Electronic Supplementary Material (ESI) for Chemical Communications.

Table of Contents

1. General Experimental Procedure

All reactions were carried out under argon atmosphere with dehydrated solvents under anhydrous conditions, unless otherwise noted. Dehydrated solvent was purchased from Kanto Chemical Co., Inc. Reagents were obtained from commercial suppliers and used without further purification, unless otherwise noted. Reactions were monitored by thin-layer chromatography (TLC) carried out on silica gel plates (Merck Kieselgel $60F_{254}$). Column chromatography was performed on Silica gel 60N (Kanto Chemical Co., Inc., spherical, neutral, 63-210 μm) and flash column chromatography was performed on Silica gel 60N (Kanto Chemical Co., Inc., spherical, neutral, 40-50 μm). Infrared spectra were obtained on a JASCO FT/IR-460Plus spectrometer. Only the strongest and/or structurally important absorption are reported as the IR data afforded in cm^{-1}.

^{1}H NMR spectra, ^{13}C NMR, and ^{31}P NMR were recorded by using a JEOL ECX 400 or a JEOL ECX 500 spectrometer. The chemical shifts (δ) of ^{1}H NMR are given from TMS (0.00 ppm) in $CDCl_3$ or THF-d_8 (3.58 ppm and 1.57 ppm for ^{1}H), as an internal reference. Coupling constant (*J*) is reported in hertz. Multiplicities are reported by using the following abbreviations: s, singlet; d, doublet; t, triplet; q, quartet; br, broad. The chemical shifts (δ) of ^{13}C NMR are given from $CDCl_3$ (77.0 ppm) as an internal reference. ^{31}P NMR spectra were recorded with 85% H_3PO_4 (0 ppm) as an external standard.

Mass spectra were recorded on a JEOL JMS-GCmate Ⅱ or a JEOL JMS-AX 505 HAD. Reaction temperature (20-25 °C) was kept with PSL-1810 (EYELA).

Trimethylphosphine (1.0 M THF solution) was purchased from Sigma-Aldrich.

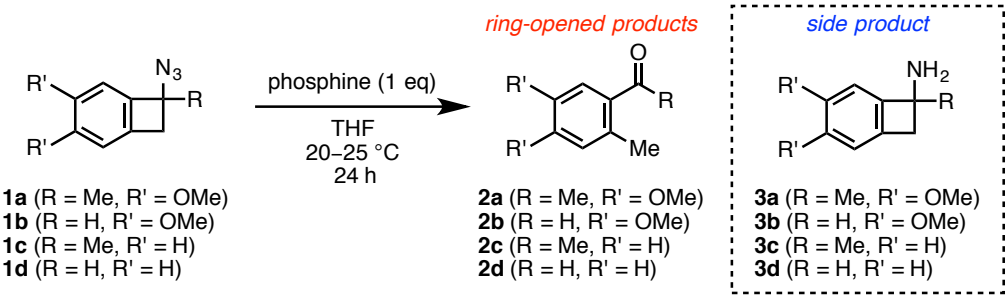
2. Experimental Procedure of 4π Ring Opening of Benzocyclobutenes (Table 1)

General Procedure A: To a solution of azide BCB **1** (**1a**: 0.125 mmol, **1b**: 0.254 mmol) in THF/H_2O (10/1, 0.25-0.33 M), phosphine[*1] (1.0 eq) was added at room temperature (20-25 °C). After 24 h, the mixture was concentrated. Yields (**2a**, **3a**) were determined by qNMR with 1,2,4,5-tetrachlorobenzene as an internal standard. The ^{1}H NMR spectra of **2a**[1] and **2b**[2] were identical with reported data.

General Procedure B: To a solution of azide BCB **1** (0.124-0.152 mmol) in THF (0.33 M), phosphine[*1] (1 eq) was added at room temperature (20-25 °C). After 24 h, the mixture was quenched with sat. NH_4Cl aq. (1.0-1.2 mL) and stirred for 1 h at room temperature. The resulting mixture was extracted with MeOH/$CHCl_3$ (1/9) or Et_2O. The combined organic layers were dried over $MgSO_4$, filtered and concentrated. Yields (**2c**, **2d**) were determined by qNMR with 1,2,4,5-tetrachlorobenzene as an internal standard.
2a, **2b**: The residue was purified by flash silica gel column chromatography (Hexane/EtOAc = 17/3 to 4/1) to afford ketone **2a** or aldehyde **2b** as a white solid. Yields (**2a**, **2b**) were determined by qNMR with 1,2,4,5-tetrachlorobenzene as an internal standard.

[*1] PMe_3: Trimethyl phosphine (1.0 M THF solution) was used. At the time, THF solvent (0.48 M) was used to adjust total concentration to 0.33 M.

Table S1



1a (R = Me, R' = OMe)
1b (R = H, R' = OMe)
1c (R = Me, R' = H)
1d (R = H, R' = H)

2a (R = Me, R' = OMe)
2b (R = H, R' = OMe)
2c (R = Me, R' = H)
2d (R = H, R' = H)

3a (R = Me, R' = OMe)
3b (R = H, R' = OMe)
3c (R = Me, R' = H)
3d (R = H, R' = H)

Entry	Substrate	R	R'	phosphine	H_2O (%v/v)	Yield (%)	Procedure
1	**1a**	Me	OMe	–	–	0[a]	–
2	**1a**	Me	OMe	PPh_3	–	7 (**2a**)	**B**
3	**1a**	Me	OMe	PMe_3	–	71 (**2a**)	**B**
4	**1a**	Me	OMe	PMe_3	10	99 (**3a**)	**A**
5	**1b**	H	OMe	–	–	0[c]	–
6	**1b**	H	OMe	PPh_3	–	43 (**2b**)	**B**
7	**1b**	H	OMe	PMe_3	–	8 (**2b**)	**B**
8	**1b**	H	OMe	PPh_3	10	0[b]	**A**
9	**1c**	Me	H	PMe_3	–	48 (**2c**)	**B**
10	**1d**	H	H	PPh_3	–	3 (**2d**)	**B**

[a] No reaction. [b]Complex mixture.

3 Experimental Details of Mechanistic Study -NMR Monitoring Experiments-

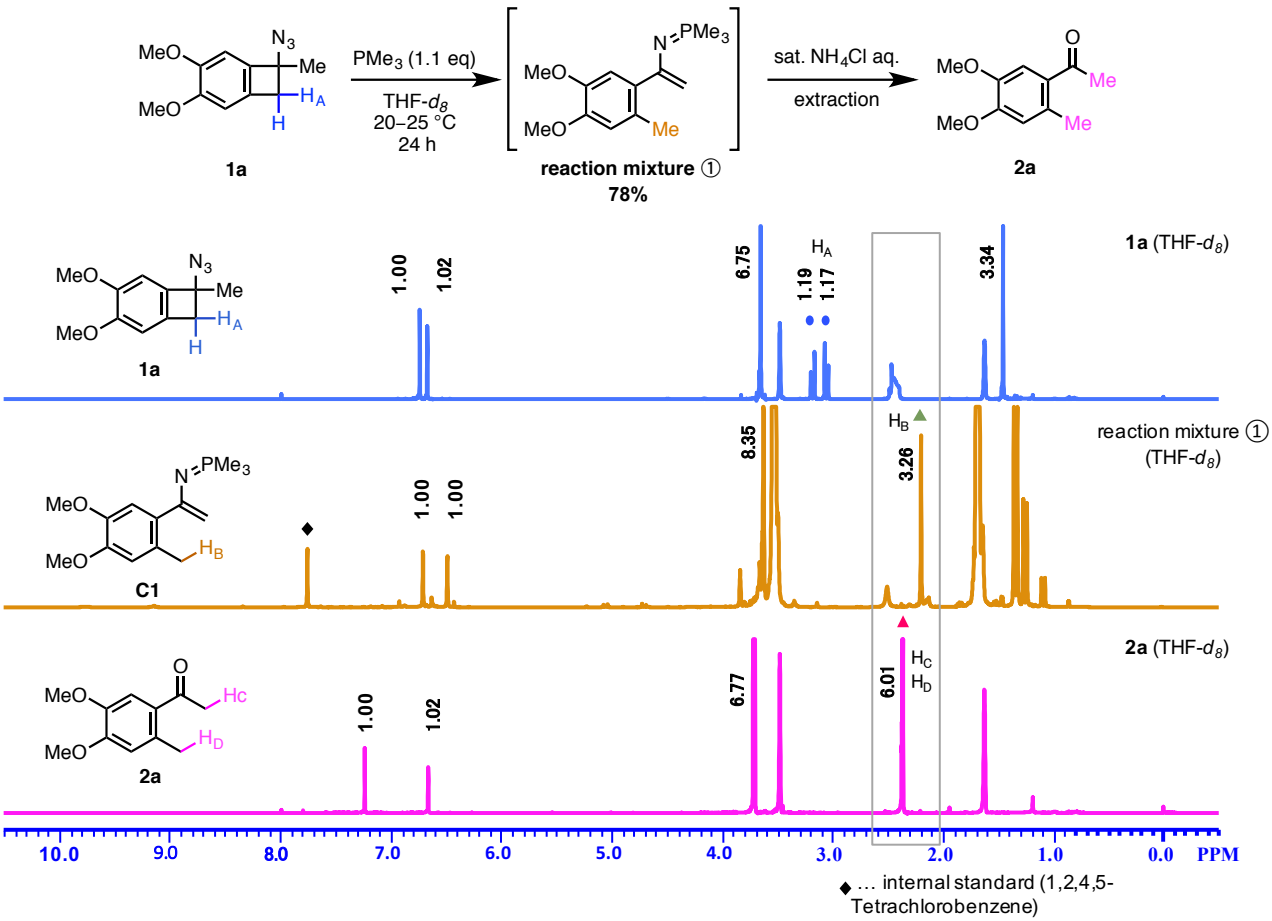


Figure S1

reaction mixture ①: To a solution of azide BCB **1a** (14.2 mg, 0.0648 mmol) in THF-d_8 (60 µL), trimethyl phosphine (1.0 M THF solution, 72 µL, 0.072 mmol) was added at room temperature (20-25 °C). After 24 h, the mixture was diluted with THF-d_8 and analyzed by ^{1}H NMR (400 MHz, THF-d_8). Yield was determined by qNMR with as an internal standard with 1,2,4,5-tetrachlorobenzene.

Note: reaction mixture ①;

- Alkene signals (2H) of enamine appeared to overlap with other signals in 3.5-3.9 ppm.
- Trimethylphosphorane signals (N=PMe$_3$, 9H) appeared in 1.4 ppm.
- Signals of trimethylphosphine oxide (O=PMe$_3$) which was generated by Staudinger reaction appeared in 1.3 ppm.

Experiment to confirm the ^{1}H-NMR spectra of enamine C1

The ^{1}H-NMR spectra of the intermediate from azide BCB **1a** and PMe_3 (the reaction mixture ①) agreed with the ^{1}H-NMR spectra of iminophosphorane from vinyl azide **S18** and PMe_3 (reaction mixture ②).

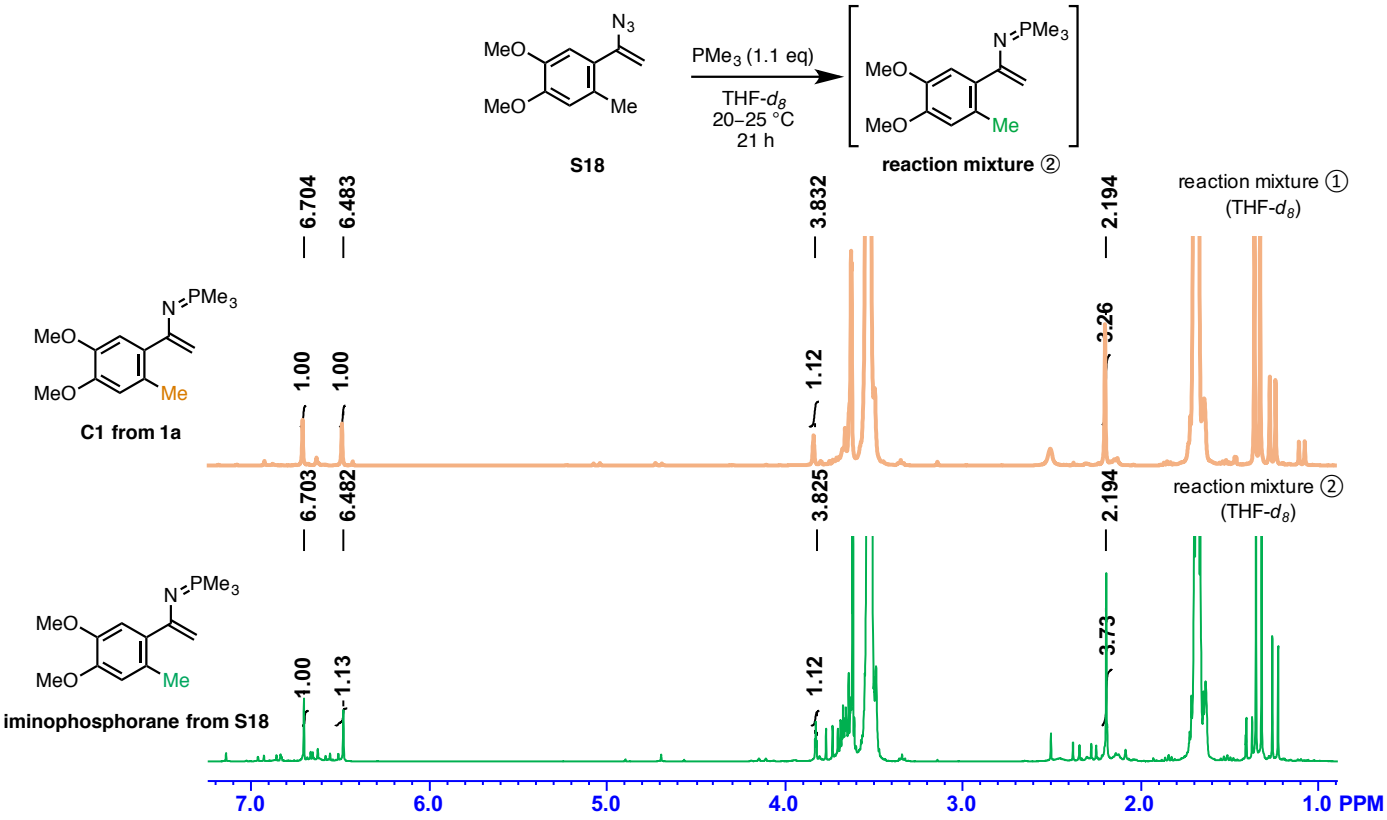


Figure S2

reaction mixture ②: To a solution of vinyl azide **18S** (15.2 mg, 0.0693 mmol) in THF-d_8 (62 µL), trimethyl phosphine (1.0 M THF solution, 76 µL, 0.076 mmol) was added at room temperature (20-25 °C). After 21 h, the mixture was diluted with THF-d_8 and analyzed by ^{1}H NMR (400 MHz, THF-d_8).

Comparison of the chemical shift of vinyl proton

S2
6.06 and 4.69 ppm
(our data)

S18
5.03 and 4.71 ppm
(our data)

4.16 and 4.07 ppm
(reported data: Org. Lett. 2009, 11, 4612.)

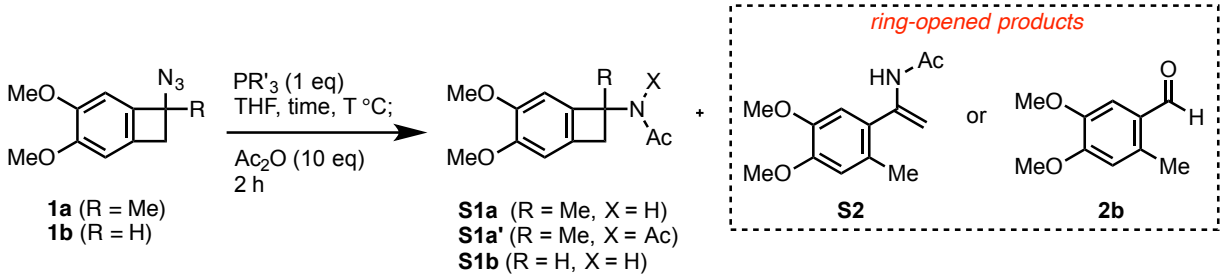
intermediate **C**
3.90 and 3.70 ppm
(our data)

4. Experimental Details of Mechanistic Study -Trapping Experiments-

4-1. Trap by Ac_2O and Lower Limit of Reaction Temperature for the Ring-opening

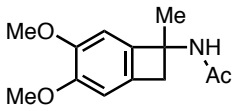
General Procedure C: To a solution of azide BCB **1a** or **1b** (0.124-0.127 mmol) in THF (0.33 M), phosphine (1 eq) was added. After 24 h, Ac_2O (10 eq) was added to the reaction mixture. After being stirred for 2 h, the mixture was concentrated. The resulting residue was purified by flash silica gel column chromatography (**S1a**: Hexane/AcOEt = 4/1 to 7/3, **S1a'**: CH_2Cl_2/EtOAc = 13/7 to 1/1, **S2**: Hexane/AcOEt = 7/3 to 3/2).

Table S2



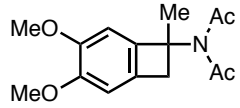
Entry	Substrate	R	PR'_3	T °C	Time (h)	Yield (%)	
						BCBs	ring-opened products
1	**1a**	Me	PMe_3	0 °C	24	58 (**S1a** + **S1a'**)	23 (**S2**)
2	**1a**	Me	PMe_3	–78 to –50 °C	28.5	76 (**S1a**)	0
3	**1b**	H	PPh_3	0 °C	24	27 (**S1b**)	23 (**2b**)
4	**1b**	H	PPh_3	20 to 25 °C	24	0	54 (**2b**)

Amide BCB (S1a)



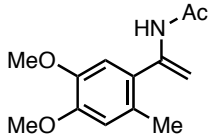
S1a: a yellow solid; R_f = 0.3 (Hexane/AcOEt = 7/3); ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.91 (1H, s), 6.72 (1H, s), 6.10 (1H, brs), 3.86 (3H, s), 3.85 (3H, s), 3.23 (2H, dd, J = 14.6 Hz, 14.6 Hz), 1.96 (3H, s), 1.74 (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.8, 150.9, 149.6, 140.2, 132.4, 107.6, 105.9, 59.7, 56.25, 56.23, 45.0, 24.2, 23.8; IR (neat): 3354, 2927, 1651, 1538, 1482 cm^{-1}; HRMS (FAB) calcd for $C_{13}H_{18}NO_3$ ($M+H^+$): 236.1287, found: 236.1288.

Amide BCB (S1a')



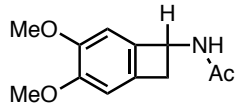
S1a': a yellow oil; R_f = 0.45 (CH_2Cl_2/EtOAc = 1/1); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.07 (1H, s), 6.65 (1H, s), 3.87 (3H, s), 3.85 (3H, s), 3.40 (1H, d, *J* = 13.5 Hz), 3.30 (1H, d, *J* = 13.5 Hz), 2.35 (6H, s), 1.83 (3H, s); IR (neat): 3593, 2935, 1667, 1590, 1481 cm^{-1}; HRMS (FAB) calcd for $C_{15}H_{19}NO_4$ (M^+): 277.1314, found: 277.1395.

Enamine (S2)



S2: a yellow solid; R_f = 0.33 (Hexane/AcOEt = 3/2); ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.75 (1H, s), 6.69 (1H, s), 6.58 (1H, brs), 6.06 (1H, s), 4.69 (1H, s), 3.87 (3H, s), 3.85 (3H, s), 2.29 (3H, s), 2.07 (3H, s); ^{13}C NMR (125 MHz, $CDCl_3$): δ168.6, 148.8, 146.8, 140.1, 130.7, 128.1, 113.3, 112.4, 102.4, 56.05, 55.92, 24.6, 19.1; IR (neat): 3355, 2933, 1667, 1513 cm^{-1}; HRMS (FAB) calcd for $C_{13}H_{18}NO_3$ (M+H^+): 236.1287, found: 236.1287.

Amide BCB (1b)



1b: a yellow solid; R_f = 0.4 (CH_2Cl_2/EtOAc = 1/1); ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.76 (1H, s), 6.70 (1H, s), 6.02 (1H, brs), 5.41 (1H, ddd, *J* = 4.8, 4.8, 1.8 Hz), 3.86 (3H, s), 3.84 (3H, s), 3.63 (1H, dd, *J* = 13.5, 4.8 Hz), 2.89 (1H, dd, *J* = 13.5, 1.8 Hz), 2.02 (3H, s); ^{13}C NMR (125 MHz, $CDCl_3$): δ 169.9, 151.1, 149.9, 136.3, 134.4, 107.1, 106.4, 56.2, 49.5, 39.8, 23.4; IR (neat): 3308, 2925, 1666, 1531, 1488 cm^{-1}; HRMS (FAB) calcd for $C_{12}H_{16}NO_3$ (M+H^+): 222.1130, found: 222.1138.

4-2. Intramoleculer Diels-Alder Trap of OQM Intermediate (Table 2)

Condition A: THF (50 mM), 24 h then H_2O, 20-25 °C, 24 h

To a solution of azide BCB **1** (**1b** or **1c**, ca. *20 mg scale*) in THF was added phosphine **4** (3 eq). After the reaction mixture was stirred at 20-25 °C for 24 h, H_2O (5%v/v) was added to the resulting solution. After being stirred at 20-25 °C for 24 h, the reaction mixture was directly purified by short silica gel column chromatography (**5**: Hexane/CH_2Cl_2 = 3/1 to $CHCl_3$/MeOH/Et_3N = 99/1/0 to 80/20/0.5, **6**: pentane/CH_2Cl_2 = 100/1 to $CHCl_3$/MeOH/Et_3N = 90/10/0 to 85/15/0.5) to separate phosphine **4** from other products containing aminophosphine oxide **5** or **6**. Yields (**5**, **6**) were determined by qNMR with 1,2,4,5-tetrabromobenzene as an internal standard.

Condition B: THF (50 mM), H_2O (5%v/v), 20-25 °C, 24 h

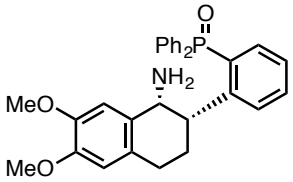
To a solution of azide BCB **1** (**1b** or **1c**, ca. *20 mg scale*) in THF and H_2O (5%v/v) was added phosphine **4**. After the reaction mixture was stirred at 20-25 °C for 24 h, the reaction mixture was directly purified by short silica gel column chromatography (**5**: Hexane/CH_2Cl_2 = 3/1 to $CHCl_3$/MeOH/Et_3N = 99/1/0 to 80/20/0.5, **6**: pentane/CH_2Cl_2 = 100/1 to $CHCl_3$/MeOH/Et_3N = 90/10/0 to 85/15/0.5) to separate phosphine **4** from other products containing aminophosphine oxide **5** or **6**. Yields (**5**, **6**) were determined by qNMR with 1,2,4,5-tetrabromobenzene as an internal standard.

Two diastereomers (*cis*-**5**, *trans*-**5**) could be partially separated by flash column chromatography ($CHCl_3$/MeOH = 1/99 to 1/4). However, *trans*-**5** was purified by repetitive flash column chromatography ($CHCl_3$/MeOH = 1/99 to 1/4).

cis-**5**: upper spot; *trans*-**5**: under spot

Relative configurations were determined by *J*-coupling values (**5** and **6**) and X-ray crystallography (See page **S21**).

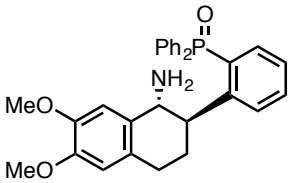
***cis*-Amino phosphine oxide (*cis*-5)**



***cis*-5**

***cis*-5**: a colorless solid; R_f = 0.45 (15% MeOH in $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ 7.70-7.36 (12H, m), 7.19-7.06 (2H, m), 6.64 (1H, s), 6.45 (1H, s), 3.93 (1H, d, *J* = 3.7 Hz), 3.87-3.72 (1H, m), 3.79 (3H, s), 3.78 (3H, s), 2.61 (1H, d, *J* = 16.5 Hz), 2.32-2.15 (2H, m), 1.54 (1H, d, *J* = 11.9 Hz), 1.48 (2H, brs); ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.1, 149.0, 147.6, 147.0, 134.3, 133.7, 133.5, 133.3, 133.2, 132.2, 132.12, 132.10, 132.0, 131.72, 131.70, 131.61, 131.58, 131.51, 131.49, 131.4, 131.3, 131.0, 129.9, 129.8, 128.4, 128.3, 127.8, 125.7, 125.6, 112.1, 110.8, 55.7, 55.6, 51.6, 43.12, 43.06, 29.0, 23.4; ^{31}P NMR (162 MHz, $CDCl_3$) 31.9; IR (KBr): 2932, 1609, 1509, 1438, 1251 cm^{-1}; HRMS (EI) calcd for $C_{30}H_{30}NO_3P$ (M^+): 483.1963, found: 483.1971.

