Electronic Supplementary Information

Magnesium-Mediated sp³ C-H Activation in Cascade Cyclization of

1-Arylethynyl-2-Alkyl-o-Carboranes: Efficient Synthesis of

Carborane-Fused Cyclopentanes

Jie Zhang,^{\dagger} Cen Tang,^{\dagger} and Zuowei Xie^{*}

Department of Chemistry and State Key Laboratory of Synthetic Chemistry, The Chinese University

of Hong Kong, Shatin, N. T., Hong Kong (China). E-mail: zxie@cuhk.edu.hk

Table of Contents

Experimental Section	S2
Deuterium Labelling Experiments	S10
Control Experiments	S15
Crystal Data and Summary of Data Collection and Refinements	S17
References	S19
NMR Spectra	S20

Experimental Section

General information. All reactions were carried out under an atmosphere of dry argon with the rigid exclusion of air and moisture using standard Schlenk techniques or in a glovebox unless otherwise specified. ¹H NMR spectra were recorded on a Bruker DPX 400 spectrometer at 400 MHz or a Bruker DPX 500 spectrometer at 500 MHz.²H NMR spectra were recorded on a Bruker DPX 400 spectrometer at 61 MHz or a Bruker DPX 500 spectrometer at 77 MHz. ¹³C{¹H} NMR spectra were recorded on a Bruker DPX 400 spectrometer at 100 MHz or a Bruker DPX 500 spectrometer at 125 MHz. ¹¹B{¹H} NMR spectra were recorded on a Bruker DPX 400 spectrometer at 128 MHz or a Bruker DPX 500 spectrometer at 160 MHz. ¹⁹F NMR spectra were recorded on a Bruker DPX 500 spectrometer at 470 MHz. All signals were reported in ppm with reference to the residual solvent resonances of the deuterated solvents for proton and carbon chemical shifts, to external BF₃·OEt₂ (0.00 ppm) for boron chemical shifts and to external $CFCl_3$ (0.00) for fluorine chemical shifts. The data were reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quadruplet, p = pentet, m = multiplet or unresolved, dd = doublet of doublets), coupling constant, integration and assignment. Mass spectra were obtained on a Thermo Q Exactive Focus Orbitrap Mass Spectrometer. All organic solvents were freshly distilled from Na-K alloy or CaH₂ immediately prior to use. 1-Arylethynyl-2-alkyl-o-carboranes 1^1 and $3,4,5,6,7,11-D_6-o$ -carborane² were synthesized according to the reported literatures. All other chemicals were purchased from either Aldrich or Acros Chemical Co. and used as received unless otherwise specified.

Synthesis of 1a- d_3 . To a THF solution (5 mL) of 1-phenylethynyl-o-carborane (244 mg, 1.0 mmol) was slowly added ^{*n*}BuLi (1.6 M in hexane, 0.69 mL, 1.1 mmol) at 0 °C, and the mixture was stirred at room temperature for 2 h. After addition of CD₃I (172 mg, 1.2 mmol) at 0°C, the reaction mixture was further stirred at room temperature for 12 h. Reaction was then quenched with water (5 mL) and extracted with diethyl ether (20 mL x 3). The ether solutions were combined and concentrated to dryness in

vacuo. The residue was subjected to flash column chromatography on silica gel (230 - 400 mesh) using *n*-hexane as eluent to give $1a-d_3$.

1a-*d*₃: White solid. Yield: 80%. ¹H NMR (400 MHz, CDCl₃): δ 7.48 (m, 2H), 7.42 (m, 1H), 7.37 (m, 2H) (aromatic CH). ²H NMR (77 MHz, CHCl₃): δ 2.30 (s, 3D) (CD₃). ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 132.3, 130.0, 128.5, 119.9 (aromatic C), 82.5, 81.7 (alkynyl C), 66.5 (cage C), another cage C and CD₃ carbon were not observed. ¹¹B{¹H} NMR (128 MHz, CDCl₃): δ -3.1 (1B), -6.5 (1B), -8.4 (2B), -10.1 (6B). HRMS (EI): *m/z* calcd for C₁₁H₁₅¹⁰B₂¹¹B₈D₃[M]⁻: 261.2605. Found: 261.2603.

Synthesis of 1a- d_6 . To a THF solution (5 mL) of 3,4,5,6,7,11-D₆-o-carborane (150 mg, 1.0 mmol) was slowly added "BuLi (1.6 M in hexane, 0.69 mL, 1.1 mmol) at 0 °C, and the mixture was stirred at room temperature for 2 h. After addition of CuCl (140 mg, 1.4 mmol), the reaction mixture was stirred at 40 °C for 1 h, to which was added phenylethynyl bromide (252 mg, 1.4 mol). The reaction was further stirred at room temperature for 12 h. After quenching with water (10 mL), the resultant solution was extracted with diethyl ether (20 mL x 3). The ether solutions were combined and concentrated to dryness in vacuo. The residue was subjected to flash column chromatography on silica gel (230 - 400 mesh) using *n*-hexane as eluent to give 1-phenylethynyl-3,4,5,6,7,11-D₆-o-carborane (245 mg, 98%).

To a THF solution (5 mL) of 1-phenylethynyl-3,4,5,6,7,11-D₆-*o*-carborane (250 mg, 1.0 mmol) was slowly added ^{*n*}BuLi (1.6 M in hexane, 0.69 mL, 1.1 mmol) at 0 °C, and the mixture was stirred at room temperature for 2 h. After addition of MeI (171 mg, 1.2 mmol) at 0°C, the reaction mixture was further stirred at room temperature for 12 h. Reaction was then quenched with water (5 mL) and extracted with diethyl ether (20 mL x 3). The ether solutions were combined and concentrated to dryness in vacuo. The residue was subjected to flash column chromatography on silica gel (230 - 400 mesh) using *n*-hexane as eluent to give 1-phenylethynyl-2-methyl-3,4,5,6,7,11-D₆-*o*-carborane **1a**-*d*₆.



1a-*d*₆: White solid. Yield: 76%. ¹H NMR (400 MHz, CDCl₃): δ 7.49 (m, 2H), 7.43 (m, 1H), 7.36 (m, 2H) (aromatic CH), 2.21 (s, 3H) (CH₃). ²H{¹¹B} NMR (77 MHz, CHCl₃): δ 2.68 (s, 2D), 2.55 (s, 2D), 2.49 (s, 2D) (BD). ${}^{13}C{}^{1}H{}$ NMR (126 MHz, CDCl₃): δ 132.3, 130.0, 128.5, 119.9 (aromatic C), 82.6, 81.6 (alkynyl C), 76.6, 66.5 (cage C), 23.8 (CH₃). ¹¹B{¹H} NMR (128 MHz, CDCl₃): δ -2.4 (1B), -5.9 (1B), -7.8 (2B), -9.6 (6B). HRMS (EI): m/z calcd for $C_{11}H_{12}^{10}B_2^{11}B_8D_6[M]^-$: 264.2794. Found: 264.2789.

Optimization of reaction conditions

	CH ₃ 1a 2 equiv MeMgBr THF/toluene (1:10) 80 °C, 36 h "Standard Conditions"	2a
Entry	Deviation from standard conditions	Yield [%] ^b
1	None	80
2	MeMgCl in place of MeMgBr	13 ^c
3	PhMgCl in place of MeMgBr	30 ^d
4	"BuLi in place of MeMgBr	0^{c}
5	24 h	60
6	No THF	0 ^e
7	No toluene	0 ^c
8	1 equiv of MeMgBr	32 ^{c,e}

Table S1. Optimization of Reaction Conditions^a

^aReactions were conducted on 0.1 mmol scale of **1a** in 0.8 mL solvent in a closed flask. ^bIsolated yield. ^cA mixture of multi-B-alkylated *o*-carboranes detected by GC-MS. ^dDeboronation detected by ¹¹B NMR. ^eStarting materials recovered.

Synthesis of Carborane-Fused Cyclopentanes 2

General synthetic procedure A. Methyl magnesium bromide (3.0 M in Et₂O, 0.067 mL, 0.2 mmol) was added to 1-arylethynyl-2-alkyl-o-carborane 1 (0.1 mmol), followed by the addition of THF (0.067 mL) and toluene (0.667 mL), and then the Schlenk flask was closed. The mixture was stirred at 80°C for 36 h. Reaction was quenched with water (1 mL) and extracted with diethyl ether (10 mL x 3). The ether solutions were combined and concentrated to dryness in vacuo. The residue was subjected to column chromatography on silica gel (230-400 mesh) using *n*-hexane as eluent to give product **2**.



2a: Colorless crystals. 80% yield. ¹H NMR (400 MHz, CDCl₃): δ 7.34 (m, 2H), 7.27 (m, 1H), 7.18 (m, 2H) (aromatic C*H*), 4.05 (p, *J*=9.7 Hz, 1H), 2.90 (dd, *J*=13.6, 9.6 Hz, 2H), 2.63 (dd, *J*=13.6,

9.9 Hz, 2H). ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 140.4, 129.1, 127.6, 127.1 (aromatic *C*), 99.9, 82.3 (cage *C*), 53.1, 43.0 (alkyl *C*). ¹¹B{¹H} NMR (128 MHz, CDCl₃): δ -7.0 (4B), -10.1 (1B), -11.0 (2B), -12.4 (1B), -13.3 (2B). HRMS: *m/z* calcd for C₁₁H₂₀¹⁰B₂¹¹B₈ [M]⁻: 260.2574. Found 260.2576.



2b: Colorless crystals. 77% yield. ¹H NMR (500 MHz, CDCl₃): δ 7.15 (d, *J* = 7.9 Hz, 2H), 7.07 (d, *J* = 8.0 Hz, 2H) (aromatic *CH*), 4.02 (p, *J* = 9.7 Hz, 1H), 2.87 (dd, *J* = 13.6, 9.7 Hz, 2H),

2.61 (dd, J = 13.6, 9.9 Hz, 2H), 2.34 (s, 3H). ¹³C {¹H} NMR (126 MHz, CDCl₃): δ 137.4, 137.3, 129.7, 126.9 (aromatic *C*), 82.34 (cage *C*), 52.8, 43.1, 21.0 (alkyl *C*). ¹¹B {¹H} NMR (160 MHz, CDCl₃): δ -6.5 (4B), -9.7 (1B), -10.6 (2B), -12.0 (1B), -12.9 (2B). HRMS: m/z calcd for C₁₂H₂₂¹⁰B₂¹¹B₈ [M]⁻: 274.2730. Found 274.2732.



2c: Colorless crystals. 78% yield. ¹H NMR (500 MHz, CDCl₃): δ 7.17 (t, J = 6.5 Hz, 2H), 7.09 (m, 2H) (aromatic CH), 4.03 (m, 1H), 2.87 (m, 2H), 2.62 (m, 4H), 1.23 (m, 3H).

¹³C{¹H} NMR (126 MHz, CDCl₃): δ 143.8, 137.6, 128.5, 127.1 (aromatic *C*), 82.4 (cage *C*), 52.8, 43.1, 28.4, 15.5 (alkyl *C*). ¹¹B{¹H} NMR (160 MHz, CDCl₃): δ -6.5 (4B), -9.7 (1B), -10.5 (2B), -12.0 (1B), -12.9 (2B). HRMS: *m/z* calcd for C₁₃H₂₄¹⁰B₂¹¹B₈ [M]⁻: 288.2887. Found 288.2890.



