Luminescent Cyclometalated Gold(III) Complexes Covalently Linked to Metal-Organic Frameworks for Heterogeneous Photocatalysis

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Supplementary Information – Table of Contents

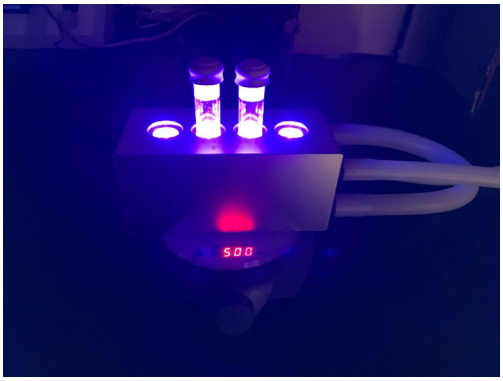
1 General information

1.1 Materials and methods

All reagents and solvents used for synthesis were purchased from commercial sources and used without further purification unless otherwise stated. [Au(C^N^C)Cl],[1] [Au(C_{np}^N^C_{np})Cl][2] and [Au(C^N^C)NHC]PF_6 [3] were synthesized according to reported methods. Me-TPDC-[Au1] crystals suitable for X-ray diffraction analysis were obtained by slowly diffusing Et_2O into the MeCN solution of the complex. Powder X-ray diffraction (PXRD) data were collected on a Rigaku MiniFlex600 diffractometer using Cu Kα radiation. The PXRD pattern was scanned over 4–30° (2θ) at a scan speed of 10°/min and a step width of 0.02°. 77 K-N_2 sorption isotherms were measured with a Micromeritics ASAP 2020 instrument. Prior to the sorption experiments, the samples were activated under a high vacuum at 100 °C for 6 h to remove guest molecules. The pore size distribution was derived from the N_2 isotherms at 77 K and analyzed by nonlocal density functional theory (NLDFT). Thermogravimetric analysis (TGA) was performed using a TA Q50 apparatus under a nitrogen atmosphere. Single crystal X-ray diffraction (SC-XRD) data were collected using a Bruker D8 VENTURE diffractometer equipped with an Excillum METALJET diffractometer using Ga Kα radiation (λ = 1.34139). Analysis of scanning electron microscope (SEM) and EDS mapping was conducted using a Zeiss Gemini 300 field emission scanning electron microscope (FE-SEM). The molar concentrations of Zr and Au were determined using an Agilent 7700 inductively coupled plasma mass spectrometer (ICP-MS). Nuclear magnetic resonance (NMR) spectra were measured on a Bruker DPX-600, DPX-500 or DPX-400 spectrometer. Chemical shifts were determined with tetramethylsilane (TMS) as an internal reference or with reference to the residual signal of a non-deuterated solvent. Coupling constants (*J*) were reported in Hertz (Hz). The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, p = pentet, m = multiplet, br = broad. X-ray photoelectron spectroscopy (XPS) was carried out on a PHI 5000 Versa Probe III supplied by ULVAC-PHI Inc., Japan equipped with a monochromatic Al Kα radiation source. Mass spectrometry measurements were performed using a Bruker Autoflex Speed MALDI TOF/TOF mass spectrometer equipped with a 355 nm solid-state smartbeam Nd:YAG laser. High-resolution mass spectra were recorded using a Q Exactive mass spectrometer (Thermo S3 Fisher Scientific, USA. Steady-state emission spectra were obtained on a Horiba Fluorolog-3 spectrophotometer. Emission quantum yields (Φ) were measured using a Hamamatsu C11347 Quantaurus-QY Absolute PL quantum yields measurement system. For absorption and emission measurements, the concentration of the solution is 2×10^{-5} mol dm^{-3}. Solutions for photophysical studies were degassed using a high vacuum line in a two-compartment cell and subjected to five freeze-pump-thaw cycles to remove oxygen. Absorption spectra were recorded on a Hewlett-Packard 8453 diode array spectrophotometer at room temperature. Irradiation was performed using 410 nm LEDs

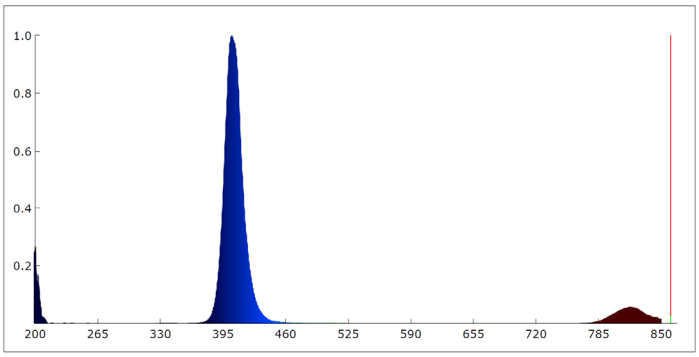
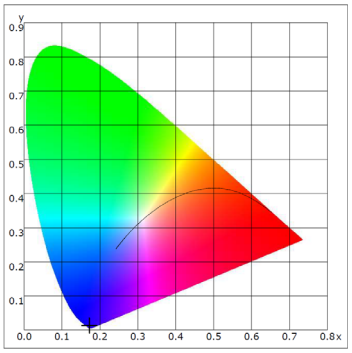
(3 W × 4) illumination instruments.

1.2 Photoreactor setup

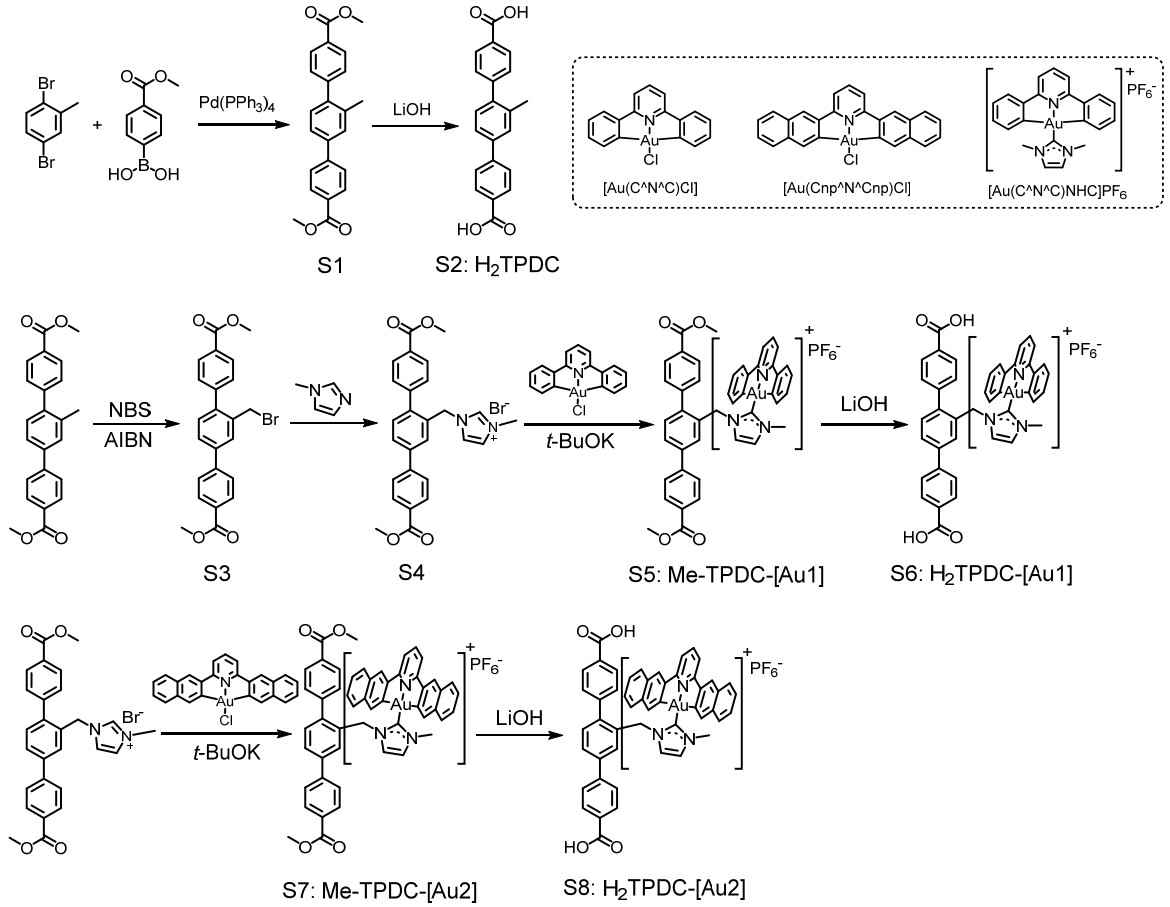


The setup used for photocatalytic studies (the reactor is cooled by running water).

1.3 LED spectral analysis

Test project:	LED spectral analysis	
Test equipment:	HOPOOCOLOR OHSP-250UV	
The test identification	Product model: 3 W LED	
	Ambient temperature: 20 °C	Ambient humidity: 65%
	Test organization: Spectro test department	
Spectral relative energy distribution curve		
		
Spectrum parameter		
Peak wavelength	404.5 nm	Chromaticity coordinate (x, y)	0.1718, 0.0132
Main wavelength	430.5 nm	Chromaticity coordinate (u, v)	0.2442, 0.0281
Centroid wavelength	434.3 nm	Color temperature	100000 K
Central wavelength	406.2 nm	Color purity	98.1%
Half-wave width	19.7 nm	Irradiance Ee (mW/cm²)	55.145
Luminous flux chromatography (RGB): 4.3, 45.2, 50.4		

2 Synthesis and Characterization of H_2TPDC and H_2TPDC-[Au1/Au2]



Scheme S1. Gold(III) complexes studied in this work and synthetic routes of organic linker H_2TPDC and **H_2TPDC-[Au1/Au2]**.

Synthesis of S1

A mixture of 2,5-dibromotoluene (4.99 g, 20 mmol), 4-(methoxycarbonyl) benzeneboronic acid (7.92 g, 44 mmol), K_2CO_3 (5.53 g, 40 mmol) and $Pd(PPh_3)_4$ (5 mol%) in H_2O/1,4-dioxane (100 mL, 1/4) was refluxed at 90 °C under argon. The reaction progress was monitored by thin-layer chromatography (TLC). After the reaction, the mixture was extracted with CH_2Cl_2. The combined organic phases were washed with H_2O, dried over $MgSO_4$, filtered, and concentrated. Further purification by column chromatography on silica gel (DCM/PE = 1: 2 v/v as eluent) to afford **S1** as a white solid (yield 85%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.13 (d, J = 5.2 Hz, 2H), 8.11 (d, J = 4.7 Hz, 2H), 7.70 (d, J = 7.9 Hz, 2H), 7.58 – 7.50 (m, 2H), 7.44 (d, J = 7.9 Hz, 2H), 7.33 (d, J = 7.9 Hz, 1H), 3.95 (s, 3H), 3.95 (s, 3H), 2.35 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.00, 146.11, 145.12, 140.76, 139.49, 135.89, 130.23, 130.15, 129.53, 129.41, 129.25, 129.00, 128.82, 127.26, 127.00, 124.82, 52.20, 52.18, 20.61. HRMS (ESI, m/z): Calcd for $[C_{23}H_{20}O_4 + Na]^+$: 383.1254, found: 383.1247.

Synthesis of S2

A mixture of **S1** (2.84 g, 7.8 mmol) and $LiOH \cdot H_2O$ (1.39 g, 31 mmol) in a mixed solvent system containing THF (75 mL) and H_2O (75 mL) was stirred at 65 °C for 12 h. After removing THF, the resulting aqueous solution was acidified with a dilute aqueous HCl solution (pH = 2 to 3). The precipitate was washed with H_2O and dried under vacuum, affording **S2** as a white solid (yield: 88%). ^{1}H NMR (600 MHz, DMSO-d_6) δ 13.00 (brs, 2H), 8.09 – 8.02 (m, 4H), 7.86 (d, J = 8.3 Hz, 2H), 7.72 (d, J = 1.9 Hz, 1H), 7.65 (dd, J = 7.9, 1.9 Hz, 1H), 7.53 (d, J = 8.2 Hz, 2H), 7.36 (d, J = 7.9 Hz, 1H), 2.34 (s, 3H). ^{13}C NMR (151 MHz, DMSO-d_6) δ 167.62, 167.60, 145.63, 144.27, 140.71, 138.89, 136.06, 130.63, 130.43, 130.15, 129.92, 129.77, 129.68, 129.54, 127.21, 125.06, 20.70. HRMS (ESI, m/z): Calcd for $[C_{21}H_{16}O_4 + Na]^+$: 355.0941, found: 355.0937.

Synthesis of S3

A mixture of **S1** (2.09 g, 5.8 mmol), NBS (1.14 g, 6.4 mmol), AIBN (99 mg, 0.6 mmol) in CCl_4 (100 mL) was refluxed for 3 h (the reaction progress was monitored by TLC). After the reaction, the insoluble substance was filtered out and the reaction solution was evaporated under reduced pressure to give an off-white solid crude product. The crude product was purified by column chromatography on silica gel (DCM/PE = 1:20 v/v as eluent) to afford **S3** as a white solid (yield 67%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.16 (d, J = 6.6 Hz, 2H), 8.14 (d, J = 6.7 Hz, 2H), 7.80 (d, J = 1.9 Hz, 1H), 7.72 (d, J = 8.4 Hz, 2H), 7.64 (dd, J = 8.0, 1.9 Hz, 1H), 7.58 (d, J = 8.3 Hz, 2H), 7.37 (d, J = 7.9 Hz, 1H), 4.49 (s, 2H), 3.97 (s, 3H), 3.96 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.85, 144.36, 144.29, 140.76, 140.32, 135.84, 130.90, 130.25, 129.90, 129.74, 129.50, 129.39, 129.09, 127.49, 127.03, 52.28, 52.24, 31.53. HRMS (ESI, m/z): Calcd for $[C_{23}H_{19}O_4Br + Na]^+$: 461.0359, found: 461.0356.

Synthesis of S4

N-Methylimidazole (0.21 g, 2.5 mmol) was added dropwise to a MeCN (60 mL) solution of **S3** (1.01 g, 2.3 mmol). The resulting mixture was stirred at 85 °C for 12 h (the reaction progress was monitored by TLC). After removing solvents, the crude product was purified by column chromatography on silica gel (MeOH/DCM = 1: 2 v/v) to afford **S4** as a white solid (yield 88%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.14 (s, 1H), 8.13 (d, J = 8.2 Hz, 2H), 8.10 (d, J = 8.4 Hz, 2H), 7.99 (d, J = 1.9 Hz, 1H), 7.78 (d, J = 8.4 Hz, 2H), 7.72 (dd, J = 8.0, 1.9 Hz, 1H), 7.39 (d, J = 8.1 Hz, 3H), 7.26 (t, J = 1.8 Hz, 1H), 6.71 (t, J = 1.8 Hz, 1H), 5.73 (s, 2H), 3.96 (s, 3H), 3.92 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.82, 166.50, 143.58, 143.46, 140.85, 140.78, 137.91, 131.21, 131.16, 130.29, 130.21, 129.94, 129.55, 129.36, 129.08, 128.36, 127.23, 123.14, 121.39, 52.44, 52.22, 51.07, 36.72. MS (MALDI-TOF): Calcd for $C_{27}H_{25}N_2O_4$: 441.51, found: 441.31.

Synthesis of S5

A mixture of **S4** (0.59 g, 1.15 mmol) and potassium *tert*-butoxide (0.238 g, 2 mmol) in MeOH (200 mL) was refluxed for 30 min, and then [Au(C^N^C)Cl] (0.69 g, 1.5 mmol) was added to give a pale yellow suspension. The resulting mixture was refluxed for another 12 h. After filtering out the insoluble substances, the filtrate was concentrated and subjected to a metathesis reaction with a saturated NH_4PF_6 solution in methanol to give a yellow solid. The crude product was collected by filtration and washed with

diethyl ether. Recrystallization from slow diffusion of diethyl ether vapor into a concentrated MeCN solution gave **S5** as a yellow crystalline solid (yield 58%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 – 7.88 (m, 3H), 7.78 (d, *J* = 8.2 Hz, 2H), 7.54 (d, *J* = 1.9 Hz, 1H), 7.50 (dd, *J* = 7.8, 1.2 Hz, 2H), 7.44 (d, *J* = 8.1 Hz, 2H), 7.36 – 7.30 (m, 3H), 7.28 – 7.23 (m, 1H), 7.22 – 7.14 (m, 3H), 7.13 – 7.03 (m, 4H), 7.00 (d, *J* = 8.0 Hz, 1H), 6.55 (dd, *J* = 7.3, 1.2 Hz, 2H), 5.48 (s, 2H), 3.92 (s, 6H), 3.68 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.79, 166.36, 164.03, 162.82, 153.16, 148.73, 143.96, 142.97, 142.93, 140.32, 139.45, 135.13, 132.96, 132.50, 131.02, 130.14, 129.79, 129.41, 129.36, 129.07, 128.20, 127.85, 127.24, 126.39, 126.24, 124.62, 123.59, 117.81, 53.51, 52.44, 52.29, 38.63. MS (MALDI-TOF): Calcd. for $[C_{44}H_{35}AuN_3O_4]^+$: 866.24, found: 866.10.

Synthesis of S6

The procedure was similar to that of **S2** except that **S5** was used instead of **S1** (yield 92%). ^{1}H NMR (600 MHz, K_3PO_4/D_2O/DMSO-d_6) δ 7.92 (t, *J* = 8.0 Hz, 1H), 7.78 (dd, *J* = 7.9, 4.9 Hz, 4H), 7.74 (d, *J* = 7.7 Hz, 2H), 7.63 (d, *J* = 8.1 Hz, 2H), 7.57 (d, *J* = 1.9 Hz, 1H), 7.40 (d, *J* = 2.1 Hz, 1H), 7.33 (td, *J* = 7.5, 1.3 Hz, 2H), 7.29 – 7.18 (m, 5H), 7.18 – 7.13 (m, 3H), 7.00 (d, *J* = 7.9 Hz, 1H), 6.66 (d, *J* = 7.2 Hz, 2H), 5.48 (s, 2H), 3.65 (s, 3H).^{13}C NMR (151 MHz, K_3PO_4/D_2O/DMSO-d_6) δ 174.16, 173.85, 165.49, 164.83, 154.87, 151.46, 146.76, 142.93, 142.51, 141.78, 140.99, 139.84, 137.39, 136.09, 134.42, 133.53, 132.19, 131.86, 130.55, 130.41, 130.33, 128.98, 127.64, 127.15, 125.16, 120.78, 55.16, 41.45. MS (MALDI-TOF): Calcd. for $[C_{42}H_{32}AuN_3O_4]^+$: 838.20, found: 838.11.

Synthesis of S7

The procedure was similar to that of **S5** except that [Au(C_{np}^N^C_{np})Cl] was used instead of [Au(C^N^C)Cl] (yield 53%). ^{1}H NMR (400 MHz, MeCN-d_3)) δ 8.26 (s, 2H), 8.13 (t, *J* = 8.0 Hz, 1H), 7.92 – 7.85 (m, 4H), 7.77 (d, *J* = 8.4 Hz, 2H), 7.62 (d, *J* = 1.9 Hz, 1H), 7.56 (d, *J* = 8.3 Hz, 2H), 7.51 – 7.40 (m, 9H), 7.22 (d, *J* = 8.4 Hz, 2H), 7.11 (s, 2H), 7.06 – 6.98 (m, 3H), 6.83 (d, *J* = 8.0 Hz, 1H), 5.52 (s, 2H), 3.94 (s, 3H), 3.87 (s, 3H), 3.73 (s, 3H). ^{13}C NMR (101 MHz, MeCN-d_3) δ 166.33, 165.86, 163.17, 157.40, 146.67, 143.40, 142.96, 142.68, 140.27, 138.96, 135.15, 134.47, 133.42, 132.02, 130.50, 129.65, 129.37, 129.19, 129.05, 129.02, 128.41, 128.11, 127.58, 126.65, 126.55, 126.15, 124.90, 123.72, 118.91, 52.19, 51.74, 51.71, 38.40. MS (MALDI-TOF): Calcd. for $[C_{52}H_{39}AuN_3O_4]^+$: 966.26, found: 966.02.

Synthesis of S8

The procedure was similar to that of **S2** except that **S7** was used instead of **S1** (yield 88%). ^{1}H NMR (600 MHz, K_3PO_4/D_2O/DMSO-d_6) δ 8.55 (s, 2H), 8.11 (d, *J* = 7.7 Hz, 1H), 8.06 (d, *J* = 7.9 Hz, 2H), 7.99 (d, *J* = 7.8 Hz, 2H), 7.81 (d, *J* = 7.7 Hz, 2H), 7.74 (d, *J* = 7.7 Hz, 2H), 7.69 (d, *J* = 7.8 Hz, 2H), 7.66 (s, 1H), 7.59 – 7.53 (m, 5H), 7.33 (s, 1H), 7.16 (s, 2H), 7.11 (d, *J* = 7.8 Hz, 2H), 7.08 (d, *J* = 7.9 Hz, 2H), 6.71 (d, *J* = 7.8 Hz, 1H), 5.60 (s, 2H), 3.77 (s, 3H). ^{13}C NMR (151 MHz, K_3PO_4/D_2O/DMSO-d_6) δ 169.54, 169.16, 162.57, 157.76, 152.54, 147.24, 143.99, 140.90, 140.21, 140.09, 139.47, 138.77, 138.43, 135.07, 134.34, 133.73, 132.24, 131.35, 129.95, 129.66, 128.76, 128.61, 128.04, 127.98, 127.08, 126.99, 126.46, 125.25, 124.93, 123.59, 119.74, 53.31,

38.73.MS (MALDI-TOF): Calcd. for $[C_{50}H_{35}AuN_3O_4]^+$: 938.23, found: 938.08.

3 Synthesis and Characterization of UiO-68-Me and UiO-68[Au1/Au2]

Using dimethylformamide as the solvent and trifluoroacetic acid as the modulator, under solvothermal conditions of 120°C and a reaction time of 48 h, **UiO-68[Au1]$_{1.2\text{-}4.5\%}$** and **UiO-68[Au2]$_{2.6\%}$** were successfully synthesized. Using a mixed-linker synthetic strategy, **UiO-68[Au1]$_{1.2\text{-}4.5\%}$** with different gold(III) complex contents was prepared and obtained as colorless crystals by varying the molar ratio of H_2TPDC-[Au1] and H_2TPDC from 1:20 to 1:5. Similarly, **UiO-68[Au2]$_{2.6\%}$** was prepared by reacting a mixture of H_2TPDC-[Au2] and H_2TPDC with a molar ratio of 1:10 under the same solvothermal conditions as **UiO-68[Au1]$_{1.2\text{-}4.5\%}$**. This reaction yields **UiO-68[Au2]$_{2.6\%}$** as a colorless and highly crystalline powder.

3.1 Synthesis of the UiO-68-Me

According to the literature,[4] $ZrCl_4$ (9.3 mg, 0.04 mmol), H_2TPDC (11.3 mg, 0.034 mmol), trifluoroacetic acid (60 μL) and DMF (2 mL) were charged in a Teflon®-capped 20 mL scintillation vial, and the mixture was sonicated for 5 min until the solid was completely dissolved. The resulting mixture was then heated in an oven at 120 °C for 48 h. After cooling to room temperature, the sample was washed with DMF and the solvent was exchanged with MeCN. UiO-68-Me was obtained as a colorless transparent crystal (yield: 67%).

3.2 Synthesis of the UiO-68[Au1/Au2]

$ZrCl_4$ (9.3 mg, 0.04 mmol), **H_2TPDC**, **H_2TPDC-[Au1]** (or **H_2TPDC-[Au2]**) (the respective amounts shown in Table S1), trifluoroacetic acid (60 μL) and DMF (2 mL) were charged in a Teflon®-capped 20 mL scintillation vial and the mixture was sonicated for 5 min until the solid was completely dissolved. The resulting mixture was then heated in an oven at 120 °C for 48 h. After cooling to room temperature, the fresh sample was washed with DMF and the solvent was exchanged with MeCN. **UiO-68[Au1/Au2]** was obtained as a colorless transparent crystal. PXRD suggested that **UiO-68[Au1]** and **UiO-68[Au2]** are isostructural with **UiO-68-Me** (Fig. S11a–14a). The concentration of gold(III) complexes covalently linked to the MOF was determined using ICP-MS (Table S2)

Table S1. The feed ratio of linkers **H_2TPDC** and **H_2TPDC-[Au1/Au2]** used in the preparation of **UiO-68[Au1/Au2]**.

MOF	Feed ratio (H_2L:$H_2L^{Au1/Au2}$)	H_2TPDC (mmol)	H_2TPDC-[Au1/Au2] (mmol)
UiO-68[Au1]$_{1.2\%}$	20:1	0.032	0.0016
UiO-68[Au1]$_{2.4\%}$	10:1	0.031	0.0031
UiO-68[Au1]$_{4.5\%}$	5:1	0.028	0.0056
UiO-68[Au2]$_{2.6\%}$	10:1	0.031	0.0031

3.3 SEM and EDS mapping of UiO-68-Me and UiO-68[Au1/Au2]

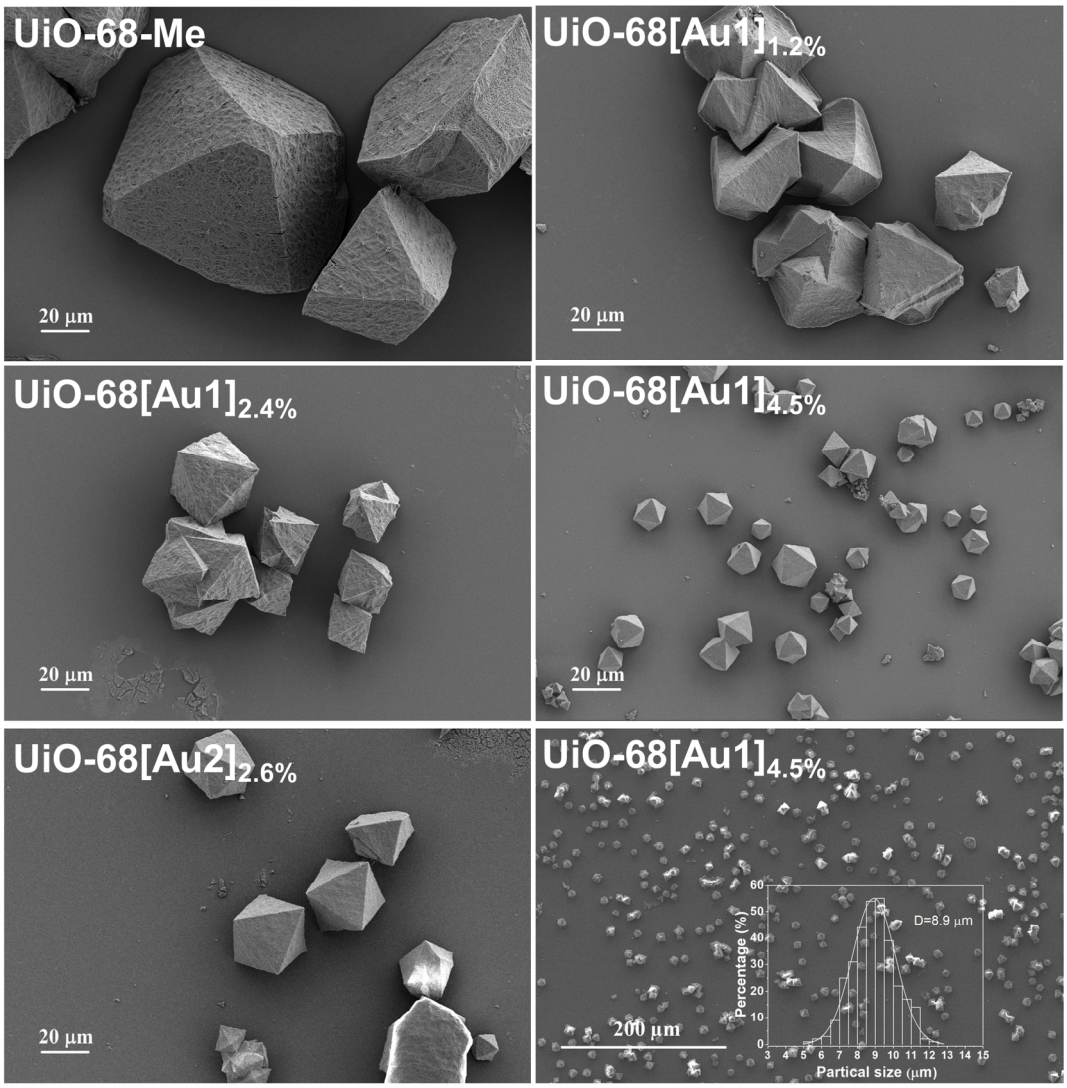
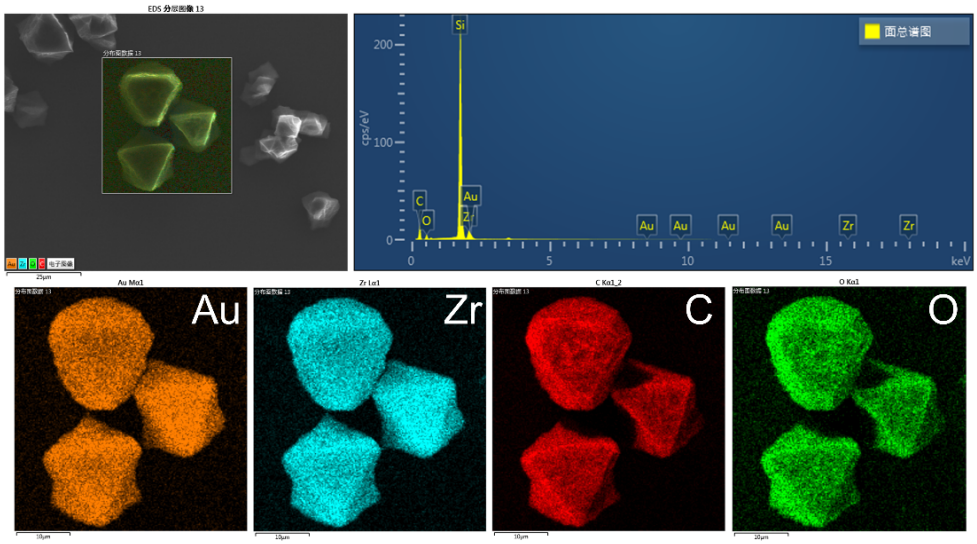
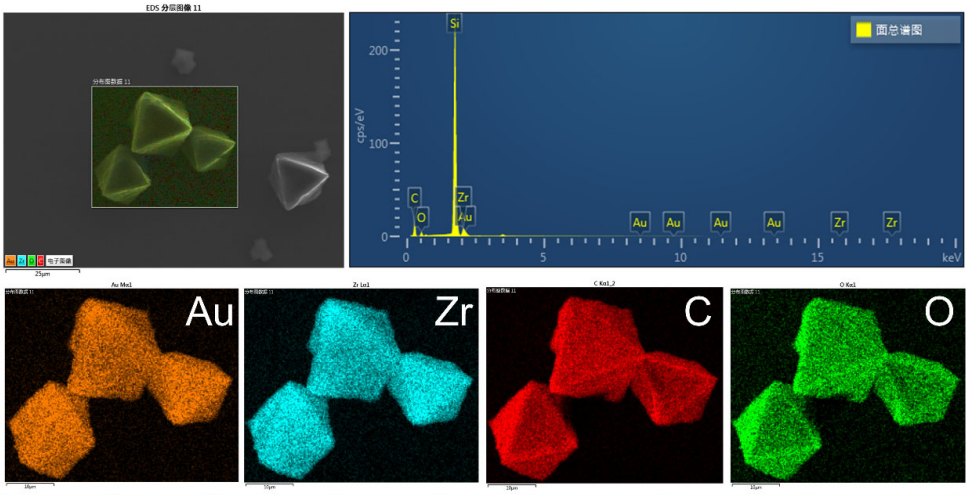


Fig. S1. SEM images of single crystal **UiO-68-Me**, **UiO-68[Au1]$_{1.2–4.5\%}$** and **UiO-68[Au2]$_{2.6\%}$**. Inset: histogram showing the particle size distribution of **UiO-68[Au1]$_{4.5\%}$** based on SEM measurements.



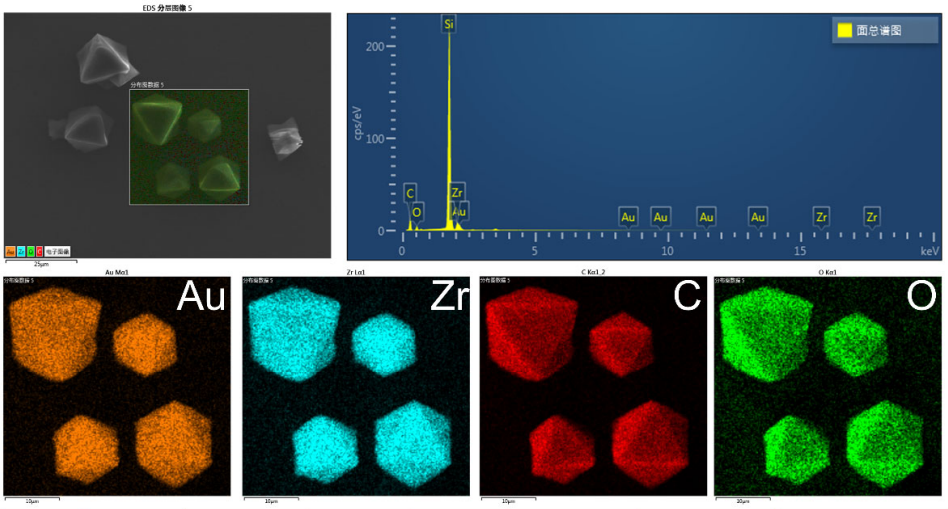
Element	Line type	Apparent concentration	K Ratio	wt%	wt% Sigma	Atomic percentage	Standard sample label
C	K	72.36	0.72356	56.19	0.10	73.85	C Vit
O	K	36.15	0.12164	7.93	0.05	7.83	SiO_2
Si	K	565.28	4.47930	31.20	0.07	17.54	SiO_2
Zr	L	47.49	0.47490	4.42	0.06	0.77	Zr
Au	M	2.77	0.02772	0.25	0.03	0.02	Au

Fig. S2. SEM-EDS mapping of **UiO-68[Au1]$_{1.2\%}$**.



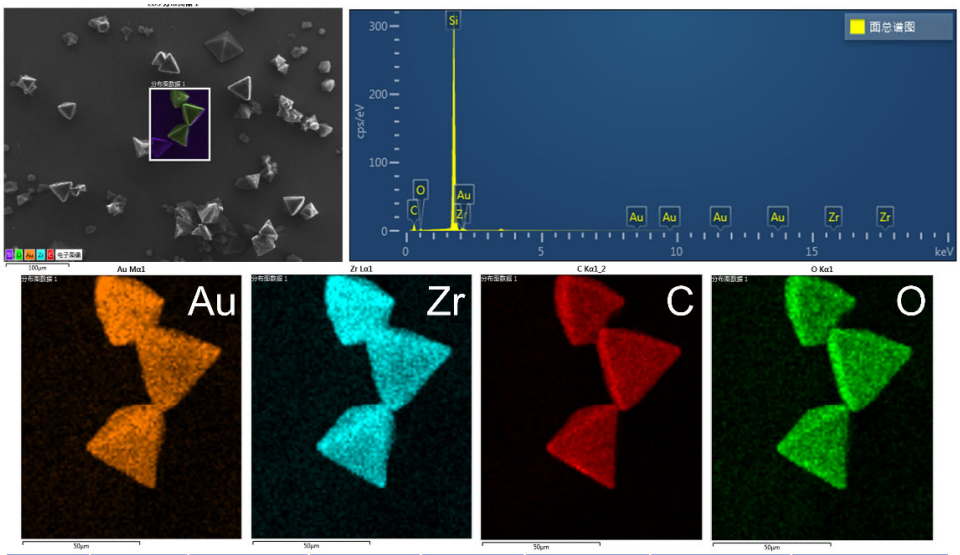
Element	Line type	Apparent concentration	K Ratio	wt%	wt% Sigma	Atomic percentage	Standard sample label
C	K	76.19	0.76194	49.21	0.09	69.14	C Vit
O	K	34.64	0.11656	6.27	0.04	6.61	SiO2
Si	K	583.14	4.62084	38.63	0.07	23.21	SiO2
Zr	L	43.11	0.43113	5.29	0.03	0.98	Zr
Au	M	5.04	0.05041	0.59	0.03	0.05	Au

Fig. S3. SEM-EDS mapping of **UiO-68[Au1]$_{2.4\%}$**.



Element	Line type	Apparent concentration	K Ratio	wt%	wt% Sigma	Atomic percentage	Standard sample label
C	K	69.24	0.69238	47.52	0.10	68.01	C Vit
O	K	33.54	0.11286	6.25	0.04	6.72	SiO_2
Si	K	571.05	4.52500	39.39	0.08	24.11	SiO_2
Zr	L	43.62	0.43622	5.61	0.04	1.06	Zr
Au	M	9.97	0.09974	1.23	0.04	0.11	Au

Fig. S4. SEM-EDS mapping of **UiO-68[Au1]**$_{4.5\%}$.



Element	Line type	Apparent concentration	K Ratio	wt%	wt% Sigma	Atomic percentage	Standard sample label
C	K	13.46	0.13461	39.03	0.13	59.58	C Vit
O	K	7.19	0.02421	4.33	0.04	4.96	SiO_2
Si	K	237.10	1.87883	53.39	0.12	34.85	SiO_2
Zr	L	5.81	0.05806	2.82	0.04	0.57	Zr
Au	M	0.94	0.00939	0.43	0.04	0.04	Au

Fig. S5. SEM-EDS mapping of **UiO-68[Au2]**$_{2.6\%}$.

3.4 XPS analysis of Au(C^N^C)Cl, Au(C_{np}^N^C_{np})Cl, UiO-68[Au1/Au2], and UiO-68[Au1] after treatment with $NaBH_4$

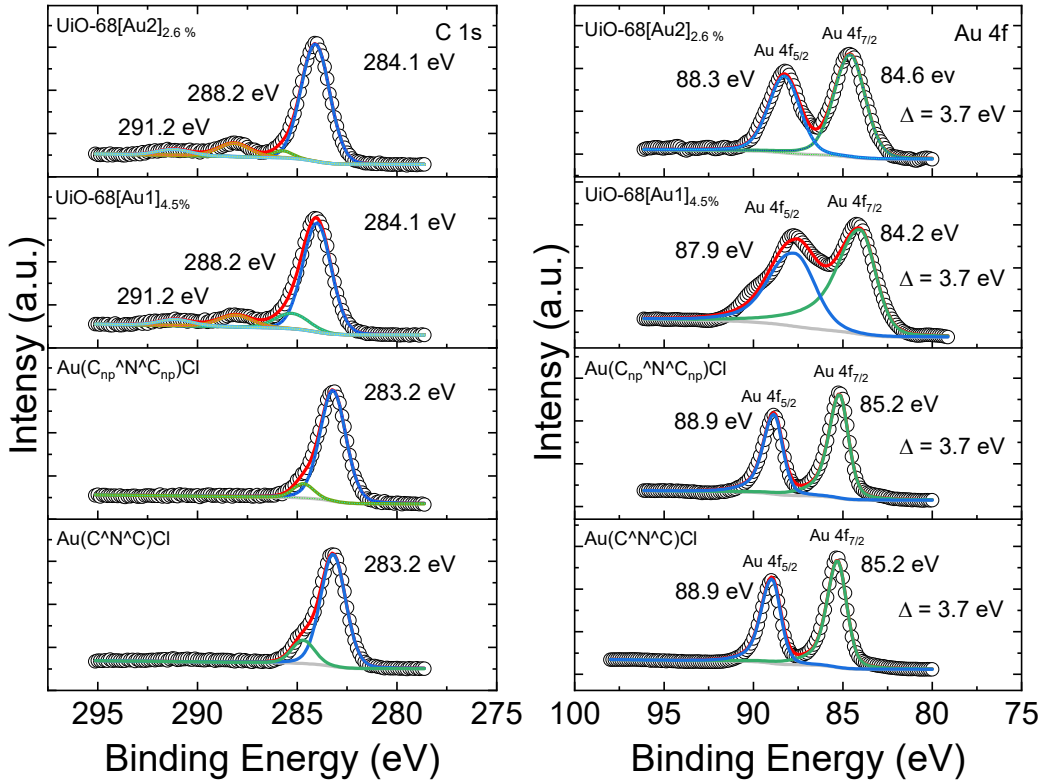


Fig. S6 XPS curve fitting of the Au 4f and C 1s photoelectron peaks in Au(C^N^C)Cl, Au(C_{np}^N^C_{np})Cl, **UiO-68[Au1]$_{4.5\%}$** and **UiO-68[Au2]$_{2.6\%}$**. (The dotted line refers to the raw data, and the solid line to the curve-fitting result. The curve fitting of the Au 4f core-level spectrum was performed by using two spin-orbit split Au $4f_{7/2}$ and Au $4f_{5/2}$ components, separated by 3.7 eV.)

Procedure for treating **UiO-68[Au1]$_{4.5\%}$** with $NaBH_4$:
Disperse 10 mg of **UiO-68[Au1]$_{4.5\%}$** in 2 mL of DMF and stir the resulting mixture in an ice bath for 0.5 h. A freshly prepared DMF solution of $NaBH_4$ (0.1 M, 1.5 mL) was added under vigorous stirring. After the addition was completed, the reaction mixture was stirred for 12 h, resulting in a purple suspension. After the reaction, the insoluble substance was collected by centrifugation.

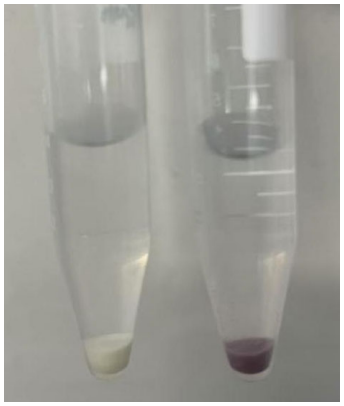


Fig. S7. Pictures of (left) **UiO-68[Au1]$_{4.5\%}$** after the [2+2] styrene (1a) cycloaddition reaction and (right) **UiO-68[Au1]$_{4.5\%}$** after treatment with $NaBH_4$.

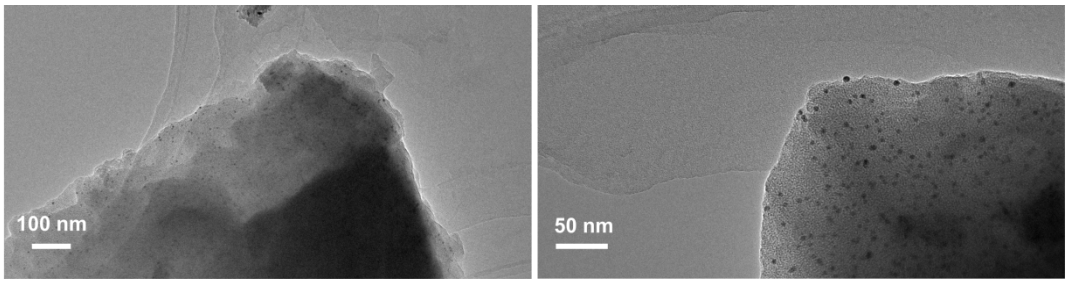


Fig. S8. TEM images of **UiO-68[Au1]$_{4.5\%}$** after treatment with $NaBH_4$.

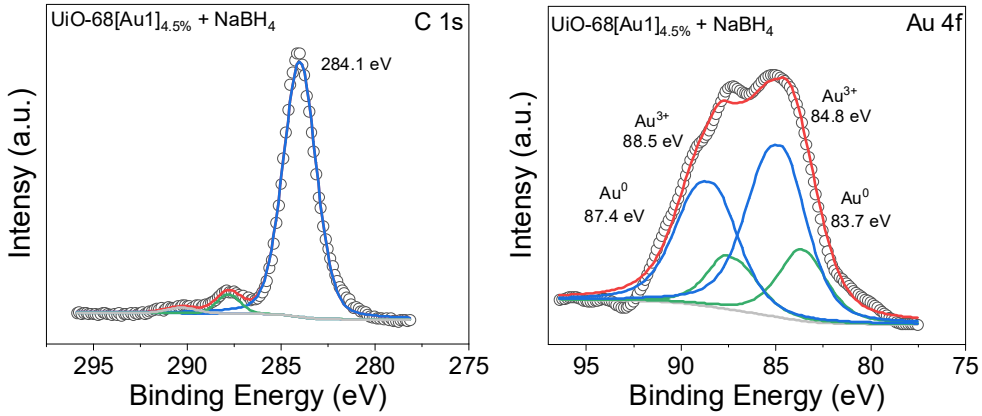


Fig. S9. XPS curve fitting of the Au 4f and C 1s photoelectron peaks in **UiO-68[Au1]$_{4.5\%}$** after treatment with $NaBH_4$. (The dotted line refers to the raw data, and the solid line to the curve-fitting result.

3.5 ICP-MS results of UiO-68[Au1/Au2]

Table S2. ICP-MS results of **UiO-68[Au1]** and **UiO-68[Au2]**.

MOF	Zr(wt%)	Au(wt%)	Zr (mol %):Au(mol %)
UiO-68[Au1]$_{1.2\%}$	13.8%	1.2%	25.6:1
UiO-68[Au1]$_{2.4\%}$	14.4%	2.4%	13.1:1
UiO-68[Au1]$_{4.5\%}$	13.1%	4.5%	6.3:1
UiO-68[Au2]$_{2.6\%}$	17.9%	2.6%	15.1:1

3.6 Digestion experiment

General procedure for the digestion experiment

A 1:1 (v/v) mixture of saturated potassium phosphate (K_3PO_4) solution in D_2O and DMSO-d_6 (total volume 1 mL) was thoroughly mixed. The activated MOF (8 mg) was then added to the resulting mixture. A clear solution was obtained after ultrasonic treatment for several minutes. The resulting sample was subjected to NMR measurements.

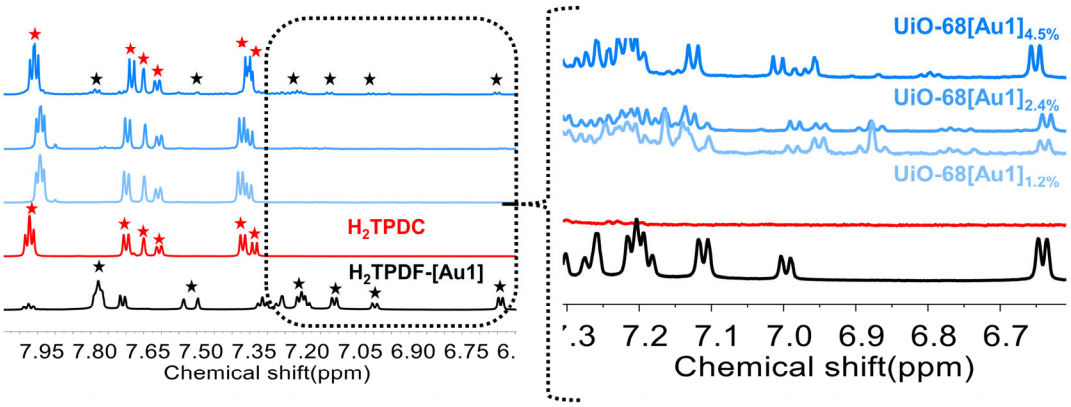


Fig. S10. Comparison of ^{1}H NMR spectra (K_3PO_4/D_2O/ DMSO-d_6, 600 MHz) of **UiO-68[Au1]$_{1.2\%–4.5\%}$**, **H_2TPDC**, and **H_2TPDC-[Au1]**.

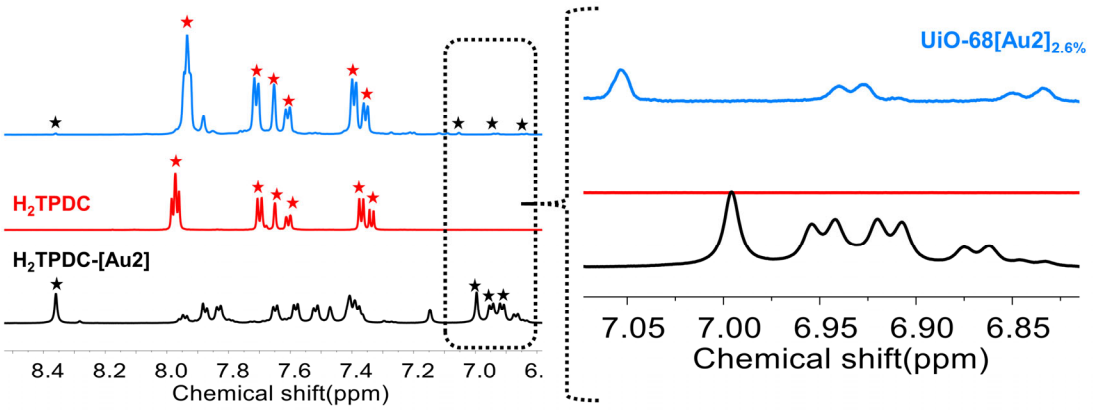


Fig. S11. Comparison of ^{1}H NMR spectra (K_3PO_4/D_2O/ DMSO-d_6, 600 MHz) of **UiO-68[Au2]$_{2.6\%}$**, **H_2TPDC**, and **H_2TPDC-[Au2]**.

3.7 PXRD patterns of UiO-68[Au1] treated under different conditions

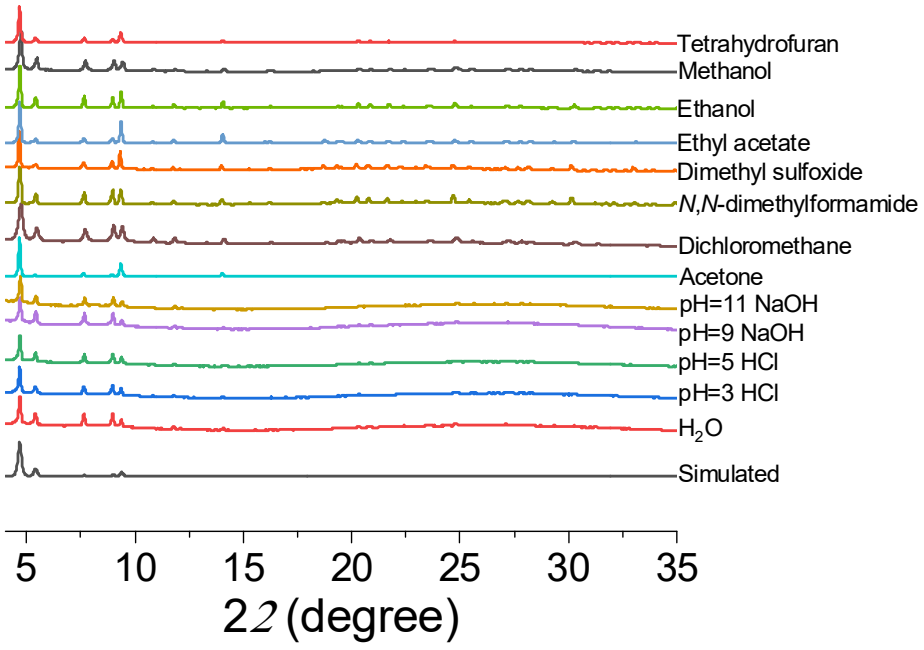


Fig. S12. PXRD patterns of **UiO-68[Au1]$_{4.5\%}$** after immersion in different solvents, HCl solution, and NaOH solution for 12 h.

3.8 PXRD patterns and TGA curves of UiO-68-Me, UiO-68[Au1], and UiO-68[Au2]

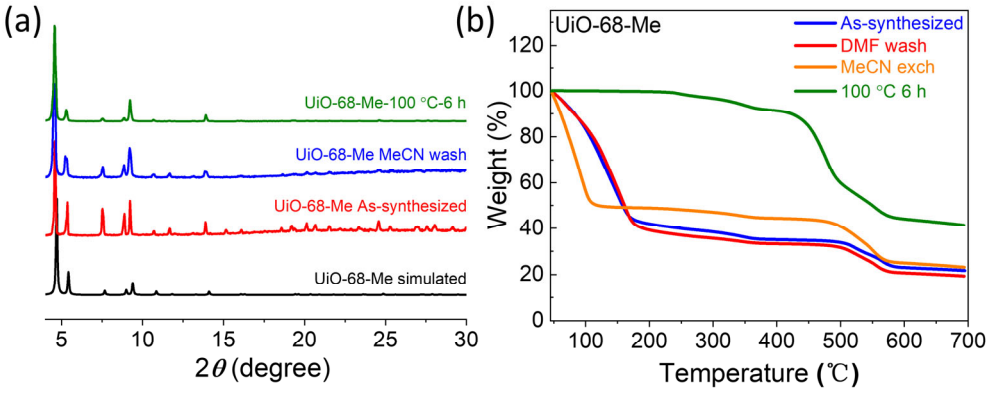


Fig. S13. PXRD patterns (a) and TGA curves (b) of **UiO-68-Me** before/after solvent (DMF and MeCN) exchange and after thermal treatment at 100 °C for 6 h.

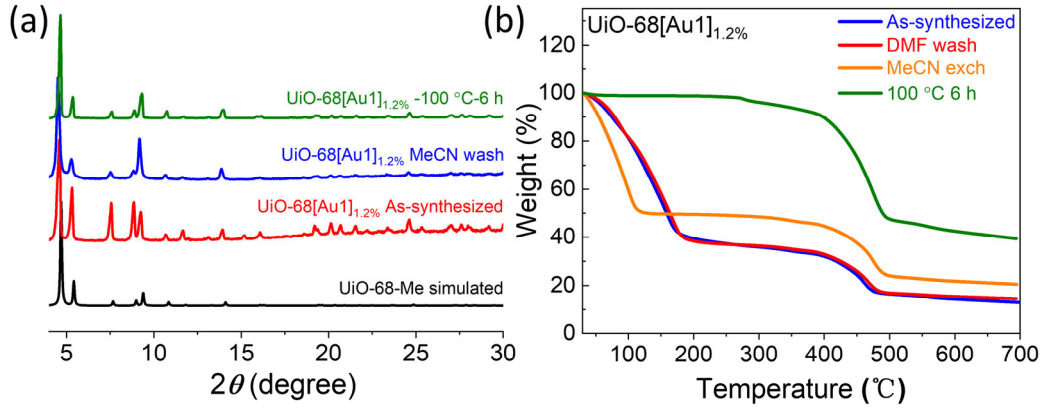


Fig. S14. PXRD patterns (a) and TGA curves (b) of **UiO-68[Au1]$_{1.2\%}$** before/after solvent (DMF and MeCN) exchange and after thermal treatment at 100 °C for 6 h.

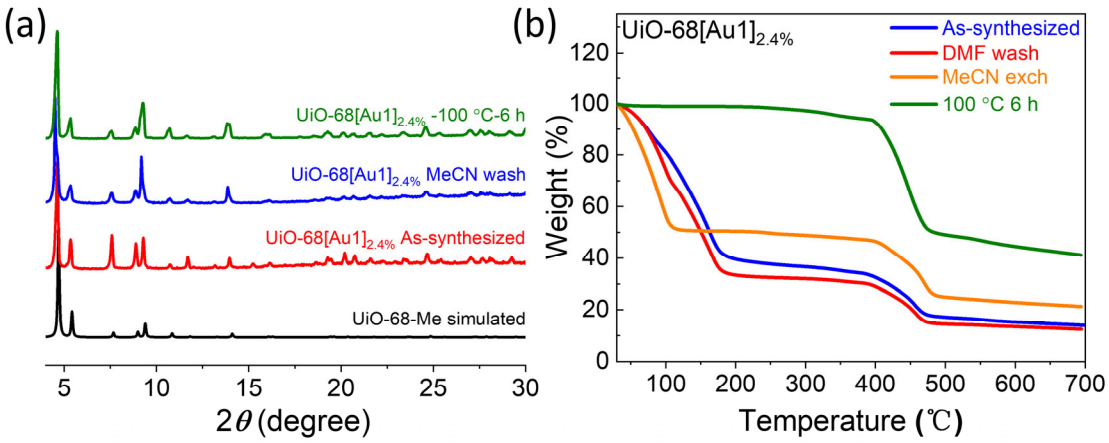


Fig. S15. PXRD patterns (a) and TGA curves (b) of **UiO-68[Au1]$_{2.4\%}$** before/after solvent (DMF and MeCN) exchange and after thermal treatment at 100 °C for 6 h.

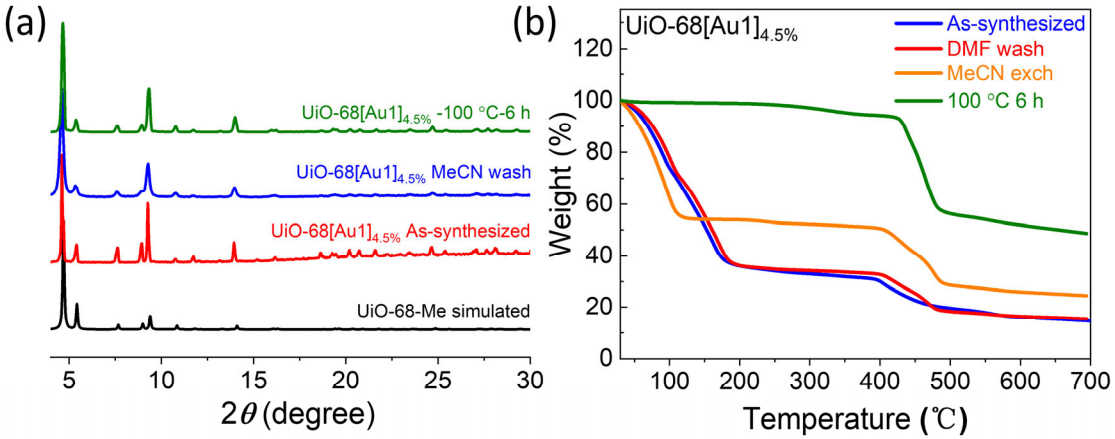


Fig. S16. PXRD patterns (a) and TGA curves (b) of **UiO-68[Au1]$_{4.5\%}$** before/after solvent (DMF and MeCN) exchange and after thermal treatment at 100 °C for 6 h.

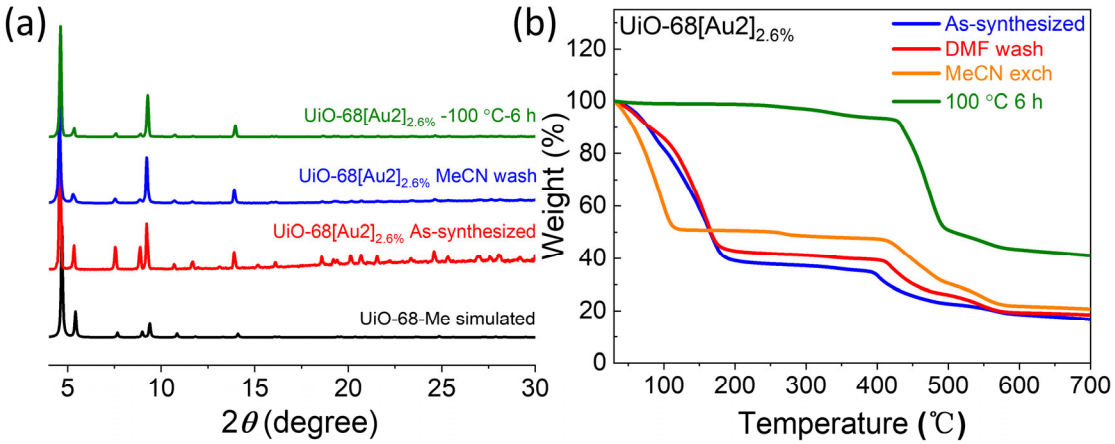
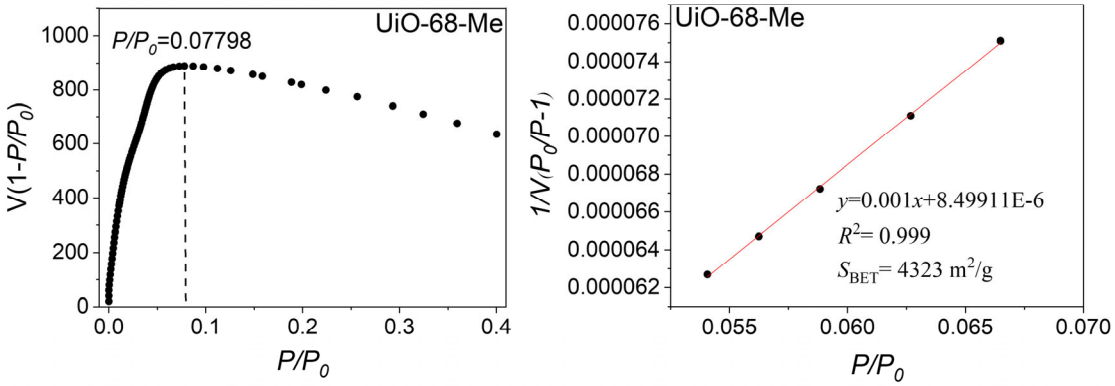


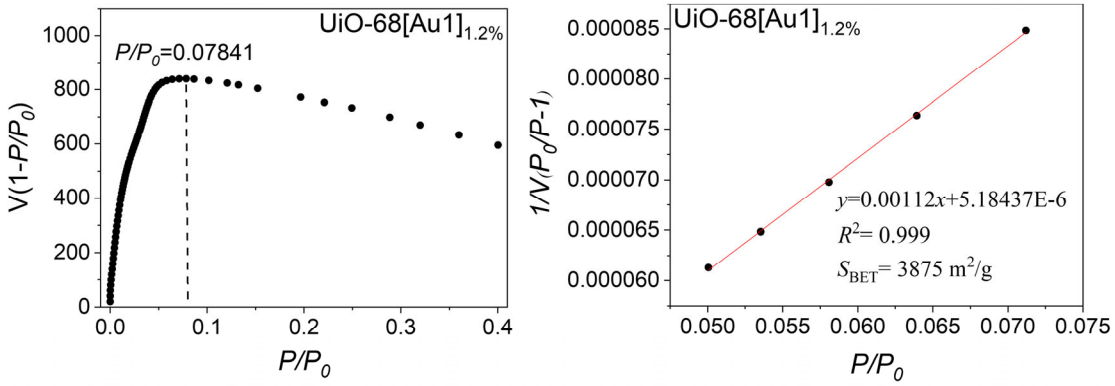
Fig. S17. PXRD patterns (a) and TGA curves (b) of **UiO-68[Au2]$_{2.6\%}$** before/after solvent (DMF and MeCN) exchange and after thermal treatment at 100 °C for 6 h.

3.9 BET surface area and pore volume of UiO-68-Me, UiO-68[Au1], and UiO-68[Au2]

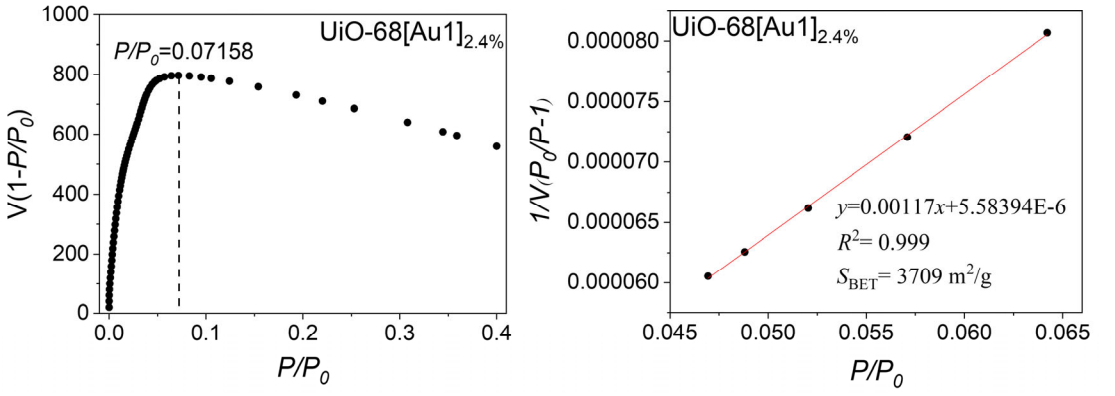
(a)



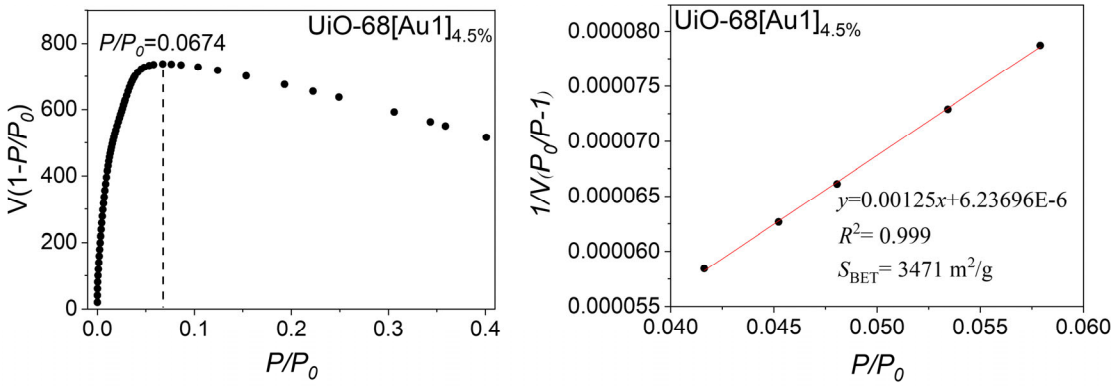
(b)



(c)



(d)



(e)

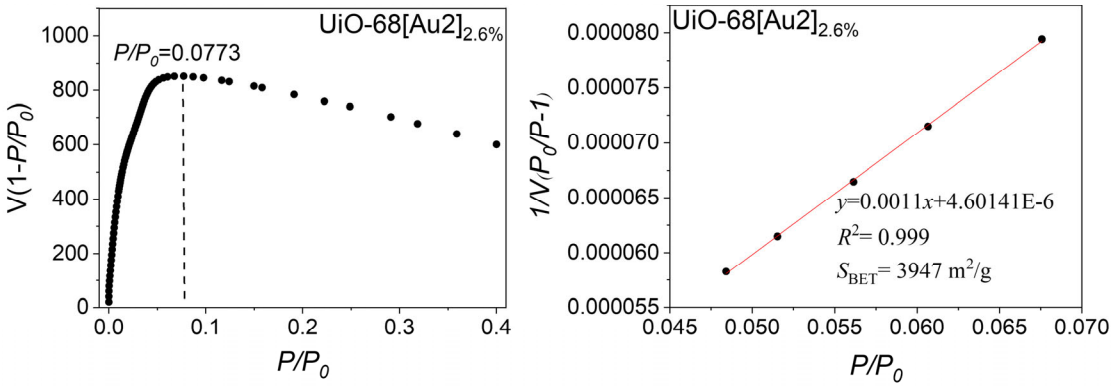


Fig. S18. BET plots of (a) **UiO-68-Me**, (b–d) **UiO-68[Au1]$_{1.2–4.5\%}$** and (e) **UiO-68[Au2]$_{2.6\%}$.** BET surface areas were calculated using the following BET equations S1 to S5, respectively.

S_{BET}(**UiO-68-Me**) =
$1/(8.49911\times10^{-6}+0.001)/22414\times6.023\times10^{23}\times0.162\times10^{-18}$ = 4323 m^2/g (S1)
S_{BET}(**UiO-68[Au1]$_{1.2\%}$**) =
$1/(5.18437\times10^{-6}+0.00112)/22414\times6.023\times10^{23}\times0.162\times10^{-18}$ = 3875 m^2/g (S2)
S_{BET}(**UiO-68[Au1]$_{2.4\%}$**) =
$1/(5.58394\times10^{-6}+0.00117)/22414\times6.023\times10^{23}\times0.162\times10^{-18}$ = 3709 m^2/g (S3)
S_{BET}(**UiO-68[Au1]$_{4.5\%}$**) =
$1/(6.23696\times10^{-6}+0.00125)/22414\times6.023\times10^{23}\times0.162\times10^{-18}$ = 3471 m^2/g (S4)
S_{BET}(**UiO-68[Au2]$_{2.6\%}$**) =
$1/(4.60141\times10^{-6}+0.0011)/22414\times6.023\times10^{23}\times0.162\times10^{-18}$ = 3947 m^2/g (S5)

Table S3. Comparison of the pore volume and BET surface area for **UiO-68-Me** and **UiO-68[Au1/Au2]**.

Samples	Pore volume[a] (cm^3/g)	S_{BET} (cm^2/g)
UiO-68-Me	1.67	4323
UiO-68[Au1]$_{1.2\%}$	1.56	3875
UiO-68[Au1]$_{2.4\%}$	1.48	3709
UiO-68[Au1]$_{4.5\%}$	1.36	3471
UiO-68[Au2]$_{2.6\%}$	1.58	3947

[a] Pore volume calculated from the maximum amounts of N_2 adsorbed.

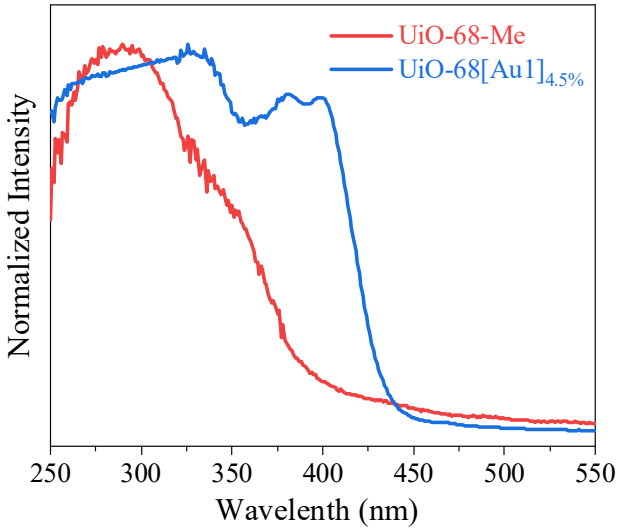


Fig. S19. UV−visible diffuse reflectance spectrum of **UiO-68-Me** and **UiO-68[Au1]$_{4.5\%}$**.

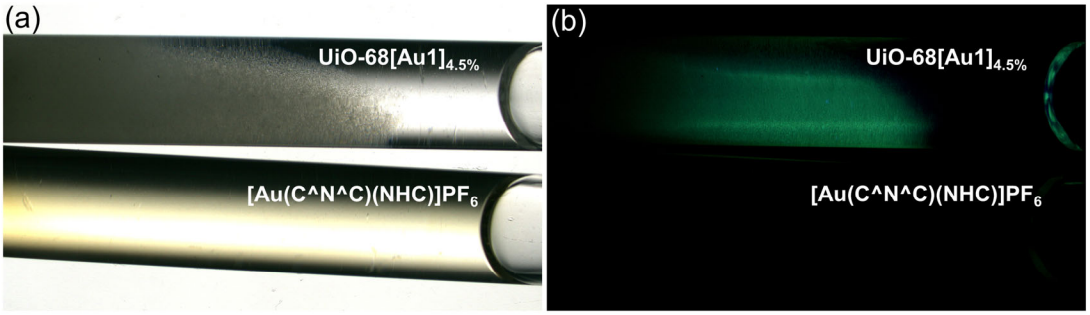
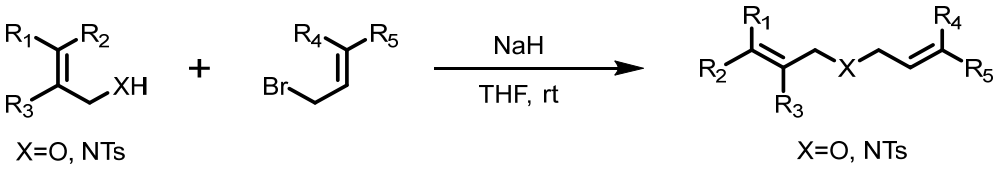


Fig. S20. Photographs of **UiO-68[Au1]$_{4.5\%}$** and [Au(C^N^C)(NHC)]PF_6 under natural light (a) and 365 nm UV light (b) under air (**UiO-68[Au1]$_{4.5\%}$** was suspended in DMF, while [Au(C^N^C)(NHC)]PF_6 was dissolved in DMF.).

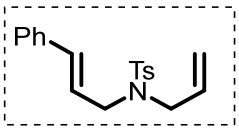
4 Synthesis and characterization of substrates

4.1 General procedure A for preparing diallyl ethers and *N*-tosylamides



To a stirred suspension of sodium hydride (60 wt% with mineral oil, 8 mmol, 2 equiv.) in 10 mL of dry THF at 0 °C, a dry THF solution (10 mL) of the corresponding alcohol or tosylamide (4 mmol, 1 equiv.) was added dropwise. The mixture was stirred at room temperature for 30 min. A solution of allyl bromide (6 mmol, 1.5 equiv.) in 10 mL of dry THF was then added dropwise to the reaction mixture. The resulting mixture was stirred at room temperature until the reaction was complete, as monitored by thin-layer chromatography (TLC). A saturated aqueous NH_4Cl solution was added to the reaction mixture, and the resulting mixture was extracted with DCM three times. The combined organic phases were dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel to afford pure diallyl ethers or *N*-tosylamides in high isolated yields.

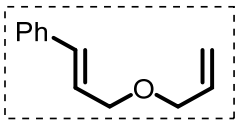
N-allyl-*N*-cinnamyl-4-methylbenzenesulfonamide (**1a**)[5]



Synthesized from *N*-cinnamyl-tosylamide and allyl bromide following general procedure A. Yield: 85 %.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.73 (d, *J* = 8.3 Hz, 2H), 7.32 – 7.27 (m, 5H), 7.25 – 7.21 (m, 2H), 6.41 (d, *J* = 16.0 Hz, 1H), 5.94 (dt, *J* = 15.9, 6.7 Hz, 1H), 5.70 – 5.60 (m, 1H), 5.19 – 5.14 (m, 2H), 3.96 (d, *J* = 6.6 Hz, 2H), 3.85 (d, *J* = 6.3 Hz, 2H), 2.42 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 143.25, 137.55, 136.27, 133.96, 132.85, 129.70, 128.57, 127.88, 127.26, 126.41, 123.84, 118.95, 49.52, 48.92, 21.50.

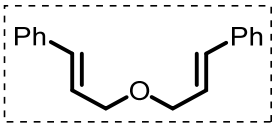
(*E*)-(3-(allyloxy)prop-1-en-1-yl)benzene (**1b**)[5]



Synthesized from cinnamyl alcohol and allyl bromide following general procedure A. Yield: 80 %.

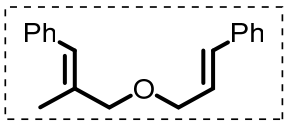
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.38 (dd, *J* = 8.1, 1.5 Hz, 2H), 7.31 (t, *J* = 7.6 Hz, 2H), 7.23 (t, *J* = 7.4 Hz, 1H), 6.61 (dt, *J* = 16.0, 1.6 Hz, 1H), 6.30 (dt, *J* = 15.9, 6.0 Hz, 1H), 6.01 – 5.88 (m, 1H), 5.31 (dq, *J* = 17.2, 1.6 Hz, 1H), 5.21 (dq, *J* = 10.4, 1.4 Hz, 1H), 4.16 (dd, *J* = 6.0, 1.5 Hz, 2H), 4.04 (dt, *J* = 5.7, 1.5 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 136.76, 134.76, 132.42, 128.55, 127.65, 126.48, 126.09, 117.12, 71.14, 70.73.

((1*E*,1'*E*)-oxybis(prop-1-ene-3,1-diyl))dibenzene (**1c**)[5]



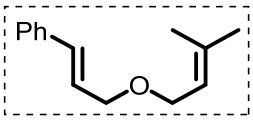
Synthesized from cinnamyl alcohol and cinnamyl bromide following general procedure A. Yield: 84 %. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.46 (d, *J* = 7.3 Hz, 2H), 7.37 (t, *J* = 7.6 Hz, 2H), 7.30 (t, *J* = 7.4 Hz, 1H), 6.70 (dt, *J* = 15.9, 1.5 Hz, 1H), 6.39 (dt, *J* = 15.9, 6.0 Hz, 1H), 4.26 (dd, *J* = 6.1, 1.5 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 136.78, 132.59, 128.60, 127.72, 126.55, 126.09, 70.78.

((*E*)-3-(cinnamyloxy)-2-methylprop-1-en-1-yl)benzene (**1d**)



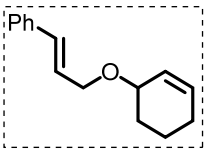
Synthesized from 2-methyl-cinnamyl alcohol and cinnamyl bromide following general procedure A. Yield: 82 %. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.40 (d, *J* = 7.3 Hz, 2H), 7.36 – 7.28 (m, 7H), 7.26 – 7.20 (m, 2H), 6.64 (d, *J* = 15.9 Hz, 1H), 6.54 (s, 1H), 6.34 (dt, *J* = 15.9, 6.0 Hz, 1H), 4.19 (dd, *J* = 6.0, 1.4 Hz, 2H), 4.09 (d, *J* = 1.2 Hz, 2H), 1.92 (d, *J* = 1.4 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 137.57, 136.78, 135.19, 132.43, 128.93, 128.56, 128.11, 127.66, 127.01, 126.50, 126.46, 126.21, 76.30, 70.51, 15.57. HRMS (ESI) Calcd for $[C_{19}H_{20}O + Na]^+$: 287.1406, found: 287.1404.

(*E*)-(3-((3-methylbut-2-en-1-yl)oxy)prop-1-en-1-yl)benzene (**1e**)[5]



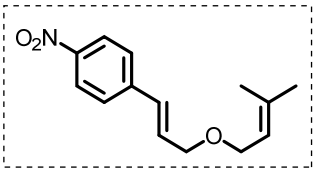
Synthesized from cinnamyl alcohol and 1-bromo-3-methyl-prop-2-ene following general procedure A. Yield: 75 %. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.42 (d, *J* = 7.4 Hz, 2H), 7.34 (t, *J* = 7.6 Hz, 2H), 7.29 – 7.24 (m, 1H), 6.64 (dt, *J* = 15.9, 1.5 Hz, 1H), 6.34 (dt, *J* = 15.9, 6.1 Hz, 1H), 5.45 – 5.41 (m, 1H), 4.17 (dd, *J* = 6.1, 1.5 Hz, 2H), 4.06 (d, *J* = 7.0 Hz, 2H), 1.80 (s, 3H), 1.73 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 137.13, 136.85, 132.29, 128.52, 127.58, 126.47, 126.45, 121.10, 70.59, 66.62, 25.82, 18.07.

(*E*)-(3-(cyclohex-2-en-1-yloxy)prop-1-en-1-yl)benzene (**1f**)[6]



Synthesized from cyclohex-2-enol and cinnamyl bromide following general procedure A. Yield: 80 %. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.38 (d, *J* = 7.4 Hz, 2H), 7.30 (t, *J* = 7.6 Hz, 2H), 7.22 (t, *J* = 7.3 Hz, 1H), 6.61 (d, *J* = 16.0 Hz, 1H), 6.31 (dt, *J* = 15.9, 6.0 Hz, 1H), 5.92 – 5.85 (m, 1H), 5.84 – 5.78 (m, 1H), 4.24 (ddd, *J* = 12.7, 5.9, 1.5 Hz, 1H), 4.19 (ddd, *J* = 12.7, 6.0, 1.5 Hz, 1H), 3.98 – 3.94 (m, 1H), 2.12 – 2.03 (m, 1H), 2.01 – 1.92 (m, 1H), 1.89 – 1.83 (m, 1H), 1.83 – 1.75 (m, 1H), 1.75 – 1.69 (m, 1H), 1.62 – 1.53 (m, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 136.90, 131.86, 130.97, 128.50, 127.77, 127.52, 126.92, 126.47, 72.27, 68.77, 28.49, 25.26, 19.29.

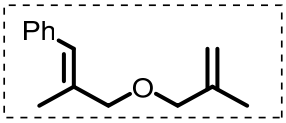
(*E*)-1-(3-((3-methylbut-2-en-1-yl)oxy)prop-1-en-1-yl)-4-nitrobenzene (**1g**) [5]



Synthesized from (*E*)-3-(4-nitrophenyl)prop-2-en-1-ol and 1-bromo-3-methylbut-2-ene following general procedure A. Yield: 85 %. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.21 – 8.15 (m, 2H), 7.52 – 7.49 (m, 2H), 6.69 (d, *J* = 16.0 Hz, 1H), 6.49 (dt, *J* = 16.0, 5.5 Hz, 1H), 5.43 – 5.38 (m, 1H), 4.18 (dd, *J* = 5.5, 1.6 Hz, 2H), 4.05 (d, *J* = 6.7 Hz, 2H), 1.78 (s, 3H), 1.70 (s, 3H). ^{13}C NMR (151

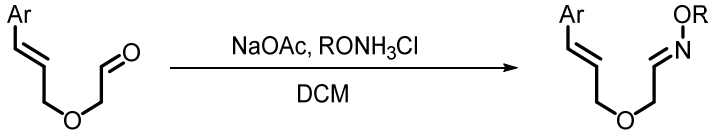
MHz, Chloroform-*d*) δ 146.92, 143.35, 137.66, 131.61, 129.43, 126.91, 124.01, 120.70, 69.93, 67.11, 25.85, 18.10. ^{13}C NMR (151 MHz, Chloroform-*d*) δ 142.32, 137.60, 135.25, 128.92, 128.10, 126.78, 126.42, 112.19, 76.01, 73.83, 19.60, 15.51.

(*E*)-(2-methyl-3-((2-methylallyl)oxy)prop-1-en-1-yl)benzene (*E*)-**1h**



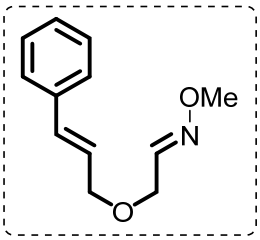
Synthesized from 2-methyl-cinnamyl alcohol and 3-bromo-2-methylprop-1-ene following general procedure A. Yield: 82 %. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.33 (t, *J* = 7.6 Hz, 2H), 7.29 (d, *J* = 7.6 Hz, 2H), 7.21 (t, *J* = 7.2 Hz, 1H), 6.51 (s, 1H), 5.01 (s, 1H), 4.92 (s, 1H), 4.01 (s, 2H), 3.92 (s, 2H), 1.90 (s, 3H), 1.78 (s, 3H). HRMS (ESI) Calcd for $[C_{14}H_{18}O + H]^+$:203.1430, found:203.1426.

4.2 General procedure B for preparing oxime



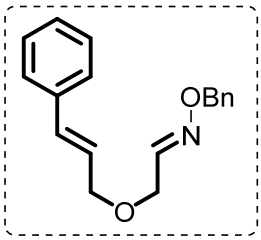
A 50-mL round-bottom flask equipped with a stir bar was charged with 2-(cinnamyloxy)acetaldehyde (1 mmol), DCM (10 mL), NaOAc (4.0 equiv.) and the corresponding hydroxylamine hydrochloride (2.0 equiv.). These reagents were added sequentially. The mixture was stirred at room temperature for 12 h. The reaction progress was monitored by TLC. A saturated aqueous $NaHCO_3$ solution was added to the reaction mixture. The resulting mixture was extracted with EA three times, and the combined organic phases were washed with brine, dried over Na_2SO_4, filtered and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel (eluent: EA/PE) to afford the product as a mixture of E/Z oxime isomers.

2-(Cinnamyloxy)acetaldehyde *o*-methyl oxime (**3a**)[7]



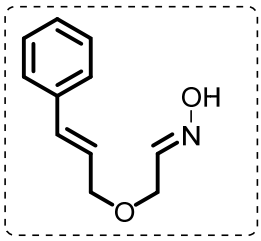
Synthesized from 2-(cinnamyloxy)acetaldehyde and *o*-methylhydroxylamine hydrochloride following general procedure B. Yield: 65 %, E/Z(oxime)=1:1.5. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.47 (t, *J* = 5.7 Hz, 1H; minor), 7.41 – 7.36 (m, 5H; major + minor), 7.35 – 7.29 (m, 5H; major + minor), 7.27 – 7.21 (m, 3H; major + minor), 6.87 (t, *J* = 3.7 Hz, 1.5H; major), 6.62 (d, *J* = 15.9 Hz, 2.5H; major + minor), 6.27 (dt, *J* = 15.8, 6.1 Hz, 2.5H; major + minor), 4.31 (d, *J* = 3.7 Hz, 3H; major), 4.19 – 4.16 (m, 5H; major + minor), 4.13 (d, *J* = 5.7 Hz, 2H; minor), 3.87 (s, 7.5H; major + minor). ^{13}C NMR (151 MHz, $CDCl_3$) δ 150.07, 146.93, 136.52, 136.47, 133.23, 133.21, 128.59, 128.58, 127.87, 127.83, 126.55, 125.23, 125.12, 71.78, 71.19, 66.68, 64.24, 62.08, 61.74.

