Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Acid-catalyzed ring-expansion of 4-(1-hydroxycyclobutyl)-1,2,3-triazoles

Mingchuan Xu, Lei Liu, Tao Wang, Han Luo, Meili Hou, Luan Du, Xiaolan Xin,

Qixing Lu and Baosheng Li*

School of Chemistry and Chemical Engineering, Chongqing University, 174 Shazheng Street, Chongqing, 400044, China.

* E-mail: libs@cqu.edu.cn

Table of Contents

1. General information

All the reactions were carried out under the argon atmosphere with magnetic stirring unless otherwise noted. Reagents were purchased from commercial sources. TsN_3 was 75% w/w in ethyl acetate solution. All solvents were dried or distilled prior to use according to the standard methods. DCM was distilled over CaH_2, THF was distilled over Na/benzophenone and toluene was distilled over Na. Glassware was dried in an oven before use. All new compounds were characterized by NMR spectroscopy, IR spectroscopy, high-resolution mass spectroscopy (HRMS).

^1H and ^{13}C NMR spectra were recorded on Bruker 500 spectrometer (^1H at 500 MHz and ^{13}C at 126 MHz) and Agilent 400MR DD2 spectrometer (^1H at 400 MHz and ^{13}C at 101 MHz). Chemical shifts for ^1H NMR spectra are reported as δ in units of parts per million (ppm) downfield from $SiMe_4$ (δ 0.00) and relative to the signal of $SiMe_4$ (δ 0.00 singlet). ^1H NMR splitting patterns are designated as singlet (s), doublet (d), triplet (t), quartet (q), multiplets (m), doublet of doublet (dd). Coupling constants are reported as a *J* value in Hz. ^{13}C NMR spectra are reported as δ in units of parts per million (ppm) downfield from $SiMe_4$ (δ 0.00), $CDCl_3$ (δ 7.60), CD_3OD (δ 3.31), DMSO-d_6 (δ 2.50), and relative to the signal of chloroform-*d* (δ 77.00 triplet), $CDCl_3$ (δ 49.00 septet) and DMSO- d_6 (δ 39.51 septet). ^{13}C NMR spectra were recorded on the same spectrometer with complete proton decoupling.

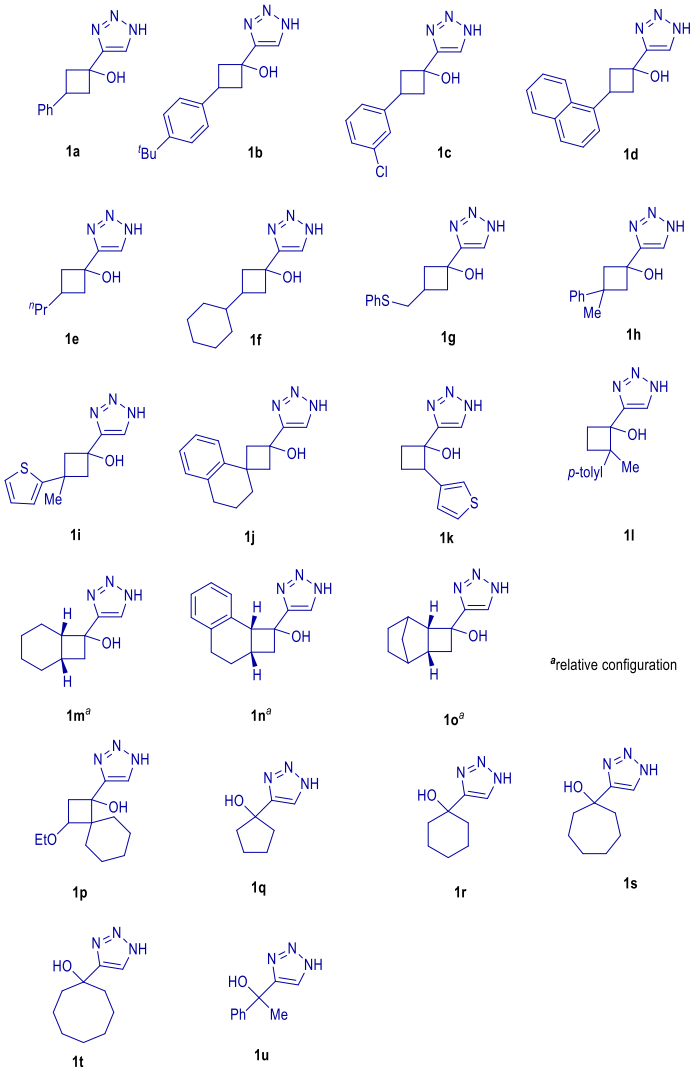
Infrared (IR) spectra were measured on Thermofisher Nicolet iN10 FM-IR spectrometer using KBr plates. High resolution mass spectral analysis (HRMS) was recorded on a FT-ICR (Fourier Transform-Ion Cyclotron Resonance) mass spectrometer by using electrospray ionization (ESI) techniques. Single crystal X-ray diffraction measurements were performed on an Agilent SuperNova-CCD X-Ray diffractometer.

Column chromatographic was performed on 200-300 mesh silica gel and reactions were monitored by thin layer chromatography (TLC) using silica gel GF254 plates. Visualization was realized by ultraviolet fluorescene (λ = 254 nm) and staining with phosphomolybdic acid.

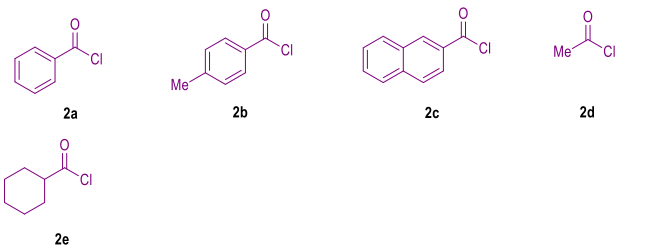
2. Preparation of substrates

4-(1-Hydroxycyclobutyl)-1,2,3-triazoles were synthesized according to the procedure A (**1q−1u**), procedure B (**1a−1j** and **1m−1o**), procedure C (**1k** and **1l**), and procedure D (**1p**), and acyl chlorides **2a−2e** are commercially available.

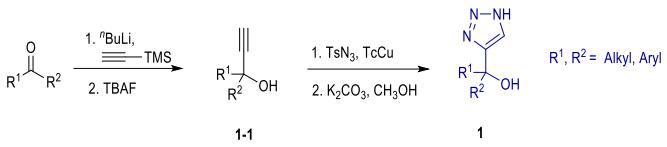
C4-Cyclobutanol-1,2,3-triazoles **1**



Acyl chlorides **2**



2.1. Procedure A: Synthesis of 4-(1-Hydroxycyclobutyl)-1,2,3-triazoles 1q−1u



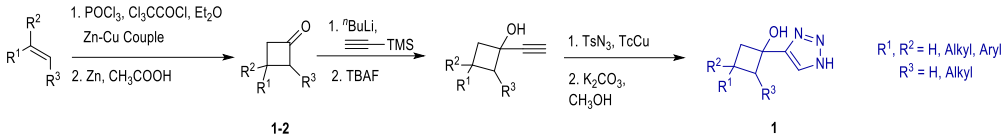
In an oven-dried round bottom, ^{n}BuLi (11 mmol, 1.1 eq.) was added dropwise to the solution of trimethylsilylacetylene (12 mmol, 1.2 eq.) in anhydrous THF (0.5 M) at -78 °C. After 30 min, a solution of ketone (10 mmol, 1.0 eq.) in anhydrous THF (1 M) was added to the reaction mixture. After the addition, the reaction was warmed to room temperature. After completion of the reaction (monitored by TCL analysis), the mixture was quenched with H_2O (5 mL), washed with sat. NH_4Cl (30 mL) and extracted with CH_2Cl_2 (3 x 30 mL). The organic phase was dried over Na_2SO_4. The solvent was removed in *vacuo* and the crude residue was directly used in the next step without further purification[1].

TBAF (15 mmol, 1.5 eq.) was added to the solution of the crude residue in THF (20 mL). After completion of the reaction (monitored by TCL analysis), the mixture was diluted with H_2O (20 mL) and extracted with CH_2Cl_2 (3 x 20 mL). The organic phase was dried over Na_2SO_4. The solvent was removed in *vacuo* and the crude residue was purified by column chromatography to afford the product **1-1**.

TsN_3 (10 mmol, 1.0 eq.) was added slowly to the solution of alkyne (10 mmol, 1.0 eq.) in toluene (2 M) at 0 °C. After the addition, the reaction was warmed to room temperature. After completion of the reaction (monitored by TCL analysis), The reaction mixture was filtered to remove inorganic compound, the solvent was dried over, concentrated and recrystallized by ethyl acetate and petroleum ether. The resulting solid was collected by filtration to afford the corresponding triazole[2].

To the solution of triazole in MeOH (0.5 M), K_2CO_3 (5% mmol) was added at room temperature into the flask. After completion of the reaction (monitored by TCL analysis), the mixture was concentrated and purified by column chromatography to afford the product **1**.

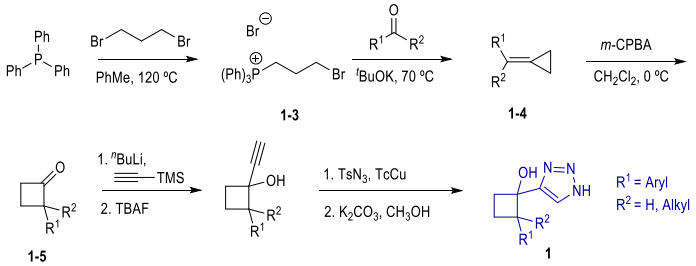
2.2. Procedure B: Synthesis of 4-(1-Hydroxycyclobutyl)-1,2,3-triazoles 1a−1j and 1m−1o



Alkene (10 mmol, 1.0 eq.) and fresh prepared Zn-Cu dust (30 mmol, 3.0 eq.) and Et_2O (20 mL) were added to an oven-dried two-neck round bottom flask with a condenser tube under argon atmosphere. A solution of $POCl_3$ (20 mmol, 2.0 eq.) and Cl_3CCOCl (20 mmol, 2.0 eq.) in Et_2O (5 mL) was added to the stirred suspension over a period of 1 h at room temperature. Then, the reaction was refluxed at 45 °C overnight. After completion of the reaction (monitored by TCL analysis), the mixture was cooled and filtered through a pad of celite. The filter pad was washed with Et_2O (2 x 20 mL), and the filtrate washed with water (2 x 30 mL), sat. $NaHCO_3$ (2 x 30 mL) and brine (1 x 30 mL). The organic phase was dried over Na_2SO_4 and concentrated in *vacuo*. The crude residue was directly used in the next step without further purification.

The crude residue was added to the suspension of Zn dust (40 mmol, 4.0 eq.) and acetic acid (20 mL) at 0 °C under argon atmosphere. After the addition was complete, the mixture was heated to 70 °C and stirred for 3 h. After completion of the reaction (monitored by TCL analysis), the mixture was cooled. The solid was filtered and washed with with CH_2Cl_2 (2 x 20mL). The combined filtrate was washed sequentially with water (2 x 20 mL) and brine (1 x 20 mL). Collect the organic phase and dried over $MgSO_4$. The solvent was concentrated under reduced pressure. The crude material was purified by column chromatography to afford the product **1-2**[3]. The subsequent steps refer to the Procedure A mentioned in 2.1.

2.3. Procedure C: Synthesis of 4-(1-Hydroxycyclobutyl)-1,2,3-triazoles 1k and 1l



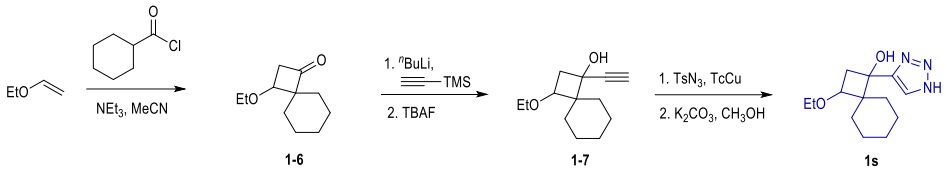
In an oven-dried two-neck round bottom flask with a condenser tube, 1,3-dibromopropane

(10 mmol, 1.0 eq.) was added to the solution of $P(Ph)_3$ (11 mmol, 1.1 eq.) in toluene (20 mL) under argon atmosphere. Then, the reaction was heated to 120 ºC overnight. The mixture was cooled to room temperature and the solid was filtered and washed with petroleum ether (3 x 30 mL) and dried over in *vacuo* to afford the product **1-3**.

To the suspension of **1-3** (10 mmol, 1.5 eq.) in anhydrous THF (20 mL), ^{t}BuOK (30 mmol, 3.0 eq.) in THF (1.3 M) was added dropwise and stirred at 70 ºC for 1h. Aldehyde/ketone (10 mmol, 1.0 eq.) was added and the reaction was proceeded under reflux condition for 6 h. After completion of the reaction (monitored by TCL analysis), H_2O (30 mL) was added and the mixture was extracted with CH_2Cl_2 (3 x 30 mL). The combined organic phase was dried over Na_2SO_4 and concentrated in *vacuo*, then the crude was purified by column chromatography to afford the product **1-4**.

In the solution of **1-4** (10 mmol, 1.0 eq.) in CH_2Cl_2 (0.15 M), *m*-CPBA (10 mmol, 1.0 eq.) in CH_2Cl_2 (0.38 M) was added dropwise at 0 ºC and stirred for 1h. After completion of the reaction (monitored by TCL analysis), the mixture was washed with saturated Na_2SO_3 (30 mL) and extracted with CH_2Cl_2 (3 x 30 mL). The combined organic phase was dried over Na_2SO_4 and concentrated in *vacum*. Then the residue was purified by column chromatography to afford the product **1-5**[4]. The subsequent steps refer to the Procedure A mentioned in 2.1.

2.4. Procedure D: Synthesis of C4-cyclobutanol-1,2,3-triazole 1p

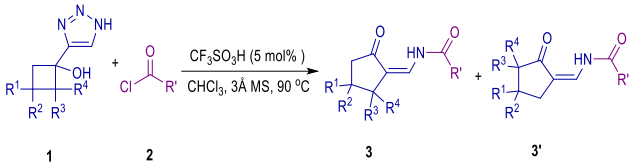


Cyclohexanecarboxylic acid chloride (10 mmol, 1.0 eq.) and anhydrous acetonitrile (0.5 M) were added to an oven-dried two-neck round bottom flask with a condenser tube under argon atmosphere. A solution of triethylamine (12 mmol, 1.2 eq.) and ethyl vinyl ether (18 mmol, 1.8 eq.) in anhydrous acetonitrile (5 mL) was added at room temperature. Then, the reaction was refluxed at 90 ºC in oil bath for 3 h. After completion of the reaction (monitored by TCL analysis), the mixture was cooled and quenched with sat. $NaHCO_3$ (30 mL). The resulting solution was extracted with CH_2Cl_2 (3 x 30 mL). The combined organic phase was

dried over Na_2SO_4 and concentrated in *vacuo*, then the residue was purified by column chromatography to afford the product **1-6**[5]. The subsequent steps refer to Procedure A mentioned in 2.1.

3. General procedure

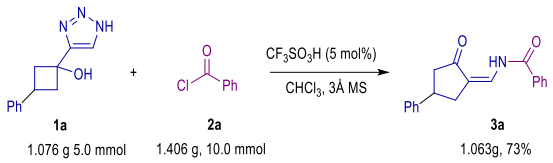
3.1. Procedure E: Synthesis of products 3



4-(1-Hydroxycyclobutyl)-1,2,3-triazoles **1** (0.10 mmol, 1.0 eq.) and 3Å MS (25.0 mg) were added to an oven-dried 10 mL reaction sealed tube and evacuated under high vacuo and backfilled with argon three times. Then, $CHCl_3$ (1 mL), acyl chloride **2** (0.2 mmol) and CF_3SO_3H (0.005 mmol) were added. The reaction was stirred at 90 °C in oil bath for 5 h. After 4-(1-hydroxycyclobutyl)-1,2,3-triazoles have been completely reacted (monitored by TCL analysis), the mixture was cooled to room temperature and quenched with 5 mL saturated $NaHCO_3$. Extracting the mixture with CH_2Cl_2 (3 x 5 mL) and the collected organic phase was dried over Na_2SO_4 and concentrated in *vacuo*. The residue was purified by column chromatography (PE/EA = 25: 1) to give the products **3**.

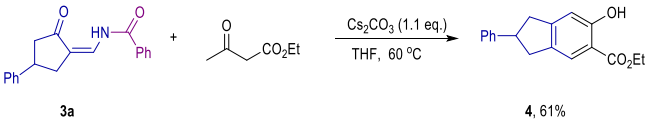
4. Application and Transformation

4.1. Procedure F: Gram-scale synthesis of 3a



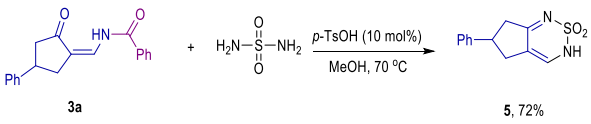
1a (1.076 g, 5.0 mmol, 1.0 eq.) and 3Å MS (1.250 g) were added to an oven-dried 200 mL reaction sealed bottle and evacuated under high vacuo and backfilled with argon three times. Then, $CHCl_3$ (50 mL), acyl chloride (1.406 g, 10.0 mmol) and CF_3SO_3H (37.5 mg, 0.25 mmol) were added in turn. The reaction was stirred at 90 °C in oil bath for 5 h. After **1a** has been completely reacted (monitored by TCL analysis), the mixture was cooled to room temperature and quenched by saturated $NaHCO_3$ (50 mL). Extracting the mixture with CH_2Cl_2 (3 x 50 mL) and the collected organic phase was dried over Na_2SO_4 and concentrated in *vacuo*. The residue was purified by column chromatography (PE/EA = 25: 1) to give the product **3a** (1.063 g) in 73% yield.

4.2. Procedure G: Synthesis of product 4



3a (29.1 mg, 0.10 mmol, 1.0 eq.), ethyl acetoacetate (14.3 mg, 0.11 mmol), Cs_2CO_3 (36 mg, 0.11 mmol), and freshly distilled THF (1 mL) were added to an oven-dried 10 mL reaction tube under argon atmosphere. The reaction was stirred at 60 °C in oil bath for 8 h. After **3a** has been completely reacted (monitored by TCL analysis), the reaction mixture was cooled to room temperature and the solvent was concentrated in *vacuo*. The residue was purified by column chromatography (PE/EA = 40: 1) to give the product **4** (17.2 mg) in 61% yield.

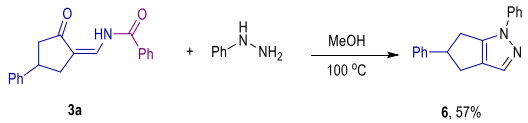
4.3. Procedure H: Synthesis of product 5



3a (29.1 mg, 0.10 mmol, 1.0 eq.), sulfamide (10.6 mg, 0.11 mmol), *p*-toluenesulfonic acid

monohydrate (1.9 mg, 0.01 mmol) and MeOH (1 mL) were added to an oven-dried 10 mL reaction sealed tube under argon atmosphere. The reaction was stirred at 70 °C in oil bath for 12 h. After **3a** has been completely reacted (monitored by TCL analysis), the reaction mixture was cooled to room temperature and the solvent was concentrated in *vacuo*. The residue was purified by column chromatography (CH_2Cl_2/MeOH = 10: 1) to give the product **5** (17.9 mg) in 72% yield.

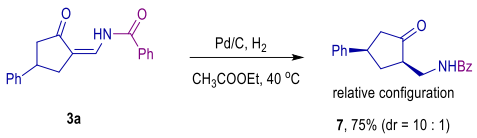
4.4. Procedure I: Synthesis of product 6



3a **6**, 57%

3a (29.1 mg, 0.10 mmol, 1.0 eq.), hydroxylamine hydrochloride (31.9 mg, 0.11 mmol) and MeOH (1 mL) were added to an oven-dried 10 mL reaction sealed tube under argon atmosphere. The reaction was stirred at 100 °C in oil bath for 12 h. After **3a** has been completely reacted (monitored by TCL analysis), the reaction mixture was cooled to room temperature. The solvent was concentrated in *vacuo*, and the residue was directly purified by column chromatography (PE/EA = 50: 1) to give product **6** (14.9 mg, 57% yield).

4.5. Procedure J: Synthesis of product 7



3a relative configuration

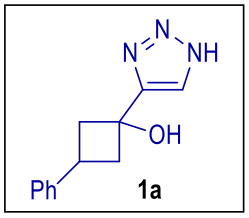
7, 75% (dr = 10 : 1)

3a (29.1 mg, 0.10 mmol, 1.0 eq.), Pd/C (3.5 mg, 12 wt%) and ethyl acetate (1 mL) were added to an oven-dried 10 mL reaction tube. Evacuating the tube under high vacuo and backfilled with argon three times and followed with H_2 two times. The reaction tube was connected to a hydrogen balloon and stirred at 40 °C in oil bath for 24 h. After **3a** has been completely reacted (monitored by TCL analysis), the reaction mixture was cooled to room temperature. The solvent was concentrated in *vacuo*, and the residue was purified by column chromatography (PE/EA = 10: 1) to give product **7** (22.0 mg, 75% yield).

5. Characterization data for compounds

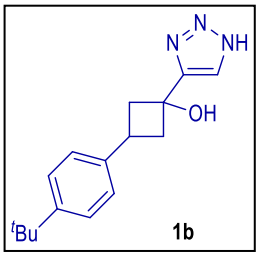
The ^{13}C signals of substrates **1a** – **1s** couldn't be got completely that the two carbon atoms on the triazole ring do not give signals as reported in literatures[6] (ref. 6a SI page S2 and ref. 6b SI page S25), even if the time is prolonged (3h) and different solvents (CD_3OD, $CDCl_3$ and DMSO- d_6) are used.

3-Phenyl-1-(1*H*-1,2,3-triazol-4-yl)cyclobutan-1-ol (**1a**)



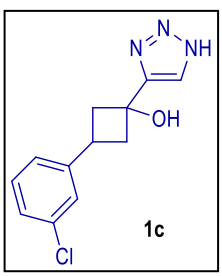
Compound **1a** was obtained by column chromatography (PE : EA = 4 : 1) as a white solid in 40% yield (861.1 mg) over 3 steps. **m.p.**: 121.4 – 123.2 °C. **^{1}H NMR (400 MHz, CD_3OD)** δ 7.87 (s, 1H), 7.29 (d, *J* = 4.4 Hz, 4H), 7.14 (m, 1H), 3.30 – 3.22 (m, 1H), 2.97 (td, *J* = 8.4, 2.8 Hz, 2H), 2.53 (td, *J* = 10.0, 2.8 Hz, 2H). **^{13}C NMR ((101 MHz, CD_3OD)** δ 146.0, 129.4, 127.6, 127.1, 67.8, 46.1, 31.2. **IR (cm^{-1})**: ν 3423, 1647, 1496, 1250, 1226, 1019, 1095,757, 702. **HRMS**: m/z: $[M + H]^+$ calculated for $C_{12}H_{14}N_3O_2^+$, 216.1131, found 216.1132.

3-(4-(Tert-butyl)phenyl)-1-(1*H*-1,2,3-triazol-4-yl)cyclobutan-1-ol (**1b**)



Compound **1b** was obtained by column chromatography (PE : EA = 4 : 1) as a white solid in 42% yield (1.2 g) over 3 steps. **m.p.**: 172.8 – 175.3 °C. **(400 MHz, DMSO- d_6)** δ 7.81 (s, 1H), 7.31 (d, *J* = 8.4 Hz, 2H), 7.23 (d, *J* = 8.4 Hz, 2H), 5.82 (s, 1H), 3.15 (p, *J* = 9.6 Hz, 1H), 2.85 (td, *J* = 8.8, 2.8 Hz, 2H), 2.43 (td, *J* = 8.8, 2.4 Hz, 2H), 1.25 (s, 9H). **^{13}C NMR (101 MHz, DMSO-d_6)** δ 157.7, 151.4, 135.8, 134.4, 75.7, 55.1, 43.5, 40.7, 38.7. **IR (cm^{-1})**: ν 3352, 2961, 1363, 1176, 1036, 1011, 832, 815. **HRMS**: m/z: $[M + H]^+$ calculated for $C_{16}H_{22}N_3O^+$, 272.1757, found 272.1768.

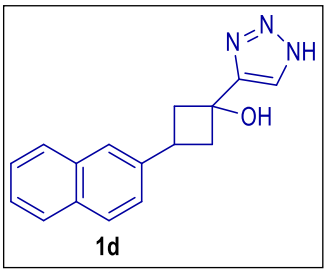
3-(3-Chlorophenyl)-1-(1*H*-1,2,3-triazol-4-yl)cyclobutan-1-ol (**1c**)



Compound **1c** was obtained by column chromatography (PE : EA = 4 : 1) as a white solid in 30% yield (749 mg) over 3 steps. **m.p.**: 141.5 – 143.6 °C. **^{1}H NMR (400 MHz, CD_3OD)** δ 7.86 (s, 1H), 7.32 – 7.17 (m, 4H), 3.31 – 3.23 (m, 1H), 2.99 (td, *J* = 8.8, 2.8 Hz, 2H), 2.51 (td, *J* = 9.2, 2.8 Hz, 2H). **^{13}C NMR (101 MHz, CD_3OD)** δ 148.5, 135.3, 130.9, 127.8, 127.2, 126.1,

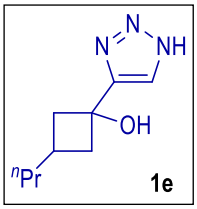
67.8, 46.0, 31.0. **IR (cm^{-1})**: ν 3218, 2935, 1597, 1419, 1252, 1094, 848, 785. **HRMS**: m/z: [M + H]$^+$ calculated for $C_{12}H_{13}ClN_3O_2^+$, 250.0742, found 250.0741.

3-(Naphthalen-1-yl)-1-(1*H*-1,2,3-triazol-4-yl)cyclobutan-1-ol (**1d**)



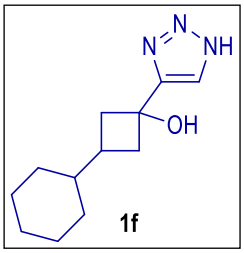
Compound **1d** was obtained by column chromatography (PE : EA = 4 : 1) as a white solid in 45% yield (1.2 g) over 3 steps. **m.p.**: 130.5 – 132.7 °C. **^{1}H NMR (400 MHz, CD$_3$OD)** δ 7.90 (s, 1H), 7.78 (d, *J* = 8.4 Hz, 3H), 7.69 (s, 1H), 7.46-7.37 (m, 3H), 3.48 – 3.39 (m, 1H), 3.05 (td, *J* = 8.8, 2.4 Hz, 2H), 2.72 – 2.57 (m, 2H). **^{13}C NMR (101 MHz, CD$_3$OD)** δ 143.4, 135.0, 133.7, 129.1, 128.6, 128.6, 127.0, 126.4, 126.3, 125.7, 67.9, 46.0, 31.4. **IR (cm^{-1})**: ν 1634, 1507, 1243, 1222, 1092, 1017, 941, 828. **HRMS**: m/z: [M + H]$^+$ calculated for $C_{16}H_{16}N_3O^+$, 266.1288, found 266.1287.

3-Propyl-1-(1*H*-1,2,3-triazol-4-yl)cyclobutan-1-ol (**1e**)



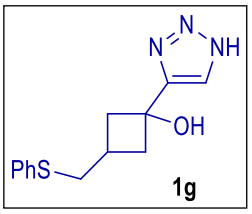
Compound **1e** was obtained by column chromatography (PE : EA = 4 : 1) as a white amorphous solid in 31% yield (562.1 mg) over 3 steps. **^{1}H NMR (400 MHz, CD$_3$OD)** δ 7.75 (s, 1H), 2.76 – 2.59 (m, 2H), 2.11 – 1.93 (m, 3H), 1.51 – 1.46 (m, 2H), 1.34 –1.24 (m, 2H), 0.91 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR (101 MHz, CD$_3$OD)** δ 44.6, 40.6, 26.5, 21.6, 14.4. **IR (cm^{-1})**: ν 1465, 1245, 1215, 1070, 1001, 933, 861, 824. **HRMS**: m/z: [M + Na]$^+$ calculated for $C_9H_{15}N_3NaO^+$, 204.1107, found 204.1107.

3-Cyclohexyl-1-(1*H*-1,2,3-triazol-4-yl)cyclobutan-1-ol (**1f**)



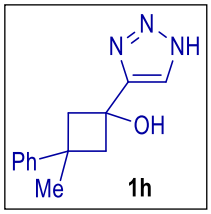
Compound **1f** was obtained by column chromatography (PE : EA = 4 : 1) as a white solid in 34% yield (752.4 mg) over 3 steps. **m.p.**: 142.1 – 143.7 °C. **^{1}H NMR (400 MHz, CD$_3$OD)** δ 7.75 (s, 1H), 2.63 (dt, *J* = 8.0, 2.8 Hz, 2H), 2.05 (dt, *J* = 9.6, 2.8 Hz, 2H), 1.77 – 1.62 (m, 6H), 1.35 – 1.18 (m, 4H), 0.89 – 0.75 (m, 2H). **^{13}C NMR (101 MHz, CD$_3$OD)** δ 67.8, 46.5, 43.0, 32.5, 31.3, 27.6, 27.2. **IR (cm^{-1})**: ν 3425, 3157, 2924, 2852, 1638, 1446, 1252, 1127. **HRMS**: m/z: [M + H]$^+$ calculated for $C_{12}H_{20}N_3O^+$, 222.1601, found 222.1601.

3-((Phenylthio)methyl)-1-(1*H*-1,2,3-triazol-4-yl)cyclobutan-1-ol (**1g**)



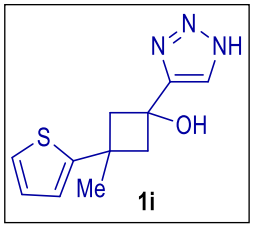
Compound **1g** was obtained by column chromatography (PE : EA = 4 : 1) as a white solid in 48% yield (1.3 g) over 3 steps. **m.p.**: 137.9–139.6 °C. **^{1}H NMR (400 MHz, CD_3OD)** δ 7.72 (s, 1H), 7.34 (d, *J* = 7.6 Hz, 2H), 7.26 (t, *J* = 7.6 Hz, 2H), 7.16 (t, *J* = 7.6 Hz, 1H), 3.11 (d, *J* = 7.2 Hz, 2H), 2.74 – 2.63 (m, 2H), 2.35 – 2.23 (m, 1H), 2.19 – 2.09 (m, 2H). **^{13}C NMR (101 MHz, CD_3OD)** δ 137.8, 130.6, 129.9, 127.0, 68.1, 44.1, 41.2, 26.5. **IR (cm^{-1})**: ν 3137, 2924, 2853, 1581, 1480, 1260, 994, 741. **HRMS**: m/z: $[M + H]^+$ calculated for $C_{13}H_{16}N_3O^+$, 262.1009, found 262.1008.

3-Methyl-3-phenyl-1-(1*H*-1,2,3-triazol-4-yl)cyclobutan-1-ol (**1h**)



Compound **1h** was obtained by column chromatography (PE : EA = 4 : 1) as a white solid in 36% yield (825.4 mg) over 3 steps. **m.p.**: 130.2 – 132.6 °C. Major isomer: **^{1}H NMR (400 MHz, CD_3OD)** δ 7.83 (s, 1H), 7.32 – 7.23 (m, 5H), 3.05 (d, *J* = 13.2 Hz, 2H), 2.59 (d, *J* = 13.2, 2H), 1.62 (s, 3H). **^{13}C NMR (101 MHz, CD_3OD)** δ 152.2, 129.2, 126.3, 126.0, 67.8, 49.8, 37.0, 33.6. Minor isomer: **^{1}H NMR (400 MHz, CD_3OD)** δ 7.47 (s, 1H), 7.21 – 7.08 (m, 5H), 2.96 (d, *J* = 13.2 Hz, 2H), 2.85 (d, *J* = 12.8 Hz, 2H), 1.29 (s, 3H). **^{13}C NMR (101 MHz, CD_3OD)** δ 152.2, 127.9, 125.0, 124.6, 65.4, 48.7, 33.7, 31.8. **IR (cm^{-1})**: ν 1181, 1118, 1063, 1009, 983, 861, 816, 701. **HRMS**: m/z: $[M + Na]^+$ calculated for $C_{13}H_{15}N_3NaO^+$, 252.1107, found 252.1107.

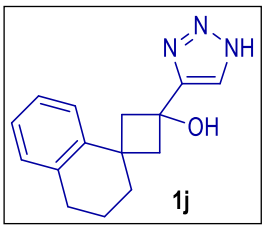
3-Methyl-3-(thiophen-2-yl)-1-(1*H*-1,2,3-triazol-4-yl)cyclobutan-1-ol (**1i**)



Compound **1i** was obtained by column chromatography (PE : EA = 4 : 1) as a white amorphous solid in 31% yield (729.4 mg) over 3 steps. Major isomer: **^{1}H NMR (400 MHz, CD_3OD)** δ 7.85–7.74 (m, 1H), 6.98 – 6.77 (m, 3H), 2.99 –2.81 (m, 4H), 1.50 – 1.38(m, 3H). **^{13}C NMR (101 MHz, CD_3OD)** δ 127.7, 127.6, 123.8, 123.0, 66.6, 52.3, 32.9, 30.5. Minor isomer: **^{1}H NMR (400 MHz, CD_3OD)** δ 7.63–7.52 (m, 1H), 7.25 – 7.05 (m, 3H), 3.35 – 3.25 (m, 1H), 3.11 – 3.01 (m, 2H), 2.73 – 2.55 (m, 2H), 1.82 – 1.70 (m, 3H). **^{13}C NMR (101 MHz, CD_3OD)** δ 157.8,

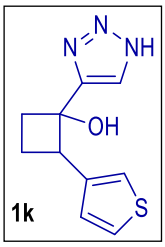
127.6, 127.3, 123.4, 52.0, 32.5, 34.5, 31.0. **IR (cm^{-1})**: ν 3855, 3676, 3387, 2934, 1638, 1418, 1232, 1025. **HRMS**: m/z: $[M + Na]^+$ calculated for $C_{11}H_{13}N_3NaOS^+$, 258.0672, found 258.0672.

3-(1*H*-1,2,3-triazol-4-yl)-3',4'-dihydro-2'*H*-spiro[cyclobutane-1,1'-naphthalen]-3-ol (**1j**)



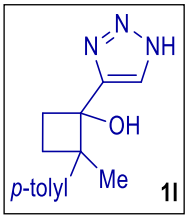
Compound **1j** was obtained by column chromatography (PE : EA = 4 : 1) as a white solid in 27% yield (510.3 mg) over 3 steps. **m.p.**: 168.7 – 171.1 °C. **^{1}H NMR (400 MHz, CD$_3$OD)** δ 7.79 (s, 1H), 7.17 – 7.05 (m, 4H), 2.95 (t, *J* = 8.8 Hz, 1H), 2.87 (dd, *J* = 12.4, 1.6 Hz, 1H), 2.80 (dt, *J* = 14.8, 3.6 Hz, 1H), 2.63 – 2.56 (m, 2H), 2.03 – 1.97 (m, 2H), 1.32 (s, 3H). **^{13}C NMR (101 MHz, CD$_3$OD)** δ 146.9, 139.1, 128.9, 127.9, 126.7, 126.3, 53.4, 50.2, 33.9, 31.5, 29.3, 23.7. **IR (cm^{-1})**: ν 3384, 2939, 2865, 1488, 1448, 1217, 1123, 1020. **HRMS**: m/z: $[M + H]^+$ calculated for $C_{15}H_{18}N_3O^+$, 256.1444, found 256.1446.