2d: Colorless crystals. 80% yield. ¹H NMR (500 MHz, CDCl₃): δ 7.35 (d, J = 8.3 Hz, 2H), 7.11 (d, J = 8.2 Hz, 2H) (aromatic CH), 4.03 (p, J = 9.7 Hz, 1H), 2.87 (dd, J = 13.6,

9.6 Hz, 2H), 2.62 (dd, *J* = 13.6, 9.9 Hz, 2H), 1.30 (s, 9H). ¹³C{¹H} NMR (126 MHz, CDCl₃): δ 150.7, 137.3, 126.8, 125.9 (aromatic *C*), 82.4 (cage *C*), 52.7, 43.0, 34.5, 31.2 (alkyl *C*). ¹¹B{¹H} NMR (160 MHz, CDCl₃): δ -6.6 (2B), -7.0 (2B), -9.7 (1B), -10.6 (2B), -12.0 (1B), -12.9 (2B). HRMS: *m/z* calcd for C₁₅H₂₈¹⁰B₂¹¹B₈ [M]⁻: 316.3200. Found 316.3201.



2e: Colorless crystals. 72% yield. ¹H NMR (500 MHz, CDCl₃): δ 7.09 (m, 2H), 6.85 (m, 2H) (aromatic CH), 4.01 (p, J = 9.7 Hz, 1H), 3.79 (s, 3H), 2.86 (dd, J = 13.6, 9.6 Hz, 2H),

2.57 (dd, J = 13.6, 9.9 Hz, 2H). ¹³C{¹H} NMR (126 MHz, CDCl₃): δ 158.9, 132.3, 128.2, 114.4 (aromatic *C*), 82.3 (cage *C*), 55.3, 52.5, 43.2 (alkyl *C*). ¹¹B{¹H} NMR (160 MHz, CDCl₃): δ -6.5 (4B), -9.8 (1B), -10.6 (2B), -12.0 (1B), -12.9 (2B). HRMS: *m/z* calcd for C₁₂H₂₂¹⁰B₂¹¹B₈O [M]⁻: 290.2683. Found 290.2679.



2f: Colorless crystals. 76% yield. ¹H NMR (500 MHz, CDCl₃): δ 7.57 (m, 4H), 7.46 (m, 2H), 7.38 (m, 1H), 7.26 (m, 2H) (aromatic C*H*), 4.11 (m, 1H), 2.94 (dd, *J* = 12.9,

10.2 Hz, 2H), 2.69 (m, 2H). ¹³C{¹H} NMR (126 MHz, CDCl₃): δ 140.6, 140.3, 139.3, 128.9, 127.7, 127.6, 127.0 (aromatic *C*), 82.3 (cage *C*), 52.8, 43.2 (alkyl *C*). ¹¹B{¹H} NMR (160 MHz, CDCl₃): δ -6.5 (4B), -9.7 (1B), -10.6 (2B), -12.0 (1B), -12.9 (2B). HRMS: *m/z* calcd for C₁₇H₂₄¹⁰B₂¹¹B₈ [M]⁻: 336.2887. Found 336.2886.



2g: Colorless crystals. 35% yield. ¹H NMR (500 MHz, CDCl₃): δ 7.15 (m, 2H), 7.02 (m, 2H) (aromatic C*H*), 4.04 (p, *J* = 9.7 Hz, 1H), 2.89 (dd, *J* = 13.6, 9.6 Hz, 2H), 2.58 (dd, *J* = 13.6,

9.9 Hz, 2H). ¹³C{¹H} NMR (126 MHz, CDCl₃): δ 162.0 (d, ¹*J*_{C-F} = 246.8 Hz), 136.1 (d, ⁴*J*_{C-F} = 3.3 Hz), 128.7 (d, ³*J*_{C-F} = 8.1 Hz), 115.9 (d, ²*J*_{C-F} = 21.5 Hz) (aromatic *C*), 82.1 (cage *C*), 52.3, 43.1 (alkyl *C*). ¹¹B{¹H} NMR (160 MHz, CDCl₃): δ -6.5 (4B), -9.7 (1B), -10.6 (2B), -12.0 (1B), -12.9 (2B). ¹⁹F NMR (470 MHz, CDCl₃): δ -114.5 (s, 1F). HRMS: *m/z* calcd for C₁₁H₁₉¹⁰B₂¹¹B₈F [M]⁻: 278.2479. Found 278.2482.



2h: Colorless crystals. 74% yield. ¹H NMR (500 MHz, CDCl₃): δ 7.30 (d, J = 8.3 Hz, 2H), 7.11 (d, J = 8.3 Hz, 2H) (aromatic CH), 4.03 (p, J = 9.7 Hz, 1H), 2.90 (dd, J = 13.6,

9.7 Hz, 2H), 2.58 (dd, J = 13.6, 9.9 Hz, 2H). ¹³C {¹H} NMR (126 MHz, CDCl₃): δ 138.8, 133.5, 129.2, 128.5 (aromatic *C*), 82.0 (cage *C*), 52.3, 42.9 (alkyl *C*). ¹¹B{¹H} NMR (160 MHz, CDCl₃): δ -6.4 (4B), -9.7 (1B), -10.6 (2B), -12.0 (1B), -12.9 (2B). HRMS: m/z calcd for C₁₁H₁₉¹⁰B₂¹¹B₈Cl [M]⁻: 294.2185. Found 294.2182.



2j: Colorless crystals. 75% yield. ¹H NMR (500 MHz, CDCl₃): δ 7.23 (dd, *J* = 11.1, 4.8 Hz, 1H), 7.09 (m, 1H), 6.98 (m, 2H) (aromatic C*H*), 4.02 (p, *J* = 9.7 Hz, 1H), 2.88 (dd, *J* = 13.6, 9.6

Hz, 2H), 2.63 (dd, J = 13.6, 9.9 Hz, 2H), 2.34 (s, 3H). ¹³C {¹H} NMR (126 MHz, CDCl₃): δ 140.3, 138.8, 128.9, 128.3, 127.8, 124.1 (aromatic *C*), 82.3 (cage *C*), 53.0, 43.0, 21.4 (alkyl *C*). ¹¹B {¹H} NMR (160 MHz, CDCl₃): δ -6.5 (4B), -9.7 (1B), -10.6 (2B), -12.0 (1B), -12.9 (2B). HRMS: *m/z* calcd for C₁₂H₂₂¹⁰B₂¹¹B₈ [M]⁻: 274.2730. Found 274.2733.



2k: Colorless crystals. 72% yield. ¹H NMR (500 MHz, CDCl₃): δ 7.30 (m, 1H), 6.97 (m, 2H), 6.88 (d, *J* = 9.6 Hz, 1H) (aromatic *CH*), 4.04 (p, *J* = 9.6 Hz, 1H), 2.91 (dd, *J* = 13.2, 10.0 Hz, 2H),

2.61 (dd, J = 13.1, 10.3 Hz, 3H). ¹³C {¹H} NMR (126 MHz, CDCl₃): δ 163.0 (d, ¹*J*_{C-F} = 247.4 Hz), 142.8 (d, ³*J*_{C-F} = 7.0 Hz), 130.7 (d, ³*J*_{C-F} = 8.4 Hz), 122.7 (d, ⁴*J*_{C-F} = 2.8 Hz), 114.6 (d, ²*J*_{C-F} = 21.0 Hz), 114.1 (d, ²*J*_{C-F} = 21.8 Hz) (aromatic *C*), 81.9 (cage *C*), 52.5, 42.8 (alkyl *C*). ¹¹B {¹H} NMR (160 MHz, CDCl₃): δ -6.4 (4B), -9.6 (1B), -10.6 (2B), -12.0 (1B), -12.9 (2B). ¹⁹F NMR (470 MHz, CDCl₃): δ -111.7 (s, 1F). HRMS: *m/z* calcd for C₁₁H₁₉¹⁰B₂¹¹B₈F [M]⁻: 278.2479. Found 278.2482.

21: Colorless crystals. 74% yield. ¹H NMR (500 MHz, CDCl₃): δ 7.27 (m, 2H), 7.17 (s, 1H), 7.07 (d, J = 6.9 Hz, 1H) (aromatic **21** Cl CH), 4.02 (p, J = 9.7 Hz, 1H), 2.91 (dd, J = 13.6, 9.7 Hz, 2H), 2.61 (dd, J = 13.6, 9.9 Hz, 2H). ¹³C{¹H} NMR (126 MHz, CDCl₃): δ 142.3, 134.9, 130.4, 127.9, 127.4, 125.3 (aromatic C), 81.9 (cage C), 52.5, 42.8 (alkyl C). ¹¹B{¹H} NMR (160 MHz, CDCl₃): δ -6.4 (4B), -9.6 (1B), -10.6 (2B), -12.0 (1B), -12.9 (2B). HRMS: m/z calcd for C₁₁H₁₉¹⁰B₂¹¹B₈Cl [M]⁻: 294.2185. Found 294.2184.



2m: Colorless crystals. 45% yield. ¹H NMR (500 MHz, CDCl₃):
δ 7.24 (m, 2H), 7.15 (m, 2H) (aromatic CH), 4.33 (p, J = 9.7 Hz, 1H), 2.84 (dd, J = 13.5, 9.6 Hz, 2H), 2.59 (dd, J = 13.5, 9.9 Hz,

2H), 2.32 (s, 3H). ¹³C{¹H} NMR (126 MHz, CDCl₃): δ 138.4, 135.4, 130.7, 127.3, 127.0, 126.1 (aromatic *C*), 82.3 (cage *C*), 48.2, 42.3, 19.7 (alkyl *C*). ¹¹B{¹H} NMR (160 MHz, CDCl₃): δ -6.5 (4B), -9.7 (1B), -10.6 (2B), -11.9 (1B), -12.9 (2B). HRMS: *m/z* calcd for C₁₂H₂₂¹⁰B₂¹¹B₈ [M]⁻: 274.2730. Found 274.2735.

2n: Colorless crystals. 43% yield. ¹H NMR (500 MHz, CDCl₃): δ 7.26 (m, 1H), 7.21 (m, 1H), 7.13 (m, 1H), 7.04 (m, 1H) (aromatic *CH*), 4.28 (p, *J* = 9.8 Hz, 1H), 2.86 (dd, *J* = 13.4, 9.6 Hz, 2H), 2.69 (dd, *J* = 13.4, 10.0 Hz, 2H). ¹³C{¹H} NMR (126 MHz, CDCl₃): δ 160.5 (d, ¹*J*_{C-F} = 246.6 Hz), 129.4 (d, ³*J*_{C-F} = 8.5 Hz), 128.5 (d, ³*J*_{C-F} = 4.1 Hz), 126.8 (d, ²*J*_{C-F} = 13.6 Hz), 124.7 (d, ⁴*J*_{C-F} = 3.6 Hz), 116.0 (d, ²*J*_{C-F} = 22.4 Hz) (aromatic *C*), 82.0 (cage *C*), 46.1, 41.1 (alkyl *C*). ¹¹B{¹H} NMR (160 MHz, CDCl₃): δ -6.5 (4B), -9.7 (1B), -10.5 (2B), -12.0 (1B), -12.9 (2B). ¹⁹F NMR (470 MHz, CDCl₃): δ -116.4 (s, 1F). HRMS: *m/z* calcd for C₁₁H₁₉¹⁰B₂¹¹B₈F [M]⁻: 278.2479. Found 278.2483.



