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Supporting Information

Rh^{I}-Catalyzed Benzo/[7+1] Cycloaddition of Cyclopropyl-Benzocyclobutenes and CO by Merging Thermal and Metal-Catalyzed C–C Bond Cleavages

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Contents

1. General

Air and moisture sensitive reactions were carried out in oven-dried glassware sealed with rubber septa under a positive pressure of dry argon or nitrogen. 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. Tetrahydrofuran, diethyl ether, and toluene were distilled from sodium and benzophenone prior to use. Dichloromethane and dichloroethane were distilled from CaH_2 prior to use. Synthetic reagents were purchased from Acros, Aldrich, Alfa Aesar and J&K Scientific, 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 followed by gentle heating. Purification of products was accomplished by flash chromatography on silica gel and the purified compounds show a single spot by analytical TLC.

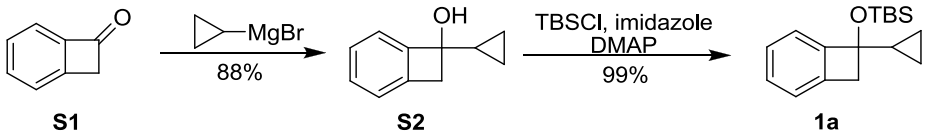
NMR spectra were measured on Bruker ARX 400 (^{1}H at 400 MHz, ^{13}C at 100 MHz) nuclear magnetic resonance spectrometers. Data for ^{1}H-NMR spectra are reported as follows: chemical shift (ppm, referenced to tetramethylsilane; s = singlet, br s = broad singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, dt = doublet of triplets, ddd = doublet of doublet of doublets, ddt = doublet of doublet of triplets, m = multiplet), coupling constant (Hz), and integration. Data for ^{13}C-NMR are reported in terms of chemical shift (ppm) relative to residual solvent peak ($CDCl_3$: 77.0 ppm). Infrared spectra were recorded on Mettler-Toledo ReactIR iC10 system with a SiComp probe and are reported in wavenumbers (cm^{-1}). High-resolution mass spectra (HRMS) were recorded on a Bruker Apex IV FTMS mass spectrometer (ESI) or a Waters GCT GC-MS (EI).

Abbreviations:
TBS = *t*-butyldimethylsilyl
TBSCl = *t*-butyldimethylsilyl chloride
DMAP = dimethylaminopyridine
Bn = benzyl
Me = methyl
Et = ethyl
Bu = butyl
TMS = trimethylsilyl
TMSCl = trimethylsilyl chloride
DCM = dichloromethane
EA = ethyl acetate
PE = petroleum ether
THF = tetrahydrofuran
DMF = dimethylformamide
TLC = thin layer chromatography
RT = room temperature
ca. = circa
brsm = based on recovered starting material

2. Experimental Procedures and Characterization Data

2.1 Synthesis of CP-BCB Substrates

CP-BCB (1a)



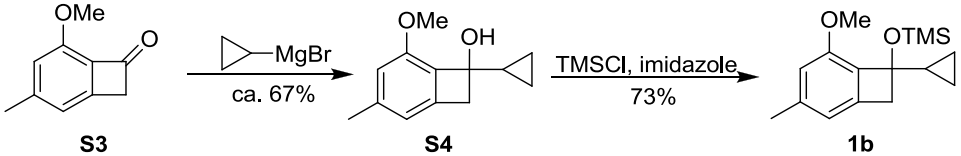
To a solution of benzocyclobutenone **S1**[1] (594 mg, 5.03 mmol) in THF (45 mL) at -78 ℃ was added cyclopropylmagnesium bromide (0.5 M solution in THF, 30 mL, 15 mmol), and the resulting solution was stirred for 1 hour. The reaction was quenched with saturated NH_4Cl solution and extracted with ether three times. The combined extract was washed with brine, dried over Na_2SO_4, filtered and concentrated under reduced pressure. The crude product was purified by flash column chromatography on silica gel (eluted with PE:EA = 20:1) to afford **S2** (706 mg, 88%).

S2: Pale yellow oil, TLC R_f = 0.33 (PE:EA = 5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30–7.23 (m, 1H), 7.22–7.11 (m, 2H), 7.08 (d, *J* = 7.3 Hz, 1H), 3.37 (d, *J* = 14.0 Hz, 1H), 3.17 (d, *J* = 14.0 Hz, 1H), 2.27 (br. s, 1H), 1.49–1.38 (m, 1H), 0.61–0.52 (m, 1H), 0.52–0.41 (m, 2H), 0.06–-0.02 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.8, 142.0, 129.4, 127.0, 123.7, 120.9, 81.8, 45.9, 18.1, 1.9, 1.7. IR (neat): υ 3351, 1458, 1345, 1138, 1047, 1026 cm^{-1}. HRMS (ESI) calcd for $C_{11}H_{12}NaO$ $(M+Na)^+$: 183.0780. Found: 183.0781.

Imidazole (257 mg, 0.74 mmol), DMAP (11 mg, 0.090 mmol), and TBSCl (455 mg, 3.01 mmol) was added to a solution of **S2** (119 mg, 0.74 mmol) in DMF (4 mL) at RT, and the resulting solution was stirred for 2 days at RT. The reaction was quenched with CH_3OH (5 mL), diluted by H_2O (15 mL) and extracted with ether three times. The combined organic phase was successively washed with water, brine, dried over Na_2SO_4, filtered and concentrated under reduced pressure. The crude product was purified by flash column chromatography on silica gel (eluted with PE:EA = 100:1) to afford CP-BCB **1a** (201 mg, 99%).

1a: Colorless oil, TLC R_f = 0.75 (PE:EA = 50:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28–7.21 (m, 1H), 7.17 (t, *J* = 7.5 Hz, 1H), 7.10 (t, *J* = 6.7 Hz, 2H), 3.34 (d, *J* = 13.9 Hz, 1H), 3.18 (d, *J* = 13.9 Hz, 1H), 1.27–1.21 (m, 1H), 0.85 (s, 9H), 0.57–0.48 (m, 1H), 0.47–0.39 (m, 1H), 0.39–0.31 (m, 1H), 0.21–0.11 (m, 1H), -0.04 (s, 3H), -0.14 (s, 3H).^{13}C NMR (100 MHz, $CDCl_3$): δ 149.6, 141.9, 128.9, 126.6, 123.6, 121.7, 81.3, 47.1, 25.7, 19.8, 18.1, 1.7, 1.2, -3.2, -3.4. IR (neat): 2928, 2856, 1472, 1459, 1251, 1176, 1143, 1067 cm^{-1}. HRMS (ESI) calcd for $C_{17}H_{26}NaOSi$ $(M+Na)^+$: 297.1645. Found: 297.1646.

CP-BCB (1b)



To a solution of crude substituted benzocyclobutenone **S3**[1] (632 mg, ca. 3.90 mmol) in THF (23 mL) at -78 ℃ was added cyclopropylmagnesium bromide (0.5 M solution in THF, 20 mL, 10 mmol), and the resulting solution was stirred for 2 hours. The reaction was quenched with saturated NH_4Cl solution and extracted with ether three times. The combined extract was washed with brine, dried over Na_2SO_4, filtered and concentrated under reduced pressure. The crude product was purified by flash column chromatography on silica gel (eluted with PE:EA = 50:1 to 10:1) to afford **S4** (530 mg, ca. 67%).

S3: White solid, TLC R_f = 0.65 (PE:EA = 5:1), m.p. 95–98 ℃.. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.84 (s, 1H), 6.60 (s, 1H), 4.08 (s, 3H), 3.84 (s, 2H), 2.37 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 184.3, 153.5, 150.6, 149.6,

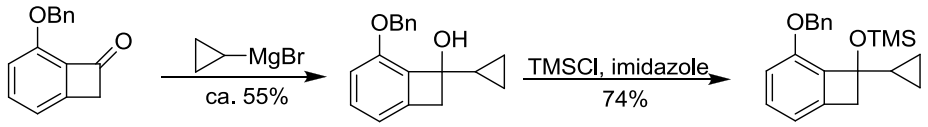
130.0, 116.3, 116.2, 59.7, 50.8, 22.5. IR (neat): 1753, 1606, 1566, 1475, 1433, 1355, 1286, 1124, 1003 cm^{-1}. HRMS (ESI) calcd for $C_{10}H_{10}NaO_2$ $(M+Na)^+$: 185.0573. Found: 183.0572.

S4: Pale yellow oil, TLC R_f = 0.51 (PE:EA = 5:1). ^1H NMR (400 MHz, $CDCl_3$) δ 6.56 (s, 1H), 6.49 (s, 1H), 3.84 (s, 3H), 3.19 (d, *J* = 13.9 Hz, 1H), 3.01 (d, *J* = 13.9 Hz, 1H), 2.59 (s, 1H), 2.31 (s, 3H), 1.47–1.36 (m, 1H), 0.68–0.58 (m, 1H), 0.53–0.46 (m, 2H), 0.26–0.17 (m, 1H).^{13}C NMR (100 MHz, $CDCl_3$): δ 153.4, 143.4, 141.2, 129.8, 116.7, 112.2, 81.0, 56.1, 44.8, 22.0, 19.0, 2.3, 2.2. IR (neat): 3380, 1606, 1577, 1477, 1419, 1343, 1301, 1225, 1125 cm^{-1}. HRMS (ESI) calcd for $C_{13}H_{16}NaO_2$ $(M+Na)^+$: 227.1043. Found: 227.1044.

Imidazole (1.07 g, 15.7 mmol), and TMSCl (1.6 mL, 1.37 g, 12.6 mmol) was added to a solution of **S4** (509 mg, 2.49 mmol) in DMF (12 mL) at RT, and the resulting solution was stirred at RT. After 13 hours, extra imidazole (0.54 g, 7.9 mmol) and TMSCl (0.8 mL, 0.69 g, 6.3 mmol) was added. The reaction was further stirred for 48 hours and then quenched with saturated $NaHCO_3$ solution, and extracted with ethyl acetate three times. The combined extract was successively washed with water, brine, dried over Na_2SO_4, filtered and concentrated under reduced pressure. The crude product was purified by flash column chromatography on silica gel (eluted with PE:EA = 100:1) to afford CP-BCB **1b** (499 mg, 73%).

1b: Colorless oil, TLC R_f = 0.79 (PE:EA = 5:1). ^1H NMR (400 MHz, $CDCl_3$): δ 6.53 (s, 1H), 6.48 (s, 1H), 3.86 (s, 3H), 3.15 (d, *J* = 13.9 Hz, 1H), 3.08 (d, *J* = 13.9 Hz, 1H), 2.30 (s, 3H), 1.30–1.27 (m, 1H), 0.58–0.51 (m, 1H), 0.45–0.42 (m, 1H), 0.42–0.39 (m, 1H), 0.28–0.20 (m, 1H), 0.04 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 153.5, 143.3, 140.9, 130.9, 116.5, 112.6, 81.6, 56.2, 45.2, 22.1, 20.5, 2.7, 2.4, 1.5. IR (neat): 2954, 1606, 1465, 1302, 1250, 1132, 1069 cm^{-1}. HRMS (ESI) calcd for $C_{16}H_{24}NaO_2Si$ $(M+Na)^+$: 299.1438. Found: 299.1435.

CP-BCB (1c)



S5 **S6** **1c**

To a solution of crude substituted benzocyclobutenone **S5**[2] (1.59 g, ca. 7.10 mmol) in THF (70 mL) at -78 ℃ was added cyclopropylmagnesium bromide (0.7 M solution in THF, 30 mL, 21 mmol), and the resulting solution was stirred for 4 hours. The reaction was quenched with saturated NH_4Cl solution and extracted with ether three times. The combined extract was washed with brine, dried over Na_2SO_4, filtered and concentrated under reduced pressure. The crude product was purified by flash column chromatography on silica gel (eluted with PE:EA = 20:1 to 10:1) to afford **S6** (1.04 g, ca. 55%).

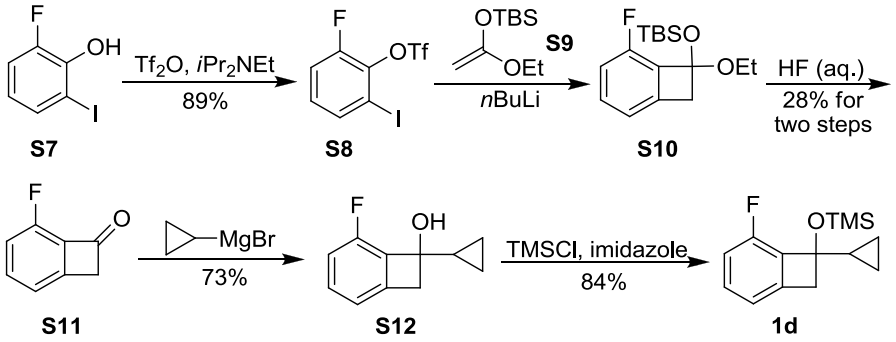
S6: Pale yellow oil, TLC R_f = 0.37 (PE:EA = 5:1). δ 7.47–7.42 (m, 2H), 7.39 (t, *J* = 7.5 Hz, 2H), 7.36–7.31 (m, 1H), 7.21 (t, *J* = 7.8 Hz, 1H), 6.82–6.73 (m, 2H), 5.18 (s, 2H), 3.29 (d, *J* = 14.0 Hz, 1H), 3.10 (d, *J* = 14.0 Hz, 1H), 2.62 (br. s, 1H), 1.52–1.43 (m, 1H), 0.79–0.70 (m, 1H), 0.59–0.50 (m, 2H), 0.36–0.27 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.7, 143.7, 137.1, 133.3, 130.8, 128.5, 127.8, 127.3, 116.4, 112.7, 81.4, 70.7, 45.3, 19.1, 2.5, 2.3. IR (neat): 3418, 2924, 1603, 1453, 1261, 1050, 1028 cm^{-1}. HRMS (ESI) calcd for $C_{18}H_{18}NaO_2$ $(M+Na)^+$: 289.1199. Found: 289.1197.

Imidazole (1.53 g, 22.5 mmol), and TMSCl (1.62 g, 14.9 mmol) was added to a solution of **S6** (1.04 g, 3.90 mmol) in DMF (40 mL) at RT, and the resulting solution was stirred for 2 days at RT. The reaction was quenched with saturated $NaHCO_3$ solution, and extracted with ethyl acetate three times. The combined extract was successively washed with water, brine, dried over Na_2SO_4, filtered and concentrated under reduced pressure. The crude product was purified by flash column chromatography on silica gel (eluted with PE:EA = 50:1) to afford CP-BCB **1c** (0.98 g, 74%).

1c: Colorless oil, TLC R_f = 0.78 (PE: EA = 10:1). ^1H NMR (400 MHz, $CDCl_3$) δ 7.47–7.42 (m, 2H), 7.38 (t, *J* =

7.3 Hz, 2H), 7.35–7.29 (m, 1H), 7.19 (dd, *J* = 8.4, 7.2 Hz, 1H), 6.74 (dd, *J* = 7.5, 5.4 Hz, 2H), 5.20 (s, 2H), 3.24 (d, *J* = 14.0 Hz, 1H), 3.17 (d, *J* = 14.0 Hz, 1H), 1.41–1.32 (m, 1H), 0.64–0.56 (m, 1H), 0.49–0.42 (m, 2H), 0.38–0.30 (m, 1H), 0.04 (s, 9H).^{13}C NMR (100 MHz, $CDCl_3$): δ 152.9, 143.5, 137.4, 134.5, 130.6, 128.5, 127.7, 127.3, 116.2, 113.2, 81.9, 71.1, 45.5, 20.6, 2.9, 2.4, 1.5. IR (neat): 1603, 1475, 1455, 1263, 1251, 1145, 1075, 1057 cm^{-1}. HRMS (ESI) calcd for $C_{21}H_{26}NaO_2Si$ $(M+Na)^+$: 361.1594. Found: 361.1594.

CP-BCB (1d)



Intermediate **S8** was prepared according to the protocol reported by Snowden:[3] To a solution of **S7**[4] (1.37 g, 4.24 mmol) in CH_2Cl_2 (12 mL) at -78 °C was added *i*Pr_2NEt (0.95 mL, 703 mg, 5.40 mmol) and Tf_2O (0.9 mL, 1.55 g, 5.49 mmol). After 10 min, the cooling bath was removed and the reaction mixture was allowed to warm to RT and stirred overnight. The reaction was quenched with H_2O (20 mL) and extracted with ether three times. The combined extract was washed with brine, dried over Na_2SO_4, filtered and concentrated under reduced pressure. The crude product was purified by flash column chromatography on silica gel (eluted with PE/EA = 50/1) to afford **S8** (1.40 g, 3.78 mmol).

Ketone **S11** was prepared by using Suzuki's method[1-2]: To a mixture of triflate **S8** (1.36 g, 3.68 mmol) and ketene silyl acetal **S9**[5] (1.13 g, 5.59 mmol) in THF (20 mL) was added *n*BuLi (1.6 M in hexane, 2.8 mL, 4.48 mmol) at -78 °C. After 10 min, the reaction was quenched with water and extracted with ethyl acetate three times. The combined extract was washed with brine, dried over Na_2SO_4, filtered and concentrated under reduced pressure. The crude product **S10** was used in the next step without further purification.

To a solution of **S10** in CH_3CN (12 mL) was added 40% aqueous HF (2 mL) at 0 °C. The reaction was stirred at RT overnight. The reaction was quenched by adding saturated $NaHCO_3$ solution and extracted by ethyl acetate three times. The combined extract was washed with brine, dried over Na_2SO_4, filtered and concentrated under reduced pressure. The crude product was purified by flash column chromatography on silica gel (eluted with PE:EA = 50:1) to afford **S11**[6] (139 g, 1.02 mmol).

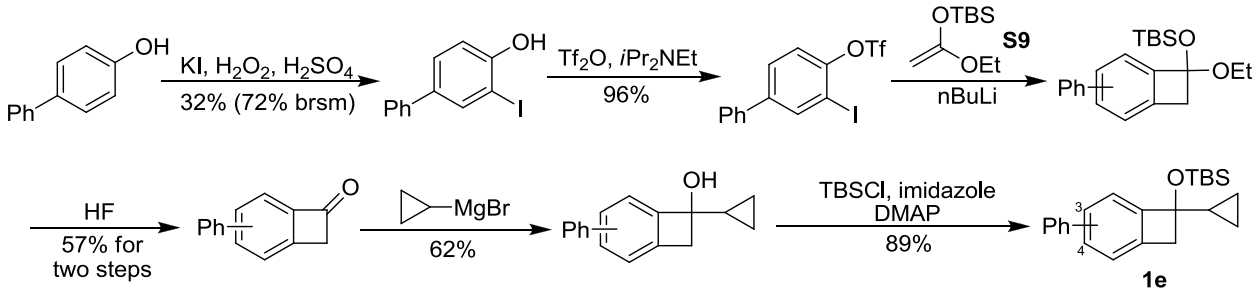
S12 (121 mg, 0.68 mmol) was prepared from **S11** (127 mg, 0.93 mmol) in 73% yield following the same procedure as **S6** from **S5**.

S12: Colorless oil, TLC R_f = 0.35 (PE: EA = 5:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.30–7.19 (m, 1H), 6.94 (dd, *J* = 7.0, 1.7 Hz, 1H), 6.83 (t, *J* = 8.5 Hz, 1H), 3.37 (d, *J* = 14.1 Hz, 1H), 3.21 (d, *J* = 14.1 Hz, 1H), 2.60 (br. s, 1H), 1.54–1.43 (m, 1H), 0.69–0.55 (m, 2H), 0.54–0.45 (m, 1H), 0.11–0.02 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.0 (d, $J_{C\text{-}F}$ = 258 Hz), 144.8 (d, $J_{C\text{-}F}$ = 8.9 Hz), 131.6 (d, $J_{C\text{-}F}$ = 16.2 Hz), 131.3 (d, $J_{C\text{-}F}$ = 6.0 Hz), 119.9 (d, $J_{C\text{-}F}$ = 4.2 Hz), 113.9 (d, $J_{C\text{-}F}$ = 20.8 Hz), 82.1, 45.8 (d, $J_{C\text{-}F}$ = 1.4 Hz), 18.7, 2.4 (d, $J_{C\text{-}F}$ = 3.2 Hz), 2.2. IR (neat): 3375, 1607, 1471, 1347, 1240, 1143, 1050, 1006 cm^{-1}. HRMS (ESI) calcd for $C_{11}H_{11}FNaO$ $(M+Na)^+$: 201.0686. Found: 201.0679.

1d (119 mg, 0.47 mmol) was prepared from **S12** (101 mg, 0.57 mmol) in 84% yield following the same procedure as **1c** from **S6**.

1d: Colorless oil, TLC R_f = 0.50 (PE: EA = 50:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.27–7.21 (m, 1H), 6.92 (dd, *J* = 7.1, 2.1 Hz, 1H), 6.82 (t, *J* = 8.6 Hz, 1H), 3.33 (d, *J* = 14.1 Hz, 1H), 3.19 (d, *J* = 14.1 Hz, 1H), 1.41–1.32 (m, 1H), 0.65–0.56 (m, 1H), 0.56–0.47 (m, 1H), 0.46–0.36 (m, 1H), 0.06 (s, 9H), 0.05–0.01 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.2 (d, J_{C-F} = 253 Hz), 144.9 (d, J_{C-F} = 9.1 Hz), 132.6 (d, J_{C-F} = 16.1 Hz), 131.2 (d, J_{C-F} = 6.1 Hz),119.8 (d, J_{C-F} = 4.2 Hz), 113.9 (d, J_{C-F} = 15.6 Hz), 82.6, 47.2 (d, J_{C-F} = 1.5 Hz), 19.9, 2.8 (d, J_{C-F} = 2.7 Hz), 1.9, 1.25 (d, J_{C-F} = 0.6 Hz). IR (neat): 1596, 1471, 1251, 1179, 1148, 1078, 1008 cm^{-1}. HRMS (ESI) calcd for $C_{14}H_{19}FNaOSi$ $(M+Na)^+$: 273.1081. Found: 273.1077.

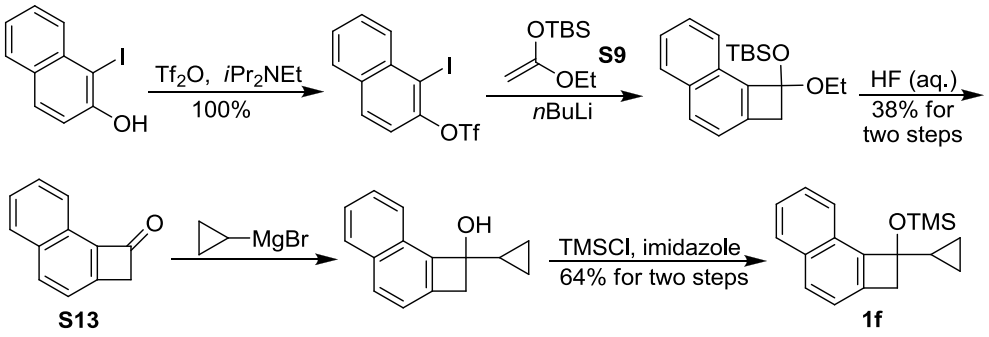
CP-BCB (1e)



1e, as a mixture (ca. 1:1) of regioisomers with the phenyl in 3 or 4 position, was prepared from 2-iodo-4-phenylphenol[7] following the same procedure as **1d** from **S7**.

1e (an inseparable mixture of compound with the phenyl at 3 or 4 position): Colorless oil, TLC R_f = 0.50 (PE: EA = 50:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59–7.40 (m, 5H), 7.34 (m, 2H), 7.18 (t, *J* = 7.9 Hz, 1H), 3.39 (d, *J* = 14.0 Hz, 0.5H), 3.38 (d, *J* = 14.0 Hz, 0.5 H), 3.23 (d, *J* = 14 Hz, 0.5 H), 3.22 (d, *J* = 14 Hz, 0.5 H), 1.33–1.25 (m, 1H), 0.88 (s, 9H), 0.62–0.52 (m, 1H), 0.51–0.43 (m, 1H), 0.43–0.33 (m, 1H), 0.27–0.17 (m, 1H), 0.02 (3H), -0.09 (3H). (We cannot determine the exact ratio of these two isomers from the NMR integrals. The approximate ratio is 1:1) ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.2, 148.5, 142.33, 142.30, 142.1, 142.0, 141.0, 140.2, 128.69, 128.66, 128.3, 127.29, 127.25, 127.04, 126.95, 126.1, 123.8, 122.5, 122.0, 120.6, 81.11, 81.08, 46.9, 46.7, 25.7, 19.86, 19.83, 18.10, 18.09, 1.84, 1.79, 1.31, -2.94, -3.09, -3.12, -3.25, -3.27. IR (neat): 2951, 2930, 2856, 1464, 1254, 1074 cm^{-1}. HRMS (ESI) calcd for $C_{23}H_{30}NaOSi$ $(M+Na)^+$: 373.1958. Found: 373.1960.

CP-BCB (1f)



The known compound **S13** [8] was prepared from 1-iodo-2-naphthol [7] as **S11** from **S7** using Suzuki's protocol.[1-2] The reaction gave the indicated isomer mostly (the ratio of **S13** and its regioisomer is greater than 15:1. The isomer of **S13**, 1-H-Cyclobuta[a]naphthalen-1-one had been reported in literature [9])

S13: White solid, TLC R_f = 0.34(PE: EA = 10:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (d, *J* = 8.1 Hz, 1H), 8.04

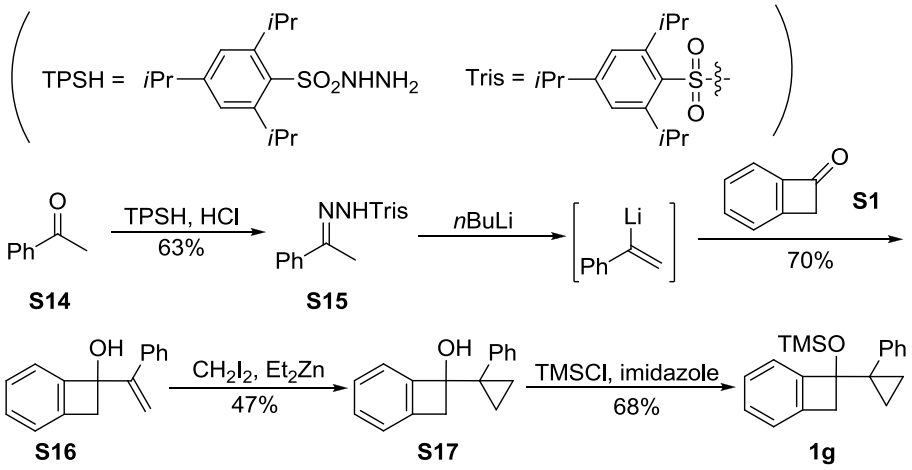
(d, J = 8.2 Hz, 1H), 7.91 (d, J = 8.2 Hz, 1H), 7.68 – 7.61 (m, 2H), 7.57 – 7.51 (m, 1H), 4.06 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 186.6, 153.6, 143.0, 136.8, 133.3, 129.18, 129.15, 126.6, 125.8, 124.0, 121.1, 51.6.

To the solution of **S13** (302 mg, 1.80 mmol) in THF (10 mL) at -78 ℃ was added cyclopropylmagnesium bromide (0.5 M solution in THF, 9.0 mL, 4.5 mmol), and the resulting solution was stirred for 1.5 hours. The reaction was quenched with saturated NH_4Cl solution and extracted with ether three times. The combined extract was washed with brine, dried over Na_2SO_4, filtered and concentrated under reduced pressure. The crude product was used directly without further purification.

1f was prepared from the corresponding alcohol following the same procedure as **1d** from **S12**.

1f: White solid, TLC R_f = 0.78 (PE: EA = 50:1), m.p. 67–69 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87–7.75 (m, 3H), 7.48 (t, J = 7.3 Hz, 1H), 7.40 (t, J = 7.4 Hz, 1H), 7.27 (d, J = 8.1 Hz, 1H), 3.38 (d, J = 13.6 Hz, 1H), 3.31 (d, J = 13.6 Hz, 1H), 1.38–1.29 (m, 1H), 0.64–0.56 (m, 1H), 0.54–0.47 (m, 2H), 0.45–0.40 (m, 1H), -0.06 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 146.0, 139.2, 133.2, 129.7, 129.5, 128.4, 126.3, 124.7, 123.6, 121.9, 81.3, 46.1, 19.8, 2.2, 1.8, 1.5. IR (neat) 2954, 1251, 1224, 1120, 1077, 1057 cm^{-1}. HRMS (ESI) calcd for $C_{18}H_{22}NaOSi$ $(M+Na)^+$: 305.1332. Found: 305.1335.

CP-BCB (1g)



Acetophenone **S14** (600 mg, 5 mmol) was added to the solution of 2,4,6-triisopropylbenzenesulfonyl hydrazide (TPSH) (1.52 g, 5.1 mmol) in methanol (20 mL). Several drops of concentrated HCl was added to catalyze the reaction. The solution was stirred at RT for 18 hours. Then saturated $NaHCO_3$ solution was added to quench the reaction and the mixture was extracted with ether three times. The combined organic phase was dried over anhydrous Na_2SO_4, concentrated, and purified by column chromatography on silica gel (eluted with PE:EA = 10:1 to 5:1) to give the pure hydrazone product **S15**[10] (1.27 g, 63%).

Alcohol **S16** was prepared by Shapiro reaction[10-11]: To the solution of **S15** (1.39 g, 3.45 mmol) in THF (23 mL) at -78 ℃ was added *n*BuLi (1.6M in hexanes, 7.6 mL, 4.75 mmol) drop by drop. After *n*BuLi was added, the solution became orange-yellow. The solution was stirred at -78 ℃ for 0.5 hour. Then the reaction was warmed to 0 ℃ and stirred for 10 minutes. Nitrogen evolution can be observed and the solution became brown. The solution was cooled to -78 ℃, and the solution of **S1** (630 mg, 5.34 mmol) in THF (10 mL) was added. The solution was stirred for further 0.5 hour and quenched by saturated NH_4Cl solution. The organic phase was seperated and the aqueous layer was extracted by ether two times. The combined organic phase was dried over anhydrous Na_2SO_4, concentrated, and eluted with PE:EA = 10:1 through a thin layer of silica gel quickly to give the crude alcohol product **S16** (533 mg, 70%). Because the intermediate **S16** was not stable, the product was used directly without further purifiaction.

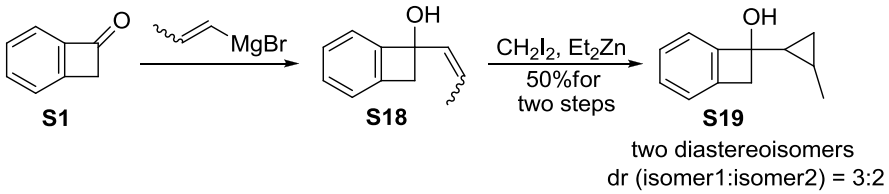
To the solution of **S16** (120 mg, 0.541 mmol) in DCM (6.5 mL) at 0 ℃ was added CH_2I_2 (0.11 mL, 1.36 mmol) and Et_2Zn (1M in THF, 2.7 mL, 2.7 mmol). The reaction was stirred at 0 °C for 2 hours and was qunenched by adding saturated NH_4Cl solution. Ether was added to the solution and the organic phase was separated. The aqueous phase was extracted by ether two times. The combined organic phase was then washed with brine and dried over Na_2SO_4, filtered and concentrated under reduced pressure. The crude product was purified by flash column chromatography on silica gel (eluted with PE/EA = 20:1 to 10:1) to afford **S17** (60.3 mg, 0.256 mmol).

S17: Colorless oil, TLC R_f = 0.33 (PE:EA = 5:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.51 (d, *J* = 8.1 Hz , 2H), 7.34 (t, *J* = 7.6 Hz, 2H), 7.27 (dd, *J* = 13.4, 4.4 Hz, 2H), 7.19 (t, *J* = 7.5 Hz, 1H), 7.14 (d, *J* = 7.2 Hz, 1H), 7.05 (d, *J* = 7.3 Hz, 1H), 3.54 (d, *J* = 14.1 Hz, 1H), 3.01 (d, *J* = 14.1 Hz, 1H), 2.41 (br s, 1H), 1.14 (m, 1H), 0.92 (m, 1H), 0.79 (m, 1H), 0.61 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.4, 142.3, 142.0, 131.2, 129.5, 128.2, 127.0, 123.7, 121.2, 83.8, 44.6, 31.6, 10.33, 10.30. IR (neat): 3390, 3068, 2927, 1600, 1494, 1458, 1210, 1050, 1026 cm^{-1}. HRMS (ESI) calcd for $C_{17}H_{16}NaO$ $(M+Na)^+$: 259.1093. Found: 259.1100.

Substrate **1g** (53.8 mg, 0.174 mmol) was prepared from **S17** (60.3 mg, 0.256 mmol) in 68% yield following the same procedure as **1c** from **S6**.

1g: Colorless oil, TLC R_f = 0.35 (PE:EA = 50:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.45 (d, *J* = 6.9 Hz, 2H), 7.31–7.14 (m, 5H), 7.10–7.02 (m, 2H), 3.41 (d, *J* = 14.2 Hz, 1H), 3.00 (d, *J* = 14.2 Hz, 1H), 1.07–0.99 (m, 1H), 0.84–0.71 (m, 2H), 0.67–0.60 (m, 1H), -0.15 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.1, 143.1, 142.4, 131.8, 129.1, 127.3, 126.4, 126.3, 123.4, 122.6, 84.7, 44.7, 32.5, 10.2, 10.1, 1.3. IR (neat): 3075, 2951, 1463, 1247, 1148, 1074 cm^{-1}. HRMS (ESI) calcd for $C_{20}H_{24}NaOSi$ $(M+Na)^+$: 331.1489. Found: 331.1488.

CP-BCB (1h)



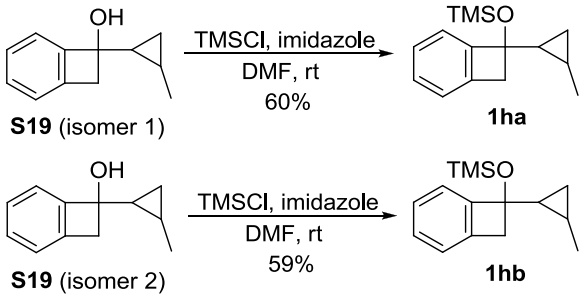
To a solution of benzocyclobutenone **S1** (408 mg, 3.46 mmol) in THF (25 mL) at -78 ℃ was added propenylmagnesium bromide (0.5 M solution in THF, 17 mL, 8.5 mmol), and the resulting solution was stirred for 1 hour. The reaction was quenched with saturated NH_4Cl solution and extracted with ether three times. The combined extract was washed with brine, dried over Na_2SO_4, filtered and concentrated under reduced pressure to give the crude procuct. The alcohol **S18** was not stable and may undergo electrocyclic reaction if stored too long, so the crude product was collected and used in the next step directly.

Alcohol **S18** was dissolved in DCM (25 mL) at 0 ℃. To the solution was added CH_2I_2 (0.7 mL, 8.67 mmol). Then Et_2Zn (1 M solution in hexanes, 17.5 mL, 17.5 mmol) was added dropwise. The solution was stired further for 1 hour and quenched with saturated NH_4Cl solution and extracted with ether three times. The combined extract was washed with brine, dried over Na_2SO_4, filtered and concentrated under reduced pressure. The crude product was purified by flash column chromatography on silica gel (eluted with PE:EA = 10:1 to 5:1) to afford **S19** (405 mg, 84%) as a mixture of two diastereoisomers which can be separated by flash column chromatography.

S19 (isomer 1): Colorless oil, TLC R_f = 0.49 (PE:EA = 5:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.29–7.19 (m, 2H), 7.18–7.10 (m, 2H), 3.44 (d, *J* = 14.1 Hz, 1H), 3.14 (d, *J* = 14.1 Hz, 1H), 2.38 (s, 1H), 1.33 (td, *J* = 8.7, 5.8 Hz, 1H), 1.04 (d, *J* = 6.4 Hz, 3H), 0.98–0.87 (m, 1H), 0.74 (td, *J* = 8.6, 4.7 Hz, 1H), 0.42 (dd, *J* = 10.6, 5.7 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.2, 141.2, 129.3, 127.2, 123.8, 121.0, 80.4, 47.2, 23.3, 12.7, 10.5, 9.6. IR

(neat): 3394, 3004, 2919, 1456, 1345, 1209, 1150, 1136, 1027 cm^{-1}. HRMS (ESI) calcd for $C_{12}H_{14}NaO$ $(M+Na)^+$: 197.0937. Found: 197.0943.

S19 (isomer 2): Colorless oil, TLC R_f = 0.39 (PE:EA = 5:1). ^1H NMR (400 MHz, $CDCl_3$): δ 7.25 (t, *J* = 7.4 Hz, 1H), 7.20–7.11 (m, 2H), 7.06 (d, *J* = 7.2 Hz, 1H), 3.35 (d, *J* = 14.0 Hz, 1H), 3.18 (d, *J* = 14.0 Hz, 1H), 2.35 (s, 1H), 1.17–1.09 (m, 1H), 1.01 (d, *J* = 6.0 Hz, 3H), 0.71–0.61 (m, 1H), 0.43 (dt, *J* = 13.7, 5.5 Hz, 1H), 0.36–0.28 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.2, 142.0, 129.3, 127.0, 123.8, 120.9, 81.6, 46.2, 26.8, 18.5, 10.3, 9.8. IR (neat): 3357, 2952, 2920, 1458, 1376, 1221, 1168, 1138, 1049, 1028 cm^{-1}. HRMS (ESI) calcd for $C_{12}H_{14}NaO$ $(M+Na)^+$: 197.0937. Found: 197.0943.

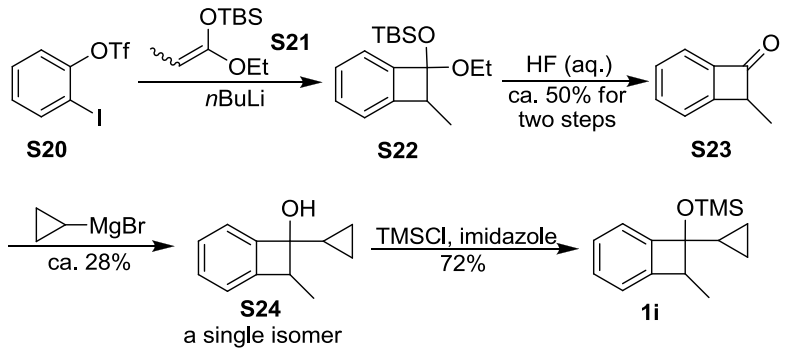


To the solution of the corresponding alcohol **S19** in DMF (1 mL for 0.2 mmol alcohol) at RT was added TMSCl (5 equiv.) and imidazole (10 equiv.). The solution was stirred at rt and monitored by TLC. When finished, the reaction was quenched with saturated $NaHCO_3$ solution and extracted with ether three times. The combined extract was washed successively with water and brine, dried over Na_2SO_4, filtered and concentrated under reduced pressure. The crude product was purified by flash column chromatography on silica gel (eluted with PE:EA = 100:1) to afford the corresponding **CP-BCB 1h** (**1ha**, 107.7 mg, 0.437 mmol, 60% yield from **S19** (isomer 1), 127 mg, 0.729 mmol; **1hb**, 64.7 mg, 0.263 mmol, 59% yield from **S19** (isomer 2), 79 mg, 0.454 mmol).

1ha: Colorless oil, TLC R_f = 0.78 (PE:EA = 50:1). ^1H NMR (400 MHz, $CDCl_3$): δ 7.28–7.24 (m, 1H), 7.21 (t, *J* = 7.1 Hz, 1H), 7.16 (d, *J* = 7.1 Hz, 1H), 7.12 (d, *J* = 7.0 Hz, 1H), 3.40 (d, *J* = 14.0 Hz, 1H), 3.25 (d, *J* = 14.0 Hz, 1H), 1.23–1.16 (m, 1H), 1.06 (d, *J* = 6.4 Hz, 3H), 0.88–0.80 (m, 1H), 0.73–0.66 (m, 1H), 0.50–0.44 (m, 1H), 0.03 (s, 9H).^{13}C NMR (100 MHz, $CDCl_3$): δ 150.9, 141.7, 128.9, 126.8, 123.8, 122.3, 81.1, 47.9, 25.3, 12.8, 10.9, 9.6, 1.7. IR (neat): 2955, 1458, 1250, 1185, 1094, 1065 cm^{-1}. HRMS (ESI) calcd for $C_{15}H_{22}NaOSi$ $(M+Na)^+$: 269.1332. Found: 269.1329.

1hb: Colorless oil, TLC R_f = 0.75 (PE: EA = 50:1). ^1H NMR (400 MHz, $CDCl_3$):δ 7.27–7.21 (m, 1H), 7.16 (t, *J* = 7.5 Hz, 1H), 7.10 (dd, *J* = 7.2, 0.6 Hz, 1H), 7.06 (d, *J* = 7.3 Hz, 1H), 3.31 (d, *J* = 13.8 Hz, 1H), 3.21 (d, *J* = 13.8 Hz, 1H), 1.06–1.01 (m, 1H), 0.98 (d, *J* = 6.0 Hz, 3H), 0.69–0.61 (m, 1H), 0.40–0.32 (m, 1H), 0.29–0.23 (m, 1H), 0.04 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.6, 142.1, 129.0, 126.6, 123.6, 122.0, 82.3, 47.2, 28.5, 18.5, 10.9, 9.6, 1.7. IR (neat): 2956, 1458, 1250, 1178, 1152, 1100, 1067 cm^{-1}. HRMS (EI) calcd for $C_{15}H_{22}NaOSi$ $(M+Na)^+$: 269.1332. Found: 269.1336.