2-(Thiophen-3-yl)-1-(1*H*-1,2,3-triazol-4-yl)cyclobutan-1-ol (**1k**)



Compound **1k** was obtained by column chromatography (PE : EA = 4 : 1) as a white amorphous solid in 18% yield (398.3 mg) over 5 steps. **^{1}H NMR (400 MHz, CD$_3$OD)** δ 7.69 (s, 1H), 7.30 (dd, *J* = 4.8, 2.8 Hz 1H), 7.15 (dt, *J* = 3.2, 1.2 Hz, 1H), 6.97 (dd, *J* = 5.2, 1.2 Hz, 1H), 4.02 (t, *J* = 9.2 Hz, 1H), 2.66 – 2.45 (m, 2H), 2.34 – 2.21 (m, 2H). **^{13}C NMR (101 MHz, CD$_3$OD)** δ 141.3, 129.2, 125.8, 122.8, 76.1, 48.3, 35.2, 23.1. **IR (cm^{-1})**: ν 3191, 2951, 1413, 1242, 1126, 1003, 852, 782. **HRMS**: m/z: $[M + Na]^+$ calculated for $C_{10}H_{11}N_3NaOS^+$, 244.0515, found 244.0515.

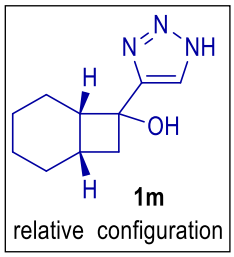
2-Methyl-2-(*p*-tolyl)-1-(1H-1,2,3-triazol-4-yl)cyclobutan-1-ol (**1l**)



Compound **1l** was obtained by column chromatography (PE : EA = 4 : 1) as a white solid in 23% yield (558.9 mg) over 5 steps. **m.p.**: 200.3 – 202.6 °C. **^{1}H NMR (400 MHz, DMSO-*d*$_6$)** δ 7.74 (s, 1H), 7.09 (s, 4H), 2.89 (d, *J* = 5.2 Hz, 1H), 2.69 (q, *J* = 9.6 Hz, 1H), 2.26 (s, 3H), 2.03 – 1.87 (m, 1H), 1.82 (t, *J* = 8.4 Hz, 1H), 1.01 (s, 3H). **^{13}C NMR (101 MHz, DMSO-*d*$_6$)** δ 127.7, 125.8, 75.7, 50.2, 29.4, 27.8, 27.1, 20.1. **IR (cm^{-1})**: ν 3161, 3116, 3028, 2951, 1515, 1160, 1072, 1027. **HRMS**: m/z:

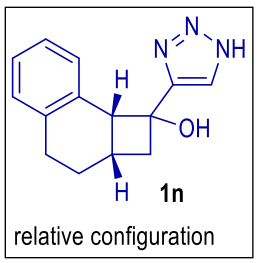
[M + Na]$^+$ calculated for $C_{14}H_{17}N_3NaO^+$, 266.1264, found 266.1263.

Cis-7-(1*H*-1,2,3-triazol-4-yl)bicyclo[4.2.0]octan-7-ol (**1m**)



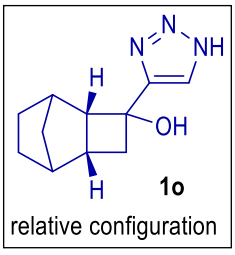
Compound **1m** was obtained by column chromatography (PE : EA = 4 : 1) as a white solid in 18% yield (444.5 mg) over 3 steps. **m.p.**: 152.5 – 155.1 °C. **^{1}H NMR (400 MHz, CD$_3$OD)** δ 7.77 (s, 1H), 2.69 – 2.62(m, 1H), 2.43 – 2.28 (m, 2H), 2.23 – 2.11 (m, 1H), 1.95 – 1.80 (m, 1H), 1.79 – 1.67 (m, 2H), 1.60 – 1.37 (m, 4H), 1.23 – 1.09 (m, 1H).**^{13}C** NMR (**101 MHz, CD$_3$OD**) δ 70.1, 44.9, 38.8, 26.9, 25.2, 23.7, 22.8, 22.6. **IR (cm^{-1})**: ν 3136, 2939, 1490, 1215, 1115, 1068, 843, 751. **HRMS**: m/z: [M + Na]$^+$ calculated for $C_{14}H_{15}N_3NaO^+$, 264.1107, found 264.1107.

Cis-1-(1*H*-1,2,3-triazol-4-yl)-1,2,2*a*,3,4,8*b*-hexahydrocyclobuta[*a*]naphthalen-1-ol (**1n**)



Compound **1n** was obtained by column chromatography (PE : EA = 4 : 1) as a white solid in 39% yield (940.4 mg) over 3 steps. **m.p.**: 161,5 – 163.6 °C. **^{1}H NMR (400 MHz, CD$_3$OD)** δ 7.74 (s, 1H), 7.33 – 6.95 (m, 4H), 3.40 – 3.24 (m, 1H), 3.10 – 2.79 (m, 3H), 2.74 – 2.58 (m, 1H), 2.43 (t, *J* = 10.4 Hz, 1H), 2.21 – 2.06 (m, 1H), 1.89 (s, 1H). **^{13}C NMR (101 MHz, CD$_3$OD)** δ 139.3, 129.5, 128.6, 127.3, 126.8, 47.2, 45.6, 29.4, 29.2, 22.5. **IR (cm^{-1})**: ν 3384 2939, 2865, 1189, 1448, 1217, 1020, 983. **HRMS**: m/z: [M + H]$^+$ calculated for $C_{15}H_{18}N_3O^+$, 256.1444, found 256.1446.

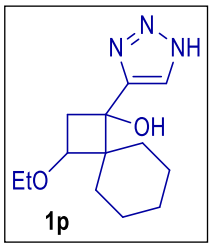
Cis-3-(1*H*-1,2,3-triazol-4-yl)tricyclo[4.2.1.02,5]nonan-3-ol (**1o**)



Compound **1o** was obtained by column chromatography (PE : EA = 4 : 1) as a white solid in 24% yield (492.5 mg) over 3 steps. **m.p.**: 187.5 – 188.8 °C. **^{1}H NMR (400 MHz, CD$_3$OD)** δ 7.67 (s, 1H), 2.59 – 2.43 (m, 2H), 2.41 – 2.31 (m, 2H), 2.20 (q, *J* = 6.8 Hz, 1H), 2.10 (s, 1H), 2.00 (dd, *J* = 13.6, 5.2 Hz, 1H), 1.60 – 1.48 (m, 2H), 1.30 (d, *J* = 10.0 Hz, 1H), 1.18 – 1.04 (m, 2H). **^{13}C NMR (101 MHz, CD$_3$OD)** δ 70.8, 55.1, 40.1, 39.8, 36.6, 35.2,

34.7, 29.1, 29.1. **IR (cm^{-1})**: ν 3417, 2958, 2872, 1637, 1459, 1164, 1141, 1026. **HRMS**: m/z: $[M+Na]^+$ calculated for $C_{12}H_{16}N_3NaO^+$, 276.0874, found 276.0873.

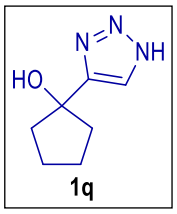
3-Ethoxy-1-(1*H*-1,2,3-triazol-4-yl)spiro[3.5]nonan-1-ol (**1p**)



1p

Compound **1p** was obtained by column chromatography (PE : EA = 4 : 1) as a white solid in 13% yield (326.5mg) over 5 steps. **m.p.**: 162.8 – 164.7 °C. **^{1}H NMR (400 MHz, CD$_3$OD)** δ 7.75 (s, 1H), 2.68 – 2.55 (m, 2H), 2.02 (td, *J* = 16.0, 6.8 Hz, 2H), 1.79 – 1.61 (m, 7H), 1.27 – 1.15 (m, 5H), 0.89 – 0.75 (m, 2H). **^{13}C NMR (101 MHz, CD$_3$OD)** δ 67.8, 46.5, 43.0, 32.5, 31.3, 27.6, 27.2. **IR (cm^{-1})**: ν 3385, 2924, 2850, 1447, 1251, 1192, 1127, 1048. **HRMS**: m/z: $[M+K]^+$ calculated for $C_{12}H_{19}N_3KO^+$, 260.1160, found 260.1169.

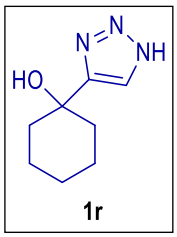
1-(1*H*-1,2,3-triazol-4-yl)cyclopentan-1-ol (**1q**)



1q

Compound **1q** was obtained by column chromatography (PE: EA = 4:1) as a white solid in 32% yield (480.2 mg) over 3 steps. **m.p.**: 122.8 – 124.7 °C. **^{1}H NMR (400 MHz, CD$_3$OD)** δ 7.70 (s, 1H), 2.15 – 1.91 (m, 6H), 1.81 (t, *J* = 7.6 Hz, 2H)**, ^{13}C NMR (101 MHz, CD$_3$OD)** δ 79.0, 41.9, 24.4. **IR (cm^{-1})**: ν 3423, 2962, 1638, 1450, 1251, 1384, 1208, 1025. **HRMS**: m/z: $[M+Na]^+$ calculated for $C_7H_{11}N_3NaO^+$, 176.0794, found 176.0789.

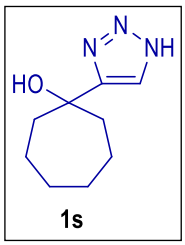
1-(1*H*-1,2,3-triazol-4-yl)cyclohexan-1-ol （**1r**）



1r

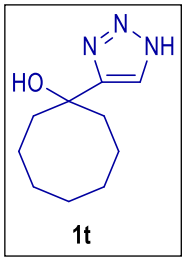
Compound **1r** was obtained by column chromatography (PE: EA = 4:1) as a white solid in 38% yield (635.4 mg) over 3 steps. **m.p.**: 127.5 – 128.9 °C, reported m.p. 128 – 129 °C. **^{1}H NMR (400 MHz, CD$_3$OD)** δ 7.70 (s, 1H), 2.05 – 1.91(m, 2H), 1.91 – 1.73 (m, 4H), 1.65 – 1.57 (m, 1H), 1.57 – 1.47 (m, 2H), 1.46 – 1.33 (m, 1H). **^{13}C NMR (101 MHz, CD$_3$OD)** δ 70.0, 39.0, 26.5, 23.0. **IR (cm^{-1})**: ν 1643, 1449, 1154, 1065, 1037, 1016, 978, 849. **HRMS**: m/z: $[M+Na]^+$ calculated for $C_8H_{13}N_3NaO^+$, 190.0951, found 190.0951.

1-(1*H*-1,2,3-triazol-4-yl)cycloheptan-1-ol (**1s**)



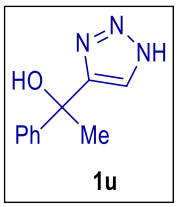
Compound **1s** was obtained by column chromatography (PE: EA = 4:1) as a white solid in 48% yield (869.4 mg) over 3 steps. **m.p.**: 129.4 – 131.3 °C. **^{1}H NMR (400 MHz, CD$_3$OD)** δ 7.68 (s, 1H), 2.21 – 2.06 (m, 2H), 1.99 (dt, *J* = 13.6, 6.4 Hz, 2H), 1.82 – 1.45 (m, 8H). **^{13}C NMR (101 MHz, CD$_3$OD)** δ 73.9, 42.8, 30.5, 22.9. **IR (cm^{-1})**: ν 3123, 2932, 2371, 2276, 1546, 1464, 1145, 1032. **HRMS**: m/z: $[M + H]^+$ calculated for $C_9H_{16}N_3^+$, 182.1288, found 182.1283.

1-(1*H*-1,2,3-triazol-4-yl)cyclooctan-1-ol (**1t**)



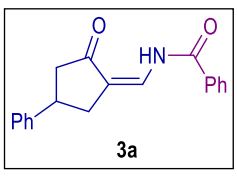
Compound **1t** was obtained by column chromatography (PE: EA = 4:1) as a white solid in 51% yield (995. 9mg) over 3 steps. **m.p.**: 136.1 – 138.5 °C. **^{1}H NMR (400 MHz, CD$_3$OD)** δ 7.69 (s, 1H), 2.10 (dd, *J* = 7.6, 3.6 Hz, 4H), 1.70 (tt, *J* = 12.8, 6.2 Hz, 5H), 1.62 – 1.40 (m, 5H). **^{13}C NMR (101 MHz, CD$_3$OD)** δ 73.7, 37.3, 29.3, 25.7, 22.8. **IR (cm^{-1})**: ν 3123, 2933, 2370, 2279, 1546, 1463, 1171, 1033. **HRMS**: m/z: $[M + H]^+$ calculated for $C_9H_{16}N_3^+$, 196.1444, found 196.1438.

1-Phenyl-1-(1*H*-1,2,3-triazol-4-yl)ethan-1-ol (**1u**)



Compound **1u** was obtained by column chromatography (PE: EA = 4:1) as a white solid in 41% yield (775.8 mg) over 3 steps. **m.p.**: 131.1 – 133.8 °C. **^{1}H NMR (400 MHz, CD$_3$OD)** δ 7.28 (s, 1H), 7.11 (d, *J* = 7.6 Hz, 2H), 6.91 (t, *J* = 7.6 Hz, 2H), 6.82 (t, *J* = 7.2 Hz, 1H), 1.60 (s, 3H). **^{13}C NMR (101 MHz, CD$_3$OD)** δ 148.0, 129.0, 128.0, 126.2, 72.5, 30.8. **IR (cm^{-1})**: ν 3386, 2935, 1636, 1448, 1373, 1214, 1128, 1028. **HRMS**: m/z: $[M + Na]^+$ calculated for $C_{10}H_{11}N_3NaO^+$, 212.0794, found 212.0794.

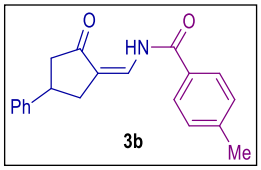
(*Z*)-*N*-((2-oxo-4-phenylcyclopentylidene)methyl)benzamide (**3a**)



According to the procedure E, **3a** was obtained by the reaction of **1a** and **2a**. Compound **3a** was obtained by column chromatography (PE : EA = 25 : 1) as a white solid in 82% yield (23.9 mg). **m.p.**: 102.6 – 104.4 °C.

^{1}H NMR (500 MHz, $CDCl_3$) δ 11.89 (d, *J* = 10.0 Hz, 1H), 7.89 (d, *J* = 7.5 Hz, 2H), 7.50 (t, *J* = 11.5 Hz, 2H), 7.42 (t, *J* = 7.0 Hz, 2H), 7.25 (t, *J* = 7.0 Hz, 2H), 7.21 – 7.14 (m, 3H), 3.47 – 3.40 (m, 1H), 3.02 (dd, *J* = 15.0, 7.5 Hz, 1H), 2.80 – 2.68 (m, 2H), 2.55 (dd, *J* = 18.0, 10.5 Hz, 1H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 208.5, 164.6, 143.1, 132.8, 132.0, 130.9, 128.8, 128.6, 127.7, 126.7, 126.6, 115.8, 46.8, 40.4, 35.6. **IR (cm^{-1})**: ν 3380, 2978, 1683, 1594, 1353, 1270, 1173, 696. **HRMS**: m/z: $[M + Na]^+$ calculated for $C_{19}H_{17}NNaO_2^+$, 314.1152, found 314.1151.

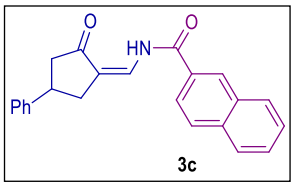
(*Z*)-4-methyl-*N*-((2-oxo-4-phenylcyclopentylidene)methyl)benzamide (**3b**)



3b

According to the procedure E, **3b** was obtained by the reaction **1a** and **2b**. Compound **3b** was obtained by column chromatography (PE : EA = 25 : 1) as a white solid in 78% yield (23.8 mg). **m.p.**: 105.8 – 107.4 °C. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 11.93 (d, *J* = 10.4 Hz, 1H), 7.88 (d, *J* = 8.4 Hz, 2H), 7.60 (d, *J* = 10.8, 11H), 7.38 – 7.22 (m, 7H), 3.60 – 3.48 (m, 1H), 3.11 (dd, *J* = 15.2, 7.6 Hz, 1H), 2.90 – 2.76 (m, 2H), 2.65 (dd, *J* = 17.6, 10.4 Hz, 1H), 2.43 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 208.5, 164.7, 143.7, 143.3, 131.2, 129.6, 129.3, 128.7, 127.8, 126.8, 126.7, 115.5, 46.9, 40.5, 35.7, 21.6. **IR (cm^{-1})**: ν 3095, 1697, 1597, 1509, 1394, 1354, 1172, 696. **HRMS**: m/z: $[M + Na]^+$ calculated for $C_{20}H_{19}NNaO_2^+$, 328.1308, found 328.1306.

(*Z*)-*N*-((2-oxo-4-phenylcyclopentylidene)methyl)-2-naphthamide (**3c**)

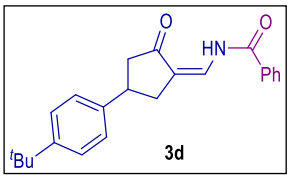


3c

According to the procedure E, **3c** was obtained by the reaction **1a** and **2c**. Compound **3c** was obtained by column chromatography (PE : EA = 25 : 1) as a white solid in 74% yield (25.3 mg). **m.p.**: 108.2 – 110.6 °C. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 12.04 (d, *J* = 10.5 Hz, 1H), 8.42 (s, 1H), 7.94 – 7.89 (m, 2H), 7.86 (d, *J* = 8.7 Hz, 1H), 7.80 (d, *J* = 9.0 Hz, 1H), 7.57 (d, *J* = 10.5 Hz, 1H), 7.54 – 7.45 (m, 2H), 7.26 (t, *J* = 7.0 Hz, 2H), 7.18 (d, *J* = 7.0Hz, 3H), 3.44 (p, *J* = 8.5 Hz, 1H), 3.03 (dd, *J* = 15.5, 7.5 Hz, 1H), 2.80 – 2.70 (m, 2H), 2.57 (dd, *J* = 17.5, 10.0 Hz, 1H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 208.6, 164.7, 143.2, 135.3, 132.5, 131.0, 129.3, 129.2, 129.0, 128.8, 128.7, 128.4, 127.7, 127.0, 126.7, 126.7, 123.6, 115.8, 46.9, 40.5, 35.7. **IR (cm^{-1})**: ν 3130, 2957, 2917,

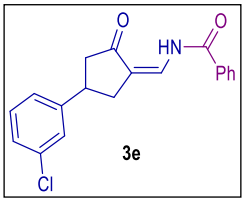
2850, 1697, 1597, 1394, 1172. **HRMS**: m/z: $[M + Na]^+$ calculated for $C_{20}H_{19}NNaO_2^+$, 364.1308, found 364.1307.

(*Z*)-N-((4-(4-(tert-butyl)phenyl)-2-oxocyclopentylidene)methyl)benzamide (**3d**)



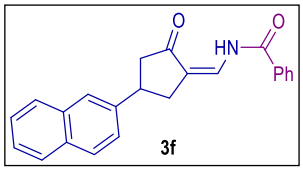
According to the procedure E, **3d** was obtained by the reaction **1b** and **2a.** Compound **3d** was obtained by column chromatography (PE : EA = 25 : 1) as a white solid in 75% yield (26. 1 mg). **m.p.**: 145.1 – 147.5 °C. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 11.90 (d, *J* = 10.0 Hz, 1H), 7.91 (d, *J* = 7.5 Hz, 2H), 7.52 (t, *J* = 9.0 Hz, 2H), 7.44 (t, *J* = 7.5 Hz, 2H), 7.29 (d, *J* = 8.0 Hz, 2H), 7.13 (d, *J* = 7.5 Hz, 2H), 3.49 – 3.39 (mz, 1H), 3.03 (dd, *J* = 15.0, 7.0 Hz, 1H), 2.81 – 2.70 (m, 2H), 2.57 (dd, *J* = 17.5, 10.0 Hz, 1H), 1.24 (s, 9H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 208.8, 164.7, 149.7, 140.1, 132.8, 132.2, 130.9, 128.9, 127.8, 126.4, 125.6, 116.0, 47.0, 40.1, 35.7, 34.4, 31.3. **IR (cm^{-1})**: ν 3108, 1697, 1604, 1264, 1169, 879, 699, 562. **HRMS**: m/z: $[M + Na]^+$ calculated for $C_{23}H_{25}NNaO_2^+$, 370.1778, found 370.1778.

(*Z*)-*N*-((4-(3-chlorophenyl)-2-oxocyclopentylidene)methyl)benzamide (**3e**)



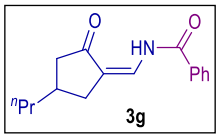
According to the procedure E, **3e** was obtained by the reaction **1c** and **2a.** Compound **3e** was obtained by column chromatography (PE : EA = 25: 1) as a white solid in 66% yield (21.5 mg). **m.p.**: 127.6 – 129.4 °C. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 11.95 (d, *J* = 10.4 Hz, 1H), 7.98 (d, *J* = 7.6 Hz, 2H), 7.66 – 7.57 (m, 2H), 7.52 (t, *J* = 8.0 Hz, 2H), 7.31 – 7.21 (m, 3H), 7.15 (d, *J* = 7.2 Hz, 1H), 3.56 – 23.47 (m, 1H), 3.13 (dd, *J* = 15.2, 7.6 Hz, 1H), 2.93 – 2.76 (m, 2H), 2.62 (dd, *J* = 18.0, 10.4 Hz, 1H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 207.9, 164.8, 145.3, 134.5, 132.9, 132.1, 131.3, 130.0, 128.9, 127.8, 127.0, 127.0, 124.9, 115.3, 46.6, 40.2, 35.5. **IR (cm^{-1})**: ν 3135, 1695, 1398, 1172, 1114, 1082, 698, 687. **HRMS**: m/z: $[M + Na]^+$ calculated for $C_{19}H_{16}ClNNaO_2^+$, 348.0759, found 348.0762.

(*Z*)-*N*-((4-(naphthalen-2-yl)-2-oxocyclopentylidene)methyl)benzamide (**3f**)



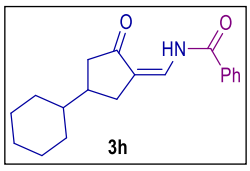
According to the procedure E, **3f** was obtained by the reaction **1d** and **2a.** Compound **3f** was obtained by column chromatography (PE : EA = 25 : 1) as a white solid in 92% yield (31.4 mg). **m.p.**: 111.5 – 113.6 °C. **^{1}H NMR (500 MHz, CDCl$_3$)** δ 11.91 (d, *J* = 10.5 Hz, 1H), 7.91 (d, *J* = 8.0 Hz, 2H), 7.77 – 7.70 (m, 3H), 7.58 (s, 1H), 7.57 – 7.47 (m, 2H), 7.42 (t, *J* = 8.0 Hz, 2H), 7.40 – 7.34 (m, 2H), 7.31 (d, *J* = 8.5Hz, 1H), 3.64 – 3.56 (m, 1H), 3.08 (dd, *J* = 15.5, 8.0Hz, 1H), 2.87 – 2.76 (m, 2H), 2.66 (dd, *J* = 18.0, 10.0 Hz, 1H).**^{13}C NMR (126 MHz, CDCl$_3$)** δ 208.5, 164.7, 140.5, 133.4, 132.8, 132.3, 132.1, 131.0, 128.9, 128.5, 127.8, 127.6, 127.6, 126.2, 125.7, 125.2, 124.9, 115.8, 46.8, 40.6, 35.6. **IR (cm^{-1})**: ν 3128, 2918, 1693, 1400, 1351, 1168, 1008, 701. **HRMS**: m/z: $[M + Na]^+$ calculated for $C_{23}H_{19}NNaO_2^+$, 364.1308, found 364.1309.

(*Z*)-*N*-((2-oxo-4-propylcyclopentylidene)methyl)benzamide (**3g**)



According to the procedure E, **3g** was obtained by the reaction **1e** and **2a.** Compound **3g** was obtained by column chromatography (PE : EA = 25 : 1) as a white amorphous solid in 72% yield (18.5 mg). **^{1}H NMR (500 MHz, CDCl$_3$)** δ 11.86 (d, *J* = 8.4 Hz, 1H), 7.89 (d, *J* = 6.0 Hz, 2H), 7.55 – 7.449 (m, 1H), 7.48 – 7.40 (m, 3H), 2.75 (dd, *J* = 15.0, 6.5 Hz, 1H), 2.49 (dd, *J* = 18.0, 7.5 Hz, 1H), 2.33 – 2.16 (m, 2H), 2.06 (dd, *J* = 18.0, 9.0 Hz, 1H), 1.45 – 1.36 (m, 2H), 1.34 – 1.28 (m, 2H), 0.87 (t, *J* = 6.8 Hz, 3H). **^{13}C NMR (126 MHz, CDCl$_3$)** δ 209.9, 164.7, 132.7, 132.2, 130.4, 128.8, 127.7, 116.4, 46.3, 37.9, 35.2, 34.1, 20.8, 14.1. **IR (cm^{-1})**: ν 3125, 1696, 1611, 1394, 1168, 1103, 1066, 703. **HRMS**: m/z: $[M + Na]^+$ calculated for $C_{23}H_{19}NNaO_2^+$, 280.1308, found 280.1309.

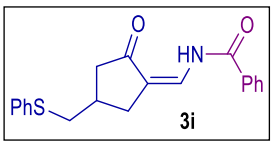
(*Z*)-*N*-((4-cyclohexyl-2-oxocyclopentylidene)methyl)benzamide (**3h**)



According to the procedure E, **3h** was obtained by the reaction **1f** and **2a.** Compound **3h** was obtained by column chromatography (PE : EA = 25 : 1) as a amorphous solid in 81% yield (24.1 mg). **m.p.**: 128.1 –

129.8 °C. **^{1}H NMR (500 MHz, CDCl$_3$)** δ 11.93 (d, *J* = 10.5 Hz, 1H), 7.96 (d, *J* = 8.0 Hz, 2H), 7.58 (t, *J* = 7.5 Hz, 1H), 7.55 – 7.47 (m, 3H), 2.78 (dd, *J* = 15.5, 7.5 Hz, 1H), 2.53 (dd, *J* = 17.5, 7.5 Hz, 1H), 2.40 – 2.32 (m, 1H), 2.16 (dd, *J* = 18.0, 11.5 Hz, 1H), 2.05 – 1.94 (m, 1H), 1.85 – 1.64 (m, 5H), 1.31 – 1.14 (m, 4H), 0.96 (q, *J* = 11.5 Hz, 2H). **^{13}C NMR (126 MHz, CDCl$_3$)** δ 209.9, 164.6, 132.7, 132.2, 130.2, 128.8, 127.7, 116.8, 44.5, 43.3, 41.6, 32.3, 31.4, 30.7, 26.4, 26.1, 26.0. **IR (cm^{-1})**: ν 3133, 2925, 2850, 1602, 1505, 1348, 1166, 704. **HRMS**: m/z: [M + Na]$^+$ calculated for $C_{19}H_{23}NNaO_2^+$, 320.1621, found 320.1620.

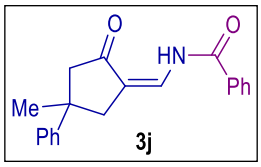
(*Z*)-*N*-((2-oxo-4-((phenylthio)methyl)cyclopentylidene)methyl)benzamide (**3i**)



3i

According to the procedure E, **3i** was obtained by the reaction **1g** and **2a.** Compound **3i** was obtained by column chromatography (PE : EA = 25 : 1) as a white solid in 80% yield (27.0 mg). **m.p.**: 125.7 – 128.1 °C. **^{1}H NMR (500 MHz, CDCl$_3$)** δ 11.91 (d, *J* = 13.0 Hz, 1H), 7.95 (d, *J* = 9.0 Hz, 2H), 7.61 – 7.48 (m, 4H), 7.37 (d, *J* = 9.5 Hz, 2H), 7.30 (t, *J* = 10.0 Hz, 2H), 7.21 (t, *J* = 9.0 Hz, 1H), 3.03 (d, *J* = 8.0 Hz, 2H), 2.90 (q, *J* = 12.5 Hz, 1H), 2.70 – 2.50 (m, 3H), 2.40 – 2.32 (m, 1H). **^{13}C NMR (126 MHz, CDCl$_3$)** δ 208.3, 164.6, 135.7, 132.8, 132.0, 131.3, 129.7, 129.0, 128.9, 127.7, 126.4, 115.3, 45.4, 39.3, 34.7, 33.3. **IR (cm^{-1})**: ν 3103,1693, 1692, 1506, 1259, 1177, 1160, 702. **HRMS**: m/z: [M + Na]$^+$ calculated for $C_{20}H_{19}NNaO_2S^+$, 360.1029, found 360.1024.

(*Z*)-*N*-((4-methyl-2-oxo-4-phenylcyclopentylidene)methyl)benzamide (**3j**)

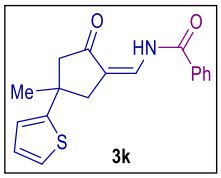


3j

According to the procedure E, **3j** was obtained by the reaction **1h** and **2a.** Compound **3j** was obtained by column chromatography (PE : EA = 25 : 1) as a white solid in 87% yield (26.7 mg). **m.p.**: 109.8 – 110.3 °C. **^{1}H NMR (500 MHz, CDCl$_3$)** δ 11.93 (d, *J* = 10.4 Hz, 1H), 7.98 (d, *J* = 7.6 Hz, 2H), 7.61 (dd, *J* = 14.8, 10.8 Hz, 2H), 7.51 (t, *J* = 7.6 Hz, 2H), 7.36 (t, *J* = 7.6 Hz, 2H), 7.33 – 7.20 (m, 3H), 3.10 (d, *J* = 14.8, 1H), 2.98 – 2.83 (m, 2H), 2.67 (d, *J* = 17.2 Hz, 1H), 1.40 (s, 3H). **^{13}C NMR (126 MHz, CDCl$_3$)** δ 208.3, 164.7, 148.2, 132.8, 132.1, 131.5, 128.9, 128.6, 127.8, 126.3, 125.4, 115.6, 53.0, 42.9, 41.3, 30.2. **IR (cm^{-1})**: ν 3133, 1693, 1613, 1510, 1401, 1348, 1401, 1171, 698. **HRMS**: m/z: [M + Na]$^+$ calculated for $C_{20}H_{19}NNaO_2^+$, 328.1308, found

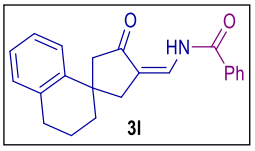
328.1311.

(*Z*)-*N*-((4-methyl-2-oxo-4-(thiophen-2-yl)cyclopentylidene)methyl)benzamid (**3k**)



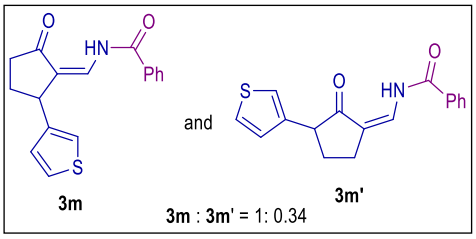
According to the procedure E, **3k** was obtained by the reaction **1i** and **2a.** Compound **3k** was obtained by column chromatography (PE : EA = 25 : 1) as a white solid in 86% yield (26.8 mg). **m.p.**: 101.4 – 103.1 °C. **^{1}H NMR** (**400 MHz, $CDCl_3$**) δ 11.89 (d, *J* = 10.4 Hz, 1H), 7.97 (d, *J* = 7.2 Hz, 2H), 7.66 – 7.56 (m, 2H), 7.51 (t, *J* = 7.6 Hz, 2H), 7.18 (d, *J* = 6.0 Hz, 1H), 6.97 – 6.91 (m, 1H), 6.90 – 6.85 (m, 1H), 3.12 (d, *J* = 14.0 Hz, 1H), 2.97 – 2.83 (m, 2H), 2.63 (d, *J* = 17.6 Hz, 1H), 1.56 (s, 3H). **^{13}C NMR** (**101 MHz, $CDCl_3$**) δ 207.7, 164.7, 153.0, 132.9, 132.1, 131.6, 128.9, 127.8, 126.7, 123.4, 122.5, 115.4, 55.1, 43.7, 41.4, 29.7. **IR (cm^{-1})**: ν 3135, 1697, 1613, 1508, 1398, 1348, 1261, 701. **HRMS**: m/z: $[M + Na]^+$ calculated for $C_{18}H_{17}NNaO_2S^+$, 334.0872, found 334.0875.

(*Z*)-*N*-((3-oxo-3',4'-dihydro-2'*H*-spiro[cyclopentane-1,1'-naphthalen]-4-ylidene)methyl)benzamide (**3l**)



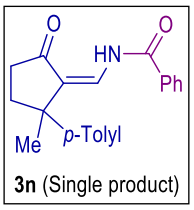
According to the procedure E, **3l** was obtained by the reaction **1j** and **2a.** Compound **3l** was obtained by column chromatography (PE : EA = 25 : 1) as a white solid in 82% yield (27.2 mg). **m.p.**: 139.4 – 141.8 °C. **^{1}H NMR** (**400 MHz, $CDCl_3$**) δ 12.00 (d, *J* = 10.4 Hz, 1H), 7.99 (d, *J* = 7.6 Hz, 2H), 7.64 – 7.50 (m, 4H), 7.32 (d, *J* = 8.0 Hz, 1H), 7.21 – 7.07 (m, 3H), 3.08 (d, *J* = 15.6 Hz, 1H), 2.93 (d, *J* = 18.4 Hz, 1H), 2.88 – 2.80 (m, 3H), 2.58 (d, *J* = 18.4 Hz, 1H), 1.94 – 1.78 (m, 4H). **^{13}C NMR** (**101 MHz, $CDCl_3$**) δ 209.0, 164.7, 142.1, 136.9, 132.7, 132.1, 131.2, 129.4, 128.9, 127.8, 126.3, 126.2, 126.1, 115.8, 55.7, 43.6, 41.6, 37.0, 30.2, 19.8. **IR (cm^{-1})**: ν 3103, 1693, 1609, 1506, 1394, 1259, 1177, 702. **HRMS**: m/z: $[M + Na]^+$ calculated for $C_{22}H_{21}NNaO_2^+$, 354.1465, found 354.1470.

