Strain-Release-Controlled [4 + 2 + 1] Reaction of Cyclopropyl-Capped Diene-ynes/Diene-enes and Carbon Monoxide Catalyzed by Rhodium

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I. General Information

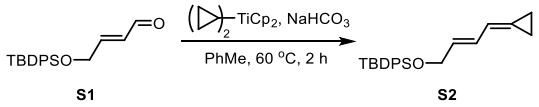
Air and moisture sensitive reactions were carried out in oven and flame-dried glassware sealed with rubber septa under a positive pressure of dry nitrogen or argon. Similarly, sensitive liquids and solutions were transferred via syringe. Reactions were stirred using Teflon-coated magnetic stir bars. 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. All other solvents were distilled from sodium and benzophenone or calcium hydride prior to use. 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 (^1H at 400 MHz, ^{13}C at 101 MHz), Bruker AVANCE III (^1H at 500 MHz, ^{13}C at 126 MHz) nuclear magnetic resonance spectrometers. Data for ^1H 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, s = singlet, brs = broad 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). High-resolution mass spectra (HRMS) were recorded on a Bruker Apex IV FTMS mass spectrometer (ESI) with an FT-ICR analyzer.

Abbreviations:

COD = (1Z,5Z)-1,5-Cyclooctadiene
DCE = 1,2-dichloroethane
DCM = dichloromethane
DIAD = diisopropyl azodicarboxylate
DIBAL-H = diisobutylaluminum hydride
dppp = 1,3-bis(diphenylphosphino)propane
EA = ethyl acetate
IPr = 1,3-Bis(2,6-diisopropylphenyl)-1,3-dihydro-2H-imidazol-2-ylidene
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

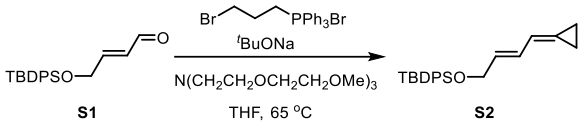
II. Preparation of Substrates

Note here: 1. We did not optimize all reactions in this part; 2. The final substrates of the [4+2+1] reaction are recommended to store at -20 °C refrigerator and use it as soon as possible. Otherwise, the substrate will gradually transform to a complex mixture.



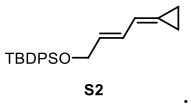
Method A: To a stirred solution of **S1** [1] (908.3 mg, 2.8 mmol) and $NaHCO_3$ (547.9 mg, 6.5 mmol) in toluene (10 mL) was added bis(cyclopentadienyl)dicyclopropyltitanium[2a] (1.70 g, 6.5 mmol) in toluene (18 mL) at 60 ºC. The reaction was monitored by TLC and stirred at the same temperature for 2 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, 200:1) to afford **S2** (683.1 mg, 70%).

Note: In this paper, **S2** was all synthesized by Method A, which was not robust enough and gave varied yields (probably due to the quality of reaction reagents). In this case, we recommend using method B below,



Method B: A more robust method[2b] could be used to synthesize **S2**, which was used by us because method A sometimes did not work well (This was found in our continuing study after submitting the present paper for publication).

Under Ar atmosphere, a solution of $BrCH_2CH_2CH_2PPh_3Br$ (1.52 g, 3.3 mmol), ^{t}BuONa (625.9 mg, 6.5 mmol) in THF (11 mL) was heated in an oil bath at 65 °C for 3 h. Then a solution of **S1** (811.2 mg, 2.5 mmol) and tris[2-(2-methoxyethoxy)ethyl)amine (93.3 mg, 0.25 mmol) in THF (4 mL) was added. The reaction mixture was further stirred in an oil bath at 65 °C for 12 h. The reaction mixture was then cooled, diluted with pentane, and passed through a short pad of silica gel with DCM. The reaction mixture was concentrated and the crude product was purified by flash column chromatography on silica gel (eluted with PE/EA, 100:1–50:1) to afford **S2** (791.5 mg, 91%).



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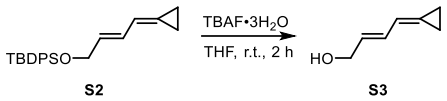
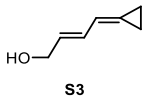
Yellow oil, TLC R_f = 0.77 (PE/EA, 10:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 – 7.67 (m, 4H), 7.45 – 7.36 (m, 6H), 6.49 – 6.35 (m, 2H), 5.78 (dt, J = 14.8, 5.0 Hz, 1H), 4.28 (d, J = 5.0 Hz, 2H), 1.18 – 1.10 (m, 4H), 1.07 (s, 9H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 135.7, 133.9, 130.2, 129.7, 129.6, 127.8, 126.7, 118.4, 64.6, 27.0, 19.4, 2.7, 2.3. HRMS (ESI): calcd. for $C_{23}H_{29}OSi$ ($[M+H]^+$): 349.1982, found 349.1972.



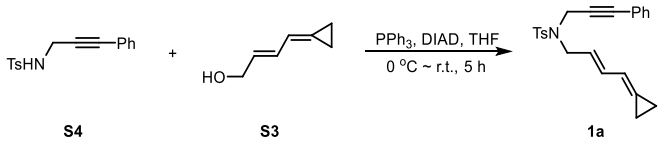
S2 **S3**

To a stirred solution of **S2** (683.1 mg, 2.0 mmol) in THF (7.5 mL) was added TBAF•3H_2O (0.95 g, 3.0 mmol). The reaction was stirred for 2 h at room temperature and monitored by TLC. Then, the resulting mixture was quenched with water (10 mL) and extracted with ether (7 mL×4). 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, 5:1) to afford **S3** (170.4 mg, 77%).



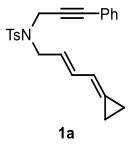
S3

Light yellow oil, TLC R_f = 0.20 (PE/EA, 5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.51 – 6.34 (m, 2H), 5.84 (dt, *J* = 15.7, 5.9 Hz, 1H), 4.21 (d, *J* = 5.9 Hz, 2H), 1.40 (brs, 1H), 1.20 – 1.09 (m, 4H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 131.3, 129.9, 127.9, 118.1, 63.7, 2.8, 2.4. HRMS (ESI): calcd. for $C_7H_{11}O$ ([M+H]$^+$): 111.0804, found 111.0804.



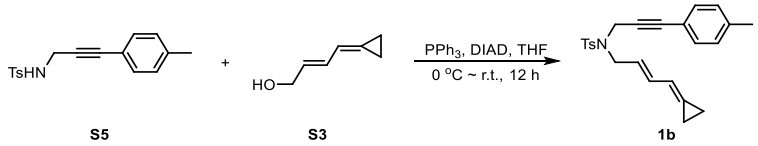
S4 **S3** **1a**

To a stirred solution of **S4** [3] (284.7 mg, 1.0 mmol), **S3** (112.8 mg, 1.0 mmol) and PPh_3 (394.5 mg, 1.5 mmol) in THF (7 mL) was added DIAD (301.1 mg, 1.5 mmol) at 0 ºC. The reaction was gradually allowed to warm to room temperature. The reaction was monitored by TLC and stirred for 5 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 **1a** (267.2 mg, 71%).



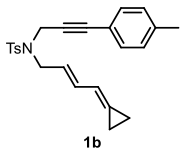
1a

Light yellow oil, TLC R_f = 0.53 (PE/EA, 5:1). ^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.75 (d, *J* = 8.2 Hz, 2H), 7.32 – 7.23 (m, 5H), 7.15 – 7.00 (m, 2H), 6.56 – 6.34 (m, 2H), 5.61 (dt, *J* = 14.1, 6.8, Hz, 1H), 4.29 (s, 2H), 3.93 (d, *J* = 6.8 Hz, 2H), 2.34 (s, 3H), 1.19 – 1.14 (m, 2H), 1.13 – 1.07 (m, 2H). ^{13}C{^{1}H} NMR (101 MHz, CD_2Cl_2) δ 144.1, 136.3, 134.8, 131.8, 129.9, 128.9, 128.8, 128.5, 128.1, 124.7, 122.6, 118.0, 85.8, 82.2, 49.1, 37.1, 21.5, 2.8, 2.5. HRMS (ESI): calcd. for $C_{23}H_{24}NO_2S^+$ ([M+H]$^+$): 378.1522, found 378.1520.



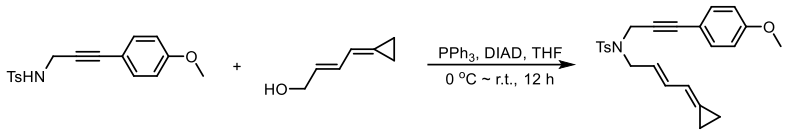
S5 **S3** **1b**

To a stirred solution of **S5** [3] (200.8 mg, 0.7 mmol), **S3** (73.6 mg, 0.7 mmol) and PPh_3 (529.4 mg, 2.0 mmol) in THF (4.7 mL) was added DIAD (403.1 mg, 2.0 mmol) at 0 ºC. 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 **1b** (144.5 mg, 55%).



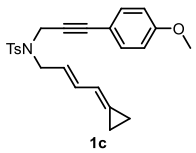
1b

Colorless oil, TLC R_f = 0.52 (PE/EA, 5:1). ^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.77 – 7.73 (m, 2H), 7.28 (d, *J* = 7.9 Hz, 2H), 7.07 (d, *J* = 7.9 Hz, 2H), 7.01 – 6.96 (m, 2H), 6.49 – 6.37 (m, 2H), 5.66 – 5.56 (m, 1H), 4.27 (s, 2H), 3.92 (d, *J* = 6.7 Hz, 2H), 2.35 (s, 3H), 2.32 (s, 3H), 1.19 – 1.14 (m, 2H), 1.13 – 1.08 (m, 2H). ^{13}C{^{1}H} NMR (101 MHz, CD_2Cl_2) δ 144.1, 139.2, 136.5, 134.8, 131.8, 130.0, 129.3, 128.9, 128.2, 124.8, 119.6, 118.1, 86.0, 81.6, 49.1, 37.2, 21.6, 21.5, 2.8, 2.5. HRMS (ESI): calcd. for $C_{24}H_{26}NO_2S$ ([M+H]$^+$): 392.1679, found 392.1678.



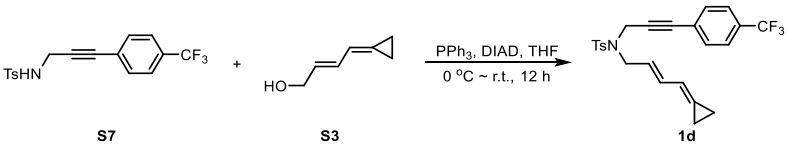
S6 **S3** **1c**

To a stirred solution of **S6** [3] (195.8 mg, 0.6 mmol), **S3** (68.7 mg, 0.6 mmol) and PPh_3 (503.6 mg, 1.9 mmol) in THF (4.3 mL) was added DIAD (383.5 mg, 1.9 mmol) at 0 ºC. 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, 40:1) to afford **1c** (151.0 mg, 60%).



1c

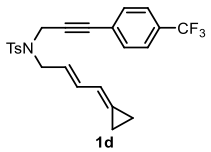
Colorless oil, TLC R_f = 0.48 (PE/EA, 5:1). ^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.78 – 7.73 (m, 2H), 7.31 – 7.26 (m, 2H), 7.08 – 6.99 (m, 2H), 6.81 – 6.76 (m, 2H), 6.49 – 6.36 (m, 2H), 5.67 – 5.55 (m, 1H), 4.27 (s, 2H), 3.92 (d, *J* = 6.7 Hz, 2H), 3.79 (s, 3H), 2.36 (s, 3H), 1.19 – 1.14 (m, 2H), 1.13 – 1.08 (m, 2H). ^{13}C{^{1}H} NMR (101 MHz, CD_2Cl_2) δ 160.2, 144.1, 136.6, 134.8, 133.4, 129.9, 128.8, 128.2, 124.9, 118.1, 114.7, 114.2, 85.8, 80.8, 55.7, 49.1, 37.2, 21.6, 2.8, 2.5. HRMS (ESI): calcd. for $C_{24}H_{26}NO_3S$ ([M+H]$^+$): 408.1628, found 408.1630.



S7 **S3** **1d**

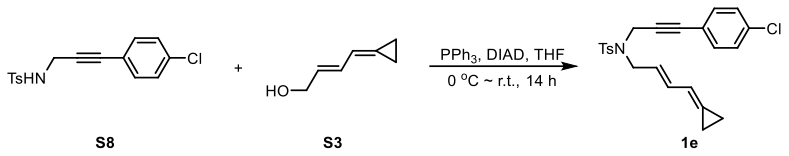
To a stirred solution of **S7** [3] (193.5 mg, 0.6 mmol), **S3** (60.2 mg, 0.6 mmol) and PPh_3 (218.0 mg,

0.8 mmol) in THF (4 mL) was added DIAD (166.2 mg, 0.8 mmol) at 0 ºC. 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 **1d** (154.2 mg, 63%).



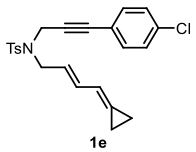
1d

Colorless oil, TLC R_f = 0.57 (PE/EA, 5:1). ^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.78 (d, J = 8.0 Hz, 2H), 7.54 (d, J = 8.1 Hz, 2H), 7.29 (d, J = 8.0 Hz, 2H), 7.21 (d, J = 8.1 Hz, 2H), 6.50 – 6.38 (m, 2H), 5.64 (dt, J = 14.0, 6.8 Hz, 1H), 4.33 (s, 2H), 3.96 (d, J = 6.8 Hz, 2H), 2.32 (s, 3H), 1.19 – 1.14 (m, 2H), 1.14 – 1.08 (m, 2H). ^{13}C{^{1}H} NMR (101 MHz, CD_2Cl_2) δ 144.2, 136.3, 135.0, 132.2, 130.18 (q, J = 32.7 Hz), 130.0, 129.0, 128.2, 126.6, 125.4 (q, J = 3.7 Hz), 124.6, 124.3 (q, J = 272.1 Hz), 118.0, 85.1, 84.5, 49.3, 37.0, 21.5, 2.8, 2.5. HRMS (ESI): calcd. for $C_{24}H_{23}F_3NO_2S$ ([M+H]$^+$): 446.1396, found 446.1394.



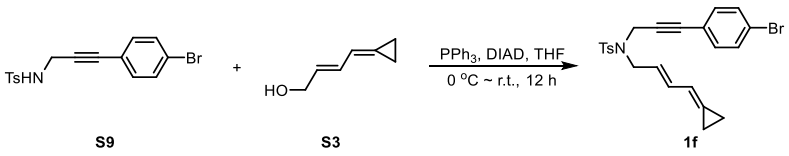
S8 **S3** **1e**

To a stirred solution of **S8** [3] (255.9 mg, 0.8 mmol), **S3** (87.6 mg, 0.8 mmol) and PPh_3 (635.5 mg, 2.4 mmol) in THF (5.6 mL) was added DIAD (484.3 mg, 2.4 mmol) at 0 ºC. 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, 50:1) to afford **1e** (184.2 mg, 56%).



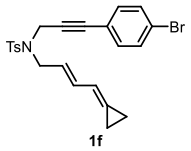
1e

Colorless oil, TLC R_f = 0.61 (PE/EA, 5:1). ^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.75 (d, J = 8.3 Hz, 2H), 7.30 – 7.23 (m, 4H), 7.06 – 7.00 (m, 2H), 6.49 – 6.35 (m, 2H), 5.61 (dt, J = 14.2, 6.8 Hz, 1H), 4.28 (s, 2H), 3.92 (d, J = 6.8 Hz, 2H), 2.34 (s, 3H), 1.19 – 1.14 (m, 2H), 1.13 – 1.07 (m, 2H). ^{13}C{^{1}H} NMR (101 MHz, CD_2Cl_2) δ 144.1, 136.5, 134.9, 134.7, 133.2, 130.0, 129.0, 128.9, 128.2, 124.7, 121.3, 118.0, 84.7, 83.5, 49.2, 37.1, 21.6, 2.8, 2.5. HRMS (ESI): calcd. for $C_{23}H_{22}ClNO_2SNa$ ([M+Na]$^+$): 434.0952, found 434.0952.



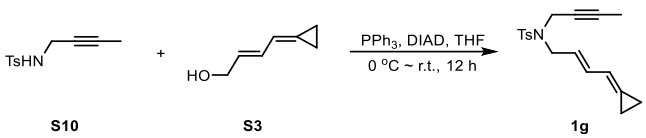
S9 **S3** **1f**

To a stirred solution of **S9** [3] (244.7 mg, 0.7 mmol), **S3** (74.0 mg, 0.7 mmol) and PPh_3 (529.7 mg, 2.0 mmol) in THF (4.7 mL) was added DIAD (403.4 mg, 2.0 mmol) at 0 ºC. 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 **1f** (137.4 mg, 45%).



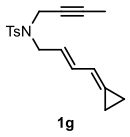
1f

Colorless oil, TLC R_f = 0.62 (PE/EA, 5:1). ^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.77 – 7.73 (m, 2H), 7.42 – 7.39 (m, 2H), 7.30 – 7.26 (m, 2H), 6.99 – 6.94 (m, 2H), 6.48 – 6.34 (m, 2H), 5.66 – 5.56 (m, 1H), 4.28 (s, 2H), 3.93 (d, *J* = 6.7 Hz, 2H), 2.35 (s, 3H), 1.20 – 1.14 (m, 2H), 1.13 – 1.07 (m, 2H). ^{13}C{^{1}H} NMR (101 MHz, CD_2Cl_2) δ 144.1, 136.4, 134.9, 133.4, 131.8, 130.0, 129.0, 128.2, 124.7, 122.9, 121.7, 118.0, 84.8, 83.7, 49.2, 37.1, 21.6, 2.8, 2.5. HRMS (ESI): calcd. for $C_{23}H_{23}BrNO_2S$ ([M+H]$^+$): 456.0627, found 456.0627.



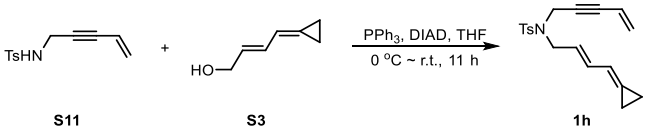
S10 **S3** **1g**

To a stirred solution of **S10** [4] (84.5 mg, 0.4 mmol), **S3** (41.7 mg, 0.4 mmol) and PPh_3 (151.1 mg, 0.6 mmol) in THF (2.7 mL) was added DIAD (114.5 mg, 0.6 mmol) at 0 ºC. 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 **1g** (86.5 mg, 72%).



1g

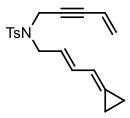
Colorless oil, TLC R_f = 0.52 (PE/EA, 5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, *J* = 8.2 Hz, 2H), 7.29 (d, *J* = 8.2 Hz, 2H), 6.43 – 6.29 (m, 2H), 5.55 (dt, *J* = 13.6, 6.9 Hz, 1H), 4.0 (q, *J* = 2.4 Hz, 2H), 3.84 (d, *J* = 6.9 Hz, 2H), 2.43 (s, 3H), 1.55 (t, *J* = 2.2 Hz, 3H), 1.19 – 1.13 (m, 2H), 1.13 – 1.07 (m, 2H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 143.3, 136.3, 134.3, 129.3, 128.4, 128.0, 124.6, 117.9, 81.6, 71.8, 48.4, 36.4, 21.6, 3.4, 2.7, 2.4. HRMS (ESI): calcd. for $C_{18}H_{22}NO_2S$ ([M+H]$^+$): 316.1366, found 316.1363.



S11 **S3** **1h**

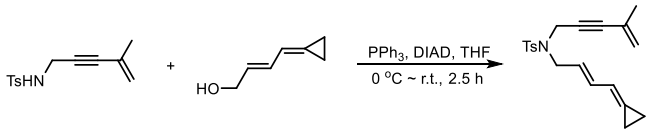
To a stirred solution of **S11** [5] (235.4 mg, 1.0 mmol), **S3** (110.2 mg, 1.0 mmol) and PPh_3 (394.6 mg,

1.5 mmol) in THF (7 mL) was added DIAD (301.0 mg, 1.5 mmol) at 0 ºC. The reaction was gradually allowed to warm to room temperature. The reaction was monitored by TLC and stirred for 11 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 **1h** (239.7 mg, 73%).



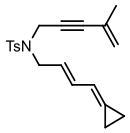
1h

Yellow oil, TLC R_f = 0.48 (PE/EA, 5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, *J* = 8.2 Hz, 2H), 7.29 (d, *J* = 8.2 Hz, 2H), 6.44 – 6.30 (m, 2H), 5.56 (dt, *J* = 14.8, 6.9 Hz, 1H), 5.51 (ddt, *J* = 17.2, 11.3, 1.2 Hz, 1H), 5.37 (dd, *J* = 11.3, 2.3 Hz, 1H), 5.32 (dd, *J* = 17.2, 2.3 Hz, 1H), 4.20 (d, *J* = 1.2 Hz, 2H), 3.86 (d, *J* = 6.9 Hz, 2H), 2.41 (s, 3H), 1.19 – 1.13 (m, 2H), 1.13 – 1.06 (m, 2H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 143.5, 136.1, 134.7, 129.5, 128.7, 128.0, 127.4, 124.3, 117.9, 116.5, 84.3, 82.8, 48.7, 36.7, 21.6, 2.8, 2.4. HRMS (ESI): calcd. for $C_{19}H_{22}NO_2S$ ([M+H]$^+$): 328.1366, found 328.1366.



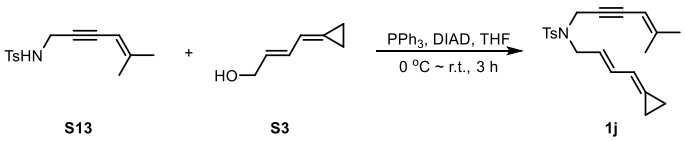
S12 **S3** **1i**

To a stirred solution of **S12** [6] (103.2 mg, 0.4 mmol), **S3** (45.0 mg, 0.4 mmol) and PPh_3 (317.4 mg, 1.2 mmol) in THF (2.9 mL) was added DIAD (239.9 mg, 1.2 mmol) at 0 ºC. The reaction was gradually allowed to warm to room temperature. The reaction was monitored by TLC and stirred for 2.5 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 **1i** (90.4 mg, 64%).



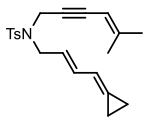
1i

Colorless oil, TLC R_f = 0.63 (PE/EA, 5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 – 7.72 (m, 2H), 7.28 (d, *J* = 8.0 Hz, 2H), 6.43 – 6.32 (m, 2H), 5.62 – 5.51 (m, 1H), 5.13 – 5.09 (m, 1H), 5.00 – 4.95 (m, 1H), 4.20 (s, 2H), 3.87 (d, *J* = 6.9 Hz, 2H), 2.40 (s, 3H), 1.65 (dd, *J* = 1.2, 1.2 Hz, 3H), 1.19 – 1.13 (m, 2H), 1.12 – 1.06 (m, 2H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 143.5, 136.2, 134.7, 129.6, 128.6, 128.0, 126.1, 124.3, 122.1, 117.9, 87.0, 81.1, 48.6, 36.7, 23.2, 21.6, 2.8, 2.4. HRMS (ESI): calcd. for $C_{20}H_{24}NO_2S$ ([M+H]$^+$): 342.1522, found 342.1521.



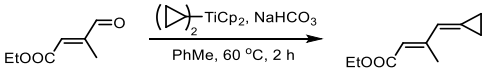
S13 **S3** **1j**

To a stirred solution of **S13** [7] (305.8 mg, 1.2 mmol), **S3** (127.7 mg, 1.2 mmol) and PPh_3 (950.1 mg, 3.6 mmol) in THF (8.4 mL) was added DIAD (723.2 mg, 3.6 mmol) at 0 ºC. 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 **1j** (287.6 mg, 74%).



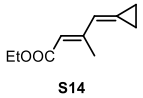
1j

Light yellow oil, TLC R_f = 0.63 (PE/EA, 5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 – 7.71 (m, 2H), 7.27 (d, *J* = 8.0 Hz, 2H), 6.44 – 6.30 (m, 2H), 5.61 – 5.51 (m, 1H), 4.99 (t, *J* = 1.6 Hz, 1H), 4.24 (d, *J* = 1.6 Hz, 2H), 3.88 (d, *J* = 6.9 Hz, 2H), 2.40 (s, 3H), 1.74 (s, 3H), 1.66 (s, 3H), 1.18 – 1.12 (m, 2H), 1.11 – 1.06 (m, 2H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 149.0, 143.4, 136.4, 134.5, 129.5, 128.4, 127.9, 124.6, 118.0, 104.6, 83.92, 83.8, 48.5, 37.0, 24.8, 21.6, 21.0, 2.8, 2.4. HRMS (ESI): calcd. for $C_{21}H_{25}NO_2SNa$ ([M+Na]$^+$): 378.1498, found 378.1499.



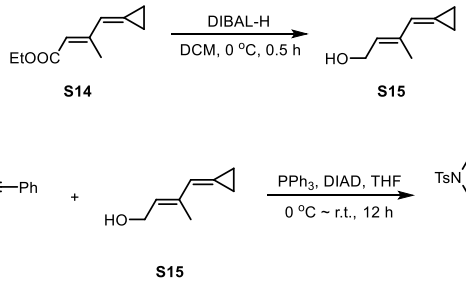
S14

To a stirred solution of (*E*)-ethyl 3-methyl-4-oxobut-2-enoate (143.8 mg, 1.0 mmol) and $NaHCO_3$ (193.3 mg, 2.3 mmol) in toluene (3.5 mL) was added bis(cyclopentadienyl)dicyclopropyltitanium (0.60 g, 2.3 mmol) in toluene (6.5 mL) at 60 ºC. The reaction was monitored by TLC and stirred at the same temperature 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, 100:1) to afford **S14** (62.9 mg, 37%).



S14

Yellow oil, TLC R_f = 0.80 (PE/EA, 5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.52 – 6.44 (m, 1H), 5.79 (s, 1H), 4.17 (q, *J* = 7.1 Hz, 2H), 2.40 (s, 3H), 1.44 – 1.39 (m, 2H), 1.29 (t, *J* = 7.1 Hz, 3H), 1.14 – 1.09 (m, 2H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 167.5, 154.1, 132.2, 122.6, 117.6, 59.7, 15.3, 14.5, 5.5, 1.0. HRMS (ESI): calcd. for $C_{10}H_{15}O_2$ ([M+H]$^+$): 167.1067, found 167.1071.



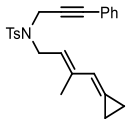
S14 **S15**

S4 **S15** **1k**

To a stirred solution of **S14** (56.8 mg, 0.3 mmol) in DCM (1.7 mL) was added DIBAL-H (1.0 M in

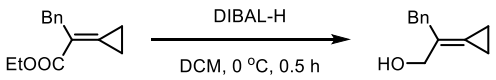
n-hexane, 0.8 mL, 0.8 mmol) at 0 ºC. The reaction was monitored by TLC and stirred for 0.5 h at the same temperature. Then, the resulting mixture was quenched with saturated potassium sodium tartrate solution (10 mL) and extracted with ether (5 mL×3). The combined organic phase was washed with brine and dried over Na_2SO_4, then filtered and concentrated. The crude residue **S15** was directly used in the next step.

To a stirred solution of **S4** [3] (97.2 mg, 0.3 mmol), **S15** (42.4 mg, 0.3 mmol) and PPh_3 (264.8 mg, 1.0 mmol) in THF (2.4 mL) was added DIAD (200.9 mg, 1.0 mmol) at 0 ºC. 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 **1k** (73.9 mg, 55%).



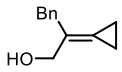
1k

Colorless oil, TLC R_f = 0.57 (PE/EA, 5:1). ^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.76 (d, *J* = 8.2 Hz, 2H), 7.32 – 7.23 (m, 5H), 7.14 – 7.02 (m, 2H), 6.42 (s, 1H), 5.42 (t, *J* = 7.4 Hz, 1H), 4.27 (s, 2H), 4.02 (d, *J* = 7.4 Hz, 2H), 2.33 (s, 3H), 1.95 (s, 3H), 1.35 – 1.28 (m, 2H), 1.08 – 1.01 (m, 2H). ^{13}C{^{1}H} NMR (101 MHz, CD_2Cl_2) δ 144.1, 140.9, 136.3, 131.8, 129.9, 128.8, 128.5, 128.2, 124.7, 122.65, 122.57, 122.5, 85.7, 82.5, 44.6, 37.0, 21.6, 13.8, 5.0, 0.8. HRMS (ESI): calcd. for $C_{24}H_{26}NO_2S$ ($[M+H]^+$): 392.1679, found 392.1675.



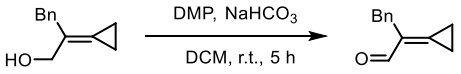
S16 **S17**

To a stirred solution of **S16** [8a] (1.77 g, 8.2 mmol) in DCM (20.0 mL) was added DIBAL-H (1.0 M in *n*-hexane, 20.0 mL, 20.0 mmol) at 0 ºC. The reaction was monitored by TLC, and stirred for 0.5 h at the same temperature. Then, the resulting mixture was quenched with saturated potassium sodium tartrate solution (100 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, 10:1) to afford **S17** (850.4 mg, 60%).



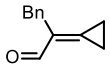
S17

Colorless oil, TLC R_f = 0.08 (PE/EA, 10:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 – 7.24 (m, 2H), 7.22 – 7.16 (m, 3H), 4.18 (s, 2H), 3.58 (s, 2H), 1.20 – 1.12 (m, 2H), 1.06 – 0.98 (m, 2H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 140.1, 129.0, 128.4, 127.4, 126.2, 119.8, 65.1, 39.0, 2.3, 1.4. HRMS (ESI): calcd. for $C_{12}H_{15}O$ ($[M+H]^+$): 175.1117, found 175.1117.



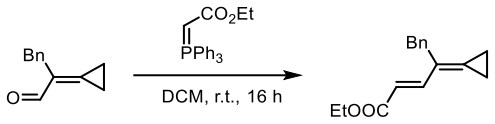
S17 **S18**

To a stirred solution of **S17** (820.1 mg, 4.7 mmol) and $NaHCO_3$ (3.95 g, 47.1 mmol) in DCM (100.0 mL) was added Dess–Martin periodinane (2.60 g, 6.1 mmol) at room temperature. The reaction was monitored by TLC, and stirred for 5.0 h at the same temperature. Then, the resulting mixture was quenched with water (100 mL) and extracted with DCM (50 mL×3). The combined organic phase was 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 20:1) to afford **S18** (559.1 mg, 69%).



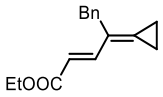
S18

Colorless oil, TLC R_f = 0.52 (PE/EA, 5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.74 (s, 1H), 7.27 – 7.22 (m, 2H), 7.21 – 7.15 (m, 3H), 3.69 (s, 2H), 1.53 – 1.38 (m, 2H), 1.21 – 1.12 (m, 2H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 193.3, 149.2, 139.6, 131.6, 129.2, 128.4, 126.2, 33.7, 2.3, 2.1. HRMS (ESI): calcd. for $C_{12}H_{13}O$ ([M+H]$^+$): 173.0961, found 173.0960.



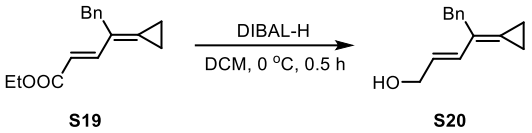
S18 **S19**

To a stirred solution of **S18** (530.2 mg, 3.0 mmol) in DCM (10.0 mL) was added Methyl(triphenylphosphoranylidene)acetate (1.07 g, 3.0 mmol) at room temperature. After stirring for 16 hours at room temperature, the reaction mixture was concentrated and purified by flash column chromatography on silica gel (eluted with PE/EA, 50:1) to afford **S19** (465.9 mg, 62%).

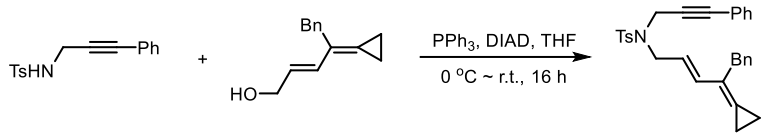


S19

Yellow oil, TLC R_f = 0.76 (PE/EA, 5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (d, J = 16.0 Hz, 1H), 7.21 – 7.13 (m, 2H), 7.11 – 7.01 (m, 3H), 5.80 (d, J = 16.0 Hz, 1H), 4.10 (q, J = 7.1 Hz, 2H), 3.64 (s, 2H), 1.25 – 1.16 (m, 2H), 1.19 (t, J = 8.0 Hz, 3H), 1.10 – 1.02 (m, 2H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 167.6, 145.6, 139.4, 137.3, 128.6, 128.4, 126.2, 125.5, 116.8, 60.3, 37.4, 14.4, 3.8, 3.2. HRMS (ESI): calcd. for $C_{16}H_{19}O_2$ ([M+H]$^+$): 243.1380, found 243.1378.



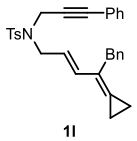
S19 S20



S4 S20 1l

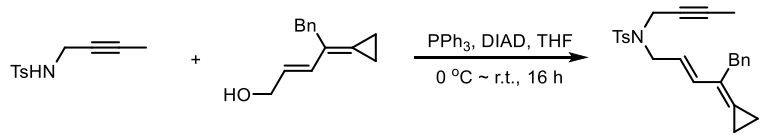
To a stirred solution of **S19** (195.4 mg, 0.8 mmol) in DCM (4.2 mL) was added DIBAL-H (1.0 M in *n*-hexane, 1.9 mL, 1.9 mmol) at 0 ºC. The reaction was monitored by TLC, and stirred for 0.5 h at the same temperature. Then, the resulting mixture was quenched with saturated potassium sodium tartrate solution (20 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 residue **S20** was directly used in the next step.

To a stirred solution of **S4** [3] (211.4 mg, 0.7 mmol), **S20** (161.5 mg, 0.8 mmol) and PPh_3 (579.6 mg, 2.2 mmol) in THF (5.2 mL) was added DIAD (442.0 mg, 2.2 mmol) at 0 ºC. The reaction was gradually allowed to warm to room temperature. The reaction was monitored by TLC and stirred for 16 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 **1l** (231.1 mg, 67%).



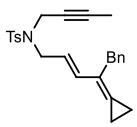
1l

Colorless oil, TLC R_f = 0.53 (PE/EA, 5:1). ^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.72 (d, J = 8.2 Hz, 2H), 7.31 – 7.22 (m, 7H), 7.19 – 7.13 (m, 3H), 7.11 – 7.05 (m, 2H), 6.48 (d, J = 15.8 Hz, 1H), 5.55 (dt, J = 15.8, 6.9 Hz, 1H), 4.12 (s, 2H), 3.89 (d, J = 6.9 Hz, 2H), 3.68 (s, 2H), 2.34 (s, 3H), 1.21 – 1.14 (m, 2H), 1.13 – 1.04 (m, 2H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 143.5, 140.1, 136.02, 136.00, 131.6, 129.6, 128.7, 128.5, 128.3, 128.22, 128.19, 128.0, 126.0, 125.4, 122.4, 121.4, 85.7, 81.9, 49.1, 38.0, 36.6, 21.6, 3.1, 2.8. HRMS (ESI): calcd. for $C_{30}H_{30}NO_2S$ ($[M+H]^+$): 468.1992, found 468.1992.



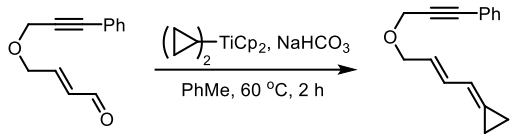
S10 S20 1m

To a stirred solution of **S10** [3] (117.9 mg, 0.5 mmol), **S20** (116.8 mg, 0.6 mmol) and PPh_3 (421.8 mg, 1.6 mmol) in THF (3.7 mL) was added DIAD (323.6 mg, 1.6 mmol) at 0 ºC. The reaction was gradually allowed to warm to room temperature. The reaction was monitored by TLC and stirred for 16 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 **1m** (164.1 mg, 77%).



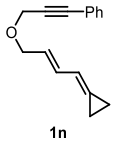
1m

Colorless oil, TLC R_f = 0.57 (PE/EA, 5:1). ^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.68 (d, J = 7.9 Hz, 2H), 7.31 (d, J = 7.9 Hz, 2H), 7.27 – 7.22 (m, 2H), 7.19 – 7.11 (m, 3H), 6.41 (d, J = 15.8 Hz, 1H), 5.48 (dt, J = 15.8, 6.8 Hz, 1H), 3.85 (s, 2H), 3.81 (d, J = 6.8 Hz, 2H), 3.65 (s, 2H), 2.42 (s, 3H), 1.54 (s, 3H), 1.22 – 1.14 (m, 2H), 1.14 – 1.06 (m, 2H). ^{13}C{^{1}H} NMR (101 MHz, CD_2Cl_2) δ 143.8, 140.7, 136.6, 135.7, 129.7, 128.9, 128.5, 128.20, 128.15, 126.2, 125.7, 121.9, 81.9, 72.0, 49.1, 38.1, 36.5, 21.6, 3.3, 3.2, 2.9. HRMS (ESI): calcd. for $C_{25}H_{28}NO_2S$ ([M+H]$^+$): 406.1835, found 406.1837.



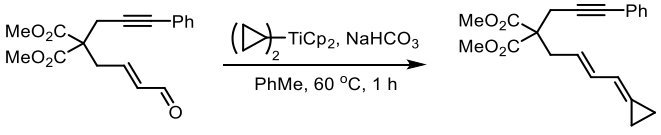
S21 **1n**

To a stirred solution of **S21** [8b] (243.7 mg, 1.2 mmol) and $NaHCO_3$ (235.4 mg, 2.8 mmol) in toluene (4 mL) was added bis(cyclopentadienyl)dicyclopropyltitanium (0.73 g, 2.8 mmol) in toluene (8 mL) at 60 ºC. The reaction was monitored by TLC and stirred at the same temperature 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, 100:1) to afford **1n** (129.7 mg, 48%).



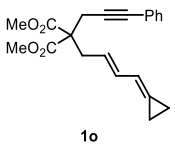
1n

Yellow oil, TLC R_f = 0.80 (PE/EA, 5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 – 7.42 (m, 2H), 7.35 – 7.28 (m, 3H), 6.58 – 6.35 (m, 2H), 5.85 – 5.76 (m, 1H), 4.39 (s, 2H), 4.20 (d, J = 6.5 Hz, 2H), 1.19 – 1.11 (m, 4H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 133.5, 131.9, 128.5, 128.40, 128.2, 126.6, 122.8, 118.2, 86.4, 85.4, 70.3, 57.8, 2.8, 2.4. HRMS (EI): calcd. for $C_{16}H_{16}O$ ([M]$^{\bullet+}$): 224.1196, found 224.1196.



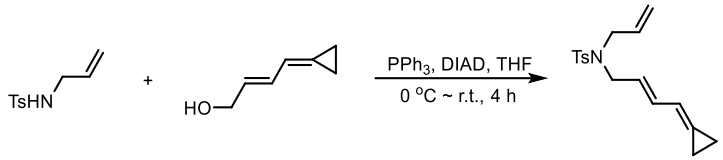
S22 **1o**

To a stirred solution of **S22** [9] (280.0 mg, 0.9 mmol) and $NaHCO_3$ (220.0 mg, 2.6 mmol) in toluene (4 mL) was added bis(cyclopentadienyl)dicyclopropyltitanium (0.55 g, 2.1 mmol) in toluene (6 mL) at 60 ºC. The reaction was monitored by TLC and stirred at the same temperature for 1 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 **1o** (150.0 mg, 50%).



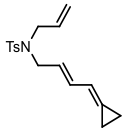
1o

Light yellow oil, TLC R_f = 0.68 (PE/EA, 5:1). ^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.40 – 7.36 (m, 2H), 7.30 – 7.27 (m, 3H), 6.40 – 6.28 (m, 2H), 5.50 (dt, *J* = 13.8, 7.8 Hz, 1H), 3.76 (s, 6H), 3.02 (s, 2H), 2.92 (d, *J* = 7.8 Hz, 2H), 1.14 – 1.07 (m, 4H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 170.5, 134.5, 131.8, 128.3, 128.1, 126.7, 124.5, 123.4, 118.5, 84.5, 83.7, 57.8, 52.9, 36.0, 23.9, 2.7, 2.3. HRMS (ESI): calcd. for $C_{21}H_{23}O_4^+$ ([M+H]+): 339.1591, found: 339.1581.



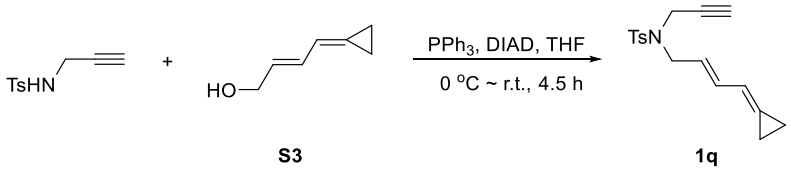
S23 **S3** **1p**

To a stirred solution of **S23** [10] (295.9 mg, 1.4 mmol), **S3** (153.5 mg, 1.4 mmol) and PPh_3 (551.9 mg, 2.1 mmol) in THF (9 mL) was added DIAD (423.4 mg, 2.1 mmol) at 0 ºC. The reaction was gradually allowed to warm to room temperature. The reaction was monitored by TLC and stirred for 4 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 **1p** (203.8 mg, 48%).



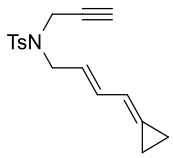
1p

Colorless oil, TLC R_f = 0.60 (PE/EA, 5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 8.1 Hz, 2H), 7.29 (d, *J* = 8.1 Hz, 2H), 6.31 (dt, *J* = 10.5, 1.7 Hz, 1H), 6.21 (dd, *J* = 15.0, 10.5 Hz, 1H), 5.62 (ddt, *J* = 16.1, 9.8, 6.3 Hz, 1H), 5.41 (dt, *J* = 15.0, 6.8 Hz, 1H), 5.17 – 5.14 (m, 1H), 5.14 – 5.11 (m, 1H), 3.86 (d, *J* = 6.8 Hz, 2H), 3.80 (d, *J* = 6.3 Hz, 2H), 2.42 (s, 3H), 1.18 – 1.10 (m, 2H), 1.10 – 1.03 (m, 2H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 143.3, 137.6, 133.9, 132.9, 129.8, 128.1, 127.4, 125.0, 119.0, 117.9, 49.3, 48.8, 21.6, 2.7, 2.3. HRMS (ESI): calcd. for $C_{17}H_{22}NO_2S$ ([M+H]$^+$): 304.1366, found 304.1366.



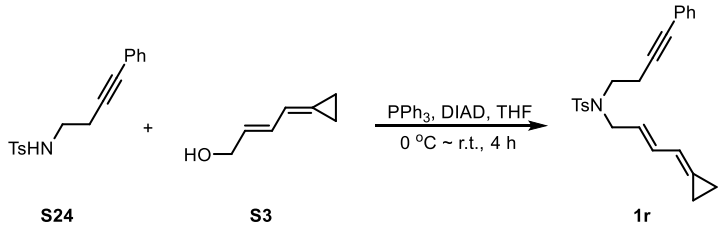
S3 **1q**

To a stirred solution of **4-methyl-N-(prop-2-yn-1-yl)benzenesulfonamide** (261.5 mg, 1.3 mmol), **S3** (125.2 mg, 1.1 mmol) and PPh_3 (596.0 mg, 2.3 mmol) in THF (10 mL) was added DIAD (459.4 mg, 2.3 mmol) at 0 ºC. The reaction was gradually allowed to warm to room temperature. The reaction was monitored by TLC and stirred for 4.5 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 **1q** (233.4 mg, 68%).



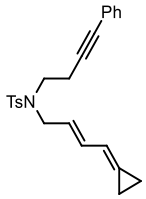
1q

Light yellow oil, TLC R_f = 0.50 (PE/EA, 5:1). ^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.72 (d, J = 8.1 Hz, 2H), 7.33 (d, J = 8.1Hz, 2H), 6.42 – 6.33 (m, 2H), 5.57 – 5.50 (m, 1H), 4.07 (d, J = 2.5 Hz, 2H), 3.87 (d, J = 6.9 Hz, 2H), 2.43 (s, 3H), 2.09 (t, J = 2.5 Hz, 1H), 1.19 – 1.14 (m, 2H), 1.13 – 1.09 (m, 2H). ^{13}C{^{1}H} NMR (101 MHz, CD_2Cl_2) δ 144.2, 136.5, 134.8, 129.9, 129.0, 128.1, 124.5, 118.0, 77.1, 73.9, 48.8, 36.2, 21.7, 2.8, 2.5. HRMS (ESI): calcd. for $C_{17}H_{20}NO_2S$ ([M+H]$^+$): 302.1209, found 302.1200.



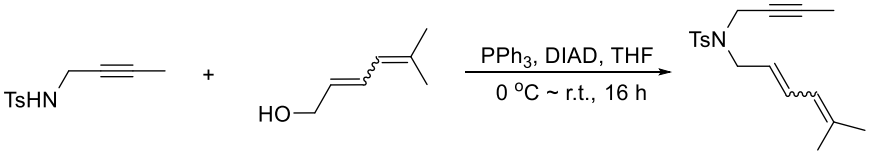
S24 **S3** **1r**

To a stirred solution of **S24** [11] (103.1 mg, 0.3 mmol), **S3** (35.8 mg, 0.3 mmol) and PPh_3 (260.2 mg, 0.6 mmol) in THF (3 mL) was added DIAD (120.1 mg, 0.6 mmol) at 0 ºC. The reaction was gradually allowed to warm to room temperature. The reaction was monitored by TLC and stirred for 4 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 **1r** (63.3 mg, 47%).



1r

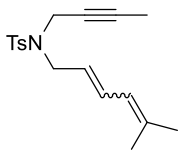
Light yellow oil, TLC R_f = 0.60 (PE/EA, 5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, J = 8.1 Hz, 2H), 7.38 – 7.33 (m, 2H), 7.28 – 7.23 (m, 5H), 6.37 – 6.20 (m, 2H), 5.53 – 5.44 (m, 1H), 3.95 (d, J = 6.8 Hz, 2H), 3.39 (dd, J = 7.4, 7.4 Hz, 2H), 2.68 (dd, J = 7.4, 7.4 Hz, 2H), 2.39 (s, 3H), 1.16 – 1.09 (m, 2H), 1.09 – 1.02 (m, 2H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 143.4, 137.1, 134.0, 131.6, 129.8, 128.5, 128.3, 128.0, 127.3, 125.2, 123.4, 117.8, 86.8, 82.3, 50.6, 46.0, 21.6, 20.4, 2.7, 2.3. HRMS (ESI): calcd. for $C_{24}H_{26}NO_2S$ ([M+H]$^+$): 392.1679, found 392.1668.



S10 **S25** **4a**

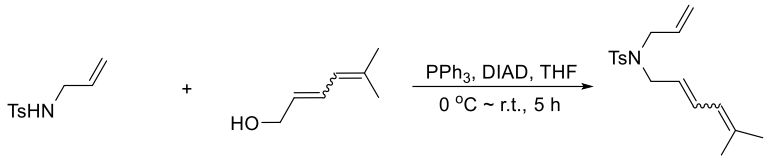
To a stirred solution of **S10** [3] (89.9 mg, 0.4 mmol), **S25** [12] (45.5 mg, 0.4 mmol) and PPh_3 (158.0

mg, 0.6 mmol) in THF (3 mL) was added DIAD (119.9 mg, 0.6 mmol) at 0 ºC. The reaction was gradually allowed to warm to room temperature. The reaction was monitored by TLC and stirred for 16 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 **4a** (110.5 mg, 86%) as an inseparable E/Z (10/1) mixture.



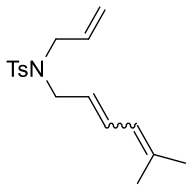
4a

Colorless oil, TLC R_f = 0.70 (PE/EA, 5:1). The E/Z ratio (10/1) of **4b** was determined by the integral at δ 2.42 and δ 2.40 in ^{1}H NMR. The following peaks are selected as (*E*)-**4a**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 8.1 Hz, 2H), 7.29 (d, *J* = 8.1 Hz, 2H), 6.39 (dd, *J* = 15.0, 10.9 Hz, 1H), 5.84 – 5.76 (m, 1H), 5.39 (ddd, *J* = 14.5, 6.9, 6.9 Hz, 1H), 4.00 (q, *J* = 2.4 Hz, 2H), 3.82 (d, *J* = 6.9 Hz, 2H), 2.42 (s, 3H), 1.76 (s, 3H), 1.72 (s, 3H), 1.55 (t, *J* = 2.4 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.3, 136.8, 136.3, 131.7, 129.3, 128.0, 124.1, 123.6, 81.5, 71.9, 48.6, 36.3, 26.1, 21.6, 18.4, 3.4. HRMS (ESI): calcd. for $C_{18}H_{24}NO_2S$ ([M+H]$^+$): 318.1522, found 318.1536.



S23 **S25** **4b**

To a stirred solution of **S23** [10] (63.4 mg, 0.3 mmol), **S25** (33.7 mg, 0.3 mmol) and PPh_3 (118.0 mg, 0.4 mmol) in THF (3 mL) was added DIAD (91.0 mg, 0.45 mmol) at 0 ºC. The reaction was gradually allowed to warm to room temperature. The reaction was monitored by TLC and stirred for 5 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 **4b** (43.7 mg, 48%) as an inseparable E/Z (10/1) mixture.

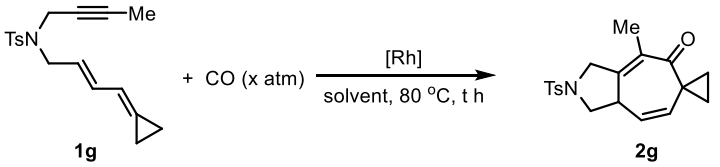


4b

Colorless oil, TLC R_f = 0.70 (PE/EA, 5:1). The E/Z ratio (10/1) of **4b** was determined by the integral at δ 2.42 and δ 2.41 in ^{1}H NMR. The following peaks are selected as (*E*)-**4b**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 8.1 Hz, 2H), 7.29 (d, *J* = 8.1 Hz, 2H), 6.25 (dd, *J* = 15.1, 11.0 Hz, 1H), 5.72 (d, *J* = 11.0 Hz, 1H), 5.68 – 5.58 (m, 1H), 5.26 (ddd, *J* = 14.5, 6.9, 6.9 Hz, 1H), 5.18 – 5.15 (m, 1H), 5.14 – 5.11 (m, 1H), 3.84 (d, *J* = 6.9 Hz, 2H), 3.79 (d, *J* = 6.3 Hz, 2H), 2.42 (s, 3H), 1.75 (s, 3H), 1.70 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.2, 137.7, 136.6, 133.1, 131.2, 129.8, 127.3, 124.1, 124.0, 118.9, 49.2, 49.0, 26.1, 21.6, 18.4. HRMS (ESI): calcd. for $C_{17}H_{24}NO_2S$ ([M+H]$^+$): 306.1522, found 306.1517.

III. General Procedure and Experimental Details of Rh(I)-Catalyzed [4+2+1] Reaction

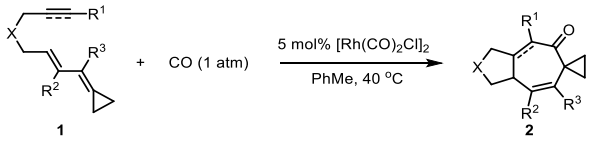
Table S1. Optimization conditions using substrate 1g



1g **2g**

Entry	Rh catalyst	x	solvent	t	yield
1	**5 mol% $[Rh(CO)_2Cl]_2$**	**1.0**	**PhMe**	**15**	**62%**
2[a]	5 mol% $[Rh(CO)_2Cl]_2$	1.0	PhMe	15	33%
3	5 mol% $[Rh(CO)_2Cl]_2$	0.5	PhMe	12	26%
4	5 mol% $[Rh(CO)_2Cl]_2$	1.0	DCE	1	25%
5	5 mol% $[Rh(CO)_2Cl]_2$	1.0	1,4-dioxane	1	trace
6	10 mol% $Rh(CO)(PPh_3)_2Cl$	1.0	PhMe	6	N.R.
7	10 mol% $Rh(CO)(PMe_3)_2Cl$	1.0	PhMe	6	N.R.
8	10 mol% $Rh(CO)(PPh_3)_2Cl$ + 12 mol% $AgSbF_6$	1.0	PhMe	1	41%
9	5 mol% $[Rh(CO)_2Cl]_2$ + 12 mol% $AgSbF_6$	1.0	PhMe	1	23%
10	10 mol% $Rh(dppp)SbF_6$	1.0	PhMe	15	11%
11[b]	10 mol% $Rh(CO)(PPh_3)_2Cl$ + 12 mol% $AgSbF_6$	1.0	PhMe	1.5	42%
12	5 mol% $[Rh(CO)_2Cl]_2$ + 10 mol% PPh_3 + 12 mol% $AgSbF_6$	1.0	PhMe	1	34%
13	5 mol% $[Rh(CO)_2Cl]_2$ + 20 mol% PPh_3 + 12 mol% $AgSbF_6$	1.0	PhMe	1	19%

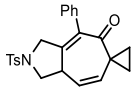
[a] substrates was stored at -20 °C for a week, [b] Substrates were slowly added in about 1 h.



1 **2**

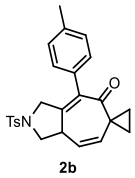
General procedure of Rh(I)-Catalyzed [4+2+1] Reaction:

Under nitrogen, 2 mL toluene was added to a flame-dried glassware containing **1** (0.1 mmol) and $[Rh(CO)_2Cl]_2$ (1.9 mg, 4.9 μmol) at room temperature. Then, the reaction mixture was bubbled with CO (1 atm) for 10 min. The glassware was immersed into an oil bath at 40 ºC 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 **2**.



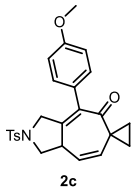
2a

Run 1: Following general procedure, 38.3 mg **1a** was used, 24 h. After flash column chromatography on silica gel (eluted with PE/EA, 5:1), 31.3 mg **2a** was obtained in 76% yield.
Run 2: Following general procedure, 38.1 mg **1a** was used, 24 h. After flash column chromatography on silica gel (eluted with PE/EA, 5:1), 31.1 mg **2a** was obtained in 76% yield.
Average yield: 76%.
White solid, m.p. = 200-201 °C, TLC R_f = 0.12 (PE/EA, 5:1) ^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.63 (d, *J* = 8.1 Hz, 2H), 7.41 – 7.29 (m, 5H), 7.01 (d, *J* = 6.8 Hz, 2H), 5.80 (dd, *J* = 9.8, 3.4 Hz, 1H), 5.43 (dd, *J* = 9.8, 2.5 Hz, 1H), 3.89 – 3.83 (m, 1H), 3.77 (dd, *J* = 16.2, 2.0 Hz, 1H), 3.67 (d, *J* = 16.2 Hz, 1H), 3.64 (dd, *J* = 10.0, 8.7 Hz, 1H), 3.26 (dd, *J* = 10.0, 6.4 Hz, 1H), 2.45 (s, 3H), 1.71 – 1.62 (m, 1H), 1.56 – 1.51 (m, 1H), 1.09 – 0.99 (m, 2H). ^{13}C{^{1}H} NMR (101 MHz, CD_2Cl_2) δ 198.3, 154.5, 144.8, 137.9, 135.5, 134.0, 133.8, 131.9, 130.2, 129.0, 128.7, 128.4, 127.9, 54.5, 53.4, 41.6, 32.9, 22.6, 22.2, 21.7. HRMS (ESI): calcd. for $C_{24}H_{24}NO_3S$ ($[M+H]^+$): 406.1471, found 406.1463.



2b

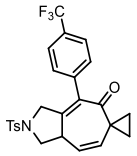
Run 1: Following general procedure, 38.2 mg **1b** was used, 24 h. After flash column chromatography on silica gel (eluted with PE/EA, 5:1), 32.6 mg **2b** was obtained in 80% yield.
Run 2: Following general procedure, 39.9 mg **1b** was used, 24 h. After flash column chromatography on silica gel (eluted with PE/EA, 5:1), 35.8 mg **2b** was obtained in 84% yield.
Average yield: 82%.
Light yellow solid, m.p. = 171-172 °C, TLC R_f = 0.14 (PE/EA, 5:1). ^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.67 – 7.61 (m, 2H), 7.40 – 7.35 (m, 2H), 7.19 – 7.13 (m, 2H), 6.94 – 6.87 (m, 2H), 5.79 (dd, *J* = 9.8, 3.4 Hz, 1H), 5.42 (dd, *J* = 9.8, 2.6 Hz, 1H), 3.88 – 3.82 (m, 1H), 3.79 (dd, *J* = 16.1, 2.4 Hz, 1H), 3.68 (d, *J* = 16.1 Hz, 1H), 3.64 (dd, *J* = 10.0, 8.2 Hz, 1H), 3.27 (dd, *J* = 10.0, 6.2 Hz, 1H), 2.45 (s, 3H), 2.36 (s, 3H), 1.65 (ddd, *J* = 9.8, 6.6, 2.9 Hz, 1H), 1.54 (ddd, *J* = 9.8, 7.0, 2.5 Hz, 1H), 1.05 (ddd, *J* = 9.3, 7.0, 2.9 Hz, 1H), 1.01 (ddd, *J* = 9.3, 6.6, 2.5 Hz, 1H). ^{13}C{^{1}H} NMR (101 MHz, CD_2Cl_2) δ 198.5, 154.2, 144.8, 137.8, 135.5, 135.0, 134.1, 133.9, 132.1, 130.2, 129.4, 128.8, 128.4, 54.6, 53.5, 41.6, 32.9, 22.7, 22.0, 21.7, 21.3. HRMS (ESI): calcd. for $C_{25}H_{26}NO_3S$ ($[M+H]^+$): 420.1628, found 420.1628.



2c

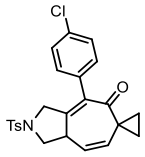
Run 1: Following general procedure, 39.9 mg **1c** was used, 24 h. After flash column chromatography on silica gel (eluted with PE/EA, 5:1), 35.0 mg **2c** was obtained in 82% yield.
Run 2: Following general procedure, 40.9 mg **1c** was used, 24 h. After flash column chromatography

on silica gel (eluted with PE/EA, 5:1), 34.4 mg **2c** was obtained in 79% yield.
Average yield: 80%.
Light yellow solid, m.p. = 90-91 °C, TLC R_f = 0.09 (PE/EA, 5:1). ^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.70 – 7.59 (m, 2H), 7.42 – 7.33 (m, 2H), 6.99 – 6.91 (m, 2H), 6.92 – 6.82 (m, 2H), 5.79 (dd, *J* = 9.8, 3.4 Hz, 1H), 5.41 (dd, *J* = 9.8, 2.6 Hz, 1H), 3.87 – 3.78 (m, 2H), 3.81 (s, 3H), 3.69 (d, *J* = 16.6 Hz, 1H), 3.64 (dd, *J* = 9.9, 8.2 Hz, 1H), 3.27 (dd, *J* = 9.9, 6.2 Hz, 1H), 2.45 (s, 3H), 1.65 (ddd, *J* = 9.7, 6.6, 2.9 Hz, 1H), 1.54 (ddd, *J* = 9.7, 7.0, 2.5 Hz, 1H), 1.05 (ddd, *J* = 9.3, 7.0, 2.9 Hz, 1H), 1.01 (ddd, *J* = 9.3, 6.6, 2.5 Hz, 1H). ^{13}C{^{1}H} NMR (101 MHz, CD_2Cl_2) δ 198.7, 159.5, 154.2, 144.8, 135.2, 134.1, 133.9, 132.1, 130.24, 130.22, 130.19, 128.4, 114.1, 55.6, 54.6, 53.5, 41.6, 32.9, 22.7, 22.1, 21.7. HRMS (ESI): calcd. for $C_{25}H_{26}NO_4S$ ([M+H]$^+$): 436.1577, found 436.1578.



2d

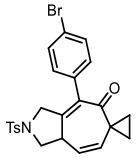
Run 1: Following general procedure, 42.9 mg **1d** was used, 48 h. After flash column chromatography on silica gel (eluted with PE/EA, 5:1), 30.7 mg **2d** was obtained in 67% yield.
Run 2: Following general procedure, 44.4 mg **1d** was used, 48 h. After flash column chromatography on silica gel (eluted with PE/EA, 5:1), 31.4 mg **2d** was obtained in 67% yield.
Average yield: 67%.
White solid, m.p. = 126-127 °C, TLC R_f = 0.17 (PE/EA, 5:1). ^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.70 – 7.61 (m, 4H), 7.39 (d, *J* = 8.0 Hz, 2H), 7.21 (d, *J* = 8.0 Hz, 2H), 5.81 (dd, *J* = 9.8, 3.3 Hz, 1H), 5.46 (dd, *J* = 9.8, 2.5 Hz, 1H), 3.96 – 3.88 (m, 1H), 3.77 (d, *J* = 16.3 Hz, 1H), 3.70 (dd, *J* = 9.9, 6.9 Hz, 1H), 3.68 (d, *J* = 16.3 Hz, 1H), 3.26 (dd, *J* = 9.9, 6.7 Hz, 1H), 2.45 (s, 3H), 1.73 – 1.66 (m, 1H), 1.58 – 1.50 (m, 1H), 1.11 – 1.03 (m, 2H). ^{13}C{^{1}H} NMR (101 MHz, CD_2Cl_2) δ 197.4, 155.8, 144.9, 141.6, 134.4, 133.9, 133.7, 131.7, 130.3, 129.79 (q, *J* = 32.2 Hz), 129.7, 128.4, 125.6 (q, *J* = 3.7 Hz), 124.6 (q, *J* = 271.9 Hz), 54.4, 53.4, 41.8, 32.9, 22.5, 22.4, 21.7. HRMS (ESI): calcd. for $C_{25}H_{23}F_3NO_3S$ ([M+H]$^+$): 474.1345, found 474.1341.



2e

Run 1: Following general procedure, 41.6 mg **1e** was used, 24 h. After flash column chromatography on silica gel (eluted with PE/EA, 5:1), 33.4 mg **2e** was obtained in 75% yield.
Run 2: Following general procedure, 41.8 mg **1e** was used, 24 h. After flash column chromatography on silica gel (eluted with PE/EA, 5:1), 32.4 mg **2e** was obtained in 73% yield.
Average yield: 74%.
White solid, m.p. = 147-148 °C. TLC R_f = 0.19 (PE/EA, 5:1). ^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.66 – 7.61 (m, 2H), 7.38 (d, *J* = 8.0 Hz, 2H), 7.36 – 7.31 (m, 2H), 7.02 – 6.97 (m, 2H), 5.79 (dd, *J* = 9.8, 3.4 Hz, 1H), 5.43 (dd, *J* = 9.8, 2.6 Hz, 1H), 3.91 – 3.85 (m, 1H), 3.76 (dd, *J* = 16.2, 2.3 Hz, 1H), 3.68 (dd, *J* = 10.0, 7.5 Hz, 1H), 3.66 (d, *J* = 16.2 Hz, 1H), 3.25 (dd, *J* = 10.0, 6.6 Hz, 1H), 2.45 (s,

3H), 1.71 – 1.65 (m, 1H), 1.55 – 1.50 (m, 1H), 1.08 – 1.01 (m, 2H). $^{13}C\{^{1}H\}$ NMR (101 MHz, CD_2Cl_2) δ 197.8, 155.3, 144.9, 136.3, 134.5, 134.0, 133.8, 133.7, 131.9, 130.6, 130.3, 128.9, 128.4, 54.4, 53.4, 41.7, 32.9, 22.5, 22.4, 21.7. HRMS (ESI): calcd. for $C_{24}H_{23}ClNO_3S$ ($[M+H]^+$): 440.1082, found 440.1081.