CP-BCB (1i)



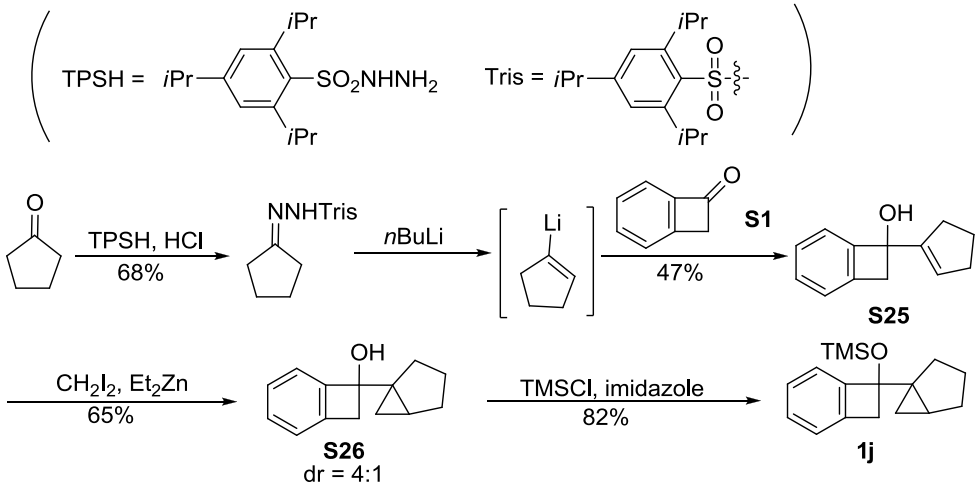
The ketone **S23** [12] was prepared from **S20** [1-2] as **S11** from **S8** using Suzuki's protocol, [1-2] with the substituted ketene silyl acetal **S21** [13] used. Alcohol **S24** was obtained as a single isomer from **S23** as **S12** from **S11**.

S24: Colorless oil, TLC R_f = 0.44 (PE: EA = 5:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.27–7.22 (m, 1H), 7.17 (dd, *J* = 11.0, 3.8 Hz, 1H), 7.10 (t, *J* = 7.3 Hz, 2H), 3.55 (q, *J* = 7.2 Hz, 1H), 2.21 (s, 1H), 1.38–1.33 (m, 1H), 1.31 (d, *J* = 7.2 Hz, 3H), 0.60–0.48 (m, 2H), 0.45–0.37 (m, 1H), -0.00–-0.07 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.3, 146.7, 129.3, 127.2, 122.4, 121.4, 82.5, 49.2, 18.1, 14.5, 1.7, 1.4. IR (neat): 3429, 3005, 2922, 1457, 1350, 1220, 1193, 1134, 1083, 1017 cm^{-1}. HRMS (ESI) calcd for $C_{12}H_{14}NaO$ $(M+Na)^+$: 197.0937. Found: 197.0944.

Substrate **1i** was prepared from **S24** following the same procedure as **1d** from **S12**.

1i: Colorless oil, TLC R_f = 0.73 (PE: EA = 50:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.24–7.20 (m, 1H), 7.14 (t, *J* = 7.4 Hz, 1H), 7.18 (t, *J* = 7.9 Hz, 2H), 3.48 (q, *J* = 7.1 Hz, 1H), 1.32–1.27 (m, 1H), 1.25 (d, *J* = 7.1 Hz, 3H), 0.55–0.45 (m, 2H), 0.39–0.30 (m, 1H), 0.08 (s, 9H), -0.10–-0.18 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.9, 146.5, 128.9, 126.6, 122.5, 122.3, 84.0, 50.3, 19.5, 14.5, 2.7, 1.9, 1.6. IR (neat): 2963, 1458, 1349, 1250, 1142, 1034, 897, 842 cm^{-1}. HRMS (ESI) calcd for $C_{15}H_{22}NaOSi$ $(M+Na)^+$: 269.1332. Found: 269.1335.

CP-BCB (1j)



Alcohol **S25** was prepared from cyclopentanone following the same procedure as **S16** from acetophenone **S14**. **S25** was not stable and was collected and used directly after being eluted with PE:EA = 10:1 through a thin layer of silica gel.

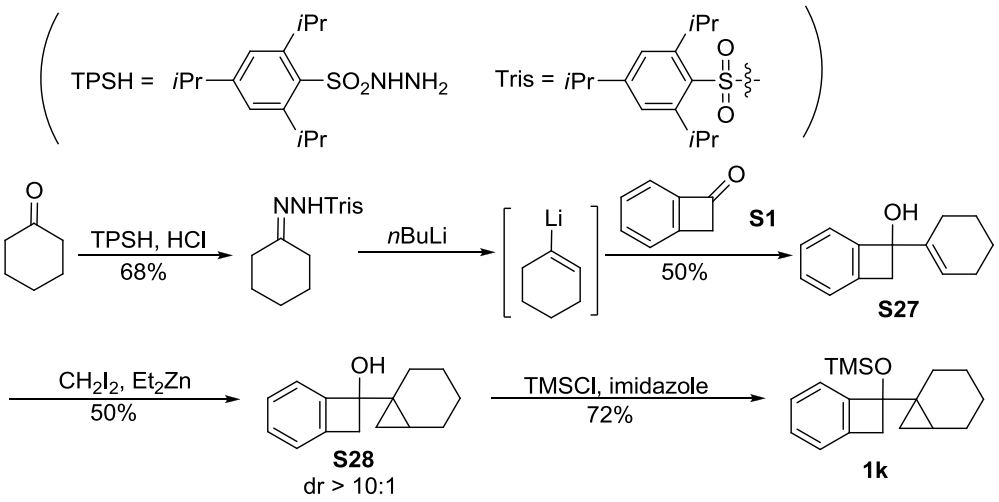
Intermediate **S26** was prepared from **S25** in 65% yield as an inseparable 4:1 mixture of two diastereoisomers, using Simmon-Smith cyclopropanation as described for **S17**.

S26: Colorless oil, TLC R_f = 0.23 (PE:EA = 5:1). The given NMR data here were read from the major isomer of **S26**. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.28–7.21 (m, 1H), 7.20–7.11 (m, 2H), 7.07 (d, *J* = 7.3 Hz, 1H), 3.40 (d, *J* = 14.0 Hz, 1H), 3.17 (d, *J* = 14.0 Hz, 1H), 2.34 (br s, 1H), 1.97–1.80 (m, 2H), 1.73–1.62 (m, 3H), 1.35–1.26 (m, 1H), 0.83–0.73 (m, 2H), 0.58–0.48 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.5, 142.5, 129.1, 126.9, 123.7, 120.8, 83.3, 45.0, 34.1, 28.2, 27.5, 21.8, 21.5, 9.7. IR (neat): 3391, 2920, 2860, 1458, 1309, 1206, 1142, 1119, 1057, 1026 cm^{-1}. HRMS (ESI) calcd for $C_{14}H_{16}NaO$ $(M+Na)^+$: 223.1093. Found: 223.1100.

Substrate **1j** as a mixture of two diastereoisomers, was prepared from **S26** following the same procedure as **1c** from acetophenone **S6**.

1j: Colorless oil, TLC R_f = 0.78 (PE:EA = 50:1). The given NMR data here were read from the major isomer of **1j**. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.24 (t, *J* = 7.4 Hz, 1H), 7.19–7.05 (m, 3H), 3.34 (d, *J* = 13.9 Hz, 1H), 3.17 (d, *J* = 13.9 Hz, 1H), 1.87–1.69 (m, 2H), 1.68–1.56 (m, 3H), 1.31–1.24 (m, 1H), 0.77–0.70 (m, 2H), 0.48–0.40 (m, 1H), 0.01 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.5, 142.8, 128.8, 126.4, 123.5, 122.3, 84.1, 45.8, 35.4, 28.5, 27.7, 21.5, 21.4, 10.1, 1.7. IR (neat): 2957, 2861, 1461, 1254, 1126, 1074 cm^{-1}. HRMS (EI) calcd for $C_{16}H_{21}OSi$ (M^+-CH_3): 257.1362. Found: 257.1366.

CP-BCB (1k)



Alcohol **S27** was prepared from cyclohexanone following the same procedure as **S16** from acetophenone **S14**. **S27** was not stable and was collected and used directly after being eluted with PE:EA = 10:1 through a thin layer of silica gel.

Intermediate **S28** was prepared from **S27** in 50% yield with dr > 10:1, using Simmon-Smith cyclopropanation as described for **S17**. The major diastereoisomer was isolated and used in the followed steps.

S28 (the major diastereoisomer): Colorless oil, TLC R_f = 0.55 (PE:EA = 5:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.27–7.22 (m, 1H), 7.16 (dd, *J* = 14.4, 7.2 Hz, 2H), 7.06 (d, *J* = 7.3 Hz, 1H), 3.35 (d, *J* = 14.0 Hz, 1H), 3.10 (d, *J* = 14.0 Hz, 1H), 2.24 (s, 1H), 2.12–2.02 (m, 1H), 1.90–1.80 (m, 1H), 1.78–1.69 (m, 1H), 1.60–1.55 (m, 1H), 1.37–1.21 (m, 4H), 0.81 (dd, *J* = 9.5, 4.6 Hz, 1H), 0.64–0.54 (m, 1H), 0.33 (t, *J* = 5.1 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.8, 142.3, 129.2, 126.9, 123.7, 120.9, 85.6, 44.2, 25.3, 24.6, 23.5, 22.0, 21.1, 14.8, 14.0. IR (neat): 3354, 2925, 2854, 1456, 1332, 1205, 1142, 1127, 1044 cm^{-1}. HRMS (ESI) calcd for $C_{15}H_{18}NaO$ $(M+Na)^+$: 237.1250. Found:237.1257.

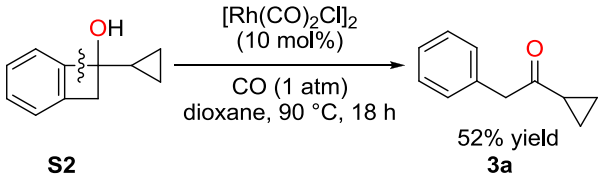
Substrate **1k** was prepared from the major diastereoisomer of **S28** in 72% yield as **1c** from **S6**.

1k: Colorless oil, TLC R_f = 0.78 (PE:EA = 50:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.22 (d, *J* = 7.6 Hz, 1H), 7.14 (t, *J* = 7.4 Hz, 1H), 7.09 (d, *J* = 7.2 Hz, 1H), 7.05 (d, *J* = 7.3 Hz, 1H), 3.28 (d, *J* = 13.9 Hz, 1H), 3.08 (d, *J* =

13.9 Hz, 1H), 1.92 (m, 1H), 1.81–1.67 (m, 2H), 1.54–1.48 (m, 1H), 1.30–1.15 (m, 4H), 0.78–0.71 (m, 1H), 0.56–0.47 (m, 1H), 0.23 (t, *J* = 5.1 Hz, 1H), -0.03 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.0, 142.7, 128.8, 126.4, 123.4, 122.3, 86.3, 44.9, 25.6, 25.5, 23.7, 22.1, 21.4, 14.4, 14.3, 1.6. IR (neat): 2926, 2858, 1461, 1254, 1204, 1145, 1071 cm^{-1}. HRMS (ESI) calcd for $C_{18}H_{26}NaOSi$ $(M+Na)^+$: 309.1645. Found: 309.1652.

2.2 Proximal C-C cleavage reaction of 1-cyclopropylbenzocyclobutenol (S2)

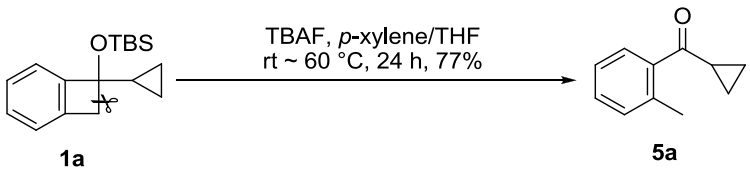
If the hydroxyl was not protected in the **CP-BCB 1a**, the compound **S2** (1-cyclopropylbenzocyclobutenol) underwent the proximal C-C cleavage reaction to give 1-cyclopropyl-2-phenylethanone,[14] rather than the desired [7+1] reaction.



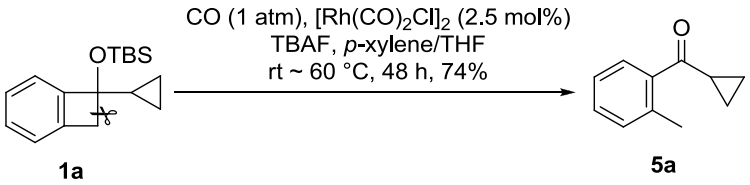
1-Cyclopropyl-2-phenylethanone (**3a**): To a solution of $[Rh(CO)_2Cl]_2$ (31 mg, 0.08 mmol) in anhydrous dioxane (8.0 mL) in a flame-dried reaction tube was added the solution of 1-cyclopropylbenzocyclobutenol (128 mg, 0.80 mmol) in dioxane (8.0 mL) under argon. Then the reaction mixture was bubbled with CO gas in a balloon for 5 min. The reaction tube was immersed into a 90 ℃ oil bath and stirred under the atmosphere pressure of CO gas. When TLC indicated the disappearance of the starting material, the reaction mixture was cooled to room temperature and concentrated under reduced pressure to remove dioxane. The residue was purified by flash column chromatography on silica gel (eluted with PE:EA = 10:1) to afford 1-cyclopropyl-2-phenylethanone (66.2 mg, 52%).

2.3 Proximal C-C cleavage reaction of 1a

In the presence of tetrabutylammonium fluoride (TBAF) with or without Rh catalyst, **1a** underwent distal C-C cleavage reaction to give (2-methyl)-phenyl cyclopropyl ketone.[15]



(2-Methyl)-phenyl cyclopropyl ketone (**5a**) (without Rh catalyst): To a solution of **1a** (53.5 mg, 0.195 mmol) in anhydrous *p*-xylene (4.0 mL) in a flame-dried reaction tube was added the solution of TBAF (1 mol/L in THF, 0.4 mL, 0.4 mmol) under argon. Then the reaction mixture was stirred at RT. Afer 12 hours, most starting material remained intact and the reaction was heated at 60 °C. After another 6 hours, there was still a large amount of starting material and TBAF $3H_2O$ (126 mg, o.4 mmol) was added. The reaction was stired at 60 °C for another 6 hours until all starting material was consumed. Then most solvent was removed under vaccum and the residue was purified by flash column chromatography on silica gel (eluted with PE:EA = 50:1) to afford (2-methyl)-phenyl cyclopropyl ketone (**5a**) (24.3 mg, 77%).

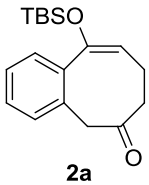


(2-Methyl)-phenyl cyclopropyl ketone (with Rh catalyst): To a solution of **1a** (53.3 mg, 0.194 mmol) and $[Rh(CO)_2Cl]_2$ (1.9 mg, 0.005 mmol) in anhydrous *p*-xylene (4.0 mL) in a flame-dried reaction tube was added the solution of TBAF (1 mol/L in THF, 0.4 mL, 0.4 mmol) under argon. Then the reaction mixture was bubbled with CO gas in a balloon for 5 min. The reaction mixture was stirred under room temperature. Afer 24 hours, most starting material remained intact and the reaction was heated at 60 ℃. After another 18 hours, there was still a large amount of starting material and TBAF $3H_2O$ (126 mg, o.4 mmol) was added. The reaction was stired at 60 ℃ for another 6 hours until all starting material was consumed. Then most solvent was removed under vaccum and the residue was purified by flash column chromatography on silica gel (eluted with PE:EA = 50:1) to afford (2-methyl)-phenyl cyclopropyl ketone (**5a**) (22.9 mg, 74%).

2.4 General Procedures for Rh(I)-Catalyzed [7 + 1] Cycloadditions

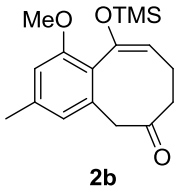
General Procedure:

To a solution of $[Rh(CO)_2Cl]_2$ (2.0 mg, 0.005 mmol for substrates **1a-f** and **1k**; or 4.0 mg, 0.01 mmol for substrate **1g-j**) in anhydrous *p*-xylene (2.0 mL) in a flame-dried reaction tube was added the solution of BCB-CP substrate (0.2 mmol) in *p*-xylene (2.0 mL) under argon. Then the reaction mixture was bubbled with CO gas in a balloon for 5 min. The reaction tube was immersed into a 140 ℃ oil bath and stirred under the atmosphere pressure of CO gas in a balloon. When TLC analysis (by phosphomolybdic acid stain) indicated the disappearance of the starting material, the reaction mixture was cooled to room temperature and concentrated under reduced pressure to remove *p*-xylene. The residue was purified by flash column chromatography on silica gel (eluted with PE:EA = 50:1) to afford the corresponding [7 + 1] cycloadduct (all reported yields were isolated yields).



2a

2a: (yield = 84%) Pale yellow oil, TLC R_f = 0.40 (PE:EA = 10:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.42–7.37 (m, 1H), 7.34–7.30 (m, 1H), 7.29–7.23 (m, 2H), 5.43 (t, *J* = 7.9 Hz, 1H), 3.79 (br. s, 2H), 2.40–2.34 (m, 2H), 2.19–2.04 (m, 2H), 0.93 (s, 9H), 0.07 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 209.0, 150.5, 137.7, 132.8, 129.6, 128.8, 128.5, 127.1, 108.5, 49.2, 40.1, 25.6, 22.9, 18.1, -4.4. IR (neat): υ 2952, 1705, 1671, 1446, 1291, 1247, 1172, 1121, 1063 cm^{-1}. HRMS (ESI) calcd for $C_{18}H_{26}NaO_2Si$ $(M+Na)^+$: 325.1594. Found: 325.1600.



2b

2b: (yield = 79%) White solid, TLC R_f = 0.53 (PE:EA = 5:1), m.p. 94–96 ℃. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.79 (s, 1H), 6.61 (s, 1H), 5.43 (t, *J* = 8.0 Hz, 1H), 4.19 (d, *J* = 10.7 Hz, 1H), 3.80 (s, 3H), 3.29 (d, *J* = 10.7 Hz, 1H), 2.38–2.32 (m, 2H), 2.32 (s, 3H), 2.21–2.11 (m, 1H), 2.01–1.87 (m, 1H), 0.13 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 209.1, 157.8, 148.4, 140.0, 134.6, 122.8, 122.5, 110.7, 108.7, 55.3, 48.9, 41.5, 23.0, 21.7, 0.6. IR (neat): 1699, 1609, 1578, 1461, 1312, 1278, 1167, 1094 cm^{-1}. HRMS (ESI) calcd for $C_{17}H_{25}O_3Si$ $(M+H)^+$:

305.1568. Found: 305.1569. The structure of **2b** was confirmed by X-ray analysis. For Cambridge X-ray data, see CCDC number: 965747.

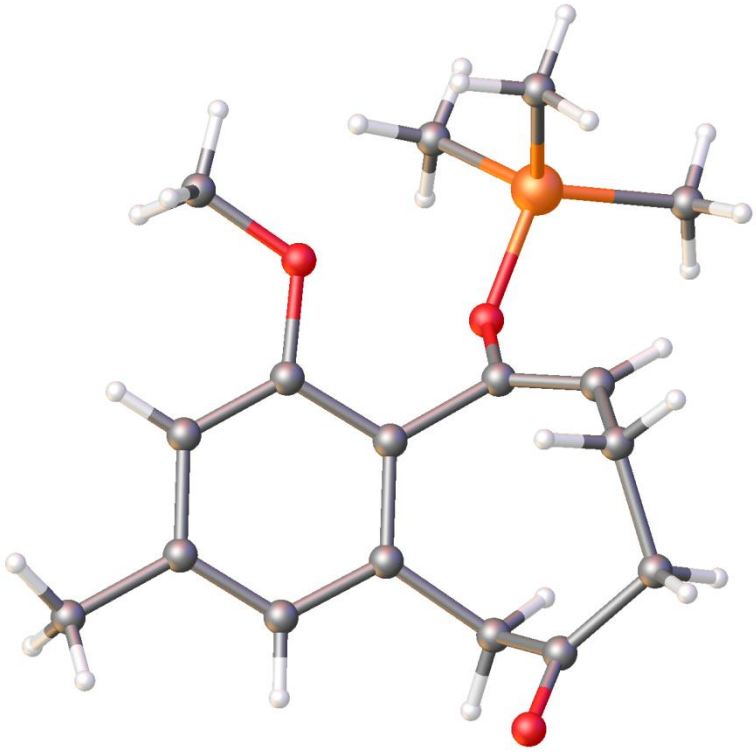
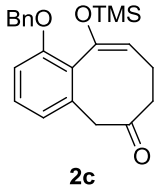


Table 1. Details of Data Collection, Processing and Structure Refinement

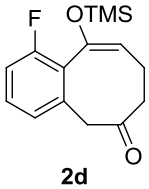
Molecular formula	$C_{17}H_{24}O_3Si$
Molecular weight	304.45
Color and habit	colorless plate
Crystal size	0.04 × 0.2 × 0.4 mm
Crystal system	monoclinic
Space group	$P2_1/n$ (No. 14)
Unit cell parameters	a = 14.647(3) Å α = 90.00° b = 6.9899(16) Å β = 99.721(7)° c = 16.919(4) Å γ = 90.00° V = 1707.4(7) Å^3 Z = 4 F(000) = 656
Density (calcd)	1.184 g/cm^3
Diffractometer	Bruker P4
Radiation	graphite-monochromatized Mo K_α, λ = 0.71073 Å

Temperature	295±2K		
Scan type	ω-scan		
Data collection range	$-1 < h < 17$, $-8 < k < 1$, $-20 < l < 20$; $\theta_{max} = 25.3°$		
Reflections measured	Total: 4123	Unique (n): 3122	Observed [$I \geq 2\sigma(I)$]: 1553
Absorption coefficient	0.145 mm^{-1}		
No. of variables, p	196		
Weighting scheme	$w = \frac{1}{\sigma^2(F_o^2) + (0.001P)^2 + 0.3P}$	$P = (F_o^2 + 2F_c^2)/3$	
$R1 = \frac{\Sigma\|\|F_o\|-\|F_c\|\|}{\Sigma\|F_o\|}$ (for all reflections)	0.1408	0.0576 (for observed data)	
$wR2 = \sqrt{\frac{\Sigma[w(F_o^2 - F_c^2)^2]}{\Sigma w(F_o^2)^2}}$ (for all reflections)	0.1088	0.0903 (for observed data)	
Goof = S = $\sqrt{\frac{\Sigma[w(F_o^2 - F_c^2)^2]}{n - p}}$	1.072		
Largest and mean Δ/σ	0.001, 0.000		
Residual extrema in final difference map	-0.236 to 0.181 e Å^{-3}		



2c

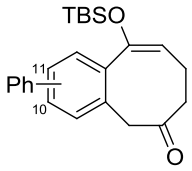
2c: (yield = 84%) Pale yellow oil, TLC R_f = 0.40 (PE:EA = 10:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.46–7.40 (m, 2H), 7.34 (t, J = 7.3 Hz, 2H), 7.31–7.26 (m, 1H), 7.17 (t, J = 8.0 Hz, 1H), 6.96 (d, J = 7.6 Hz, 1H), 6.81 (d, J = 8.2 Hz, 1H), 5.42 (dd, J = 8.9, 7.6 Hz, 1H), 5.13 (s, 2H), 4.23 (d, J = 10.7 Hz, 1H), 3.36 (d, J = 10.7 Hz, 1H), 2.41–2.29 (m, 2H), 2.25–2.11 (m, 1H), 2.02–1.87 (m, 1H), 0.15 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 208.5, 156.6, 148.4, 137.0, 134.8, 129.4, 128.3, 127.6, 127.0, 126.1, 121.9, 111.4, 108.0, 69.8, 48.9, 41.4, 22.9, 0.3. IR (neat): 1703, 1652, 1578, 1452, 1265, 1251, 1131, 1062 cm^{-1}. HRMS (ESI) calcd for $C_{22}H_{27}O_3Si$ $(M+H)^+$: 367.1724. Found: 367.1723.



2d

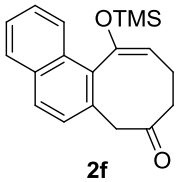
2d: (yield = 73%) White solid, TLC R_f = 0.42 (PE:EA = 10:1), m.p. 65–68 ℃. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.29–7.22 (m, 1H), 7.15 (d, J = 7.5 Hz, 1H), 6.98 (t, J = 9.3 Hz, 1H), 5.49 (t, J = 8.0 Hz, 1H), 4.21 (d, J = 11.0 Hz, 1H), 3.40 (d, J = 11.0 Hz, 1H), 2.45–2.31 (m, 2H), 2.22 (m, 1H), 1.94 (m, 1H), 0.22 (s, 9H). ^{13}C NMR (100

MHz, $CDCl_3$): δ 207.9, 160.6 (d, $J_{C\text{-}F}$ = 250.1 Hz), 146.2, 135.6 (d, $J_{C\text{-}F}$ = 3.8 Hz), 130.0 (d, $J_{C\text{-}F}$ = 9.0 Hz), 125.2 (d, $J_{C\text{-}F}$ = 3.2 Hz), 125.0 (d, $J_{C\text{-}F}$ = 16.0 Hz), 114.6 (d, $J_{C\text{-}F}$ = 21.6 Hz), 109.7, 48.6 (d, $J_{C\text{-}F}$ = 2.1 Hz), 40.9, 22.8, 0.3. IR (neat): 2957, 1708, 1655, 1460, 1252, 1195, 1131, 1011 cm^{-1}. HRMS (ESI) calcd for $C_{15}H_{20}FO_2Si$ $(M+H)^+$: 279.1211. Found: 279.1211.



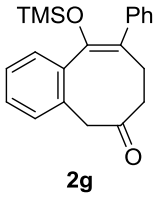
2e

2e (an inseparable mixture of compound with the phenyl at 10 or 11 position): (yield = 72%) Colorless oil, TLC R_f = 0.50 (PE:EA = 5:1). ^1H NMR (400 MHz, $CDCl_3$): δ 7.64–7.57 (m, 3H), 7.52–7.35 (m, 5H), 5.465 (t, *J* = 8 Hz, 0.5H), 5.455 (t, *J* = 8 Hz, 0.5H), 3.85 (s, 2H), 2.43–2.36 (m, 2H), 2.22–2.11 (m, 2H), 0.95 (s, 9H), 0.11 (s, 6H). (We cannot determine the exact ratio of these two isomers from the NMR integrals. The approximate ratio is 1:1) ^{13}C NMR (100 MHz, $CDCl_3$): δ 208.8, 150.2, 150.0, 141.2, 140.4, 140.2, 140.0, 137.9, 136.4, 133.7, 132.3, 130.2, 129.3, 128.9, 128.8, 128.3, 127.6, 127.44, 127.38, 127.2, 127.1, 126.9, 125.8, 108.56, 108.55, 49.1, 48.6, 40.24, 40.15, 25.7, 23.09, 23.07, 18.1, -4.29, -4.32. IR (neat): 2960, 2926, 2859, 1711, 1649, 1489, 1356, 1257, 1124 cm^{-1}. HRMS (ESI) calcd for $C_{24}H_{31}O_2Si$ $(M+H)^+$: 379.2088. Found: 379.2089.



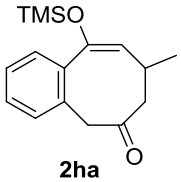
2f

2f: (yield = 80%) White solid, TLC R_f = (PE:EA = 5:1), m.p. 105–107 ℃. ^1H NMR (400 MHz, $CDCl_3$): δ ^1H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, *J* = 8.0 Hz, 1H), 7.82–7.73 (m, 2H), 7.52–7.42 (m, 3H), 5.67 (dd, *J* = 8.9, 7.7 Hz, 1H), 4.45 (d, *J* = 10.7 Hz, 1H), 3.50 (d, *J* = 10.7 Hz, 1H), 2.49–2.29 (m, 2H), 2.27–2.13 (m, 1H), 1.97–1.82 (m, 1H), 0.09 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 208.4, 149.4, 133.4, 132.9, 131.7, 130.9, 129.2, 128.0, 127.3, 126.6, 126.3, 125.8, 109.8, 49.6, 41.3, 23.1, 0.4. IR (neat): 2962, 1706, 1253, 1189, 1005 cm^{-1}. HRMS (ESI) calcd for $C_{19}H_{23}O_2Si$ $(M+H)^+$: 311.1462. Found: 311.1464.



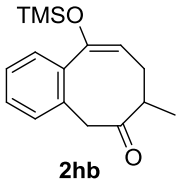
2g

2g: (yield = 50%) White solid, m.p. 97–99 ℃, TLC R_f = 0.53 (PE:EA = 5:1). ^1H NMR (400 MHz, $CDCl_3$): δ 7.51 (d, *J* = 7.4 Hz, 2H), 7.43–7.37 (m, 4H), 7.33–7.27 (m, 3H), 4.43 (d, *J* = 10.8 Hz, 1H), 3.45 (d, *J* = 10.8 Hz, 1H), 2.59–2.46 (m, 2H), 2.41–2.24 (m, 2H), -0.07 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 208.3, 145.1, 139.7, 138.4, 133.4, 129.9, 129.2, 129.1, 128.8, 128.2, 127.2, 126.8, 120.7, 49.1, 39.7, 29.5, 0.8. IR (neat): 3064, 2955, 1705, 1253, 1146, 911, 844, 731 cm^{-1}. HRMS (ESI) calcd for $C_{21}H_{25}O_2Si$ $(M+H)^+$: 337.1618. Found: 337.1619.



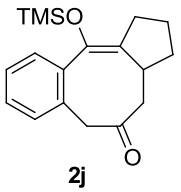
2ha

2ha: (for **1ha**, yield = 56%, **2ha**:**2hb** = 1.7:1; for **1hb**, yield = 53%, **2ga**:**2gb** = 1.5:1) Colorless oil, TLC R_f = 0.62 (PE:EA = 5:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.41–7.37 (m, 1H), 7.33–7.29 (m, 1H), 7.29–7.24 (m, 2H), 5.14 (d, *J* = 7.7 Hz, 1H), 4.09 (d, *J* = 11.2 Hz, 1H), 3.46 (d, *J* = 11.2 Hz, 1H), 2.45–2.35 (m, 1H), 2.25–2.20 (m, 1H), 2.18–2.12 (m, 1H), 1.02 (d, *J* = 6.8 Hz, 3H), 0.17 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 208.5, 148.0, 137.6, 133.2, 129.6, 128.8, 128.7, 127.1, 116.1, 48.74, 48.66, 29.4, 24.1, 0.5. IR (neat): 2958, 1707, 1648, 1320, 1252, 1217, 1139, 1072 cm^{-1}. HRMS (ESI) calcd for $C_{16}H_{23}O_2Si$ $(M+H)^+$: 275.1462. Found: 275.1468.



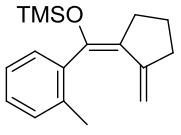
2hb

2hb: Colorless oil, TLC R_f = 0.66 (PE:EA = 5:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.39–7.34 (m, 2H), 7.28–7.24 (m, 2H), 5.46 (t, *J* = 8.2 Hz, 1H), 3.90 (br. s, 1H), 3.67 (br. s, 1H), 2.58–2.50 (m, 1H), 2.12–2.03 (m, 1H), 1.95–1.85(m, 1H), 1.03 (d, *J* = 6.8 Hz, 3H), 0.18 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 210.8, 149.9, 137.1, 133.9, 129.6, 128.7, 128.6, 127.0, 107.8, 47.6, 42.3, 31.2, 15.9, 0.4. IR (neat): 2961, 1708, 1650, 1446, 1356, 1252, 1139, 1088 cm^{-1}. HRMS (ESI) calcd for $C_{16}H_{23}O_2Si$ $(M+H)^+$: 275.1462. Found: 275.1463.



2j

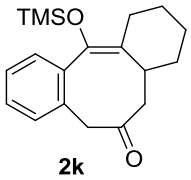
2j: (yield = 51%) White solid, m.p. 81–84 ℃, TLC R_f = 0.53 (PE:EA = 5:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.42–7.38 (m, 1H), 7.34–7.30 (m, 1H), 7.26–7.20 (m, 2H), 4.07 (d, *J* = 10.9 Hz, 1H), 3.38 (d, *J* = 10.8 Hz, 1H), 2.74–2.62 (m, 1H), 2.56–2.45 (m, 2H), 2.44–2.35 (m, 1H), 2.23–2.13 (m, 1H), 1.82–1.72 (m, 3H), 1.50–1.41 (m, 1H), 0.02 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 209.3, 140.7, 139.0, 132.7, 129.8, 128.6, 128.2, 128.1, 126.8, 48.6, 46.3, 38.6, 36.2, 28.7, 23.1, 0.7. IR (neat): 2956, 1708, 1667, 1272, 1251, 1169, 1118, 1075 cm^{-1}. HRMS (ESI) calcd for $C_{18}H_{25}O_2Si$ $(M+H)^+$: 301.1618. Found: 301.1623.



4j

In the case of benzo/[7+1] of CP-BCB **1j**, besides the [7+1] cycloadduct **2j**, we have also observed the production of **4j** originating from the β-elimination of the proposed rhodacyclooctene intermediate (Note: We have tried our best to purify **4j** but the spectra still indicates the presence of some impurities (some may be attributed to petroleum ether)). **4j**: (yield = 35%) Colorless oil, TLC R_f = 0.95 (PE:EA = 5:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.22–7.13 (m, 4H), 5.82 (d, *J* = 10.0 Hz, 1H), 5.55–5.48 (m, 1H), 2.51 (dt, *J* = 12.2, 6.2 Hz, 2H),

2.27 (s, 3H), 2.12 (d, J = 4.2 Hz, 2H), 1.75 (dd, J = 12.4, 6.2 Hz, 2H), -0.05 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 145.0, 137.5, 137.2, 130.7, 130.0, 127.9, 126.2, 125.5, 125.0, 117.9, 25.6, 23.8, 22.4, 19.8, 0.3. IR (neat): 2931, 2857, 1650, 1632, 1449, 1379, 1274, 1254 cm^{-1}. HRMS (ESI) calcd for $C_{17}H_{25}OSi$ $(M+H)^+$: 273.1669. Found: 273.1670.



2k

2k: (yield = 62%) White solid, m.p. 82–84 ℃, TLC R_f = 0.58 (PE:EA = 5:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.40–7.36 (m, 1H), 7.30–7.25 (m, 1H), 7.25–7.20 (m, 2H), 4.01 (d, J = 11.0 Hz, 1H), 3.33 (d, J = 11.0 Hz, 1H), 3.04–2.95 (m, 1H), 2.84–2.73 (m, 1H), 2.46–2.38 (m, 1H), 2.16–2.04 (m, 2H), 1.82–1.76 (m, 1H), 1.56–1.49 (m, 1H), 1.47–1.40 (m, 2H), 1.40–1.33 (m, 2H), -0.04 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 208.9, 140.9, 138.2, 133.5, 129.53, 129.51, 128.3, 127.1, 121.7, 49.1, 45.8, 34.5, 33.3, 26.0, 22.7, 21.3, 0.8. IR (neat): 2930, 2856, 1706, 1288, 1251, 1141, 1069, 842 cm^{-1}. HRMS (ESI) calcd for $C_{19}H_{27}O_2Si$ $(M+H)^+$: 315.1775. Found: 315.1784. Some tiny inseparable impurity in **2k** can be seen in the ^{1}H and ^{13}C NMR spectra.

The reaction of **1k** gave the desired benzo/[7+1] product **2k** together with other unidentified mixture, which could include β–H elimination product , as judged by crude NMR.

2.5 References:

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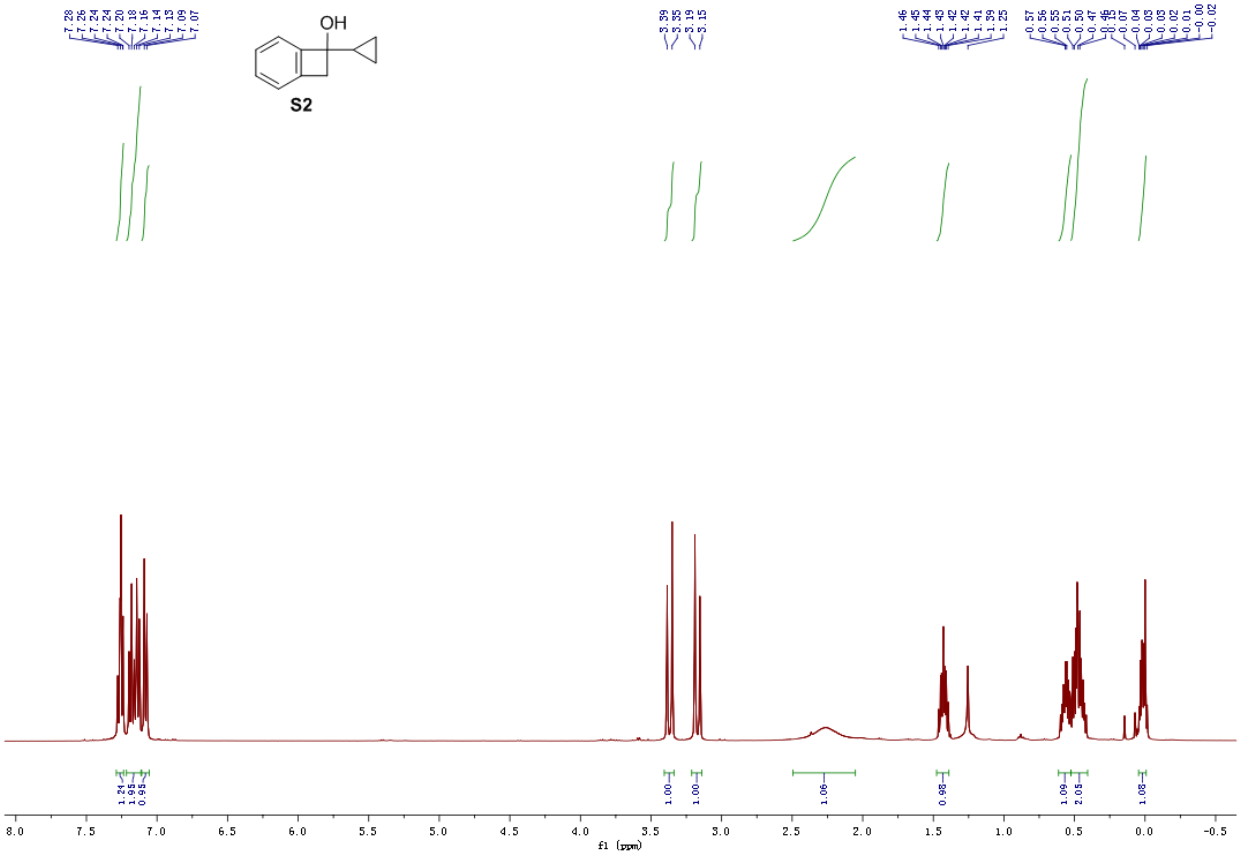
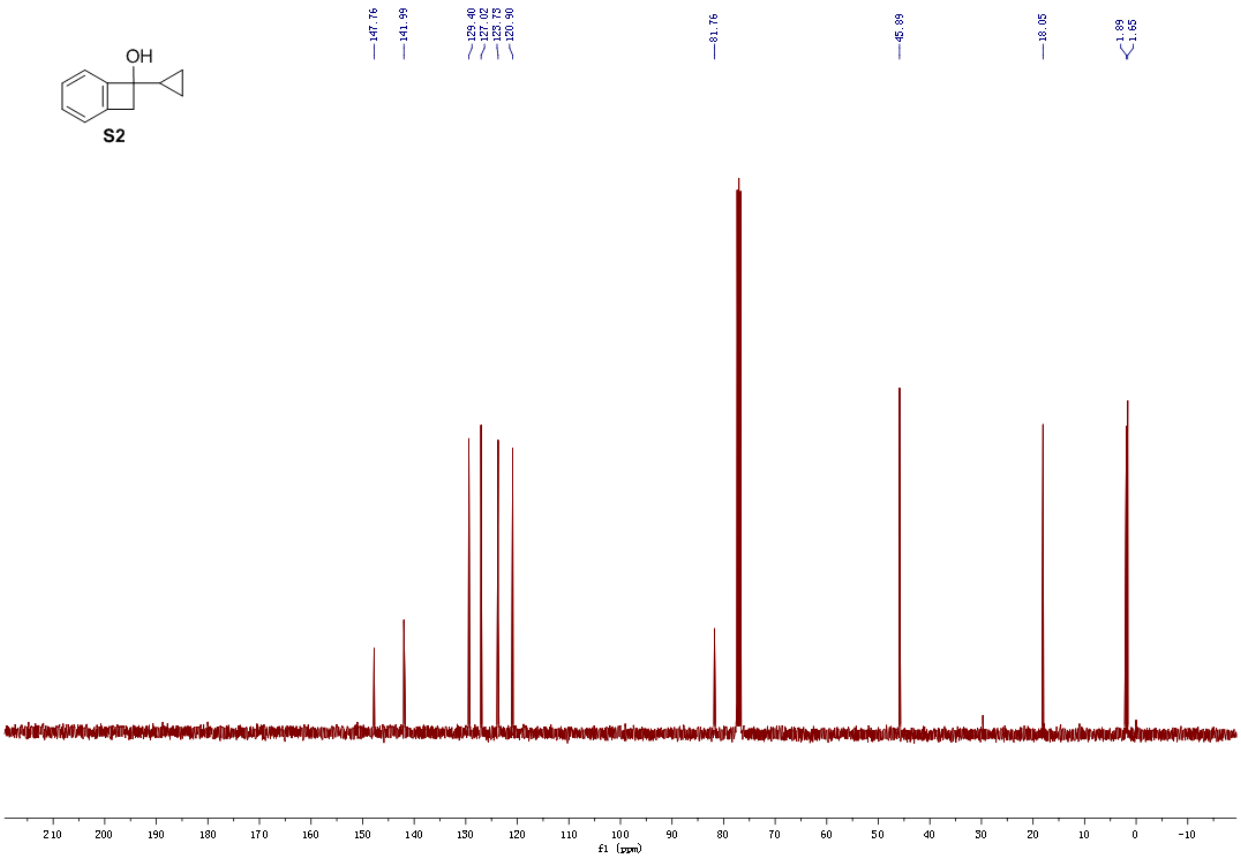
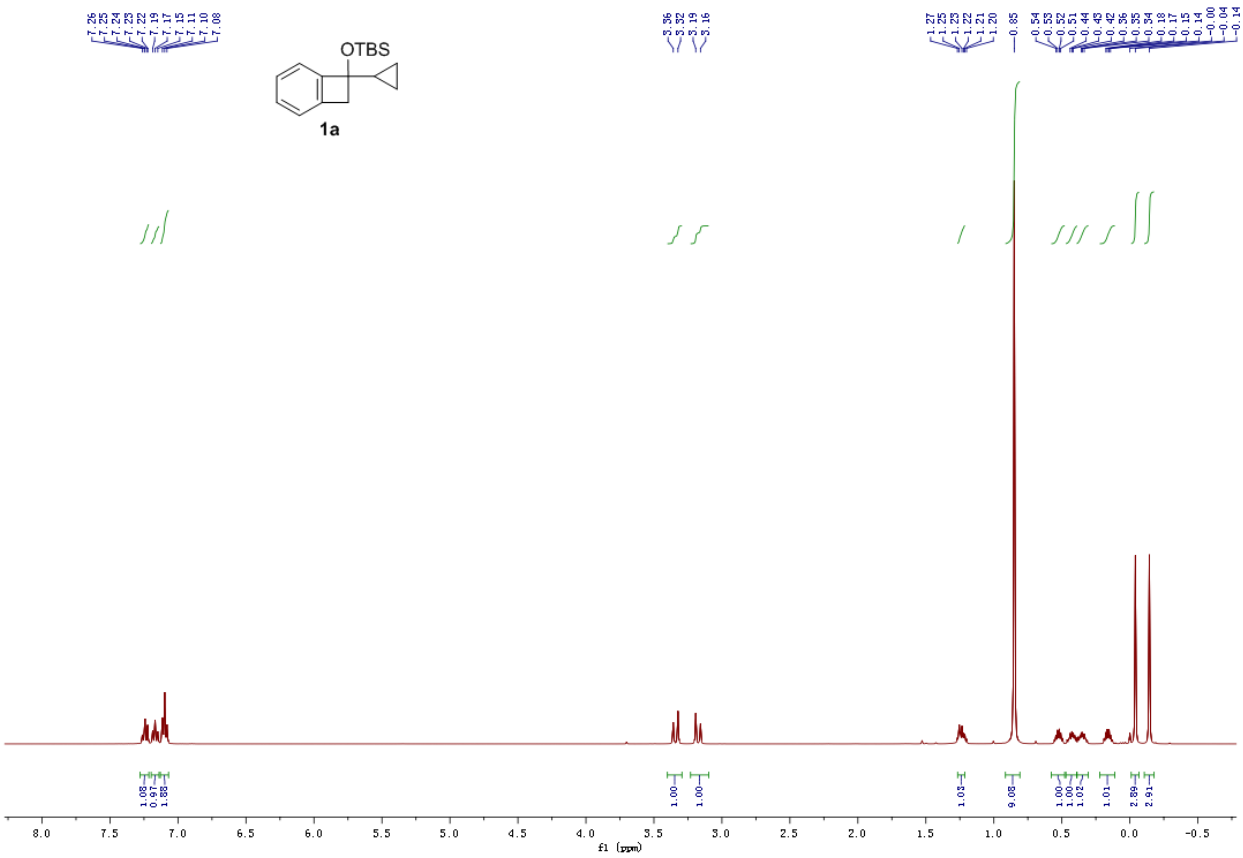
3. ^{1}H and ^{13}C-NMR Spectra for New Compounds



