Electronic Supplementary Material (ESI) for Chemical Communications.

KO^{t}Bu-catalyzed lithiation of PMDTA and the direct functionalization of bridged alkenes under mild conditions

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Supporting Information

1. General Information

All the commercial reagents were used without further purification unless otherwise stated. Reaction solvents were all obtained from the Solvent Purification System. Glass flasks were dried in oven at 125 ^{o}C for at least 3 h before use. All the reactions were carried out under a positive pressure of argon or nitrogen. Organic solutions were concentrated under reduced pressure on a rotary evaporator.

Flash chromatography was performed on silica gel 100-200 vm. The solvent system was used as petroleum ether/EA, increasing in polarity to EA. Thin layer chromatography (TLC) was performed on glass backed plates pre-coated with silica (GF254), which were developed using standard visualizing agents.

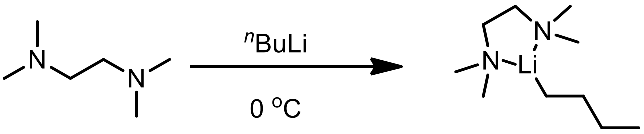
^{1}H-NMR spectra were recorded on a 400 MHz spectrometer. Chemical shifts are reported in ppm with internally referenced to residual protic $CDCl_3$ (δ 7.26 ppm) unless stated. Data are reported as follows: chemical shift, multiplicity (s =singlet, d = doublet, t = triplet, q = quartet, br = broad, m = multiplet, sept = sepetet), integration, coupling constants (*J*) in Hz. ^{13}C-NMR spectra were recorded on a 400 MHz (101 MHz) spectrometer with complete proton decoupling. Data are reported in ppm in terms of chemical shifts relative to $CDCl_3$ (δ 77.0 ppm) unless stated. High-resolution mass spectra (HRMS) recorded for accurate mass analysis, were performed on a Q-TOF micro spectrometer.

2. Experimental Section

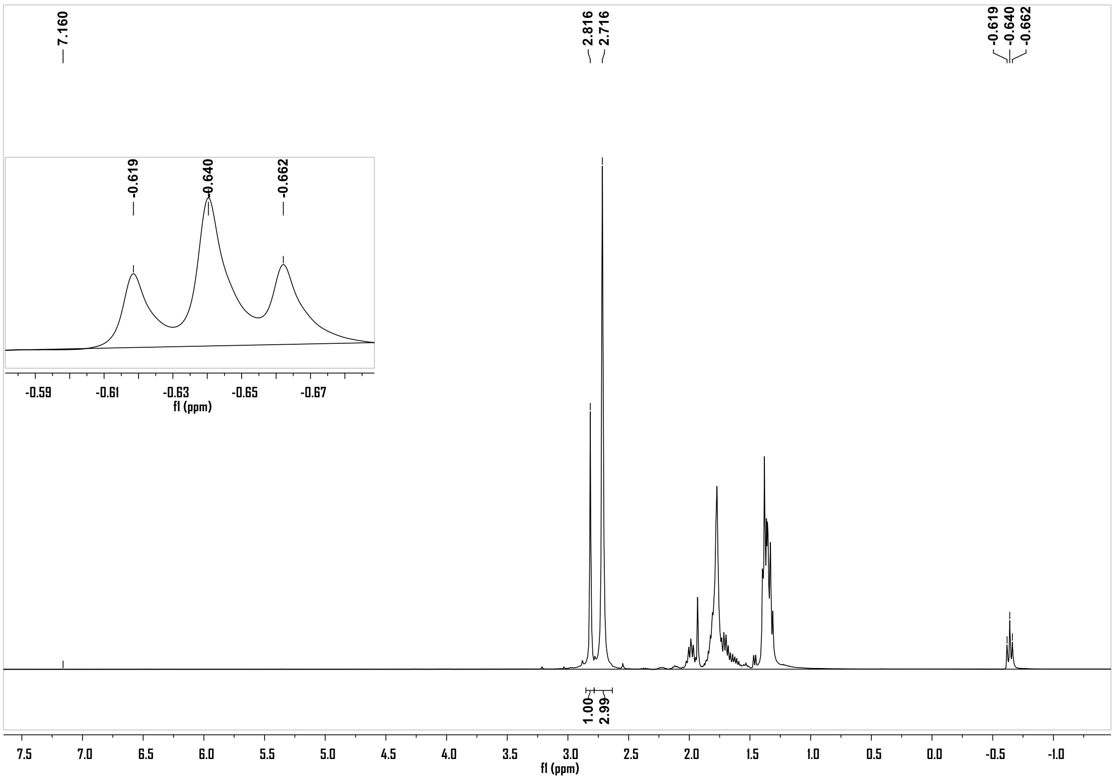
2.1 NMR Studies of organolithium reagents

All the NMR samples were prepared in NMR tubes with glass capillary tubes containing C_6D_6 and sealed with parafilm in the glovebox. All the NMR spectroscopic data were collected at room temperature.

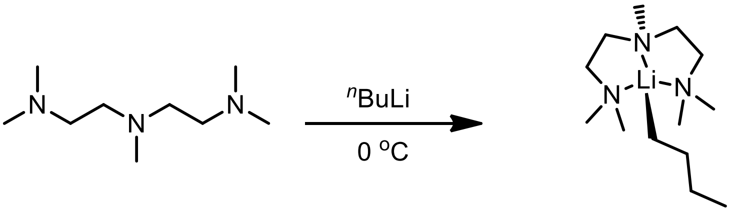
2.1.1 ^{1}H NMR of ^{n}BuLi + TMEDA



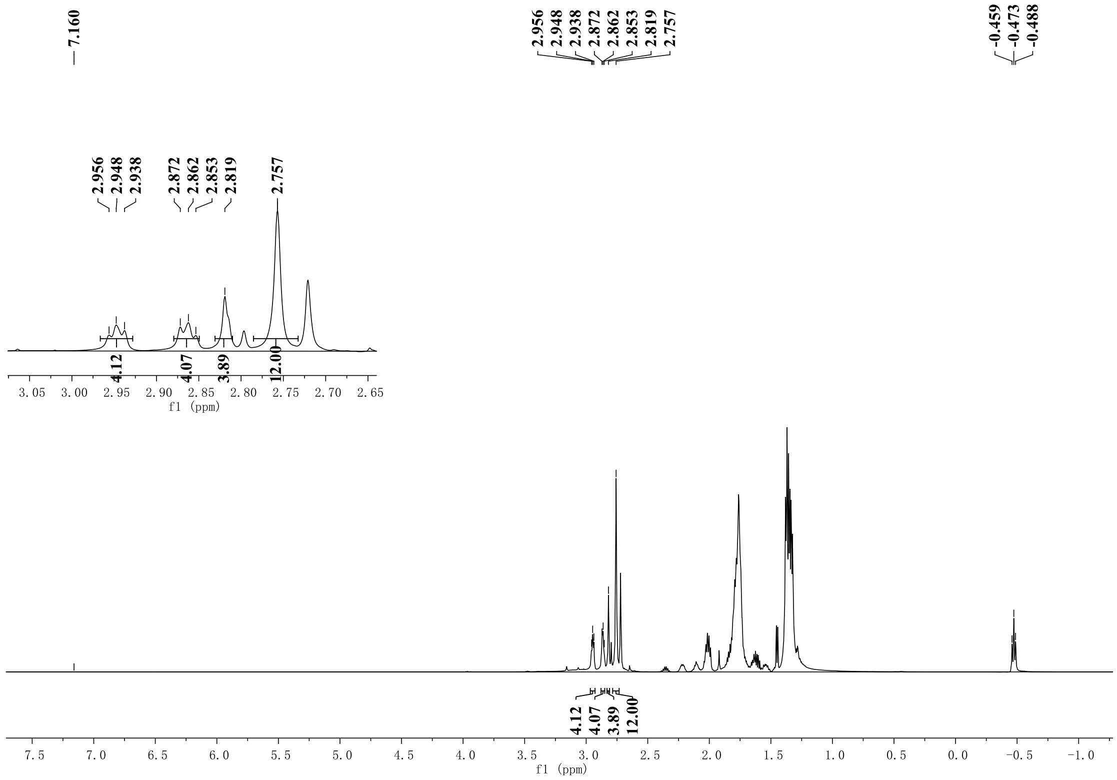
A 10 mL well-dried round-bottomed flask with a solution of TMEDA (116 mg, 1 mmol) in n-hexane (1.0 mL), ^{n}BuLi (c = 2.4 mol/L in hexanes, 0.625 mL, 1.5 equiv.) was added dropwise at 0 °C, stirred for 30 min. The ^{1}H NMR spectrum is shown below.

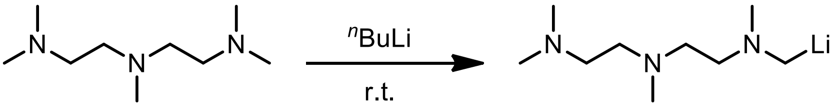


21.2 Prepare and NMR Studies of PMDTALi

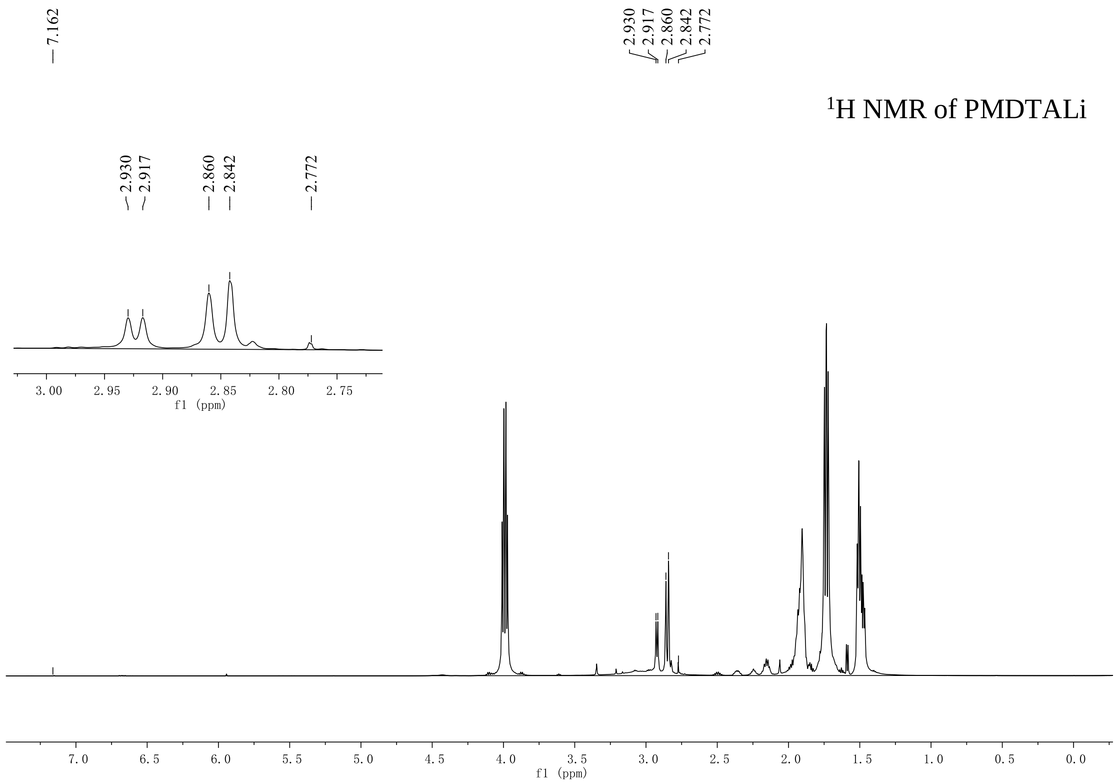


A 10 mL well-dried round-bottomed flask with a solution of PMDTA (173 mg, 1mmol) in n-hexane (1 mL), ^{n}BuLi (c = 2.4 mol/L in hexanes, 0.625 mL, 1.5 equiv.) was added dropwise at 0 °C temperature, stirred 1 h at 0 °C. The ^{1}H NMR spectrum is shown below.

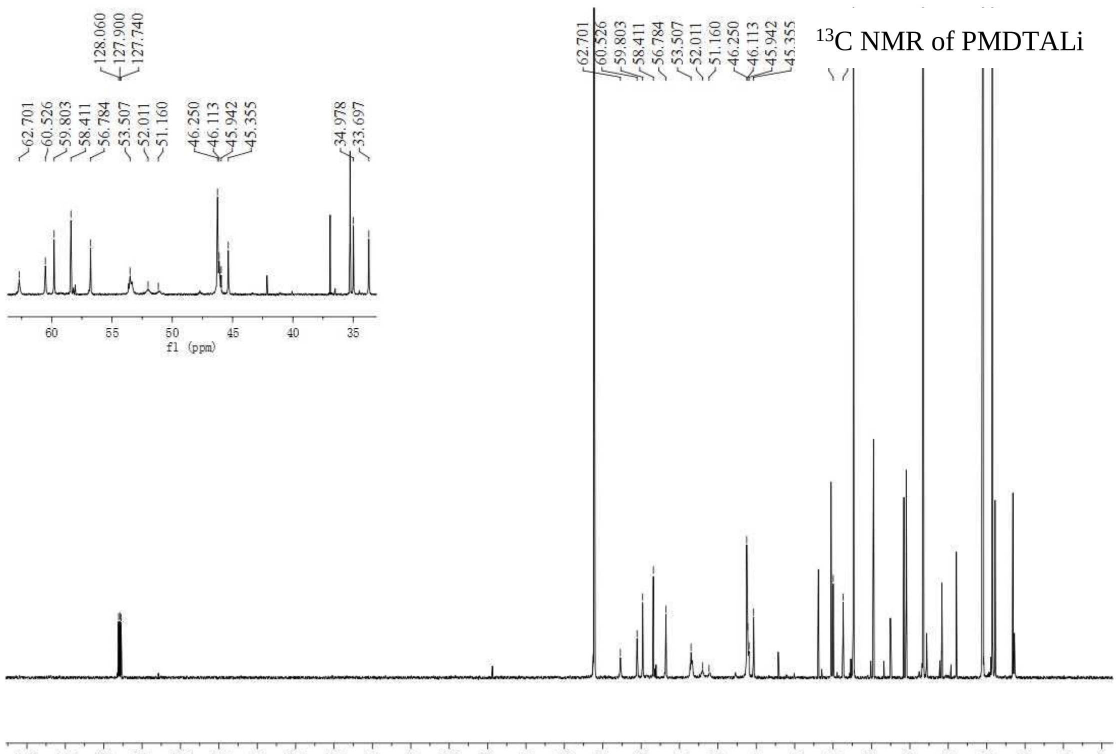




A 10 mL well-dried round-bottomed flask with a solution of PMDTA (173 mg, 1 mmol) in diethyl ether (1 mL), ^{n}BuLi (c = 2.4 mol/L in hexanes, 0.625 mL, 1.5 equiv.) was added dropwise at 0 ^{o}C, stirred 1 h at room temperature, The ^{1}H, ^{13}C and ^{7}Li NMR spectra are shown below.

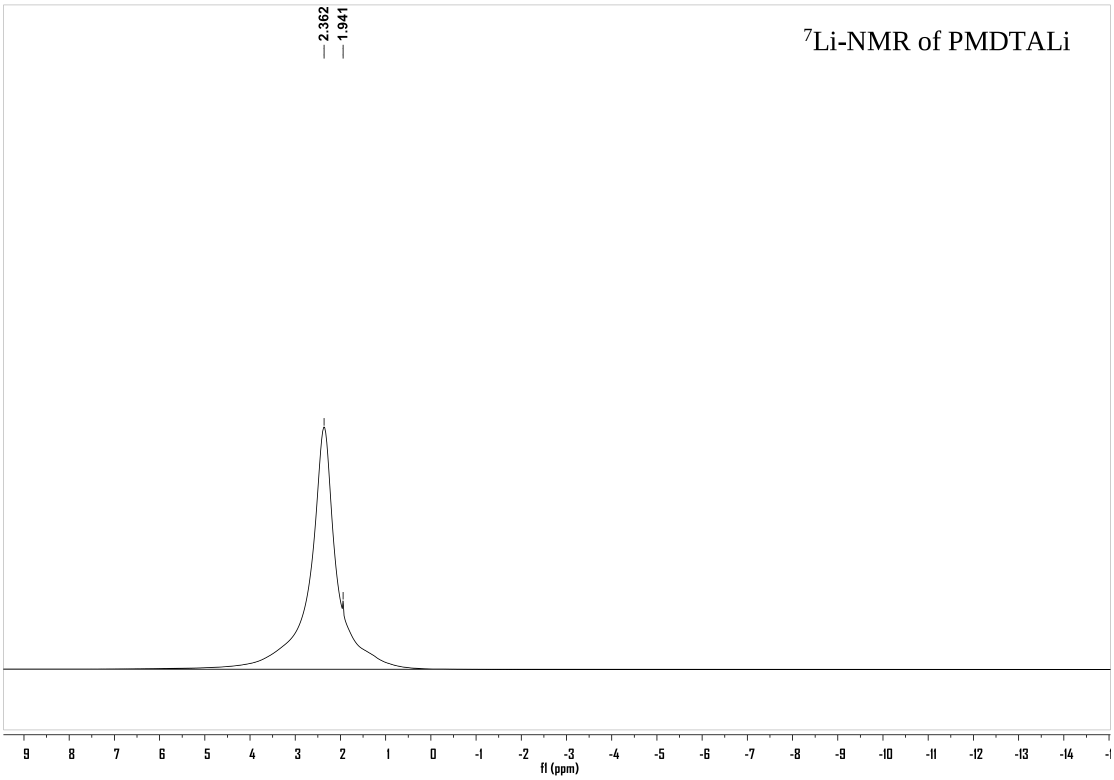


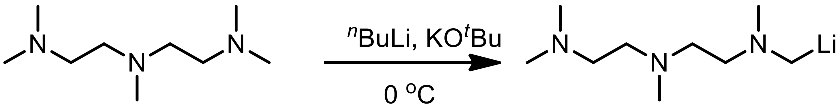
^{1}H NMR of PMDTALi



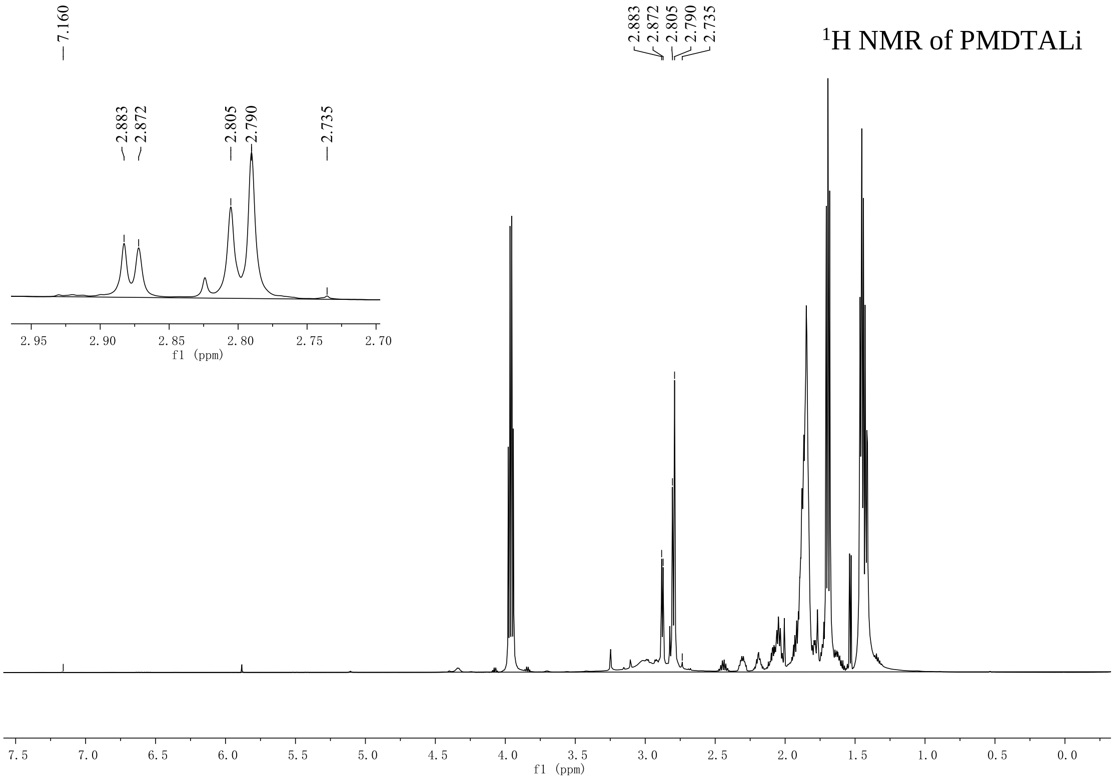
^{13}C NMR of PMDTALi

^{13}C NMR (151 MHz, C_6D_6) δ 62.70 (NCH_2, A), 60.53 (NCH_2, B), 59.80 (NCH_2, A+B), 58.41 (NCH_2, B), 56.78 (N(2)Me, A), 53.51 (N(2)Me, B), 52.01 (NCH_2, A), 51.16 (NCH$_2$, B), 46.25 (N(3)Me, A), 46.11 (N(3)Me$_2$, B), 45.94 (N(1)Me, B), 45.36 (N(1)Me, A), 34.98 (N(3)Me$_2$, A or B), 33.70 (N(3)Me$_2$, B or A).

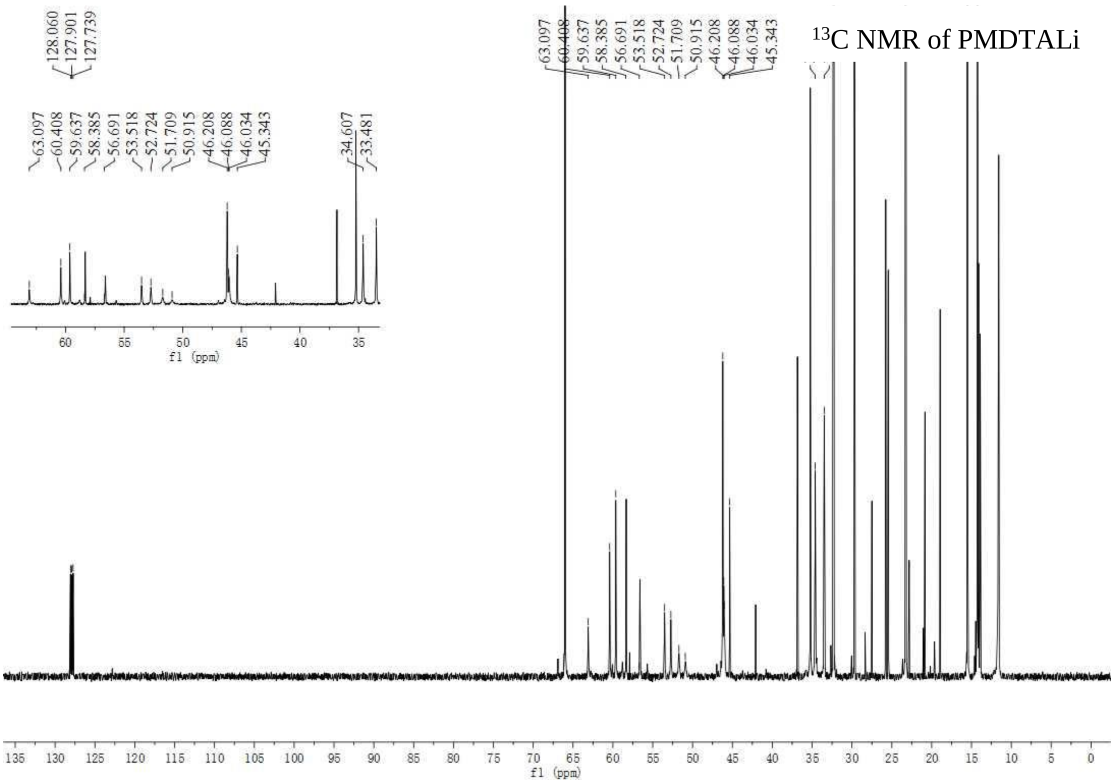




A 10 mL well-dried round-bottomed flask was transferred to the glovebox, to a solution of PMDTA (173 mg, 1 mmol), KO*t*Bu (28 mg, 0.25 equiv.) in diethyl ether (1.0 mL), *n*BuLi (c = 2.4 mol/L in hexanes, 0.625 mL, 1.5 equiv.) was added dropwise and stirred at 0 ^{o}C for 1 h. The ^{1}H, ^{13}C and ^{7}Li NMR spectra are shown below.