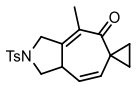
2f

Run 1: Following general procedure, 45.6 mg **1f** was used, 24 h. After flash column chromatography on silica gel (eluted with PE/EA, 5:1), 34.4 mg **2f** was obtained in 71% yield.

Run 2: Following general procedure, 44.5 mg **1f** was used, 24 h. After flash column chromatography on silica gel (eluted with PE/EA, 5:1), 33.6 mg **2f** was obtained in 71% yield.

Average yield: 71%.

White solid, m.p. = 159-160 °C, TLC R_f = 0.19 (PE/EA, 5:1). ^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.67 – 7.59 (m, 2H), 7.54 – 7.43 (m, 2H), 7.38 (d, J = 8.0 Hz, 2H), 6.98 – 6.87 (m, 2H), 5.79 (dd, J = 9.8, 3.4 Hz, 1H), 5.43 (dd, J = 9.8, 2.6 Hz, 1H), 3.91 – 3.84 (m, 1H), 3.75 (dd, J = 16.3, 2.4 Hz, 1H), 3.67 (dd, J = 10.0, 7.5 Hz, 1H), 3.66 (d, J = 16.3 Hz, 1H), 3.24 (dd, J = 10.0, 6.6 Hz, 1H), 2.45 (s, 3H), 1.71 – 1.64 (m, 1H), 1.55 – 1.49 (m, 1H), 1.08 – 1.00 (m, 2H). $^{13}C\{^{1}H\}$ NMR (101 MHz, CD_2Cl_2) δ 197.7, 155.3, 144.9, 136.8, 134.5, 134.0, 133.7, 132.0, 131.9, 130.9, 130.3, 128.4, 122.1, 54.5, 53.4, 41.8, 32.9, 22.5, 22.4, 21.7. HRMS (ESI): calcd. for $C_{24}H_{23}BrNO_3S$ ($[M+H]^+$): 484.0577, found 484.0578.



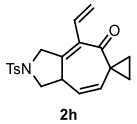
2g

Run 1: Following general procedure, 31.7 mg **1g** was used, 80 °C, 15 h. After flash column chromatography on silica gel (eluted with PE/EA, 10:1), 21.9 mg **2g** was obtained in 63% yield.

Run 2: Following general procedure, 31.3 mg **1g** was used, 80 °C, 15 h. After flash column chromatography on silica gel (eluted with PE/EA, 10:1), 20.7 mg **2g** was obtained in 61% yield.

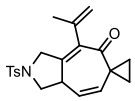
Average yield: 62%.

White solid, m.p. = 104-105 °C, TLC R_f = 0.24 (PE/EA, 5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, J = 8.0 Hz, 2H), 7.37 (d, J = 8.0 Hz, 2H), 5.70 (dd, J = 9.8, 3.2 Hz, 1H), 5.34 (dd, J = 9.8, 2.4 Hz, 1H), 3.93 (s, 2H), 3.83 – 3.75 (m, 1H), 3.69 (dd, J = 9.1, 8.7 Hz, 1H), 3.14 (dd, J = 9.1, 7.5 Hz, 1H), 2.45 (s, 3H), 1.80 – 1.75 (m, 1H), 1.71 (s, 3H), 1.45 – 1.37 (m, 1H), 1.00 – 0.92 (m, 2H). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 198.6, 152.3, 144.4, 133.6, 133.5, 131.7, 130.0, 129.9, 128.2, 54.1, 52.8, 41.3, 32.0, 22.2, 21.7, 21.6, 15.9. HRMS (ESI): calcd. for $C_{19}H_{22}NO_3S$ ($[M+H]^+$): 344.1315, found 344.1309.



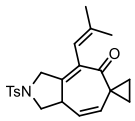
2h

Run 1: Following general procedure, 32.2 mg **1h** was used, 3 h. After flash column chromatography on silica gel (eluted with PE/EA, 5:1), 34.1 mg **2h** was obtained in 97% yield.
Run 2: Following general procedure, 33.7 mg **1h** was used, 3 h. After flash column chromatography on silica gel (eluted with PE/EA, 5:1), 35.5 mg **2h** was obtained in 97% yield.
Average yield: 97%.
White solid, m.p. = 55-56 °C, TLC R_f = 0.25 (PE/EA, 5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, *J* = 8.0 Hz, 2H), 7.35 (d, *J* = 8.0 Hz, 2H), 6.17 (dd, *J* = 17.4, 11.4 Hz, 1H), 5.70 (dd, *J* = 9.9, 3.6 Hz, 1H), 5.28 – 5.20 (m, 3H), 4.19 (dd, *J* = 15.8, 1.5 Hz, 1H), 3.86 (d, *J* = 15.8 Hz, 1H), 3.72 – 3.65 (m, 1H), 3.46 (dd, *J* = 9.8, 8.2 Hz, 1H), 3.30 (dd, *J* = 9.8, 4.9 Hz, 1H), 2.44 (s, 3H), 1.82 (ddd, *J* = 10.1, 7.2, 3.3 Hz, 1H), 1.53 (ddd, *J* =10.1, 7.3, 3.0 Hz, 1H), 1.08 (ddd, *J* = 9.6, 7.3, 3.3 Hz, 1H), 0.97 (ddd, *J* = 9.6, 7.2, 3.0 Hz, 1H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 200.2, 151.0, 144.4, 134.2, 132.8, 131.7, 131.5, 131.1, 130.0, 128.2, 118.7, 53.8, 51.9, 40.9, 33.2, 25.0, 21.7, 21.0. HRMS (ESI): calcd. for $C_{20}H_{22}NO_3S$ ([M+H]$^+$): 356.1315, found 356.1312.



2i

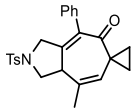
Run 1: Following general procedure, 34.0 mg **1i** was used, 24 h. After flash column chromatography on silica gel (eluted with PE/EA, 5:1), 21.2 mg **2i** was obtained in 58% yield.
Run 2: Following general procedure, 34.2 mg **1i** was used, 24 h. After flash column chromatography on silica gel (eluted with PE/EA, 5:1), 22.8 mg **2i** was obtained in 62% yield.
Average yield: 60%.
Colorless oil, TLC R_f = 0.24 (PE/EA, 5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, *J* = 8.2 Hz, 2H), 7.36 (d, *J* = 8.2 Hz, 2H), 5.74 (dd, *J* = 9.8, 3.5 Hz, 1H), 5.32 (dd, *J* = 9.8, 2.6 Hz, 1H), 5.11 – 5.05 (m, 1H), 4.69 – 4.63 (m, 1H), 4.05 (dd, *J* = 16.0, 2.2 Hz, 1H), 3.81 (d, *J* = 16.0 Hz, 1H), 3.76 – 3.68 (m, 1H), 3.50 (dd, *J* = 9.8, 8.1 Hz, 1H), 3.30 (dd, *J* = 9.8, 5.4 Hz, 1H), 2.44 (s, 3H), 1.74 (s, 3H), 1.71 (ddd, *J* = 9.8, 6.7, 2.6 Hz, 1H), 1.54 (ddd, *J* = 9.8, 7.1, 2.1 Hz, 1H), 1.01 (ddd, *J* = 9.3, 7.1, 2.6 Hz, 1H), 0.96 (ddd, *J* = 9.3, 6.7, 2.1 Hz, 1H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 198.1, 152.0, 144.4, 142.4, 137.3, 134.0, 133.6, 131.7, 130.0, 128.2, 116.4, 54.1, 52.9, 41.0, 32.7, 22.6, 22.2, 21.9, 21.7. HRMS (ESI): calcd. for $C_{21}H_{24}NO_3S$ ([M+H]$^+$): 370.1471, found 370.1471.



2j

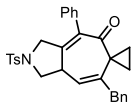
Run 1: Following general procedure, 35.1 mg **1j** was used, 48 h. After flash column chromatography on silica gel (eluted with PE/EA, 5:1), 25.9 mg **2j** was obtained in 68% yield.
Run 2: Following general procedure, 34.9 mg **1j** was used, 48 h. After flash column chromatography on silica gel (eluted with PE/EA, 5:1), 24.1 mg **2j** was obtained in 64% yield.
Average yield: 66%.
Colorless oil, TLC R_f = 0.26 (PE/EA, 5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 – 7.69 (m, 2H), 7.35 (d, *J* = 8.0 Hz, 2H), 5.70 (dd, *J* = 9.8, 3.3 Hz, 1H), 5.67 – 5.64 (m, 1H), 5.30 (dd, *J* = 9.8, 2.5 Hz, 1H), 3.85 – 3.80 (m, 2H), 3.75 – 3.68 (m, 1H), 3.65 (dd, *J* = 9.5, 8.4 Hz, 1H), 3.18 (dd, *J* = 9.5, 6.3

Hz, 1H), 2.44 (s, 3H), 1.77 (d, *J* = 1.3 Hz, 3H), 1.68 (ddd, *J* = 9.8, 6.8, 3.0 Hz, 1H), 1.57 (ddd, *J* = 9.8, 7.2, 2.6 Hz, 1H), 1.41 (d, *J* = 1.0 Hz, 3H), 1.03 (ddd, *J* = 9.3, 7.2, 3.0 Hz, 1H), 0.95 (ddd, *J* = 9.3, 6.8, 2.6 Hz, 1H). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 199.4, 152.9, 144.3, 137.9, 133.8, 133.6, 132.3, 132.0, 129.9, 128.2, 120.4, 54.1, 52.8, 40.9, 32.4, 25.5, 23.7, 22.2, 21.7, 20.2. HRMS (ESI): calcd. for $C_{22}H_{26}NO_3S$ ($[M+H]^+$): 384.1628, found 384.1629.



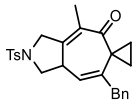
2k

Run 1: Following general procedure, 40.1 mg **1k** was used, 5 h. After flash column chromatography on silica gel (eluted with PE/EA, 5:1), 35.3 mg **2k** was obtained in 82% yield.
Run 2: Following general procedure, 39.9 mg **1k** was used, 5 h. After flash column chromatography on silica gel (eluted with PE/EA, 5:1), 37.0 mg **2k** was obtained in 86% yield.
Average yield: 84%.
White solid, m.p. = 193-194 °C, TLC R_f = 0.23 (PE/EA, 5:1). ^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.65 (d, *J* = 8.2 Hz, 2H), 7.43 – 7.26 (m, 5H), 7.09 – 6.94 (m, 2H), 5.34 (s, 1H), 4.00 – 3.94 (m, 1H), 3.88 (dd, *J* = 16.0, 2.0 Hz, 1H), 3.75 (dd, *J* = 10.2, 3.5 Hz, 1H), 3.48 (d, *J* = 16.0 Hz, 1H), 3.19 (dd, *J* = 10.2, 7.6 Hz, 1H), 2.45 (s, 3H), 1.91 (s, 3H), 1.82 – 1.74 (m, 1H), 1.38 – 1.30 (m, 1H), 1.05 – 0.97 (m, 2H). $^{13}C\{^{1}H\}$ NMR (101 MHz, CD_2Cl_2) δ 198.1, 155.7, 144.8, 143.0, 137.7, 134.7, 131.7, 130.2, 129.0, 128.6, 128.5, 128.4, 127.9, 52.6, 50.6, 44.3, 32.3, 22.9, 21.7, 21.0, 19.1. HRMS (ESI): calcd. for $C_{25}H_{26}NO_3S$ ($[M+H]^+$): 420.1628, found 420.1627.



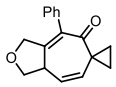
2l

Run 1: Following general procedure, 47.7 mg **1l** was used, 5 h. After flash column chromatography on silica gel (eluted with PE/EA, 5:1), 36.4 mg **2l** was obtained in 72% yield.
Run 2: Following general procedure, 47.0 mg **1l** was used, 5 h. After flash column chromatography on silica gel (eluted with PE/EA, 5:1), 33.8 mg **2l** was obtained in 68% yield.
Average yield: 70%.
White solid, m.p. = 79-80 °C, TLC R_f = 0.17 (PE/EA, 5:1). ^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.66 (d, *J* = 8.3 Hz, 2H), 7.39 (d, *J* = 8.3 Hz, 2H), 7.37 – 7.30 (m, 3H), 7.29 – 7.24 (m, 2H), 7.22 – 7.17 (m, 1H), 7.13 (d, *J* = 7.1 Hz, 2H), 6.92 – 6.82 (m, 2H), 5.84 (d, *J* = 4.0 Hz, 1H), 4.11 – 4.03 (m, 1H), 3.82 (dd, *J* = 16.5, 2.3 Hz, 1H), 3.73 (d, *J* = 16.5 Hz, 1H), 3.67 (dd, *J* = 10.1, 8.4 Hz, 1H), 3.37 (d, *J* = 15.2 Hz, 1H), 3.34 (dd, *J* = 10.1, 6.0 Hz, 1H), 3.24 (d, *J* = 15.2 Hz, 1H), 2.44 (s, 3H), 1.69 (ddd, *J* = 9.8, 7.0, 4.4 Hz, 1H), 1.17 (ddd, *J* = 9.3, 6.9, 4.4 Hz, 1H), 1.08 (ddd, *J* = 9.8, 6.9, 2.8 Hz, 1H), 1.03 (ddd, *J* = 9.3, 7.0, 2.8 Hz, 1H). $^{13}C\{^{1}H\}$ NMR (101 MHz, CD_2Cl_2) δ 194.7, 156.6, 144.8, 141.6, 139.2, 137.6, 134.9, 134.0, 132.2, 130.3, 129.1, 129.0, 128.8, 128.6, 128.4, 127.8, 126.8, 54.2, 53.4, 41.8, 41.6, 35.8, 21.7, 21.0, 13.5. HRMS (ESI): calcd. for $C_{31}H_{30}NO_3S$ ($[M+H]^+$): 496.1941, found 496.1940.



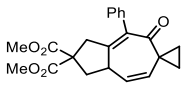
2m

Run 1: Following general procedure, 40.3 mg **1m** was used, 5 h. After flash column chromatography on silica gel (eluted with PE/EA, 10:1), 19.8 mg **2m** was obtained in 46% yield.
Run 2: Following general procedure, 38.4 mg **1m** was used, 5 h. After flash column chromatography on silica gel (eluted with PE/EA, 10:1), 20.1 mg **2m** was obtained in 49% yield.
Average yield: 48%.
White solid, m.p. = 68-69 °C, TLC R_f = 0.26 (PE/EA, 5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, *J* = 8.2 Hz, 2H), 7.37 (d, *J* = 8.2 Hz, 2H), 7.25 – 7.14 (m, 3H), 7.00 (d, *J* = 7.0 Hz, 2H), 5.58 (d, *J* = 3.6 Hz, 1H), 4.03 – 3.90 (m, 3H), 3.75 (dd, *J* = 9.7, 8.9 Hz, 1H), 3.26 (d, *J* = 15.8 Hz, 1H), 3.21 (d, *J* = 15.8 Hz, 1H), 3.11 (dd, *J* = 9.7, 7.8 Hz, 1H), 2.44 (s, 3H), 1.74 (ddd, *J* = 9.8, 6.9, 4.8 Hz, 1H), 1.64 (d, *J* = 1.4 Hz, 3H), 1.07 (ddd, *J* = 9.5, 6.7, 4.8 Hz, 1H), 0.94 (ddd, *J* = 9.8, 6.7, 3.1 Hz, 1H), 0.90 (ddd, *J* = 9.5, 6.9, 3.1 Hz, 1H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 194.6, 154.2, 144.4, 141.4, 138.6, 133.9, 132.0, 130.0, 128.8, 128.6, 128.4, 128.2, 126.5, 53.8, 52.8, 41.6, 41.4, 35.7, 21.7, 19.2, 15.0, 12.0. HRMS (ESI): calcd. for $C_{26}H_{28}NO_3S$ ([M+H]$^+$): 434.1784, found 434.1784.



2n

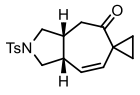
Run 1: Following general procedure, 22.6 mg **1n** was used, 5 h. After flash column chromatography on silica gel (eluted with PE/EA, 20:1), 14.6 mg **2n** was obtained in 57% yield.
Run 2: Following general procedure, 22.2 mg **1n** was used, 5 h. After flash column chromatography on silica gel (eluted with PE/EA, 20:1), 13.4 mg **2n** was obtained in 54% yield.
Average yield: 56%.
Colorless oil, TLC R_f = 0.41 (PE/EA, 5:1). ^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.36 – 7.31 (m, 2H), 7.30 – 7.25 (m, 1H), 7.15 – 7.01 (m, 2H), 5.88 (dd, *J* = 9.8, 3.2 Hz, 1H), 5.49 (dd, *J* = 9.8, 2.7 Hz, 1H), 4.32 (dd, *J* = 10.0, 8.0 Hz, 1H), 4.27 – 4.21 (m, 2H), 4.01 – 3.95 (m, 1H), 3.91 (dd, *J* = 8.4, 6.3 Hz, 1H), 1.76 – 1.69 (m, 1H), 1.64 – 1.59 (m, 1H), 1.11 – 1.05 (m, 2H). ^{13}C{^{1}H} NMR (101 MHz, CD_2Cl_2) δ 198.8, 158.7, 138.4, 134.1, 133.7, 133.4, 129.2, 128.5, 127.7, 75.0, 72.2, 43.1, 32.9, 22.4, 22.2. HRMS (ESI): calcd. for $C_{17}H_{17}O_2$ ([M+H]$^+$): 253.1223, found 253.1218.



2o

Run 1: Following general procedure, 36.0 mg **1o** was used, 48 h. After flash column chromatography on silica gel (eluted with PE/EA, 5:1), 20.2 mg **2o** was obtained in 52% yield.
Run 2: Following general procedure, 36.0 mg **1o** was used, 48 h. After flash column chromatography on silica gel (eluted with PE/EA, 5:1), 21.5 mg **2o** was obtained in 55% yield.
Average yield: 54%.
Colorless oil, TLC R_f = 0.46 (PE/EA, 5:1). ^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.37 – 7.32 (m, 2H), 7.30 – 7.25 (m, 1H), 7.17 – 7.04 (m, 2H), 5.83 (dd, *J* = 9.8, 3.4 Hz, 1H), 5.40 (dd, *J* = 9.8, 2.7 Hz, 1H), 3.96 – 3.89 (m, 1H), 3.70 (s, 3H), 3.69 (s, 3H), 2.99 (dd, *J* = 18.2, 2.7 Hz, 1H), 2.86 – 2.78 (m, 2H),

2.38 (dd, J = 13.2, 7.8 Hz, 1H), 1.71 – 1.65 (m, 1H), 1.60 – 1.56 (m, 1H), 1.07 – 1.00 (m, 2H). $^{13}C\{^1H\}$ NMR (101 MHz, CD_2Cl_2) δ 198.9, 171.5, 171.4, 159.5, 139.4, 136.4, 136.1, 133.3, 129.5, 128.5, 127.3, 59.3, 53.2, 53.1, 42.2, 41.4, 40.7, 32.8, 22.5, 22.3. HRMS(ESI): calcd. for $C_{22}H_{23}O_5$ ($[M+H]^+$): 367.1540, found: 367.1539.

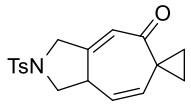


2p

Run 1: Following general procedure, 30.4 mg **1p** was used, 80 °C, 15 h. After flash column chromatography on silica gel (eluted with PE/EA, 5:1), 14.0 mg **2p** was obtained in 42% yield.
Run 2: Following general procedure, 30.1 mg **1p** was used, 80 °C, 15 h. After flash column chromatography on silica gel (eluted with PE/EA, 5:1), 14.4 mg **2p** was obtained in 44% yield.
Average yield: 43%.

Gram scale:
Run 1: Following general procedure, 1.06 g **1p** was used, 80 °C, 17 h. After flash column chromatography on silica gel (eluted with PE/EA, 5:1), 501.7 mg **2p** was obtained in 43% yield.
Run 2: Following general procedure, 1.06 g **1p** was used, 80 °C, 17 h. After flash column chromatography on silica gel (eluted with PE/EA, 5:1), 532.6 mg **2p** was obtained in 46% yield.
Average yield: 45%.

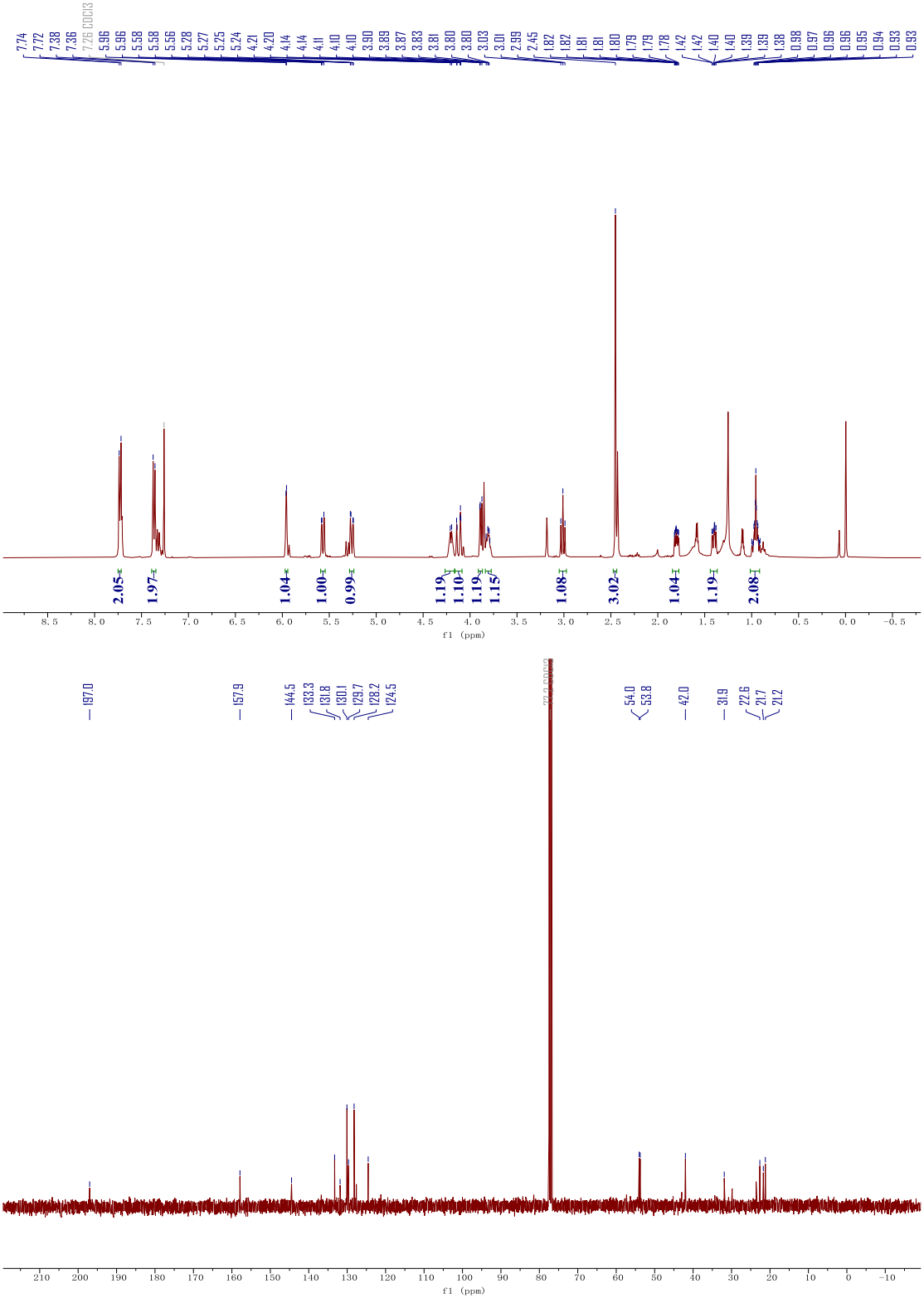
Light yellow solid, m.p. = 128-129 °C, TLC R_f = 0.10 (PE/EA, 5:1). ^1H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, J = 8.1 Hz, 2H), 7.33 (d, J = 8.1 Hz, 2H), 5.45 (dd, J = 10.9, 4.7 Hz, 1H), 5.29 (dd, J = 10.9, 2.2 Hz, 1H), 3.54 (dd, J = 10.0, 7.5 Hz, 1H), 3.46 (dd, J = 10.0, 6.9 Hz, 1H), 3.25 (dd, J = 10.0, 4.8 Hz, 1H), 3.07 – 3.02 (m, 1H), 2.99 (dd, J = 10.0, 7.6 Hz, 1H), 2.73 (dd, J = 11.5, 11.5 Hz, 1H), 2.56 – 2.47 (m, 1H), 2.44 (s, 3H), 2.34 (dd, J = 11.5, 4.5 Hz, 1H), 1.68 (ddd, J = 10.1, 7.2, 3.2 Hz, 1H), 1.33 (ddd, J = 10.1, 7.3, 3.1 Hz, 1H), 0.95 (ddd, J = 9.2, 7.3, 3.2 Hz, 1H), 0.87 (ddd, J = 9.2, 7.2, 3.1 Hz, 1H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 208.9, 143.8, 133.7, 133.5, 129.9, 129.8, 127.7, 53.8, 53.3, 43.7, 40.5, 40.4, 31.4, 24.1, 21.7, 20.7. HRMS (ESI): calcd. for $C_{18}H_{22}NO_3S$ ($[M+H]^+$): 332.1315, found 332.1307.

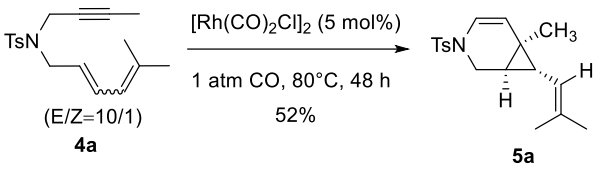


2q

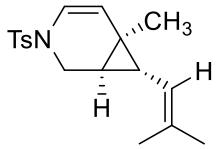
Following general procedure, 30.1 mg **1q** was used, 40 °C, 16 h. A series of unidentified products together with **2q**, which was also contaminated by inseparable impurities, can be seen from TLC. After flash column chromatography on silica gel (eluted with PE/EA, 5:1), 3.8 mg mixture was obtained, which consists of **2q** (<12% yield) and some impurities from substrate decomposition. The following peaks selected from this mixture can be used to judge that [4+2+1] cycloadduct **2q** was generated. ^1H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, J = 8.1 Hz, 2H), 7.37 (d, J = 8.1 Hz, 2H), 5.99 – 5.93 (m, 1H), 5.57 (dd, J = 10.5, 2.4 Hz, 1H), 5.26 (dd, J = 10.5, 2.7 Hz, 1H), 4.27 – 4.16 (m, 1H), 4.17 – 4.08 (m, 1H), 3.92 – 3.85 (m, 1H), 3.85 – 3.77 (m, 1H), 3.01 (dd, J = 8.8, 8.8 Hz, 1H), 2.45 (s, 3H), 1.80 (ddd, J = 9.6, 5.8, 2.3 Hz, 1H), 1.45 – 1.36 (m, 1H), 1.02 – 0.90 (m, 2H). ^{13}C NMR (101 MHz,

$CDCl_3$) δ 197.0, 157.9, 144.5, 133.3, 131.8, 130.1, 129.7, 128.2, 124.5, 54.0, 53.8, 42.0, 31.9, 22.6, 21.7, 21.2. HRMS (ESI): calcd. for $C_{18}H_{20}NO_3S$ ($[M+H]^+$): 330.1158, found 332.1174.



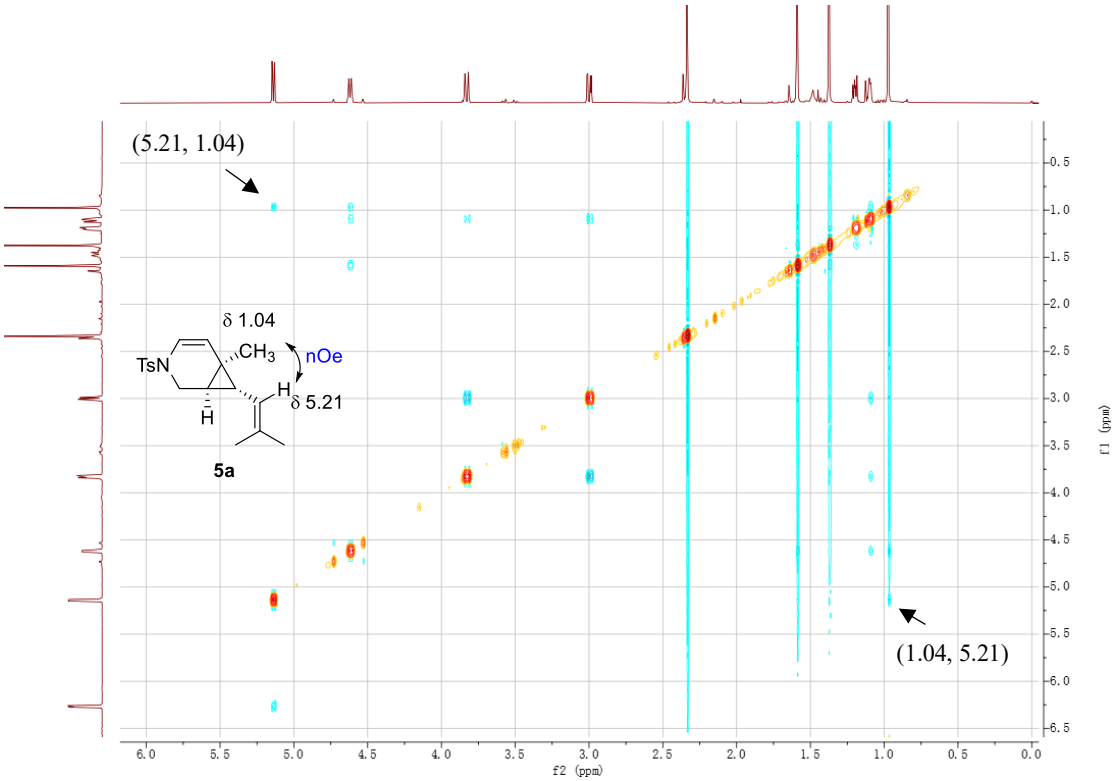


Run 1: Following general procedure, 31.0 mg **4a** was used, 80 °C, 48 h. After flash column chromatography on silica gel (eluted with PE/EA, 20:1), 15.6 mg **5a** was obtained in 50% yield.
Run 2: Following general procedure, 31.0 mg **4a** was used, 80 °C, 48 h. After flash column chromatography on silica gel (eluted with PE/EA, 20:1), 16.4 mg **5a** was obtained in 53% yield.
Average yield: 52%.

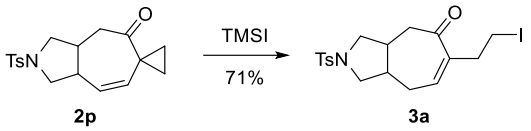


5a

Colorless oil, TLC R_f = 0.80 (PE/EA, 5:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.66 (d, J = 8.2 Hz, 2H), 7.30 (d, J = 8.2 Hz, 2H), 6.33 (dd, J = 8.1, 1.0 Hz, 1H), 5.21 (dd, J = 8.2, 1.0 Hz, 1H), 4.69 (ddd, J = 8.5, 1.4, 1,4 Hz, 1H), 3.90 (d, J = 11.6 Hz, 1H), 3.06 (dd, J = 11.6, 2.8 Hz, 1H), 2.41 (s, 3H), 1.66 (s, 3H), 1.44 (s, 3H), 1.29 – 1.24 (m, 1H), 1.19 – 1.15 (m, 1H), 1.04 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 143.7, 135.2, 134.8, 129.9, 127.2, 121.7, 120.0, 117.4, 40.3, 33.3, 31.0, 25.7, 21.6, 19.2, 18.6, 18.4.
HRMS (ESI): calcd. for $C_{18}H_{24}NO_2S$ ($[M+H]^+$): 318.1522, found 318.1524.
The relative configuration of **5a** was proposed by nuclear Overhauser effect spectroscopy (NOESY):

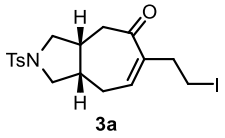


IV. Further Transformations of [4+2+1] Adduct



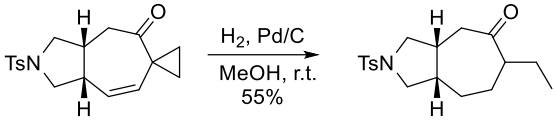
2p **3a**

To a stirred solution of **2p** (16.6 mg, 0.05 mmol) in CCl_4/DCM (0.5 mL/0.2 mL) was added TMSI (12.0 mg, 8.6 μL) slowly at -20 °C. After stirring for 1 h, the reaction mixture was warmed to room temperature. The reaction was monitored by TLC and stirred for another 1 h. The solution was diluted with ether and washed with saturated $NaSO_3$ solution. The organic phase was removed and dried, filtered, concentrated, purified by flash column chromatography on silica gel (eluted with PE/EA, 4:1) to afford **3a** as yellow solid. Run 1: **3a** (15.8 mg, 69%); Run 2: **3a** (16.7 mg, 73%). Average yield: 71%.



3a

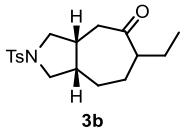
Yellow solid, m.p. = 62-65 °C, TLC R_f = 0.33 (PE/EA, 2:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, J = 8.0 Hz, 2H), 7.34 (d, J = 8.0 Hz, 2H), 6.59 (dd, J = 8.5, 5.0 Hz, 1H), 3.55 – 3.42 (m, 2H), 3.27 – 3.15 (m, 2H), 2.85 (dd, J = 10.1, 5.3 Hz, 1H), 2.80 (dd, J = 10.1, 6.6 Hz, 1H), 2.70 – 2.62 (m, 2H), 2.62 – 2.47 (m, 4H), 2.45 (s, 3H), 2.43 – 2.31 (m, 2H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 199.5, 144.3, 144.1, 142.4, 132.4, 129.9, 128.0, 54.0, 53.5, 45.5, 40.9, 36.8, 36.4, 30.5, 21.7, 6.6. HRMS (ESI): calcd. for $C_{18}H_{23}INO_3S$ ([M+H]$^+$): 460.0438, found 460.0433.



2p **3b**

To a solution of **2p** (10.0 mg, 0.03 mmol) in MeOH (0.6 mL) was added Pd/C (32.0 mg, 10% on dry basis, 0.03 mmol) and bubbled by H_2 (1 atm) for 10 min. The reaction mixture was stirred at room temperature under balloon pressure gas of H_2 (1 atm) for 24 h. The mixture was filtered through silica gel by washing with EA, then concentrated, and purified by column chromatography (PE/EA = 5:1) to give the product **3b** as a colorless oil. Run 1:**3b** (5.4 mg, 53%); Run 2: **3b** (5.7 mg, 56%).

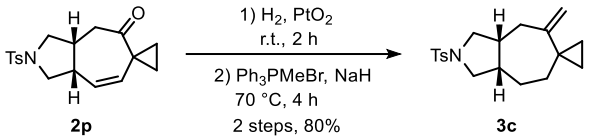
Average yield: 55%



3b

Colorless oil, TLC R_f = 0.10 (PE/EA, 5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, J = 8.1 Hz, 2H), 7.33 (d, J = 8.1 Hz, 2H), 3.42 (ddd, J = 13.8, 10.0, 7.3 Hz, 2H), 2.99 – 2.90 (m, 2H), 2.52 – 2.44 (m, 1H), 2.43 (s, 3H), 2.41 – 2.28 (m, 3H), 2.11 (dd, J = 13.8, 3.6 Hz, 1H), 1.80 – 1.67 (m, 1H), 1.66 – 1.39 (m, 4H), 1.33 – 1.26 (m, 1H), 0.82 (t, J = 7.4 Hz, 3H). ^{13}C{^{1}H} (101 MHz, $CDCl_3$) δ 213.1,

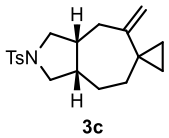
143.8, 133.0, 129.8, 127.8, 54.4, 53.2, 51.7, 42.2, 40.3, 37.6, 26.3, 25.5, 24.9, 21.7, 11.8. HRMS (ESI): calcd. for $C_{18}H_{26}NO_3S$ ($[M+H]^+$): 332.1628, found 332.1626.



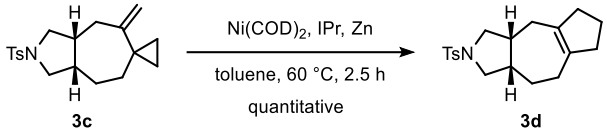
To a stirred solution of **2p** (39.2 mg, 0.1 mmol) in MeOH (2 mL) was added PtO_2 (4.6 mg, 20 μmol), then the reaction mixture was evacuated and refilled with H_2 (1 atm), and stirred at room temperature under the atmosphere pressure of H_2. The reaction was monitored by TLC and stirred for 2 h. Upon completion, the reaction mixture was purified by TLC to yield the hydrogenation product, and directly used for the next step.

Under nitrogen, to a mixture of NaH (60% dispersion in mineral oil, 19.0 mg, 0.45 mmol) and Ph_3PMeBr (142.5 mg, 0.4 mmol) was added dry THF (1.6 mL), and stirred at 70 °C for 4 hours. The reaction mixture was then added a solution of the hydrogenation product in dry THF (0.5 mL) and 2-methyl-2-butanol (0.1 mL). The reaction was monitored by TLC, and stirred at the same temperature for 4 h. Upon completion, the reaction mixture was purified by TLC to yield **3c**. Run 1: **3c** (30.2 mg, 77%); Run 2: **3c** (32.1 mg, 82%).

Average yield: 80%



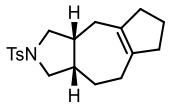
White solid, m.p. = 94-95 °C, TLC R_f = 0.46 (PE/EA, 5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, J = 7.8 Hz, 2H), 7.33 (d, J = 7.8 Hz, 2H), 4.60 (s, 1H), 4.59 (s, 1H), 3.51 – 3.43 (m, 2H), 2.84 – 2.74 (m, 2H), 2.44 (s, 3H), 2.37 – 2.30 (m, 1H), 2.29 – 2.22 (m, 2H), 2.17 – 2.06 (m, 1H), 1.65 – 1.56 (m, 1H), 1.54 – 1.40 (m, 2H), 1.15 – 1.04 (m, 1H), 0.78 – 0.72 (m, 1H), 0.49 – 0.42 (m, 1H), 0.41 – 0.30 (m, 2H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 151.6, 143.5, 133.2, 129.7, 127.9, 109.6, 54.7, 53.6, 42.0, 41.6, 37.3, 37.0, 28.4, 26.9, 21.7, 15.4, 15.2. HRMS (ESI): calcd. for $C_{19}H_{26}NO_2S$ ($[M+H]^+$): 332.1679, found 332.1681.



In a glovebox, dry, degassed toluene (0.5 mL) was added to a flame-dried glassware containing $Ni(COD)_2$ (27.5 mg, 0.1 mmol), IPr (79.6 mg, 0.2 mmol) and Zn (6.5 mg, 0.1 mmol). The resulting solution was stirred under room temperature for 4 h to give $Ni(IPr)_2$.

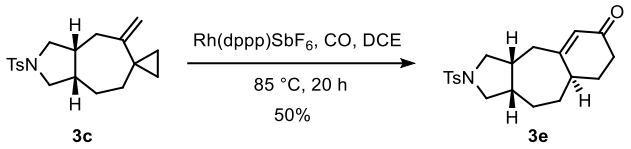
Under nitrogen, to a solution of **3c** (19.4 mg, 0.06 mmol) in dry, degassed toluene (0.3 mL) was added the prepared solution of $Ni(IPr)_2$ (0.06 mL, 20 mol%). The reaction mixture was then heated to 60 °C. The reaction was monitored by TLC, and stirred at the same temperature for 2.5 h. Upon completion, the reaction mixture was purified by TLC to yield **3d**. Run 1: **3d** (20.4 mg, >99%); Run 2: **3d** (19.4 mg, 100%)

Average yield: quantitative.



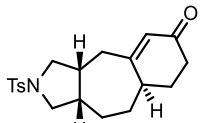
3d

White solid, m.p. = 83-84 °C, TLC R_f = 0.48 (PE/EA, 5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, *J* = 8.0 Hz, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 3.47 (ddd, *J* = 17.7, 9.8, 7.6 Hz, 2H), 2.78 (dd, *J* = 9.8, 4.4 Hz, 1H), 2.72 (t, *J* = 9.8 Hz, 1H), 2.53 – 2.45 (m, 1H), 2.43 (s, 3H), 2.38 – 2.30 (m, 1H), 2.29 – 2.19 (m, 3H), 2.18 – 2.06 (m, 2H), 2.06 – 1.98 (m, 2H), 1.76 – 1.66 (m, 4H), 1.61 – 1.50 (m, 1H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 143.5, 136.7, 134.0, 133.1, 129.7, 127.9, 55.0, 53.5, 41.7, 41.0, 39.7, 39.0, 29.5, 28.3, 27.1, 22.2, 21.7. HRMS (ESI): calcd. for $C_{19}H_{26}NO_2S$ ([M+H]$^+$): 332.1679, found 332.1681.



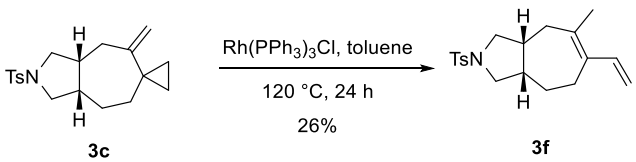
3c **3e**

In a glovebox, dry DCE (0.9 mL) was added to a flame-dried glassware containing $[Rh(CO)_2Cl]_2$ (1.8 mg, 4.5 μmol), $AgSbF_6$ (3.7 mg, 11 μmol), and dppp (4.5 mg, 11 μmol). The resulting mixture was then stirred at room temperature for 10 min to give the Rh^+ catalyst (0.01 M, 10 mol%).
Under nitrogen, to a solution of **3c** (29.1 mg, 0.1 mmol) and 4 Å MS (52.8 mg) in dry DCE (0.9 mL) was added the prepared solution of the Rh^+ catalyst. The reaction mixture was then bubbled with a mixture of CO (0.2 atm) and N_2 (0.8 atm) for 10 min and heated to 85 °C. The reaction was monitored by TLC, and stirred at the same temperature under CO (0.2 atm) for 22.5 h. Upon completion, the reaction mixture was purified by TLC to yield **3e**. Run 1: **3e** (16.2 mg, 51%); Run 2: **3e** (15.6 mg, 49%).
Average yield: 50%.



3e

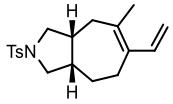
White solid, m.p. = 124-125 °C, TLC R_f = 0.45 (PE/EA, 1:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 8.1 Hz, 2H), 7.33 (d, *J* = 8.1 Hz, 2H), 5.80 (s, 1H), 3.44 (ddd, *J* = 22.9, 10.0, 7.2 Hz, 2H), 2.89 (ddd, *J* = 17.2, 10.0, 5.9 Hz, 2H), 2.44 (s, 3H), 2.40 – 2.29 (m, 4H), 2.27 – 2.13 (m, 3H), 2.11 – 2.03 (m, 2H), 1.92 (ddd, *J* = 13.3, 7.7, 5.2 Hz, 1H), 1.85 – 1.73 (m, 1H), 1.69 – 1.59 (m, 1H), 1.54 – 1.40 (m, 2H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 199.6, 166.3, 143.8, 133.0, 129.8, 127.9, 127.2, 54.6, 53.5, 41.7, 41.3, 41.1, 38.1, 34.9, 30.5, 29.3, 27.0, 21.7. HRMS (ESI): calcd. for $C_{20}H_{26}NO_3S$ ([M+H]$^+$): 360.1628, found 360.1627.



3c **3f**

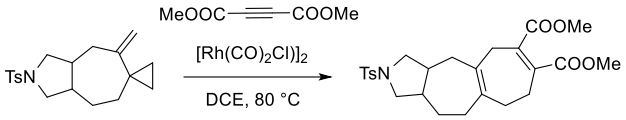
Under Ar, 2 mL toluene was added to a flame-dried glassware containing **3c** (33.2 mg, 0.1 mmol)

and $Rh(PPh_3)_3Cl$ (4.4 mg, 0.005 mmol). The reaction mixture was stirred at 120 °C for 24 h. The mixture was concentrated, and purified by TLC to give the product **3f**. Run 1: **3f** (8.0 mg, 24%); Run 2: **3f** (9.1 mg, 27%).
Average yield: 26%



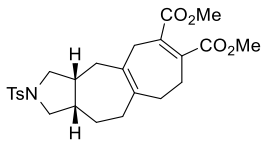
3f

White solid, m.p. = 200-201 °C, TLC R_f = 0.12 (PE/EA, 5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 8.0 Hz, 2H), 7.30 (d, *J* = 8.0 Hz, 2H), 6.65 (dd, *J* = 17.3, 11.0 Hz, 1H), 5.04 (d, *J* = 17.3 Hz, 1H), 4.94 (d, *J* = 11.0 Hz, 1H), 3.33 (ddd, *J* = 9.2, 6.8, 2.0 Hz, 2H), 3.09 (dd, *J* = 9.8, 6.5 Hz, 1H), 2.99 (dd, *J* = 9.8, 5.5 Hz, 1H), 2.41 (s, 3H), 2.32 – 2.21 (m, 3H), 2.19 – 2.09 (m, 2H), 2.06 – 1.97 (m, 1H), 1.76 (s, 3H), 1.53 – 1.43 (m, 1H), 1.27 – 1.19 (m, 1H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 143.4, 134.9, 134.6, 134.2, 134.0, 129.7, 127.6, 111.1, 53.0, 52.3, 41.5, 38.1, 35.9, 25.7, 23.8, 21.6, 21.1. HRMS (ESI): calcd. for $C_{19}H_{26}NO_2S$ ($[M+H]^+$): 332.1679, found 332.1681.



3c **3g**

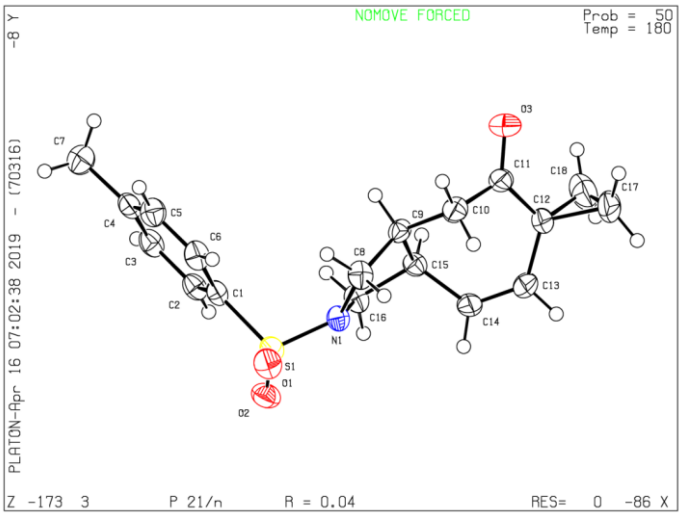
Under Ar, 1 mL DCE and dimethyl acetylenedicarboxylate (7.1 mg, 0.05 mmol) were added to a flame-dried glassware containing **3c** (16.6 mg, 0.05 mmol) and $[Rh(CO)_2Cl]_2$ (1.0 mg, 2.5 μmol) at room temperature. The glassware was immersed into an oil bath at 80 ºC. The reaction was monitored by TLC and stirred for 5 h. Upon completion, the reaction mixture was concentrated and purified by flash column chromatography on silica gel to afford **3g** as colorless oil. Run 1: **3g** (11.5 mg, 49%); Run 2: **3g** (11.1 mg, 47%).
Average yield: 48%.

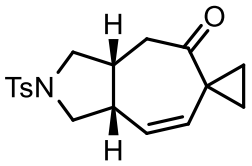


3g

Colorless oil, TLC R_f = 0.06 (PE/EA, 5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 8.2 Hz, 2H), 7.32 (d, *J* = 8.2 Hz, 2H), 3.77 (s, 3H), 3.75 (s, 3H), 3.42 – 3.34 (m, 2H), 3.16 (d, *J* = 17.1 Hz, 1H), 2.99 – 2.88 (m, 3H), 2.55 – 2.46 (m, 2H), 2.44 (s, 3H), 2.37 – 2.29 (m, 2H), 2.27 – 2.16 (m, 3H), 2.08 – 1.93 (m, 3H), 1.54 – 1.46 (m, 1H), 1.24 – 1.17 (m, 1H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 169.0, 143.3, 137.9, 137.8, 136.5, 133.6, 130.1, 129.6, 127.6, 53.3, 52.8, 52.4, 52.2, 41.4, 39.2, 36.9, 35.6, 32.7, 31.9, 27.4, 26.1, 21.5. HRMS (ESI): calcd. for $C_{25}H_{32}NO_6S$ ($[M+H]^+$): 474.1945, found 474.1945.

V. X-ray Crystal Analysis





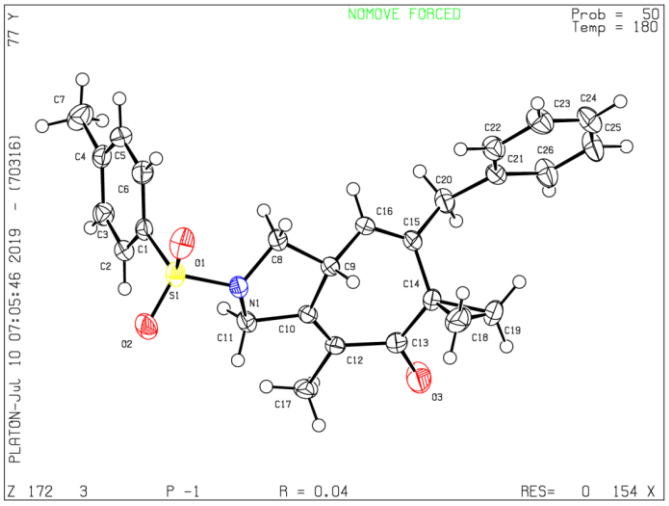
2p

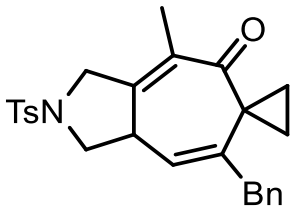
Ellipsoids are drawn at 50% probability

CCDC number: 2201275

Crystal data	
Chemical formula	$C_{18}H_{21}NO_3S$
M_r	331.42
Crystal system, space group	Monoclinic, $P2_1/n$
Temperature (K)	180
a, b, c (Å)	15.3948 (5), 5.9225 (2), 19.4092 (6)
β (°)	111.289 (4)
V (Å^3)	1648.89 (10)
Z	4
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.21
Crystal size (mm)	0.24 × 0.12 × 0.10
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.037, 0.106, 1.03
No. of reflections	3776
No. of parameters	209
H-atom treatment	H-atom parameters constrained

$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.33, −0.32



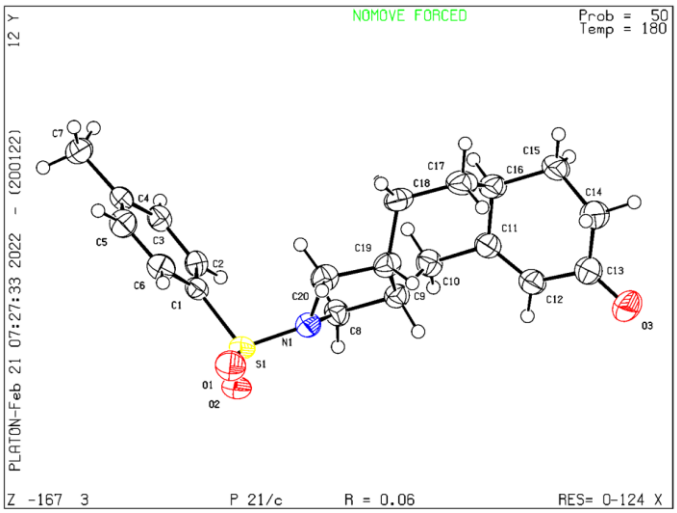


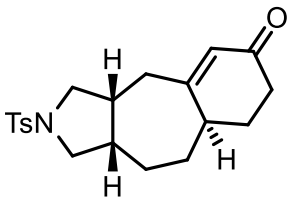
2m

Ellipsoids are drawn at 50% probability **CCDC number: 2201276**

Crystal data	
Chemical formula	$C_{26}H_{27}NO_3S$
M_r	433.54
Crystal system, space group	Triclinic, $P\bar{1}$
Temperature (K)	180
a, b, c (Å)	5.7108 (2), 11.2232 (4), 17.6058 (5)
α, β, γ (°)	99.264 (2), 91.591 (2), 98.733 (3)
V (Å^3)	1099.21 (6)
Z	2
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.18
Crystal size (mm)	0.45 × 0.15 × 0.05
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.042, 0.115, 1.01
No. of reflections	5044
No. of parameters	282
H-atom treatment	H-atom parameters constrained

$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.39, −0.40





3e

Ellipsoids are drawn at 50% probability **CCDC number: 2201274**

Crystal data

Chemical formula	$C_{20}H_{25}NO_3S$
M_r	359.47
Crystal system, space group	Monoclinic, $P2_1/c$
Temperature (K)	180
a, b, c (Å)	21.1372 (13), 7.1928 (3), 12.3409 (7)
β (°)	103.966 (6)
V (Å^3)	1820.79 (18)
Z	4
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.20
Crystal size (mm)	0.21 × 0.08 × 0.03

Refinement

$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.061, 0.177, 1.06
No. of reflections	4694
No. of parameters	227
H-atom treatment	H-atom parameters constrained

$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.42, −0.29

VI. DFT Calculations

All possible reaction paths of [4+2+1] reactions and [2+2+1] reactions are calculated (Figure S1). The different configurations of the key transition states are also considered. The competing transition states with Cl/CO exchanging of their coordination positions, namely **TS4-LE** and **TS5-CO-LE** are disfavored and can be excluded for consideration. Other transition states such as **TS5-CO-B** and **TS5-B** are also disfavored. We conclude that **TS4** is the most favored transition state for cyclopropyl-capped diene-yne substrate, while **TS5-CO-d** is the most favored transition state of yne−diene substrate, indicating [4+2+1] cycloaddition is favored in our system, but [2+2+1] cycloaddition is favored in yne−diene system.

[2+2+1] reaction could start from **IN1** and **IN3**, but both two process are disfavored (Figure S2): the cyclometallation via **TS1b** has higher free energy than **TS1** by 12.5 kcal/mol while **TS1c** is higher than **TS1** by 18.5 kcal/mol, the energy difference is probably attributed to the absence of coordination effect of the MCP part in **TS1b** and **TS1c**.

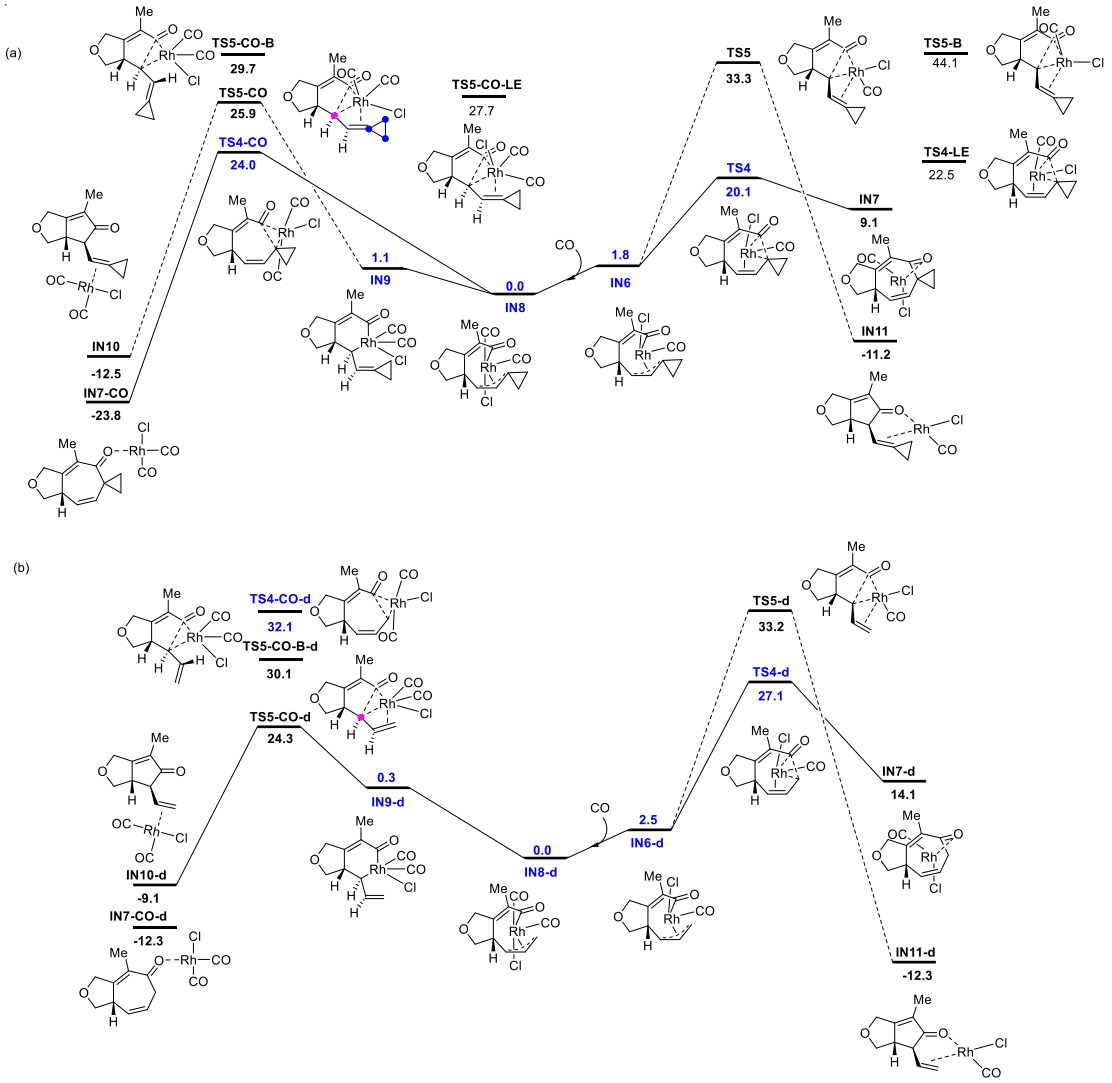


Figure S1. All possible reaction paths of [4+2+1] reactions and [2+2+1] reactions: (a) CP-capped diene-yne substrate. (b) yne−diene substrate. Computed at DLPNO-CCSD(T)-SMD(PhMe)//BMK/def2-SVP level.

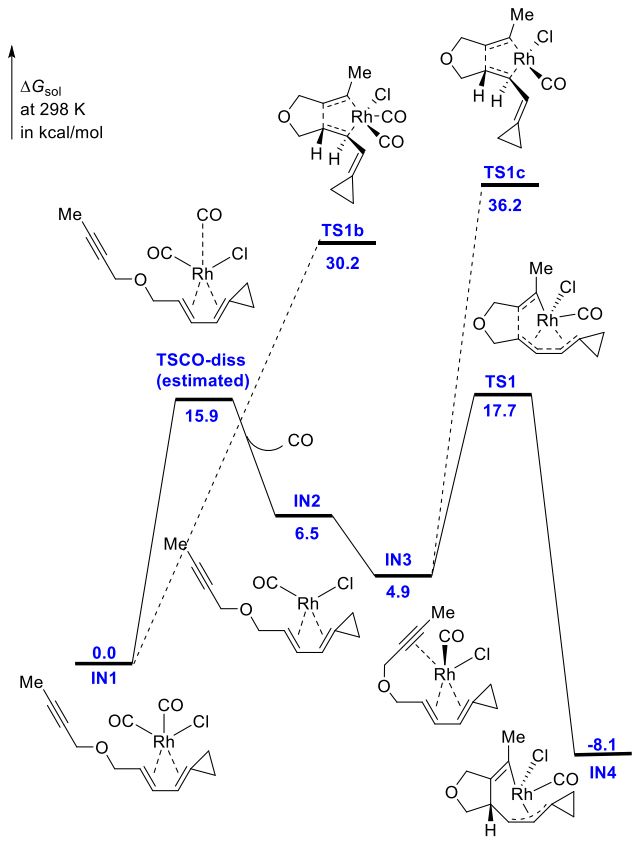


Figure S2. Other [2+2+1] pathways via TS1b and TS1c.

We have also studied whether the preference of [4+2+1] over [2+2+1] cycloaddition is possible or not for dimethyl diene-yne, if this substrate could undergo CO insertion process (experimentally, cyclopropanation is favored, see the experimental part). The computational results below (Figure S2) show that [2+2+1] is favored over [4+2+1] cycloaddition by 5.5 kcal/mol. Therefore, we can conclude the electronic effects brought by two methyl groups in the substrates cannot overturn the intrinsic preference of [2+2+1] over [4+2+1] cycloaddition (there are other possible approaches to give both [4+2+1] and [2+2+1] products, as those shown in the main text. These pathways were expected to be disfavored too and were not computed).

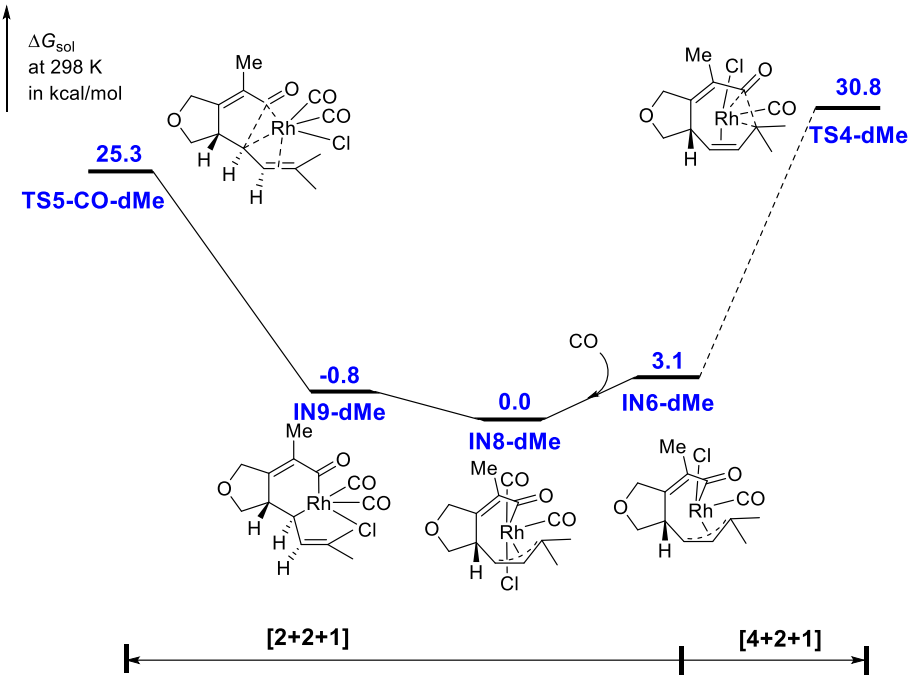


Figure S3. The competition of [4+2+1] and [2+2+1] cycloadditions for CO and dimethyl diene-yne. Computed at DLPNO-CCSD(T)-SMD(PhMe)//BMK/def2-SVP level.

