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Supporting Information

A Formal [3 + 3 + 1] Reaction of Enyne-Methylenecyclopropanes through Au(I)-Catalyzed Enyne Cycloisomerization and Rh(I)-Catalyzed [6 + 1] Reaction of Vinylspiropentanes and CO

Chen-Long Li, Yusheng Yang, Yi Zhou, and Zhi-Xiang Yu*This manuscript is part of a special collection celebrating the 10th Anniversary of the Asian Journal of Organic Chemistry.

A Formal [3+3+1] Reaction of Enyne-Methylenecyclopropanes through Au(I)-Catalyzed Enyne Cycloisomerization and Rh(I)-Catalyzed [6+1] Reaction of Vinylspiropentanes and CO

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I. General Information

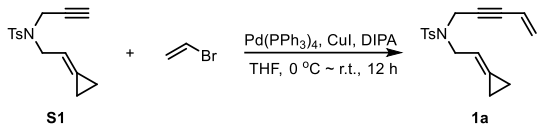
Air and moisture sensitive reactions were carried out in oven and flame-dried glassware sealed with rubber septa under a positive pressure of dry nitrogen or argon. Similarly, sensitive liquids and solutions were transferred via syringe. Reactions were stirred using Teflon-coated magnetic stir bars. Elevated temperatures were maintained using Thermostat-controlled silicone oil baths. Organic solutions were concentrated using a Büchi rotary evaporator with a desktop vacuum pump. DCE was superdry (water ≤ 30 ppm), which could be purchased from J&K. Chloro(dimethylsulfide)gold(I) and all ligands were purchased from Strem, and used without further purification. Other synthetic reagents were purchased from J&K and Acros, and used without further purification, unless otherwise indicated. Analytical TLC was performed with 0.25 mm silica gel G plates with a 254 nm fluorescent indicator. The TLC plates were visualized by ultraviolet light and treatment with phosphomolybdic acid stain or $KMnO_4$ stain followed by gentle heating. Purification of products was accomplished by flash chromatography on silica gel and the purified compounds show a single spot by analytical TLC.

NMR spectra were measured on Bruker ARX 400 (^{1}H at 400 MHz, ^{13}C at 101 MHz), Bruker AVANCE III (^{1}H at 500 MHz, ^{13}C at 126 MHz, ^{31}P NMR at 202 MHz) and Bruker AVANCE III (^{1}H at 700 MHz, ^{13}C at 176 MHz, ^{31}P NMR at 283 MHz) nuclear magnetic resonance spectrometers. Data for ^{1}H NMR spectra were reported as follows: chemical shift (ppm, referenced to residual solvent peak ($CDCl_3$ = δ 7.26 ppm, CD_2Cl_2 = δ 5.32 ppm, $(CD_3)_2SO$ = δ 2.50 ppm; s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, dt = doublet of triplets, ddd = doublet of doublet of doublets, ddt = doublet of doublet of triplets, dm = doublet of multiplet, tt = triplet of triplets, tq = triplet of quartets, m = multiplet), coupling constant (Hz), and integration. Data for ^{13}C NMR were reported in terms of chemical shift (ppm) relative to residual solvent peak ($CDCl_3$ = δ 77.16 ppm, CD_2Cl_2 = δ 53.84 ppm, $(CD_3)_2SO$ = δ 39.52 ppm). Infrared spectra were recorded on a Mettler-Toledo ReactIR iC10 system with a SiComp probe and were reported in wavenumbers (cm^{-1}). High-resolution mass spectra (HRMS) were recorded on a Bruker Apex IV FTMS mass spectrometer (ESI, EI or MALDI) with an FT-ICR analyzer. The enantiomer excesses (e.e.) of the products were determined by chiral HPLC analysis using Agilent Technologies 1200 series.

Abbreviations:
BAr^F_4 = tetrakis(3,5-bis(trifluoromethyl)phenyl)borate
Bs = *p*-bromobenzenesulfonyl
dba = dibenzylideneacetone
DCE = 1,2-dichloroethane
DCM = dichloromethane
DIAD = diisopropyl azodiformate
DIPA = diisopropylamine
dppe = 1,2-bis(diphenylphosphino)ethane
dppp = 1,3-bis(diphenylphosphino)propane
EA = ethyl acetate
e.e. = enantiomeric excess
JohnPhos = 2-(di-*t*-butylphosphino)biphenyl
MCP = methylenecyclopropane

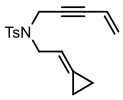
m.p. = melting point
MS = molecular sieves
Ms = methylsulfonyl
N_2 = nitrogen
Ns = *p*-nitrobenzenesulfonyl
PE = petroleum ether
r.t. = room temperature
TBAF = Tetrabutylammonium fluoride
TBDPS = *t*-butyldiphenylsilyl
THF = tetrahydrofuran
TLC = thin layer chromatography
Ts = *p*-toluenesulfonyl

II. Preparation of Substrates



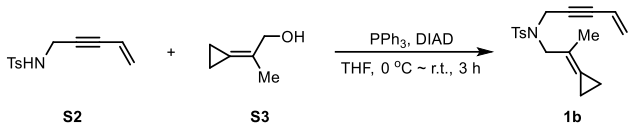
S1 1a

CuI (14.5 mg, 0.08 mmol) and $Pd(PPh_3)_4$ (32.9 mg, 0.03 mmol) were dissolved in diisopropylamine (DIPA, 2 mL). Bromoethene (3.8 mL, 1.0 M in THF) was added to the above solution at 0 ℃. After being stirred for 5 min, **S1** [1] (517.2 mg, 1.9 mmol) in DIPA (8 mL) and THF (2 mL) were added to the solution at 0 ℃. The reaction was gradually allowed to warm to room temperature overnight. The reaction was monitored by TLC and stirred for 12 h. Upon completion, 2M HCl solution (30 mL) was added to quench the reaction. The resulting mixture was extracted with ether (15 mL×3), and the combined organic phase was washed with brine, then dried over Na_2SO_4, then filtered and concentrated. The crude product was purified by flash column chromatography on silica gel (eluted with PE/EA, 20:1) to afford **1a** (507.4 mg, 90%).



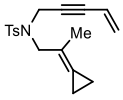
1a

Light yellow oil, TLC R_f = 0.45 (PE/EA, 5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, *J* = 8.2 Hz, 2H), 7.29 (d, *J* = 8.2 Hz, 2H), 5.77 – 5.67 (m, 1H), 5.50 (ddt, *J* = 17.2, 11.3, 1.8 Hz, 1H), 5.36 (dd, *J* = 11.3, 2.4 Hz, 1H), 5.31 (dd, *J* = 17.2, 2.4 Hz, 1H), 4.17 (d, *J* = 1.8 Hz, 2H), 3.96 (d, *J* = 6.9 Hz, 2H), 2.41 (s, 3H), 1.13 – 1.03 (m, 4H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 143.4, 136.2, 129.5, 128.9, 128.0, 127.2, 116.5, 112.1, 84.1, 83.0, 48.1, 36.6, 21.6, 2.8, 2.0. IR (neat): 2982, 2920, 1598, 1347, 1251, 1161, 1096, 1036, 970, 925 cm^{-1}. HRMS (EI): calcd. for $C_{17}H_{19}NO_2S$ ([M•]$^+$): 301.1131, found 301.1127.



S2 S3 1b

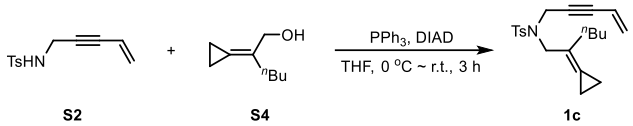
To a stirred solution of **S2** [2] (535.7 mg, 2.3 mmol) and PPh_3 (897.1 mg, 3.4 mmol) in THF (20 mL) was added DIAD (692.0 mg, 3.4 mmol) at 0 ℃. After being stirred for 5 min, to the solution was added **S3** [3] (245.4 mg, 2.5 mmol) in THF (6 mL). The reaction was gradually allowed to warm to room temperature. The reaction was monitored by TLC and stirred for 3 h. Upon completion, the reaction mixture was concentrated and the crude product was purified by flash column chromatography on silica gel (eluted with PE/EA, 50:1) to afford **1b** (543.1 mg, 76%).



1b

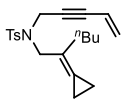
Colorless oil, TLC R_f = 0.53 (PE/EA, 5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, *J* = 8.2 Hz, 2H),

7.29 (d, *J* = 8.2 Hz, 2H), 5.46 (ddt, *J* = 17.2, 11.2, 1.8 Hz, 1H), 5.33 (dd, *J* = 11.2, 2.4 Hz, 1H), 5.27 (dd, *J* = 17.2, 2.4 Hz, 1H), 4.08 (d, *J* = 1.8 Hz, 2H), 3.89 (s, 2H), 2.41 (s, 3H), 1.07 – 1.00 (m, 4H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 143.3, 136.2, 129.5, 128.0, 127.1, 123.0, 118.5, 116.5, 84.0, 82.9, 51.9, 36.2, 21.6, 18.2, 2.8, 2.4. IR (neat): 2928, 2856, 2254, 1731, 1465, 1349, 1162, 1093, 909 cm^{-1}. HRMS (ESI): calcd. for $C_{18}H_{22}NO_2S$ ($[M+H]^+$): 316.1366, found 316.1370.



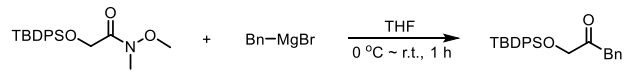
S2 **S4** **1c**

To a stirred solution of **S2** [2] (800.1 mg, 3.4 mmol), **S4** [3] (509.8 mg, 3.6 mmol) and PPh_3 (1.3377 g, 5.1 mmol) in THF (26 mL) was added DIAD (1.0315 g, 5.1 mmol) at 0 ℃. The reaction was gradually allowed to warm to room temperature. The reaction was monitored by TLC and stirred for 3 h. Upon completion, the reaction mixture was concentrated and the crude product was purified by flash column chromatography on silica gel (eluted with PE/EA, 50:1) to afford **1c** (892.9 mg, 73%).



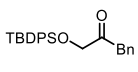
1c

Light yellow oil, TLC R_f = 0.62 (PE/EA, 5:1). ^1H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, *J* = 8.2 Hz, 2H), 7.28 (d, *J* = 8.2 Hz, 2H), 5.46 (ddt, *J* = 17.2, 11.2, 1.5 Hz, 1H), 5.33 (dd, *J* = 11.2, 2.4 Hz, 1H), 5.26 (dd, *J* = 17.2, 2.4 Hz, 1H), 4.08 (d, *J* = 1.5 Hz, 2H), 3.90 (s, 2H), 2.41 (s, 3H), 2.20 (t, *J* = 7.6 Hz, 2H), 1.52 (tt, *J* = 7.6, 7.4 Hz, 2H), 1.30 (tq, *J* = 7.4, 7.3 Hz, 2H), 1.12 – 1.06 (m, 2H), 1.03 – 0.97 (m, 2H), 0.90 (t, *J* = 7.3 Hz, 3H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 143.3, 136.3, 129.4, 128.0, 127.0, 122.7, 122.4, 116.5, 84.1, 83.0, 50.6, 36.2, 31.8, 29.7, 22.7, 21.6, 14.1, 3.0, 1.8. IR (neat): 2925, 2859, 1599, 1434, 1348, 1161, 1094, 1055, 976, 905 cm^{-1}. HRMS (ESI): calcd. for $C_{21}H_{28}NO_2S$ ($[M+H]^+$): 358.1835, found 358.1835.



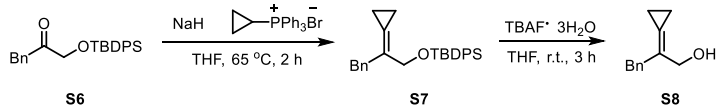
S5 **S6**

To a stirred solution of **S5** [4] (2.1430 g, 6.0 mmol) in THF (18 mL) was added dropwise the benzylmagnesium bromide (21 mL, 1.0 M in THF, 21 mmol) at 0 ℃. The reaction was gradually allowed to warm to room temperature. The reaction was monitored by TLC and stirred for 1 h. The reaction was quenched at 0 ℃ with saturated NH_4Cl (20 mL) and extracted with ether (20 mL×3). The combined organic phase was washed with brine and dried over Na_2SO_4, then filtered and concentrated. The crude product was purified by flash column chromatography on silica gel (eluted with PE/EA, 50:1) to afford **S6** (1.9417 g, 83%).



S6

Colorless oil, TLC R_f = 0.62 (PE/EA, 5:1). ^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.68 – 7.62 (m, 4H), 7.49 – 7.44 (m, 2H), 7.43 – 7.37 (m, 4H), 7.33 – 7.23 (m, 3H), 7.16 – 7.09 (m, 2H), 4.30 (s, 2H), 3.81 (s, 2H), 1.11 (s, 9H). ^{13}C{^{1}H} NMR (101 MHz, CD_2Cl_2) δ 207.2, 135.9, 134.4, 133.1, 130.3, 123.0, 128.8, 128.2, 127.2, 69.8, 45.8, 26.9, 19.5. IR (neat): 3071, 3030, 2958, 2932, 2892, 2858, 1732, 1589, 1496, 1472, 1428, 1391, 1361, 1150, 1112, 1049, 999 cm^{-1}. HRMS (ESI): calcd. for $C_{25}H_{32}NO_2Si$ ([M+NH_4]$^+$): 406.2197, found 406.2198.



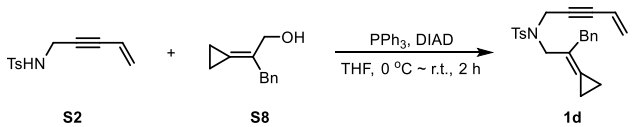
S6 **S7** **S8**

To a flame-dried glassware containing NaH (413.5 mg, 10.3 mmol, 60% in oil) and cyclopropyltriphenylphosphonium bromide (3.9630 g, 10.3 mmol) was added THF (9.5 mL) at room temperature. After being stirred for 10 h at 65 ℃, a solution of **S6** (1.8413 g, 4.7 mmol) in THF (3 mL) was added. The reaction was monitored by TLC, and stirred for 2 h at the same temperature. Then, the resulting mixture was quenched with water (15 mL) and extracted with ether (10 mL×3). The combined organic phase was washed with brine and dried over Na_2SO_4, then filtered and concentrated. The residue was purified by flash column chromatography on silica gel (eluted with PE) to afford crude **S7**, which was then used in the next step.

To a stirred solution of **S7** in THF (13 mL) was added TBAF·3H_2O (1.46769 g, 4.7 mmol). The reaction was monitored by TLC, and stirred for 3 h at room temperature. Then, the resulting mixture was quenched with water (20 mL) and extracted with ether (10 mL×3). The combined organic phase was washed with brine and dried over Na_2SO_4, then filtered and concentrated. The residue was purified by flash column chromatography on silica gel (eluted with PE/EA, 10:1) to afford **S8** (376.1 mg, 46% over two steps).

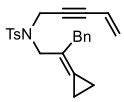
S8

Yellow oil, TLC R_f = 0.25 (PE/EA, 5:1). ^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.31 – 7.25 (m, 2H), 7.24 – 7.16 (m, 3H), 4.15 (s, 2H), 3.58 (s, 2H), 1.73 – 1.65 (m, 1H), 1.19 – 1.13 (m, 2H), 1.06 – 1.01 (m, 2H). ^{13}C{^{1}H} NMR (101 MHz, CD_2Cl_2) δ 140.7, 129.3, 128.6, 127.8, 126.3, 119.9, 65.1, 39.0, 2.4, 1.5. IR (neat): 3313, 3059, 3027, 2977, 2923, 2868, 1494, 1453, 1433, 1014, 988 cm^{-1}. HRMS (ESI): calcd. for $C_{12}H_{15}O$ ([M+H]$^+$): 175.1117, found 175.1113.



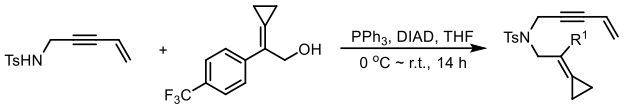
S2 **S8** **1d**

To a stirred solution of **S2** [2] (400.6 mg, 1.7 mmol), **S8** (318.1 mg, 1.8 mmol) and PPh_3 (668.9 mg, 2.6 mmol) in THF (10 mL) was added DIAD (515.3 mg, 2.5 mmol) at 0 ℃. The reaction was gradually allowed to warm to room temperature. The reaction was monitored by TLC and stirred for 2 h. Upon completion, the reaction mixture was concentrated and the crude product was purified by flash column chromatography on silica gel (eluted with PE/EA, 50:1) to afford **1d** (585.0 mg, 88%).



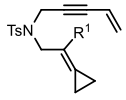
1d

Colorless oil, TLC R_f = 0.52 (PE/EA, 5:1). ^{1}H NMR (400 MHz, $(CD_3)_2SO$) δ 7.68 (d, *J* = 8.2 Hz, 2H), 7.39 (d, *J* = 8.2 Hz, 2H), 7.31 – 7.24 (m, 2H), 7.23 – 7.15 (m, 3H), 5.56 (ddt, *J* = 17.2, 11.2, 1.4 Hz, 1H), 5.42 (dd, *J* = 11.2, 2.3 Hz, 1H), 5.25 (dd, *J* = 17.2, 2.3 Hz, 1H), 4.03 (d, *J* = 1.4 Hz, 2H), 3.77 (s, 2H), 3.44 (s, 2H), 2.37 (s, 3H), 1.10 – 0.96 (m, 4H). ^{13}C{^{1}H} NMR (101 MHz, $(CD_3)_2SO$) δ 143.4, 139.4, 135.2, 129.6, 129.0, 128.2, 127.8, 127.5, 126.0, 124.8, 121.2, 116.3, 83.8, 83.0, 49.8, 38.0, 36.2, 21.0, 2.5, 2.1. IR (neat): 3059, 3027, 2919, 2849, 1597, 1491, 1447, 1346, 1185, 1159, 1113, 1090, 1053, 999, 900 cm^{-1}. HRMS (ESI): calcd. for $C_{24}H_{26}NO_2S$ ([M+H]$^+$): 392.1679, found 392.1678.



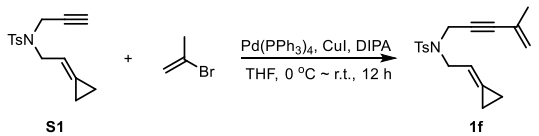
S2 **S9** **1e**, R^1 = 4-$CF_3C_6H_4$

To a stirred solution of **S2** [2] (190.2 mg, 0.8 mmol), **S9** [5] (184.0 mg, 0.8 mmol) and PPh_3 (319.6 mg, 1.2 mmol) in THF (6 mL) was added DIAD (245.3 mg, 1.2 mmol) at 0 ℃. The reaction was gradually allowed to warm to room temperature. The reaction was monitored by TLC and stirred for 14 h. Upon completion, the reaction mixture was concentrated and the crude product was purified by flash column chromatography on silica gel (eluted with PE/EA, 20:1) to afford **1e** (135.7 mg, 38%).



1e, R^1 = 4-$CF_3C_6H_4$

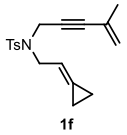
White solid, m.p. = 134-135 ℃, TLC R_f = 0.45 (PE/EA, 5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 8.2 Hz, 2H), 7.79 (d, *J* = 8.1 Hz, 2H), 7.61 (d, *J* = 8.2 Hz, 2H), 7.32 (d, *J* = 8.1 Hz, 2H), 5.44 (dd, *J* = 17.1, 11.2 Hz, 1H), 5.35 (dd, *J* = 11.2, 2.4 Hz, 1H), 5.24 (dd, *J* = 17.1, 2.4 Hz, 1H), 4.43 (s, 2H), 4.01 (s, 2H), 2.43 (s, 3H), 1.55 – 1.50 (m, 2H), 1.29 – 1.19 (m, 2H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 143.7, 140.7, 135.2, 131.2, 129.5, 128.9 (q, *J* = 32.1 Hz), 128.1, 127.2, 126.5, 125.3 (q, *J* = 3.5 Hz), 124.4 (q, *J* = 271.4 Hz), 120.0, 116.2, 84.6, 82.3, 49.3, 36.1, 21.6, 5.8, 1.6. IR (neat): 2977, 2924, 1736, 1615, 1599, 1495, 1453, 1411, 1347, 1327, 1245, 1163, 1122, 1092, 1068, 1035, 1016, 973 cm^{-1}. HRMS (ESI): calcd. for $C_{24}H_{23}F_3NO_2S$ ([M+H]$^+$): 446.1396, found 446.1396.



S1 **1f**

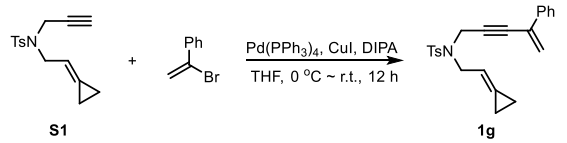
CuI (15.2 mg, 0.08 mmol) and $Pd(PPh_3)_4$ (34.8 mg, 0.03 mmol) were dissolved in diisopropylamine (DIPA, 2 mL). 2-Bromoprop-1-ene (0.36 mL, 4.1 mmol) in THF (4 mL) was added to the above

solution at 0 ℃. After being stirred for 5 min, **S1** [1] (554.0 mg, 2.0 mmol) in DIPA (8 mL) and THF (2 mL) were added to the solution at 0 ℃. The reaction was gradually allowed to warm to room temperature overnight. The reaction was monitored by TLC and stirred for 12 h. Upon completion, 2M HCl solution (30 mL) was added to quench the reaction. The resulting mixture was extracted with ether (15 mL×3), and the combined organic phase was washed with brine, then dried over Na_2SO_4, then filtered and concentrated. The crude product was purified by flash column chromatography on silica gel (eluted with PE/EA, 50:1) to afford **1f** (498.6 mg, 79%).



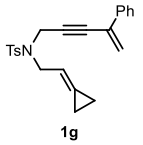
1f

Colorless oil, TLC R_f = 0.56 (PE/EA, 5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, *J* = 8.2 Hz, 2H), 7.28 (d, *J* = 8.2 Hz, 2H), 5.78 – 5.66 (m, 1H), 5.11 – 5.08 (m, 1H), 4.97 – 4.94 (m, 1H), 4.18 (s, 2H), 3.97 (d, *J* = 6.9 Hz, 2H), 2.40 (s, 3H), 1.65 – 1.62 (m, 3H), 1.13 – 1.04 (m, 4H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 143.4, 136.3, 129.6, 128.8, 128.0, 126.2, 122.0, 112.2, 86.7, 81.3, 48.0, 36.6, 23.2, 21.6, 2.8, 2.0. IR (neat): 2954, 2919, 2851, 1613, 1598, 1446, 1345, 1305, 1289, 1162, 1129, 1099, 1032 cm^{-1}. HRMS (ESI): calcd. for $C_{18}H_{22}NO_2S$ ([M+H]$^+$): 316.1366, found 316.1366.



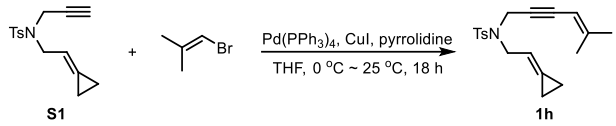
S1 **1g**

CuI (15.2 mg, 0.08 mmol) and $Pd(PPh_3)_4$ (34.9 mg, 0.03 mmol) were dissolved in diisopropylamine (DIPA, 2 mL). α-Bromostyrene (0.52 mL, 4.0 mmol) in THF (4 mL) was added to the above solution at 0 ℃. After being stirred for 5 min, **S1** [1] (550.9 mg, 2.0 mmol) in DIPA (8 mL) and THF (2 mL) were added to the solution at 0 ℃. The reaction was gradually allowed to warm to room temperature overnight. The reaction was monitored by TLC and stirred for 12 h. Upon completion, 2M HCl solution (30 mL) was added to quench the reaction. The resulting mixture was extracted with ether (15 mL×3), and the combined organic phase was washed with brine, then dried over Na_2SO_4, then filtered and concentrated. The crude product was purified by flash column chromatography on silica gel (eluted with PE/EA, 50:1) to afford **1g** (441.9 mg, 59%).



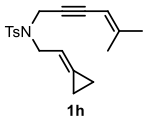
1g

Yellow oil, TLC R_f = 0.50 (PE/EA, 5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 8.1 Hz, 2H), 7.40 – 7.35 (m, 2H), 7.31 – 7.27 (m, 3H), 7.17 (d, *J* = 8.1 Hz, 2H), 5.79 (s, 1H), 5.79 – 5.73 (m, 1H), 5.33 (s, 1H), 4.31 (s, 2H), 4.03 (d, *J* = 6.9 Hz, 2H), 2.27 (s, 3H), 1.13 – 1.07 (m, 2H), 1.06 – 1.01 (m, 2H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 143.5, 136.8, 136.2, 130.1, 129.6, 128.9, 128.5, 128.4, 127.9, 126.0, 121.0, 112.2, 84.7, 83.7, 48.3, 36.7, 21.6, 2.8, 2.0. IR (neat): 3058, 2982, 2920, 2863, 1692, 1597, 1493, 1446, 1404, 1345, 1250, 1161, 1095, 1028, 968, 900 cm^{-1}. HRMS (ESI): calcd. for $C_{23}H_{24}NO_2S$ ([M+H]$^+$): 378.1522, found 378.1522.



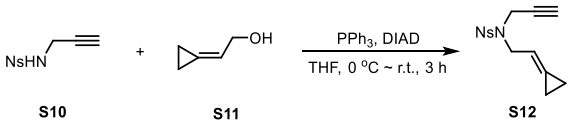
S1 1h

CuI (57.0 mg, 0.3 mmol) and $Pd(PPh_3)_4$ (115.5 mg, 0.1 mmol) were dissolved in pyrrolidine (2 mL). 1-Bromo-2-methylprop-1-ene (0.41 mL, 4.0 mmol) was added to the above solution at 0 ℃. After being stirred for 5 mins, **S1** [1] (548.5 mg, 2.0 mmol) in THF (1.5 mL) was added to the solution at 0 ℃. The reaction was gradually allowed to warm to 25 ℃ overnight. The reaction was monitored by TLC and stirred for 18 h. Upon completion, 2M HCl solution (10 ml) was added to quench the reaction. The resulting mixture was extracted with ether (10 mL×3), and the combined organic phase was washed with brine, then dried over Na_2SO_4, then filtered and concentrated. The crude product was purified by flash column chromatography on silica gel (eluted with PE/EA, 20:1) to afford **1h** (509.3 mg, 78%).



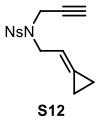
1h

Light yellow oil, TLC R_f = 0.55 (PE/EA, 5:1). ^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.71 (d, *J* = 8.2 Hz, 2H), 7.30 (d, *J* = 8.2 Hz, 2H), 5.76 – 5.63 (m, 1H), 5.00 (s, 1H), 4.18 (s, 2H), 3.95 (d, *J* = 6.8 Hz, 2H), 2.40 (s, 3H), 1.73 (s, 3H), 1.64 (s, 3H), 1.12 – 1.03 (m, 4H). ^{13}C{^{1}H} NMR (101 MHz, CD_2Cl_2) δ 149.4, 143.9, 136.7, 129.8, 128.9, 128.0, 112.5, 104.6, 84.3, 83.6, 48.3, 37.2, 24.7, 21.6, 20.9, 2.8, 2.2. IR (neat): 2980, 2912, 2858, 1598, 1494, 1445, 1379, 1348, 1306, 1248, 1203, 1162, 1117, 1098, 1031, 969, 924, 901 cm^{-1}. HRMS (ESI): calcd. for $C_{19}H_{27}N_2O_2S$ ($[M+NH_4]^+$): 347.1788, found 347.1791.



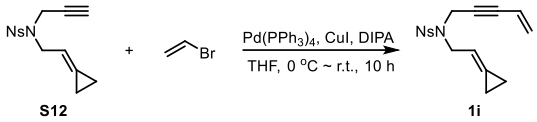
S10 S11 S12

To a stirred solution of **S10** [6] (985.3 mg, 4.1 mmol), **S11** [1] (450.1 mg, 5.4 mmol) and PPh_3 (1.6146 g, 6.2 mmol) in THF (24 mL) was added DIAD (1.2434 g, 6.1 mmol) at 0 ℃. The reaction was gradually allowed to warm to room temperature. The reaction was monitored by TLC and stirred for 3 h. Upon completion, the reaction mixture was concentrated and the crude product was purified by flash column chromatography on silica gel (eluted with PE/DCM, 4:1) to afford **S12** (1.1453 g, 91%).



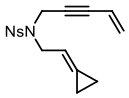
S12

White solid, m.p. = 114-117 ℃, TLC R_f = 0.41 (PE/EA, 5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.36 (d, *J* = 8.8 Hz, 2H), 8.06 (d, *J* = 8.8 Hz, 2H), 5.78 – 5.68 (m, 1H), 4.14 (d, *J* = 2.3 Hz, 2H), 4.02 (d, *J* = 6.8 Hz, 2H), 1.98 (t, *J* = 2.3 Hz, 1H), 1.17 – 1.06 (m, 4H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 150.3, 145.2, 130.1, 129.1, 124.2, 111.3, 76.2, 74.1, 48.2, 35.9, 2.9, 2.2. IR (neat): 3258, 3106, 2917, 2850, 1606, 1529, 1476, 1426, 1401, 1347, 1312, 1164, 1106, 1035, 1010, 969, 923 cm^{-1}. HRMS (ESI): calcd. for $C_{14}H_{15}N_2O_4S$ ($[M+H]^+$): 307.0747, found 307.0746.



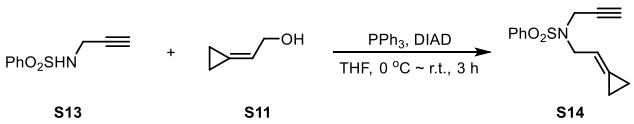
S12 1i

CuI (7.7 mg, 0.04 mmol) and $Pd(PPh_3)_4$ (17.3 mg, 0.015 mmol) were dissolved in diisopropylamine (DIPA, 1 mL). Bromoethene (2.0 mL, 1.0 M in THF) was added to the above solution at 0 ℃. After being stirred for 5 min, **S12** (305.7 mg, 1.0 mmol) in DIPA (4 mL) and THF (2 mL) were added to the solution at 0 ℃. The reaction was gradually allowed to warm to room temperature overnight. The reaction was monitored by TLC and stirred for 10 h. Upon completion, 2M HCl solution (15 mL) was added to quench the reaction. The resulting mixture was extracted with ether (10 mL×3), and the combined organic phase was washed with brine, then dried over Na_2SO_4, then filtered and concentrated. The crude product was purified by flash column chromatography on silica gel (eluted with PE/EA, 20:1) to afford **1i** (257.7 mg, 78%).



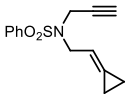
1i

Yellow oil, TLC R_f = 0.45 (PE/EA, 5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.36 – 8.31 (m, 2H), 8.08 – 8.03 (m, 2H), 5.76 – 5.69 (m, 1H), 5.46 (ddt, *J* = 17.0, 11.2, 1.6 Hz, 1H) 5.37 (dd, *J* = 11.2, 2.5 Hz, 1H), 5.30 (dd, *J* = 17.0, 2.5 Hz, 1H), 4.22 (d, *J* = 1.6 Hz, 2H), 3.99 (d, *J* = 6.8 Hz, 2H), 1.16 – 1.05 (m, 4H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 150.2, 145.1, 129.9, 129.2, 128.1, 124.1, 116.0, 111.4, 84.6, 82.1, 48.4, 36.8, 2.9, 2.0. IR (neat): 3105, 2983, 2918, 2866, 1606, 1530, 1478, 1429, 1402, 1350, 1312, 1251, 1166, 1106, 1037, 1012, 972, 924, 900 cm^{-1}. HRMS (ESI): calcd. for $C_{16}H_{17}N_2O_4S$ ($[M+H]^+$): 333.0904, found 333.0903.



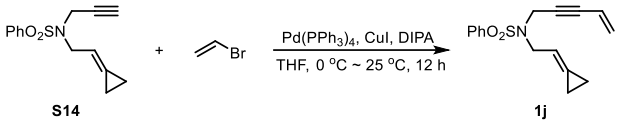
S13 S11 S14

To a stirred solution of **S13** [6] (1.0162 g, 5.2 mmol), **S11** [1] (561.1 mg, 6.7 mmol) and PPh_3 (2.0460 g, 7.8 mmol) in THF (30 mL) was added DIAD (1.5751 g, 7.8 mmol) at 0 ℃. The reaction was gradually allowed to warm to room temperature. The reaction was monitored by TLC and stirred for 3 h. Upon completion, the reaction mixture was concentrated and the crude product was purified by flash column chromatography on silica gel (eluted with PE/EA, 30:1) to afford **S14** (759.5 mg, 56%).



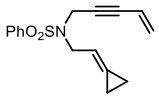
S14

Colorless oil, TLC R_f = 0.46 (PE/EA, 5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 – 7.84 (m, 2H), 7.60 – 7.55 (m, 1H), 7.53 – 7.48 (m, 2H), 5.77 – 5.64 (m, 1H), 4.08 (d, *J* = 2.4 Hz, 2H), 4.00 (d, *J* = 6.9 Hz, 2H), 1.95 (t, *J* = 2.4 Hz, 1H), 1.14 – 1.03 (m, 4H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 139.3, 132.8, 129.2, 129.0, 127.8, 111.9, 76.8, 73.4, 48.0, 35.8, 2.8, 2.1. IR (neat): 3279, 3061, 2983, 2919, 1480, 1447, 1348, 1252, 1164, 1102, 1073, 1036, 968, 925 cm^{-1}. HRMS (MALDI): calcd. for $C_{14}H_{16}NO_2S$ ($[M+H]^+$): 262.0896, found 262.0900.



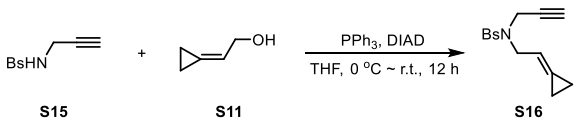
S14 1j

CuI (16.9 mg, 0.09 mmol) and $Pd(PPh_3)_4$ (38.2 mg, 0.03 mmol) were dissolved in diisopropylamine (DIPA, 2.2 mL). Bromoethene (4.4 mL, 1.0 M in THF) was added to the above solution at 0 ℃. After being stirred for 5 min, **S14** (580.9 mg, 2.2 mmol) in DIPA (8.8 mL) and THF (2.2 mL) were added to the solution at 0 ℃. The reaction was gradually allowed to warm to 25 ℃ overnight. The reaction was monitored by TLC and stirred for 12 h. Upon completion, 2M HCl solution (30 mL) was added to quench the reaction. The resulting mixture was extracted with ether (30 mL×3), and the combined organic phase was washed with brine, then dried over Na_2SO_4, then filtered and concentrated. The crude product was purified by flash column chromatography on silica gel (eluted with PE/EA, 20:1) to afford **1j** (531.7 mg, 83%).



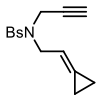
1j

Light yellow oil, TLC R_f = 0.44 (PE/EA, 5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 – 7.84 (m, 2H), 7.59 – 7.54 (m, 1H), 7.53 – 7.47 (m, 2H), 5.76 – 5.68 (m, 1H), 5.48 (ddt, *J* = 16.9, 11.5, 1.7 Hz, 1H), 5.34 (dd, *J* = 11.5, 2.4 Hz, 4H), 5.32 (dd, *J* = 16.9, 2.4 Hz, 1H), 4.19 (d, *J* = 1.7 Hz, 2H), 3.98 (d, *J* = 6.9 Hz, 2H), 1.13 – 1.03 (m, 4H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 139.2, 132.7, 129.0, 128.9, 127.9, 127.4, 116.4, 112.0, 84.2, 82.7, 48.1, 36.7, 2.8, 2.0. IR (neat): 3059, 2983, 2916, 2861, 1598, 1439, 1340, 1160, 1096, 1028, 971 cm^{-1}. HRMS (ESI): calcd. for $C_{16}H_{18}NO_2S$ ([M+H]$^+$): 288.1053, found 288.1054.



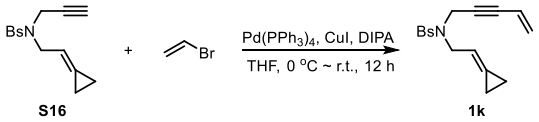
S15 S11 S16

To a stirred solution of **S15** [6] (1.6456 g, 6.0 mmol), **S11** [1] (606.2 mg, 7.2 mmol) and PPh_3 (2.3627 g, 9.0 mmol) in THF (36 mL) was added DIAD (1.8190 g, 9.0 mmol) at 0 ℃. The reaction was gradually allowed to warm to room temperature. The reaction was monitored by TLC and stirred for 12 h. Upon completion, the reaction mixture was concentrated and the crude product was purified by flash column chromatography on silica gel (eluted with PE/EA, 50:1) to afford **S16** (1.3876 g, 68%).



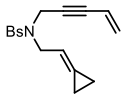
S16

White solid, m.p. = 58-60 ℃, TLC R_f = 0.58 (PE/EA, 5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 8.7 Hz, 2H), 7.64 (d, *J* = 8.7 Hz, 2H), 5.74 – 5.67 (m, 1H), 4.08 (d, *J* = 2.4 Hz, 2H), 3.97 (d, *J* = 6.8 Hz, 2H), 2.00 (t, *J* = 2.4 Hz, 1H), 1.15 – 1.04 (m, 4H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 138.3, 132.2, 129.5, 129.4, 127.8, 111.6, 76.5, 73.8, 48.0, 35.8, 2.8, 2.1. IR (neat): 3275, 2955, 2918, 2869, 2849, 1573, 1538, 1467, 1387, 1349, 1274, 1162, 1098, 1068, 1035, 1008, 967, 924 cm^{-1}. HRMS (ESI): calcd. for $C_{14}H_{15}BrNO_2S$ ([M+H]$^+$): 340.0001, found 339.9995.



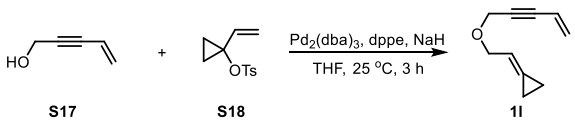
S16 1k

CuI (15.3 mg, 0.08 mmol) and $Pd(PPh_3)_4$ (34.8 mg, 0.03 mmol) were dissolved in diisopropylamine (DIPA, 2 mL). Bromoethene (4.0 mL, 1.0 M in THF) was added to the above solution at 0 ℃. After being stirred for 5 min, **S16** (679.7 mg, 2.0 mmol) in DIPA (8 mL) and THF (2 mL) were added to the solution at 0 ℃. The reaction was gradually allowed to warm to room temperature overnight. The reaction was monitored by TLC and stirred for 12 h. Upon completion, 2M HCl solution (35 mL) was added to quench the reaction. The resulting mixture was extracted with ether (15 mL×3), and the combined organic phase was washed with brine, then dried over Na_2SO_4, then filtered and concentrated. The crude product was purified by flash column chromatography on silica gel (eluted with PE/EA, 50:1) to afford **1k** (545.8 mg, 75%).



1k

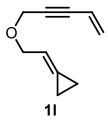
Light yellow oil, TLC R_f = 0.61 (PE/EA, 5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 – 7.70 (m, 2H), 7.66 – 7.61 (m, 2H), 5.76 – 5.68 (m, 1H), 5.50 (ddt, *J* = 17.0, 11.2, 1.6 Hz, 1H), 5.40 (dd, *J* = 11.2, 2.4 Hz, 1H), 5.32 (dd, *J* = 17.0, 2.4 Hz, 1H), 4.18 (d, *J* = 1.6 Hz, 2H), 3.95 (d, *J* = 6.9 Hz, 2H), 1.15 – 1.04 (m, 4H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 138.2, 132.2, 129.5, 129.4, 127.8, 127.7, 116.2, 111.7, 84.4, 82.4, 48.2, 36.6, 2.8, 2.0. IR (neat): 3089, 3054, 2982, 1573, 1470, 1428, 1389, 1351, 1296, 1275, 1163, 1095, 1068, 1036, 1009, 970, 924 cm^{-1}. HRMS (ESI): calcd. for $C_{16}H_{17}BrNO_2S$ ($[M+H]^+$): 366.0158, found 366.0156.



S17 S18 1l

To a flame-dried glassware containing NaH (120.0 mg, 3.0 mmol, 60% in oil) was added **S17** [7] (221.2 mg, 2.7 mmol) in THF (3 mL) at 0 ℃. After being stirred for 20 min at 25 ℃, this solution was then used in the next procedure.

S18 [1] (238.9 mg, 1.0 mmol), $Pd_2(dba)_3$ (18.4 mg, 0.02 mmol) and dppe (8.1 mg, 0.02 mmol) were dissolved in THF (2 mL) at 25 ℃. The reaction was stirred at 25 ℃ for 15 min, then the above prepared solution was added dropwise at the same temperature. The reaction was monitored by TLC, and stirred for 3 h. The reaction was quenched with water (5 mL) and extracted with ether (5 mL×3). The combined organic phase was washed with brine and dried over Na_2SO_4, then filtered and concentrated. The crude product was purified by flash column chromatography on silica gel (eluted with PE/EA, 100:1) to afford **1l** (68.3 mg, 46%).

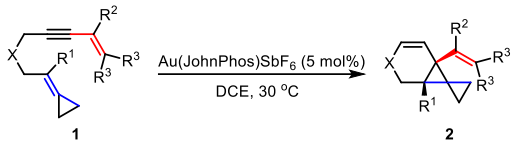


1l

Yellow oil, TLC R_f = 0.76 (PE/EA, 5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.99 – 5.88 (m, 1H), 5.82 (ddt, *J* = 17.6, 11.0, 1.8 Hz, 1H), 5.65 (dd, *J* = 17.6, 2.1 Hz, 1H), 5.49 (dd, *J* = 11.0, 2.1 Hz, 1H),

4.25 (d, *J* = 1.8 Hz, 2H), 4.20 (d, *J* = 6.8 Hz, 2H), 1.11 (s, 4H). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 128.1, 127.4, 116.8, 114.2, 86.1, 84.8, 69.9, 57.6, 2.5, 1.9. IR (neat): 3054, 2924, 2852, 1603, 1454, 1411, 1354, 1252, 1156, 1073, 1005, 968, 923 cm^{-1}. HRMS (ESI): calcd. for $C_{10}H_{13}O$ ($[M+H]^+$): 149.0961, found 149.0959.

III. General Procedure and Experimental Details of Au(I)-Catalyzed Cycloisomerization

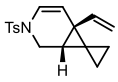


1 2

General procedure A:

Preparation of solution of cationic Au(I) catalyst: Anhydrous DCE (2.0 mL) was added to a mixture of Au(JohnPhos)Cl (5.3 mg, 10.0 μmol) and $AgSbF_6$ (4.1 mg, 11.9 μmol) under nitrogen. The mixture was stirred at room temperature for 30 min. The resulting suspension was left to stand until the formed AgCl precipitated. The supernatant was used in Au(I)-catalyzed cycloisomerization reactions as the catalyst precursor.

General procedure of Au(I)-catalyzed cycloisomerization: Under nitrogen, the above $Au(I)^+$ solution (2.0 mL, 10.0 μmol) was added to a flame-dried glassware containing **1** (0.2 mmol) at 30 ℃. The reaction was monitored by TLC. Upon completion, the reaction mixture was purified by flash column chromatography on silica gel to afford **2**.



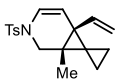
2a

Run 1: Following general procedure A, 60.6 mg **1a** was used, 1 h. After flash column chromatography on silica gel (eluted with PE/EA, 20:1), 33.9 mg **2a** was obtained in 56% yield.

Run 2: Following general procedure A, 60.2 mg **1a** was used, 1 h. After flash column chromatography on silica gel (eluted with PE/EA, 20:1), 33.6 mg **2a** was obtained in 56% yield.

Average yield: 56%.

Colorless oil, TLC R_f = 0.50 (PE/EA, 5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (d, *J* = 8.2 Hz, 2H), 7.31 (d, *J* = 8.2 Hz, 2H), 6.56 (d, *J* = 8.4 Hz, 1H), 5.56 (dd, *J* = 17.4, 10.9 Hz, 1H), 5.27 (d, *J* = 8.4 Hz, 1H), 5.03 (d, *J* = 17.4 Hz, 1H), 4.98 (d, *J* = 10.9 Hz, 1H), 3.77 (d, *J* = 11.4 Hz, 1H), 3.03 (dd, *J* = 11.4, 2.9 Hz, 1H), 2.43 (s, 3H), 1.87 (s, 1H), 0.81 (ddd, *J* = 9.1, 5.2, 5.2 Hz, 1H), 0.76 (ddd, *J* = 8.7, 5.2, 5.2 Hz, 1H), 0.54 (ddd, *J* = 9.1, 5.2, 5.2 Hz, 1H), 0.44 (ddd, *J* = 8.7, 5.2, 5.2 Hz, 1H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 143.9, 140.8, 135.2, 129.9, 127.3, 122.0, 112.1, 108.4, 39.7, 31.4, 29.2, 23.7, 21.7, 5.8, 3.5. IR (neat): 2920, 2855, 1634, 1464, 1411, 1349, 1265, 1166, 1102, 989, 941 cm^{-1}. HRMS (ESI): calcd. for $C_{17}H_{20}NO_2S$ ($[M+H]^+$): 302.1209, found 302.1217.



2b

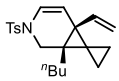
Run 1: Following general procedure A, 63.3 mg **1b** was used, 1 h. After flash column chromatography on silica gel (eluted with PE/EA, 50:1), 31.4 mg **2b** was obtained in 50% yield.

Run 2: Following general procedure A, 65.0 mg **1b** was used, 1 h. After flash column chromatography on silica gel (eluted with PE/EA, 50:1), 29.6 mg **2b** was obtained in 46% yield.

Average yield: 48%.

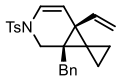
Colorless oil, TLC R_f = 0.64 (PE/EA, 5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, *J* = 8.2 Hz, 2H), 7.31 (d, *J* = 8.2 Hz, 2H), 6.53 (d, *J* = 8.3 Hz, 1H), 5.65 (dd, *J* = 16.8, 11.5 Hz, 1H), 5.23 (d, *J* = 8.3 Hz, 1H), 5.11 (dd, *J* = 11.5, 1.1 Hz, 1H), 5.10 (dd, *J* = 16.8, 1.1 Hz, 1H), 3.65 (d, *J* = 11.2 Hz, 1H),

2.68 (d, *J* = 11.2 Hz, 1H), 2.43 (s, 3H), 1.11 (s, 3H), 0.73 (ddd, *J* = 9.0, 4.4, 4.4 Hz, 1H), 0.68 (ddd, *J* = 8.7, 4.4, 4.4 Hz, 1H), 0.61 (ddd, *J* = 9.0, 4.4, 4.4 Hz, 1H), 0.55 (ddd, *J* = 8.7, 4.4, 4.4 Hz, 1H). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 143.8, 138.0, 135.2, 129.9, 127.2, 122.0, 114.8, 109.8, 45.5, 34.9, 32.7, 27.6, 21.7, 16.5, 4.9, 4.0. IR (neat): 2924, 2858, 1728, 1625, 1455, 1349, 1271, 1165, 1113, 1014, 951, 905 cm^{-1}. HRMS (ESI): calcd. for $C_{18}H_{22}NO_2S$ ($[M+H]^+$): 316.1366, found 316.1359.