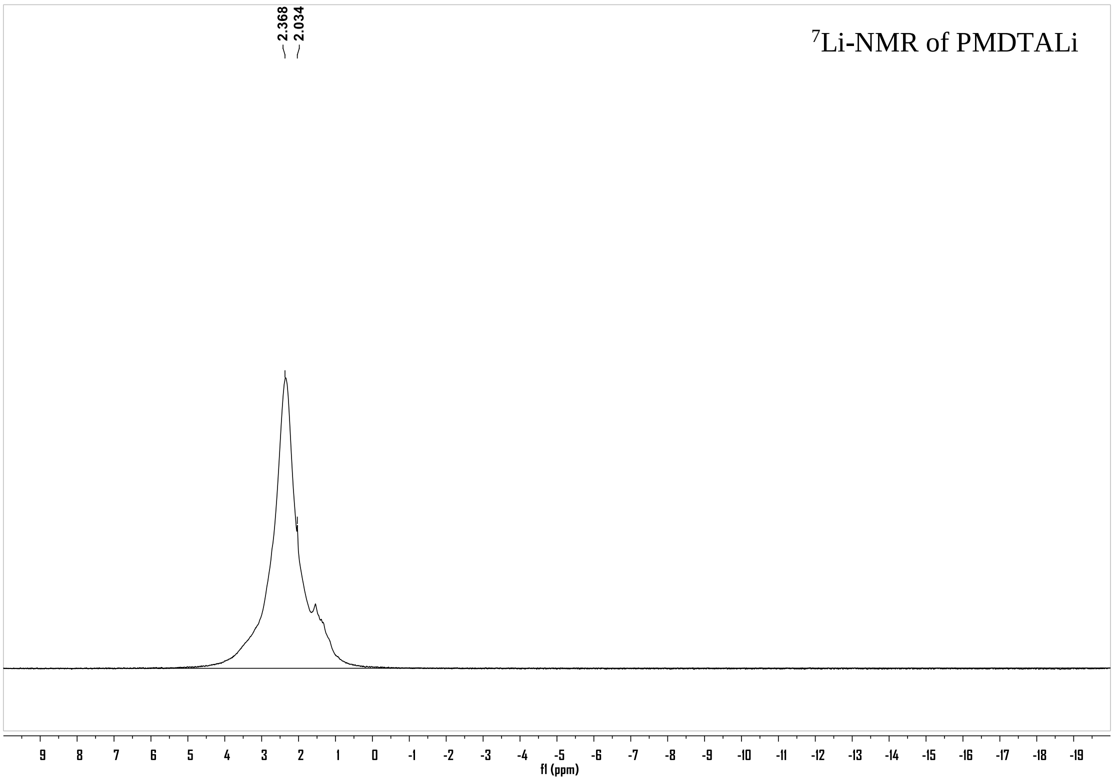


^{1}H NMR of PMDTALi



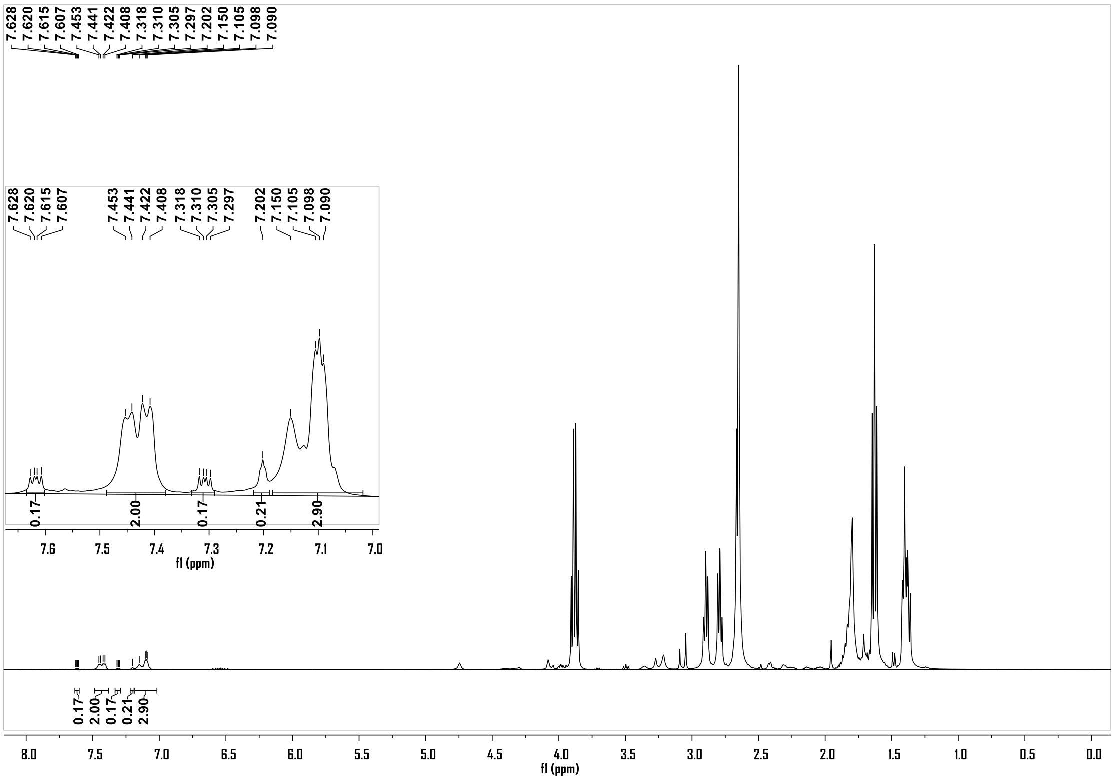
^{13}C NMR of PMDTALi

^{13}C NMR (151 MHz, C_6D_6) δ 63.10 (NCH$_2$, A), 60.41 (NCH$_2$, B), 59.64 (NCH$_2$, A+B), 58.38 (NCH$_2$, B), 56.69 (N(2)Me, A), 53.52 (N(2)Me, B), 51.71 (NCH$_2$, A), 50.91 (NCH$_2$, B), 46.21 (N(3)Me, A), 46.09 (N(3)Me$_2$, B), 46.03 (N(1)Me, B), 45.34 (N(1)Me, A), 34.61 (N(3)Me$_2$, A or B), 33.48 (N(3)Me$_2$, B or A).



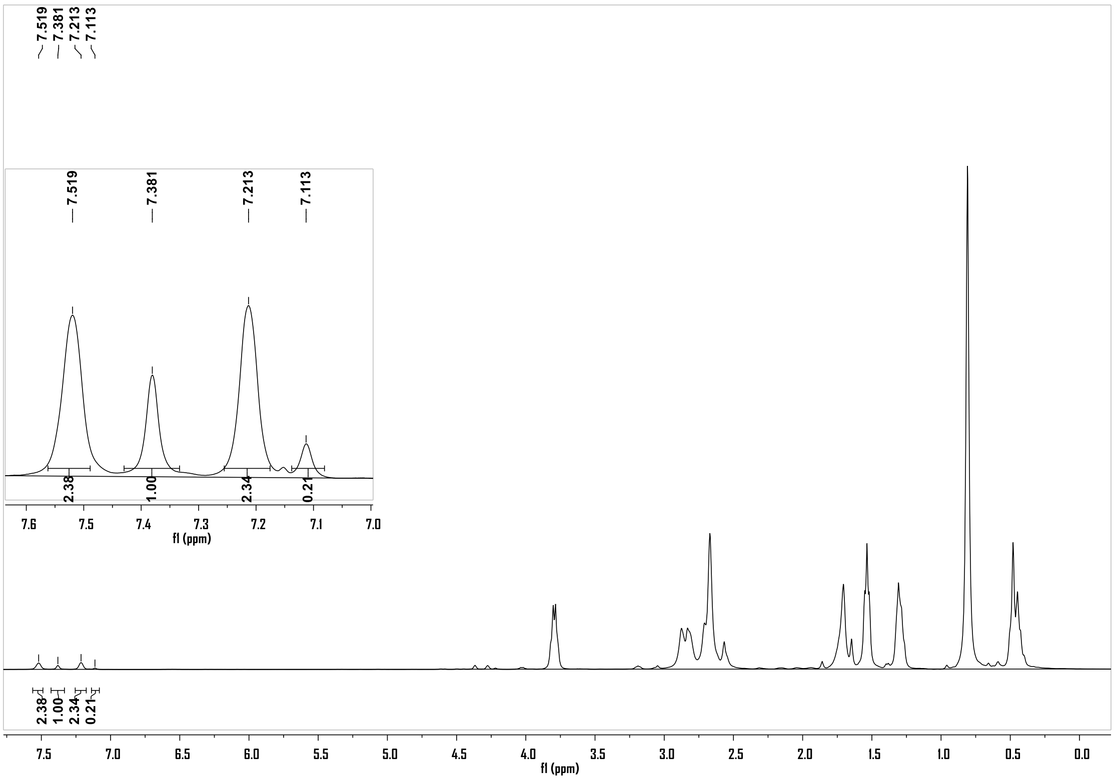
^{1}H NMR spectrum of benzonorbornene Li

Add benzonorbornene (71 mg, 0.5 mmol) to the flask of which have prepared PMDTALi used the method above, stirred 25 min. The ^{1}H NMR spectrum is shown below.

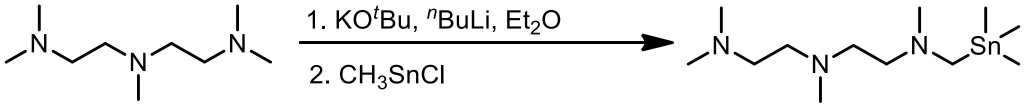


^{1}H NMR spectrum of benzonorbornene-SiMe$_3$

Add TMS-Cl (163 mg, 1.5 mmol)to the flask of which have prepared benzonorbornene Li, stirred 10 min. The ^{1}H NMR spectrum is shown below.



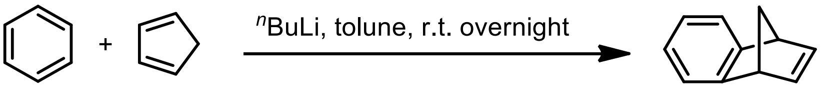
Preparation of N1-(2-(dimethylamino)ethyl)-N1,N2-dimethyl-N2-((trimethylstannyl)methyl)ethane-1,2-diamine



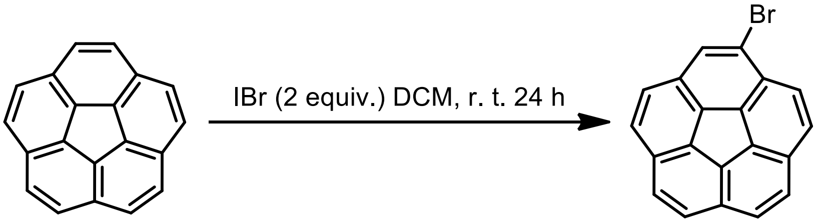
A 10 mL well-dried round–bottomed flask was charged with nitrogen through Schlenk line. To a solution of PMDTA (82 mg, 0.5 mmol) and KO^{t}Bu (28 mg, 0.5 equiv.) in diethyl ether, ^{n}BuLi (c = 2.4 mol/L in hexanes, 0.31 mL, 1.5 equiv.) was added dropwise at 0 °C, add trimethyltin chloride (200 mg, 2 equiv.) after1 h, the reaction was stirred for 1 h. The crude products were purified by using diatomite (DCM / triethylamine 9:1) to get the crude product (140 mg, 83%), as a yellow oil.

^{1}H-NMR (400 MHz, $CDCl_3$) δ 2.60 (s, 2H), 2.53–2.43 (m, 4H), 2.39 (d, *J* = 7.0 Hz, 4H), 2.24 (d, *J* = 12.0 Hz, 12H), 0.13 (s, 9H). ^{13}C-NMR (101 MHz, $CDCl_3$) δ 77.3, 77.0, 76.7, 58.8, 57.5, 56.4, 56.2, 48.5, 46.8, 45.9, 43.0, -8.4.

2.2 Preparation of substrates



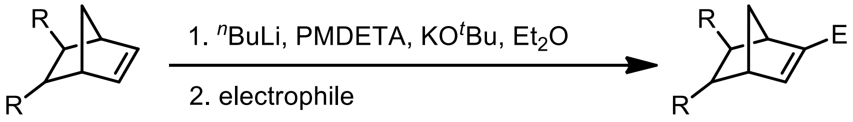
A 250 mL well-dried round–bottomed flask was charged with nitrogen through Schlenk line. To a solution of 1,2-dibromobenzene (9.44 g, 40 mmol), freshly distilled cyclopentadiene (2.64 g, 40 mmol) in toluene (40 mL). The flask was cooled to 0 °C and a solution of ^{n}BuLi (c = 2.4 mol/L in hexanes, 40 mmol) was added dropwise over a period of 30 min. After the resulting white suspension had been stirred at 0 °C for additional 10 min, the mixture was allowed to warm to room temperature and stirred overnight. Water (30 mL) was added and the layers were separated. The aqueous layer was extracted with petroleum ether (20 mL × 3) and the combined organic layers were dried with Na_2SO_4, filtered and concentrated under vacuum. The crude product was purified by flash chromatography to give product, as a colorless oil.[1]



IBr (1.78 g, 2.0 equiv.) was added to the solution of corannulene (1.0 g, 4.3 mmol) in DCM (65 mL) in portion. The reaction mixture was stirred at room temperature for 24 h and poured into saturated aqueous $Na_2S_2O_3$ (30 mL), extracted with DCM (30 mL x 3), dried over anhydrous Na_2SO_4, filtered and concentrated under vacuum. The residue (1.4 g) was the mixture of corannulene and 1-bromocorannulene (90% purity). The yield of corannulene bromide as 77% according to ^{1}H-NMR.[2]

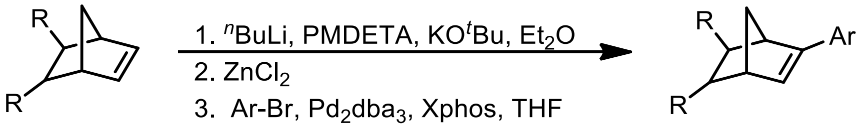
2.3 Preparation of Norbornene and norbornadiene derivatives.

General Procedure A:



A 10 mL well-dried round–bottomed flask was charged with nitrogen through Schlenk line. To a solution of norbornenes (0.5 mmol), KO^{t}Bu (11 mg, 0.2 equiv.) and PMDTA (173 mg, 2.0 equiv.) in Et$_2$O, ^{n}BuLi (c = 2.4 mol/L in hexanes, 0.42 mL, 2.0 equiv.) was added dropwise at 0 °C. After the resulting dark blue suspension had been stirred at 0 °C for additional 1 h, cool down to -78 ^{o}C and add electrophiles or add LiBr (109 mg, 2.5 equiv.) which was dissolved in dry THF, and then cool down to -78 ^{o}C and add electrophiles, quenched with saturated aqueous NH$_4$Cl after 1 h. The mixture was extracted with Et$_2$O (5 mL × 3), dried over anhydrous Na$_2$SO$_4$, filtered and concentrated under vacuum. The residue was purified by column chromatography (petroleum ether / EA) to give the product.

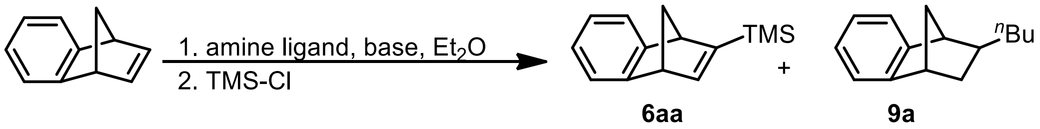
General Procedure B:



A 10 mL well-dried round–bottomed flask was charged with nitrogen through Schlenk line. To a solution of norbornene (0.2 mmol), KO^{t}Bu (4.5 mg, 0.2 equiv.) and PMDTA (69 mg, 2.0 equiv.) in Et_2O, ^{n}BuLi (c = 2.4 mol·L^{-1} in hexanes, 0.17 mL, 2.0 equiv.) was added dropwise at 0 °C. After the resulting dark blue suspension had been stirred at 0 °C for additional 1 h, add $ZnCl_2$ (150 mg, 2.5 equiv.) which was dissolved in dry THF (1.5 mol/L), after 5 min, add all those to another flask which Ar-X (2.5 equiv.), $Pd_2(dba)_3$ (4.5 mg, 5 mmol%), Xphos (9.6 mg, 10 mmol%) were dissolved in THF (0.2 mL) under nitrogen. The reaction was stirred overnight at room temperature and quenched with saturated aqueous NH_4Cl. The mixture was extracted with Et_2O (5 mL × 3), dried over anhydrous Na_2SO_4, filtered and concentrated under vacuum. The residue was purified by column chromatography (petroleum ether/EA) to give the desired product.

2.4 Reaction condition screening:

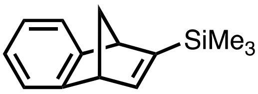
Optimization of Conditions



Entry	Base	Ligand/Additive	Yield of **6aa** (%)	Yield of **9a** (%)
1	^{n}BuLi	----	0	0
2	LiTMP	----	0	0
3	^{n}BuLi	TMEDA	42	53
4	^{s}BuLi	TMEDA	41	59
5	^{t}BuLi	----	28	0

6	^{n}BuLi	KO^{t}Bu	78	0
7	PMEDTLi	----	85	0
8	^{n}BuLi/KO^{t}Bu	PMDTA	79	0
9	^{n}BuLi	PMDTA	74	13
^{a}10	**^{n}BuLi/KO^{t}Bu**	**PMDTA**	**88**	**0**

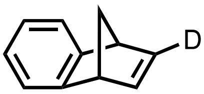
Reaction conditions: Substrate **5a** (0.5 mmol), RLi (1.0 mmol), ligand (1.0 mmol), in Et_2O (0.5 mL) for 2 h. ^{a}KO^{t}Bu (0.1 mmol) was used. then quenched with TMSCl.



6aa

(1,4-Dihydro-1,4-methanonaphthalen-2-yl)trimethylsilane 6aa

Following the general procedure A, benzonorbornene (71 mg, 0.5 mmol) was added, and quenched with chlorotrimethylsilane (136 mg, 2.5 equiv.), (1,4-dihydro-1,4-methanonaphthalen-2-yl) trimethylsilane **6aa** (94 mg, 88%) was isolated as a colorless oil; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.24–7.15 (m, 2H), 7.01 (dd, J = 3.0, 0.5 Hz, 1H), 6.96–6.88 (m, 2H), 4.00 (s, 1H), 3.93 (s, 1H), 2.19 (t, J = 1.5 Hz, 2H), 0.06 (s, 9H). ^{13}C-NMR (101 MHz, $CDCl_3$) δ 157.5, 154.1, 153.9, 153.2, 126.0, 125.9, 123.3, 123.3, 71.4, 55.2, 53.8, 0.0. HRMS (ESI) $[M + H]^+$ calculated for ($C_{14}H_{18}Si$) 215.1256, found 215.1253.

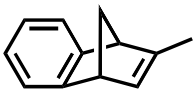


6ab

1,4-Dihydro-1,4-methanonaphthalene 6ab

Following the general procedure A, benzonorbornene (71 mg, 0.5 mmol) was added, and quenched with D_2O (25 mg, 2.5 equiv.), 1,4-dihydro-1,4-methanonaphtha

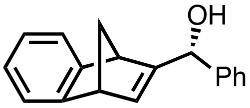
-lene **6ab** (66 mg, 93%) was isolated as a colorless oil; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.24–7.17 (m, 2H), 6.95–6.89 (m, 2H), 6.78 (s, 1H), 3.88 (s, 2H), 2.31 (dt, *J* = 7.0, 1.5 Hz, 1H), 2.23 (dt, *J* = 7.0, 1.5 Hz, 1H). ^{13}C-NMR (101 MHz, $CDCl_3$) δ 151.8, 142.9, 124.2, 121.5, 70.2, 50.3, 50.2. HRMS (ESI) $[M + H]^+$ calculated for ($C_{11}H_9D$) 144.0924, found 144.0922.



6ac

2-Methyl-1,4-dihydro-1,4-methanonaphthalene 6ac

Following the general procedure A, benzonorbornene (71 mg, 0.5 mmol) was added, and quenched with methyl iodide (177 mg, 2.5 equiv), 2-methyl-1,4-dihydro-1,4-methanonaphthalene **6ac** (70 mg, 90%) was isolated as a colorless oil;^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.24 (d, *J* = 7.0 Hz, 1H), 7.17 (d, *J* = 6.0 Hz, 1H), 6.97–6.88 (m, 2H), 6.19 (s, 1H), 3.78 (s, 1H), 3.52 (s, 1H), 2.30 (d, *J* = 7.0 Hz, 1H), 2.20 (d, *J* = 7.0 Hz, 1H), 1.82 (s, 3H). ^{13}C-NMR (101 MHz, $CDCl_3$) δ 153.7, 152.6, 151.6, 134.7, 124.3, 123.9, 121.2, 120.9, 68.6, 55.0, 50.4, 16.4. HRMS (ESI) $[M + H]^+$ calculated for ($C_{12}H_{12}$) 157.1017, found 157.1015.

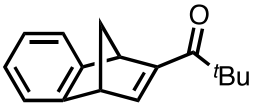


6ad

(1,4-Dihydro-1,4-methanonaphthalen-2-yl)(phenyl)methanol 6ad

Following the general procedure A, benzonorbornene (71 mg, 0.5 mmol) was added, lithium bromide (96 mg, 2.2 equiv.) which dissolved in THF was added, and quenched with benzaldehyde (133 mg, 2.5 equiv.), (1,4-dihydro-1,4-methanonaph

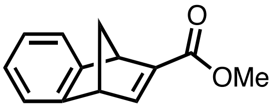
-thalen-2-yl)(phenyl)methanol **6ad** and **6ad’** (76 mg, 61%, dr = 9/1) was isolated as a colorless oil; ^{1}H-NMR (400 MHz, CDCl$_3$) (dr: 9:1)δ 7.32–7.23 (m, 4H), 7.22–7.15 (m, 3H), 6.95–6.85 (m, 2H), 6.82 (td, *J* = 7.5, 1.0 Hz, 1H), 6.59–6.55 (s, 0.1H), 6.53–6.44 (s, 0.9H), 5.44 (s, 0.9H), 5.33 (s, 0.1H), 3.88 (s, 1H), 3.70 (s, 0.9H), 3.63 (s, 0.1H), 2.33 (dt, *J* = 7.0 Hz, 1H), 2.19 (d, *J* = 7.0 Hz, 1H), 1.89 (d, *J* = 4.0 Hz, 0.1H), 1.85 (d, *J* = 4.0 Hz, 0.9H). ^{13}C-NMR (101 MHz, CDCl$_3$) δ 158.7, 151.5, 151.4, 140.9, 136.6, 128.3, 127.7, 126.7, 124.2, 124.0, 121.7, 121.1, 73.6, 68.9, 50.9, 50.2. HRMS (ESI) [M + H]$^+$ calculated for ($C_{18}H_{16}O$) 249.1279, found 249.1280.