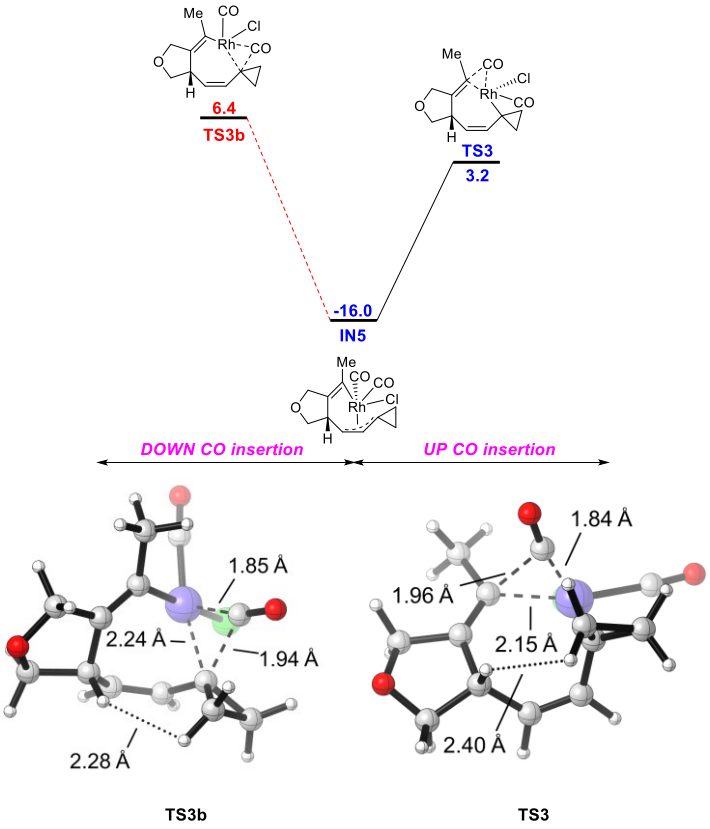
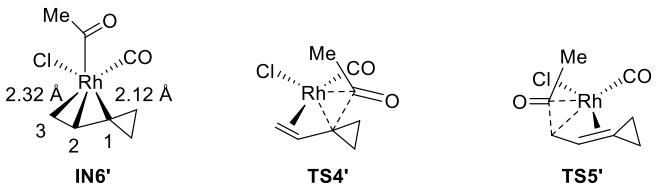
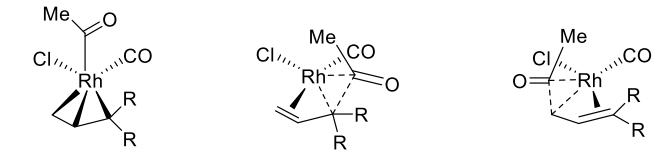


Figure S4. Comparison of the two CO insertion pathways (UP CO insertion vs. DOWN CO insertion).





R=H	0.0	23.6	24.7
R=Me	0.0	27.2	23.4
R=OMe	0.0	34.8	23.6
R=NMe_2	0.0	45.4	25.0

Figure S5. The Gibbs energies of model reactants with different substituents in the reductive elimination steps. Computed at BMK/def2-SVP in the gas phase.

We have studied several model reactants with different substituents in the reductive elimination steps shown in **Figure S5**. The different ligands Cl and CO at *trans*-positions have small effects on the regiochemistry of reductive elimination (23.6 kcal/mol vs. 24.7 kcal/mol). The reductive elimination at C1 with CP is favored over that at C3 by 6.4 kcal/mol due to the strain release, which is consistent with the real [4+2+1] reaction. Besides, the reductive elimination at C1 with electron-donating groups require higher activation free energies (27.2 kcal/mol for R=Me, 34.8 kcal/mol for R=OMe and 45.4 kcal/mol for R=NMe_2) probably due to the steric hinderance around the rhodium center, while the reductive elimination at C3 requires similar activation free energies (23.4 - 25.0 kcal/mol).

We have also considered that CO and Cl could exchange their positions to form **IN6-LE**, which then undergoes reductive elimination **(Figure S6)**. This is not favored and can be ruled out for considerations.

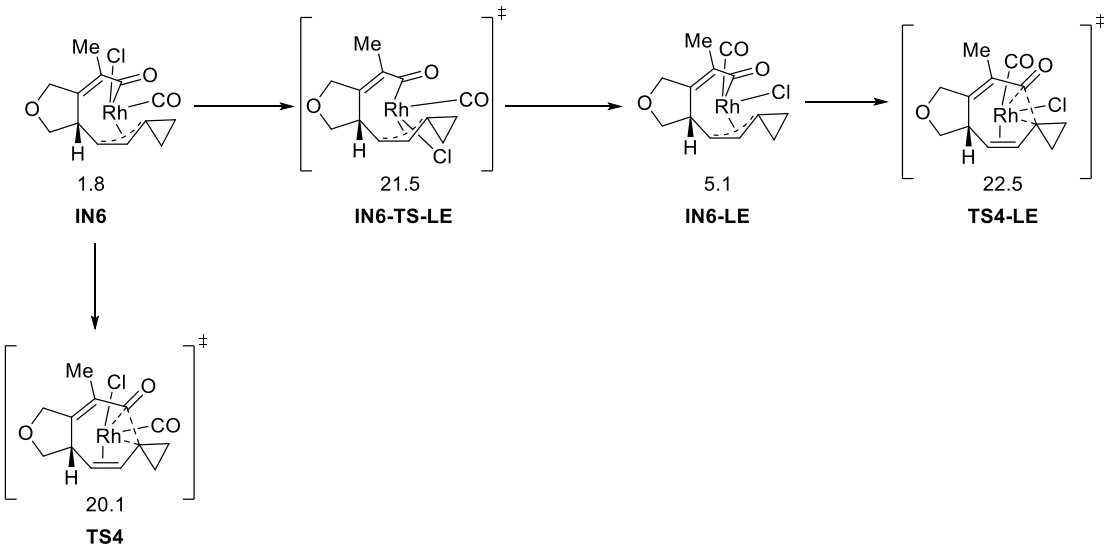


Figure S6. The Gibbs free energy profile of ligand exchange of Cl and CO, computed at DLPNO-

CCSD(T)-SMD(PhMe)/def2-TZVPP//BMK/def2-SVP level.

Table S2. Computed Energies of the Stationary Points.

Entry	SPE[a]	TCG[a]	G[a]	SPE[b]	SPE[c]
CO	-113.172745	-0.01386	-113.186605	-113.168349	-113.158173
IN1	-1298.38407	0.1865	-1298.19757	-1298.40163	-1298.3356
IN2	-1185.18206	0.181871	-1185.00019	-1185.20063	-1185.1503
IN3	-1185.1915	0.18627	-1185.00523	-1185.20844	-1185.15888
IN4	-1185.21766	0.189061	-1185.0286	-1185.23784	-1185.17925
IN5	-1298.4221	0.194477	-1298.22762	-1298.43756	-1298.37113
IN6	-1298.42792	0.196023	-1298.2319	-1298.44872	-1298.36727
IN7-CO	-1411.67475	0.202999	-1411.47175	-1411.68916	-1411.59064
IN8	-1411.62564	0.202364	-1411.42327	-1411.64284	-1411.54935
IN9	-1411.61864	0.199963	-1411.41868	-1411.6377	-1411.54337
IN10	-1411.64507	0.200617	-1411.44445	-1411.66383	-1411.56589
IN7	-1298.43094	0.197889	-1298.23305	-1298.4491	-1298.36
TS1	-1185.17296	0.187787	-1184.98517	-1185.1903	-1185.13969
TS1b	-1298.340152	0.188937	-1298.151215	-1298.357846	-1298.28973
TS1c	-1185.141516	0.183126	-1184.958390	-1185.160382	-1185.10395
TS2	-1185.19021	0.189254	-1185.00096	-1185.20895	-1185.1534
TS3	-1298.3917	0.195049	-1298.19665	-1298.4098	-1298.33845
TS3b	-1298.388889	0.196586	-1298.192303	-1298.40745	-1298.334454
TS4	-1298.40422	0.197189	-1298.20703	-1298.42315	-1298.34116
TS4-LE	-1298.39296	0.196307	-1298.196651	-1298.41202	-1298.33606
TS5-B	-1298.37451	0.196224	-1298.178286	-1298.39242	-1298.30264
TS5-CO	-1411.58086	0.200967	-1411.3799	-1411.60018	-1411.50457
TS5-CO-B	-1411.576479	0.200295	-1411.376184	-1411.594939	-1411.498814
TS5-CO-LE	-1411.57709	0.201306	-1411.375788	-1411.59333	-1411.50505
P	-615.216259	0.196938	-615.01932	-615.230446	-615.024243
S	-501.921826	0.175952	-501.745874	-501.936928	-501.762518
IN6-d	-1221.16625	0.166009	-1221.00024	-1221.18501	-1221.13477
IN7-d	-1334.39382	0.172848	-1334.22097	-1334.40856	-1334.33844
IN8-d	-1334.36489	0.172358	-1334.19253	-1334.37995	-1334.31802
IN9-d	-1334.35829	0.170215	-1334.18807	-1334.37431	-1334.31439
IN10-d	-1334.38594	0.170697	-1334.21525	-1334.40213	-1334.3363
IN7-CO-d	-1221.16107	0.166837	-1220.99424	-1221.17781	-1221.1189
TS4-d	-1221.13359	0.166744	-1220.96685	-1221.15225	-1221.09629
TS5-CO-d	-1334.32205	0.171881	-1334.15017	-1334.33836	-1334.2776
TS5-CO-d-B	-1334.312410	0.170301	-1334.142109	-1334.328404	-1334.266999
IN11	-1298.46145	0.197825	-1298.26363	-1298.48325	-1298.38861
TS4-CO	-1411.58905	0.203725	-1411.38532	-1411.60696	-1411.51182
TS5	-1298.37761	0.196052	-1298.18156	-1298.39672	-1298.31879
TS4-CO-d	-1334.31525	0.171131	-1334.14412	-1334.33229	-1334.26366

IN11-d	-1221.19635	0.167574	-1221.02877	-1221.2158	-1221.1541
TS5-d	-1221.11664	0.165556	-1220.95108	-1221.13329	-1221.08743
IN6-dMe	-1299.673171	0.220074	-1299.453097	-1299.693383	-1299.618191
IN8-dMe	-1412.87457	0.227315	-1412.647254	-1412.890522	-1412.803938
IN9-dMe	-1412.868134	0.223907	-1412.644226	-1412.886052	-1412.799854
TS4-dMe	-1299.636298	0.221239	-1299.41506	-1299.654436	-1299.577349
TS5-CO-dMe	-1412.828405	0.224268	-1412.604137	-1412.846002	-1412.758882
IN11'	-615.197316	0.191965	-615.005351	-615.213945	-615.0026167
IN11-d'	-537.937083	0.162176	-537.774907	-537.94987	-537.7757368
INT-TS-LE	-1298.396319	0.195167	-1298.201152	-1298.416174	-1298.336005
IN6-LE	-1298.423019	0.195984	-1298.227035	-1298.442923	-1298.362884

[a]Computed at the BMK/def2-SVP level.

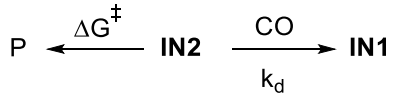
[b]Computed at the SMD(PhMe)/BMK/def2-SVP//BMK/def2-SVP level.

[c]Computed at the DLPNO-CCSD(T)/def2-TZVPP//BMK/def2-SVP level. We used 7.4 mM [14] as the concentration of CO and 1.0 M for other species:

$$\Delta G_{\text{std}} = -RT\ln\left(\frac{V_1}{V_2}\right) = -RT\ln\left(\frac{\frac{1}{24.46}}{1}\right) = 1.89\ \text{kcal/mol}$$

$$\Delta G_{\text{CO}} = -RT\ln\left(\frac{V_1}{V_2}\right) - RT\ln\left(\frac{c_1}{c_2}\right) = -RT\ln\left(\frac{\frac{1}{24.46}}{1}\right) - RT\ln\left(\frac{1}{0.0074}\right) = -1.01\ \text{kcal/mol}$$

TSCO-diss has an estimated free energy of 16.0 kcal/mol if we assume its reverse reaction of CO coordination is diffusion-controlled [13] (the CO concentration is estimated to be 7.4 mM [14]) and apply the following equation:



k_d[CO][**IN2**]=(k_BT/h)*exp(-ΔG/RT)[**IN2**]

k_d=10^8 L/mol

k_B=1.38*10^{-23} J/K

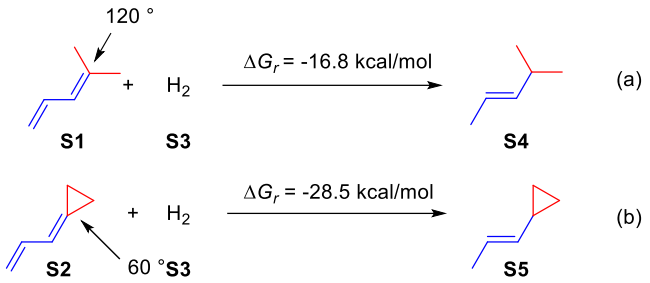
T=298.15 K

[CO]=0.182 (Ostwald solubility according to ref 14) / 24.46 = 7.4 mM

h=6.63*10^{-34} J*s

R=8.314 J/(mol*K)

Thus, $\Delta G^{\neq}$=9.4 kcal/mol, the estimated activation free energy of CO coordination (from **IN2** to **IN1**; **IN4** to **IN5**; **IN6** to **IN8**; **IN6-d** to **IN8-d**) is 9.4 kcal/mol, and the estimated Gibbs free energy of **TSCO-diss** is (9.4+6.5=)15.9 kcal/mol.



Scheme S1. Evaluation of Strain Release of MCP by Comparing the Hydrogenation Reactions of a and b.

Table S2. Computed Energies of the Stationary Points.

Entry	SPE[a] (Hartree)	TCG[a] (Hartree)	SPE[b] (Hartree)
S1	-234.260857	0.11061	-234.1842503
S2	-233.006338	0.088705	-232.9232617
S3	-1.162819	-0.001427	-1.172276056
S4	-235.481046	0.13393	-235.4079759
S5	-234.243437	0.1116	-234.1652863

[a]Computed at the BMK/def2-SVP level.

[b]Computed at the DLPNO-CCSD(T)/def2-TZVPP//BMK/def2-SVP.

Entry	SPE[a] (Hartree)	TCG[a] (Hartree)	SPE[a] (Hartree)
IN6'	-1030.646438	0.120712	-1030.525725
TS4'	-1030.620041	0.119863	-1030.500179
TS5'	-1030.606844	0.11995	-1030.486894
IN6'-H	-953.385845	0.089904	-953.295941
TS4'-H	-953.346578	0.088318	-953.25826
TS5'-H	-953.346043	0.089416	-953.256627
IN6'-Me	-1031.893047	0.141371	-1031.751676
TS4'-Me	-1031.852598	0.144345	-1031.708252
TS5'-Me	-1031.857808	0.143476	-1031.714332
IN6'-OMe	-1182.145039	0.148113	-1181.996926
TS4'-OMe	-1182.090981	0.149555	-1181.941426
TS5'-OMe	-1182.108726	0.149403	-1181.959323
IN6'-NMe2	-1220.942845	0.226318	-1220.716527
TS4'-NMe2	-1220.874225	0.230011	-1220.644214
TS5'-NMe2	-1220.905796	0.227526	-1220.678269

[a]Computed at the BMK/def2-SVP level.

Cartesian coordinates of the stationary point

CO

C	0.000000	0.000000	-0.643398
O	0.000000	0.000000	0.482549

IN1

Rh	-0.899576	-0.227228	-0.105000

Cl	-2.323743	-1.992719	-1.027618
C	0.557899	-1.207404	-1.129356
O	1.280185	-1.836451	-1.724184
C	-0.735307	-1.123369	1.609873
O	-0.692856	-1.619369	2.626792
C	-2.040752	1.453666	-0.922128
C	-2.507010	1.001608	0.371838
C	-3.895533	0.785305	0.891552
H	-4.731056	1.245167	0.350684
H	-4.127173	-0.187774	1.336580
C	-2.917016	1.717651	1.649663
H	-2.508996	1.365509	2.603733
H	-3.098284	2.797892	1.603282
H	-2.643233	1.346135	-1.830781
C	-0.663954	1.760535	-1.008716
C	0.114368	1.613196	0.211322
H	-0.304806	2.065903	1.118326
H	-0.183848	1.898568	-1.982989
C	1.622064	1.743226	0.140128
H	1.907745	2.819290	0.124779
H	2.078694	1.300293	1.047250
O	2.104170	1.116055	-1.014945
C	3.491841	1.174287	-1.184219
H	3.838904	2.228619	-1.173639
H	3.701584	0.766063	-2.186213
C	4.252109	0.407264	-0.174531
C	4.884781	-0.219684	0.647361
C	5.657396	-0.984124	1.631180
H	6.732605	-0.758987	1.535937
H	5.345782	-0.732030	2.658246
H	5.519330	-2.067984	1.484212

IN10-d

Rh	1.699395	-0.138738	0.352755
Cl	3.375867	-0.962771	-1.081355
O	-4.338156	-1.174264	0.967303
C	-4.237504	0.226241	0.794576
H	-5.087832	0.623049	0.206128
H	-4.252128	0.711761	1.787092
C	-3.407040	-1.844704	0.145008
H	-3.801067	-1.988512	-0.883452
H	-3.212274	-2.831954	0.590050
C	-2.194290	-0.897922	0.122924
H	-1.681339	-0.978767	1.097816
C	-1.208934	-0.815451	-1.045956
H	-1.664273	-1.306798	-1.931318
C	0.174831	-1.399570	-0.913152
H	0.784502	-1.343478	-1.823543
C	0.646758	-2.154516	0.135719
C	-2.936264	0.419862	0.063757
C	-2.390781	1.334694	-0.759195
C	-2.813654	2.731711	-1.097204
H	-2.826499	2.873315	-2.190599
H	-3.807018	2.969484	-0.686827
H	-2.087410	3.457655	-0.692142
C	-1.208619	0.699550	-1.424825
O	-0.435578	1.228412	-2.174774
C	0.439815	0.528851	1.582236
O	-0.287112	0.934105	2.361383
C	2.952815	1.296198	0.705205
O	3.720494	2.109840	0.866449
H	1.571175	-2.727261	0.013327
H	0.021676	-2.382592	1.005095

IN10

Rh	-1.618710	-0.123531	0.272851
Cl	-3.304988	0.197259	-1.344711
O	4.352581	1.314021	0.651969
C	4.313922	-0.093544	0.788383
H	5.183504	-0.570934	0.295729
H	4.345544	-0.350791	1.862622
C	3.390298	1.748999	-0.285136
H	3.778619	1.689700	-1.324198
H	3.149707	2.798691	-0.058064
C	2.222550	0.766319	-0.093816
H	1.696526	1.037549	0.837650
C	1.244685	0.392429	-1.212177
H	1.676800	0.707250	-2.185138
C	-0.167343	0.932689	-1.188078
H	-0.771502	0.706946	-2.075654
C	-0.664146	1.846211	-0.294028
C	-0.283902	2.900642	0.701105
C	-1.578722	3.017956	-0.163952
H	-2.538202	2.882972	0.344972
H	-1.597380	3.733240	-0.994566
H	-0.422996	2.697927	1.769270
H	0.570281	3.547375	0.466016
C	3.025112	-0.497401	0.124408
C	2.526674	-1.589959	-0.483577

C	3.015995	-3.005539	-0.522554
H	3.041002	-3.372524	-1.562029
H	4.017293	-3.105547	-0.076174
H	2.322121	-3.663635	0.028772
C	1.318340	-1.165417	-1.261357
O	0.574660	-1.879210	-1.876097
C	-0.355184	-0.409133	1.637191
O	0.372663	-0.579492	2.498156
C	-2.846687	-1.454061	0.976526
O	-3.599173	-2.214556	1.340343

IN7-d

Rh	1.246736	-0.215571	-0.100610
C	1.734673	-0.672829	1.734882
O	1.960188	-0.883153	2.824854
C	-0.645915	-1.559062	-0.918752
O	0.291002	-2.236047	-0.475544
C	-0.505903	-0.950643	-2.314867
C	0.346996	0.283677	-2.030212
C	-0.150774	1.201811	-1.100609
C	-1.598137	1.230691	-0.636358
C	-2.234826	0.016478	0.017926
C	-1.838468	-1.268037	-0.071603
C	-2.366265	-2.401957	0.775773
H	-1.530124	-2.885751	1.307423
H	-3.102840	-2.051514	1.513412
H	-2.848237	-3.174054	0.151164
C	-3.269776	0.564728	0.994054
O	-3.191189	1.959741	0.893597
C	-1.906965	2.290752	0.442833
H	-1.922440	3.319666	0.053507
H	-1.151274	2.224779	1.254185
H	-4.298911	0.242700	0.756547
H	-3.033306	0.221442	2.023321
H	-2.211149	1.491069	-1.526917
H	0.370546	2.161969	-1.016810
H	1.181535	0.541261	-2.691503
Cl	2.707470	1.579020	0.065661
H	-1.481779	-0.701465	-2.764239
H	0.030025	-1.670711	-2.950520

IN7

Rh	-1.323392	0.203428	0.165245
C	-2.065619	-0.975562	1.538181
O	-2.445574	-1.730820	2.292291
C	0.848443	1.174597	0.850177
O	-0.073385	1.367934	1.653530
C	0.856058	1.975581	-0.444507
C	0.972970	3.491014	-0.382943
C	2.114702	2.660871	-0.981427
H	3.036589	2.562970	-0.397095
H	2.257015	2.676889	-2.066904
H	1.124775	3.954735	0.597092
H	0.332915	4.063603	-1.062308
C	-0.146659	1.271943	-1.320783
C	0.059705	-0.101942	-1.524858
C	1.386849	-0.800629	-1.272609
C	2.051087	-0.780235	0.093449
C	1.849545	0.097777	1.095734
C	2.370815	-0.057702	2.505447
H	1.532350	0.004353	3.218678
H	2.885966	-1.019520	2.645135
H	3.080537	0.748752	2.759905
C	2.824713	-2.089449	0.198249
O	2.582099	-2.777685	-0.997562
C	1.364973	-2.323306	-1.522385
H	1.317532	-2.590643	-2.588640
H	0.493690	-2.773434	-1.000752
H	3.912425	-1.937686	0.313709
H	2.466352	-2.668770	1.075339
H	2.111426	-0.364200	-1.993818
H	-0.564131	-0.591472	-2.281254
H	-0.844079	1.847688	-1.940389
Cl	-3.001255	-0.541218	-1.252420

IN2

Rh	0.957390	0.264789	-0.272398
Cl	1.883552	2.405913	0.027124
C	-0.686295	1.056376	-0.956806
O	-1.580175	1.571264	-1.421086
C	2.194624	-1.469653	-0.738973
C	2.780733	-0.774310	0.325580
C	4.124355	-0.277450	0.736802
H	5.009957	-0.871132	0.481275
H	4.261383	0.810784	0.732199
C	3.135731	-0.847048	1.792284
H	2.666038	-0.134285	2.479798
H	3.345485	-1.835705	2.218947
H	2.701666	-1.508554	-1.710697

C	0.792383	-1.802487	-0.683721
C	0.089416	-1.477932	0.520877
H	0.595879	-1.622082	1.484165
H	0.271780	-2.154719	-1.577850
C	-1.408303	-1.653520	0.612512
H	-1.636192	-2.675380	0.991659
H	-1.816473	-0.935687	1.352865
O	-1.995242	-1.466381	-0.640683
C	-3.392481	-1.553881	-0.655264
H	-3.723214	-2.533160	-0.250443
H	-3.695374	-1.513048	-1.713966
C	-4.066039	-0.470147	0.090342
C	-4.619790	0.419426	0.699053
C	-5.290005	1.505321	1.420175
H	-6.270119	1.724211	0.965018
H	-5.452469	1.239956	2.477782
H	-4.683897	2.425571	1.383069

IN3

Rh	0.173439	0.126341	0.027227
Cl	1.290361	2.231451	0.601283
C	0.149544	-0.296847	1.920539
O	0.204785	-0.558943	3.020271
C	1.277185	-0.392406	-1.794067
C	1.944943	-0.724295	-0.545137
C	3.375970	-0.566079	-0.130313
H	4.126168	-0.390576	-0.910536
H	3.573090	-0.046232	0.812579
C	2.698244	-1.957319	-0.068080
H	2.457937	-2.364619	0.920379
H	2.990688	-2.707544	-0.812055
H	1.667735	0.346511	-2.501934
C	-0.038062	-0.890492	-1.916467
C	-0.554383	-1.682051	-0.814950
H	0.102789	-2.471687	-0.431592
H	-0.694007	-0.507742	-2.708325
C	-2.039690	-2.008808	-0.715374
H	-2.611930	-1.492316	-1.512306
H	-2.200918	-3.092208	-0.837890
O	-2.565571	-1.684432	0.552653
C	-3.037315	-0.381771	0.686656
H	-3.182441	-0.199071	1.763984
H	-4.022451	-0.265356	0.186941
C	-2.148253	0.674448	0.118710
C	-1.720524	1.652676	-0.490717
C	-1.415825	2.890629	-1.216246
H	-0.581557	3.412035	-0.719511
H	-1.119398	2.665717	-2.254099
H	-2.311302	3.533939	-1.233379

IN4

Rh	-0.913148	-0.162803	-0.357940
Cl	-1.041119	-2.352438	-1.281452
C	-2.370319	-0.438804	0.851540
O	-3.257641	-0.572084	1.540615
C	-0.099831	1.526673	-1.518568
C	-0.664734	1.908817	-0.242158
C	-1.515999	3.094279	0.150239
H	-1.552136	3.955670	-0.527504
H	-2.446259	2.916459	0.700406
C	-0.182221	2.803603	0.878765
H	-0.224804	2.418673	1.902817
H	0.659815	3.477225	0.681595
H	-0.722133	1.639552	-2.419085
C	0.975911	0.645309	-1.576980
C	2.054203	0.606935	-0.514063
H	2.318066	1.646791	-0.239498
H	1.181604	0.152278	-2.534675
C	3.355815	-0.138040	-0.857520
H	3.116687	-1.107915	-1.342882
H	4.038980	0.429124	-1.509487
O	3.981294	-0.314774	0.386887
C	3.011850	-0.548140	1.386220
H	3.277191	0.052492	2.275541
H	2.994729	-1.615034	1.682298
C	1.684849	-0.137777	0.755449
C	0.440686	-0.502667	1.071353
C	0.056863	-1.314934	2.281896
H	-0.469095	-2.238350	1.984989
H	0.951917	-1.599530	2.861571
H	-0.605519	-0.746497	2.958832

IN5

Rh	-0.728546	-0.251978	-0.040383
Cl	-2.802076	-0.583305	-1.373521
O	4.254458	-0.190073	-0.268844
C	3.550841	-0.037621	0.952752
H	3.698259	-0.921911	1.601045
H	3.958583	0.844204	1.482310

C	3.360687	-0.297891	-1.349112
H	3.055499	-1.351817	-1.527673
H	3.865780	0.079104	-2.253242
C	2.141748	0.530705	-0.910960
H	2.423360	1.600579	-0.979222
C	0.834307	0.334294	-1.660783
H	0.862358	-0.284309	-2.567278
C	-0.240062	1.237847	-1.569234
H	-1.023637	1.182664	-2.333435
C	-0.586736	1.849216	-0.322647
C	0.010431	2.888927	0.591435
C	-1.430251	3.041602	0.031902
H	-2.263504	2.907505	0.729421
H	-1.609863	3.795443	-0.743404
H	0.127315	2.642606	1.651607
H	0.792389	3.543309	0.189200
C	2.097081	0.124168	0.542179
C	0.951494	-0.217323	1.147812
C	0.898020	-0.686988	2.585865
H	1.903860	-0.804976	3.025283
H	0.350746	0.037595	3.217533
H	0.369974	-1.652765	2.684804
C	-0.496542	-2.237905	-0.214435
O	-0.381057	-3.352092	-0.341715
C	-1.970151	-0.148987	1.447882
O	-2.725458	-0.038120	2.279834

IN6-d

Rh	-1.138122	-0.493027	0.129822
Cl	-1.158753	0.629821	2.200239
O	4.201234	-0.310874	-0.007272
C	3.518301	0.909923	0.089353
H	3.591234	1.333404	1.114874
H	3.973031	1.629182	-0.611732
C	3.307868	-1.323864	0.351428
H	3.177169	-1.374271	1.454195
H	3.702081	-2.288556	-0.001947
C	1.963991	-0.924069	-0.306585
H	2.014839	-1.200854	-1.376479
C	0.757544	-1.596321	0.330399
H	0.928675	-1.958546	1.351808
C	-0.204523	-2.324068	-0.425150
H	-0.760544	-3.118623	0.094425
C	-0.775183	-1.807216	-1.615735
C	2.064165	0.590229	-0.225509
C	1.079589	1.477565	-0.435068
C	1.250000	2.979252	-0.392843
H	0.598560	3.409303	0.387290
H	2.289254	3.263416	-0.171942
H	0.949025	3.422840	-1.355998
C	-0.304110	1.038573	-0.821031
O	-0.980523	1.667124	-1.580861
C	-2.949437	0.259946	-0.320093
O	-3.971458	0.673991	-0.552397
H	-1.616131	-2.344903	-2.064351
H	-0.176159	-1.214770	-2.316968

IN6

Rh	-1.038087	-0.070051	-0.523105
Cl	-0.709119	-2.119164	-1.662087
O	4.243829	0.592716	-0.105310
C	3.686769	-0.587323	0.407681
H	3.892586	-1.453549	-0.258736
H	4.137784	-0.796104	1.391570
C	3.310147	1.151933	-0.981797
H	3.303845	0.616881	-1.956219
H	3.574790	2.205094	-1.159850
C	1.939196	0.965286	-0.283457
H	1.818156	1.763255	0.470787
C	0.766219	1.012631	-1.249964
H	1.016271	0.753139	-2.286224
C	-0.342531	1.877678	-1.081552
H	-0.912277	2.160261	-1.980587
C	-1.024916	1.967975	0.164438
C	-0.756906	2.493314	1.556248
C	-2.010184	2.937290	0.757591
H	-2.980473	2.559873	1.097207
H	-2.033309	3.960433	0.364037
H	-0.910015	1.815824	2.402940
H	0.049209	3.224687	1.688079
C	2.188110	-0.334490	0.465102
C	1.270779	-1.076896	1.103352
C	1.565903	-2.334827	1.887414
H	1.036557	-3.191911	1.436363
H	2.642204	-2.561156	1.899806
H	1.204723	-2.228712	2.923411
C	-0.168451	-0.648653	1.159922
O	-0.835830	-0.783839	2.143730
C	-2.778882	-0.704299	0.205608
O	-3.775825	-1.054835	0.598967

IN7-CO-d

O	-4.735646	-1.294069	0.994679
C	-3.392069	-1.414633	1.364293
C	-2.646843	-0.413246	0.497071
C	-1.395289	0.055319	0.724848
C	-0.779288	1.070869	-0.157894
O	0.432517	1.289958	-0.132809
C	-1.579023	1.916248	-1.144794
C	-2.994384	2.324954	-0.799834
C	-3.947675	1.415384	-0.576308
C	-3.594245	-0.059786	-0.640316
H	-3.109892	-0.271662	-1.611878
C	-4.764212	-1.035126	-0.381319
H	-5.747296	-0.615139	-0.643379
H	-4.612350	-1.968014	-0.961854
H	-4.973346	1.706140	-0.323144
H	-3.220307	3.395305	-0.758122
C	-0.546838	-0.453971	1.870145
H	0.070910	0.352580	2.295220
H	-1.168485	-0.874640	2.673979
H	0.136772	-1.242511	1.509593
H	-3.298091	-1.213045	2.442967
H	-3.001966	-2.438689	1.167328
Rh	2.176240	0.031711	-0.096293
C	3.635645	-1.116228	-0.235672
O	4.497932	-1.847987	-0.342514
C	3.150435	1.312270	0.898207
O	3.723361	2.093737	1.495075
Cl	0.900178	-1.521842	-1.331773
H	-0.943733	2.781623	-1.381021
H	-1.588632	1.286914	-2.062377

IN7-CO

O	-4.296728	-2.149795	0.463917
C	-3.010752	-2.183552	1.015315
C	-2.359365	-0.884520	0.576286
C	-1.235548	-0.325670	1.075697
C	-0.705318	0.942350	0.524445
O	0.515425	1.161822	0.560199
C	-1.580074	2.012810	-0.048465
C	-3.065510	2.029133	0.131888
C	-3.839871	0.962791	-0.103548
C	-3.211390	-0.339985	-0.556087
H	-2.573341	-0.155921	-1.440694
C	-4.198537	-1.505689	-0.778841
H	-5.203147	-1.176867	-1.085734
H	-3.799374	-2.194995	-1.550331
H	-4.923427	1.005189	0.055605
H	-3.515785	2.976615	0.449164
C	-1.035293	2.486167	-1.477197
C	-0.876445	3.362699	-0.281988
H	-1.529589	4.237367	-0.196022
H	0.121397	3.472076	0.148505
H	-1.818445	2.714807	-2.205928
H	-0.178092	1.913383	-1.847192
C	-0.389883	-1.009867	2.128738
H	0.040398	-0.279516	2.832430
H	-0.984881	-1.736992	2.701357
H	0.452214	-1.551823	1.660141
H	-3.089812	-2.286405	2.109643
H	-2.422083	-3.044380	0.626174
Rh	2.127539	-0.095099	-0.073247
C	3.468265	-1.164896	-0.800192
O	4.256188	-1.832324	-1.273725
C	3.231781	0.506276	1.337355
O	3.879750	0.883042	2.193589
Cl	0.687956	-0.790783	-1.821959

IN8-d

Rh	-1.005966	-0.068567	-0.071278
Cl	-2.775207	-1.674548	0.672361
O	4.255503	-1.136998	0.004440
C	3.902337	0.176642	0.346233
H	4.027029	0.357145	1.435843
H	4.567838	0.874140	-0.190295
C	3.100882	-1.922353	0.049018
H	2.831868	-2.192665	1.093992
H	3.277411	-2.848679	-0.518574
C	1.991703	-1.028134	-0.551112
H	2.146402	-1.003044	-1.646886
C	0.587421	-1.547766	-0.270145
H	0.544554	-2.318581	0.511131
C	-0.383062	-1.725770	-1.311771
H	-1.126316	-2.518467	-1.182681
C	-0.693431	-0.681815	-2.205693
C	2.434995	0.331216	-0.033958
C	1.717196	1.467080	-0.001048
C	2.288562	2.814425	0.381289

H	1.734603	3.249981	1.230806
H	3.352278	2.754535	0.654583
H	2.170542	3.515014	-0.461771
C	0.275170	1.490224	-0.439775
O	-0.183234	2.516174	-0.888067
C	-0.816202	0.192894	1.859941
O	-0.712232	0.281582	2.979858
C	-2.554709	1.180549	-0.414793
O	-3.445406	1.836416	-0.619801
H	-1.571237	-0.796070	-2.849009
H	0.069783	0.019005	-2.560326

IN8

Rh	-0.925318	-0.131638	-0.227840
Cl	-2.660082	0.501850	-1.920283
O	4.316882	0.968606	-0.649298
C	3.997105	-0.304274	-0.154498
H	4.196385	-1.092686	-0.912584
H	4.629846	-0.512670	0.724679
C	3.167255	1.504715	-1.235521
H	2.989446	1.075497	-2.246280
H	3.292698	2.593667	-1.334569
C	2.011963	1.094767	-0.292686
H	2.050876	1.751245	0.596211
C	0.639405	1.236410	-0.936924
H	0.660619	1.312461	-2.032517
C	-0.423837	1.970690	-0.324317
H	-1.166979	2.438369	-0.979702
C	-0.824447	1.693508	0.999894
C	-0.323160	1.797847	2.418620
C	-1.715736	2.353133	2.008598
H	-2.595685	1.809448	2.367620
H	-1.848056	3.439448	1.945434
H	-0.303894	0.890984	3.031454
H	0.478061	2.516638	2.627107
C	2.509273	-0.266367	0.167665
C	1.805651	-1.205350	0.822282
C	2.407502	-2.468660	1.395765
H	1.928967	-3.364905	0.963859
H	3.490476	-2.533935	1.214435
H	2.218308	-2.502993	2.481249
C	0.342408	-1.000272	1.120917
O	-0.126135	-1.497613	2.120727
C	-0.567795	-1.552794	-1.542555
O	-0.371602	-2.324359	-2.342005
C	-2.476279	-0.959135	0.745934
O	-3.376171	-1.370837	1.282099

IN9-d

Rh	-1.094677	0.329784	0.065095
Cl	-1.848750	0.210324	-2.149970
O	4.191515	-0.005612	-0.077569
C	3.541473	-1.244313	-0.108183
H	3.727373	-1.776249	-1.066518
H	3.927175	-1.876817	0.709992
C	3.297404	0.958500	-0.565460
H	3.226278	0.925069	-1.673920
H	3.651561	1.955474	-0.265616
C	1.934776	0.569591	0.055411
H	1.973429	0.881798	1.118276
C	0.695165	1.102097	-0.640385
H	0.704893	0.786117	-1.695748
C	0.440827	2.573874	-0.560214
H	-0.255152	2.955072	-1.320303
C	0.927994	3.442099	0.347149
C	2.053275	-0.942772	0.021729
C	1.076319	-1.874168	0.032830
C	1.348902	-3.363269	-0.033213
H	0.793957	-3.816267	-0.871411
H	2.419159	-3.579130	-0.161583
H	0.995208	-3.861578	0.884964
C	-0.380271	-1.546911	0.156962
O	-1.207398	-2.400119	0.302481
C	-0.513035	0.631878	1.866533
O	-0.181057	0.832217	2.930078
C	-3.092208	-0.346842	0.502941
O	-4.145185	-0.727204	0.601686
H	1.641216	3.141085	1.123333
H	0.637398	4.496804	0.328728

IN9

Rh	-1.057373	0.530021	-0.021681
Cl	-2.013642	0.385734	-2.157839
O	3.528333	-2.106842	-0.233346
C	2.411977	-2.924317	-0.021841
H	2.254760	-3.623586	-0.871666
H	2.572406	-3.528696	0.887732
C	3.085679	-0.933069	-0.860832
H	2.897576	-1.096041	-1.943908

H	3.857689	-0.157261	-0.749744
C	1.759924	-0.588587	-0.144757
H	2.037804	-0.161641	0.838595
C	0.804943	0.322345	-0.894038
H	0.582790	-0.111609	-1.881527
C	1.205461	1.756745	-1.052796
H	0.745313	2.287890	-1.896758
C	2.018051	2.455797	-0.250547
C	2.931853	2.485874	0.926096
C	2.672605	3.755407	0.045176
H	2.073556	4.564934	0.480945
H	3.486023	4.096647	-0.607285
H	2.505270	2.470842	1.937621
H	3.914772	2.002304	0.849619
C	1.216194	-1.985511	0.088920
C	-0.058572	-2.380716	0.291596
C	-0.456239	-3.829592	0.487672
H	-1.247428	-4.108330	-0.227779
H	0.396297	-4.510783	0.353865
H	-0.875422	-3.982476	1.496445
C	-1.214149	-1.431505	0.394176
O	-2.305201	-1.802737	0.719827
C	-0.225887	0.819382	1.679249
O	0.262209	1.017537	2.682211
C	-3.098437	0.883069	0.573967
O	-4.198857	1.019224	0.758874

IN11-d

Rh	-1.707559	-0.047303	0.154467
Cl	-2.905736	1.742145	-0.771107
O	4.554788	-1.201609	-0.836204
C	4.406405	0.200785	-0.784584
H	5.120592	0.660186	-0.071982
H	4.606242	0.622316	-1.786029
C	3.528895	-1.836411	-0.101181
H	3.770779	-1.875563	0.982274
H	3.428706	-2.864072	-0.479469
C	2.305403	-0.938353	-0.340562
H	1.896639	-1.126640	-1.352089
C	1.158310	-0.749687	0.665540
H	1.575405	-0.946319	1.674883
C	-0.172559	-1.480432	0.499365
H	-0.177014	-2.309913	-0.217928
C	-1.099831	-1.467611	1.579667
C	2.990082	0.412604	-0.324790
C	2.250059	1.407954	0.214983
C	2.506961	2.877756	0.358486
H	3.502043	3.154600	-0.020269
H	1.743797	3.444743	-0.201715
H	2.427380	3.188570	1.413687
C	0.974490	0.767032	0.601668
O	-0.102685	1.317253	0.784904
C	-2.969551	-1.189693	-0.582900
O	-3.736904	-1.892480	-1.038393
H	-1.814828	-2.287715	1.704389
H	-0.835641	-0.956991	2.515430

IN11

Rh	1.578357	-0.229345	-0.127036
Cl	2.766266	-2.239165	-0.371440
O	-4.720437	1.033089	-1.062802
C	-4.641054	-0.306054	-0.624940
H	-5.308991	-0.492028	0.240058
H	-4.955039	-0.973956	-1.447026
C	-3.599001	1.767432	-0.616673
H	-3.737671	2.125618	0.425660
H	-3.480875	2.638064	-1.278017
C	-2.451170	0.748748	-0.679551
H	-2.126360	0.616778	-1.729519
C	-1.231300	0.764261	0.254574
H	-1.545678	1.262967	1.195668
C	0.116577	1.320413	-0.198010
H	0.120045	1.918432	-1.117902
C	1.103894	1.537566	0.799887
C	1.122323	1.802984	2.281073
C	1.997460	2.637457	1.301225
H	1.702449	3.674895	1.104176
H	3.079399	2.466603	1.330510
H	0.249645	2.292024	2.733922
H	1.636984	1.090465	2.935345
C	-3.200695	-0.488561	-0.230025
C	-2.467148	-1.344760	0.517722
C	-2.788046	-2.688840	1.098743
H	-3.826082	-2.985511	0.887020
H	-2.108818	-3.449097	0.676427
H	-2.631864	-2.690755	2.190587
C	-1.130737	-0.716504	0.616807
O	-0.071579	-1.270078	0.878732
C	2.858731	0.603482	-1.184674
O	3.634673	1.120249	-1.832524

P

O	-3.286989	-0.431372	-0.192765
C	-2.653654	0.810959	-0.060512
C	-1.174086	0.485676	0.092059
C	-0.135706	1.325685	-0.083192
C	1.294017	0.893598	0.086557
O	2.116614	1.721579	0.418894
C	1.746855	-0.535934	-0.182336
C	0.900387	-1.533273	-0.913780
C	-0.391801	-1.761116	-0.650849
C	-1.100787	-0.994941	0.447283
H	-0.543316	-1.135857	1.391421
C	-2.596895	-1.336940	0.623378
H	-2.851650	-2.360886	0.309107
H	-2.891146	-1.211913	1.686440
H	-0.959926	-2.493407	-1.236170
H	1.398420	-2.111475	-1.701038
C	2.687778	-1.094393	0.953456
C	3.269883	-0.663060	-0.360434
H	3.604339	-1.438728	-1.057086
H	3.827256	0.276924	-0.380252
H	2.595804	-2.162067	1.174823
H	2.828943	-0.431959	1.813350
C	-0.305418	2.803720	-0.356215
H	0.239867	3.098549	-1.269011
H	-1.362378	3.084706	-0.470220
H	0.132014	3.386628	0.470773
H	-2.875704	1.420890	-0.950296
H	-3.022961	1.357066	0.836644

S

O	-1.109548	-0.256067	-0.913573
C	-0.963814	-1.279161	0.022164
C	0.450035	-1.343986	0.527660
C	1.441538	-0.522310	0.140811
C	2.809660	-0.608782	0.655284
C	3.793751	0.208162	0.271141
C	5.216159	0.615349	0.380466
H	5.546785	1.146304	1.282169
H	5.985111	-0.019351	-0.078002
C	4.214757	1.354273	-0.575714
H	3.892483	2.365088	-0.295506
H	4.331320	1.198967	-1.655726
H	3.027923	-1.389586	1.395597
H	1.225721	0.257978	-0.597012
H	0.647923	-2.130625	1.267924
H	-1.656217	-1.129272	0.879149
H	-1.240717	-2.259583	-0.429957
C	-2.383413	-0.150934	-1.469409
C	-3.432932	0.269711	-0.513210
C	-4.299909	0.608262	0.262973
C	-5.346619	1.030623	1.198712
H	-5.892900	0.162389	1.603089
H	-6.073557	1.690822	0.697036
H	-4.909622	1.586823	2.044641
H	-2.312750	0.594870	-2.278072
H	-2.690388	-1.113517	-1.932005

TS1

Rh	-0.492100	-0.266206	-0.260203
Cl	0.578284	-2.297676	-1.151706
C	-2.100728	-1.247954	-0.079758
O	-3.055026	-1.852446	0.020027
C	-0.938567	1.525682	-1.508378
C	-1.318801	1.630153	-0.107759
C	-2.518667	2.272131	0.538104
H	-3.128918	2.962894	-0.056542
H	-3.084921	1.693591	1.276227
C	-1.093098	2.723818	0.927949
H	-0.707881	2.430212	1.910887
H	-0.763941	3.710529	0.581172
H	-1.656307	1.544374	-2.336588
C	0.383424	1.093826	-1.713684
C	1.319849	1.099959	-0.556250
H	1.211955	2.004397	0.056564
H	0.729230	0.741002	-2.690492
C	2.775461	0.795278	-0.877635
H	2.844267	-0.177774	-1.406229
H	3.198843	1.589821	-1.512378
O	3.482286	0.793595	0.324393
C	2.861136	-0.097009	1.190518
H	3.195381	0.112174	2.219280
H	3.120615	-1.143712	0.929600
C	1.354398	0.005556	1.104074
C	0.291291	-0.515530	1.614850
C	-0.194991	-1.232171	2.827395
H	-0.389647	-2.288136	2.572422
H	0.543931	-1.194625	3.644527

H	-1.141249	-0.796620	3.187769

TS2

Rh	-0.995417	-0.251573	-0.006714
Cl	-2.489549	-2.063402	-0.006887
O	3.883642	-0.834316	-0.782871
C	3.032376	0.051977	-1.481862
H	3.412964	1.093496	-1.435206
H	3.013026	-0.251950	-2.544768
C	3.288183	-1.238287	0.423709
H	3.456013	-0.500246	1.236234
H	3.727548	-2.203589	0.719190
C	1.779402	-1.303358	0.079953
H	1.624550	-2.205439	-0.543238
C	0.770197	-1.317185	1.201414
H	0.551535	-2.290001	1.655438
C	0.219904	-0.207420	1.819225
H	-0.390001	-0.348862	2.718823
C	0.198494	1.105079	1.147241
C	-0.449639	2.332609	1.788837
C	1.048925	2.337109	1.518852
H	1.439660	2.983896	0.727770
H	1.732476	2.185459	2.361071
H	-1.075266	2.962647	1.147136
H	-0.817132	2.237577	2.817851
C	1.691398	-0.066166	-0.786273
C	0.663547	0.804402	-0.689362
C	0.557041	2.055800	-1.529520
H	1.550668	2.484642	-1.751706
H	0.077555	1.818738	-2.494970
H	-0.054356	2.835579	-1.046827
C	-2.323049	0.728572	-0.972867
O	-3.132870	1.321549	-1.500085

TS3

Rh	-1.016898	-0.269356	-0.044014
Cl	-1.497941	-2.278691	-1.262106
O	4.325523	-0.085549	-0.053621
C	3.396590	-1.085407	0.252964
H	3.447026	-1.925624	-0.475692
H	3.618744	-1.492998	1.253396
C	3.720133	0.774586	-0.971145
H	3.719999	0.334302	-1.992465
H	4.283881	1.719420	-0.998135
C	2.260034	0.940158	-0.483870
H	2.235079	1.701507	0.318795
C	1.308445	1.348264	-1.584164
H	1.691421	1.307044	-2.611863
C	0.041076	1.764309	-1.378281
H	-0.577108	2.036890	-2.243725
C	-0.587297	1.759262	-0.036278
C	-0.120240	2.716591	1.065527
C	-1.502674	2.888032	0.420959
H	-2.377374	2.646900	1.034859
H	-1.652011	3.735085	-0.259772
H	-0.072559	2.380637	2.105877
H	0.652421	3.445483	0.793419
C	2.023911	-0.421404	0.176144
C	0.889941	-1.029913	0.584617
C	0.961131	-2.451317	1.126675
H	1.559600	-3.090525	0.455890
H	1.427864	-2.473714	2.128805
H	-0.036265	-2.909848	1.194086
C	-0.485924	-0.203497	1.713828
O	-0.335413	-0.097882	2.847881
C	-2.938605	0.119450	-0.297835
O	-4.051911	0.274621	-0.394496

TS4-d

Rh	1.048319	-0.300555	0.117399
Cl	1.608364	-2.076045	-1.272012
O	-3.958023	-0.796168	-0.458891
C	-3.361546	0.386765	-0.912278
H	-3.125398	0.330284	-1.996325
H	-4.063015	1.225282	-0.760061
C	-2.940774	-1.631021	0.015360
H	-2.386007	-2.119039	-0.814356
H	-3.386891	-2.409396	0.652679
C	-1.991505	-0.684269	0.780525
H	-2.508744	-0.412010	1.725543
C	-0.646005	-1.320381	1.109522
H	-0.616523	-2.412566	1.017040
C	0.294751	-0.732390	1.975163
H	0.992078	-1.306189	2.593375
C	0.317929	0.750768	1.982993
C	-2.063866	0.537160	-0.122937
C	-1.187199	1.551763	-0.281189
C	-1.406718	2.695581	-1.246203
H	-2.379983	2.628232	-1.752013

H	-1.346009	3.658938	-0.713807
H	-0.612429	2.709480	-2.011810
C	0.129037	1.641883	0.439881
O	0.822568	2.625662	0.387114
C	2.747250	0.534121	-0.437511
O	3.769289	0.935291	-0.704229
H	-0.649986	1.197785	2.273311
H	1.147575	1.228756	2.515749

TS4

Rh	-1.011270	-0.490443	-0.103704
Cl	-1.359115	-2.749720	0.350146
O	4.100543	-0.860749	0.035930
C	3.489380	-0.064364	1.014482
H	3.364205	-0.621802	1.966529
H	4.130646	0.811740	1.215792
C	3.091625	-1.447169	-0.736509
H	2.622568	-2.311344	-0.219013
H	3.528022	-1.794238	-1.685574
C	2.049353	-0.324048	-0.914485
H	2.491955	0.413158	-1.616392
C	0.726152	-0.805067	-1.487560
H	0.748963	-1.813281	-1.918534
C	-0.273190	0.052557	-1.968500
H	-0.969245	-0.247712	-2.760363
C	-0.497554	1.300394	-1.236262
C	-1.342085	2.461792	-1.689095
C	0.155537	2.688650	-1.520595
H	0.785470	2.719487	-2.415366
H	0.495426	3.301868	-0.681593
H	-1.765236	2.417875	-2.698535
H	-1.983803	2.910960	-0.924671
C	2.116357	0.308654	0.461674
C	1.187945	1.023594	1.125065
C	1.425513	1.603043	2.503095
H	2.449559	1.418168	2.856991
H	1.241401	2.689862	2.493628
H	0.717453	1.172745	3.231534
C	-0.207017	1.287108	0.620359
O	-0.926451	2.088598	1.169515
C	-2.716072	-0.138734	0.823698
O	-3.734211	0.030808	1.281753

TS5-CO-d

Rh	1.192395	-0.188711	0.281201
Cl	2.796965	-0.536454	-1.457932
O	-4.269978	-0.711627	0.149435
C	-3.826605	0.614654	0.342739
H	-4.363139	1.321000	-0.320976
H	-4.026838	0.909901	1.388835
C	-3.312272	-1.437421	-0.583621
H	-3.405534	-1.258754	-1.675352
H	-3.461617	-2.508748	-0.383027
C	-1.963912	-0.887404	-0.065874
H	-1.835368	-1.288685	0.955939
C	-0.710363	-1.057863	-0.888652
H	-0.874306	-1.007985	-1.973148
C	0.270942	-2.103717	-0.541432
H	0.940084	-2.394700	-1.356554
C	0.526705	-2.649469	0.695937
C	-2.351754	0.574240	0.011926
C	-1.497769	1.506230	-0.429217
C	-1.724328	2.984988	-0.572827
H	-1.495813	3.293047	-1.606604
H	-2.760866	3.260997	-0.325509
H	-1.048163	3.550870	0.091541
C	-0.237939	0.940359	-1.043939
O	0.289873	1.413519	-1.995292
C	0.185969	0.119267	1.874253
O	-0.343318	0.310633	2.859034
C	2.551749	1.011043	0.841276
O	3.381066	1.730532	1.128681
H	-0.135120	-2.522839	1.557815
H	1.336824	-3.376287	0.799566

TS5-CO

Rh	-1.189648	-0.159058	0.170357
Cl	-2.717471	-0.376686	-1.643579
O	4.258477	0.625300	-0.095248
C	3.890516	-0.601218	0.500572
H	4.477778	-1.444215	0.086333
H	4.090610	-0.546311	1.586237
C	3.264418	1.040204	-1.003473
H	3.381423	0.551051	-1.993265
H	3.348369	2.129633	-1.132986
C	1.948810	0.588033	-0.334389
H	1.775448	1.269405	0.517033
C	0.686670	0.414128	-1.153468
H	0.878335	0.067643	-2.179434

C	-0.253317	1.584366	-1.209895
H	-0.945281	1.595358	-2.057457
C	-0.346548	2.599755	-0.326684
C	0.174330	3.350183	0.853521
C	-0.983745	3.908381	-0.037799
H	-1.995035	3.917079	0.386138
H	-0.759946	4.756538	-0.696916
H	-0.076611	3.012632	1.866897
H	1.158255	3.830575	0.773344
C	2.422589	-0.751627	0.177135
C	1.618500	-1.811323	0.030351
C	1.899673	-3.255676	0.332034
H	1.706799	-3.864956	-0.566383
H	2.939613	-3.402562	0.661948
H	1.228996	-3.626957	1.126452
C	0.361701	-1.495527	-0.745078
O	-0.136488	-2.254145	-1.511308
C	-0.216263	0.113668	1.783812
O	0.298765	0.302816	2.778088
C	-2.624877	-0.991816	1.091325
O	-3.487292	-1.528076	1.597100

TS4-CO-d

Rh	1.440815	0.055881	-0.315806
Cl	3.038801	1.692214	0.163255
O	-4.402414	0.779636	0.127615
C	-3.470689	0.799867	1.172479
H	-3.153039	1.840366	1.344709
H	-3.917451	0.410864	2.114263
C	-4.381014	-0.509769	-0.414515
H	-4.869988	-0.489342	-1.400549
H	-4.928986	-1.222439	0.236631
C	-2.887428	-0.898861	-0.478063
H	-2.762455	-1.985378	-0.317529
C	-2.198727	-0.497447	-1.770237
H	-2.769536	0.074456	-2.510905
C	-0.911089	-0.805651	-1.991667
H	-0.423365	-0.498038	-2.923408
C	-0.082753	-1.541709	-0.982218
C	-2.333256	-0.109781	0.709336
C	-1.104715	-0.165302	1.259271
C	-0.716962	0.596302	2.510916
H	0.194752	1.196785	2.346131
H	-1.521576	1.261429	2.855381
H	-0.485317	-0.124550	3.313510
C	0.027968	-1.045326	0.768762
O	0.564954	-1.857526	1.491282
C	2.902050	-1.275896	0.105416
O	3.758102	-1.963408	0.353220
C	0.295642	1.584005	-0.771332
O	-0.272664	2.526980	-1.018576
H	-0.672298	-2.364664	-0.544769
H	0.794988	-2.049836	-1.414711

TS4-CO

Rh	-1.411250	-0.167890	-0.297230
Cl	-2.974127	-1.923123	-0.371778
O	4.452793	-0.908120	-0.082420
C	3.503895	-1.337921	0.854420
H	3.222841	-2.377704	0.622449
H	3.920485	-1.311967	1.885513
C	4.379363	0.489320	-0.130532
H	4.887902	0.839660	-1.041953
H	4.880160	0.943044	0.750196
C	2.870699	0.814292	-0.102840
H	2.672830	1.770815	0.408449
C	2.223061	0.820319	-1.474217
H	2.832400	0.513050	-2.332977
C	0.929940	1.135901	-1.649981
H	0.500549	1.101397	-2.660056
C	-0.000708	1.508753	-0.533271
C	-0.846807	2.804606	-0.788976
C	0.324538	2.904556	0.125388
H	1.231984	3.383176	-0.255739
H	0.137310	3.005681	1.197897
H	-0.767669	3.215523	-1.802261
H	-1.845723	2.887430	-0.355532
C	2.342841	-0.353500	0.726373
C	1.111467	-0.517109	1.240180
C	0.728972	-1.685627	2.128621
H	-0.195984	-2.172211	1.772944
H	1.526939	-2.440496	2.180040
H	0.526236	-1.316078	3.148599
C	-0.043761	0.456908	1.091877
O	-0.523780	1.013188	2.054357
C	-2.875160	0.845712	0.651278
O	-3.731583	1.341713	1.188019
C	-0.248107	-1.443276	-1.256816
O	0.319415	-2.253128	-1.798830

TS5-d

Rh	1.379110	-0.278143	-0.167155
Cl	1.443306	1.912399	-1.038937
O	-4.352941	-0.847651	-0.444786
C	-3.975827	0.505395	-0.333107
H	-4.035287	1.025560	-1.311160
H	-4.666580	1.006705	0.365965
C	-3.210445	-1.646965	-0.601869
H	-2.838514	-1.626448	-1.648889
H	-3.473971	-2.682076	-0.338714
C	-2.166315	-0.999236	0.334231
H	-2.352623	-1.310763	1.379039
C	-0.699595	-1.148902	-0.019461
H	-0.602256	-1.103663	-1.123480
C	0.327847	-1.986409	0.593965
H	0.324922	-2.137883	1.679628
C	1.392188	-2.434233	-0.217807
C	-2.544568	0.467863	0.152983
C	-1.590641	1.372101	0.392792
C	-1.628406	2.870917	0.398739
H	-2.627538	3.241615	0.123292
H	-1.375888	3.245882	1.405570
H	-0.874709	3.265073	-0.301200
C	-0.401998	0.616569	0.939781
O	0.002449	0.650168	2.051449
C	3.241559	-0.162887	0.111534
O	4.351218	-0.055420	0.326754
H	2.223692	-2.965373	0.255888
H	1.234004	-2.655014	-1.280047

TS5

Rh	1.202598	-0.225149	0.052949
Cl	0.907325	-2.307294	1.140240
O	-4.312212	1.517613	0.276357
C	-4.209570	0.117307	0.386883
H	-4.341573	-0.218114	1.436251
H	-5.004079	-0.343562	-0.224206
C	-3.031620	2.089220	0.318153
H	-2.649580	2.158677	1.359287
H	-3.091146	3.102158	-0.106822
C	-2.152883	1.110954	-0.494427
H	-2.291538	1.291108	-1.576839
C	-0.681369	1.023997	-0.141510
H	-0.576992	1.092771	0.958521
C	0.473889	1.578526	-0.838717
H	0.485589	1.673695	-1.930839
C	1.611359	1.831331	-0.036935
C	1.960915	2.674001	1.165878
C	2.839778	2.686058	-0.119235
H	2.804198	3.574792	-0.759754
H	3.825180	2.212200	-0.058030
H	1.338171	3.552565	1.373531
H	2.371495	2.179803	2.052558
C	-2.812639	-0.205782	-0.093841
C	-2.070835	-1.312533	-0.190451
C	-2.411018	-2.753976	0.043853
H	-3.456250	-2.864402	0.370947
H	-2.267616	-3.327666	-0.887943
H	-1.732676	-3.178562	0.800931
C	-0.774787	-0.911493	-0.853529
O	-0.432574	-1.182314	-1.952443
C	3.001316	-0.673812	-0.287307
O	4.068556	-0.969369	-0.539822

IN6-dMe

Rh	-1.011783	-0.064307	-0.511416
Cl	-0.530469	-1.977357	-1.797782
O	4.246219	0.702689	-0.290117
C	3.748196	-0.405427	0.411289
H	3.978972	-1.354514	-0.117816
H	4.226655	-0.444148	1.405108
C	3.229768	1.169843	-1.130085
H	3.123696	0.534252	-2.035734
H	3.470799	2.197235	-1.442925
C	1.945201	1.069618	-0.275991
H	1.993457	1.893245	0.460228
C	0.660500	1.171660	-1.084533
H	0.839933	1.112876	-2.166392
C	-0.482347	1.977284	-0.749876
H	-1.078719	2.312098	-1.613004
C	-1.172162	2.005890	0.490919
C	2.237389	-0.216980	0.473374
C	1.371151	-1.049556	1.074952
C	1.783890	-2.289100	1.839170
H	1.326545	-3.184002	1.383520
H	2.875561	-2.420796	1.846818
H	1.421015	-2.231223	2.878344
C	-0.112453	-0.814349	1.084736
O	-0.803820	-1.202752	1.983355

C	-2.753837	-0.894361	0.108791
O	-3.724358	-1.366603	0.434913
C	-0.508872	2.015959	1.859472
H	-0.441651	3.061927	2.212987
H	-1.120100	1.457567	2.586410
H	0.501246	1.588437	1.874945
C	-2.547539	2.660541	0.511933
H	-3.195681	2.179232	1.262723
H	-2.459226	3.725649	0.796781
H	-3.051936	2.608231	-0.466086

IN8-dMe

Rh	0.884208	0.091693	-0.277156
Cl	2.633038	-1.070850	-1.644037
O	-4.281980	-1.269987	-0.368496
C	-4.036603	0.089609	-0.121931
H	-4.291934	0.711639	-1.005870
H	-4.673371	0.420101	0.717391
C	-3.084200	-1.865813	-0.774357
H	-2.861833	-1.655517	-1.843880
H	-3.165172	-2.955410	-0.640261
C	-2.004777	-1.211422	0.115774
H	-2.139072	-1.634378	1.129392
C	-0.581136	-1.485570	-0.353697
H	-0.553174	-2.000995	-1.323885
C	0.514170	-1.895550	0.492800
H	1.259723	-2.522680	-0.006157
C	0.973495	-1.242136	1.659668
C	-2.545606	0.205885	0.172697
C	-1.883711	1.341673	0.457701
C	-2.562258	2.684959	0.616306
H	-2.138610	3.424701	-0.084592
H	-3.648085	2.628213	0.450581
H	-2.373607	3.073910	1.630491
C	-0.394420	1.356064	0.695709
O	0.079079	2.249310	1.363075
C	0.401227	0.919519	-1.973744
O	0.130902	1.339506	-2.986218
C	2.433505	1.287247	0.263277
O	3.324218	1.909126	0.558119
C	0.095367	-0.667695	2.757633
H	0.064428	-1.401382	3.584725
H	0.525095	0.264747	3.155692
H	-0.935887	-0.459332	2.447191
C	2.372671	-1.606570	2.136162
H	2.823509	-0.766714	2.690260
H	2.322894	-2.464813	2.831464
H	3.030022	-1.868677	1.292294

IN9-dMe

Rh	1.103531	-0.023743	0.045957
Cl	1.878018	0.377995	-2.140756
O	-4.163342	0.505722	-0.182271
C	-3.473320	1.723620	-0.142472
H	-3.618180	2.301752	-1.080963
H	-3.861579	2.331373	0.692756
C	-3.291170	-0.463284	-0.698623
H	-3.200407	-0.383466	-1.803153
H	-3.682373	-1.461355	-0.449235
C	-1.929079	-0.149904	-0.040859
H	-1.989073	-0.504097	1.003839
C	-0.692069	-0.642943	-0.769043
H	-0.688965	-0.186717	-1.770504
C	-0.308956	-2.081614	-0.913409
H	0.296389	-2.242404	-1.815287
C	-0.475923	-3.180822	-0.128593
C	-1.999094	1.368521	0.010980
C	-0.991324	2.259678	0.119371
C	-1.211853	3.758315	0.146213
H	-0.602134	4.247089	-0.631671
H	-2.266836	4.022377	-0.015425
H	-0.884740	4.178549	1.112072
C	0.451980	1.872669	0.284310
O	1.286467	2.688781	0.552627
C	0.484770	-0.451380	1.806650
O	0.138999	-0.715544	2.852921
C	3.081569	0.484729	0.552444
O	4.146244	0.817455	0.698674
C	0.145850	-4.499491	-0.537425
H	-0.637862	-5.254557	-0.734247
H	0.766714	-4.400896	-1.440722
H	0.775171	-4.905185	0.276230
C	-1.266322	-3.257454	1.158486
H	-1.930624	-4.140087	1.139033
H	-0.590609	-3.400024	2.023223
H	-1.887394	-2.374993	1.355051

