

Supporting Information

Efficient conversion of carbon dioxide at atmospheric pressure to 2-oxazolidinones promoted by bifunctional Cu(II)-substituted polyoxometalate-based ionic liquid

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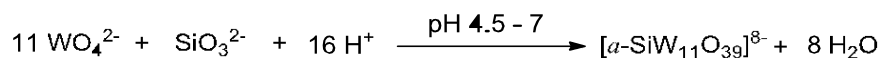
1. General Experimental Methods

General analytic methods. ^1H NMR spectra was recorded on 400 MHz spectrometers using CDCl_3 as solvent referenced to CDCl_3 (7.26 ppm). ^{13}C NMR was recorded at 101 MHz in CDCl_3 (77.00 ppm). Multiplets were assigned as singlet, doublet, triplet, doublet of doublet, multiplet and broad singlet. FT-IR was recorded on a Bruker Tensor 27 FT-IR spectrophotometer with KBr pellets. Mass spectra were recorded on a Shimadzu GCMS-QP2010 equipped with a RTX-5MS capillary column at an ionization voltage of 70 eV. The data are given as mass units per charge (m/z). Electrospray ionization mass spectra (ESI-MS) were recorded with an Agilent 6520 Q-TOF mass spectrometer.

Materials. All starting materials were obtained from TCI, Aladdin or Alfa Aesar and used as received. Unless otherwise noted, carbon dioxide (99.99%). Propargylic amines and transition metal-substituted polyoxometalate-based ionic liquids were synthesized as previously described.

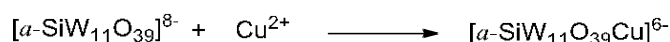
1.1 Procedure for the synthesis of transition metal substituted-polyoxometalate-based ionic liquids.

1.1.1 The preparation of $\text{K}_8[\alpha\text{-SiW}_{11}\text{O}_{39}]\cdot 13\text{H}_2\text{O}$ ¹



To a solution of $\text{Na}_2\text{WO}_4\cdot 2\text{H}_2\text{O}$ (32.99 g, 100 mmol) in H_2O (100 mL) was added $\text{Na}_2\text{SiO}_3\cdot 9\text{H}_2\text{O}$ (2.58 g, 9.1 mmol) in H_2O (15 mL) at 70-80 °C, with stirring and maintaining this temperature for 1 h. Then the mixture was adjusted the pH to 4.5 with 4 mol/L hydrochloric acid at 75 °C, and a small amount of insoluble substance was removed by filtration. After a half of water was removed in vacuum from the filtrate, saturated KCl solution was dropped to give the $\text{K}_8[\alpha\text{-SiW}_{11}\text{O}_{39}]\cdot 13\text{H}_2\text{O}$ as a white solid. Yield: 28.40 g (60%); IR (KBr, pellet): 3592, 3434, 3384, 1622, 1393, 1358, 999, 961, 896, 794, 729 cm^{-1} ; (Ref. IR (KBr, pellet): 1000, 952, 885, 870 (sh), 797, 725, 625 (sh), 540, 520, 472 (sh), 430 (sh), 368, 332 cm^{-1}). The $\text{K}_8[\alpha\text{-SiW}_{11}\text{O}_{39}]\cdot 13\text{H}_2\text{O}$ was used for the next step without further purification, while as a catalyst, the crystal water was removed by heating at 120 °C for 4 h.

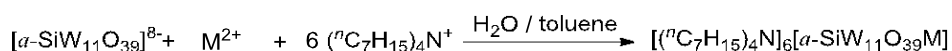
1.1.2 Typical procedures for the preparation of $\text{K}_6[\alpha\text{-SiW}_{11}\text{O}_{39}\text{Cu}]$ ²



To a stirred solution of 2.415 g (0.75 mmol) $\text{K}_8[\alpha\text{-SiW}_{11}\text{O}_{39}]\cdot 13\text{H}_2\text{O}$ in 10 mL of water was added in 0.1282 g (0.75 mmol) $\text{CuCl}_2\cdot 2\text{H}_2\text{O}$. The solution was stirred for 1 h at room temperature

and then cooled to 0 °C. To the cold solution was added 30 mL cold methanol. The precipitated slightly blue solid $K_6[\alpha\text{-SiW}_{11}\text{O}_{39}\text{Cu}(\text{H}_2\text{O})]\cdot 2\text{H}_2\text{O}$ was filtered off, washed with a 2:1 (v/v) cold methanol/water mixture. Yield: 1.62 g (67%); IR (KBr pellet): 3551, 3477, 3414, 1637, 1618, 1398, 1384, 1012, 960, 901, 798, 740 cm^{-1} . The water of $K_6[\alpha\text{-SiW}_{11}\text{O}_{39}\text{Cu}(\text{H}_2\text{O})]\cdot 2\text{H}_2\text{O}$ was removed by heating at 120 °C for 4 h.

1.1.3 General procedures for the preparation of transition metal substituted-polyoxometalate-based ionic liquids^{3,4}



25 mL of 20 mM aqueous $K_8[\alpha\text{-SiW}_{11}\text{O}_{39}]$ solution and 50 mL of a 10 mM aqueous MCl_2 ($\text{M} = \text{Cu(II)}, \text{Co(II)}, \text{Fe(II)}, \text{Mn(II)}, \text{Zn(II)}, \text{Ni(II)}$) solution were mixed and stirred for 15 min. Then the solution was treated with tetraheptylammonium bromide (2.47 g, 3 mmol) dissolved in 60 mL toluene. After the two phases was allowed to settle for 10 minutes, the organic layer was decanted and washed seven times with 20 mL water portions. The wet toluene was removed by heating to 40 °C under vacuum. Then 30 mL dry toluene was added and evaporated under reduced pressure to remove the traces of water. These transition metal substituted-polyoxometalate-based ionic liquids were characterized by FT-IR and Elemental Analysis.

$[(^n\text{C}_7\text{H}_{15})_4\text{N}]_6 [\alpha\text{-SiW}_{11}\text{O}_{39}\text{Cu}]$: blue viscous liquid, IR (neat, KBr): 2955, 2927, 2856, 1638, 1618, 1465, 1383, 1265, 949, 898, 798, 739 cm^{-1} . Anal. Calcd for $[(^n\text{C}_7\text{H}_{15})_4\text{N}]_6 [\alpha\text{-SiW}_{11}\text{O}_{39}\text{Cu}]$ (MW = 5202): C 38.78, H 6.98, N 1.62, Found: C 38.19, H 6.80, N 1.66.

$[(^n\text{C}_7\text{H}_{15})_4\text{N}]_6 [\alpha\text{-SiW}_{11}\text{O}_{39}\text{Zn}]$: light yellow viscous liquid, IR (neat, KBr): 2955, 2927, 2856, 1637, 1618, 1466, 1378, 995, 949, 900, 800, 724 cm^{-1} .

$[(^n\text{C}_7\text{H}_{15})_4\text{N}]_6 [\alpha\text{-SiW}_{11}\text{O}_{39}\text{Mn}]$: burgundy viscous liquid, IR (neat, KBr): 2955, 2927, 2857, 1638, 1618, 1466, 1380, 1265, 1000, 953, 912, 871, 790, 742 cm^{-1} .

$[(^n\text{C}_7\text{H}_{15})_4\text{N}]_6 [\alpha\text{-SiW}_{11}\text{O}_{39}\text{Fe}]$: light yellow viscous liquid, IR (neat, KBr): 2955, 2927, 2857, 1638, 1618, 1466, 1377, 998, 955, 909, 875, 795 cm^{-1} .

$[(^n\text{C}_7\text{H}_{15})_4\text{N}]_6 [\alpha\text{-SiW}_{11}\text{O}_{39}\text{Ni}]$: light green viscous liquid, IR (neat, KBr): 2955, 2927, 2857, 1637, 1466, 1378, 992, 947, 900, 801, 721 cm^{-1} .

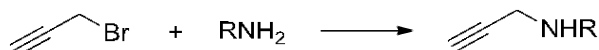
$[(^n\text{C}_7\text{H}_{15})_4\text{N}]_6 [\alpha\text{-SiW}_{11}\text{O}_{39}\text{Co}]$: deep green viscous liquid, IR (neat, KBr): 2954, 2926, 2856, 1633, 1465, 1371, 988, 944, 897, 800 cm^{-1} .

$[(^{13}\text{C}_4\text{H}_9)_4\text{N}]_6[\alpha\text{-SiW}_{11}\text{O}_{39}\text{Cu}]$: light blue solid, IR (neat, KBr): 2961, 2874, 1619, 1474, 1380, 952, 907, 804, 738 cm^{-1} .

$[(^{13}\text{C}_{16}\text{H}_{33})(\text{CH}_3)_3\text{N}]_6[\alpha\text{-SiW}_{11}\text{O}_{39}\text{Cu}]$: light blue solid, IR (neat, KBr): 2918, 2850, 1650, 1625, 1588, 1482, 1469, 1007, 952, 900, 800, 768 cm^{-1} .

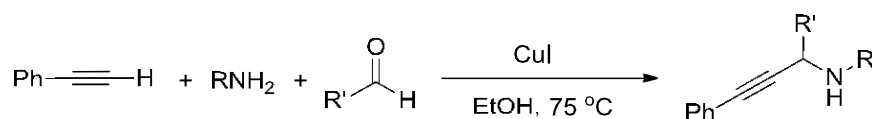
1.2. Procedure for the synthesis of propargylic amines.

1.2.1 Procedures for the preparation of 1a and 1b⁵



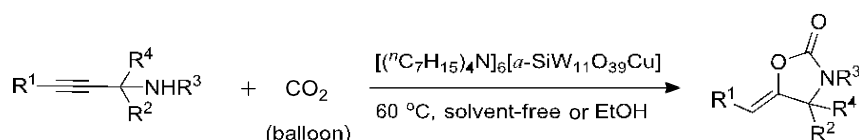
Propargyl bromide (3 mL, 27 mmol) was added to benzyl amine (18 mL, 162 mmol) or n-butylamine (16 mL, 162 mmol) over thirty minutes via addition funnel, and allowed to stir overnight. The resulting mixture was diluted in Et_2O , and extracted with saturated aq. NaHCO_3 and dried over MgSO_4 . The reaction mixture was concentrated and chromatographed, eluting with 9:1 hexanes/ EtOAc , to afford the corresponding pale yellow liquid.

1.2.2 Procedures for the preparation of 1c - 1g⁶



In a typical experiment, CuI (0.6 mmol) was charged in a Schlenk flask with a magnetic stirrer. The flask was sealed and flushed with N_2 and then was charged with alkyne (2 mmol), aldehyde (2 mmol), and amine (2 mmol). The test tube was then placed in an oil bath of 75°C and was allowed to stir overnight. The crude reaction mixture was purified by silica gel column chromatography to provide the desired propargylic amine.

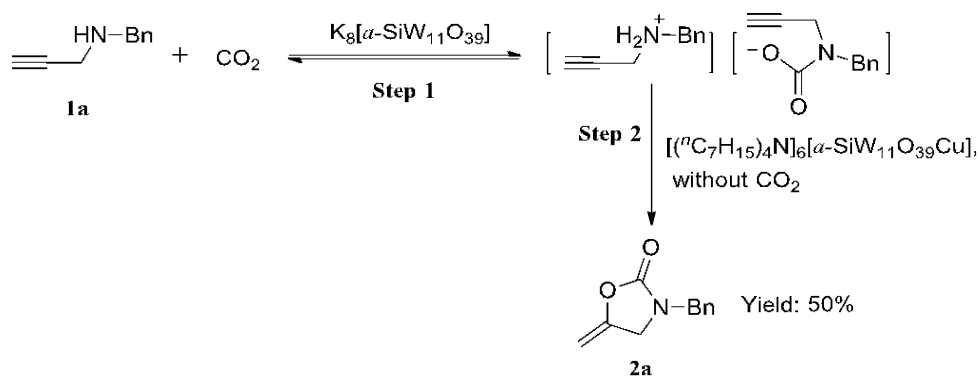
1.3 General procedure for the synthesis of 5-alkylideneoxazolidin-2-ones



$[(^{13}\text{C}_7\text{H}_{15})_4\text{N}]_6[\alpha\text{-SiW}_{11}\text{O}_{39}\text{Cu}]$ (130.0 mg, 0.025 mmol) and propargylic amine (1 mmol) were added to a 10 mL Schlenk tube equipped with a magnetic stir bar. The flask was capped and sealed. Then a gas-exchanging process was conducted using the “freeze-pump-thaw” method. The reaction mixture was stirred at 60°C for 20 h under CO_2 balloon (99.999%). Upon completion, product yield was determined by ^1H NMR technique using 1,1,2,2-tetrachloroethane as an internal

standard. Then the reaction mixture was diluted with dichloromethane (2 mL). The organic phase was collected and then purified by column chromatography on silica gel using petroleum ether/ethyl acetate as an eluent to afford the desired product.

1.4 Exploration of the carbamate intermediate



Reaction conditions: Step 1: **1a** (0.2904 g, 2 mmol), K₈[α-SiW₁₁O₃₉] (0.1494 g, 0.05 mmol), CO₂ balloon, 0 °C, 10 min; Step 2: Carbamate A (0.3344 g, 1 mmol), [(ⁿC₇H₁₅)₄N]₆[α-SiW₁₁O₃₉Cu] (0.2600 g, 0.05 mmol), 60 °C, 20 h, the yield was relative to **1a**.

Scheme S1. Carbamate intermediate for the carboxylative cyclization reaction

Although K₈[α-SiW₁₁O₃₉] were found to be ineffective, but it was also worth mentioning that K₈[α-SiW₁₁O₃₉] allowed the reaction to produce the carbamate rather than 2-oxazolidinone **2a**. To explore the reaction progress, a stepwise experiment was carried out (Scheme S1). At first, **1a** was reacted with CO₂ balloon in the exist of K₈[α-SiW₁₁O₃₉] (Step 1), and the white solid carbamate was afforded in only 10 min (Fig. S1). Then the carbamate was dealt with [(ⁿC₇H₁₅)₄N]₆[α-SiW₁₁O₃₉Cu] under no CO₂ condition (Step 2). To our surprise, 50% yield of **2a** was obtained, which indicated that the carbamate probably is the intermediate of this carboxylative cyclization reaction. In fact, the carbamate could also be formed without any catalyst for at least 6 h. We thought that the formation of carbamate intermediate was accelerated due to the activation of propargylic amine and CO₂ by [α-SiW₁₁O₃₉Cu]⁶⁻. In addition, these results also indicated that Cu(II) played a key role in the subsequent intramolecular cyclization.

