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Catalyst-Controlled Selective Borocarbonylation of Benzylidenecyclopropanes: Regiodivergent Synthesis of γ -vinylboryl ketones and β -cyclopropylboryl ketones

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1. General information

Reagents, solvents, and analytical methods:

Unless otherwise noted, all reactions were carried out under a carbon monoxide or nitrogen atmosphere. The benzylidenecyclopropanes were synthesized according to existing method, and reagents were ordered from Sigma-Aldrich, TCI, ABCR, and Acros, and used without purification. All solvents were dried by standard techniques and distilled prior to use. Column chromatography was performed on silica gel (200-300 meshes) using N-pentane (bp. 36.1 °C), dichloromethane and ethyl acetate as eluent. All NMR spectra were recorded at ambient temperature using Bruker Avance III HD 300 NMR (1H, 300 MHz; 13C{1H}, 75 MHz; 11B, 96 MHz, 19F, 282 MHz), Bruker ARX 400 NMR spectrometers (1H, 400 MHz; 13C{1H}, 101 MHz, 11B, 128 MHz, 19F 376 MHz). 1H NMR chemical shifts are reported relative to TMS and were referenced via residual proton resonances of the corresponding deuterated solvent (CDCl₃: 7.26 ppm) whereas ¹³C{¹H} NMR spectra are reported relative to TMS via the carbon signals of the deuterated solvent (CDCl₃: 77.0 ppm). Data for ¹H are reported as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = doubletquartet, quint = quintet, m = multiplet, br = broad), coupling constant (Hz), and integration. All ¹³C NMR spectra were broad-band ¹H decoupled. However, signals for the carbon attach to boron, C(alkyl)-B or C(vinyl)-B, are usually too broad to observe in the ¹³C{¹H} NMR spectra. High resolution mass spectra (HRMS) were recorded on an Agilent 6210 system. Gas chromatography (GC) analyses were performed on an Agilent HP-7890A instrument with an FID detector and HP-5 capillary column (polydimethylsiloxane with 5% phenyl groups, 30 m, 0.32 mm i.d. 0.25 µm film thickness) using argon as carrier gas.

Because of the high toxicity of carbon monoxide, all the reactions should be performed in an autoclave. The laboratory should be well-equipped with a CO detector and alarm system.



2. Optimization of borocarbonylation

2.1 Optimization of ligand for γ -vinylboryl ketones **3a**.

Entry	Ligand	3a (%)	4a (%)	r.r. (3a:4a)
1	None	0	0	-
2	DPPBz (L1)	0	0	-
3	DPPE (L2)	0	0	-
4	DPPP (L3)	22	22	1:1
5	DPPB (L4)	4	2	2:1
6	DPPF (L5)	19	10	2:1
7	DPEphos (L6)	39	18	2:1
8	PPh ₃ (L7)	0	5	-
9	$BuPAd_2$ (L8)	64	0	>20:1
10	IPr (L9)	81	2	>20:1
11	IMes (L10)	0	0	-

2.2 Optimization of palladium source for γ -vinylboryl ketones **3a**.

Entry	[Pd]	3a (%)	4a (%)	r.r. (3a:4a)
1	Pd(OAc) ₂	80	5	16:1
2	$Pd(TFA)_2$	79	5	20:1
3	$PdCl_2$	58	0	>20:1
4	PdI_2	58	0	>20:1
5	$[Pd(\eta^3-cinnamyl)Cl]_2(1 mol\%)$	64	0	>20:1
6	$[Pd(\eta^3-C_3H_5)Cl]_2 (1 \text{ mol}\%)$	77	5	15:1

2.3 Optimization of temperature for γ -vinylboryl ketones **3a**.

Entry	temperature	3a (%)	4a (%)	r.r. (3a:4a)
1	90 ℃	63	5	12:1
2	80 °C	81	2	>20:1
3	70 °C	62	2	>20:1
4	60 °C	47	11	4:1

2.4 Optimization of the loading of B_2pin_2 , NaO'Bu and PhI for γ -vinylboryl ketones ${\bf 3a}$.

Entry	B ₂ pin ₂	NaO ^t Bu	PhI	3a (%)	4a (%)	r.r. (3a:4a)
1	1.2	1.5	1.5	73	5	15:1
2	1.7	1.5	1.5	74	3	>20:1
3	2.0	1.5	1.5	75	3	>20:1
4	1.5	1.2	1.5	50	5	10:1
5	1.5	1.7	1.5	82	3	>20:1
6	1.5	2.0	1.5	75	1	>20:1
7	1.5	1.5	1.2	72	2	>20:1
8	1.5	1.5	1.5	81	2	>20:1
9	1.5	1.5	1.7	85	2	>20:1
10	1.5	1.5	2.0	76	5	13:1

2.5 Optimization of ligand for β -cyclopropylboryl ketone **4a**.

Entry	Ligand	3a (%)	4a (%)	r.r. (3a:4a)
1	None	2	25	1:13
2	DPEphos (L6)	5	35	1:7
3	PPh ₃ (L7)	4	31	1:8
4	$BuPAd_2$ (L8)	29	2	10:1
5	IPr·HCl (L9)	44	23	2:1
6	Xantphos (L11)	7	50	1:7
7	Nixantphos (L12)	4	26	1:7
8	Sixantphos (L13)	4	33	1:8
9	BINAP (L14)	10	36	1:4
10	L15	3	31	1:10
11	L16	4	26	1:7
12	L17	2	17	1:9
13	L18	3	21	1:7
14	L19	4	26	1:7
15	L20	4	37	1:9
16	L21	4	21	1:5
17	L22	3	21	1:7
18	L23	3	36	1:12
19	L24	4	38	1:10
20	L25	2	29	1:15
21	(S,S)-Ph-BPE (L26)	2	0	-

2.6 Optimization of palladium source for β -cyclopropylboryl ketone **4a**.

Entry	[Pd]	3a (%)	4a (%)	r.r. (3a:4a)
1	Pd(OAc) ₂	7	50	1:8
2	$Pd(TFA)_2$	7	57	1:8
3	$PdCl_2$	8	29	1:4
4	[Pd(cinnamyl)Cl] ₂ (1 mol%)	7	61	1:9
5	$[Pd(\eta^3-C_3H_5)Cl]_2(1 \text{ mol}\%)$	6	54	1:9

2.7 Optimization of CO pressure.

Entry	CO (bar)	3a (%)	4a (%)	r.r. (3a:4a)
1	20	7	55	1:8
2	10	7	61	1:9
3	6	9	64	1:7
4	3	4	76	1:19
5	1	5	73	1:15

Entry	CO (bar)	3a (%)	4a (%)	r.r. (3a:4a)
1	20	84	2	>20:1
2	10	85	2	>20:1
3	6	91	7	13:1
4	3	91	9	10:1
5	1	70	9	8:1

3. General procedure of borocarbonylation

3.1 general borocarbonylation I (ring-opening).

A 4 mL screw-cap vial was charged with IPrCuCl (9.7 mg, 10 mol%), Pd(dppp)Cl₂ (2.4 mg, 2 mol%), B₂pin₂ (76.2 mg, 1.5 equiv.), NaO'Bu (28.8 mg, 1.5 equiv.) and an oven-dried stir bar. The vial was closed with a Teflon septum and cap and connected to the atmosphere via a needle. After toluene (1.0 mL), aryl iodides (1.7 equiv.) and BCP (0.2 mmol) were added with a syringe under argon atmosphere, the vial was moved to an alloy plate and put into a Parr 4560 series autoclave (300 mL) under argon atmosphere. At room temperature, the autoclave was flushed with CO three times and charged with 10 bar CO. The autoclave was placed on a heating plate equipped with a magnetic stirrer and an aluminum block. The reaction mixture was heated to 80 °C for 20 h. The reaction was then quenched upon addition of water (10 mL) and the mixture was extracted with EA (10 mL). The combined organic was dried using Na₂SO₄ and then concentrated in vacuo. The crude product was purified by column chromatography on silica gel to afford the corresponding product.

3.2 general borocarbonylation II (ring-remaining).

A 4 mL screw-cap vial was charged with Cu(dppp)Cl (10.2 mg, 10 mol%), $[Pd(\eta^3\text{-cinnamyl})Cl]_2$ (1.0 mg, 1 mol%), Xantphos (2.3 mg, 2 mol%) B_2pin_2 (76.2 mg, 1.5 equiv.), NaO'Bu (28.8 mg, 1.5 equiv.) and an oven-dried stir bar. The vial was closed with a Teflon septum and cap and connected to the atmosphere via a needle. After toluene (1.0 mL), aryl iodides (1.5 equiv.) and BCP (0.2 mmol) were added with a syringe under argon atmosphere, the vial was moved to an alloy plate and put into a Parr 4560 series autoclave (300 mL) under argon atmosphere. At room temperature, the autoclave was flushed with CO three times and charged with 10 bar CO. The autoclave was placed on a heating plate equipped with a magnetic stirrer and an aluminum block. The reaction mixture was heated to 80 °C for 20 h. The reaction was then quenched upon addition of water (10 mL) and the mixture was extracted with EA (10 mL). The combined organic was dried using Na₂SO₄ and then concentrated in vacuo. The crude product was purified by column chromatography on silica gel to afford the corresponding product.

3.3 general borocarbonylation III (ring-remaining).

A 4 mL screw-cap vial was charged with Cu(dppp)Cl (10.2 mg, 10 mol%), $[Pd(\eta^3\text{-cinnamyl})Cl]_2$ (1.0 mg, 1 mol%), Xantphos (2.3 mg, 2 mol%) B_2pin_2 (76.2 mg, 1.5 equiv.), NaOBu (28.8 mg, 1.5 equiv.) and an oven-dried stir bar. The vial was closed with a Teflon septum and cap and connected to the atmosphere via a needle. After toluene (1.0 mL), aryl iodides (1.5 equiv.) and BCP (0.2 mmol) were added with a syringe under argon atmosphere, the vial was moved to an alloy plate and put into a Parr 4560 series autoclave (300 mL) under argon atmosphere. At room temperature, the autoclave was flushed with CO three times and charged with 10 bar CO. The autoclave was placed on a heating plate equipped with a magnetic stirrer and an aluminum block. The reaction mixture was heated to 80 °C for 20 h. The reaction was then quenched upon addition of water (10 mL) and the mixture was extracted with EA (10 mL) and then concentrated in vacuo. The crude product in THF (2 mL) and water (2 mL) was added NaBO3·4H2O (153.0 mg. 5 equiv). The reaction mixture was stirred vigorously at room temperature and determined by TLC analysis (2 h – 12 h). The reaction mixture was quenched with water and then extracted with ethyl acetate (5 mL). The combined organic layers were washed with brine (15 mL), dried over Na2SO4 and concentrated. The crude product was purified by column chromatography on silica gel to afford the corresponding product.

4. General procedure for preparing BCPs

Representative Procedure¹: To a 500 mL round bottom flask, 1,3-dibromopropane (41.6 g, 200 mmol), triphenylphosphine (52.5 g, 200 mmol) and toluene (100 mL) were added. The mixture was heated at 110 °C and maintained with stirring for 16 h. The white precipitate was filtered and washed with additional 50 mL of toluene and dried overnight in a vacuum stove, yielding 3-bromopropyltriphenylphosphonium bromide quantitatively. A flame-dried scintillation vial equipped with a stir bar was charged with (3-bromopropyl)triphenylphosphonium bromide (1.40 g, 3.0 mmol, 1.2 equiv) and KO'Bu (700 mg, 6.0 mmol, 2.4 equiv). The solids were suspended in THF (10 mL), and the mixture was allowed to stir at 60 °C for 1 h. After the solution had cooled to room temperature, benzaldehyde (265 mg, 2.5 mmol, 1.0 equiv) was added to the suspension dropwise over 2 min. The vial was sealed, and the suspension was allowed to stir at 60 °C for 12 h. The reaction mixture was cooled to room temperature and filtered through a celite pad, which was subsequently rinsed with Et2O (3 × 20 mL). The filtrate was concentrated, and the resulting crude mixture was purified by flash chromatography (*n*-pentane) to provide BCP substrate 1a (195 mg, 60% yield) as a colorless oil.