TS4-dMe

Rh	-0.952144	-0.504050	-0.067984

Cl	-1.214210	-2.801404	0.198174
O	3.984522	-0.989529	0.103307
C	3.421973	-0.098496	1.026764
H	3.232383	-0.595107	2.001296
H	4.127668	0.733127	1.201410
C	2.946577	-1.521254	-0.671996
H	2.384419	-2.313009	-0.132764
H	3.374352	-1.949162	-1.591398
C	2.021249	-0.314021	-0.934126
H	2.572491	0.341526	-1.641182
C	0.684310	-0.700274	-1.542712
H	0.692080	-1.678917	-2.038114
C	-0.356868	0.155767	-1.932301
H	-1.064379	-0.147924	-2.712165
C	-0.560678	1.472088	-1.255580
C	2.093654	0.355143	0.425904
C	1.192438	1.133143	1.062604
C	1.444589	1.712984	2.437973
H	2.473026	1.532140	2.780436
H	1.258005	2.799170	2.430418
H	0.744734	1.281614	3.173940
C	-0.195738	1.431480	0.554237
O	-0.930386	2.162613	1.173584
C	-2.567309	-0.309064	1.038539
O	-3.545434	-0.243558	1.601533
C	0.520402	2.544066	-1.569770
H	0.401202	2.807276	-2.634616
H	0.344423	3.449270	-0.967517
H	1.551103	2.207834	-1.412586
C	-1.945574	2.082496	-1.493838
H	-1.944582	2.644410	-2.443725
H	-2.730886	1.313691	-1.545930
H	-2.191729	2.779611	-0.678734

TS5-CO-dMe

Rh	-1.087653	-0.273952	0.216070
Cl	-2.673098	-0.611470	-1.554818
O	4.248794	1.148375	-0.075225
C	4.048433	-0.175758	0.372021
H	4.703638	-0.887775	-0.167584
H	4.296520	-0.231298	1.447553
C	3.179824	1.543269	-0.902049
H	3.309388	1.183842	-1.944553
H	3.135137	2.642626	-0.907466
C	1.950430	0.869844	-0.253637
H	1.761226	1.412559	0.684345
C	0.691770	0.650593	-1.061691
H	0.916926	0.397356	-2.107351
C	-0.478664	1.571236	-1.042413
H	-1.103221	1.425878	-1.928176
C	-1.011275	2.461047	-0.132266
C	2.591184	-0.458132	0.084343
C	1.912420	-1.589182	-0.141766
C	2.389815	-3.007399	-0.004145
H	2.225930	-3.544526	-0.952991
H	3.456366	-3.050015	0.265324
H	1.815263	-3.539695	0.773803
C	0.588024	-1.368600	-0.834199
O	0.161721	-2.106203	-1.661231
C	-0.110364	-0.024860	1.827473
O	0.409921	0.105275	2.828308
C	-2.309549	-1.429123	1.087598
O	-3.050229	-2.142065	1.570377
C	-0.374827	3.055355	1.107683
H	0.590625	2.622014	1.391441
H	-0.216175	4.136872	0.937068
H	-1.056526	2.974497	1.971558
C	-2.332637	3.112917	-0.493736
H	-2.980346	3.194311	0.395616
H	-2.166434	4.141400	-0.866835
H	-2.870449	2.534486	-1.260129

S1

C	0.913923	-0.052492	0.000005
C	-0.363776	-0.498075	-0.000034
C	-1.585690	0.309068	0.000033
C	-2.823405	-0.217603	-0.000013
H	-1.482112	1.399989	0.000198
H	-0.522988	-1.584569	-0.000087
H	-3.713960	0.417369	0.000098
H	-2.979782	-1.302483	-0.000125
C	2.072323	-1.023720	0.000025
H	1.732537	-2.070884	0.000332
H	2.714232	-0.866595	-0.886566
H	2.714520	-0.866238	0.886362
C	1.318241	1.403534	-0.000024
H	1.941055	1.625808	-0.885855
H	0.466495	2.097216	-0.000543
H	1.940310	1.626116	0.886236

S2

C	-2.876829	-0.008383	-0.000180
C	-1.584680	0.360489	0.000215
C	-0.462041	-0.582036	0.000175
C	0.817011	-0.198787	0.000029
H	-0.697965	-1.654025	0.000258
H	-1.321634	1.425931	0.000461
H	-3.165165	-1.065794	-0.000479
H	-3.682321	0.731587	-0.000306
C	1.791577	0.923752	-0.000107
C	2.251125	-0.576489	-0.000051
H	1.933057	1.500727	-0.922652
H	1.932954	1.500916	0.922334
H	2.691900	-0.975456	-0.922317
H	2.692183	-0.975157	0.922211

S3

H	0.000000	0.000000	0.377859
H	0.000000	0.000000	-0.377859

S4

C	1.098127	-0.047407	0.423750
C	-0.365138	-0.439053	0.367939
C	-1.384325	0.301027	-0.089937
C	-2.822000	-0.150356	-0.131775
H	-1.185280	1.313070	-0.465232
H	-0.585723	-1.451783	0.738345
H	-3.213393	-0.134486	-1.164841
H	-2.934882	-1.173118	0.262970
C	1.947698	-1.074855	-0.352371
H	1.768704	-2.101084	0.011026
H	1.695782	-1.048460	-1.427004
H	3.024392	-0.859132	-0.245029
C	1.379623	1.378970	-0.064462
H	1.108245	1.490968	-1.128950
H	0.809719	2.125128	0.513638
H	2.451717	1.616663	0.036202
H	1.403800	-0.109386	1.487585
H	-3.466987	0.521663	0.462433

S5

C	2.796668	0.076427	-0.197217
C	1.335626	0.332215	0.066065
C	0.416215	-0.621020	0.274735
C	-1.041397	-0.402603	0.515181
H	0.738532	-1.672664	0.267212
H	1.021480	1.384188	0.092340
H	3.024387	-1.001797	-0.192210
H	3.102701	0.488540	-1.175694
C	-1.747244	0.897653	0.141466
C	-2.027282	-0.368466	-0.668935
H	-2.528283	1.267037	0.813600
H	-1.161296	1.686448	-0.340513
H	-2.996766	-0.863686	-0.551956
H	-1.597845	-0.428517	-1.674669
H	3.428029	0.566824	0.565304
H	-1.426457	-0.911612	1.408818

TS1b

O	-1.764153	3.246640	-0.715875
C	-2.581924	2.295288	-0.088125
C	-1.754049	1.184130	0.462139
C	-1.516843	0.366198	1.422848
C	-1.965520	-0.084069	2.767948
H	-2.682436	0.623488	3.215507
H	-1.107268	-0.201371	3.450074
H	-2.453957	-1.068521	2.665411
H	-3.136753	2.749291	0.757695
H	-3.314815	1.910880	-0.817743
C	-0.435878	3.071302	-0.340627
C	0.032097	1.656033	-0.671837
C	1.093864	0.979476	0.057179
C	2.360850	0.627399	-0.633924
C	3.540800	0.515574	-0.024705
C	4.994838	0.234800	-0.126109
H	5.648516	0.989196	-0.581545
H	5.325279	-0.800653	-0.276838
C	4.316128	0.591184	1.242299
H	4.528547	1.577188	1.674768
H	4.206018	-0.212580	1.981197
H	2.316548	0.462303	-1.719614
H	1.237681	1.318949	1.092378
H	0.036824	1.520907	-1.762242
H	0.166247	3.773356	-0.942496
H	-0.265011	3.297747	0.730598
Rh	-0.409349	-0.504172	-0.082997
C	0.119145	-1.250976	-1.895137
O	0.325764	-1.737804	-2.892252

Cl	-2.327010	-1.996912	-0.559205
C	0.434166	-1.877019	1.011025
O	0.894441	-2.653940	1.692675

TS1c

O	2.752200	2.585715	0.558112
C	3.285297	1.323312	0.281439
C	2.196298	0.389271	-0.166544
C	1.861181	-0.511908	-1.033655
C	2.344602	-1.289864	-2.206232
H	3.408131	-1.103285	-2.429345
H	1.742431	-1.023645	-3.091823
H	2.178092	-2.364683	-2.028839
H	4.028638	1.372004	-0.539256
H	3.792716	0.941178	1.184187
C	1.460049	2.677901	0.046403
C	0.618442	1.502836	0.554463
C	-0.568387	1.070857	-0.195991
C	-1.930473	1.272652	0.344485
C	-3.020723	1.300481	-0.423763
C	-4.496487	1.407561	-0.525344
H	-4.963405	2.392523	-0.401182
H	-5.107905	0.566260	-0.176042
C	-3.594017	1.184220	-1.788625
H	-3.477049	2.024229	-2.484775
H	-3.608944	0.195223	-2.263230
H	-2.039591	1.399953	1.429910
H	-0.513024	1.205619	-1.285903
H	0.480688	1.602491	1.640136
H	1.021148	3.613349	0.431172
H	1.446790	2.715572	-1.061336
Rh	0.327275	-0.699395	0.292917
C	-0.860677	-1.054026	1.864450
O	-1.476080	-1.397148	2.749492
Cl	-0.417393	-2.777195	-0.533663

TS3b

Rh	-0.863038	-0.370640	-0.159313
Cl	-2.923086	0.137127	-1.381662
O	4.343593	-0.309629	-0.324593
C	3.494989	-0.934311	0.614196
H	3.560115	-2.036429	0.528401
H	3.831285	-0.652843	1.629376
C	3.580585	0.214597	-1.376036
H	3.340356	-0.556395	-2.140393
H	4.158117	1.019547	-1.858163
C	2.289701	0.694090	-0.692257
H	2.557631	1.589417	-0.094401
C	1.138062	1.064209	-1.586615
H	1.280832	0.981990	-2.672125
C	-0.033527	1.609470	-1.154791
H	-0.795708	1.885133	-1.891346
C	-0.423400	1.781666	0.274550
C	0.357103	2.659807	1.242504
C	-1.043247	3.082623	0.754081
H	-1.863311	3.047271	1.477723
H	-1.116199	3.889701	0.017102
H	0.455596	2.342109	2.285614
H	1.226112	3.191478	0.840415
C	2.080897	-0.448274	0.287868
C	0.915440	-0.996327	0.676440
C	0.900318	-2.136646	1.679971
H	1.894872	-2.338910	2.111158
H	0.220012	-1.912971	2.520842
H	0.538451	-3.076584	1.223831
C	-1.262598	0.475469	1.431239
O	-1.582047	0.725004	2.506281
C	-1.514020	-2.175819	-0.250088
O	-1.966644	-3.211398	-0.272573

TS5-CO-B

Rh	0.947839	-0.666923	-0.327138
Cl	2.777433	-0.059343	1.105593
O	-4.211121	1.358964	-0.584852
C	-4.146881	0.019231	-0.142283
H	-4.766605	-0.138428	0.762099
H	-4.532127	-0.641485	-0.940311
C	-3.011602	2.031976	-0.277735
H	-3.006621	2.408535	0.766524
H	-2.908371	2.884807	-0.965007
C	-1.928840	0.945742	-0.458770
H	-1.827145	0.782543	-1.548714
C	-0.561287	1.094480	0.186977
H	-0.590152	1.639781	1.142179
C	0.432663	1.770022	-0.726189
H	0.324102	1.607789	-1.805899
C	1.366864	2.631936	-0.308273
C	2.042749	3.293115	0.829284
C	2.527269	3.488335	-0.649841

H	2.351731	4.460752	-1.126379
H	3.456030	2.986308	-0.948316
H	1.542457	4.141149	1.314463
H	2.643729	2.653085	1.486949
C	-2.683842	-0.206730	0.155008
C	-2.024387	-1.006271	1.000797
C	-2.548245	-2.131443	1.845946
H	-2.283929	-1.955500	2.901743
H	-3.640373	-2.230214	1.749831
H	-2.086196	-3.089429	1.550380
C	-0.620354	-0.526419	1.273344
O	-0.096330	-0.614948	2.335097
C	-0.260673	-1.338444	-1.627171
O	-0.929525	-1.781953	-2.431649
C	2.153041	-2.114308	-0.613691
O	2.866414	-2.986645	-0.735825

TS5-CO-d-B

Rh	1.212463	-0.053825	-0.329008
Cl	2.780704	0.848705	1.240453
O	-4.324710	0.631313	-0.471281
C	-3.922038	-0.690956	-0.177823
H	-4.472509	-1.097524	0.692903
H	-4.138385	-1.334022	-1.050381
C	-3.327186	1.545445	-0.077025
H	-3.402718	1.798167	1.001269
H	-3.449333	2.465411	-0.668015
C	-2.011245	0.788532	-0.356613
H	-1.887669	0.766442	-1.456252
C	-0.709029	1.203145	0.313609
H	-0.856671	1.651228	1.307475
C	0.059725	2.177164	-0.555257
H	-0.150185	2.120401	-1.630470
C	0.882543	3.148299	-0.119385
C	-2.445989	-0.574231	0.118295
C	-1.592563	-1.263968	0.882289
C	-1.793685	-2.571101	1.592766
H	-1.583305	-2.445410	2.667658
H	-2.820148	-2.945278	1.458486
H	-1.093609	-3.334396	1.210999
C	-0.367341	-0.458616	1.234550
O	0.159944	-0.510592	2.296529
C	0.220039	-0.861742	-1.733185
O	-0.320655	-1.360597	-2.599089
C	2.730939	-1.151965	-0.661812
O	3.633736	-1.820358	-0.811951
H	1.139932	3.255232	0.938139
H	1.350252	3.835743	-0.830282

IN6'-H

Rh	-0.101075	0.005687	-0.382280
Cl	1.756015	1.454721	-0.604824
C	-1.704537	1.517107	-0.126688
H	-1.568678	2.500088	-0.586759
C	-2.155888	0.442550	-0.926077
H	-2.196037	0.605674	-2.013670
C	-2.120329	-0.899985	-0.467125
C	-0.064139	-0.283226	1.597865
O	-0.518052	-1.261506	2.097725
C	1.006766	-1.585602	-0.604061
O	1.652015	-2.503483	-0.732056
H	-2.319764	-1.695877	-1.191722
H	-2.355714	-1.142640	0.572803
H	-1.909956	1.519689	0.950191
C	0.628855	0.824372	2.385402
H	0.261930	1.814692	2.081446
H	0.467201	0.641037	3.458733
H	1.701055	0.799768	2.132359

IN6'-Me

Rh	-0.235594	0.118679	-0.368811
Cl	-2.531170	0.041925	-0.917738
C	0.419788	-1.738860	-1.325358
H	-0.104103	-2.035015	-2.238960
C	1.430978	-0.742373	-1.425999
H	1.476204	-0.179898	-2.372271
C	2.074220	-0.147949	-0.309802
C	-0.442841	-0.638646	1.458946
O	0.052502	-0.093300	2.395469
C	-0.414515	1.914786	0.432624
O	-0.528254	2.948483	0.872087
H	0.493172	-2.517690	-0.559662
C	-1.354282	-1.853987	1.586087
H	-1.094220	-2.640673	0.865473
H	-1.299656	-2.226356	2.620321
H	-2.373585	-1.515198	1.336479
C	2.920771	1.094874	-0.538839
H	2.907633	1.744992	0.351322
H	3.975159	0.811922	-0.717341

H	2.572503	1.682940	-1.403149
C	2.518904	-0.968735	0.888258
H	1.944642	-1.898267	1.013837
H	3.580371	-1.245081	0.744850
H	2.441358	-0.391060	1.821164

IN6'-NMe2

Rh	1.136572	-0.258817	-0.316677
Cl	3.407635	0.302623	-0.766790
C	0.205305	0.961863	-1.677558
H	0.654058	0.920305	-2.679336
C	-0.798762	-0.081550	-1.402143
H	-0.807205	-0.933469	-2.092637
C	-1.946970	-0.042822	-0.548262
C	0.748837	0.967223	1.167944
O	-0.234146	0.831536	1.844479
C	1.634551	-1.677557	0.968932
O	1.995308	-2.445213	1.723571
H	0.032413	1.992260	-1.353088
C	1.749439	2.093210	1.408652
H	1.858533	2.691328	0.490323
H	1.404097	2.711739	2.251877
H	2.741521	1.657653	1.604240
N	-2.492678	1.092461	-0.042457
N	-2.576744	-1.211486	-0.220824
C	-3.039726	1.153673	1.304871
H	-2.841401	0.216432	1.836777
H	-2.521670	1.953917	1.858906
H	-4.125033	1.363347	1.296378
C	-2.373111	2.386137	-0.684570
H	-3.333224	2.920392	-0.575496
H	-1.584586	3.005513	-0.217624
H	-2.157252	2.270561	-1.753556
C	-1.924660	-2.495039	-0.369503
H	-2.403346	-3.217540	0.310753
H	-1.997012	-2.890541	-1.401185
H	-0.860633	-2.405685	-0.104864
C	-4.012612	-1.280848	-0.003289
H	-4.485137	-0.327175	-0.269470
H	-4.439919	-2.065385	-0.652141
H	-4.266841	-1.524618	1.044179

IN6'-OMe

Rh	0.802230	-0.275558	-0.295257
Cl	3.067800	0.259164	-0.700640
C	-0.083252	0.626341	-1.922177
H	0.404983	0.400225	-2.879179
C	-1.074304	-0.362328	-1.466803
H	-1.098109	-1.362207	-1.909219
C	-2.129449	-0.043396	-0.599508
C	0.330695	1.134626	0.992219
O	-0.545846	0.949108	1.790378
C	1.305313	-1.477949	1.233684
O	1.667950	-2.133796	2.082378
H	-0.360058	1.683881	-1.828717
C	1.124844	2.431056	0.921229
H	1.010831	2.870977	-0.082261
H	0.761413	3.122384	1.697218
H	2.195374	2.204596	1.042964
C	-3.314526	1.533502	0.708873
H	-2.934127	1.146686	1.664898
H	-3.344553	2.629747	0.730956
H	-4.316536	1.130493	0.499072
C	-2.663581	-2.294440	-0.112694
H	-3.377202	-2.789436	0.558017
H	-2.816315	-2.652543	-1.144058
H	-1.627951	-2.506135	0.205448
O	-2.922056	-0.911242	-0.016744
O	-2.415691	1.199824	-0.341839

IN6'

Rh	-0.242662	-0.047319	-0.375529
Cl	-2.573908	-0.304092	-0.777489
C	0.346853	-2.289836	-0.261079
H	-0.266027	-3.019935	-0.796923
C	1.287515	-1.524985	-0.951765
H	1.310790	-1.605378	-2.049991
C	1.858083	-0.351382	-0.355863
C	2.880845	-0.119630	0.735206
C	3.101376	0.434286	-0.693118
H	3.017280	1.517691	-0.829501
H	3.863233	-0.042458	-1.321460
H	2.633728	0.594369	1.526119
H	3.488456	-0.975593	1.051767
C	-0.300871	0.130892	1.609118
O	0.371814	0.916848	2.195725
C	-0.316978	1.881431	-0.482366
O	-0.351087	3.007501	-0.562171
C	-1.364233	-0.730745	2.287357

H	-1.157332	-0.752272	3.368450
H	-2.333839	-0.245082	2.085204
H	-1.425922	-1.741150	1.864385
H	0.424503	-2.406275	0.824727

TS4'-H

Rh	-0.287643	-0.128309	-0.058599
Cl	-2.482269	-0.468269	0.597871
C	0.220881	-2.294432	-0.124443
H	-0.631686	-2.971656	-0.221341
C	0.633376	-1.553128	-1.233861
H	0.172479	-1.671561	-2.220299
C	1.725878	-0.540700	-1.072841
C	1.846552	0.512896	0.292336
O	2.079712	1.658768	0.015500
C	-0.797530	1.754370	-0.304705
O	-1.158519	2.803806	-0.516852
H	2.680316	-1.012030	-0.769833
H	1.879312	0.098206	-1.950512
C	2.298522	-0.096389	1.616872
H	1.678776	0.338621	2.418115
H	2.213629	-1.189667	1.654546
H	3.343988	0.208522	1.793425
H	0.870081	-2.462233	0.739725

TS4'-Me

Rh	-0.580274	-0.155400	0.011929
Cl	-2.789991	-0.842658	0.161938
C	0.224990	-2.221911	-0.035163
H	-0.502426	-2.982416	-0.331062
C	0.746035	-1.360681	-1.004100
H	0.490729	-1.467868	-2.064957
C	1.702360	-0.262006	-0.616615
C	1.296357	0.750736	0.805161
O	1.444690	1.926475	0.601886
C	-1.317126	1.644364	-0.264066
O	-1.791791	2.640662	-0.509755
C	1.457214	0.186034	2.218626
H	0.729924	0.718838	2.851730
H	1.281214	-0.892324	2.304432
H	2.467706	0.433249	2.585885
H	0.710302	-2.377296	0.932651
C	3.025962	-0.828338	-0.033792
H	3.533658	-1.364301	-0.853335
H	3.689181	-0.019707	0.312699
H	2.864411	-1.541232	0.785555
C	1.999824	0.681835	-1.785578
H	2.643814	1.513935	-1.468942
H	2.519190	0.115257	-2.577401
H	1.077569	1.104764	-2.210888

TS4'-NMe2

Rh	-1.225320	-0.235496	0.160894
Cl	-3.271920	-1.090541	-0.533982
C	-0.231761	-2.100714	-0.299245
H	-0.911438	-2.800915	-0.791910
C	0.286140	-1.020653	-1.029460
H	0.101730	-0.913766	-2.103044
C	1.349165	-0.134323	-0.406817
C	0.742371	0.506605	1.228736
O	0.785647	1.707709	1.295670
C	-2.141094	1.499235	0.339583
O	-2.707020	2.479818	0.334877
C	0.778779	-0.361894	2.487422
H	-0.253881	-0.439489	2.872344
H	1.155673	-1.372790	2.291014
H	1.389489	0.139875	3.256281
H	0.268732	-2.458220	0.606171
N	2.458926	-0.904576	0.073679
N	1.661380	0.992553	-1.215215
C	3.448653	-0.413148	1.020117
H	3.642035	-1.182567	1.791580
H	4.416286	-0.188046	0.531899
H	3.125604	0.502688	1.529358
C	3.037758	-1.862612	-0.854154
H	2.259054	-2.377905	-1.431417
H	3.741159	-1.379519	-1.565968
H	3.598461	-2.625515	-0.287366
C	2.848672	1.771332	-0.925583
H	2.794698	2.307969	0.043594
H	3.750864	1.145187	-0.945974
H	2.964151	2.525985	-1.718451
C	0.596799	1.797004	-1.794803
H	-0.270539	1.185514	-2.070205
H	0.252922	2.591397	-1.104157
H	0.972976	2.275572	-2.714664

TS4'-OMe

Rh	-0.918029	-0.181894	0.153295
Cl	-3.061037	-0.962227	-0.272803
C	-0.077973	-2.178259	-0.216069
H	-0.835569	-2.866790	-0.598193
C	0.447769	-1.201338	-1.060626
H	0.200324	-1.152161	-2.125604
C	1.544045	-0.309883	-0.554656
C	1.157578	0.523097	1.023918
O	1.283790	1.716495	0.989928
C	-1.735503	1.597259	0.314132
O	-2.251651	2.604306	0.313917
C	1.344442	-0.266497	2.315798
H	0.441380	-0.118934	2.932809
H	1.501435	-1.338185	2.149068
H	2.200409	0.161442	2.865444
H	0.437237	-2.476229	0.701742
O	1.969952	0.667909	-1.388092
O	2.610197	-1.027755	-0.093069
C	1.063437	1.519501	-2.045448
H	0.366443	0.965096	-2.695704
H	0.494141	2.122912	-1.322423
H	1.674905	2.187725	-2.667877
C	3.836162	-0.357138	0.119376
H	3.717451	0.532720	0.763918
H	4.494979	-1.084522	0.612848
H	4.277746	-0.038094	-0.836668

TS4'

Rh	-0.550840	-0.129476	-0.069728
Cl	-2.812372	-0.653902	0.101937
C	0.188395	-2.323025	-0.060383
H	-0.516539	-3.083428	-0.406607
C	0.807752	-1.505289	-0.993055
H	0.600874	-1.641880	-2.061894
C	1.547093	-0.294780	-0.585718
C	2.333550	0.568909	-1.548357
C	3.109557	-0.178311	-0.484530
H	3.645049	-1.090904	-0.764916
H	3.540749	0.393027	0.342939
H	2.396769	0.236135	-2.590120
H	2.231122	1.648811	-1.402058
C	1.142323	0.507090	0.997818
O	1.385655	1.690765	0.997139
C	-1.120813	1.720071	-0.295446
O	-1.478799	2.773652	-0.489256
H	0.518222	-2.402887	0.976847
C	1.410423	-0.357199	2.236575
H	1.997777	0.251601	2.941000
H	0.456549	-0.632828	2.715763
H	1.963018	-1.275023	1.989372

TS4-LE

Rh	-1.047148	-0.315150	-0.038052
Cl	-2.269322	0.374149	1.892282
O	3.969375	-1.291181	0.207268
C	3.424454	-0.358783	1.100949
H	3.239257	-0.815932	2.097149
H	4.141986	0.468172	1.234554
C	2.908487	-1.911435	-0.455425
H	2.419483	-2.675963	0.188154
H	3.293866	-2.407272	-1.359492
C	1.905149	-0.774860	-0.755117
H	2.296534	-0.195012	-1.612578
C	0.506825	-1.289669	-1.095708
H	0.429788	-2.385283	-1.105049
C	-0.389299	-0.589080	-1.966815
H	-1.112482	-1.087232	-2.620606
C	-0.386354	0.831886	-1.763366
C	-1.053628	1.964414	-2.468505
C	0.484028	1.962991	-2.321355
H	1.083064	1.688303	-3.196861
H	0.931795	2.713929	-1.666361
H	-1.514850	1.783547	-3.445935
H	-1.576247	2.675460	-1.817198
C	2.100560	0.085136	0.488149
C	1.315448	1.066147	0.976017
C	1.629240	1.871076	2.216678
H	2.584986	1.576664	2.673909
H	1.659483	2.944942	1.968669
H	0.823160	1.737129	2.958834
C	0.020796	1.468335	0.327328
O	-0.449961	2.558341	0.421660
C	-2.169898	-1.949670	0.231735
O	-2.866231	-2.824558	0.390944

TS5'-H

Rh	-0.340225	0.170682	-0.177910
Cl	-0.262529	-2.138914	-0.648773
C	1.478125	1.401560	-0.653132

H	1.424680	1.237827	-1.740390
C	0.407132	2.172319	-0.034051
H	0.552129	2.562177	0.978774
C	-0.852402	2.214292	-0.658992
C	1.689843	-0.163233	0.637558
O	1.703074	0.213176	1.762545
C	-2.041197	-0.237084	0.578006
O	-3.019063	-0.513567	1.080520
H	-1.685890	2.694363	-0.136833
H	-0.940309	2.160114	-1.751252
H	2.505305	1.581274	-0.317054
C	2.629905	-1.191233	0.043352
H	2.432643	-2.154443	0.536653
H	2.486119	-1.308908	-1.036899
H	3.657924	-0.868155	0.281125

TS5'-Me

Rh	0.013122	0.213581	0.082792
Cl	1.710450	1.572958	0.984195
C	0.202098	-1.991515	0.442004
H	0.193992	-1.933020	1.539257
C	-1.014139	-1.634498	-0.293377
H	-1.061418	-1.919854	-1.349790
C	-1.992373	-0.767634	0.229877
C	1.613343	-1.098283	-0.659317
O	1.445973	-1.308606	-1.818392
C	-0.622959	1.797844	-0.754929
O	-0.943975	2.736141	-1.307348
H	0.742003	-2.883338	0.103855
C	2.957015	-1.146529	0.040681
H	3.559950	-0.304021	-0.329829
H	2.863220	-1.058002	1.129270
H	3.444020	-2.093084	-0.249352
C	-3.121812	-0.327149	-0.686782
H	-3.994450	-0.991157	-0.545905
H	-3.451502	0.696822	-0.447109
H	-2.826655	-0.363227	-1.746797
C	-2.327155	-0.665453	1.710775
H	-3.205743	-1.305995	1.919241
H	-1.510842	-0.985129	2.373134
H	-2.600824	0.367592	1.979420

TS5'-NMe2

Rh	-0.806116	0.243355	-0.182400
Cl	-2.515344	0.066000	-1.789086
C	-0.423778	-1.623142	0.824632
H	-0.382125	-2.117096	-0.160551
C	0.707252	-0.710101	1.168302
H	0.696624	-0.325139	2.189978
C	1.849259	-0.439436	0.376130
C	-1.922389	-0.675330	1.406876
O	-1.739620	-0.150490	2.473862
C	-0.730298	2.100356	-0.499844
O	-0.785324	3.231226	-0.634908
H	-0.701166	-2.380384	1.571844
C	-3.242224	-1.332454	1.031730
H	-3.977613	-0.532589	0.853232
H	-3.168730	-1.935674	0.118144
H	-3.576272	-1.935944	1.892626
N	2.665244	0.613714	0.689861
N	2.223668	-1.180128	-0.718078
C	4.072765	0.640752	0.334221
H	4.676430	0.842709	1.236467
H	4.381405	-0.330746	-0.071630
H	4.297733	1.426287	-0.410985
C	2.237547	1.642799	1.613950
H	1.166256	1.857152	1.476316
H	2.396180	1.353012	2.670454
H	2.810721	2.562400	1.416449
C	2.545776	-0.527417	-1.975828
H	2.493601	0.563485	-1.860878
H	3.553242	-0.804040	-2.338234
H	1.805447	-0.820681	-2.744346
C	2.010838	-2.608509	-0.813554
H	1.857611	-3.040565	0.184381
H	1.146942	-2.866040	-1.456423
H	2.908433	-3.075199	-1.258210

TS5'-OMe

Rh	0.441742	0.265283	-0.020403
Cl	2.192446	1.565177	0.839716
C	0.242840	-1.695712	0.916661
H	0.167915	-1.250932	1.923209
C	-0.942445	-1.490884	0.045073
H	-0.984176	-2.029382	-0.902165
C	-1.989837	-0.644668	0.404528
C	1.682796	-1.475360	-0.306539
O	1.454154	-2.025143	-1.348145
C	0.175016	1.613535	-1.317598

O	0.104453	2.391510	-2.145723
H	0.611104	-2.726112	1.009684
C	3.046197	-1.491004	0.362578
H	3.709192	-0.823031	-0.208654
H	3.008487	-1.130984	1.398081
H	3.437877	-2.520396	0.303393
C	-2.937069	-0.611897	-1.761119
H	-1.992749	-0.260373	-2.213057
H	-3.030156	-1.700965	-1.905256
H	-3.790463	-0.104364	-2.228439
C	-2.791406	0.998438	1.897573
H	-2.270094	1.819726	1.375103
H	-3.841832	0.953613	1.575336
H	-2.733043	1.154798	2.981813
O	-2.977390	-0.280177	-0.390888
O	-2.126039	-0.228944	1.645627

TS5'

Rh	0.017854	0.175096	-0.038832
Cl	-1.584266	1.620560	-1.004402
C	-0.198314	-2.049044	-0.323225
H	-0.063497	-2.045113	-1.414579
C	0.945636	-1.685300	0.493798
H	0.973586	-1.945022	1.557581
C	1.885600	-0.807482	-0.077865
C	2.779401	-0.752106	-1.292114
C	3.315472	-0.418709	0.133200
H	3.977182	-1.144411	0.619890
H	3.559237	0.628334	0.341856
H	3.075021	-1.704477	-1.748608
H	2.667429	0.080672	-1.994372
C	-1.773109	-0.966886	0.544160
O	-1.771071	-1.094766	1.722084
C	0.721618	1.765376	0.745857
O	1.085962	2.707924	1.260671
C	-2.986702	-1.086796	-0.354857
H	-3.688150	-0.283626	-0.084523
H	-2.725387	-0.992702	-1.414936
H	-3.456712	-2.061627	-0.139087
H	-0.846351	-2.860460	0.023288

TS5-B

Rh	-1.350770	-0.313110	-0.264398
Cl	-1.226853	0.780685	1.797836
O	3.938148	0.223453	0.795131
C	3.483553	-1.104289	0.897171
H	4.125541	-1.800718	0.319001
H	3.513029	-1.417293	1.956743
C	3.133058	0.936199	-0.116729
H	3.461001	0.766494	-1.164675
H	3.219994	2.008678	0.111499
C	1.716347	0.368404	0.105317
H	1.290878	0.800217	1.030980
C	0.692091	0.396224	-1.010584
H	1.125872	-0.032691	-1.929685
C	-0.018887	1.655810	-1.405954
H	-0.539038	1.622333	-2.372255
C	-0.028108	2.812174	-0.734035
C	0.370636	3.595007	0.459801
C	-0.523406	4.211227	-0.670334
H	-1.584381	4.378115	-0.446438
H	-0.071598	4.963958	-1.328460
H	-0.109584	3.334890	1.410720
H	1.404819	3.954561	0.540842
C	2.081627	-1.081240	0.339025
C	1.284604	-2.055846	-0.143925
C	1.509174	-3.544513	-0.146767
H	2.533811	-3.789233	0.173334
H	0.806672	-4.051333	0.537090
H	1.340978	-3.955344	-1.156250
C	0.079968	-1.499901	-0.794896
O	-0.637911	-1.921740	-1.693155
C	-2.932451	-1.143533	0.458400
O	-3.795995	-1.706549	0.927189

TS5-CO-LE

Rh	1.288926	-0.118040	-0.276949
Cl	-0.027845	-0.241706	-2.265874
O	-4.335445	0.473520	-0.319251
C	-3.718709	-0.792520	-0.385378
H	-4.284806	-1.549926	0.192990
H	-3.677222	-1.121296	-1.440289
C	-3.602049	1.335641	0.517397
H	-3.895084	1.215465	1.582302
H	-3.808141	2.371818	0.210093
C	-2.134245	0.907792	0.315994
H	-1.763203	1.276777	-0.658042
C	-1.128009	1.139186	1.402576
H	-1.474841	1.029176	2.437043

C	0.128756	1.714009	1.202205
H	0.742042	1.816117	2.111164
C	0.785136	1.976818	-0.042764
C	0.376835	2.903767	-1.166942
C	1.680768	3.159882	-0.376290
H	2.629397	2.972586	-0.891053
H	1.701923	4.015000	0.311222
H	0.449473	2.527826	-2.192133
H	-0.458358	3.592338	-0.987403
C	-2.340216	-0.582998	0.184563
C	-1.403568	-1.420275	0.640300
C	-1.393447	-2.924749	0.590304
H	-1.106199	-3.343645	1.568716
H	-2.388902	-3.303677	0.311452
H	-0.675802	-3.291936	-0.164507
C	-0.224552	-0.781520	1.320793
O	0.354901	-1.148985	2.288857
C	1.728027	-1.959357	-0.741108
O	2.012242	-2.988766	-1.114746
C	2.642957	0.099126	1.069256
O	3.480216	0.234902	1.820839

INT-TS-LE

Rh	1.046337	-0.013573	-0.203423
Cl	2.878038	-0.785703	-1.608097
O	-4.215962	-0.848930	-0.823258
C	-3.832301	0.487891	-0.642777
H	-3.893241	1.056470	-1.596261
H	-4.519138	0.960786	0.079065
C	-3.074971	-1.582172	-1.159176
H	-2.796329	-1.430796	-2.225214
H	-3.279788	-2.651266	-0.998019
C	-1.957687	-1.016176	-0.248187
H	-2.079838	-1.445751	0.762202
C	-0.563529	-1.334536	-0.747044
H	-0.497931	-1.534105	-1.826387
C	0.431886	-1.973653	0.051148
H	1.186809	-2.611602	-0.420552
C	0.699427	-1.388157	1.324289
C	0.100489	-1.263156	2.700078
C	1.565608	-1.741725	2.492702
H	2.352543	-1.032912	2.773371
H	1.817376	-2.797058	2.650413
H	-0.034239	-0.262267	3.121468
H	-0.652588	-2.003776	2.993370
C	-2.389403	0.441096	-0.162935
C	-1.654907	1.445702	0.341177
C	-2.162202	2.850425	0.566853
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H	-3.229239	2.954227	0.319086
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C	-0.250791	1.169653	0.814166
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IN6-LE

Rh	-1.033549	-0.194402	-0.402362
Cl	-3.368564	-0.566083	-0.068605
O	4.244814	0.898105	-0.473141
C	3.882574	-0.296511	0.165373
H	4.162500	-1.182635	-0.445496
H	4.417872	-0.364062	1.127297
C	3.170366	1.305787	-1.271878
H	3.132124	0.726720	-2.220735
H	3.295563	2.371198	-1.516689
C	1.908056	1.003041	-0.430368
H	1.791848	1.804070	0.322629
C	0.623708	0.893582	-1.239645
H	0.806374	0.651830	-2.296236
C	-0.485919	1.796303	-1.029732
H	-1.110718	2.064035	-1.894226
C	-1.065543	1.946043	0.229787
C	-0.838790	2.333350	1.667959
C	-2.130806	2.741676	0.900916
H	-3.051372	2.205001	1.159529
H	-2.258788	3.792399	0.615333
H	-0.933731	1.561796	2.439202
H	-0.090460	3.108788	1.873203
C	2.371441	-0.235699	0.315666
C	1.581871	-1.050276	1.031676
C	2.057660	-2.198777	1.891216
H	1.574664	-3.144534	1.590689
H	3.147896	-2.330686	1.824341
H	1.780290	-2.016687	2.942910
C	0.115865	-0.739910	1.132039
O	-0.505147	-0.912062	2.137875
C	-0.786966	-1.970631	-1.143283
O	-0.653404	-2.991492	-1.610678

VII. References

(1) Adamson, N. J.; Wilbur, K. C. E.; Malcolmson, S. J. Enantioselective Intermolecular Pd-Catalyzed Hydroalkylation of Acyclic 1,3-Dienes with Activated Pronucleophiles. *J. Am. Chem. Soc.* **2018**, *140*, 2761–2764.

(2) (a) Hönig, M.; Carreira, E. M., Total Synthesis and Structural Revision of a Harziane Diterpenoid. *Angew. Chem., Int. Ed.* **2020,** *59*, 1192–1196. (b) Stafford, J. A.; McMurry, J. E., An efficient method for the preparation of alkylidenecyclopropanes. *Tetrahedron Lett.* **1988**, *29*, 2531-2534.

(3) Nayak, S.; Ghosh, N.; Sahoo, A. K. Access to Cyclobutene-Fused Azepines through Au-Catalyzed Cycloisomerization of Stable Alkyne Tethered Ketene N,N-Acetals. *Org. Lett.* **2014**, *16*, 2996.

(4) Zhang, Q.; Xu, W.; Lu, X. Cycloisomerization of 1,6-Enynes Using Acetate as a Nucleophile under Palladium(II) Catalysis. *J. Org. Chem.* **2005**, *70*, 1505.

(5) Geary, L. M.; Leung, J. C.; Krische, M. J. Ruthenium-Catalyzed Reductive Coupling of 1,3-Enynes and Aldehydes by Transfer Hydrogenation: *anti*-Diastereoselective Carbonyl Propargylation. *Chem. Eur. J.* **2012**, *18*, 16823.

(6) Dong, Z.; Liu, C.-H.; Wang, Y.; Lin, M.; Yu, Z.-X. Gold(I)-Catalyzed *endo*-Selective Intramolecular α-Alkenylation of β-Yne-Furans: Synthesis of Seven-Membered-Ring-Fused Furans and DFT Calculations. *Angew. Chem., Int. Ed.* **2013**, *52*, 14157.

(7) Li, C.-L.; Yu, Z.-X. Asymmetric Synthesis of Azepine-Fused Cyclobutanes from Yne-Methylenecyclopropanes Involving Cyclopropanation/C−C Cleavage/Wagner−Meerwein Rearrangement and Reaction Mechanism. *J. Org. Chem.* **2019**, *84*, 9913.

(8) (a) Huang, X.; Zhou, H. Novel Tunable CuX_2-Mediated Cyclization Reaction of Cyclopropylideneacetic Acids and Esters for the Facile Synthesis of 4-Halomethyl-2(5H)-furanones and 4-Halo-5,6-dihydro-2H-pyran-2-ones. *Org. Lett.* **2002**, *4*, 4419–4422. (b) Zhao, L.; Lu, X.; Xu, W. Palladium(II)-Catalyzed Enyne Coupling Reaction Initiated by Acetoxypalladation of Alkynes and Quenched by Protonolysis of the Carbon-Palladium Bond. *J. Org. Chem.* **2005**, *70*, 4059.

(9) Shu, X.-Z.; Li, X.; Shu, D.; Huang, S.; Schienebeck, C. M.; Zhou, X.; Robichaux, P. J.; Tang, W. Rhodium-Catalyzed Intra- and Intermolecular [5+2] Cycloaddition of 3-Acyloxy-1,4-enyne and Alkyne with Concomitant 1,2-Acyloxy Migration. *J. Am. Chem. Soc.* **2012**, *134*, 5211.

(10) Tang, X.; Huang, L.; Qi, C.; Wu, X.; Wu, W.; Jiang, H. Copper-Catalyzed Sulfonamides Formation from Sodium Sulfinates and Amines. *Chem. Commun.* **2013**, *49*, 6102.

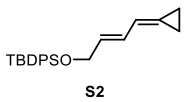
(11) Vinoth, P.; Nagarajan, S.; Maheswari, C. U.; Sudalai, A.; Pace, V.; Sridharan, V., Palladium-Catalyzed Internal Nucleophile-Assisted Hydration–Olefin Insertion Cascade: Diastereoselective Synthesis of 2,3-Dihydro-1H-inden-1-ones. *Org. Lett.* **2016**, *18*, 3442–3445.

(12) Curti, C.; Sartori, A.; Battistini, L.; Brindani, N.; Rassu, G.; Pelosi, G.; Lodola, A.; Mor, M.; Casiraghi, G.; Zanardi, F., Pushing the Boundaries of Vinylogous Reactivity: Catalytic Enantioselective Mukaiyama Aldol Reactions of Highly Unsaturated 2-Silyloxyindoles. *Chem.-Eur. J.* **2015**, *21*, 6433-6442.

(13) Limanto, J.; Tallarico, J. A.; Porter, J. R.; Khuong, K. S.; Houk, K. N.; Snapper, M. L. Intramolecular Cycloadditions of Cyclobutadiene with Olefins. *J. Am. Chem. Soc.* **2002**, *124*, 14748-14758.

(14) Skirrow, F. W. Über die Löslichkeit von Kohlenoxyd in binären organischen Gemischen. *Z. Phys. Chem. Stoechiom. Verwandtschaftsl.* **1902**, *41*, 139.

VIII. NMR Spectra



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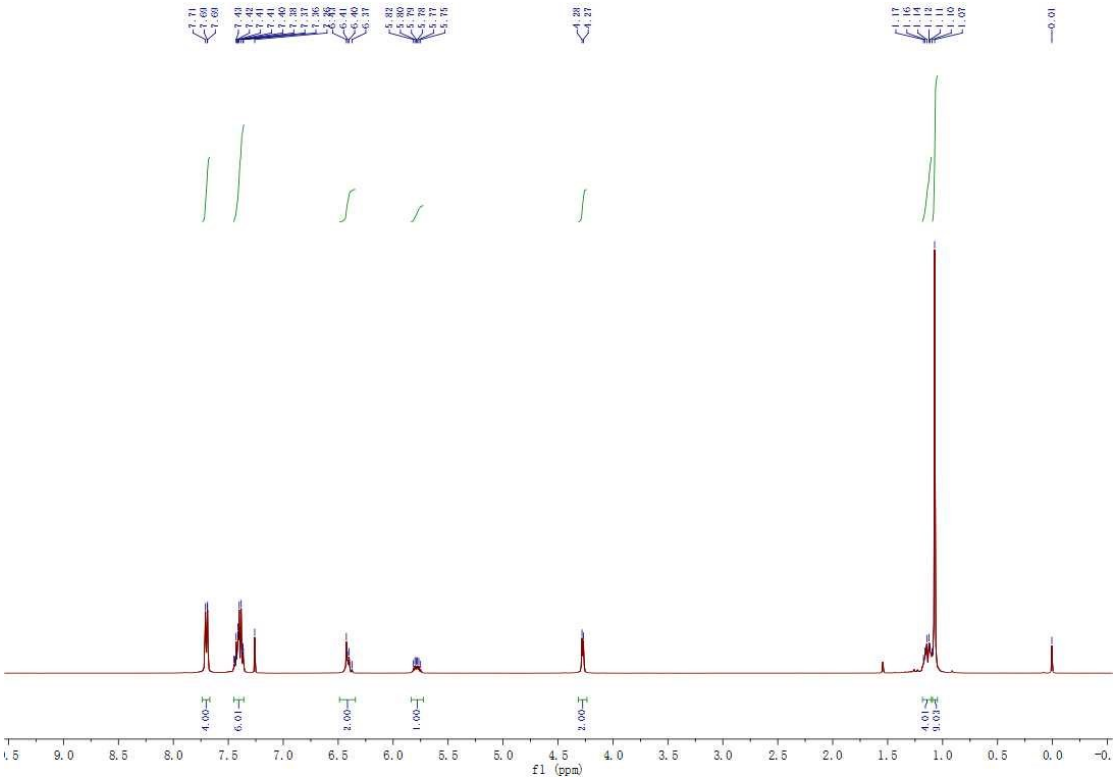

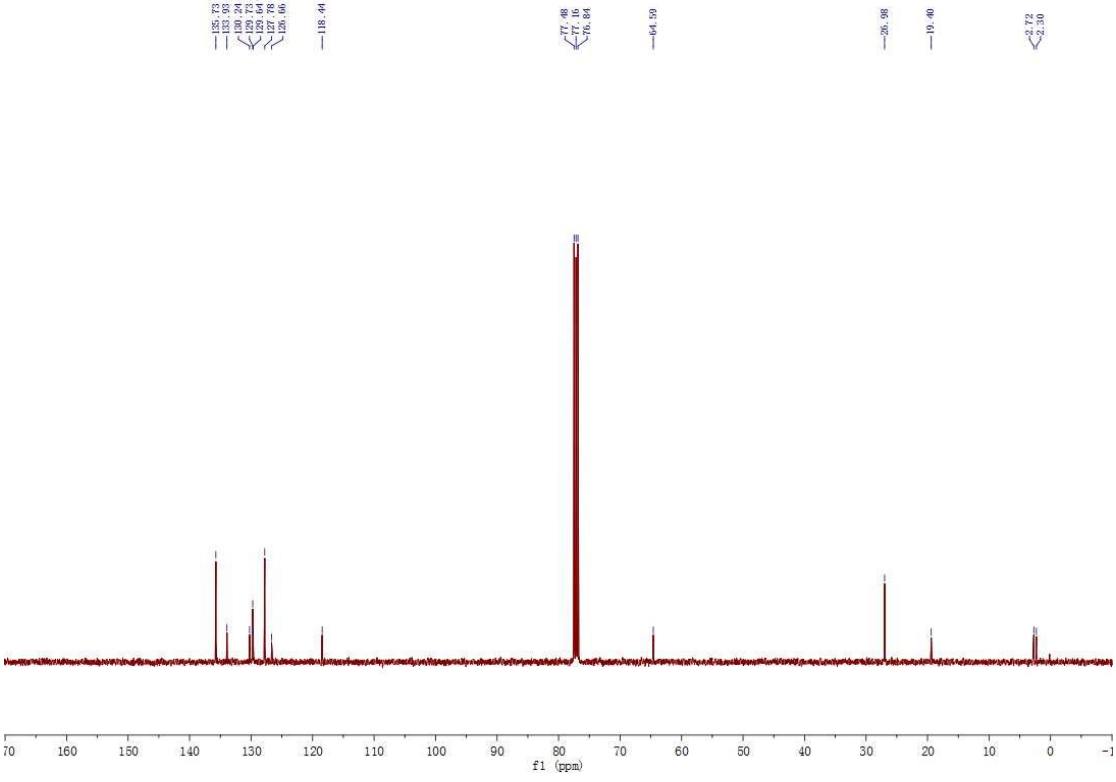

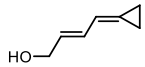

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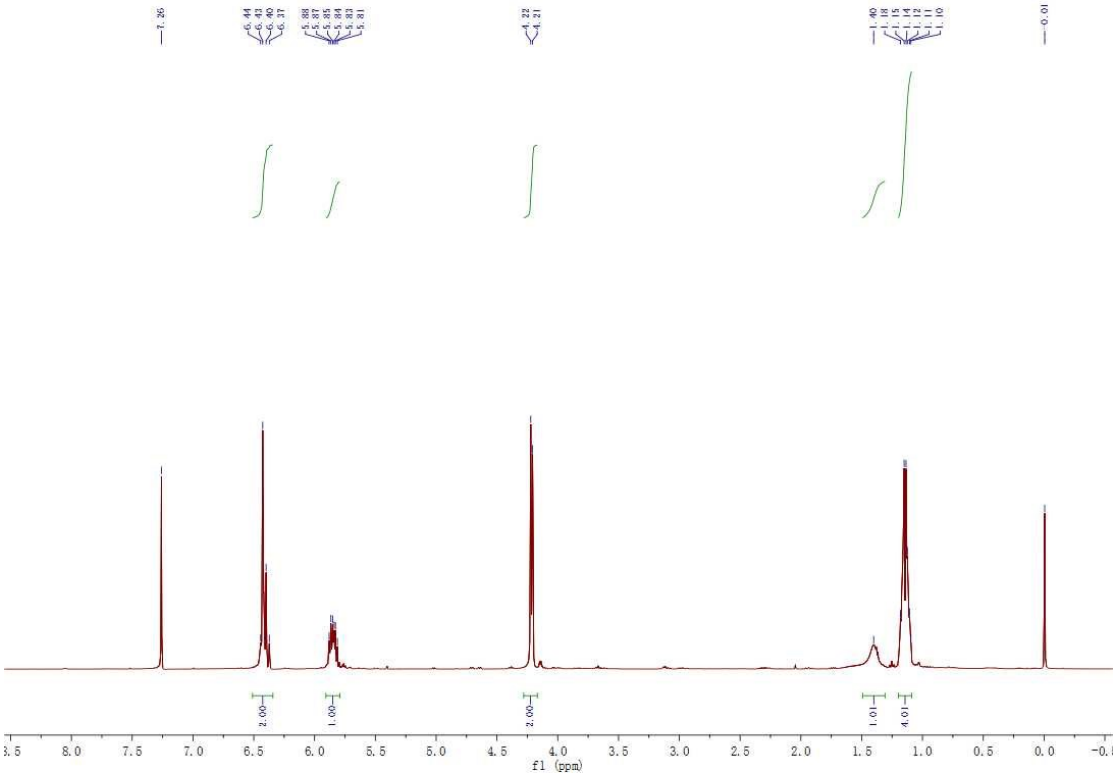

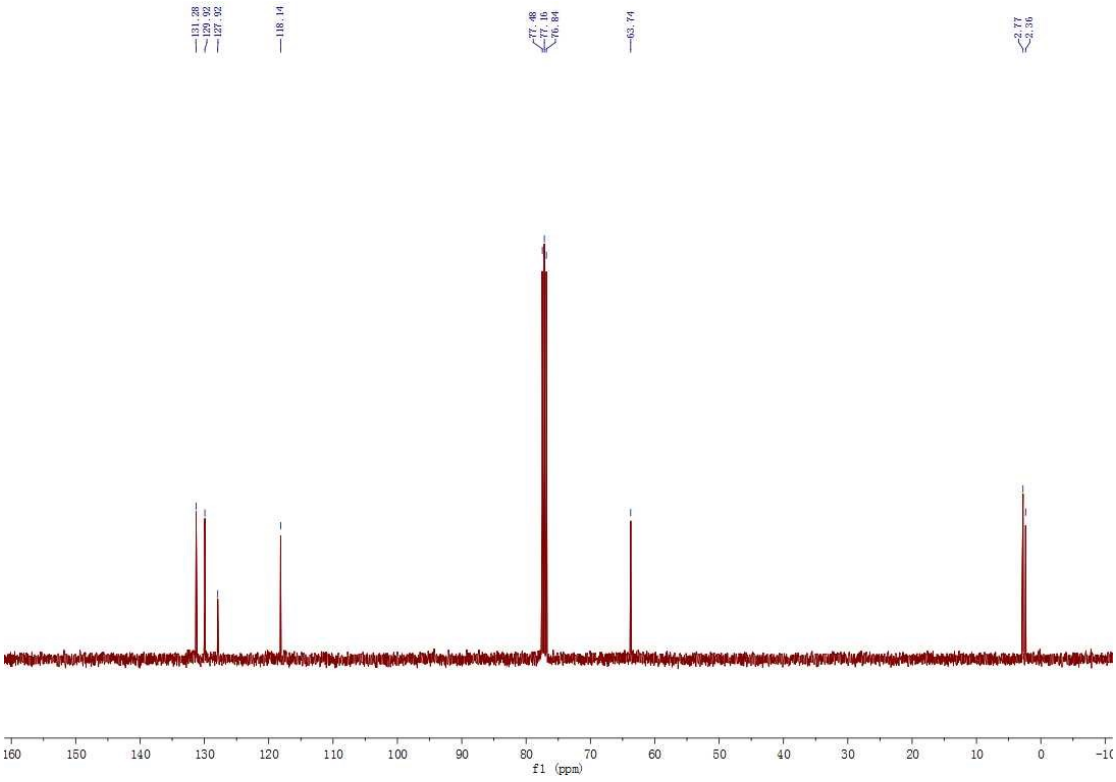

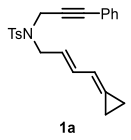

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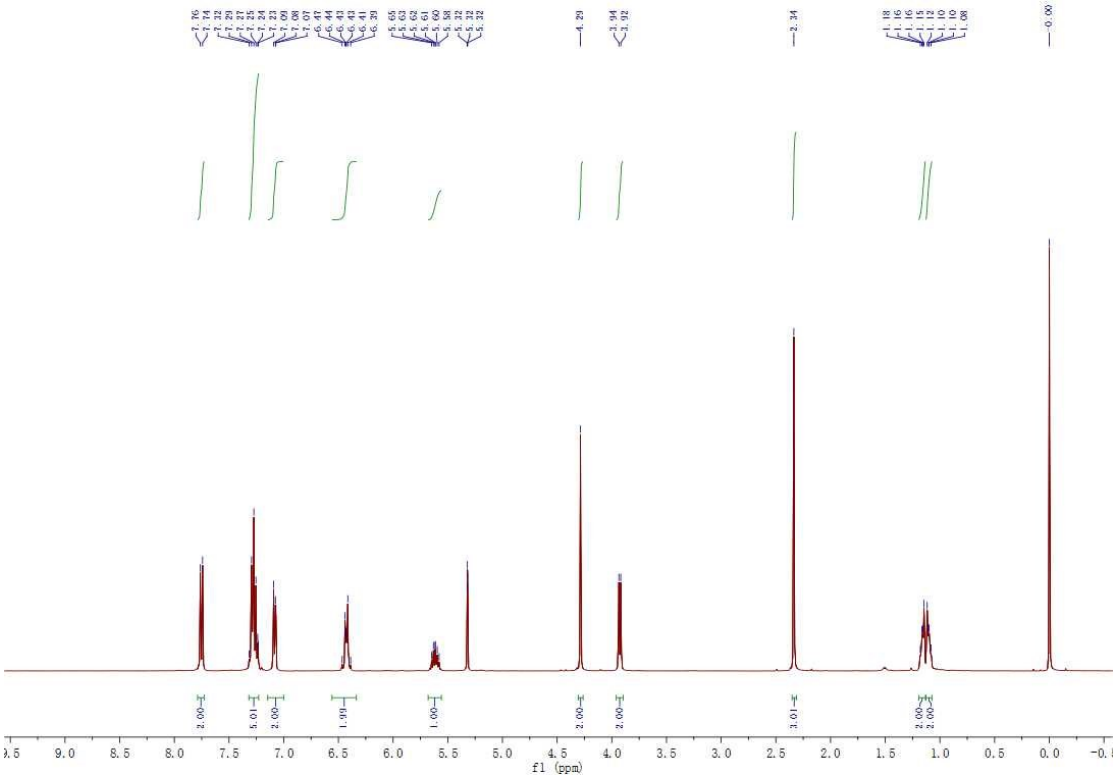

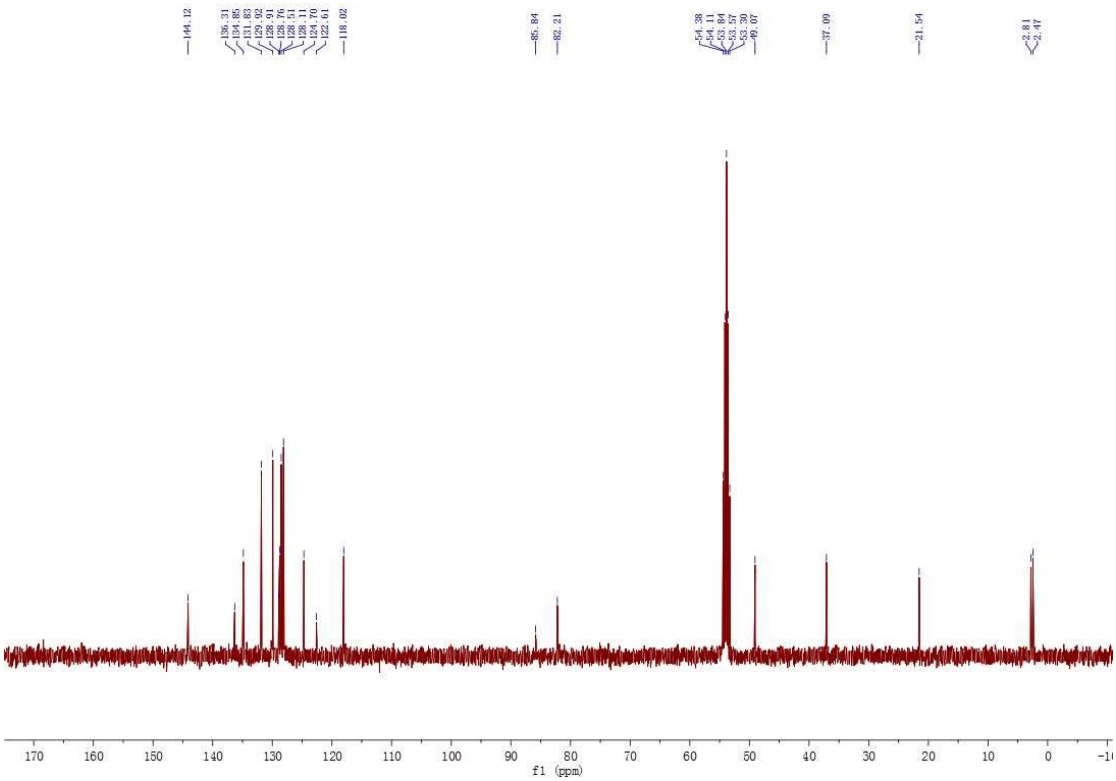

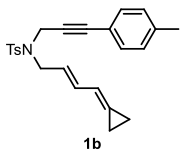

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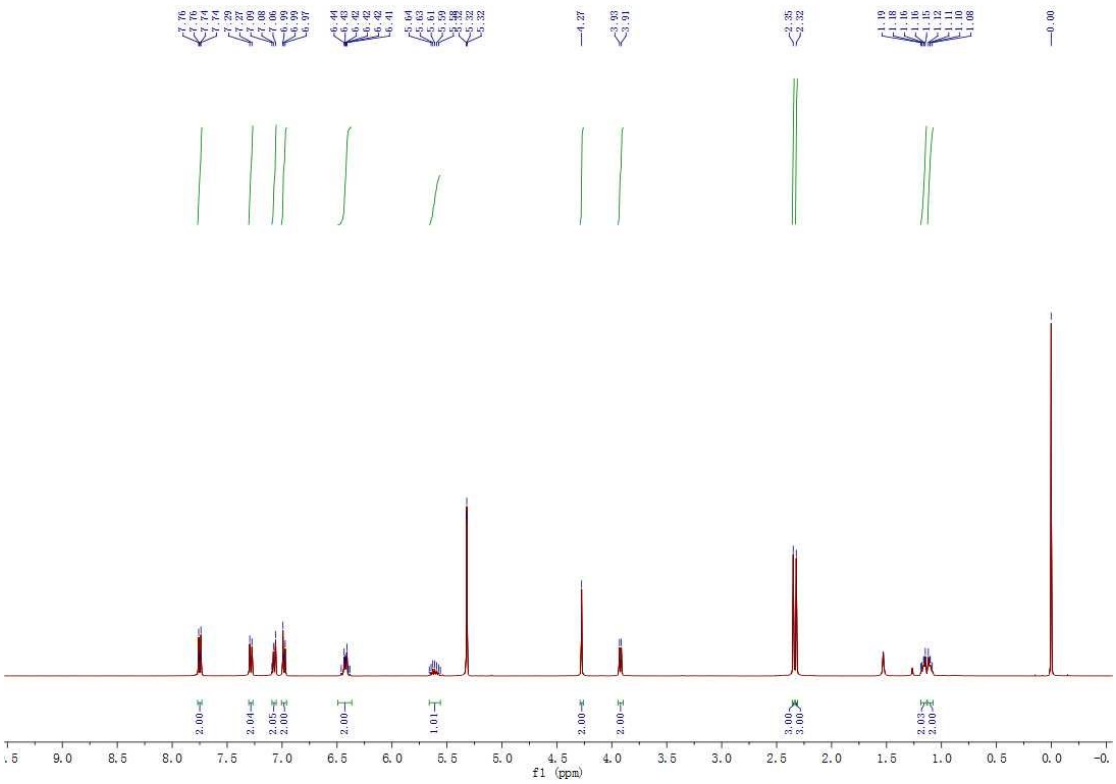