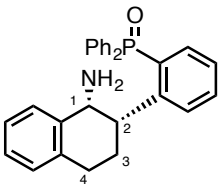
***trans*-Amino phosphine oxide (*trans*-5)**



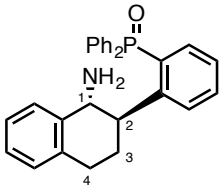
***trans*-5**

***trans*-5**: a colorless solid; R_f = 0.45 (15% MeOH in $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$): δ 7.72-7.63 (4H, m), 7.60-7.54 (3H, m), 7.51-7.46 (5H, m), 7.33 (1H, s), 7.21 (1H, ddd, *J* = 7.8, 7.7, 2.3 Hz), 7.05 (1H, ddd, *J* = 14.2, 7.8, 1.3 Hz), 6.46 (1H, s), 4.08 (1H, d, *J* = 10.2 Hz), 3.87 (3H, s), 3.83 (3H, s), 3.58 (1H, dd, J = 11.5, 10.2 Hz), 2.46 (1H, ddd, *J* = 14.5, 4.7, 2.3 Hz), 2.24-2.12 (3H, m, containing NH_2), 1.80 (1H, dddd, *J* = 14.5, 12.3, 11.5, 4.7 Hz), 1.58-1.52 (1H, m); ^{13}C NMR (125 MHz, $CDCl_3$): δ 149.74, 149.67, 147.7, 147.5, 134.1, 133.5, 133.4, 133.3, 133.08, 133.06, 133.0, 132.3, 132.23, 132.17, 132.07, 132.05, 131.93, 131.91, 131.63, 131.55, 131.5, 131.0, 128.69, 128.65, 128.59, 128.56, 128.1, 128.0, 126.2, 126.1, 110.9, 110.7, 56.8, 56.2, 55.8, 47.7, 47.6, 30.7, 29.5; ^{31}P NMR (162 MHz, $CDCl_3$) 32.8; IR (KBr): 3419, 2932, 1510, 1438, 1262 cm^{-1}; HRMS (EI) calcd for $C_{30}H_{30}NO_3P$ (M^+): 483.1963, found: 483.1918.

Amino phosphine oxide (6)



***cis*-6**



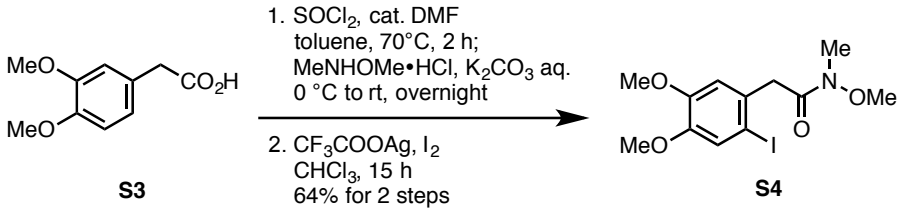
***trans*-6**

6 (mixture of *cis* : *trans* = 3 : 7): a colorless solid; R_f = 0.55 (15% MeOH in $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.80-7.36 (12H, m), 7.19-6.95 (6H, m), 4.09 (0.3H, d, *J* = 9.7 Hz, $H1_{trans}$), 4.01 (0.7H, d, *J* = 3.8 Hz, $H1_{cis}$), 3.90 (0.7H, d, *J* = 11.6 Hz, $H2_{cis}$), 3.67-3.58 (0.3H, m, $H2_{trans}$), 2.73 (0.7H, dd, *J* = 16.3, 2.6 Hz, $H4_{cis}$), 2.55 (0.3H, dd, J = 11.6, 1.7 Hz, $H4_{trans}$), 2.38 (0.7H, ddd, *J* = 16.5, 11.6, 4.7 Hz, $H3_{cis}$), 2.33-2.18 (1H, m, $H3'_{cis,trans}$), 1.84-1.74 (0.3H, m, $H3_{trans}$), 1.68-1.52 (1H, m, $H4'_{cis,trans}$), 1.37 (2H, brs, NH_2); ^{13}C NMR (125 MHz, $CDCl_3$): δ 150.5, 150.4, 149.2, 149.1, 140.7, 140.5, 136.3, 135.9, 134.4, 134.3, 133.6, 133.54, 133.50, 133.4, 133.2, 133.1, 133.0, 132.8, 132.7, 132.3, 132.2, 132.1, 132.0, 131.9, 131.7, 131.54, 131.46, 131.4, 131.1, 130.1, 130.1, 129.3, 129.4, 128.4, 128.33, 128.27, 128.2, 127.62, 127.55, 127.5, 126.4, 126.1, 125.8, 125.70, 125.67, 125.62, 125.56, 56.8, 51.7, 48.1, 48.0, 42.91, 42.87, 30.5, 29.8, 29.4, 23.7; ^{31}P NMR (202 MHz, $CDCl_3$) 31.8, 31.2; IR (KBr): 3060, 3011, 2975, 1591, 1568, 1487, 1472, 1438, 1217 cm^{-1}; HRMS (FAB) calcd for $C_{28}H_{27}NOP$ ($M+H^+$): 424.1830, found: 424.1837.

5. Preparation of Substrates

Azide BCBs were prepared by directly azidation[3] of benzocyclobutenols. The benzocyclobutenols were prepared from benzocyclobutenone **S5**[4] prepared according to the literature procedure.

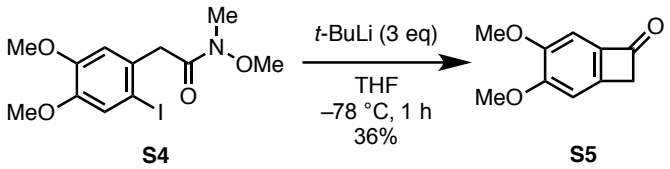
N,O-Dimethyl-4,5-dimethoxy-2-iodobenzylamide (S4)[4]



To a solution 3,4-dimethoxyphenylacetic acid **S3** (22.6 g, 115 mmol) in toluene (110 mL) was added thionyl cloride (10.0 mL, 138 mmol). The reaction mixture was stirred for 2 h at 70 °C. After the mixture was cooled to 0 °C, K_2CO_3 aq. (8 M, 57.0 mL) and *N,O*-dimethylhydroxylamine hydorochloride (14.6 g, 150 mmol) were added at 0 °C. After being stirred at 0 °C to room temperature overnight, the mixture was quenched with 2 M HCl aq., extracted with Et_2O. The combined organic layers were dried over $MgSO_4$, filtered and concentrated under reduced pressure. The resulting residue was purified by passing through a plug of silica (Hexane/EtOAc = 1/1) to afford the crude Weinreb amide (28.3 g). To a solution of crude Weinreb amide (12.5 g, 55.5 mmol) in $CHCl_3$ (159 ml) were added CF_3CO_2Ag (14.7 g, 66.6 mmol) and iodine (16.9 g, 66.6 mmol) at room temperature, then, the mixture was stirred for 15 h at room temperature. After the mixture was filtered through a pad of Celite®, the filtrate was washed with 10% (w/w) $Na_2S_2O_3$ aq.. After the combined organic layers were dried over $MgSO_4$ and concentrated. The resulting residue was purified by silica gel column chromatography (CH_2Cl_2/EtOAc = 30/1 to 10/1) to afford aryl iodide **S4** (13.1 g, 37.5 mmol, 64% for 2 steps) as a pale yellow solid.

S4: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.24 (1H, s), 6.83 (1H, s), 3.85 (8H, s), 3.73 (3H, s), 3.23 (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.7, 149.3, 148.4, 130.7, 121.5, 113.1, 89.2, 61.5, 56.1, 55.9, 43.9, 32.4; IR (KBr): 2968, 1663, 1599, 1505, 1379, 1257 cm^{-1}; HRMS (FAB) calcd for $C_{12}H_{17}INO_4$ ($M+H^+$): 366.0203, found: 366.0209.

4,5-Dimethoxybenzocyclobuten-1-one (S5)[4]

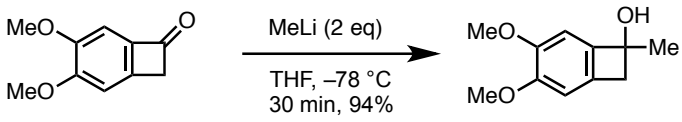


S4 **S5**

To a solution of **S4** (4.62 g, 13.2 mmol) in THF (68 mL) was added *t*-BuLi (1.9 M Pentane solution, 20.7 mL, 39.5 mmol) at –78 °C. After being stirred for 1 h at –78 °C, the reaction mixture was quenched with saturated NH_4Cl aq.. The resulting mixture was extracted with CH_2Cl_2. The combined organic layers were dried over $MgSO_4$ and concentrated. The resulting residue was purified by flash silica gel column chromatography (Hexane/Acetone = 5/1 to 4/1) to afford benzocyclobutenone **S5** (843 mg, 4.73 mmol, 36%) as a pale yellow solid. ^{1}H NMR spectrum data of benzocyclobutenone **S5** was identical with reported data[4].

S5: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.01 (1H, s), 6.82 (1H, s), 3.98 (3H, s), 3.86 (5H, s).

Benzocyclobutenol (S6a)

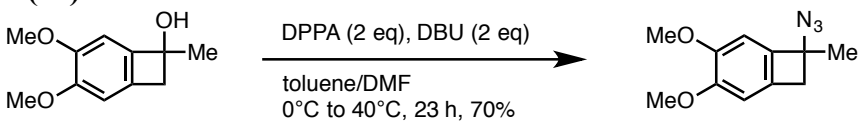


S5 **S6a**

To a solution of **S5** (939 mg, 5.27 mmol) in THF (37 mL) was added MeLi (1.1 M Et_2O solution, 9.6 mL, 10.5 mmol) at –78 °C. After being stirred for 30 min at –78 °C, the reaction mixture was quenched with 1 M HCl aq.. The organic layers were washed with sat. Na_2CO_3 aq., dried over $MgSO_4$ and concentrated. The residue was purified by flash silica gel column chromatography (Hexane/EtOAc = 3/2) to afford alcohol **S6a** (964 mg, 4.97 mmol, 94%) as a pale yellow solid.

S6a: ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.78 (1H, s), 6.74 (1H, s), 3.864 (3H, s), 3.860 (3H, s), 3.28 (1H, d, J = 13.6 Hz), 3.14 (1H, d, J = 13.6 Hz), 2.21 (1H, s), 1.65 (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.4, 148.9, 141.9, 131.9, 107.3, 104.1, 76.6, 55.63, 55.60, 47.0, 25.4; IR (neat): 3447, 3019, 1591, 1484, 1310 cm^{-1}; HRMS (EI) calcd for $C_{11}H_{14}O_3$ (M^+): 194.0943, found: 194.0974.

Azide BCB (1a)[3]

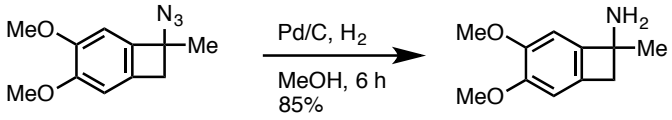


S6a **1a**

To a solution of **S6a** (214 mg, 1.11 mmol) in toluene (1.0 mL) and DMF (2.0 mL) was added DPPA (0.48 mL, 2.2 mmol) and DBU (0.35 mL, 2.2 mmol) at 0 °C. After being stirred at 0 °C for 2 h and at 40 °C for 20 h, the reaction mixture was cooled to room temperature, quenched with H_2O and extracted with Et_2O. The organic layers were washed with H_2O and 1 M HCl aq., dried over $MgSO_4$ and concentrated. The residue was purified by flash silica gel column chromatography (Hexane/CH_2Cl_2 = 7/3 to 3/2) to afford azide **1a** (171 mg, 0.778 mmol, 70%) as a dark green solid.

1a: ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.77 (1H, s), 6.74 (1H, s), 3.873 (3H, s), 3.869 (3H, s), 3.34 (1H, d, *J* = 13.4 Hz), 3.20 (1H, d, *J* = 13.4 Hz), 1.63 (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$): δ 151.5, 149.9, 137.9, 131.9, 107.4, 104.6, 66.7, 56.12, 56.08, 44.3, 24.0; IR (neat): 2925, 2100, 1591, 1484 cm^{-1}; HRMS (FAB) calcd for $C_{11}H_{13}O_2N_3$ (M^+): 219.1008, found: 219.1034.

Amino BCB (3a)

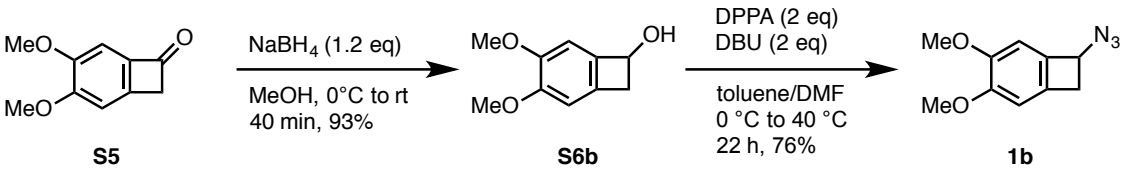


1a **3a**

To a solution of **1a** (41 mg, 0.19 mmol) in MeOH (1.3 mL) was added Palladium 10 wt% on activated Carbon (9.0 mg, 0.029 mmol) and stirred under H_2 atmosphere at room temperature for 6 h. The mixture was filtered through Celite®, extracted with MeOH and concentrated. The residue was purified by recrystallization (Hexane/Et_2O = 3/7) to afford amine **3a** (31 mg, 0.16 mmol, 85%) as a white solid.

3a: ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.80 (1H, s), 6.72 (1H, s), 3.852 (3H, s), 3.845 (3H, s), 3.22 (1H, d, *J* = 13.5 Hz), 3.06 (1H, d, *J* = 13.5 Hz), 2.93 (2H, brs), 1.59 (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.8, 149.7, 142.0, 131.8, 107.8, 104.7, 59.9, 56.2, 47.0, 26.0; IR (neat): 3419, 2965, 1636, 1593, 1484 cm^{-1}; HRMS (EI) calcd for $C_{11}H_{15}O_2N$ (M^+): 193.1103, found: 193.1123.

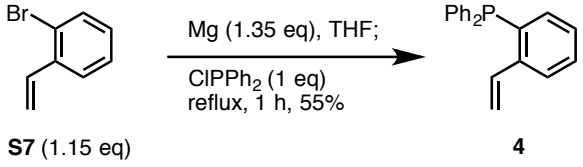
Azide BCB (1b)[3]



To a solution of **S5** (201 mg, 1.12 mmol) in MeOH (11 mL) was added $NaBH_4$ (51.4 mg, 1.34 mmol) at 0 °C. After being stirred for 40 min at room temperature, the reaction mixture was quenched with sat. NH_4Cl aq. and extracted with EtOAc (x5). The organic layers were washed with brine, dried over $MgSO_4$ and concentrated The residue was purified by open silica gel column chromatography (Hexane/EtOAc = 1/1) to afford alcohol **S6b** (188 mg, 1.04 mmol, 93%) as a pale yellow solid. To a solution of alcohol **S6b** (251 mg, 1.39 mmol) in toluene (1.2 mL) and DMF (2.5 mL) were added DPPA (0.60 mL, 2.8 mmol) and DBU (0.40 mL, 2.8 mmol) at 0 °C. After being stirred at 0 °C for 2 h and 40 °C for 20 h, the reaction mixture was cooled to room temperature. The mixture was quenched with H_2O and extracted with Et_2O. The organic layer was washed with H_2O and 1 M HCl aq., dried over $MgSO_4$ and concentrated in *vacuo*. The residue was purified by flash silica gel column chromatography (Pentane/Et_2O = 5/1) to afford azide BCB **1b** (216 mg, 1.05 mmol, 76%) as a blue oily solid.

1b: ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.79 (1H, s), 6.70 (1H, s), 4.75 (1H, d, J = 4.4 Hz), 3.85 (3H, s), 3.84 (3H, s), 3.49 (1H, dd, J = 13.7, 4.4 Hz), 3.12 (1H, d, J = 13.7 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 151.7, 149.9, 133.8, 106.8, 106.3, 58.4, 56.1, 56.0, 37.9; IR (neat): 3003, 2930, 2832, 2100, 1591, 1486 cm^{-1}; HRMS (EI) calcd for $C_{10}H_{11}N_3O_2$ (M^+): 205.0851, found: 205.0849.

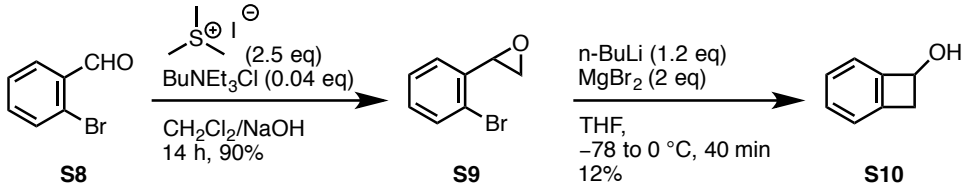
Styryl phosphine (4)[5]



Magnesium (0.13 g, 5.4 mmol) and 1-bromo-2-vinylbenzene **S7** (0.60 mL, 4.6 mol) were mixed in THF (2.0 mL) under argon atmosphere. After 5 min, the reaction mixture produced heat. Subsequently the mixture was cooled with an ice bath and stirred until all Mg was dissolved. chlorodiphenylphosphine (0.74 mL, 4.0 mmol), dissolved in THF (1.2 mL) was slowly added to keep the solution gently boiling. After being stirred for 1 h

under reflux, the reaction mixture was quenched with water and ice. The product was extracted with Et_2O. Purification was done by flash silica gel column chromatography (CH_2Cl_2/*n*-Pentane = 1/1) to afford styryl phosphine **10** (0.65 g, 2.2 mmol, 55%) as a white solid. ^{1}H NMR spectrum data of styryl phosphine **10** was identical with reported data[5].

Benzocyclobutenol (S10)[6]

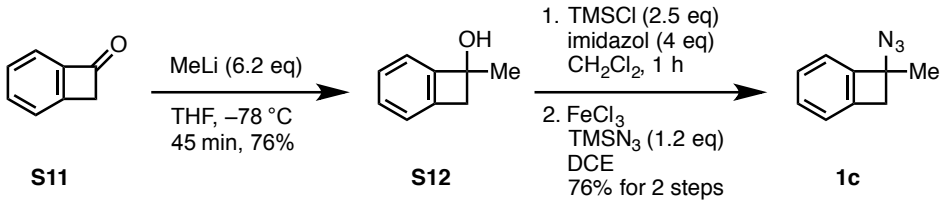


To a solution of 2-bromobenzaldehyde **S8** (5.35 g, 28.9 mmol) in CH_2Cl_2 (40 mL) were added Me_3SI (15.9 g, 72.3 mmol) and $BuNEt_3Cl$ (263 mg, 1.15 mmol), then 50% NaOH aq. (40 ml) at 0 °C. After being stirred for 14 h at room temperature, H_2O was added to the reaction mixture and the resulting solution was extracted with CH_2Cl_2. The organic layers were washed with H_2O, brine, dried over $MgSO_4$ and concentrated. The residue was purified by open silica gel column chromatography (short column, Hexane/Et_2O = 20/1 to 10/1) to afford epoxide **S9** (5.16 g, 25.9 mmol, 90%) as a colorless oil. To a solution of $MgBr_2$ (3.01 g, 16.4 mmol) in THF (100 ml), a solution of epoxide **S9** (1.63 g, 8.18 mmol) in THF (25+6+5 mL) was cannulated at -78 °C. To the resulting solution was added *n*-BuLi (6.14 ml, 1.6 M hexane solution, 9.82 mmol) at -78 °C. After being stirred at -78 °C for 20 min, the reaction mixture was warmed up to 0 °C and stirred for 20 min at 0 °C. The mixture was quenched with sat. NH_4Cl aq. and extracted with Et_2O. The organic layer was washed with brine, dried over $MgSO_4$ and concentrated. The residue was purified by open silica gel column chromatography (Pentane/CH_2Cl_2 = 1/2 to CH_2Cl_2) to afford benzocyclobutenol **S10** (141 mg, 1.00 mmol, 12%) as a colorless solid.

S10: R_f = 0.25 (CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.33-7.22 (3H, m), 7.15 (1H, d, J = 7.3 Hz), 5.30 (1H, dd, J = 8.0, 4.4 Hz), 3.63 (1H, dd, J = 14.3, 4.4 Hz), 3.04 (1H, J = 14.3 Hz), 2.26-2.12 (1H, m); ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.7, 142.3, 129.5, 127.2, 123.6, 122.2, 71.2, 42.5; IR (neat): 3304, 2925, 1600, 1457 cm^{-1}; HRMS (EI) calcd for C_8H_9O ($M+H^+$): 121.0654, found: 121.0653.

Azide BCB (1c)

*With DPPA, alcohol **S13** could not be converted to azide **1d** only to afford phosphate as an intermediate. Therefore, we chose another method to convert alcohol **S12** to azide **1c**.[7]



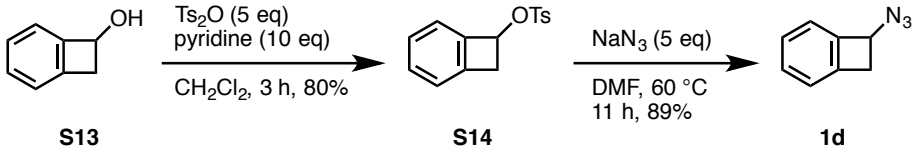
To a solution of **S11**[8] (91.6 mg, 0.775 mmol) in THF (5.5 mL) was added MeLi (1.1 M Et_2O solution, 1.4 mL, 1.6 mmol) at –78 °C. After the reaction mixture was stirred for 30 min at –78 °C, to the reaction mixture was added MeLi (1.1 M Et_2O solution, 3.0 mL, 3.3 mmol) at –78 °C. After being stirred for 30 min at –78 °C, the reaction mixture was quenched with 1 M HCl aq. and extracted with Et_2O. The organic layers were washed with brine, dried over $MgSO_4$ and concentrated. The residue was purified by flash silica gel column chromatography (Pentane/Et_2O = 4/1 to 1/1) to afford alcohol **S12**[73] (78.8 mg, 0.587 mmol, 76%) as a colorless solid. To a solution of alcohol **S12** (93.8 mg, 0.699 mmol) in CH_2Cl_2 (7 mL) were added imidazole (190 mg, 2.79 mmol) and TMSCl (220 μl, 1.74 mmol) at 0 °C. After being stirred for 1 h at room temperature, the reaction mixture was quenched with H_2O and extracted with CH_2Cl_2. The organic layer was washed with brine, dried over Na_2SO_4 and concentrated. The residue was purified by silica gel column chromatography (short column, Pentane/Et_2O = 8/1) to afford silyl ether (125 mg, 0.606 mmol) as a colorless oil. To a solution of silyl ether (125 mg, 0.606 mmol) in DCE (3 mL) were added $TMSN_3$ (95.5 μl, 0.727 mmol) and $FeCl_3$ (a half micro spatula) at room temperature. After being stirred for 10 min at room temperature, the reaction mixture was quenched with H_2O and extracted with CH_2Cl_2. The organic layer was washed with H_2O and brine, dried over $MgSO_4$ and concentrated. The residue was purified by flash silica gel column chromatography (Pentane/Et_2O = 50/0 to 50/1) to afford azide BCB **1c** (84.6 mg, 0.531 mmol) as a colorless oil.

1c: R_f = 0.25 (Hexane/EtOAc = 100/1); ^1H NMR (400 MHz, $CDCl_3$): δ 7.36-7.23 (2H, m), 7.20 (1H, d, *J* = 7.3 Hz), 7.17 (1H, d, *J* = 7.3 Hz), 3.42 (1H, d, *J* = 14.0 Hz), 3.29 (1H, d, *J* = 14.0 Hz), 1.67 (3H, s); ^{13}C NMR (125 MHz, $CDCl_3$): δ 147.0, 140.7, 129.8, 127.6, 123.9, 120.9, 67.3, 45.1, 24.0; IR (neat): 3445, 2086, 1634, 1458 cm^{-1}; HRMS (FAB)

calcd for C_9H_9N (M-N_2^+): 131.0735, found: 131.0736.

Azide BCB (1d)[9]

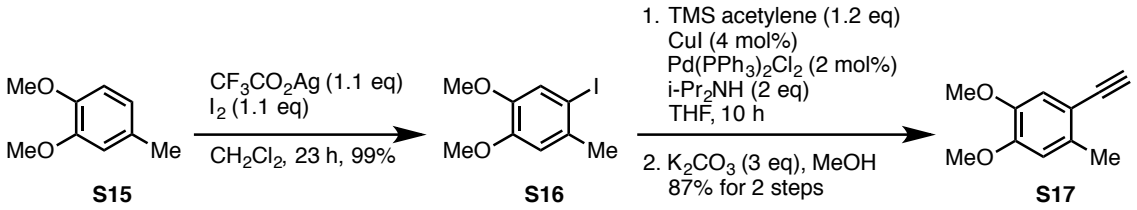
*With DPPA, alcohol **S13** could not be converted to azide **1d** only to afford phosphate as an intermediate. Therefore, we chose another method to convert alcohol **S13** to azide **1d**.