1-(Cyclopropylidenemethyl)-2-methylbenzene (M-1)

¹H NMR (300 MHz, CDCl₃) δ 7.75 (ddd, J = 7.4, 1.3, 0.6 Hz, 1H), 7.24 – 7.09 (m, 3H), 6.98 (p, J = 2.1 Hz, 1H), 2.41 (s, 3H), 1.46 – 1.39 (m, 2H), 1.23 – 1.17 (m, 2H).

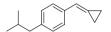
¹³C NMR (75 MHz, CDCl₃) δ 136.6, 134.9, 130.3, 126.6, 125.9, 125.8, 125.0, 115.5, 19.7, 4.1, 0.8.



1-(Cyclopropylidenemethyl)-3-methylbenzene (M-2)

¹**H NMR** (300 MHz, CDCl₃) δ 7.34 – 7.27 (m, 2H), 7.21 – 7.13 (m, 1H), 7.02 – 6.95 (m, 1H), 6.68 (p, J = 2.1 Hz, 1H), 2.32 (s, 3H), 1.42 – 1.34 (m, 2H), 1.15 – 1.09 (m, 2H).

¹³C NMR (75 MHz, CDCl₃) δ 138.2, 137.9, 128.3, 127.5, 127.3, 124.0, 123.7, 118.3, 21.5, 4.2, 0.5.



1-(Cyclopropylidenemethyl)-4-isobutylbenzene (M-3)

¹H NMR (300 MHz, CDCl₃) δ 7.47 – 7.43 (m, 2H), 7.13 – 7.09 (m, 2H), 6.73 (q, J = 2.0 Hz, 1H), 2.47 (d, J = 7.2 Hz, 2H), 1.94 – 1.80 (m, 1H), 1.46 – 1.38 (m, 2H), 1.20 – 1.13 (m, 2H), 0.92 (s, 3H), 0.90 (s, 3H).

¹³C NMR (75 MHz, CDCl₃) δ 140.3, 135.7, 129.2, 126.3, 123.1, 118.1, 45.2, 30.2, 22.4, 4.1, 0.5.

5-(Cyclopropylidenemethyl)benzo[d][1,3]dioxole (M-4)

¹H NMR (400 MHz, CDCl₃) δ 7.04 (d, J = 1.7 Hz, 1H), 6.80 (dd, J = 7.8, 1.5 Hz, 1H), 6.66 (d, J = 8.4 Hz, 1H), 6.56 (q, J = 2.1 Hz, 1H), 5.82 (s, 2H), 1.27 (ddd, J = 9.4, 5.3, 2.2 Hz, 2H), 1.07 – 1.02 (m, 2H).

¹³C NMR (101 MHz, CDCl₃) δ 147.8, 146.4, 132.8, 122.1, 120.8, 117.8, 108.1, 106.1, 100.8, 4.0, 0.4.

1-(Cyclopropylidenemethyl)-4-methoxybenzene (M-5)

¹**H NMR** (300 MHz, CDCl₃) δ 7.55 – 7.45 (m, 2H), 6.95 – 6.86 (m, 2H), 6.72 (t, J = 2.1 Hz, 1H), 3.83 (s, 3H), 1.45 – 1.36 (m, 2H), 1.23 – 1.13 (m, 2H).

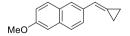
¹³C NMR (75 MHz, CDCl₃) δ 158.5, 131.2, 127.6, 121.6, 117.5, 113.9, 55.2, 4.0, 0.4.



1-(Cyclopropylidenemethyl)-3,5-dimethoxybenzene (M-6)

¹**H NMR** (**400 MHz, CDCl**₃) δ 6.70 (dd, J = 13.0, 2.1 Hz, 3H), 6.37 (t, J = 2.3 Hz, 1H), 3.81 (s, 6H), 1.45 – 1.41 (m, 2H), 1.19 (ddd, J = 10.3, 5.9, 2.1 Hz, 2H).

¹³C NMR (101 MHz, CDCl₃) δ 160.8, 140.2, 125.0, 118.2, 104.7, 98.9, 55.2, 26.9, 4.2, 0.6.



2-(Cyclopropylidenemethyl)-6-methoxynaphthalene (M-7)

¹H NMR (400 MHz, CDCl₃) δ 7.84 – 7.75 (m, 2H), 7.75 – 7.66 (m, 2H), 7.18 – 7.09 (m, 2H), 6.89 (p, J = 2.1 Hz, 1H), 3.92 (s, 3H), 1.50 (ddd, J = 9.5, 5.6, 2.3 Hz, 2H), 1.24 – 1.20 (m, 2H).

¹³C NMR (101 MHz, CDCl₃) δ 157.4, 133.8, 133.6, 129.4, 129.1, 126.8, 125.6, 125.0, 123.7, 118.8, 118.4, 105.8, 55.3, 4.3, 0.6.

(4-(Cyclopropylidenemethyl)phenyl)(methyl)sulfane (M-8)

¹H NMR (400 MHz, CDCl₃) δ 7.48 – 7.44 (m, 2H), 7.25 – 7.21 (m, 2H), 6.71 (p, J = 2.1 Hz, 1H), 2.49 (s, 3H), 1.44 – 1.39 (m, 2H), 1.18 (ddd, J = 10.1, 5.7, 2.1 Hz, 2H).

¹³C NMR (101 MHz, CDCl₃) δ 136.4, 135.4, 127.0, 126.8, 123.8, 117.6, 16.0, 4.1, 0.5.



1-(tert-Butyl)-4-(cyclopropylidenemethyl)benzene (M-9)

¹H NMR (300 MHz, CDCl₃) δ 7.45 – 7.39 (m, 2H), 7.34 – 7.28 (m, 2H), 6.72 – 6.64 (m, 1H), 1.34 (dd, J = 14.4, 2.2 Hz, 2H), 1.27 (s, 9H), 1.12 – 1.07 (m, 2H).

¹³C NMR (**75 MHz, CDCl**₃) δ 149.6, 135.5, 126.3, 125.3, 123.3, 117.9, 34.5, 31.3, 4.1, 0.5.



1-(Cyclopropylidenemethyl)naphthalene (M-10)

¹H NMR (300 MHz, CDCl₃) δ 8.25 (dd, J = 8.9, 1.1 Hz, 1H), 7.93 – 7.84 (m, 2H), 7.76 (d, J = 8.2 Hz, 1H), 7.60 – 7.45 (m, 4H), 1.52 – 1.44 (m, 2H), 1.35 – 1.27 (m, 2H).

¹³C NMR (75 MHz, CDCl₃) δ 134.6, 133.8, 131.0, 128.6, 127.1, 126.7, 125.8, 125.6, 125.5, 123.8, 123.6, 114.7, 4.1, 1.5.



1-Chloro-4-(cyclopropylidenemethyl)benzene (M-11)

¹H NMR (300 MHz, CDCl₃) δ 7.49 – 7.42 (m, 2H), 7.35 – 7.24 (m, 2H), 6.71 (p, J = 2.1 Hz, 1H), 1.45 – 1.38 (m, 2H), 1.22 – 1.15 (m, 2H).

¹³C NMR (75 MHz, CDCl₃) δ 136.7, 132.2, 128.6, 127.7, 125.2, 117.2, 4.1, 0.6.



1-(Cyclopropylidenemethyl)-3-fluorobenzene (M-12)

¹H NMR (300 MHz, CDCl₃) δ 7.27 – 7.19 (m, 3H), 6.94 – 6.81 (m, 1H), 6.70 (p, J = 1.2 Hz, 1H), 1.45 – 1.37 (m, 2H), 1.21 – 1.14 (m, 2H).

¹³C NMR (75 MHz, CDCl₃) δ 163.1 (d, J = 244.4 Hz), 140.6 (d, J = 7.7 Hz), 129.8 (d, J = 8.6 Hz), 126.0, 122.5 (d, J = 2.5 Hz), 117.4 (d, J = 2.8 Hz), 113.4 (d, J = 21.6 Hz), 112.8 (d, J = 21.8 Hz), 4.2, 0.6.



3-(Cyclopropylidenemethyl)benzo[b]thiophene (M-13)

¹H NMR (400 MHz, CDCl₃) δ 7.97 – 7.94 (m, 1H), 7.84 (ddd, J = 7.8, 1.3, 0.7 Hz, 1H), 7.51 (s, 1H), 7.40 – 7.30 (m, 2H), 7.06 (q, J = 2.0 Hz, 1H), 1.40 – 1.35 (m, 2H), 1.26 (ddd, J = 8.7, 4.9, 1.5 Hz, 2H).

¹³C NMR (**101 MHz, CDCl₃**) δ 140.1, 137.9, 134.0, 125.2, 124.2, 124.0, 122.7, 121.7, 120.8, 110.5, 4.2, 2.0.

(4-(Cyclopropylidenemethyl)phenyl)(trifluoromethyl)sulfane (M-14)

¹H NMR (400 MHz, CDCl₃) δ 7.59 (q, J = 8.4 Hz, 4H), 6.77 (p, J = 2.0 Hz, 1H), 1.50 – 1.40 (m, 2H), 1.23 (ddd, J = 9.8, 5.7, 1.5 Hz, 2H).

¹³C NMR (101 MHz, CDCl₃) δ 140.9, 136.5, 129.6 (q, J = 308.3 Hz), 127.8, 127.4, 121.8 (q, J = 2.2 Hz), 117.3, 4.3, 0.7.

4-(Cyclopropylidenemethyl)benzonitrile (M-15)

¹**H NMR** (300 MHz, CDCl₃) δ 7.58 (s, 4H), 6.77 (p, J = 1.9 Hz, 1H), 1.51 – 1.42 (m, 2H), 1.29 – 1.19 (m, 2H).

¹³C NMR (**75 MHz, CDCl**₃) δ 142.6, 132.2, 129.7, 126.9, 119.2, 117.2, 109.7, 4.4, 0.8.

3-(Cyclopropylidenemethyl)-1-tosyl-1*H*-pyrrole (M-16)

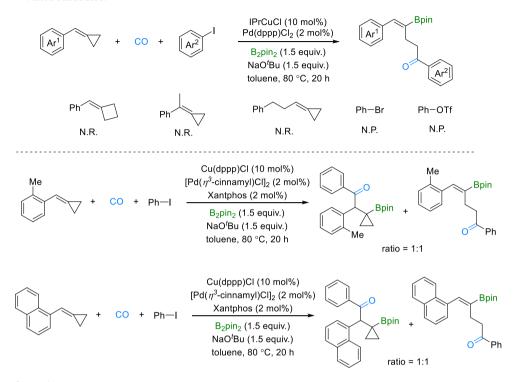
¹H NMR (300 MHz, CDCl₃) δ 7.62 – 7.55 (m, 2H), 7.20 – 7.13 (m, 3H), 7.07 (dd, J = 2.4, 1.8 Hz, 1H), 6.37 (ddq, J = 3.5, 1.7, 0.6 Hz, 1H), 6.15 (td, J = 3.3, 0.7 Hz, 1H), 2.27 (s, 3H), 1.12 – 1.04 (m, 4H).

¹³C NMR (75 MHz, CDCl₃) δ 144.8, 136.3, 133.6, 129.9, 126.8, 125.5, 122.0, 112.3, 111.3, 107.5, 21.6, 3.5, 2.2.

5. Spectroscopic data of products

5.1 Failed substrates.

Failed substrates:



5.2 date of products.

(Z)-1,5-Diphenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pent-4-en-1-one (3a)

The title compound was prepared from (cyclopropylidenemethyl)benzene (27 uL, 0.2 mmol) and iodobenzene (39 uL, 0.34 mmol), according to general borocarbonylation I (ring open). The crude residue was purified by flash chromatography (pentane/EA = 20:1, Rf = 0.35) to give the product as a white solid (47.7 mg, 70%). X-ray (single-crystal) colorless block crystals of X-ray diffraction quality were obtained by slow evaporation of saturated solution of 3a in ethyl acetate/n-pentane (CCDC 2123095).