6ae

1-(1,4-Dihydro-1,4-methanonaphthalen-2-yl)-2,2-dimethylpropan-1-one 6ae

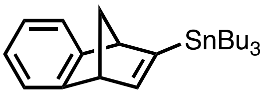
Following the general procedure A, benzonorbornene (71 mg, 0.5 mmol) was added, lithium bromide (96 mg, 2.2 equiv.) which dissolved in THF was added, and quenched with pivaloyl chloride (151 mg, 2.5 equiv.), 1-(1,4-dihydro-1,4-methan-onaphthalen-2-yl)-2,2-dimethylpropan-1-one **6ae** (47 mg, 42%) was isolated as a colorless oil; ^{1}H-NMR (400 MHz, CDCl$_3$) δ 7.44 (d, *J* = 3.5 Hz, 1H), 7.35 (m, 1H), 7.23 (m, 1H), 6.98–6.93 (m, 2H), 4.28 (s, 1H), 4.06 (s, 1H), 2.34 (m, 1H), 2.23 (m, 1H), 1.17 (s, 9H). ^{13}C-NMR (101 MHz, CDCl$_3$) δ 203.8, 153.6, 150.7, 149.1, 124.9, 124.4, 122.4, 121.9, 67.8, 52.0, 51.5, 43.8, 27.8. HRMS (ESI) [M + H]$^+$ calculated for ($C_{16}H_{18}O$) 227.1436, found 227.1435.



6af

Methyl 1,4-dihydro-1,4-methanonaphthalene-2-carboxylate 6af

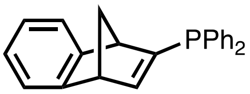
Following the general procedure A, benzonorbornene (71 mg, 0.5 mmol) was added, lithium bromide (96 mg, 2.2 equiv.) which dissolved in THF was added, and quenched with methyl chloroformate (119 mg, 2.5 equiv.), methyl.1,4-dihydro-1,4-methanonaphthalene-2-carboxylate **6af** (63 mg, 63%) was isolated as a colorless oil; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.63 (d, *J* = 3.5 Hz, 1H), 7.35 (m, 1H), 7.30–7.22 (m, 1H), 7.00–6.86 (m, 2H), 4.22 (s, 1H), 4.10–4.01 (m, 1H), 3.71 (s, 3H), 2.46 (dt, *J* = 7.5, 1.5 Hz, 1H), 2.34 (dd, *J* = 7.5, 1.0 Hz, 1H). ^{13}C-NMR (101 MHz, $CDCl_3$) δ 165.1, 154.3, 150.5, 149.1, 148.7, 124.9, 124.7, 122.4, 122.3, 69.5, 51.6, 51.5, 50.1. HRMS (ESI) $[M + H]^+$ calculated for ($C_{13}H_{12}O_2$) 201.0916, found 201.0915.



6ag

Tributyl(1,4-dihydro-1,4-methanonaphthalen-2-yl)stannane 6ag

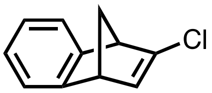
Following the general procedure A, benzonorbornene (71 mg, 0.5 mmol) was added, and quenched with chlorotributyltin (407 mg, 2.5 equiv.), tributyl(1,4-dihydro-1,4-methanonaphthalen-2-yl)stannane **6ag** (192 mg, 89%) was isolated as a colorless oil; ^{1}H-NMR (400 MHz, CDCl3) δ 7.20–7.15 (m, 1H), 7.15–7.10 (m, 1H), 6.98 (d, J = 3.0 Hz, 1H), 6.90–6.85 (m, 2H), 3.99 (s, 1H), 3.90 (s, 1H), 2.19 (s, 2H), 1.46–1.38 (m, 6H), 1.26 (m, 6H), 0.86 (m, 15H). ^{13}C-NMR (101 MHz, CDCl3) δ 155.1, 153.5, 151.8, 151.5, 123.9, 123.9, 121.5, 121.2, 69.5, 56.0, 51.9, 29.2, 27.3, 13.7, 9.4. HRMS (ESI) $[M + H]^+$ calculated for ($C_{23}H_{36}Sn$) 433.1917, found 433.1918.



6ah

(1,4-Dihydro-1,4-methanonaphthalen-2-yl)diphenylphosphine 6ah

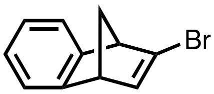
Following the general procedure A, benzonorbornene (71 mg, 0.5 mmol) was added, and quenched with chlorodiphenylphosphine (276 mg, 2.5 equiv.), (1,4-dihydro-1,4-methanonaphthalen-2-yl)diphenylphosphine **6ah** (139 mg, 85%) was isolated as a colorless oil; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.42–7.23 (m, 10H), 7.17 (d, *J* = 6.5 Hz, 1H), 6.95–6.88 (m, 2H), 6.88–6.82 (m, 1H), 6.73–6.67 (m, 1H), 3.96 (s, 1H), 3.83 (s, 1H), 2.47 (dt, *J* = 7.5, 1.5 Hz, 1H), 2.26 (d, *J* = 7.5 Hz, 1H) ^{13}C-NMR (101 MHz, $CDCl_3$) δ 150.9, 150.8, 150.8, 150.5, 133.9, 133.8, 133.7, 133.6, 128.9, 128.7, 128.5, 128.4, 128.3, 128.3, 124.4, 124.1, 122.0, 121.2, 68.8, 54.0, 53.9, 51.9, 51.9. HRMS (ESI) $[M + H]^+$ calculated for ($C_{23}H_{19}P$) 327.1303, found 327.1303.



6ai

2-Chloro-1,4-dihydro-1,4-methanonaphthalene 6ai

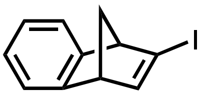
Following the general procedure A, benzonorbornene (71 mg, 0.5 mmol) was added, lithium bromide (96 mg, 2.2 equiv.) which dissolved in THF was added, and quenched with 4-methylbenzene-1-sulfonyl chloride (238 mg, 2.5 equiv.), 2-chloro-1,4-dihydro-1,4-methanonaphthalene **6ai** (52 mg, 59%) was isolated as a colorless oil; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.34 (d, *J* = 5.0 Hz, 1H), 7.22 (d, *J* = 6.0 Hz, 1H), 7.05 – 6.90 (m, 2H), 6.72 (s, 1H), 3.91 (s, 1H), 3.81 (s, 1H), 2.65 – 2.44 (m, 1H), 2.30 (d, *J* = 7.0 Hz, 1H). ^{13}C-NMR (101 MHz, $CDCl_3$) δ 149.9, 149.5, 140.3, 136.3, 125.2, 124.6, 122.1, 121.6, 69.0, 58.4, 51.7. HRMS (ESI) $[M + H]^+$ calculated for ($C_{11}H_9{}^{35}Cl$) 177.0471, found 177.0472.



6aj

2-Bromo-1,4-dihydro-1,4-methanonaphthalene 6aj

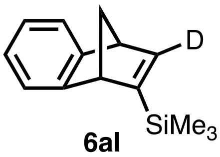
Following the general procedure A, benzonorbornene (71 mg, 0.5 mmol) was added, lithium bromide (96 mg, 2.2 equiv.) which dissolved in THF was added, and quenched with 1,2-dibromoethane (233 mg, 2.5 equiv.), 2-bromo-1,4-dihydro-1,4-methanonaphthalene **6aj** (40 mg, 36%) was isolated as a colorless oil; ^{1}H-NMR (400 MHz, CDCl$_3$) δ 7.33 (dd, *J* = 6, 2.0 Hz, 1H), 7.22 (dd, *J* = 6, 2.0 Hz, 1H), 7.04–6.91 (m, 2H), 6.48 (d, *J* = 3.5 Hz, 1H), 3.92 (s, 1H), 3.71 (s, 1H), 2.57 (d, *J* = 6.5 Hz, 1H), 2.32 (d, *J* = 6.5 Hz, 1H). ^{13}C-NMR (101 MHz, CDCl$_3$) δ 150.3, 149.5, 148.4, 135.6, 125.2, 124.6, 122.1, 121.6, 68.8, 56.7, 50.7. HRMS (ESI) [M + H]$^+$ calculated for ($C_{11}H_9{}^{79}Br$) 220.9966, found 220.9969.



6ak

2-Iodo-1,4-dihydro-1,4-methanonaphthalene 6ak

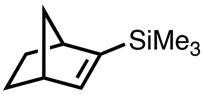
Following the general procedure A, benzonorbornene (71 mg, 0.5 mmol) was added, lithium bromide (96 mg, 2.2 equiv.) which dissolved in THF was added, and quenched with iodine (316 mg, 2.5 equiv.), 2-iodo-1,4-dihydro-1,4-methanonaphthalene **6ak** (63 mg, 47%) was isolated as a colorless oil; ^{1}H-NMR (400 MHz, CDCl$_3$) δ 7.32 (d, *J* = 6.5, 1H), 7.20 (d, *J* = 6.5, 1H), 7.07 (d, *J* = 3.0 Hz, 1H), 6.98 (pd, *J* = 7.5, 1.5Hz, 2H), 3.91 (s, 1H), 3.87 (s, 1H), 2.57–2.50 (m, 1H), 2.23 (m, 1H). ^{13}C-NMR (101 MHz, CDCl$_3$) δ 149.6, 149.5, 149.2, 125.1, 124.6, 122.1, 121.6, 106.0, 69.2, 61.4, 52.9. HRMS (ESI) [M + H]$^+$ calculated for ($C_{11}H_9Br$) 268.9827, found 268.9826.



6al

((1R,4R)-1,4-dihydro-1,4-methano-3-deuteratednaphthalen-2-yl)trimethylsilane 6al

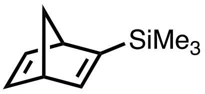
Following the general procedure A, 1,4-dihydro-1,4-methanonaphthalene (71 mg, 0.5 mmol) was added, and quenched with chlorotrimethylsilane (136 mg, 2.5 equiv.), norbornene **6al** (36 mg, 86%) was isolated as a colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24–7.15 (m, 2H), 6.96–6.88 (m, 2H), 4.00 (s, 1H), 3.93 (s, 1H), 2.19 (t, *J* = 1.5 Hz, 2H), 0.08–0.04 (m, 9H). ^{13}C-NMR (101 MHz, $CDCl_3$) δ 157.5, 154.1, 153.9, 153.2, 126.0, 125.9, 123.3, 123.3, 71.4, 55.2, 53.8, 0.0. HRMS (ESI) [M + H]+ calculated for ($C_{14}H_{17}SiD$) 216.1319, found 216.1318.



6ba

Bicyclo[2.2.1]hept-2-en-2-yltrimethylsilane 6ba

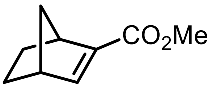
Following the general procedure A, norbornene (47 mg, 0.5 mmol) was added, and quenched with chlorotrimethylsilane (136 mg, 2.5 equiv.), bicyclo[2.2.1]hept-2-en-2-yltrimethylsilane **6ba** (70 mg, 85%) was isolated as a colorless oil; The analytical data for **6ba** are consistently agreed with those have been previously reported in the literature.[3]



6ca

Bicyclo[2.2.1]hepta-2,5-dien-2-yltrimethylsilane 6ca

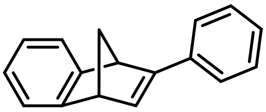
Following the general procedure A, norbornadiene (46 mg, 0.5 mmol) was added, and quenched with chlorotrimethylsilane (136 mg, 2.5 equiv.), bicyclo[2.2.1]hepta-2,5-di-en-2-yltrimethylsilane **6ca** (76 mg, 93%) was isolated as a colorless oil; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 6.96 (d, *J* = 3.0 Hz, 1H), 6.68 (s, 2H), 3.64 (s, 1H), 3.58 (s, 1H), 1.84 (d, *J* = 6.0 Hz, 1H), 1.78 (d, *J* = 6.0 Hz, 1H), 0.00 (s, 9H). ^{13}C-NMR (101 MHz, $CDCl_3$) δ 157.5, 154.1, 153.9, 153.2, 126.0, 125.9, 123.3, 123.3, 71.4, 55.2, 53.8, -0.3. HRMS (ESI) $[M + H]^+$ calculated for ($C_{10}H_{16}Si$) 165.1100, found 165.1103.



6bb

(1S,4R)-Methyl bicyclo[2.2.1]hept-2-ene-2-carboxylate 6bb

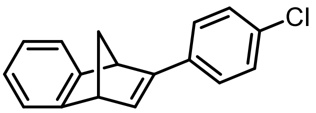
Following the general procedure A, norbornene (47 mg, 0.5 mmol) was added, lithium bromide (96 mg, 2.2 equiv.) which dissolved in THF was added, and quenched with methyl chloroformate (119 mg, 2.5 equiv.), (1S,4R)-methylbicyclo-[2.2.1]hept-2-ene-2-carboxylate **6bb** (35 mg, 47%) was isolated as a colorless oil; The analytical data for **6bb** are consistently agreed with those have been previously reported in the literature.[6]



10aa

2-Phenyl-1,4-dihydro-1,4-methanonaphthalene 10aa

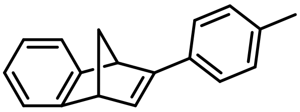
Following the general procedure B, 2-phenyl-1,4-dihydro-1,4-methanonaphthalene **10aa** (26 mg, 59%) was isolated as a colorless oil; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.49–7.41 (m, 2H), 7.36 (dd, *J* = 6.0, 2.1 Hz, 1H), 7.33–7.27 (m, 2H), 7.25–7.16 (m, 2H), 6.93 (ddd, *J* = 8.0, 3.0, 2.5 Hz, 3H), 4.27 (s, 1H), 4.01 (s, 1H), 2.46 (dt, *J* = 7.5, 1.5 Hz, 1H), 2.37 (d, *J* = 7.5 Hz, 1H). ^{13}C-NMR (101 MHz, $CDCl_3$) δ 155.8, 151.5, 150.9, 135.9, 135.6, 128.5, 127.2, 124.7, 124.5, 124.3, 121.6, 121.3, 68.0, 51.8, 51.0. HRMS (ESI) $[M + H]^+$ calculated for ($C_{17}H_{14}$) 219.1174, found 219.1175.



10ab

2-(4-Chlorophenyl)-1,4-dihydro-1,4-methanonaphthalene 10ab

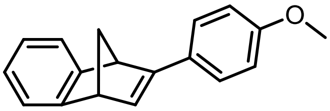
Following the general procedure B, 2-(4-chlorophenyl)-1,4-dihydro-1,4-methanonaphthalene **10ab** (27 mg, 53%) was isolated as a colorless oil; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.37–7.32 (m, 3H), 7.28–7.26 (m, 1H), 7.24 (dt, *J* = 5.5, 2.6 Hz, 2H), 6.96–6.92 (m, 2H), 6.91 (d, *J* = 3.0 Hz, 1H), 4.21 (s, 1H), 4.00 (dd, *J* = 2.5, 1.5 Hz, 1H), 2.45 (dt, *J* = 7.0, 1.6 Hz, 1H), 2.36 (d, *J* = 6.5 Hz, 1H). ^{13}C-NMR (101 MHz, $CDCl_3$) δ 154.7, 151.3, 150.6, 136.6, 134.1, 132.9, 128.6, 126.0, 124.6, 124.4, 121.5, 121.4, 68.0, 51.8, 51.1. HRMS (ESI) $[M + H]^+$ calculated for ($C_{17}H_{13}{}^{35}Cl$) 253.1784, found 253.1784.



10ac

2-(*p*-Tolyl)-1,4-dihydro-1,4-methanonaphthalene 10ac

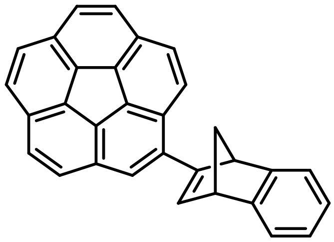
Following the general procedure B, 2-(4-chlorophenyl)-1,4-dihydro-1,4-methanonaphthalene **10ac** (27 mg, 53%) was isolated as a colorless oil; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.33 (dd, *J* = 8.5, 2.1 Hz, 3H), 7.23–7.18 (m, 1H), 7.11 (d, *J* = 8.0 Hz, 2H), 6.96–6.87 (m, 2H), 6.84 (d, *J* = 3.0 Hz, 1H), 4.24 (s, 1H), 3.98 (dd, *J* = 3.0, 1.5 Hz, 1H), 2.44 (dt, *J* = 7.0, 1.6 Hz, 1H), 2.35 (t, *J* = 7.0 Hz, 1H), 2.31 (s, 3H). ^{13}C-NMR (101 MHz, $CDCl_3$) δ 155.6, 151.6, 151.0, 137.1, 134.7, 132.8, 129.2, 124.7, 124.4, 124.2, 121.5, 121.2, 67.9, 51.8, 50.9, 21.2. HRMS (ESI) $[M + H]^+$ calculated for ($C_{18}H_{16}$) 233.1330, found 233.1333.



10ad

2-(4-Methoxyphenyl)-1,4-dihydro-1,4-methanonaphthalene 10ad

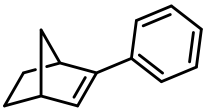
Following the general procedure B, 2-(4-methoxyphenyl)-1,4-dihydro-1,4-methanonaphthalene 10ad (33 mg, 66%) was isolated as a colorless oil; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.40–7.35 (m, 2H), 7.34 (dd, *J* = 5.5, 2.8 Hz, 1H), 7.23–7.19 (m, 1H), 6.96–6.88 (m, 2H), 6.87–6.82 (m, 2H), 6.76 (d, *J* = 3.0 Hz, 1H), 4.22 (s, 1H), 3.98 (s, 1H), 3.79 (s, 3H), 2.44 (dt, *J* = 7.0, 1.6 Hz, 1H), 2.34 (d, *J* = 7.0 Hz, 1H). ^{13}C-NMR (101 MHz, $CDCl_3$) δ 159.0, 155.2, 151.8, 151.0, 133.4, 128.5, 126.0, 124.5, 124.2 121.5, 121.2, 113.9, 67.8, 55.3, 51.9, 50.9. HRMS (ESI) $[M + H]^+$ calculated for ($C_{18}H_{16}O$) 249.1279, found 249.1282.



10ae

1-(1,4-Dihydro-1,4-methanonaphthalen-2-yl)dibenzo[ghi,mno]fluoranthene 10ae

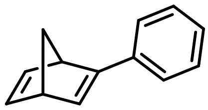
Following the general procedure B, 1-(1,4-dihydro-1,4-methanonaphthalen-2-yl)dibenzo[ghi,mno]fluoranthene **10ae** (16 mg, 20%) was isolated as a yellow solid, Mp 97-100 °C; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.02 (d, *J* = 9.0 Hz, 1H), 7.82–7.73 (m, 8H), 7.56 (dd, *J* = 5.0, 3.1 Hz, 1H), 7.35 (dd, *J* = 5.5, 3.0 Hz, 2H), 7.07–6.91 (m, 2H), 4.34 (s, 1H), 4.20 (s, 1H), 2.63 (dt, *J* = 7.5, 1.5 Hz, 1H), 2.47 (d, *J* = 7.5 Hz, 1H). ^{13}C-NMR (101 MHz, $CDCl_3$) δ 154.3, 151.1, 150.9, 141.5, 136.5, 136.3, 136.0, 135.6, 135.3, 135.1, 130.9, 130.6, 130.5, 128.8, 127.6, 127.3, 127.2, 127.1, 127.0, 127.0, 126.8, 126.8, 124.8, 124.5, 121.9, 121.8, 121.5, 68.2, 54.2, 51.7. HRMS (ESI) $[M + H]^+$ calculated for ($C_{31}H_{18}$) 390.1487, found 391.1489.



10ba

2-Phenylbicyclo[2.2.1]hept-2-ene 10ba

Following the general procedure B, 2-phenylbicyclo[2.2.1]hept-2-ene **10ba** (21 mg, 63%) was isolated as a colorless oil; The analytical data for **10ba** are consistently agreed with those have been previously reported in the literature.[4]

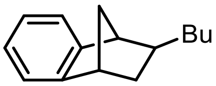


10ca

2-Phenylbicyclo[2.2.1]hepta-2,5-diene 10ca

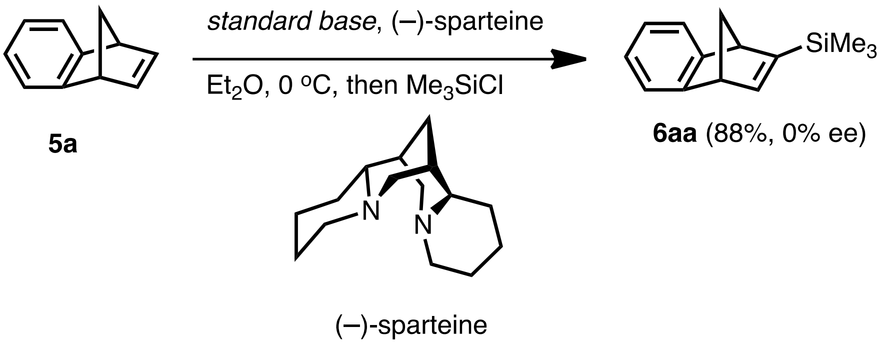
Following the general procedure B, 2-phenylbicyclo[2.2.1]hepta-2,5-diene **10ca** (210 mg, 59%) was isolated as a colorless oil**;** the analytical data for **10ca** are consistently agreed with those have been previously reported in the literature.[5]

Preparation of 2-butyl-1,2,3,4-tetrahydro-1,4-methanonaphthalene



A 10 mL well-dried round–bottomed flask was charged with nitrogen through Schlenk line. To a solution of benzonorbornene (72 mg, 0.5 mmol) KO*ᵗ*Bu (28 mg, 0.5 equiv.) and TMEDA (116 mg, 2 equiv.) in Et_2O (1 mL), ^{n}BuLi (c = 2.4 mol/L in hexanes, 0.42 mL, 2 equiv.) was added dropwise at 0 °C. After the resulting dark blue suspension had been stirred at 0 °C for additional 1 h, add TMSCl (148 mg, 2.5 equiv.), quenched with saturated aqueous NH_4Cl after 1 h. The mixture was extracted with Et_2O (5 mL x 3), dried over anhydrous Na_2SO_4, filtered and concentrated under vacuum. The residue was purified by column chromatography (petroleum ether) to get the byproduct as a colorless oil; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.14 (m, 2H), 7.05–7.01 (m, 2H), 3.28 (s, 1H), 3.02 (s, 1H), 1.78–1.65 (m, 2H), 1.36 (m, 8H), 0.89 (m, 4H). ^{13}C-NMR (101 MHz, $CDCl_3$) δ 149.3, 148.5, 125.3, 125.2, 120.6, 120.2, 48.4, 46.0, 44.0, 40.7, 36.3, 35.3, 30.7, 22.9, 14.2. HRMS (ESI) $[M + H]^+$ calculated for ($C_{15}H_{20}$) 201.1643, found 201.1640.