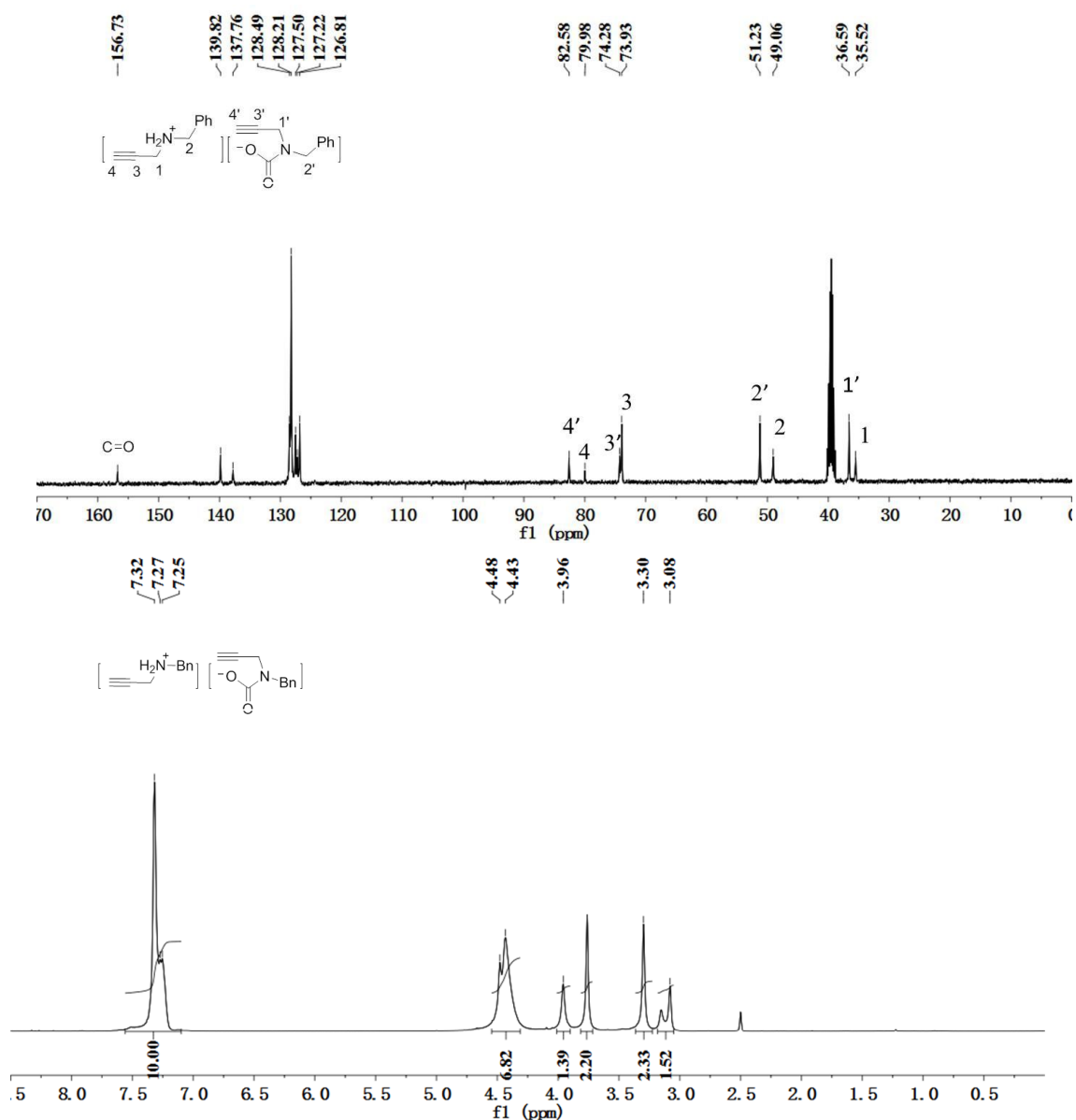
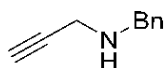


Fig. S1. ¹³C NMR and ¹H NMR of carbamate in *d*-DMSO .

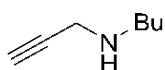
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- [5] O. P. Pereshivko, V. A. Peshkov and E. V. Van der Eycken, *Org. Lett.*, 2010, **12**, 2638-2641.
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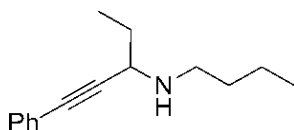
2. Characterization Data of Propargylic Amines, Carbamate and 5-Alkylideneoxazolidin-2-ones



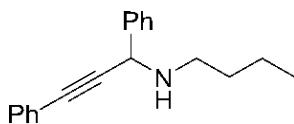
N-benzylprop-2-yn-1-amine **1a**: pale yellow oil, 86% yield; ^1H NMR (400 MHz, CDCl_3): δ 3.91 (s, 2H), 3.45 (d, $J = 2.4$ Hz, 2H), 2.30 (t, $J = 2.4$ Hz, 1H), 1.69 (s, NH, 1H) ppm. ^{13}C NMR (101 MHz, CDCl_3): δ 139.4, 128.5, 128.5, 127.2, 82.1, 71.6, 52.3, 37.4 ppm. MS (ESI): calcd $[\text{M}+\text{H}]^+$ ($\text{C}_{10}\text{H}_{11}\text{N}$) 146.20, found 146.07.



N-(prop-2-yn-1-yl)butan-1-amine **1b**: pale yellow oil, 55% yield; ^1H NMR (400 MHz, CDCl_3): δ 3.26 (d, $J = 2.4$ Hz, 2H), 2.52 (t, $J = 7.2$ Hz, 2H), 2.07 (t, $J = 2.4$ Hz, 1H), 1.32 (m, 2H), 1.20 (m, 2H), 1.12 (s, NH, 1H), 0.76 (t, $J = 7.2$ Hz, 3H) ppm. ^{13}C NMR (101 MHz, CDCl_3): δ 82.2, 71.0, 48.2, 38.0, 31.8, 20.2, 13.8 ppm. MS (ESI): calcd $[\text{M}+\text{H}]^+$ ($\text{C}_7\text{H}_{13}\text{N}$) 112.19, found 112.20.

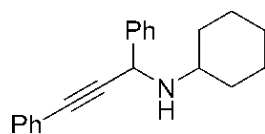


N-butyl-1-phenylpent-1-yn-3-amine **1c**: yellow oil, 67% yield; ^1H NMR (400 MHz, CDCl_3): δ 7.42 (m, 2H), 7.29 (m, 3H), 3.52 (t, $J = 7.2$ Hz, 1H), 2.96-2.89 (m, 1H), 2.69-2.63 (m, 1H), 1.83-1.63 (m, 2H), 1.58-1.45 (m, 2H), 1.43-1.34 (m, 2H), 1.25 (s, 1H), 1.08 (t, $J = 7.2$ Hz, 3H), 0.94 (t, $J = 7.2$ Hz, 3H) ppm. ^{13}C NMR (101 MHz, CDCl_3): δ 131.8, 128.54, 128.3, 127.9, 123.6, 91.2, 83.7, 52.4, 47.5, 32.4, 29.3, 20.7, 14.1, 10.7 ppm. MS (ESI): calcd $[\text{M}+\text{H}]^+$ ($\text{C}_{15}\text{H}_{21}\text{N}$) 216.34, found 216.07.

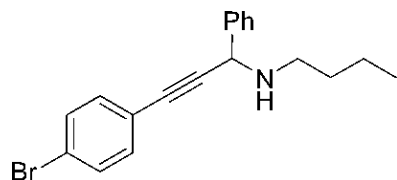


N-(1,3-diphenylprop-2-yn-1-yl)butan-1-amine **1d**: yellow oil, 61% yield; ^1H NMR (400 MHz, CDCl_3): δ 7.60 (d, $J = 7.2$ Hz, 2H), 7.46 (d, $J = 7.2$ Hz, 2H), 7.38 (t, $J = 7.2$ Hz, $J = 7.6$ Hz, 2H), 7.32-7.31 (m, 4H), 4.81 (s, 1H), 2.89-2.83 (m, 1H), 2.76-2.70 (m, 1H), 1.57-1.48 (m, 3H), 1.43-1.34 (m, 2H), 0.92 (t, $J = 7.2$ Hz, 3H) ppm. ^{13}C NMR (101 MHz, CDCl_3): δ 140.7, 131.8, 128.6, 128.4, 128.2, 127.8, 127.7, 123.3, 89.7, 85.4, 54.9, 47.4, 32.2, 20.6, 14.1 ppm. MS (ESI):

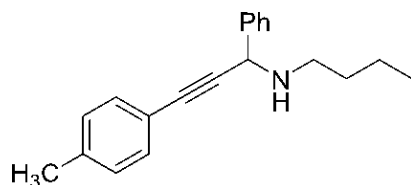
calcd $[M+H]^+$ ($C_{19}H_{21}N$) 264.38, found 263.87.



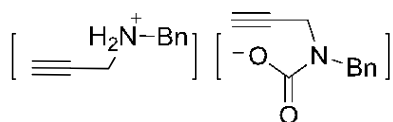
N-(1,3-diphenylprop-2-yn-1-yl)cyclohexanamine **1e**: yellow oil, 70% yield; 1H NMR (400 MHz, $CDCl_3$): δ 7.57 (d, $J = 7.2$ Hz, 2H), 7.45-7.43 (m, 2H), 7.33 (t, $J = 7.2$ Hz, $J = 7.6$ Hz, 2H), 7.27-7.24 (m, 4H), 4.87(s, 1H), 2.87-2.81 (m, 1H), 1.98 (d, $J = 12.4$ Hz, 1H), 1.83 (d, $J = 11.6$ Hz, 1H), 1.74-1.71 (m, 2H), 1.61-1.58 (d, $J = 12.0$ Hz, 1H), 1.38 (s, 1H), 1.30-1.09 (m, 5H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ 141.1, 131.6, 128.4, 128.1, 128.0, 127.56, 127.50, 123.2, 89.9, 84.9, 54.2, 51.5, 33.9, 32.6, 26.1, 24.9, 24.7 ppm. MS (ESI): calcd $[M+H]^+$ ($C_{21}H_{23}N$) 290.42, found 290.00.



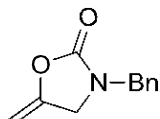
N-(3-(4-bromophenyl)-1-phenylprop-2-yn-1-yl)butan-1-amine **1f**: yellow oil, 43% yield; 1H NMR (400 MHz, $CDCl_3$): δ 7.61-7.29 (m, 9H), 4.81(d, $J = 9.2$ Hz, 1H), 2.90-2.84 (m, 1H), 2.77-2.71 (m, 1H), 1.56-1.54 (m, 3H), 1.42-1.38 (m, 2H), 0.95 (t, $J = 7.2$ Hz, 3H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ 140.4, 133.3, 131.6, 128.7, 127.9, 127.6, 122.4, 122.2, 90.9, 84.3, 54.9, 47.2, 32.2, 20.6, 14.1 ppm. MS (ESI): calcd $[M+H]^+$ ($C_{19}H_{20}BrN$) 342.29, 344.29, found 341.93, 344.00.



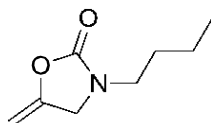
N-(1-phenyl-3-(p-tolyl)prop-2-yn-1-yl)butan-1-amine **1g**: yellow oil, 79% yield; 1H NMR (400 MHz, $CDCl_3$): δ 7.60 (d, $J = 2.8$ Hz, 2H), 7.38 (d, $J = 6.8$ Hz, 4H), 7.32 (d, $J = 6.1$ Hz, 1H), 7.13 (d, $J = 6.1$ Hz, 2H), 4.81(s, 1H), 2.89-2.86 (m, 1H), 2.76-2.72 (m, 1H), 1.57-1.50 (m, 3H), 1.42-1.36 (m, 2H), 0.93 (t, $J = 6.8$ Hz, 3H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ 140.8, 138.2, 131.7, 129.1, 128.6, 127.7, 120.2, 88.9, 85.4, 54.8, 47.1, 32.2, 21.6, 20.6, 14.1 ppm. MS (ESI): calcd $[M+H]^+$ ($C_{20}H_{23}N$) 278.41, found 278.00.



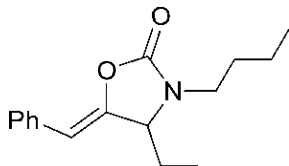
N-benzylprop-2-yn-1-aminium benzyl(prop-2-yn-1-yl)carbamate: white solid; ^1H NMR (400 MHz, CDCl_3): δ 7.25-7.32 (m, 10H), 4.48-4.43 (m, 6H), 3.96 (s, 1H), 3.76 (s, 2H), 3.30 (s, 2H), 3.08 (s, 1H) ppm. ^{13}C NMR (101 MHz, CDCl_3): δ 156.7, 139.8, 137.7, 128.4, 128.2, 127.5, 127.2, 126.8, 82.5, 79.9, 74.2, 73.9, 51.2, 49.0, 36.5, 35.5 ppm.



3-benzyl-5-methyleneoxazolidin-2-one **2a**: white crystalline solid, m.p. 53-54 °C; ^1H NMR (400 MHz, CDCl_3): δ 7.40-7.27 (m, 5H), 4.72 (dd, $J = 5.6$ Hz, $J = 2.8$ Hz, 1H), 4.47 (s, 2H), 4.20 (dd, $J = 5.2$ Hz, $J = 2.4$ Hz, 1H), 4.02 (t, $J = 2.4$ Hz, 2H) ppm. ^{13}C NMR (101 MHz, CDCl_3): δ 155.6, 148.8, 134.8, 128.98, 128.9, 128.2, 128.1, 86.7, 47.8, 47.1 ppm. GC-MS (EI, 70 eV) m/z (%) = 189 (19), 92 (52), 91 (100), 65 (16).