(*Z*)-*N*-((2-oxo-5-(thiophen-3-yl)cyclopentylidene)methyl)benzamide (**3m**) and (Z)-N-((2-oxo-3-(thiophen-3-yl)cyclopentylidene)methyl)benzamide (**3m'**)



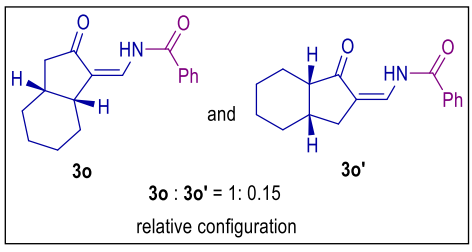
According to the procedure E, **3m** was obtained by the reaction **1k** and **2a.** Compound **3m** and **3m'** were obtained by column chromatography (PE : EA = 25 : 1) as a white amorphous solid in 71% yield (21.1 mg), the mixture could not be isolated by column chromatography. For major product **3m**: **^{1}H NMR (400 MHz, $CDCl_3$)** δ 12.11 (d, *J* = 10.4 Hz, 1H), 7.96 (d, *J* = 7.6 Hz, 2H), 7.58 (q, *J* = 7.2 Hz,1H), 7.54 – 7.44 m, 2H), 7.41 – 7.32 (m, 2H), 7.13 – 7.15 (m, 1H), 6.99 (d, *J* = 4.4 Hz, 1H), 4.22 (t, *J* = 7.4 Hz, 1H), 2.78 (d, *J* = 8.1 Hz, 1H), 2.59 – 2.47 (m, 2H), 2.11 – 1.95 (m, 1H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 209.5, 164.8, 144.0, 133.0, 132.9, 133.7, 128.9, 127.9, 126.7, 126.6, 121.4, 120.0, 41.4, 38.4, 30.8. **IR (cm^{-1})**: ν 3099, 1693, 1610, 1506, 1394, 1259, 1066, 703. **HRMS**: m/z: $[M + Na]^+$ calculated for $C_{17}H_{15}NNaO_2S^+$, 320.0716, found 320.0718.

(*Z*)-*N*-((2-methyl-5-oxo-2-(p-tolyl)cyclopentylidene)methyl)benzamide (**3n**)



According to the procedure E, **3n** was obtained by the reaction **1l** and **2a.** Compound **3n** was obtained by column chromatography (PE : EA = 25 : 1) as a white solid in 74% yield (23.6 mg). **m.p.**: 178.5 – 180.8 °C. **^{1}H NMR (400 MHz, $CDCl_3$)**) δ 12.25 (d, *J* = 10.4 Hz, 1H), 8.00 (d, *J* = 7.2 Hz, 2H), 7.60 (t, *J* = 7.6 Hz, 1H), 7.56 – 7.46 (m, 3H), 7.29 – 7.22 (m, 2H), 7.13 (d, *J* =8.0 Hz, 2H), 2.50 – 2.37 (m, 3H), 2.33 (s,, 3H), 2.12 – 2.02 (m, 1H), 1.64 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 210.0, 164.9, 144.4, 136.0, 132.9, 132.7, 132.2, 129.1, 128.9, 127.8, 126.2, 124.9, 47.1, 38.1, 36.8, 29.0, 20.8. **IR (cm^{-1})**: ν 3104, 1608, 1508, 1506, 1398, 1261, 1182, 819. **HRMS**: m/z: $[M + Na]^+$ calculated for $C_{21}H_{21}NNaO_2^+$, 342.1465, found 342.1466.

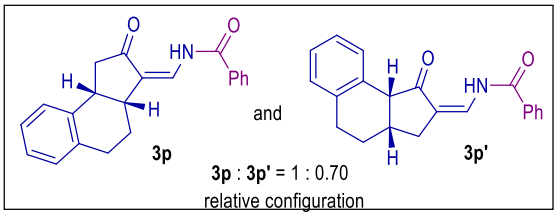
Cis-*N*-2-oxooctahydro-1H-inden-1-ylidene)methyl)benzamide (**3o**) and *Cis*-(*Z*)-*N*-((2-oxooctahydro-1*H*-inden-1-ylidene)methyl)benzamide (**3o'**)



According to the procedure E, **3o** was obtained by the reaction **1m** and **2a.** Compound **3o** and **3o'** were obtained by column chromatography (PE : EA = 25 : 1) as a white amorphous solid in 82% yield (21.9 mg),

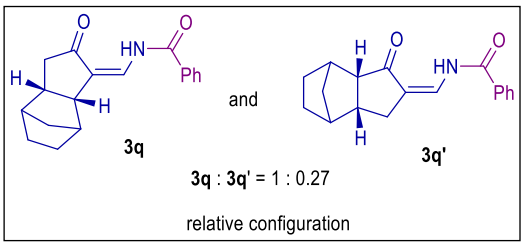
the mixture could not be isolated by column chromatography and distinguished by ^{1}H NMR. For major product **3o**: **^{1}H NMR (400 MHz, $CDCl_3$)** δ 11.97 (d, *J* = 10.4 Hz, 1H), 7.98 (d, *J* = 7.2 Hz, 2H), 7.61 – 7.54 (m, 1H), 7.54 – 7.41 (m, 3H), 2.98 (d, *J* = 4.0 Hz, 1H), 2.42 (dd, *J* = 17.2, 6.8 Hz, 1H), 2.37 – 2.28 (m, 1H), 2.18 (dd, *J* = 17.2, 3.6 Hz, 1H), 1.91 – 1.80 (m, 1H), 1.74 – 1.52 (m, 3H), 1.45 – 1.16 (m, 4H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 210.9, 164.7, 132.7, 132.3, 130.3, 128.8, 127.7, 119.1, 45.0, 39.3, 34.8, 28.4, 26.7, 23.6, 21.1. **IR (cm^{-1})**: ν 3099, 1693, 1610, 1506, 1394, 1259, 1066, 703. **HRMS**: m/z: $[M + Na]^+$ calculated for $C_{17}H_{19}NNaO_2^+$, 292.1308, found 292.1306.

Cis-(*Z*)-*N*-((2-oxo-1,2,3*a*,4,5,9*b*-hexahydro-3*H*-cyclopenta[*a*]naphthalen-3-ylidene)methyl)benzamide (**3p**) and *Cis*-(*Z*)-*N*-((1-oxo-1,3,3*a*,4,5,9*b*-hexahydro-2*H*-cyclopenta[*a*]naphthalen-2-ylidene)methyl)benzamide (**3p'**)



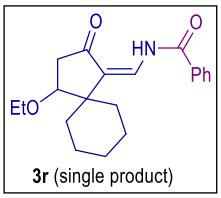
According to the procedure E, **3p** was obtained by the reaction **1n** and **2a**. Compound **3p** and **3p'** were obtained by column chromatography (PE : EA = 25 : 1) as a white amorphous solid in 74% yield (23.6 mg), the mixture could not be isolated by column chromatography and distinguished by ^{1}H NMR. For major product **3p**: **^{1}H NMR (400 MHz, $CDCl_3$)** δ 12.03 (d, *J* = 10.4 Hz, 1H), 7.97 (d, *J* = 7.6 Hz, 2H), 7.72 – 7.56 (m, 2H), 7.55 – 7.45 (m, 2H), 7.25 – 7.04 (m, 4H), 3.69 – 3.55 (m, 1H), 3.21 (dd, *J* = 14.0, 7.6 Hz, 1H), 2.98 – 2.53 (m, 4H), 2.06 – 1.75 (m, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 211.1, 164.7, 137.8, 136.3, 132.8, 132.1, 131.8, 128.9, 128.9, 128.7, 127.8, 126.4, 126.2, 114.9, 49.3, 37.4, 35.2, 28.0, 21.8. **HRMS**: m/z: $[M + Na]^+$ calculated for $C_{21}H_{19}NNaO_2^+$, 340.1308, found 340.1314.

Cis-(*Z*)-*N*-((2-oxooctahydro-1*H*-4,7-methanoinden-1-ylidene)methyl)benzamide (**3q**) and *Cis*-(*Z*)-*N*-((1-oxooctahydro-2H-4,7-methanoinden-2-ylidene)methyl)benzamide (**3q'**)



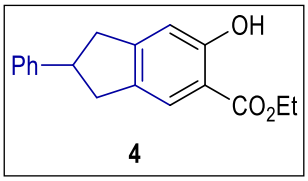
According to the procedure E, **3q** was obtained by the reaction **1o** and **2a.** Compound **3q** + **3q'** were obtained by column chromatography (PE: EA = 25: 1) as a white amorphous solid in 72% yield (20.2 mg), the mixture could not be isolated by column chromatography and distinguished by ^{1}H NMR. For major product **3q**: **^{1}H NMR (400 MHz, $CDCl_3$)** δ 12.26 – 12.12 (m, 1H), 8.12 – 7.92 (m, 2H), 7.62 – 7.46 (m, 4H), 3.09 – 2.65 (m, 2H), 2.43 – 2.02 (m, 4H), 1.64 – 1.49 (m, 2H), 1.36 – 1.19 (m, 3H), 1.17 – 1.09 (m, 1H). **^{13}C NMR (101 MHz, $CDCl_3$)**δ 211.9, 164.8, 132.8, 132.4, 132.2, 130.9, 127.8, 120.1, 48.5, 45.3, 44.7, 43.3, 40.4, 32.5, 28.8, 28.2. **IR (cm^{-1})**: ν 3104, 1691, 1600, 1398, 1353, 1256, 1128, 703. **HRMS**: m/z: $[M + Na]^+$ calculated for $C_{18}H_{19}NNaO_2^+$, 304.1308, found 304.1312.

(*Z*)-*N*-((4-ethoxy-2-oxospiro[4.5]decan-1-ylidene)methyl)benzamide (**3r**)



According to the procedure E, **3r** was obtained by the reaction **1p** and **2a.** Compound **3r** was obtained by column chromatography (PE : EA = 25 : 1) as a white amorphous solid in 74% yield (24.1 mg). **m.p.**: 147.2 – 149.8 °C. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 11.93 (d, *J* = 10.0 Hz, 1H), 7.96 (d, *J* = 7.2 Hz, 2H), 7.64 – 7.44 (m, 4H), 2.79 (dd, *J* = 15.6, 7.6 Hz, 1H), 2.54 (dd, *J* = 18.0, 7.6 Hz, 1H), 2.42 – 2.32 (m, 1H), 2.17 (dd, *J* = 17.6, 10.8 Hz, 1H), 2.06 – 1.93 (m, 1H), 1.86 – 1.62 (m, 6H), 1.35 – 1.11 (m, 5H), 1.04 – 0.91 (m, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 210.0, 164.7, 132.73, 132.3, 130.3, 128.9, 127.8, 116.9, 44.6, 43.4, 41.7, 32.3, 31.5, 30.8, 26.4, 26.1. **IR (cm^{-1})**: ν 3158, 1670, 1597, 1504, 1398, 1353, 1262, 703. **HRMS**: m/z: $[M + Na]^+$ calculated for $C_{20}H_{25}NNaO_3^+$, 350.1727, found 350.1727.

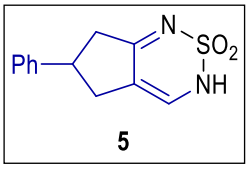
Ethyl 6-hydroxy-2-phenyl-2,3-dihydro-1*H*-indene-5-carboxylate (**4**)



According to the procedure G, **4** was obtained by column chromatography (PE : EA = 40 : 1) as colorless oil in 61% yield (17.2 mg). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 10.89 (s, 1H), 7.69 (s, 1H), 7.34 – 7.19 (m, 5H), 6.87 (s, 1H), 4.40 (q, *J* = 7.2 Hz, 2H),

3.68 (p, J = 8.4 Hz, 1H), 3.38 – 3.24 (m, 2H), 3.11 – 2.94 (m, 2H), 1.42 (t, J = 7.2 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** 170.5, 161.2, 152.1, 144.9, 134.7, 128.5, 126.9, 126.4, 124.7, 113.0, 110.6, 61.2, 45.5, 41.2, 39.7, 14.2. **IR (cm^{-1})**: ν 3209, 1670, 1398, 1267, 1059, 1179, 796, 699. **HRMS**: m/z: $[M + H]^+$ calculated for $C_{18}H_{19}O_3^+$, 283.1328, found 283.1326.

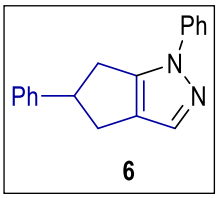
6-Phenyl-3,5,6,7-tetrahydrocyclopenta[*c*][1,2,6]thiadiazine 2,2-dioxide (**5**)



5

According to the procedure H, **5** was obtained by column chromatography (CH_2Cl_2 : MeOH = 10 : 1) as a white solid in 72% yield (17.9 mg). **m.p.**: 99.8 – 101.7 °C. **^{1}H NMR (400 MHz, CD_3OD)** δ 7.47 (s, 1H), 7.20 – 7.14 (m, 4H), 7.11 – 7.14 (dq, J = 6.4, 3.2 Hz, 1H), 3.51 (p, J = 8.2 Hz, 1H), 2.96– 2.79 (m, 2H), 2.62 (dd, J = 16.8, 8.4 Hz, 1H), 2.55 (dd, J = 13.6, 7.6 Hz, 1H). **^{13}C NMR (101 MHz, CD_3OD)** δ 175.7, 154.1, 146.4, 129.5, 127.8, 127.3, 109.3, 44.2, 44.1, 37.6. **IR (cm^{-1})**: ν 3148, 2551, 1646, 1522, 1398, 1171, 1116, 700. **HRMS**: m/z: $[M + Na]^+$ calculated for $C_{12}H_{12}N_2NaO_2S^+$, 271.0512, found 271.0515.

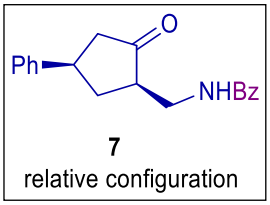
1,5-Diphenyl-1,4,5,6-tetrahydrocyclopenta[*c*]pyrazole (**6**)



6

According to the procedure I, **6** was obtained by column chromatography (PE : EA = 50 : 1) as colorless oil in 57% yield (14.8 mg). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.65 (d, J = 8.0 Hz, 2H), 7.59 (s, 1H), 7.42 (t, J = 7.6 Hz, 2H), 7.33 (d, J = 4.4 Hz, 3H), 7.27 – 7.20 (m, 3H), 4.04 (p, J = 8.4 Hz, 1H), 3.28 (dd, J = 16.4, 8.4 Hz, 1H), 3.19 (dd, J = 16.0, 8.0 Hz, 1H), 2.97 (dd, J = 15.2, 8.0 Hz, 1H), 2.84 (dd, J = 15.2, 8.0 Hz, 1H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 162.2, 145.2, 140.9, 129.4, 128.6, 127.0, 126.4, 125.9, 125.6, 120.6, 118.6, 50.3, 33.3, 32.1. **HRMS**: m/z: $[M + H]^+$ calculated for $C_{18}H_{17}N_2^+$, 261.1386, found 261.1386.

Cis-N-((2-oxo-4-phenylcyclopentyl)methyl)benzamide (**7**)

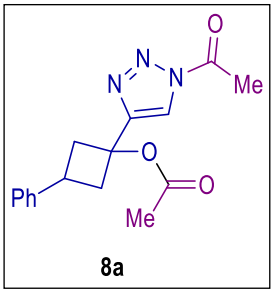


7
relative configuration

According to the procedure J, **7** was obtained by column chromatography (PE : EA = 10 : 1) as colorless oil in 75% yield (22.0 mg). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.79 (d, J = 7.6 Hz, 2H), 7.55 –

7.48 (m, 1H), 7.47 –7.41(m, 2H), 7.33 (t, *J* = 7.6 Hz, 2H), 7.23 (s, 2H), 7.14 (s, 1H), 4.06 – 3.95 (m, 1H), 3.51 – 3.36 m, 2H), 2.88 – 2.78 (m, 1H), 2.71 – 2.57 (m, 2H), 2.43 – 2.31 (m, 1H), 1.79 (d, *J* = 11.9 Hz, 1H). **^{13}C NMR (101 MHz, CDCl$_3$)** δ 167.4, 142.2, 134.2, 131.5, 128.7, 128.6, 126.9, 126.9, 126.7, 50.5, 45.8, 39.9, 39.1, 35.4. **IR (cm^{-1})**: ν 3096, 1697, 1597, 1509, 1394, 1354, 1270, 696. **HRMS**: m/z: $[M + Na]^+$ calculated for $C_{19}H_{19}NNaO_2^+$, 316.1308, found 316.1306.

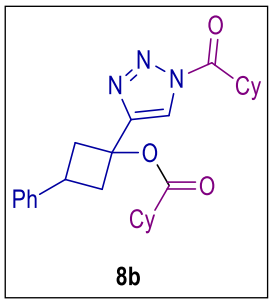
1-(2-acetyl-2*H*-1,2,3-triazol-4-yl)-3-phenylcyclobutyl acetate (**8a**)



8a

According to the procedure E, **8a** was obtained by column chromatography (PE: EA = 40: 1) as colorless oil in 69% yield (20.6 mg). **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.97 (s, 1H), 7.38 – 7.31 (m, 2H), 7.26 – 7.21 (m, 3H), 3.47 – 3.35 (m, 1H), 3.28 – 3.25 (m, 2H), 2.85 (s, 3H), 2.72 (td, *J* = 10.0, 2.8 Hz, 2H), 2.08 (s, 3H). **^{13}C NMR (101 MHz, CDCl$_3$)** δ 169.7, 166.1, 154.2, 143.3, 137.2, 128.5, 126.5, 126.4, 72.0, 42.3, 31.7, 22.2, 21.2. **IR (cm^{-1})**: ν 3473, 2927, 1765, 1741, 1287, 1251, 1224, 935. **HRMS**: m/z: $[M + H]^+$ calculated for $C_{16}H_{18}N_3O_3^+$, 300.1343, found 300.1328.

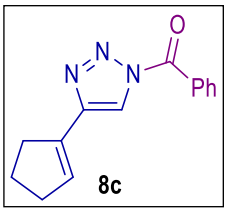
1-(2-(cyclohexanecarbonyl)-2*H*-1,2,3-triazol-4-yl)-3-phenylcyclobutyl cyclohexanecarboxylate (**8b**)



8b

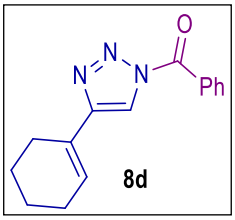
According to the procedure E, **8b** was obtained by column chromatography (PE: EA = 40: 1) as colorless oil in 42% yield (18.2 mg). **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.91 (s, 1H), 7.38 – 7.31 (m, 2H), 7.24 (d, J = 7.6 Hz, 3H), 3.66 (tt, J = 11.7, 3.4 Hz, 1H), 3.50 – 3.39 (m, 1H), 3.28 – 3.25 (m, 2H), 2.68 (td, J = 10.0, 2.8 Hz, 2H), 2.32 (tt, J = 11.2, 3.6 Hz, 1H), 2.11 – 2.02 (m, 2H), 1.95 – m, 4H), 1.81 – 1.71 (m, 3H), 1.65 (dd, J = 12.0, 3.2 Hz, 2H), 1.51 – 1.35 (m, 4H), 1.34 – 1.23 (m, 5H). **^{13}C NMR (101 MHz, CDCl$_3$)** δ 174.8, 171.7, 154.1, 143.6, 136.6, 128.5, 126.4, 126.4, 72.0, 43.0, 42.4, 42.3, 31.8, 29.1, 28.8, 25.6, 25.4, 25.3, 25.3. **IR (cm^{-1})**: ν 2933, 2856, 1751, 1705, 1449, 1317, 1254, 937. **HRMS**: m/z: $[M + H]^+$ calculated for $C_{26}H_{34}N_3O_3^+$, 436.2595, found 436.2574.

(4-(Cyclopent-1-en-1-yl)-1*H*-1,2,3-triazol-1-yl)(phenyl)methanone (**8c**)



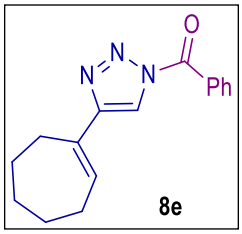
Compound **8a** was obtained by column chromatography (PE: EA = 40: 1) as colorless oil in 71% yield (17.0 mg). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.10 – 8.00 (m, 2H), 7.50 – 7.42 (m, 3H), 6.97 (s, 1H), 6.29 – 6.21 (m, 1H), 2.70 – 2.53 (m, 4H), 2.04 (p, *J* = 7.6 Hz, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 160.7, 149.4, 130.1, 129.9, 128.7, 127.9, 127.5, 126.2, 124.0, 33.2, 32.1, 23.2. **IR (cm^{-1})**: ν 3440, 2955, 1683, 1448, 1481, 1448, 1128, 712. **HRMS**: m/z: $[M+Na]^+$ calculated for $C_{14}H_{14}N_3O^+$, 240.1131, found 240.1131.

(4-(Cyclohex-1-en-1-yl)-1*H*-1,2,3-triazol-1-yl)(phenyl)methanone (**8d**)



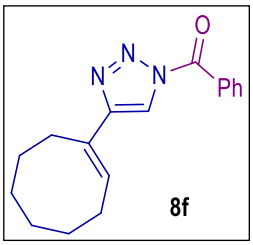
Compound **8d** was obtained by column chromatography (PE: EA = 40: 1) as colorless oil in 68% yield (17.2 mg).**^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.05 – 8.02 (m, 2H), 7.47 – 7.42 (m, 3H), 6.96 (s, 1H), 6.47 – 6.40 (m, 1H), 2.32 (s, 2H), 2.23 (s, 2H), 1.81 – 1.74 (m, 2H), 1.73 – 1.66 (m, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 160.3, 152.5, 130.0, 128.7, 127.7, 126.1, 124.9, 122.0, 25.2, 24.6, 22.1, 22.1. **IR (cm^{-1})**: ν 1727, 1684, 1683, 1449, 1482, 1449, 1250, 1026. **HRMS**: m/z: $[M+Na]^+$ calculated for $C_{15}H_{15}N_3NaO^+$, 276.1107, found 276.1104.

(4-(cyclohept-1-en-1-yl)-1*H*-1,2,3-triazol-1-yl)(phenyl)methanone (**8e**)



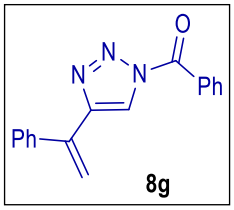
Compound **8d** was obtained by column chromatography (PE: EA = 40: 1) as colorless oil in 74% yield (19.8 mg).**^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.05 – 8.02 (m, 2H), 7.47 – 7.42 (m, 3H), 6.96 (s, 1H), 6.47 – 6.40 (m, 1H), 2.32 (s, 2H), 2.23 (s, 2H), 1.81 – 1.74 (m, 2H), 1.73 – 1.66 (m, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.6, 153.1, 131.5, 130.0, 129.7, 128.7, 127.6, 126.1, 122.7, 32.3, 29.6, 28.5, 26.6, 26.5. **IR (cm^{-1})**: ν 2922, 1562, 1537, 1486, 1448, 1132, 1069, 710. **HRMS**: m/z: $[M-H]^-$ calculated for $C_{16}H_{16}N_3O^-$, 266.1294, found 266.1300.

(4-(cyclooct-1-en-1-yl)-1*H*-1,2,3-triazol-1-yl)(phenyl)methanone (**8f**)



Compound **8f** was obtained by column chromatography (PE: EA = 40: 1) as colorless oil in 72% yield (20.2 mg).**^{1}H NMR (400 MHz, CDCl$_3$)** δ 8.04 (m, 2H), 7.43 (dd, J = 7.2, 3.6 Hz, 3H), 6.99 (d, J = 3.6 Hz, 1H), 6.41 (td, J = 8.4, 3.2 Hz, 1H), 2.56 – 2.49 (m, 2H), 2.37 – 2.27 (m, 2H), 1.69 – 1.56 (m, 4H), 1.56 – 1.48 (m, 4H). **^{13}C NMR (101 MHz, CDCl$_3$)** δ 160.4, 152.4, 132.3, 130.0, 128.7, 127.9, 127.6, 126.1, 122.6, 30.0, 29.0, 26.6, 26.5, 26.0, 25.9. **IR (cm^{-1})**: ν 2925, 1684, 1636, 1561, 1537, 1469, 1285, 774. **HRMS**: m/z: $[M - H]^-$ calculated for $C_{17}H_{18}N_3O^-$, 280.1450, found 280.1462.

Phenyl(4-(1-phenylvinyl)-1*H*-1,2,3-triazol-1-yl)methanone (**8g**)



Compound **8c** was obtained by column chromatography (PE: EA = 40: 1) as colorless oil in 51% yield (13.9 mg). **^{1}H NMR (400 MHz, CDCl$_3$)** δ 8.13 – 8.05 (m, 2H), 7.48 – 7.41 (m, 5H), 7.44 – 7.39 (m, 3H), 7.00 (s, 1H), 5.88 (s, 1H), 5.39 (s, 1H). **^{13}C NMR (101 MHz, CDCl$_3$)** δ 161.5, 151.1, 138.3, 136.7, 130.5, 128.8, 128.5, 128.2, 128.0, 127.3, 126.9, 126.4, 113.9. **IR (cm^{-1})**: ν 3448, 2956, 1727, 1646, 1482, 1484, 1448, 1248. **HRMS**: m/z: $[M + Na]^+$ calculated for $C_{17}H_{13}N_3NaO^+$, 298.0951, found 298.0954.

6. X-ray structure.

The single crystal was obtained by slow evaporation of a saturated solution in ethyl acetate in a lossely capped vial. Structure information was deposited at the Cambridge Crystallographic Data Center (CCDC).

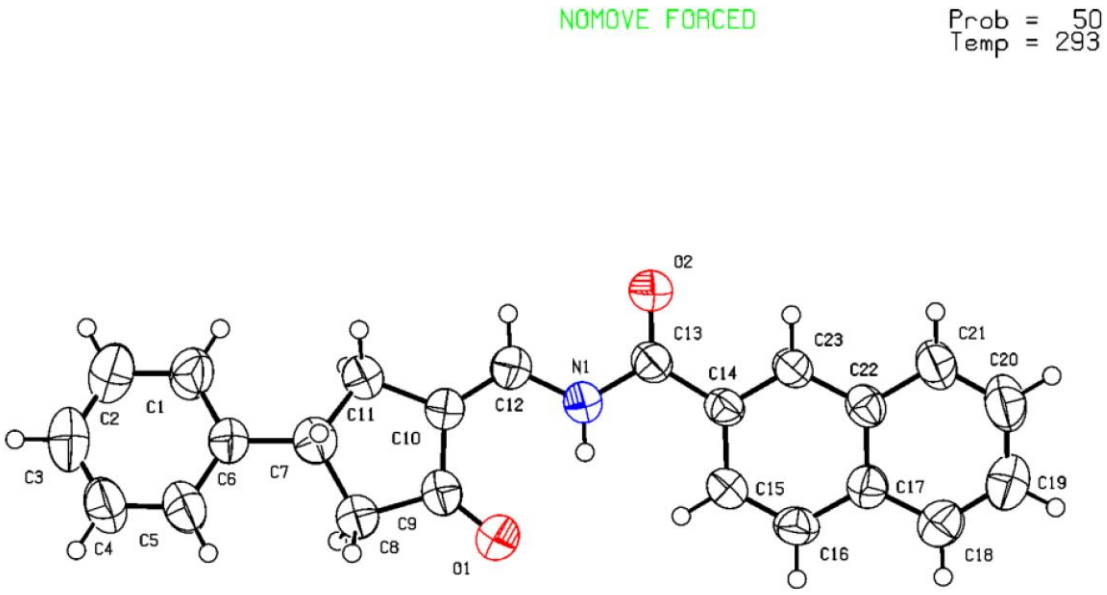


Fig. 1. X-ray crystallographic structure of **3c** (CCDC 2113582) showing thermal ellipsoid probability at 50%.

The crystal was prepared by slow evaporation using petroleum ether and ethyl acetate solvent mixture (m.p: 108.2 – 110.6 °C). A single crystal of **3c** was mounted and the diffraction data was collected at 293 K on a Rigaku SuperNova diffractometer using CrysAlisPro software, which coupled with a Mo source (λ = 0.71073 Å). The structure of the crystal was solved by ShelXT[7] and refined by ShelXL[8] program based on the Olex2[9] software. The ORTEP image of compound **3c** and crystallographic refinement parameters are given below.

Crystal Data for $C_{23}H_{19}NO_2$ (M = 341.39 g/mol): monoclinic, space group $P2_{1/c}$ (no. 14), a = 10.1851(6) Å, b = 9.5684(6) Å, c = 18.3153(10) Å, β = 96.013(5)°, V = 1775.10(18) Å^3, Z = 4, T = 293 (2)K, μ(Mo Kα) = 0.081 mm^{-1}, *Dcalc* = 1.277 g/cm^3, 7866 reflections measured (7.112° ≤ 2θ ≤ 57.99°), 4059 unique (R_{int} = 0.0423, R_{sigma} = 0.1153) which were used in all calculations. The final $R1$ was 0.0652 (I > 2σ(I)) and wR_2 was 0.1955.

7. References

1 A. L. Featherston, C. R. Shugrue, B. Mercado and S. J. Miller, *ACS Catal.,* 2019, **9**, 242.

2 Q.-S. Tian, B. Chen and G,-Z. Zhang, *Green Chem*., 2016,**18**, 6236.

3 J. Raushel and V. V. Fokin, *Org. Lett*., 2010, **12**, 4952.

4 J. M. Medina, T. Kang, T. G. Erbay, H. Shao, G. M. Gallego, S. Yang, M. Tran-Dubé, P. F. Richardson, J. Derosa and R. T. Helsel, *ACS Catal*., 2019, **9**, 11130.

5 C. R. Shugrue and S. J. Miller, *Angew. Chem., Int. Ed*., 2015, **54**, 11173.

6 (*a*) J. Barluenga, C. Valdés, G. Beltrán, M. Escribano and F. Aznar, *Angew. Chem., Int. Ed.*, 2006, **45**, 6893; (*b*) E. J. Yoo, M. Ahlquist, S. H. Kim, I. Bae, V. V. Fokin, K. B. Sharpless and S. Chang, *Angew. Chem*., *Int. Ed.*, 2007, **46**, 1730.

7 G. M. Sheldrick, *Acta Cryst.* 2015, A71, 3–8.

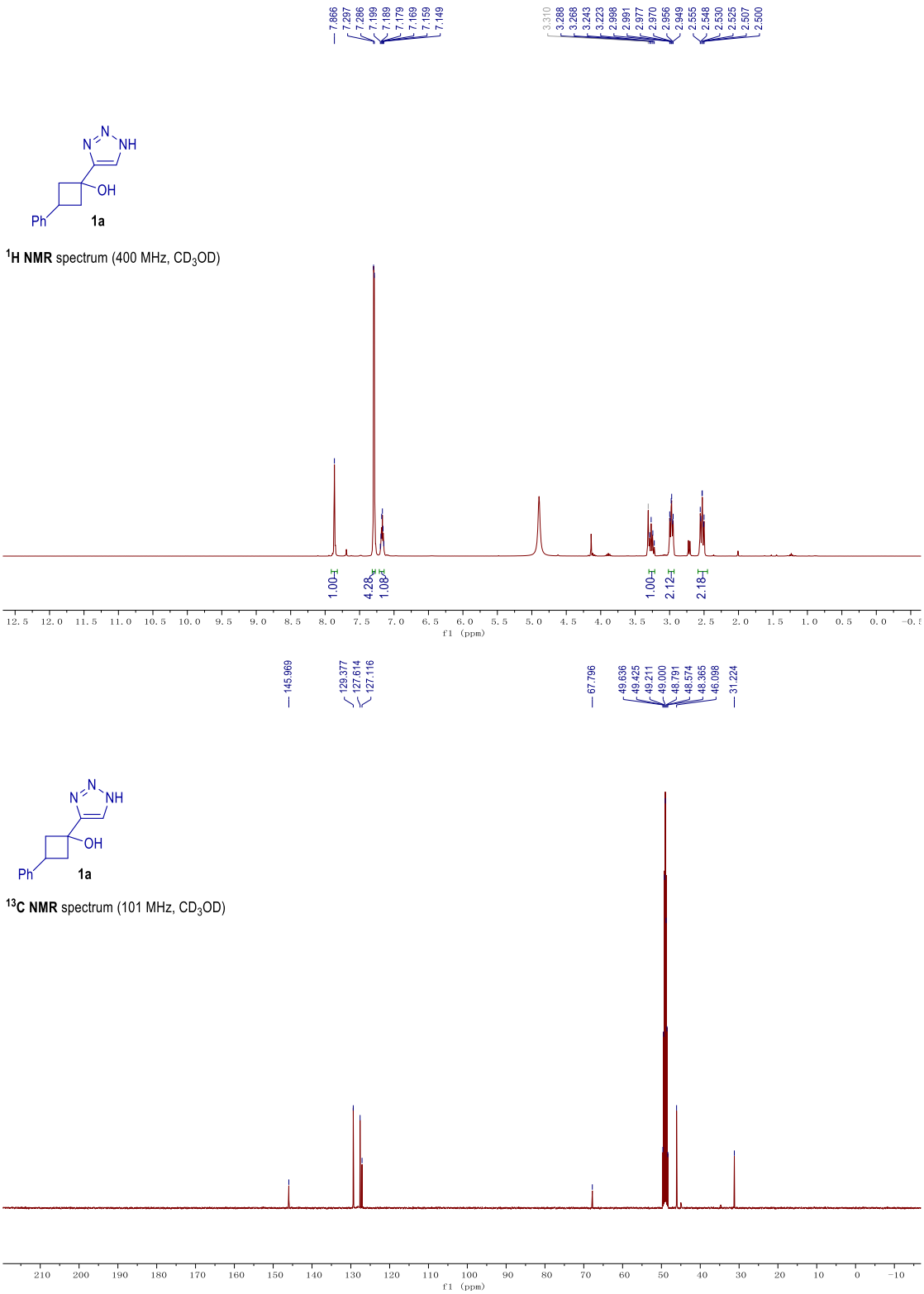
8 G. M. Sheldrick, *Acta Cryst*. 2015, C71, 3–8.

9 O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. J. Puschmann, *Appl. Cryst.* 2009, **42**, 339.

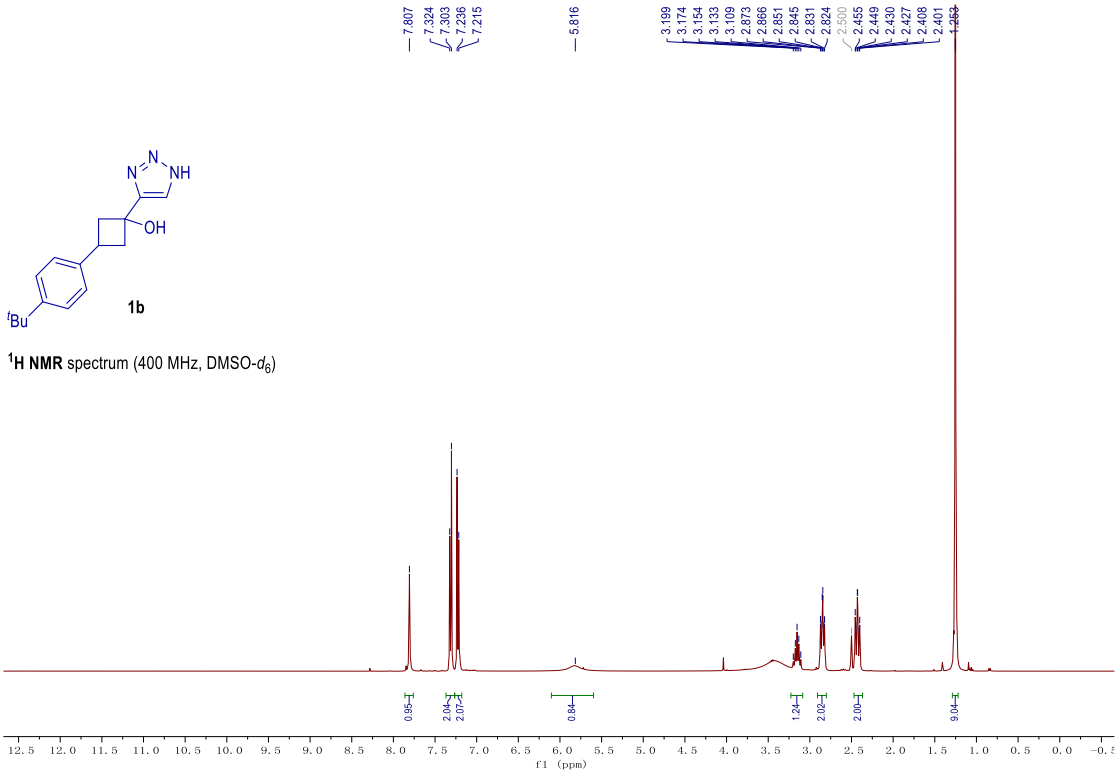
8. Copies of NMR spectra

The ^{13}C signals of substrates **1a** – **1s** couldn't be got completely that the two carbon atoms on the triazole ring do not give signals as reported in literatures[6] (ref. 6a SI page S2 and ref. 6b SI page S25), even if the time was prolonged (3h) and different solvents (CD_3OD, $CDCl_3$ and DMSO-d_6) were used.