¹H NMR (300 MHz, CDCl₃) δ 7.90 – 7.83 (m, 2H), 7.45 – 7.38 (m, 1H), 7.35 – 7.27 (m, 2H), 7.23 – 7.16 (m, 5H), 7.15 – 7.09 (m, 1H), 3.08 – 2.97 (m, 2H), 2.76 – 2.64 (m, 2H), 1.20 (s, 12H).

¹³C NMR (75 MHz, CDCl₃) δ 200.0, 143.3, 137.5, 136.8, 132.8, 128.9, 128.4, 128.2, 128.2, 127.3, 83.5, 38.8, 24.8, 24.7.

¹¹B NMR (96 MHz, CDCl₃) δ 30.3.

HRMS (**ESI**): calcd for [M+Na]⁺ C₂₃H₂₇BO₃ 384.1987, found: 384.1991.

IR (**ATR**): 2920, 2851, 1678, 1448, 1351, 1313, 1142, 747, 721, 688 cm⁻¹.

Mp: 56-58 °C

$(Z)-1-(4-Ethylphenyl)-5-phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pent-4-en-1-one \\ (3b)$

The title compound was prepared from (cyclopropylidenemethyl)benzene (27 uL, 0.2 mmol) and 1-ethyl-4-iodobenzene (49 uL, 0.34 mmol), according to general borocarbonylation I (ring open). The crude residue was purified by flash chromatography (pentane/EA = 20:1, Rf = 0.36) to give the product as a colorless oil (47.8 mg, 61%).

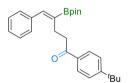
¹H NMR (300 MHz, CDCl₃) δ 7.98 – 7.85 (m, 2H), 7.36 – 7.28 (m, 5H), 7.27 (d, J = 0.6 Hz, 1H), 7.26 – 7.18 (m, 2H), 3.21 – 3.04 (m, 2H), 2.88 – 2.76 (m, 2H), 2.70 (q, J = 7.6 Hz, 2H), 1.33 (s, 12H), 1.26 (t, J = 7.6 Hz, 3H).

¹³C NMR (75 MHz, CDCl₃) δ 199.7, 149.7, 143.2, 137.5, 134.6, 128.9, 128.4, 128.2, 127.9, 127.3, 83.5, 38.8, 28.9, 24.9, 24.8, 15.2.

¹¹B NMR (96 MHz, CDCl₃) δ 30.3.

HRMS (**ESI**): calcd for [M+Na]⁺ C₂₅H₃₁BO₃ 412.2300, found: 412.2305.

IR (ATR): 2970, 1673, 1350, 1319, 1142, 701 cm⁻¹.



(Z)-1-(4-(tert-Butyl)phenyl)-5-phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pent-4-en-1-one (3c)

The title compound was prepared from (cyclopropylidenemethyl)benzene (27 uL, 0.2 mmol) and 1-(tert-butyl)-4-iodobenzene (60 uL, 0.34 mmol), according to general borocarbonylation I (ring open). The crude residue was purified by flash chromatography (pentane/EA = 20:1, Rf = 0.38) to give the product as a white solid (58.9 mg, 70%).

¹H NMR (300 MHz, CDCl₃) δ 8.00 – 7.86 (m, 2H), 7.49 – 7.41 (m, 2H), 7.36 – 7.28 (m, 5H), 7.25 – 7.13 (m, 1H), 3.19 – 3.07 (m, 2H), 2.90 – 2.76 (m, 2H), 1.35 (s, 9H), 1.33 (s, 12H).

¹³C NMR (**75 MHz, CDCl**₃) δ 199.7, 156.4, 143.2, 137.5, 134.3, 128.9, 128.2, 128.2, 127.3, 125.4, 83.5, 38.7, 35.0, 31.1, 24.8, 24.8.

¹¹B NMR (96 MHz, CDCl₃) δ 30.2.

HRMS (**ESI**): calcd for [M+Na]⁺ C₂₇H₃₅BO₃ 440.2612, found: 440.2616.

IR (ATR): 2965, 1679, 1370, 1313, 1266, 1140, 750, 703, 683, 492 cm⁻¹.

Mp: 115-117 ℃

(Z) - 1 - (4-Methoxyphenyl) - 5-phenyl - 4 - (4,4,5,5-tetramethyl - 1,3,2-dioxaborolan - 2-yl) pent - 4-en-1-one (3d)

The title compound was prepared from (cyclopropylidenemethyl)benzene (27 uL, 0.2 mmol) and 1-iodo-4-methoxybenzene (79.6 mg, 0.34 mmol), according to general borocarbonylation I (ring open). The crude residue was purified by flash chromatography (pentane/EA = 15:1, Rf = 0.30) to give the product as a yellow oil (65.4 mg, 83%).

¹H NMR (300 MHz, CDCl₃) δ 8.04 – 7.88 (m, 2H), 7.36 – 7.28 (m, 5H), 7.26 – 7.19 (m, 1H), 6.96 – 6.84 (m, 2H), 3.86 (s, 3H), 3.17 – 3.03 (m, 2H), 2.88 – 2.72 (m, 2H), 1.32 (s, 12H).

¹³C NMR (**75 MHz, CDCl**₃) δ 198.7, 163.2, 143.1, 137.5, 130.5, 130.0, 128.9, 128.2, 127.3, 113.6, 83.5, 55.4, 38.6, 25.0, 24.8.

¹¹**B NMR (96 MHz, CDCl₃)** δ 30.1.

HRMS (**ESI**): calcd for [M+Na]⁺ C₂₄H₂₉BO₄ 414.2092, found: 414.2090.

IR (**ATR**): 1671, 1597, 1254, 1167, 1027, 698 cm⁻¹.

(Z)-1-(4-(Benzyloxy)phenyl)-5-phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pent-4-en-1-one (3e)

The title compound was prepared from (cyclopropylidenemethyl)benzene (27 uL, 0.2 mmol) and 1-(benzyloxy)-4-iodobenzene (105.4 mg, 0.34 mmol), according to general borocarbonylation I (ring open). The crude residue was purified by flash chromatography (pentane/EA = 15:1, Rf = 0.30) to give the product as a colorless oil (78.6 mg, 84%).

¹**H NMR (300 MHz, CDCl₃)** δ 8.02 – 7.94 (m, 2H), 7.47 – 7.28 (m, 10H), 7.27 – 7.21 (m, 1H), 7.03 – 6.96 (m, 2H), 5.13 (s, 2H), 3.16 – 3.04 (m, 2H), 2.90 – 2.74 (m, 2H), 1.33 (s, 12H).

¹³C NMR (75 MHz, CDCl₃) δ 198.6, 162.3, 143.1, 137.4, 136.2, 130.5, 130.1, 128.9, 128.6, 128.2, 128.2, 127.4, 127.2, 114.4, 83.5, 70.0, 38.6, 25.0, 24.8.

¹¹B NMR (96 MHz, CDCl₃) δ 30.1.

HRMS (**ESI**): calcd for [M+Na]⁺ C₃₀H₃₃BO₄ 490.2405, found: 490.2402.

IR (ATR): 2976, 1674, 1598, 1256, 1206, 1168, 1140, 964, 740, 696, 685 cm⁻¹.

$(Z)-1-(4-Chlorophenyl)-5-phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pent-4-en-1-one \\ (3f)$

The title compound was prepared from (cyclopropylidenemethyl)benzene (27 uL, 0.2 mmol) and 1-chloro-4-iodobenzene (80.9 mg, 0.34 mmol), according to general borocarbonylation I (ring open). The crude residue was purified by flash chromatography (pentane/EA = 20:1, Rf = 0.38) to give the product as a white solid (54.0 mg, 68%).

¹H NMR (300 MHz, CDCl₃) δ 7.98 – 7.86 (m, 2H), 7.43 – 7.36 (m, 2H), 7.36 – 7.28 (m, 5H), 7.26 – 7.19 (m, 1H), 3.16 – 3.06 (m, 2H), 2.86 – 2.74 (m, 2H), 1.32 (s, 12H).

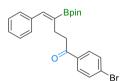
¹³C NMR (75 MHz, CDCl₃) δ 198.8, 143.5, 139.2, 137.4, 135.1, 129.7, 128.8, 128.7, 128.3, 127.3, 83.6, 38.8, 24.8, 24.8.

¹¹**B NMR (96 MHz, CDCl₃)** δ 30.3.

HRMS (**ESI**): calcd for [M+Na]⁺ C₂₃H₂₆BClO₃ 418.1597, found: 418.1600.

IR (**ATR**): 2974, 1683, 1380, 1350, 1317, 1201, 1139, 1082, 698, 682 cm⁻¹.

Mp: 82-83 ℃



(Z) - 1 - (4 - Bromophenyl) - 5 - phenyl - 4 - (4,4,5,5 - tetramethyl - 1,3,2 - dioxaborolan - 2 - yl) pent - 4 - en - 1 - one (3g)

The title compound was prepared from (cyclopropylidenemethyl)benzene (27 uL, 0.2 mmol) and 1-bromo-4-iodobenzene (95.9 mg, 0.34 mmol), according to general borocarbonylation I (ring open). The crude residue was purified by flash chromatography (pentane/EA = 20:1, Rf = 0.37) to give the product as a colorless oil (59.8 mg, 68%).

¹**H NMR** (**300 MHz, CDCl₃**) δ 7.88 – 7.79 (m, 2H), 7.61 – 7.52 (m, 2H), 7.37 – 7.28 (m, 5H), 7.27 – 7.21 (m, 1H), 3.14 – 3.03 (m, 2H), 2.84 – 2.70 (m, 2H), 1.32 (s, 12H).

¹³C NMR (**75 MHz, CDCl**₃) δ 199.0, 143.5, 137.4, 135.5, 131.7, 129.8, 128.8, 128.3, 127.9, 127.3, 83.6, 38.8, 24.8, 24.8.

¹¹B NMR (96 MHz, CDCl₃) δ 30.0.

HRMS (**ESI**): calcd for [M+Na]⁺ C₂₃H₂₆BBrO₃ 462.1092, found: 462.1097.

IR (ATR): 2975, 1683, 1584, 1370, 1351, 1310, 1141, 1069, 1009, 750, 697 cm⁻¹.

(Z)-1-(2-Methoxyphenyl)-5-phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pent-4-en-1-one (3h)

The title compound was prepared from (cyclopropylidenemethyl)benzene (27 uL, 0.2 mmol) and 1-iodo-2-methoxybenzene (75.9 mg, 0.34 mmol), according to general borocarbonylation I (ring open). The crude residue was purified by flash chromatography (pentane/EA = 15:1, Rf = 0.30) to give the product as a yellow oil (56.5 mg, 72%).

¹H NMR (300 MHz, CDCl₃) δ 7.66 (dd, J = 7.7, 2.2 Hz, 1H), 7.46 – 7.39 (m, 1H), 7.35 – 7.27 (m, 5H), 7.22 (ddd, J = 6.7, 5.6, 2.3 Hz, 1H), 6.97 (td, J = 7.4, 1.0 Hz, 1H), 6.92 (dd, J = 8.3, 1.1 Hz, 1H), 3.81 (s, 3H), 3.25 – 3.10 (m, 2H), 2.86 – 2.68 (m, 2H), 1.30 (s, 12H).

¹³C NMR (**75 MHz, CDCl**₃) δ 202.3, 158.4, 142.6, 137.6, 133.0, 130.2, 129.0, 128.6, 128.1, 127.1, 120.5, 111.4, 83.4, 55.3, 43.6, 24.8, 24.5.

¹¹B NMR (96 MHz, CDCl₃) δ 30.3.

HRMS (**ESI**): calcd for [M+Na]⁺ C₂₄H₂₉BO₄ 414.2092, found: 414.2093.