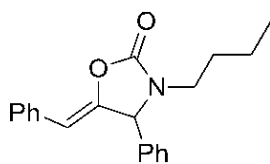


3-butyl-5-methyleneoxazolidin-2-one **2b**: pale yellow oil; 3-benzyl-5-methyleneoxazolidin-2-one **2a**: ^1H NMR (400 MHz, CDCl_3): δ 4.65 (d, $J = 2.4$ Hz, 1H), 4.24 (d, $J = 2.4$ Hz, 2H), 4.12 (d, $J = 2.4$ Hz, 2H), 3.24 (t, $J = 7.2$ Hz, 2H), 1.52-1.44 (m, 2H), 1.33-1.24 (m, 2H), 0.88 (t, $J = 7.2$ Hz, 3H) ppm. ^{13}C NMR (101 MHz, CDCl_3): δ 155.4, 149.1, 86.1, 47.6, 43.3, 29.1, 19.6, 13.5 ppm. GC-MS (EI, 70 eV) m/z (%) = 155 (90), 113 (27), 112 (100), 98 (11), 84 (37).

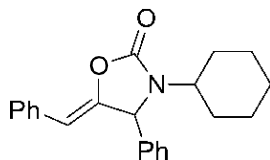


(*Z*)-5-benzylidene-3-butyl-4-ethyloxazolidin-2-one **2c**: pale yellow oil; ^1H NMR (400 MHz, CDCl_3): δ 7.62 (d, $J = 7.6$ Hz, 2H), 7.35 (dd, $J = 7.2$ Hz, $J = 12.8$ Hz, 2H), 7.22 (dd, $J = 6.8$ Hz, $J = 12.8$ Hz, 1H), 5.48 (s, 1H), 4.56 (s, 1H), 3.66-3.56 (m, 1H), 3.06-2.98 (m, 1H), 1.97-1.93 (m, 1H), 1.78-1.75 (m, 1H), 1.62-1.54 (m, 2H), 1.41-1.34 (m, 2H), 0.99-0.87 (m, 6H) ppm. ^{13}C NMR (101 MHz, CDCl_3): δ 155.3, 146.7, 133.7, 128.3, 126.7, 102.3, 59.0, 41.1, 29.2, 24.9, 19.9, 13.7,

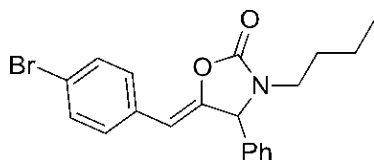
6.5 ppm. GC-MS (EI, 70 eV) m/z (%) = 259 (14), 230 (100), 174 (51), 118 (26), 90 (22).



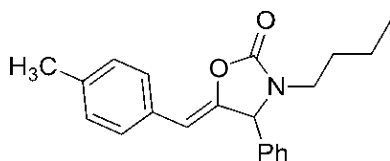
(Z)-5-benzylidene-3-butyl-4-phenyloxazolidin-2-one **2d**: white crystalline solid, m.p. 103-104 °C; ^1H NMR (400 MHz, CDCl_3): δ 7.56 (d, J = 7.6 Hz, 2H), 7.46 (d, J = 6.0 Hz, 3H), 7.37-7.29 (m, 4H), 7.21 (m, 1H), 5.41 (s, 1H), 5.28 (s, 1H), 3.58-3.50 (m, 1H), 2.89-2.82 (m, 1H), 1.52-1.45 (m, 2H), 1.37-1.26 (m, 2H), 0.91 (t, J = 7.2 Hz, 6H) ppm. ^{13}C NMR (101 MHz, CDCl_3): δ 155.1, 147.8, 137.4, 133.5, 129.46, 129.42, 128.5, 128.4, 127.9, 127.0, 104.6, 63.9, 41.7, 29.0, 19.9, 13.7 ppm. GC-MS (EI, 70 eV) m/z (%) = 333 (22), 208 (56), 207 (70), 180 (100), 179 (44).



(Z)-5-benzylidene-3-cyclohexyl-4-phenyloxazolidin-2-one **2e**: white crystalline solid, m.p. 121-123 °C; ^1H NMR (400 MHz, CDCl_3): δ 7.53 (d, J = 8 Hz, 2H), 7.44-7.38 (m, 5H), 7.30 (t, J = 7.6 Hz, 2H), 7.19 (t, J = 7.6 Hz, 1H), 5.42 (s, 1H), 5.18 (s, 1H), 3.56 (t, J = 7.2 Hz, 1H), 1.81-1.56 (m, 6H), 1.29-0.96 (m, 4H) ppm. ^{13}C NMR (101 MHz, CDCl_3): δ 154.7, 148.4, 139.6, 133.6, 129.2, 128.4, 128.3, 127.8, 126.8, 104.2, 63.2, 54.7, 31.2, 30.0, 25.7, 25.1 ppm. GC-MS (EI, 70 eV) m/z (%) = 307 (33), 262 (10), 208 (29), 207 (28), 180 (100), 179 (66).



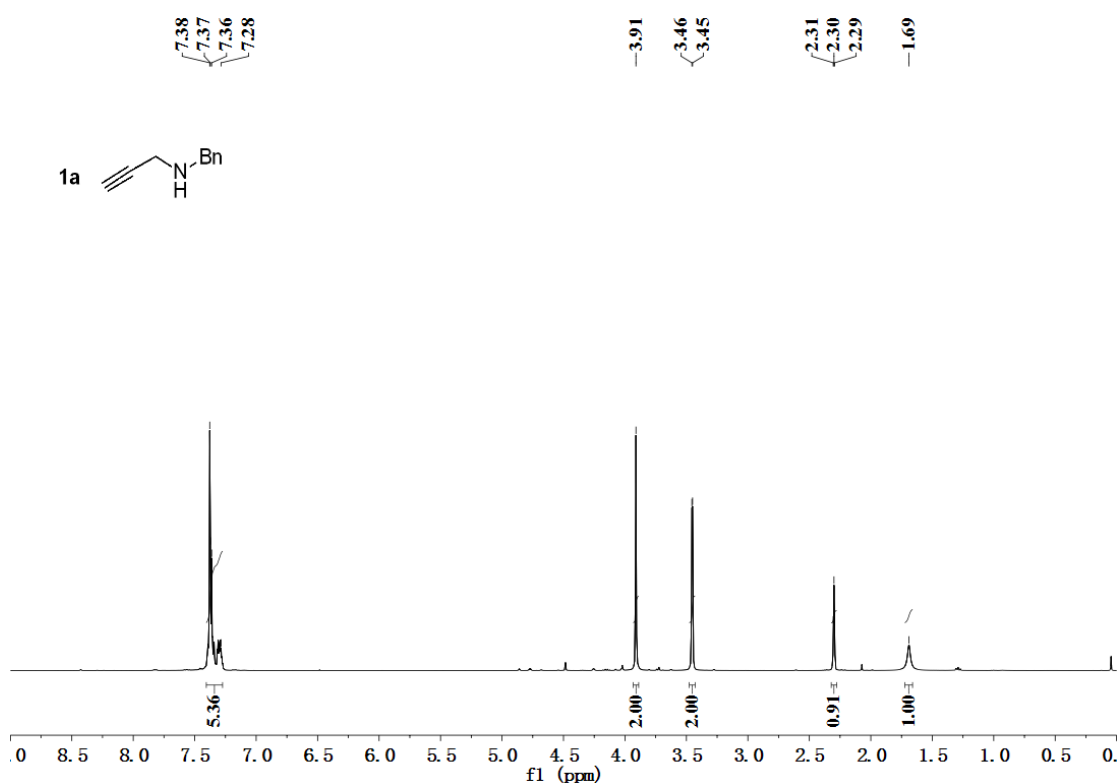
(Z)-5-(4-bromobenzylidene)-3-butyl-4-phenyloxazolidin-2-one **2f**: white crystalline solid, m.p. 119-120 °C; ^1H NMR (400 MHz, CDCl_3): δ 7.42-7.31 (m, 9H), 5.36 (s, 1H), 5.18 (s, 1H), 3.54-3.47 (m, 1H), 2.85-2.78 (m, 1H), 1.46-1.41 (m, 2H), 1.29-1.24 (m, 2H), 0.87 (t, J = 7.2 Hz, 3H) ppm. ^{13}C NMR (101 MHz, CDCl_3): δ 154.9, 148.5, 137.1, 132.5, 131.6, 129.9, 129.6, 129.5, 127.9, 120.7, 103.5, 64.0, 41.7, 29.0, 19.9, 13.7 ppm. GC-MS (EI, 70 eV) m/z (%) = 387 (33), 385 (33), 288 (17), 286 (17), 261 (14), 259 (14), 178 (100), 179 (91).

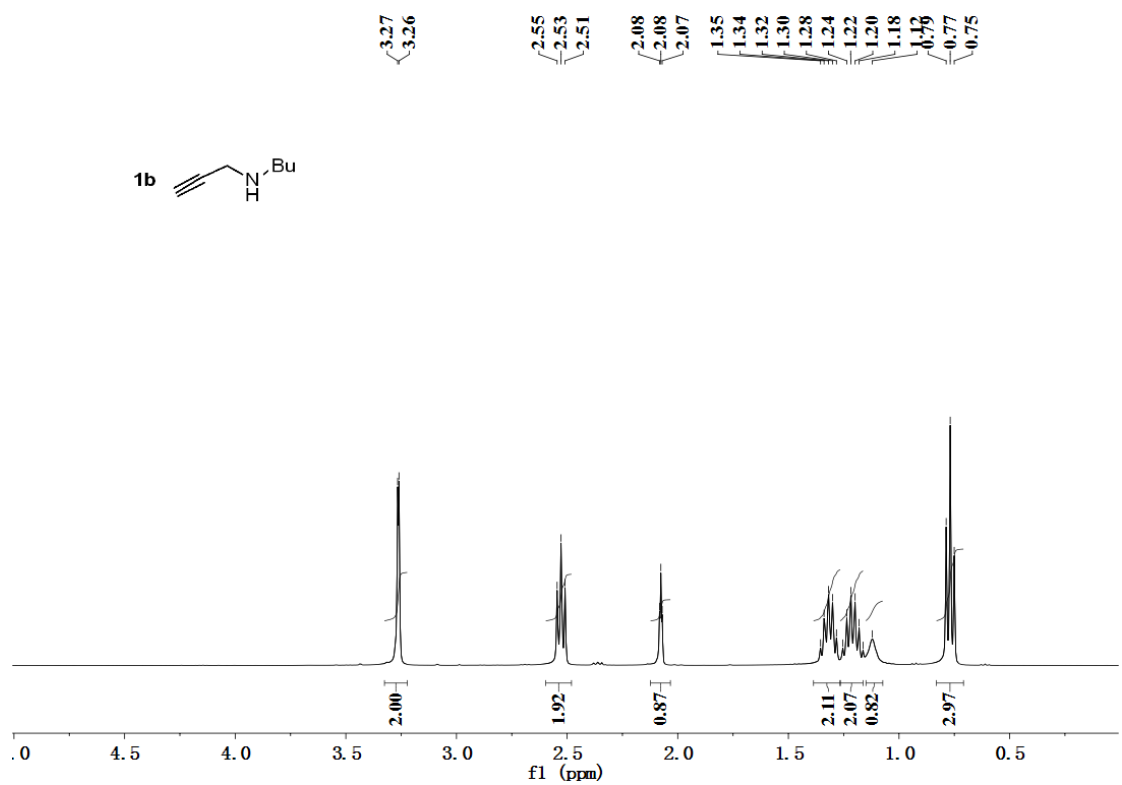
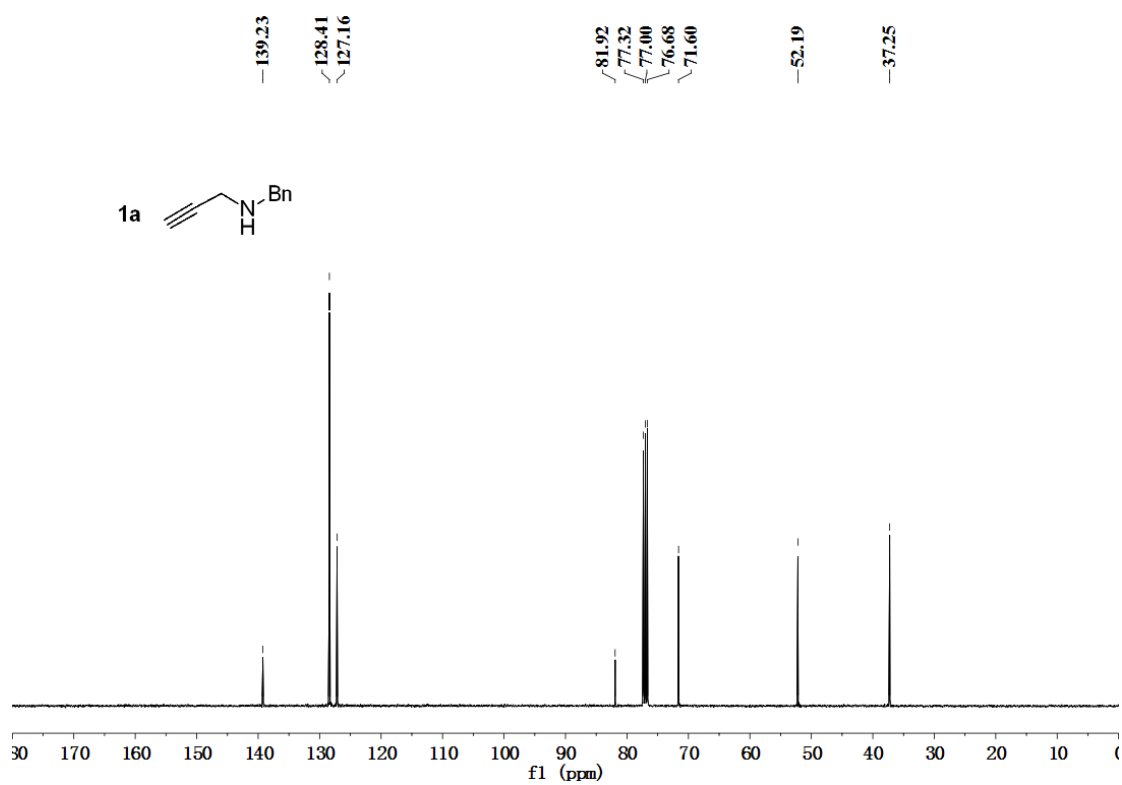