2-(Cinnamyloxy)acetaldehyde *o*-benzyl oxime (**3b**)[7]

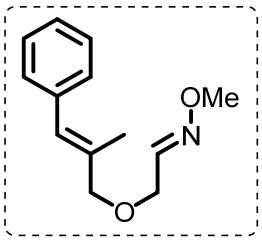


Synthesized from 2-(cinnamyloxy)acetaldehyde and *o*-benzylhydroxylamine hydrochloride following general procedure B. Yield: 71 %, E/Z(oxime) = 1:1.3.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (t, *J* = 5.7 Hz, 1H, minor), 7.42 – 7.28 (m, 20H; major + minor), 7.28 – 7.21 (m, 2H; major + minor), 6.92 (t, *J* = 3.6 Hz, 1.3H; major), 6.60 (dd, *J* = 15.9, 11.1 Hz, 2.3H; major + minor), 6.31 – 6.20 (m, 2.3H; major + minor), 5.10 (d, *J* = 1.9 Hz, 4.6H; major + minor), 4.36 (d, *J* = 3.7 Hz, 2.6H; major), 4.19 – 4.14 (m, 4.6H; major + minor), 4.13 (d, *J* = 5.7 Hz, 2H, minor). ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.73, 147.56, 137.59, 137.34, 136.51, 136.45, 133.25, 133.21, 128.59, 128.58, 128.45, 128.43, 128.28, 128.06, 127.98, 127.96, 127.87, 127.83, 126.55, 126.54, 125.20, 125.11, 76.32, 76.08, 71.77, 71.09, 66.65, 64.51.

2-(Cinnamyloxy)acetaldehyde oxime (**3c**)[7]

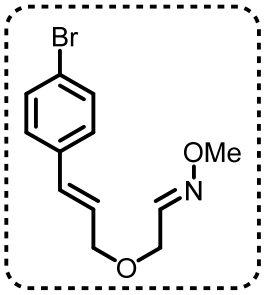


Synthesized from 2-(cinnamyloxy)acetaldehyde and hydroxylamine hydrochloride following general procedure B. Yield: 75%, E/Z(oxime) = 1.1:1.
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.12 (s, 1H; minor), 7.84 (s, 1.1H; major), 7.54 (t, *J* = 5.6 Hz, 1.1H; major), 7.41 – 7.37 (m, 4.2H; major + minor), 7.34 – 7.29 (m, 4.2H; major + minor), 7.27 – 7.24 (m, 2.1H; major + minor), 6.95 (t, *J* = 3.7 Hz, 1H; minor), 6.63 (dd, *J* = 15.9, 8.6 Hz, 2.1H; major + minor), 6.27 (dq, *J* = 15.9, 6.2 Hz, 2.1H; major + minor), 4.40 (d, *J* = 3.7 Hz, 2H; minor), 4.19 (ddd, *J* = 8.0, 6.2, 1.4 Hz, 4.2H; major + minor), 4.15 (d, *J* = 5.6 Hz, 2.2H; major). ^{13}C NMR (151 MHz, $CDCl_3$) δ 151.33, 148.58, 136.49, 136.45, 133.33, 133.29, 128.60, 128.58, 127.89, 127.86, 126.57, 126.56, 125.13, 125.04, 71.86, 71.21, 66.61, 63.88.2-(Cinnamyloxy)acetaldehyde *o*-methyl oxime (**3d**)[7]



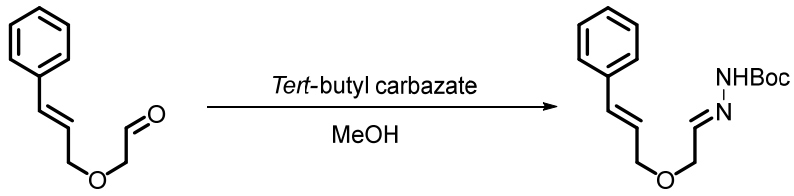
Synthesized from (*E*)-2-((2-methyl-3-phenylallyl)oxy)acetaldehyde and *o*-methylhydroxylamine hydrochloride following general procedure B. Yield: 85 %, E/Z(oxime) = 1:1.
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.48 (t, *J* = 5.7 Hz, 1H; major), 7.33 (td, *J* = 7.7, 2.4 Hz, 4H; major + minor), 7.28 (dd, *J* = 7.0, 4.3 Hz, 4H; major + minor), 7.24 – 7.20 (m, 2H; major + minor), 6.88 (t, *J* = 3.6 Hz, 1H; minor), 6.51 (s, 2H; major + minor), 4.29 (d, *J* = 3.7 Hz, 2H; minor), 4.11 (d, *J* = 5.7 Hz, 2H; major), 4.05 (s, 4H; major + minor), 3.87 (d, *J* = 2.2 Hz, 6H; major + minor), 1.92 – 1.88 (m, 6H; major + minor). ^{13}C NMR (151 MHz, $CDCl_3$) δ 150.19, 147.05, 137.35, 137.29, 134.48, 134.35, 128.92, 128.15, 128.13, 127.69, 127.66, 126.62, 126.58, 77.39, 76.81, 66.54, 64.04, 62.08, 61.72, 15.49, 15.45.

2-(((*E*)-3-(4-Bromophenyl)allyl)oxy)acetaldehyde *o*-methyl oxime(**3e**)[7]



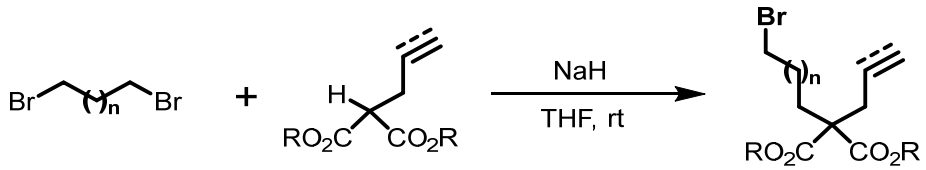
Synthesized from (*E*)-2-((3-(4-bromophenyl)allyl)oxy)acetaldehyde and *o*-methylhydroxylamine hydrochloride following general procedure B. Yield: 72 %, E/Z(oxime) = 1:1.3. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.47 (t, *J* = 5.7 Hz, 1H, minor), 7.45 – 7.42 (m, 4.6H; major + minor), 7.26 – 7.22 (m, 4.6H; major + minor), 6.86 (t, *J* = 3.7 Hz, 1.3H; major), 6.56 (dd, *J* = 16.0, 1.7 Hz, 2.3H; major + minor), 6.26 (dt, *J* = 15.9, 6.0 Hz, 2.3H; major + minor), 4.31 (d, *J* = 3.7 Hz, 2.6H; major), 4.16 (dt, *J* = 6.0, 1.8 Hz, 4.6H; major + minor), 4.12 (d, *J* = 5.7 Hz, 2H, minor), 3.87 (d, *J* = 1.0 Hz, 6.9H; major + minor). ^{13}C NMR (151 MHz, $CDCl_3$) δ 149.90, 146.79, 135.48, 135.43, 131.79, 131.77, 131.72, 131.70, 128.05, 128.04, 126.12, 126.00, 121.66, 121.61, 71.56, 70.93, 66.83, 64.38, 62.10, 61.76.

4.3 Synthesis of *tert*-butyl 2-(2-(cinnamyloxy)ethylidene)hydrazine-1-carboxylate (3f)[7]



A 50-mL round-bottom flask equipped with a stir bar was charged with 2-(cinnamyloxy)acetaldehyde (1 mmol.), methanol (10 mL), and *tert*-butyl carbazate (1.5 mmol). These chemicals were added sequentially. The mixture was stirred at room temperature for 12 h. A saturated aqueous $NaHCO_3$ solution was added to the reaction mixture. The resulting mixture was extracted with EA three times, and the combined organic phases were washed with brine, dried over Na_2SO_4, filtered and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel using EA and PE as eluents, affording the pure product as a mixture of E/Z oxime isomers. Yield: 60%, E/Z(oxime) = 2.5:1. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.78 (s, 2.5H; major), 7.42 – 7.35 (m, 7H; major + minor), 7.34 – 7.28 (m, 7H; major + minor), 7.26 – 7.22 (m, 3.5H; major + minor), 6.65 (d, *J* = 4.1 Hz, 1H; minor), 6.61 (d, *J* = 15.9 Hz, 2.5H; major), 6.31 – 6.22 (m, 3.5H; major + minor), 4.24 – 4.20 (m, 7H; major + minor), 4.20 – 4.15 (m, 7H; major + minor), 1.51 (s, 31.5H; major + minor). ^{13}C NMR (151 MHz, $CDCl_3$) δ 152.21, 152.20, 142.90, 139.06, 136.54, 136.11, 134.25, 133.09, 128.66, 128.56, 128.16, 127.80, 126.61, 126.53, 125.32, 124.12, 81.55, 81.53, 71.75, 71.31, 69.23, 66.64, 28.25.

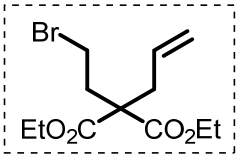
4.4 General procedure C for preparing halogenated alkyl malonates



n=0 or 1 R=Me or Et

To a stirred suspension of sodium hydride (60 wt% with mineral oil, 10 mmol, 2 equiv.) in 15 mL of dry THF at 0 °C, a solution of diethyl 2-allylmalonate (5 mmol, 1 equiv.) in 15 mL of dry THF was added dropwise. The mixture was stirred at room temperature for 30 min. Then, a solution of the corresponding alkyl bromides (20 mmol, 4 equiv.) in 15 mL of dry THF was added dropwise to the reaction mixture. The resulting mixture was stirred at room temperature until the reaction was complete, as monitored by TLC. A saturated aqueous NH_4Cl solution was then added to the reaction mixture. The resulting mixture was extracted with diethyl ether three times. The organic layer was combined, dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel using EA and hexane as eluents, affording pure halogenated alkyl malonates in good isolated yields.

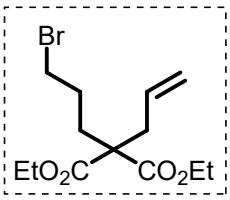
Diethyl 2-allyl-2-(2-bromoethyl)malonate (**9a**)[8]



Synthesized from diethyl 2-allylmalonate and 1,2-dibromoethane following general procedure C. Yield: 70 %.

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.71 – 5.58 (m, 1H), 5.19 – 5.12 (m, 2H), 4.21 (q, J = 7.1 Hz, 4H), 3.40 – 3.32 (m, 2H), 2.66 (dt, J = 7.5, 1.2 Hz, 2H), 2.49 – 2.39 (m, 2H), 1.27 (t, J = 7.1 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.20, 131.76, 119.67, 61.61, 57.45, 37.73, 36.18, 27.06, 14.05.

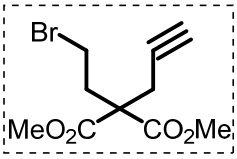
Diethyl 2-allyl-2-(3-bromopropyl)malonate (**9b**)[8]



Synthesized from diethyl 2-allylmalonate and 1,3-dibromopropane following general procedure C. Yield: 65%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.69 – 5.53 (m, 1H), 5.13 – 5.03 (m, 2H), 4.16 (q, J = 7.1 Hz, 4H), 3.35 (t, J = 6.5 Hz, 2H), 2.61 (d, J = 7.4 Hz, 2H), 2.01 – 1.93 (m, 2H), 1.80 – 1.70 (m, 2H), 1.22 (t, J = 7.1 Hz, 7H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.86, 132.09, 119.20, 61.32, 56.82, 37.13, 33.18, 31.04, 27.52, 14.10.

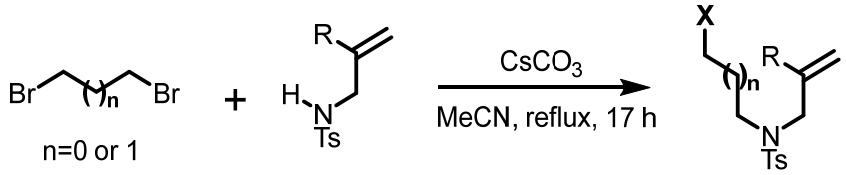
Dimethyl 2-(2-bromoethyl)-2-(prop-2-yn-1-yl)malonate (**9c**)[9]



Synthesized from dimethyl 2-(prop-2-yn-1-yl)malonate and 1,2-dibromoethane following general procedure C. Yield: 40 %.

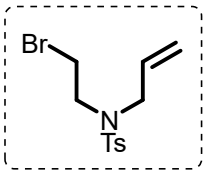
^{1}H NMR (400 MHz, $CDCl_3$) δ 3.77 (s, 6H), 3.43 – 3.37 (m, 2H), 2.86 (d, J = 2.7 Hz, 2H), 2.69 – 2.63 (m, 2H), 2.07 (t, J = 2.7 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.73, 78.04, 72.17, 56.74, 53.10, 35.84, 26.80, 23.46.

4.5 General procedure D for preparing halogenated alkyl *N*-tosylamides



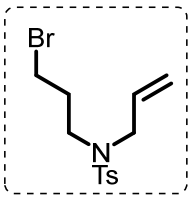
To a suspension of *N*-allyl-4-methylbenzenesulfonamide (106 mg, 0.5 mmol) and Cs_2CO_3 (244 mg, 0.75 mmol) in 2 mL of MeCN at room temperature, 1,2-dibromoethane or 1,3-dibromopropane (5 mmol) was added. The mixture was stirred at 80 ºC for 17 h. After the reaction, the mixture was filtered. The filtrate was collected and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel using EA and PE as eluents, affording pure halogenated alkyl *N*-tosylamides as colorless oil.

N-allyl-*N*-(2-bromoethyl)-4-methylbenzenesulfonamide (**9d**)[8]



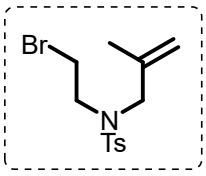
Synthesized from *N*-allyl-4-methylbenzenesulfonamide and 1,2-dibromoethane following general procedure D. Yield: 65 %.
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.73 (d, *J* = 7.9 Hz, 2H), 7.34 (d, *J* = 7.9 Hz, 2H), 5.75 – 5.64 (m, 1H), 5.25 – 5.19 (m, 2H), 3.84 (d, *J* = 6.5 Hz, 2H), 3.52 – 3.39 (m, 4H), 2.46 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 143.71, 136.36, 132.89, 129.86, 127.19, 119.67, 52.02, 48.96, 29.25, 21.53.

N-allyl-*N*-(3-bromopropyl)-4-methylbenzenesulfonamide (**9e**)



Synthesized from *N*-allyl-4-methylbenzenesulfonamide and 1,3-dibromopropane following general procedure D. Yield: 67 %.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, *J* = 8.3 Hz, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 5.71 – 5.57 (m, 1H), 5.26 – 5.12 (m, 2H), 3.80 (dt, *J* = 6.4, 1.3 Hz, 2H), 3.42 (t, *J* = 6.5 Hz, 2H), 3.24 (dd, *J* = 7.7, 6.3 Hz, 2H), 2.44 (s, 3H), 2.13 (p, *J* = 6.5 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 143.46, 136.49, 132.90, 129.79, 127.22, 119.41, 51.60, 46.09, 31.83, 30.46, 21.55. HRMS (ESI) Calcd for $[C_{13}H_{18}NO_2SBr + Na]^+$: 354.0134, found: 354.0131.

N-(2-bromoethyl)-4-methyl-*N*-(2-methylallyl)benzenesulfonamide (**9f**)[10]



Synthesized from 4-methyl-*N*-(2-methylallyl)benzenesulfonamide and 1,2-dibromoethane following general procedure D. Yield: 62 %.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, *J* = 8.3 Hz, 2H), 7.34 (d, *J* = 8.0 Hz, 2H), 4.94 (d, *J* = 19.7 Hz, 2H), 3.72 (s, 2H), 3.48 – 3.42 (m, 2H), 3.42 – 3.37 (m, 2H), 2.46 (s, 3H), 1.75 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.70, 140.48, 136.11, 129.84, 127.19, 115.40, 55.88, 49.55, 28.95, 21.56, 19.76.

5 Activity and stability of UiO-68[Au1] for photo-induced [2+2] styrene(1a) cycloaddition.

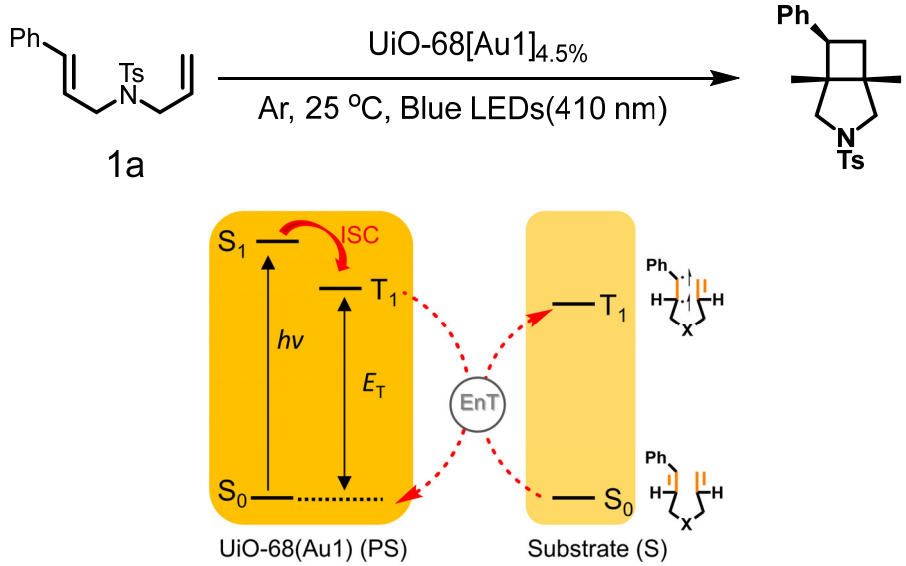


Fig. S21. Sensitization through triplet energy transfer from a sensitizer (left) to a substrate (right).[11]

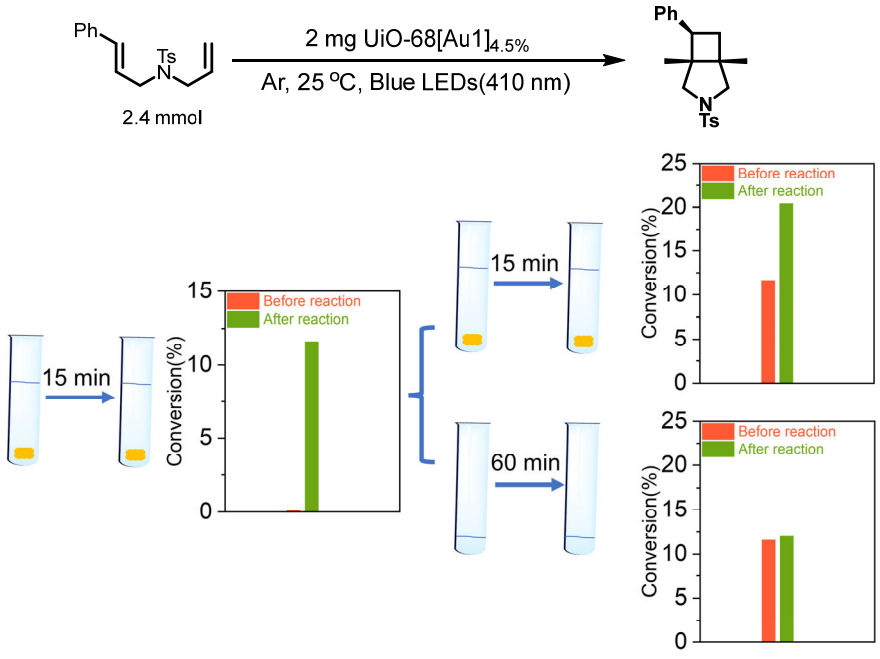
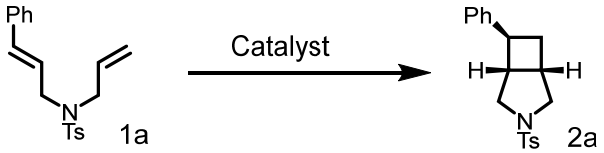


Fig. S22. Schematic representation of the leaching experiment.

Table S4. Evaluation of reaction conditions for visible-light-driven [2+2] cycloaddition reaction of **1a**.



Entry	Catalyst	Condition	Yield (%)
1	**UiO-68[Au1]$_{4.5\%}$**	argon, MeCN	95[d]
2	**UiO-68[Au1]$_{4.5\%}$**	argon, THF	95[d]
3	**UiO-68[Au1]$_{4.5\%}$**	air, MeCN	88[d]
4	**UiO-68[Au1]$_{4.5\%}$**	argon, lack of light, MeCN	trace[d]
5	**UiO-68[Au1]$_{4.5\%}$**	argon, MeCN	85[c]
6	**UiO-68[Au1]$_{4.5\%}$**	argon, MeCN	96[e]
7	**[Au(C^N^C)(NHC)]PF_6**	argon, MeCN	96
8	**[Au(C^N^C)(NHC)]PF_6**	argon, THF	95
9	**UiO-68-Me**	argon, MeCN	trace
10	**No Catalyst**	argon, MeCN	trace
11	**UiO-68[Au2]$_{2.6\%}$**	argon, MeCN	92[b]
12	**Ir[(dFppy)$_2$dtbbpy]PF_6**	argon, MeCN	96[a]
13	**Thioxanthone**	argon, MeCN	95[a]

Reaction conditions: 1a (0.1 mmol), UiO-68[Au1]$_{4.5\%}$ (0.5−2 mol%)/UiO-68[Au2]$_{2.6\%}$ (1.8 mol%)/UiO-68-Me (5 mg)/[Au(C^N^C)(NHC)]PF_6 (1.5 mol%)/Ir[(dFppy)$_2$dtbbpy]PF_6 (1 mol%)/thioxanthone (1 mol%), MeCN/THF (2 mL), 25°C, 410 nm LED irradiation, 15 min/2 h[a]/30 h[b]; 0.5 mol%[c], 1 mol%[d] or 2 mol%[e] of UiO-68[Au1]$_{4.5\%}$ was used. Yields were determined by ^{1}H NMR analysis of the unpurified reaction mixture using chlorodiphenylmethane as an internal standard.

Table S5. ICP-MS results of **UiO-68[Au1]$_{4.5\%}$** before and after [2+2] styrene (1a) cycloaddition reaction.

MOF	Zr(wt%)	Au(wt%)	Zr (mol %):Au(mol %)
UiO-68[Au1]$_{4.5\%}$	13.1%	4.5%	6.3:1
recycled **UiO-68[Au1]$_{4.5\%}$** (after ten reaction runs)	14.6%	4.3%	7.3:1

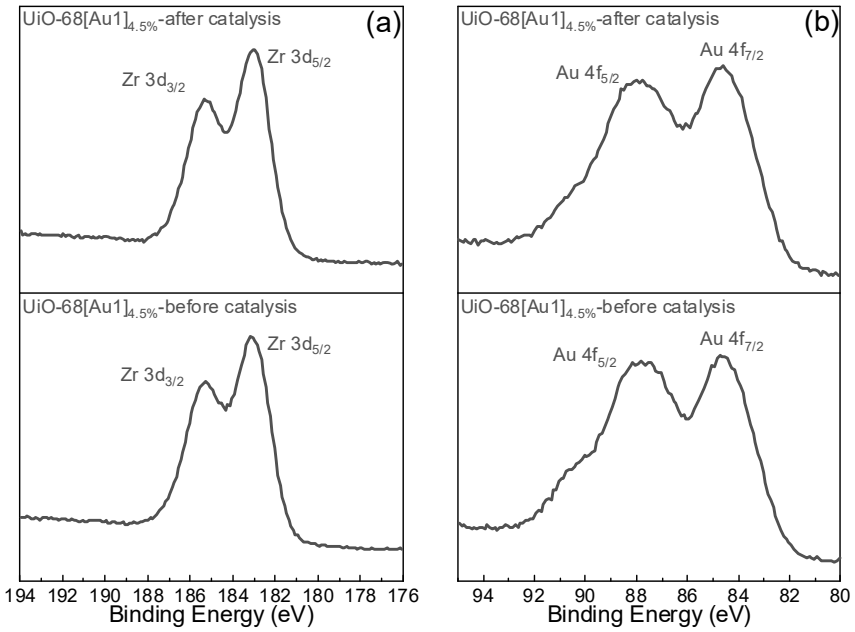


Fig. S23. XPS spectra of the Zr 3d (a) and the Au 4f (b) photoelectron peaks in the freshly prepared **UiO-68[Au1]$_{4.5\%}$** and the recycled **UiO-68[Au1]$_{4.5\%}$** (used in the [2+2] styrene (**1a**) cycloaddition reaction for ten runs). Referenced to C(1s) at 284.7 eV.

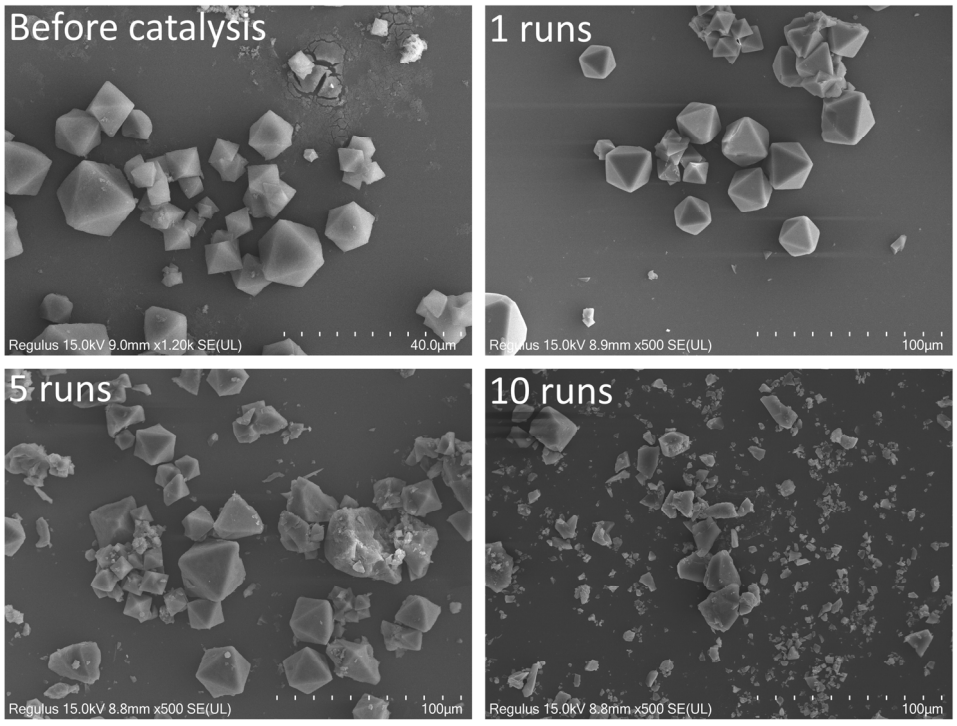


Fig. S24. SEM images of **UiO-68[Au1]$_{4.5\%}$** before and after the [2+2] styrene (**1a**) cycloaddition reaction.

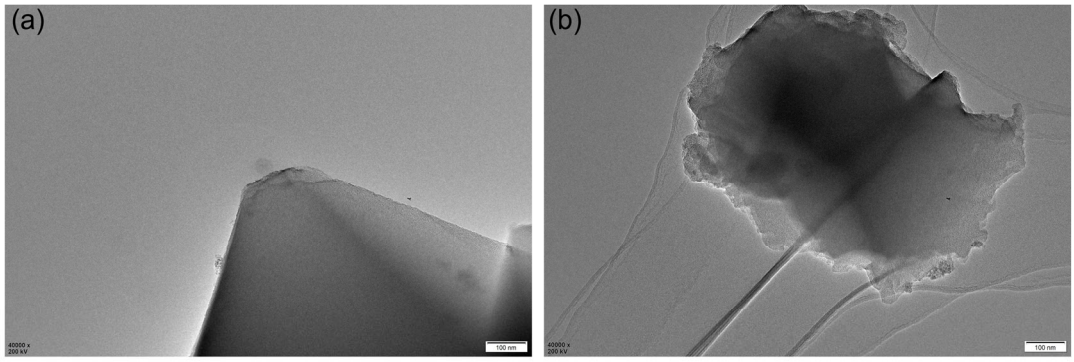


Fig. S25. TEM images of **UiO-68[Au1]$_{4.5\%}$** before (a) and after (b) the [2+2] styrene (**1a**) cycloaddition reaction (10 reaction runs).

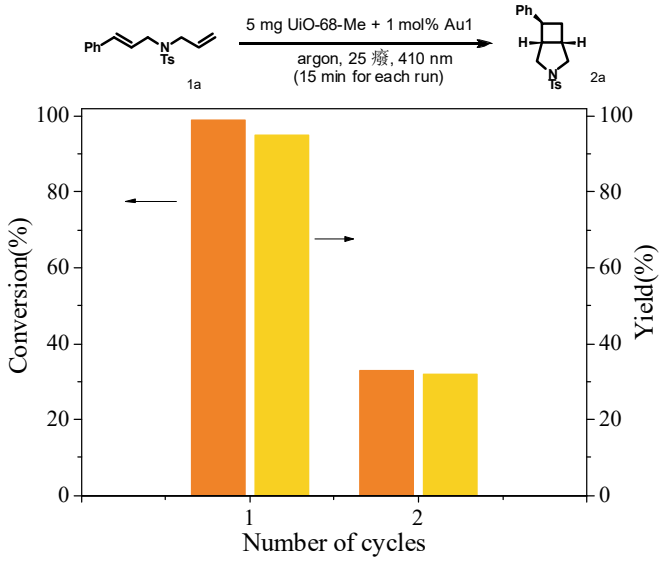
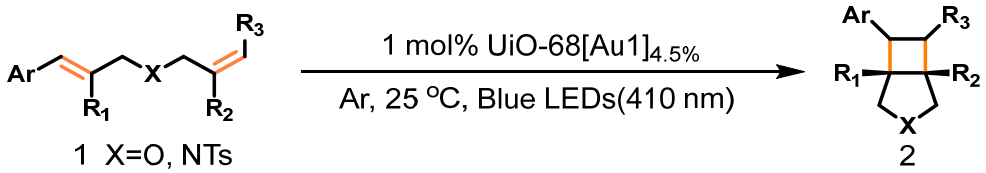


Fig. S26. Substrate conversion and product yields in recycling experiments with two reaction runs using the physically mixed system (**UiO-68-Me** and **Au1**) as the photocatalyst in the given reaction.

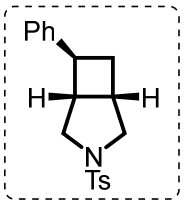
6 General procedure E for visible-light-driven [2+2] styrene cycloaddition



Diallyl ethers or *N*-tosylamides (**1**, 0.1 mmol) and **UiO-68[Au1]$_{4.5\%}$** (1 mol%) were weighted and transferred into a 10 mL reaction tube equipped with a stir bar. 2 mL of

dry MeCN was added to the tube. The reaction mixture was degassed by bubbling argon and then stirred at room temperature under irradiation from a 410 nm LED with cooling by running water. After the indicated reaction time, the tube was opened and chlorodiphenylmethane (0.1 mmol) was added as an internal standard. Diastereomer ratios and yields were determined using ^{1}H NMR spectroscopy. The mixture was purified by column chromatography on silica gel (eluent: EA/PE) to afford the pure product **2**. **UiO-68[Au1]$_{4.5\%}$** was recovered by washing with MeCN several times. The recovered MOF catalyst was then used in subsequent reactions for cycle tests, with fresh substrates added.

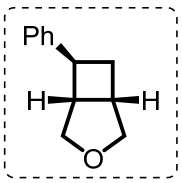
6-Phenyl-3-tosyl-3-azabicyclo[3.2.0]heptane (**2a**)[5]



The synthesis followed the general procedure E with the use of **1a** as the starting material. The reaction time was 15 min, with d.r. of 6:1 and a yield of 95%.

Diastereomer (major product): ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.73 (d, *J* = 8.2 Hz, 2H), 7.34 (d, *J* = 8.0 Hz, 2H), 7.31 (t, *J* = 7.7 Hz, 2H), 7.22 – 7.16 (m, 3H), 3.60 (d, *J* = 9.8 Hz, 1H), 3.54 (d, *J* = 9.7 Hz, 1H), 3.42 – 3.36 (m, 1H), 2.91 – 2.81 (m, 2H), 2.75 (dd, *J* = 9.8, 6.5 Hz, 1H), 2.67 (dd, *J* = 9.8, 5.4 Hz, 1H), 2.44 (s, 3H), 2.38 – 2.24 (m, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 145.34, 143.60, 132.04, 129.55, 128.51, 128.11, 126.36, 126.15, 54.50, 54.37, 45.68, 41.94, 34.09, 31.77, 21.54.

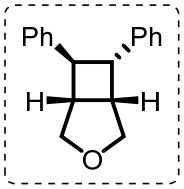
6-Phenyl-3-oxabicyclo[3.2.0]heptane (**2b**)[5]



The synthesis followed the general procedure E with the use of **1b** as the starting material. The reaction time was 1 h, with d.r. of 5:1 and a yield of 95%.

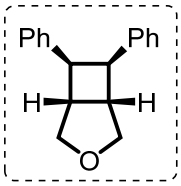
Diastereomer (major product): ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.32 (t, *J* = 7.7 Hz, 2H), 7.26 (d, *J* = 8.2 Hz, 2H), 7.19 (td, *J* = 7.2, 1.4 Hz, 1H), 3.99 (t, *J* = 10.0 Hz, 2H), 3.62 (dd, *J* = 9.2, 5.8 Hz, 1H), 3.52 (dd, *J* = 9.3, 4.8 Hz, 1H), 3.29 – 3.20 (m, 1H), 3.05 – 2.99 (m, 1H), 2.99 – 2.93 (m, 1H), 2.34 – 2.27 (m, 1H), 2.17 (ddd, *J* = 12.9, 9.5, 4.0 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 146.09, 128.43, 126.41, 125.94, 74.48, 74.02, 47.24, 41.96, 35.33, 31.83.

6,7-Diphenyl-3-oxabicyclo[3.2.0]heptane (**2c**)[5]



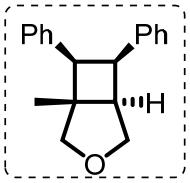
The synthesis followed the general procedure E with the use of **1c** as the starting material. The reaction time was 1 h, with d.r. of 3:1 and a yield of 96%.

Diastereomer (major product): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36 – 7.28 (m, 4H), 7.28 – 7.24 (m, 4H), 7.24 – 7.18 (m, 2H), 4.04 (d, *J* = 9.1 Hz, 1H), 3.87 – 3.78 (m, 2H), 3.67 (dd, *J* = 9.7, 6.7 Hz, 1H), 3.54 (dd, *J* = 9.1, 4.1 Hz, 1H), 3.49 (dd, *J* = 10.0, 6.9 Hz, 1H), 3.26 (q, *J* = 7.7 Hz, 1H), 3.13 (td, *J* = 7.0, 4.1 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 144.45, 140.33, 128.49, 128.46, 127.78, 126.47, 126.32, 126.26, 72.98, 68.44, 45.91, 45.57, 44.16, 40.74.



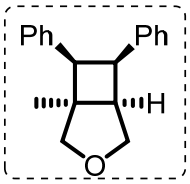
Diastereomer (minor product): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.11 – 7.04 (m, 4H), 7.03 – 6.96 (m, 2H), 6.96 – 6.90 (m, 4H), 4.10 (d, *J* = 9.5 Hz, 2H), 3.75 (d, *J* = 4.2 Hz, 2H), 3.72 (dd, *J* = 3.4, 1.7 Hz, 1H), 3.70 (dd, *J* = 3.4, 1.8 Hz, 1H), 3.37 – 3.25 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 140.80, 128.12, 127.72, 125.63, 74.03, 47.19, 42.13.

1-Methyl-6,7-diphenyl-3-oxabicyclo[3.2.0]heptane (**2d**)



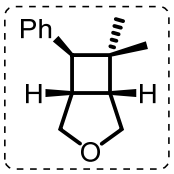
The synthesis followed the general procedure E with the use of **1d** as the starting material. The reaction time was 1 h, with d.r. of 1.1:1 and a yield of 84%.

Diastereomer (major product): ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.35 – 7.30 (m, 2H), 7.30 – 7.28 (m, 2H), 7.27 – 7.24 (m, 4H), 7.24 – 7.17 (m, 2H), 4.00 (d, *J* = 9.2 Hz, 1H), 3.76 (d, *J* = 9.7 Hz, 1H), 3.68 (dd, *J* = 9.2, 4.1 Hz, 1H), 3.61 (dd, *J* = 9.7, 6.6 Hz, 1H), 3.50 (d, *J* = 9.7 Hz, 1H), 3.12 (d, *J* = 9.7 Hz, 1H), 2.66 (dd, *J* = 6.6, 4.0 Hz, 1H), 1.45 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 144.59, 140.20, 128.49, 128.49, 127.56, 126.55, 126.46, 126.19, 74.46, 72.73, 53.79, 50.99, 47.68, 42.76, 24.67. HRMS (ESI) Calcd for $[C_{19}H_{20}O + Na]^+$: 287.1406, found: 287.1405.



Diastereomer (minor product): ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.17 (t, *J* = 7.6 Hz, 2H), 7.12 – 7.07 (m, 1H), 7.06 – 7.02 (m, 3H), 6.95 (d, *J* = 8.3 Hz, 2H), 6.80 – 6.76 (m, 2H), 4.14 (d, *J* = 9.1 Hz, 1H), 4.04 (d, *J* = 9.1 Hz, 1H), 3.93 (dd, *J* = 10.2, 6.8 Hz, 1H), 3.86 (dd, *J* = 9.4, 4.5 Hz, 2H), 3.51 (d, *J* = 9.0 Hz, 1H), 3.13 – 3.05 (m, 1H), 0.94 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 140.49, 138.95, 130.52, 127.89, 127.60, 127.24, 125.77, 125.48, 82.00, 51.92, 48.25, 47.29, 43.06, 18.97. HRMS (ESI) Calcd for $[C_{19}H_{20}O + Na]^+$: 287.1406, found: 287.1403.

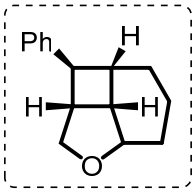
6,6-Dimethyl-7-phenyl-3-oxabicyclo[3.2.0]heptane (**2e**)[5]



The synthesis followed the general procedure E with the use of **1e** as the starting material. The reaction time was 1 h, with d.r. > 10:1 and a yield of 87%.

Diastereomer (major product): ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.30 (t, *J* = 7.6 Hz, 2H), 7.20 (t, *J* = 7.5 Hz, 1H), 7.14 (d, *J* = 7.5 Hz, 2H), 4.17 (d, *J* = 10.0 Hz, 1H), 3.79 (d, *J* = 9.0 Hz, 1H), 3.51 (dd, *J* = 10.1, 6.7 Hz, 1H), 3.44 (dd, *J* = 9.0, 4.5 Hz, 1H), 3.27 (td, *J* = 7.7, 4.5 Hz, 1H), 2.99 (d, *J* = 7.3 Hz, 1H), 2.40 (t, *J* = 7.4 Hz, 1H), 1.11 (s, 3H), 0.74 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 140.63, 128.00, 127.65, 125.92, 72.09, 69.13, 51.93, 46.62, 38.01, 37.28, 26.22, 24.24.

3-Phenyloctahydro-2*H*-cyclobuta[cd]benzofuran (**2f**)[6]

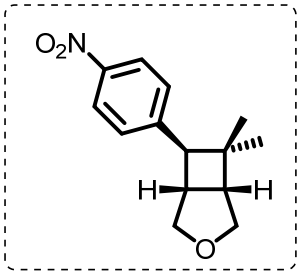


The synthesis followed the general procedure E with the use of **1f** as the starting material. The reaction time was 1 h, with d.r. > 10:1 and a yield of 96%.

Diastereomer (major product): ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.30 (t, *J* = 7.5 Hz, 2H), 7.22 (d, *J* = 7.6 Hz, 2H), 7.19 (t, *J* = 7.3 Hz, 1H), 4.03 (dd, *J* = 6.9, 3.2 Hz, 1H), 3.95 (d, *J* = 9.1 Hz, 1H), 3.58 (dd, *J* = 9.1, 3.8 Hz, 1H), 3.25 (t, *J* = 7.9 Hz, 1H), 2.96 – 2.89 (m, 1H), 2.67 (q, *J* = 7.7 Hz, 1H), 2.51 (q, *J* = 8.3

Hz, 1H), 2.09 (dd, *J* = 14.6, 3.3 Hz, 1H), 1.98 (qt, *J* = 15.9, 4.7 Hz, 1H), 1.59 (d, *J* = 14.4 Hz, 1H), 1.54 – 1.33 (m, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 145.31, 128.37, 126.65, 125.94, 75.57, 72.81, 45.22, 43.57, 35.25, 35.03, 27.44, 25.82, 14.74.

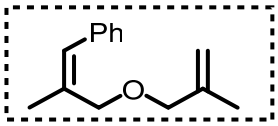
6,6-dimethyl-7-(4-nitrophenyl)-3-oxabicyclo[3.2.0]heptane (**2g**) [5]



The synthesis followed the general procedure E with the use of **1g** as the starting material. The reaction time was 1 h, with d.r. > 10:1 and a yield of 85%.

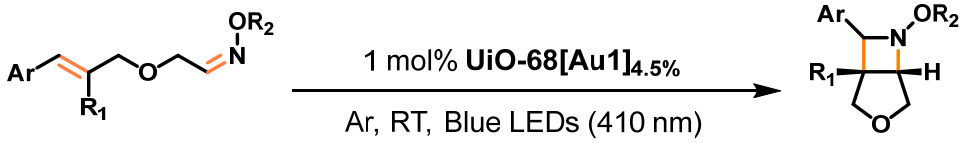
Diastereomer (major product): ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.17 (d, *J* = 8.7 Hz, 2H), 7.28 (d, *J* = 8.4 Hz, 2H), 4.19 (d, *J* = 10.2 Hz, 1H), 3.81 (d, *J* = 9.2 Hz, 1H), 3.53 (dd, *J* = 10.2, 6.6 Hz, 1H), 3.47 (dd, *J* = 9.2, 4.4 Hz, 1H), 3.31 (td, *J* = 7.7, 4.4 Hz, 1H), 3.10 (d, *J* = 7.3 Hz, 1H), 2.46 (t, *J* = 7.4 Hz, 1H), 1.15 (s, 3H), 0.74 (s, 3H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 148.64, 146.36, 128.23, 123.37, 71.87, 69.06, 51.86, 46.62, 37.99, 26.24, 24.24.

(*Z*)-(2-methyl-3-((2-methylallyl)oxy)prop-1-en-1-yl)benzene (***Z***)-1h



The synthesis followed the general procedure E with the use of **1h** as the starting material. The reaction time was 1 h, with a yield of 50%. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.31 (m, 2H), 7.25 – 7.16 (m, 2H), 6.52 (s,1H), 4.92 (s, 1H), 4.86 (s, 1H), 4.06 (s, 2H), 3.84 (s, 2H), 1.98 (s, 3H), 1.74 (s, 3H).

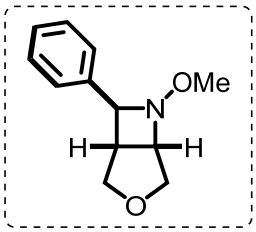
7 General procedure F for visible-light-driven [2+2] cycloaddition reaction between imines and alkenes



3 4

Substrate (**3**, 0.1 mmol) and **UiO-68[Au1]$_{4.5\%}$** (1 mol%) were weighted and added to a 10 mL reaction tube equipped with a stir bar. 2 mL of MeCN was added to the tube. The reaction mixture was degassed by bubbling argon and then stirred at room temperature under irradiation from a 410 nm LED with cooling by running water. After the indicated reaction time, the tube was opened and chlorodiphenylmethane (0.1 mmol) was added as an internal standard. Diastereomer ratios and yields were determined using ^{1}H NMR spectroscopy. The mixture was purified by column chromatography on silica gel (eluent: EA/PE) to afford the pure product **4**.

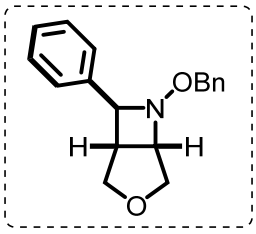
6-Methoxy-7-phenyl-3-oxa-6-azabicyclo[3.2.0]heptane (**4a**)[7]



The synthesis followed the general procedure F with the use of **3a** as the starting material. The reaction time was 0.5 h, with d.r. > 20:1 and a yield of 98%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (d, *J* = 6.9 Hz, 2H), 7.38 (t, *J* = 7.5 Hz, 2H), 7.34 – 7.27 (m, 1H), 4.77 (d, *J* = 10.7 Hz, 1H), 4.55 (t, *J* = 5.6 Hz, 1H), 4.43 (d, *J* = 5.9 Hz, 1H), 3.98 (d, *J* = 9.4 Hz, 1H), 3.59 (dd, *J* = 10.6, 5.3 Hz, 1H), 3.55 – 3.51 (m, 1H), 3.46 (s, 3H), 2.73 (td, *J* = 5.9, 3.6 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.82, 128.46, 127.45, 126.29, 73.74, 70.67, 67.34, 67.04, 60.49, 42.03.

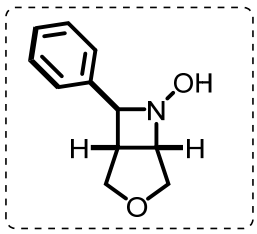
6-(Benzyloxy)-7-phenyl-3-oxa-6-azabicyclo[3.2.0]heptane (**4b**)[7]



The synthesis followed the general procedure F with the use of **3b** as the starting material. The reaction time was 0.5 h, with d.r. > 20:1 and a yield of 97%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.38 (m, 2H), 7.38 – 7.33 (m, 2H), 7.33 – 7.25 (m, 6H), 4.79 (d, *J* = 10.6 Hz, 1H), 4.65 (s, 2H), 4.51 (d, *J* = 5.8 Hz, 1H), 4.33 (t, *J* = 5.6 Hz, 1H), 3.98 (d, *J* = 9.4 Hz, 1H), 3.55 – 3.45 (m, 2H), 2.68 (td, *J* = 5.9, 3.5 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.73, 138.24, 128.51, 128.38, 128.18, 127.60, 127.37, 126.38, 75.47, 73.98, 70.69, 68.38, 67.43, 42.49.

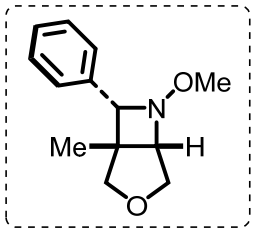
7-Phenyl-3-oxa-6-azabicyclo[3.2.0]heptan-6-ol (**4c**)[7]



The synthesis followed the general procedure F with the use of **3c** as the starting material. The reaction time was 2 h, with d.r. > 20:1 and a yield of 91%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.31 (m, 4H), 7.30 – 7.26 (m, 1H), 4.81 (d, *J* = 10.8 Hz, 1H), 4.36 (d, *J* = 4.7 Hz, 1H), 4.34 (t, *J* = 5.6 Hz, 1H), 3.93 (d, *J* = 9.4 Hz, 1H), 3.52 – 3.45 (m, 2H), 2.75 (td, *J* = 5.9, 3.5 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 140.85, 128.51, 127.75, 126.76, 75.35, 70.63, 69.03, 66.68, 41.73.

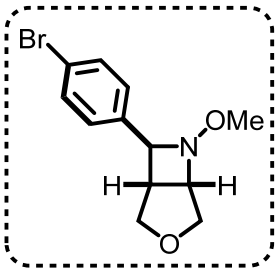
6-Methoxy-1-methyl-7-phenyl-3-oxa-6-azabicyclo[3.2.0]heptane (**4d**)[7]



The synthesis followed the general procedure F with the use of **3d** as the starting material. The reaction time was 0.5 h, with d.r. of 1.3:1 and a yield of 98%.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.41 (d, *J* = 7.5 Hz, 2H), 7.36 (t, *J* = 7.5 Hz, 2H), 7.28 (d, *J* = 7.2 Hz, 1H), 4.48 (s, 1H), 4.11 (d, *J* = 9.8 Hz, 1H), 3.83 (d, *J* = 2.6 Hz, 1H), 3.54 – 3.50 (m, 5H), 2.98 (d, *J* = 9.8 Hz, 1H), 1.44 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 138.59, 128.39, 127.36, 126.66, 77.50, 77.09, 72.82, 72.38, 61.62, 44.86, 22.53.

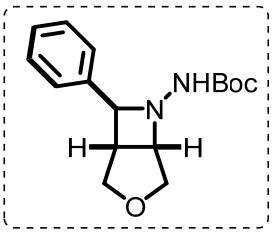
7-(4-Bromophenyl)-6-methoxy-3-oxa-6-azabicyclo[3.2.0]heptane (**4e**)[7]



The synthesis followed the general procedure F with the use of **3e** as the starting material. The reaction time was 0.5 h, with d.r. >20:1 and a yield of 93%.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.48 (d, *J* = 8.2 Hz, 2H), 7.29 (d, *J* = 8.2 Hz, 2H), 4.73 (d, *J* = 10.6 Hz, 1H), 4.51 (t, *J* = 5.5 Hz, 1H), 4.34 (d, *J* = 5.7 Hz, 1H), 3.94 (d, *J* = 9.5 Hz, 1H), 3.55 (dd, *J* = 10.6, 5.3 Hz, 1H), 3.49 (dd, *J* = 9.5, 3.5 Hz, 1H), 3.41 (s, 3H), 2.65 (td, *J* = 5.8, 3.6 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 140.86, 131.55, 128.05, 121.29, 73.06, 70.54, 67.36, 66.98, 60.54, 42.09.

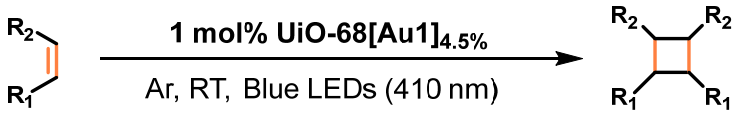
Tert-butyl-7-phenyl-3-oxa-6-azabicyclo[3.2.0]heptan-6-yl)carbamate (**4f**)[7]



The synthesis followed the general procedure F with the use of **3f** as the starting material. The reaction time was 1 h, with d.r. of 5.6:1 and a yield of 83%.

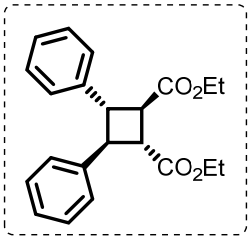
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.53 (d, *J* = 7.5 Hz, 2H), 7.39 (t, *J* = 7.6 Hz, 2H), 7.30 (t, *J* = 8.4 Hz, 1H), 5.92 (s, 1H), 4.65 – 4.61 (m, 1H), 4.51 (d, *J* = 11.5 Hz, 1H), 4.25 (d, *J* = 4.8 Hz, 1H), 4.06 (d, *J* = 9.5 Hz, 1H), 3.53 (dd, *J* = 9.5, 4.0 Hz, 1H), 3.50 (dd, *J* = 11.5, 4.1 Hz, 1H), 2.78 (q, *J* = 4.9 Hz, 1H), 1.44 (s, 9H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 141.42, 128.46, 127.34, 125.83, 80.17, 71.74, 68.54, 67.40, 43.07, 28.29.

8 General procedure G for visible-light-driven [2+2] intermolecular cycloaddition reactions.



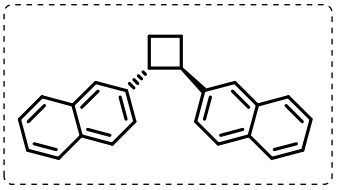
Substrate (0.2 mmol) and **UiO-68[Au1]$_{4.5\%}$** (1 mol%) were weighted and added to a 10 mL reaction tube equipped with a stir bar. 2 mL of MeCN was added to the tube. The reaction mixture was degassed by bubbling argon and then stirred at room temperature under irradiation from a 410 nm LED with cooling by running water. After the indicated reaction time, the tube was opened and chlorodiphenylmethane (0.1 mmol) was added as an internal standard. Diastereomer ratios and yields were determined using ^{1}H NMR spectroscopy. The mixture was purified by column chromatography on silica gel (eluent: EA/PE) to afford the pure product.

Diethyl-3,4-diphenylcyclobutane-1,2-dicarboxylate (**7a**)[12]



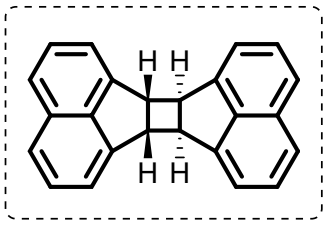
Synthesized from ethyl cinnamate. Reaction time: 30 h, d.r. 10 :1, conversion: 87%, yield: 68%.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.19 (m, 10H), 4.20 (q, *J* = 7.1 Hz, 4H), 3.79 – 3.72 (m, 2H), 3.48 – 3.42 (m, 2H), 1.26 (t, *J* = 7.1 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.60, 141.20, 128.62, 127.08, 126.86, 61.03, 47.00, 44.86, 14.26.

1,2-Di(naphthalen-2-yl)cyclobutene (**7b**)[13]

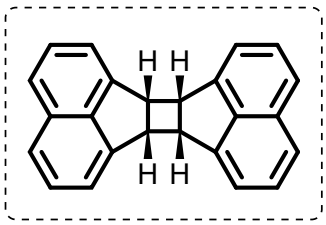


Synthesized from 2-vinylnaphthalene. Reaction time: 16 h, d.r. 5 :1, conversion: 99%, yield: 43%.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 – 7.77 (m, 6H), 7.71 (s, 2H), 7.51 – 7.39 (m, 6H), 3.92 – 3.78 (m, 2H), 2.54 – 2.41 (m, 2H), 2.40 – 2.28 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.02, 133.53, 132.24, 127.98, 127.66, 127.62, 125.97, 125.53, 125.27, 124.71, 48.19, 25.94.

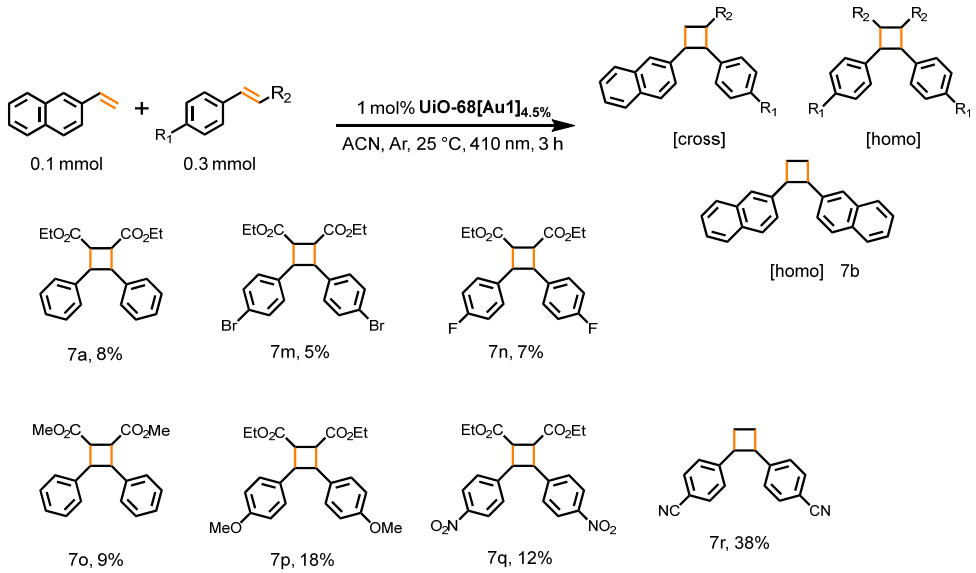
Tetrahydrocyclobuta[1,2-a:3,4-a']diacenaphthylene (**7c**)[14]



Synthesized from acenaphthylene. Reaction time: 1 h, d.r. 1.2 :1, conversion: 99%, yield: 98%.
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.74 (d, *J* = 8.1 Hz, 4H), 7.62 – 7.58 (m, 4H), 7.52 (d, *J* = 6.8 Hz, 4H), 4.09 (s, 4H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 147.66, 139.57, 132.12, 128.38, 123.18, 119.24, 52.51.

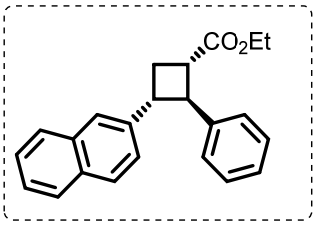


^{1}H NMR (600 MHz, $CDCl_3$) δ 7.18 (d, *J* = 8.1 Hz, 4H), 7.13 (t, *J* = 7.5 Hz, 4H), 7.01 (d, *J* = 6.7 Hz, 4H), 4.83 (s, 4H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 144.62, 141.73, 130.95, 126.94, 122.16, 120.27, 47.30.

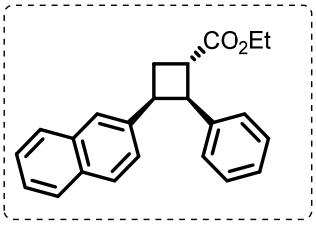


2-Vinylnaphthalene (0.1 mmol), cinnamate (or other substituted styrenes, 0.3 mmol) and **UiO-68[Au1]$_{4.5\%}$** (1 mol%) were weighted and added to a 10 mL reaction tube equipped with a stir bar. 2 mL of MeCN was added to the tube. The reaction mixture was degassed by bubbling argon and then stirred at room temperature under irradiation from a 410 nm LED with cooling by running water. After the indicated reaction time, the tube was opened and chlorodiphenylmethane (0.1 mmol) was added as an internal standard. Diastereomer ratios and yields were determined using ^{1}H NMR spectroscopy. The mixture was purified by column chromatography on silica gel (eluent: EA/PE) to afford the pure product.

Ethyl-3-(naphthalen-2-yl)-2-phenylcyclobutane-1-carboxylate (**7d**)[15]

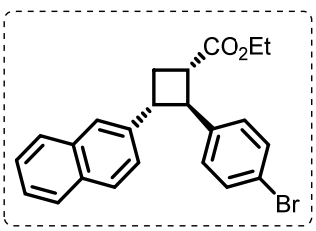


Synthesized from 2-vinylnaphthalene and ethyl cinnamate. Reaction time: 3 h, d.r. 1.8:1, conversion: 99%, yield: 76%.
Diastereomer (major product): ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.79 (m, 3H), 7.71 (s, 1H), 7.48 – 7.40 (m, 3H), 7.33 – 7.26 (m, 4H), 7.24 – 7.20 (m, 1H), 4.20 (q, *J* = 7.1 Hz, 2H), 3.97 (t, *J* = 9.7 Hz, 1H), 3.69 (q, *J* = 9.6 Hz, 1H), 3.24 (q, *J* = 9.3 Hz, 1H), 2.70 (dt, *J* = 10.7, 8.3 Hz, 1H), 2.51 (q, *J* = 10.3 Hz, 1H), 1.29 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 174.20, 142.24, 140.69, 133.46, 132.42, 128.50, 128.20, 127.69, 127.64, 126.69, 126.64, 126.10, 125.51, 125.41, 125.20, 60.67, 50.67, 43.67, 41.76, 29.68, 14.32. HRMS (ESI) Calcd for $[C_{23}H_{22}O_2 + Na]^+$: 353.1512, found: 353.1516.

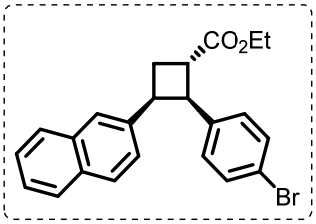


Diastereomer (minor product): ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.73 (dd, *J* = 17.5, 8.0 Hz, 2H), 7.58 (s, 1H), 7.55 (d, *J* = 8.5 Hz, 1H), 7.42 (m, 2H), 7.06 (t, *J* = 7.6 Hz, 2H), 7.03 – 6.94 (m, 4H), 4.39 (t, *J* = 9.2 Hz, 1H), 4.24 (t, *J* = 6.9 Hz, 2H), 4.28 – 4.16 (m, 1H), 3.78 (q, *J* = 8.9 Hz, 1H), 2.91 (dt, *J* = 12.0, 8.7 Hz, 1H), 2.79 – 2.71 (m, 1H), 1.32 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 174.78, 139.26, 138.21, 133.23, 131.93, 127.83, 127.61, 127.59, 127.48, 127.34, 127.16, 126.07, 125.92, 125.73, 125.23, 60.71, 47.49, 42.38, 41.12, 27.29, 14.30. HRMS (ESI) Calcd for $[C_{23}H_{22}O_2 + Na]^+$: 353.1512, found: 353.1516.

Ethyl-2-(4-bromophenyl)-3-(naphthalen-2-yl)cyclobutane-1-carboxylate (**7e**)

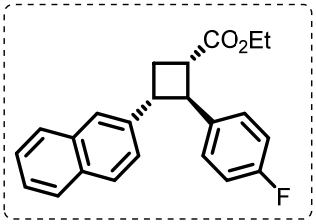


Synthesized from 2-vinylnaphthalene and ethyl (*E*)-3-(4-bromophenyl)acrylate. Reaction time: 3 h, d.r. 1.6:1, conversion: 99%, yield: 74%.
Diastereomer (major product): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (m, 3H), 7.68 (s, 1H), 7.51 – 7.35 (m, 5H), 7.15 (d, *J* = 8.4 Hz, 2H), 4.20 (q, *J* = 7.1 Hz, 2H), 3.89 (t, *J* = 9.8 Hz, 1H), 3.69 – 3.57 (m, 1H), 3.20 (q, *J* = 9.8, 8.2 Hz, 1H), 2.70 (dt, *J* = 10.8, 8.2 Hz, 1H), 2.51 (q, *J* = 10.4 Hz, 1H), 1.29 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 173.91, 141.15, 140.21, 133.43, 132.46, 131.59, 128.42, 128.32, 127.68, 127.65, 126.20, 125.63, 125.23, 125.18, 120.55, 60.78, 50.24, 43.73, 41.65, 29.56, 14.30. HRMS (ESI) Calcd for $[C_{23}H_{21}BrO_2 + Na]^+$:431.0617, found: 431.0623.



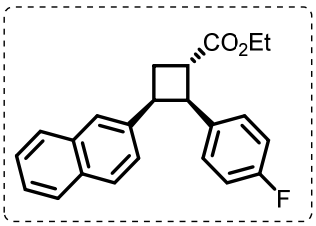
Diastereomer (minor product): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (t, *J* = 7.0 Hz, 2H), 7.55 (m, 2H), 7.47 – 7.35 (m, 2H), 7.14 (d, *J* = 8.4 Hz, 2H), 6.94 (dd, *J* = 8.4, 1.9 Hz, 1H), 6.79 (d, *J* = 8.5 Hz, 2H), 4.29 (t, *J* = 9.3 Hz, 1H), 4.24 – 4.16 (m, 2H), 4.16 – 4.08 (m, 1H), 3.69 (q, *J* = 9.3 Hz, 1H), 2.87 (dt, *J* = 12.1, 8.8 Hz, 1H), 2.75 – 2.65 (m, 1H), 1.28 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 174.44, 138.36, 137.74, 133.23, 132.01, 130.93, 129.34, 127.67, 127.59, 127.55, 127.02, 125.93, 125.89, 125.45, 120.05, 60.81, 46.92, 42.23, 41.31, 27.14, 14.29. HRMS (ESI) Calcd for [$C_{23}H_{21}BrO_2$ + Na]$^+$:431.0617, found: 431.0618.

Ethyl-2-(4-fluorophenyl)-3-(naphthalen-2-yl)cyclobutane-1-carboxylate (**7f**)



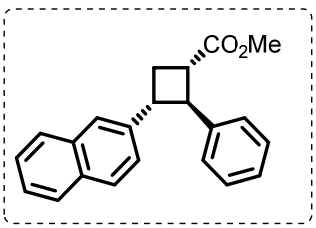
Synthesized from 2-vinylnaphthalene and ethyl (*E*)-3-(4-fluorophenyl)acrylate. Reaction time: 3 h, d.r. 1.8:1, conversion: 99%, yield: 84%.

Diastereomer (major product): ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.80 (m, 3H), 7.68 (s, 1H), 7.45 (m, 2H), 7.40 (d, *J* = 8.3 Hz, 1H), 7.24 (dd, *J* = 8.3, 5.6 Hz, 2H), 6.98 (t, *J* = 8.6 Hz, 2H), 4.20 (q, *J* = 7.1 Hz, 2H), 3.91 (t, *J* = 9.8 Hz, 1H), 3.63 (q, *J* = 9.9 Hz, 1H), 3.19 (q, *J* = 9.4 Hz, 1H), 2.69 (dt, *J* = 10.9, 8.2 Hz, 1H), 2.50 (q, *J* = 10.4 Hz, 1H), 1.29 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 174.02, 161.72 (d, *J* = 244.8 Hz), 140.36, 137.92 (d, *J* = 3.4 Hz), 133.45, 132.45, 128.28, 128.16, 128.10, 127.66 (d, *J* = 3.9 Hz), 126.17, 125.59, 125.29, 125.18, 115.30 (d, *J* = 21.3 Hz), 60.73, 50.10, 43.92, 41.96, 29.57, 14.31. HRMS (ESI) Calcd for [$C_{23}H_{21}FO_2$ + Na]$^+$: 371.1418, found: 371.1419.



Diastereomer (minor product): ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.71 (dd, *J* = 12.3, 8.0 Hz, 2H), 7.55 (s, 1H), 7.53 (d, *J* = 8.6 Hz, 1H), 7.45 – 7.36 (m, 2H), 6.93 (d, *J* = 8.4 Hz, 1H), 6.87 (dd, *J* = 8.4, 5.4 Hz, 2H), 6.70 (t, *J* = 8.6 Hz, 2H), 4.31 (t, *J* = 9.3 Hz, 1H), 4.24 – 4.16 (m, 1H), 4.20 (t, *J* = 6.7 Hz, 1H), 4.12 (td, *J* = 9.2, 3.9 Hz, 1H), 3.68 (q, *J* = 9.0 Hz, 1H), 2.86 (dt, *J* = 12.3, 8.8 Hz, 1H), 2.71 (m, 1H), 1.28 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 174.55, 161.27 (d, *J* = 244.2 Hz), 137.85, 134.99 (d, *J* = 3.2 Hz), 133.23, 131.97, 129.06 (d, *J* = 7.8 Hz), 127.57, 127.52, 127.11, 125.87, 125.39, 114.66 (d, *J* = 21.2 Hz), 60.77, 46.82, 42.34, 41.48, 26.97, 14.29. HRMS (ESI) Calcd for [$C_{23}H_{21}FO_2$ + Na]$^+$: 371.1418, found: 371.1420.

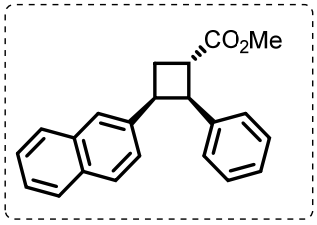
Methyl 3-(naphthalen-2-yl)-2-phenylcyclobutane-1-carboxylate (**7g**)



Synthesized from 2-vinylnaphthalene and methyl cinnamate. Reaction time: 3 h, d.r. 1.7 :1, conversion: 99%, yield: 73%.

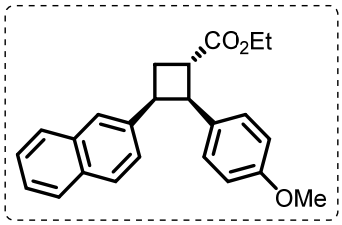
Diastereomer (major product): ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.79 (m, 3H), 7.70 (s, 1H), 7.47 – 7.39 (m, 3H), 7.33 – 7.25 (m, 4H), 7.22 (t, *J* = 7.0 Hz, 1H), 3.97 (t, *J* = 9.7 Hz, 1H), 3.74 (s, 3H), 3.68 (q, *J* = 9.6 Hz, 1H), 3.27 (q, *J* = 9.3 Hz, 1H), 2.70 (dt, *J* = 10.4, 8.3 Hz, 1H), 2.52 (q, *J* = 10.4 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 174.63, 142.11, 140.58, 133.46, 132.43, 128.53, 128.22, 127.70, 127.64,

126.76, 126.62, 126.12, 125.53, 125.40, 125.22, 51.90, 50.79, 43.88, 41.45, 29.66. HRMS (ESI) Calcd for $[C_{22}H_{20}O_2 + Na]^+$: 339.1356, found: 339.1360.



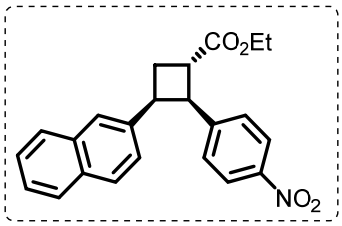
Diastereomer (minor product): ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.69 (dd, *J* = 18.2, 8.0 Hz, 2H), 7.55 (s, 1H), 7.51 (d, *J* = 8.5 Hz, 1H), 7.38 (dt, *J* = 22.5, 7.1 Hz, 2H), 7.02 (m, 2H), 6.99 – 6.96 (m, 1H), 6.95 – 6.90 (m, 3H), 4.36 (t, *J* = 9.3 Hz, 1H), 4.15 (td, *J* = 9.3, 4.1 Hz, 1H), 3.77 (q, *J* = 9.0 Hz, 1H), 3.74 (s, 3H), 2.89 (dt, *J* = 12.1, 8.8 Hz, 1H), 2.75 – 2.68 (m, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 175.19, 139.11, 138.08, 133.22, 131.94, 127.86, 127.60, 127.59, 127.48, 127.36, 127.15, 126.14, 125.89, 125.75, 125.26, 51.95, 47.59, 42.41, 40.86, 27.16. HRMS (ESI) Calcd for $[C_{22}H_{20}O_2 + Na]^+$: 339.1356, found: 339.1359.

Ethyl-2-(4-methoxyphenyl)-3-(naphthalen-2-yl)cyclobutane-1-carboxylate (**7h**)



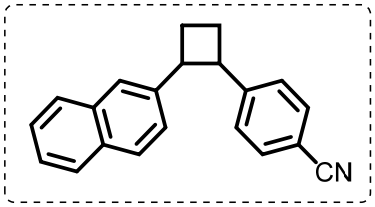
Synthesized from 2-vinylnaphthalene and ethyl (*E*)-3-(4-methoxyphenyl)acrylate. Reaction time: 3 h, d.r. 5:1, conversion: 99%, yield: 70%.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (dd, *J* = 11.8, 7.8 Hz, 2H), 7.57 (s, 1H), 7.53 (d, *J* = 8.5 Hz, 1H), 7.47 – 7.34 (m, 2H), 6.95 (dd, *J* = 8.5, 1.8 Hz, 1H), 6.87 – 6.80 (m, 2H), 6.59 – 6.53 (m, 2H), 4.29 (t, *J* = 9.2 Hz, 1H), 4.19 (qt, *J* = 7.1, 3.7 Hz, 2H), 4.11 (td, *J* = 9.1, 4.1 Hz, 1H), 3.68 (q, *J* = 9.2 Hz, 1H), 3.64 (s, 3H), 2.84 (dt, *J* = 12.0, 8.7 Hz, 1H), 2.76 – 2.66 (m, 1H), 1.28 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 174.71, 157.76, 138.19, 133.17, 131.86, 131.37, 128.61, 127.53, 127.42, 127.29, 127.26, 125.70, 125.64, 125.13, 113.18, 60.57, 54.97, 46.90, 42.33, 41.56, 26.90, 14.21. HRMS (ESI) Calcd for $[C_{24}H_{24}O_3 + Na]^+$: 383.1618, found:383.1620.

Ethyl-3-(naphthalen-2-yl)-2-(4-nitrophenyl)cyclobutane-1-carboxylate (**7i**)



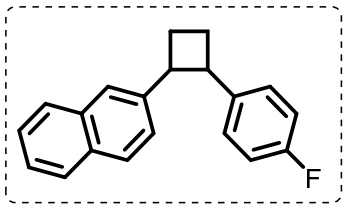
Synthesized from 2-vinylnaphthalene and ethyl (*E*)-3-(4-nitrophenyl)acrylate. Reaction time: 3 h, d.r. 2.3:1, conversion: 99%, yield: 71%.^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 – 7.88 (m, 2H), 7.77 – 7.69 (m, 2H), 7.60 (s, 1H), 7.56 (d, *J* = 8.5 Hz, 1H), 7.49 – 7.39 (m, 2H), 7.14 – 7.08 (m, 2H), 6.97 (dd, *J* = 8.5, 1.8 Hz, 1H), 4.47 (t, *J* = 9.4 Hz, 1H), 4.25 (dd, *J* = 7.1, 2.8 Hz, 2H), 4.29 – 4.17 (m, 1H) 3.83 (q, *J* = 9.1 Hz, 1H), 2.96 (dt, *J* = 12.2, 8.9 Hz, 1H), 2.82 – 2.69 (m, 1H), 1.32 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 174.02, 147.16, 146.27, 137.14, 133.19, 132.07, 128.32, 127.96, 127.59, 127.53, 126.54, 126.19, 126.02, 125.72, 123.12, 61.02, 47.08, 42.51, 41.06, 27.29, 14.28. HRMS (ESI) Calcd for $[C_{23}H_{21}NO_4 + Na]^+$:398.1363, found: 398.1369.

2-(Naphthalen-2-yl)cyclobutyl)benzonitrile (**7j**)



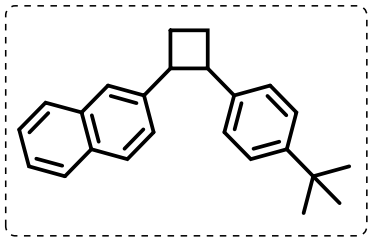
Synthesized from 2-vinylnaphthalene and 4-vinylbenzonitrile. Reaction time: 3 h, d.r. > 20:1, conversion: 99%, yield: 44%. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.80 (q, *J* = 6.9, 6.4 Hz, 3H), 7.64 (d, *J* = 1.6 Hz, 1H), 7.57 (d, *J* = 8.2 Hz, 2H), 7.51 – 7.41 (m, 2H), 7.35 (dd, *J* = 8.5, 1.8 Hz, 1H), 7.31 (d, *J* = 8.2 Hz, 2H), 3.79 – 3.65 (m, 2H), 2.47 – 2.38 (m, 2H), 2.35 – 2.25 (m, 1H), 2.25 – 2.14 (m, 1H).^{13}C NMR (126 MHz, Chloroform-*d*) δ 149.95, 140.99, 133.46, 132.35, 132.25, 128.26, 127.67, 127.63, 127.37, 126.20, 125.55, 125.19, 124.84, 119.15, 109.89, 48.31, 47.72, 26.11, 25.43. HRMS (ESI) Calcd for $[C_{21}H_{17}N + H]^+$: 284.1434, found: 284.1427.

2-(2-(4-Fluorophenyl)cyclobutyl)naphthalene (**7k**)



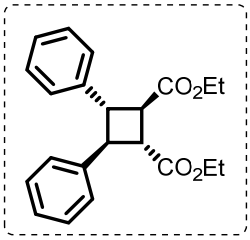
Synthesized from 2-vinylnaphthalene and 4-vinylbenzonitrile. Reaction time: 3 h, d.r. > 20:1, conversion: 99%, yield: 17%. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.86 – 7.79 (m, 3H), 7.67 (d, *J* = 1.7 Hz, 1H), 7.53 – 7.41 (m, 2H), 7.39 (dd, *J* = 8.5, 1.8 Hz, 1H), 7.23 (dd, *J* = 8.5, 5.5 Hz, 2H), 7.05 – 6.95 (m, 2H), 3.77 – 3.61 (m, 2H), 2.48 – 2.36 (m, 2H), 2.31 – 2.23 (m, 1H), 2.23 – 2.15 (m, 1H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 161.39 (d, *J* = 243.8 Hz), 141.70, 140.20 (d, *J* = 3.2 Hz), 133.48, 132.24, 128.04, 128.00 (d, *J* = 4.7 Hz), 127.63, 126.02, 125.41, 125.33, 124.70, 115.07 (d, *J* = 21.2 Hz), 48.58, 47.27, 26.03, 25.87. HRMS (ESI) Calcd for $[C_{20}H_{17}F + H]^+$:277.1387, found:277.1448.

2-(2-(4-(Tert-butyl)phenyl)cyclobutyl)naphthalene (**7l**)



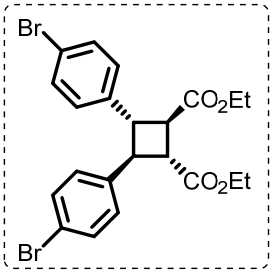
Synthesized from 2-vinylnaphthalene and 4-vinylbenzonitrile. Reaction time: 3 h, d.r. 6:1, conversion: 90%, yield: 10%.^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.82 – 7.74 (m, 3H), 7.71 – 7.63 (m, 0.45H), 7.46 – 7.35 (m, 3H), 7.32 (d, *J* = 8.3 Hz, 2H), 7.20 (d, *J* = 8.0 Hz, 2H), 7.05 (d, *J* = 8.4 Hz, 0.3H), 6.99 – 6.92 (m, 0.3H), 6.89 (d, *J* = 8.3 Hz, 0.3H), 4.19 – 4.01 (m, 0.3H), 3.79 – 3.60 (m, 2H), 2.45 – 2.30 (m, 2H), 2.27 – 2.08 (m, 2H), 2.01 (q, *J* = 6.5 Hz, 0.3H), 1.31 (s, 9H), 1.16 (s, 1.35H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 148.90, 142.21, 141.58, 133.49, 132.18, 127.88, 127.63, 127.60, 126.29, 125.91, 125.58, 125.22, 125.19, 124.69, 48.11, 47.27, 34.41, 31.41, 26.13, 25.99. HRMS (ESI) Calcd for $[C_{24}H_{26} + H]^+$: 315.2107, found:315.2101.

Diethyl-3,4-diphenylcyclobutane-1,2-dicarboxylate (**7a**)[12]



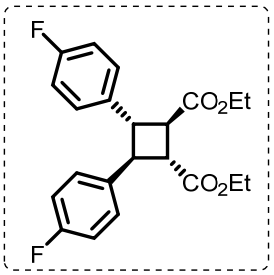
Synthesized from ethyl cinnamate. Reaction time: 3 h, d.r. > 20:1, yield: 8%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.19 (m, 10H), 4.20 (q, *J* = 7.1 Hz, 4H), 3.79 – 3.72 (m, 2H), 3.48 – 3.42 (m, 2H), 1.26 (t, *J* = 7.1 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.60, 141.20, 128.62, 127.08, 126.86, 61.03, 47.00, 44.86, 14.26.

Diethyl-3,4-bis(4-bromophenyl)cyclobutane-1,2-dicarboxylate (**7m**)[12]



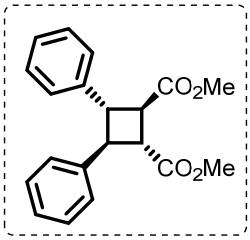
Synthesized from ethyl (*E*)-3-(4-bromophenyl)acrylate. Reaction time: 3 h, d.r. > 20:1, yield: 5%. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.45 (d, *J* = 8.2 Hz, 4H), 7.14 (d, *J* = 8.1 Hz, 4H), 4.20 (qd, *J* = 7.1, 1.6 Hz, 4H), 3.64 – 3.58 (m, 2H), 3.41 – 3.35 (m, 2H), 1.26 (t, *J* = 7.1 Hz, 7H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 172.17, 139.71, 131.81, 128.52, 121.17, 61.21, 46.59, 44.62, 14.22.

Diethyl-3,4-bis(4-fluorophenyl)cyclobutane-1,2-dicarboxylate (**7n**)[12]



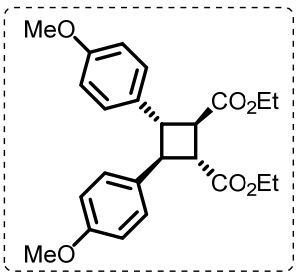
Synthesized from ethyl (*E*)-3-(4-fluorophenyl)acrylate. Reaction time: 3 h, d.r. > 20:1, yield: 17%. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.27 – 7.21 (m, 4H), 7.01 (t, *J* = 8.6 Hz, 4H), 4.20 (qd, *J* = 7.1, 1.6 Hz, 4H), 3.68 – 3.62 (m, 2H), 3.42 – 3.35 (m, 2H), 1.27 (t, *J* = 7.1 Hz, 7H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 172.34, 161.98 (d, *J* = 245.6 Hz), 136.63 (d, *J* = 3.3 Hz), 128.34 (d, *J* = 8.1 Hz), 115.52 (d, *J* = 21.3 Hz), 61.13, 46.65, 44.94, 14.23.

Dimethyl-3,4-diphenylcyclobutane-1,2-dicarboxylate (**7o**)[12]



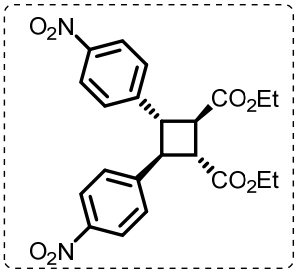
Synthesized from methyl cinnamate. Reaction time: 3 h, d.r. > 20:1, yield: 9%. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.37 – 7.22 (m, 11H), 3.77 – 3.71 (m, 9H), 3.52 – 3.47 (m, 2H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 173.01, 140.96, 128.66, 127.17, 126.84, 52.24, 47.35, 44.43.

Diethyl-3,4-bis(4-methoxyphenyl)cyclobutane-1,2-dicarboxylate (**7p**)[12]



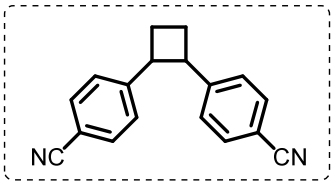
Synthesized from ethyl (*E*)-3-(4-methoxyphenyl)acrylate. Reaction time: 3 h, d.r. > 20:1, yield: 18%. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.24 (d, *J* = 8.2 Hz, 4H), 6.88 (d, *J* = 8.2 Hz, 4H), 4.22 (q, *J* = 7.1 Hz, 4H), 3.82 (s, 6H), 3.68 – 3.62 (m, 2H), 3.42 – 3.37 (m, 2H), 1.29 (t, *J* = 7.1 Hz, 6H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 172.60, 158.57, 133.28, 127.85, 113.89, 60.84, 55.20, 46.85, 44.93, 14.18.

Diethyl -3,4-bis(4-nitrophenyl)cyclobutane-1,2-dicarboxylate (**7q**)[12]



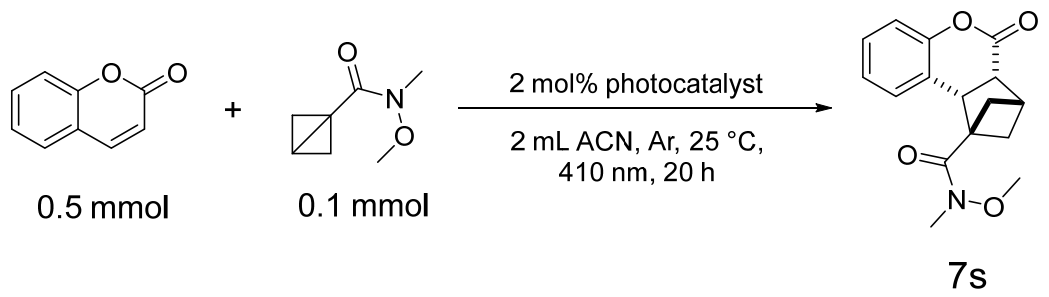
Synthesized from ethyl (*E*)-3-(4-nitrophenyl)acrylate.. Reaction time: 3 h, d.r. > 20:1, yield: 12%.
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.25 – 8.19 (m, 4H), 7.49 – 7.43 (m, 4H), 4.24 (qd, *J* = 7.1, 1.5 Hz, 4H), 3.88 – 3.83 (m, 2H), 3.54 – 3.47 (m, 2H), 1.29 (t, *J* = 7.1 Hz, 6H).

4,4'-(Cyclobutane-1,2-diyl)dibenzonitrile (**7r**)[16]



Synthesized from 4-vinylbenzonitrile. Reaction time: 3 h, d.r. 3:1, yield: 38%.
Diastereomer (major product):^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.60 (d, *J* = 8.2 Hz, 4H), 7.29 (d, *J* = 8.1 Hz, 4H), 3.61 (td, *J* = 10.5, 9.5, 5.3 Hz, 2H), 2.47 – 2.35 (m, 2H), 2.27 – 2.14 (m, 2H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 148.91, 132.41, 127.32, 118.90, 110.36, 47.70, 25.64. Diastereomer (minor product): ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.40 (d, *J* = 8.1 Hz, 4H), 7.01 (d, *J* = 8.1 Hz, 4H), 4.18 – 4.07 (m, 2H), 2.64 – 2.53 (m, 2H), 2.51 – 2.40 (m, 2H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 146.38, 131.82, 128.40, 118.82, 109.89, 45.21, 23.78.

Table S6. Intermolecular [2π+2σ]-photocycloaddition.

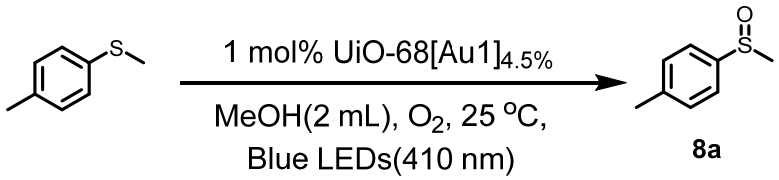


Entry	PC	7s yield (%)
1	UiO-68[Au1]$_{4.5\%}$	6%
2	[Au(C^N^C)(NHC)]PF_6	21%

Reaction conditions: 0.5 mmol 2*H*-chromen-2-one, 0.1 mmol *N*-methoxy-*N*-methylbicyclo[1.1.0]butane-1-carboxamide (prepared according to the literature[11]), 2 mol% photocatalyst, 2 mL MeCN, 25 °C, 20 h; Yield was determined by ^{1}H NMR spectroscopy using CH_2Br_2 as an internal standard.

