*-dibenzo[*b*,*f*][1,2,3]triazolo[4,5-*d*]azocine were prepared according to the procedure for preparation of **S8** using 5-acetyl-5*H*,6*H*-11,12-didehydrodibenzo[*b*,*f*]azocin (**S9**) instead of **S7** to afford major isomer **S10** (12.7 mg, 24.4 µmol, 50.4%) and minor isomer **S10’** (11.3 mg, 21.7 µmol, 44.8%).

*The SPAAC click reaction of azide **2c** with BCN derivative **S7** to prepare the authentic sample of triazole **S11** for kinetic studies*



(5a*S*,6*S*,6a*R*)-1-(2,6-diisopropylphenyl)-6-(hydroxymethyl)-1,4,5,5a,6,6a,7,8-octahydrocyclopropa[5,6]cycloocta[1,2-*d*][1,2,3]triazole (**S11**) (16.2 mg, 45.8 µmol, 91.4%) was prepared according to the procedure for preparation of **S8** using 2,6-diisopropylphenyl azide (**2c**) instead of **2o**.

*The SPAAC reaction of azide **2c** with DIBAC derivative **S9** to prepare the authentic samples of triazole **S12** and **S12’** for a competition experiment*

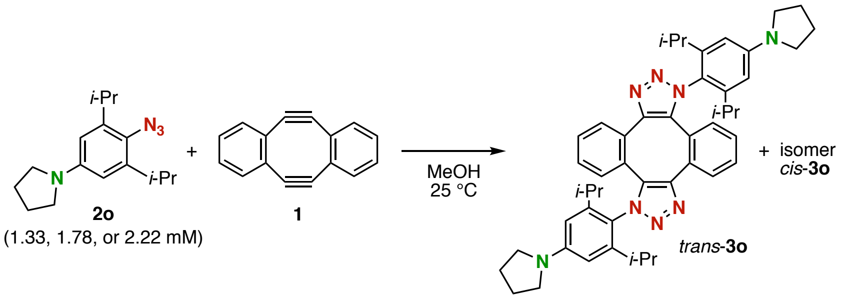


major isomer **S12** + minor isomer **S12’**

8-Acetyl-1-(2,6-diisopropylphenyl)-8,9-dihydro-1*H*-dibenzo[*b*,*f*][1,2,3]triazolo[4,5-*d*]azocine and 8-acetyl-3-(2,6-diisopropylphenyl)-8,9-dihydro-3*H*-dibenzo[*b*,*f*][1,2,3]triazolo[4,5-*d*]azocine were prepared according to the procedure for preparation of **S8**, using 2,6-diisopropylphenyl azide (**2c**) and 5-acetyl-5*H*,6*H*-11,12-didehydrodibenzo[*b*,*f*]azocin (**S9**) instead of **2o** and **S7**, respectively, to afford major isomer **S12** (12.7 mg, 28.2 µmol, 54.4%) and minor isomer **S12’** (10.4 mg, 23.1 µmol, 44.6%).

Kinetic Studies

A typical experimental procedure for the kinetic study on double-click reaction of diyne ***1*** *with azide* ***2o*** *(Table 2, Entry 10)*



The rate measurement of the first cycloaddition in the double-click reaction was performed by monitoring the absorbance of diyne **1** in the presence of an excess amount of phenyl azides **2**.

To 600 µL of 1.24 mM (final concentration at 0.248 mM) solution of diyne **1** in MeOH placed in a quartz cuvette (10 mm light path, temperature kept at 25 °C) was added 2.40 mL of MeOH solution of 2,6-diisopropyl-4-pyrrolidinophenyl azide (**2o**) in three different concentrations (final concentration at 1.33, 1.78, or 2.22 mM, respectively). The consumption of diyne **1** was monitored by UV spectroscopy focusing at 351.5 nm, which is a wavelength that characteristic absorbance for the diyne (logε = 3.22) is observed but almost no significant absorption for azide **2o** and bis-cycloadducts **3o**.

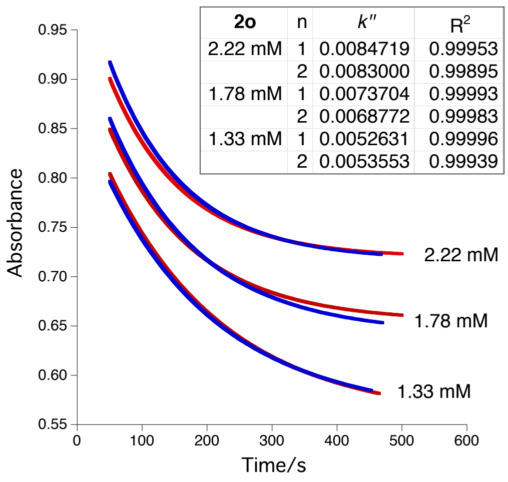
The monitoring was continued for 50–500 s and the experiments were repeated in duplicate for each concentration of azide **2o**. The observed absorbance data at 351.5 nm, which contains absorbance of diyne **1** and azide **2o**, were plotted versus time and fitted to a first order exponential decay curve. The pseudo-first order rate constants (*k*”) were determined by least-squares fitting of the data to the following exponential equation using KaleidaGraph ver. 4.1.1.

$$y = a*\exp(-k''*(t + t_0)) + b*\exp(-2*k''*(t + t_0)) + y_0$$

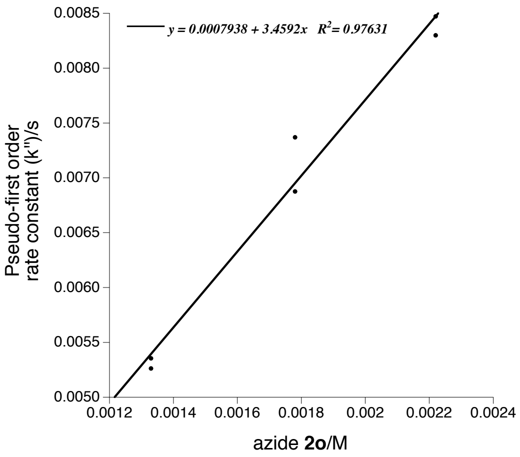
a: absorption of diyne ***1*** *(0.248 mM)*
b: absorption of azide ***2o*** *(1.33, 1.78, or 2.22 mM)*
t: time (s) from the starting point of the observation
t_0: *time (s) between the starting point of the reaction and the observation*

The pseudo-first order rate constants (*k*”) were plotted versus concentrations of azide **2o** and fitted to a straight line by linear regression method using KaleidaGraph ver. 4.1.1. The slope of the straight line indicates the second order rate constant (*k*) for the first cycloaddition in the double-click reaction of diyne **1** and azide **2o**, which is the rate-determining step of the reaction.

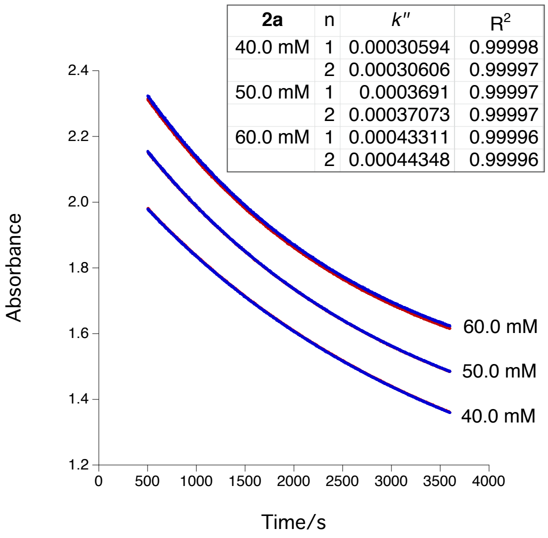
Time-dependent absorbance of diyne **1** (initial concentration of 0.248 mM) at 351.5 nm of wavelength was monitored in duplicate during the reaction with azide **2o** in three different concentrations (1.33, 1.78, or 2.22 mM) (left graph). A plot of pseudo-first order rate constants (*k*") versus the concentration of azide **2o** (right graph).



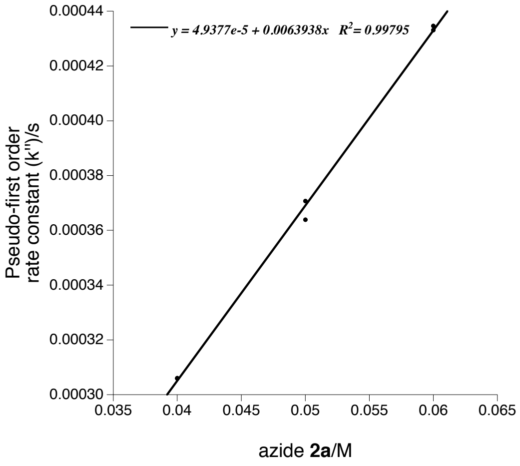
2o	n	*k*"	R^2
2.22 mM	1	0.0084719	0.99953
	2	0.0083000	0.99895
1.78 mM	1	0.0073704	0.99993
	2	0.0068772	0.99983
1.33 mM	1	0.0052631	0.99996
	2	0.0053553	0.99939



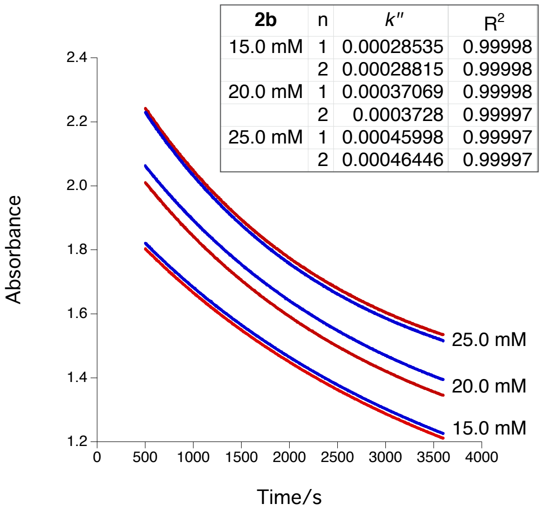
The kinetic study for double-click reaction of diyne **1** with phenyl azide (**2a**) in MeCN was similarly conducted by the method described for **2o** in MeOH. Time-dependent absorbance of diyne **1** (initial concentration of 0.500 mM) at 351.5 nm of wavelength was monitored in duplicate during the reaction with azide **2a** in three different concentrations (40.0, 50.0, or 60.0 mM) (left graph). A plot of pseudo-first order rate constants (*k*") versus the concentration of azide **2a** (right graph).



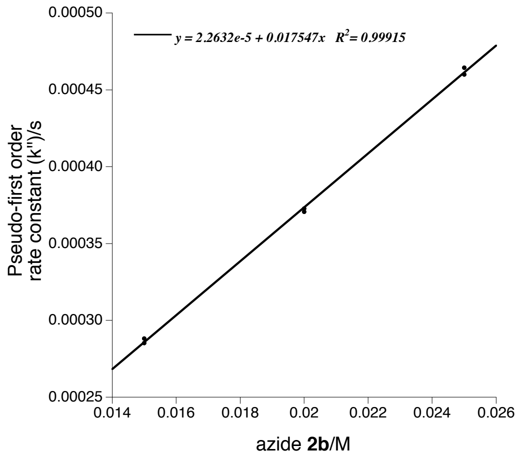
2a	n	*k*"	R^2
40.0 mM	1	0.00030594	0.99998
	2	0.00030606	0.99997
50.0 mM	1	0.0003691	0.99997
	2	0.00037073	0.99997
60.0 mM	1	0.00043311	0.99996
	2	0.00044348	0.99996



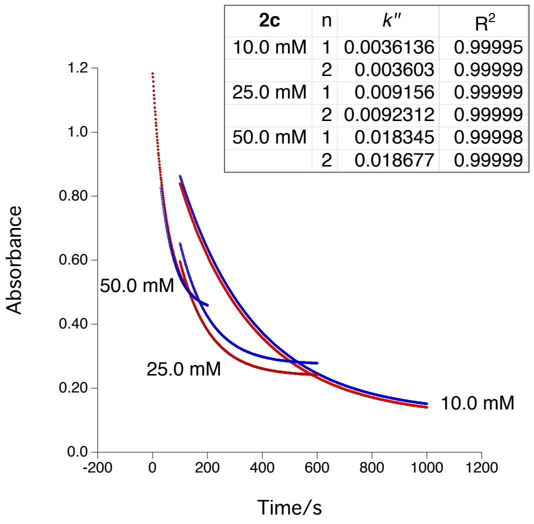
The kinetic study for double-click reaction of diyne **1** with 4-methoxyphenyl azide (**2b**) in MeCN was similarly conducted by the method described for **2o** in MeOH. Time-dependent absorbance of diyne **1** (initial concentration of 0.500 mM) at 351.5 nm of wavelength was monitored in duplicate during the reaction with azide **2b** in three different concentrations (15.0, 20.0, or 25.0 mM) (left graph). A plot of pseudo-first order rate constants (*k*") versus the concentration of azide **2b** (right graph).



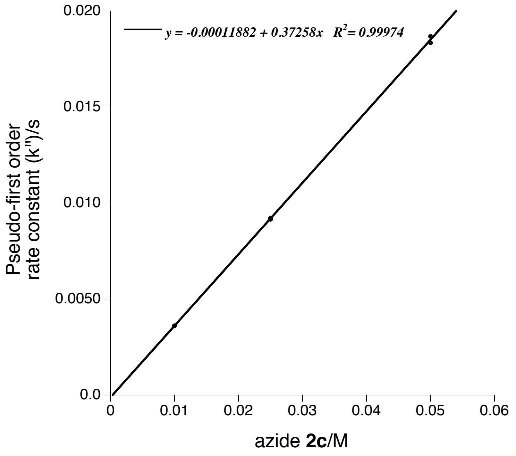
2b	n	*k''*	R^2
15.0 mM	1	0.00028535	0.99998
	2	0.00028815	0.99998
20.0 mM	1	0.00037069	0.99998
	2	0.0003728	0.99997
25.0 mM	1	0.00045998	0.99997
	2	0.00046446	0.99997



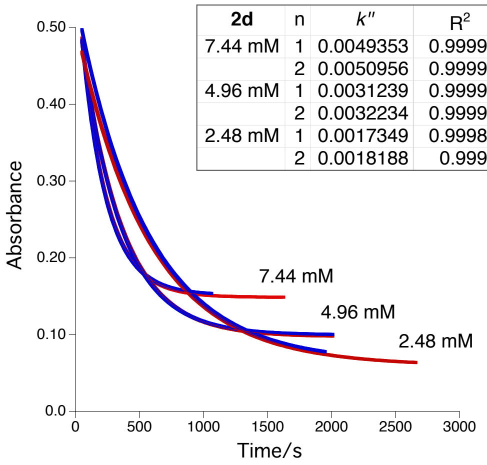
The kinetic study for double-click reaction of diyne **1** with 2,6-diisopropylphenyl azide (**2c**) in MeCN was similarly conducted by the method described for **2o** in MeOH. Time-dependent absorbance of diyne **1** (initial concentration of 0.500 mM) at 351.5 nm of wavelength was monitored in duplicate during the reaction with azide **2c** in three different concentrations (10.0, 25.0, or 50.0 mM) (left graph). A plot of pseudo-first order rate constants (*k*") versus the concentration of azide **2c** (right graph).



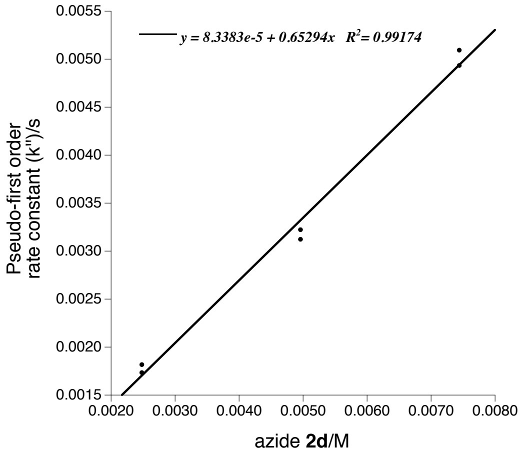
2c	n	*k''*	R^2
10.0 mM	1	0.0036136	0.99995
	2	0.003603	0.99999
25.0 mM	1	0.009156	0.99999
	2	0.0092312	0.99999
50.0 mM	1	0.018345	0.99998
	2	0.018677	0.99999



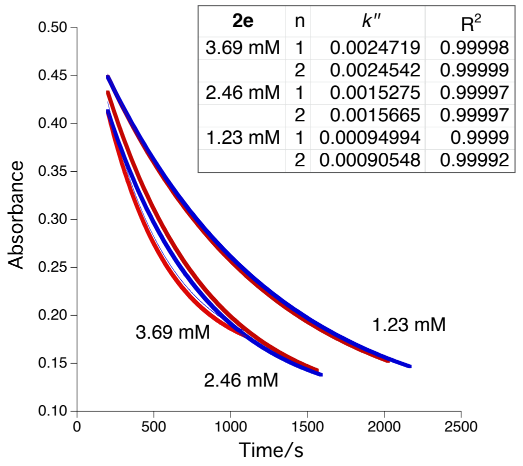
The kinetic study for double-click reaction of diyne **1** with 4-bromo-2,6-diisopropylphenyl azide (**2d**) in MeOH was similarly conducted by the method described for **2o**. Time-dependent absorbance of diyne **1** (initial concentration of 0.250 mM) at 351.5 nm of wavelength was monitored in duplicate during the reaction with azide **2d** in three different concentrations (2.48, 4.96, or 7.44 mM) (left graph). A plot of pseudo-first order rate constants (*k*”) versus the concentration of azide **2d** (right graph).



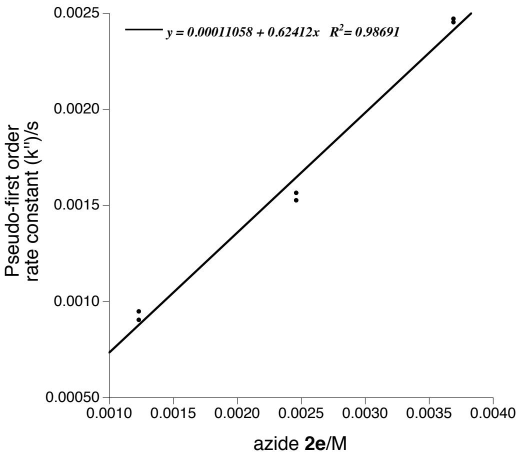
2d	n	*k"*	R^2
7.44 mM	1	0.0049353	0.99996
	2	0.0050956	0.99999
4.96 mM	1	0.0031239	0.99996
	2	0.0032234	0.99996
2.48 mM	1	0.0017349	0.99989
	2	0.0018188	0.9999



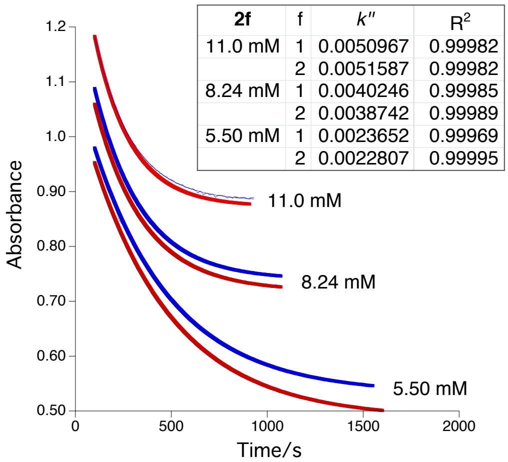
The kinetic study for double-click reaction of diyne **1** with 4-iodo-2,6-diisopropylphenyl azide (**2e**) in MeOH was similarly conducted by the method described for **2o**. Time-dependent absorbance of diyne **1** (initial concentration of 0.200 mM) at 351.5 nm of wavelength was monitored in duplicate during the reaction with azide **2e** in three different concentrations (1.23, 2.46, or 3.69 mM) (left graph). A plot of pseudo-first order rate constants (*k*”) versus the concentration of azide **2e** (right graph).



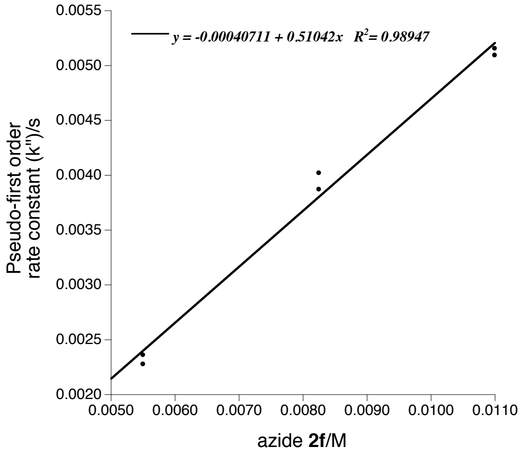
2e	n	*k"*	R^2
3.69 mM	1	0.0024719	0.99998
	2	0.0024542	0.99999
2.46 mM	1	0.0015275	0.99997
	2	0.0015665	0.99997
1.23 mM	1	0.00094994	0.9999
	2	0.00090548	0.99992



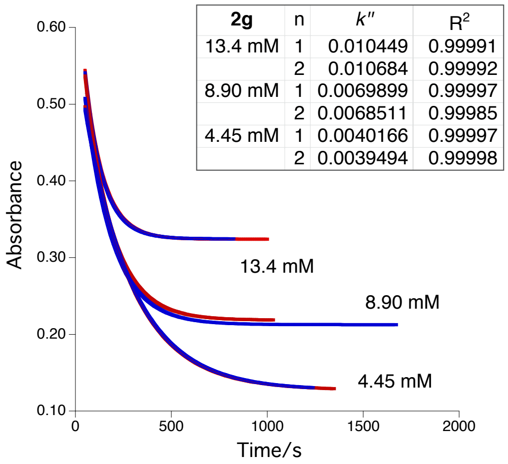
The kinetic study for double-click reaction of diyne **1** with 2,6-diisopropyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl azide (**2f**) in MeOH was similarly conducted by the method described for **2o**. Time-dependent absorbance of diyne **1** (initial concentration of 0.200 mM) at 351.5 nm of wavelength was monitored in duplicate during the reaction with azide **2f** in three different concentrations (5.50, 8.24, or 11.0 mM) (left graph). A plot of pseudo-first order rate constants (*k*") versus the concentration of azide **2f** (right graph).



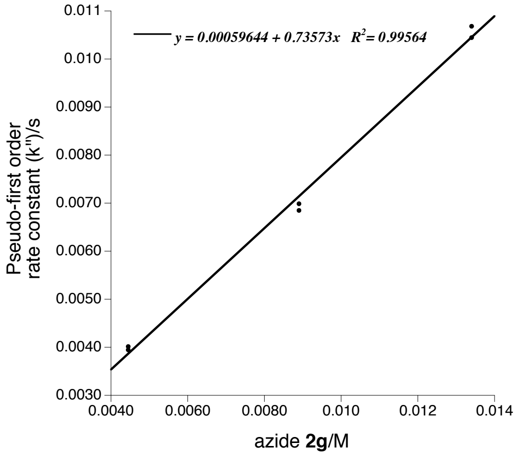
2f	f	*k*"	R^2
11.0 mM	1	0.0050967	0.99982
	2	0.0051587	0.99982
8.24 mM	1	0.0040246	0.99985
	2	0.0038742	0.99989
5.50 mM	1	0.0023652	0.99969
	2	0.0022807	0.99995



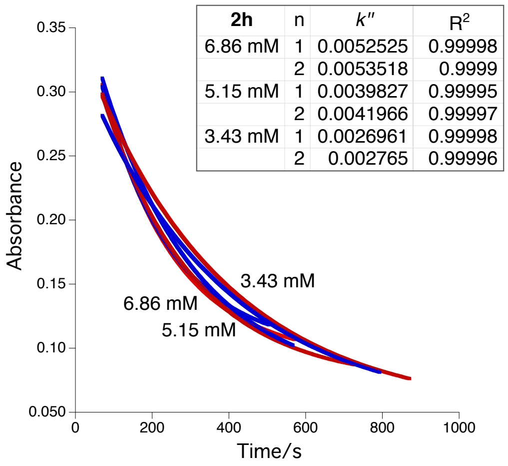
The kinetic study for double-click reaction of diyne **1** with 2,6-diisopropyl-4-phenylphenyl azide (**2g**) in MeOH was similarly conducted by the method described for **2o**. Time-dependent absorbance of diyne **1** (initial concentration of 0.210 mM) at 351.5 nm of wavelength was monitored in duplicate during the reaction with azide **2g** in three different concentrations (4.45, 8.90, or 13.4 mM) (left graph). A plot of pseudo-first order rate constants (*k*") versus the concentration of azide **2g** (right graph).



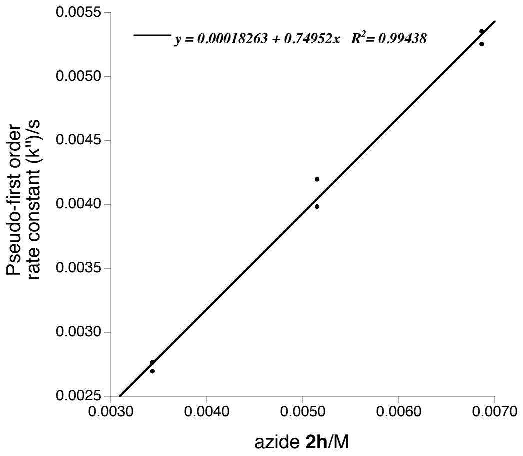
2g	n	*k*"	R^2
13.4 mM	1	0.010449	0.99991
	2	0.010684	0.99992
8.90 mM	1	0.0069899	0.99997
	2	0.0068511	0.99985
4.45 mM	1	0.0040166	0.99997
	2	0.0039494	0.99998



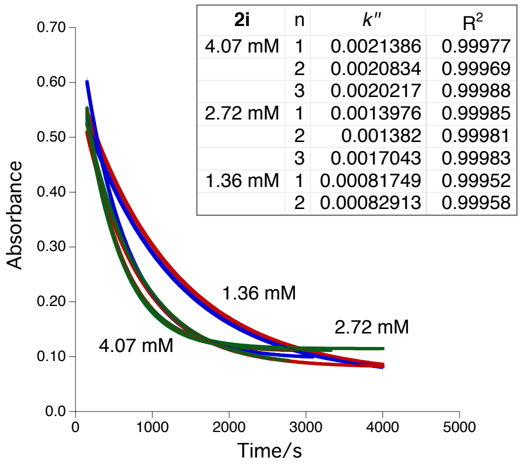
The kinetic study for double-click reaction of diyne **1** with 4-(2,6-dimethylphenyl)-2,6-diisopropylphenyl azide (**2h**) in MeOH was similarly conducted by the method described for **2o**. Time-dependent absorbance of diyne **1** (initial concentration of 0.200 mM) at 351.5 nm of wavelength was monitored in duplicate during the reaction with azide **2h** in three different concentrations (3.43, 5.15, or 6.86 mM) (left graph). A plot of pseudo-first order rate constants (*k*") versus the concentration of azide **2h** (right graph).



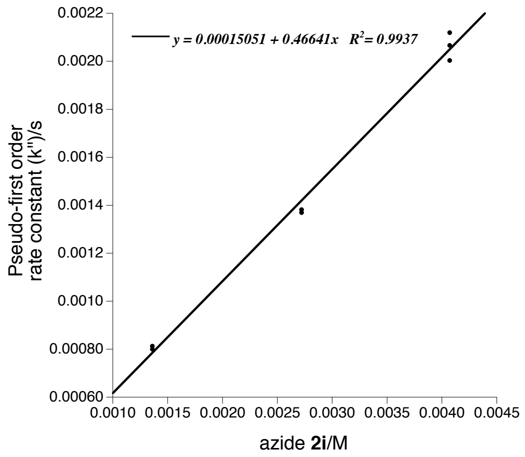
2h	n	*k"*	R^2
6.86 mM	1	0.0052525	0.99998
	2	0.0053518	0.9999
5.15 mM	1	0.0039827	0.99995
	2	0.0041966	0.99997
3.43 mM	1	0.0026961	0.99998
	2	0.002765	0.99996



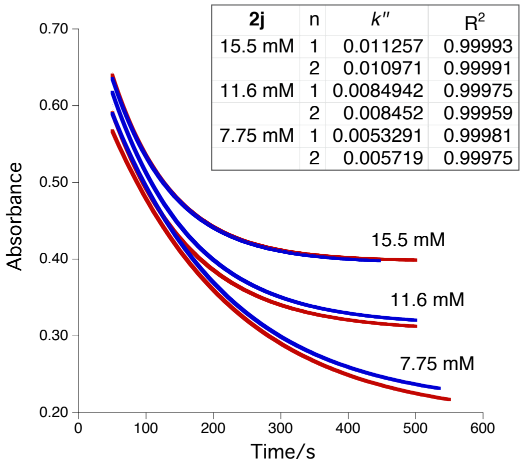
The kinetic study for double-click reaction of diyne **1** with 2,6-diisopropyl-4-(4-(trifluoromethyl)-phenyl)phenyl azide (**2i**) in MeOH was similarly conducted by the method described for **2o**. Time-dependent absorbance of diyne **1** (initial concentration of 0.260 mM) at 351.5 nm of wavelength was monitored in triplicate or duplicate during the reaction with azide **2i** in three different concentrations (1.36, 2.72, or 4.07 mM) (left graph). A plot of pseudo-first order rate constants (*k*") versus the concentration of azide **2i** (right graph).



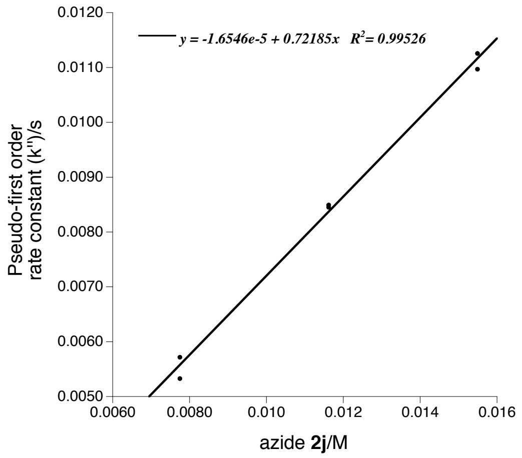
2i	n	*k"*	R^2
4.07 mM	1	0.0021386	0.99977
	2	0.0020834	0.99969
	3	0.0020217	0.99988
2.72 mM	1	0.0013976	0.99985
	2	0.001382	0.99981
	3	0.0017043	0.99983
1.36 mM	1	0.00081749	0.99952
	2	0.00082913	0.99958



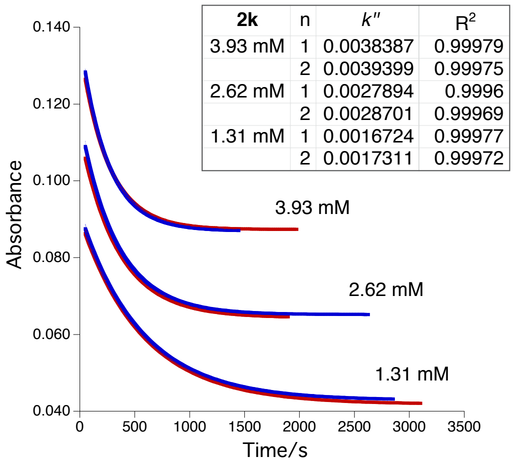
The kinetic study for double-click reaction of diyne **1** with 2,6-diisopropyl-4-(4-methoxyphenyl)-phenyl azide (**2j**) in MeOH was similarly conducted by the method described for **2o**. Time-dependent absorbance of diyne **1** (initial concentration of 0.250 mM) at 351.5 nm of wavelength was monitored in duplicate during the reaction with azide **2j** in three different concentrations (7.75, 11.6, or 15.5 mM) (left graph). A plot of pseudo-first order rate constants (*k*") versus the concentration of azide **2j** (right graph).



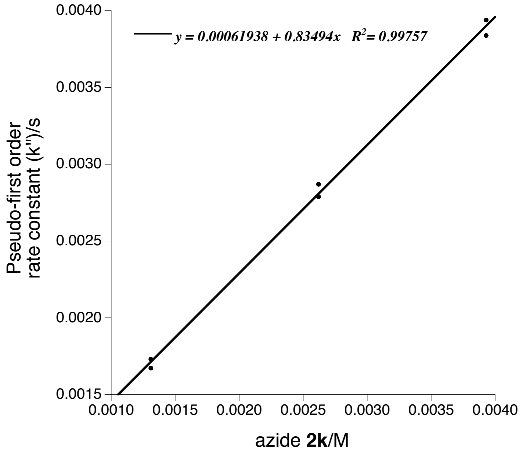
2j	n	*k*″	R^2
15.5 mM	1	0.011257	0.99993
	2	0.010971	0.99991
11.6 mM	1	0.0084942	0.99975
	2	0.008452	0.99959
7.75 mM	1	0.0053291	0.99981
	2	0.005719	0.99975



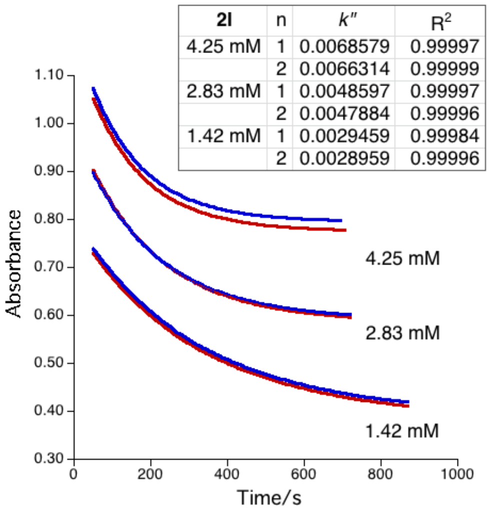
The kinetic study for double-click reaction of diyne **1** with 4-(4-(dimethylamino)phenyl)-2,6-diisopropylphenyl azide (**2k**) in MeOH was similarly conducted by the method described for **2o**. Time-dependent absorbance of diyne **1** (initial concentration of 0.110 mM) at 400.0 nm of wavelength was monitored in duplicate during the reaction with azide **2k** in three different concentrations (1.31, 2.62, or 3.93 mM) (left graph). A plot of pseudo-first order rate constants (*k*") versus the concentration of azide **2k** (right graph).



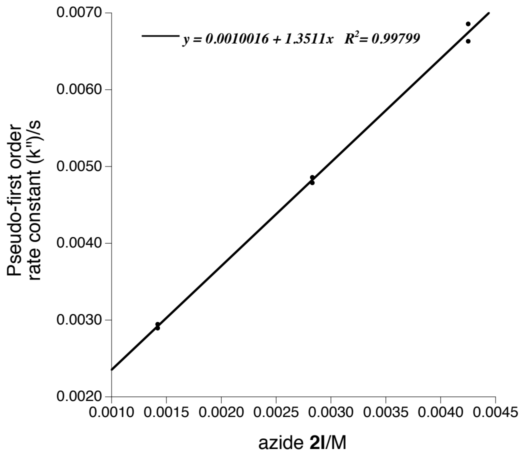
2k	n	*k*″	R^2
3.93 mM	1	0.0038387	0.99979
	2	0.0039399	0.99975
2.62 mM	1	0.0027894	0.9996
	2	0.0028701	0.99969
1.31 mM	1	0.0016724	0.99977
	2	0.0017311	0.99972



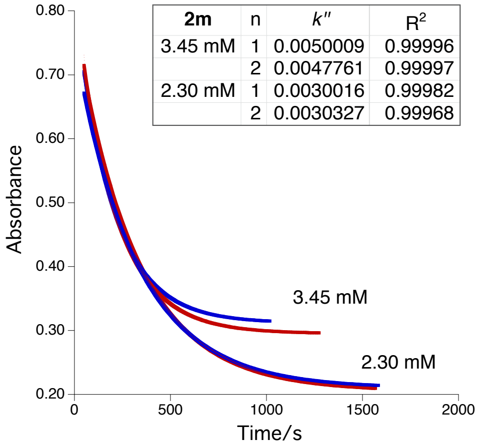
The kinetic study for double-click reaction of diyne **1** with 2,6-diisopropyl-4-(*N*-methyl-*N*-phenylamino)phenyl azide (**2l**) in MeOH was similarly conducted by the method described for **2o**. Time-dependent absorbance of diyne **1** (initial concentration of 0.250 mM) at 351.5 nm of wavelength was monitored in duplicate during the reaction with azide **2l** in three different concentrations (1.42, 2.83, or 4.25 mM) (left graph). A plot of pseudo-first order rate constants (*k*") versus the concentration of azide **2l** (right graph).



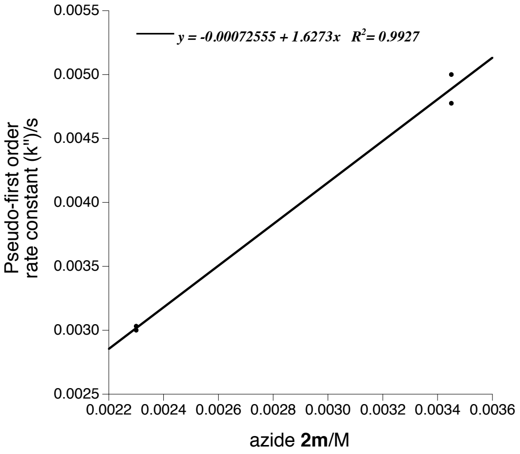
2l	n	*k"*	R^2
4.25 mM	1	0.0068579	0.99997
	2	0.0066314	0.99999
2.83 mM	1	0.0048597	0.99997
	2	0.0047884	0.99996
1.42 mM	1	0.0029459	0.99984
	2	0.0028959	0.99996



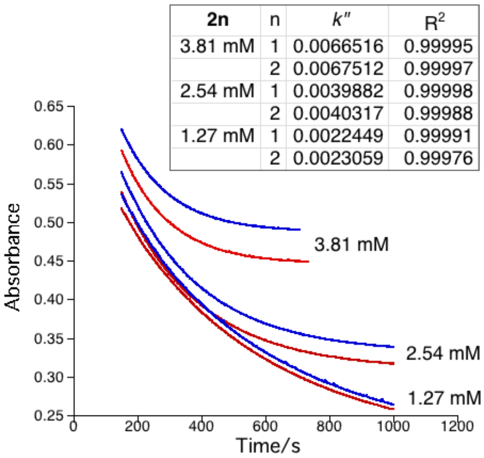
The kinetic study for double-click reaction of diyne **1** with 2,6-diisopropyl-4-morpholinophenyl azide (**2m**) in MeOH was similarly conducted by the method described for **2o**. Time-dependent absorbance of diyne **1** (initial concentration of 0.250 mM) at 351.5 nm of wavelength was monitored in duplicate during the reaction with azide **2m** in two different concentrations (2.30 or 3.45 mM) (left graph). A plot of pseudo-first order rate constants (*k*") versus the concentration of azide **2m** (right graph).



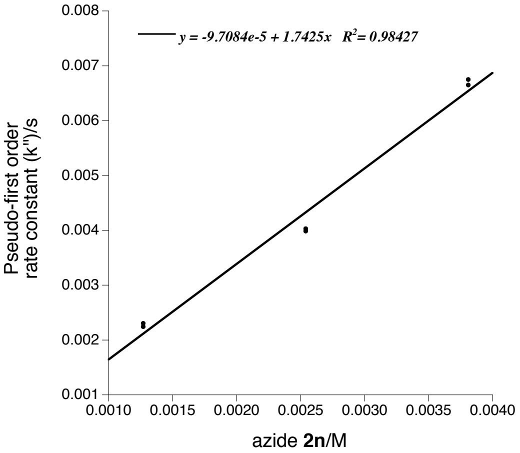
2m	n	*k"*	R^2
3.45 mM	1	0.0050009	0.99996
	2	0.0047761	0.99997
2.30 mM	1	0.0030016	0.99982
	2	0.0030327	0.99968



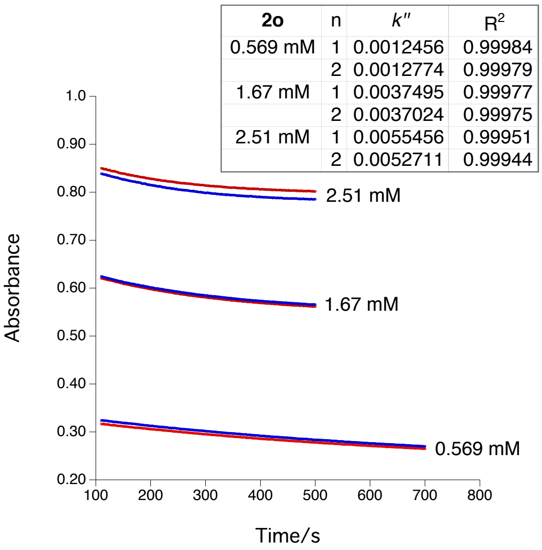
The kinetic study for double-click reaction of diyne **1** with 2,6-diisopropyl-4-piperidinophenyl azide (**2n**) in MeOH was similarly conducted by the method described for **2o**. Time-dependent absorbance of diyne **1** (initial concentration of 0.240 mM) at 351.5 nm of wavelength was monitored in duplicate during the reaction with azide **2n** in three different concentrations (1.27, 2.54, or 3.81) (left graph). A plot of pseudo-first order rate constants (*k*") versus the concentration of azide **2n** (right graph).



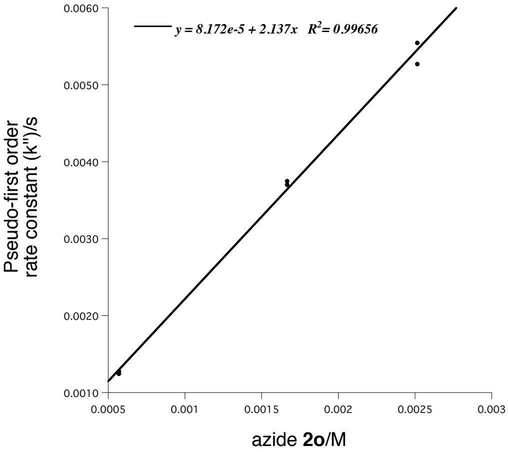
2n	n	*k*"	R^2
3.81 mM	1	0.0066516	0.99995
	2	0.0067512	0.99997
2.54 mM	1	0.0039882	0.99998
	2	0.0040317	0.99988
1.27 mM	1	0.0022449	0.99991
	2	0.0023059	0.99976



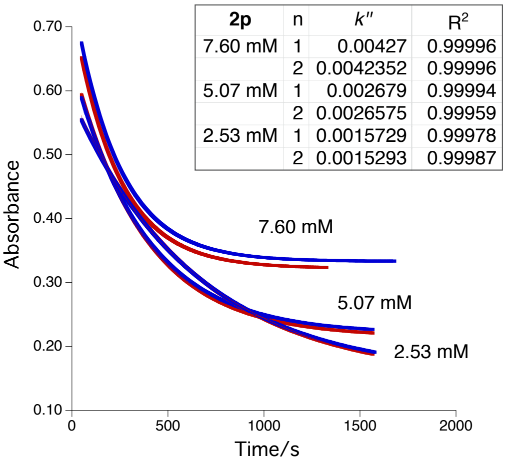
The kinetic study for double-click reaction of diyne **1** with 2,6-diisopropyl-4-pyrrolidinophenyl azide (**2o**) in MeCN was similarly conducted by the method described for **2o** in MeOH. Time-dependent absorbance of diyne **1** (initial concentration of 0.0835 mM) at 351.5 nm of wavelength was monitored in duplicate during the reaction with azide **2o** in three different concentrations (0.569, 1.67, or 2.51 mM) (left graph). A plot of pseudo-first order rate constants (*k*") versus the concentration of azide **2o** (right graph).

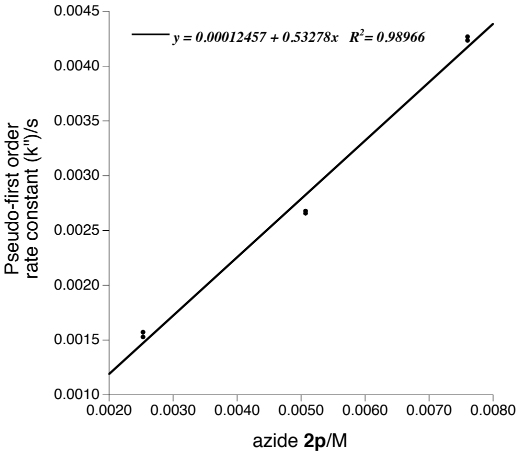


2o	n	*k*"	R^2
0.569 mM	1	0.0012456	0.99984
	2	0.0012774	0.99979
1.67 mM	1	0.0037495	0.99977
	2	0.0037024	0.99975
2.51 mM	1	0.0055456	0.99951
	2	0.0052711	0.99944

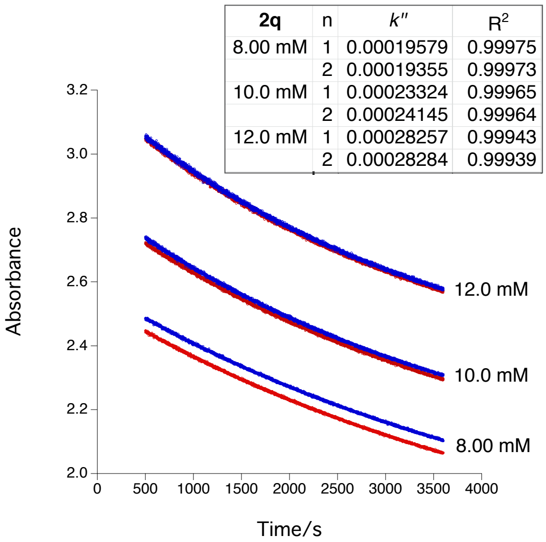


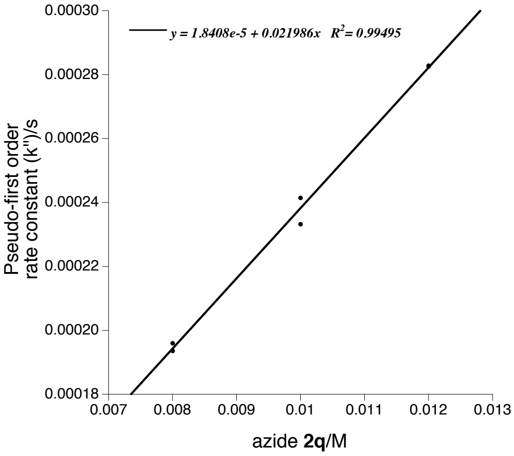
The kinetic study for double-click reaction of diyne **1** with 4-(4-acetyl-5-methyl-1*H*-1,2,3-triazol-1-yl)-2,6-diisopropylphenyl azide (**2p**) in MeOH was similarly conducted by the method described for **2o**. Time-dependent absorbance of diyne **1** (initial concentration of 0.220 mM) at 351.5 nm of wavelength was monitored in duplicate during the reaction with azide **2p** in three different concentrations (2.53, 5.07, or 7.60 mM) (left graph). A plot of pseudo-first order rate constants (*k*") versus the concentration of azide **2p** (right graph).


2p	n	*k*"	R^2
7.60 mM	1	0.00427	0.99996
	2	0.0042352	0.99996
5.07 mM	1	0.002679	0.99994
	2	0.0026575	0.99959
2.53 mM	1	0.0015729	0.99978
	2	0.0015293	0.99987

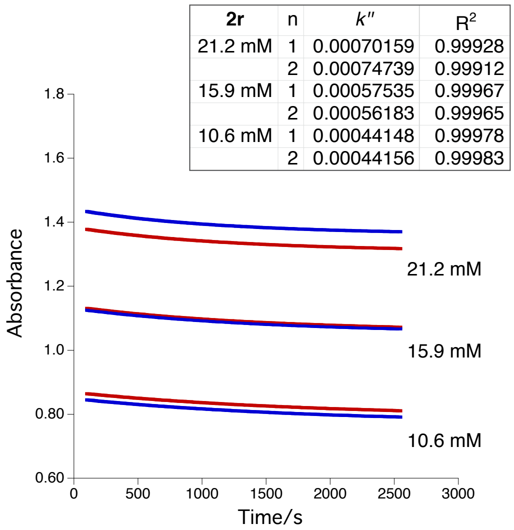


The kinetic study for double-click reaction of diyne **1** with 4-morpholinophenyl azide (**2q**) in MeCN was similarly conducted by the method described for **2o** in MeOH. Time-dependent absorbance of diyne **1** (initial concentration of 0.500 mM) at 351.5 nm of wavelength was monitored during the reaction with azide **2q** in three different concentrations (8.0, 10.0, or 12.0 mM) (left graphs). A plot of pseudo-first order rate constants (*k*") versus the concentration of azide **2q** (right graph).

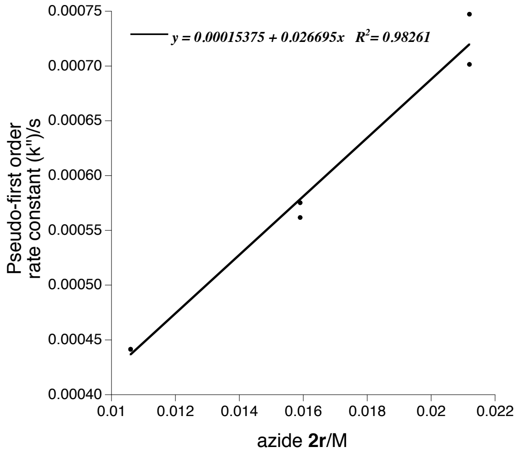

2q	n	*k*"	R^2
8.00 mM	1	0.00019579	0.99975
	2	0.00019355	0.99973
10.0 mM	1	0.00023324	0.99965
	2	0.00024145	0.99964
12.0 mM	1	0.00028257	0.99943
	2	0.00028284	0.99939



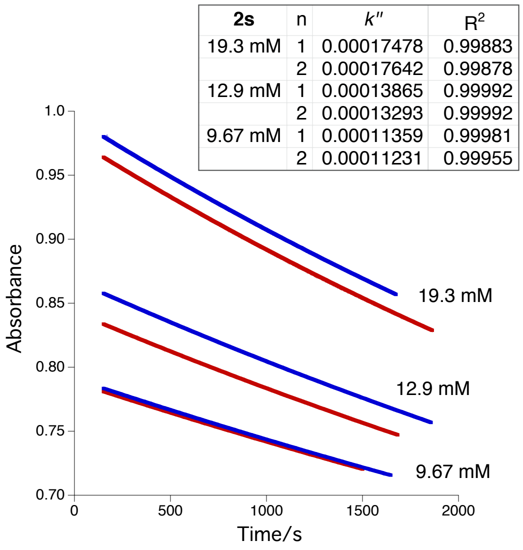
The kinetic study for double-click reaction of diyne **1** with 4-azidoaniline (**2r**) in MeOH was similarly conducted by the method described for **2o**. Time-dependent absorbance of diyne **1** (initial concentration of 0.250 mM) at 400.0 nm of wavelength was monitored in duplicate during the reaction with azide **2r** in three different concentrations (10.6, 15.9, or 21.2 mM) (left graph). A plot of pseudo-first order rate constants (*k*”) versus the concentration of azide **2r** (right graph).



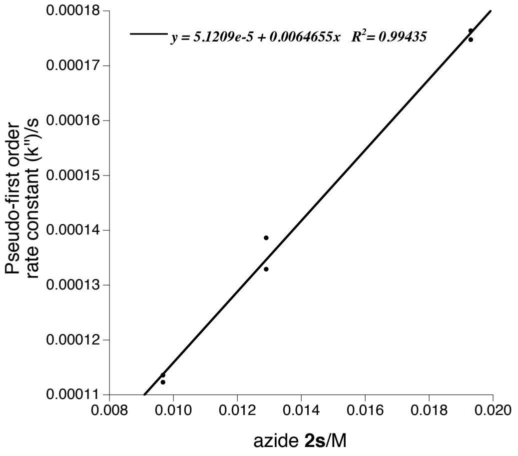
2r	n	*k''*	R^2
21.2 mM	1	0.00070159	0.99928
	2	0.00074739	0.99912
15.9 mM	1	0.00057535	0.99967
	2	0.00056183	0.99965
10.6 mM	1	0.00044148	0.99978
	2	0.00044156	0.99983



The kinetic study for double-click reaction of diyne **1** with 4-azidoaniline hydrochloride (**2s**) in MeOH was similarly conducted by the method described for **2o**. Time-dependent absorbance of diyne **1** (initial concentration of 0.280 mM) at 351.5 nm of wavelength was monitored in duplicate during the reaction with azide **2s** in three different concentrations (9.67, 12.9, or 19.3 mM) (left graph). A plot of pseudo-first order rate constants (*k*”) versus the concentration of azide **2s** (right graph).



2s	n	*k''*	R^2
19.3 mM	1	0.00017478	0.99883
	2	0.00017642	0.99878
12.9 mM	1	0.00013865	0.99992
	2	0.00013293	0.99992
9.67 mM	1	0.00011359	0.99981
	2	0.00011231	0.99955



The rate measurement of the reaction between equimolar amounts of 2,6-diisopropyl-4-pyrrolidinophenyl azide (**2o**) and (1α,8α,9α)-bicyclo[6.1.0]non-4-yn-9-ylmethanol (**S7**) that afforded (5a*S*,6*S*,6a*R*)-1-(2,6-diisopropyl-4-pyrrolidinophenyl)-6-(hydroxymethyl)-1,4,5,5a,6,6a,7,8-octahydrocyclopropa[5,6]cycloocta[1,2-*d*][1,2,3]triazole (**S8**) was performed by monitoring the reaction in CD_3OD by ^1H NMR at 23 °C.