2p: Colorless crystals. 77% yield. ¹H NMR (500 MHz, CDCl₃): δ 7.34 (t, *J* = 7.2 Hz, 2H), 7.28 (d, *J* = 7.4 Hz, 1H), 7.19 (d, *J* = 7.2 Hz, 2H) (aromatic C*H*), 3.36 (m, 1H), 2.80 (m, 2H), 2.54 (m, 1H), 1.51 (m, 1H), 1.40 (m, 2H), 1.11 (m, 1H), 0.76 (t, *J* = 6.3 Hz, 3H).

¹³C {¹H} NMR (126 MHz, CDCl₃): δ 140.1, 129.0, 127.7, 127.7 (aromatic *C*), 86.3, 82.1 (cage *C*), 60.5, 53.5, 43.2, 35.5, 20.7, 13.8 (alkyl *C*). ¹¹B {¹H} NMR (160 MHz, CDCl₃): δ -5.9 (2B), -6.7 (2B), -10.3 (2B), -11.8 (1B), -13.4 (3B). HRMS: *m/z* calcd for $C_{14}H_{26}^{10}B_2^{11}B_8$ [M]⁻: 302.3043. Found 302.3045.



2q: Colorless oil. 27% yield. ¹H NMR (400 MHz, CDCl₃): δ 7.30 (m, 5H), 7.20 (m, 3H), 7.12 (d, *J* = 6.8 Hz, 2H) (aromatic *CH*), 4.24 (m, 1H), 4.14 (d, *J* = 10.8 Hz, 1H), 3.01 (dd, *J* = 13.7, 9.0 Hz, 1H), 2.81 (dd, *J* = 13.7, 9.9 Hz, 1H). ¹³C{¹H} NMR (126 MHz,

CDCl₃): δ 139.0, 135.1, 128.9, 128.8, 128.6, 128.0, 127.7, 127.3 (aromatic *C*), 85.9, 80.2 (cage *C*), 59.4, 57.8, 42.3 (alkyl *C*). ¹¹B{¹H} NMR (160 MHz, CDCl₃): δ -5.9 (1B), -7.1 (3B), -10.3 (4B), -13.4 (2B). HRMS: *m/z* calcd for C₁₇H₂₄¹⁰B₂¹¹B₈ [M]⁻: 336.2887. Found 336.2889.



1-Bn-2-C₆H₅CH=C-*o*-C₂B₁₀H₁₂ was also isolated as colorless oil in 60% yield. ¹H NMR (400 MHz, CDCl₃): δ 7.48 (m, 2H), 7.42 (m, 3H), 7.31 (m, 3H), 7.12 (m, 2H) (aromatic CH), 7.07 (d, J = 15.7 Hz, 1H), 6.39 (d, J = 15.7 Hz, 1H) (alkenyl CH), 3.44 (s,

2H). ¹³C{¹H} NMR (126 MHz, CDCl₃): δ 141.8, 135.4, 134.2, 130.2, 129.9, 129.0, 128.5, 127.9, 127.2, 120.8 (aromatic *C*), 80.8, 79.8 (cage *C*), 41.3 (*C*H₂). ¹¹B{¹H} NMR (160 MHz, CDCl₃): δ -3.9 (2B), -10.2 (8B). HRMS: *m/z* calcd for C₁₇H₂₄¹⁰B₂¹¹B₈ [M]⁻: 336.2887. Found 336.2888.

General synthetic procedure B. A suspension of $MgH_2(THF)_{0.23}^3$ (8.5 mg, 0.2 mmol) and 1-arylethynyl-2-methyl-*o*-carborane **1** (0.1 mmol) in a mixed solvent of THF (0.067 mL) and toluene (0.666 mL) in a closed Schlenk was stirred at 80°C for 36 h. Reaction was then quenched with water (1 mL) and extracted with diethyl ether (10 mL x 3). The ether solutions were combined and concentrated to dryness in vacuo. The residue was subjected to column chromatography on silica gel (230-400 mesh) using *n*-hexane as eluent to give product **2**.

2i: Colorless crystals. 60% yield. ¹H NMR (500 MHz, CDCl₃): δ 7.60 (d, J = 8.1 Hz, 2H), 7.30 (d, J = 8.1 Hz, 2H) (aromatic CH), 4.11 (p, J = 9.7 Hz, 1H), 2.94 (dd, J = 13.6,

9.7 Hz, 2H), 2.63 (dd, J = 13.6, 9.9 Hz, 2H). ¹³C {¹H} NMR (126 MHz, CDCl₃): δ 144.3, 130.1 (q, ² $J_{C-F} = 32.7$ Hz), 127.6, 126.1 (q, ³ $J_{C-F} = 3.7$ Hz), 124.0 (q, ¹ $J_{C-F} = 272.1$ Hz) (aromatic *C*), 81.8 (cage *C*), 52.5, 42.8 (alkyl *C*). ¹¹B {¹H} NMR (160 MHz, CDCl₃): δ -6.4 (4B), -9.6 (1B), -10.6 (2B), -12.0 (1B), -12.9 (2B). ¹⁹F NMR (470 MHz, CDCl₃): δ -62.7 (s, 3F). HRMS: *m/z* calcd for C₁₂H₁₉¹⁰B₂¹¹B₈F₃ [M]⁻: 328.2448. Found 328.2449.

20: Colorless crystals. 75% yield. ¹H NMR (400 MHz, CDCl₃): δ 7.32 (dd, *J* = 5.0, 2.9 Hz, 1H), 6.99 (m, 1H), 6.91 (dd, *J* = 5.0, 1.3 Hz, 1H) (aromatic C*H*), 4.17 (p, *J* = 9.6 Hz, 1H), 2.90 (dd, *J* = 13.5,

9.6 Hz, 2H), 2.61 (dd, J = 13.5, 9.7 Hz, 2H). ¹³C {¹H} NMR (126 MHz, CDCl₃): δ 141.4, 127.2, 125.9, 120.9 (aromatic *C*), 82.1 (cage *C*), 47.9, 42.4 (alkyl *C*). ¹¹B {¹H} NMR

(160 MHz, CDCl₃): δ -6.5 (4B), -9.7 (1B), -10.6 (2B), -11.9 (1B), -12.9 (2B). HRMS: *m/z* calcd for C₉H₁₈¹⁰B₂¹¹B₈S [M]⁻: 266.2138. Found 266.2141.



2r: Colorless crystals. 82% yield. ¹H NMR (500 MHz, CDCl₃): δ 7.29 (t, *J* = 7.5 Hz, 2H), 7.21 (t, *J* = 7.3 Hz, 1H), 7.12 (d, *J* = 7.2 Hz, 2H) (aromatic C*H*), 2.88 (m, 1H), 2.68 (m, 2H), 2.54

(m, 2H), 2.20 (m, 2H), 1.76 (m, 2H). ¹³C {¹H} NMR (126 MHz, CDCl₃): δ 140.7, 128.6, 128.1, 126.3 (aromatic *C*), 83.0 (cage *C*), 47.4, 41.2, 37.9, 34.2 (alkyl *C*). ¹¹B {¹H} NMR (160 MHz, CDCl₃): δ -6.8 (4B), -9.5 (1B), -10.7 (2B), -11.5 (1B), -12.9 (2B). HRMS: *m/z* calcd for C₁₃H₂₄¹⁰B₂¹¹B₈ [M-H]⁻: 287.2808. Found 287.2812.

Deuterium labelling experiments

Reaction of 1a with MeMgBr in a mixed solvent of THF- d_8 /toluene- d_8 (0.8 mL, 1/10 in V/V). A suspension of MeMgBr (3.0 M in Et₂O, 0.067 mL, 0.2 mmol) and 1phenylethynyl-2-methyl-o-carborane (1a; 25.8 mg, 0.1 mmol) in a mixed solvent of THF- d_8 (0.067 mL) and toluene- d_8 (0.667 mL) in a closed Schlenk flask was stirred at 80°C for 36 h. Reaction was then quenched with water (1 mL) and extracted with diethyl ether (10 mL x 3). The ether solutions were combined and concentrated to dryness in vacuo. The residue was subjected to column chromatography on silica gel (230-400 mesh) using *n*-hexane as eluent to give product **2a** (20.8 mg, 80%).

Reaction of 1a with C₂D₅MgBr. A suspension of C₂D₅MgBr⁴ (1.0 M in THF, 0.2 mL, 0.2 mmol) and 1-phenylethynyl-2-methyl-*o*-carborane (**1a**; 25.8 mg, 0.1 mmol) in toluene (0.6 mL) in a closed Schlenk flask was stirred at 80°C for 36 h. Reaction was then quenched with water (1 mL) and extracted with diethyl ether (10 mL x 3). The ether solutions were combined and concentrated to dryness in vacuo. The residue was subjected to column chromatography on silica gel (230-400 mesh) using *n*-hexane as eluent to give product **2a** (13.0 mg, 50%).

Quenching with D₂O. A suspension of MeMgBr (3.0 M in Et₂O, 0.067 mL, 0.2 mmol) and 1-phenylethynyl-2-methyl-o-carborane (**1a**; 25.8 mg, 0.1 mmol) in a mixed solvent of THF (0.067 mL) and toluene (0.667 mL) in a closed Schlenk flask was stirred at 80°C for 36 h. Reaction was then quenched with D₂O (1 mL) and extracted with

diethyl ether (10 mL x 3). The ether solutions were combined and concentrated to dryness in vacuo. The residue was subjected to column chromatography on silica gel (230-400 mesh) using *n*-hexane as eluent to give product $2a - d_1$ (20.4 mg, 78%).

2a- d_1 : Colorless crystals. 78% yield. ¹H NMR (500 MHz, CDCl₃): δ 7.34 (m, 2H), 7.28 (m, 1H), 7.18 (dd, J = 5.2, 3.3 Hz, 2H) (aromatic CH), 4.04 (m, 1H), 2.90 (dd, J = 13.6, 9.6 Hz, 1H), 2.63 (dd, J = 13.5, 9.9 Hz, 2H). ²H NMR (77 MHz, CHCl₃): 2.92 (s, 1D). ¹³C{¹H} NMR (126 MHz, CDCl₃): δ 140.4, 129.1, 127.6, 127.1 (aromatic C), 82.3, 82.2 (cage C), 53.0, 43.0, 42.7 (t, $J_{C-D} = 21.1$ Hz) (alkyl C). ¹¹B{¹H} NMR (160 MHz, CDCl₃): δ -6.5 (4B), -9.7 (1B), -10.6 (2B), -12.0 (1B), -12.9 (2B). HRMS: m/z calcd for C₁₁H₁₉D¹⁰B₂¹¹B₈ [M]⁻: 261.2636. Found 261.2638.



a)

Figure S1. a) ²H NMR spectrum of **2a**- d_1 in CHCl₃; b) ¹H NMR spectrum of **2a**- d_1 in CDCl₃.

Reaction of 1a- d_3 with MeMgBr. A suspension of MeMgBr (3.0 M in Et₂O, 0.067 mL, 0.2 mmol) and 1-(PhC=C)-2-CD₃-o-carborane (1a- d_3 ; 26.1 mg, 0.1 mmol) in a mixed solvent of THF (0.067 mL) and toluene (0.667 mL) in a closed Schlenk flask was stirred at 80°C for 36 h. Reaction was then quenched with water (1 mL) and

extracted with diethyl ether (10 mL x 3). The ether solutions were combined and concentrated to dryness in vacuo. The residue was subjected to column chromatography on silica gel (230-400 mesh) using *n*-hexane as eluent to give product $2a-d_3$ (20.0 mg, 76%).

