

# Supporting Information

## **Alkyne Activation by a Porous Silver Coordination Polymer for Heterogeneous Catalysis of Carbon Dioxide Cycloaddition**

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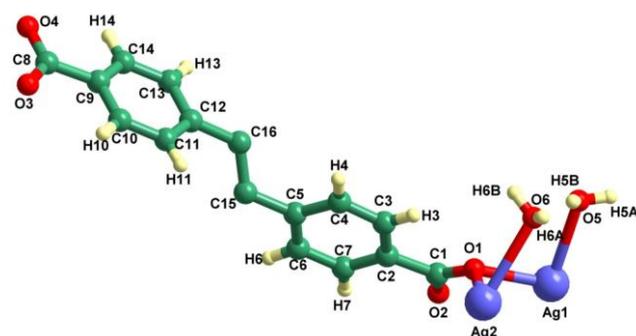
- 1. Supplementary Structural Figures.**
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- 5. <sup>1</sup>H NMR and <sup>13</sup>C NMR Spectra for the Products and Substrates**

**Table S1.** Crystal data and structure refinements

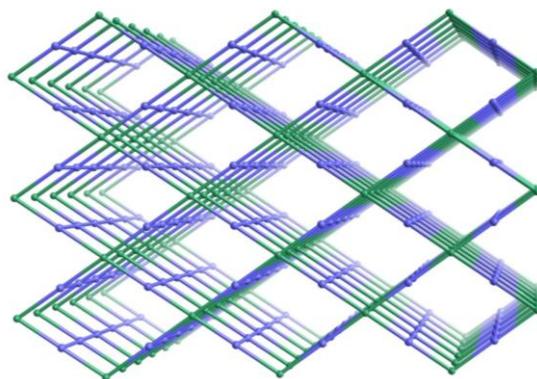
Compounds	Ag-TCPE	Ag-TCPE@1a
Empirical formula	C <sub>15</sub> H <sub>12</sub> O <sub>6</sub> Ag <sub>2</sub>	C <sub>54.5</sub> H <sub>45</sub> O <sub>10</sub> Ag <sub>4</sub> Cl <sub>5</sub>
Formula weight	503.99	1468.64
<i>T</i> /K	220(2)	200(2)
Crystal system	Monoclinic	Monoclinic
Space group	<i>C2/c</i>	<i>P2(1)/n</i>
<i>a</i> /Å	26.064(3)	11.2473(3)
<i>b</i> /Å	19.397(2)	18.5148(6)
<i>c</i> /Å	11.0996(12)	26.3786(8)
$\alpha$ <sup>o</sup>	90	90
$\beta$ <sup>o</sup>	97.166(2)	97.2988(13)
$\gamma$ <sup>o</sup>	90	90
<i>V</i> /Å <sup>3</sup>	5567.71(10)	5448.6(3)
<i>Z</i>	8	4
<i>D</i> <sub>calc</sub> /Mg m <sup>-3</sup>	1.203	1.790
$\mu$ /mm <sup>-1</sup>	0.441	1.719
<i>F</i> (000)	1952	2900
<i>R</i> <sub>int</sub>	0.0347	0.0455
Data/parameters	4898 / 209	9557 / 665
GOF	1.116	0.908
<i>R</i> [ <i>I</i> > 2σ( <i>I</i> )] <sup>a</sup>	<i>R</i> <sub>1</sub> = 0.0661	<i>R</i> <sub>1</sub> = 0.0966
	<i>wR</i> <sub>2</sub> = 0.1864	<i>wR</i> <sub>2</sub> = 0.2573
<i>R</i> indices (all data) <sup>b</sup>	<i>R</i> <sub>1</sub> = 0.0769	<i>R</i> <sub>1</sub> = 0.1421
	<i>wR</i> <sub>2</sub> = 0.1952	<i>wR</i> <sub>2</sub> = 0.2827
$\Delta\rho_{\max,\min}$ /eÅ <sup>-3</sup>	4.672 / -2.500	4.902 / -2.083
CCDC number	1494374	1494395

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

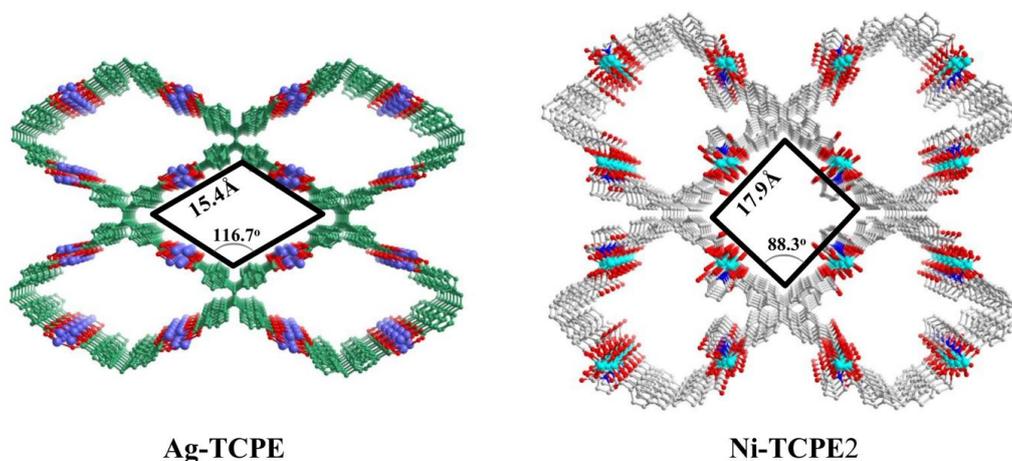
## 1. Supplementary Structural Figures



**Figure S1.** Ball-and-stick representation of **Ag-TCPE** in an asymmetric unit with atomic-numbering scheme and the selective bond distance (Å) and angle (°) in **Ag-TCPE**: Ag(1)-O(1) 2.192(5), Ag(1)-O(2) 2.172(4), Ag(1)-O(5) 2.557(8), Ag(1)-O(6) 2.388(10), Ag(2)-O(1) 2.568(6), Ag(2)-O(3) 2.161(5), Ag(2)-O(4) 2.220(4), O(1)-C(1) 1.251(9), O(2)-C(1) 1.256(8), C(1)-C(2) 1.506(8), C(5)-C(15) 1.491(6); O(2)-Ag(1)-O(5) 98.7(2), O(1)-Ag(1)-O(5) 89.5(2), O(4)-Ag(2)-O(1) 82.38(17), O(4)-Ag(2)-O(6) 86.2(2), O(1)-Ag(2)-O(6) 85.9(2).

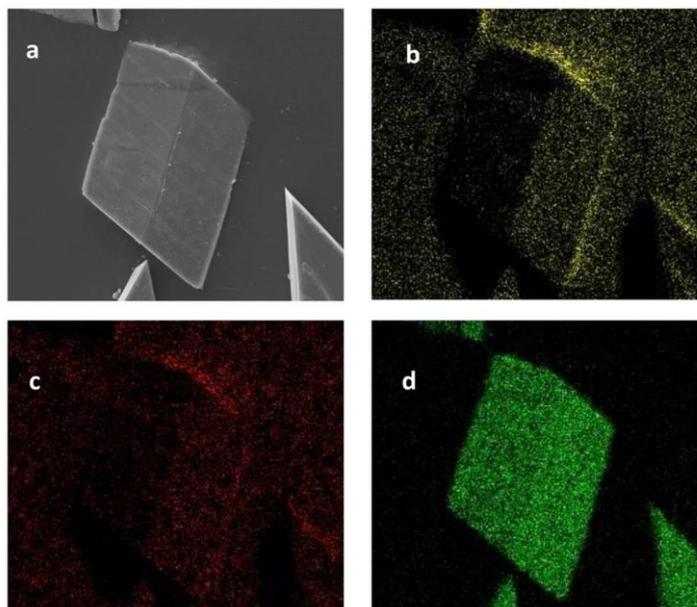


**Figure S2.** The truncated 3D structure and schematic representation of **Ag-TCPE** network.

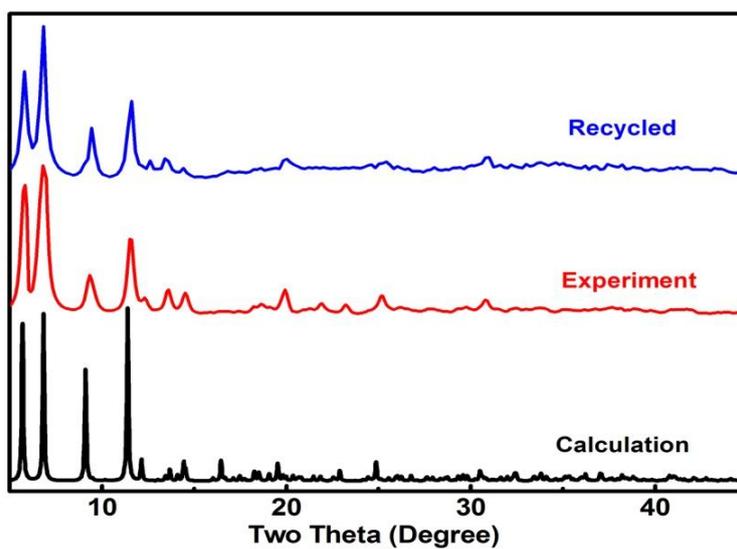


**Figure S3.** The comparison of the framework between the **Ag-TCPE** and the reported **Ni-TCPE2**.

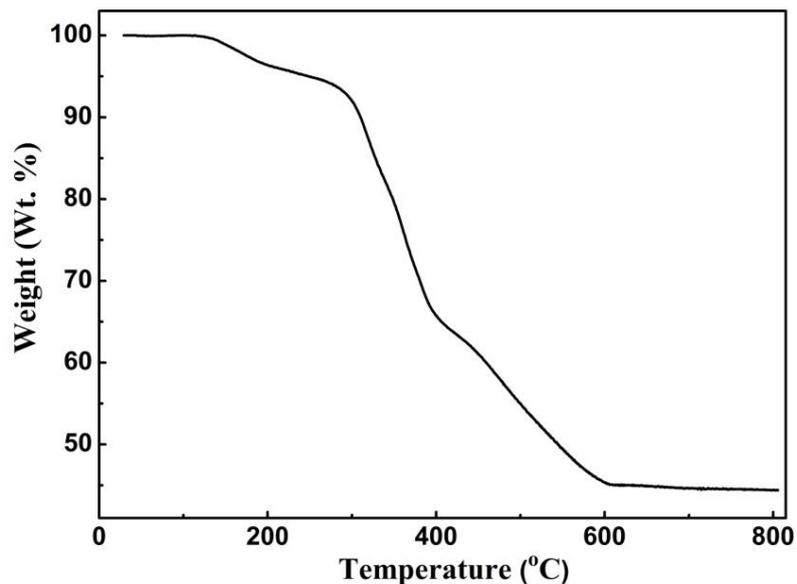
## 2. Characterizations of Catalysts



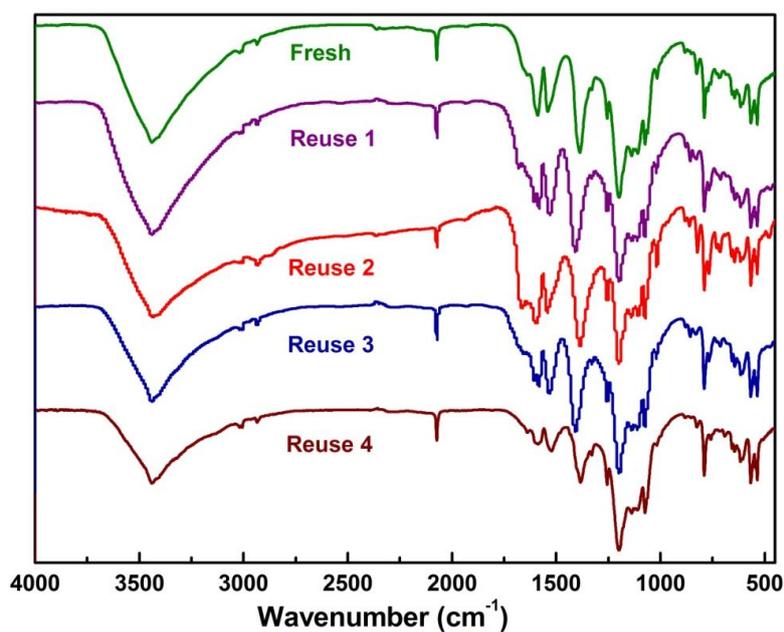
**Figure S4.** Element maps for Ag-TCPE, (a) SEM image; (b) C (yellow); (c) O (red); (d) Ag (green).



**Figure S5.** PXRD patterns of Ag-TCPE (red), its calculated pattern based on the single-crystal simulation (black) and the recycled catalyst after reactions (blue).



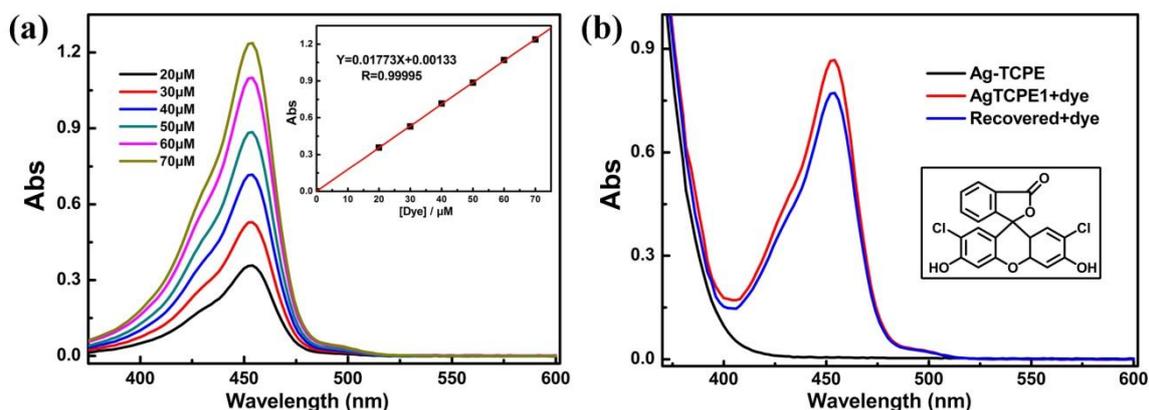
**Figure S6.** TG curve of Ag-TCPE, exhibiting two steps of weight loss processes. The first weight loss of 6.7 % (cacl. 7.2 %) between 25 and 260 °C is attributed to the loss of coordinated water molecules. The second weight loss of 49.1 % (cacl. 50.0 %) up to 600 °C is assigned to the decomposition of ligand TCPE.



**Figure S7.** IR spectra of fresh Ag-TCPE and the sample after each reused, showing that the main skeleton has been maintained.