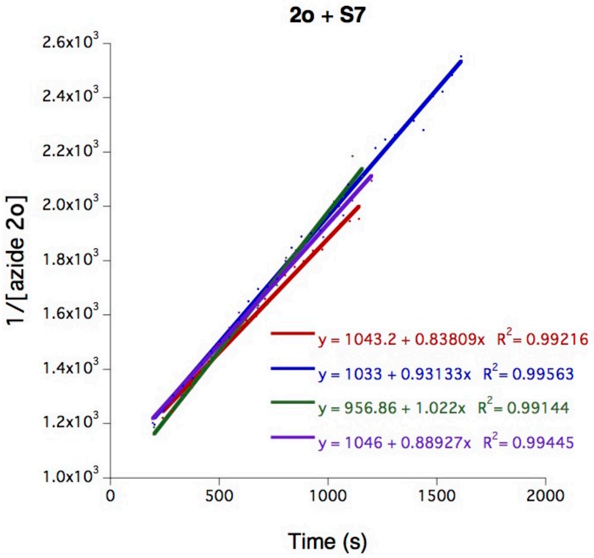
To 0.30 mL of CD_3OD solution of 2,6-diisopropyl-4-pyrrolidinophenyl azide (**2o**) (2.00 mM; final concentration at 1.00 mM) placed in an NMR tube (temperature kept at 23 °C) was added 0.30 mL of CD_3OD solution of (1α,8α,9α)-bicyclo[6.1.0]non-4-yn-9-ylmethanol (**S7**) (2.00 mM; final concentration at 1.00 mM). The formation of **S8** and consumption of azide **2o** were monitored by ^1H NMR analysis (500 MHz). Since triazole **S8** was obtained quantitatively as the sole product, the amount of triazole **S8** formed was equated to the decreased amount of azide **2o** determined by the integrations.

The second-order rate constant (*k*) was determined by plotting 1/[observed concentrations of azide **2o**] versus time. The points fitted to a linear regression and the slope corresponds to the second-order rate constant (*k*), which was determined by linear regression analysis using KaleidaGraph ver. 4.1.4 (graph below).

$1/[A] = 1/[A_0] + kt$

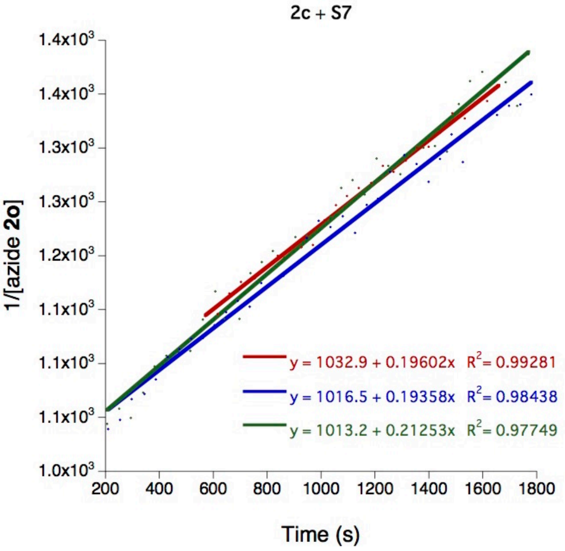
*A: concentration of 2,6-diisopropyl-4-pyrrolidinophenyl azide (**2o**)*

t: time (s) from the starting point of the observation

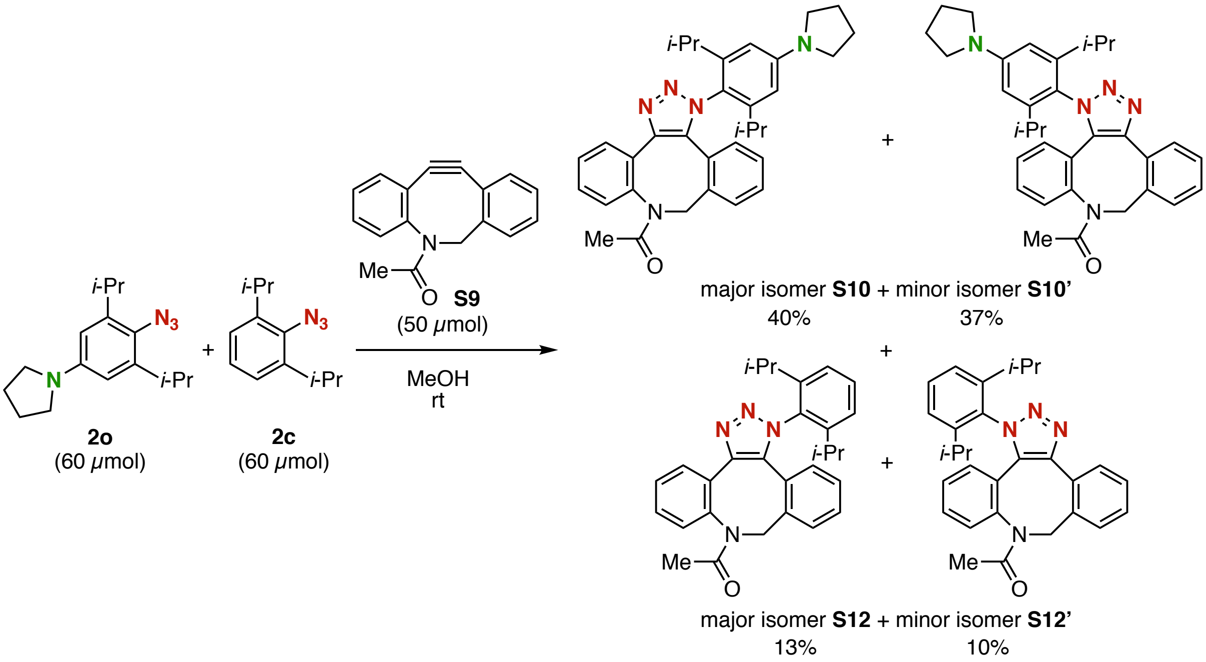


The experiment was quadruplicated and the average indicates the second-order rate constant (*k*) to be 0.92 ± 0.07 $M^{-1}s^{-1}$ for the reaction between azide **2o** and cycloalkyne **S7**.

The rate measurement of the reaction between equimolar amounts of 2,6-diisopropylphenyl azide (**2c**) and (1α,8α,9α)-bicyclo[6.1.0]non-4-yn-9-ylmethanol (**S7**) that afforded (5a*S*,6*S*,6a*R*)-1-(2,6-diisopropylphenyl)-6-(hydroxymethyl)-1,4,5,5a,6,6a,7,8-octahydrocyclopropa[5,6]cycloocta[1,2-*d*][1,2,3]triazole (**S11**) was performed according to the method described for the reaction between azide **2o** and cycloalkyne **S7** (final concentration at 1.00 mM). The experiment was triplicated and the average indicates the second-order rate constant (*k*) to be 0.201 ± 0.008 $M^{-1}s^{-1}$ for the reaction between azide **2o** and cycloalkyne **S9**.



Competition Experiment

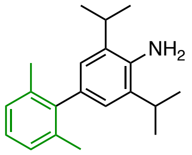


To a solution of 5-acetyl-5*H*,6*H*-11,12-didehydrodibenzo[*b*,*f*]azocin (**S9**) (12.4 mg, 50.1 μmol) dissolved in MeOH (1.3 mL) was added a solution of 2,6-diisopropyl-4-pyrrolidinophenyl azide (**2o**) (16.3 mg, 59.8 μmol) and 2,6-diisopropylphenyl azide (**2c**) (12.2 mg, 60.0 μmol) dissolved in MeOH (5.0 mL) at room temperature. After stirring for 1.5 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 a mixture of **S10** and **S12** (12.3 mg; **S10** 20 μmol, **S12** 3.2 μmol), **S10'** and **S12'** (12.3 mg; **S10'** 19 μmol, **S12'** 5.6 μmol), and **S12** (1.4 mg, 3.1 μmol).

Characterization Data of New Compounds

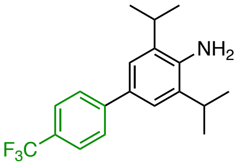
4-Azidoaniline (**2r**)[S14] and 2,6-diisopropyl-4-phenylaniline[S15] were identical in the spectra data with those reported in the literature.

4-(2,6-Dimethylphenyl)-2,6-diisopropylaniline



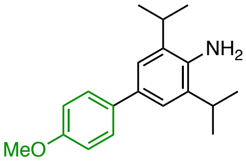
Pale yellow solid; Mp 67–68 ℃; R_f = 0.46 (*n*-hexane/EtOAc = 10/1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.26 (d, 12H, *J* = 6.8 Hz), 2.07 (s, 6H), 2.98 (sept, 2H, *J* = 6.8 Hz), 3.59–3.87 (br, 2H), 6.80 (s, 2H), 7.09–7.15 (m, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 21.3 (2C), 22.9 (4C), 28.2 (2C), 123.7 (2C), 126.7 (1C), 127.4 (2C), 131.1 (1C), 132.7 (2C), 136.9 (2C), 138.6 (1C), 143.3 (1C); IR (KBr, cm^{-1}) 1251, 1463, 1460, 1621, 2959, 3383, 3461; HRMS (ESI$^+$) *m*/*z* 282.2202 ([M+H]$^+$, $C_{20}H_{28}N^+$ requires 282.2216).

2,6-Diisopropyl-4-(4-(trifluoromethyl)phenyl)aniline



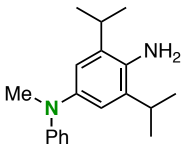
Pale brown solid; Mp 91–92 ℃; R_f = 0.34 (*n*-hexane/EtOAc = 10/1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.33 (d, 12H, *J* = 6.8 Hz), 2.98 (sept, 2H, *J* = 6.8 Hz), 3.89 (br s, 2H), 7.28 (s, 2H), 7.62–7.67 (m, 4H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 22.6 (4C), 28.3 (2C), 122.1 (2C), 124.7 (q, 1C, J_{C-F} = 272.0 Hz), 125.7 (q, 2C, J_{C-F} = 3.7 Hz), 126.9 (2C), 128.2 (q, 1C, J_{C-F} = 32.1 Hz), 129.9 (1C), 133.0 (2C), 141.0 (1C), 146.0 (1C); ^{19}F NMR (376 MHz, $CDCl_3$) δ –62.4 (s); IR (KBr, cm^{-1}); 1108, 1325, 1463, 1615, 2873, 2964, 3412, 3491; HRMS (ESI$^+$) *m*/*z* 322.1785 ([M+H]$^+$, $C_{19}H_{23}F_3N^+$ requires 322.1777).

2,6-Diisopropyl-4-(4-methoxyphenyl)aniline



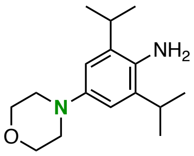
Pale yellow solid; Mp 69–70 ℃; R_f = 0.38 (*n*-hexane/EtOAc = 10/1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.32 (d, 12H, *J* = 6.8 Hz), 2.98 (sept, 2H, *J* = 6.8 Hz), 3.63–3.92 (br, 2H), 3.84 (s, 3H), 6.93–6.97 (AA'BB', 2H), 7.22 (s, 2H), 7.46–7.50 (AA'BB', 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 22.7 (4C), 28.3 (2C), 55.6 (1C), 114.2 (2C), 121.7 (2C), 127.9 (2C), 131.4 (1C), 133.0 (2C), 135.3 (1C), 139.5 (1C), 158.5 (1C); IR (KBr, cm^{-1}) 1178, 1240, 1463, 1461, 1627, 2960, 3402, 3485; HRMS (ESI$^+$) *m*/*z* 284.1997 ([M+H]$^+$, $C_{19}H_{26}NO^+$ requires 284.2009).

2,6-Diisopropyl-4-(*N*-methyl-*N*-phenylamino)aniline



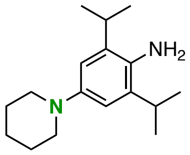
Pale purple oil; R_f = 0.36 (*n*-hexane/EtOAc = 9/1); ^{1}H NMR (500 MHz, CDCl$_3$) δ 1.24 (d, 12H, J = 6.8 Hz), 2.93 (sept, 2H, J = 6.8 Hz), 3.26 (s, 3H), 3.59–3.80 (br, 2H), 6.64–6.75 (m, 3H), 6.87 (s, 2H), 7.12–7.20 (AA'BB'C, 2H); ^{13}C NMR (126 MHz, CDCl$_3$) δ 22.5 (4C), 28.1 (2C), 40.4 (1C), 113.9 (2C), 116.8 (1C), 112.1 (2C), 128.8 (2C), 133.8 (2C), 137.5 (1C), 140.0 (1C), 150.0 (1C); IR (KBr, cm^{-1}) 694, 748, 1356, 1443, 1464, 1499, 1593, 1620, 2961; HRMS (ESI$^+$) *m*/*z* 283.2156 ([M+H]$^+$, $C_{19}H_{27}N_2^+$ requires 283.2169).

2,6-Diisopropyl-4-morpholinoaniline



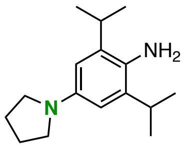
Brown solid; Mp 108–114 ℃; R_f = 0.39 (*n*-hexane/EtOAc = 2/1); ^{1}H NMR (500 MHz, CDCl$_3$) δ 1.27 (d, 12H, J = 6.8 Hz), 2.96 (sept, 2H, J = 6.8 Hz), 3.03–3.08 (m, 4H), 3.37–3.63 (br, 2H), 3.84–3.89 (m, 4H), 6.69 (s, 2H); ^{13}C NMR (126 MHz, CDCl$_3$) δ 22.5 (4C), 28.2 (2C), 51.4 (2C), 67.2 (2C), 112.3 (2C), 133.7 (2C), 134.5 (1C), 144.3 (1C); IR (KBr, cm^{-1}) 980, 1119, 1445, 1470, 1601, 2959; HRMS (ESI$^+$) *m*/*z* 263.2116 ([M+H]$^+$, $C_{16}H_{27}N_2O^+$ requires 263.2118).

2,6-Diisopropyl-4-piperidinoaniline



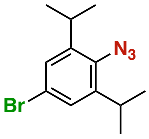
Brown solid; Mp 46–47 ℃; R_f = 0.41 (*n*-hexane/EtOAc = 5/1); ^{1}H NMR (500 MHz, CDCl$_3$) δ 1.26 (d, 12H, J = 6.8 Hz), 1.50–1.57 (m, 2H), 1.70–1.77 (m, 4H), 2.95 (sept, 2H, J = 6.8 Hz), 2.98–3.03 (m, 4H), 3.05–3.95 (br, 2H), 6.73 (s, 2H); ^{13}C NMR (126 MHz, CDCl$_3$) δ 22.8 (4C), 24.5 (1C), 26.6 (2C), 28.4 (2C), 53.3 (2C), 113.6 (2C), 133.7 (2C), 134.3 (1C), 146.0 (1C); IR (KBr, cm^{-1}) 971, 1229, 1364, 1443, 1604, 2935; HRMS (ESI$^+$) *m*/*z* 261.2323 ([M+H]$^+$, $C_{17}H_{29}N_2^+$ requires 261.2325).

2,6-Diisopropyl-4-pyrrolidinoaniline



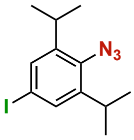
Brown solid; Mp 67–68 ℃; R_f = 0.41 (*n*-hexane/EtOAc = 5/1); ^{1}H NMR (500 MHz, CDCl$_3$) δ 1.27 (d, 12H, J = 6.8 Hz), 1.92–2.02 (m, 4H), 2.81–3.19 (br, 2H), 3.19–3.46 (br, 6H), 6.36 (s, 2H); ^{13}C NMR (126 MHz, CDCl$_3$) δ 22.9 (4C), 25.5 (2C), 28.4 (2C), 48.5 (2C), 107.3 (2C), 130.4 (1C), 134.9 (2C), 142.4 (1C); IR (KBr, cm^{-1}) 832, 1008, 1246, 1380, 1459, 1605, 2958; HRMS (ESI$^+$) *m*/*z* 247.2172 ([M+H]$^+$, $C_{16}H_{27}N_2^+$ requires 247.2169).

4-Bromo-2,6-diisopropylphenyl azide (**2d**)



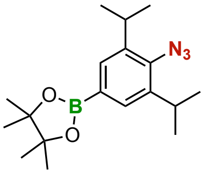
Brown oil; R_f = 0.63 (*n*-hexane); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.25 (d, 12H, *J* = 6.9 Hz), 3.31 (sept, 2H, *J* = 6.9 Hz), 7.23 (s, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 23.5 (4C), 29.1 (2C), 120.8 (1C), 127.4 (2C), 134.6 (1C), 145.6 (2C); IR (KBr, cm^{-1}) 1329, 1454, 2091, 2955; HRMS (ESI$^+$) *m*/*z* 254.0539 ($[M+H–N_2]^+$, $C_{12}H_{17}{}^{79}BrN^+$ requires 254.0539).

4-Iodo 2,6-diisopropylphenyl azide (**2e**)



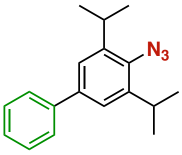
Brown oil; R_f = 0.65 (*n*-hexane); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.24 (d, 12H, *J* = 6.8 Hz), 3.28 (sept, 2H, *J* = 6.8 Hz), 7.42 (s, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 23.3 (4C), 28.7 (2C), 92.3 (1C), 133.3 (2C), 135.3 (1C), 145.5 (2C); IR (KBr, cm^{-1}) 865, 1071, 1234, 1332, 1438, 1565, 2102, 2124, 2930, 2964; Anal. calcd. for $C_{12}H_{16}IN_3$: C, 43.78; H, 4.90; N, 12.77%; Found: C, 43.61; H, 5.20; N, 12.53%.

2,6-Diisopropyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl azide (**2f**)



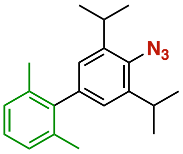
Pale brown oil; R_f = 0.53 (*n*-hexane/EtOAc = 10/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.29 (d, 12H, *J* = 6.9 Hz), 1.34 (s, 12H), 3.35 (sept, 2H, *J* = 6.9 Hz), 7.57 (s, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 23.7 (4C), 25.0 (4C), 29.0 (2C), 84.0 (2C), 130.8 (2C), 138.3 (1C), 142.4 (2C) (The signal for the carbon attached to the boron atom was not observed); IR (KBr, cm^{-1}) 692, 852, 966, 1146, 1378, 1463, 1601, 2117, 2933, 2967; Anal. calcd. for $C_{18}H_{28}BN_3O_2$: C, 65.66; H, 8.57; N, 12.76%; Found: C, 65.67; H, 8.86; N, 12.83%.

2,6-Diisopropyl-4-phenylphenyl azide (**2g**)



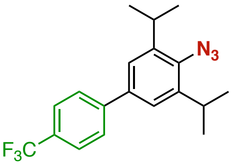
Pale yellow solid; Mp 34–35 ℃; R_f = 0.49 (*n*-hexane); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.32 (d, 12H, *J* = 6.8 Hz), 3.41 (sept, 2H, *J* = 6.8 Hz), 7.33 (s, 2H), 7.33–7.37 (AA'BB'C, 1H), 7.42–7.47 (AA'BB'C, 2H), 7.54–7.57 (AA'BB'C, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 23.8 (4C), 29.2 (2C), 123.1 (2C), 127.4 (2C), 127.5 (2C), 129.0 (2C), 134.8 (1C), 140.0 (1C), 141.4 (1C), 143.6 (1C); IR (KBr, cm^{-1}) 881, 1315, 1234, 1446, 2117, 2964; Anal. calcd. for $C_{18}H_{21}N_3$: C, 77.38; H, 7.58; N, 15.04 %; Found: C, 77.39; H, 7.38; N, 15.17 %.

4-(2,6-Dimethylphenyl)-2,6-diisopropylphenyl azide (**2h**)



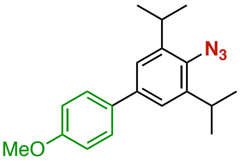
Yellow solid; Mp 35–36 ℃; R_f = 0.47 (*n*-hexane); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.26 (d, 12H, *J* = 6.8 Hz), 2.03 (s, 6H), 3.39 (sept, 2H, *J* = 6.8 Hz), 6.92 (s, 2H), 7.10–7.19 (m, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 21.1 (2C), 23.8 (4C), 29.0 (2C), 124.9 (2C), 127.3 (1C), 127.6 (2C), 133.8 (1C), 136.3 (2C), 139.5 (1C), 142.0 (1C), 143.3 (2C); IR (KBr, cm^{-1}) 1307, 1461, 2117, 2965; HRMS (ESI$^+$) *m*/*z* 280.2052 ($[M+H–N_2]^+$, $C_{20}H_{26}N^+$ requires 280.2060).

2,6-Diisopropyl-4-(4-(trifluoromethyl)phenyl)phenyl azide (**2i**)



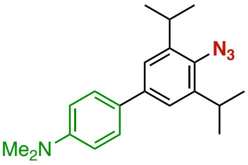
Pale brown solid; Mp 34–39 ℃; R_f = 0.61 (*n*-hexane); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.33 (d, 12H, *J* = 6.9 Hz), 3.42 (sept, 2H, *J* = 6.9 Hz), 7.33 (s, 2H), 7.63–7.67 (AA'BB', 2H), 7.68–7.71 (AA'BB', 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 23.7 (4C), 29.2 (2C), 123.2 (2C), 124.5 (q, 1C, $J_{C–F}$ = 272.6 Hz), 125.9 (q, 2C, $J_{C–F}$ = 3.6 Hz), 127.6 (2C), 129.6 (q, 1C, $J_{C–F}$ = 32.6 Hz), 135.7 (1C), 138.5 (1C), 144.0 (2C), 144.9 (1C); ^{19}F NMR (376 MHz, $CDCl_3$) δ –62.7 (s); IR (KBr, cm^{-1}) 1071, 1126, 1167, 1325, 2120, 2968; HRMS (ESI$^+$) *m*/*z* 348.1686 ($[M+H]^+$, $C_{19}H_{21}F_3N_3^+$ requires 348.1682).

2,6-Diisopropyl-4-(4-methoxyphenyl)phenyl azide (**2j**)



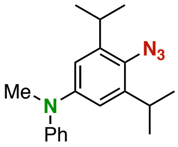
Brown solid; Mp 33–34 ℃; R_f = 0.46 (*n*-hexane); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.32 (d, 12H, *J* = 6.8 Hz), 3.40 (sept, 2H, *J* = 6.8 Hz), 3.86 (s, 3H), 6.96–7.00 (AA'BB', 2H), 7.28 (s, 2H), 7.47–7.51 (AA'BB', 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 23.8 (4C), 29.1 (2C), 55.6 (1C), 114.4 (2C), 122.7 (2C), 128.4 (2C), 133.9 (1C), 134.3 (1C), 139.6 (1C), 143.6 (2C), 159.4 (1C); IR (KBr, cm^{-1}) 1179, 1250, 1440, 1515, 2107, 2964; HRMS (ESI$^+$) *m*/*z* 332.1724 ($[M+Na]^+$, $C_{19}H_{23}N_3NaO^+$ requires 332.1733).

4-(4-(Dimethylamino)phenyl)-2,6-diisopropylphenyl azide (**2k**)



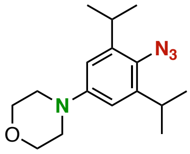
Orange solid; Mp 60–64 ℃; R_f= 0.51 (*n*-hexane/EtOAc = 10/1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.31 (d, 12H, *J* = 6.8 Hz), 3.00 (s, 6H), 3.39 (sept, 2H, *J* = 6.8 Hz), 6.79–6.83 (AA'BB', 2H), 7.29 (s, 2H), 7.44–7.48 (AA'BB', 2H); ^{13}C NMR (126 MHz, $CDCl_3$) *δ* 23.8 (4C), 29.1 (2C), 40.8 (2C), 113.0 (2C), 122.3 (2C), 127.9 (2C), 129.4 (1C), 133.7 (1C), 140.0 (1C), 143.4 (2C), 150.2 (1C); IR (KBr, cm^{-1}) 1441, 1524, 1612, 2118, 2964; HRMS (ESI$^+$) *m*/*z* 323.2234 ([M+H]$^+$, $C_{20}H_{27}N_4^+$ requires 323.2230).

2,6-Diisopropyl-4-(*N*-methyl-*N*-phenylamino)phenyl azide (**2l**)



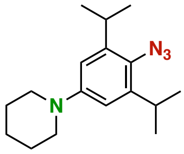
Brown oil; R_f = 0.21 (*n*-hexane); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.25 (d, 12H, *J* = 6.9 Hz), 3.29–3.39 (m, 5H), 6.85 (s, 2H), 6.92–6.97 (AA'BB'C, 1H), 6.97–7.01 (AA'BB'C, 2H), 7.26–7.31 (AA'BB'C, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 23.7 (4C), 29.2 (2C), 40.5 (1C), 117.3 (2C), 119.2 (2C), 120.7 (1C), 129.3 (2C), 129.6 (1C), 144.3 (2C), 147.6 (1C), 149.1 (1C); IR (KBr, cm^{-1}) 1356, 1496, 1590, 2116, 2964; HRMS (ESI$^+$) *m*/*z* 281.1999 ([M+H–N$_2$]$^+$, $C_{19}H_{25}N_2^+$ requires 281.2012).

2,6-Diisopropyl-4-morpholinophenyl azide (**2m**)



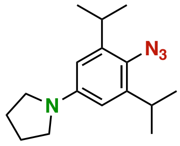
Brown oil; R_f = 0.31 (*n*-hexane); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.26 (d, 12H, *J* = 6.8 Hz), 3.13–3.16 (m, 4H), 3.33 (sept, 2H, *J* = 6.8 Hz), 3.85–3.89 (m, 4H), 6.67 (s, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 23.7 (4C), 29.3 (2C), 49.9 (2C), 67.2 (2C), 111.6 (2C), 128.3 (1C), 144.1 (2C), 150.2 (1C); IR (KBr, cm^{-1}) 1122, 1252, 1448, 1600, 2117, 2961; HRMS (ESI$^+$) *m*/*z* 289.2018 ([M+H]$^+$, $C_{16}H_{25}N_4O^+$ requires 289.2023).

2,6-Diisopropyl-4-piperidinophenyl azide (**2n**)



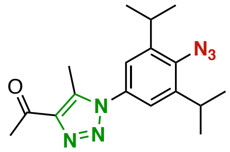
Brown oil; R_f = 0.41 (*n*-hexane/EtOAc = 5/1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.25 (d, 12H, *J* = 6.8 Hz), 1.52–1.61 (m, 2H), 1.69–1.76 (m, 4H), 3.10–3.13 (m, 4H), 3.31 (sept, 2H, *J* = 6.8 Hz), 6.70 (s, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 23.7 (4C), 24.4 (1C), 26.2 (2C), 29.3 (2C), 51.3 (2C), 112.5 (2C), 127.6 (1C), 143.7 (2C), 151.3 (1C); IR (KBr, cm^{-1}) 1252, 1466, 1598, 2119, 2964; HRMS (ESI$^+$) *m*/*z* 287.2216 ([M+H]$^+$, $C_{17}H_{27}N_4^+$ requires 287.2230).

2,6-Diisopropyl-4-pyrrolidinophenyl azide (**2o**)



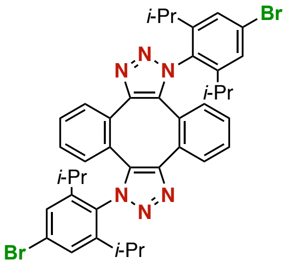
Brown oil; R_f = 0.64 (*n*-hexane/EtOAc = 5/1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.27 (d, 12H, *J* = 6.8 Hz), 1.97–2.02 (m, 4H), 3.24–3.37 (m, 6H), 6.31 (s, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 23.8 (4C), 25.7 (2C), 29.3 (2C), 47.9 (2C), 107.0 (2C), 124.3 (1C), 144.1 (2C), 146.8 (1C); IR (KBr, cm^{-1}) 1279, 1476, 1603, 2100, 2963; HRMS (ESI$^+$) *m*/*z* 245.2008 ([M+H–N$_2$]$^+$, $C_{16}H_{25}N_2^+$ requires 245.2012).

4-(4-Acetyl-5-methyl-1*H*-1,2,3-triazol-1-yl)-2,6-diisopropylphenyl azide (**2p**)



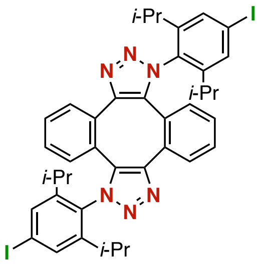
Yellow solid; Mp 54–55 °C; R_f = 0.38 (*n*-hexane/EtOAc = 5/1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.30 (d, 12H, *J* = 6.8 Hz), 2.58 (s, 3H), 2.76 (s, 3H), 3.44 (sept, 2H, *J* = 6.8 Hz), 7.18 (s, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 10.4 (1C), 23.5 (4C), 28.1 (1C), 29.2 (2C), 121.3 (2C), 133.9 (1C), 136.9 (1C), 137.6 (1C), 143.9 (1C), 145.3 (2C), 194.6 (1C); IR (KBr, cm^{-1}) 1332, 1479, 1683, 2116, 2968; HRMS (ESI$^+$) *m*/*z* 349.1740 ([M+Na]$^+$, $C_{17}H_{22}N_6NaO^+$ requires 349.1747).

1,8-Bis(4-bromo-2,6-diisopropylphenyl)-1,8-dihydrodibenzo[3,4:7,8]cycloocta[1,2-*d*:5,6-*d*']bis-([1,2,3]triazole) (*trans*-**3d**)



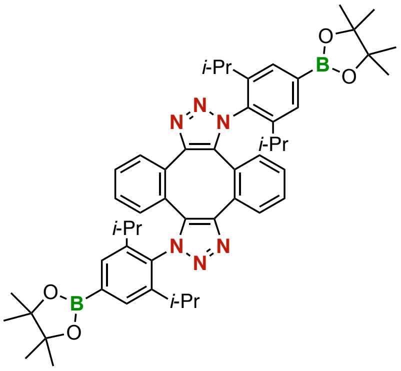
Colorless solid; Mp 293–294 °C; R_f = 0.33 (*n*-hexane/EtOAc = 5/1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.71 (d, 6H, *J* = 6.8 Hz), 0.76 (d, 6H, *J* = 6.8 Hz), 1.37–1.42 (m, 12H), 1.89 (qq, 2H, *J* = 6.8, 6.8 Hz), 2.60 (qq, 2H, *J* = 6.8, 6.8 Hz), 6.81–6.84 (m, 2H), 7.17 (d, 2H, *J* = 2.1 Hz), 7.22 (ddd, 2H, *J* = 1.1, 7.7, 7.7 Hz), 7.42–7.48 (m, 4H), 7.80 (d, 2H, *J* = 7.7 Hz); ^{13}C NMR (126 MHz, $CDCl_3$) δ 22.3 (2C), 22.9 (2C), 24.4 (2C), 26.2 (2C), 28.7 (2C), 29.6 (2C), 125.4 (2C), 126.2 (2C), 127.6 (2C), 127.7 (2C), 129.0 (2C), 129.7 (2C), 130.2 (2C), 130.9 (2C), 131.8 (2C), 132.5 (2C), 136.2 (2C), 144.4 (2C), 148.1 (2C), 149.4 (2C); IR (KBr, cm^{-1}) 991, 1360, 1467, 1573, 2970; HRMS (ESI$^+$) *m*/*z* 763.1718 ([M+H]$^+$, $C_{40}H_{41}{}^{79}Br_2N_6^+$ requires 763.1754).

1,8-Bis(4-iodo-2,6-diisopropylphenyl)-1,8-dihydrodibenzo[3,4:7,8]cycloocta[1,2-*d*:5,6-*d*']bis-([1,2,3]triazole) (*trans*-**3e**)



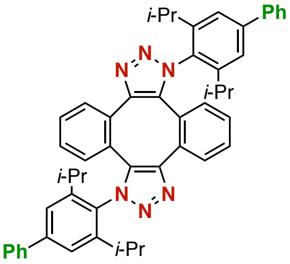
Colorless solid; Mp 293–295 °C; R_f = 0.36 (*n*-hexane/EtOAc = 5/1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.70 (d, 6H, *J* = 6.8 Hz), 0.75 (d, 6H, *J* = 6.8 Hz), 1.37–1.41 (m, 12H), 1.85 (qq, 2H, *J* = 6.8, 6.8 Hz), 2.55 (qq, 2H, *J* = 6.8, 6.8 Hz), 6.81–6.84 (m, 2H), 7.22 (ddd, 2H, *J* = 0.9, 7.7, 7.7 Hz), 7.36 (d, 2H, *J* = 1.8 Hz), 7.45 (ddd, 2H, *J* = 0.9, 7.7, 7.7 Hz), 7.66 (d, 2H, *J* = 1.8 Hz), 7.79 (dd, 2H, *J* = 0.9, 7.7 Hz); ^{13}C NMR (126 MHz, $CDCl_3$) δ 22.3 (2C), 22.9 (2C), 24.4 (2C), 26.2 (2C), 28.6 (2C), 29.5 (2C), 97.9 (2C), 126.2 (2C), 129.0 (2C), 129.7 (2C), 130.2 (2C), 131.7 (2C), 131.8 (2C), 132.5 (2C), 133.7 (2C), 133.8 (2C), 136.1 (2C), 144.4 (2C), 148.0 (2C), 149.3 (2C); IR (KBr, cm^{-1}) 992, 1362, 1466, 1567, 2963; HRMS (ESI$^+$) *m*/*z* 859.1439 ([M+H]$^+$, $C_{40}H_{41}I_2N_6^+$ requires 859.1477).

1,8-Bis(2,6-diisopropyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)-1,8-dihydrodibenzo-[3,4:7,8]cycloocta[1,2-*d*:5,6-*d*']bis([1,2,3]triazole) (*trans*-**3f**)



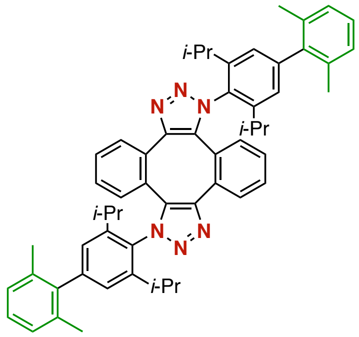
Colorless solid; Mp >300 ℃; R_f = 0.52 (*n*-hexane/EtOAc = 2/1); ^{1}H NMR (500 MHz, CDCl$_3$) δ 0.75 (d, 6H, *J* = 6.8 Hz), 0.82 (d, 6H, *J* = 6.8 Hz), 1.36 (s, 24H), 1.42 (d, 6H, *J* = 6.8 Hz), 1.45 (d, 6H, *J* = 6.8 Hz), 1.95 (qq, 2H, *J* = 6.8, 6.8 Hz), 2.62 (qq, 2H, *J* = 6.8, 6.8 Hz), 6.84–6.87 (m, 2H), 7.15 (ddd, 2H, *J* = 1.0, 7.6, 7.6 Hz), 7.40 (ddd, 2H, *J* = 1.0, 7.6, 7.6 Hz), 7.49 (d, 2H, *J* = 0.8 Hz), 7.76 (d, 2H, *J* = 0.8 Hz), 7.79 (dd, 2H, *J* = 1.0, 7.6 Hz); ^{13}C NMR (126 MHz, CDCl$_3$) δ 22.5 (2C), 23.0 (2C), 24.7 (2C), 25.1 (8C), 26.3 (2C), 28.6 (2C), 29.5 (2C), 84.3 (4C), 126.5 (2C), 128.7 (2C), 129.9 (2C+2C, two signals overlapped), 130.5 (2C), 130.6 (2C), 131.8 (2C), 132.7 (2C), 134.3 (2C), 136.1 (2C), 144.3 (2C), 144.9 (2C), 146.1 (2C) (The signals for the two carbons attached to the boron atoms were not observed); IR (KBr, cm^{-1}) 1144, 1314, 1377, 1408, 1634, 2967, 3418; HRMS (ESI$^+$) *m*/*z* 859.5225 ([M+H]$^+$, $C_{52}H_{65}{}^{11}B_2N_6O_4^+$ requires 859.5248).

1,8-Bis(2,6-diisopropyl-4-phenylphenyl)-1,8-dihydrodibenzo[3,4:7,8]cycloocta[1,2-*d*:5,6-*d*']bis-([1,2,3]triazole) (*trans*-**3g**)



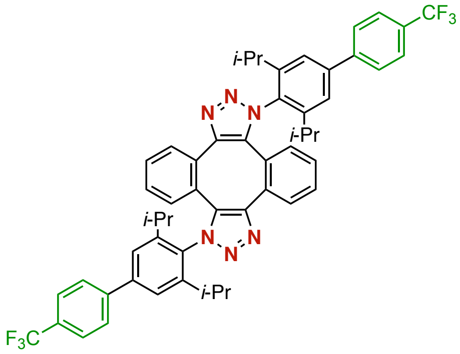
Colorless solid; Mp >300 ℃; R_f = 0.50 (*n*-hexane/EtOAc = 3/1); ^{1}H NMR (500 MHz, CDCl$_3$) δ 0.80 (d, 6H, *J* = 6.8 Hz), 0.85 (d, 6H, *J* = 6.8 Hz), 1.47 (d, 6H+6H, *J* = 6.8 Hz, two signals overlapped), 2.03 (qq, 2H, *J* = 6.8, 6.8 Hz), 2.71 (qq, 2H, *J* = 6.8, 6.8 Hz), 6.91–6.95 (m, 2H), 7.20 (ddd, 2H, *J* = 1.1, 7.7, 7.7 Hz), 7.27 (d, 2H, *J* = 1.9 Hz), 7.36–7.41 (AA'BB'C, 2H), 7.41–7.49 (m, 6H), 7.55 (d, 2H, *J* = 1.9 Hz), 7.57–7.63 (AA'BB'C, 4H), 7.82–7.85 (m, 2H); ^{13}C NMR (126 MHz, CDCl$_3$) δ 22.6 (2C), 23.1 (2C), 24.7 (2C), 26.4 (2C), 28.7 (2C), 29.6 (2C), 123.02 (2C), 123.05 (2C), 126.6 (2C), 127.5 (4C), 128.0 (2C), 128.8 (2C), 129.0 (4C), 129.9 (2C), 130.0 (2C), 131.0 (2C), 131.8 (2C), 132.7 (2C), 136.2 (2C), 140.9 (2C), 143.6 (2C), 144.4 (2C), 146.2 (2C), 147.4 (2C); IR (KBr, cm^{-1}) 994, 1366, 1471, 1599, 2967; HRMS (ESI$^+$) *m*/*z* 781.3950 ([M+Na]$^+$, $C_{52}H_{50}N_6Na^+$ requires 781.3989).

1,8-Bis(4-(2,6-dimethylphenyl)-2,6-diisopropylphenyl)-1,8-dihydrodibenzo[3,4:7,8]cycloocta-[1,2-*d*:5,6-*d'*]bis([1,2,3]triazole) (*trans*-**3h**)



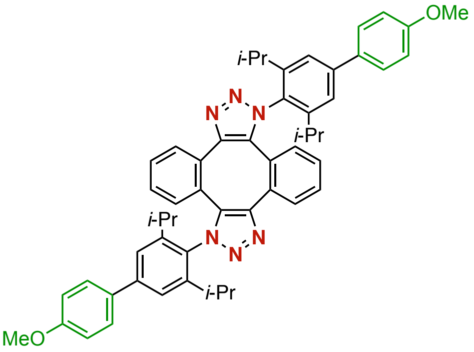
Colorless solid; Mp >300 ℃; R_f = 0.50 (*n*-hexane/EtOAc = 5/1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.74–0.79 (m, 12H), 1.40 (d, 6H, J = 6.8 Hz), 1.43 (d, 6H, J = 6.8 Hz), 1.94 (s, 6H), 2.01 (qq, 2H, J = 6.8, 6.8 Hz), 2.08 (s, 6H), 2.70 (qq, 2H, J = 6.8, 6.8 Hz), 6.86 (d, 2H, J = 1.7 Hz), 6.91–6.94 (m, 2H), 7.10–7.22 (m, 10H), 7.45 (ddd, 2H, J = 0.9, 7.7, 7.7 Hz), 7.85 (dd, 2H, J = 0.9, 7.7 Hz); ^{13}C NMR (126 MHz, $CDCl_3$) δ 20.7 (2C), 21.0 (2C), 22.4 (2C), 23.1 (2C), 24.7 (2C), 26.4 (2C), 28.7 (2C), 29.5 (2C), 124.97 (2C), 125.00 (2C), 126.6 (2C), 127.56 (2C), 127.61 (2C), 127.7 (2C), 128.2 (2C), 130.1 (4C), 130.2 (2C), 131.8 (2C), 132.9 (2C), 135.9 (2C), 136.0 (2C), 136.2 (2C), 141.6 (2C), 143.5 (2C), 144.4 (2C), 146.0 (2C), 147.3 (2C); IR (KBr, cm^{-1}) 995, 1364, 1463, 2967; HRMS (ESI$^+$) *m*/*z* 837.4611 ([M+Na]$^+$, $C_{56}H_{58}N_6Na^+$ requires 837.4615).

1,8-Bis(2,6-diisopropyl-4-(4-(trifluoromethyl)phenyl)phenyl)-1,8-dihydrodibenzo[3,4:7,8]cycloocta-[1,2-*d*:5,6-*d'*]bis([1,2,3]triazole) (*trans*-**3i**)



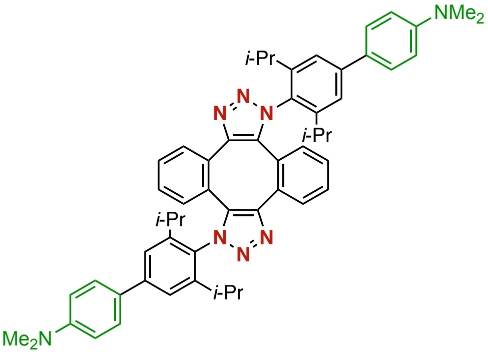
Colorless solid; Mp 182–184 ℃; R_f = 0.38 (*n*-hexane/EtOAc = 4/1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.81 (d, 6H, J = 6.8 Hz), 0.87 (d, 6H, J = 6.8 Hz), 1.49 (d, 6H+6H, J = 6.8 Hz, two signals overlapped), 2.05 (qq, 2H, J = 6.8, 6.8 Hz), 2.73 (qq, 2H, J = 6.8, 6.8 Hz), 6.91–6.95 (m, 2H), 7.22 (ddd, 2H, J = 1.0, 7.6, 7.6 Hz), 7.27 (d, 2H, J = 1.9 Hz), 7.46 (ddd, 2H, J = 1.0, 7.6, 7.6 Hz), 7.56 (d, 2H, J = 1.9 Hz), 7.69–7.74 (m, 8H), 7.85 (dd, 2H, J = 1.0, 7.6 Hz); ^{13}C NMR (126 MHz, $CDCl_3$) δ 22.6 (2C), 23.1 (2C), 24.7 (2C), 26.4 (2C), 28.8 (2C), 29.7 (2C), 123.2 (2C), 123.3 (2C), 124.4 (q, 2C, $J_{C\text{–}F}$ = 272.7 Hz), 126.0 (q, 4C, $J_{C\text{–}F}$ = 3.8 Hz), 126.5 (2C), 127.8 (4C), 128.9 (2C), 129.9 (2C), 130.0 (q, 2C, $J_{C\text{-}F}$ = 32.3 Hz), 130.1 (2C), 131.84 (2C), 131.85 (2C), 132.7 (2C), 136.3 (2C), 142.3 (2C), 144.4 (2C), 144.5 (2C), 146.6 (2C), 147.9 (2C); ^{19}F NMR (376 MHz, $CDCl_3$) δ –62.7 (s); IR (KBr, cm^{-1}) 842, 994, 1071, 1129, 1169, 1325, 2966; HRMS (ESI$^+$) *m*/*z* 895.3885 ([M+H]$^+$, $C_{54}H_{49}F_6N_6^+$ requires 895.3917).

1,8-Bis(2,6-diisopropyl-4-(4-methoxyphenyl)phenyl)-1,8-dihydrodibenzo[3,4:7,8]cycloocta[1,2-*d*:5,6-*d*']bis([1,2,3]triazole) (*trans*-**3j**)



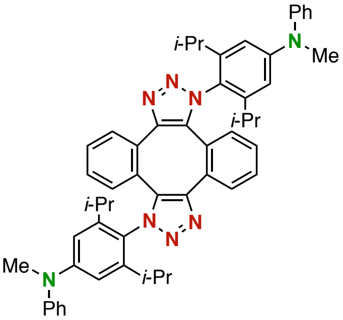
Colorless solid; Mp >300 ℃; R_f = 0.36 (*n*-hexane/EtOAc = 3/1); ^{1}H NMR (500 MHz, CDCl$_3$) δ 0.79 (d, 6H, J = 6.8 Hz), 0.84 (d, 6H, J = 6.8 Hz), 1.47 (d, 6H+6H, J = 6.8 Hz, two signals overlapped), 2.01 (qq, 2H, J = 6.8, 6.8 Hz), 2.70 (qq, 2H, J = 6.8, 6.8 Hz), 3.86 (s, 6H), 6.91–6.95 (m, 2H), 6.97–7.02 (AA'BB', 4H), 7.20 (ddd, 2H, J = 1.0, 7.7, 7.7 Hz), 7.22 (d, 2H, J = 1.9 Hz), 7.43 (ddd, 2H, J = 1.0, 7.7, 7.7 Hz), 7.50 (d, 2H, J = 1.9 Hz), 7.52–7.58 (AA'BB', 4H), 7.83 (dd, 2H, J = 1.0, 7.7 Hz); ^{13}C NMR (126 MHz, CDCl$_3$) δ 22.6 (2C), 23.1 (2C), 24.7 (2C), 26.4 (2C), 28.7 (2C), 29.6 (2C), 55.6 (2C), 114.5 (4C), 122.52 (2C), 122.53 (2C), 126.6 (2C), 128.5 (4C), 128.8 (2C), 129.9 (2C), 130.0 (2C), 130.5 (2C), 131.8 (2C), 132.7 (2C), 133.3 (2C), 136.2 (2C), 143.1 (2C), 144.4 (2C), 146.1 (2C), 147.3 (2C), 159.8 (2C); IR (KBr, cm^{-1}) 1029, 1256, 1462, 1516, 1606, 2958; HRMS (ESI$^+$) *m*/*z* 841.4171 ([M+Na]$^+$, $C_{54}H_{54}N_6NaO_2^+$ requires 841.4200).

1,8-Bis(4-(4-(dimethylamino)phenyl)-2,6-diisopropylphenyl)-1,8-dihydrodibenzo[3,4:7,8]cycloocta[1,2-*d*:5,6-*d*']bis([1,2,3]triazole) (*trans*-**3k**)



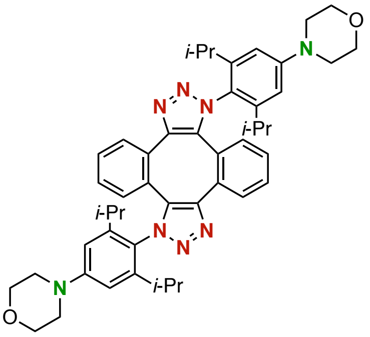
Colorless solid; Mp 200–201℃; R_f = 0.40 (*n*-hexane/EtOAc = 2/1); ^{1}H NMR (500 MHz, CDCl$_3$) δ 0.79 (d, 6H, J = 6.8 Hz), 0.84 (d, 6H, J = 6.8 Hz), 1.457 (d, 6H, J = 6.8 Hz), 1.462 (d, 6H, J = 6.8 Hz), 2.00 (qq, 2H, J = 6.8, 6.8 Hz), 2.68 (qq, 2H, J = 6.8, 6.8 Hz), 3.00 (s, 12H), 6.79–6.83 (AA'BB', 4H), 6.92–6.95 (m, 2H), 7.19 (ddd, 2H, J = 0.8, 7.7, 7.7 Hz), 7.22 (d, 2H, J = 1.7 Hz), 7.42 (ddd, 2H, J = 0.8, 7.7, 7.7 Hz), 7.49–7.54 (m, 6H), 7.80–7.84 (m, 2H); ^{13}C NMR (126 MHz, CDCl$_3$) δ 22.6 (2C), 23.1 (2C), 24.7 (2C), 26.4 (2C), 28.6 (2C), 29.6 (2C), 40.7 (4C), 112.9 (4C), 122.0 (2C+2C, two signals overlapped), 126.7 (2C), 128.0 (4C), 128.6 (2C), 128.7 (2C), 129.87 (2C), 129.88 (2C), 130.0 (2C), 131.7 (2C), 132.8 (2C), 136.2 (2C), 143.4 (2C), 144.4 (2C), 145.9 (2C), 147.1 (2C), 150.5 (2C); IR (KBr, cm^{-1}) 1360, 1472, 1525, 1612, 2965; HRMS (ESI$^+$) *m*/*z* 867.4810 ([M+Na]$^+$, $C_{56}H_{60}N_8Na^+$ requires 867.4833).

1,8-Bis(2,6-diisopropyl-4-(*N*-methyl-*N*-phenylamino)phenyl)-1,8-dihydrodibenzo[3,4:7,8]cycloocta-[1,2-*d*:5,6-*d'*]bis([1,2,3]triazole) (*trans*-**3l**)



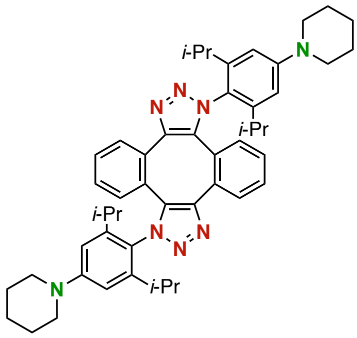
Colorless solid; Mp 135–137 °C; R_f = 0.25 (*n*-hexane/EtOAc = 5/1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.66–0.72 (m, 12H), 1.32 (d, 6H, *J* = 6.8 Hz), 1.36 (d, 6H, *J* = 6.8 Hz), 1.89 (qq, 2H, *J* = 6.8, 6.8 Hz), 2.59 (qq, 2H, *J* = 6.8, 6.8 Hz), 3.34 (s, 6H), 6.58 (d, 2H, *J* = 2.6 Hz), 6.86 (d, 2H, *J* = 2.6 Hz), 6.91–6.94 (m, 2H), 7.03–7.07 (AA'BB'C, 2H), 7.08–7.12 (AA'BB'C, 4H), 7.23 (ddd, 2H, *J* = 1.0, 7.7, 7.7 Hz), 7.29–7.34 (AA'BB'C, 4H), 7.43 (ddd, 2H, *J* = 1.0, 7.7, 7.7 Hz), 7.80 (dd, 2H, *J* = 1.0, 7.7 Hz); ^{13}C NMR (126 MHz, $CDCl_3$) δ 22.5 (2C), 23.0 (2C), 24.5 (2C), 26.2 (2C), 28.6 (2C), 29.5 (2C), 40.4 (2C), 113.3 (2C), 113.4 (2C), 122.8 (4C), 123.1 (2C), 124.1 (2C), 126.9 (2C), 128.5 (2C), 129.6 (4C), 129.8 (2C), 130.0 (2C), 131.6 (2C), 132.9 (2C), 136.3 (2C), 144.3 (2C), 146.6 (2C), 147.7 (2C), 148.5 (2C), 150.4 (2C); IR (KBr, cm^{-1}) 1358, 1495, 1589, 2964; HRMS (ESI$^+$) *m*/*z* 839.4486 ([M+Na]$^+$, $C_{54}H_{56}N_8Na^+$ requires 839.4520).

1,8-Bis(2,6-diisopropyl-4-morpholinophenyl)-1,8-dihydrodibenzo[3,4:7,8]cycloocta[1,2-*d*:5,6-*d'*]bis-([1,2,3]triazole) (*trans*-**3m**)



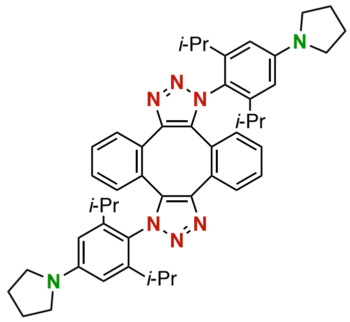
Colorless solid; Mp 199–201 °C; R_f = 0.46 (*n*-hexane/EtOAc = 1/1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.72 (d, 6H, *J* = 6.8 Hz), 0.76 (d, 6H, *J* = 6.8 Hz), 1.37–1.43 (m, 12H), 1.91 (qq, 2H, *J* = 6.8, 6.8 Hz), 2.62 (qq, 2H, *J* = 6.8, 6.8 Hz), 3.18–3.24 (m, 8H), 3.84–3.90 (m, 8H), 6.54 (d, 2H, *J* = 2.6 Hz), 6.82 (d, 2H, *J* = 2.6 Hz), 6.86–6.90 (m, 2H), 7.18 (ddd, 2H, *J* = 1.0, 7.8, 7.8 Hz), 7.40 (ddd, 2H, *J* = 1.0, 7.8, 7.8 Hz), 7.78 (dd, 2H, *J* = 1.0, 7.8 Hz); ^{13}C NMR (126 MHz, $CDCl_3$) δ 22.6 (2C), 23.1 (2C), 24.6 (2C), 26.4 (2C), 28.7 (2C), 29.7 (2C), 49.1 (4C), 67.0 (4C), 110.6 (2C+2C, two signals overlapped), 124.2 (2C), 126.8 (2C), 128.6 (2C), 129.8 (2C), 129.9 (2C), 131.6 (2C), 132.8 (2C), 136.3 (2C), 144.3 (2C), 146.7 (2C), 147.8 (2C), 152.7 (2C); IR (KBr, cm^{-1}) 979, 1223, 1258, 1363, 1477, 1599, 2962; HRMS (ESI$^+$) *m*/*z* 799.4399 ([M+Na]$^+$, $C_{48}H_{56}N_8NaO_2^+$ requires 799.4418).