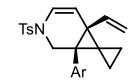
2c

Run 1: Following general procedure A, 72.8 mg **1c** was used, 1 h. After flash column chromatography on silica gel (eluted with PE/EA, 50:1), 36.2 mg **2c** was obtained in 50% yield.
Run 2: Following general procedure A, 71.1 mg **1c** was used, 1 h. After flash column chromatography on silica gel (eluted with PE/EA, 50:1), 35.3 mg **2c** was obtained in 50% yield.
Average yield: 50%.
Colorless oil, TLC R_f = 0.51 (PE/EA, 10:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, *J* = 8.0 Hz, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 6.52 (d, *J* = 8.2 Hz, 1H), 5.70 (dd, *J* = 17.4, 10.8 Hz, 1H), 5.23 (d, *J* = 8.2 Hz, 1H), 5.11 (d, *J* = 17.4 Hz, 1H), 5.10 (d, *J* = 10.8 Hz, 1H), 3.68 (d, *J* = 11.2 Hz, 1H), 2.77 (d, *J* = 11.2 Hz, 1H), 2.43 (s, 3H), 1.54 – 1.42 (m, 2H), 1.31 – 1.15 (m, 4H), 0.86 (t, *J* = 6.9 Hz, 3H), 0.78 – 0.66 (m, 2H), 0.61 – 0.55 (m, 1H), 0.52 – 0.47 (m, 1H). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 143.8, 138.1, 135.4, 129.9, 127.2, 121.9, 114.8, 110.2, 43.7, 38.5, 32.7, 31.8, 28.3, 27.8, 23.2, 21.7, 14.1, 4.6, 3.9. IR (neat): 3085, 3065, 2957, 2929, 2860, 1649, 1625, 1598, 1494, 1459, 1402, 1349, 1306, 1270, 1169, 1100, 1019, 975, 902 cm^{-1}. HRMS (ESI): calcd. for $C_{21}H_{28}NO_2S$ ($[M+H]^+$): 358.1835, found 358.1836.



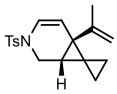
2d

Run 1: Following general procedure A, 78.5 mg **1d** was used, 1 h. After flash column chromatography on silica gel (eluted with PE/EA, 50:1), 38.2 mg **2d** was obtained in 49% yield.
Run 2: Following general procedure A, 78.8 mg **1d** was used, 1 h. After flash column chromatography on silica gel (eluted with PE/EA, 50:1), 42.7 mg **2d** was obtained in 54% yield.
Average yield: 52%.
Colorless oil, TLC R_f = 0.35 (PE/EA, 10:1). ^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.55 (d, *J* = 8.2 Hz, 2H), 7.31 – 7.23 (m, 4H), 7.22 – 7.14 (m, 1H), 7.03 (d, *J* = 7.2 Hz, 2H), 6.53 (d, *J* = 8.3 Hz, 1H), 5.86 (dd, *J* = 17.4, 10.8 Hz, 1H), 5.29 (d, *J* = 8.3 Hz, 1H), 5.23 (d, *J* = 17.4 Hz, 1H), 5.20 (d, *J* = 10.8 Hz, 1H), 3.51 (d, *J* = 11.6 Hz, 1H), 2.93 (d, *J* = 15.5 Hz, 1H), 2.85 (d, *J* = 15.5 Hz, 1H), 2.68 (d, *J* = 11.6 Hz, 1H), 2.42 (s, 3H), 0.90 (ddd, *J* = 8.7, 5.4, 5.4 Hz, 1H), 0.86 (ddd, *J* = 8.7, 5.4, 5.4 Hz, 1H), 0.61 (ddd, *J* = 9.0, 5.4, 5.4 Hz, 1H), 0.49 (ddd, *J* = 9.0, 5.4, 5.4 Hz, 1H). $^{13}C\{^{1}H\}$ NMR (101 MHz, CD_2Cl_2) δ 144.4, 138.6, 138.5, 135.4, 130.1, 129.0, 128.8, 127.3, 126.7, 122.5, 115.5, 110.0, 44.1, 38.7, 37.9, 32.7, 28.2, 21.7, 4.9, 4.4. IR (neat): 3063, 3028, 2984, 2921, 1647, 1625, 1598, 1495, 1453, 1402, 1349, 1306, 1272, 1168, 1103, 1051, 1019, 978, 906 cm^{-1}. HRMS (ESI): calcd. for $C_{24}H_{26}NO_2S$ ($[M+H]^+$): 392.1679, found 392.1680.



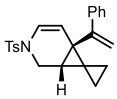
2e, Ar = 4-$CF_3C_6H_4$

Run 1: Following general procedure A, 88.9 mg **1e** was used, 17 h. After flash column chromatography on silica gel (eluted with PE/EA, 50:1), 41.1 mg **2e** was obtained in 46% yield.
Run 2: Following general procedure A, 89.1 mg **1e** was used, 17 h. After flash column chromatography on silica gel (eluted with PE/EA, 50:1), 41.5 mg **2e** was obtained in 47% yield.
Average yield: 46%.
White solid, m.p. = 144-145 ℃, TLC R_f = 0.63 (PE/EA, 5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, *J* = 8.2 Hz, 2H), 7.55 (d, *J* = 8.2 Hz, 2H), 7.31 (d, *J* = 8.0 Hz, 2H), 7.25 (d, *J* = 8.0 Hz, 1H), 6.67 (d, *J* = 8.4 Hz, 1H), 5.43 (d, *J* = 8.4 Hz, 1H), 5.13 – 5.08 (m, 2H), 5.00 (dd, *J* = 8.3, 4.0 Hz, 1H), 3.89 (d, *J* = 11.5 Hz, 1H), 2.91 (d, *J* = 11.5 Hz, 1H), 2.43 (s, 3H), 1.15 – 1.10 (m, 1H), 0.93 – 0.88 (m, 1H), 0.86 – 0.81 (m, 1H), 0.79 – 0.74 (m, 1H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 144.1, 142.2, 138.6, 135.0, 130.4, 130.0, 129.5 (q, *J* = 32.4 Hz), 127.2, 125.5 (q, *J* = 3.8 Hz), 124.2 (q, *J* = 271.2 Hz), 123.1, 113.8, 108.8, 47.5, 42.5, 31.8, 29.3, 21.6, 5.1, 4.4. IR (neat): 2926, 2858, 1724, 1622, 1497, 1409, 1327, 1166, 1124, 1070, 1019, 968, 922 cm^{-1}. HRMS (ESI): calcd. for $C_{24}H_{23}F_3NO_2S$ ($[M+H]^+$): 446.1396, found 446.1396.



2f

Run 1: Following general procedure A, 63.1 mg **1f** was used, 12 h. After flash column chromatography on silica gel (eluted with PE/EA, 20:1), 57.2 mg **2f** was obtained in 91% yield.
Run 2: Following general procedure A, 63.2 mg **1f** was used, 12 h. After flash column chromatography on silica gel (eluted with PE/EA, 20:1), 56.3 mg **2f** was obtained in 89% yield.
Average yield: 90%.
Colorless oil, TLC R_f = 0.47 (PE/EA, 10:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (d, *J* = 8.2 Hz, 2H), 7.30 (d, *J* = 8.2 Hz, 2H), 6.53 (d, *J* = 8.5 Hz, 1H), 5.25 (d, *J* = 8.5 Hz, 1H), 4.84 – 4.76 (m, 2H), 3.75 (d, *J* = 11.4 Hz, 1H), 3.01 (dd, *J* = 11.4, 2.9 Hz, 1H), 2.42 (s, 3H), 1.99 (s, 1H), 1.67 (s, 3H), 0.92 (ddd, *J* = 9.1, 5.4, 5.4 Hz, 1H), 0.86 (ddd, *J* = 8.8, 5.4, 5.4 Hz, 1H), 0.51 (ddd, *J* = 9.1, 5.4, 5.4 Hz, 1H), 0.40 (ddd, *J* = 8.8, 5.4, 5.4 Hz, 1H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 145.4, 143.8, 135.2, 129.8, 127.2, 121.5, 110.2, 110.0, 39.6, 28.5, 27.4, 26.2, 21.7, 20.5, 7.4, 3.7. IR (neat): 3066, 2986, 2923, 2858, 1645, 1626, 1597, 1495, 1454, 1402, 1346, 1306, 1292, 1262, 1185, 1168, 1101, 1048, 1018, 991, 940 cm^{-1}. HRMS (ESI): calcd. for $C_{18}H_{22}NO_2S$ ($[M+H]^+$): 316.1366, found 316.1368.

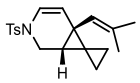


2g

Run 1: Following general procedure A, 75.7 mg **1g** was used, 12 h. After flash column chromatography on silica gel (eluted with PE/EA, 20:1), 54.9 mg **2g** was obtained in 73% yield.
Run 2: Following general procedure A, 75.5 mg **1g** was used, 12 h. After flash column chromatography on silica gel (eluted with PE/EA, 20:1), 59.0 mg **2g** was obtained in 78% yield.

Average yield: 76%.

Colorless oil, TLC R_f = 0.37 (PE/EA, 10:1). ^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.68 (d, *J* = 8.2 Hz, 2H), 7.36 (d, *J* = 8.0 Hz, 2H), 7.31 – 7.23 (m, 3H), 7.20 – 7.14 (m, 2H), 6.46 (d, *J* = 8.4 Hz, 1H), 5.44 (s, 1H), 5.11 (s, 1H), 5.09 (d, *J* = 8.4 Hz, 1H), 3.83 (d, *J* = 11.4 Hz, 1H), 3.14 (dd, *J* = 11.4, 2.7 Hz, 1H), 2.45 (s, 3H), 2.17 (s, 1H), 0.83 – 0.70 (m, 3H), 0.49 – 0.43 (m, 1H). ^{13}C{^{1}H} NMR (101 MHz, CD_2Cl_2) δ 149.3, 144.4, 139.5, 135.5, 130.2, 128.7, 128.0, 127.4, 126.9, 121.4, 112.5, 112.4, 39.9, 29.0, 28.8, 26.4, 21.7, 6.8, 3.7. IR (neat): 3060, 2995, 2923, 2864, 1640, 1597, 1493, 1445, 1399, 1344, 1302, 1260, 1167, 1103, 1039, 1017, 987, 941, 903 cm^{-1}. HRMS (ESI): calcd. for $C_{23}H_{24}NO_2S$ ([M+H]$^+$): 378.1522, found 378.1522.



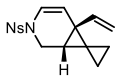
2h

Run 1: Following general procedure A, 64.3 mg **1h** was used, 1 h. After flash column chromatography on silica gel (eluted with PE/EA, 50:1), 51.6 mg **2h** was obtained in 80% yield.

Run 2: Following general procedure A, 65.3 mg **1h** was used, 1 h. After flash column chromatography on silica gel (eluted with PE/EA, 50:1), 55.4 mg **2h** was obtained in 85% yield.

Average yield: 82%.

White solid, m.p. = 78-81 ℃, TLC R_f = 0.57 (PE/EA, 5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, *J* = 8.2 Hz, 2H), 7.30 (d, *J* = 8.2 Hz, 2H), 6.44 (d, *J* = 8.2 Hz, 1H), 5.17 (s, 1H), 5.06 (d, *J* = 8.2 Hz, 1H), 3.74 (d, *J* = 11.4 Hz, 1H), 3.10 (dd, *J* = 11.4, 2.8 Hz, 1H), 2.43 (s, 3H), 1.74 (s, 1H), 1.66 (s, 3H), 1.57 (s, 3H), 0.77 (ddd, *J* = 9.0, 5.2, 5.2 Hz, 1H), 0.65 (ddd, *J* = 8.8, 5.2, 5.2 Hz, 1H), 0.53 (ddd, *J* = 9.0, 5.2, 5.2 Hz, 1H), 0.34 (ddd, *J* = 8.8, 5.2, 5.2 Hz, 1H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 143.7, 137.4, 135.5, 129.8, 127.2, 125.6, 120.4, 113.8, 39.8, 30.8, 28.1, 25.3, 21.7, 20.5, 19.4, 5.6, 4.0. IR (neat): 3060, 2976, 2921, 2862, 1638, 1600, 1452, 1393, 1348, 1265, 1167, 1104, 1027, 1001, 942 cm^{-1}. HRMS (ESI): calcd. for $C_{19}H_{24}NO_2S$ ([M+H]$^+$): 330.1522, found 330.1519.



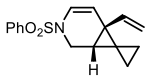
2i

Run 1: Following general procedure A, 66.5 mg **1i** was used, 12 h. After flash column chromatography on silica gel (eluted with PE/EA, 20:1), 40.3 mg **2i** was obtained in 61% yield.

Run 2: Following general procedure A, 66.3 mg **1i** was used, 12 h. After flash column chromatography on silica gel (eluted with PE/EA, 20:1), 44.0 mg **2i** was obtained in 66% yield.

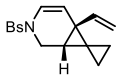
Average yield: 64%.

Yellow oil, TLC R_f = 0.40 (PE/EA, 5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.40 – 8.35 (m, 2H), 8.00 – 7.95 (m, 2H), 6.54 (d, *J* = 8.4 Hz, 1H), 5.56 (dd, *J* = 17.4, 10.7 Hz, 1H), 5.40 (d, *J* = 8.4 Hz, 1H), 5.04 (dd, *J* = 17.4, 0.7 Hz, 1H), 5.01 (dd, *J* = 10.7, 0.7 Hz, 1H), 3.82 (d, *J* = 11.6 Hz, 1H), 3.14 (dd, *J* = 11.6, 3.0 Hz, 1H), 1.91 (s, 1H), 0.84 (ddd, *J* = 9.2, 5.3, 5.3 Hz, 1H), 0.78 (ddd, *J* = 8.9, 5.3, 5.3 Hz, 1H), 0.51 (ddd, *J* = 9.2, 5.3, 5.3 Hz, 1H), 0.33 (ddd, *J* = 8.9, 5.3, 5.3 Hz, 1H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 150.3, 143.8, 140.2, 128.4, 124.6, 121.0, 112.6, 110.9, 40.1, 31.2, 29.4, 23.7, 5.9, 3.4. IR (neat): 3105, 2989, 2869, 1627, 1607, 1531, 1463, 1403, 1350, 1312, 1267, 1171, 1106, 1059, 1013, 993, 938 cm^{-1}. HRMS (ESI): calcd. for $C_{16}H_{17}N_2O_4S$ ([M+H]$^+$): 333.0904, found 333.0909.



2j

Run 1: Following general procedure A, 57.2 mg **1j** was used, 1 h. After flash column chromatography on silica gel (eluted with PE/EA, 20:1), 34.0 mg **2j** was obtained in 59% yield.
Run 2: Following general procedure A, 57.4 mg **1j** was used, 1 h. After flash column chromatography on silica gel (eluted with PE/EA, 20:1), 34.2 mg **2j** was obtained in 60% yield.
Average yield: 60%.
Colorless oil, TLC R_f = 0.44 (PE/EA, 5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 – 7.73 (m, 2H), 7.62 – 7.57 (m, 1H), 7.55 – 7.49 (m, 2H), 6.57 (d, *J* = 8.4 Hz, 1H), 5.56 (dd, *J* = 17.4, 10.7 Hz, 1H), 5.30 (d, *J* = 8.4 Hz, 1H), 5.04 (dd, *J* = 17.4, 0.8 Hz, 1H), 4.99 (dd, *J* = 10.7, 0.8 Hz, 1H), 3.78 (d, *J* = 11.5 Hz, 1H), 3.07 (dd, *J* = 11.5, 2.9 Hz, 1H), 1.87 (s, 1H), 0.81 (ddd, *J* = 9.1, 5.4, 5.4 Hz, 1H), 0.75 (ddd, *J* = 8.8, 5.4, 5.4 Hz, 1H), 0.51 (ddd, *J* = 9.1, 5.4, 5.4 Hz, 1H), 0.36 (ddd, *J* = 8.8, 5.4, 5.4 Hz, 1H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 140.7, 138.1, 133.0, 129.3, 127.2, 121.9, 112.2, 108.8, 39.7, 31.5, 29.3, 23.7, 5.8, 3.4. IR (neat): 3067, 2998, 2859, 1626, 1447, 1409, 1347, 1311, 1266, 1170, 1102, 1059, 990, 939 cm^{-1}. HRMS (ESI): calcd. for $C_{16}H_{18}NO_2S$ ([M+H]$^+$): 288.1053, found 288.1054.

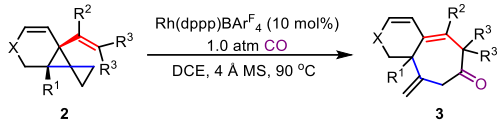


2k

Run 1: Following general procedure A, 73.5 mg **1k** was used, 1 h. After flash column chromatography on silica gel (eluted with PE/EA, 50:1), 44.4 mg **2k** was obtained in 60% yield.
Run 2: Following general procedure A, 73.7 mg **1k** was used, 1 h. After flash column chromatography on silica gel (eluted with PE/EA, 50:1), 43.7 mg **2k** was obtained in 59% yield.
Average yield: 60%.
Colorless oil, TLC R_f = 0.68 (PE/EA, 5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 – 7.62 (m, 4H), 6.52 (d, *J* = 8.4 Hz, 1H), 5.56 (dd, *J* = 17.4, 10.7 Hz, 1H), 5.32 (d, *J* = 8.4 Hz, 1H), 5.04 (dd, *J* = 17.4, 0.8 Hz, 1H), 5.00 (dd, *J* = 10.7, 0.8 Hz, 1H), 3.77 (d, *J* = 11.4 Hz, 1H), 3.06 (dd, *J* = 11.4, 2.9 Hz, 1H), 1.88 (s, 1H), 0.83 (ddd, *J* = 9.2, 5.4, 5.4 Hz, 1H), 0.77 (ddd, *J* = 8.8, 5.4, 5.4 Hz, 1H), 0.54 (ddd, *J* = 9.2, 5.4, 5.4 Hz, 1H), 0.42 (ddd, *J* = 8.8, 5.4, 5.4 Hz, 1H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 140.5, 137.1, 132.6, 128.7, 128.1, 121.5, 112.3, 109.5, 39.8, 31.3, 29.3, 23.7, 5.9, 3.5. IR (neat): 2954, 2919, 2869, 2849, 1651, 1626, 1462, 1363, 1169, 990, 938 cm^{-1}. HRMS (ESI): calcd. for $C_{16}H_{17}BrNO_2S$ ([M+H]$^+$): 366.0158, found 366.0155.

Following general procedure A, 30.2 mg **1l** was used, 1 h. But only a complex mixture was obtained, which was determined by ^{1}H NMR and ^{13}C NMR.

IV. General Procedure and Experimental Details of Rh(I)-Catalyzed [6+1] Cycloaddition



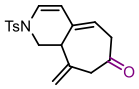
2 3

General procedure B:

Preparation of solution of cationic Rh(I) catalyst: Anhydrous DCE (2.0 mL) was added to a mixture of $[Rh(CO)_2Cl]_2$ (3.9 mg, 10.0 μmol), $NaBAr^F_4$ (21.2 mg, 23.9 μmol), dppp (8.2 mg, 19.9 μmol), and the newly activated 4 Å MS (0.06 g) under nitrogen. The mixture was stirred at room temperature for 30 min. The resulting suspension was filtered to afford the supernatant, which was further used in Rh(I)-catalyzed [6+1] cycloaddition reactions as the catalyst precursor.

General procedure of Rh(I)-catalyzed [6+1] cycloaddition: Under nitrogen, the above $Rh(I)^+$ solution (2.0 mL, 20.0 μmol) was added to a flame-dried glassware containing **2** (0.2 mmol) and the newly activated 4 Å MS (0.06 g) at room temperature. Then, the reaction mixture was bubbled with CO (1.0 atm) for 10 min. The glassware was immersed into an oil bath at 90 ℃ and reacted under the atmosphere pressure of CO. The reaction was monitored by TLC. Upon completion, the reaction mixture was purified by flash column chromatography on silica gel to afford **3**.

(**Attention**: The present reaction is sensitive to solvent and very highly anhydrous DCE must be used. Molecular sieves also should be activated before the reaction. If the reaction system were not dry, products **3** would be obtained in lower yields.)



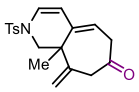
3a

Run 1: Following general procedure B, 60.6 mg **2a** was used, 24 h. After flash column chromatography on silica gel (eluted with PE/EA, 5:1), 52.7 mg **3a** was obtained in 80% yield.

Run 2: Following general procedure B, 60.5 mg **2a** was used, 24 h. After flash column chromatography on silica gel (eluted with PE/EA, 5:1), 52.3 mg **3a** was obtained in 79% yield.

Average yield: 80%.

Colorless oil, TLC R_f = 0.27 (PE/EA, 5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, *J* = 8.2 Hz, 2H), 7.33 (d, *J* = 8.2 Hz, 2H), 6.65 (d, *J* = 8.0 Hz, 1H), 5.46 (d, *J* = 8.0 Hz, 1H), 5.38 (ddd, *J* = 8.2, 5.6, 2.2 Hz, 1H), 5.08 (s, 2H), 3.71 (dd, *J* = 12.0, 4.7 Hz, 1H), 3.50 (ddd, *J* = 14.9, 5.6, 1.6 Hz, 1H), 3.29 (dm, *J* = 12.0 Hz, 1H), 3.14 (d, *J* = 16.8 Hz, 1H), 3.06 (d, *J* = 16.8 Hz, 1H), 2.90 (dd, *J* = 12.0, 12.0 Hz, 1H), 2.81 (dd, *J* = 14.9, 8.2 Hz, 1H), 2.44 (s, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 206.2, 144.4, 141.5, 134.6, 133.8, 130.2, 127.2, 124.6, 118.2, 117.0, 112.1, 48.4, 48.3, 43.6, 41.2, 21.7. IR (neat): 2956, 2920, 2852, 1713, 1644, 1606, 1494, 1461, 1389, 1353, 1308, 1262, 1231, 1166, 1095, 983, 920 cm^{-1}. HRMS (ESI): calcd. for $C_{18}H_{20}NO_3S$ ($[M+H]^+$): 330.1158, found 330.1163.



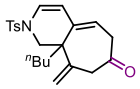
3b

Run 1: Following general procedure B, 61.9 mg **2b** was used, 24 h. After flash column chromatography on silica gel (eluted with PE/EA, 5:1), 38.1 mg **3b** was obtained in 57% yield.

Run 2: Following general procedure B, 59.2 mg **2b** was used, 24 h. After flash column

chromatography on silica gel (eluted with PE/EA, 5:1), 37.6 mg **3b** was obtained in 58% yield.
Average yield: 58%.

Colorless oil, TLC R_f = 0.18 (PE/EA, 5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, *J* = 8.2 Hz, 2H), 7.33 (d, *J* = 8.2 Hz, 2H), 6.66 (d, *J* = 8.2 Hz, 1H), 5.38 (d, *J* = 8.2 Hz, 1H), 5.33 (dd, *J* = 8.6, 6.0 Hz, 1H), 5.26 (s, 1H), 5.11 (s, 1H), 3.50 (dd, *J* = 14.8, 6.0 Hz, 1H), 3.32 (d, *J* = 11.4 Hz, 1H), 3.18 (d, *J* = 16.2 Hz, 1H), 3.03 (d, *J* = 16.2 Hz, 1H), 2.73 (d, *J* = 11.4 Hz, 1H), 2.69 (dd, *J* = 14.8, 8.6 Hz, 1H), 2.43 (s, 3H), 1.30 (s, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 206.9, 146.5, 144.4, 138.7, 134.8, 130.1, 127.2, 123.3, 116.2, 115.8, 110.5, 53.4, 48.6, 43.2, 40.8, 22.4, 21.7. IR (neat): 3093, 2967, 2922, 2853, 1716, 1637, 1608, 1456, 1402, 1350, 1306, 1262, 1226, 1169, 1093, 1052, 1023, 978, 942, 918 cm^{-1}. HRMS (ESI): calcd. for $C_{19}H_{22}NO_3S$ ([M+H]$^+$): 344.1315, found 344.1316.



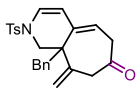
3c

Run 1: Following general procedure B, 70.6 mg **2c** was used, 24 h. After flash column chromatography on silica gel (eluted with PE/EA, 5:1), 29.6 mg **3c** was obtained in 39% yield.

Run 2: Following general procedure B, 71.0 mg **2c** was used, 24 h. After flash column chromatography on silica gel (eluted with PE/EA, 5:1), 28.6 mg **3c** was obtained in 37% yield.

Average yield: 38%.

Colorless oil, TLC R_f = 0.32 (PE/EA, 5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, *J* = 8.2 Hz, 2H), 7.32 (d, *J* = 8.2 Hz, 2H), 6.61 (d, *J* = 8.2 Hz, 1H), 5.45 (dd, *J* = 8.5, 5.7 Hz, 1H), 5.37 (d, *J* = 8.2 Hz, 1H), 5.17 (s, 1H), 5.13 (s, 1H), 3.36 (dd, *J* = 15.3, 5.7 Hz, 1H), 3.32 (d, *J* = 11.7 Hz, 1H), 3.12 (d, *J* = 16.0 Hz, 1H), 3.03 (d, *J* = 16.0 Hz, 1H), 2.82 (d, *J* = 11.7 Hz, 1H), 2.75 (dd, *J* = 15.3, 8.5 Hz, 1H), 2.43 (s, 3H), 1.57 – 1.46 (m, 2H), 1.43 – 1.34 (m, 1H), 1.20 – 1.13 (m, 2H), 1.10 – 1.02 (m, 1H), 0.82 (t, *J* = 7.3 Hz, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 206.9, 144.3, 143.0, 136.6, 134.9, 130.1, 127.2, 122.8, 118.2, 116.1, 110.7, 53.3, 49.2, 46.7, 41.7, 33.4, 25.1, 23.0, 21.7, 14.0. IR (neat): 2955, 2922, 2852, 1716, 1644, 1521, 1462, 1402, 1353, 1263, 1168, 1095, 995, 919 cm^{-1}. HRMS (ESI): calcd. for $C_{22}H_{28}NO_3S$ ([M+H]$^+$): 386.1784, found 386.1785.



3d

Run 1: Following general procedure B, 77.6 mg **2d** was used, 24 h. After flash column chromatography on silica gel (eluted with PE/EA, 10:1), 20.9 mg **3d** was obtained in 25% yield.

Run 2: Following general procedure B, 78.5 mg **2d** was used, 24 h. After flash column chromatography on silica gel (eluted with PE/EA, 10:1), 18.1 mg **3d** was obtained in 22% yield.

Average yield: 24%.

Colorless oil, TLC R_f = 0.18 (PE/EA, 5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 8.3 Hz, 2H), 7.34 (d, *J* = 8.1 Hz, 2H), 7.16 – 7.08 (m, 5H), 6.72 (d, *J* = 8.2 Hz, 1H), 5.61 (s, 1H), 5.48 (d, *J* = 8.2 Hz, 1H), 5.34 (s, 1H), 5.32 (dd, *J* = 8.8, 5.6 Hz, 1H), 3.53 (d, *J* = 11.6 Hz, 1H), 3.17 (d, *J* = 15.5 Hz, 1H), 3.13 (d, *J* = 13.9 Hz, 1H), 2.94 (d, *J* = 15.5 Hz, 1H), 2.89 (d, *J* = 13.9 Hz, 1H), 2.78 (d, *J* = 11.6 Hz, 1H), 2.43 (s, 3H), 2.11 (dd, *J* = 16.0, 8.8 Hz, 1H), 1.84 (dd, *J* = 16.0, 5.6 Hz, 1H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 206.7, 144.5, 142.6, 136.7, 134.8, 134.7, 131.4, 130.2, 127.7, 127.2, 126.7, 123.0, 121.0, 117.1, 111.0, 53.6, 49.7, 49.1, 40.8, 38.2, 21.8. IR (neat): 3090, 3031, 2927,

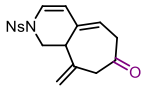
1714, 1636, 1607, 1494, 1450, 1402, 1353, 1261, 1167, 1121, 1097, 1057, 1002, 966, 913 cm^{-1}. HRMS (ESI): calcd. for $C_{25}H_{26}NO_3S$ ($[M+H]^+$): 420.1628, found 420.1627.

Following general procedure B, 89.0 mg **2e** was used, 24 h. But only a complex mixture was obtained, which was determined by ^1H NMR.

Following general procedure B, 63.4 mg **2f** was used, 24 h. But only a complex mixture was obtained, which was determined by ^1H NMR.

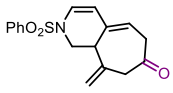
Following general procedure B, 76.2 mg **2g** was used, 24 h. But only a complex mixture was obtained, which was determined by ^1H NMR.

Following general procedure B, 66.2 mg **2h** was used, 24 h. But only a complex mixture was obtained, which was determined by ^1H NMR.



3i

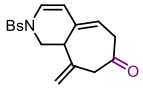
Run 1: Following general procedure B, 67.2 mg **2i** was used, 26 h. After flash column chromatography on silica gel (eluted with PE/EA, 5:1), 45.4 mg **3i** was obtained in 62% yield.
Run 2: Following general procedure B, 66.6 mg **2i** was used, 26 h. After flash column chromatography on silica gel (eluted with PE/EA, 5:1), 45.8 mg **3i** was obtained in 63% yield.
Average yield: 62%.
Yellow solid, m.p. = 152-153 ℃, TLC R_f = 0.12 (PE/EA, 5:1). ^1H NMR (400 MHz, CD_2Cl_2) δ 8.44 – 8.33 (m, 2H), 8.10 – 7.88 (m, 2H), 6.63 (d, *J* = 8.0 Hz, 1H), 5.58 (d, *J* = 8.0 Hz, 1H), 5.47 (ddd, *J* = 8.0, 5.6, 2.1 Hz, 1H), 5.12 (s, 1H), 5.10 (s, 1H), 3.76 (dd, *J* = 12.0, 4.7 Hz, 1H), 3.49 (ddd, *J* = 14.9, 5.6, 1.2 Hz, 1H), 3.30 (dm, *J* = 12.0 Hz, 1H), 3.14 (d, *J* = 16.8 Hz, 1H), 3.06 (d, *J* = 16.8 Hz, 1H), 3.00 (dd, *J* = 12.0, 12.0 Hz, 1H), 2.80 (dd, *J* = 14.9, 8.0 Hz, 1H). $^{13}C\{^1H\}$ NMR (101 MHz, CD_2Cl_2) δ 205.7, 150.8, 143.3, 141.5, 133.5, 128.7, 125.1, 123.4, 118.9, 118.4, 113.9, 48.7, 48.5, 43.8, 41.4. IR (neat): 3104, 3037, 2983, 2872, 1713, 1646, 1608, 1530, 1477, 1456, 1402, 1351, 1302, 1260, 1232, 1172, 1096, 1077, 1012, 985, 955, 924 cm^{-1}. HRMS (MALDI): calcd. for $C_{17}H_{17}N_2O_5S$ ($[M+H]^+$): 361.0853, found 361.0854.



3j

Run 1: Following general procedure B, 57.1 mg **2j** was used, 24 h. After flash column chromatography on silica gel (eluted with PE/EA, 5:1), 44.9 mg **3j** was obtained in 72% yield.
Run 2: Following general procedure B, 57.4 mg **2j** was used, 24 h. After flash column chromatography on silica gel (eluted with PE/EA, 5:1), 46.4 mg **3j** was obtained in 74% yield.
Average yield: 73%.
Colorless oil, TLC R_f = 0.23 (PE/EA, 5:1). ^1H NMR (400 MHz, $CDCl_3$) δ 7.83 – 7.78 (m, 2H), 7.66 – 7.61 (m, 1H), 7.59 – 7.53 (m, 2H), 6.67 (d, *J* = 8.0 Hz, 1H), 5.48 (d, *J* = 8.0 Hz, 1H), 5.40 (ddd, *J* = 8.3, 5.6, 2.3 Hz, 1H), 5.09 (s, 1H), 5.08 (s, 1H), 3.73 (dd, *J* = 12.1, 4.7 Hz, 1H), 3.50 (ddd, *J* =

14.9, 5.6, 1.6 Hz, 1H), 3.27 (dm, *J* = 12.1 Hz, 1H), 3.14 (d, *J* = 16.8 Hz, 1H), 3.06 (d, *J* = 16.8 Hz, 1H), 2.93 (dd, *J* = 12.1, 12.1 Hz, 1H), 2.81 (dd, *J* = 14.9, 8.3 Hz, 1H). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 206.2, 141.4, 137.6, 133.7, 133.5, 129.6, 127.2, 124.4, 118.2, 117.2, 112.3, 48.4, 48.3, 43.6, 41.2. IR (neat): 3087, 2955, 2920, 2851, 1712, 1644, 1608, 1447, 1422, 1399, 1353, 1311, 1263, 1232, 1170, 1097, 1075, 1026, 983, 956, 922 cm^{-1}. HRMS (ESI): calcd. for $C_{17}H_{18}NO_3S$ ($[M+H]^+$): 316.1002, found 316.1001.



3k

Run 1: Following general procedure B, 73.3 mg **2k** was used, 24 h. After flash column chromatography on silica gel (eluted with PE/EA, 5:1), 57.1 mg **3k** was obtained in 72% yield.

Run 2: Following general procedure B, 73.4 mg **2k** was used, 24 h. After flash column chromatography on silica gel (eluted with PE/EA, 5:1), 57.6 mg **3k** was obtained in 73% yield.

Average yield: 72%.

Yellow oil, TLC R_f = 0.26 (PE/EA, 5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 – 7.62 (m, 4H), 6.61 (d, *J* = 8.1 Hz, 1H), 5.49 (d, *J* = 8.1 Hz, 1H), 5.41 (ddd, *J* = 8.2, 5.5, 2.2 Hz, 1H), 5.09 (s, 2H), 3.71 (dd, *J* = 12.0, 4.7 Hz, 1H), 3.51 (ddd, *J* = 14.8, 5.5, 1.3 Hz, 1H), 3.30 (dm, *J* = 12.0 Hz, 1H), 3.14 (d, *J* = 16.8 Hz, 1H), 3.07 (d, *J* = 16.8 Hz, 1H), 2.91 (dd, *J* = 12.0, 12.0 Hz, 1H), 2.82 (dd, *J* = 14.8, 8.2 Hz, 1H). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 206.0, 141.2, 136.5, 133.4, 132.9, 128.6, 124.0, 118.4, 117.7, 112.7, 48.3, 43.6, 41.2. IR (neat): 2955, 2922, 2858, 1707, 1641, 1611, 1575, 1462, 1384, 1349, 1268, 1165, 1099, 1069, 981 cm^{-1}. HRMS (ESI): calcd. for $C_{17}H_{17}BrNO_3S$ ($[M+H]^+$): 394.0107, found 394.0103.

V. Studies of Au(I)-Catalyzed Enantioselective Cycloisomerization

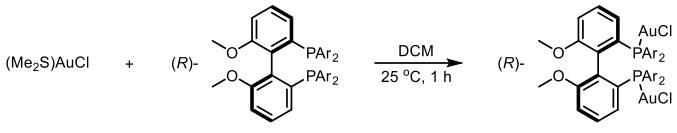
1. Preparation of Chiral Gold Pre-Catalysts

2. Optimization of Au(I)-Catalyzed Enantioselective Cycloisomerization

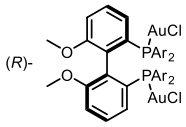
3. The Enantioselective Cycloisomerization of **1i**

1. Preparation of Chiral Gold Pre-Catalysts

The chiral gold pre-catalysts **L1**AuCl [8], **L2**Au_2Cl_2 [8], **L4**Au_2Cl_2 [9], **L5**Au_2Cl_2 [10], **L7**Au_2Cl_2 [10], **L8**Au_2Cl_2 [9], and **L10**Au_2Cl_2 [11] were synthesized according to their reported literature. By using a similar procedure [12], **L3**Au_2Cl_2, **L6**Au_2Cl_2, and **L9**Au_2Cl_2 were then synthesized here.

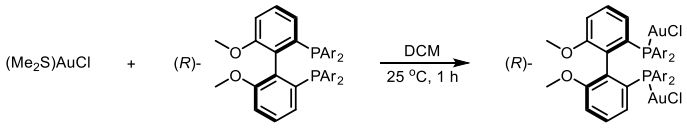


To a flame-dried glassware containing (Me_2S)AuCl (60.4 mg, 0.21 mmol) and **L3** (93.7 mg, 0.10 mmol) was added DCM (2.5 mL) at room temperature. After being stirred for 1 h at 25 ℃, the solution was concentrated. The residue was recrystallized from DCM/Et_2O to afford **L3**Au_2Cl_2 (21.7 mg, 16%).

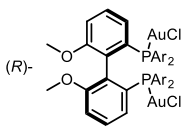


L3Au_2Cl_2

White solid, m.p. = 103-105 ℃. ^{1}H NMR (700 MHz, CD_2Cl_2) δ 7.58 – 7.55 (m, 2H), 7.05 – 7.02 (m, 2H), 7.02 – 7.00 (m, 2H), 6.75 – 6.70 (m, 4H), 6.60 – 6.55 (m, 4H), 3.81 (s, 6H), 3.80 (s, 6H), 3.78 (s, 12H), 3.69 (s, 12H), 3.22 (s, 6H). ^{13}C{^{1}H, ^{31}P} NMR (176 MHz, CD_2Cl_2) δ 158.8, 153.7, 141.21, 141.18, 130.46, 130.45, 130.35, 129.4, 127.9, 125.1, 123.7, 114.8, 112.1, 111.9, 61.0, 60.9, 56.7, 56.6, 55.2. ^{31}P{^{1}H} NMR (283 MHz, CD_2Cl_2) δ 27.3. IR (neat): 2998, 2939, 2834, 1575, 1499, 1458, 1403, 1310, 1243, 1187, 1123, 1042, 1000 cm^{-1}. HRMS (ESI): calcd. for $C_{50}H_{60}Au_2Cl_2NO_{14}P_2$ ($[M+NH_4]^+$): 1424.2192, found 1424.2152.

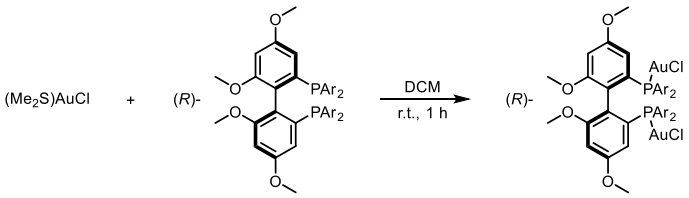


To a flame-dried glassware containing (Me_2S)AuCl (106.0 mg, 0.36 mmol) and **L6** (100.0 mg, 0.16 mmol) was added DCM (4.1 mL) at room temperature. After being stirred for 1 h at 25 ℃, the solution was concentrated. The residue was recrystallized from DCM/Et_2O to afford **L6**Au_2Cl_2 (137.3 mg, 79%).



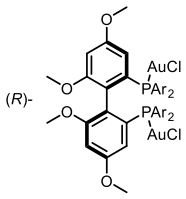
L6Au_2Cl_2

White solid, m.p. = 192-194 ℃. ^{1}H NMR (700 MHz, CD_2Cl_2) δ 7.53 – 7.47 (m, 2H), 7.45 – 7.34 (m, 8H), 7.30 – 7.19 (m, 8H), 6.98 – 6.86 (m, 4H), 2.91 (s, 6H), 2.40 (s, 6H), 2.38 (s, 6H). ^{13}C{^{1}H, ^{31}P} NMR (176 MHz, CD_2Cl_2) δ 158.8, 142.5, 142.2, 135.0, 130.1, 129.9, 127.9, 126.7, 126.4, 114.0, 54.6, 21.6. ^{31}P{^{1}H} NMR (202 MHz, CD_2Cl_2) δ 22.5. IR (neat): 3017, 2921, 2868, 2835, 1598, 1566, 1498, 1460, 1433, 1417, 1398, 1310, 1282, 1264, 1188, 1155, 1100, 1046, 1019, 996, 954 cm^{-1}. HRMS (ESI): calcd. for $C_{42}H_{44}Au_2Cl_2NO_2P_2$ ($[M+NH_4]^+$): 1120.1550, found 1120.1549.



L9, Ar = 4-MeO-3,5-(^{t}Bu)$_2$C$_6$H$_2$ — **L9**Au_2Cl_2

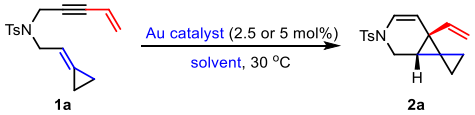
To a flame-dried glassware containing $(Me_2S)AuCl$ (48.6 mg, 0.16 mmol) and **L9** (100.0 mg, 0.08 mmol) was added DCM (2 mL) at room temperature. After being stirred for 1 h at room temperature, the solution was concentrated to afford **L9**Au_2Cl_2 in quantitative yield.



L9Au_2Cl_2

Light yellow solid, m.p. = 192-194 ℃. ^{1}H NMR (700 MHz, CD_2Cl_2) δ 7.47 – 7.40 (m, 4H), 7.31 – 7.07 (m, 4H), 6.48 – 6.41 (m, 2H), 6.37 – 6.30 (m, 2H), 3.70 (s, 6H), 3.68 (s, 6H), 3.62 (s, 6H), 2.70 (s, 6H), 1.36 (s, 36H), 1.35 (s, 36H). ^{13}C{^{1}H, ^{31}P} NMR (176 MHz, CD_2Cl_2) δ 163.0, 162.8, 161.3, 160.5, 144.8, 144.5, 133.6, 133.4, 130.4, 124.4, 123.9, 122.9, 111.6, 102.1, 65.03, 64.99, 55.7, 54.2, 36.4, 36.2, 32.1. ^{31}P{^{1}H} NMR (283 MHz, CD_2Cl_2) δ 23.3. IR (neat): 3004, 2961, 2871, 2835, 1592, 1565, 1454, 1431, 1409, 1395, 1362, 1299, 1263, 1215, 1191, 1161, 1144, 1117, 1074, 1048, 1008 cm^{-1}. HRMS (ESI): calcd. for $C_{76}H_{112}Au_2Cl_2NO_8P_2$ ($[M+NH_4]^+$): 1692.6566, found 1692.6516.

2. Optimization of Au(I)-Catalyzed Enantioselective Cycloisomerization



1a — **2a**

General procedure C:

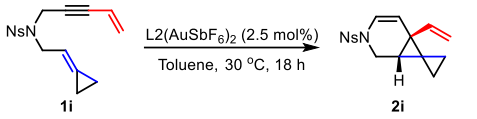
Preparation of solution of cationic Au(I) catalyst: Under nitrogen, anhydrous solvent (2.0 mL) was added to a mixture of chiral gold pre-catalyst (2.5 or 5.0 μmol **L1**AuCl or **L2**-**L10**Au_2Cl_2) and salt (using one of the following silver salts: $AgSbF_6$, $NaBAr^F{}_4$, $AgBF_4$, AgOTf, $AgNTf_2$, $AgPF_6$, 1.2 equiv. vs. gold) to abstract Cl anion. The mixture was stirred at room temperature for 30 min. The resulting suspension was left to stand until the formed solid precipitated. The supernatant was used in Au(I)-catalyzed enantioselective cycloisomerization reactions as the catalyst precursor.

General procedure of Au(I)-catalyzed enantioselective cycloisomerization: Under nitrogen, the above $Au(I)^+$ solution (2.0 mL, 2.5 or 5.0 μmol) was added to a flame-dried glassware containing

1a (0.1 mmol) at 30 ℃. The reaction was monitored by TLC. Upon completion, the reaction mixture was purified by flash column chromatography on silica gel to afford **2a**.

Following general procedure C, 60.5 mg **1a**, 8.0 mg **L2**Au_2Cl_2 and 4.1 mg $AgSbF_6$ were used, 6 h. After flash column chromatography on silica gel (eluted with PE/EA, 50:1), 33.5 mg **2a** was obtained in 55% yield and 78% e.e., as determined by HPLC analysis (chiral OD-3, hexane/^{i}PrOH = 100/1, 0.6 mL/min, 210 nm, 25 ℃), t_r, 17.43 min (major), 19.01 min (minor).

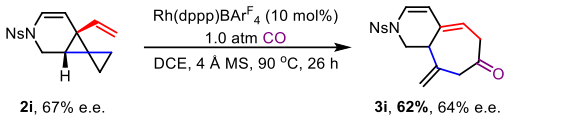
3. The Enantioselective Cycloisomerization of **1i** (attention: only relative configuration was given, not the absolute configuration for both **2i** and **3i**)



Run 1: **65%**, 67% e.e.
Run 2: **64%**, 66% e.e.

Run 1: Following general procedure C, 66.3 mg **1i** was used, 18 h. After flash column chromatography on silica gel (eluted with PE/EA, 35:1), 43.0 mg **2i** was obtained in 65% yield and 67% e.e., as determined by HPLC analysis (chiral OD-3, hexane/^{i}PrOH = 95/5, 0.6 mL/min, 210 nm, 25 ℃), t_r, 38.23 min (major), 41.61 min (minor).
Run 2: Following general procedure C, 66.5 mg **1i** was used, 18 h. After flash column chromatography on silica gel (eluted with PE/EA, 35:1), 42.7 mg **2i** was obtained in 64% yield and 66% e.e..

We performed the Rh(I)-catalyzed [6+1] cycloaddition of chiral **2i** and CO, in which desired **3i** was obtained in 62% yield and 64% e.e.. **3i** was a yellow solid and we then tried to recrystallize it to improve its e.e. value. However, it was a pity that the recrystallization from DCM/^{n}hexane only offered **3i** in a similar 65% e.e..

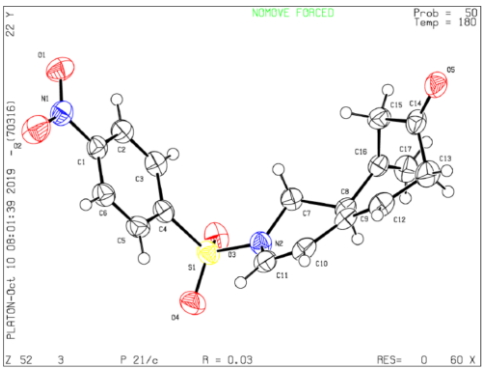


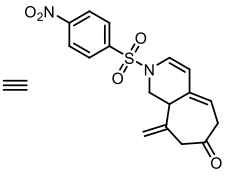
recrystallization from DCM/^{n}hexane:
65% e.e.

Following general procedure B, 66.4 mg **2i** (67% e.e.) was used, 26 h. After flash column chromatography on silica gel (eluted with PE/EA, 5:1), 45.0 mg **3i** was obtained in 62% yield and 64% e.e., as determined by HPLC analysis (chiral OD-3, hexane/^{i}PrOH = 80/20, 0.5 mL/min, 210 nm, 25 ℃), t_r, 62.26 min (major), 66.55 min (minor).

VI. X-ray Crystal Analysis

Crystallographic Data of Compound **3i**





3i
CCDC number: 2105972

Table S1 Crystal data and structure refinement for compound **3i**

Identification code	3i
Empirical formula	$C_{17}H_{16}N_2O_5S$
Formula weight	360.38
Temperature/K	179.98(11)
Crystal system	Monoclinic
Space group	$P2_1/c$
a/Å	13.5958(2)
b/Å	7.67610(10)
c/Å	15.8863(2)
α/°	90
β/°	97.4480(10)
γ/°	90
Volume/Å^3	1643.95(4)
Z	4
ρ_{calc}g/cm^3	1.456
μ/mm^{-1}	2.038
F(000)	752.0
Crystal size/mm^3	0.43 × 0.4 × 0.22
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	11.234 to 133.146
Index ranges	$-16 \le h \le 16$, $-9 \le k \le 4$, $-18 \le l \le 18$
Reflections collected	8854
Independent reflections	2879 [R_{int} = 0.0194, R_{sigma} = 0.0181]
Data/restraints/parameters	2879/0/226
Goodness-of-fit on F^2	1.026
Final R indexes [I>=2σ (I)]	R_1 = 0.0334, wR_2 = 0.0952

Final R indexes [all data] $R_1 = 0.0345$, $wR_2 = 0.0962$

Largest diff. peak/hole / e $Å^{-3}$ 0.20/-0.37

VII. DFT Calculations

1. Energy profile for the [6+1] reaction of **2a'**
2. The barrierless β–C elimination of **Int3**
3. The direct reductive elimination of **Int5**
4. Discussion of CO concentration to the computed energy surface
5. Energy data
6. Cartesian coordinates of all stationary points

1. Energy profile for the [6+1] reaction of **2a'**

Here, we present Gibbs free energies and enthalpies in the gas phase (ΔG_{gas} and ΔH_{gas}) for the [6+1] reaction of **2a'** in Figure S1.