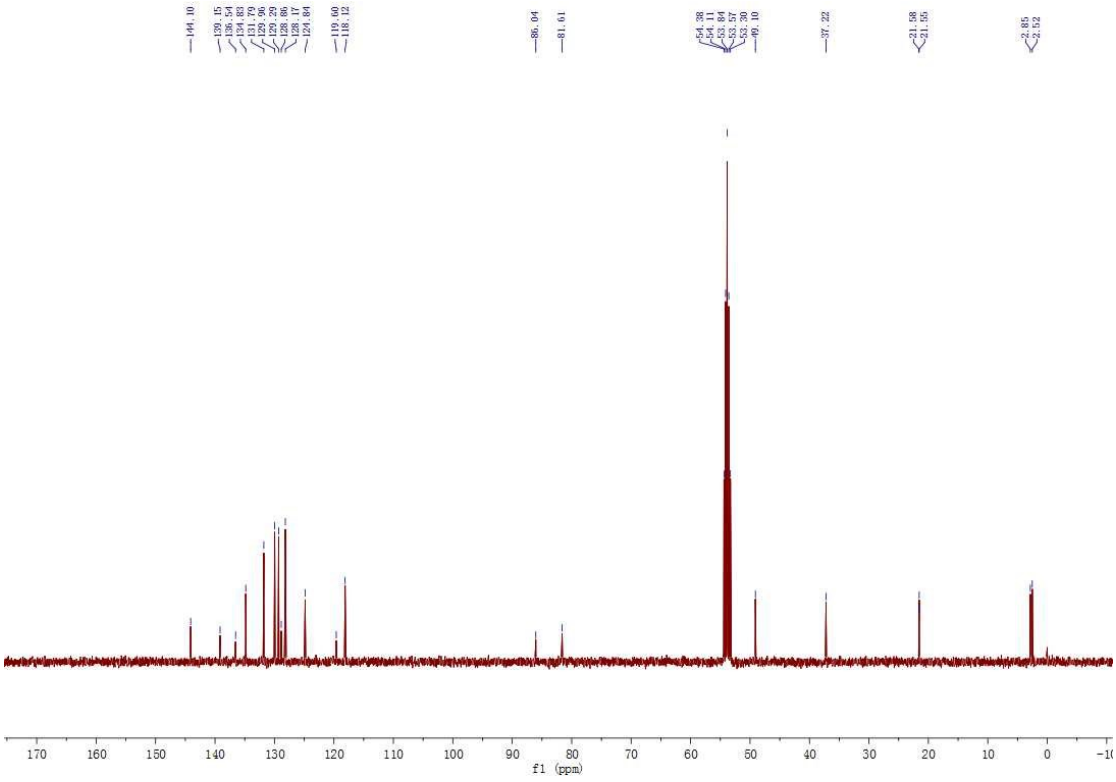

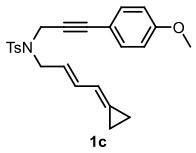
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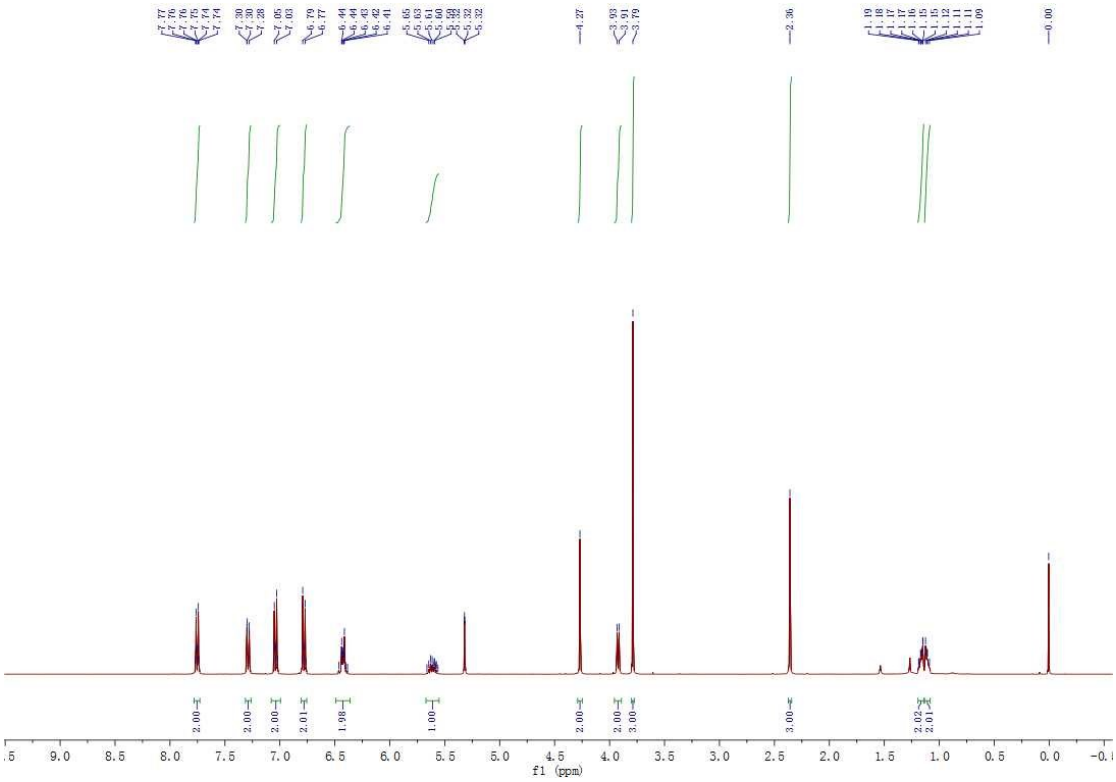
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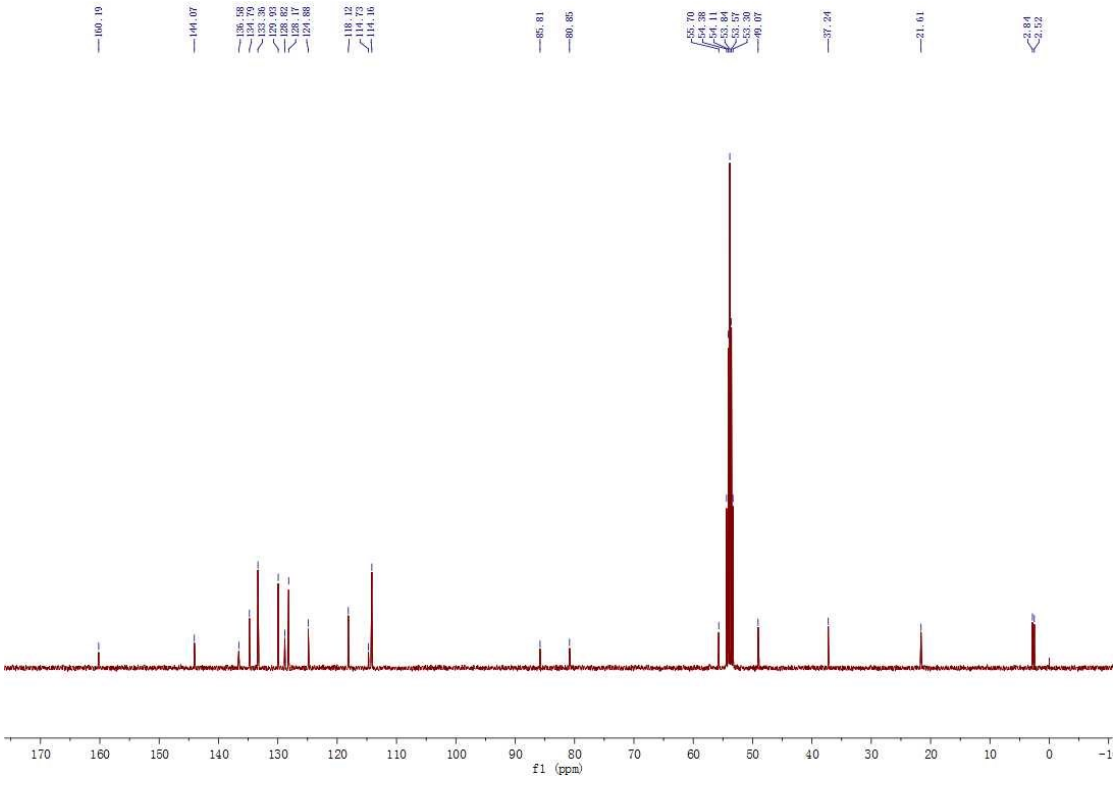
f1 (ppm)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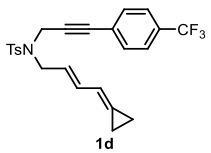

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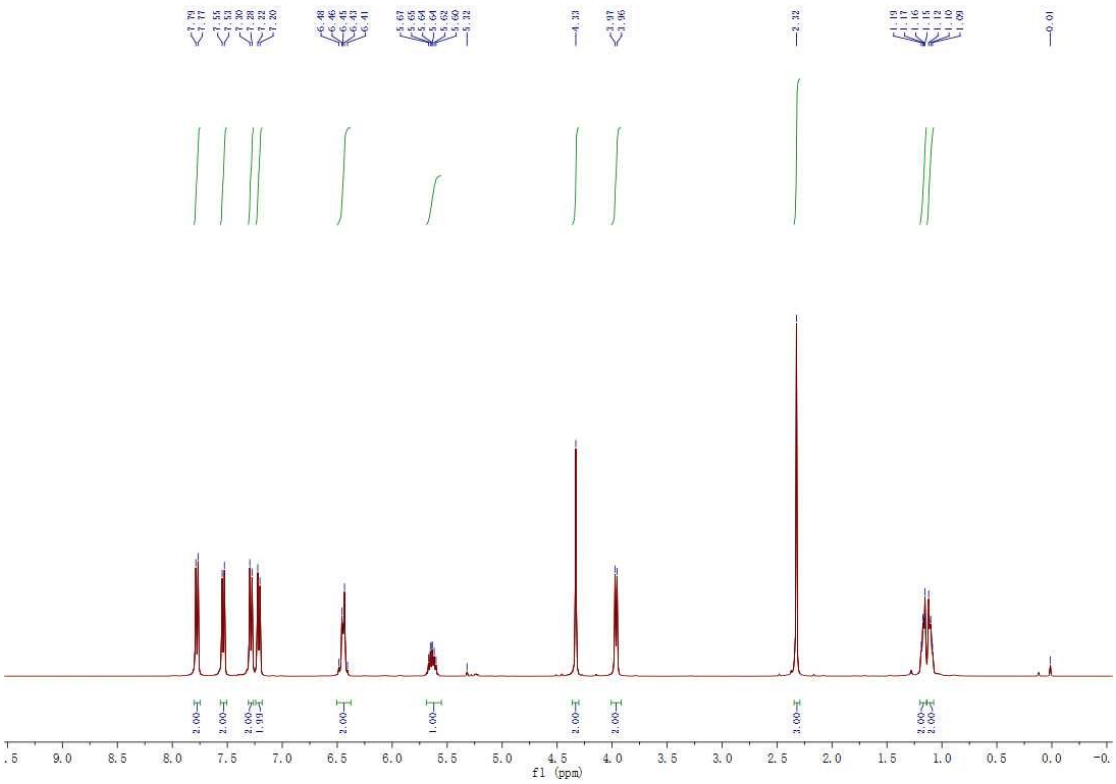

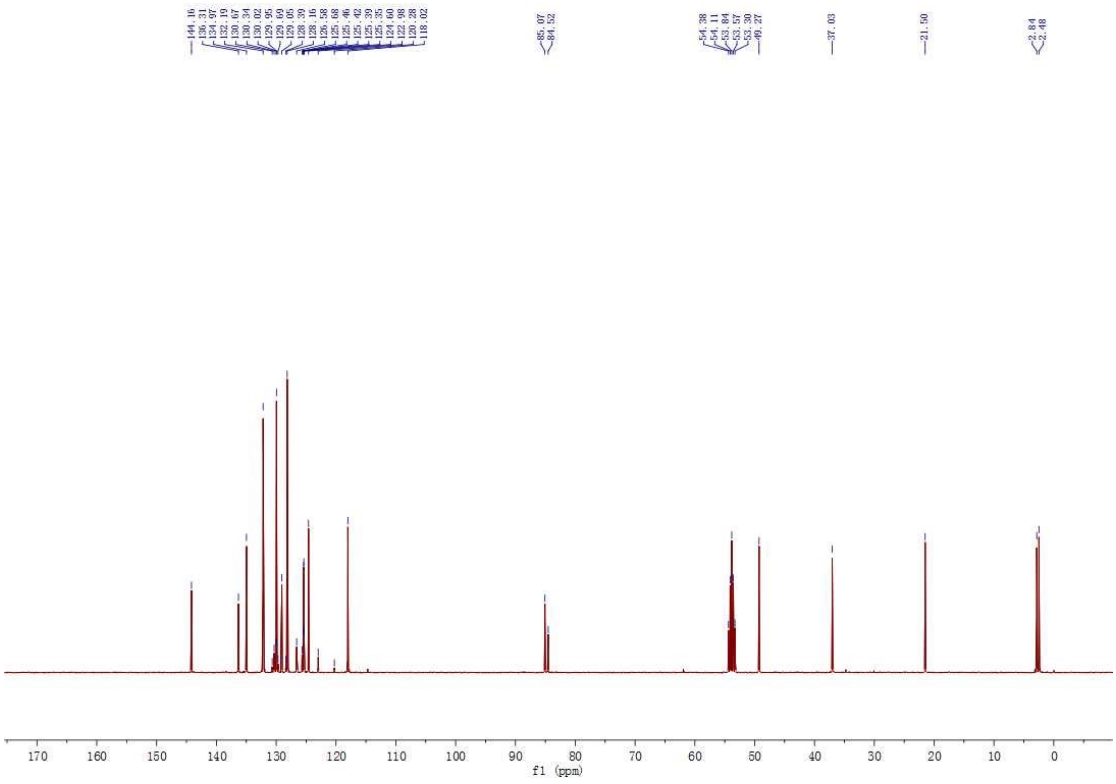

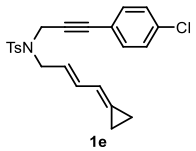

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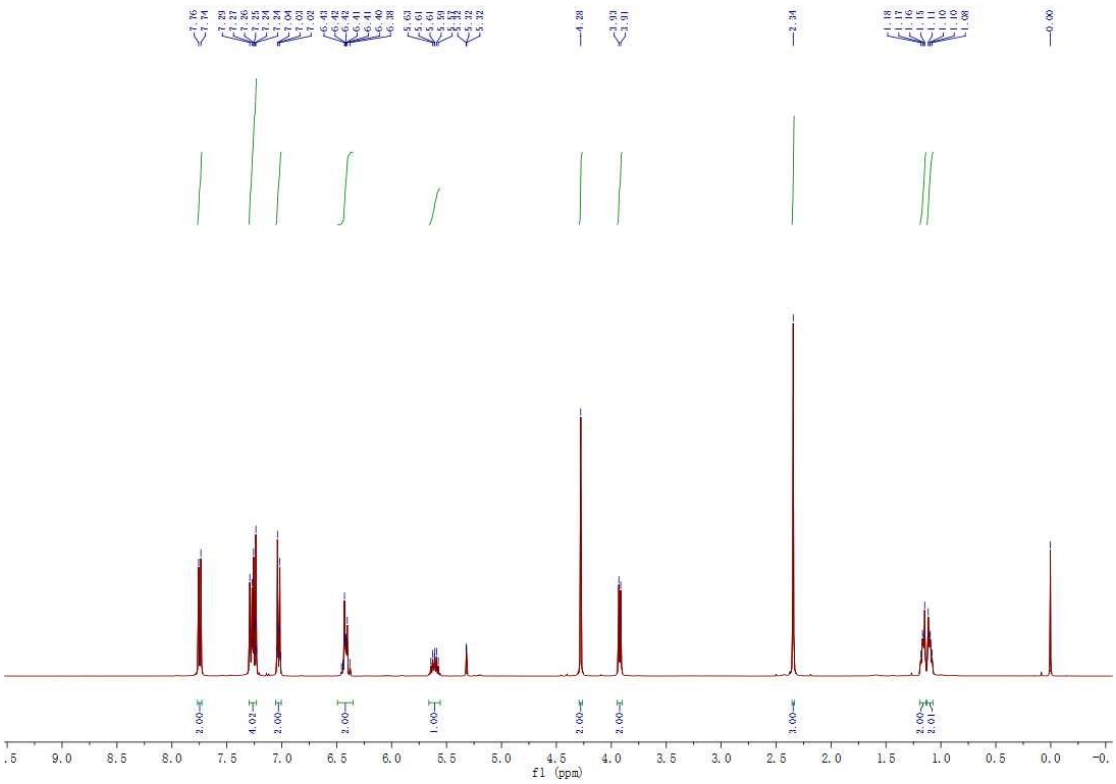

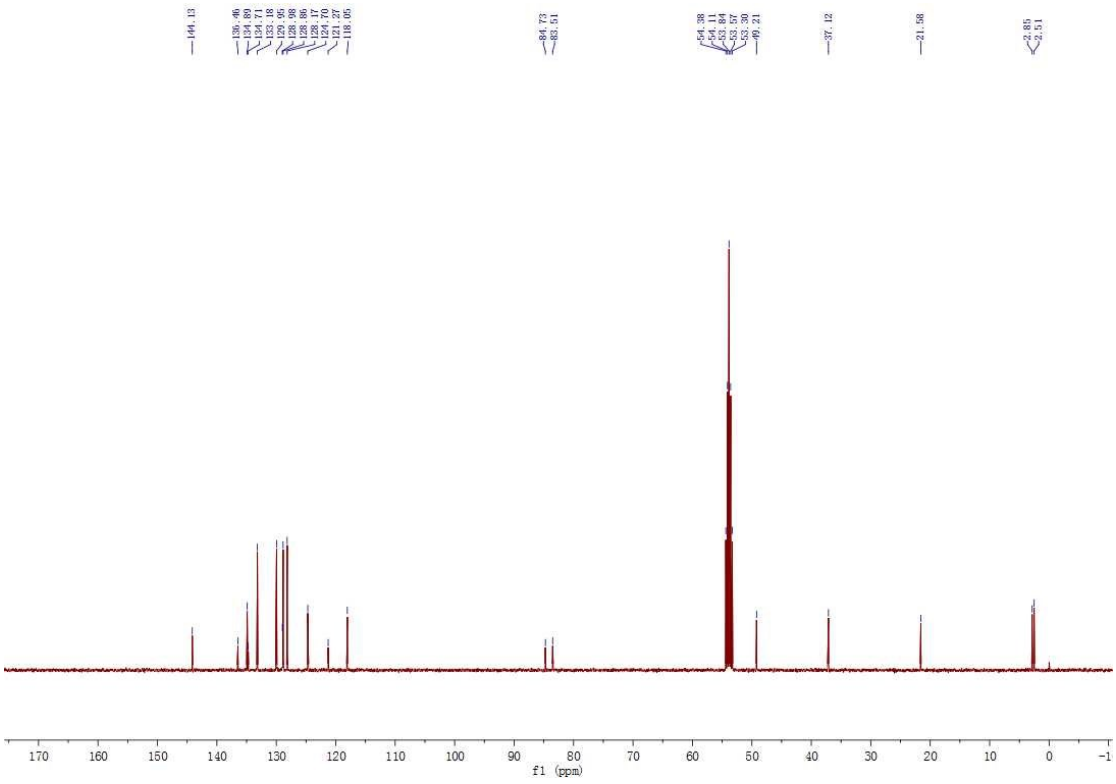

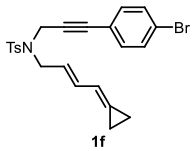

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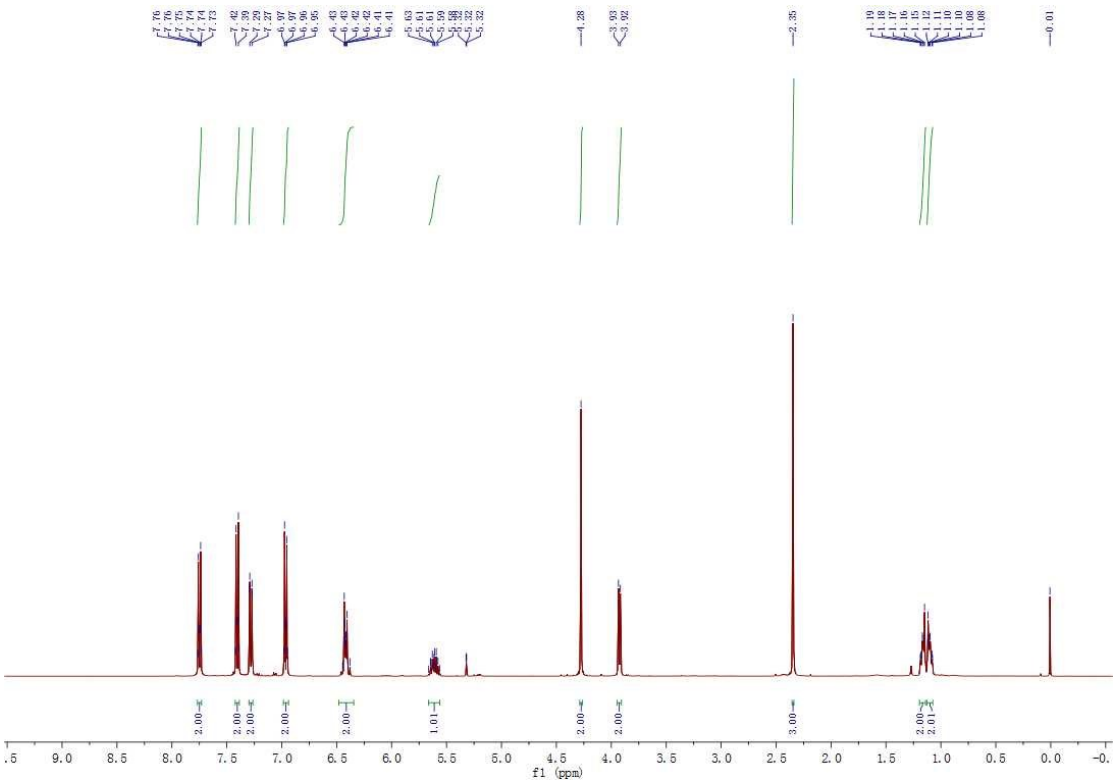

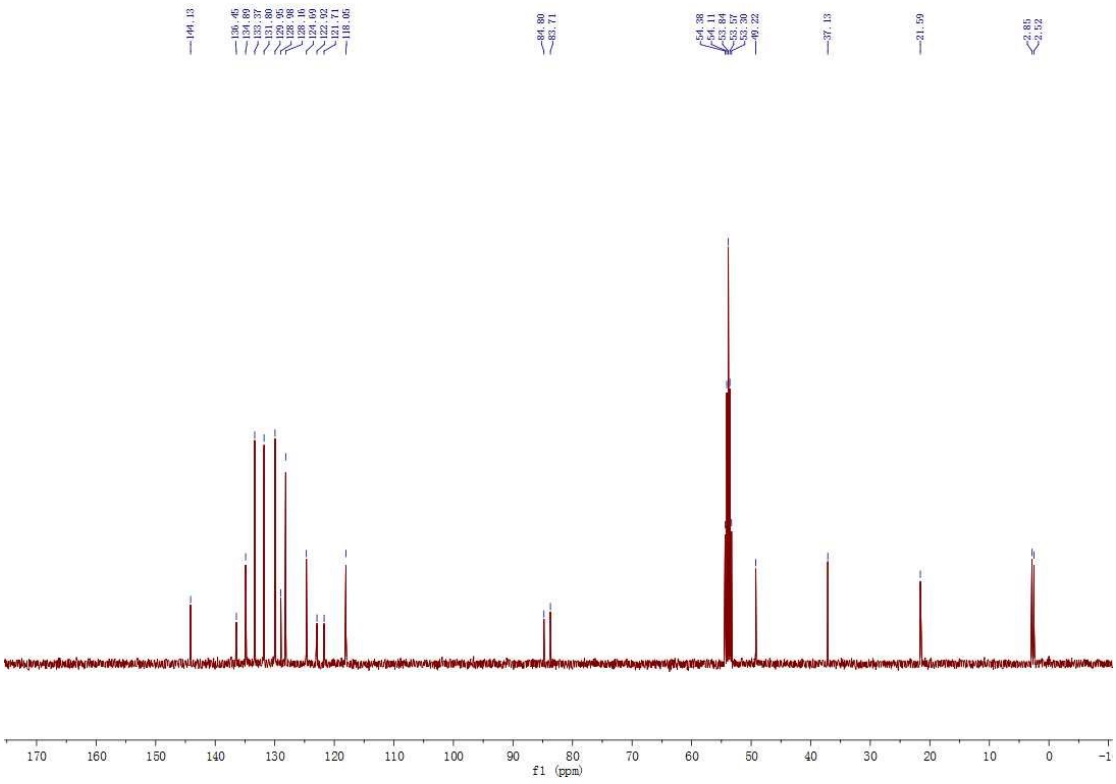

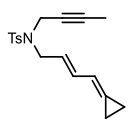
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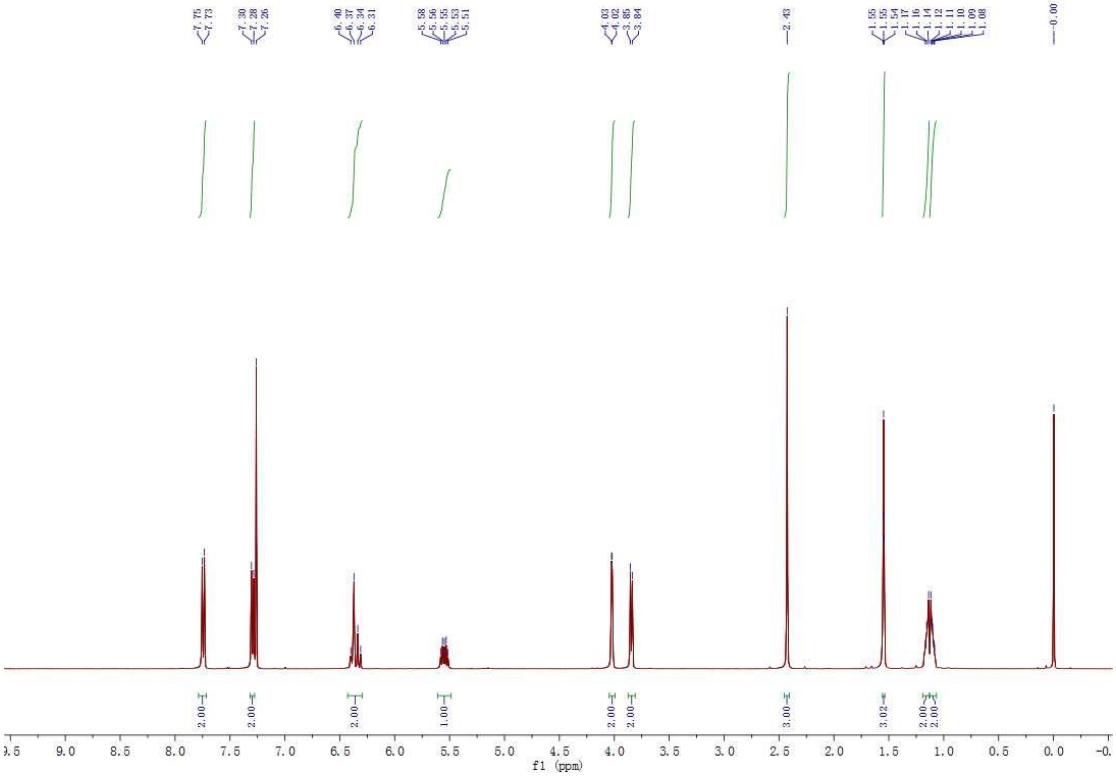
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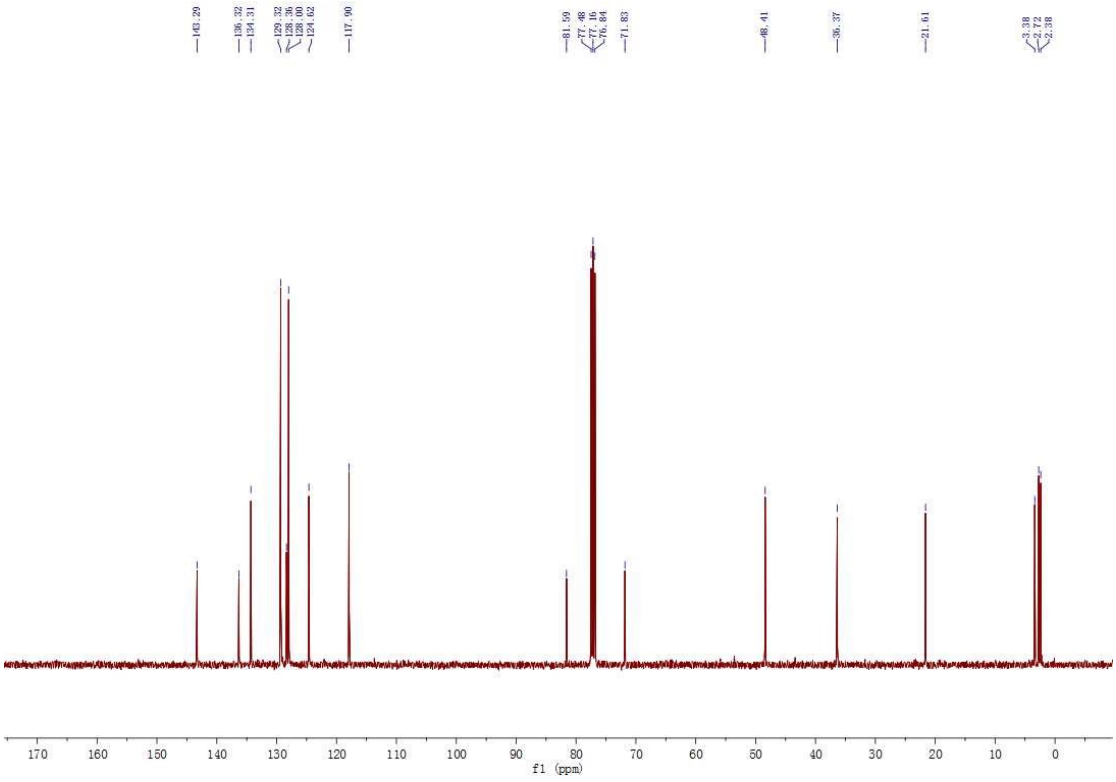
f1 (ppm)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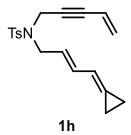

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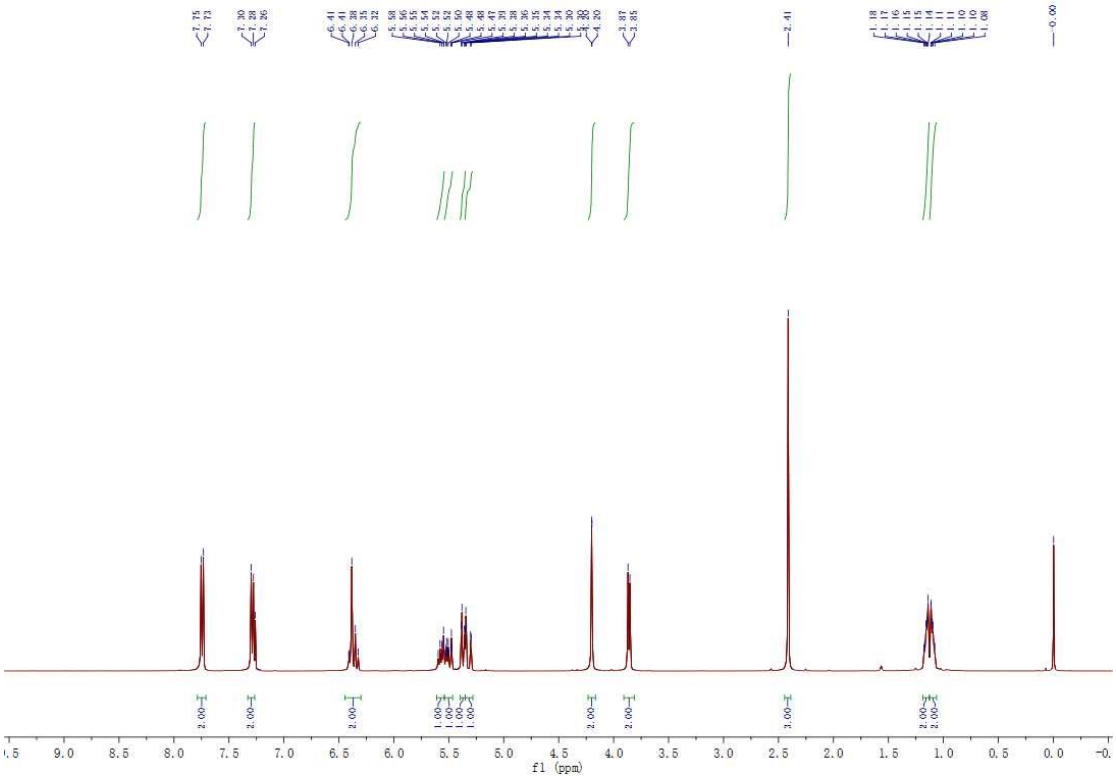

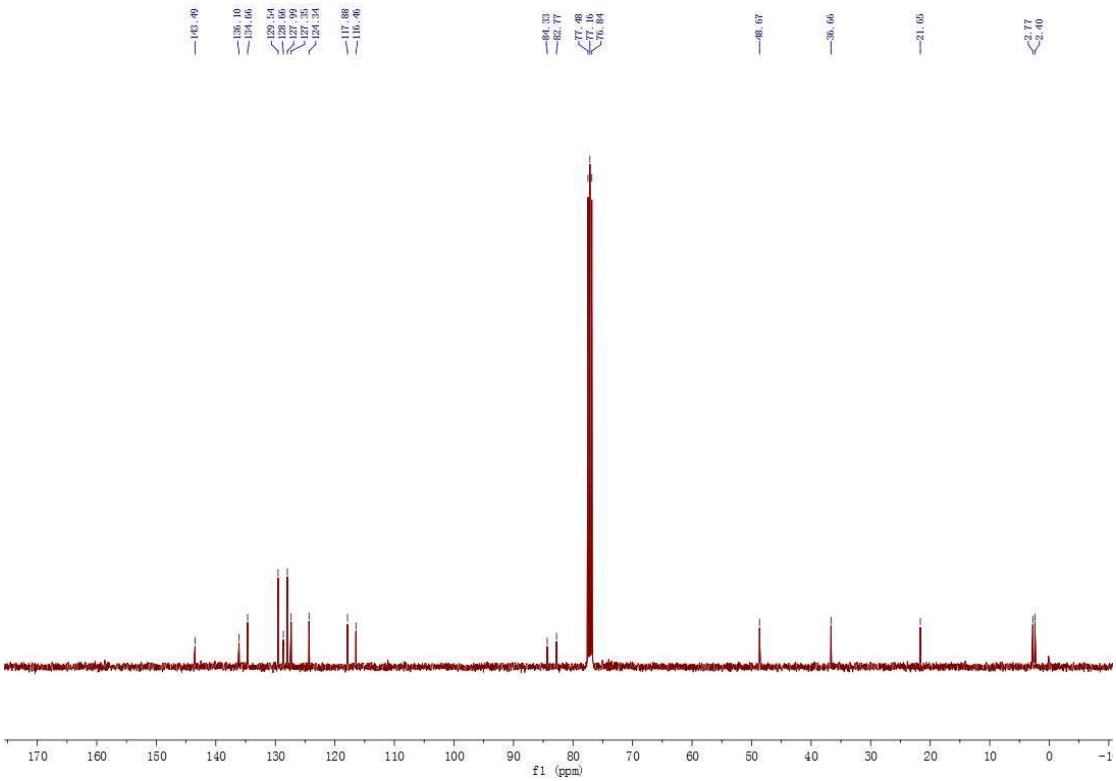

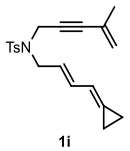

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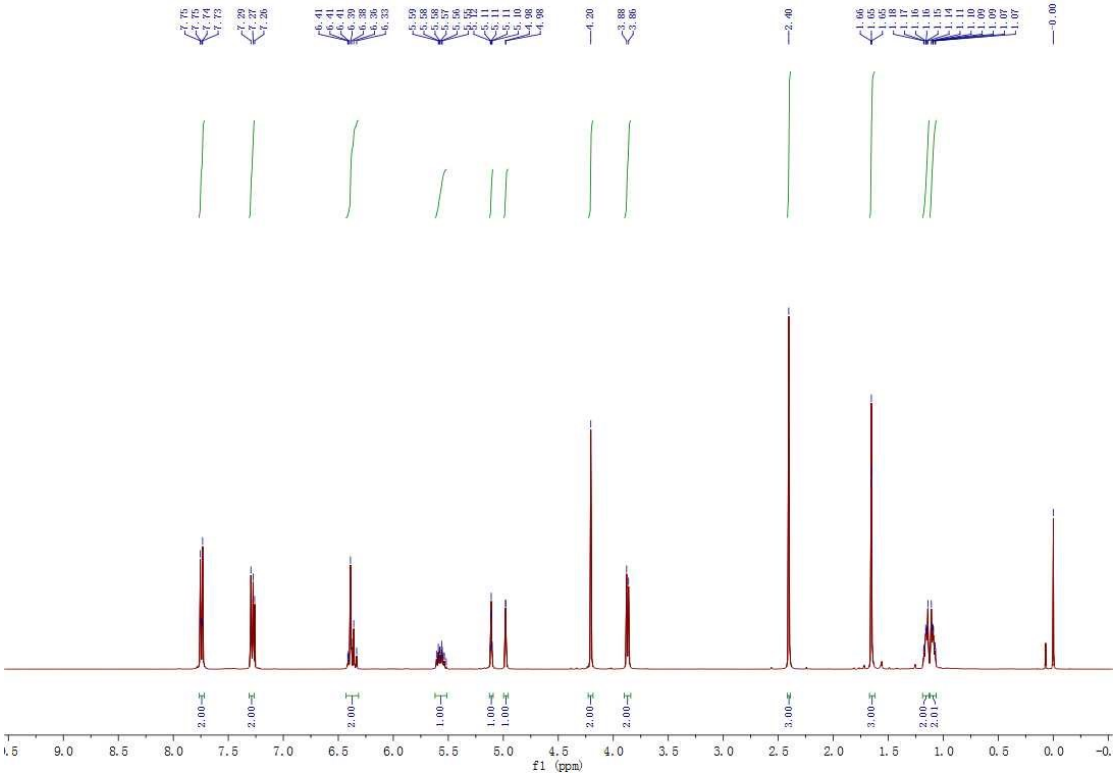

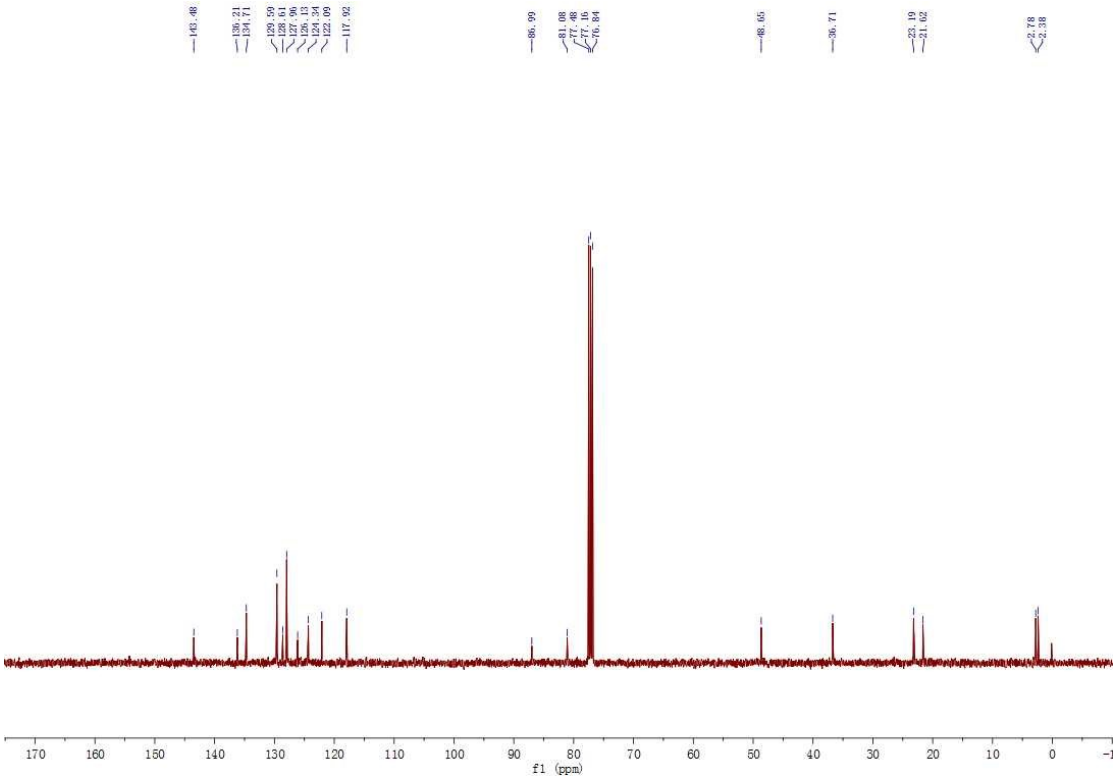

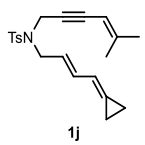

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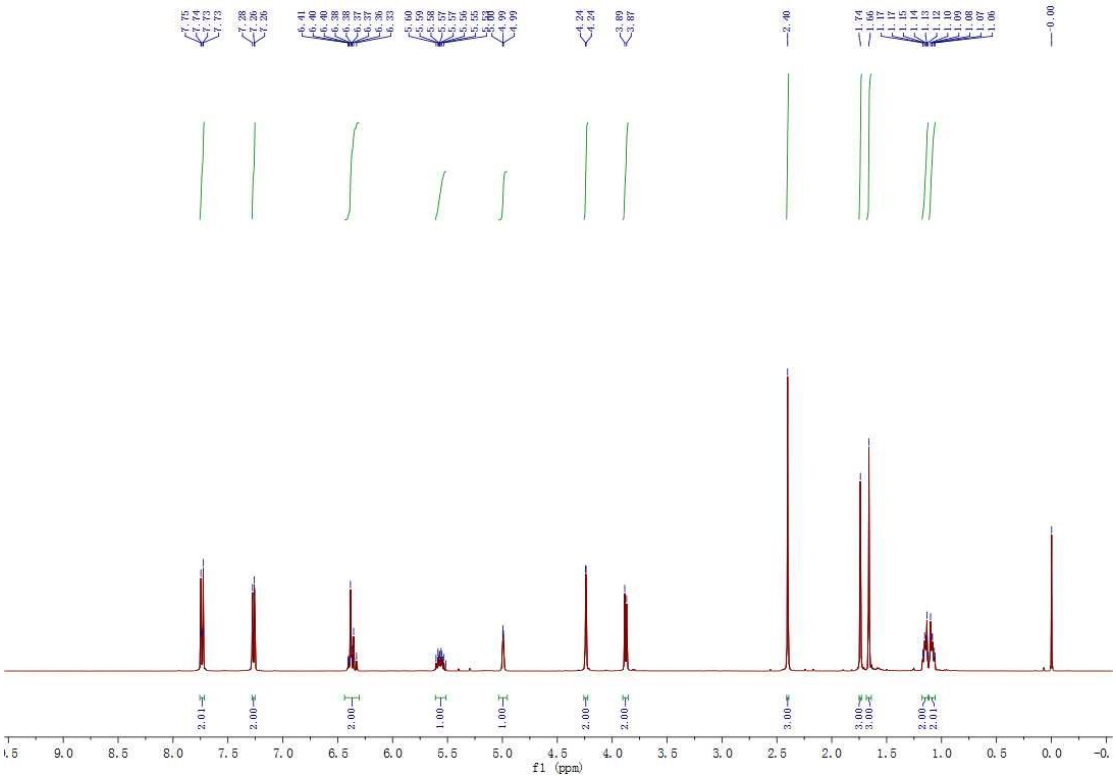

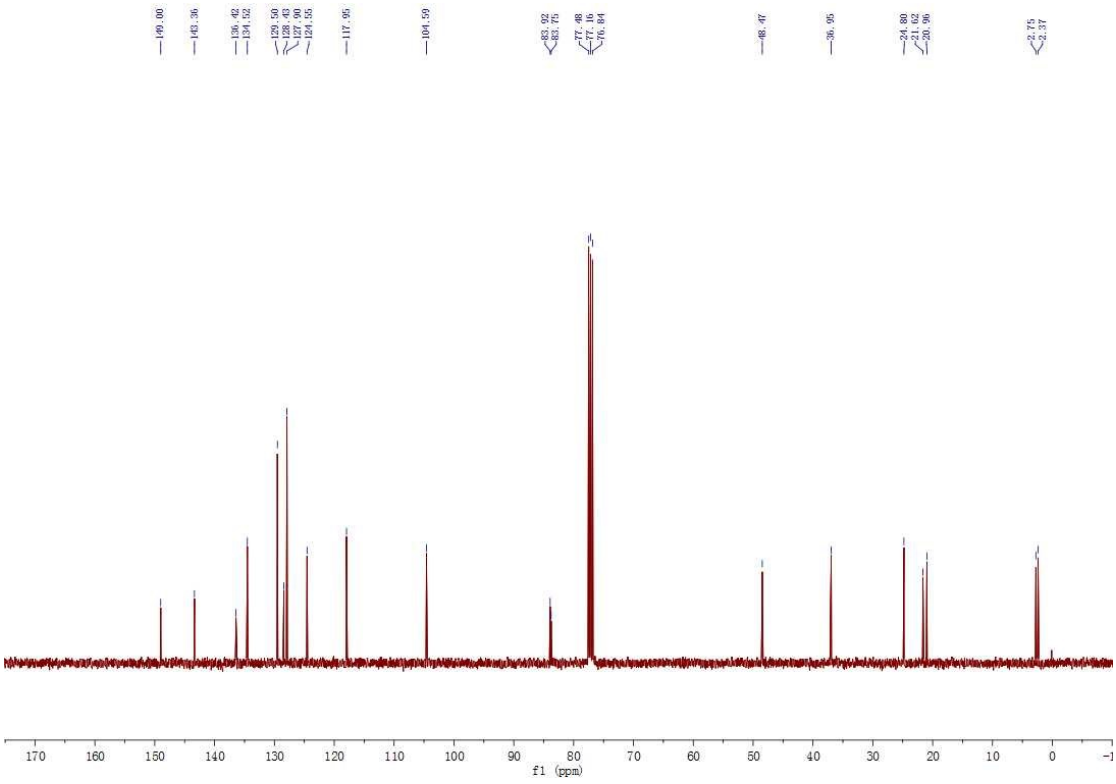

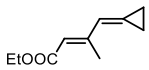
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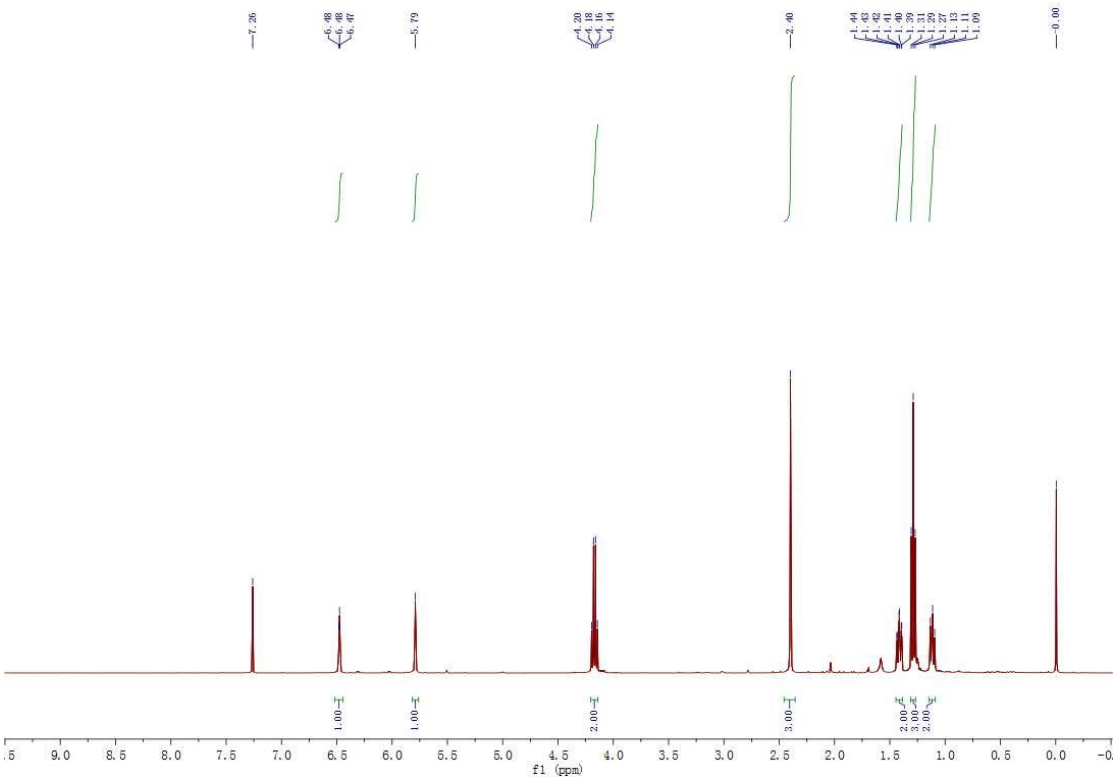
S14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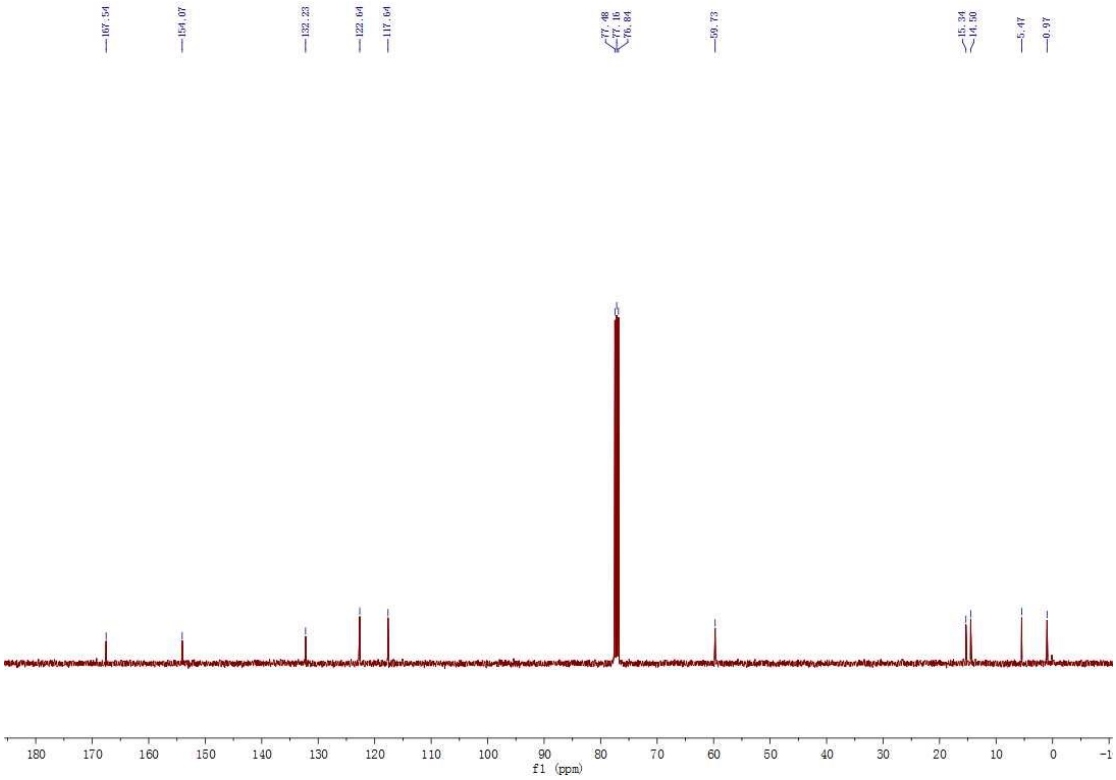
4.16
4.14
2.40
1.44
1.43
1.42
1.41
1.40
1.39
1.31
1.29
1.27
1.13
1.11
1.09
0.00
1.00
1.00
2.09
3.00
2.09
3.00
2.00
f1 (ppm)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154.07
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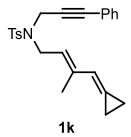
122.64
117.64
77.48
77.16
76.84
59.73
15.34
14.50
5.47
0.97
f1 (ppm)



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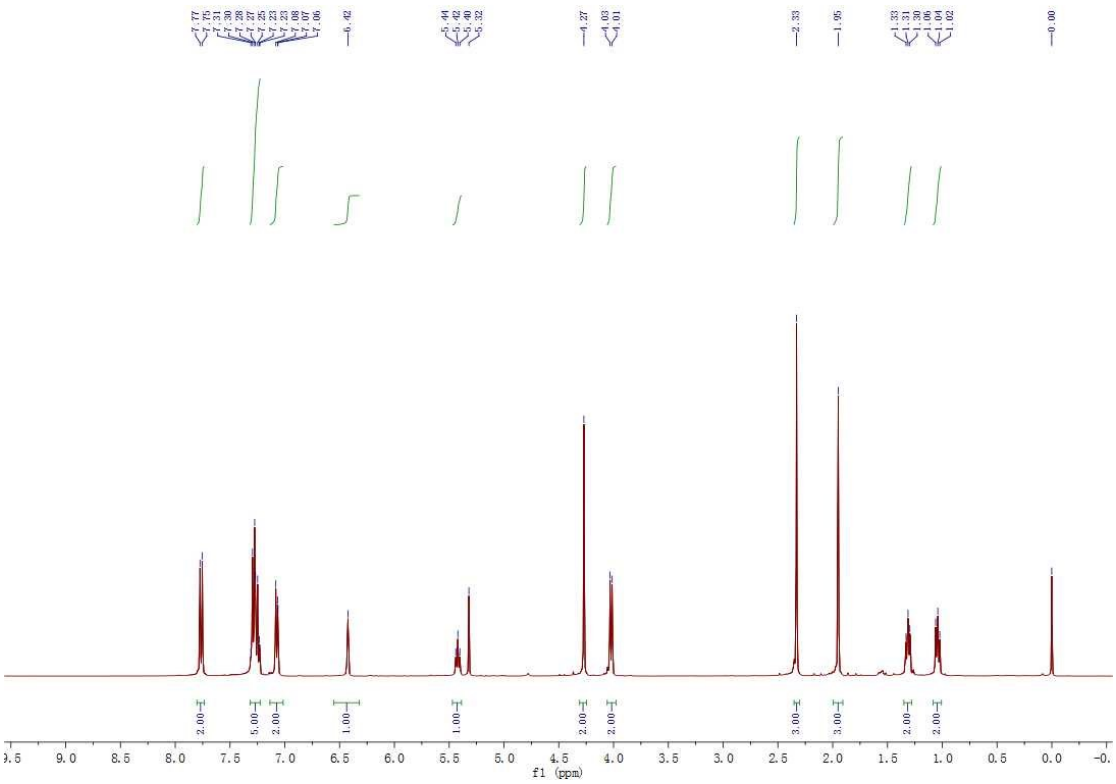
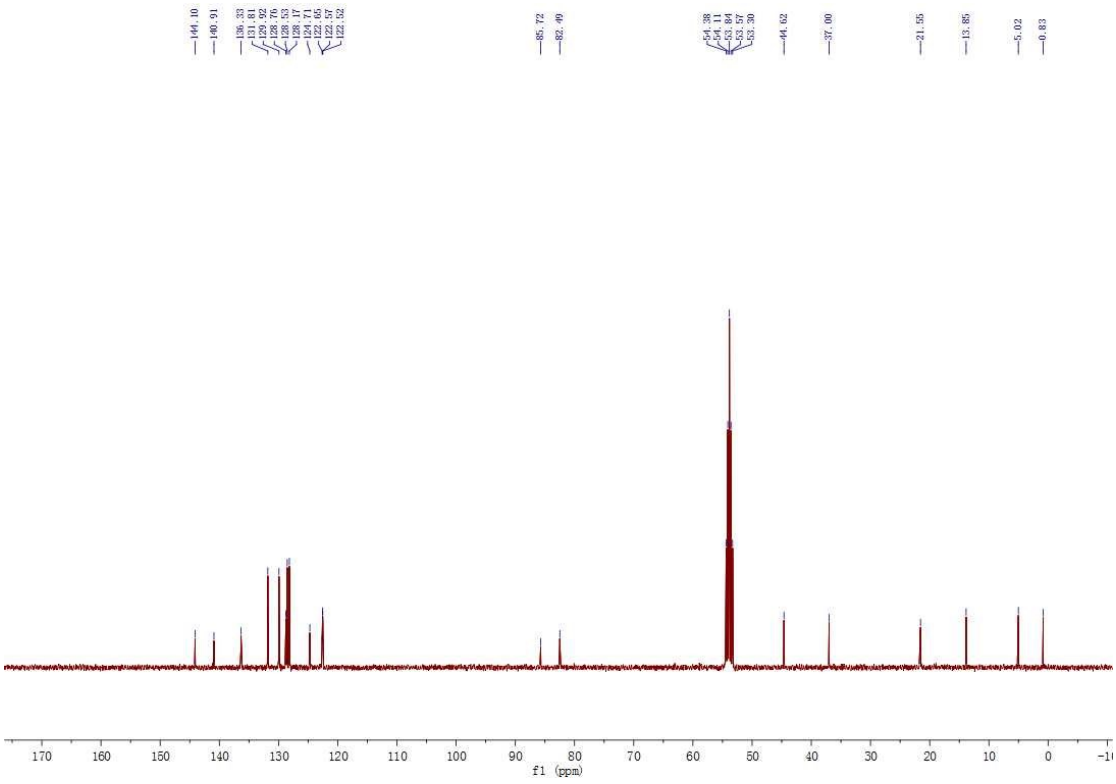
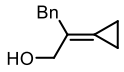
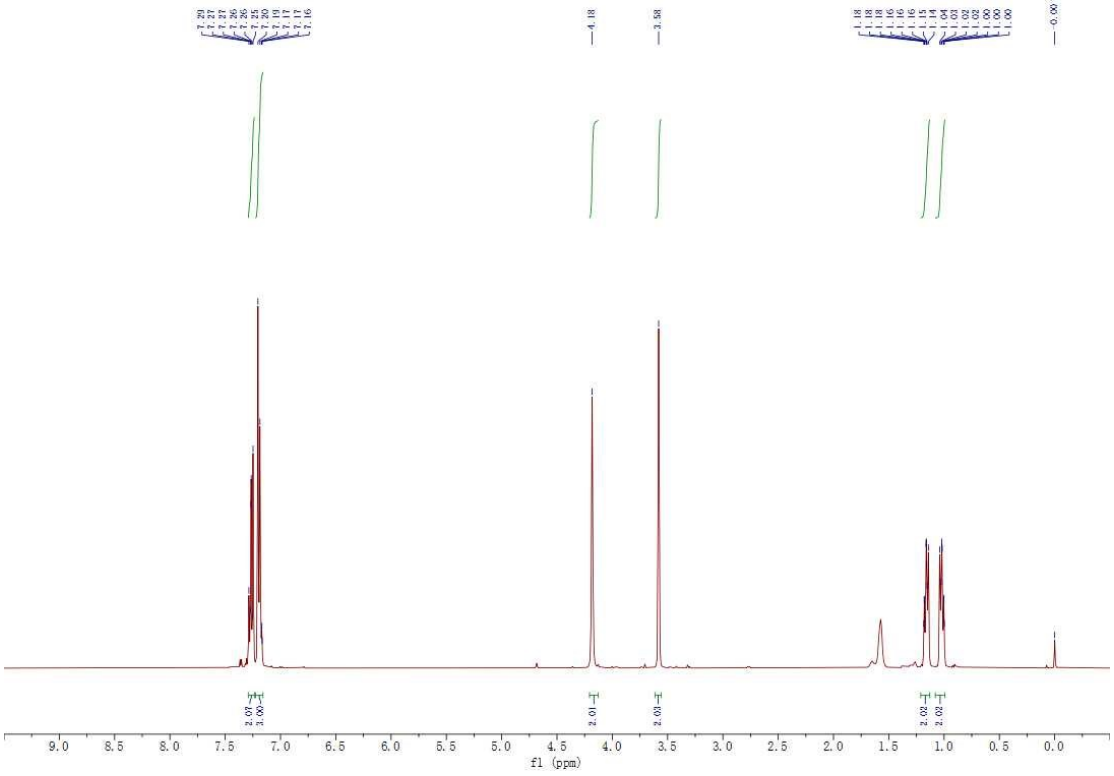
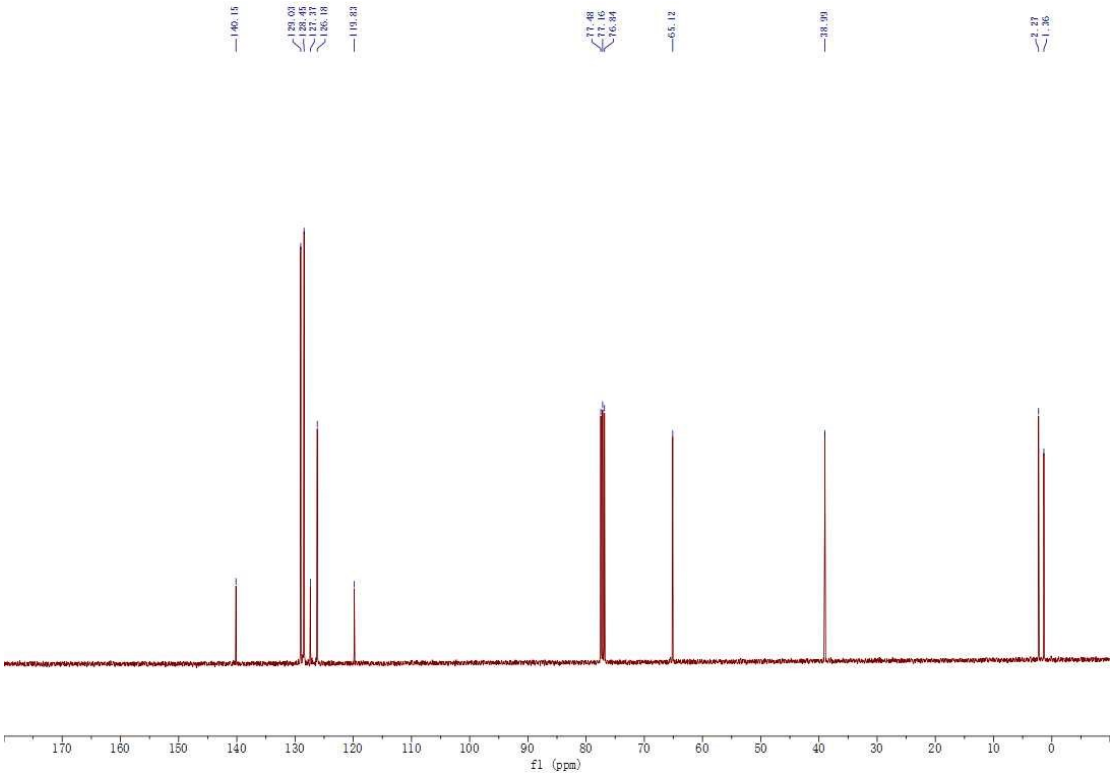