1,8-Bis(2,6-diisopropyl-4-piperidinophenyl)-1,8-dihydrodibenzo[3,4:7,8]cycloocta[1,2-*d*:5,6-*d*']bis([1,2,3]triazole) (*trans*-**3n**)



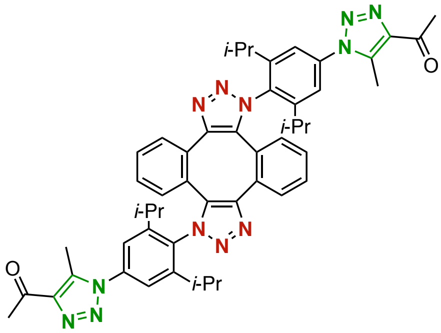
Colorless solid; Mp 287–289 ℃; R_f = 0.52 (*n*-hexane/EtOAc = 3/1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.72 (d, 6H, *J* = 6.8 Hz), 0.75 (d, 6H, *J* = 6.8 Hz), 1.37–1.42 (m, 12H), 1.56–1.62 (m, 4H), 1.68–1.76 (m, 8H), 1.90 (qq, 2H, *J* = 6.8, 6.8 Hz), 2.60 (qq, 2H, *J* = 6.8, 6.8 Hz), 3.16–3.22 (m, 8H), 6.56 (d, 2H, *J* = 2.6 Hz), 6.84 (d, 2H, *J* = 2.6 Hz), 6.87–6.90 (m, 2H), 7.16 (ddd, 2H, *J* = 1.0, 7.7, 7.7 Hz), 7.38 (ddd, 2H, *J* = 1.0, 7.7, 7.7 Hz), 7.77 (dd, 2H, *J* = 1.0, 7.7 Hz); ^{13}C NMR (126 MHz, $CDCl_3$) δ 22.6 (2C), 23.1 (2C), 24.4 (2C), 24.6 (2C), 26.0 (4C), 26.4 (2C), 28.6 (2C), 29.6 (2C), 50.4 (4C), 111.4 (2C), 111.5 (2C), 123.4 (2C), 126.9 (2C), 128.5 (2C), 129.6 (2C), 130.0 (2C), 131.5 (2C), 132.9 (2C), 136.3 (2C), 144.3 (2C), 146.3 (2C), 147.4 (2C), 153.6 (2C); IR (KBr, cm^{-1}) 1257, 1479, 1598, 2964; HRMS (ESI$^+$) *m*/*z* 773.4980 ([M+H]$^+$, $C_{50}H_{61}N_8^+$ requires 773.5014).

1,8-Bis(2,6-diisopropyl-4-pyrrolidinophenyl)-1,8-dihydrodibenzo[3,4:7,8]cycloocta[1,2-*d*:5,6-*d*']bis([1,2,3]triazole) (*trans*-**3o**)



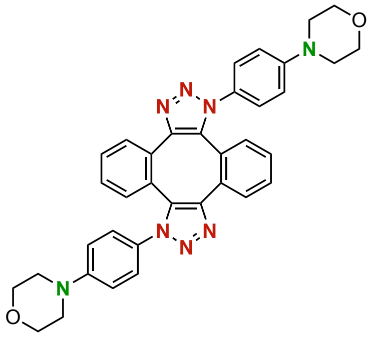
Colorless solid; Mp >300 ℃; R_f = 0.43 (CH_2Cl_2/MeOH = 50/1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.74 (d, 6H, *J* = 6.7 Hz), 0.76 (d, 6H, *J* = 6.7 Hz), 1.37–1.43 (m, 12H), 1.90 (qq, 2H, *J* = 6.7, 6.7 Hz), 1.98–2.04 (m, 8H), 2.59 (qq, 2H, *J* = 6.7, 6.7 Hz), 3.29–3.34 (m, 8H), 6.16 (d, 2H, *J* = 2.5 Hz), 6.43 (d, 2H, *J* = 2.5 Hz), 6.90–6.93 (m, 2H), 7.18 (ddd, 2H, *J* = 0.9, 7.6, 7.6 Hz), 7.38 (ddd, 2H, *J* = 0.9, 7.6, 7.6 Hz), 7.77 (dd, 2H, *J* = 0.9, 7.6 Hz); ^{13}C NMR (126 MHz, $CDCl_3$) δ 22.7 (2C), 23.1 (2C), 24.7 (2C), 25.7 (4C), 26.5 (2C), 28.6 (2C), 29.6 (2C), 47.8 (4C), 106.6 (2C), 106.7 (2C), 120.5 (2C), 127.1 (2C), 128.5 (2C), 129.5 (2C), 130.1 (2C), 131.5 (2C), 133.0 (2C), 136.4 (2C), 144.2 (2C), 146.6 (2C), 147.7 (2C), 149.1 (2C); IR (KBr, cm^{-1}) 1389, 1485, 1606, 2969; HRMS (ESI$^+$) *m*/*z* 767.4485 ([M+Na]$^+$, $C_{48}H_{56}N_8Na^+$ requires 767.4520).

1,8-Bis(4-(4-acetyl-5-methyl-1*H*-1,2,3-triazol-1-yl)-2,6-diisopropylphenyl)-1,8-dihydrodibenzo-[3,4:7,8]cycloocta[1,2-*d*:5,6-*d'*]bis([1,2,3]triazole) (*trans*-**3p**)



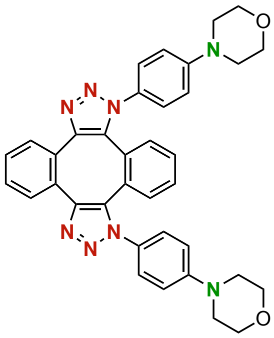
Colorless solid; Mp >300 ℃; R_f = 0.30 (*n*-hexane/EtOAc = 3/2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.78 (d, 6H, *J* = 6.8 Hz), 0.83 (d, 6H, *J* = 6.8 Hz), 1.44–1.51 (m, 12H), 2.07 (qq, 2H, *J* = 6.8, 6.8 Hz), 2.61 (s, 6H), 2.70–2.82 (m, 8H), 6.88–6.92 (m, 2H), 7.16 (d, 2H, *J* = 2.3 Hz), 7.28 (ddd, 2H, *J* = 1.0, 7.7, 7.7 Hz), 7.48 (d, 2H, *J* = 2.3 Hz), 7.51 (ddd, 2H, *J* = 1.0, 7.7, 7.7 Hz), 7.86 (dd, 2H, *J* = 1.0, 7.7 Hz); ^{13}C NMR (126 MHz, $CDCl_3$) δ 10.5 (2C), 22.2 (2C), 23.0 (2C), 24.4 (2C), 26.3 (2C), 28.1 (2C), 29.0 (2C), 29.9 (2C), 121.0 (2C), 121.4 (2C), 126.0 (2C), 129.2 (2C), 129.6 (2C), 130.5 (2C), 132.0 (2C), 132.4 (2C), 132.9 (2C), 136.3 (2C), 137.51 (2C), 137.53 (2C), 144.1 (2C), 144.5 (2C), 148.2 (2C), 149.7 (2C), 194.5 (2C); IR (KBr, cm^{-1}) 762, 995, 1078, 1368, 1485, 1685, 2967; HRMS (ESI$^+$) *m*/*z* 875.4195 ([M+Na]$^+$, $C_{50}H_{52}N_{12}NaO_2^+$ requires 875.4228).

1,8-Bis(4-morpholinophenyl)-1,8-dihydrodibenzo[3,4:7,8]cycloocta[1,2-*d*:5,6-*d'*]bis([1,2,3]triazole) (*trans*-**3q**)



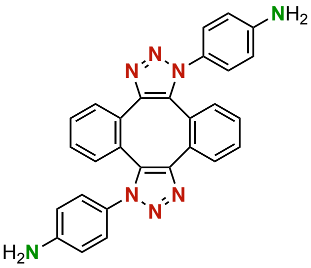
Colorless solid; Mp >300℃; R_f= 0.49 (EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.16–3.21 (m, 8H), 3.83–3.88 (m, 8H), 6.81–6.85 (AA'BB', 4H), 6.87 (dd, 2H, *J* = 0.8, 7.8 Hz), 7.17–7.24 (m, 6H), 7.46 (ddd, 2H, *J* = 0.8, 7.8, 7.8 Hz), 7.80 (dd, 2H, *J* = 0.8, 7.8 Hz); ^{13}C NMR (126 MHz, $CDCl_3$) δ 48.7 (4C), 66.9 (4C), 115.4 (4C), 126.2 (4C), 127.2 (2C), 128.1 (2C), 129.0 (2C), 130.0 (2C), 131.1 (2C), 131.4 (2C), 132.3 (2C), 134.2 (2C), 145.9 (2C), 151.5 (2C); IR (KBr, cm^{-1}) 928, 1123, 1238, 1269, 1518, 2853, 2924; HRMS (ESI$^+$) *m*/*z* 631.2523 ([M+Na]$^+$, $C_{36}H_{32}N_8NaO_2^+$ requires 631.2540).

1,10-Bis(4-morpholinophenyl)-1,10-dihydrodibenzo[3,4:7,8]cycloocta[1,2-*d*:5,6-*d*']bis([1,2,3]triazole) (*cis*-**3q**)



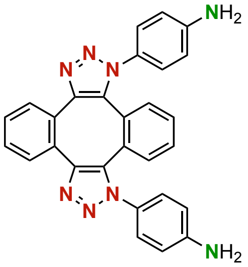
Colorless solid; Mp >300℃; R_f = 0.63 (CH_2Cl_2/MeOH/NEt_3= 90/9/1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.18–3.27 (m, 8H), 3.82–3.91 (m, 8H), 6.87–6.93 (m, 6H), 7.12–7.17 (m, 2H), 7.22–7.26 (AA'BB', 4H), 7.51–7.56 (m, 2H), 7.76–7.80 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 48.7 (4C), 66.9 (4C), 115.4 (4C), 126.3 (4C), 128.1 (2C), 128.6 (2C), 129.5 (2C+2C, two signals overlapped), 130.8 (2C), 130.9 (2C), 131.8 (2C), 133.5 (2C), 146.5 (2C), 151.7 (2C); IR (KBr, cm^{-1}) 835, 927, 1122, 1240, 1351, 1450, 1521, 1606, 2833, 2964; HRMS (ESI$^+$) *m*/*z* 631.2529 ([M+Na]$^+$, $C_{36}H_{32}N_8NaO_2^+$ requires 631.2540).

1,8-Bis(4-aminophenyl)-1,8-dihydrodibenzo[3,4:7,8]cycloocta[1,2-*d*:5,6-*d*']bis([1,2,3]triazole) (*trans*-**3r**)



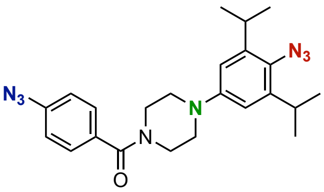
Colorless solid; Mp >300℃; R_f = 0.61 (EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.83 (br s, 4H), 6.58–6.63 (AA'BB', 4H), 6.87 (dd, 2H, *J* = 1.0, 7.8 Hz), 7.04–7.09 (AA'BB', 4H), 7.21 (ddd, 2H, *J* = 1.0, 7.8, 7.8 Hz), 7.45 (ddd, 2H, *J* = 1.0, 7.8, 7.8 Hz), 7.79 (dd, 2H, *J* = 1.0, 7.8 Hz); ^{13}C NMR (126 MHz, $CDCl_3$) δ 114.9 (4C), 126.3 (4C), 126.9 (2C), 127.0 (2C), 128.6 (2C), 129.7 (2C), 130.8 (2C), 131.1 (2C), 132.1 (2C), 134.0 (2C), 145.5 (2C), 147.0 (2C); IR (KBr, cm^{-1}) 828, 995, 1295, 1516, 1623, 3340; HRMS (ESI$^+$) *m*/*z* 491.1689 ([M+Na]$^+$, $C_{28}H_{20}N_8Na^+$ requires 491.1703).

1,10-Bis(4-aminophenyl)-1,10-dihydrodibenzo[3,4:7,8]cycloocta[1,2-*d*:5,6-*d'*]bis([1,2,3]triazole) (*cis*-**3r**)



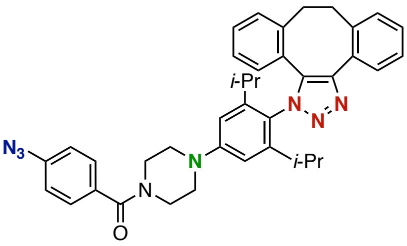
Colorless solid; Mp >300℃; R_f = 0.51 (EtOAc); ^{1}H NMR (500 MHz, DMSO-d_6) δ 5.57 (br s, 4H), 6.52–6.61 (br, 4H), 7.01–7.12 (m, 6H), 7.20–7.28 (br, 2H), 7.56–7.61 (br, 2H), 7.61–7.68 (br, 2H); ^{13}C NMR (126 MHz, DMSO-d_6) δ 113.8 (4C), 124.3 (2C), 127.3 (4C), 128.2 (2C), 129.6 (2C), 129.8 (2C), 130.8 (2C), 131.0 (2C), 131.8 (2C), 134.3 (2C), 145.2 (2C), 150.4 (2C); IR (KBr, cm^{-1}) 723, 837, 1142, 1204, 1518, 1607, 2853, 2924; HRMS (ESI$^+$) *m*/*z* 491.1686 ([M+Na]$^+$, $C_{28}H_{20}N_8Na^+$ requires 491.1703).

1-(4-Azidobenzoyl)-4-(4-azido-3,5-diisopropylphenyl)piperazine (**6**)



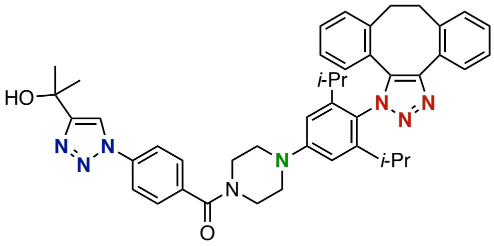
Brown solid; Mp 75–77 °C; R_f = 0.29 (*n*-hexane); ^{1}H NMR (500 MHz, CDCl$_3$) δ 1.25 (d, 12H, *J* = 6.9 Hz), 3.06–3.28 (br, 4H), 3.33 (sept, 2H, *J* = 6.9 Hz), 3.55–4.02 (br, 4H), 6.68 (s, 2H), 7.06–7.10 (AA'BB', 2H), 7.45–7.49 (AA'BB', 2H); ^{13}C NMR (126 MHz, CDCl$_3$) δ 23.7 (4C), 29.3 (2C), 50.4 (br, 2C+2C, two signals overlapped), 112.8 (2C), 119.3 (2C), 128.9 (1C), 129.4 (2C), 132.1 (1C), 142.1 (1C), 144.2 (2C), 149.9 (1C), 169.8 (1C); IR (KBr, cm^{-1}) 1288, 1463, 1602, 2124, 2964; HRMS (ESI$^+$) *m*/*z* 455.2275 ([M+Na]$^+$, $C_{23}H_{28}N_8NaO^+$ requires 455.2278).

1-(4-Azidobenzoyl)-4-(4-(8,9-dihydro-1*H*-dibenzo[3,4:7,8]cycloocta[1,2-*d*][1,2,3]triazol-1-yl)-3,5-diisopropylphenyl)piperazine (**S5**)



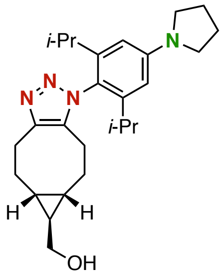
Yellow solid; Mp 129–130 °C; R_f = 0.29 (*n*-hexane/EtOAc = 2/1); ^{1}H NMR (500 MHz, CDCl$_3$) δ 0.62–1.47 (m, 12H), 2.29–2.45 (br, 2H), 3.06–3.46 (br, 8H), 3.46–4.07 (br, 4H), 6.68–6.74 (m, 3H), 6.95 (ddd, 1H, *J* = 1.0, 7.5, 7.5 Hz), 7.07–7.11 (AA'BB', 2H), 7.17–7.28 (m, 4H), 7.29 (d, 1H, *J* = 7.7 Hz), 7.46–7.50 (AA'BB', 2H), 7.65–7.58 (m, 1H); ^{13}C NMR (126 MHz, CDCl$_3$) δ 22.7 (2C), 25.6 (br, 2C), 29.0 (2C), 32.8 (1C), 37.1 (1C), 42.4 (br, 1C), 47.7 (br, 1C), 49.5 (1C+1C, two signals overlapped), 111.7 (2C), 119.2 (2C), 125.0 (1C), 126.09 (1C), 126.11 (1C), 126.3 (1C), 128.1 (1C), 129.0 (1C), 129.3 (2C), 129.5 (1C), 129.89 (1C), 129.91 (1C), 131.1 (1C), 132.0 (1C), 132.7 (1C), 135.3 (1C), 137.6 (1C), 141.6 (1C), 142.1 (1C), 146.2 (1C), 147.4 (br, 2C), 152.4 (1C), 169.8 (1C); IR (KBr, cm^{-1}) 842, 908, 977, 1012, 1034, 1284, 1367, 1455, 1601, 2127, 2964; HRMS (ESI$^+$) *m*/*z* 659.3200 ([M+Na]$^+$, $C_{39}H_{40}N_8NaO^+$ requires 659.3217).

4-(4-(8,9-Dihydro-1*H*-dibenzo[3,4:7,8]cycloocta[1,2-*d*][1,2,3]triazol-1-yl)-3,5-diisopropylphenyl)-1-(4-(4-(2-hydroxypropan-2-yl)-1*H*-1,2,3-triazol-1-yl)benzoyl)piperazine (**9**)



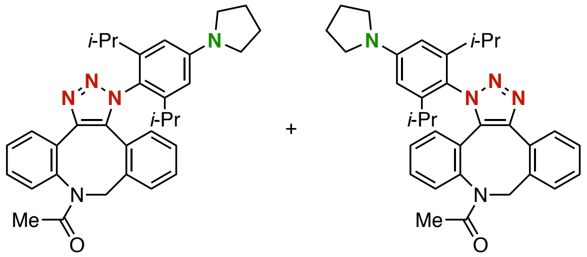
Pale yellow solid; Mp 161–162 °C; R_f = 0.25 (EtOAc); ^{1}H NMR (500 MHz, CDCl$_3$) δ 0.68–1.32 (br, 12H), 1.72 (s, 6H), 2.29–2.45 (br, 2H), 2.83 (br s, 1H), 2.97–3.51 (br, 8H), 3.51–3.78 (br, 2H), 3.78–4.09 (br, 2H), 6.68–6.75 (m, 3H), 6.95 (ddd, 1H, *J* = 0.9, 7.4, 7.4 Hz), 7.17–7.26 (m, 4H), 7.30 (d, 1H, *J* = 7.4 Hz), 7.59–7.64 (AA'BB', 2H), 7.64–7.68 (m, 1H), 7.80–7.84 (AA'BB', 2H), 7.97 (s, 1H); ^{13}C NMR (126 MHz, CDCl$_3$) δ 22.7 (2C), 25.6 (br, 2C), 29.1 (2C), 30.7 (2C), 32.8 (1C), 37.1 (1C), 42.5 (br, 1C), 47.8 (br, 1C), 49.3 (br, 1C), 49.7 (br, 1C), 68.9 (1C), 111.8 (2C), 117.7 (1C), 120.6 (2C), 125.1 (1C), 126.2 (2C+1C, two signals overlapped), 126.3 (1C), 128.2 (1C), 129.0 (1C), 129.1 (2C), 129.6 (1C), 129.87 (1C), 129.93 (1C), 131.1 (1C), 132.7 (1C), 135.4 (1C), 135.8 (1C), 137.6 (1C), 138.2 (1C), 141.7 (1C), 146.2 (1C), 147.4 (1C), 152.4 (1C), 157.0 (1C), 169.2 (1C); IR (KBr, cm^{-1}) 989, 1013, 1036, 1159, 1256, 1284, 1367, 1434, 1599, 2964, 3340; HRMS (ESI$^+$) *m*/*z* 743.3762 ([M+Na]$^+$, $C_{44}H_{48}N_8NaO_2^+$ requires 743.3792).

(5a*S*,6*S*,6a*R*)-1-(2,6-Diisopropyl-4-pyrrolidinophenyl)-6-(hydroxymethyl)-1,4,5,5a,6,6a,7,8-octahydro cyclopropa[5,6]cycloocta[1,2-*d*][1,2,3]triazole (**S8**)



Colorless oil; R_f = 0.36 (*n*-hexane/EtOAc = 1/4); ^{1}H NMR (500 MHz, CDCl$_3$) δ 0.71–0.77 (m, 1H), 0.80–0.90 (m, 1H), 0.93–1.00 (m, 1H), 1.08 (d, 3H, *J* = 6.9 Hz), 1.106 (d, 3H, *J* = 6.8 Hz), 1.110 (d, 3H, *J* = 6.9 Hz), 1.114 (d, 3H, *J* = 6.8 Hz), 1.18–1.38 (m, 2H), 1.33–1.42 (m, 1H), 1.99–2.11 (m, 6H), 2.23–2.30 (m, 1H), 2.40 (ddd, 1H, *J* = 16.0, 10.6, 2.1 Hz), 2.45–2.53 (m, 1H), 2.55 (ddd, 1H, *J* = 16.2, 7.3, 2.1 Hz), 2.89 (ddd, 1H, *J* = 15.8, 10.4, 2.4 Hz), 3.27 (ddd, 1H, *J* = 15.8, 7.7, 2.2 Hz), 3.33–3.40 (m, 4H), 3.46 (dd, 1H, *J* = 11.1, 7.1 Hz), 3.54 (dd, 1H, *J* = 11.1, 6.7 Hz), 6.38 (s, 2H); ^{13}C NMR (126 MHz, CDCl$_3$) δ 23.0 (2C), 23.2 (1C), 23.29 (1C), 23.31 (1C), 24.7 (2C), 25.3 (2C), 26.4 (1C), 27.4 (1C), 27.9 (1C), 28.0 (1C), 28.37 (1C), 28.41 (1C), 47.6 (2C), 66.5 (1C), 106.3 (1C), 106.4 (1C), 120.4 (1C), 136.2 (1C), 144.2 (1C), 147.1 (1C), 147.3 (1C), 148.9 (1C); IR (KBr, cm^{-1}) 735, 835, 1032, 1396, 1458, 1487, 1604, 3370; HRMS (ESI$^+$) *m*/*z* 445.2925 ([M+Na]$^+$, $C_{26}H_{38}N_4NaO^+$ requires 445.2938).

The cycloadducts obtained from the SPAAC reaction between **2o** and **S9**



major isomer **S10** + minor isomer **S10'**

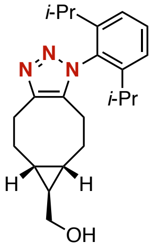
Major isomer **S10**

Colorless solid; Mp 231–235 °C; R_f = 0.30 (*n*-hexane/EtOAc = 2/1); ^{1}H NMR (500 MHz, CDCl$_3$) δ 0.67–0.86 (m, 3H), 0.91–1.10 (m, 3H), 1.30–1.38 (m, 3H), 1.38–1.48 (m, 3H), 1.60 (s, 3H), 1.97–2.08 (m, 4H), 2.25–2.38 (m, 1H), 2.46–2.64 (m, 1H), 3.29–3.37 (m, 4H), 4.39 (d, 1H, *J* = 14.8 Hz), 6.10–6.27 (m, 1H), 6.32 (d, 1H, *J* = 14.8 Hz), 6.39–6.54 (m, 1H), 6.78 (dd, 1H, *J* = 7.9, 0.8 Hz), 6.93–6.98 (m, 1H), 7.10–7.17 (m, 2H), 7.36–7.40 (m, 1H), 7.46–7.52 (m, 2H), 7.80–7.84 (m, 1H); ^{13}C NMR (126 MHz, CDCl$_3$) δ 22.1 (1C), 22.4 (1C), 22.8 (1C), 24.4 (1C), 25.5 (2C), 26.3 (1C), 28.6 (1C), 29.4 (1C), 47.6 (2C), 51.3 (1C), 106.6 (1C+1C, two signals overlapped), 120.8 (1C), 124.5 (1C), 126.6 (1C), 127.3 (1C), 128.8 (1C), 129.1 (1C), 129.2 (1C), 130.1 (1C), 130.3 (1C), 131.7 (1C), 132.4 (1C), 135.8 (1C), 136.0 (1C), 141.0 (1C), 141.6 (1C), 146.0 (1C), 147.4 (1C), 148.8 (1C), 170.3 (1C); IR (KBr, cm^{-1}) 733, 758, 1300, 1393, 1483, 1605, 1668; HRMS (ESI$^+$) *m*/*z* 542.2882 ([M+Na]$^+$, $C_{33}H_{37}N_5NaO^+$ requires 542.2890).

Minor isomer **S10'**

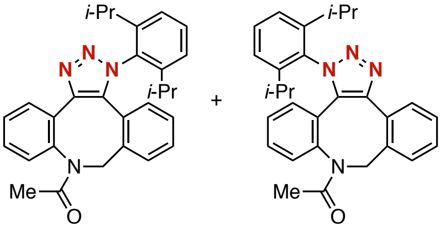
Colorless solid; Mp 202–208 °C; R_f = 0.29 (*n*-hexane/EtOAc = 3/2); ^{1}H NMR (500 MHz, CDCl$_3$) δ 0.77–1.47 (m, 12H), 1.71 (s, 0.8H × 3), 1.98–2.08 (m, 4H), 2.13 (s, 0.2H × 3), 2.16–2.38 (m, 2H), 3.30–3.43 (m, 4H), 4.46–4.97 (m, 0.8H), 5.02–5.20 (m, 0.2H × 2), 5.20–5.59 (m, 0.8H), 6.16–6.64 (m, 2H), 6.86–7.01 (m, 1H), 7.04–7.43 (m, 6H), 7.79 (d, 0.8H, *J* = 7.5 Hz), 8.10 (d, 0.2H, *J* = 6.3 Hz); ^{13}C NMR (126 MHz, CDCl$_3$) δ 22.1, 23.1, 25.5, 29.1, 47.6, 54.1, 106.3, 120.7, 127.8, 128.0, 128.3, 129.7 , 129.8, 130.0, 131.1, 131.4, 133.6, 133.7, 141.7, 145.4 , 149.1, 170.2: Some signals were not observed clearly due to the existence of rotamers; IR (KBr, cm^{-1}) 731, 1393, 1485, 1605, 2359; HRMS (ESI$^+$) *m*/*z* 542.2886 ([M+Na]$^+$, $C_{33}H_{37}N_5NaO^+$ requires 542.2890).

(5a*S*,6*S*,6a*R*)-1-(2,6-Diisopropylphenyl)-6-(hydroxymethyl)-1,4,5,5a,6,6a,7,8-octahydrocyclopropa[5,6]cycloocta[1,2-*d*][1,2,3]triazole (**S11**)



Colorless solid; Mp 42–67 °C; R_f = 0.31 (*n*-hexane/EtOAc = 2/3); ^{1}H NMR (500 MHz, CDCl$_3$) δ 0.72–0.80 (m, 1H), 0.80–0.89 (m, 1H), 0.92–1.01 (m, 1H), 1.06–1.16 (m, 12H), 1.21–1.32 (m, 1H), 1.34–1.42 (m, 1H), 1.51 (br s, 1H), 2.04–2.17 (m, 2H), 2.24–2.36 (m, 1H), 2.42 (ddd, 1H, *J* = 16.2, 10.5, 2.4 Hz), 2.46–2.56 (m, 2H), 2.91 (ddd, 1H, *J* = 15.8, 10.4, 2.5 Hz), 3.29 (ddd, 1H, *J* = 15.8, 7.7, 2.4 Hz), 3.47 (dd, 1H, J = 11.1, 6.9 Hz), 3.54 (dd, 1H, J = 11.1, 6.9 Hz), 7.28 (d, 2H, J = 7.8 Hz), 7.48 (t, 1H, J = 7.8 Hz); ^{13}C NMR (126 MHz, CDCl$_3$) δ 22.9 (2C), 23.1 (1C), 23.2 (2C), 24.6 (1C), 24.7 (1C), 26.3 (1C), 27.3 (1C), 27.86 (1C), 27.89 (1C), 28.2 (1C), 28.3 (1C), 66.4 (1C), 123.89 (1C), 123.92 (1C), 130.7 (1C), 132.0 (1C), 135.7 (1C), 144.5 (1C), 146.5 (1C), 146.7 (1C); IR (KBr, cm^{-1}) 735, 806, 1032, 1101, 1240, 1364, 1474, 3354; HRMS (ESI$^+$) m/z 376.2361 ([M+Na]$^+$, $C_{22}H_{31}N_3NaO^+$ requires 376.2359).

The cycloadducts obtained from the SPAAC reaction between **2c** and **S9**



major isomer **S12** + minor isomer **S12'**

Major isomer **S12**

Colorless solid; Mp 238–241 °C; R_f = 0.43 (n-hexane/EtOAc = 1/1); ^{1}H NMR (500 MHz, CDCl$_3$) δ 0.70–0.83 (m, 3H), 0.83–1.06 (m, 3H), 1.27–1.48 (m, 6H), 1.60 (s, 3H), 2.28–2.47 (m, 1H), 2.52–2.68 (m, 1H), 4.41 (d, 1H, J = 15.9 Hz), 6.36 (d, 1H, J = 15.9 Hz), 6.70 (dd, 1H, J = 7.9, 1.4 Hz), 6.90–6.94 (m, 1H), 7.08–7.20 (m, 3H), 7.32–7.45 (m, 3H), 7.49–7.54 (m, 2H), 7.82–7.86 (m, 1H); ^{13}C NMR (126 MHz, CDCl$_3$) δ 21.9 (1C), 22.3 (1C), 22.8 (1C), 24.4 (1C), 26.2 (1C), 28.5 (1C), 29.3 (1C), 51.2 (1C), 123.8 (1C), 124.1 (1C+1C, two signals overlapped), 126.5 (1C), 127.3 (1C), 129.1 (1C), 129.2 (1C), 129.3 (1C), 130.1 (1C), 130.5 (1C), 130.6 (1C), 131.6 (1C), 132.05 (1C), 132.09 (1C), 135.8 (1C), 136.0 (1C), 141.1 (1C), 141.7 (1C), 145.3 (1C), 146.7 (1C), 170.3 (1C); IR (KBr, cm^{-1}) 733, 907, 995, 1300, 1364, 1393, 1456, 1663, 3416; HRMS (ESI$^+$) m/z 473.2303 ([M+Na]$^+$, $C_{29}H_{30}N_4NaO^+$ requires 473.2312).

Minor isomer **S12'**

Colorless oil; R_f = 0.34 (n-hexane/EtOAc = 1/1); ^{1}H NMR (500 MHz, CDCl$_3$) δ 0.69–1.44 (m, 12H), 1.74 (s, 0.7H × 3), 2.14 (s, 0.3H × 3), 2.17–2.45 (m, 2H), 4.48–5.00 (m, 0.7H), 5.00–5.21 (m, 0.3H × 2), 5.21–5.68 (m, 0.7H), 6.77 (d, 0.3H, J = 6.7 Hz), 6.88 (d, 0.7H, J = 7.7 Hz), 7.00–7.13 (m, 1H), 7.14–7.55 (m, 8H), 7.84 (d, 0.7H, J = 7.4 Hz), 8.14 (d, 0.3H, J = 6.8 Hz); ^{13}C NMR (126 MHz, CDCl$_3$) δ 22.1, 22.6, 23.1, 25.4, 28.4, 29.0, 53.4, 54.3, 124.1, 126.4, 127.8, 128.0, 128.5, 129.7, 129.9, 130.3, 130.6, 131.1, 131.5, 132.4, 133.2, 133.6, 141.9, 145.6, 170.1: Some signals were not observed clearly due to the existence of rotamers; IR (KBr, cm^{-1}) 735, 752, 995, 1277, 1366, 1450, 1670; HRMS (ESI$^+$) m/z 473.2300 ([M+Na]$^+$, $C_{29}H_{30}N_4NaO^+$ requires 473.2312).

Computations

The geometrical structures and their energies shown in Table 5, and Kohn–Sham orbital amplitude plots (Table S3) were obtained from a density functional theory (DFT) (B3LYP/6-31G(d)) method using the GAMESS suite of program codes.[S16] All the stationary geometries were confirmed to be energy minima by achieving vibrational frequency analyses. Transition structures were also confirmed to be true transition states on the potential energy surfaces by achieving vibrational frequency analyses and intrinsic reaction coordinate approaches.

Table S3. Kohn–Sham orbital amplitude plots and their energies (in eV) for HOMO, HOMO–1, LUMO, and LUMO+1 of the diyne **1**, azides **2a**, **2c**, and **2m**–**o**.

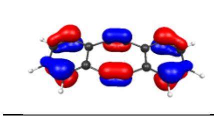
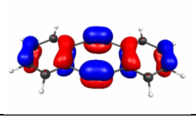
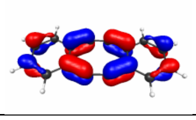
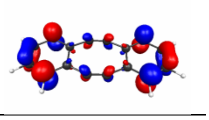
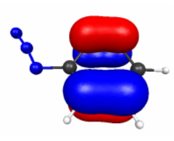
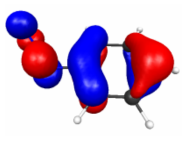
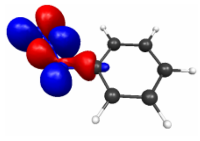
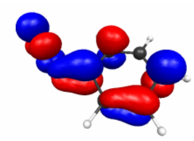
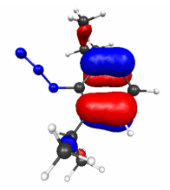
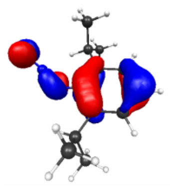
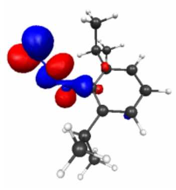
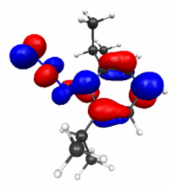
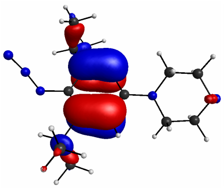
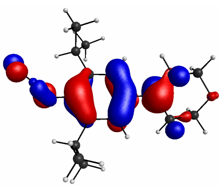
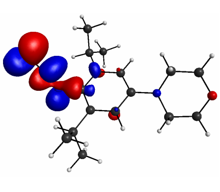
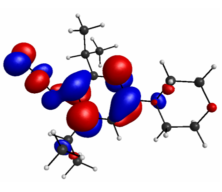
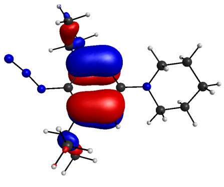
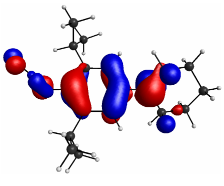
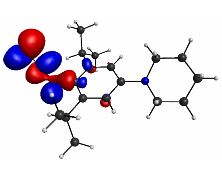
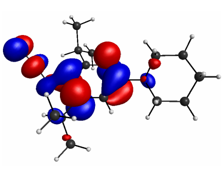
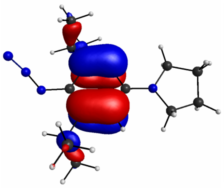
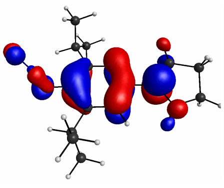
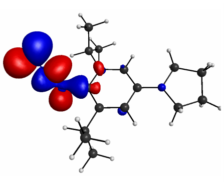
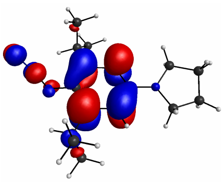
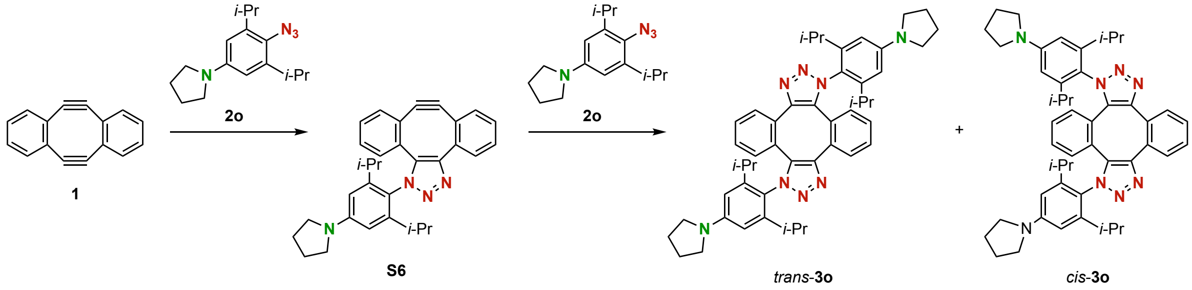
	HOMO–1	**HOMO**	**LUMO**	**LUMO+1**
1				
	–6.335 (B2g)	**–5.344 (B1u)**	**–1.861 (Au)**	**–0.727 (B3g)**
2a				
	–7.026 (a”)	**–6.109 (a”)**	**–0.944 (a’)**	**–0.792 (a”)**
2c				
	–6.482 (a)	**–6.185 (a)**	**–0.746 (a)**	**–0.278 (a)**
2m				
	–6.444 (a)	**–5.285 (a)**	**–0.648 (a)**	**–0.139 (a)**
2n				
	–6.346 (a)	**–5.159 (a)**	**–0.577 (a)**	**–0.052 (a)**
2o				
	–6.226 (a)	**–4.846 (a)**	**–0.438 (a)**	**–0.177 (a)**

Table S4. Distortion, interaction, and activation energies, and heat of formation (in kcal mol^{-1}) for each cycloaddition in the double-click reaction of Sondheimer diyne (**1**) with 2,6-diisopropyl-4-pyrrolidinophenyl azide (**2o**) at the B3LYP/6-31G(d) level of theory.



Reactants	**2o** + **1**		**2o** + **S6**			
Product	monoyne, **S6**		*trans*-**3o**		*cis*-**3o**	
Distorted reactants[a]	+13.8	+2.7	+9.9	+1.6	+11.1	+2.0
Distortion energy[b]	+16.5		+11.5		+13.1	
Interaction energy[c]	–8.6		–7.0		–7.2	
Activation energy[d]	+7.9		+4.5		+5.9	
Activation energy (+ZPCs)[e]	+8.7		+5.1		+6.9	
Heat of Formation	–62.4		–79.6		–67.9	

[a] The energy differences of each fragment between the optimized and the transition geometries.

[b] The energy required to distort the geometries of reactants to those of the transition state.

[c] The interaction energy between the distorted fragments at the transition state.

[d] The energy differences of the dissociation limit and the transition state.

[e] The values including zero-point corrections (ZPCs).

Geometries of stationary points

Sondheimer diyne (**1**)

Point group: D_{2h}
Total Energy: –613.991263 [hartree]
ZPCs: 0.180223 [hartree]

C	−0.72178	−1.91509	0.00000
C	0.72178	−1.91509	0.00000
C	−0.72178	1.91509	0.00000
C	0.72178	1.91509	0.00000
C	−1.40337	−3.13071	0.00000
C	1.40337	−3.13071	0.00000
C	−1.40337	3.13071	0.00000
C	1.40337	3.13071	0.00000
H	−2.48946	−3.12983	0.00000
H	2.48946	−3.12983	0.00000
H	−2.48946	3.12983	0.00000
H	2.48946	3.12983	0.00000
C	−0.69622	−4.34041	0.00000
C	0.69622	−4.34041	0.00000
C	−0.69622	4.34041	0.00000
C	0.69622	4.34041	0.00000
H	−1.24130	−5.28029	0.00000
H	1.24130	−5.28029	0.00000
H	−1.24130	5.28029	0.00000
H	1.24130	5.28029	0.00000
C	−1.31903	−0.60960	0.00000
C	1.31903	−0.60960	0.00000
C	−1.31903	0.60960	0.00000
C	1.31903	0.60960	0.00000

Phenyl azide (**2a**)

Point group: C_S
Total Energy: –395.608799 [hartree]
ZPCs: 0.103778 [hartree]

N	−1.40284	−0.87178	0.00000
N	−2.35000	−0.07613	0.00000
N	−3.31143	0.53994	0.00000
C	−0.07960	−0.35164	0.00000
C	0.94936	−1.30130	0.00000
C	0.22497	1.01662	0.00000
C	2.27724	−0.88156	0.00000
C	1.55870	1.42316	0.00000
H	3.07169	−1.62317	0.00000
H	1.79014	2.48520	0.00000
C	2.58942	0.48072	0.00000
H	3.62628	0.80457	0.00000
H	−0.57214	1.75568	0.00000
H	0.69085	−2.35561	0.00000

2,6-Diisopropylphenyl azide (**2c**)

Point group: C_1
Total Energy: –631.313351 [hartree]
ZPCs: 0.273989 [hartree]

N	1.81350	−1.60404	1.68632
N	2.22127	−0.50296	2.06619
N	2.46388	0.57710	2.35055
C	2.59950	−2.78515	1.94768
C	1.93960	−3.83892	2.61402
C	3.92646	−2.90446	1.47987
C	2.66331	−5.01192	2.85613
C	4.60492	−4.09701	1.76139
H	2.18320	−5.83389	3.38054
H	5.63289	−4.21073	1.42844
C	3.98762	−5.14056	2.44576
H	4.53510	−6.05715	2.64970
C	4.62520	−1.79975	0.69040
H	3.86859	−1.07220	0.37758
C	5.27178	−2.32682	−0.60563
H	5.67850	−1.49031	−1.18624
H	6.09905	−3.01647	−0.40238
H	4.54069	−2.85230	−1.22957
C	5.66410	−1.05822	1.55759
H	6.14336	−0.25585	0.98402
H	5.20461	−0.61166	2.44573
H	6.44902	−1.74500	1.89703
C	0.49679	−3.70699	3.09208
H	0.09562	−2.78300	2.66440
C	0.43274	−3.57428	4.62730
H	1.02233	−2.71957	4.97777
H	−0.60308	−3.43118	4.95858
H	0.82291	−4.47308	5.12066
C	−0.38911	−4.86567	2.59846
H	−0.35803	−4.95269	1.50670
H	−0.07799	−5.82874	3.02094
H	−1.43099	−4.69808	2.89686

2,6-Diisopropyl-4-morpholinophenyl azide (**2m**)

Point group: C_1
Total Energy: –917.739346 [hartree]
ZPCs: 0.389190 [hartree]

N	1.77892	–1.63734	1.57207
N	2.16011	–0.49222	1.83001
N	2.37903	0.61881	1.98901
C	2.59501	–2.76294	1.95588
C	1.97865	–3.76333	2.72754
C	3.92494	–2.90775	1.50012
C	2.73245	–4.88379	3.09620
C	4.63375	–4.04199	1.89241
H	2.26332	–5.63126	3.72566
H	5.64535	–4.17476	1.52255
C	4.06733	–5.04414	2.69960
C	4.59034	–1.88605	0.57841
H	3.81505	–1.20834	0.20664
C	5.21978	–2.54275	–0.66596
H	5.56943	–1.77027	–1.36123
H	6.08449	–3.16572	–0.40905
H	4.49488	–3.17307	–1.19247
C	5.63251	–1.03797	1.33635
H	6.08825	–0.29757	0.66801
H	5.18174	–0.50090	2.17779
H	6.43372	–1.67210	1.73481
C	0.53345	–3.63309	3.19988
H	0.11916	–2.73742	2.72694
C	0.45791	–3.42740	4.72619
H	1.03811	–2.55148	5.03758
H	–0.58144	–3.27686	5.04281
H	0.85081	–4.29675	5.26776
C	–0.32957	–4.82904	2.75656
H	–0.29755	–4.95979	1.66922
H	0.00413	–5.76692	3.21726
H	–1.37475	–4.67220	3.04953
N	4.82836	–6.18862	3.03108
C	4.14273	–7.31249	3.66433
C	5.03178	–8.55535	3.60673
O	6.29523	–8.32778	4.21417
C	6.97075	–7.25640	3.57036
C	6.15208	–5.96882	3.62999
H	3.88549	–7.09921	4.71882
H	3.21283	–7.51497	3.12280
H	4.56663	–9.38022	4.15554
H	5.16559	–8.85974	2.55533
H	7.17615	–7.51439	2.51784
H	7.92291	–7.12871	4.09490
H	6.05497	–5.64951	4.68370
H	6.67826	–5.17795	3.09050

2,6-Diisopropyl-4-piperidinophenyl azide (**2n**)

Point group: C_1
Total Energy: –881.851357 [hartree]
ZPCs: 0.413234 [hartree]

N	1.78770	–1.63555	1.56537
N	2.17610	–0.49342	1.82527
N	2.40436	0.61566	1.98563
C	2.59489	–2.76690	1.95387
C	1.97153	–3.75860	2.73076
C	3.92340	–2.92352	1.49722
C	2.71781	–4.88273	3.10445
C	4.62390	–4.06065	1.89533
H	2.24486	–5.62401	3.73844
H	5.63461	–4.20619	1.52702
C	4.05198	–5.05455	2.70970
C	4.59383	–1.91230	0.56743
H	3.82318	–1.22924	0.19572
C	5.21083	–2.58222	–0.67606
H	5.57252	–1.81768	–1.37410
H	6.06475	–3.21944	–0.41824
H	4.47449	–3.20153	–1.19979
C	5.64768	–1.06984	1.31570
H	6.10593	–0.33635	0.64138
H	5.20621	–0.52500	2.15722
H	6.44580	–1.70889	1.71258
C	0.52852	–3.61381	3.20563
H	0.11922	–2.71923	2.72622
C	0.45866	–3.39371	4.73015
H	1.04564	–2.51893	5.03205
H	–0.57877	–3.23338	5.04841
H	0.84753	–4.26068	5.27853
C	–0.34456	–4.80729	2.77583
H	–0.31703	–4.94730	1.68951
H	–0.01542	–5.74360	3.24292
H	–1.38763	–4.64104	3.07141
N	4.81383	–6.19605	3.05323
C	4.10174	–7.34149	3.61869
C	4.95793	–8.61144	3.53658
C	7.01561	–7.17161	3.64665
C	6.10002	–5.94641	3.72431
H	3.81529	–7.16181	4.67467
H	3.17613	–7.48647	3.05285
H	4.40872	–9.44229	3.99817
H	5.10799	–8.86756	2.47937
H	7.28416	–7.34792	2.59624
H	7.94483	–6.96359	4.19216
H	5.92993	–5.68180	4.78681
H	6.58192	–5.08497	3.25753
C	6.31656	–8.41208	4.21815
H	6.16399	–8.27639	5.29936
H	6.94618	–9.30243	4.09765

2,6-Diisopropyl-4-pyrrolidinophenyl azide (**2o**)
Point group: C_1
Total Energy: –842.566866 [hartree]
ZPCs: 0.383367 [hartree]

N	1.77602	–1.63102	1.60610
N	2.12020	–0.49295	1.93653
N	2.31147	0.61366	2.15493
C	2.60043	–2.75858	1.97669
C	1.99199	–3.78269	2.72879
C	3.93239	–2.88089	1.52914
C	2.75026	–4.90048	3.07864
C	4.65898	–4.01244	1.90264
H	2.28588	–5.67411	3.68034
H	5.68175	–4.10730	1.55566
C	4.09812	–5.03841	2.69039
C	4.59872	–1.82071	0.65281
H	3.81994	–1.14062	0.29208
C	5.25842	–2.42398	–0.60268
H	5.61551	–1.62218	–1.26025
H	6.12232	–3.05095	–0.35293
H	4.54868	–3.03791	–1.16799
C	5.61550	–0.98551	1.45868
H	6.07788	–0.21910	0.82467
H	5.13970	–0.48127	2.30656
H	6.41463	–1.62371	1.85484
C	0.53968	–3.67922	3.18726
H	0.12289	–2.77326	2.73649
C	0.44235	–3.52267	4.71763
H	1.00881	–2.65092	5.06441
H	–0.60243	–3.39381	5.02613
H	0.83947	–4.40448	5.23548
C	–0.30763	–4.86807	2.69672
H	–0.25824	–4.96637	1.60658
H	0.02789	–5.81612	3.13465
H	–1.35845	–4.72791	2.97851
N	4.83953	–6.14244	3.05666
C	4.29773	–7.25936	3.82485
C	5.42670	–8.30076	3.79767
C	6.69769	–7.43916	3.71845
C	6.27668	–6.26462	2.82090
H	4.05499	–6.95707	4.85790
H	3.37317	–7.64109	3.37176
H	5.40517	–8.96028	4.67057
H	5.33592	–8.92629	2.90130
H	7.56295	–7.98076	3.32343
H	6.96273	–7.06795	4.71600
H	6.80119	–5.33697	3.08620
H	6.49292	–6.46952	1.75925

Monoyne **S6**

Point group: C_1

Total Energy: –1456.664537 [hartree]

ZPCs: 0.570514 [hartree]

C	–1.37157	1.61554	0.50493
C	0.02455	1.69680	0.77138
C	–2.14846	2.77542	0.38619
H	–3.21129	2.67794	0.18609
C	0.58904	2.97386	0.88974
C	–1.55898	4.03111	0.51222
H	1.64744	3.05426	1.11129
H	–2.16452	4.92818	0.41523
C	–0.18803	4.12664	0.75544
H	0.28242	5.10199	0.84830
C	–1.84491	0.29712	0.27692
C	–1.71494	–0.87447	–0.02271
C	0.88645	0.51686	1.08670
C	1.04303	–0.82699	0.68024
C	–0.91406	–1.91670	–0.56749
C	0.48688	–1.77152	–0.33788
C	–1.39814	–2.92818	–1.40545
H	–2.47019	–3.01854	–1.55143
C	1.34767	–2.60871	–1.05813
C	–0.51410	–3.77675	–2.07175
H	2.41877	–2.48929	–0.95157
H	–0.89818	–4.55407	–2.72684
C	0.85905	–3.59847	–1.91634
H	1.55973	–4.23034	–2.45494
N	2.04204	–1.28904	1.51993
N	2.46822	–0.31387	2.35629
N	1.79427	0.75707	2.08672
C	2.59458	–2.60736	1.71523
C	1.85026	–3.57799	2.41325
C	3.91861	–2.85685	1.29785
C	2.44601	–4.81389	2.66477
C	4.48050	–4.10149	1.57517
H	1.88232	–5.55804	3.21553
H	5.49369	–4.30235	1.24692
C	3.76572	–5.10485	2.26345
C	4.75161	–1.79251	0.58396
H	4.06618	–1.01567	0.22814
C	5.49798	–2.33630	–0.64952
H	5.97841	–1.51129	–1.18848
H	6.28693	–3.04628	–0.37421
H	4.82038	–2.84579	–1.34487
C	5.73131	–1.11635	1.56473
H	6.29713	–0.32644	1.05530
H	5.19045	–0.66784	2.40299
H	6.44866	–1.84446	1.96297
C	0.44938	–3.30307	2.95662
H	0.10788	–2.34485	2.55574
C	0.48209	–3.15942	4.49223
H	1.17848	–2.37094	4.79754
H	–0.51417	–2.90233	4.87199
H	0.79625	–4.09405	4.97319
C	–0.57439	–4.36639	2.51623
H	–0.62070	–4.44746	1.42502
H	–0.33293	–5.35754	2.91885
H	–1.57347	–4.09831	2.87987
N	4.33898	–6.32593	2.53853
C	3.62716	–7.42369	3.19070
H	3.40228	–7.18654	4.24396
H	2.67186	–7.62486	2.68923
C	4.60286	–8.60459	3.07998
H	4.45568	–9.12130	2.12392
H	4.46459	–9.33554	3.88241
C	5.98059	–7.92318	3.10800
H	6.25901	–7.68010	4.14077
H	6.77845	–8.54052	2.68385
C	5.75155	–6.62943	2.31090
H	5.96199	–6.77521	1.23883
H	6.39231	–5.81019	2.66192

Bis-cycloadduct *trans*-**3o**
Point group: C_1
Total Energy: –2299.365639 [hartree]
ZPCs: 0.961287 [hartree]