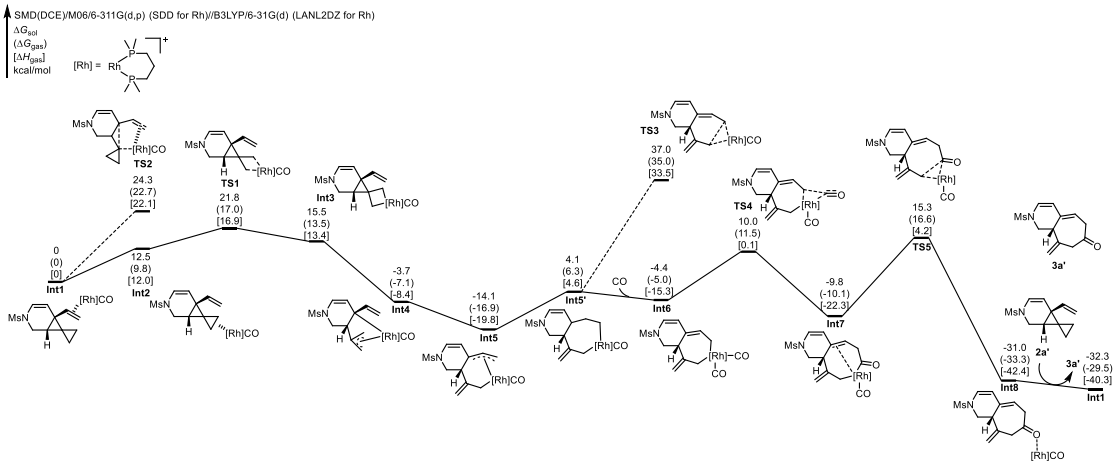
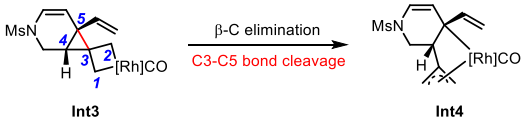


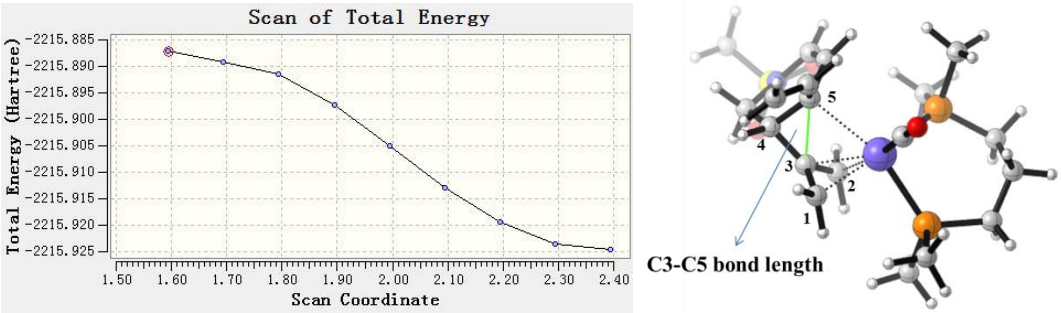
Figure S1 Energy profile for the [6+1] reaction of **2a'**

2. The barrierless β–C elimination of **Int3**

Efforts to locate a transition state of the β–C elimination (C3-C5 bond cleavage, Scheme S1) from **Int3** failed. Then, we did a relaxed scan of the C3-C5 bond at B3LYP/6-31G(d) (LANL2DZ for Rh) level in Scheme S2. The single-point energies only decrease with the C3-C5 bond increasing from 1.6 Å to 2.4 Å, which indicates that it is a barrierless process.



Scheme S1 The β–C elimination of **Int3**



Scheme S2 The scan of C3-C5 bond in **Int3**

3. The direct reductive elimination of **Int5**

A direct reductive elimination (via **TS3**) of **Int5** to afford an aza-6/6 bicyclic compound is also taken into consideration. As shown in Figure 1a or Figure S2, it has a barrier of 51.5 kcal/mol, which is higher than that of the CO insertion/reductive elimination process (29.4 kcal/mol). Therefore, this direct reductive elimination of **Int5** can be excluded for consideration.

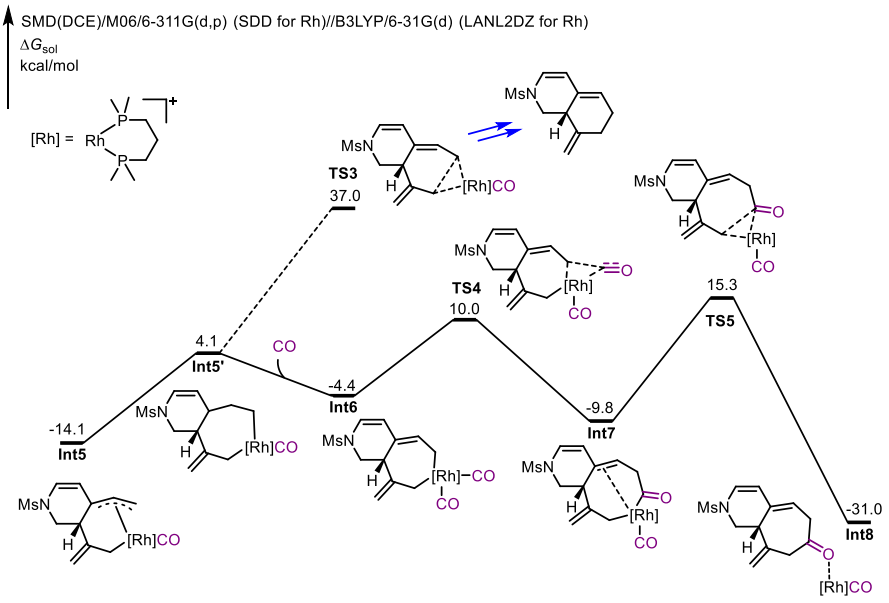


Figure S2 The direct reductive elimination of **Int5**

4. Discussion of CO concentration to the computed energy surface

Experimentally, we used 1.0 atm CO and the concentration of CO in the reaction system is near 5.5 mM [13]. As we all know, the free-energy change of 1.0 mol of an ideal gas from 1.0 atm (24.46 L/mol) to 1.0 M (1.0 mol/L) is given by

$$\Delta G^{gas\rightarrow sol} = RT\ln\frac{V^{gas}}{V^{sol}} = RT\ln\frac{24.46}{1.0} = 1.89\ \text{kcal/mol}$$

So in the case for 5.5 mM of CO,

$$\Delta G^{gas\rightarrow sol} = RT\ln\frac{\frac{1.0\times 0.0055}{1.0}}{\frac{24.46}{24.46\times 24.46}} = 8.314\times 298.15\times\ln(24.46\times 0.0055)\div 4186$$

$$\Delta G^{gas\rightarrow sol} = 1.89 - 3.08 = \Delta G^{gas} - 1.19\ \text{kcal/mol}$$

In Figure 1, we used 5.5 mM of CO to draw the surface of free energy of the [6+1] reaction. If we used 1.0 M of CO, the relative energies of all species after **Int5'** will be declined by 3.1 kcal/mol in Figure S3. The overall activation free energy of this [6+1] reaction is therefore 26.3 kcal/mol at room temperature.

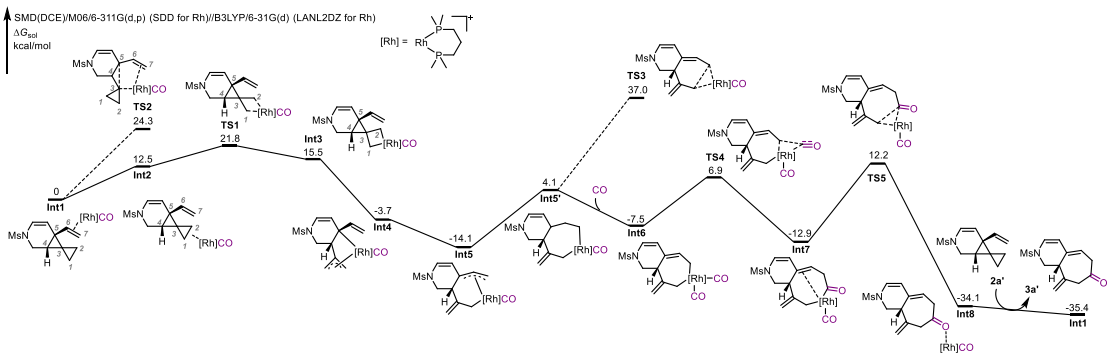


Figure S3 Energy profile for the [6+1] reaction of **2a'** at 1.0 M CO

5. Energy data [a]

	E [b]	H [b]	G [b]	E [c]	$\Delta G_{solvation}$ [d]
Int1	-2214.452827	-2213.920573	-2214.021149	-2215.056675	-0.083018
Int2	-2214.436968	-2213.905267	-2214.009200	-2215.037078	-0.078792
TS1	-2214.425721	-2213.896176	-2213.996452	-2215.027054	-0.075534
TS2	-2214.413718	-2213.883299	-2213.981437	-2215.021179	-0.080391
Int3	-2214.436663	-2213.905692	-2214.006078	-2215.034024	-0.079953
Int4	-2214.465272	-2213.933366	-2214.031882	-2215.069724	-0.077617
Int5	-2214.489231	-2213.956681	-2214.052649	-2215.088556	-0.078544
Int5'	-2214.454173	-2213.923122	-2214.021020	-2215.048148	-0.086575
TS3	-2214.405723	-2213.875725	-2213.973881	-2215.001057	-0.079918
CO	-113.306914	-113.298573	-113.321016	-113.283642	0.005575
Int6	-2327.788566	-2327.245495	-2327.349066	-2328.367279	-0.081336
TS4	-2327.765044	-2327.223293	-2327.325022	-2328.341444	-0.084779
Int7	-2327.803597	-2327.259482	-2327.359836	-2328.379539	-0.082033
TS5	-2327.756463	-2327.214022	-2327.314028	-2328.335699	-0.084474
Int8	-2327.852209	-2327.306243	-2327.411522	-2328.413475	-0.078730
2a'	-1031.394460	-1031.133460	-1031.191963	-1031.137245	-0.020122
3a'	-1144.782221	-1144.507517	-1144.568120	-1144.490619	-0.023955

[a] in a.u.

[b] Computed at the B3LYP/6-31G(d) (LANL2DZ for Rh) level

[c] Computed at the M06/6-311G(d,p) (SDD for Rh) level

[d] Computed at the SMD(DCE)/B3LYP/6-31G(d) (LANL2DZ for Rh) level

6. Cartesian coordinates of all stationary points

Int1

C	3.91963100	1.37328500	-0.70907800
C	1.46715000	0.41797400	-0.74613900
C	1.66191200	0.31222400	0.72977800
C	2.87359000	0.37172300	1.30607100
C	2.30292000	-0.50074400	-1.61906700
C	0.17592600	1.00159200	-1.19913300
C	-0.57170300	0.61608400	-2.28955800
C	2.99535900	-1.80243000	-1.43845900
C	2.20082300	-1.51968800	-2.70639000
N	4.03429700	0.69789000	0.58950600
S	5.51635900	-0.02306900	1.03487800
O	5.21649400	-0.90072700	2.16373400
O	6.15463400	-0.51581200	-0.18754300
H	3.83019900	2.45607500	-0.54145800
H	4.83888400	1.18937600	-1.27187900

H	0.79775700	0.09044700	1.34838200
H	3.02422300	0.16825700	2.35930600
H	-0.06199500	1.94997100	-0.71683200
H	-1.31382500	1.27833800	-2.72235800
H	-0.24917000	-0.20758900	-2.91656400
H	4.08069800	-1.81410000	-1.49290600
H	2.57199100	-2.51303600	-0.73275500
H	1.27635400	-2.07342100	-2.84369500
H	2.74617400	-1.32961300	-3.62817400
C	6.49018800	1.36987800	1.63334700
H	7.47290700	0.97661300	1.90488100
H	6.59068400	2.10818800	0.83522400
H	5.99496900	1.79703600	2.50693200
C	2.72080100	0.90886100	-1.52402200
H	2.52130100	1.54385100	-2.38824400
H	-1.90665500	-1.90453100	2.76740400
C	-2.87432700	-1.40816300	2.64936300
P	-3.33480400	-1.37828500	0.86219300
H	-2.78305700	-0.39322400	3.04512700
H	-3.62646500	-1.95237300	3.23156200
C	-5.07810800	-0.74390700	0.84949400
C	-3.59235900	-3.16234600	0.47214000
C	-5.27778700	0.73951000	1.20110900
H	-5.48465900	-0.95025000	-0.14894000
H	-5.64186500	-1.36731900	1.55515600
H	-3.92631500	-3.27588300	-0.56345800
H	-4.34719000	-3.59198800	1.13933300
H	-2.65766400	-3.71624100	0.59543600
H	-4.83245900	0.96659100	2.17814700
H	-6.35408500	0.90722400	1.32565200
C	-4.77393900	1.72868900	0.13699500
P	-2.93388900	1.82471600	-0.07537400
H	-5.19512700	1.46817600	-0.84259000
H	-5.12756200	2.73942300	0.37589700
C	-2.35734600	2.68364400	1.45626300
C	-2.78605700	3.14295000	-1.36138200
H	-2.89395600	3.62831500	1.59653300
H	-2.51497500	2.05204200	2.33495000
H	-1.28574200	2.89125300	1.38311100
H	-1.73728000	3.39385600	-1.54354800
H	-3.23130000	2.80335000	-2.30141800
H	-3.30688300	4.04879200	-1.03357700
Rh	-1.76827000	-0.25624800	-0.49311200
C	-0.87916600	-1.91468600	-0.76428400
O	-0.35516200	-2.92542700	-0.92041100

Int2

C	-3.99261200	-0.45513600	1.09970400
C	-3.41298400	1.97244700	0.32759400
C	-4.09711500	1.54398300	-0.92578700
C	-4.29942000	0.25845200	-1.24788000
C	-2.08947400	1.28183800	0.61616100
C	-3.61884300	3.39022300	0.75180100
C	-3.05856600	4.00550100	1.79698500
C	-1.06370900	0.66129800	-0.24756000
C	-0.70611000	1.73975900	0.86519800
N	-4.00778500	-0.78577500	-0.33340400
S	-3.20869700	-2.16950700	-0.89757000
O	-2.76590300	-1.89196400	-2.26300500
O	-2.24601600	-2.58658700	0.13673700
H	-5.03037600	-0.35889000	1.44361800
H	-3.52791900	-1.28421000	1.63733700
H	-4.42185300	2.31302700	-1.62012600
H	-4.72823900	-0.04501400	-2.19574600
H	-4.30586700	3.95464700	0.12255400
H	-3.28639400	5.04259300	2.02164800
H	-2.36854400	3.50796100	2.47474400
H	-0.85022600	-0.39088400	-0.08390800
H	-1.05173100	0.97518900	-1.28703400
H	-0.45462000	2.74479500	0.53823700
H	-0.22688300	1.43106900	1.79198700
C	-4.50287200	-3.41922900	-0.95575400
H	-4.04270100	-4.34709300	-1.30384600
H	-4.91465700	-3.55074600	0.04665400
H	-5.27380500	-3.09083300	-1.65525000
C	-3.26513300	0.85102400	1.38879000
H	-3.33897100	1.18273300	2.42459300
H	4.94153200	2.10489000	-0.11716300
C	5.06482500	1.02401700	-0.00250400
P	3.69521100	0.15954600	-0.88532400
H	5.04818400	0.79503800	1.06597000
H	6.03572600	0.72914800	-0.41667100
C	4.15607600	-1.63597600	-0.82324800
C	4.02419100	0.56290600	-2.65362400
C	4.11709400	-2.32580600	0.55010800
H	3.49242200	-2.15639000	-1.52533900
H	5.17108000	-1.70303200	-1.23595300
H	3.28829500	0.06651800	-3.29262700

H	5.02844900	0.22967800	-2.93661400
H	3.95334900	1.64187000	-2.81648900
H	4.74354000	-1.78221300	1.26867000
H	4.58745400	-3.30986800	0.43799900
C	2.70747100	-2.54517000	1.12495900
P	1.78185700	-1.00143300	1.56733700
H	2.08690500	-3.08868700	0.40111400
H	2.76823400	-3.16903000	2.02552300
C	2.65018900	-0.37398300	3.07260300
C	0.21102500	-1.67310200	2.26263600
H	2.71514000	-1.15700800	3.83610400
H	3.65856100	-0.03106400	2.82720300
H	2.09985100	0.47700600	3.48512800
H	-0.37453200	-0.86427300	2.71033600
H	-0.39511600	-2.14910500	1.48659100
H	0.43814400	-2.40730500	3.04353300
Rh	1.59956400	0.67009000	-0.17547900
C	1.53339200	2.12043100	-1.40865200
O	1.46795400	3.03798000	-2.09755900

TS1

C	-3.82070300	-0.08987800	1.13430800
C	-2.75969300	2.17628400	0.44553200
C	-3.49389000	1.93663600	-0.82948900
C	-3.96650700	0.73448100	-1.19217800
C	-1.56465500	1.22325400	0.68135500
C	-2.64262100	3.59772400	0.88428400
C	-2.47877100	4.04960400	2.13028100
C	-0.84028300	0.40562100	-0.31397900
C	-0.20320900	1.53544900	1.15769900
N	-3.93121900	-0.37049200	-0.30479200
S	-3.50201500	-1.89867500	-0.89801900
O	-3.20588600	-1.73688200	-2.31976900
O	-2.50066900	-2.47958800	0.01805500
H	-4.80708700	0.21834500	1.50386400
H	-3.53797400	-1.01265200	1.64563200
H	-3.62730400	2.77388800	-1.50779300
H	-4.42907100	0.55171300	-2.15434200
H	-2.67652100	4.32140400	0.06935500
H	-2.37922400	5.11199100	2.32993600
H	-2.45572200	3.39623000	2.99936800
H	-0.91256800	-0.67037800	-0.19585100
H	-0.89111600	0.75685600	-1.34268600
H	0.13135600	2.56231900	1.02735900
H	0.10769800	1.06680000	2.08857800
C	-5.00817800	-2.86641900	-0.71822700
H	-4.78317500	-3.87927400	-1.06091800
H	-5.30315100	-2.87925800	0.33291300
H	-5.78547100	-2.41618600	-1.33800900
C	-2.82686500	1.02173000	1.44137300
H	-2.79918700	1.28958600	2.49752100
H	0.03906500	-2.91487300	-0.28312300
C	1.08396600	-2.96428700	0.03910800
P	1.46601300	-1.50627900	1.10647300
H	1.71891700	-2.97725900	-0.85057900
H	1.23204900	-3.89430400	0.59932300
C	3.05834500	-1.96109100	1.94390200
C	0.24611200	-1.70574700	2.47828700
C	4.30743200	-1.99526700	1.04678900
H	3.20830300	-1.24861500	2.76560100
H	2.91030200	-2.94693900	2.40240200
H	0.39774200	-0.94449200	3.24942000
H	0.35752900	-2.69403300	2.93705600
H	-0.76975600	-1.62376500	2.08196100
H	4.14911000	-2.67172100	0.19741100
H	5.12156900	-2.44281300	1.62913500
C	4.79106200	-0.62035300	0.55594400
P	3.72688600	0.22893400	-0.70420000
H	4.88689200	0.06735000	1.40606600
H	5.79076800	-0.71793300	0.11357600
C	3.98802600	-0.74828100	-2.24904600
C	4.68909500	1.77095500	-1.02147700
H	5.05668700	-0.84261200	-2.47242600
H	3.55475500	-1.74765000	-2.15372400
H	3.49268500	-0.24562100	-3.08496200
H	4.26156900	2.31418500	-1.86906500
H	4.65000400	2.42042100	-0.14193300
H	5.73486200	1.53448100	-1.24519700
Rh	1.43453000	0.57910300	-0.13611000
C	1.42775300	2.12951900	-1.24054600
O	1.39910400	3.05121800	-1.92662600

TS2

C	3.44785400	-1.61631000	0.02805100
C	0.99885200	-1.07641800	-0.59462600
C	1.57466700	-0.10264300	-1.52383000
C	2.88050000	0.24167800	-1.49695500
C	1.25904500	-0.64467400	1.12924100

C	-0.26514600	-1.71698100	-0.95826200
C	-0.95630800	-2.57965400	-0.06524500
C	1.87281900	0.53195000	1.79227500
C	1.04700300	-0.45945700	2.60720000
N	3.79978300	-0.36655400	-0.65384900
S	5.25498000	0.44797900	-0.25285300
O	5.14575800	1.77557700	-0.85116900
O	5.45969800	0.25120000	1.18246700
H	3.68174700	-2.46390200	-0.63044000
H	4.05740900	-1.70024100	0.93100400
H	0.91880200	0.38868000	-2.23343200
H	3.28340200	1.02177200	-2.13165500
H	-0.52384300	-1.67783700	-2.01122800
H	-1.74283500	-3.21479200	-0.46162700
H	-0.46450200	-2.99130100	0.81080700
H	2.95260800	0.54154600	1.92641800
H	1.45043000	1.51965500	1.63112000
H	0.09573700	-0.12294800	2.99839300
H	1.57367400	-1.15313200	3.26182000
C	6.52013700	-0.48475900	-1.13118300
H	7.47916100	-0.02128700	-0.88632300
H	6.50725600	-1.52106100	-0.78746900
H	6.32751300	-0.41849400	-2.20339500
C	1.95999000	-1.70367200	0.38736700
H	1.70363400	-2.72416100	0.67753700
H	0.67937200	2.40739000	-0.58783800
C	-0.32249300	2.81784300	-0.73686700
P	-1.54845100	1.93752800	0.33125900
H	-0.58827600	2.68310200	-1.79033300
H	-0.31256200	3.88951200	-0.50931400
C	-3.14298500	2.77142500	-0.13528800
C	-1.26988500	2.69104200	1.99780800
C	-3.87261900	2.17000800	-1.34500900
H	-3.79987500	2.73566200	0.74302500
H	-2.91723400	3.82964300	-0.31503600
H	-2.05158400	2.34911700	2.68330600
H	-1.30360100	3.78457400	1.93838700
H	-0.30339200	2.39420100	2.41156600
H	-3.20209500	2.10580800	-2.21269700
H	-4.67334000	2.85831300	-1.63998700
C	-4.50884800	0.80349200	-1.04760900
P	-3.36226400	-0.65266800	-0.97149300
H	-5.04543100	0.84311100	-0.09112200
H	-5.25382500	0.55727300	-1.81468900
C	-3.11543000	-1.07872000	-2.75171800
C	-4.51035600	-1.97875500	-0.39839000
H	-4.08540500	-1.16669300	-3.25327800
H	-2.52291100	-0.30851000	-3.25310500
H	-2.59235200	-2.03456600	-2.84534500
H	-4.02089800	-2.95468700	-0.44456600
H	-4.80649300	-1.79425800	0.63800500
H	-5.40722800	-2.00286100	-1.02712900
Rh	-1.46011700	-0.49924100	0.34073100
C	-2.37181800	-0.81681300	2.12276100
O	-3.07484500	-1.23414400	2.93038700

Int3

C	-3.41766400	-0.20717900	1.00666000
C	-2.61240900	1.98701500	-0.10694200
C	-3.18606800	1.37266000	-1.33655100
C	-3.47348500	0.06641200	-1.44884400
C	-1.29084800	1.31034000	0.42582200
C	-2.76994700	3.46578600	-0.00108600
C	-2.92858000	4.18726200	1.11129700
C	-0.53781000	0.30194500	-0.39342500
C	-0.15855900	2.09368200	1.08112700
N	-3.36284000	-0.80540500	-0.33623800
S	-2.75585400	-2.36966100	-0.54884100
O	-2.25776500	-2.45597500	-1.92186500
O	-1.86675000	-2.66554100	0.59063700
H	-4.46501200	0.02571700	1.23981600
H	-3.06599000	-0.94831500	1.72698700
H	-3.36827300	2.01699700	-2.19152300
H	-3.83038100	-0.38013300	-2.36907800
H	-2.73941500	3.98854300	-0.95808700
H	-3.01876300	5.26835900	1.06836900
H	-2.99113200	3.74063600	2.10053500
H	-0.55321100	-0.72654600	-0.03991800
H	-0.65998300	0.35464700	-1.47524600
H	-0.14861700	3.15592100	0.82962900
H	-0.09767200	1.97429300	2.16456100
C	-4.20073100	-3.42977100	-0.38756700
H	-3.85990100	-4.46179500	-0.50014900
H	-4.64199700	-3.28114000	0.59992300
H	-4.91039500	-3.17364000	-1.17636000
C	-2.61023500	1.08005600	1.10695000
H	-2.71975800	1.56612600	2.07629700
H	4.93946900	0.99153300	-1.43702900

C	4.74197600	-0.04852500	-1.15868100
P	2.92822900	-0.39281800	-1.27751500
H	5.09846800	-0.19642700	-0.13490600
H	5.30959300	-0.70548000	-1.82698900
C	2.80479700	-2.21686100	-0.96460300
C	2.61206900	-0.28773300	-3.09337000
C	3.00056900	-2.65407700	0.49821300
H	1.81846000	-2.53799600	-1.32249600
H	3.54914100	-2.71199600	-1.60113800
H	1.56544600	-0.53010300	-3.30240400
H	3.25340900	-0.98310900	-3.64549500
H	2.80759300	0.72885900	-3.44870000
H	3.94432800	-2.25770500	0.89549700
H	3.11876900	-3.74410100	0.50357400
C	1.83429300	-2.32116500	1.44560700
P	1.57646400	-0.53939400	1.89748200
H	0.88550500	-2.67472000	1.02130900
H	1.97186300	-2.85961000	2.39200200
C	3.03157600	-0.09299400	2.94418700
C	0.19960100	-0.69117800	3.11223800
H	3.16022900	-0.81817200	3.75524900
H	3.94788900	-0.06557700	2.34749100
H	2.87895100	0.89920600	3.38011700
H	-0.05171600	0.27979100	3.54529400
H	-0.68147200	-1.10329700	2.61258000
H	0.49459200	-1.37159000	3.91799900
Rh	1.38867800	1.01894400	0.07441100
C	1.27312000	2.36939100	-1.30365600
O	1.21984700	3.18570900	-2.10437500

Int4

C	-3.00649300	1.43005600	0.67455600
C	-0.96119000	1.68034700	-0.89533700
C	-1.70900800	0.77319300	-1.75428400
C	-2.79014900	0.06486200	-1.35184600
C	-0.51841100	1.27573300	1.42254200
C	-0.36356900	2.83234800	-1.60290300
C	-0.22993200	4.10113100	-1.18521600
C	-0.46753000	-0.12653100	1.62768900
C	0.66899000	2.00889000	1.67057600
N	-3.30169200	0.19811600	-0.06394800
S	-4.29414300	-1.01479900	0.60521800
O	-4.16056200	-2.16292600	-0.29081200
O	-3.94659200	-1.09091300	2.02376300
H	-3.66693100	2.22413000	0.30257400
H	-3.22172200	1.26269500	1.73220200
H	-1.40900500	0.69239300	-2.79381000
H	-3.30465700	-0.63482500	-1.99951200
H	-0.03728300	2.60184500	-2.61758400
H	0.19472600	4.85236000	-1.84331100
H	-0.53895800	4.45216200	-0.20502100
H	-1.31039200	-0.74444500	1.34370800
H	0.11369600	-0.50378600	2.46257700
H	0.72924400	3.05191900	1.37613300
H	1.30790800	1.72713400	2.50077400
C	-5.96823300	-0.36442300	0.46941100
H	-6.63315400	-1.10847100	0.91524500
H	-6.03449700	0.57459800	1.02286400
H	-6.20929800	-0.22228100	-0.58562200
C	-1.55044800	1.91073500	0.50378700
H	-1.57919600	2.98106000	0.72382200
H	0.14061300	-0.66156700	-3.42189500
C	0.96342500	-1.30223900	-3.10041200
P	0.90928500	-1.55627800	-1.27034900
H	1.90473100	-0.81928700	-3.38128300
H	0.88846100	-2.26137600	-3.62409300
C	2.30552500	-2.76942400	-1.03445900
C	-0.53946500	-2.66731200	-1.01748400
C	3.70330000	-2.18475100	-0.76803500
H	2.02296400	-3.43638500	-0.21011300
H	2.32285600	-3.39135100	-1.93769600
H	-1.47589200	-2.14830300	-1.22449200
H	-0.56153000	-3.00605000	0.02272200
H	-0.46378400	-3.54105700	-1.67405100
H	3.89635500	-1.31489800	-1.40993200
H	4.44946200	-2.93538300	-1.05388600
C	3.93644400	-1.83435700	0.70987600
P	2.99591500	-0.35495800	1.35280200
H	3.65885200	-2.69539800	1.33051200
H	5.00171700	-1.64753200	0.89212300
C	4.30776800	0.94608800	1.43693800
C	2.76864400	-0.80056500	3.13453500
H	5.14022300	0.62105400	2.07051700
H	4.68976800	1.15479300	0.43304700
H	3.89256000	1.87407200	1.84034600
H	2.35140200	0.03768700	3.70047300
H	2.08871000	-1.65296500	3.22777600
H	3.73159600	-1.07095600	3.58148200

Rh	1.02515800	0.46816600	0.04905500
C	2.19854600	1.42000900	-1.15111300
O	2.92455400	1.97592600	-1.84665600

Int5

C	-3.25106900	-1.28420700	-0.81398200
C	-1.25187500	-1.42093300	0.70546100
C	-2.09235200	-0.82406400	1.70081400
C	-3.29074600	-0.24686100	1.39459100
C	-1.00471300	-0.13054600	-1.45163100
C	-0.11514000	-2.15098000	1.07554700
C	0.89530800	-2.67914800	0.20502600
C	-1.64382000	0.93988700	-1.94870200
C	0.47057300	-0.32524100	-1.58516300
N	-3.84365800	-0.33630000	0.14404800
S	-5.31459600	0.48446900	-0.22198300
O	-5.48858200	1.46492200	0.84438300
O	-5.21866200	0.85560500	-1.63086000
H	-3.61727800	-2.29187200	-0.57185900
H	-3.58615600	-1.02089500	-1.81768300
H	-1.75519400	-0.78926100	2.73173400
H	-3.86992500	0.30624700	2.12548300
H	0.02503600	-2.28854500	2.14635900
H	1.60140000	-3.37389300	0.65285100
H	0.64678300	-2.92231000	-0.82432100
H	-2.71629500	1.08818500	-1.88776400
H	-1.08865500	1.71231100	-2.47629500
H	0.67414400	-1.25025700	-2.13637600
H	0.89964000	0.50114200	-2.15645300
C	-6.57538900	-0.79197100	-0.05568500
H	-7.52877600	-0.32314700	-0.31265300
H	-6.35981300	-1.60464700	-0.75234400
H	-6.59112500	-1.14315600	0.97770700
C	-1.71351600	-1.29079600	-0.74913400
H	-1.40981000	-2.20460400	-1.27736000
H	1.91803100	2.10168900	3.00806900
C	2.37621600	2.47857700	2.08845800
P	1.42905600	1.86232400	0.62287400
H	3.41234300	2.12846100	2.06020000
H	2.37593400	3.57343100	2.12141800
C	2.24133900	2.76936700	-0.78185500
C	-0.17878100	2.74185800	0.82258000
C	3.65935400	2.28998300	-1.15562300
H	1.57899600	2.69948200	-1.65312500
H	2.28066300	3.83074100	-0.50586600
H	-0.65365700	2.41286800	1.75224400
H	-0.84883300	2.49682000	-0.00511900
H	-0.02738400	3.82606100	0.86537400
H	4.30206700	2.27122800	-0.26582000
H	4.09908700	3.04987300	-1.81257100
C	3.74528400	0.94416800	-1.90371800
P	3.42634600	-0.59553300	-0.91274000
H	3.04501400	0.93805700	-2.74705200
H	4.74953300	0.83261300	-2.33321600
C	4.96639900	-0.79627800	0.08254000
C	3.58584700	-1.92734700	-2.17547800
H	5.84946500	-0.78861000	-0.56568700
H	5.05884600	0.01030000	0.81542400
H	4.93374500	-1.74705900	0.62294100
H	3.55475900	-2.90338600	-1.68285300
H	2.76210500	-1.87291800	-2.89224900
H	4.53342600	-1.83109100	-2.71680500
Rh	1.44234000	-0.56727000	0.32594700
C	2.32836600	-0.81704600	2.08389100
O	2.83811300	-0.96633900	3.10020300

Int5'

C	-3.36553500	-0.45804000	1.17105500
C	-1.86606600	1.53309100	0.72855000
C	-3.01013400	2.12766100	0.10054700
C	-4.13271200	1.41727700	-0.20396800
C	-1.12270500	-0.70772900	-0.12071200
C	-0.73340300	2.25807800	0.99535800
C	0.48291400	1.77268100	1.59814400
C	-1.67157800	-1.03129500	-1.30663400
C	0.26915200	-1.09967000	0.21720600
N	-4.29057200	0.10241700	0.17649800
S	-5.70133900	-0.77124200	-0.28061800
O	-6.23983300	-0.06661900	-1.43940800
O	-5.30086600	-2.17358300	-0.32255300
H	-3.69404900	-0.14126200	2.17144100
H	-3.41456900	-1.54575900	1.10805700
H	-2.96634600	3.16931400	-0.20159200
H	-4.94556100	1.83688400	-0.78514400
H	-0.75343000	3.31421800	0.72499000
H	1.10457500	2.58722800	1.96476100
H	0.34162200	1.00900800	2.38840500
H	-2.69838800	-0.80039700	-1.56482400

H	-1.10399200	-1.58451500	-2.05186700
H	0.30275200	-1.56727200	1.21874300
H	0.62810600	-1.83404000	-0.50779900
C	-6.82823000	-0.54140600	1.10792100
H	-7.73759500	-1.09831900	0.86807400
H	-6.37148100	-0.94480100	2.01395300
H	-7.05219200	0.52181800	1.21309700
C	-1.91353600	0.02985500	0.96811700
H	-1.41653800	-0.18401900	1.92251100
H	2.99727200	3.24884500	-0.95865300
C	3.21545400	2.38906600	-1.59891400
P	1.90697800	1.10649000	-1.37931600
H	4.19873400	1.99705700	-1.32484000
H	3.24575600	2.72483400	-2.64149600
C	2.33137700	-0.18098400	-2.64954700
C	0.42251800	1.91061800	-2.09632300
C	3.58268200	-1.04825100	-2.40433100
H	1.44610200	-0.81655000	-2.77013300
H	2.45267200	0.36825200	-3.59250400
H	0.22227700	2.84888500	-1.57479200
H	-0.44953900	1.25935600	-1.99515700
H	0.60111400	2.12070400	-3.15667400
H	4.43935400	-0.41942300	-2.12809600
H	3.85369600	-1.49737200	-3.36719500
C	3.40900000	-2.19755700	-1.39399100
P	3.35360900	-1.68800100	0.39402100
H	2.48390700	-2.74590200	-1.61049000
H	4.23004900	-2.91642500	-1.50940000
C	5.13984100	-1.47168000	0.81934500
C	2.93087300	-3.26941200	1.25183600
H	5.71318200	-2.37540200	0.58604900
H	5.56729100	-0.63105600	0.26419100
H	5.24121700	-1.25710800	1.88778600
H	3.04202800	-3.13977000	2.33297400
H	1.89392800	-3.54840900	1.04314600
H	3.58920300	-4.08185100	0.92497300
Rh	1.84668100	0.26508900	0.75675200
C	3.34158800	1.34862100	1.48610400
O	4.21142700	1.97199200	1.89557300

TS3

C	3.65603800	-1.46501700	-0.44529200
C	1.92333600	-0.26836100	-1.85488600
C	2.92379300	0.73740200	-2.05072300
C	4.03183300	0.81145300	-1.26167900
C	1.19304000	-1.05189600	0.36255000
C	0.66610700	-0.19781700	-2.40772500
C	-0.33027600	-1.15625200	-2.06610300
C	1.63299900	-0.56706500	1.53712600
C	-0.24193200	-1.38365100	0.15405200
N	4.32357800	-0.15931700	-0.32978000
S	5.62785200	0.05424000	0.77195100
O	5.92265900	1.48291300	0.75972500
O	5.23430700	-0.66022400	1.98397300
H	4.14359700	-2.03119000	-1.25088400
H	3.78608000	-2.00623900	0.49288500
H	2.74464500	1.53082300	-2.76883000
H	4.71155100	1.65529900	-1.29092500
H	0.38492300	0.66544600	-3.00610300
H	-1.30847300	-1.06271600	-2.54449600
H	-0.03710900	-2.19663400	-1.98930600
H	2.67994600	-0.36897500	1.74311300
H	0.94794600	-0.39205000	2.36348900
H	-0.42605100	-2.45096400	0.02821300
H	-0.81198400	-1.04791100	1.03698500
C	7.00019200	-0.83192200	0.01134000
H	7.84498900	-0.74969400	0.69998700
H	6.72494100	-1.88056400	-0.11826900
H	7.24201100	-0.36065400	-0.94318400
C	2.16309600	-1.33397100	-0.79861600
H	1.88747900	-2.31475200	-1.21143500
H	-2.19778100	3.85319000	-0.98421300
C	-2.46307100	3.48770100	0.01263500
P	-1.48354900	1.97020300	0.40337900
H	-3.53497500	3.27169500	0.01975100
H	-2.25548900	4.27675600	0.74373800
C	-2.04936500	1.54559000	2.14461500
C	0.20438900	2.67470400	0.65184000
C	-3.42576600	0.84624700	2.30929900
H	-1.26069500	0.93093700	2.59705800
H	-2.06221200	2.48853100	2.70795900
H	0.53468200	3.13593300	-0.28426000
H	0.91144200	1.88347900	0.91063200
H	0.19948400	3.43693500	1.43969200
H	-4.16652800	1.29740900	1.63765500
H	-3.77079500	1.08912900	3.32176100
C	-3.47455900	-0.70050600	2.20178700
P	-3.61299000	-1.47912700	0.49602300

H	-2.58233800	-1.13314800	2.67341300
H	-4.33191500	-1.06843300	2.78182100
C	-5.41826000	-1.39180000	0.12076700
C	-3.37302000	-3.27600600	0.85632700
H	-6.00181100	-1.88614100	0.90515600
H	-5.74227900	-0.35040500	0.03896600
H	-5.61984300	-1.88602800	-0.83463200
H	-3.58117700	-3.85690800	-0.04762400
H	-2.34041900	-3.46988700	1.16042600
H	-4.04522500	-3.61099300	1.65453600
Rh	-2.08586600	-0.07126100	-0.63647000
C	-3.49612000	0.79846100	-1.46246600
O	-4.33196000	1.30642800	-2.07679500

CO

C	0.00000000	0.00000000	-0.65013500
O	0.00000000	0.00000000	0.48760100

Int6

C	3.49818900	-1.05387000	0.74035300
C	1.89368000	-1.15061800	-1.21565200
C	2.97926700	-0.59985800	-1.99146300
C	4.09870100	-0.08226200	-1.42745100
C	1.15973600	0.07874500	0.85926500
C	0.75547700	-1.62347800	-1.79745600
C	-0.35764300	-2.22481400	-1.08547400
C	1.66450100	1.31644900	1.01418500
C	-0.21730500	-0.24462600	1.34197700
N	4.31438300	-0.12917900	-0.05801500
S	5.73672100	0.54633700	0.61357500
O	6.19595100	1.54211300	-0.35035100
O	5.40151900	0.88299900	1.99421500
H	3.89214800	-2.07262500	0.61268800
H	3.58495600	-0.76821900	1.78953000
H	2.87959200	-0.55144600	-3.07153100
H	4.86505200	0.42225700	-2.00373600
H	0.67530100	-1.56230500	-2.88288600
H	-0.99847300	-2.82695200	-1.72717600
H	-0.04171000	-2.81408000	-0.22579300
H	2.68645700	1.56853700	0.75465500
H	1.07888600	2.10987900	1.47317600
H	-0.16077900	-1.08828000	2.03715700
H	-0.62086100	0.60838800	1.89096100
C	6.91954000	-0.81543600	0.63448400
H	7.84144000	-0.42468800	1.07242200
H	6.52720900	-1.62563300	1.25259000
H	7.09842200	-1.14717900	-0.39010700
C	2.01496700	-1.06796500	0.30397300
H	1.61548500	-1.99418900	0.73582000
H	-2.69525100	0.70855700	-3.44253100
C	-2.76556700	1.49406800	-2.68408400
P	-1.45310900	1.24568400	-1.40297500
H	-3.76696400	1.45680100	-2.24662500
H	-2.63436400	2.46321700	-3.17726700
C	-1.52360300	2.83333200	-0.43753100
C	0.07379000	1.50121500	-2.39695300
C	-2.82296500	3.16694900	0.31604600
H	-0.67125700	2.82858000	0.25018700
H	-1.32632700	3.62597300	-1.16999800
H	0.13491800	0.75350300	-3.18954300
H	0.96077000	1.42214500	-1.76729500
H	0.03286800	2.49837600	-2.84848800
H	-3.68788200	3.08727200	-0.35481400
H	-2.77135500	4.22505300	0.59892900
C	-3.06430200	2.35799000	1.60063800
P	-3.47303900	0.56564600	1.34995400
H	-2.17624300	2.40301400	2.24335100
H	-3.88754100	2.80392500	2.17336900
C	-5.23800200	0.59017600	0.80039000
C	-3.59750600	-0.04550300	3.08844000
H	-5.86141500	1.15561700	1.50179400
H	-5.32851200	1.04138800	-0.19238700
H	-5.61784300	-0.43479300	0.74190600
H	-4.00746800	-1.06002800	3.10289600
H	-2.60493200	-0.06812400	3.54896100
H	-4.24881100	0.60255700	3.68476400
Rh	-1.84705300	-0.79522600	-0.07082500
C	-3.20453800	-1.39683600	-1.42528700
O	-3.92876300	-1.81801200	-2.20261100
O	-2.25470300	-3.21267300	1.78857200
C	-2.10911300	-2.32096400	1.08789200

TS4

C	-3.44331600	-1.18202200	-0.74101600
C	-1.71844300	-1.33500500	1.09056300
C	-2.69487400	-0.67769900	1.92876500
C	-3.82979000	-0.12245400	1.43941700
C	-1.10430400	-0.08335300	-1.03076000

C	-0.62494100	-1.94933600	1.61802200
C	0.33176400	-2.77733400	0.88323100
C	-1.66254700	1.09911900	-1.35155100
C	0.31994500	-0.34752700	-1.41738400
N	-4.16559700	-0.21317400	0.09549800
S	-5.56380300	0.56697000	-0.50067500
O	-5.92195600	1.56578900	0.50270000
O	-5.26358300	0.92139700	-1.88643900
H	-3.85347000	-2.18477100	-0.55516700
H	-3.60482400	-0.92161400	-1.78823400
H	-2.51254600	-0.61603600	2.99737600
H	-4.52526800	0.43276100	2.05692700
H	-0.46542600	-1.87904100	2.69374500
H	0.92346000	-3.43057200	1.52297000
H	-0.11363100	-3.33315100	0.05768900
H	-2.71121700	1.32352700	-1.19896700
H	-1.08171400	1.87402300	-1.84682300
H	0.38798800	-1.26521800	-2.00984100
H	0.66732100	0.47466000	-2.04355000
C	-6.83004200	-0.71640700	-0.51172000
H	-7.73940600	-0.25734800	-0.90764400
H	-6.51012700	-1.53258000	-1.16265300
H	-6.99401000	-1.06251200	0.51054000
C	-1.93127600	-1.22725000	-0.41992800
H	-1.57542500	-2.15267900	-0.89229000
H	2.32705000	1.43239900	3.40696800
C	2.46101200	2.09930200	2.54953000
P	1.29761700	1.61065000	1.19223700
H	3.50350900	2.02641300	2.22528200
H	2.26591300	3.12655000	2.87584200
C	1.50019300	3.00948800	-0.01613100
C	-0.33677500	1.95900700	1.96809500
C	2.85337600	3.07502900	-0.75174300
H	0.68022200	2.94100700	-0.74016700
H	1.34779300	3.94114500	0.54311600
H	-0.47574200	1.29969700	2.82918300
H	-1.14238000	1.76814900	1.25728800
H	-0.38106800	3.00047400	2.30540100
H	3.68328100	3.03100300	-0.03484900
H	2.92659600	4.06489700	-1.21746100
C	3.05315200	2.03646100	-1.87195000
P	3.35609200	0.28222900	-1.34648400
H	2.18401900	2.03646300	-2.54002000
H	3.91620400	2.32184300	-2.48764800
C	5.09975500	0.28587000	-0.75061500
C	3.44834800	-0.64027700	-2.93418400
H	5.76610900	0.69715600	-1.51671600
H	5.19691100	0.88437700	0.15966500
H	5.41260800	-0.73811800	-0.52523100
H	3.72056100	-1.68130900	-2.73639000
H	2.47578500	-0.62686400	-3.43360600
H	4.19635100	-0.19274800	-3.59744200
Rh	1.81781300	-0.63747200	0.18267200
C	3.12901600	-0.94716300	1.66840600
O	3.87373200	-1.15234000	2.51113400
O	2.23121500	-3.41235400	-0.95488700
C	1.86677000	-2.46981300	-0.37430900

Int7

C	-3.31365500	-1.43280900	-0.62909100
C	-1.31434600	-1.34846600	0.89565900
C	-2.10909400	-0.49223000	1.74195200
C	-3.30720900	0.01415700	1.34438200
C	-1.05465200	-0.40217500	-1.42218100
C	-0.21402400	-2.00726500	1.39438500
C	0.58421100	-3.10736500	0.71270100
C	-1.68965600	0.60173800	-2.04803400
C	0.41669600	-0.61719600	-1.58100300
N	-3.89166700	-0.32526600	0.14837500
S	-5.35079300	0.43552900	-0.35404700
O	-5.49594000	1.60793000	0.50317300
O	-5.26865100	0.52746700	-1.80926600
H	-3.69068700	-2.38006000	-0.21855000
H	-3.64600900	-1.34293300	-1.66405200
H	-1.75333400	-0.25203300	2.73888600
H	-3.87256700	0.70713500	1.95730300
H	-0.03075200	-1.89640500	2.46189400
H	0.84549400	-3.90656100	1.41846600
H	0.03817200	-3.57919100	-0.11444800
H	-2.76023200	0.76480900	-2.00126000
H	-1.13227700	1.29371300	-2.67556800
H	0.62290300	-1.61830900	-1.97609400
H	0.80782700	0.10587100	-2.30149900
C	-6.63299600	-0.75778500	0.06704300
H	-7.58109500	-0.32568000	-0.26336400
H	-6.44404600	-1.69271300	-0.46439300
H	-6.63953500	-0.90564900	1.14851900
C	-1.77460500	-1.44933100	-0.56083200

H	-1.48267600	-2.43145500	-0.95463700
H	1.17692500	2.21499800	3.09353300
C	1.64947000	2.71442000	2.24170100
P	0.95159900	2.05012900	0.65598900
H	2.72665600	2.53171100	2.30188400
H	1.47174100	3.79194900	2.32825800
C	1.75175700	3.16919900	-0.59814100
C	-0.76123300	2.73984700	0.70817800
C	3.22953300	2.87479900	-0.90958100
H	1.15949700	3.10750500	-1.52011100
H	1.65124600	4.19833100	-0.23069300
H	-1.30616100	2.31136700	1.55282600
H	-1.29889000	2.47907500	-0.20610400
H	-0.72957000	3.82951000	0.81845200
H	3.81577400	2.79804300	0.01562800
H	3.63806800	3.74337500	-1.43955700
C	3.46399900	1.64717500	-1.80642000
P	3.35744100	-0.04094600	-1.04490900
H	2.75844200	1.66143700	-2.64636900
H	4.46841500	1.69689800	-2.24705700
C	4.93280900	-0.25593000	-0.12009800
C	3.57726200	-1.13053000	-2.50833200
H	5.78848000	-0.09967400	-0.78572200
H	4.99996100	0.44662600	0.71531800
H	4.96701400	-1.27798700	0.26845900
H	3.64436200	-2.16750400	-2.17591100
H	2.73550400	-1.02402700	-3.19673900
H	4.50004000	-0.85045900	-3.02742700
Rh	1.49949500	-0.49030100	0.29128200
C	2.47309300	-0.46231100	2.03797000
O	3.03093500	-0.45774300	3.03727200
O	2.82266000	-3.11336800	-0.22982200
C	1.85610000	-2.49990700	0.14499700