1a

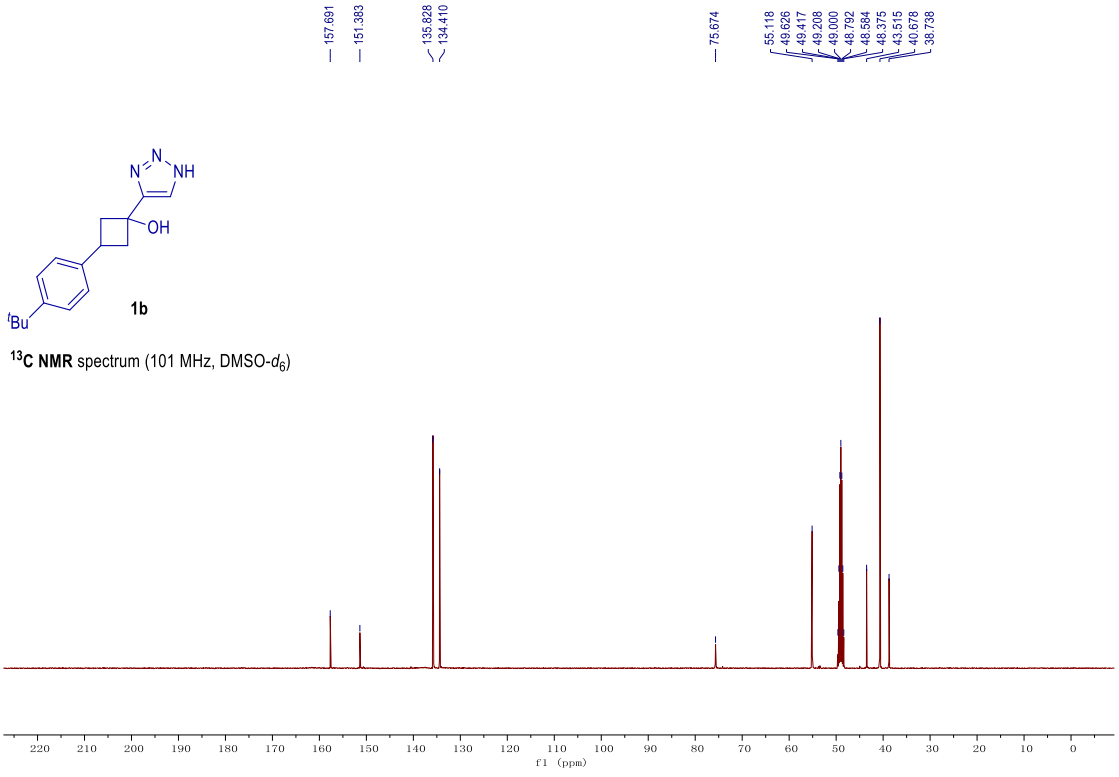


1b



1b

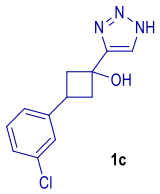
^{1}**H NMR** spectrum (400 MHz, DMSO-d_6)



1b

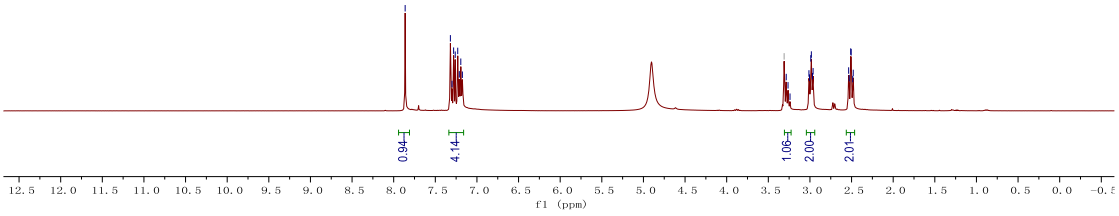
^{13}**C NMR** spectrum (101 MHz, DMSO-d_6)

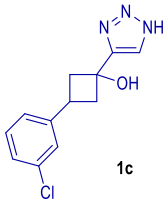
1c



1c

^{1}H NMR spectrum (400 MHz, CD_3OD)

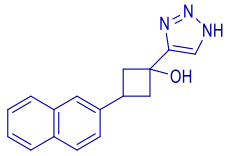




1c

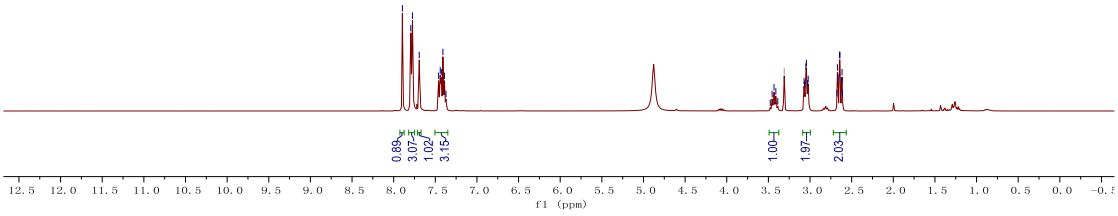
^{13}C NMR spectrum (101 MHz, CD_3OD)

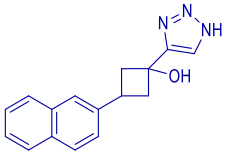
1d



1d

^{1}H NMR spectrum (400 MHz, CD_3OD)





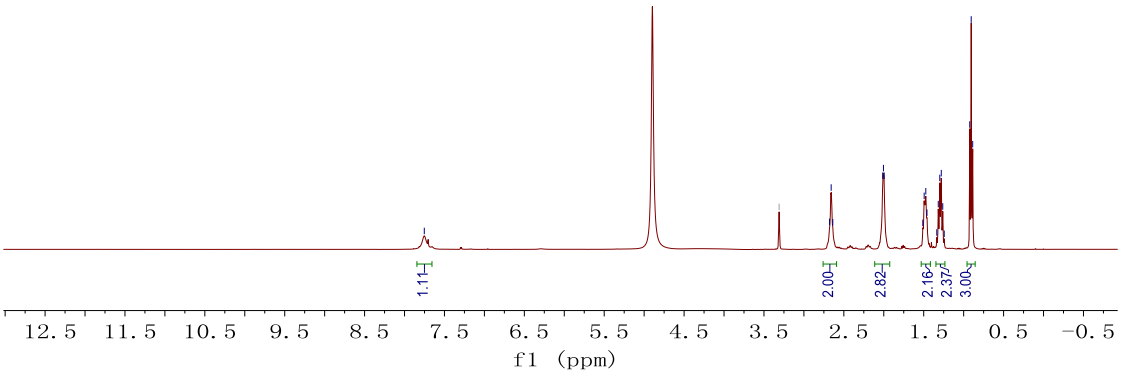
1d

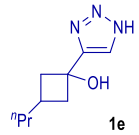
^{13}C NMR spectrum (101 MHz, CD_3OD)

1e

1e

^{1}H NMR spectrum (400 MHz, CD_3OD)

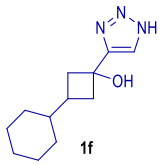




1e

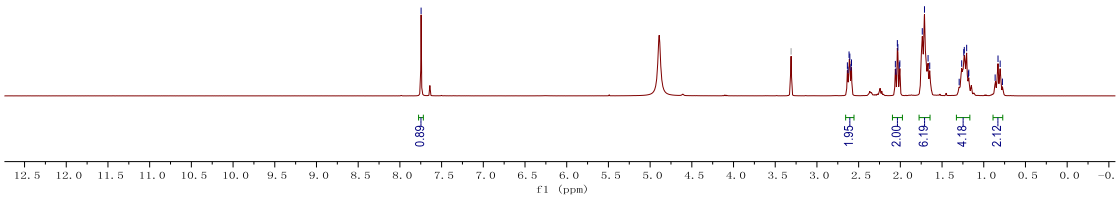
^{13}C NMR spectrum (101 MHz, CD_3OD)

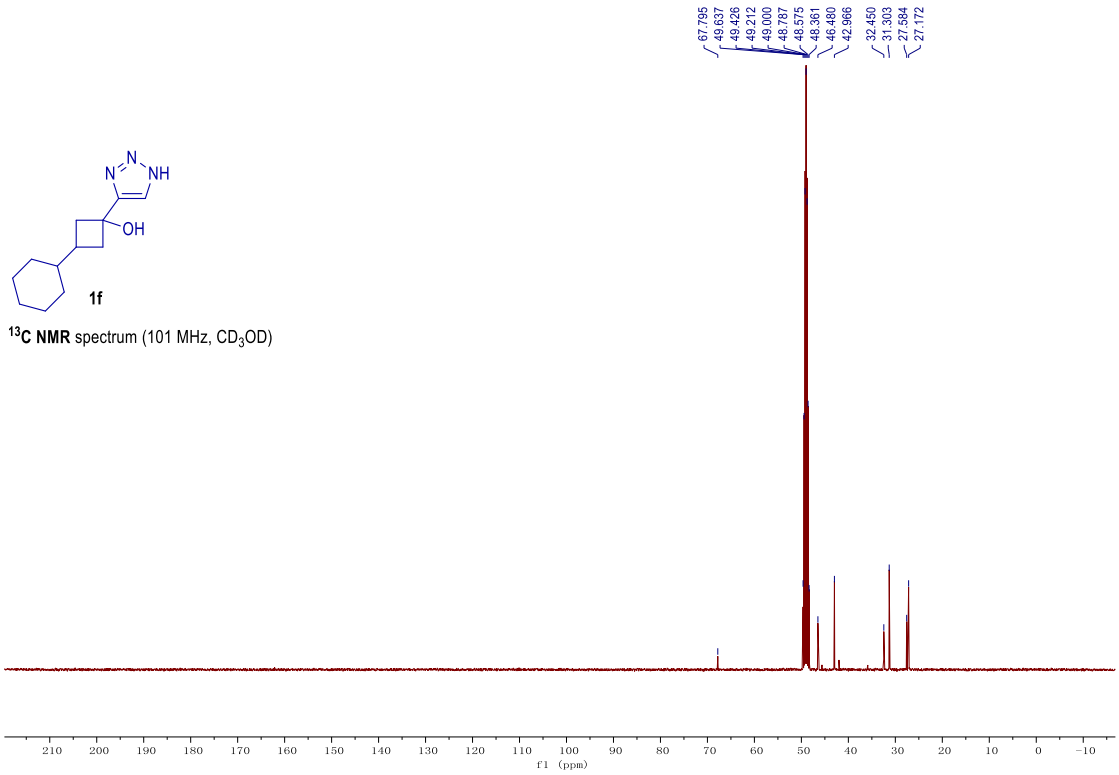
1f



1f

^{1}**H NMR** spectrum (400 MHz, CD_3OD)

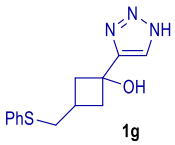




1f

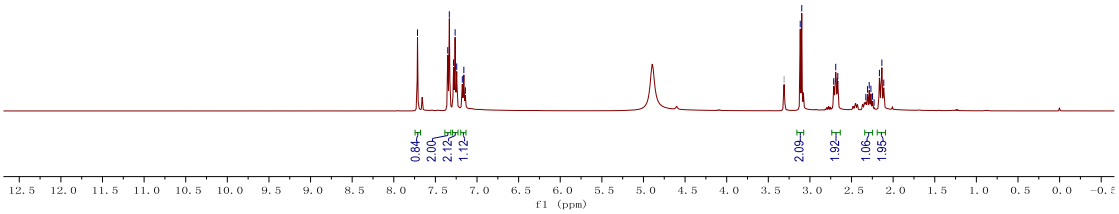
^{13}**C NMR** spectrum (101 MHz, CD_3OD)

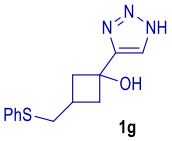
1g



1g

^{1}**H NMR** spectrum (400 MHz, CD_3OD)

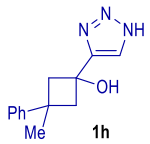




1g

^{13}**C NMR** spectrum (101 MHz, CD_3OD)

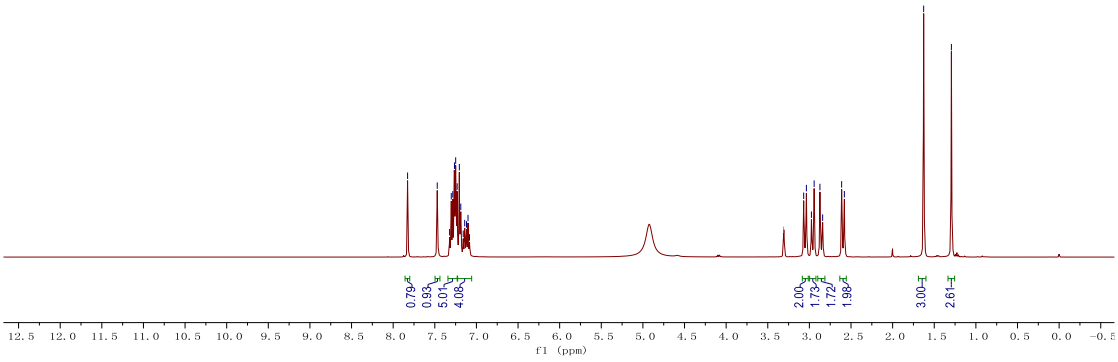
1h

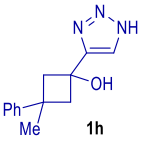


1h

major : minor = 1: 0.9

^{1}H NMR spectrum (400 MHz, CD_3OD)



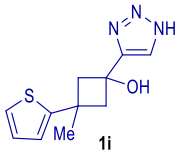


1h

major : minor = 1: 0.9

^{13}C NMR spectrum (101 MHz, CD_3OD)

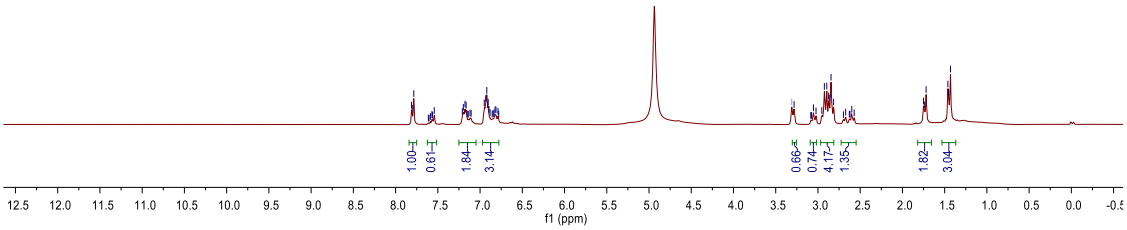
1i

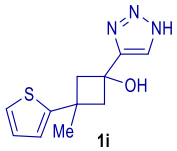


1i

major : minor = 1: 0.6

^{1}H NMR spectrum (400 MHz, CD_3OD)

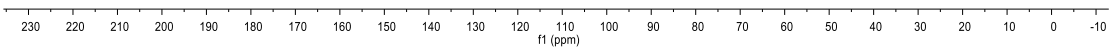




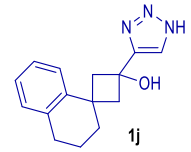
1i

major : minor = 1: 0.6

^{13}C NMR spectrum (101 MHz, CD_3OD)

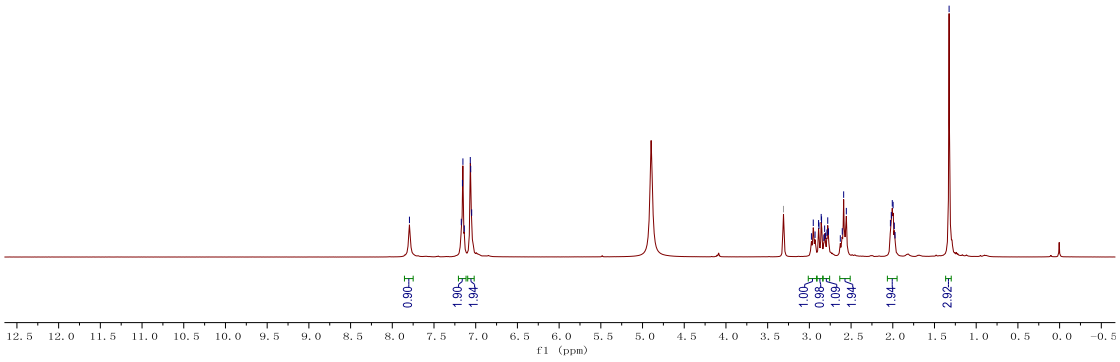


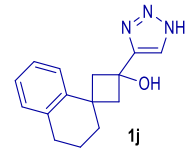
1j



1j

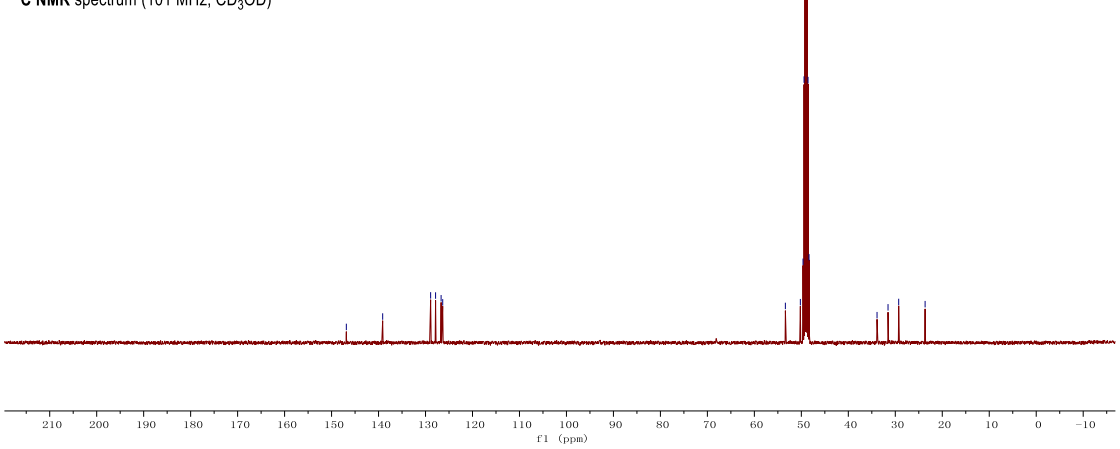
^{1}H NMR spectrum (400 MHz, CD_3OD)



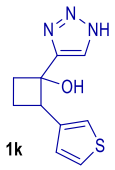


1j

^{13}C NMR spectrum (101 MHz, CD_3OD)

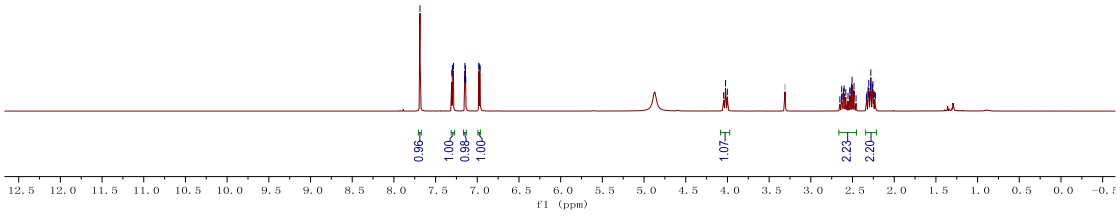


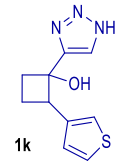
1k



1k

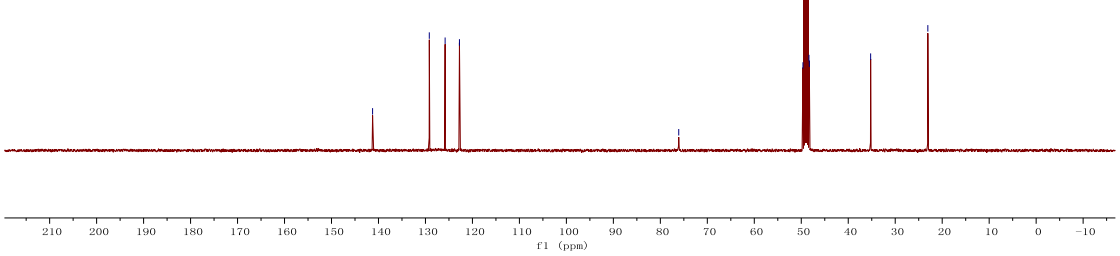
^{1}**H NMR** spectrum (400 MHz, CD_3OD)



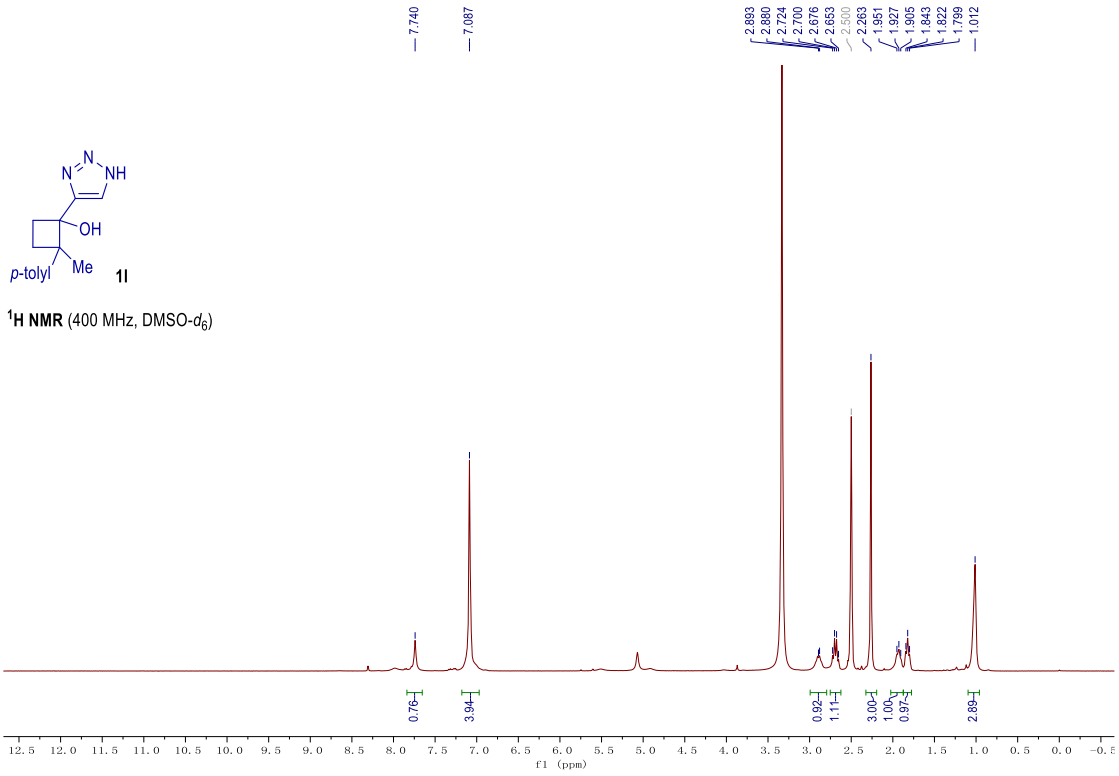


1k

^{13}**C NMR** spectrum (101 MHz, CD_3OD)

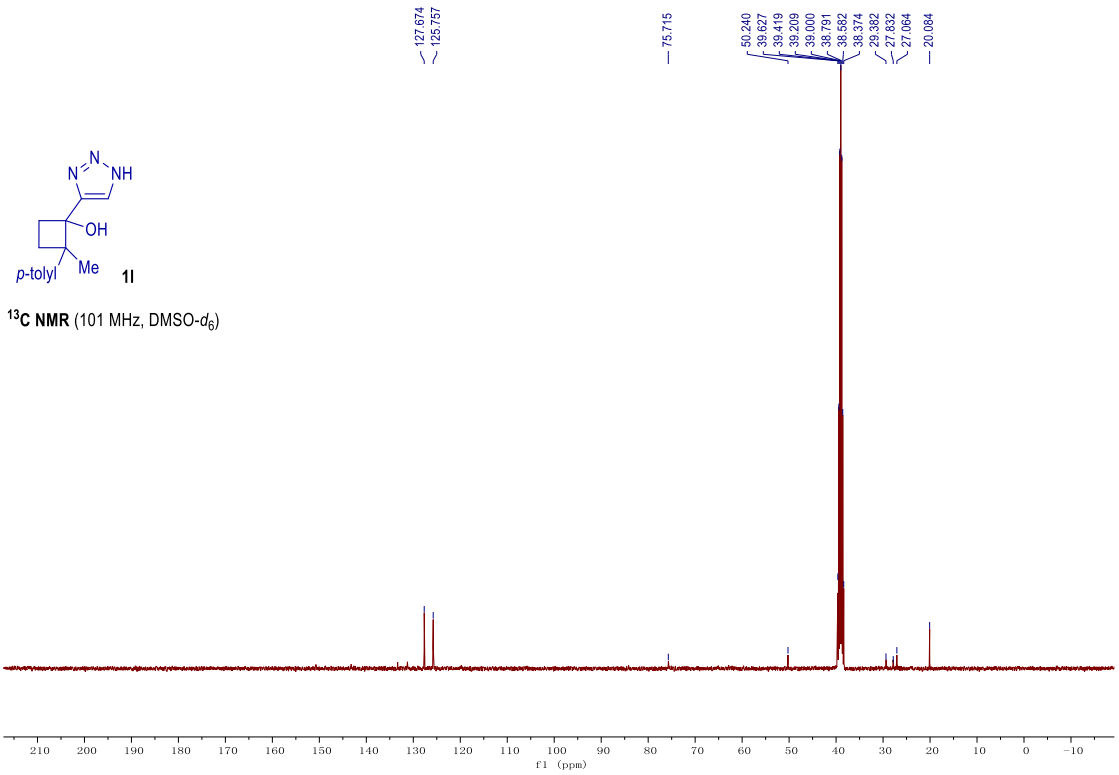


1l



1l

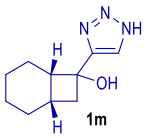
^{1}H NMR (400 MHz, DMSO-d_6)



1l

^{13}C NMR (101 MHz, DMSO-d_6)

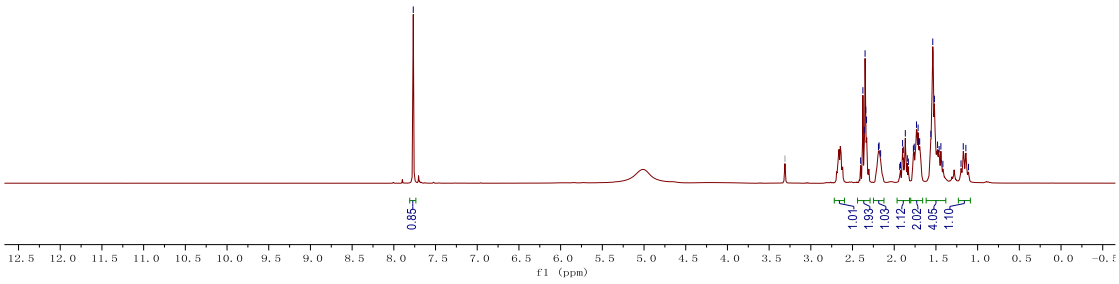
1m

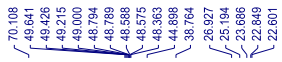


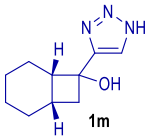
1m

relative configuration

^{1}H NMR spectrum (400 MHz, CD_3OD)



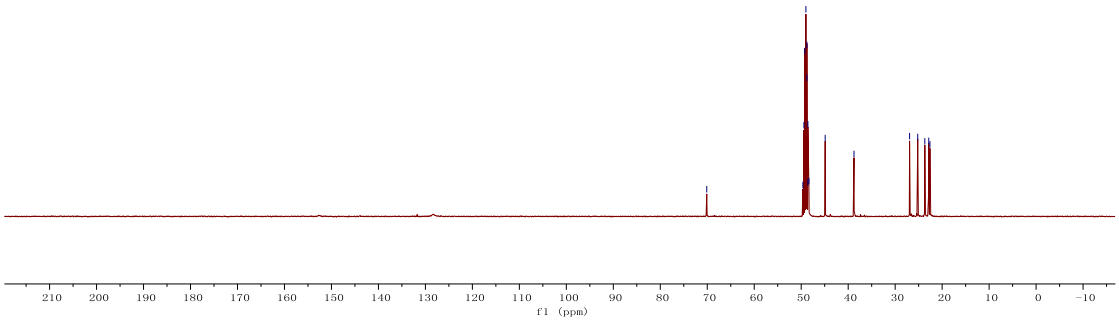




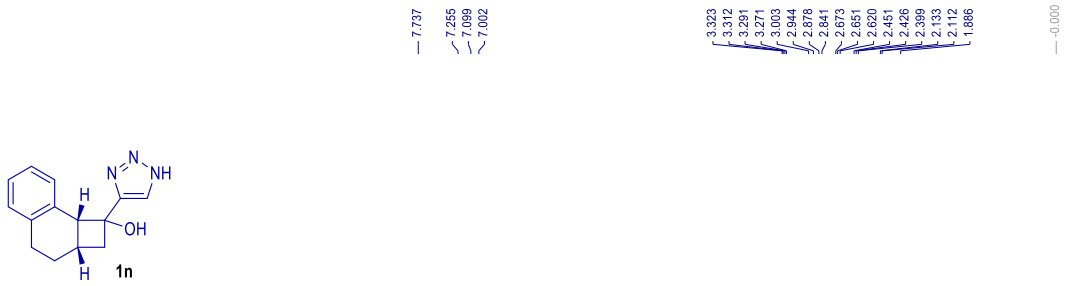
1m

relative configuration

^{13}C NMR spectrum (101 MHz, CD_3OD)



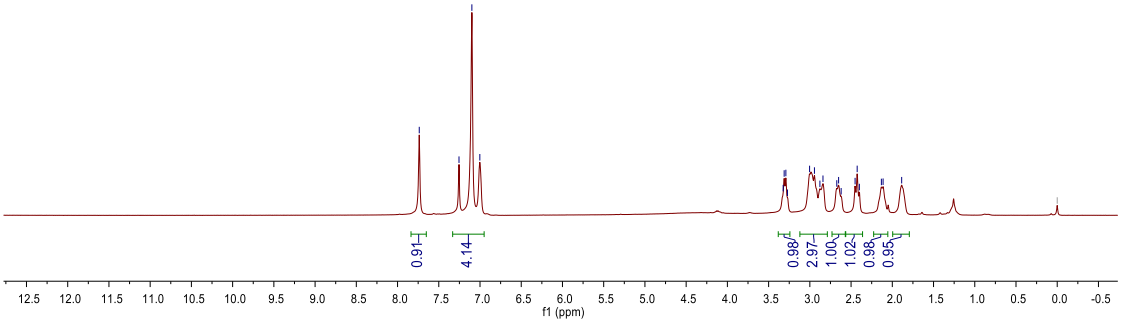
1n

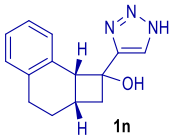


1n

relative configuration

^{1}H NMR spectrum (400 MHz, CD_3OD)



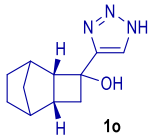


1n

relative configuration

^{13}C NMR spectrum (101 MHz, CD_3OD)

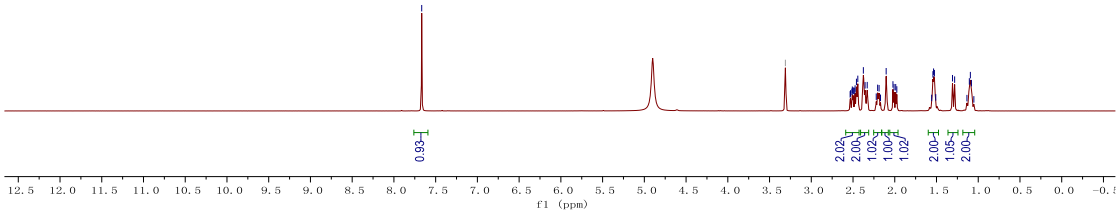
1o

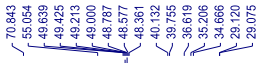


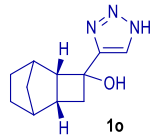
1o

relative configuration

^{1}H NMR spectrum (400 MHz, CD_3OD)



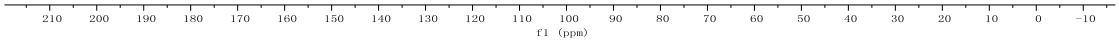




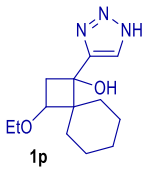
1o

relative configuration

^{13}C NMR spectrum (101 MHz, CD_3OD)

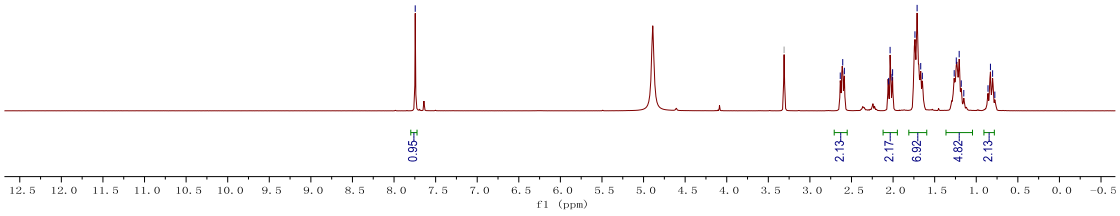


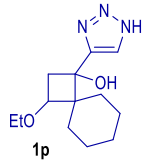
1p



1p

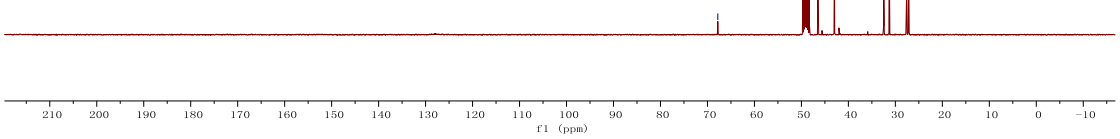
^{1}**H NMR** spectrum (400 MHz, CD_3OD)