Reactions with chiral ligands



A 10 mL well-dried round–bottomed flask was charged with nitrogen through Schlenk line. To a solution of PMDTA (82 mg, 0.5 mmol) and KO^{t}Bu (28 mg, 0.5 equiv.) in diethyl ether, ^{n}BuLi (c = 2.4 mol/L in hexanes, 0.31 mL, 1.5 equiv.) was added dropwise at 0 °C, after 1 h, add the mixture solution of benzonorbornene (35 mg, 0.25 mmol) with sparteine (117 mg, 2 equiv.), add TMSCl after 1 h, and then via HPLC using a Chiralpak AY-RH column (250 mm length) with H_2O/CH_3CN as eluting solvent (50/50) with detection at = 254 nm, retention times: 31 min, 37 min.

References

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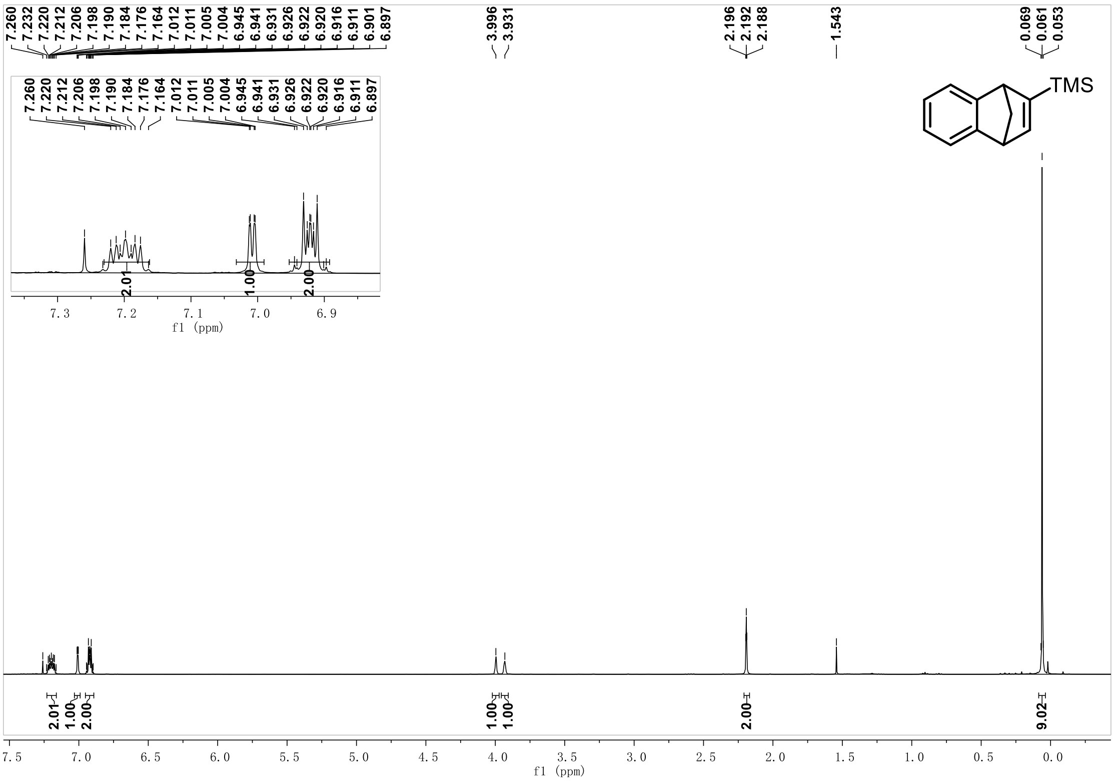
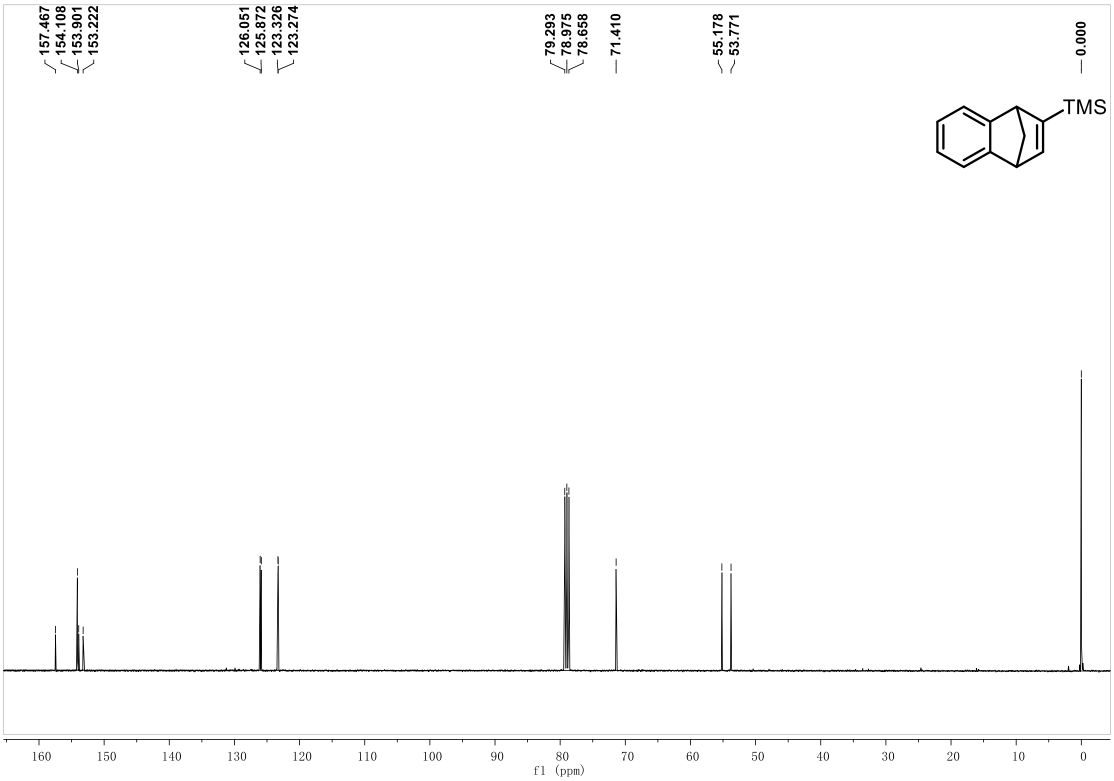
[6] Shen, P.-X.; Wang, X.-C.; Wang, P.; Zhu, R.-Y.; Yu, J.-Q. *J. Am. Chem. Soc.* **2015**, *137*, 11574.