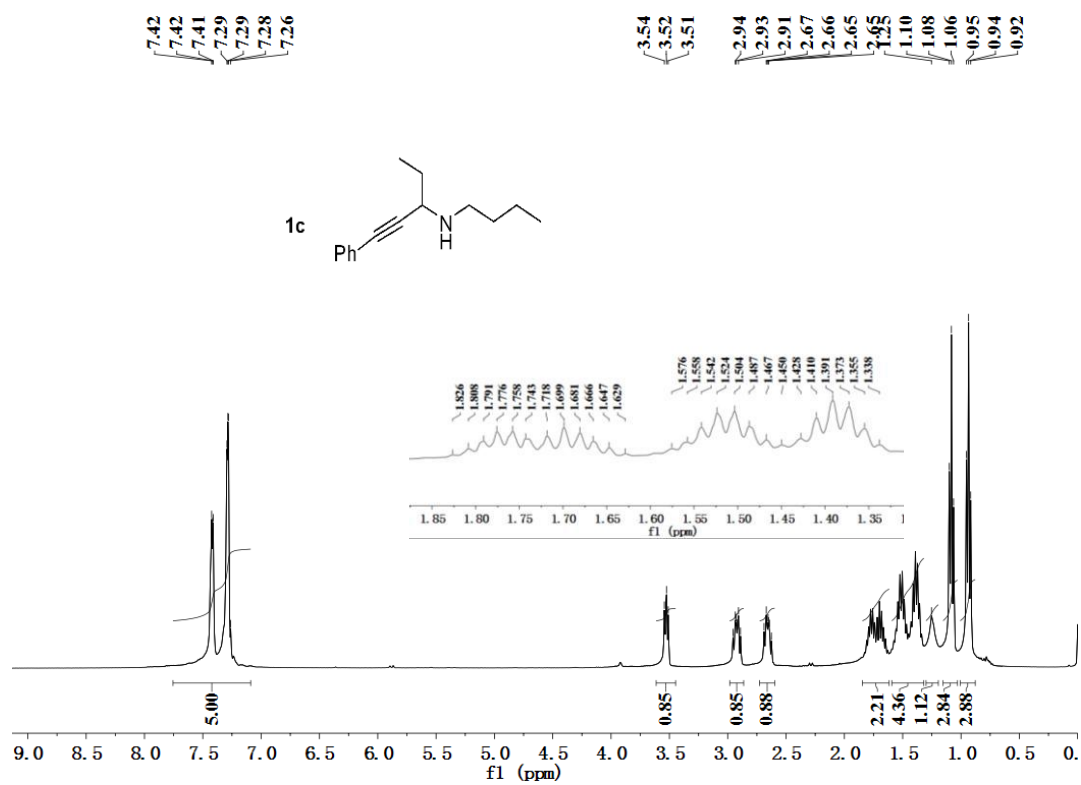
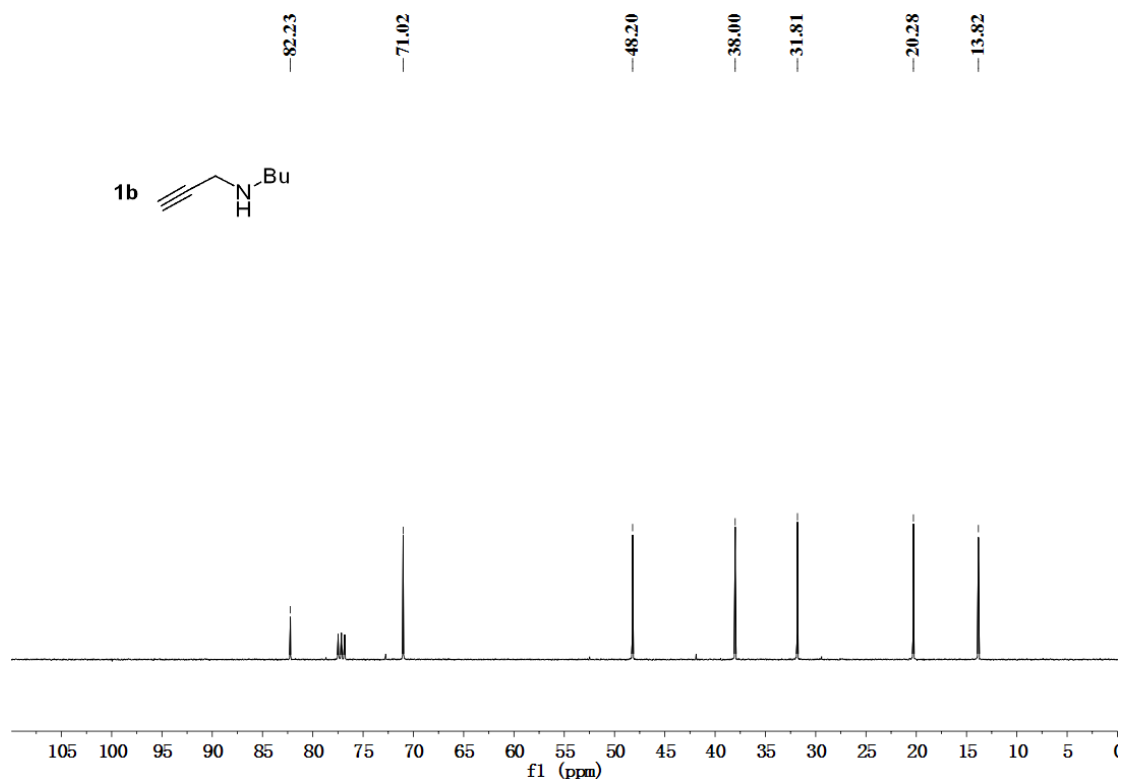
(*Z*)-3-butyl-5-(4-methylbenzylidene)-4-phenyloxazolidin-2-one **2g**: white crystalline solid, m.p. 125-126 °C; ^1H NMR (400 MHz, CDCl_3): δ 7.42-7.40 (m, 5H), 7.33 (d, $J = 7.2$ Hz, 2H), 7.11-7.09 (d, $J = 7.2$ Hz, 2H), 5.37 (s, 1H), 5.22 (s, 1H), 3.54-3.47 (m, 1H), 2.85-2.78 (m, 1H), 2.31 (s, 1H), 1.51-1.40 (m, 2H), 1.33-1.23 (m, 2H), 0.87 (t, $J = 7.2$ Hz, 3H) ppm. ^{13}C NMR (101 MHz, CDCl_3): δ 155.2, 147.0, 137.5, 136.8, 130.7, 129.4, 129.2, 128.3, 127.9, 104.6, 63.9, 41.7, 29.0, 21.3, 19.9, 13.7 ppm. GC-MS (EI, 70 eV) m/z (%) = 321 (44), 207 (24), 194 (100), 179 (64), 132 (19).

3. NMR, IR Spectrum.

3.1 ^1H NMR and ^{13}C NMR







5.62
C13CPD

131.75
128.31
127.93
123.58

91.23

83.73

52.41

47.48

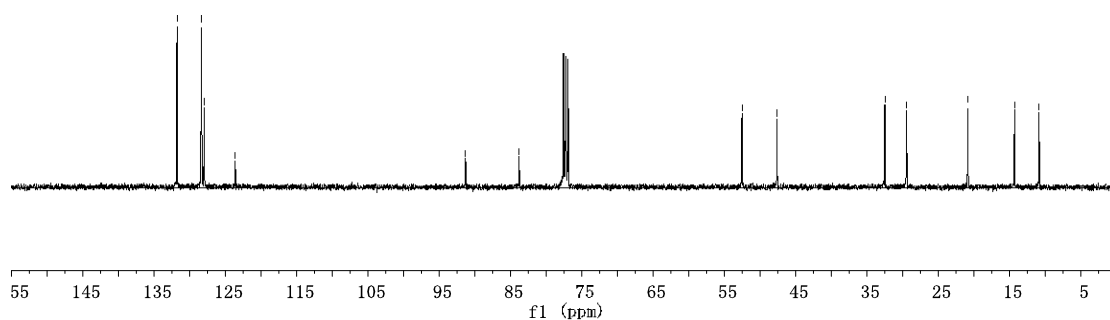
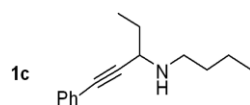
32.35

29.30

20.66

14.14

10.69

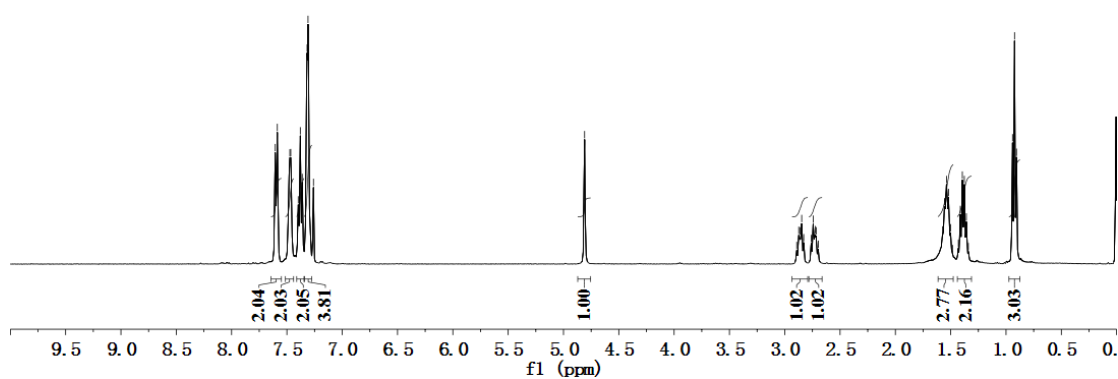
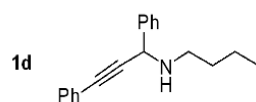


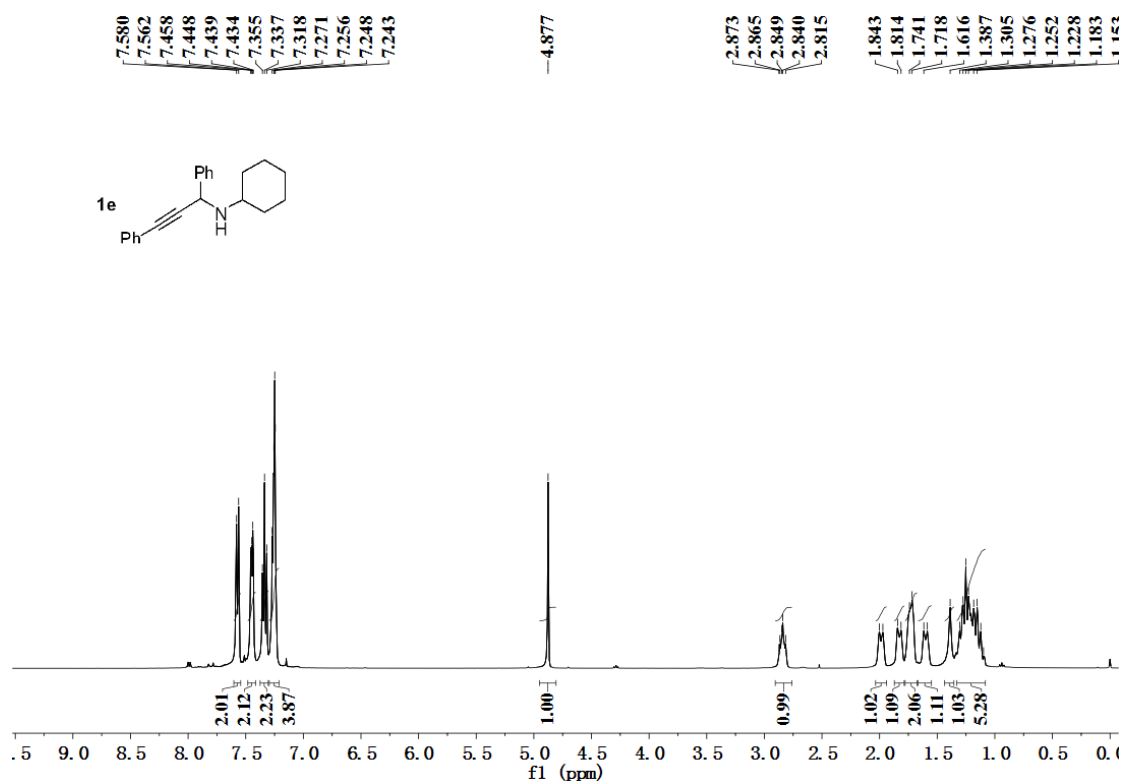
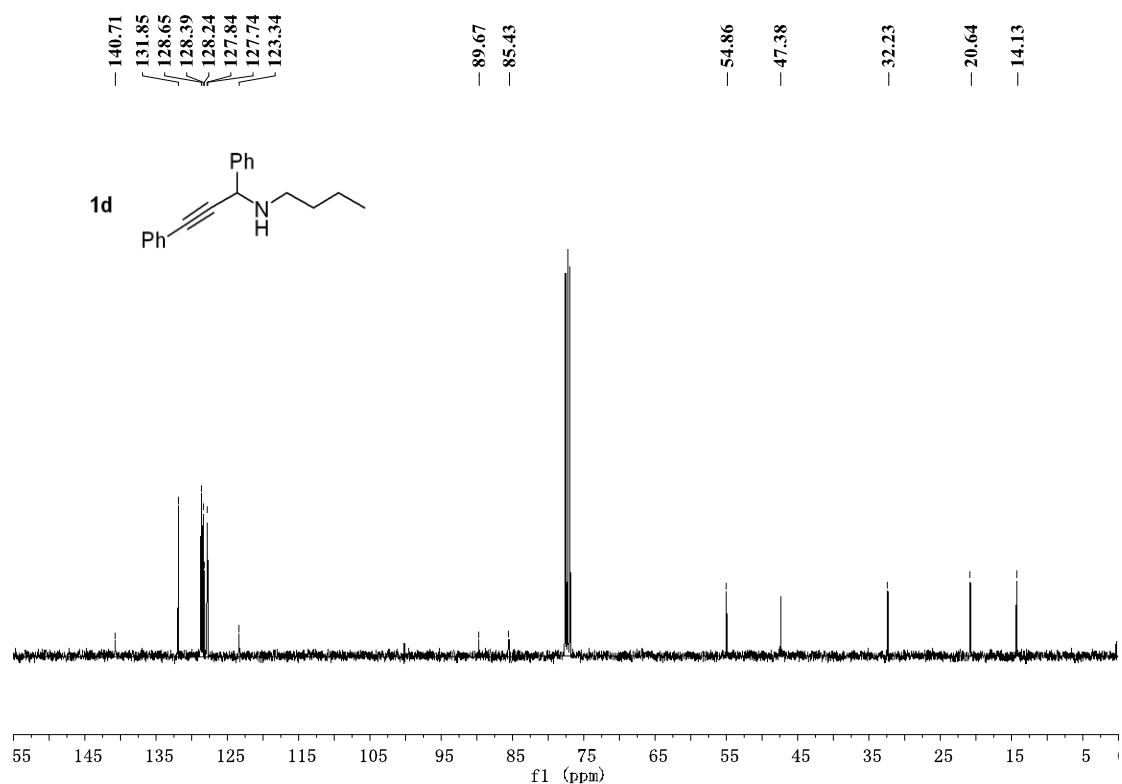
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7.59
7.47
7.47
7.40
7.38
7.36
7.32
7.31
7.26