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7.25
7.24
7.24
7.23
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7.19
7.17
7.15
7.11
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7.08
3.36
3.32
3.19
3.16
1.27
1.25
1.23
1.22
1.21
1.20
0.85
0.54
0.53
0.52
0.51
0.44
0.45
0.42
0.36
0.35
0.34
0.18
0.17
0.15
0.14
-0.00
-0.04
-0.14
1.08
0.97
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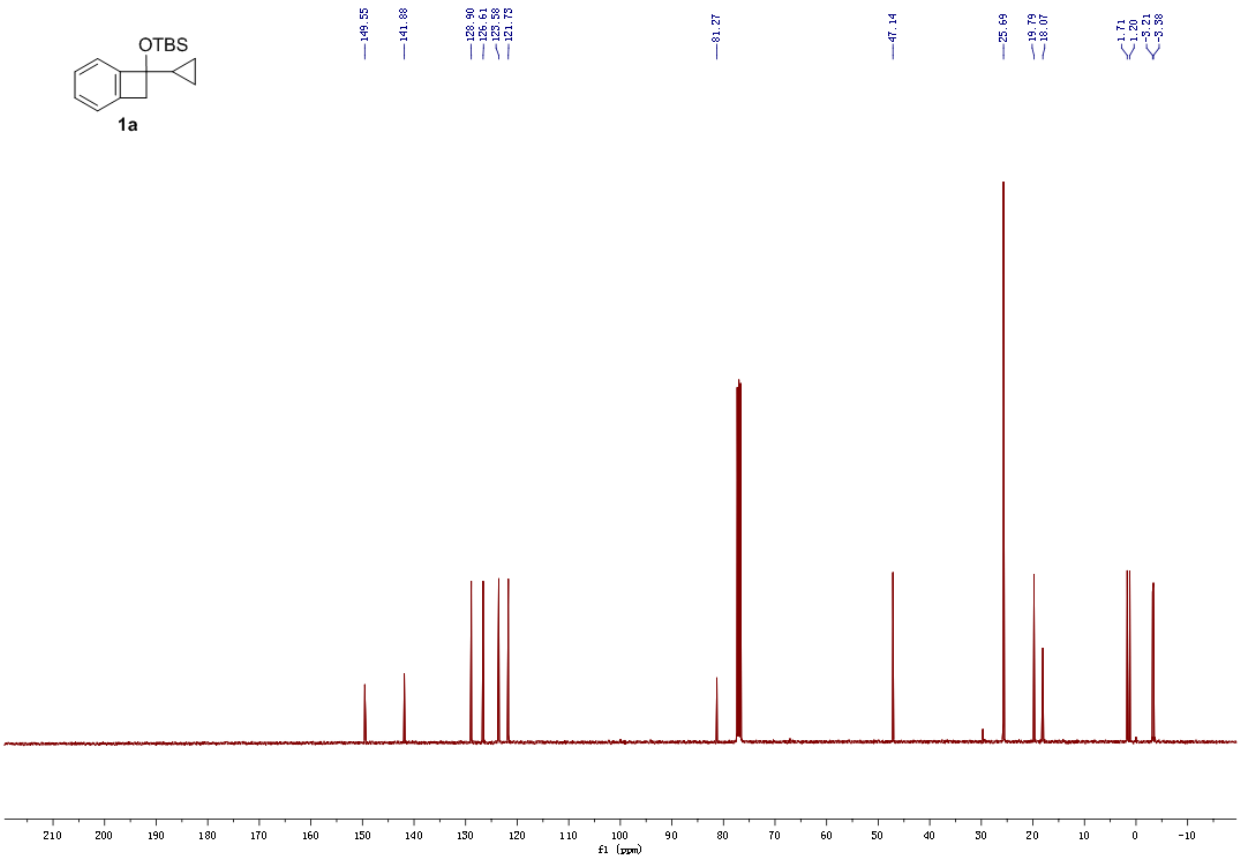
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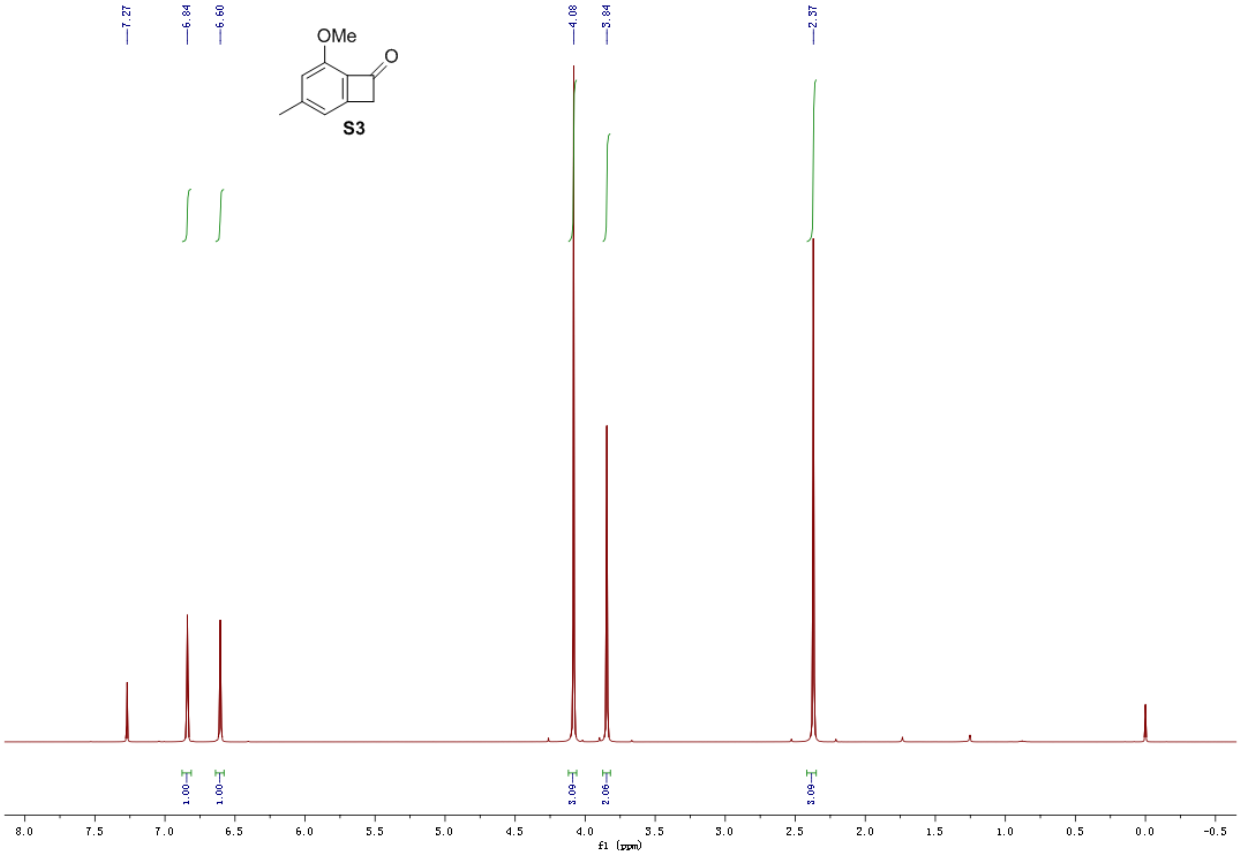
-3.38
f1 (ppm)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O
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3.09
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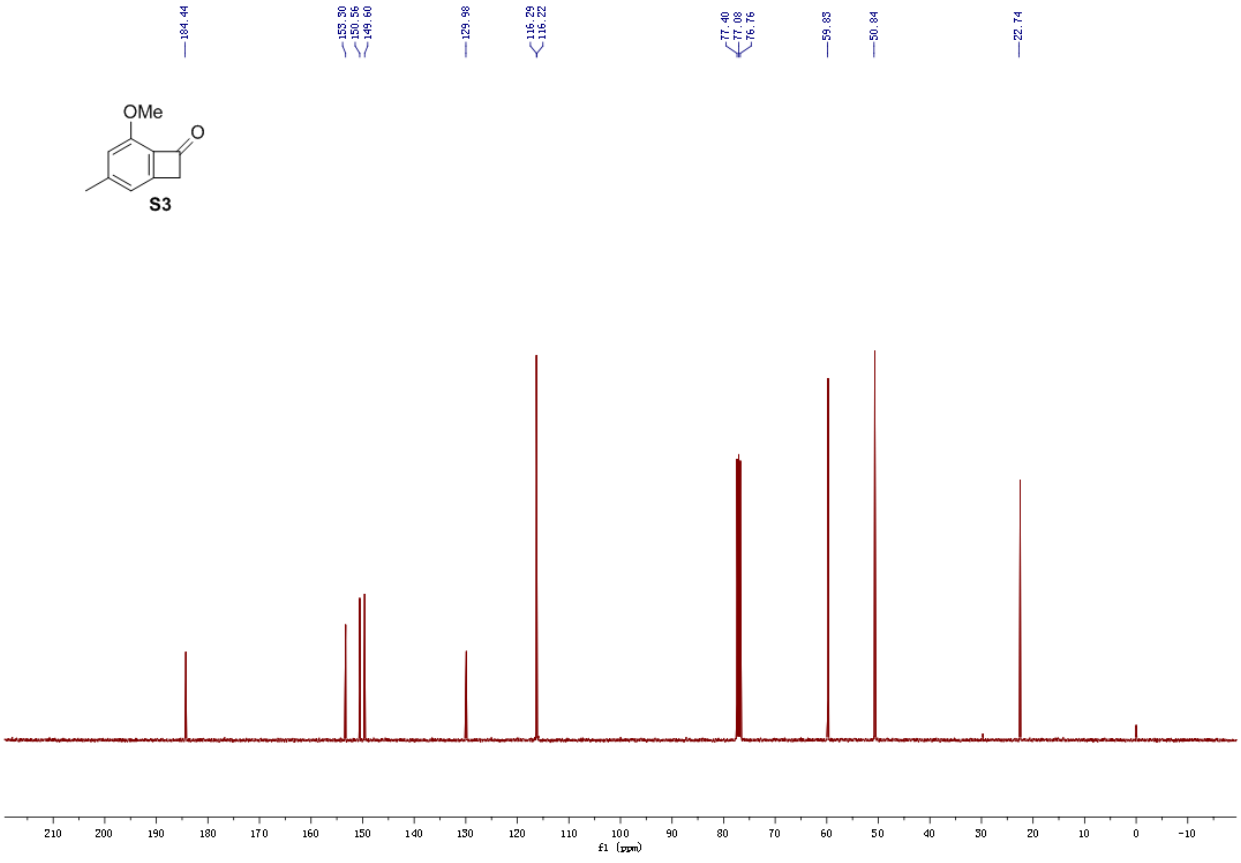
3.09
f1 (ppm)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149.60
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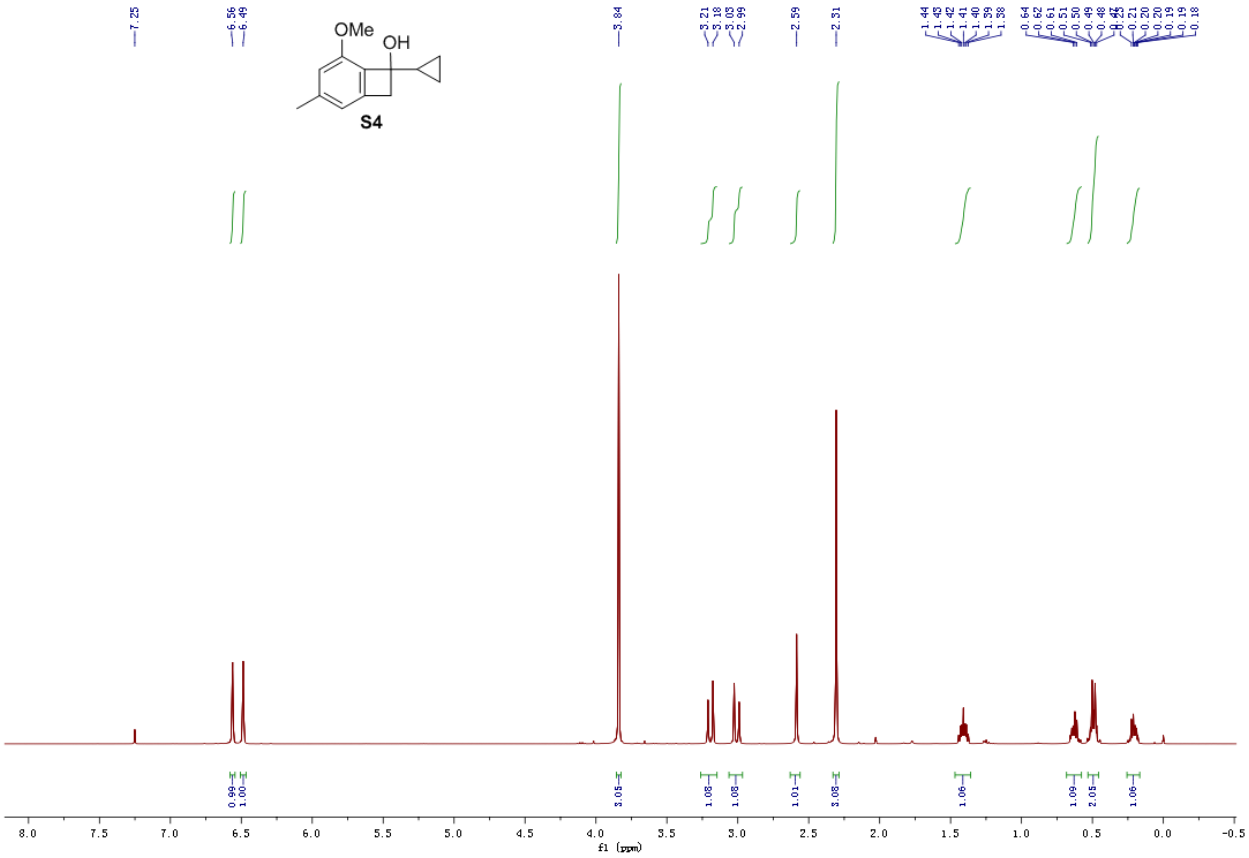
77.08
76.76
59.83
50.84
22.74
OMe
O
S3
f1 (ppm)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2.99
2.59
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1.44
1.43
1.42
1.41
1.40
1.39
1.38
0.64
0.62
0.61
0.51
0.50
0.49
0.48
0.21
0.20
0.19
0.19
0.18
0.99
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1.01
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1.09
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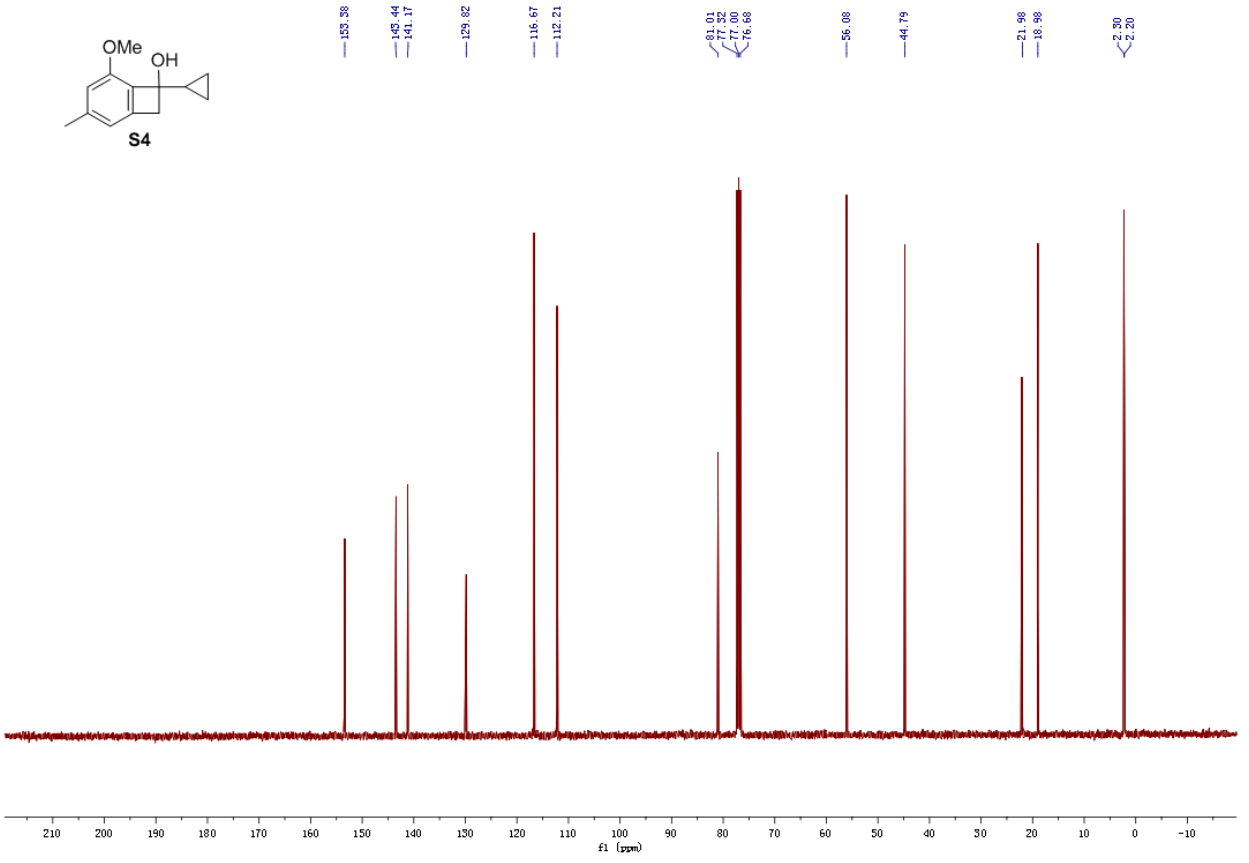
1.06
f1 (ppm)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2.20
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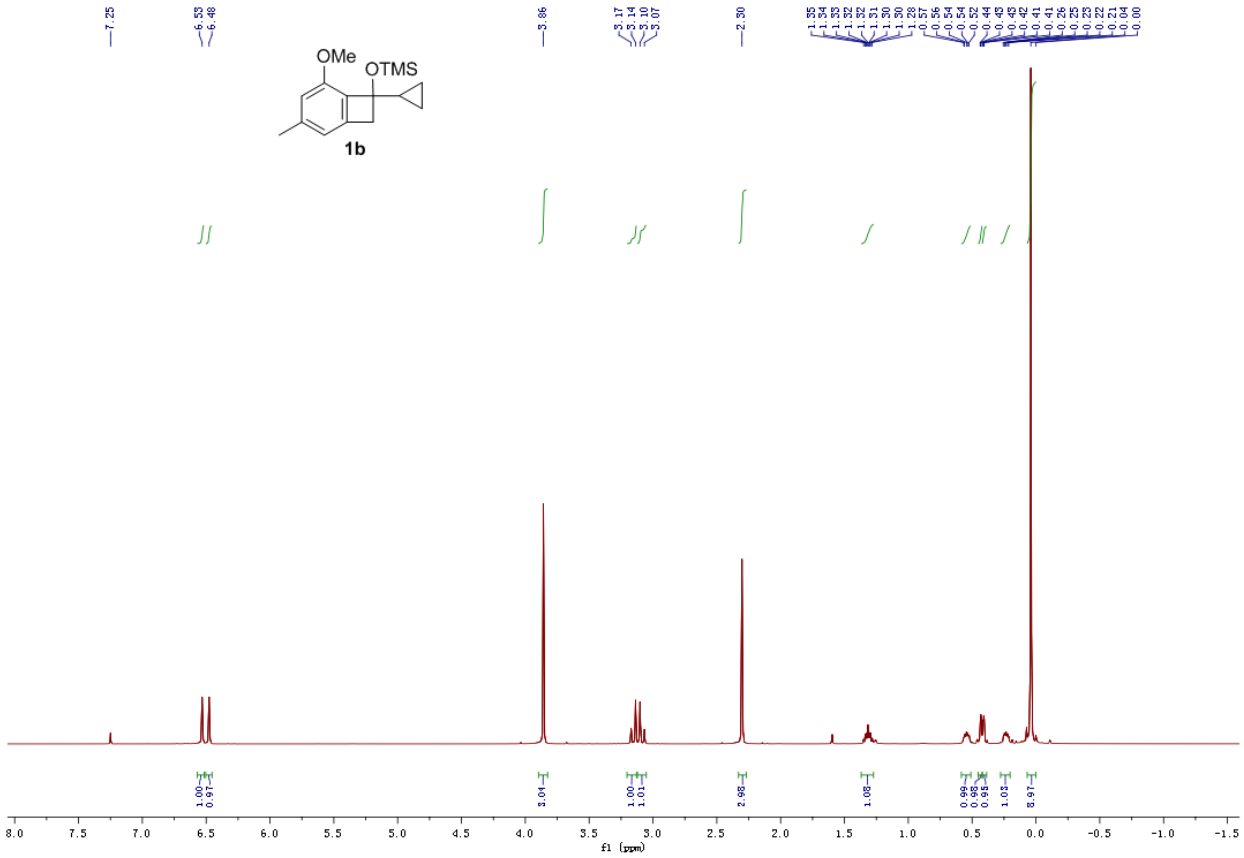
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1b
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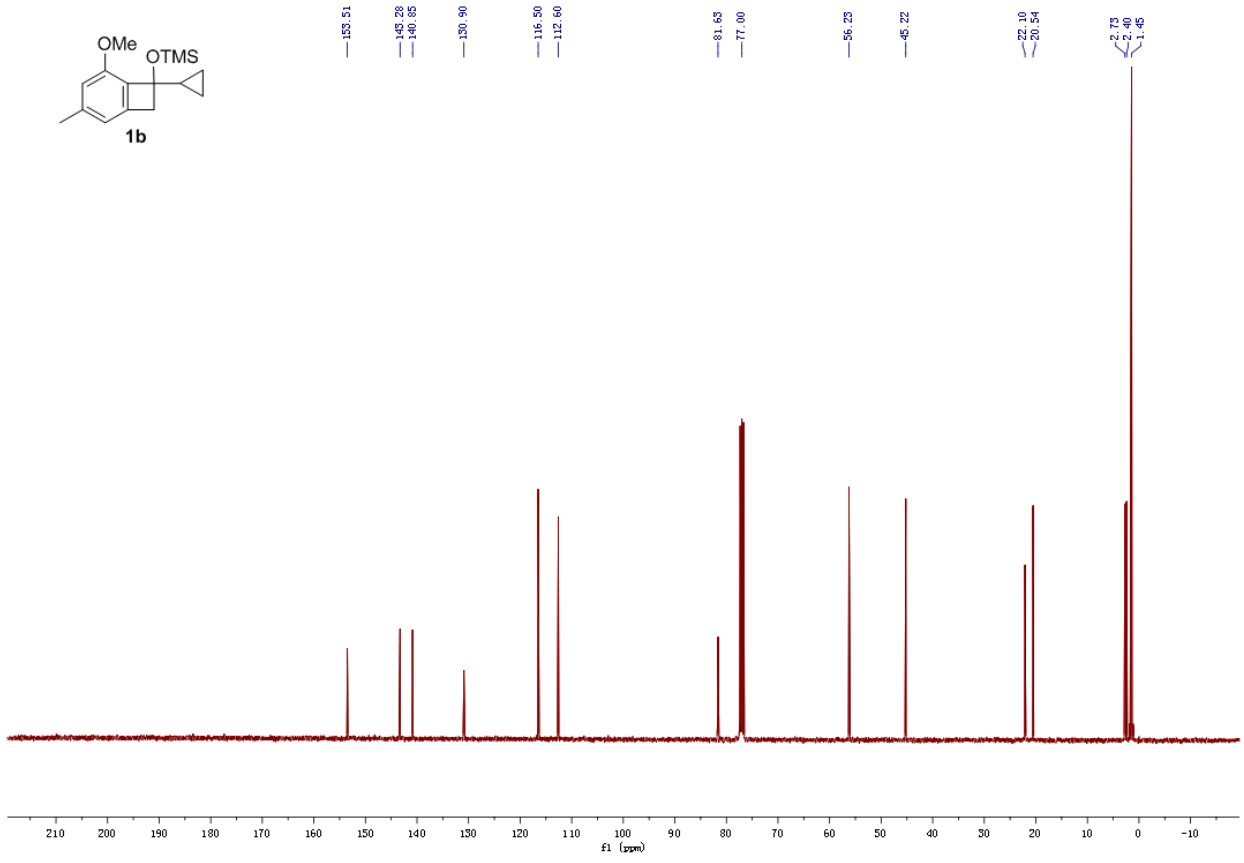
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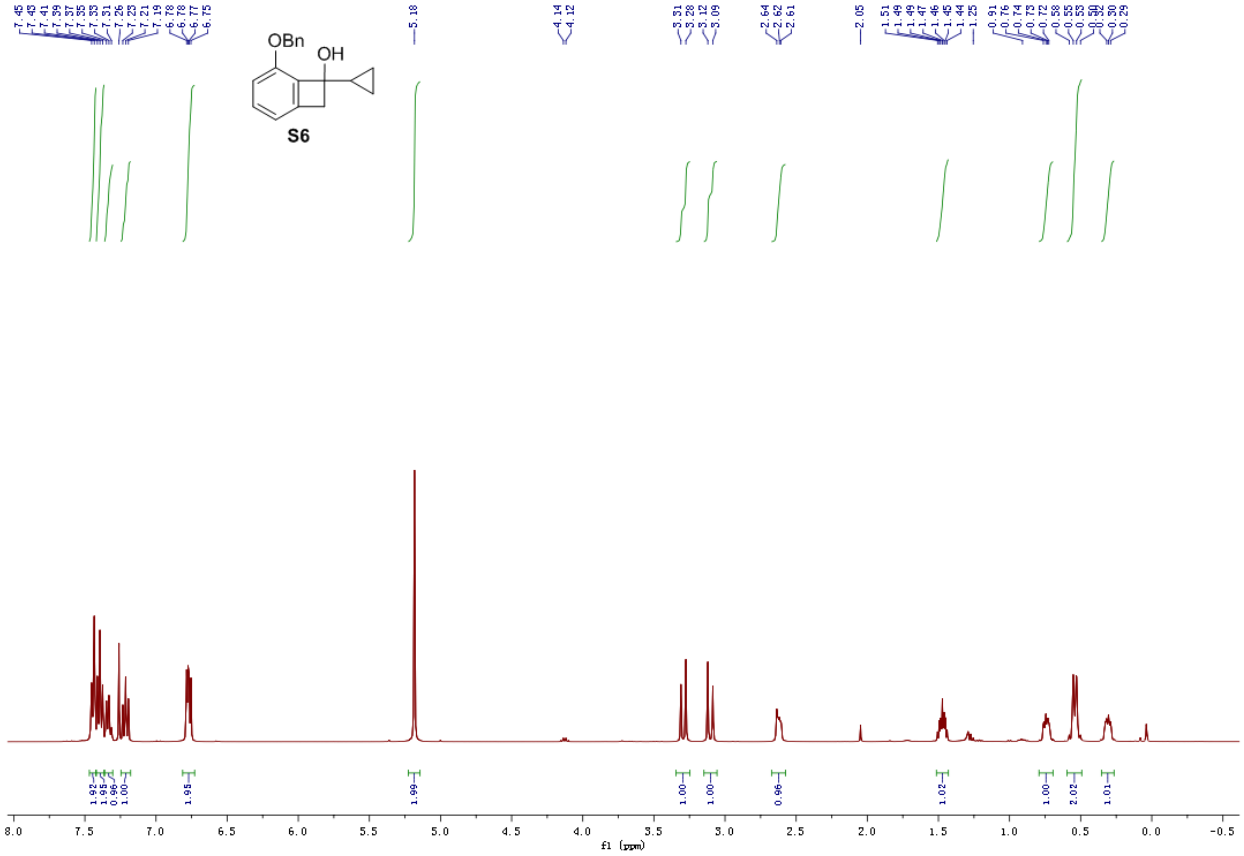
OTMS
1b
f1 (ppm)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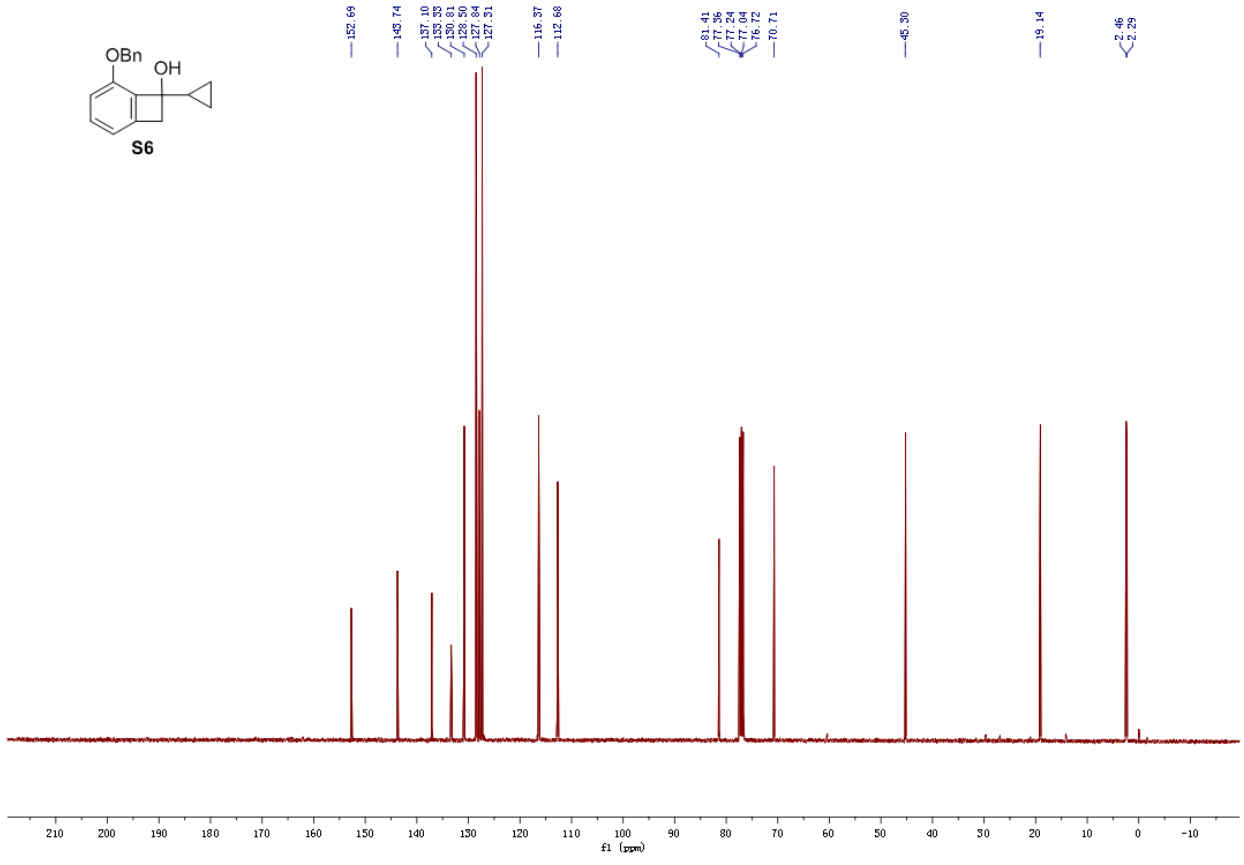
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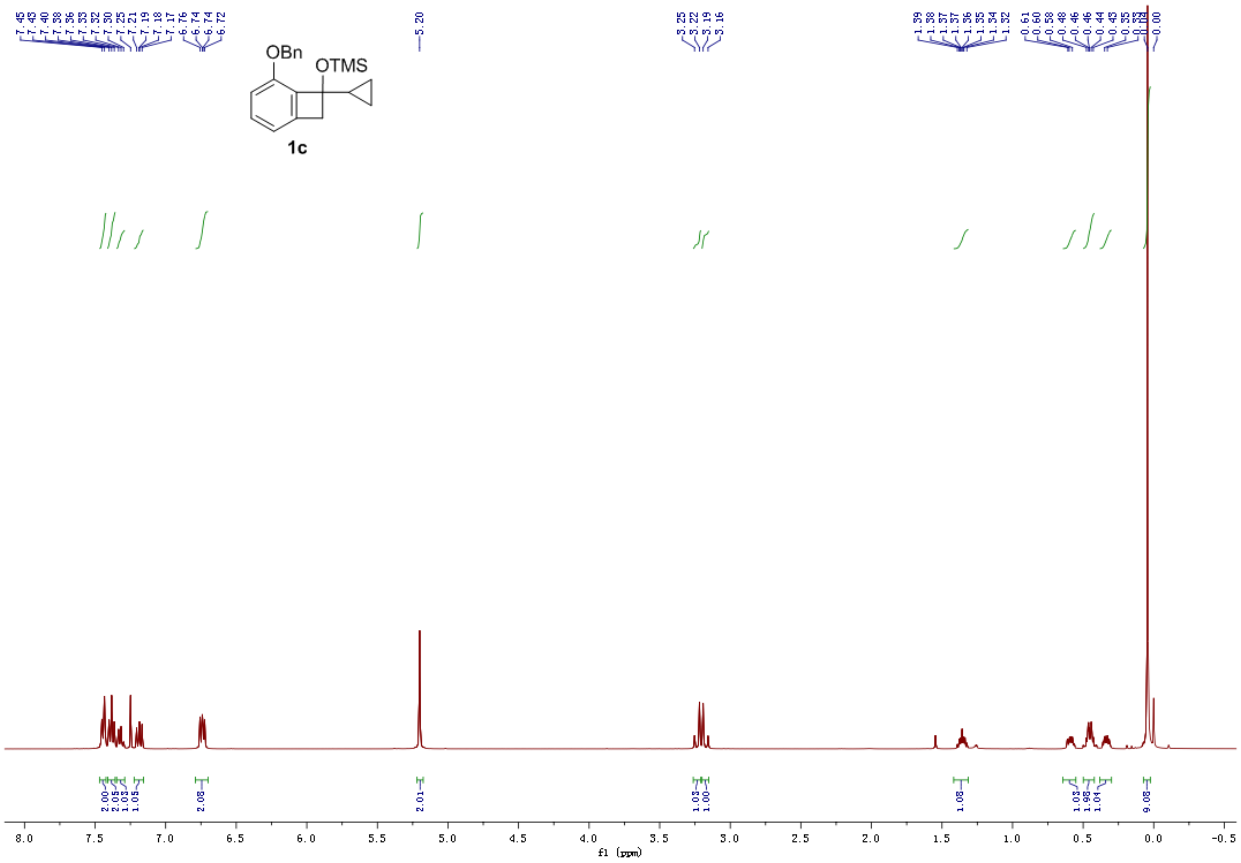
f1 (ppm)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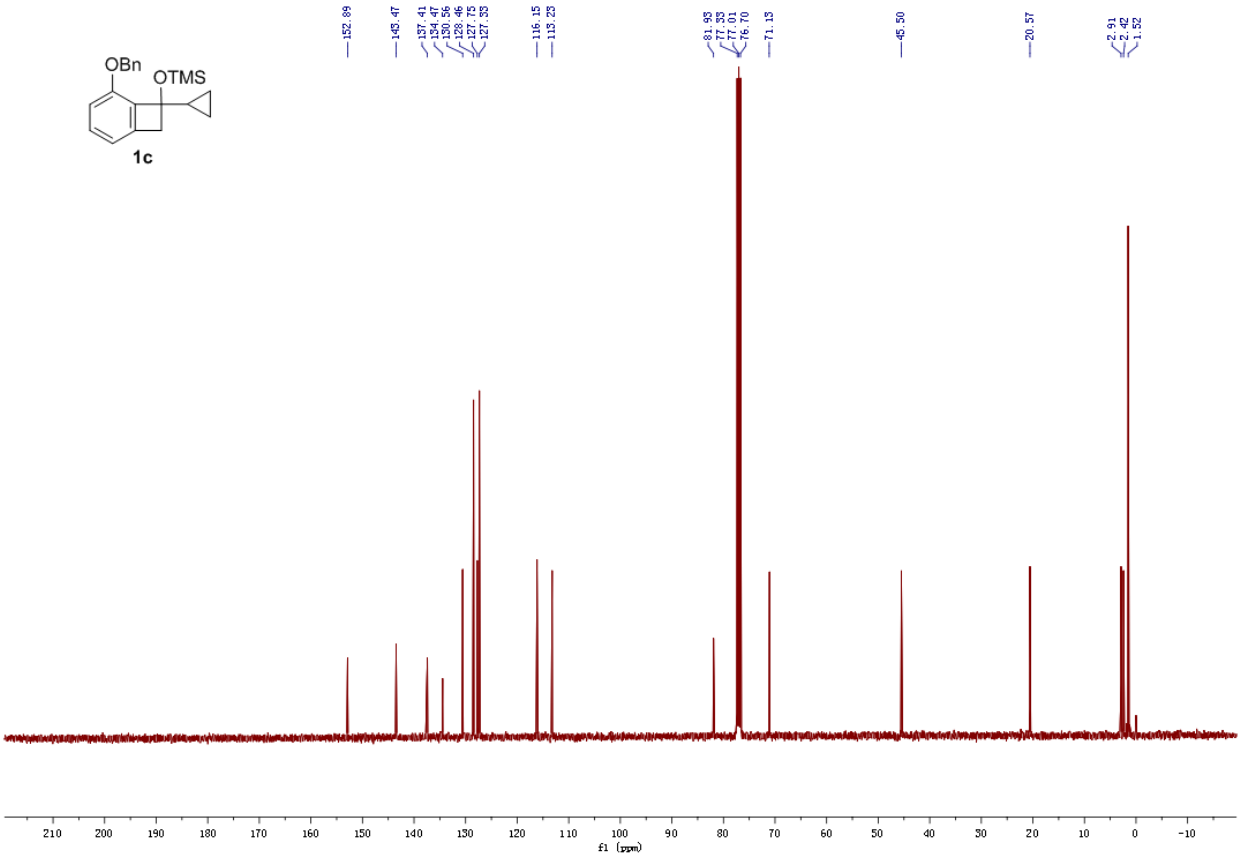
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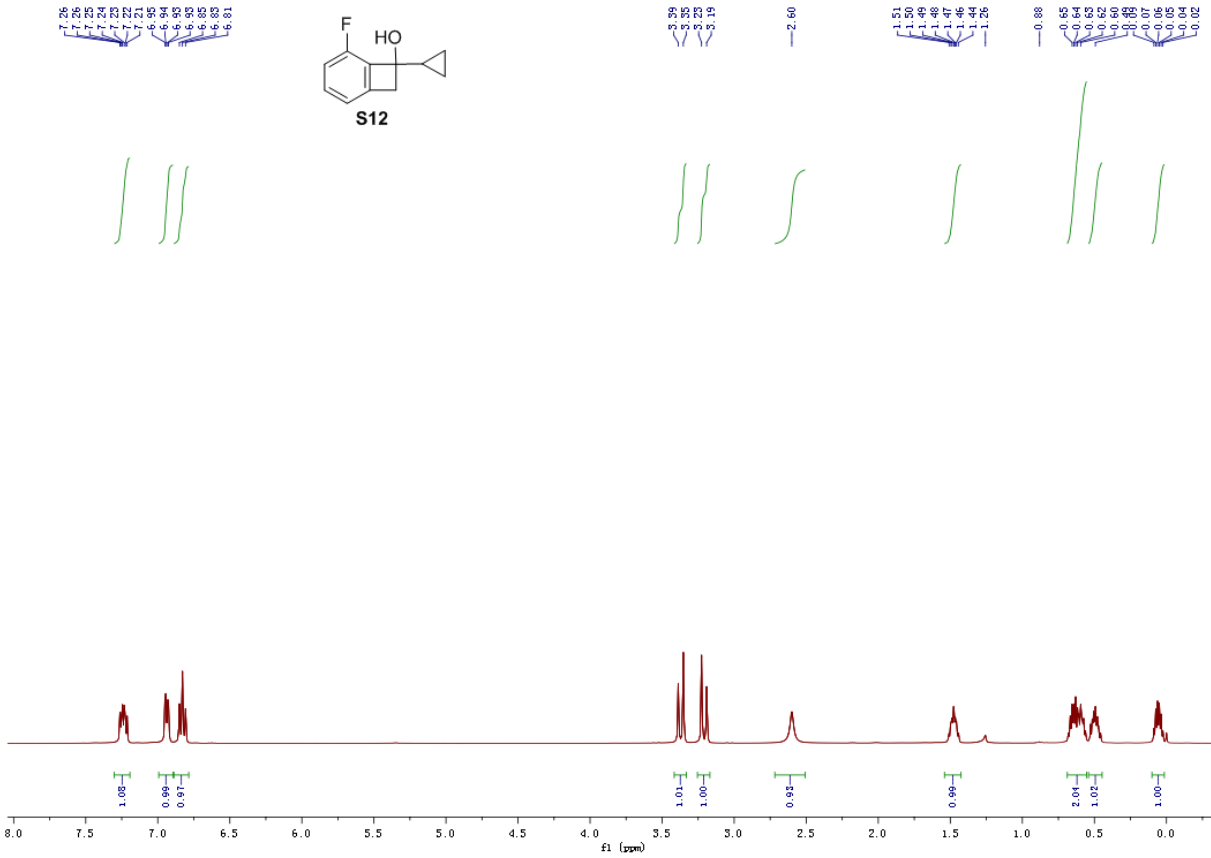
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S12