IR (**ATR**): 2973, 1670, 1596, 1484, 1464, 1436, 1284, 1243, 1179, 1156, 1111, 1022, 948, 754, 698 cm⁻¹.

(Z)-5-Phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1-(*m*-tolyl)pent-4-en-1-one (3i)

The title compound was prepared from (cyclopropylidenemethyl)benzene (27 uL, 0.2 mmol) and 1-iodo-3-methylbenzene (49 uL, 0.34 mmol), according to general borocarbonylation I (ring open). The crude residue was purified by flash chromatography (pentane/EA = 20:1, Rf = 0.35) to give the product as a white solid ($50.6 \, \text{mg}$, 67%).

¹H NMR (300 MHz, CDCl₃) δ 7.83 – 7.74 (m, 2H), 7.38 – 7.26 (m, 7H), 7.25 – 7.14 (m, 1H), 3.20 – 3.07 (m, 2H), 2.88 – 2.74 (m, 2H), 2.40 (s, 3H), 1.33 (s, 12H).

¹³C NMR (75 MHz, CDCl₃) δ 200.2, 143.2, 138.2, 137.5, 136.9, 133.5, 128.9, 128.7, 128.3, 128.2, 127.3, 125.4, 83.5, 38.9, 24.8, 24.8, 21.3.

¹¹**B NMR (96 MHz, CDCl₃)** δ 30.1.

HRMS (**ESI**): calcd for [M+Na]⁺ C₂₄H₂₉BO₃ 398.2143, found: 398.2151.

IR (**ATR**): 2979, 1677, 1371, 1339, 1315, 1282, 1156, 1141, 771, 758, 701, 690, 684 cm⁻¹.

Mp: 94-96 ℃

(Z)-5-Phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1-(3-(trifluoromethyl)phenyl)pent-4-en-1-one (3j)

The title compound was prepared from (cyclopropylidenemethyl)benzene (27 uL, 0.2 mmol) and 1-iodo-3-(trifluoromethyl)benzene (49 uL, 0.34 mmol), according to general borocarbonylation I (ring open). The crude residue was purified by flash chromatography (pentane/EA = 20:1, Rf = 0.35) to give the product as a colorless oil (43.0 mg, 50%).

¹H NMR (300 MHz, CDCl₃) δ 8.24 (dt, J = 1.8, 1.1 Hz, 1H), 8.17 – 8.13 (m, 1H), 7.79 (ddt, J = 7.8, 1.2, 0.6 Hz, 1H), 7.57 (tt, J = 7.8, 0.8 Hz, 1H), 7.35 – 7.29 (m, 5H), 7.26 – 7.20 (m, 1H), 3.22 – 3.11 (m, 2H), 2.89 – 2.76 (m, 2H), 1.32 (s, 12H).

¹³C NMR (75 MHz, CDCl₃) δ 198.7, 143.7, 137.4, 137.3, 131.4 (q. J = 1.3 Hz), 131.1 (q. J = 32.9 Hz), 130.1, 129.2 (d, J = 3.7 Hz), 129.1, 128.3, 127.4, 125.1 (q. J = 3.6 Hz), 123.7 (d. J = 272.5 Hz), 83.7, 38.9, 24.8, 24.1.

¹¹**B NMR (96 MHz, CDCl₃)** δ 30.3.

¹⁹F NMR (282 MHz, CDCl₃) δ -62.7.

HRMS (**ESI**): calcd for [M+Na]⁺ C₂₄H₂₆BF₃O₃ 452.1860, found: 452.1865.

IR (ATR): 2977, 1689, 1372, 1327, 1255, 1165, 1125, 1071, 755, 693, 654 cm⁻¹.

(Z)-1-(3,4-Dimethylphenyl)-5-phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pent-4-en-1-one (3k)

The title compound was prepared from (cyclopropylidenemethyl)benzene (27 uL, 0.2 mmol) and 4-iodo-1,2-dimethylbenzene (48 uL, 0.34 mmol), according to general borocarbonylation I (ring open). The crude residue was purified by flash chromatography (pentane/EA = 20:1, Rf = 0.32) to give the product as a white solid (55.0 mg, 71%).

¹**H NMR** (300 MHz, CDCl₃) δ 7.82 – 7.65 (m, 2H), 7.40 – 7.27 (m, 5H), 7.26 – 7.21 (m, 1H), 7.19 (d, J = 7.6 Hz, 1H), 3.18 – 3.06 (m, 2H), 2.88 – 2.75 (m, 2H), 2.30 (s, 6H), 1.33 (s, 12H).

¹³C NMR (75 MHz, CDCl₃) δ 200.0, 143.1, 142.2, 137.5, 136.7, 134.8, 129.7, 129.3, 128.9, 128.2, 127.3, 126.0, 83.5, 38.8, 25.0, 24.8, 20.0, 19.8.

¹¹B NMR (96 MHz, CDCl₃) δ 30.1.

HRMS (**ESI**): calcd for [M+Na]⁺ C₂₅H₃₁BO₃ 412.2300, found: 412.2300.

IR (ATR): 2977, 1681, 1377, 1352, 1341, 1315, 1278, 1140, 699, 686 cm⁻¹.

Mp: 114-116 °C

(Z)-1-(3,4-Dichlorophenyl)-5-phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pent-4-en-1-one (3l)

The title compound was prepared from (cyclopropylidenemethyl)benzene (27 uL, 0.2 mmol) and 1,2-dichloro-4-iodobenzene (92.8 mg, 0.34 mmol), according to general borocarbonylation I (ring open). The crude residue was purified by flash chromatography (pentane/EA = 20:1, Rf = 0.40) to give the product as a colorless oil (37.9 mg, 44%).

¹H NMR (300 MHz, CDCl₃) δ 8.08 (d, J = 2.0 Hz, 1H), 7.79 (dd, J = 8.4, 2.1 Hz, 1H), 7.50 (d, J = 8.4 Hz, 1H), 7.36 – 7.28 (m, 5H), 7.26 – 7.20 (m, 1H), 3.11 – 3.03 (m, 2H), 2.78 (dd, J = 8.3, 6.5 Hz, 2H), 1.33 (s, 12H).

¹³C NMR (75 MHz, CDCl₃) δ 197.9, 143.7, 137.3, 136.3, 133.1, 130.6, 130.4, 128.8, 128.3, 127.4, 127.3, 83.7, 39.0, 24.9, 24.8.

¹¹B NMR (96 MHz, CDCl₃) δ 30.5.

HRMS (**ESI**): calcd for [M+Na]⁺ C₂₃H₂₅BCl₂O₃ 452.1207, found: 452.1204.

IR (ATR): 2975, 1686, 1372, 1350, 1310, 1269, 1140, 1029, 752, 698, 674 cm⁻¹.

(Z) - 1 - (Naphthalen - 1 - yl) - 5 - phenyl - 4 - (4,4,5,5 - tetramethyl - 1,3,2 - dioxaborolan - 2 - yl) pent - 4 - en - 1 - one (3m)

The title compound was prepared from (cyclopropylidenemethyl)benzene (27 uL, 0.2 mmol) and 1-iodonaphthalene (50 uL, 0.34 mmol), according to general borocarbonylation I (ring open). The crude residue was purified by flash chromatography (pentane/EA = 20:1, Rf = 0.35) to give the product as a yellow oil (61.6 mg, 75%).

¹H NMR (300 MHz, CDCl₃) δ 8.61 (ddd, J = 8.0, 1.7, 0.8 Hz, 1H), 7.99 – 7.93 (m, 1H), 7.91 – 7.84 (m, 2H), 7.62 – 7.51 (m, 2H), 7.51 – 7.45 (m, 1H), 7.38 – 7.28 (m, 5H), 7.27 – 7.19 (m, 1H), 3.33 – 3.20 (m, 2H), 2.99 – 2.80 (m, 2H), 1.32 (s, 12H).

¹³C NMR (75 MHz, CDCl₃) δ 204.3, 143.2, 137.4, 135.9, 133.9, 132.3, 130.2, 128.9, 128.3, 128.2, 127.7, 127.6, 127.3, 126.3, 125.9, 124.3, 83.5, 42.2, 25.0, 24.8.

¹¹B NMR (96 MHz, CDCl₃) δ 30.0.

HRMS (**ESI**): calcd for [M+Na]⁺ C₂₇H₂₉BO₃ 434.2163, found: 434.2141.

IR (ATR): 2972, 1677, 1380, 1371, 1313, 1282, 1136, 1098, 787, 772, 749, 698, 686, 482 cm⁻¹.

Ethyl (Z)-2-methyl-2-(4-(5-phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pent-4-enoyl)phenoxy)propanoate (3n)

The title compound was prepared from (cyclopropylidenemethyl)benzene (27 uL, 0.2 mmol) and ethyl 2-(4-iodophenoxy)-2-methylpropanoate (113.6 mg, 0.34 mmol), according to general borocarbonylation I (ring open). The crude residue was purified by flash chromatography (pentane/EA = 15:1, Rf = 0.25) to give the product as a colorless oil (61.2 mg, 62%).

¹H NMR (300 MHz, CDCl₃) δ 7.94 – 7.87 (m, 2H), 7.35 – 7.27 (m, 5H), 7.26 – 7.19 (m, 1H), 6.85 – 6.75 (m, 2H), 4.22 (q, J = 7.2 Hz, 2H), 3.14 – 3.02 (m, 2H), 2.78 (dd, J = 9.8, 7.9 Hz, 2H), 1.65 (s, 6H), 1.31 (s, 12H), 1.21 (t, J = 7.2 Hz, 3H).

¹³C NMR (75 MHz, CDCl₃) δ 198.6, 173.7, 159.5, 143.2, 137.4, 130.5, 130.0, 128.9, 128.2, 127.3, 117.3, 83.5, 79.2, 61.6, 38.6, 25.3, 24.9, 24.8, 14.0.

¹¹B NMR (96 MHz, CDCl₃) δ 29.8.

HRMS (**ESI**): calcd for [M+H]⁺ C₂₉H₃₇BO₆ 492.2798, found: 492.2809.

IR (**ATR**): 2979, 1732, 1676, 1597, 1367, 1286, 1244, 1169, 1137, 1021, 966, 835, 699, 493 cm⁻¹.

(Z)-5-Phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1-(4-

(trifluoromethoxy)phenyl)pent-4-en-1-one (30)

The title compound was prepared from (cyclopropylidenemethyl)benzene (27 uL, 0.2 mmol) and 1-iodo-4-(trifluoromethoxy)benzene (51 uL, 0.34 mmol), according to general borocarbonylation I (ring open). The crude residue was purified by flash chromatography (pentane/EA = 20:1, Rf = 0.40) to give the product as a colorless oil (59.0 mg, 66%).

¹H NMR (400 MHz, CDCl₃) δ 8.01 – 7.85 (m, 2H), 7.28 – 7.20 (m, 5H), 7.19 – 7.12 (m, 3H), 3.08 – 2.98 (m, 2H), 2.77 – 2.66 (m, 2H), 1.23 (s, 12H).

¹³C NMR (101 MHz, CDCl₃) δ 198.5, 152.4 (q, J = 1.8 Hz), 143.5, 137.4, 135.0, 130.2, 128.8, 128.3, 127.4, 120.3, 120.3 (q, J = 258.5 Hz), 83.6, 38.9, 24.8, 24.7.

¹¹B NMR (128 MHz, CDCl₃) δ 30.6.

¹⁹F NMR (376 MHz, CDCl₃) δ -57.59.

HRMS (**ESI**): calcd for [M+Na]⁺ C₂₄H₂₆BF₃O₄ 468.1810, found: 468.1813.

IR (ATR): 1686, 1372, 1251, 1204, 1162, 1141, 1109, 1082, 859, 750, 698 cm⁻¹.