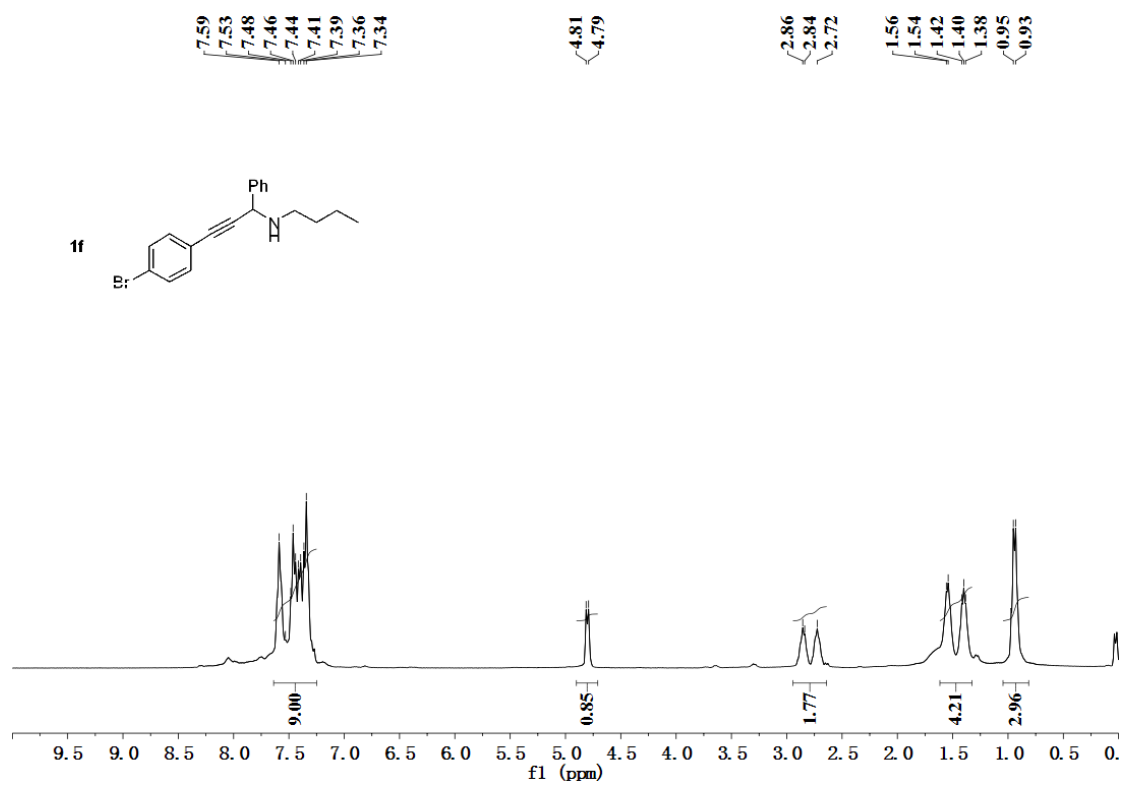
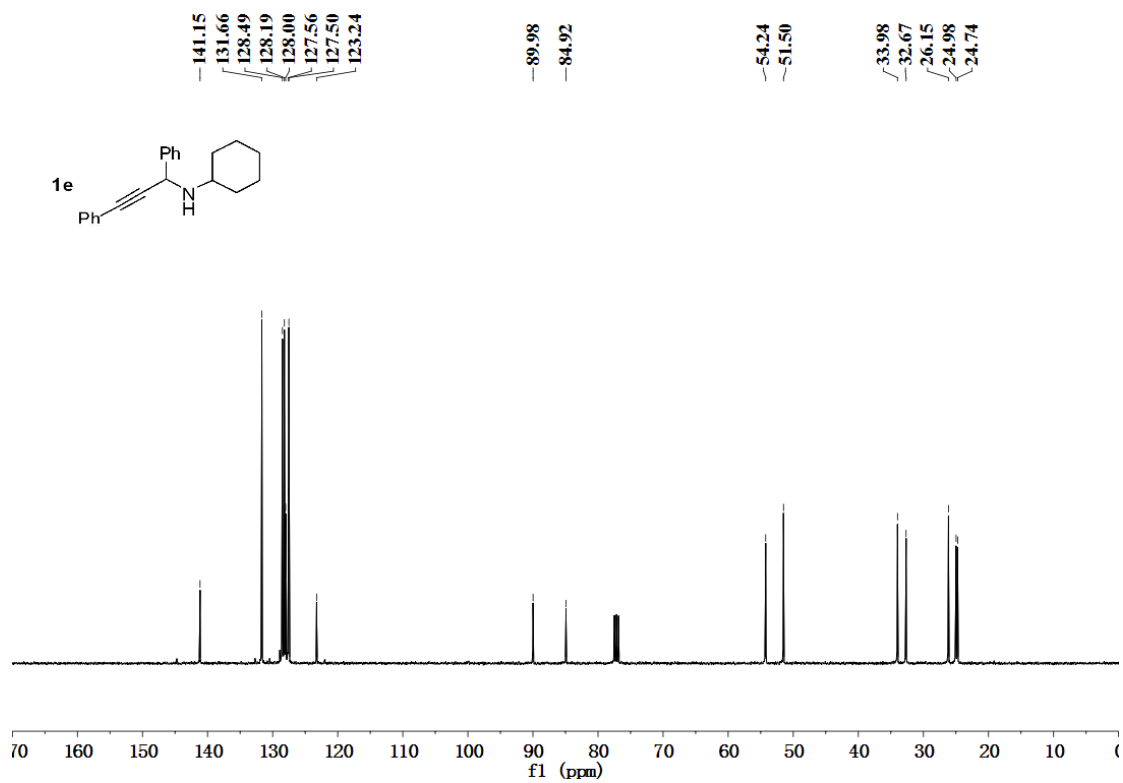
4.81

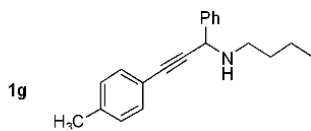
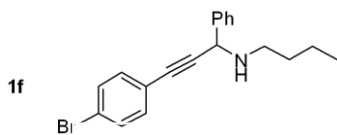
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2.87
2.86
2.85
2.83
2.76
2.74
2.72
2.72
2.70

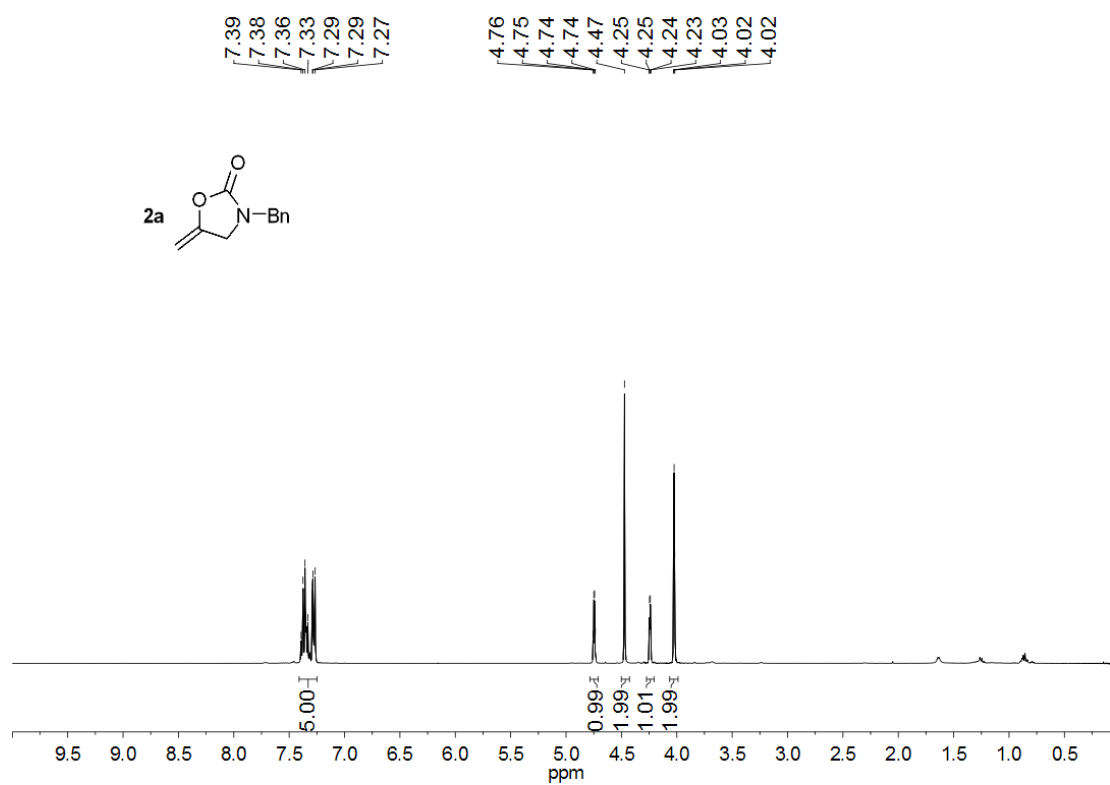
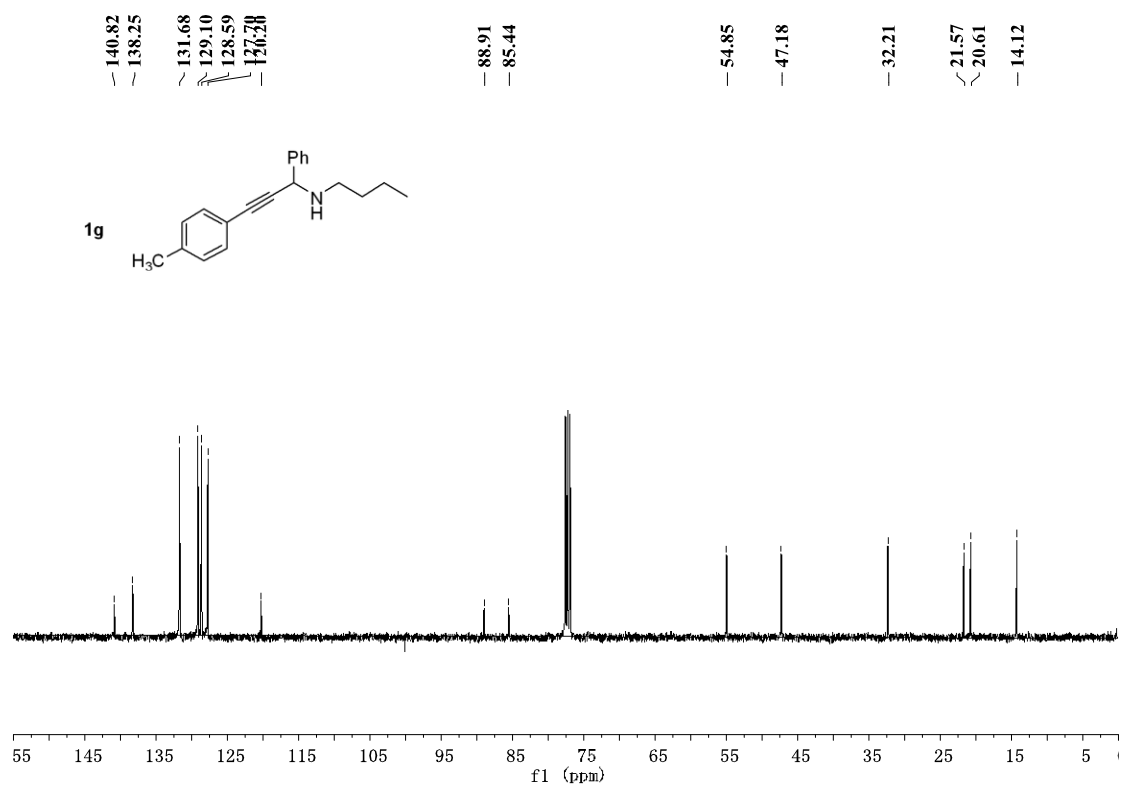
1.56
1.54
1.52
1.41
1.39
1.38
1.36
0.94
0.92
0.91