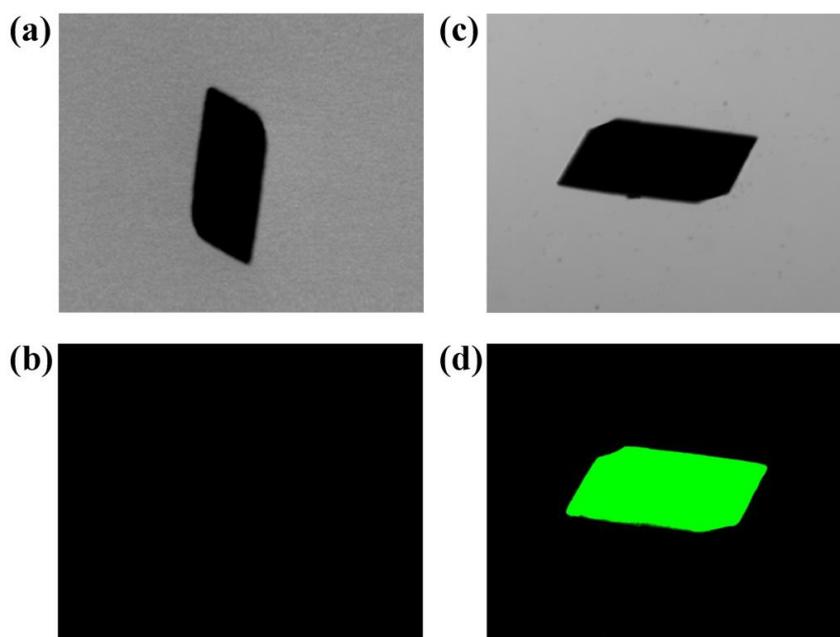
### Typical Procedure for Dye Uptake and Confocal Laser Scanning Microscopy of Ag-TCPE:

**Dye Uptake:** Before the dye uptake experiments, **Ag-TCPE** was firstly soaked in methanol solution (72 hours) for guest molecules exchange and fully dried out the methanol molecules in a vacuum oven (100 °C, 2 hours). Then, the dried-out crystals **Ag-TCPE** (2 mg) were soaked in a methanol solution of 2', 7'-dichlorofluorescein dye (24 mM, 2 mL) on a constant temperature oscillation incubator overnight. The resulting crystals were washed with methanol thoroughly to remove any dye from the crystals' surfaces until the solution become colorless, and then dried under a stream of air. The dried samples were dissociated by concentrated hydrochloric acid, and the relevant clear solution with the light of olivine color was diluted to 25 mL and adjusted to a pH of 0.2. Absorption experiment was performed on a UV-vis spectrophotometer. The concentration of 2', 7'-dichlorofluorescein dye was determined by comparing the UV-vis absorption with a standard curve.

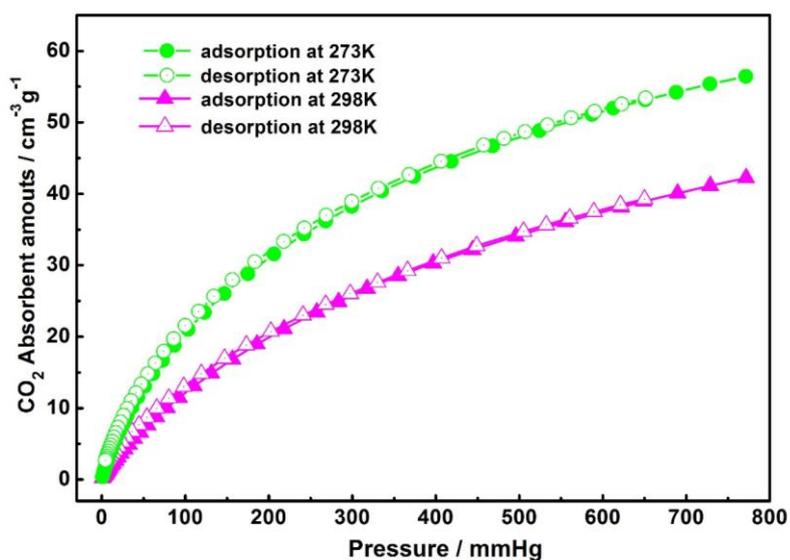


**Figure S8.** (a) UV-vis spectra of different concentration of 2', 7'-dichlorofluorescein dye; inside: The standard linear relationship between the absorption and the concentration. (b) UV-vis measurements of 2', 7'-dichlorofluorescein dye released from **Ag-TCPE**.

**Confocal Laser Scanning Microscopy:** The crystals of **Ag-TCPE** were soaked in a methanol solution of 2', 7'-dichlorofluorescein dye and conducted using the same procedure with the experiments of dye uptake. The brightfield images and confocal images of the obtained samples were scanned at  $\lambda_{em} = 510-610$  nm, excited by 488 nm through a 405/488 nm filter.



**Figure S9.** Confocal images of empty (a and b) and soaked (c and d) 2', 7'-dichlorofluorescein dye of Ag-TCPE.

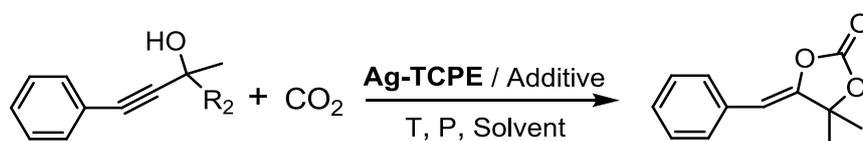


**Figure S10.** Gas sorption isotherms of Ag-TCPE of CO<sub>2</sub> measured at 273 and 298 K, respectively. Filled shape, adsorption; open shape, desorption.

### 3. Catalysis Details

#### 3.1 Typical procedure for the reaction of carboxylic cyclization of propargylic alcohols with CO<sub>2</sub>.

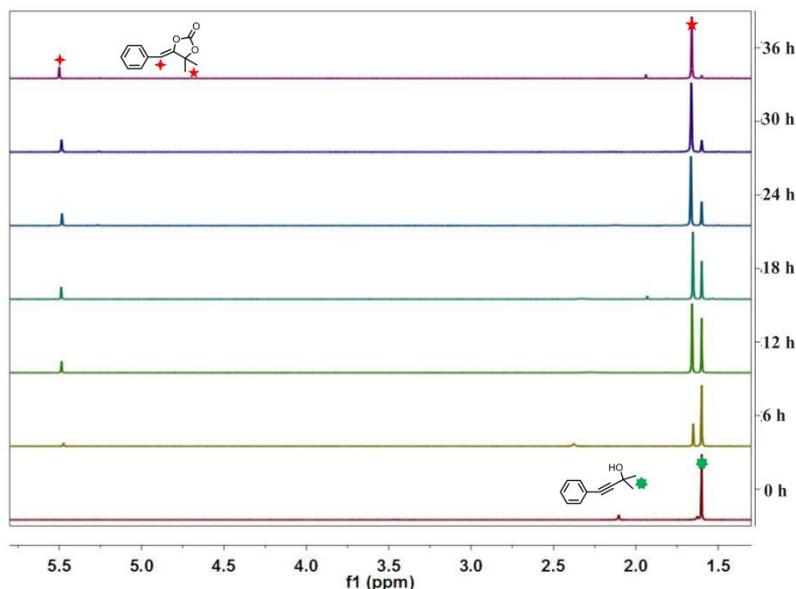
In a typical reaction, the catalytic reaction was conducted in a 25 mL autoclave reactor, purged with 0.5 MPa CO<sub>2</sub> under a constant pressure for 10 min to allow the system to equilibrate. The vessel was set in an oil bath with frequent stirring at the temperature of 50 °C for 36 h. At the end of the reaction, the reactor was placed in an ice bath for 20 min and then opened. The catalysts were separated by centrifugation, and a small aliquot of the supernatant reaction mixture was taken to be analyzed by <sup>1</sup>H NMR to calculate the yields of the reaction. The organic phase was collected and then purified by flash column chromatography on silica gel using petroleum ether–ethyl acetate as an eluent to give the desired products.



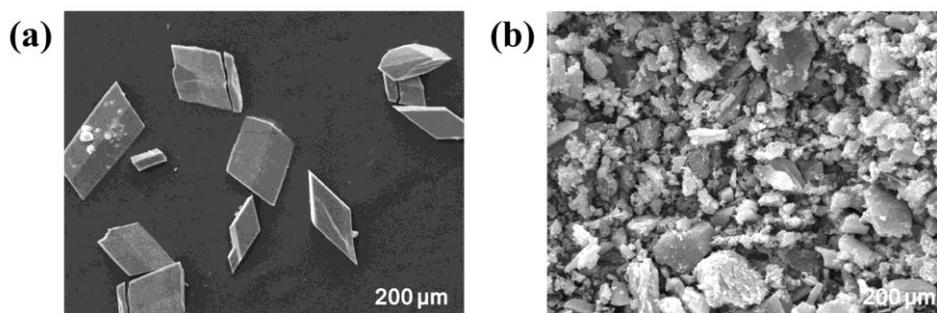
**Table S2.** Control experiments of carboxylic cyclization of propargylic alcohols with CO<sub>2</sub> <sup>[a]</sup>

Entry	Solvent	<i>T</i> (°C)	<i>P</i> (MPa)	<i>t</i> (h)	Yield <sup>[b]</sup> (%)
<b>1</b> <sup>[c]</sup>	CH <sub>3</sub> CN	50	0.5	36	-
<b>2</b>	CH <sub>3</sub> CN	25	0.1	36	5
<b>3</b>	CH <sub>3</sub> CN	50	0.1	36	14
<b>4</b>	CH <sub>3</sub> CN	50	1	36	91
<b>5</b>	CH <sub>3</sub> CN	25	0.5	36	5
<b>6</b>	CH <sub>3</sub> CN	80	0.5	36	91
<b>7</b> <sup>[d]</sup>		50	0.5	36	-
<b>8</b>	CH <sub>2</sub> Cl <sub>2</sub>	50	0.5	36	5
<b>9</b>	PhMe	50	0.5	36	17

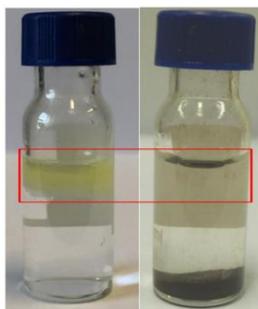
[a] Reaction conditions: propargylic alcohols (2 mmol), catalyst (0.5 mol% loading, based on each Ag site), and additive (Ph<sub>3</sub>P, 2.5 mol%) under purged with CO<sub>2</sub>. [b] The yields were determined by <sup>1</sup>H NMR analysis using durene as internal standard. [c] without the addition of catalyst Ag-TCPE. [d] solvent free.



**Figure S11.**  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz) monitoring of the cycloaddition reaction progress using catalyst **Ag-TCPE**, showing the increasing tendency of the peaks at around 1.68 and 5.49 ppm, while the gradual vanish of the peak at around 1.60, with the proceeding of the reaction.



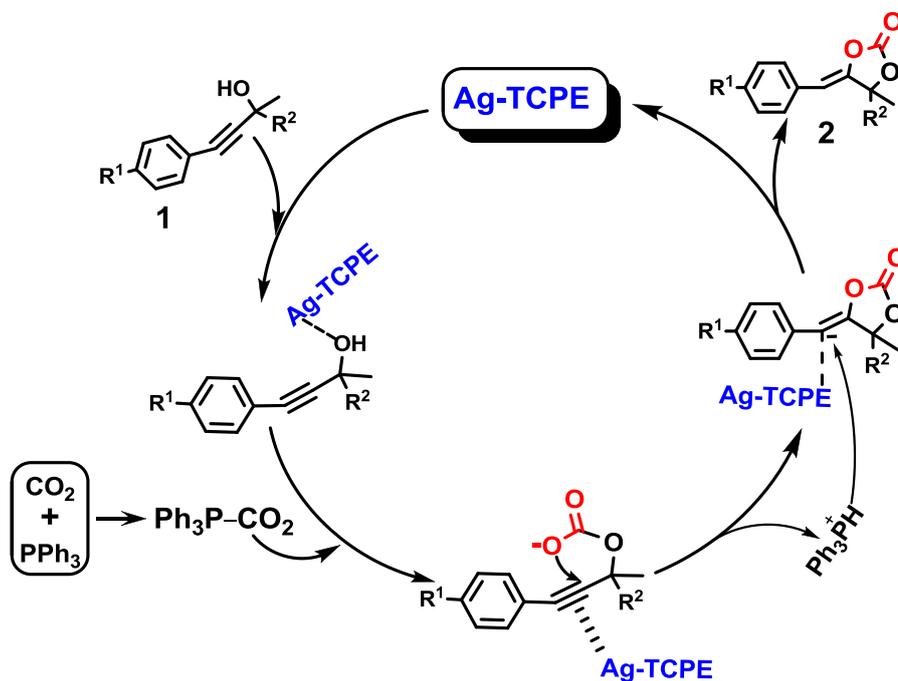
**Figure S12.** SEM images for initial crystals **Ag-TCPE** with the size about 0.1 mm (a) and the grinding sample with the size about 5-20  $\mu\text{m}$  (b) showing the similar catalytic ability under the same conditions.



**Figure S13.** The pictures of phenylacetylene before (left) and after (right) adsorption by **Ag-TCPE**.

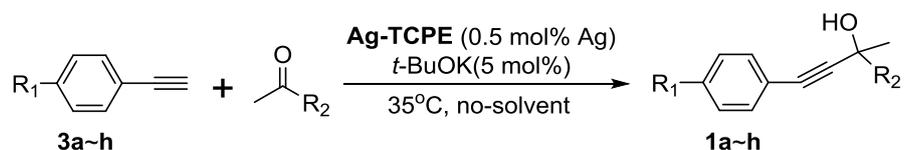
### 3.2 Proposed mechanism for the reaction of carboxylic cyclization of propargylic alcohols with CO<sub>2</sub>.

In a typical reaction, there are two steps in the carboxylative cycloaddition. In the first step, the alcoholic hydroxyl was activated by the Ag-TCPE, and CO<sub>2</sub> was activated by Ph<sub>3</sub>P to form the carbonate intermediate. The O atom in hydroxyl group is more favorable to the electrophilic attack of the C atom in CO<sub>2</sub>. For the next intramolecular ring-closing step, a nucleophilic attack to the silver propargylic carbonate intermediate that generated the Ag...C≡C bonds by π-activation was occurred. The corresponding carboxylative cyclization product is thus yielded with the process of proto-demetalation and the regeneration of Ph<sub>3</sub>P.



### 3.3 Typical procedure for the synthesis of propargylic alcohols via terminal alkynes.

In a typical reaction, the catalytic reaction was conducted in a 2 mL glass vial with the cover of tetrafluoroethylene. 2 mmol phenylacetylene and acetone (1.5 eq, 0.22 mL) in the presence of catalyst **Ag-TCPE** (0.5 mol%) and the additive *t*-BuOK (5 mol%) were added into the reactor. The vial was stirred at 35 °C for 24 h. At the end of the reaction, CH<sub>2</sub>Cl<sub>2</sub> was added into the system and then the catalysts were separated by centrifugation. The solvent was removed by vacuum evaporation and taken to be analyzed by <sup>1</sup>H NMR to calculate the yields of the reaction using durene as internal standard. The yields of the general reactions with different substrates were indicated in Table S3.

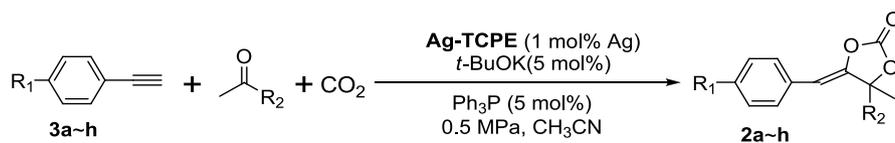


**Table S3.** The synthesis of propargylic alcohols via terminal alkynes catalyzed by **Ag-TCPE**.

Entry	Alkyne	Ketone	Product	Yield (%)
1				93
2				87
3				84
4				73
5				64
6				97
7				78
8				53

### 3.4 Typical procedure for the tandem conversion of alkyne and CO<sub>2</sub> to $\alpha$ -methylene cyclic carbonates.

In a typical reaction, the catalytic reaction was conducted in a 25 mL autoclave reactor, with the addition of 2 mmol phenylacetylene and acetone (1.5 eq, 0.22 mL) in the presence of catalyst **Ag-TCPE** (1.0 mol%), *t*-BuOK (5 mol%), Ph<sub>3</sub>P (5 mol%) and 1 mL CH<sub>3</sub>CN were directly added into the reactor, then purged with 0.5 MPa CO<sub>2</sub> under a constant pressure for 10 min to allow the system to equilibrate. The vessel was set in an oil bath with frequent stirring at the temperature of 40 °C for 72 h. At the end of the reaction, the reactor was placed in an ice bath for 20 min and then opened. The catalysts were separated by centrifugation, and a small aliquot of the supernatant reaction mixture was taken to be analyzed by <sup>1</sup>H NMR to calculate the yields of the reaction using durene as internal standard. The yields of the general reactions with different substrates were indicated in Table S4.