 $\begin{array}{l} \textbf{2a-}d_3: \mbox{ Colorless crystals. 76\% yield. ^1H NMR (400 MHz, CDCl_3): }\delta \\ \hline \textbf{7.34 (t, J = 7.3 Hz, 2H), 7.28 (d, J = 7.2 Hz, 1H), 7.18 (d, J = 7.3 Hz, 2H) (aromatic CH), 4.03 (d, J = 9.5 Hz, 1H), 2.88 (d, J = 9.5 Hz, 1H). \\ \ ^2H \mbox{ NMR (77 MHz, CHCl_3): }2.88 (s, 1D), 2.61 (s, 2D). ^{13}C{^1H} \mbox{ NMR (126 MHz, CDCl_3): }\delta 140.3, 129.1, 127.6, 127.1 (aromatic C), 82.2 (cage C), 52.8, 42.7 (t, J_{C-D} = 21.0 Hz) (alkyl C). ^{11}B{^1H} \mbox{ NMR (128 MHz, CDCl_3): }\delta -6.9 (4B), -10.1 (1B), -11.0 (2B), -12.5 (1B), -13.3 (2B). \mbox{ HRMS: }m/z \ calcd \ for \ C_{11}H_{17}D_3^{10}B_2^{11}B_8 \ \mbox{ [M]}^{-1}: 263.2762. \mbox{ Found 263.2758.} \end{array}$





Figure S2. a) ²H NMR spectrum of $2a-d_3$ in CHCl₃; b) ¹H NMR spectrum of $2a-d_3$ in CDCl₃.

Reaction of 1a- d_6 with MeMgBr. A suspension of MeMgBr (3.0 M in Et₂O, 0.067 mL, 0.2 mmol) and 1-phenylethynyl-2-methyl-3,4,5,6,7,11-D₆-o-carborane (1a- d_6 ; 26.4mg, 0.1 mmol) in a mixed solvent of THF (0.067 mL) and toluene (0.667 mL) in a closed Schlenk flask was stirred at 80°C for 24 h. Reaction was then quenched with water (1 mL) and extracted with diethyl ether (10 mL x 3). The ether solutions were

combined and concentrated to dryness in vacuo. The residue was subjected to column chromatography on silica gel (230-400 mesh) using *n*-hexane as eluent to give the starting material **1a**- d_6 (10.0 mg, 38%), product **2a**- d_7 (6.7 mg, 25%) and a mixture of **3** and **2a**- d_7 (1.6 mg, 6%). In addition, an inseparable mixture of multi-B-methylated *o*-carboranes **1a**-Me_n (24%) were detected by GC-MS.

2a- d_7 : Colorless crystals. 25% yield. ¹H NMR (500 MHz, CDCl₃): δ 7.34 (t, J = 7.4 Hz, 2H), 7.28 (d, J = 7.4 Hz, 1H), 7.18 (d, J = 7.4 Hz, **2a**- d_7 2H) (aromatic CH), 4.04 (p, J = 9.5 Hz, 0.44H), 2.90 (dd, J = 13.6, 9.4 Hz, 2H), 2.63 (dd, J = 13.5, 9.1 Hz, 2H). ²H{¹¹B} NMR (77 MHz, CDCl₃): 4.04 (s, 0.56D) (CD), 2.39 (s, 4D), 2.29 (s, 2D) (BD). ¹³C{¹H} NMR (126 MHz, CDCl₃): δ 141.8, 140.4, 140.3, 129.1, 127.6, 127.1 (aromatic C), 82.1 (cage C), 53.0, 52.7 (t, J_{C-D} = 20.3 Hz), 42.9 (alkyl C). ¹¹B{¹H} NMR (160 MHz, CDCl₃): δ -6.6 (4B), -9.8 (1B), -10.7 (2B), -12.0 (1B), -13.0 (2B). HRMS: m/z calcd for C₁₁H₁₃D₇¹⁰B₂¹¹B₈ [M-H]⁻: 266.2940. Found 266.2950.





Figure S3. a) ${}^{2}H{}^{11}B{}$ NMR spectrum of 2a- d_7 in CHCl₃; b) ${}^{1}H$ NMR spectrum of 2a-

 d_7 in CDCl₃.



3 was obtained as a mixture of **3** with 60% D incorporation and **2a**- d_7 in a molar ration of 0.15:1 by ¹H NMR. Compared ¹H NMR spectra of the mixture, **2a**- d_7 and 1-phenylethenyl-2-methyl-*o*-carborane, the resonances at 7.40 (m, 0.75H) (aromatic CH), 6.98

(m, 0.15H), 6.27 (d, J = 15.6 Hz, 0.06H) (alkenyl CH), 1.98 (s, 0.46H) (CH₃) ppm were assigned to **3** (Figure S4b). A resonance at 6.30 ppm in ²H NMR spectrum of the mixture supported the incorporation of D at the alkenyl C (Figure S4a).

a)







Figure S4. a) ²H NMR spectrum of the mixture of 3 and 2a-d₇ in CHCl₃; b) ¹H NMR spectrum of the mixture of 3 and 2a-d₇ in CDCl₃; c) ¹H NMR spectrum of 1phenylethenyl-2-methyl-o-carborane in CDCl₃.

Control experiments

c)

Reaction of 1a with MeMgBr in the presence of 1,1-diphenylethylene. A suspension of MeMgBr (3.0 M in Et₂O, 0.067 mL, 0.2 mmol), 1-phenylethynyl-2-methyl-*o*-carborane (1a; 25.8 mg, 0.1 mmol) and 1,1-diphenylethylene (36.0 mg, 0.2 mmol) in a mixed solvent of THF (0.067 mL) and toluene (0.667 mL) in a closed Schlenk flask was stirred at 80°C for 36 h. Reaction was then quenched with water (1 mL) and extracted with diethyl ether (10 mL x 3). The ether solutions were combined and concentrated to dryness in vacuo. The residue was subjected to column chromatography on silica gel (230-400 mesh) using *n*-hexane as eluent to give product 2a (20.8 mg, 80%).

Quenching with TMSCI. A suspension of MeMgBr (3.0 M in Et₂O, 0.067 mL, 0.2 mmol) and 1-phenylethynyl-2-methyl-*o*-carborane (**1a**; 25.8 mg, 0.1 mmol) in a mixed solvent of THF (0.067 mL) and toluene (0.667 mL) in a closed Schlenk flask was stirred at 80°C for 18 h. Reaction mixture was then treated with TMSCI (21.7 mg, 0.2 mmol). After further stirring at room temperature for 12 h, the reaction was quenched with water and extracted with diethyl ether (10 mL x 3). The ether solutions were combined and concentrated to dryness in vacuo. The residue was subjected to column chromatography on silica gel (230-400 mesh) using *n*-hexane as eluent to give product **2a** (9.9 mg, 38%) and **4** (11.6 mg, 35%).

4: Colorless crystals. 35% yield. ¹H NMR (400 MHz, CDCl₃): δ 7.45 (m, 2H), 7.39 (m, 3H) (aromatic CH), 6.98 (d, J = 15.7 Hz, 1H), 6.31 (d, J = 15.7 Hz, 1H) (alkenyl CH), 1.59 (s, 2H), 0.14 (s, 9H). ¹³C{¹H}

NMR (100 MHz, CDCl₃): δ 141.4, 134.4, 129.7, 128.9, 127.2, 121.2 (aromatic and alkenyl *C*), 81.4, 81.1 (cage *C*), 26.3 (*C*H₂). ¹¹B{¹H} NMR (160 MHz, CDCl₃): δ -4.0 (1B), -5.1 (1B), -9.0 (2B), -10.6 (6B). HRMS: *m/z* calcd for C₁₄H₂₈¹⁰B₂¹¹B₈Si [M-H]⁻: 331.2892. Found 331.2885.

Ph

-TMS

Quenching with I2. A suspension of MeMgBr (3.0 M in Et₂O, 0.067 mL, 0.2 mmol) and 1-phenylethynyl-2-methyl-*o*-carborane (**1a**; 25.8 mg, 0.1 mmol) in a mixed solvent of THF (0.067 mL) and toluene (0.667 mL) in a closed Schlenk flask was stirred at 80°C for 36 h. Reaction mixture was then treated with I₂ (50.8 mg, 0.2 mmol). After further stirring at room temperature for 12 h, the reaction was quenched with water and extracted with diethyl ether (10 mL x 3). The ether solutions were combined and concentrated to dryness in vacuo. The residue was subjected to column chromatography on silica gel (230-400 mesh) using *n*-hexane as eluent to give product **5** (25.1 mg, 65%).

5: Colorless crystals. 65% yield. ¹H NMR (500 MHz, CDCl₃): δ 7.37
Fh (m, 3H), 7.24 (m, 2H) (aromatic CH), 4.71 (d, J = 9.6 Hz, 1H), 4.03 (q, J = 9.8 Hz, 1H), 2.78 (d, J = 9.8 Hz, 2H). ¹³C {¹H} NMR (126 MHz, CDCl₃): δ 136.8, 129.3, 129.1, 128.5, 127.6, 127.1 (aromatic C), 84.0, 82.2 (cage C), 65.9, 42.9, 29.7 (alkyl C). ¹¹B {¹H} NMR (160 MHz, CDCl₃): δ -5.6 (1B), -6.5 (3B), -7.9 (1B), -9.4 (1B), -10.4(1B), -13.1 (3B). HRMS: *m/z* calcd for C₁₁H₁₉¹⁰B₂¹¹B₈I [M-H]⁻: 385.1462. Found 385.1461.

Reaction of 1i with MeMgBr. A suspension of MeMgBr (3.0 M in Et₂O, 0.067 mL, 0.2 mmol) and 1-[(4-trifluoromethyl)phenylethynyl]-2-methyl-*o*-carborane (**1i**; 32.6 mg, 0.1 mmol) in a mixed solvent of THF (0.067 mL) and toluene (0.667 mL) in a closed Schlenk flask was stirred at 80°C for 36 h. Reaction was then quenched with D_2O (1 mL) and extracted with diethyl ether (10 mL x 3). The ether solutions were combined and concentrated to dryness in vacuo. The residue was subjected to column chromatography on silica gel (230-400 mesh) using *n*-hexane as eluent to give **2i**-*d*₁

(2.3 mg, 7%) and **1i** (26.1 mg, 80%) without any D incorporation, suggesting that the cage-CH₃ proton was not deprotonated by MeMgBr.

X-ray structure determination. The data of **2a**, **2p** and **2r** were collected on a Bruker APEX DUO diffractometer. An empirical absorption correction was applied using the SADABS program.⁵ All structures were solved by direct methods and subsequent Fourier difference techniques and refined anisotropically for all non-hydrogen atoms by full-matrix least-squares on F^2 using the SHELXTL program package.⁶ All hydrogen atoms were geometrically fixed using the riding model. Crystal data and details of data collection and structure refinements were given in Table S2.

CCDC 1998059-1998061 (**2a**, **2p** and **2r**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via <u>www.ccdc.cam.ac.uk/data_request/cif</u>.