TS5

C	3.32808100	-1.60656700	0.30816000
C	1.20301900	-1.48233500	-1.05987400
C	1.93672800	-0.57314000	-1.89899900
C	3.09554600	0.01402200	-1.49488100
C	1.02509700	-1.10462200	1.42700900
C	0.01966100	-2.06342200	-1.47810400
C	-0.73088100	-3.13732700	-0.70592900
C	1.57248800	-0.22556900	2.27596500
C	-0.40102300	-1.57641400	1.59220000
N	3.72461700	-0.34082100	-0.32558200
S	5.04405100	0.58801900	0.26882300
O	4.93089800	1.88177200	-0.39875400
O	5.00431700	0.44273300	1.72150300
H	3.77945500	-2.42865300	-0.26419000
H	3.72028400	-1.63106500	1.32487100
H	1.52102500	-0.29009500	-2.86048100
H	3.57430100	0.79780900	-2.07115000
H	-0.24404100	-1.93370300	-2.52507000
H	-1.43099000	-3.66574100	-1.36015800
H	-0.06699200	-3.89719300	-0.26680000
H	2.60735500	0.09546800	2.22398900
H	0.98462200	0.19029700	3.09035400
H	-0.36419100	-2.58462900	2.02190700
H	-0.94899800	-0.98109200	2.32330600
C	6.50618200	-0.26347100	-0.34902300
H	7.37157500	0.28793400	0.02762200
H	6.51572900	-1.28451400	0.03774900
H	6.49234300	-0.24845700	-1.44042600
C	1.80153000	-1.80594500	0.31466700
H	1.66521900	-2.88479700	0.47961100
H	1.76204500	2.38100600	-0.51510500
C	0.83771800	2.78130200	-0.93993100
P	-0.63290600	2.07683900	-0.05997100
H	0.80215700	2.52090900	-2.00195800
H	0.85545400	3.87279000	-0.84324200
C	-1.98206200	3.21684400	-0.70248900
C	-0.34867900	2.75298600	1.64559000
C	-3.42411200	2.67450100	-0.71903900
H	-1.93942900	4.14121000	-0.11197300
H	-1.70206800	3.49141300	-1.72624800
H	0.54328500	2.28904100	2.07373500
H	-1.19601500	2.53249300	2.30199400
H	-0.20251300	3.83864600	1.61596900
H	-3.55545600	1.99363100	-1.56725700
H	-4.09578000	3.51856200	-0.91408900
C	-3.88040200	1.98725400	0.58371700
P	-3.42457300	0.18964200	0.72794900
H	-3.47837600	2.51139200	1.45888700
H	-4.97301000	2.02723100	0.67397800
C	-4.86940100	-0.72905300	0.06253100
C	-3.48236300	-0.16813800	2.52845400
H	-5.76295700	-0.50235100	0.65430200
H	-5.05326100	-0.45712500	-0.98034800

H	-4.65107700	-1.79832000	0.12559300
H	-3.33598700	-1.24142000	2.67408800
H	-2.70940400	0.38772000	3.06627500
H	-4.46388200	0.12178000	2.92000800
Rh	-1.42589700	-0.43254700	-0.31815600
C	-2.34307000	-0.40929100	-1.96524800
O	-2.83750000	-0.38464800	-3.00748000
O	-2.54878100	-2.90864800	0.91350600
C	-1.55763800	-2.44411600	0.37510800

Int8

C	4.50137500	1.16646400	-0.42154200
C	2.89517400	1.19142700	1.54203600
C	3.71210200	0.11118400	2.06110600
C	4.58824200	-0.57478500	1.29268600
C	1.92702300	1.06581800	-0.77582800
C	1.92640800	1.77745600	2.28263400
C	0.95629500	2.80939100	1.74037900
C	1.98543700	0.02095000	-1.60688100
C	0.63954400	1.88209700	-0.67419100
N	4.86654100	-0.19511100	-0.01403600
S	5.85344700	-1.16558700	-1.01019500
O	5.86129000	-2.49043600	-0.39633900
O	5.38720200	-0.93642200	-2.37706300
H	5.22260100	1.86976700	0.01844800
H	4.55958800	1.23307100	-1.50872300
H	3.55174400	-0.21763600	3.08283800
H	5.09832100	-1.46513900	1.64044100
H	1.76470600	1.45062800	3.30683800
H	0.32029600	3.20426100	2.53539700
H	1.47830600	3.64716700	1.25816600
H	2.89195400	-0.55253700	-1.76518900
H	1.11902700	-0.27456000	-2.19355400
H	0.83428700	2.89074900	-1.07710700
H	-0.14567000	1.42008100	-1.27993000
C	7.50234500	-0.45237500	-0.85496600
H	8.16125000	-1.03694800	-1.50188600
H	7.47919300	0.58743600	-1.18759300
H	7.82555200	-0.53049800	0.18487100
C	3.09549700	1.57039000	0.06807700
H	3.08266000	2.66898200	0.00102800
H	-2.17252600	-0.08663800	3.39425700
C	-2.56665400	-1.04151200	3.03458300
P	-2.01150500	-1.30876800	1.29468500
H	-3.65852100	-0.99526100	3.08096200
H	-2.21308700	-1.84768100	3.68688300
C	-2.67826400	-2.98172300	0.86032400
C	-0.20413300	-1.63092600	1.46597500
C	-4.14182600	-2.99829300	0.38918200
H	-2.03311600	-3.39434600	0.07409500
H	-2.55638000	-3.62638500	1.73951100
H	0.29211400	-0.75530500	1.89247600
H	0.24062900	-1.82954000	0.48677700
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H	-4.46651600	-4.04381800	0.33223200
C	-4.35602400	-2.36107600	-0.99486500
P	-4.31535500	-0.50693900	-1.07011300
H	-3.59941200	-2.73239200	-1.69791300
H	-5.33226000	-2.66166500	-1.39598600
C	-5.96868600	-0.01202300	-0.41599900
C	-4.46442800	-0.20253900	-2.88225100
H	-6.77114100	-0.52209300	-0.96051900
H	-6.04512600	-0.25591800	0.64747000
H	-6.09666000	1.06902900	-0.52261400
H	-4.62953100	0.86186700	-3.07250500
H	-3.54076900	-0.50209900	-3.38607100
H	-5.30217100	-0.77021800	-3.30172500
Rh	-2.59315600	0.59004200	-0.04849600
C	-3.06754500	2.18079400	-0.98824300
O	-3.34337800	3.16481000	-1.51548900
O	-1.01951500	1.66892300	1.06633900
C	0.09383000	2.08935800	0.72548200

2a'

C	0.22358300	-0.11553600	1.25092800
C	-1.89976600	-0.64940500	-0.21130500
C	-0.90043300	-1.15966200	-1.19140800
C	0.40791600	-0.88205600	-1.10629300
C	-1.89393600	0.85147600	0.02380600
C	-3.16856700	-1.42707300	-0.09199600
C	-4.27485100	-1.06892600	0.56698500
C	-1.53527500	2.04402000	-0.78015700
C	-2.88018400	1.96030800	-0.06343000
N	0.94774500	-0.13877700	-0.03348700
S	2.60731800	0.17100700	-0.00753200
O	3.04140600	0.26889200	-1.40034600
O	2.81760500	1.25568900	0.95070600

H	0.42106400	-1.04149400	1.81568200
H	0.60742300	0.72746000	1.83016100
H	-1.25713900	-1.71961700	-2.05091500
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H	-3.76972200	1.80506400	-0.66990700
H	-3.03667600	2.59059900	0.81026500
C	3.35938800	-1.32086400	0.68776300
H	4.43809400	-1.15061800	0.71954700
H	2.97691000	-1.48336600	1.69763400
H	3.12985300	-2.16995100	0.04056600
C	-1.27877400	-0.00245500	1.05098600
H	-1.84024900	-0.16825400	1.97045900

3a'

C	-1.23599300	-1.32579000	-0.06398700
C	-2.49071000	-1.81852500	-0.10627700
C	-3.71945400	-1.10369200	0.39759700
C	-0.94964300	0.05865300	0.52571500
C	-3.77763600	0.41901500	0.18253100
O	-4.54590000	1.10311800	0.82884500
H	-2.64718300	-2.79356700	-0.56519700
H	-4.60491300	-1.50609000	-0.11597100
H	-3.90731100	-1.28413500	1.46621200
H	-1.55237900	0.16218200	1.44150000
C	0.50646400	0.15115000	1.00258500
C	-0.10389400	-2.00633800	-0.67526200
C	1.13606600	-1.47522300	-0.71041500
N	1.44000800	-0.27781500	-0.04897100
S	3.03107700	0.29390800	-0.02589900
O	3.66632000	-0.18544700	-1.25190400
O	2.95343900	1.71549500	0.31049400
H	0.61949500	-0.50933600	1.87565600
H	0.75754800	1.16969600	1.29910600
H	-0.27989500	-2.94080800	-1.19954700
H	1.95124000	-1.91561100	-1.27142200
C	3.81464800	-0.55132600	1.36765500
H	4.84638000	-0.19562800	1.41947200
H	3.28419700	-0.29637200	2.28751300
H	3.79368300	-1.62796800	1.18669300
C	-2.86308000	1.01783400	-0.88596600
H	-3.26474100	1.99326300	-1.17133200
H	-2.88904500	0.35628500	-1.76389500
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C	-0.66401200	2.19028300	-0.81751000
H	0.38171600	2.29906900	-0.54938400
H	-1.07795200	2.96527300	-1.45770300

VIII. References

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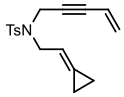
IX. NMR Spectra



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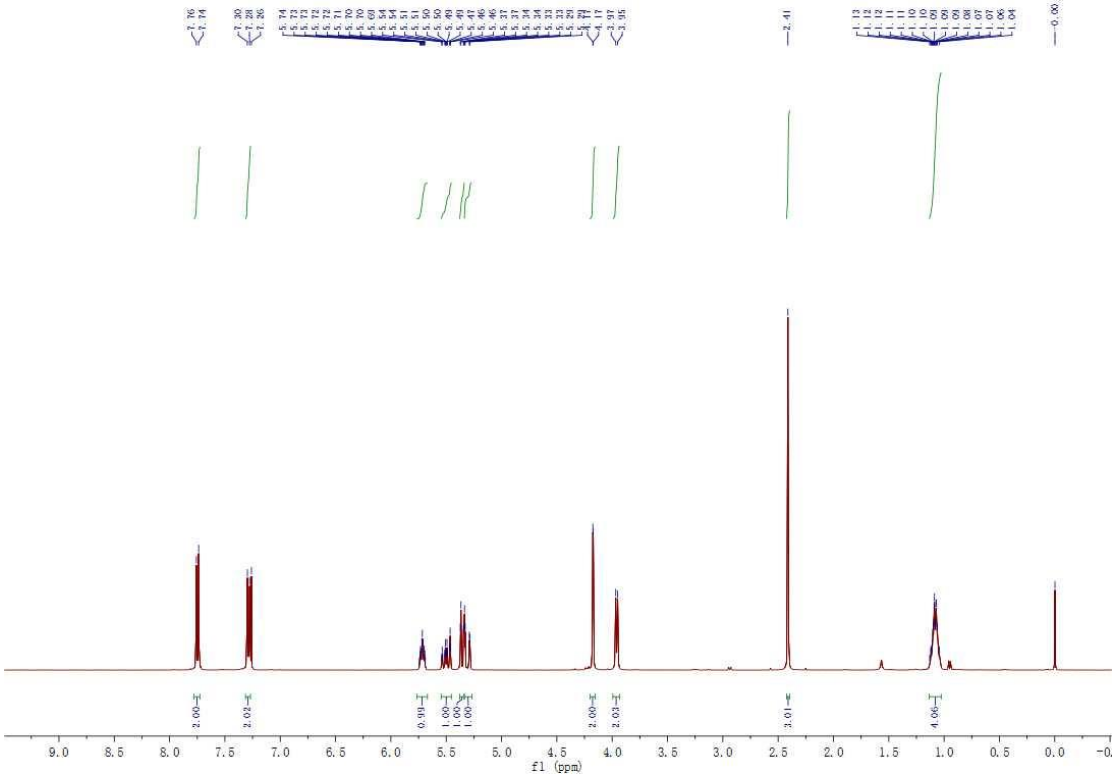

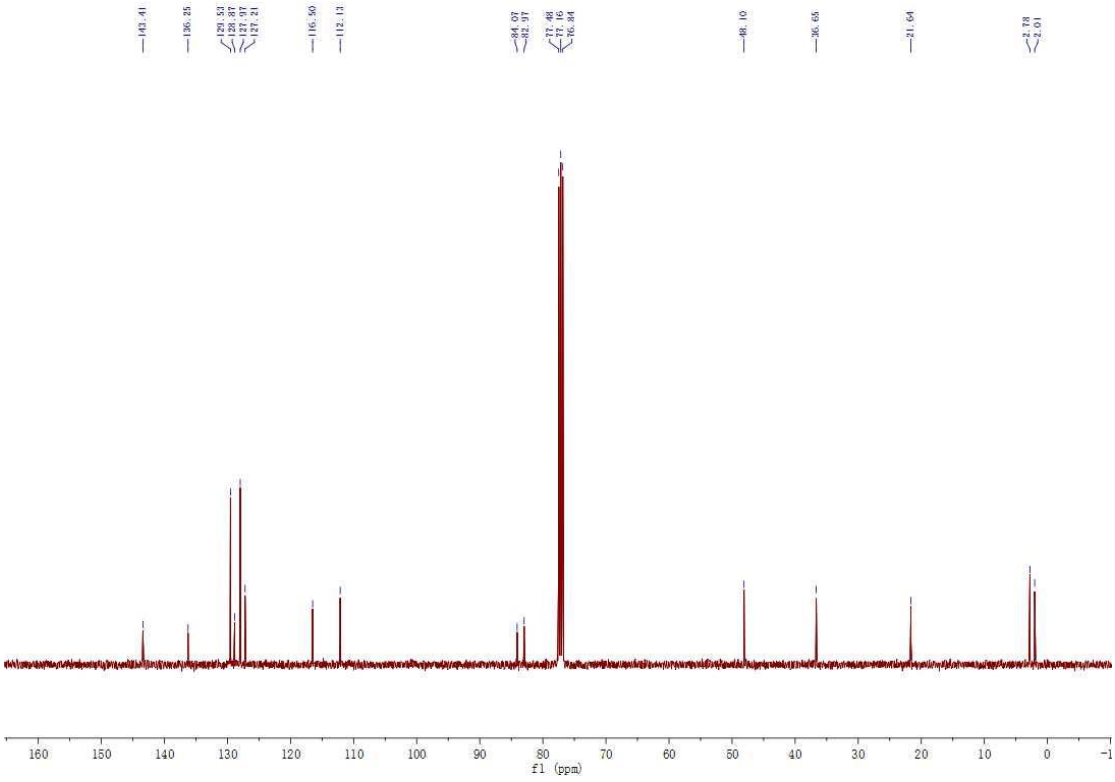

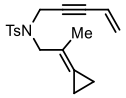

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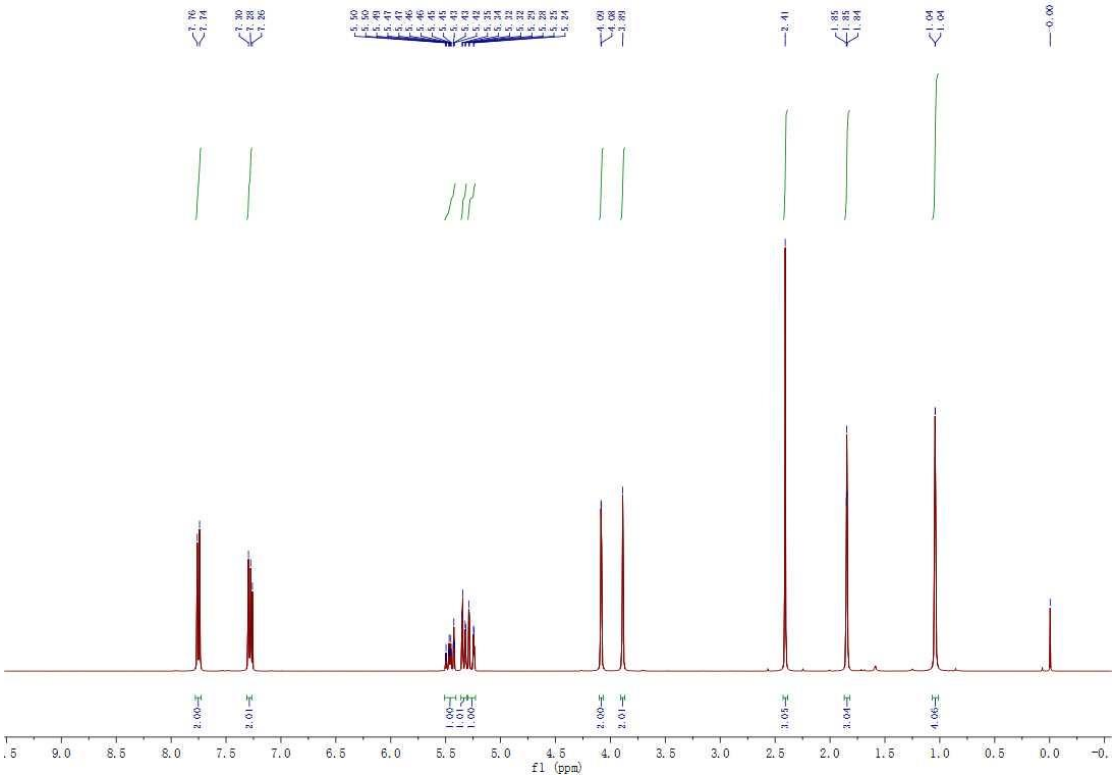

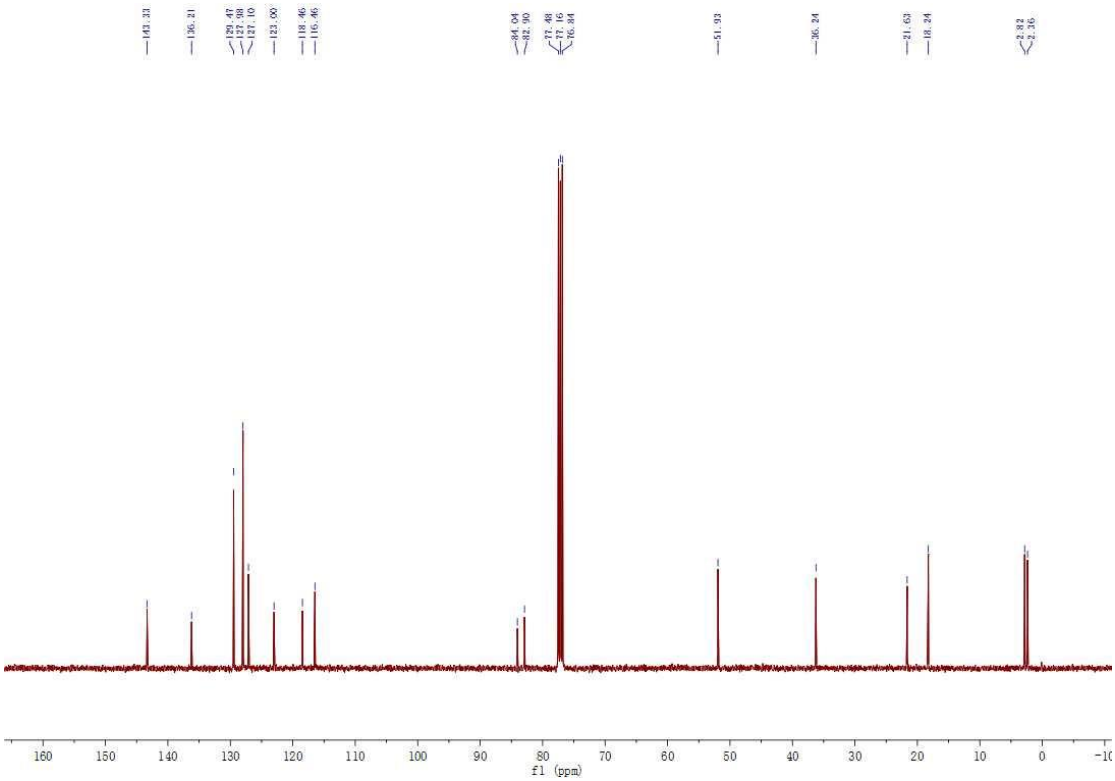

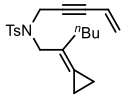

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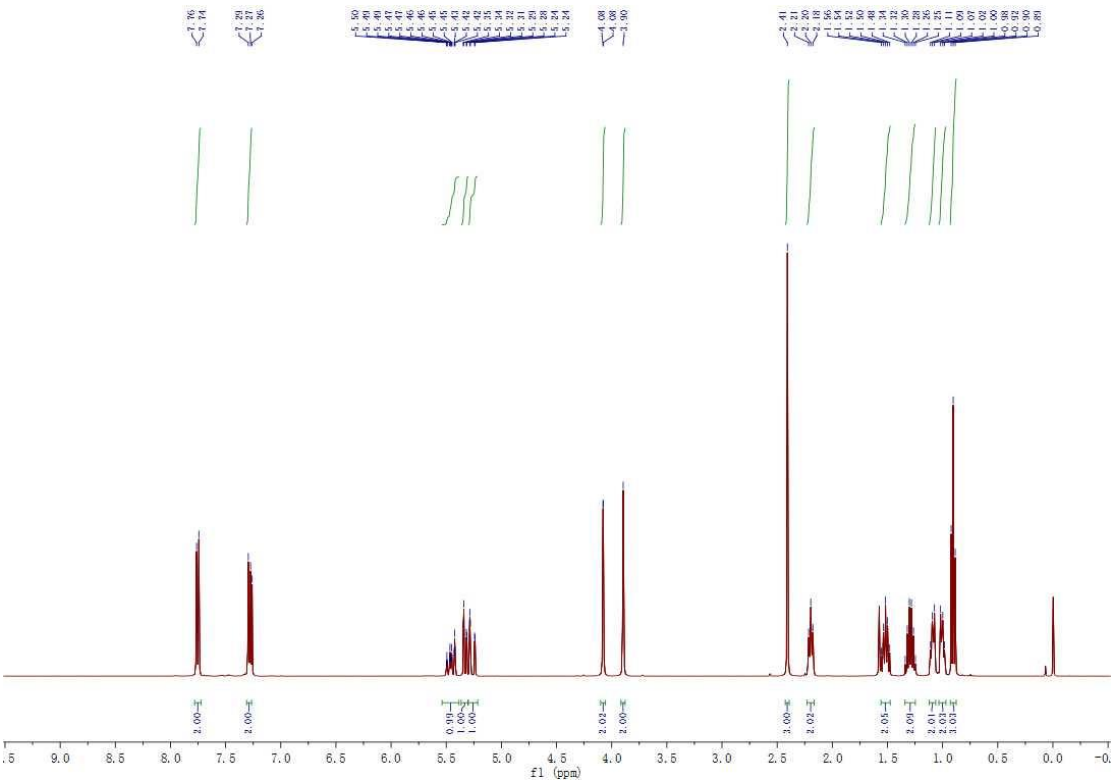

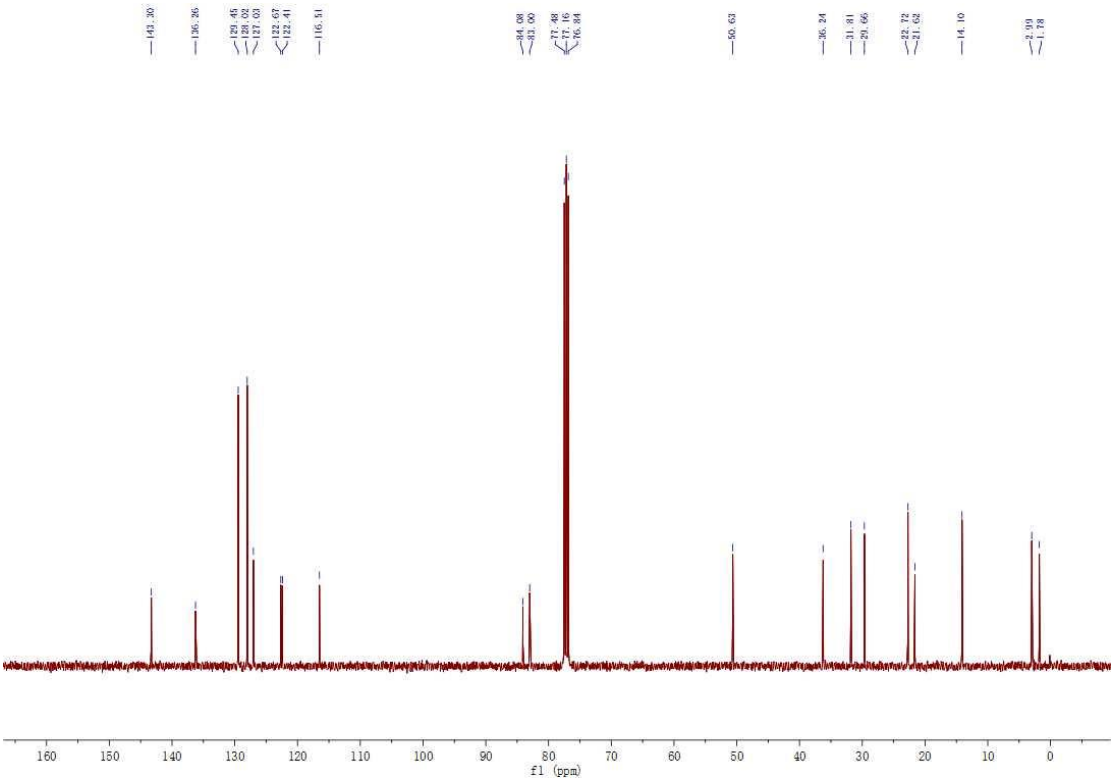

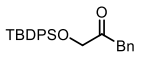

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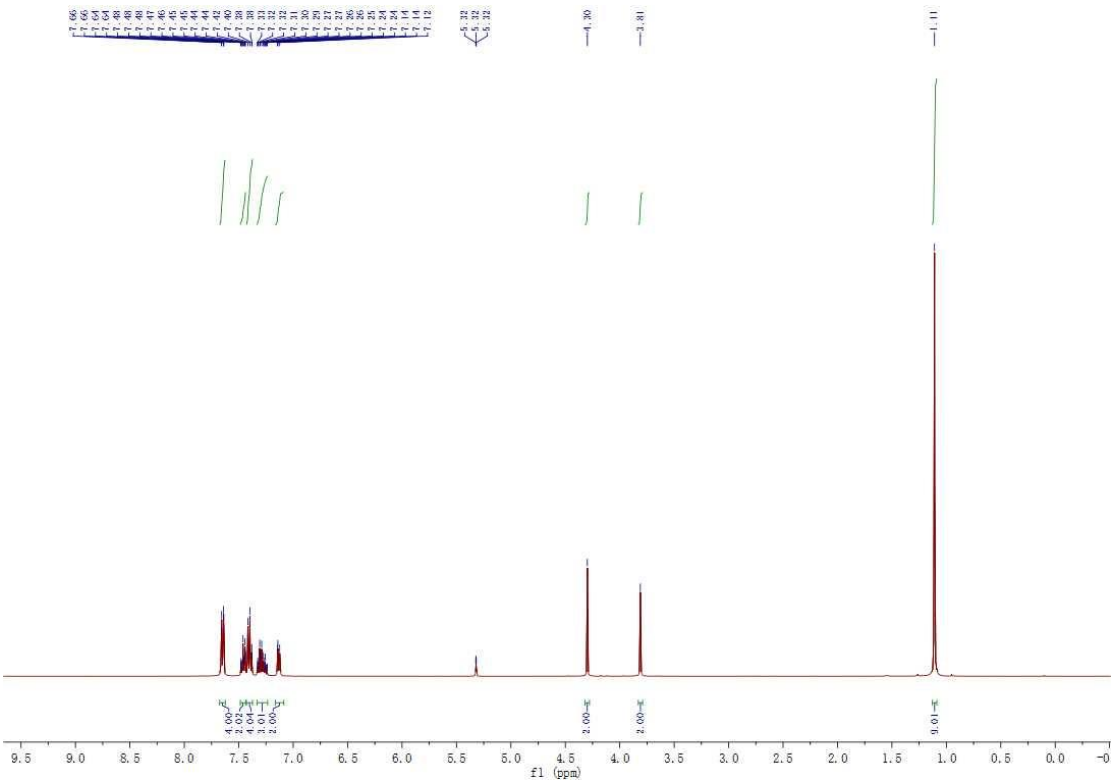

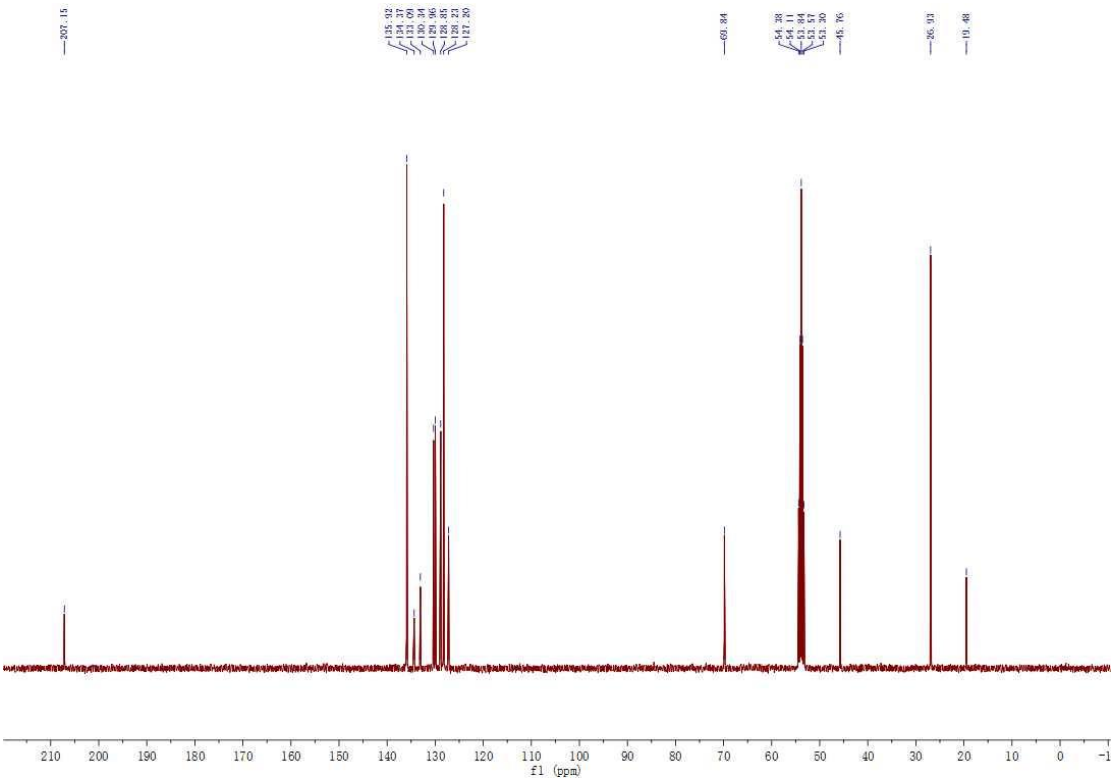

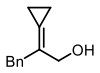

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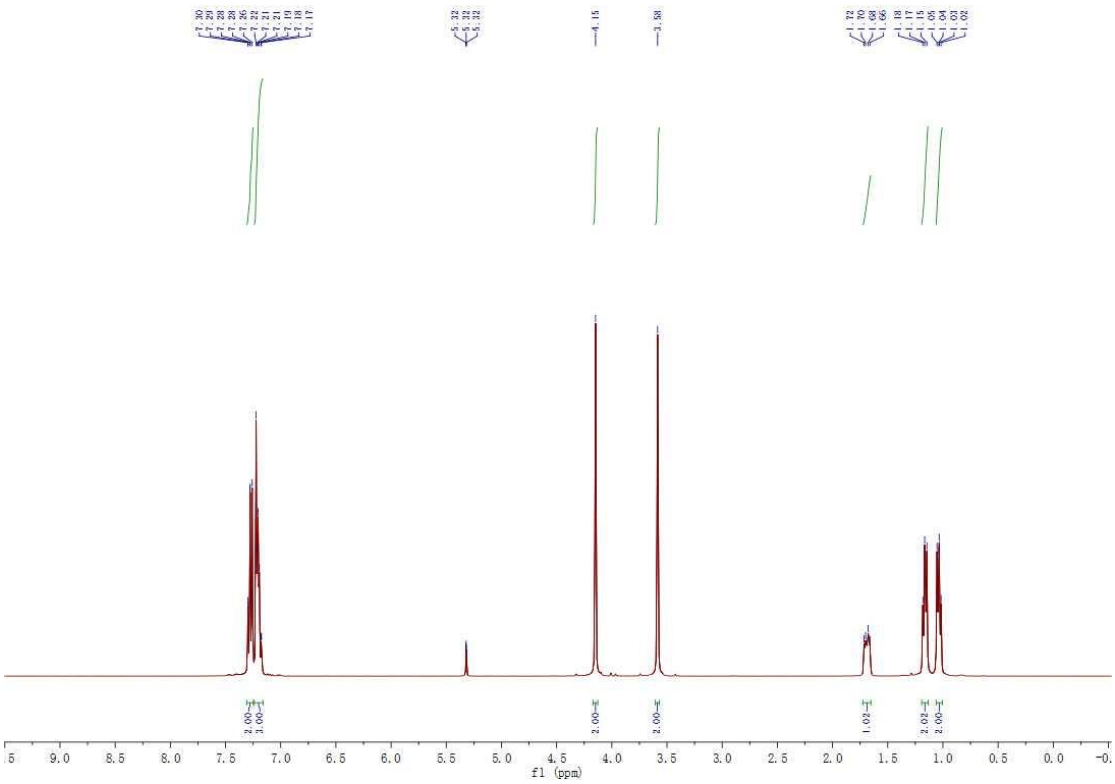

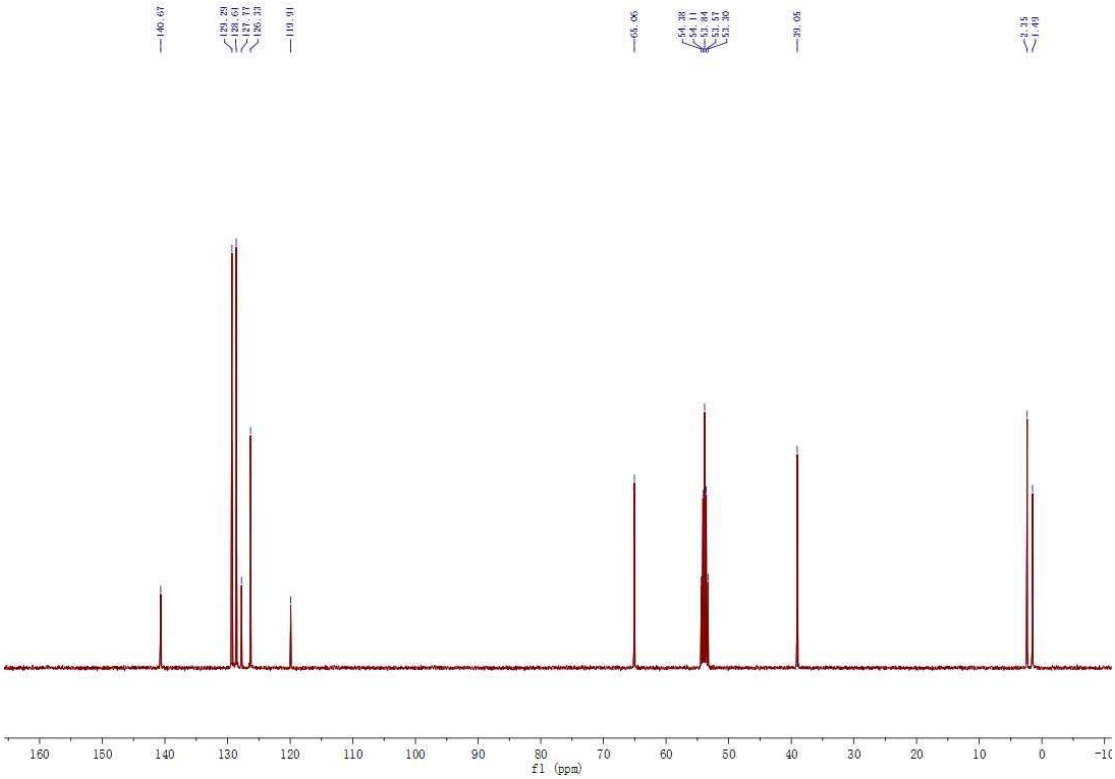

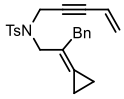

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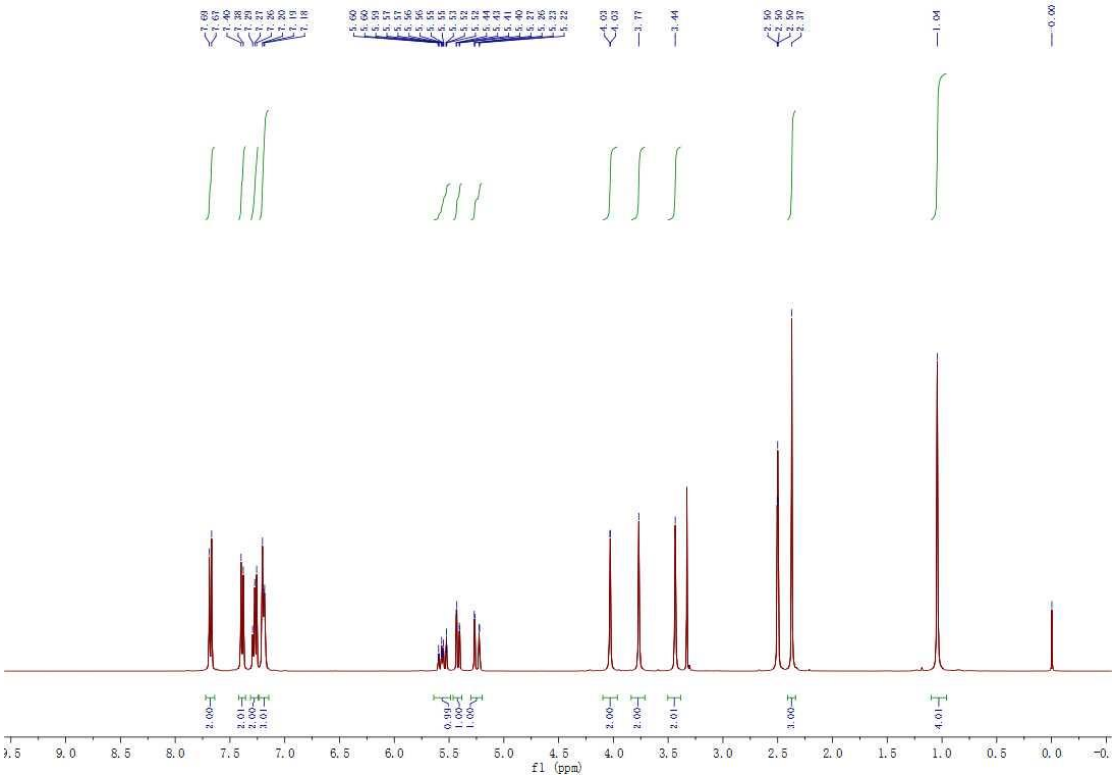

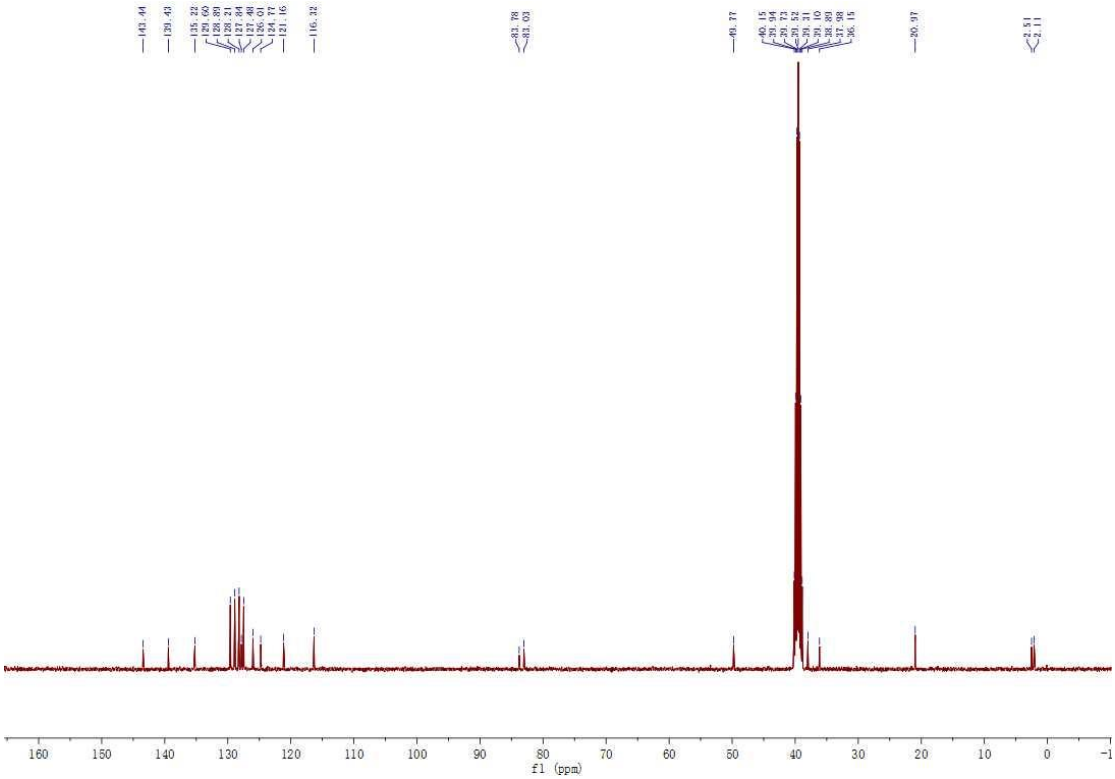

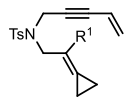

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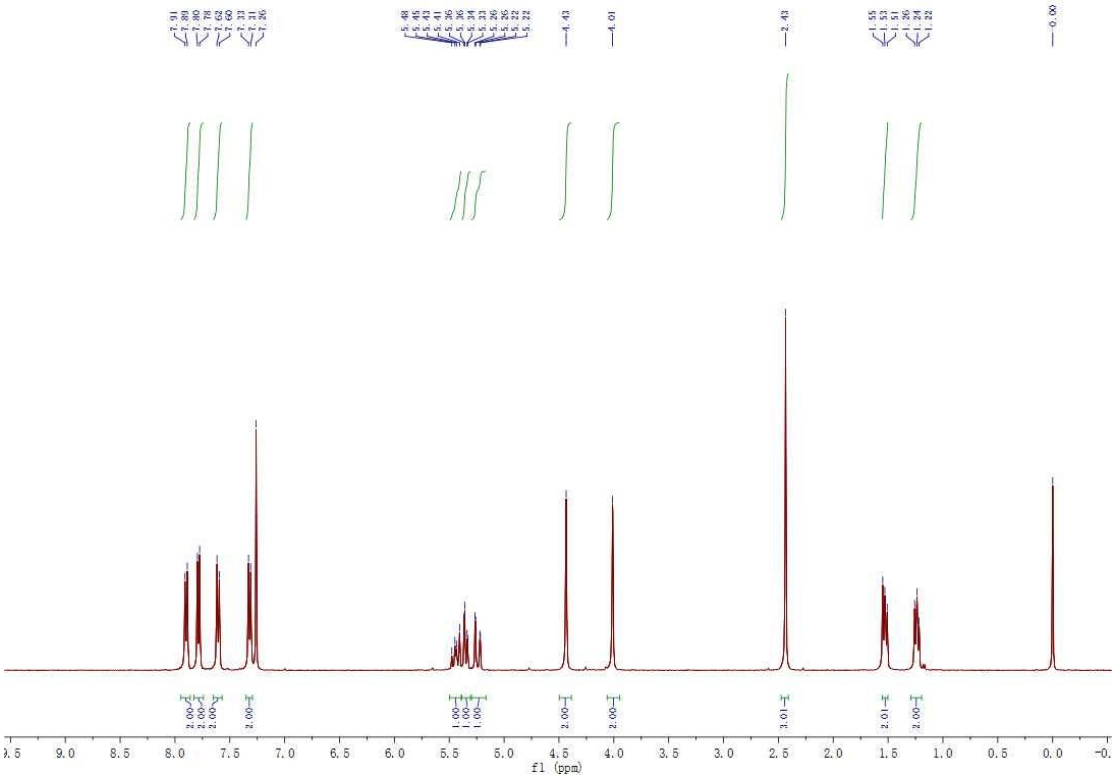

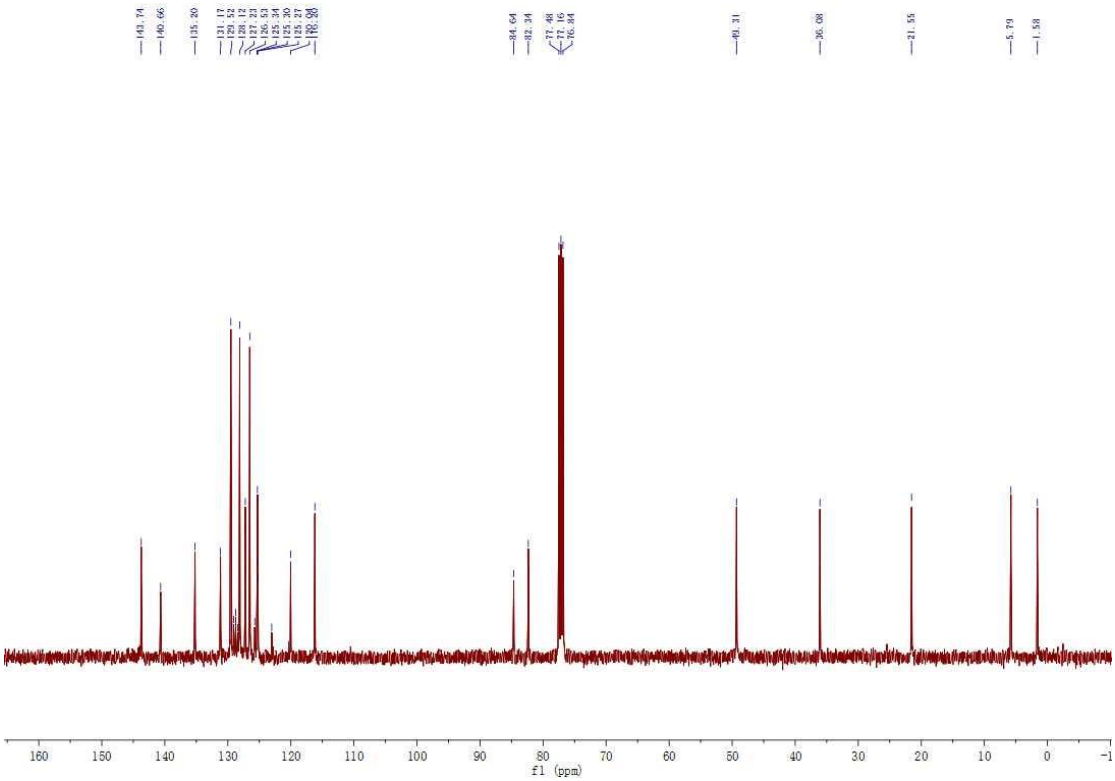

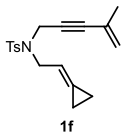

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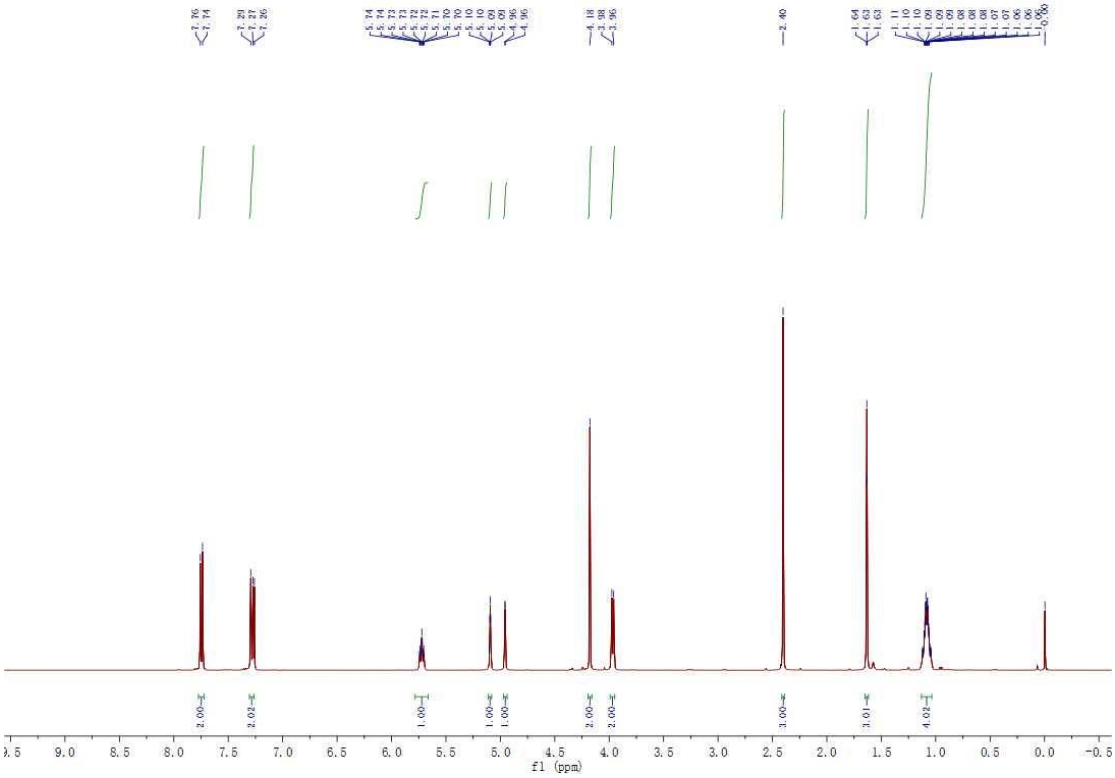