To a solution of alcohol **S13** (97.1 mg, 0.808 mmol) in CH_2Cl_2 (8.1 mL) were added Ts_2O (1.31 g, 4.04 mmol) and pyridine (0.648 ml, 8.08 mmol) at 0 °C. After being stirred for 3 h at room temperature, the reaction mixture was quenched with sat. $NaHCO_3$ aq. and extracted with Et_2O. The organic layers were washed with brine, dried over $MgSO_4$ and concentrated. The residue was purified by flash silica gel column chromatography (Hexane/Et_2O = 15/1) to afford tosylate **S14** (178 mg, 0.647 mmol, 80%) as a white solid. To a solution of alcohol tosylate **S14** (178 mg, 0.647 mmol) in DMF (13 mL) was added NaN_3 (214 mg, 3.23 mmol). After being stirred for 11 h at 60 °C, the reaction mixture was cooled to room temperature. The mixture was quenched with H_2O and extracted with Et_2O. The organic layer was washed with H_2O, dried over $MgSO_4$ and concentrated. The residue was purified by flash silica gel column chromatography (Pentane/Et_2O = 100/1 to 10/1) to afford azide **1d** (83.6 mg, 0.575 mmol, 89%) as a blue oil.

1d: R_f = 0.4 (Hexane/EtOAc = 10/1); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.34 (1H, dd, *J* = 7.4, 7.4 Hz), 7.28 (1H, dd, *J* = 7.4, 7.4 Hz), 7.24 (1H, d, *J* = 7.4 Hz), 7.15 (1H, d, *J* = 7.4 Hz), 4.88 (1H, dd, *J* = 4.9, 2.3 Hz), 3.61 (1H, dd, *J* = 14.3, 4.9 Hz), 3.23 (1H, dd, *J* = 14.3, 2.3 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ 143.0, 142.4, 129.9, 127.6, 123.5, 122.7, 59.0, 38.7; IR (neat): 2931, 2100, 1603, 1457 cm^{-1}; HRMS (EI) calcd for $C_8H_7N_3$ (M^+): 145.0640, found: 145.0658.

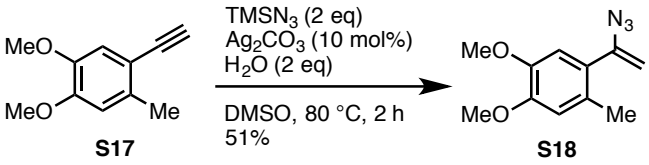
Phenyl acetylene (S17)



To a solution of 3,4-dimethoxy toluene **S15** (1.93 g, 12.6 mmol) in $CHCl_3$ (50 mL) were added iodine (3.52 g, 13.9 mmol) and CF_3CO_2Ag (3.08 g 13.9 mmol) at room temperature. After being stirred for 23 h at room temperature, the reaction mixture was quenched with 10% $Na_2S_2O_3$ aq. and diluted with CH_2Cl_2. The resulting mixture was filtered through a Celite pad. The filtrate was washed with 10% $Na_2S_2O_3$ aq. and brine, dried over $MgSO_4$ and concentrated. The residue was purified by silica gel column chromatography (Hexane/EtOAc = 8/1) to afford aryl iodide **S16** (3.49 g, 12.5 mmol, 99%) as a colorless oil. To a solution of aryl iodide **S16** (3.49 g, 12.5 mmol) in THF (34 mL) were added CuI (95.2 mg, 0.500 mmol), $Pd(PPh_3)_2Cl_2$ (175 mg, 0.250 mmol). After being stirred for 10.5 h, the reaction mixture was quenched with sat. NH_4Cl aq. and extracted with EtOAc. The organic layer was washed with sat. NH_4Cl aq. and concentrated. The residue was dissolved in MeOH in 80 ml and to the resulting solution, K_2CO_3 (5.18 g, 37.5 mmol) was added. After being stirred for 3 h, the reaction mixture was quenched with 1 N HCl aq. (30 ml) and sat. NH_4Cl aq.. The resulting solution was extracted with Et_2O and the organic layer was washed with brine, dried over $MgSO_4$ and concentrated. The residue was purified by flash silica gel column chromatography (Hexane/Et_2O = 8/1 to 4/1) to afford phenyl acetylene **S17** (1.93 g, 10.9 mmol, 87% for 2 steps) as a white solid.

S17: R_f = 0.45 (Hexane/EtOAc = 4/1); ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.95 (1H, s), 6.69 (1H, s), 3.88 (3H, s), 3.85 (3H, s), 3.20 (1H, s), 2.40 (3H, s); ^{13}C NMR (125 MHz, $CDCl_3$): δ 149.5, 146.6, 134.2, 114.9, 113.3, 112.4, 82.8, 79.3, 56.0, 55.8, 20.1; IR (neat): 3307, 2365, 2345, 1605, 1508 cm^{-1}; HRMS (EI) calcd for $C_{11}H_{12}O_2$ (M^+): 176.0837, found: 176.0808.

Vinyl azide (S18)[10]



To a solution of phenyl acetylene **S17** (357 mg, 2.02 mmol) in DMSO (8.1 mL) were added H_2O (73 μl, 4.0 mmol), $TMSN_3$ (0.53 ml, 4.0 mmol), and Ag_2CO_3 (55.7 mg, 0.202 mmol) at room temperature. After being stirred for 2 h at 80 °C, the reaction mixture was cooled to room temperature and extracted with Et_2O. The organic layer was washed with brine, dried over $MgSO_4$ and concentrated. The residue was purified by flash silica gel column chromatography (Hexane/EtOAc = 10/1 to 2/1) to afford vinyl azide **S18** (225 mg, 1.02 mmol, 51%) as an orange oil.

S18: R_f = 0.5 (Hexane/EtOAc = 4/1); ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.78 (1H, s), 6.71 (1H, s), 5.03 (1H, d, *J* = 0.9 Hz), 4.71 (1H, d, *J* = 0.9 Hz), 3.89 (3H, s), 3.87 (3H, s), 2.34 (3H, s); ^{13}C NMR (125 MHz, $CDCl_3$): δ 149.2, 146.7, 145.1, 128.5, 126.8, 113.2, 112.3, 102.4, 56.0, 55.9, 19.3; IR (neat): 3002, 2936, 2848, 2090, 1631, 1606, 1515 cm^{-1}; HRMS (EI) calcd for $C_{11}H_{13}N_3O_2$ (M^+): 219.1008, found: 219.1021.

6. References

1. Solomek, T.; Klan, P., *et al*., *J. Org. Chem.* **2010,** *75*, 7300-7309.
2. Le, T. N.; Cho, W.-J., *Chem. Pharm. Bull.* **2008,** *56*, 1026 -1029.
3. Thompson, A. S.; Grabowski, E. J. J., *et al*., *J. Org. Chem.* **1993,** *58*, 5886-5888.
4. Aidhen, I. S.; Ahuja, J. R., *Tetrahedron Lett.* **1992,** *33*, 5431-5432.
5. Lexer, C.; N. G.; Slugovc, C., *et al*., *J. Organomet. Chem.* **2011,** *696*, 2466-2470.
6. Ting, C. P.; Maimone, T. J., *Angew. Chem. Int. Ed. Engl.* **2014,** *53*, 3115-3119.
7. Sawama, Y.; Sajiki, H. *et al*., *Chem. Eur. J*. **2012**, *18*, 16608-16611.
8. Hosoya, T.; Suzuki, K. *et al.*, *Synlett*, **1995**, 177-179.
9. Iida, K.; Yoshioka, M., *et al.*, *J. Org. Chem.* **1999**, *64*, 7407-7411.
10. Liu, Z.; Liao, P.; Bi, X. *Org. Lett.* **2014**, *16*, 3668-3671.

7. X-ray Crystal Graphic Data

cis-**5** was crystalized as a BF_4 salt from MeOH : toluene.

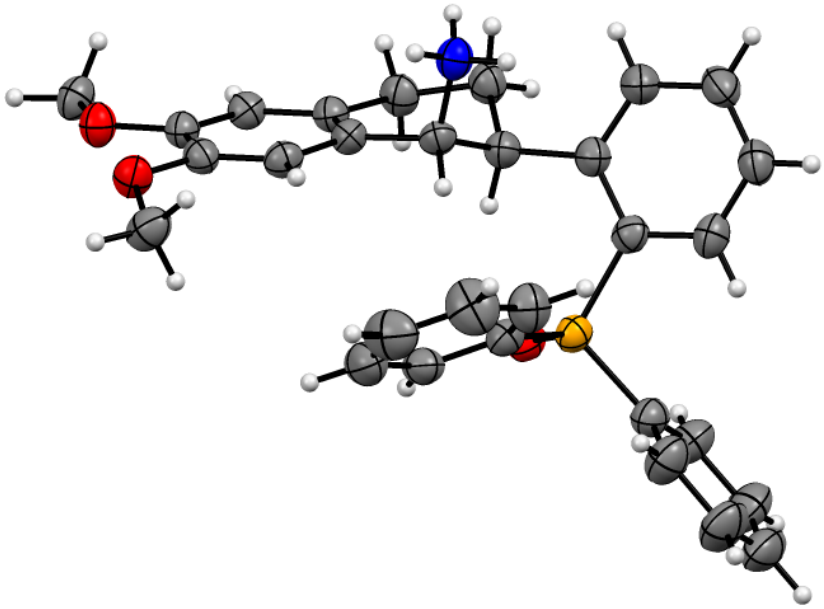


Figure S3: ORTEP drawing of *cis*-**5** (R_1 = 6.8%).

A. Crystal Data

Empirical Formula	$C_{30}H_{33}BF_4NO_4P$
Formula Weight	589.37
Crystal Color, Habit	colorless, platelet
Crystal Dimensions	0.200 X 0.100 X 0.020 mm
Crystal System	orthorhombic
Lattice Type	Primitive
Lattice Parameters	a = 10.49949(19) Å
	b = 15.8323(3) Å
	c = 35.2366(6) Å
	V = 5857.41(18) $Å^3$
Space Group	Pbca (#61)
Z value	8
D_{calc}	1.337 g/cm^3

F_{000}	2464.00
m(CuKa)	13.703 cm^{-1}

B. Intensity Measurements

Diffractometer	R-AXIS RAPID
Radiation	CuKa (l = 1.54187 Å)
	multi-layer mirror monochromated
Voltage, Current	40kV, 30mA
Temperature	-100.0°C
Detector Aperture	460.0 x 256.0 mm
Data Images	300 exposures
w oscillation Range (c=54.0, f=0.0)	80.0 - 260.0°
Exposure Rate	30.0 sec./°
w oscillation Range (c=54.0, f=90.0)	80.0 - 260.0°
Exposure Rate	30.0 sec./°
w oscillation Range (c=54.0, f=180.0)	80.0 - 260.0°
Exposure Rate	30.0 sec./°
w oscillation Range (c=54.0, f=270.0)	80.0 - 260.0°
Exposure Rate	30.0 sec./°
w oscillation Range (c=0.0, f=0.0)	80.0 - 260.0°
Exposure Rate	30.0 sec./°
Detector Position	127.00 mm
Pixel Size	0.100 mm
2qmax	136.4°
No. of Reflections Measured	Total: 63297
	Unique: 5355 (Rint = 0.0653)
Corrections	Lorentz-polarization
	Absorption
	(trans. factors: 0.680 - 0.973)

C. Structure Solution and Refinement

Structure Solution	Direct Methods (SHELXT Version 2014/5)
Refinement	Full-matrix least-squares on F^2

Function Minimized	$S\ w\ (Fo^2 - Fc^2)^2$
Least Squares Weights	$w = 1/ [\ s^2(Fo^2) + (0.1027\ .\ P)^2$
	$+ 5.2183\ .\ \ P\ ]$
	where $P = (Max(Fo^2,0) + 2Fc^2)/3$
2qmax cutoff	136.4^o
Anomalous Dispersion	All non-hydrogen atoms
No. Observations (All reflections)	5355
No. Variables	391
Reflection/Parameter Ratio	13.70
Residuals: R1 (I>2.00s(I))	0.0687
Residuals: R (All reflections)	0.0970
Residuals: wR2 (All reflections)	0.2004
Goodness of Fit Indicator	1.041
Max Shift/Error in Final Cycle	0.000
Maximum peak in Final Diff. Map	1.09 e-/$Å^3$
Minimum peak in Final Diff. Map	-0.39 e-/$Å^3$

trans-**5** was crystalized as a BF_4 salt from MeOH : toluene.

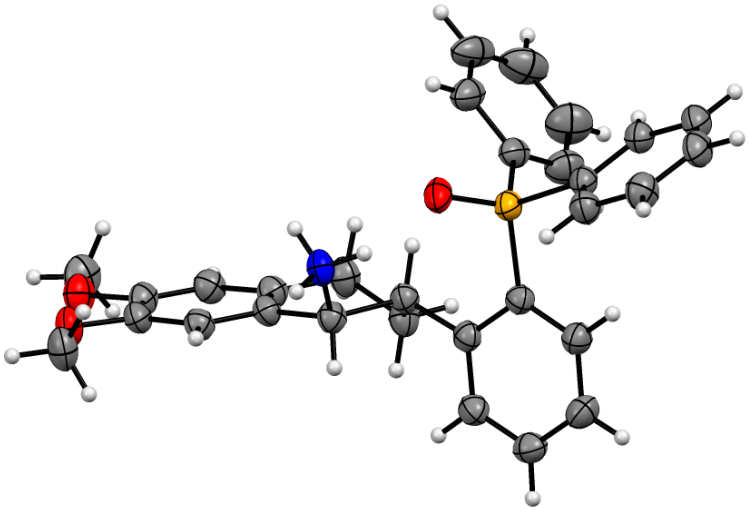


Figure S4: ORTEP drawing of *trans*-**5** (R_1 = 5.4%).

A. Crystal Data

Empirical Formula	$C_{37}H_{39}BF_4NO_3P$
Formula Weight	663.50
Crystal Color, Habit	colorless, platelet
Crystal Dimensions	0.180 X 0.150 X 0.060 mm
Crystal System	triclinic
Lattice Type	Primitive
Lattice Parameters	a = 7.93080(14) Å
	b = 13.1455(2) Å
	c = 17.4250(3) Å
	a = 76.619(5) ^{o}
	b = 88.302(6) ^{o}
	g = 73.541(5) ^{o}
	V = 1693.64(8) Å3
Space Group	P-1 (#2)
Z value	2
Dcalc	1.301 g/cm^3
F000	696.00
m(CuKa)	12.235 cm^{-1}

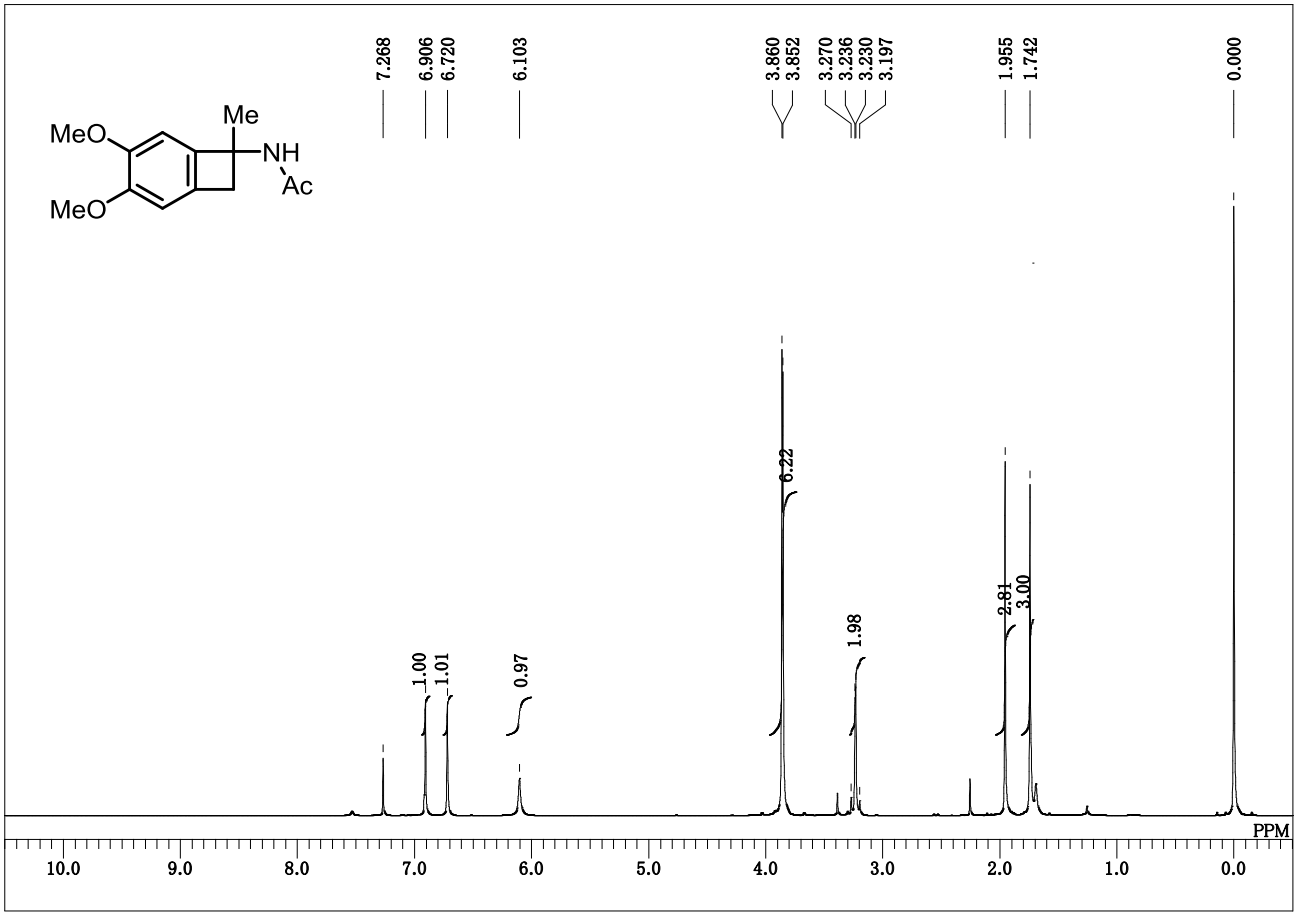
B. Intensity Measurements

Diffractometer	R-AXIS RAPID
Radiation	CuKa (l = 1.54187 Å)
	multi-layer mirror monochromated
Voltage, Current	40kV, 30mA
Temperature	-100.0°C
Detector Aperture	460.0 x 256.0 mm
Data Images	100 exposures
w oscillation Range (c=54.0, f=0.0)	80.0 - 260.0°
Exposure Rate	15.0 sec./°
w oscillation Range (c=54.0, f=90.0)	80.0 - 260.0°
Exposure Rate	15.0 sec./°
w oscillation Range (c=54.0, f=180.0)	80.0 - 260.0°
Exposure Rate	15.0 sec./°
w oscillation Range (c=54.0, f=270.0)	80.0 - 260.0°
Exposure Rate	15.0 sec./°
w oscillation Range (c=0.0, f=0.0)	80.0 - 260.0°
Exposure Rate	15.0 sec./°
Detector Position	127.00 mm
Pixel Size	0.100 mm
2qmax	136.5°
No. of Reflections Measured	Total: 19539
	Unique: 6073 (Rint = 0.0438)
Corrections	Lorentz-polarization
	Absorption
	(trans. factors: 0.662 - 0.929)

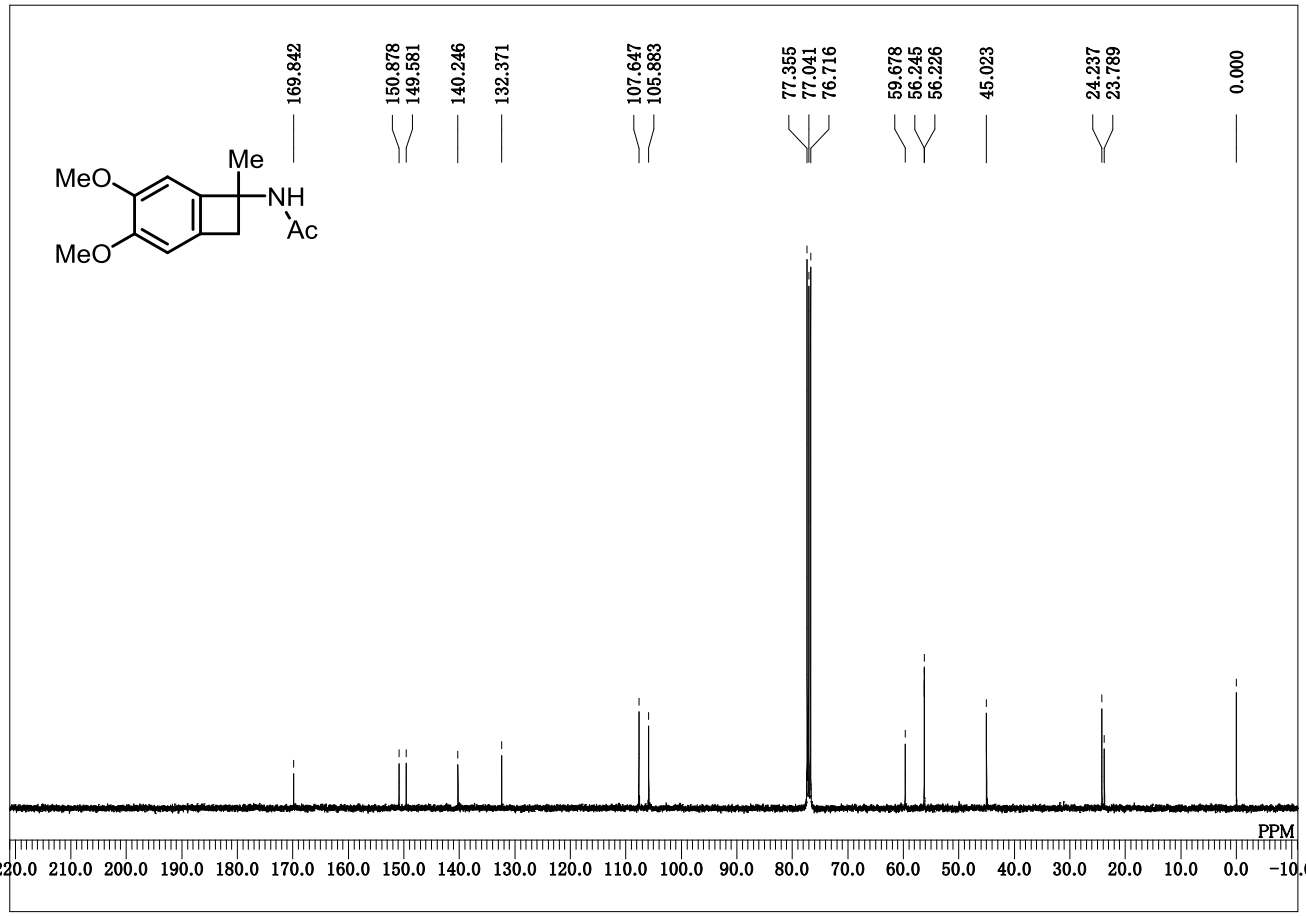
C. Structure Solution and Refinement

Structure Solution	Direct Methods (SHELXT Version 2018/2)
Refinement	Full-matrix least-squares on F2
Function Minimized	S w $(Fo^2 - Fc^2)^2$
Least Squares Weights	w = 1/ [$s^2(Fo^2)$ + $(0.0935 . P)^2$ + 0.1158 . P] where P = $(Max(Fo^2,0) + 2Fc^2)/3$
2qmax cutoff	136.5°
Anomalous Dispersion	All non-hydrogen atoms
No. Observations (All reflections)	6073
No. Variables	454
Reflection/Parameter Ratio	13.38
Residuals: R1 (I>2.00s(I))	0.0542
Residuals: R (All reflections)	0.0713
Residuals: wR2 (All reflections)	0.1644
Goodness of Fit Indicator	1.081
Max Shift/Error in Final Cycle	0.000
Maximum peak in Final Diff. Map	0.35 $e^-/Å^3$
Minimum peak in Final Diff. Map	-0.32 $e^-/Å^3$