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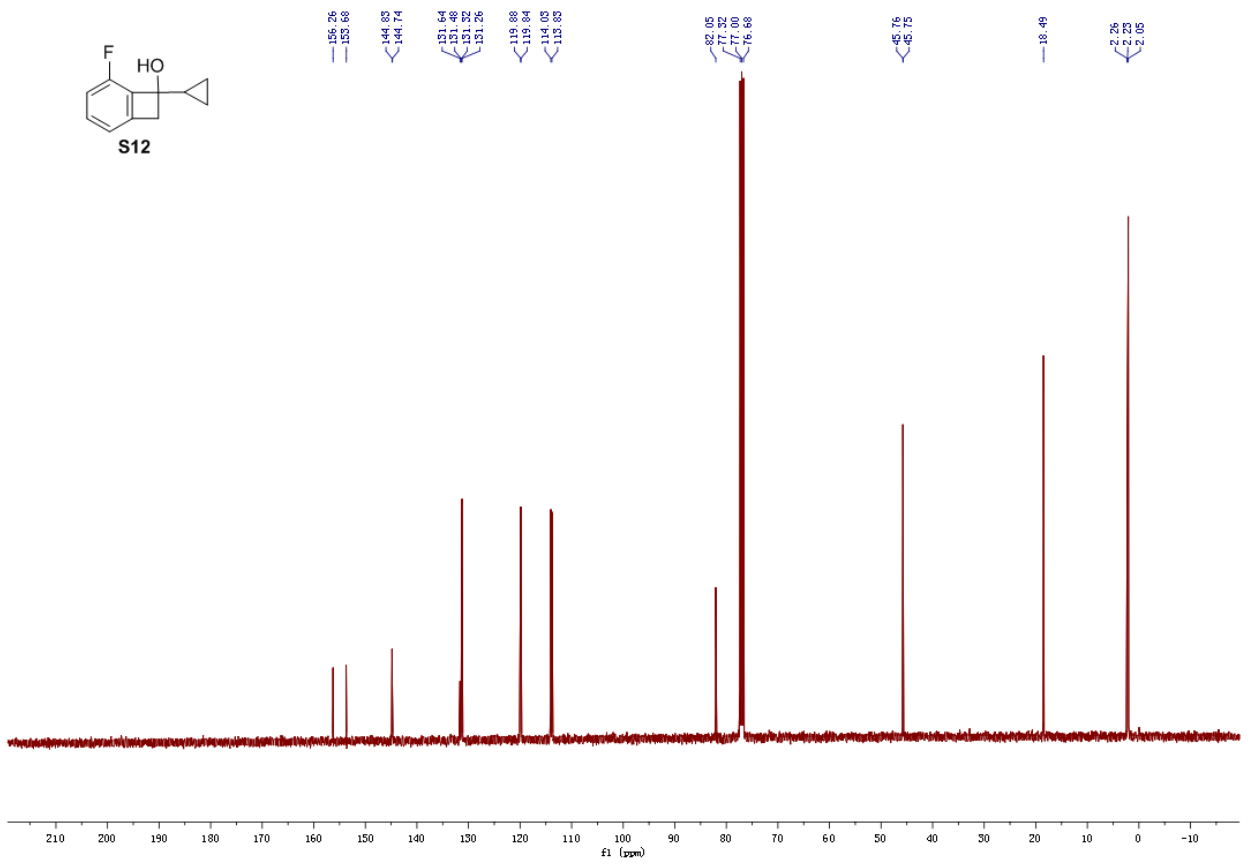
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HO
S12
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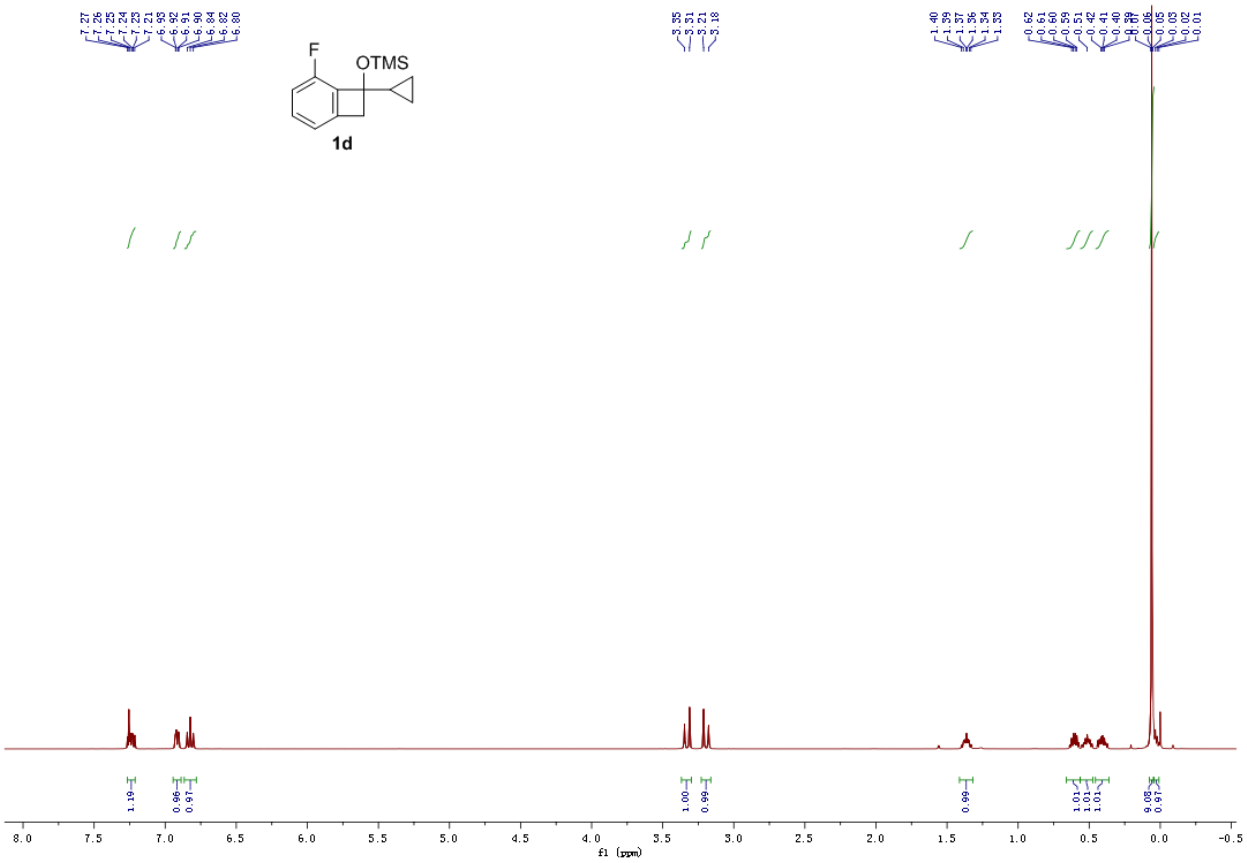
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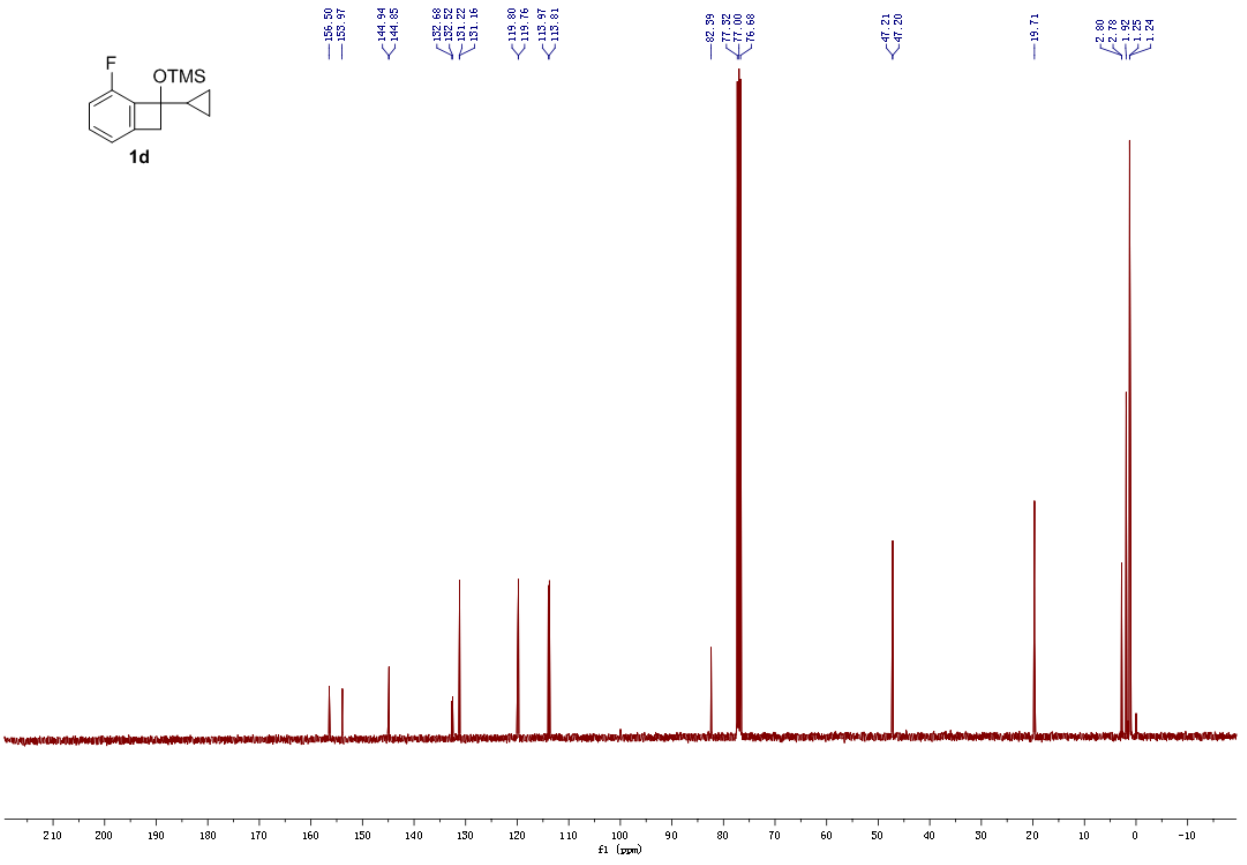
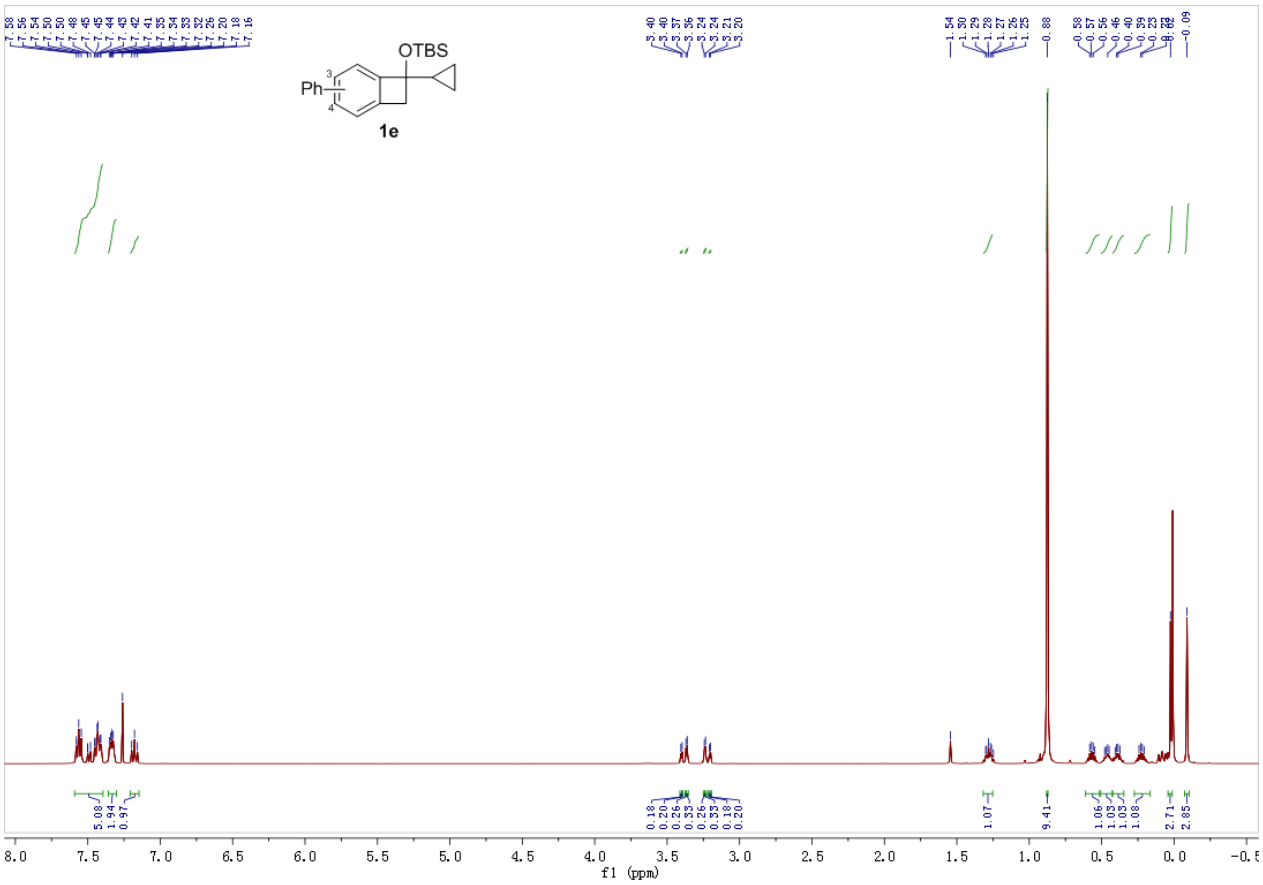
1d
f1 (ppm)


F
OTMS
1d
f1 (ppm)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Ph
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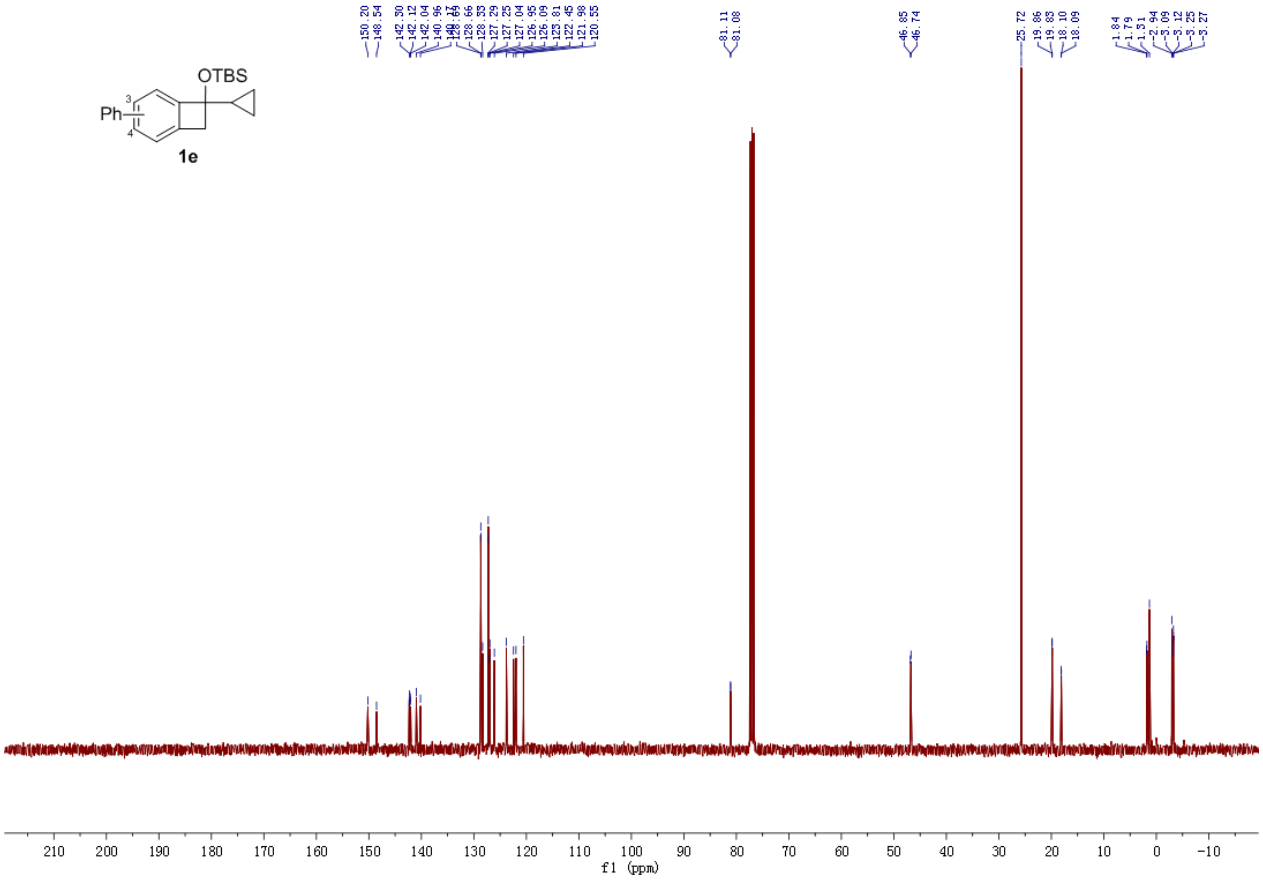
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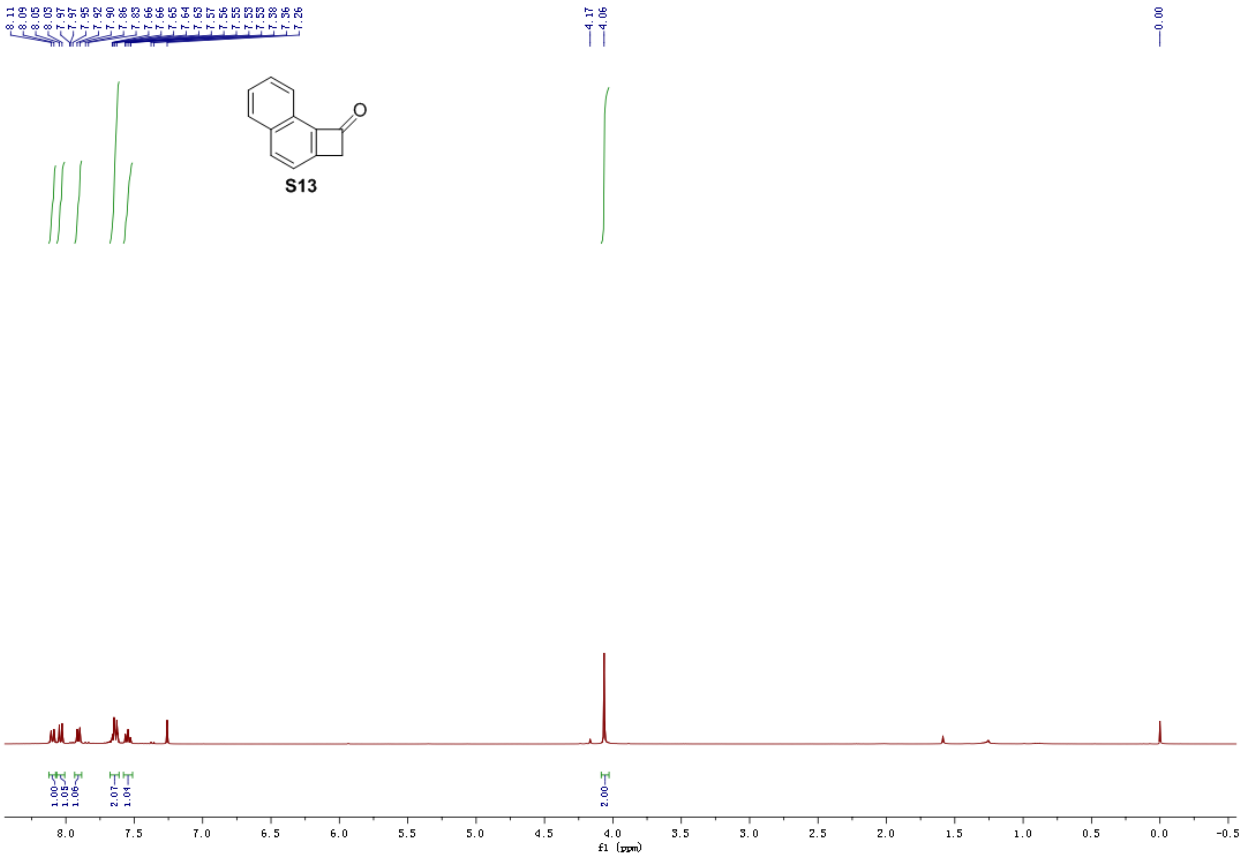
Ph
1e
f1 (ppm)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7.64
7.63
7.57
7.56
7.55
7.53
7.38
7.36
7.26
4.17
4.06
0.00
S13
1.00
1.05
1.06
2.01
1.04
2.00
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
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3.0
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2.0
1.5
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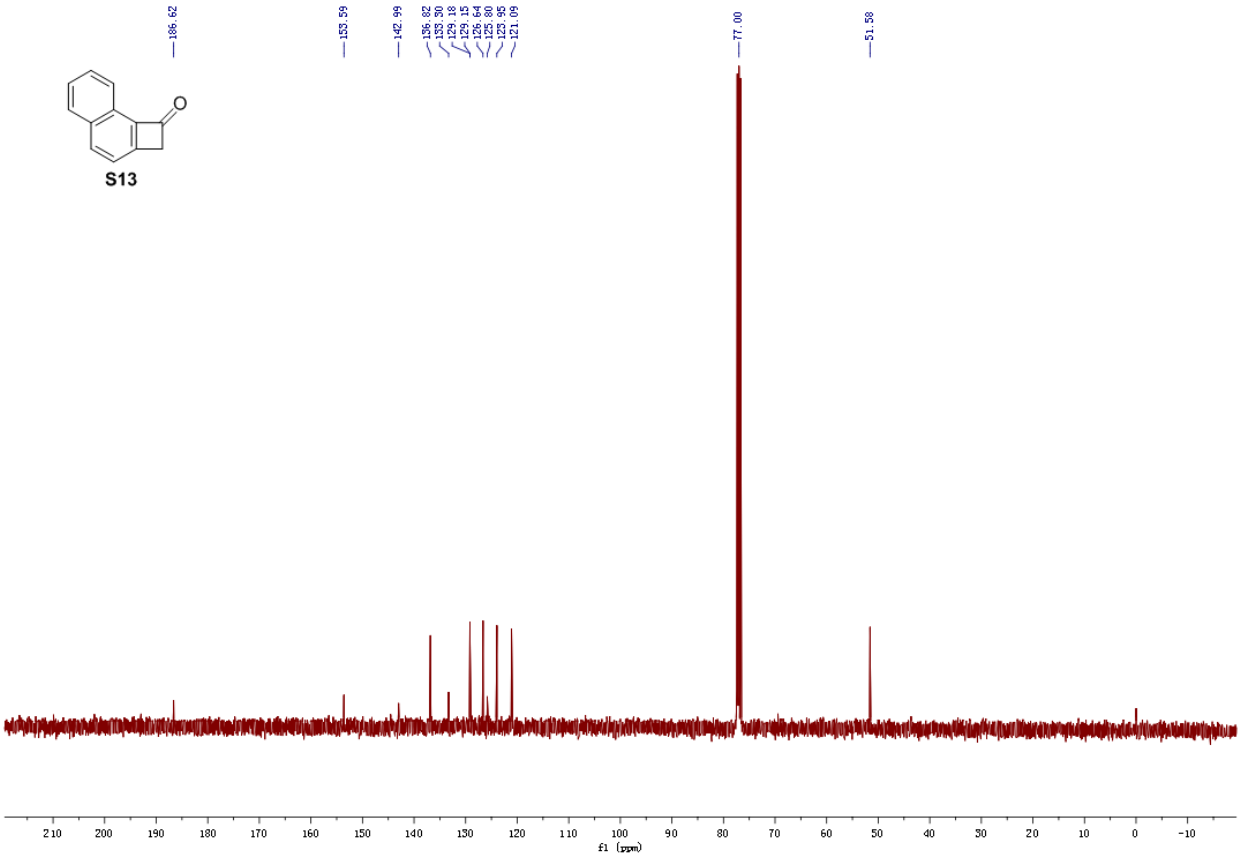
0.5
0.0
-0.5
f1 (ppm)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123.95
121.09
77.00
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200
190
180
170
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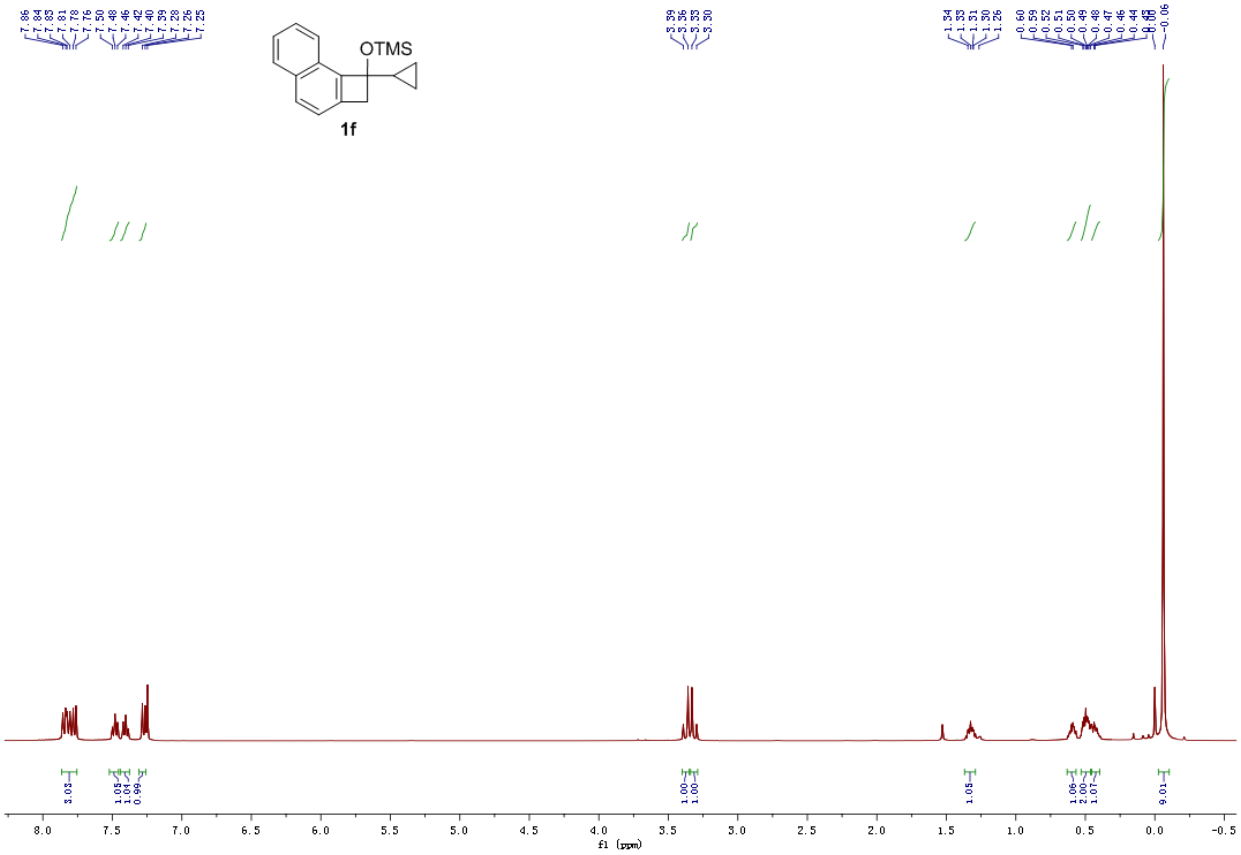
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1f
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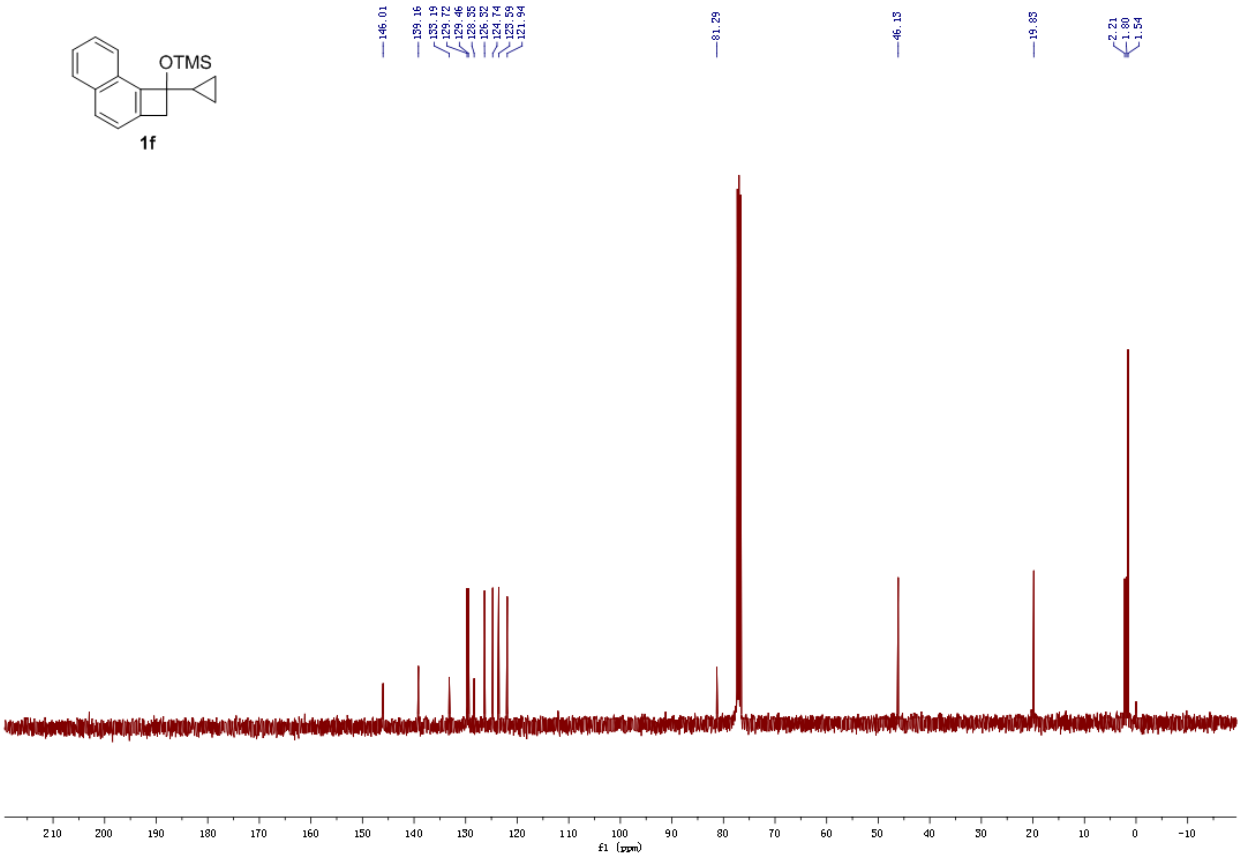
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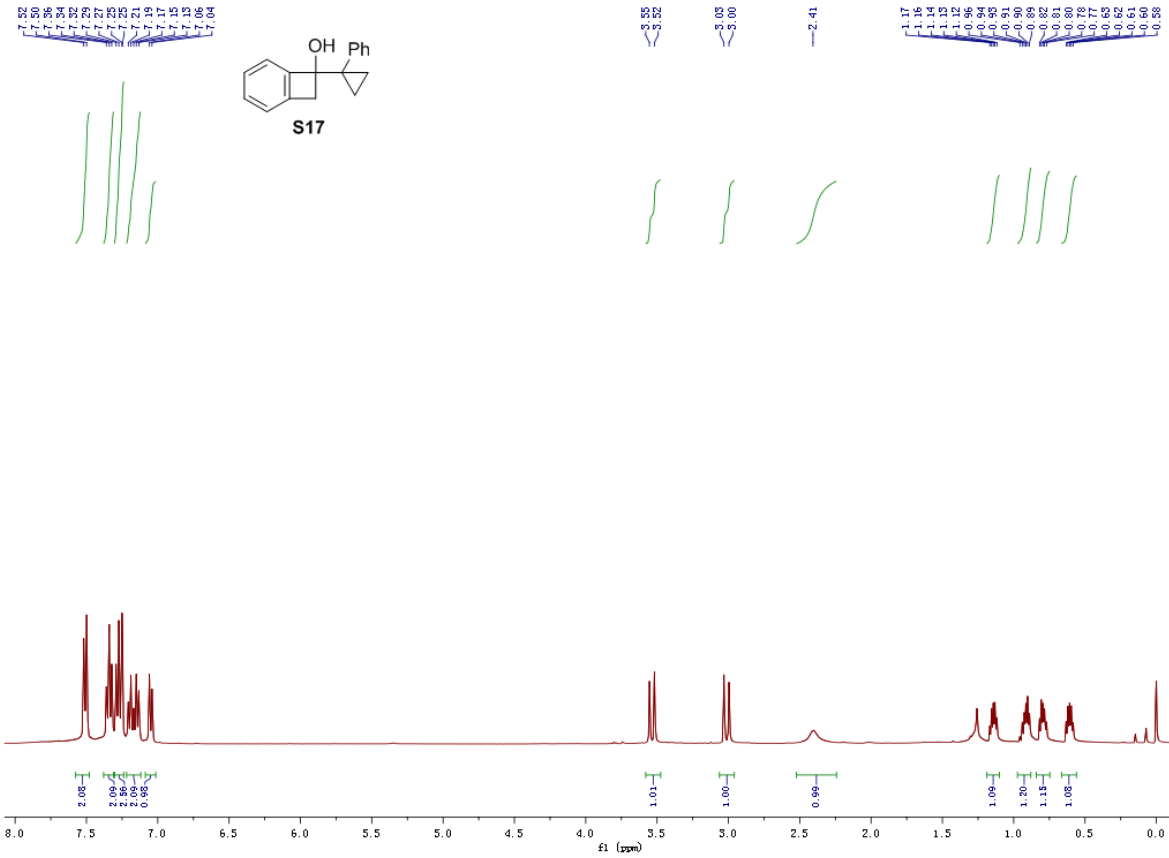
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Ph
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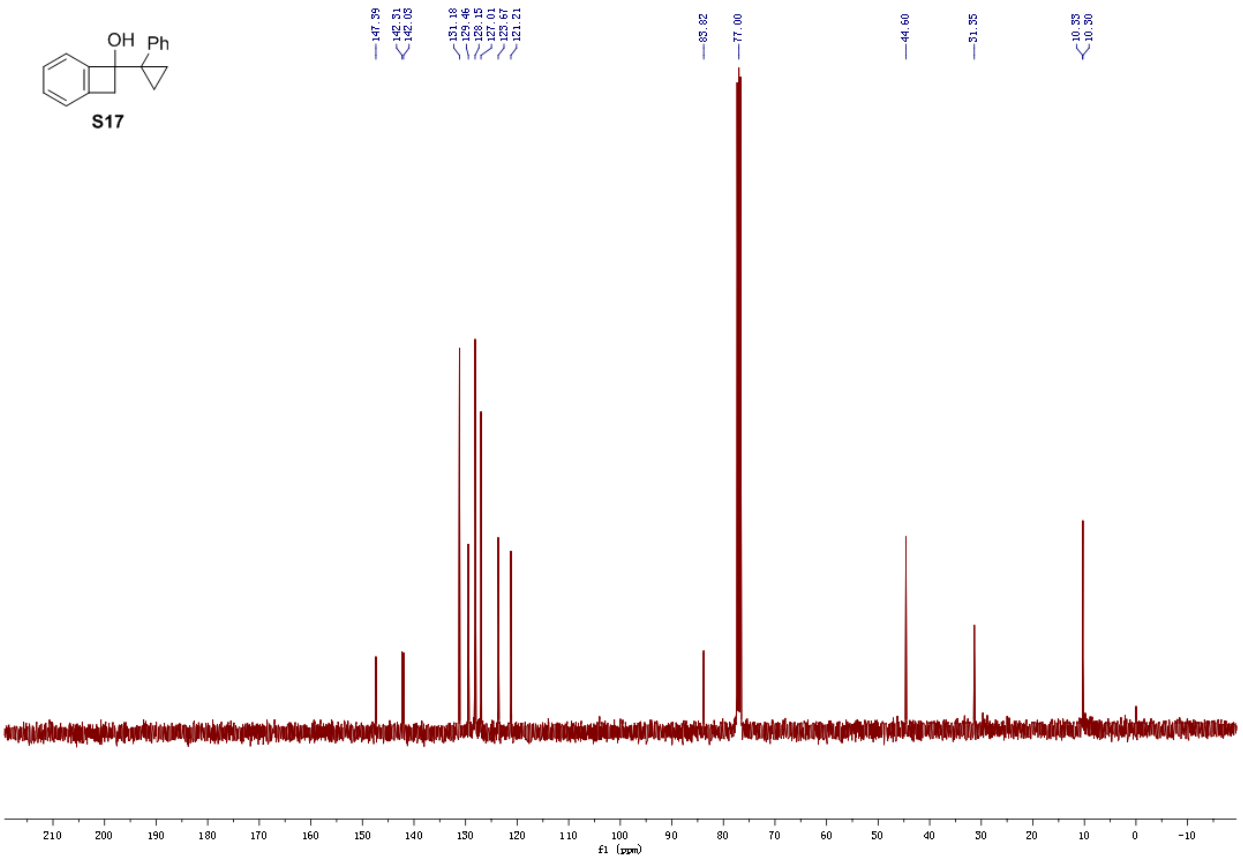
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Ph
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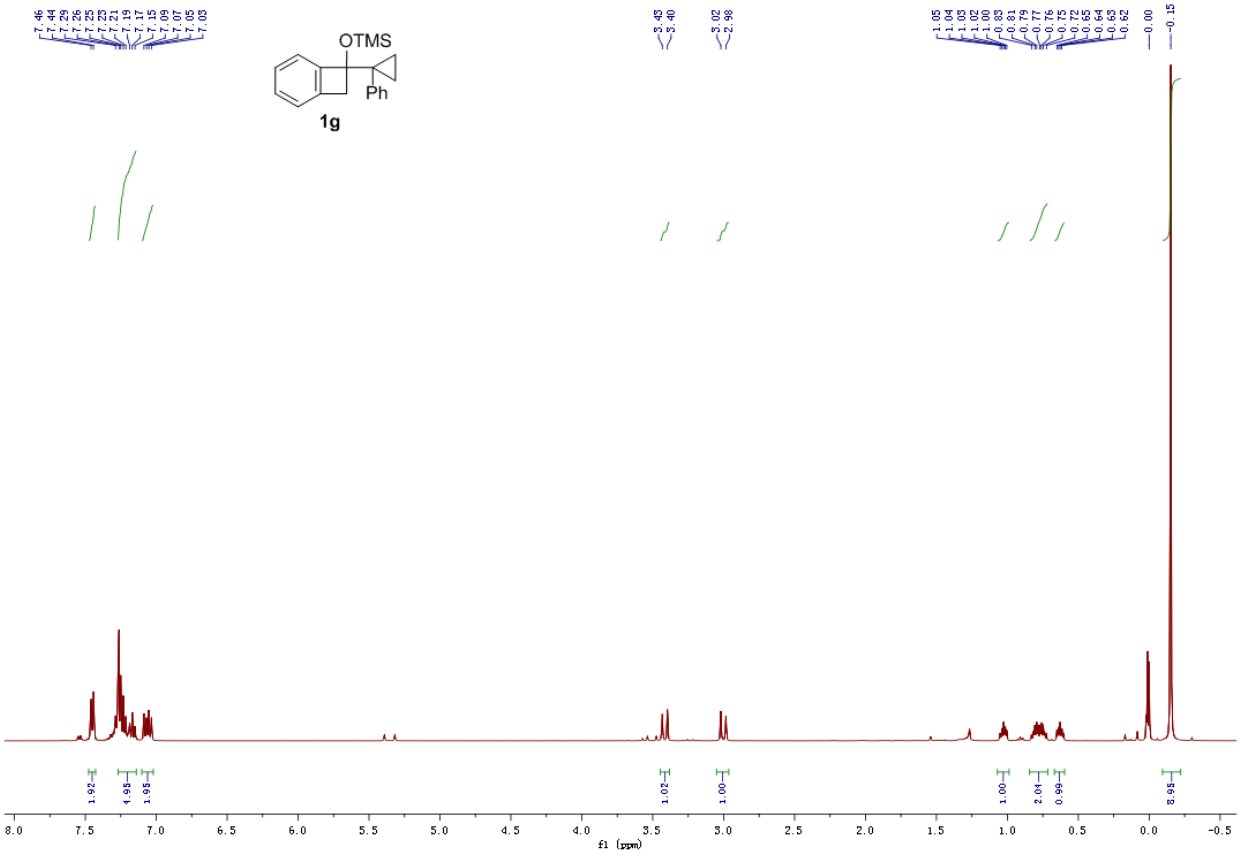
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Ph
1g
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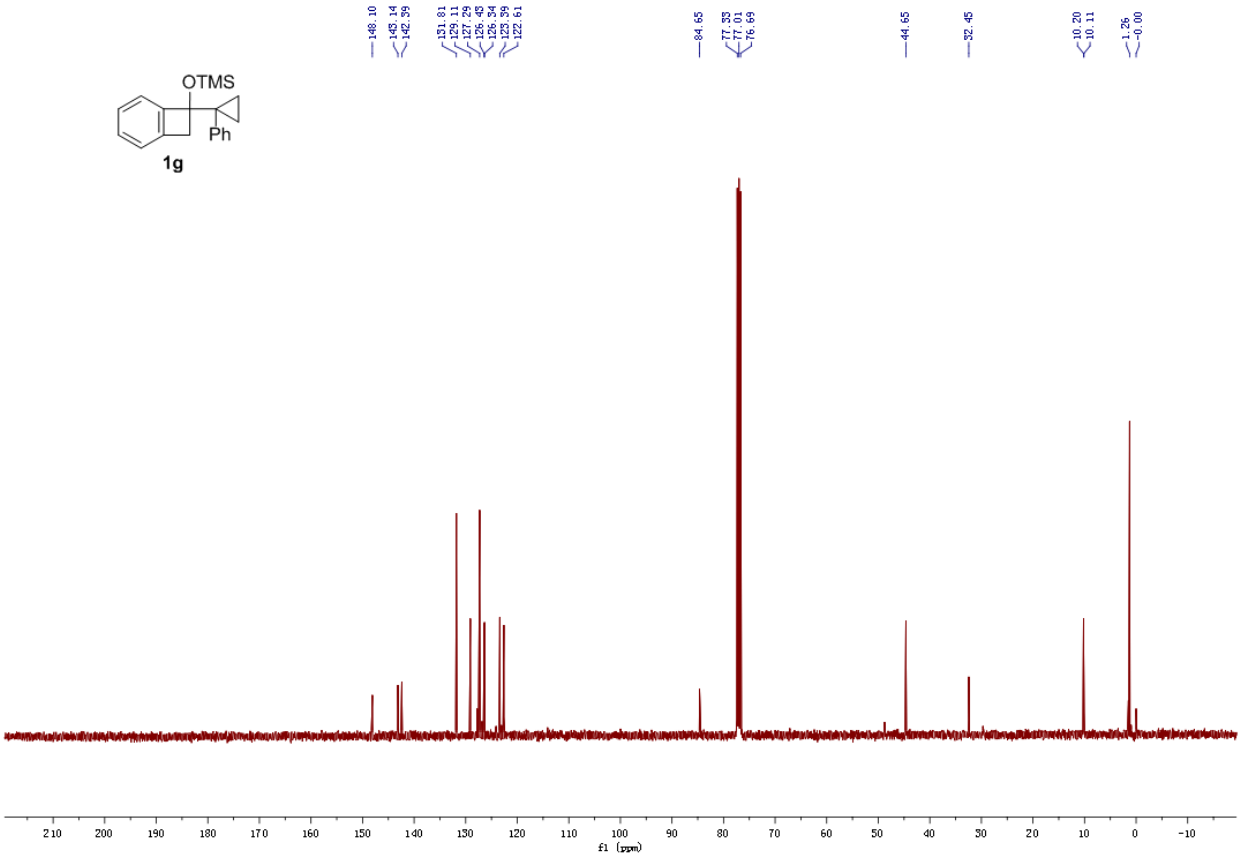
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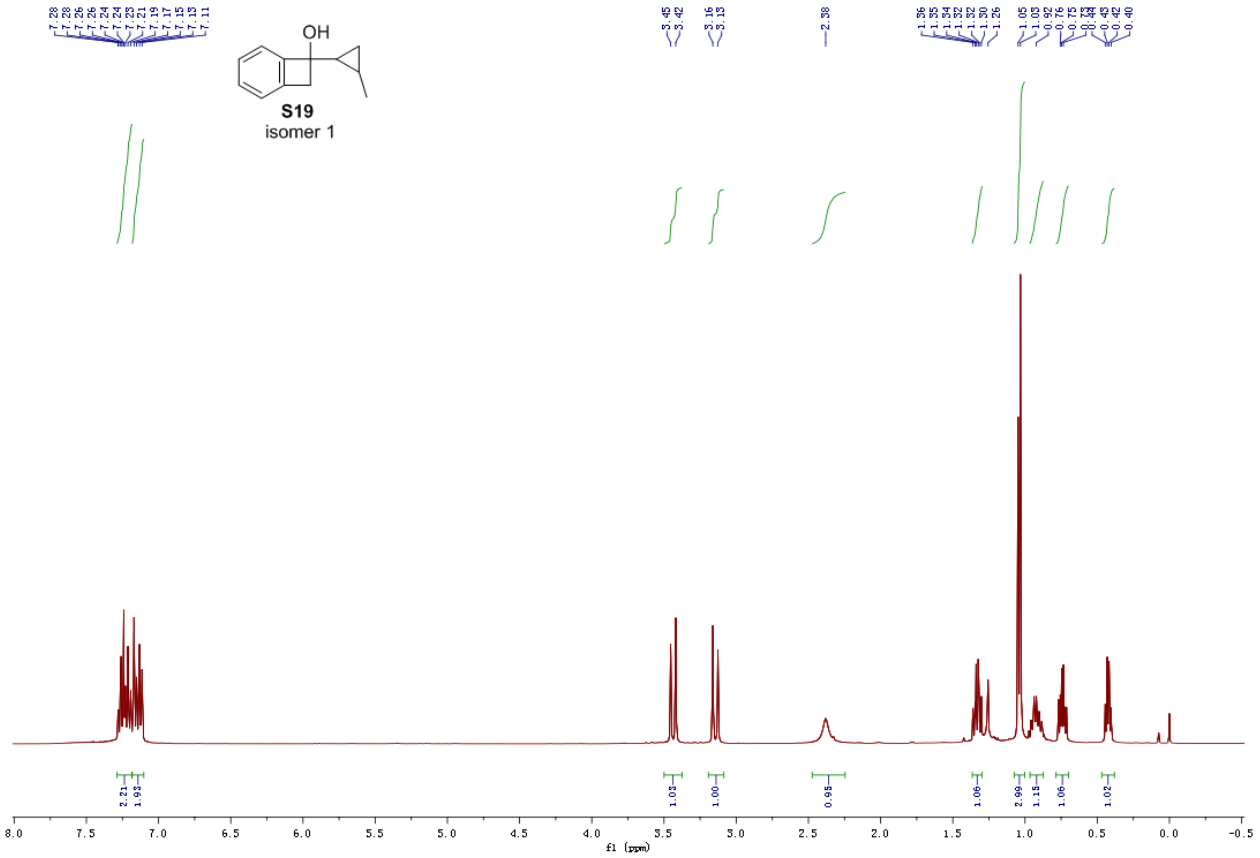
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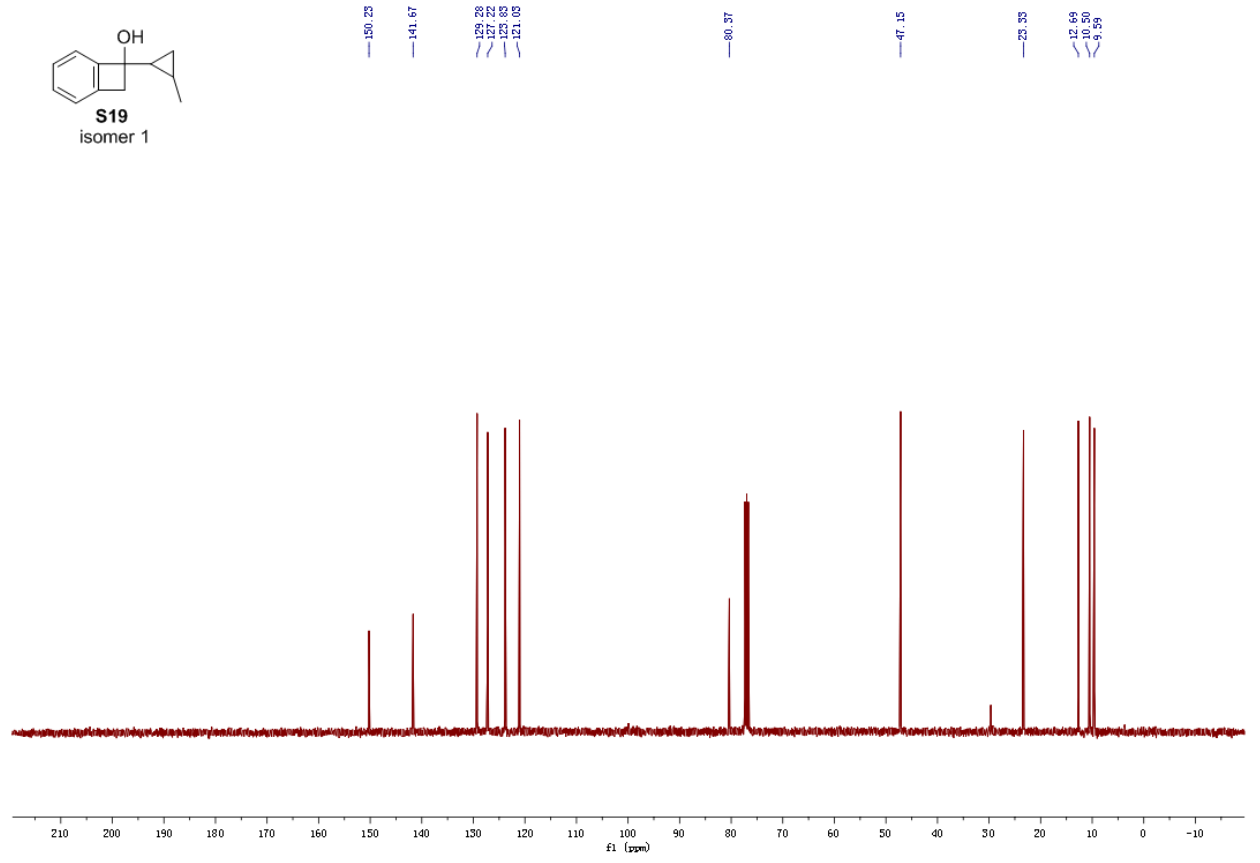
S19
isomer 1
f1 (ppm)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S19
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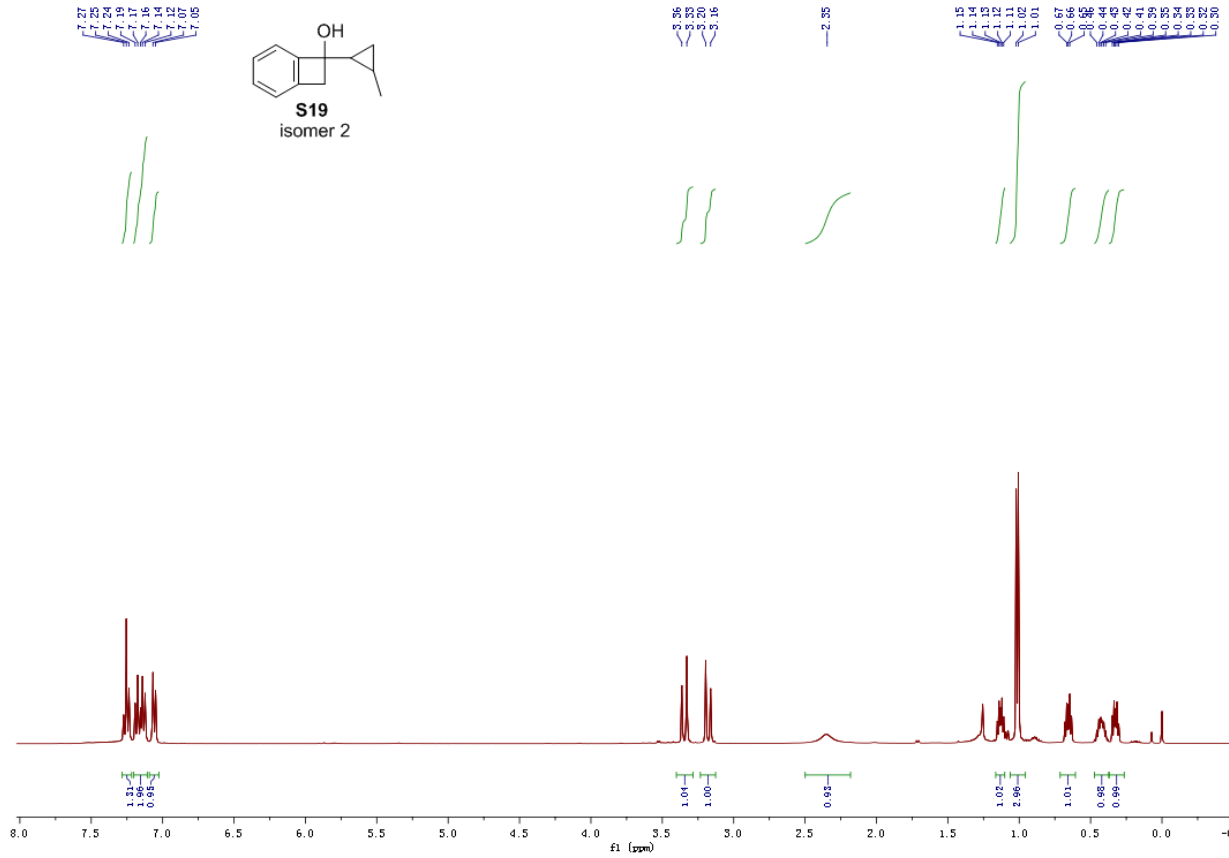
f1 (ppm)