C	1.11748	–1.25501	1.35025
C	–0.38873	2.03768	1.15767
C	2.07172	–0.21402	1.30665
C	–1.33935	0.99274	1.12694
C	1.35944	–2.36636	2.17434
C	–0.68994	3.21116	1.86866
H	0.62062	–3.15902	2.22295
H	0.04442	4.00844	1.90874
C	3.25441	–0.34028	2.05190
C	–2.57387	1.17371	1.76970
C	2.52813	–2.46656	2.92490
C	–1.91141	3.36712	2.51857
H	3.99195	0.45343	1.98424
H	–3.30597	0.37408	1.71229
H	2.69113	–3.33548	3.55696
H	–2.11932	4.28386	3.06416
C	3.48635	–1.45384	2.85414
C	–2.86328	2.34773	2.45953
H	4.40761	–1.52745	3.42624
H	–3.82441	2.46339	2.95380
C	–0.09936	–1.21036	0.51639
C	0.88946	1.93146	0.42806
C	1.91091	0.98958	0.46942
C	–1.11709	–0.27202	0.40069
N	–0.48413	–2.21525	–0.33649
N	1.34988	2.87173	–0.45987
N	2.57580	2.52034	–0.93178
N	–1.66570	–1.90400	–0.93497
N	2.91721	1.40196	–0.36178
N	–2.05085	–0.74797	–0.47956
C	0.17837	–3.44596	–0.67879
C	0.72567	4.07390	–0.94576
C	1.26520	–3.42050	–1.57560
C	–0.28427	3.98507	–1.92386
C	–0.32028	–4.65647	–0.15717
C	1.19056	5.31961	–0.47690
C	1.86418	–4.63100	–1.92016
C	–0.84119	5.16812	–2.40790
C	0.30143	–5.84656	–0.53220
C	0.61460	6.47937	–0.99254
H	2.69211	–4.62081	–2.61925
H	–1.60883	5.10471	–3.17040
H	–0.07151	–6.78046	–0.12805
H	0.96052	7.44017	–0.62990
C	1.40413	–5.86407	–1.41198
C	–0.41085	6.43444	–1.96066
C	–1.53695	–4.69331	0.76591
C	2.32347	5.42394	0.54375
H	2.43729	4.44248	1.01733
H	–1.71183	–3.67495	1.12921
C	3.65997	5.74374	–0.15655
C	–2.79890	–5.11507	–0.01338
H	3.61011	6.71263	–0.66888
H	–2.68986	–6.13008	–0.41540
H	4.47560	5.78925	0.57606
H	–3.67726	–5.10348	0.64395
H	3.90184	4.97403	–0.89517
H	–2.98466	–4.43210	–0.84778
C	–1.33090	–5.58704	2.00382
C	2.03153	6.43790	1.66540
H	–0.42625	–5.31111	2.55808
H	1.06920	6.23967	2.15170
H	–2.18794	–5.48882	2.68032
H	2.81541	6.38745	2.43046
H	–1.24686	–6.64714	1.73693
H	2.00896	7.46871	1.29287
C	1.74033	–2.12546	–2.23152
C	–0.73176	2.64848	–2.51244
H	1.34514	–1.28530	–1.65375
H	–0.32561	1.84724	–1.88889
C	1.15311	–2.00993	–3.65378
C	–0.13946	2.46180	–3.92460
H	1.52208	–2.81732	–4.29868
H	–0.51524	3.22619	–4.61612
H	0.05927	–2.06825	–3.63204
H	0.95364	2.53404	–3.90419
H	1.43724	–1.05375	–4.11050
H	–0.41139	1.47818	–4.32724
C	3.27065	–1.97055	–2.23989
C	–2.26105	2.47655	–2.51587
H	3.68634	–2.07510	–1.23224
H	–2.68001	2.63096	–1.51591
H	3.75634	–2.70871	–2.89010
H	–2.74994	3.17768	–3.20351
H	3.54042	–0.97432	–2.60687
H	–2.52247	1.46018	–2.82964
N	–0.97094	7.59057	–2.45601
C	–2.10209	7.60940	–3.38151
H	–1.80991	7.24568	–4.38083
H	–2.91424	6.96430	–3.02245
C	–2.51004	9.08977	–3.42369
H	–3.21640	9.30513	–2.61249
H	–2.99147	9.36252	–4.36804
C	–1.18239	9.82553	–3.18115
H	–0.60135	9.86800	–4.11034
H	–1.31360	10.85029	–2.82003
C	–0.46559	8.92968	–2.15869
H	–0.70566	9.22810	–1.12455
H	0.62616	8.97307	–2.26590
N	2.00965	–7.04825	–1.76799
C	1.49551	–8.36497	–1.39605
H	1.64236	–8.56340	–0.32119
H	0.41908	–8.44006	–1.59783
C	2.31570	–9.33471	–2.26158
H	1.82398	–9.47482	–3.23194
H	2.42540	–10.31898	–1.79613
C	3.65070	–8.59656	–2.44858
H	4.28009	–8.72131	–1.55885
H	4.22150	–8.94433	–3.31512
C	3.22282	–7.12690	–2.57966
H	3.02204	–6.85909	–3.63047
H	3.99068	–6.43681	–2.20756

Bis-cycloadduct *cis*-**3o**
Point group: C_1
Total Energy: –2299.347796 [hartree]
ZPCs: 0.962073 [hartree]

C	0.13811	–0.51381	–1.22502
C	0.07434	–0.60968	0.19671
C	3.30393	0.61130	–1.02782
C	3.27982	0.40842	0.36200
C	–0.52055	–1.49720	–1.98707
C	–0.66108	–1.67196	0.75517
C	4.50928	0.41525	–1.72485
C	4.45686	0.00531	1.01650
H	–0.46391	–1.44537	–3.06500
H	–0.70733	–1.76186	1.83057
H	4.52364	0.60087	–2.79406
H	4.42949	–0.12359	2.09375
C	–1.24448	–2.53329	–1.40788
C	–1.32072	–2.61785	–0.02120
C	5.66677	0.01151	–1.06663
C	5.63948	–0.19929	0.31356
H	–1.73435	–3.26837	–2.04064
H	–1.87383	–3.42007	0.46008
H	6.58573	–0.13481	–1.62841
H	6.53664	–0.51258	0.84127
C	0.85895	0.55222	–1.95821
C	0.77555	0.29170	1.14223
C	2.14520	1.06708	–1.81962
C	2.10786	0.69499	1.20668
N	0.36200	1.21870	–3.06913
N	0.24619	0.75762	2.33593
N	2.34829	2.00786	–2.79405
N	2.30919	1.36767	2.38060
N	1.29097	2.09937	–3.53590
N	1.20098	1.41048	3.04979
C	–0.73194	0.92036	–3.96903
C	–1.03864	0.59897	2.97469
C	–0.46385	0.07848	–5.07193
C	–1.19250	–0.41336	3.94594
C	–1.98672	1.54138	–3.81604
C	–2.05921	1.54119	2.73483
C	–1.48855	–0.18108	–5.98068
C	–2.42037	–0.53177	4.59575
C	–2.98750	1.25007	–4.74283
C	–3.27490	1.38578	3.39900
H	–1.27941	–0.81675	–6.83279
H	–2.55120	–1.31763	5.32983
H	–3.96198	1.70289	–4.62057
H	–4.06372	2.10636	3.22512
C	–2.77077	0.38434	–5.83502
C	–3.49128	0.34474	4.32649
C	0.92574	–0.50486	–5.33351
C	–0.03504	–1.32599	4.35385
H	1.50767	–0.43231	–4.40892
H	0.71929	–1.29684	3.55954
C	1.66314	0.32940	–6.40246
C	0.64246	–0.78837	5.63307
H	1.12437	0.30157	–7.35779
H	–0.06508	–0.77710	6.47156
H	2.67101	–0.06987	–6.57003
H	1.48975	–1.42707	5.91098
H	1.75257	1.37217	–6.08576
H	1.01077	0.22976	5.47861
C	0.90159	–1.99408	–5.72771
C	–0.44333	–2.79992	4.53751
H	0.35687	–2.60363	–4.99746
H	–0.96973	–3.19581	3.66110
H	1.92703	–2.37752	–5.78528
H	0.45015	–3.41387	4.69935
H	0.44021	–2.15428	–6.70913
H	–1.09419	–2.94114	5.40829
C	–2.23297	2.57245	–2.71703
C	–1.80760	2.77186	1.86731
H	–1.69699	2.23610	–1.81968
H	–1.12660	2.48187	1.05781
C	–1.64277	3.93985	–3.12885
C	–1.10229	3.86875	2.69883
H	–1.77367	4.67035	–2.32077
H	–0.88884	4.74305	2.07143
H	–2.15655	4.32404	–4.01906
H	–1.74935	4.19087	3.52430
H	–0.57660	3.86599	–3.35920
H	–0.16125	3.50957	3.12306
C	–3.71490	2.72985	–2.34152
C	–3.07745	3.34595	1.22332
H	–3.81181	3.42062	–1.50014
H	–2.80378	4.12234	0.49998
H	–4.16920	1.77432	–2.05436
H	–3.65792	2.57832	0.70163
H	–4.30027	3.15220	–3.16704
H	–3.73041	3.82094	1.96596
N	–4.70259	0.20253	4.96447
C	–5.88163	1.00970	4.65713
H	–5.75932	2.05090	4.99985
H	–6.06412	1.04093	3.57531
C	–7.01208	0.30236	5.41899
H	–7.43737	–0.49746	4.80018
H	–7.82500	0.98357	5.68910
C	–6.29062	–0.29605	6.63752
H	–6.14229	0.47620	7.40194
H	–6.83472	–1.12531	7.10002
C	–4.93225	–0.73244	6.06541
H	–4.96328	–1.77408	5.70557
H	–4.13013	–0.66719	6.81197
N	–3.77700	0.10926	–6.73310
C	–3.63574	–0.82401	–7.84885
H	–2.95297	–0.42947	–8.62000
H	–3.22653	–1.78435	–7.51007
C	–5.06739	–0.95944	–8.38862
H	–5.60191	–1.74054	–7.83433
H	–5.09092	–1.22462	–9.45005
C	–5.68302	0.41779	–8.09248
H	–5.37100	1.13999	–8.85649
H	–6.77696	0.40819	–8.06776
C	–5.06773	0.79716	–6.73640
H	–5.70018	0.46241	–5.89805
H	–4.93739	1.88236	–6.63374

Geometries of transition structures

First cycloaddition of **2o** with diyne **1**
Point group: C_1
Total Energy: –1456.545602 [hartree]
ZPCs: 0.564935 [hartree]
Imaginary frequency: *i* 280.8 [cm^{-1}]

C	–1.19205	2.23324	–0.27917
C	0.00060	1.97867	0.48343
C	–1.69797	3.52976	–0.37797
H	–2.60148	3.70116	–0.95583
C	0.63305	3.06161	1.09782
C	–1.04498	4.59424	0.25153
H	1.53079	2.88448	1.67647
H	–1.44621	5.60053	0.16612
C	0.11754	4.35843	0.97994
H	0.63210	5.18212	1.46766
C	–1.74941	1.08350	–0.91590
C	–1.80045	–0.08069	–1.26596
C	0.47298	0.60141	0.55868
C	0.41533	–0.57998	0.15906
C	–1.31199	–1.41850	–1.37908
C	–0.10579	–1.67389	–0.63734
C	–1.88171	–2.42540	–2.15825
H	–2.79586	–2.21481	–2.70563
C	0.48499	–2.93390	–0.75294
C	–1.27655	–3.68350	–2.24210
H	1.40273	–3.13829	–0.21586
H	–1.72711	–4.46003	–2.85435
C	–0.09425	–3.93043	–1.54906
H	0.38766	–4.90191	–1.62008
N	1.82400	–1.61824	1.78581
N	2.08265	–0.51251	2.33275
N	1.80078	0.62047	2.25448
C	2.57952	–2.80053	2.03455
C	1.94704	–3.87434	2.70121
C	3.89885	–2.93550	1.54055
C	2.65997	–5.05354	2.90768
C	4.58434	–4.12548	1.77495
H	2.18136	–5.86526	3.44430
H	5.59710	–4.22578	1.40166
C	3.99017	–5.20666	2.46231
C	4.57899	–1.79429	0.78914
H	3.79647	–1.09349	0.47982
C	5.29117	–2.25727	–0.49528
H	5.67300	–1.38808	–1.04394
H	6.14651	–2.90897	–0.28167
H	4.60784	–2.80217	–1.15607
C	5.55299	–1.03148	1.71110
H	5.99028	–0.17335	1.18610
H	5.04718	–0.65773	2.60817
H	6.37282	–1.68431	2.03544
C	0.52255	–3.73878	3.23233
H	0.10309	–2.82734	2.79555
C	0.52293	–3.55943	4.76419
H	1.12571	–2.69394	5.06146
H	–0.49841	–3.40559	5.13367
H	0.93564	–4.44261	5.26764
C	–0.38422	–4.90858	2.81024
H	–0.40023	–5.02358	1.72084
H	–0.06011	–5.86091	3.24769
H	–1.41247	–4.72764	3.14590
N	4.68547	–6.37440	2.68285
C	4.08390	–7.58313	3.24379
H	3.88669	–7.46991	4.32267
H	3.12576	–7.80572	2.75721
C	5.13693	–8.66993	2.97740
H	4.97726	–9.10682	1.98405
H	5.09664	–9.48188	3.71016
C	6.46181	–7.89105	3.00638
H	6.77742	–7.72246	4.04316
H	7.27732	–8.40267	2.48623
C	6.09693	–6.55200	2.34713
H	6.24792	–6.58767	1.25531
H	6.70145	–5.72119	2.73368

Second *trans*-cycloaddition of **2o** with monoyne **S6**

Point group: C_1

Total Energy: –2299.224206 [hartree]

ZPCs: 0.954891 [hartree]

Imaginary frequency: *i* 258.9 [cm^{-1}]

C	0.93848	–1.52334	1.13594
C	–1.27767	1.58501	0.51369
C	1.75246	–0.39532	0.83942
C	–2.04945	0.41096	0.73843
C	1.46807	–2.51735	1.96931
C	–1.84321	2.85022	0.73840
H	0.84936	–3.36426	2.24243
H	–1.23959	3.73274	0.55421
C	3.07346	–0.34285	1.30417
C	–3.37103	0.56290	1.18154
C	2.77297	–2.43815	2.45987
C	–3.15597	2.97169	1.18772
H	3.68150	0.51543	1.03785
H	–3.97128	–0.32887	1.32771
H	3.15267	–3.22545	3.10539
H	–3.57946	3.95737	1.36239
C	3.58450	–1.35994	2.10874
C	–3.91974	1.82445	1.41105
H	4.60773	–1.30114	2.47072
H	–4.94585	1.90957	1.75943
C	–0.40875	–1.70672	0.53017
C	0.08826	1.39225	0.14226
C	1.12163	0.71113	0.17907
C	–1.59012	–0.96111	0.39482
N	–0.72804	–2.91294	–0.06029
N	0.78565	3.09292	–1.44549
N	1.93307	2.58954	–1.51854
N	–2.00649	–2.91043	–0.51117
N	2.60639	1.68888	–1.21662
N	–2.52135	–1.75584	–0.22416
C	0.10548	–4.04781	–0.36569
C	0.53622	4.48634	–1.59293
C	1.01325	–3.96562	–1.44056
C	–0.42357	4.88288	–2.55065
C	–0.05852	–5.23948	0.36835
C	1.14630	5.44367	–0.74445
C	1.79358	–5.08316	–1.73386
C	–0.72117	6.23791	–2.68640
C	0.73446	–6.33784	0.03889
C	0.83240	6.78887	–0.91959
H	2.48327	–5.03023	–2.56846
H	–1.44115	6.53981	–3.43901
H	0.62039	–7.25423	0.60567
H	1.29864	7.52193	–0.27156
C	1.68517	–6.28333	–1.00201
C	–0.09667	7.22107	–1.89181
C	–1.10514	–5.36249	1.47478
C	2.14329	5.02694	0.33518
H	1.99416	3.95964	0.52883
H	–1.39751	–4.34931	1.77257
C	3.59635	5.21978	–0.14843
C	–2.37484	–6.05788	0.94167
H	3.80117	6.27861	–0.34981
H	–2.14881	–7.07847	0.60819
H	4.30549	4.87652	0.61483
H	–3.13770	–6.11925	1.72790
H	3.79336	4.66037	–1.06895
H	–2.79270	–5.50259	0.09698
C	–0.58006	–6.07288	2.73636
C	1.91896	5.74767	1.67722
H	0.34465	–5.61590	3.10811
H	0.88447	5.64063	2.02209
H	–1.33017	–6.01780	3.53411
H	2.57727	5.32076	2.44300
H	–0.37738	–7.13545	2.55688
H	2.14516	6.81893	1.61597
C	1.11364	–2.72835	–2.33027
C	–1.12170	3.86307	–3.44626
H	0.56718	–1.91333	–1.84824
H	–0.75823	2.87340	–3.15437
C	0.42375	–2.98755	–3.68623
C	–0.76239	4.07210	–4.93029
H	0.92778	–3.78912	–4.24014
H	–1.12180	5.04092	–5.29843
H	–0.62248	–3.27871	–3.54425
H	0.32175	4.03600	–5.08731
H	0.44767	–2.08186	–4.30431
H	–1.22178	3.29042	–5.54757
C	2.56199	–2.24273	–2.52407
C	–2.64829	3.87181	–3.23768
H	3.05469	–2.06353	–1.56283
H	–2.90465	3.67922	–2.19044
H	3.16568	–2.96568	–3.08650
H	–3.09025	4.83464	–3.52349
H	2.56822	–1.30095	–3.08449
H	–3.12061	3.09418	–3.85011
N	–0.38898	8.55769	–2.04762
C	–1.41515	9.06150	–2.95845
H	–1.10786	8.94695	–4.01111
H	–2.35801	8.51446	–2.83142
C	–1.55006	10.54212	–2.57163
H	–2.28294	10.65081	–1.76292
H	–1.88122	11.16449	–3.40859
C	–0.14433	10.90397	–2.06555
H	0.52105	11.10750	–2.91380
H	–0.13160	11.78269	–1.41323
C	0.30971	9.62848	–1.33927
H	0.03058	9.65208	–0.27274
H	1.39758	9.48986	–1.38856
N	2.47501	–7.37117	–1.30263
C	2.36581	–8.66168	–0.62624
H	2.67353	–8.58868	0.43069
H	1.33144	–9.02925	–0.64059
C	3.31457	–9.56970	–1.42249
H	2.78391	–10.00848	–2.27632
H	3.71256	–10.39019	–0.81746
C	4.39845	–8.59609	–1.91308
H	5.12051	–8.40461	–1.10983
H	4.95464	–8.96541	–2.78039
C	3.60976	–7.31448	–2.22425
H	3.27293	–7.29452	–3.27362
H	4.20753	–6.40946	–2.05570

Second *cis*-cycloaddition of **2o** with monoyne **S6**
Point group: C_1
Total Energy: –2299.221929 [hartree]
ZPCs: 0.955391 [hartree]
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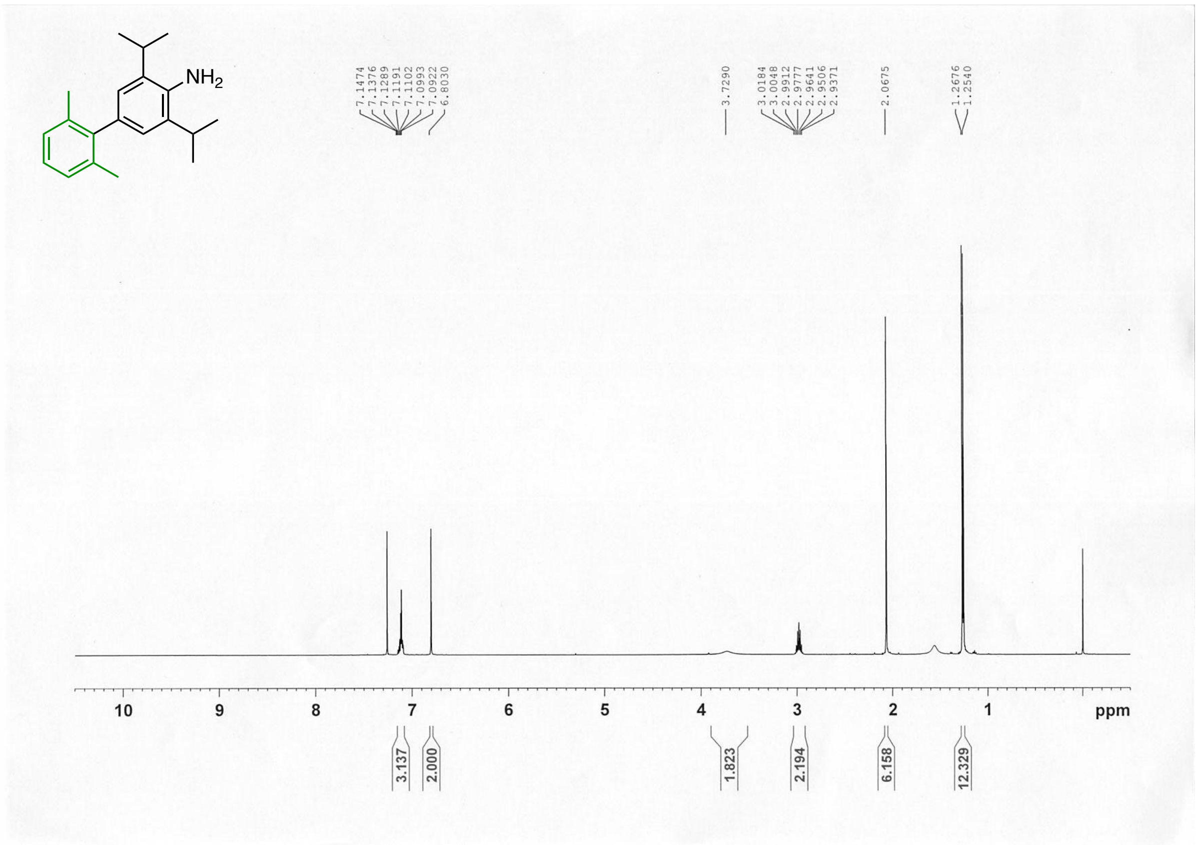
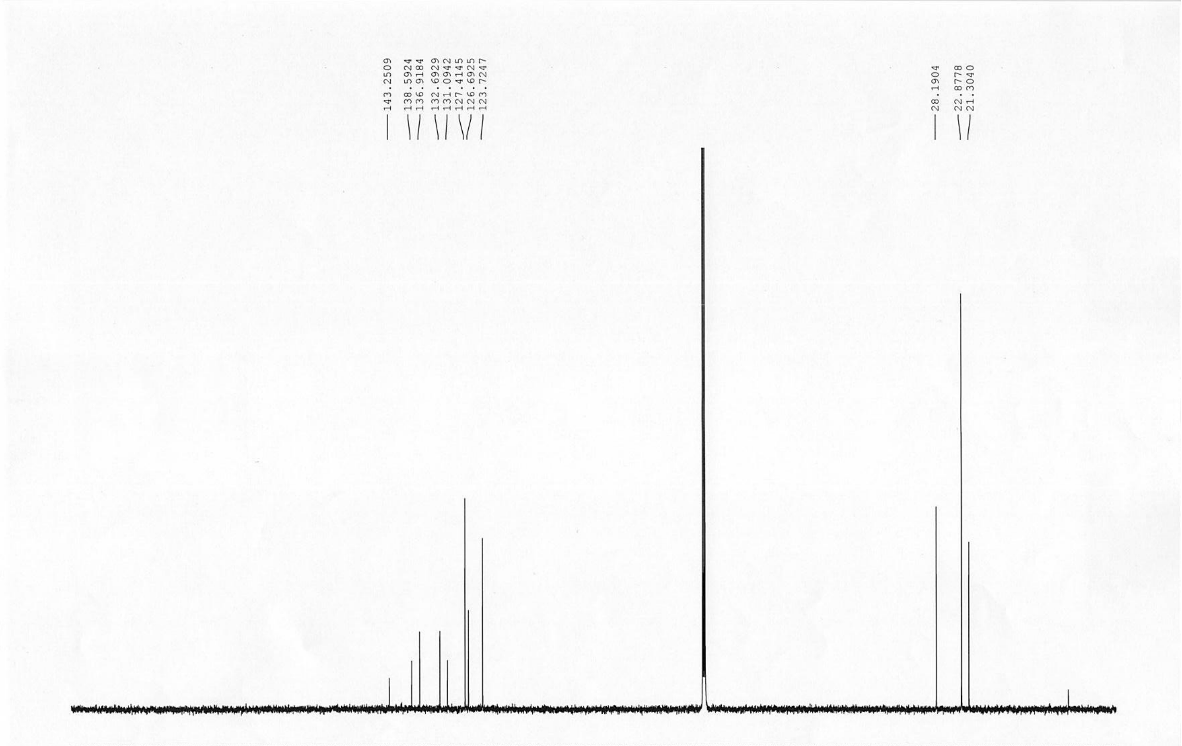
^{1}H and ^{13}C NMR Spectra of Compounds

^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of 4-(2,6-dimethylphenyl)-2,6-diisopropylaniline ($CDCl_3$)





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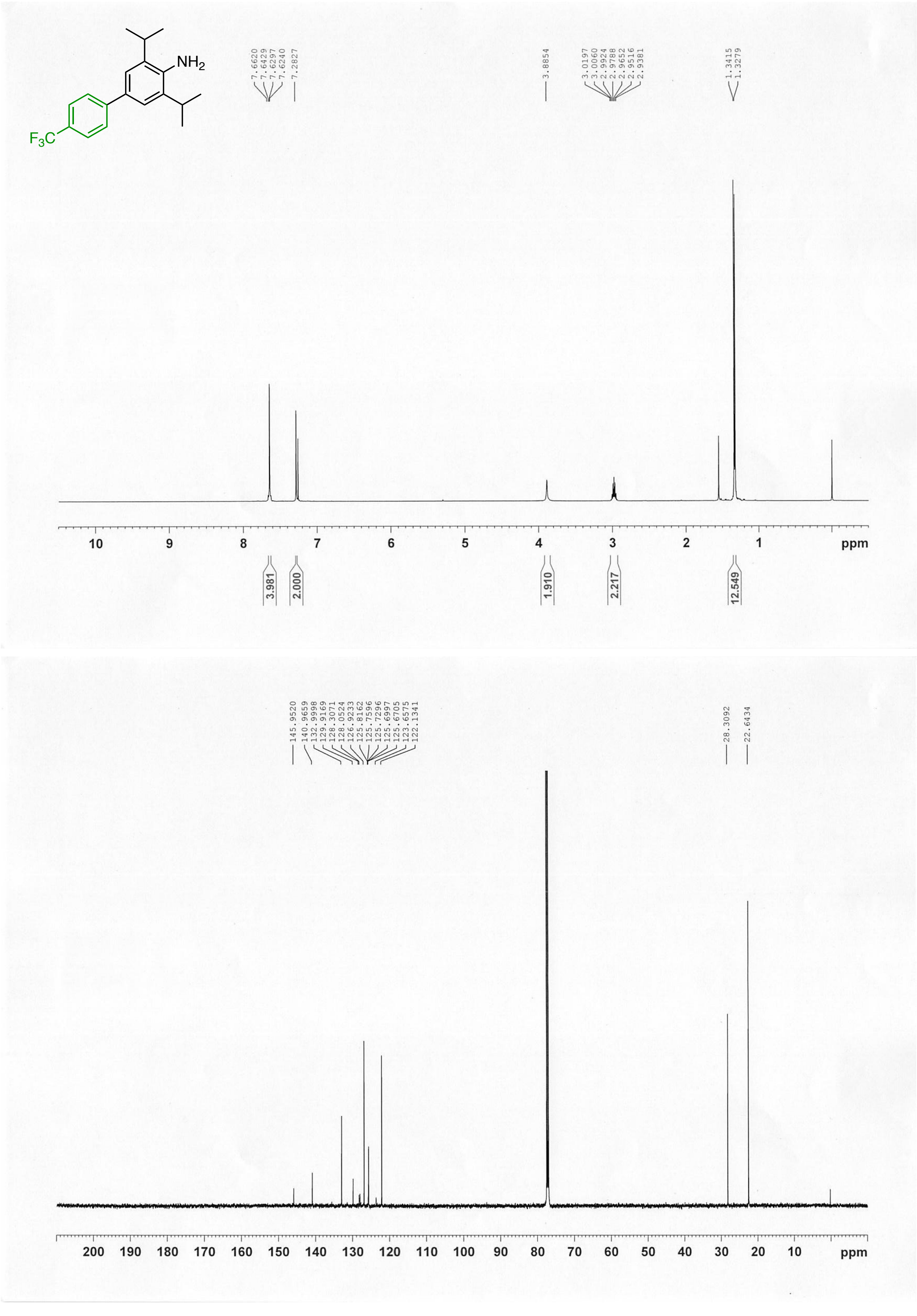

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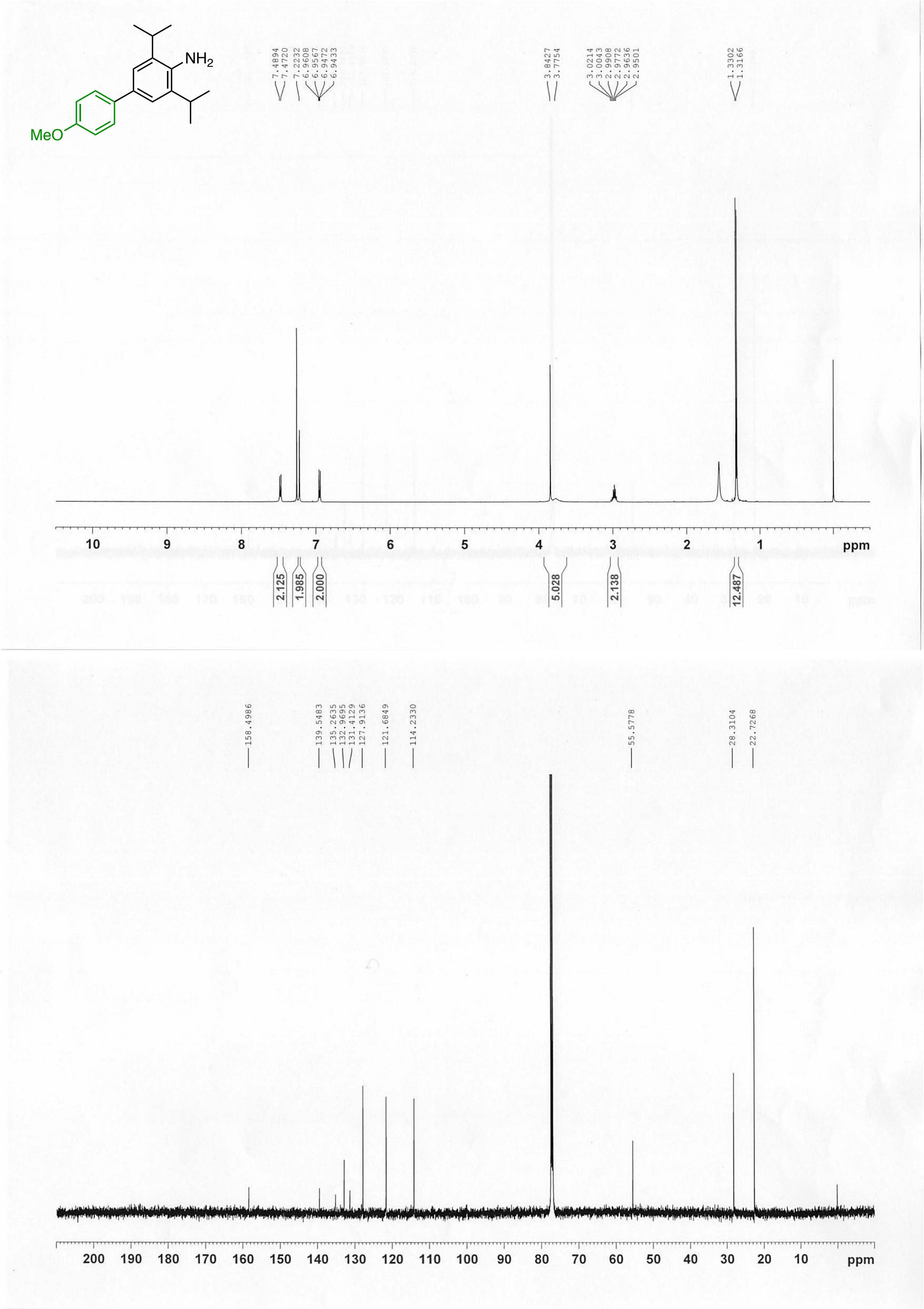

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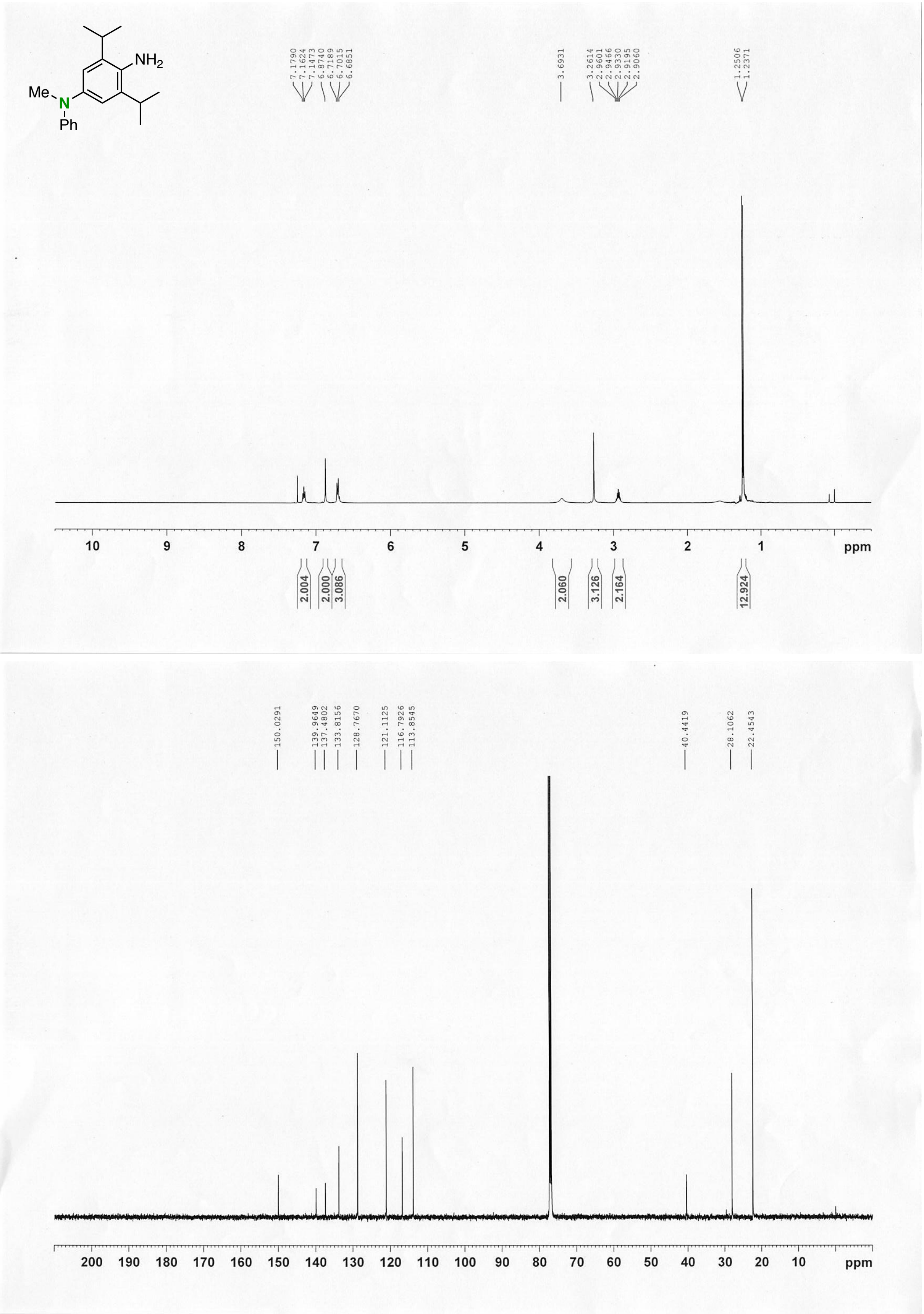

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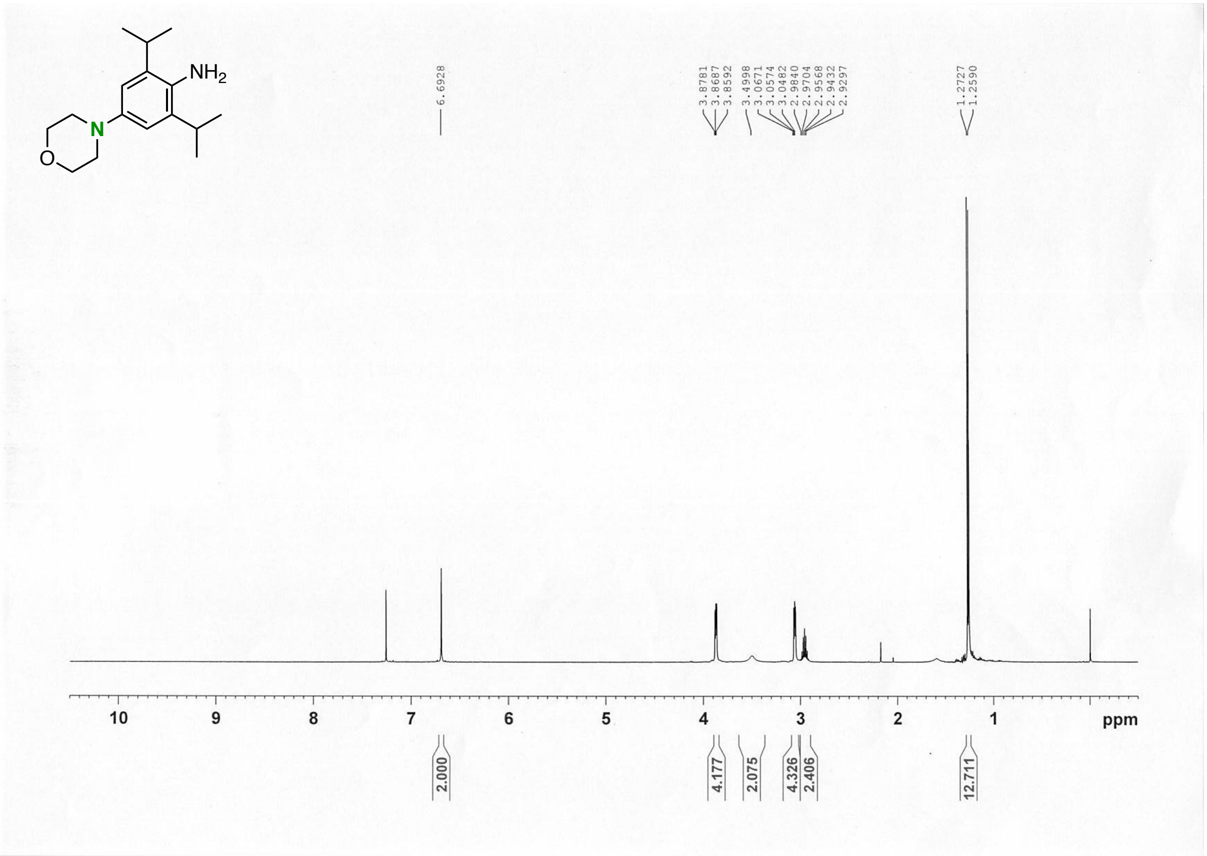

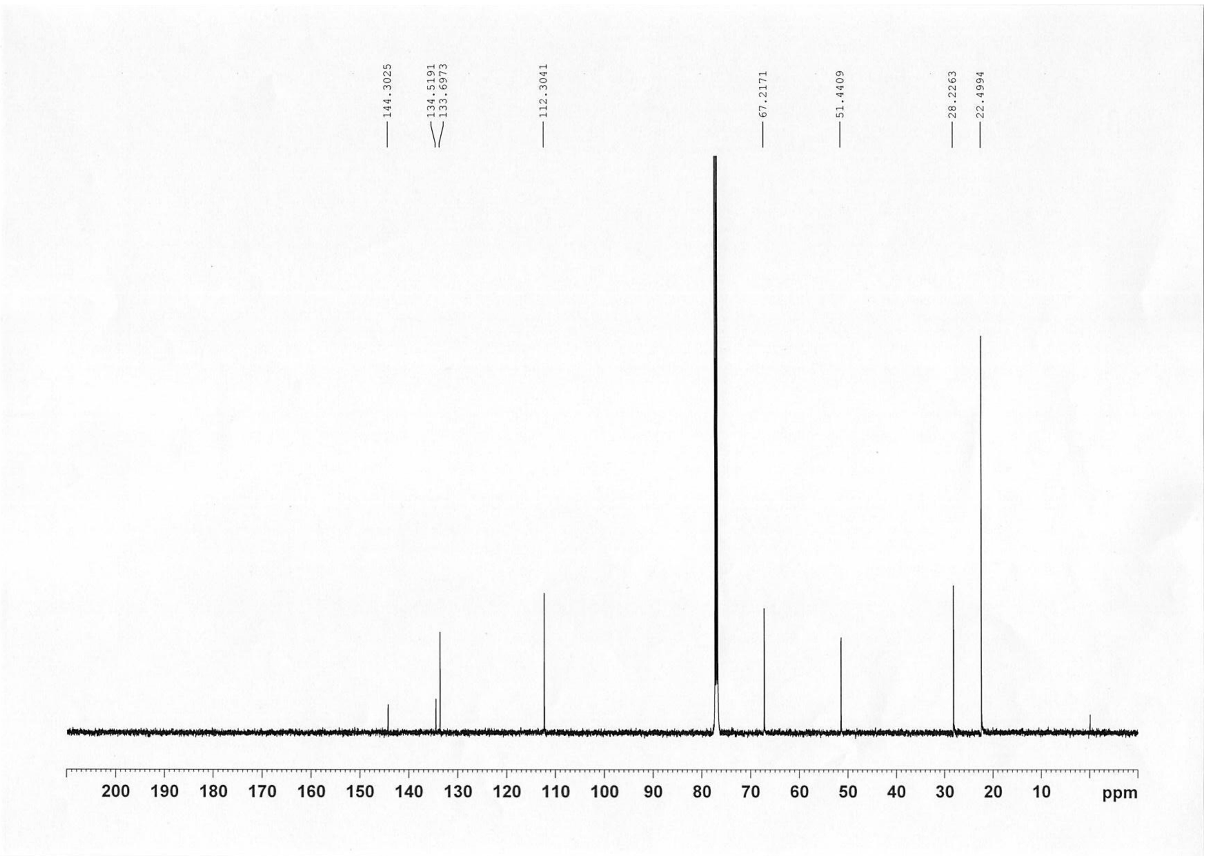

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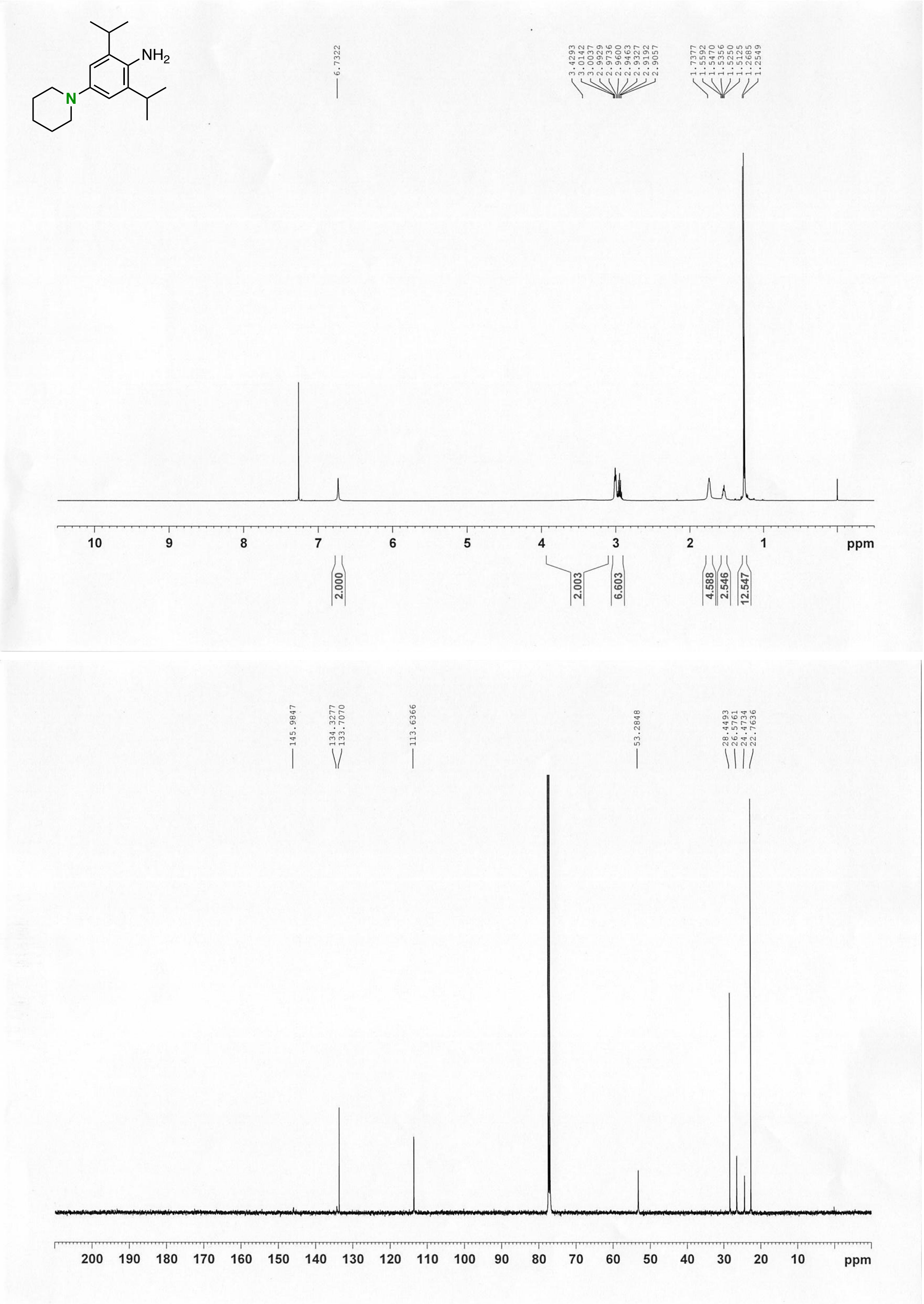

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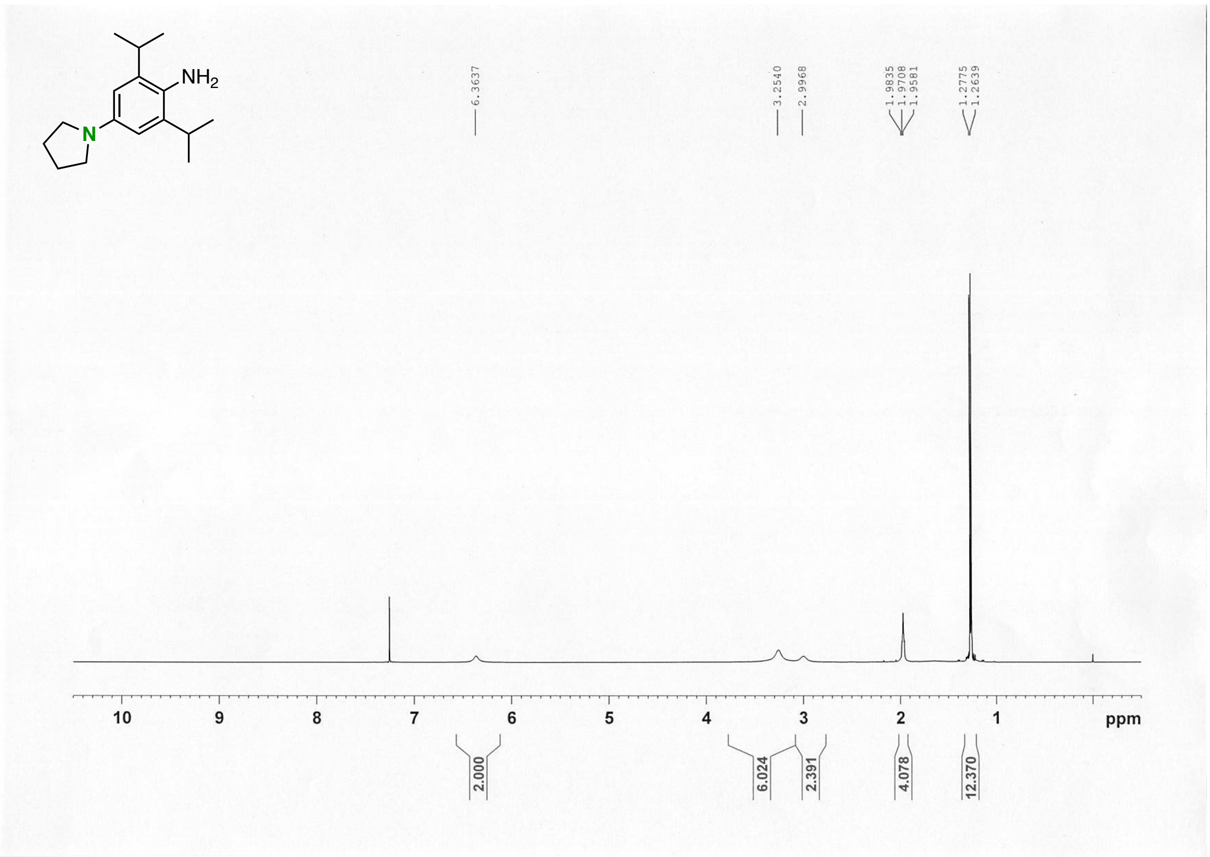

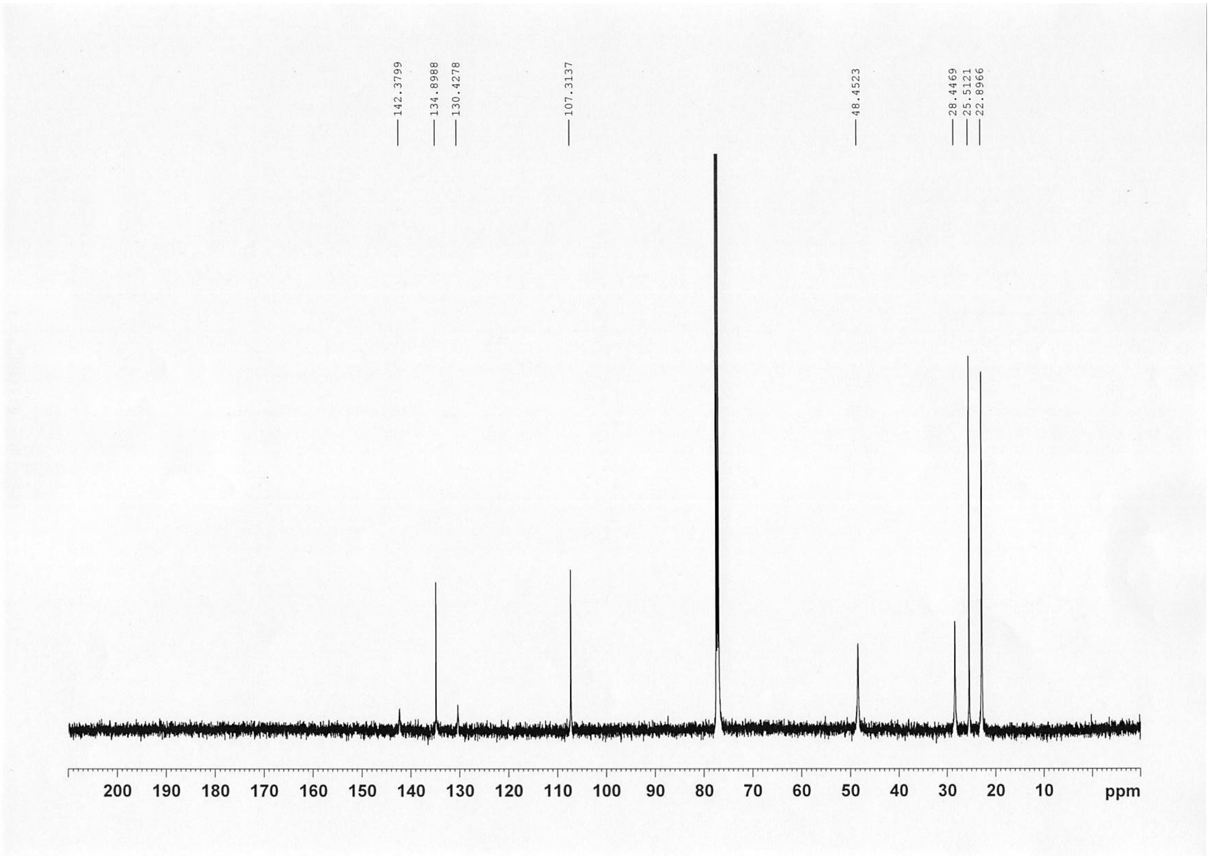

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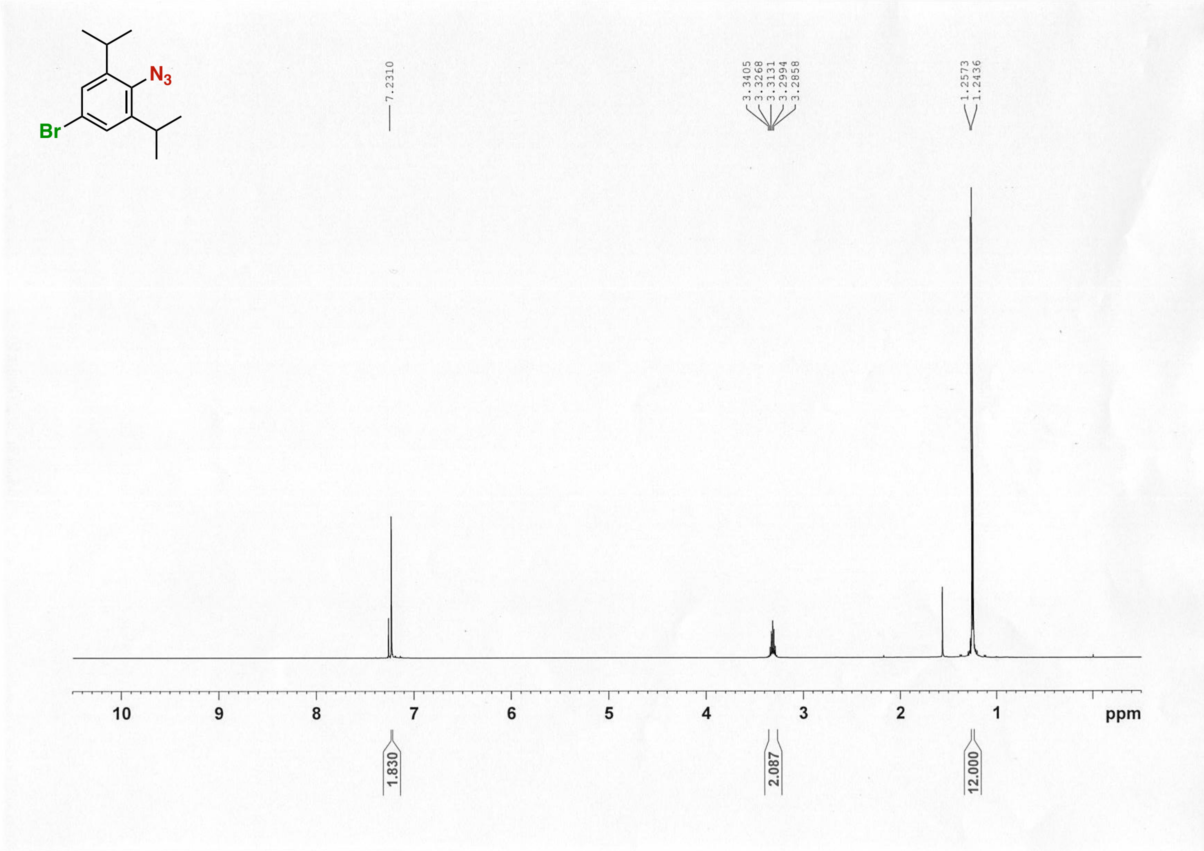