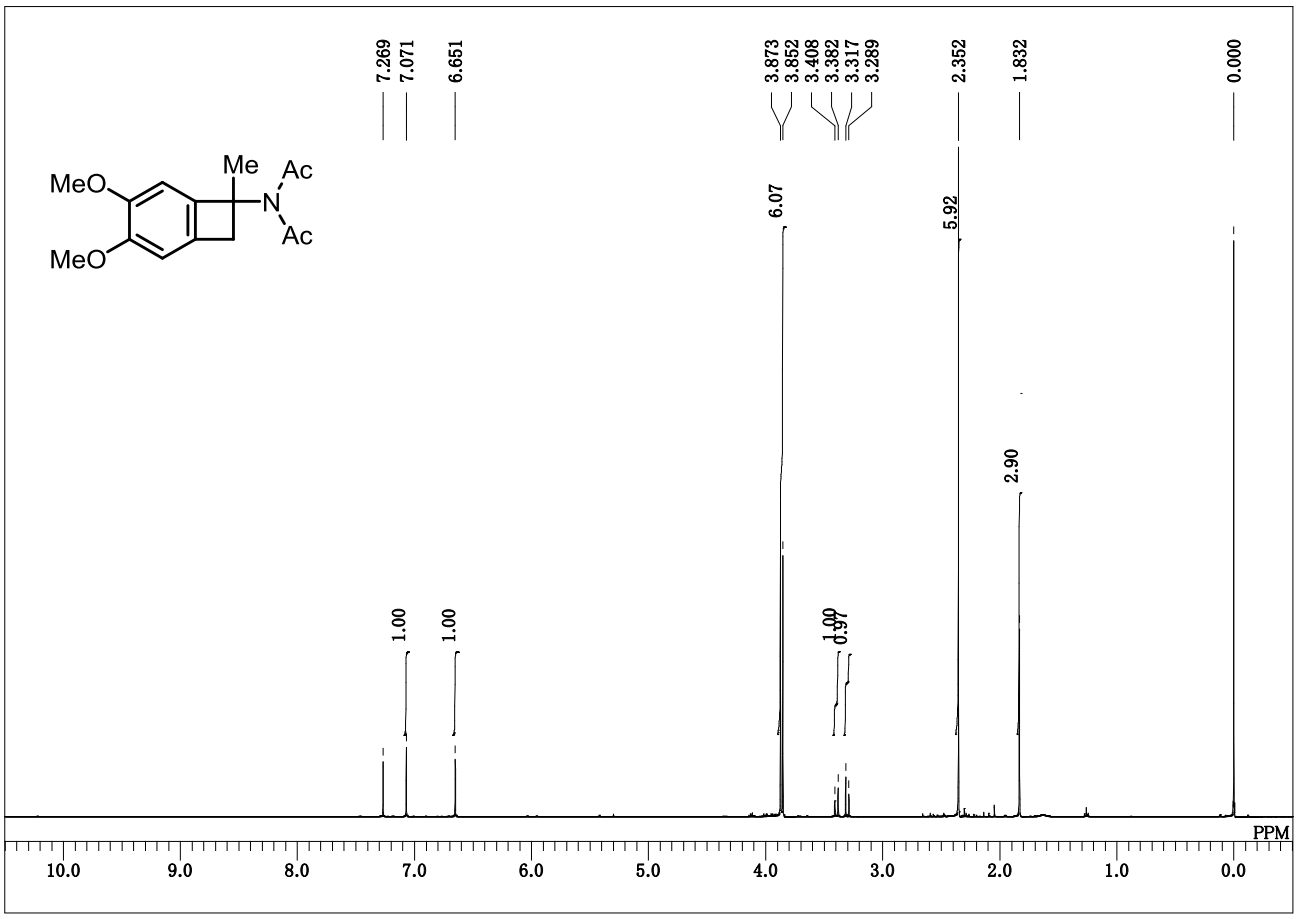
Amide BCB Me-1H



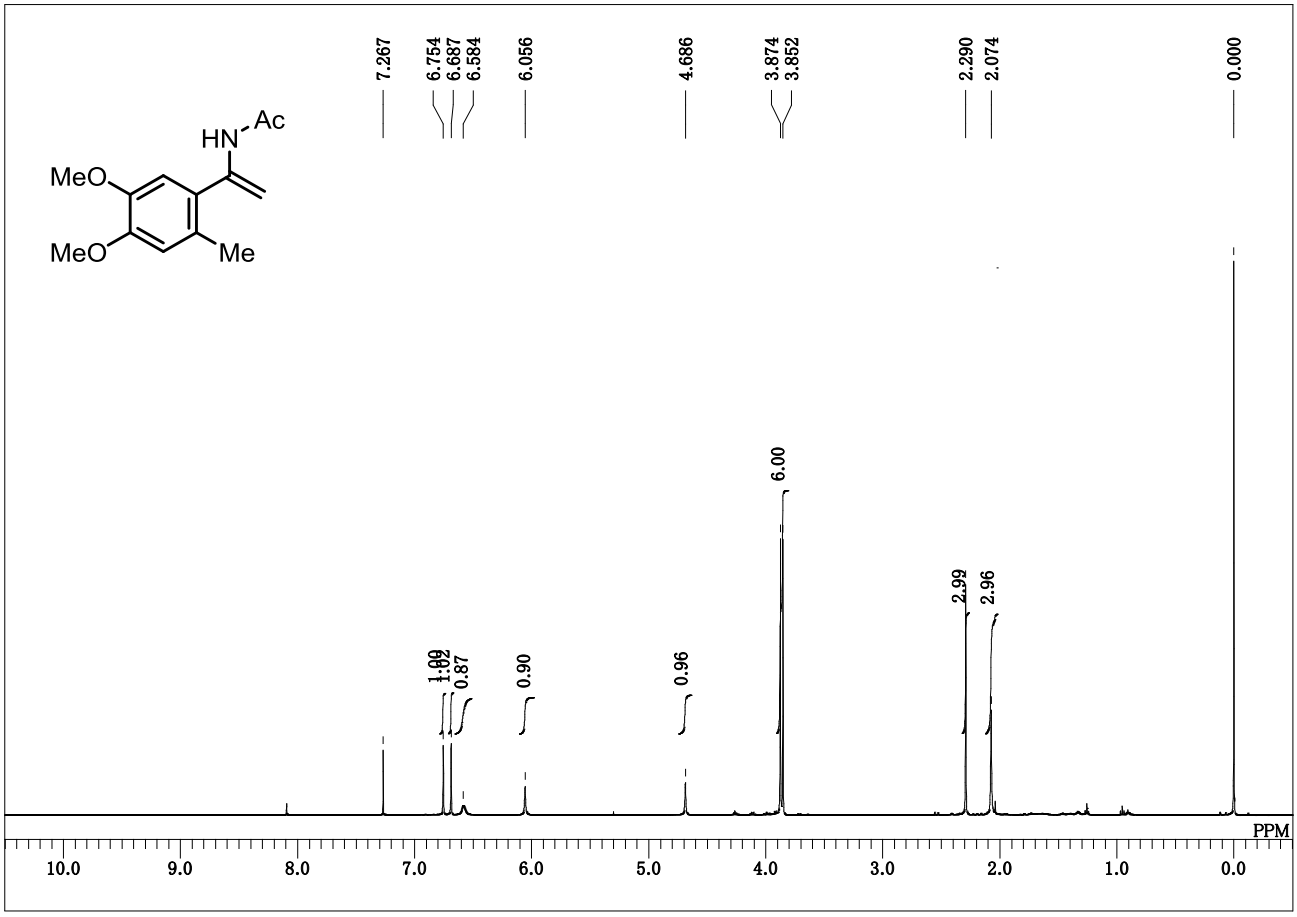
Amide BCB Me-13C



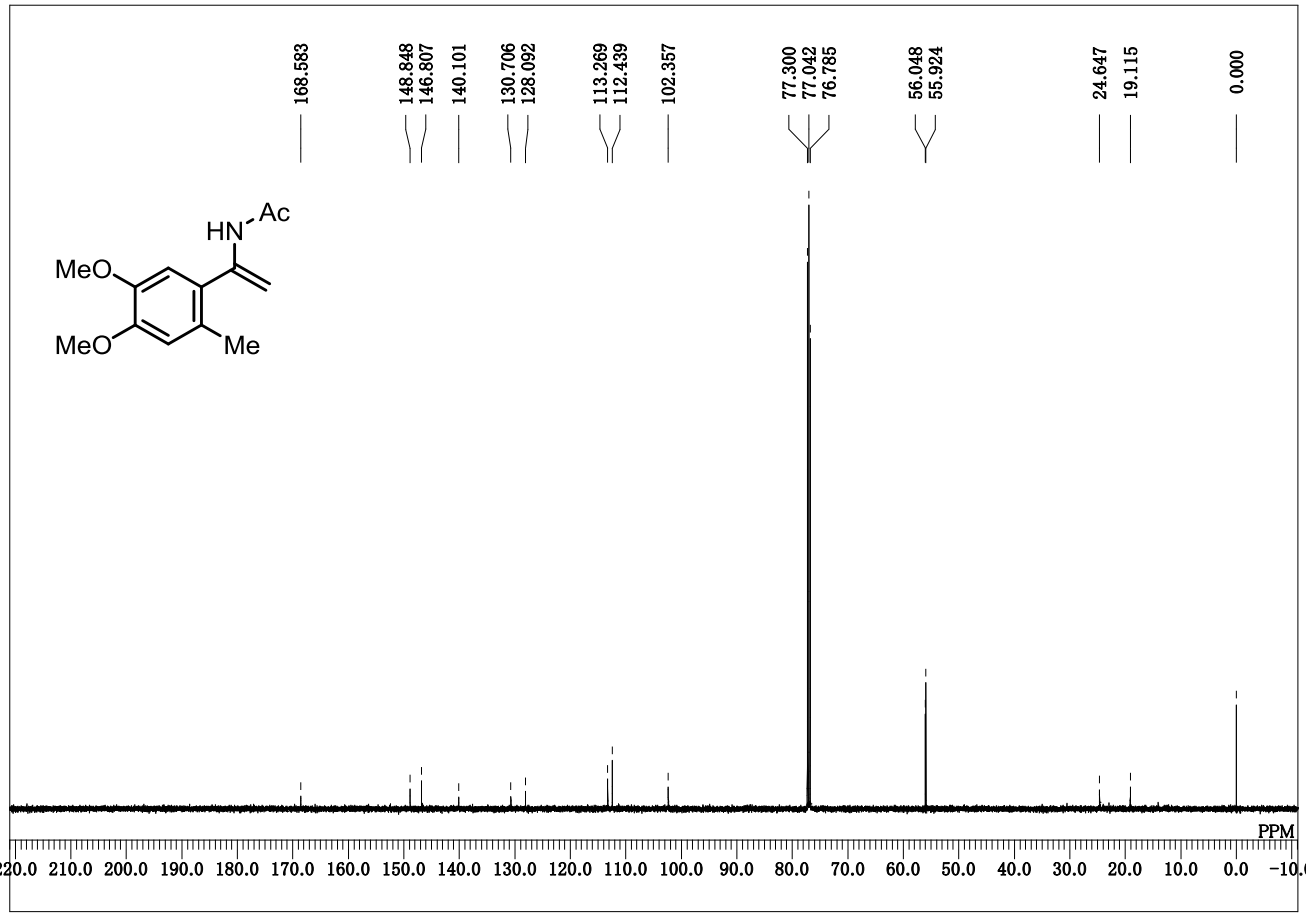
Diamide BCB Me-1H



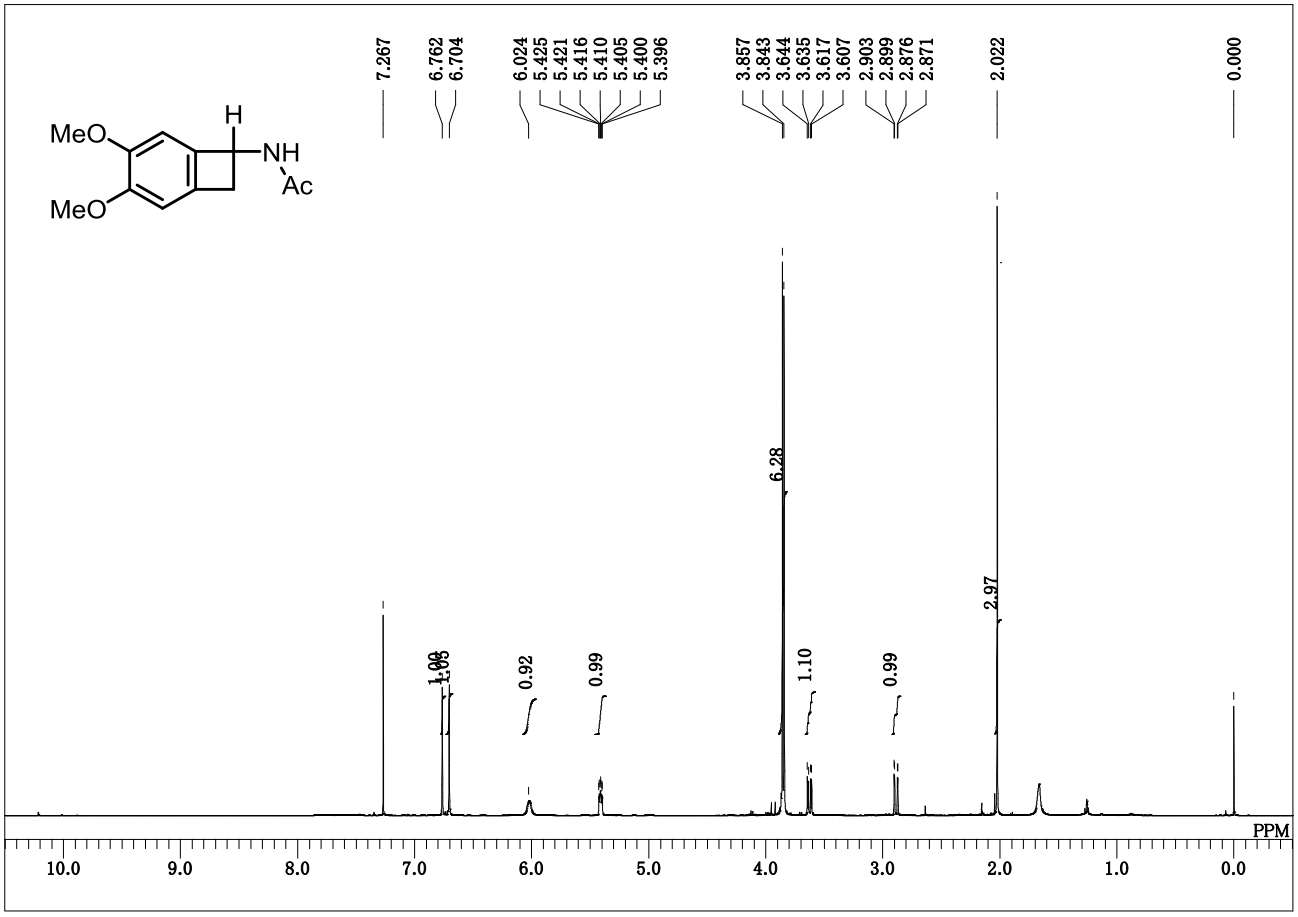
Enamine-1H



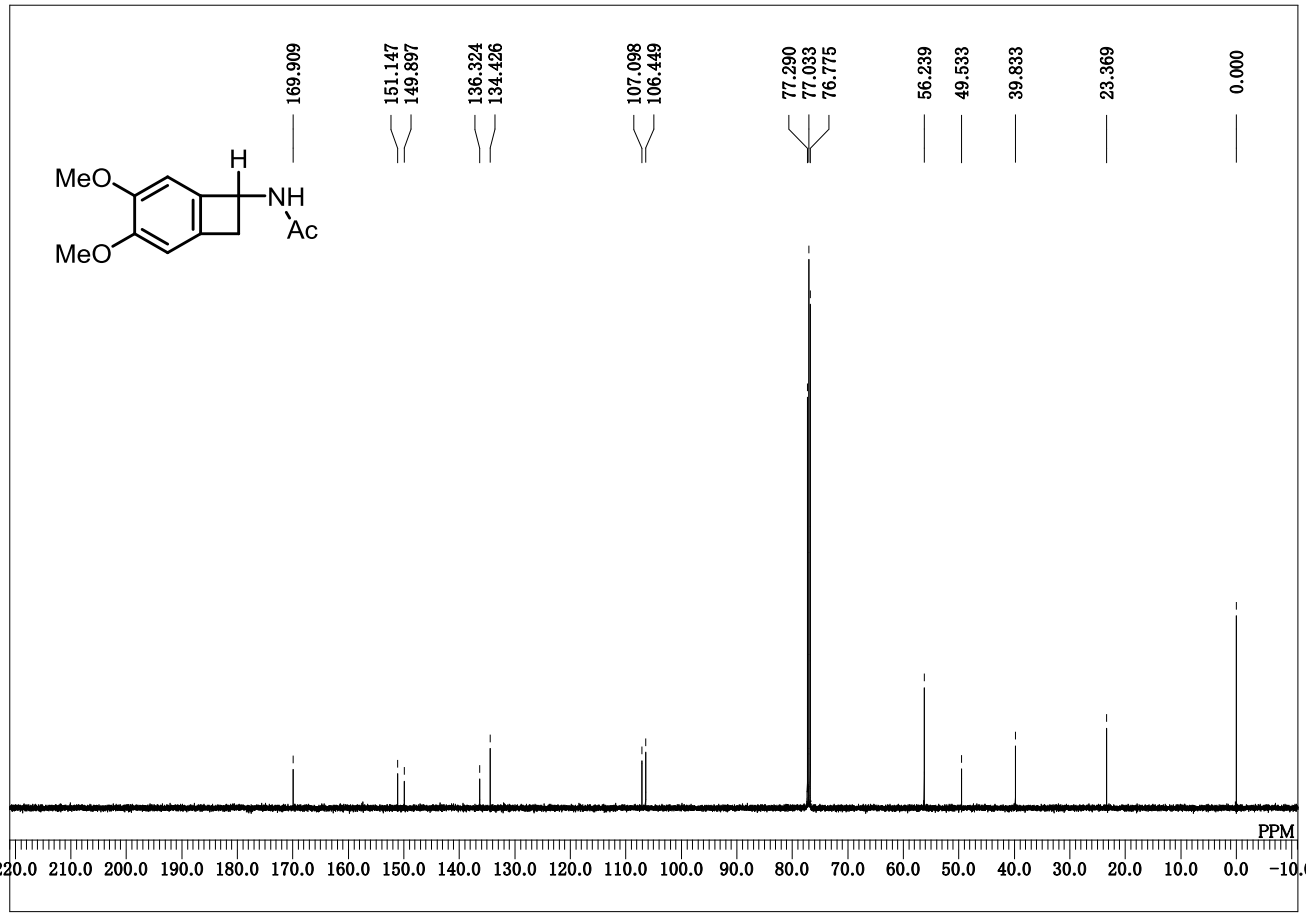
Enamine-13C



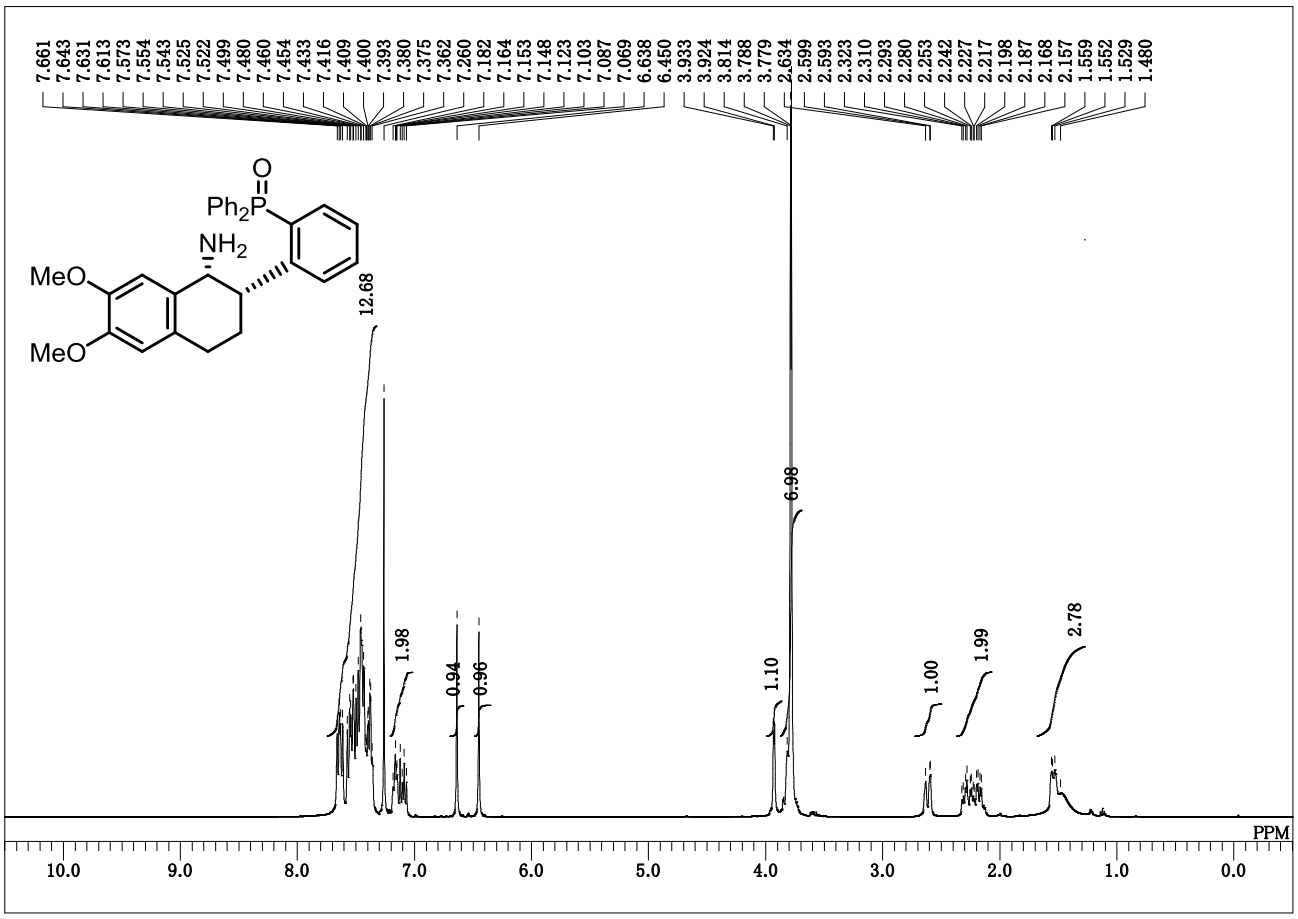
Amide BCB H-1H



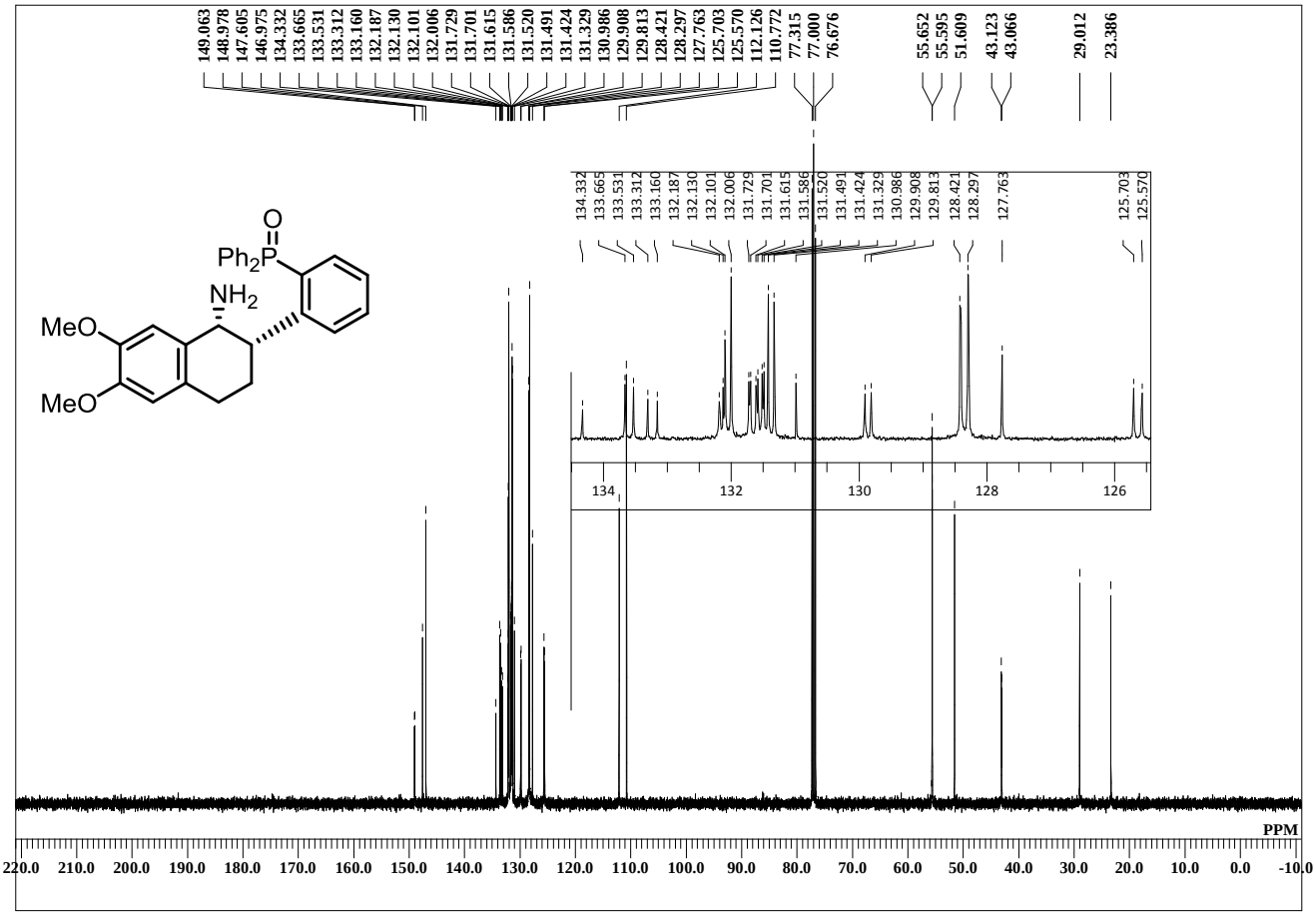
Amide BCB H-13C



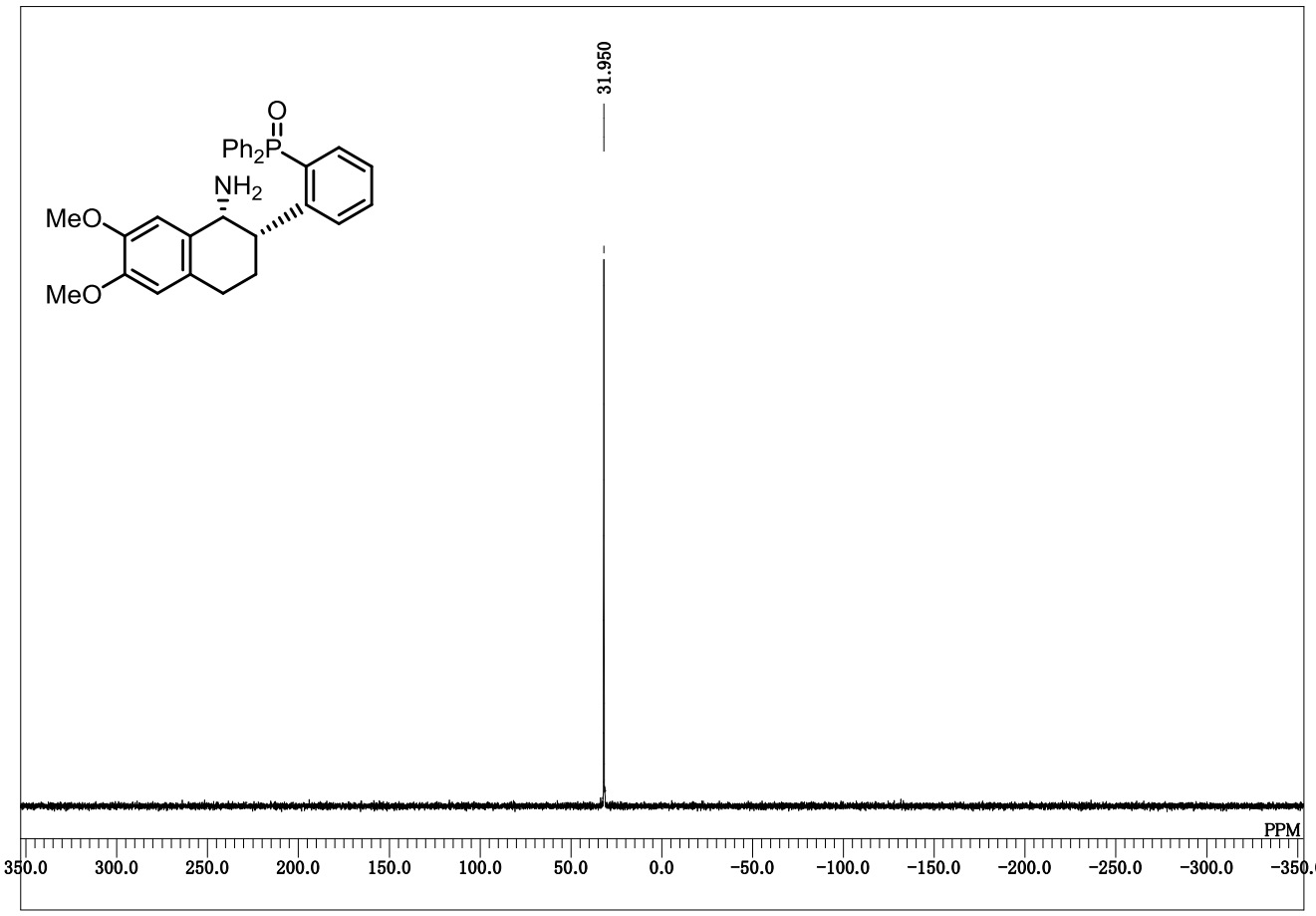