OH
S19
isomer 2
7.27
7.25
7.24
7.19
7.17
7.16
7.14
7.12
7.07
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3.53
3.20
3.16
2.55
1.15
1.14
1.13
1.12
1.11
1.02
1.01
0.67
0.66
0.46
0.45
0.44
0.43
0.42
0.41
0.39
0.38
0.35
0.34
0.33
0.32
0.30
1.31
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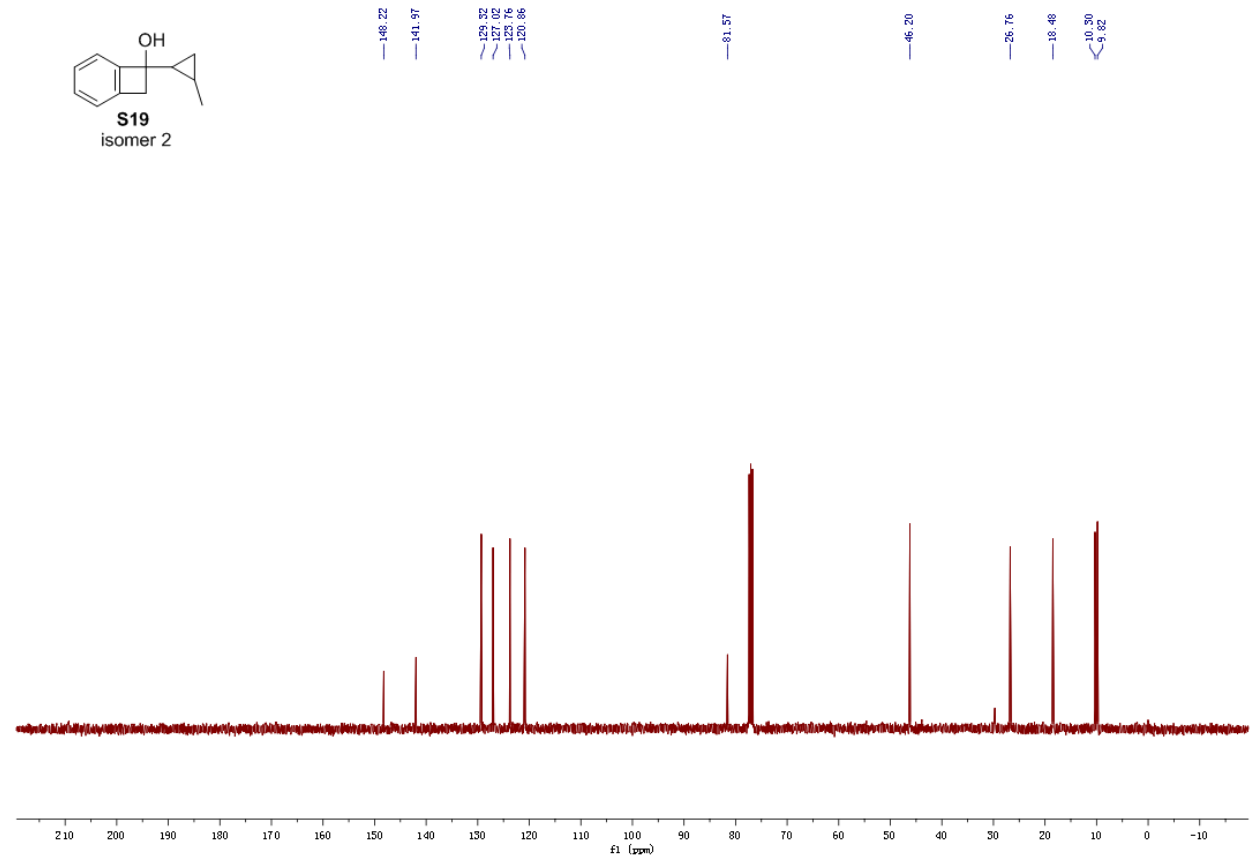
0.99
f1 (ppm)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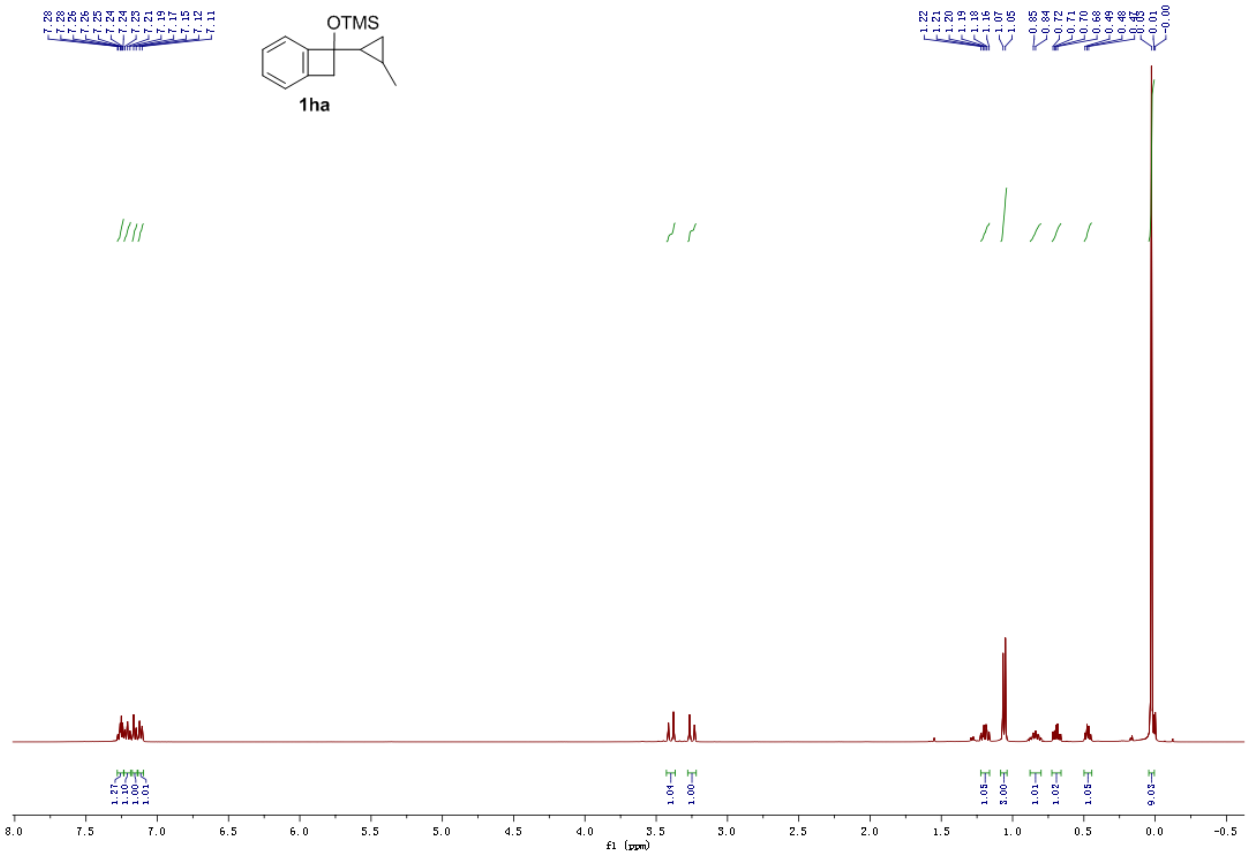
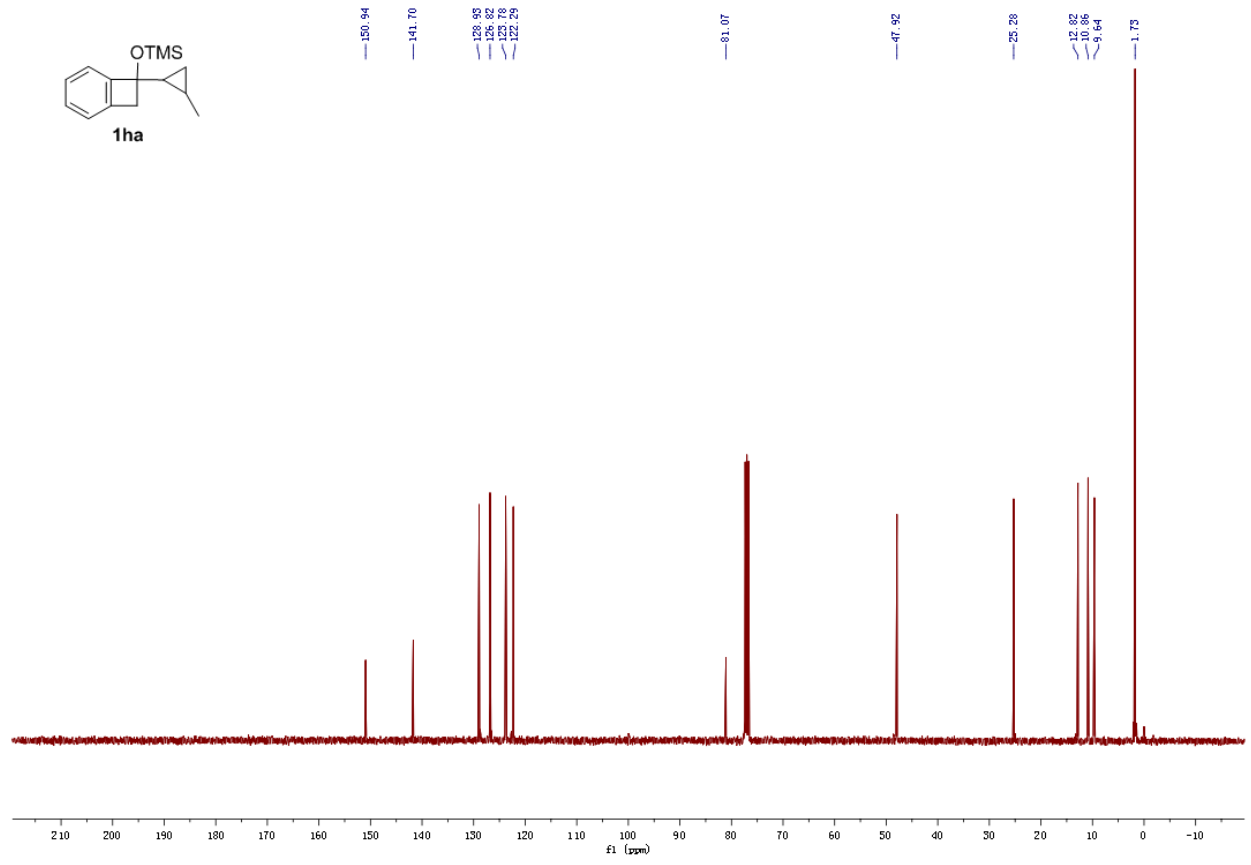
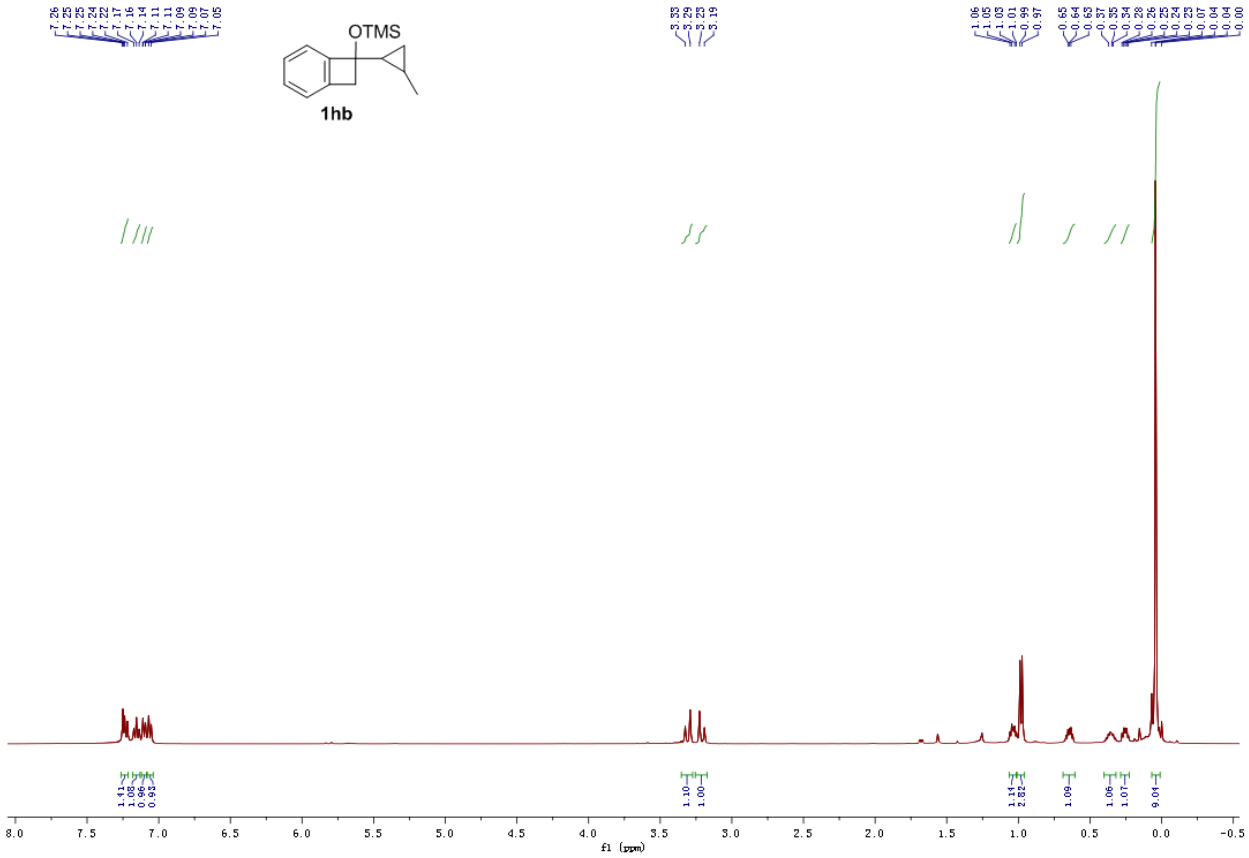
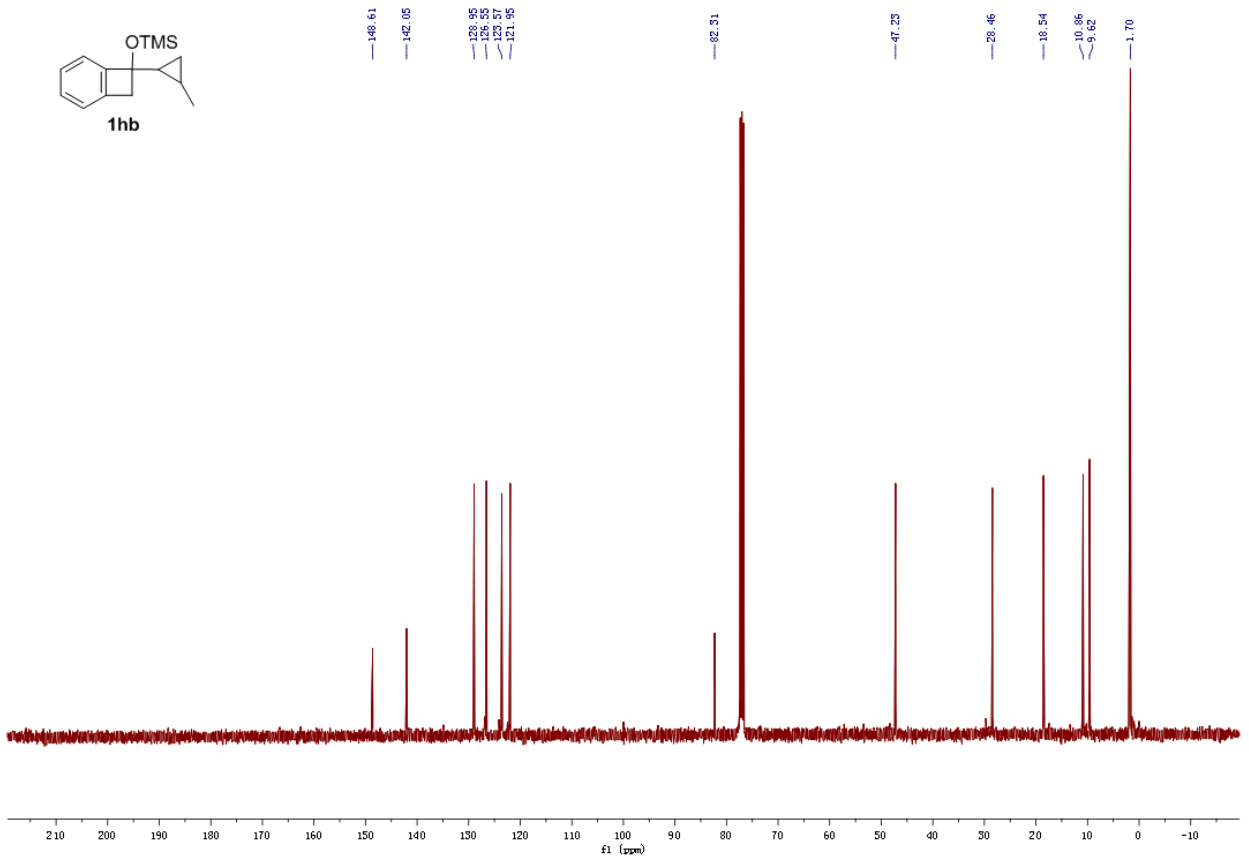
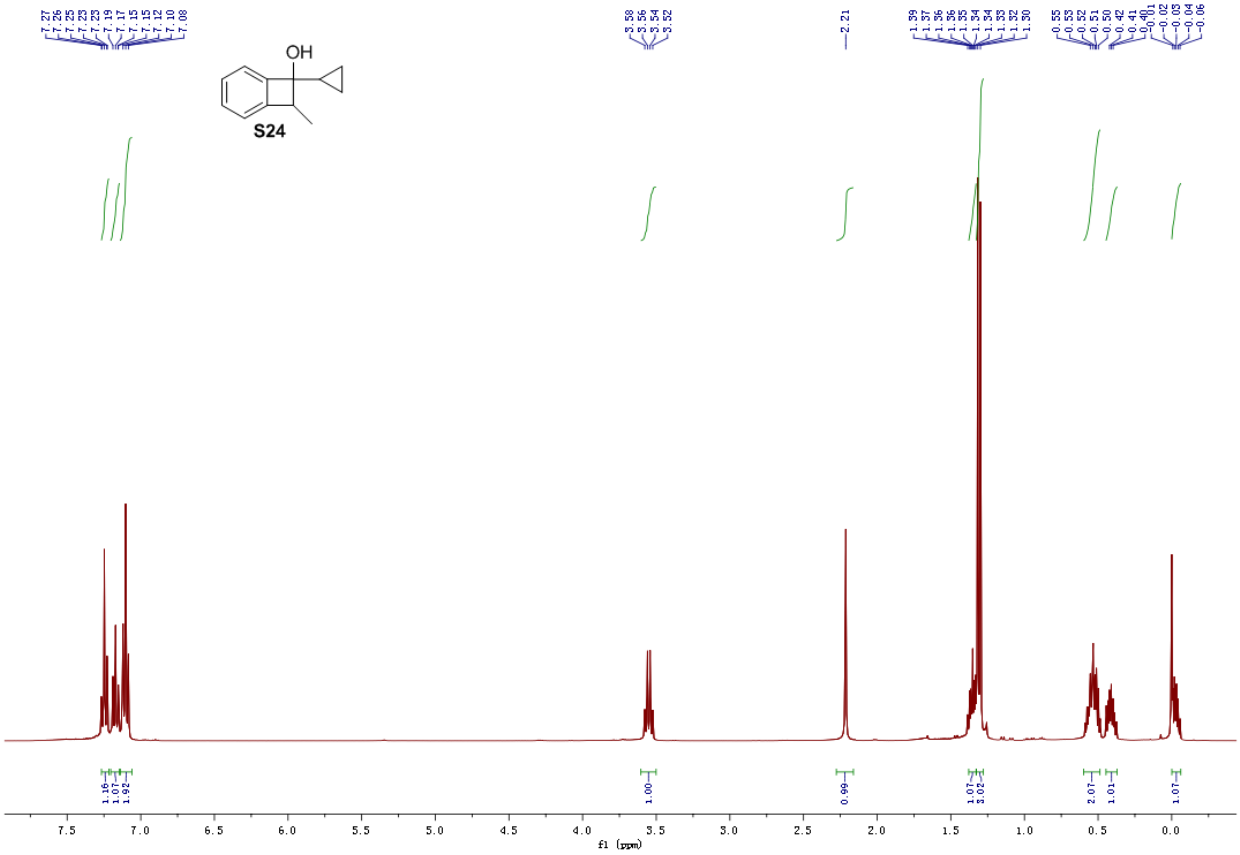
9.82
f1 (ppm)

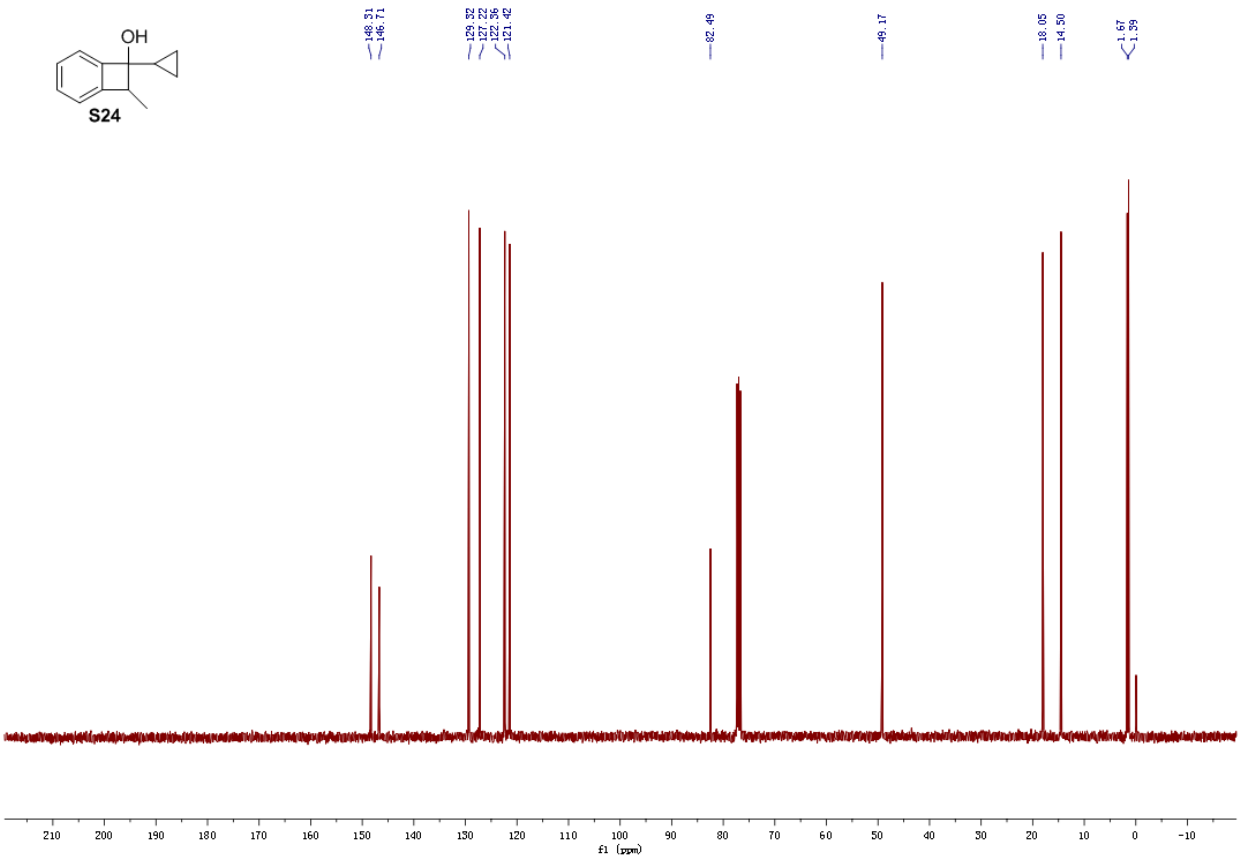

OTMS
1ha
f1 (ppm)

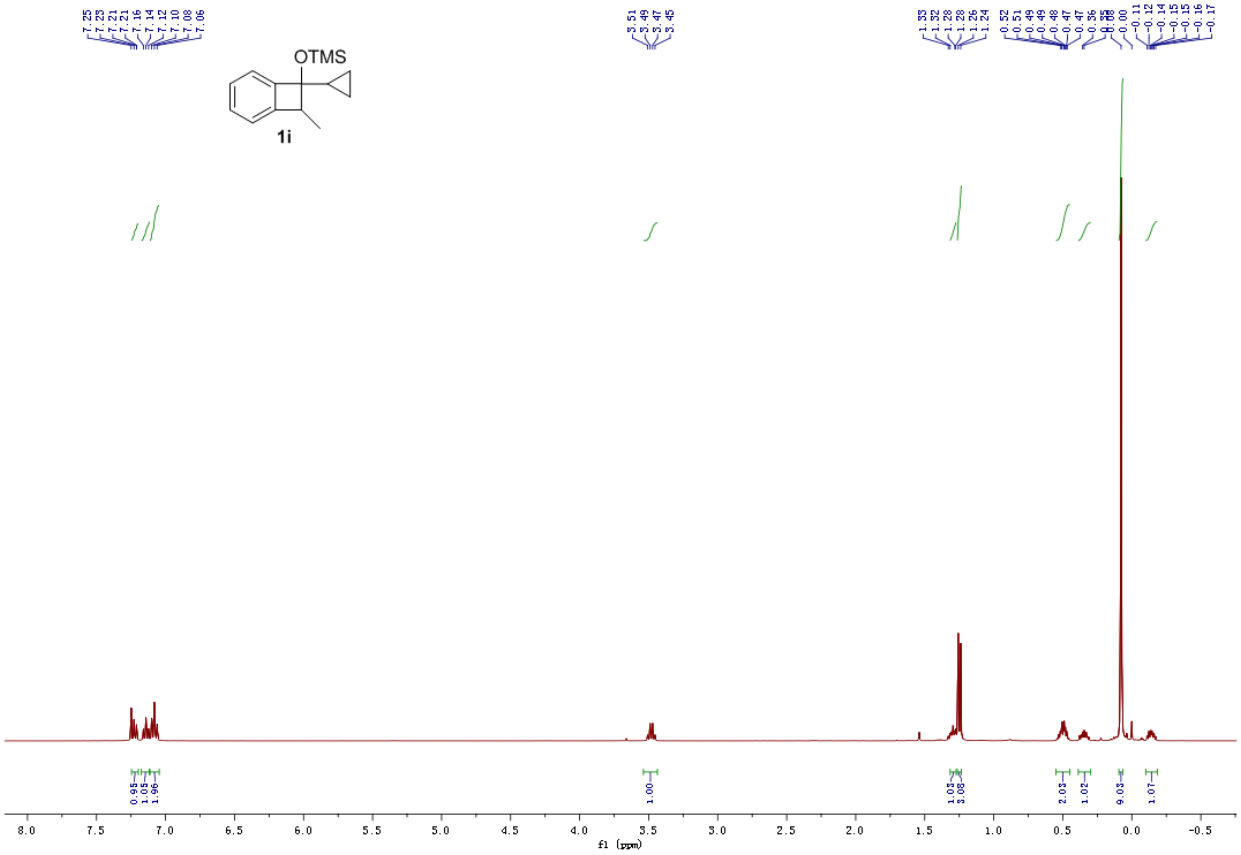

OTMS
1ha
f1 (ppm)