	2a	2p	2r
formula	$C_{11}H_{20}B_{10}$	$C_{14}H_{26}B_{10}$	$C_{13}H_{24}B_{10}$
crystal size (mm)	0.50×0.40×0.30	0.50×0.40×0.30	0.50×0.40×0.30
fw	260.37	302.45	288.42
crystal system	Monoclinic	Monoclinic	Orthorhombic
space group	<i>P</i> 2 ₁ /c	P21/n	Pca21
<i>a</i> , Å	7.7202(4)	9.7246(5)	18.2149(7)
b, Å	21.9059(12)	9.0634(4)	8.1437(4)
<i>c</i> , Å	9.0867(6)	21.3352(10)	12.0108(4)
α , deg	90	90	90
β , deg	98.1207(17)	96.9612(15)	90
γ, deg	90	90	90
<i>V</i> , Å ³	1521.31(15)	1866.58(15)	1781.64(13)
Z	4	4	4
$D_{\text{calcd}}, \text{Mg/m}^3$	1.137	1.076	1.075
radiation (λ) Å	0.71073	0.71073	0.71073
2θ range, deg	2.448 to 25.238	2.423 to 25.250	2.236 to 25.249
μ , mm ⁻¹	0.054	0.052	0.052
<i>F</i> (000)	544	640	608
no. of obsd reflns	2749	3366	3208
no. of params refnd	190	217	208
goodness of fit	1.054	1.107	1.064
R1	0.0701	0.0624	0.0409
wR2	0.1889	0.1804	0.1066

 Table S2. Crystal Data and Summary of Data Collection and Refinement

Reference

1 J. X. Guo, D. Q. Liu, J. H. Zhang, J. J. Zhang, Q. Miao and Z. Xie, *Chem. Commun.*, 2015, **51**, 12004-12007.

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4 E. Johansson, P. T. Hurley, B. S. Brunschwig and N. S. Lewis, *J. Phys. Chem. C*, 2009, **113**, 15239-15245.

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																		Solvent	CDCI3
																		Temperature	295.2
																		Pulse Sequence	e zg2h
																		Experiment	1D
																		Number of Scans	32
																		Receiver Gain	64
																		Relaxation Delay	0.0500
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							[Acquisition Time	90.9996
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					Solvent	CDCl3
					Temperature	294.7
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					Number of Scans	24
					Receiver Gain	203
					Relaxation Delay	2.0000
					Pulse Width	9.5000
					Acquisition Time	1.1010
					Spectrometer Frequency	100.64
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																		Number of Scans	32
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				Spectral Width	29761.9
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00 190 180 170 160 150 140 130	120 110 100 90 80 f1 (ppm)	70 60 50 40 30	20 10 0		

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								Temperature	294.6
								Pulse Sequence	e zgig
								Experiment	1D
								Number of Scans	36
								Receiver Gain	181
								Relaxation Dela	ay 1.0000
								Pulse Width	28.5000
		~						Acquisition Tim	e 1.2845
								Spectrometer Frequency	128.38
								Spectral Width	25510.2
		-						Lowest Frequency	-12755.3
								Nucleus	11B
	СН							Acquired Size	32768
	1a -d ₆							Spectral Size	03330
			\mathcal{M}						
		1.06	1.04 2.07	6.00					
15	10 5	Ó	-5 1 (ppm)	-10	-15	-20	-25	-30	

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S28





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S31

							Parameter Title	Value zhiie190315-4-
88 88	38	0 m 0 %	m	8	~		nio	Me-wu-p-cdcl3-C
37.38	9.6 9.9	2.33	6.79	.08.	.98		Spectrometer	spect
		び 28 12 12 12 12 12 12 12 12 12 12 12 12 12	23 	4	- 20		Solvent	CDCI3
Ŷ			I	I	I		Temperature	298.0
							Pulse Sequence	; zgpg30
							Experiment	1D
							Number of Scans	256
							Receiver Gain	207
							Relaxation Delay	2.0000
							Pulse Width	10.0000
							Acquisition Time	∋ 1.1010
							Spectrometer Frequency	125.77
							Spectral Width	29761.9
2b	1						Lowest Frequency	-2310.2
							Nucleus	13C
							Acquired Size	32768
							Spectral Size	65536
		II						
		<u> </u>		· · · · · · · · · · · · · · · · · · ·				
00 190 180 170 160 150 140	130 120 110 100 90 f1 (ppm)	80 70 60	50	40 30	20	10 0)	

			Parameter	Value
	50	2 2 3 3	Title	zhjie190315-4- Me-wu-p-cdcl3-B
	5.510	4 0 0 1 1 2 4 0 0 0	Spectrometer	spect
	Ϋ́		Solvent	CDCI3
	I		Temperature	298.0
			Pulse Sequence	zgpg30
			Experiment	1D
			Number of Scans	16
			Receiver Gain	207
			Relaxation Delay	1.0000
			Pulse Width	15.0000
			Acquisition Time	0.6816
			Spectrometer Frequency	160.46
			Spectral Width	24038.5
			Lowest Frequency	-12040.1
			Nucleus	11B
₩ 2h			Acquired Size	16384
ZŊ			Spectral Size	32768





						Parameter	Value
28 32 73 28	4 10 0 10		0	4	~	Title	zhjie181220-4-Et- wu-cdcl3-C
		. 83	.00.	.40	. 507	Spectrometer	spect
	8773	- 52	43	- 28	- 15	Solvent	CDCl3
			I			Temperature	298.0
						Pulse Sequence	zgpg30
						Experiment	1D
						Number of Scans	128
						Receiver Gain	207
						Relaxation Delay	2.0000
						Pulse Width	10.0000
						Acquisition Time	9 1.1010
						Spectrometer Frequency	125.76
						Spectral Width	29761.9
						Lowest Frequency	-2309.1
						Nucleus	13C
	ų •					Acquired Size	32768
2c						Spectral Size	65536
1							
				l			
	1						
	· · · · · · · · ·		· · ·				
190 180 170 160 150 140 130 120 110	100 90 80 70 f1 (ppm)	0 60 50	40	30 20	10 0	1	

//----

			Parameter	Value
	4	4 25 85 00	Title	zhjie181220-4-Et- wu-cdcl3-B
	9.50	2.90	Spectrometer	spect
	Ψ I		Solvent	None
	I	r r l l	Temperature	298.0
			Pulse Sequence	zgpg30
			Experiment	1D
			Number of Scans	16
			Receiver Gain	207
			Relaxation Delay	1.0000
			Pulse Width	15.0000
			Acquisition Time	0.6816
			Spectrometer Frequency	160.46
			Spectral Width	24038.5
			Lowest Frequency	-12040.1
			Nucleus	11B
			Acquired Size	16384
2c			Spectral Size	32768
	\bigwedge			
		M_{M}		
	~			




					Parameter Title	Value zhjie181220-4-
5 5 5	0400	0	ы С	m		tBu-wu-cdcl3-C
5.9.7 3 25.9.7 3 25.9.7 3	2.36 5.74 255	5.68	3.03 4.50	1.25	Spectrometer	spect
		2	Η Α φ	ю 	Solvent	CDCl3
	אור ו	ļ	1 1	1	Temperature	298.0
					Pulse Sequence	zgpg30
					Experiment	1D
					Number of Scans	88
					Receiver Gain	207
					Relaxation Delay	2.0000
					Pulse Width	10.0000
					Acquisition Time	1.1010
					Spectrometer Frequency	125.76
					Spectral Width	29761.9
	_				Lowest Frequency	-2309.6
					Nucleus	13C
					Acquired Size	32768
20					Spectral Size	65536
190 180 170 160 150 140 130	20 110 100 90 80 f1 (ppm)	70 60 50	40	30 20 10 0		

		980	ú		Parameter Title	Value zhjie181220-4- tBu-wu-cdcl3-B
	.557	0.61 2.00 2.00			Spectrometer	spect
	φφ	9444	•		Solvent	None
) (()	1		Temperature	298.0
					Pulse Sequence	e zgpg30
					Experiment	1D
					Number of Scans	16
					Receiver Gain	207
					Relaxation Delay	1.0000
					Pulse Width	15.0000
					Acquisition Time	e 0.6816
					Spectrometer Frequency	160.46
					Spectral Width	24038.5
					Lowest Frequency	-12040.1
					Nucleus	11B
					Acquired Size	16384
 ₩					Spectral Size	32768
20						
	μ.		\land			





																				Parameter	Value
			3.928			2.355 3.167		1.366		966	254 000	2	319	483	213					Title	zhjie190314-4- MeO-wu-p-cdcl3- C
			- 156			- 132		- 11		8	7 7 7 7 7 7		5	-22	43.					Spectrometer	spect
			I							· · · ·										Solvent	CDCI3
																				Temperature	298.0
																				Pulse Sequence	e zgpg30
																				Experiment	1D
																				Number of Scans	256
																				Receiver Gain	207
																				Relaxation Delay	2.0000
																				Pulse Width	10.0000
																				Acquisition Time	e 1.1010
																				Spectrometer Frequency	125.77
																				Spectral Width	29761.9
			£.				/													Lowest Frequency	-2308.4
				XI –	\succ		-0				ų									Nucleus	13C
					·						- 1									Acquired Size	32768
			•		2e															Spectral Size	65536
								1							I						
														1							
			ļ			!								ĺ							
•								ـــــ			╢┈╢										
//	, , , , ,			· · · ·	· · · ·	· · ·	· .	· · · ·			1	· · · · ·			· · ·	·	·	· · · ·			
1	90 180	170	160	150	140	130	120	110 1 f1 (p	00 opm)	90	80	70	60	50	40	30	20	10	0		

		→ 2e	~_0∕	—-6.495					Pi Title Spec Solv Temp Pulse Expe Num Scar Rela Dela Pulse Acqu Spec Freq Nucl Acqu Spec	arameter ertometer ent erature e Sequence eriment ber of is eiver Gain xation y e Width isition Tim strometer uency etral Width st uency eus ired Size stral Size	Value zhjie190314-4- MeO-wu-p-cdcl3- B spect CDCl3 298.0 e zgpg30 1D 16 207 1.0000 15.0000 e 0.6816 160.46 24038.5 -12040.1 11B 16384 32768
				4.05	1.02 1 1.95 1 1.00 1	2.05 1					
15	10	5	0	-5 f1 (ppm)	-10	-15	-20	-25	-30		



					Parameter	Value
	271 254 746	760	019		Title	zhjie181116- wu-4-Ph-cdcl3- C
4 4 8 9 9 9 9 9 9 9 9 9 9 9 9 9 9 9 9 9	-242782.	- 52.	.64		Spectrometer	spect
					Solvent	CDCl3
					Temperature	298.0
					Pulse Sequence	zgpg30
					Experiment	1D
					Number of Scans	100
					Receiver Gain	207
					Relaxation Delay	2.0000
					Pulse Width	10.0000
					Acquisition Time	1.1010
					Spectrometer Frequency	125.76
					Spectral Width	29761.9
					Lowest Frequency	-2310.7
					Nucleus	13C
					Acquired Size	32768
2f					Spectral Size	65536
1			1			
1						
				<u> </u>		
180 170 160 150 140 130 120 110	100 90 80 70 60 f1 (ppm)	50	40	30 20 10 0		