aminophos-cis-1H



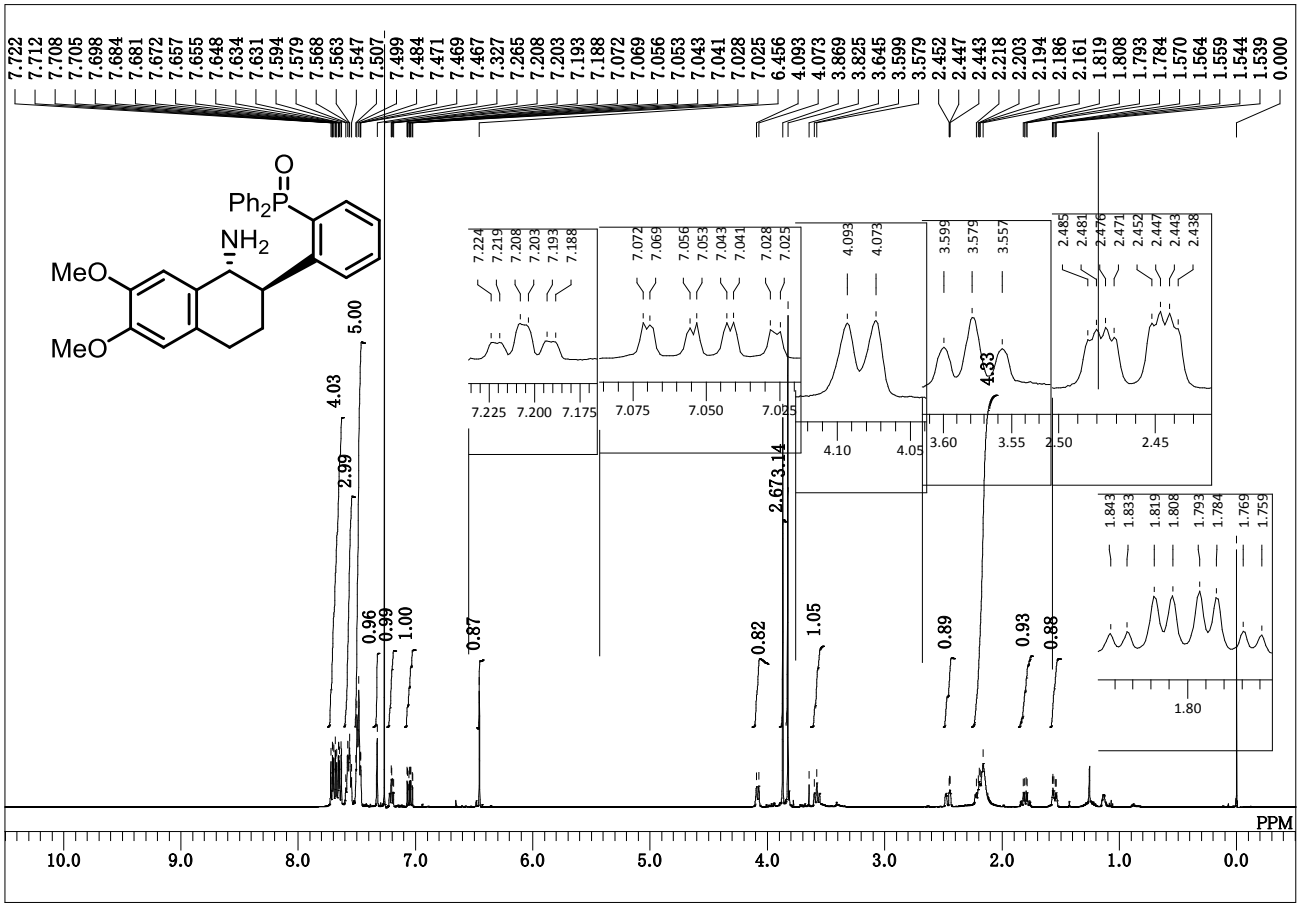
aminophos-cis-13C



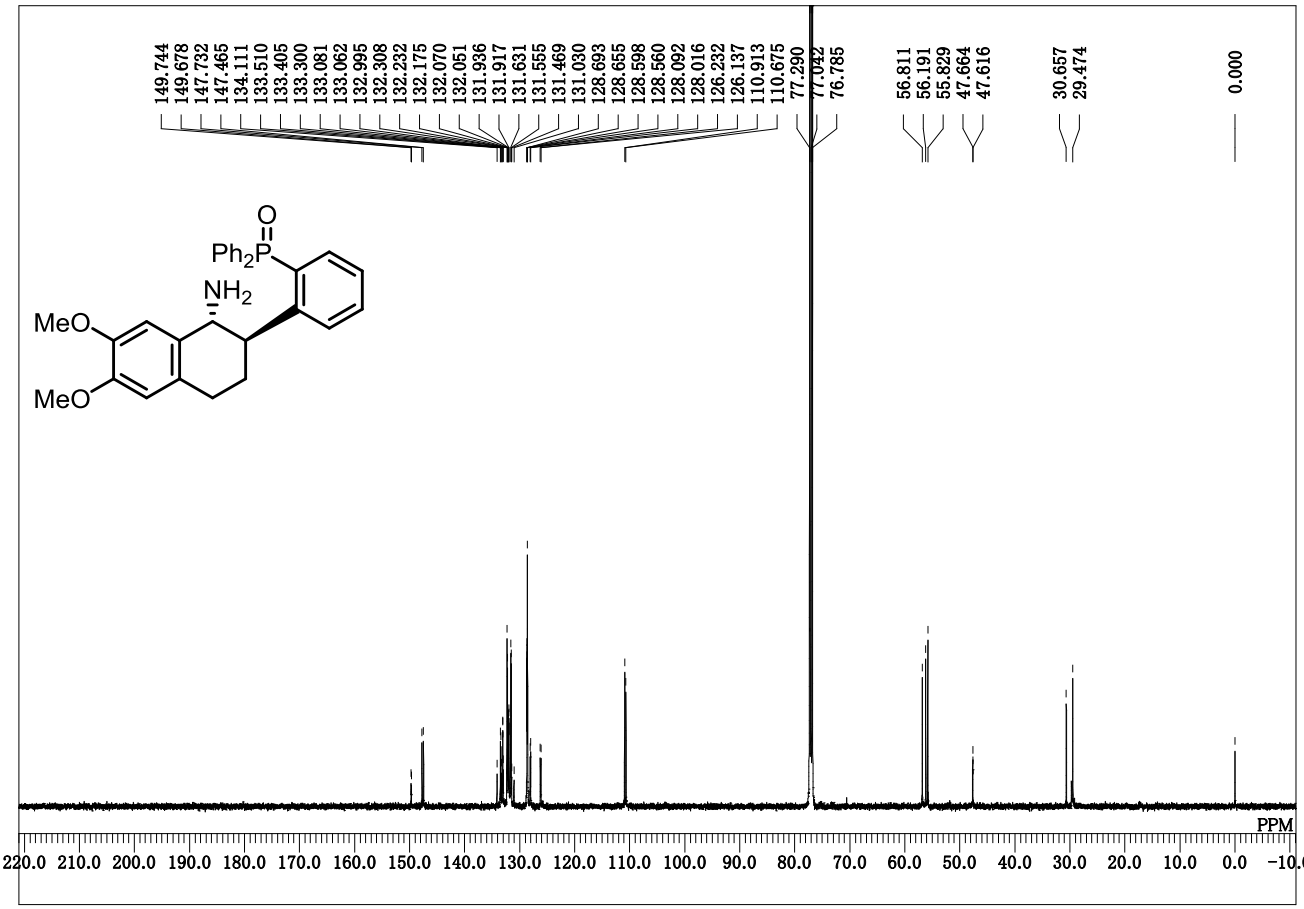
aminophos-cis-31P



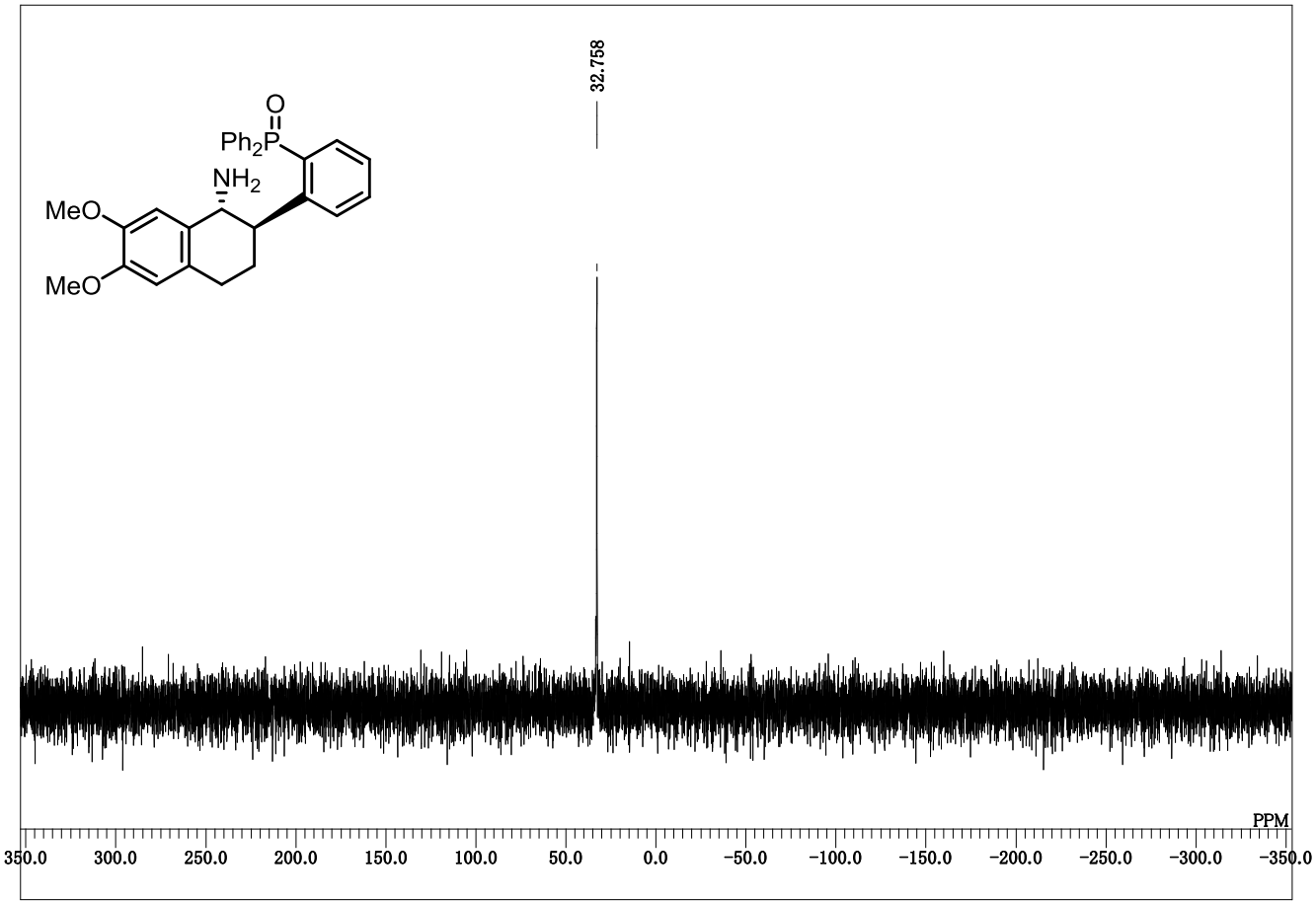
aminophos-trans-1H



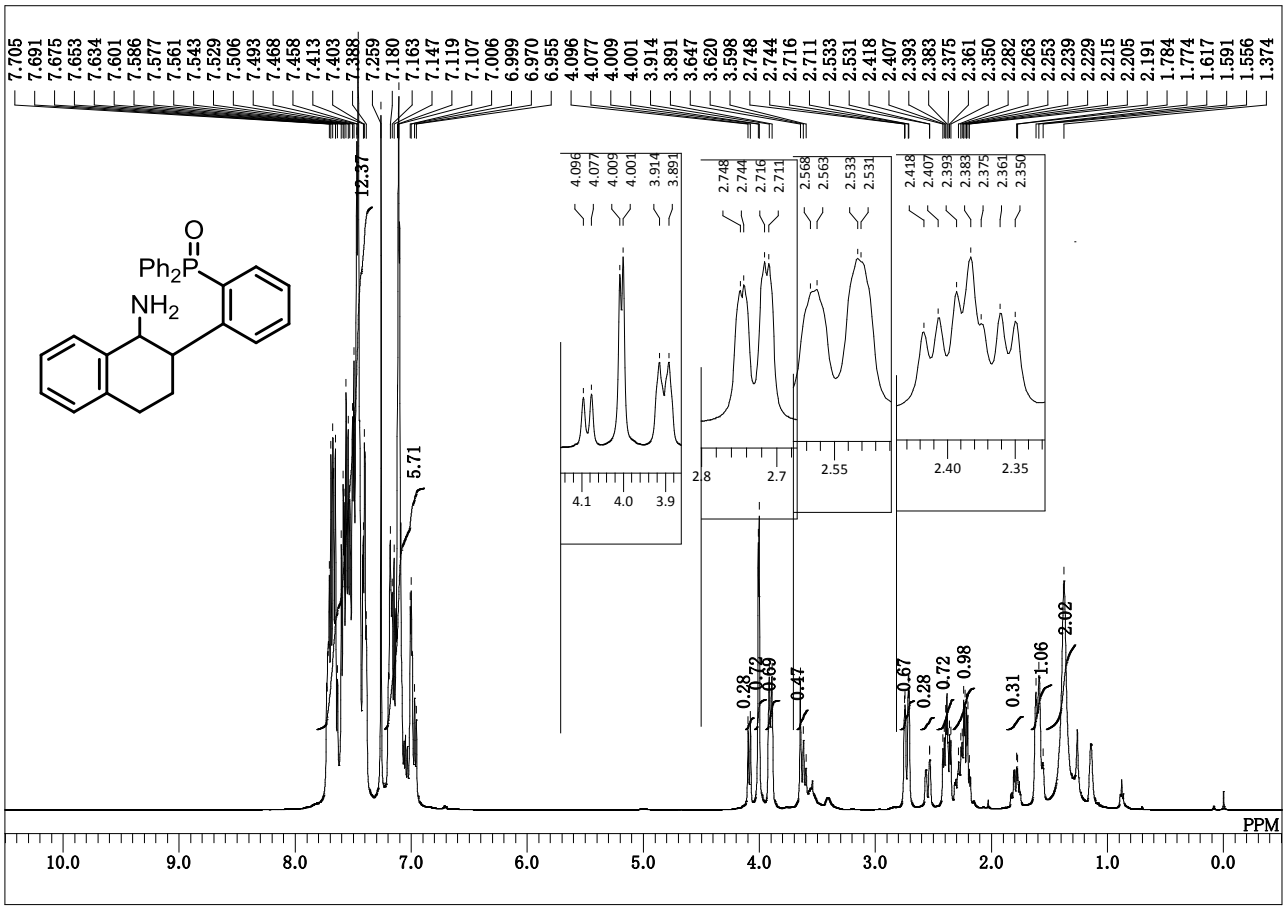
aminophos-trans-13C



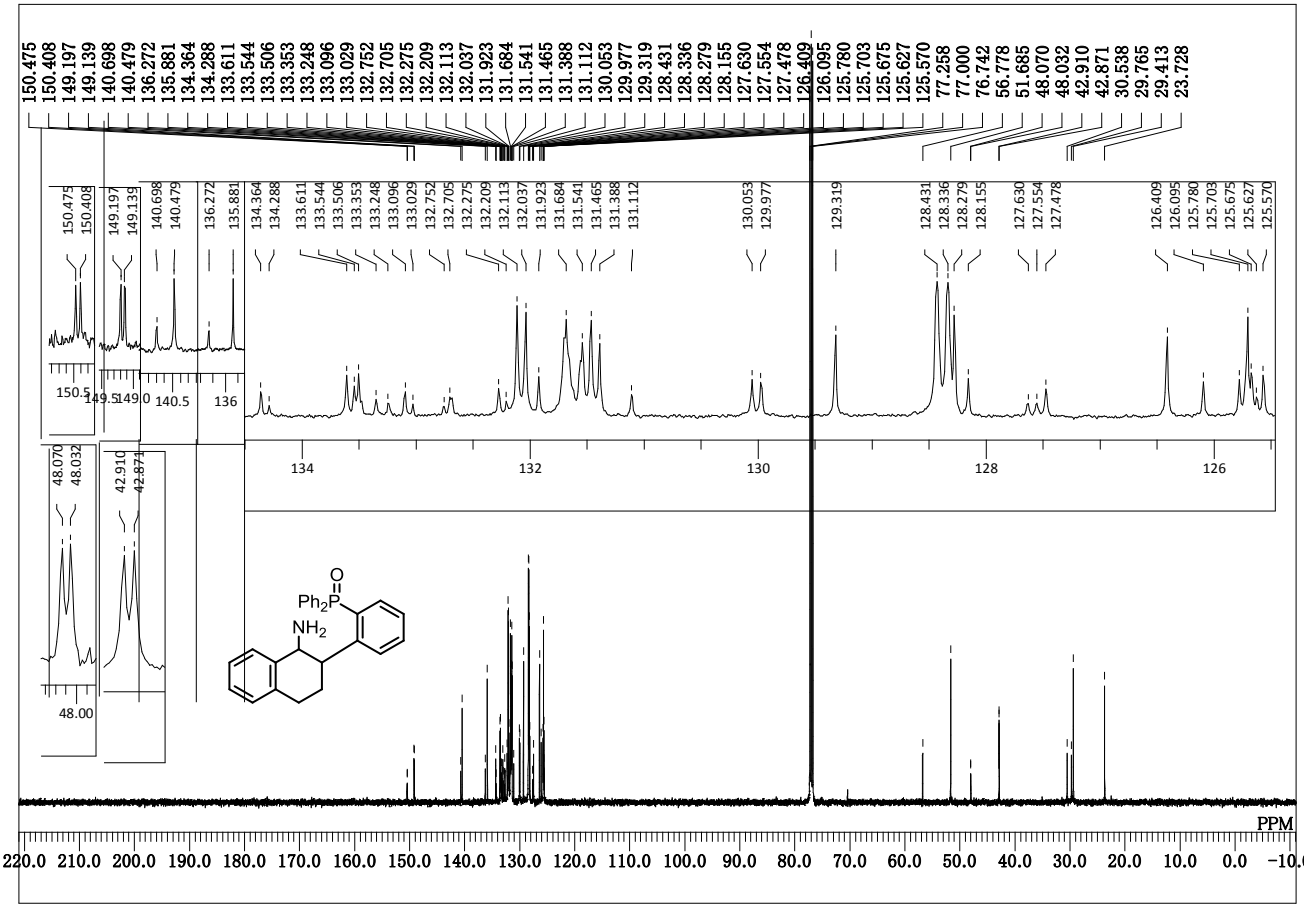
aminophos-trans-31P



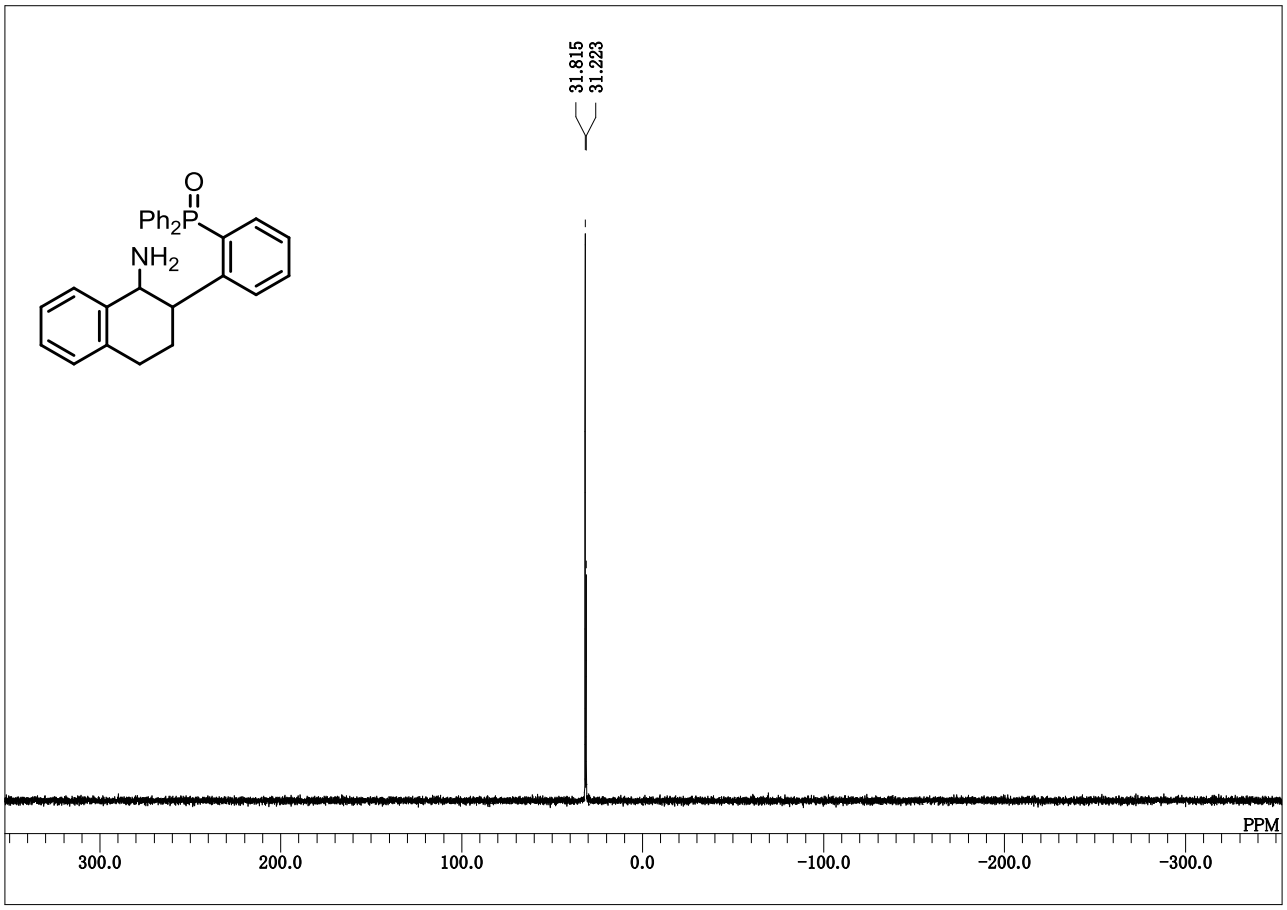
aminophosphine oxide mixture cis/trans-1H