(Z)-5-Phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)pent-4-en-1-one (3p)

The title compound was prepared from (cyclopropylidenemethyl)benzene (27 uL, 0.2 mmol) and 2-(4-iodophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (111.2 mg, 0.34 mmol), according to general borocarbonylation I (ring open). The crude residue was purified by flash chromatography (pentane/EA = 20:1, Rf = 0.18) to give the product as a yellow oil (83.8 mg, 86%).

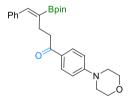
¹H NMR (300 MHz, CDCl₃) δ 7.98 – 7.93 (m, 2H), 7.90 – 7.84 (m, 2H), 7.36 – 7.29 (m, 5H), 7.26 – 7.19 (m, 1H), 3.20 – 3.09 (m, 2H), 2.81 (dd, J = 9.6, 6.9 Hz, 2H), 1.36 (s, 12H), 1.32 (s, 12H).

¹³C NMR (**75 MHz, CDCl**₃) δ 200.3, 143.3, 138.8, 137.5, 134.8, 128.9, 128.2, 127.3, 127.2, 124.2, 84.1, 83.6, 39.0, 25.0, 24.9, 24.8, 24.8.

¹¹B NMR (96 MHz, CDCl₃) δ 30.1.

HRMS (**ESI**): calcd for [M+Na]⁺ C₂₉H₃₈B₂O₅ 509.2875, found: 509.2886.

IR (**ATR**): 2976, 1678, 1598, 1367, 1204, 1153, 1108, 948, 882, 828, 743, 697, 550, 495 cm⁻¹.



(Z)-1-(4-Morpholinophenyl)-5-phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pent-4-en-1-one (3q)

The title compound was prepared from (cyclopropylidenemethyl)benzene (27 uL, 0.2 mmol) and 4-(4-iodophenyl)morpholine (97.9 mg, 0.34 mmol), according to general borocarbonylation I (ring open). The crude residue was purified by flash chromatography (pentane/EA = 10:1, Rf = 0.25) to give the product as a yellow oil (80.0 mg, 89%).

¹H NMR (300 MHz, CDCl₃) δ 7.96 – 7.87 (m, 2H), 7.37 – 7.28 (m, 5H), 7.26 – 7.19 (m, 1H), 6.88 – 6.81 (m, 2H), 3.88 – 3.82 (m, 4H), 3.32 – 3.24 (m, 4H), 3.11 – 3.03 (m, 2H), 2.86 – 2.71 (m, 2H), 1.32 (s, 12H).

¹³C NMR (75 MHz, CDCl₃) δ 198.3, 154.0, 142.9, 137.5, 130.2, 128.9, 128.2, 127.8, 127.2, 113.3, 83.5, 66.5, 47.6, 38.3, 25.1, 24.8.

¹¹**B NMR (96 MHz, CDCl₃)** δ 30.0.

HRMS (**ESI**): calcd for [M+H]⁺ C₂₇H₃₄BNO₄ 447.2695, found: 447.2703.

IR (**ATR**): 2973, 1666, 1596, 1186, 1140, 1112, 926 cm⁻¹.

(Z) - 1 - (4 - (1H-Pyrrol-1-yl)phenyl) - 5 - phenyl - 4 - (4,4,5,5 - tetramethyl-1,3,2 - dioxaborolan-2-yl)pent-4 - en-1-one (3r)

The title compound was prepared from (cyclopropylidenemethyl)benzene (27 uL, 0.2 mmol) and 1-(4-iodophenyl)-1H-pyrrole (91.1 mg, 0.34 mmol), according to general borocarbonylation I (ring open). The crude residue was purified by flash chromatography (pentane/EA = 20:1, Rf = 0.30) to give the product as a yellow oil (72.6 mg, 85%).

¹H NMR (300 MHz, CDCl₃) δ 8.10 – 8.02 (m, 2H), 7.48 – 7.39 (m, 2H), 7.34 (d, J = 4.5 Hz, 5H), 7.28 – 7.21 (m, 1H), 7.19 – 7.14 (m, 2H), 6.43 – 6.34 (m, 2H), 3.20 – 3.07 (m, 2H), 2.92 – 2.76 (m, 2H), 1.33 (s, 12H).

¹³C NMR (**75 MHz, CDCl**₃) δ 198.7, 143.8, 143.4, 137.4, 133.7, 130.1, 128.9, 128.3, 127.3, 119.3, 119.0, 111.5, 83.6, 38.8, 25.0, 24.8.

¹¹**B NMR (96 MHz, CDCl₃)** δ 30.1.

HRMS (**ESI**): calcd for [M+Na]⁺ C₂₇H₃₀BNO₃ 449.2252, found: 449.2260.

IR (**ATR**): 1610, 1517, 1351, 1329, 1145, 1130, 1062, 1045, 840, 730, 696 cm⁻¹.



$(Z)-5-Phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1-(thiophen-2-yl)pent-4-en-1-one \\ (3s)$

The title compound was prepared from (cyclopropylidenemethyl)benzene (27 uL, 0.2 mmol) and 2-iodothiophene (38 uL, 0.34 mmol), according to general borocarbonylation I (ring open). The crude residue was purified by flash chromatography (pentane/EA = 20:1, Rf = 0.25) to give the product as a yellow oil (47.6 mg, 65%).

¹H NMR (300 MHz, CDCl₃) δ 7.73 (dd, J = 3.8, 1.1 Hz, 1H), 7.60 (dd, J = 5.0, 1.2 Hz, 1H), 7.37 – 7.28 (m, 5H), 7.27 – 7.21 (m, 1H), 7.10 (dd, J = 5.0, 3.9 Hz, 1H), 3.14 – 3.03 (m, 2H), 2.87 – 2.76 (m, 2H), 1.32 (s, 12H).

¹³C NMR (**75 MHz, CDCl**₃) δ 193.0, 144.4, 143.4, 137.4, 133.3, 131.9, 128.9, 128.3, 127.9, 127.3, 83.6, 39.5, 25.1, 24.8.

¹¹**B NMR (96 MHz, CDCl₃)** δ 30.4.

HRMS (**ESI**): calcd for [M+Na]+ C₂₁H₂₅BO₃S 390.1551, found: 390.1552.

IR (ATR): 2975, 1659, 1413, 1371, 1351, 1310, 1267, 1141, 1081, 755, 722, 699 cm⁻¹.

(Z)-1-(4-((1H-Indol-1-yl)methyl)phenyl)-5-phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pent-4-en-1-one (3t)

The title compound was prepared from (cyclopropylidenemethyl)benzene (27 uL, 0.2 mmol) and 1-(3-iodobenzyl)-1H-indole (113.2 mg, 0.34 mmol), according to general borocarbonylation I (ring open). The crude residue was purified by flash chromatography (pentane/EA = 20:1, Rf = 0.15) to give the product as a colorless oil (78.0 mg, 79%).

¹H NMR (300 MHz, CDCl₃) δ 7.82 – 7.75 (m, 2H), 7.58 (ddd, J = 7.4, 1.5, 0.8 Hz, 1H), 7.29 – 7.21 (m, 6H), 7.21 – 7.13 (m, 2H), 7.13 – 7.01 (m, 4H), 6.49 (dd, J = 3.2, 0.9 Hz, 1H), 5.27 (s, 2H), 3.09 – 2.97 (m, 2H), 2.74 (dd, J = 9.1, 6.6 Hz, 2H), 1.23 (s, 12H).

¹³C NMR (75 MHz, CDCl₃) δ 199.6, 143.3, 138.1, 137.4, 137.2, 136.1, 131.0, 129.0, 128.9, 128.7, 128.2, 128.0, 127.6, 127.3, 126.5, 121.8, 121.0, 119.6, 109.5, 102.0, 83.5, 49.8, 38.8, 24.8, 24.6.

¹¹**B NMR (96 MHz, CDCl₃)** δ 29.9.

HRMS (**ESI**): calcd for [M+Na]⁺ C₃₂H₃₄BNO₃ 513.2565, found: 513.2568.

IR (**ATR**): 1681, 1462, 1348, 1311, 1254, 1141, 738, 690, 425 cm⁻¹.

(Z)-1-(1-Methyl-1H-indol-5-yl)-5-phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pent-4-en-1-one (3u)

The title compound was prepared from (cyclopropylidenemethyl)benzene (27 uL, 0.2 mmol) and 5-iodo-1-methyl-1H-indole (87.0 mg, 0.34 mmol), according to general borocarbonylation I (ring open). The crude residue was purified by flash chromatography (pentane/EA = 5:1, Rf = 0.25) to give the product as a red solid (56.9 mg, 57%).

¹H NMR (300 MHz, CDCl₃) δ 8.37 (dd, J = 1.7, 0.7 Hz, 1H), 7.94 (dd, J = 8.7, 1.7 Hz, 1H), 7.40 – 7.29 (m, 6H), 7.26 – 7.19 (m, 1H), 7.11 (d, J = 3.1 Hz, 1H), 6.59 (dd, J = 3.2, 0.9 Hz, 1H), 3.81 (s, 3H), 3.29 – 3.19 (m, 2H), 2.94 – 2.81 (m, 2H), 1.35 (s, 12H).

¹³C NMR (75 MHz, CDCl₃) δ 200.1, 142.9, 139.0, 137.5, 130.2, 129.0, 128.9, 128.2, 127.8, 127.2, 123.0, 121.9, 109.0, 102.9, 83.5, 38.8, 33.0, 25.4, 24.8.

¹¹B NMR (96 MHz, CDCl₃) δ 30.4.

HRMS (**ESI**): calcd for [M+H]⁺ C₂₆H₃₀BNO₃ 415.2433, found: 415.2441.

IR (**ATR**): 1666, 1346, 1312, 1299, 1137, 732, 685 cm⁻¹.

Mp: 99-101 ℃

(Z)-5-Phenyl-1-(pyridin-3-yl)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pent-4-en-1-one (3v)

The title compound was prepared from (cyclopropylidenemethyl)benzene (27 uL, 0.2 mmol) and 3-iodopyridine (69.7 mg, 0.34 mmol), according to general borocarbonylation I (ring open). The crude residue was purified by flash chromatography (pentane/EA = 5:1, Rf = 0.20) to give the product as a yellow oil (41.9 mg, 58%).

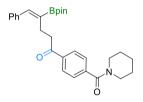
¹**H NMR** (**300 MHz, DMSO**) δ 9.08 (br, 1H), 8.29 (d, J = 7.8 Hz, 1H), 7.63 (br, 1H), 7.41 – 7.23 (m, 5H), 7.18 (s, 1H), 3.30 – 3.14 (m, 2H), 2.66 (t, J = 7.3 Hz, 2H), 1.23 (s, 12H).

¹³C NMR (**75** MHz, DMSO) δ 198.9, 142.6, 136.8, 135.6, 128.8, 128.4, 127.6, 83.4, 38.3, 24.6, 24.1.

¹¹B NMR (**96** MHz, CDCl₃) δ 30.4.

HRMS (**ESI**): calcd for [M+Na]⁺ C₂₂H₂₆BNO₃ 386.1902, found: 386.1903.

IR (ATR): 1685, 1373, 1314, 1144, 1052, 1023, 1004, 821, 758, 704, 620 cm⁻¹.



$(Z)\hbox{-}5\hbox{-}Phenyl\hbox{-}1\hbox{-}(4\hbox{-}(piperidine}\hbox{-}1\hbox{-}carbonyl)phenyl)\hbox{-}4\hbox{-}(4,4,5,5\hbox{-}tetramethyl\hbox{-}1,3,2\hbox{-}dioxaborolan-}2\hbox{-}yl)pent\hbox{-}4\hbox{-}en\hbox{-}1\hbox{-}one\ (3w)$

The title compound was prepared from (cyclopropylidenemethyl)benzene (27 uL, 0.2 mmol) and (4-iodophenyl)(piperidin-1-yl)methanone (107.1 mg, 0.34 mmol), according to general borocarbonylation I (ring open). The crude residue was purified by flash chromatography (pentane/EA = 2:1, Rf = 0.20) to give the product as a brown oil (80.7 mg, 85%).