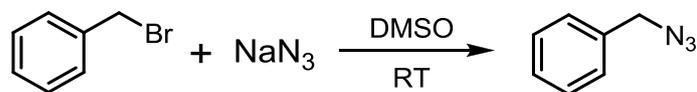


**Table S4.** Tandem conversion of alkyne and CO<sub>2</sub> to  $\alpha$ -methylene cyclic carbonates catalyzed by **Ag-TCPE**.

Entry	Alkyne	Ketone	Product	Conversion (%)	Selectivity (%)
1				93	73
2				93	71
3				90	67
4				85	62
5				85	55
6				90	68
7				87	62
8				trace	-

### 3.5 Typical procedure for the azide-alkyne cycloaddition.

Benzyl azide was synthesized according to the reported procedure.<sup>[S1]</sup> **Caution:** Sodium azide ( $\text{NaN}_3$ ) may be toxic, the operation need more carefully due to its explosion when heat or vibration.

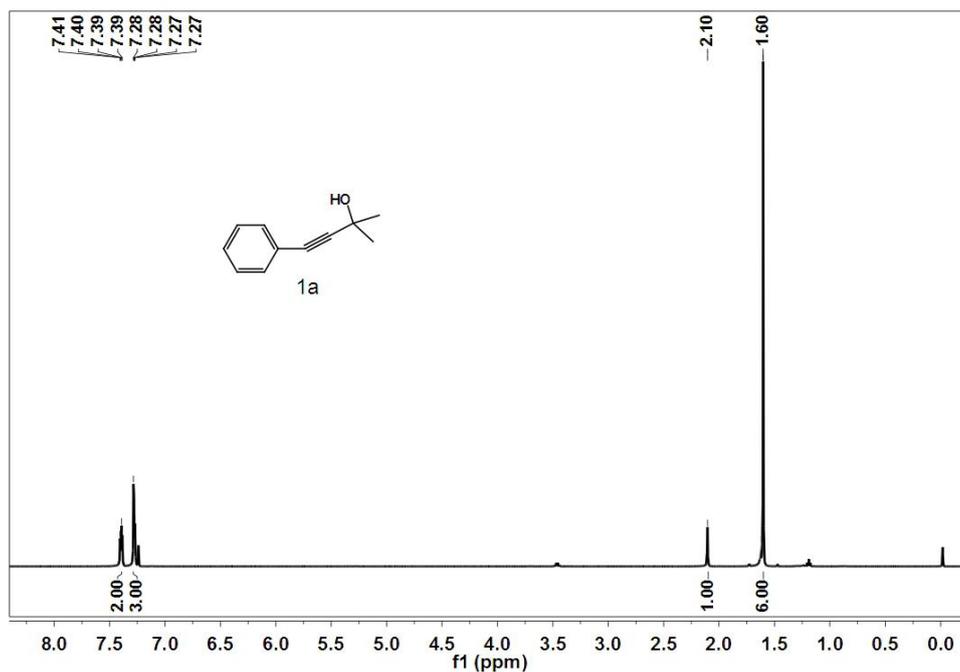


In a typical reaction, the catalytic reaction was as conducted in a 2 mL glass vial with the cover of tetrafluoroethylene. To a mixture of phenylacetylene (1 mmol) and benzyl azide (1 mmol, 1 eq) in 0.1 mL of water were added sequentially catalyst (0.5 mol%). The mixture was then stirred at 50 °C for 24 h. The reaction mixture was diluted with dichloromethane (10 mL). The catalysts were separated by centrifugation. Subsequently, the filtrate was carried out by adding 10 mL of water, and the organic layer was extracted with dichloromethane and dried over anhydrous sodium sulphate. The organic phase was concentrated under reduced pressure and purified through silica gel column chromatography (ethyl acetate/ hexanes) to afford the pure product. All reported yields are isolated yields.

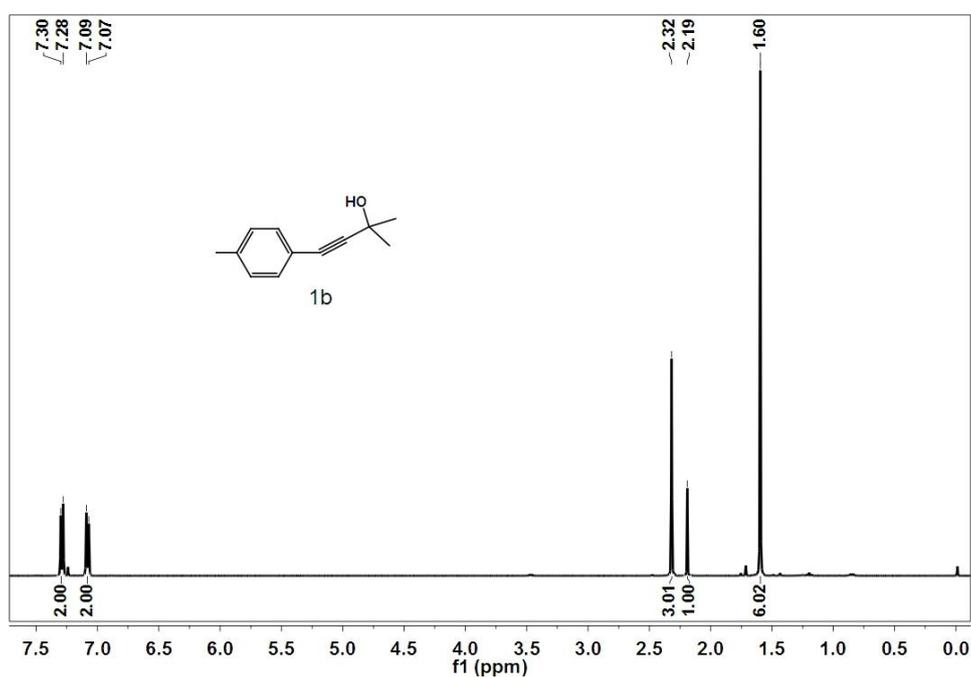
#### 4. References:

[S1] McNulty, J.; Keskar, K.; Vemula, R. *Chem. Eur. J.* **2011**, *17*, 14727–14730.

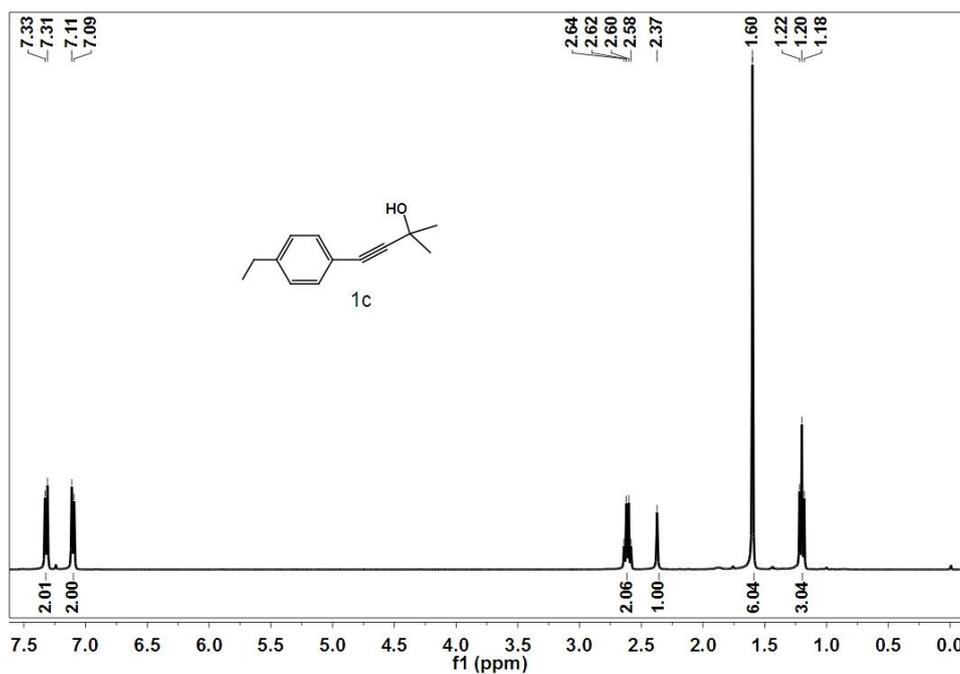
## 5. $^1\text{H}$ NMR Spectra and Analysis for the Products and Substrates



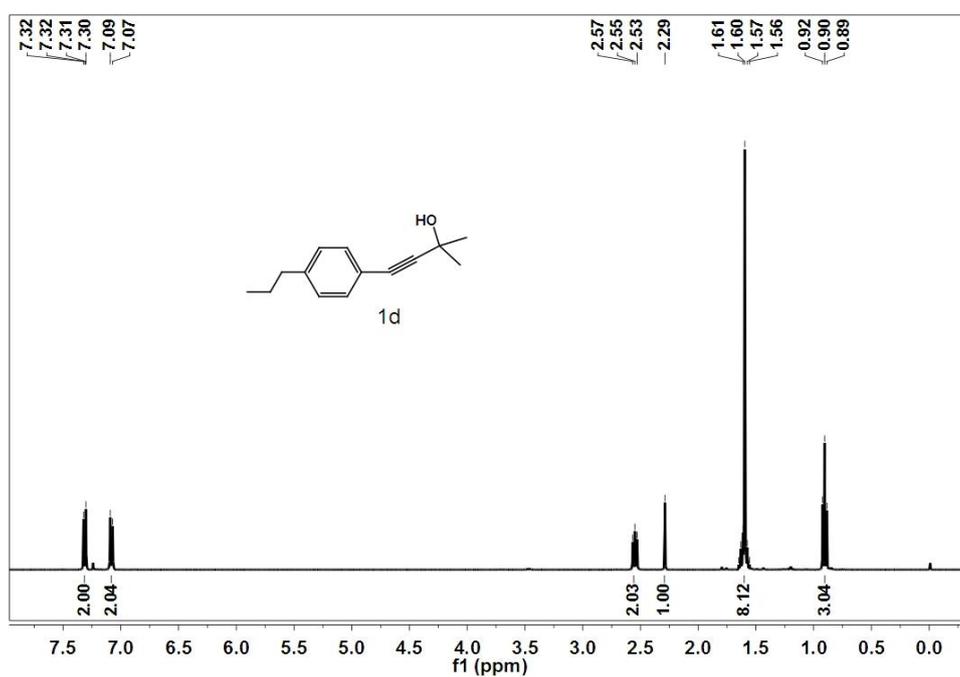
**1a:**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ =7.39–7.41 (m, 2H), 7.27–7.28 (m, 3H), 2.10 (s, 1H), 1.60 (s, 6H).



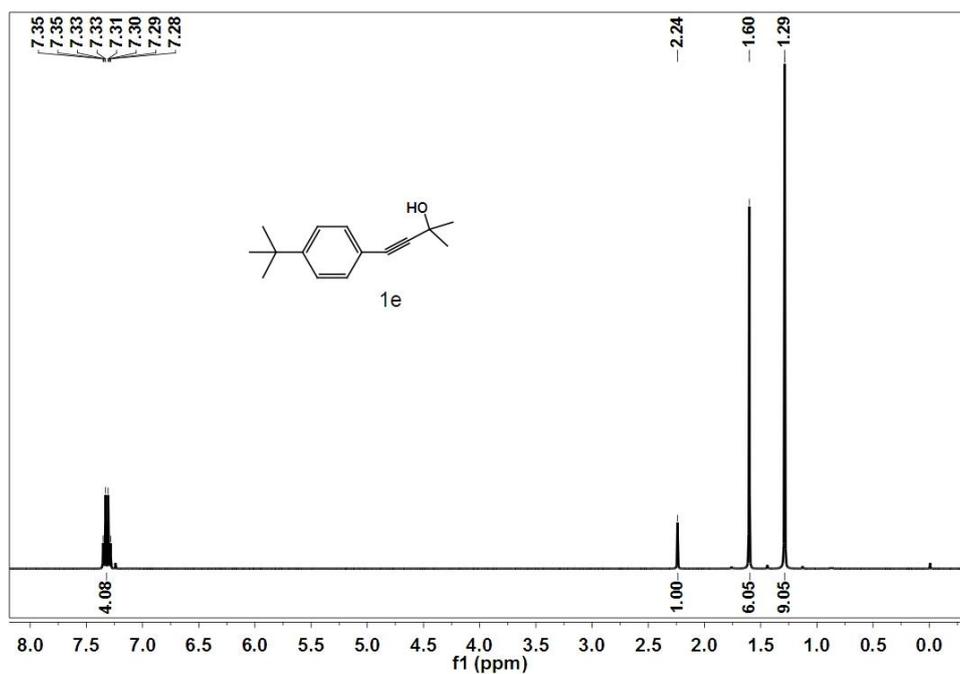
**1b:**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ =7.29 (d,  $J$  = 8.0 Hz, 2H), 7.08 (d,  $J$  = 7.9 Hz, 2H), 2.32 (s, 3H), 2.19 (s, 1H), 1.60 (s, 6H).



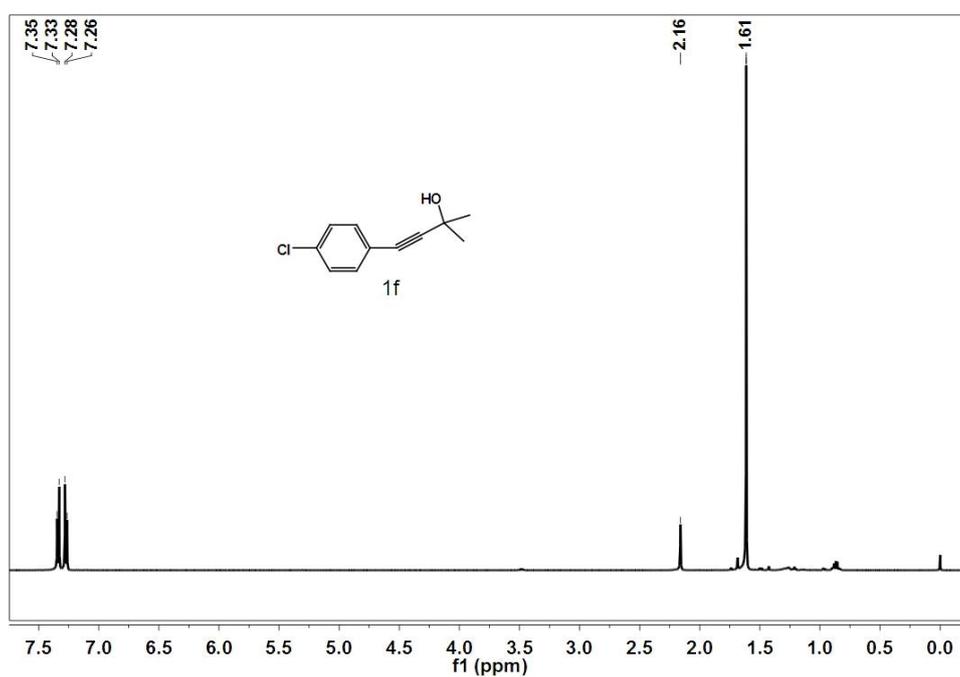
**1c:**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ =7.32 (d,  $J$ =7.8, 2H), 7.10 (d,  $J$ =7.8, 2H), 2.61 (q,  $J$ =7.6, 2H), 2.37 (s, 1H), 1.60 (s, 6H), 1.20 (t,  $J$ =7.6, 3H).