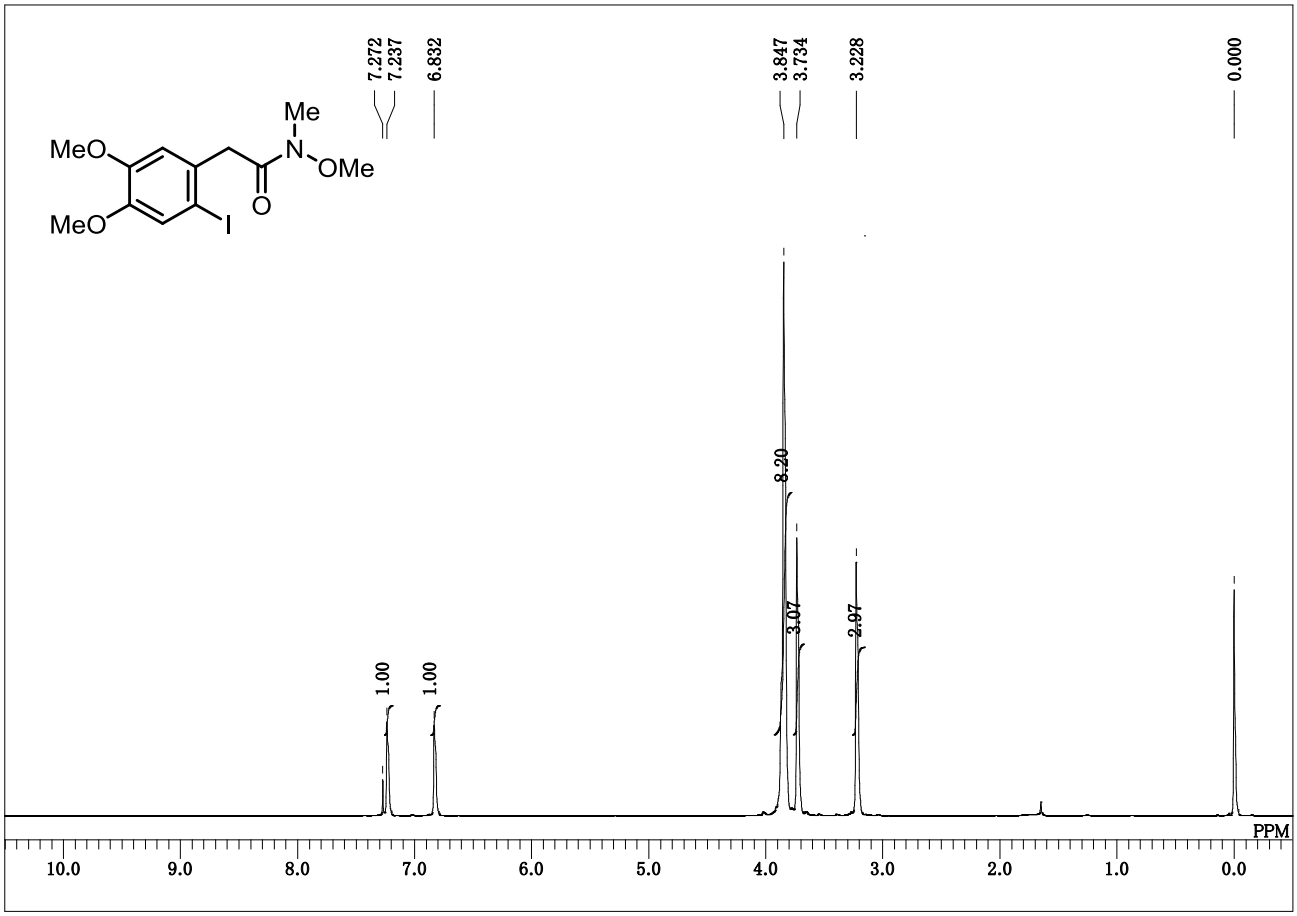
aminophosphine oxide mixture-cis/trans-13C