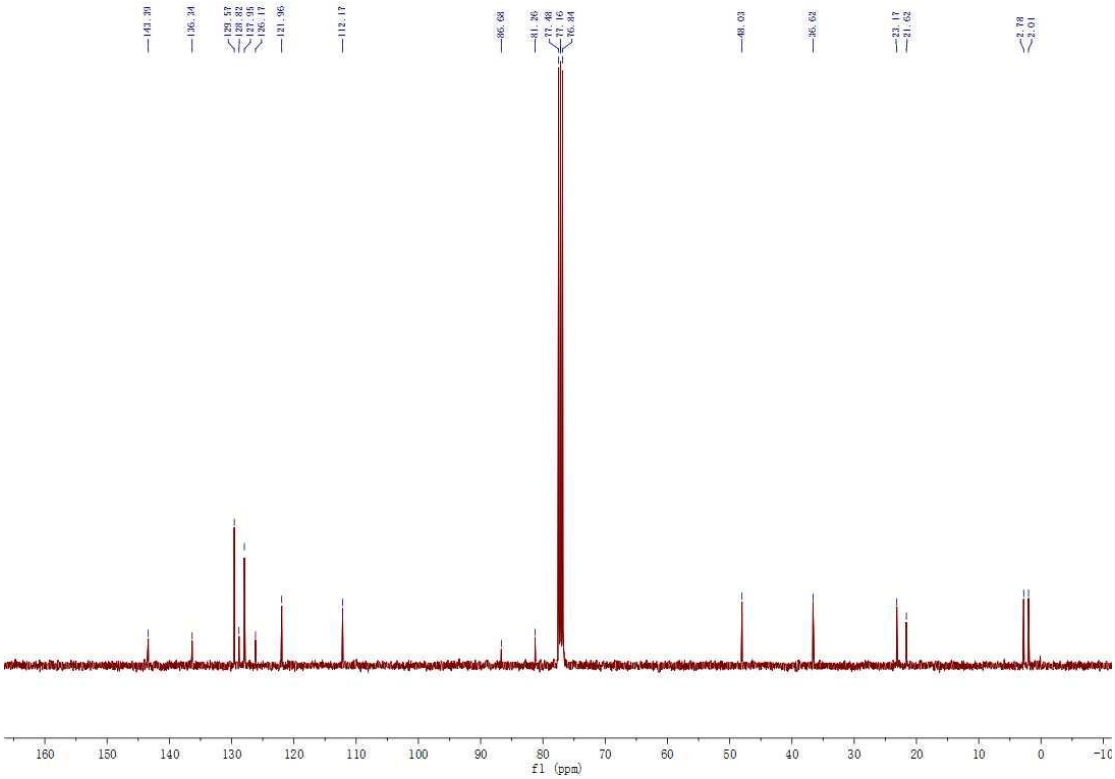

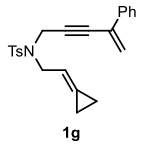

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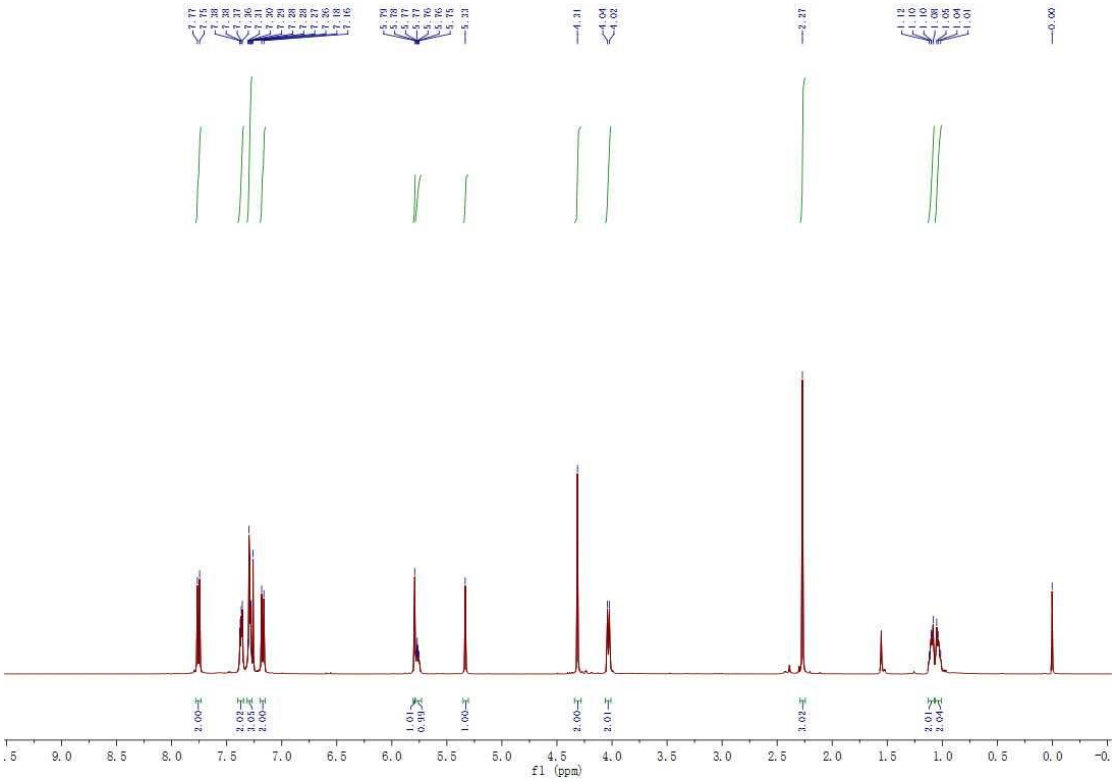

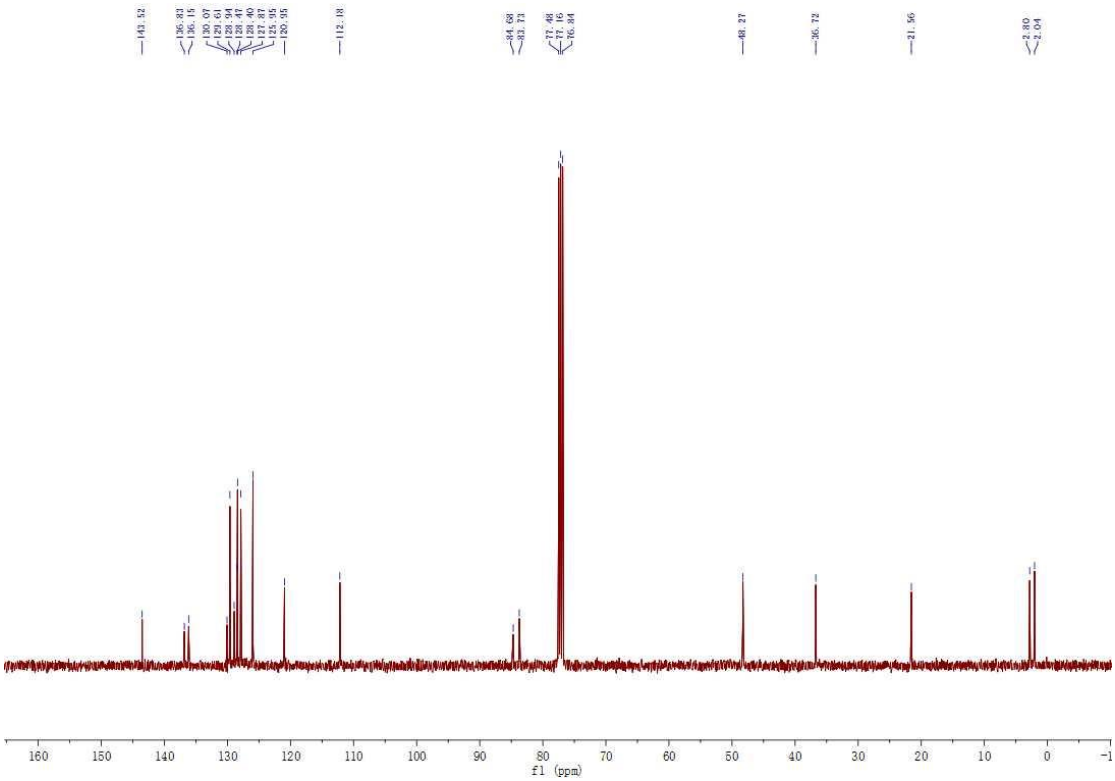

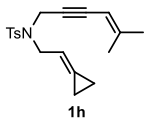

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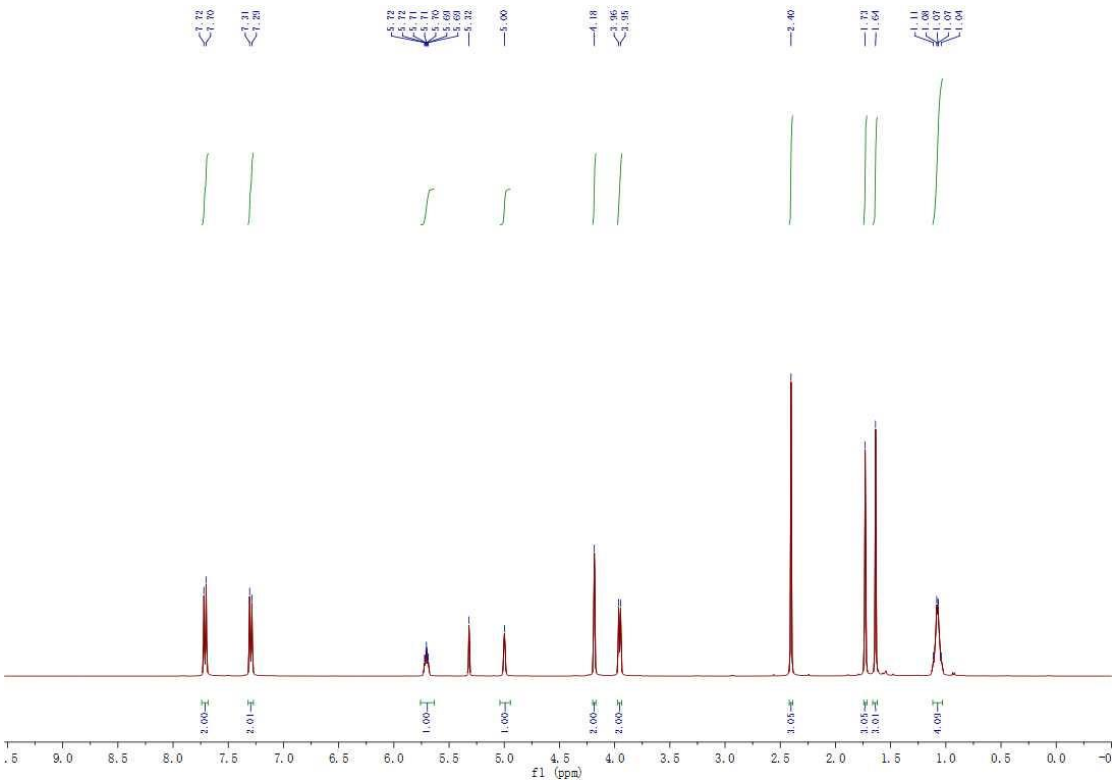
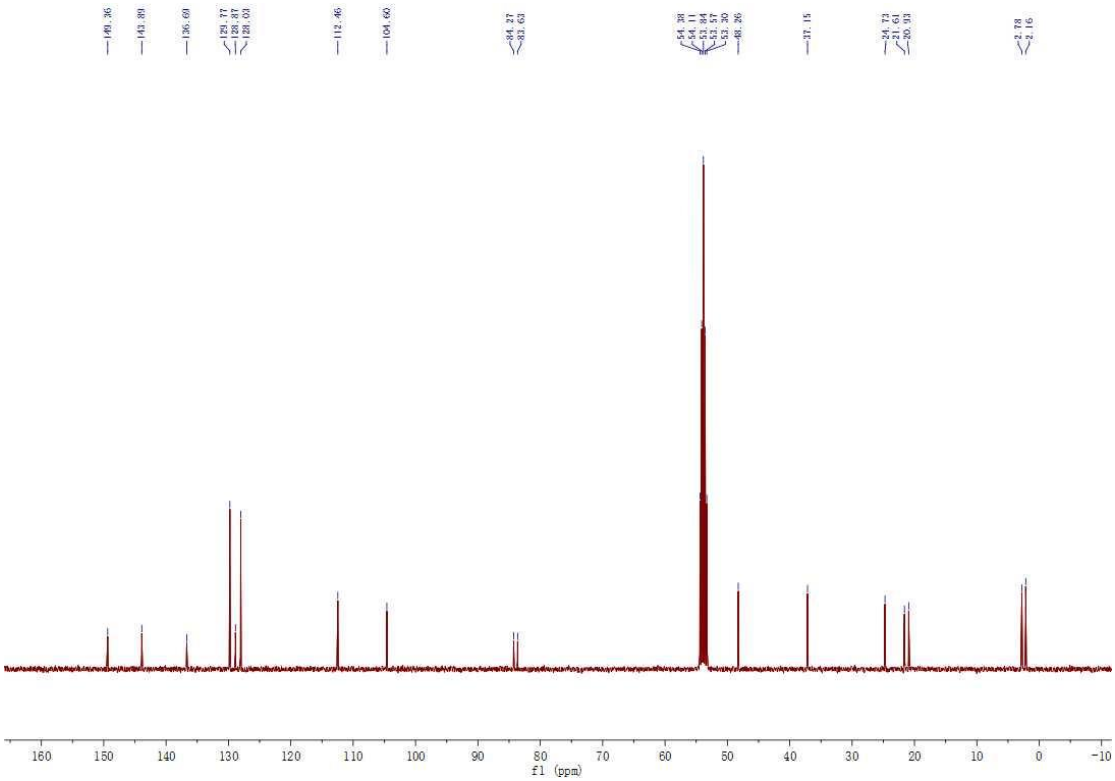
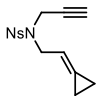
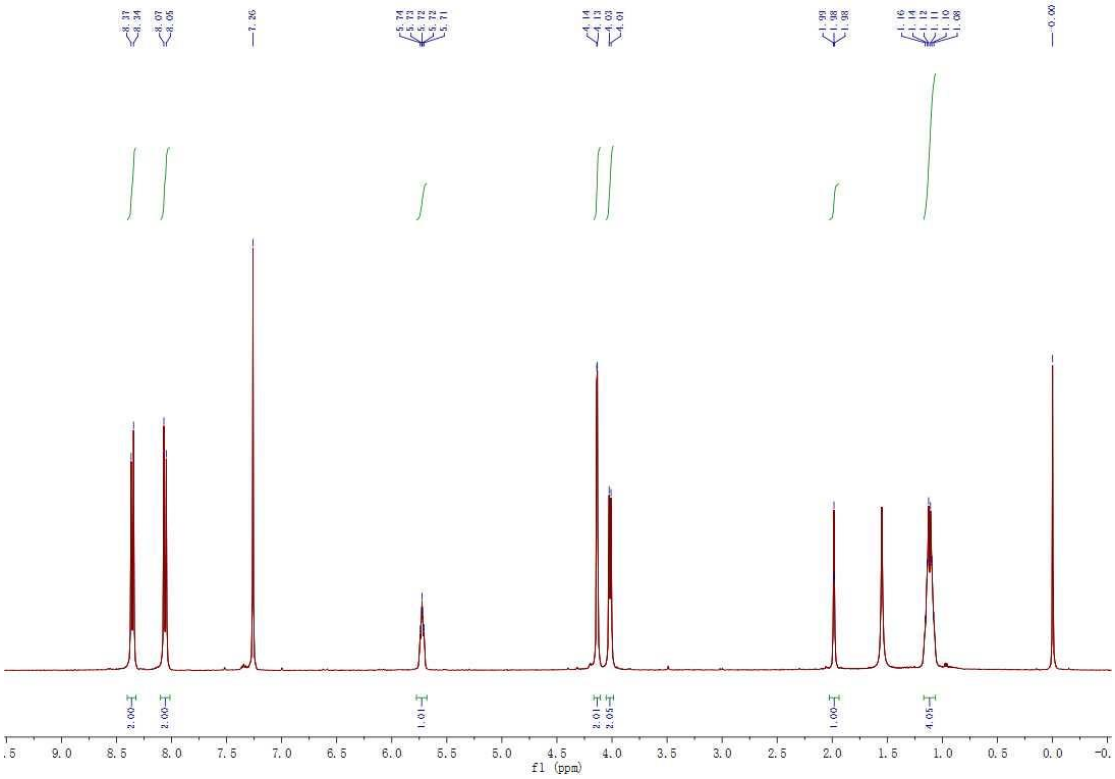





NsN

S12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1.98
1.98
1.16
1.14
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2.01
2.05
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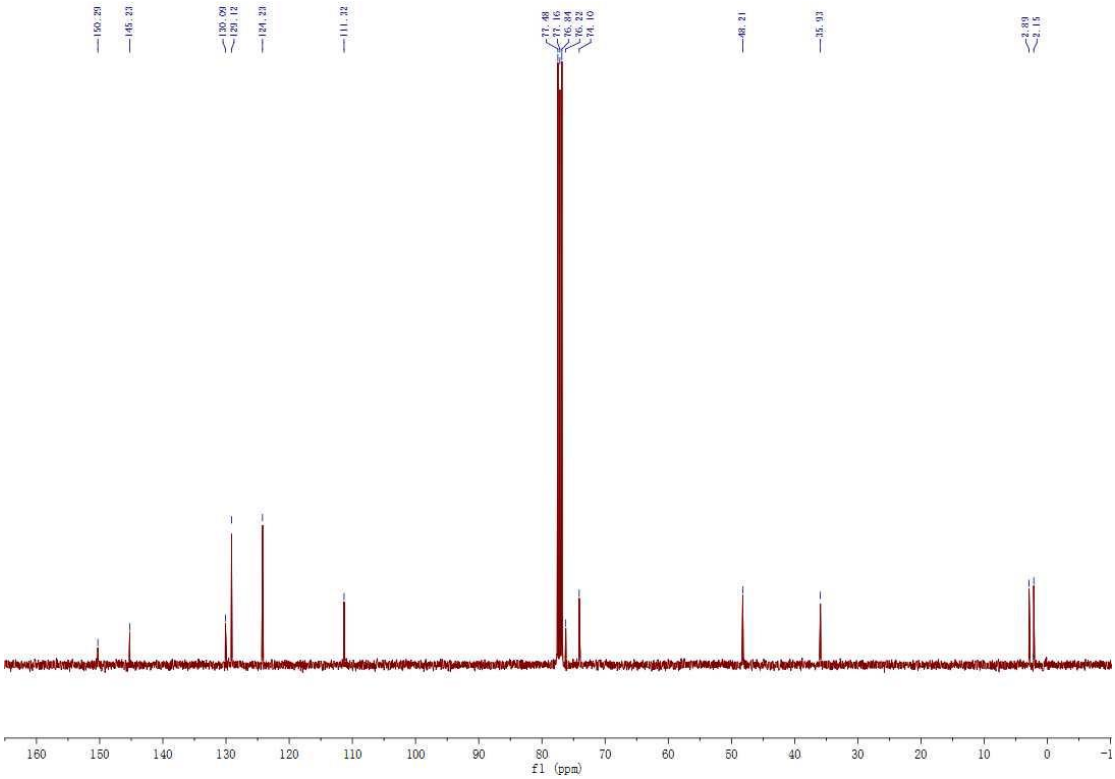
4.05
f1 (ppm)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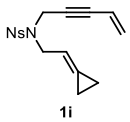
f1 (ppm)



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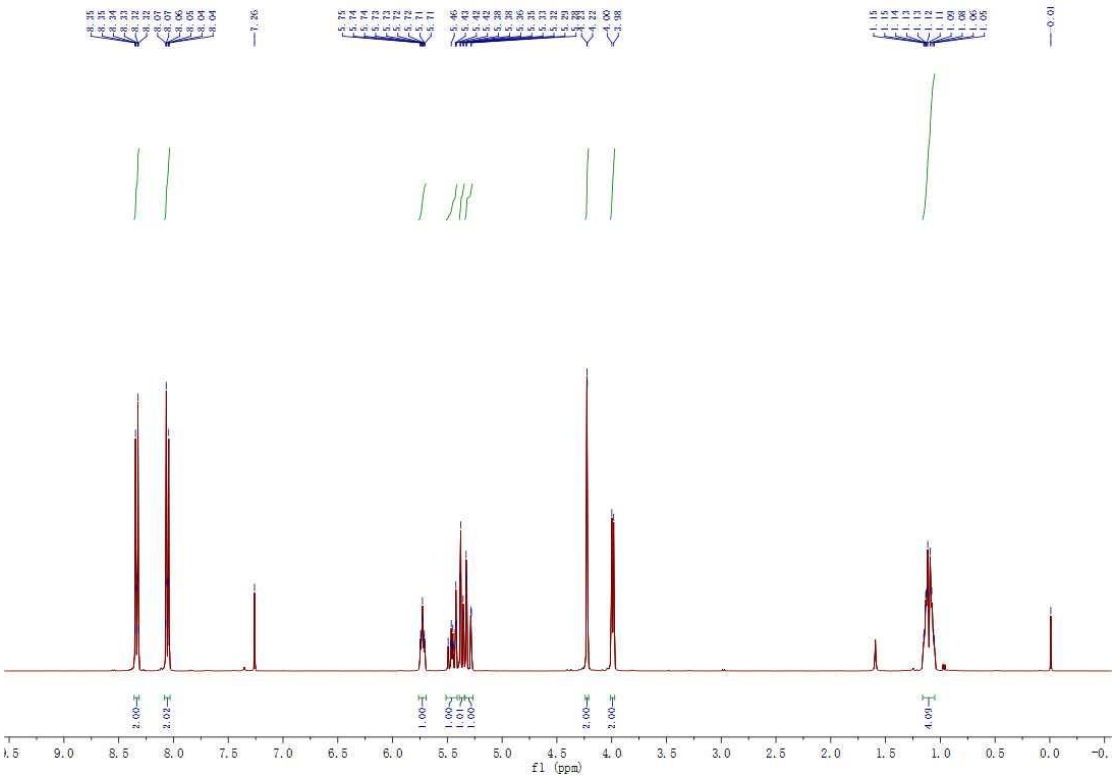

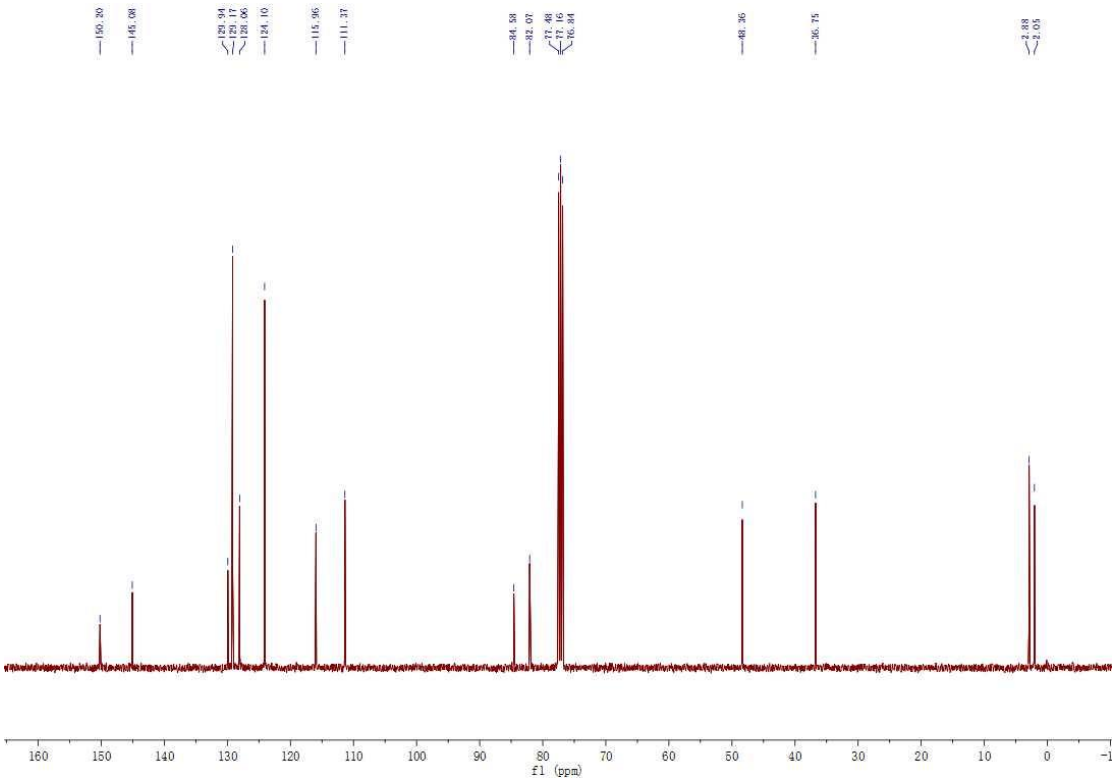

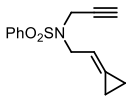

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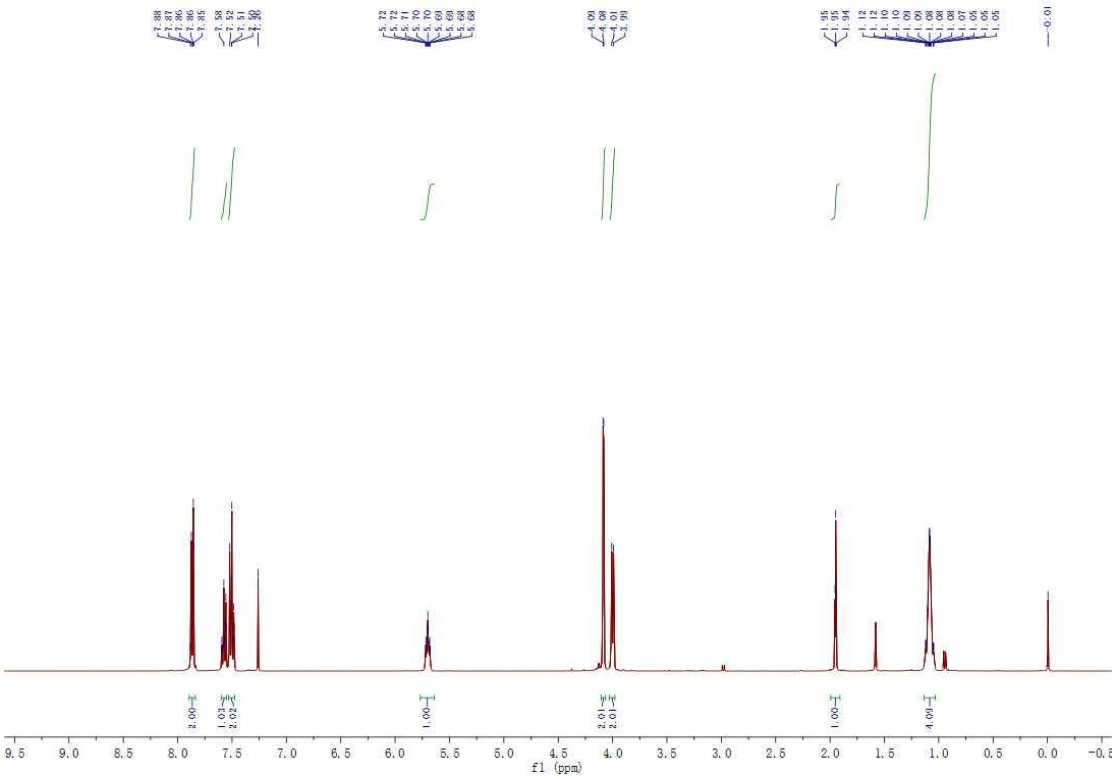

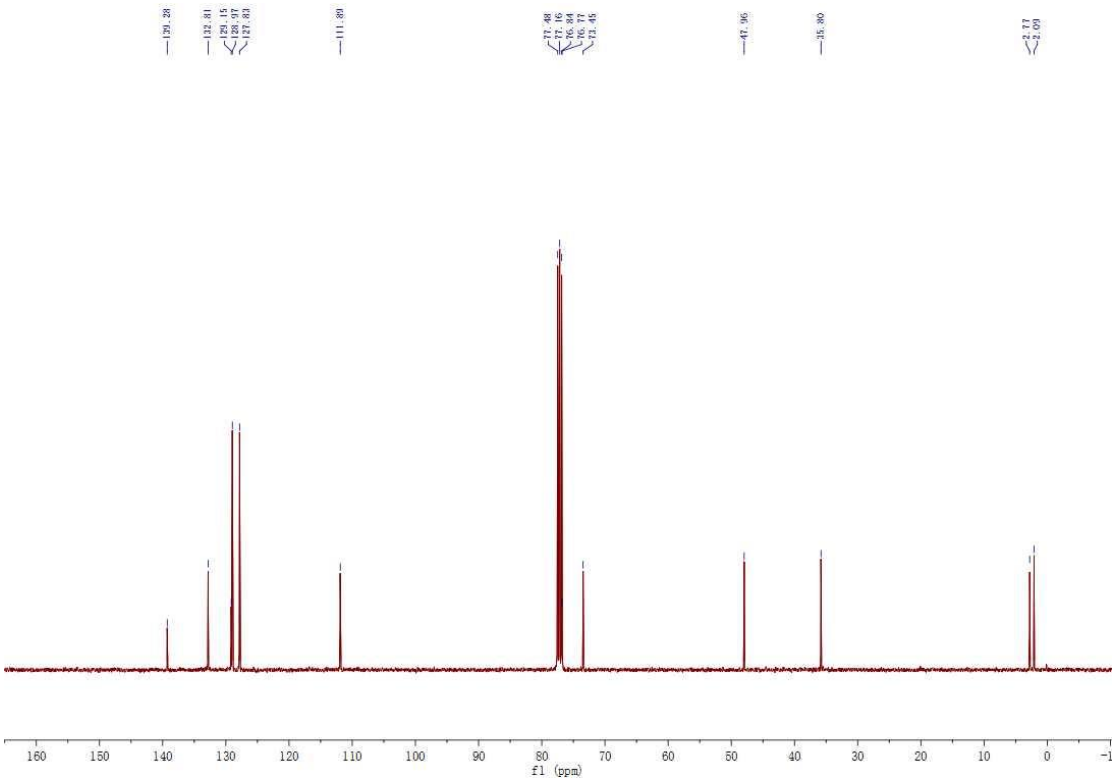

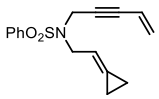

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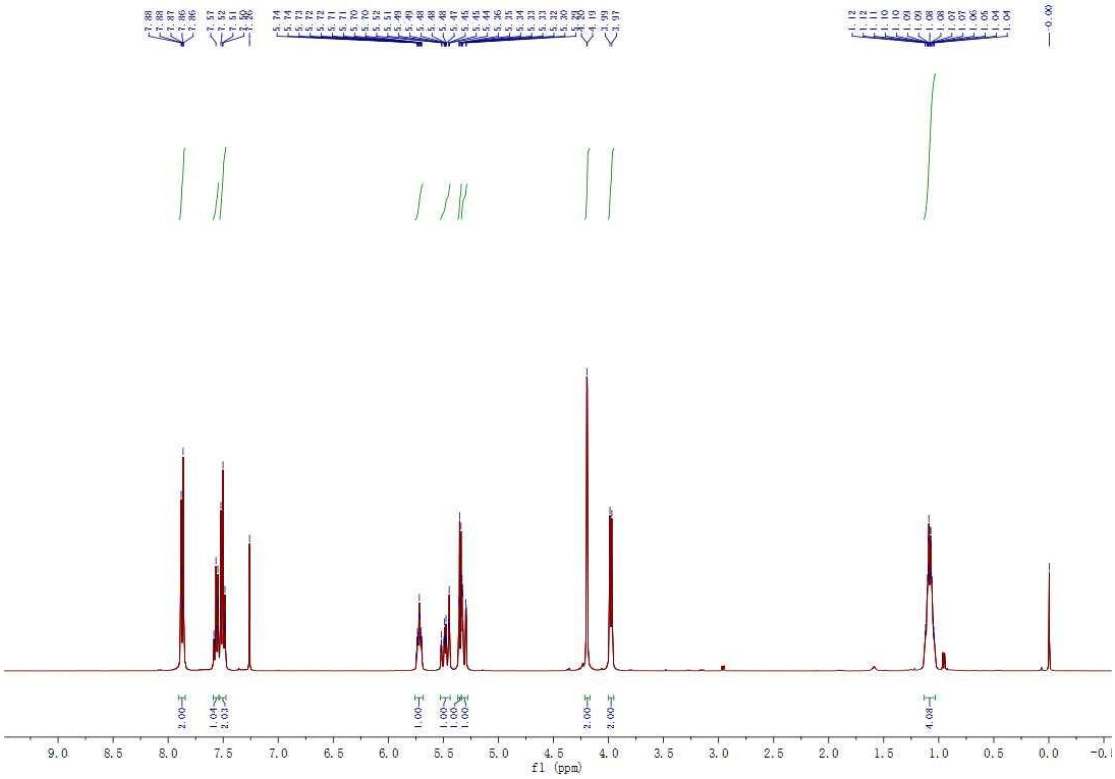

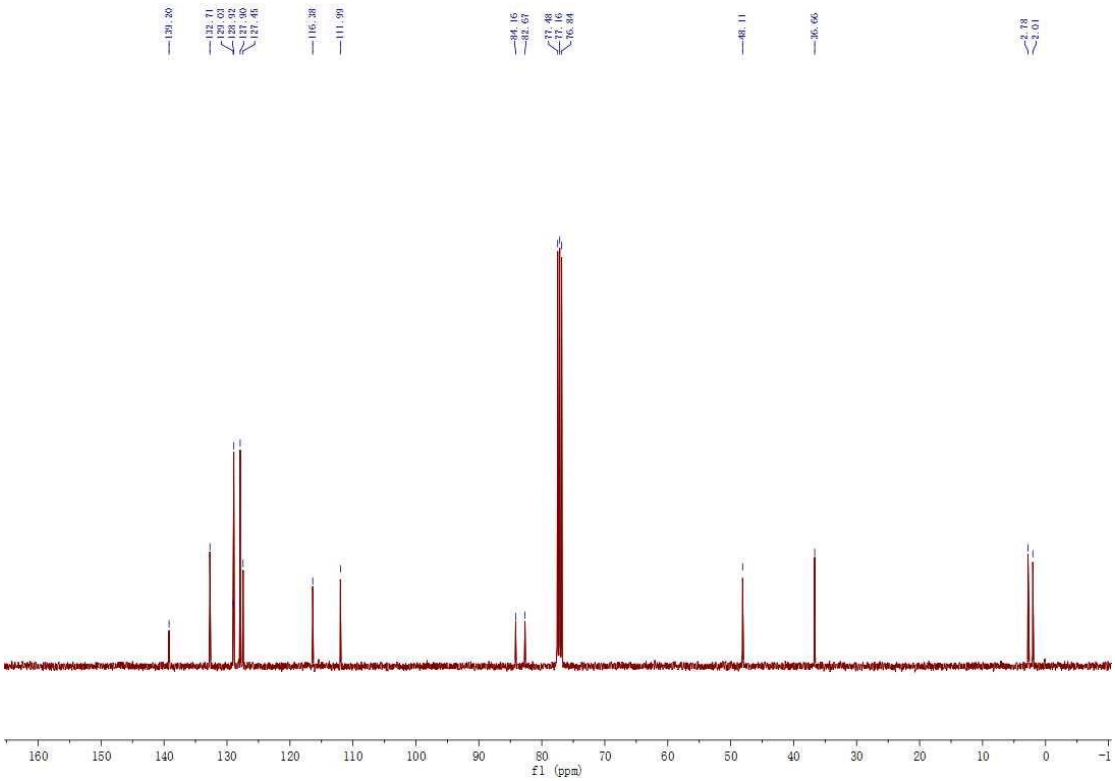

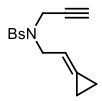

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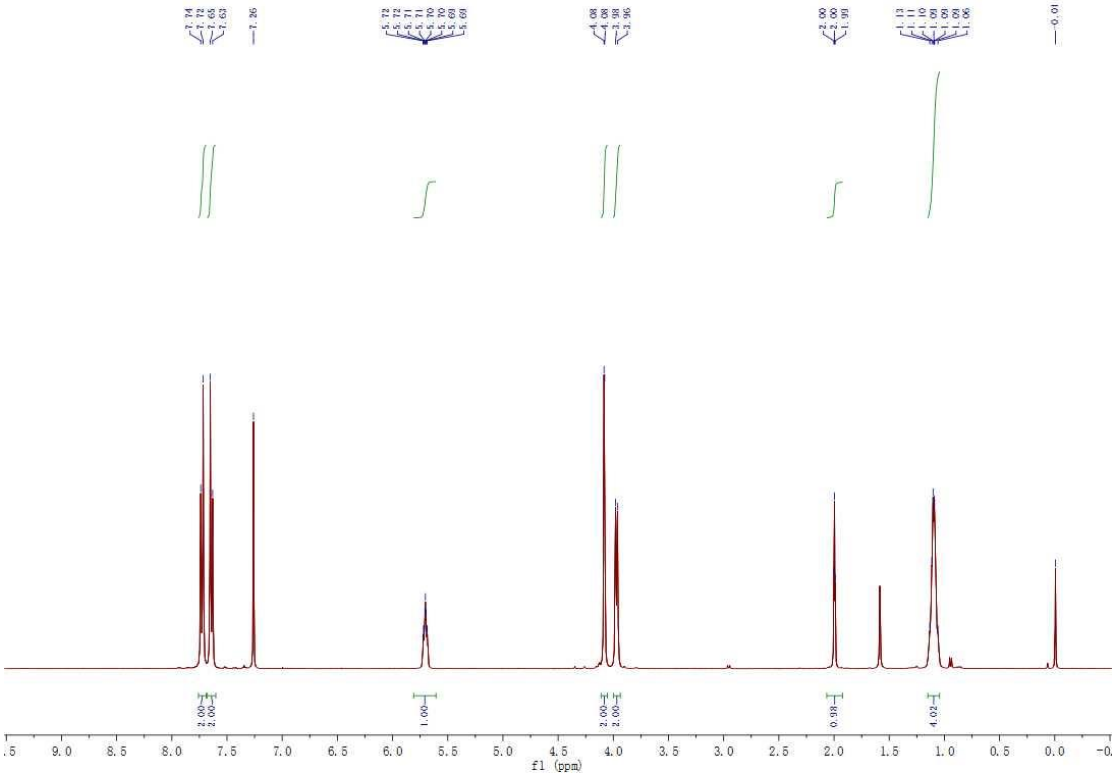

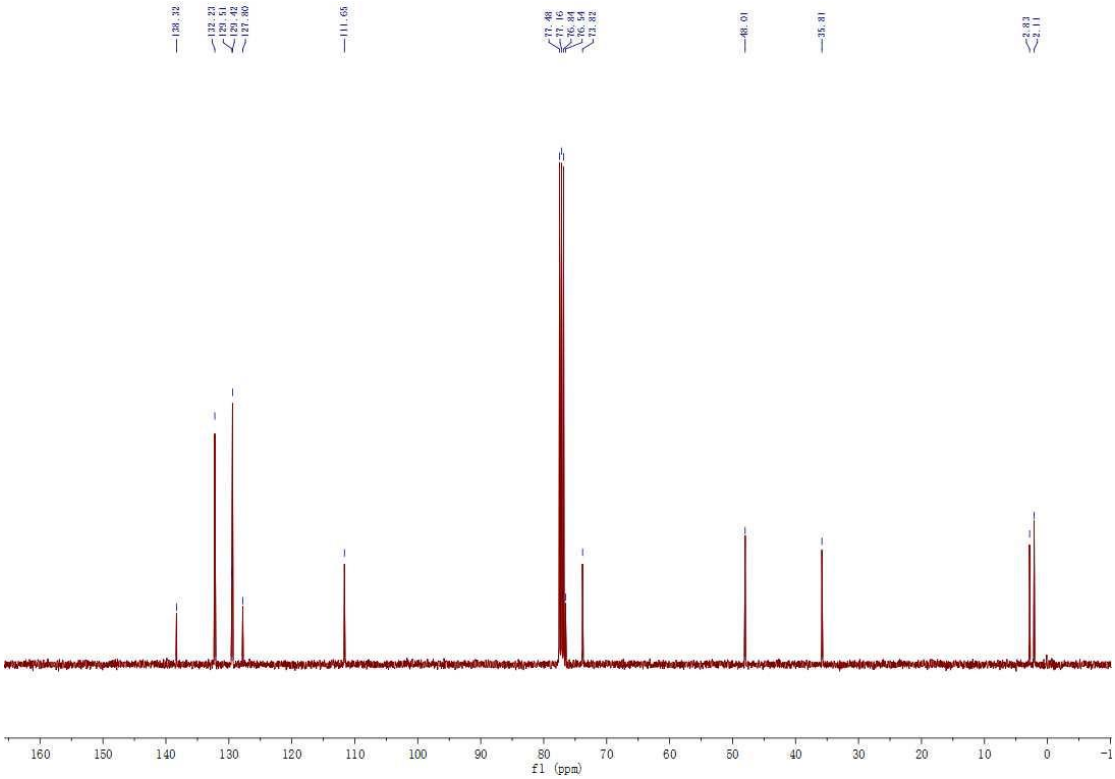

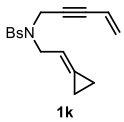

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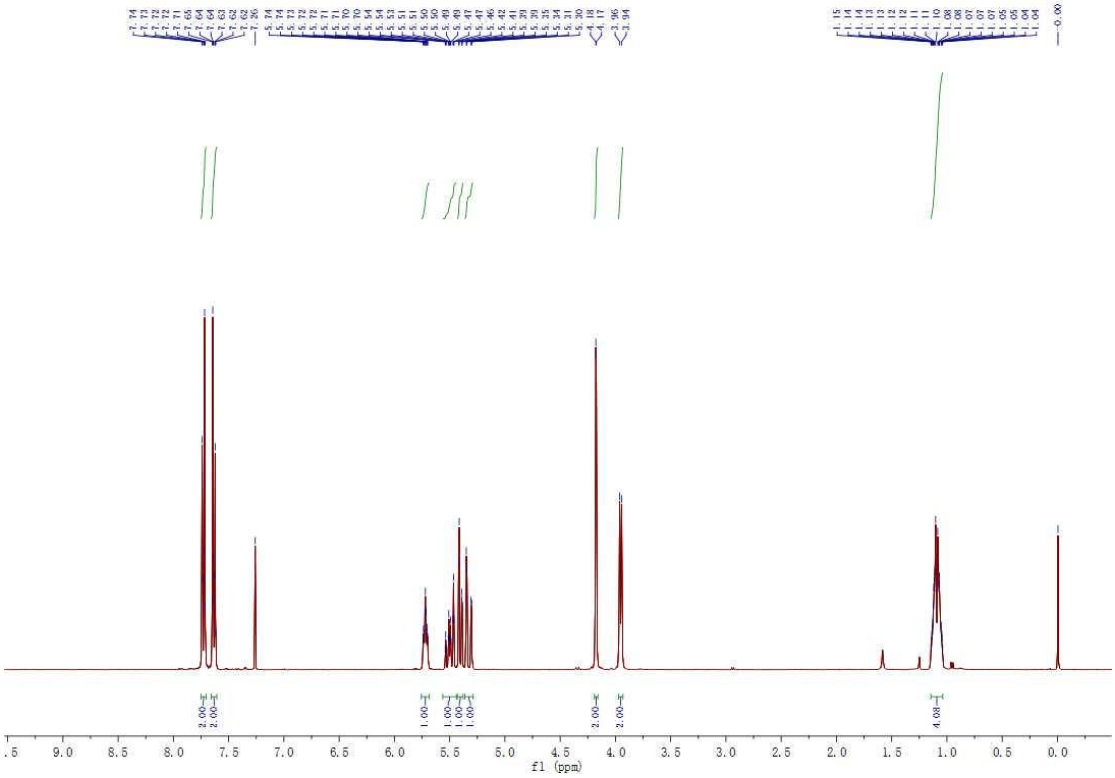