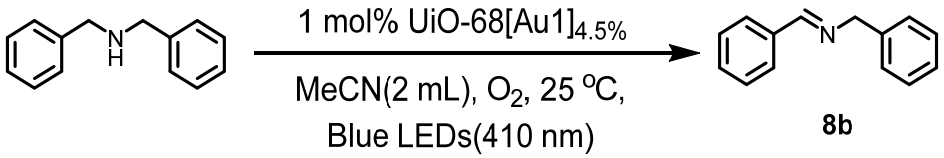
9 General procedure H for visible-light-driven oxidative organic transformations

9.1 Oxidation of sulfides (8a)[17]



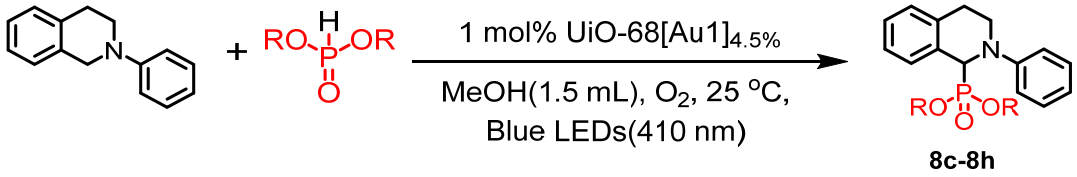
Methyl(*p*-tolyl)sulfane (0.1 mmol) and **UiO-68[Au1]$_{4.5\%}$** (1 mol%) were weighted and added to a 10 mL reaction tube equipped with a stir bar. 2 mL of methanol was added to the tube. The reaction mixture was degassed by bubbling O_2 and then stirred at room temperature under irradiation from a 410 nm LED with cooling by running water. After 30 min, the tube was opened and chlorodiphenylmethane (0.1 mmol) was added as an internal standard. Conversion and yields were determined using ^{1}H NMR spectroscopy. The crude product was purified by column chromatography on silica gel (eluent: EA/PE) to afford the pure product. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, J = 8.2 Hz, 2H), 7.34 (d, J = 8.2 Hz, 2H), 2.71 (s, 3H), 2.43 (s, 3H).

9.2 Oxidation of dibenzylamine (8b)[18]



Dibenzylamine (0.1 mmol) and **UiO-68[Au1]$_{4.5\%}$** (1 mol%) were weighted and added to a 10 mL reaction tube equipped with a stir bar. 2 mL of MeCN was added to the tube. The reaction mixture was degassed by bubbling O_2 and then stirred at room temperature under irradiation from a 410 nm LED with cooling by running water. After 2 h, the tube was opened and chlorodiphenylmethane (0.1 mmol) was added as an internal standard. Conversion and yields were determined using ^{1}H NMR spectroscopy. The crude product was purified by column chromatography on silica gel (eluent: EA/PE) to afford the pure product. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.43 (s, 1H), 7.84 – 7.78 (m, 2H), 7.47 – 7.42 (m, 3H), 7.39 – 7.34 (m, 4H), 7.32 – 7.29 (m, 1H), 4.86 (s, 2H).

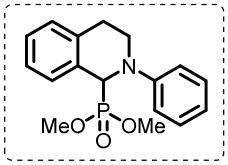
9.3 Visible-light-driven cross-dehydrogenative coupling reactions.



8c-8h

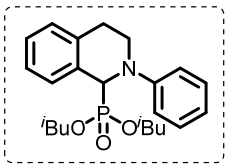
2-Phenyl-1,2,3,4-tetrahydroisoquinoline (0.1 mmol), phosphite (0.3 mmol) and **UiO-68[Au1]$_{4.5\%}$** (1 mol%) were weighted and added to a 10 mL reaction tube equipped with a stir bar. 1.5 mL of MeOH was added to the reaction tube. The reaction mixture was degassed by bubbling O_2 and then stirred at room temperature under irradiation from a 410 nm LED with cooling by running water. After the indicated reaction time, the tube was opened and chlorodiphenylmethane (0.1 mmol) was added as an internal standard. Conversion and yields were determined using ^{1}H NMR spectroscopy. The crude product was purified by column chromatography on silica gel (eluent: EA/PE) to afford the pure product **8c-8h**. (The catalyst **UiO-68[Au1]$_{4.5\%}$** was recovered by washing with MeOH several times. The recovered MOF catalyst was then used in subsequent reactions for cycle tests, with fresh substrates added.)

Dimethyl (2-phenyl-1,2,3,4-tetrahydroisoquinolin-1-yl)phosphonate (**8c**)[19]



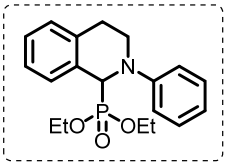
Synthesized from 2-phenyl-1,2,3,4-tetrahydroisoquinoline and dimethyl phosphonate, yield: 97%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.34 (m, 1H), 7.30 – 7.15 (m, 5H), 6.98 (d, J = 8.2 Hz, 2H), 6.82 (t, J = 7.3 Hz, 1H), 5.21 (d, J = 20.0 Hz, 1H), 4.07 – 3.98 (m, 1H), 3.71 – 3.62 (m, 7H), 3.15 – 2.95 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.25 (d, J = 6.1 Hz), 136.43 (d, J = 5.6 Hz), 130.39, 129.28, 128.87 (d, J = 2.6 Hz), 127.96 (d, J = 4.6 Hz), 127.58 (d, J = 3.6 Hz), 126.09 (d, J = 2.9 Hz), 118.70, 114.78, 58.76 (d, J = 159.7 Hz), 53.99 (d, J = 7.1 Hz), 52.98 (d, J = 7.7 Hz), 43.58, 26.69.

Diisobutyl (2-phenyl-1,2,3,4-tetrahydroisoquinolin-1-yl)phosphonate (**8d**)[19]



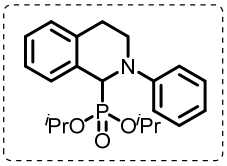
Synthesized from 2-phenyl-1,2,3,4-tetrahydroisoquinoline and diisobutyl phosphonate, yield: 89%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.36 (m, 1H), 7.28 – 7.13 (m, 5H), 6.98 (d, J = 8.2 Hz, 2H), 6.79 (t, J = 7.3 Hz, 1H), 5.22 (d, J = 19.8 Hz, 1H), 4.07 – 3.97 (m, 1H), 3.85 – 3.71 (m, 2H), 3.70 – 3.59 (m, 2H), 3.53 (dt, J = 9.7, 6.2 Hz, 1H), 3.13 – 2.95 (m, 2H), 1.92 – 1.68 (m, 2H), 0.88 (dd, J = 6.7, 3.8 Hz, 6H), 0.80 (dd, J = 6.7, 4.6 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 149.30 (d, J = 5.4 Hz), 136.41 (d, J = 5.4 Hz), 130.80, 129.14, 128.74 (d, J = 2.7 Hz), 128.14 (d, J = 4.7 Hz), 127.43 (d, J = 3.4 Hz), 125.87 (d, J = 2.9 Hz), 118.38, 114.73, 72.99 (d, J = 7.8 Hz), 72.08 (d, J = 8.2 Hz), 58.73 (d, J = 159.0 Hz), 43.46, 29.24 (d, J = 5.9 Hz), 26.83, 18.73 (d, J = 5.8 Hz), 18.63 (d, J = 4.3 Hz).

Diethyl (2-phenyl-1,2,3,4-tetrahydroisoquinolin-1-yl)phosphonate (**8e**)[20]



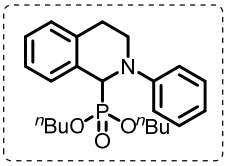
Synthesized from 2-phenyl-1,2,3,4-tetrahydroisoquinoline and diethyl phosphonate, yield: 85%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.36 (m, 1H), 7.30 – 7.12 (m, 5H), 6.98 (d, *J* = 7.9 Hz, 2H), 6.80 (t, *J* = 7.3 Hz, 1H), 5.19 (d, *J* = 20.0 Hz, 1H), 4.17 – 3.83 (m, 5H), 3.69 – 3.58 (m, 1H), 3.15 – 2.94 (m, 2H), 1.25 (t, *J* = 7.1 Hz, 3H), 1.15 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 149.40 (d, *J* = 5.8 Hz), 136.46 (d, *J* = 5.5 Hz), 130.65, 129.15, 128.76 (d, *J* = 2.8 Hz), 128.13 (d, *J* = 4.6 Hz), 127.44 (d, *J* = 3.5 Hz), 125.88 (d, *J* = 2.8 Hz), 118.46, 114.78, 63.35 (d, *J* = 7.3 Hz), 62.35 (d, *J* = 7.7 Hz), 58.82 (d, *J* = 159.4 Hz), 43.49, 26.76, 16.48 (d, *J* = 5.4 Hz), 16.39 (d, *J* = 5.9 Hz).

Diisopropyl (2-phenyl-1,2,3,4-tetrahydroisoquinolin-1-yl)phosphonate (**8f**)[20]



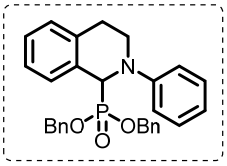
Synthesized from 2-phenyl-1,2,3,4-tetrahydroisoquinoline and diisopropyl phosphonate, yield: 92%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 – 7.37 (m, 1H), 7.26 – 7.09 (m, 5H), 6.96 (d, *J* = 8.2 Hz, 2H), 6.77 (t, *J* = 7.3 Hz, 1H), 5.14 (d, *J* = 21.2 Hz, 1H), 4.71 – 4.55 (m, 2H), 4.12 – 4.00 (m, 1H), 3.70 – 3.61 (m, 1H), 3.10 – 2.92 (m, 2H), 1.30 (dd, *J* = 7.4, 6.2 Hz, 6H), 1.17 (d, *J* = 6.2 Hz, 3H), 0.95 (d, *J* = 6.2 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 149.56 (d, *J* = 6.5 Hz), 136.44 (d, *J* = 5.6 Hz), 130.90 (d, *J* = 1.3 Hz), 129.01, 128.73 (d, *J* = 2.6 Hz), 128.44 (d, *J* = 4.5 Hz), 127.29 (d, *J* = 3.5 Hz), 125.64 (d, *J* = 2.9 Hz), 118.28, 115.05, 72.28 (d, *J* = 7.7 Hz), 70.88 (d, *J* = 8.3 Hz), 58.77 (d, *J* = 161.2 Hz), 43.49, 26.57, 24.62 (d, *J* = 2.8 Hz), 24.16 (d, *J* = 3.2 Hz), 23.76 (d, *J* = 5.7 Hz), 23.33 (d, *J* = 5.5 Hz).

Dibutyl (2-phenyl-1,2,3,4-tetrahydroisoquinolin-1-yl)phosphonate (**8g**)[20]



Synthesized from 2-phenyl-1,2,3,4-tetrahydroisoquinoline and dibutyl phosphonate, yield: 76%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.35 (m, 1H), 7.27 – 7.12 (m, 5H), 6.97 (d, *J* = 8.2 Hz, 2H), 6.79 (t, *J* = 7.3 Hz, 1H), 5.20 (d, *J* = 19.9 Hz, 1H), 4.07 – 3.93 (m, 3H), 3.93 – 3.84 (m, 1H), 3.84 – 3.75 (m, 1H), 3.69 – 3.59 (m, 1H), 3.13 – 2.93 (m, 2H), 1.61 – 1.52 (m, 2H), 1.50 – 1.41 (m, 2H), 1.39 – 1.19 (m, 4H), 0.89 (t, *J* = 7.4 Hz, 3H), 0.82 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 149.34 (d, *J* = 5.6 Hz), 136.42 (d, *J* = 5.4 Hz), 130.75, 129.12, 128.74 (d, *J* = 2.7 Hz), 128.11 (d, *J* = 4.6 Hz), 127.42 (d, *J* = 3.5 Hz), 125.87 (d, *J* = 3.0 Hz), 118.40, 114.74, 66.94 (d, *J* = 7.5 Hz), 65.97 (d, *J* = 8.0 Hz), 58.74 (d, *J* = 158.9 Hz), 43.45, 32.61 (d, *J* = 5.7 Hz), 32.54 (d, *J* = 5.6 Hz), 26.82, 18.68 (d, *J* = 8.0 Hz), 13.59 (d, *J* = 5.4 Hz).

Dibenzyl (2-phenyl-1,2,3,4-tetrahydroisoquinolin-1-yl)phosphonate (**8h**)[19]



Synthesized from 2-phenyl-1,2,3,4-tetrahydroisoquinoline and dibenzyl phosphonate, yield: 81%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38 – 7.09 (m, 16H), 6.99 (d, *J* = 8.3 Hz, 2H), 6.82 (t, *J* = 7.3 Hz, 1H), 5.31 (d, *J* = 19.6 Hz, 1H), 5.07 – 4.76 (m, 4H), 4.10 – 4.00 (m, 1H), 3.70 – 3.61 (m, 1H), 3.15 – 2.96 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 149.22 (d, *J* = 5.5 Hz), 136.53 (d, *J* = 5.5 Hz), 136.35 (d, *J* = 6.0 Hz), 136.22 (d, *J* = 6.0 Hz), 130.37, 129.22, 128.82 (d, *J* = 2.7 Hz), 128.42 (d, *J* = 10.8 Hz), 128.29, 128.21, 128.19, 128.17, 128.03 (d, *J* = 6.2 Hz), 127.58 (d, *J* = 3.5 Hz), 126.00 (d, *J* = 2.9 Hz), 118.63,

114.86, 68.66 (d, J = 7.3 Hz), 67.74 (d, J = 7.8 Hz), 59.02 (d, J = 158.2 Hz), 43.57, 26.83.

9.3.1 Control experiment

Table S7. Control experiment for visible-light-driven cross-dehydrogenative coupling reactions.

a b

Entry	Catalyst	Conditions	Yield(%)
1	**UiO-68[Au1]$_{4.5\%}$**	O_2, blue LEDs (410 nm)	98
2	**UiO-68[Au1]$_{4.5\%}$**	argon, blue LEDs (410 nm)	5.7
3	**UiO-68[Au1]$_{4.5\%}$**	O_2, lack of light	1.3
4	[Au(C^N^C)(NHC)]PF_6	O_2, blue LEDs (410 nm)	97
5	**UiO-68[Au1]$_{4.5\%}$**	O_2, blue LEDs (410 nm)	84[a]
6	No Catalyst	O_2, blue LEDs (410 nm)	13[a]
7	**UiO-68[Au1]$_{4.5\%}$**	Air, blue LEDs (410 nm)	93

Reaction conditions: 0.1 mmol **a**, 0.3 mmol **b**, 5 mg **UiO-68[Au1]$_{4.5\%}$** (or 1.5 mol% [Au(C^N^C)(NHC)]PF_6), 1.5 mL MeOH, 25 °C, 30 min (or 5 min[a]); Yields were determined by ^{1}H NMR spectroscopy using chlorodiphenylmethane as an internal standard.

9.3.2 Cycle experiment

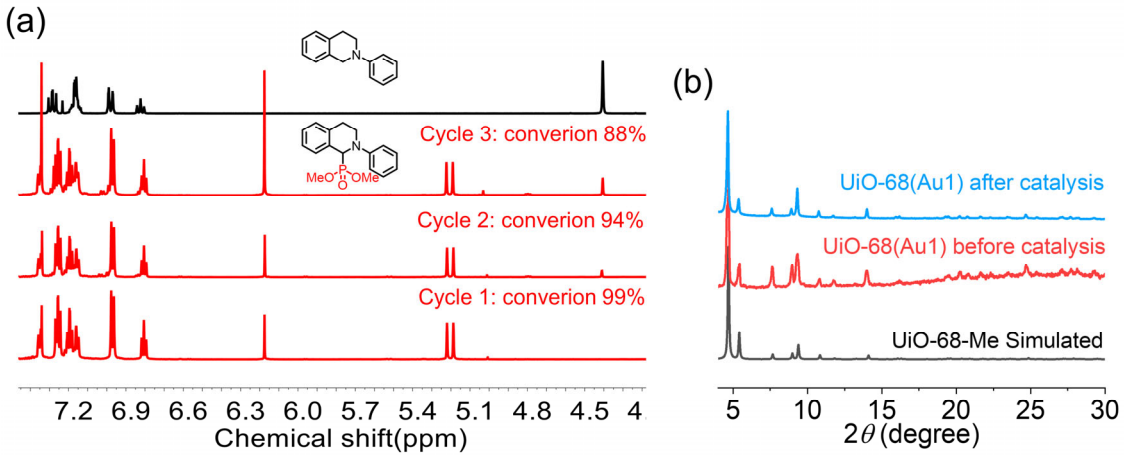
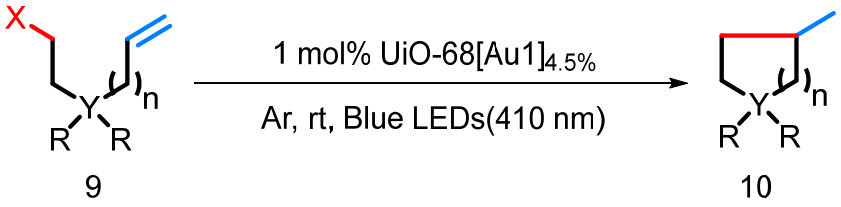


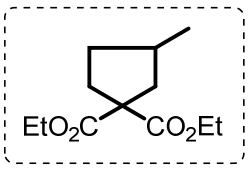
Fig. S27. (a) ^{1}H NMR spectra of crude product obtained from cycle experiments. (b) PXRD patterns of **UiO-68[Au1]$_{4.5\%}$** before and after cross-dehydrogenative coupling reactions (three reaction runs).

10 General procedure I for visible-light-driven cyclization of alkyl halide



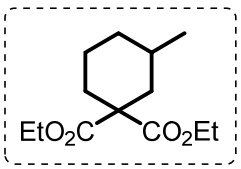
Alkyl halide (0.05 mmol, **9a**–**9f**), DIPEA (0.1 mmol), 1,4-CHD (0.1 mmol) and **UiO-68[Au1]$_{4.5\%}$** (1 mol%, 2.5 mg) were weighted and added to a 10 mL reaction tube equipped with a stir bar. 2 mL of solvent (MeCN/MeOH = 1:1 v/v) was added to the tube. The reaction mixture was degassed by bubbling argon and then stirred at room temperature under irradiation from a 410 nm LED with cooling by running water. After the indicated reaction time, the tube was opened and chlorodiphenylmethane (0.1 mmol) was added as an internal standard. Conversion and yields were determined using ^{1}H NMR spectroscopy. The crude product was purified by column chromatography on silica gel (eluent: EA/PE) to afford the pure product **10a**–**10f**.

Diethyl 3-methylcyclopentane-1,1-dicarboxylate (**10a**)[8]



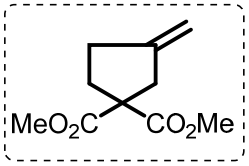
Synthesized from **9a**, yield: 97%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.17 (q, *J* = 7.1 Hz, 4H), 2.44 (dd, *J* = 13.1, 7.1 Hz, 1H), 2.32 (ddd, *J* = 13.7, 8.5, 3.8 Hz, 1H), 2.14 (ddd, *J* = 13.6, 9.4, 7.5 Hz, 1H), 2.09 – 1.99 (m, 1H), 1.90 – 1.79 (m, 1H), 1.66 (dd, *J* = 13.3, 10.1 Hz, 1H), 1.25 (d, *J* = 7.1 Hz, 6H), 1.22 (s, 1H), 1.01 (d, *J* = 6.6 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 172.89, 61.25, 60.34, 42.54, 34.47, 34.17, 34.04, 19.61, 14.06.

Diethyl 3-methylcyclohexane-1,1-dicarboxylate (**10b**)[8]



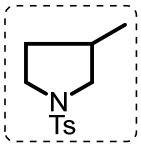
Synthesized from **9b**, yield: 85%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.20 (q, *J* = 7.1 Hz, 2H), 4.14 (q, *J* = 7.1 Hz, 2H), 2.37 – 2.24 (m, 2H), 1.75 – 1.66 (m, 1H), 1.65 – 1.46 (m, 3H), 1.41 (tt, *J* = 13.3, 3.4 Hz, 1H), 1.30 – 1.23 (m, 6H), 1.21 (d, *J* = 7.1 Hz, 2H), 0.90 (d, *J* = 6.6 Hz, 3H), 0.88 – 0.80 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.68, 171.31, 61.23, 60.96, 55.40, 39.36, 33.97, 30.91, 28.88, 22.70, 22.56, 14.10, 14.03.

Dimethyl 3-methylenecyclopentane-1,1-dicarboxylate (**10c**)[21]



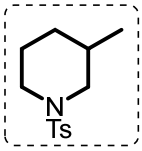
Synthesized from **9c**, yield: 96%. ^{1}H NMR (600 MHz, $CDCl_3$) δ 4.93 – 4.87 (m, 2H), 3.73 (s, 6H), 2.92 (q, *J* = 2.0 Hz, 2H), 2.43 (td, *J* = 7.6, 2.0 Hz, 2H), 2.28 (t, *J* = 7.6 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 172.16, 148.18, 107.00, 60.09, 52.74, 40.77, 33.86, 31.19.

3-Methyl-1-tosylpyrrolidine (**10d**)[8]



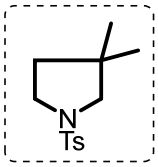
Synthesized from **9d**, yield: 97%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.71 (d, *J* = 8.3 Hz, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 3.42 (dd, *J* = 9.6, 7.2 Hz, 1H), 3.34 (ddd, *J* = 9.8, 8.1, 4.1 Hz, 1H), 3.26 – 3.18 (m, 1H), 2.75 (dd, *J* = 9.7, 7.8 Hz, 1H), 2.44 (s, 3H), 2.18 – 2.06 (m, 1H), 1.96 – 1.84 (m, 1H), 1.35 (dq, *J* = 12.3, 8.4 Hz, 1H), 0.92 (d, *J* = 6.7 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 143.25, 133.97, 129.60, 127.51, 54.76, 47.62, 33.31, 33.25, 21.55, 17.65.

3-Methyl-1-tosylpiperidine (**10e**)[22]



Synthesized from **9e**, yield: 90%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (d, *J* = 8.3 Hz, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 3.71 – 3.56 (m, 2H), 2.44 (s, 3H), 2.20 (td, *J* = 11.3, 2.9 Hz, 1H), 1.87 (t, *J* = 10.7 Hz, 1H), 1.80 – 1.53 (m, 4H), 0.87 (d, *J* = 6.5 Hz, 3H), 0.85 – 0.76 (m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 143.28, 133.28, 129.56, 127.68, 53.22, 46.46, 32.09, 30.70, 24.70, 21.54, 19.02.

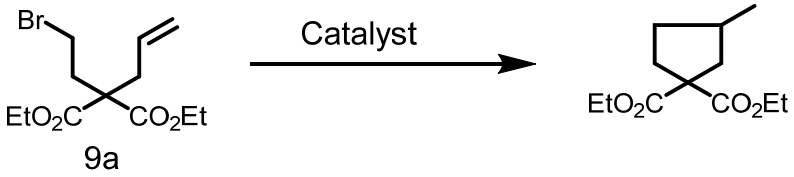
3,3-Dimethyl-1-tosylpyrrolidine (**10f**)[23]



Synthesized from **9f**, yield: 95%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.72 (d, *J* = 8.3 Hz, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 3.33 (t, *J* = 7.1 Hz, 2H), 2.98 (s, 2H), 2.43 (s, 3H), 1.55 (t, *J* = 7.1 Hz, 2H), 0.92 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 143.23, 134.09, 129.57, 127.44, 60.20, 46.99, 39.13, 38.63, 26.06, 21.56.

10.1 Control experiments

Table S8. Control experiments for visible-light-driven cyclization of alkyl halide.



9a

Entry	Catalyst	Conditions	Yield(%)
1	**UiO-68[Au1]$_{4.5\%}$**	Ar	82%
2	**UiO-68[Au1]$_{4.5\%}$**	Air	trace
3	**UiO-68[Au1]$_{4.5\%}$**	Ar, lack of DIPEA	trace
4	**UiO-68[Au1]$_{4.5\%}$**	Ar, lack of light	trace
5	[Au(C^N^C)(NHC)]PF_6	Ar	84%
6	**UiO-68-Me**	Ar	trace
7	No Catalyst	Ar	trace

Reaction conditions: 0.1 mmol **9a**, 0.2 mmol DIPEA, 5 mg **UiO-68[Au1]$_{4.5\%}$**/5 mg **UiO-68-Me**/1.5 mol% [Au(C^N^C)(NHC)]PF_6, 2 mL MeCN, under argon (or air), 25 °C, 410 nm LED irradiation, 2 h; Yields were determined by ^{1}H NMR using chlorodiphenylmethane as an internal standard.

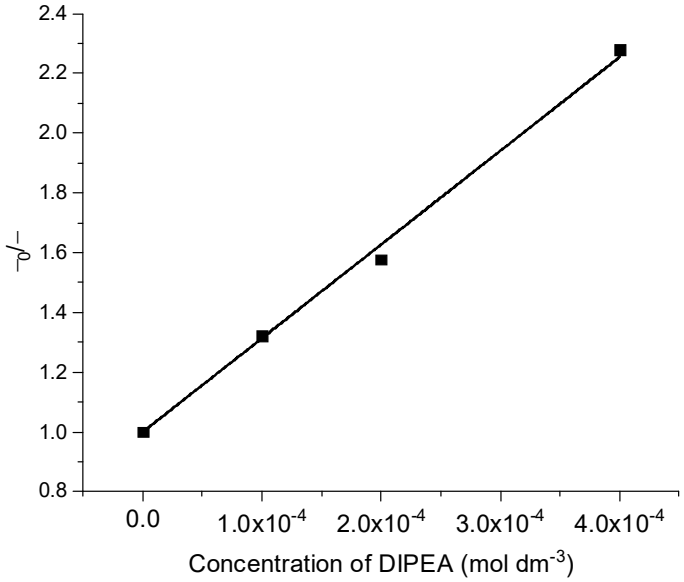


Fig. S28. Stern-Volmer plots of emission quenching of **Au1** (2×10^{-5} mol dm^{-3} in MeCN) by DIPEA. The k_q value was fitted to be 7.7×10^9 dm^3 mol^{-1} s^{-1}.

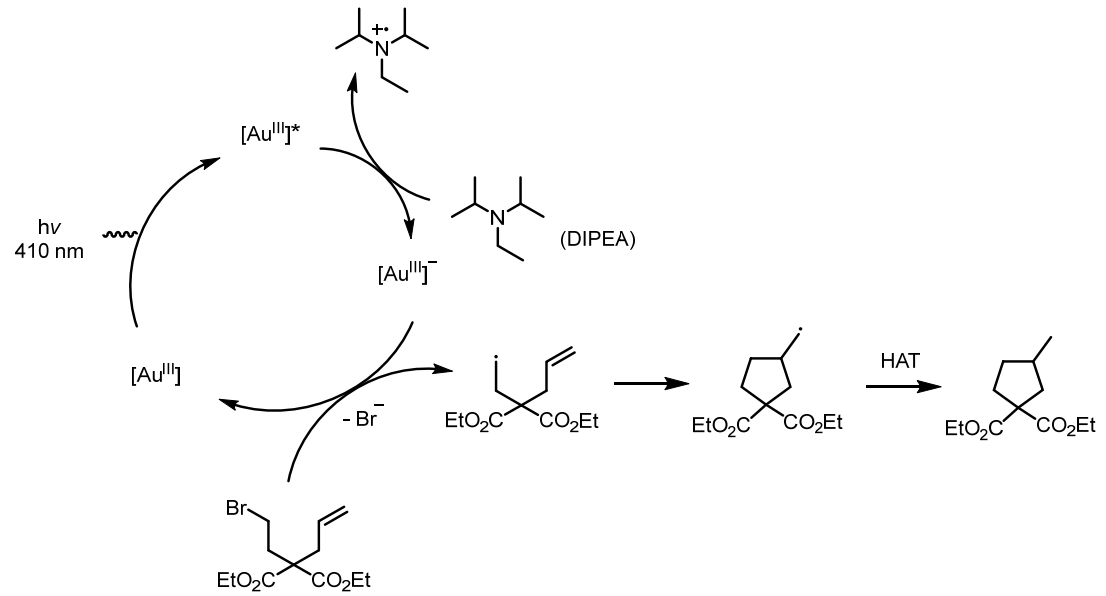


Fig. S29. Proposed mechanism of visible-light-driven cyclization of alkyl halide (path A).

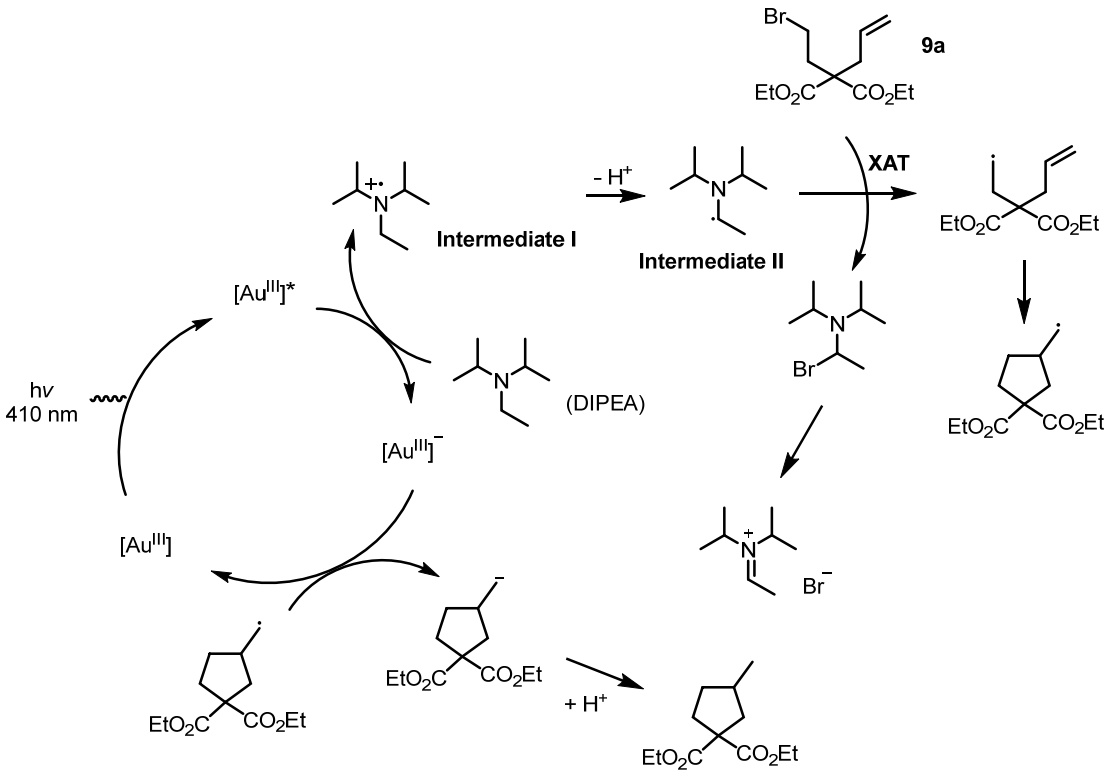


Fig. S30. Proposed mechanism of visible-light-driven cyclization of alkyl halide (path B).

Comparison of the anodic peak current originated from the oxidation of DIPEA before and after the addition of alkyl bromide **9a** (50 mM):

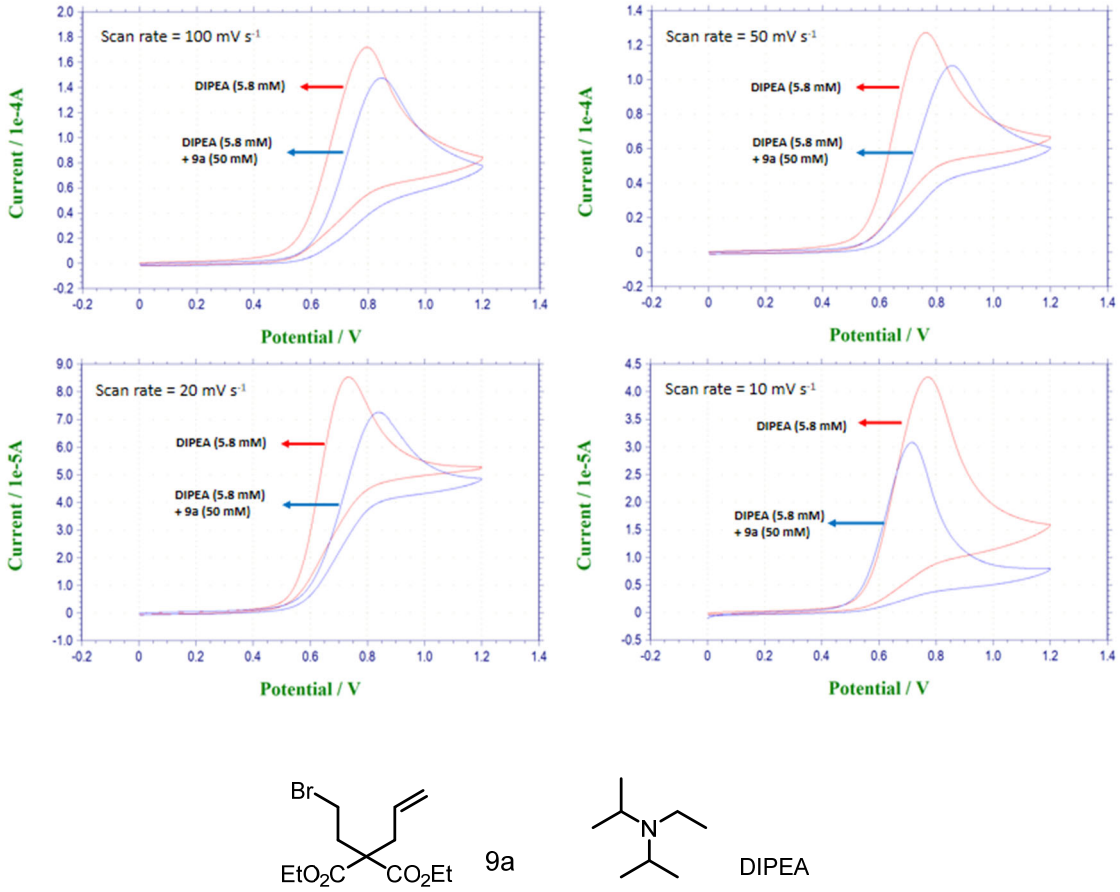


Fig. S31. CV experiments of DIPEA and **9a** performed under different conditions at different scan rates (20–100 mV s^{-1}).

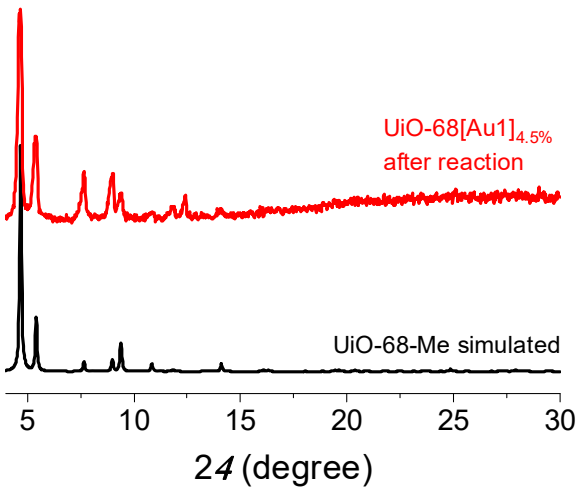
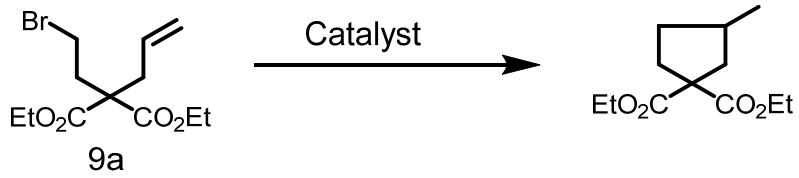


Fig. S32. PXRD patterns of **UiO-68[Au1]$_{4.5\%}$** after the photo-induced cyclization reaction of alkyl halide.

Table S9. Optimization of reaction conditions for visible-light-driven cyclization of alkyl halide.



Entry	9a (mmol)	Hydrogen donors	Solvent	Yield
1	0.1	--	MeCN	62%
2	0.1	--	MeCN	61%[a]
3	0.1	HCOOH	MeCN	45%
4	0.05	CHD	MeCN	Trace
5	0.05	CHD	MeCN/MeOH (1:1 v/v)	97%
6	0.05	--	MeCN/MeOH (1:1 v/v)	71%
7	0.05	--	MeOH	76%

Reaction conditions: **9a** (1 equiv.), DIPEA (2 equiv.), 1,3-CHD (2 equiv.), 2.5 mg **UiO-68[Au1]$_{4.5\%}$**, 2 mL solvent, argon, 25 °C, 410 nm, 2 h (or 30 min[a]); Yields were determined by ^{1}H NMR using chlorodiphenylmethane as an internal standard.

References

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Single crystal data

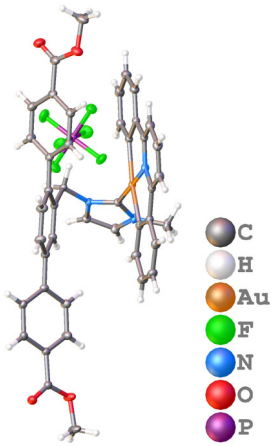


Fig. S33. Single crystal structure of **Me-TPDC-[Au1]**.

Table S10. Crystallographic data and structure refinement details.

Complex	**Me-TPDC-[Au1]**
CCDC Number	2376582
Formula	$C_{44}H_{35}O_4N_3PF_6Au$
Formula weight	1011.68
Temperature (K)	100.0
Crystal system	Monoclinic
Space group	$P2_1/c$
a/Å	14.4088(11)
b/Å	17.1693(13)
c/Å	16.0777(12)
α/°	90
β/°	104.518(2)
γ/°	90
V/Å^3	3850.4(5)
Z	4
D_c /g cm^{-3}	1.745
reflns coll.	99384
unique reflns	11497
R_{int}	0.0548
R_1 $[I > 2\sigma(I)]$[a]	0.0236
wR_2 $[I > 2\sigma(I)]$[b]	0.0619
R_1 (all data)	0.0242
wR_2 (all data)	0.0623
GOF	1.067

[a] $R_1 = \sum||F_o|-F_c||/\sum|F_o|$. [b] $wR_2 = [\sum[w(F_o^2-F_c^2)^2]/\sum[(F_o^2)^2]]^{1/2}$

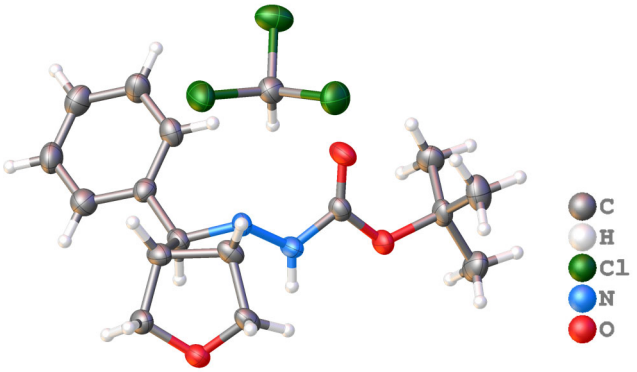


Fig. S34. Single crystal structure of **4f**.

Table S11. Crystallographic data and structure refinement details.

Complex	**4f**
CCDC Number	2376581
Formula	$C_{17}H_{23}Cl_3N_2O_3$
Formula weight	409.72
Temperature (K)	100.0
Crystal system	Triclinic
Space group	*P*-1
a/Å	10.7577(7)
b/Å	12.0667(8)
c/Å	16.1638(9)
α/°	92.851(3)
β/°	97.765(3)
γ/°	101.579(3)
V/Å^3	2030.3(2)
Z	4
D_c /g cm^{-3}	1.340
reflns coll.	44831
unique reflns	6929
R_{int}	0.1421
R_1 [$I > 2\sigma(I)$][a]	0.0637
wR_2 [$I > 2\sigma(I)$][b]	0.1551
R_1 (all data)	0.1180
wR_2 (all data)	0.1863
GOF	1.018

[a] $R_1 = \sum||F_o|-F_c||/\sum|F_o|$. [b] $wR_2 = [\sum[w(F_o^2-F_c^2)^2]/\sum[(F_o^2)^2]]^{1/2}$

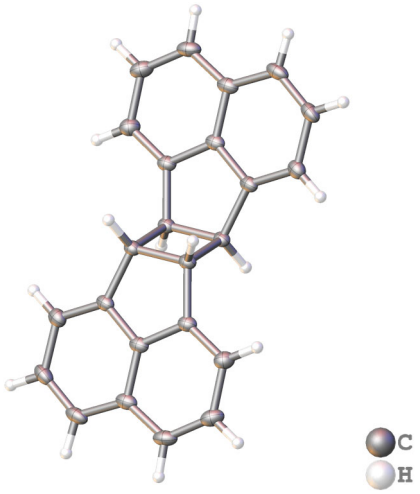


Fig. S35. Single crystal structure of **7c**.

Table S12. Crystallographic data and structure refinement details.

Complex	**7c**
CCDC Number	2376583
Formula	$C_{24}H_{16}$
Formula weight	304.37
Temperature (K)	100.0(2)
Crystal system	Monoclinic
Space group	$P2_1/n$
a/Å	7.7763(7)
b/Å	4.8289(4)
c/Å	20.0609(18)
α/°	90
β/°	92.476(4)
γ/°	90
V/Å^3	752.60(11)
Z	2
D_c /g cm^{-3}	1.343
reflns coll.	16840
unique reflns	1871
R_{int}	0.0666
R_1 $[I > 2\sigma(I)]$[a]	0.0432
wR_2 $[I > 2\sigma(I)]$[b]	0.1175
R_1 (all data)	0.0483
wR_2 (all data)	0.1214
GOF	1.060

[a] $R_1 = \sum||F_o|-F_c||/\sum|F_o|$. [b] $wR_2 = [\sum[w(F_o^2-F_c^2)^2]/\sum[(F_o^2)^2]]^{1/2}$

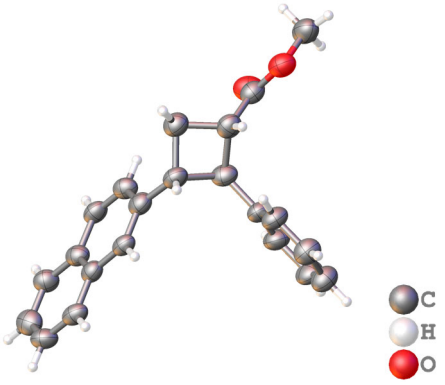


Fig. S36. Single crystal structure of **7g**.

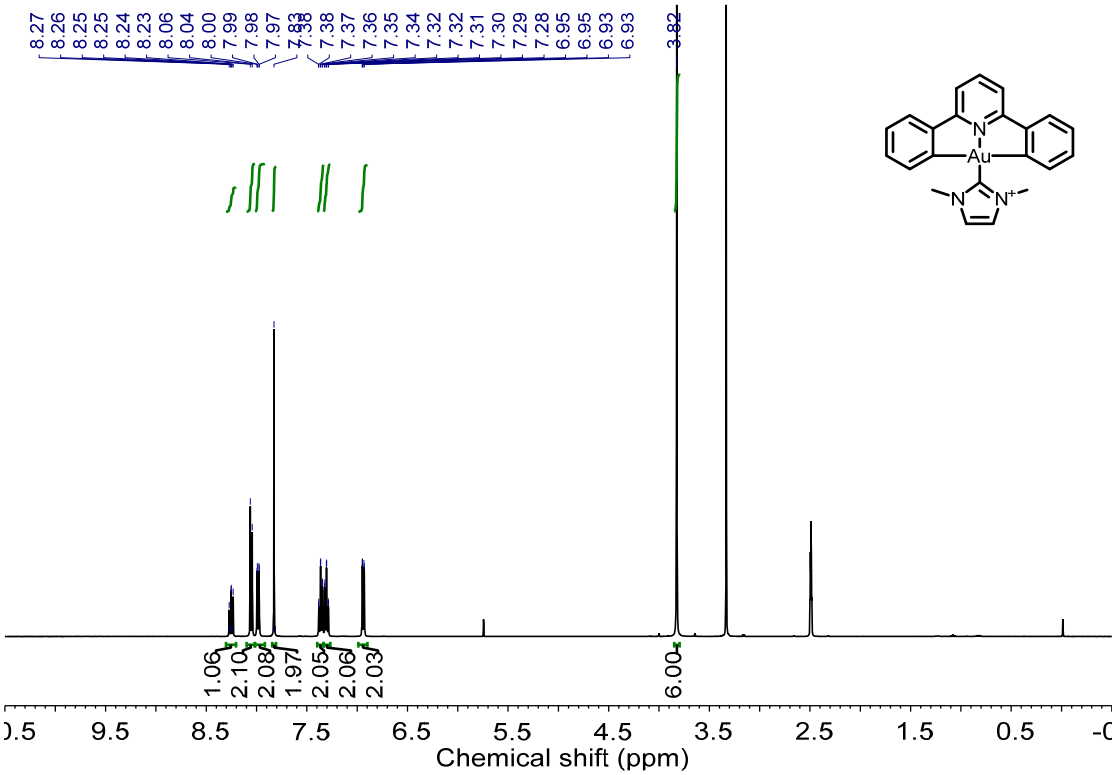
Table S13. Crystallographic data and structure refinement details.

Complex	**7g**
CCDC Number	2376584
Formula	$C_{22}H_{20}O_2$
Formula weight	316.38
Temperature (K)	100.0(2)
Crystal system	Monoclinic
Space group	$P2_1/c$
a/Å	8.8211(4)
b/Å	5.6037(2)
c/Å	34.2588(14)
α/°	90
β/°	94.5040(10)
γ/°	90
V/Å^3	1688.21(12)
Z	4
D_c /g cm^{-3}	1.245
reflns coll.	50854
unique reflns	4900
R_{int}	0.0591
R_1 $[I > 2\sigma(I)]$[a]	0.0401
wR_2 $[I > 2\sigma(I)]$[b]	0.1134
R_1 (all data)	0.0420
wR_2 (all data)	0.1155
GOF	1.058

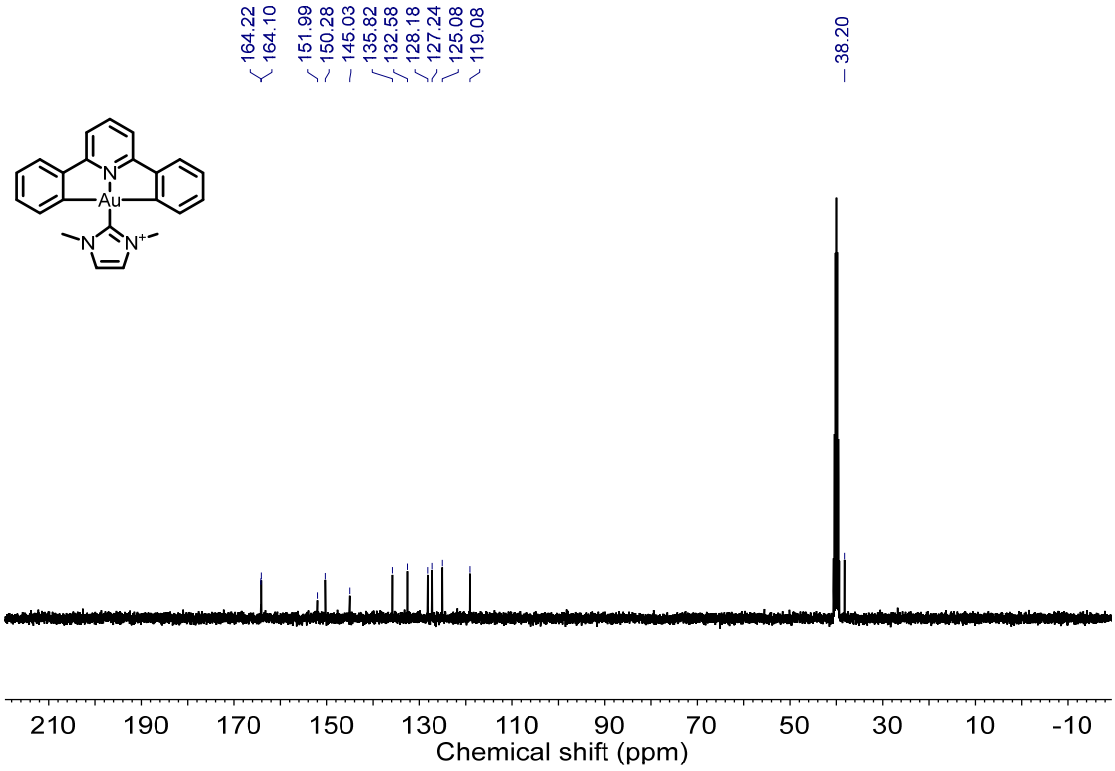
[a] $R_1 = \sum||F_o|-F_c||/\sum|F_o|$. [b] $wR_2 = [\sum[w(F_o^2-F_c^2)^2]/\sum[(F_o^2)^2]]^{1/2}$

NMR spectra

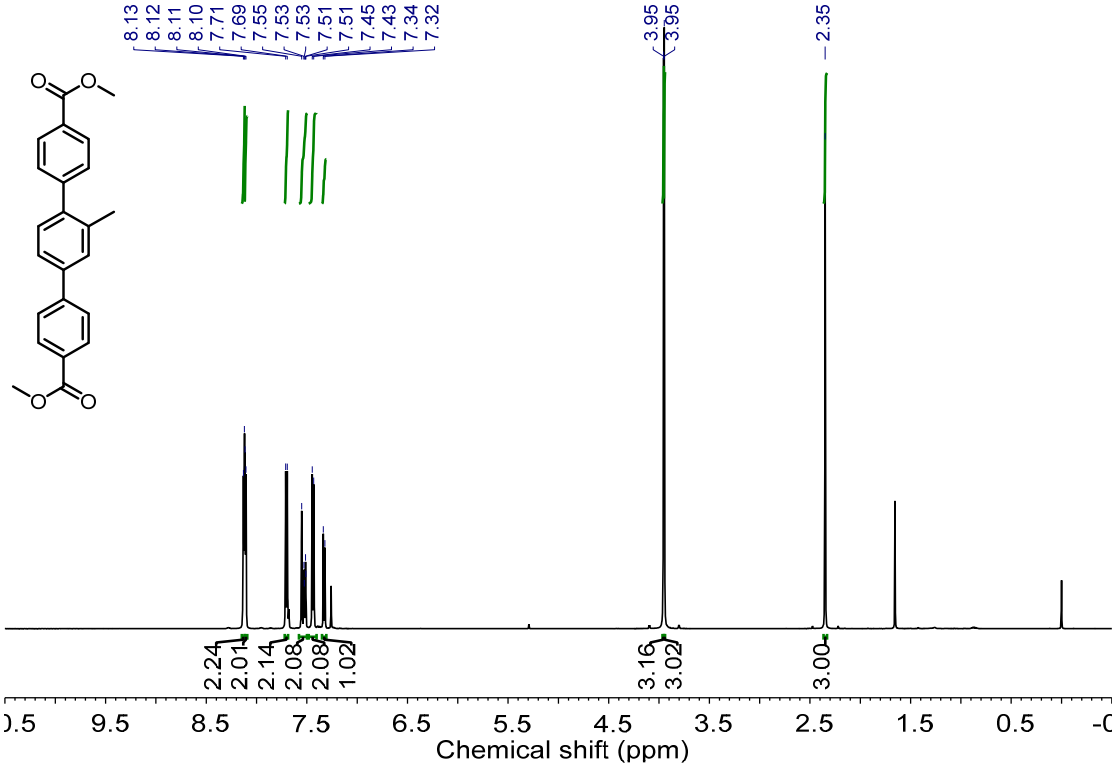
[Au(C^N^C)(NHC)]PF_6, ^{1}H NMR (400 MHz, DMSO-d_6)



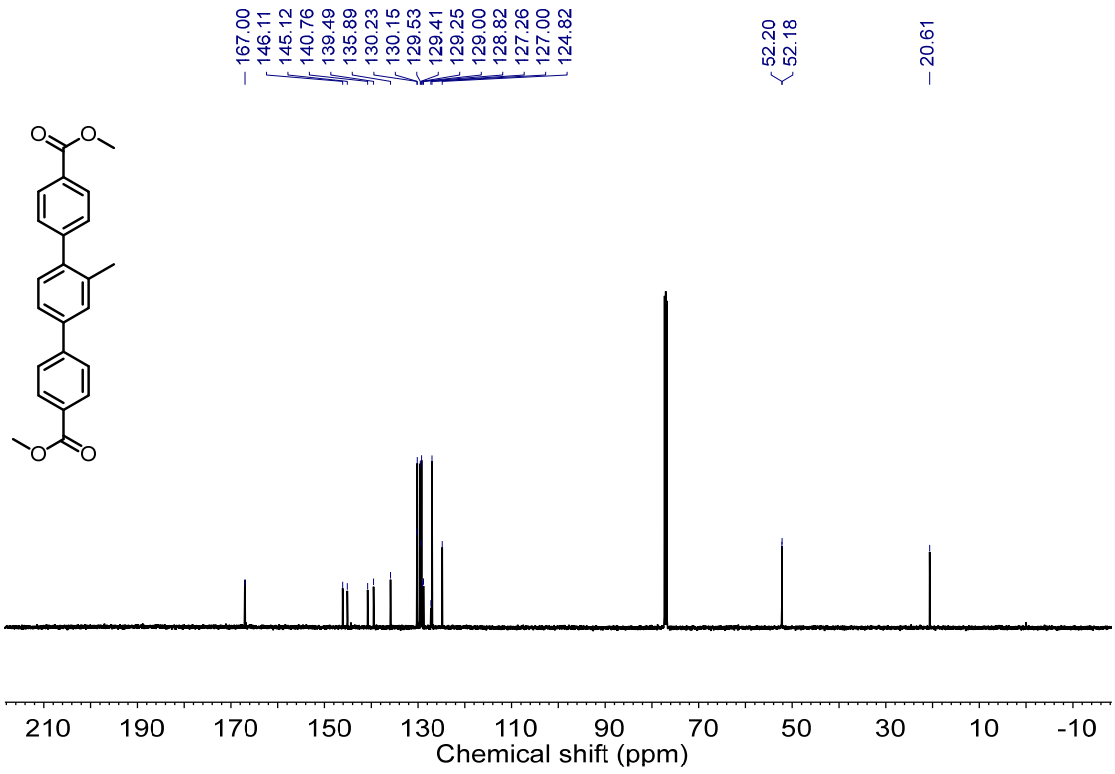
[Au(C^N^C)(NHC)]PF_6, ^{13}C NMR (101 MHz, DMSO-d_6)



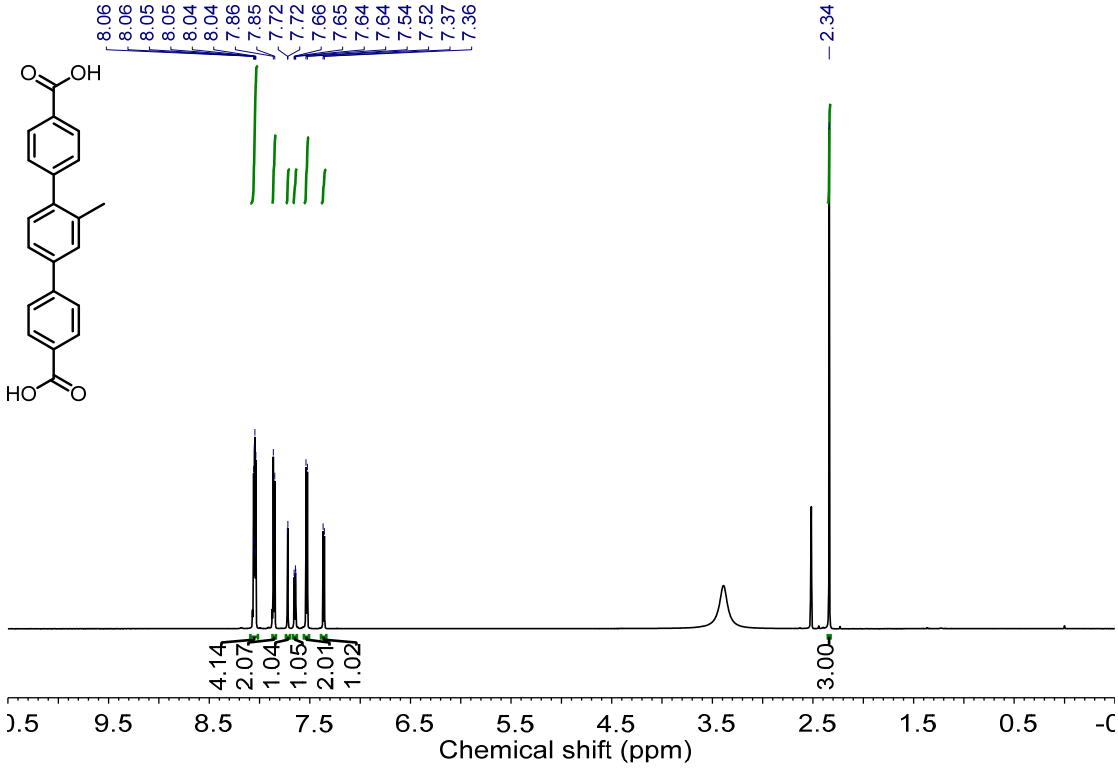
S1, ^{1}H NMR (500 MHz, $CDCl_3$)



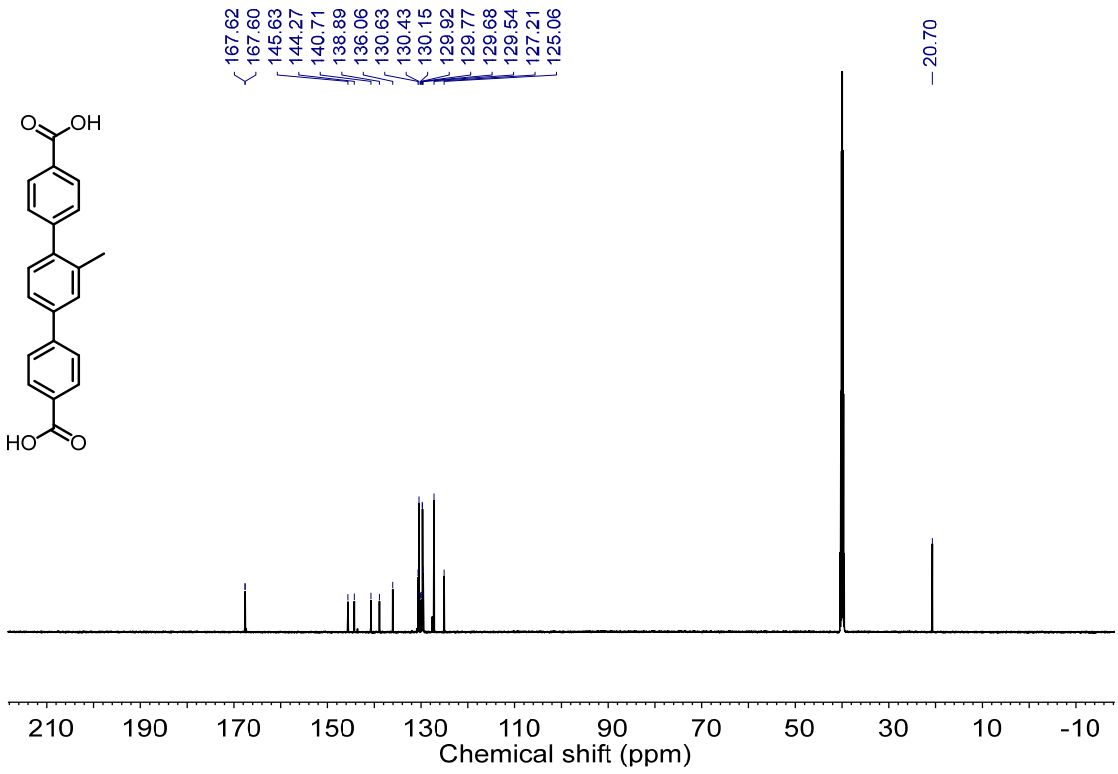
S1, ^{13}C NMR (126 MHz, $CDCl_3$)



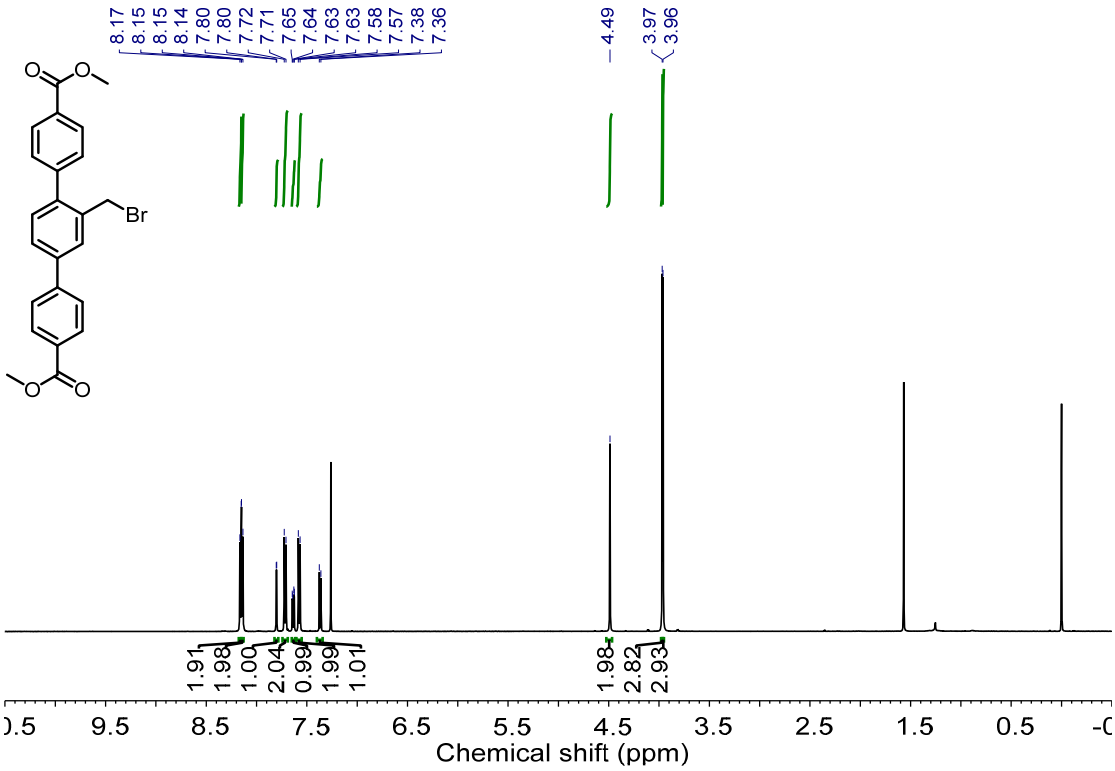
S2, ^{1}H NMR (600 MHz, DMSO-d_6)



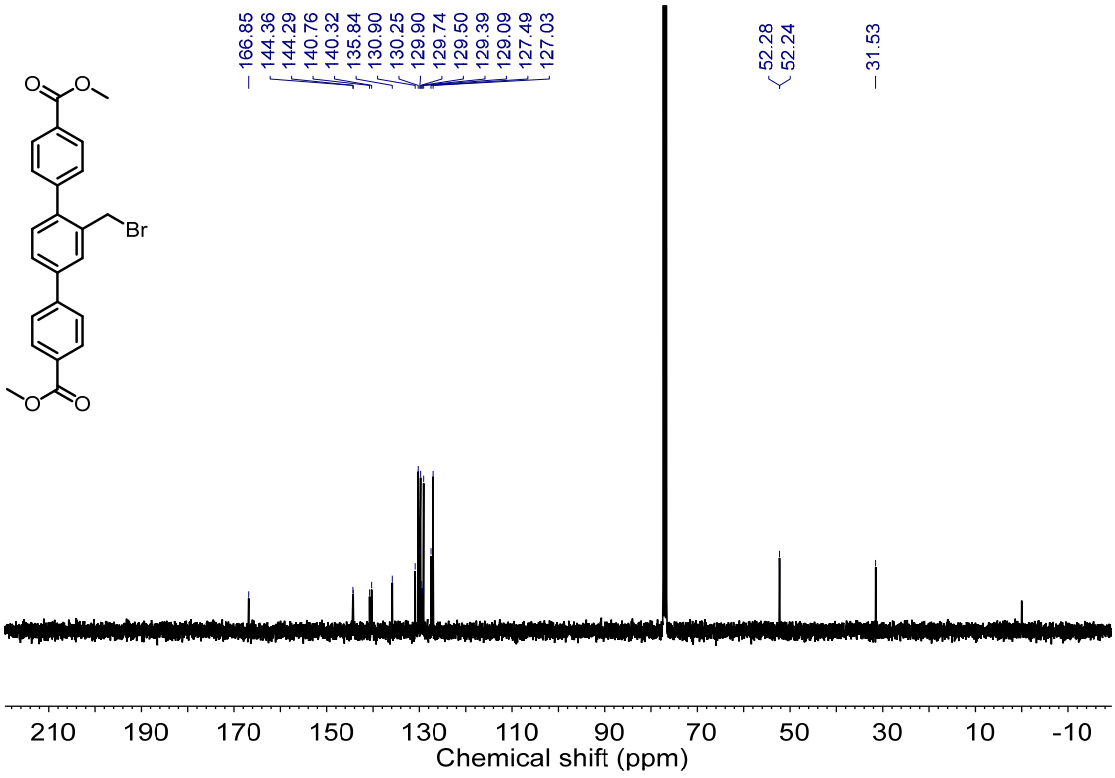
S2, ^{13}C NMR (151 MHz, DMSO-d_6)



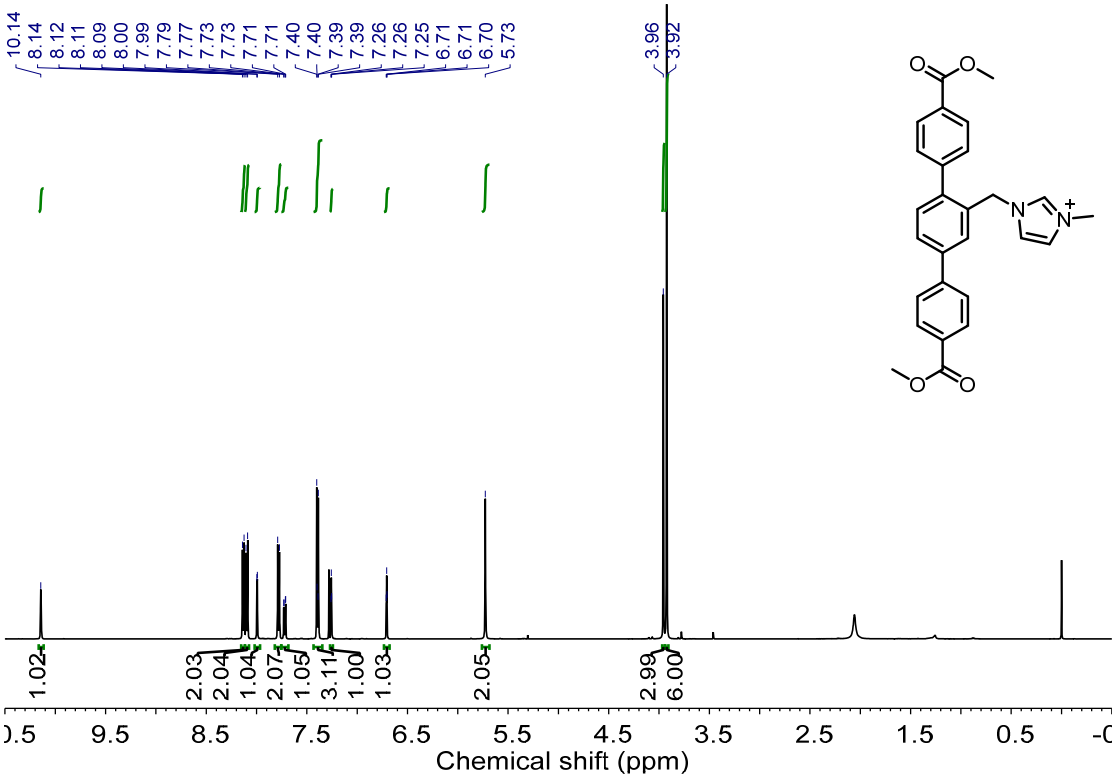
S3, ^{1}H NMR (500 MHz, $CDCl_3$)



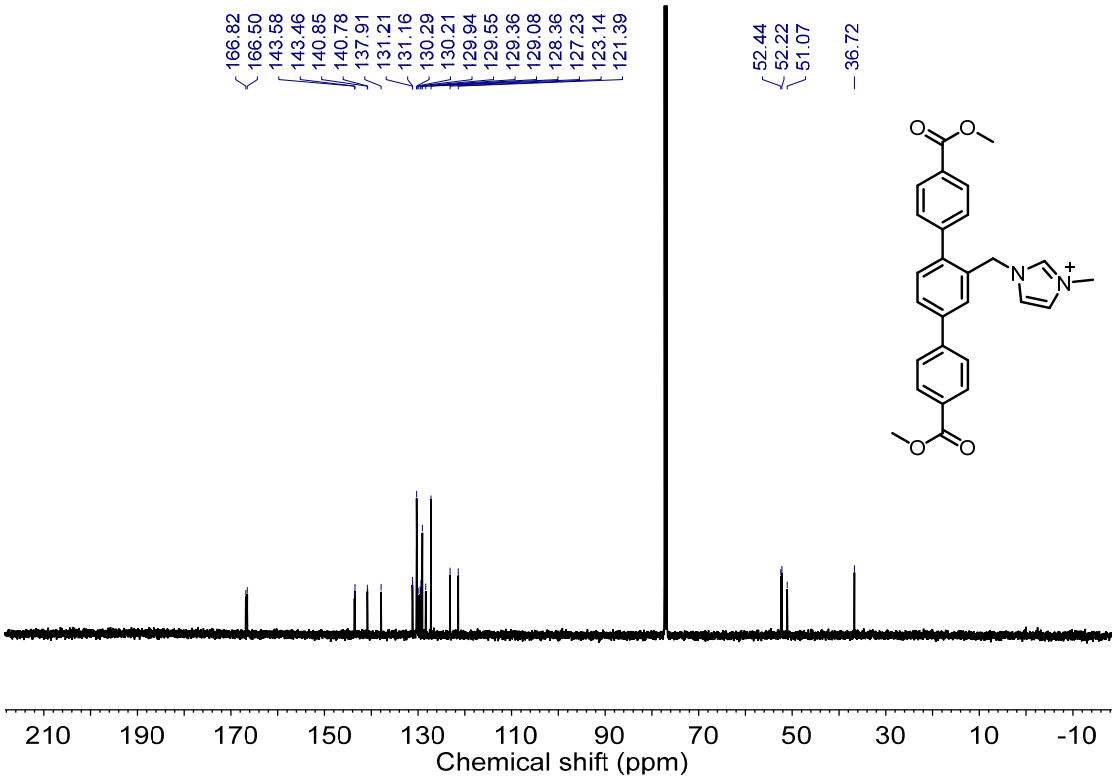
S3, ^{13}C NMR (101 MHz, $CDCl_3$)



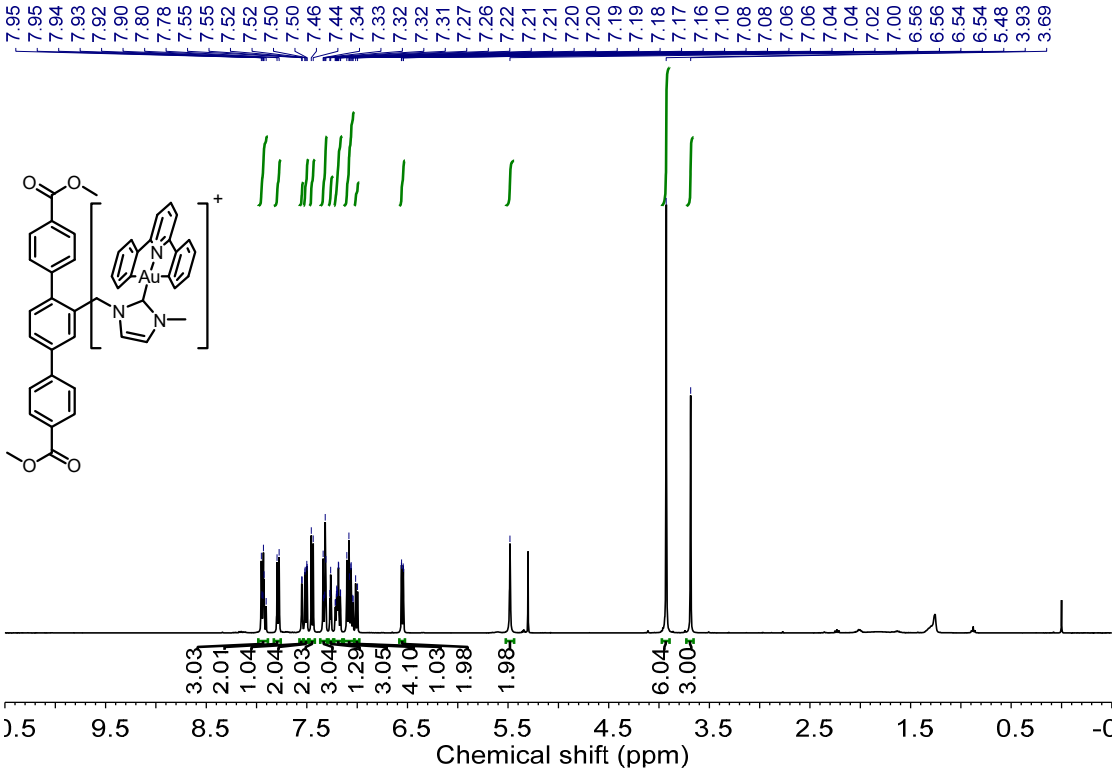
S4, ^{1}H NMR (500 MHz, $CDCl_3$)



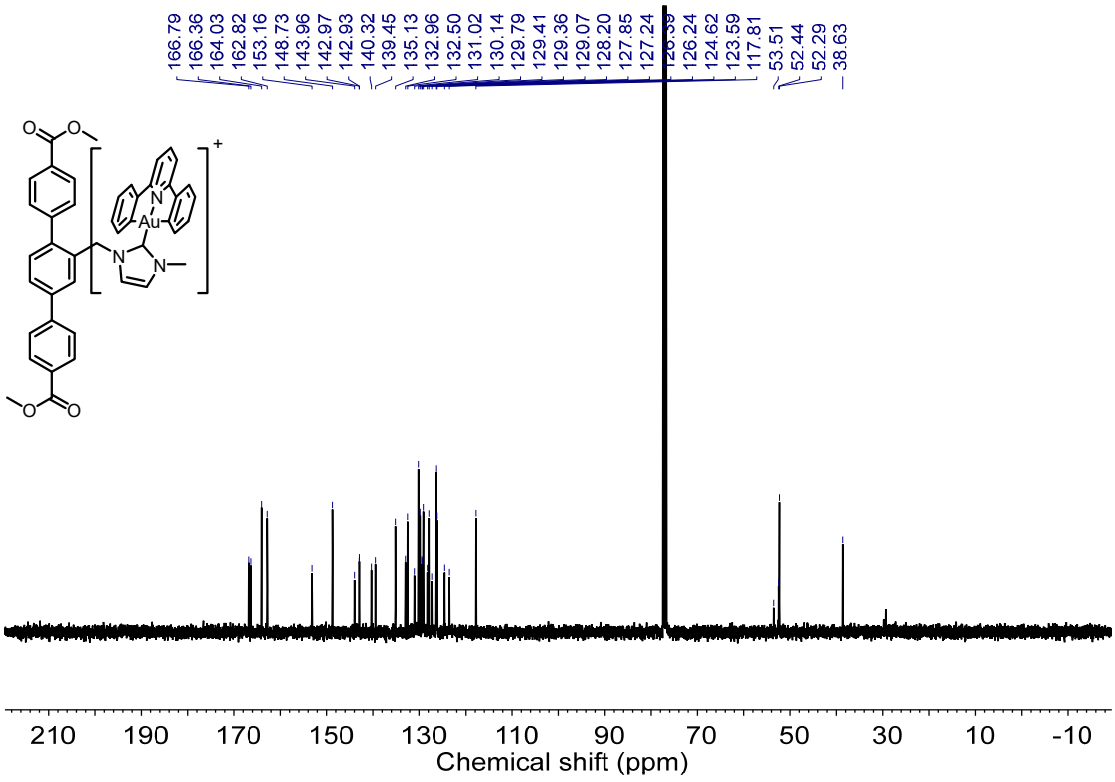
S4, ^{13}C NMR (126 MHz, $CDCl_3$)



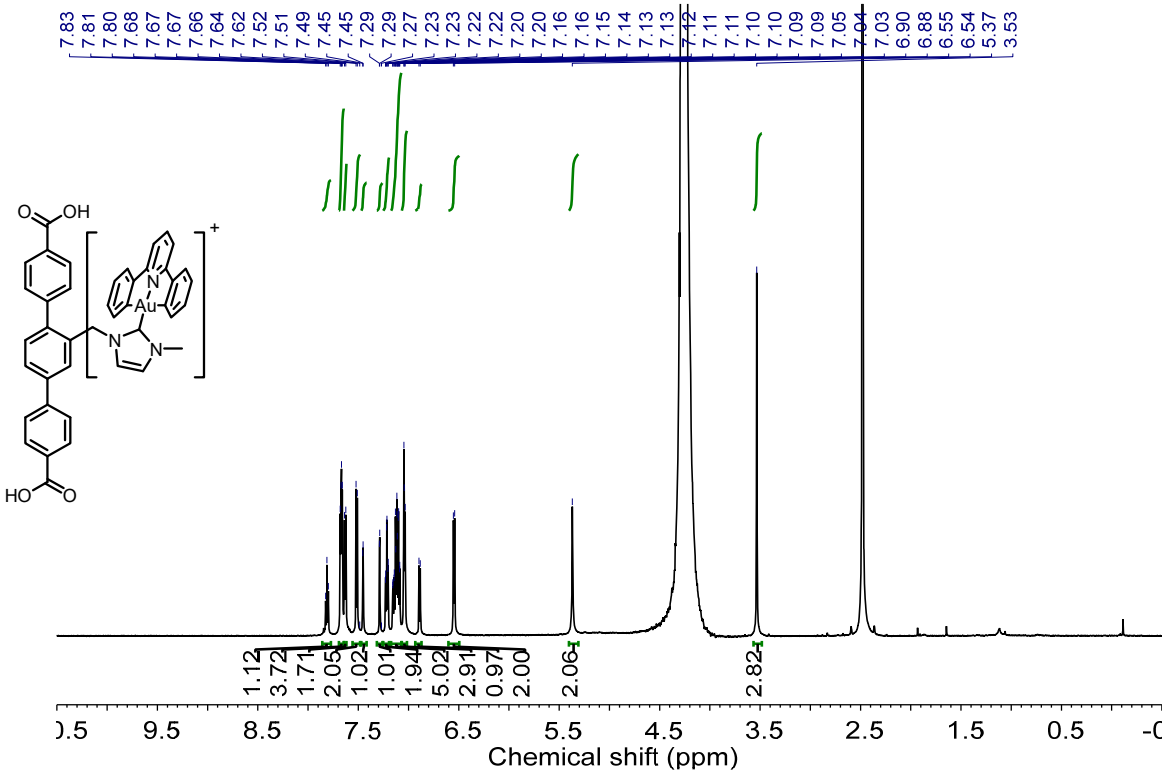
S5, ^{1}H NMR (400 MHz, $CDCl_3$)



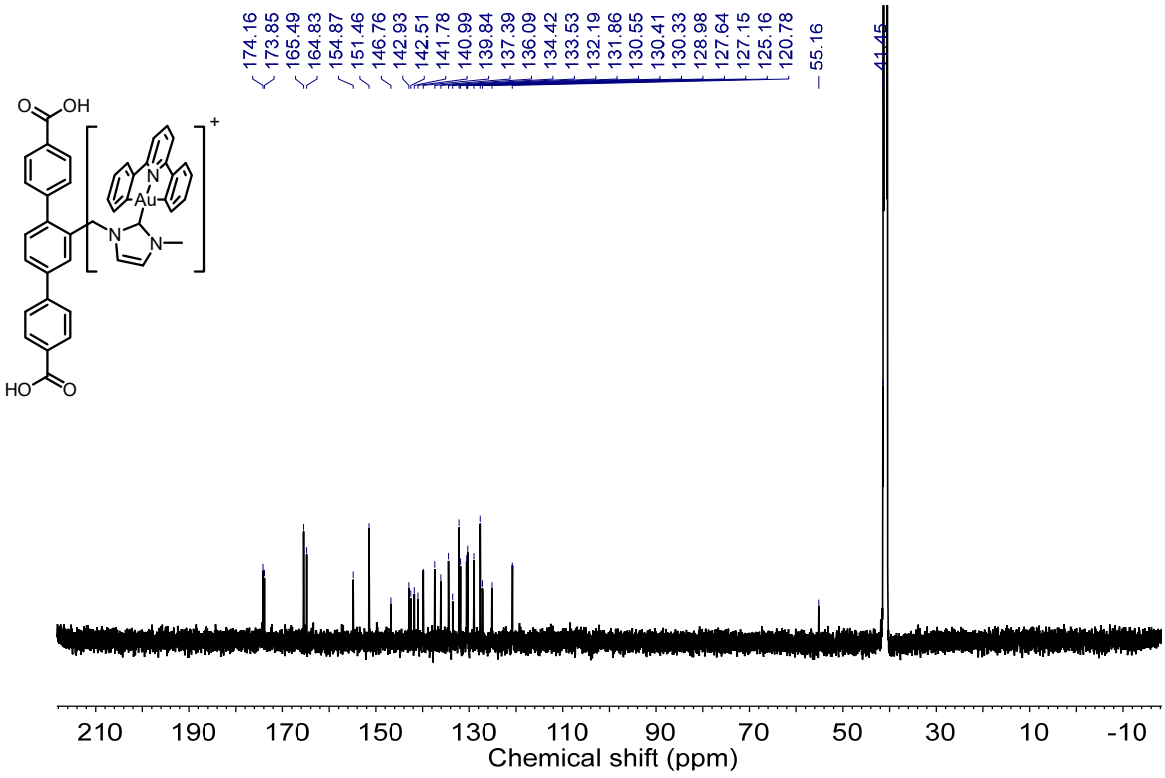
S5, ^{13}C NMR (101 MHz, $CDCl_3$)



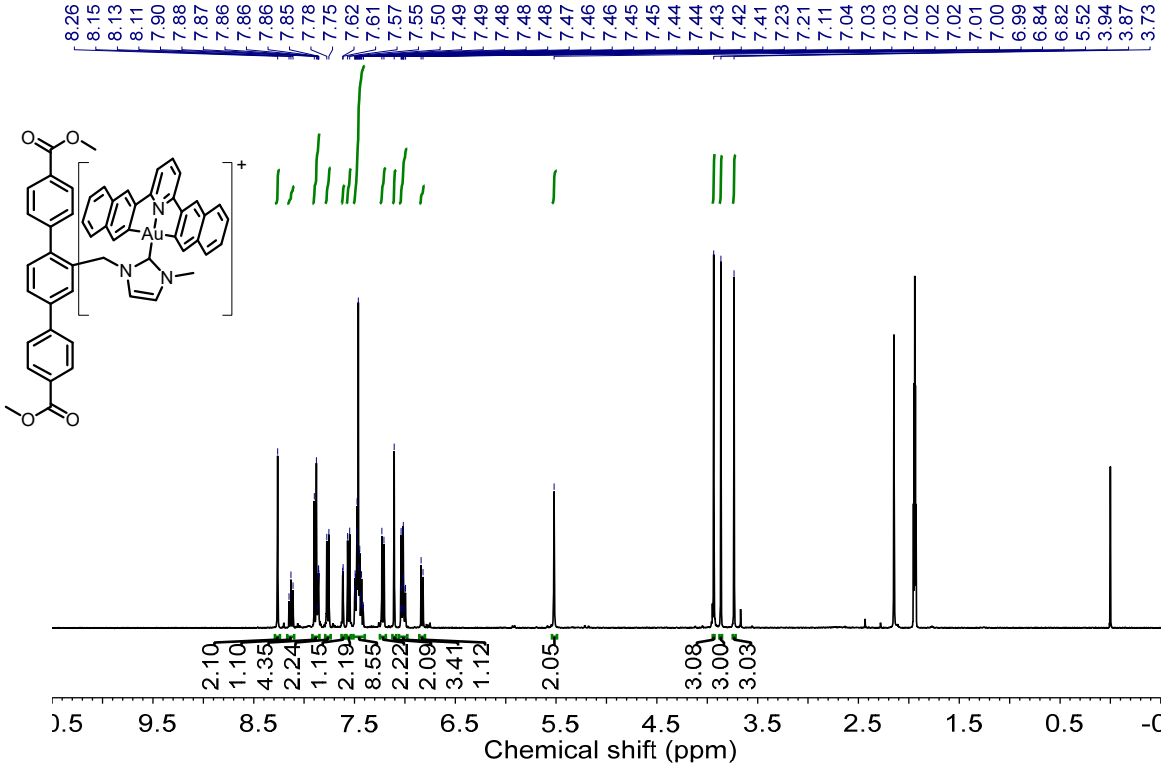
S6, ^{1}H NMR (600 MHz, K_3PO_4/D_2O/DMSO-d_6)