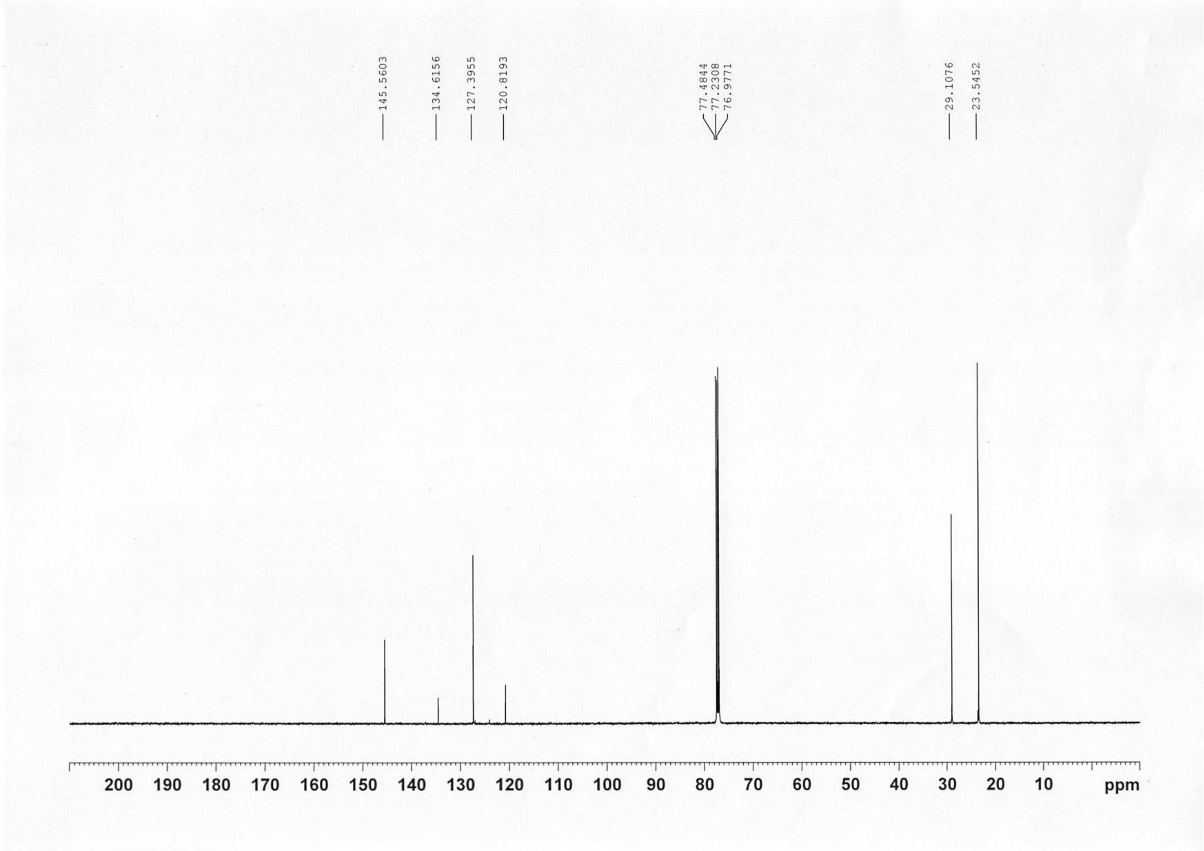

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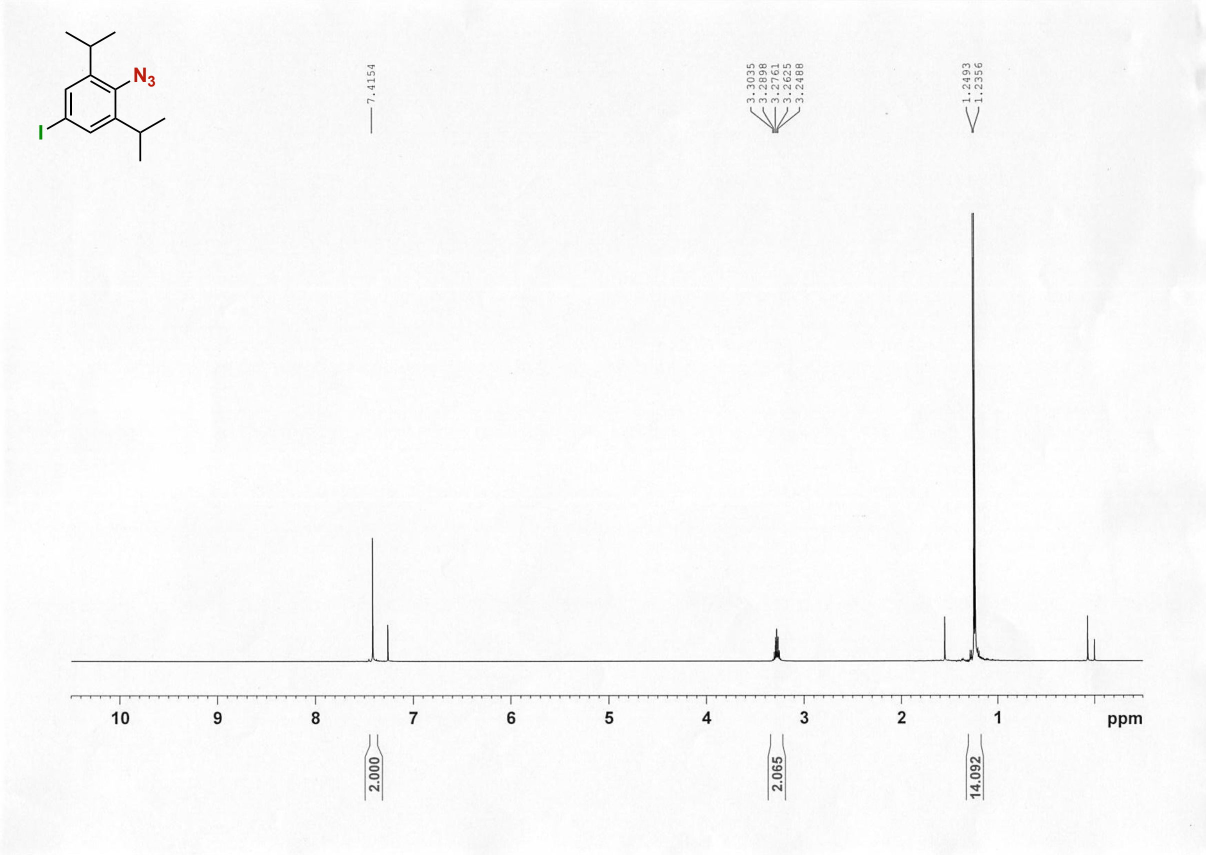

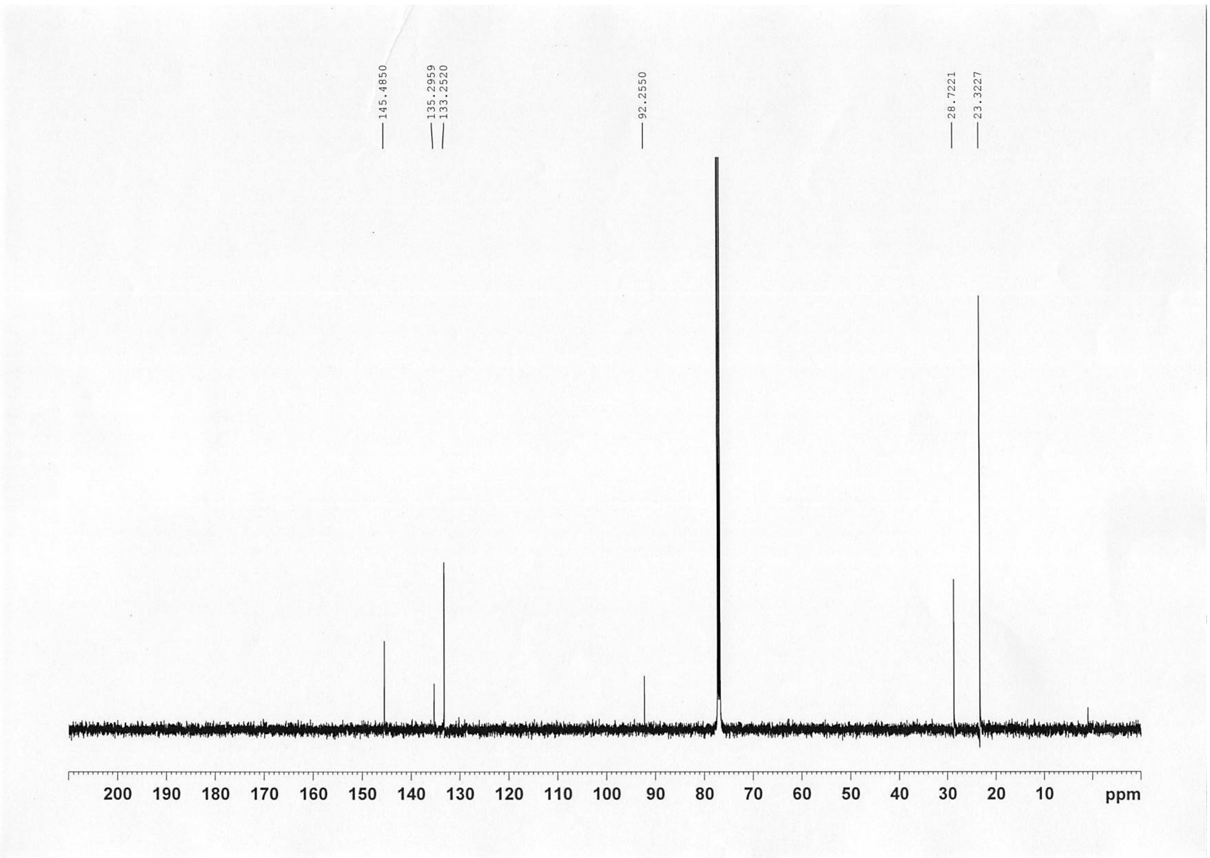

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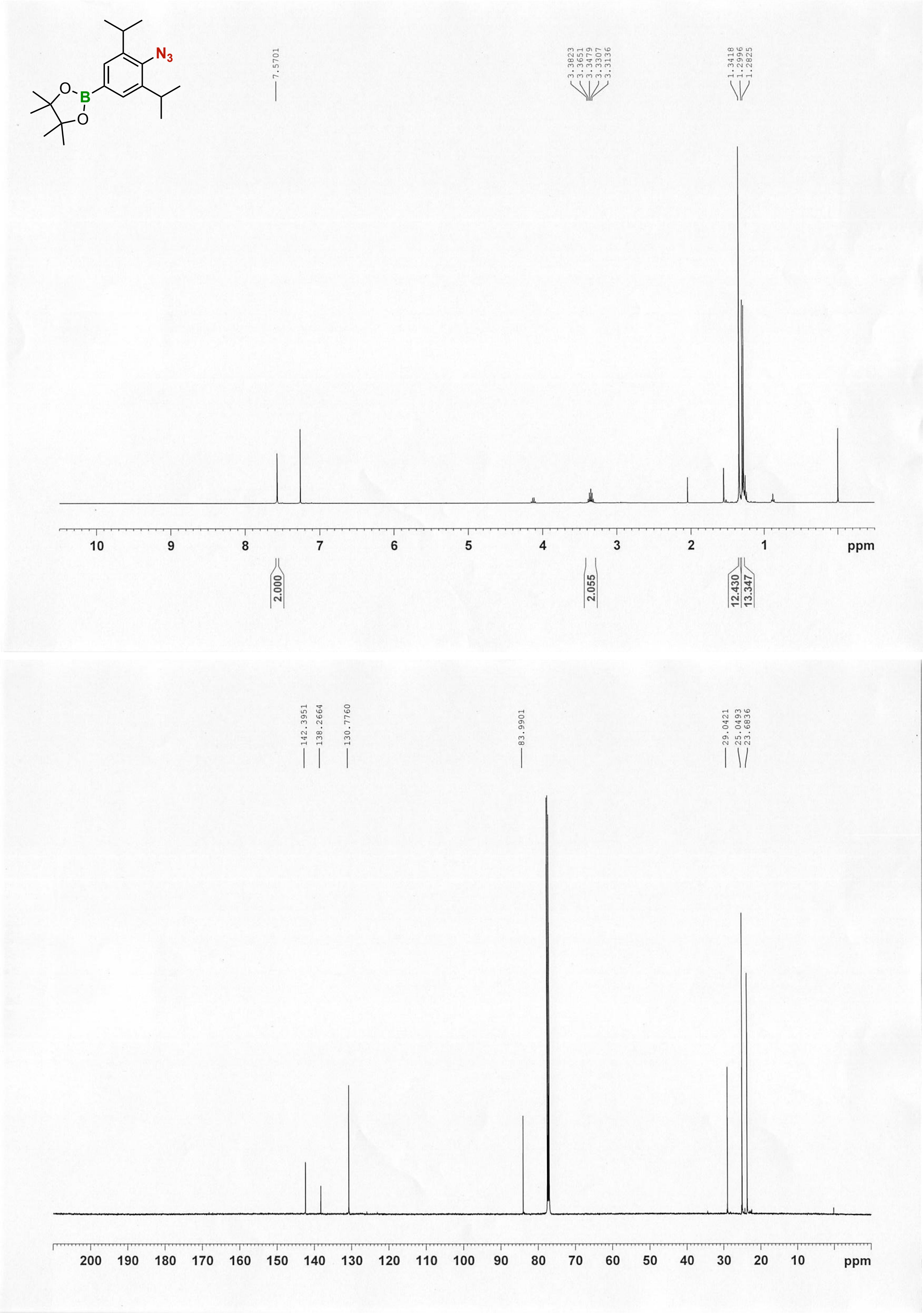

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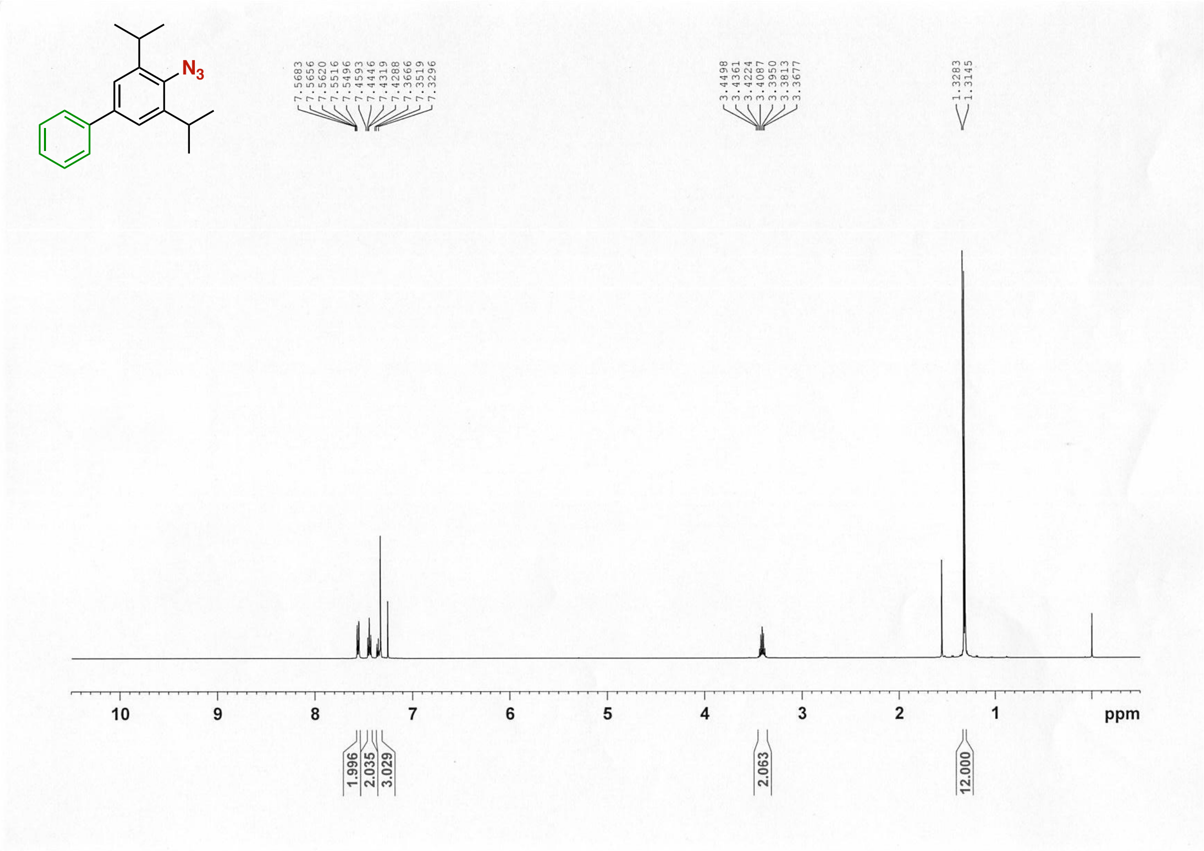

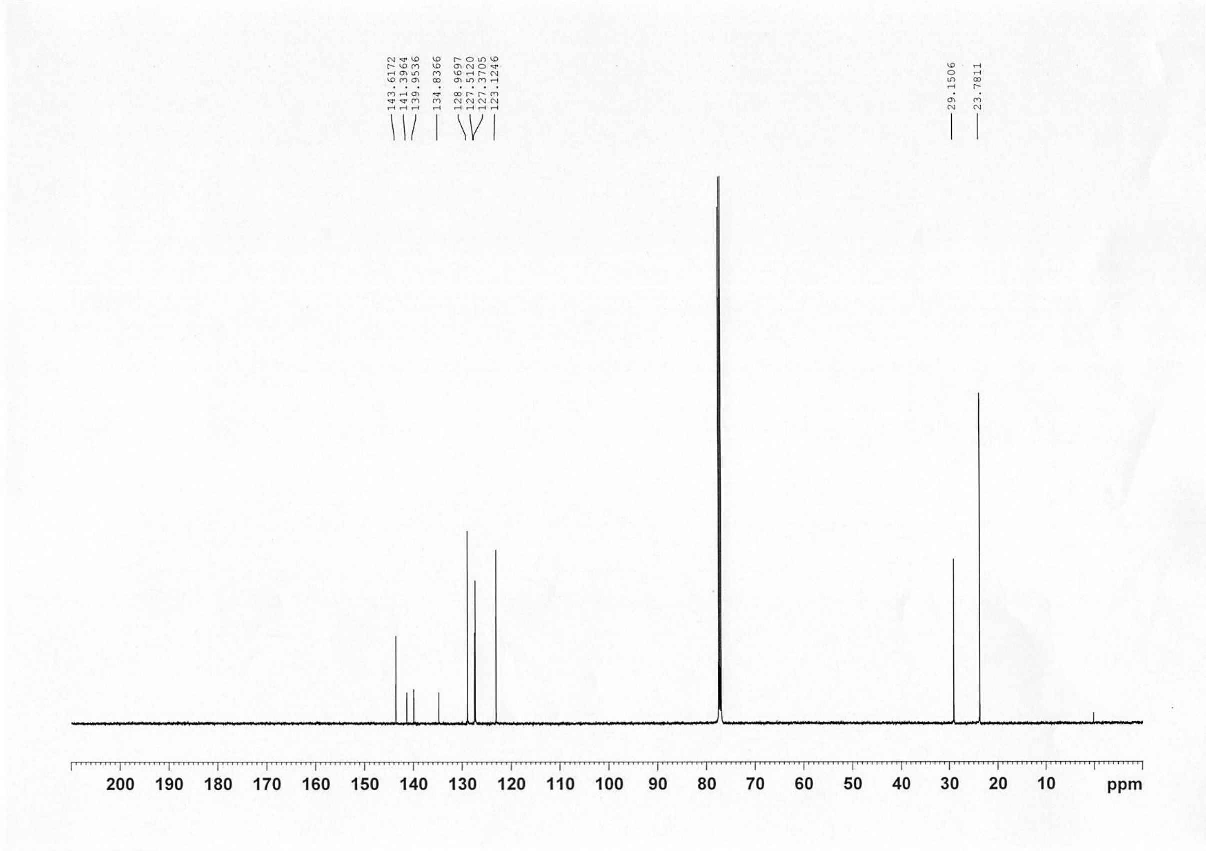

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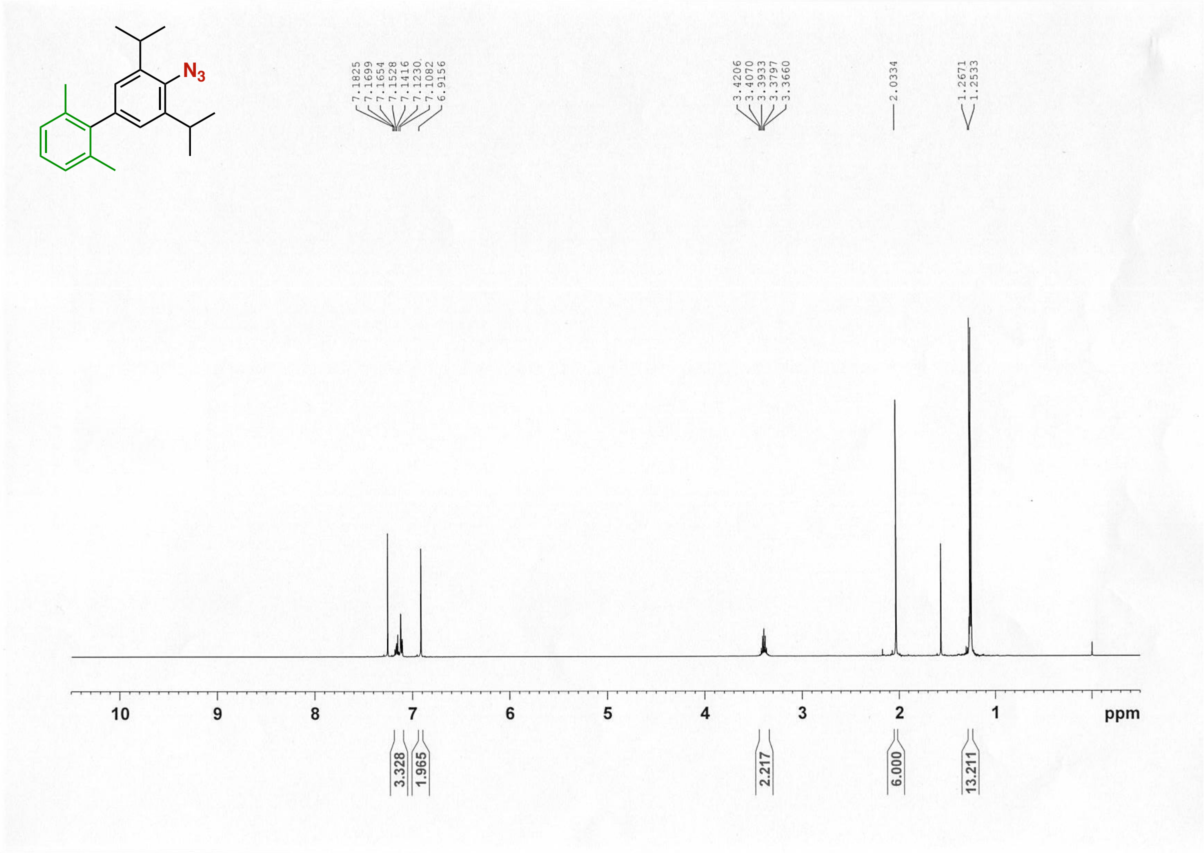

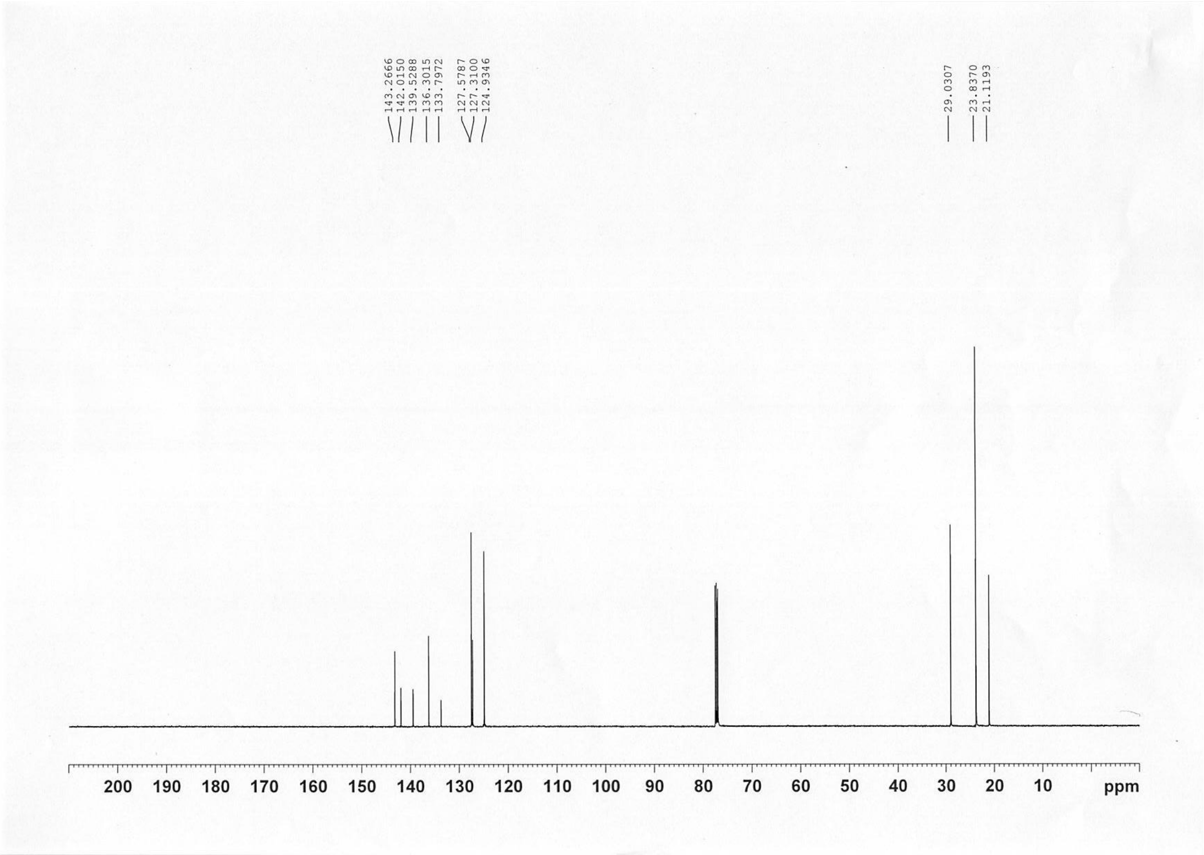

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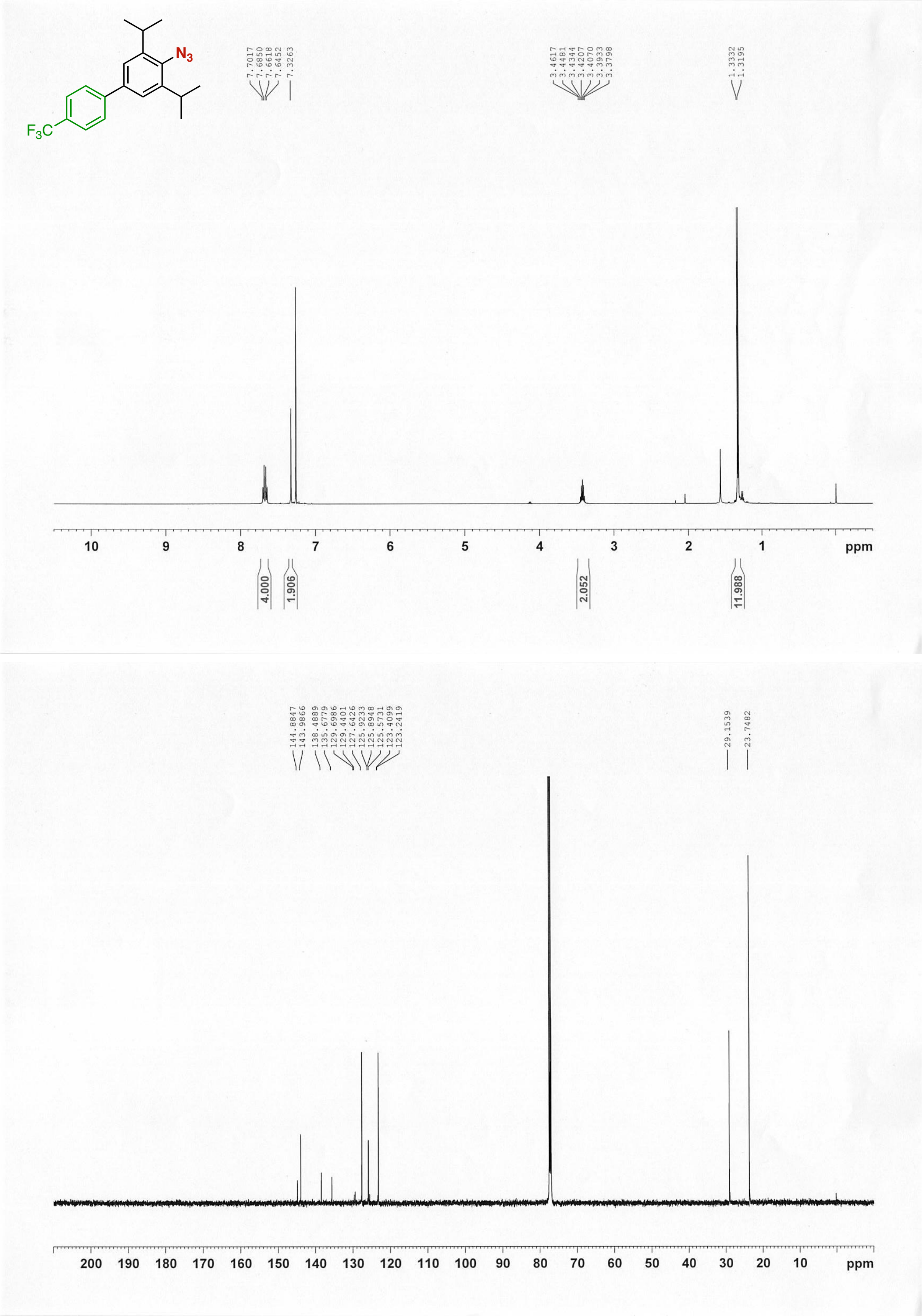

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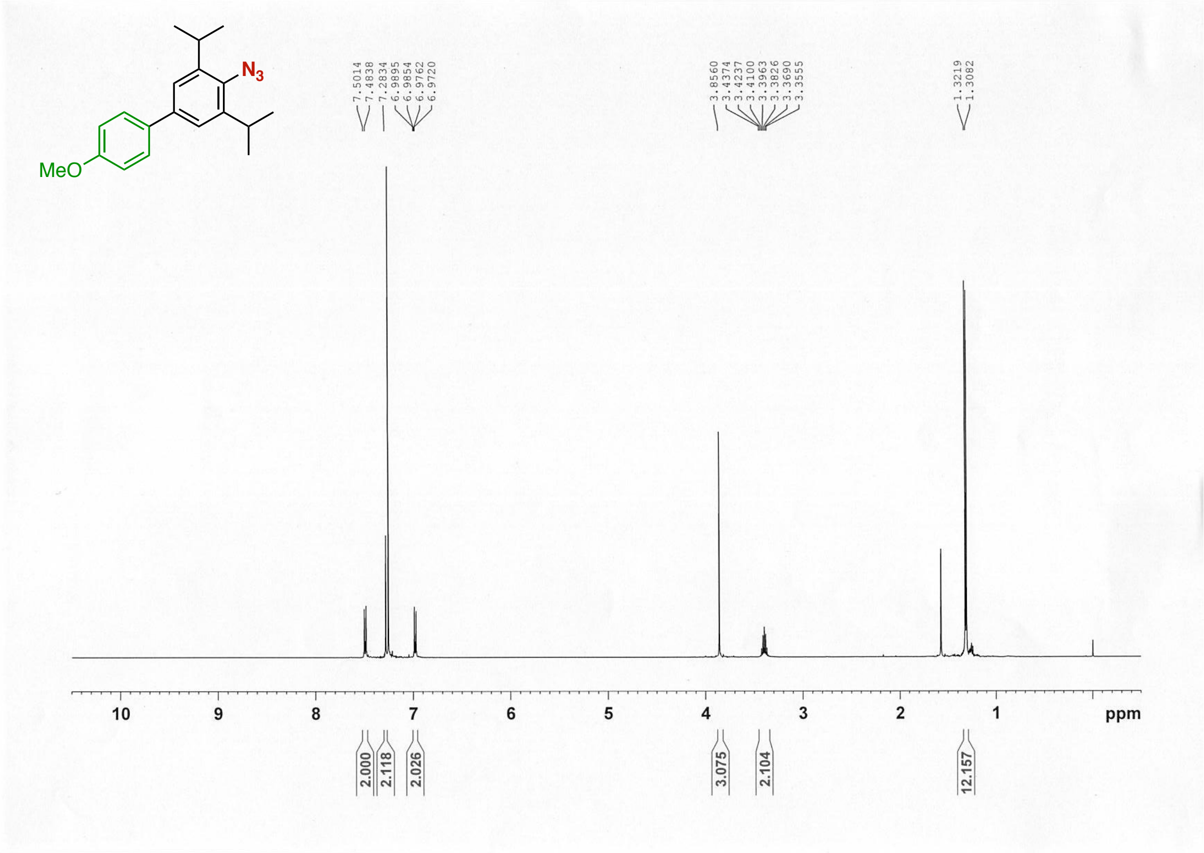

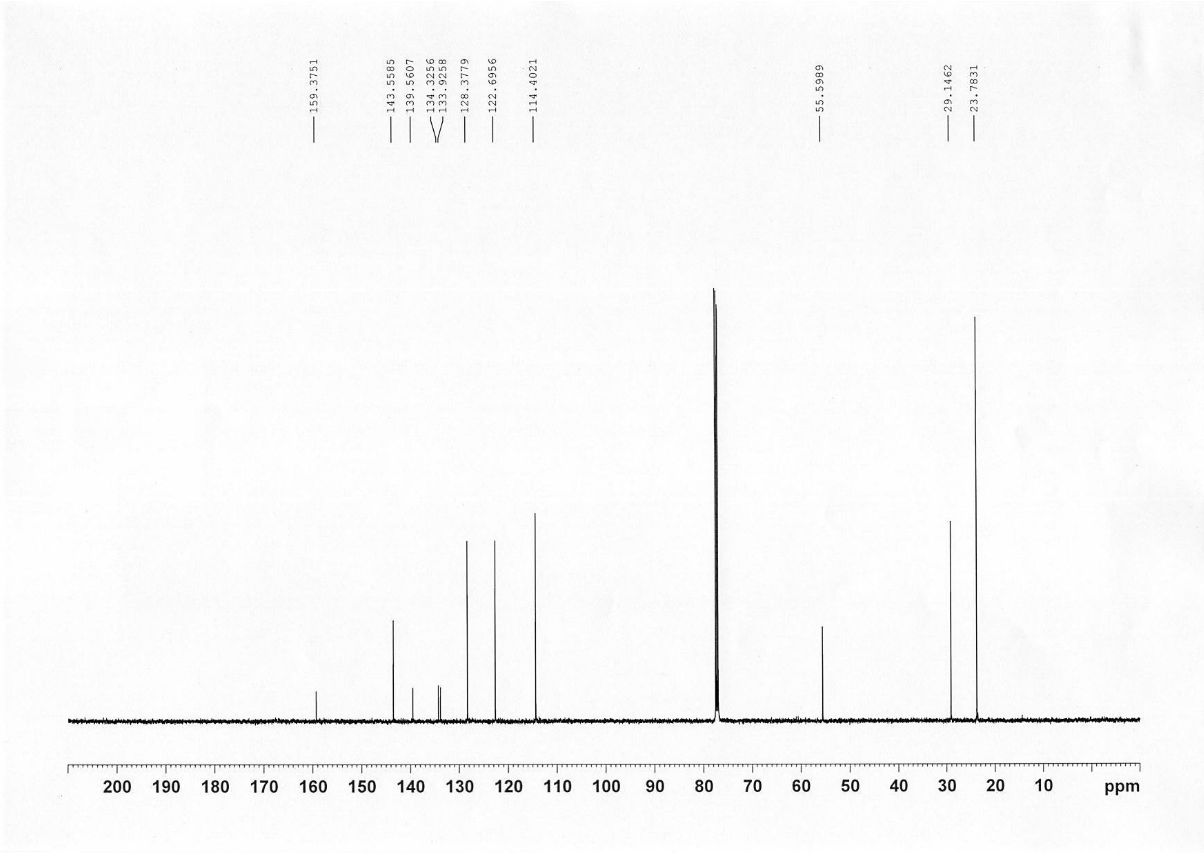

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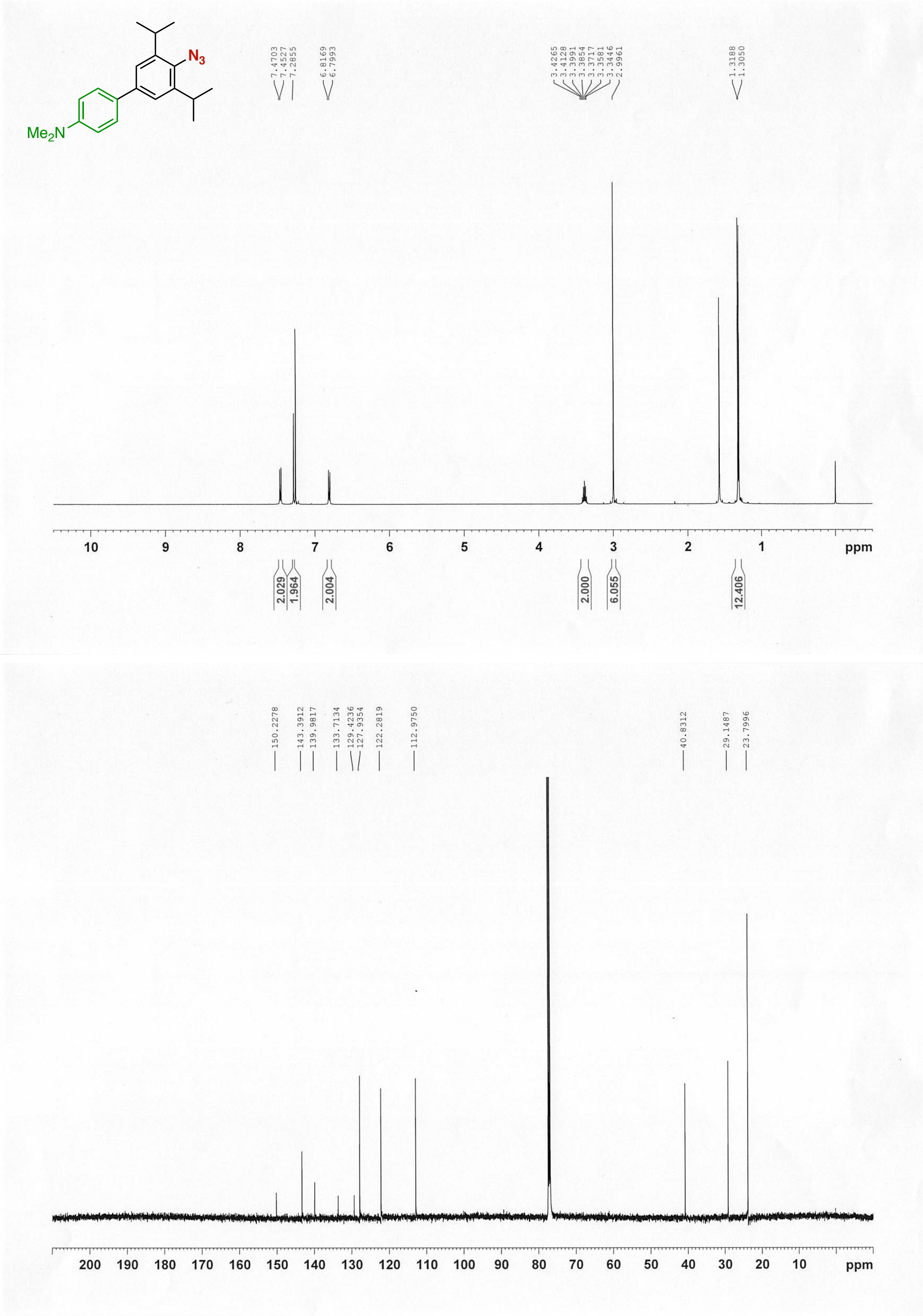

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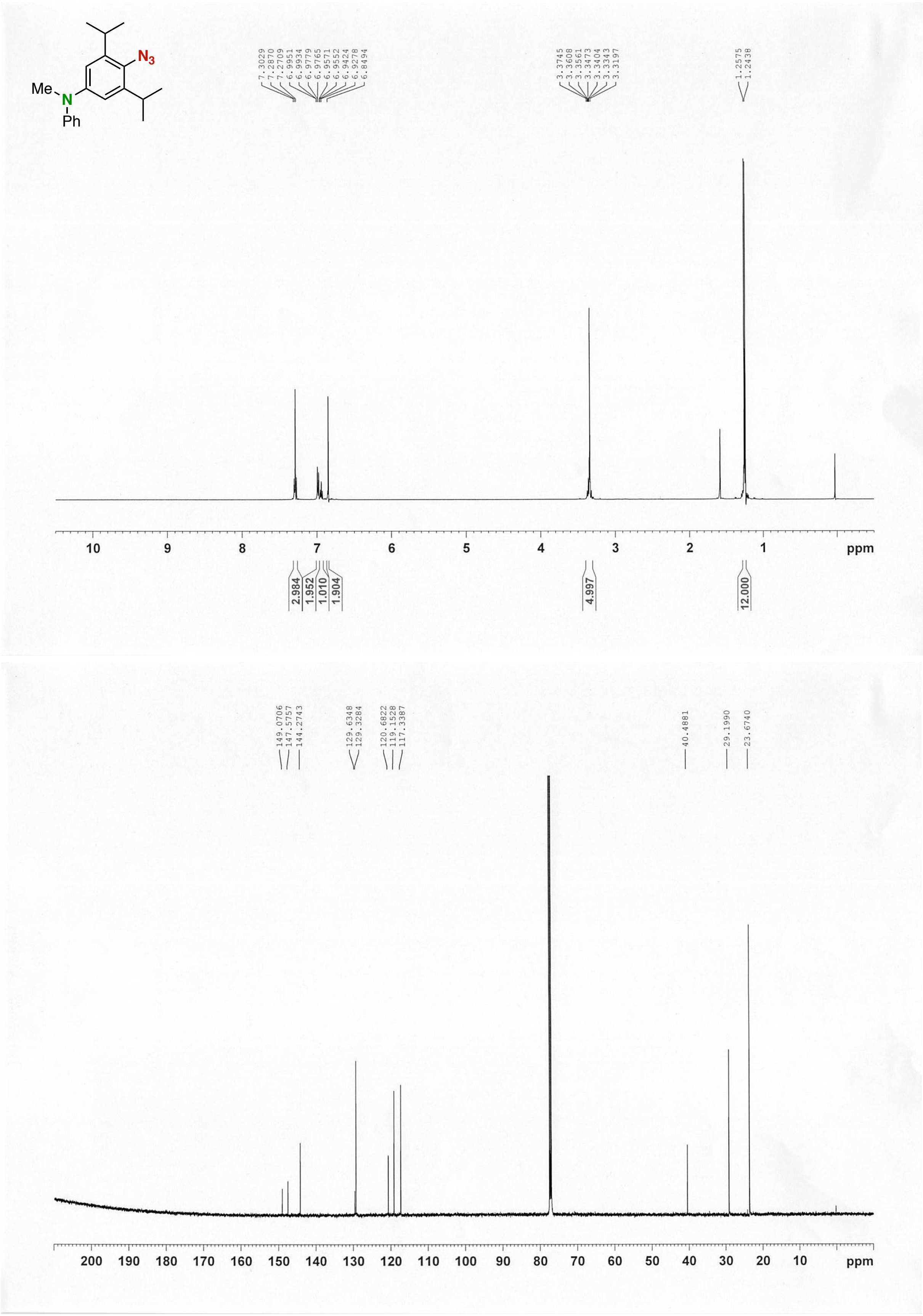

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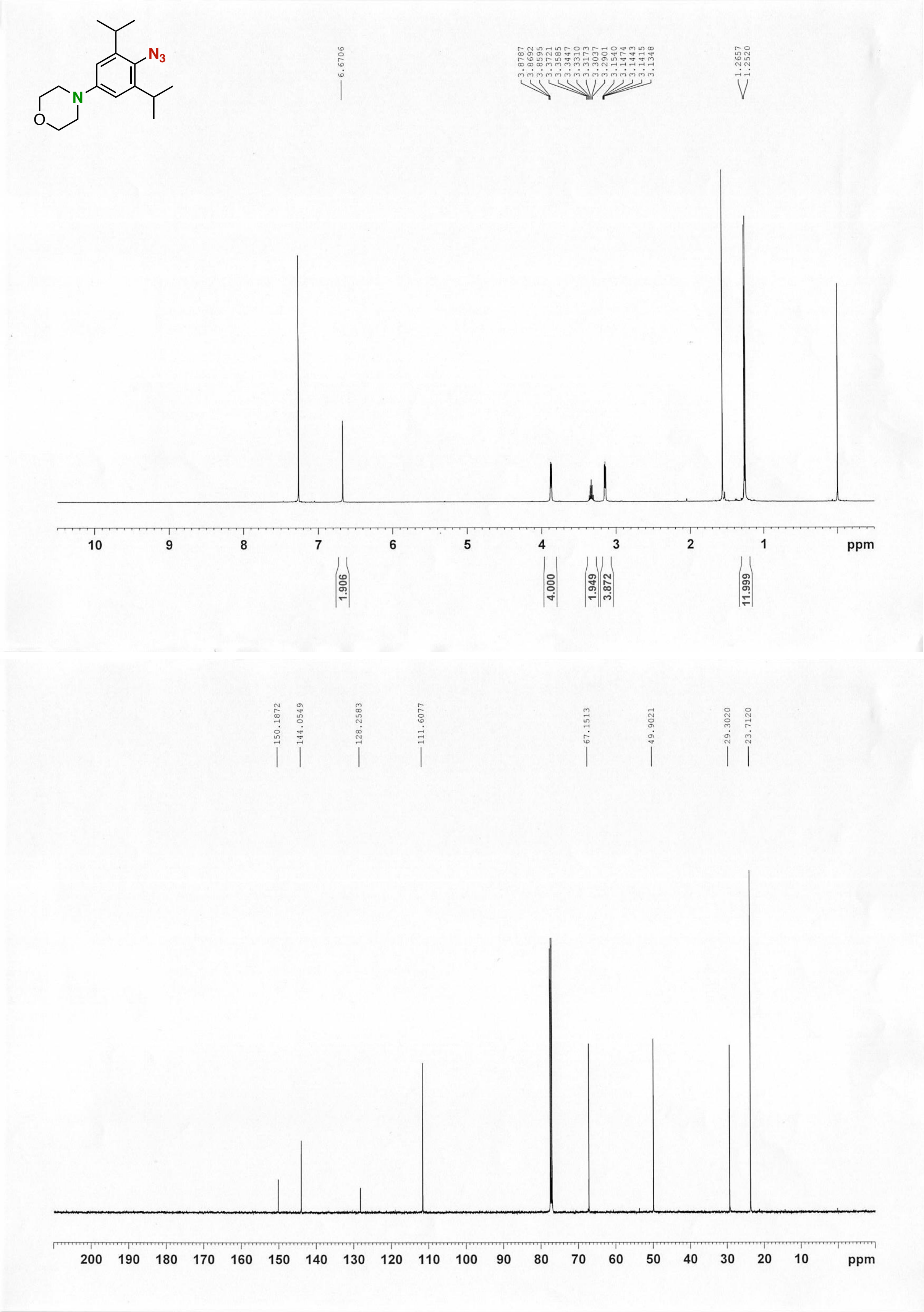