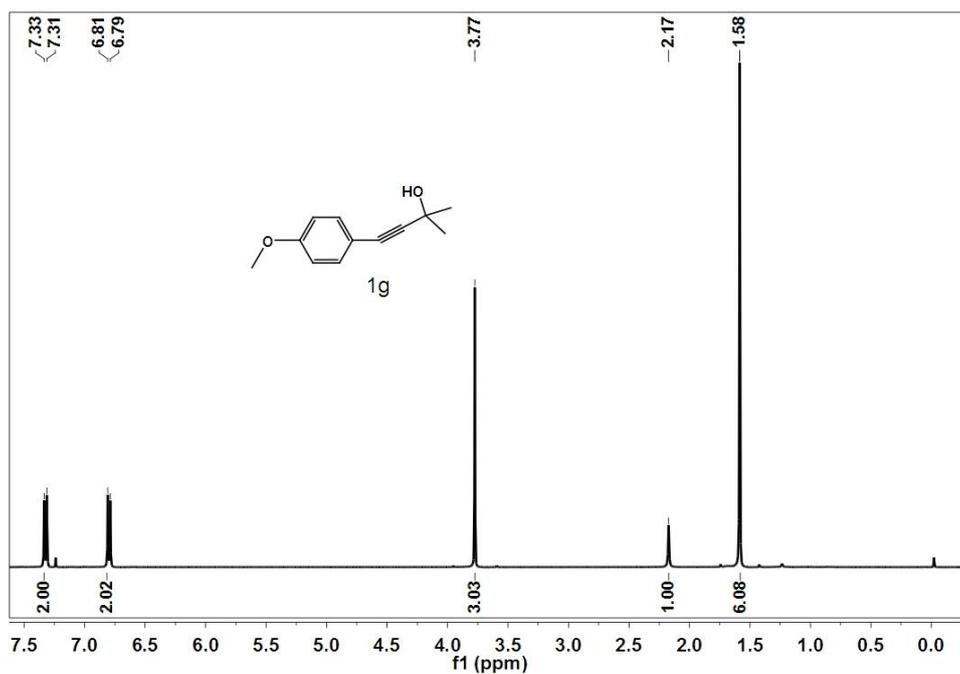
**1d:**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ =7.31 (d,  $J$ =8.2, 2H), 7.08 (d,  $J$ =8.3, 2H), 2.57–2.53 (m, 2H), 2.29 (s, 1H), 1.61–1.56 (m, 8H), 0.90 (t,  $J$ =7.3, 3H).



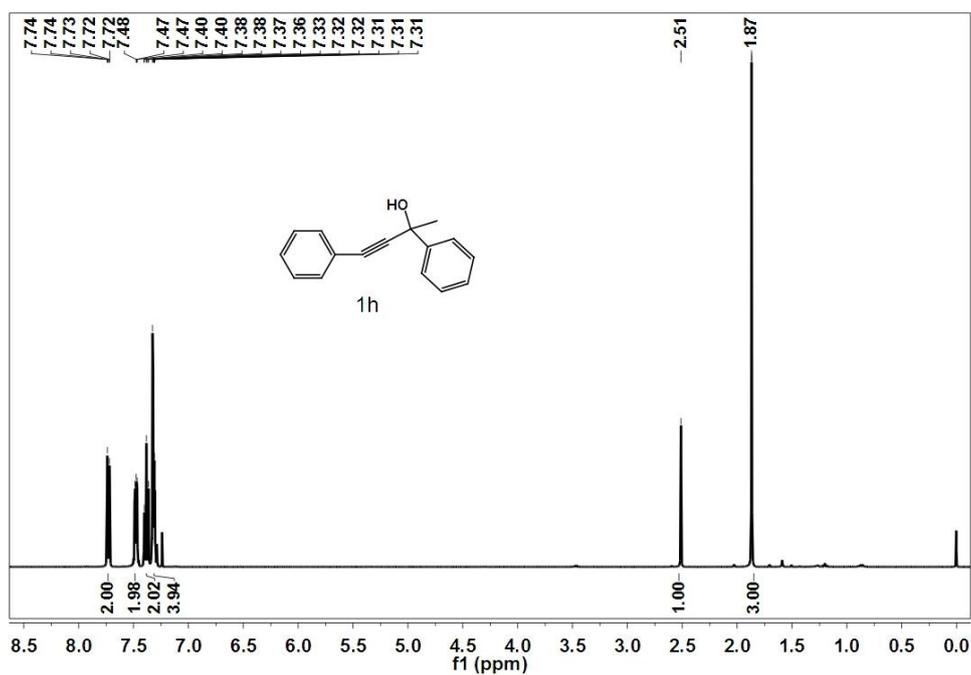
**1e**:  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$ =7.35–7.28 (m, 4H), 2.24 (s, 1H), 1.60 (s, 6H), 1.29 (s, 9H).



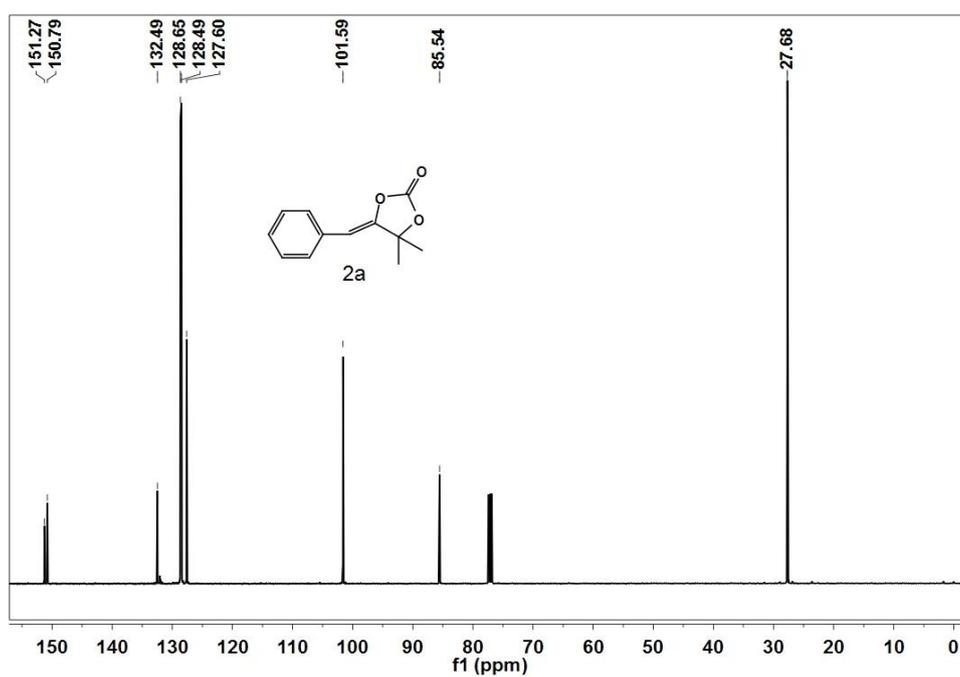
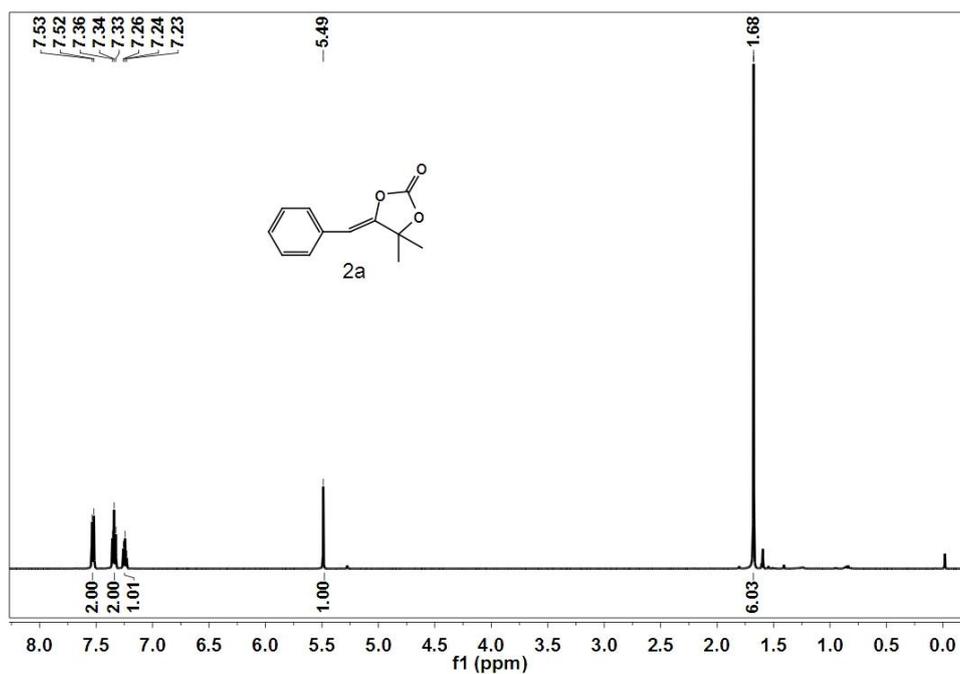
**1f**:  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$ =7.34 (d,  $J$ =8.6, 2H), 7.27 (d,  $J$ =8.6, 2H), 2.16 (s, 1H), 1.61 (s, 6H).



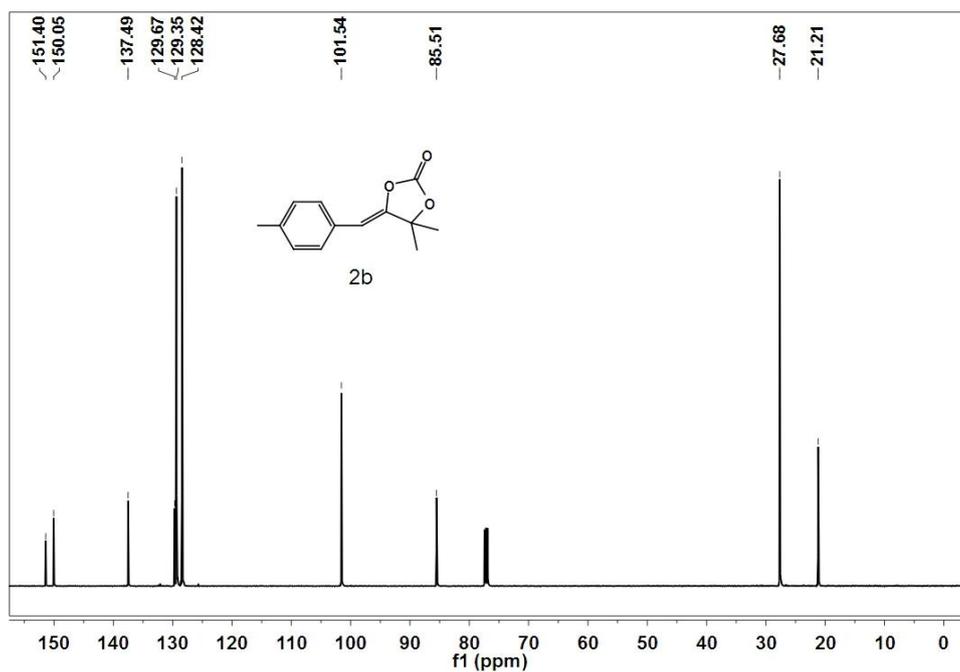
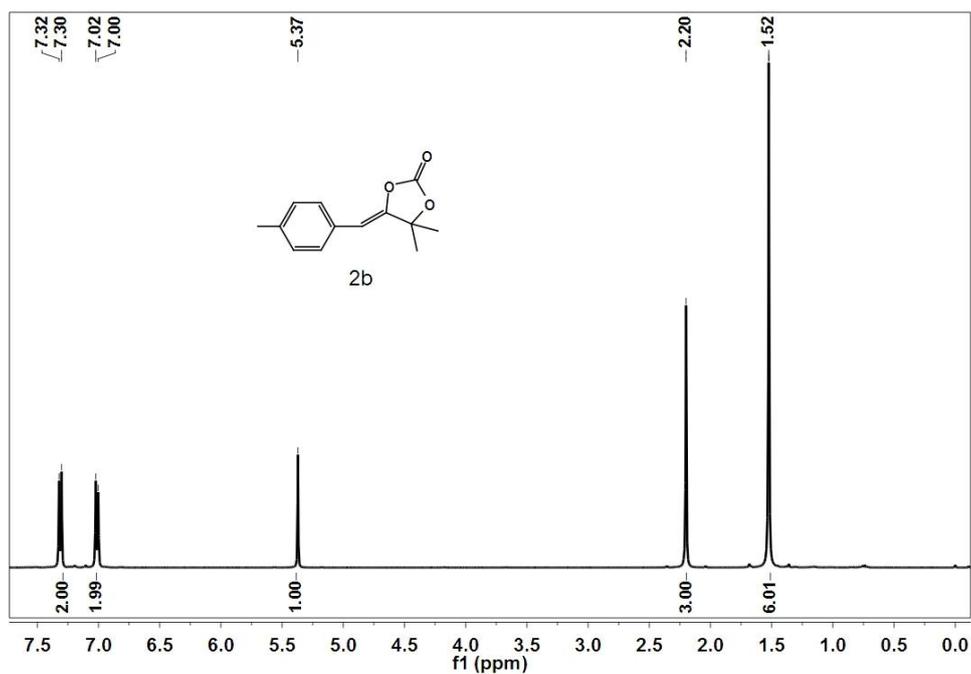
**1g**:  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$ =7.32 (d,  $J=8.7$ , 2H), 6.80 (d,  $J=8.7$ , 2H), 3.77 (s, 3H), 2.17 (s, 1H), 1.58 (s, 6H).



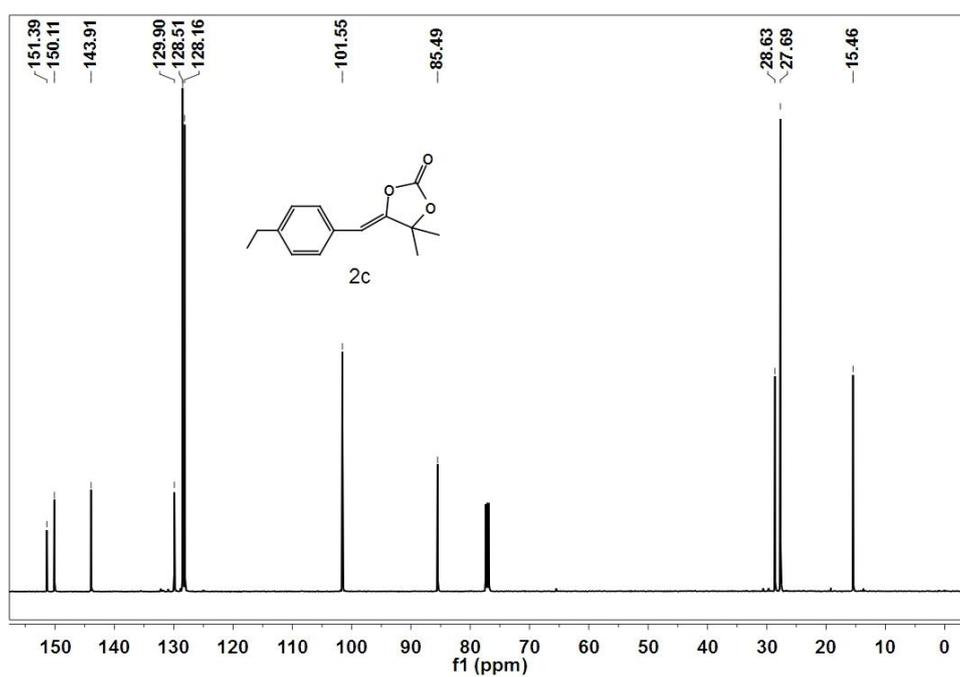
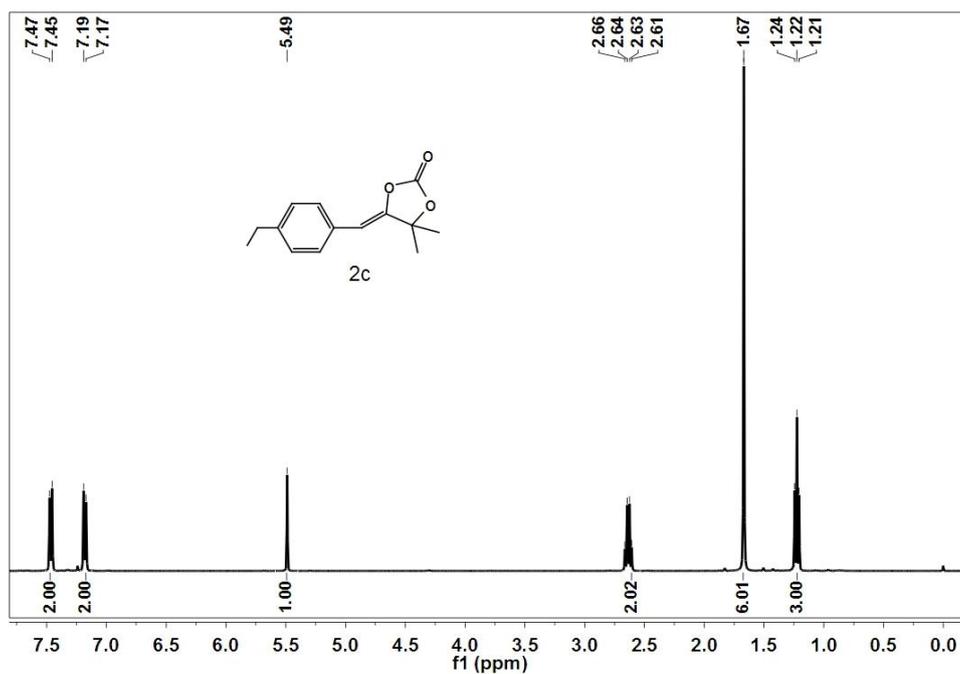
**1h**:  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$ =7.78–7.68 (m, 2H), 7.52–7.46 (m, 2H), 7.41–7.35 (m, 2H), 7.35–7.28 (m, 4H), 2.51 (s, 1H), 1.87 (s, 3H).