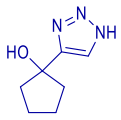


1p

^{13}**C NMR** spectrum (101 MHz, CD_3OD)

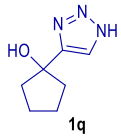


1q



1q

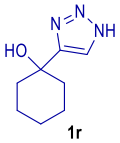
^{1}H NMR (400 MHz, CD_3OD)



1q

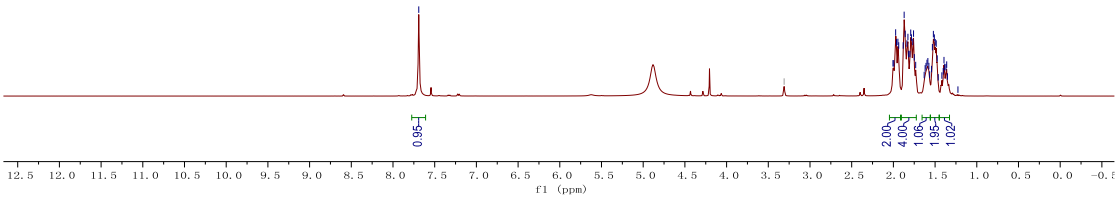
^{13}C NMR (101 MHz, CD_3OD)

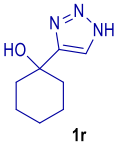
1r



1r

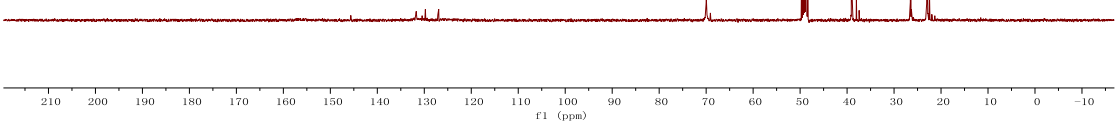
^{1}**H NMR** (400 MHz, CD_3OD)





1r

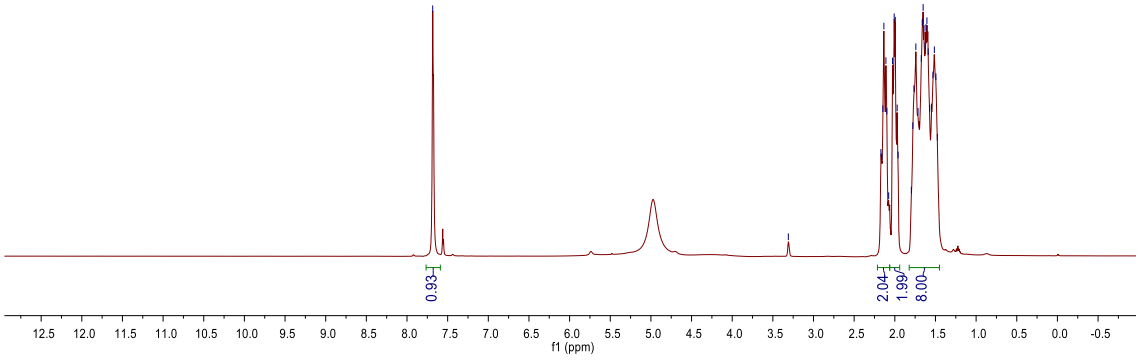
^{13}**C NMR** (101 MHz, CD_3OD)

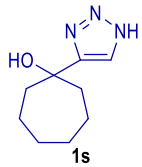


1s

1s

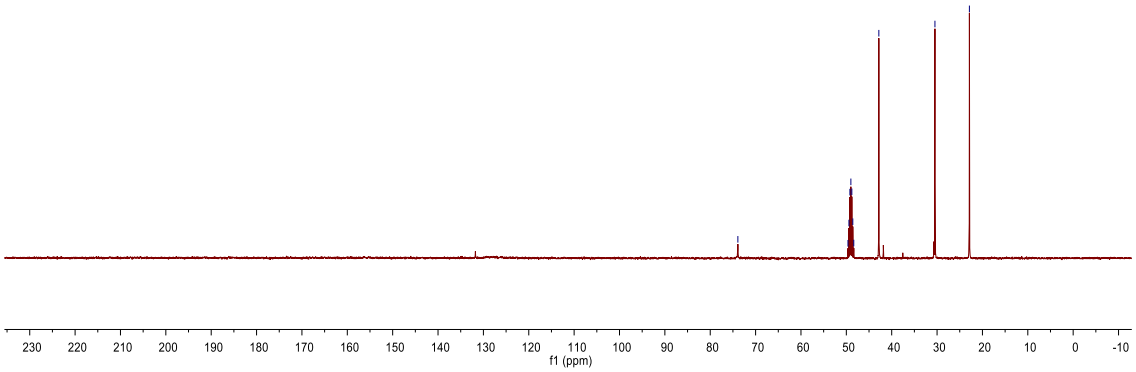
^{1}H NMR (400 MHz, CD_3OD)



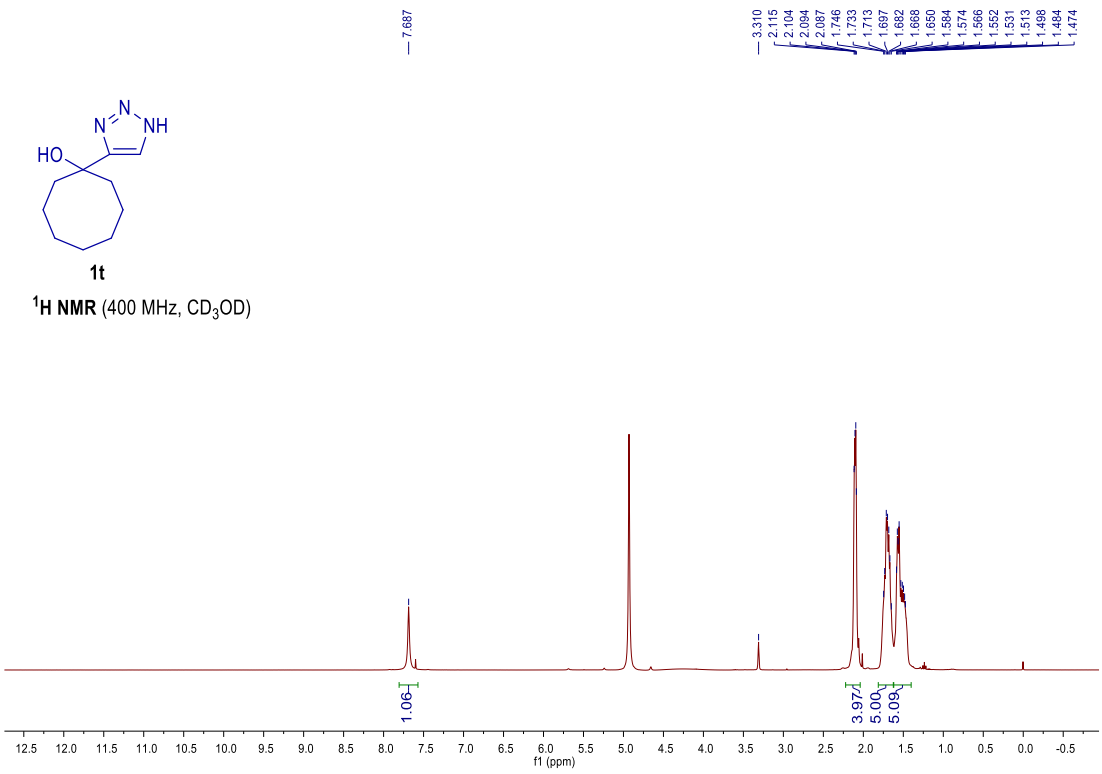


1s

^{13}C NMR (101MHz, CD_3OD)

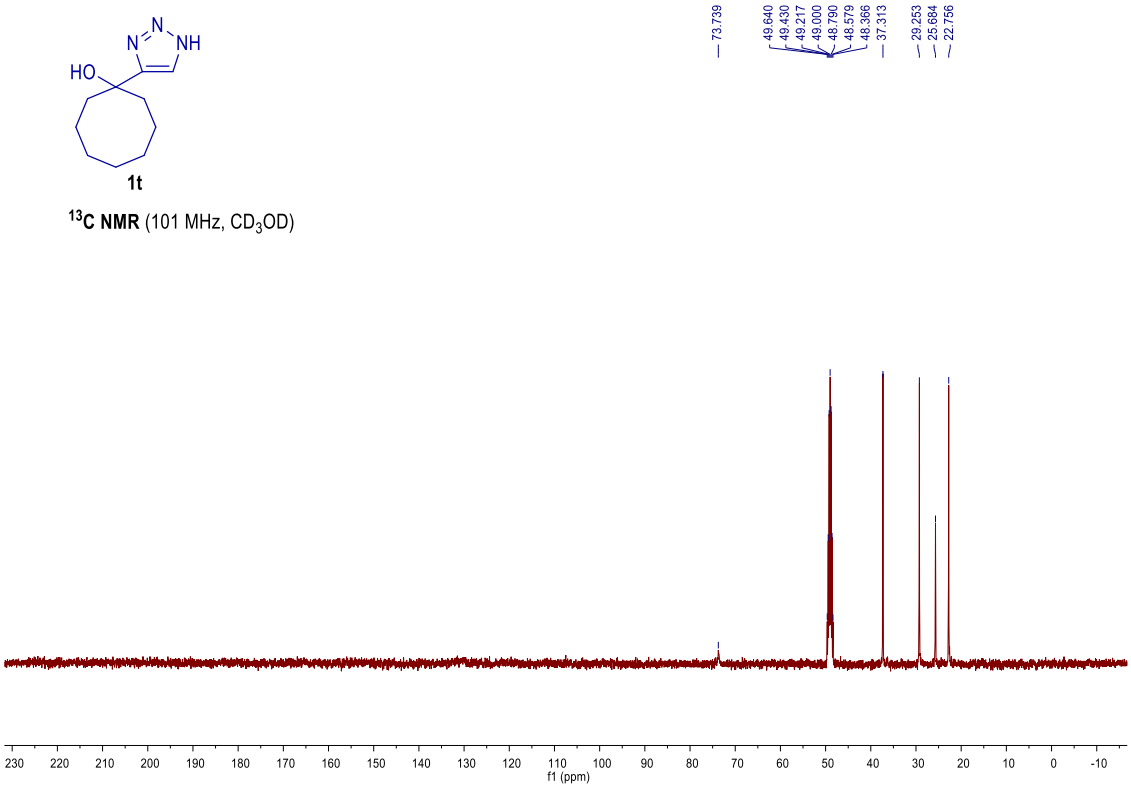


1t



1t

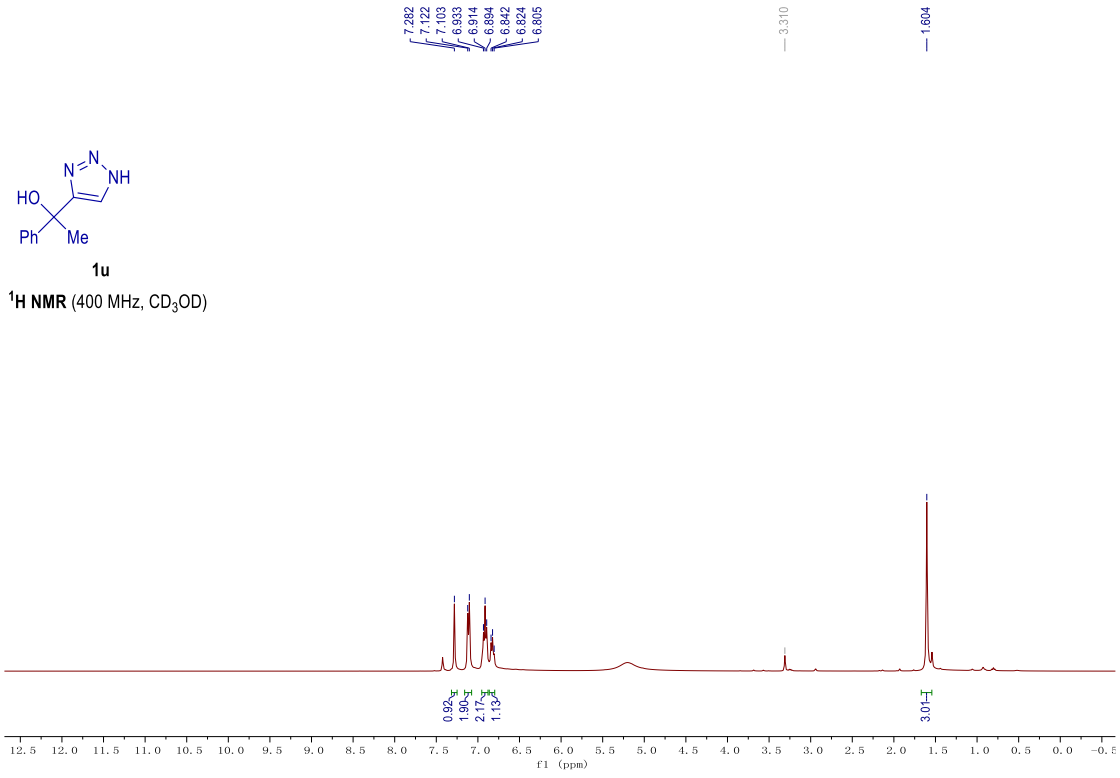
^{1}H NMR (400 MHz, CD_3OD)



1t

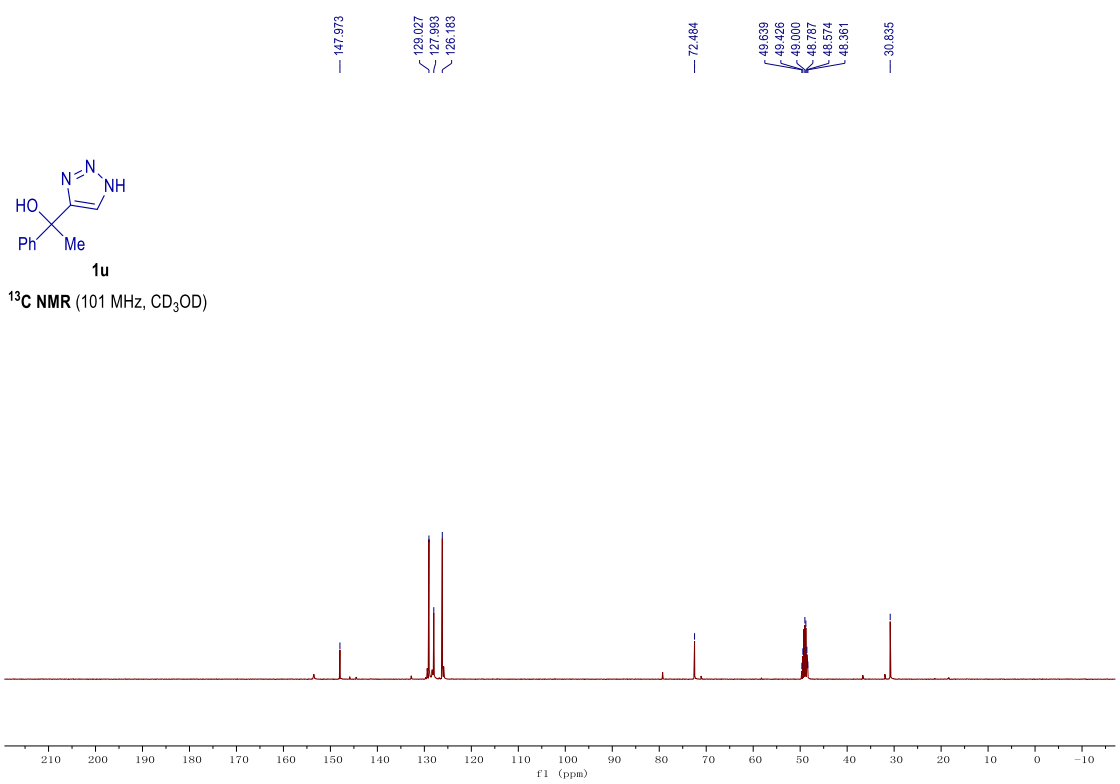
^{13}C NMR (101 MHz, CD_3OD)

1u



1u

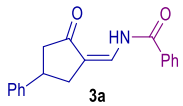
^{1}H NMR (400 MHz, CD_3OD)



1u

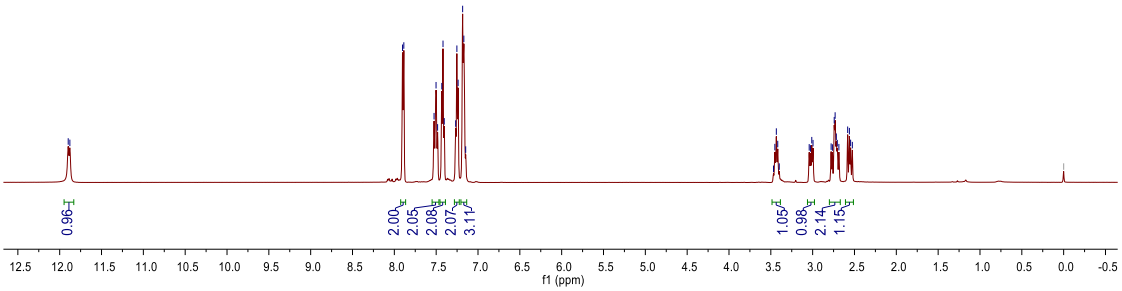
^{13}C NMR (101 MHz, CD_3OD)

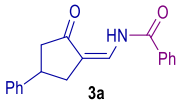
3a



3a

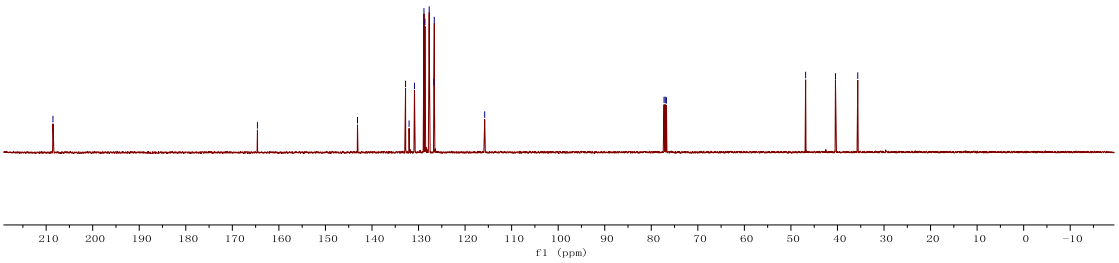
^{1}**H NMR** spectrum (500 MHz, $CDCl_3$)



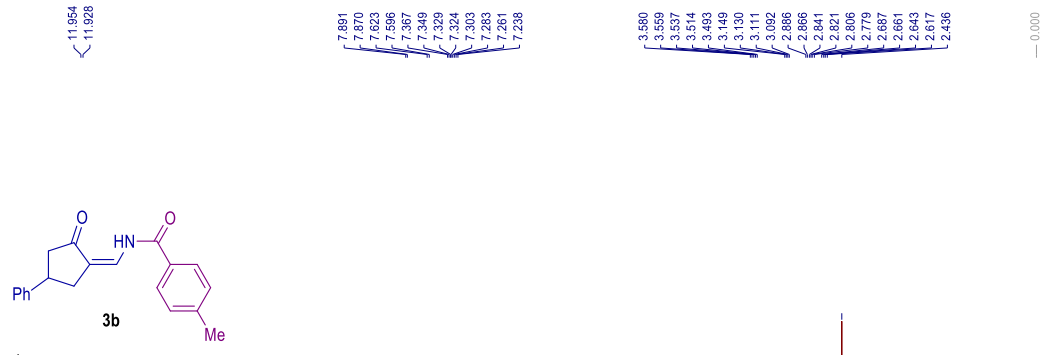


3a

^{13}**C NMR** spectrum (126 MHz, $CDCl_3$)

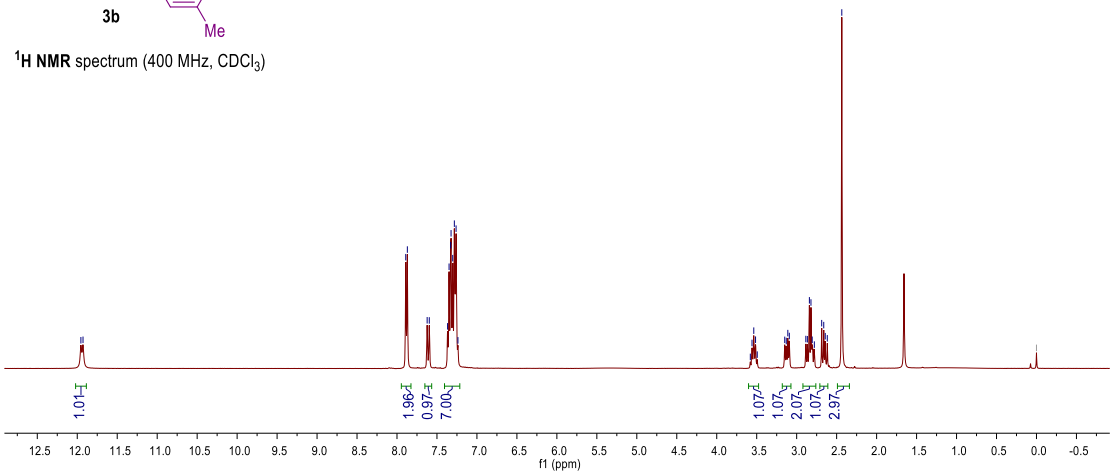


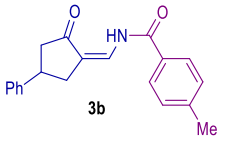
3b



3b

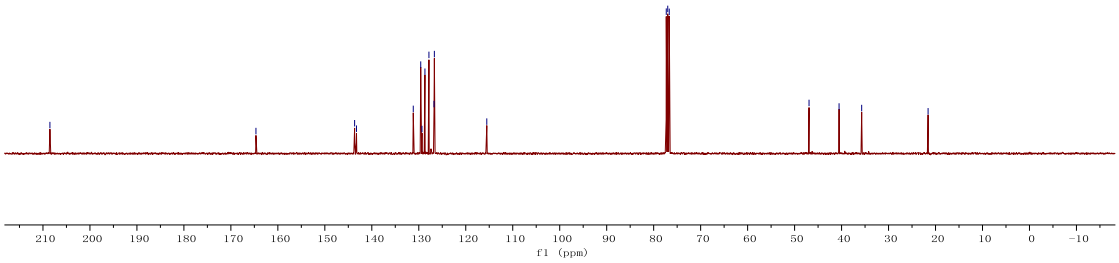
^{1}H NMR spectrum (400 MHz, $CDCl_3$)



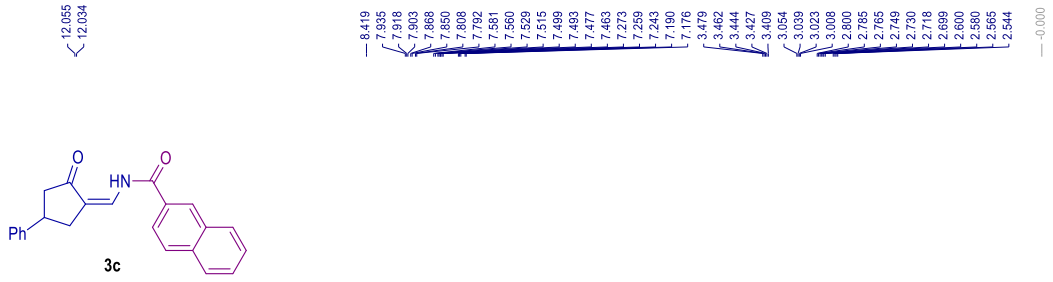


3b

^{13}C NMR spectrum (400 MHz, $CDCl_3$)

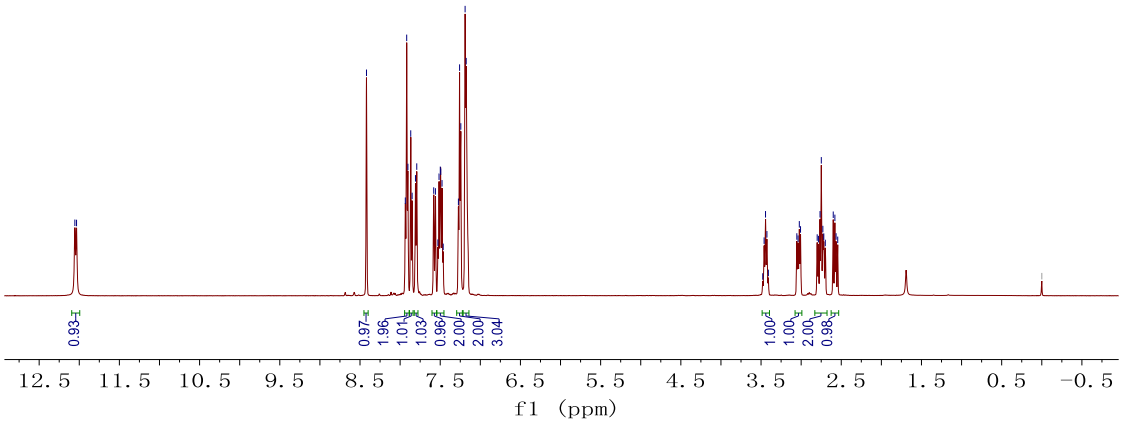


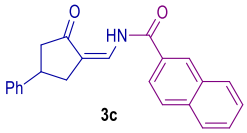
3c



3c

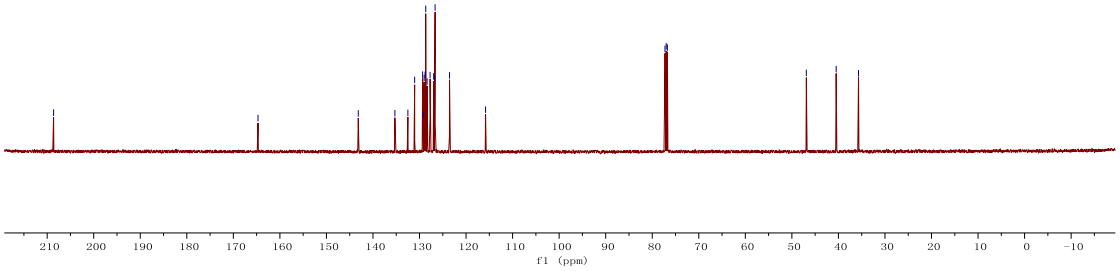
^{1}H NMR spectrum (500 MHz, $CDCl_3$)



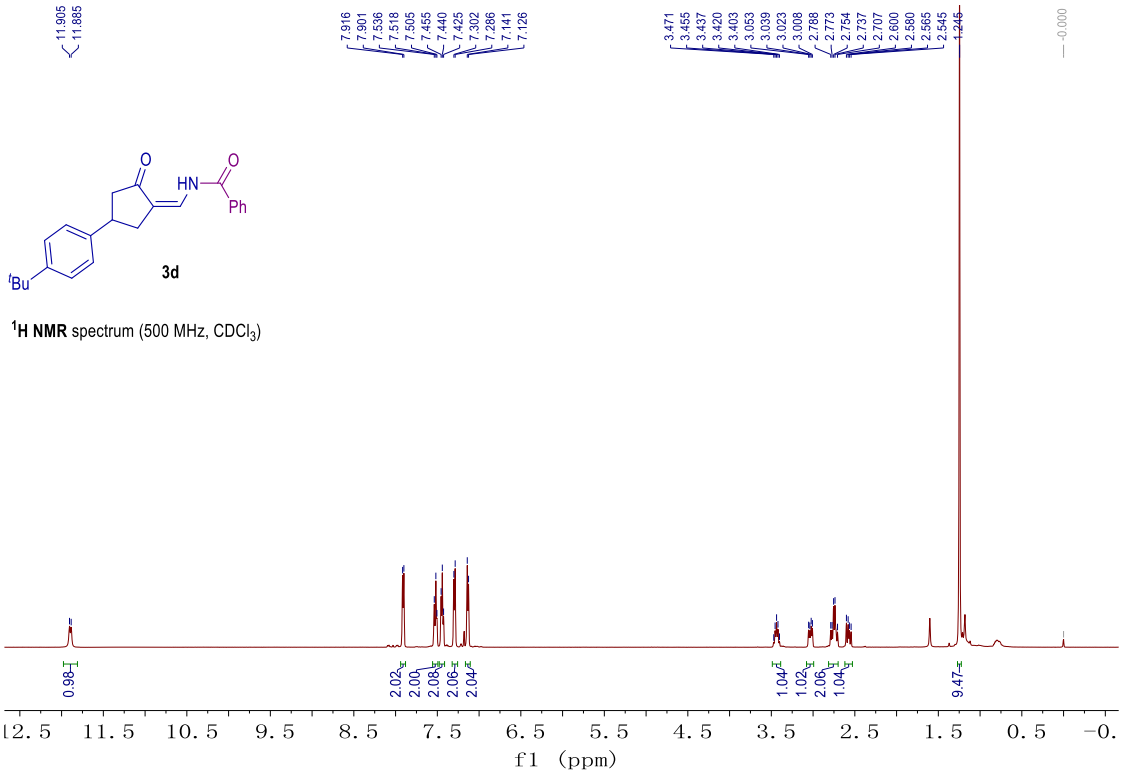


3c

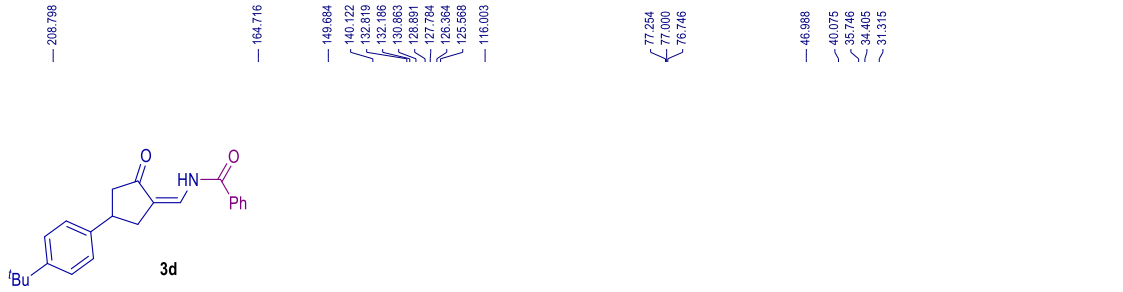
^{13}C NMR spectrum (126 MHz, $CDCl_3$)



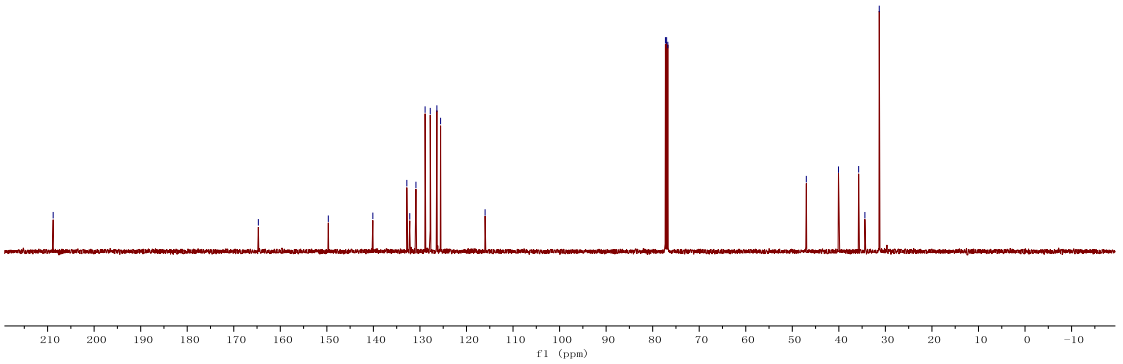
3d



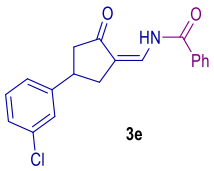
^{1}H NMR spectrum (500 MHz, $CDCl_3$)



^{13}C NMR spectrum (126 MHz, $CDCl_3$)

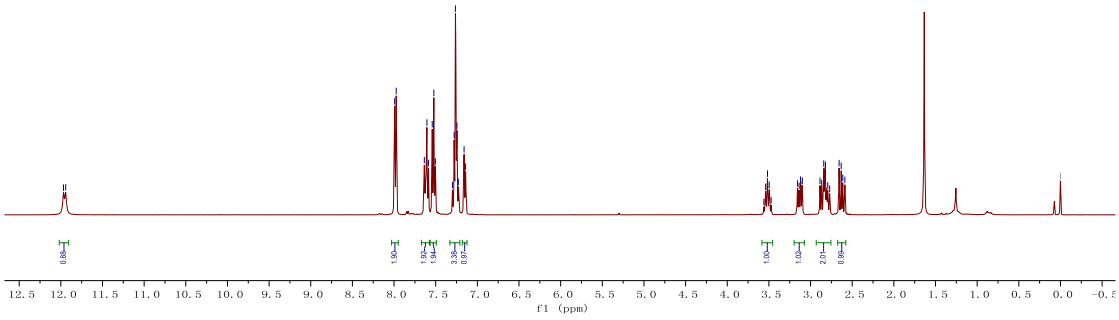


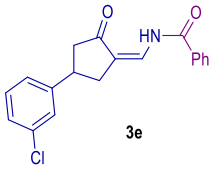
3e



3e

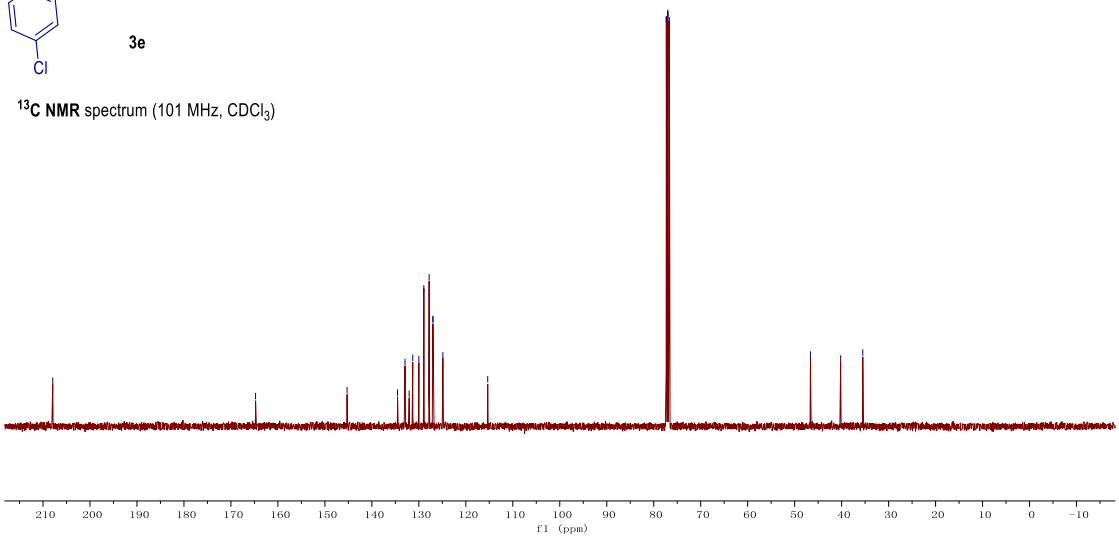
^{1}H NMR spectrum (400 MHz, $CDCl_3$)