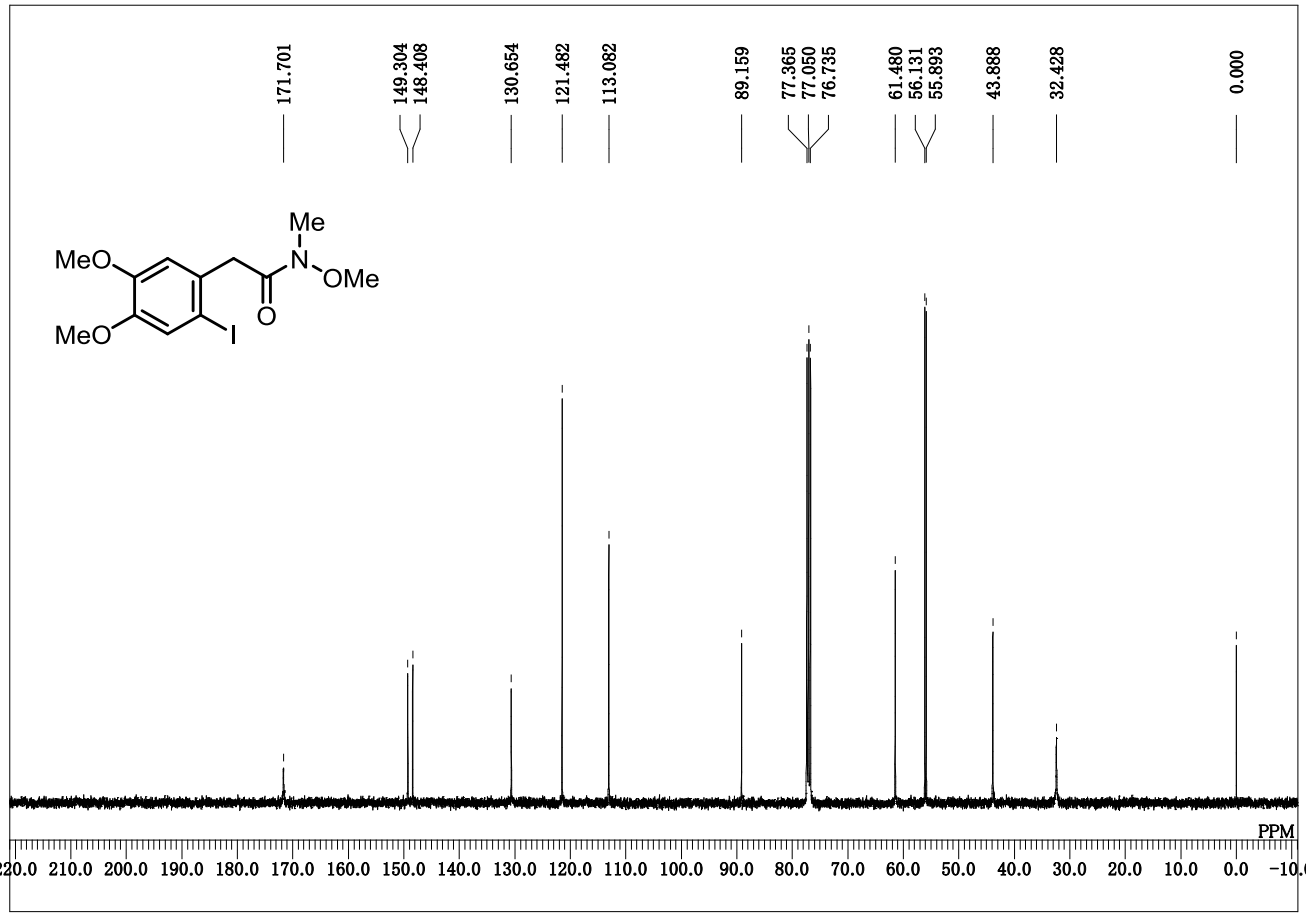
aminophosphineoxide-31p



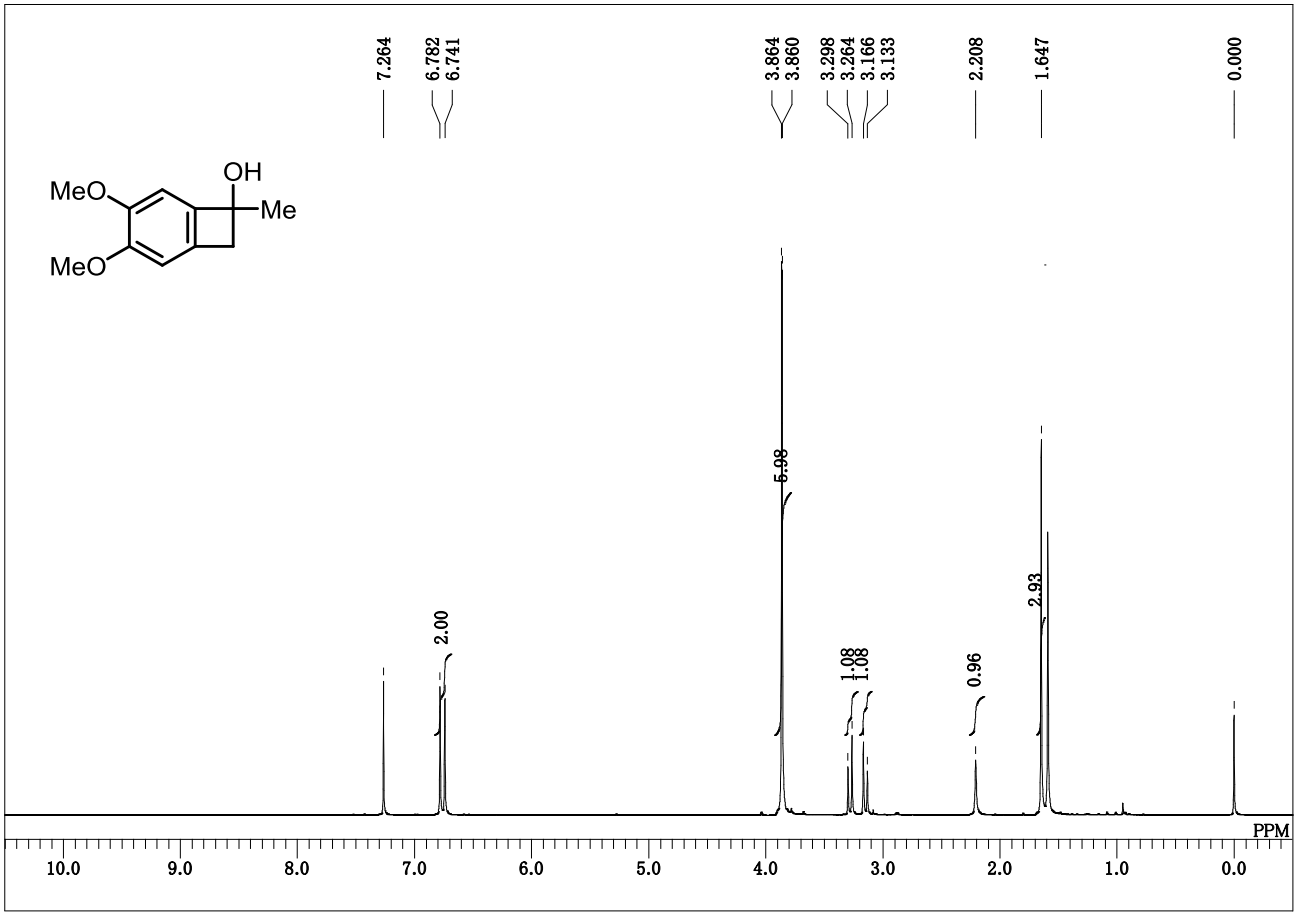
Iodobenzylamide-1H



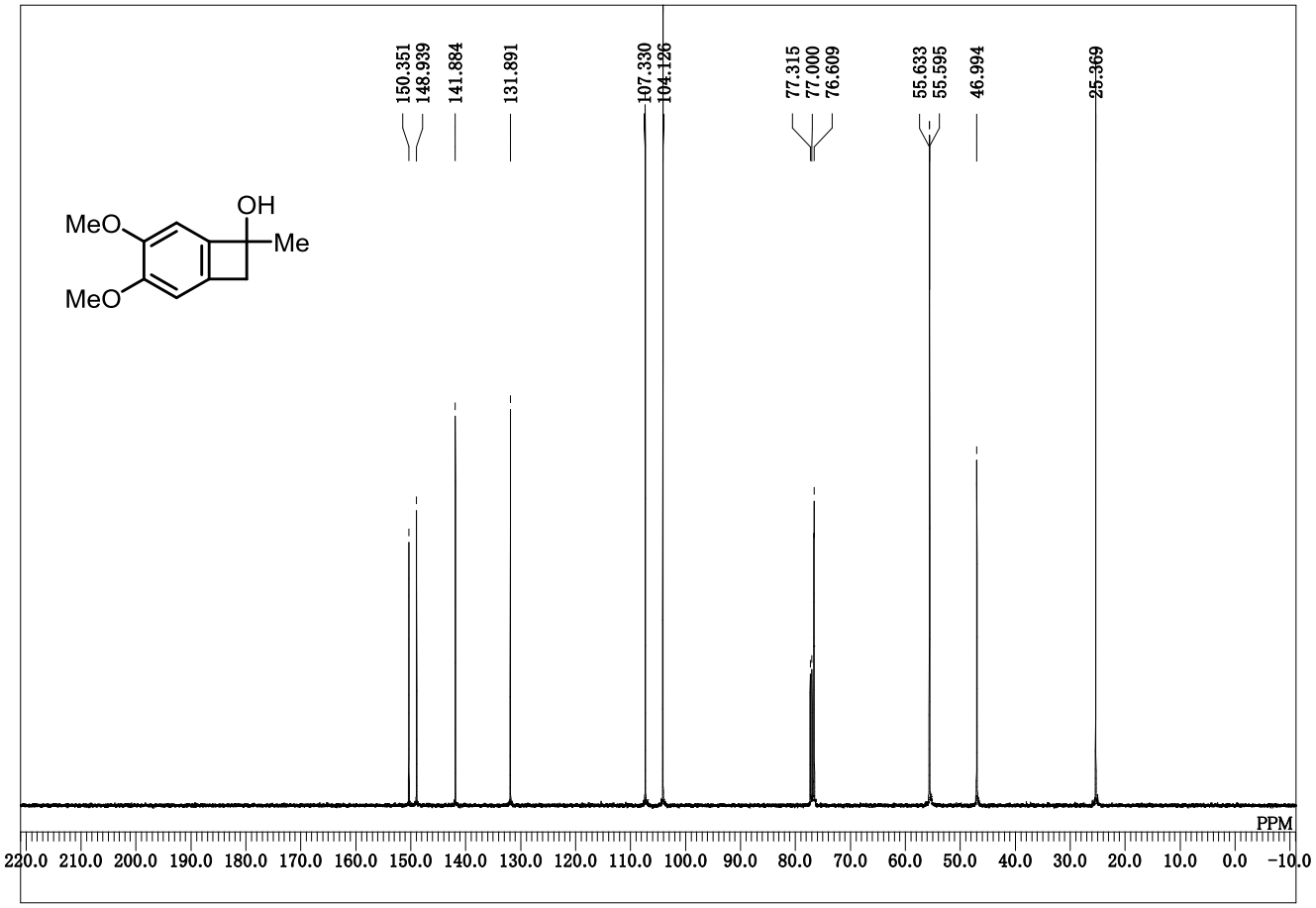
Iodobenzylamide-13C



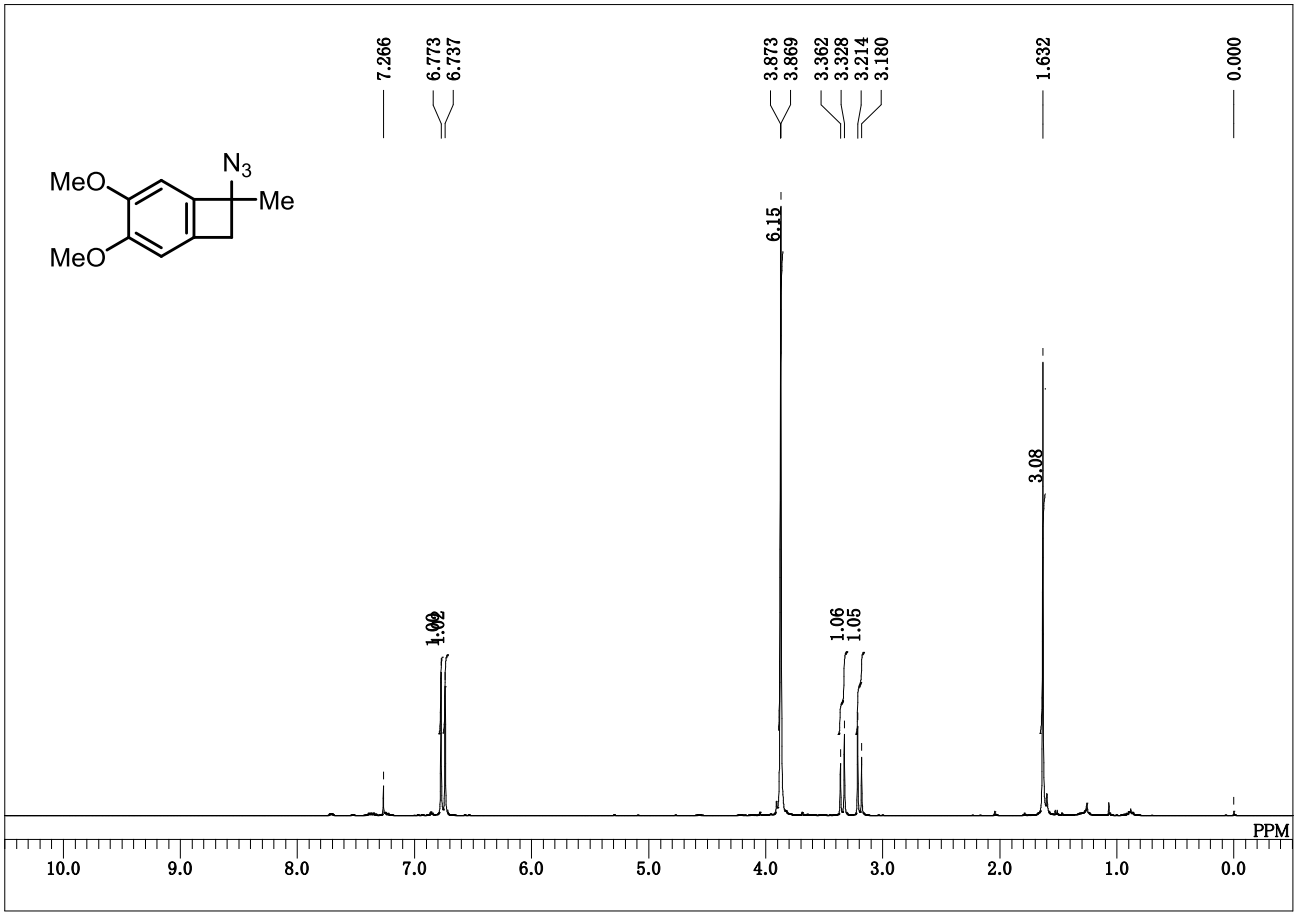
OH BCB Me-1H



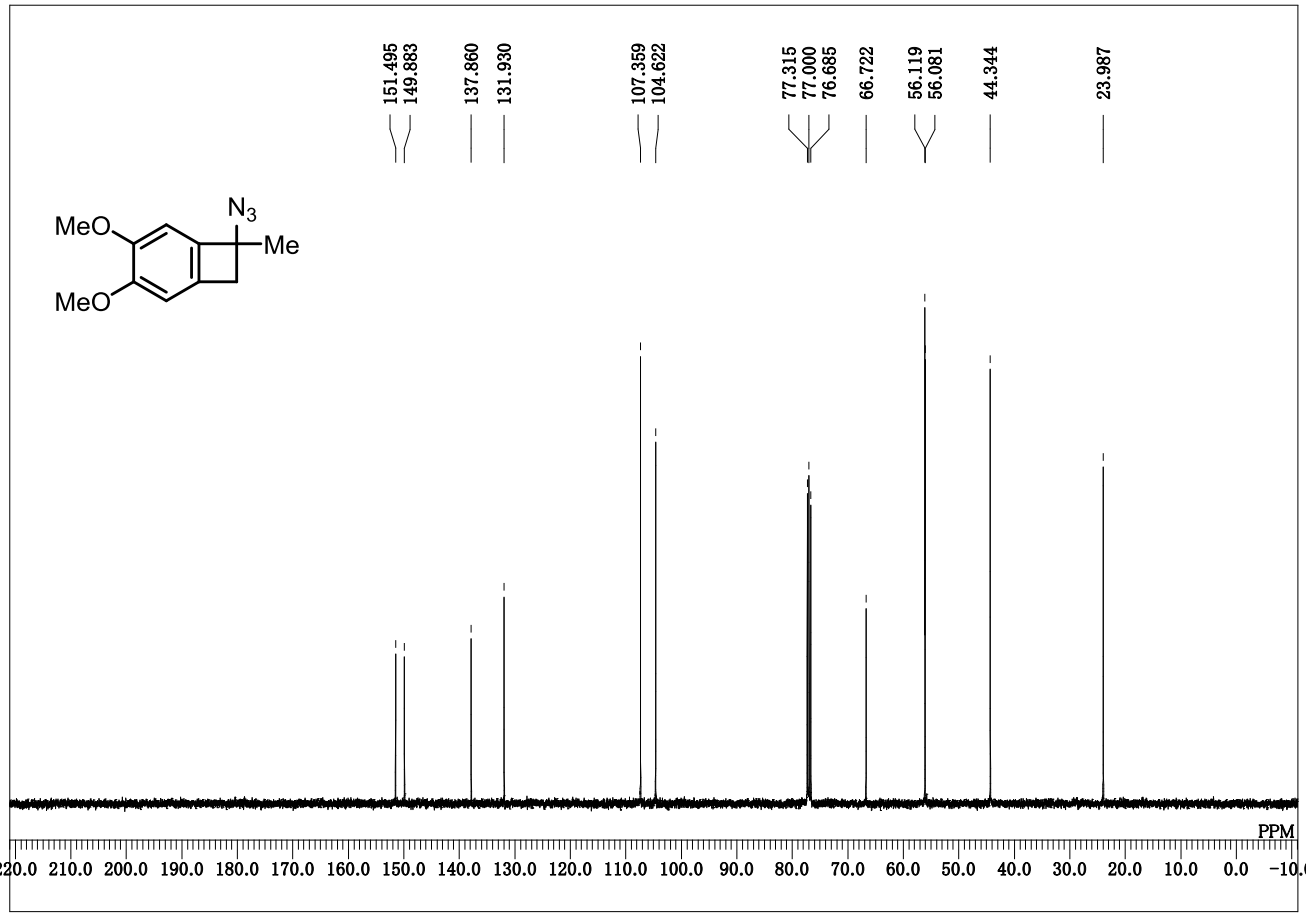
OH BCB Me-13C



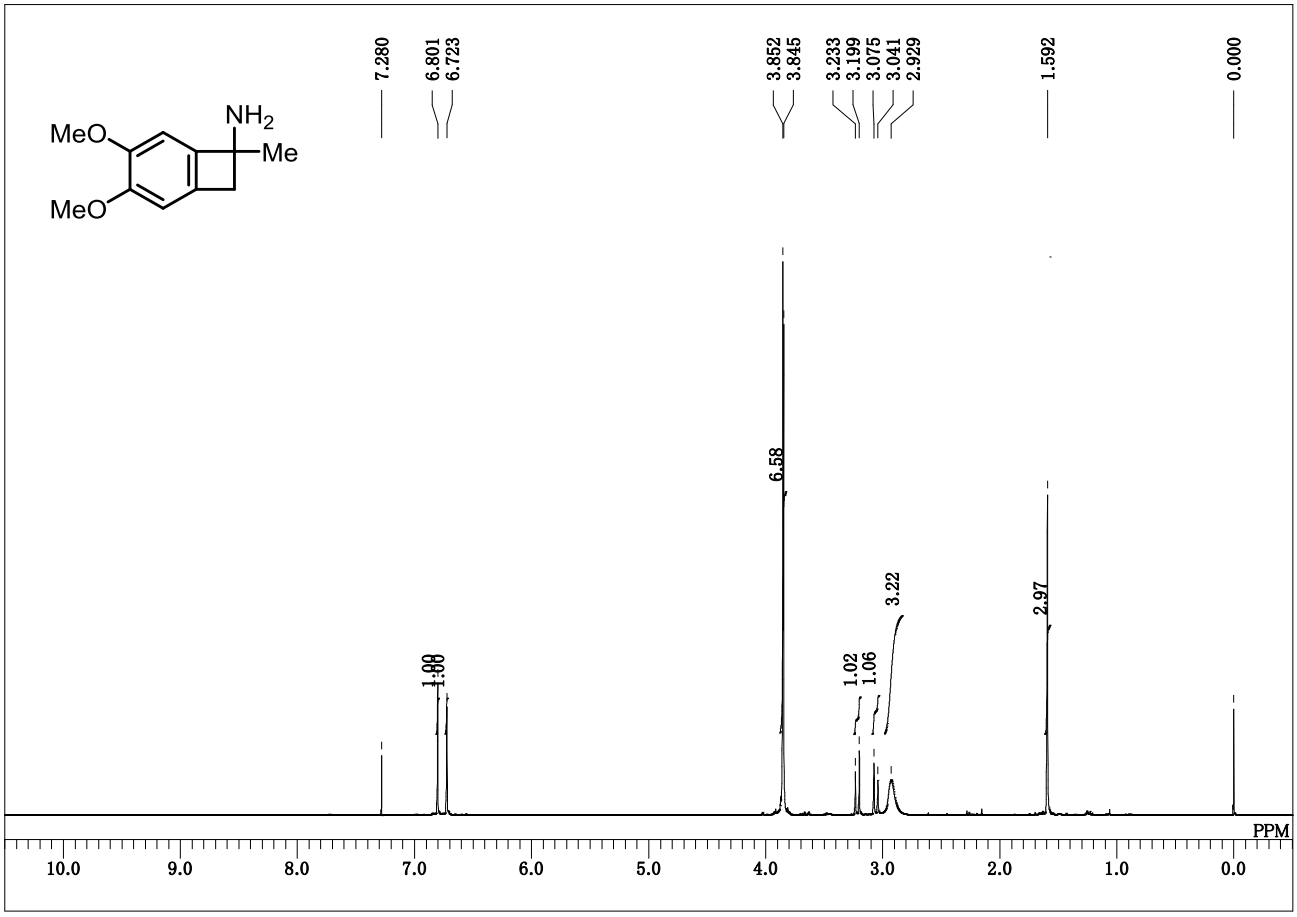
azide BCB Me 1H



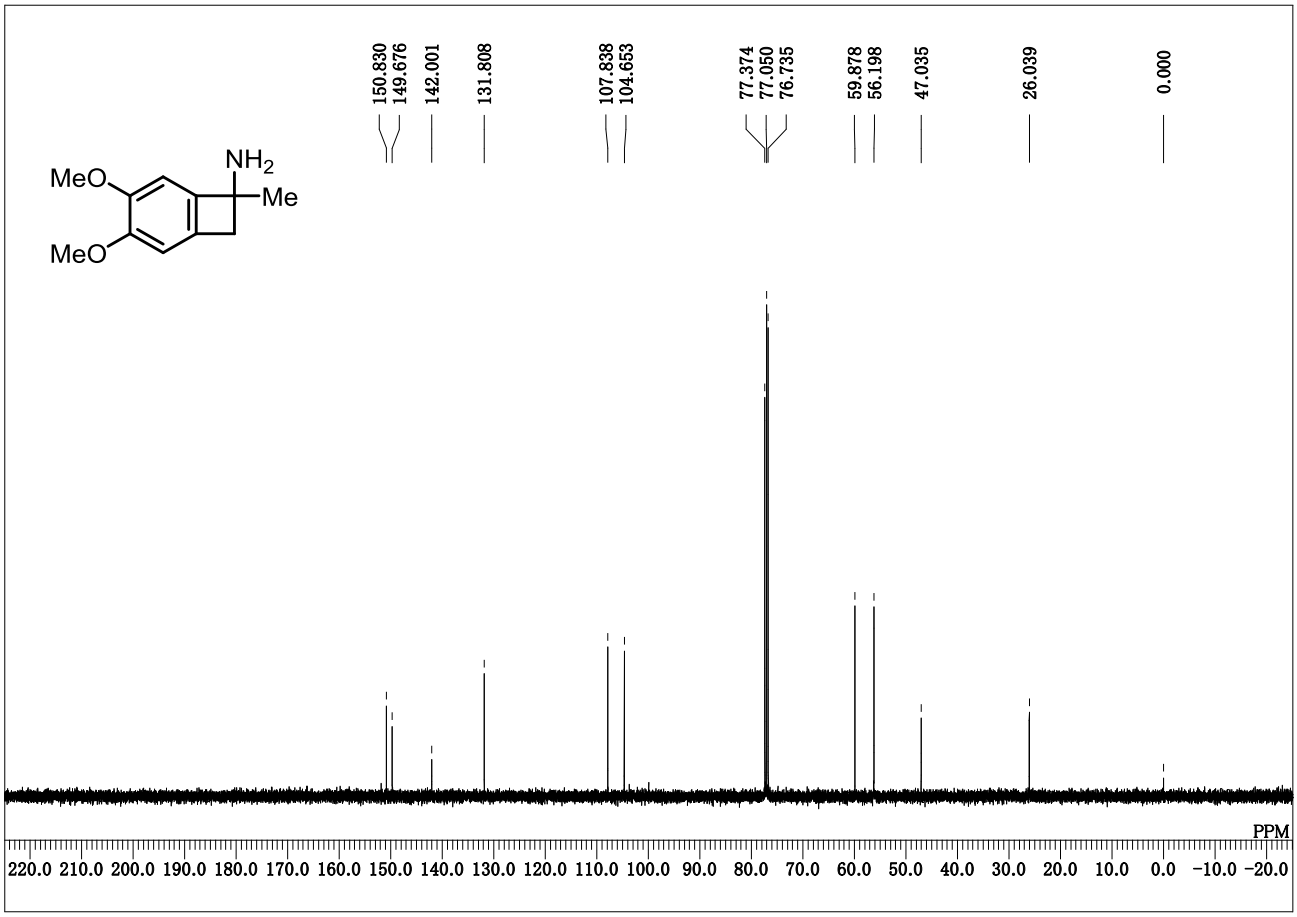
Azide BCB Me-13C



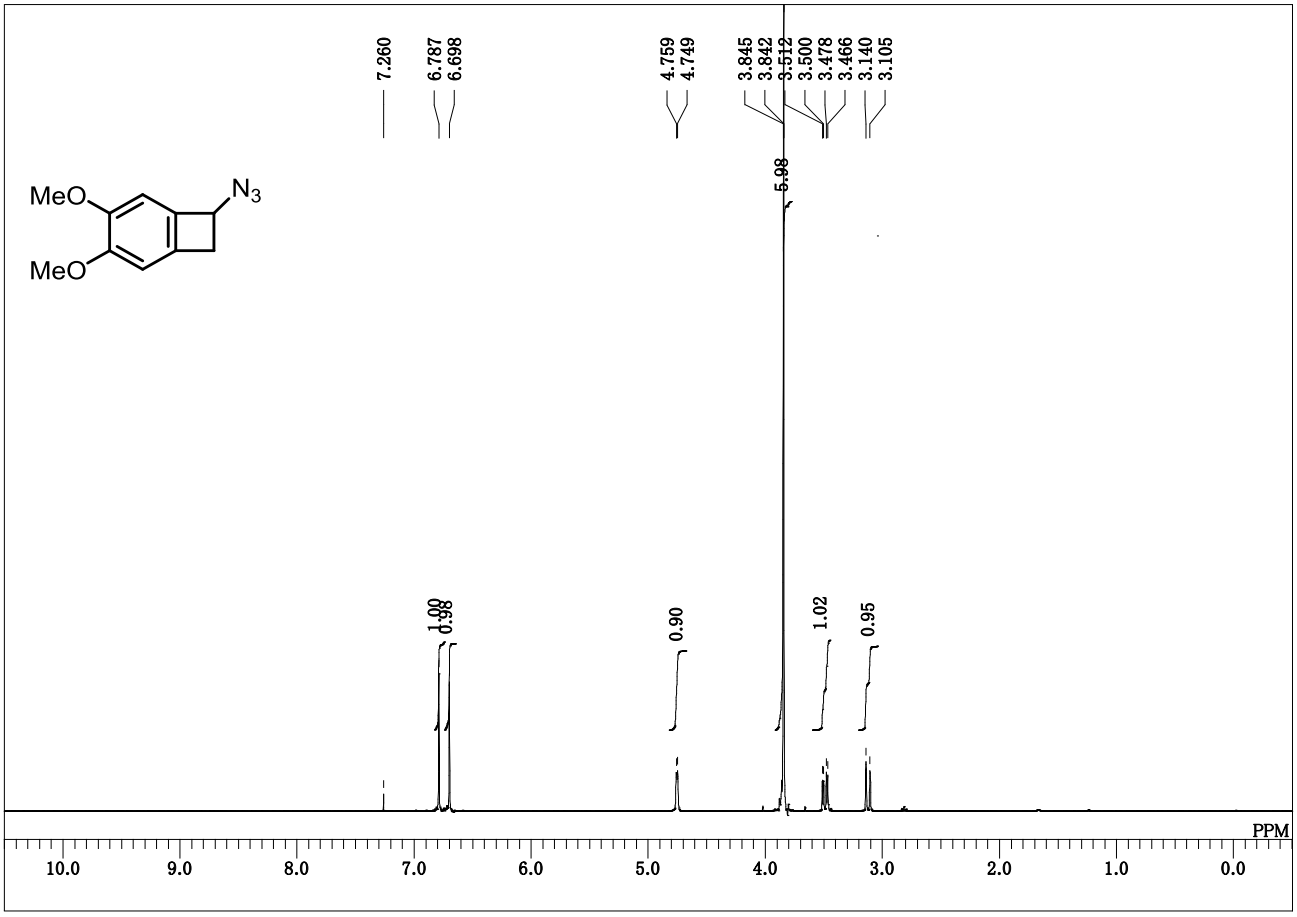
NH2 BCB Me-1H



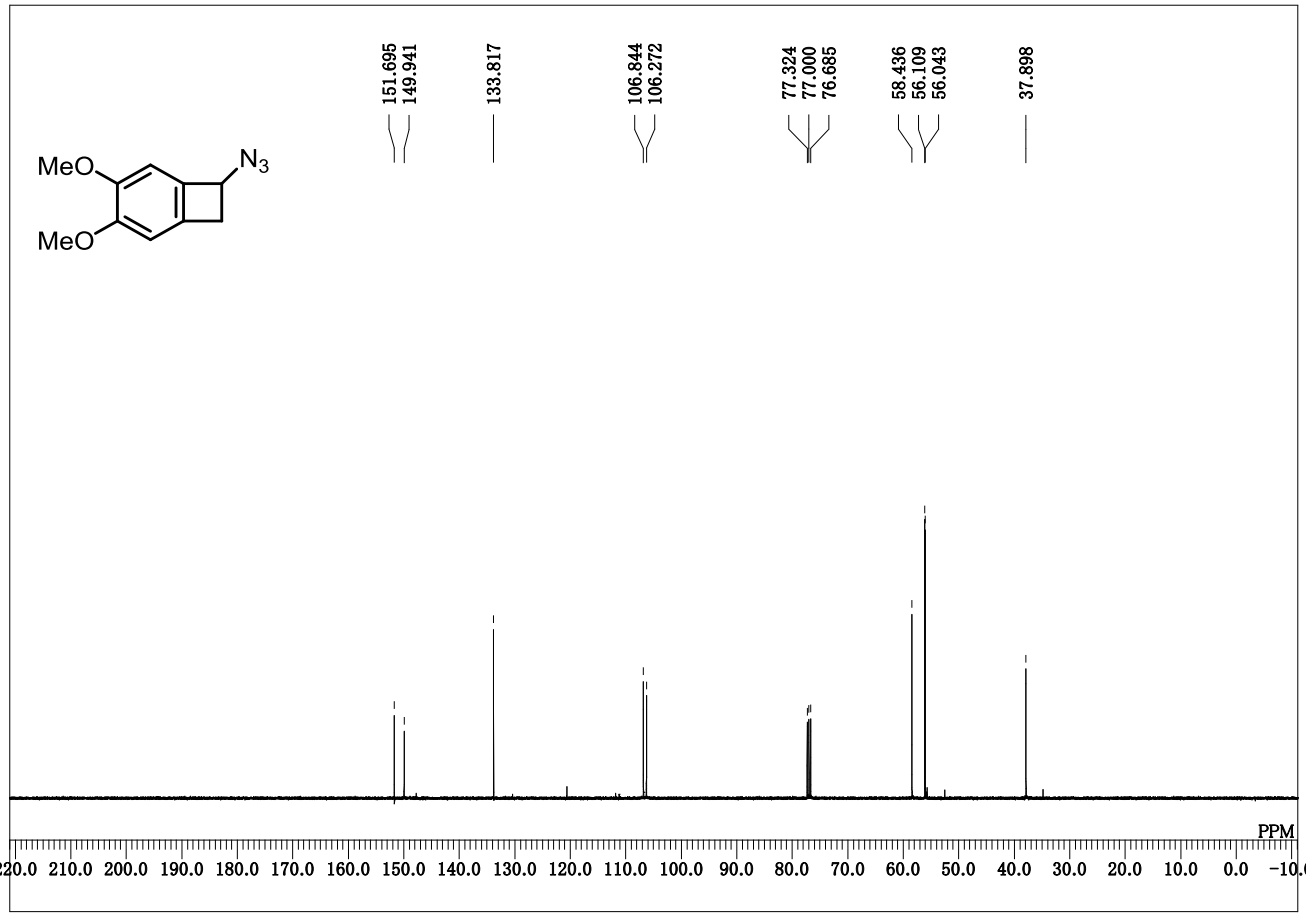
NH2 BCB Me-13C



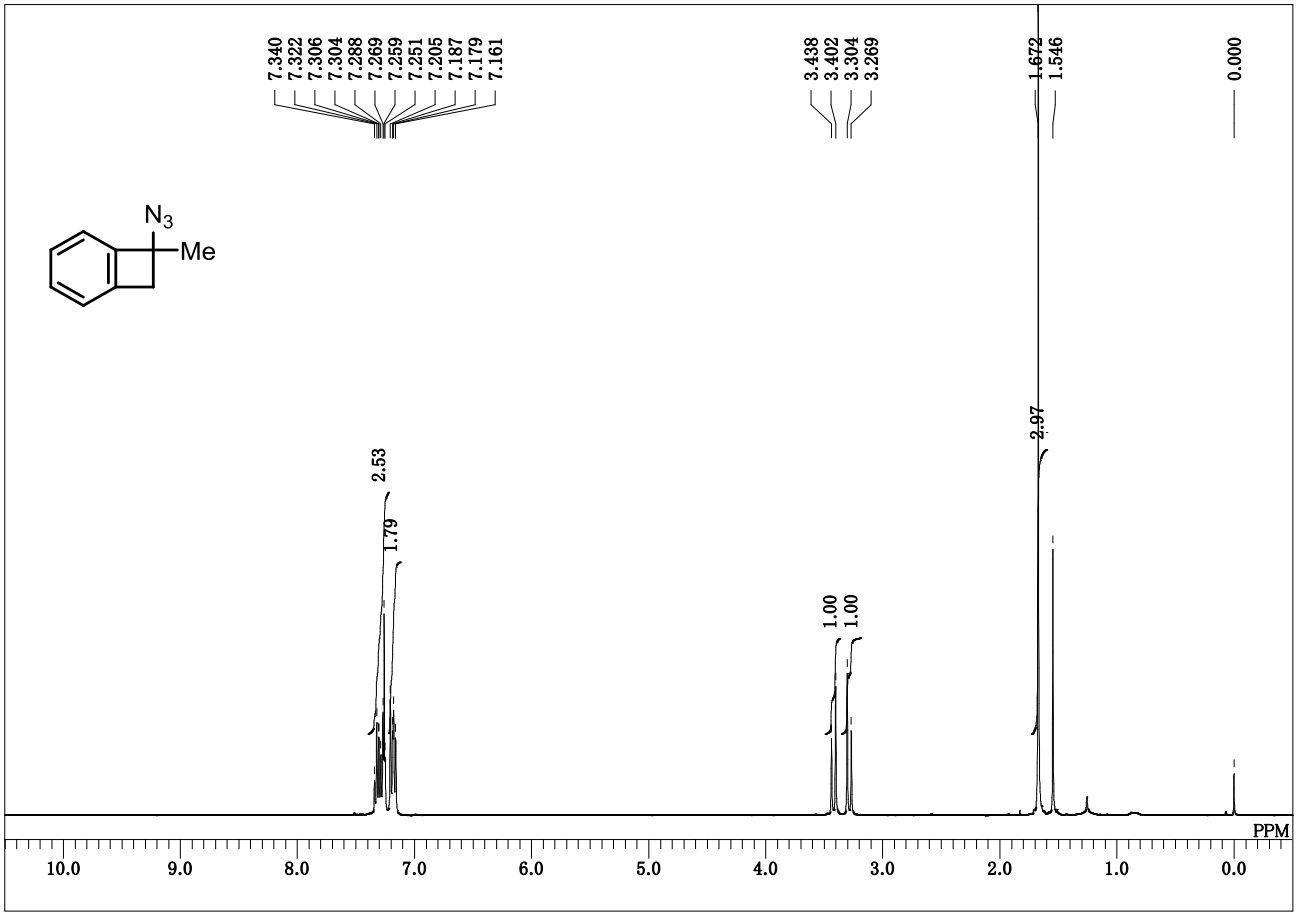