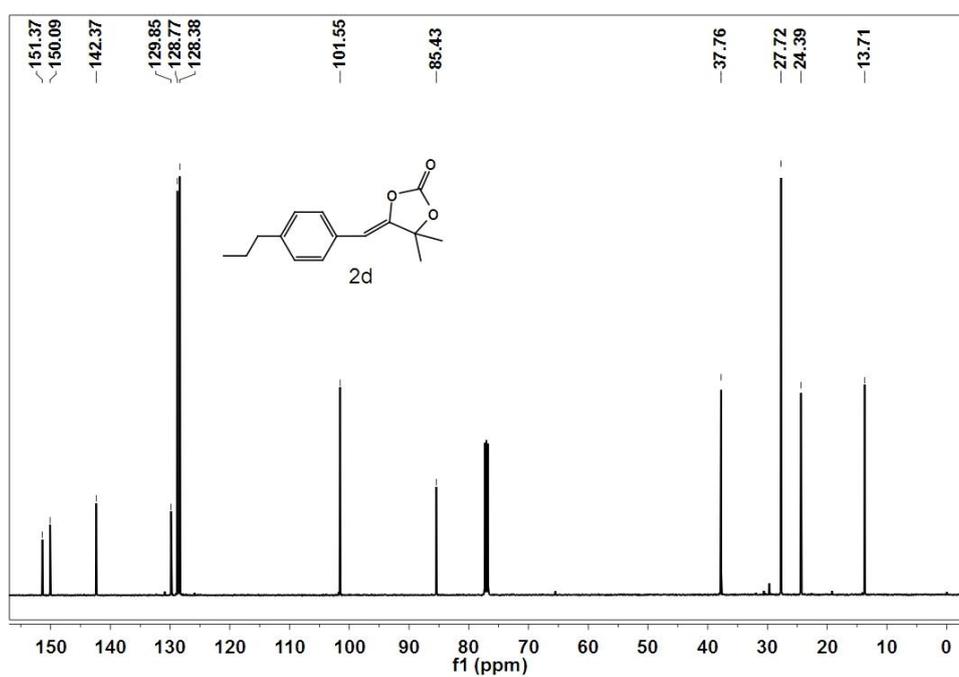
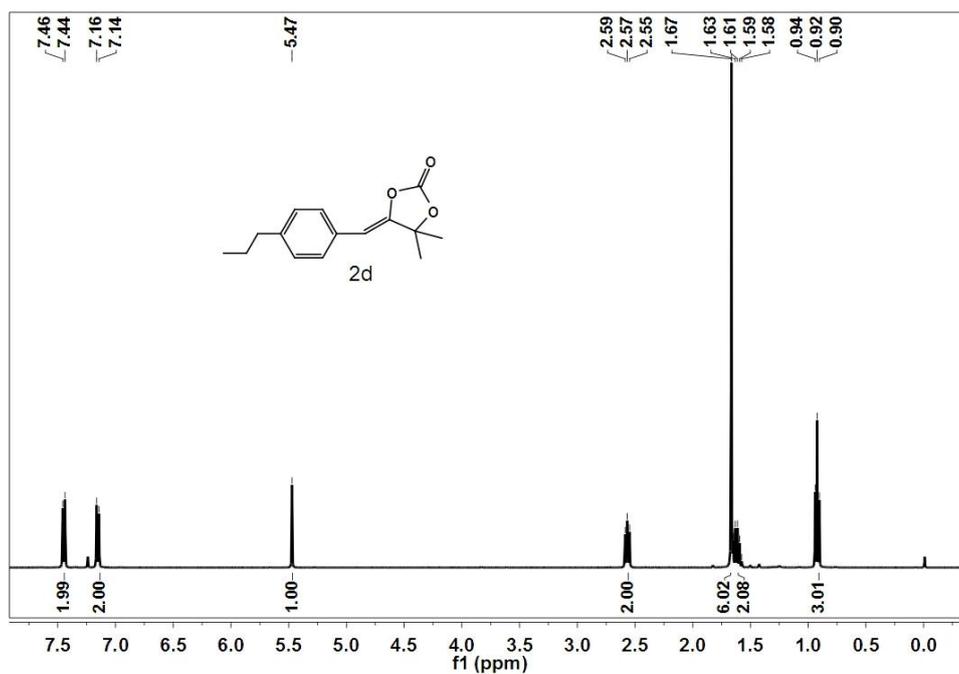
**2a:** <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ=7.53 (d, *J*=7.5, 2H), 7.34 (t, *J*=7.7, 2H), 7.25 (d, *J*=7.4, 1H), 5.49 (s, 1H), 1.68 (s, 6H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ=151.25, 150.79, 132.49, 128.65, 128.49, 127.60, 101.59, 85.54, 27.68.



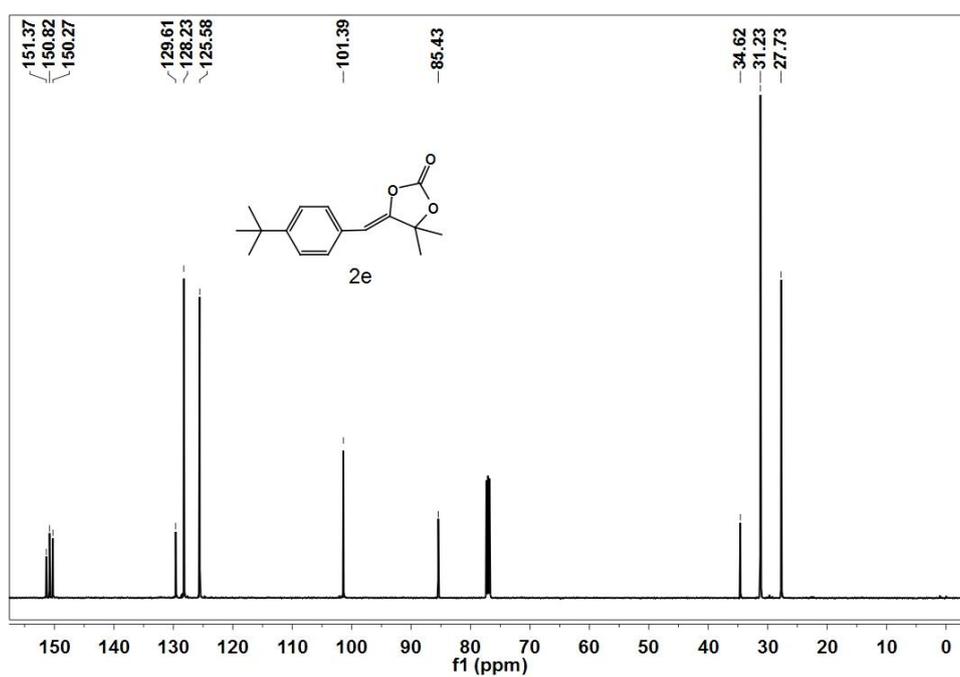
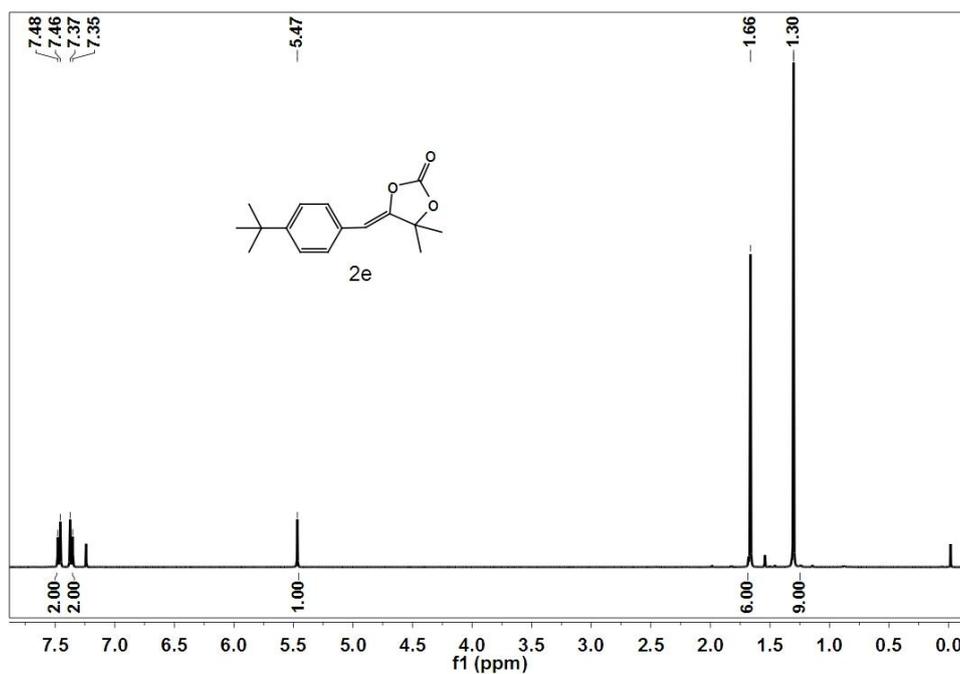
**2b**:  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ =7.31 (d,  $J$ =8.1, 2H), 7.01 (d,  $J$ =8.0, 2H), 5.37 (s, 1H), 2.20 (s, 3H), 1.52 (s, 6H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$ =151.40, 150.05, 137.49, 129.67, 129.35, 128.42, 101.54, 85.51, 27.68, 21.21.



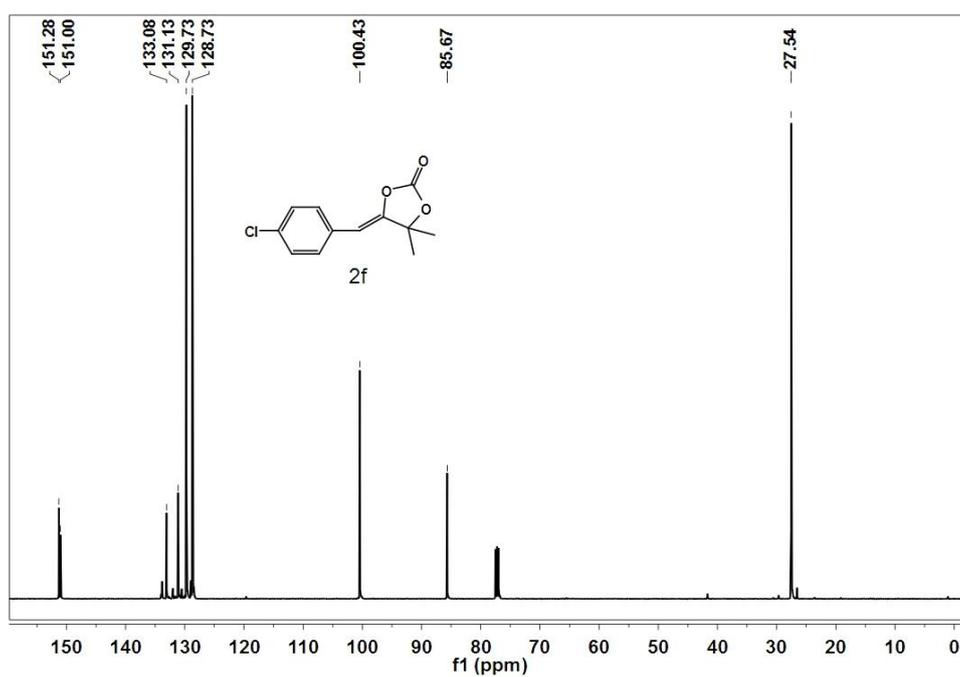
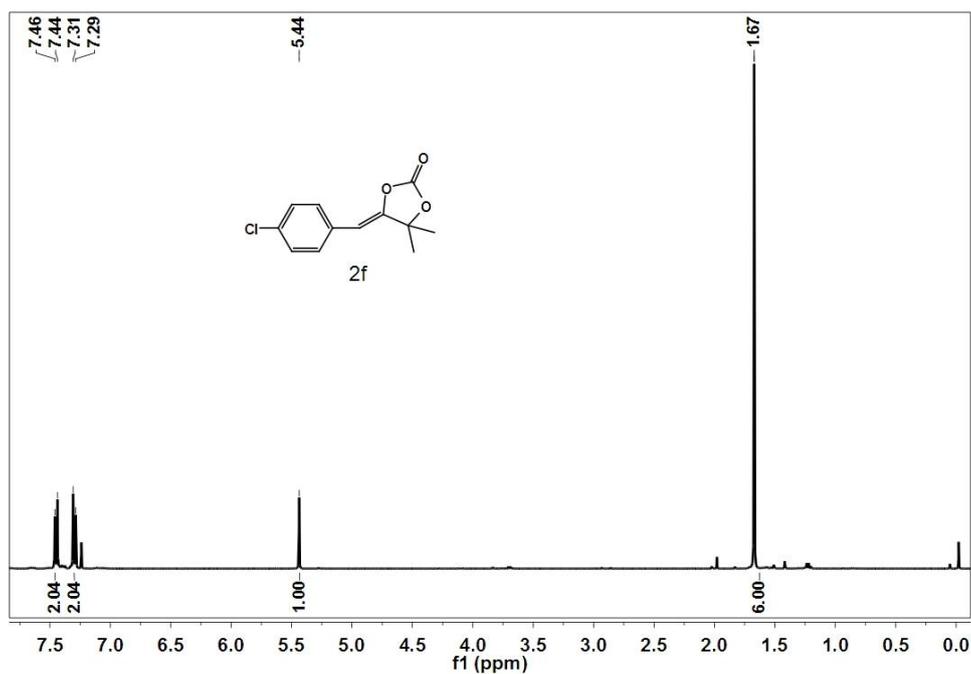
**2c:**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ =7.46 (d,  $J$ =8.1, 2H), 7.18 (d,  $J$ =8.0, 2H), 5.49 (s, 1H), 2.64 (q,  $J$ =7.6, 2H), 1.67 (s, 6H), 1.22 (t,  $J$ =7.6, 3H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$ =151.39, 150.11, 143.91, 129.90, 128.51, 128.16, 101.55, 85.49, 28.63, 27.69, 15.46.