					0 10 0					Parameter Title	Value zhjie181116- wu-4-Ph-cdcl3-
				502	701 560 97						В
				0.						Spectrometer	spect
					$\langle \langle \rangle \rangle$					Solvent	CDCl3
										Temperature	298.0
										Pulse Sequence	zgpg30
										Experiment	1D
										Number of Scans	32
										Receiver Gain	207
										Relaxation Delay	1.0000
										Pulse Width	15.0000
										Acquisition Time	0.6816
										Spectrometer Frequency	160.46
										Spectral Width	24038.5
			<u> </u>							Lowest Frequency	-12040.1
			<u>}</u>							Nucleus	11B
		\mathbb{N} // \mathbb{N}	$\sim //$							Acquired Size	16384
										Spectral Size	32768
	21			M	M	X					
				4.00	1.00 2.03 1.03 1.03 1.03 1.03						
15	10	5	0 f1	-5 (ppm)	-10	-15	-20	-25	-30		





The second se	6.458		Parameter Title Spectrometer Solvent Temperature Pulse Sequence Experiment Number of Scans Receiver Gain Relaxation Delay Pulse Width Acquisition Time Spectrometer Frequency Spectral Width Lowest Frequency Nucleus Acquired Size Spectral Size	Value 2hjie190613-4-F- wi-p-cdcl3-B spect CDCl3 298.0 2gpg30 1D 16 207 1.0000 15.0000 0.6816 160.46 24038.5 -12040.1 11B 16384 32768
-9	M	MM		



								Parameter	Value
				74				Title	zhjie190618-4-F- wu-cdcl3-F(c)
				4.4				Spectrometer	spect
				- 11				Solvent	CDCl3
								Temperature	298.0
								Pulse Sequence	e zgflqn
								Experiment	1D
								Number of Scans	16
								Receiver Gain	7
								Relaxation Delay	1.0000
								Pulse Width	15.0000
								Acquisition Time	e 0.5767
	•							Spectrometer Frequency	470.59
	E A	/=						Spectral Width	113636.4
		\succ	—F					Lowest Frequency	-103877.4
								Nucleus	19F
		2a						Acquired Size	65536
		-9						Spectral Size	131072
		105			· · · · ·	· · · · · ·			
-95	-100	-102	-110 f1 (ppm)	-115	-120	-125	-130		

//----

				Parameter	Value
2 S 0 1 4	88 7 7 1 5 88	61 00 20 20 45 75 75	Ŋ	Title	zhjie190102-4-Cl- wu-cdcl3-H
22 27 27 27 27 27 27 27 27 27 27 27 27 2	4 4 4 4 0 0 0 0 0 0		1.55	Spectrometer	spect
				Solvent	CDCI3
				Temperature	298.0
				Pulse Sequence	zg30
				Experiment	1D
				Number of Scans	16
				Receiver Gain	31
				Relaxation Delay	1.0000
				Pulse Width	11.2500
				Acquisition Time	3.2768
				Spectrometer Frequency	500.13
				Spectral Width	10000.0
				Lowest Frequency	-1924.7
				Nucleus	1H
				Acquired Size	32768
2h				Spectral Size	65536
	j.			_	
2.00 一 二 2.00 一 二	1.07년	2.09- <u>∓</u> 2.10- <u>∓</u>			

2.5

2.0

1.5

Т

4.0

3.5

3.0

4.5 f1 (ppm)

Г

).0

8.5

8.0

7.5

7.0

6.5

6.0

5.5

5.0

0.5

0.0

					Parameter	Value
2 7 8 0		-	~		litte	wu-cdcl3-C
28.5 23.3 28.7 28.7 28.7 28.7 28.7 28.7 28.7 28.7	5.746 5.746	2.340	2.94		Spectrometer	spect
		й 	4		Solvent	CDCl3
ור ר ז	זור ו	I	I		Temperature	298.0
					Pulse Sequence	zgpg30
					Experiment	1D
					Number of Scans	128
					Receiver Gain	207
					Relaxation Delay	2.0000
					Pulse Width	10.0000
					Acquisition Time	1.1010
					Spectrometer Frequency	125.77
					Spectral Width	29761.9
					Lowest Frequency	-2309.6
					Nucleus	13C
2h					Acquired Size	32768
211					Spectral Size	65536
	6					
1	l l l l l l l l l l l l l l l l l l l					
		i				
	1					
	ll					
		· · · ·	· · · ·			
180 170 160 150 140 130 120 1	110 100 90 80 70 60 f1 (ppm)	50	40 30	20 10 0		

									Pa	rameter	Value
				4 M	9 20	13 13			Title		zhjie190102-4-Cl- wu-cdcl3-B
				5.45 5.86	9.65	[2.9			Spect	rometer	spect
				ų ų \					Solve	nt	CDCI3
				11		1 1			Temp	erature	298.0
									Pulse	Sequenc	e zgpg30
									Exper	iment	1D
									Numb Scans	er of S	16
									Recei	ver Gain	207
									Relax Delay	ation	1.0000
									Pulse	Width	15.0000
									Acqui	sition Tim	e 0.6816
									Spect Frequ	rometer iency	160.46
									Spect	ral Width	24038.5
		\sim $=$	\backslash						Lowes Frequ	st Jency	-12040.1
		$\rightarrow \sim$	/∕—CI						Nucle	us	11B
		\checkmark \checkmark	/						Acqui	red Size	16384
	\checkmark								Spect	ral Size	32768
						\vee					
				4.02	1.01 2.00 1.01- 1.01-	2.07					
15	10	5	0	-5	-10	-15	-20	-25	-30		
15	10	5	v	f1 (ppm)	10	-15	20	23	50		

					Parameter	Value
	2 2 3 2 2 7	33 12 23 13 23 13	2 4 2 4 2 2 8 8 8	20	Title	zhjie190710-4- CF3-wu-cdcl3-H
	2 2 2 3 3 2 0 2 2 2 5 3 3 2 0	44444	5 5 5 5 5 5 5 5 5 5 5 5 5 5 5 5 5 5 5	.1.5	Spectrometer	spect
	$\langle \langle \langle \langle \rangle \rangle \rangle$				Solvent	CDCI3
					Temperature	298.0
					Pulse Sequence	e zg30
					Experiment	1D
					Number of Scans	32
					Receiver Gain	64
					Relaxation Delay	1.0000
					Pulse Width	11.2500
					Acquisition Time	e 3.2768
					Spectrometer Frequency	500.13
					Spectral Width	10000.0
	\sim				Lowest Frequency	-1924.7
					Nucleus	1H
	₩				Acquired Size	32768
	21				Spectral Size	65536
		ML				
	5.00 上 2.00 上 2.00	1.06 1	2.00 <u>∓</u> 2.13 <u>∓</u>			
8.5 8.0	7.5 7.0 6.5 6.0 5.5 5.0 4 f1	.5 4.0 3.5 (ppm)	3.0 2.5 2.0	1.5 1.0 0.5 0.0		



			Parameter	Value
	419	589 	Title	zhjie190618-4- CF3-wu-p-cdcl3- B
		6, 9, 9, 9, 9, 9, 9, 9, 9, 9, 9, 9, 9, 9,	Spectrometer	spect
			Solvent	CDCI3
			Temperature	298.0
			Pulse Sequence	zgpg30
			Experiment	1D
			Number of Scans	16
			Receiver Gain	207
			Relaxation Delay	1.0000
			Pulse Width	15.0000
			Acquisition Time	0.6816
			Spectrometer Frequency	160.46
			Spectral Width	24038.5
\sim			Lowest Frequency	-12040.1
			Nucleus	11B
			Acquired Size	16384
21			Spectral Size	32768



		Parameter	Value
	99	Title	zhjie190710-4- CF3-wu-cdcl3-F
	5.0	Spectrometer	spect
		Solvent	CDCI3
		Temperature	298.0
		Pulse Sequence	zgflqn
		Experiment	1D
		Number of Scans	32
		Receiver Gain	7
		Relaxation Delay	1.0000
		Pulse Width	15.0000
		Acquisition Time	0.5767
		Spectrometer Frequency	470.59
		Spectral Width	113636.4
		Lowest Frequency	-103877.4
$\left \begin{array}{c} \begin{array}{c} \begin{array}{c} \end{array} \\ \end{array} \\ \end{array} \right $		Nucleus	19F
		Acquired Size	65536
		Spectral Size	131072
2 i			
	_L		

0 -5 -10 -15 -20 -25 -30 -35 -40 -45 -50 -55 -60 -65 -70 -75 -80 -85 -90 -95 -105 -115 f1 (ppm)



						Parameter	Value
22	12 23 38	0 4 0 %	-	~	m	Title	zhjie190313-3- Me-wu-p-cdcl3-C
04 0 10 10 10 10 10 10 10 10 10 10 10 10 10 1	88 80 77 45 96 88 47	2.25.	.07	86	<u>6</u>	Spectrometer	spect
1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1		び ((() () () () () () ()	5	4	- 21	Solvent	CDCl3
	אר ר		I	I	I	Temperature	298.0
						Pulse Sequence	zgpg30
						Experiment	1D
						Number of Scans	128
						Receiver Gain	207
						Relaxation Delay	2.0000
						Pulse Width	10.0000
						Acquisition Time	9 1.1010
						Spectrometer Frequency	125.76
						Spectral Width	29761.9
	\sim					Lowest Frequency	-2310.7
						Nucleus	13C
	\sim					Acquired Size	32768
•	21					Spectral Size	65536
	2 j						
		4					
				1			
			i				
		· · · · · · · ·			<u> </u>		
180 170 160 150 140	130 120 110 100 90 f1 (ppm)	80 70 60	50	40 30	20 10 0		

										Paramete Title	Value zhjie190313-3-
					505 329	724 .573 .984 .899				Spectromete	Ne-wu-p-cdcl3-B
					- 9 - 9					Solvent	CDCI3
					17	$\langle \langle \rangle \rangle$				Temperature	298.0
										Pulse Seque	nce zgpg30
										Experiment	1D
										Number of Scans	16
										Receiver Ga	in 207
										Relaxation Delay	1.0000
										Pulse Width	15.0000
										Acquisition T	me 0.6816
										Spectromete Frequency	r 160.46
										Spectral Wid	th 24038.5
										Lowest Frequency	-12040.1
				/\						Nucleus	11B
				\neg						Acquired Size	e 16384
			2j		Å					Spectral Size	32768
					4.06	1.02 1.96 1.00 2.03 1					
20	15	10	5	0	-5 f1 (ppm)	-10	-15	-20	-25	-30	



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	Parameter	Value
-	Title	zhjie190315-3-f wu-p-cdcl3-F
:	Spectrometer	spect
:	Solvent	CDCI3
	Temperature	298.0
I	Pulse Sequence	zgflqn
I	Experiment	1D
	Number of Scans	16
	Receiver Gain	7
	Relaxation Delay	1.0000
I	Pulse Width	15.0000
	Acquisition Time	0.5767
:	Spectrometer Frequency	470.55
:	Spectral Width	113636.4
	Lowest Frequency	-103877.4
I	Nucleus	19F
	Acquired Size	65536
:	Spectral Size	131072