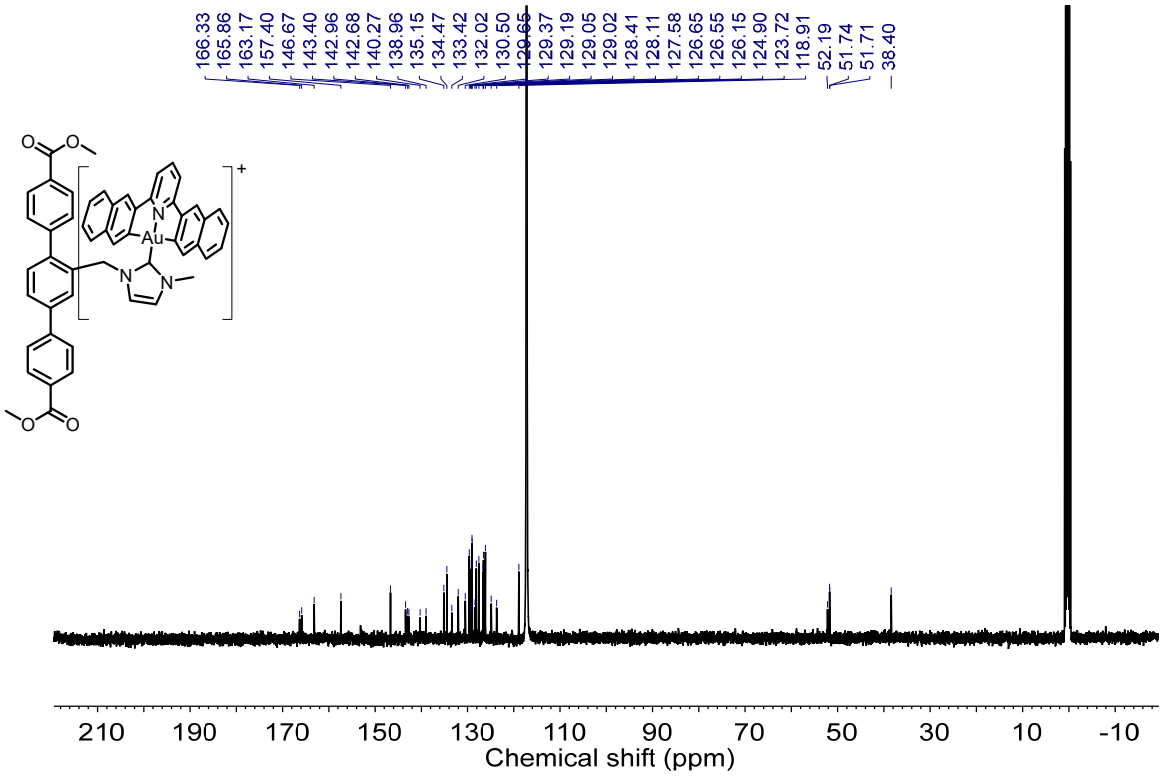
S6, ^{13}C NMR (151 MHz, K_3PO_4/D_2O/DMSO-d_6)



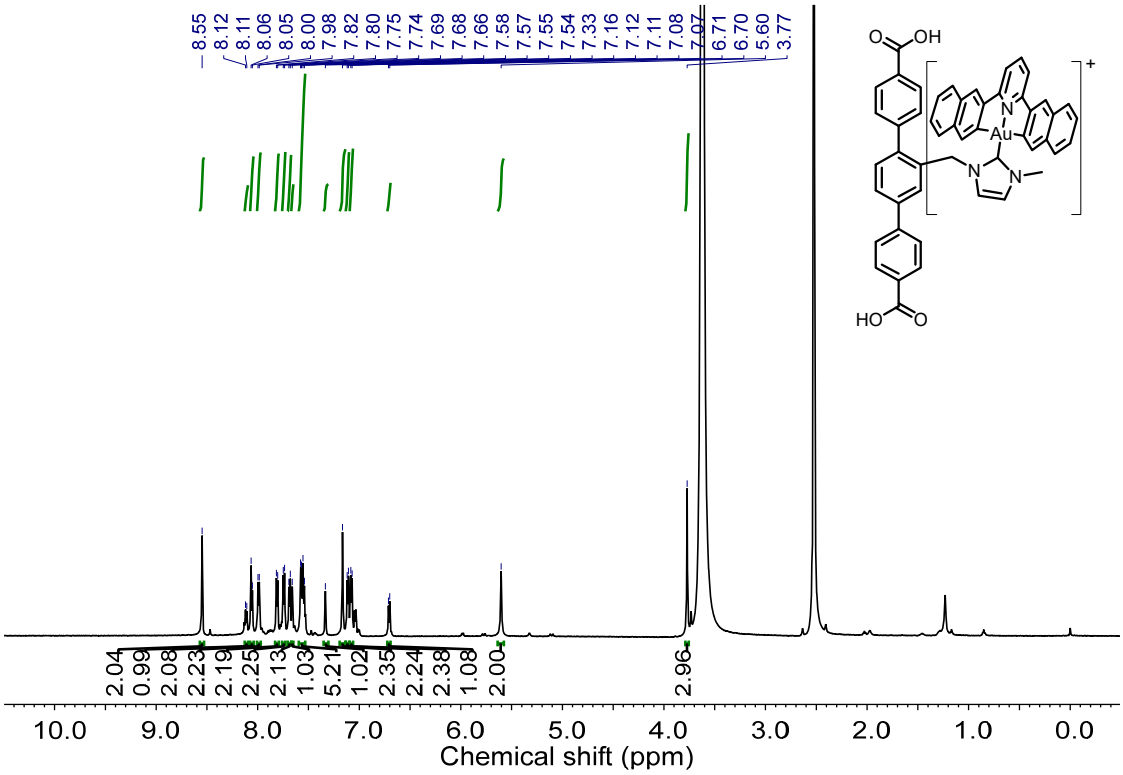
S7, ^{1}H NMR (400 MHz, MeCN-d_3)



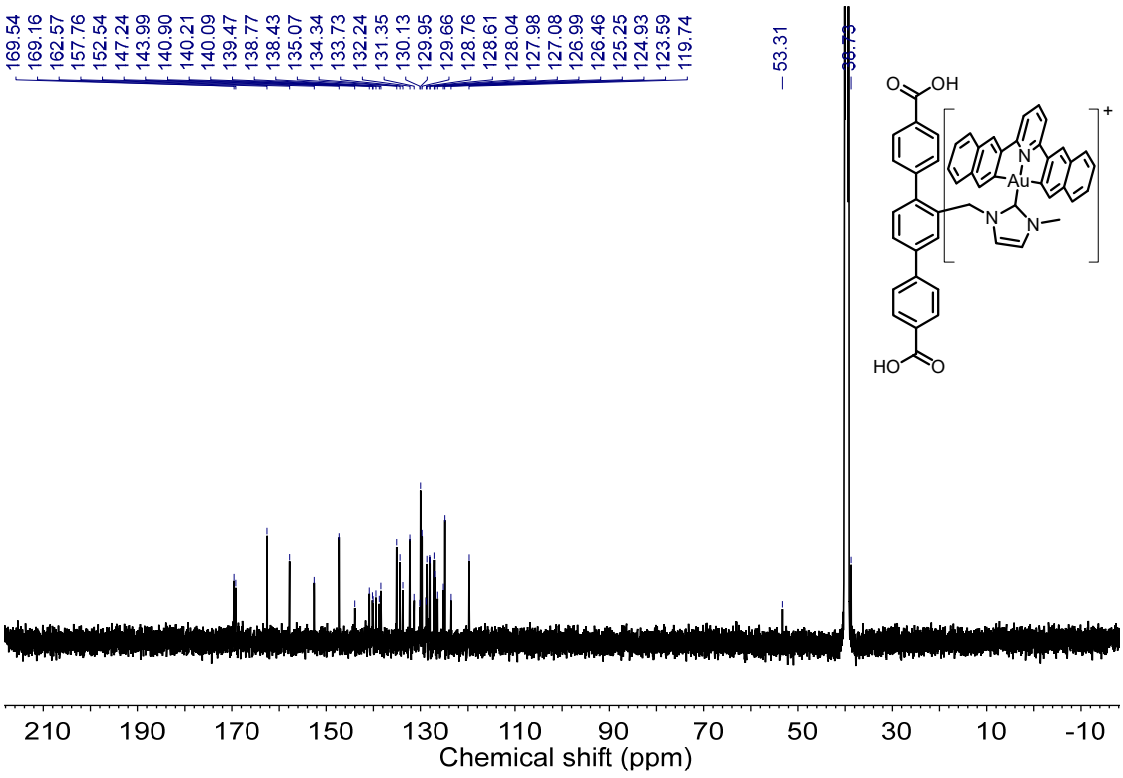
S7, ^{13}C NMR (101 MHz, MeCN-d_3)



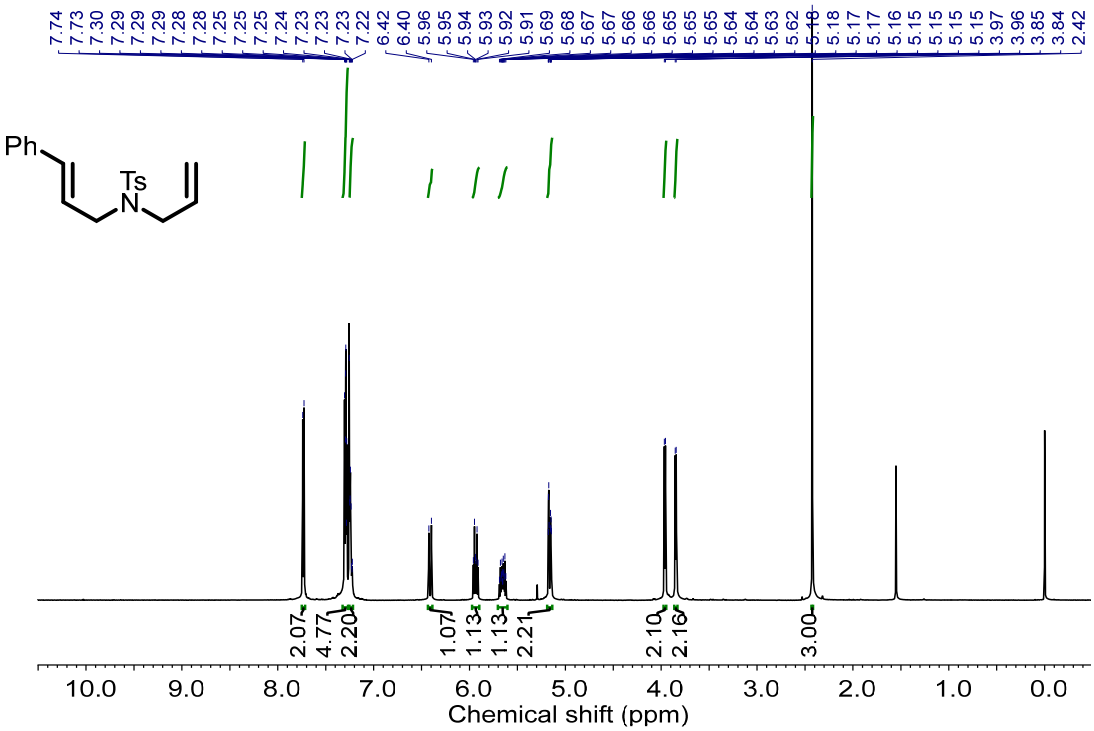
S8, ^{1}H NMR (600 MHz, K_3PO_4/D_2O/DMSO-d_6)



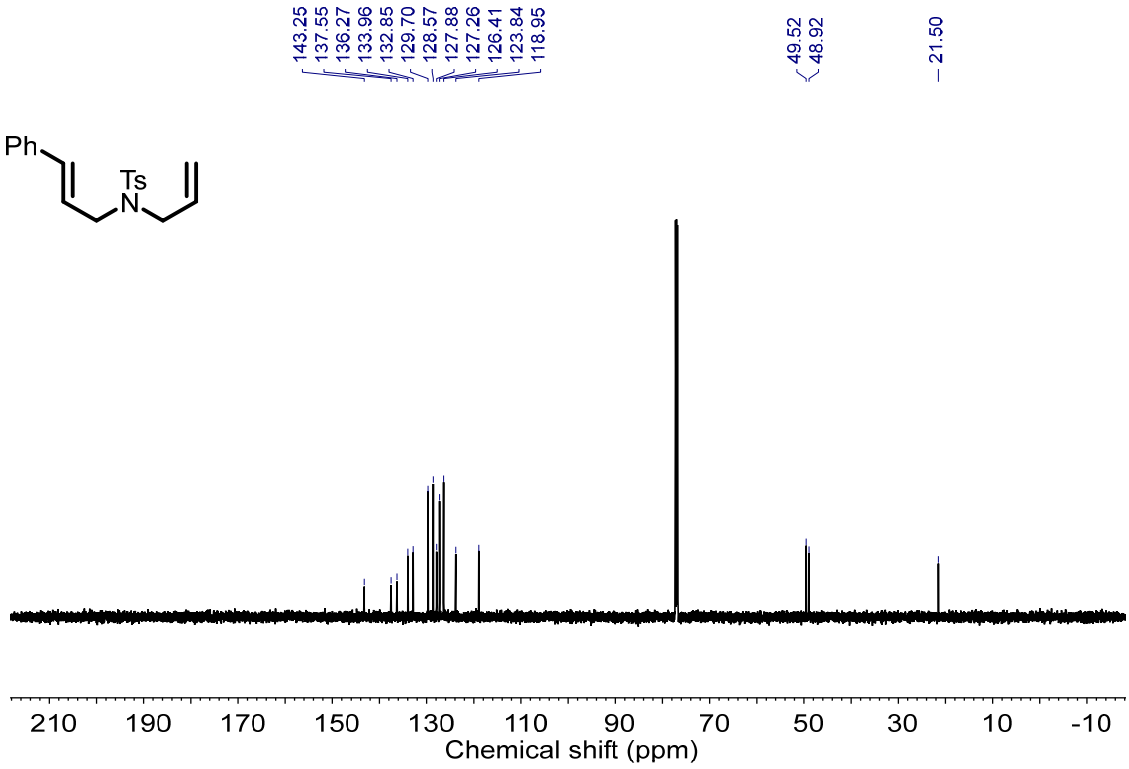
S8, ^{13}C NMR (151 MHz, K_3PO_4/D_2O/DMSO-d_6)



1a, ^{1}H NMR (600 MHz, $CDCl_3$)



1a, ^{13}C NMR (151 MHz, $CDCl_3$)



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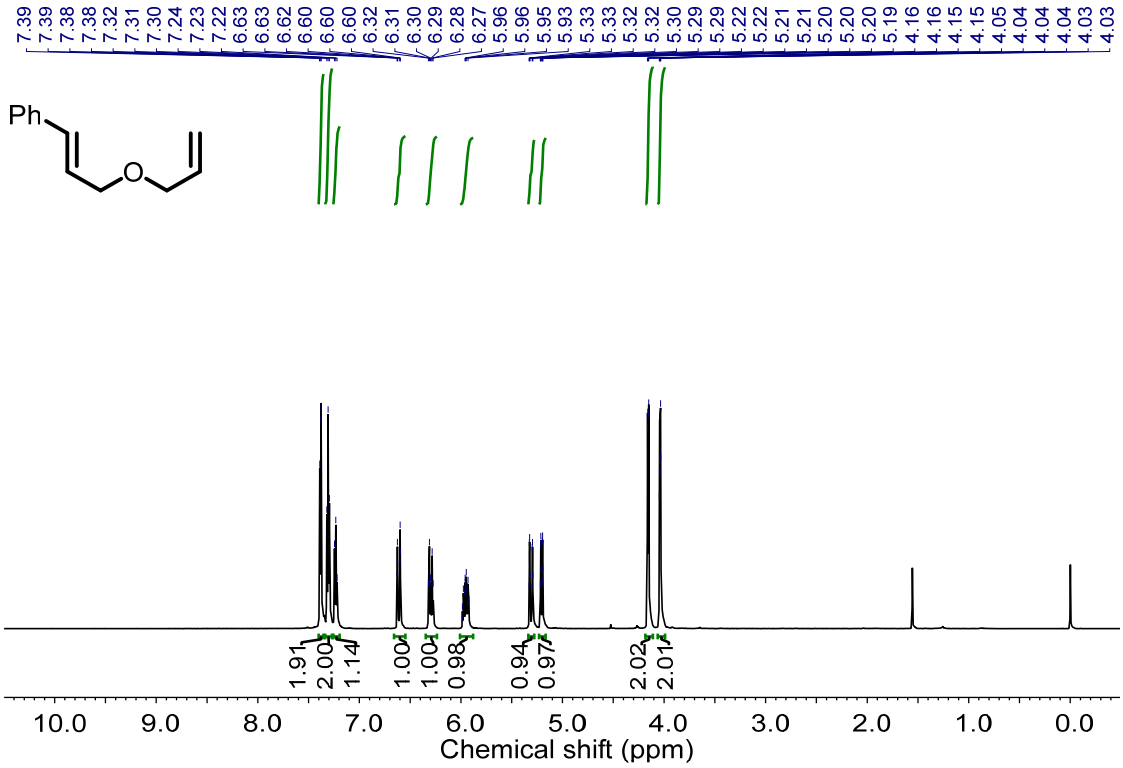

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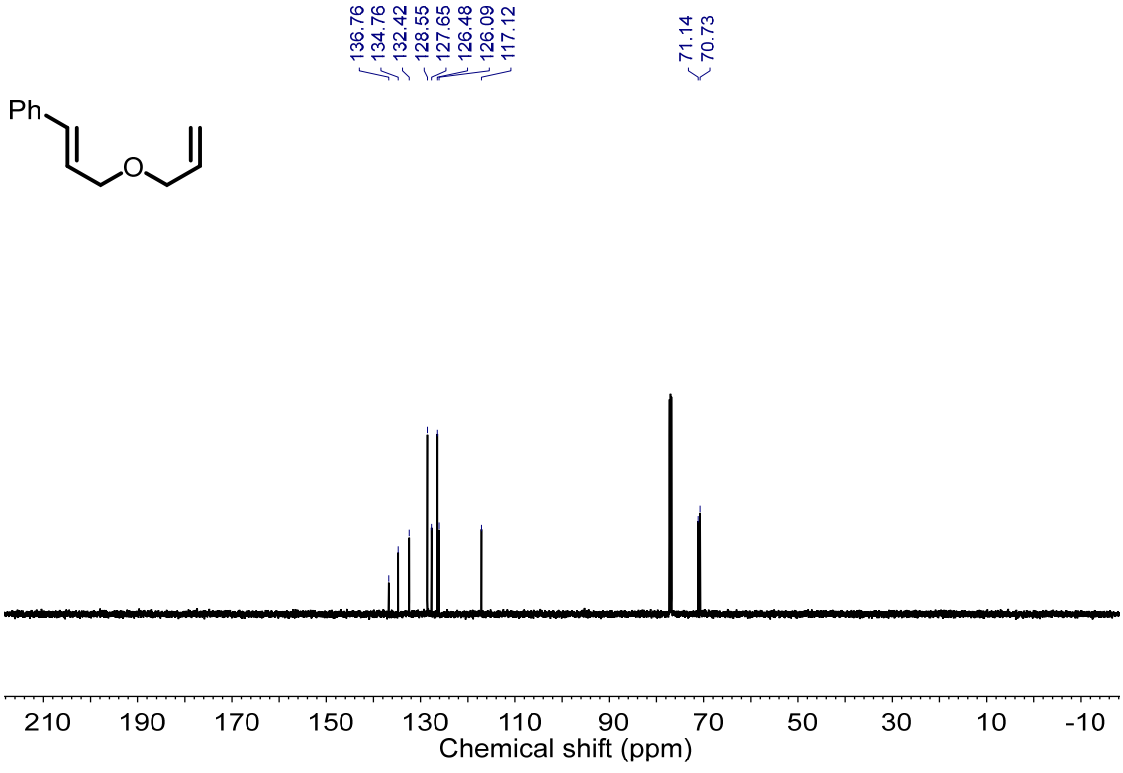

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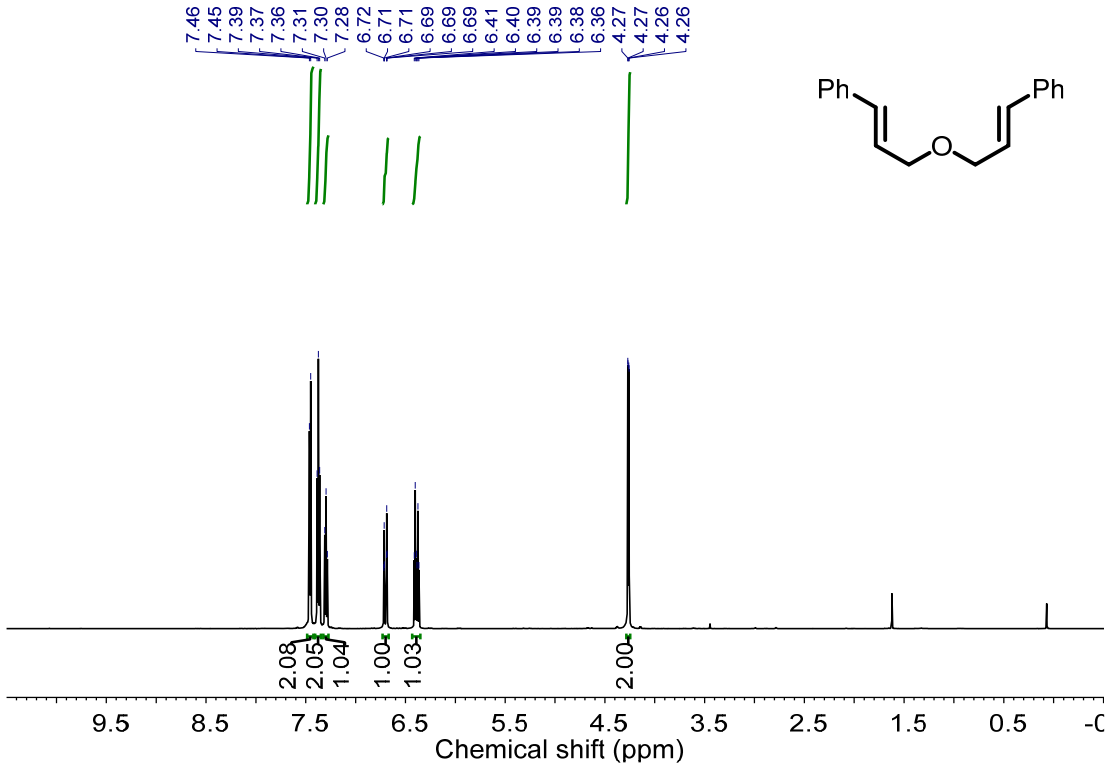

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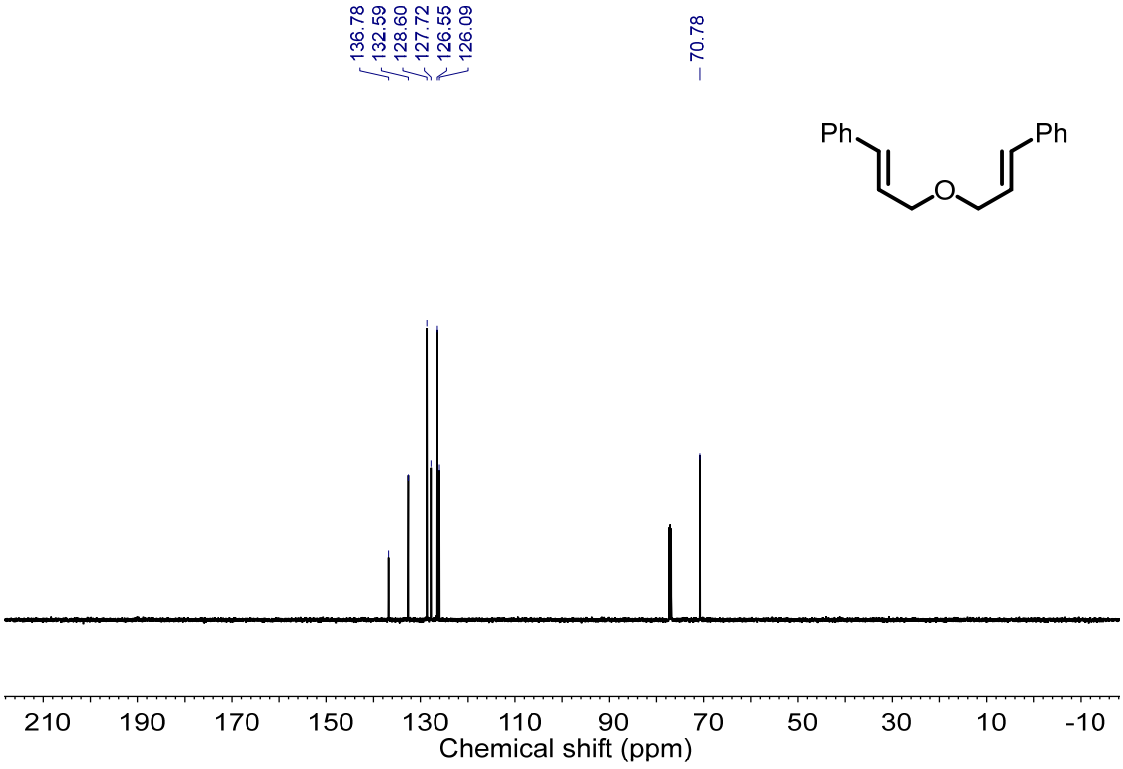

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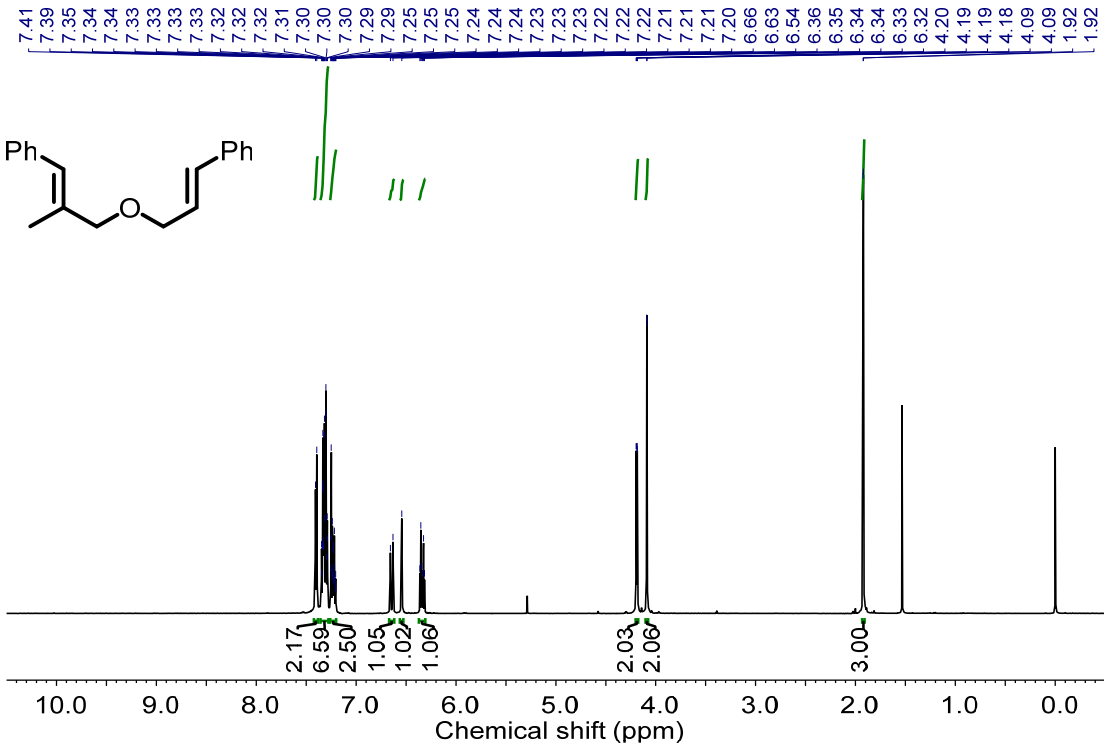

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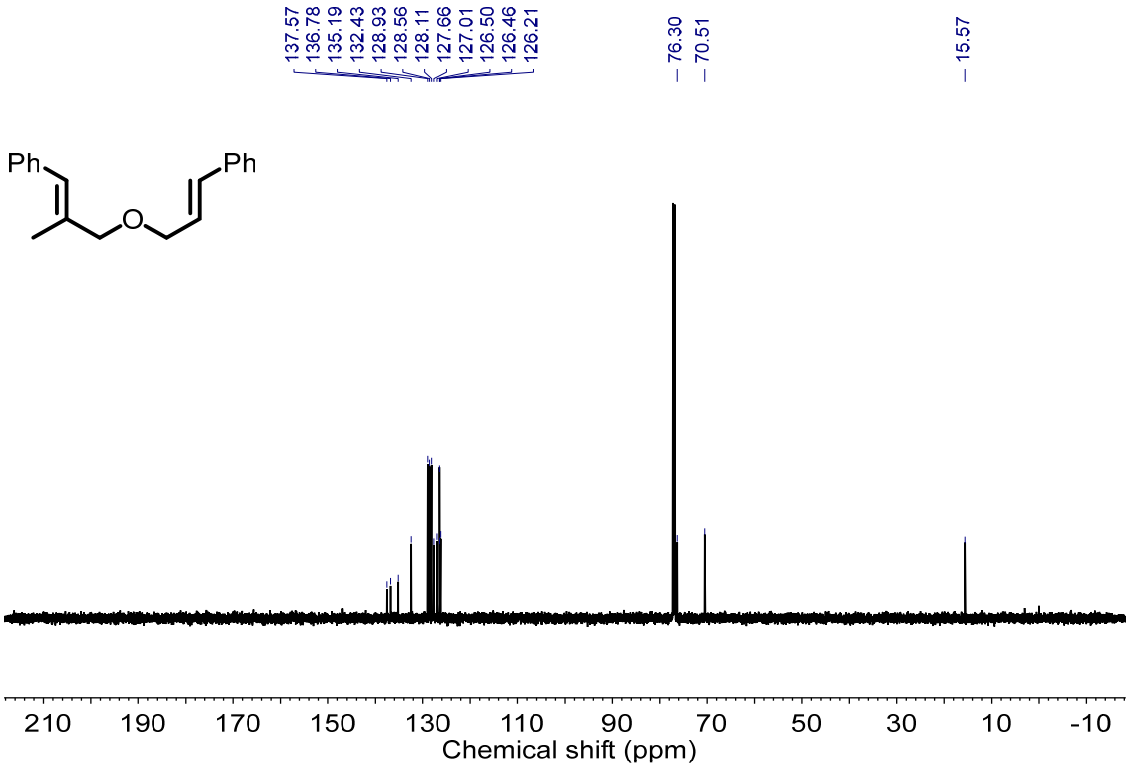

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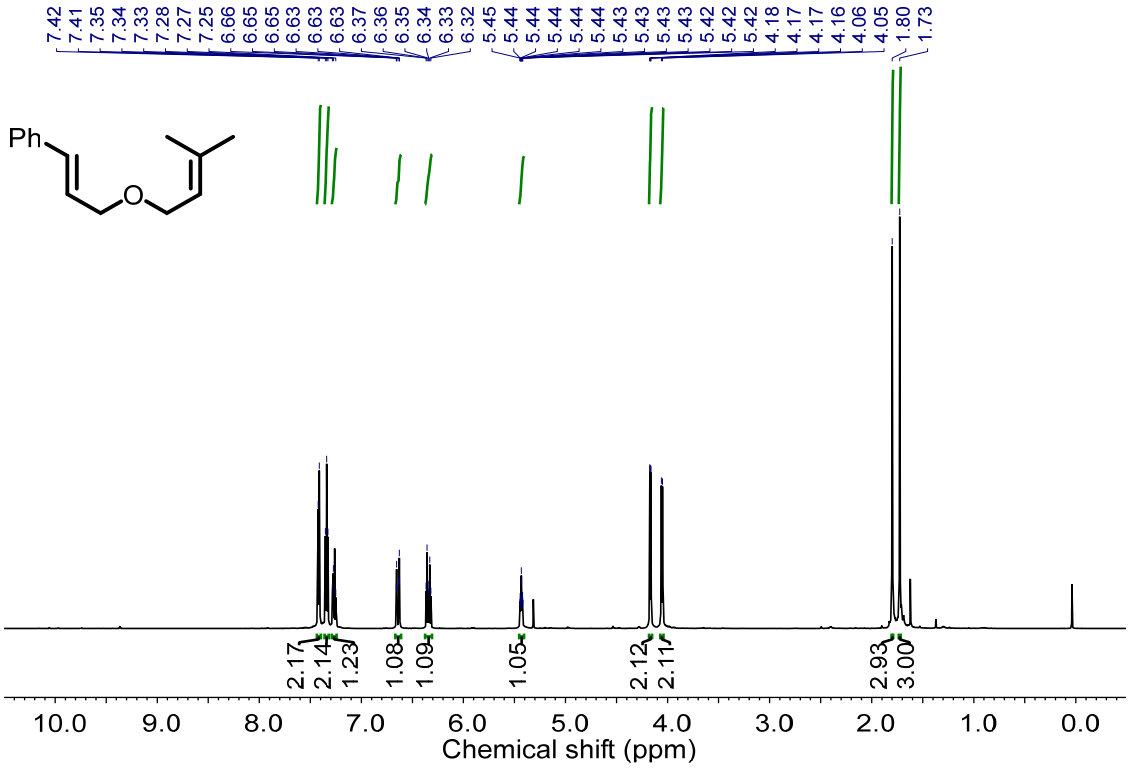

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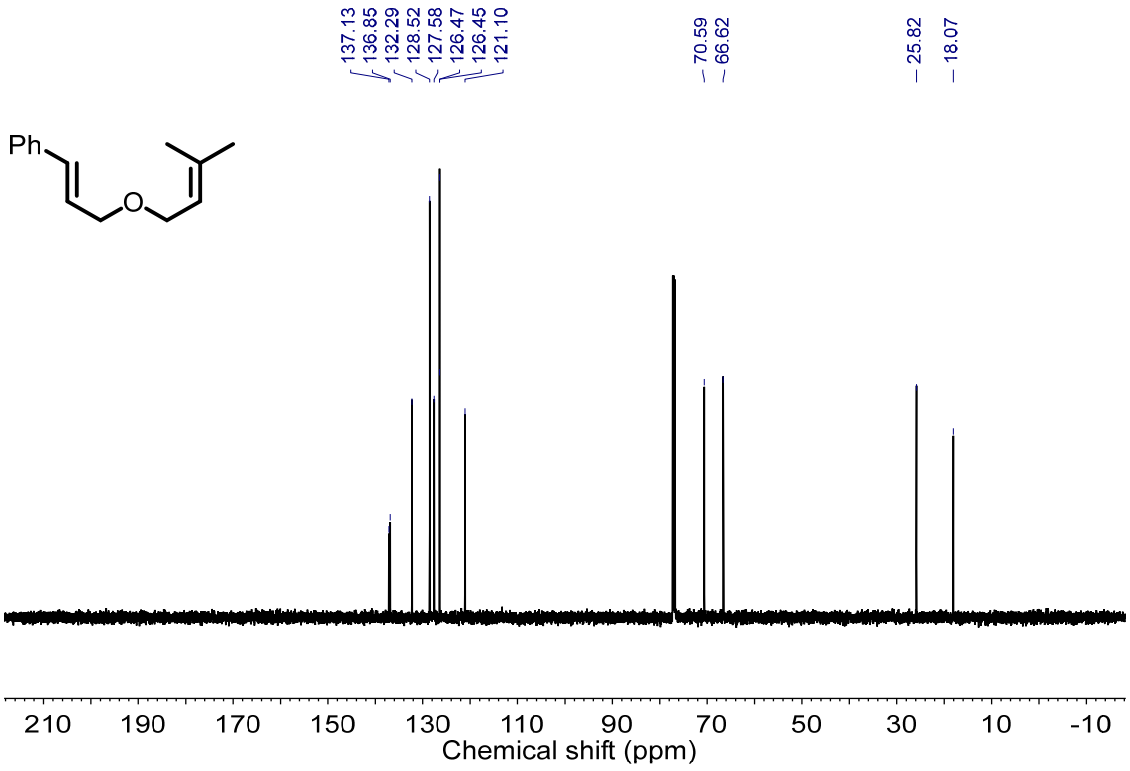

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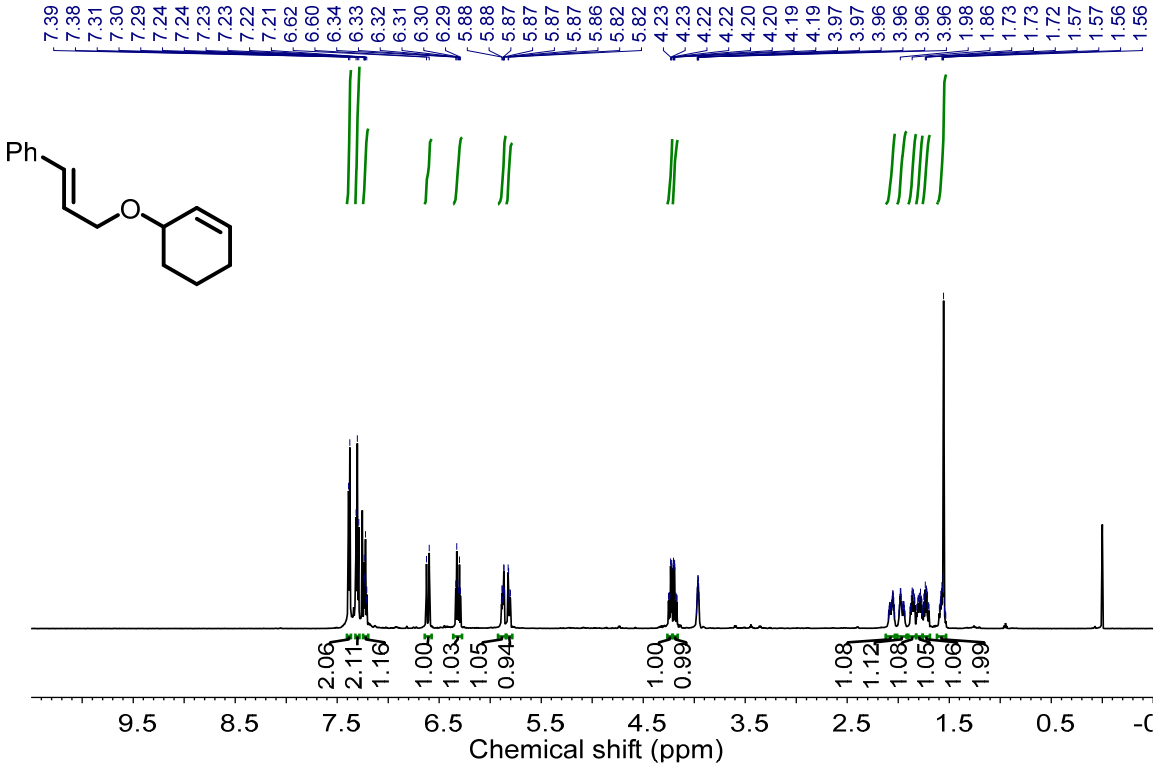

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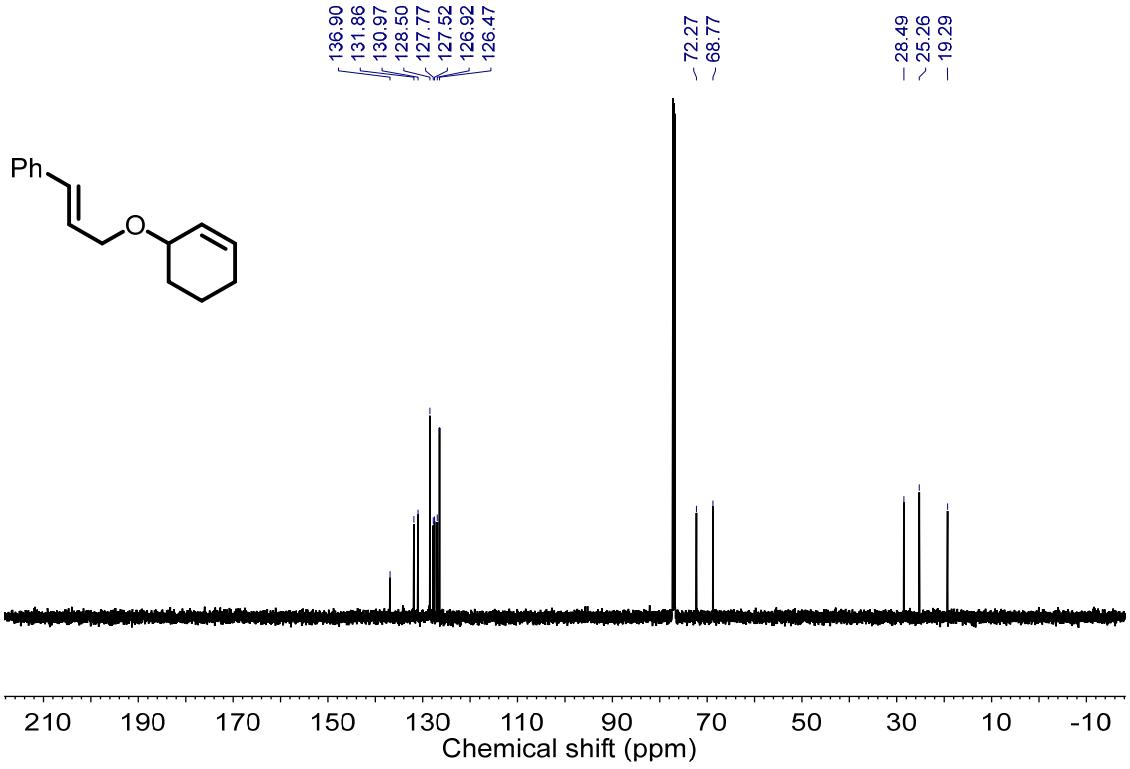
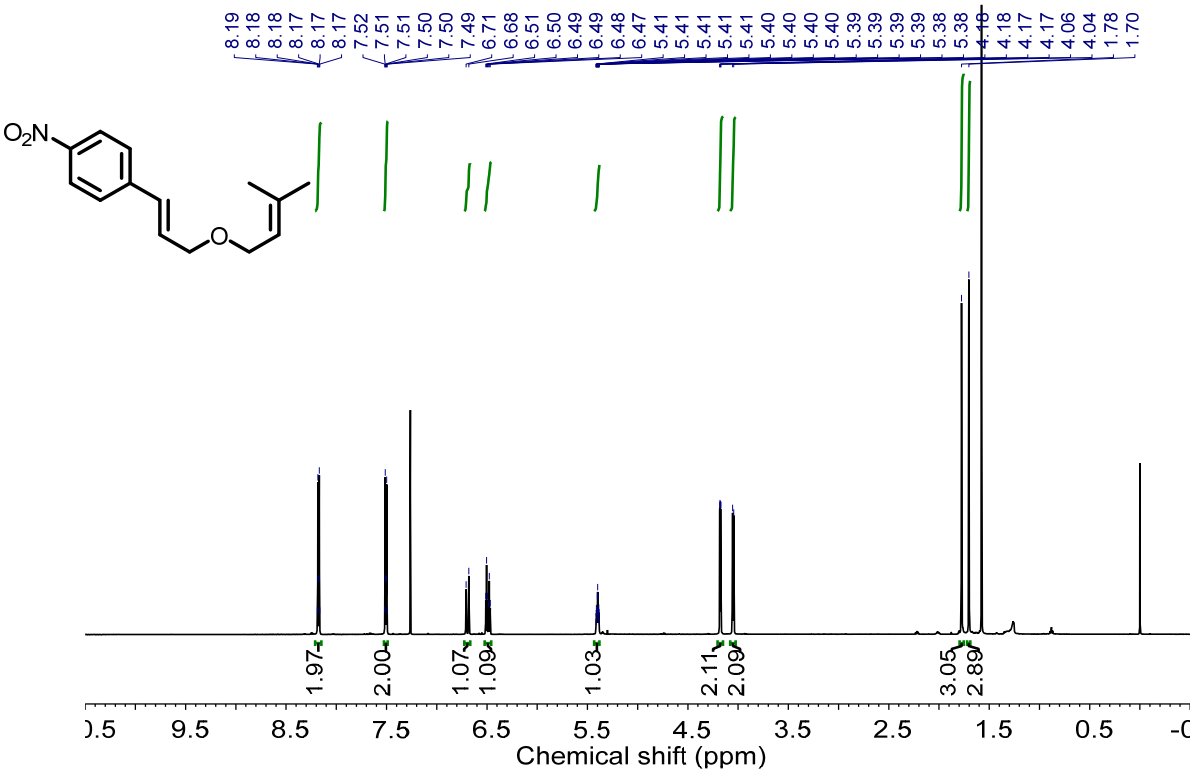
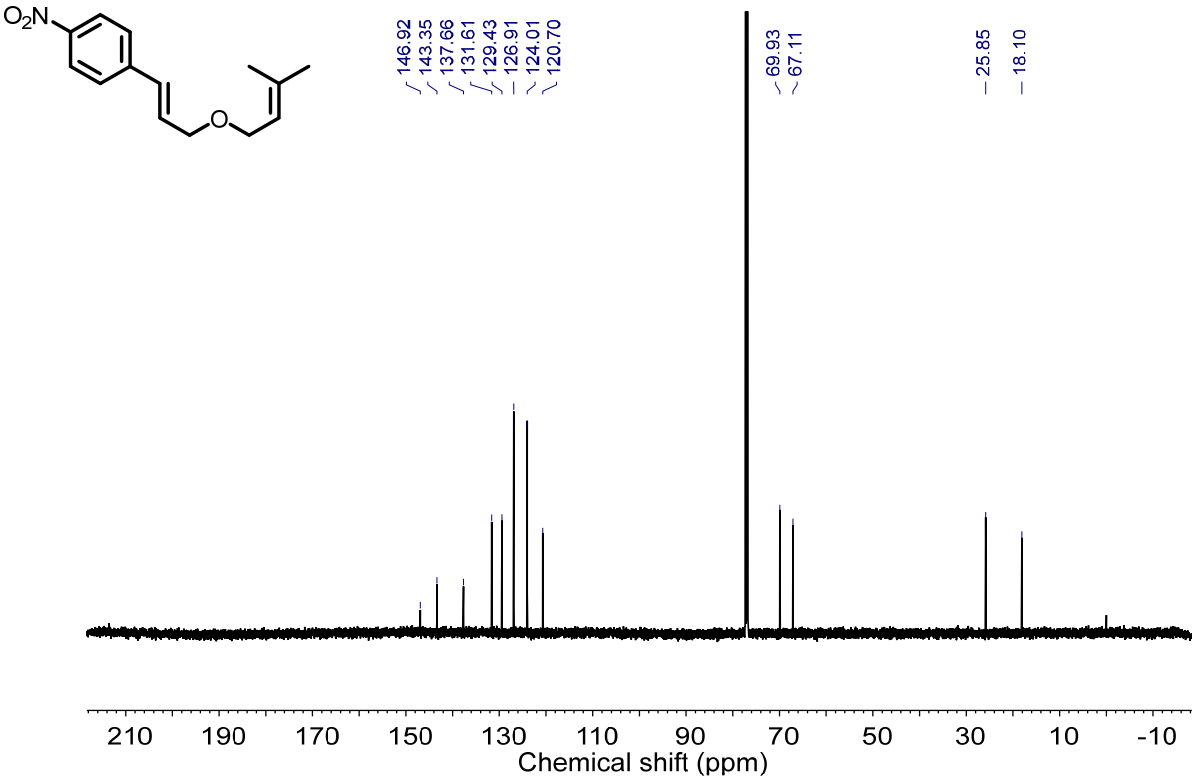


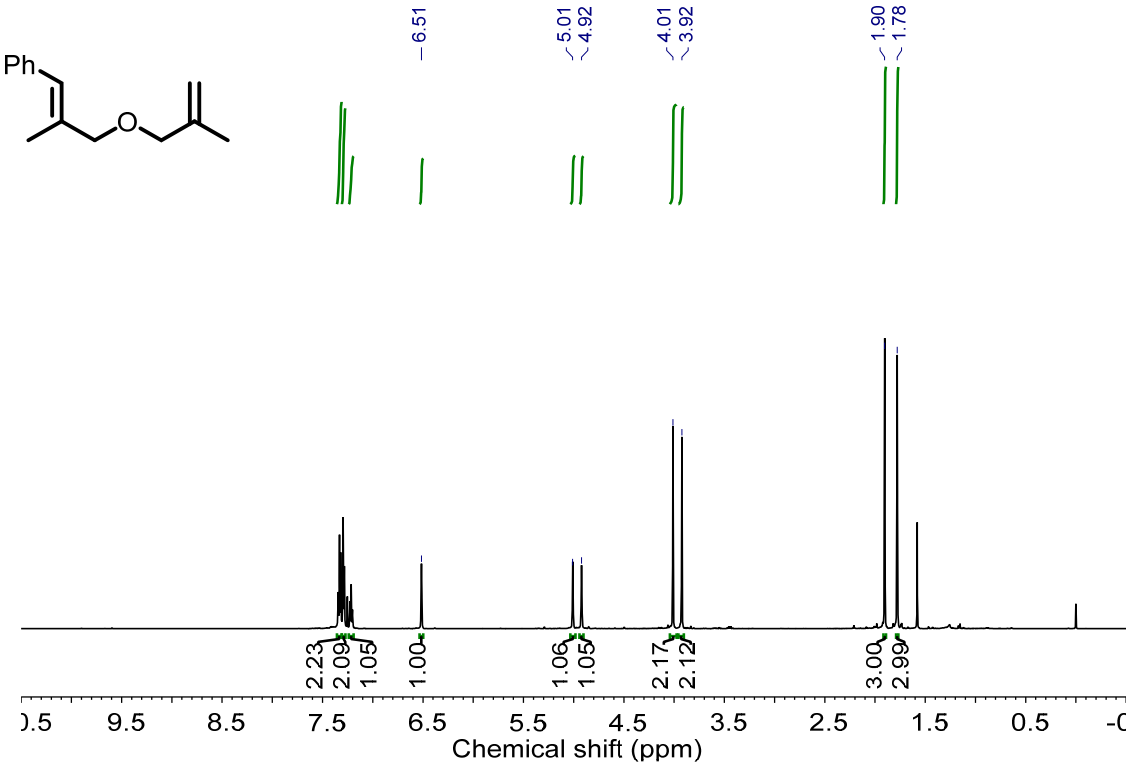
1g, ^{1}H NMR (600 MHz, Chloroform-*d*)



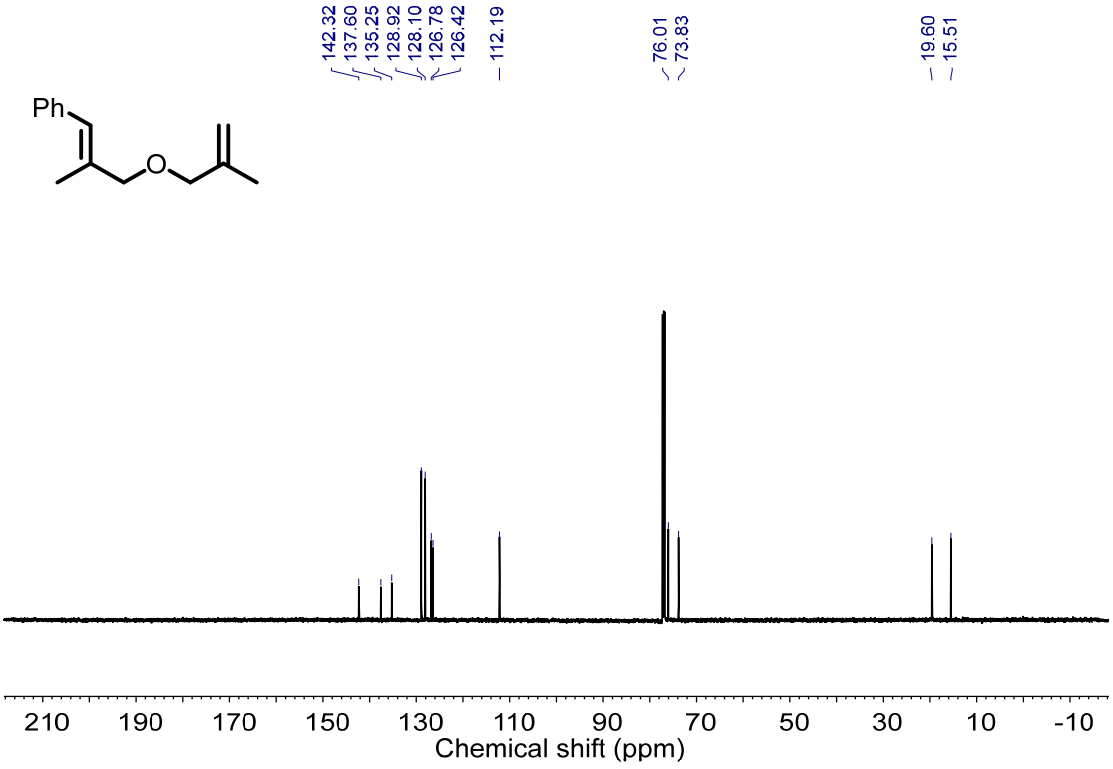
1g, ^{13}C NMR (151 MHz, Chloroform-*d*)



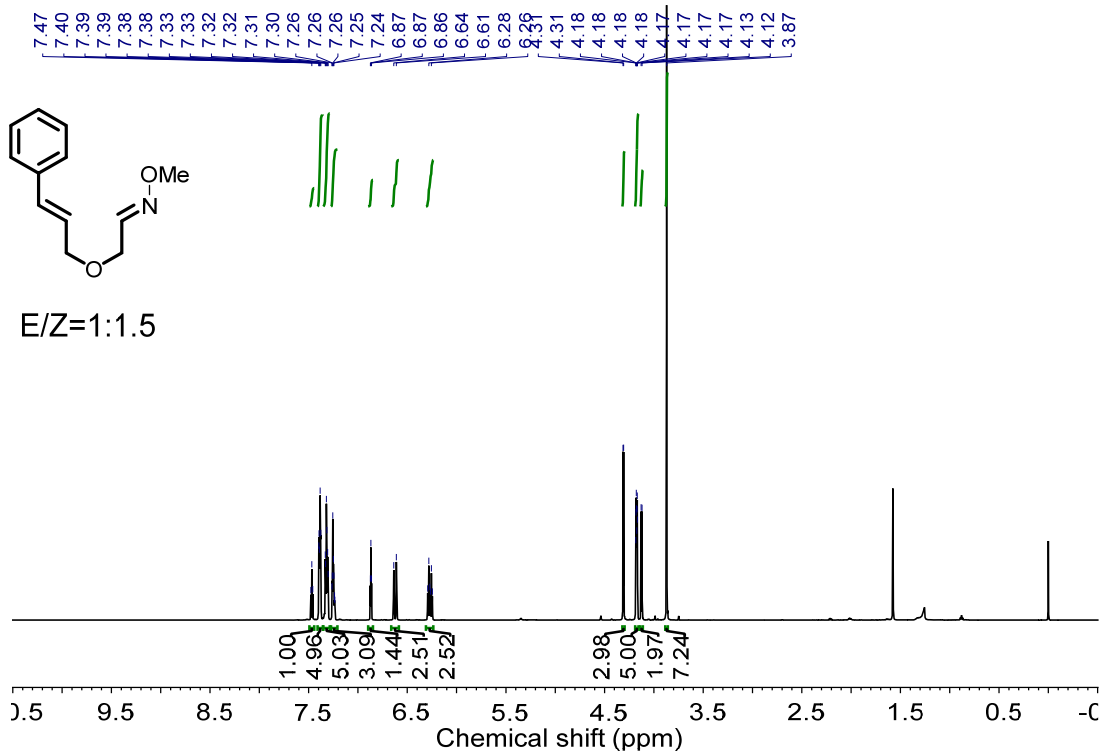
(*E*)-1h, ^{1}H NMR (600 MHz, Chloroform-*d*)



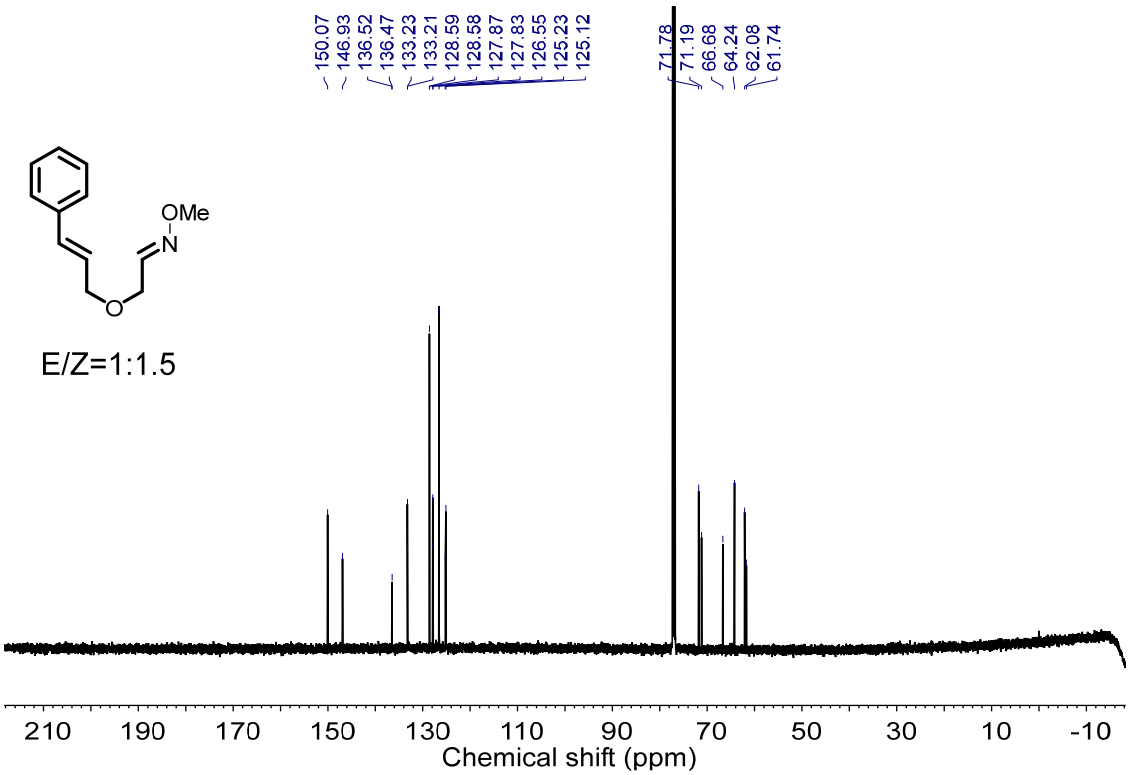
(*E*)-1h, ^{13}C NMR (151 MHz, Chloroform-*d*)



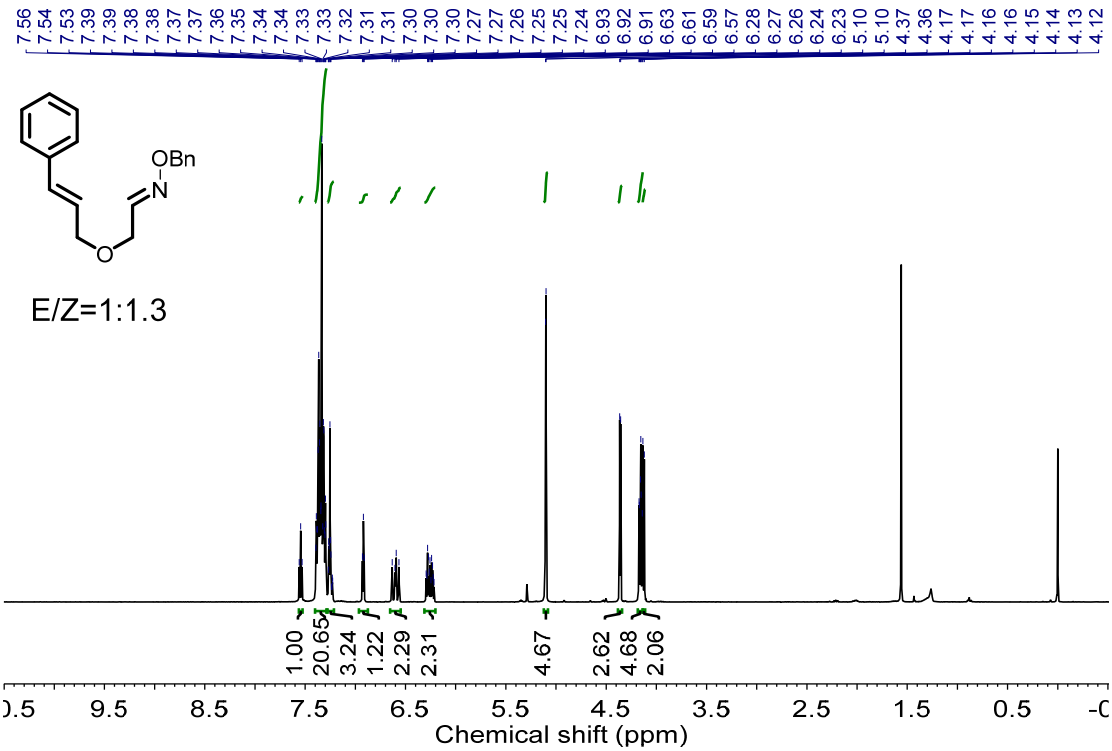
3a, ^{1}H NMR (600 MHz, $CDCl_3$)



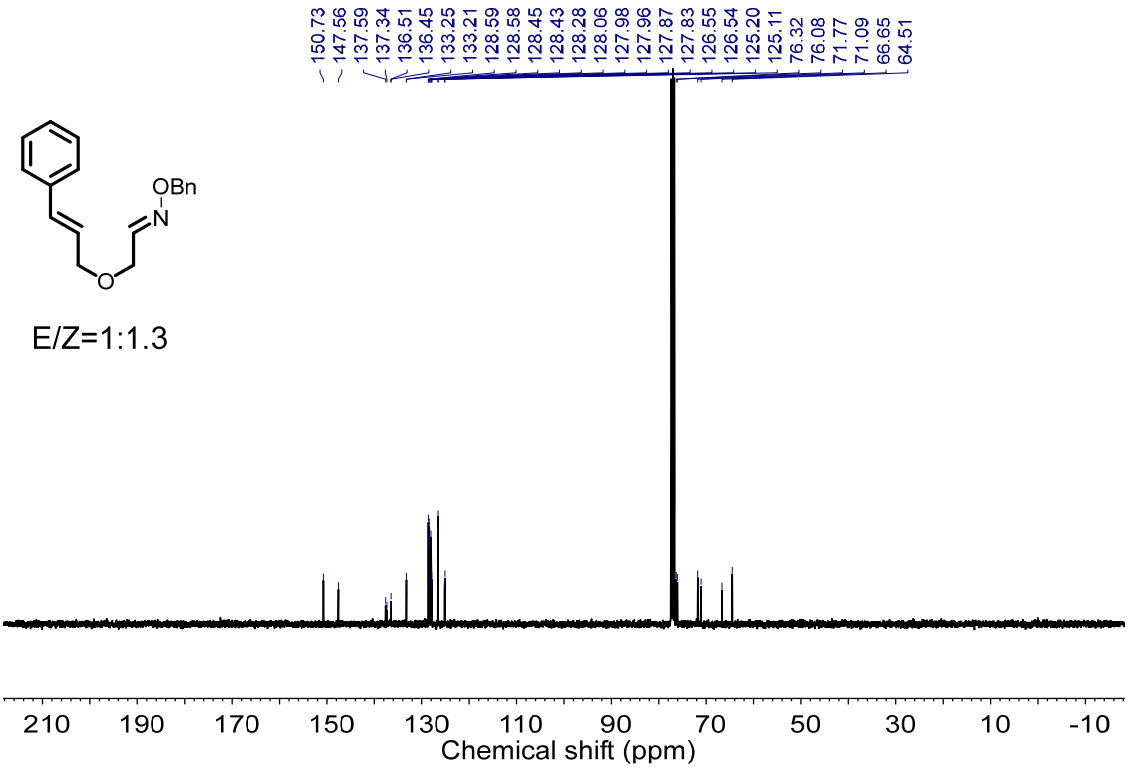
3a, ^{13}C NMR (151 MHz, $CDCl_3$)



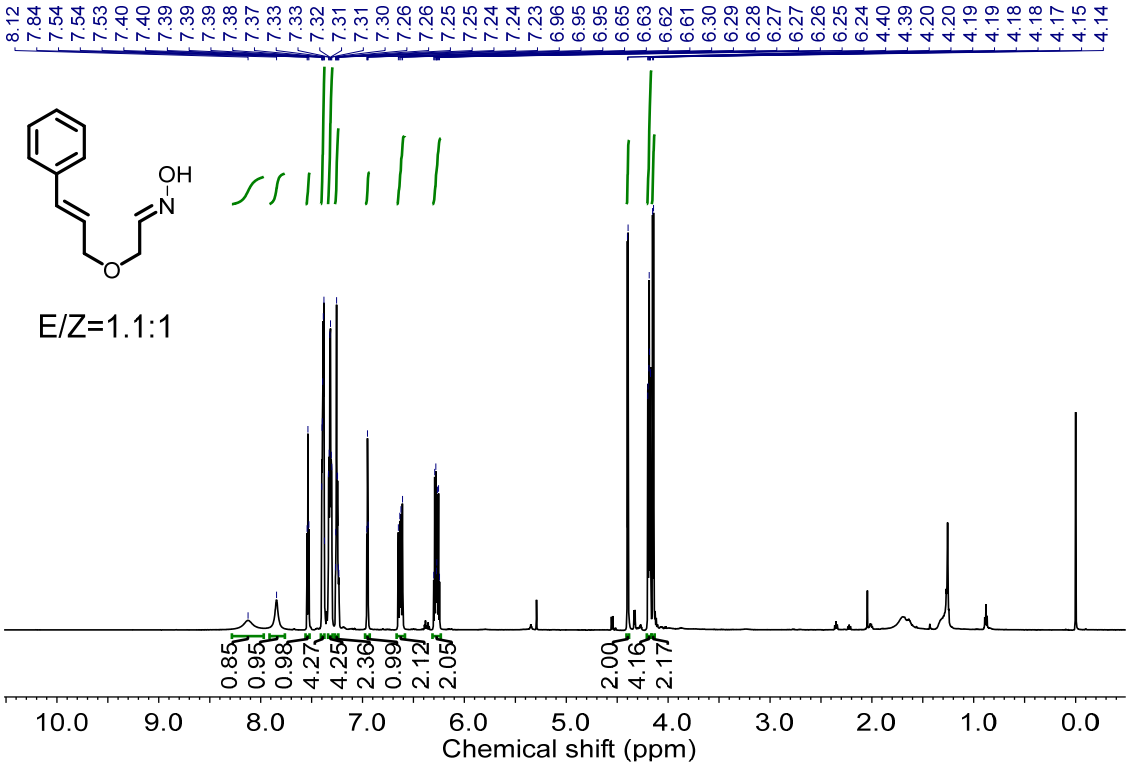
3b, ^{1}H NMR (400 MHz, $CDCl_3$)



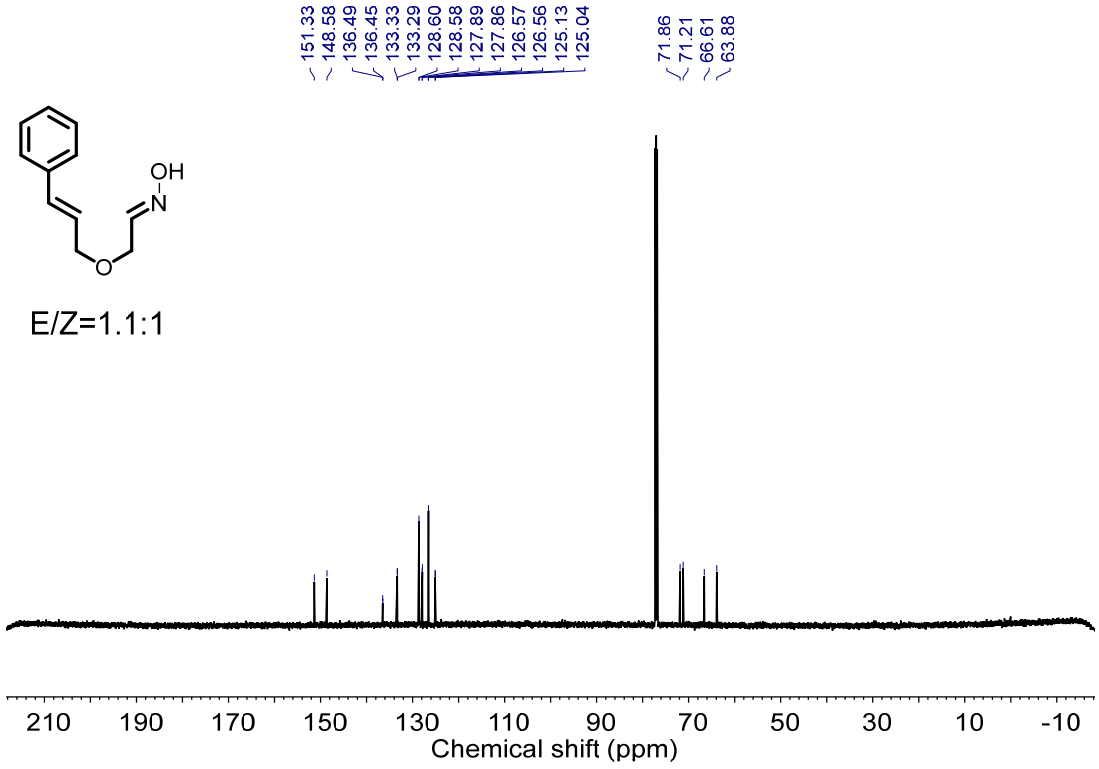
3b, ^{13}C NMR (101 MHz, $CDCl_3$)



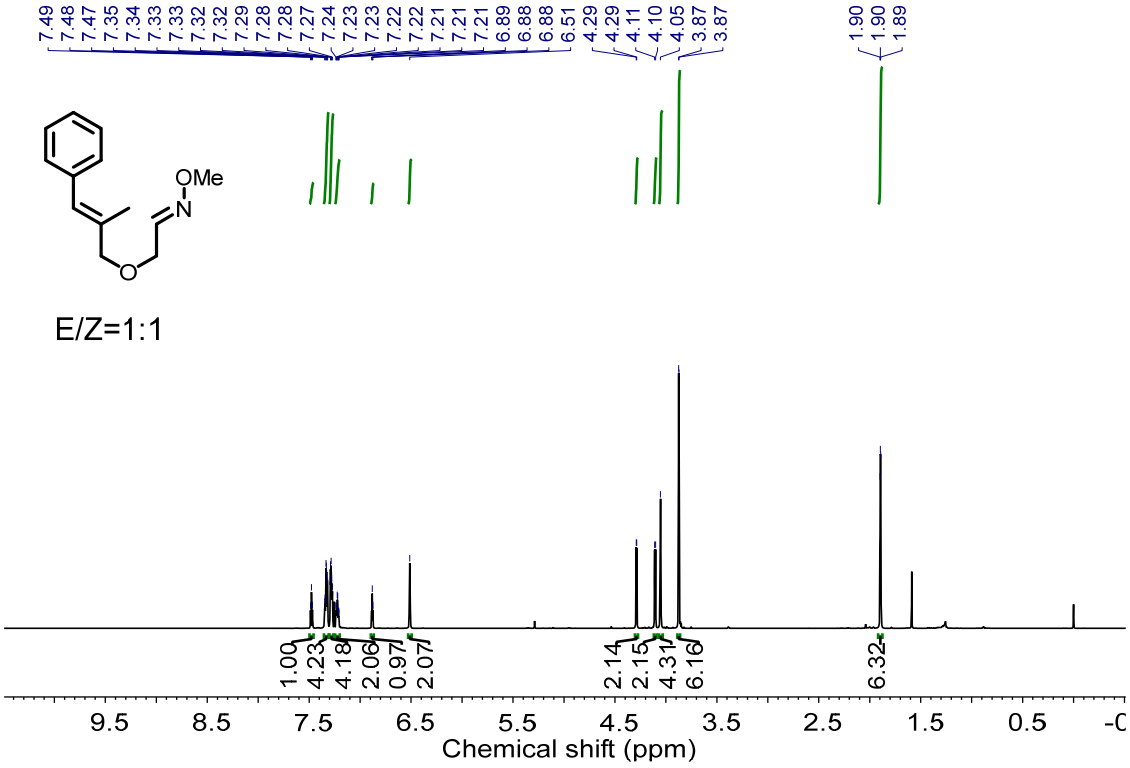
3c, ^{1}H NMR (600 MHz, $CDCl_3$)



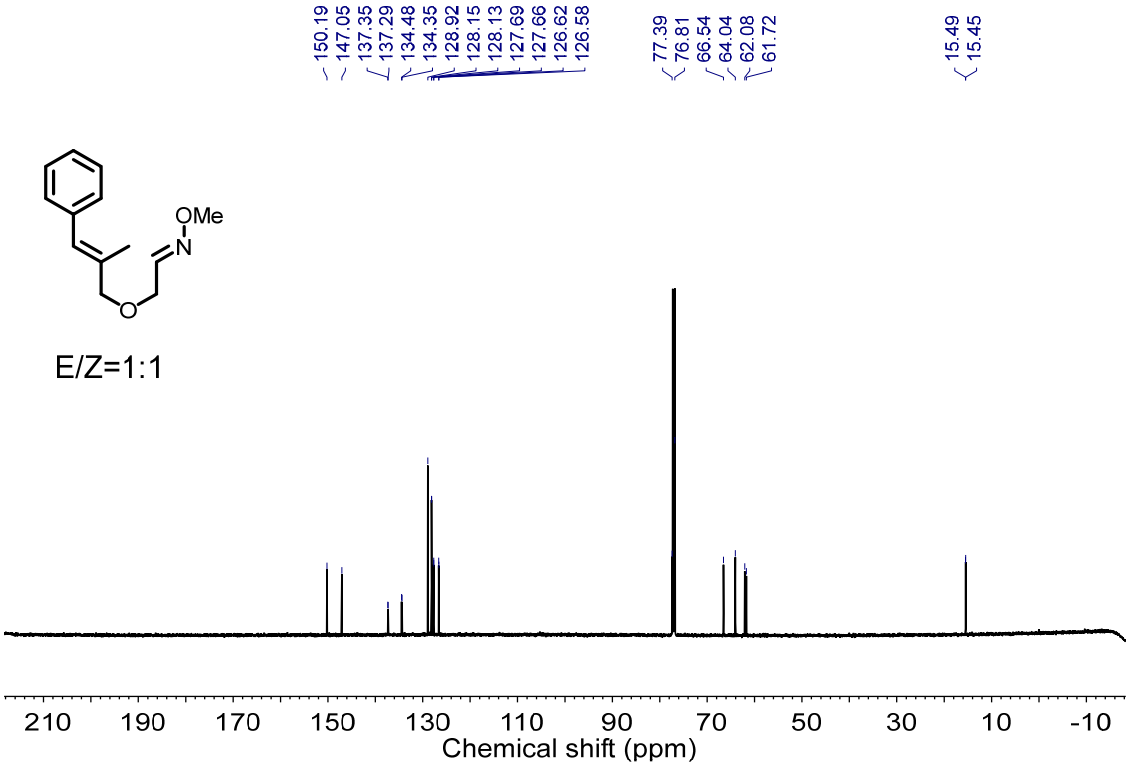
3c, ^{13}C NMR (151 MHz, $CDCl_3$)



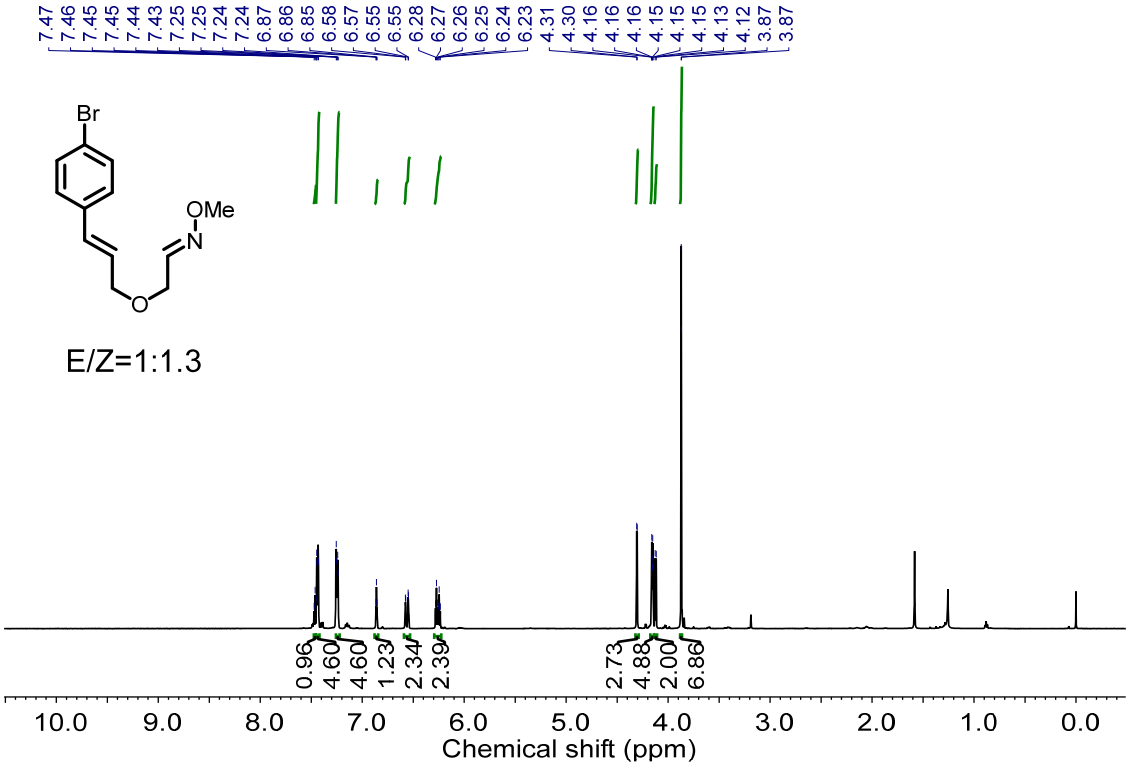
3d, ^{1}H NMR (600 MHz, $CDCl_3$)



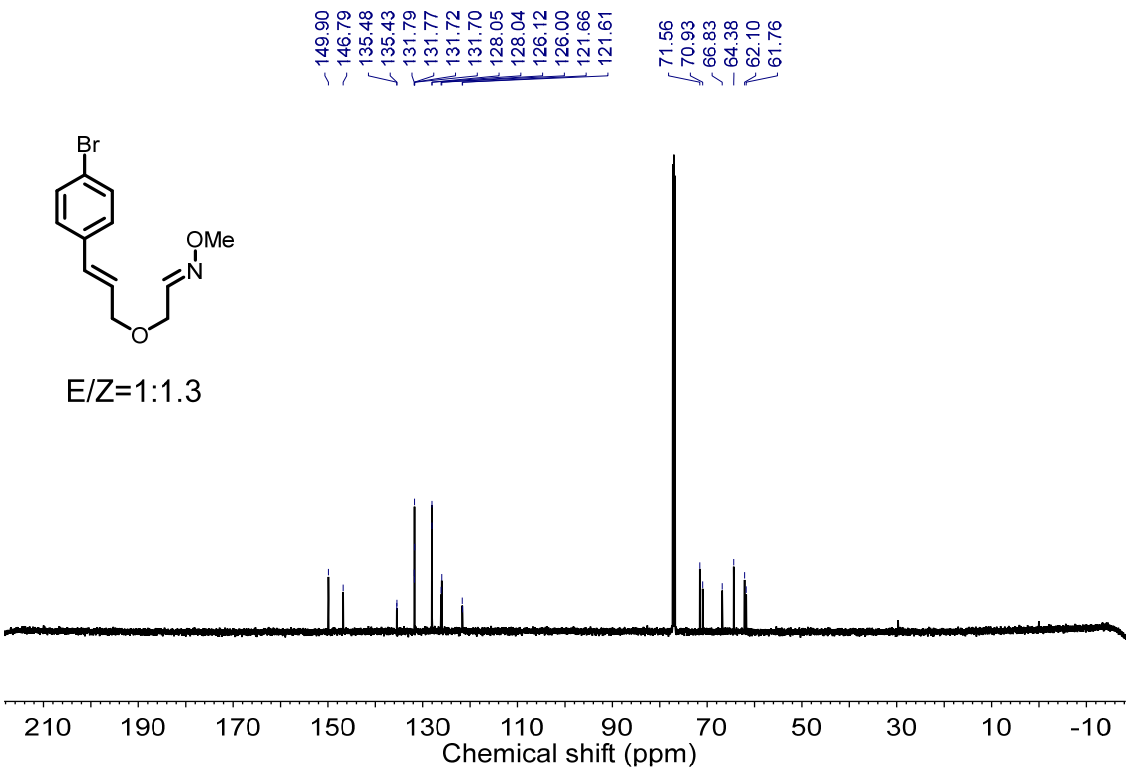
3d, ^{13}C NMR (151 MHz, $CDCl_3$)



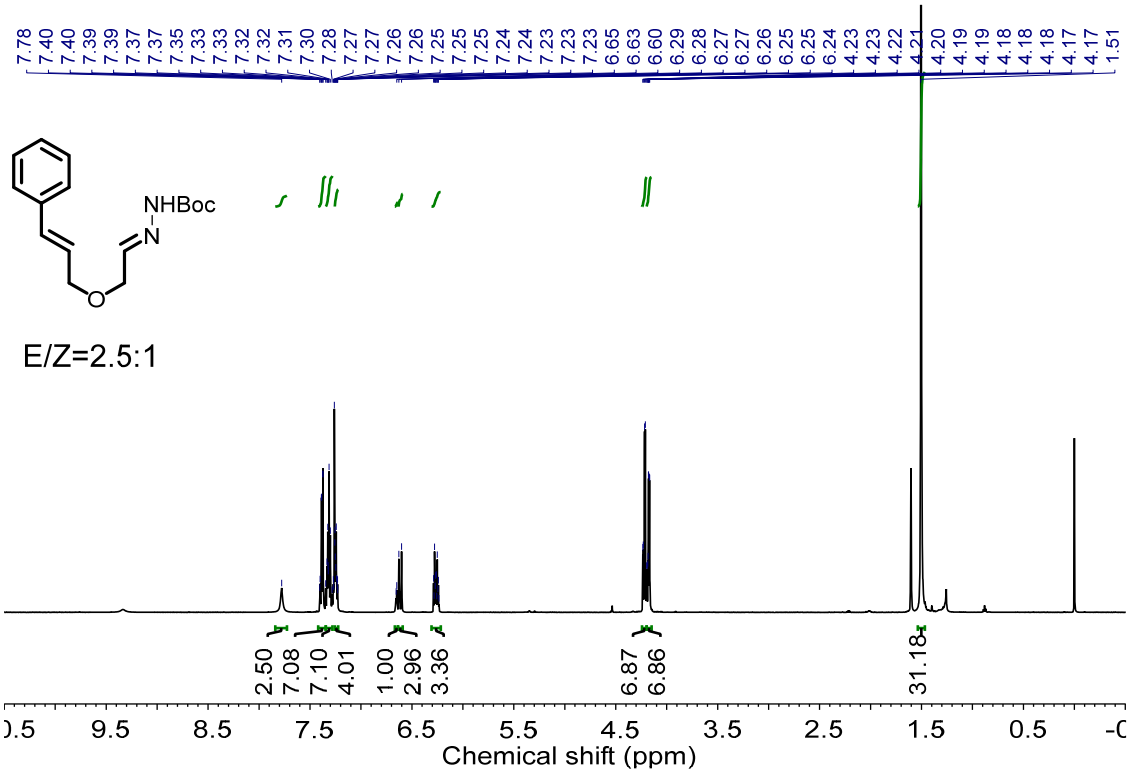
3e, ^{1}H NMR (600 MHz, $CDCl_3$)