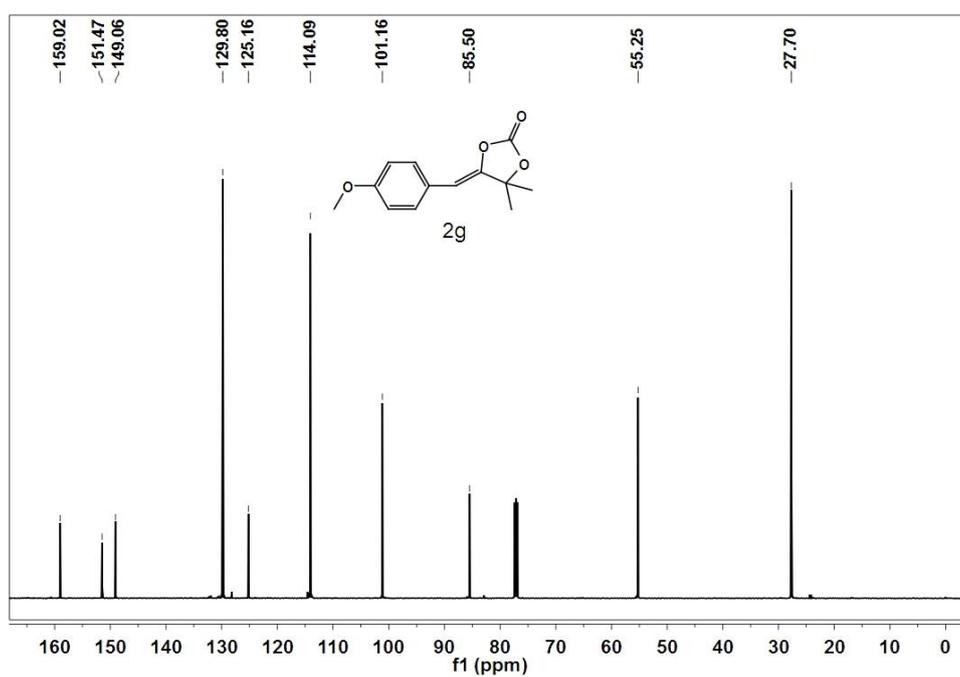
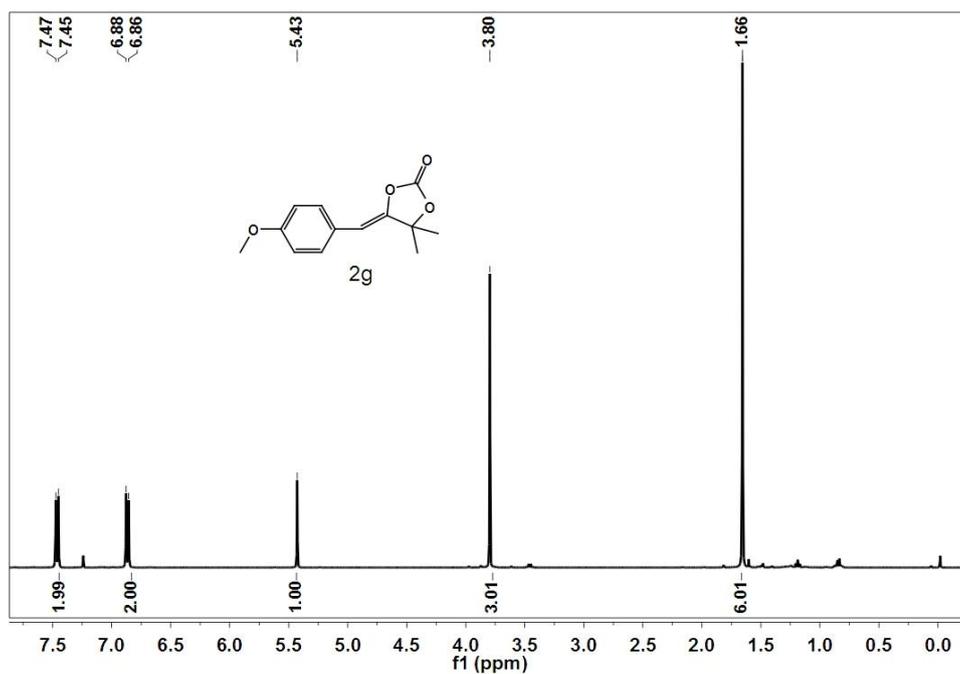
**2d**:  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ =7.45 (d,  $J$ =8.2, 2H), 7.15 (d,  $J$ =8.2, 2H), 5.47 (s, 1H), 2.59–2.55 (m, 2H), 1.67 (s, 6H), 1.61 (dt,  $J$ =14.8, 7.4, 2H), 0.92 (t,  $J$ =7.3, 3H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$ =151.37, 150.09, 142.37, 129.85, 128.77, 128.38, 101.55, 85.43, 37.76, 27.72, 24.39, 13.71.



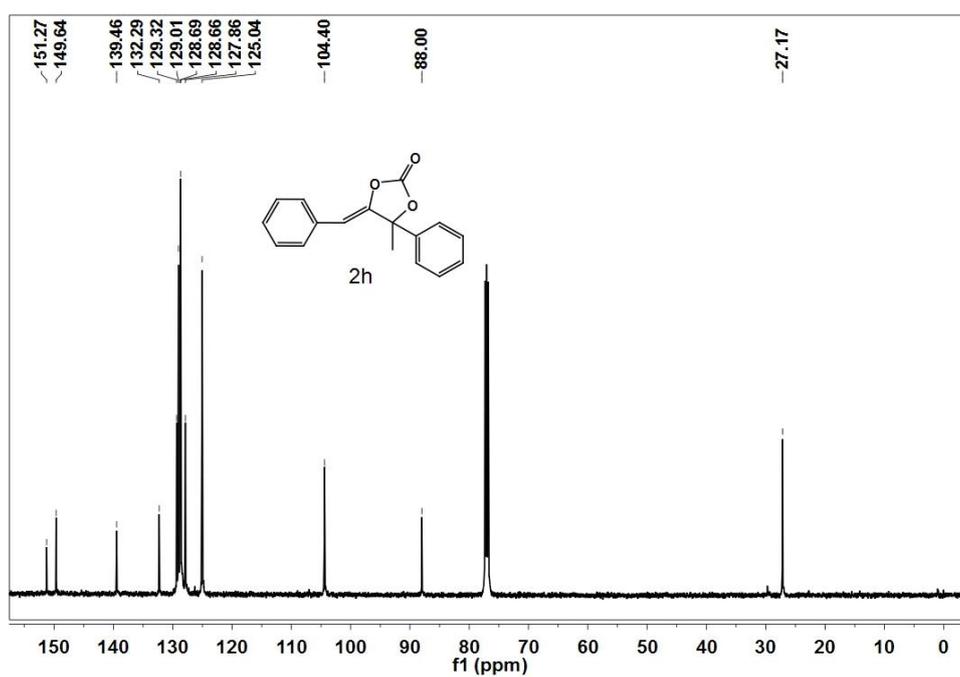
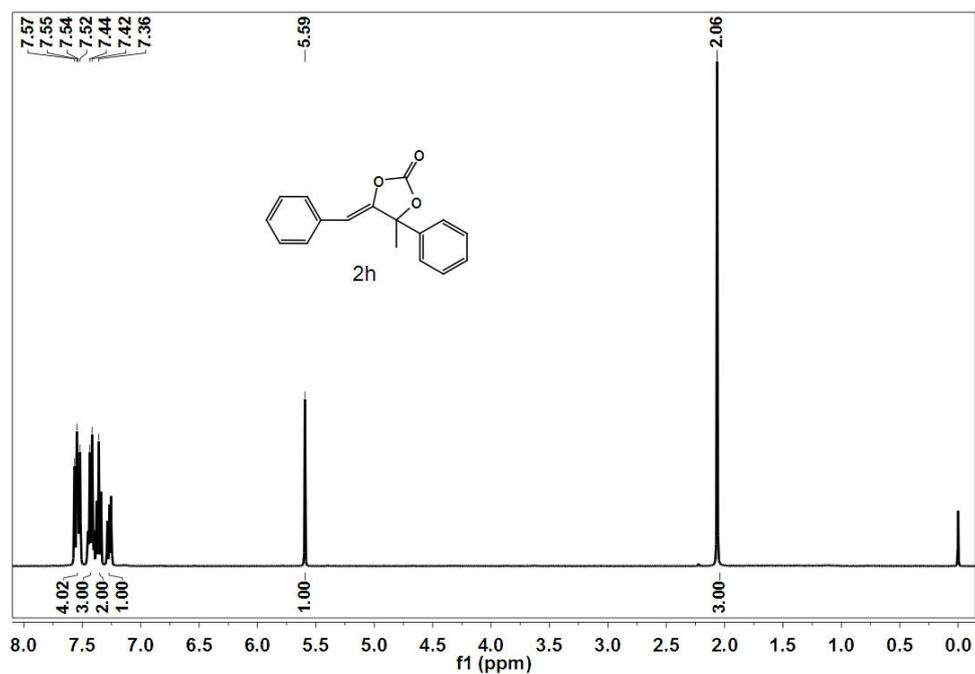
**2e:**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ =7.47 (d,  $J$ =8.5, 2H), 7.36 (d,  $J$ =8.5, 2H), 5.47 (s, 1H), 1.66 (s, 6H), 1.30 (s, 9H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$ =151.37, 150.82, 150.27, 129.61, 128.23, 125.58, 101.39, 85.43, 34.62, 31.23, 27.73.



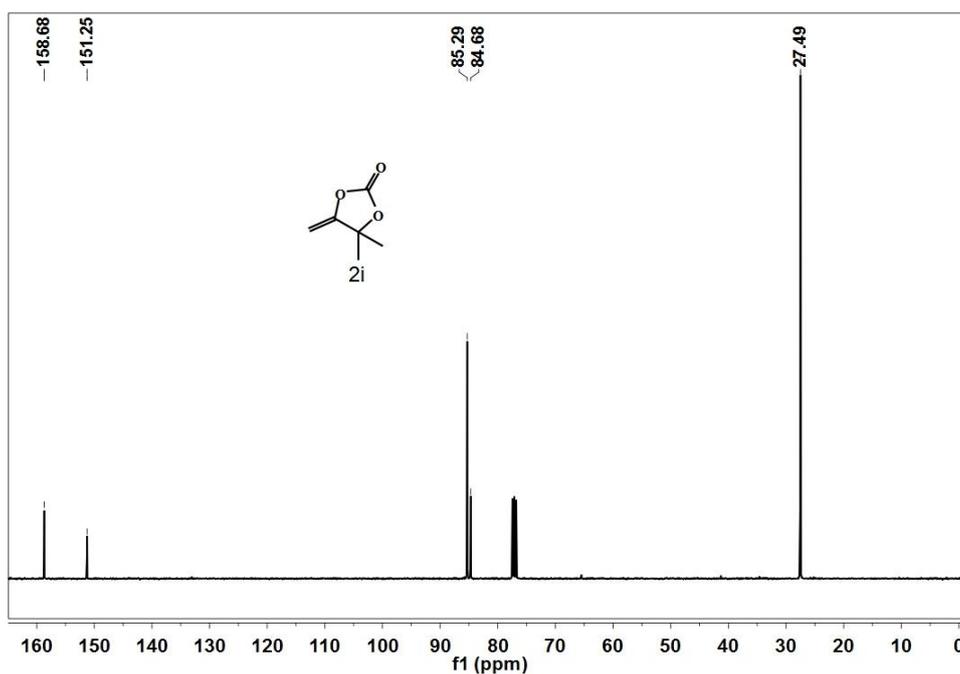
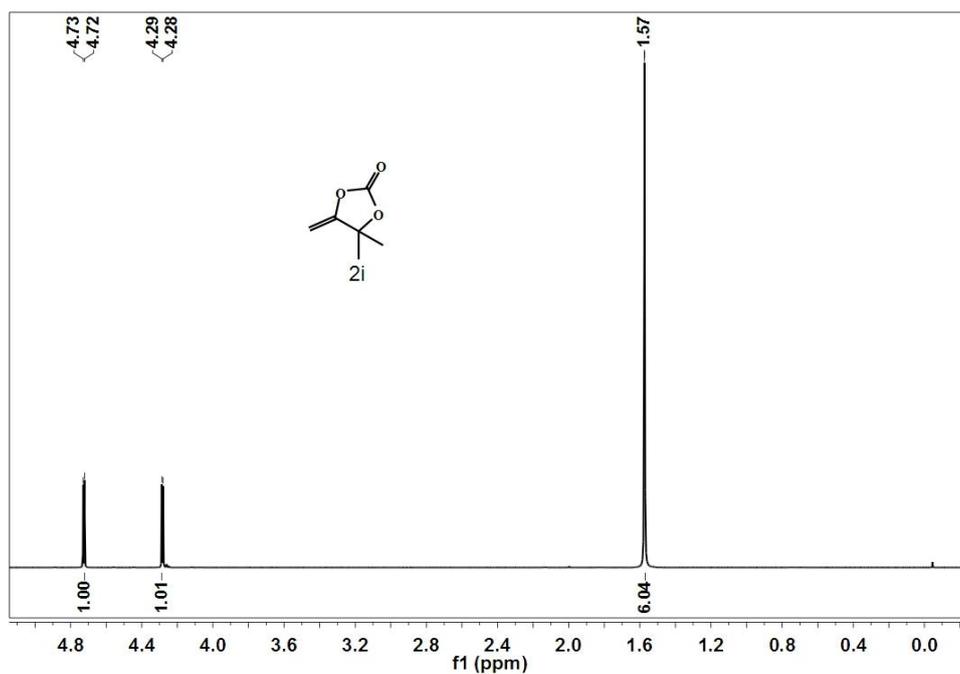
**2f:**  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$ =7.45 (d,  $J$ =8.5, 2H), 7.30 (d,  $J$ =8.6, 2H), 5.44 (s, 1H), 1.67 (s, 6H).  $^{13}\text{C NMR}$  (126 MHz,  $\text{CDCl}_3$ )  $\delta$ =151.28, 151.00, 133.08, 131.13, 129.73, 128.73, 100.43, 85.67, 27.54.



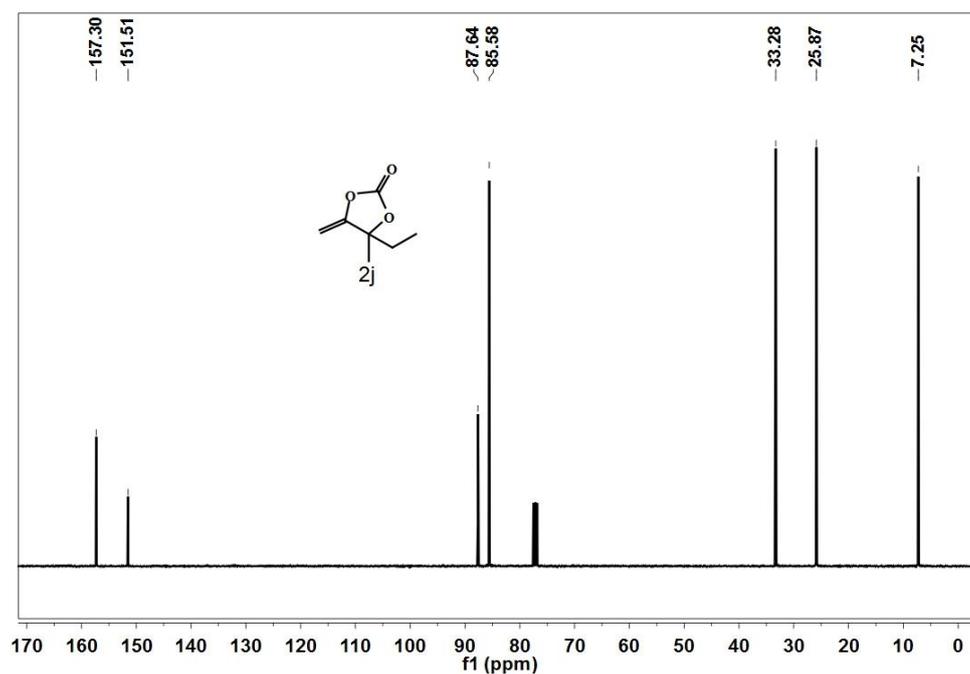
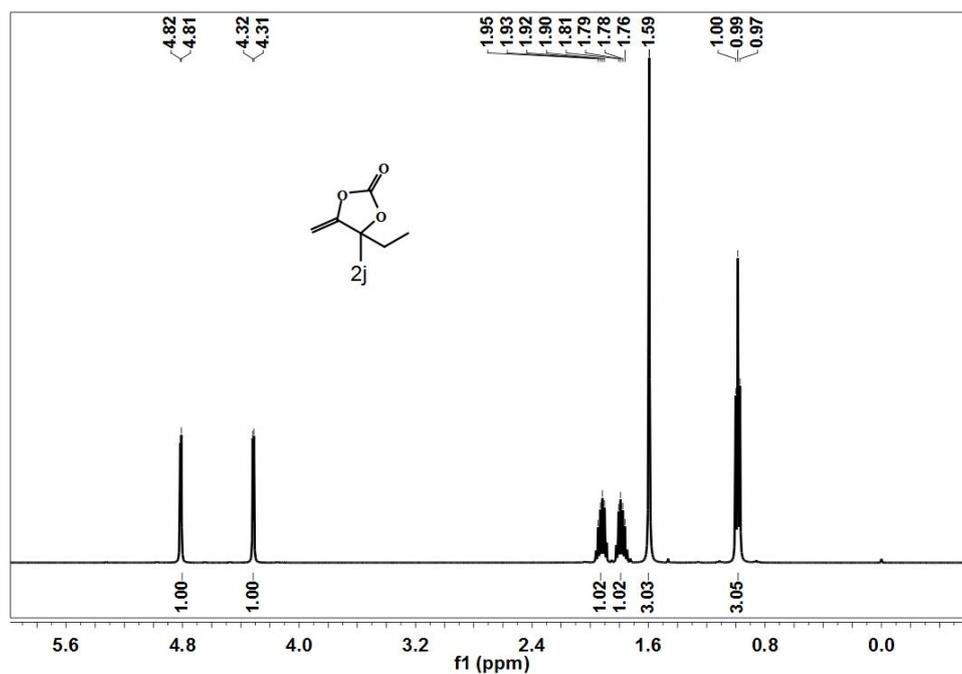
**2g**:  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ =7.46 (d,  $J$ =8.8, 2H), 6.87 (d,  $J$ =8.8, 2H), 5.43 (s, 1H), 3.80 (s, 3H), 1.66 (s, 6H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$ =159.02, 151.47, 149.06, 129.80, 125.16, 114.09, 101.16, 85.50, 55.25, 27.70.