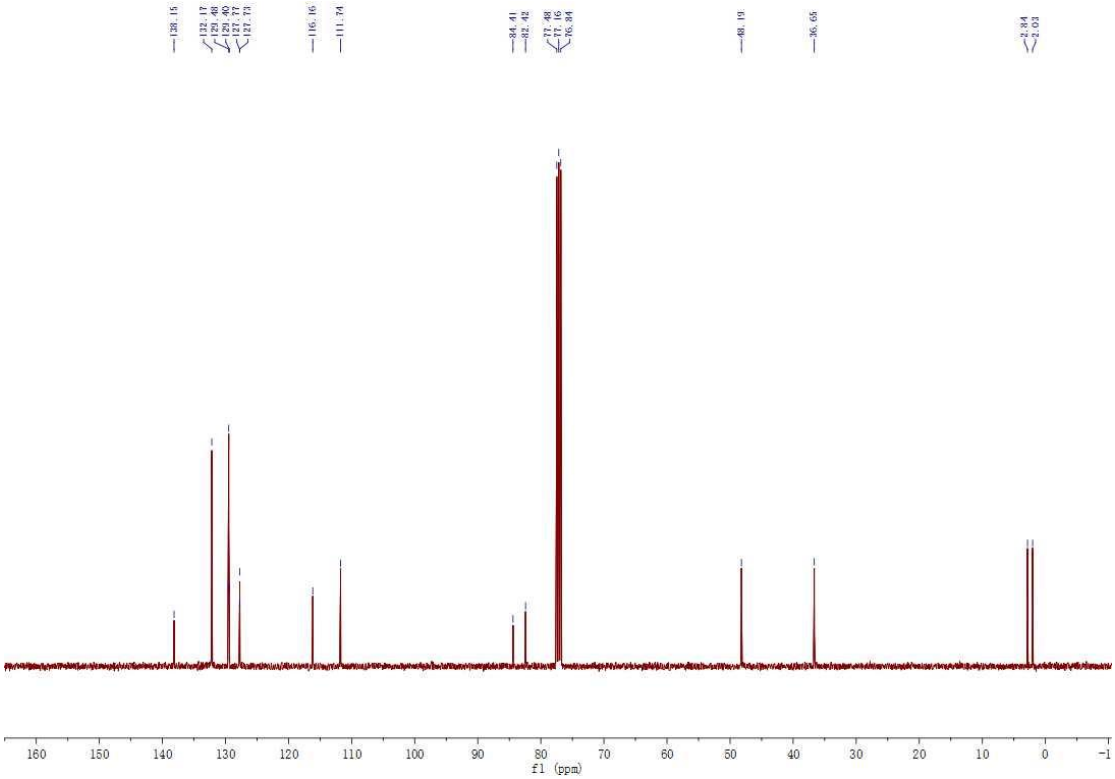

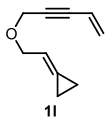

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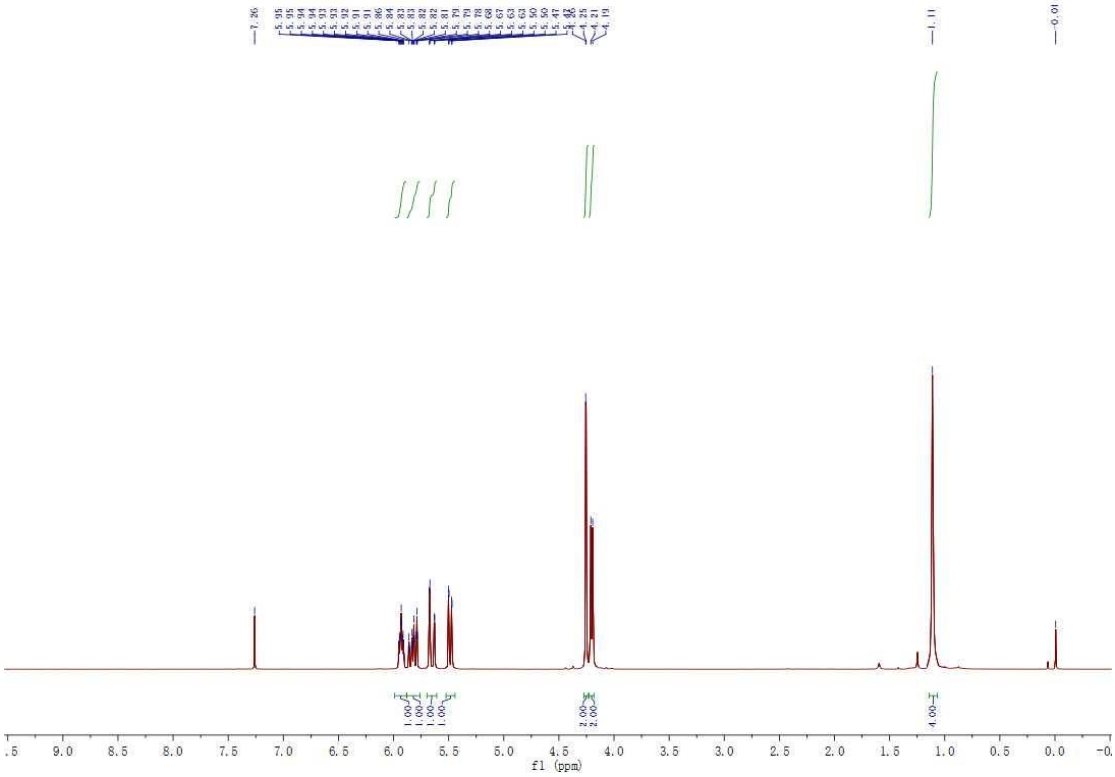
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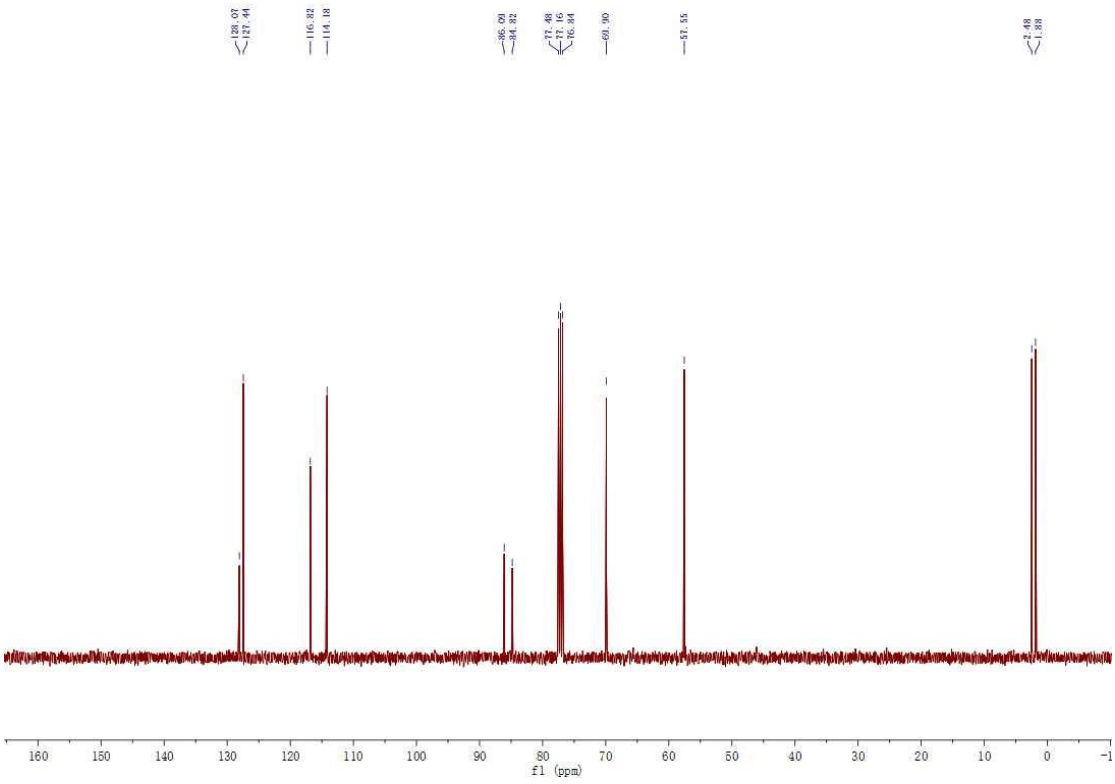
2.00
2.00
4.00
f1 (ppm)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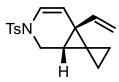
1.88
f1 (ppm)



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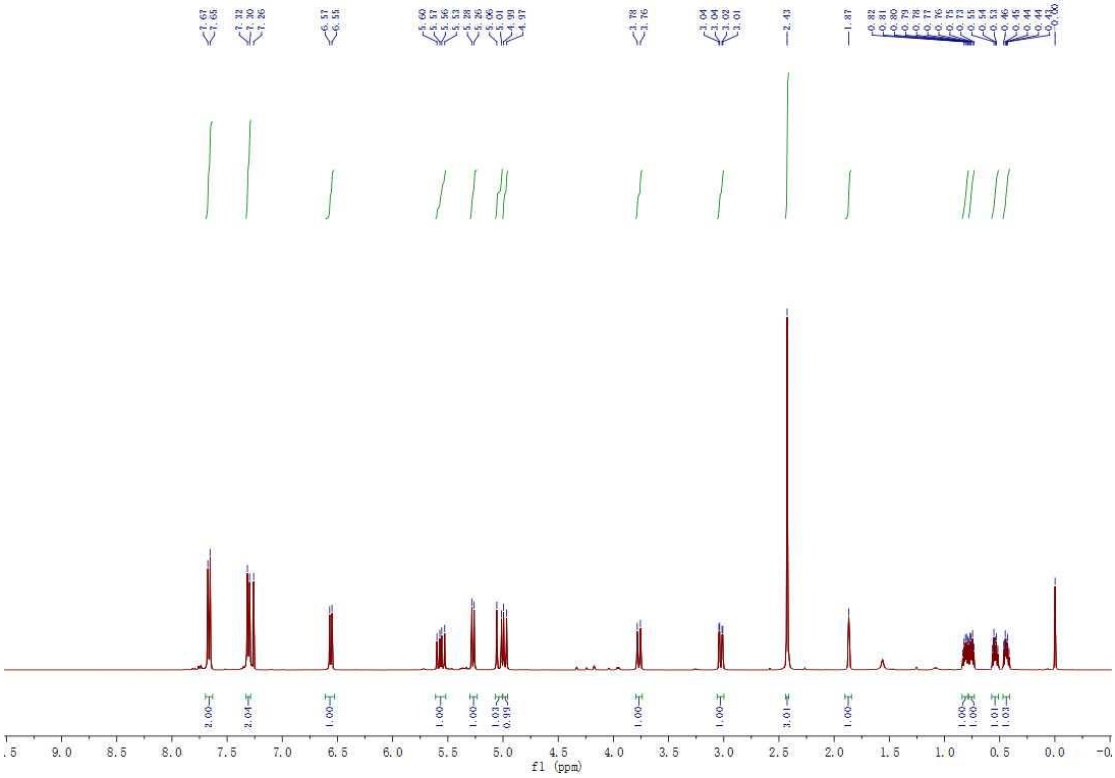

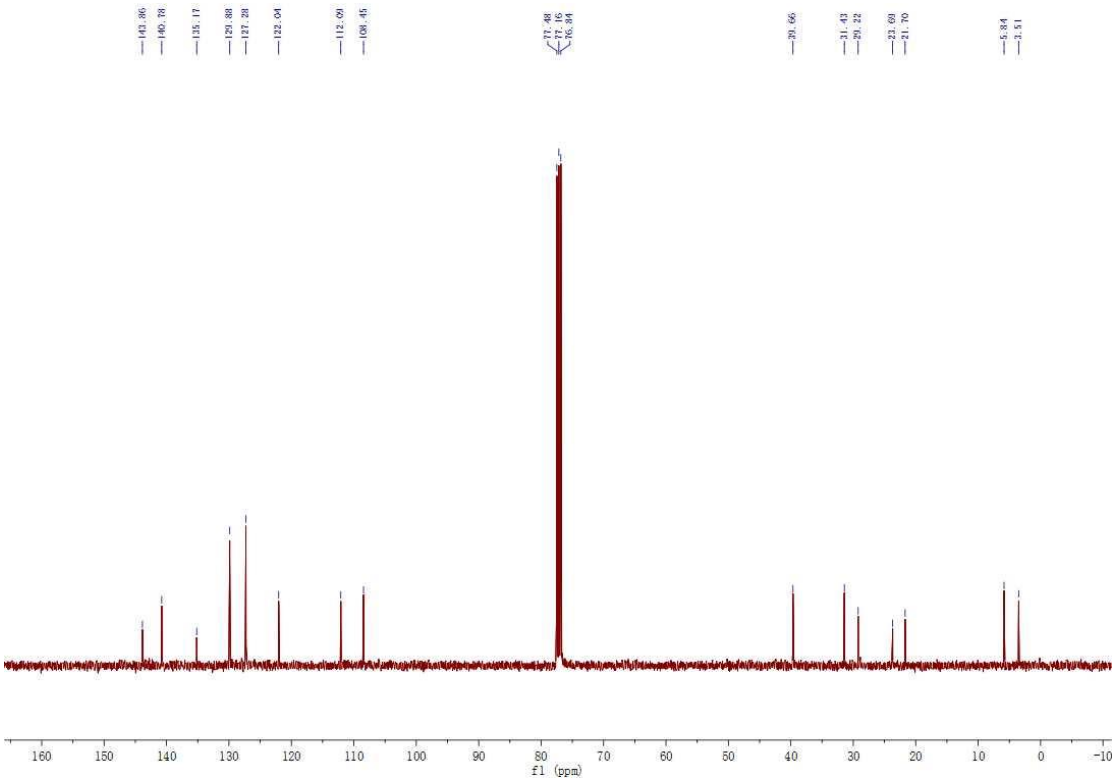

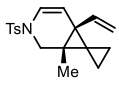

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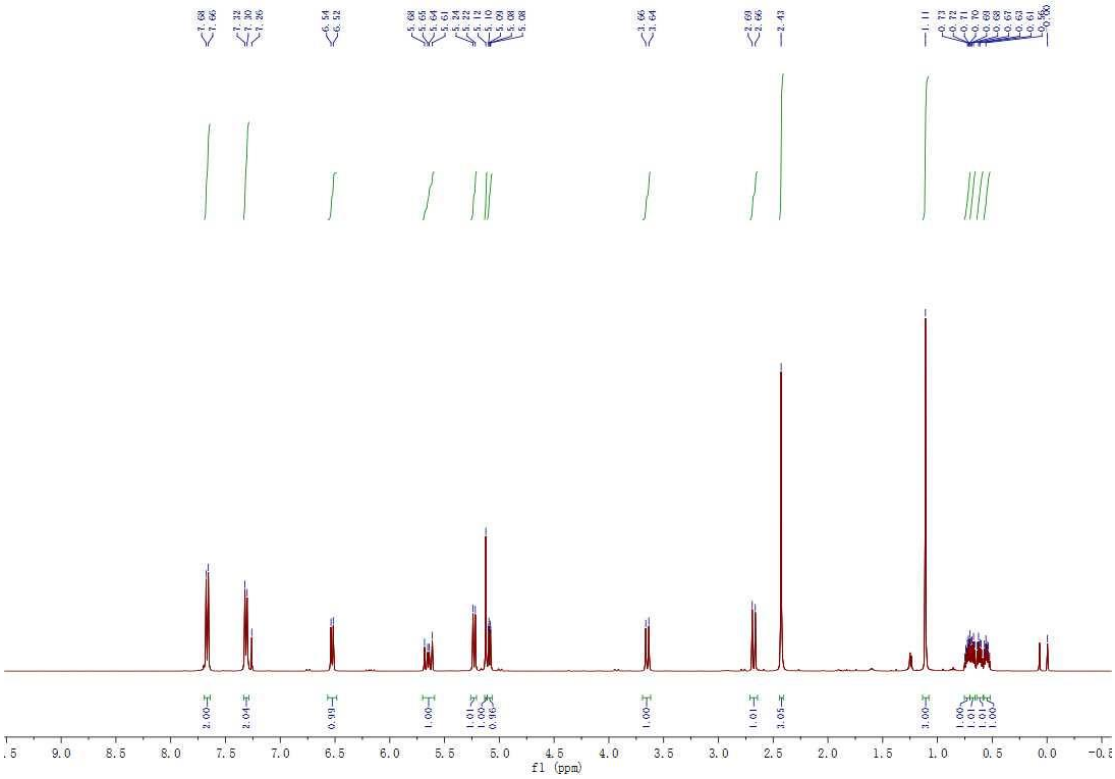

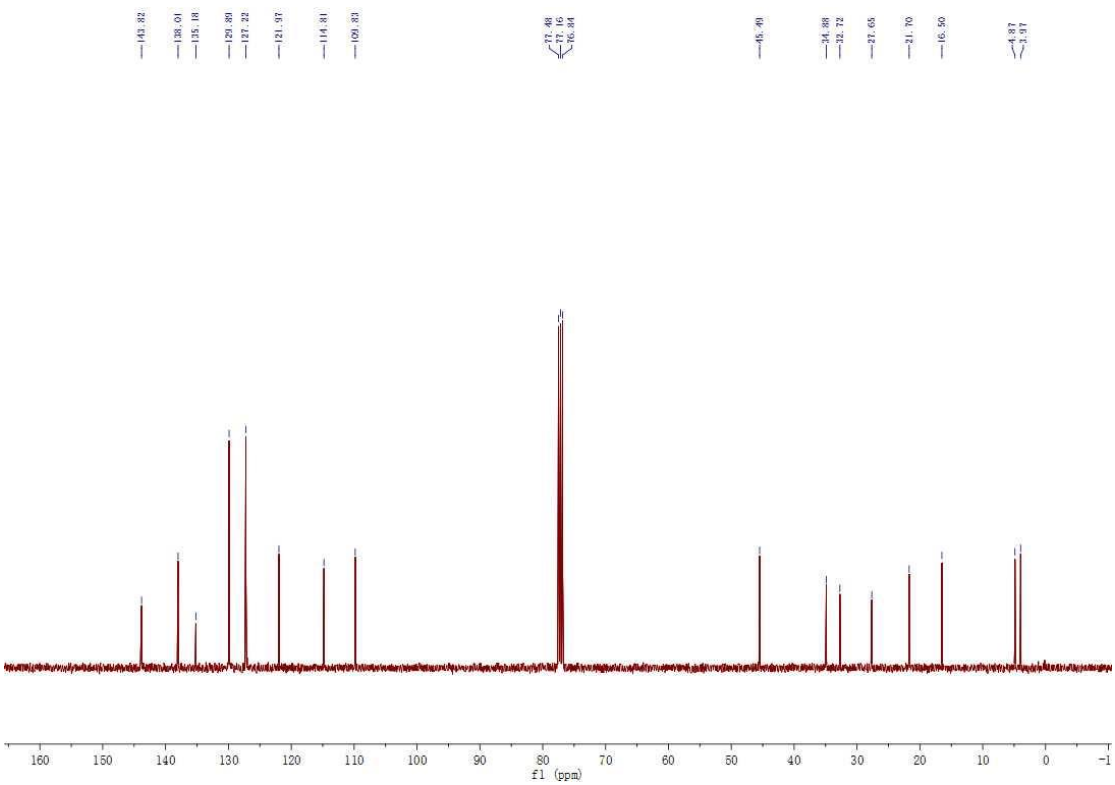

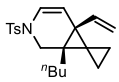

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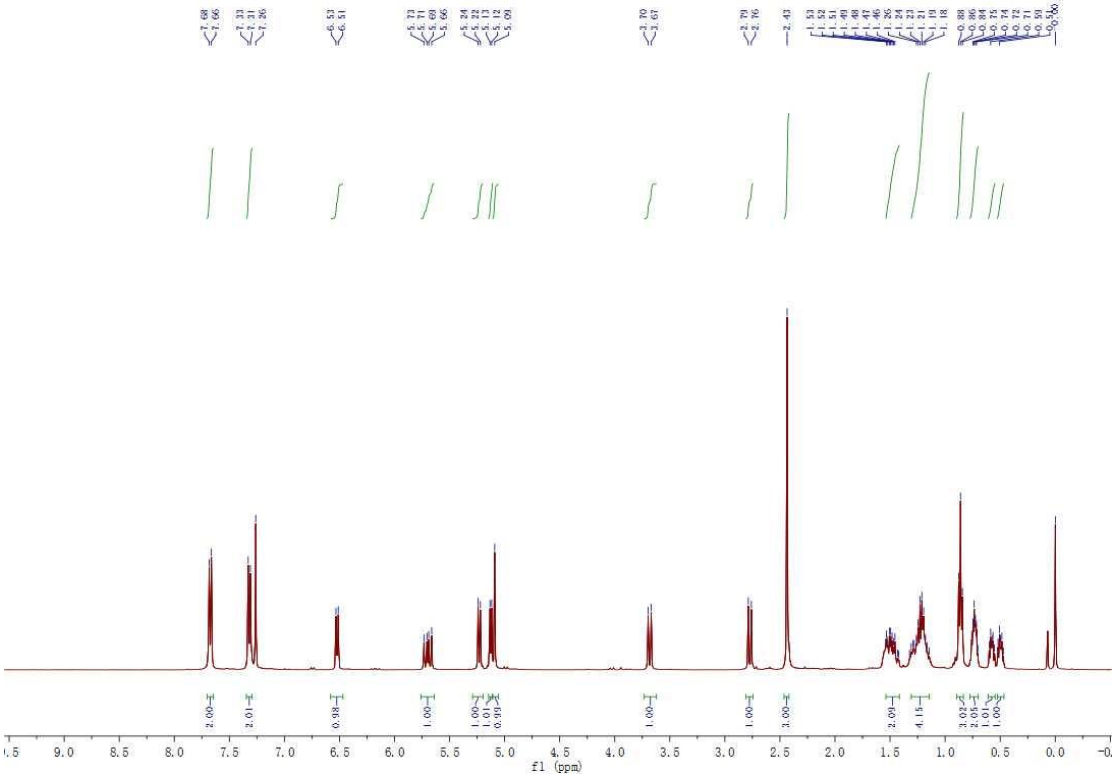

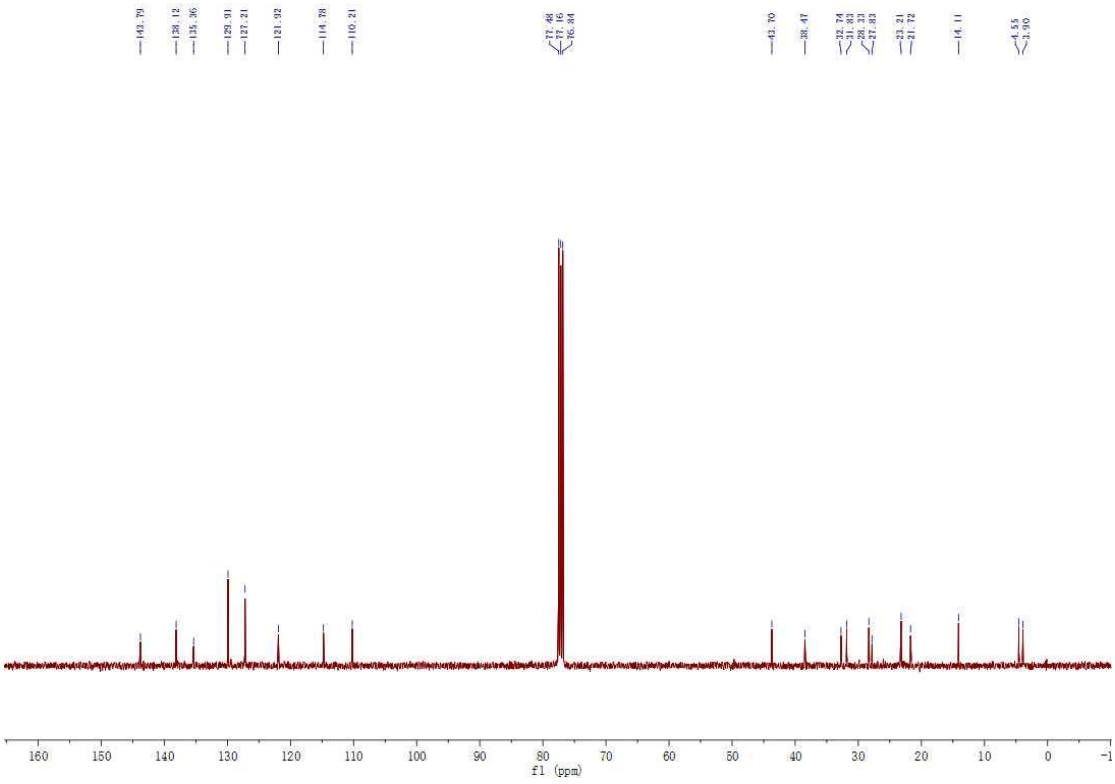

S62

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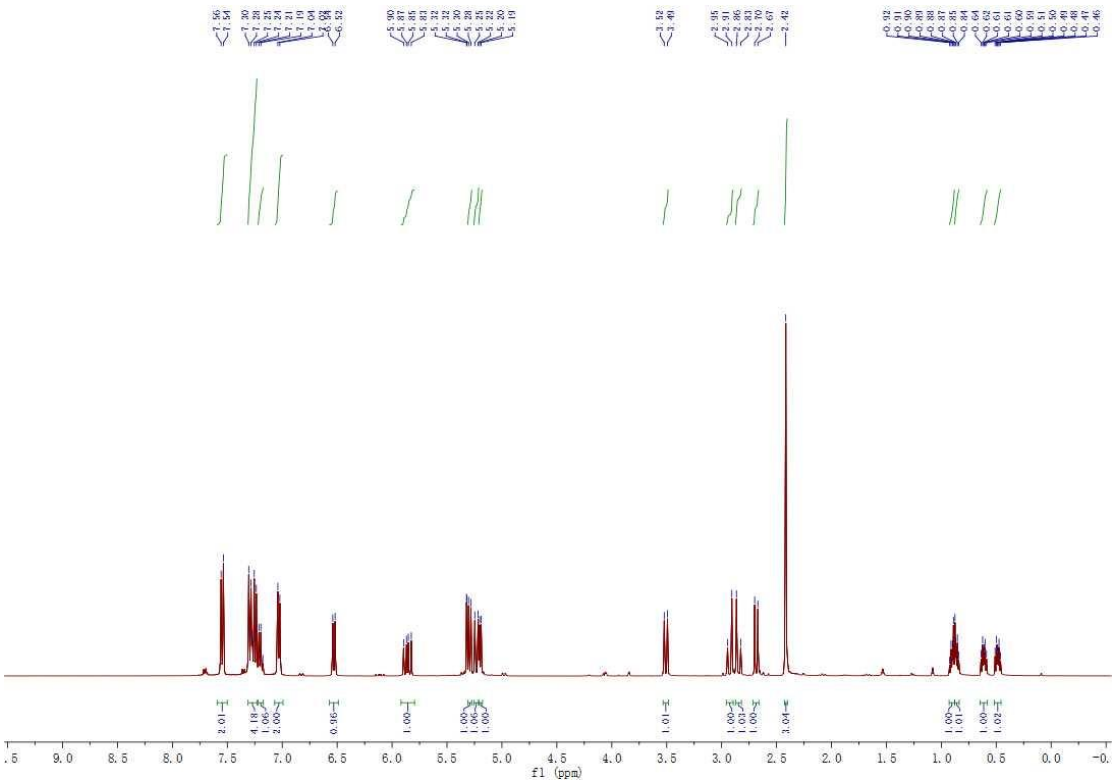
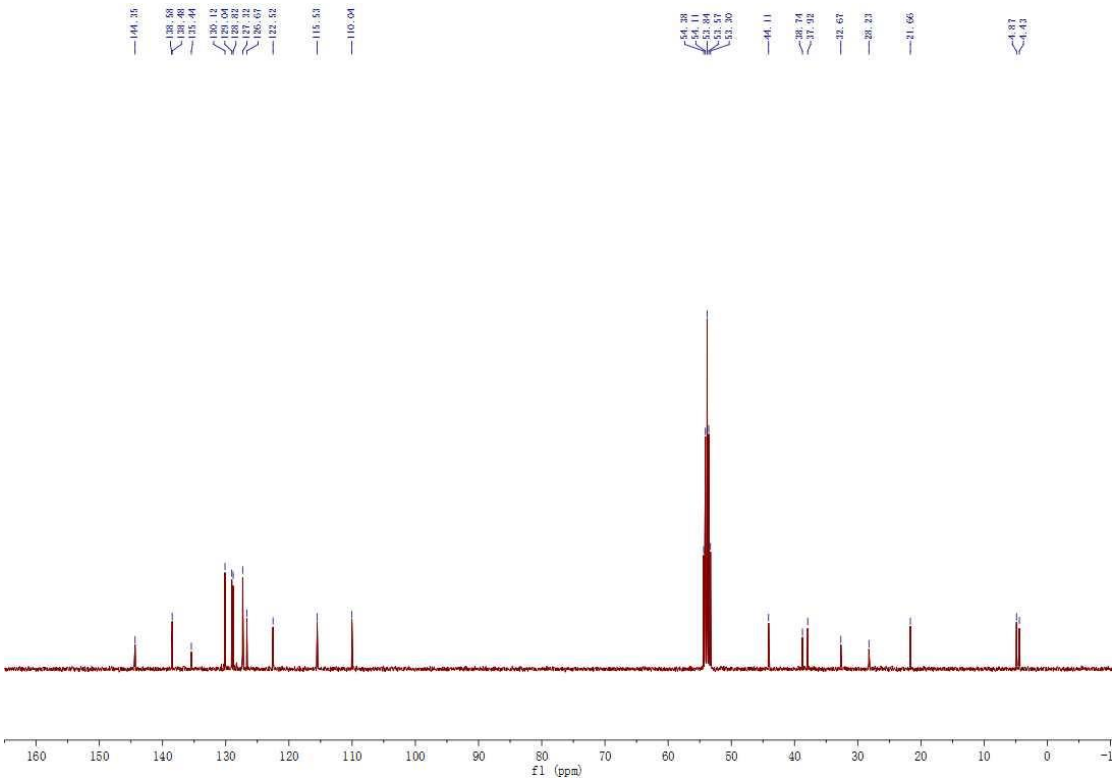
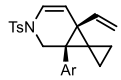
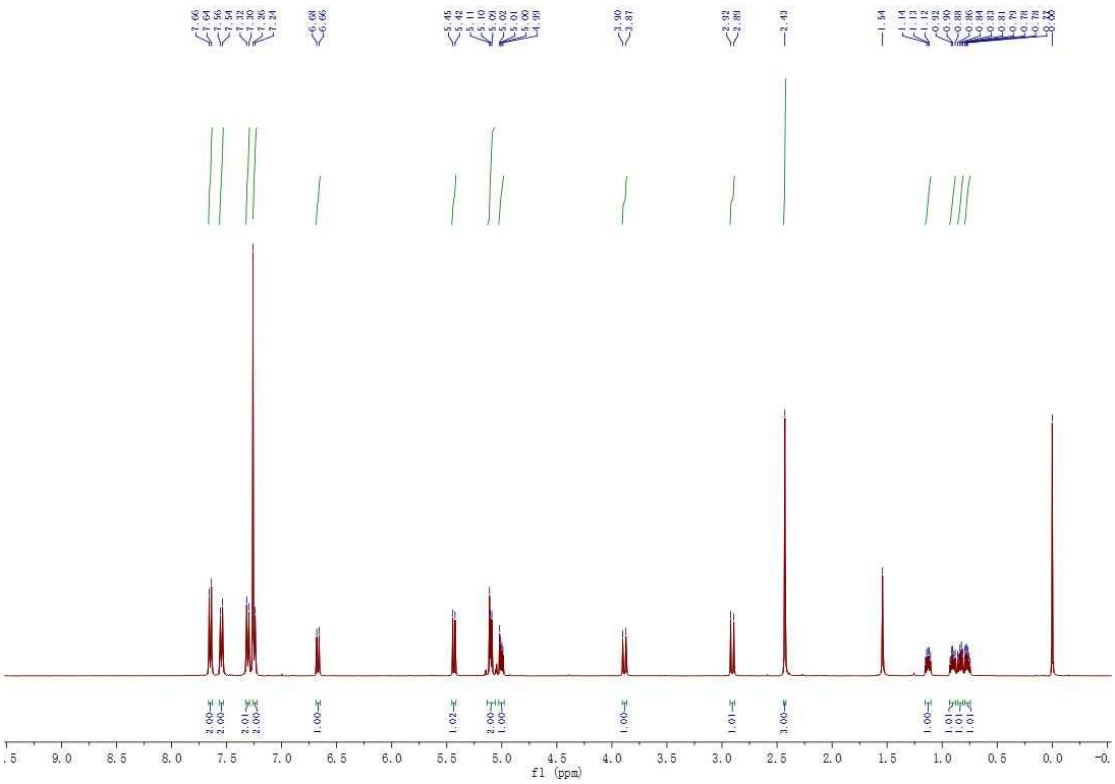
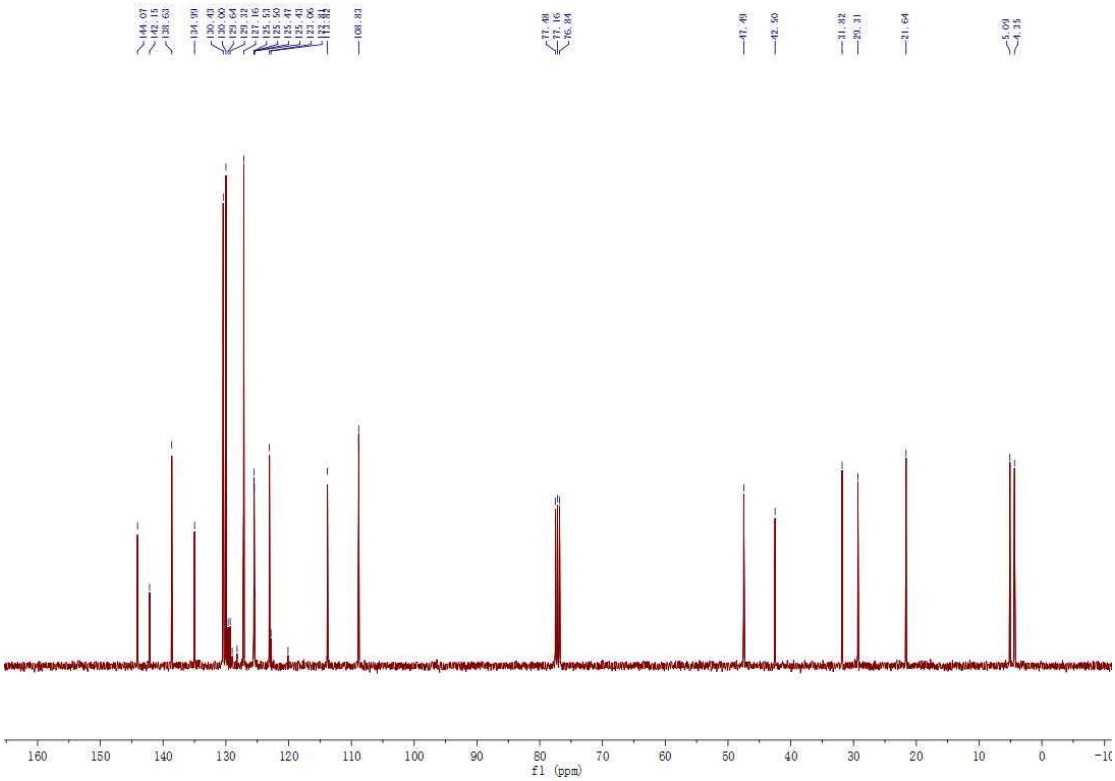


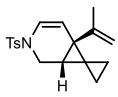




2e, Ar = 4-$CF_3C_6H_4$







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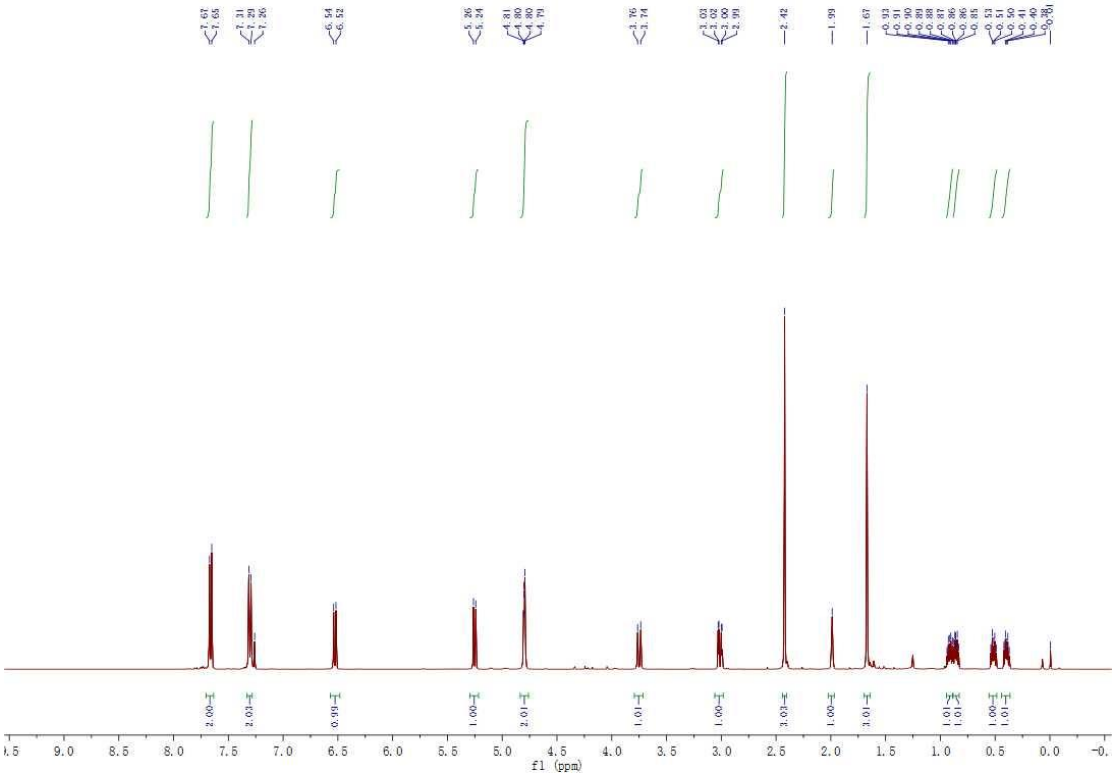

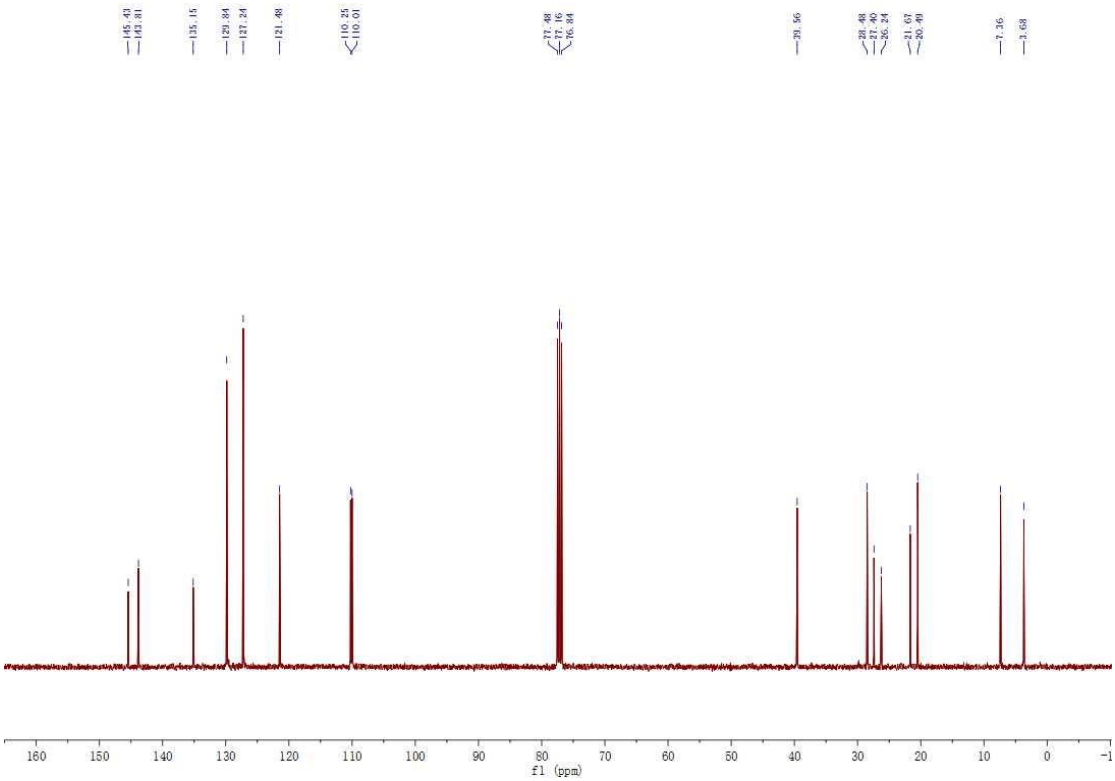

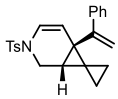

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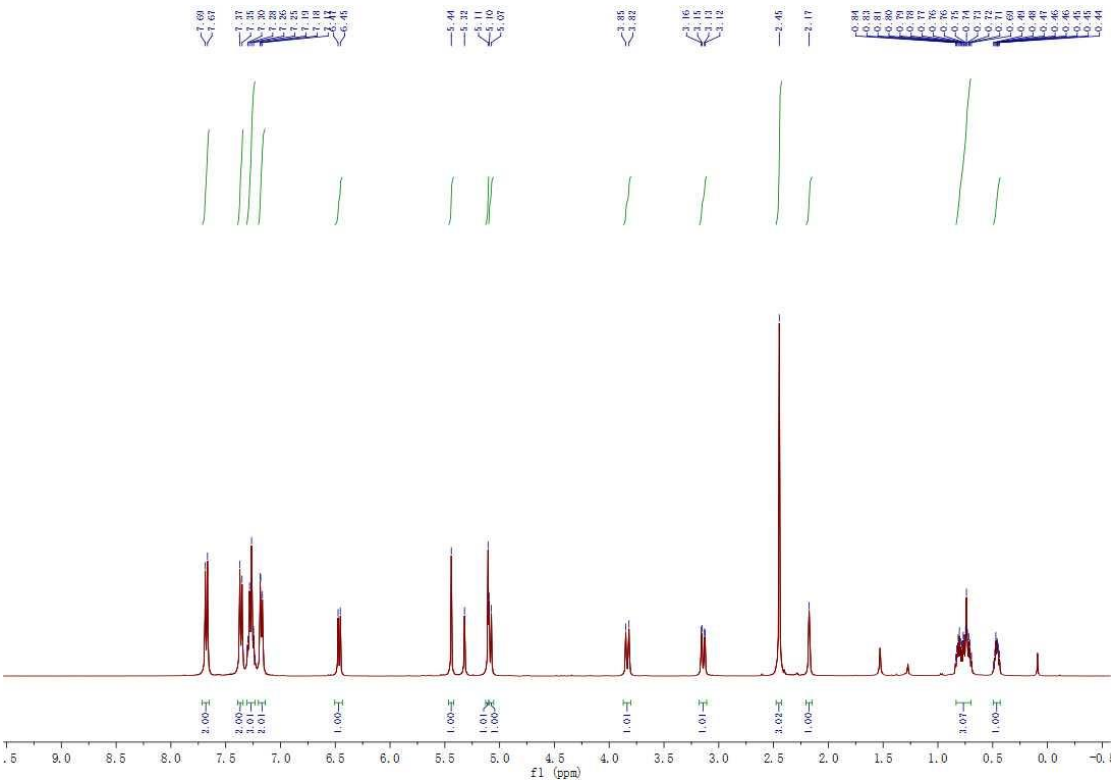
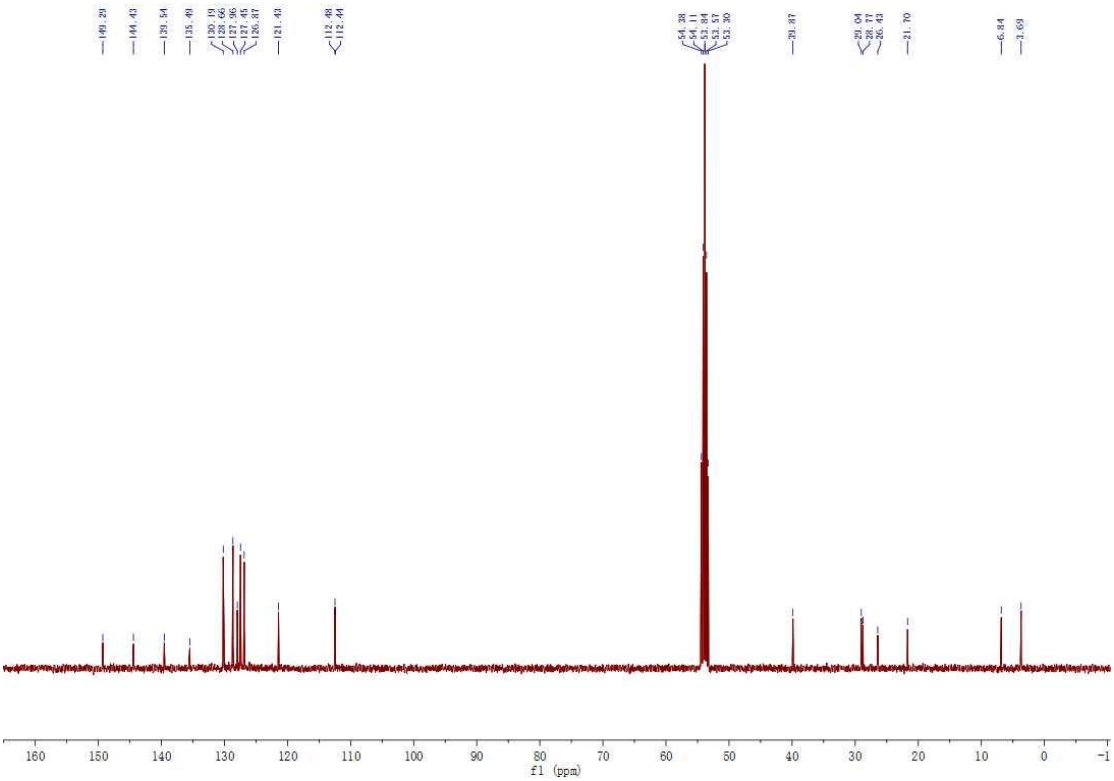
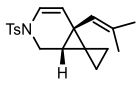
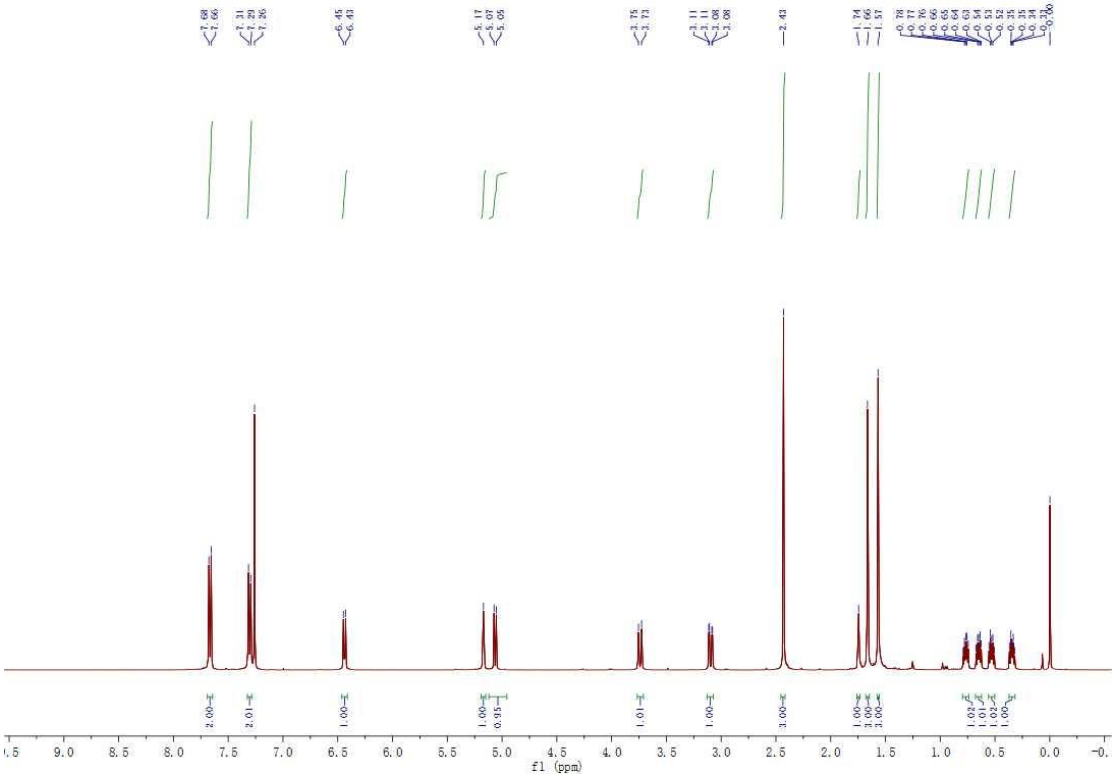
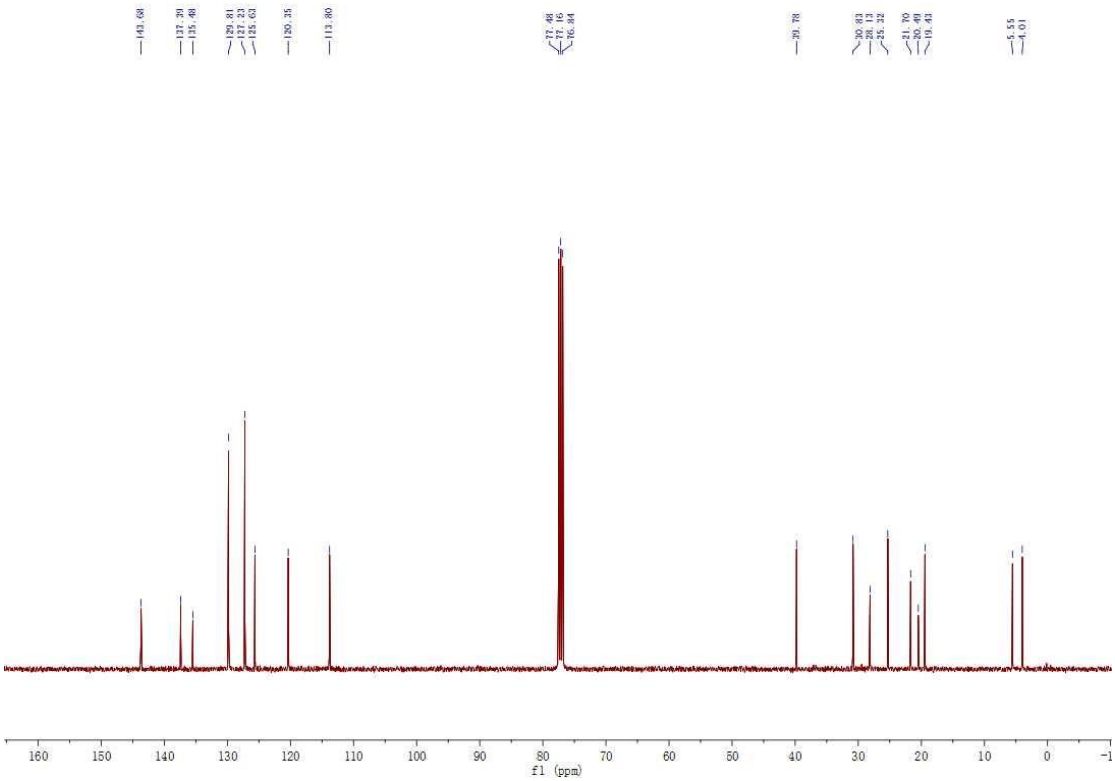