Spectral Data

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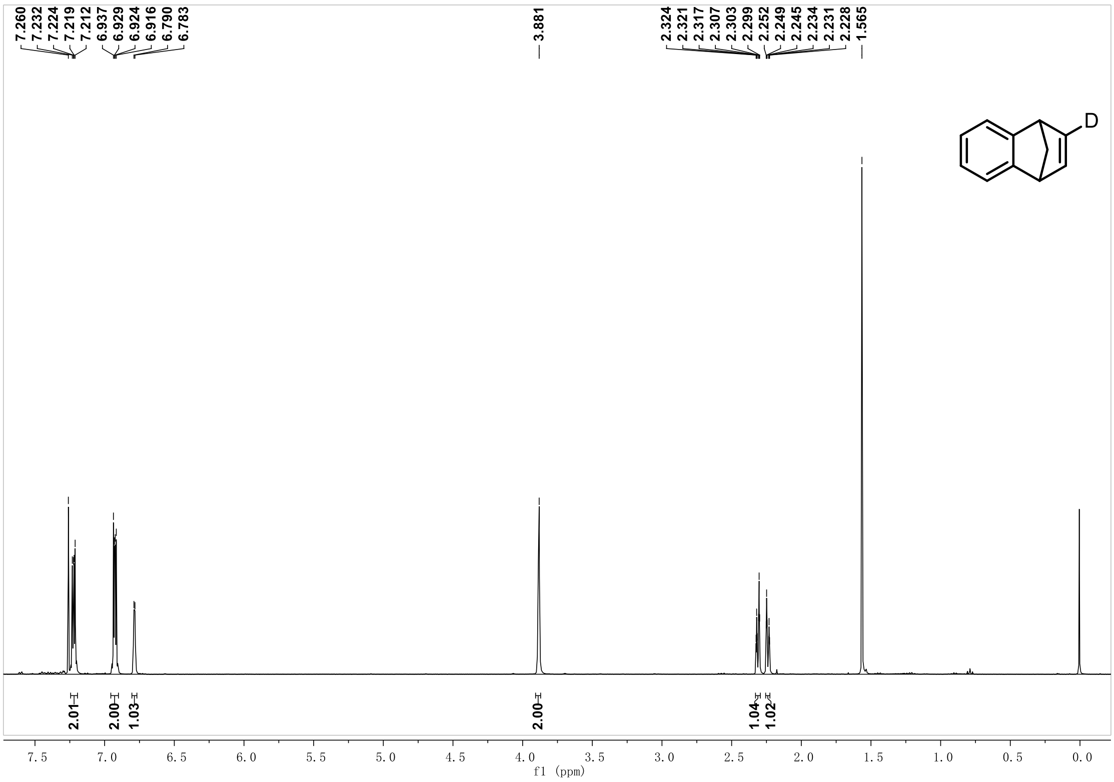
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2.245
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2.228
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D
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1.03
2.00
1.04
1.02
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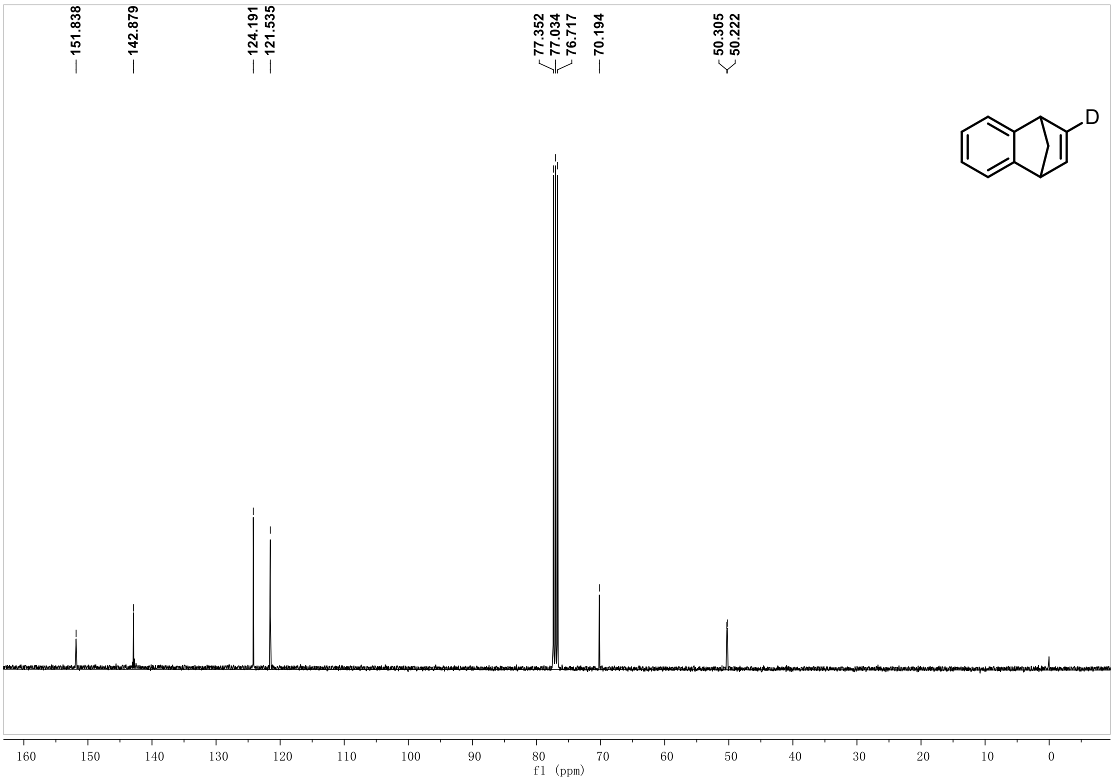
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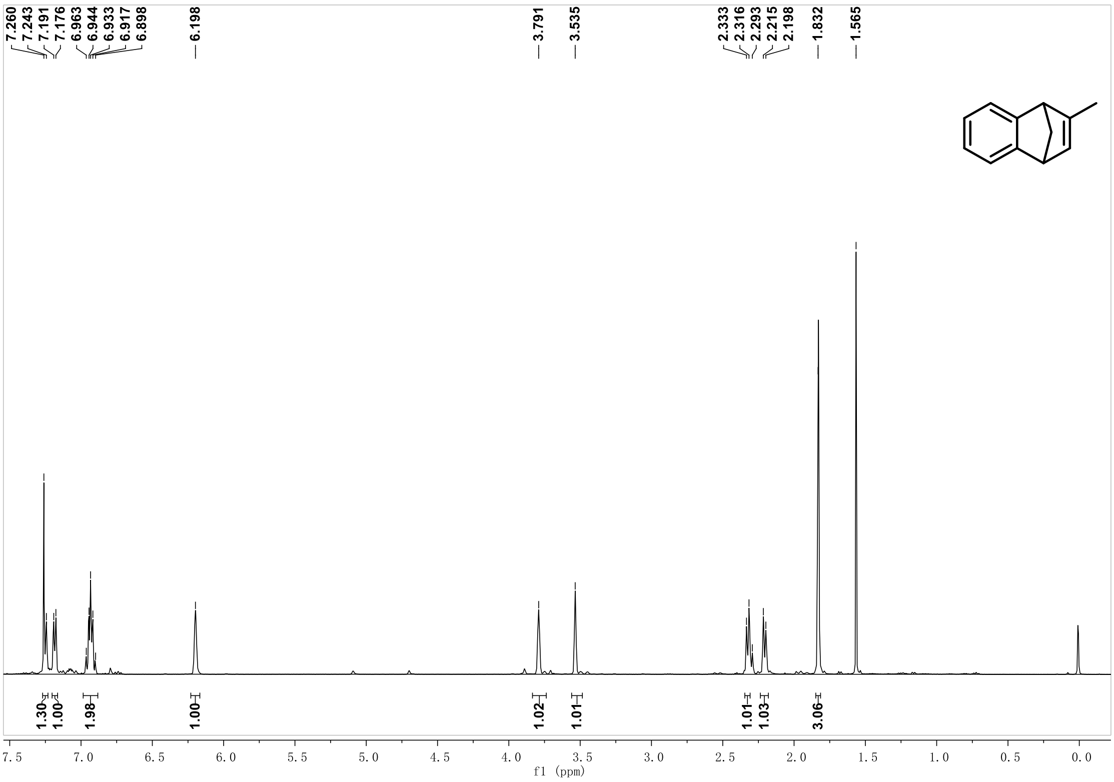
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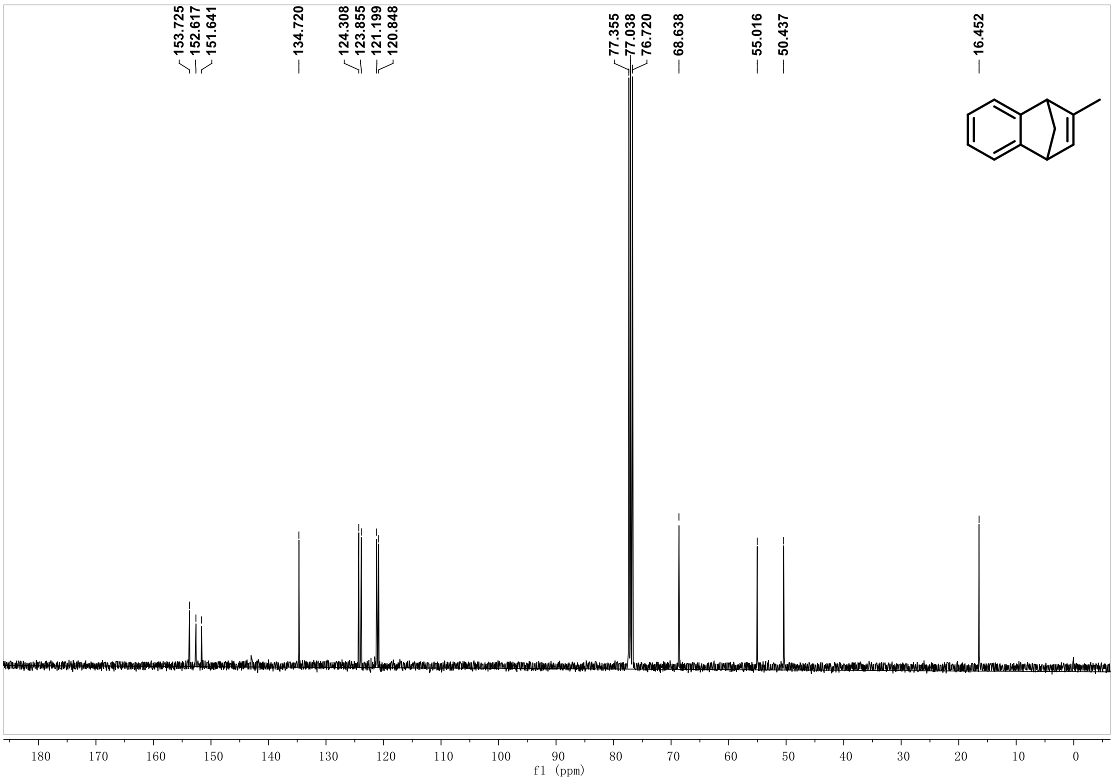
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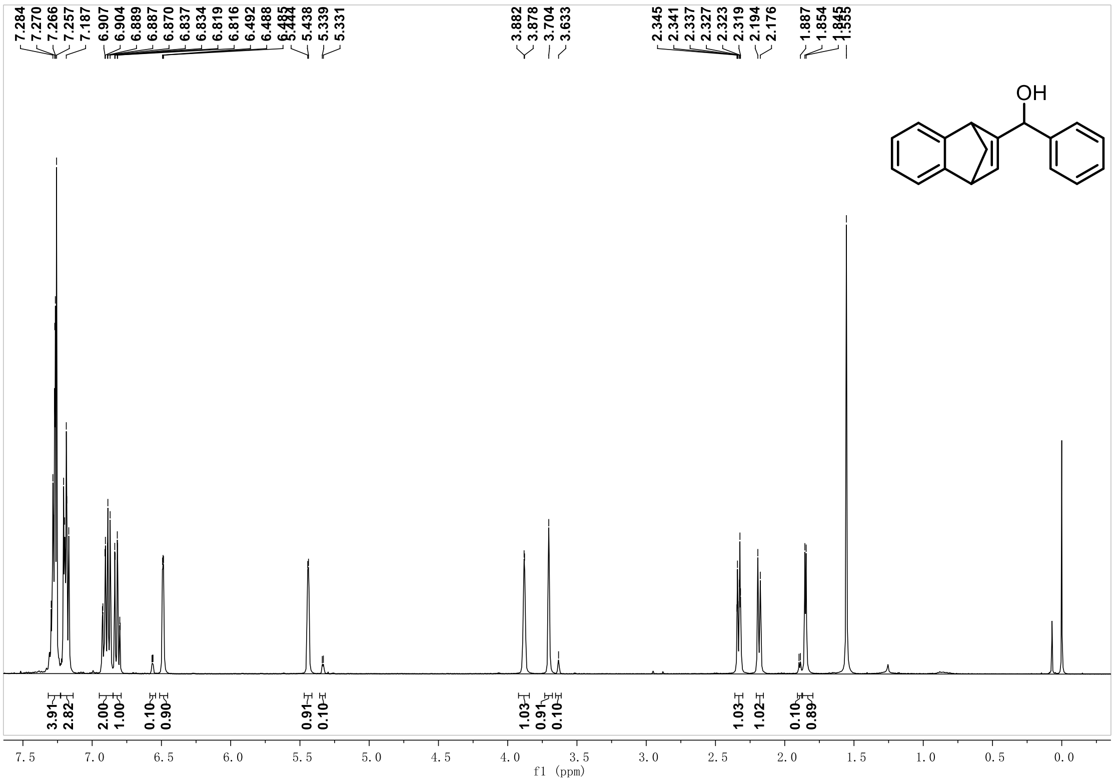
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3.704
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1.854
1.845
1.555
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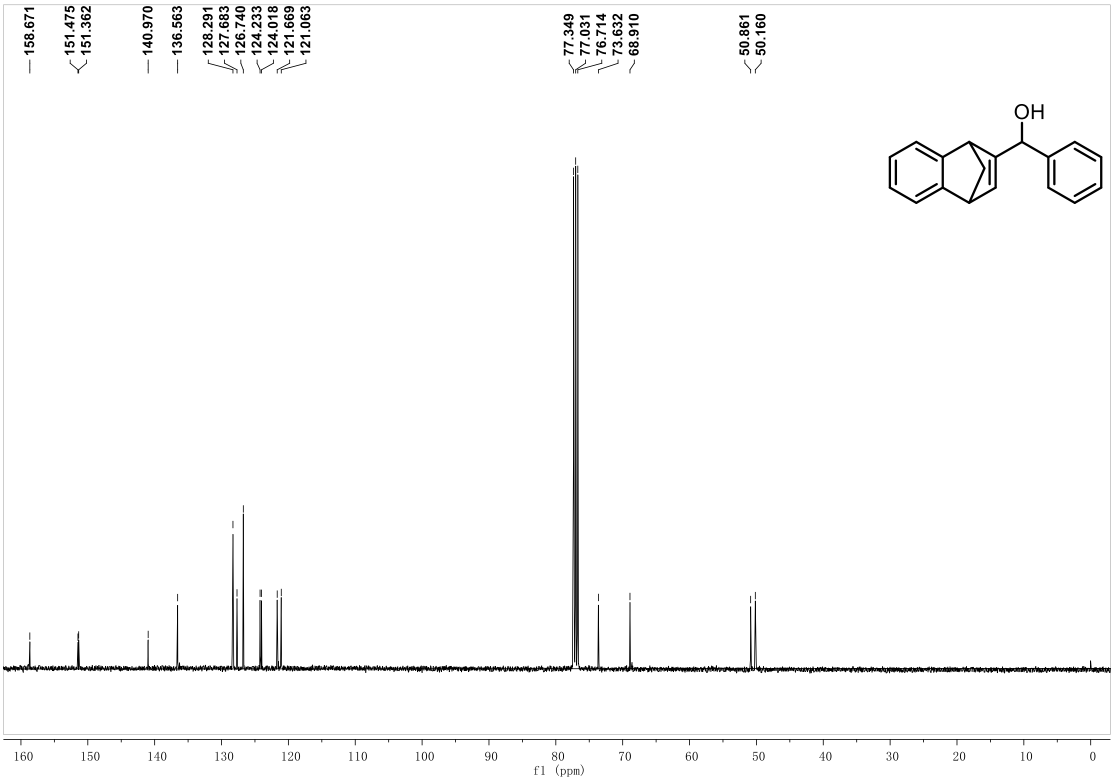
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77.031
76.714
73.632
68.910
50.861
50.160
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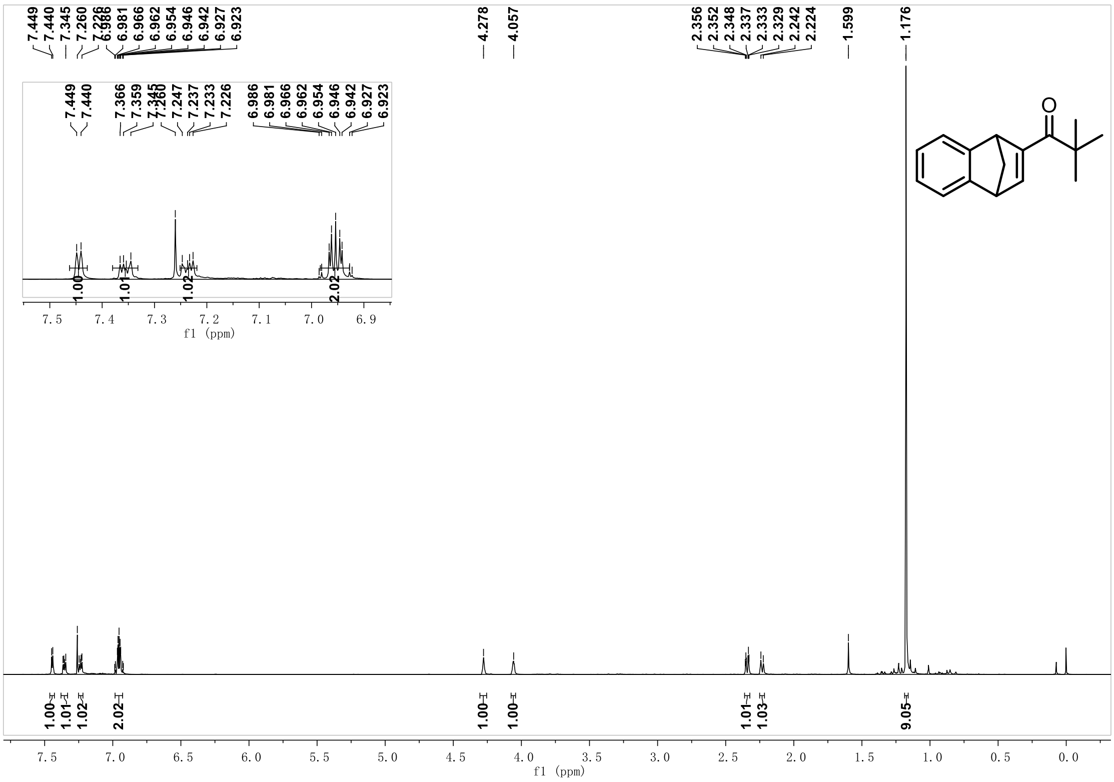
f1 (ppm)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6.954
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6.927
6.923
4.278
4.057
2.356
2.352
2.348
2.337
2.333
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2.224
1.599
1.176
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7.366
7.359
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7.260
7.247
7.237
7.233
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6.966
6.962
6.954
6.946
6.942
6.927
6.923
1.00
1.01
1.02
2.02
7.5
7.4
7.3
7.2
7.1
7.0
6.9
f1 (ppm)
O
1.00
1.01
1.02
2.02
1.00
1.00
1.01
1.03
9.05
7.5
7.0
6.5
6.0
5.5
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1.0
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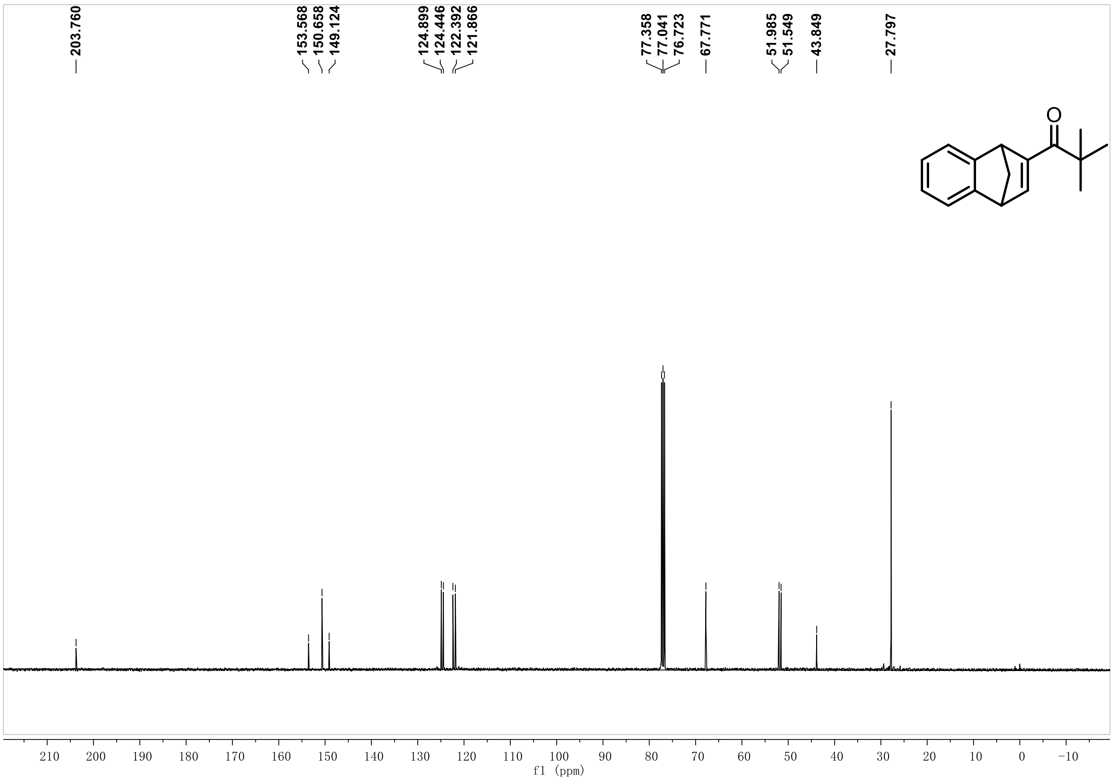
f1 (ppm)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43.849
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O
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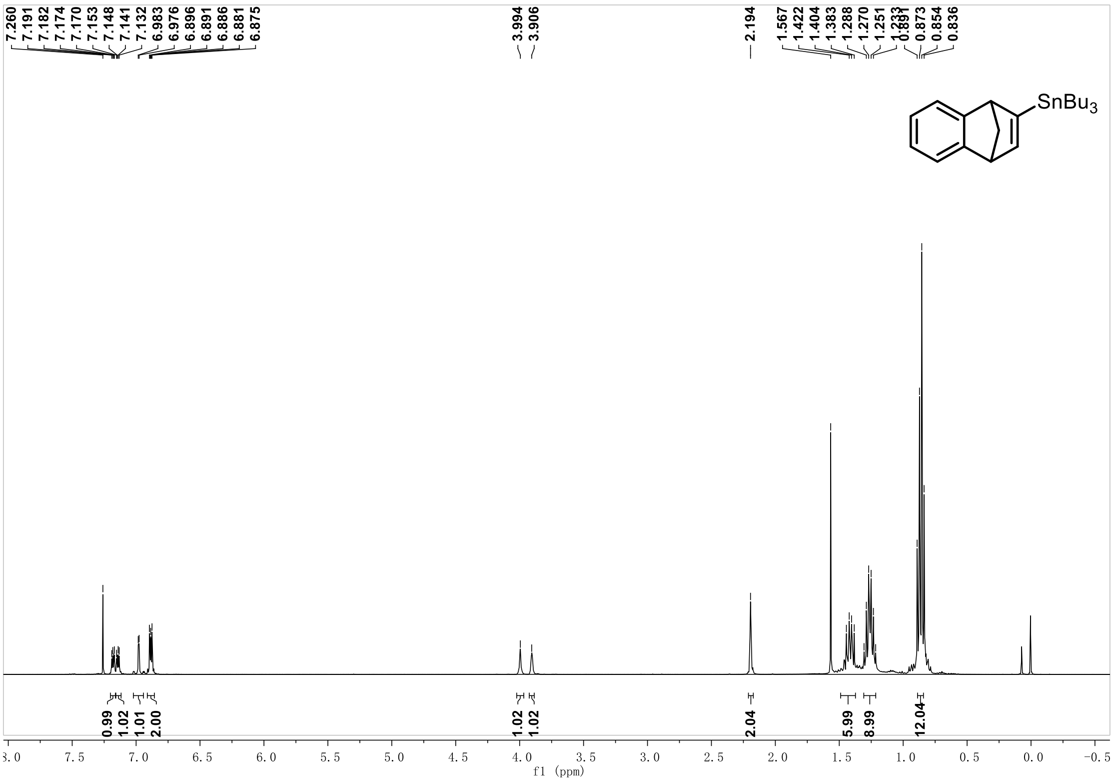
f1 (ppm)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6.881
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3.906
2.194
1.567
1.422
1.404
1.383
1.288
1.270
1.251
1.233
0.891
0.873
0.854
0.836
SnBu3
0.99
1.02
1.01
2.00
1.02
1.02
2.04
5.99
8.99
12.04
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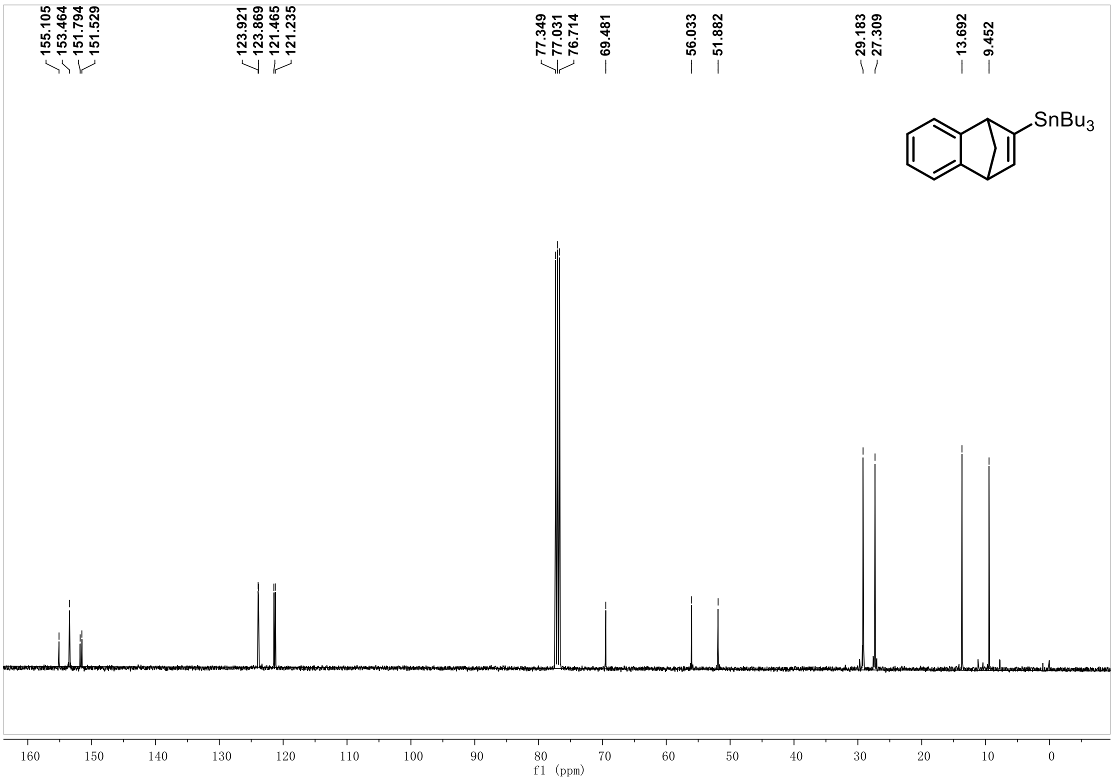
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69.481
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27.309
13.692
9.452
SnBu$_3$
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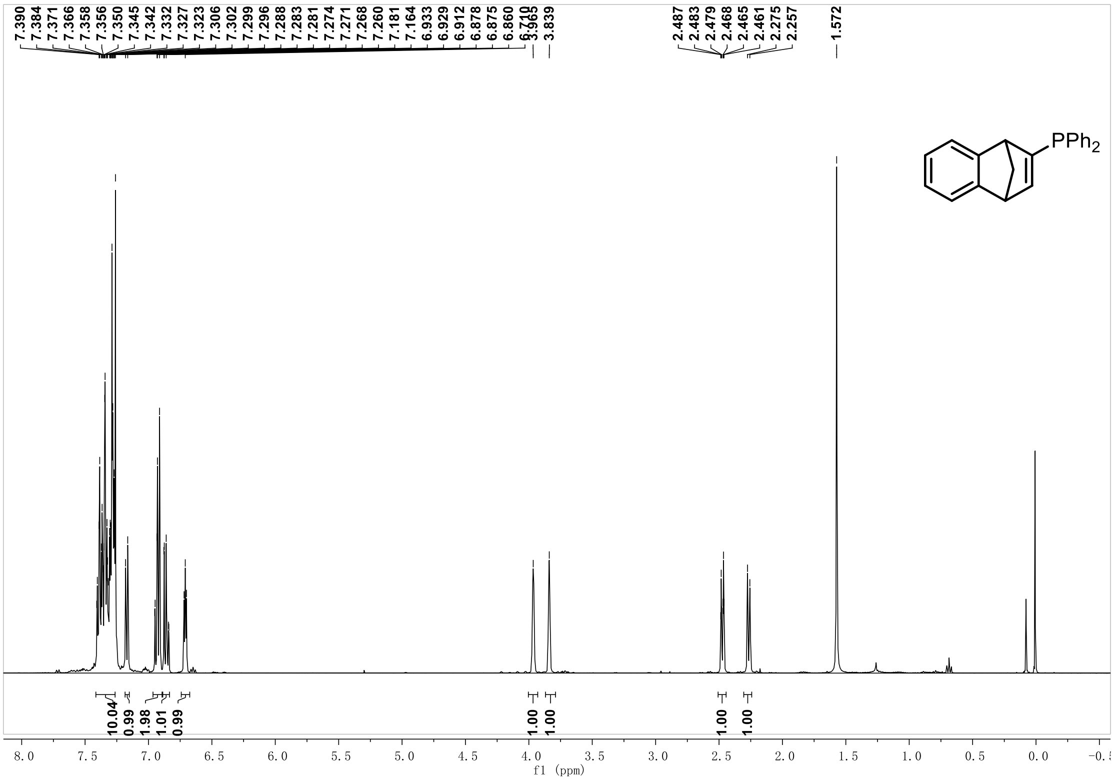
f1 (ppm)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7.302
7.299
7.296
7.288
7.283
7.281
7.274
7.271
7.268
7.260
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7.164
6.933
6.929
6.912
6.878
6.875
6.860
6.710
3.965
3.839
2.487
2.483
2.479
2.468
2.465
2.461
2.275
2.257
1.572
PPh$_2$
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1.01
0.99
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1.00
1.00
1.00
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
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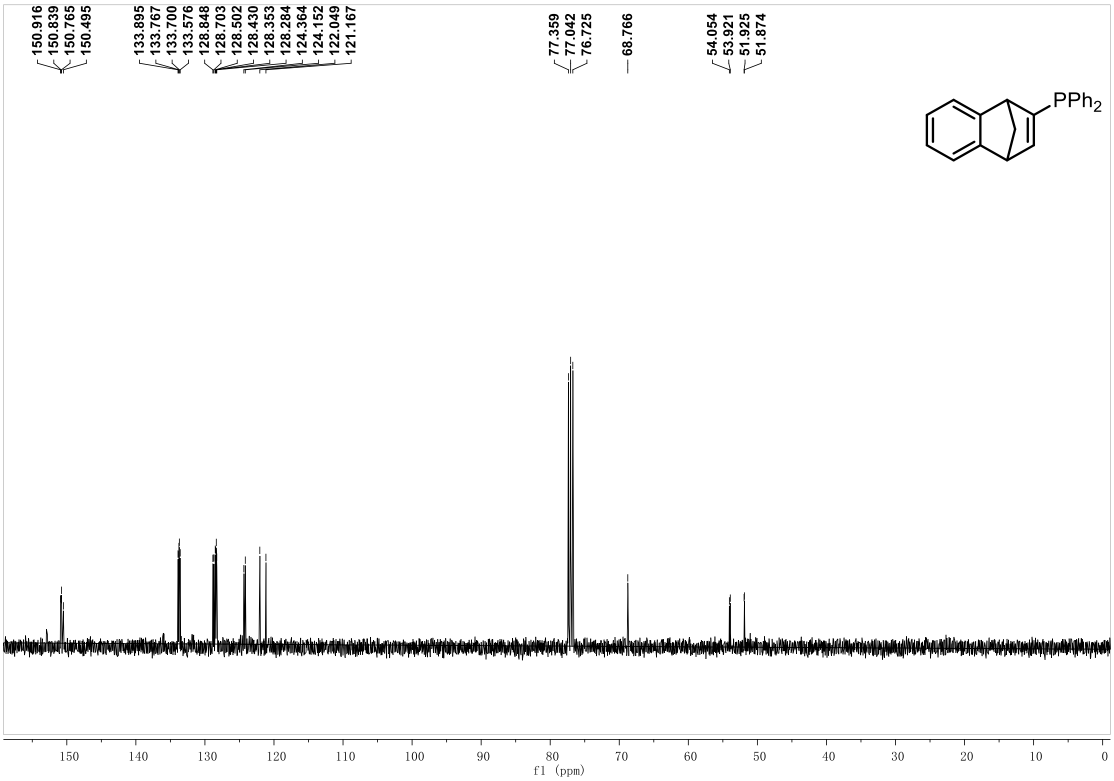
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128.353
128.284
124.364
124.152
122.049
121.167
77.359
77.042
76.725
68.766
54.054
53.921
51.925
51.874
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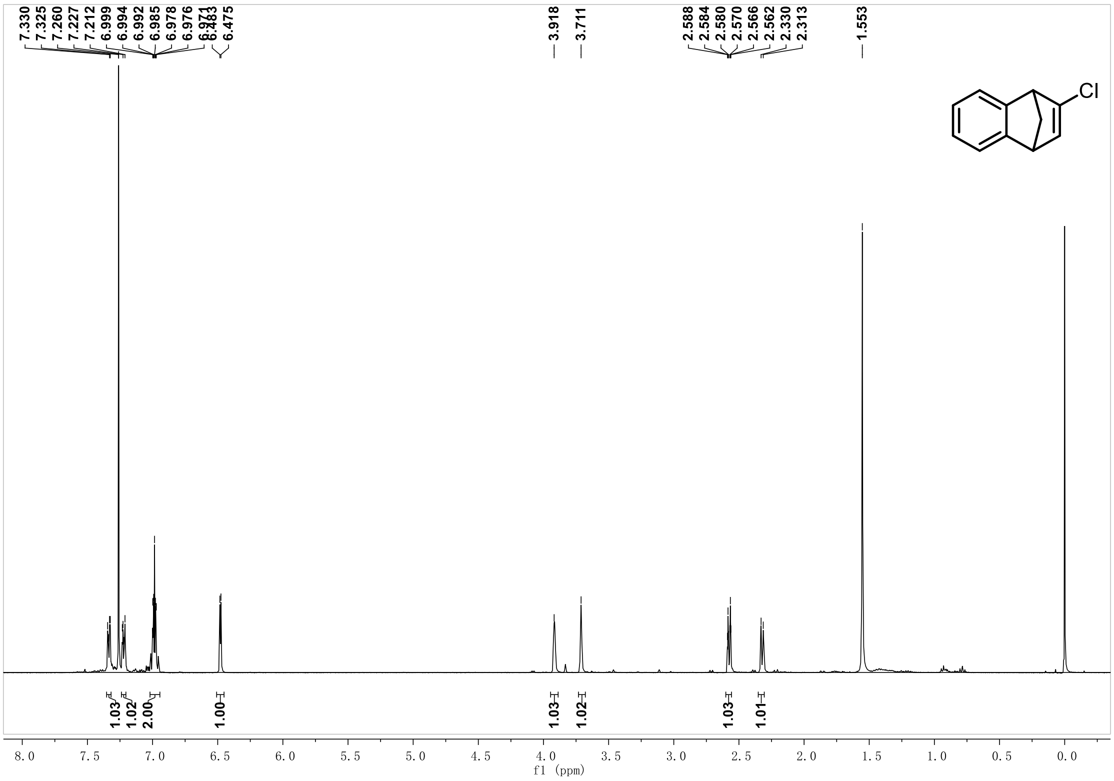
20
10
0
f1 (ppm)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6.971
6.483
6.475
3.918
3.711
2.588
2.584
2.580
2.570
2.566
2.562
2.330
2.313
1.553
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1.02
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1.00
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1.03
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6.0
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1.0
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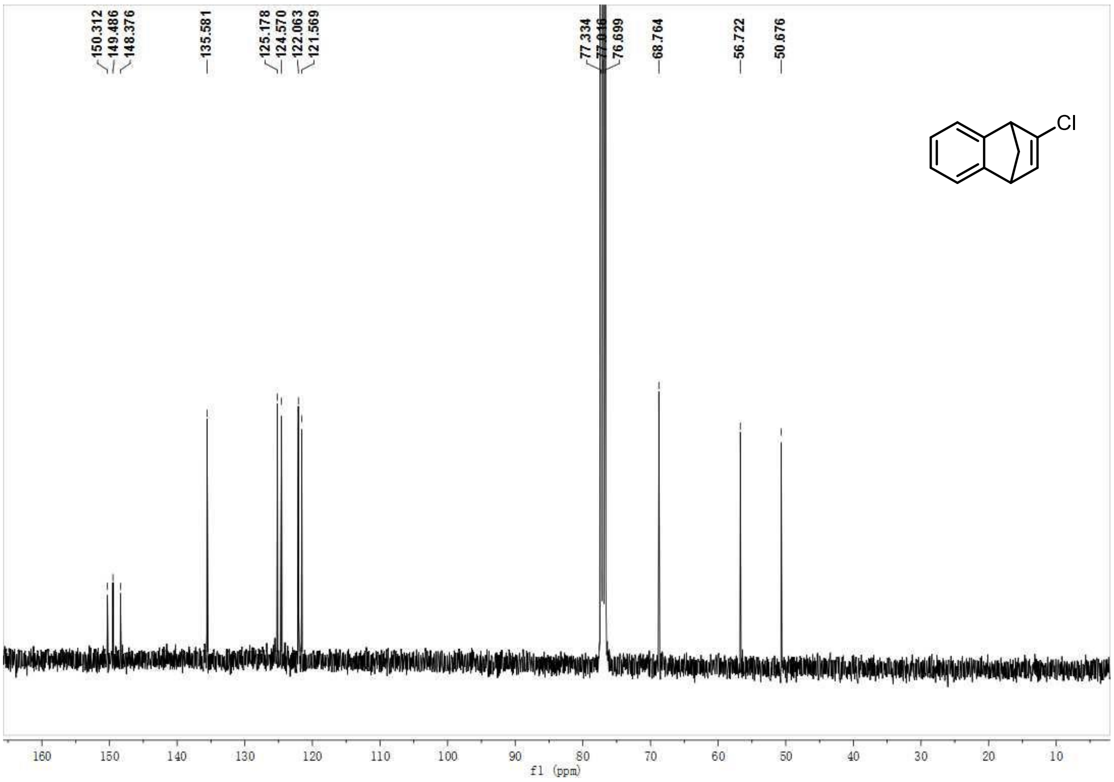
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56.722
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30
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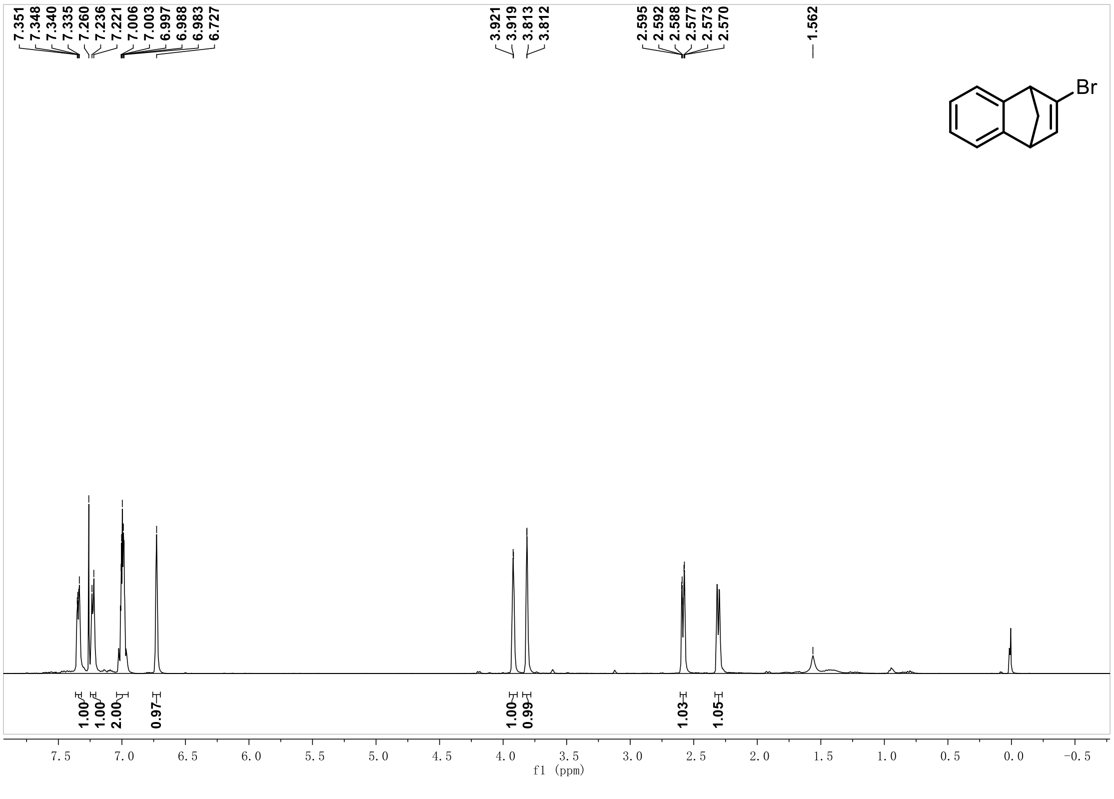
f1 (ppm)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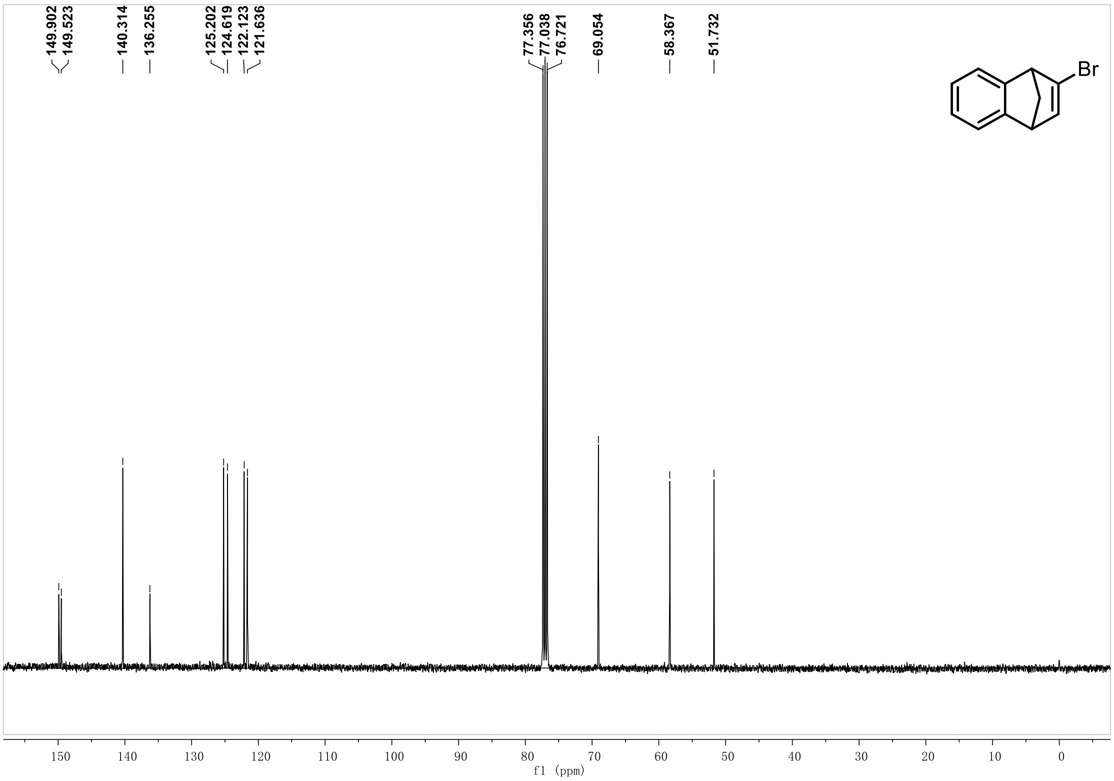
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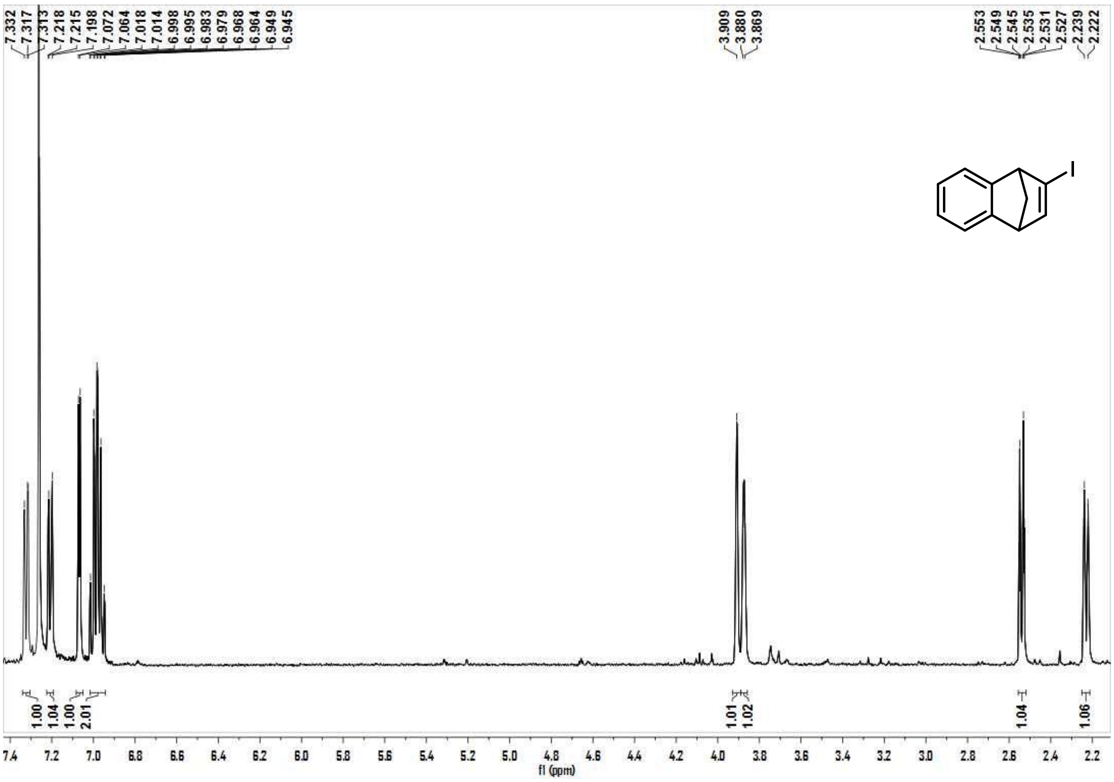
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1.00
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1.04
1.06
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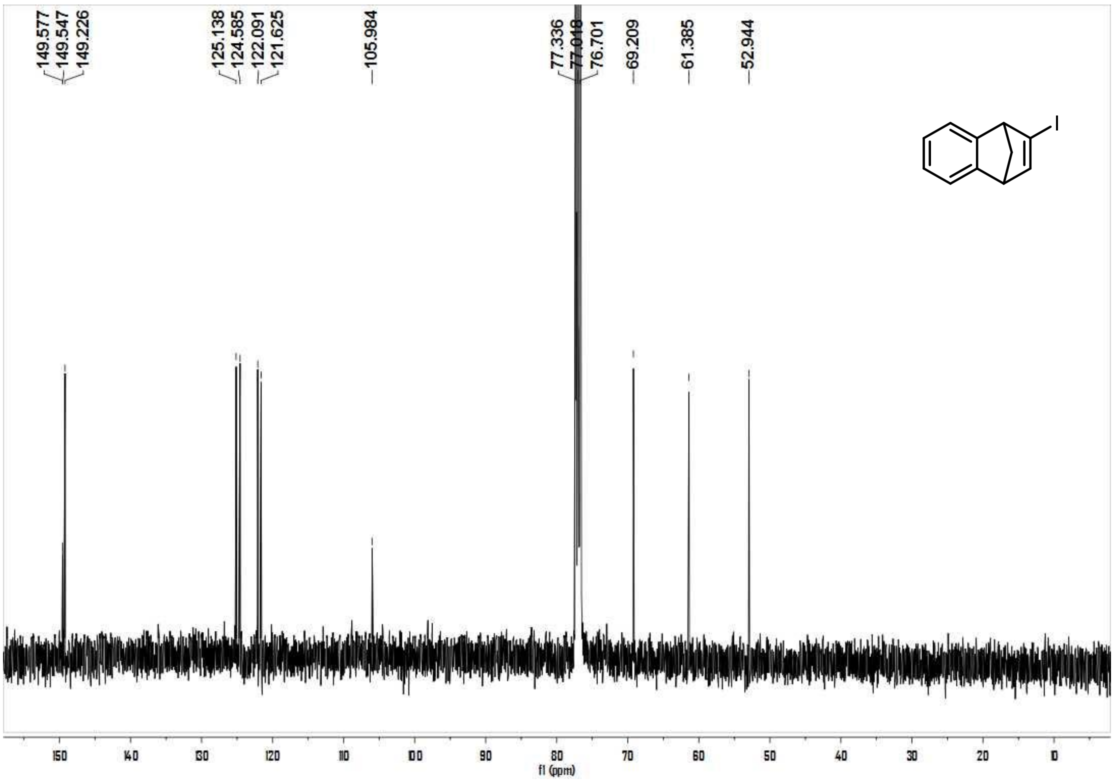
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105.984
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69.209
61.385
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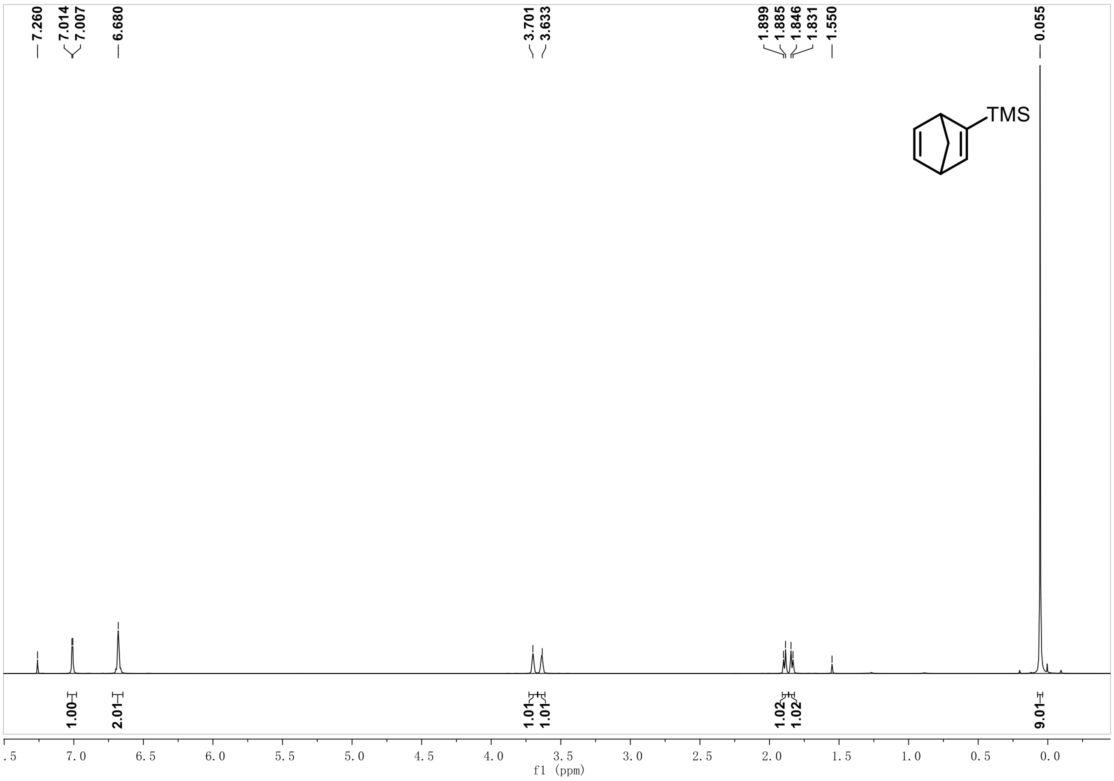
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TMS
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2.01
1.01
1.01
1.02
1.02
9.01
.5
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6.5
6.0
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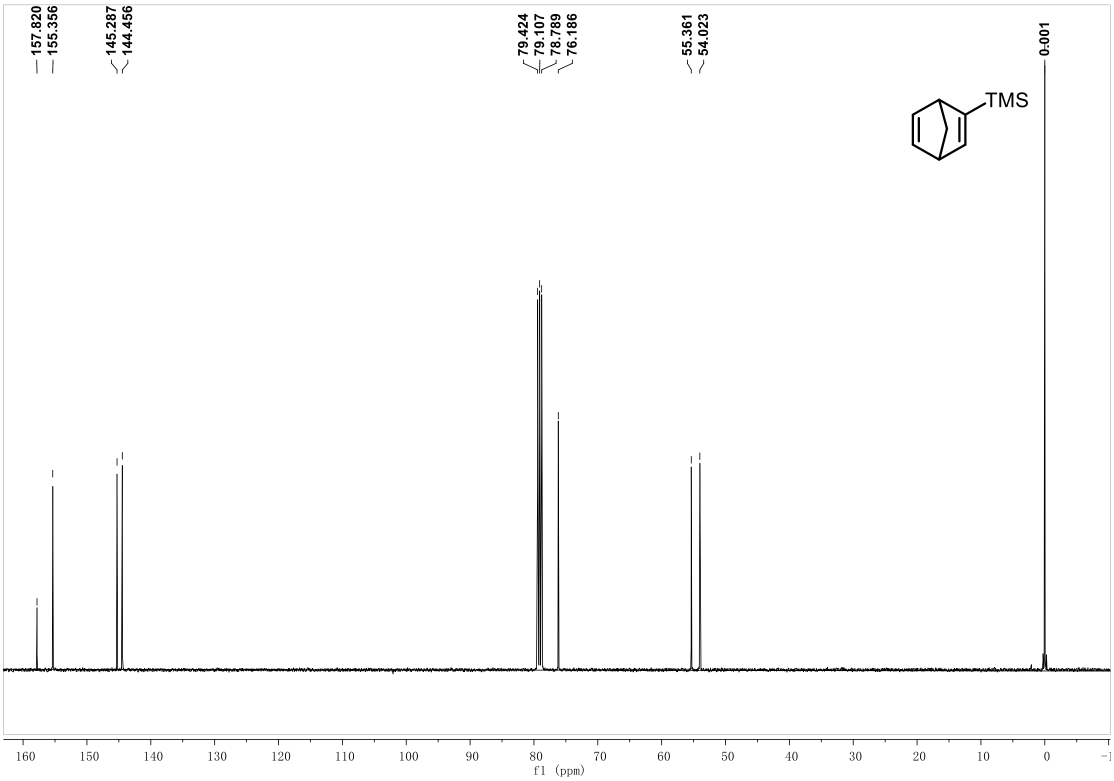
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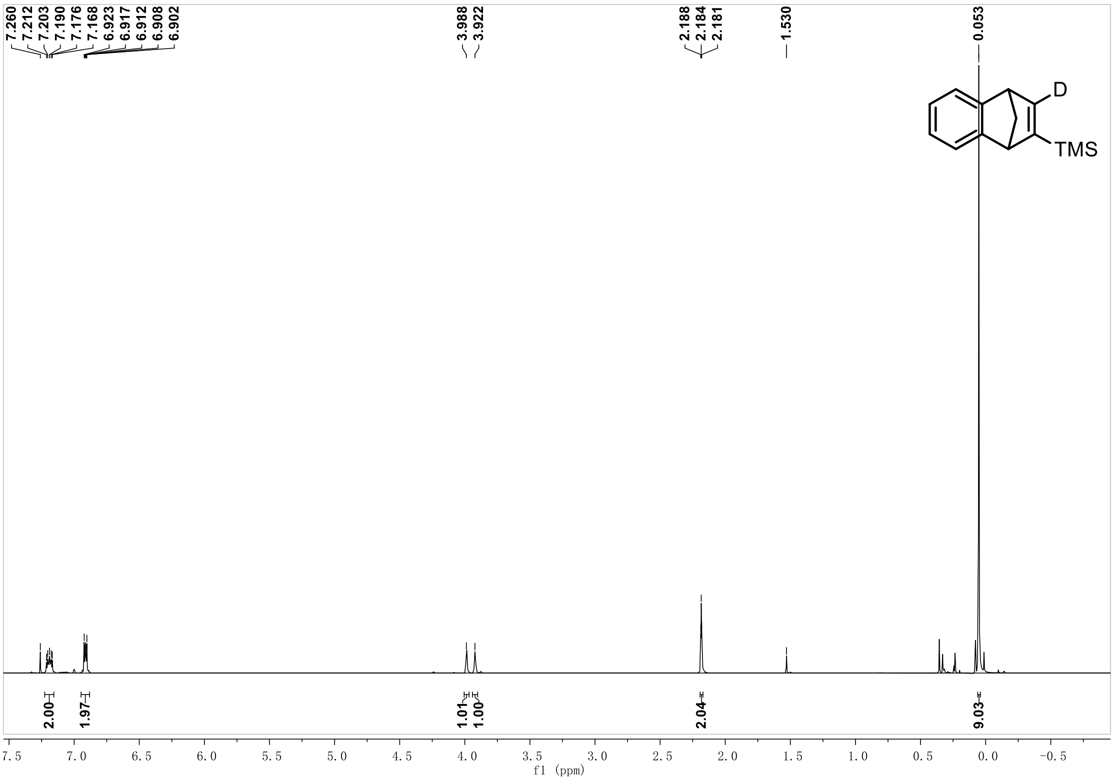
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2.184
2.181
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D
TMS
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1.00
2.04
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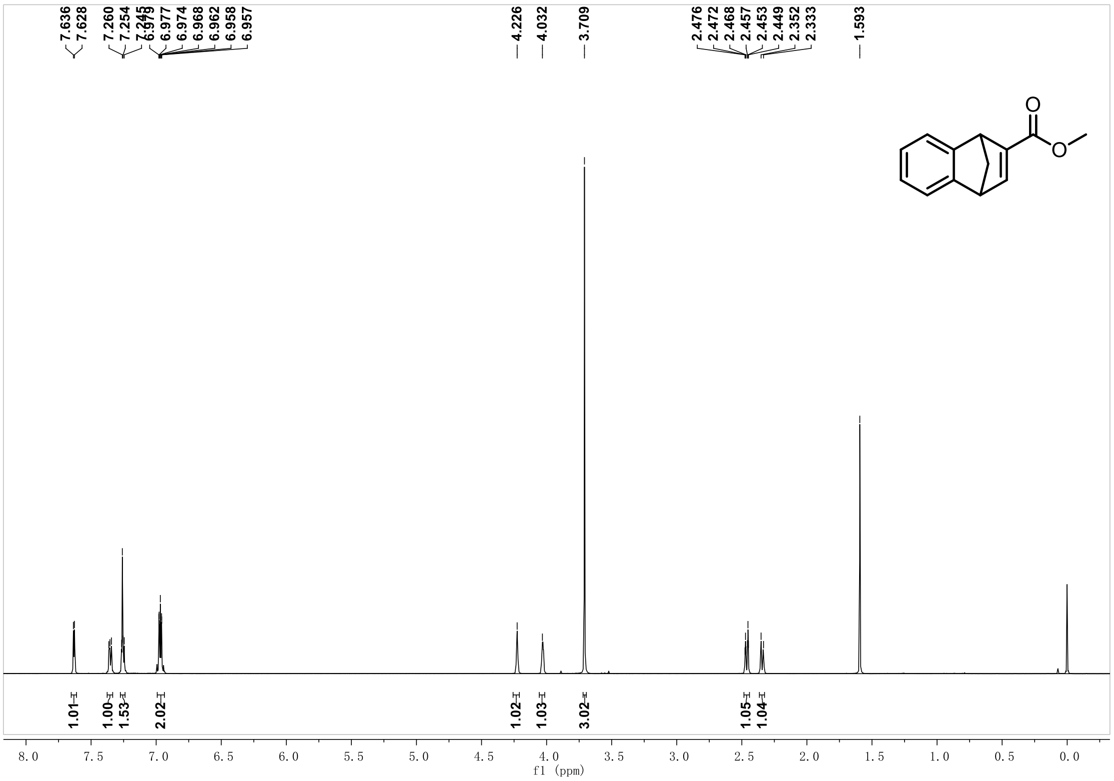
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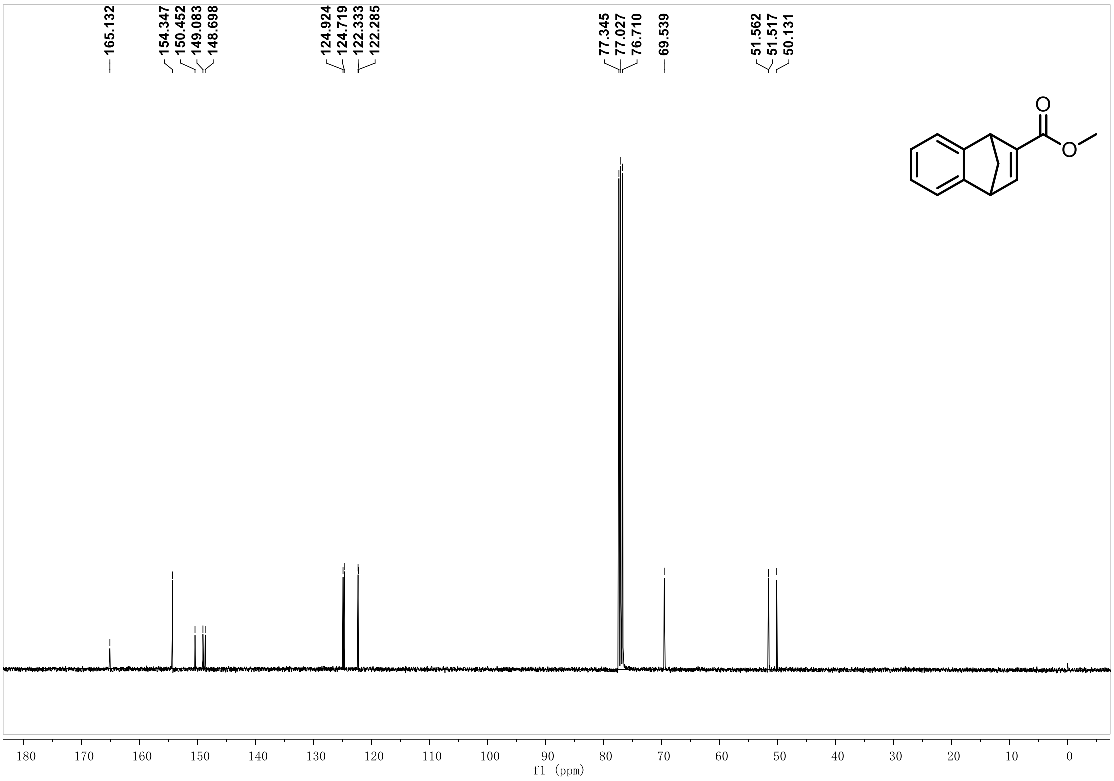
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O
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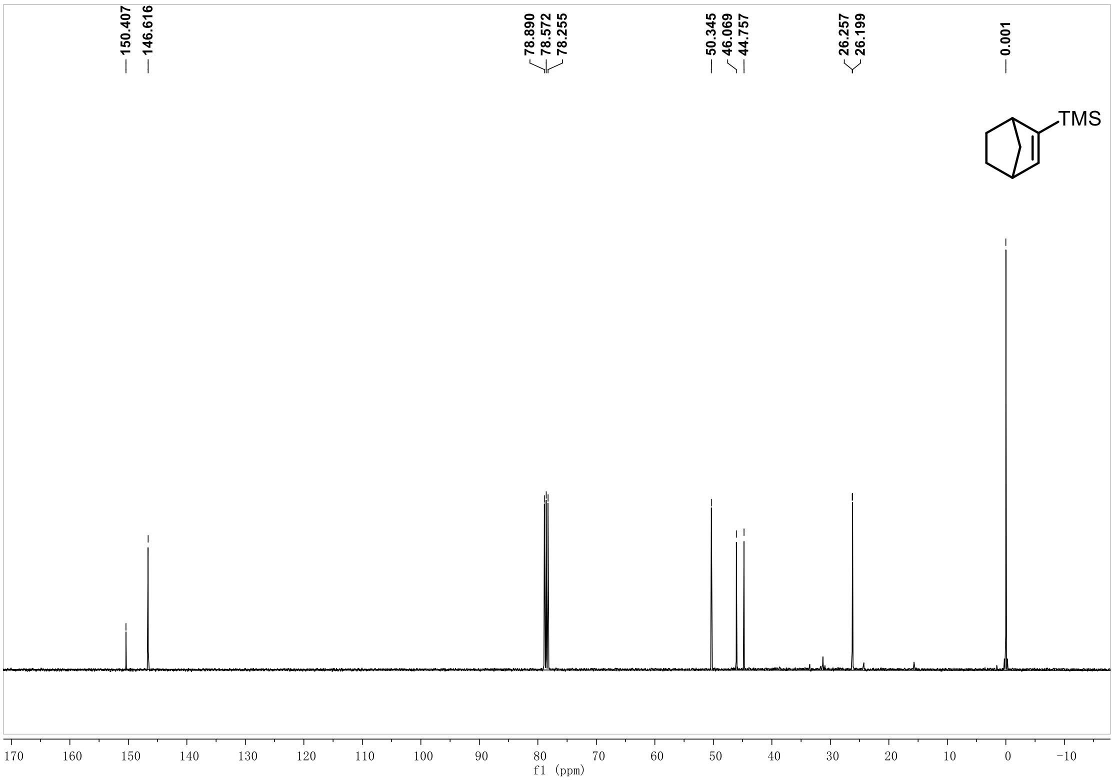
20
10
0
f1 (ppm)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26.199
0.001
TMS
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140
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100
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30
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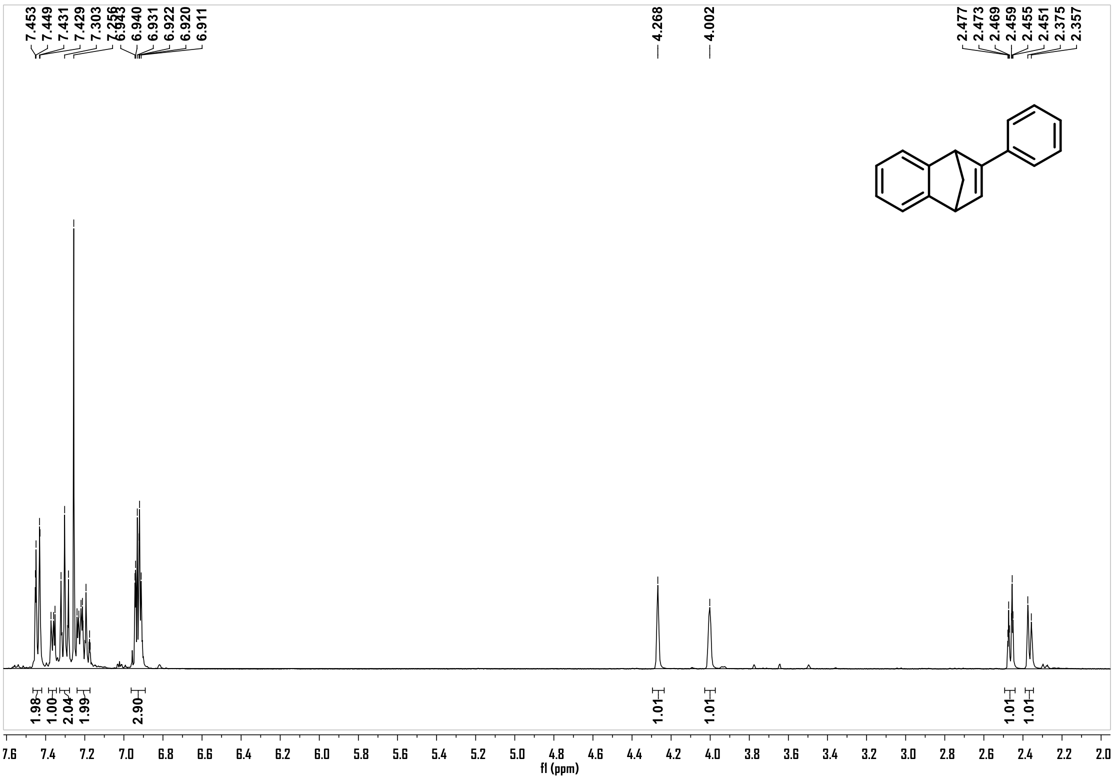
−10
f1 (ppm)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6.911
4.268
4.002
2.477
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2.459
2.455
2.451
2.375
2.357
1.98
1.00
2.04
1.99
2.90
1.01
1.01
1.01
1.01
7.6
7.4
7.2
7.0
6.8
6.6
6.4
6.2
6.0
5.8
5.6
5.4
5.2
5.0
4.8
4.6
4.4
4.2
4.0
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3.4
3.2
3.0
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2.4
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2.0
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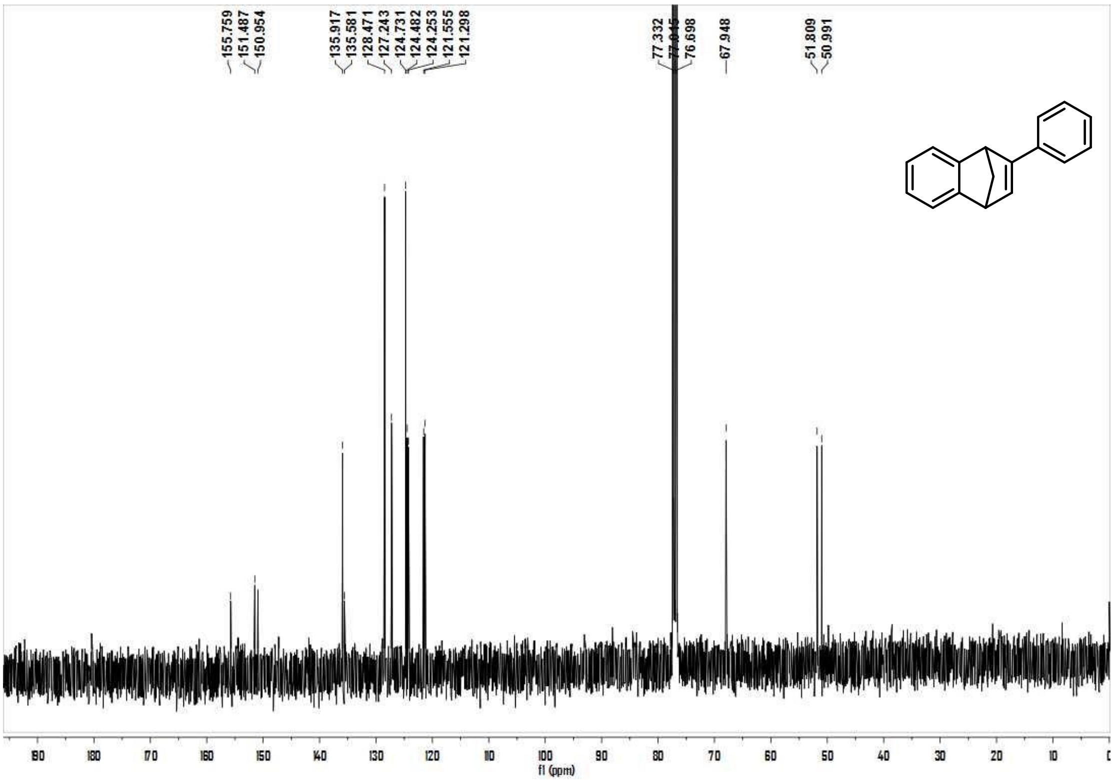
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124.731
124.482
124.253
121.555
121.298
77.332
77.015
76.698
67.948
51.809
50.991
190
180
170
160
150
140
130
120
110
100
90
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70
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50
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30
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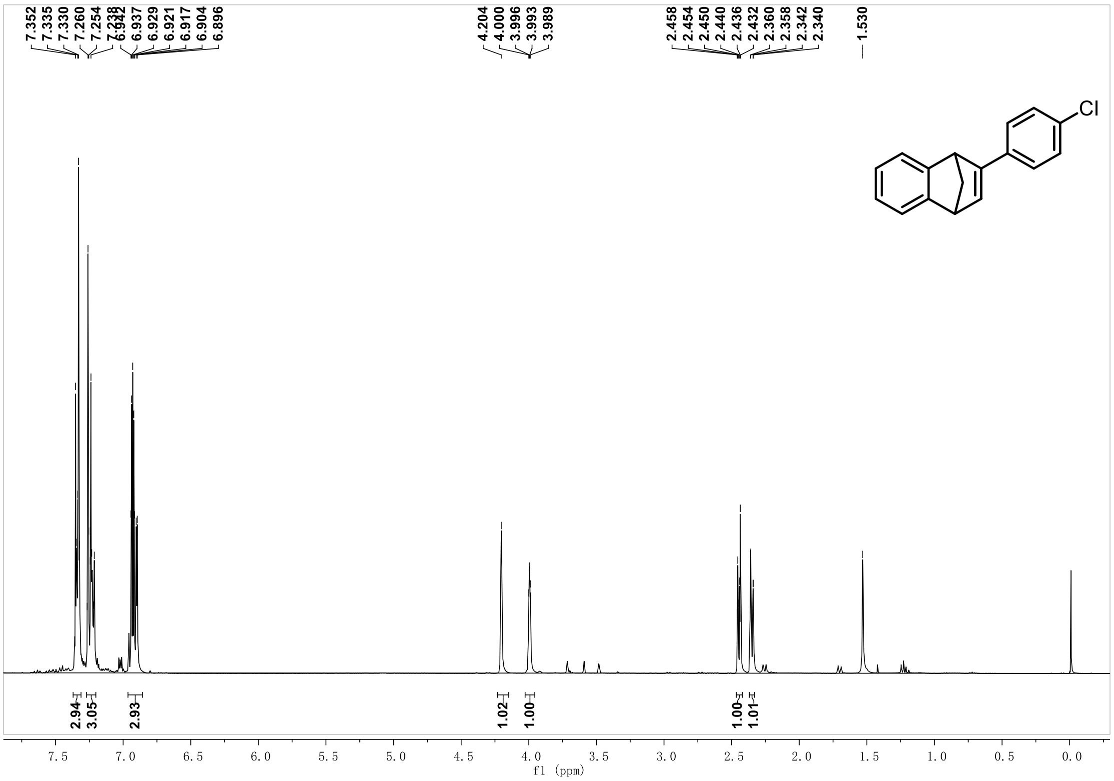
f1 (ppm)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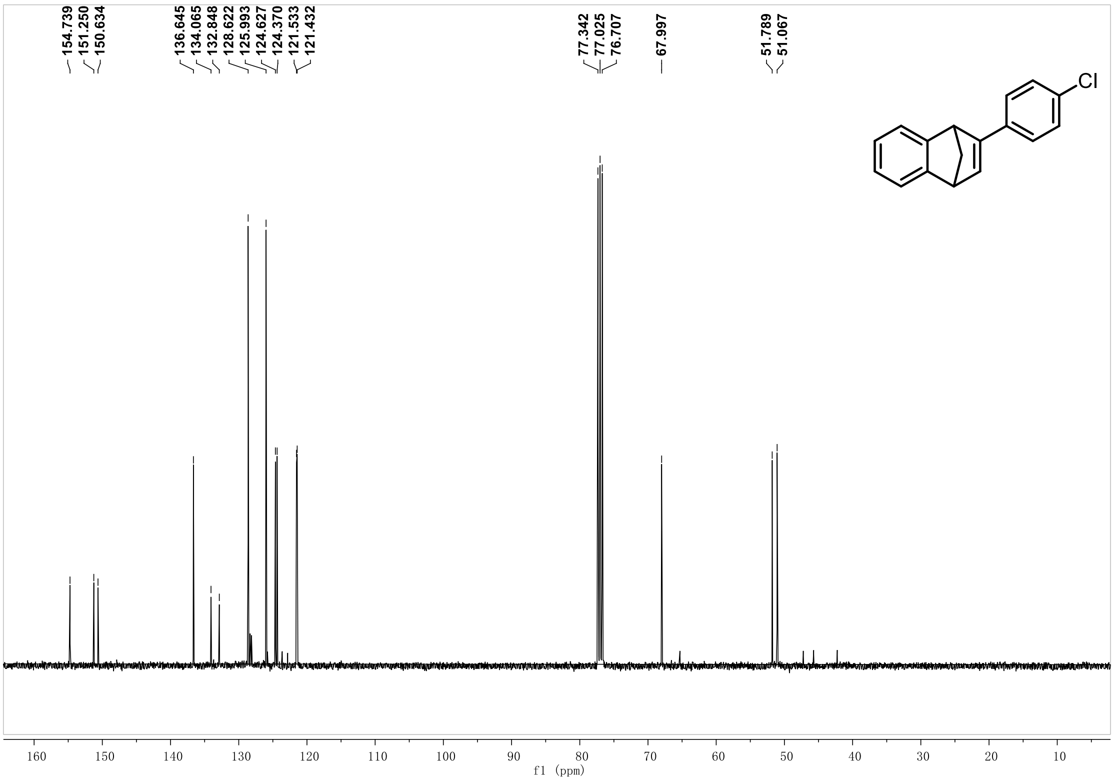
7.330
7.260
7.254
7.238
6.942
6.937
6.929
6.921
6.917
6.904
6.896
4.204
4.000
3.996
3.993
3.989
2.458
2.454
2.450
2.440
2.436
2.432
2.360
2.358
2.342
2.340
1.530
Cl
2.94
3.05
2.93
1.02
1.00
1.00
1.01
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