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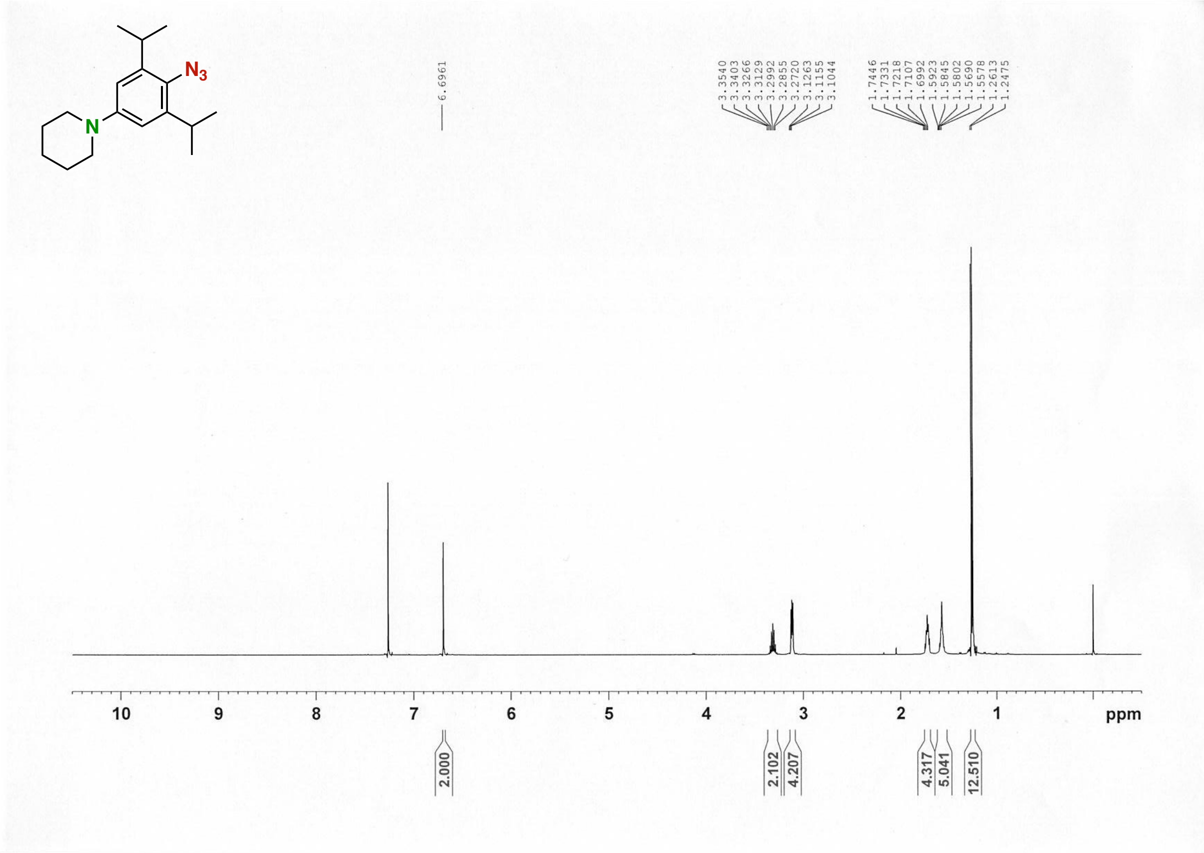
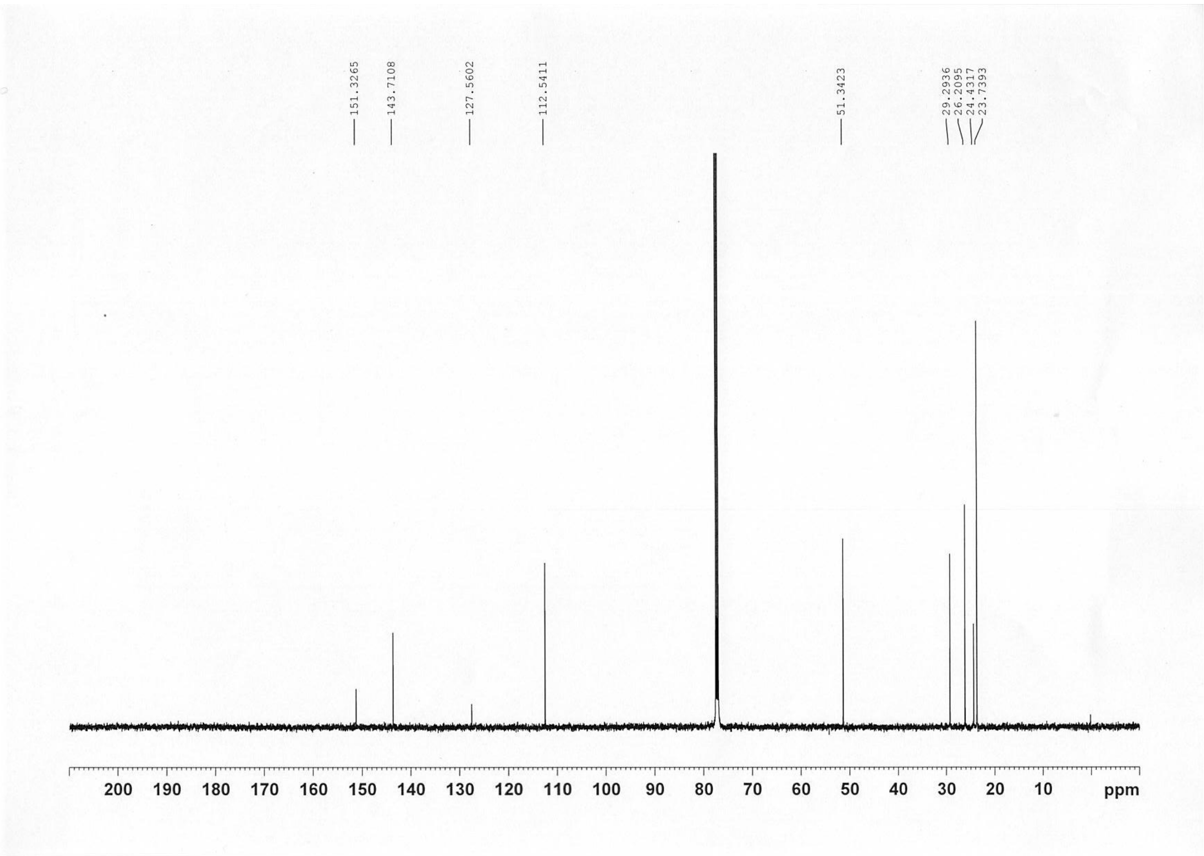
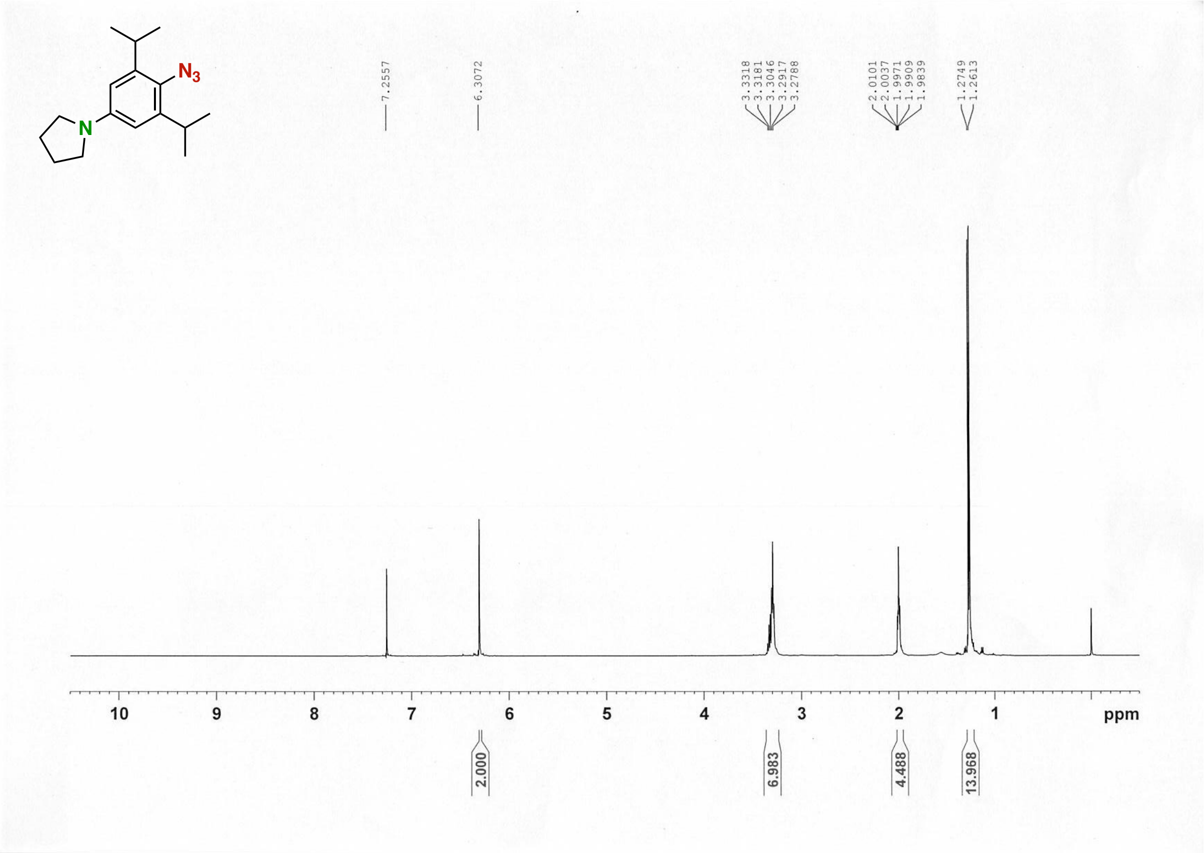
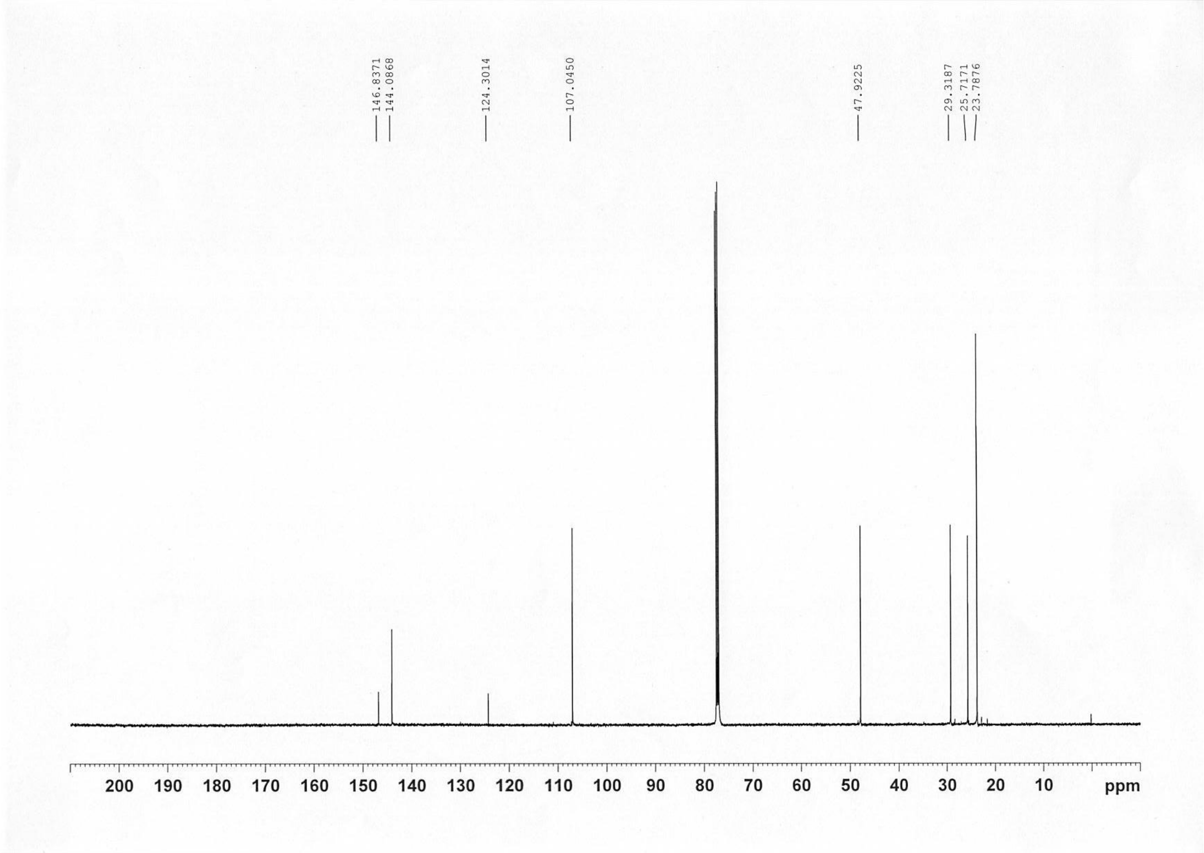




^1H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of **2o** ($CDCl_3$)





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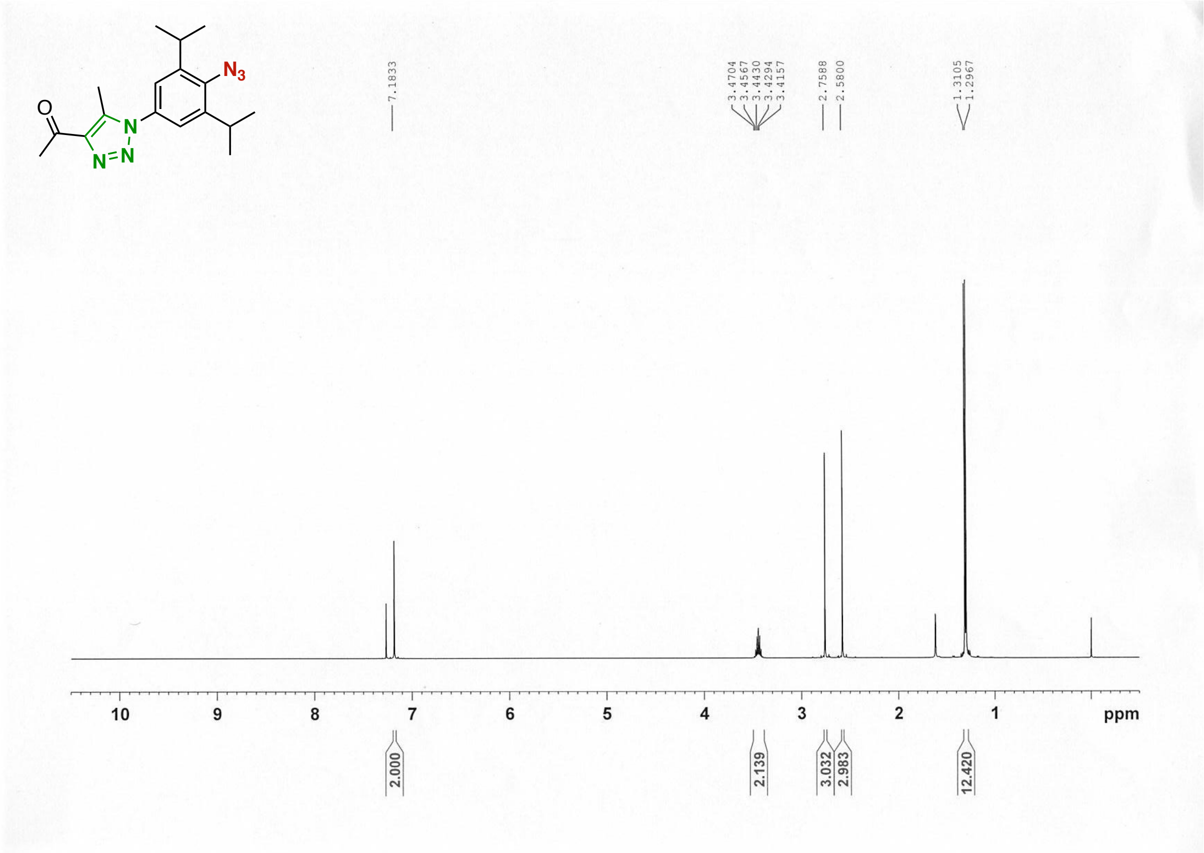

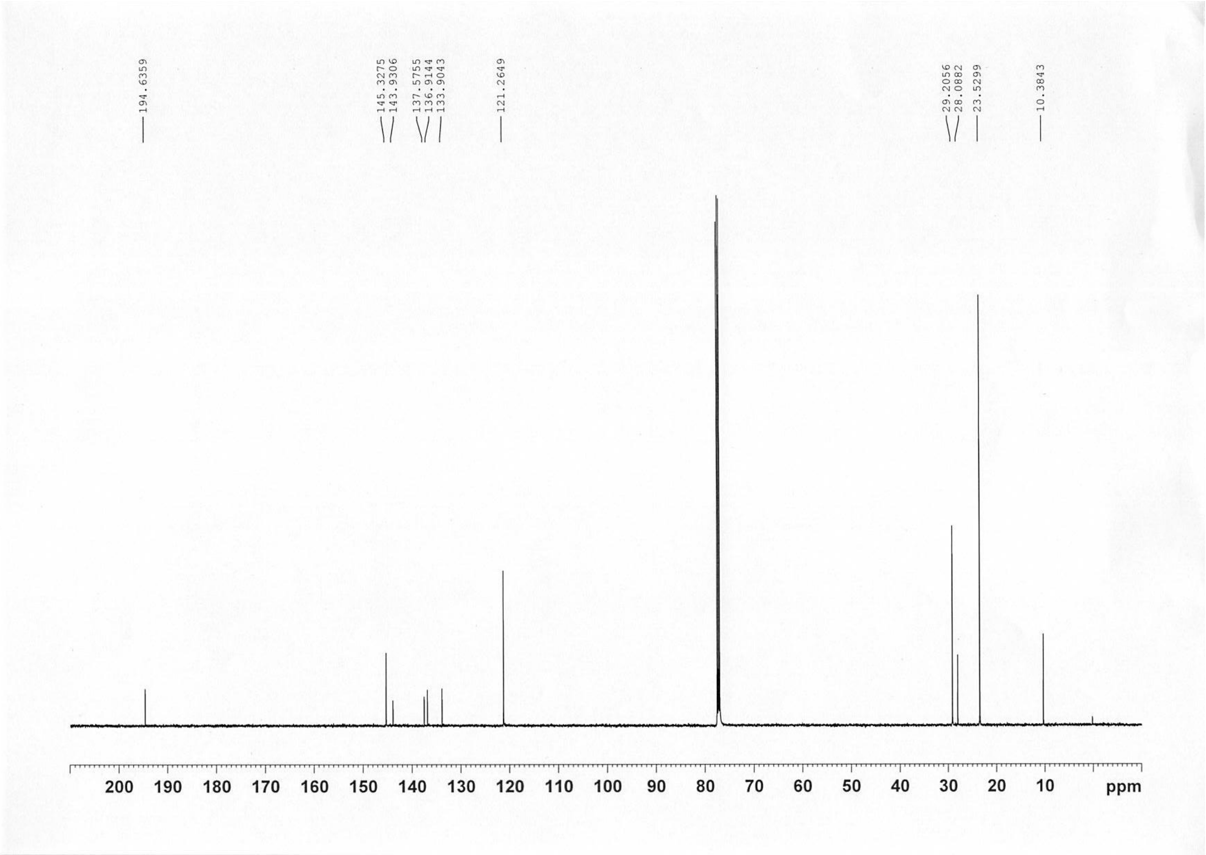

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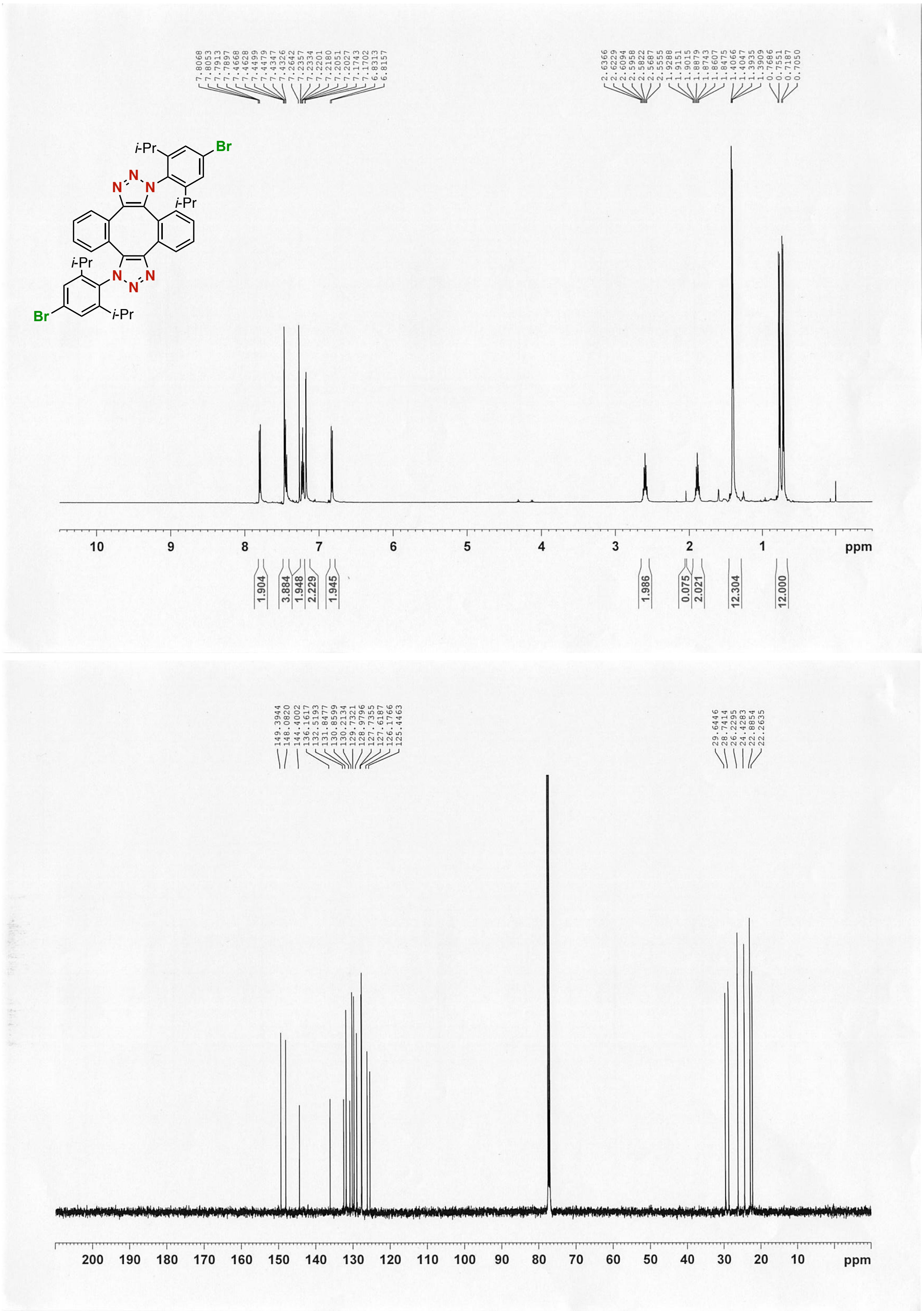

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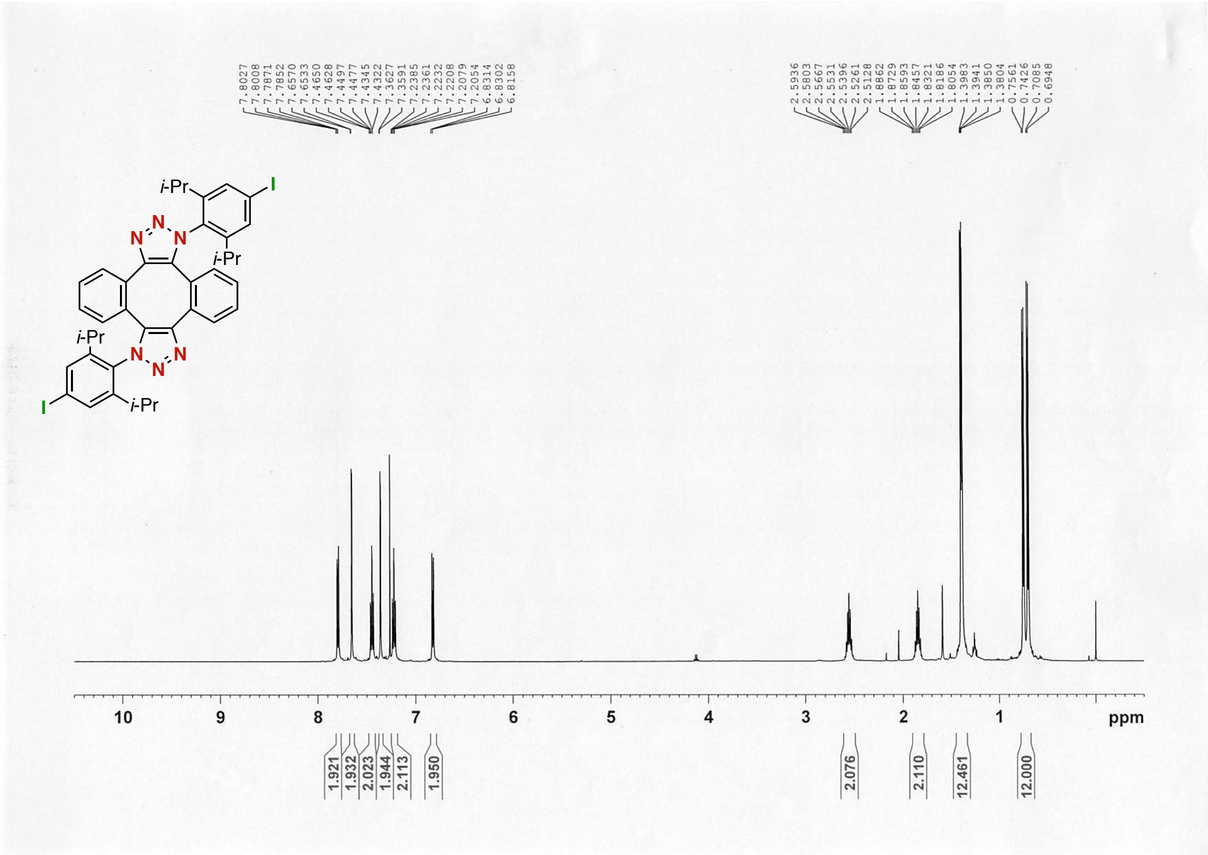

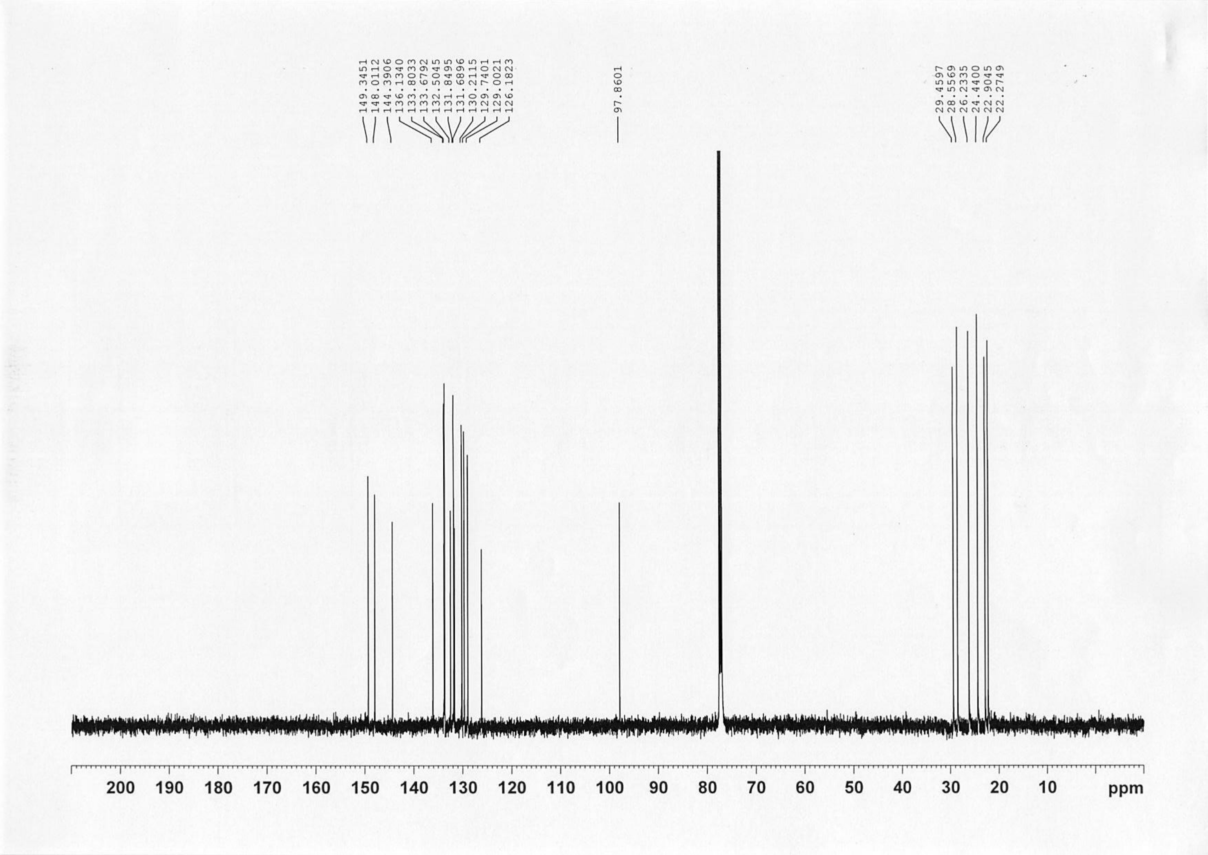

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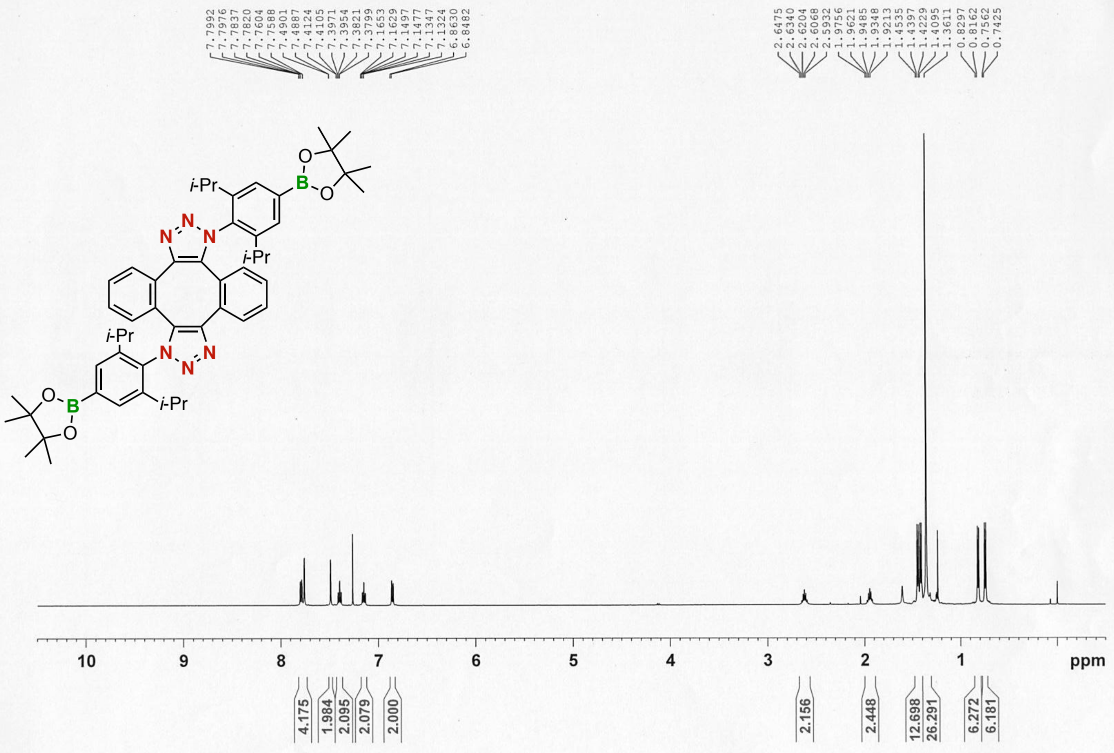

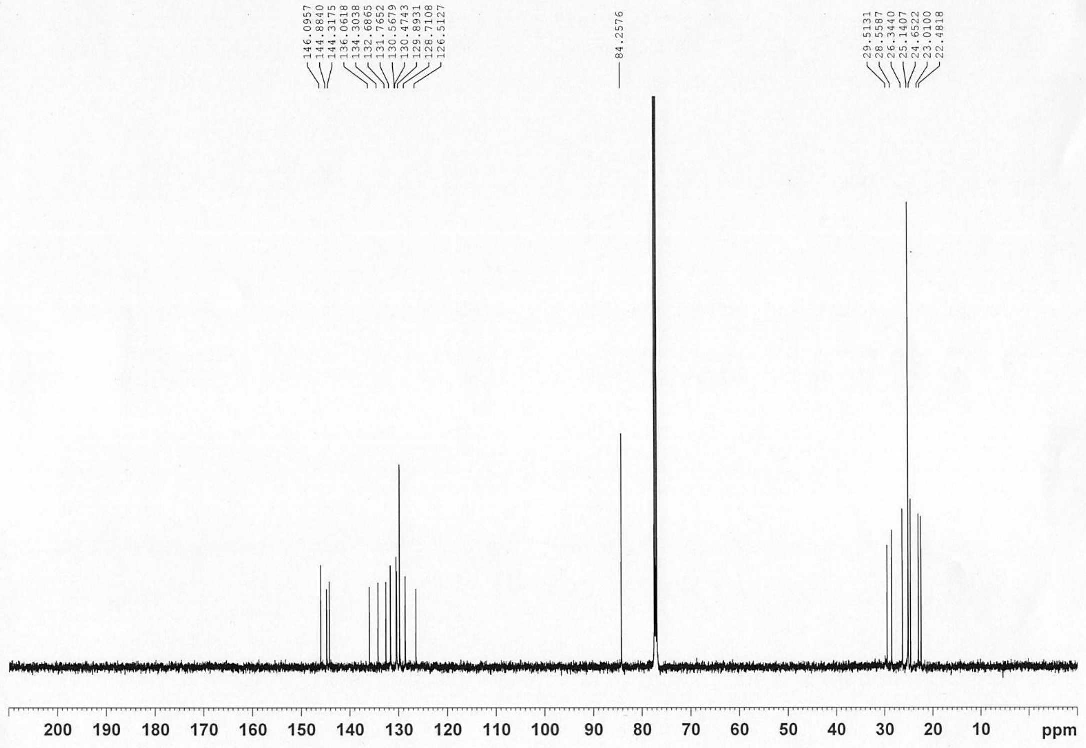

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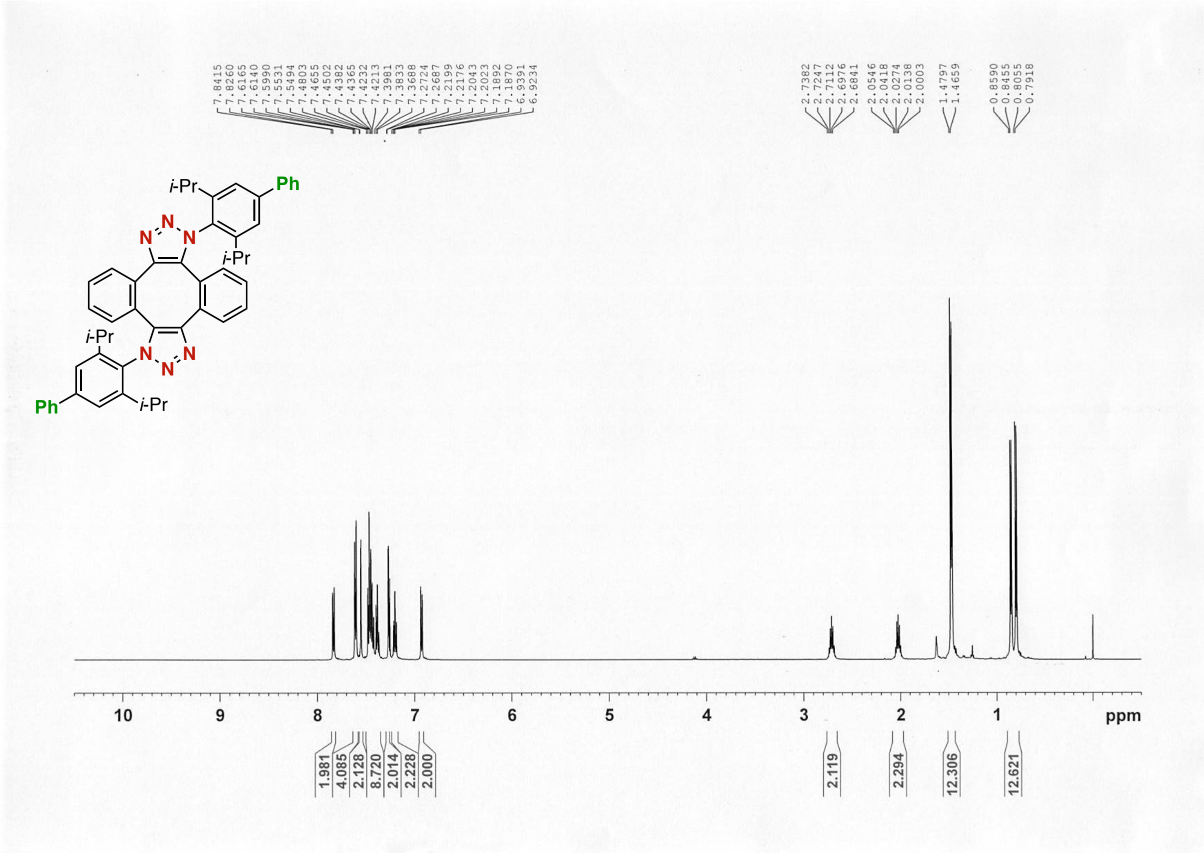
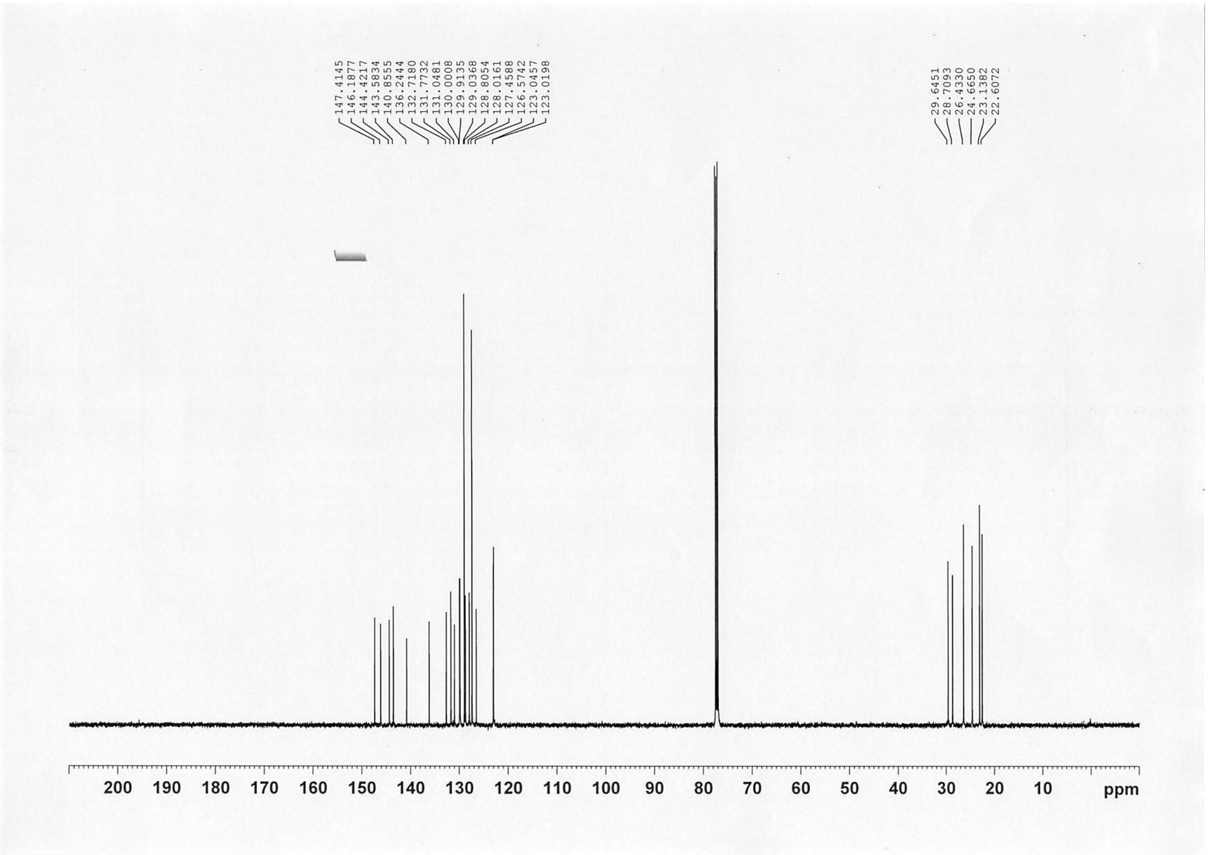
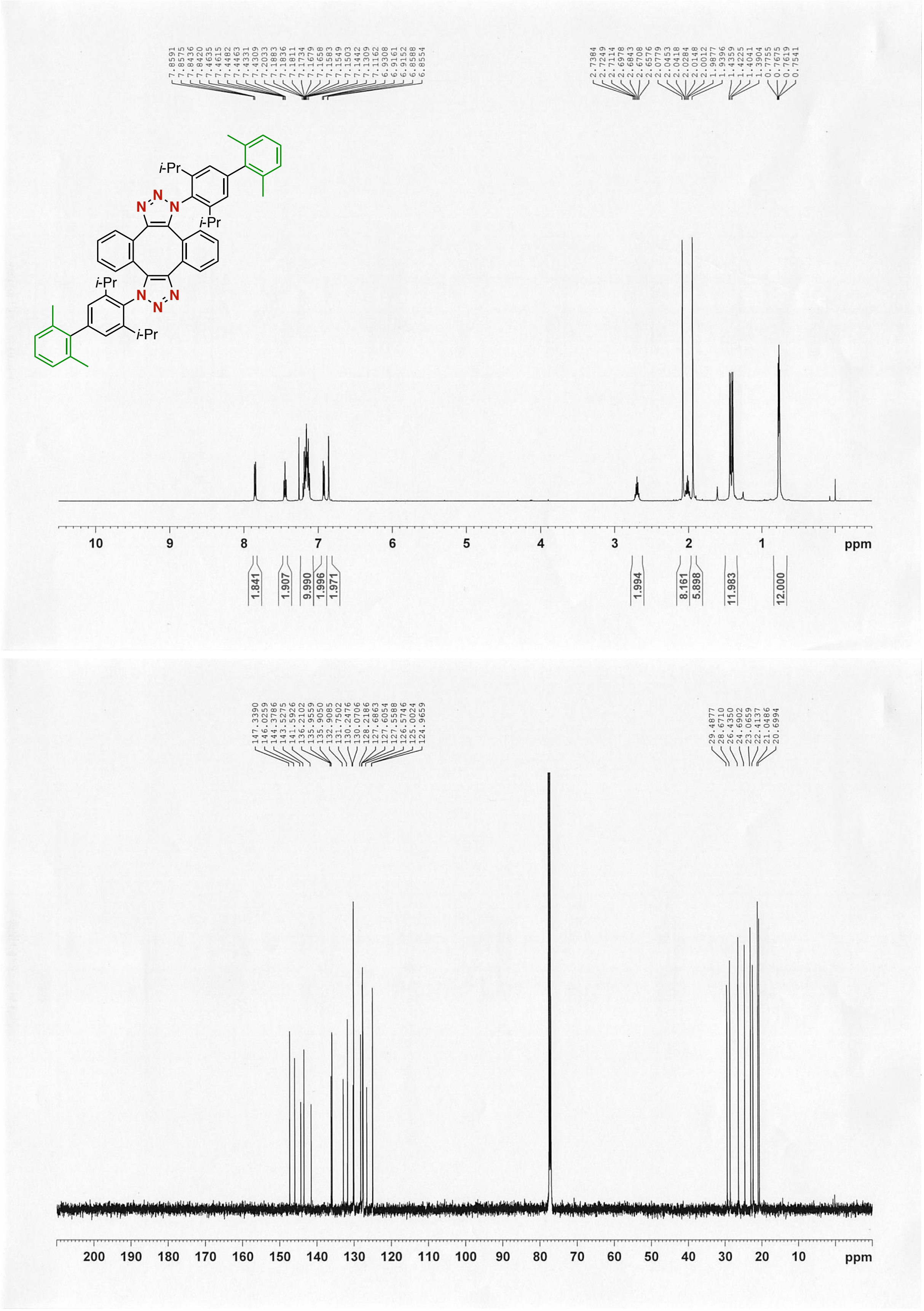
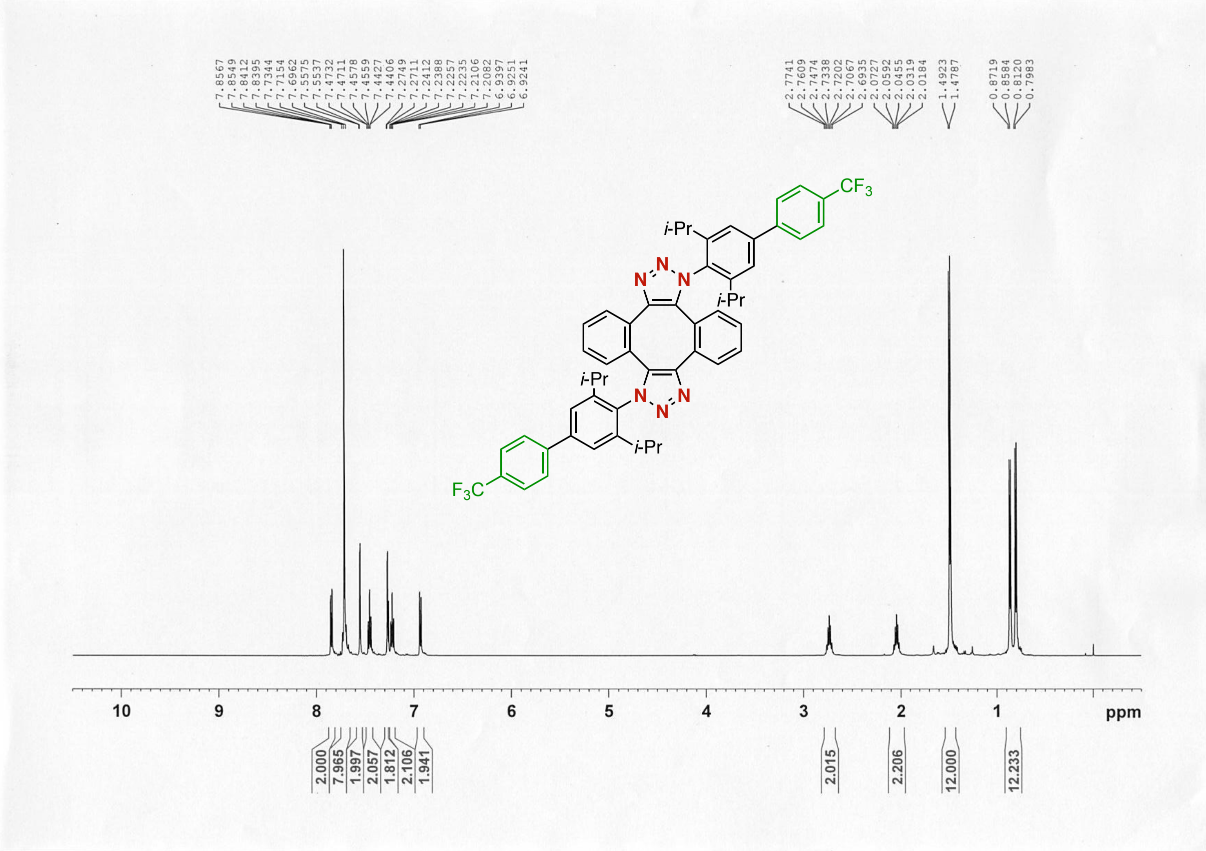


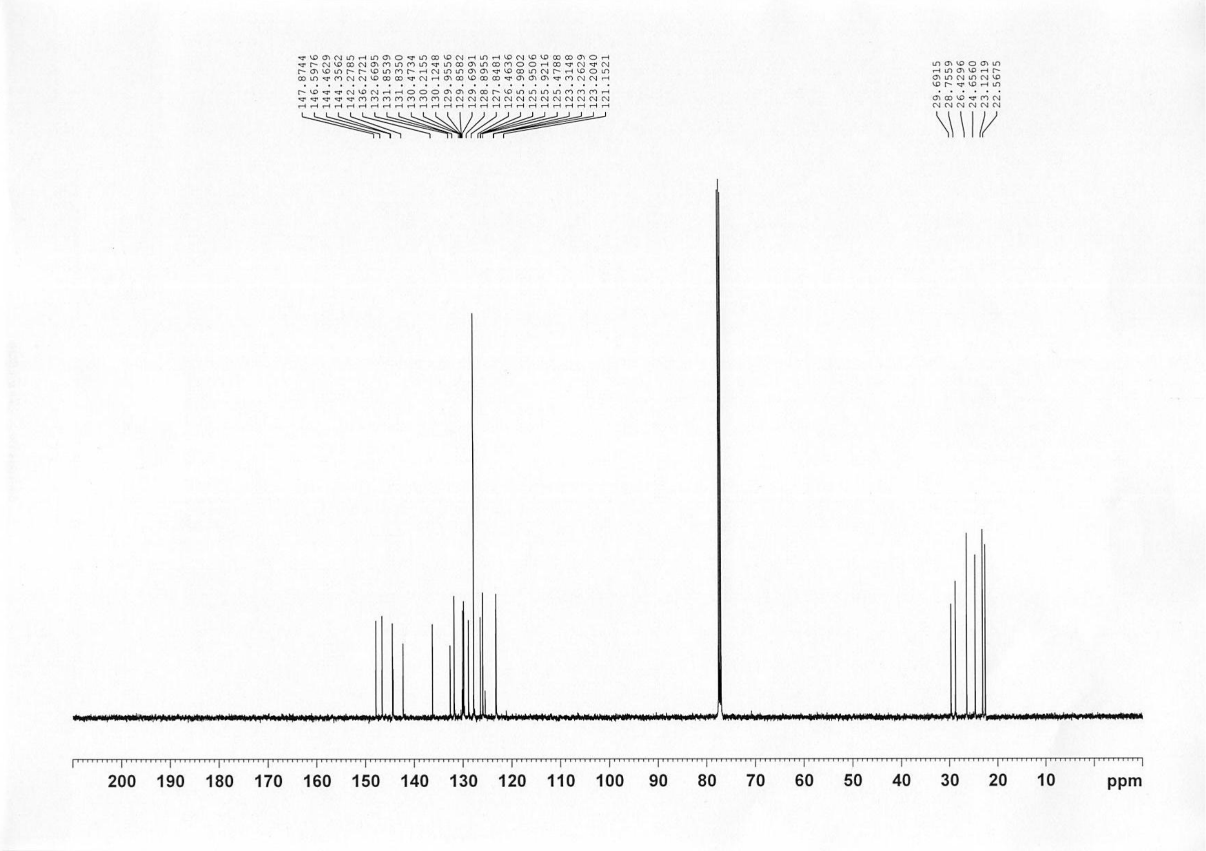


^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of *trans*-**3h** ($CDCl_3$)

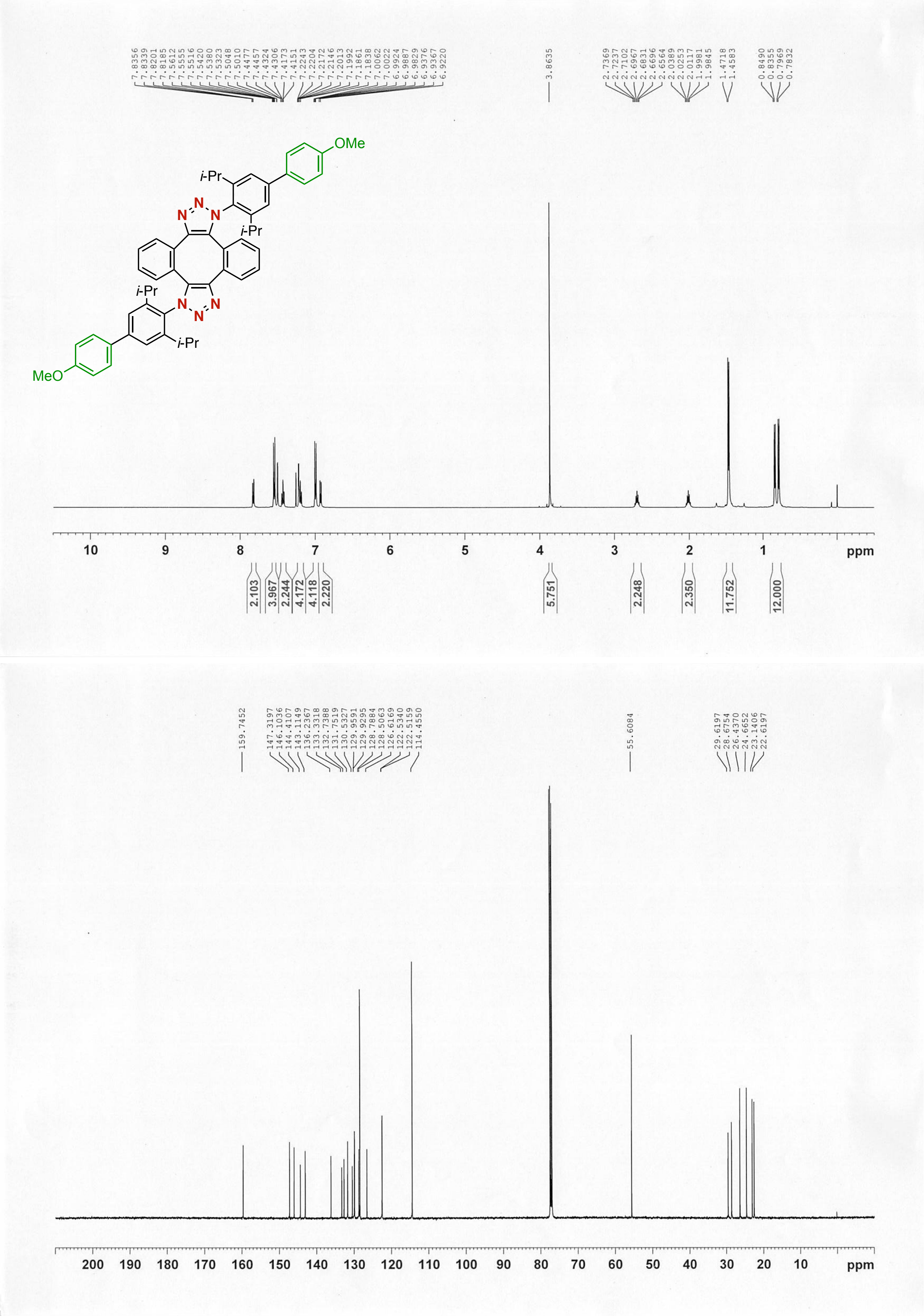


^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of *trans*-**3i** ($CDCl_3$)