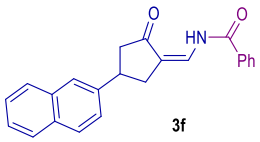


3e

^{13}C NMR spectrum (101 MHz, $CDCl_3$)

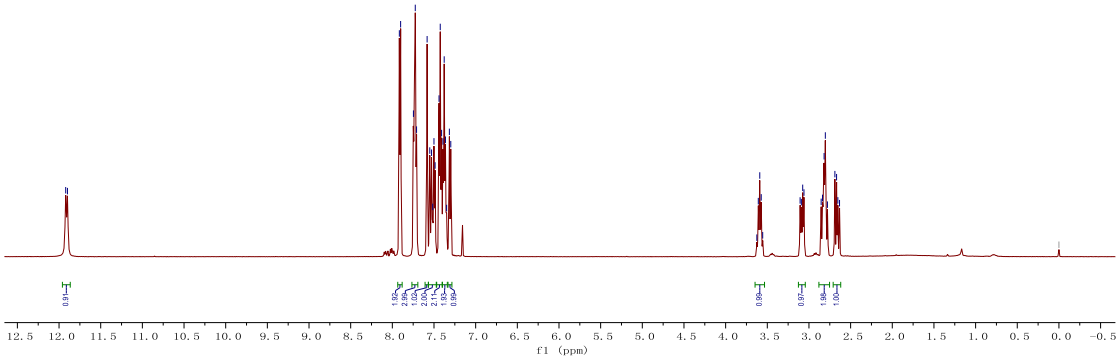


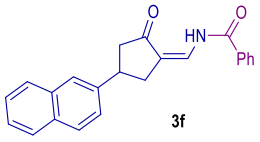
3f



3f

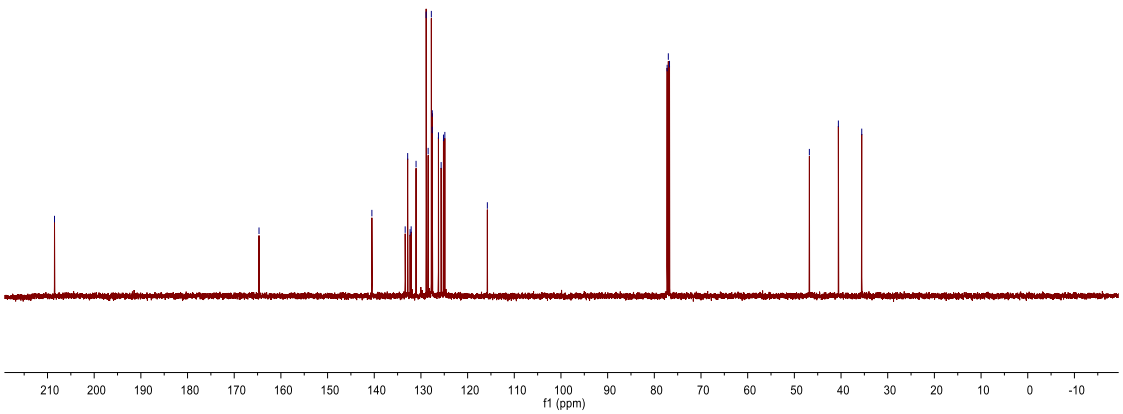
^{1}H NMR spectrum (500 MHz, $CDCl_3$)



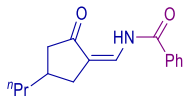


3f

^{13}C NMR spectrum (126 MHz, $CDCl_3$)

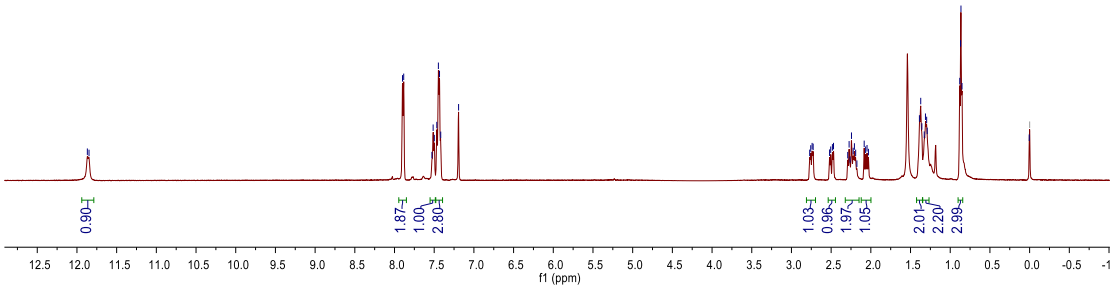


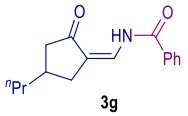
3g



3g

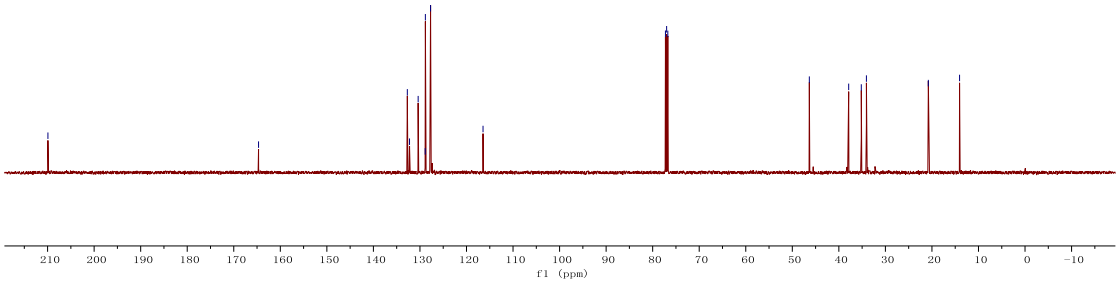
^{1}**H NMR** spectrum (500 MHz, $CDCl_3$)



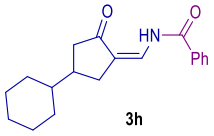


3g

^{13}**C NMR** spectrum (126 MHz, $CDCl_3$)

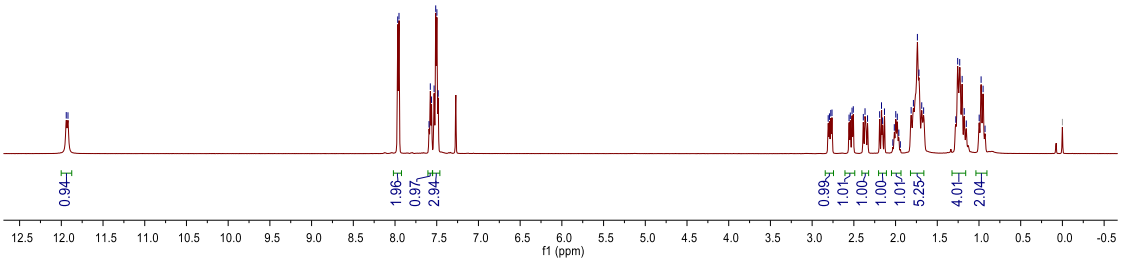


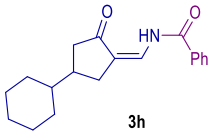
3h



3h

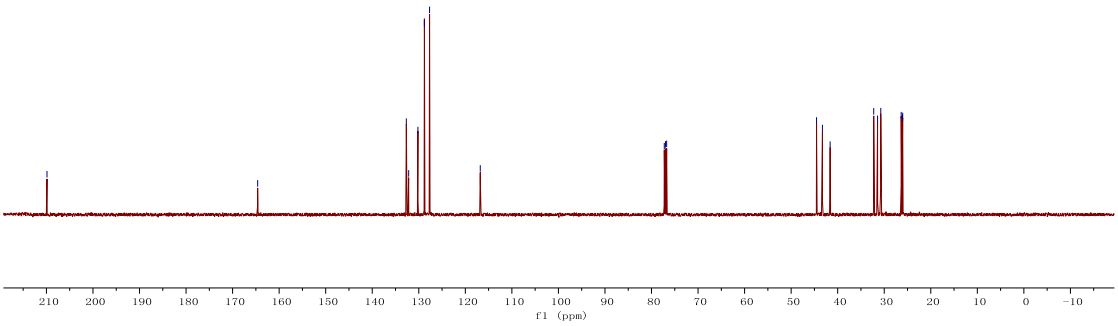
^{1}H NMR spectrum (500 MHz, $CDCl_3$)



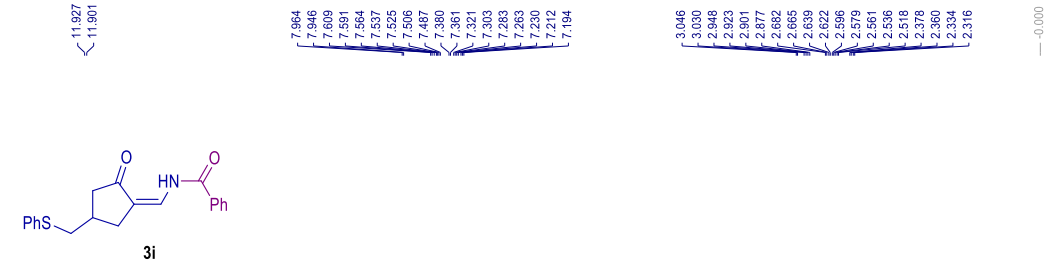


3h

^{13}C NMR spectrum (126 MHz, $CDCl_3$)

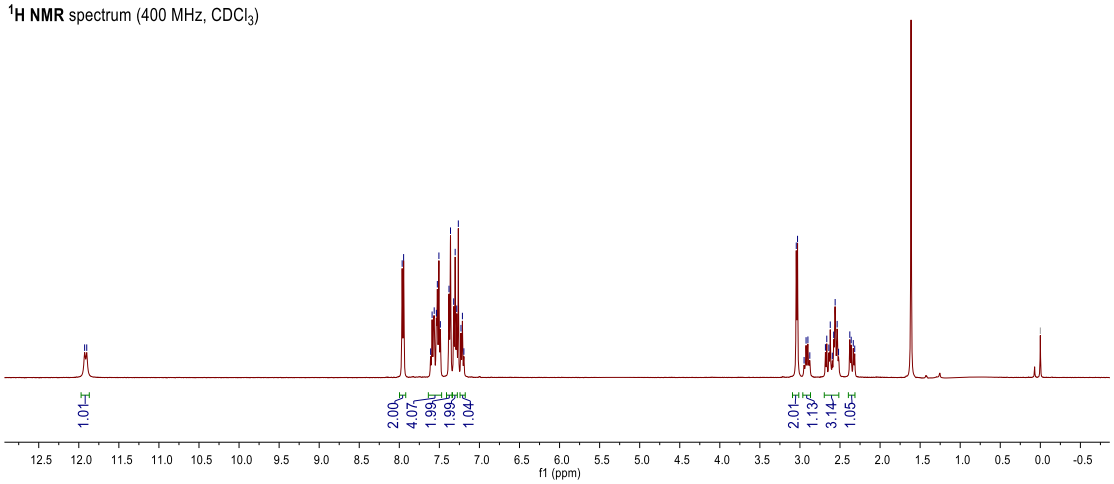


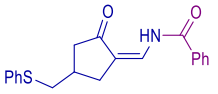
3i



3i

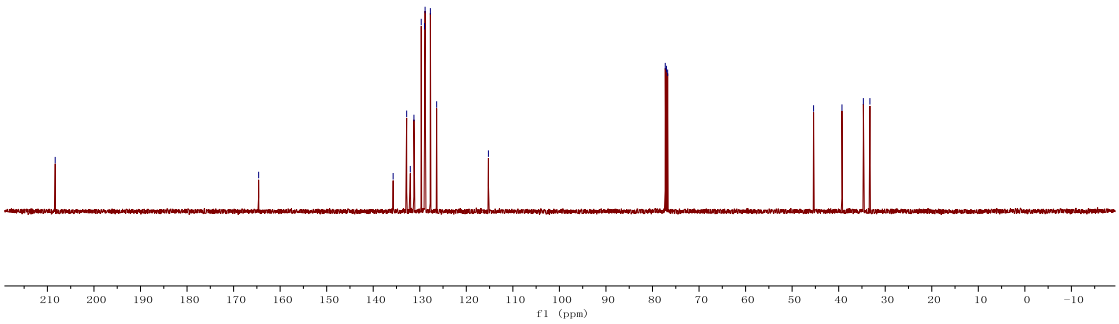
^{1}**H NMR** spectrum (400 MHz, $CDCl_3$)



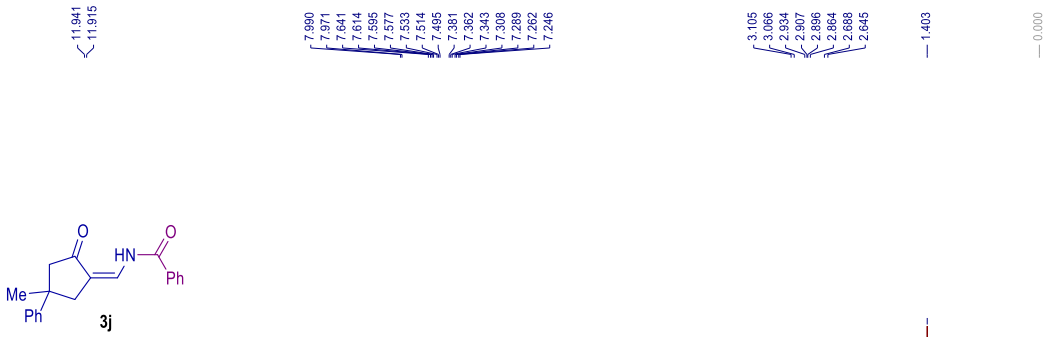


3i

^{13}**C NMR** spectrum (126 MHz, $CDCl_3$)

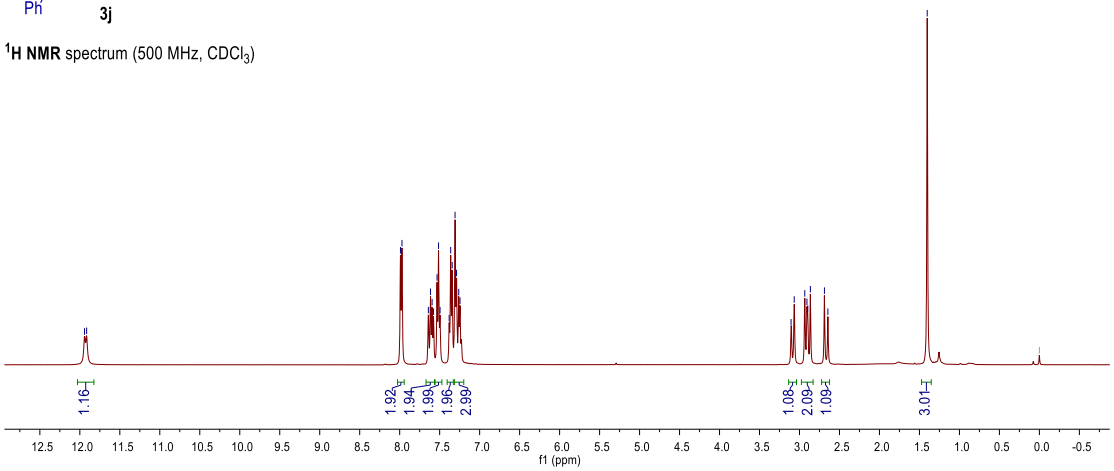


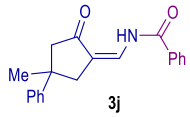
3j



3j

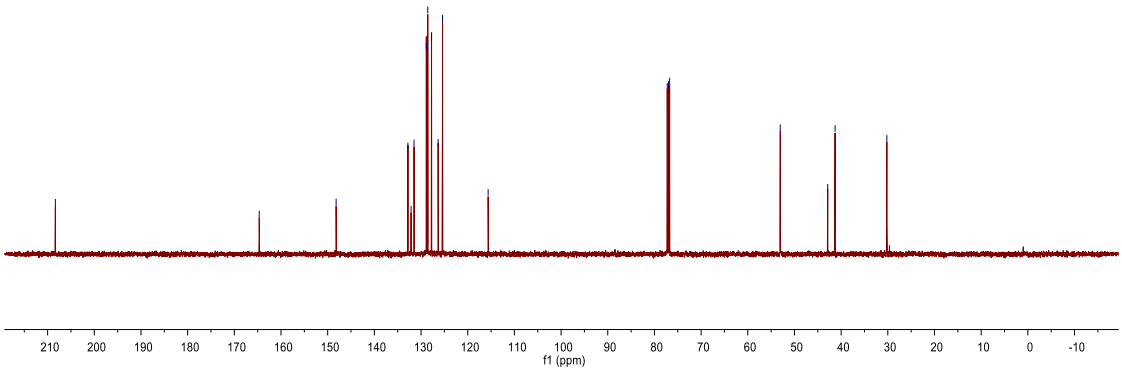
^{1}H NMR spectrum (500 MHz, $CDCl_3$)



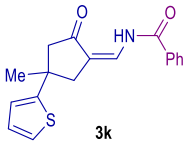


3j

^{13}C NMR spectrum (126 MHz, $CDCl_3$)

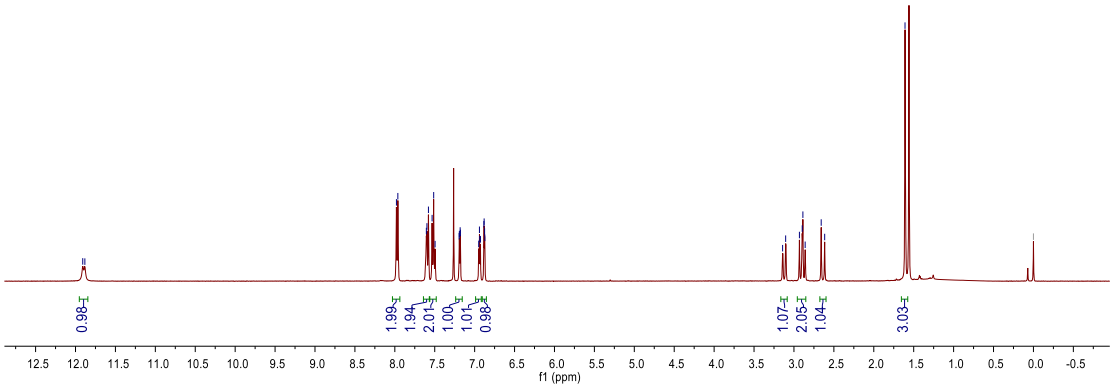


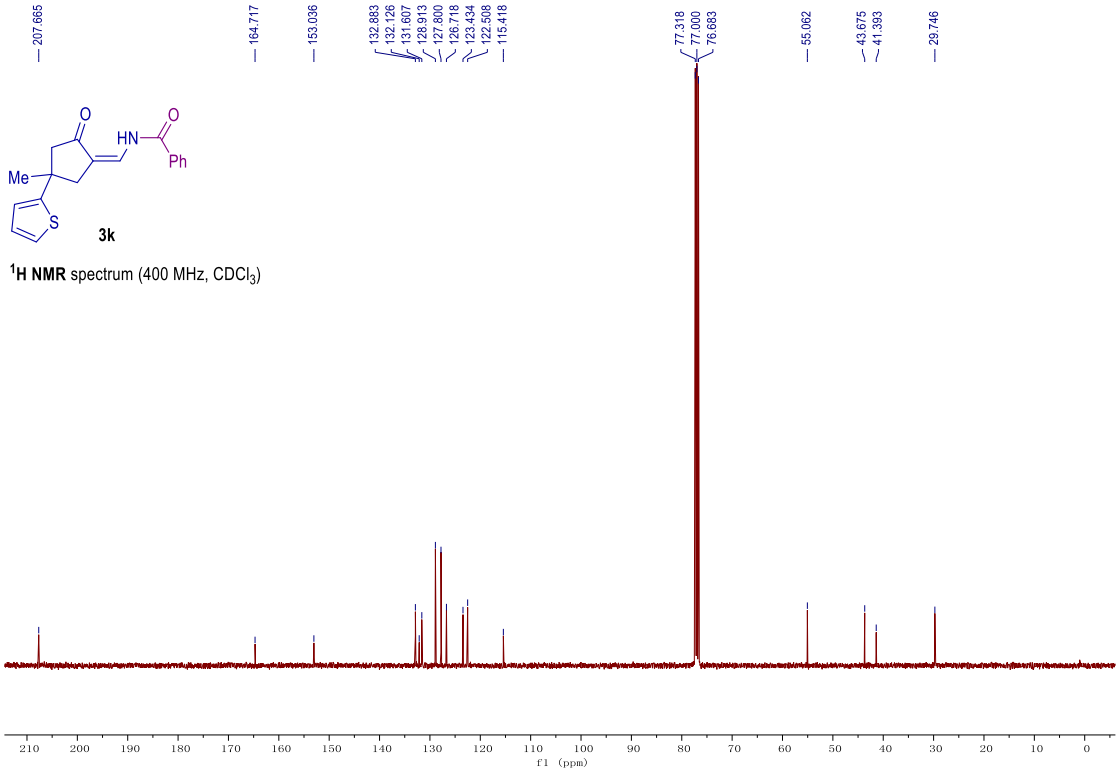
3k



3k

^{13}C NMR spectrum (101 MHz, $CDCl_3$)

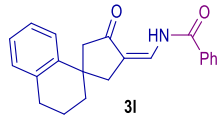




3k

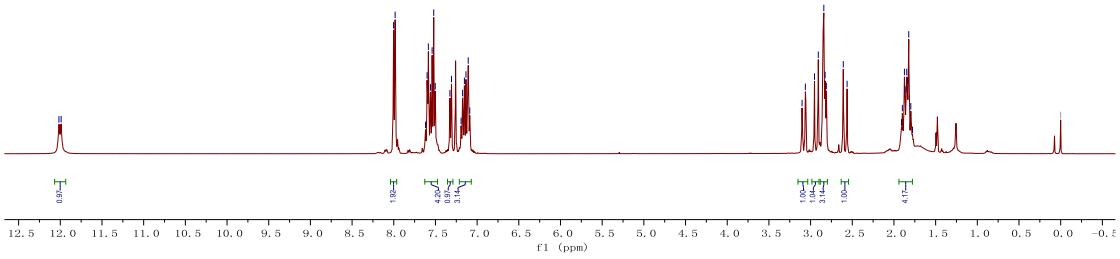
^{1}H NMR spectrum (400 MHz, $CDCl_3$)

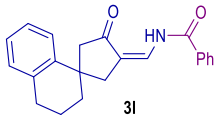
3l



3l

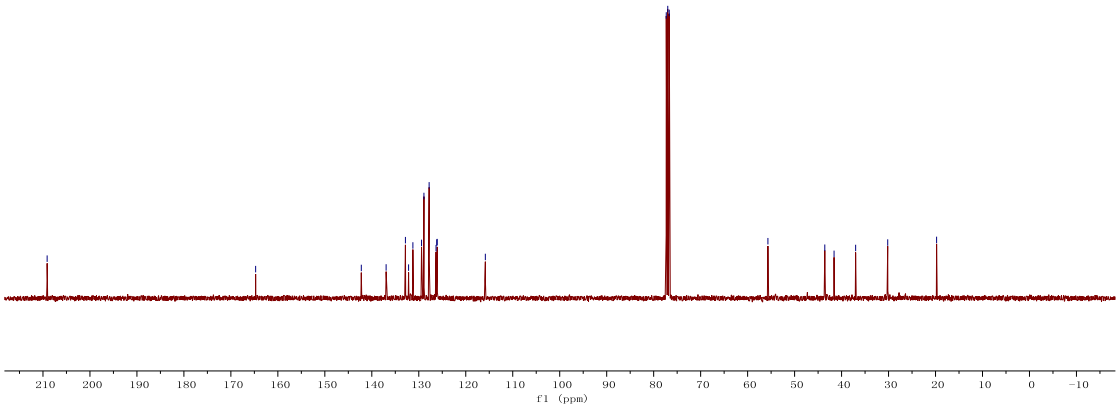
^{1}H NMR spectrum (400 MHz, $CDCl_3$)



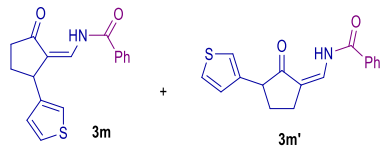


3l

^{13}C NMR spectrum (101 MHz, $CDCl_3$)

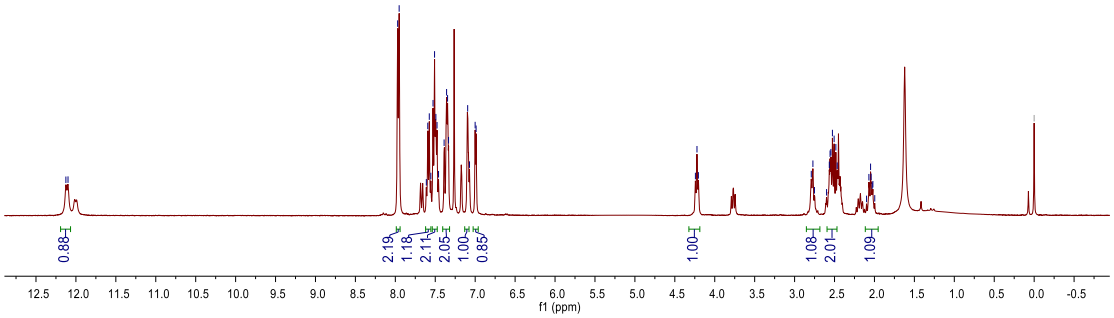


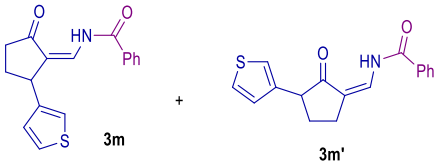
3m and **3m'**



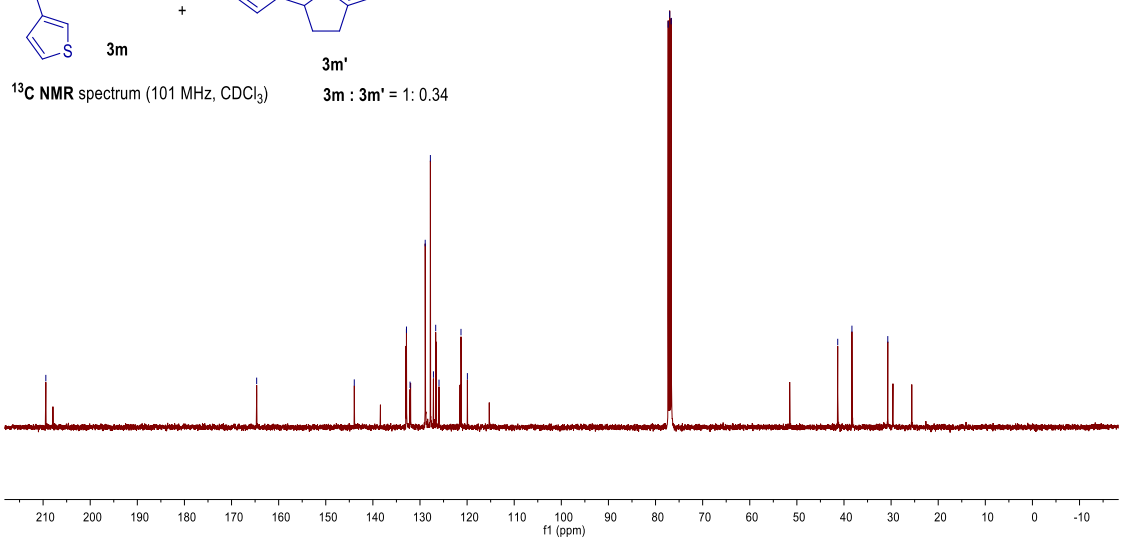
^{1}**H NMR** spectrum (400 MHz, $CDCl_3$) **3m : 3m'** = 1: 0.34

Compounds **3m** and **3m'** could not be isolates through silicagel column or plate with various eluent, such as EA/PE, $CHCl_3$/PE, DCE/PE, MeOH/PE and EA/toluene, even so three-compnent solvent system (EA/DCM/PE, EA/DCM/toluene).

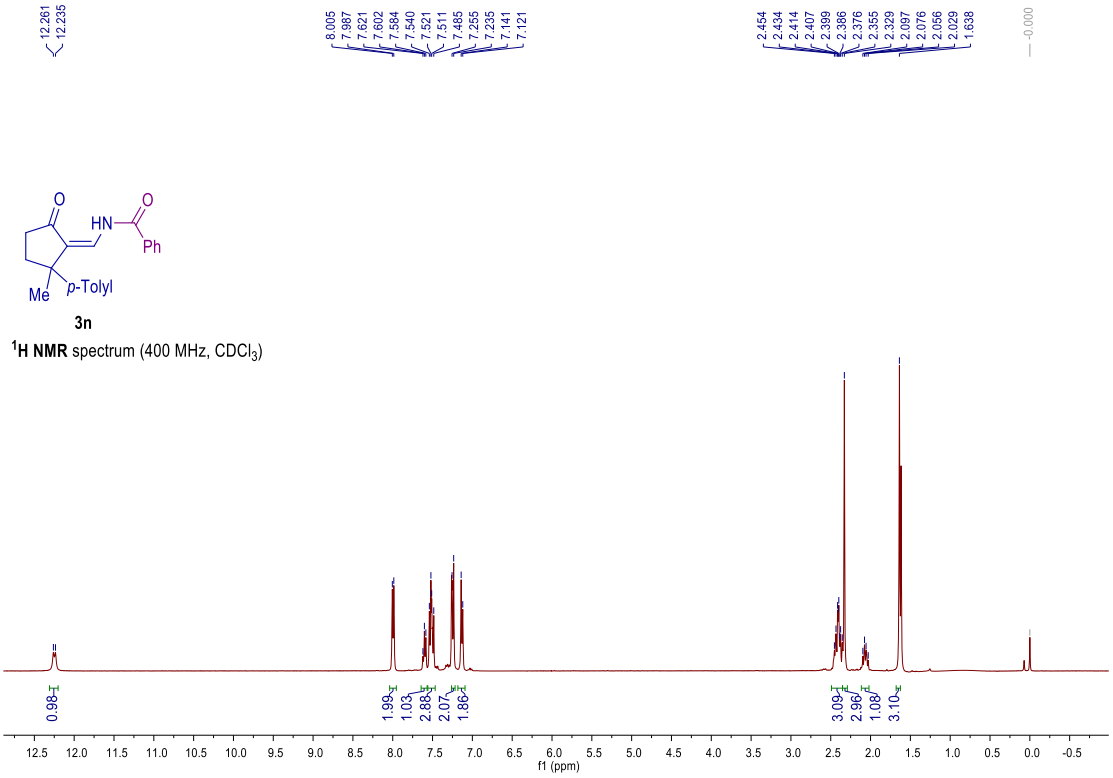




^{13}**C NMR** spectrum (101 MHz, $CDCl_3$) **3m : 3m'** = 1: 0.34

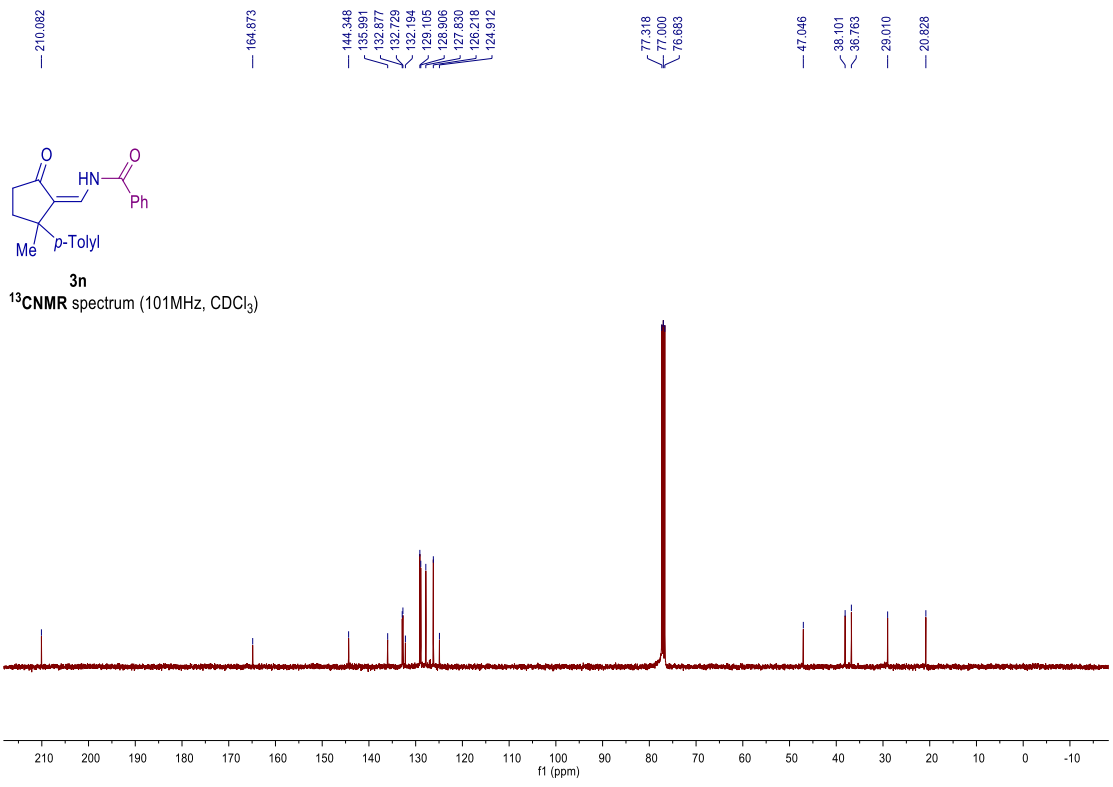


3n



3n

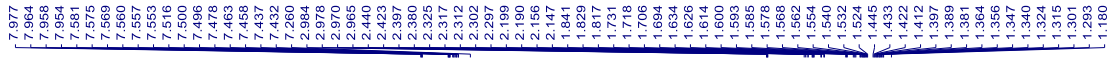
^{1}H NMR spectrum (400 MHz, $CDCl_3$)

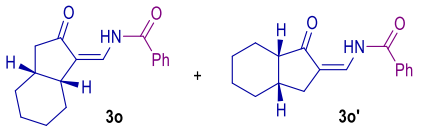


3n

^{13}CNMR spectrum (101MHz, $CDCl_3$)

3o and **3o'**



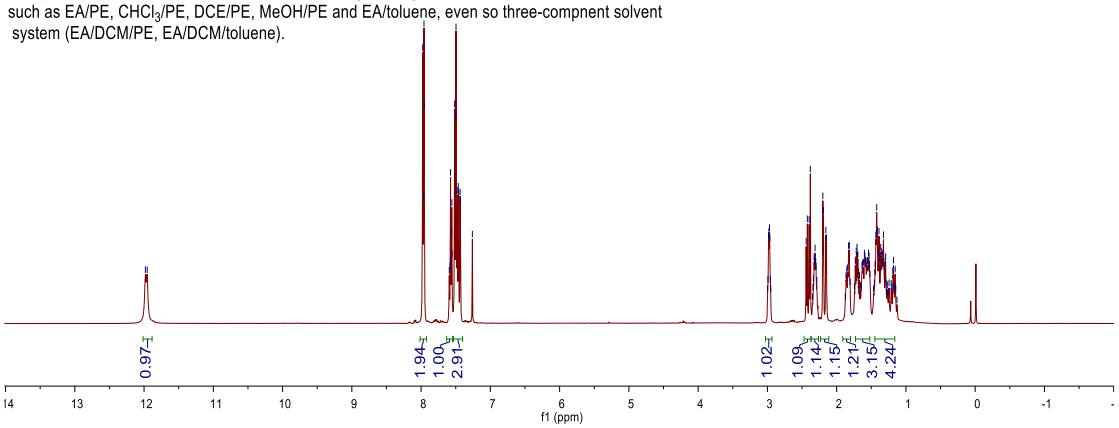


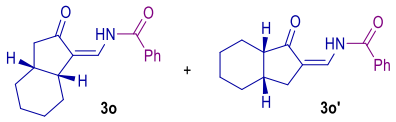
3o **3o'**

relative configuration

^{1}H NMR spectrum (500 MHz, $CDCl_3$) **3o : 3o'** = 1: 0.15

Compounds **3o** and **3o'** could not be isolated through silicagel column or plate with various eluent, such as EA/PE, $CHCl_3$/PE, DCE/PE, MeOH/PE and EA/toluene, even so three-compnent solvent system (EA/DCM/PE, EA/DCM/toluene).