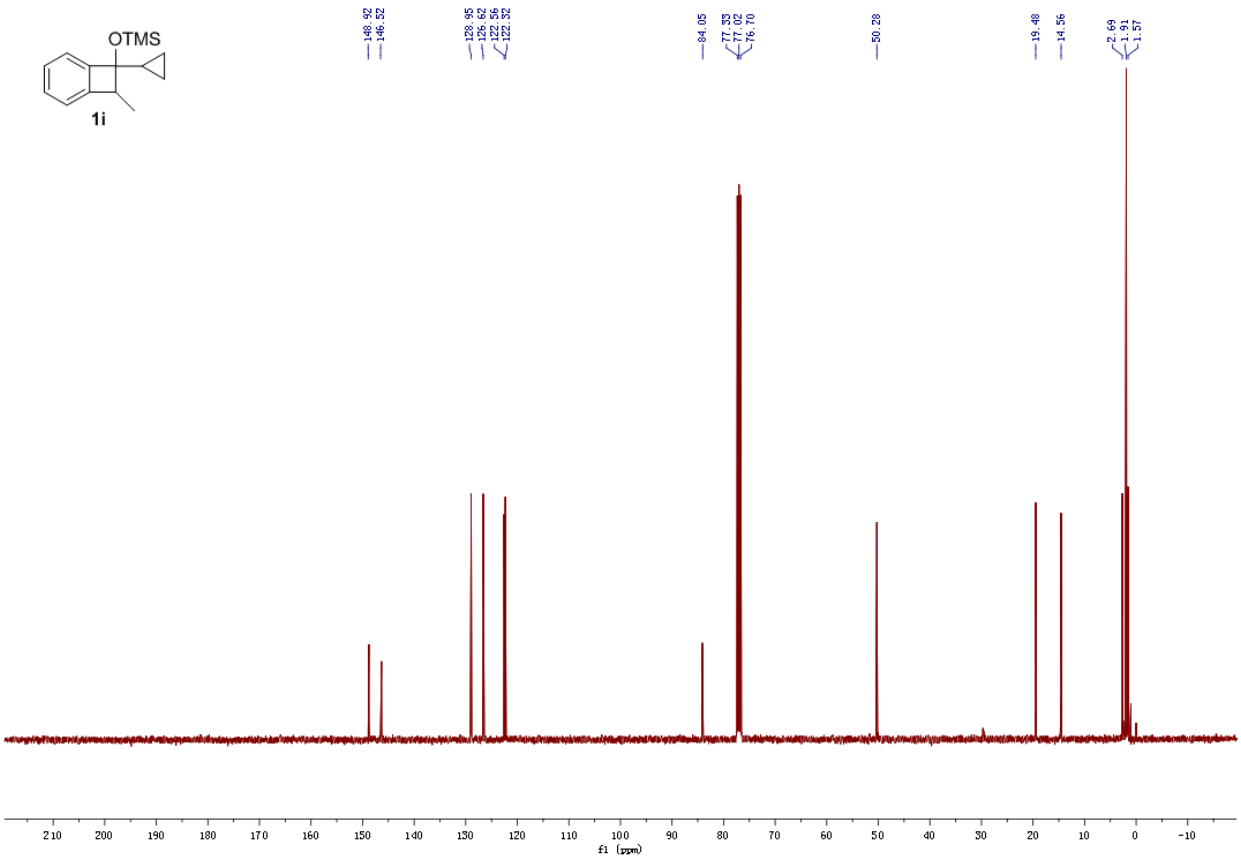

OTMS
1hb
f1 (ppm)


OTMS
1hb
f1 (ppm)


OH
S24
7.27
7.26
7.25
7.23
7.23
7.19
7.17
7.15
7.15
7.12
7.10
7.08
3.58
3.56
3.54
3.52
2.21
1.39
1.37
1.36
1.35
1.34
1.33
1.32
1.30
0.55
0.53
0.52
0.51
0.50
0.42
0.41
0.40
0.01
0.02
0.03
0.04
0.06
1.16
1.00
1.92
1.00
0.99
1.07
3.02
2.07
1.01
1.07
f1 (ppm)

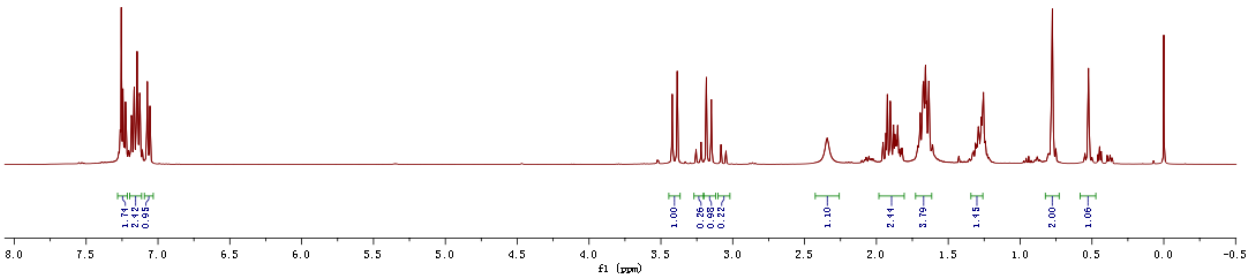

OH
S24
148.31
146.71
129.52
127.22
122.36
121.42
82.49
49.17
18.05
14.50
1.67
1.39
f1 (ppm)

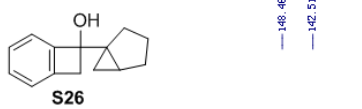

OTMS
1i
f1 (ppm)


OTMS
1i
f1 (ppm)

S26

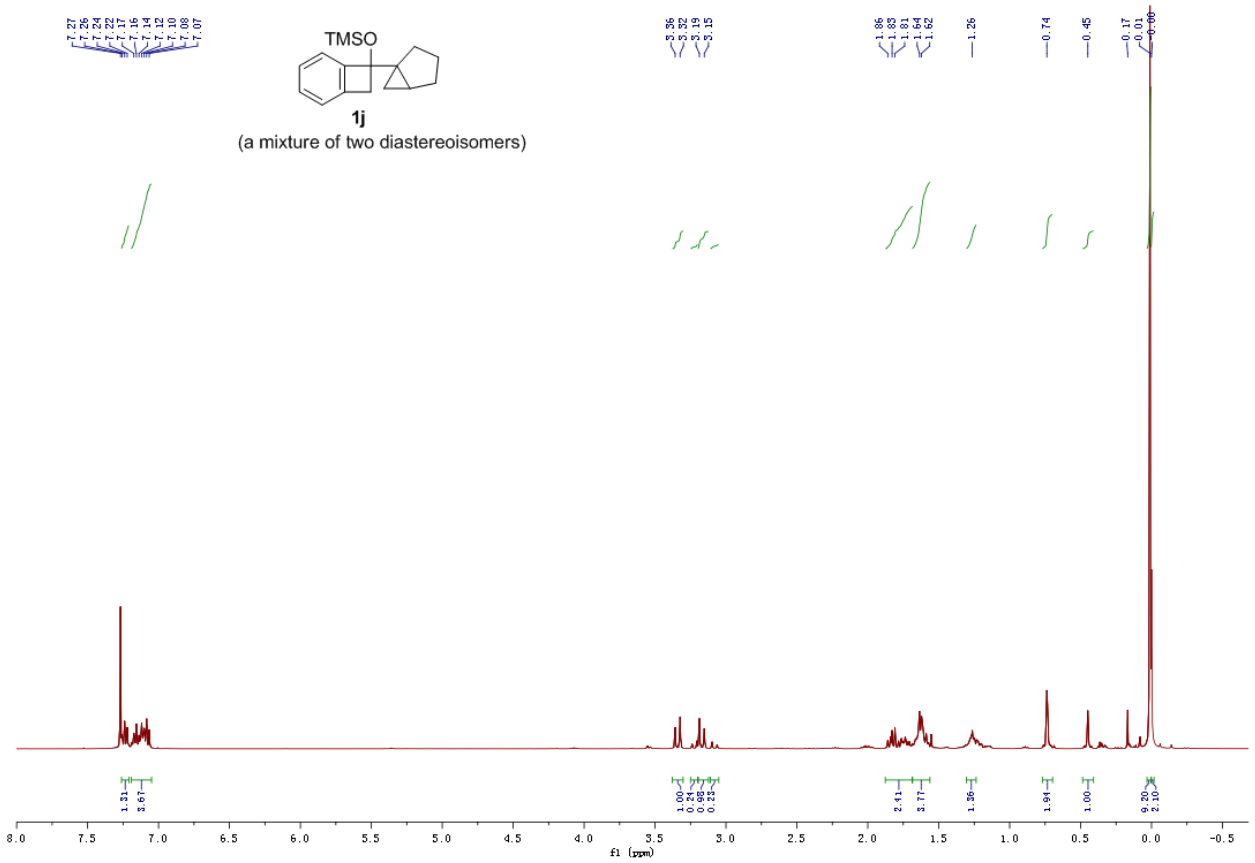
(a mixture of two diastereoisomers)

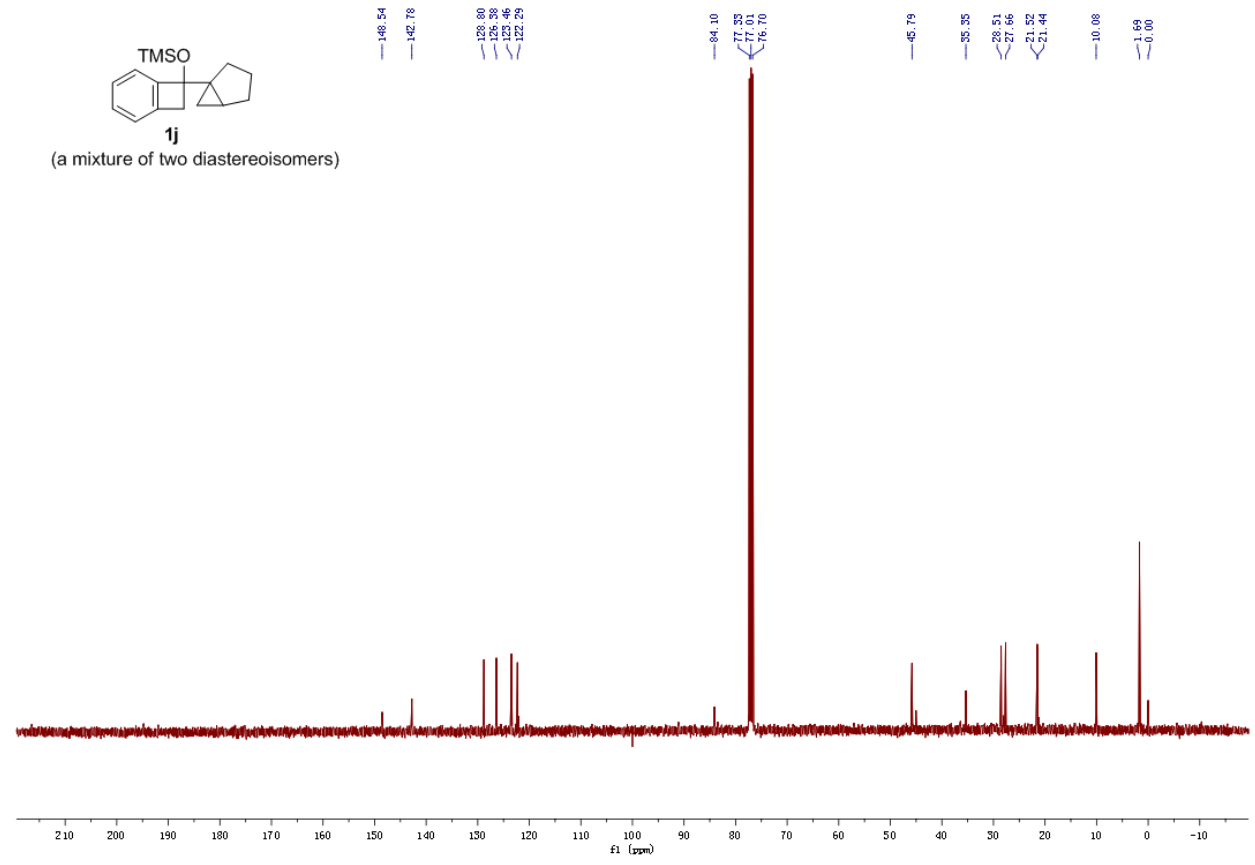


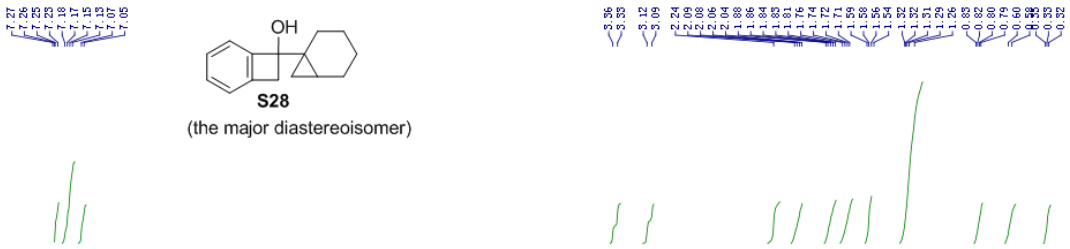


S26

(a mixture of two diastereoisomers)

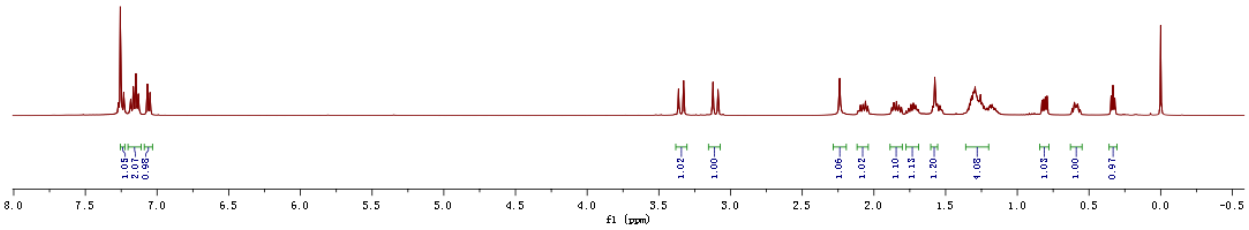

TMSO
1j
(a mixture of two diastereoisomers)
f1 (ppm)

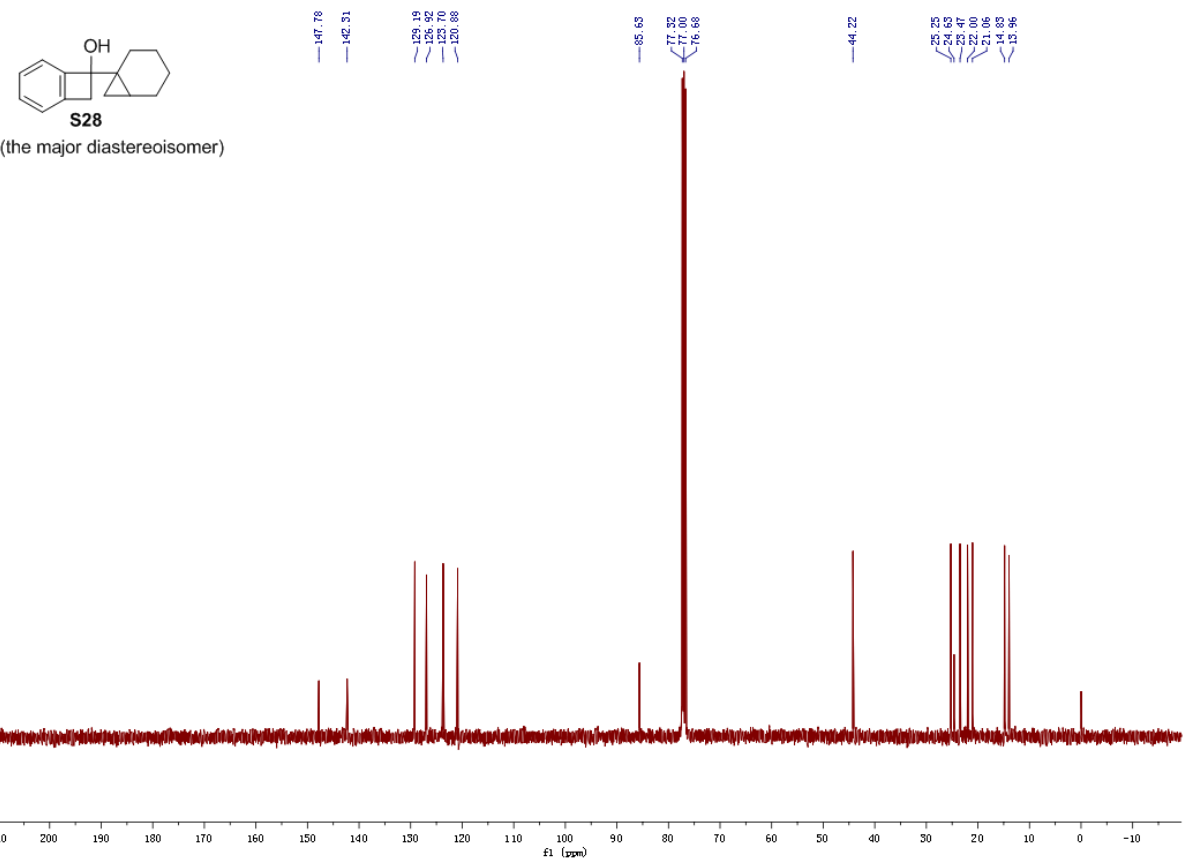

TMSO
1j
(a mixture of two diastereoisomers)
f1 (ppm)



S28

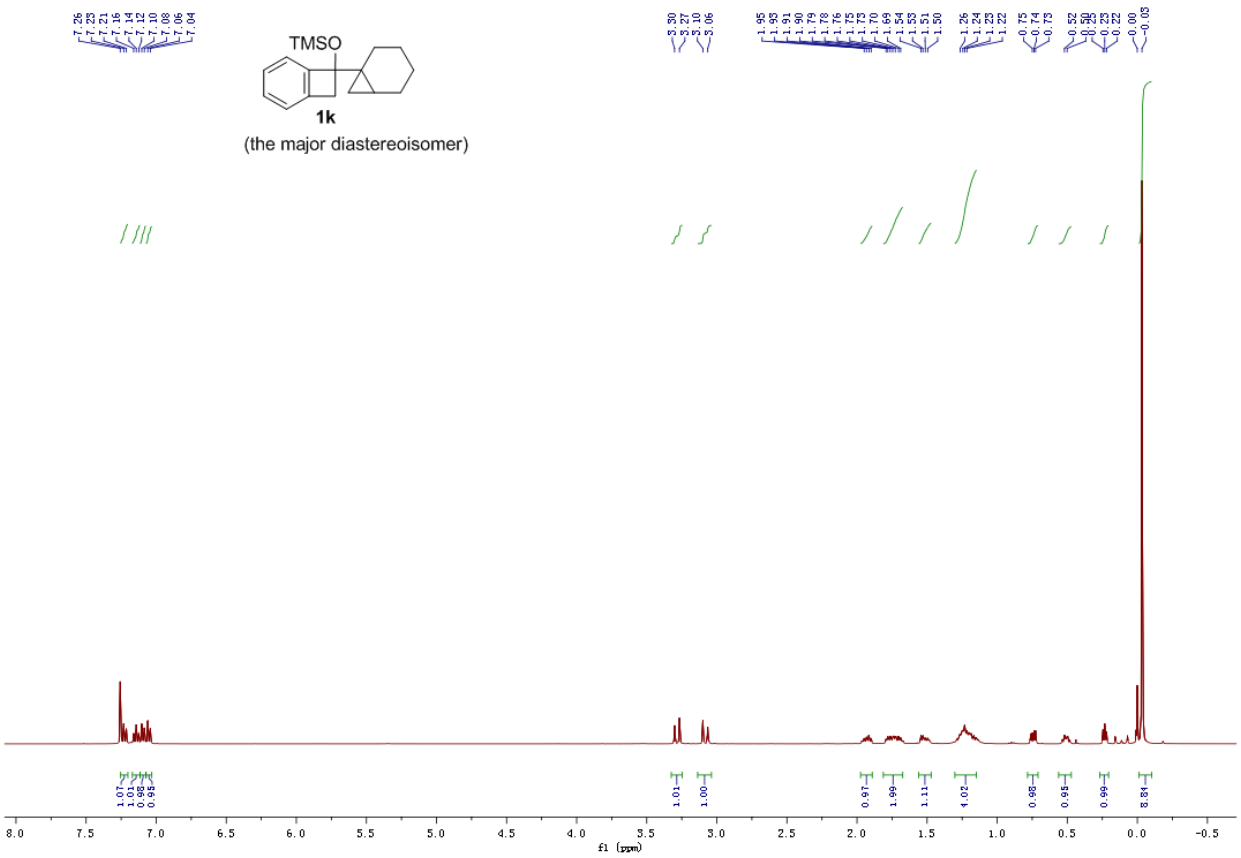
(the major diastereoisomer)

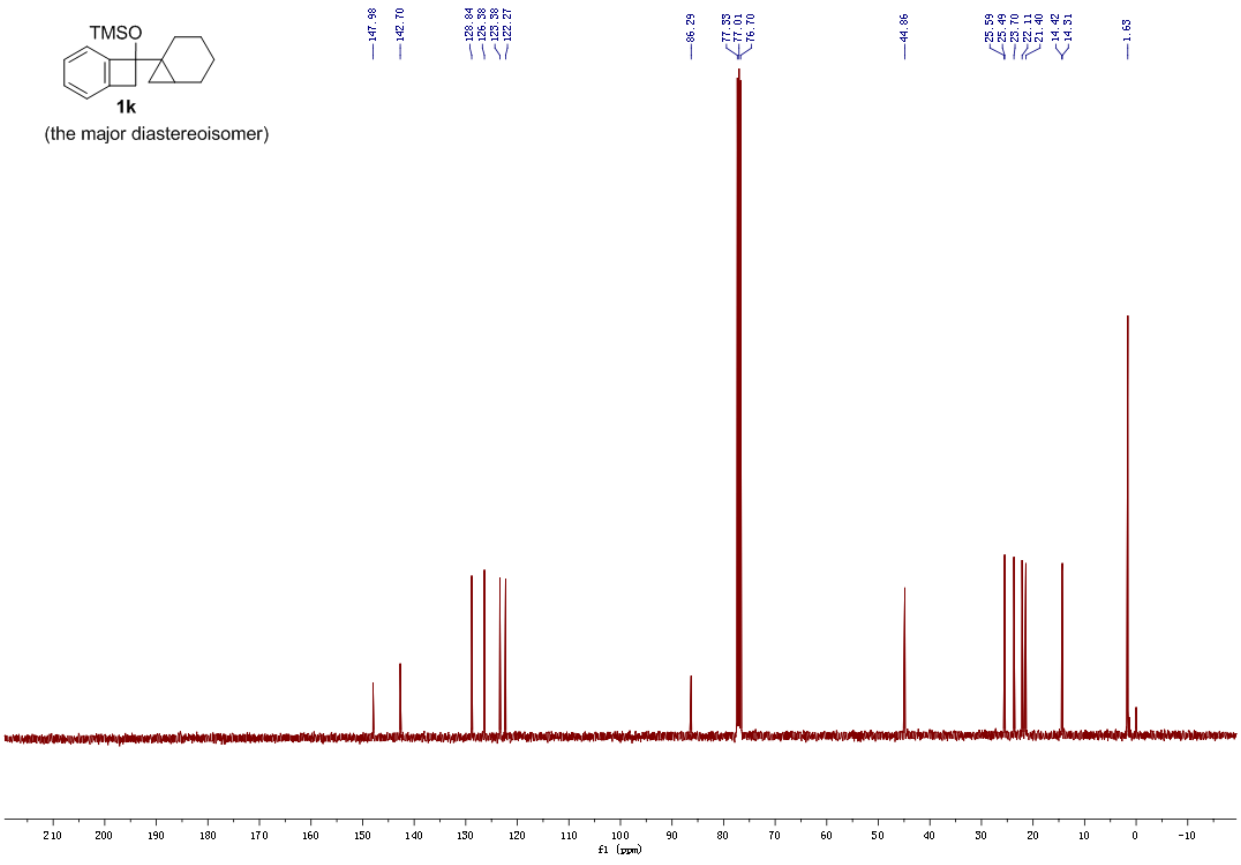


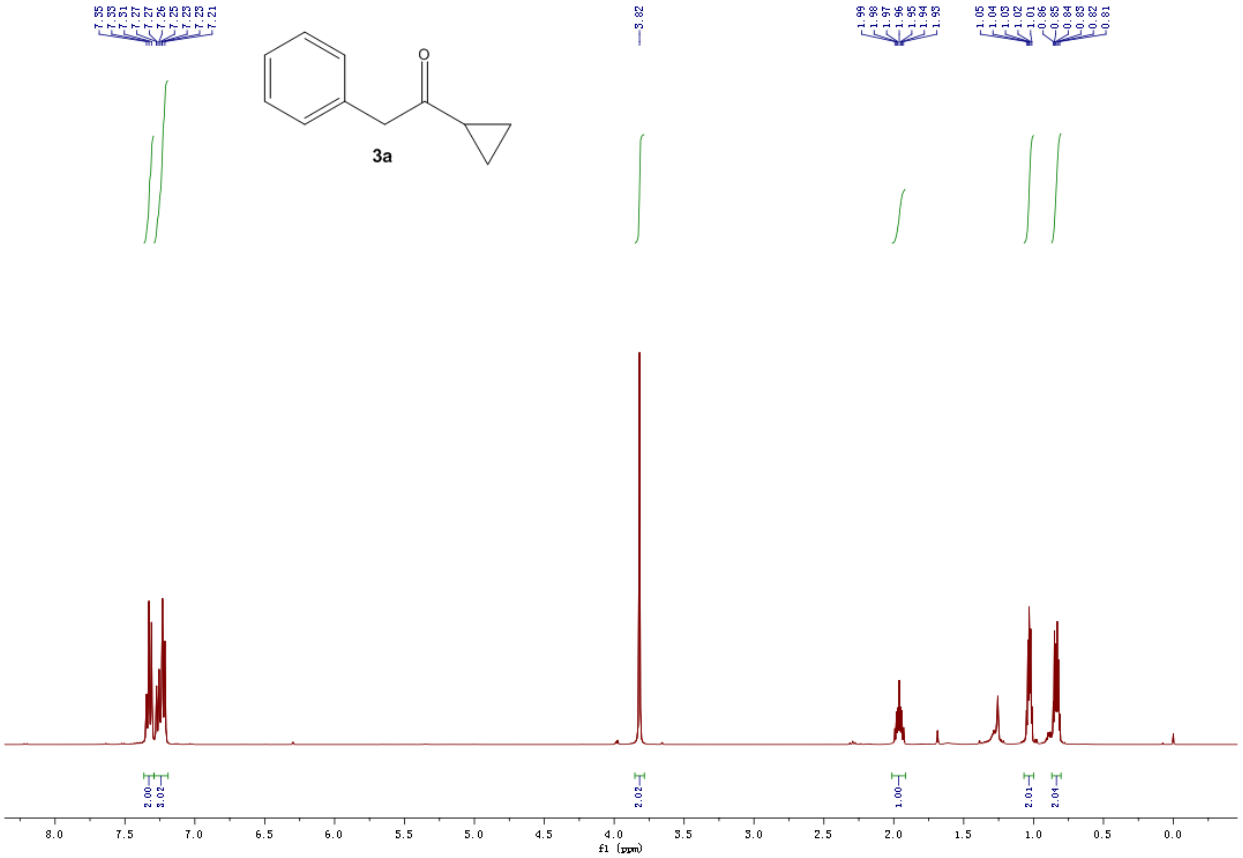


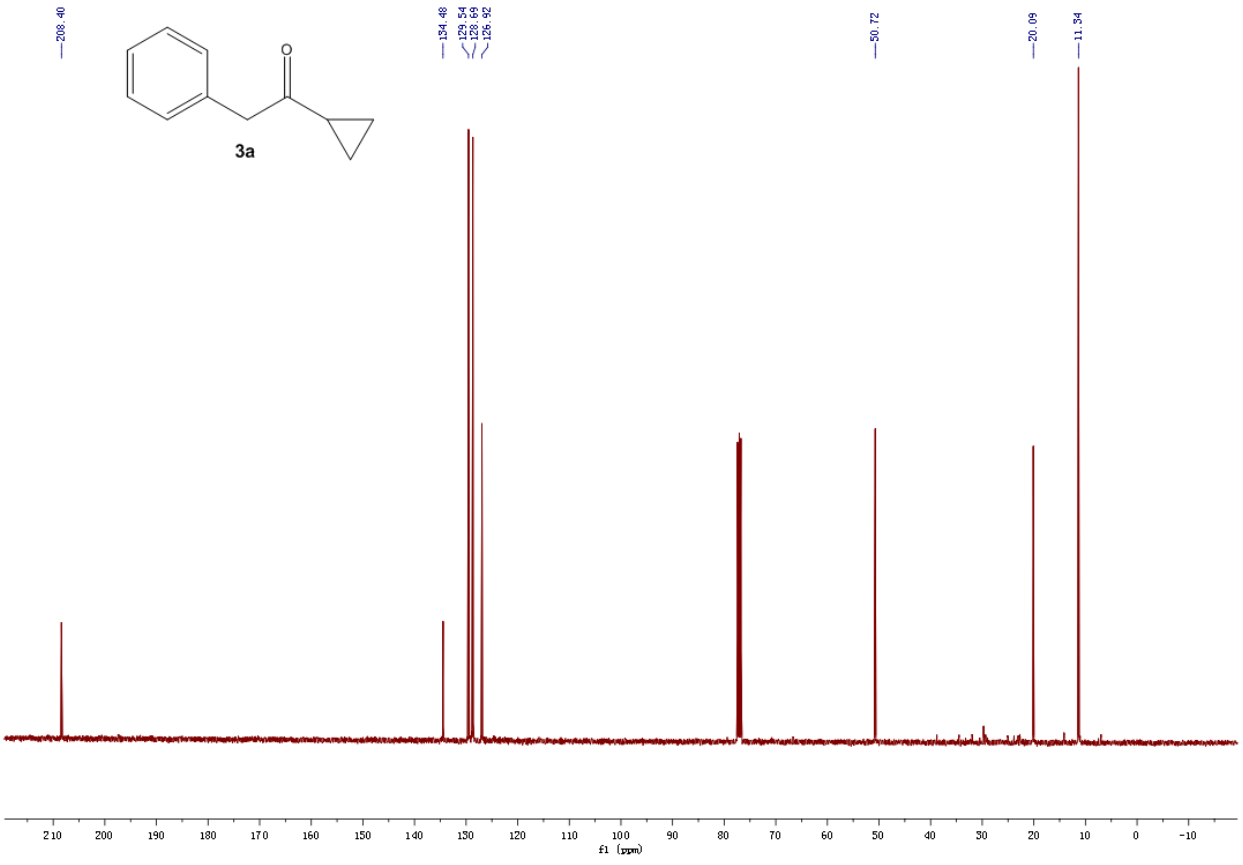
S28

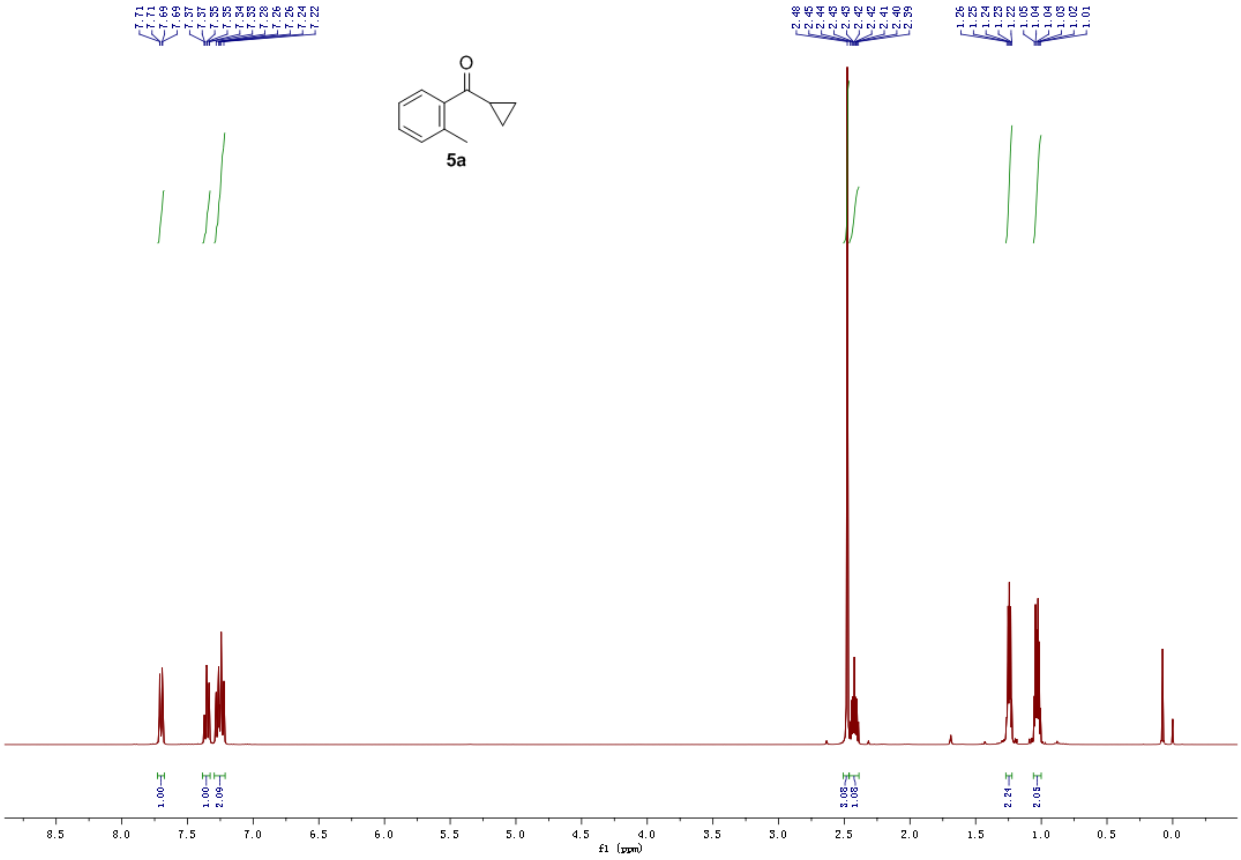
(the major diastereoisomer)

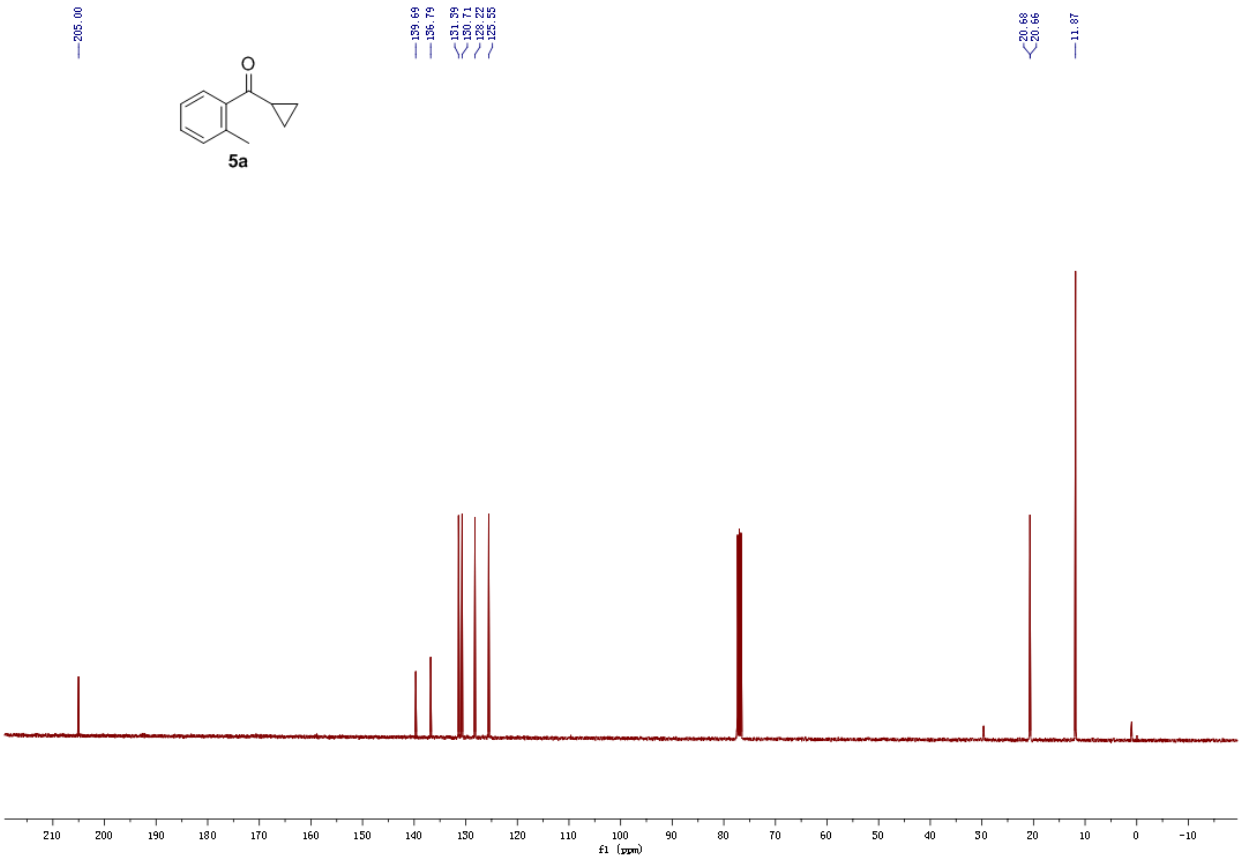

TMSO
1k
(the major diastereoisomer)
f1 (ppm)

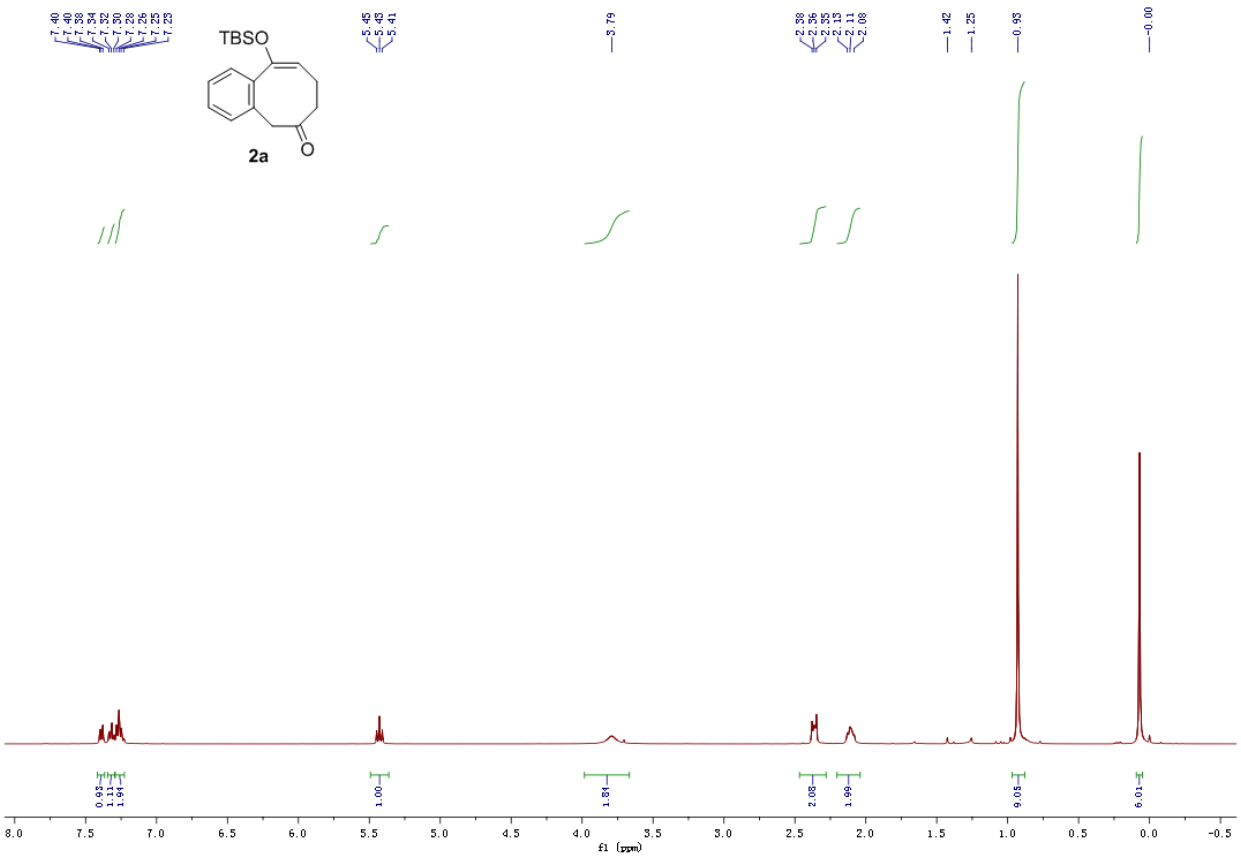

TMSO
1k
(the major diastereoisomer)
f1 (ppm)