154.739
151.250
150.634
136.645
134.065
132.848
128.622
125.993
124.627
124.370
121.533
121.432
77.342
77.025
76.707
67.997
51.789
51.067
Cl
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
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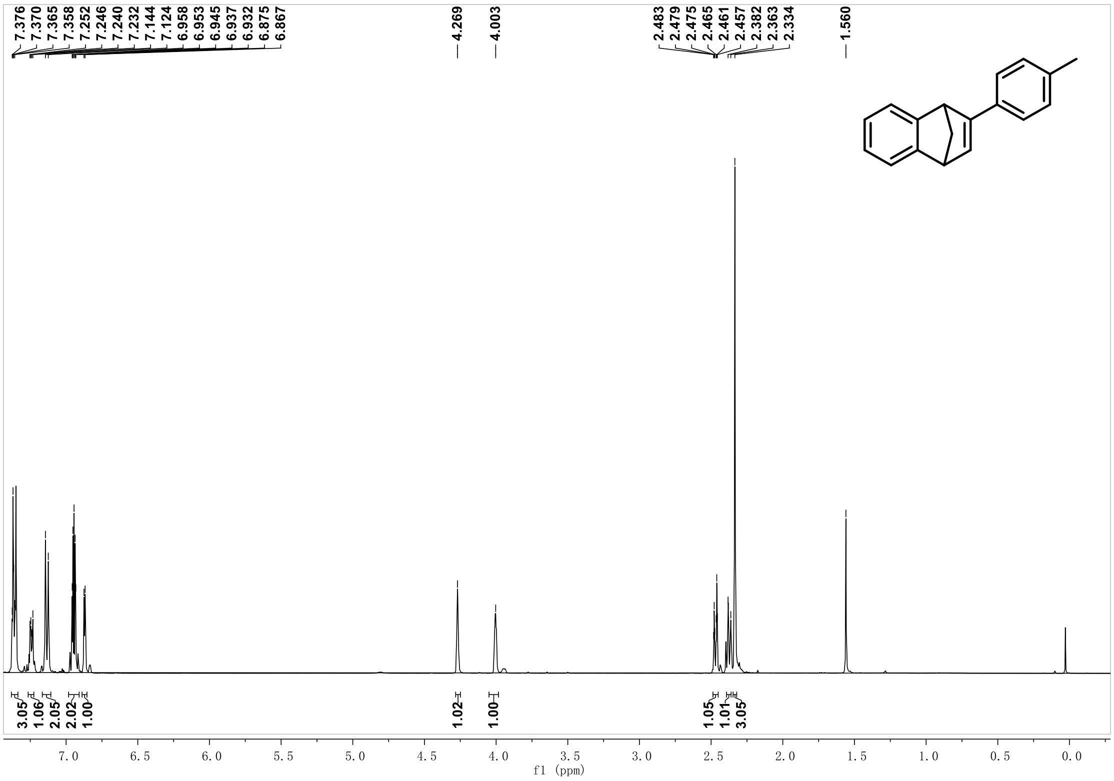
f1 (ppm)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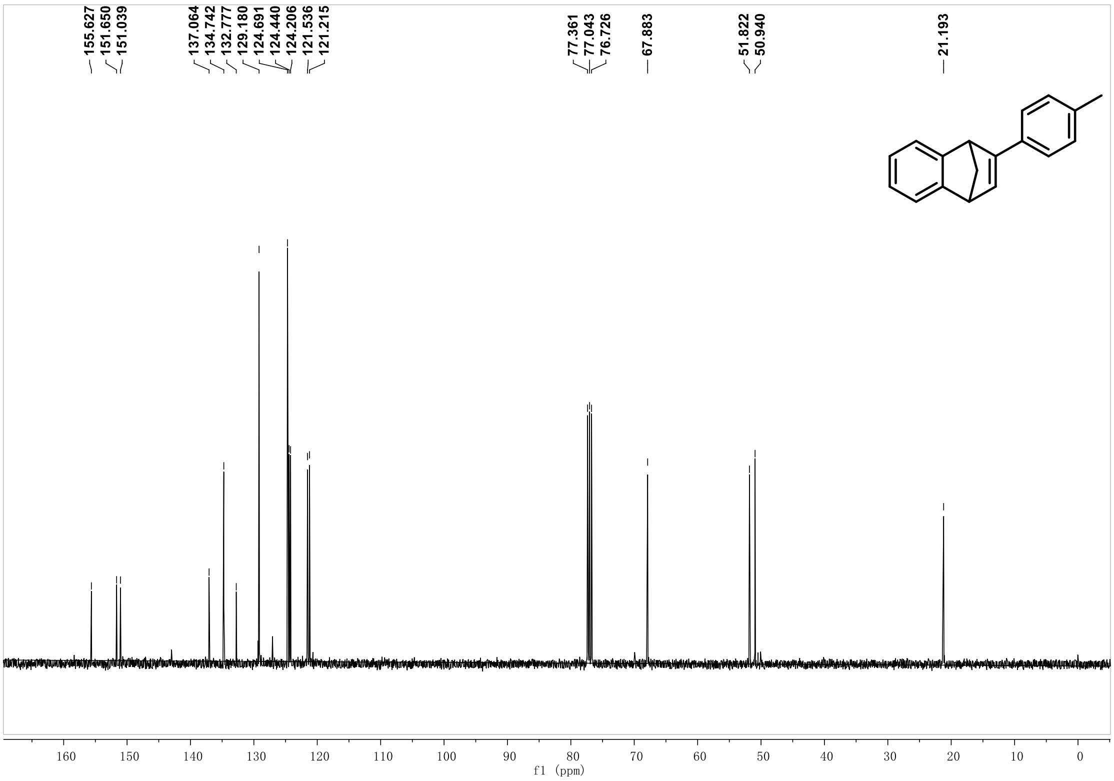
7.370
7.365
7.358
7.252
7.246
7.240
7.232
7.144
7.124
6.958
6.953
6.945
6.937
6.932
6.875
6.867
4.269
4.003
2.483
2.479
2.475
2.465
2.461
2.457
2.382
2.363
2.334
1.560
3.05
1.06
2.05
2.02
1.00
1.02
1.00
1.05
1.01
3.05
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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151.039
137.064
134.742
132.777
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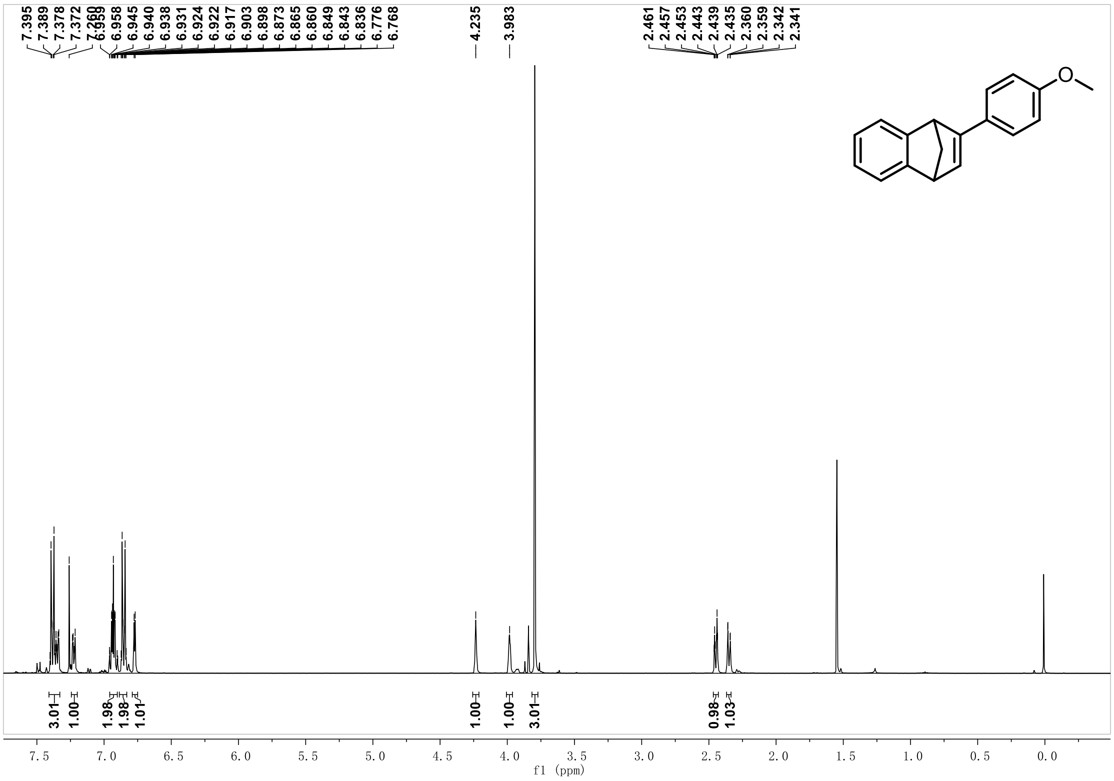
124.691
124.440
124.206
121.536
121.215
77.361
77.043
76.726
67.883
51.822
50.940
21.193
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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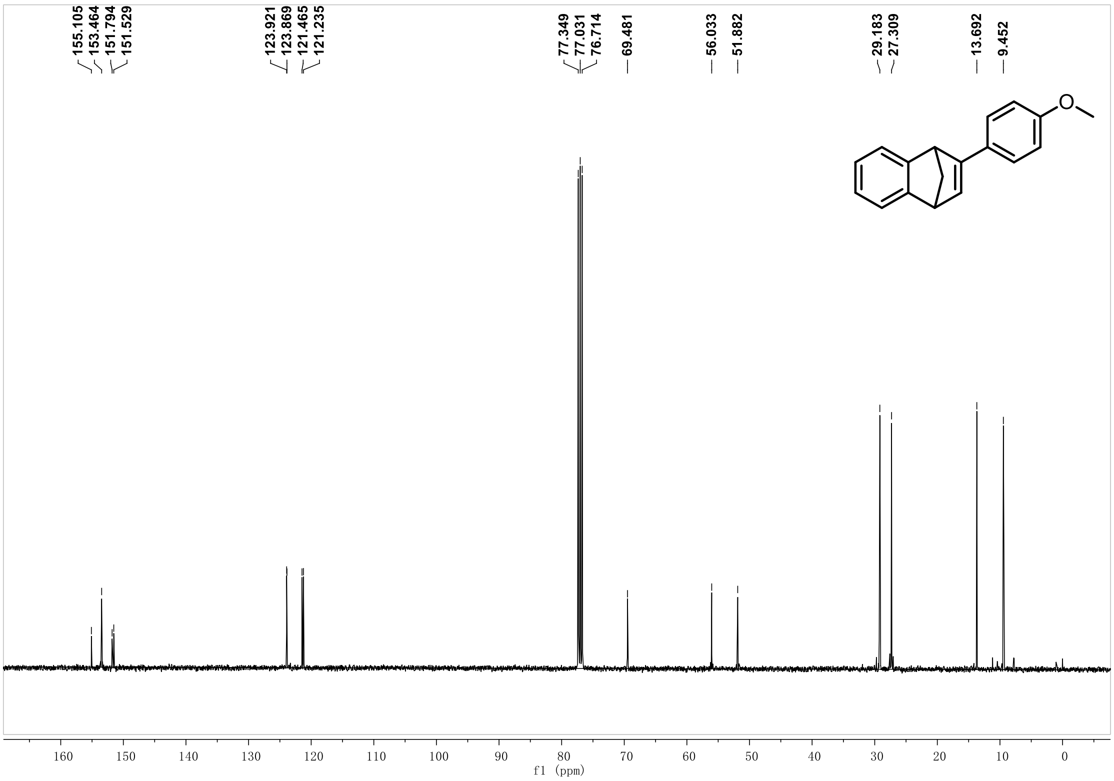
7.378
7.372
7.260
6.959
6.958
6.945
6.940
6.938
6.931
6.924
6.922
6.917
6.903
6.898
6.873
6.865
6.860
6.849
6.843
6.836
6.776
6.768
4.235
3.983
2.461
2.457
2.453
2.443
2.439
2.435
2.360
2.359
2.342
2.341
3.01
1.00
1.98
1.98
1.01
1.00
1.00
3.01
0.98
1.03
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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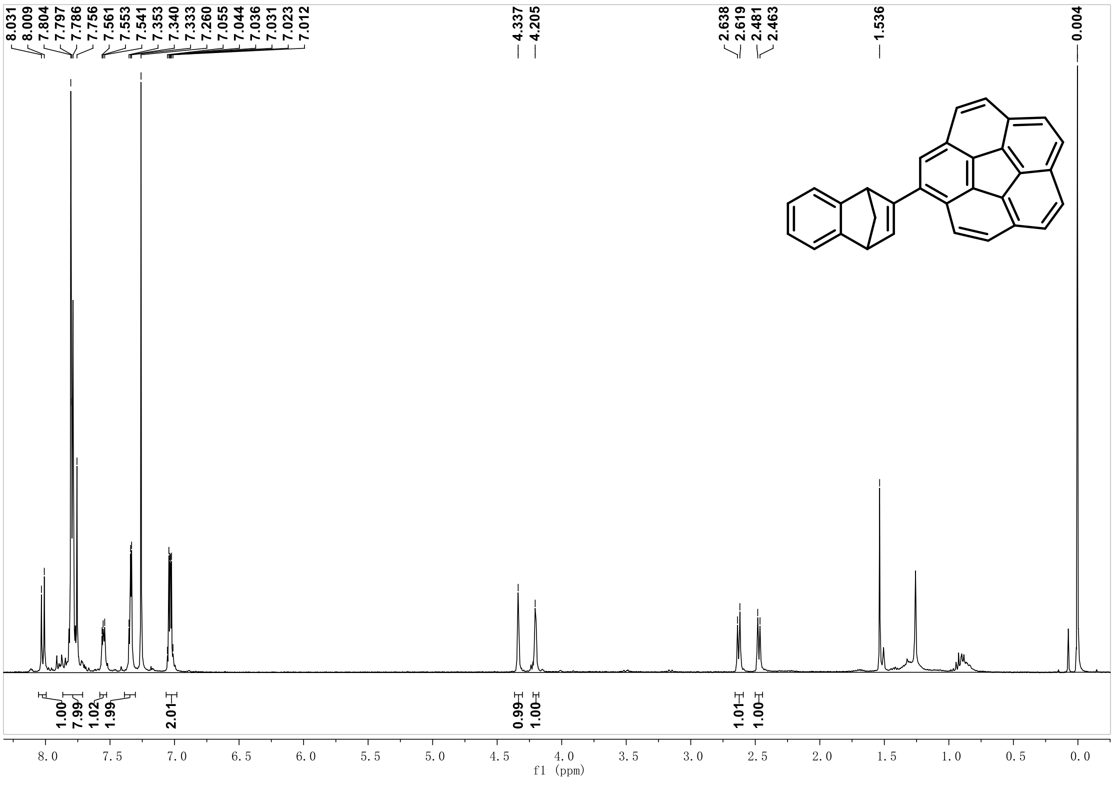
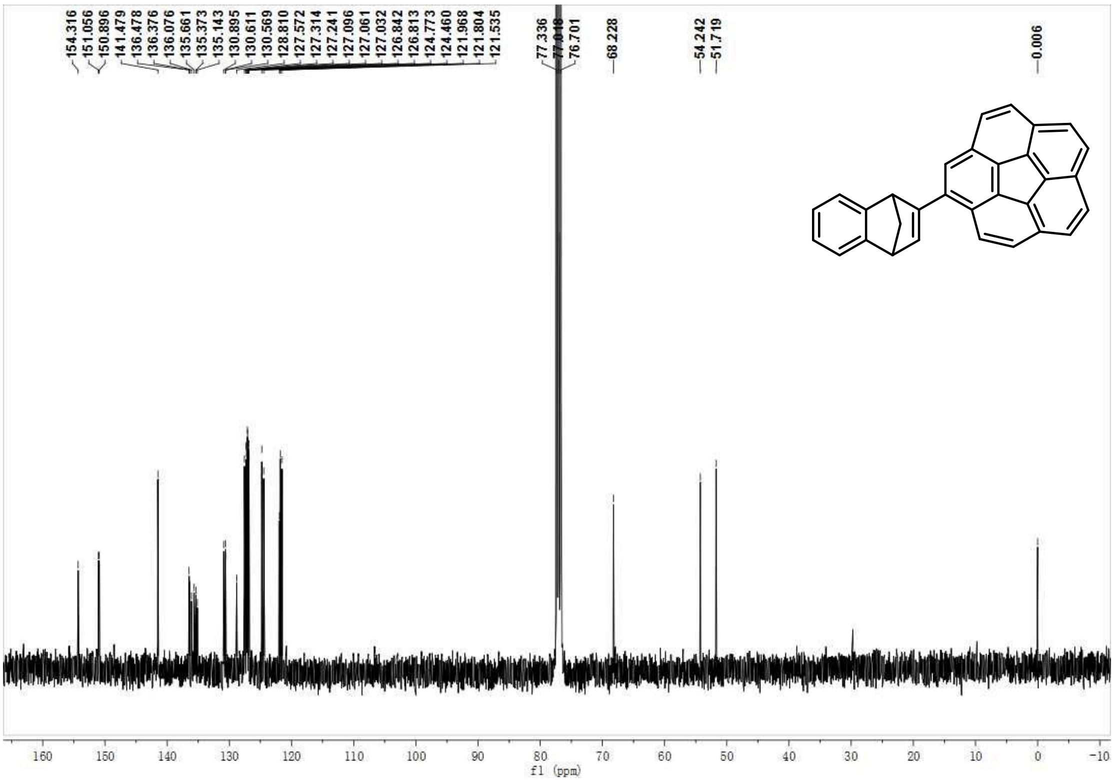
151.794
151.529
123.921
123.869
121.465
121.235
77.349
77.031
76.714
69.481
56.033
51.882
29.183
27.309
13.692
9.452
O
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