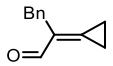




S17






Bn
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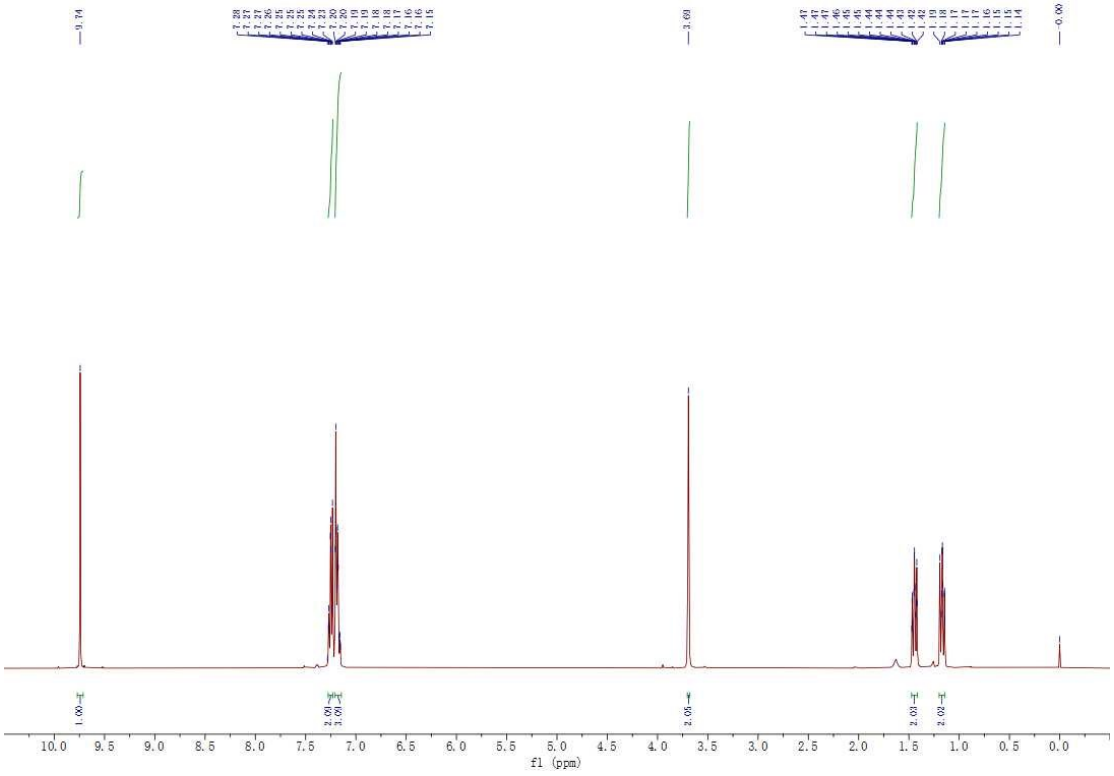
S18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7.18
7.17
7.16
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1.18
1.17
1.16
1.15
1.14
0.00
1.00
2.09
3.09
2.05
2.01
2.02
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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2.5
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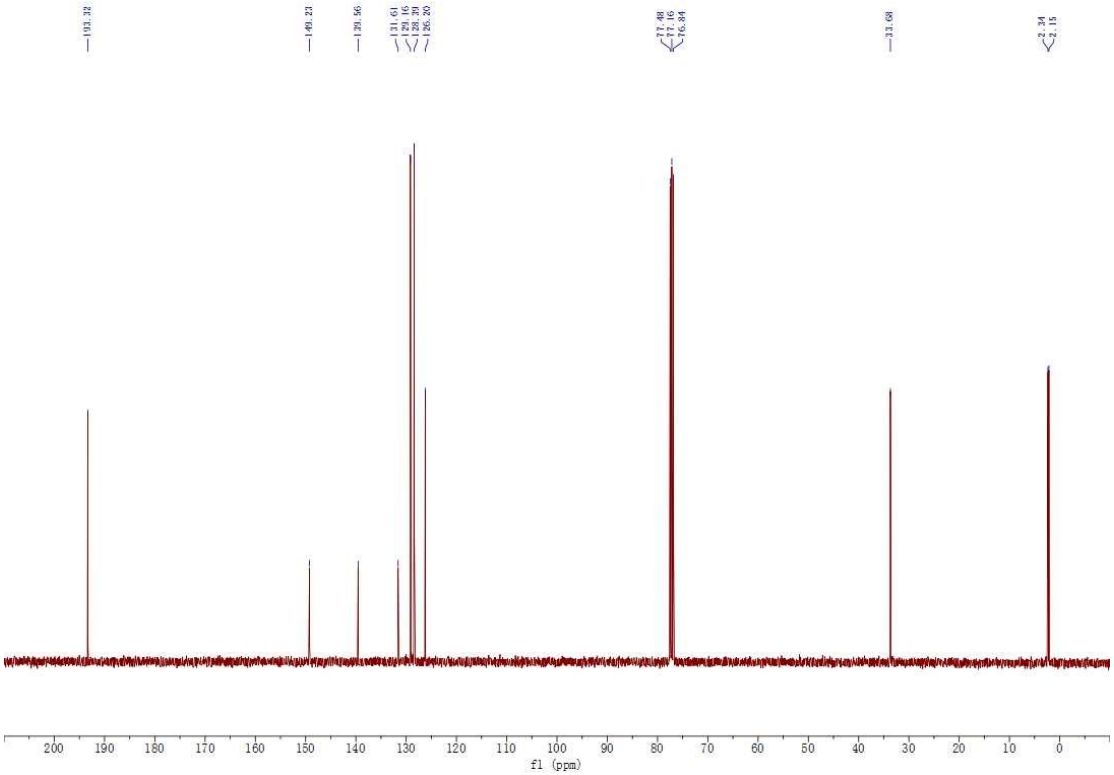
1.0
0.5
0.0
f1 (ppm)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76.84
33.68
2.34
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200
190
180
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130
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90
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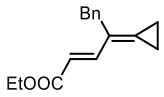
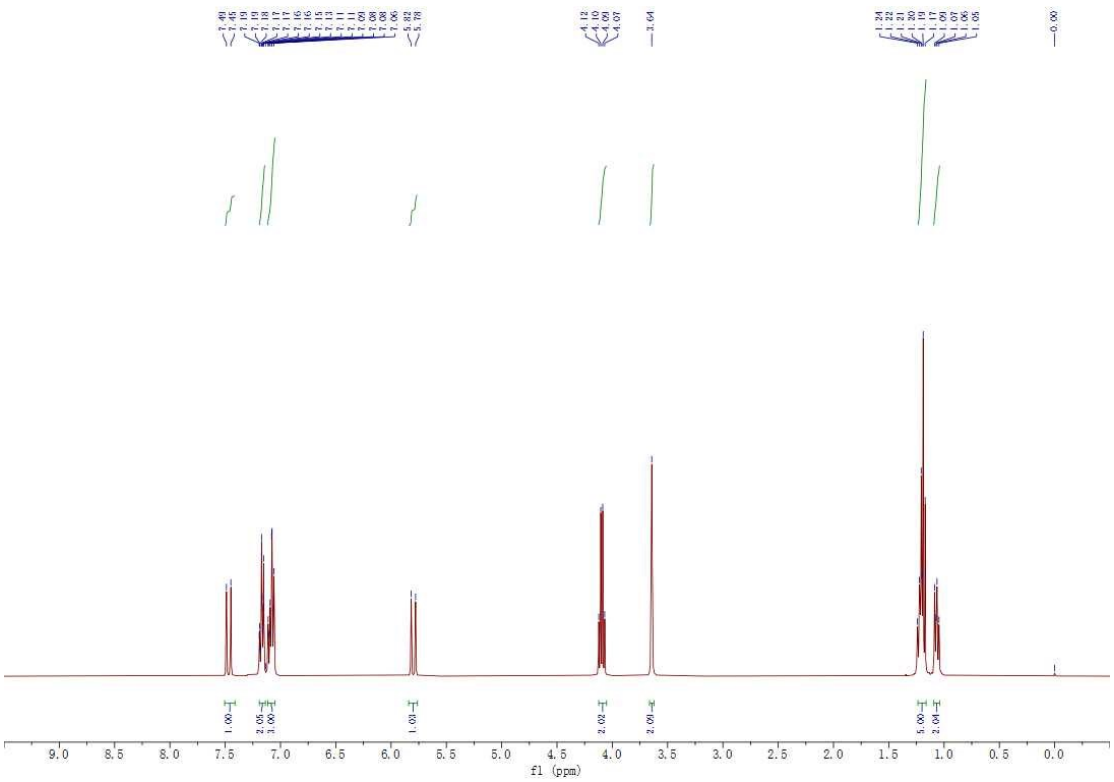
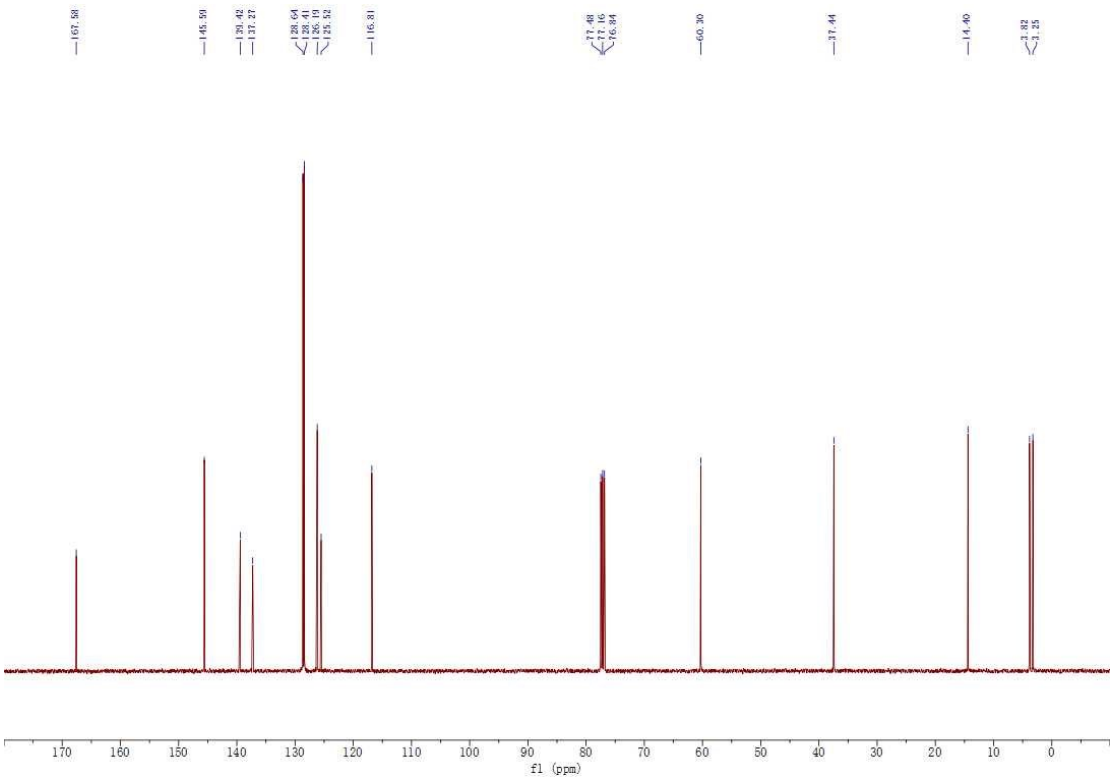
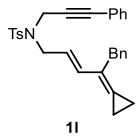
f1 (ppm)



S19







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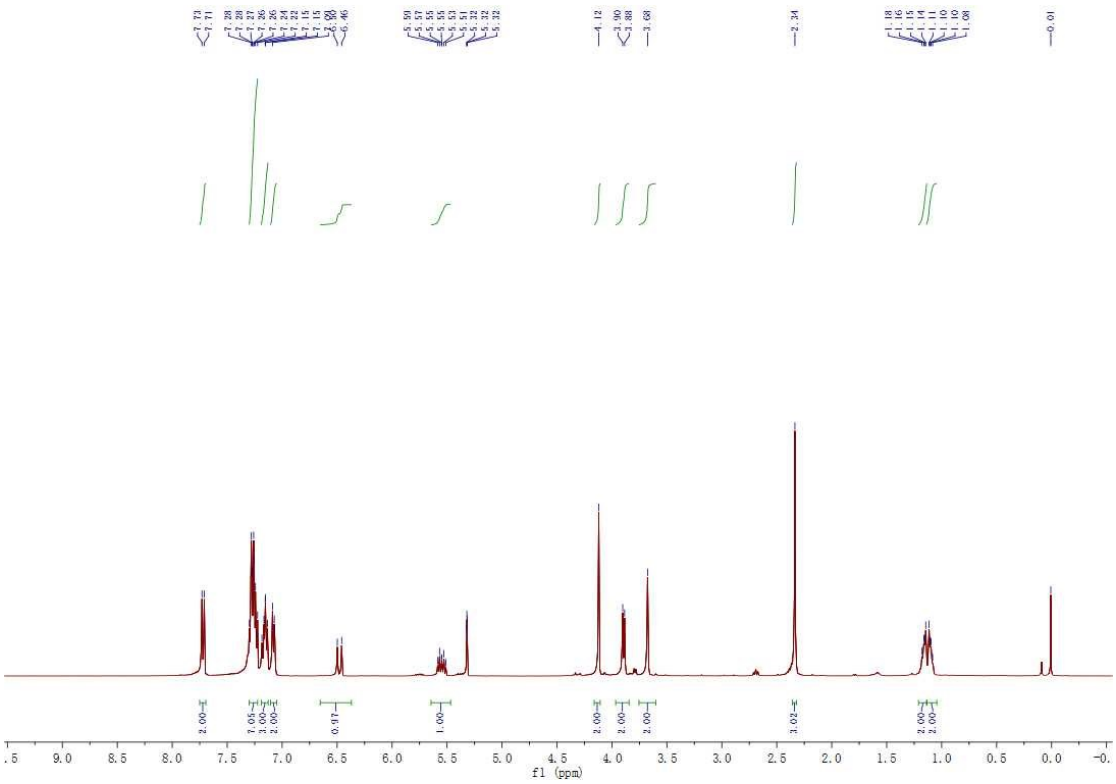
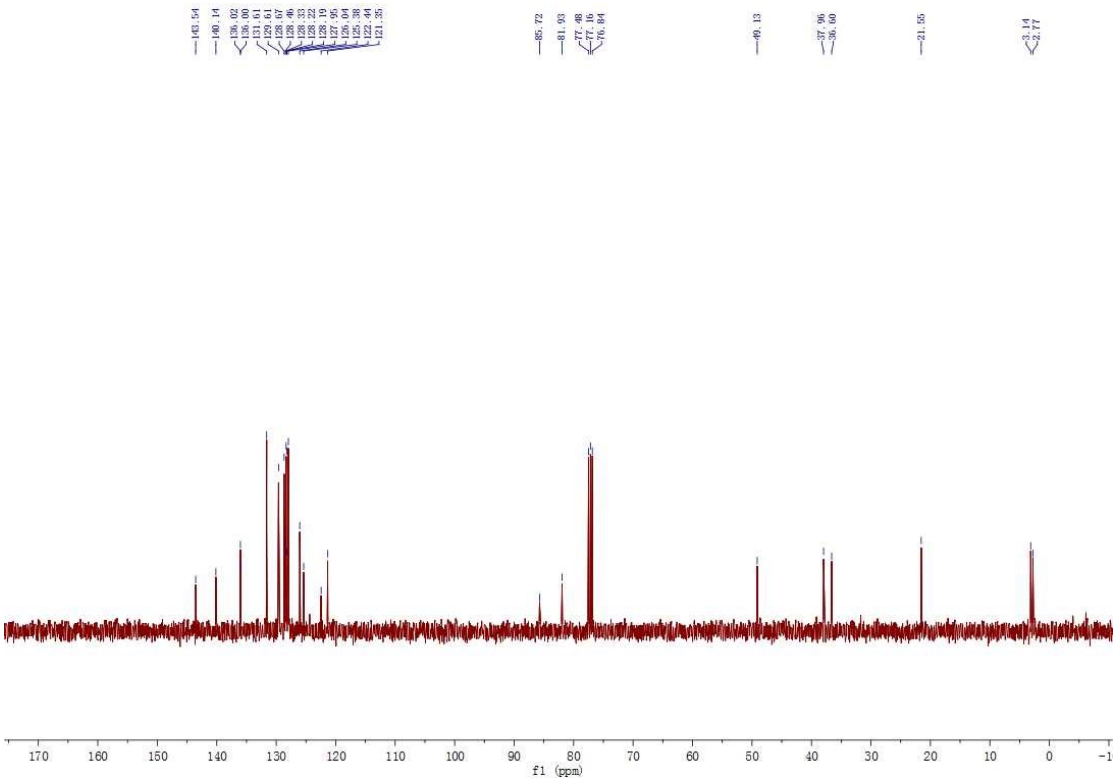
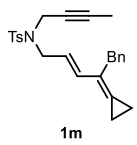
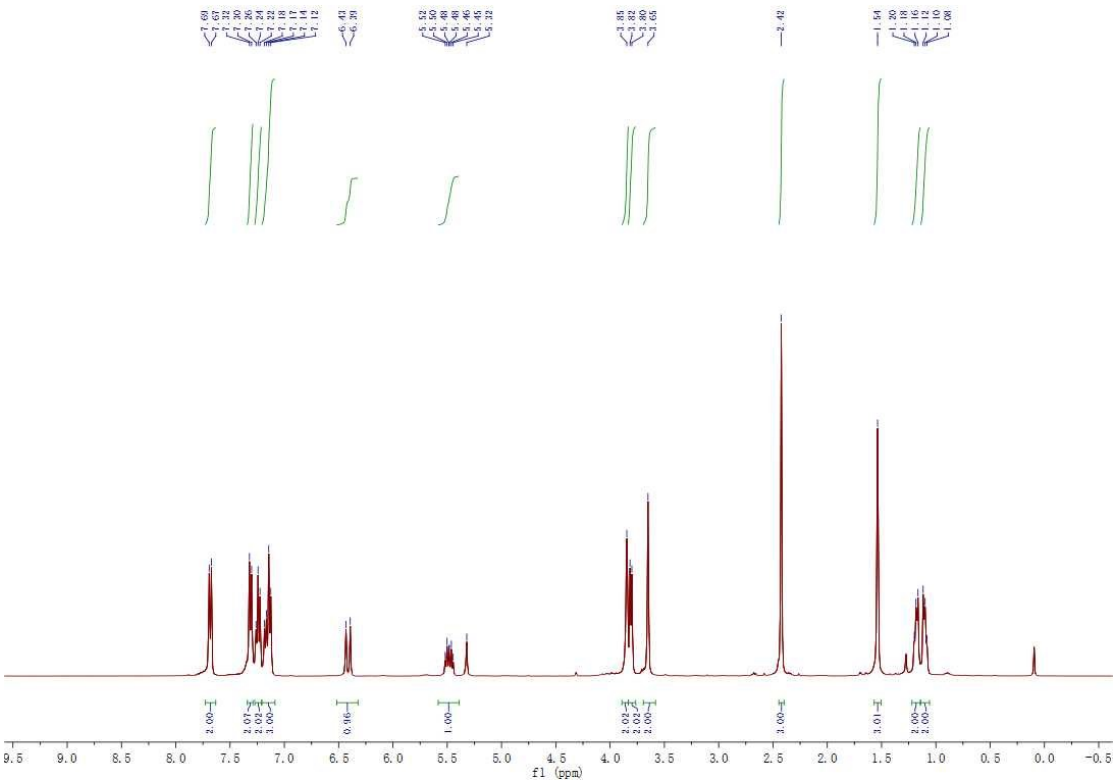
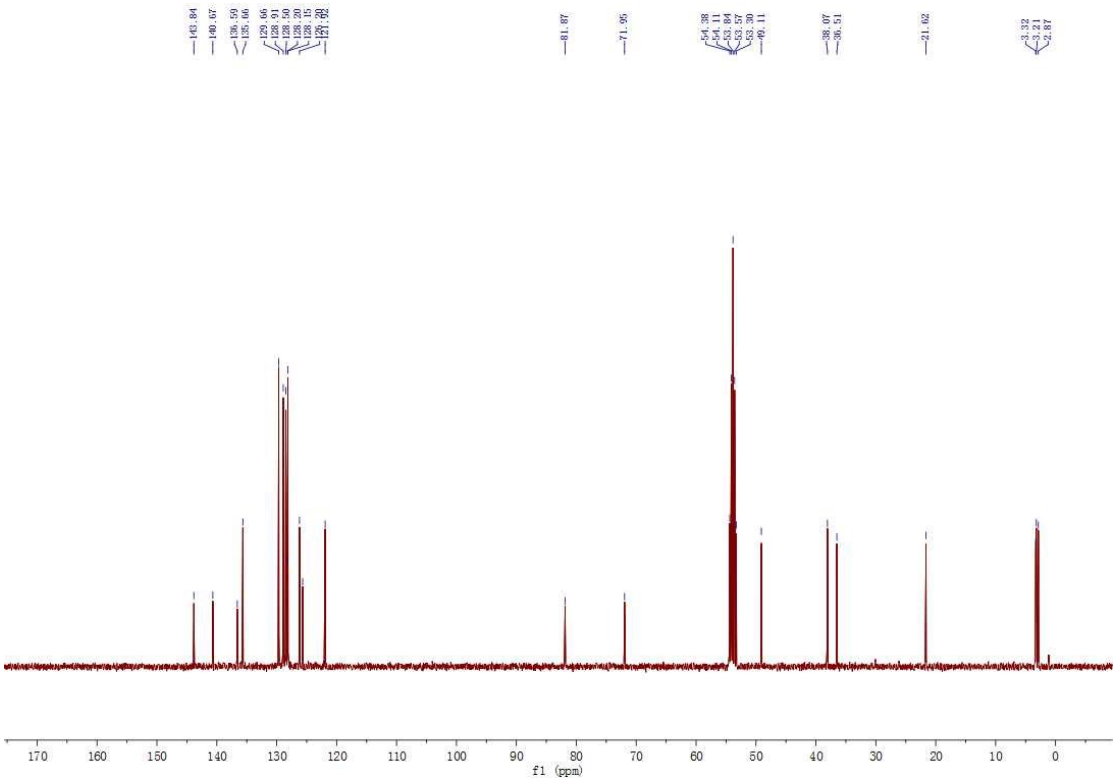


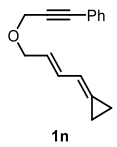




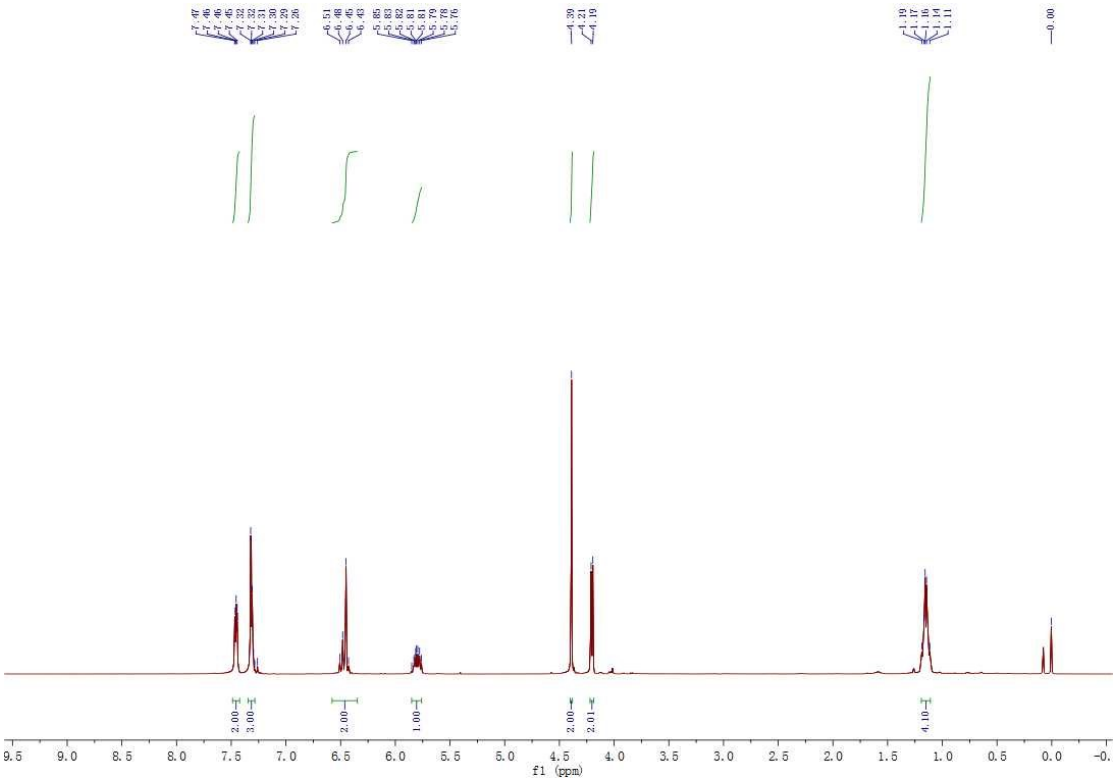
1m






Ph
O

1n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5.82
5.81
5.81
5.79
5.78
5.76
4.39
4.21
4.19
1.19
1.17
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1.14
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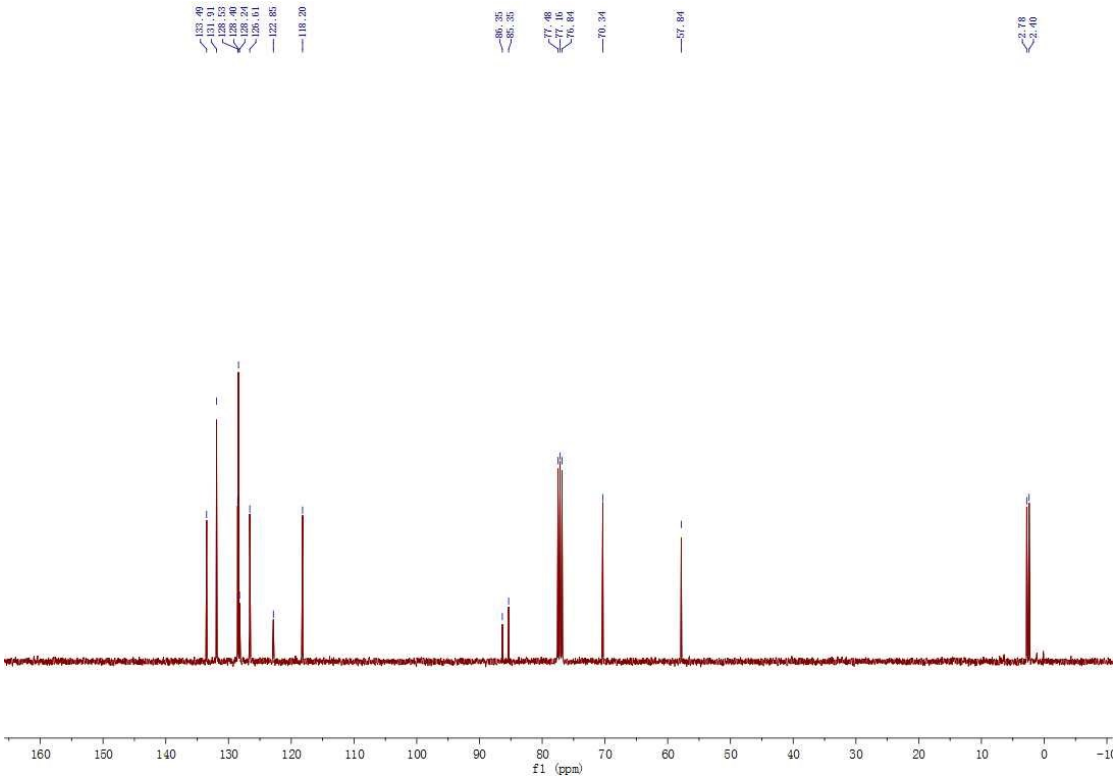
4.10
f1 (ppm)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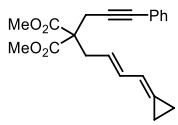
2.40
f1 (ppm)



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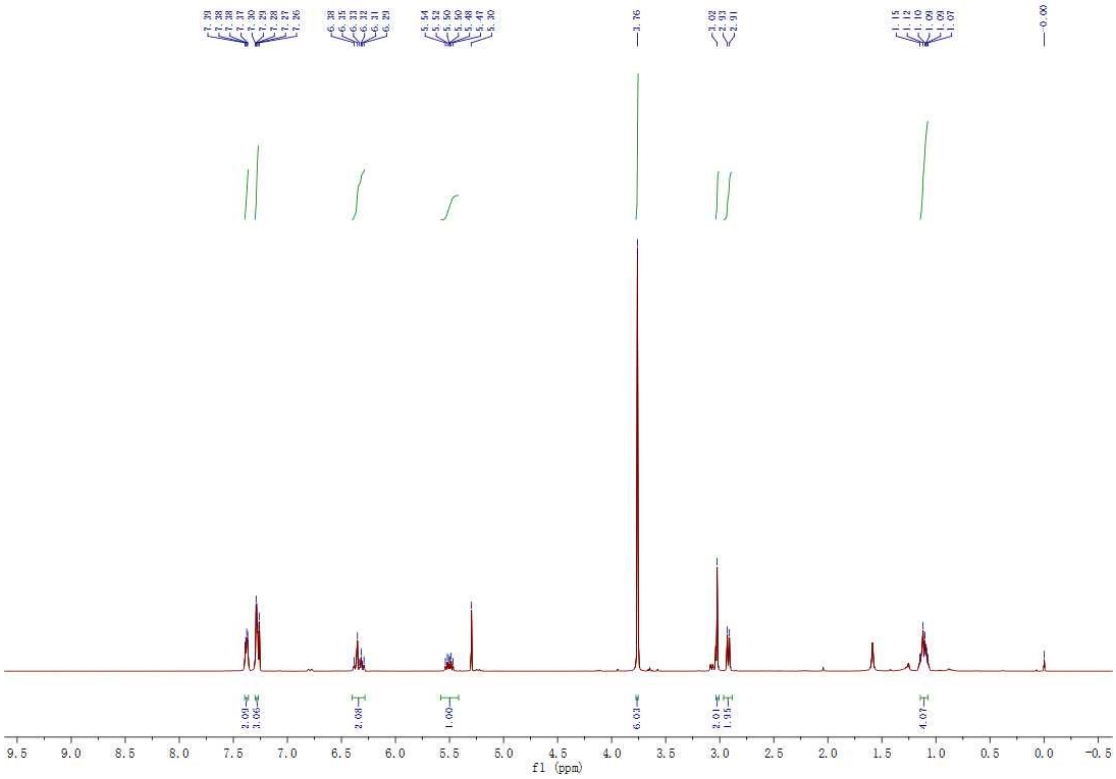

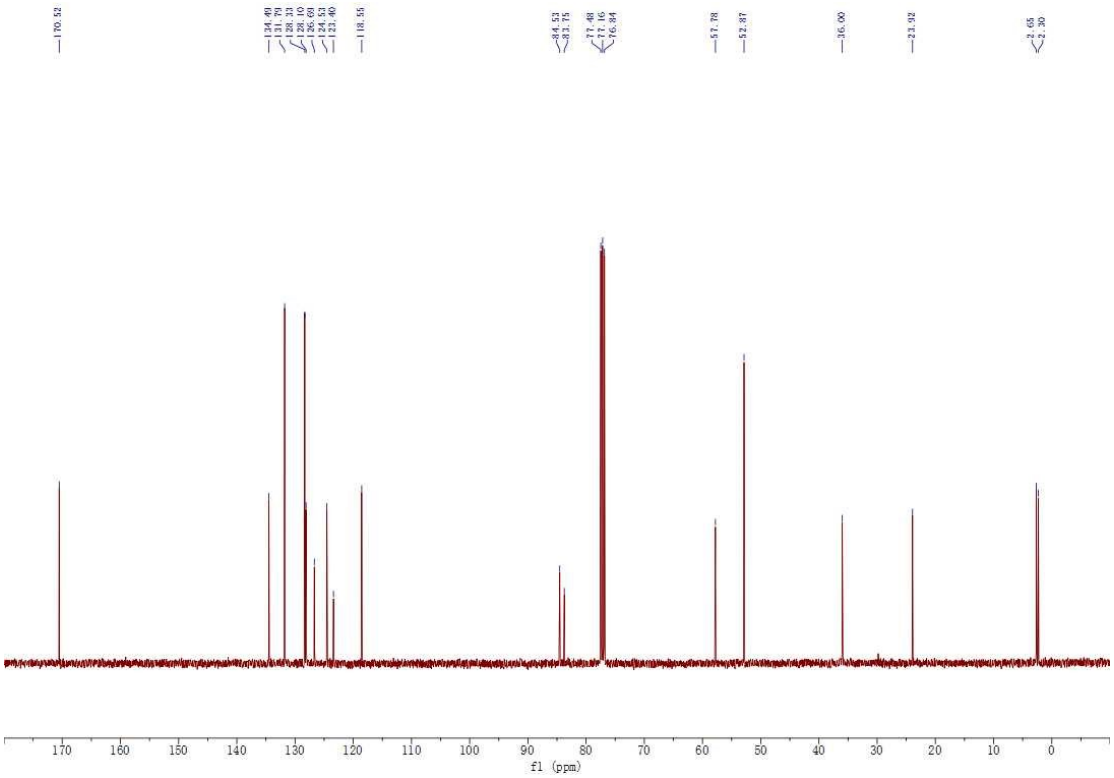

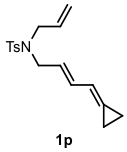

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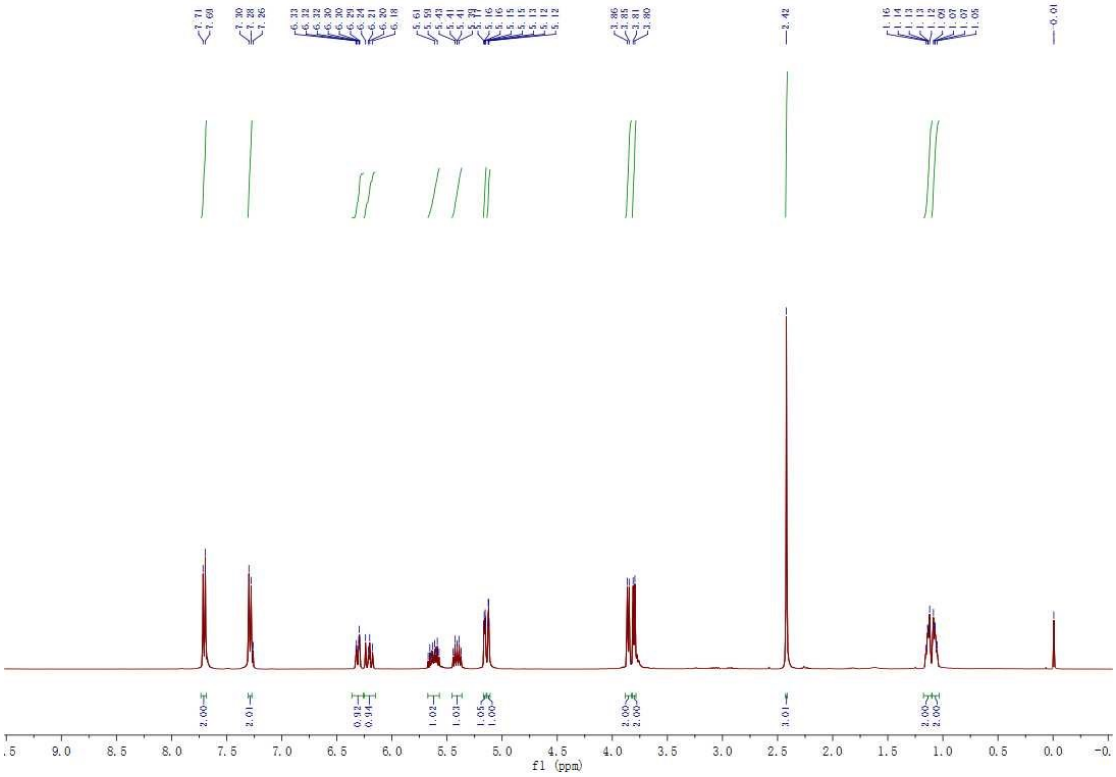

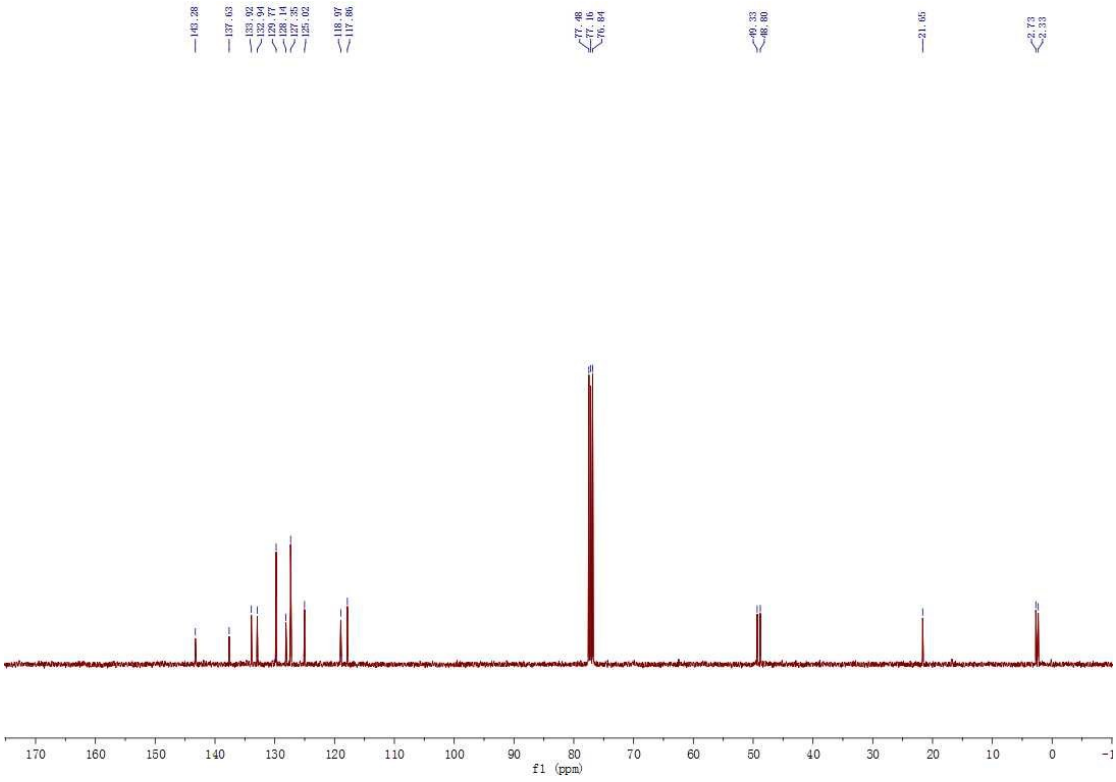

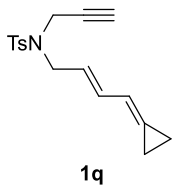

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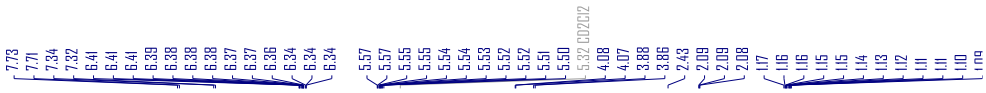
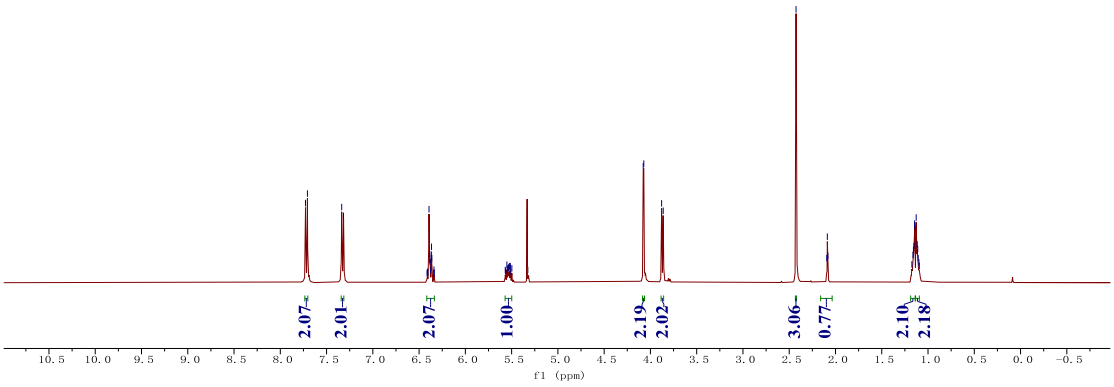
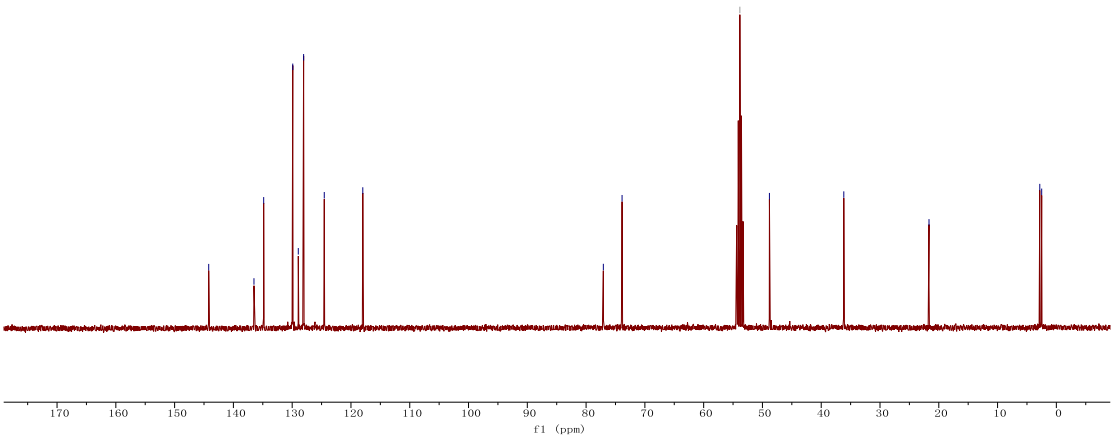
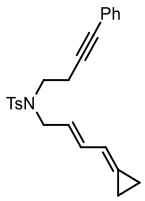
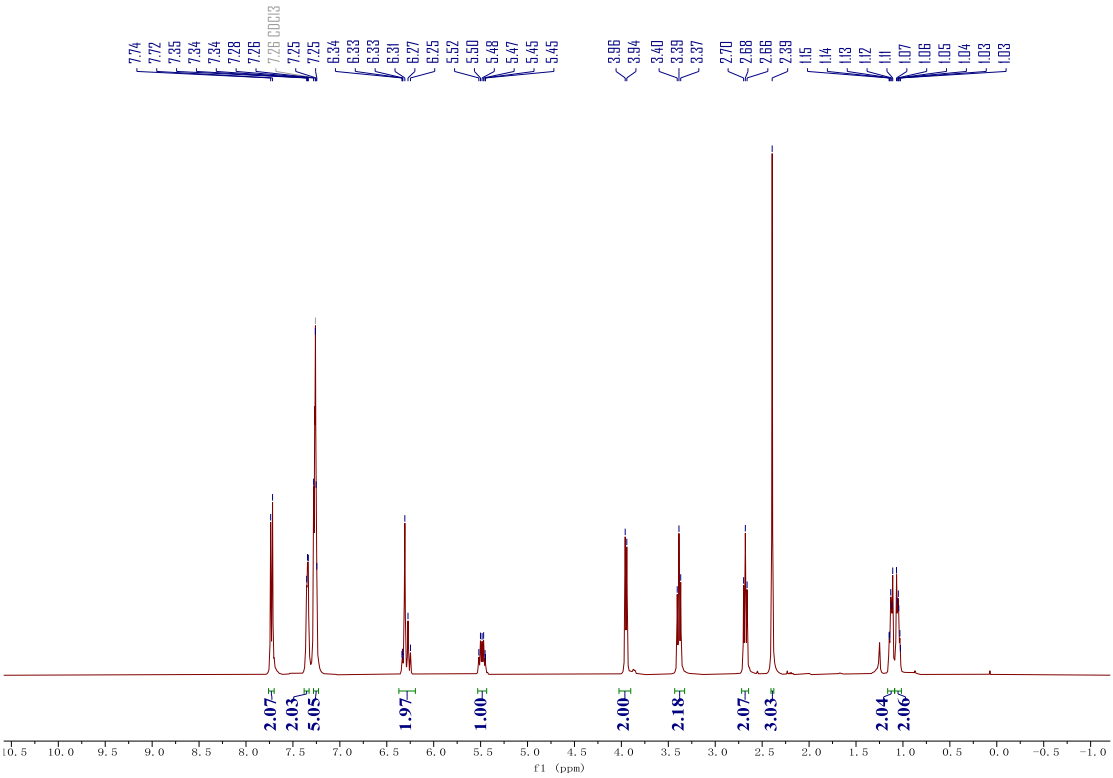







Ph
TsN

1r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5.47
5.45
5.45
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3.94
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3.39
3.37
2.70
2.68
2.66
2.39
1.15
1.14
1.13
1.12
1.11
1.07
1.06
1.05
1.04
1.03
1.03
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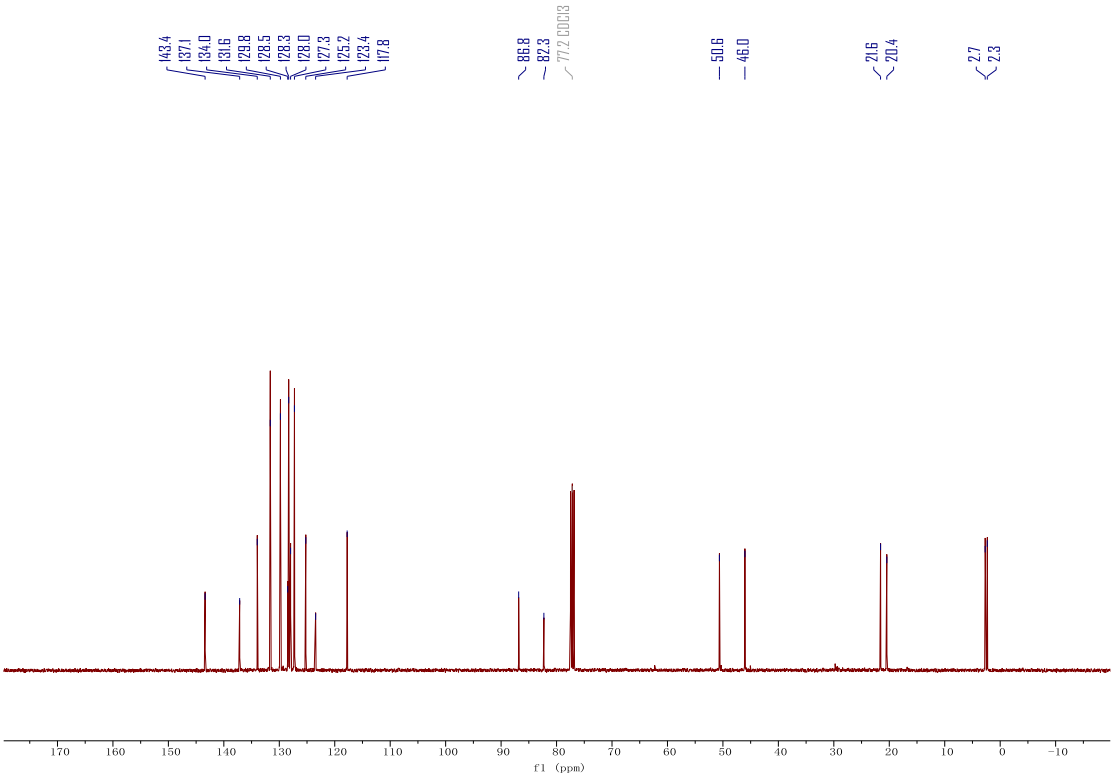
2.07
3.03
2.04
2.06
f1 (ppm)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128.0
127.3
125.2
123.4
117.8
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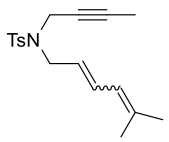
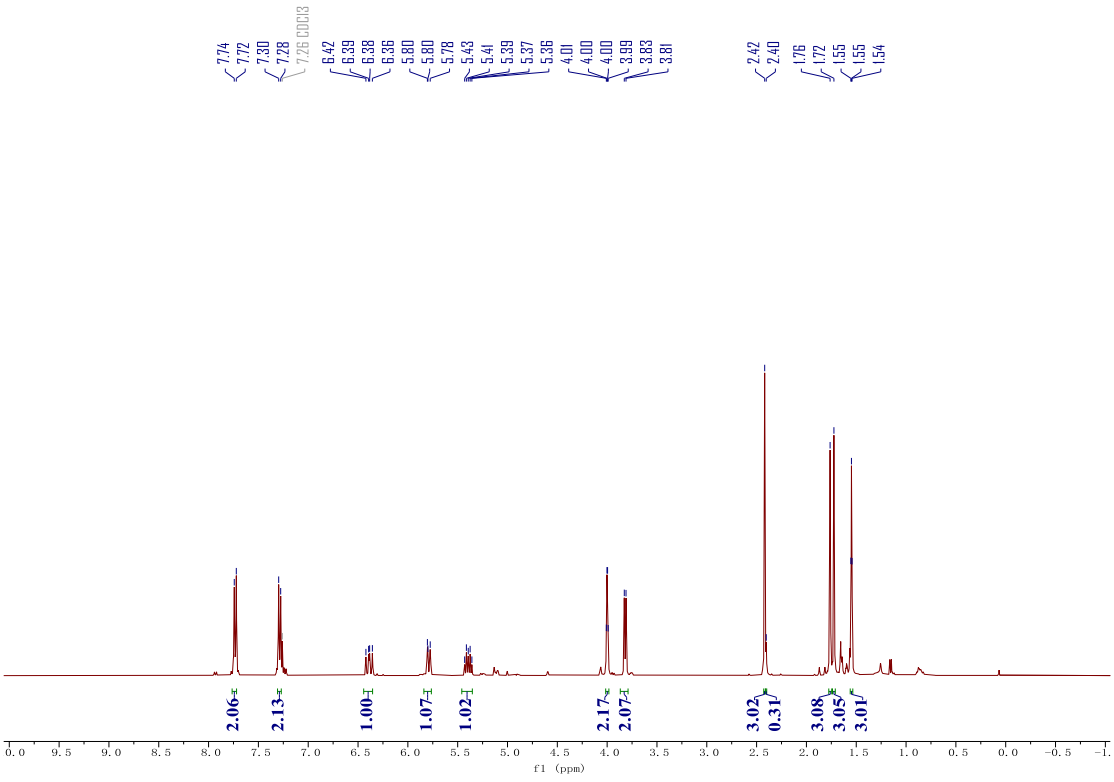
82.3
77.2
50.6
46.0
21.6
20.4
2.7
2.3
f1 (ppm)


TsN

4a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7.26 CDCl3
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5.80
5.78
5.43
5.41
5.39
5.37
5.36
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4.00
4.00
3.99
3.83
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2.40
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1.72
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1.54
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3.02
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3.08
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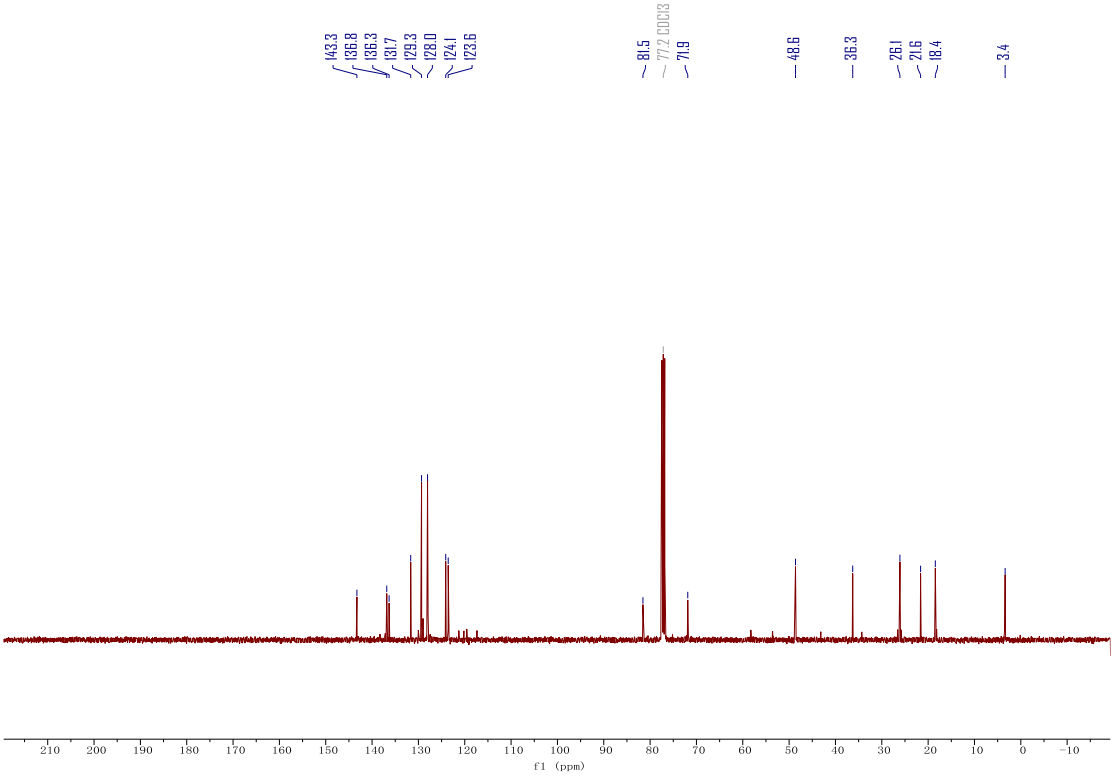
3.01
f1 (ppm)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124.1
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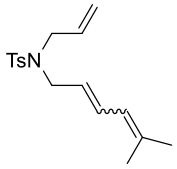
3.4
f1 (ppm)


TsN

4b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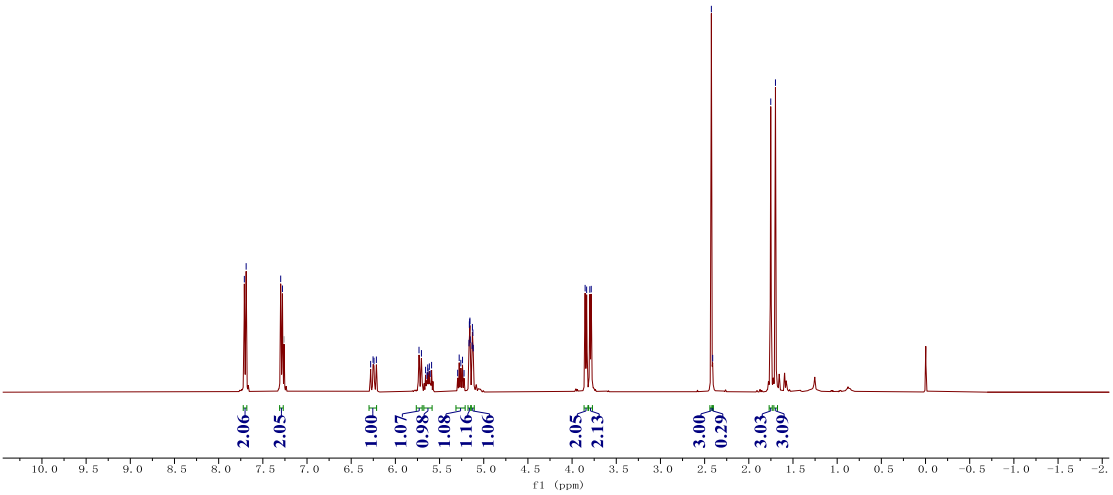
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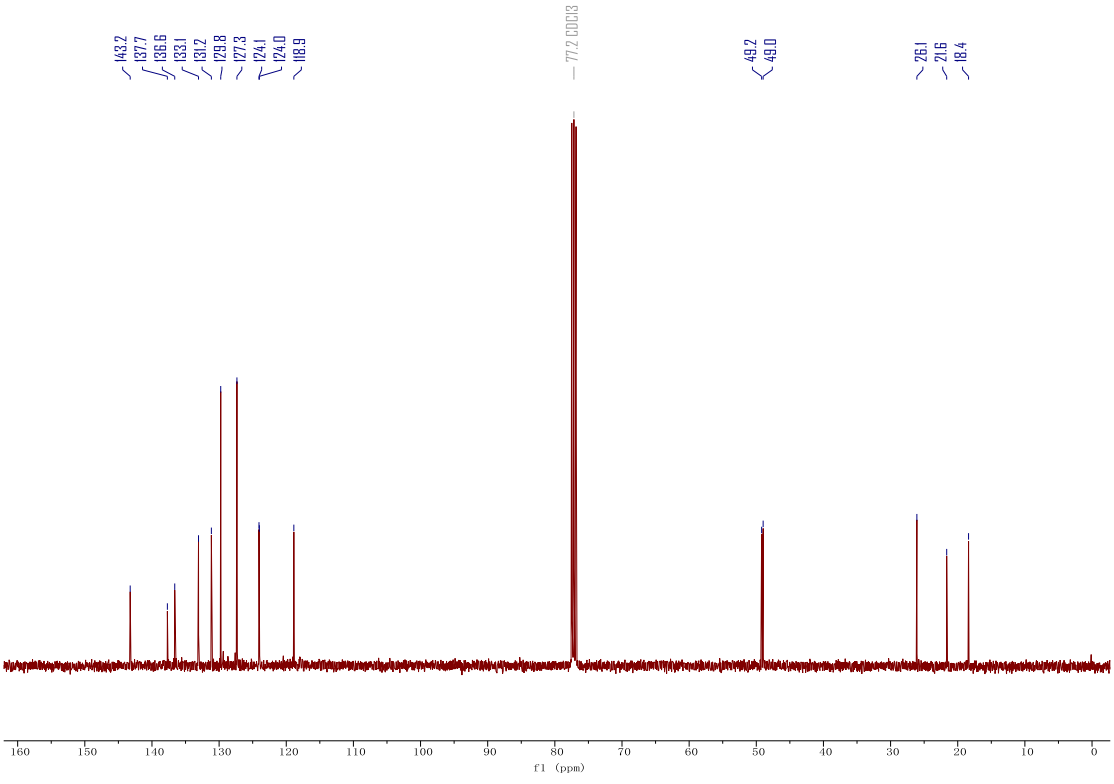
f1 (ppm)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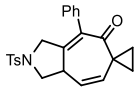
f1 (ppm)



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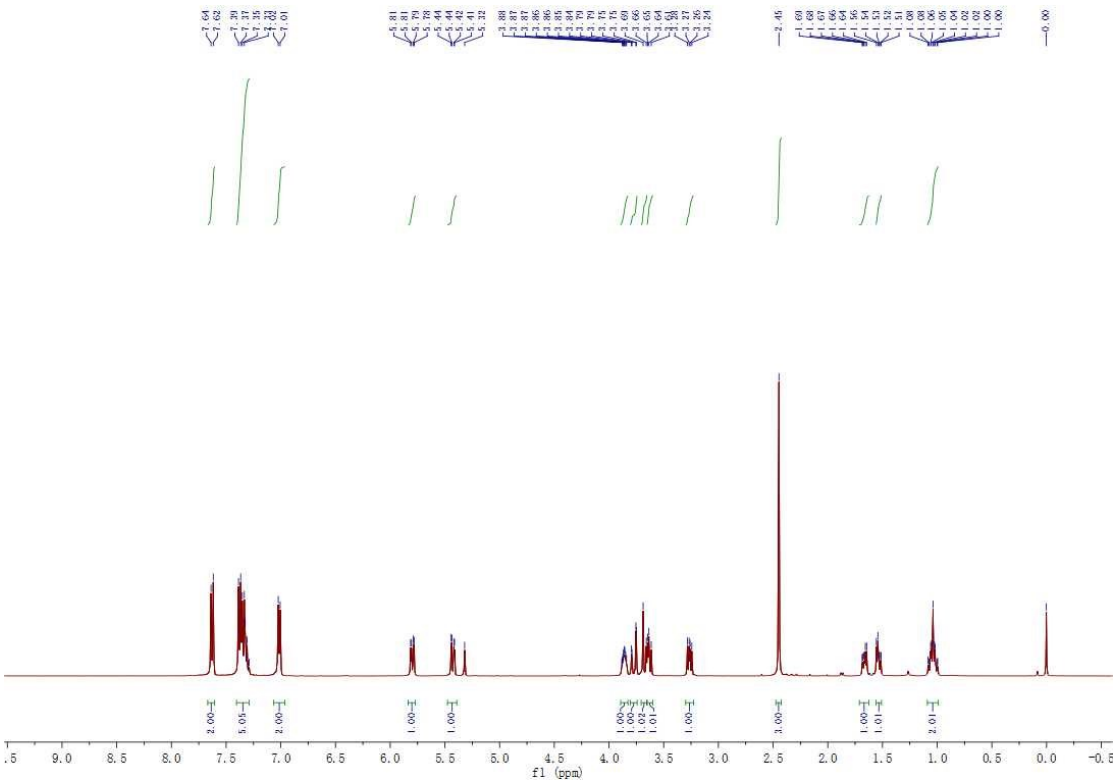

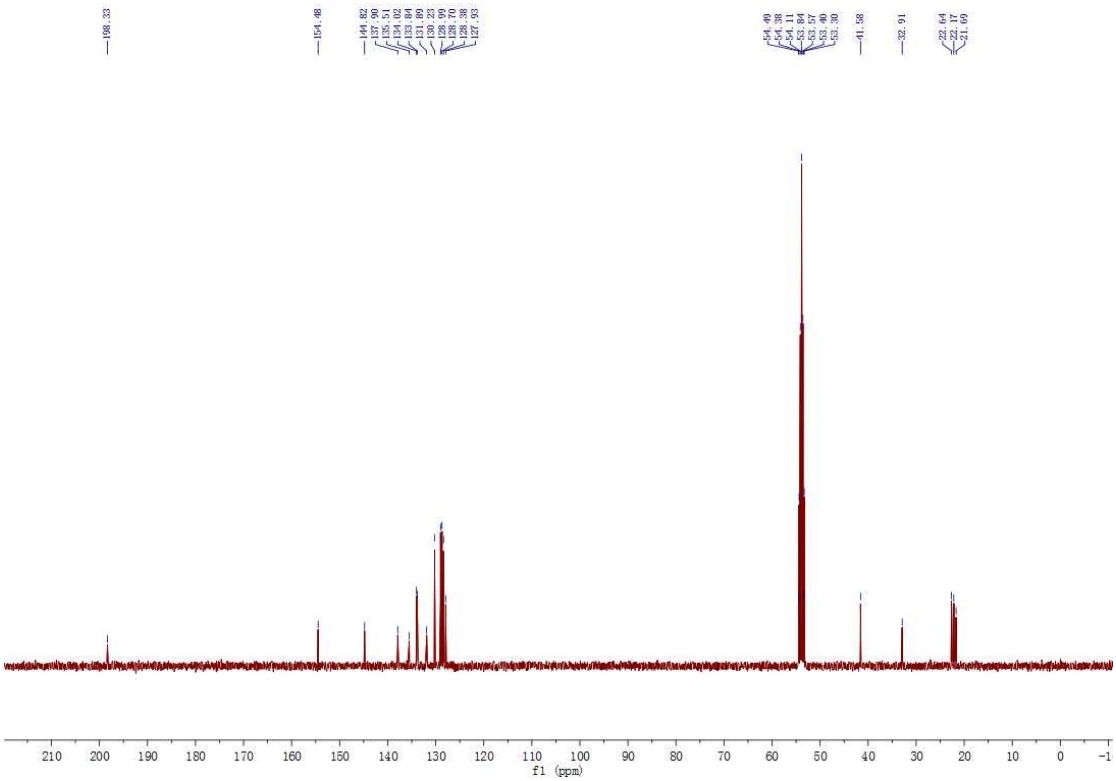

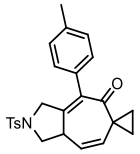

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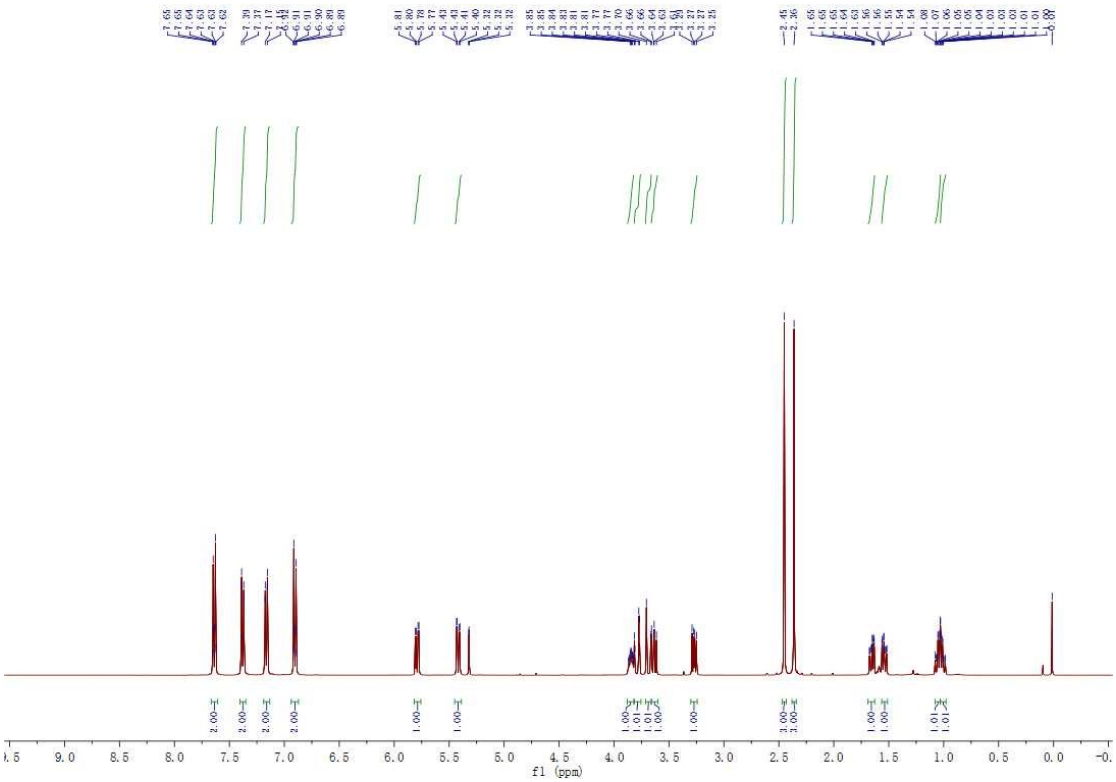