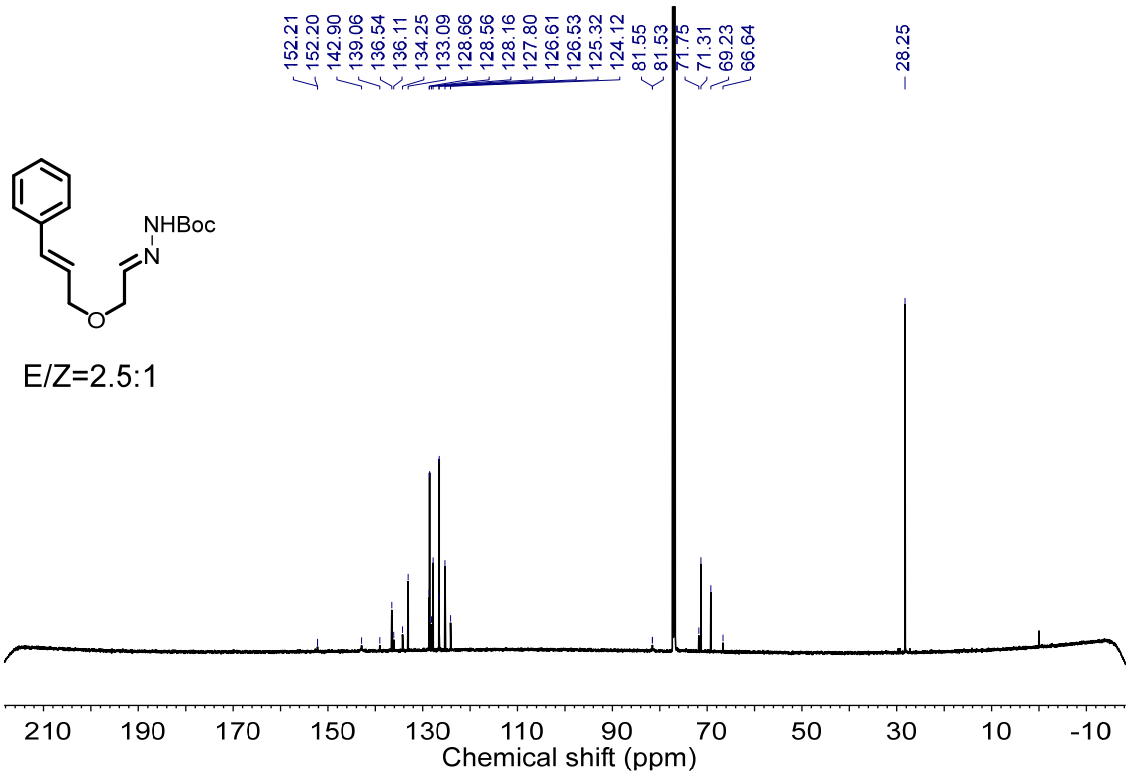
3e, ^{13}C NMR (151 MHz, $CDCl_3$)



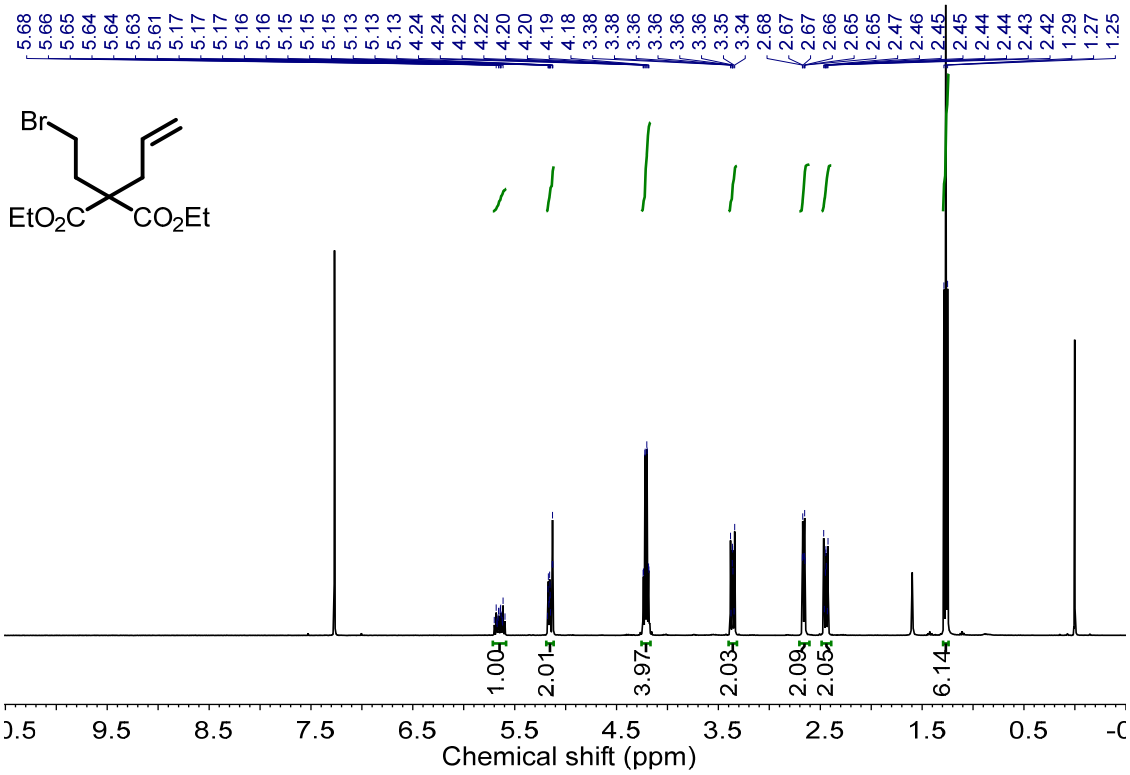
3f, ^{1}H NMR (600 MHz, $CDCl_3$)



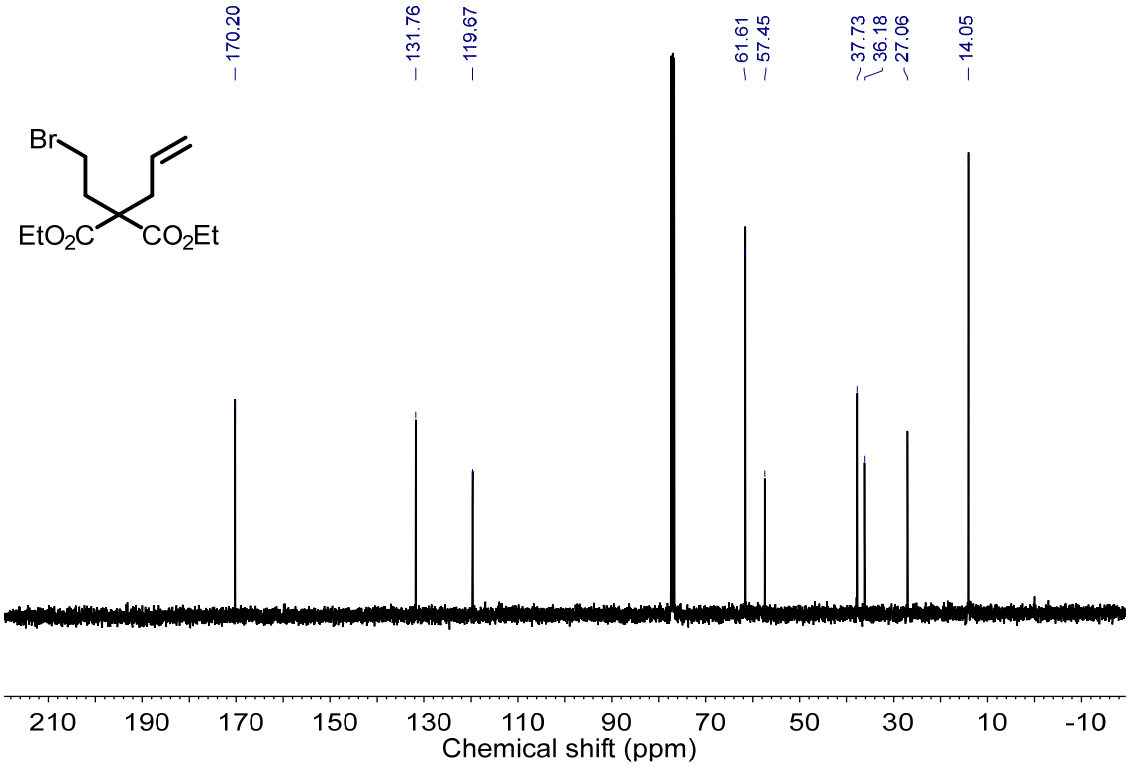
3f, ^{13}C NMR (151 MHz, $CDCl_3$)



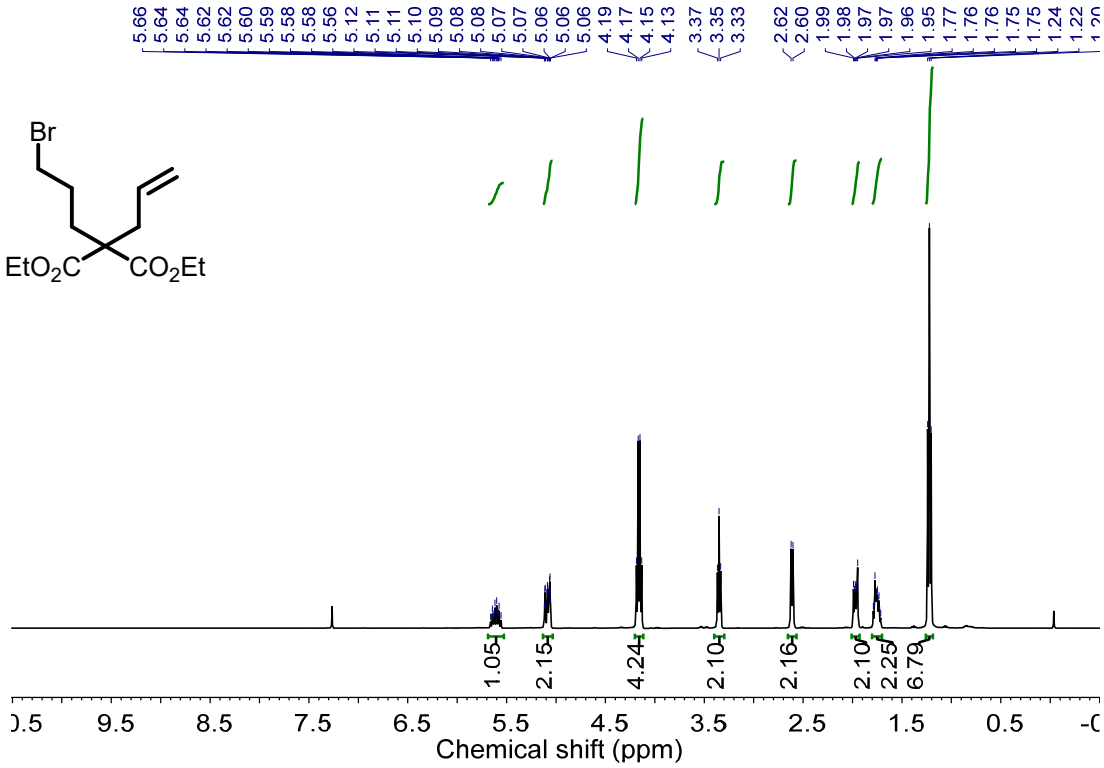
9a, ^{1}H NMR (400 MHz, $CDCl_3$)



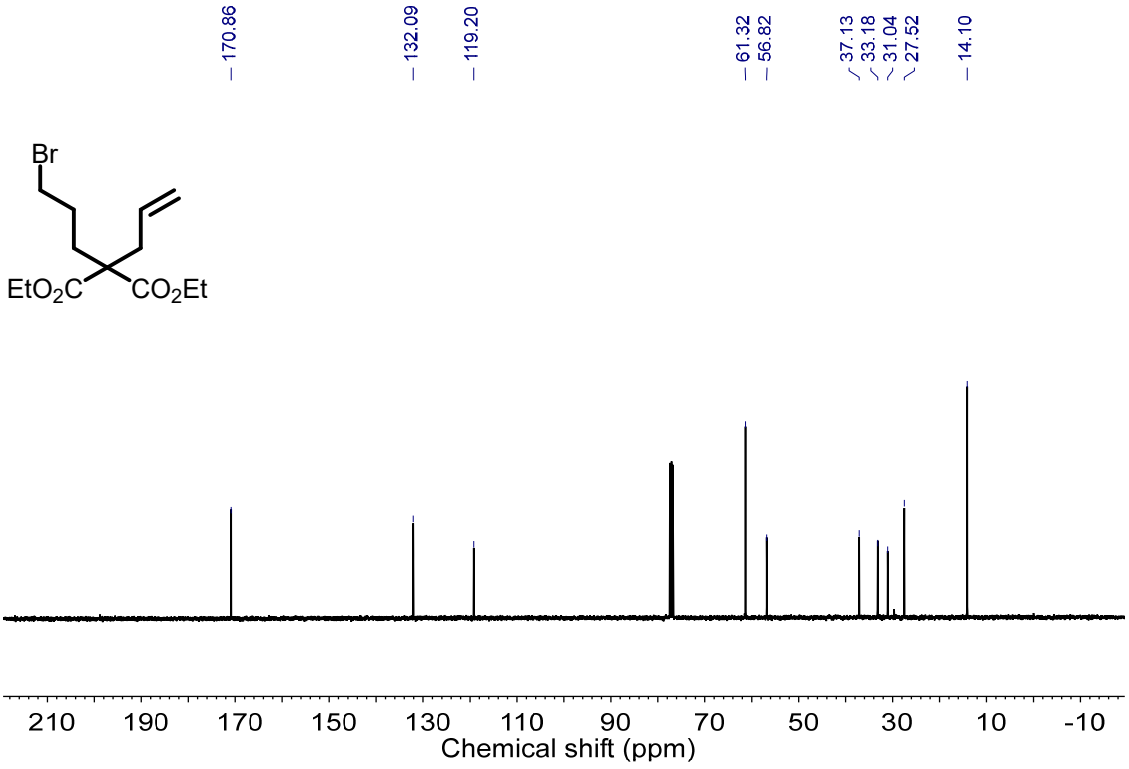
9a, ^{13}C NMR (101 MHz, $CDCl_3$)



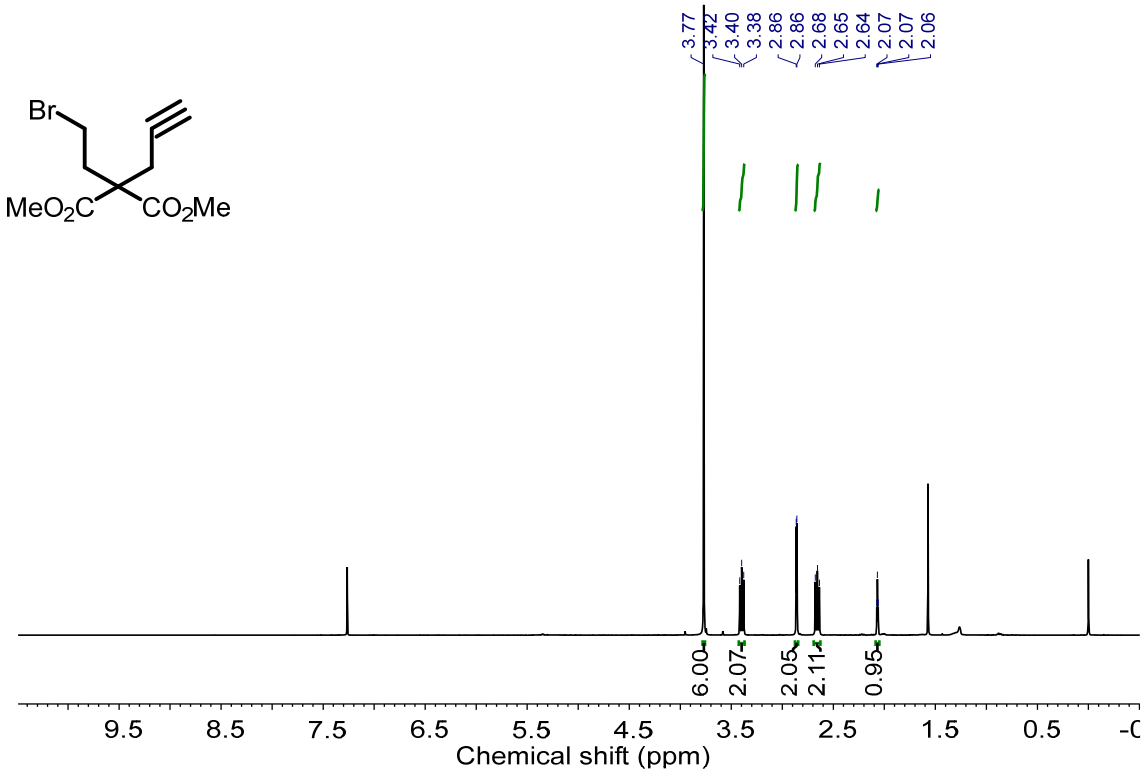
9b, ^{1}H NMR (400 MHz, $CDCl_3$)



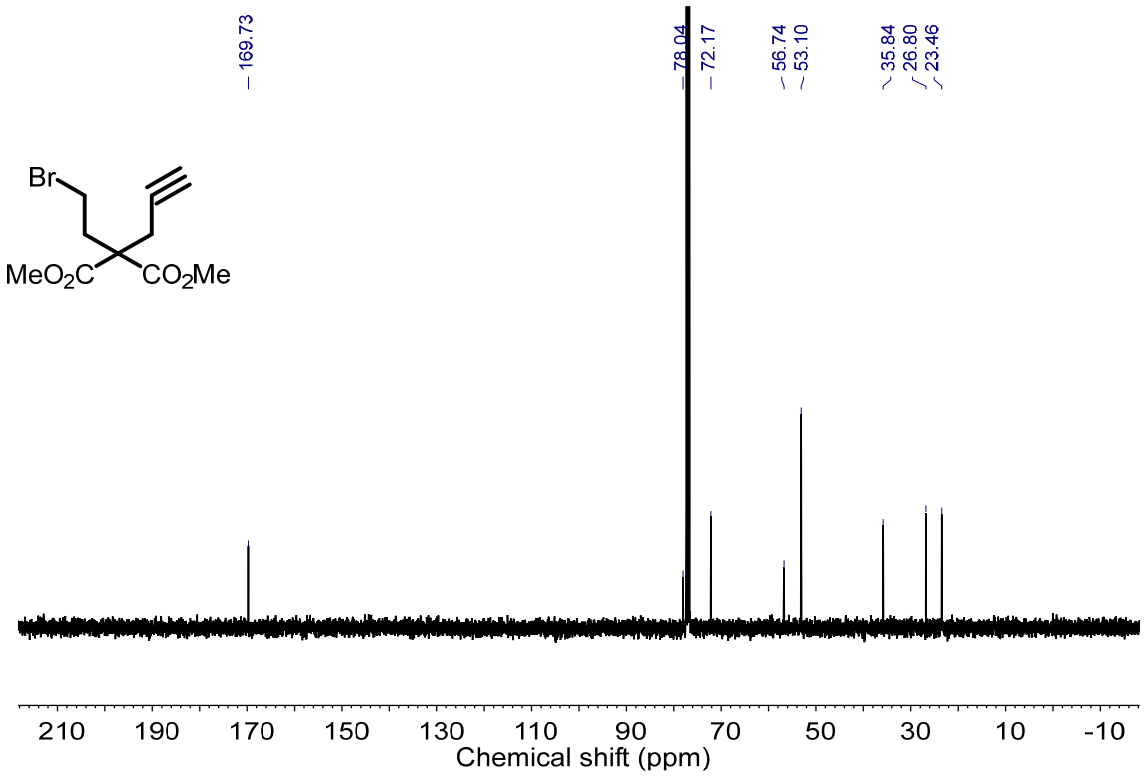
9b, ^{13}C NMR (101 MHz, $CDCl_3$)



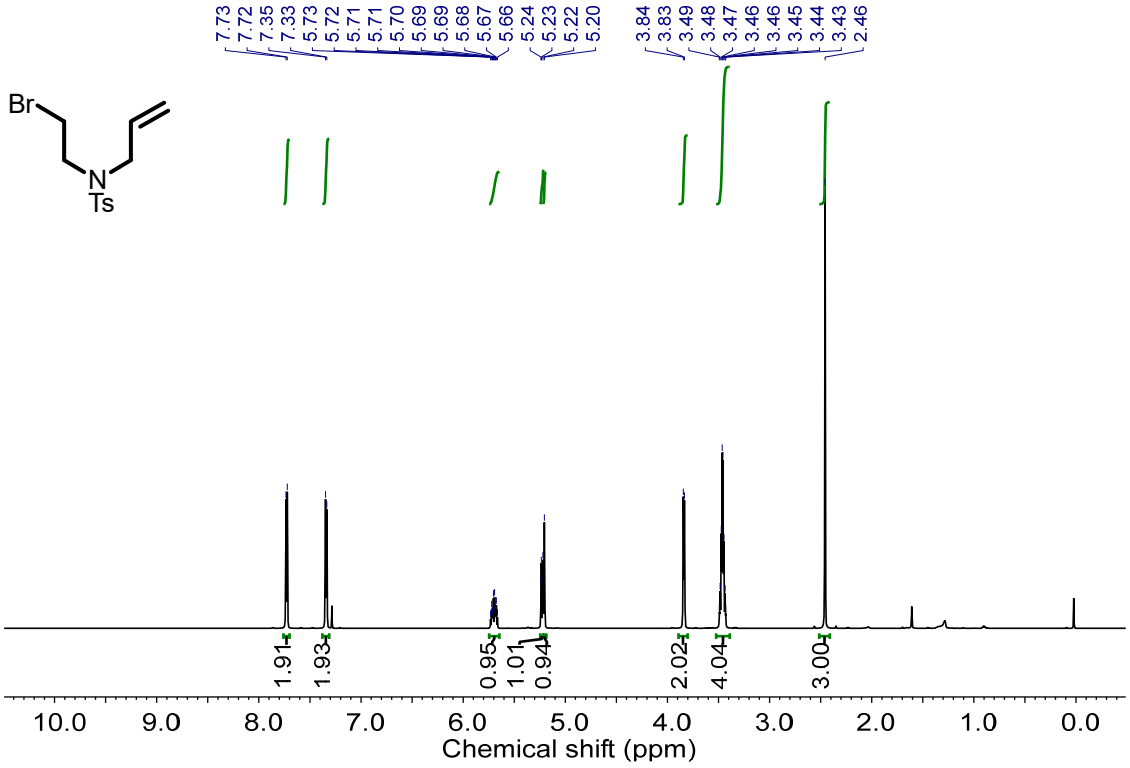
9c, ^{1}H NMR (400 MHz, $CDCl_3$)



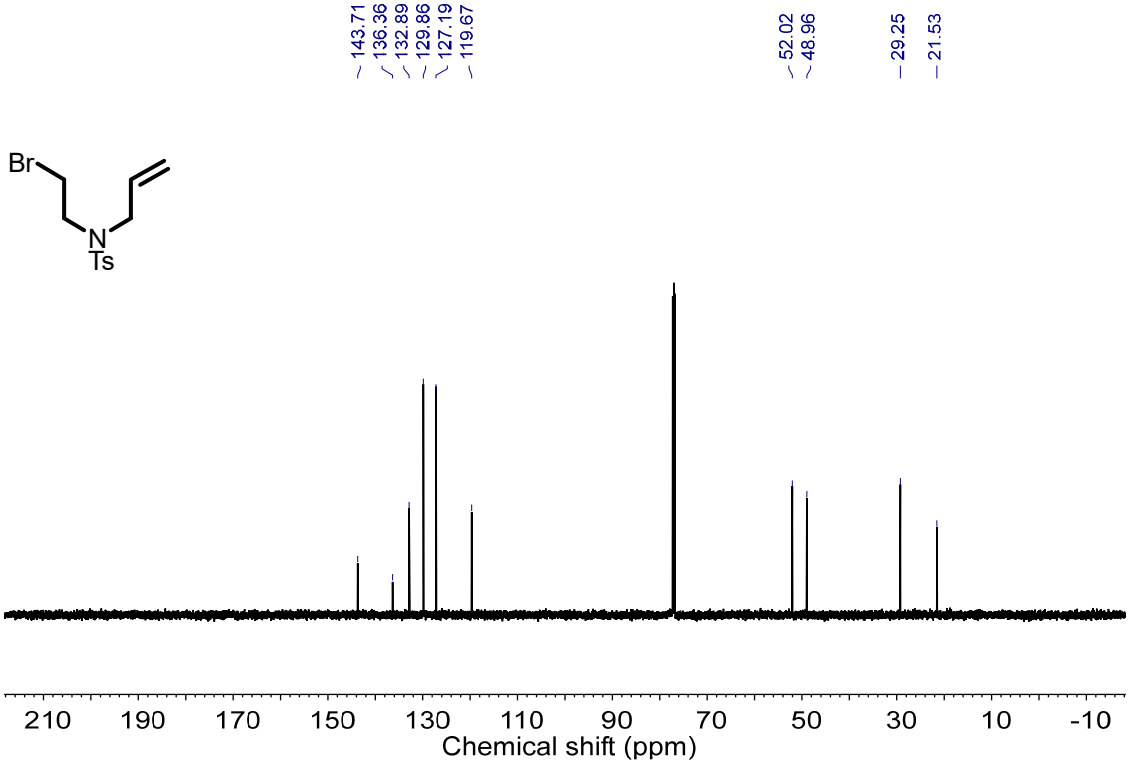
9c, ^{13}C NMR (101 MHz, $CDCl_3$)



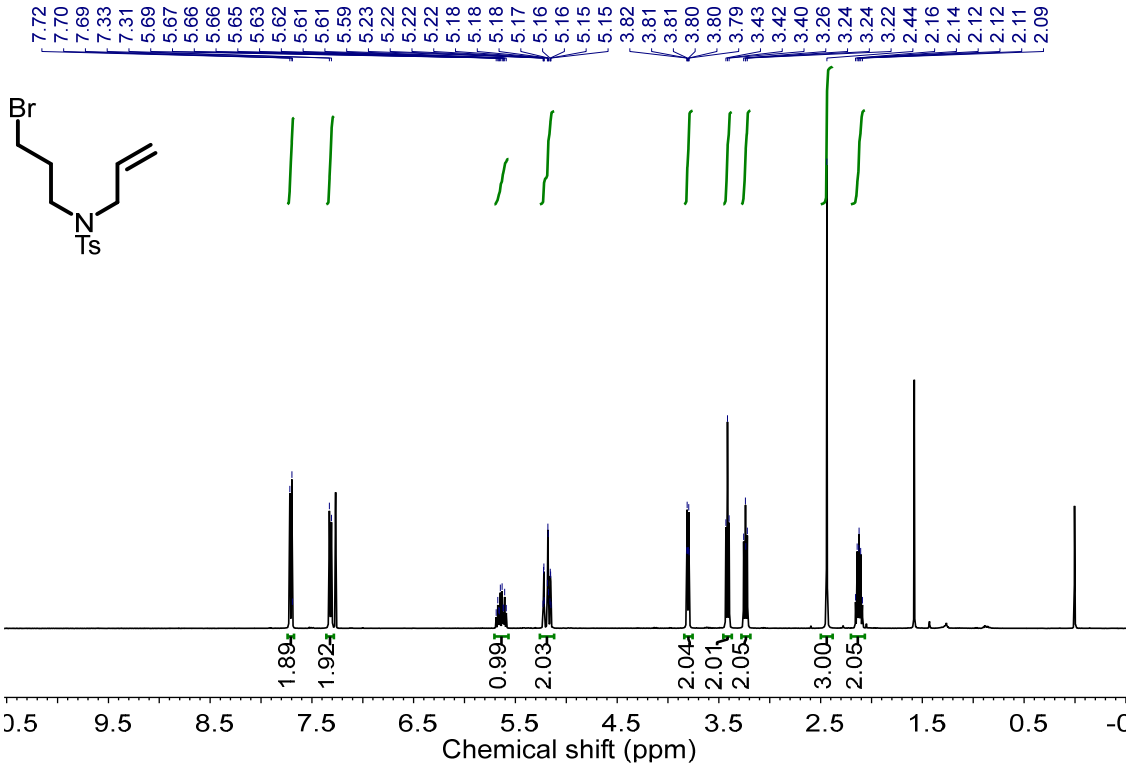
9d, ^{1}H NMR (600 MHz, $CDCl_3$)



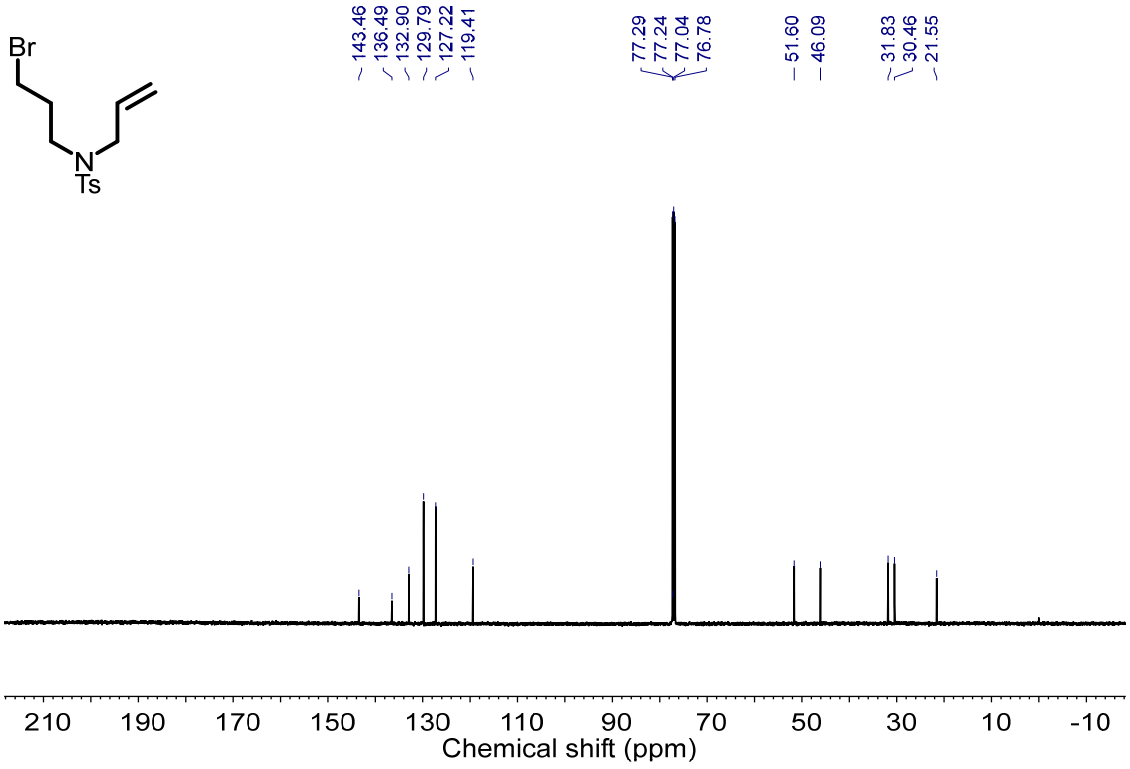
9d, ^{13}C NMR (151 MHz, $CDCl_3$)



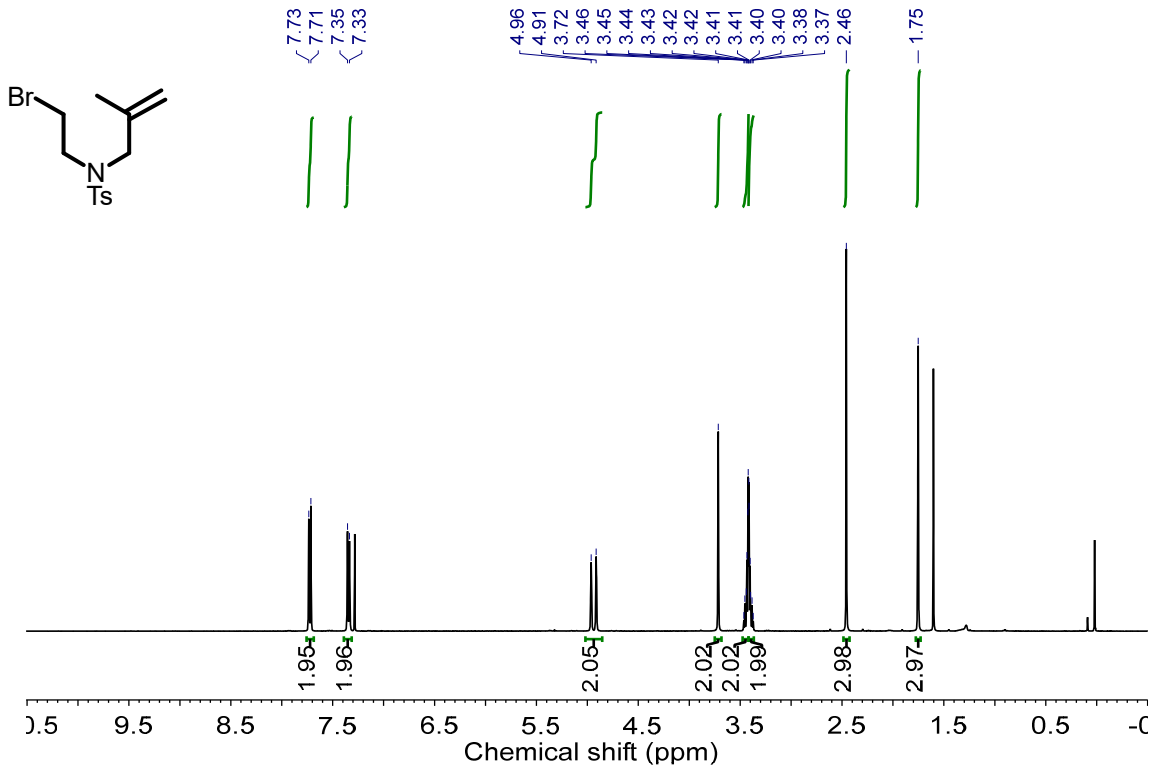
9e, ^{1}H NMR (400 MHz, $CDCl_3$)



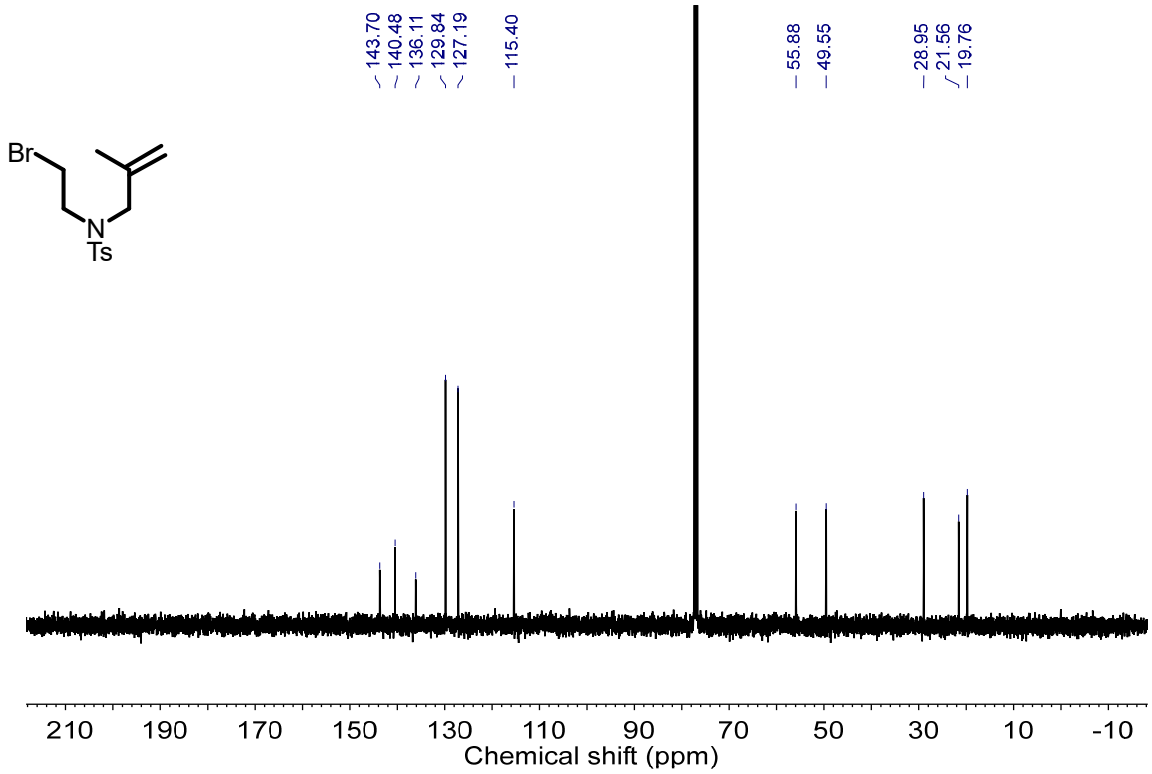
9e, ^{13}C NMR (126 MHz, $CDCl_3$)



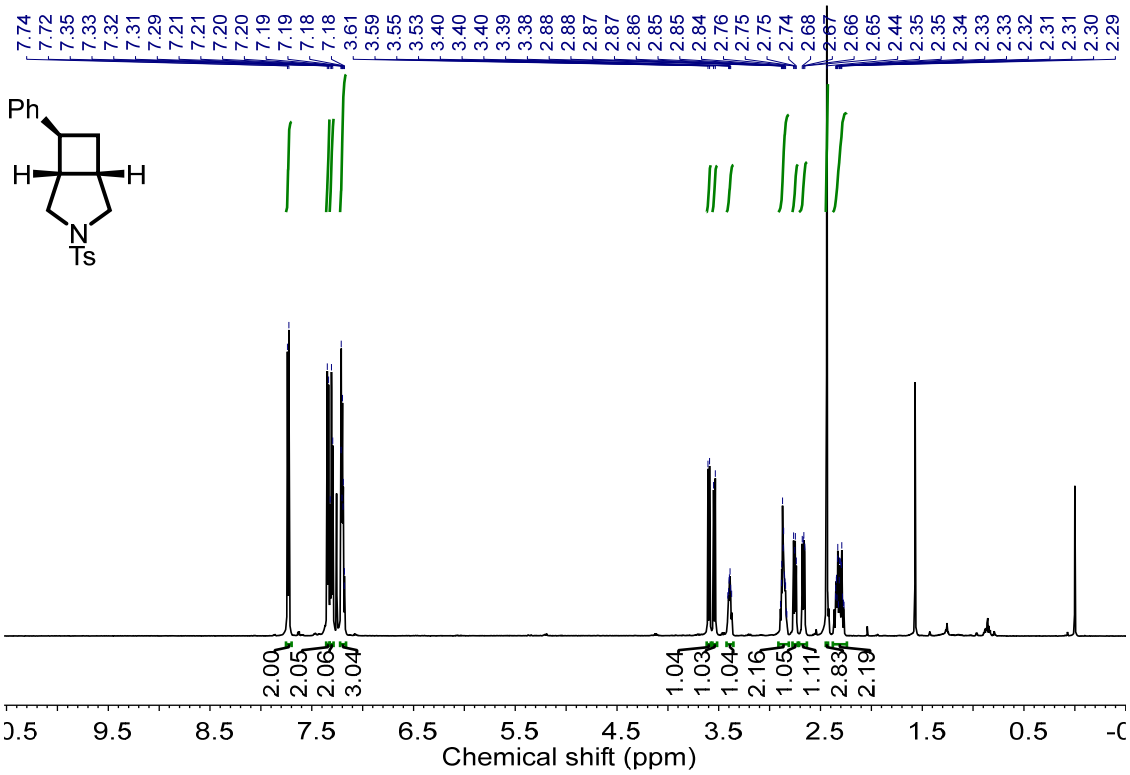
9f, ^{1}H NMR (400 MHz, $CDCl_3$)



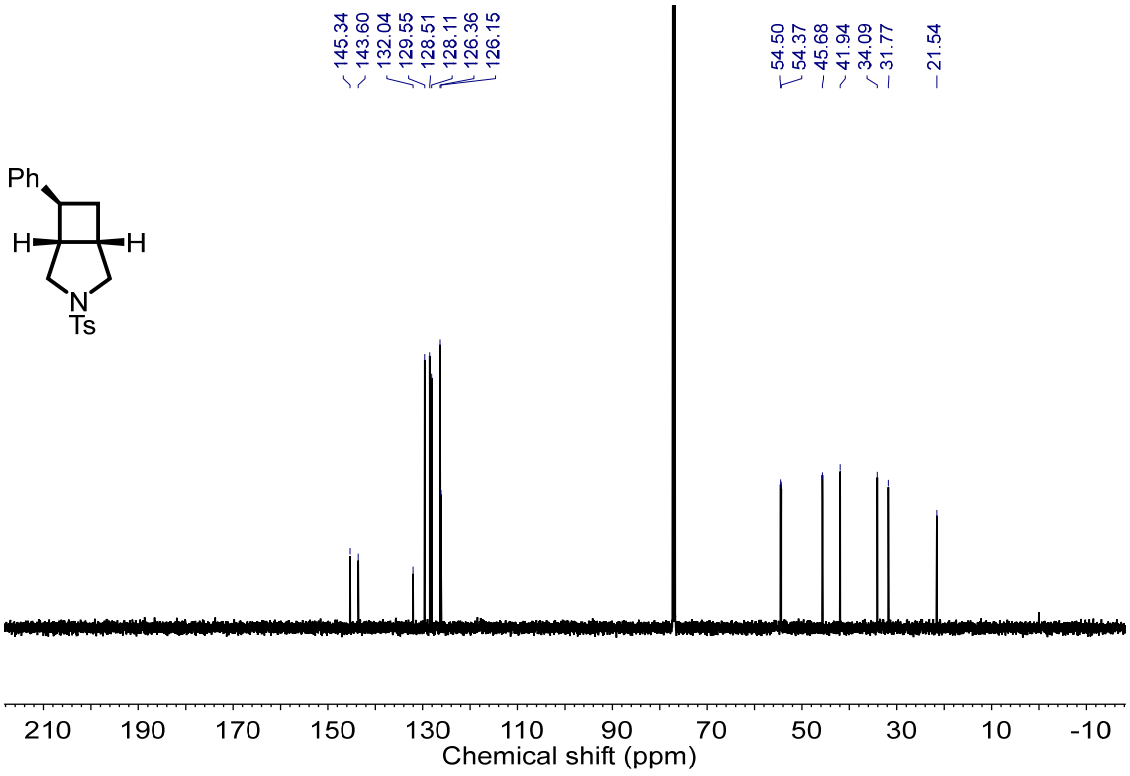
9f, ^{13}C NMR (101 MHz, $CDCl_3$)



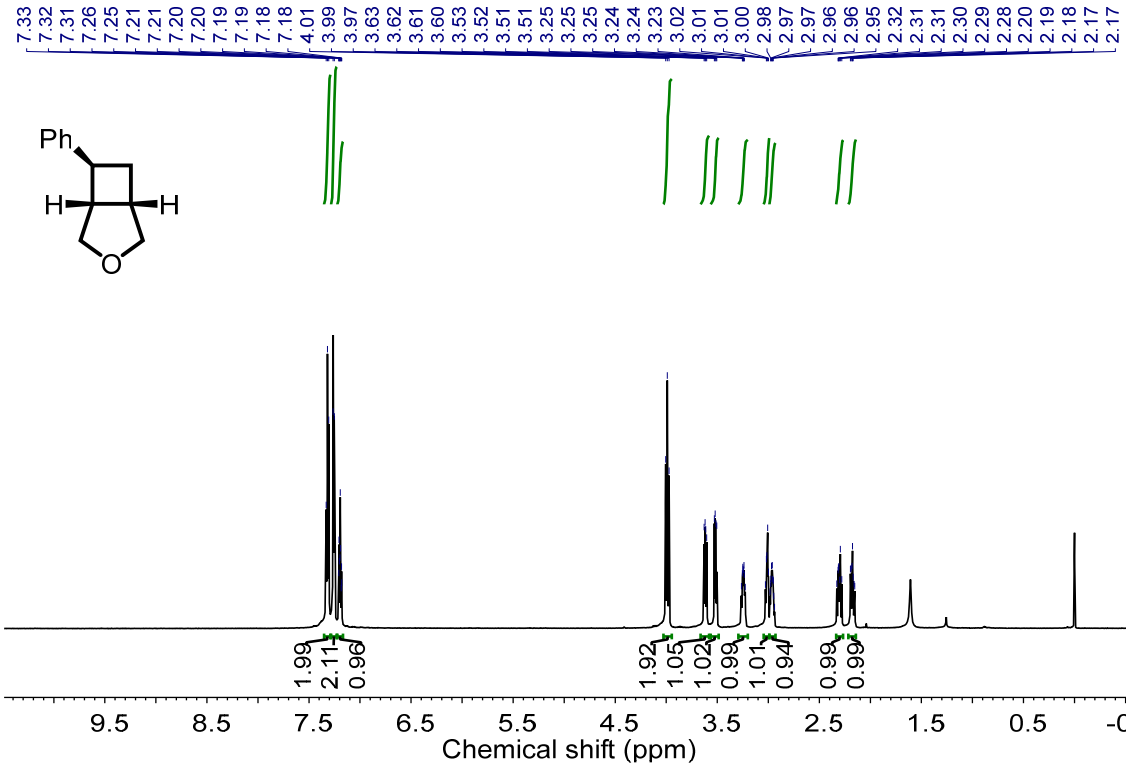
2a, ^{1}H NMR (600 MHz, $CDCl_3$)



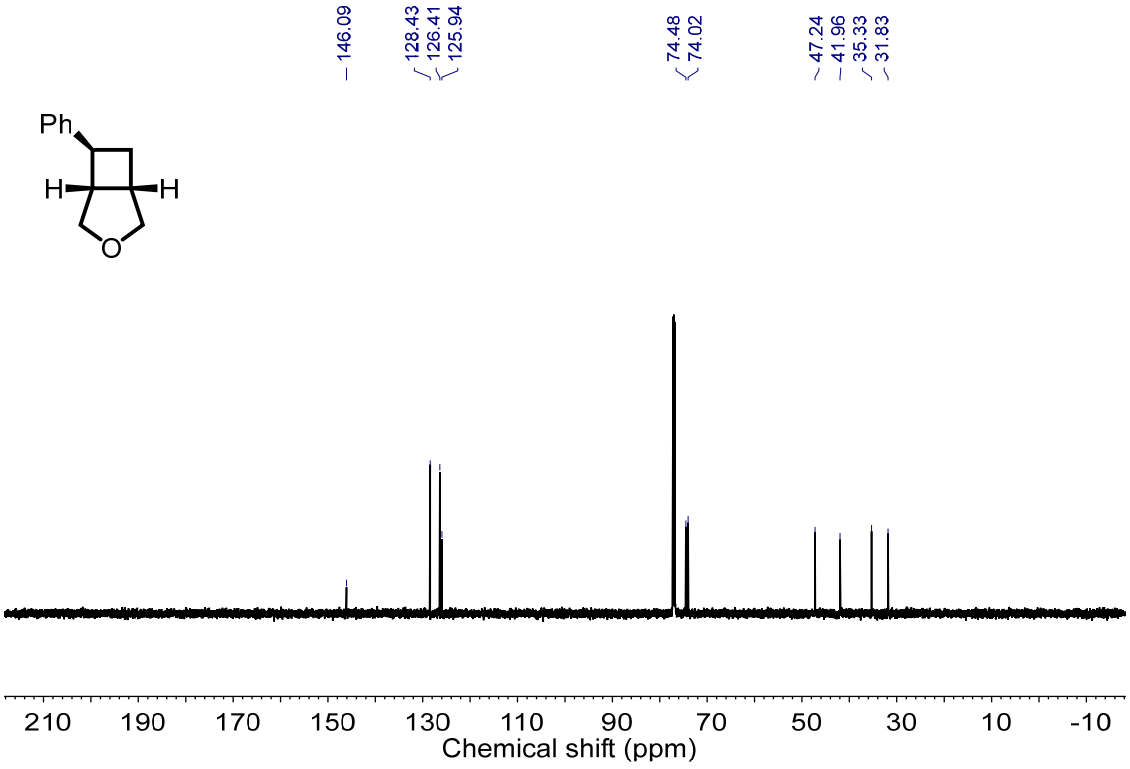
2a, ^{13}C NMR (151 MHz, $CDCl_3$)



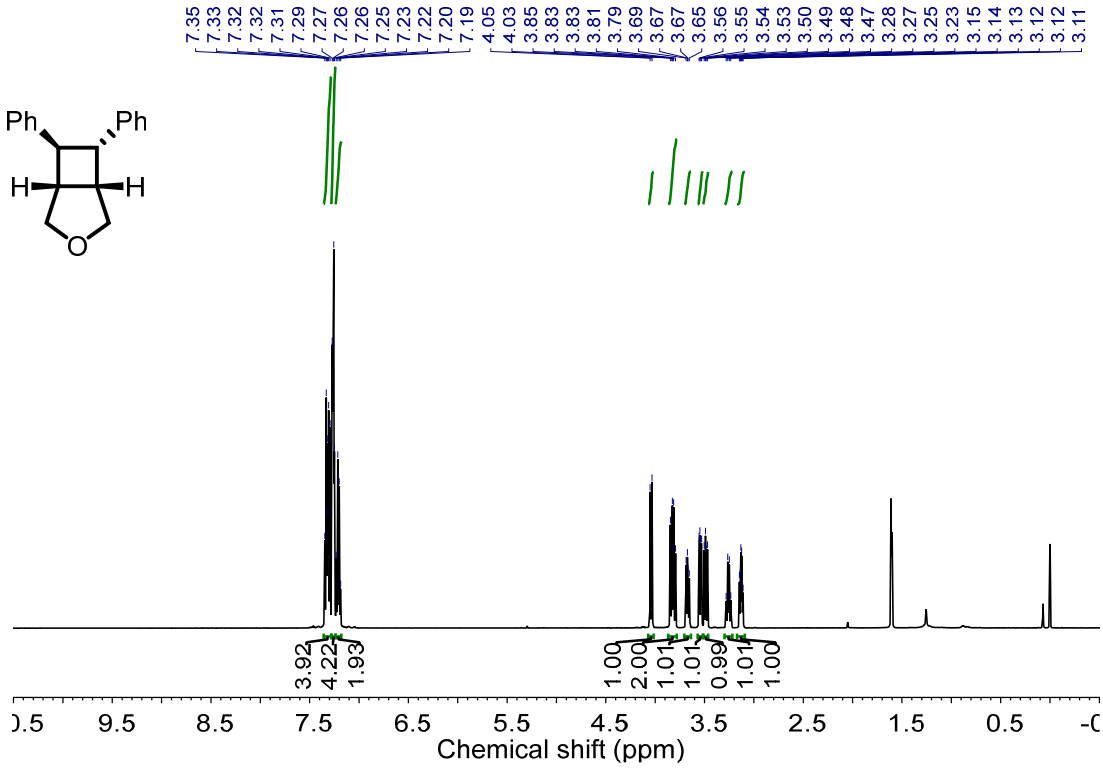
2b, ^{1}H NMR (600 MHz, $CDCl_3$)



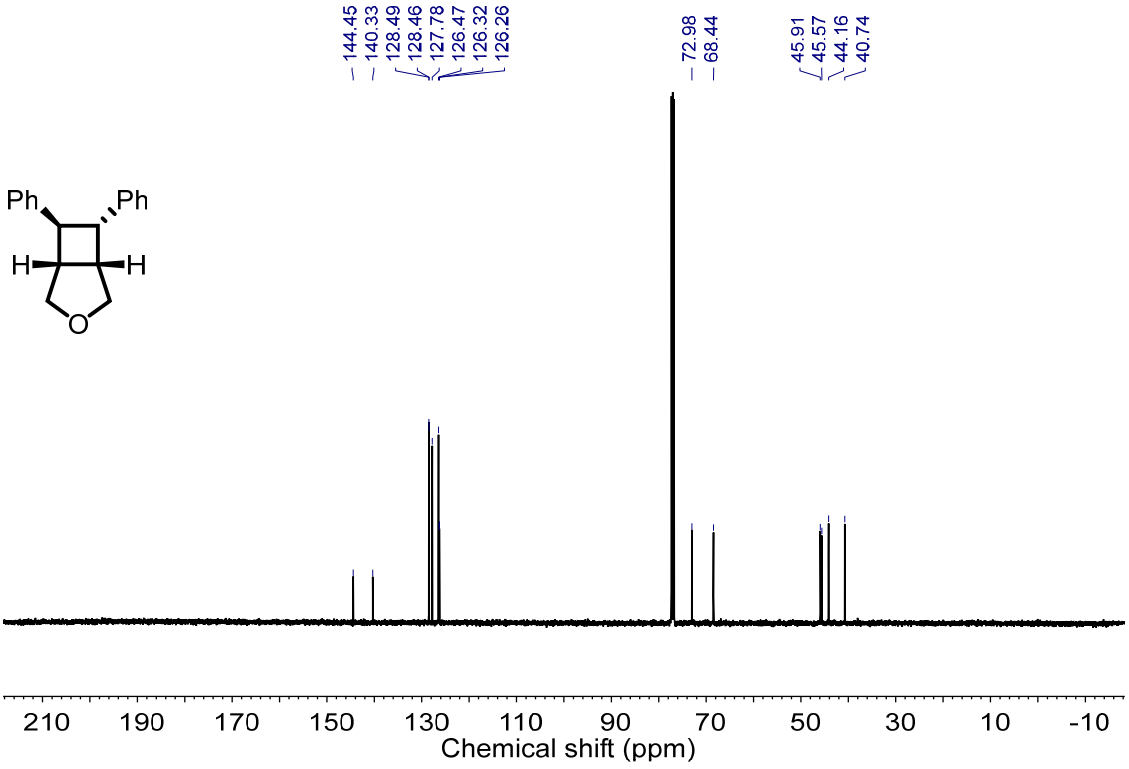
2b, ^{13}C NMR (151 MHz, $CDCl_3$)



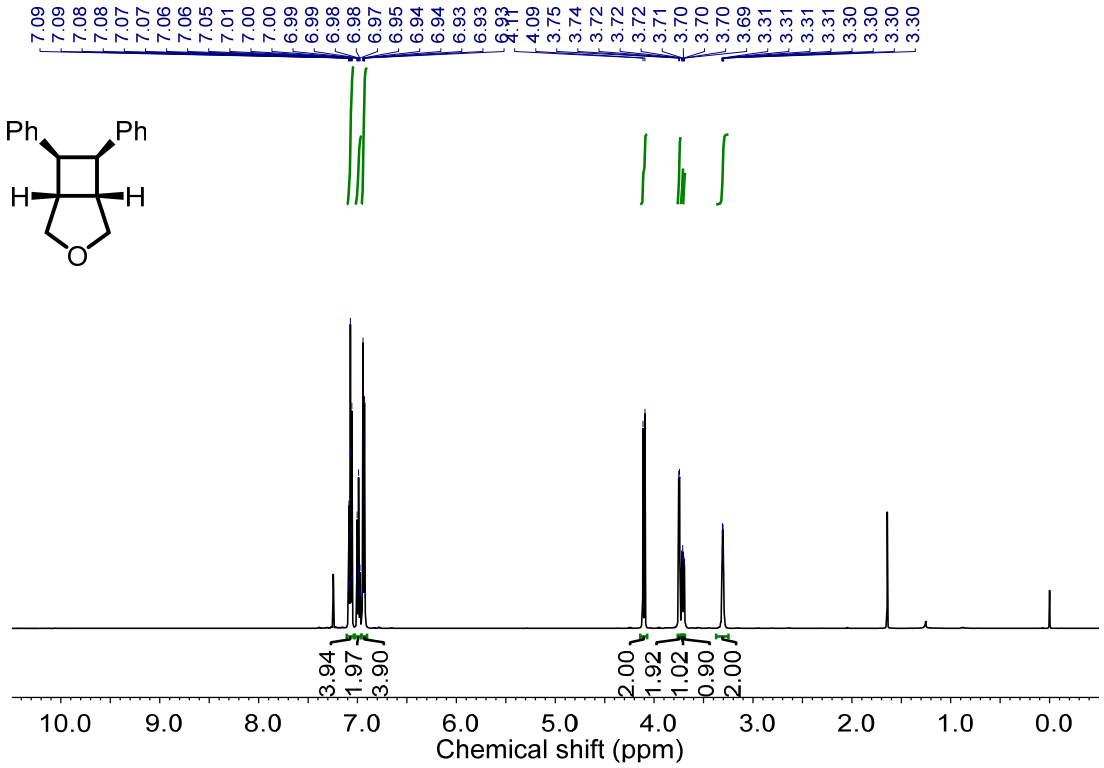
2c, ^{1}H NMR (500 MHz, $CDCl_3$)



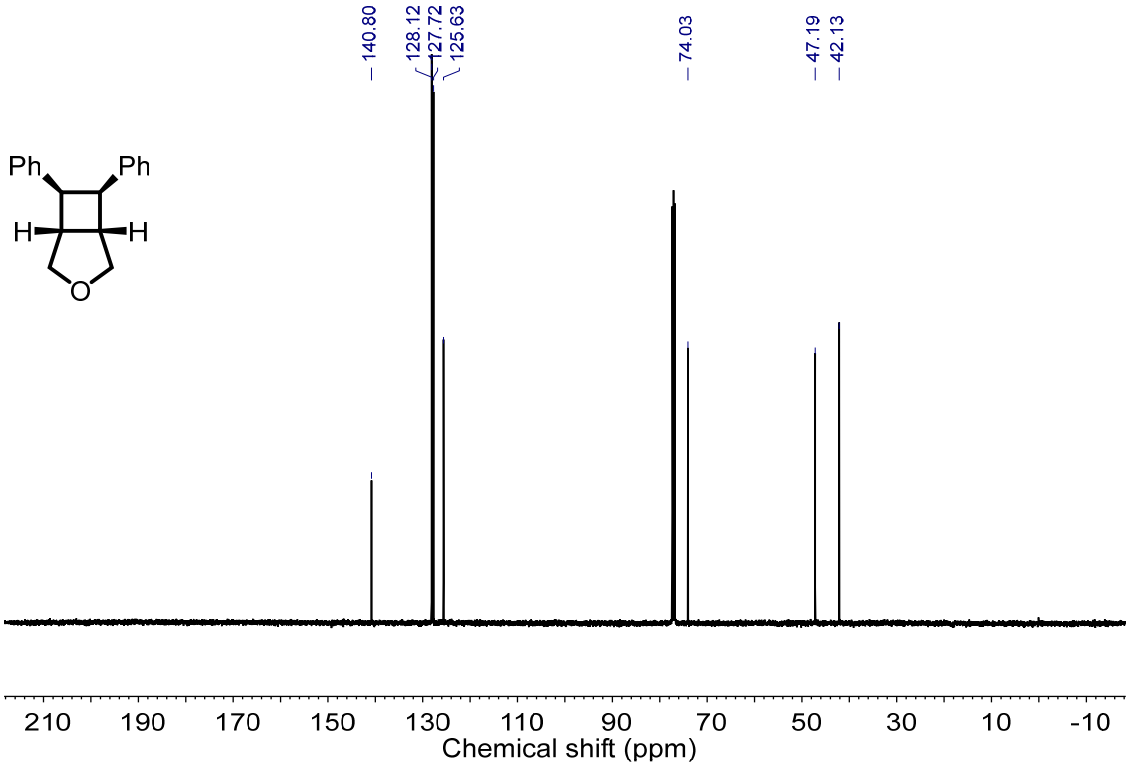
2c, ^{13}C NMR (126 MHz, $CDCl_3$)



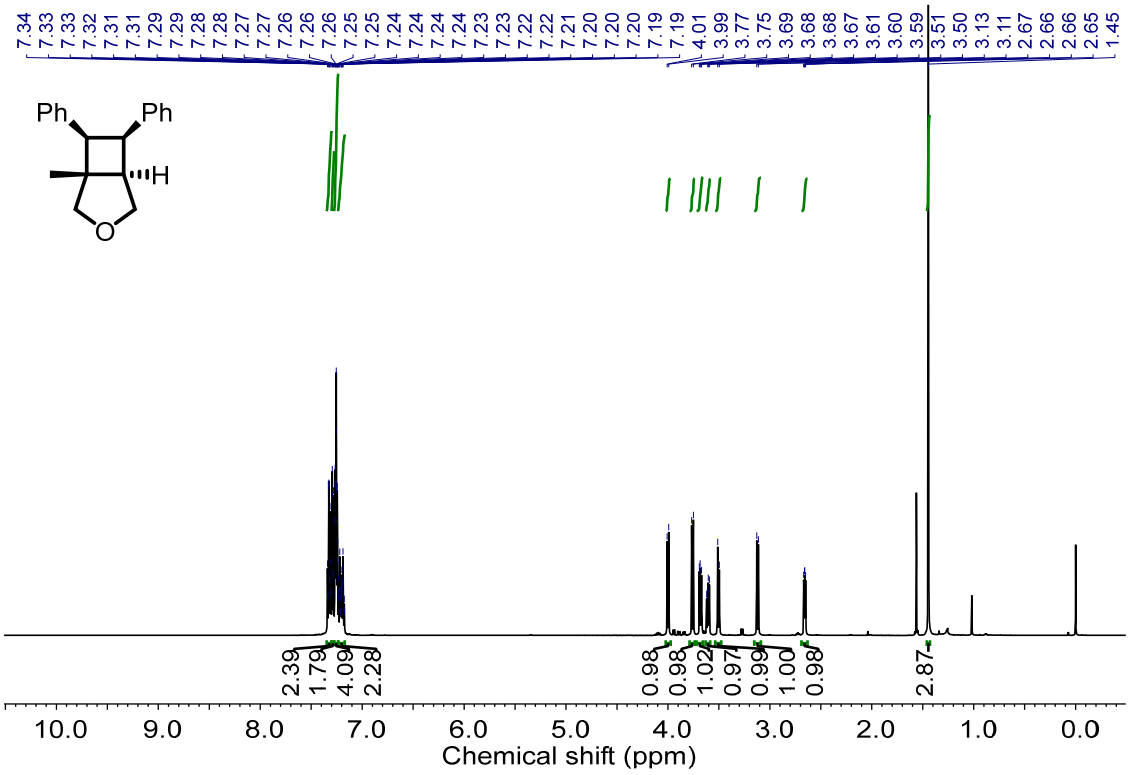
2c, ^{1}H NMR (500 MHz, $CDCl_3$)



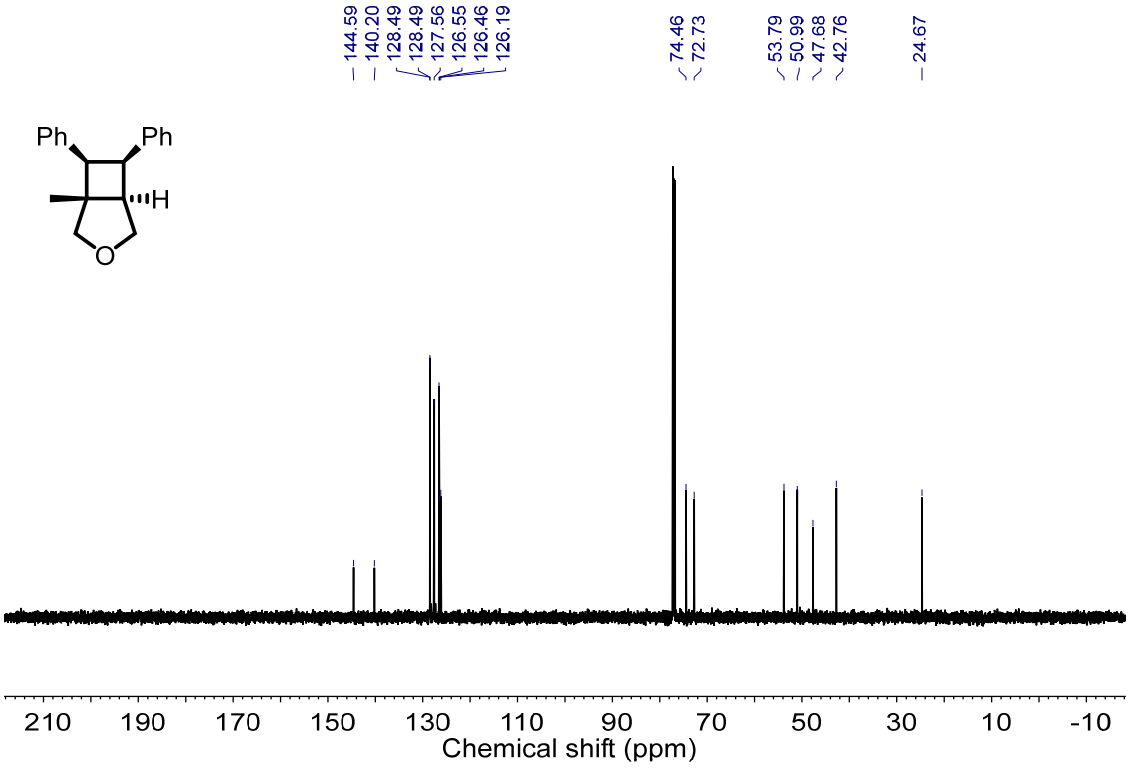
2c, ^{13}C NMR (126 MHz, $CDCl_3$)



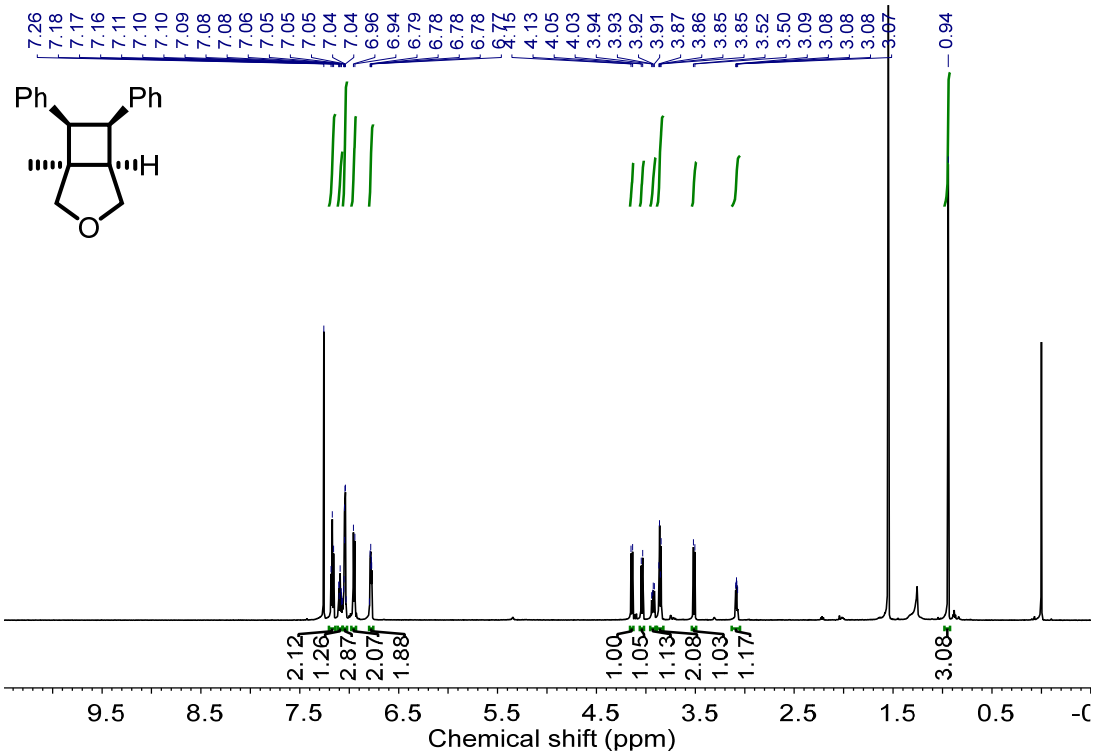
2d, ^{1}H NMR (600 MHz, $CDCl_3$)



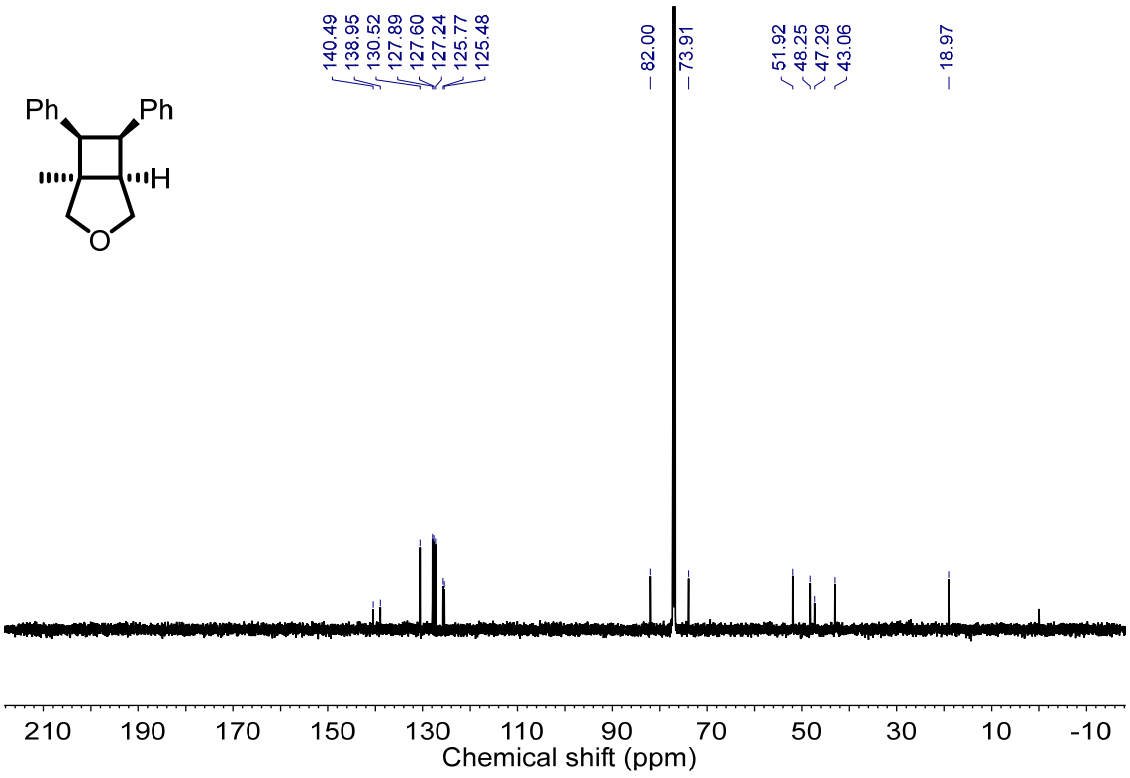
2d, ^{13}C NMR (151 MHz, $CDCl_3$)



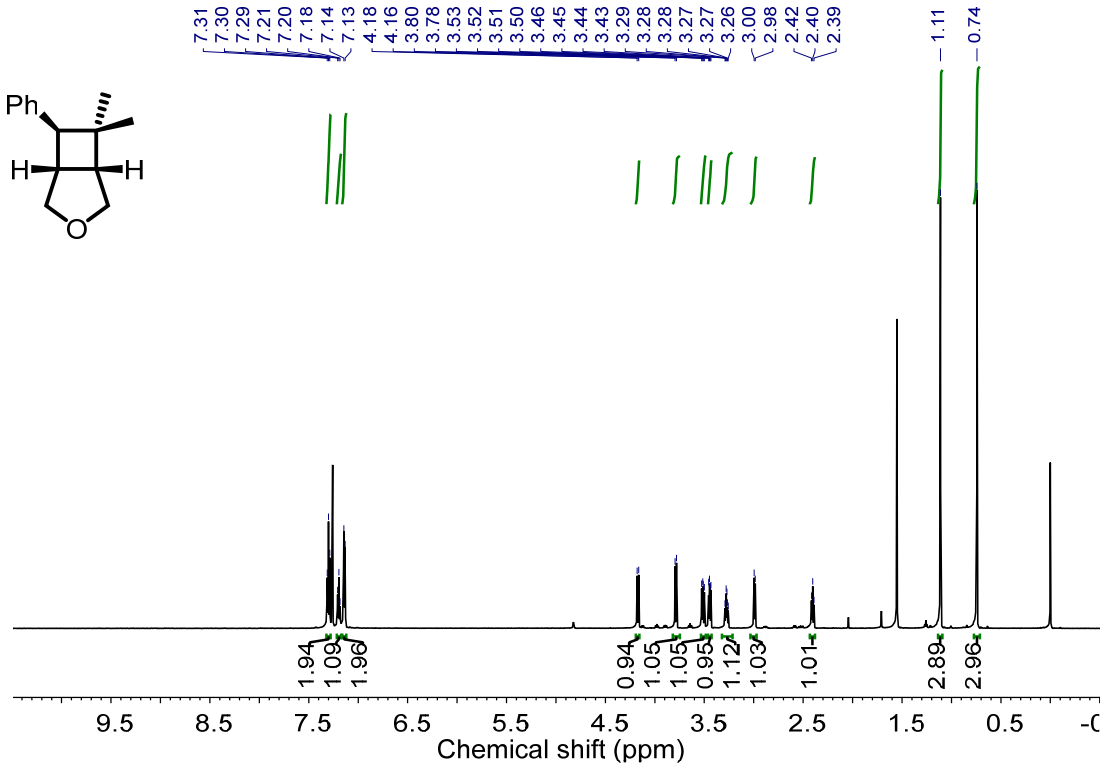
2d, ^{1}H NMR (600 MHz, $CDCl_3$)



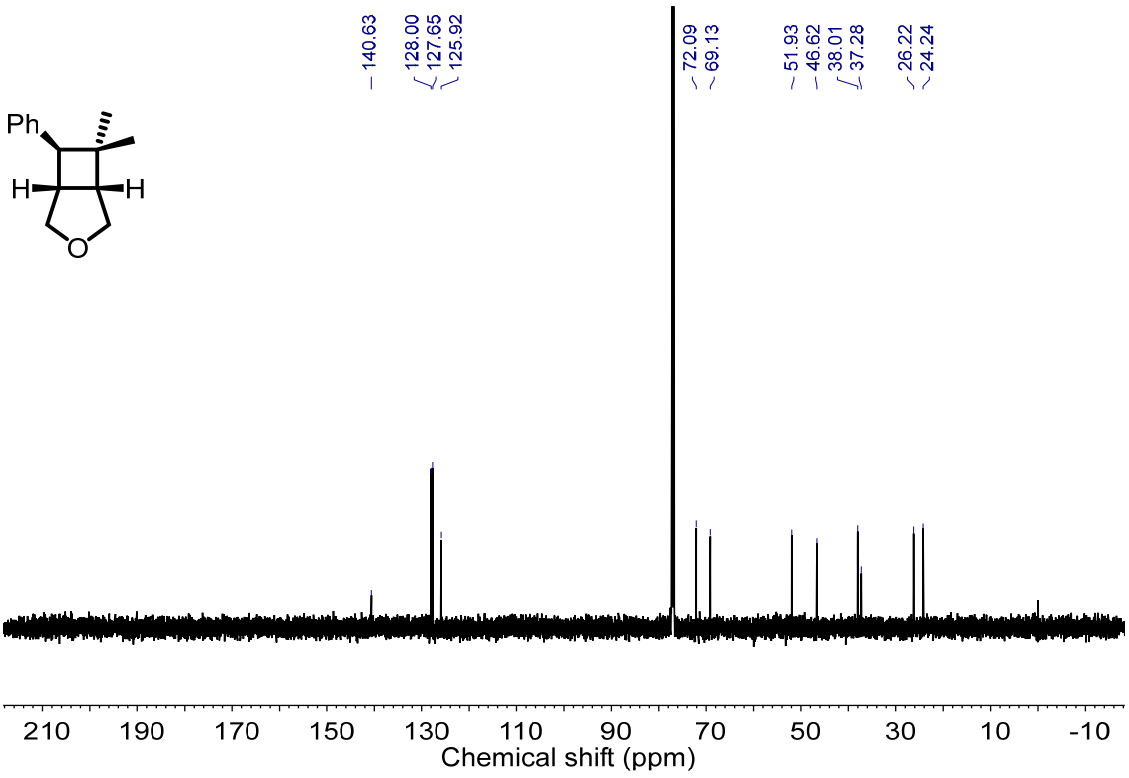
2d, ^{13}C NMR (151 MHz, $CDCl_3$)



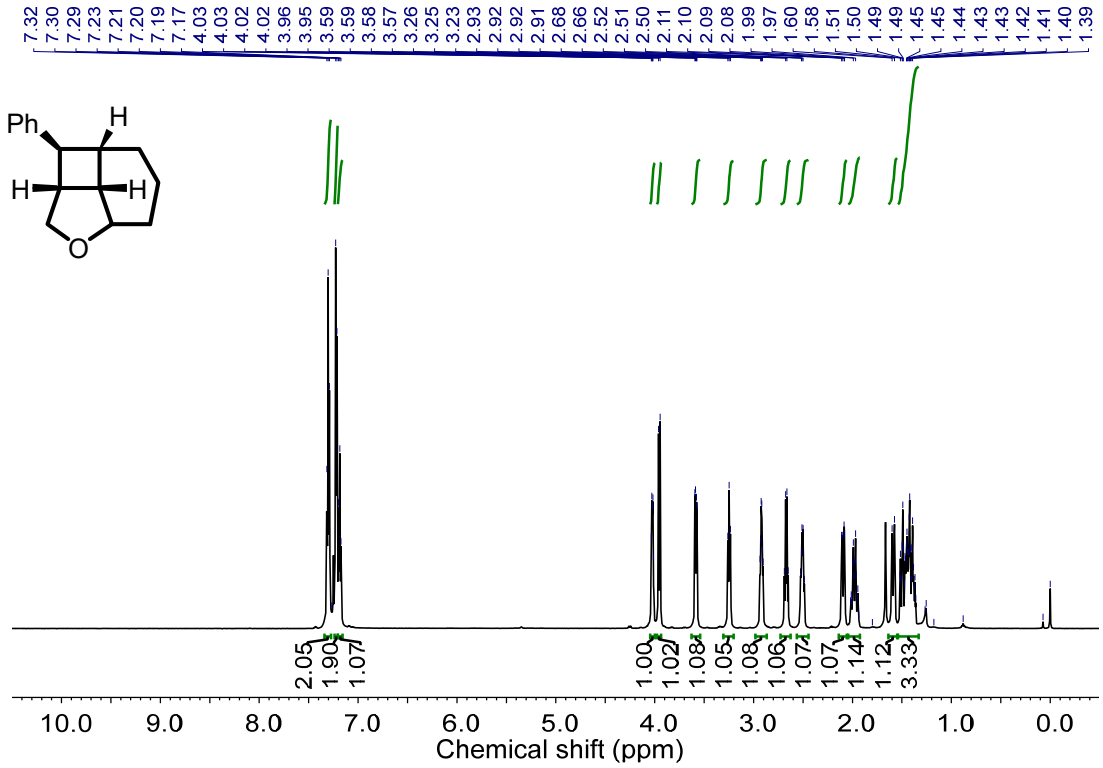
2e, ^{1}H NMR (600 MHz, $CDCl_3$)



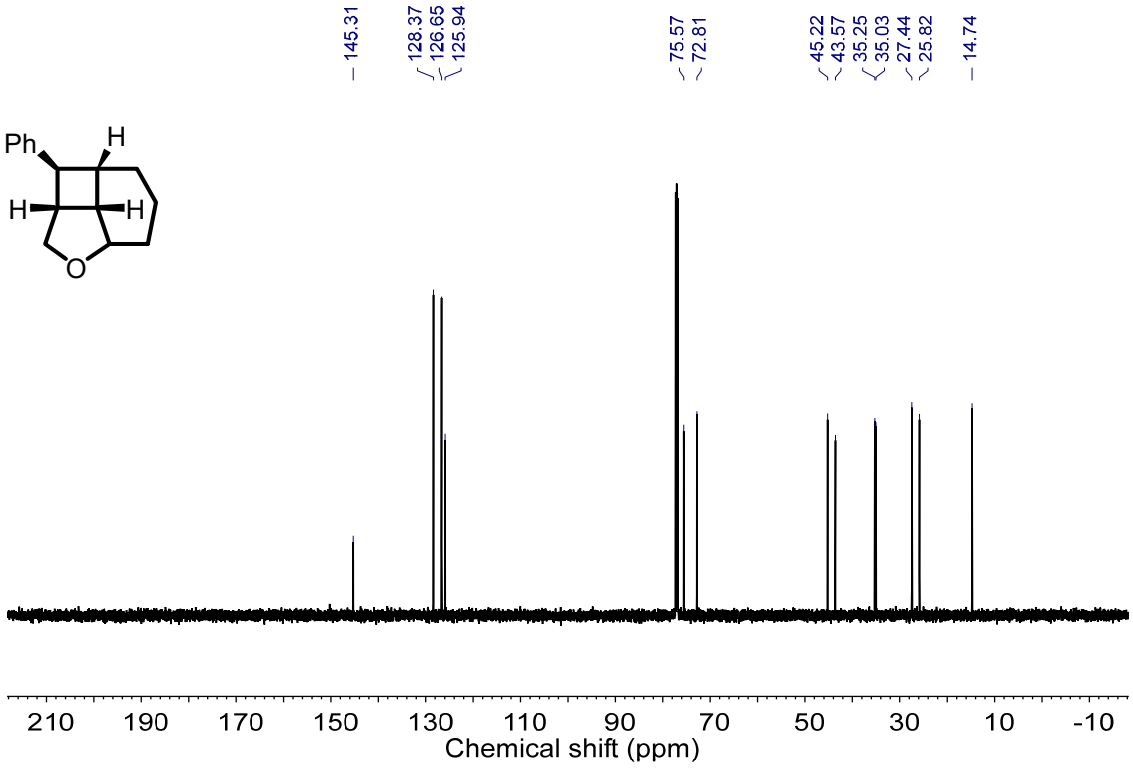
2e, ^{13}C NMR (151 MHz, $CDCl_3$)



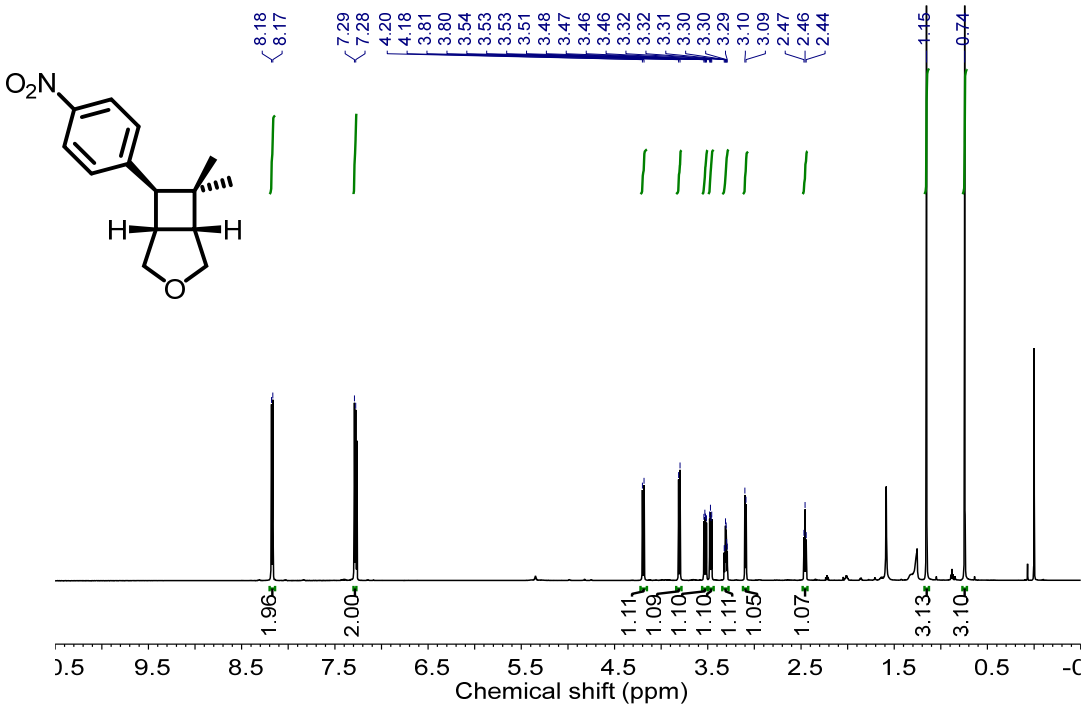
2f, ^{1}H NMR (600 MHz, $CDCl_3$)