¹H NMR (300 MHz, CDCl₃) δ 8.03 – 7.97 (m, 2H), 7.47 – 7.41 (m, 2H), 7.32 (d, J = 4.2 Hz, 5H), 7.26 – 7.20 (m, 1H), 3.71 (br, 2H), 3.29 (br, 2H), 3.18 – 3.09 (m, 2H), 2.87 – 2.75 (m, 2H), 1.68 – 1.52 (m, 6H), 1.31 (s, 12H).

¹³C NMR (**75 MHz, CDCl**₃) δ 199.4, 169.2, 143.4, 140.6, 137.4, 137.3, 128.8, 128.4, 128.3, 127.3, 126.9, 83.6, 48.6, 39.0, 25.6, 24.8, 24.8, 24.5.

¹¹**B NMR (96 MHz, CDCl₃)** δ 29.7.

HRMS (**ESI**): calcd for [M+H]⁺ C₂₉H₃₆BNO₄ 473.2852, found: 473.2861.

IR (ATR): 2934, 1682, 1618, 1371, 1350, 1310, 1272, 1141, 751, 699 cm⁻¹.

(Z)-1-(4-((((1R,2S,5R)-2-Isopropyl-5-methylcyclohexyl)oxy)methyl)phenyl)-5-phenyl-4-<math>(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pent-4-en-1-one (3x)

The title compound was prepared from (cyclopropylidenemethyl)benzene (27 uL, 0.2 mmol) and 1-iodo-4-((((1R,2S,5R)-2-isopropyl-5-methylcyclohexyl)oxy)methyl)benzene (126.4 mg, 0.34 mmol), according to general borocarbonylation I (ring open). The crude residue was purified by flash chromatography (pentane/EA = 20:1, Rf = 0.30) to give the product as a colorless oil (65.0 mg, 61%). ¹H NMR (300 MHz, CDCl₃) δ 8.01 – 7.90 (m, 2H), 7.46 – 7.37 (m, 2H), 7.37 – 7.28 (m, 5H), 7.27 –

7.20 (m, 1H), 4.71 (d, J = 12.4 Hz, 1H), 4.45 (d, J = 12.4 Hz, 1H), 3.27 – 3.07 (m, 3H), 2.81 (dd, J = 9.8, 6.9 Hz, 2H), 2.30 (pd, J = 7.0, 2.7 Hz, 1H), 2.24 – 2.13 (m, 1H), 1.72 – 1.58 (m, 2H), 1.32 (s, 14H), 0.97 – 0.87 (m, 9H), 0.74 (d, J = 7.0 Hz, 3H).

¹³C NMR (75 MHz, CDCl₃) δ 199.7, 144.4, 143.2, 137.4, 135.9, 128.9, 128.3, 128.2, 127.4, 127.3, 83.5, 79.2, 69.7, 48.3, 40.2, 38.9, 34.5, 31.5, 25.6, 24.8, 23.2, 22.3, 21.0, 16.1.

¹¹**B NMR (96 MHz, CDCl₃)** δ 29.9.

HRMS (**ESI**): calcd for [M+Na]⁺ C₃₄H₄₇BO₄ 552.3500, found: 552.3511.

IR (ATR): 2952, 2920, 1681, 1370, 1351, 1309, 1269, 1142, 1107, 1084, 962, 751, 698 cm⁻¹.

(Z)-1-Phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-5-(*o*-tolyl)pent-4-en-1-one (3y)

The title compound was prepared from 1-(cyclopropylidenemethyl)-3-methylbenzene (32 uL, 0.2 mmol) and iodobenzene (39 uL, 0.34 mmol), according to general borocarbonylation I (ring open). The crude residue was purified by flash chromatography (pentane/EA = 20:1, Rf = 0.35) to give the product as a colorless oil ($46.9 \, \text{mg}$, 62%).

¹H NMR (300 MHz, CDCl₃) δ 8.06 – 7.89 (m, 2H), 7.58 – 7.50 (m, 1H), 7.48 – 7.39 (m, 2H), 7.29 (d, J = 1.1 Hz, 1H), 7.22 (dd, J = 8.2, 7.3 Hz, 1H), 7.17 – 7.11 (m, 2H), 7.09 – 7.02 (m, 1H), 3.20 – 3.08 (m, 2H), 2.81 (dd, J = 7.7, 6.7 Hz, 2H), 2.32 (s, 3H), 1.32 (s, 12H).

¹³C NMR (75 MHz, CDCl₃) δ 200.1, 143.4, 137.7, 137.4, 136.9, 132.8, 129.7, 128.4, 128.2, 128.1, 128.1, 125.9, 83.5, 38.9, 24.8, 24.8, 21.4.

¹¹**B NMR (96 MHz, CDCl₃)** δ 30.1.

HRMS (**ESI**): calcd for [M+Na]⁺ C₂₄H₂₉BO₃ 398.2143, found: 398.2149.

IR (ATR): 2974, 1682, 1371, 1340, 1309, 1267, 1141, 1079, 963, 743, 687 cm⁻¹.

(Z)-5-(4-(tert-Butyl)phenyl)-1-phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pent-4-en-1-one (3z)

The title compound was prepared from 1-(tert-butyl)-4-(cyclopropylidenemethyl)benzene (40 uL, 0.2 mmol) and iodobenzene (39 uL, 0.34 mmol), according to general borocarbonylation I (ring open). The crude residue was purified by flash chromatography (pentane/EA = 20:1, Rf = 0.35) to give the product as a white solid (42.7 mg, 51%).

¹H NMR (300 MHz, CDCl₃) δ 8.06 – 7.95 (m, 2H), 7.58 – 7.51 (m, 1H), 7.48 – 7.41 (m, 2H), 7.35 (d, J = 8.1 Hz, 2H), 7.32 – 7.26 (m, 3H), 3.25 – 3.11 (m, 2H), 2.92 – 2.76 (m, 2H), 1.32 (s, 12H), 1.31 (s, 9H).

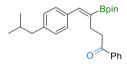
¹³C NMR (75 MHz, CDCl₃) δ 200.2, 150.3, 143.1, 136.9, 134.5, 132.8, 128.8, 128.4, 128.2, 125.2, 83.5, 38.9, 34.5, 31.3, 24.9, 24.8.

¹¹**B NMR (96 MHz, CDCl₃)** δ 30.1.

HRMS (**ESI**): calcd for [M+Na]⁺ C₂₇H₃₅BO₃ 440.2612, found: 440.2613.

IR (ATR): 1684, 1378, 1335, 1319, 1280, 1204, 1139, 1078, 746, 686 cm⁻¹.

Mp: 147-149 ℃



(Z)-5-(4-Isobutylphenyl)-1-phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pent-4-en-1-one (3aa)

The title compound was prepared from 1-(cyclopropylidenemethyl)-4-isobutylbenzene (37.2 mg, 0.2 mmol) and iodobenzene (39 uL, 0.34 mmol), according to general borocarbonylation I (ring open). The crude residue was purified by flash chromatography (pentane/EA = 20:1, Rf = 0.35) to give the product as a colorless oil (46.0 mg, 55%).

¹H NMR (300 MHz, CDCl₃) δ 7.93 – 7.86 (m, 2H), 7.47 – 7.39 (m, 1H), 7.37 – 7.29 (m, 2H), 7.19 – 7.15 (m, 2H), 7.14 (d, J = 1.7 Hz, 1H), 7.02 – 6.96 (m, 2H), 3.11 – 2.99 (m, 2H), 2.83 – 2.63 (m, 2H), 2.34 (d, J = 7.2 Hz, 2H), 1.74 (hept, J = 6.6 Hz, 1H), 1.20 (s, 12H), 0.78 (d, J = 6.6 Hz, 6H).

¹³C NMR (**75 MHz, CDCl₃**) δ 200.1, 143.3, 141.0, 136.9, 134.8, 132.8, 129.0, 128.8, 128.4, 128.2, 83.5, 45.2, 38.8, 30.1, 24.8, 22.4.

¹¹B NMR (96 MHz, CDCl₃) δ 30.3.

HRMS (**ESI**): calcd for [M+Na]⁺ C₂₇H₃₅BO₃ 440.2612, found: 440.2611.

IR (**ATR**): 2953, 1681, 1371, 1346, 1309, 1268, 1141, 688 cm⁻¹.

(Z)-5-(3,5-Dimethoxyphenyl)-1-phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pent-4-en-1-one (3bb)

The title compound was prepared from 1-(cyclopropylidenemethyl)-3,5-dimethoxybenzene (38 uL, 0.2 mmol) and iodobenzene (39 uL, 0.34 mmol), according to general borocarbonylation I (ring open). The crude residue was purified by flash chromatography (pentane/EA = 20:1, Rf = 0.15) to give the product as a yellow oil (73.2 mg, 87%).

¹H NMR (300 MHz, CDCl₃) δ 8.05 – 7.92 (m, 2H), 7.59 – 7.49 (m, 1H), 7.48 – 7.39 (m, 2H), 7.24 (s, 1H), 6.49 (dd, J = 2.3, 0.7 Hz, 2H), 6.37 (t, J = 2.3 Hz, 1H), 3.76 (s, 6H), 3.25 – 3.06 (m, 2H), 2.91 – 2.73 (m, 2H), 1.32 (s, 12H).

¹³C NMR (**75 MHz, CDCl**₃) δ 200.0, 160.5, 143.2, 139.3, 136.8, 132.8, 128.4, 128.2, 106.7, 99.9, 83.6, 55.3, 38.9, 25.1, 24.8.

¹¹**B NMR (128 MHz, CDCl₃)** δ 30.8.

HRMS (**ESI**): calcd for [M+Na]⁺ C₂₅H₃₁BO₅ 444.2198, found: 444.2204.

IR (ATR): 1680, 1588, 1449, 1371, 1290, 1203, 1140, 1060, 967, 832, 747, 686 cm⁻¹.

(Z)-5-(6-Methoxynaphthalen-2-yl)-1-phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pent-4-en-1-one (3cc)

The title compound was prepared from 2-(cyclopropylidenemethyl)-6-methoxynaphthalene (42.0 mg, 0.2 mmol) and iodobenzene (39 uL, 0.34 mmol), according to general borocarbonylation I (ring open). The crude residue was purified by flash chromatography (pentane/EA = 20:1, Rf = 0.15) to give the product as a colorless oil (55.1 mg, 62%).

¹H NMR (400 MHz, CDCl₃) δ 7.99 (dd, J = 8.4, 1.3 Hz, 2H), 7.75 (s, 1H), 7.69 (dd, J = 8.8, 3.8 Hz, 2H), 7.56 – 7.50 (m, 1H), 7.48 – 7.38 (m, 4H), 7.16 – 7.08 (m, 2H), 3.92 (s, 3H), 3.24 – 3.14 (m, 2H), 2.97 – 2.87 (m, 2H), 1.34 (s, 12H).

¹³C NMR (101 MHz, CDCl₃) δ 200.1, 157.9, 143.3, 136.8, 133.7, 132.8, 132.8, 129.8, 128.7, 128.4, 128.2, 128.1, 127.5, 126.6, 118.9, 105.5, 83.5, 55.3, 38.8, 24.9, 24.8.

¹¹B NMR (128 MHz, CDCl₃) δ 30.5.

HRMS (**ESI**): calcd for [M+Na]+ C₂₈H₃₁BO₄ 464.2249, found: 464.2252.

IR (**ATR**): 1680, 1595, 1370, 1352, 1306, 1263, 1140, 849, 687 cm⁻¹.

(Z) - 5 - (4 - Methoxyphenyl) - 1 - phenyl - 4 - (4,4,5,5 - tetramethyl - 1,3,2 - dioxaborolan - 2 - yl) pent - 4 - en - 1 - one (3dd)

The title compound was prepared from 1-(cyclopropylidenemethyl)-4-methoxybenzene (28 uL, 0.2 mmol) and iodobenzene (39 uL, 0.34 mmol), according to general borocarbonylation I (ring open). The crude residue was purified by flash chromatography (pentane/EA = 20:1, Rf = 0.20) to give the product as a white solid (60.6 mg, 77%).