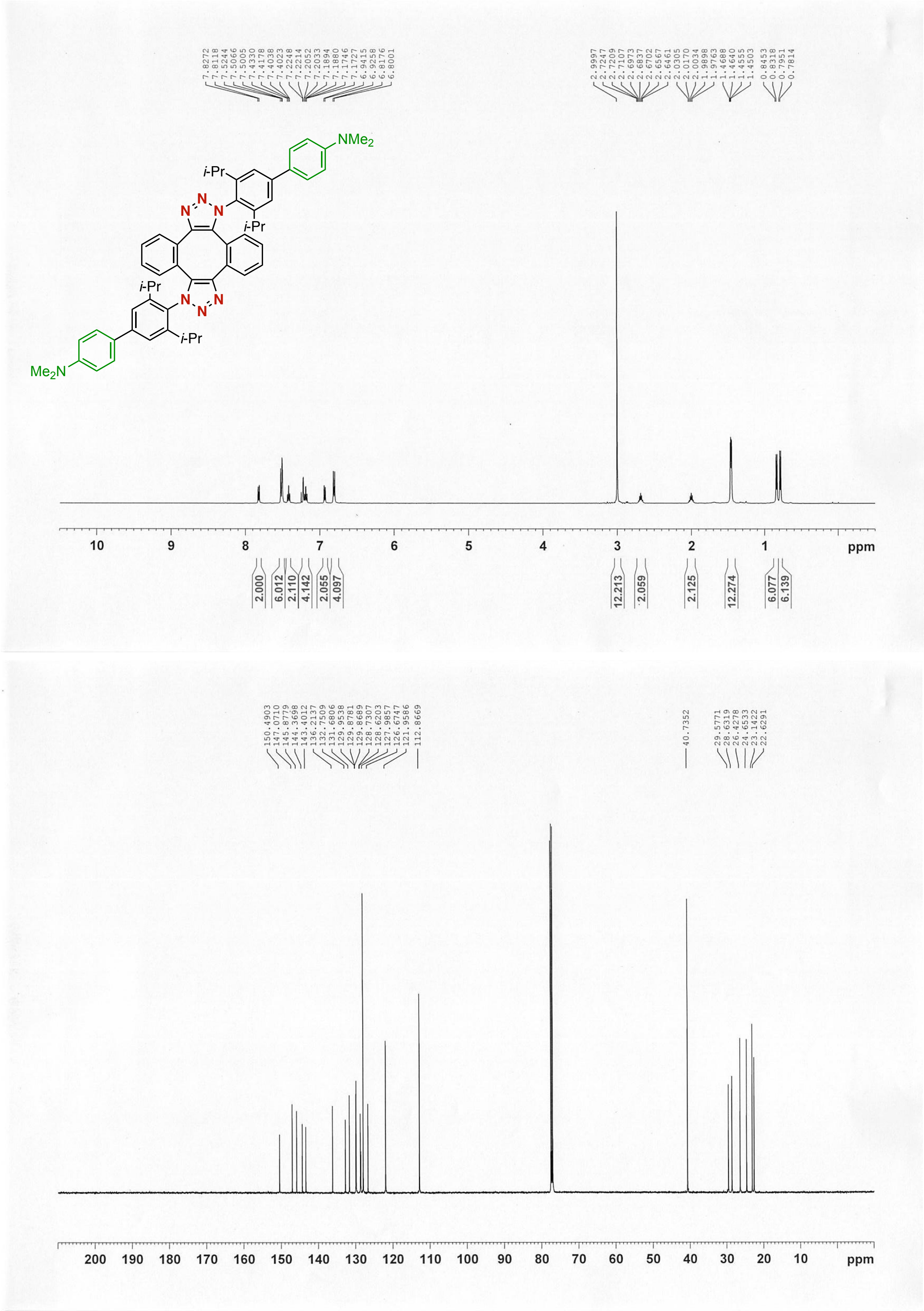




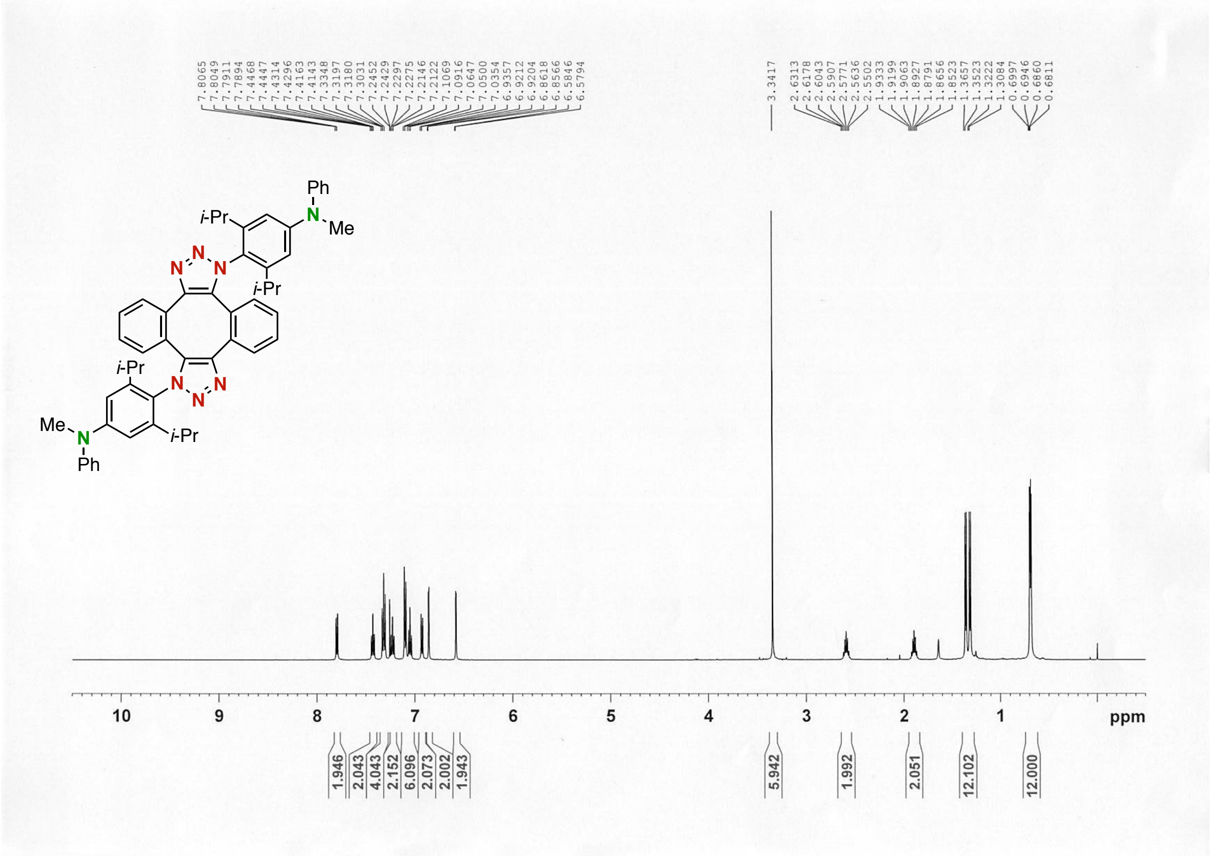
^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of *trans*-**3j** ($CDCl_3$)

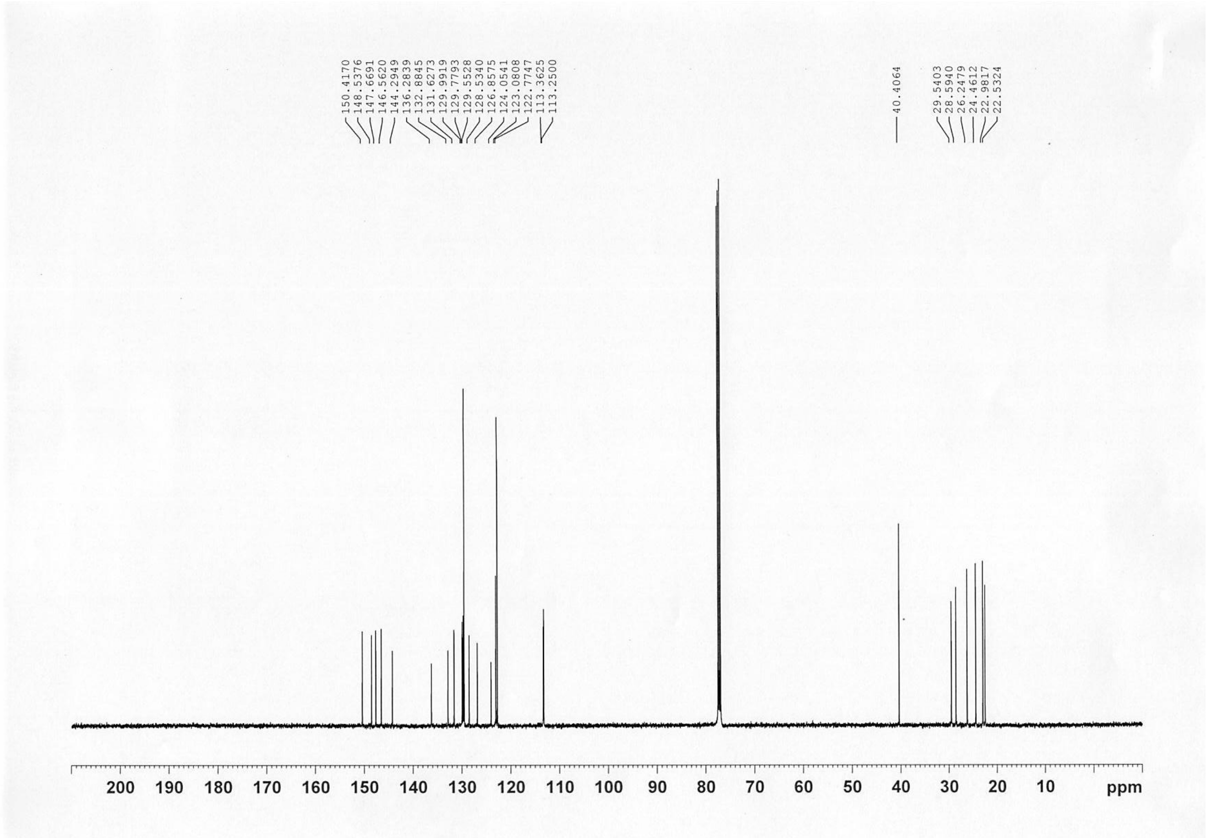


^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of *trans*-**3k** ($CDCl_3$)

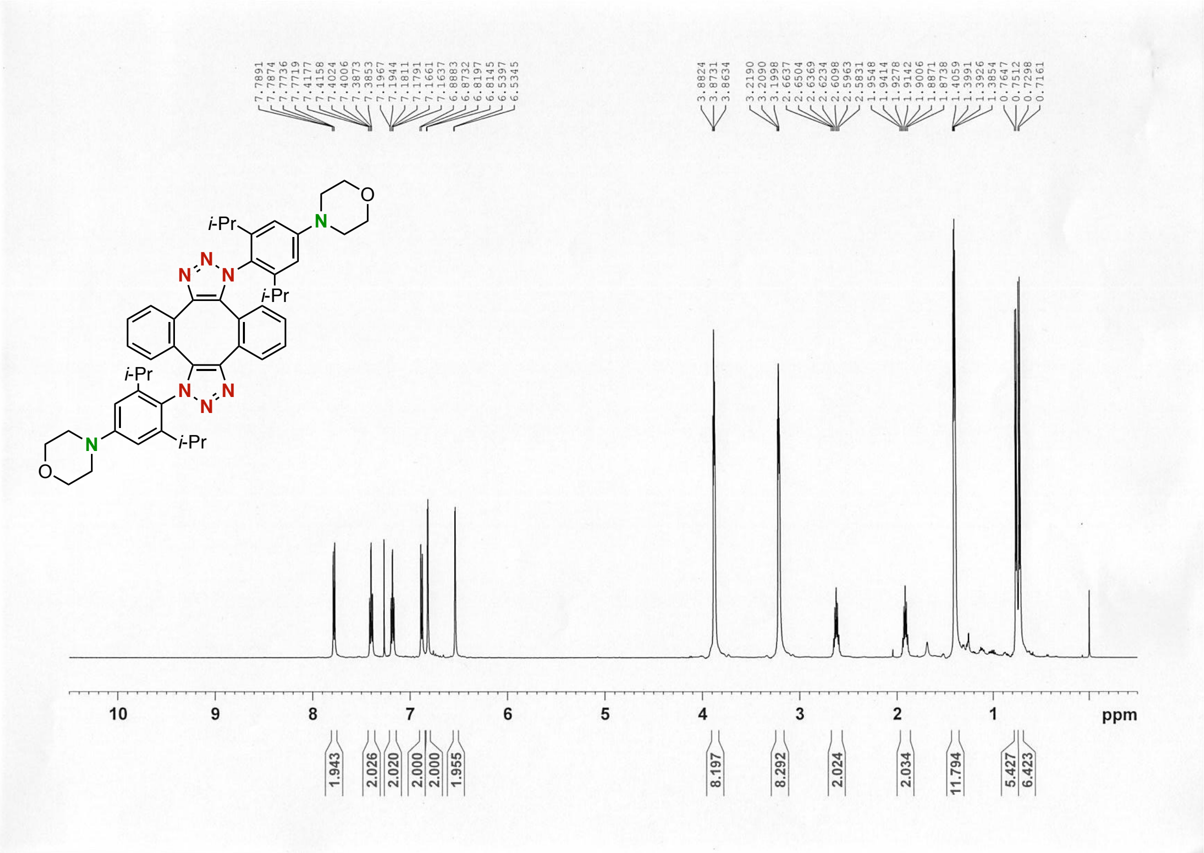


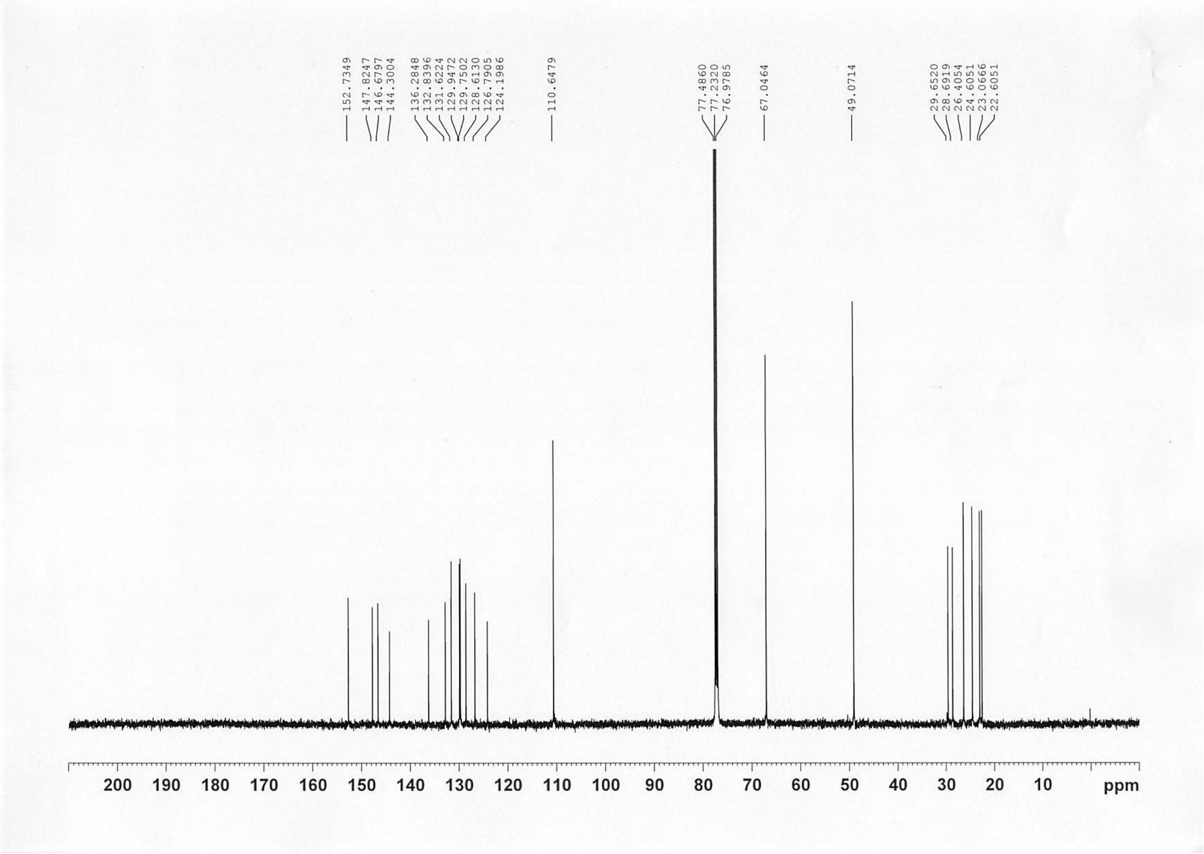
^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of *trans*-**3l** ($CDCl_3$)



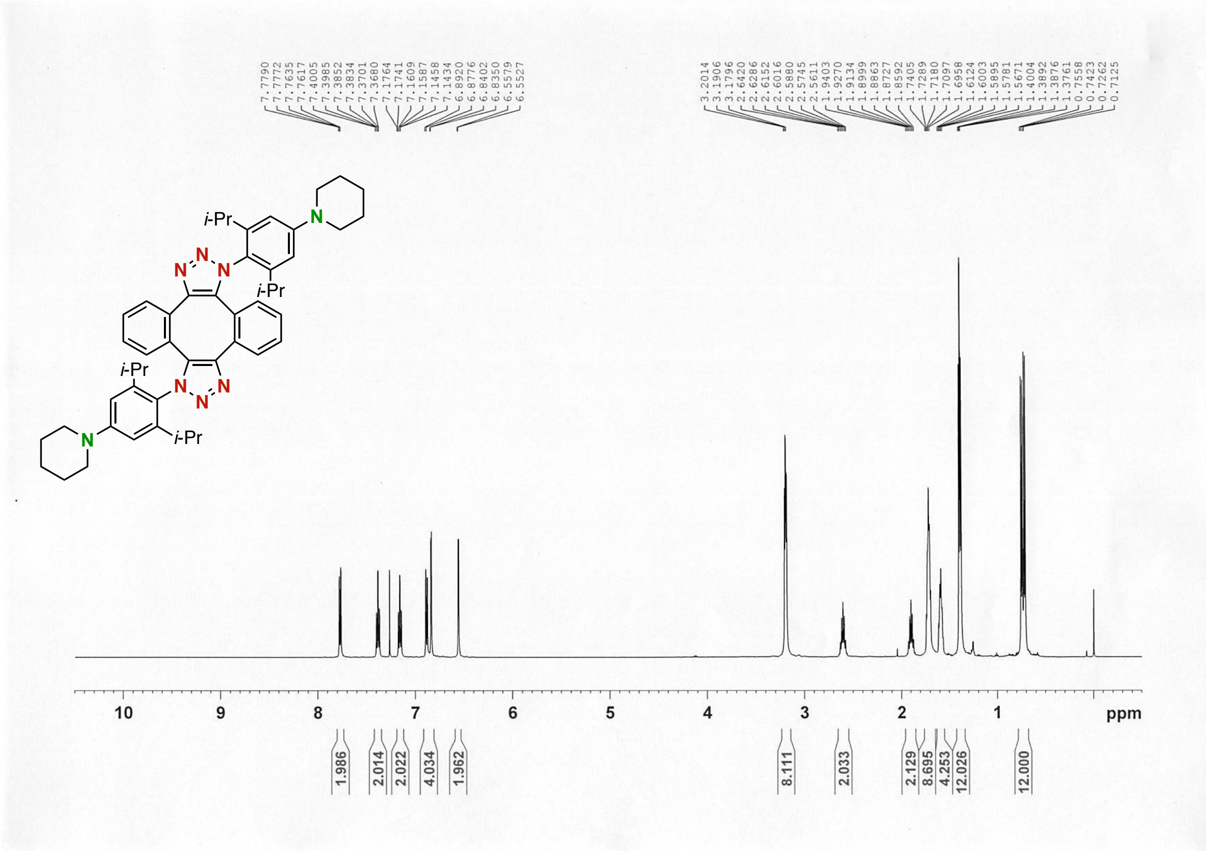


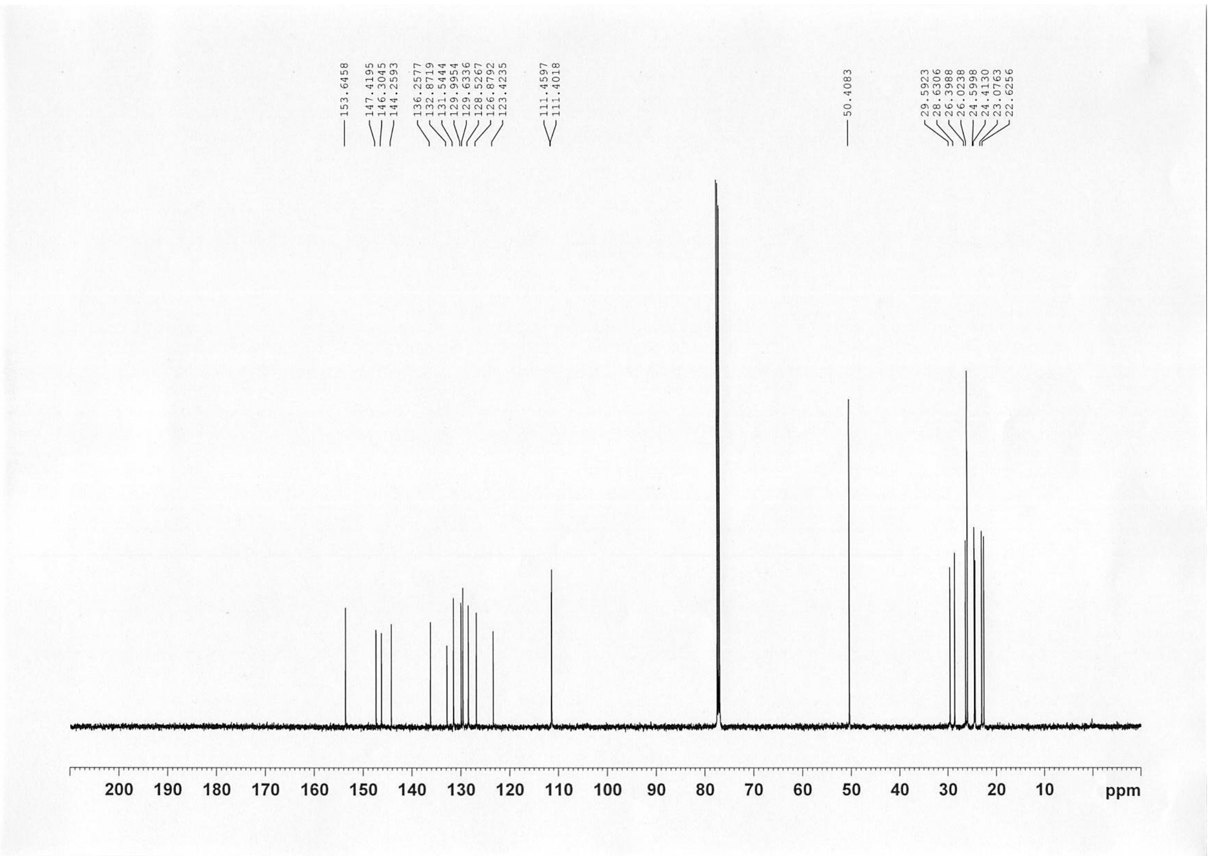
^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of *trans*-**3m** (CDCl$_3$)



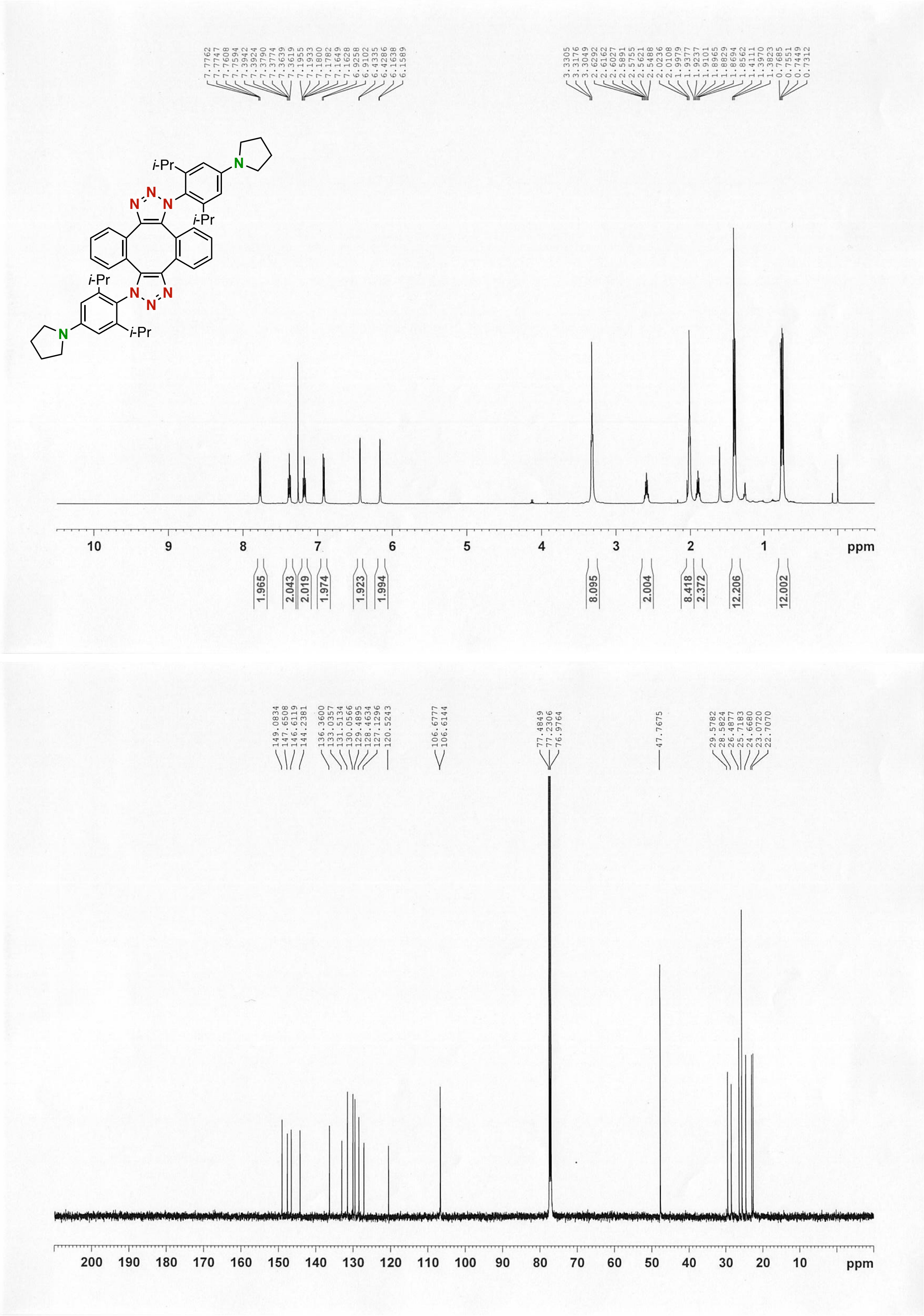


^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of *trans*-**3n** ($CDCl_3$)

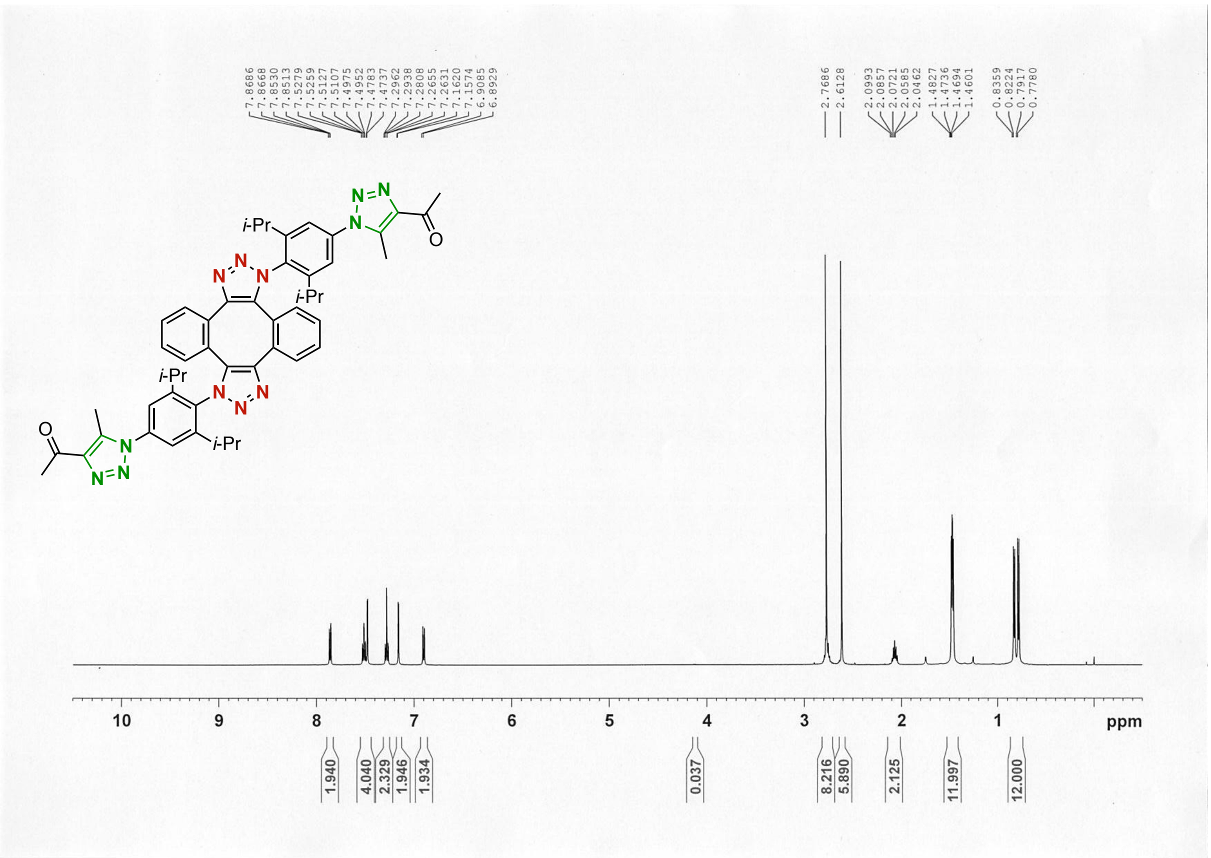


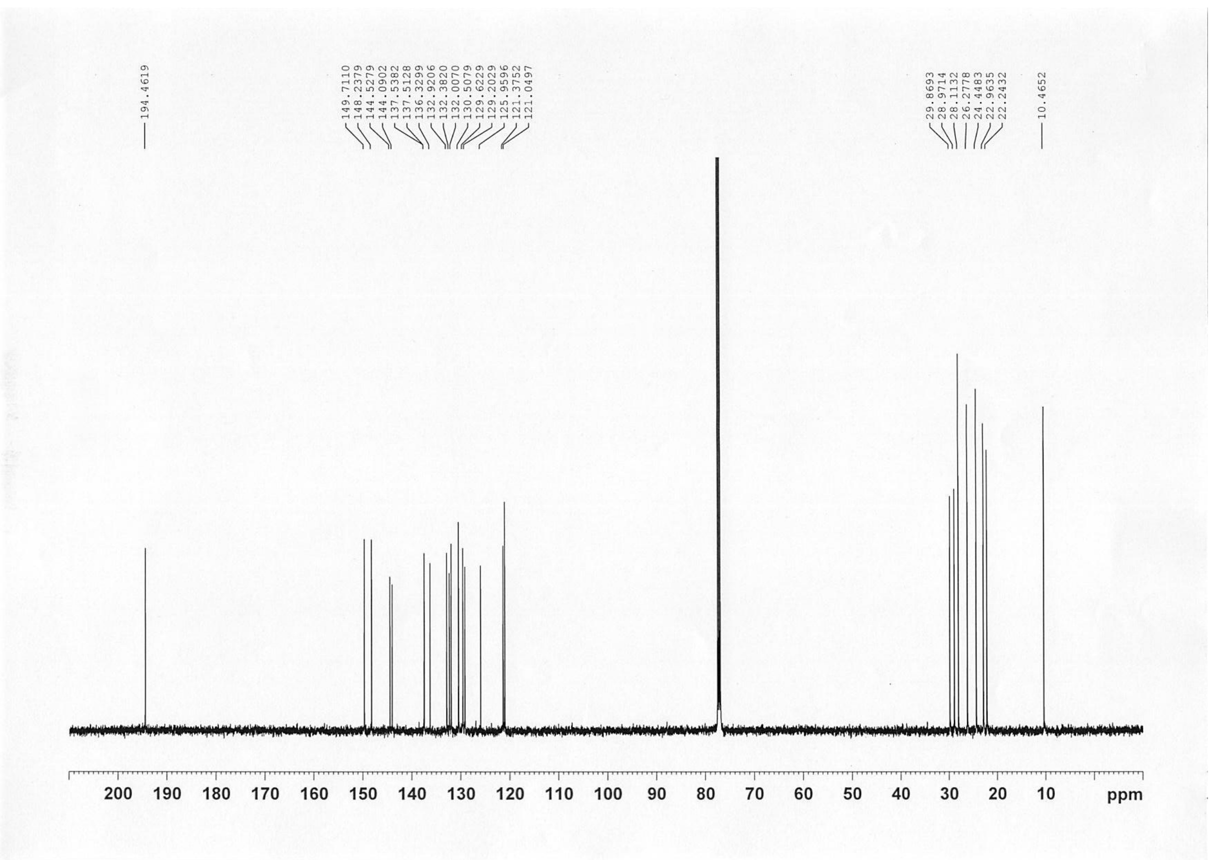


^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of *trans*-**3o** ($CDCl_3$)

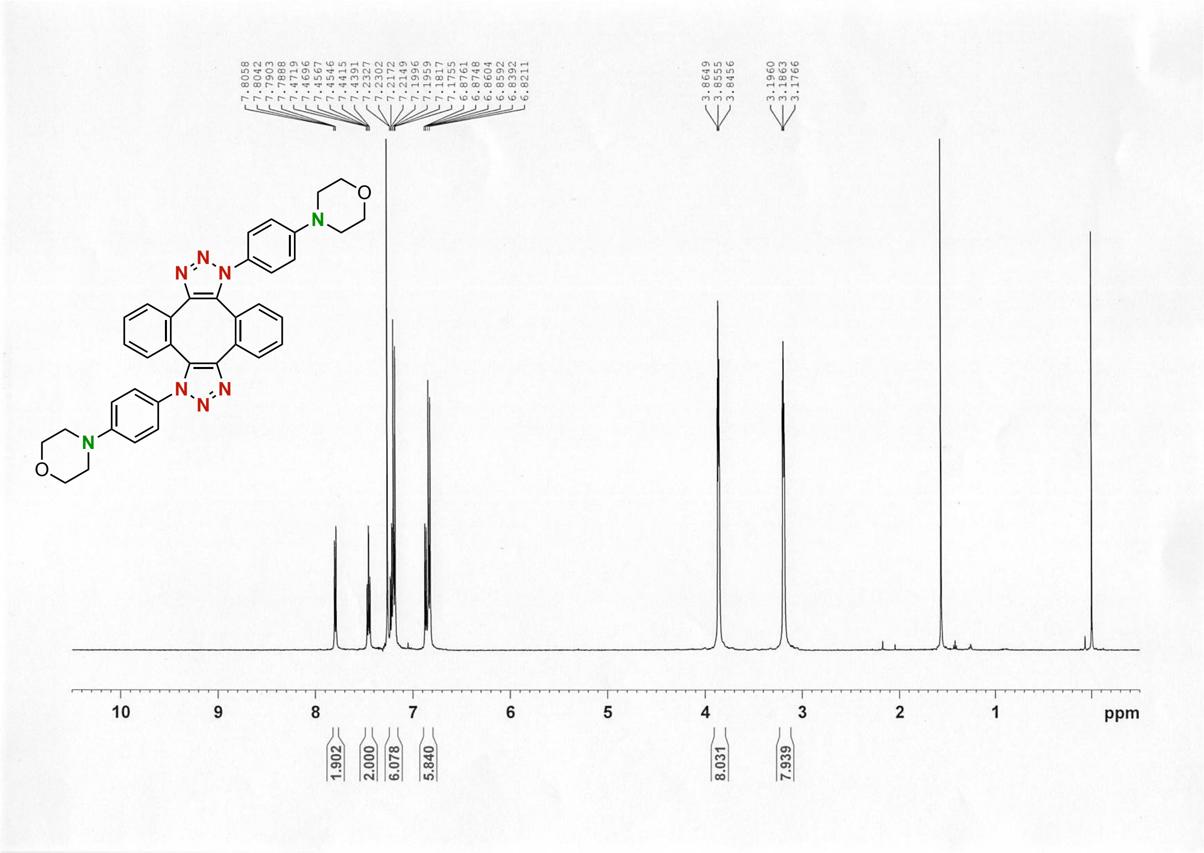


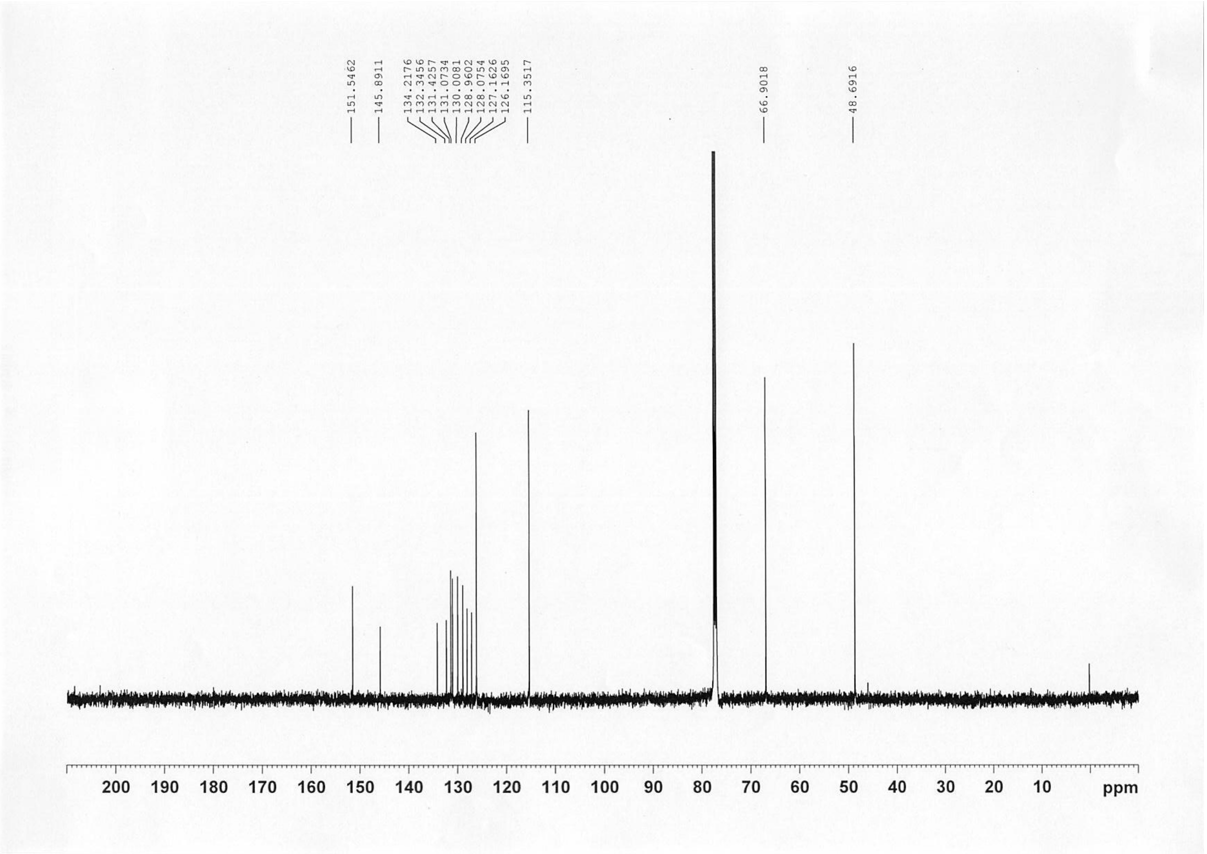
^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of *trans*-**3p** (CDCl$_3$)



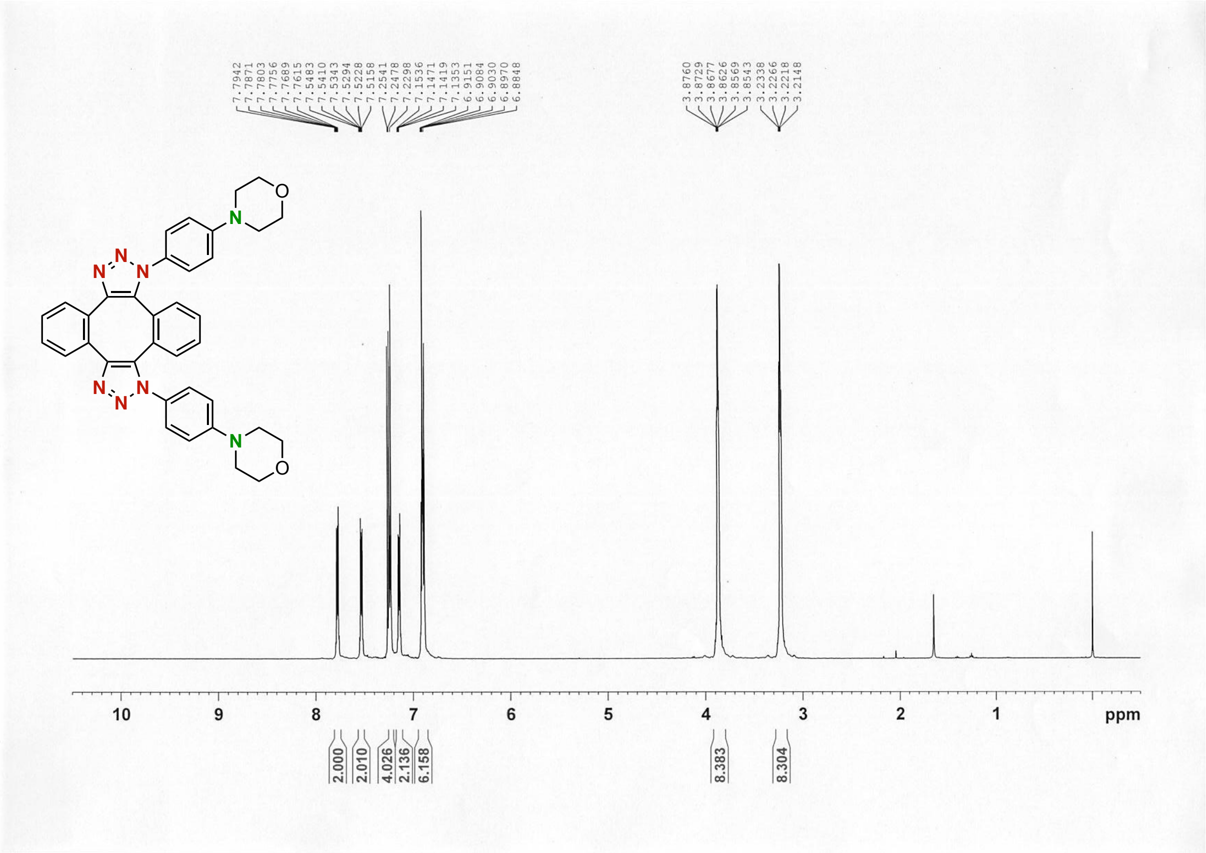


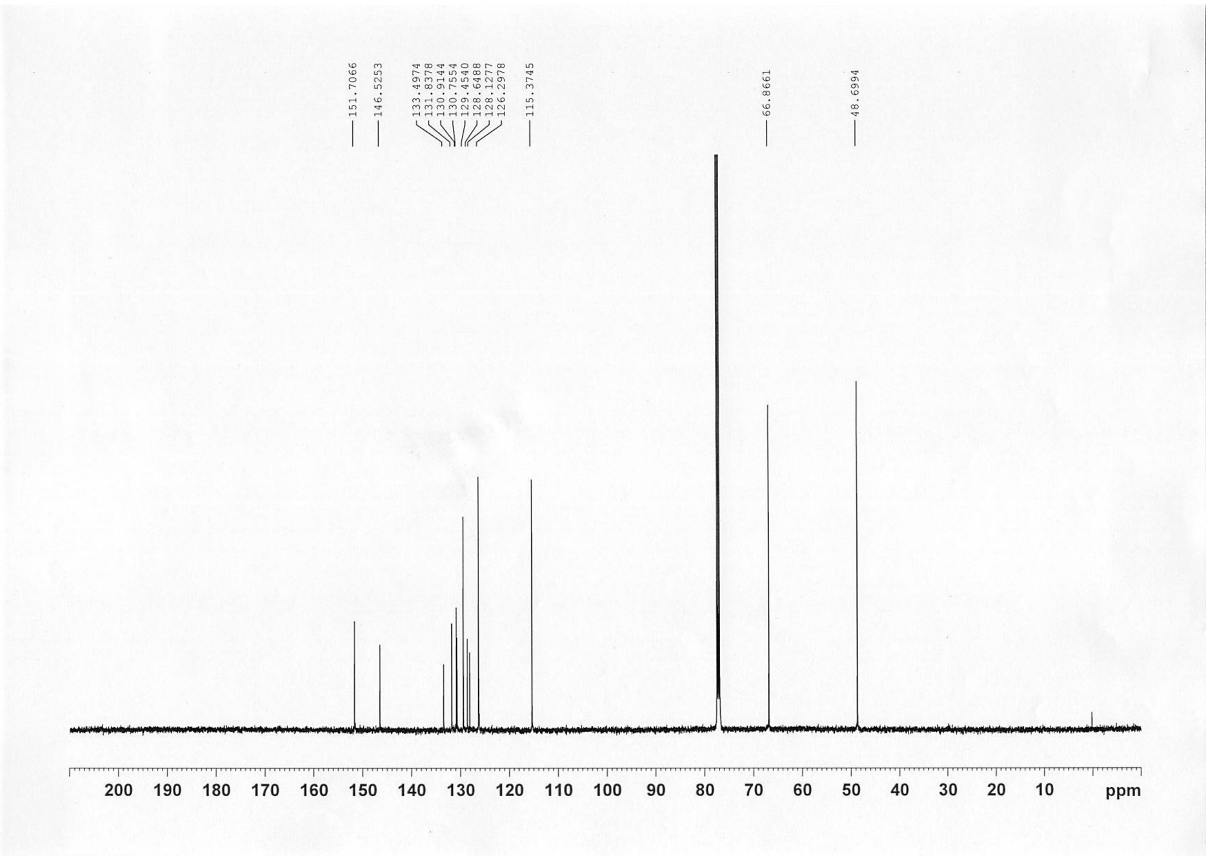
^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of *trans*-**3q** ($CDCl_3$)



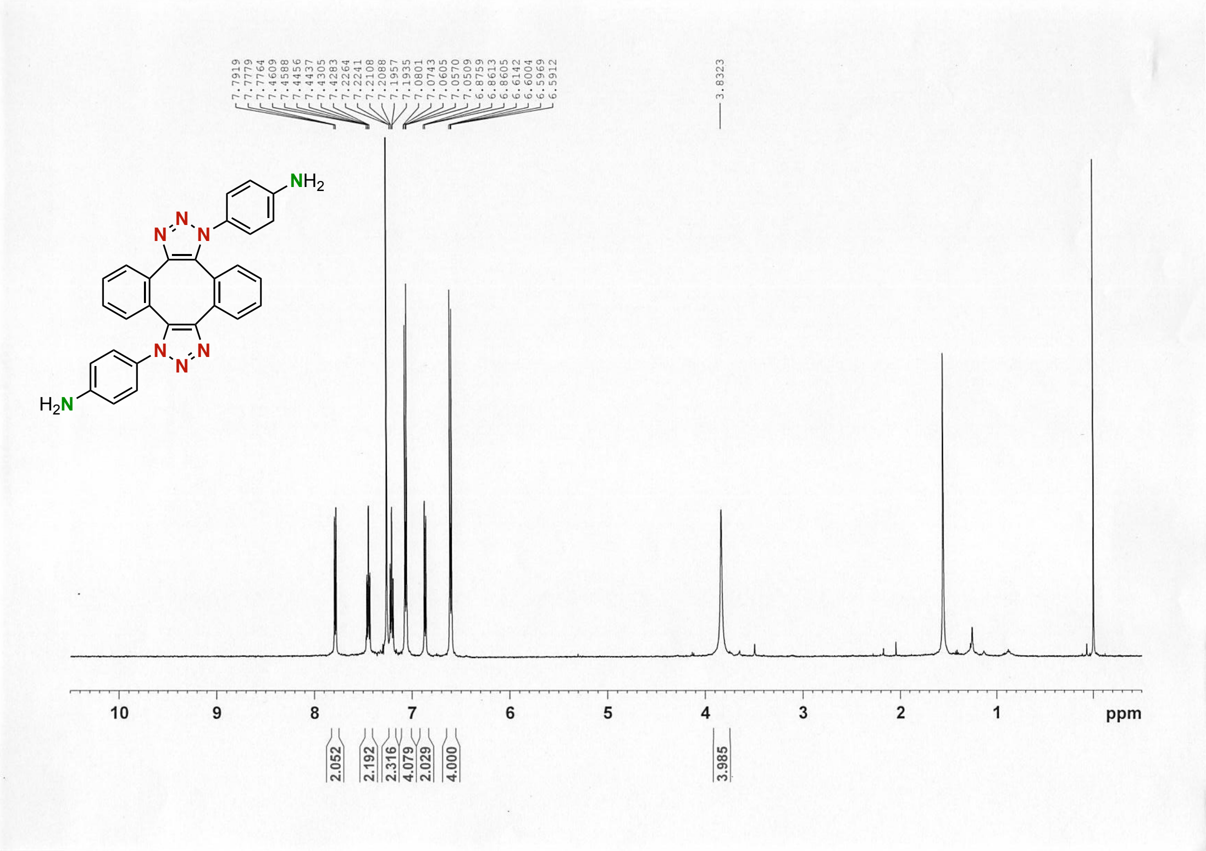


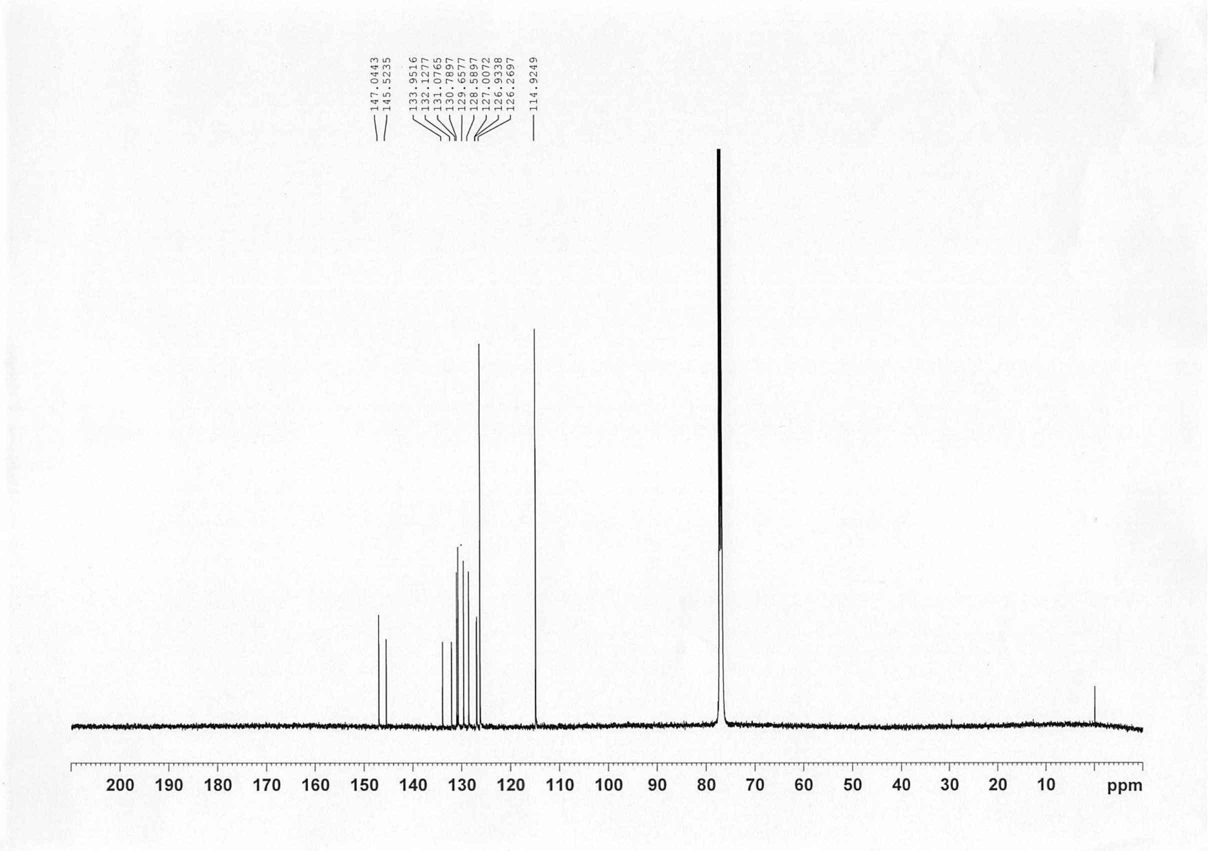
^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of *cis*-**3q** (CDCl$_3$)