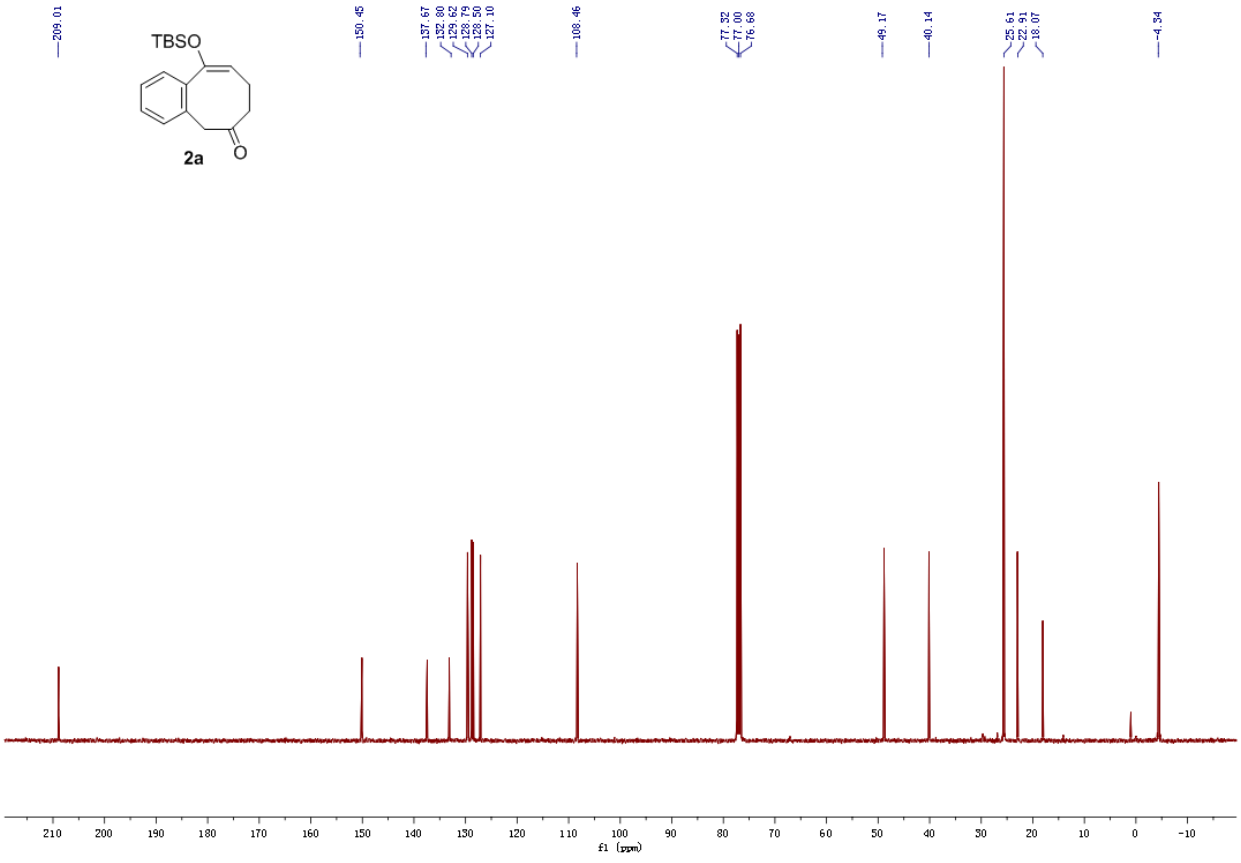

7.35
7.33
7.31
7.27
7.27
7.26
7.25
7.23
7.23
7.21
3.82
1.99
1.98
1.97
1.96
1.95
1.94
1.93
1.05
1.04
1.03
1.02
1.01
0.86
0.85
0.84
0.83
0.82
0.81
O
3a
2.00
3.02
2.02
1.00
2.01
2.04
f1 (ppm)

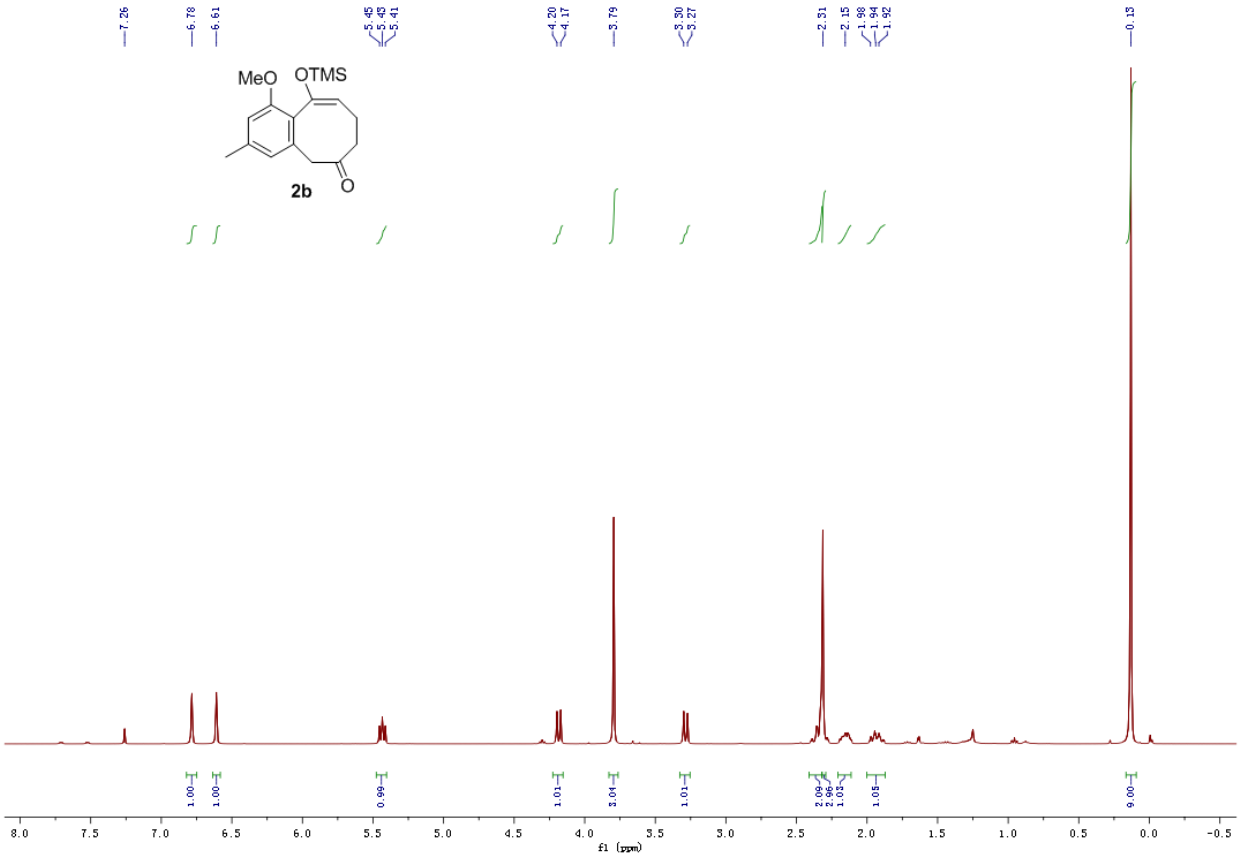

208.40
134.48
129.54
128.69
126.92
50.72
20.09
11.34
O
3a
f1 (ppm)

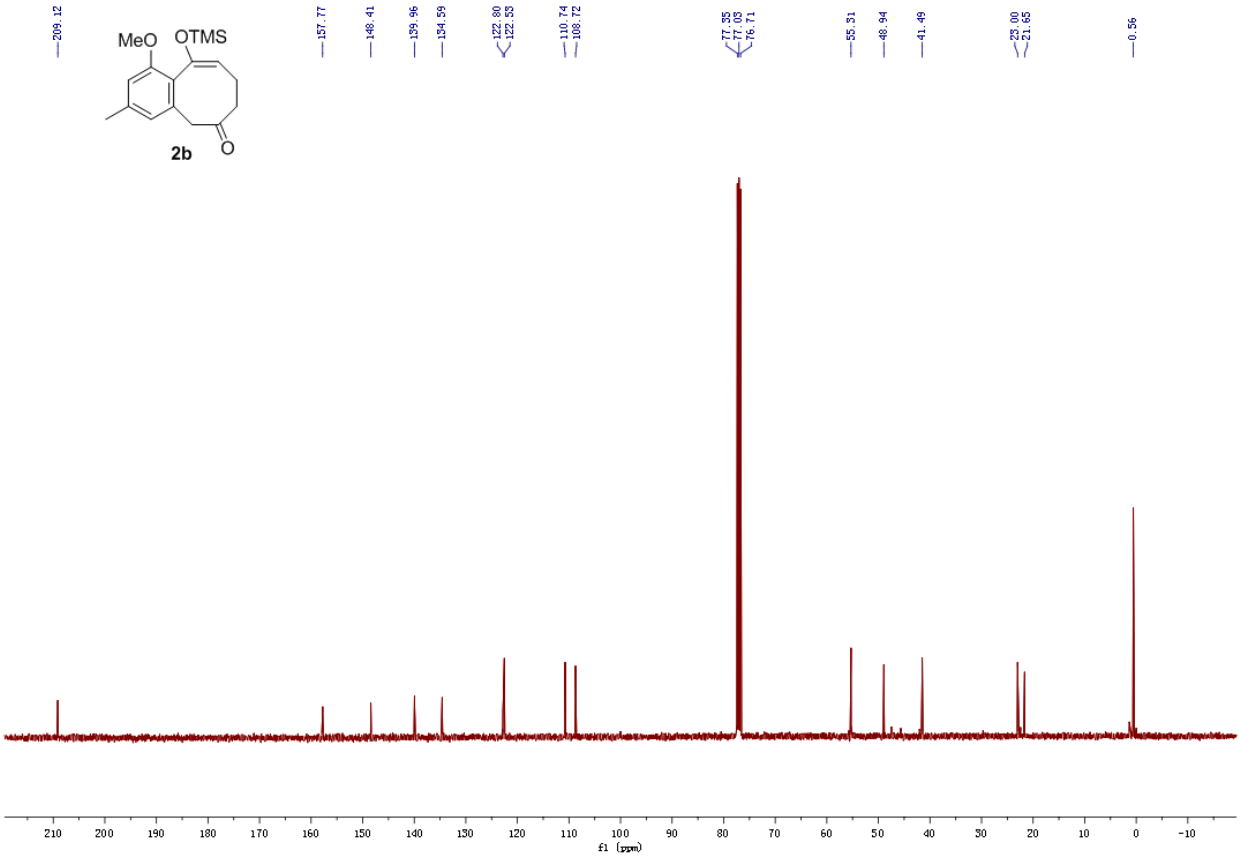

7.71
7.71
7.69
7.69
7.37
7.37
7.35
7.35
7.34
7.33
7.28
7.26
7.26
7.24
7.22
2.48
2.45
2.44
2.43
2.43
2.42
2.42
2.41
2.40
2.39
1.26
1.25
1.24
1.23
1.22
1.05
1.04
1.04
1.03
1.02
1.01
O
5a
1.00
1.00
2.09
3.08
1.08
2.24
2.05
f1 (ppm)

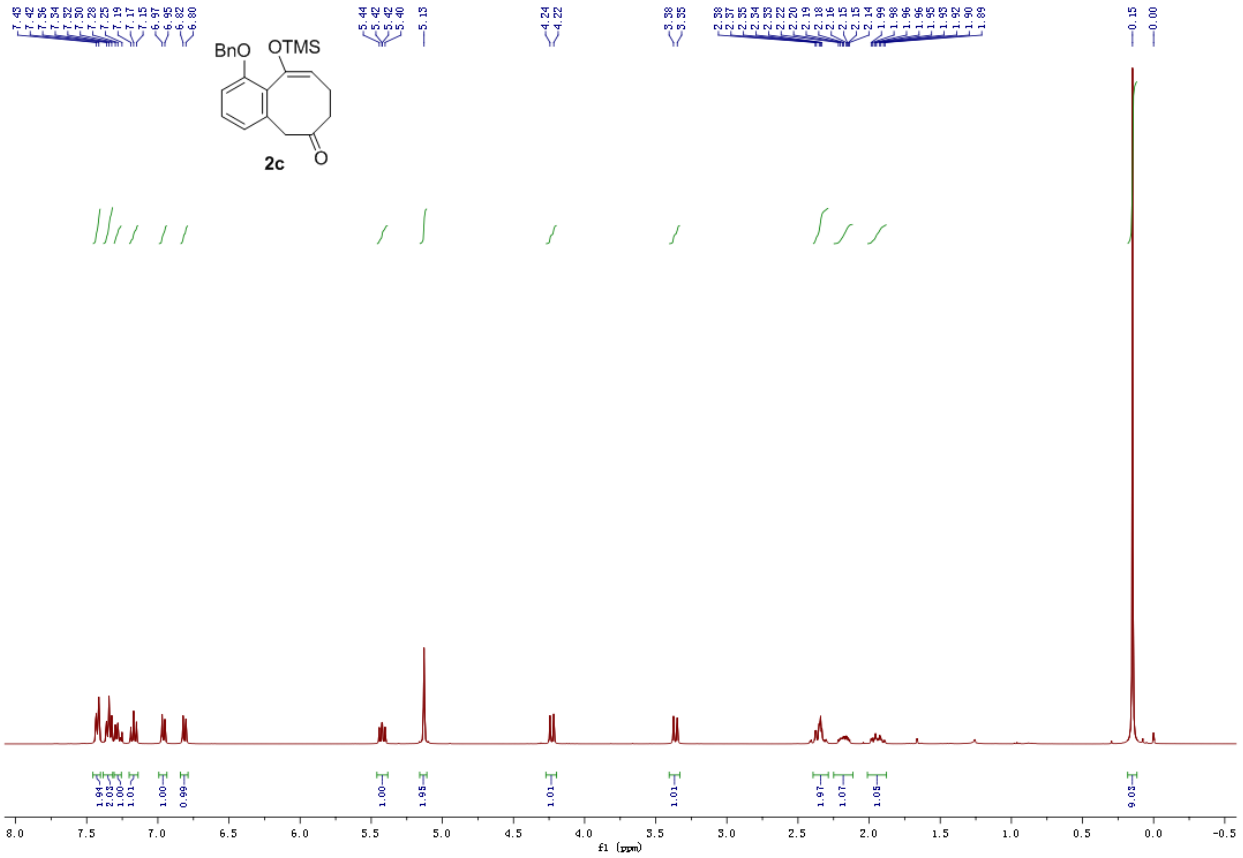

205.00
159.69
136.79
131.39
130.71
129.22
125.55
20.68
20.66
11.87
O
5a
f1 (ppm)

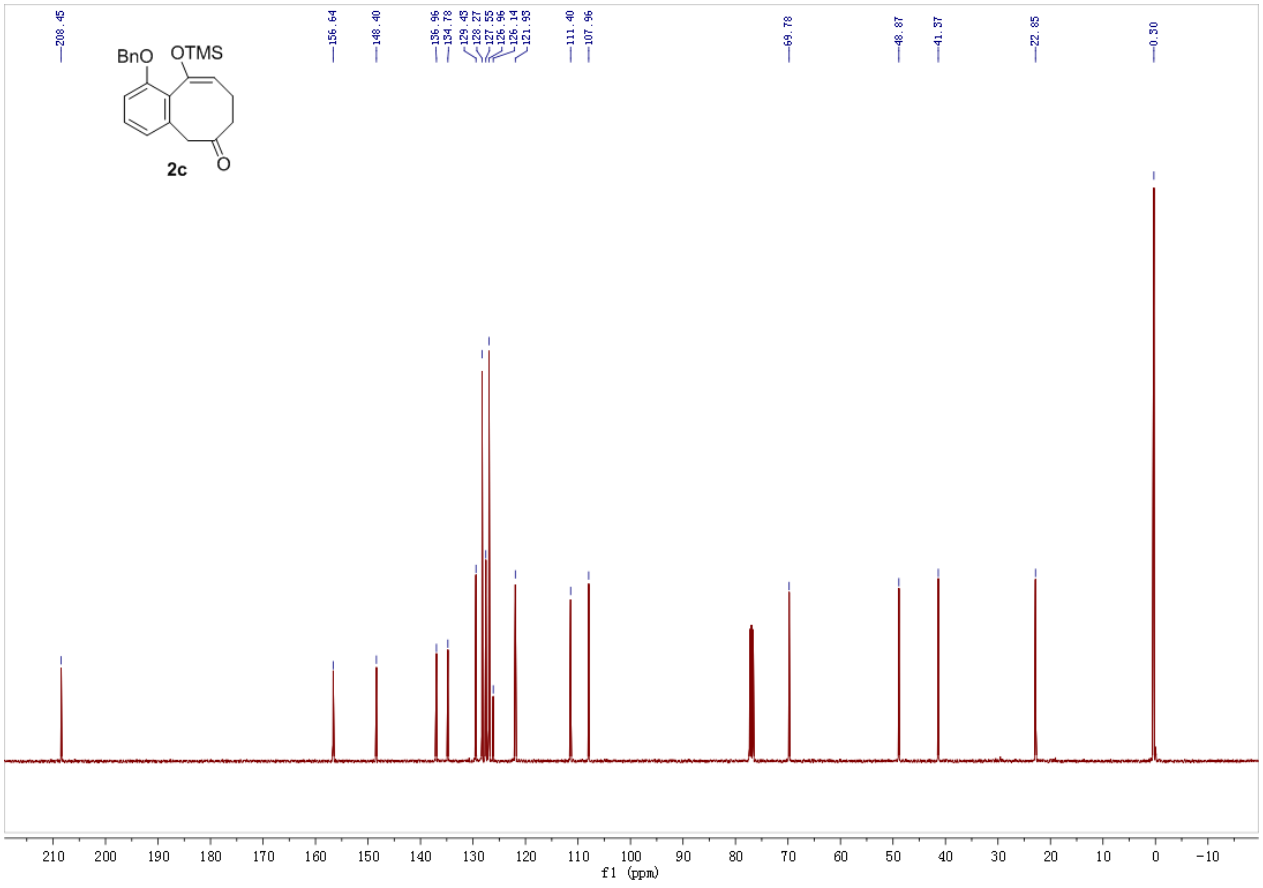

TBSO
O
2a
f1 (ppm)

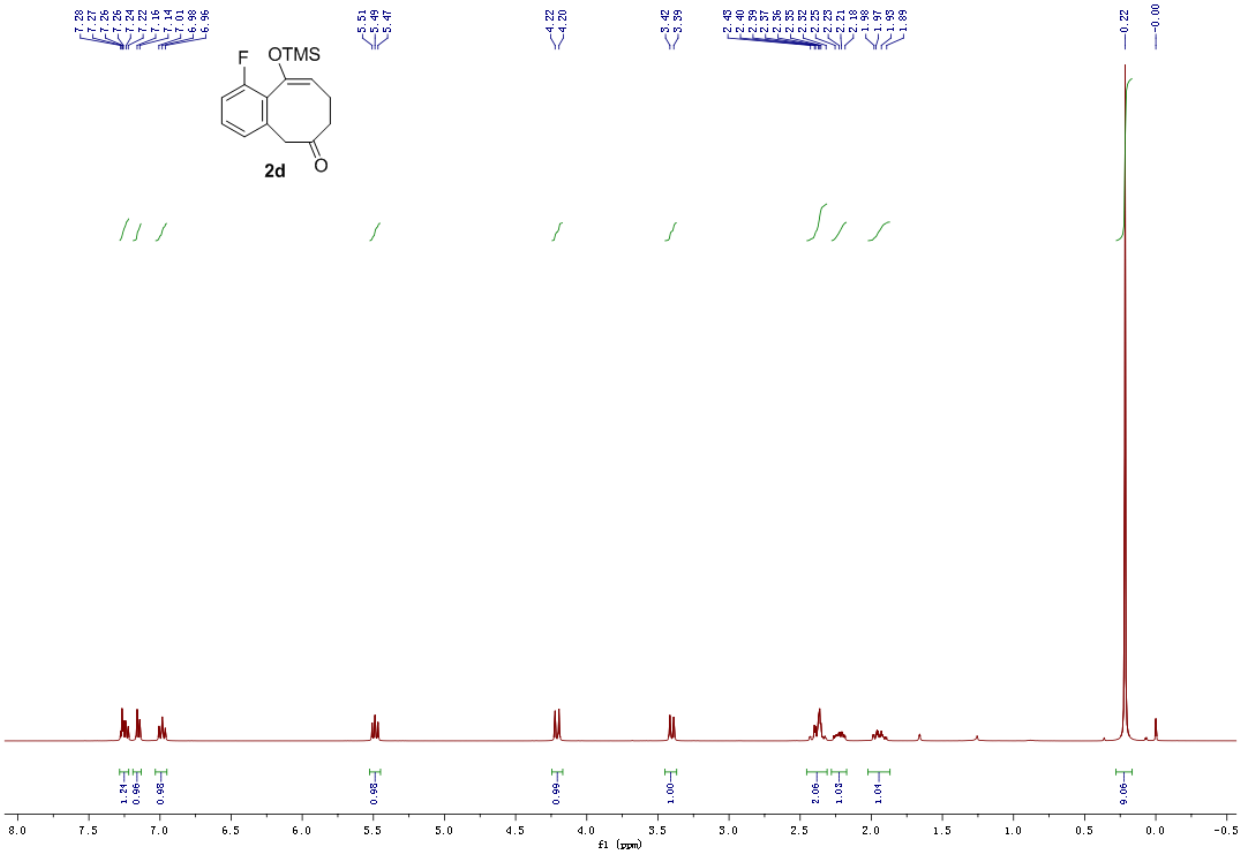

TBSO
O
2a
f1 (ppm)

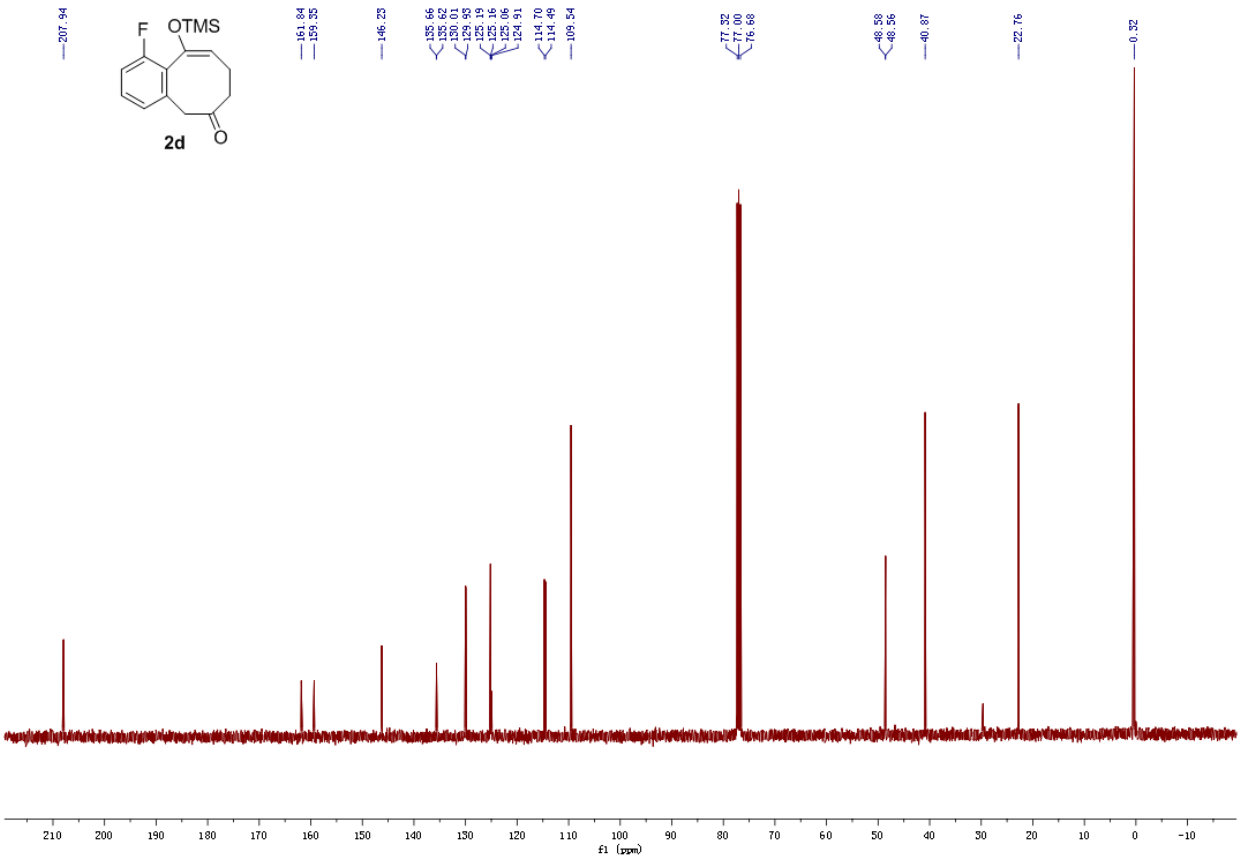

7.26
6.78
6.61
5.45
5.43
5.41
4.20
4.17
3.79
3.50
3.27
2.31
2.15
1.98
1.94
1.92
0.13
MeO
OTMS
O
2b
1.00
1.00
0.99
1.01
3.04
1.01
2.04
2.05
1.04
1.08
9.00
f1 (ppm)

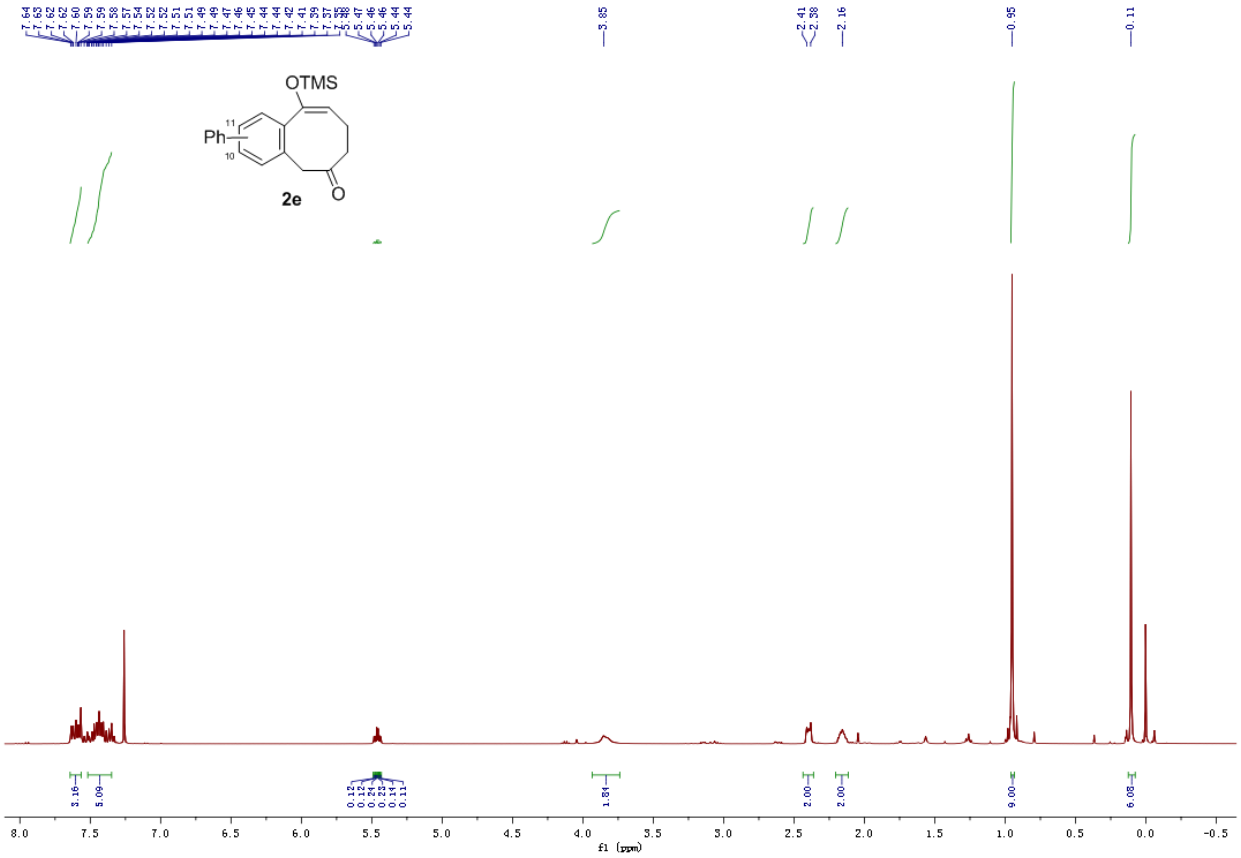

209.12
157.77
146.41
139.96
134.59
122.80
122.53
110.74
108.72
77.35
77.03
76.71
55.31
48.94
41.49
28.00
21.65
0.56
MeO
OTMS
O
2b
f1 (ppm)

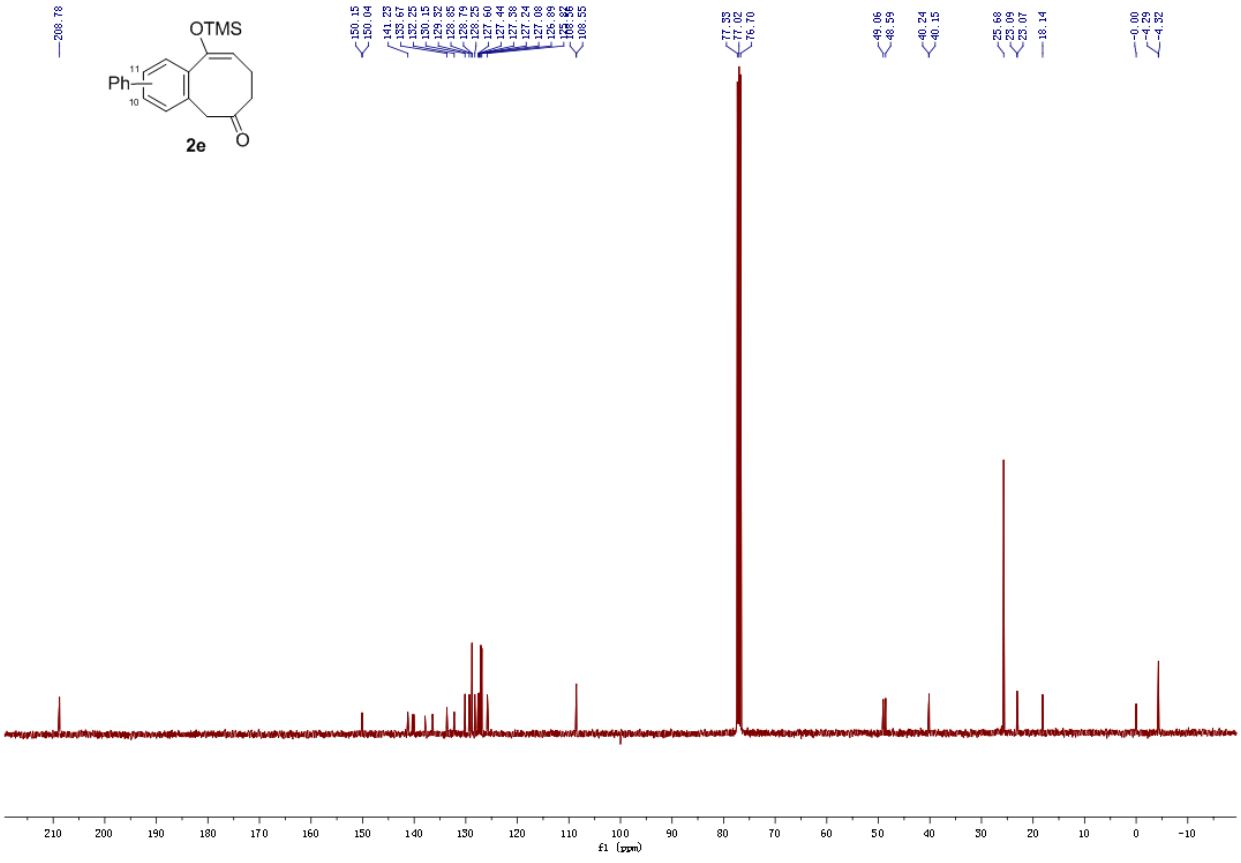

BnO
OTMS
O
2c
f1 (ppm)

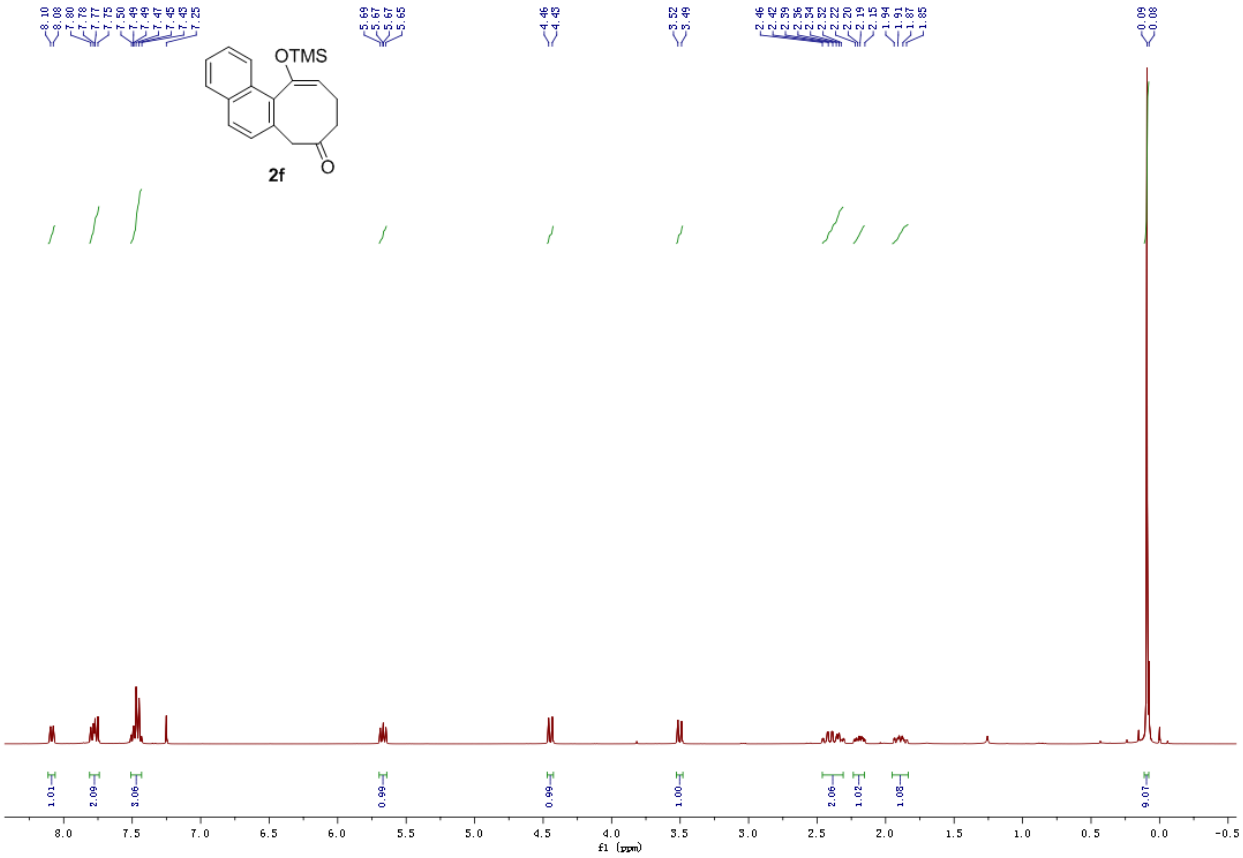

BnO
OTMS
O
2c
f1 (ppm)

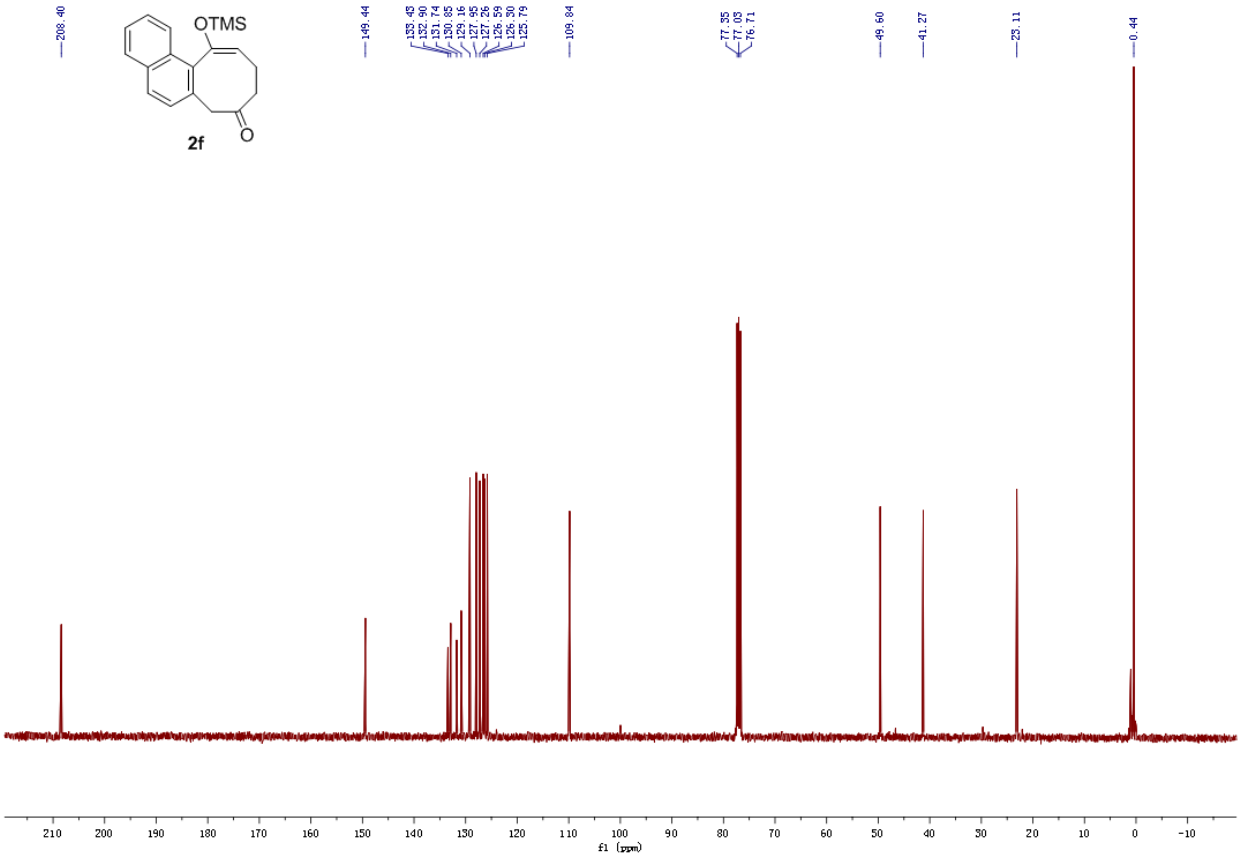

F
OTMS
O
2d
7.28
7.27
7.26
7.25
7.24
7.22
7.16
7.14
7.01
6.98
6.96
5.51
5.49
5.47
4.22
4.20
3.42
3.39
2.43
2.40
2.39
2.37
2.36
2.35
2.32
2.25
2.23
2.21
2.18
1.98
1.97
1.93
1.89
0.22
0.00
1.24
0.96
0.98
0.98
0.99
1.00
2.06
1.05
1.04
9.06
f1 (ppm)