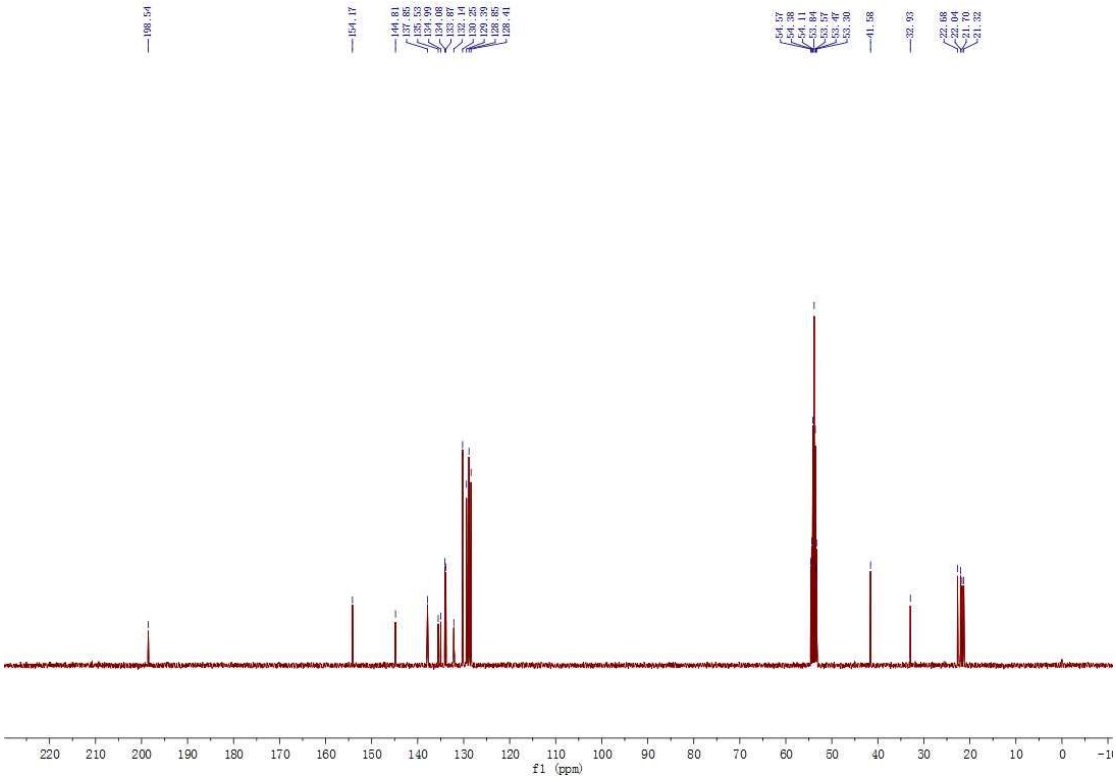

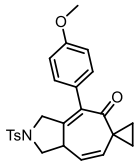

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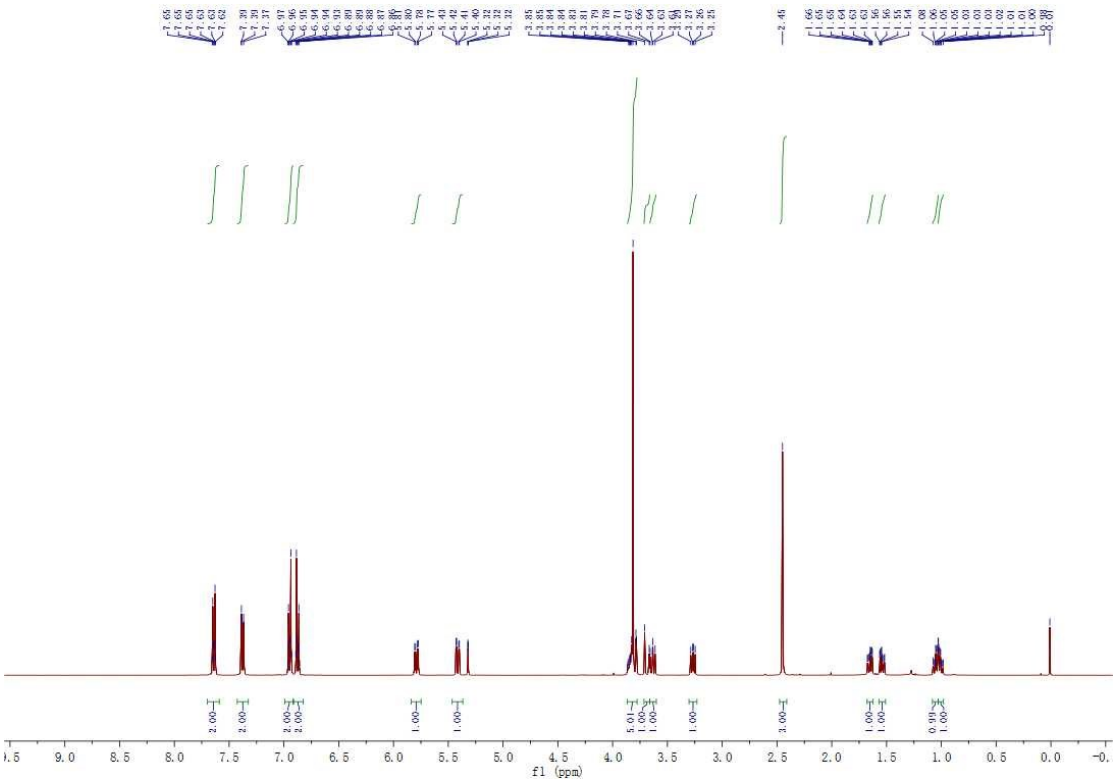

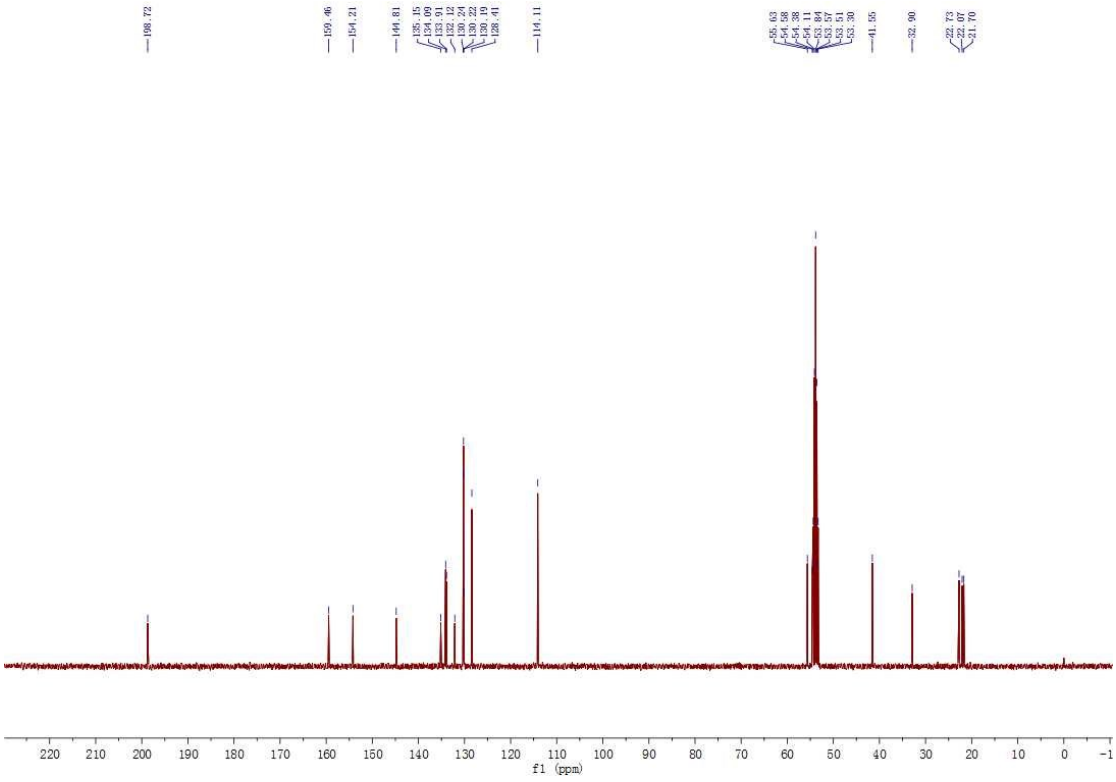

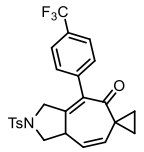

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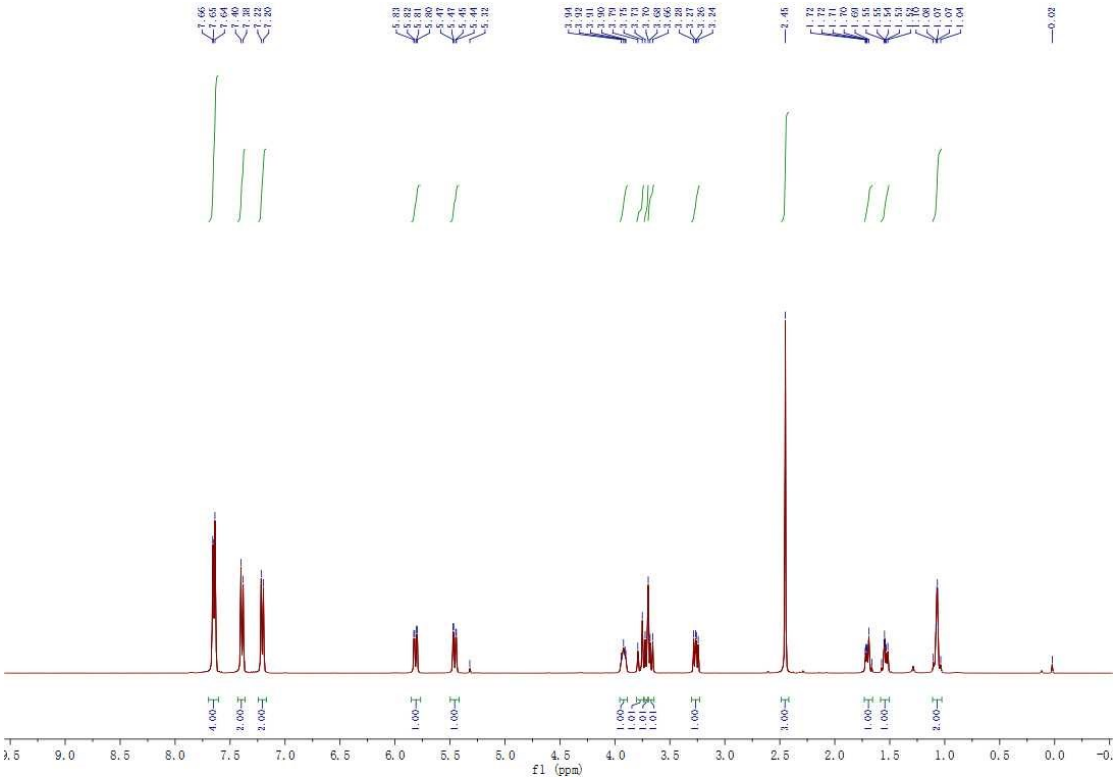

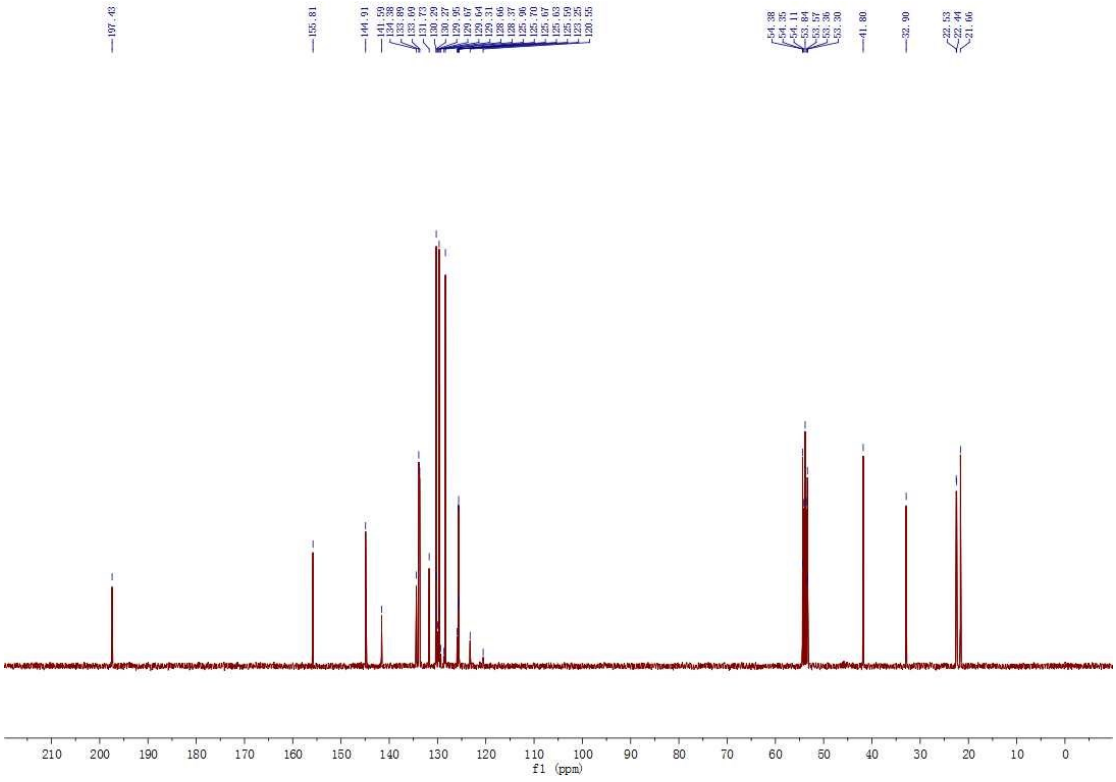

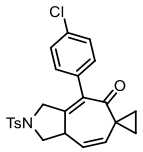

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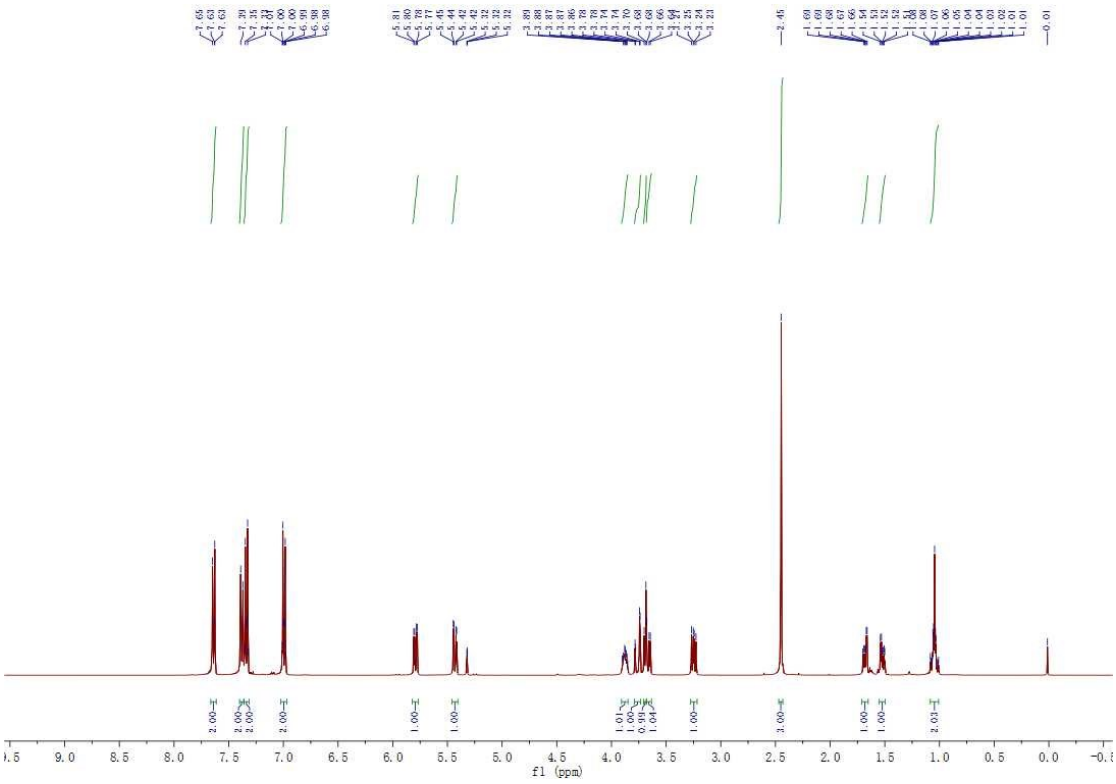

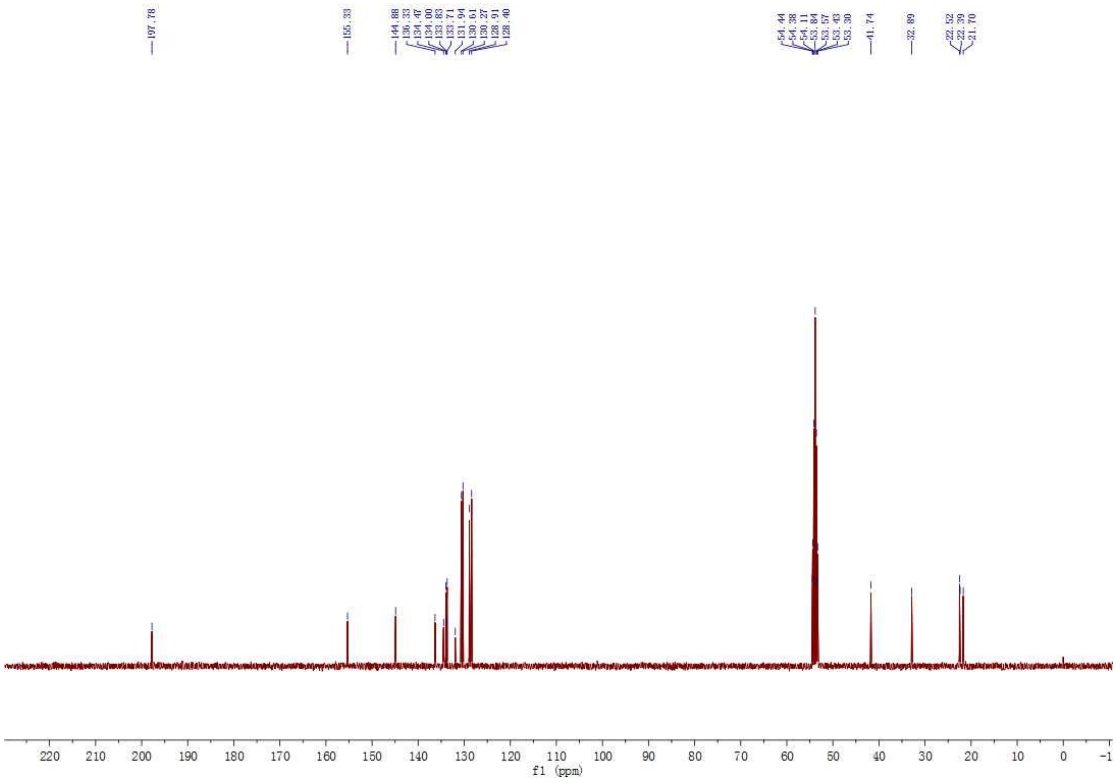

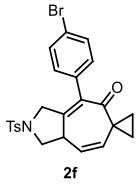

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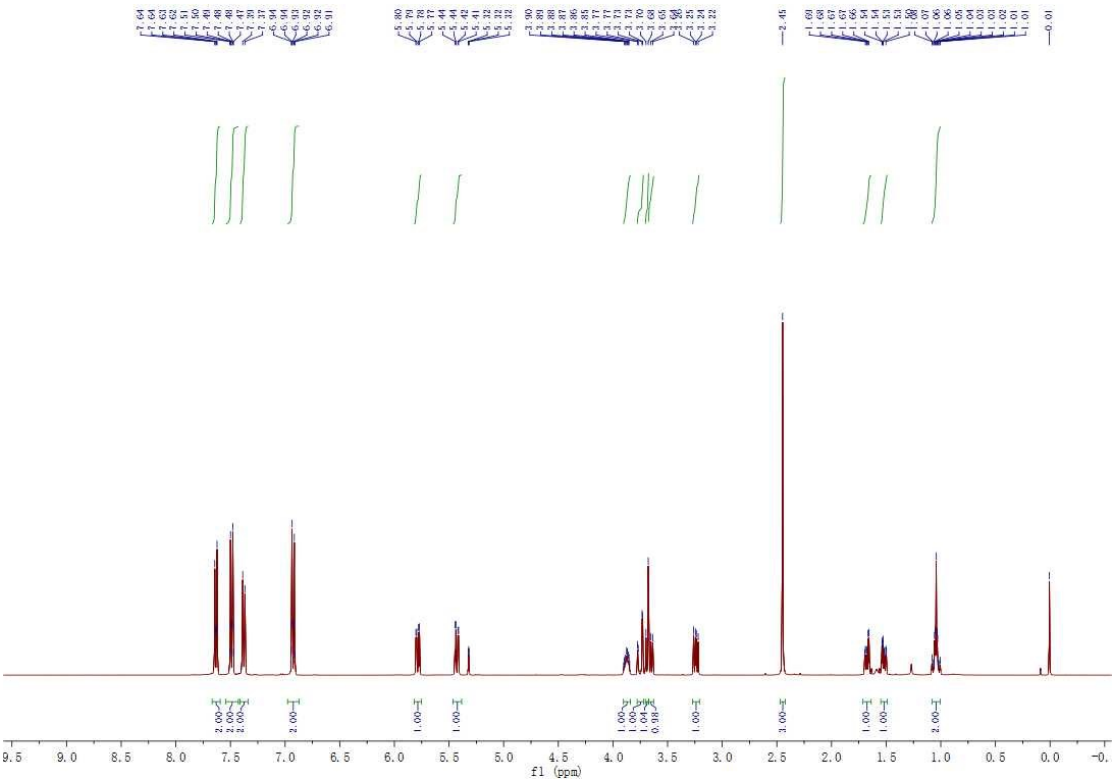

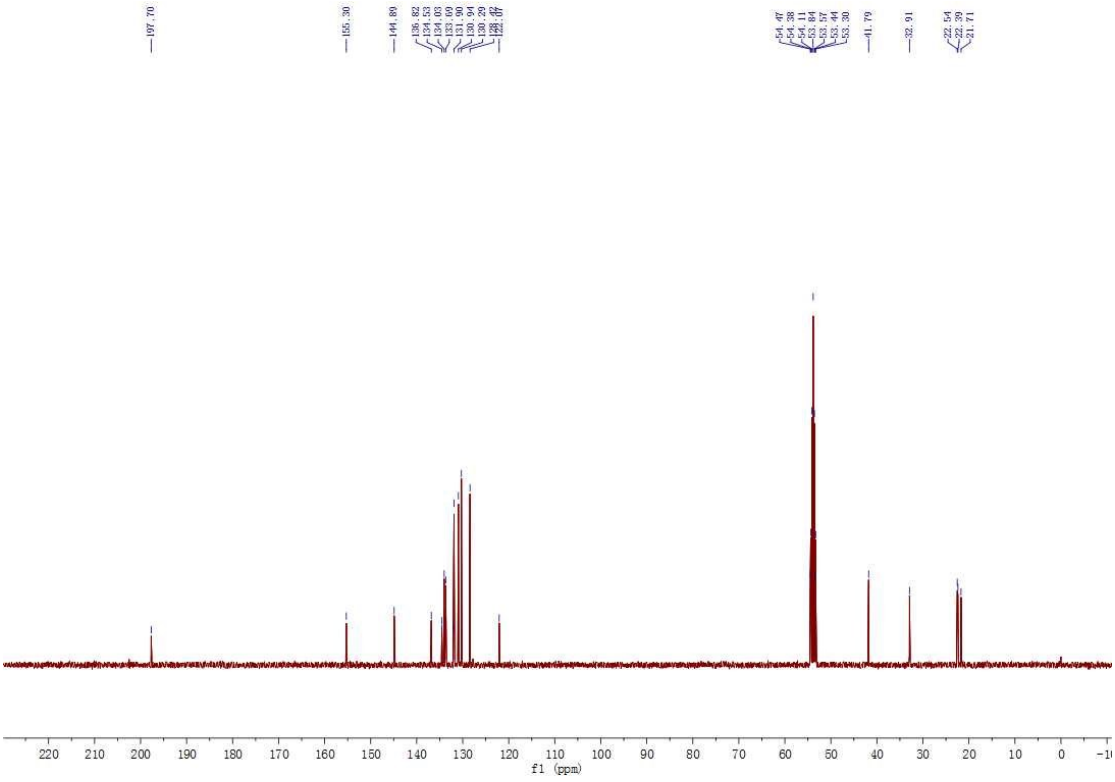

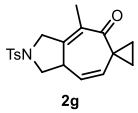

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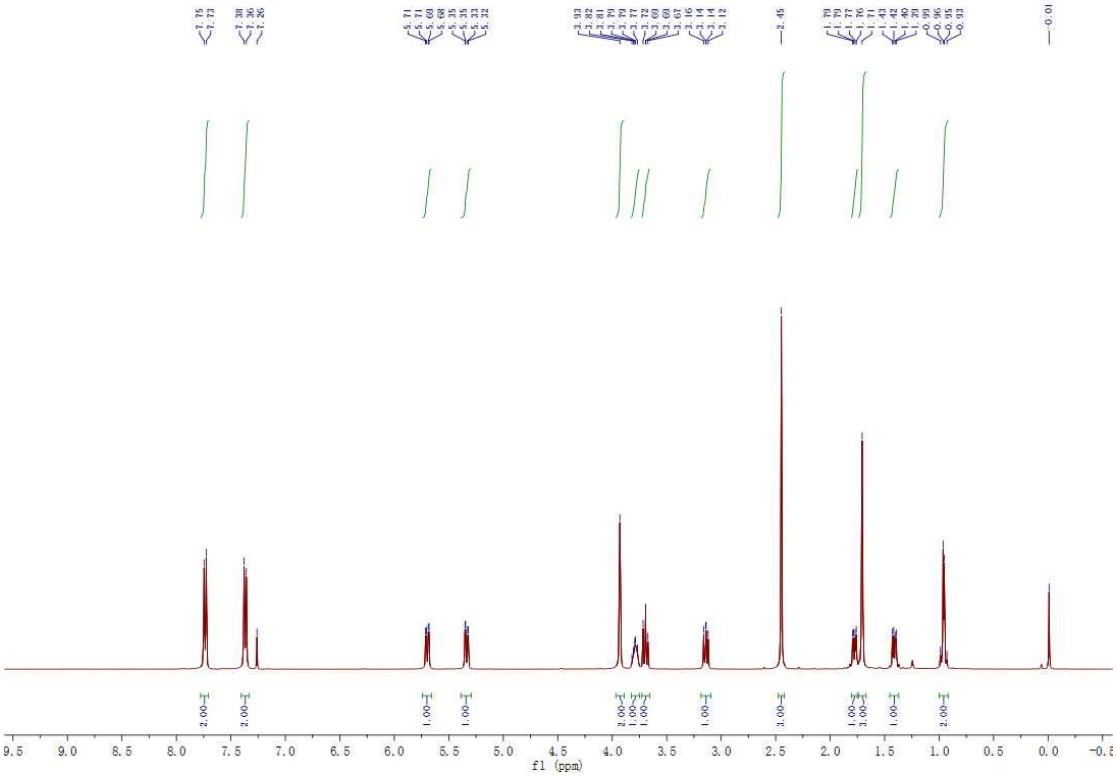

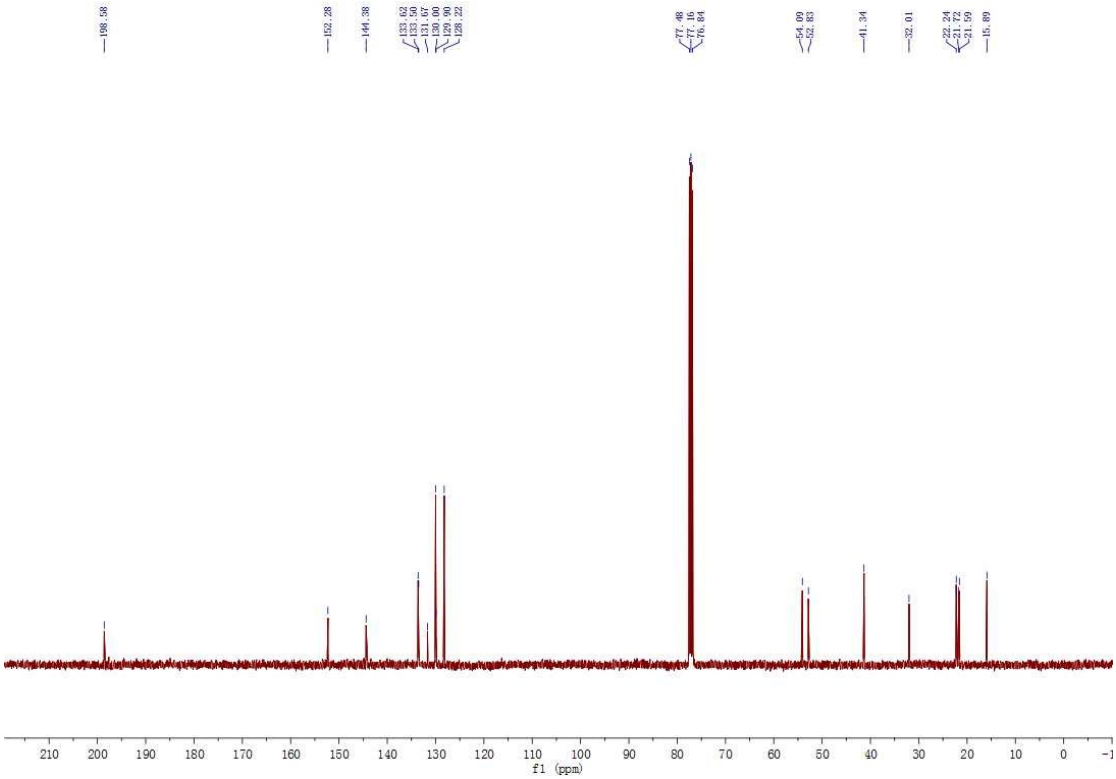

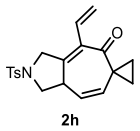

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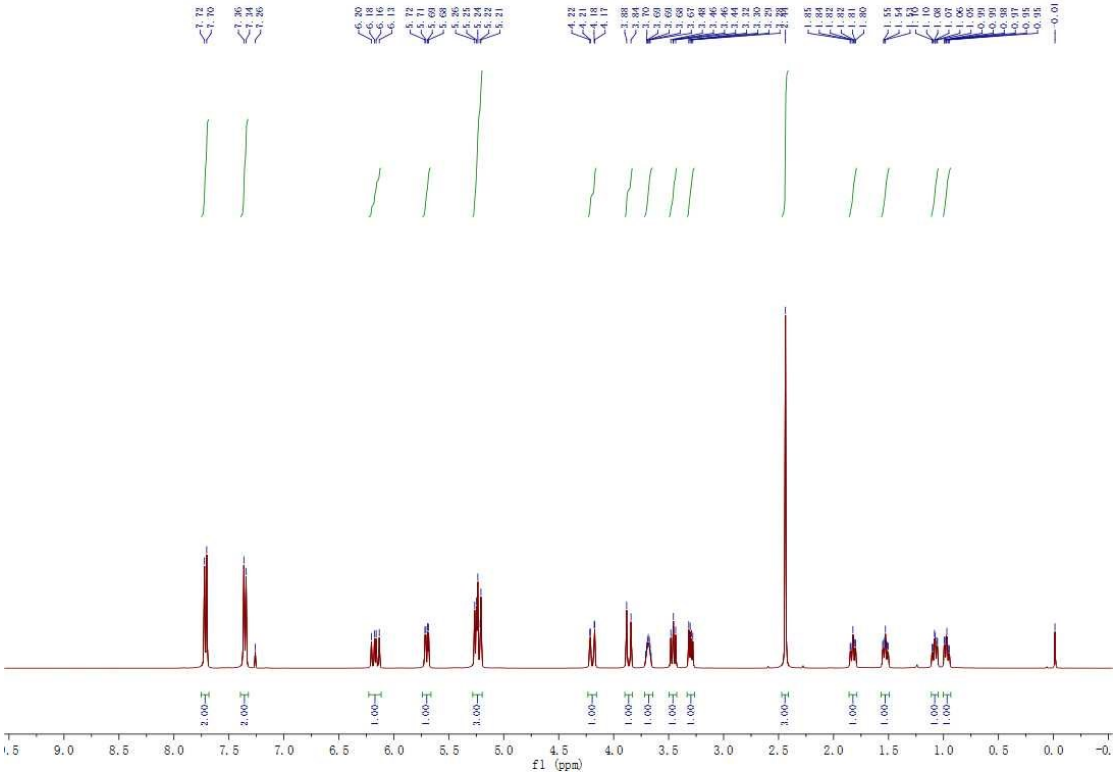

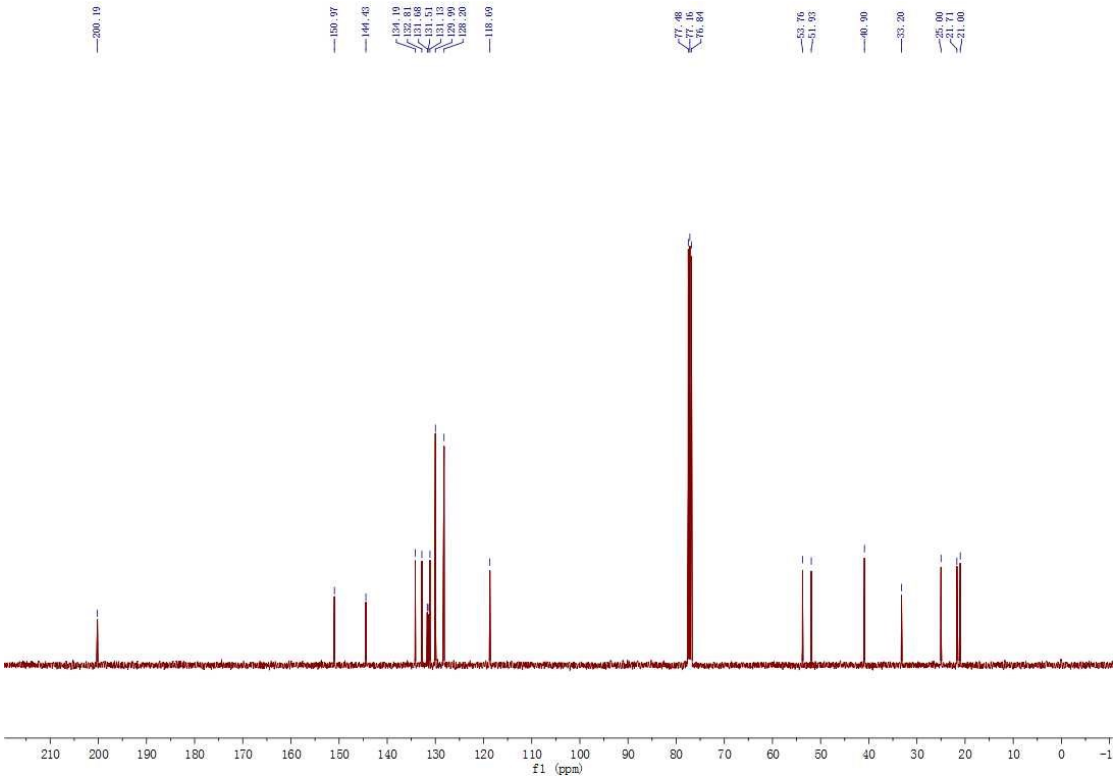

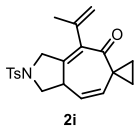

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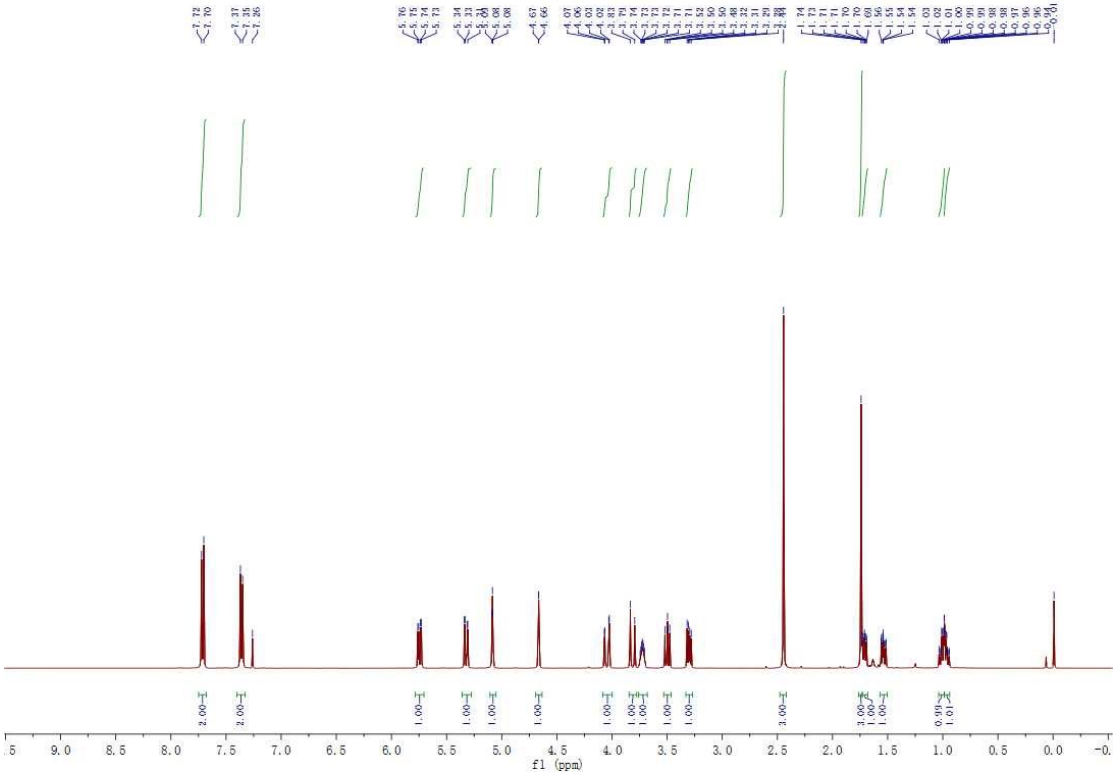

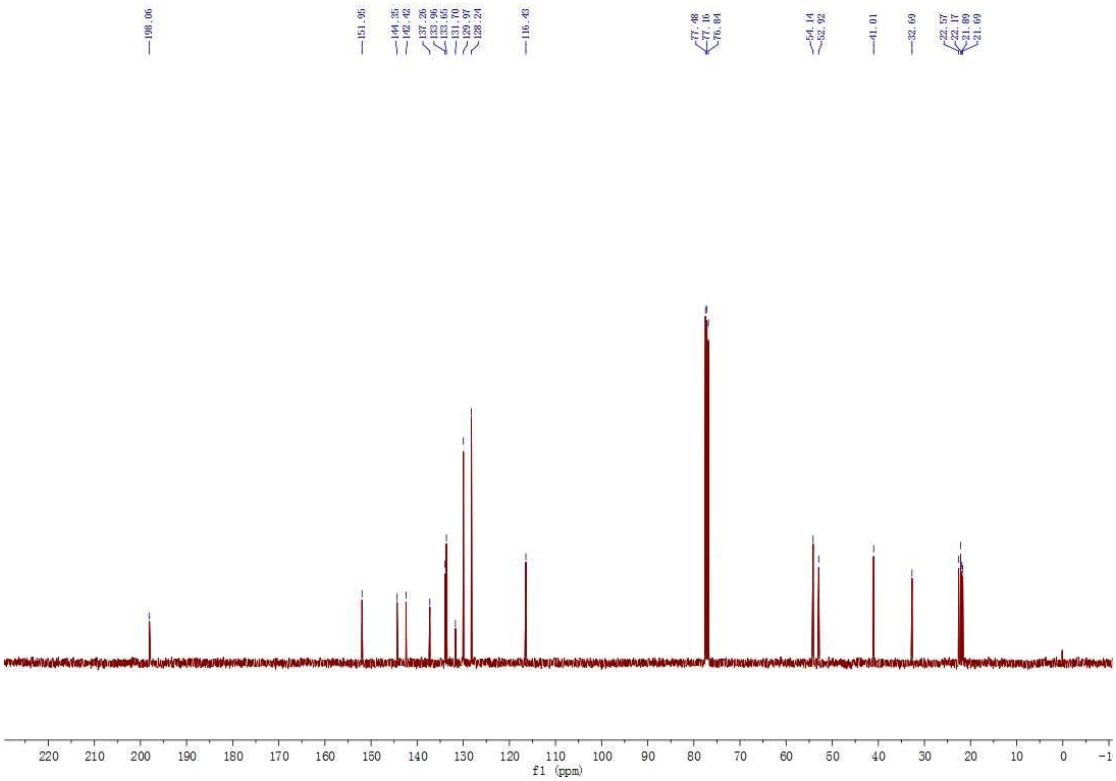

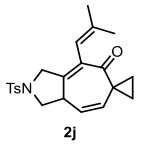

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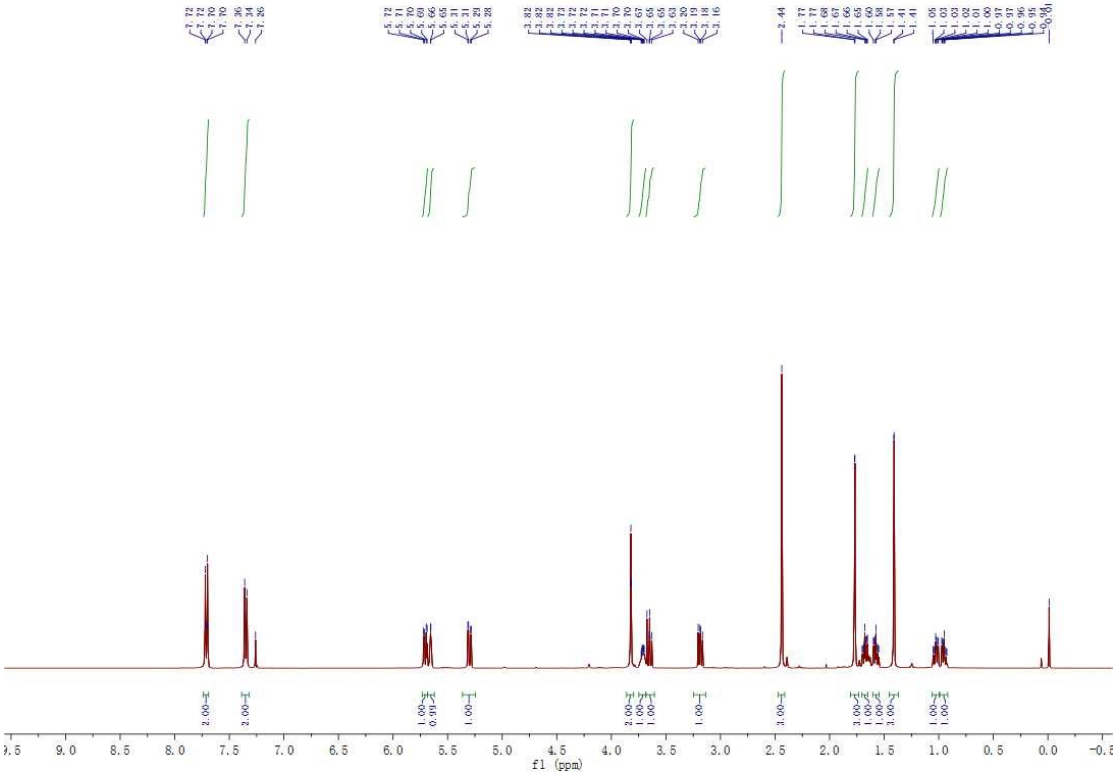

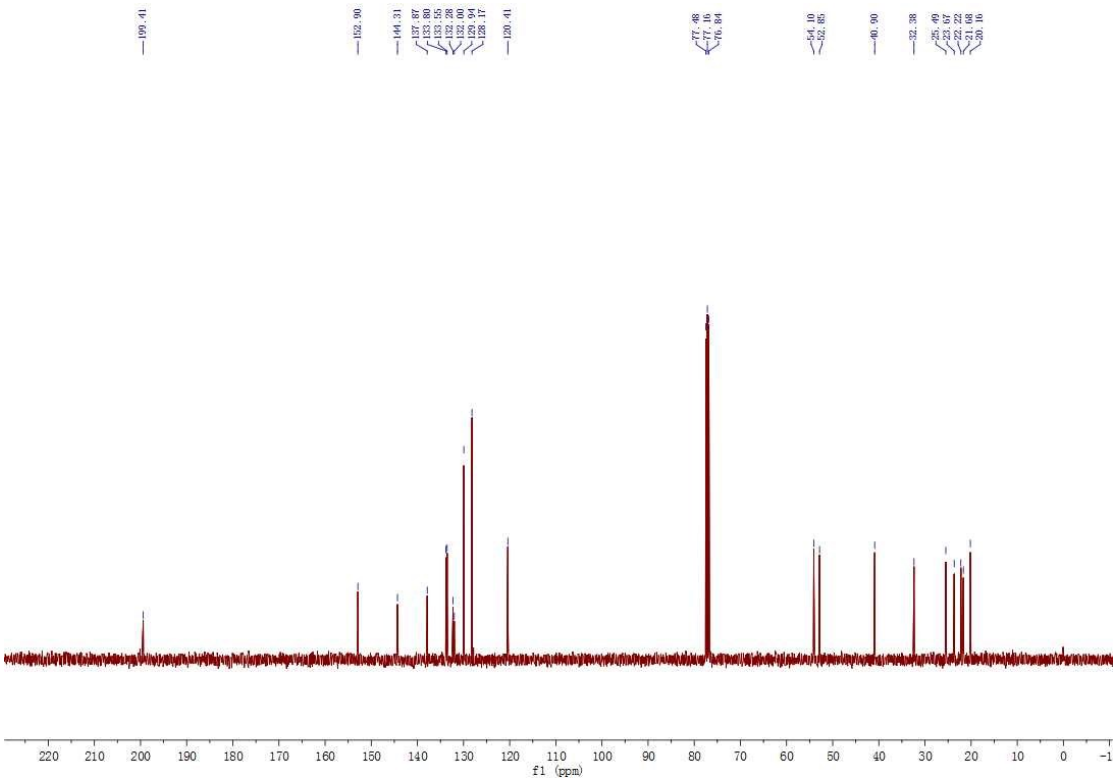

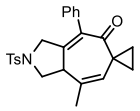

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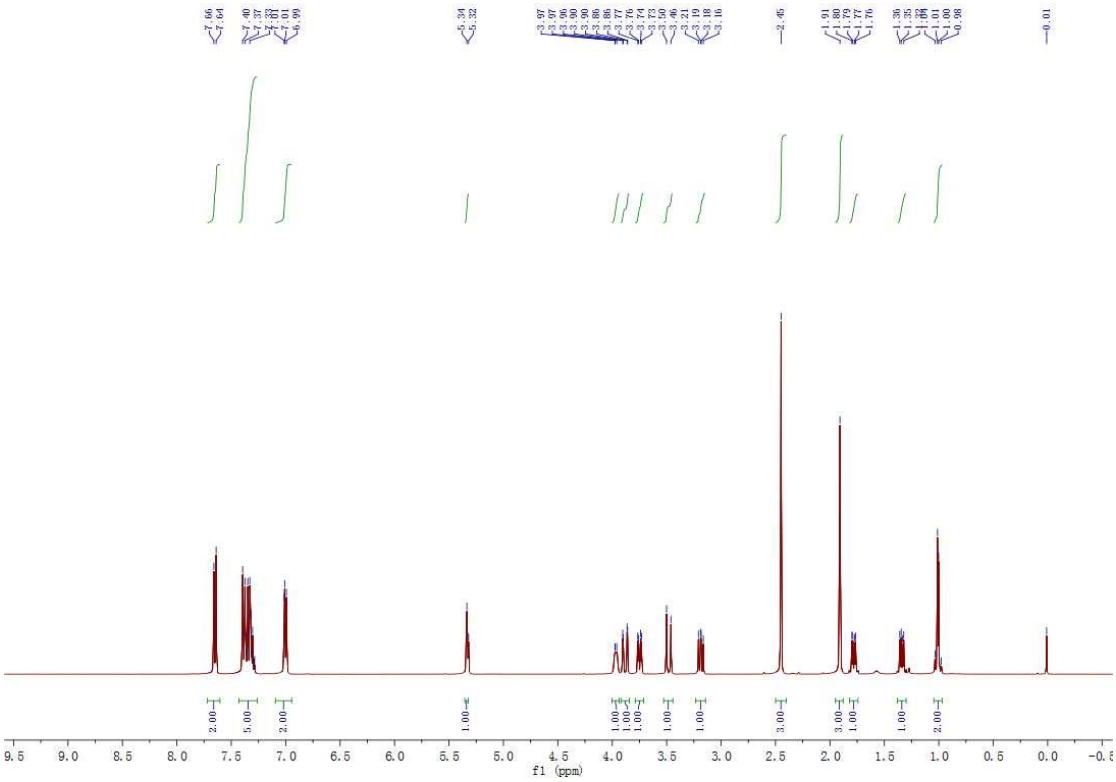

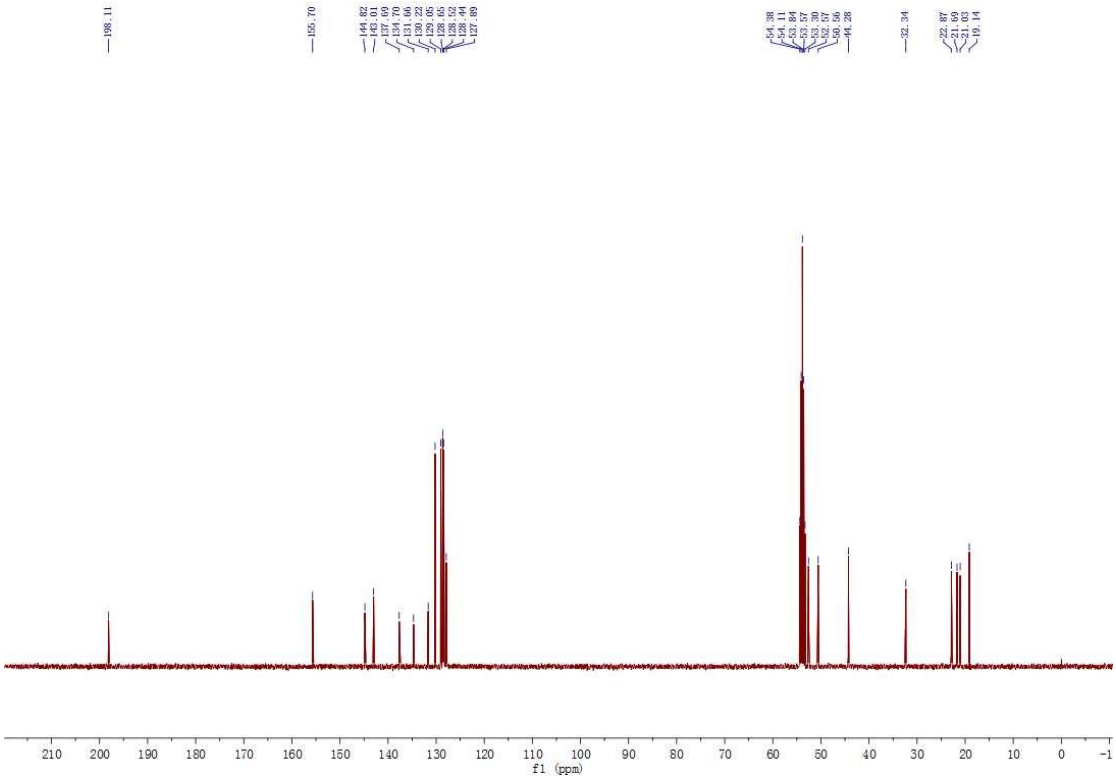

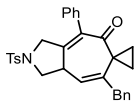

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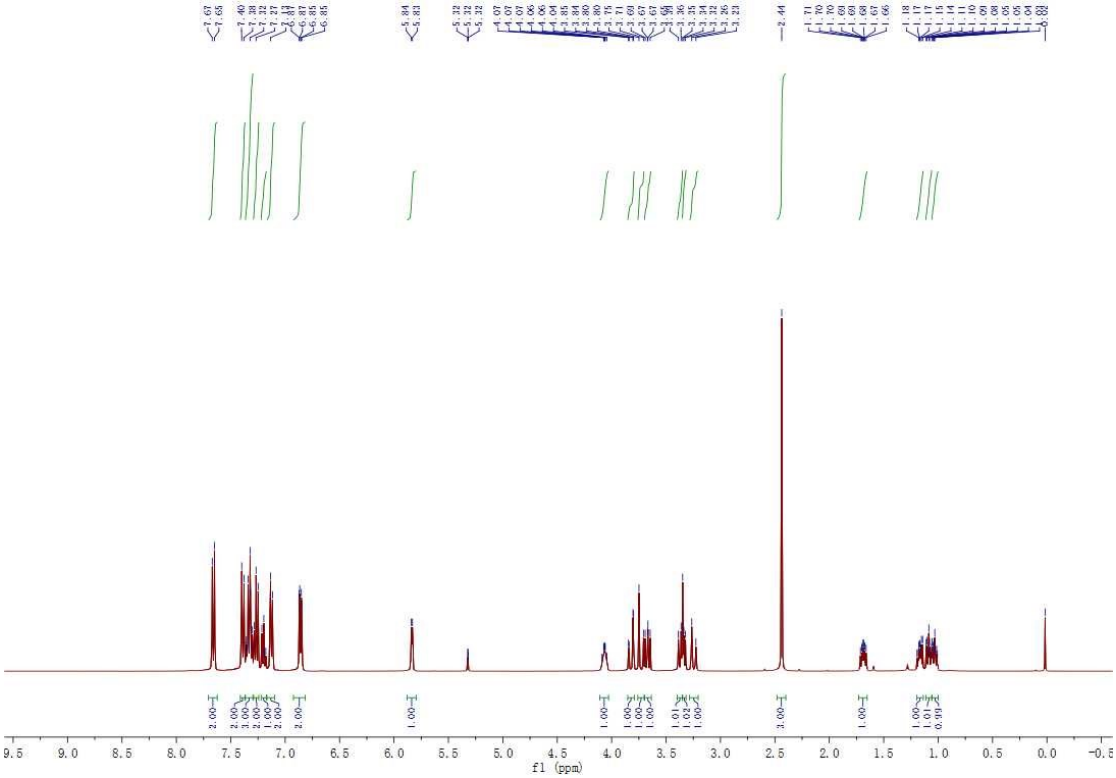
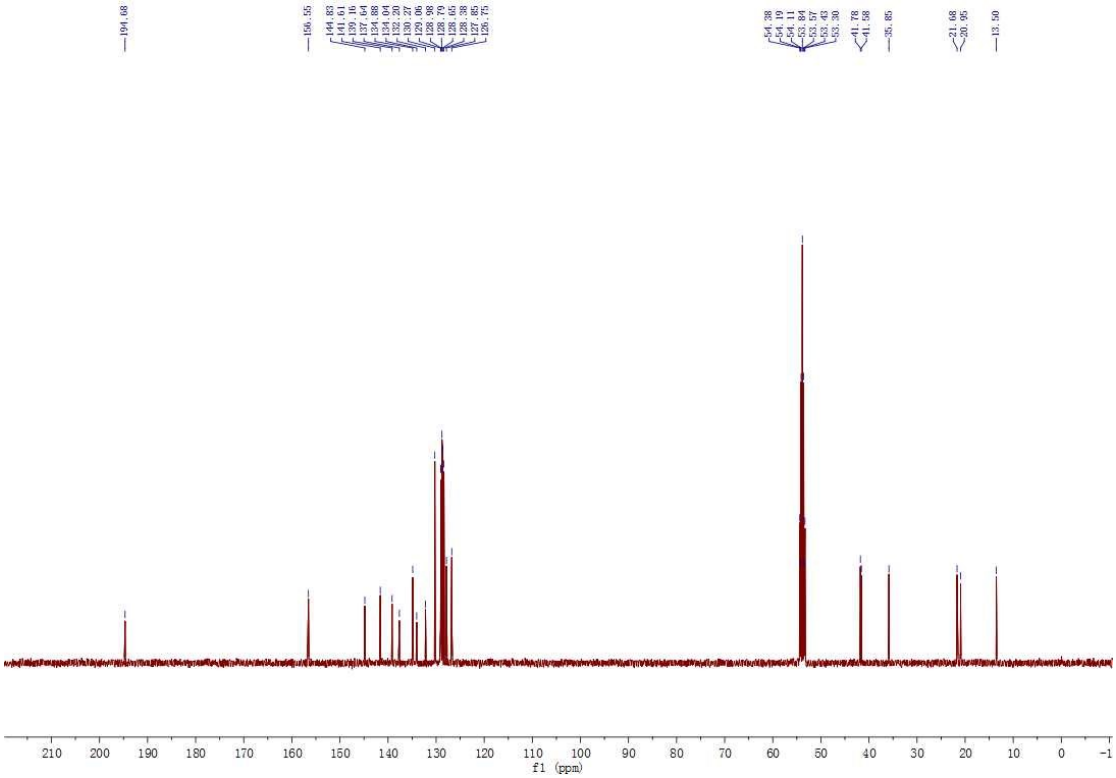
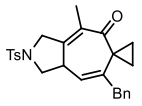
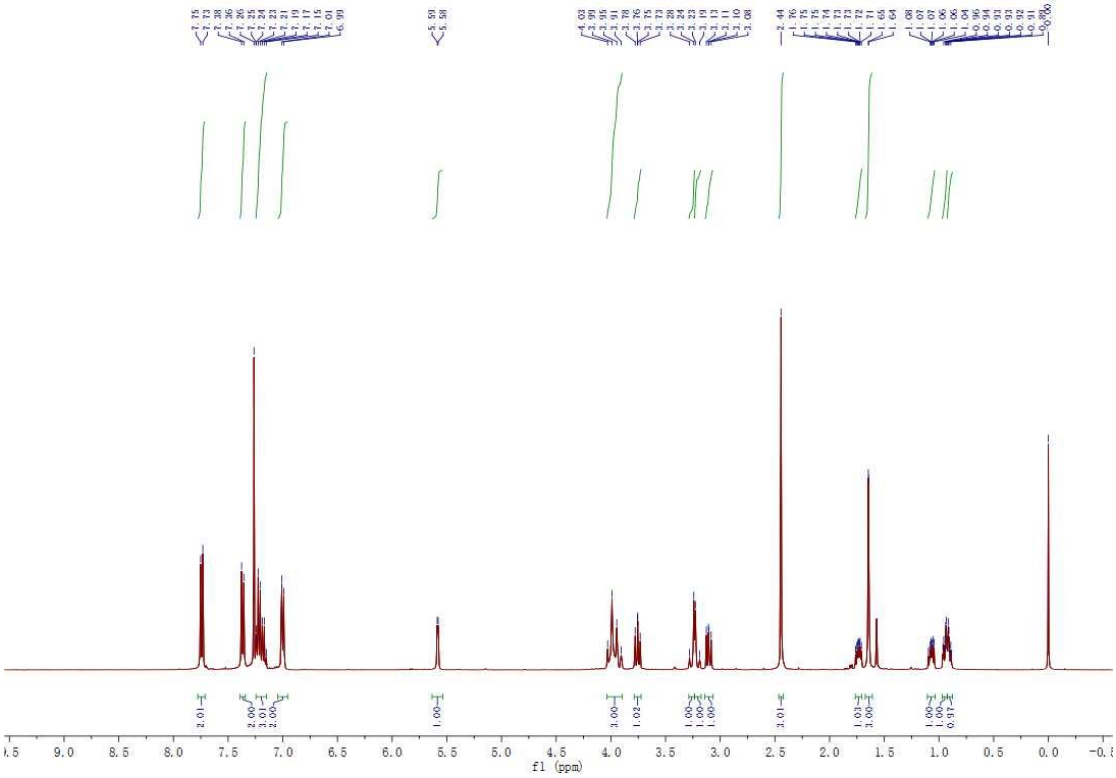
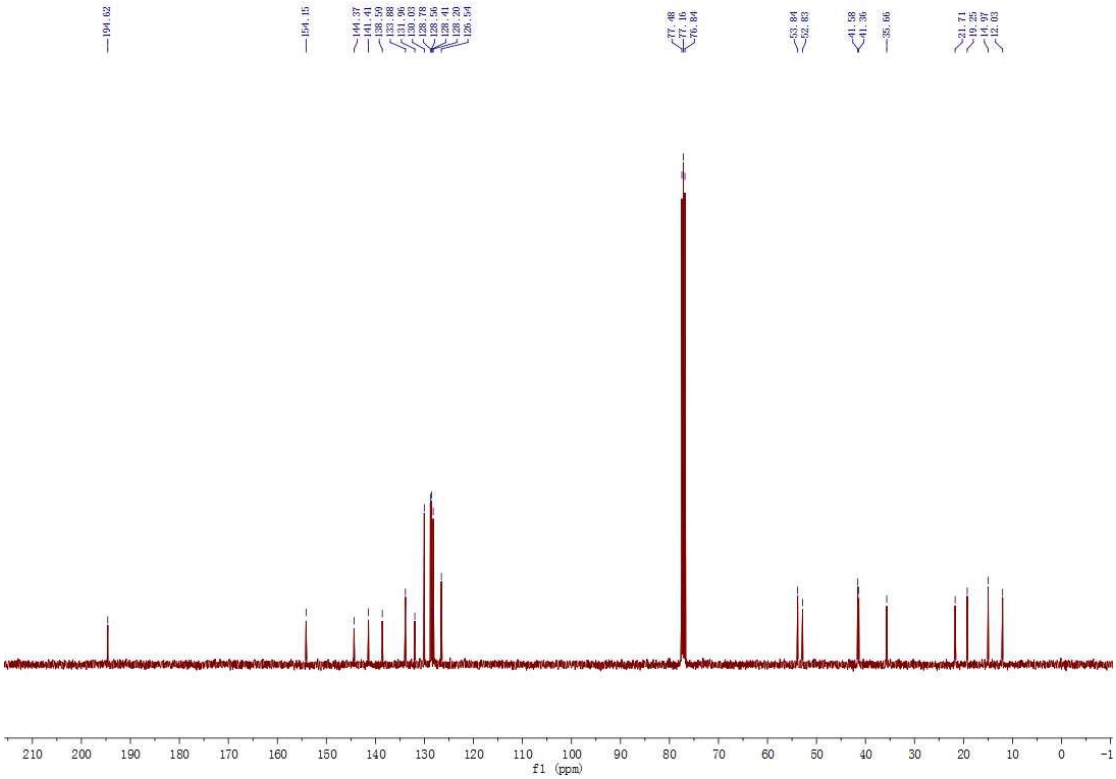