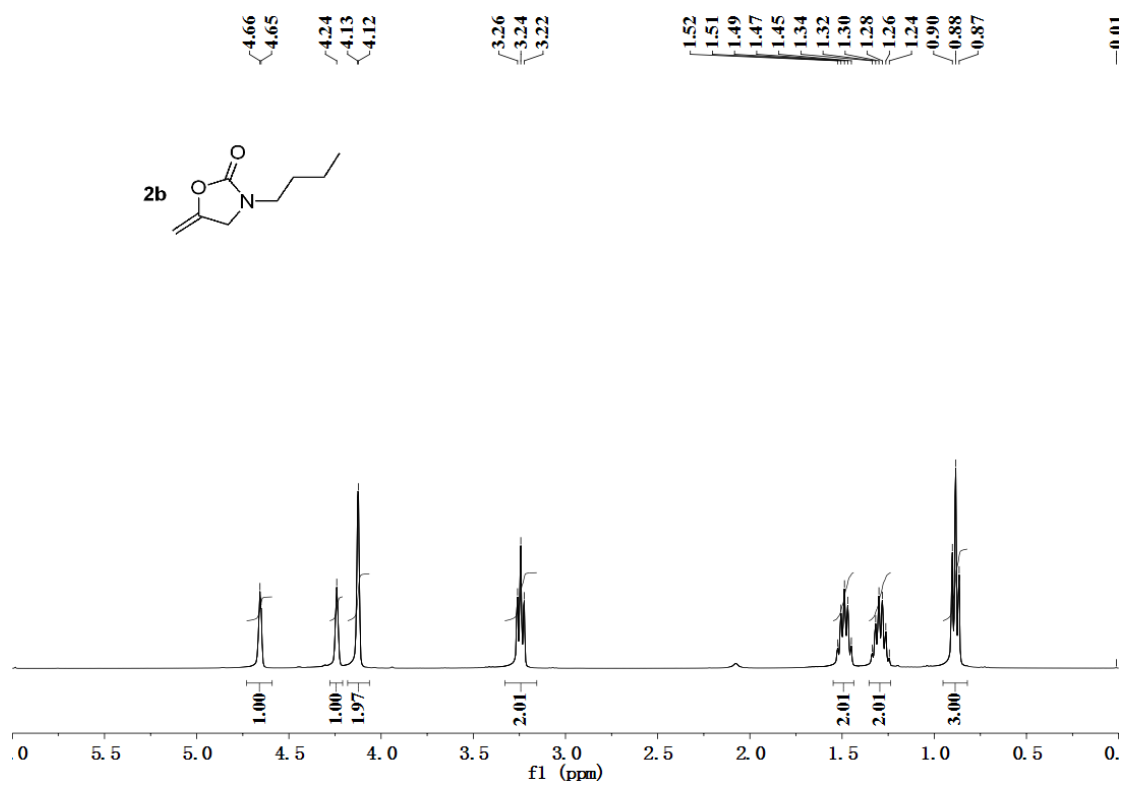
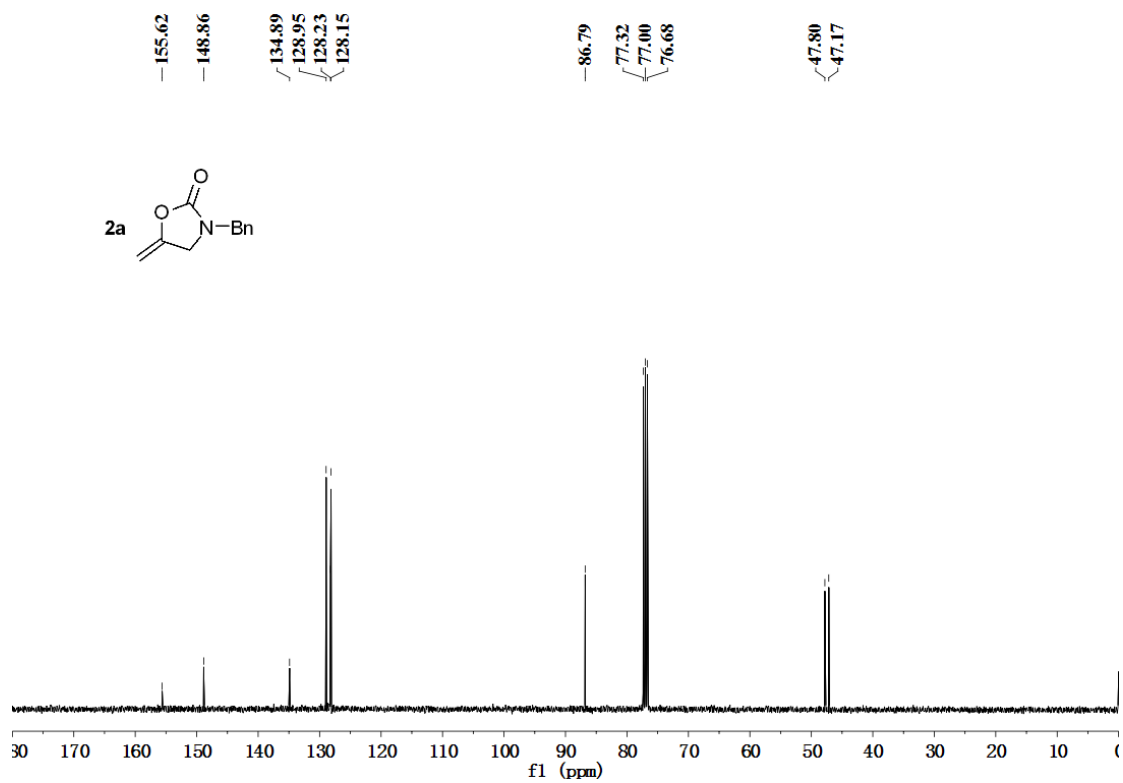


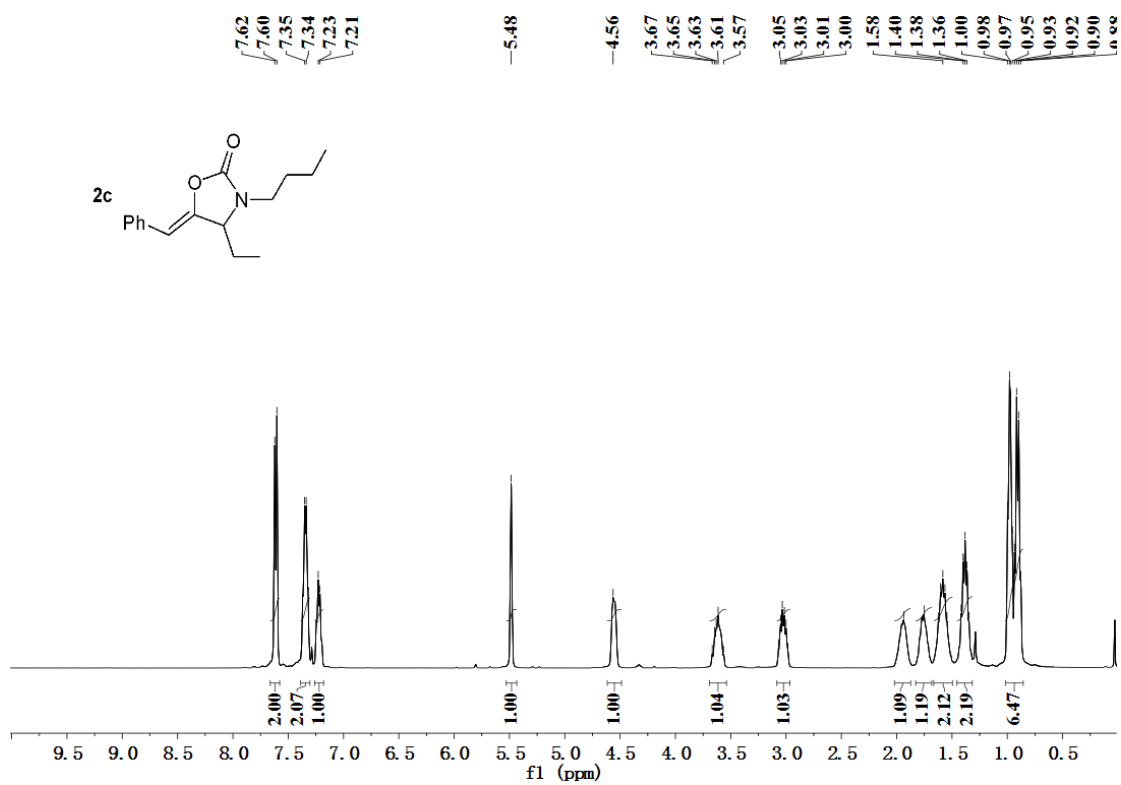
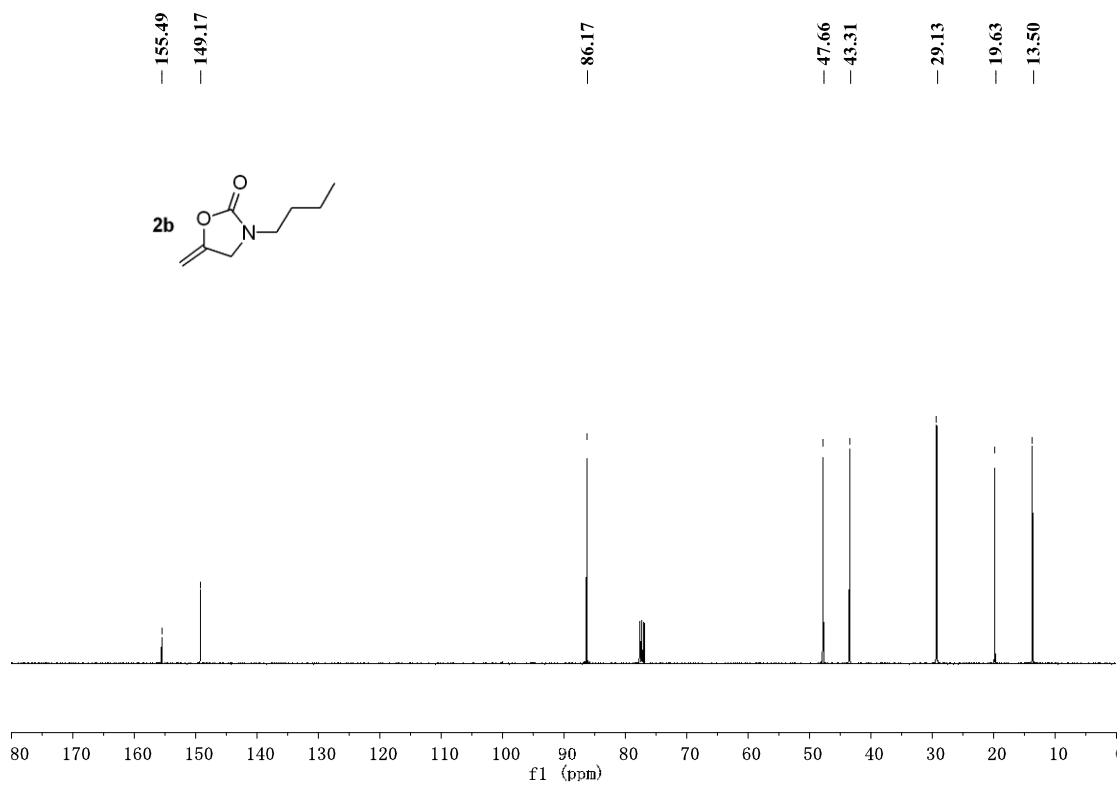