8.031
8.009
7.804
7.797
7.786
7.756
7.561
7.553
7.541
7.353
7.340
7.333
7.260
7.055
7.044
7.036
7.031
7.023
7.012
4.337
4.205
2.638
2.619
2.481
2.463
1.536
0.004
1.00
7.99
1.02
1.99
2.01
0.99
1.00
1.01
1.00
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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150.896
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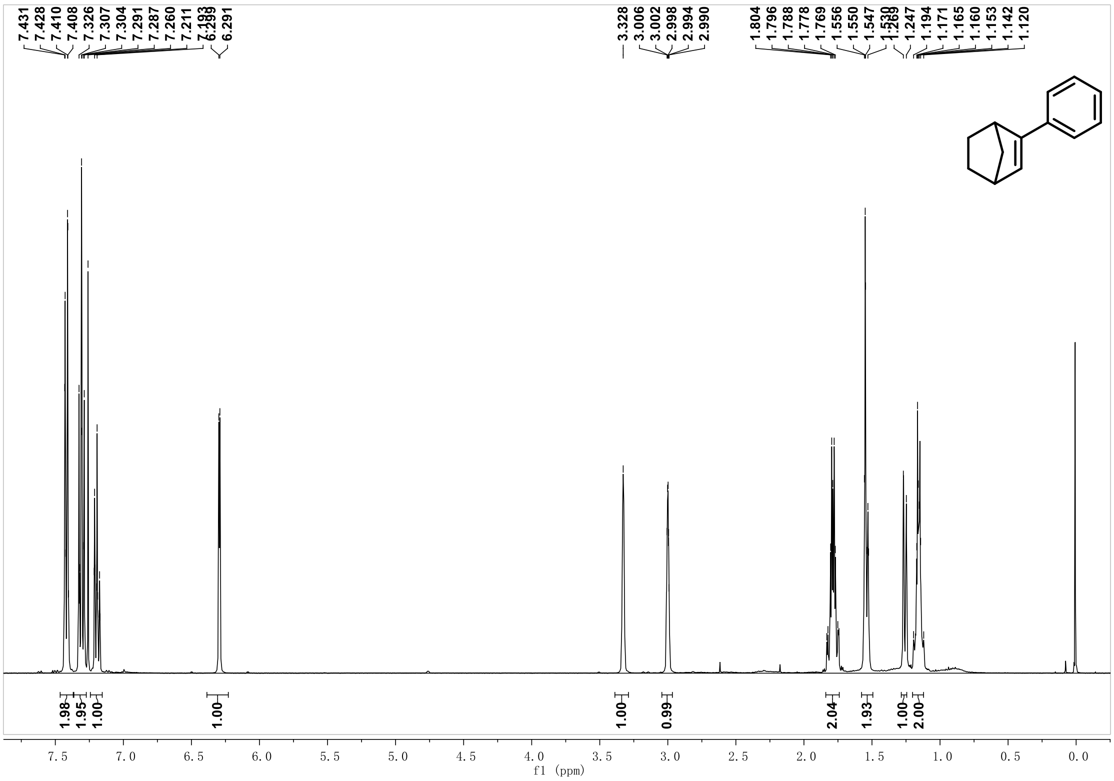
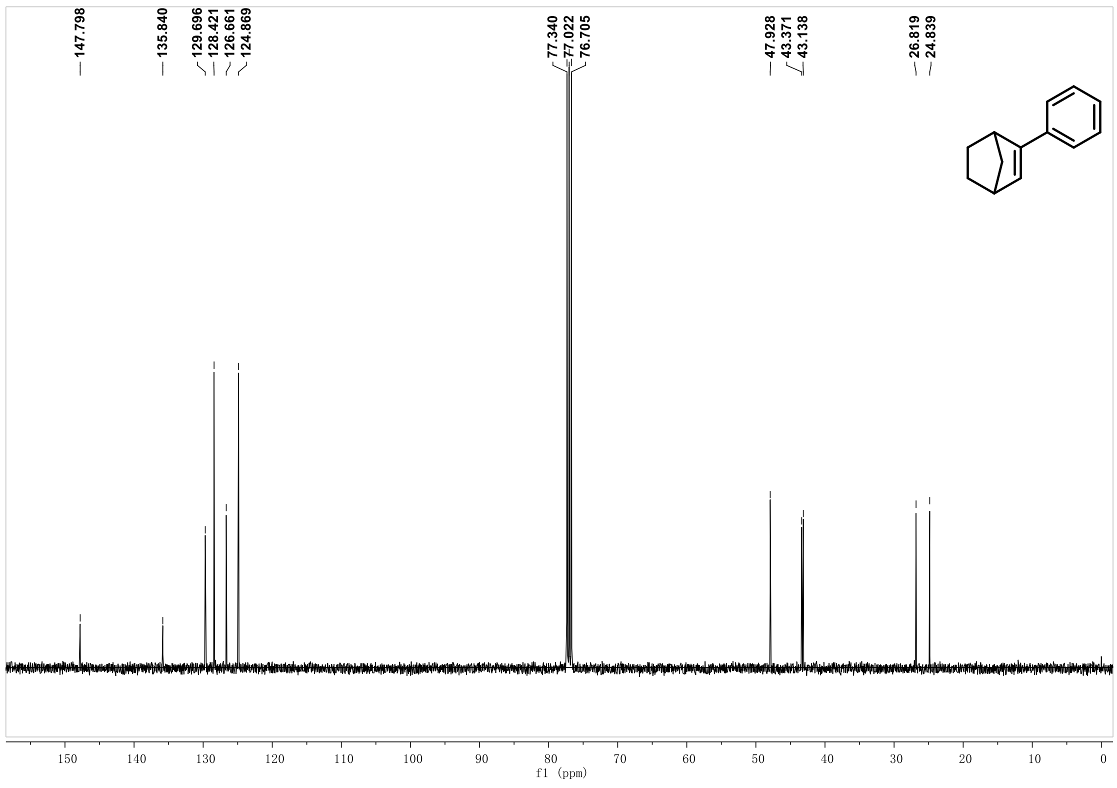
136.478
136.376
136.076
135.661
135.373
135.143
130.895
130.611
130.569
128.810
127.572
127.314
127.241
127.096
127.061
127.032
126.842
126.813
124.773
124.460
121.968
121.804
121.535
77.336
77.018
76.701
68.228
54.242
51.719
0.006
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