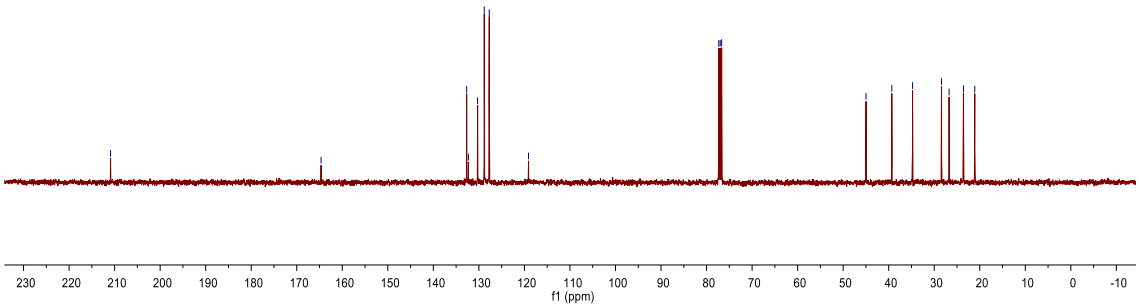




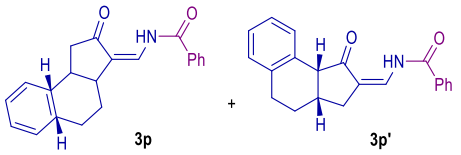
3o **3o'**

relative configuration

^{13}C NMR spectrum (126 MHz, $CDCl_3$) **3o : 3o'** = 1: 0.15



3p and **3p'**

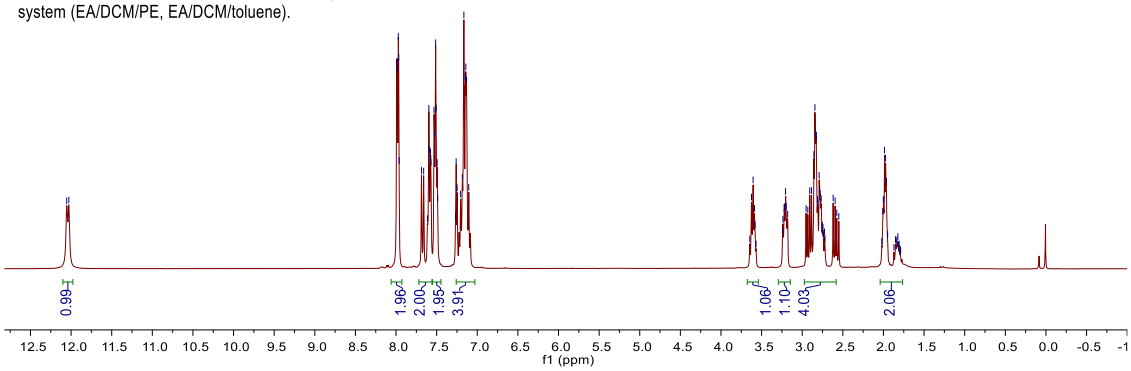


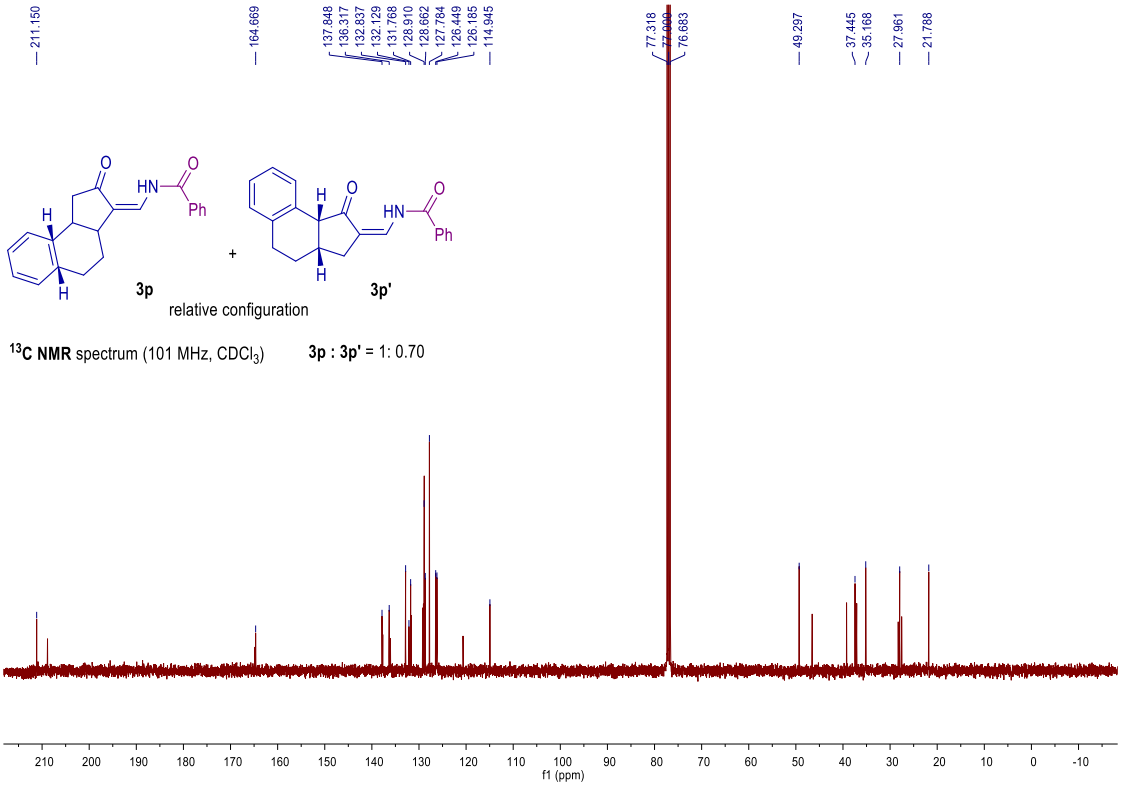
3p **3p'**

relative configuration

^{1}H NMR spectrum (400 MHz, $CDCl_3$) **3p : 3p'** = 1: 0.70

Compounds **3q** and **3q'** could be not isolates through silicagel column or plate with various eluent, such as EA/PE, $CHCl_3$/PE, DCE/PE, MeOH/PE and EA/toluene, even so three-compnent solvent system (EA/DCM/PE, EA/DCM/toluene).



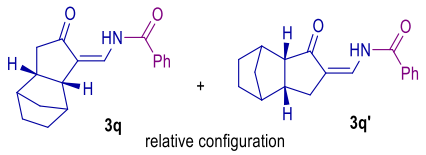


3p **3p'**

relative configuration

^{13}C NMR spectrum (101 MHz, $CDCl_3$) **3p : 3p'** = 1: 0.70

3q and **3q'**

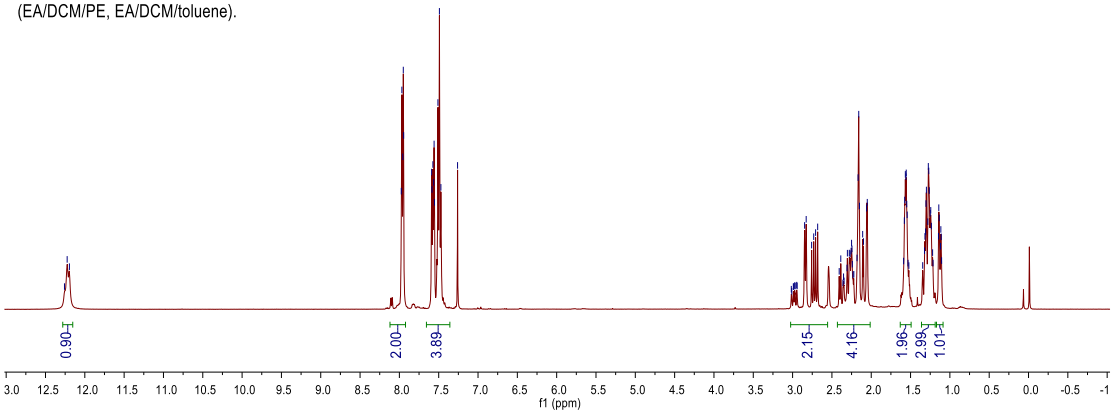


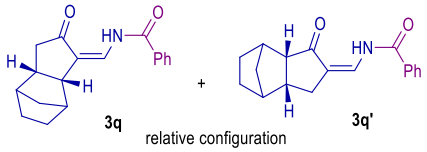
3q **3q'**

relative configuration

^{1}H NMR spectrum (400 MHz, $CDCl_3$) **3q : 3q'** = 1: 0.27

Compounds **3r** and **3r'** could not be isolated through silicagel column or plate with various eluent, such as EA/PE, $CHCl_3$/PE, DCE/PE, MeOH/PE and EA/toluene, even so three-compnent solvent system (EA/DCM/PE, EA/DCM/toluene).

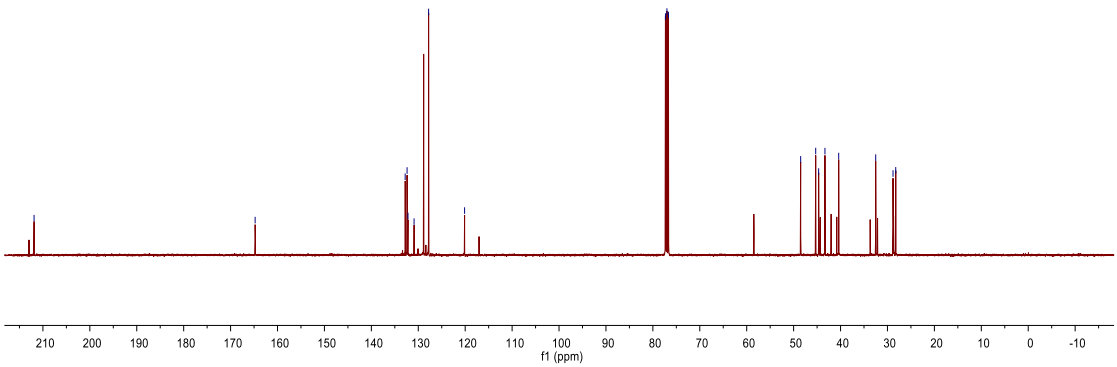




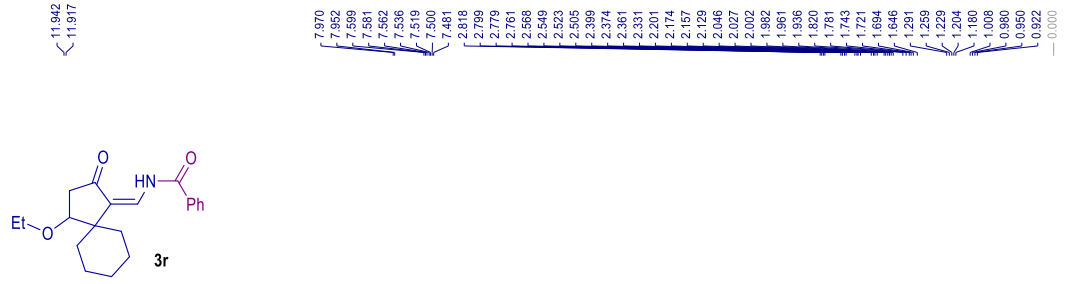
3q **3q'**

relative configuration

^{13}C NMR spectrum (101 MHz, $CDCl_3$) **3q : 3q'** = 1: 0.27

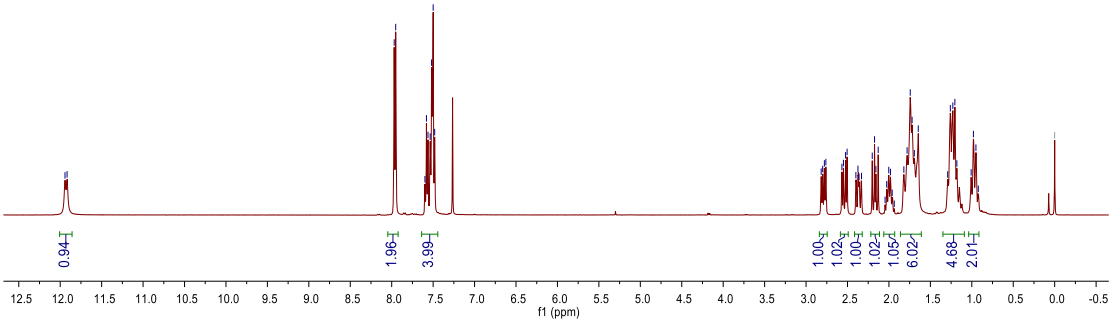


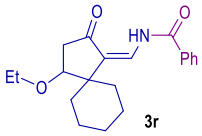
3r



3r

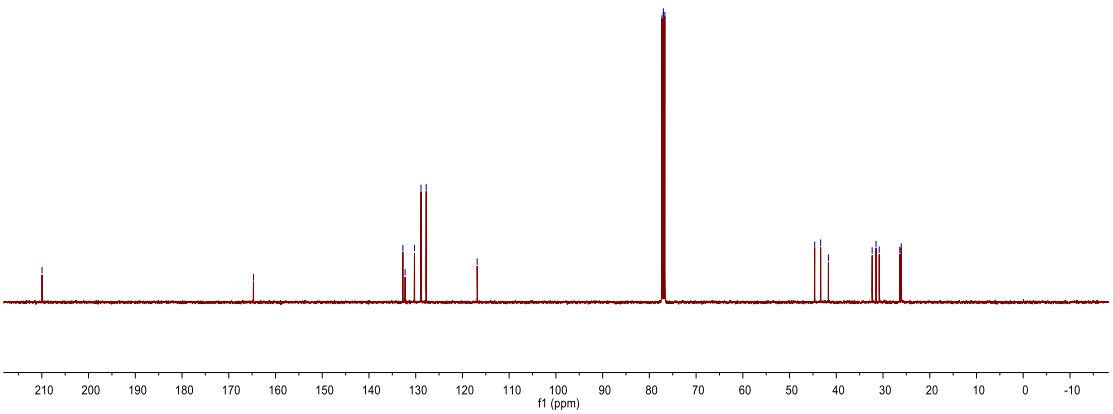
^{1}**H NMR** spectrum (400 MHz, $CDCl_3$)



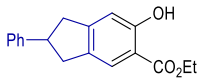


3r

^{13}**C NMR** spectrum (101 MHz, $CDCl_3$)

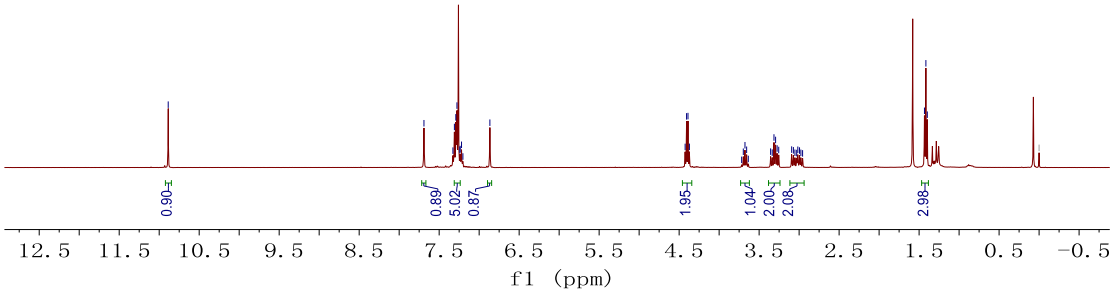


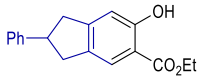
4



4

^{1}**H NMR** spectrum (400 MHz, $CDCl_3$)

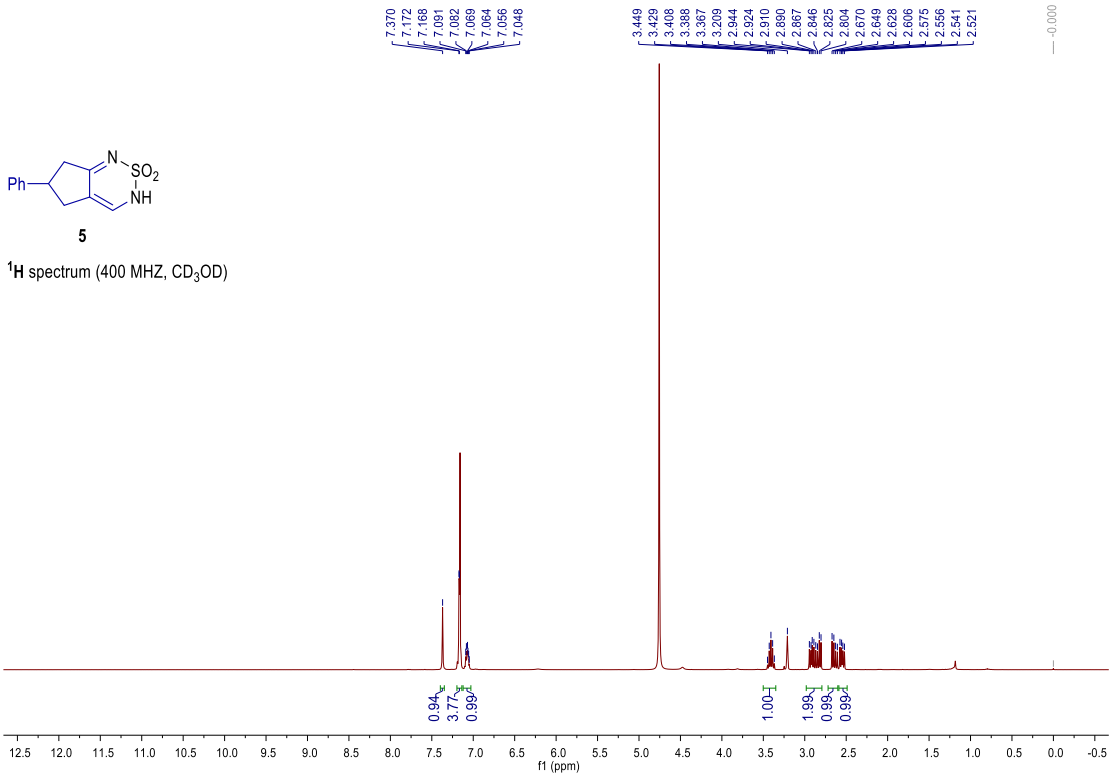




4

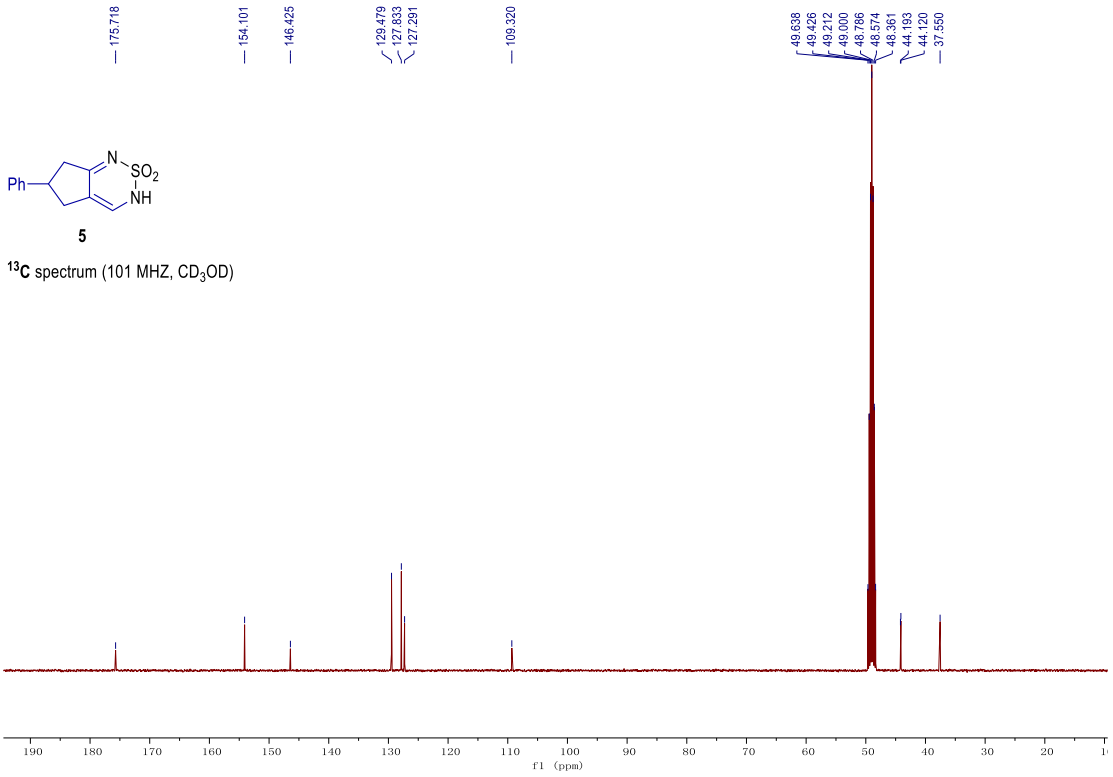
^{13}**C NMR** spectrum (101 MHz, $CDCl_3$)

5



5

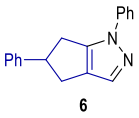
^{1}H spectrum (400 MHZ, CD_3OD)



5

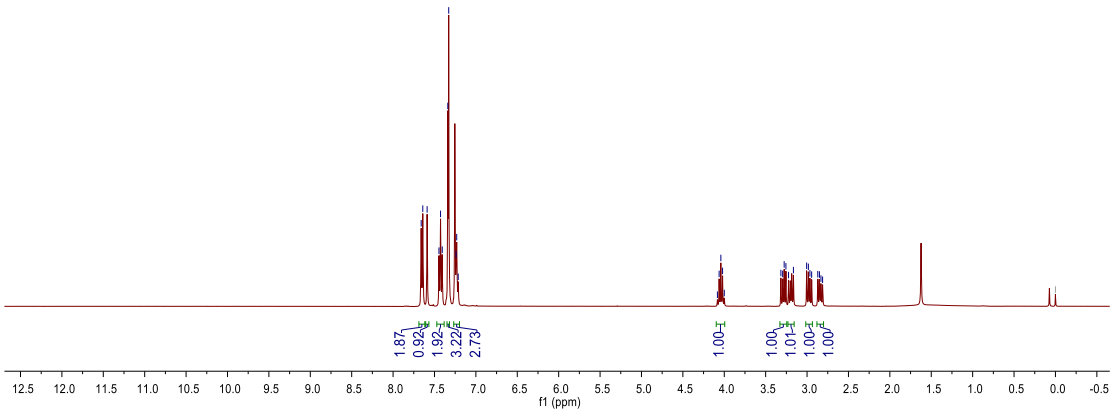
^{13}C spectrum (101 MHZ, CD_3OD)

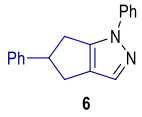
6



6

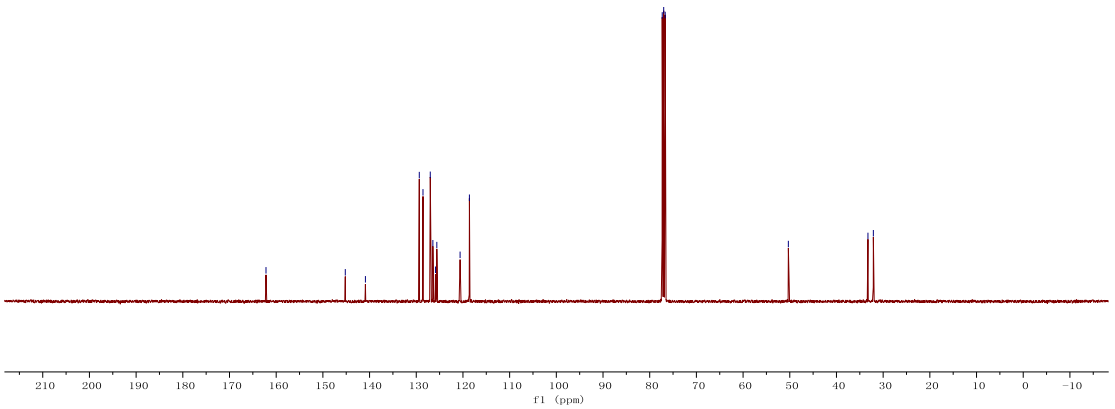
^{1}**H NMR** spectrum (400 MHz, $CDCl_3$)



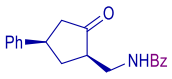


6

^{13}**C NMR** spectrum (101 MHz, $CDCl_3$)

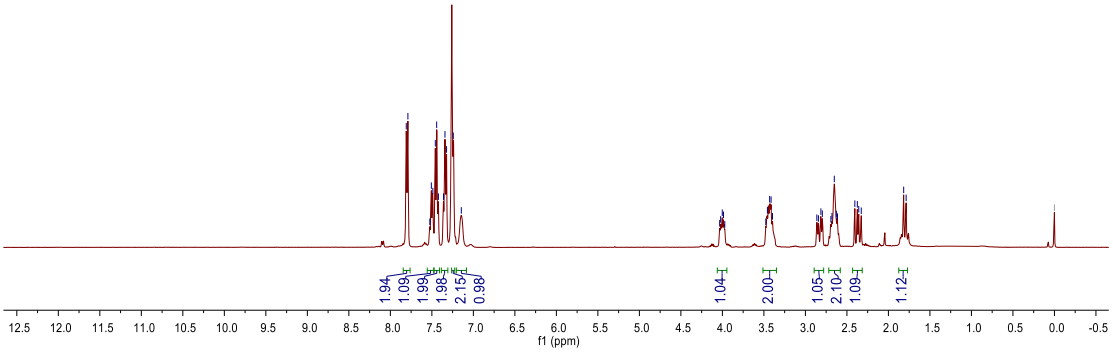


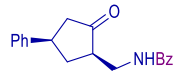
7



7
relative configuration

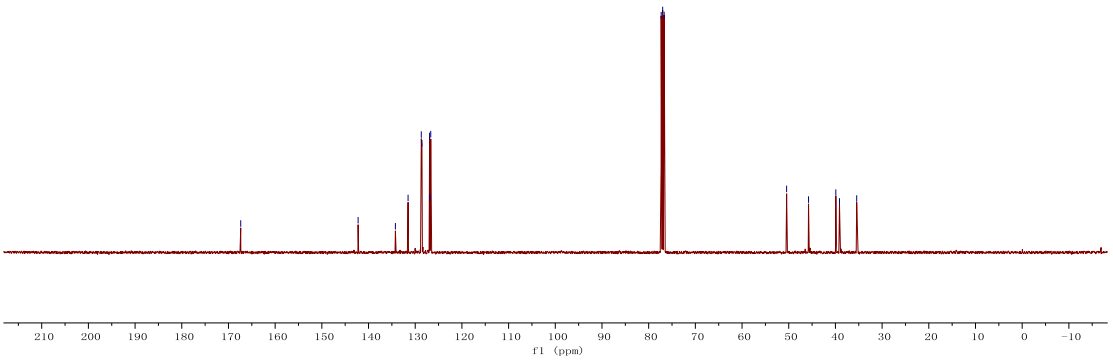
^{1}H NMR spectrum (400 MHz, $CDCl_3$)



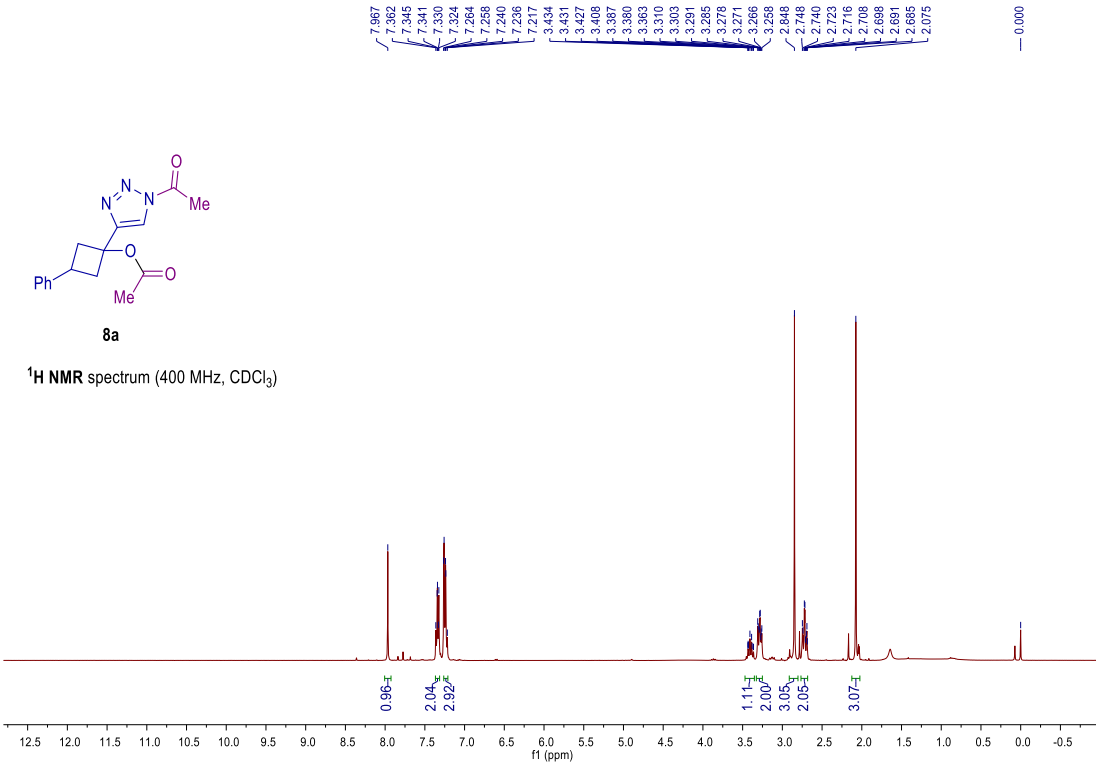


7
relative configuration

^{13}C NMR spectrum (101 MHz, $CDCl_3$)

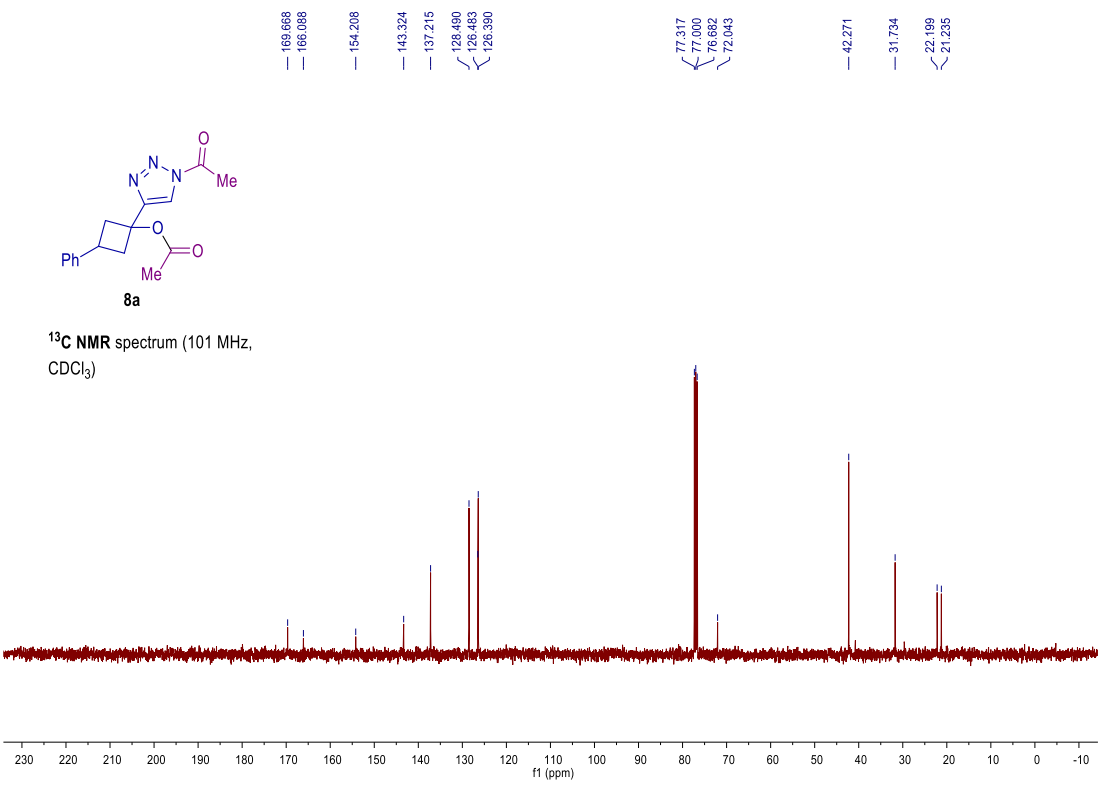


8a



8a

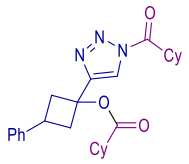
^{1}H NMR spectrum (400 MHz, $CDCl_3$)