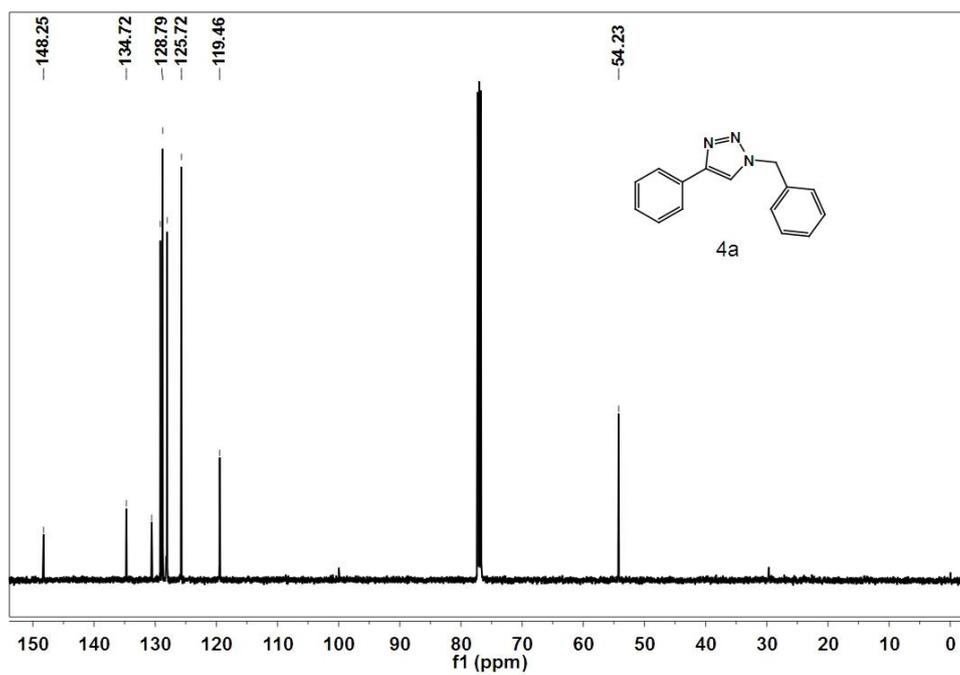
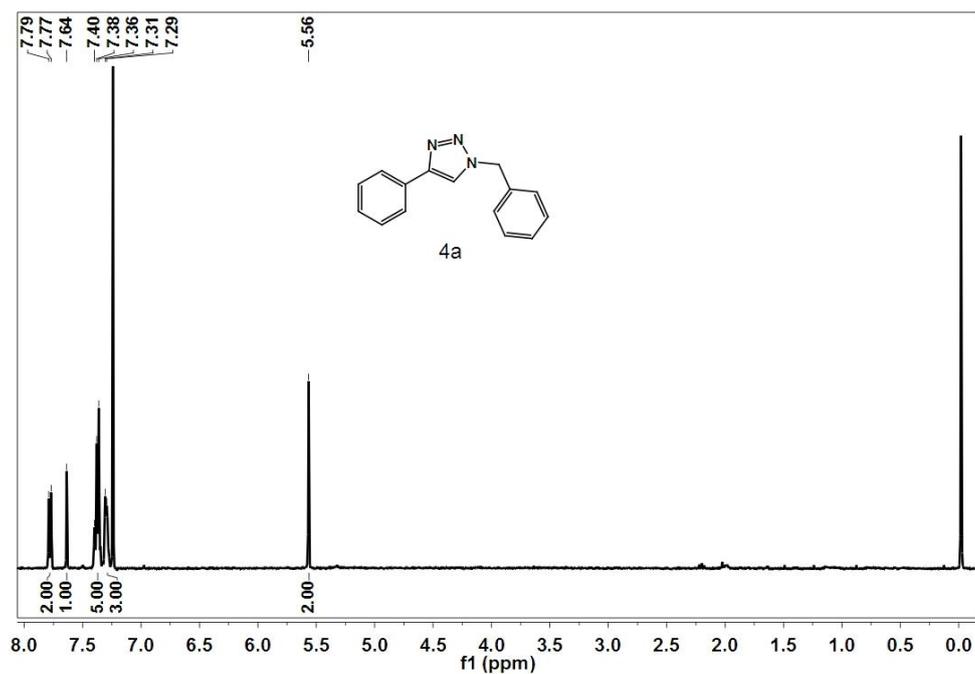
**2h**: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ=7.54 (dd, *J*=11.2, 7.4, 4H), 7.48–7.38 (m, 3H), 7.36 (t, *J*=7.6, 2H), 7.29–7.25 (m, 1H), 5.59 (s, 1H), 2.06 (s, 3H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ=151.27, 149.64, 139.46, 132.29, 129.32, 129.01, 128.69, 128.66, 127.86, 125.04, 104.40, 88.00, 27.17.



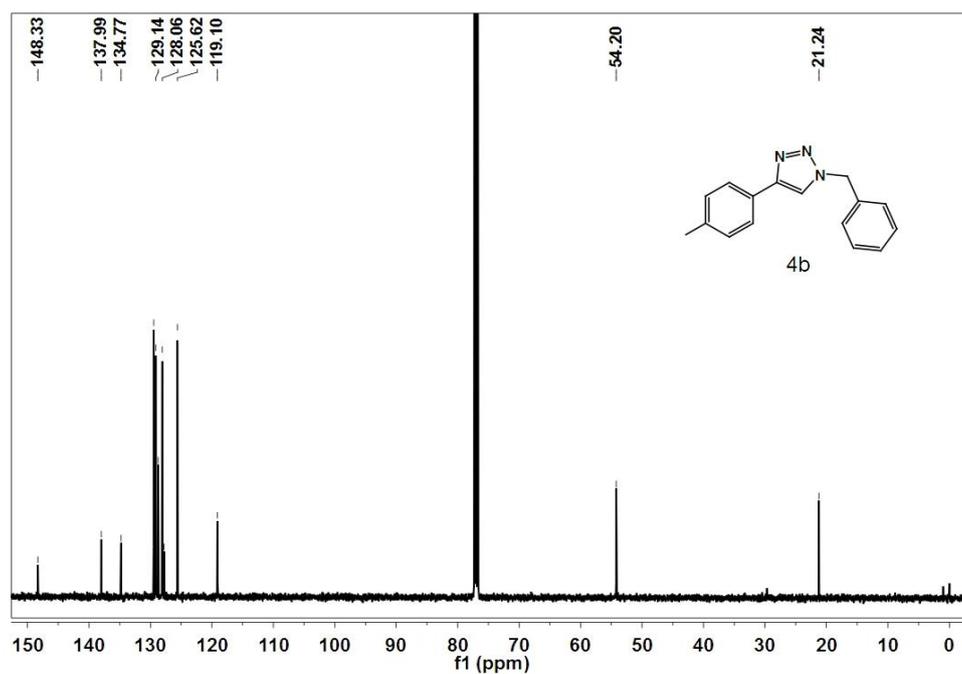
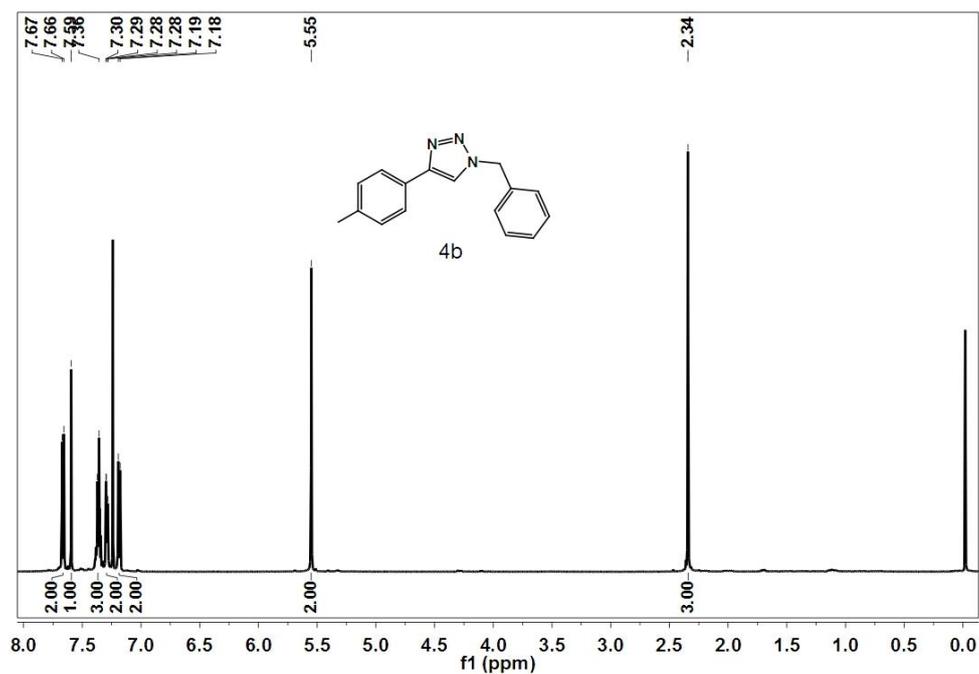
**2i**:  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$ =4.73 (d,  $J$  = 3.2, 1H), 4.28 (d,  $J$  = 3.2, 1H), 1.57 (s, 6H).  $^{13}\text{C NMR}$  (126 MHz,  $\text{CDCl}_3$ )  $\delta$ =158.68, 151.25, 85.29, 84.68, 27.49.



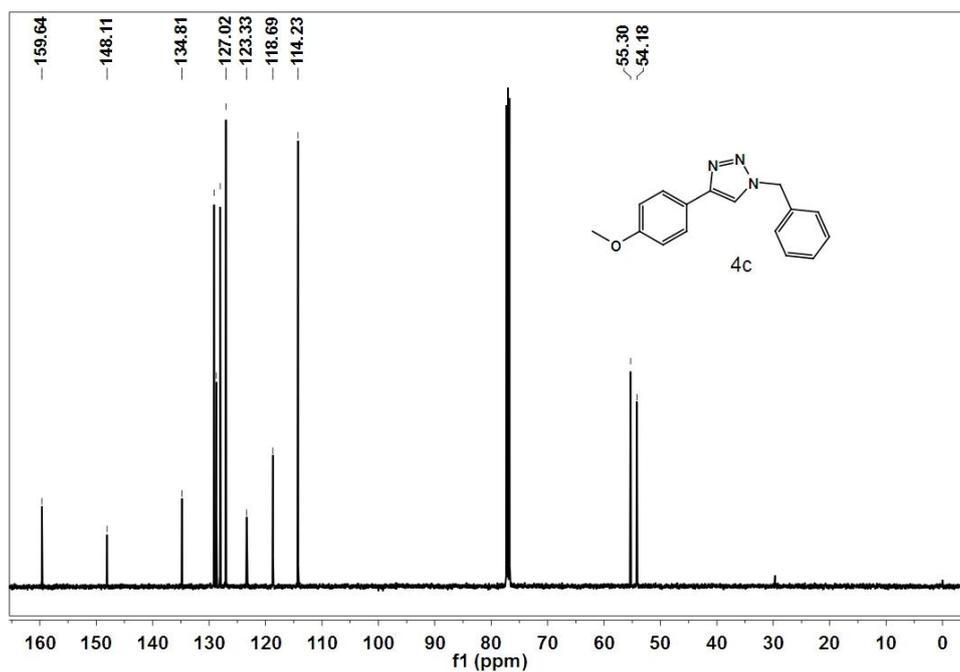
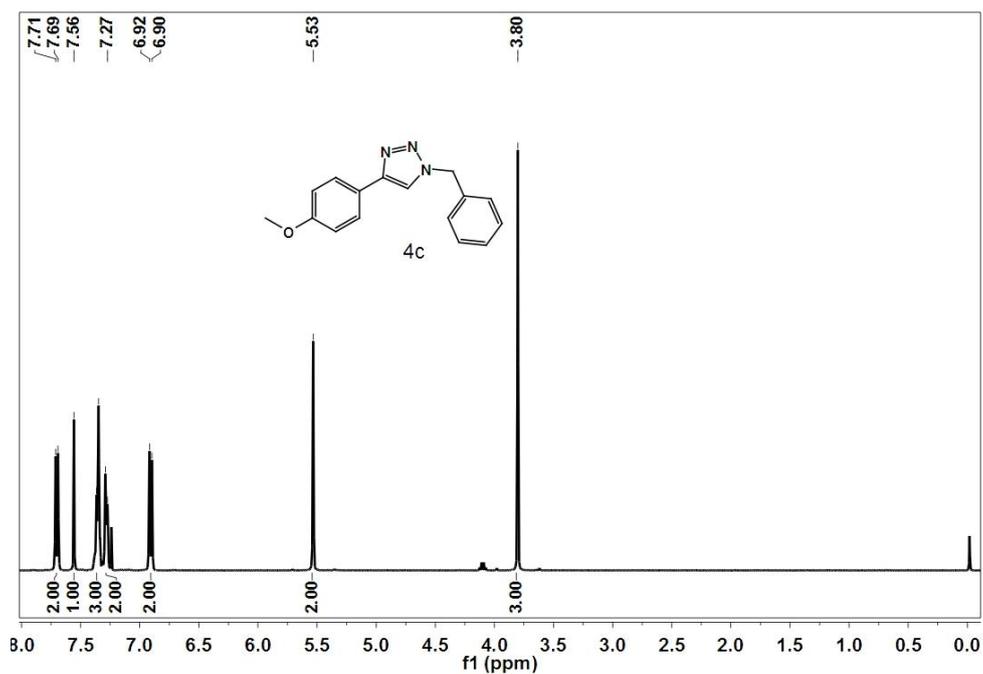
**2j**:  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ =4.81 (d,  $J$  = 3.9, 1H), 4.31 (d,  $J$  = 3.9, 1H), 1.92 (dd,  $J$  = 14.6, 7.3, 1H), 1.78 (dd,  $J$  = 14.6, 7.4, 1H), 1.59 (s, 3H), 0.99 (t,  $J$  = 7.4, 3H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$ =157.30, 151.51, 87.64, 85.58, 33.28, 25.87, 7.25.