					Parameter	Value
33 0 55 8 27 17	°° + ⊂ '0	0	4		Title	zhjie190313-3-Cl- wu-p-cdcl3-C
び 本のだがら で、 8月18日 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 -		8	22.7		Spectrometer	spect
	8 ススを	- 23	4		Solvent	CDCI3
) M	I	I		Temperature	298.0
					Pulse Sequence	zgpg30
					Experiment	1D
					Number of Scans	128
					Receiver Gain	207
					Relaxation Delay	2.0000
					Pulse Width	10.0000
					Acquisition Time	: 1.1010
*					Spectrometer Frequency	125.76
					Spectral Width	29761.9
					Lowest Frequency	-2311.0
					Nucleus	13C
2					Acquired Size	32768
_ , 01					Spectral Size	65536
	II.					
			1			
	i i					
			متعامل والمعارك فالمترك والمعارك والمعارك والمعارك والمعارك	,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,		
			- <u> </u>			
00 190 180 170 160 150 140 130 120 110 100 f1 (pp) 90 80 70 m)	60 50	40 30	20 10 0		

		21	CI	6.414	7-9.623 10.560 11.981					Parameter Title Spectrometer Solvent Temperature Pulse Sequence Experiment Number of Scans Receiver Gain Relaxation Delay Pulse Width Acquisition Time Spectrometer Frequency Spectral Width Lowest Frequency Nucleus Acquired Size Spectral Size	Value zhjije190313-3-Cl- wu-p-cdcl3-B spect CDCl3 298.0 298.0 299.0 1D 16 207 1.0000 0.6816 160.46 24038.5 -12040.1 11B 16384 32768
				4.16	1.18-T 2.11-T 1.00-T 2.12-T						
15	10	5	0	-5 f1 (ppm)	-10	-15	-20	-25	-30		

<u>2</u>0





			Parameter	Value
	10	2 2 3 3 3 3	Title	zhjie190314-2- Me-wu-p-cdcl3-B
	481		Spectrometer	spect
	φ I		Solvent	CDCI3
	ļ		Temperature	298.0
			Pulse Sequence	; zgpg30
			Experiment	1D
			Number of Scans	16
			Receiver Gain	207
			Relaxation Delay	1.0000
			Pulse Width	15.0000
			Acquisition Time	÷ 0.6816
			Spectrometer Frequency	160.46
			Spectral Width	24038.5
			Lowest Frequency	-12040.1
			Nucleus	11B
			Acquired Size	16384
~			Spectral Size	32768
2m /				









										Parameter	Value
			~ ~	22	1 0					Title	zhjie190613-2-F- wu-P-cdcl3-B
			.950	.737	2.93					Spectrometer	spect
			φ φ \	0 1	 					Solvent	CDCl3
				1 1	1 1					Temperature	298.0
										Pulse Sequence	e zgpg30
										Experiment	1D
										Number of Scans	16
										Receiver Gain	207
										Relaxation Delay	1.0000
										Pulse Width	15.0000
										Acquisition Time	e 0.6816
										Spectrometer Frequency	160.46
										Spectral Width	24038.5
	^									Lowest Frequency	-12040.1
		-\								Nucleus	11B
		\rightarrow								Acquired Size	16384
	2n F										
			1								
			<u> </u>	\mathcal{M}							
			4.00	1.00 2.03	1.07 √ 2.10 √						
· · ·	· · · · · ·	1		1							
15	10 5 0	0 f	-5 1 (ppm)	-10		-15	-20	-25	-30		
	Parameter	Value									
----	---------------------------	--------------------------------									
66	Title	zhjie190618-2-F- wu-cdcl3-F									
õ.	Spectrometer	spect									
	Solvent	CDCI3									
	Temperature	298.0									
	Pulse Sequence	zgflqn									
	Experiment	1D									
	Number of Scans	32									
	Receiver Gain	7									
	Relaxation Delay	1.0000									
	Pulse Width	15.0000									
	Acquisition Time	0.5767									
	Spectrometer Frequency	470.59									
	Spectral Width	113636.4									
	Lowest Frequency	-103877.4									
	Nucleus	19F									
	Acquired Size	65536									
	Spectral Size	131072									







					Parameter	Value
1.373	7.193 5.928 0.891	.140 255 747	894	.371	Title	zhjie190921-wu- thiophene-p- cdcl3-C
	- 12	28.7.7.82	- 47.	- 42.	Spectrometer	spect
	<	$\langle \rangle$			Solvent	CDCl3
					Temperature	295.2
					Pulse Sequence	e zgpg30
					Experiment	1D
					Number of Scans	110
					Receiver Gain	207
					Relaxation Del	ay 2.0000
					Pulse Width	9.7500
					Acquisition Tim	e 1.1010
					Spectrometer Frequency	125.76
					Spectral Width	29761.9
	c				Lowest Frequency	-2312.1
					Nucleus	13C
	≺∖				Acquired Size	32768
					Spectral Size	65536
20						
		h				
		ľ				
	11					
	ii i		ļ			
		!				
	de la serie de la section d La section de la section de	<u>ئەرما</u> ⁶ ەروپۇرۇر يۈۈمىدىنىتىرىنى بورۇر بەر بەر بەر بەر بەر بەر بەر بەر بەر بە	ويربع أبارت مرشد معيا الفاتين والرجاب فالبدائيل مستعالي			
//	· · · · · ·			· · · · · · ·		
190 180 170 160 150 140) 130 120	110 100 90 80 f1 (ppm)	70 60 50	40 30 20	10 0	

			Parameter	Value
	511	660 1.563 1.938 1.904	Title	zhjie191101- wup-thiophene- cdcl3-B
	.9-		Spectrometer	spect
		$\langle \langle \rangle \rangle$	Solvent	CDCl3
			Temperature	295.3
			Pulse Sequence	zgpg30
			Experiment	1D
			Number of Scans	16
			Receiver Gain	207
			Relaxation Delay	1.0000
			Pulse Width	16.0000
			Acquisition Time	0.6816
			Spectrometer Frequency	160.46
			Spectral Width	24038.5
			Lowest Frequency	-12040.1
S_			Nucleus	11B
			Acquired Size	16384
			Spectral Size	32768
-				





Parameter	Value
Title	zhjie190313- ynePh-Bu-wu-p- cdcl3-H
Spectrometer	spect
Solvent	CDCI3
Temperature	298.0
Pulse Sequence	zg30
Experiment	1D
Number of Scans	16
Receiver Gain	51
Relaxation Delay	1.0000
Pulse Width	11.2500
Acquisition Time	3.2768
Spectrometer Frequency	500.13
Spectral Width	10000.0
Lowest Frequency	-1924.7

1H

32768

65536

Nucleus

Acquired Size

Spectral Size

 $\begin{array}{c} 1.557\\ 1.531\\ 1.531\\ 1.533\\ 1.400\\ 1.120\\ 1.106\\ 0.755\\ 0.755\end{array}$



7.351 7.335 7.322 7.290 7.276 7.195 7.181



									Parameter	Value
085		330 115 000 746	501	554	231	515	720	904	Title	zhjie190313- ynePh-Bu-wu-p- cdcl3-C
140	127.127.127.	86.3 77.2 76.7	60.1	23.1	4	35.5	20.7	13.8	Spectrometer	spect
	$\leq V$	$\langle \langle \cdot \rangle \rangle$							Solvent	CDCI3
									Temperature	298.0
									Pulse Sequence	zgpg30
									Experiment	1D
									Number of Scans	128
									Receiver Gain	207
									Relaxation Delay	2.0000
									Pulse Width	10.0000
									Acquisition Time	1.1010
									Spectrometer Frequency	125.76
									Spectral Width	29761.9
									Lowest Frequency	-2309.2
\mathbf{V}	\backslash								Nucleus	13C
	}								Acquired Size	32768
	∖ 2p								Spectral GZE	
			ł				i			
		, , <u>, , , ,</u>	-					· · · · · · · · · · · · · · · · · · ·		
00 190 180 170 160 150 140	130 120 110 100 9 f1 (ppm)	90 80 70	60	50	40	30	20	10 0		

					Pa	^v arameter	Value
	10 Cl ~~	36	26	ŝ	Title		zhjie190102-4-Br- wu-cdcl3-B
	1910	0.3	1.7	3.3	Spec	ctrometer	spect
	$\langle \langle \rangle$	- -		- I	Solve	'ent	None
	1 1 (I	I	I	Temp	perature	298.0
					Pulse	e Sequence :	zgpg30
					Expe	eriment	1D
					Num Scan	nber of ns	16
					Rece	eiver Gain	207
					Rela: Delay	axation ay	1.0000
					Pulse	e Width	15.0000
					Acqu	uisition Time	0.6816
					Spec Frequ	ctrometer quency	160.46
					Spec	ctral Width	24038.5
					Lowe Frequ	est · quency	-12040.1
\mathbf{V}					Nucle	leus	11B
>					Acqu	uired Size	16384
<					Spec	ctral Size	32768
\ 2p							







					Parameter	Value
	904 264	.330	.416	T	lītle	zhjie200505- bnhplc-5-cdcl3- B
	5.	10	- 	S	Spectrometer	spect
		I		S	Solvent	None
				r	Temperature	295.2
				F	Pulse Sequence	zgpg30
				E	Experiment	1D
				۱ ۲	Number of Scans	500
				F	Receiver Gain	207
				F	Relaxation Delay	1.0000
				F	Pulse Width	16.0000
				l l l l l l l l l l l l l l l l l l l	Acquisition Time	0.6816
				S	Spectrometer Frequency	160.46
				S	Spectral Width	24038.5
				L	_owest Frequency	-12040.1
₩ \				1	Nucleus	11B
				l l l l l l l l l l l l l l l l l l l	Acquired Size	16384
2q				S	Spectral Size	32768
		\checkmark	Ļ			



				Parameter	Value
z μ z μ z z z z z z z z z z z z z z z z	Q.	36	ñ	Title	zhjie190115-Bn- p1-cdcl3-H
スススススススススススススススムの54 36 4 4 4 4 4 4 4 7 7 7 7 1 1 1 2 8 54 36	ю. 4.	1.56	1.26	Spectrometer	spect
				Solvent	CDCl3
				Temperature	294.9
				Pulse Sequence	zg30
				Experiment	1D
				Number of Scans	16
				Receiver Gain	90
				Relaxation Delay	1.0000
				Pulse Width	12.8000
				Acquisition Time	4.0894
				Spectrometer Frequency	400.23
				Spectral Width	8012.8
				Lowest Frequency	-1544.8
				Nucleus	1H
				Acquired Size	32768
				Spectral Size	65536
	I				
			impurity in		
			/hexane		
		I			
NA II Ni ii					
			l .		
	Ť				
0.0000 0.0000 0.0000	1.9				
			· · · · · · · · · · · · · · · · · · ·		

' 3.5

4.0

4.5 f1 (ppm)

3.0

2.5

2.0

1.5

1.0

0.5

0.0

).0

8.5

8.0

, 7.5

7.0

5.5

5.0

6.0

6.5





			Parameter	Value
7,310 7,295 7,229 7,113 7,113 7,113	2.928 2.910 2.877 2.877 2.873 2.873 2.873 2.873 2.675 2.649 2.553 2.553 2.553 2.553 2.553 2.553 2.553	2.221 2.203 2.1267 1.757 1.751 1.736 1.557	Title	zhjie-7175- CH2CH2Ph-p2- cdcl3-H
			Spectrometer	spect
			Solvent	CDCl3
			Temperature	298.0
			Pulse Sequence	zg30
			Experiment	1D
			Number of Scans	16
			Receiver Gain	31
			Relaxation Delay	1.0000
			Pulse Width	11.2500
			Acquisition Time	3.2768
•			Spectrometer Frequency	500.13
			Spectral Width	10000.0
			Lowest Frequency	-1924.2
			Nucleus	1H
2r			Acquired Size	32768
			Spectral Size	65536
		H H		
	1.16 2.24 2.02	2.26-		
0.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 f1 (ppn	4.0 3.5 3.0 2.5 n)	2.0 1.5 1.0 0.5 0.0		