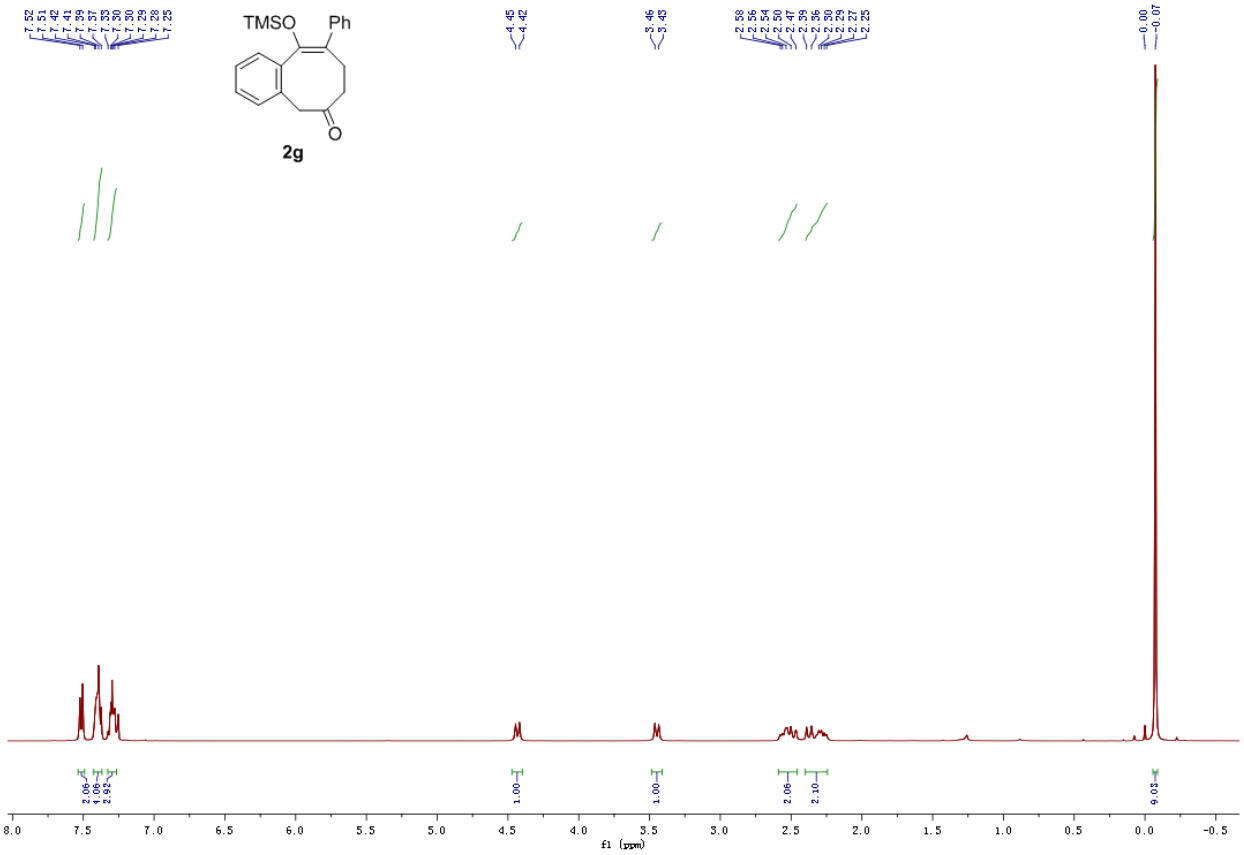

F
OTMS
O
2d
207.94
161.84
159.35
146.23
135.66
135.62
130.01
129.95
125.19
125.16
125.06
124.91
114.70
114.49
109.54
77.32
77.00
76.68
48.58
48.56
40.87
22.76
0.32
f1 (ppm)

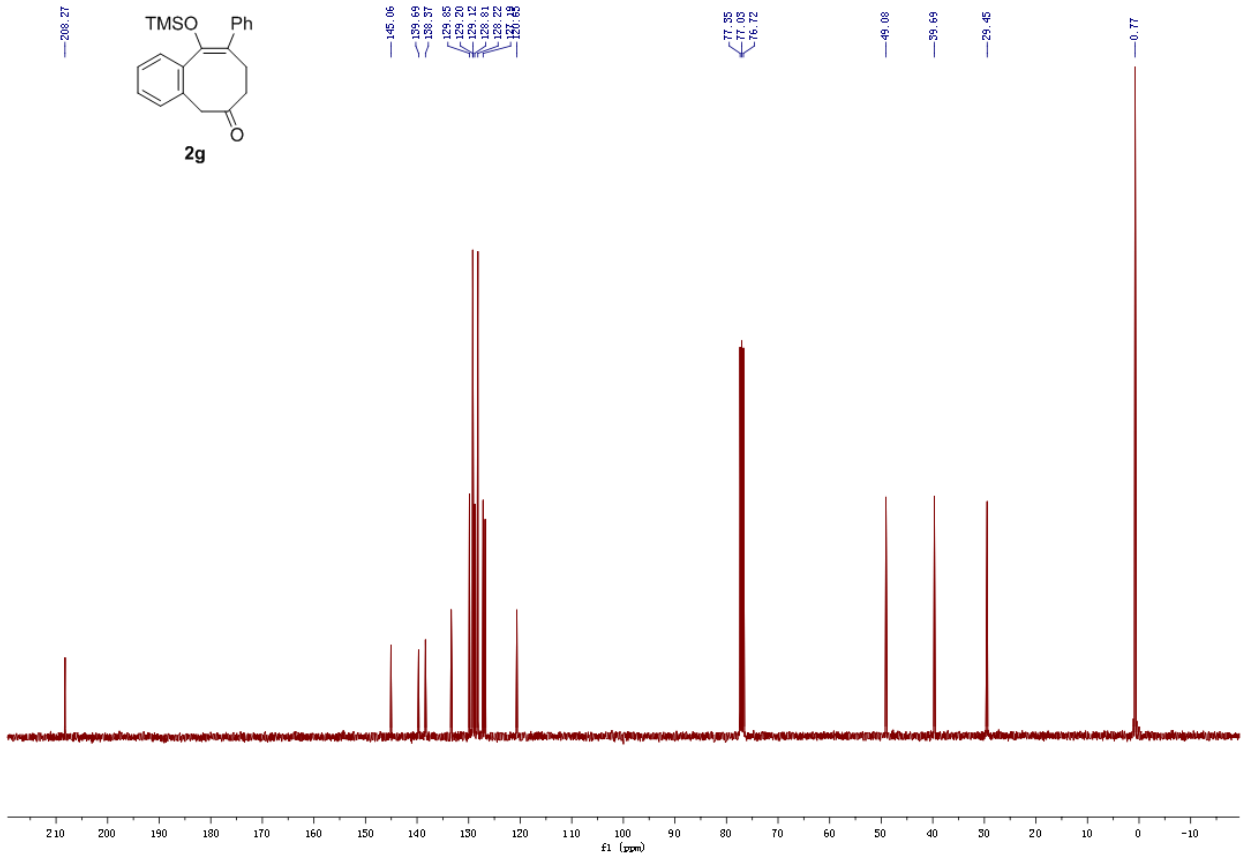

OTMS
Ph
11
10
O
2e
f1 (ppm)

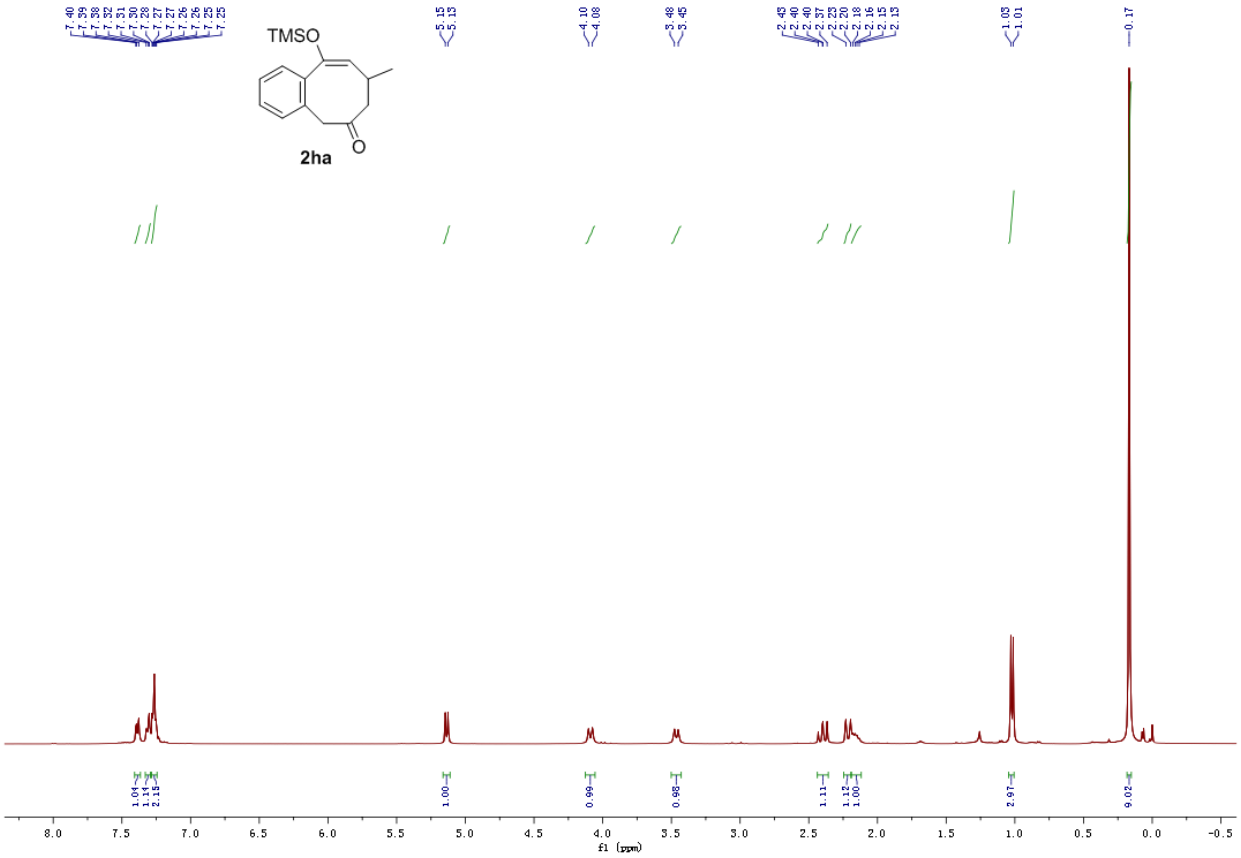

OTMS
Ph
11
10
O
2e
f1 (ppm)

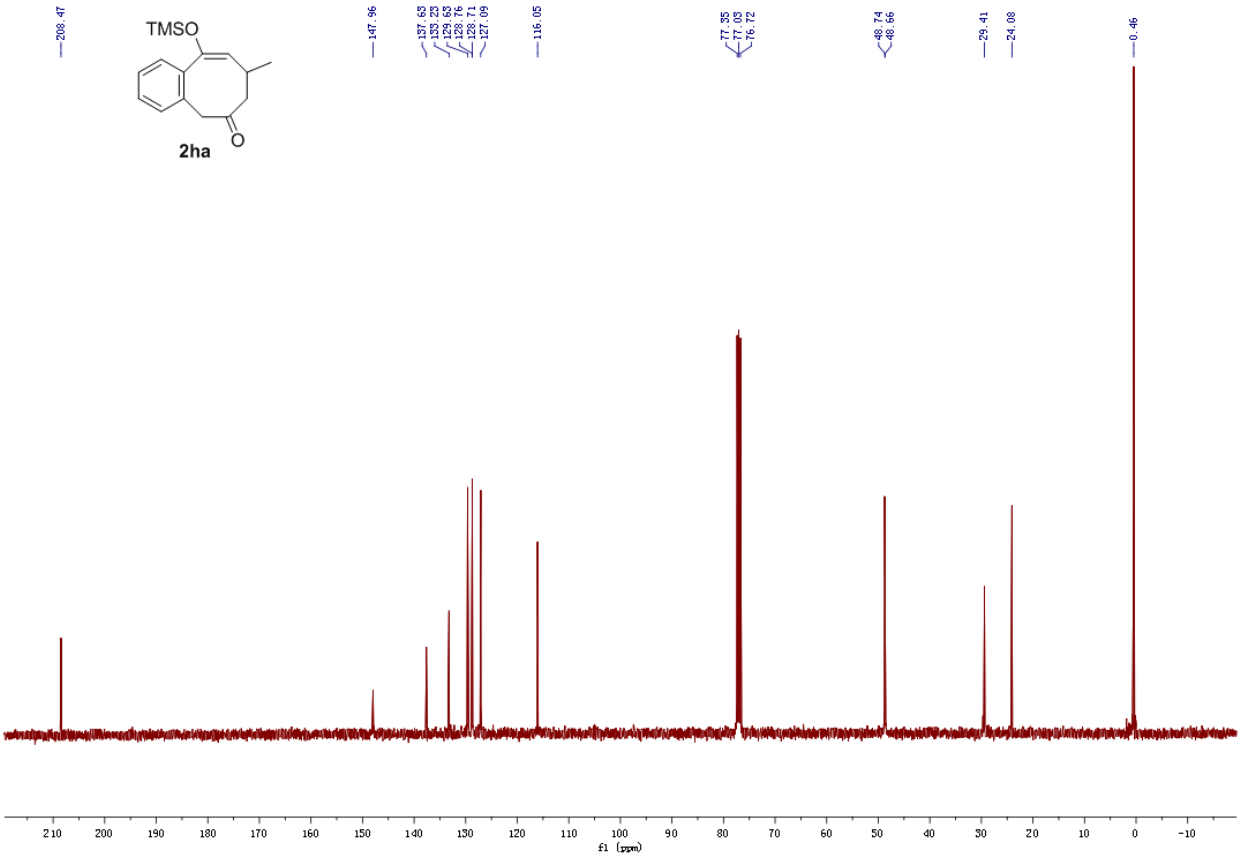

OTMS
O
2f
8.10
8.08
7.80
7.78
7.77
7.75
7.50
7.49
7.49
7.47
7.47
7.45
7.43
7.25
5.69
5.67
5.67
5.65
4.46
4.43
3.52
3.49
2.46
2.42
2.39
2.36
2.34
2.32
2.22
2.20
2.19
2.15
1.94
1.91
1.87
1.85
0.09
0.08
1.01
2.09
3.06
0.99
0.99
1.00
2.06
1.02
1.08
9.07
f1 (ppm)

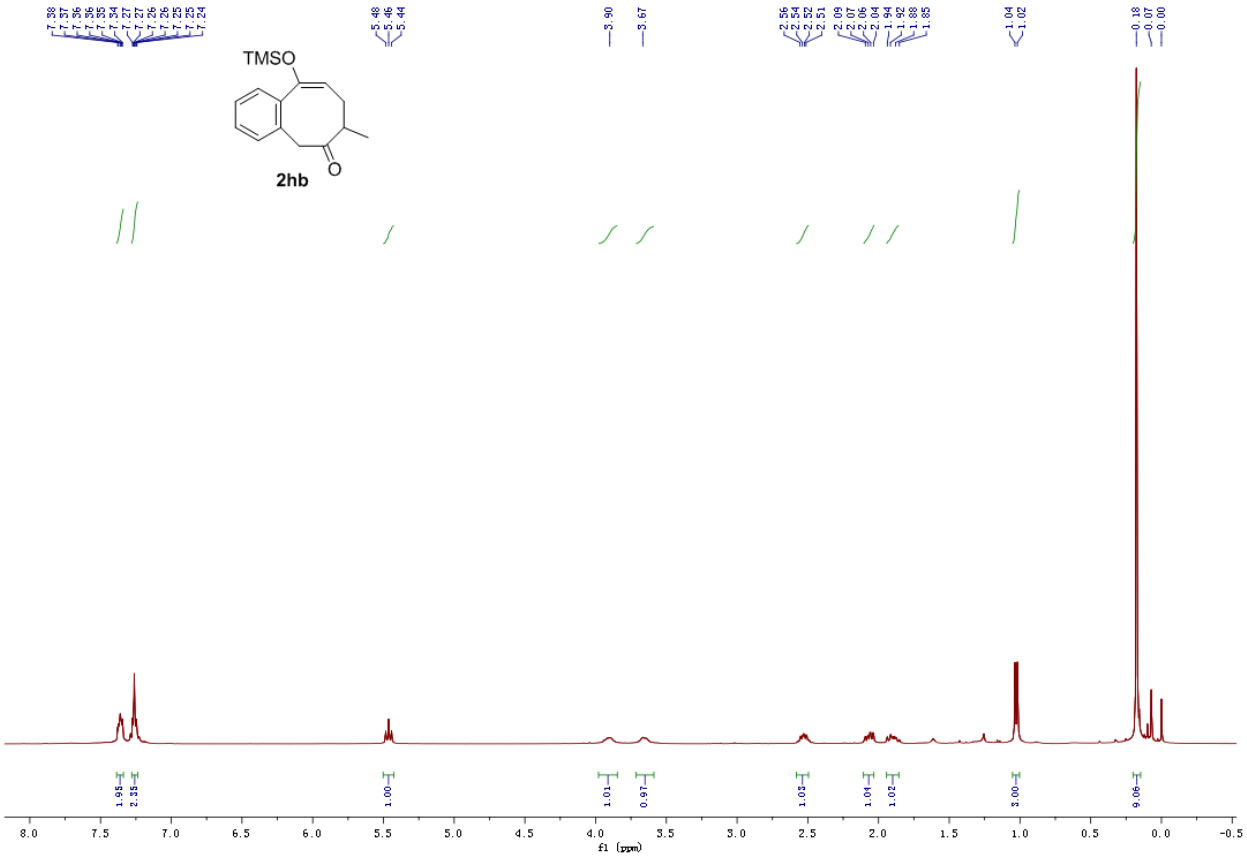

OTMS
O
2f
208.40
149.44
133.43
132.90
131.74
130.85
129.16
127.95
127.26
126.59
126.30
125.79
109.84
77.35
77.03
76.71
49.60
41.27
23.11
0.44
f1 (ppm)

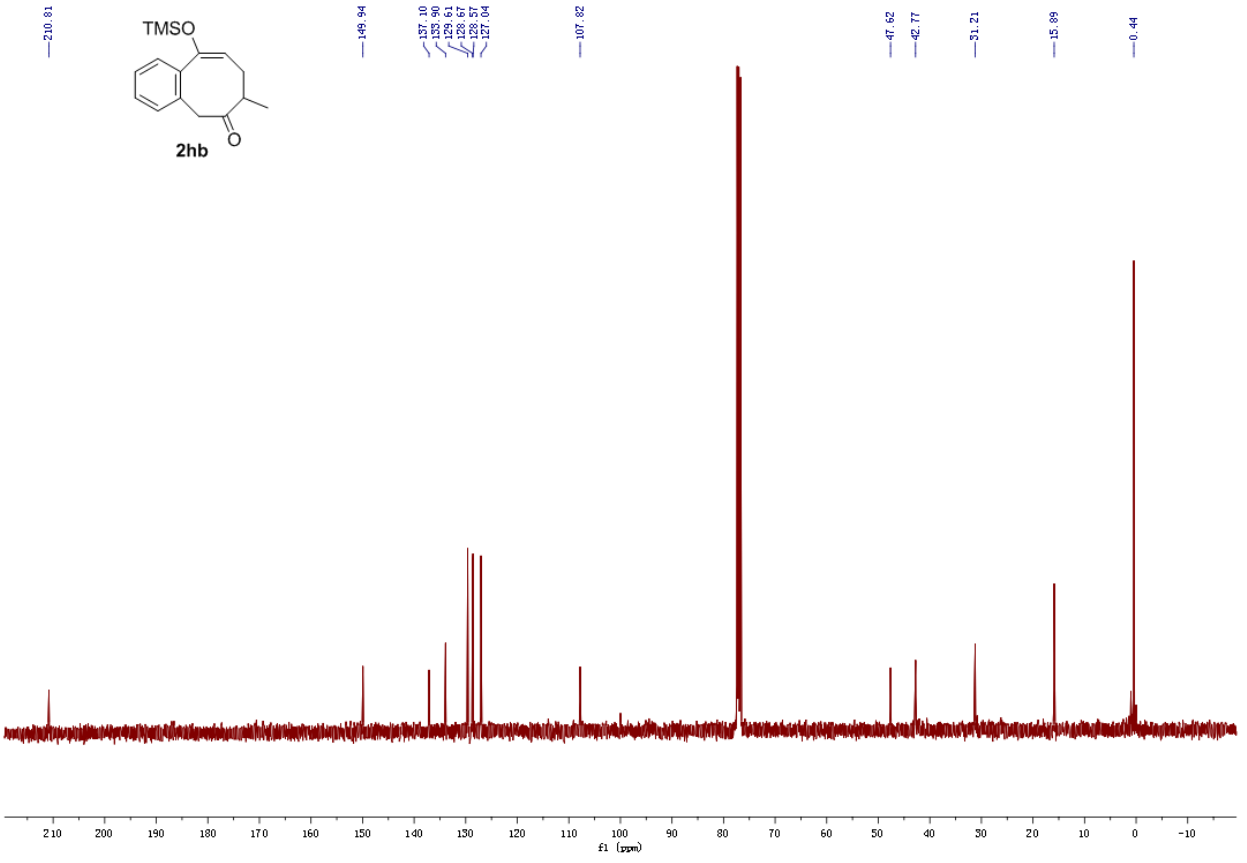

TMSO
Ph
O
2g
f1 (ppm)

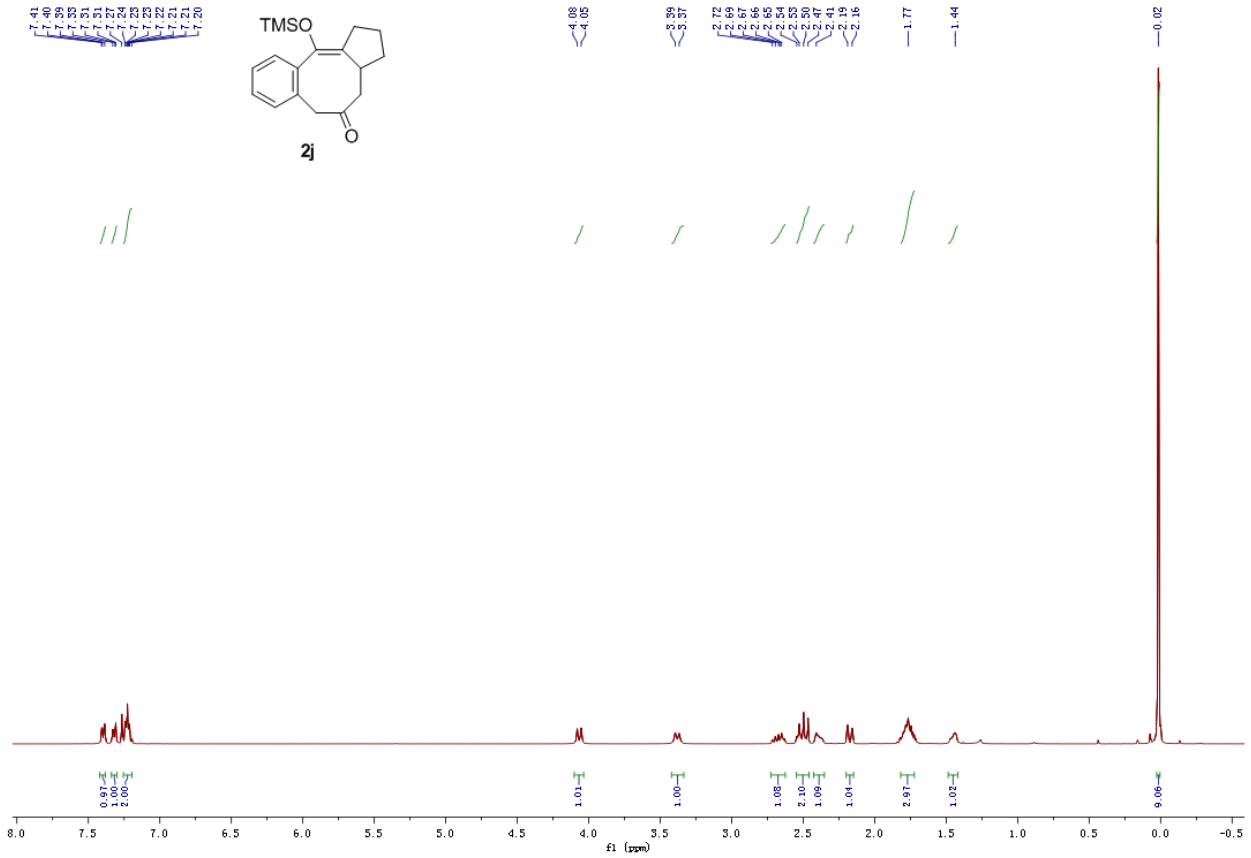

TMSO
Ph
O
2g
f1 (ppm)


TMSO
O
2ha
f1 (ppm)


TMSO
O
2ha
f1 (ppm)


TMSO
O
2hb
7.38
7.37
7.36
7.36
7.35
7.34
7.27
7.27
7.26
7.26
7.26
7.25
7.25
7.24
5.48
5.46
5.44
3.90
3.67
2.56
2.54
2.52
2.51
2.09
2.07
2.06
2.04
1.94
1.92
1.88
1.85
1.04
1.02
0.18
0.07
0.00
1.95
2.35
1.00
1.01
0.97
1.05
1.04
1.05
3.00
9.06
f1 (ppm)


TMSO
O
2hb
210.81
149.94
137.10
135.90
129.61
128.67
128.57
127.04
107.82
47.62
42.77
31.21
15.89
0.44
f1 (ppm)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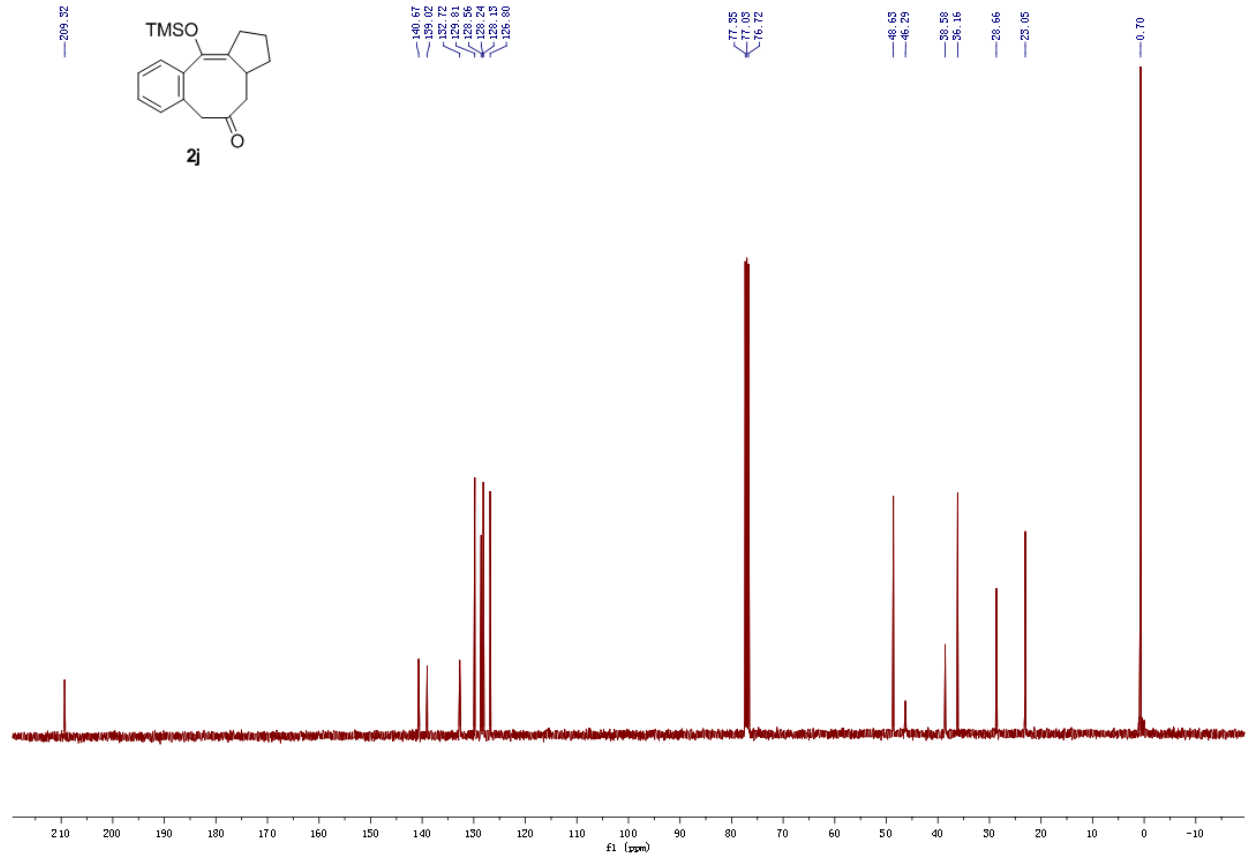
2j
f1 (ppm)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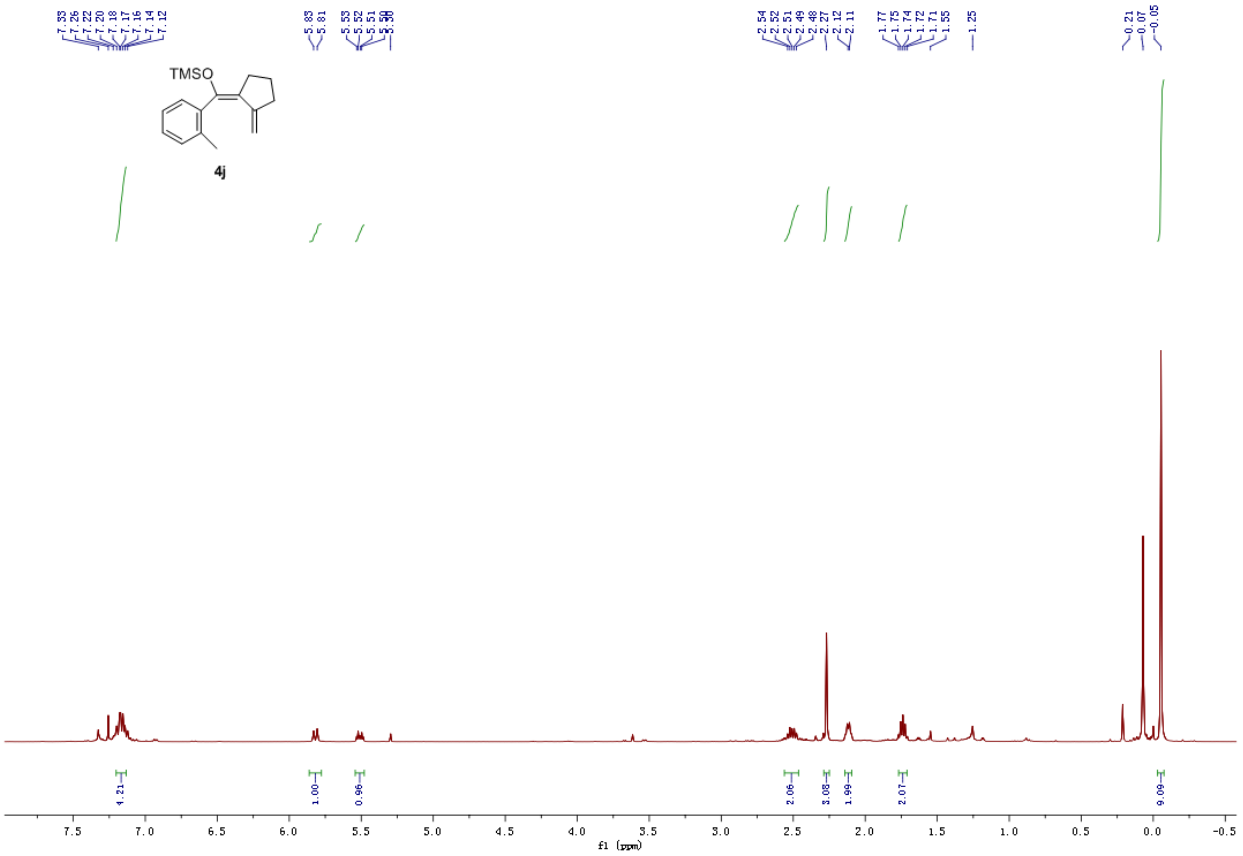
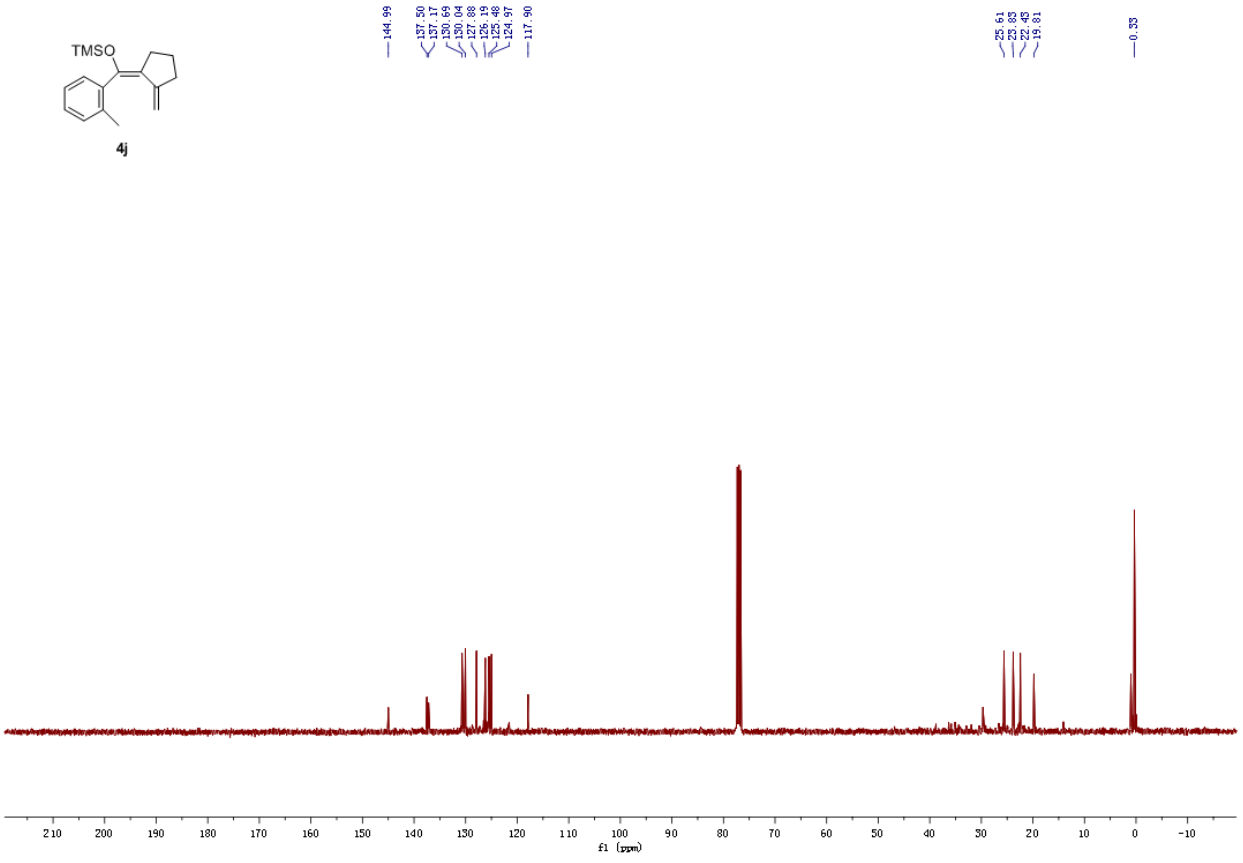
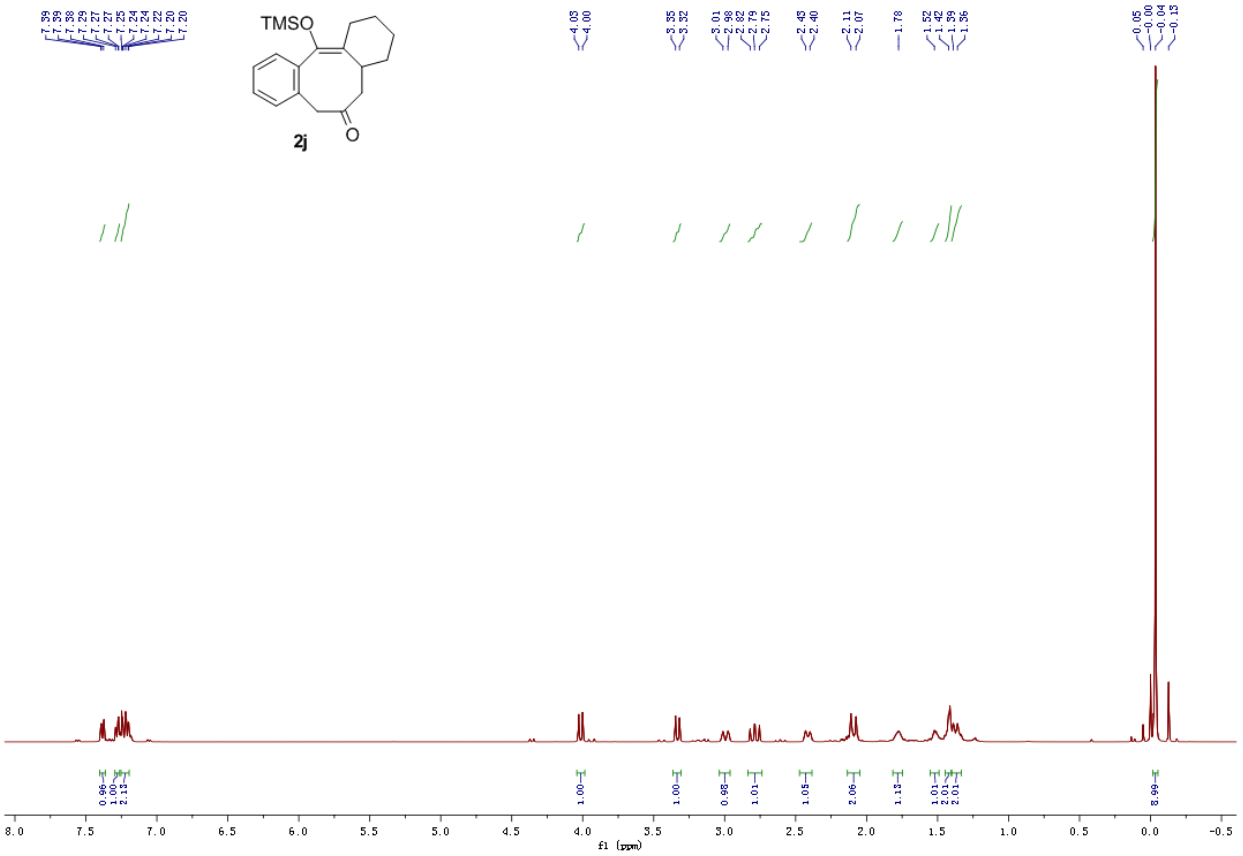
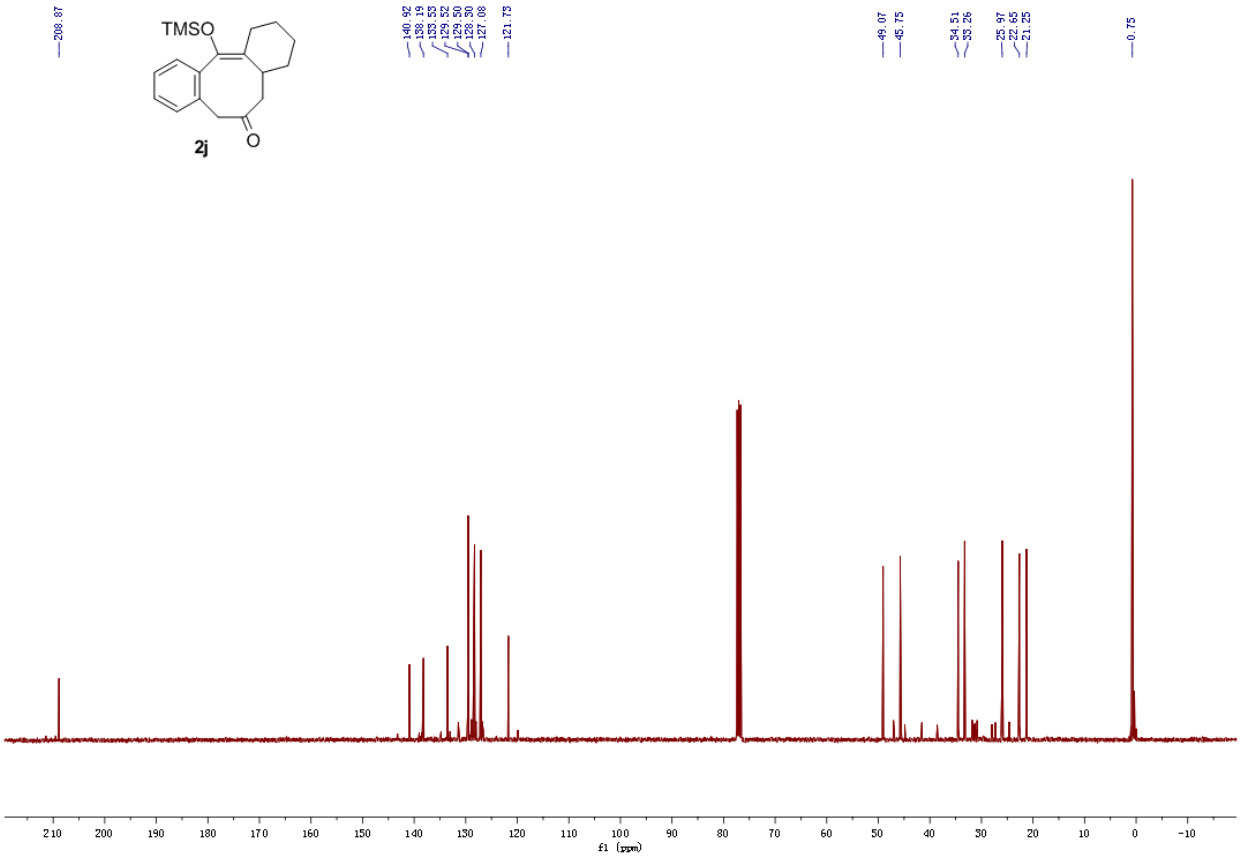
O
2j
f1 (ppm)


7.33
7.25
7.22
7.20
7.18
7.17
7.16
7.14
7.12
5.83
5.81
5.53
5.52
5.51
5.50
2.54
2.52
2.51
2.49
2.48
2.27
2.12
2.11
1.77
1.75
1.74
1.72
1.71
1.55
1.25
0.21
0.07
-0.05
TMSO
4j
4.21
1.00
0.96
2.06
3.08
1.99
2.07
9.09
f1 (ppm)


144.99
137.50
137.17
130.69
130.04
127.88
126.19
125.46
124.97
117.90
25.61
23.83
22.45
19.81
0.33
TMSO
4j
f1 (ppm)


TMSO
O
2j
f1 (ppm)


TMSO
O
2j
f1 (ppm)