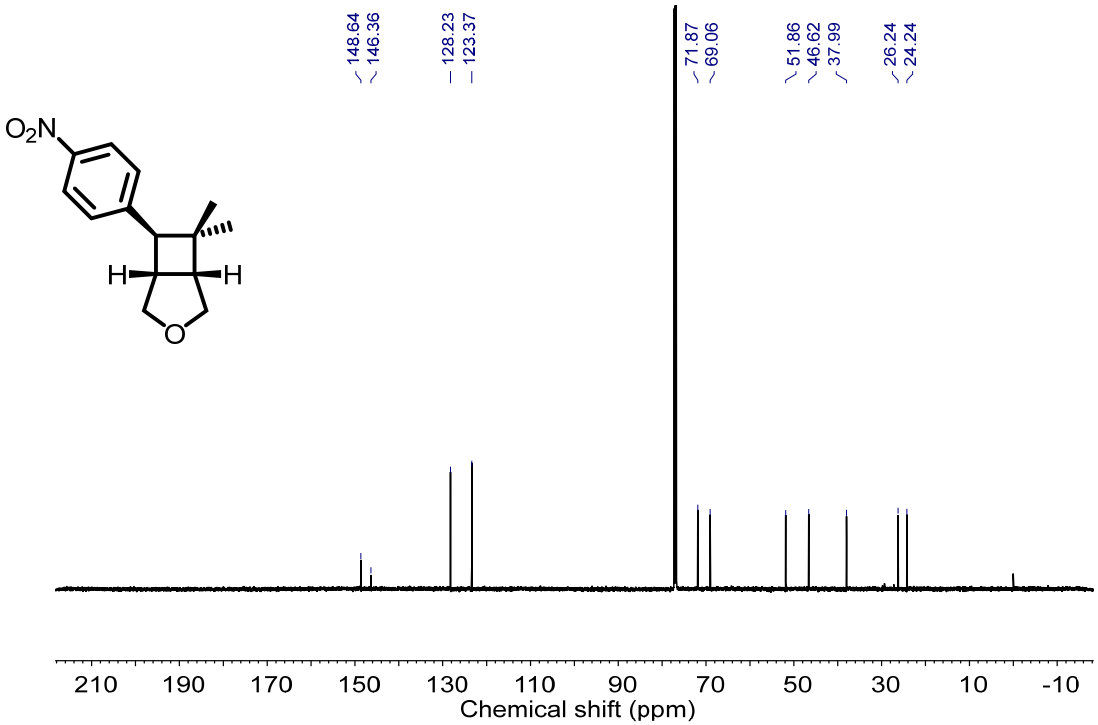
2f, ^{13}C NMR (151 MHz, $CDCl_3$)



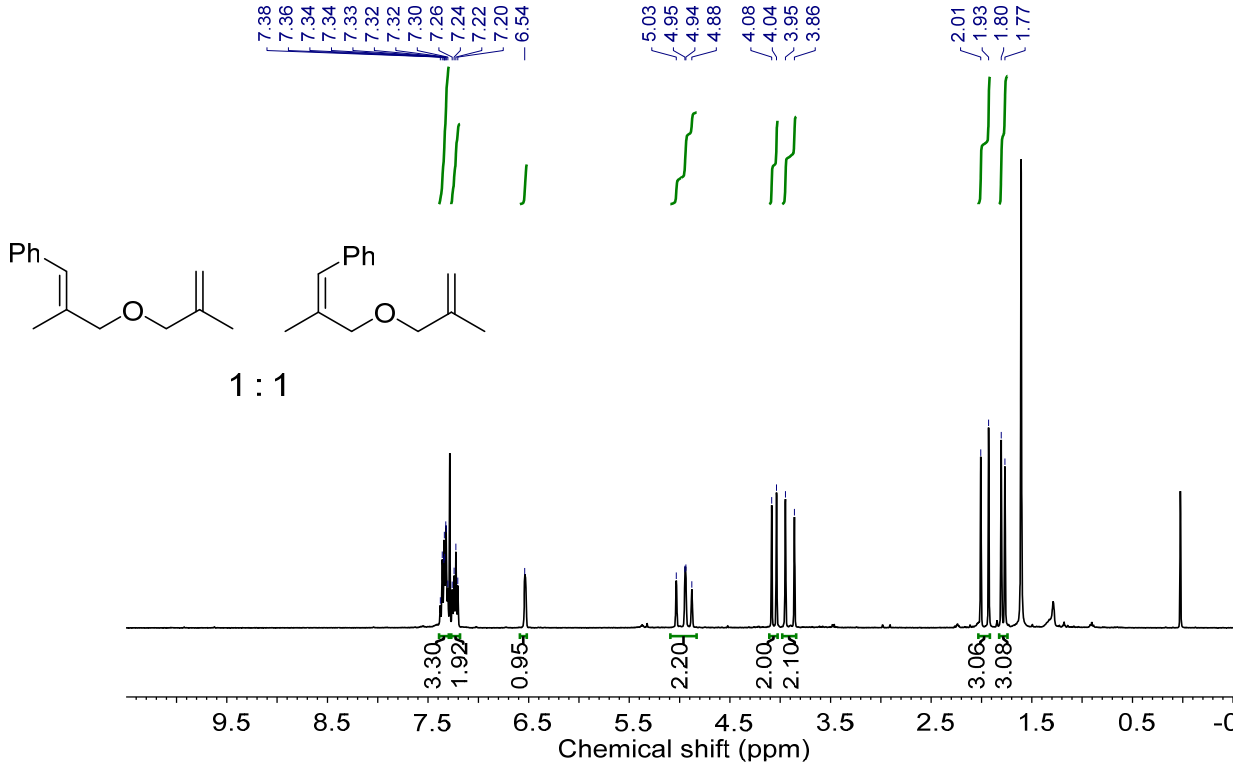
2g, ^{1}H NMR (600 MHz, Chloroform-*d*)



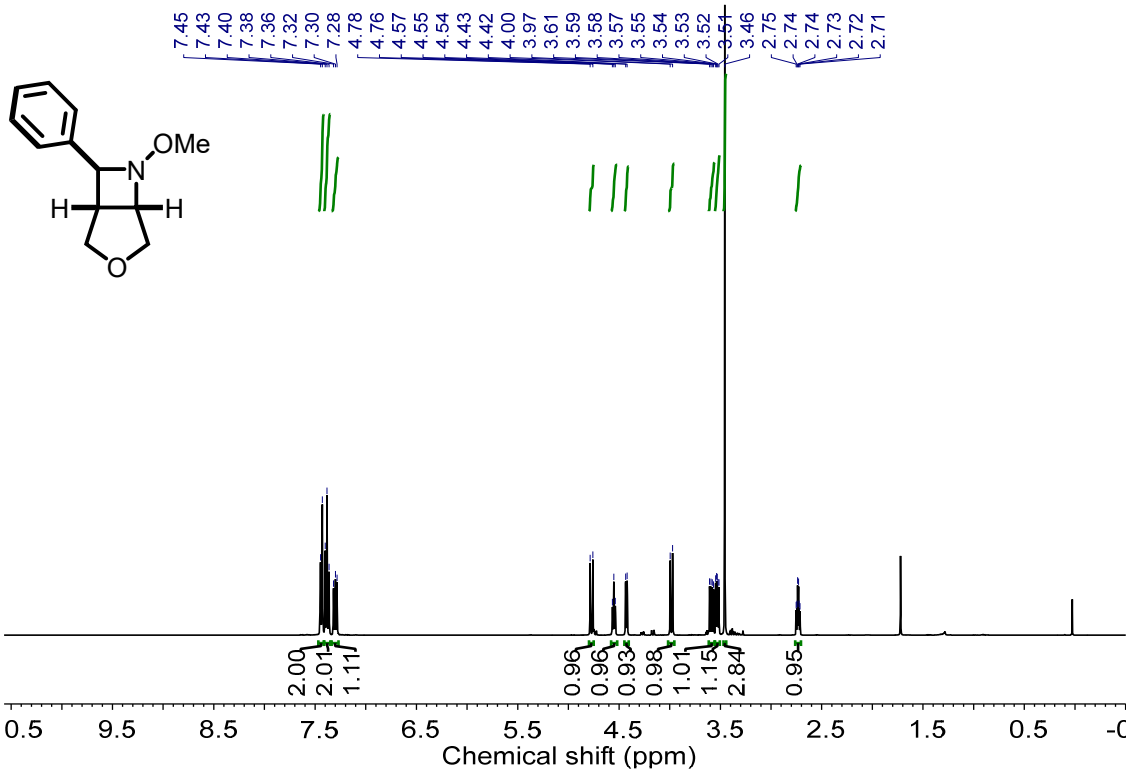
2g, ^{13}C NMR (151 MHz, Chloroform-*d*)



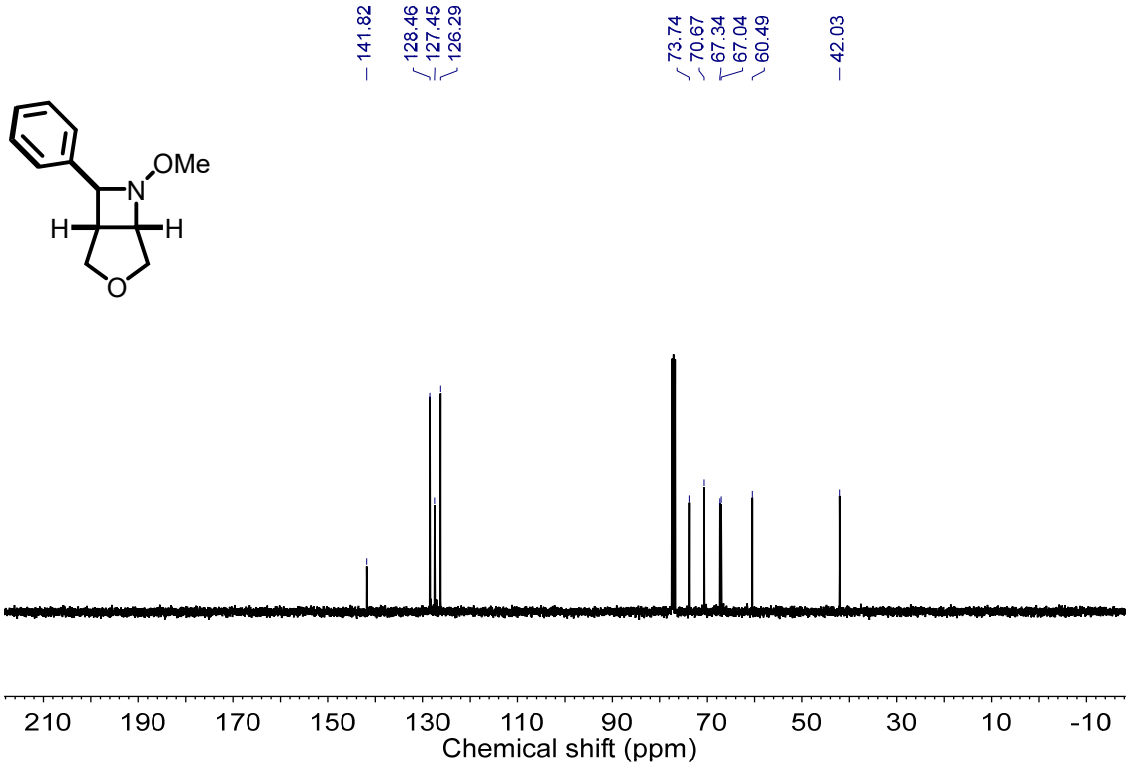
(*E*)-1h and (*Z*)-1h, ^{1}H NMR (400 MHz, Chloroform-*d*)



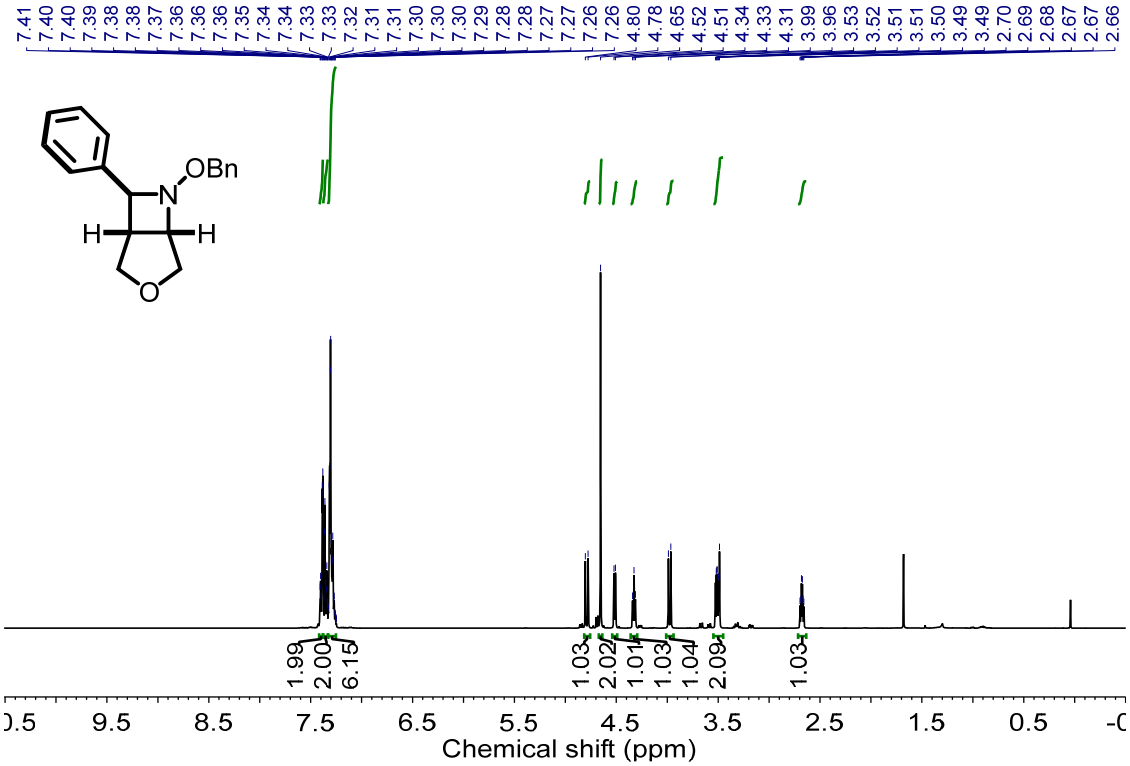
4a, ^{1}H NMR (400 MHz, $CDCl_3$)



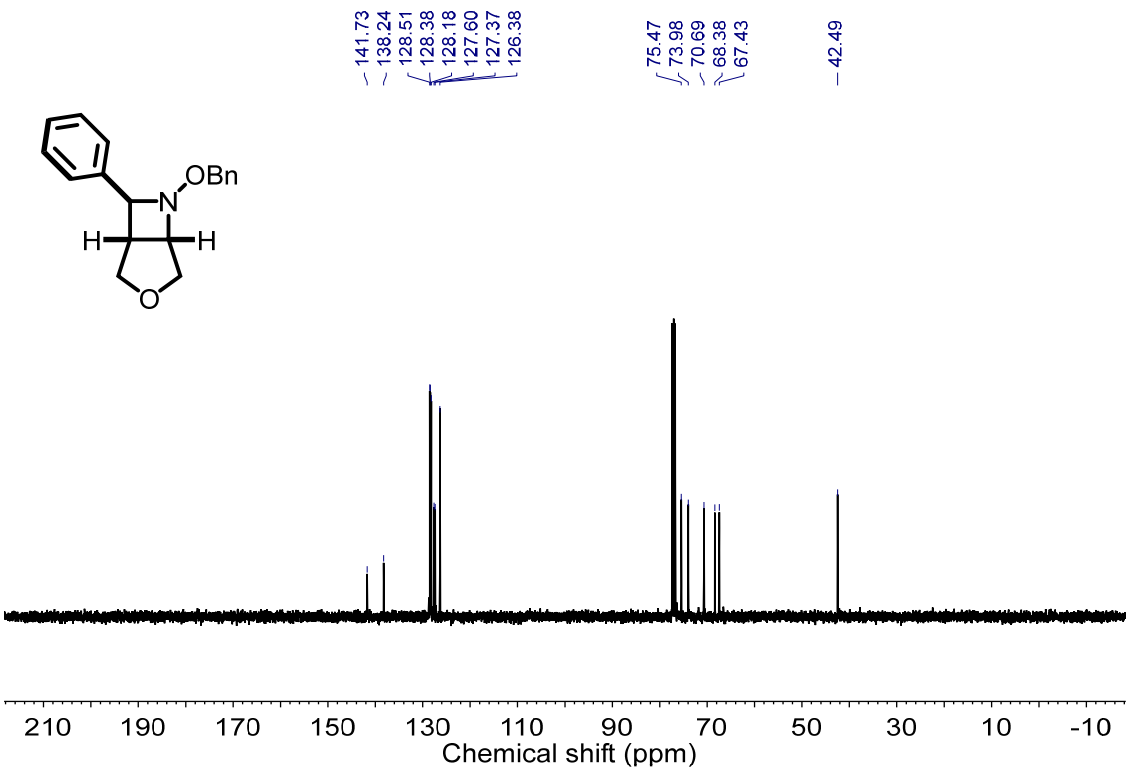
4a, ^{13}C NMR (101 MHz, $CDCl_3$)



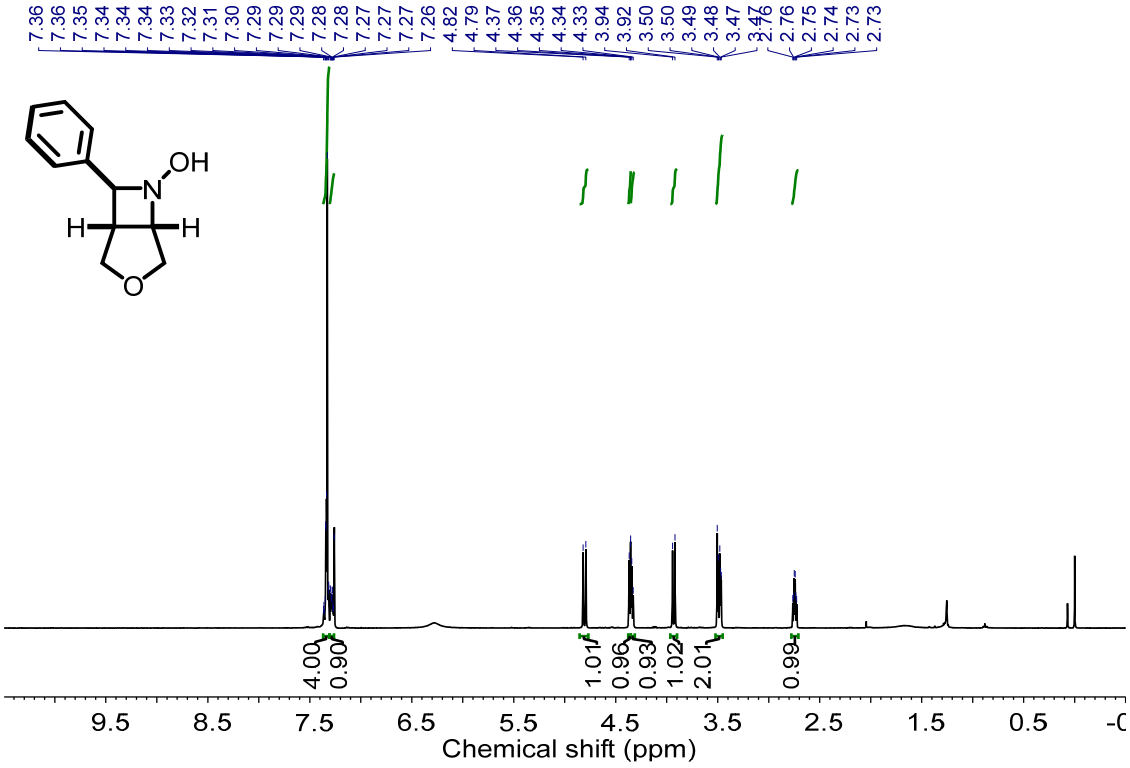
4b, ^{1}H NMR (400 MHz, $CDCl_3$)



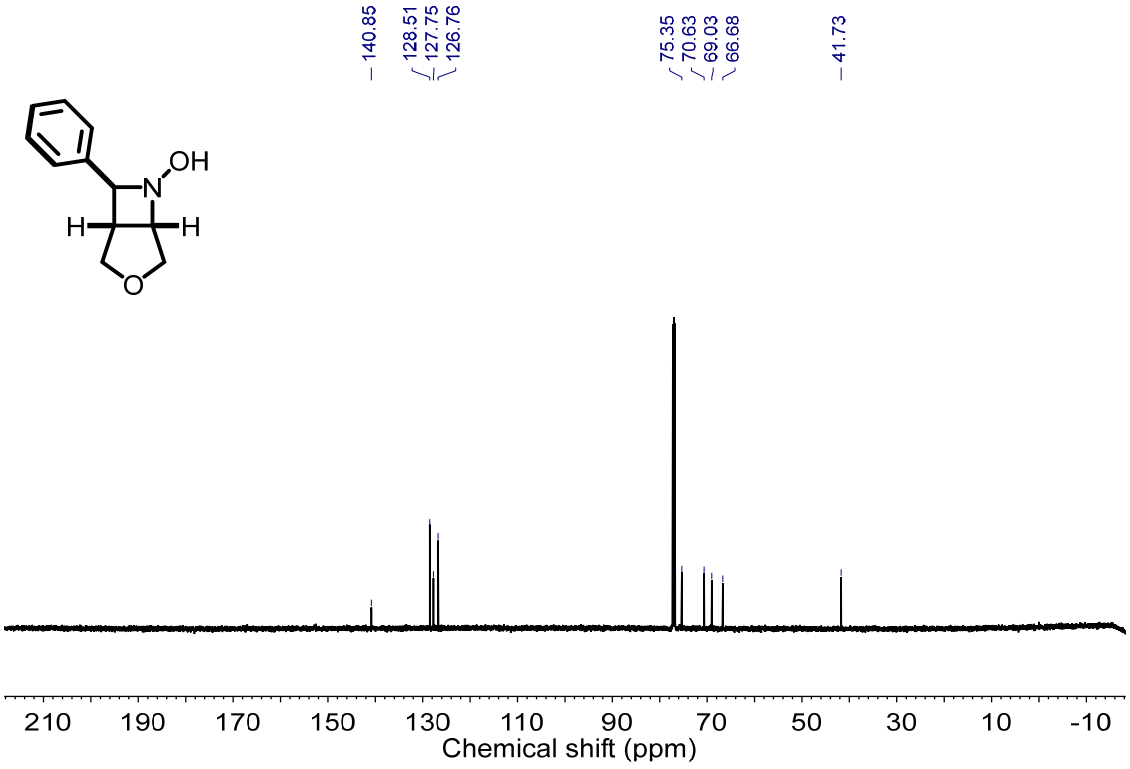
4b, ^{13}C NMR (101 MHz, $CDCl_3$)



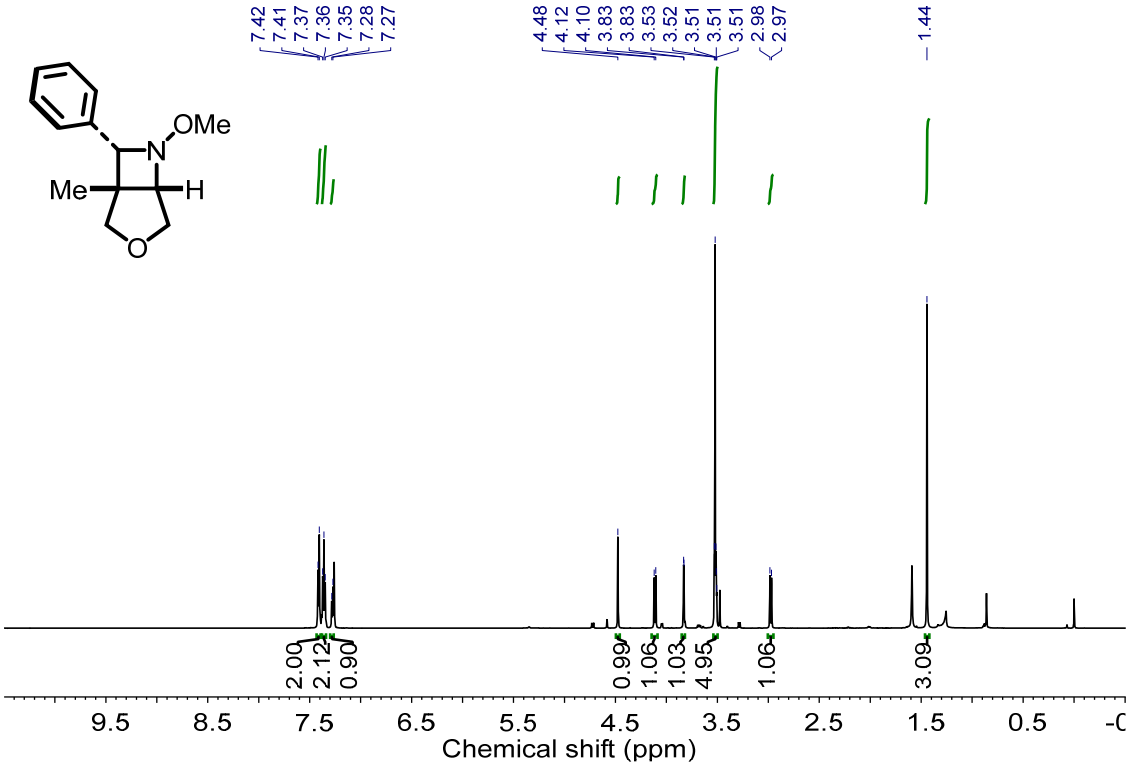
4c, ^{1}H NMR (400 MHz, $CDCl_3$)



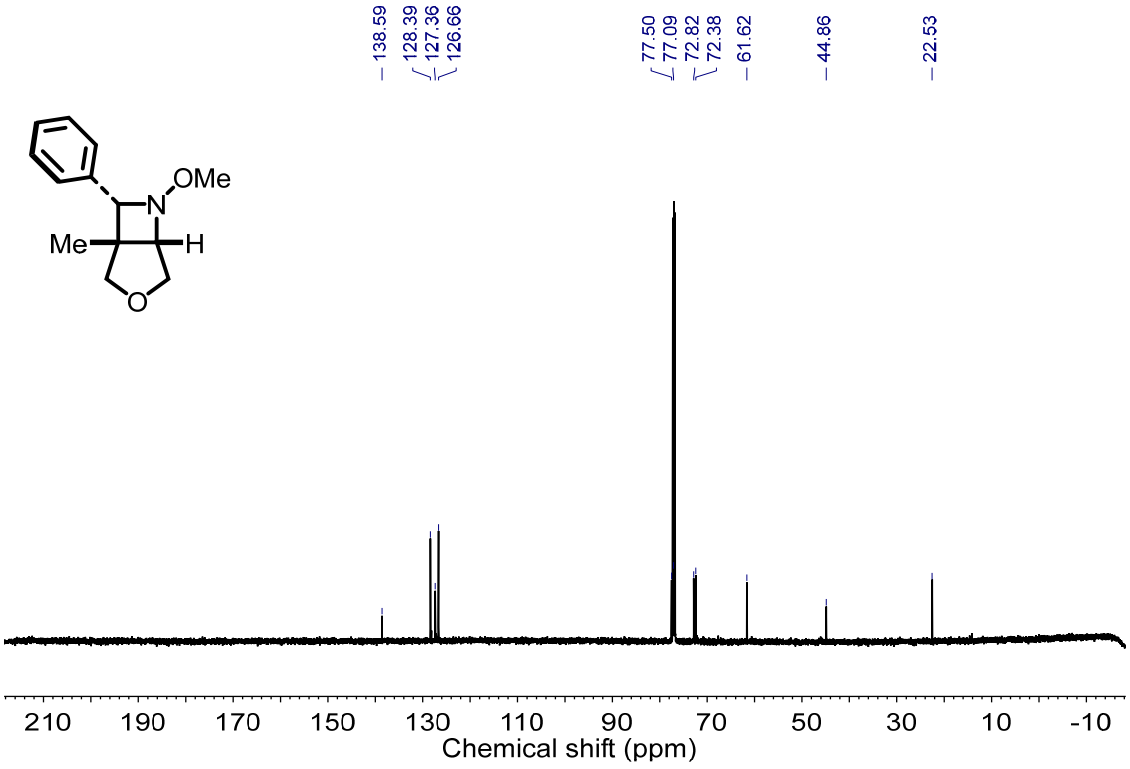
4c, ^{13}C NMR (151 MHz, $CDCl_3$)



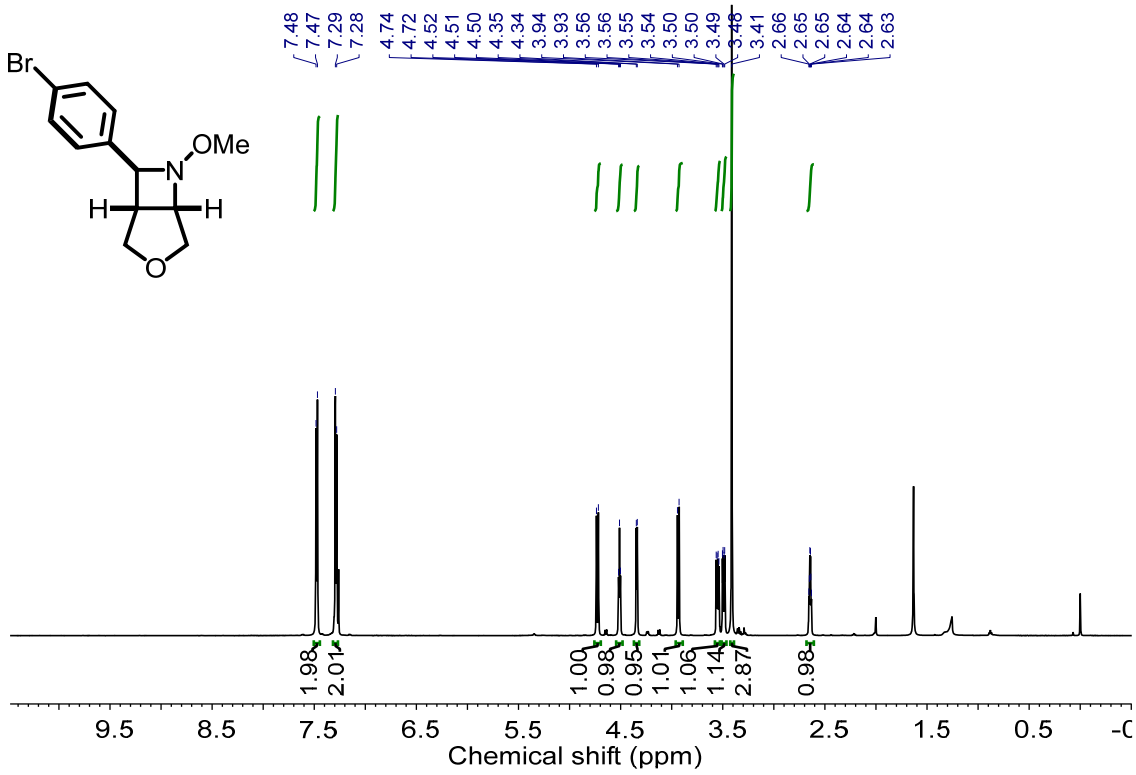
4d, ^{1}H NMR (600 MHz, $CDCl_3$)



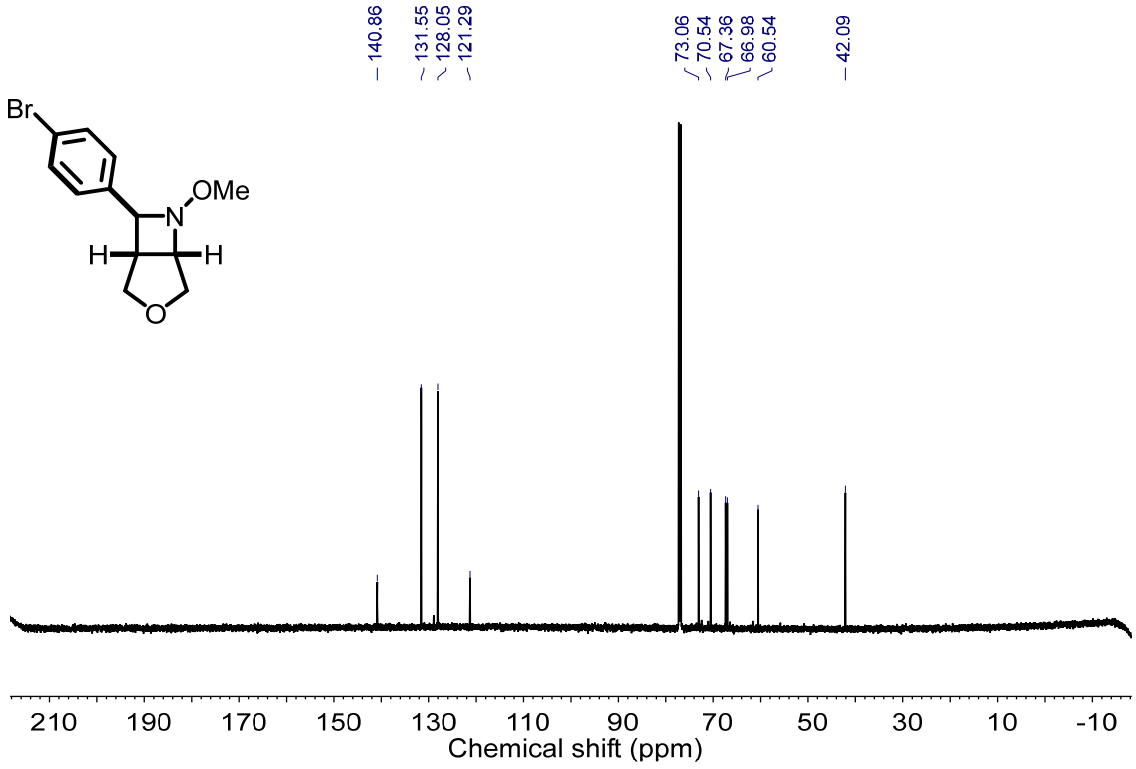
4d, ^{13}C NMR (151 MHz, $CDCl_3$)



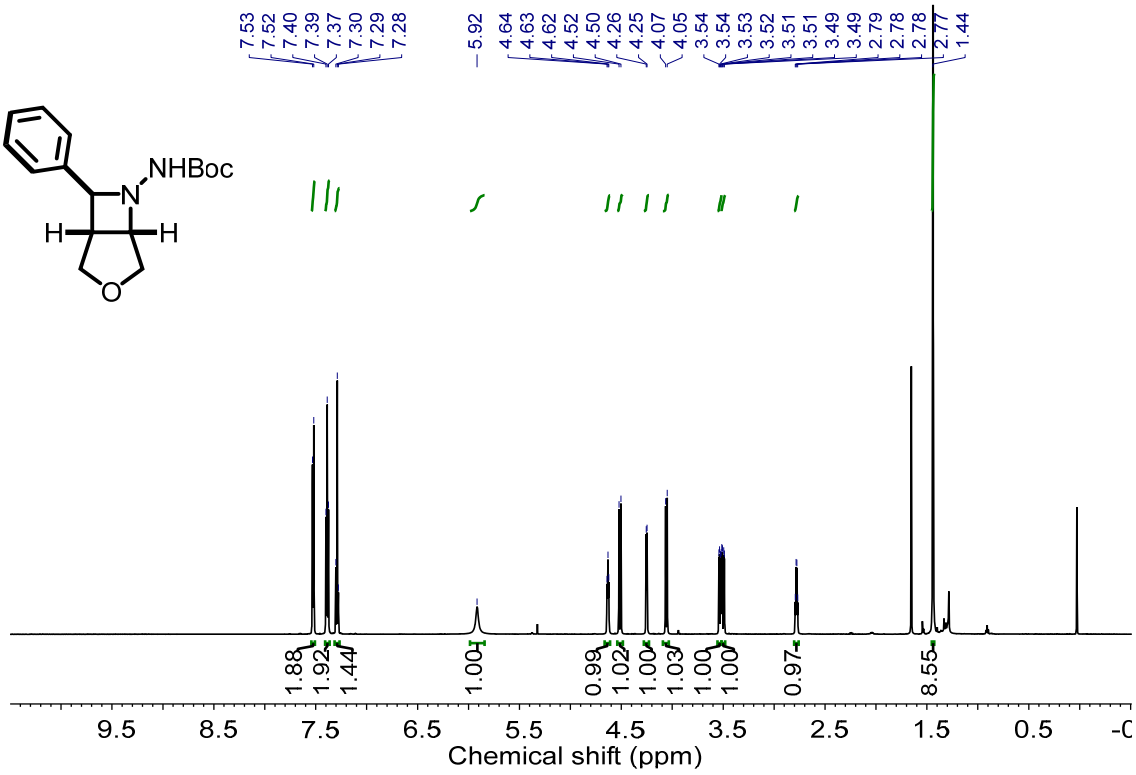
4e, ^{1}H NMR (600 MHz, $CDCl_3$)



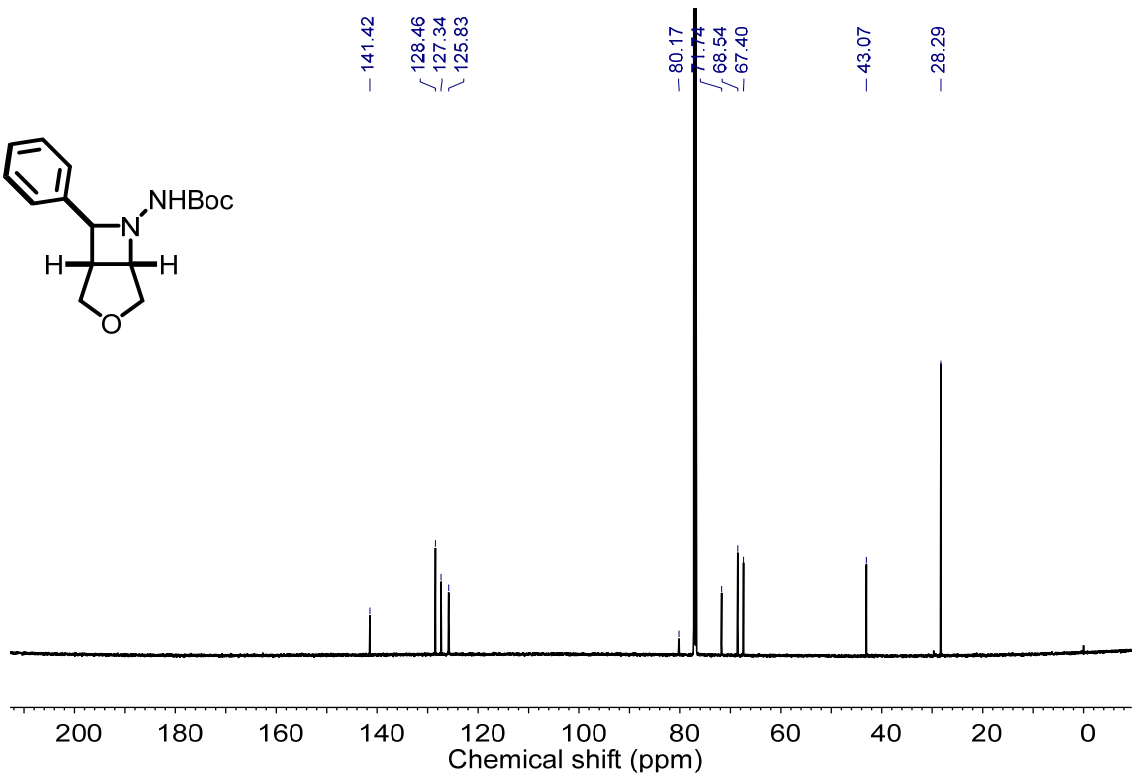
4e, ^{13}C NMR (151 MHz, $CDCl_3$)



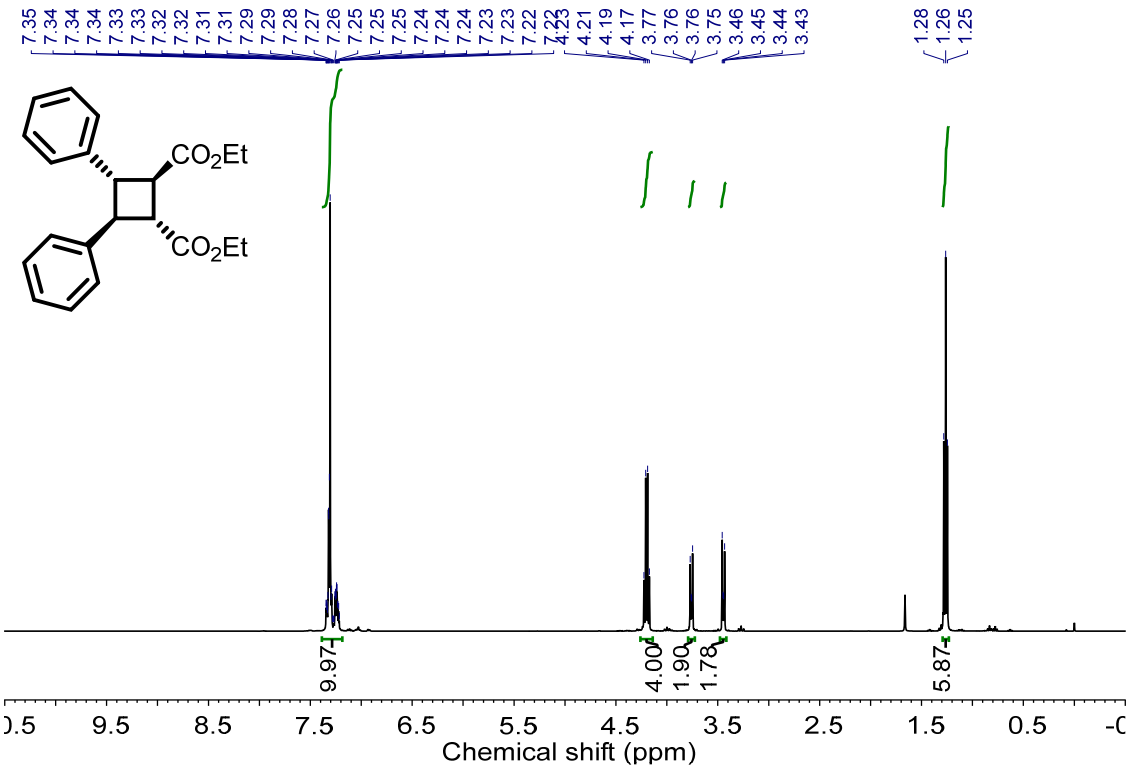
4f, ^{1}H NMR (600 MHz, $CDCl_3$)



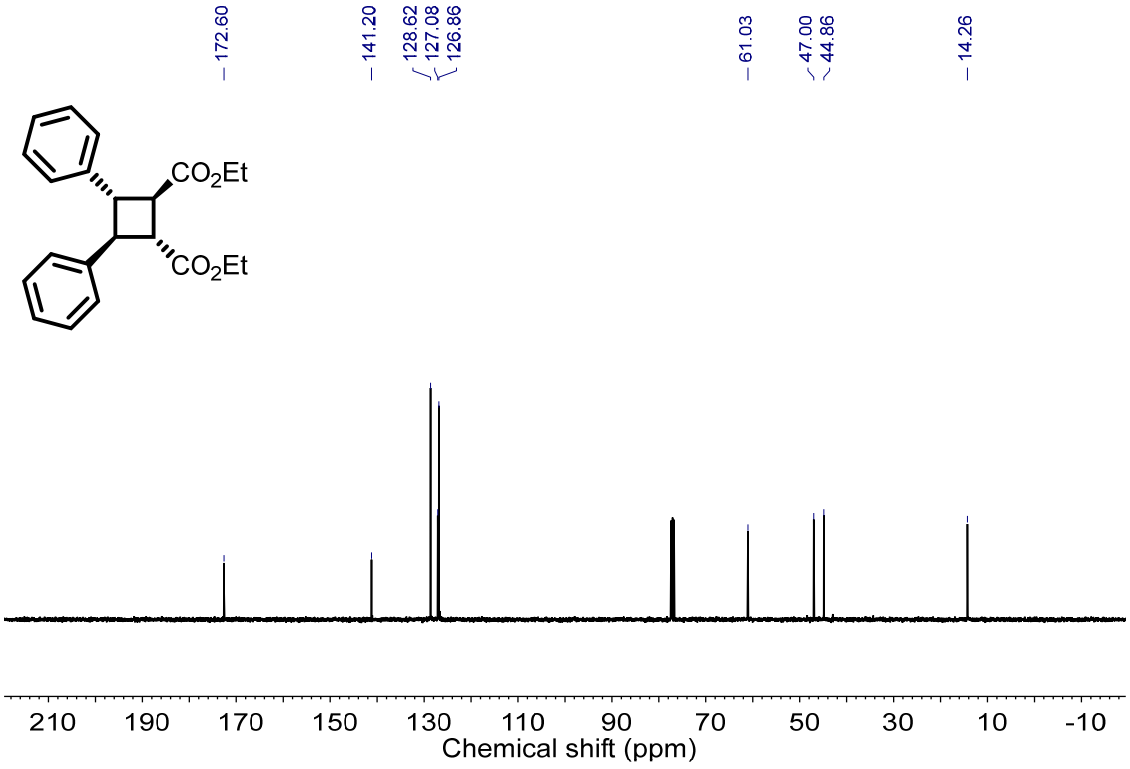
4f, ^{13}C NMR (151 MHz, $CDCl_3$)



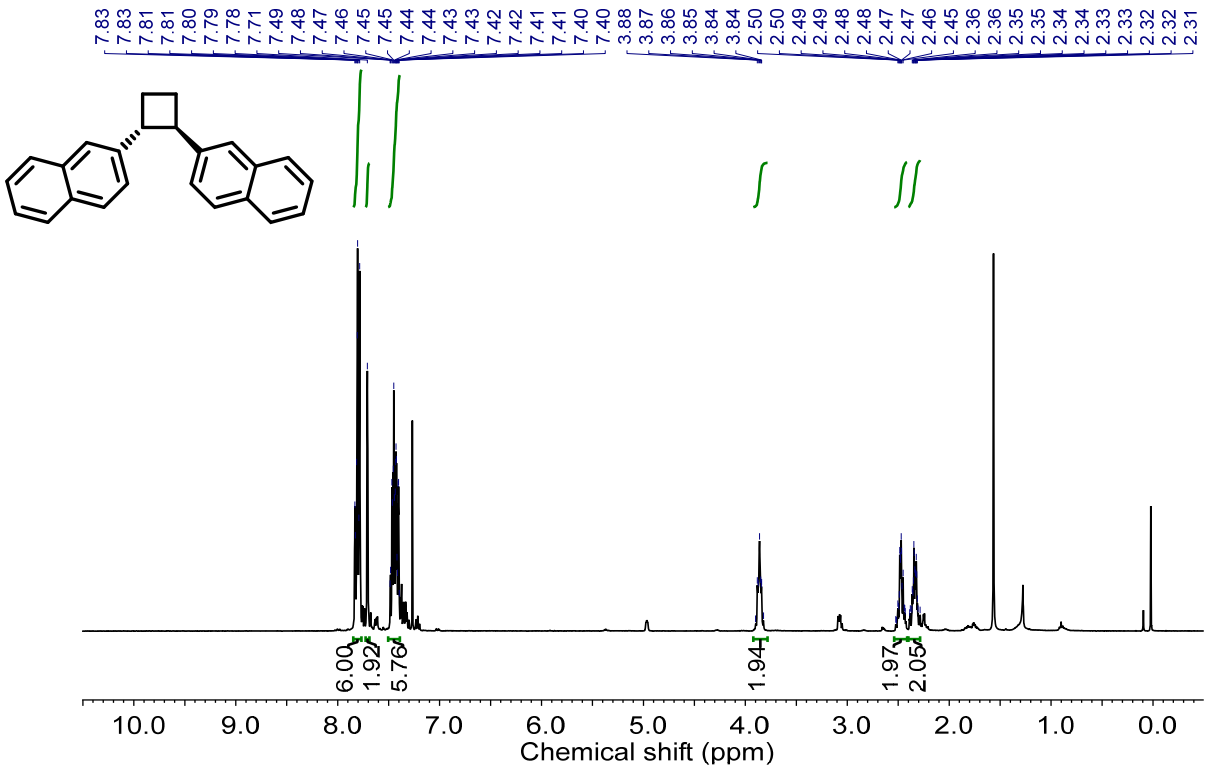
7a, ^{1}H NMR (400 MHz, $CDCl_3$)



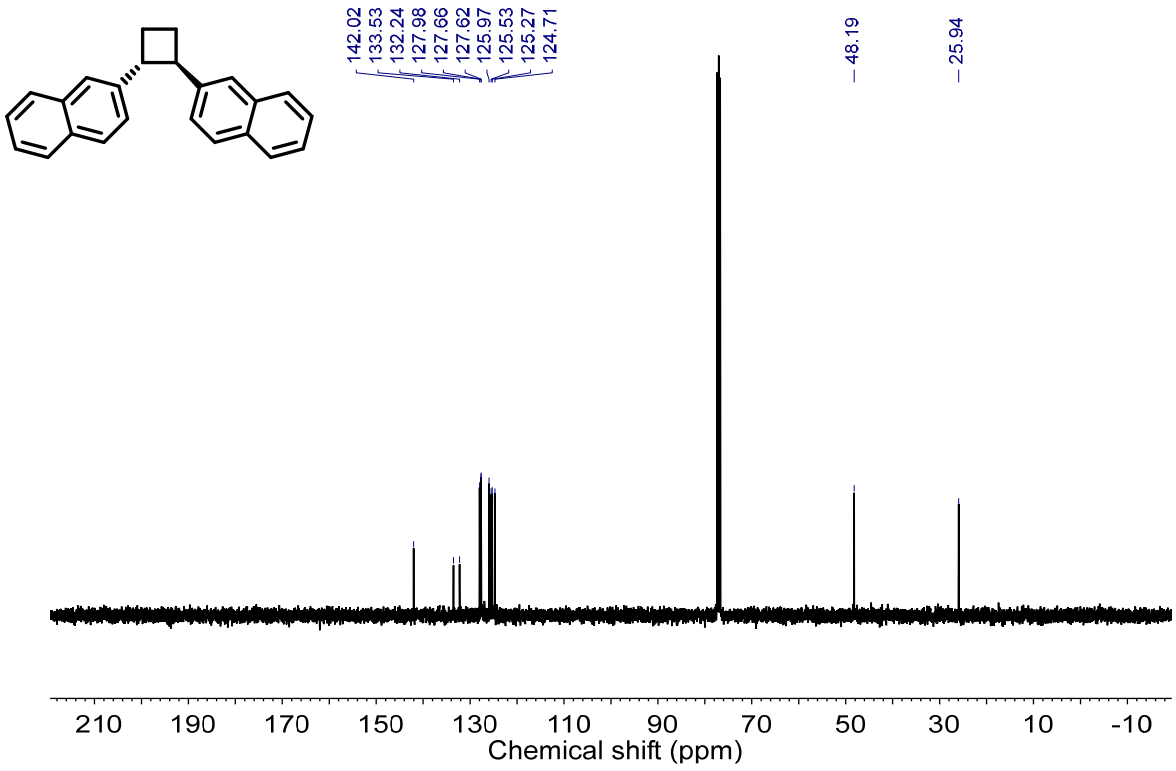
7a, ^{13}C NMR (101 MHz, $CDCl_3$)



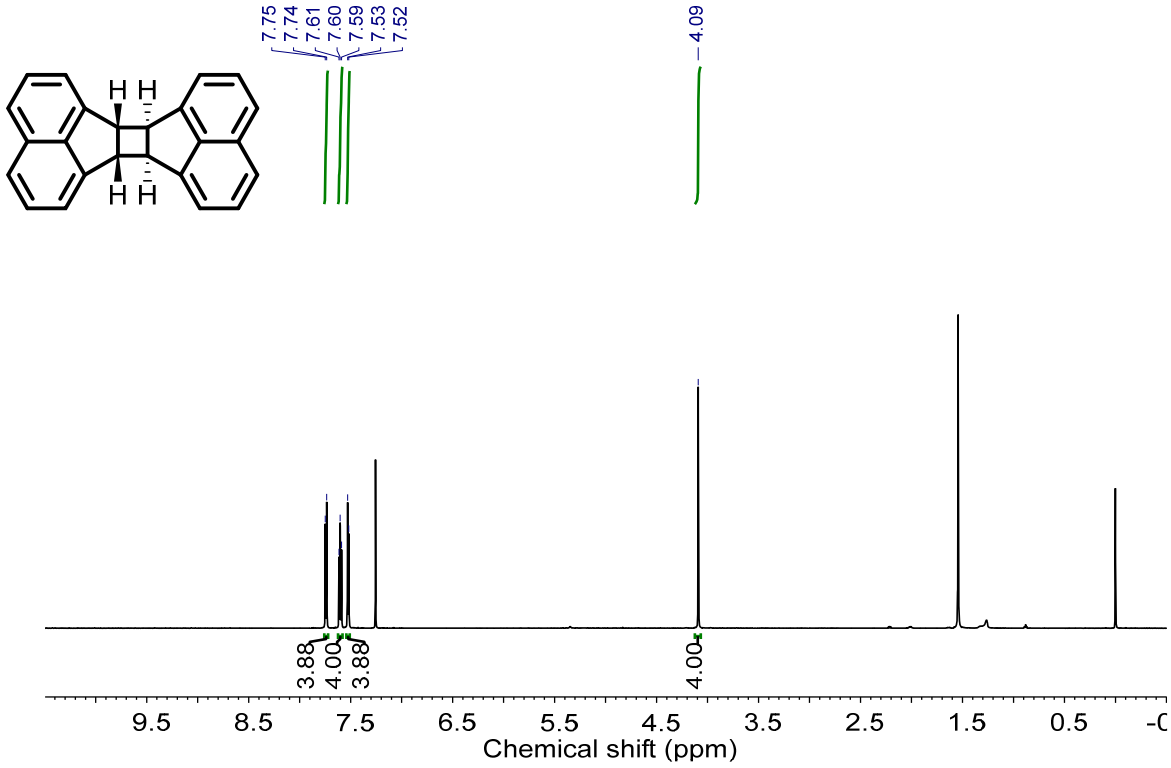
7b, ^{1}H NMR (400 MHz, $CDCl_3$)



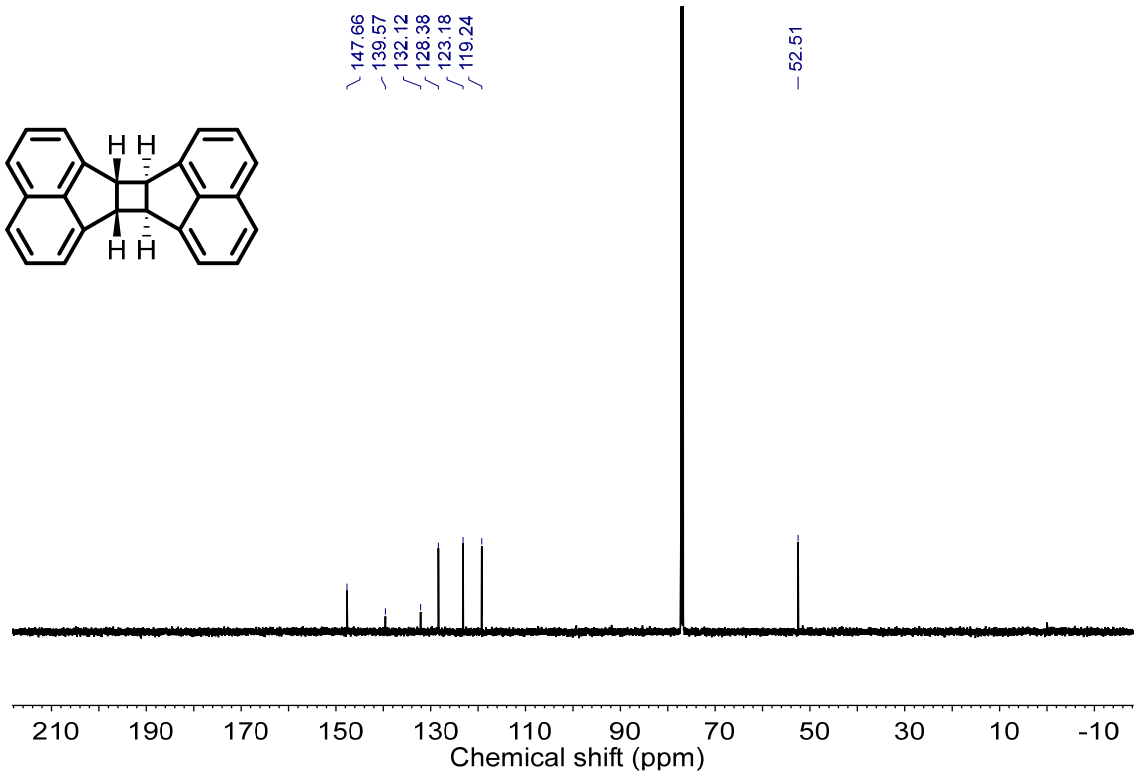
7b, ^{13}C NMR (101 MHz, $CDCl_3$)



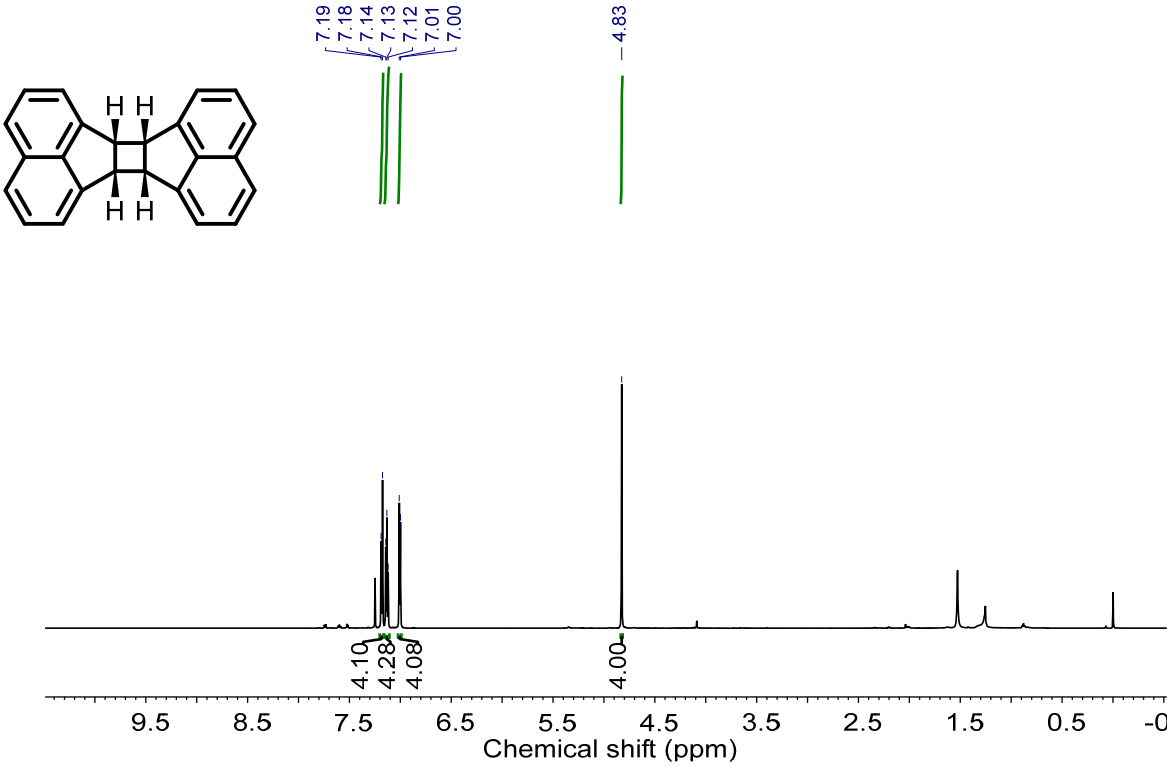
7c, ^{1}H NMR (600 MHz, $CDCl_3$)



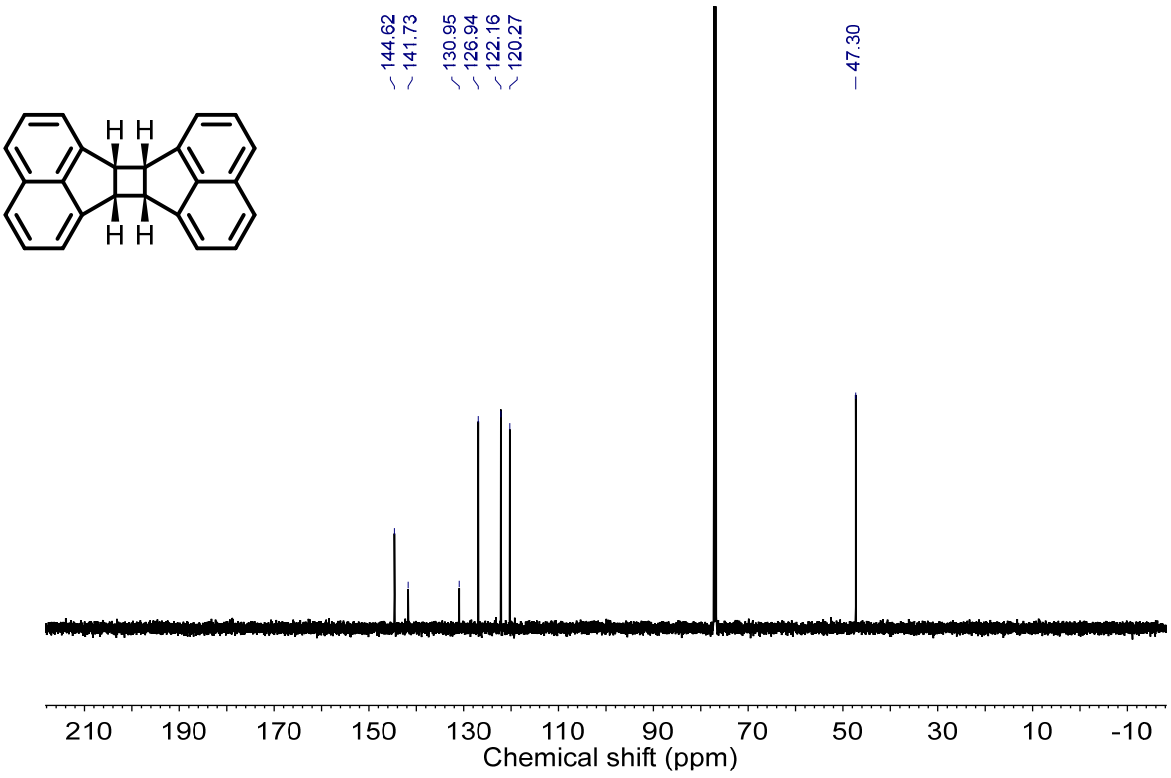
7c, ^{13}C NMR (151 MHz, $CDCl_3$)



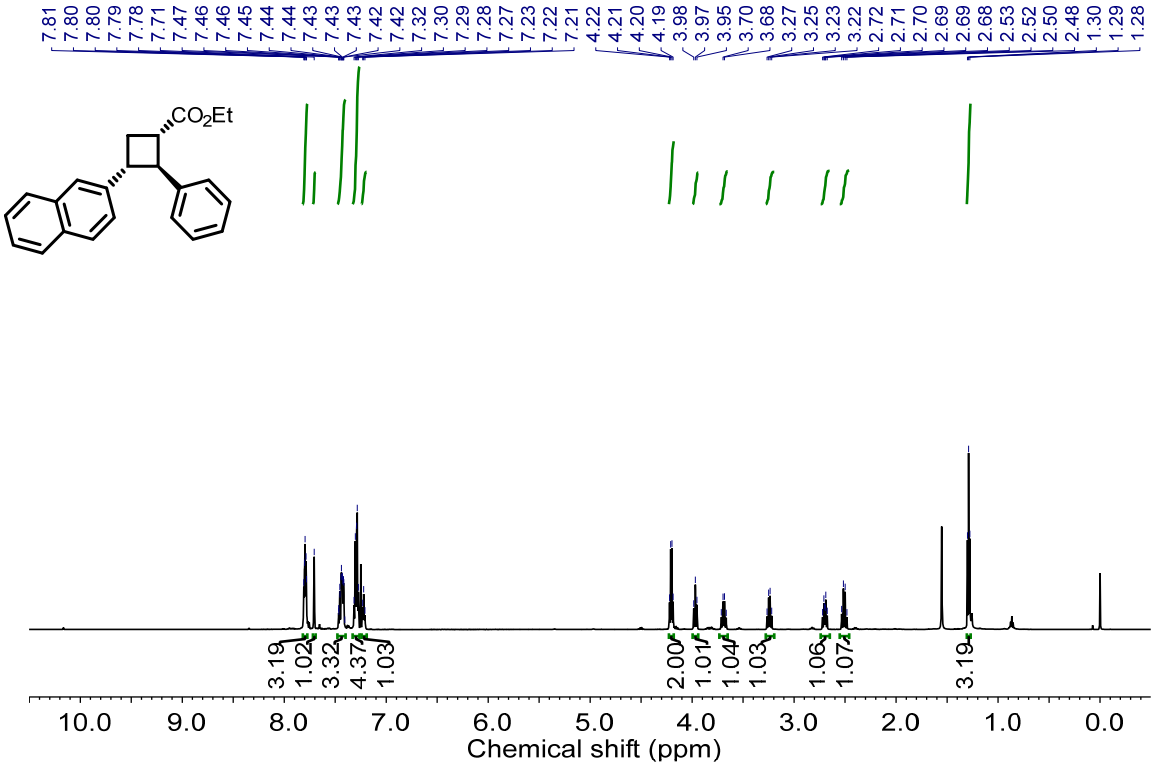
7c, ^{1}H NMR (600 MHz, $CDCl_3$)



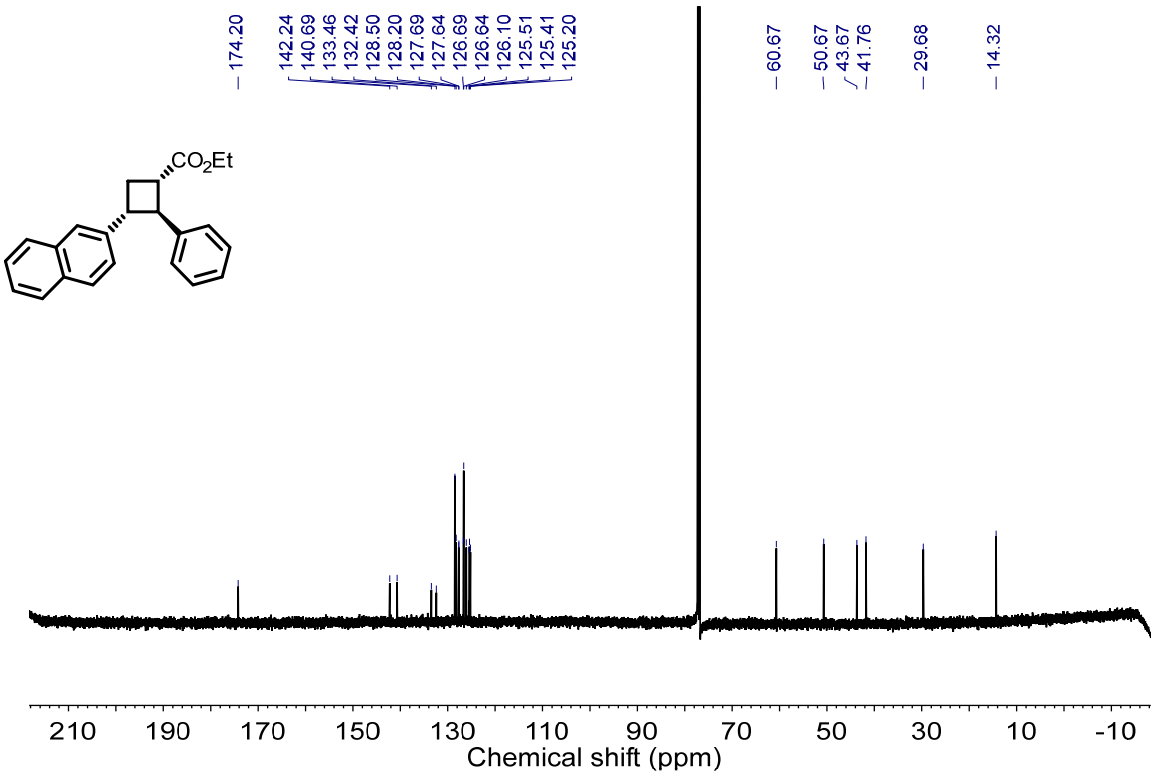
7c, ^{13}C NMR (151 MHz, $CDCl_3$)



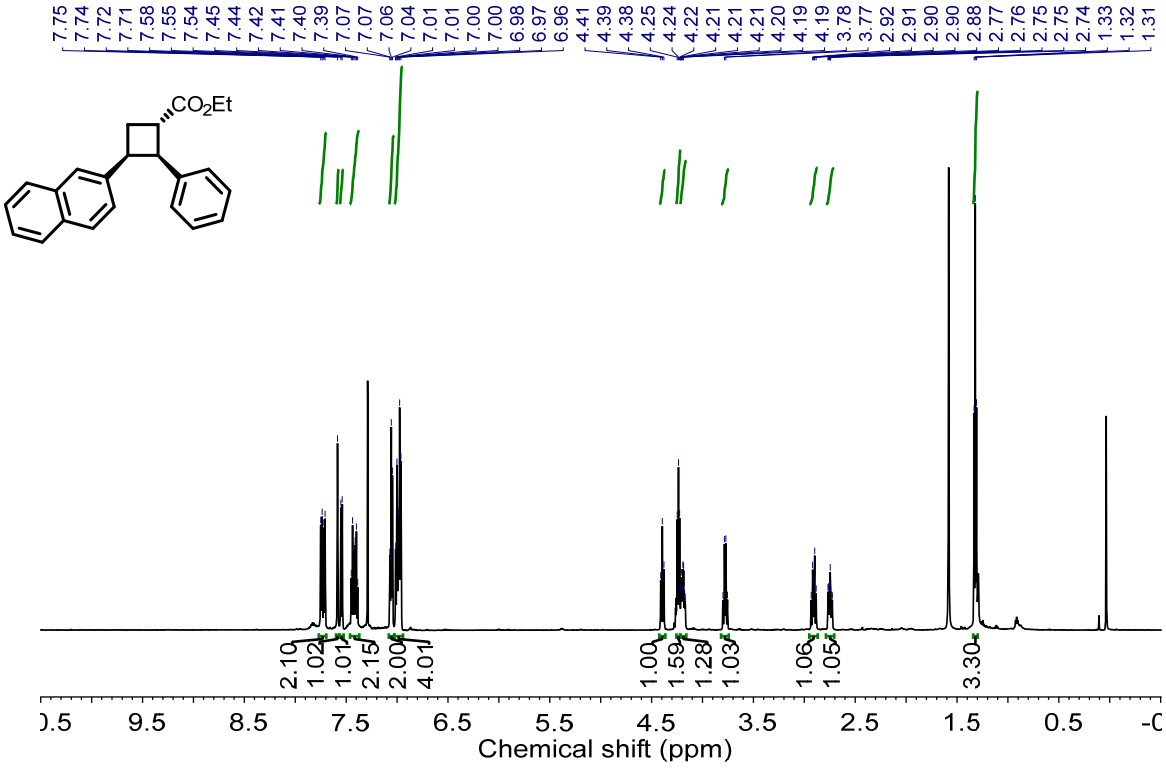
7d, ^{1}H NMR (600 MHz, $CDCl_3$)



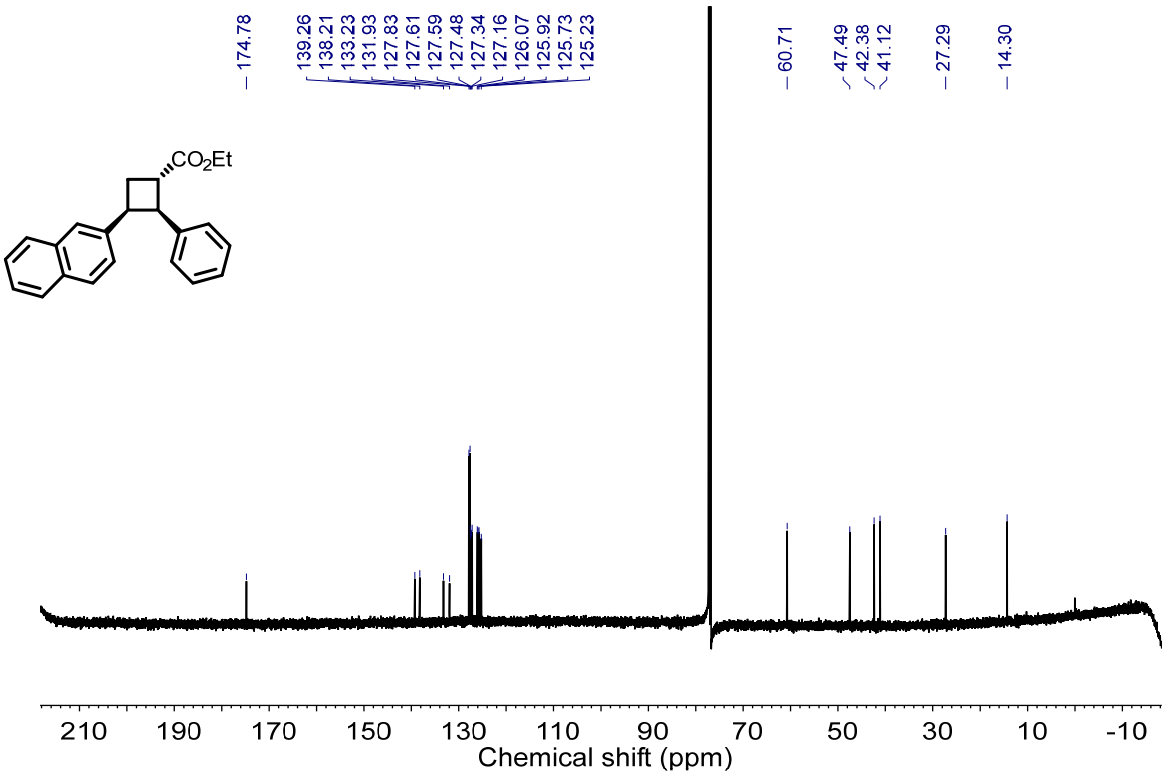
7d, ^{13}C NMR (151 MHz, $CDCl_3$)



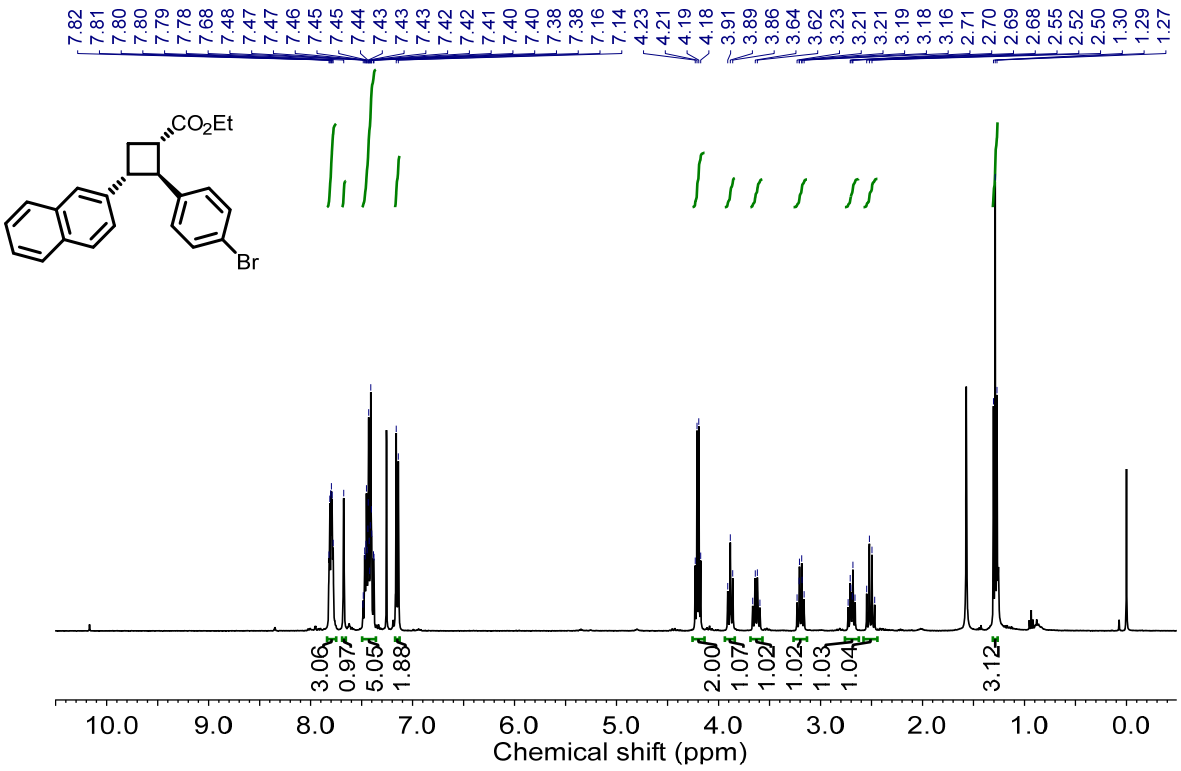
7d, ^{1}H NMR (600 MHz, $CDCl_3$)



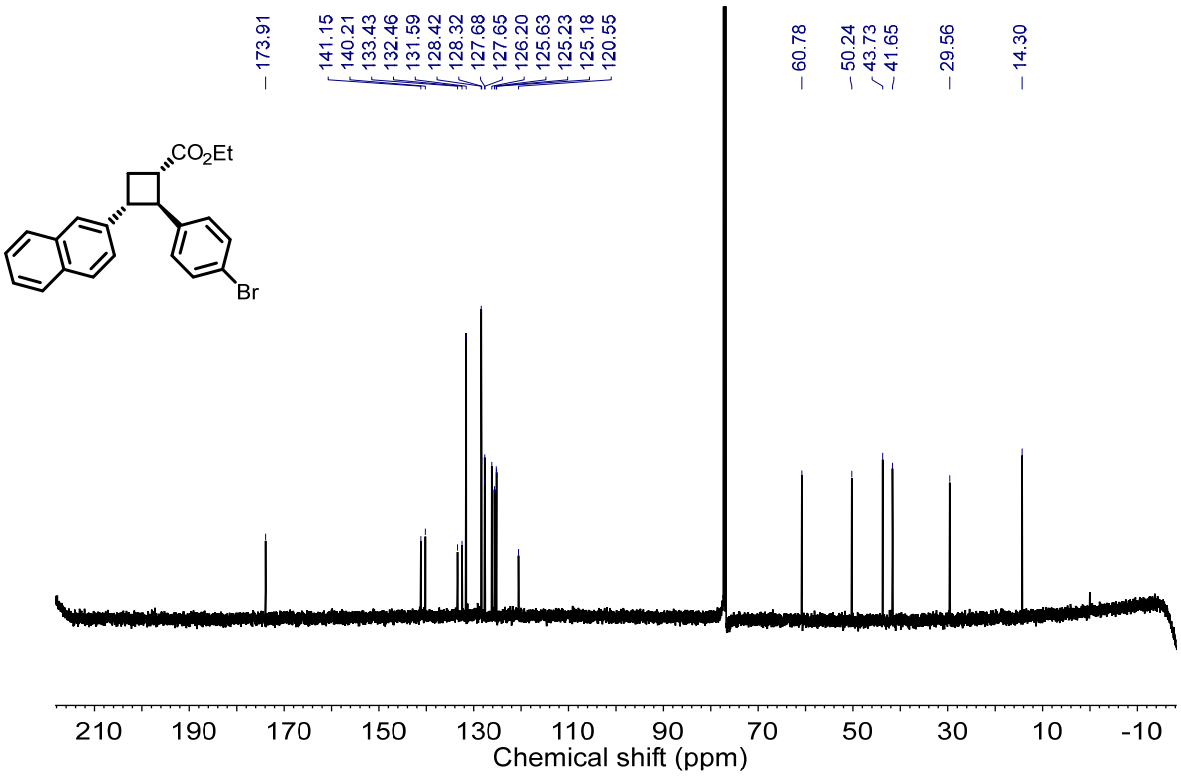
7d, ^{13}C NMR (151 MHz, $CDCl_3$)



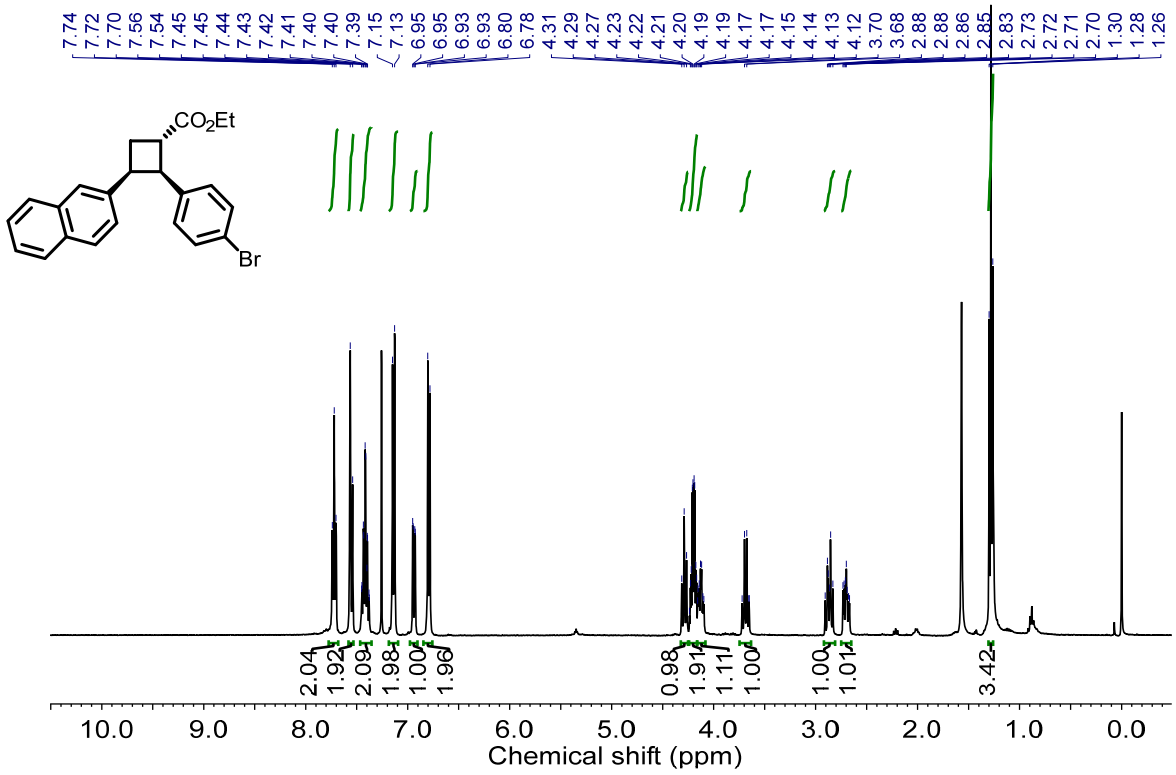
7e, ^{1}H NMR (400 MHz, $CDCl_3$)



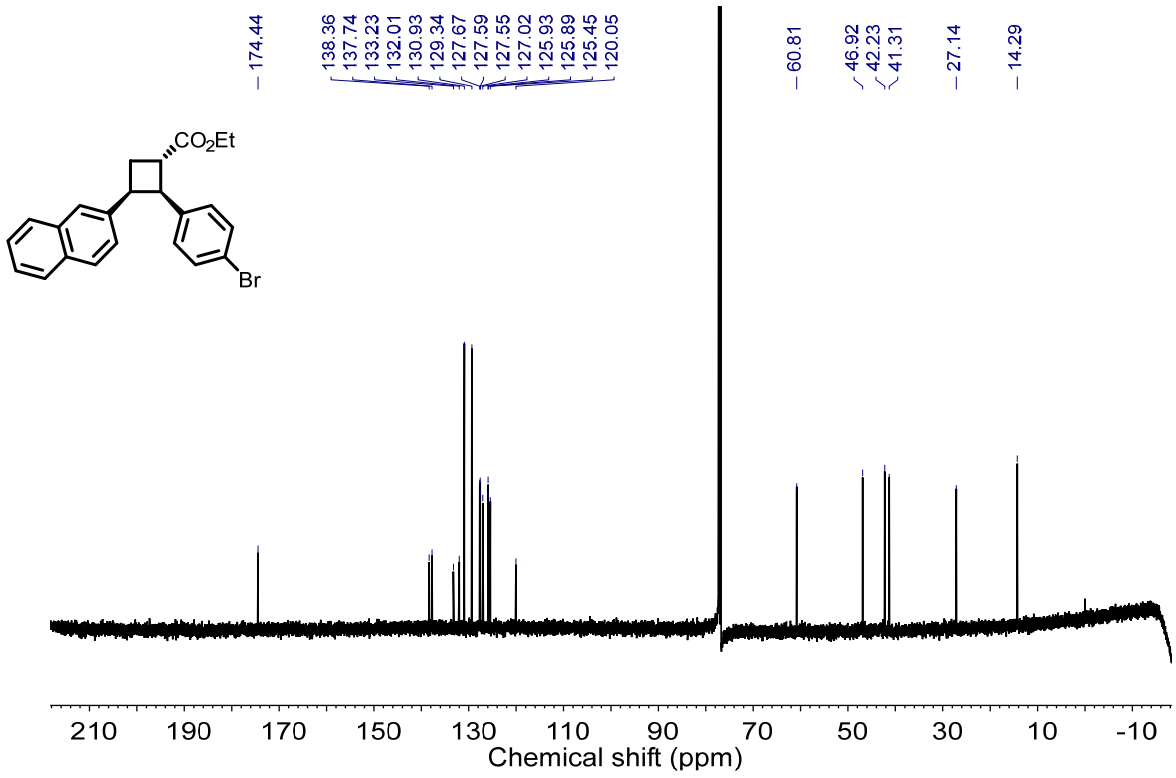
7e, ^{13}C NMR (151 MHz, $CDCl_3$)