						Parameter	Value
0.665 0.565 0.581	8.119 5.275		427	.230 889 .164		Title	zhjie-7175- CH2CH2Ph-p2- cdcl3-C-
			-47.	- 41		Spectrometer	spect
			I	$\langle + \rangle$		Solvent	CDCI3
						Temperature	298.0
						Pulse Sequence	zgpg30
						Experiment	1D
						Number of Scans	64
						Receiver Gain	207
						Relaxation Delay	2.0000
						Pulse Width	10.0000
						Acquisition Time	1.1010
						Spectrometer Frequency	125.76
						Spectral Width	29761.9
	\rightarrow					Lowest Frequency	-2310.8
2r		<u>h</u>				Nucleus	13C
						Acquired Size	32768
						Spectral Size	65536
				1			
				Ì			
	1						
			1				
ĺ							
******	<u>ار بالاست میں بار دور ایک کار اور ایک ایک ایک کار کا کار کار کار ایک کار کار کار کار کار کار کار کار کار کا</u>	market and a free of the sector of the secto	-	,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,	<u></u>		
		· · · · · · ·					
170 160 150 140 130	0 120 110 100 90 f1 (ppm)	80 70 60 50	0	40 30	20 10 0		

00

190 180

1

										Paramet	er Value
					.827	.500 0.718 1.532 2.931				Title	zhjie-7175- CH2CH2Ph-p2- cdcl3-B-
					o I	6, 5, 5, 7, 7				Spectromet	er spect
					I	\sim				Solvent	CDCl3
										Temperature	e 298.0
										Pulse Seque	ence zgpg30
										Experiment	1D
										Number of Scans	16
										Receiver G	ain 207
										Relaxation Delay	1.0000
										Pulse Width	15.0000
										Acquisition	Time 0.6816
										Spectromet Frequency	er 160.46
										Spectral Wi	dth 24038.5
										Lowest Frequency	-12040.1
		·)r							Nucleus	11B
			21							Acquired Siz	ze 16384
										Spectral Siz	e 32768
					⊢	┝╼╣╾ᠸ᠊ᡟᠵ᠋ᡰᡃ					
· · · ·					4.00-	1.05- 1.97- 1.00- 2.08-		1	· · · · · · · · · · · · · · · · · · ·		
20	15	10	5	0	-5 f1 (ppm)	-10	-15	-20	-25	-30	



2 2 2	$\sqrt{\frac{4}{3}}$			Nucleus Acquired Size Spectral Size	2H 1535 4096
20					4030
~					
	v Za	$\mathbf{D}_{\mathbf{f}_{2}}$	$ \begin{array}{c} $	$ \underbrace{D}_{4} \underbrace{D}_{5} \underbrace{D}_{2} \underbrace{D}_{3} \underbrace{D}_{2} \underbrace{D}_{3} \underbrace{D}_{2} \underbrace{D}_{3} \underbrace{D}_{2} \underbrace{D}_{3} \underbrace{D}_{3} \underbrace{D}_{2} \underbrace{D}_{3} $	Puse Sequence Experime Number of Scans Receiver Gain Relaxation Delay Puse Width Acquisition Time Spectrometer Frequency Spectral Width Lowest Frequency Nucleus $2\mathbf{a} - d_1$ Spectral Size

Parameter

Title

Value CF-20200327-

Research



			Parameter	Value
	0	ب 0 % 1 	lītle	zhjie181116-wu- D-cdcl3-B
		5.1990	Spectrometer	spect
	Ϋ́		Solvent	CDCl3
	I		Temperature	298.0
		F	Pulse Sequence	zgpg30
		E	Experiment	1D
		1 2	Number of Scans	32
		F	Receiver Gain	207
		F	Relaxation Delay	1.0000
		F	Pulse Width	15.0000
		/	Acquisition Time	0.6816
		s F	Spectrometer Frequency	160.46
D		\$	Spectral Width	24038.5
5		L F	_owest =requency	-12040.1
		1	Nucleus	11B
		/	Acquired Size	16384
2a -d ₁		9	Spectral Size	32768





Parameter	Value
Title	CF-20200327- Research Service Xie 52
Spectrometer	spect
Solvent	CDCI3
Temperature	295.2
Pulse Sequence	zg2h
Experiment	1D
Number of Scans	32
Receiver Gain	64
Relaxation Delay	0.0500
Pulse Width	300.0000
Acquisition Time	e 0.9996
Spectrometer Frequency	76.77
Spectral Width	1535.6
Lowest Frequency	-212.0
Nucleus	2H
Acquired Size	1535
Spectral Size	4096





—2.876 —2.610



											Parameter	Value
					943	144 012	.487			r	lītle	zhjie-7041-2- cd3wu-16-cdcl3- B
					- -	10	12			S	Spectrometer	spect
										5	Solvent	CDCl3
										٦	Temperature	295.3
										F	Pulse Sequence	zgdc
										E	Experiment	1D
										N	Number of Scans	24
										F	Receiver Gain	287
										F	Relaxation Delay	2.0000
										F	Pulse Width	7.5000
										ŀ	Acquisition Time	1.3631
			Þ							S F	Spectrometer Frequency	128.41
			1 5							5	Spectral Width	24038.5
			4-P	h						L	_owest Frequency	-12091.7
										١	Nucleus	11B
			D							ŀ	Acquired Size	32768
			2a -d ₃							9	Spectral Size	65536
						۲Ÿ						
					3:99	1.00 ⁷	2.12					
20	15	10	5	0	-5 f1 (ppm)	-10	-15	-20	-25	-30		

															Parameter	Value
	7.353 7.338 7.323 7.285 7.270	.175				1.085 1.066 1.047		918 2.899 2.872	2.652 2.633 2.606		551				Title	zhije-8153- wud7-cry- cdcl3-H
											Ī				Spectrometer	spect
															Solvent	CDCl3
															Temperature	295.2
															Pulse Sequence	zg30
															Experiment	1D
															Number of Scans	s 16
															Receiver Gain	103
															Relaxation Delay	1.0000
															Pulse Width	10.0000
															Acquisition Time	3.2768
			1 5	H/D											Spectrometer Frequency	500.13
		\mathbf{N}^{\wedge}	\mathbf{X}												Spectral Width	10000.0
			4	Ph											Lowest Frequency	-1924.7
		Ŭ	5												Nucleus	1H
			2a -d ₇												Acquired Size	32768
															Spectral Size	65536
	2.03 2.00 2.00 2.00							2.04	2.15 壬							
8.5 8.0) 7.5 7.1	0 6.5	6.0	5.5	5.0	4.5 4.0 f1 (ppm)) 3.5	3.0	2.5	2.0	1.5	1.0	0.5	0.0		

			Parameter	Value
	.040	2.391	Title	CF-20200327- Research Service Xie 55
			Spectrometer	spect
			Solvent	CDCl3
			Temperature	295.4
			Pulse Sequence	e zgig2h
			Experiment	1D
			Number of Scans	32
			Receiver Gain	207
			Relaxation Delay	0.0500
			Pulse Width	300.0000
			Acquisition Tim	e 0.9996
H/D			Spectrometer Frequency	76.77
			Spectral Width	1535.6
2 3 4 PII			Lowest Frequency	-226.5
2a -d ₇			Nucleus	2H
			Acquired Size	1535
			Spectral Size	4096





Parameter	Value
Title	zhije-8153- wud7-cry- cdcl3-B
Spectrometer	spect
Solvent	CDCI3
Temperature	295.1
Pulse Sequence	zgpg30
Experiment	1D
Number of Scans	32
Receiver Gain	207
Relaxation Delay	1.0000
Pulse Width	16.0000
Acquisition Time	0.6816
Spectrometer Frequency	160.46
Spectral Width	24038.5
Lowest Frequency	-12040.1
Nucleus	11B
Acquired Size	16384
Spectral Size	32768





-9.804 -10.718 -12.030 -13.023

—-6.581





									Parame	eter Value
				4 3	22 3				Title	zhjie-6183-1-wu- tms-cdcl3-B
				. 96.	3.95 0.5				Spectrome	ter spect
				р Р Р	φ 1				Solvent	CDCI3
					1 1				Temperatur	re 295.1
									Pulse Sequ	ience zgpg30
									Experiment	t 1D
									Number of Scans	128
									Receiver C	Sain 207
									Relaxation Delay	1.0000
									Pulse Widt	h 16.0000
									Acquisition	Time 0.6816
									Spectrome Frequency	ter 160.46
									Spectral W	<i>l</i> idth 24038.5
			Ph						Lowest Frequency	-12040.1
									Nucleus	11B
			1S						Acquired S	ize 16384
		•							Spectral Si	ze 32768
						~				
					2.00-					
15	10	5	0	-5 f1 (ppm)	-10	-15	-20	-25	-30	

20

															Parameter	Value
		2 0 8 2 2	0 II 9				<u>୭</u> ୧	2 7 7 5 S		32		ß	00		Title	zhjie-6183-2-wu- I-cdcl3-H
		22.2.2.3	7.27				4.7	4 4 4 4 0 0 0 0		2.7		1.56	1.20		Spectrometer	spect
							$\langle \rangle$			\mathbf{Y}					Solvent	CDCI3
															Temperature	295.2
															Pulse Sequence	zg30
															Experiment	1D
															Number of Scans	12
															Receiver Gain	93
															Relaxation Delay	1.0000
															Pulse Width	10.0000
															Acquisition Time	3.2768
						_									Spectrometer Frequency	500.13
					,										Spectral Width	10000.0
				¢.											Lowest Frequency	-1911.7
				X -	X.	∕—Ph									Nucleus	1H
															Acquired Size	32768
				•	F										Spectral Size	65536
												ł	impuri hexar	ity in ne		
		/Vh						₩	·							
·							1.00-五	- 1.14- <u>T</u>	, <u>, ,</u>	2.12 -≖						
0.0	8.5 8.	0 7.5	7.0	6.5	6.0	5.5 5	.0 4.5 f1 (ppr	4.0 n)	3.5	3.0 2.5	2.0	1.5	1.0	0.5 0.0		



	Parameter Value	
	Title zhjie-6183-2 I-cdcl3-B	.'-wu-
3.00 . 47	Spectrometer spect	
	Solvent CDCl3	
	Temperature 295.3	
	Pulse Sequence zgpg30	
	Experiment 1D	
	Number of 16 Scans	
	Receiver Gain 207	
	Relaxation 1.0000 Delay	
	Pulse Width 16.0000	
	Acquisition Time 0.6816	
	Spectrometer 160.46 Frequency	
ļ	Spectral Width 24038.5	
	Lowest -12040.1 Frequency	
Ph	Nucleus 11B	
	Acquired Size 16384	
÷ _	Spectral Size 32768	
3.12 11:000		
20 15 10 5 0 -5 -10 -15 -20 f1 (ppm)	-25 -30	