¹H NMR (300 MHz, CDCl₃) δ 8.04 – 7.97 (m, 2H), 7.58 – 7.50 (m, 1H), 7.48 – 7.40 (m, 2H), 7.35 – 7.28 (m, 2H), 7.24 (s, 1H), 6.90 – 6.83 (m, 2H), 3.80 (s, 3H), 3.20 – 3.12 (m, 2H), 2.90 – 2.78 (m, 2H), 1.31 (s, 12H).

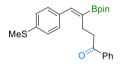
¹³C NMR (75 MHz, CDCl₃) δ 200.1, 158.8, 142.8, 136.9, 132.8, 130.5, 130.1, 128.4, 128.2, 113.7, 83.4, 55.2, 38.8, 24.8, 24.7.

¹¹B NMR (96 MHz, CDCl₃) δ 30.2.

HRMS (EI): calcd for [M] C₂₄H₂₉BO₄ 392.21534, found: 392.21632.

IR (**ATR**): 1681, 1602, 1508, 1347, 1248, 1175, 1140, 688 cm⁻¹.

Mp: 62-63 ℃



(Z)-5-(4-(Methylthio)phenyl)-1-phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pent-4-en-1-one (3ee)

The title compound was prepared from (4-(cyclopropylidenemethyl)phenyl)(methyl)sulfane (35.2 mg, 0.2 mmol) and iodobenzene (39 uL, 0.34 mmol), according to general borocarbonylation I (ring open). The crude residue was purified by flash chromatography (pentane/EA = 20:1, Rf = 0.20) to give the product as a yellow oil (74.5 mg, 91%).

¹H NMR (400 MHz, CDCl₃) δ 8.02 – 7.93 (m, 2H), 7.57 – 7.51 (m, 1H), 7.44 (tt, J = 6.7, 1.4 Hz, 2H), 7.30 – 7.26 (m, 2H), 7.24 (s, 1H), 7.22 – 7.17 (m, 2H), 3.20 – 3.11 (m, 2H), 2.87 – 2.77 (m, 2H), 2.47 (s, 3H), 1.31 (s, 12H).

¹³C NMR (101 MHz, CDCl₃) δ 200.0, 142.5, 137.7, 136.8, 134.1, 132.8, 129.4, 128.4, 128.2, 126.1, 83.5, 38.7, 24.8, 24.7, 15.5.

¹¹B NMR (128 MHz, CDCl₃) δ 30.6.

HRMS (**ESI**): calcd for [M+Na]+ C₂₄H₂₉BO₃S 430.1864, found: 430.1861.

IR (**ATR**): 1685, 1371, 1309, 1140, 1076, 964, 742, 685, 502 cm⁻¹.

(Z)-5-(Benzo[d][1,3]dioxol-5-yl)-1-phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pent-4-en-1-one (3ff)

The title compound was prepared from 5-(cyclopropylidenemethyl)benzo[d][1,3]dioxole (34.8 mg, 0.2 mmol) and iodobenzene (39 uL, 0.34 mmol), according to general borocarbonylation I (ring open). The crude residue was purified by flash chromatography (pentane/EA = 20:1, Rf = 0.20) to give the product as a colorless oil (62.9 mg, 77%).

¹H NMR (300 MHz, CDCl₃) δ 8.06 – 7.93 (m, 2H), 7.60 – 7.51 (m, 1H), 7.48 – 7.40 (m, 2H), 7.20 (s, 1H), 6.89 – 6.73 (m, 3H), 5.94 (s, 2H), 3.23 – 3.06 (m, 2H), 2.87 – 2.75 (m, 2H), 1.30 (s, 12H).

¹³C NMR (75 MHz, CDCl₃) δ 200.0, 147.5, 146.8, 142.8, 136.9, 132.8, 131.6, 128.4, 128.2, 123.1,

109.1, 108.2, 101.0, 83.5, 38.7, 24.8, 24.7.

¹¹**B NMR (96 MHz, CDCl₃)** δ 30.1.

HRMS (**ESI**): calcd for [M+Na]⁺ C₂₄H₂₇BO₅ 428.1885, found: 428.1887.

IR (ATR): 1681, 1487, 1444, 1358, 1307, 1235, 1203, 1141, 1101, 1036, 926, 744, 688 cm⁻¹.

(Z) - 5 - (4 - (dimethylamino)phenyl) - 1 - phenyl - 4 - (4,4,5,5 - tetramethyl - 1,3,2 - dioxaborolan - 2 - yl)pent - 4 - en - 1 - one (3gg)

The title compound was prepared from 4-(cyclopropylidenemethyl)-N,N-dimethylaniline (34.6 mg, 0.2 mmol) and iodobenzene (39 uL, 0.34 mmol), according to general borocarbonylation I (ring open). The crude residue was purified by flash chromatography (pentane/EA = 10:1, Rf = 0.30) to give the product as a yellow oil (32.4 mg, 40%).

¹**H NMR (300 MHz, CDCl₃)** δ 8.13 – 7.96 (m, 2H), 7.61 – 7.49 (m, 1H), 7.49 – 7.41 (m, 2H), 7.36 – 7.30 (m, 2H), 7.20 (s, 1H), 6.68 (d, J = 9.0 Hz, 2H), 3.23 – 3.12 (m, 2H), 2.96 (s, 6H), 2.91 – 2.84 (m, 2H), 1.31 (s, 12H).

¹³C NMR (101 MHz, CDCl₃) δ 200.4, 149.6, 143.3, 137.0, 132.7, 130.6, 128.5, 128.4, 128.3, 111.9, 83.3, 40.3, 38.8, 24.9, 24.8.

¹¹B NMR (128 MHz, CDCl₃) δ 30.6.

HRMS (**ESI**): calcd for [M+Na]⁺ C₂₅H₃₂BNO₃ 427.2408, found: 427.2414.

IR (**ATR**): 1682, 1595, 1519, 1348, 1163, 1141, 946, 815, 747, 689 cm⁻¹.

(Z)-1-Phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-5-(o-tolyl)pent-4-en-1-one (3hh)

The title compound was prepared from 1-(cyclopropylidenemethyl)-2-methylbenzene (32 uL, 0.2 mmol) and iodobenzene (39 uL, 0.34 mmol), according to general borocarbonylation I (ring open). The crude residue was purified by flash chromatography (pentane/EA = 20:1, Rf = 0.33) to give the product as a colorless oil (49.2 mg, 66%).

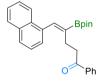
¹H NMR (300 MHz, CDCl₃) δ 7.98 – 7.85 (m, 2H), 7.56 – 7.48 (m, 1H), 7.44 – 7.37 (m, 2H), 7.35 (s, 1H), 7.20 – 7.10 (m, 4H), 3.11 – 2.98 (m, 2H), 2.70 – 2.56 (m, 2H), 2.26 (s, 3H), 1.33 (s, 12H).

¹³C NMR (75 MHz, CDCl₃) δ 200.0, 143.3, 137.0, 136.8, 136.0, 132.7, 129.8, 128.5, 128.4, 128.2, 127.2, 125.4, 83.5, 39.0, 25.0, 24.8, 19.9.

¹¹**B NMR (96 MHz, CDCl₃)** δ 30.3.

HRMS (**ESI**): calcd for [M+Na]⁺ C₂₄H₂₉BO₃ 398.2143, found: 398.2147.

IR (**ATR**): 1683, 1370, 1330, 1312, 1284, 1139, 1080, 744, 684 cm⁻¹.



$(Z)-5-(Naphthalen-1-yl)-1-phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pent-4-en-1-one \\ (3ii)$

The title compound was prepared from 1-(cyclopropylidenemethyl)naphthalene (36.0 mg, 0.2 mmol) and iodobenzene (39 uL, 0.34 mmol), according to general borocarbonylation I (ring open). The crude residue was purified by flash chromatography (pentane/EA = 20:1, Rf = 0.20) to give the product as a colorless oil (32.0 mg, 39%).

¹H NMR (300 MHz, CDCl₃) δ 8.00 – 7.94 (m, 1H), 7.88 – 7.75 (m, 5H), 7.52 – 7.45 (m, 3H), 7.42 (d, J = 8.5 Hz, 1H), 7.37 – 7.30 (m, 3H), 3.11 – 2.97 (m, 2H), 2.71 – 2.54 (m, 2H), 1.37 (s, 12H).

¹³C NMR (75 MHz, CDCl₃) δ 200.0, 142.2, 136.7, 135.0, 133.5, 132.6, 131.5, 128.3, 128.3, 128.1, 127.6, 125.9, 125.8, 125.8, 125.3, 125.2, 83.6, 39.1, 25.4, 24.9.

¹¹**B NMR (96 MHz, CDCl₃)** δ 29.9.

HRMS (**ESI**): calcd for [M+Na]⁺ C₂₇H₂₉BO₃ 434.2143, found: 434.2145.

IR (ATR): 1679, 1370, 1350, 1309, 1263, 1139, 781, 741, 687 cm⁻¹.

(Z)-5-(4-Fuorophenyl)-1-phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pent-4-en-1-one (3jj)

The title compound was prepared from 1-(cyclopropylidenemethyl)-4-fluorobenzene (28 uL, 0.2 mmol) and iodobenzene (39 uL, 0.34 mmol), according to general borocarbonylation I (ring open). The crude residue was purified by flash chromatography (pentane/EA = 20:1, Rf = 0.35) to give the product as a colorless oil (64.1 mg, 84%).

¹H NMR (300 MHz, CDCl₃) δ 8.06 – 7.90 (m, 2H), 7.59 – 7.51 (m, 1H), 7.49 – 7.40 (m, 2H), 7.34 – 7.24 (m, 3H), 7.07 – 6.95 (m, 2H), 3.25 – 3.08 (m, 2H), 2.79 (dd, J = 8.8, 6.4 Hz, 2H), 1.31 (s, 12H). ¹³C NMR (75 MHz, CDCl₃) δ 199.9, 161.9 (d, J = 247.1 Hz), 142.0, 136.8, 133.5 (d, J = 3.3 Hz), 132.9, 130.6 (d, J = 8.1 Hz), 128.5, 128.2, 115.2 (d, J = 21.2 Hz), 83.6, 38.6, 24.8, 24.6.

¹¹B NMR (128 MHz, CDCl₃) δ 30.5.

¹⁹F NMR (282 MHz, CDCl₃) δ -114.31 (ddd, J = 14.5, 9.2, 5.3 Hz).

HRMS (**ESI**): calcd for [M+Na]+ C₂₃H₂₆BFO₃ 402.1892, found: 402.1896.

IR (**ATR**): 1686, 1505, 1344, 1312, 1203, 1140, 1024, 742, 687, 524 cm⁻¹.

$(Z)-5-(3-Fluorophenyl)-1-phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pent-4-en-1-one \\ (3kk)$

The title compound was prepared from 1-(cyclopropylidenemethyl)-3-fluorobenzene (28 uL, 0.2 mmol) and iodobenzene (39 uL, 0.34 mmol), according to general borocarbonylation I (ring open). The crude residue was purified by flash chromatography (pentane/EA = 20:1, Rf = 0.35) to give the product as a colorless oil (53.5 mg, 70%).

¹H NMR (300 MHz, CDCl₃) δ 7.85 – 7.70 (m, 2H), 7.39 – 7.30 (m, 1H), 7.24 (ddt, J = 8.3, 6.8, 1.2 Hz, 2H), 7.13 – 7.03 (m, 2H), 6.90 (ddd, J = 8.4, 1.7, 0.9 Hz, 1H), 6.85 – 6.78 (m, 1H), 6.77 – 6.69 (m, 1H), 3.00 – 2.91 (m, 2H), 2.65 – 2.55 (m, 2H), 1.12 (s, 12H).