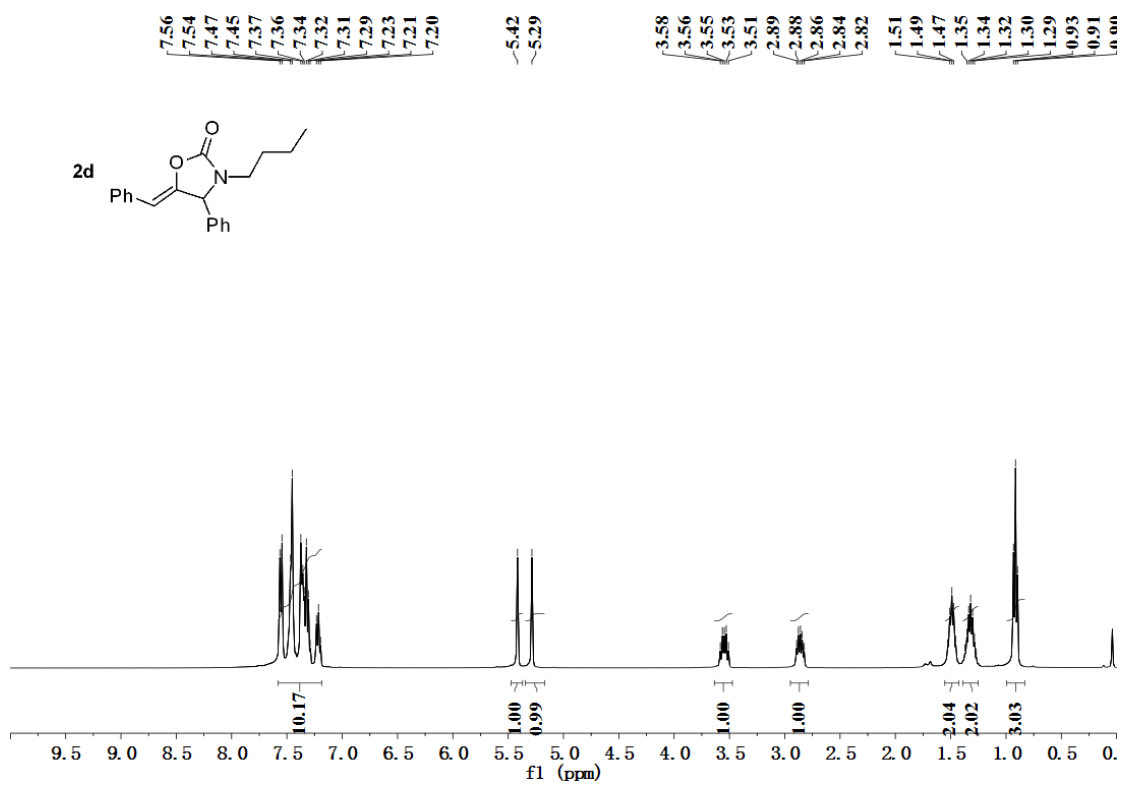
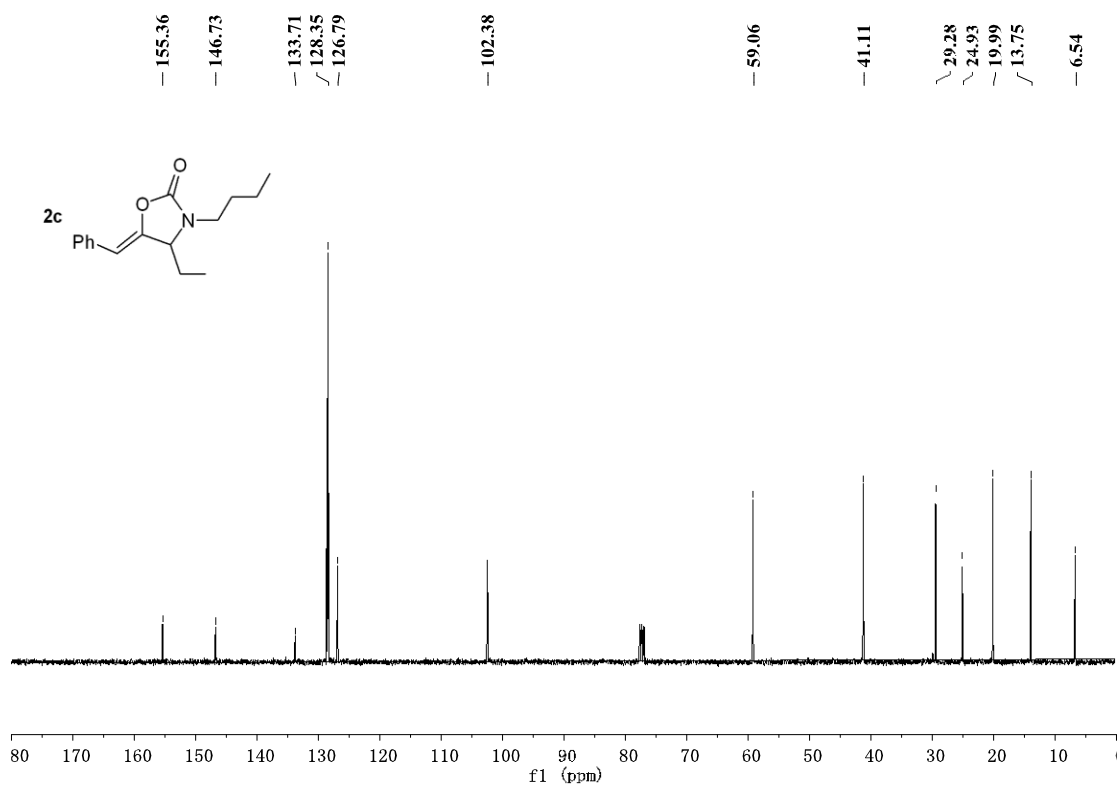


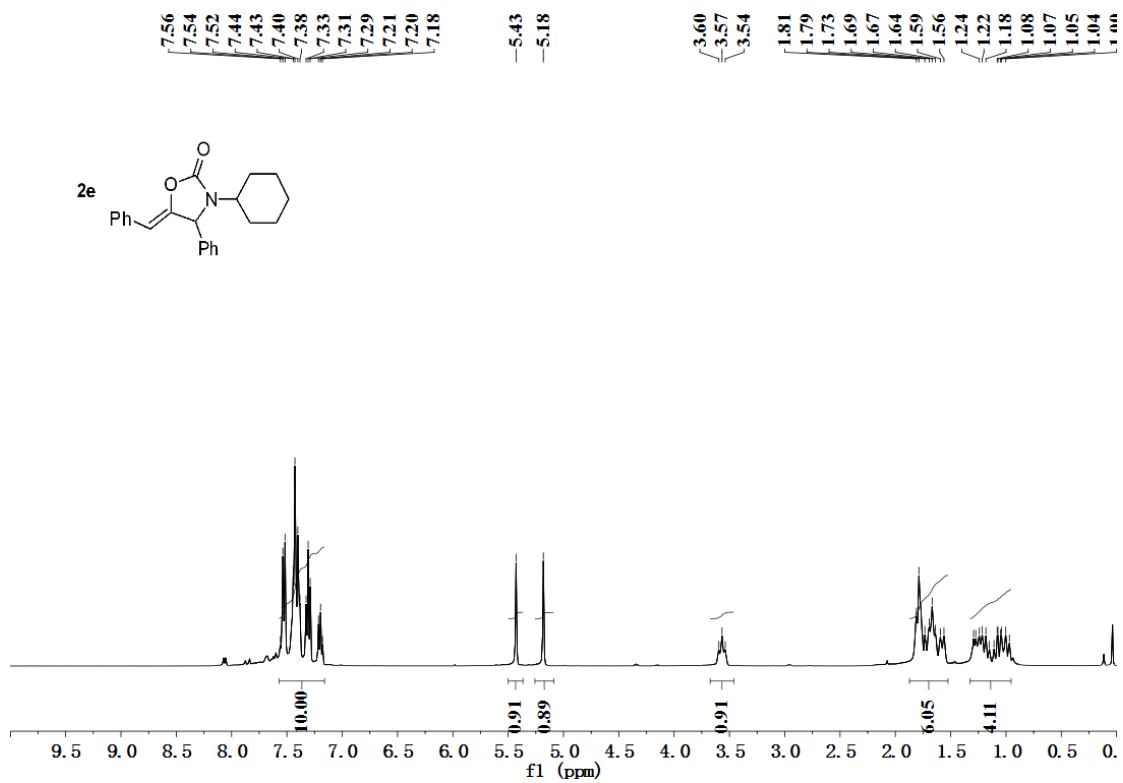
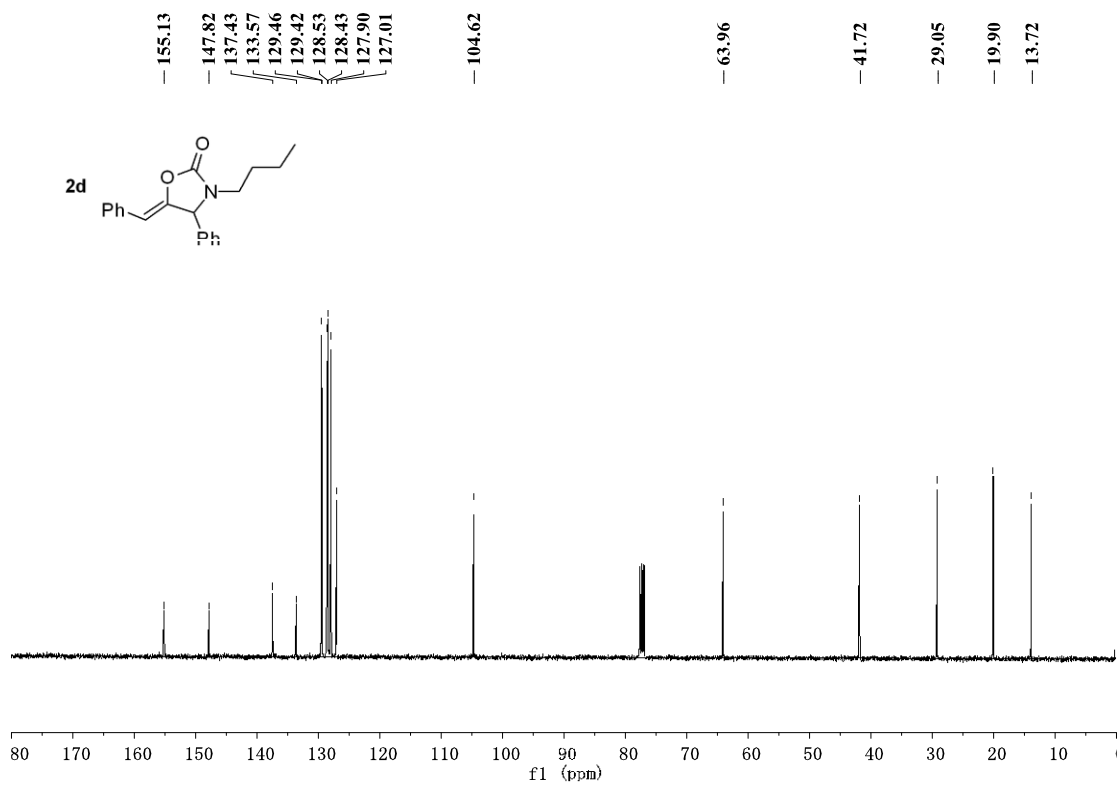


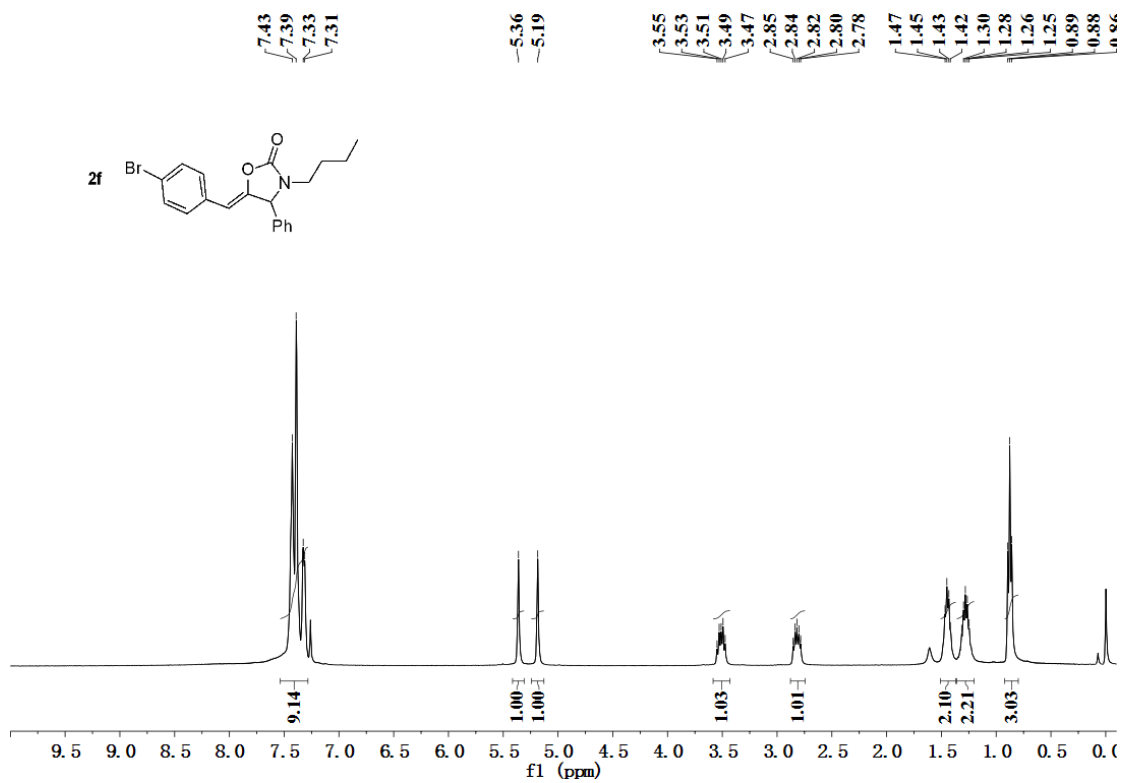
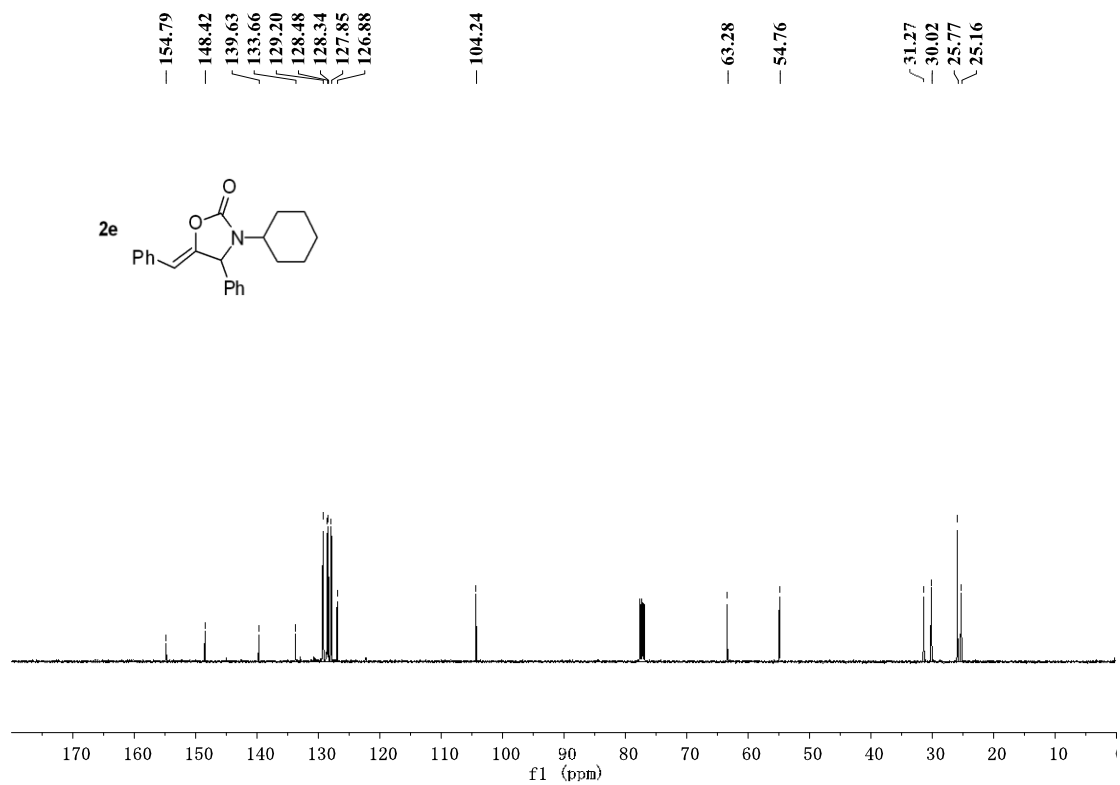