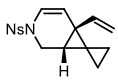




2h







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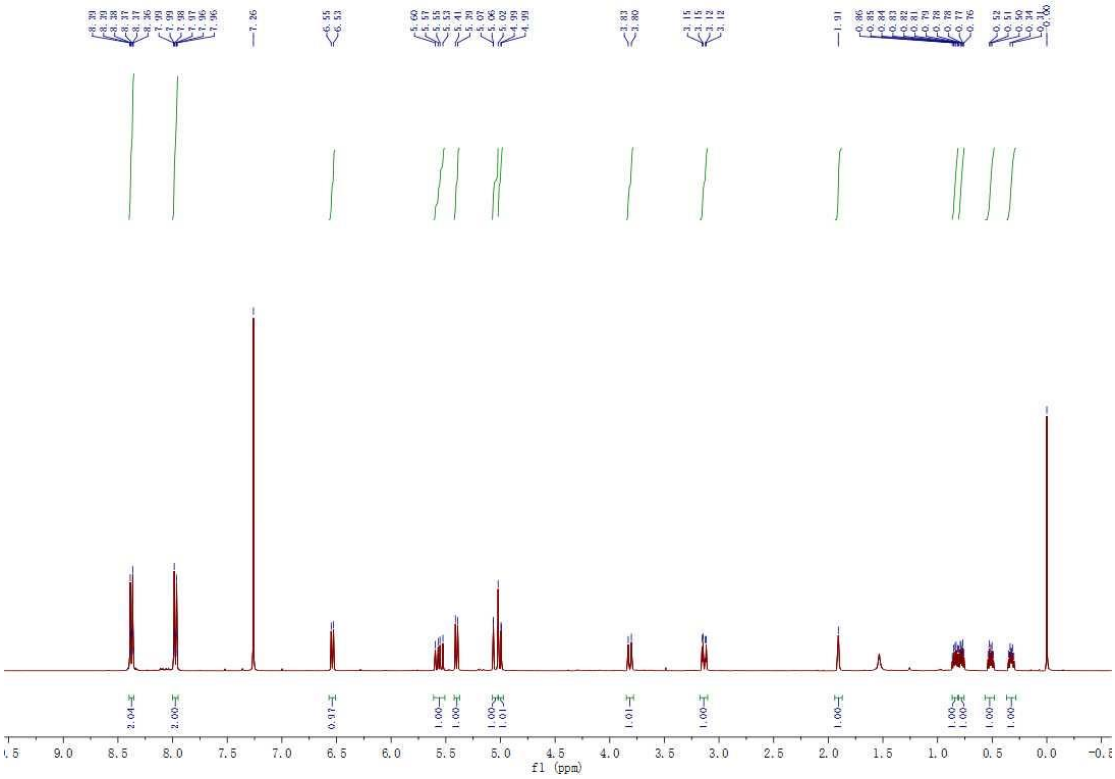

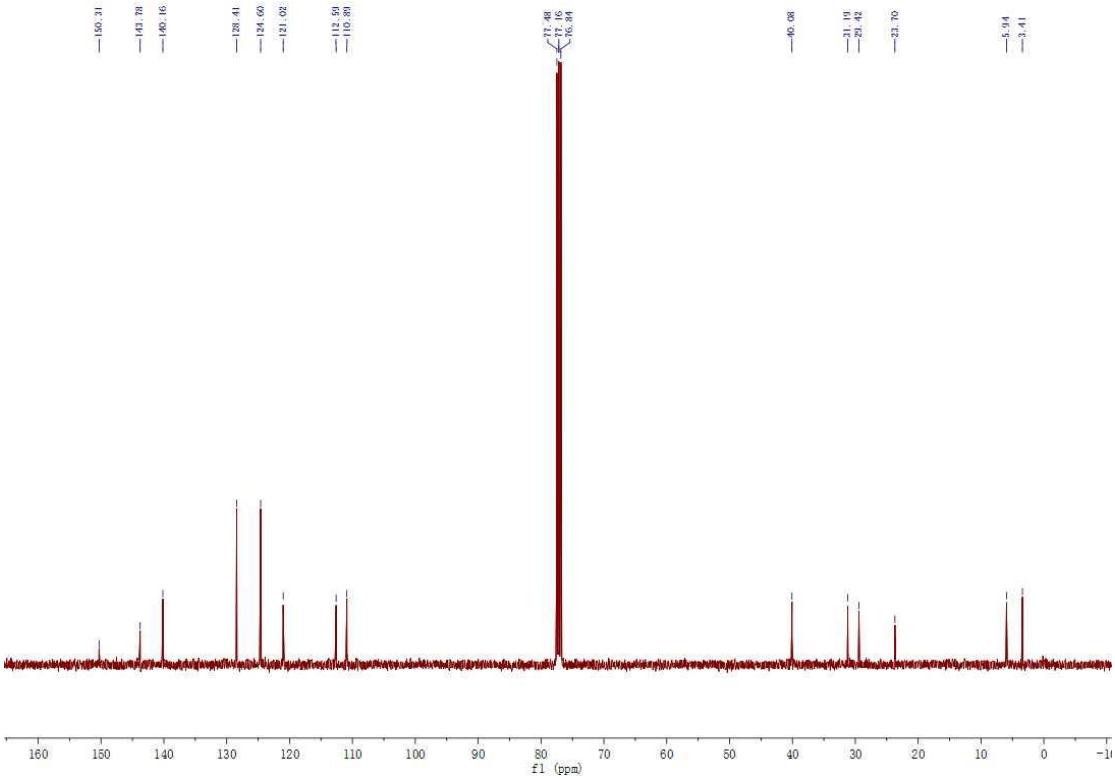

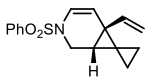

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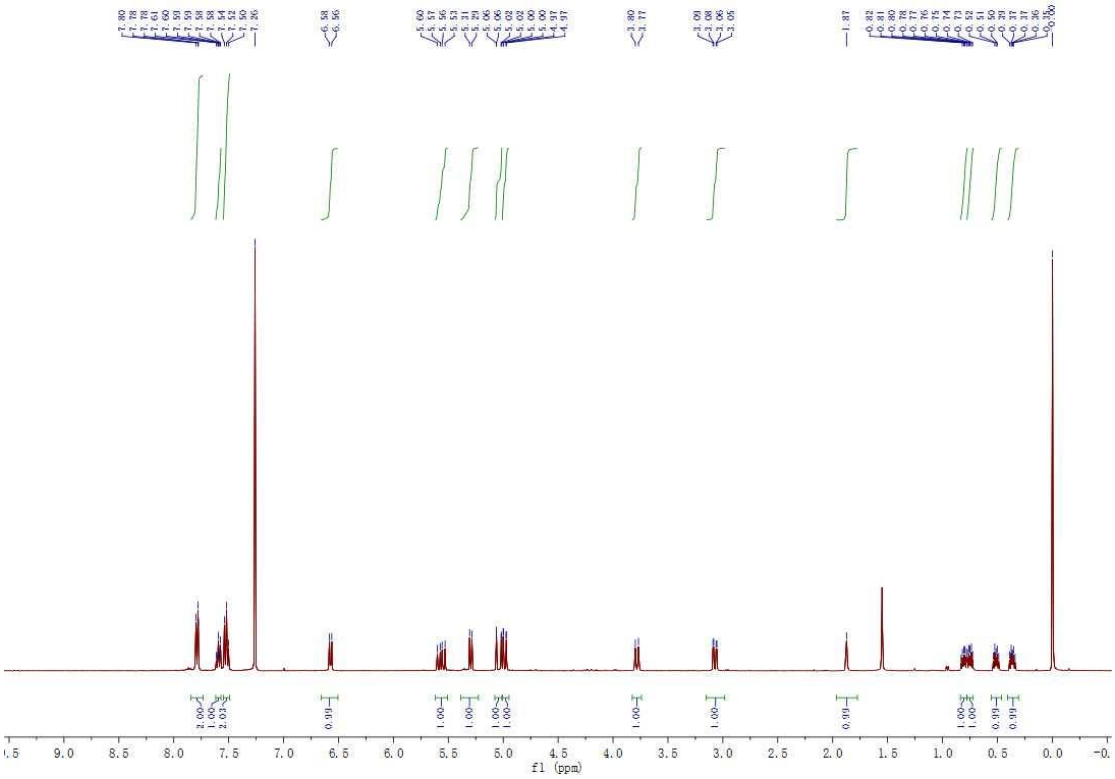

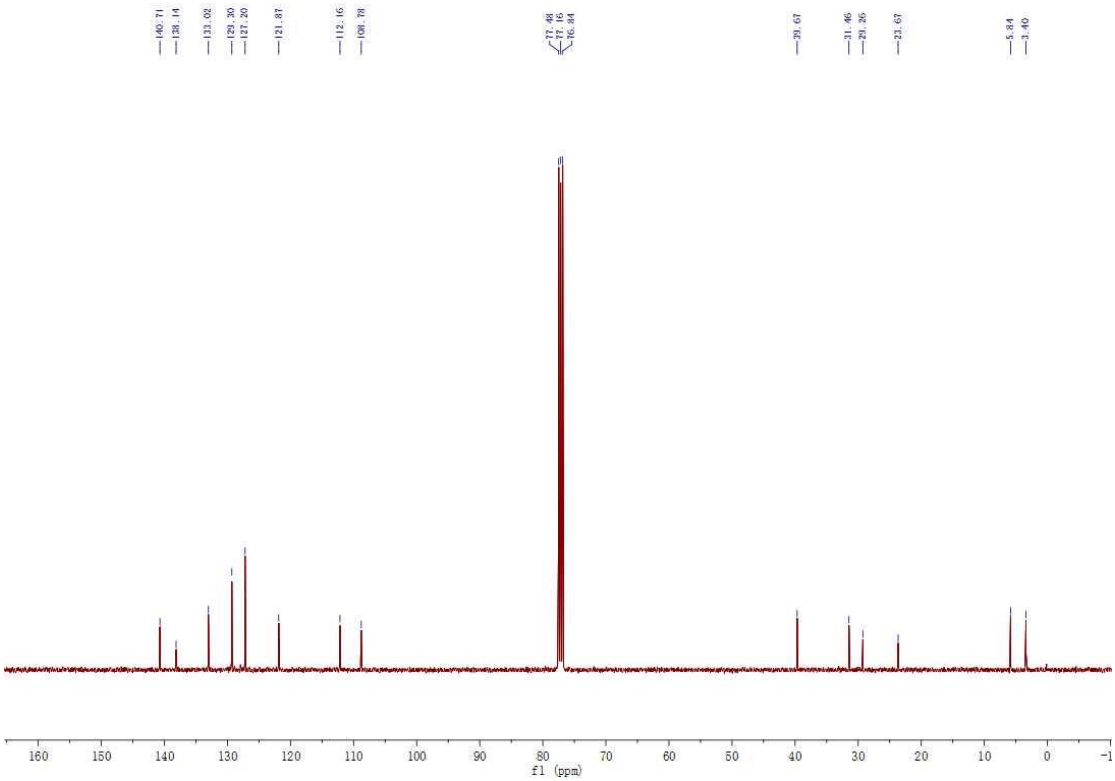

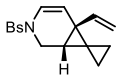

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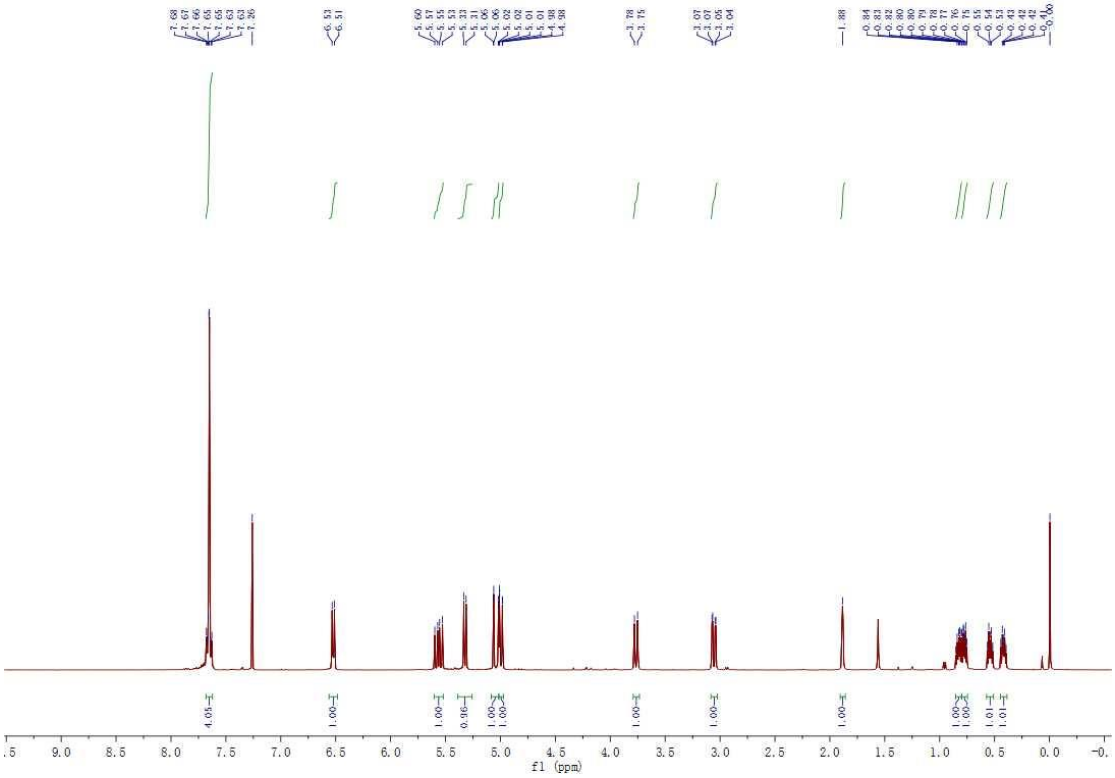

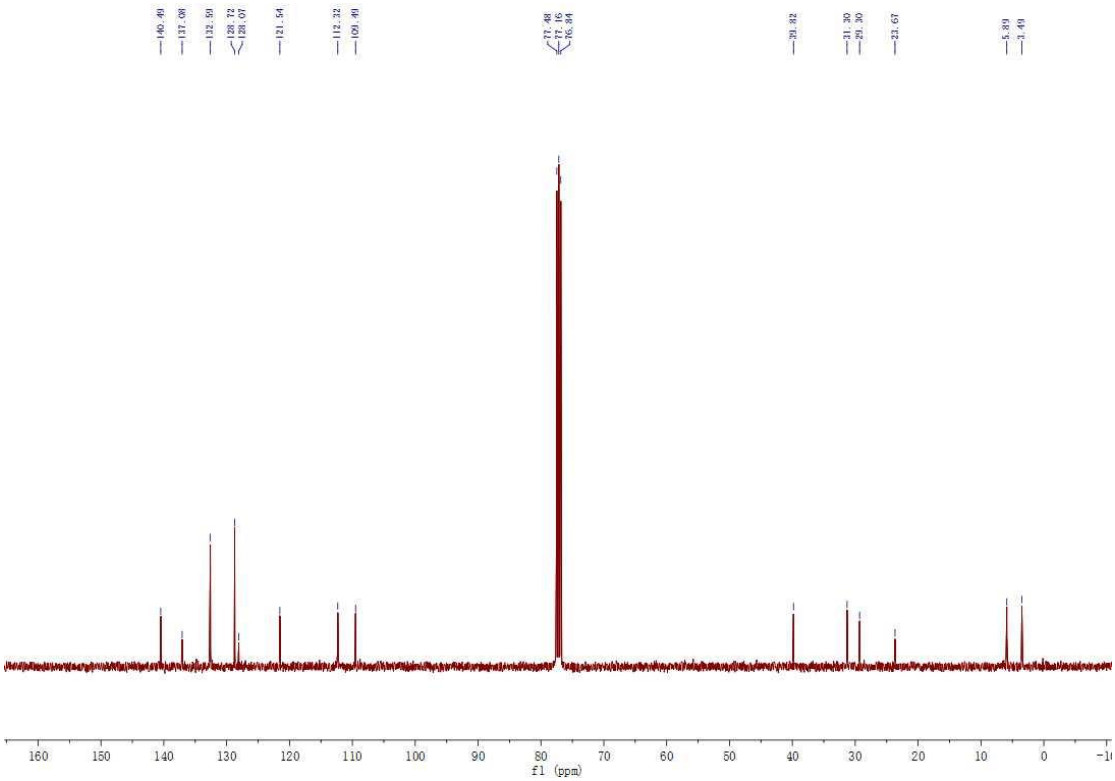

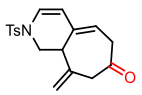

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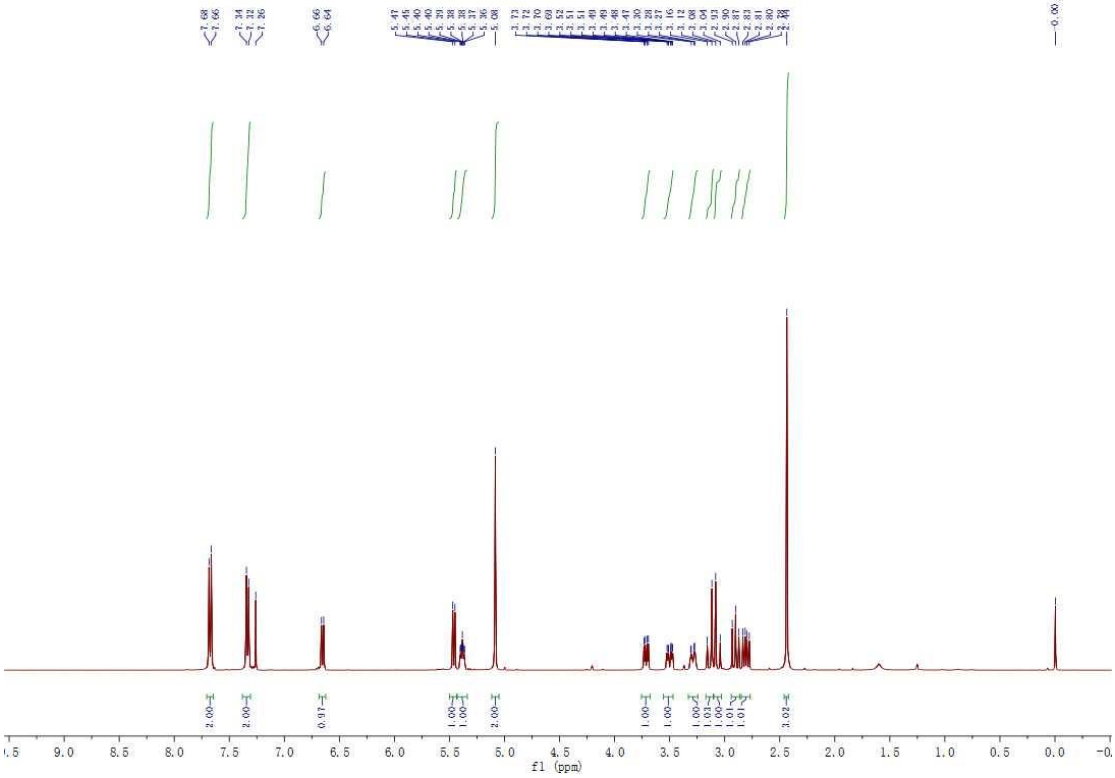
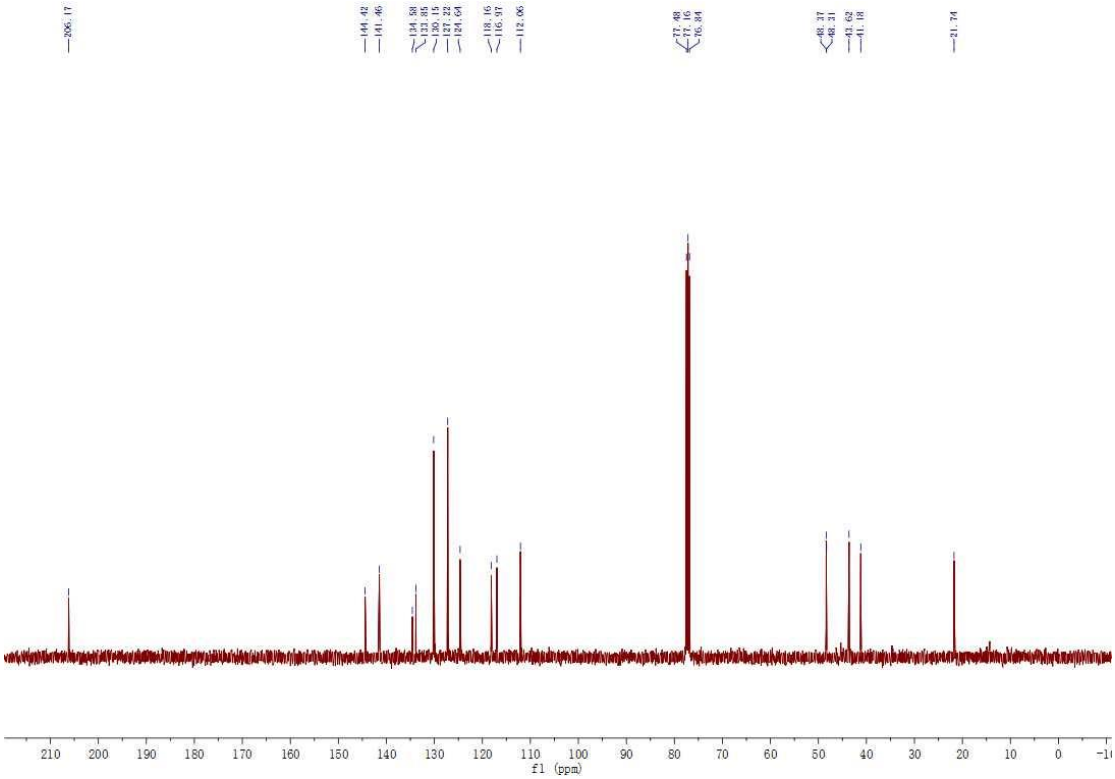
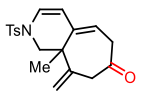
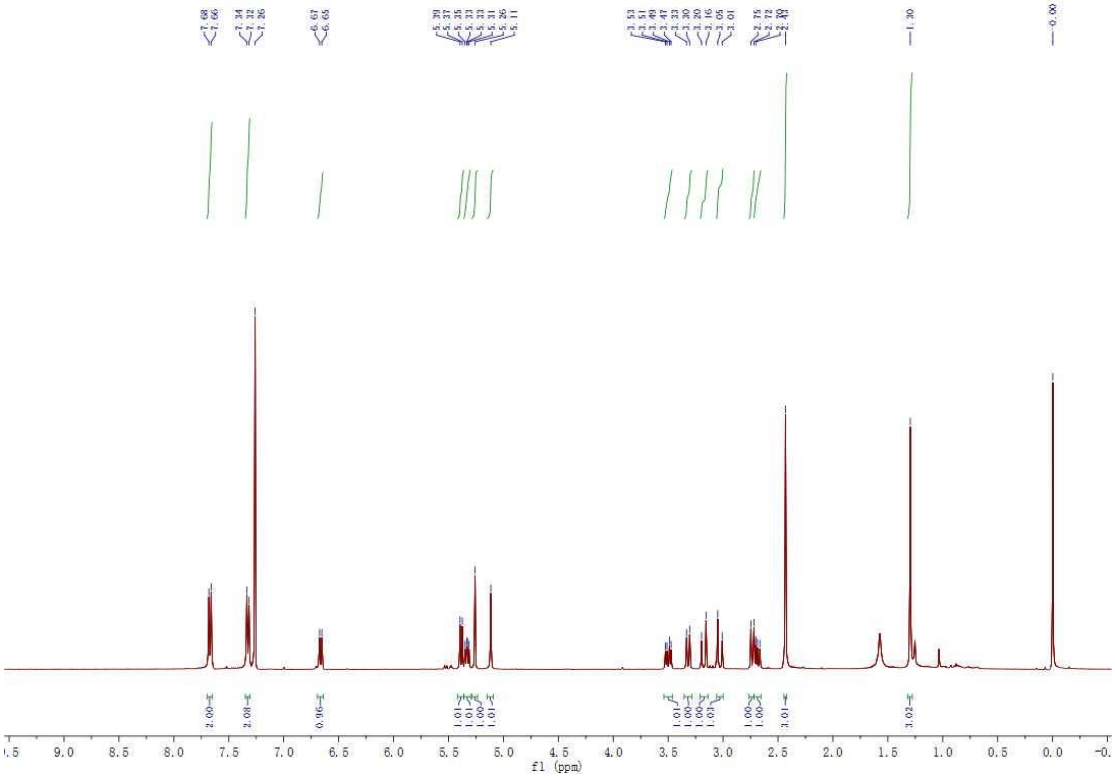
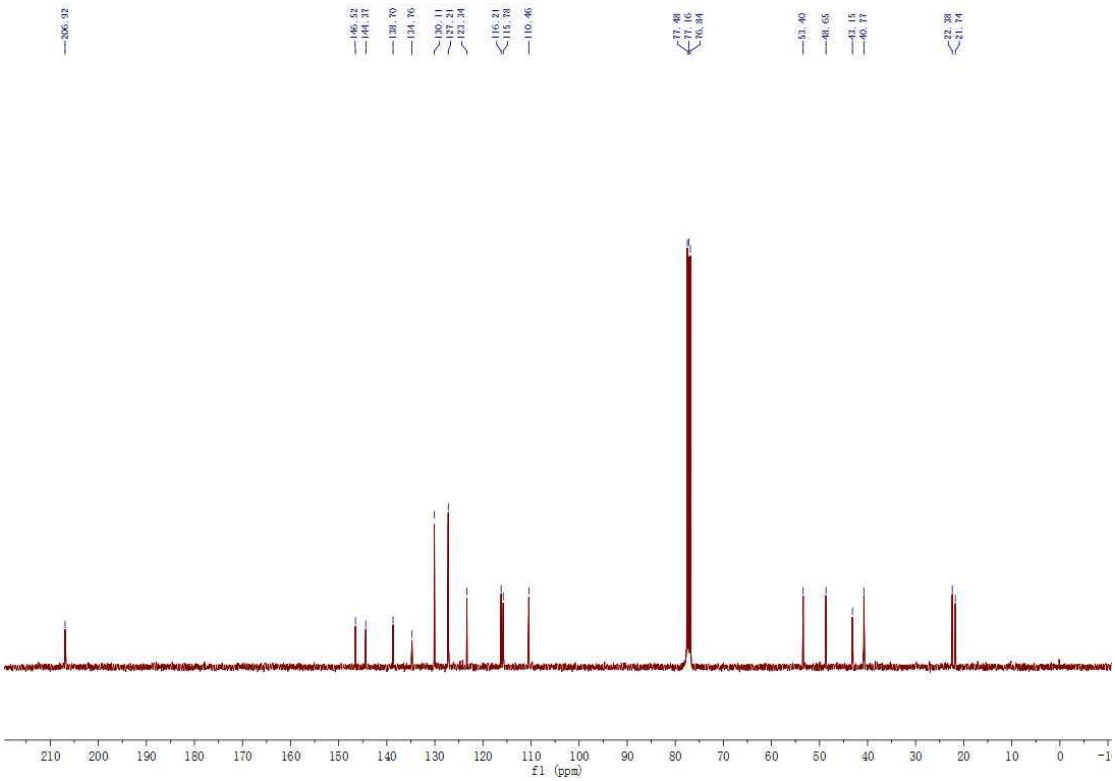


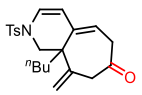




3b







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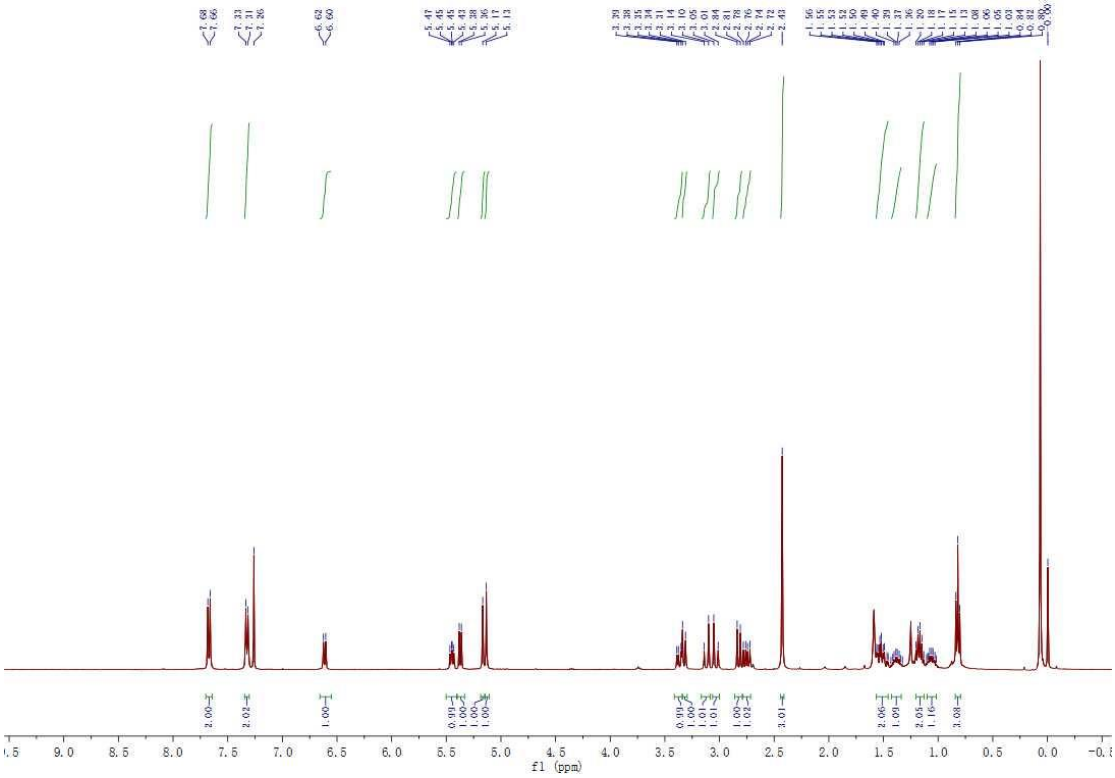

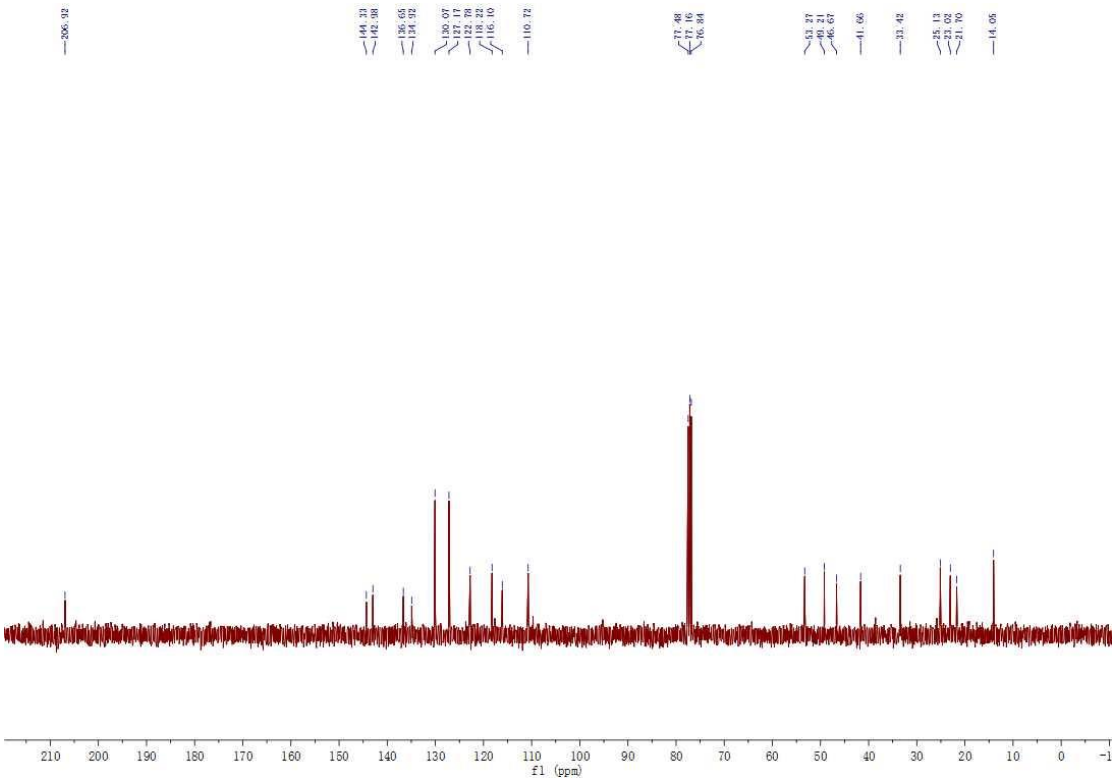

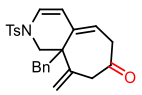

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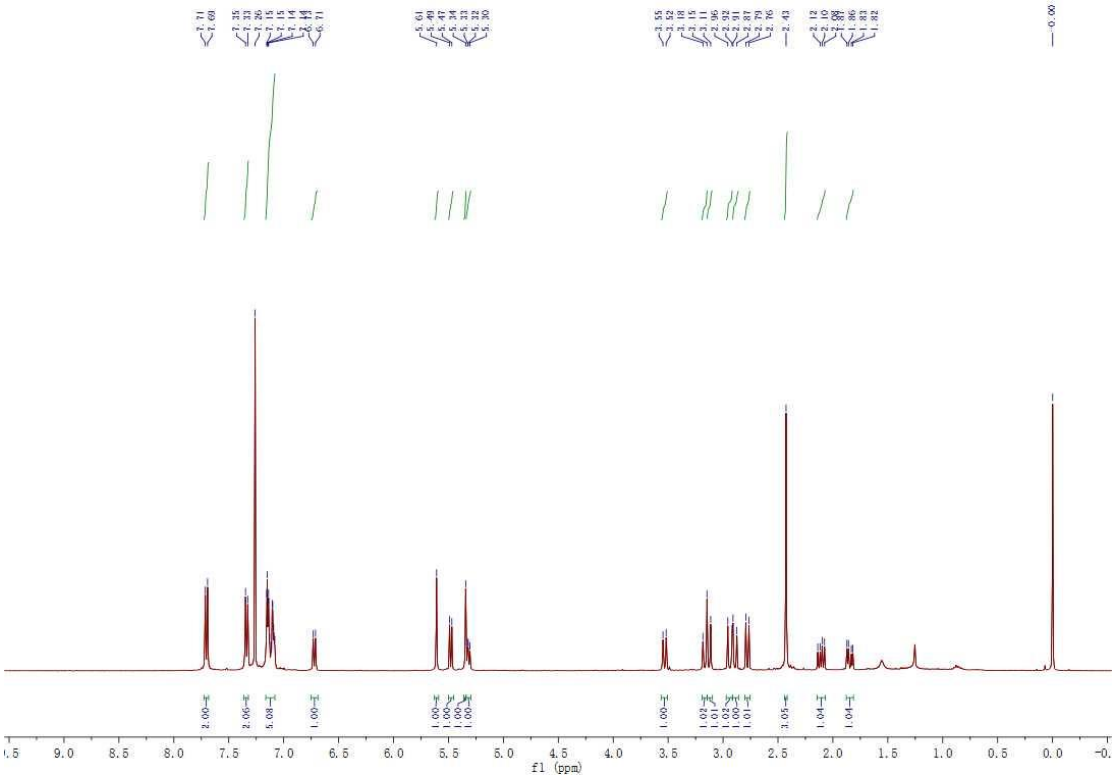

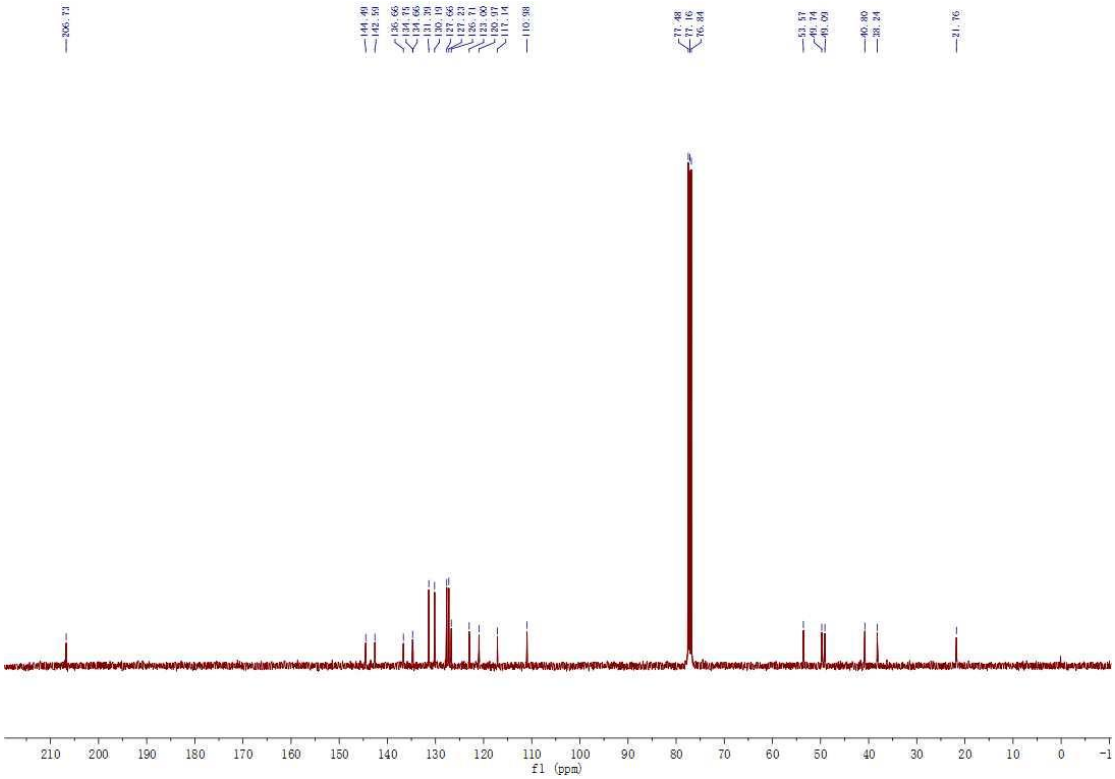

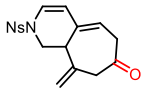

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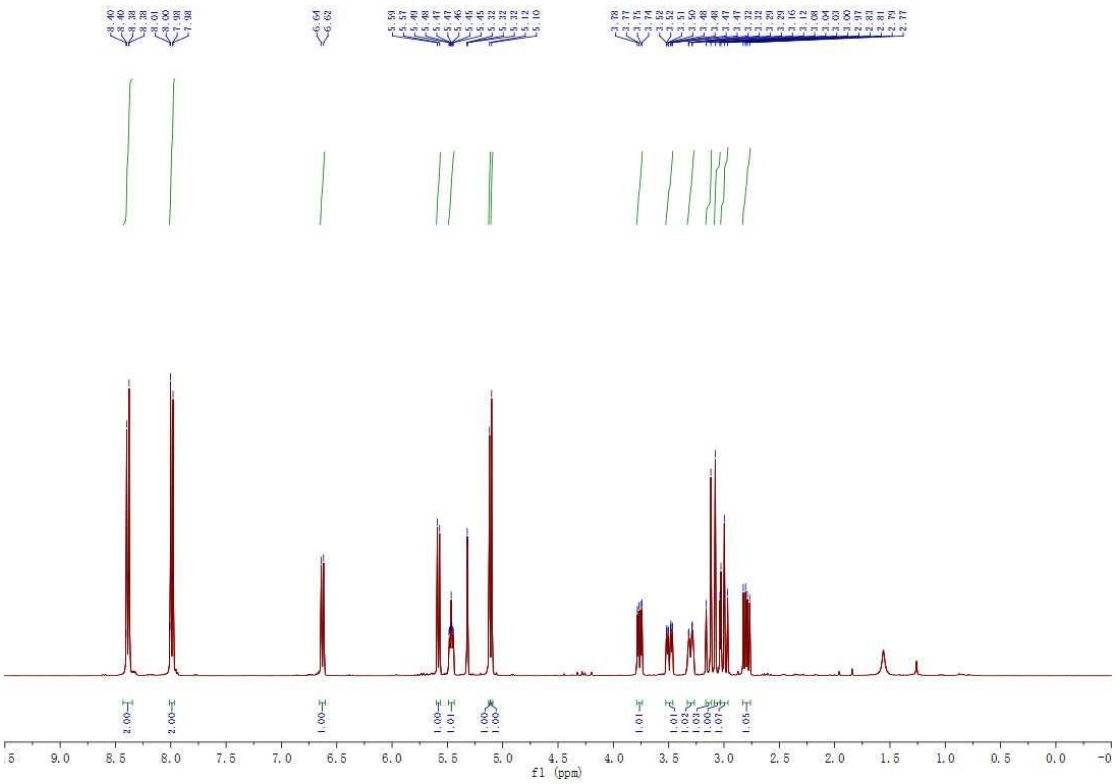

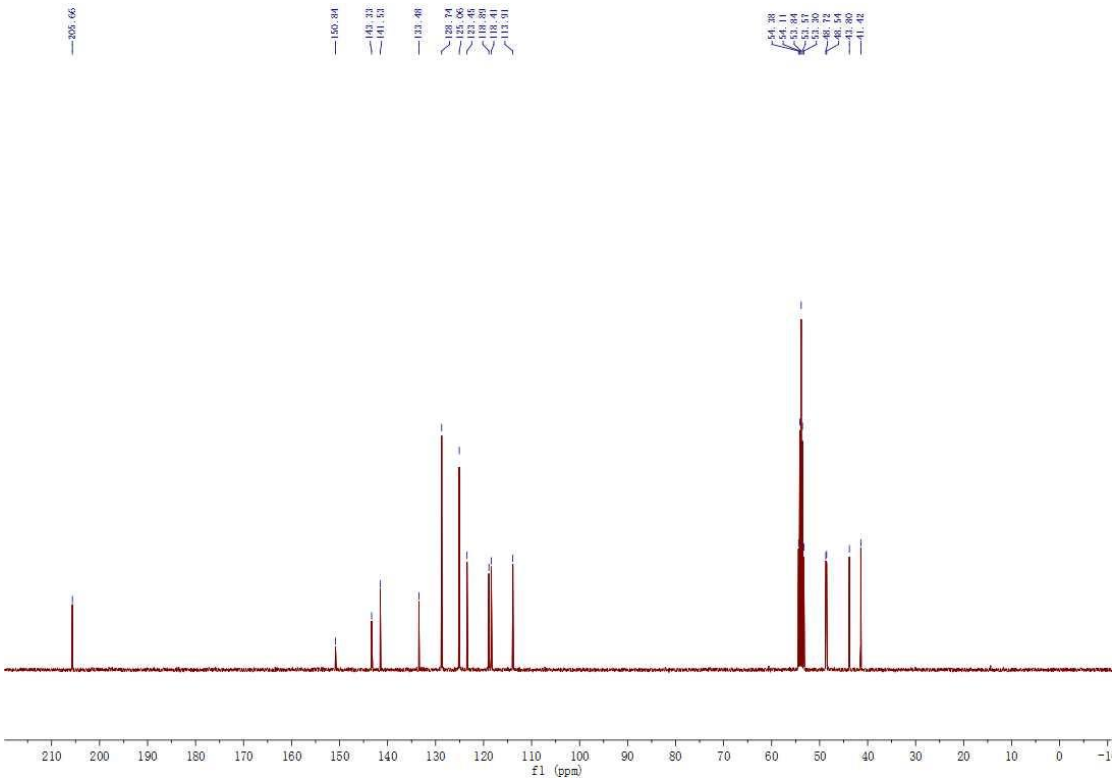

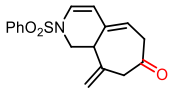

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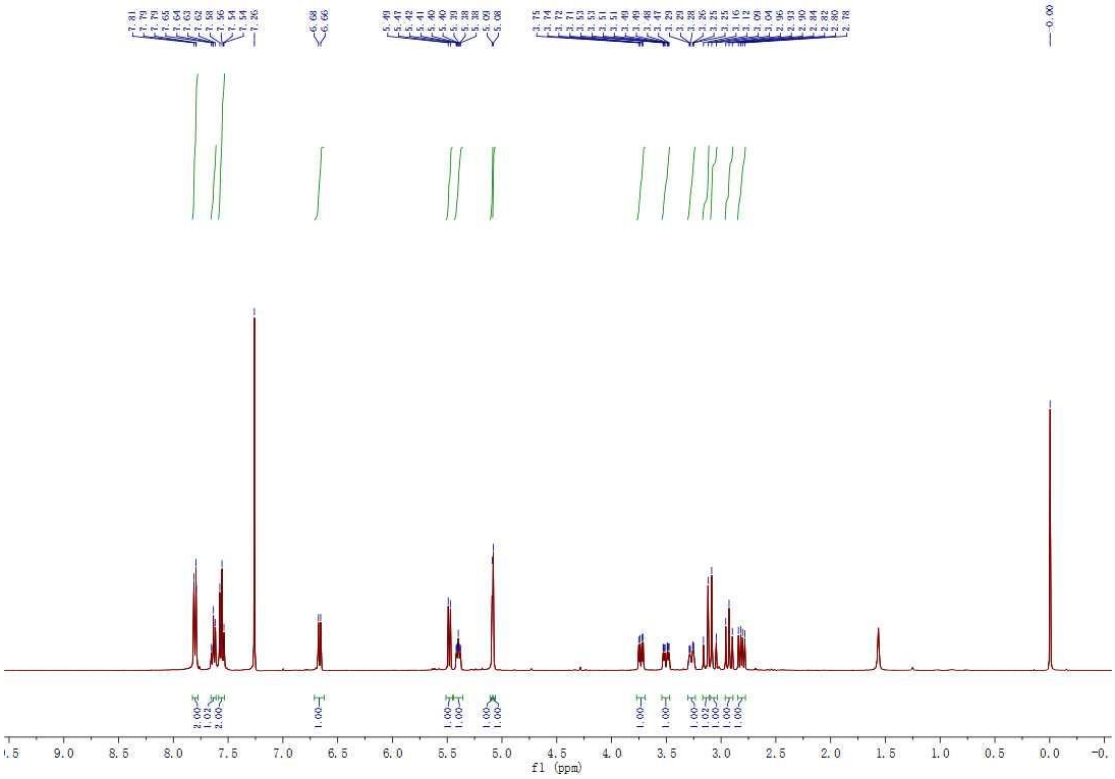