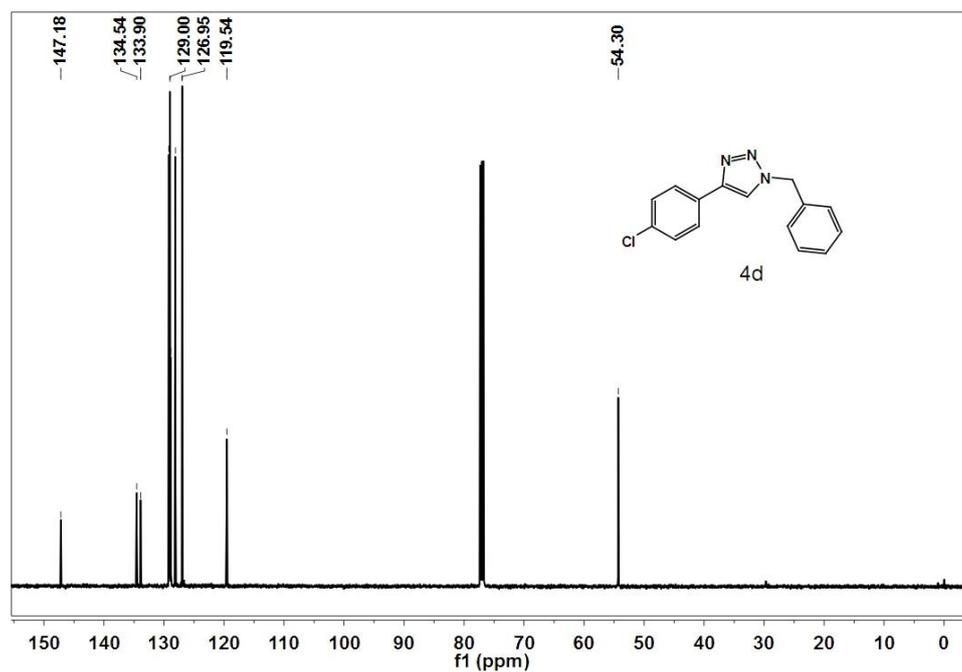
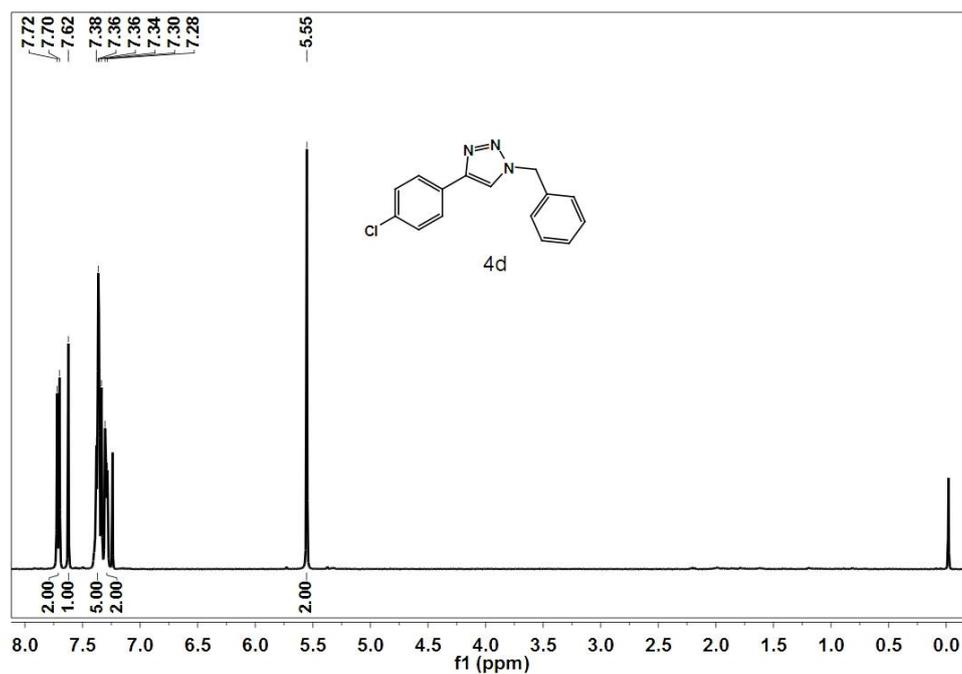
**4a:**  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$ =7.78 (d,  $J$ =7.8, 2H), 7.64 (s, 1H), 7.42–7.32 (m, 5H), 7.30 (d,  $J$ =5.2, 3H), 5.56 (s, 2H).  $^{13}\text{C NMR}$  (126 MHz,  $\text{CDCl}_3$ )  $\delta$ =148.25, 134.72, 130.58, 129.15, 128.79, 128.15, 128.06, 125.72, 119.46, 54.23.



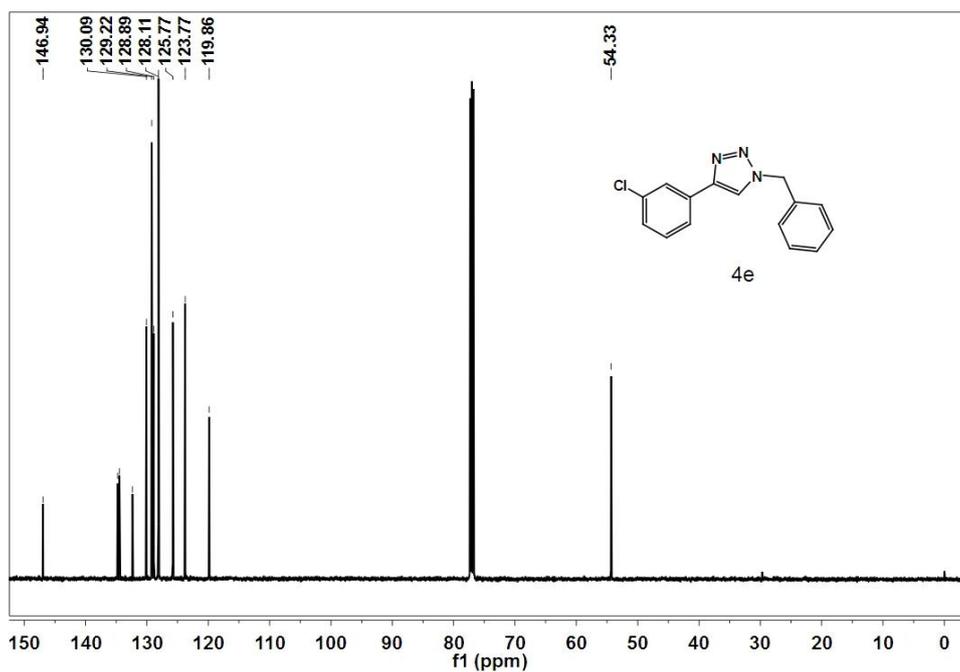
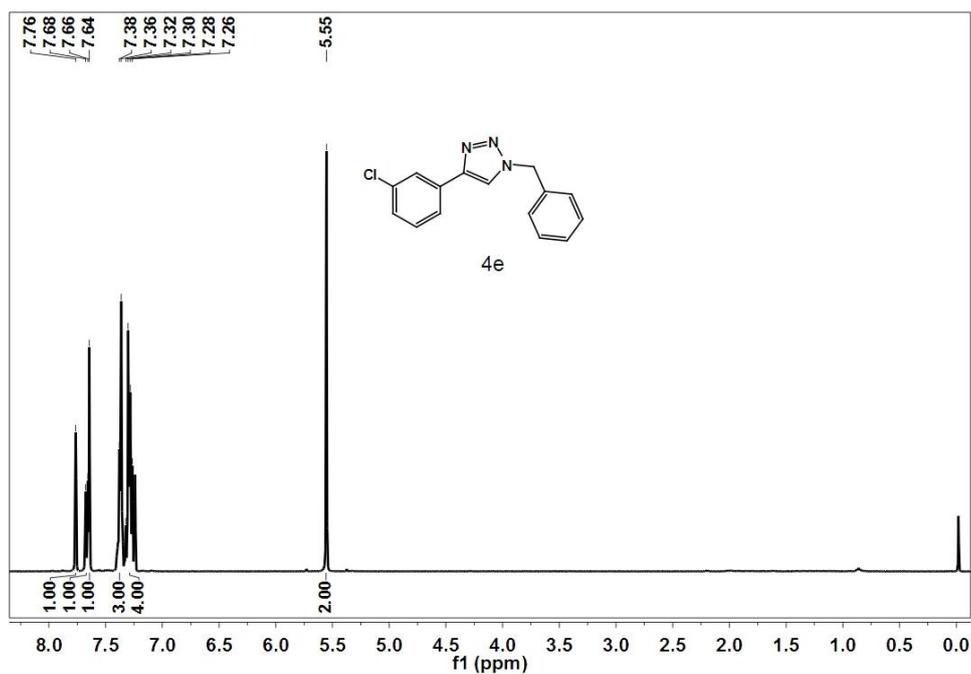
**4b**:  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  = 7.66 (d,  $J$  = 6.5, 2H), 7.59 (s, 1H), 7.36 (dd,  $J$  = 6.4, 1.7, 3H), 7.29 (dd,  $J$  = 6.1, 1.3, 2H), 7.19 (d,  $J$  = 6.3, 2H), 5.55 (s, 2H), 2.34 (s, 3H).  $^{13}\text{C NMR}$  (126 MHz,  $\text{CDCl}_3$ )  $\delta$  = 148.33, 137.99, 134.77, 129.46, 129.14, 128.74, 128.06, 127.76, 125.62, 119.10, 54.20, 21.24.



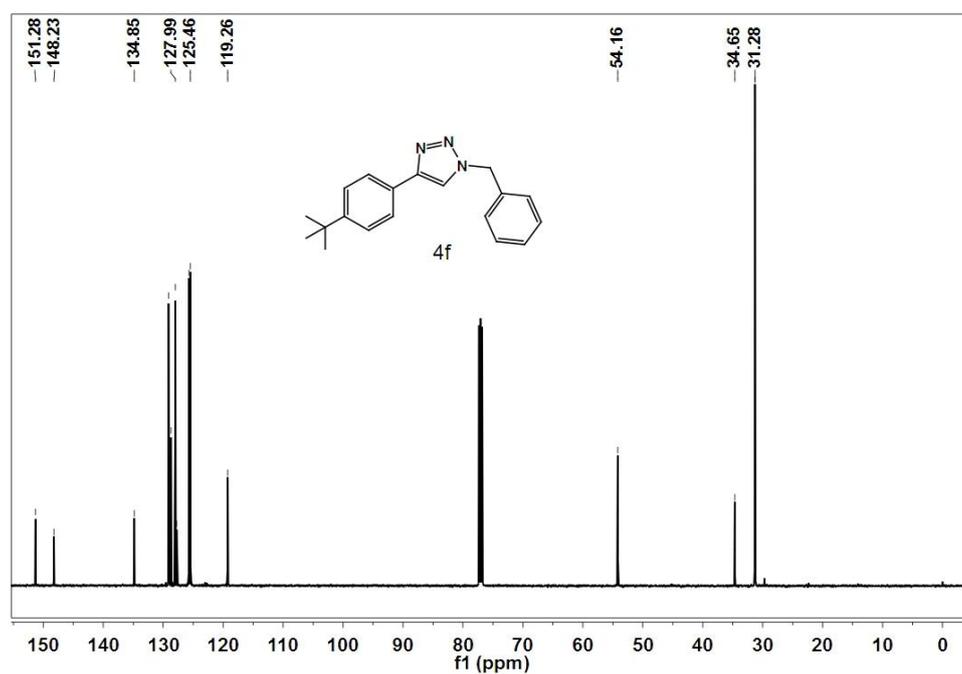
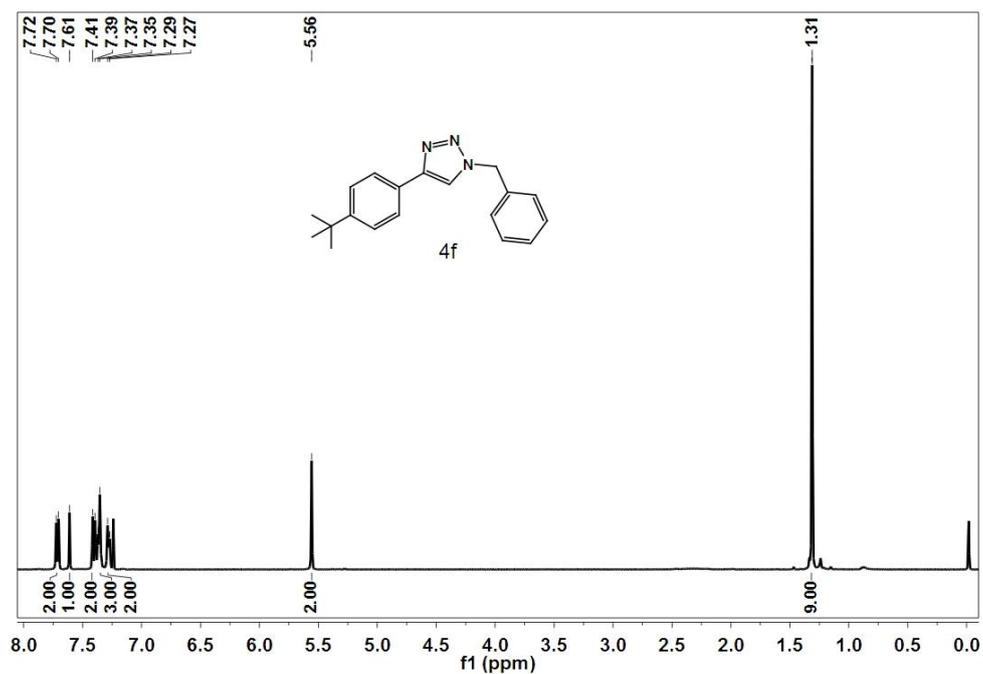
**4c:**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ =7.70 (d,  $J$ =8.3, 2H), 7.56 (s, 1H), 7.36 (d,  $J$ =6.7, 3H), 7.28 (d,  $J$ =7.3, 2H), 6.91 (d,  $J$ =8.3, 2H), 5.53 (s, 2H), 3.80 (s, 3H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$ =159.64, 148.11, 134.81, 129.12, 128.72, 128.04, 127.02, 123.33, 118.69, 114.23, 55.30, 54.18.



**4d:**  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$ =7.71 (d,  $J$ =8.2, 2H), 7.62 (s, 1H), 7.36 (dd,  $J$ =10.2, 7.7, 5H), 7.29 (d,  $J$ =7.7, 2H), 5.55 (s, 2H).  $^{13}\text{C NMR}$  (126 MHz,  $\text{CDCl}_3$ )  $\delta$ =147.18, 134.54, 133.90, 129.20, 129.12, 129.00, 128.87, 128.10, 126.95, 119.54, 54.30.



**4e:**  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$ =7.76 (s, 1H), 7.67 (d,  $J$ =7.5, 1H), 7.64 (s, 1H), 7.42–7.34 (m, 3H), 7.29 (q,  $J$ =7.8, 4H), 5.55 (s, 2H).  $^{13}\text{C NMR}$  (126 MHz,  $\text{CDCl}_3$ )  $\delta$ =146.94, 134.78, 134.49, 132.36, 130.09, 129.22, 128.89, 128.11, 125.77, 123.77, 119.86, 54.33.



**4f:**  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  = 7.71 (d,  $J$  = 7.7, 2H), 7.61 (s, 1H), 7.40 (d,  $J$  = 7.8, 2H), 7.36 (d,  $J$  = 6.4, 3H), 7.28 (d,  $J$  = 7.1, 2H), 5.56 (s, 2H), 1.31 (s, 9H).  $^{13}\text{C NMR}$  (126 MHz,  $\text{CDCl}_3$ )  $\delta$  = 151.28, 148.23, 134.85, 129.12, 128.71 (s, 3H), 127.99, 127.77, 125.71, 125.46, 119.26, 54.16, 34.65, 31.28.