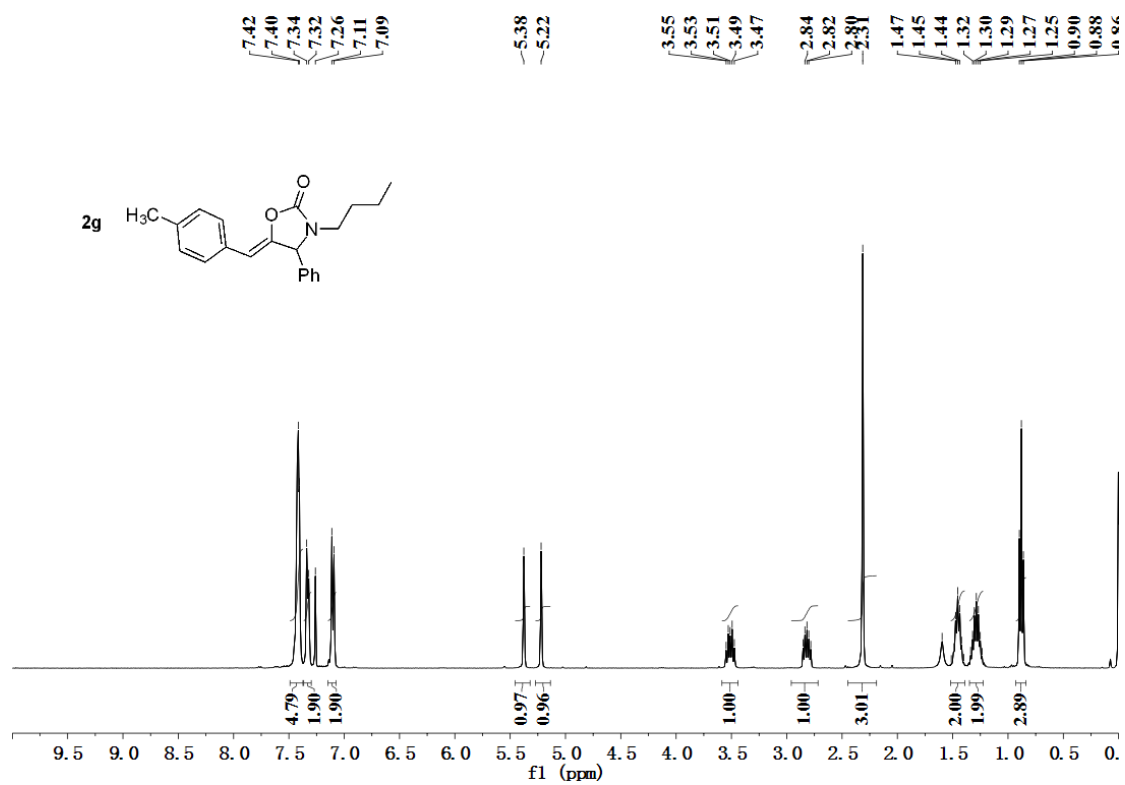
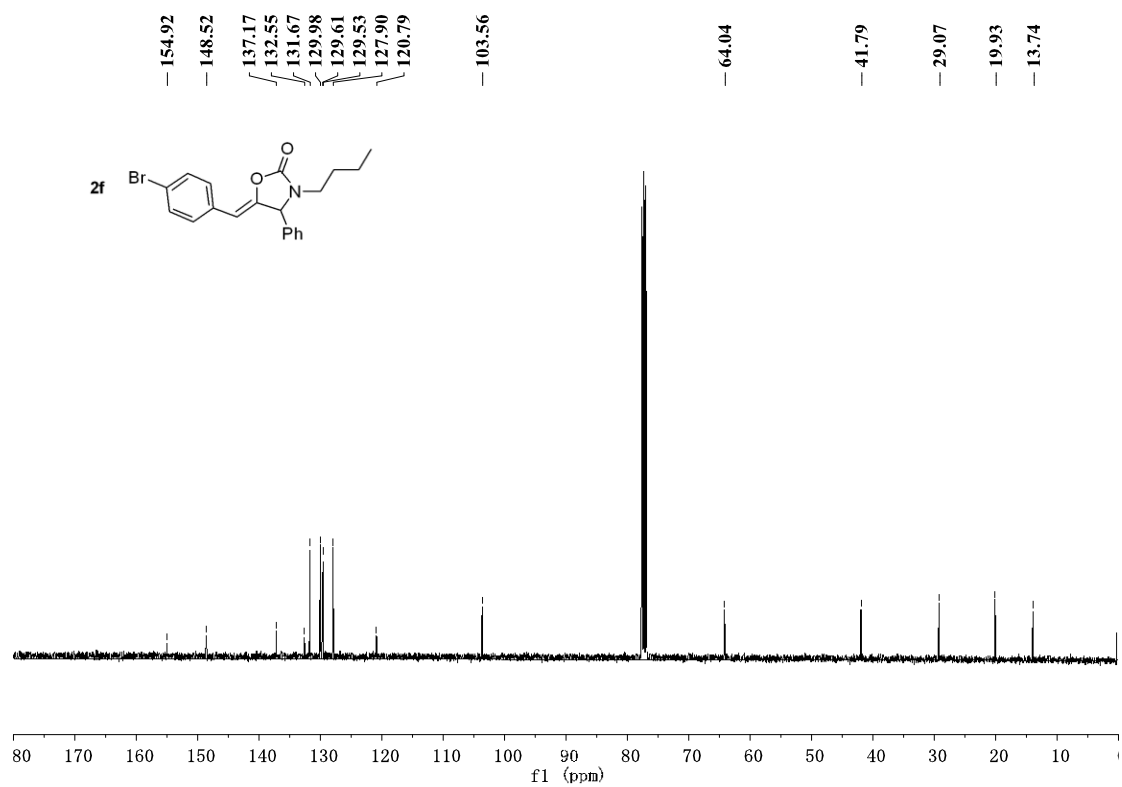


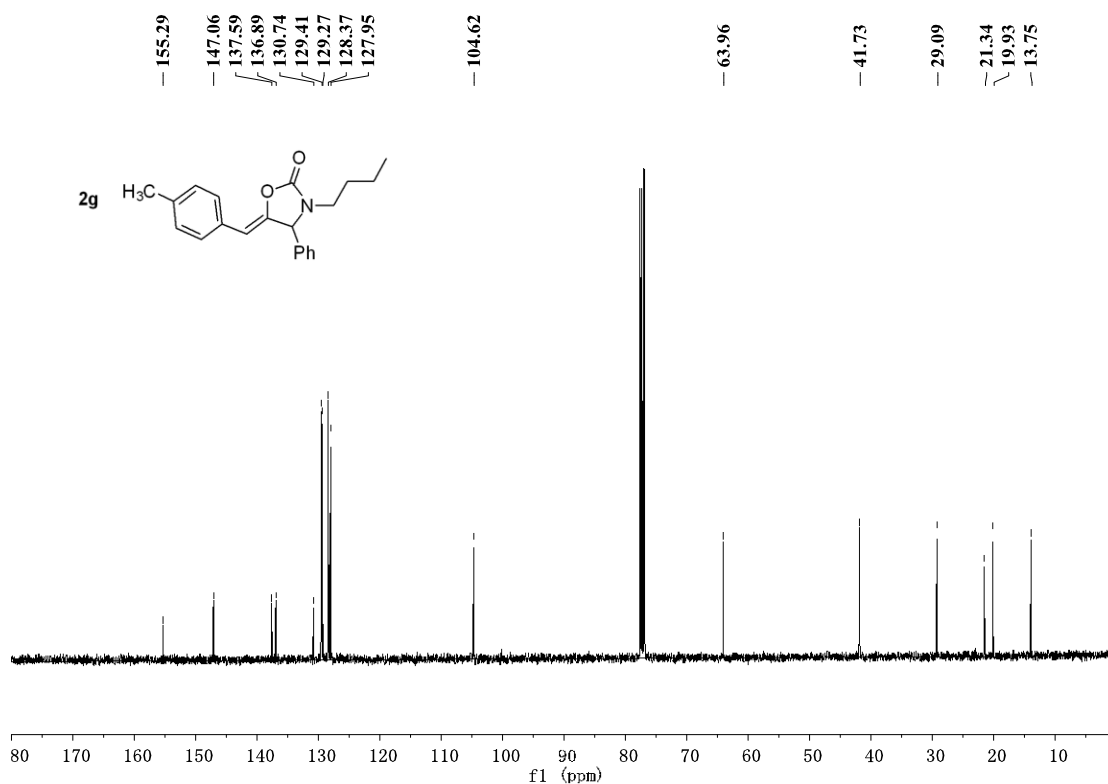












3.2 IR spectrum of transition metal substituted-polyoxometalate-based ionic liquids.

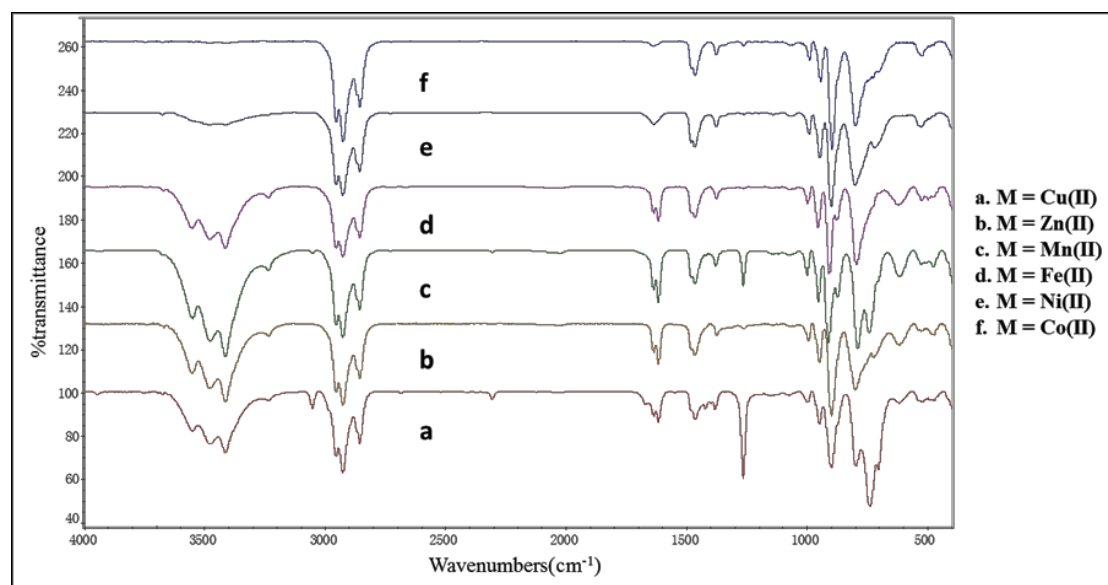


Fig. S2 FT-IR spectra of $[(^nC_7H_{15})_4N]_6[\alpha-SiW_{11}O_{39}M]$ ($M = Cu(II), Co(II), Fe(II), Ni(II), Zn(II), Mn(II)$).

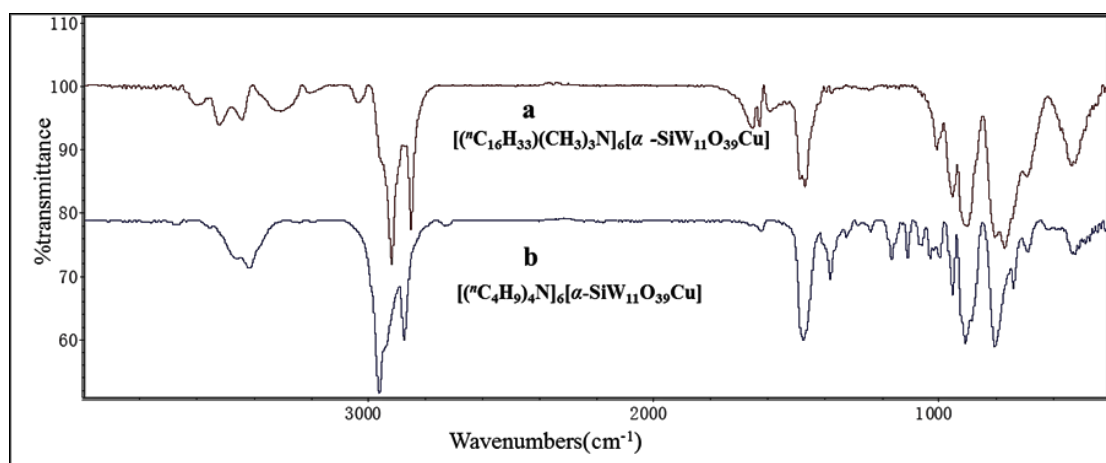


Fig. S3 FT-IR spectroscopy of $[(^{13}\text{C}_4\text{H}_9)_4\text{N}]_6[\alpha\text{-SiW}_{11}\text{O}_{39}\text{Cu}]$ and $[(^{13}\text{C}_{16}\text{H}_{33})(\text{CH}_3)_3\text{N}]_6[\alpha\text{-SiW}_{11}\text{O}_{39}\text{Cu}]$