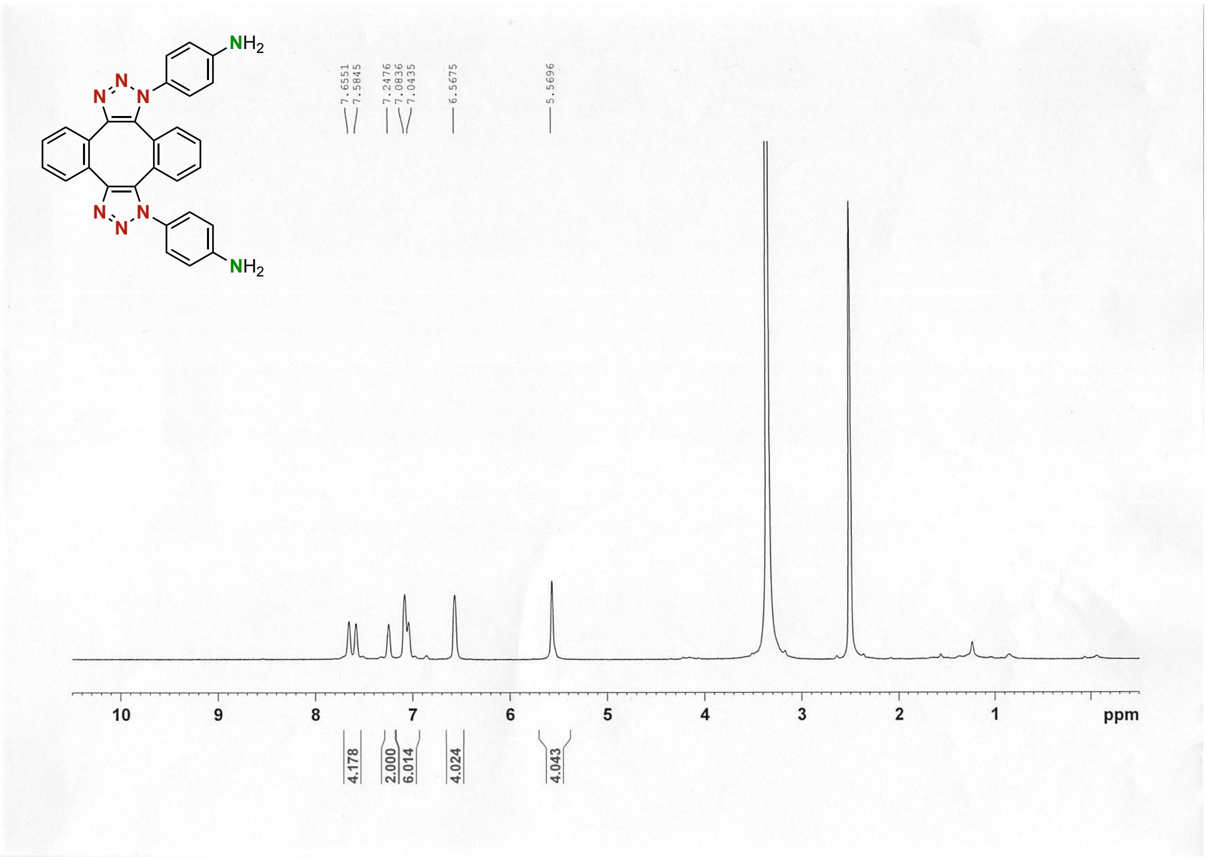


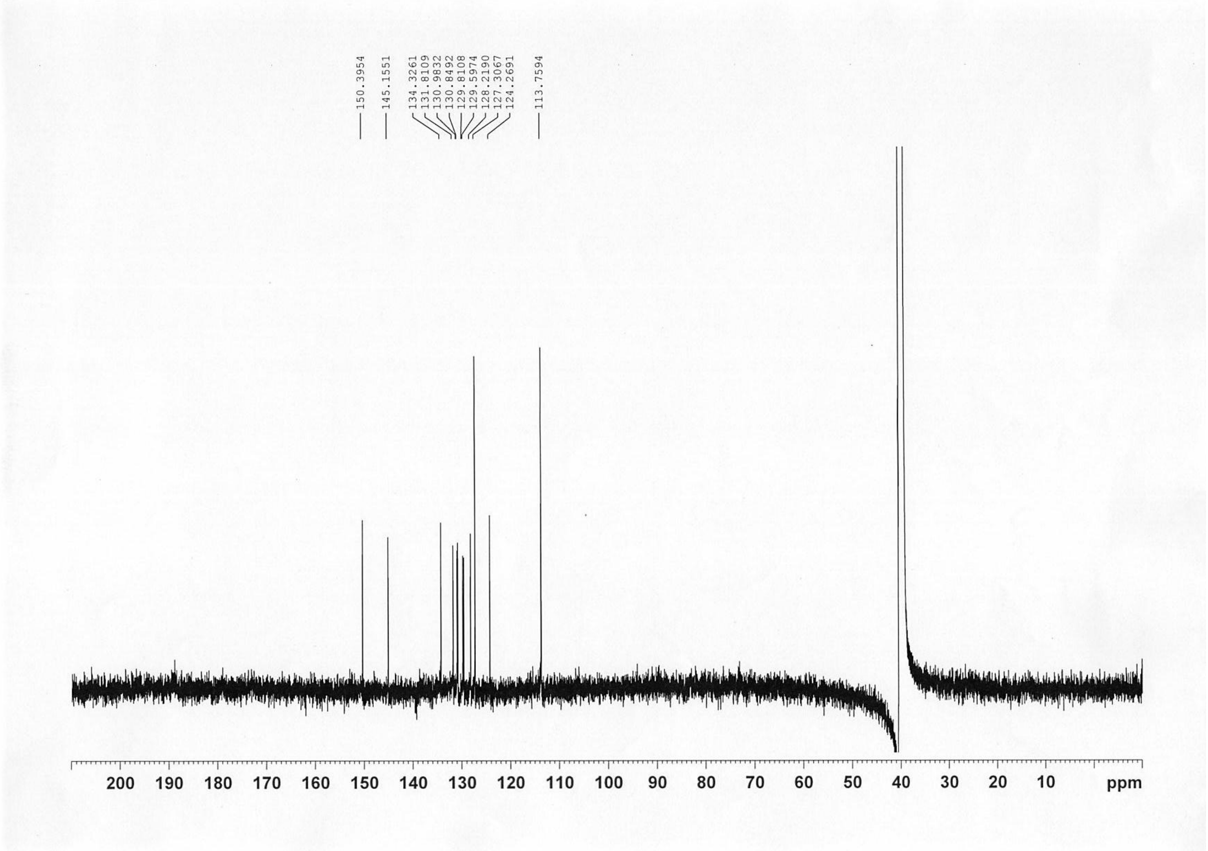
^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of *trans*-**3r** ($CDCl_3$)



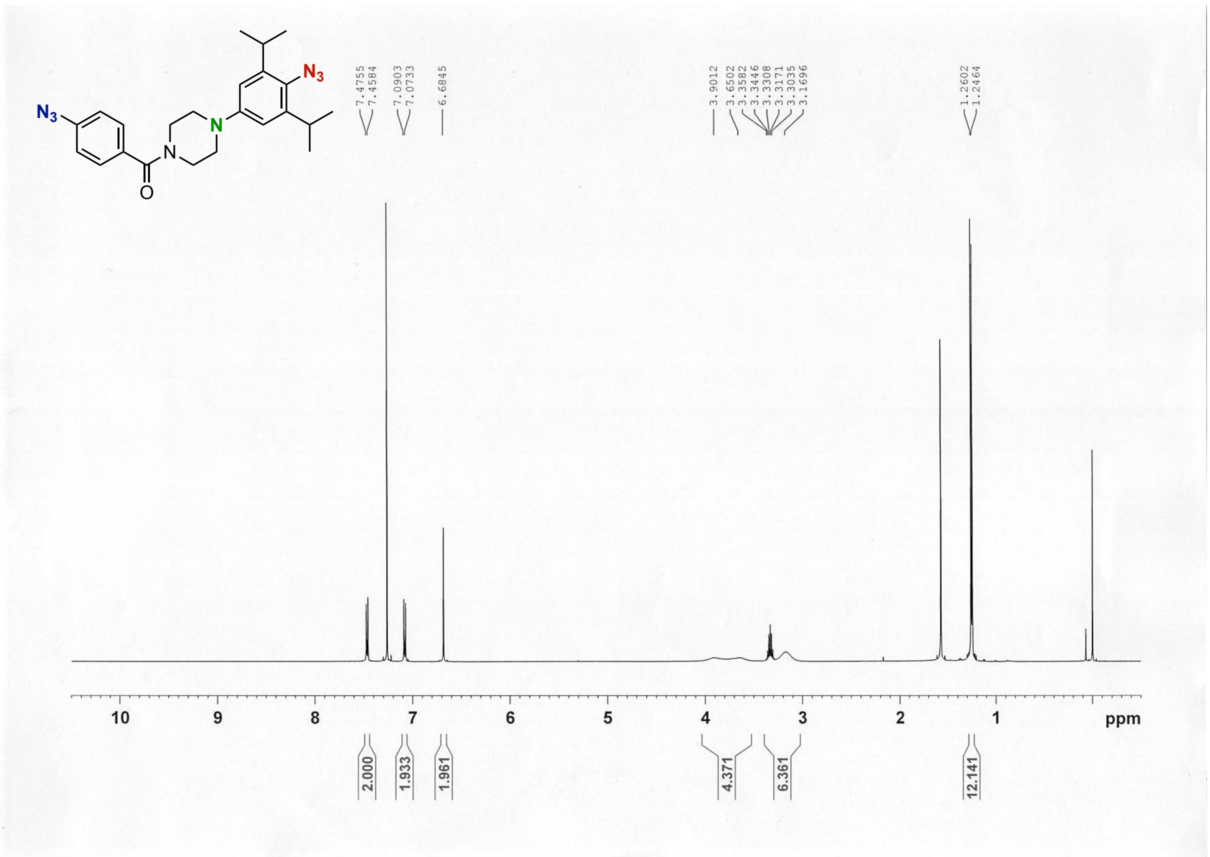


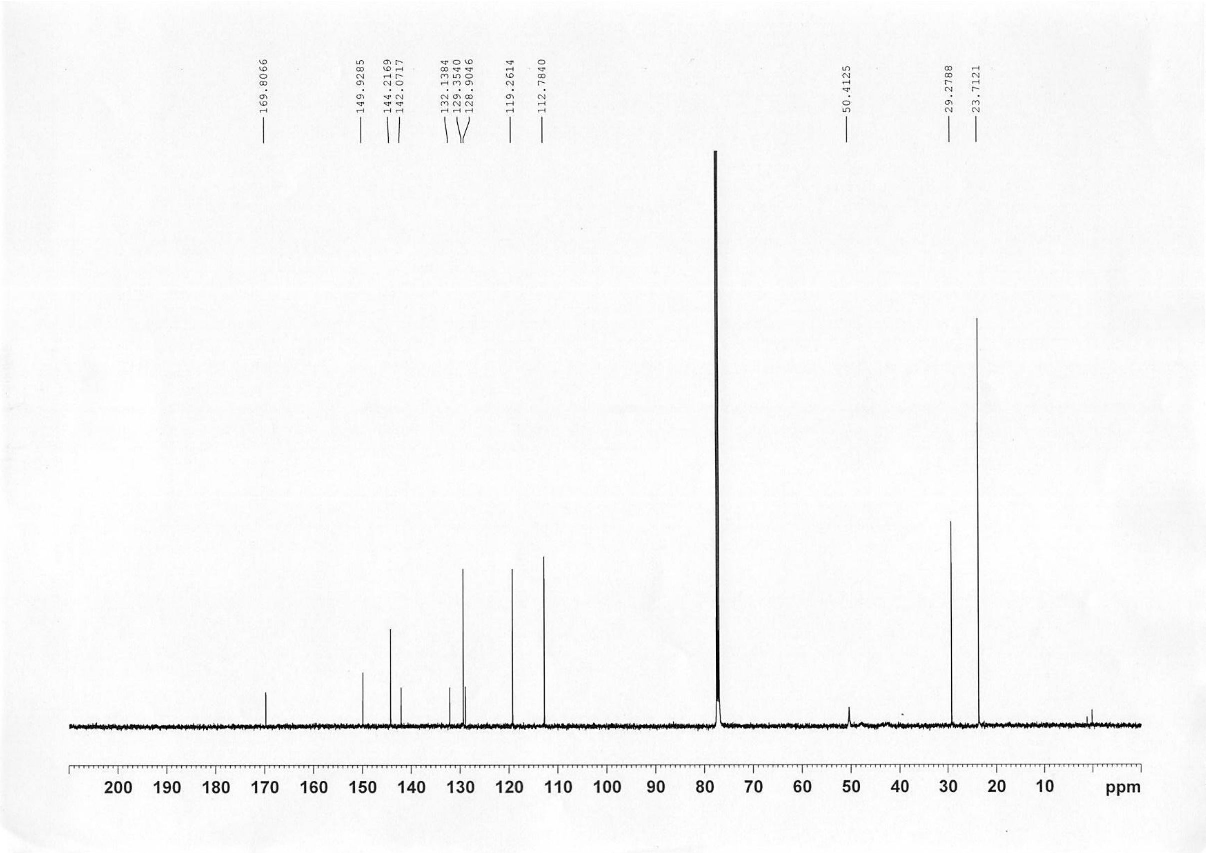
^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of *cis*-**3r** (DMSO-d_6)



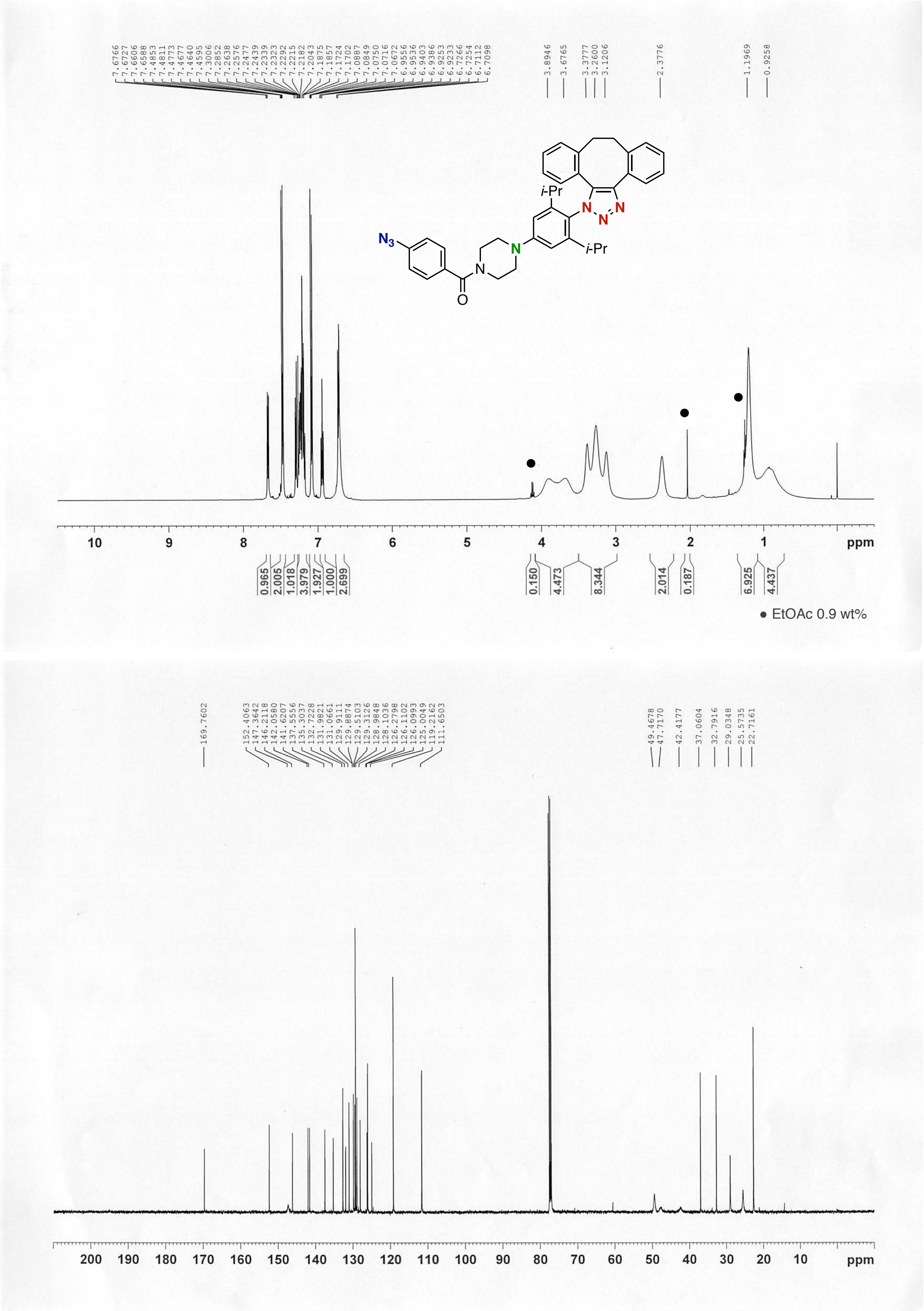


^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of **6** (CDCl$_3$)

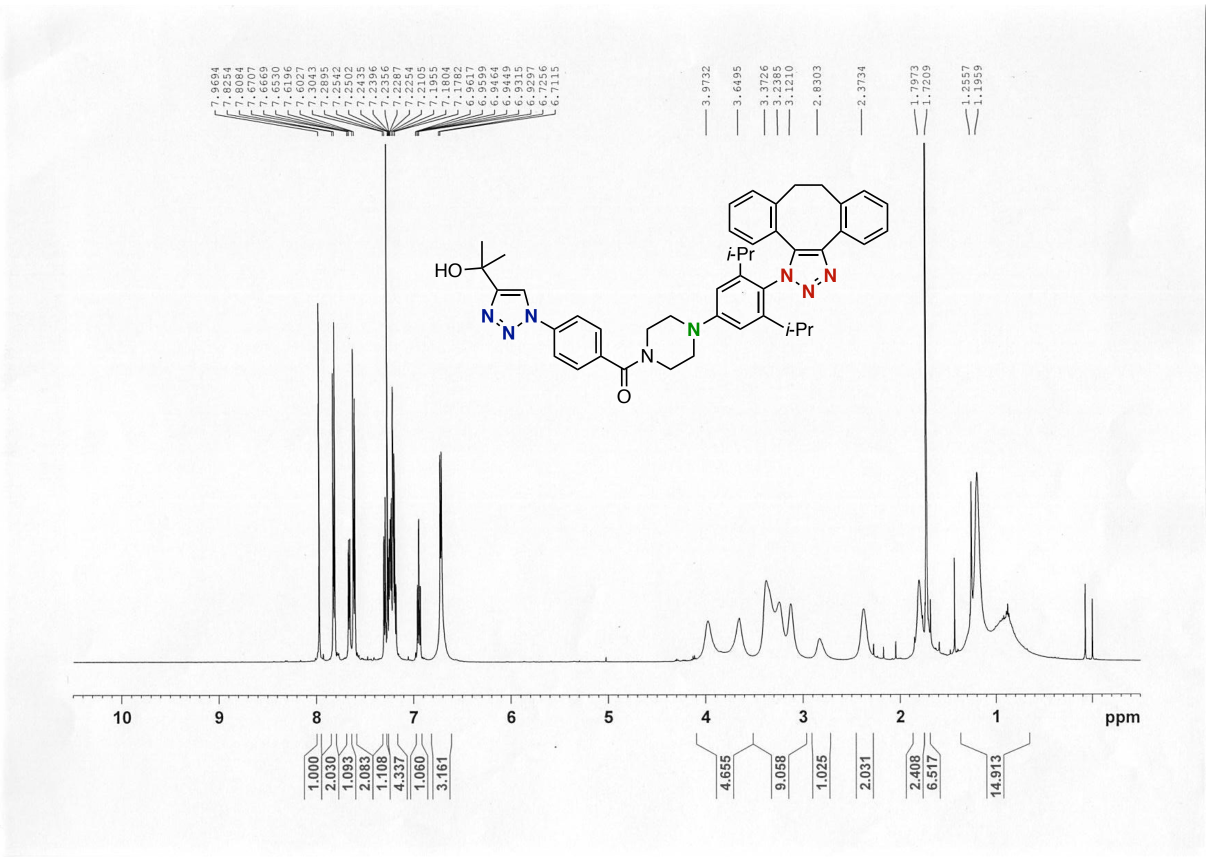


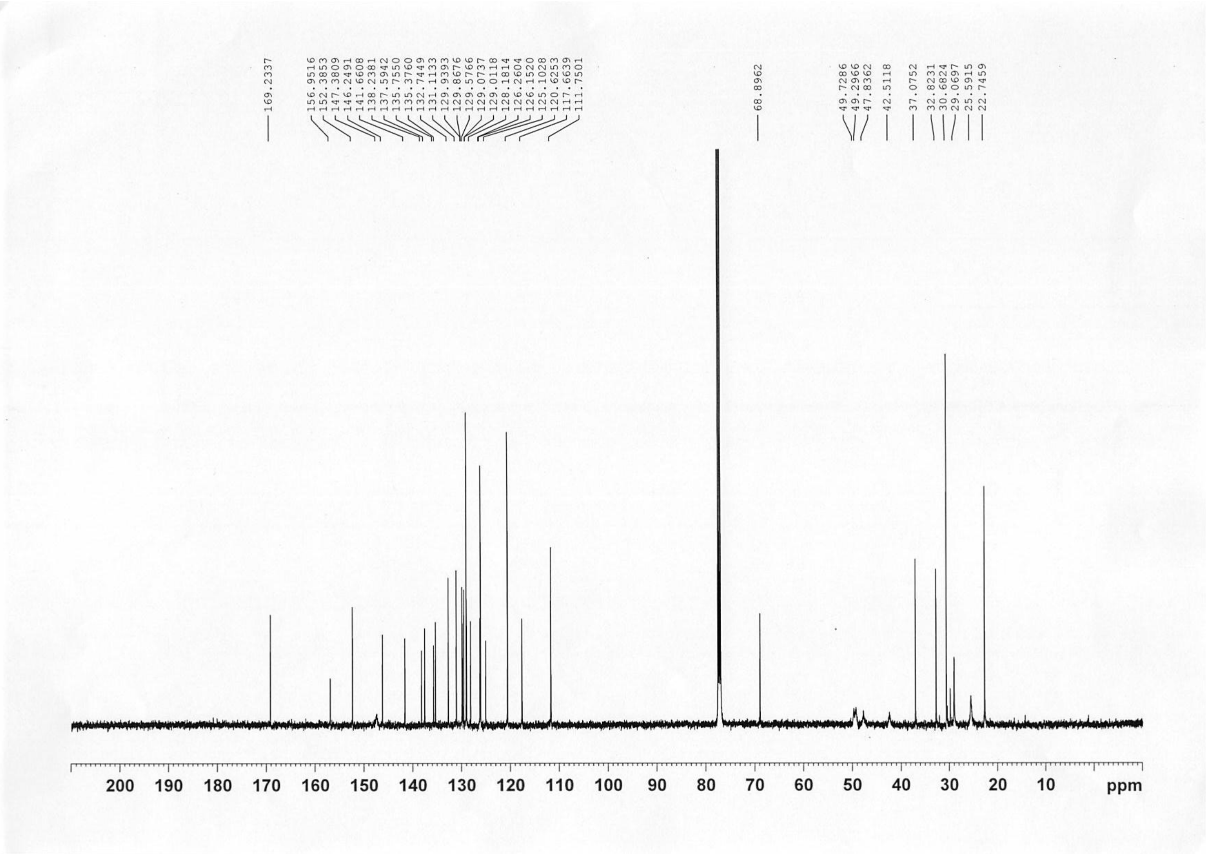


^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of **S5** ($CDCl_3$)

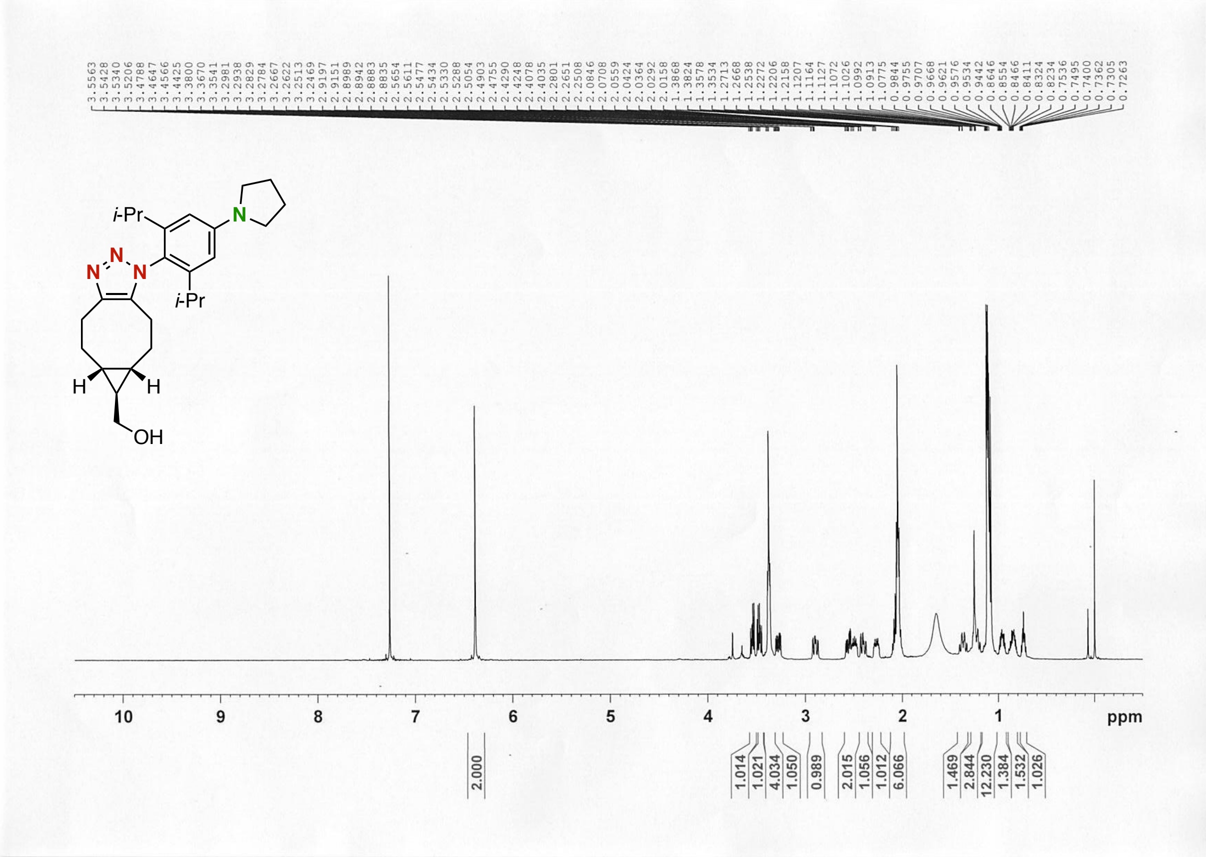


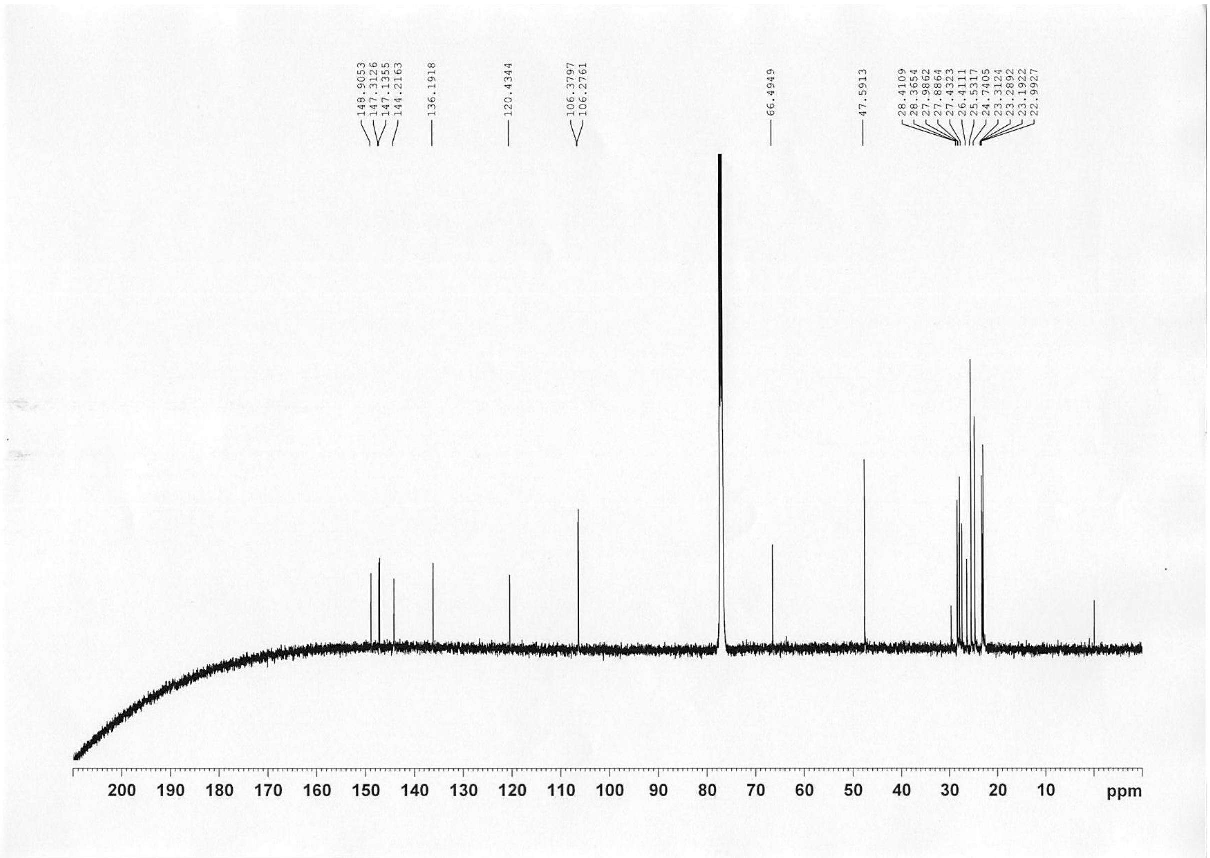
^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of **9** ($CDCl_3$)



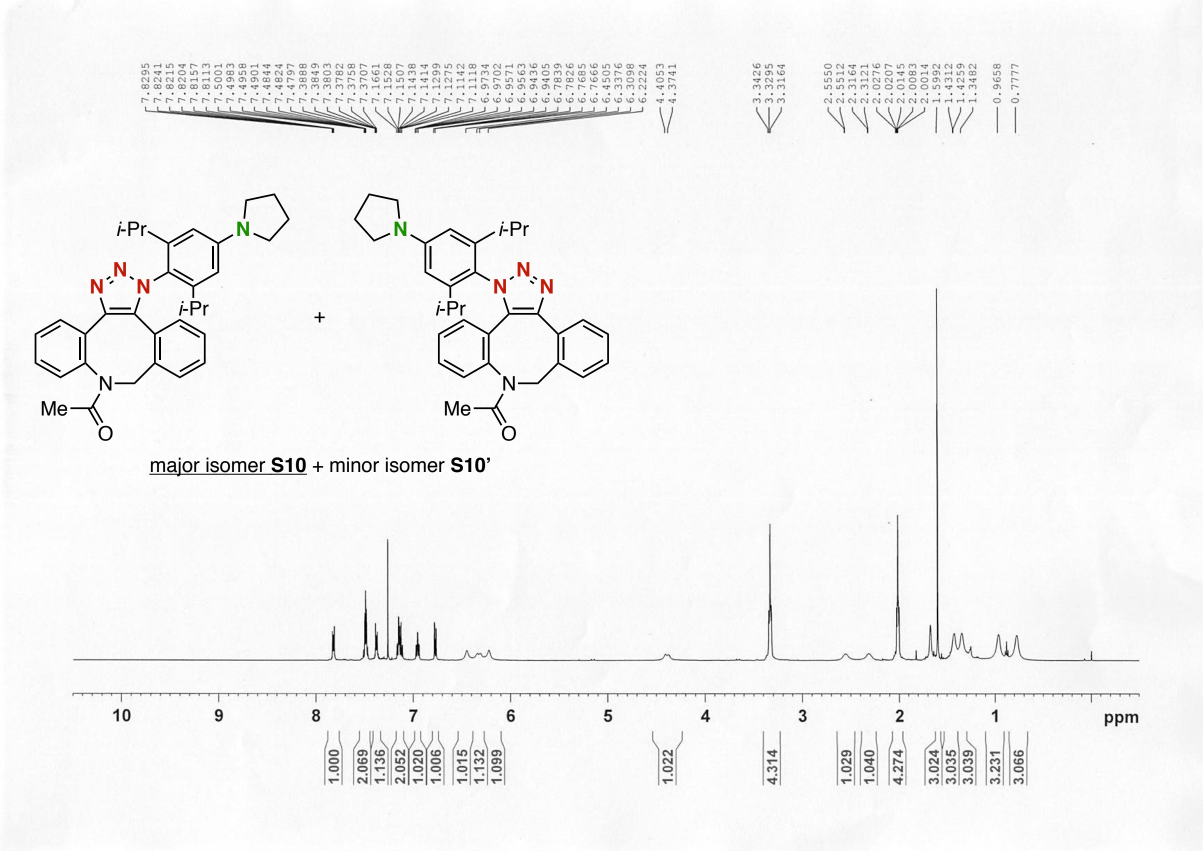


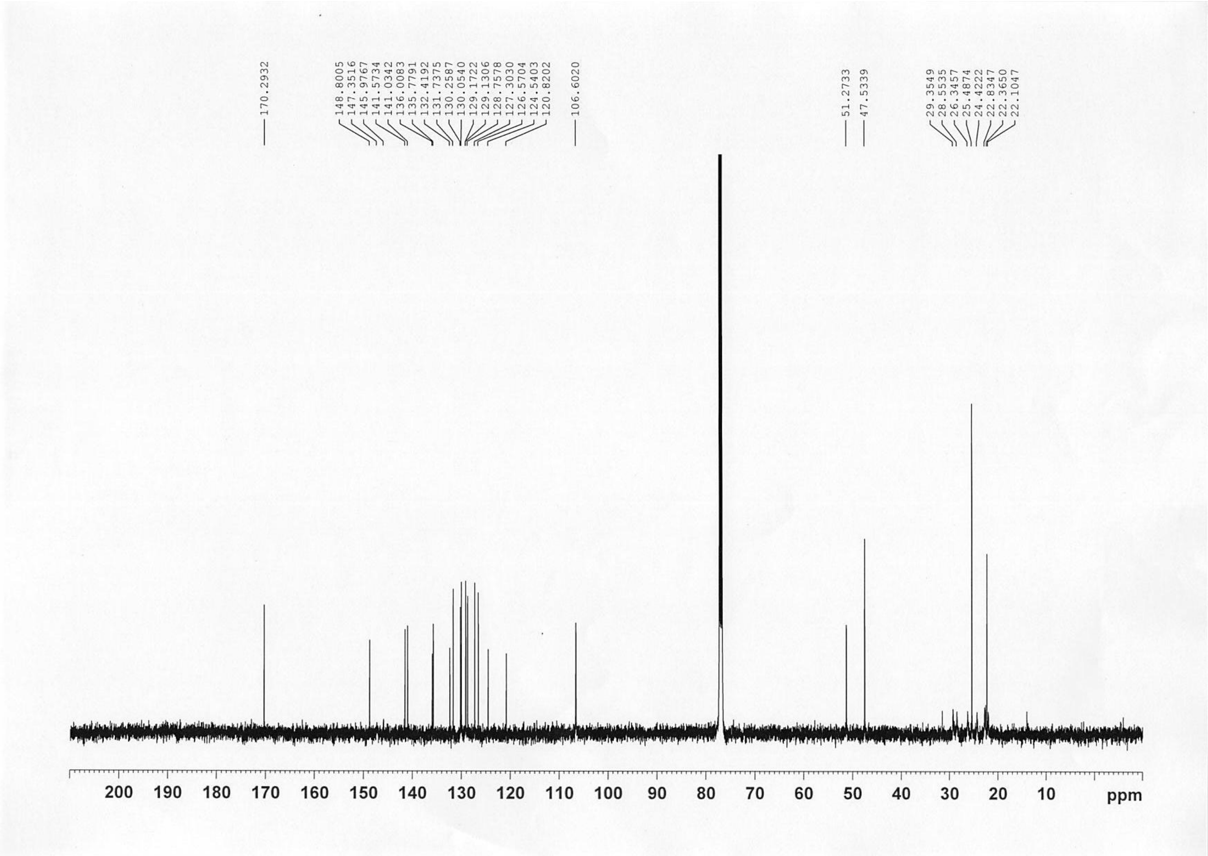
^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of **S8** (CDCl$_3$)



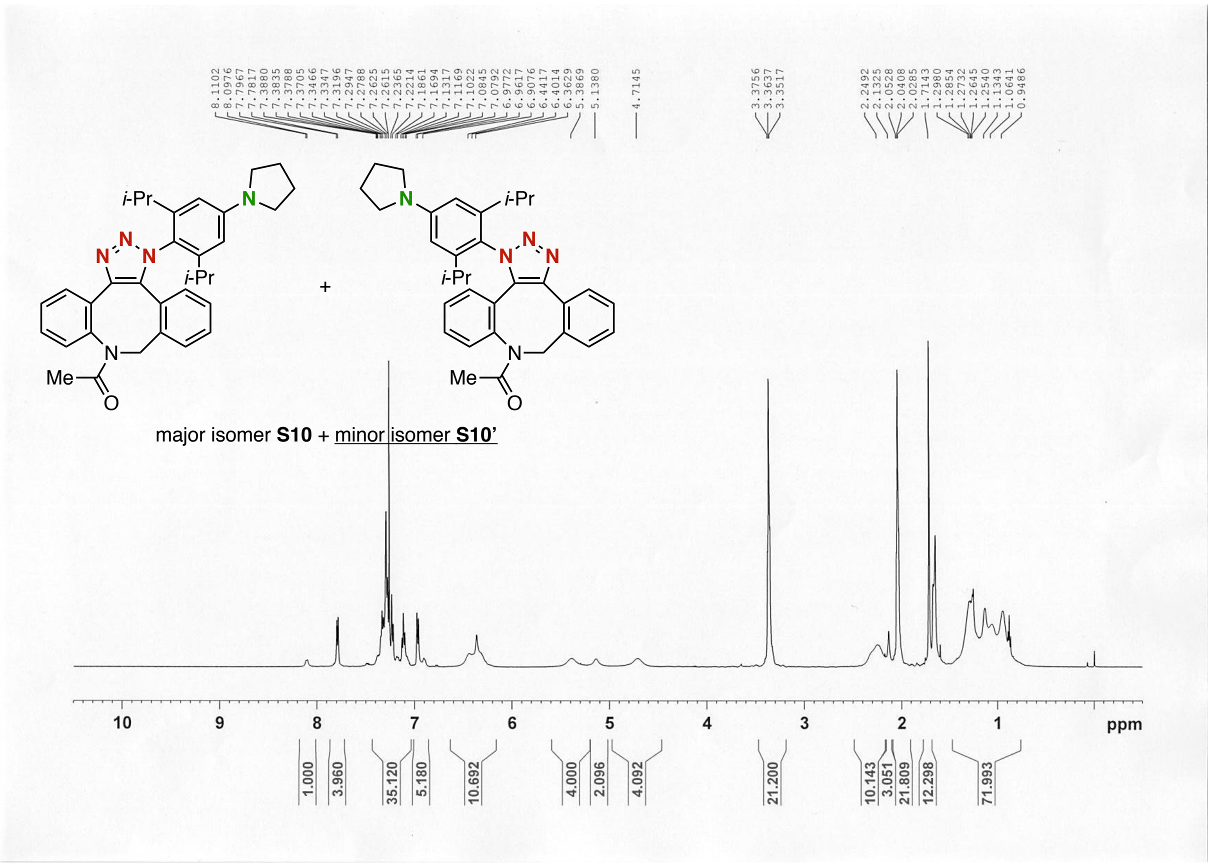


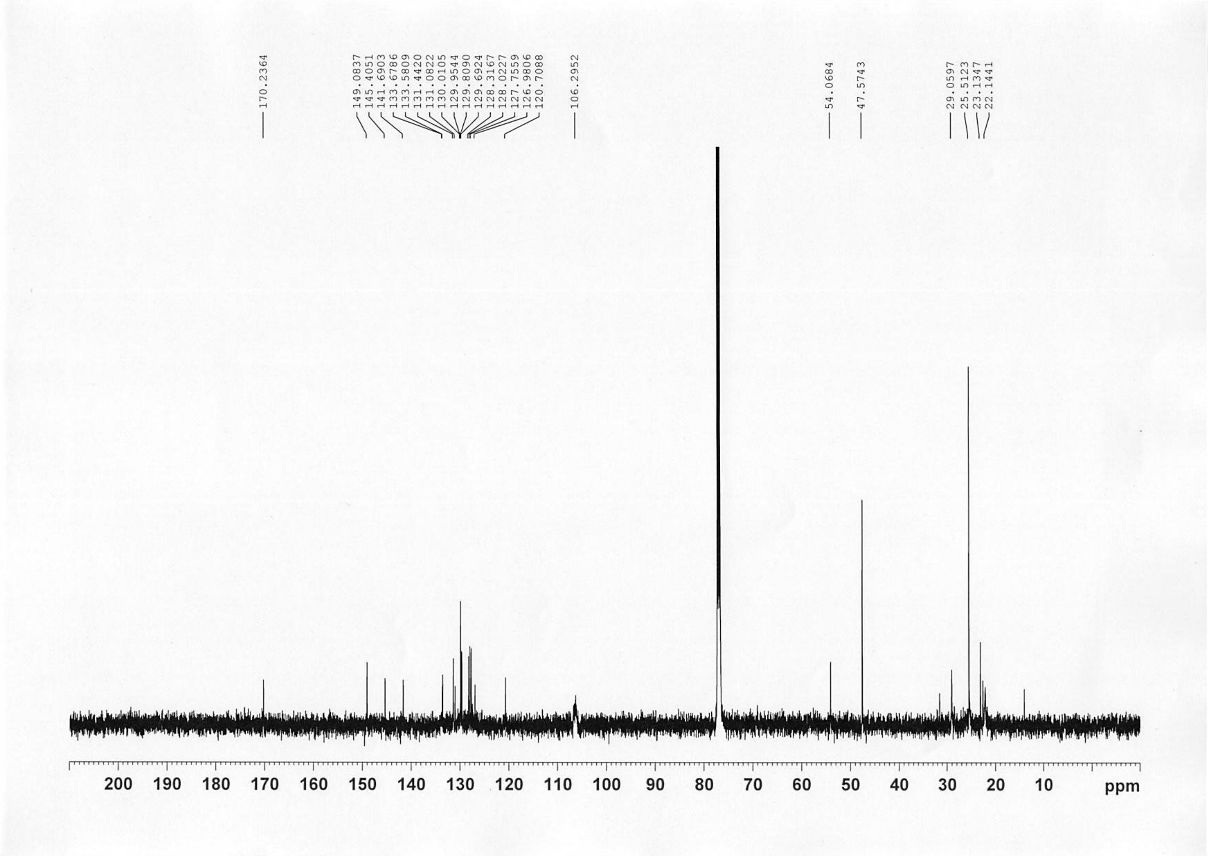
^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of major isomer **S10** ($CDCl_3$)



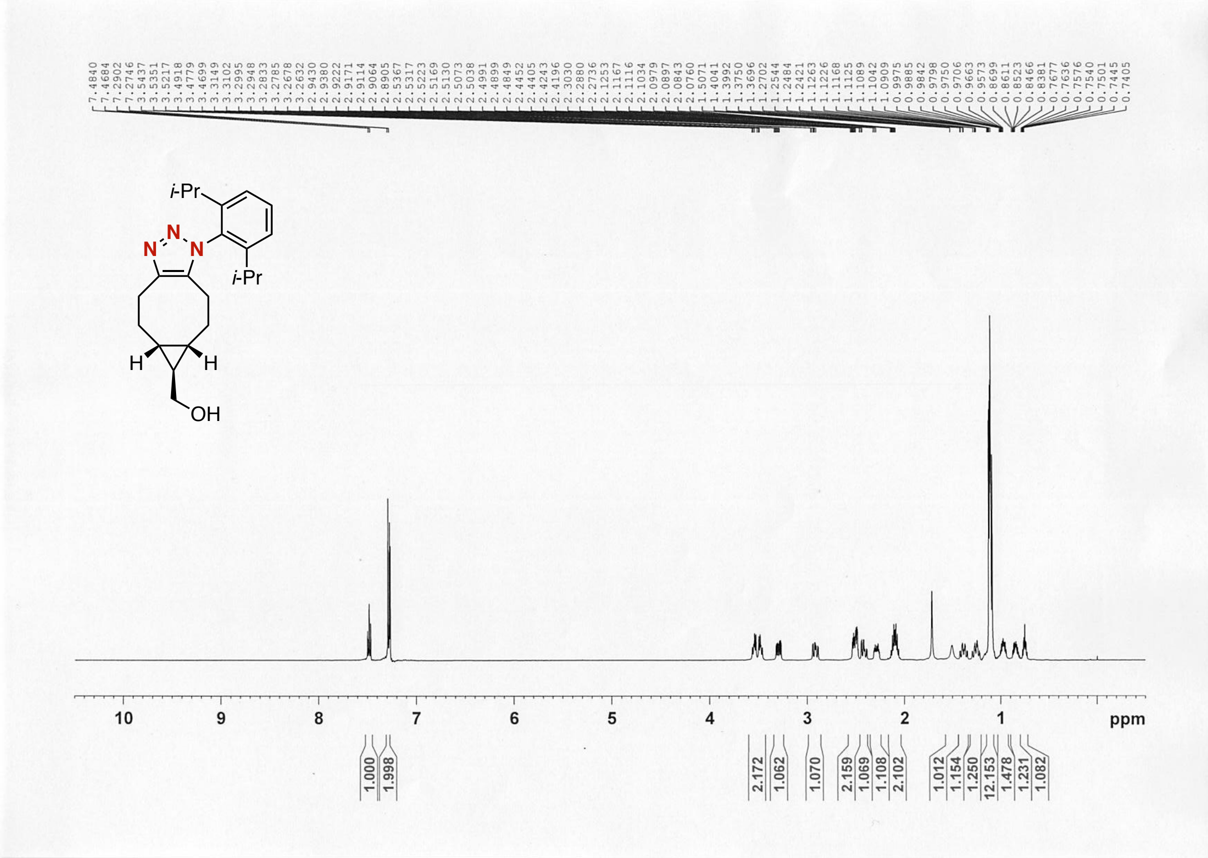


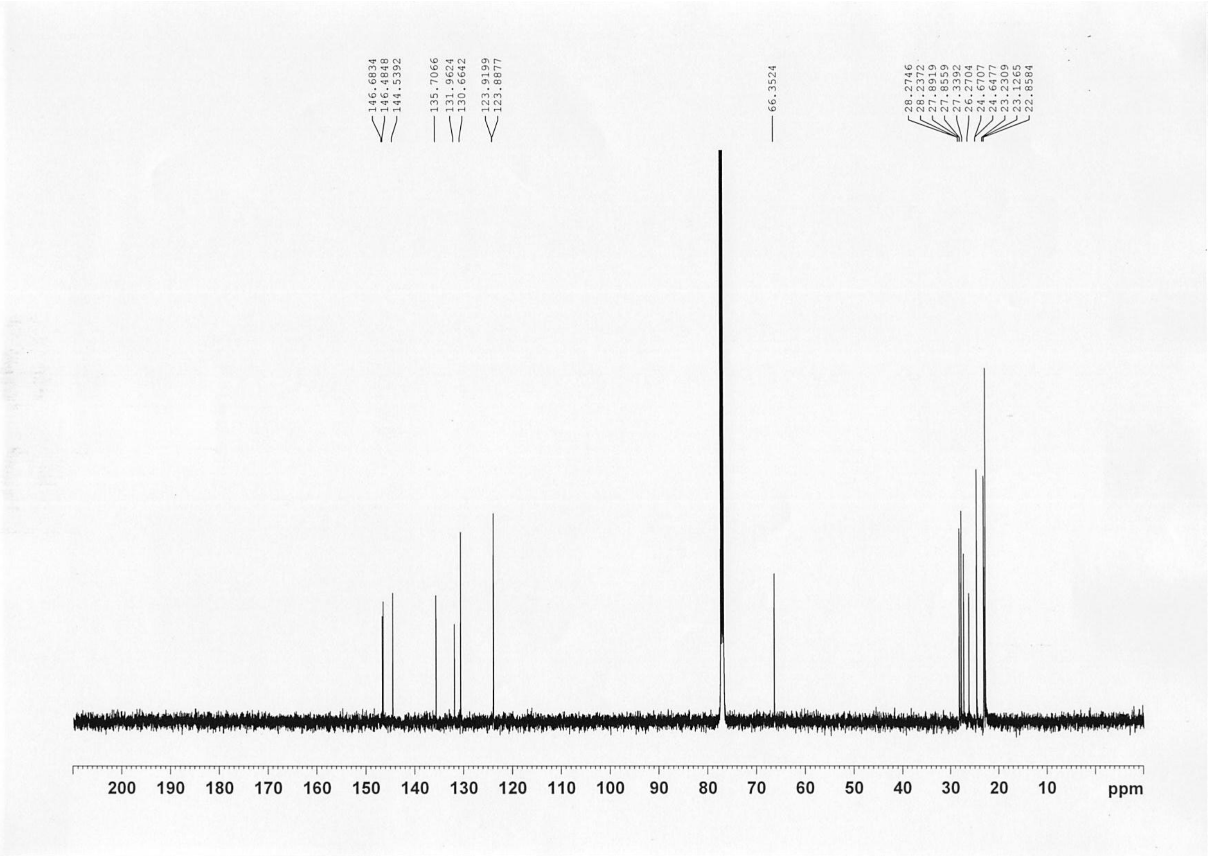
^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of minor isomer **S10’** ($CDCl_3$)



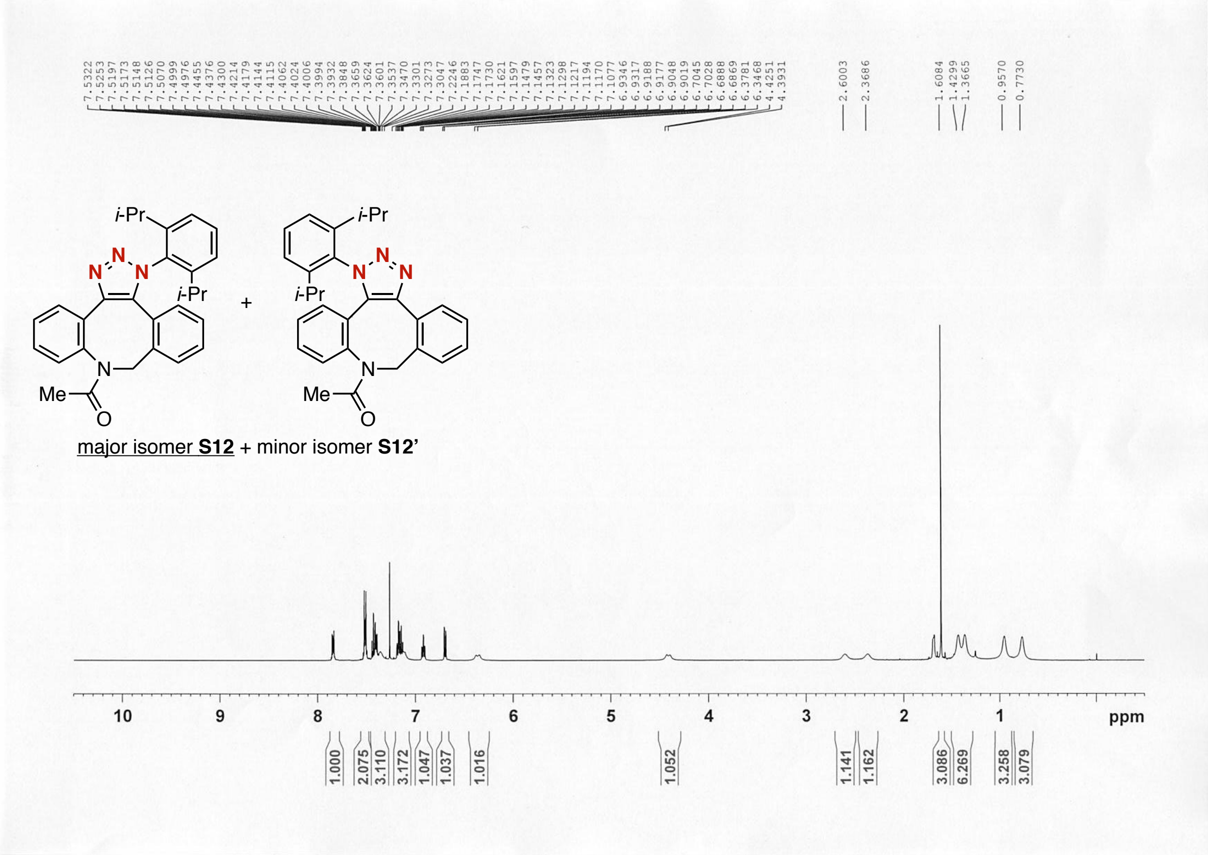


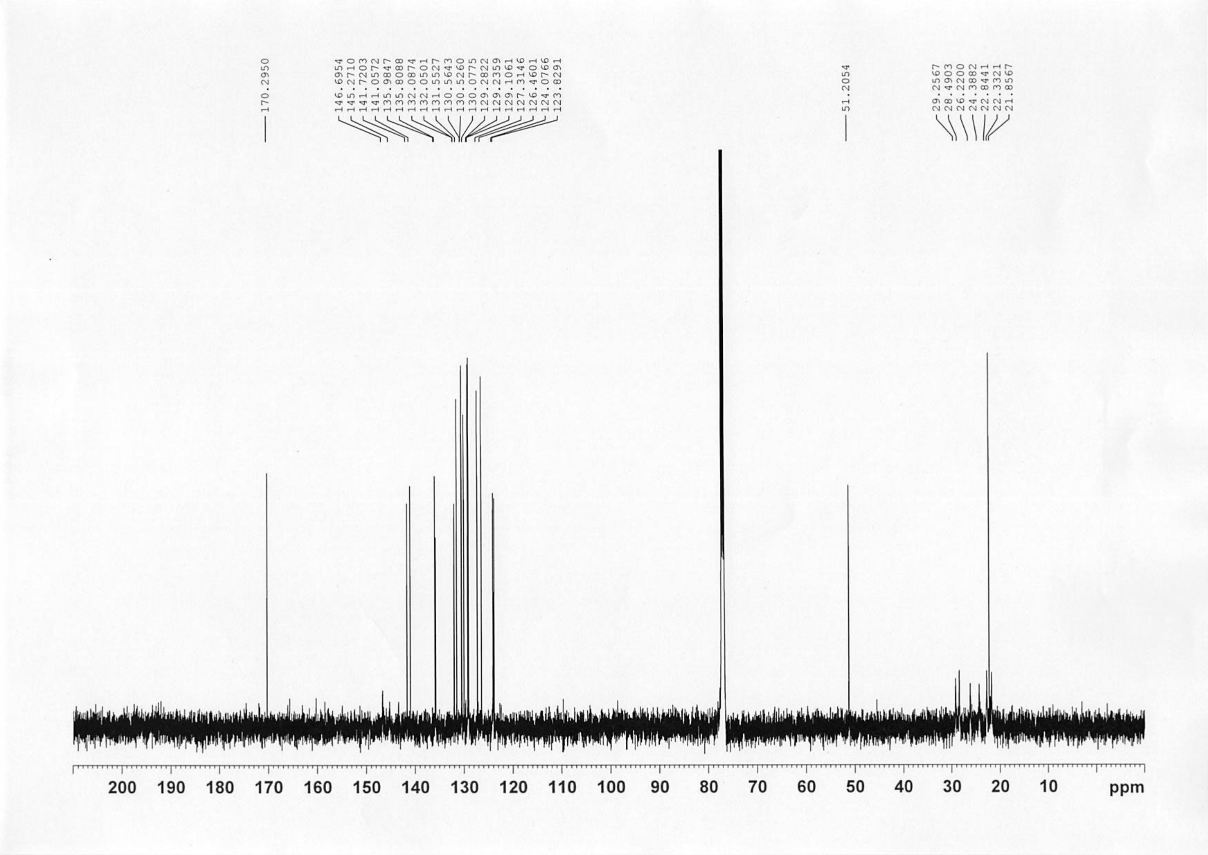
^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of **S11** ($CDCl_3$)





^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of major isomer **S12** ($CDCl_3$)





^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of minor isomer **S12’** ($CDCl_3$)