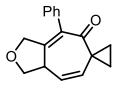




2m







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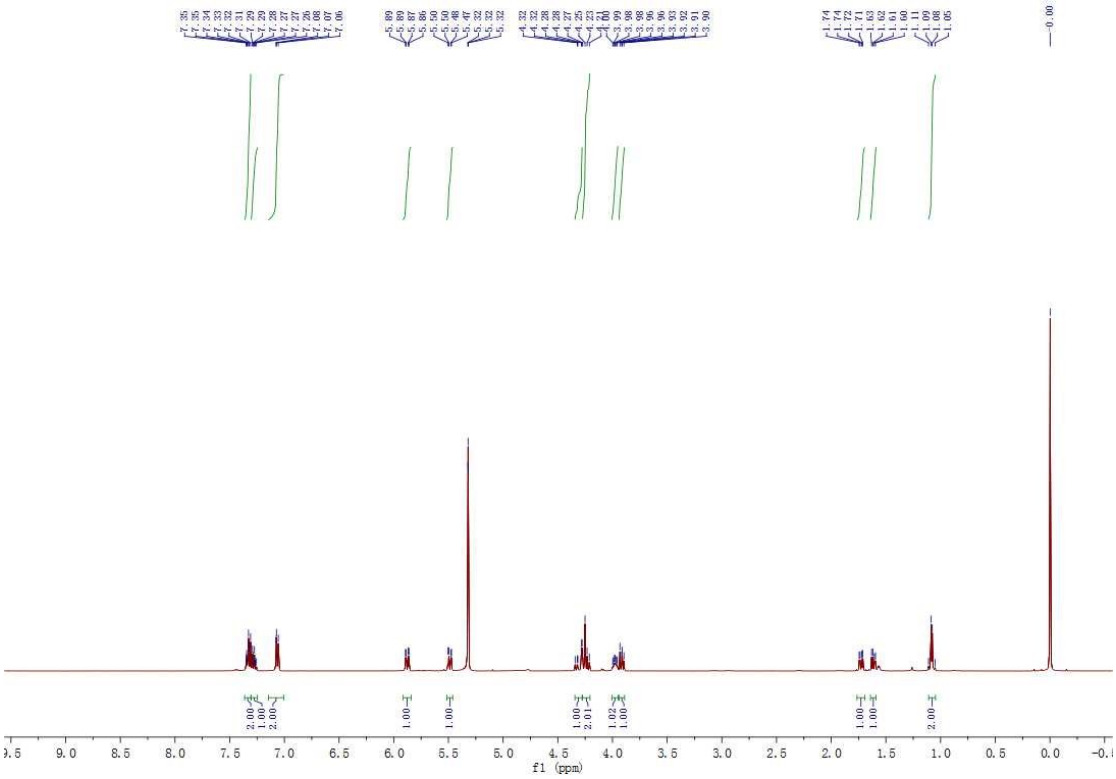
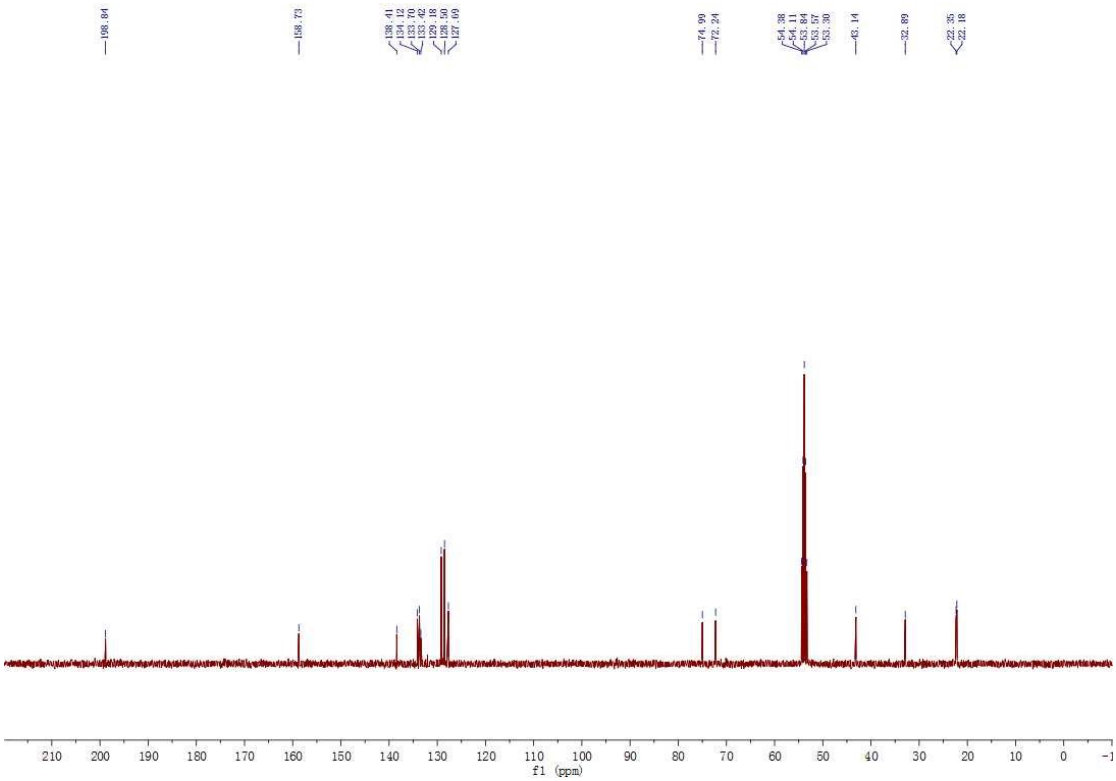
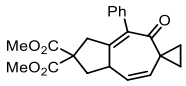
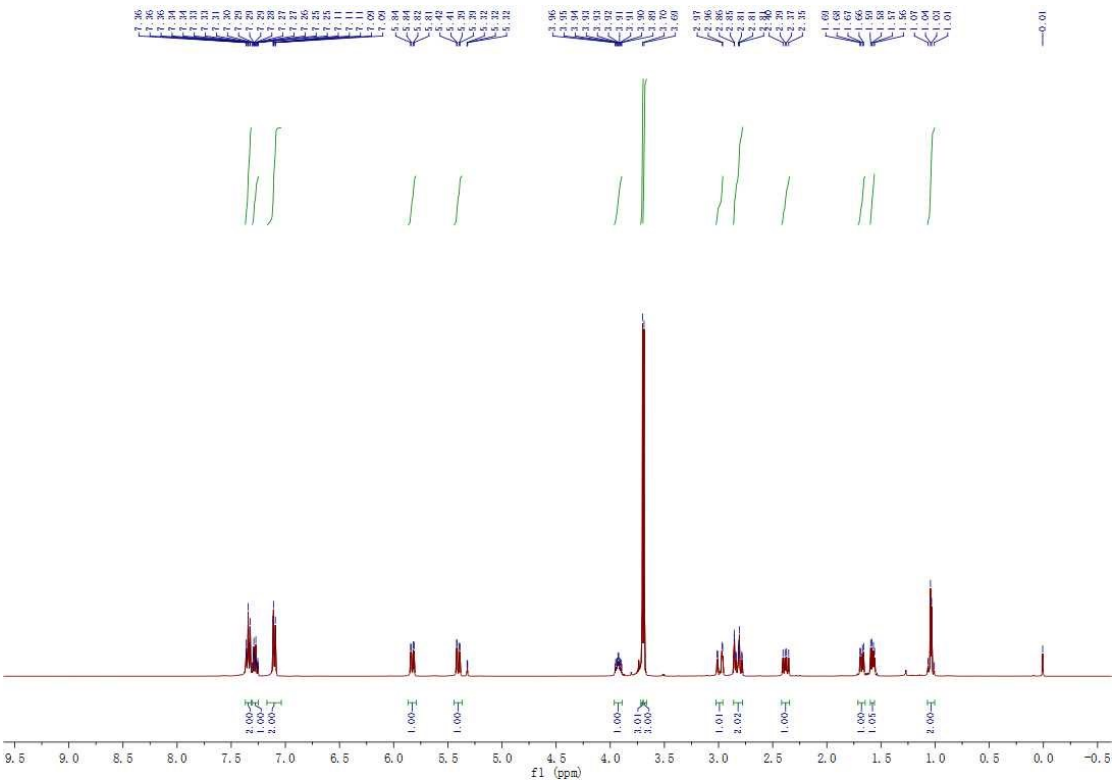
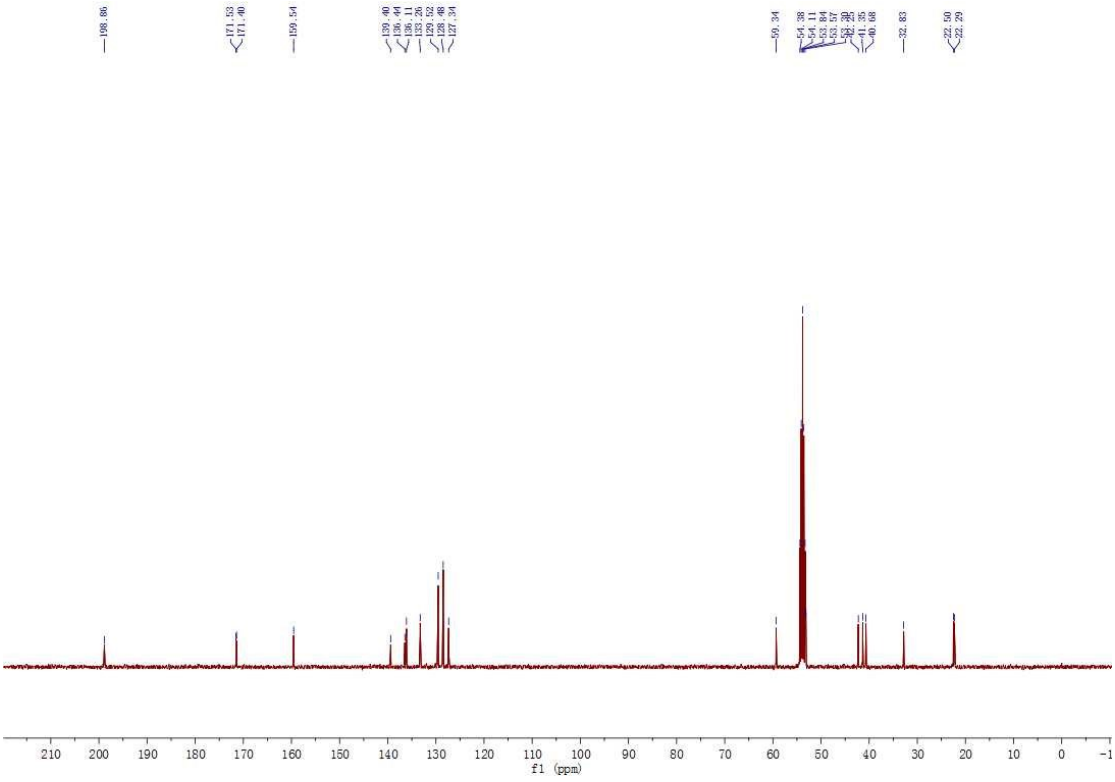





Ph
O
MeO2C
MeO2C

2o


9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5
f1 (ppm)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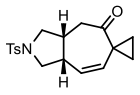
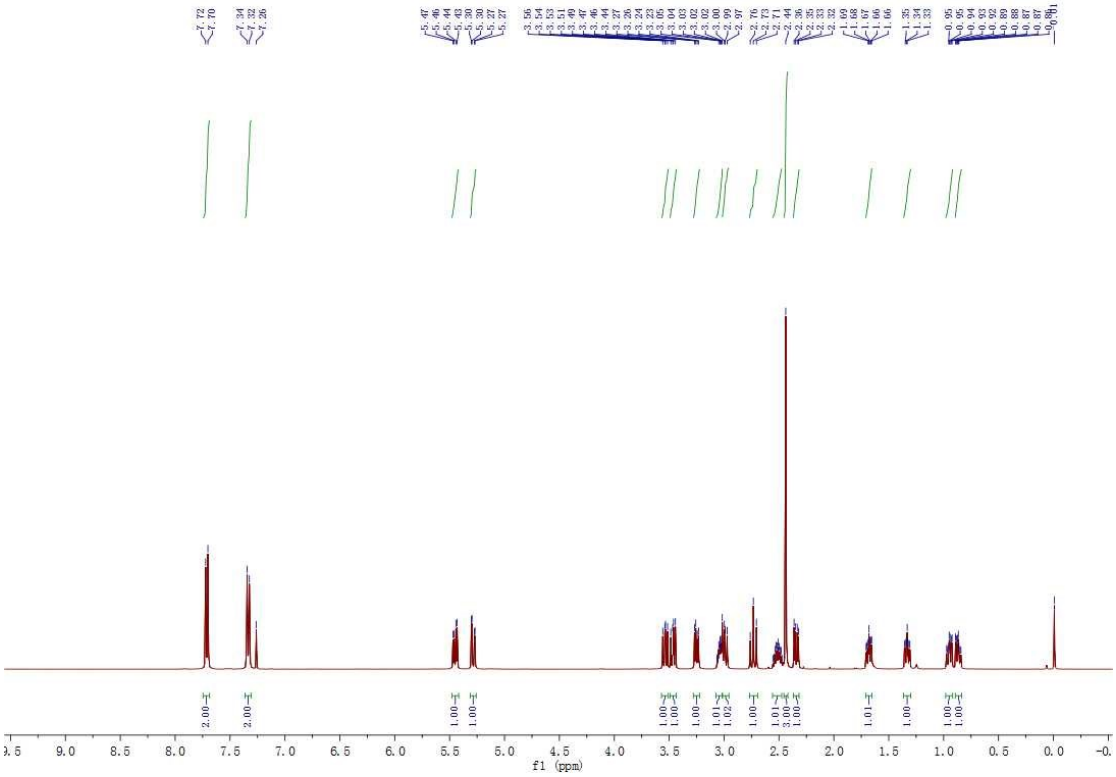
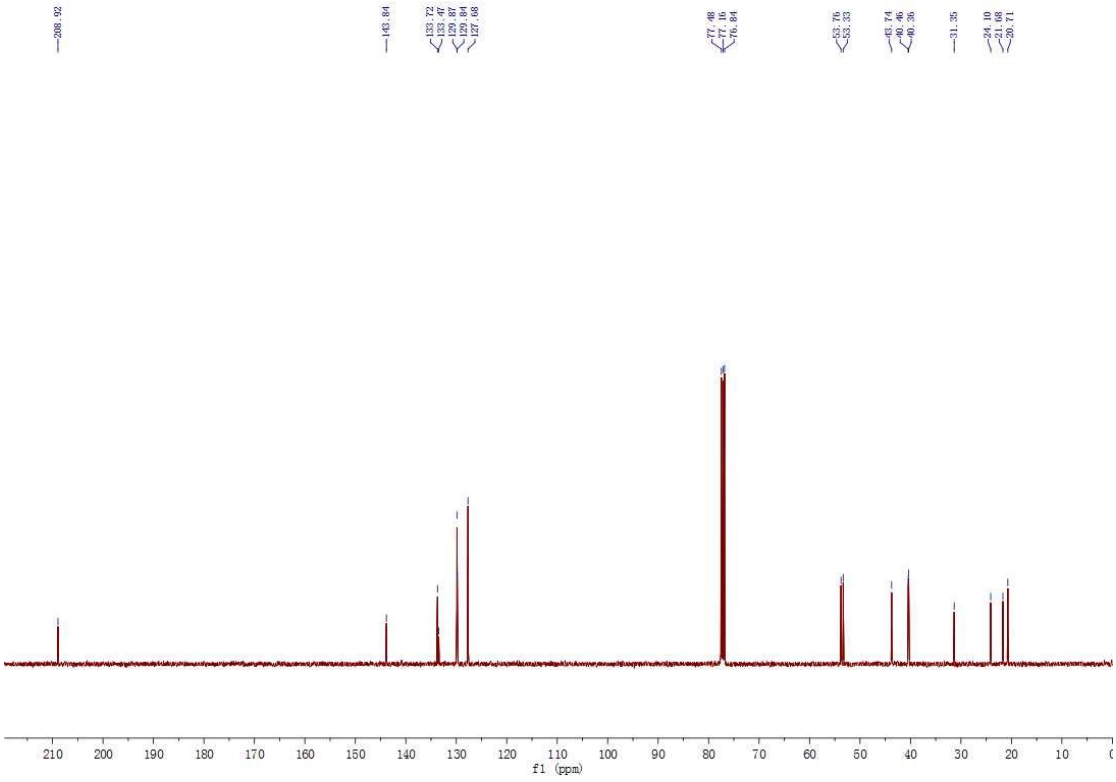
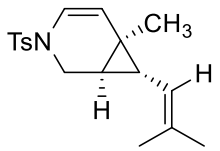
f1 (ppm)



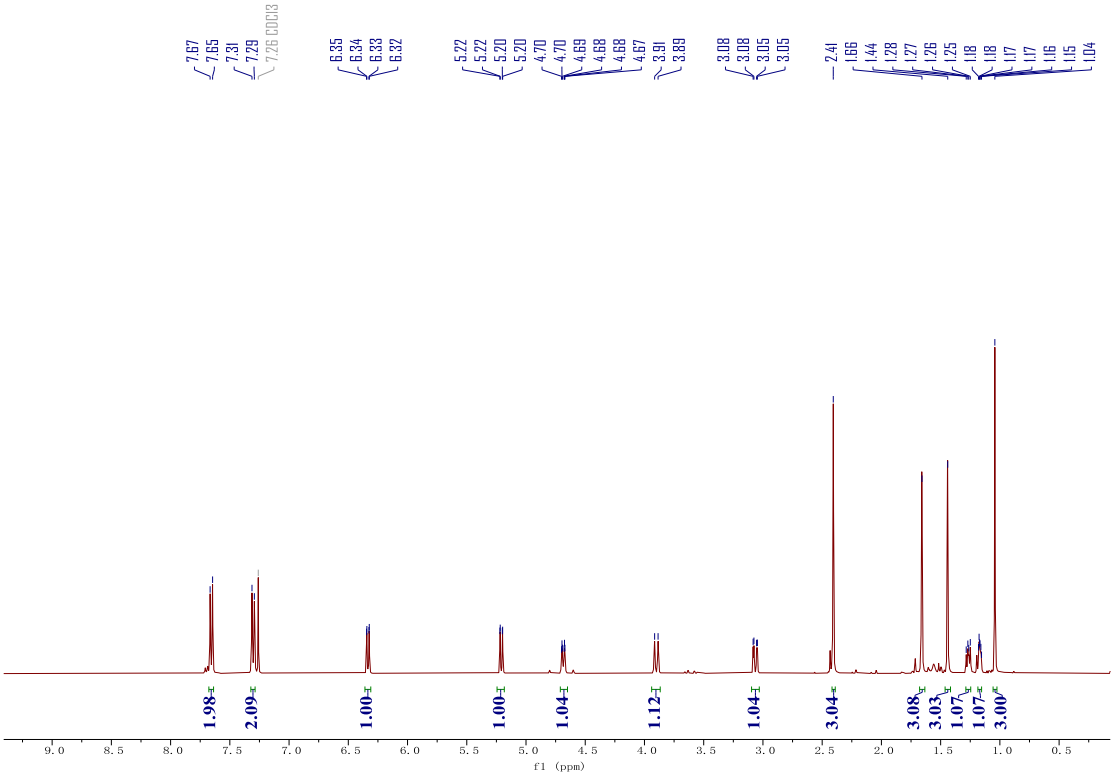
2p






TsN
CH3
H
H

5a


7.67
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7.26 CDCl3
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5.20
5.20
4.70
4.70
4.69
4.68
4.68
4.67
3.91
3.89
3.08
3.08
3.05
3.05
2.41
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1.44
1.28
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1.26
1.25
1.18
1.18
1.17
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1.16
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1.04
1.98
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3.04
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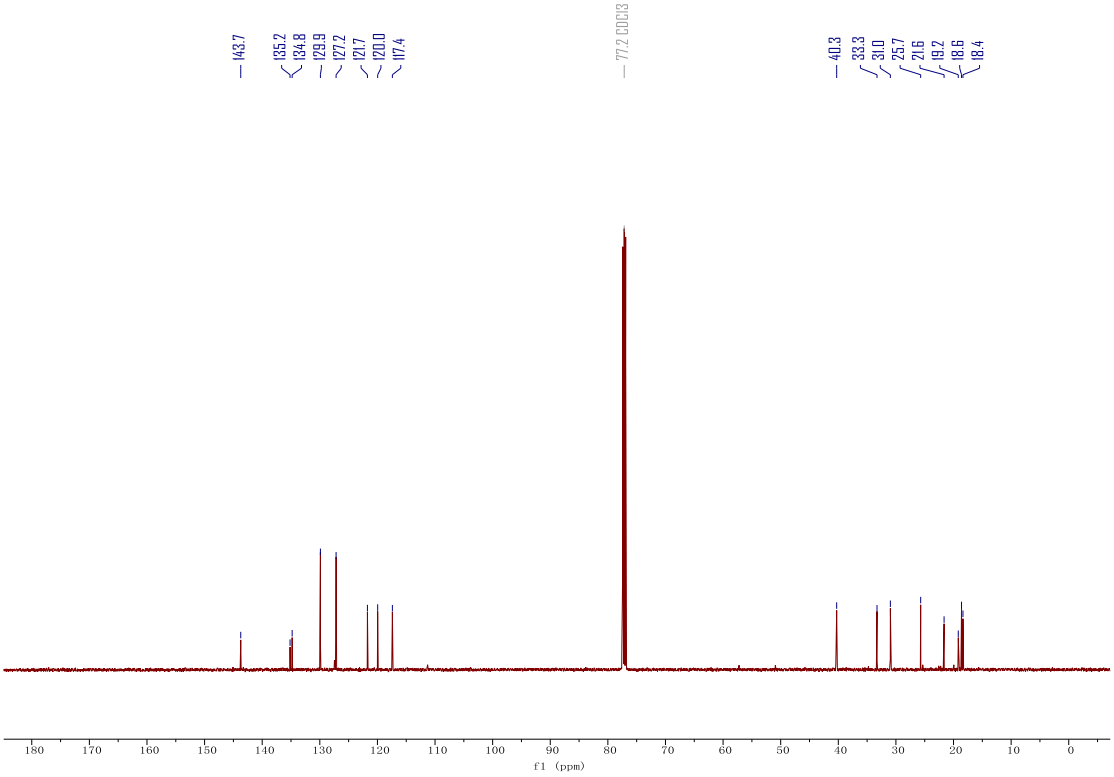
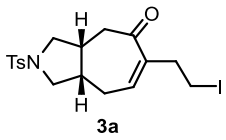
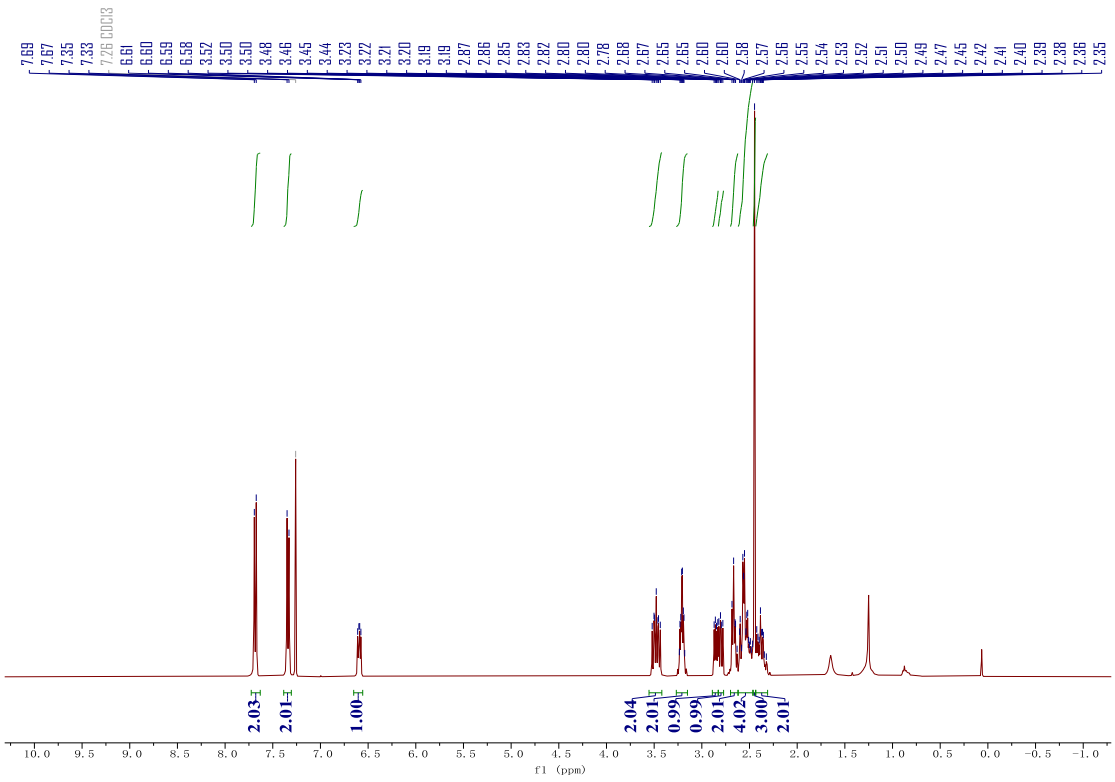
3.00
f1 (ppm)


143.7
135.2
134.8
129.9
127.2
121.7
120.0
117.4
77.2 CDCl3
40.3
33.3
31.0
25.7
21.6
19.2
18.6
18.4
f1 (ppm)


H
O
TsN
I
H

3a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7.67
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7.26 CDCl3
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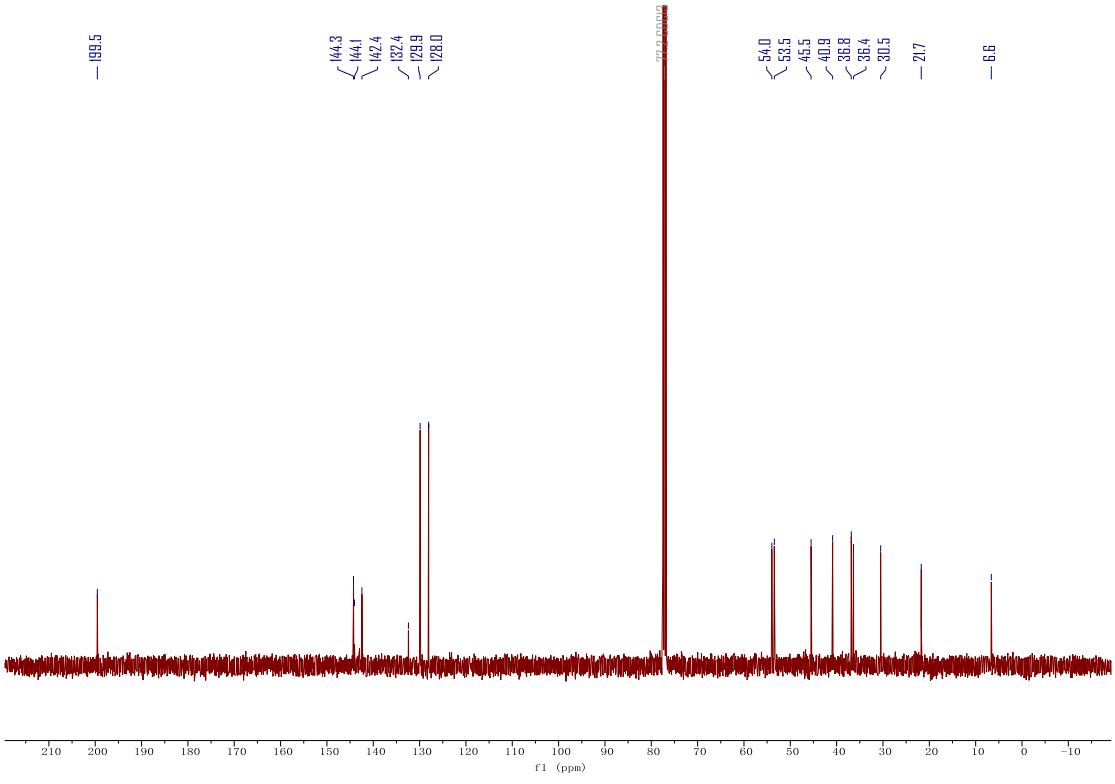
2.39
2.38
2.36
2.35
2.03
2.01
1.00
2.04
2.01
0.99
0.99
2.01
4.02
3.00
2.01
f1 (ppm)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144.1
142.4
132.4
129.9
128.0
77.0 CDCl3
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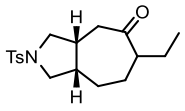
53.5
45.5
40.9
36.8
36.4
30.5
21.7
6.6
f1 (ppm)



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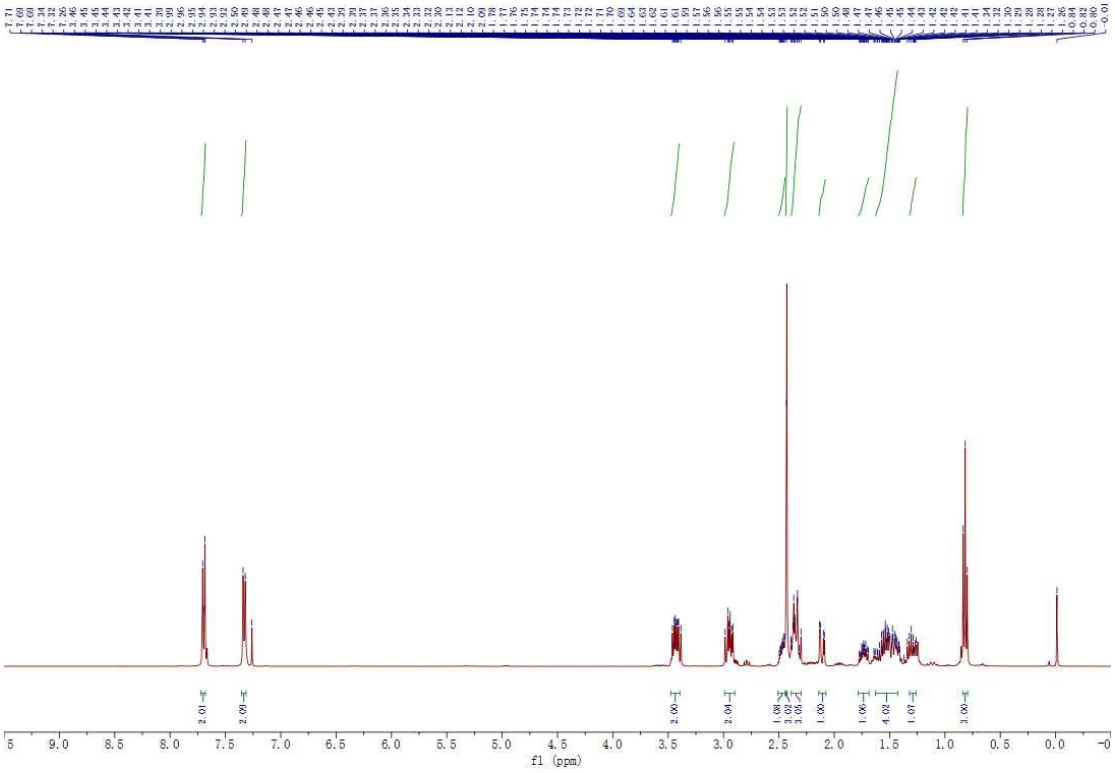

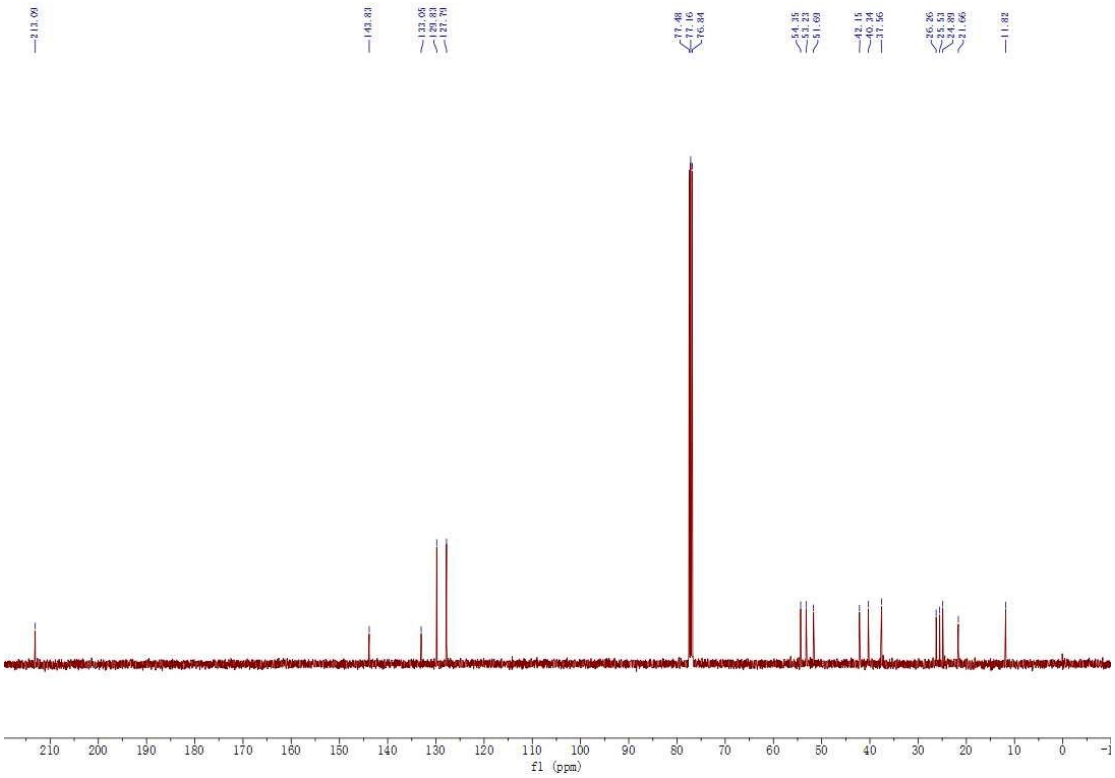

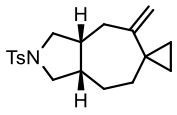

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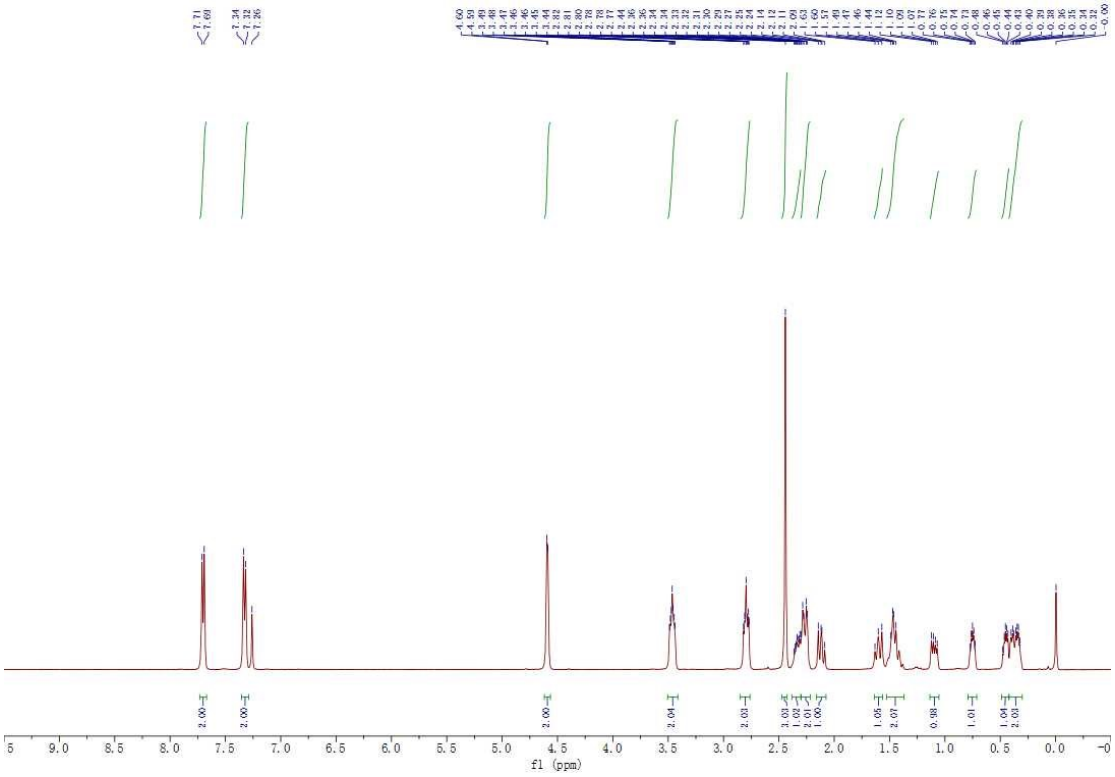

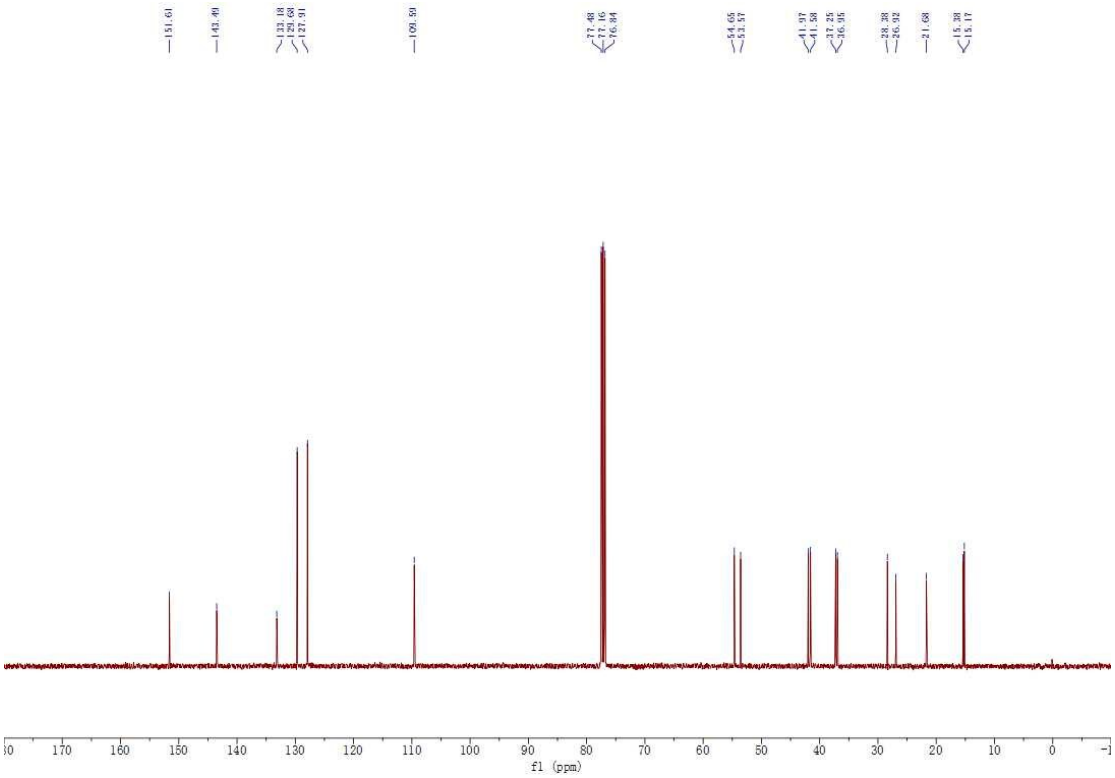

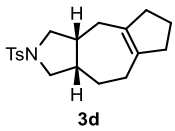

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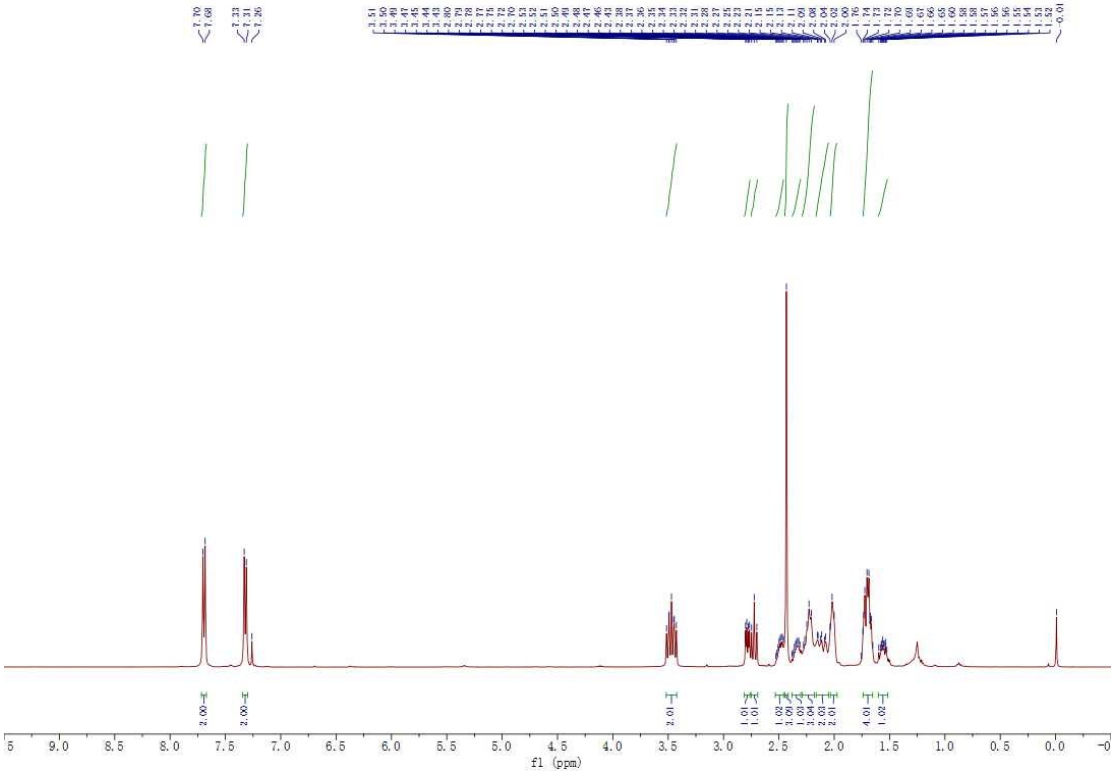

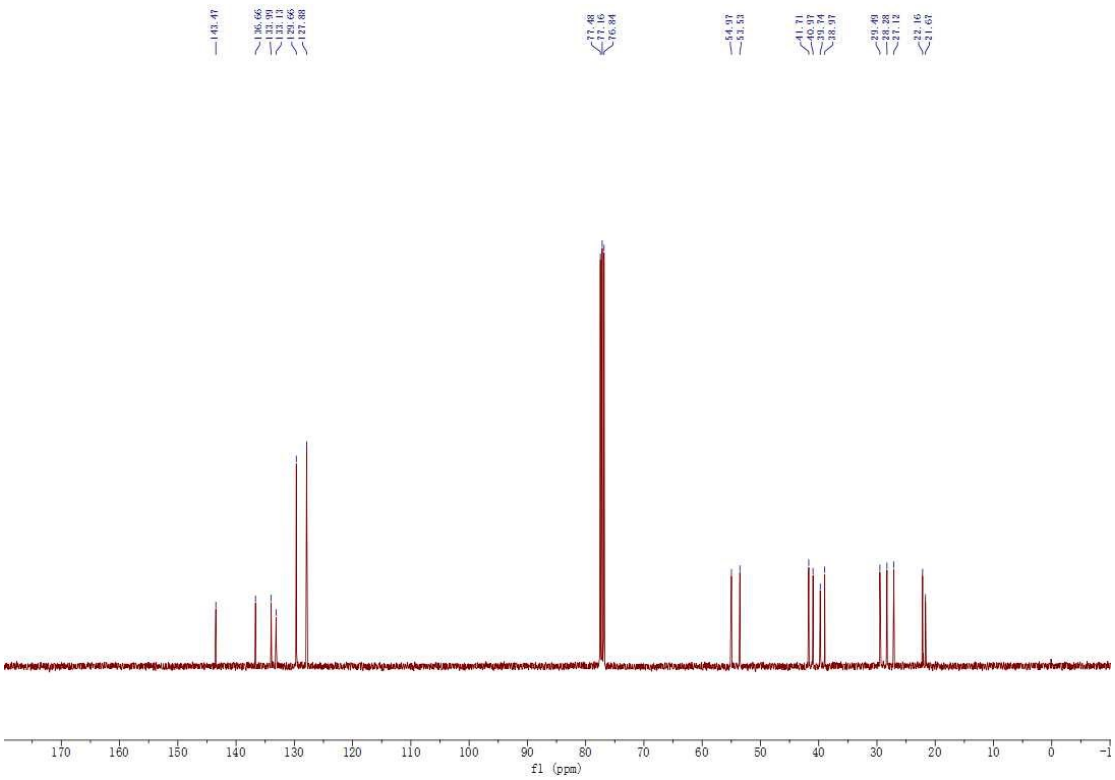

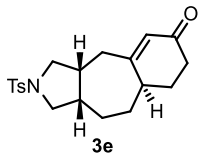

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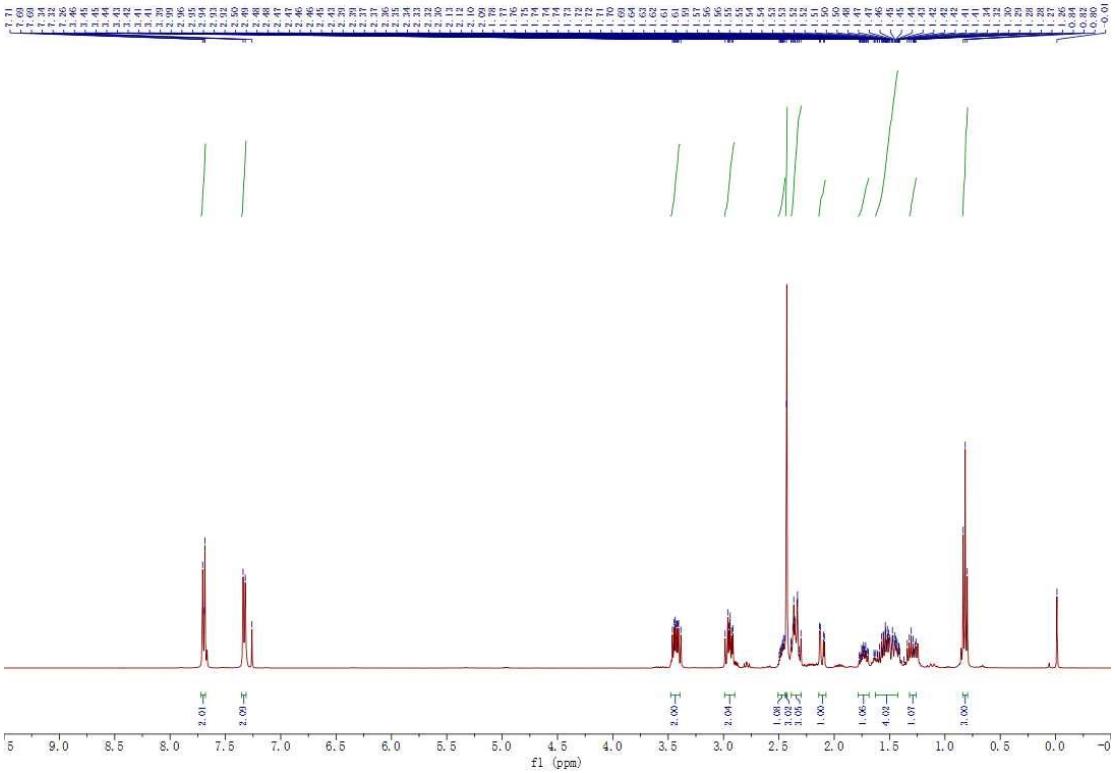

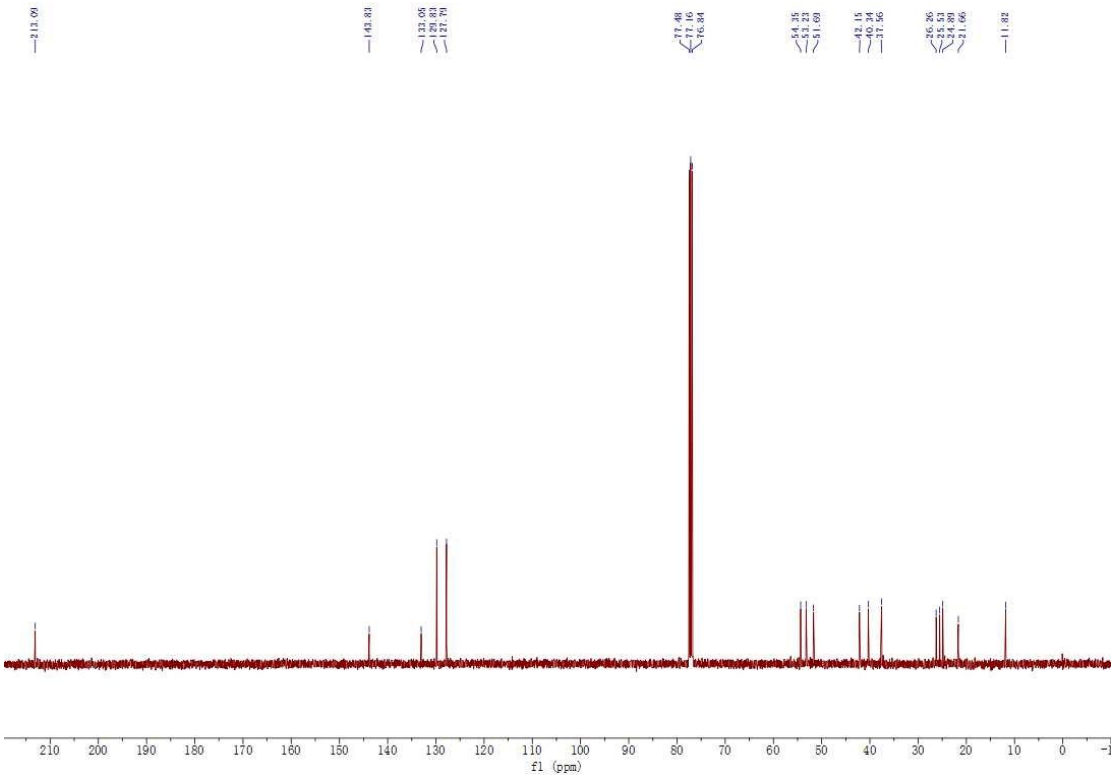

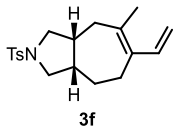

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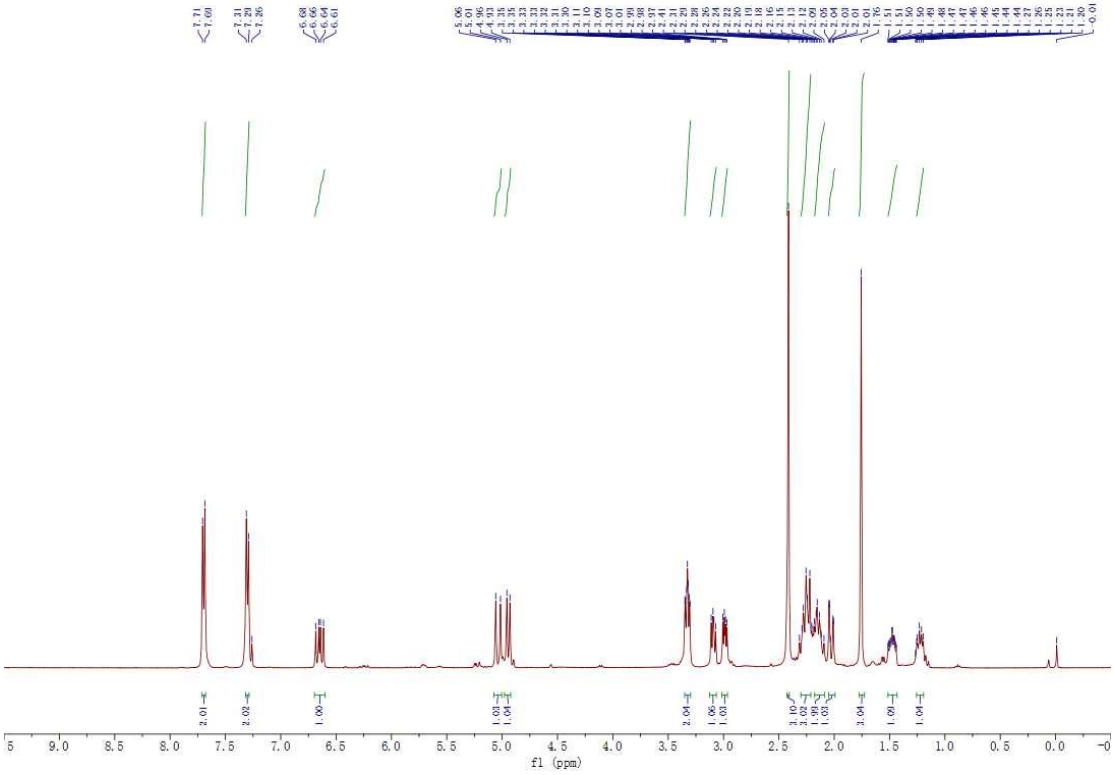
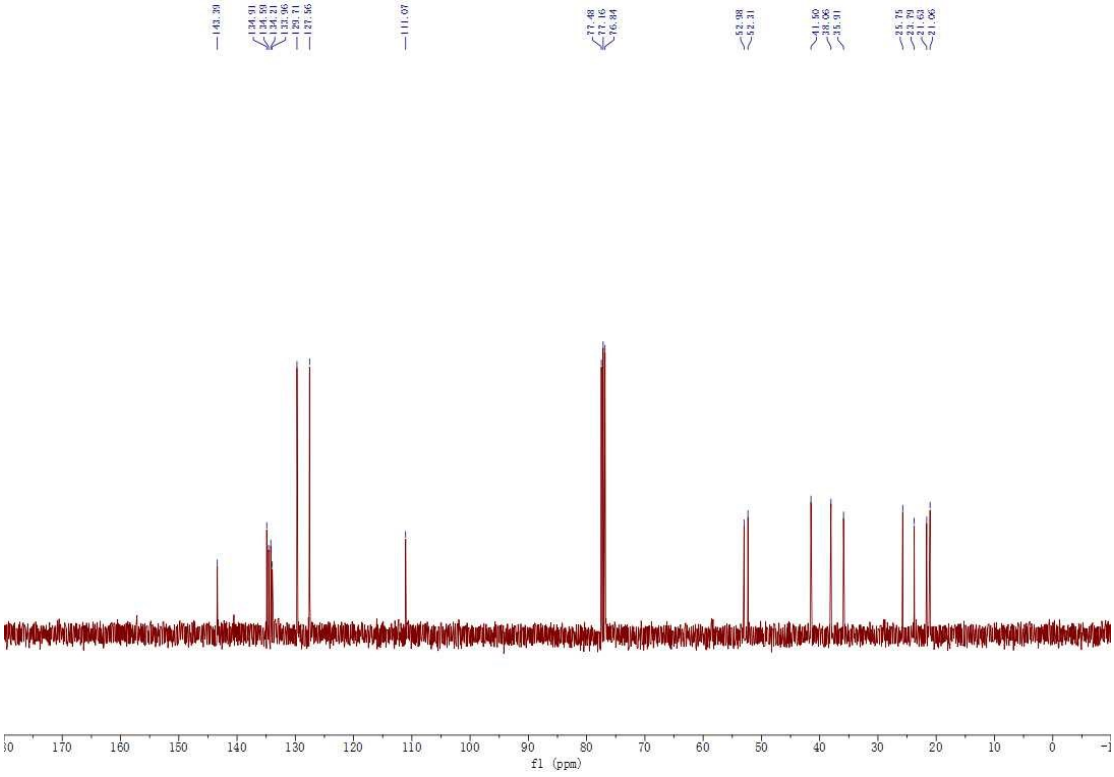
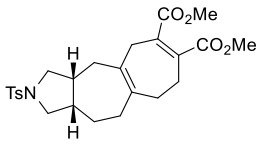
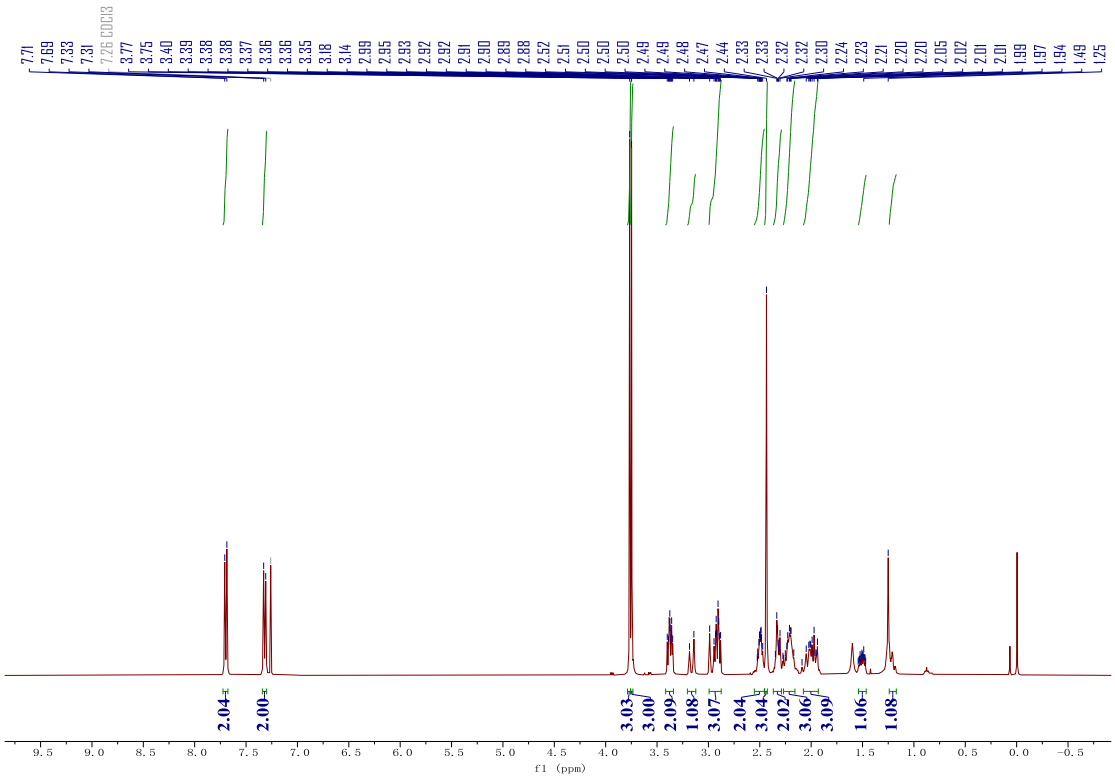





CO2Me
CO2Me
H
TsN
H

3g


7.71
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7.26 CDCl3
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3.38
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3.36
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2.50
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2.49
2.48
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2.32
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2.21
2.20
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2.01
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1.94
1.49
1.25
2.04
2.00
3.03
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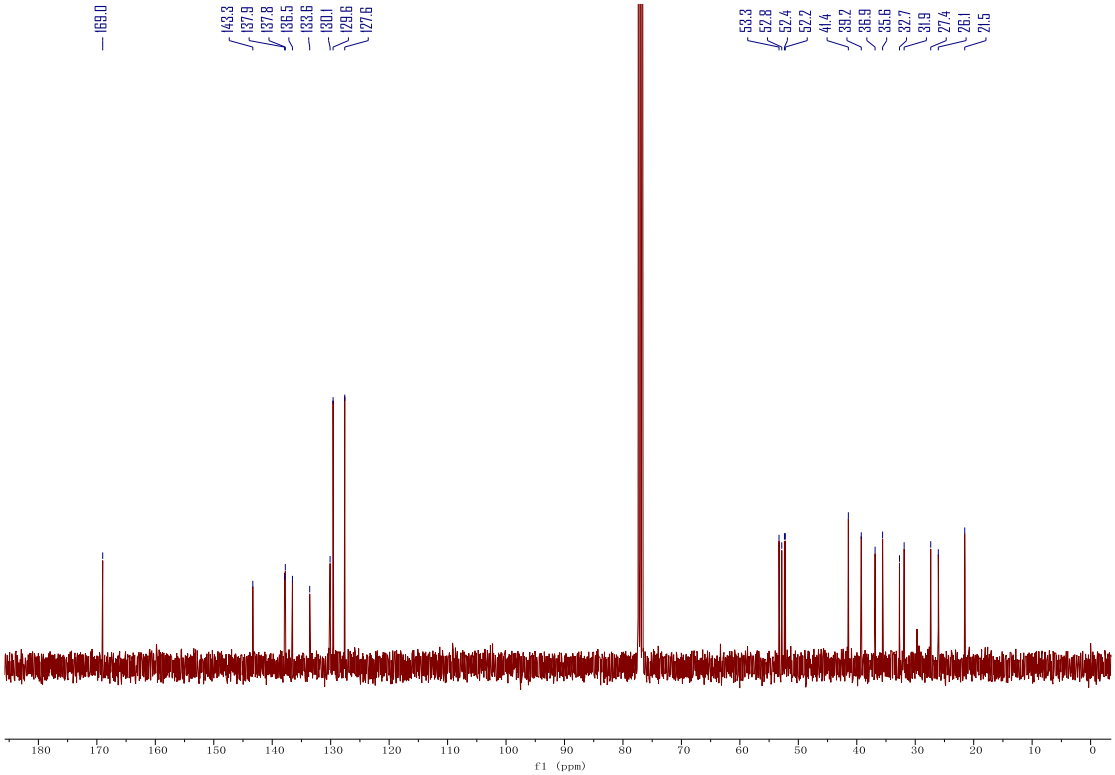
3.07
2.04
3.04
2.02
3.06
3.09
1.06
1.08
f1 (ppm)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137.9
137.8
136.5
133.6
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129.6
127.6
53.3
52.8
52.4
52.2
41.4
38.2
36.9
35.6
32.7
31.9
27.4
26.1
21.5
f1 (ppm)