azide BCB-1H



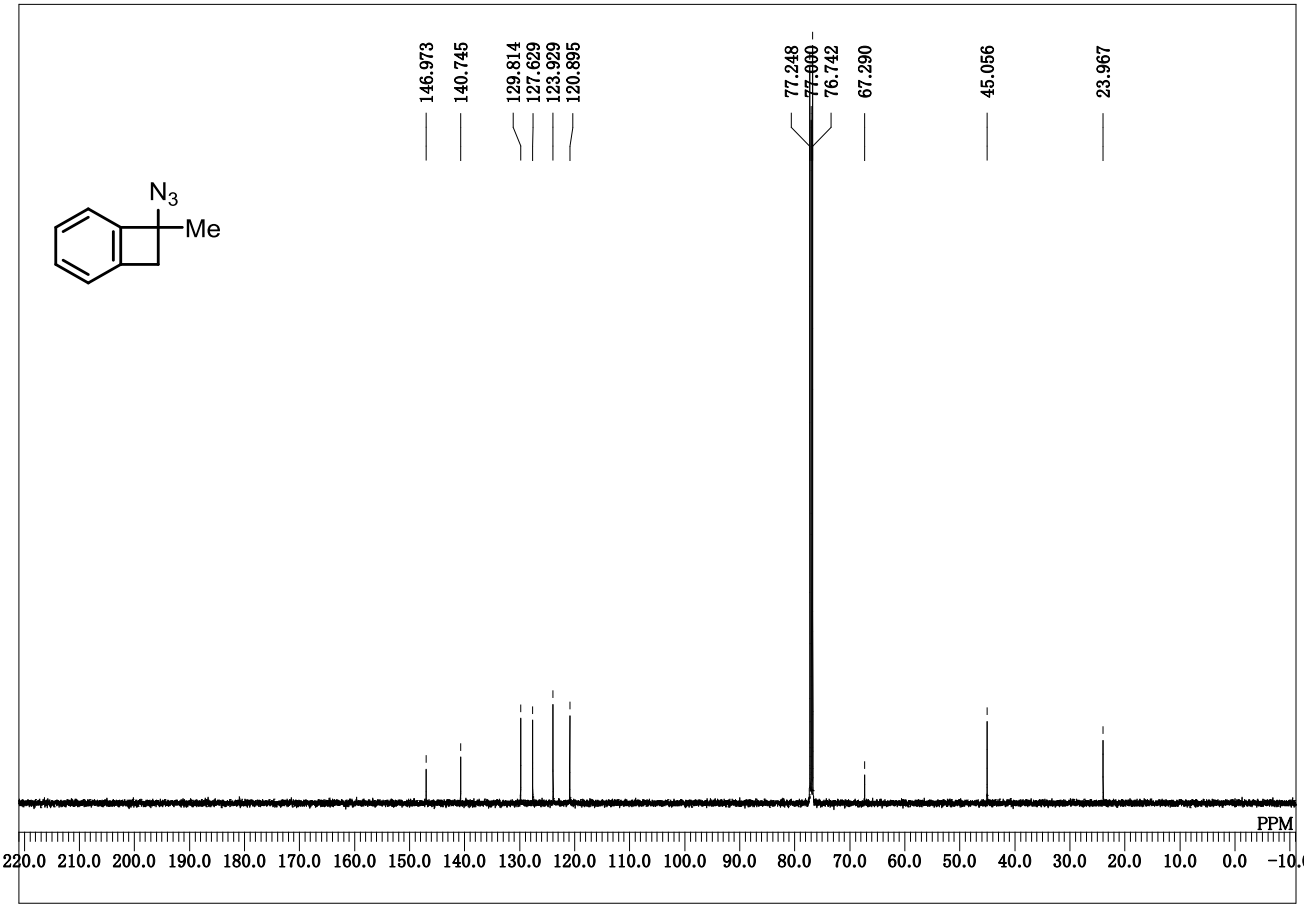
azide BCB-13C



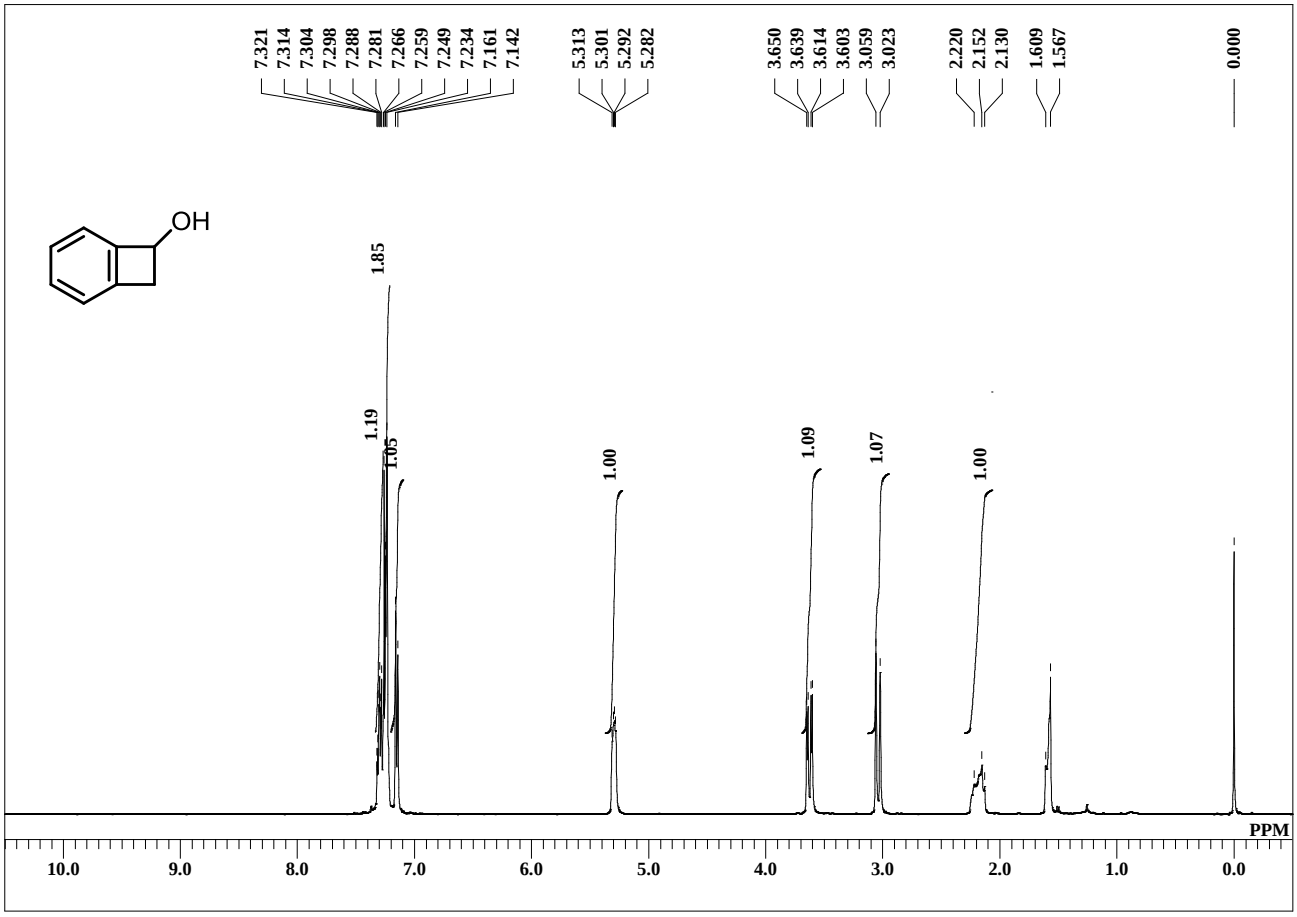
azide BCB 1c-1H



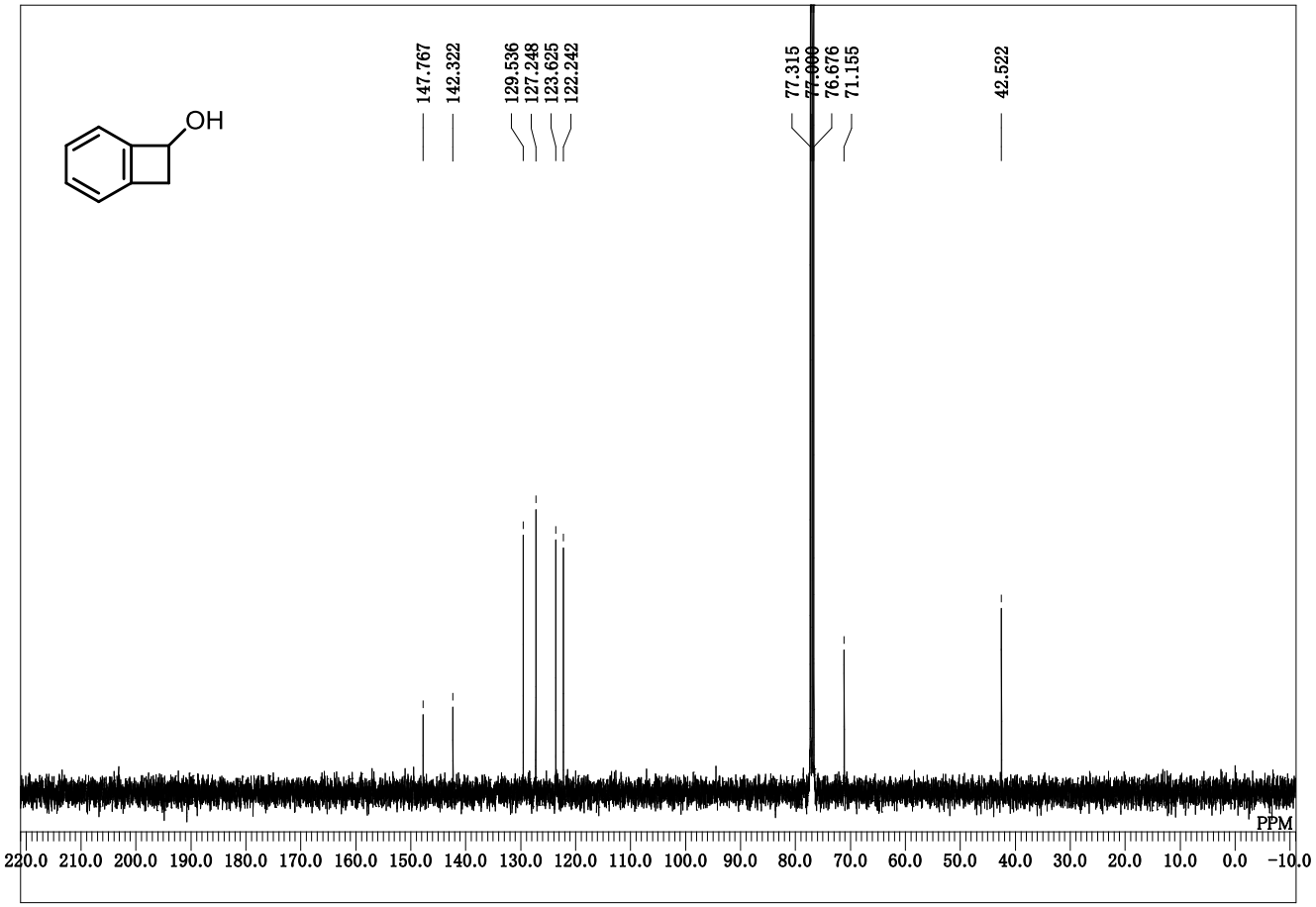
azide BCB 1c-13C



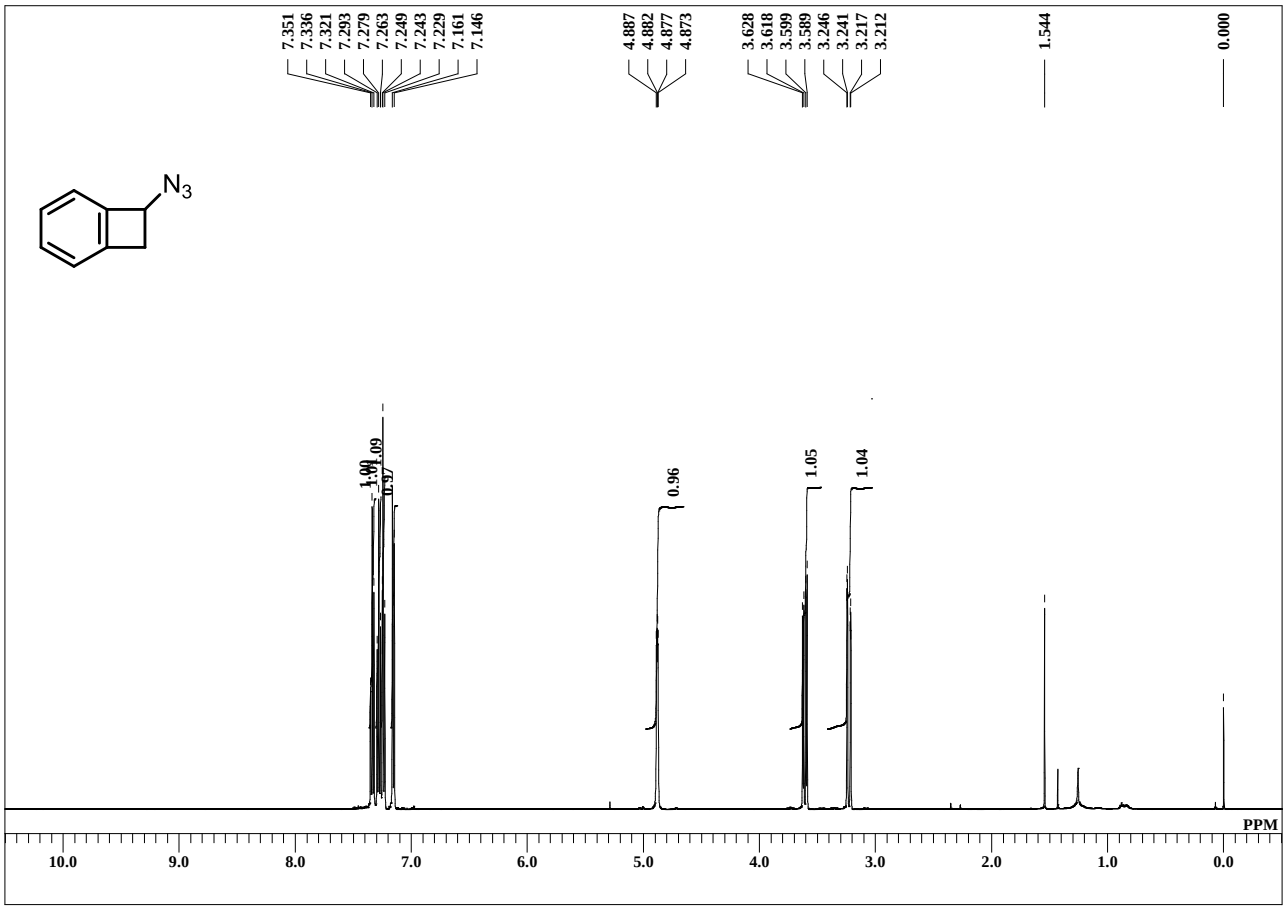
benzocyclobutenol-1H



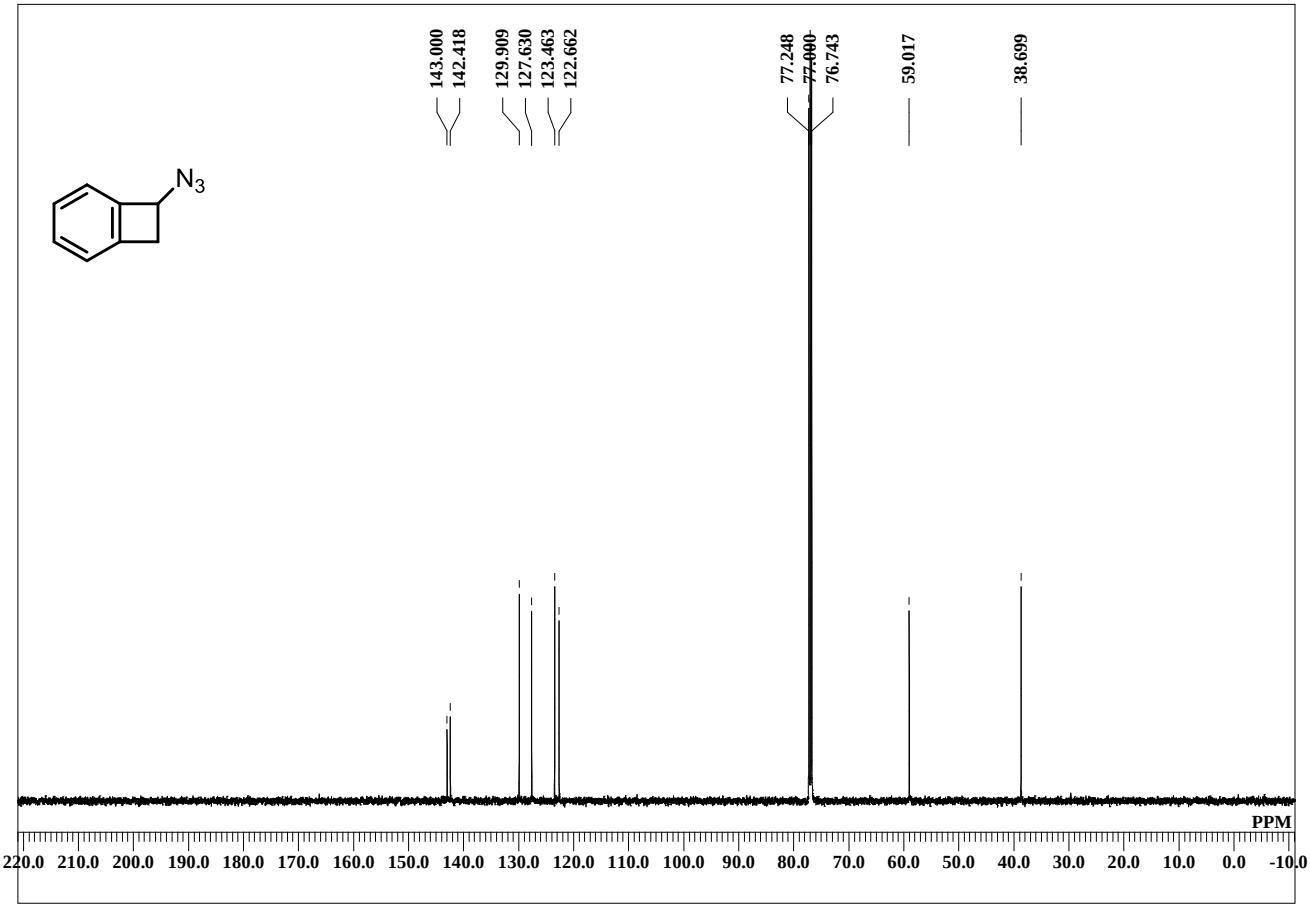
benzocyclobutenol-13C



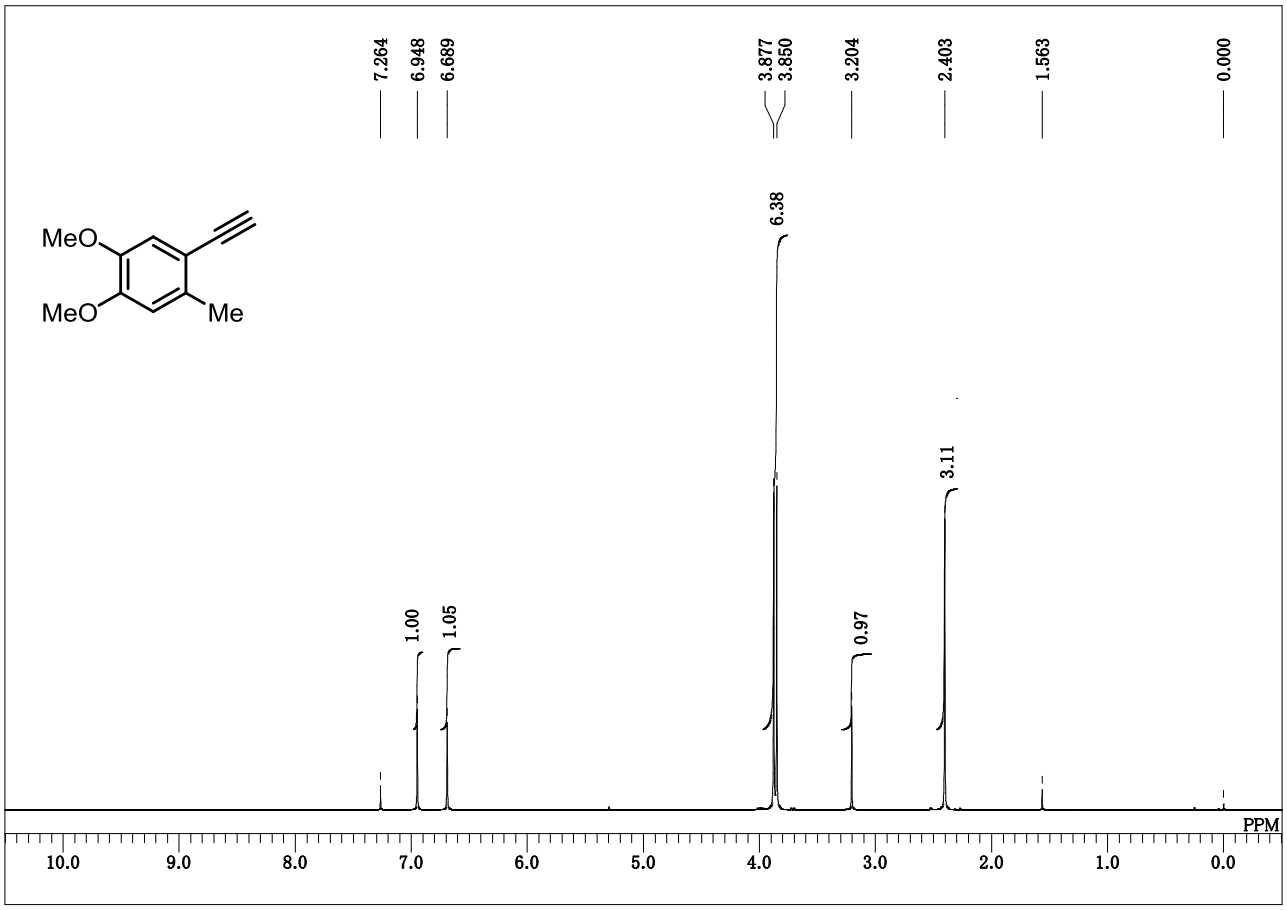
azide BCB 1d-1H



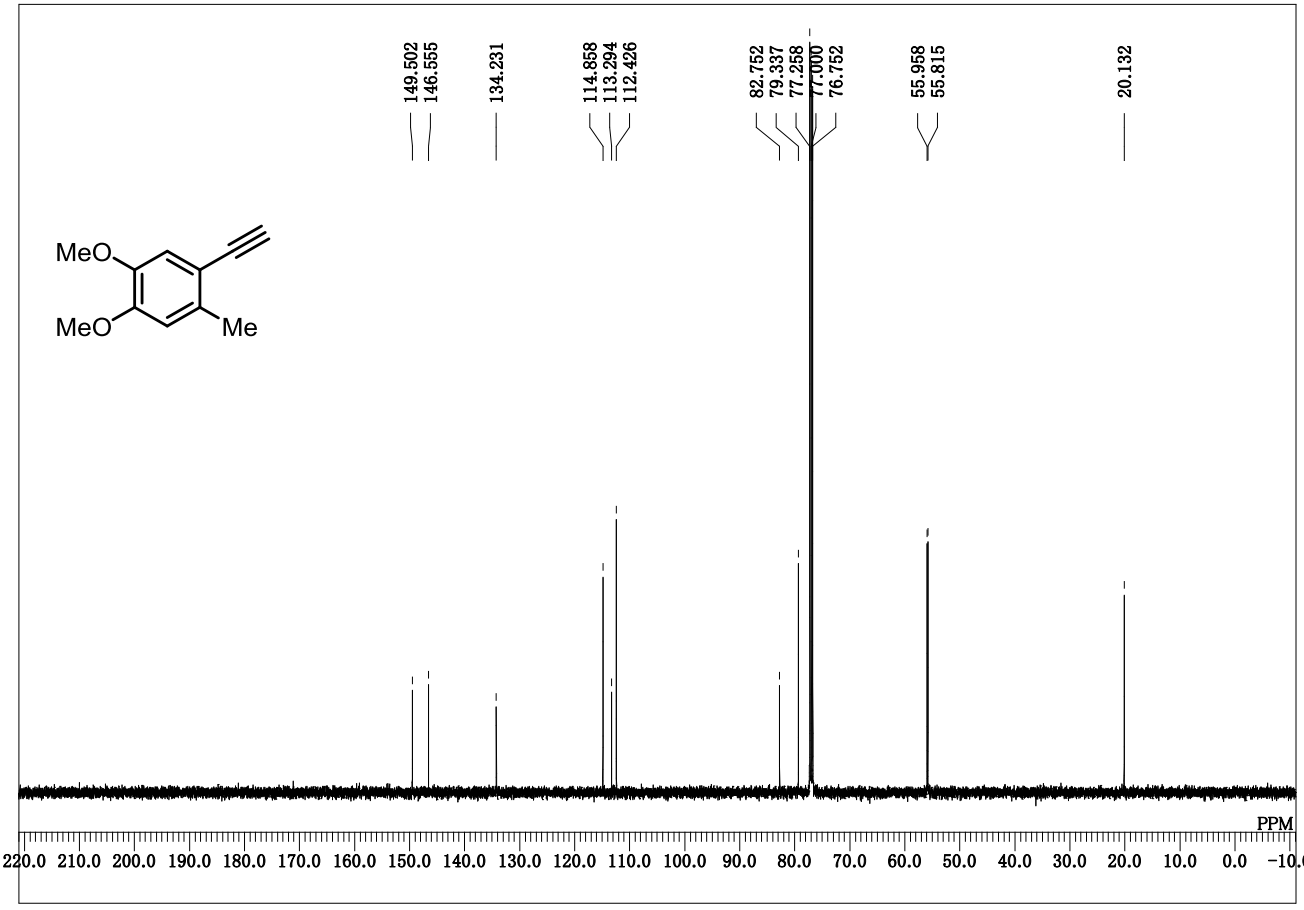
azide BCB 1d-13C



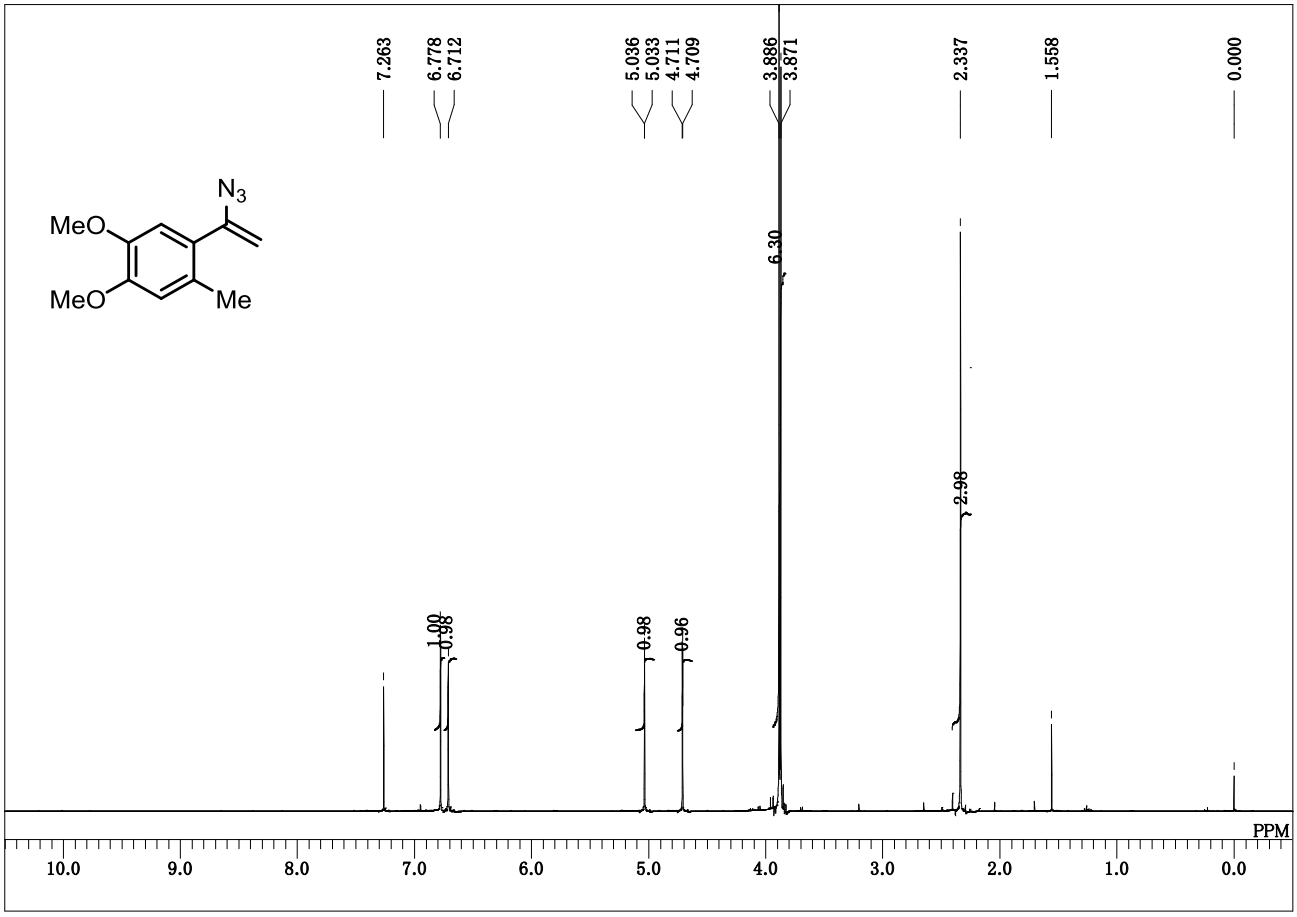
phenyl acetylene 1H



phenyl acetylene 13C



vinyl azide-1H



vinyl azide-13C