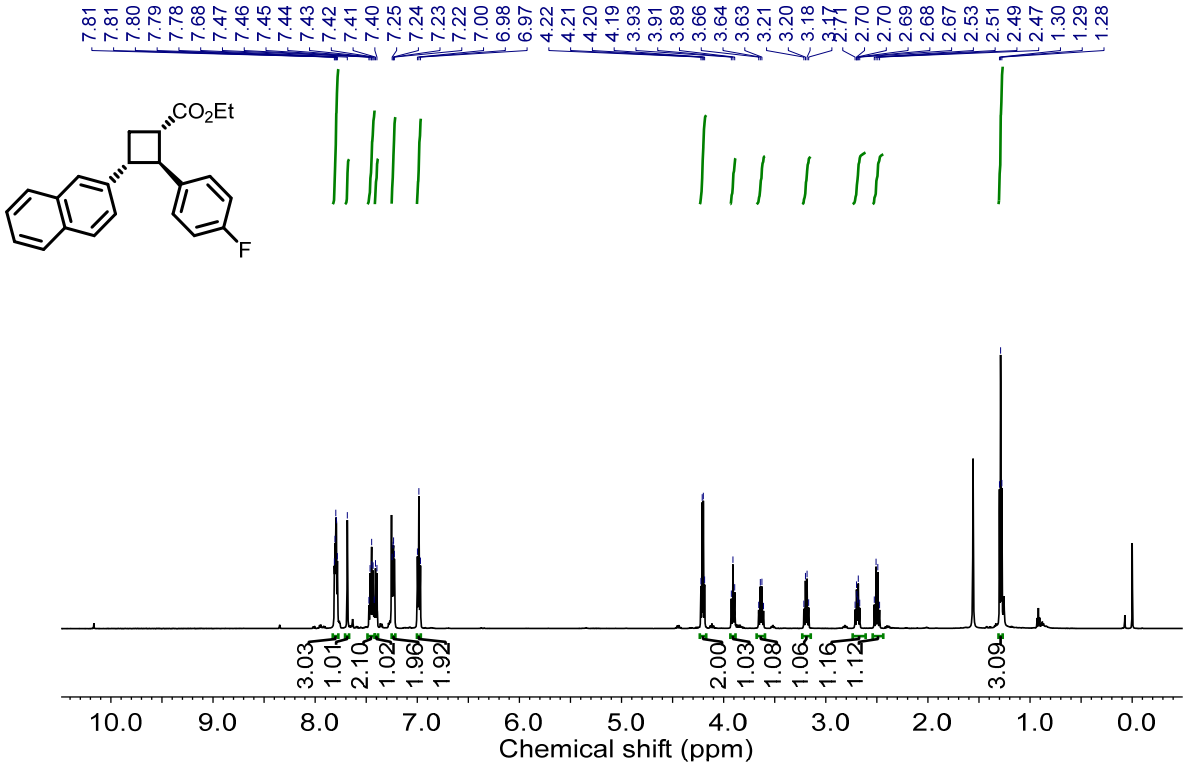
7e, ^{1}H NMR (400 MHz, $CDCl_3$)



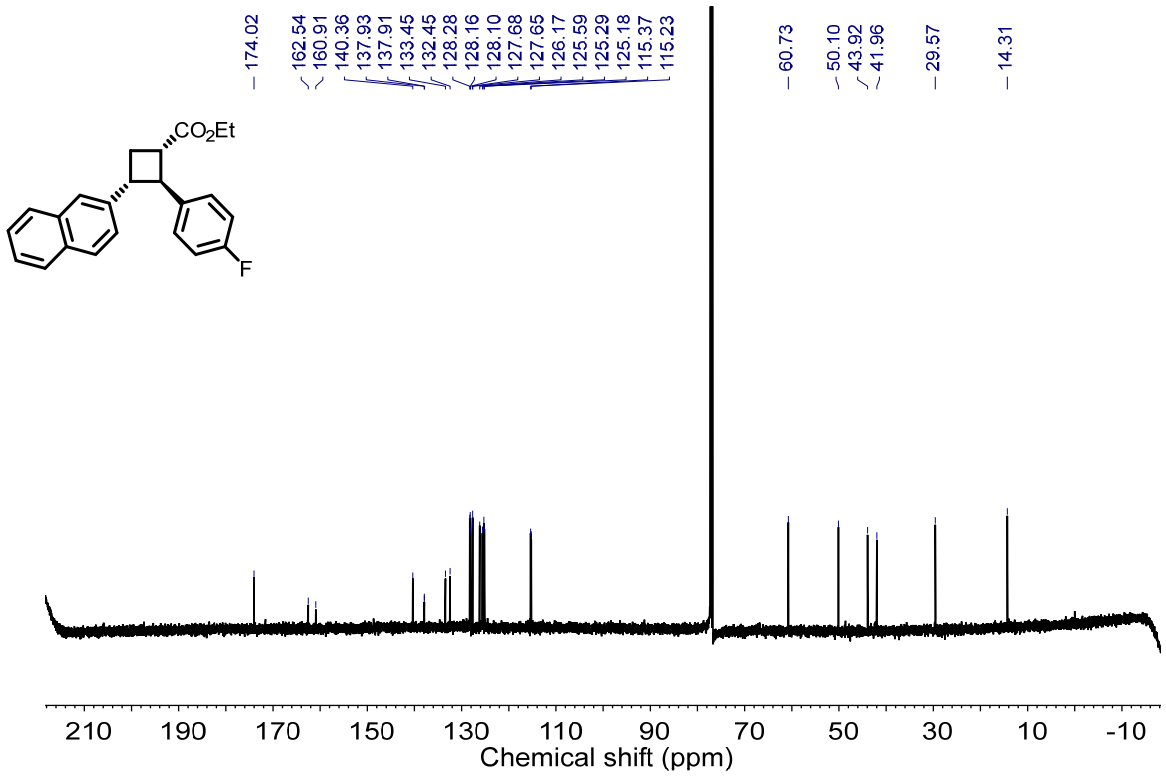
7e, ^{13}C NMR (151 MHz, $CDCl_3$)



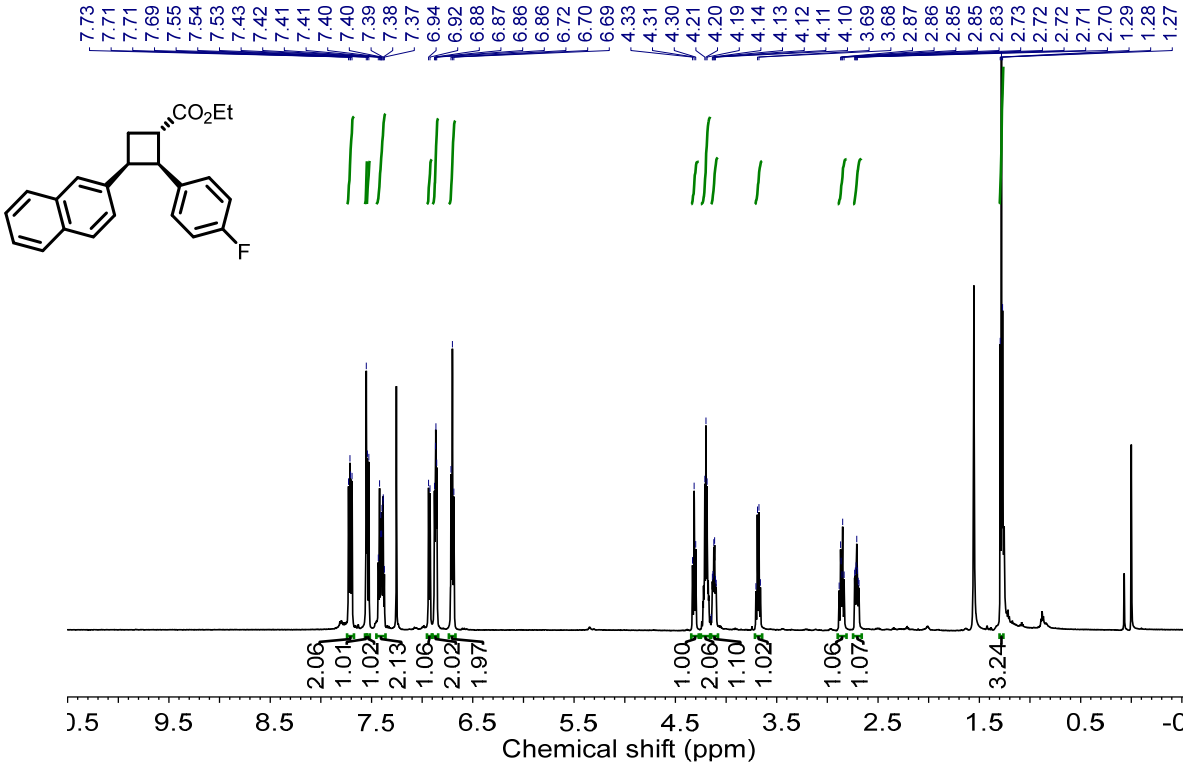
7f, ^{1}H NMR (600 MHz, $CDCl_3$)



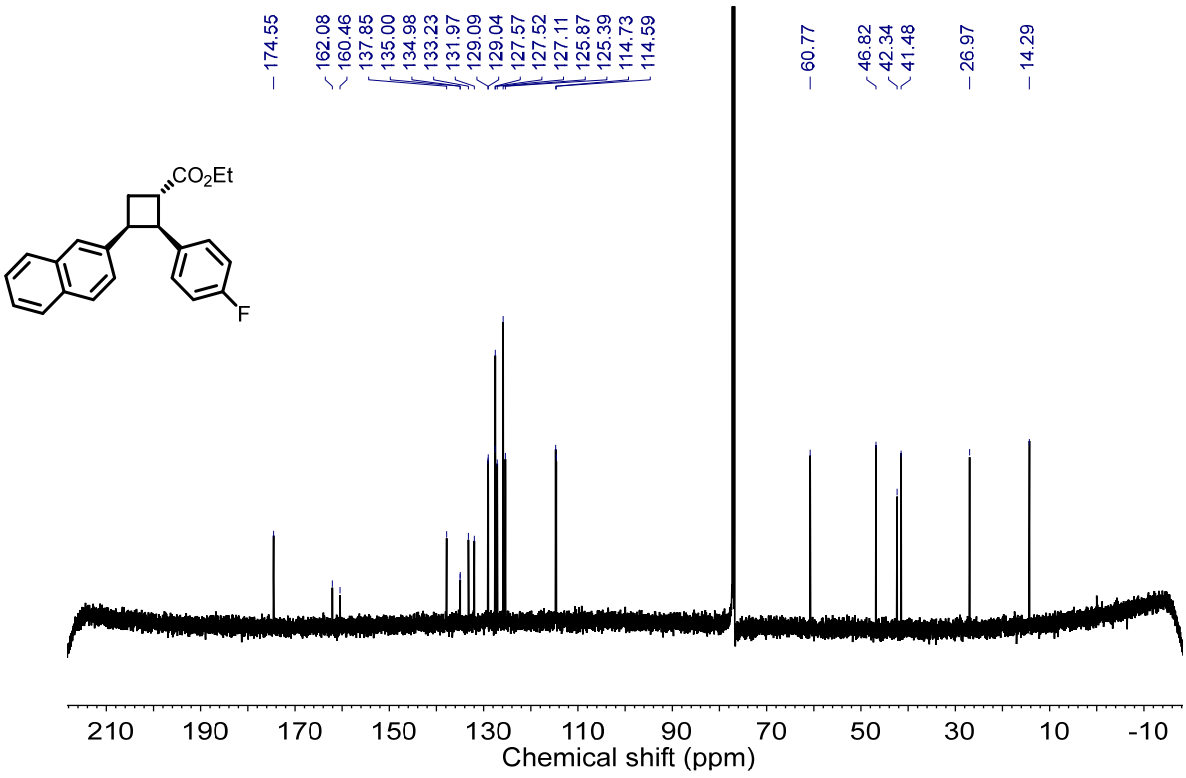
7f, ^{13}C NMR (151 MHz, $CDCl_3$)



7f, ^{1}H NMR (600 MHz, $CDCl_3$)



7f, ^{13}C NMR (151 MHz, $CDCl_3$)



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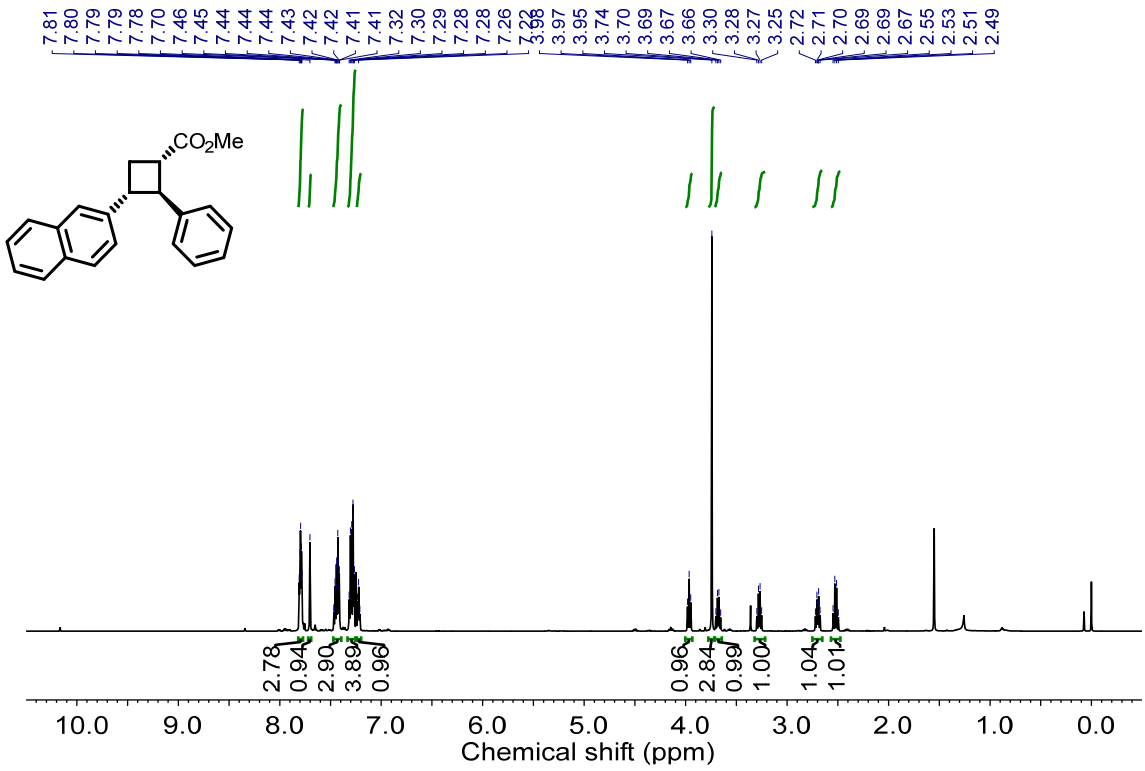
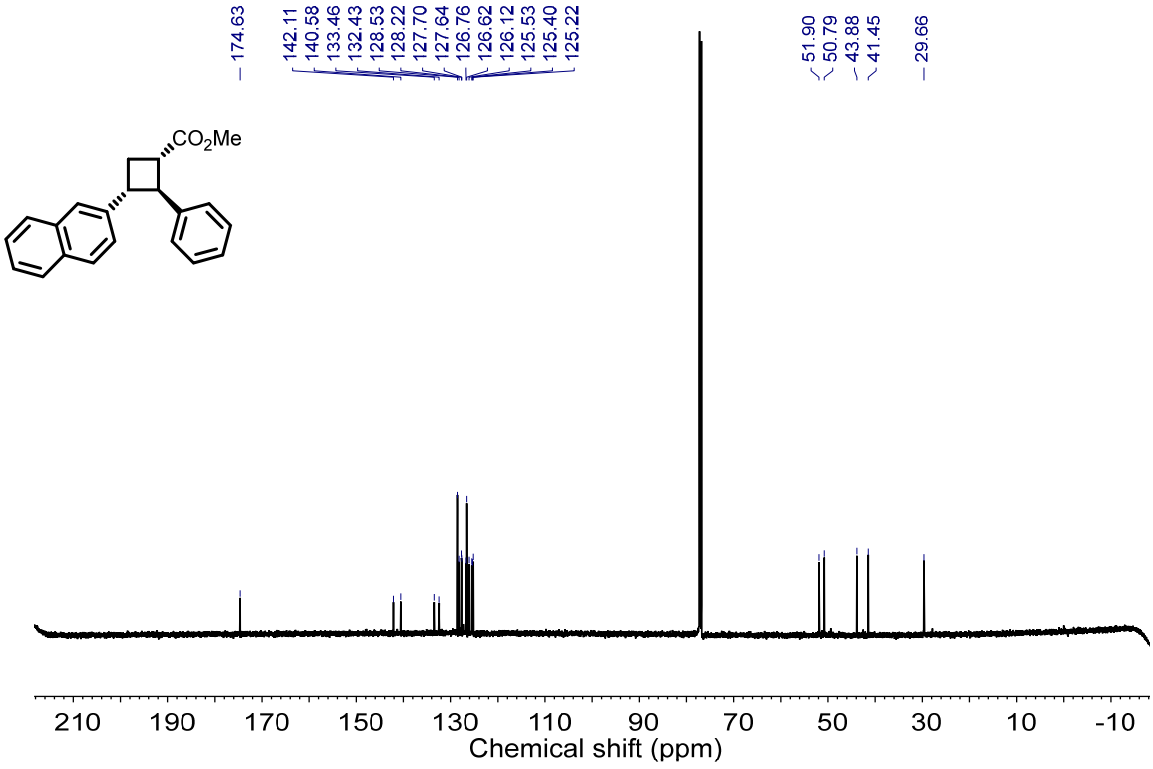
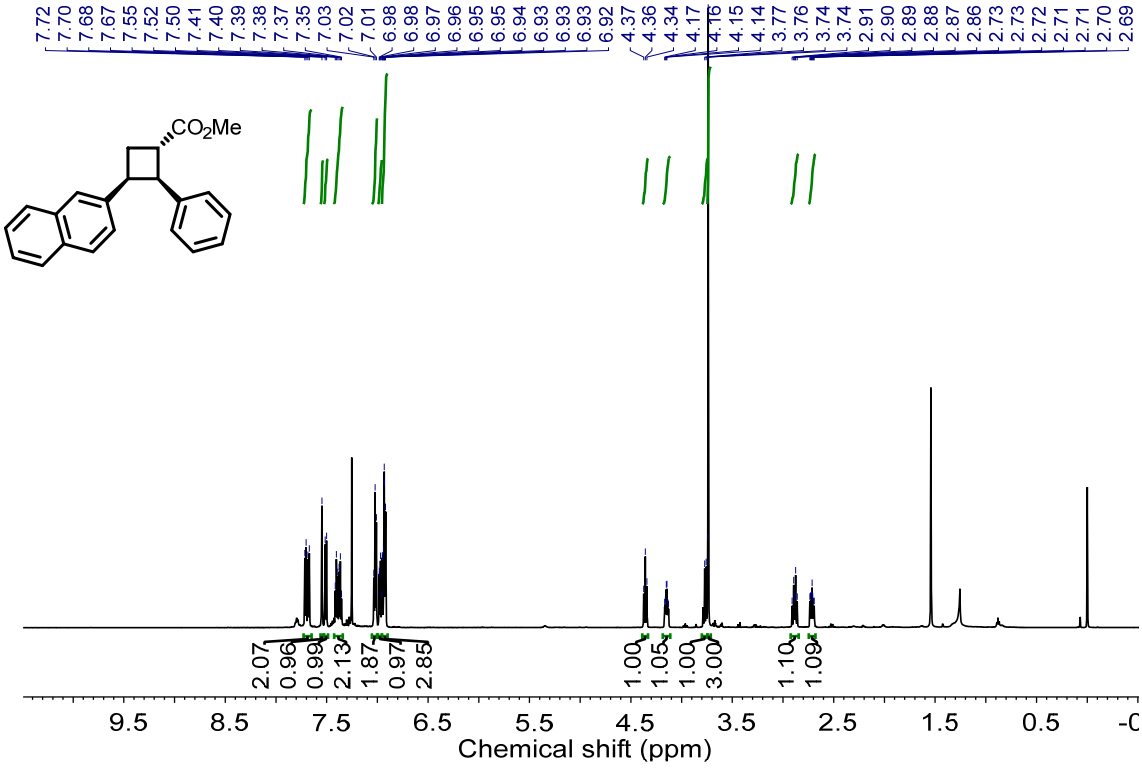


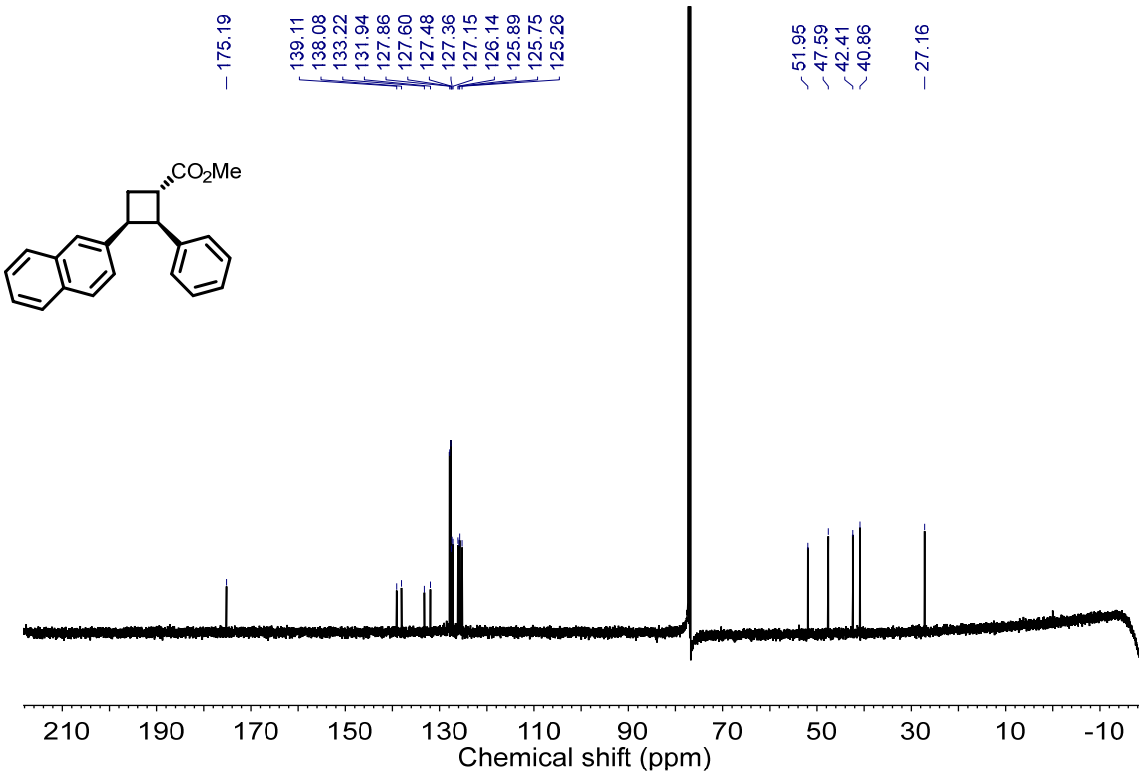
7g, ^{13}C NMR (151 MHz, $CDCl_3$)



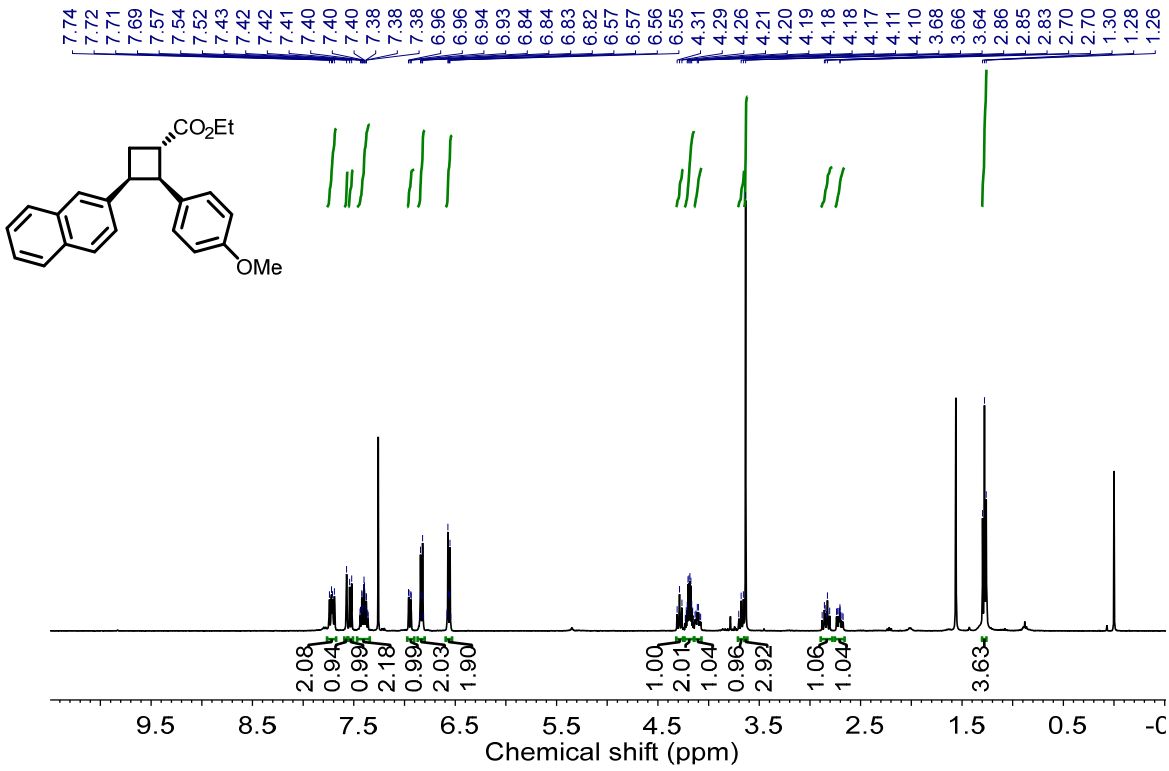
7g, ^{1}H NMR (600 MHz, $CDCl_3$)



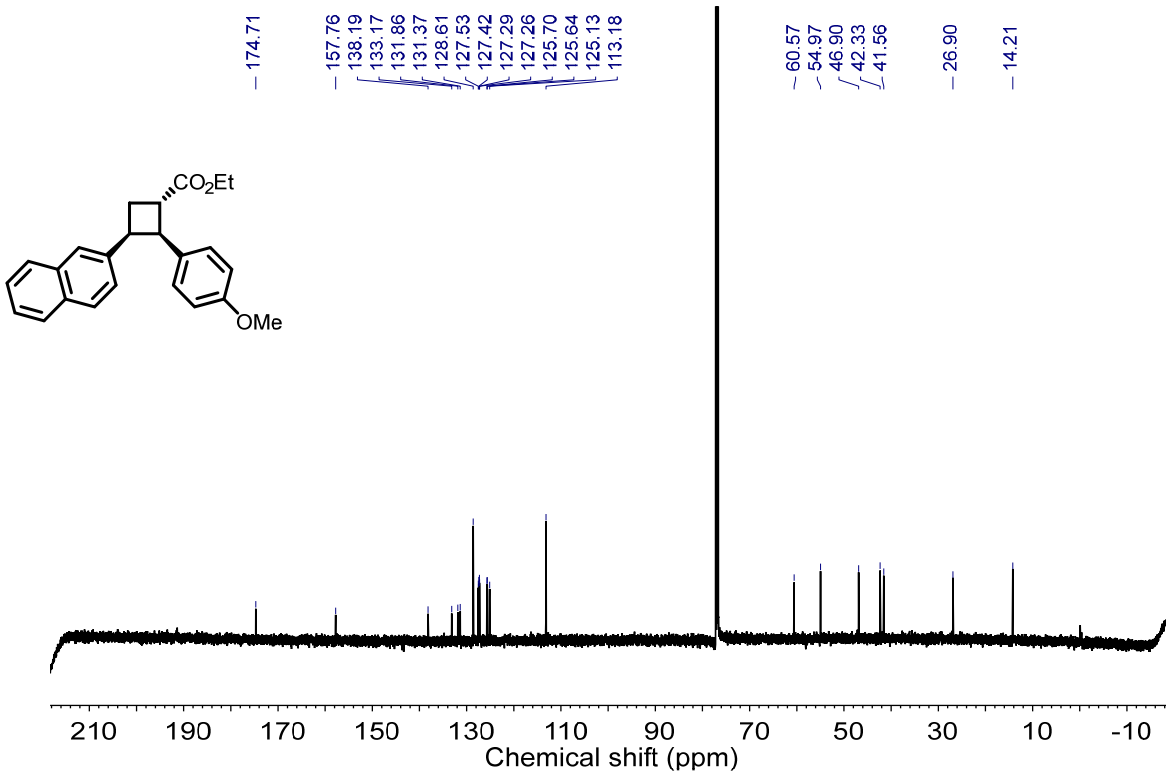
7g, ^{13}C NMR (151 MHz, $CDCl_3$)



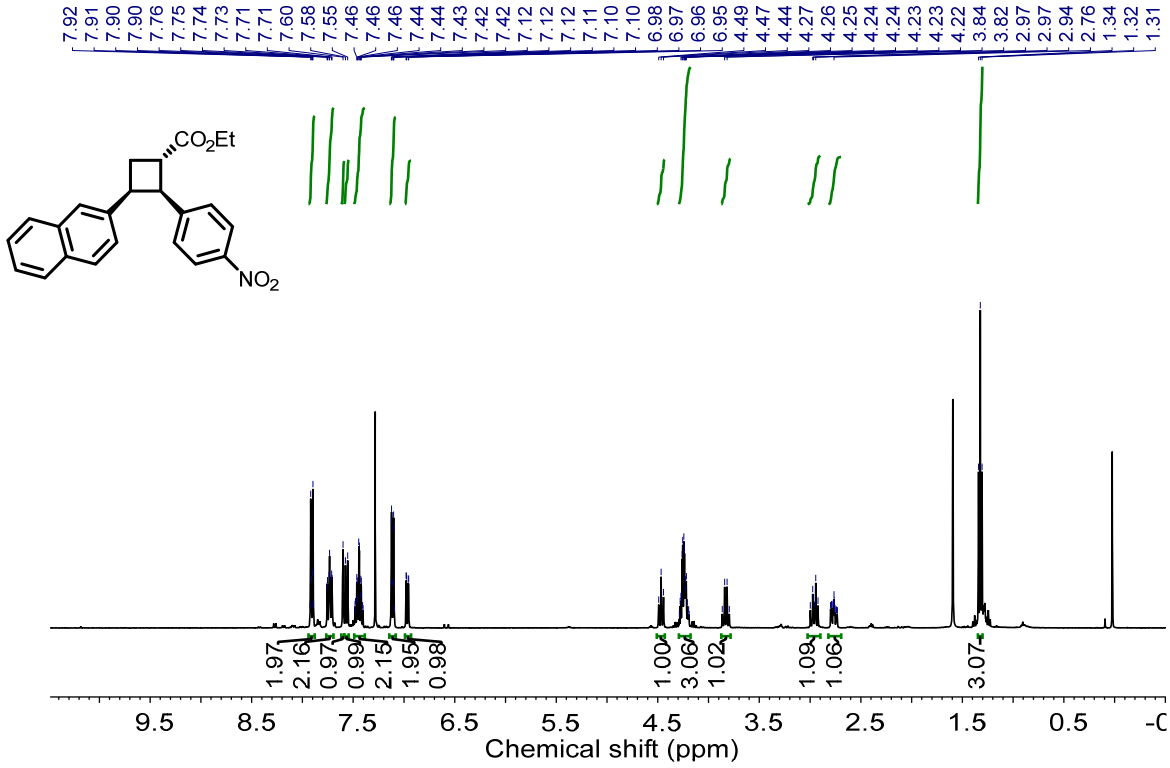
7h, ^{1}H NMR (400 MHz, $CDCl_3$)



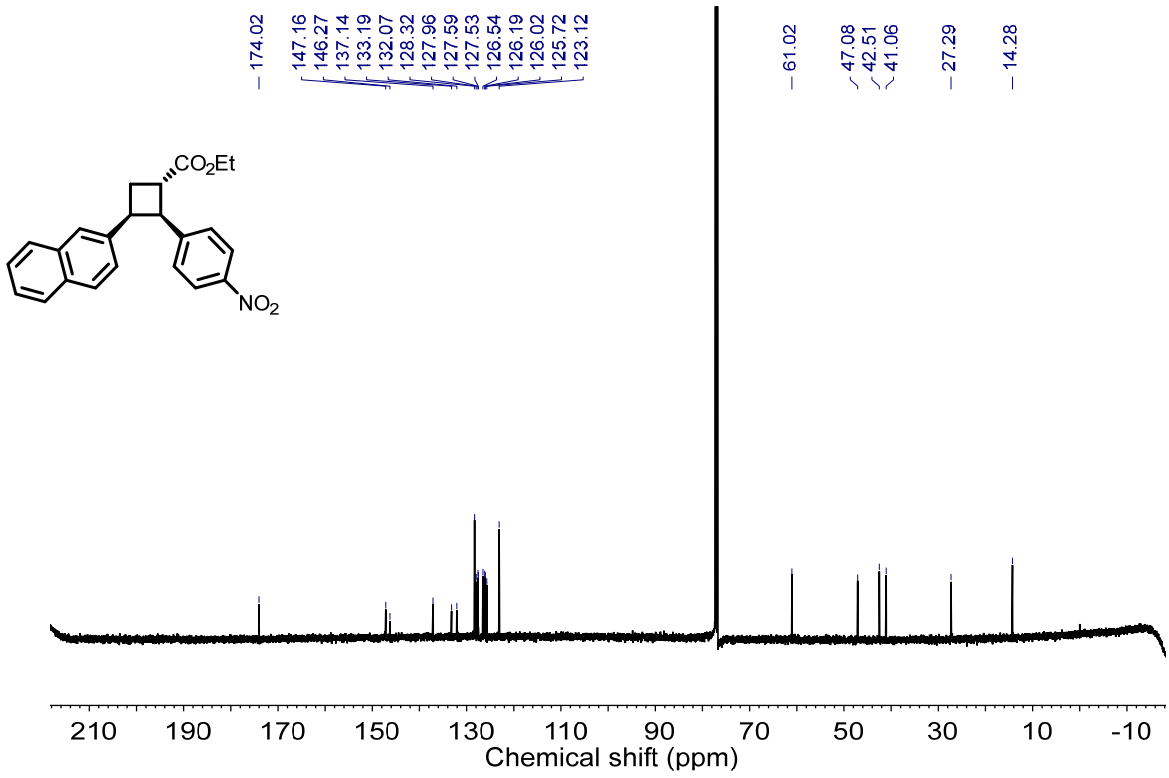
7h, ^{13}C NMR (151 MHz, $CDCl_3$)



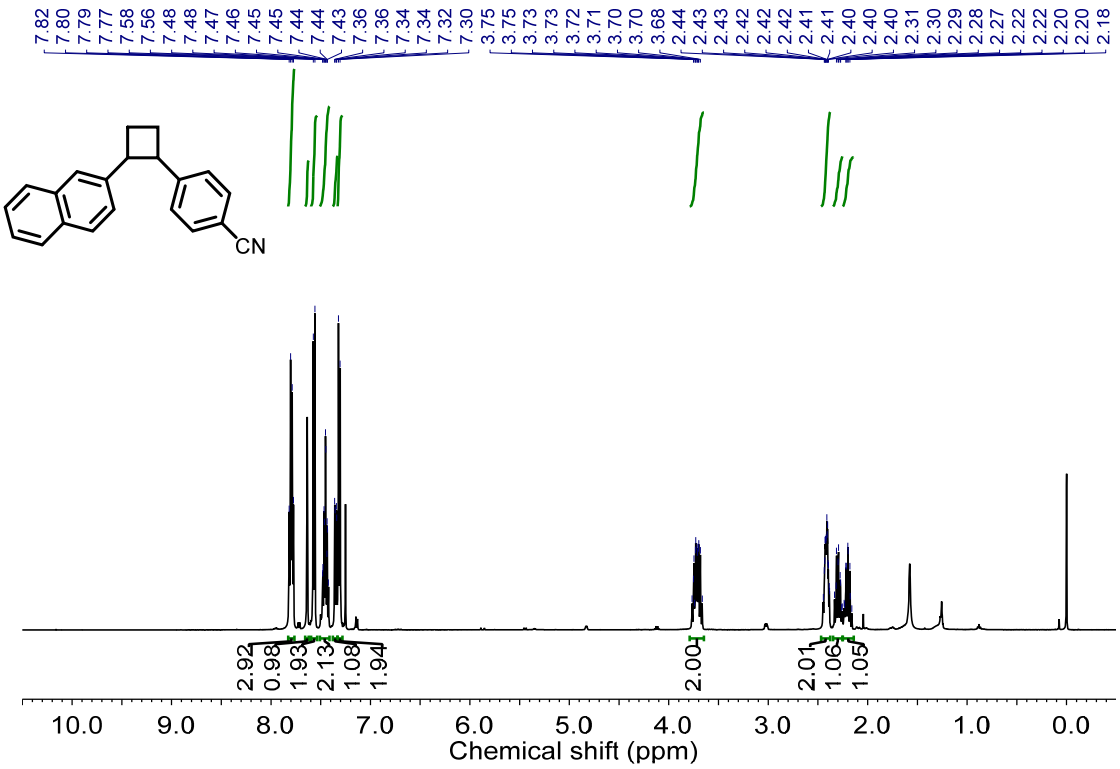
7i, ^{1}H NMR (400 MHz, $CDCl_3$)



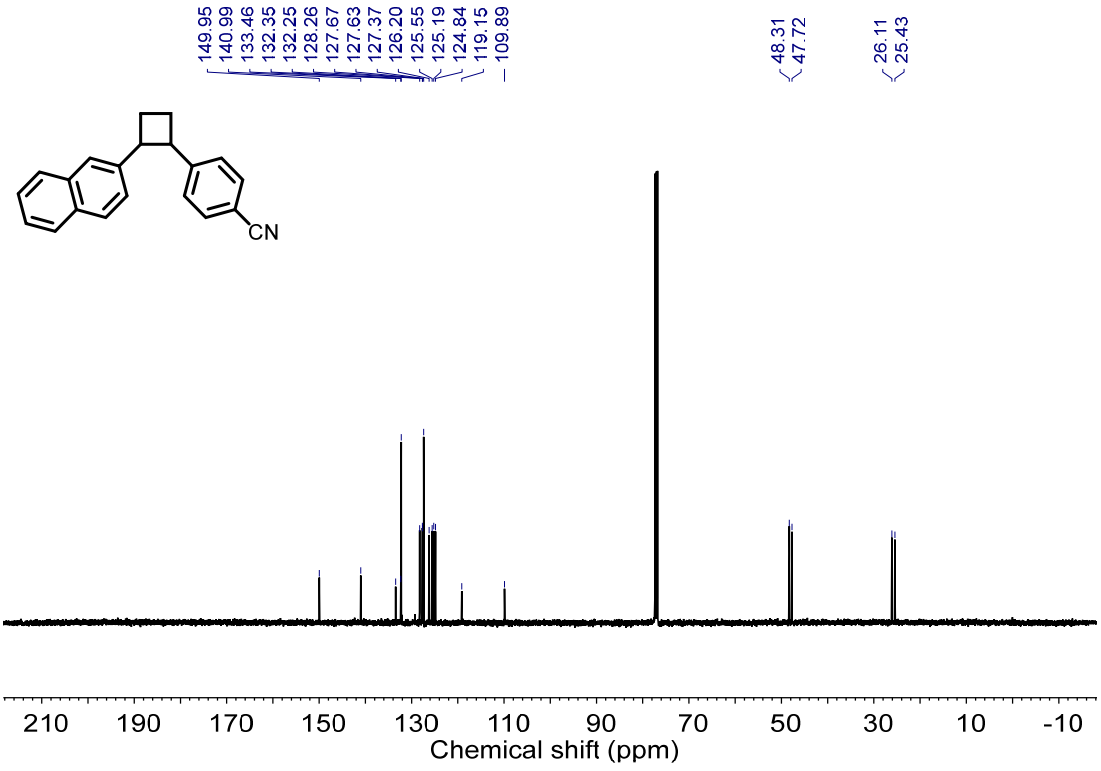
7i, ^{13}C NMR (151 MHz, $CDCl_3$)



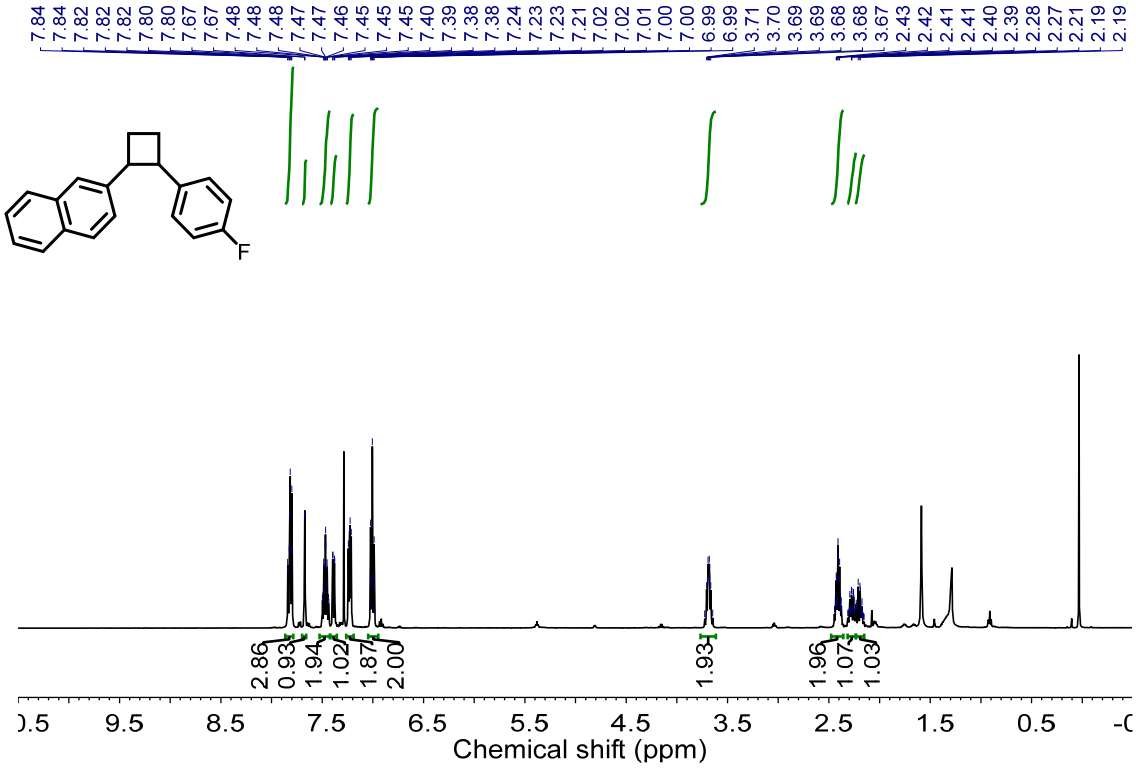
7j, ^{1}H NMR (500 MHz, Chloroform-*d*)



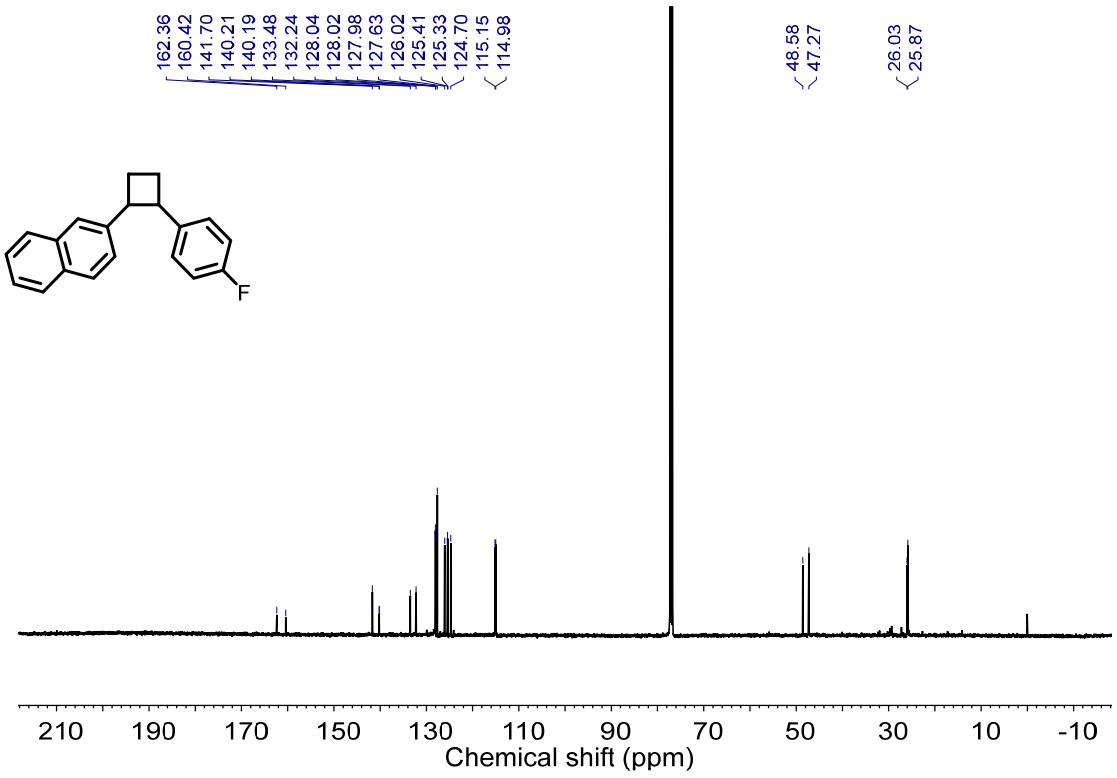
7j, ^{13}C NMR (126 MHz, Chloroform-*d*)



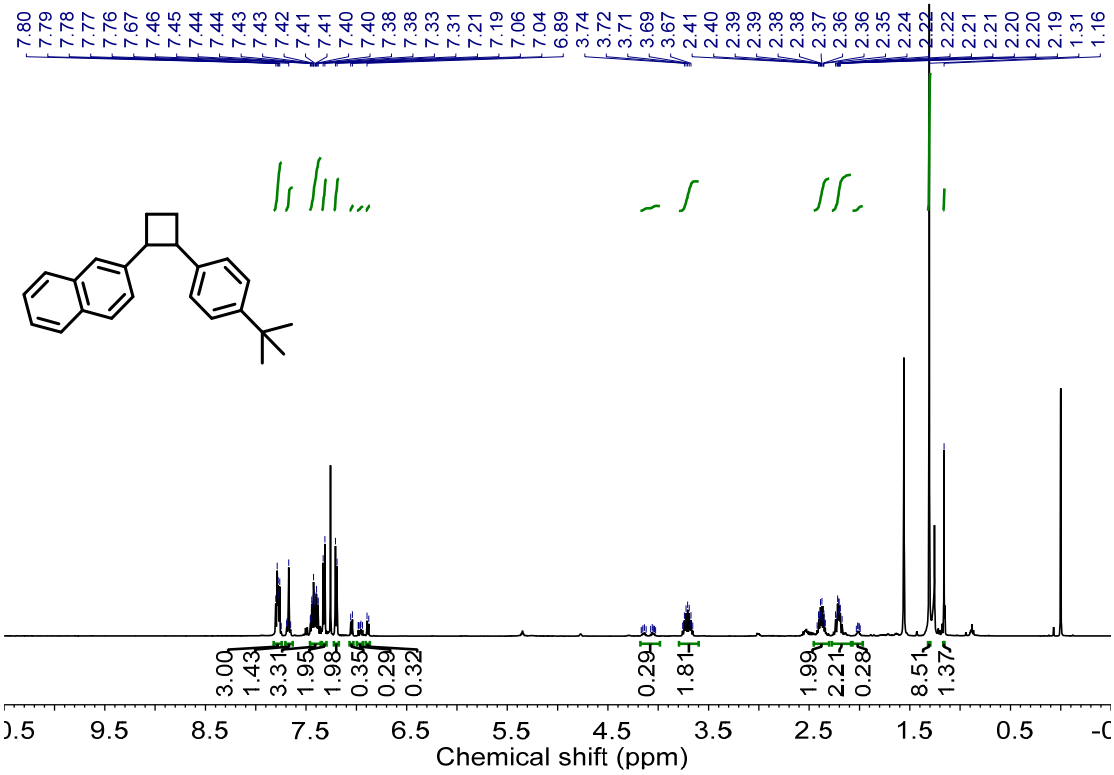
7k, ^{1}H NMR (500 MHz, Chloroform-*d*)



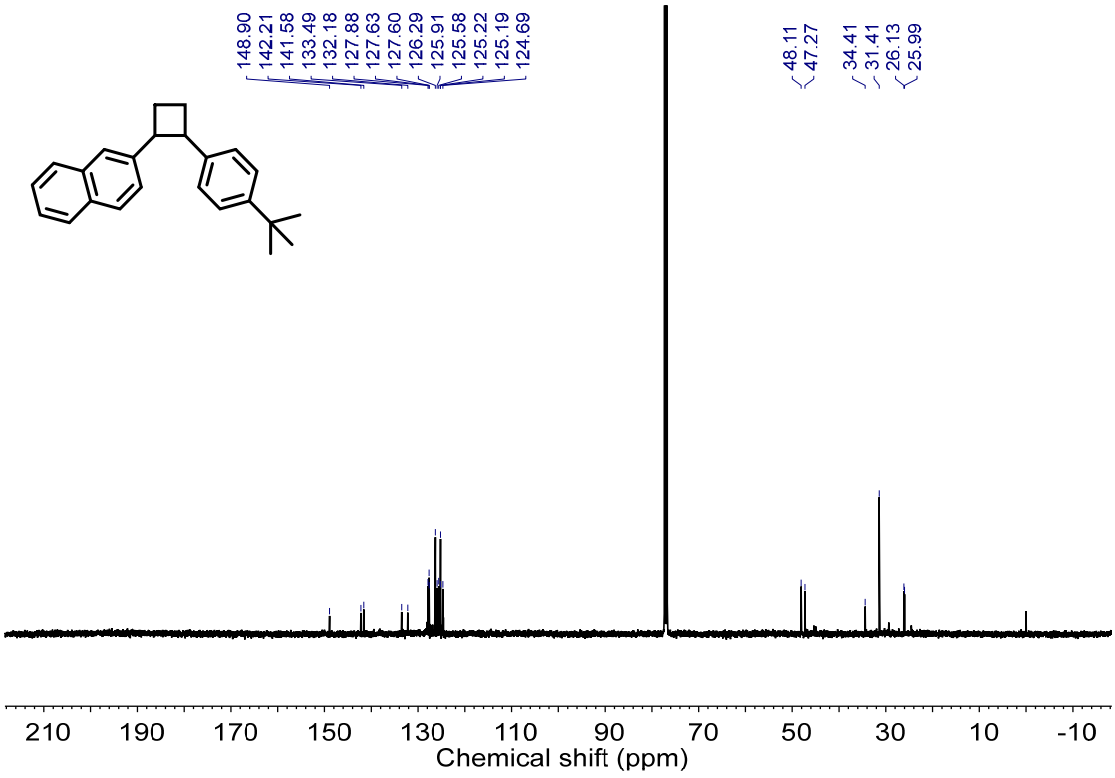
7k, ^{13}C NMR (126 MHz, Chloroform-*d*)



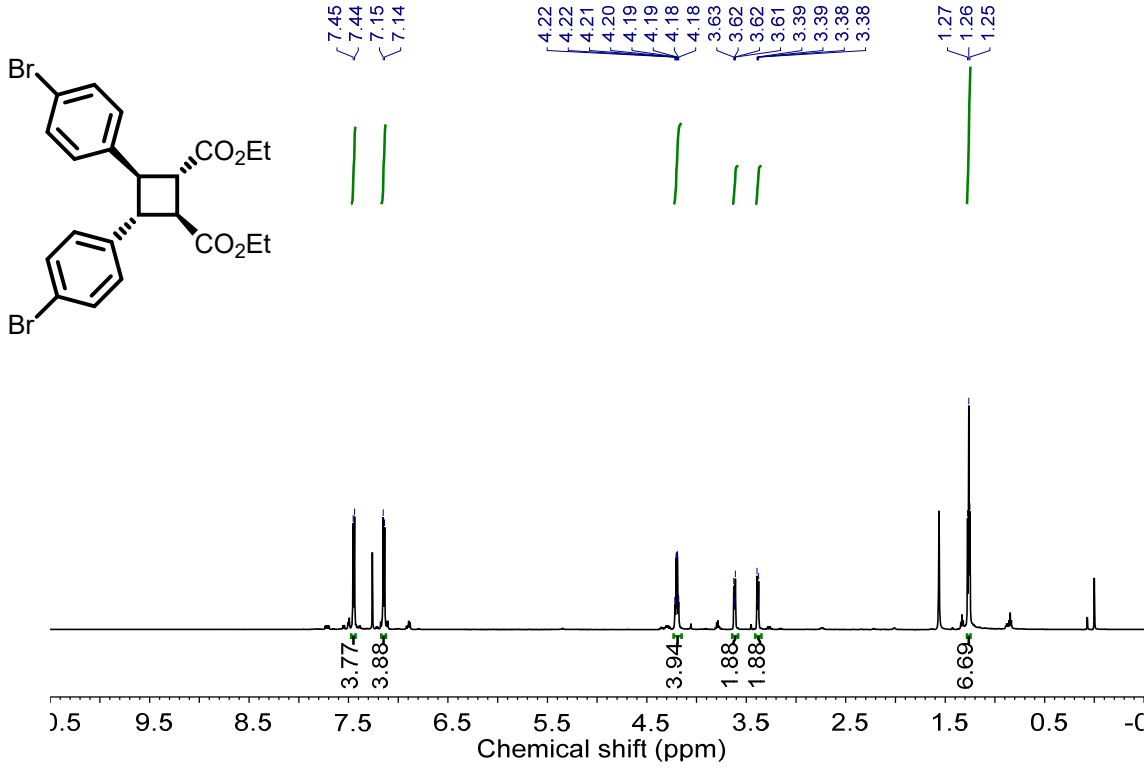
7l, ^{1}H NMR (500 MHz, Chloroform-*d*)



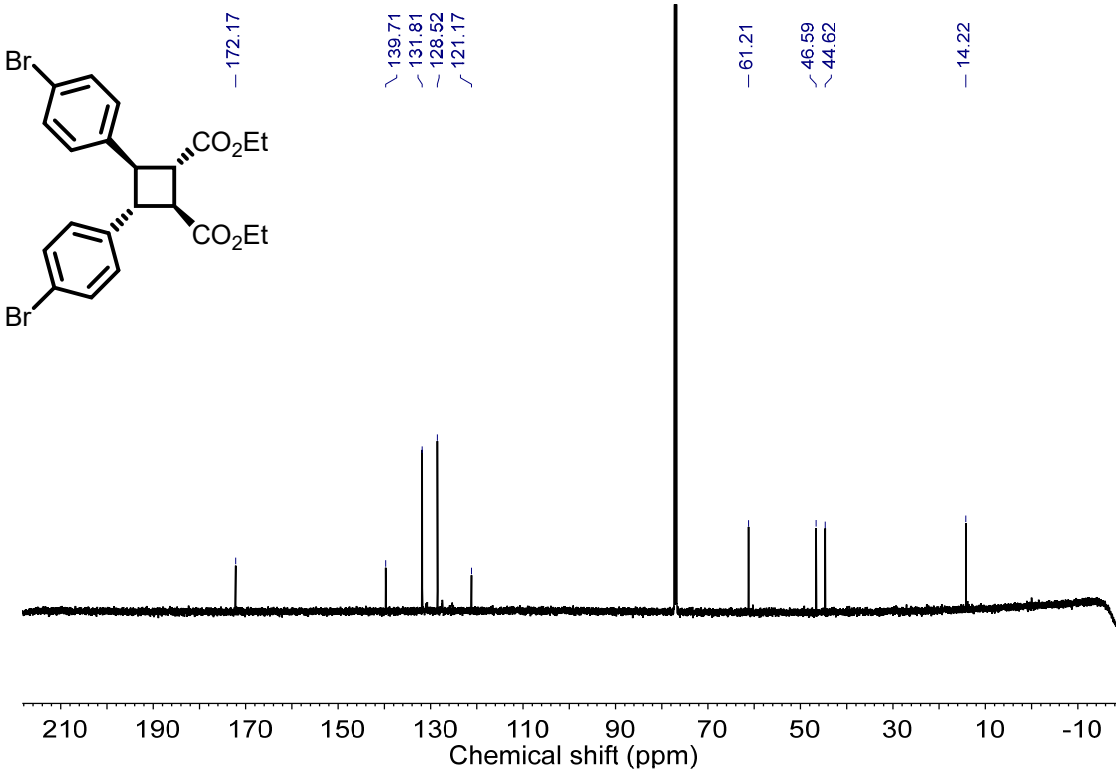
7l, ^{13}C NMR (126 MHz, Chloroform-*d*)



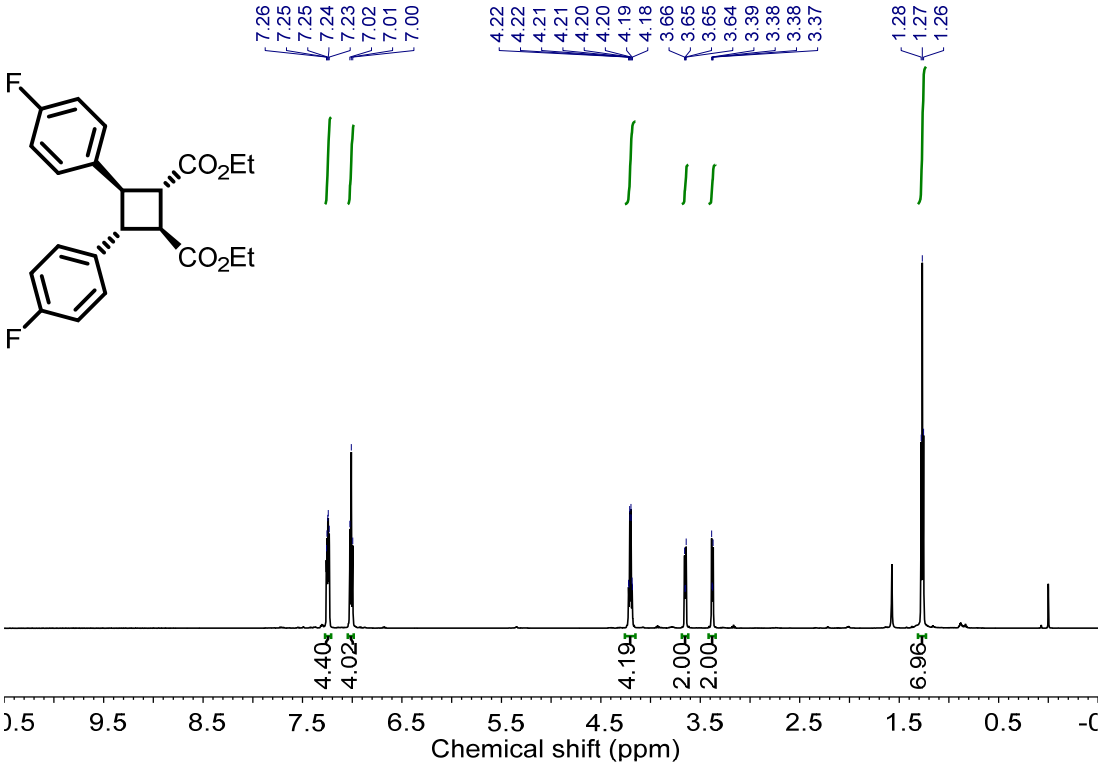
7m, ^{1}H NMR (600 MHz, Chloroform-*d*)



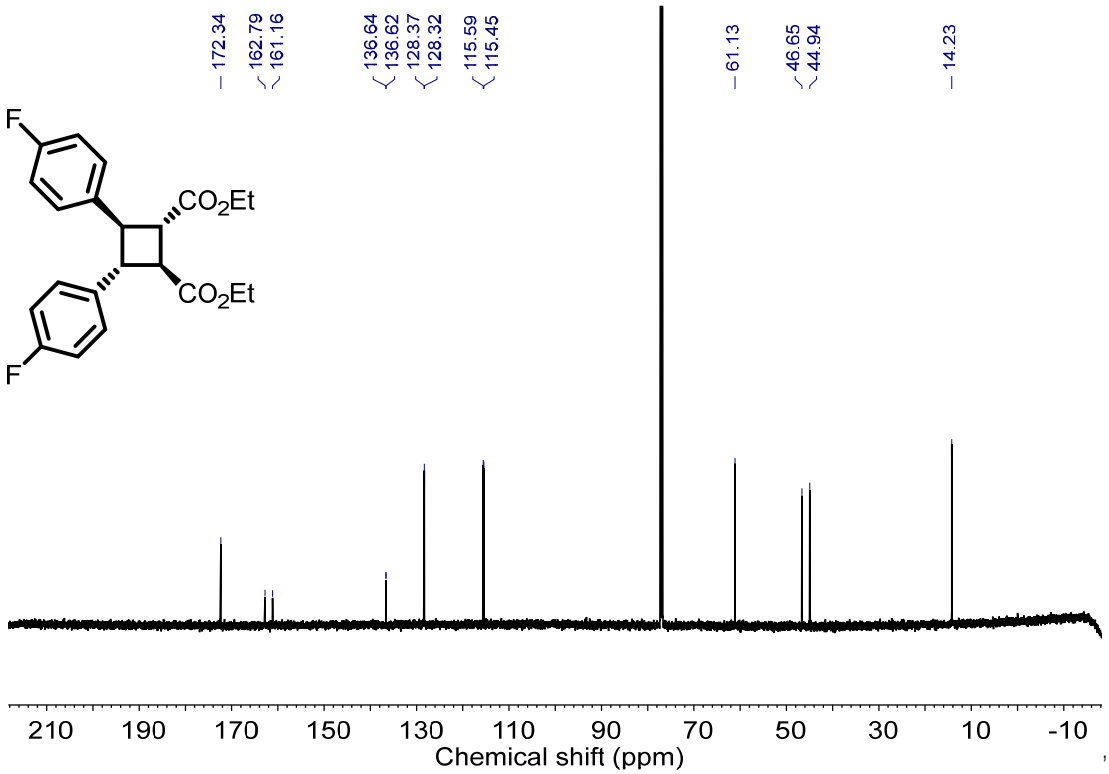
7m, ^{13}C NMR (151 MHz, Chloroform-*d*)



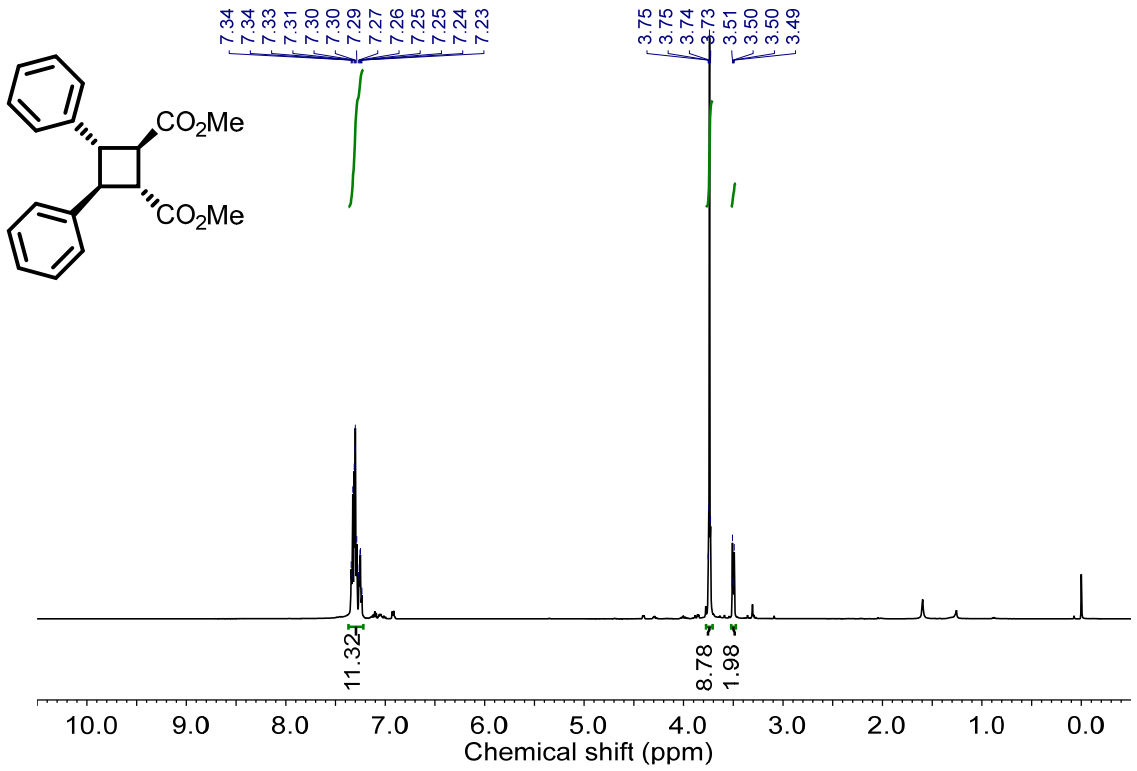
7n, ^{1}H NMR (600 MHz, Chloroform-*d*)



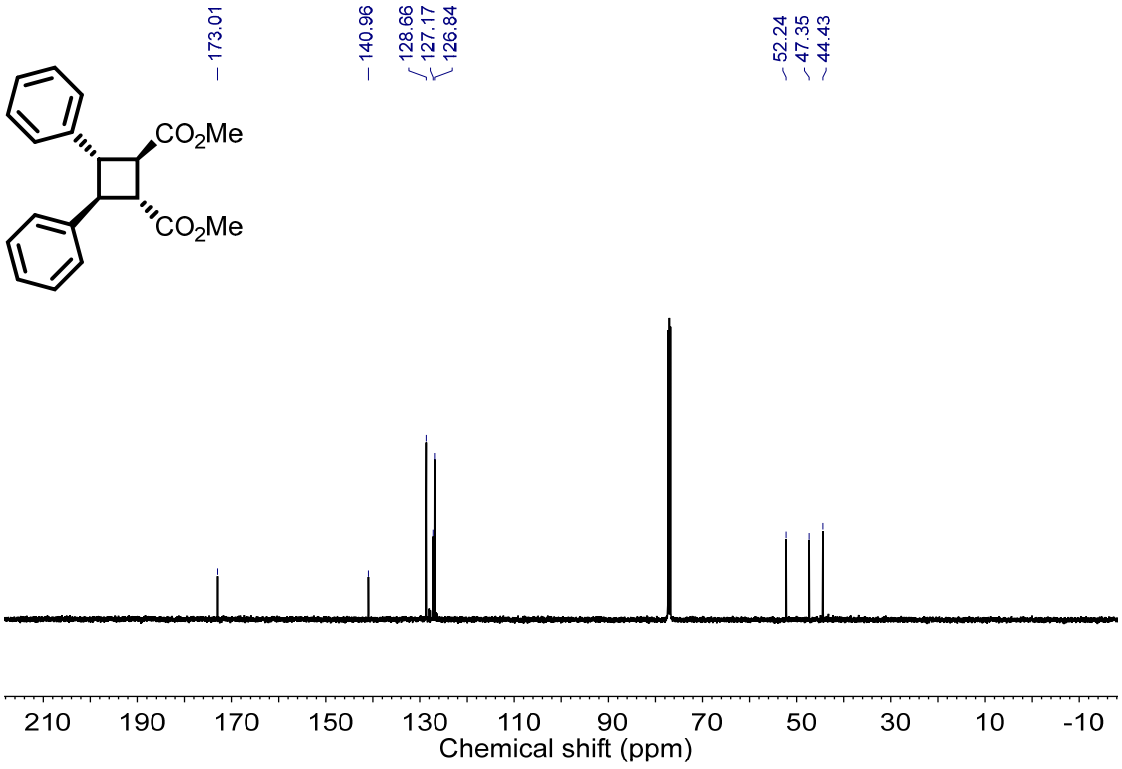
7n, ^{13}C NMR (151 MHz, Chloroform-*d*)



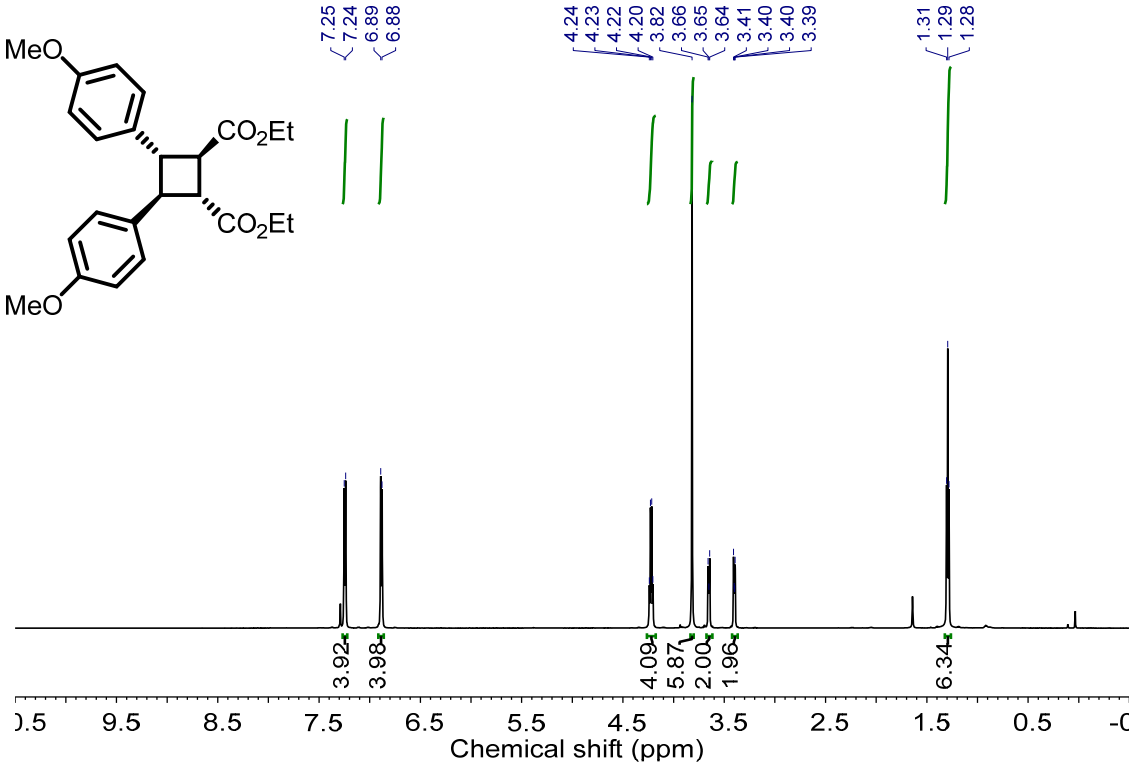
7o, ^{1}H NMR (500 MHz, Chloroform-*d*)



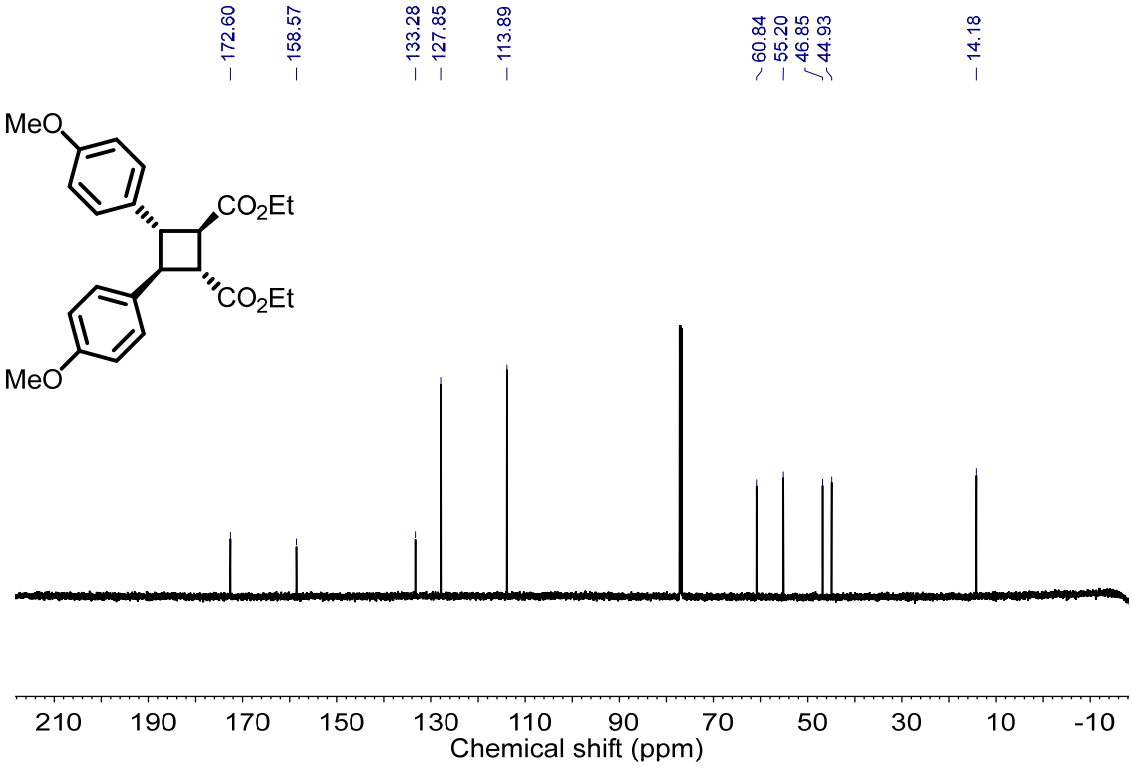
7o, ^{13}C NMR (126 MHz, Chloroform-*d*)



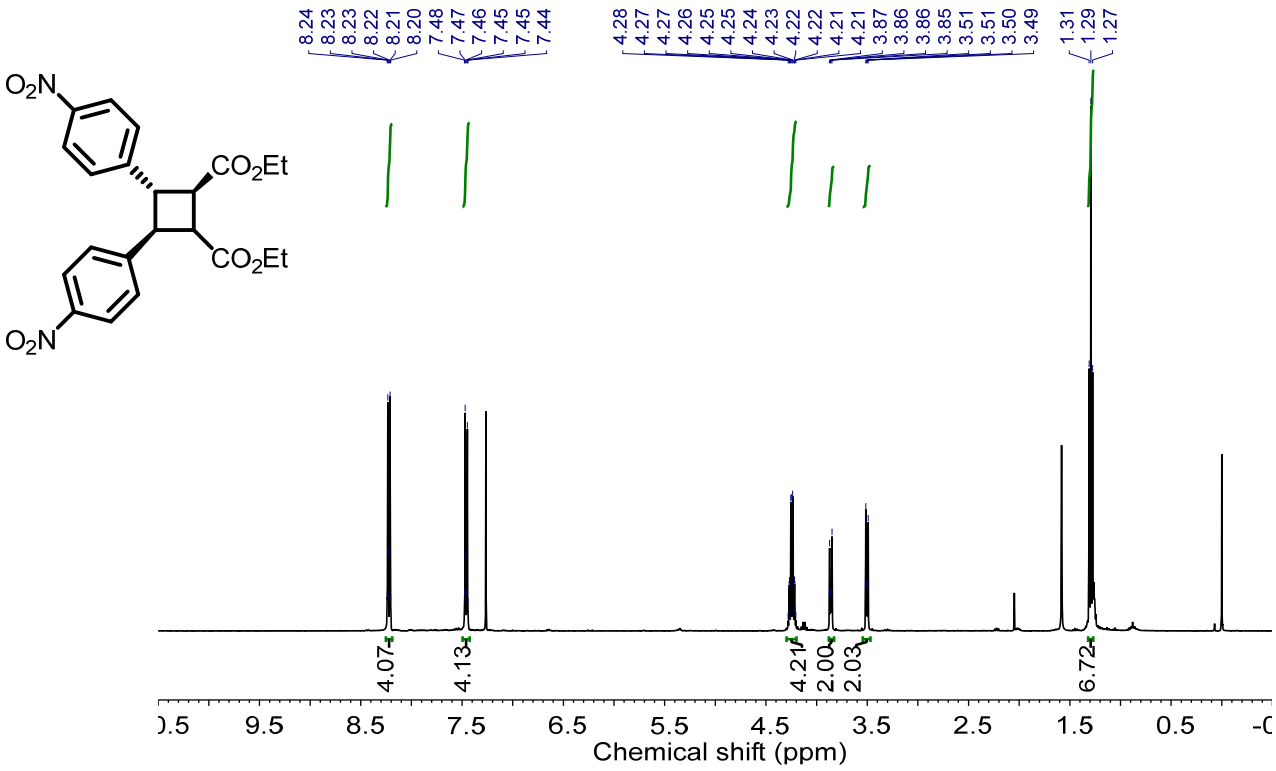
7p, ^{1}H NMR (600 MHz, Chloroform-*d*)



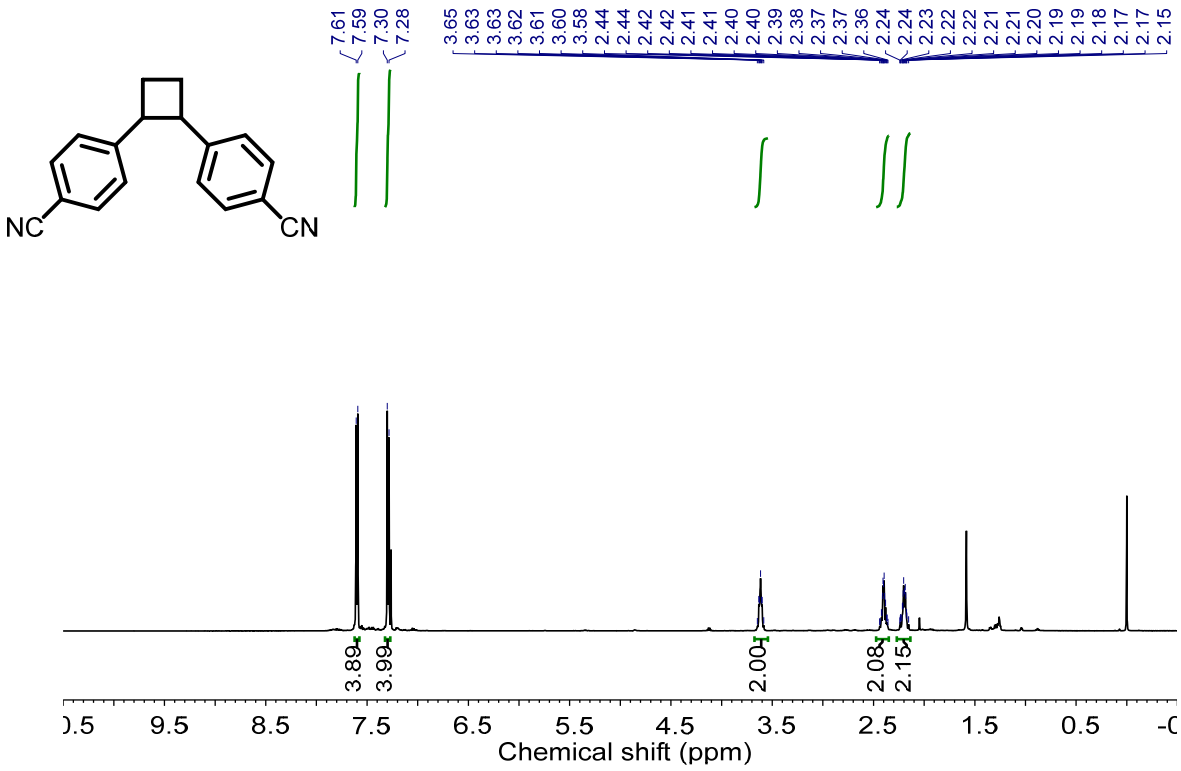
7p, ^{13}C NMR (151 MHz, Chloroform-*d*)



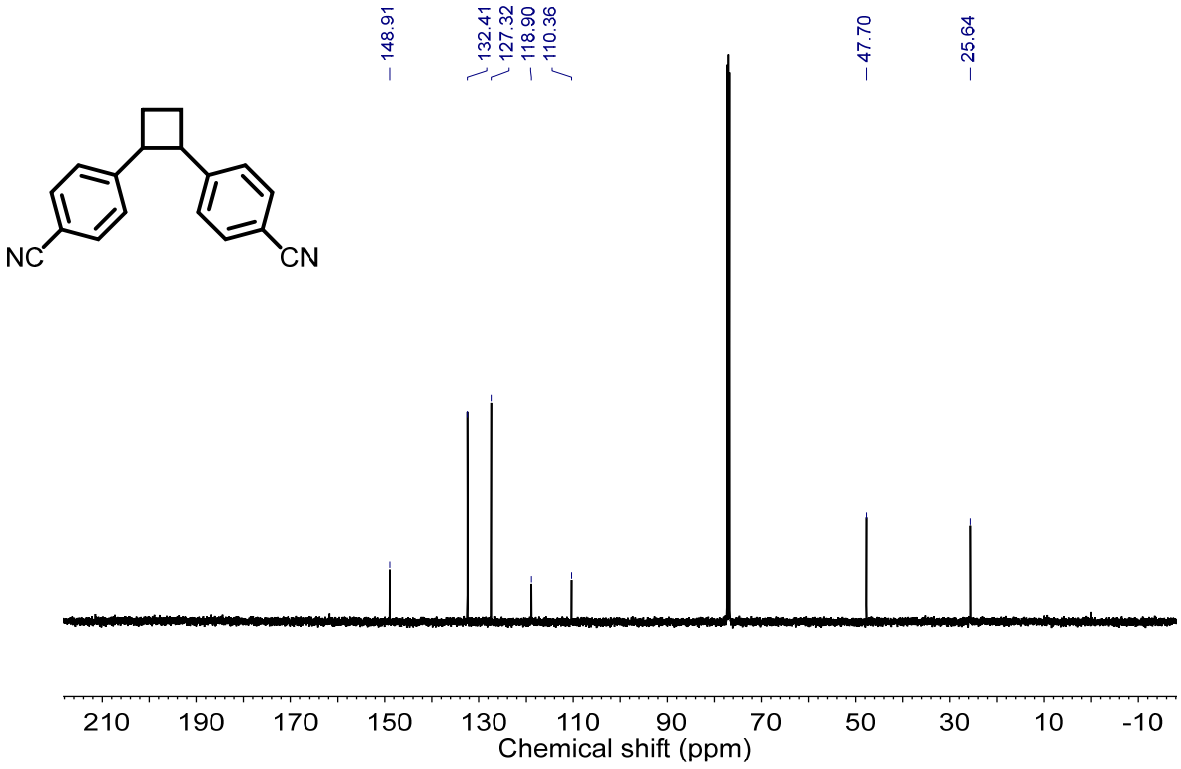
7q, ^{1}H NMR (400 MHz, Chloroform-*d*)



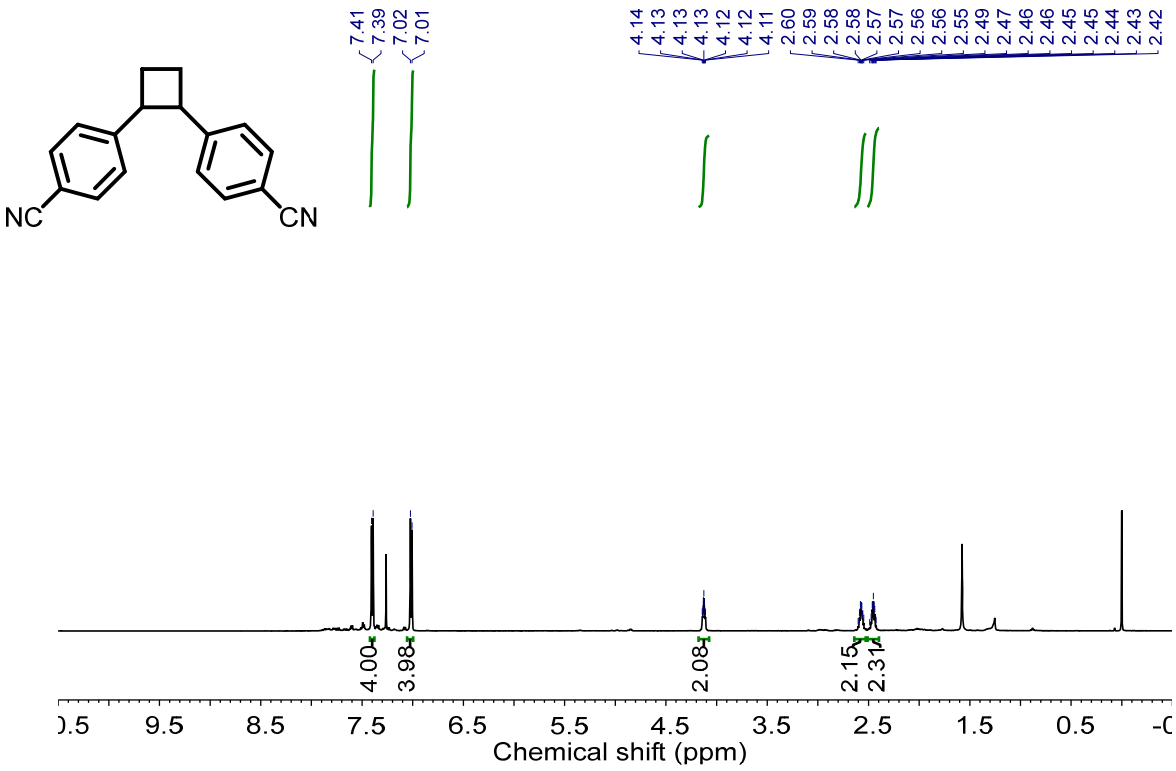
7r (major product), ^{1}H NMR (500 MHz, Chloroform-*d*)