7.431
7.428
7.410
7.408
7.326
7.307
7.304
7.291
7.287
7.260
7.211
7.193
6.293
6.291
3.328
3.006
3.002
2.998
2.994
2.990
1.804
1.796
1.788
1.778
1.769
1.556
1.550
1.547
1.539
1.269
1.247
1.194
1.171
1.165
1.160
1.153
1.142
1.120
1.98
1.95
1.00
1.00
1.00
0.99
2.04
1.93
1.00
2.00
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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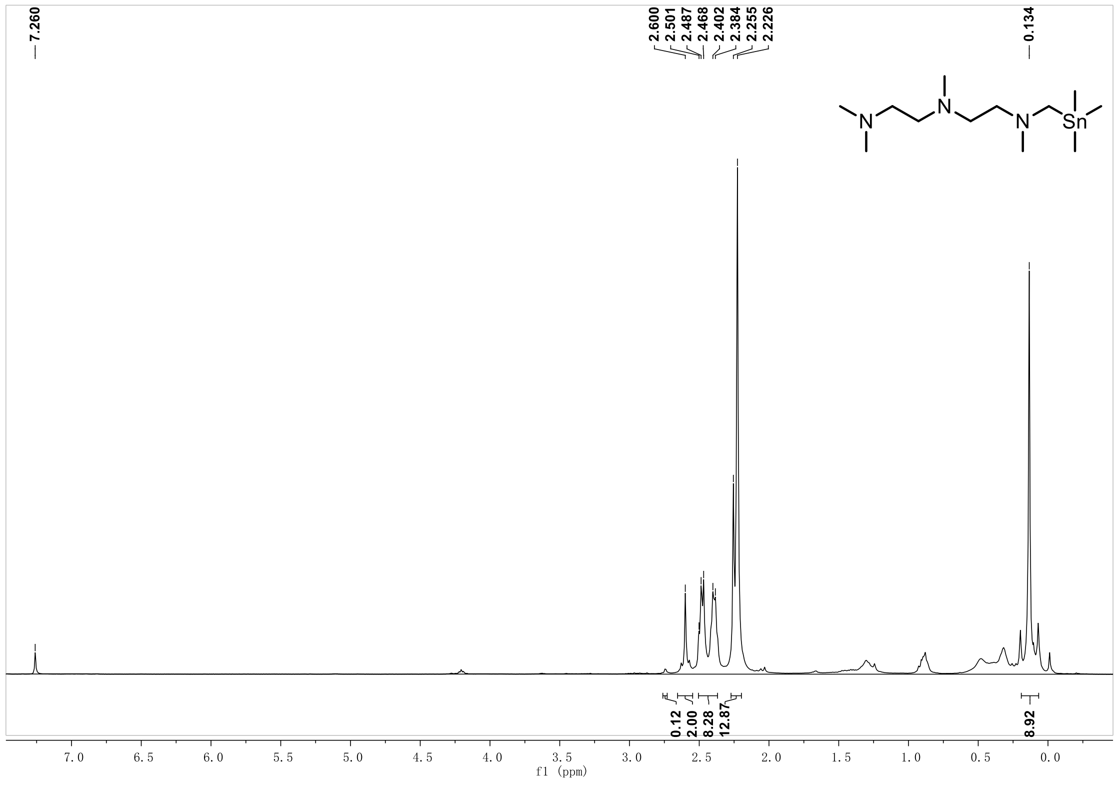
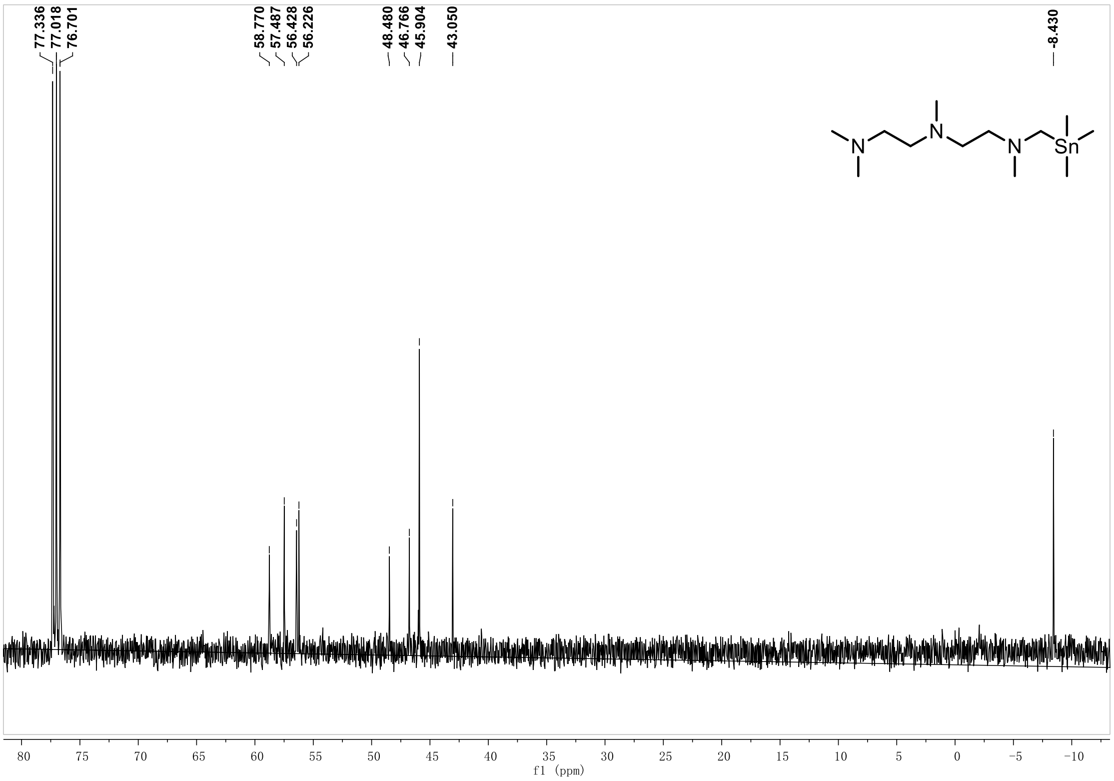
128.421
126.661
124.869
77.340
77.022
76.705
47.928
43.371
43.138
26.819
24.839
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.260
2.600
2.501
2.487
2.468
2.402
2.384
2.255
2.226
0.134
N
N
N
Sn
0.12
2.00
8.28
12.87
8.92
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


77.336
77.018
76.701
58.770
57.487
56.428
56.226
48.480
46.766
45.904
43.050
-8.430
N
N
N
Sn
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
0
−5
−10
f1 (ppm)