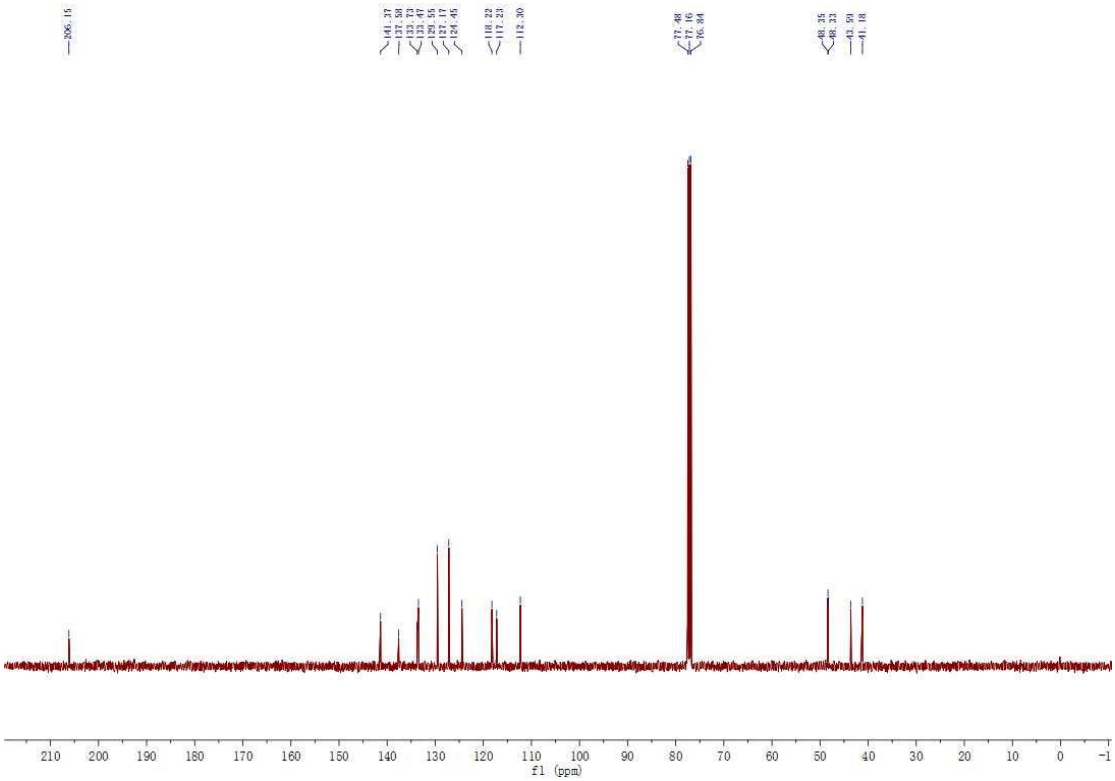

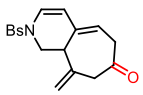

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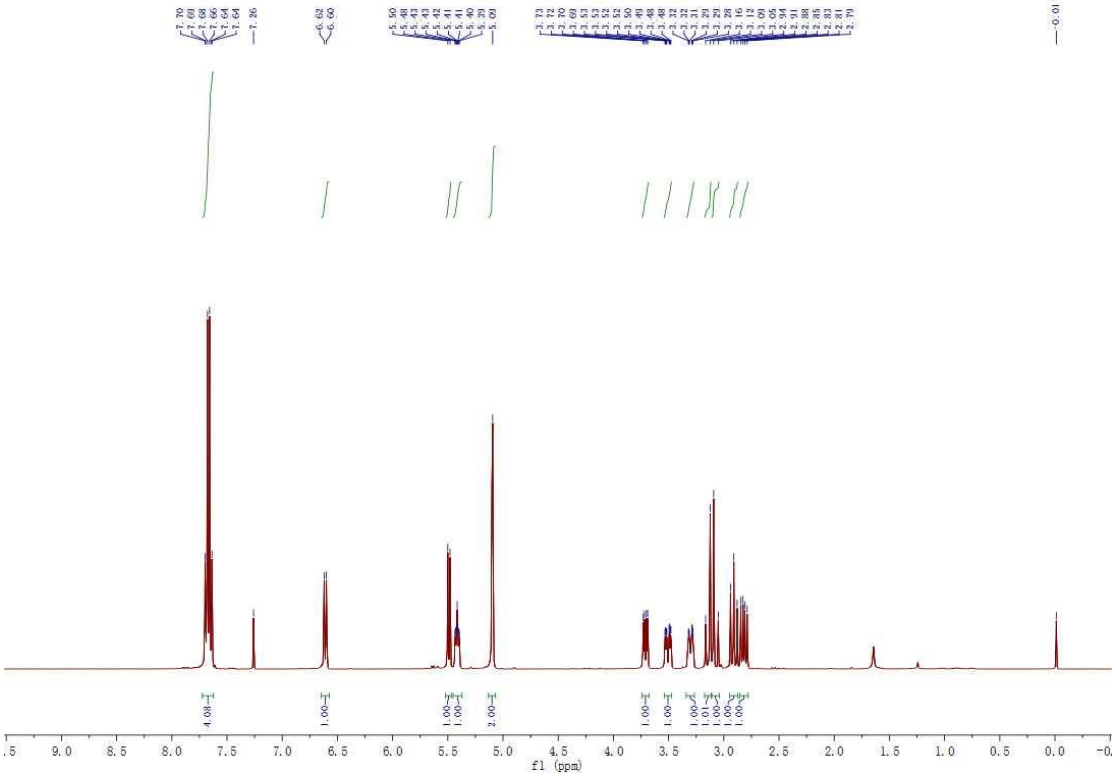
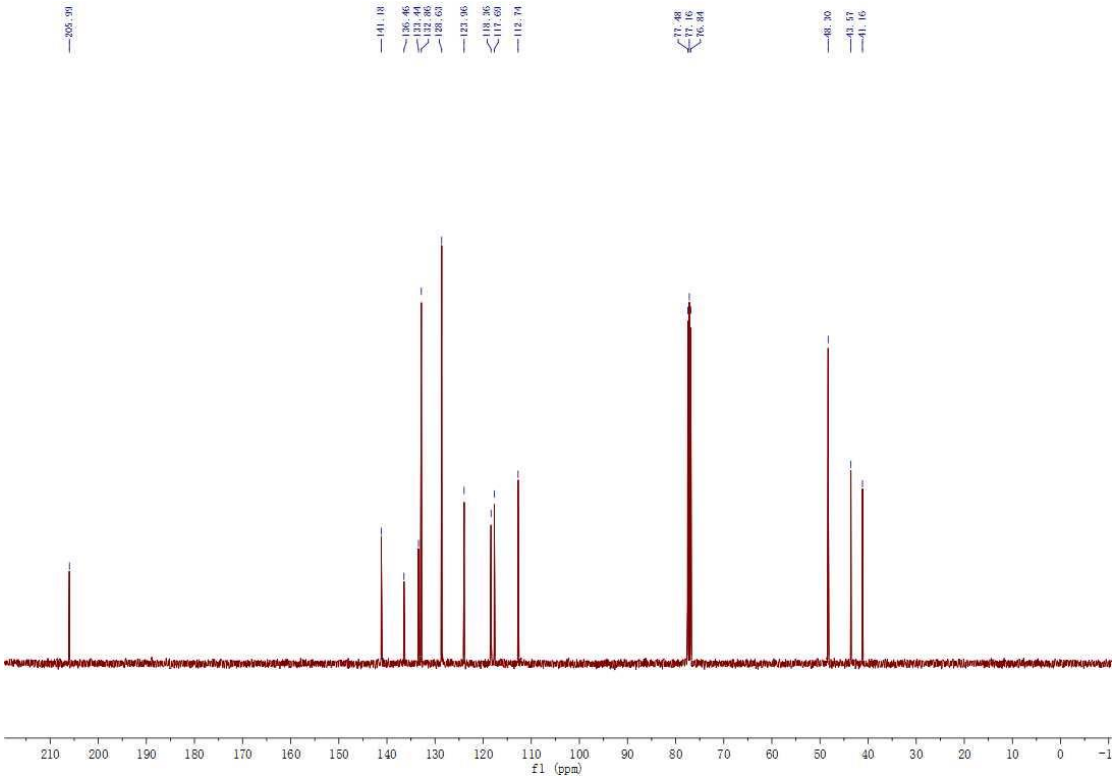
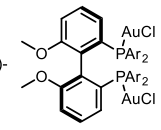
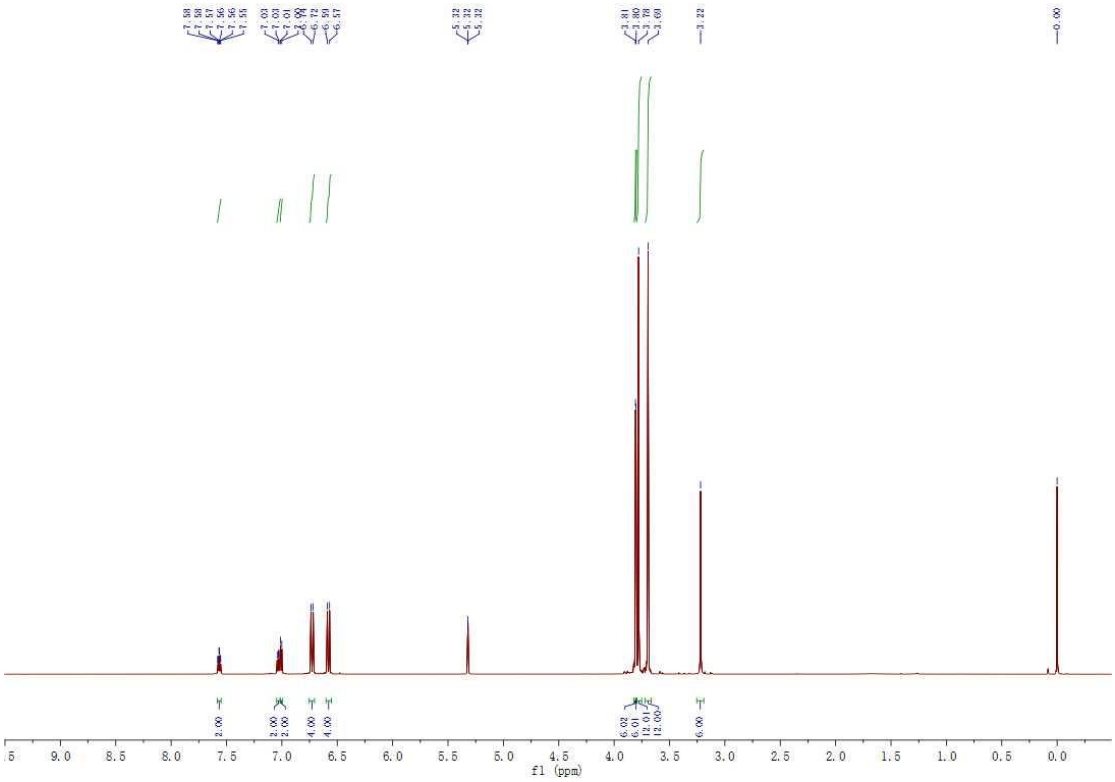


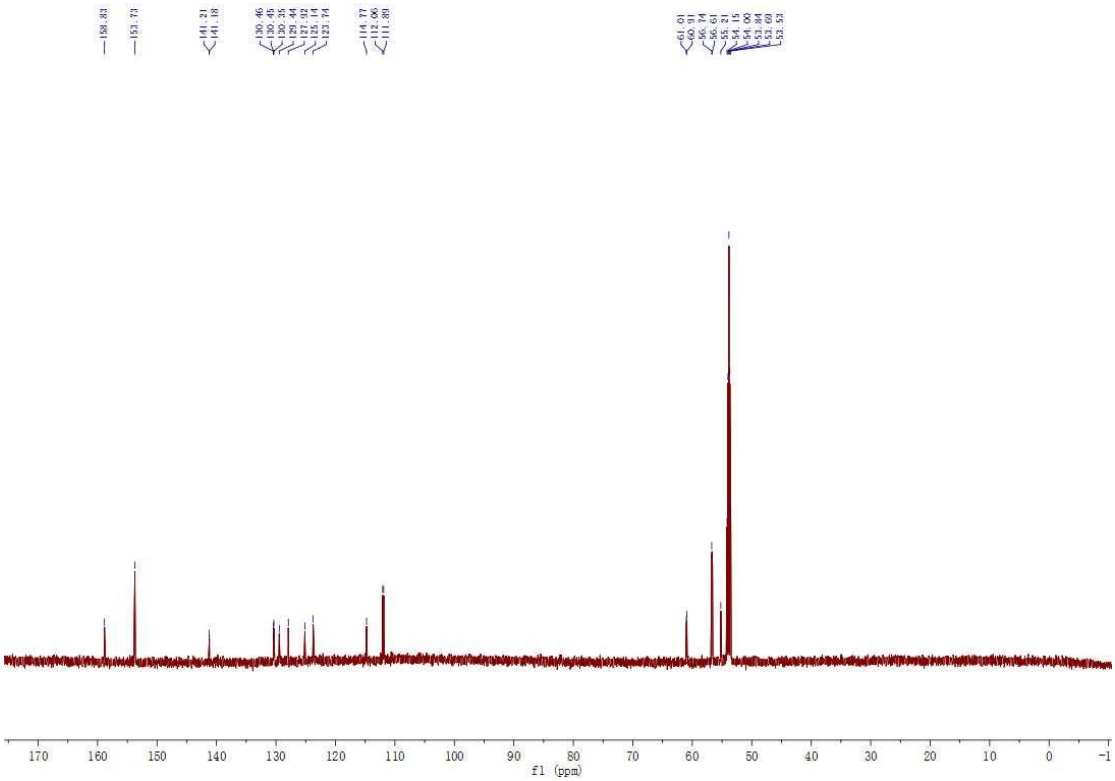


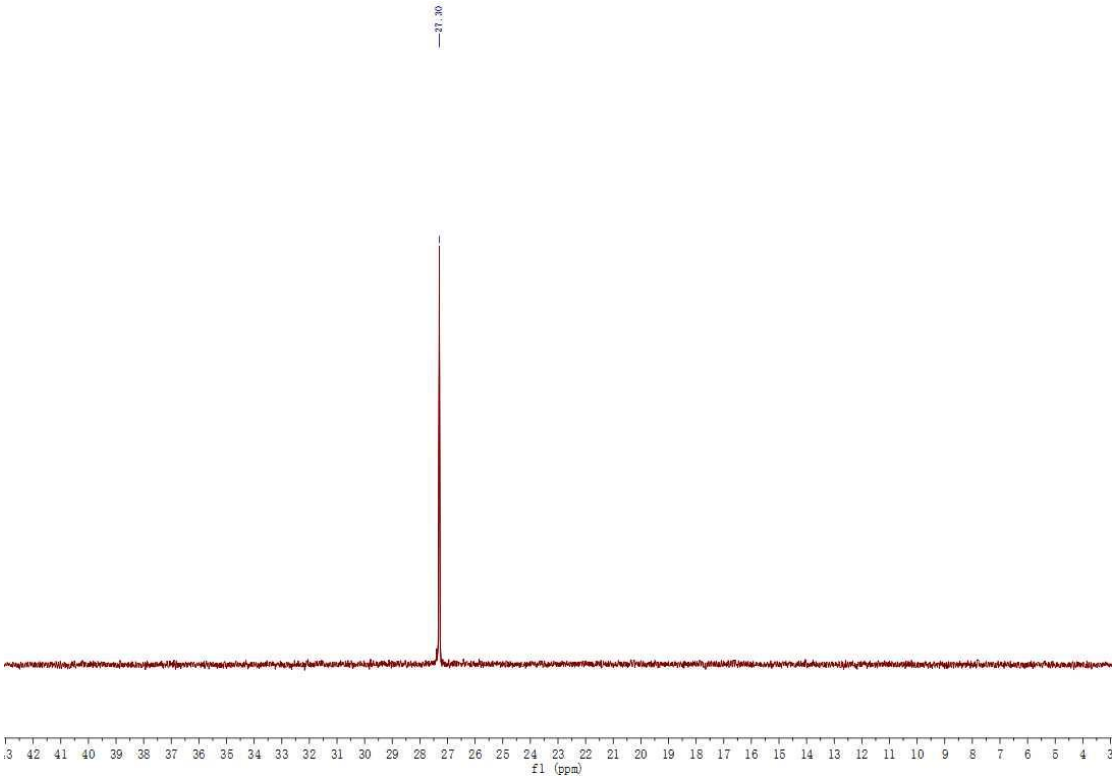
(*R*)-

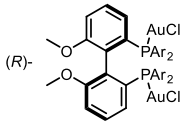


$L3Au_2Cl_2$

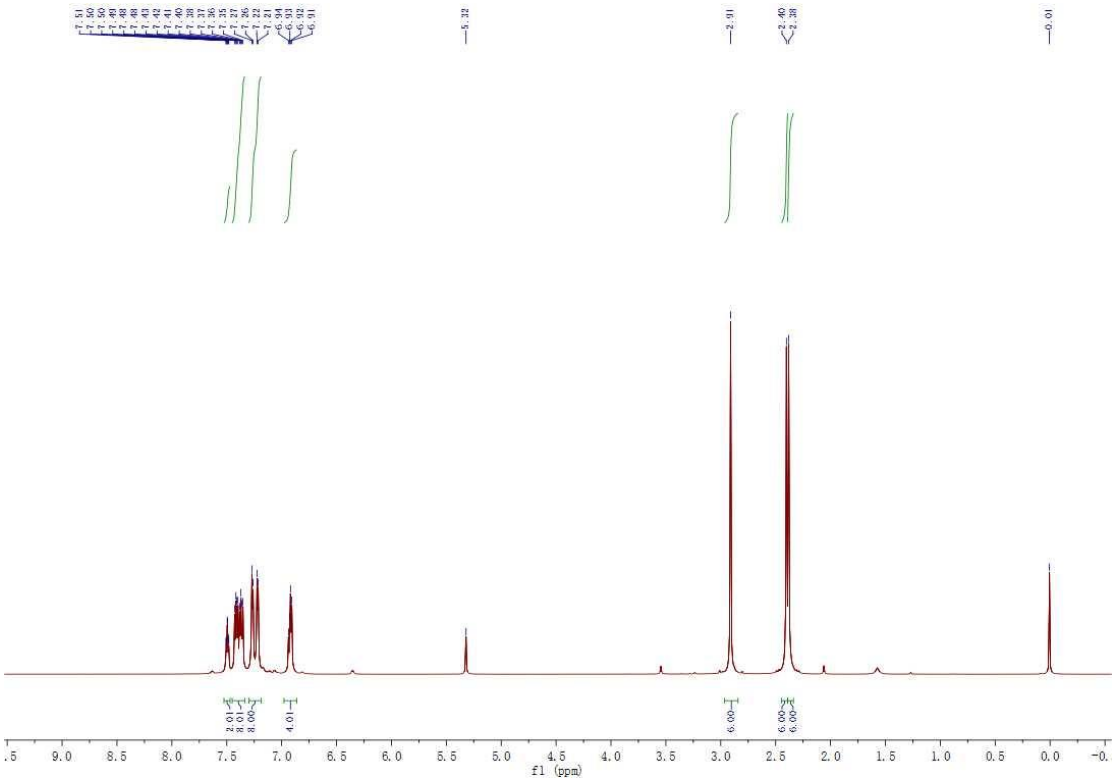


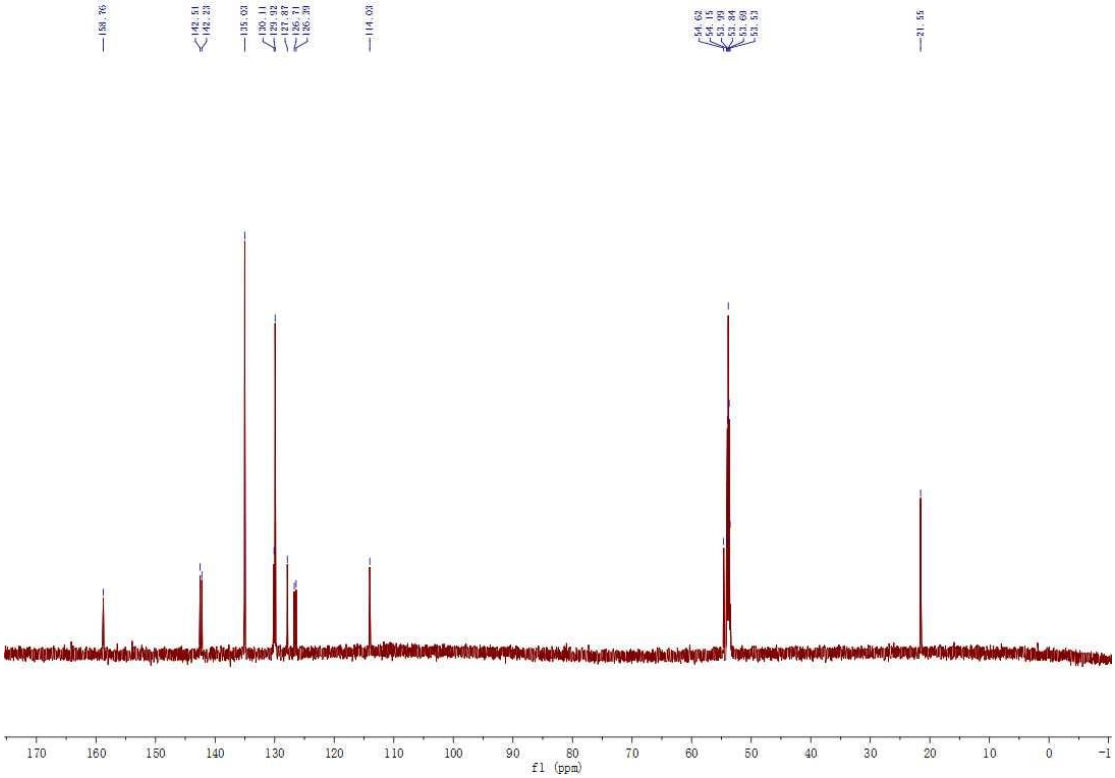


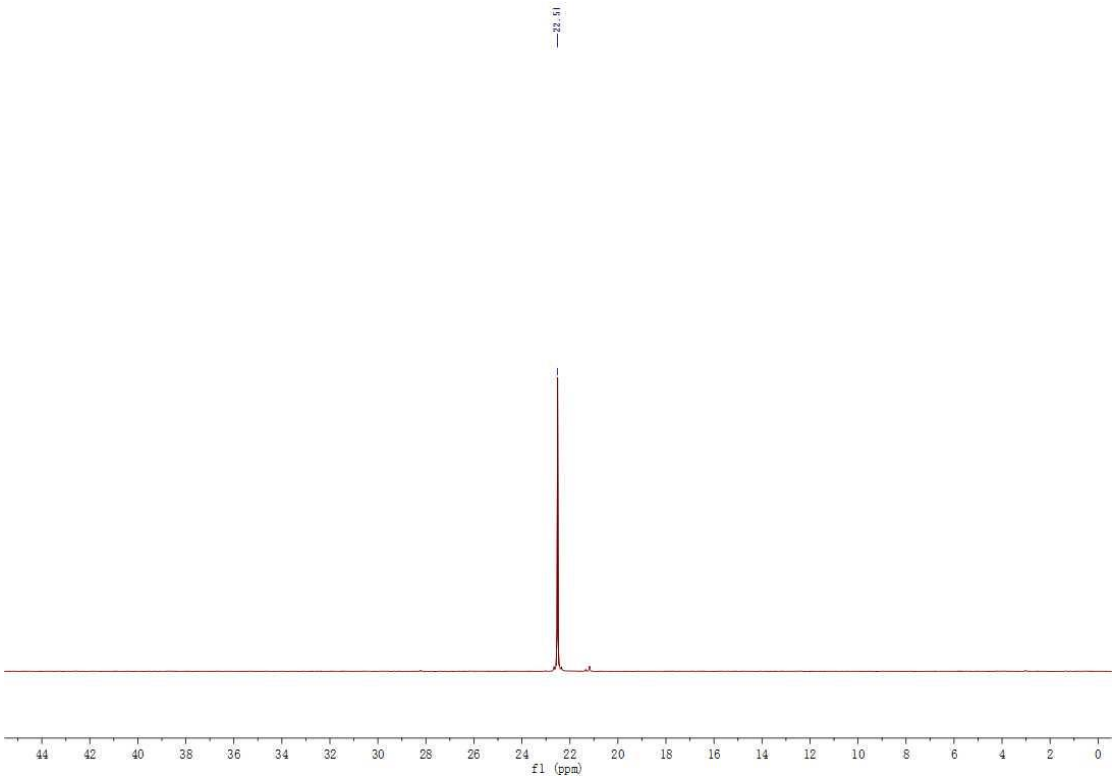

27.30
f1 (ppm)

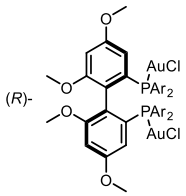

(R)-
AuCl
PAr2
PAr2
AuCl

$L6Au_2Cl_2$

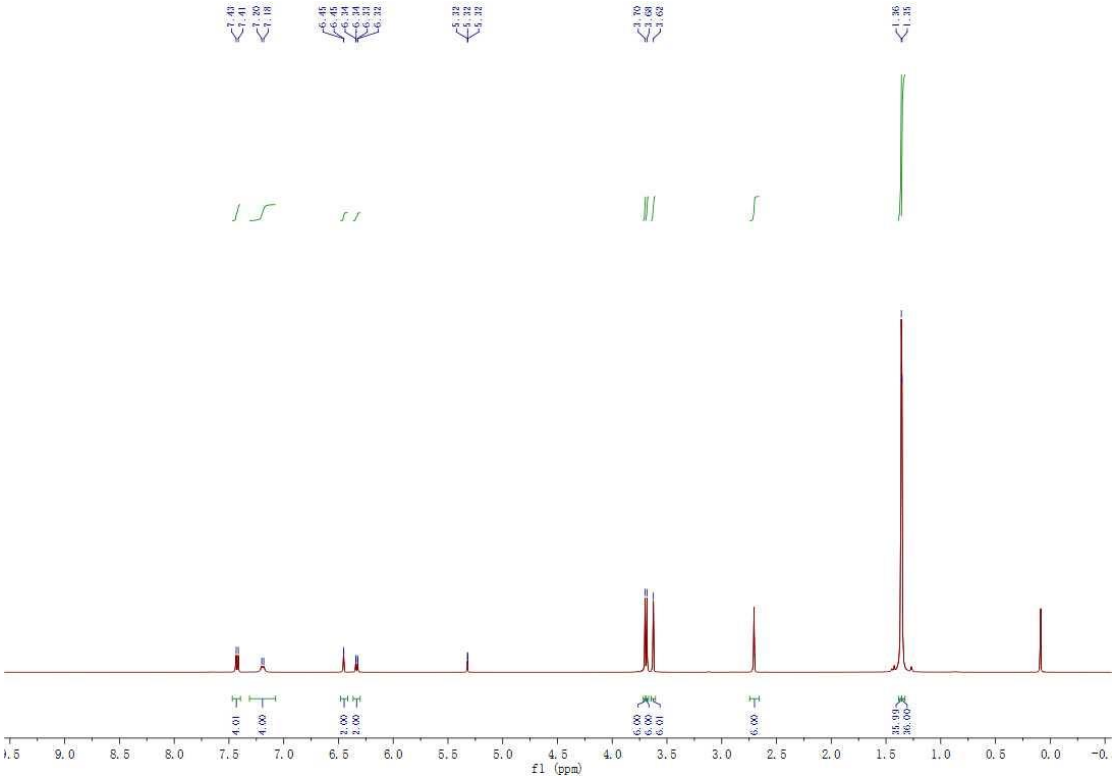

7.51
7.50
7.50
7.49
7.48
7.43
7.42
7.41
7.40
7.38
7.37
7.36
7.35
7.27
7.26
7.22
7.21
6.94
6.93
6.92
6.91
5.32
2.91
2.40
2.39
0.01
2.01
2.00
8.00
4.01
6.00
6.00
6.00
f1 (ppm)

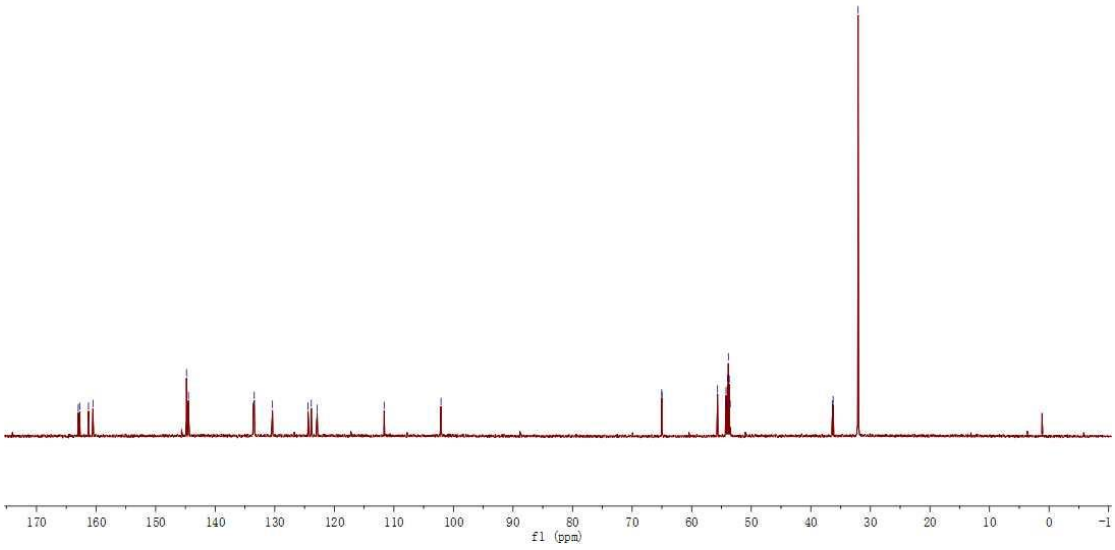

158.76
142.51
142.23
135.03
130.11
129.92
127.87
125.71
120.39
114.03
54.62
54.15
53.99
53.84
53.69
53.53
21.55
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
f1 (ppm)

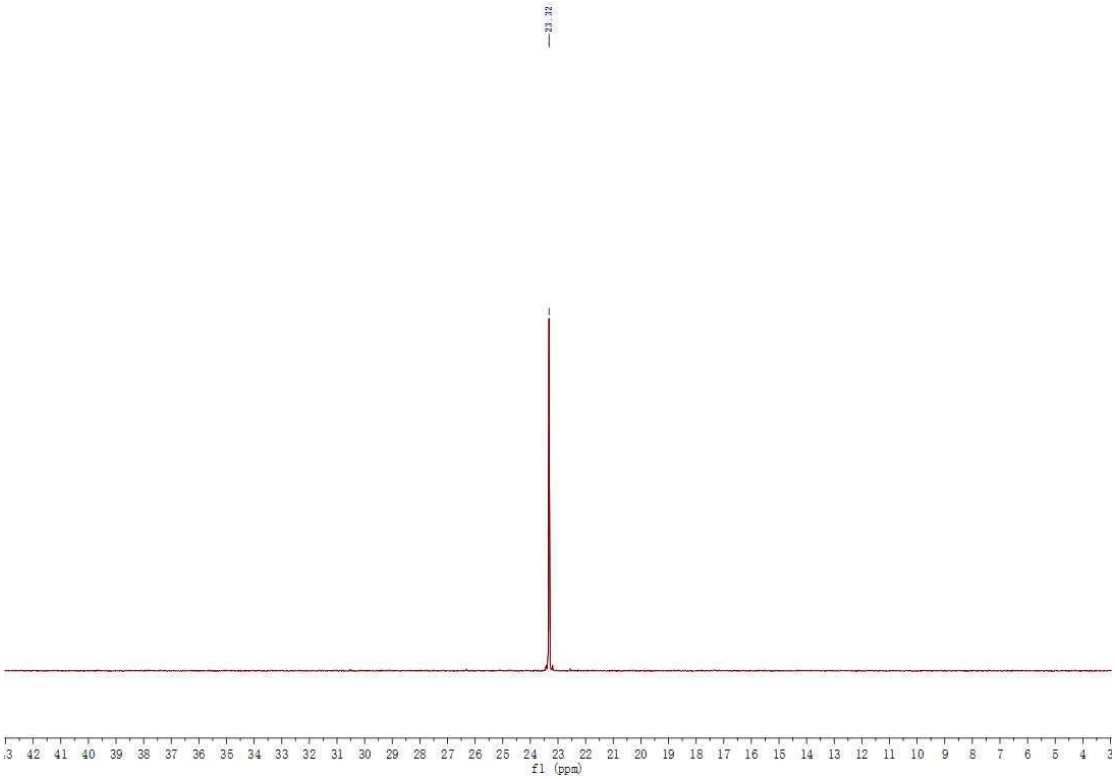

22.51
44
42
40
38
36
34
32
30
28
26
24
22
20
18
16
14
12
10
8
6
4
2
0
f1 (ppm)



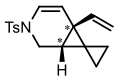
$L9Au_2Cl_2$



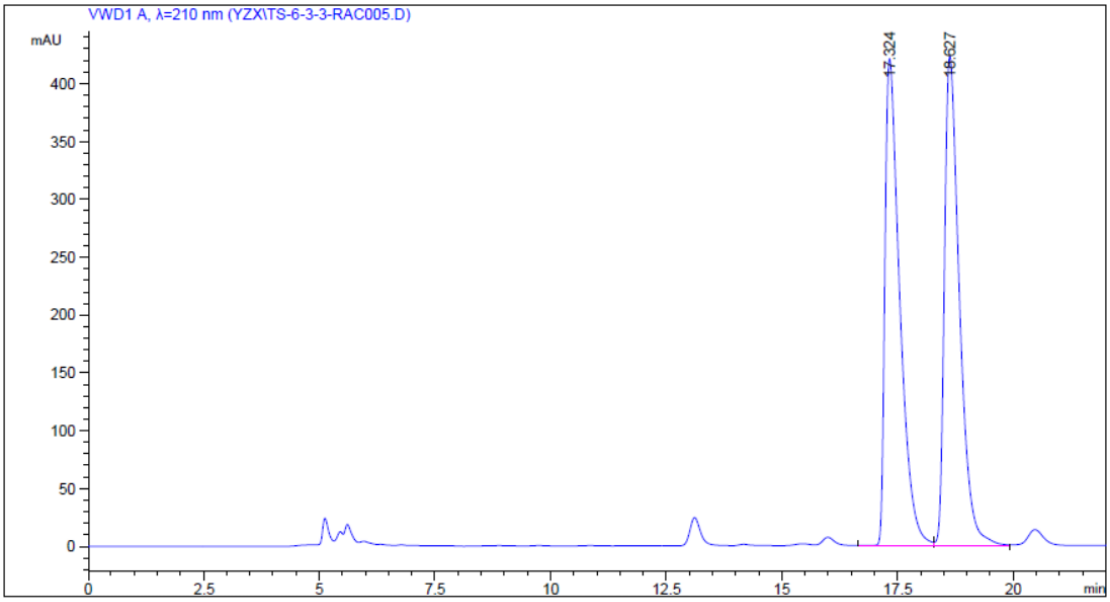



23.32
43 42 41 40 39 38 37 36 35 34 33 32 31 30 29 28 27 26 25 24 23 22 21 20 19 18 17 16 15 14 13 12 11 10 9 8 7 6 5 4 3
f1 (ppm)

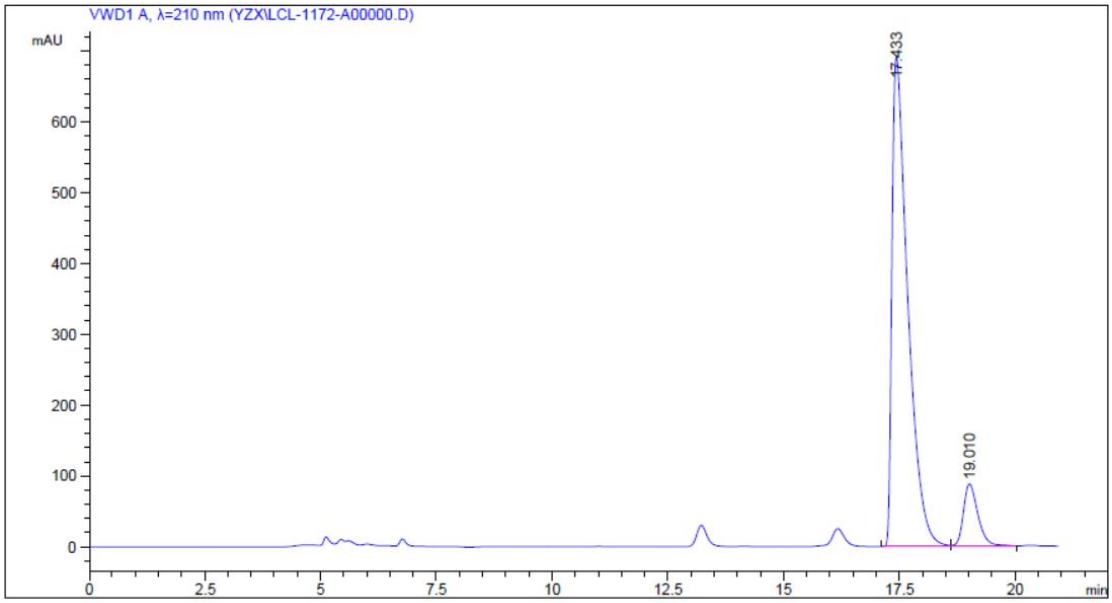
X. High Performance Liquid Chromatography (HPLC) Data



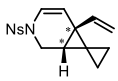
2a



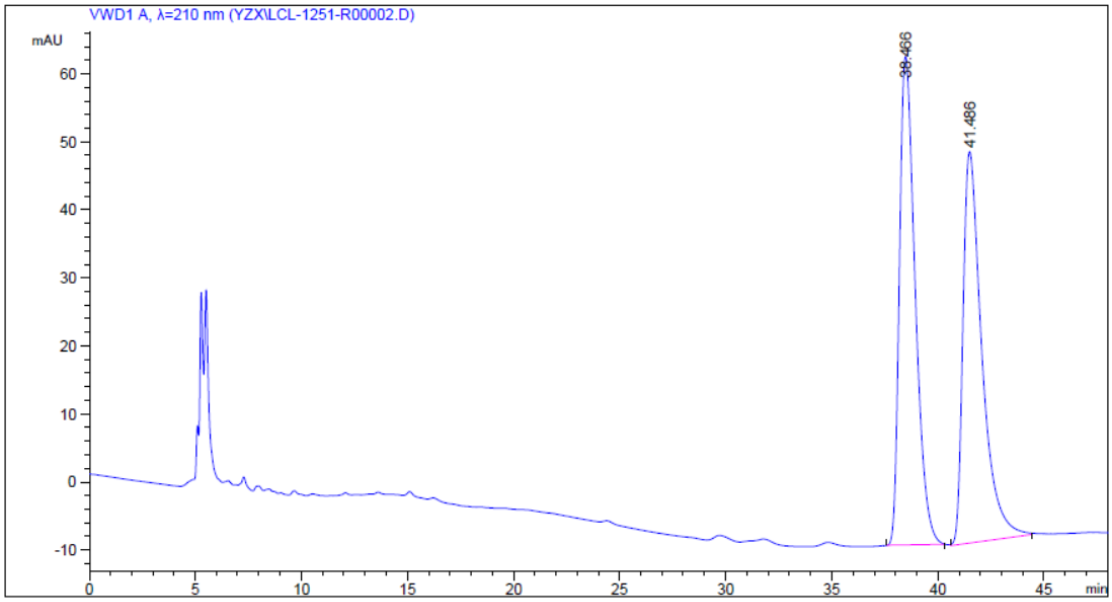
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	17.324	VV	0.3329	9386.77637	421.06326	49.5395
2	18.627	VB	0.3422	9561.29590	423.17770	50.4605



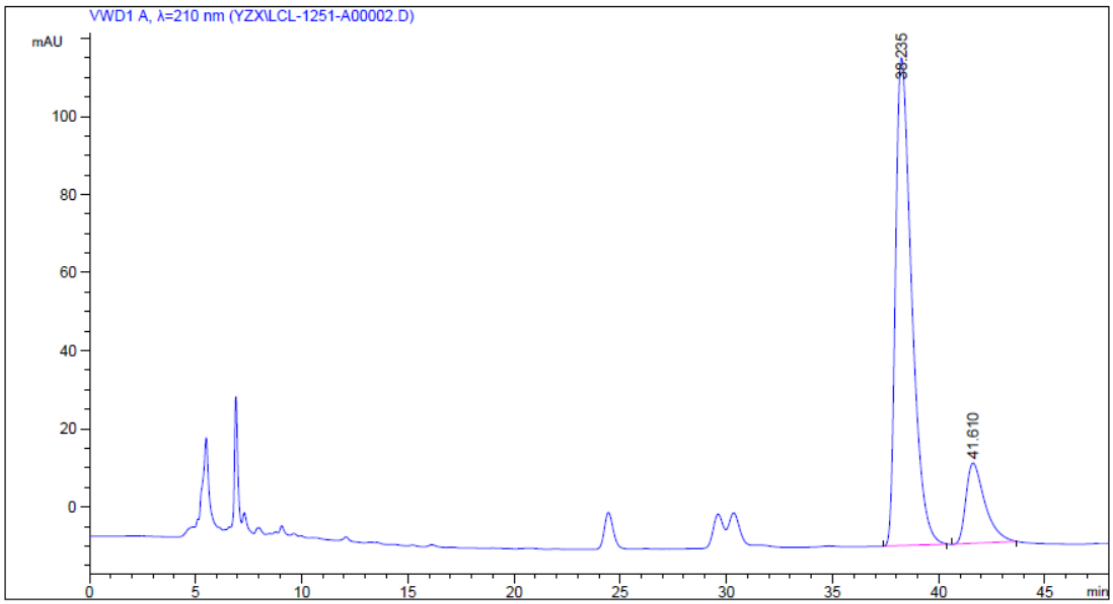
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	17.433	BV	0.3498	1.64247e4	691.88519	89.2341
2	19.010	VV	0.3399	1981.60242	88.49050	10.7659



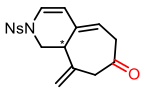
2i



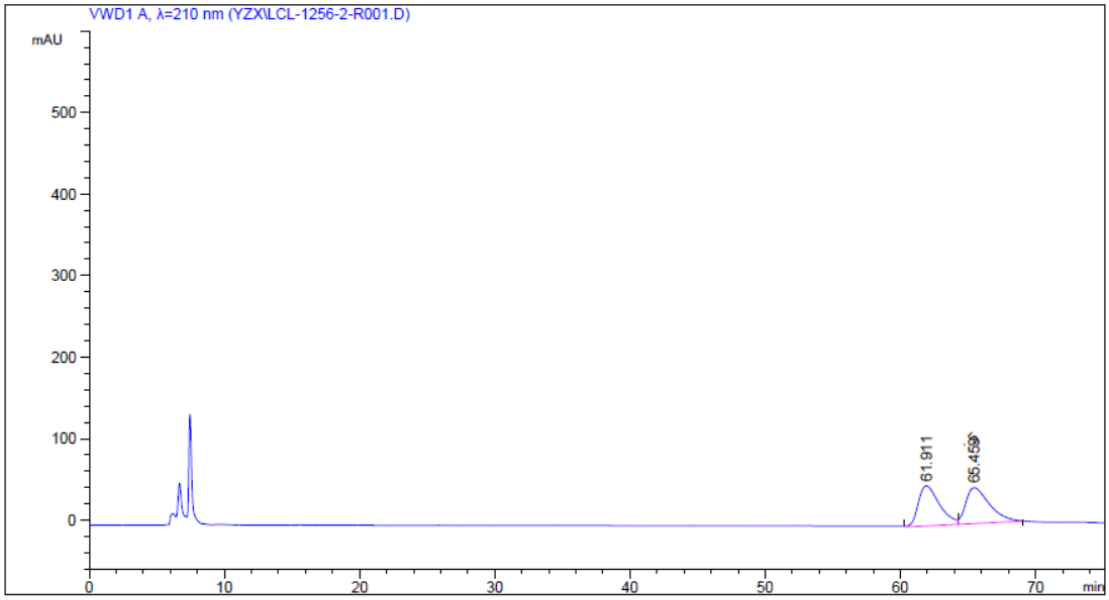
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	38.466	BB	0.7875	3703.25708	71.86938	50.8850
2	41.486	MM	1.0342	3574.44336	57.60526	49.1150



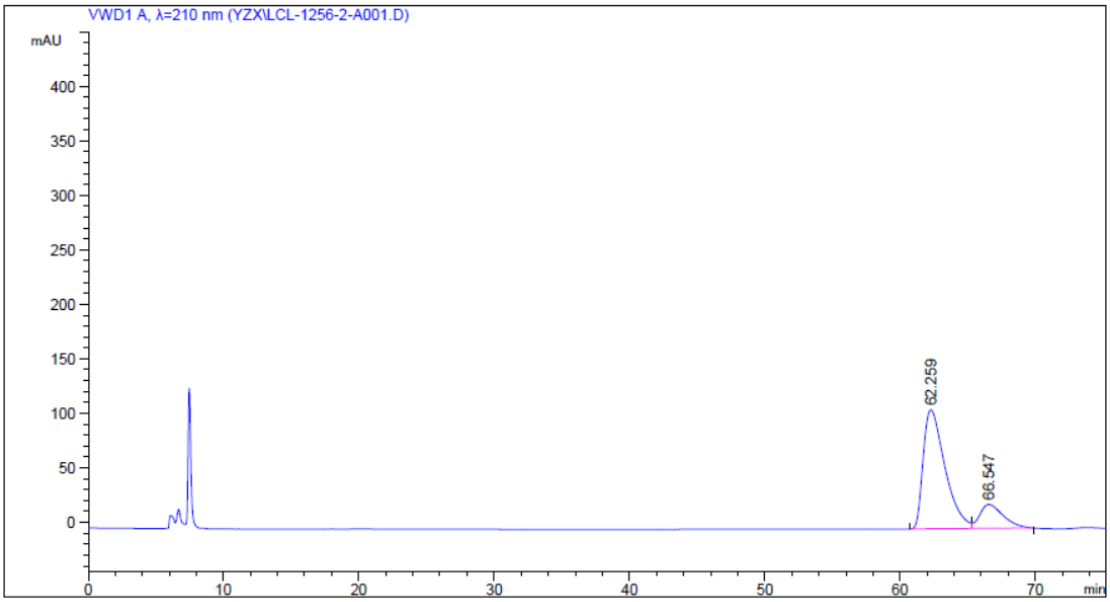
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	38.235	BB	0.8005	6592.24756	124.93335	83.6089
2	41.610	BB	0.8901	1292.37659	20.61604	16.3911



3i



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	61.911	MF	1.8235	5411.50391	49.46181	49.6347
2	65.459	FM	2.0593	5491.15625	44.44169	50.3653



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	62.259	BB	1.6722	1.22606e4	109.21660	82.1249
2	66.547	BB	1.5101	2668.59717	22.01785	17.8751