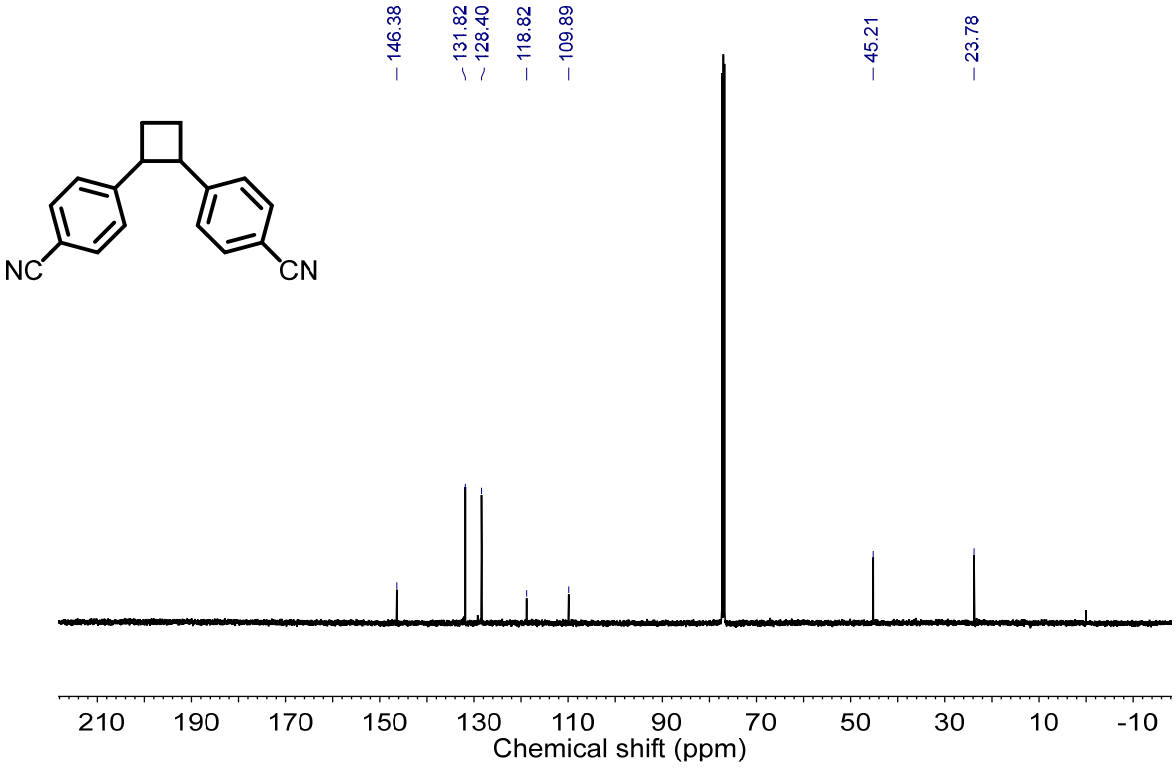
7r (major product), ^{13}C NMR (126 MHz, Chloroform-*d*)



7r (minor product), ^{1}H NMR (500 MHz, Chloroform-*d*)

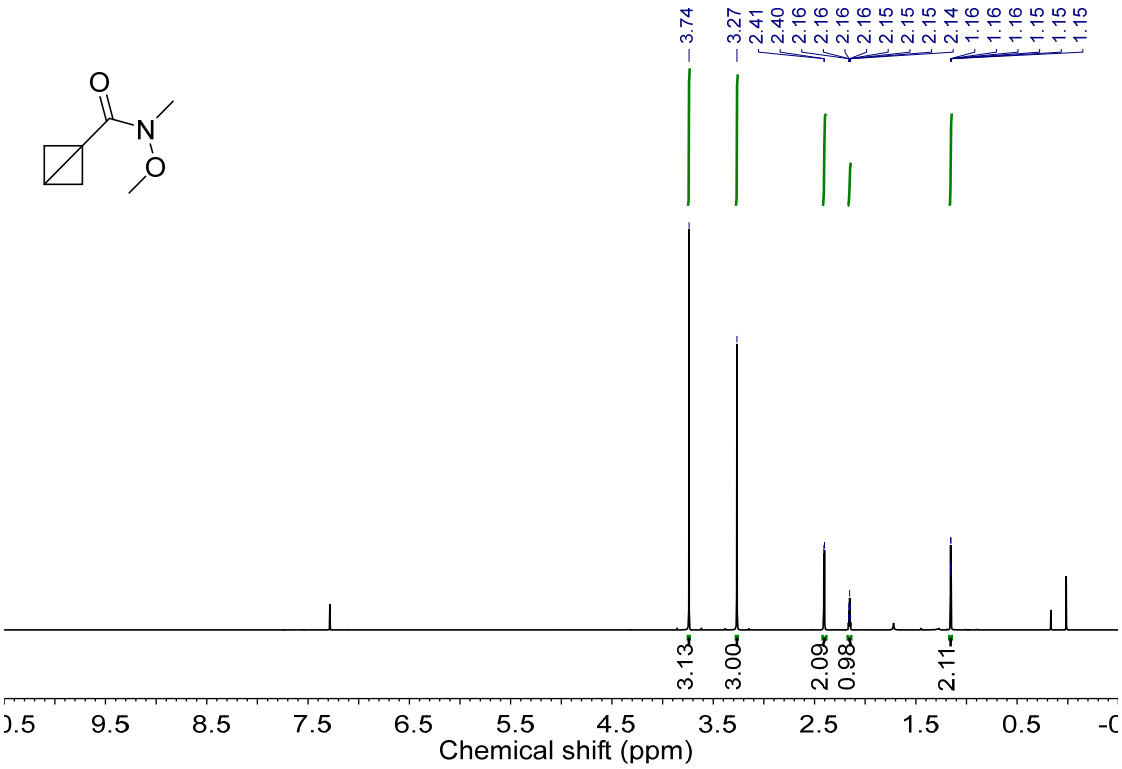


7r (minor product), ^{13}C NMR (126 MHz, Chloroform-*d*)



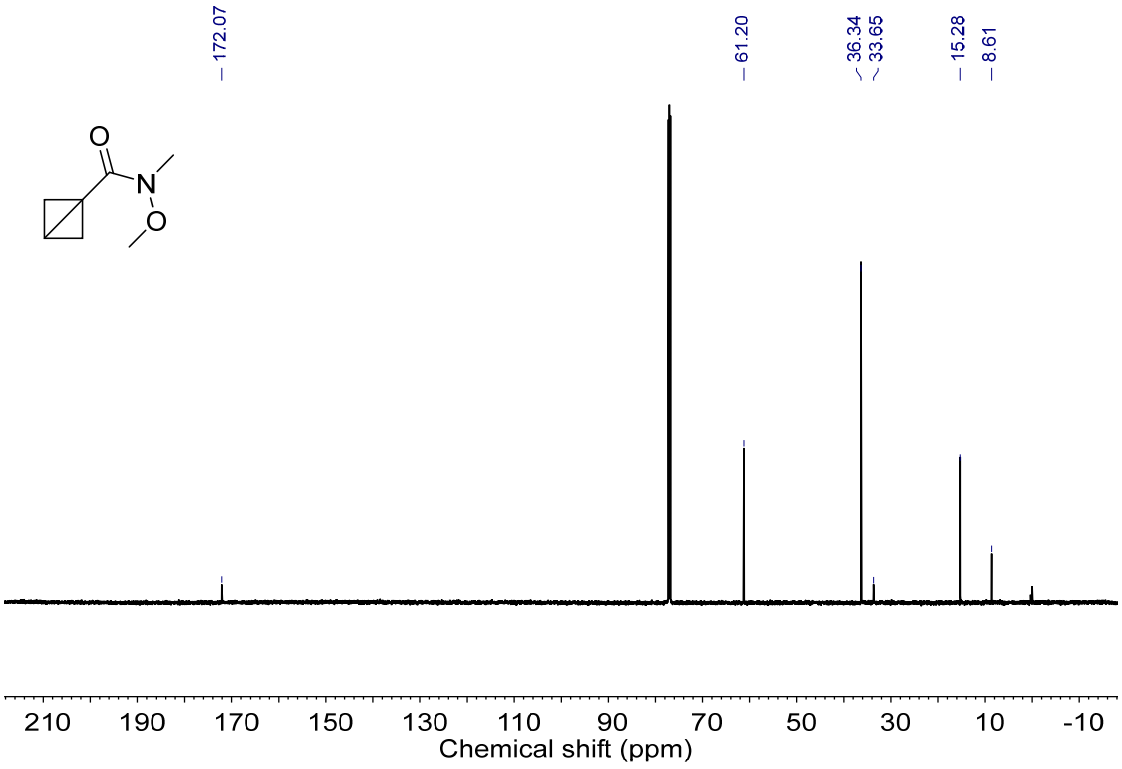
N-methoxy-*N*-methylbicyclo[1.1.0]butane-1-carboxamide

^{1}H NMR (600 MHz, Chloroform-*d*)

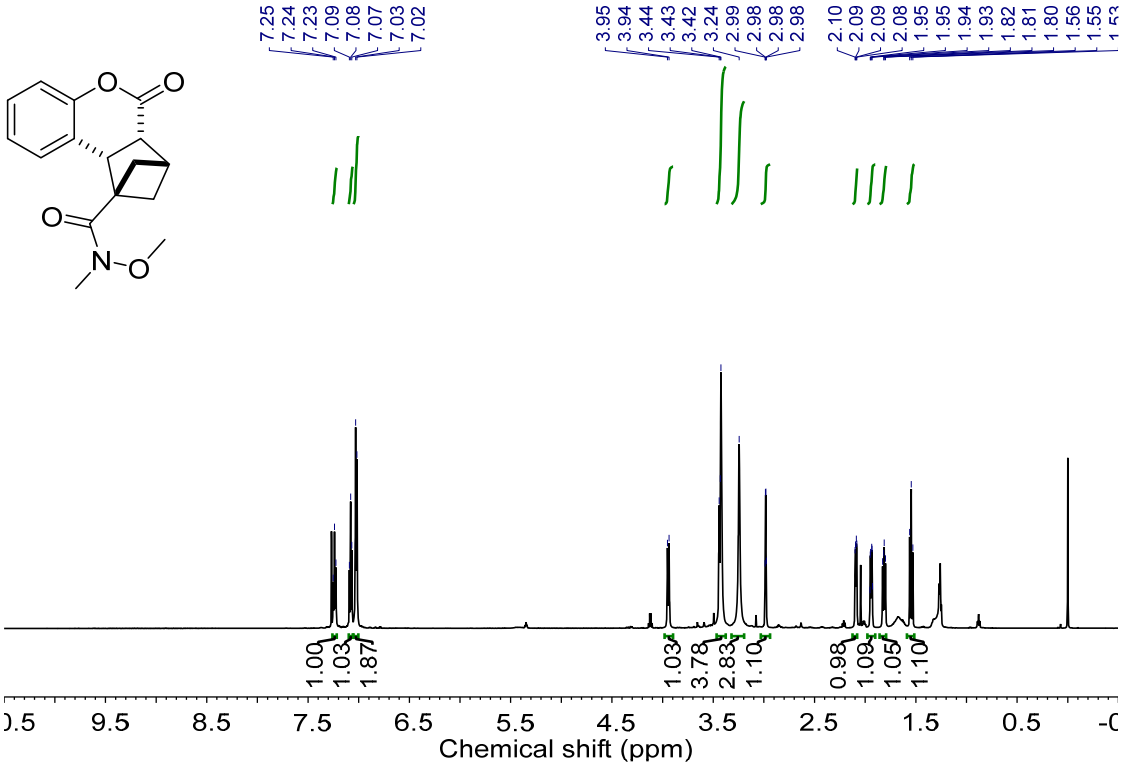


N-methoxy-*N*-methylbicyclo[1.1.0]butane-1-carboxamide

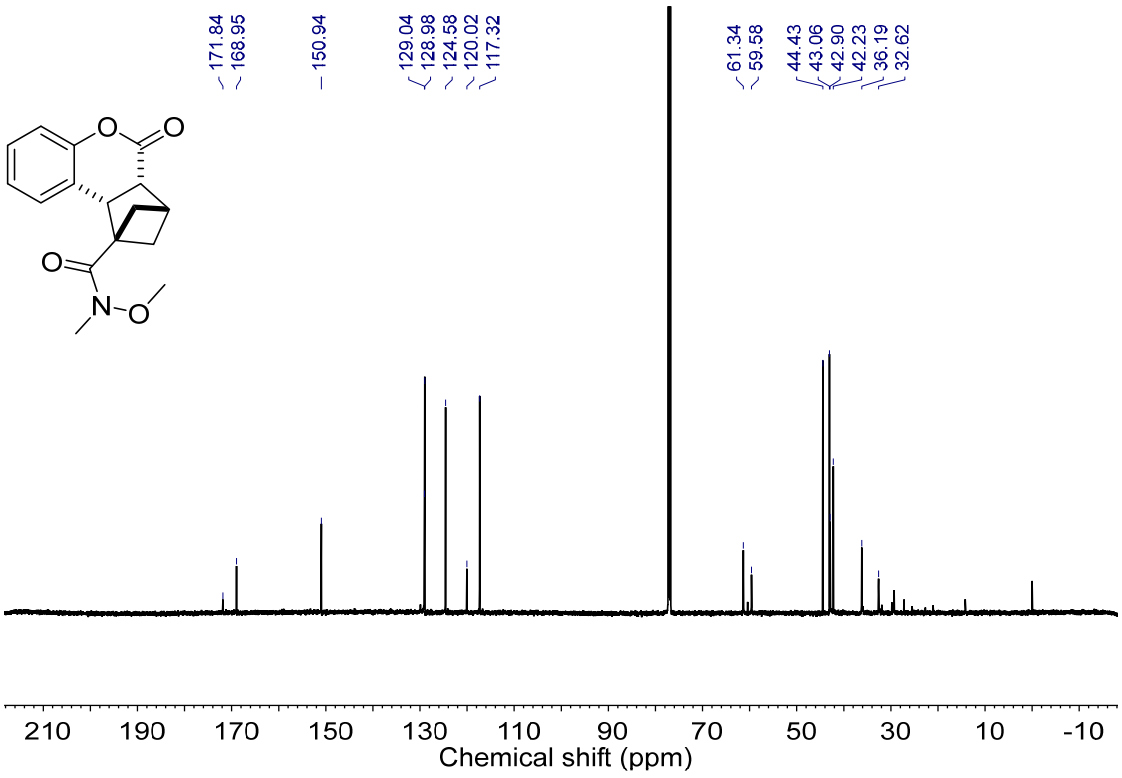
^{13}C NMR (151 MHz, Chloroform-*d*)



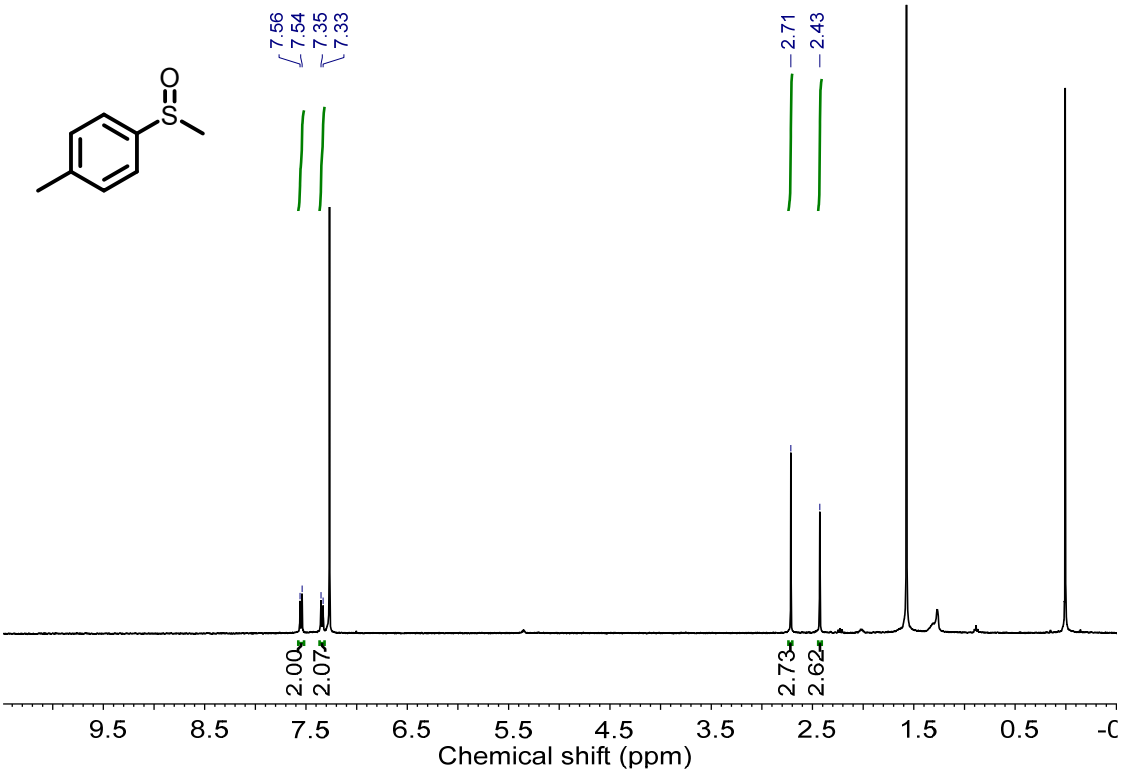
7s, ^{1}H NMR (600 MHz, Chloroform-*d*)



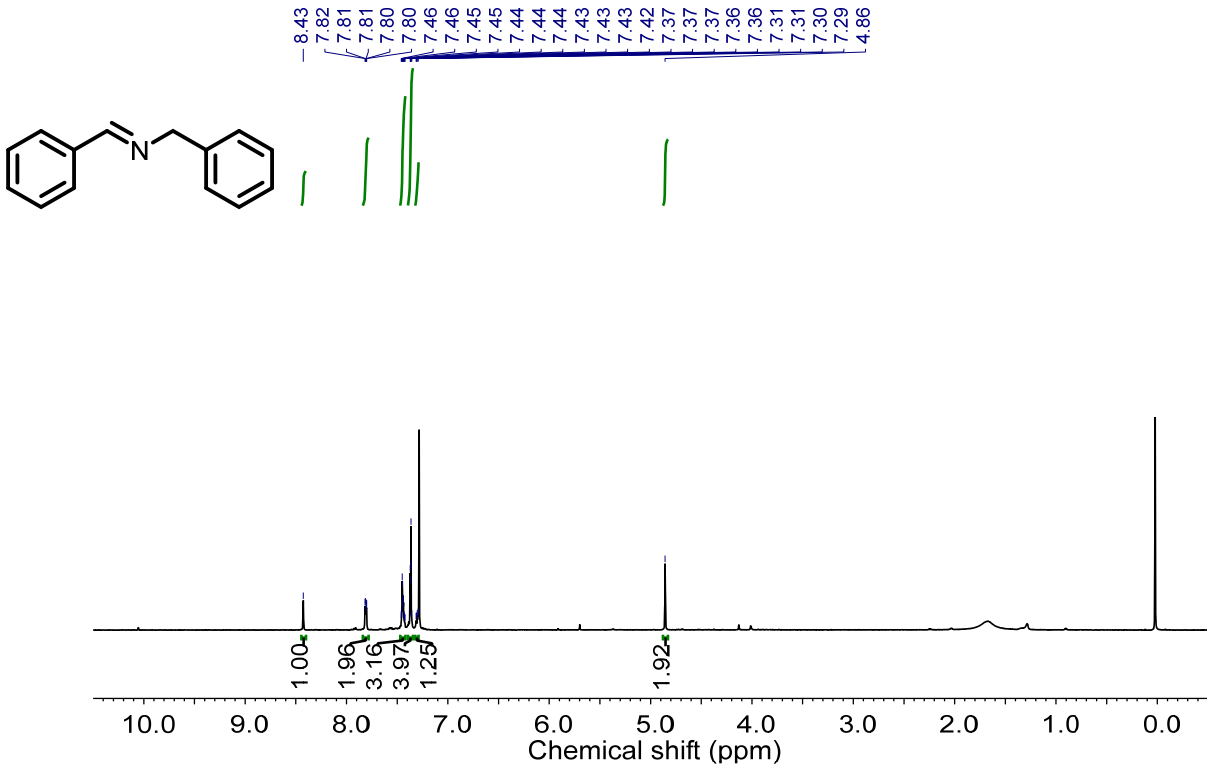
7s, ^{13}C NMR (151 MHz, Chloroform-*d*)



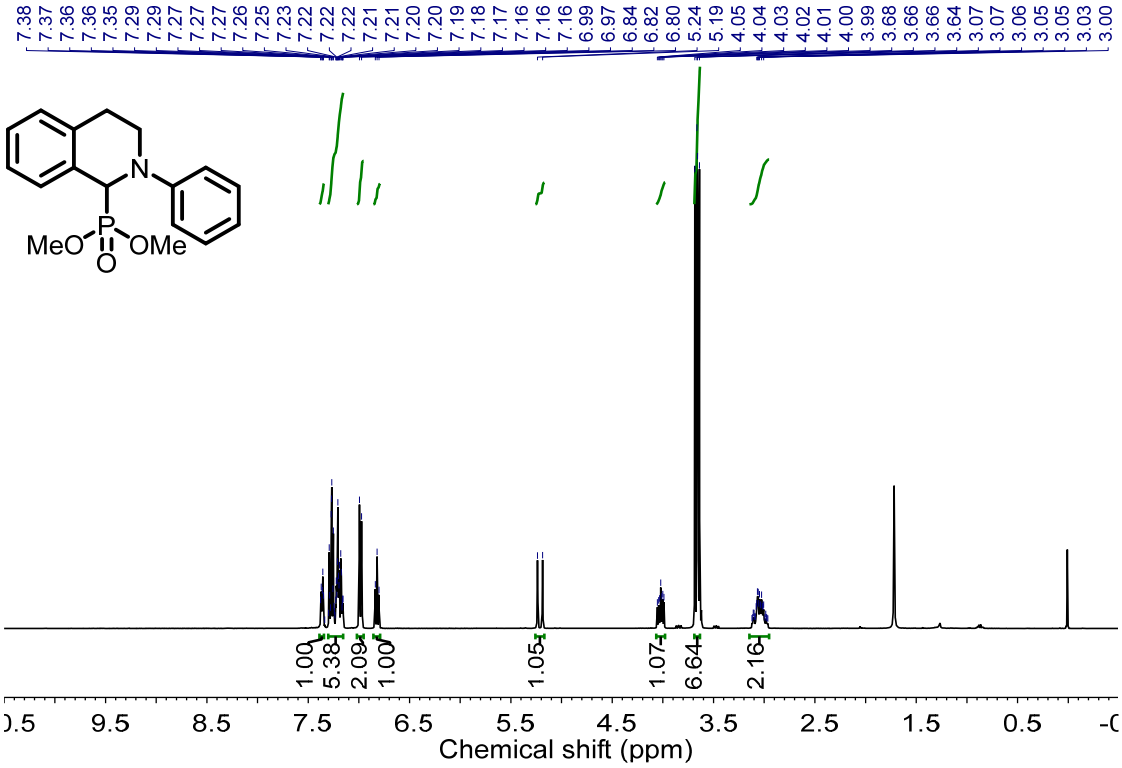
8a, ^{1}H NMR (400 MHz, $CDCl_3$)



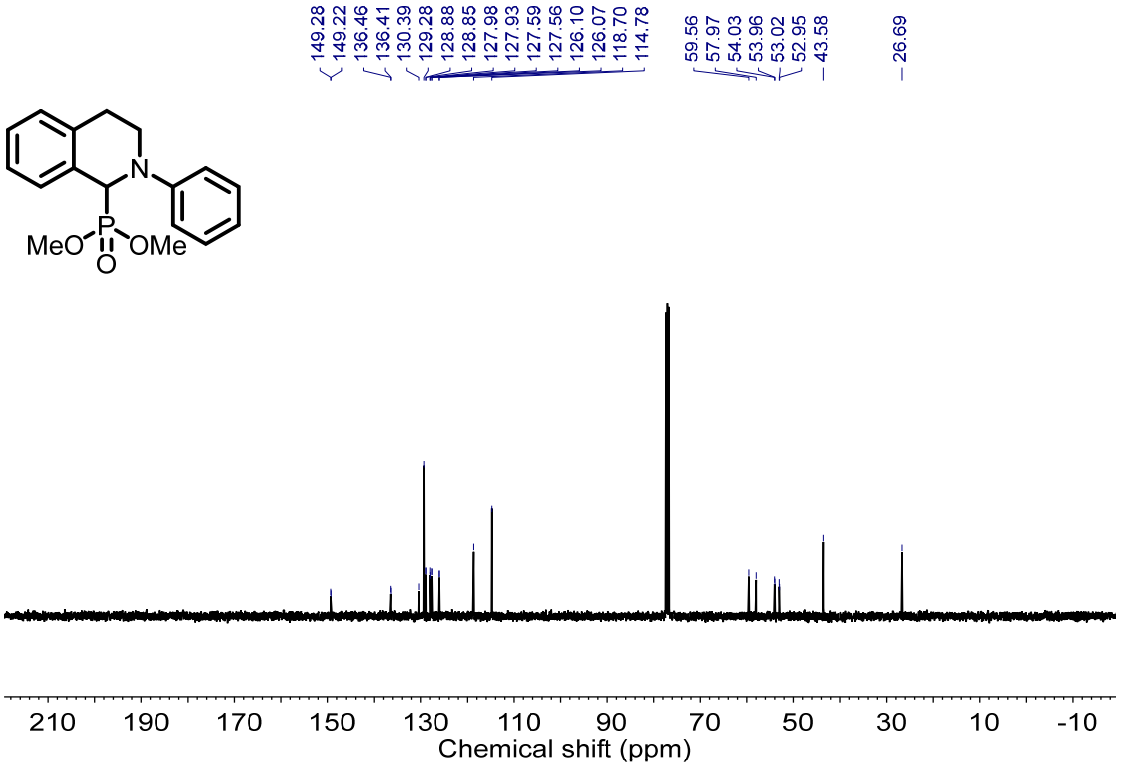
8b, ^{1}H NMR (600 MHz, $CDCl_3$)



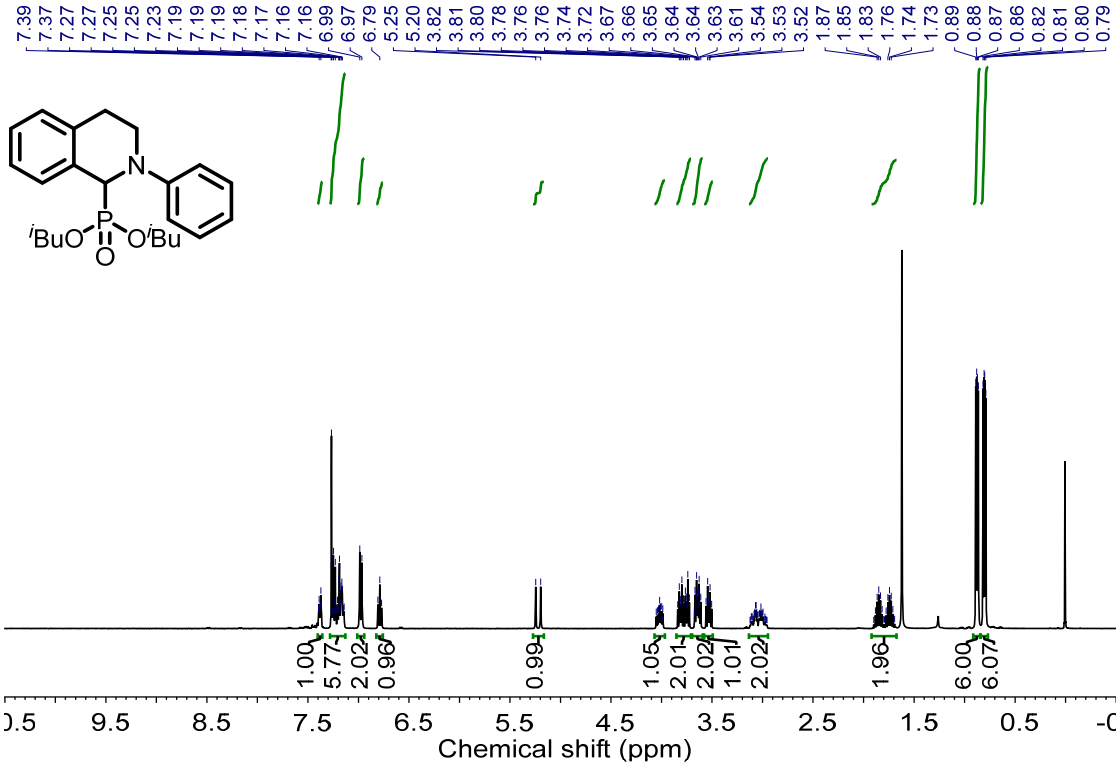
8c, ^{1}H NMR (400 MHz, $CDCl_3$)



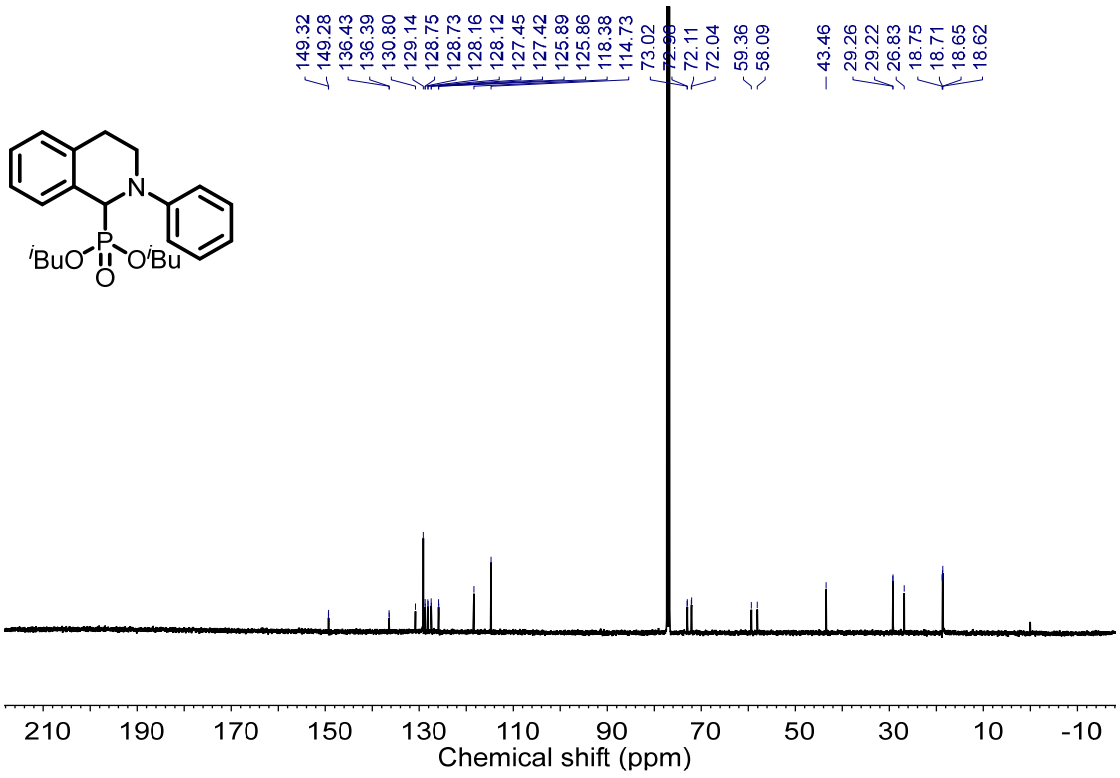
8c, ^{13}C NMR (101 MHz, $CDCl_3$)



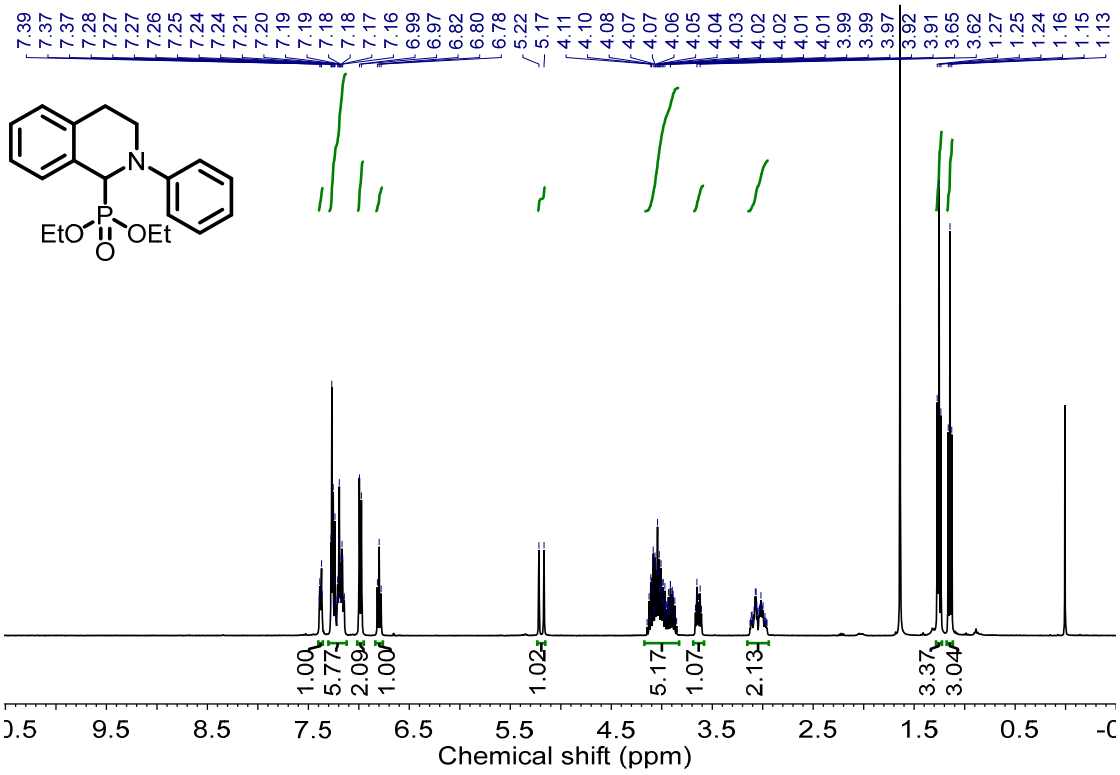
8d, ^{1}H NMR (400 MHz, $CDCl_3$)



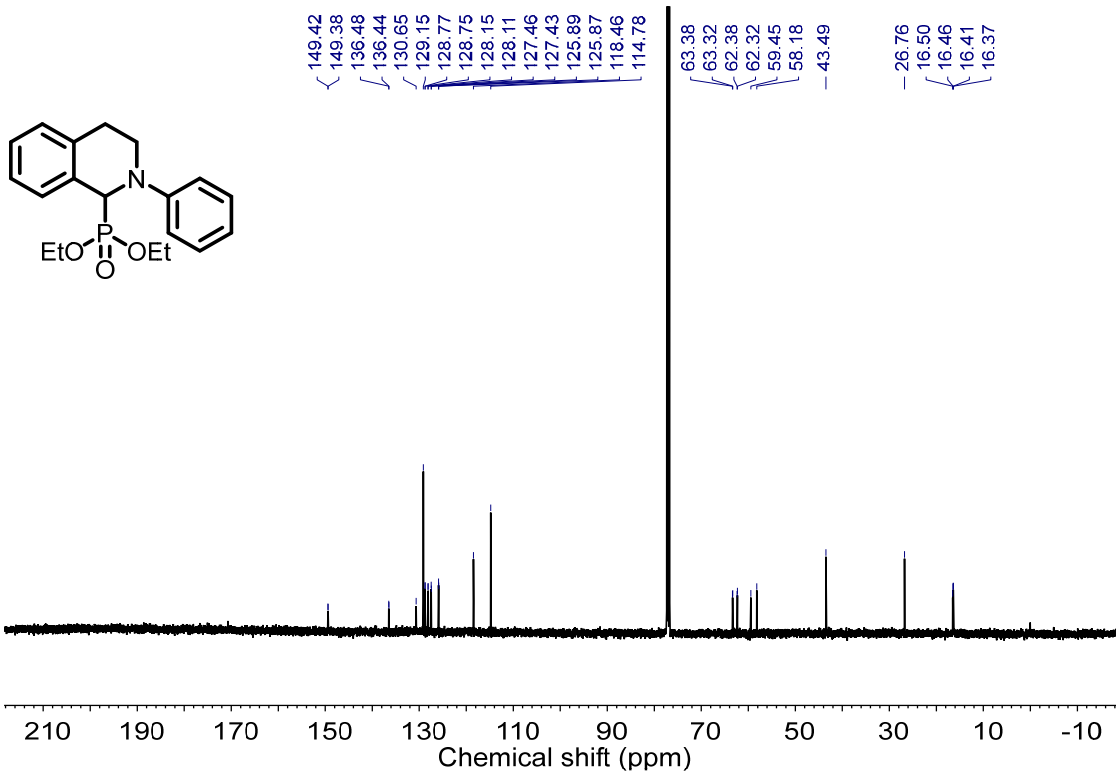
8d, ^{13}C NMR (126 MHz, $CDCl_3$)



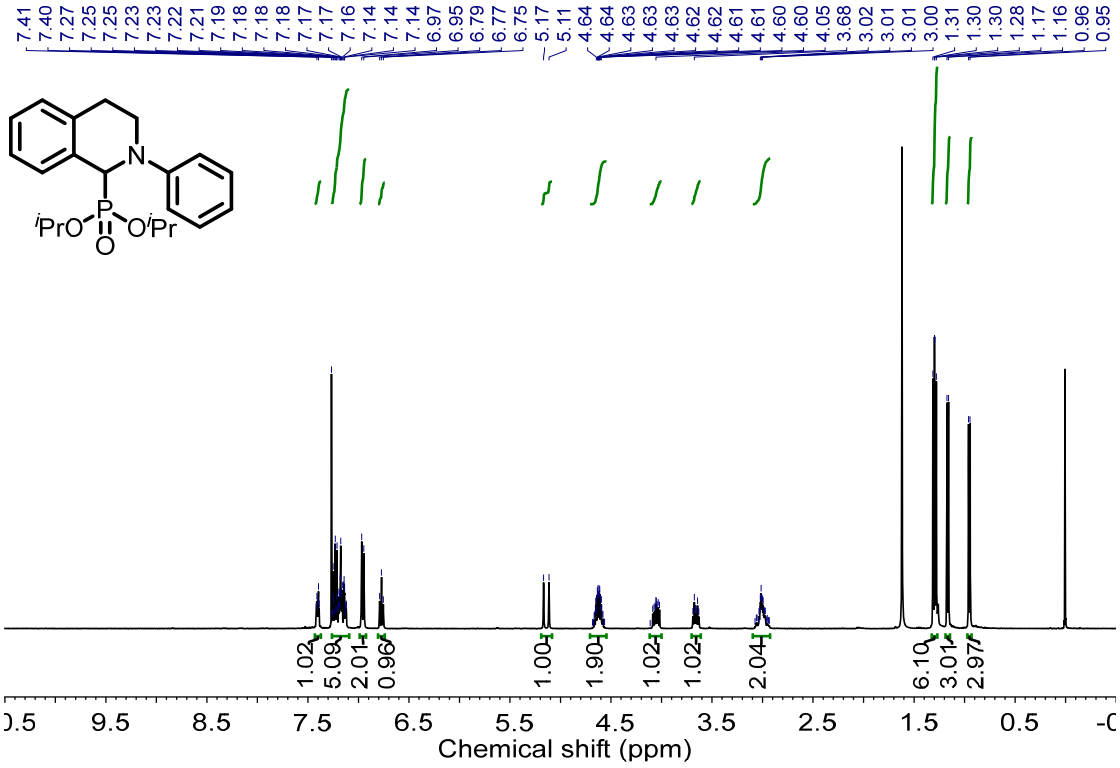
8e, ^{1}H NMR (400 MHz, $CDCl_3$)



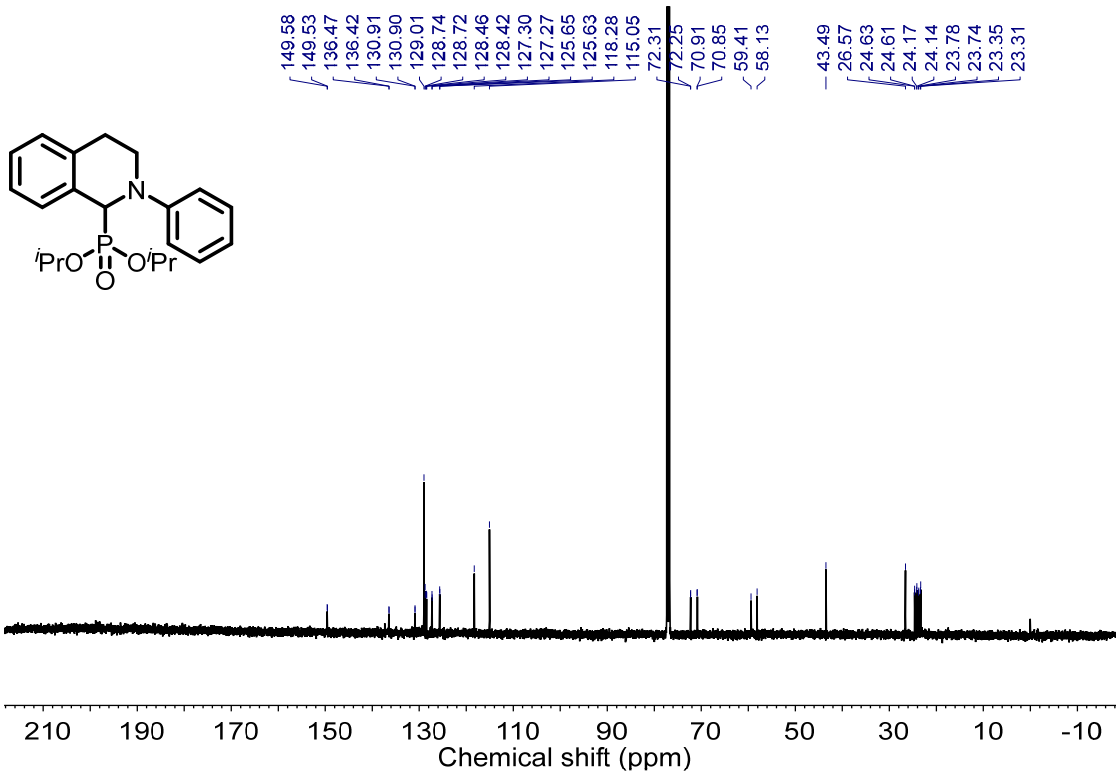
8e, ^{13}C NMR (126 MHz, $CDCl_3$)



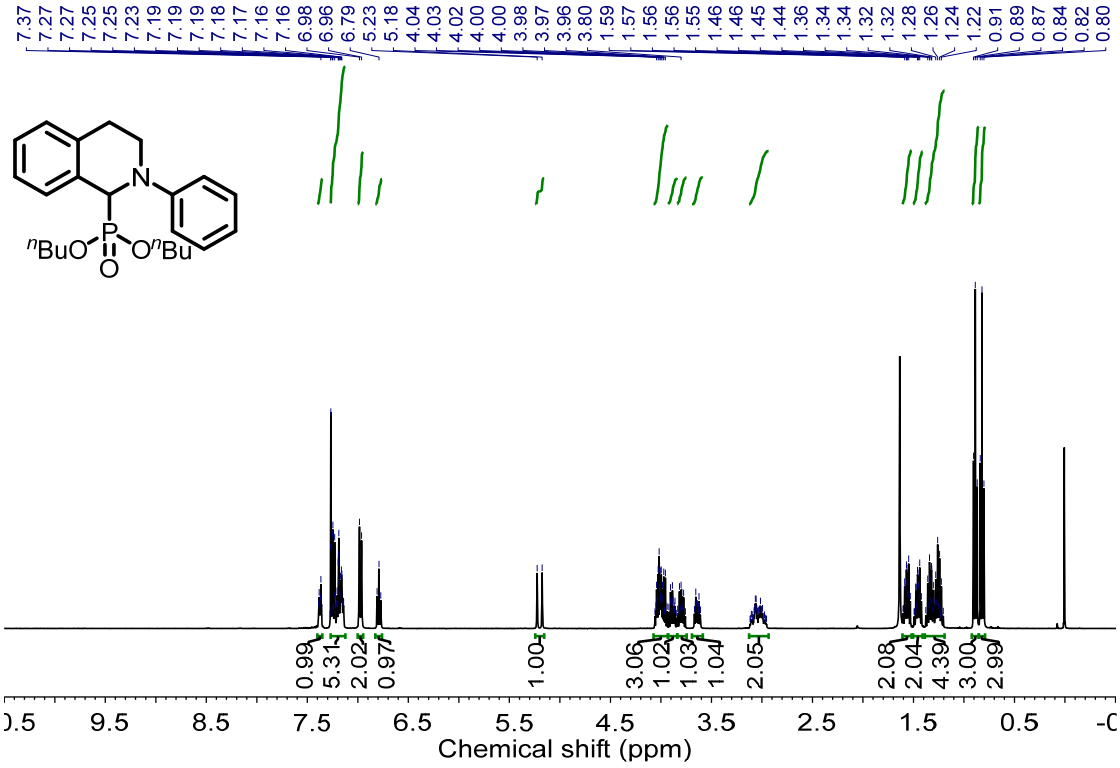
8f, ^{1}H NMR (400 MHz, $CDCl_3$)



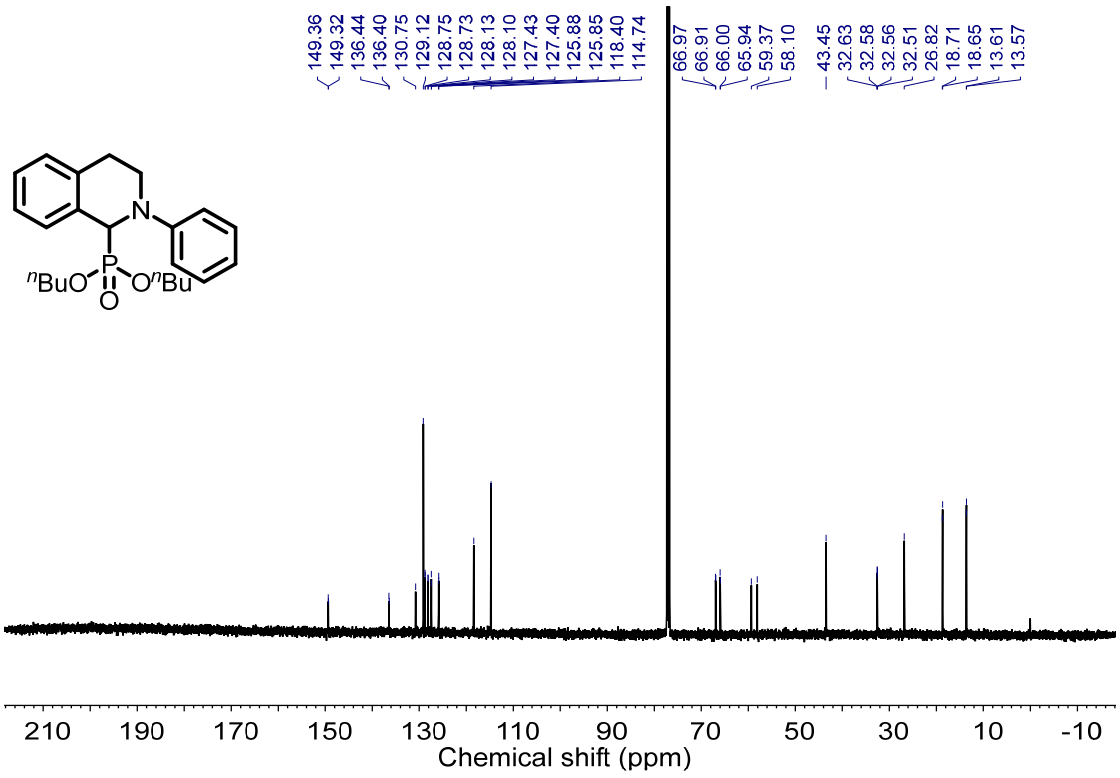
8f, ^{13}C NMR (126 MHz, $CDCl_3$)



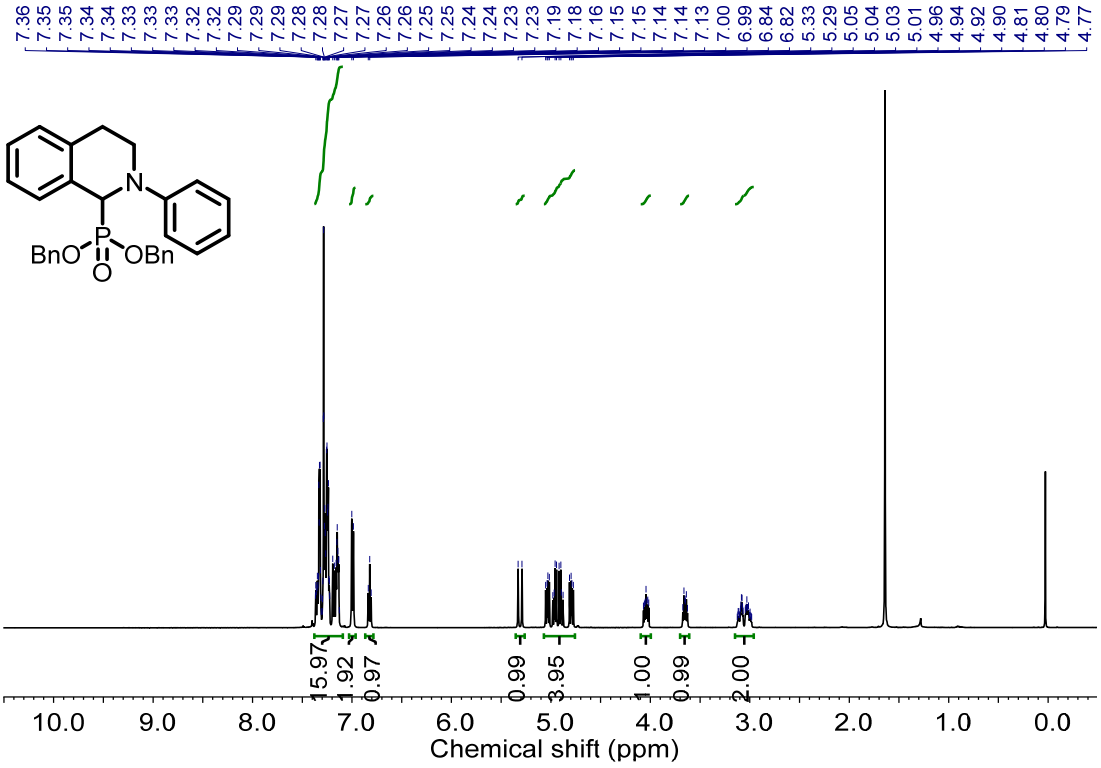
8g, ^{1}H NMR (400 MHz, $CDCl_3$)



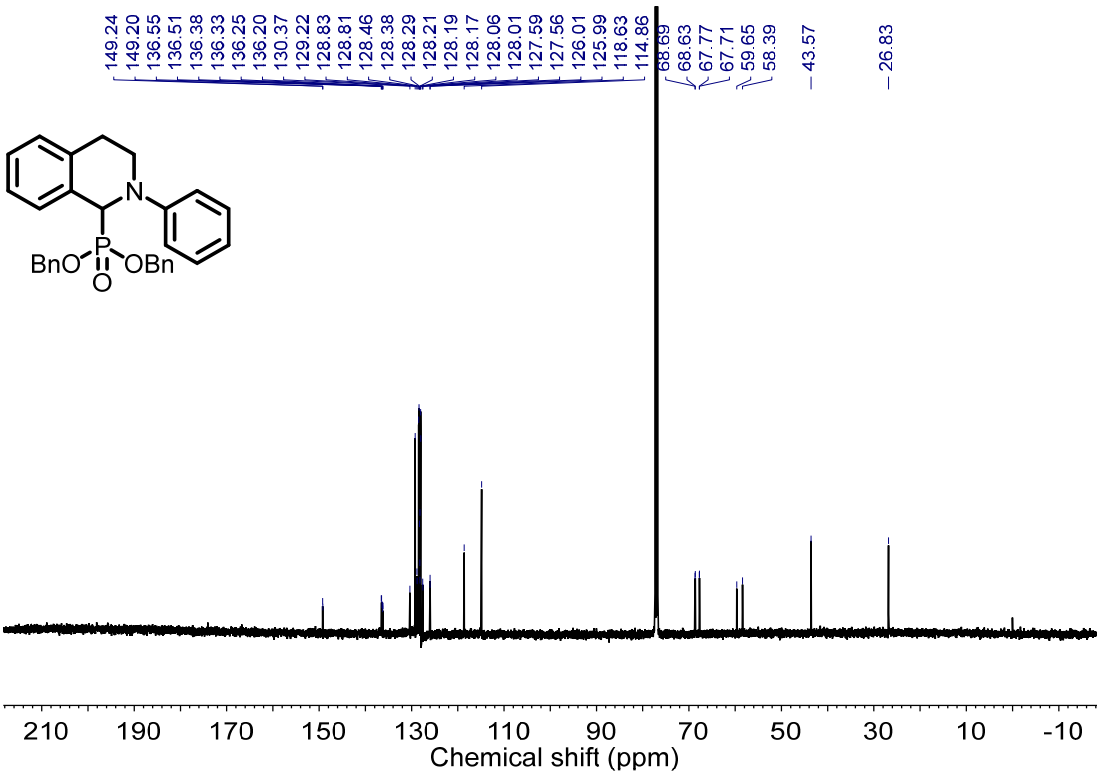
8g, ^{13}C NMR (126 MHz, $CDCl_3$)



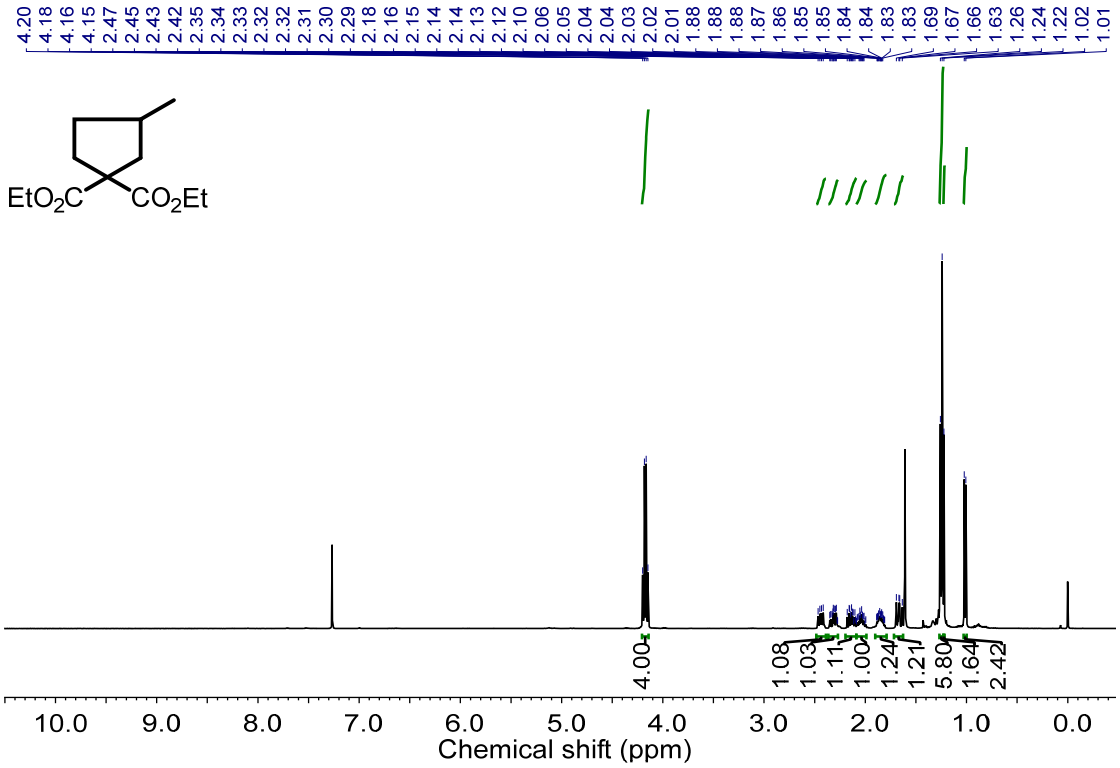
8h, ^{1}H NMR (500 MHz, $CDCl_3$)



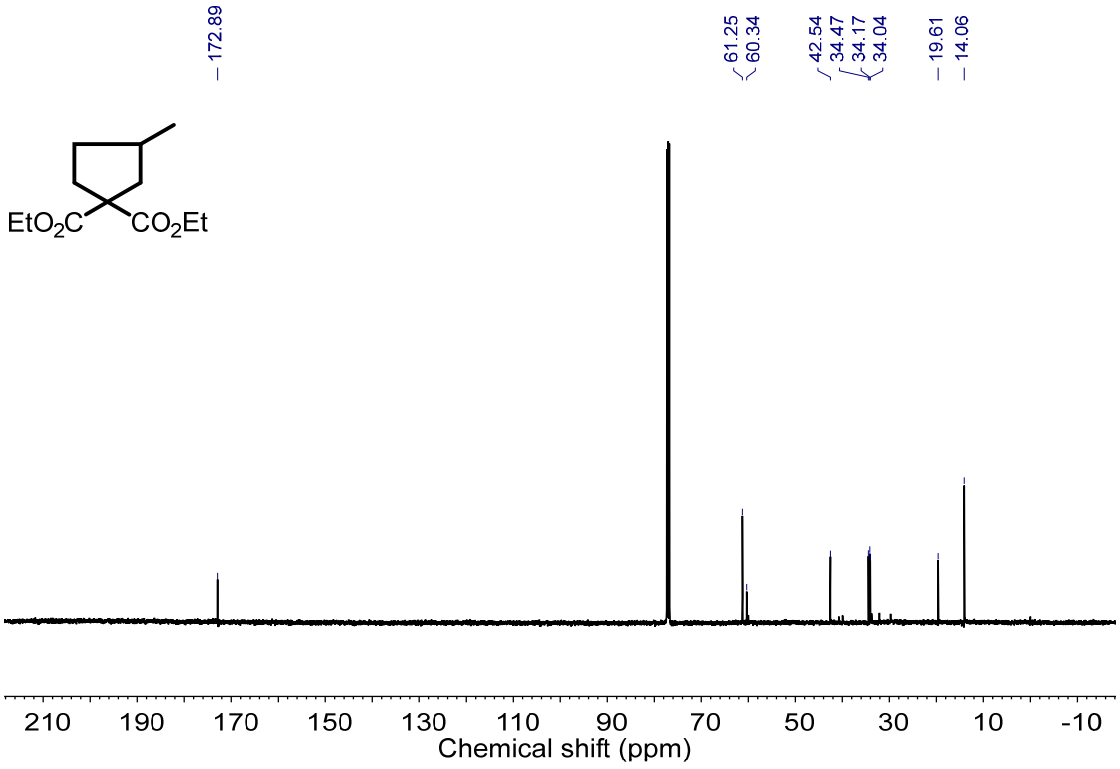
8h, ^{13}C NMR (126 MHz, $CDCl_3$)



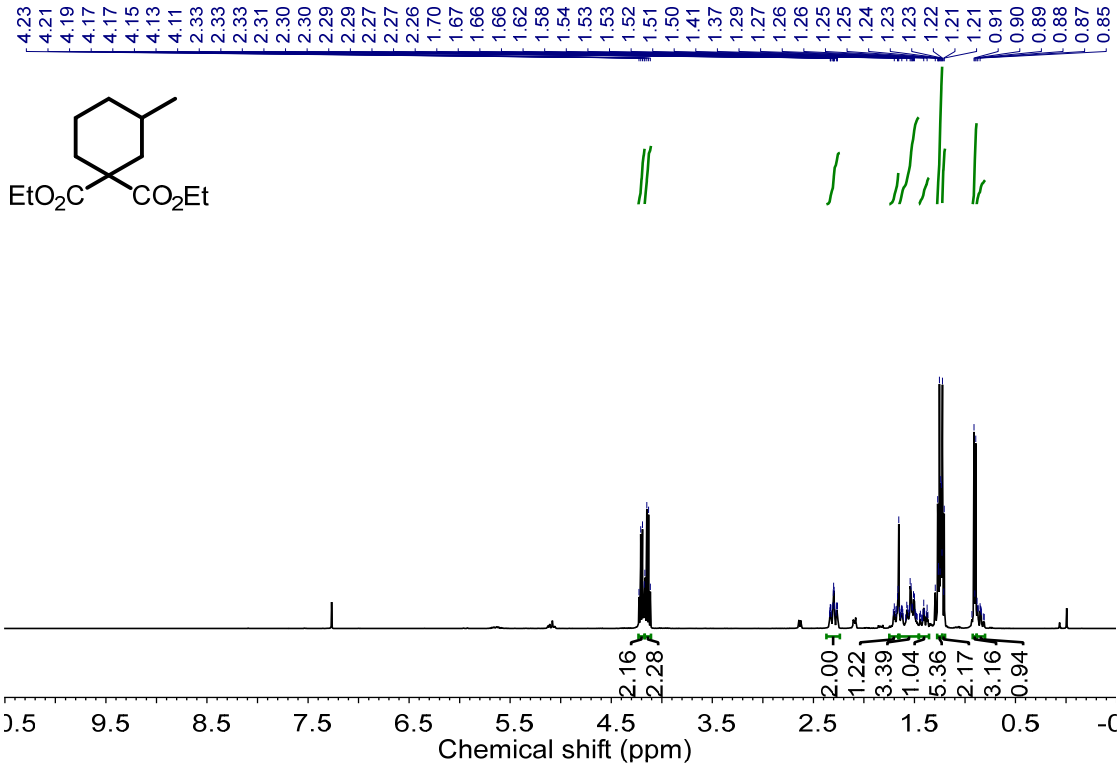
10a, ^{1}H NMR (400 MHz, $CDCl_3$)



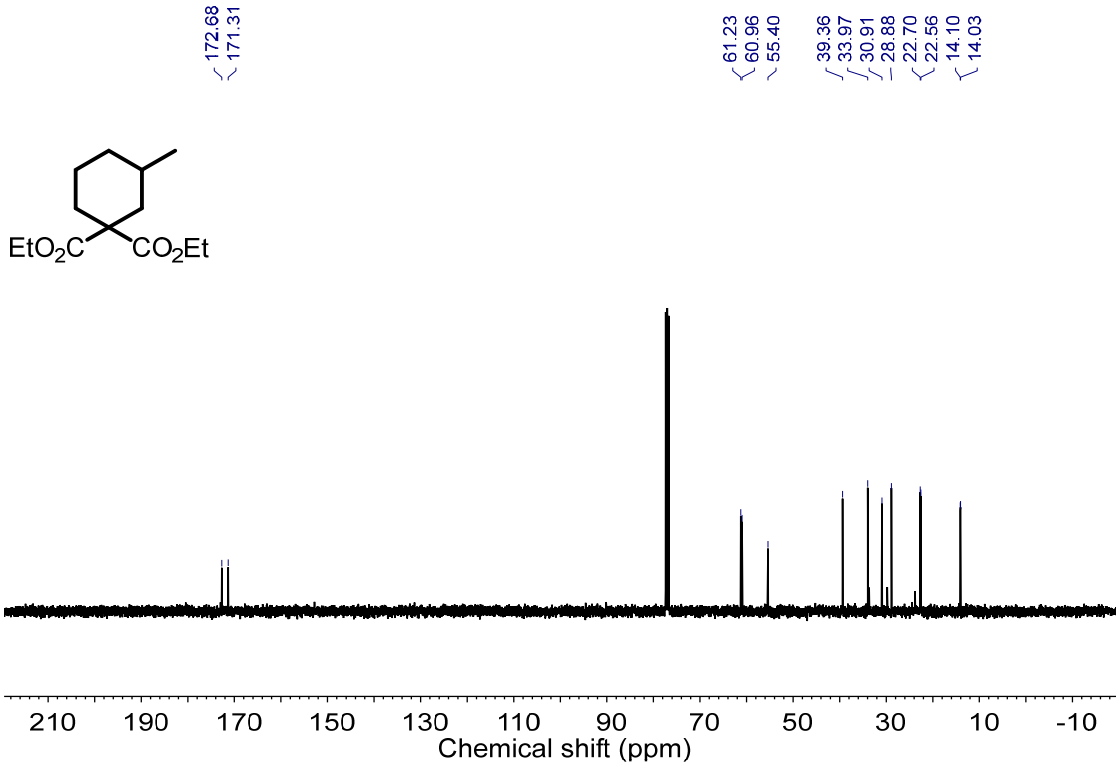
10a, ^{13}C NMR (126 MHz, $CDCl_3$)



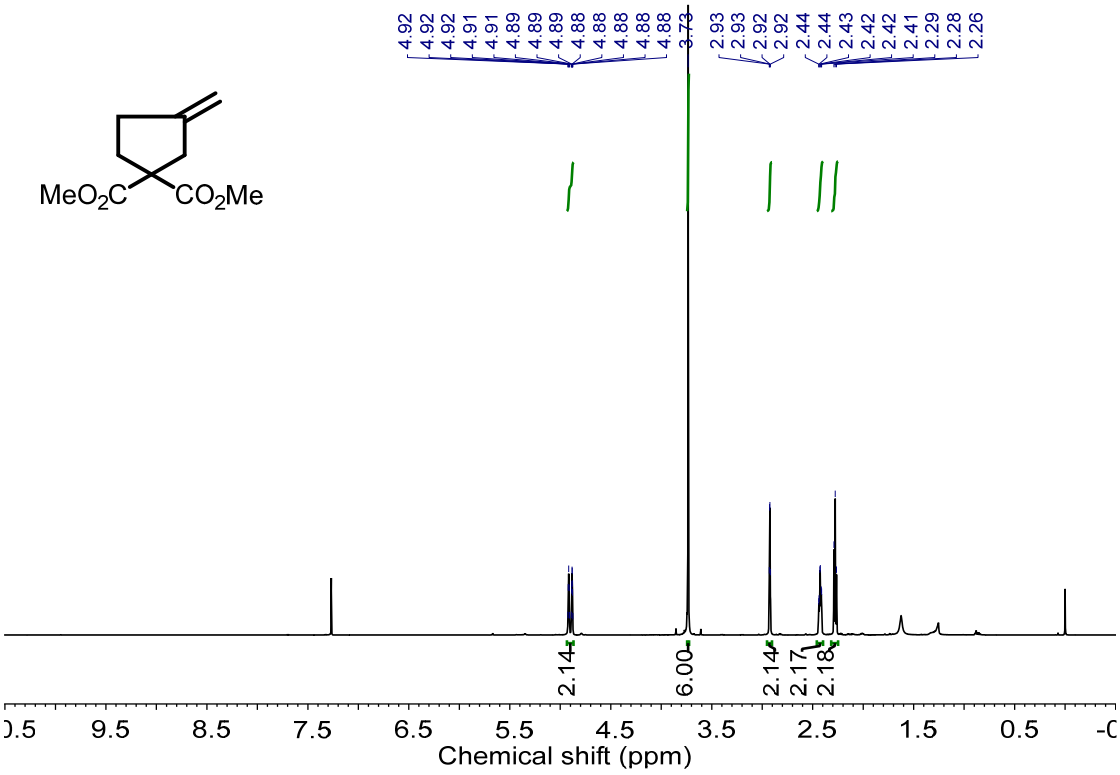
10b, ^{1}H NMR (400 MHz, $CDCl_3$)



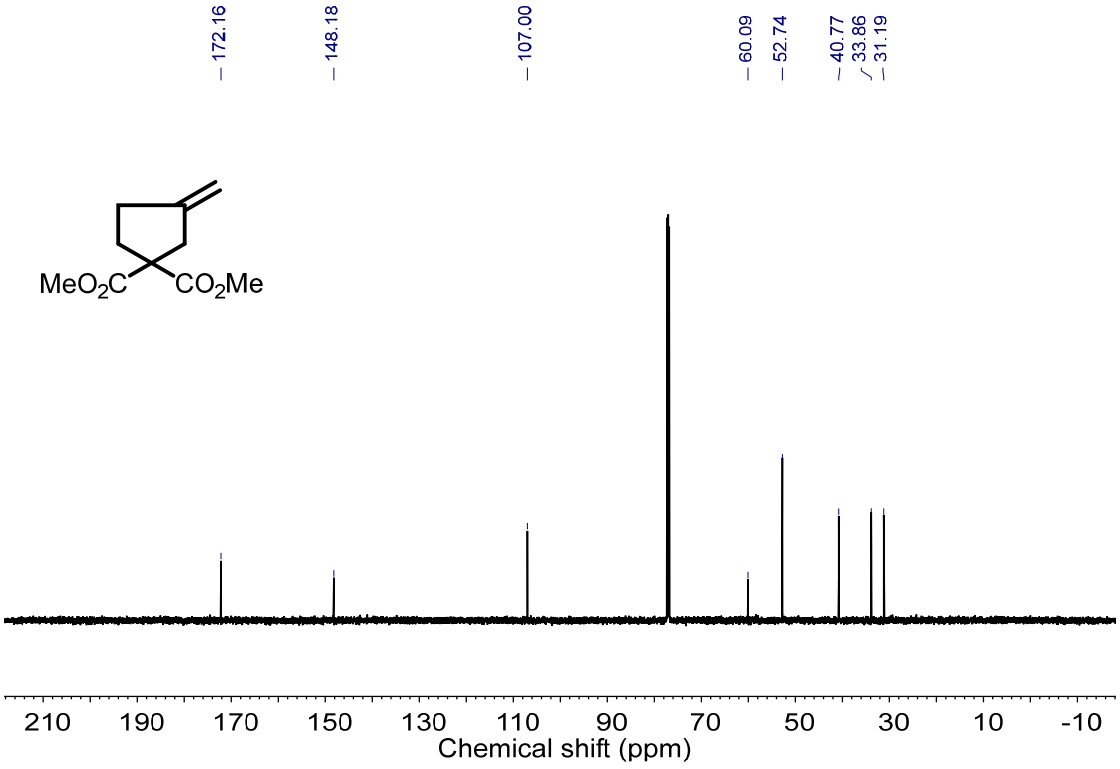
10b, ^{13}C NMR (151 MHz, $CDCl_3$)



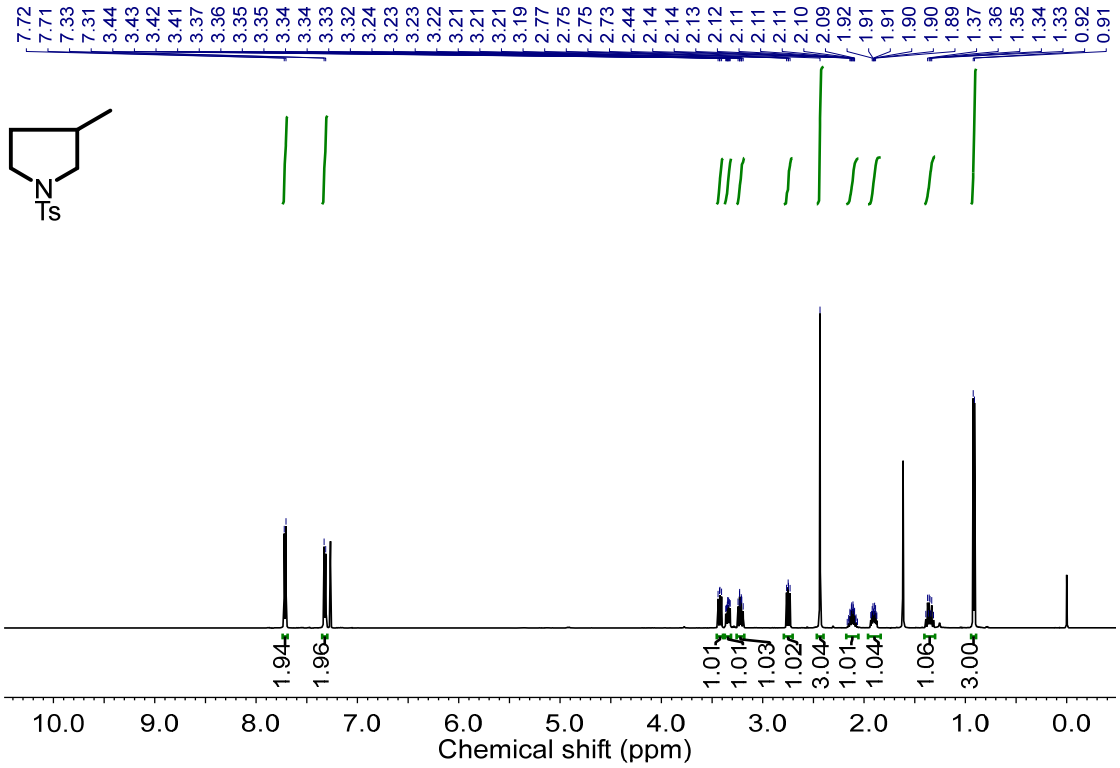
10c, ^{1}H NMR (600 MHz, $CDCl_3$)



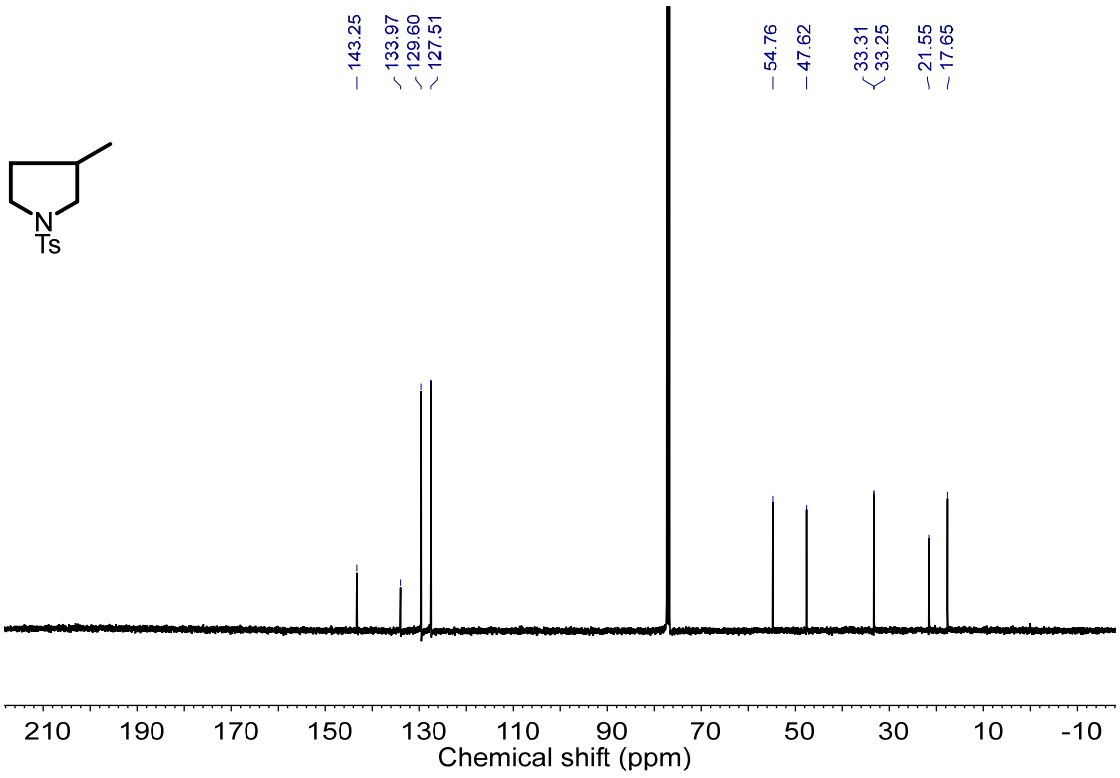
10c, ^{13}C NMR (151 MHz, $CDCl_3$)



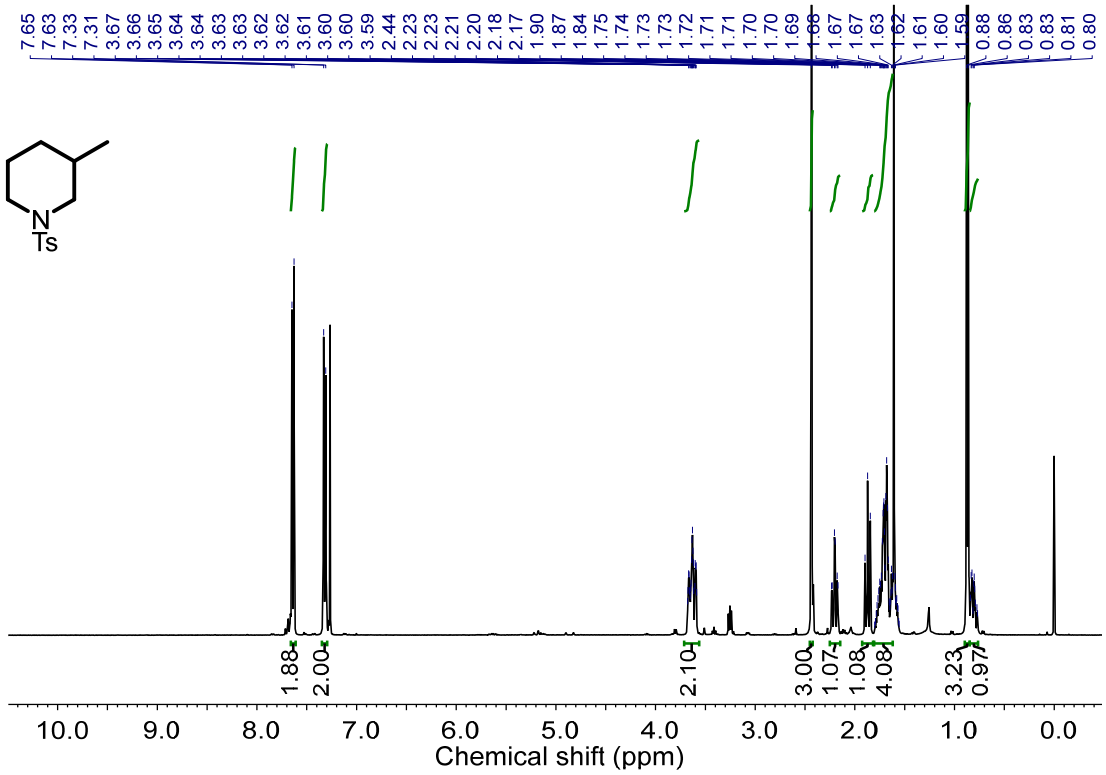
10d, ^{1}H NMR (500 MHz, $CDCl_3$)



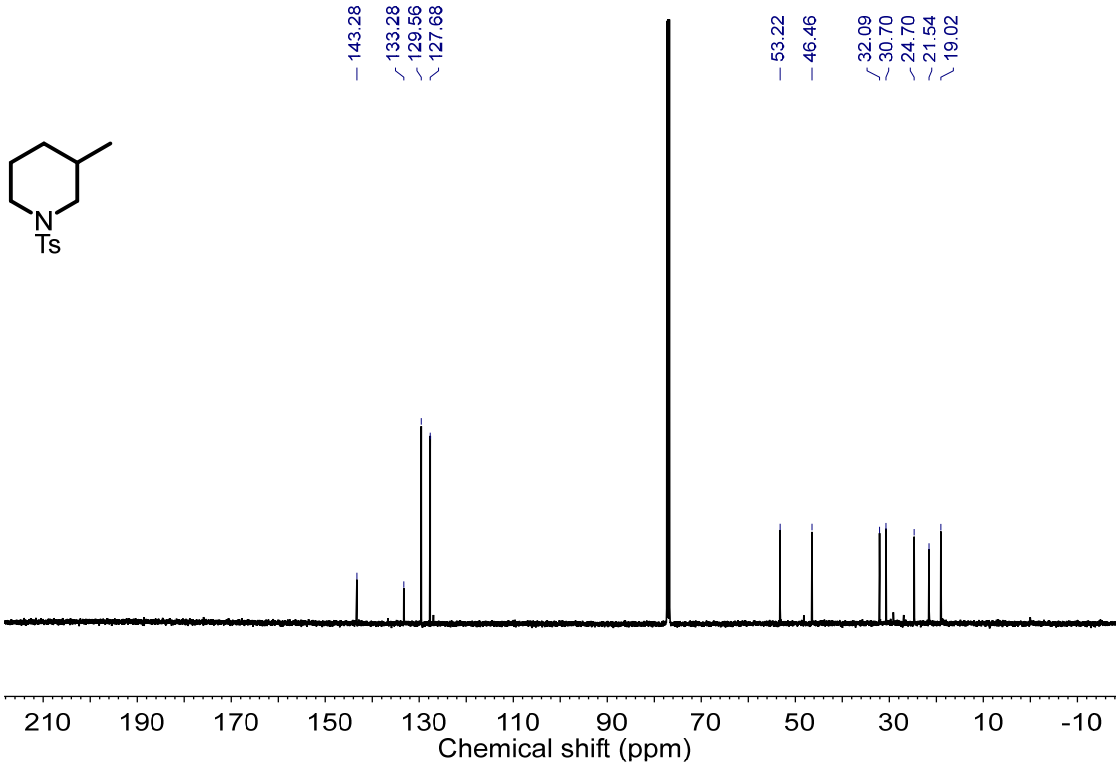
10d, ^{13}C NMR (126 MHz, $CDCl_3$)



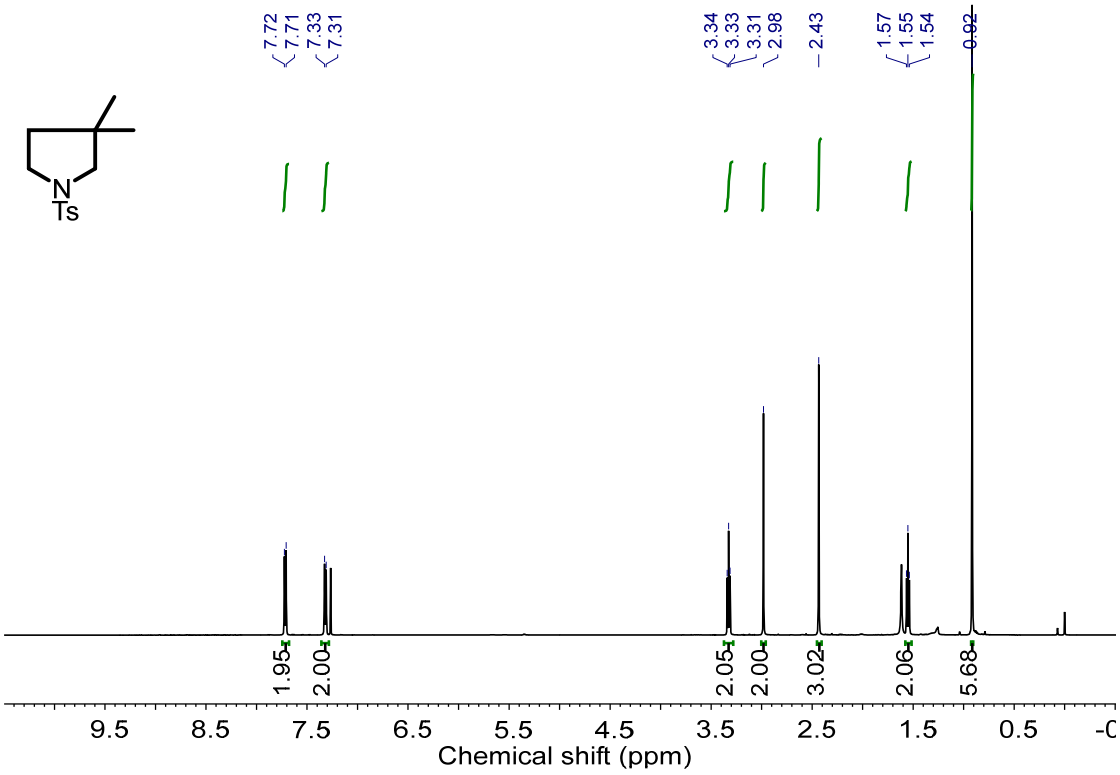
10e, ^{1}H NMR (400 MHz, $CDCl_3$)



10e, ^{13}C NMR (126 MHz, $CDCl_3$)



10f, ^{1}H NMR (500 MHz, $CDCl_3$)



10f, ^{13}C NMR (126 MHz, $CDCl_3$)