8a

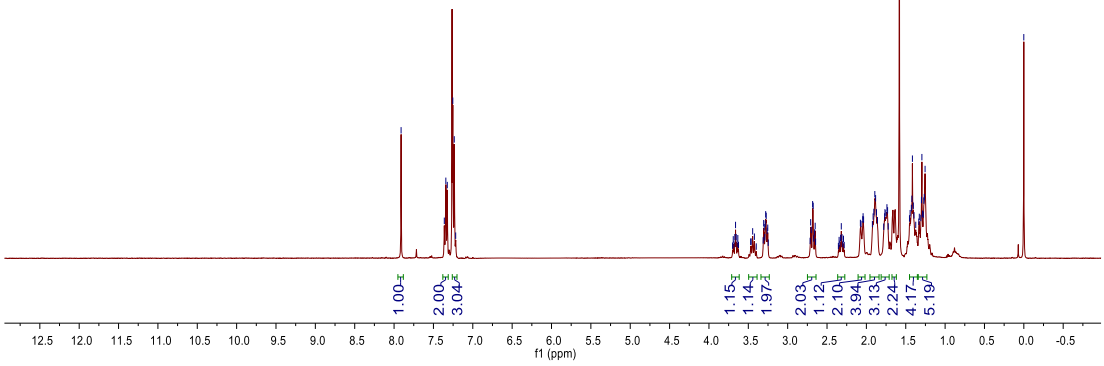
^{13}C NMR spectrum (101 MHz, $CDCl_3$)

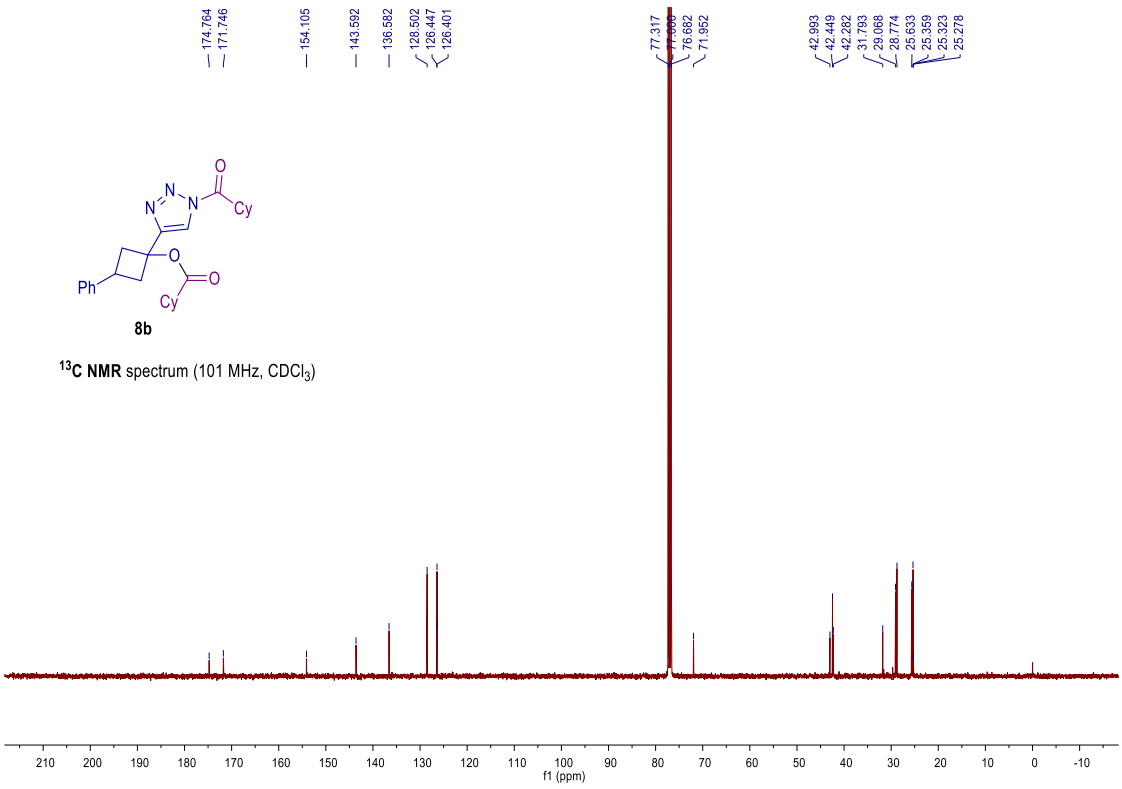
8b



8b

^{1}H NMR spectrum (400 MHz, $CDCl_3$)

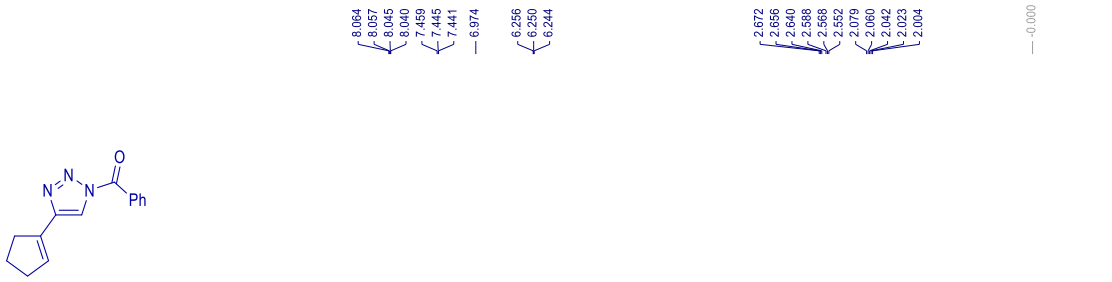




8b

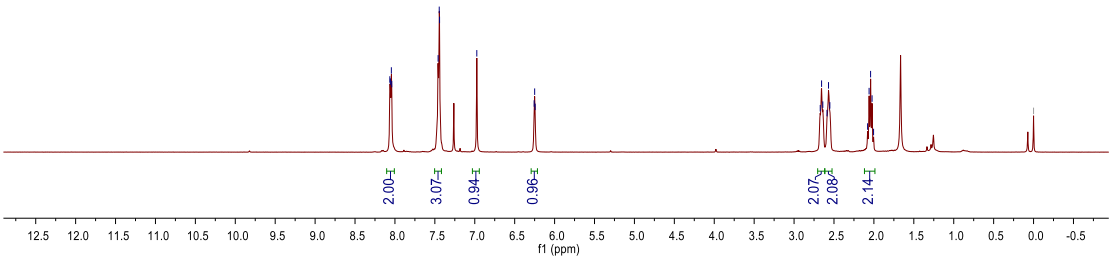
^{13}C NMR spectrum (101 MHz, $CDCl_3$)

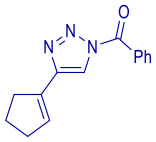
8c



8c

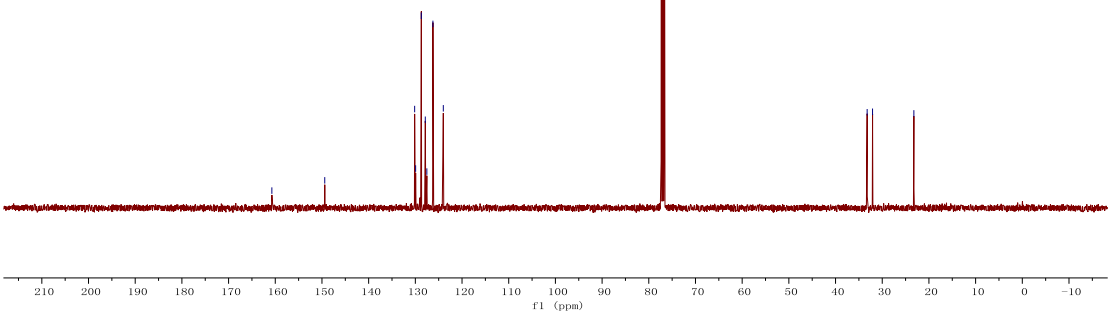
^{1}H NMR (400 MHz, $CDCl_3$)



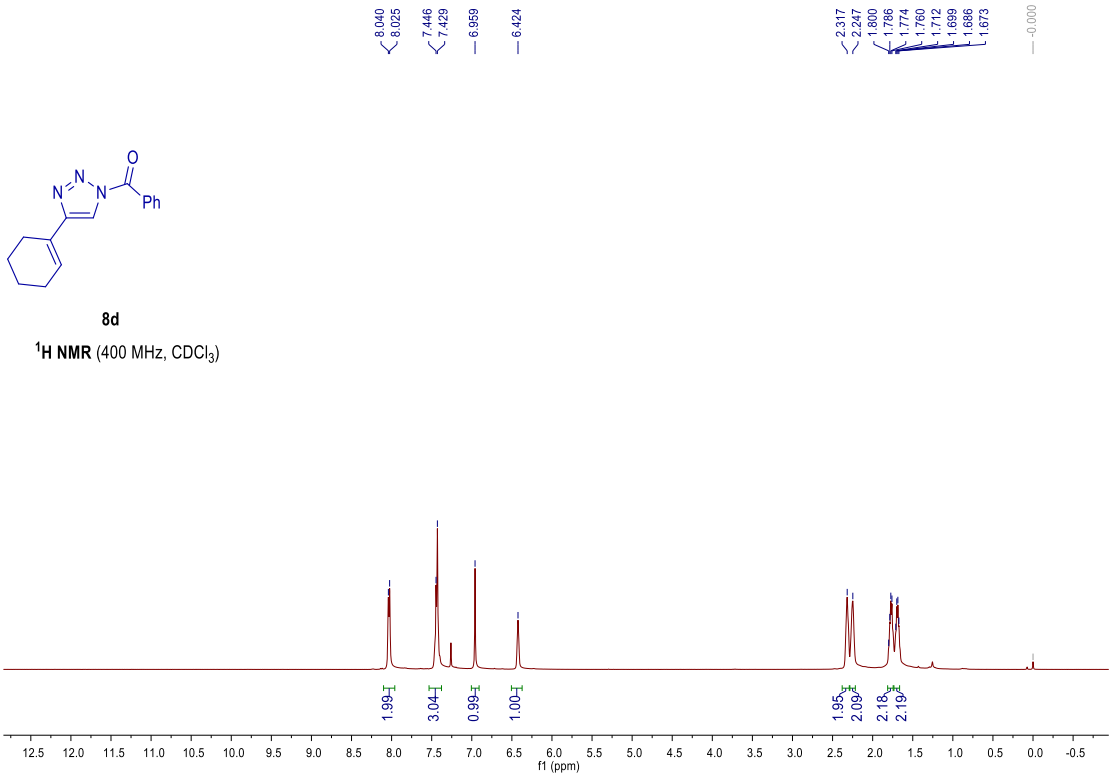


8c

^{13}C NMR (101 MHz, $CDCl_3$)

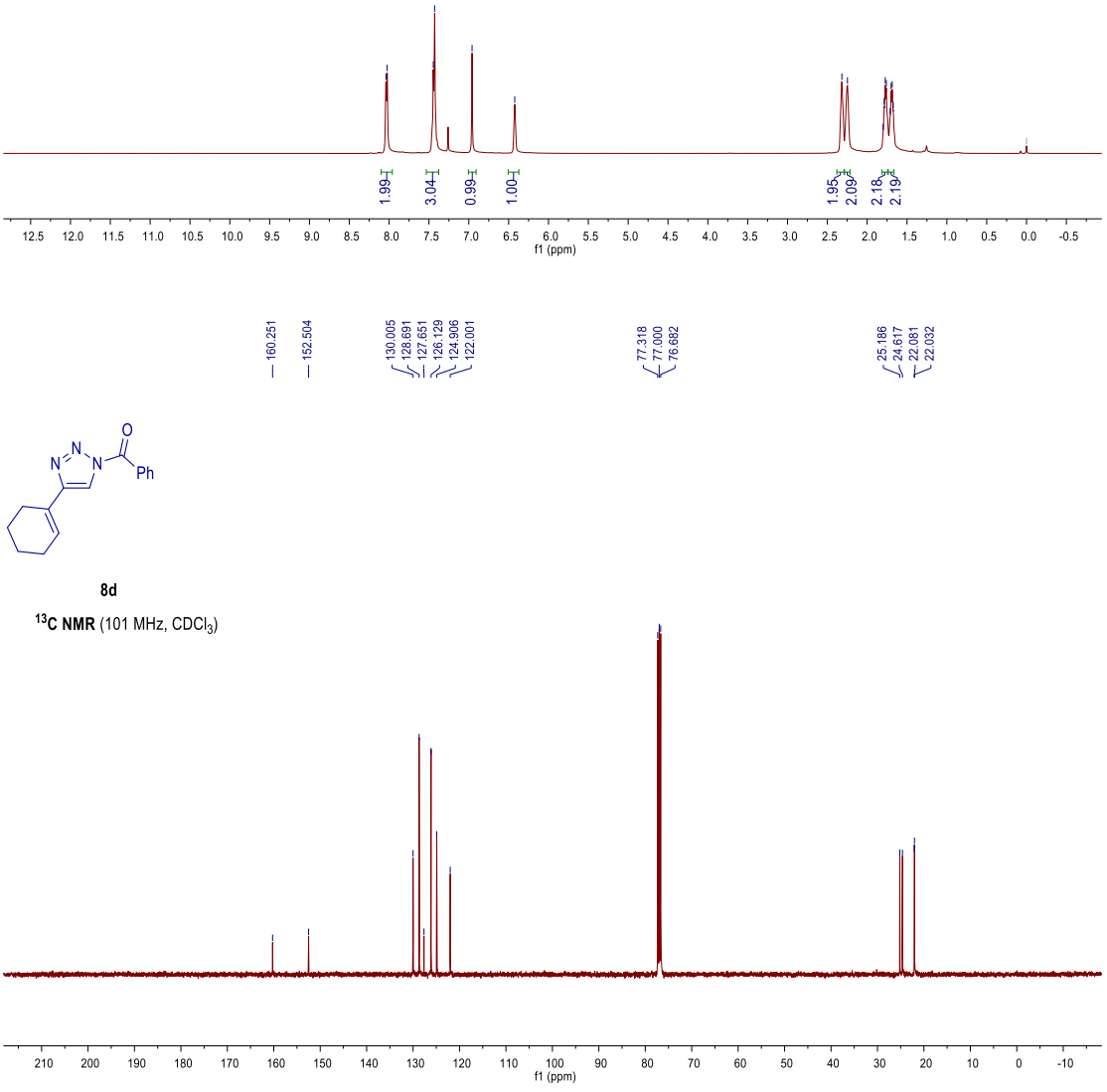


8d



8d

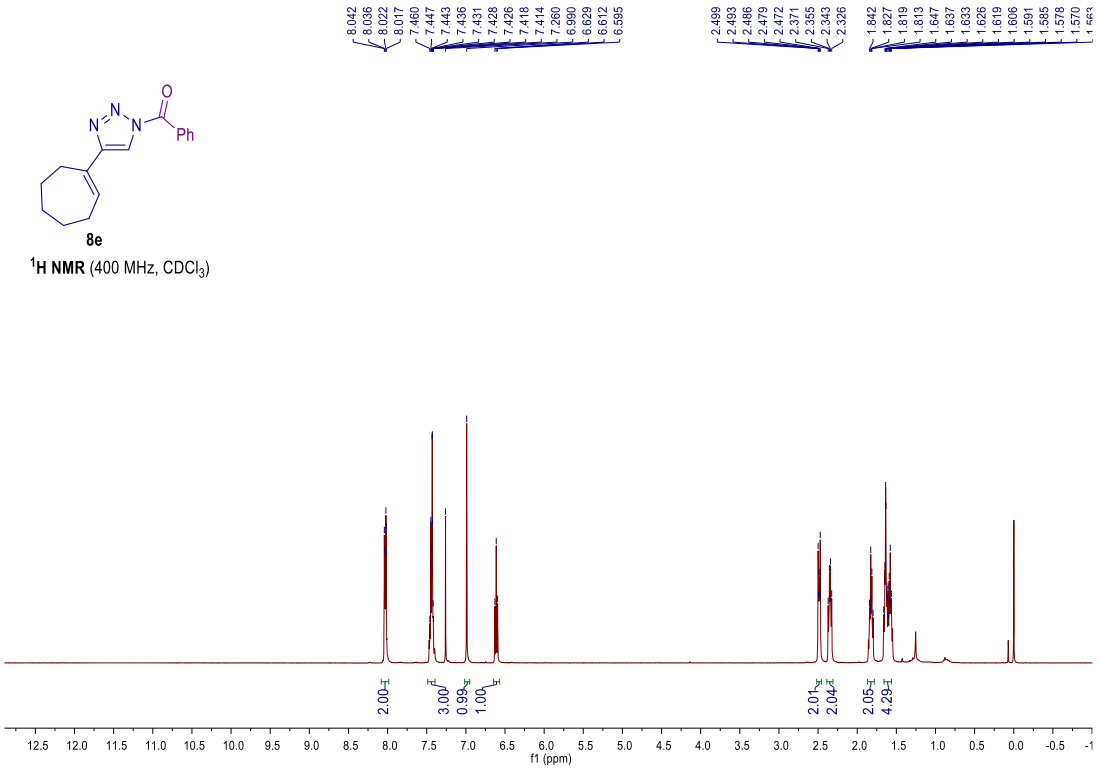
^{1}H NMR (400 MHz, $CDCl_3$)

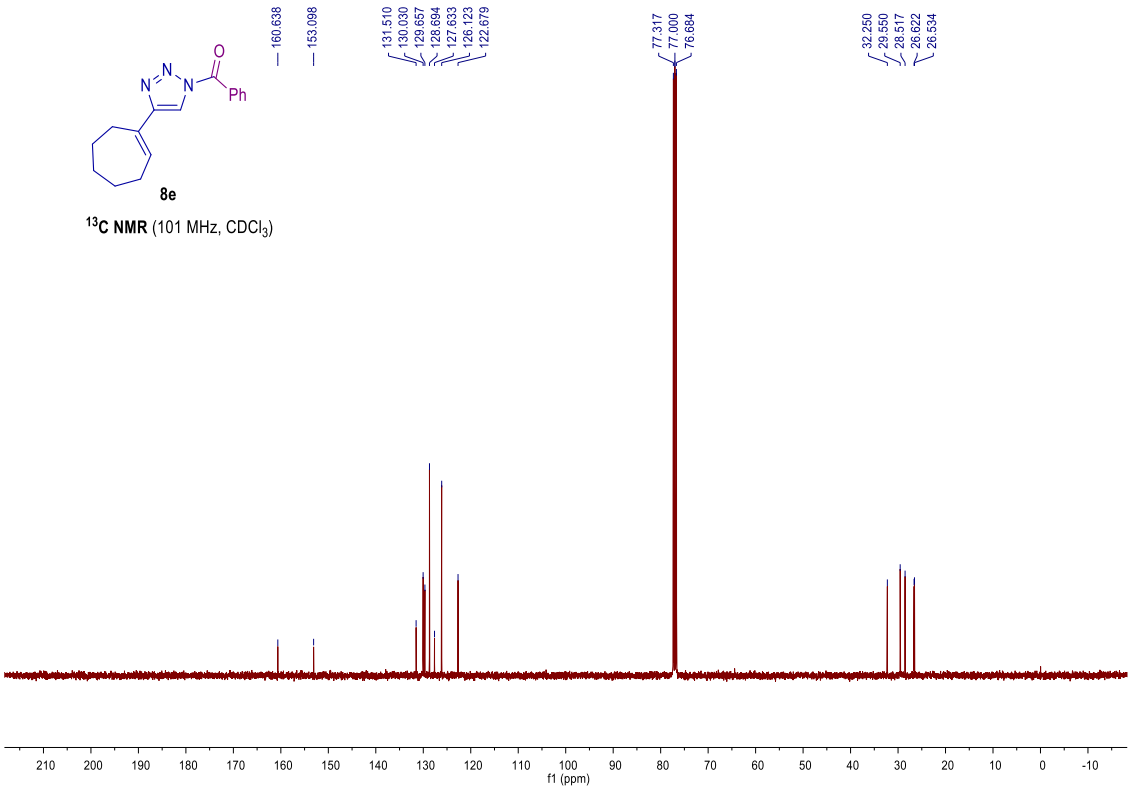


8d

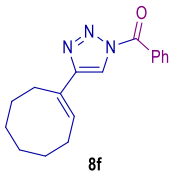
^{13}C NMR (101 MHz, $CDCl_3$)

8e


8.042
8.036
8.022
8.017
7.460
7.447
7.443
7.436
7.431
7.428
7.426
7.418
7.414
7.260
6.990
6.629
6.612
6.595
2.499
2.493
2.486
2.479
2.472
2.371
2.355
2.343
2.326
1.842
1.827
1.819
1.813
1.647
1.637
1.633
1.626
1.619
1.606
1.591
1.585
1.578
1.570
O
N
N
N
Ph
8e
1H NMR (400 MHz, CDCl3)
2.00
3.00
0.99
1.00
2.01
2.04
2.05
4.29
f1 (ppm)

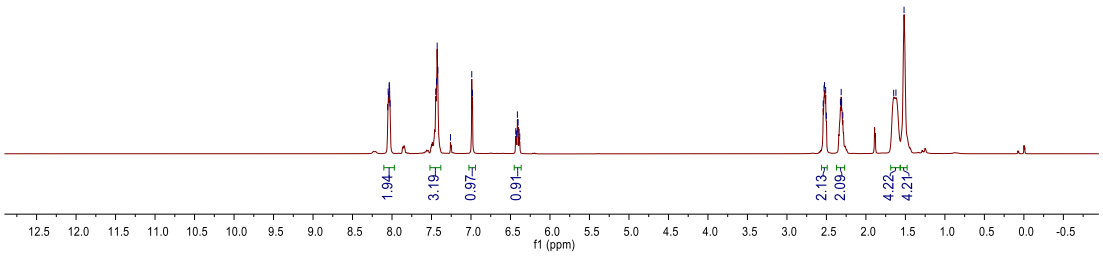

160.638
153.098
131.510
130.030
129.657
128.694
127.633
126.123
122.679
77.317
77.000
76.684
32.250
29.550
28.517
26.622
26.534
O
N
N
N
Ph
8e
13C NMR (101 MHz, CDCl3)
f1 (ppm)

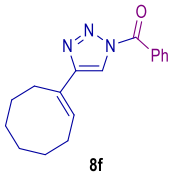
8f



8f

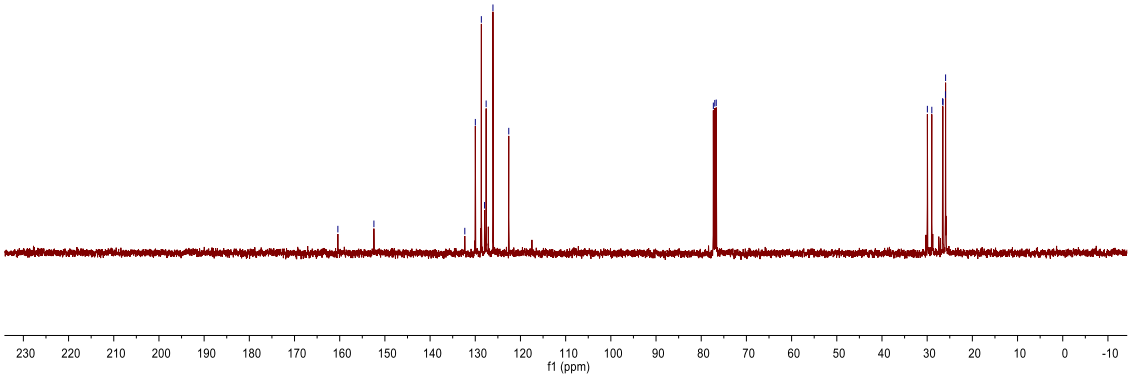
^{1}H NMR (400 MHz, $CDCl_3$)



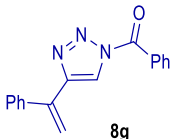


8f

^{13}C NMR (101 MHz, $CDCl_3$)

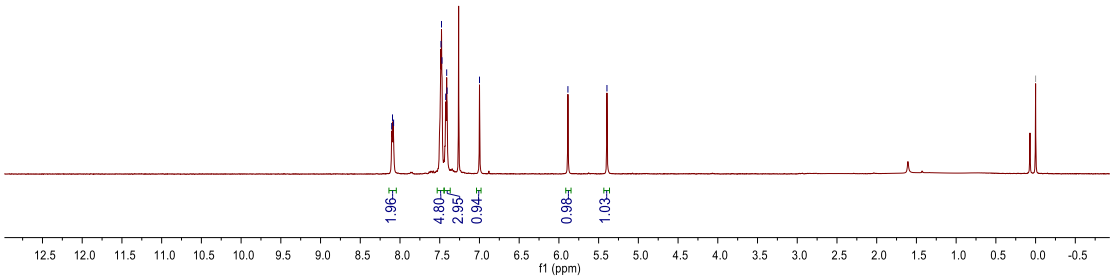


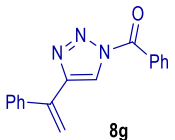
8g



8g

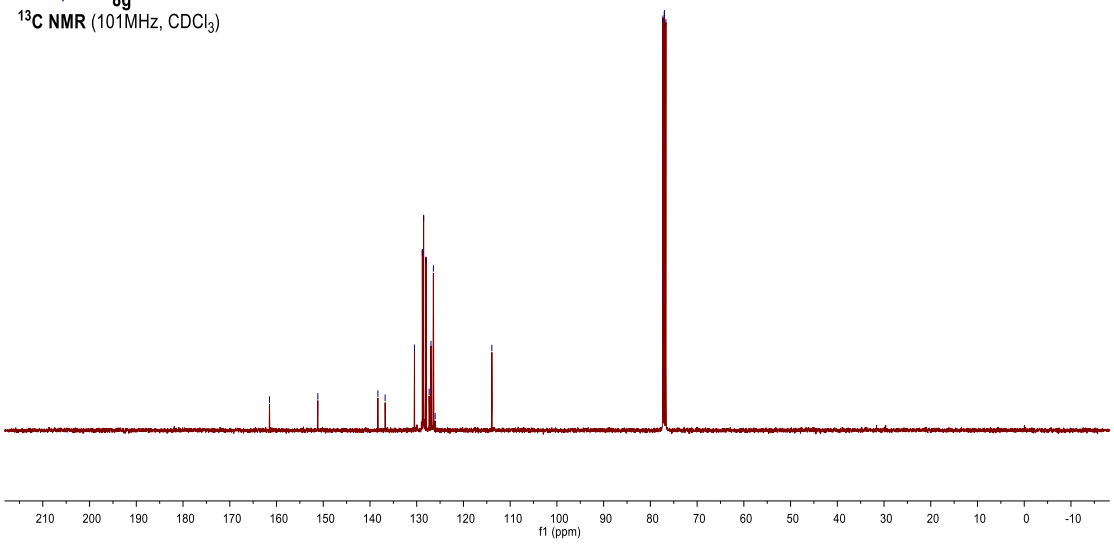
^{1}H NMR (400 MHz, $CDCl_3$)





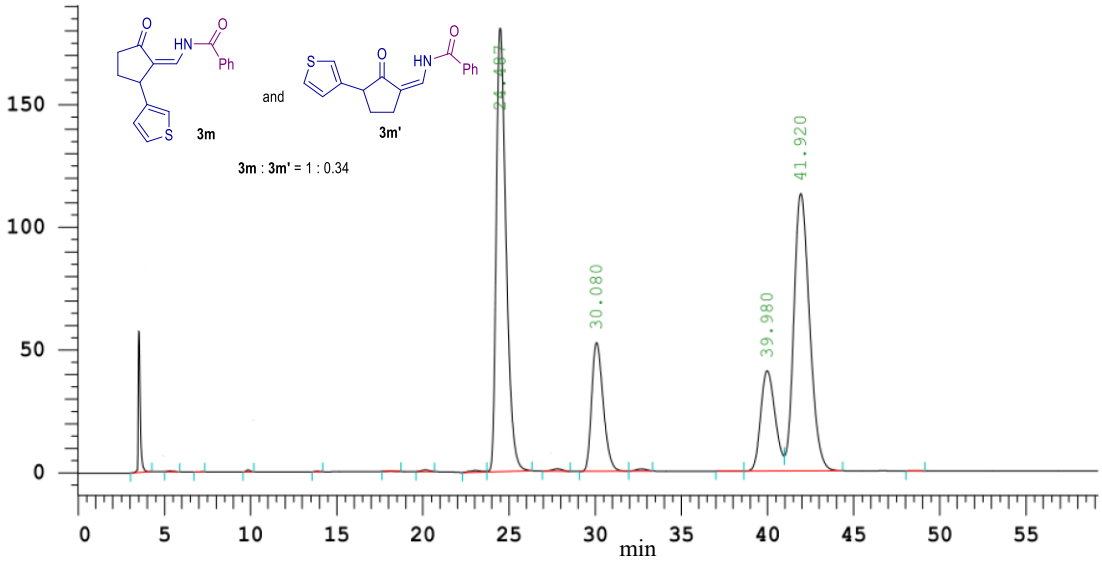
8g

^{13}C NMR (101MHz, $CDCl_3$)



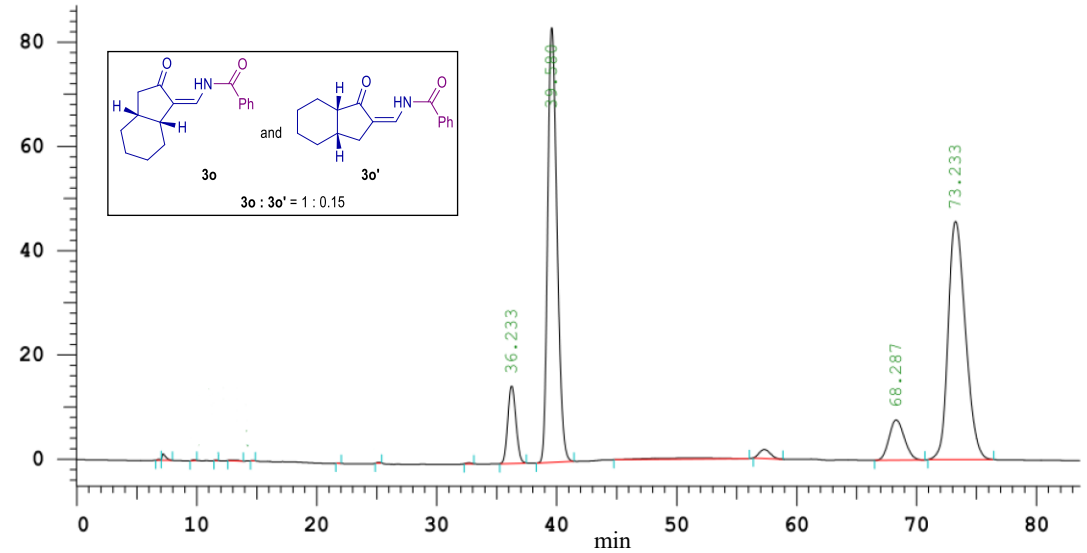
9. HPLC analysis

HPLC conditions: Chiralpak IC, ^{n}hexane/2-propanol = 96:4 (v/v), 1.0 mL/min, 254 nm, 30 °C



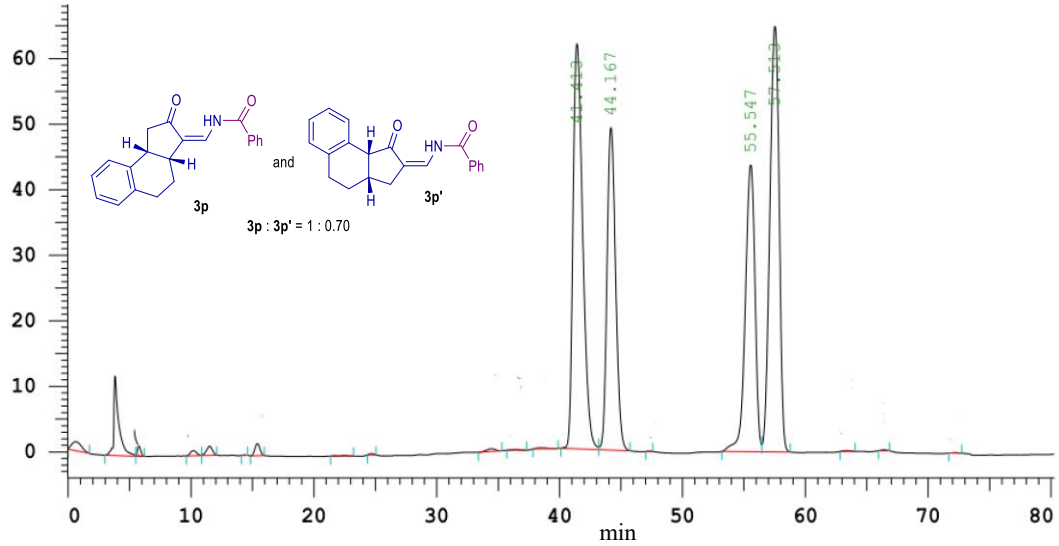
Peak#	Ret. Time	Area	Area%
1	24.287	6989377	37.130
2	30.080	2398912	12.744
3	39.980	2341764	12.440
4	41.920	7094146	37.686

HPLC conditions: Chiralpak IC, ^{n}hexane/2-propanol = 97:3 (v/v), 0.5 mL/min, 254 nm, 30 °C



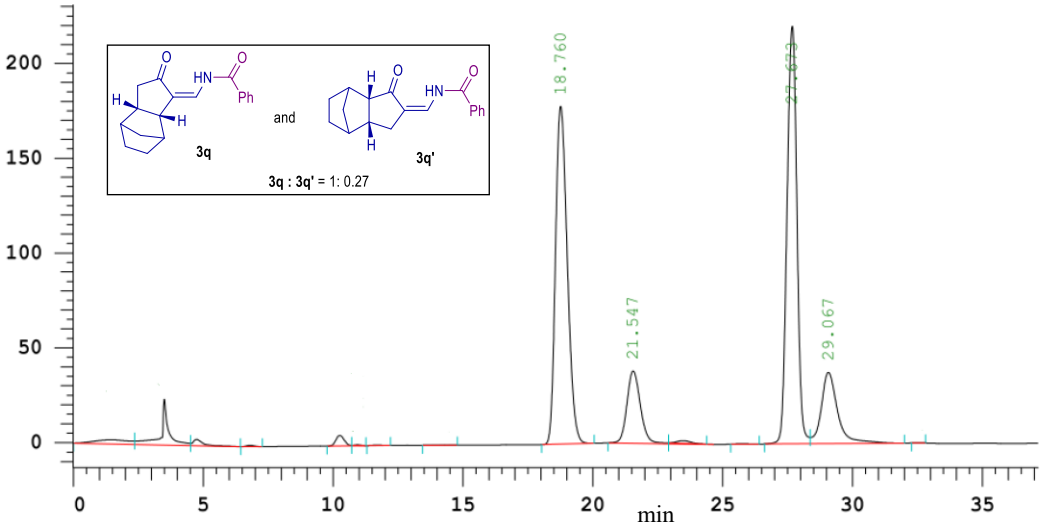
Peak#	Ret. Time	Area	Area%
1	36.233	679329	6.614
2	39.580	4401971	42.861
3	68.287	673865	6.560
4	73.233	4515454	43.965

HPLC conditions: Chiralpak IC, ^{n}hexane/2-propanol = 98:2 (v/v), 1.0 mL/min, 254 nm, 30 °C



Peak#	Ret. Time	Area	Area%
1	41.413	3299932	29.073
2	44.167	2348976	20.695
3	55.547	2343344	20.645
4	57.513	3358213	29.587

HPLC conditions: Chiralpak IC, ^{n}hexane/2-propanol = 97:3 (v/v), 1.0 mL/min, 254 nm, 30 °C



Peak#	Ret. Time	Area	Area%
1	18.760	5557395	38.812
2	21.547	1375415	9.606
3	27.673	5749260	40.152
4	29.067	1636524	11.428