¹³C NMR (75 MHz, CDCl₃) δ 199.8, 162.63 (d, J = 245.4 Hz), 141.8 (d, J = 2.4 Hz), 139.7 (d, J = 7.4 Hz), 136.8, 132.8, 129.7 (d, J = 8.4 Hz), 128.5, 128.2, 124.5 (d, J = 2.7 Hz), 115.6 (d, J = 21.5 Hz), 114.1 (d, J = 21.2 Hz), 83.7, 38.6, 24.8, 24.7.

¹¹B NMR (96 MHz, CDCl₃) δ 30.0.

HRMS (ESI): calcd for [M+Na]+ C₂₃H₂₆BFO₃ 402.1892, found: 402.1901.

IR (**ATR**): 2976, 1682, 1579, 1371, 1341, 1313, 1270, 1248, 1204, 1139, 1081, 964, 784, 743, 687 cm⁻¹.

(Z) - 1 - Phenyl - 4 - (4,4,5,5 - tetramethyl - 1,3,2 - dioxaborolan - 2 - yl) - 5 - (2,4,5 - trifluorophenyl) pent - 4 - en - 1 - one (3ll)

The title compound was prepared from 1-(cyclopropylidenemethyl)-2,4,5-trifluorobenzene (36.8 mg, 0.2 mmol) and iodobenzene (39 uL, 0.34 mmol), according to general borocarbonylation I (ring open). The crude residue was purified by flash chromatography (pentane/EA = 20:1, Rf = 0.35) to give the product as a colorless oil (58.0 mg, 70%).

¹H NMR (400 MHz, CDCl₃) δ 7.99 – 7.93 (m, 2H), 7.57 – 7.52 (m, 1H), 7.47 – 7.41 (m, 2H), 7.16 – 7.05 (m, 2H), 6.90 (ddd, J = 10.3, 9.1, 6.7 Hz, 1H), 3.18 – 3.10 (m, 2H), 2.71 – 2.60 (m, 2H), 1.31 (s, 12H).

¹³C NMR (101 MHz, CDCl₃) δ 199.7, 154.9 (ddd, J = 246.7, 9.4, 2.0 Hz), 149.4 (ddd, J = 251.8, 14.4, 12.6 Hz), 146.4 (ddd, J = 245.0, 12.5, 3.9 Hz), 136.8, 133.8, 132.9, 128.5, 128.1, 121.5 (d, J = 18.0 Hz), 117.9 (dd, J = 19.3, 4.9 Hz), 105.6 (dd, J = 28.7, 20.6 Hz), 83.9, 38.1, 25.2, 24.8.

¹¹B NMR (128 MHz, CDCl₃) δ 30.5.

HRMS (**ESI**): calcd for [M+Na]⁺ C₂₃H₂₄BF₃O₃ 438.1704, found: 438.1712.

IR (**ATR**): 1683, 1504, 1372, 1312, 1268, 1200, 1141, 1078, 843, 744, 688 cm⁻¹.

(Z) - 1 - Phenyl - 4 - (4,4,5,5 - tetramethyl - 1,3,2 - dioxaborolan - 2 - yl) - 5 - (4 - (trifluoromethyl)phenyl)pent - 4 - en - 1 - one (3mm)

The title compound was prepared from 1-(cyclopropylidenemethyl)-4-(trifluoromethyl)benzene (35 uL, 0.2 mmol) and iodobenzene (39 uL, 0.34 mmol), according to general borocarbonylation I (ring open). The crude residue was purified by flash chromatography (pentane/EA = 20:1, Rf = 0.35) to give the product as a colorless oil (54.0 mg, 63%).

¹**H NMR (400 MHz, CDCl₃)** δ 7.99 – 7.93 (m, 2H), 7.60 – 7.52 (m, 3H), 7.46 – 7.39 (m, 4H), 7.31 (s, 1H), 3.20 – 3.10 (m, 2H), 2.86 – 2.75 (m, 2H), 1.32 (s, 12H).

¹³C NMR (101 MHz, CDCl₃) δ 199.7, 141.6, 141.0, 136.7, 132.9, 129.1 (q, J = 32.3 Hz), 129.0, 128.5, 128.1, 125.2 (q, J = 4.0 Hz), 124.1 (q, J = 272.0 Hz), 83.8, 38.5, 24.8, 24.7.

¹¹**B NMR (128 MHz, CDCl₃)** δ 30.6.

¹⁹F NMR (376 MHz, CDCl₃) δ -62.5.

HRMS (EI): calcd for [M] C₂₄H₂₆BF₃O₃ 430.19216, found: 430.19251.

IR (**ATR**): 1683, 1372, 1320, 1268, 1163, 1141, 1121, 1065, 1016, 962, 833, 743, 688, 596 cm⁻¹.

(Z)-1-Phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-5-(4-

((trifluoromethyl)thio)phenyl)pent-4-en-1-one (3nn)

The title compound was prepared from (4-(cyclopropylidenemethyl)phenyl)(trifluoromethyl)sulfane (46.0 mg, 0.2 mmol) and iodobenzene (39 uL, 0.34 mmol), according to general borocarbonylation I (ring open). The crude residue was purified by flash chromatography (pentane/EA = <math>20:1, Rf = 0.35) to give the product as a colorless oil (60.1 mg, 65%).

¹H NMR (400 MHz, CDCl₃) δ 8.00 – 7.94 (m, 2H), 7.60 (d, J = 8.2 Hz, 2H), 7.57 – 7.52 (m, 1H), 7.44 (tt, J = 7.7, 1.8 Hz, 2H), 7.38 – 7.33 (m, 2H), 7.28 (s, 1H), 3.20 – 3.12 (m, 2H), 2.80 (dd, J = 8.9, 7.0 Hz, 2H), 1.32 (s, 12H).

¹³C NMR (101 MHz, CDCl₃) δ 199.7, 141.5, 140.1, 136.7, 136.1, 132.9, 129.8, 129.5 (q, J = 308.3 Hz), 128.5, 128.1, 122.9 (q, J = 2.2 Hz), 83.8, 38.5, 24.8, 24.7.

¹¹B NMR (128 MHz, CDCl₃) δ 30.8.

¹⁹F NMR (376 MHz, CDCl₃) δ -42.6.

HRMS (**EI**): calcd for [M] C₂₄H₂₆BF₃O₃S 462.16423, found: 462.16553.

IR (**ATR**): 1683, 1372, 1342, 1314, 1266, 1112, 1083, 962, 744, 688 cm⁻¹.

(Z)-5-(4-Chlorophenyl)-1-phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pent-4-en-1-one (300)

The title compound was prepared from 1-chloro-4-(cyclopropylidenemethyl)benzene (32.8 mg, 0.2 mmol) and iodobenzene (39 uL, 0.34 mmol), according to general borocarbonylation I (ring open). The crude residue was purified by flash chromatography (pentane/EA = 20:1, Rf = 0.35) to give the product as a colorless oil (58.4 mg, 74%).

¹H NMR (300 MHz, CDCl₃) δ 7.90 – 7.75 (m, 2H), 7.44 – 7.37 (m, 1H), 7.33 – 7.26 (m, 2H), 7.17 – 7.08 (m, 5H), 3.05 – 2.92 (m, 2H), 2.71 – 2.58 (m, 2H), 1.16 (s, 12H).

¹³C NMR (75 MHz, CDCl₃) δ 199.8, 141.8, 136.8, 135.8, 133.1, 132.9, 130.2, 128.5, 128.4, 128.2, 83.7, 38.6, 24.8, 24.6.

¹¹B NMR (96 MHz, CDCl₃) δ 30.2.

HRMS (**ESI**): calcd for [M+Na]⁺ C₂₃H₂₆BClO₃ 418.1597, found: 418.1600.

IR (ATR): 2974, 1683, 1370, 1339, 1314, 1281, 1137, 1091, 1076, 812, 746, 686, 501 cm⁻¹.

(Z) - 4 - (5 - Oxo - 5 - phenyl - 2 - (4,4,5,5 - tetramethyl - 1,3,2 - dioxaborolan - 2 - yl) pent - 1 - en - 1 - yl) benzonitrile (3pp)

The title compound was prepared from 4-(cyclopropylidenemethyl)benzonitrile (31.0 mg, 0.2 mmol) and iodobenzene (39 uL, 0.34 mmol), according to general borocarbonylation I (ring open). The crude residue was purified by flash chromatography (pentane/EA = 10:1, Rf = 0.20) to give the product as a white solid (37.4 mg, 48%).

¹H NMR (300 MHz, CDCl₃) δ 8.04 – 7.89 (m, 2H), 7.64 – 7.57 (m, 2H), 7.57 – 7.51 (m, 1H), 7.47 – 7.37 (m, 4H), 7.26 (d, J = 1.7 Hz, 1H), 3.21 - 3.07 (m, 2H), 2.83 - 2.71 (m, 2H), 1.31 (s, 12H).

¹³C NMR (**75 MHz, CDCl**₃) δ 199.5, 142.1, 141.0, 136.7, 133.0, 132.0, 129.4, 128.5, 128.1, 118.9, 110.7, 83.9, 38.3, 24.8, 24.7.

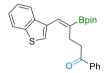
¹¹**B NMR (96 MHz, CDCl₃)** δ 30.0.

¹⁹**F NMR (376 MHz, CDCl₃)** δ -115.16 (ddt, J = 15.0, 10.9, 4.8 Hz), -134.23 (dtd, J = 22.5, 9.5, 4.4 Hz), -142.80 (dddd, J = 21.8, 14.3, 10.9, 6.8 Hz).

HRMS (**ESI**): calcd for [M+H]⁺ C₂₄H₂₆BNO₃ 387.2120, found: 387.2122.

IR (**ATR**): 2222, 1678, 1088, 853, 745, 688, 553 cm⁻¹.

decomposition: 177 °C



(Z)-5-(Benzo[b]thiophen-3-yl)-1-phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pent-4-en-1-one (3qq)

The title compound was prepared from 3-(cyclopropylidenemethyl)benzo[b]thiophene (37.2 mg, 0.2 mmol) and iodobenzene (39 uL, 0.34 mmol), according to general borocarbonylation I (ring open). The crude residue was purified by flash chromatography (pentane/EA = 20:1, Rf = 0.20) to give the product as a colorless oil (76.1 mg, 90%).

¹H NMR (400 MHz, CDCl₃) δ 7.96 (dd, J = 8.4, 1.3 Hz, 2H), 7.90 – 7.81 (m, 2H), 7.57 – 7.51 (m, 1H), 7.48 (d, J = 3.1 Hz, 2H), 7.45 – 7.33 (m, 4H), 3.29 – 3.09 (m, 2H), 2.97 – 2.79 (m, 2H), 1.34 (s, 12H).

¹³C NMR (101 MHz, CDCl₃) δ 200.0, 139.5, 139.0, 136.8, 134.8, 132.8, 132.5, 128.4, 128.2, 124.6, 124.4, 124.1, 122.5, 122.3, 83.6, 38.6, 25.8, 24.8.

¹¹**B NMR (128 MHz, CDCl₃)** δ 30.9.

HRMS (**ESI**): calcd for [M+Na]⁺ C₂₅H₂₇BO₃S 440.1707, found: 440.1707.

IR (**ATR**): 1687, 1355, 1315, 1136, 760, 744, 732, 688, 678, 667 cm⁻¹.

(*Z*)-1-Phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-5-(1-tosyl-1H-pyrrol-3-yl)pent-4-en-1-one (3rr)

The title compound was prepared from 3-(cyclopropylidenemethyl)-1-tosyl-1H-pyrrole (54.6 mg, 0.2 mmol) and iodobenzene (39 uL, 0.34 mmol), according to general borocarbonylation I (ring open). The crude residue was purified by flash chromatography (pentane/EA = 10:1, Rf = 0.30) to give the product as a yellow oil (94.8 mg, 94%).

¹H NMR (300 MHz, CDCl₃) δ 8.00 – 7.87 (m, 2H), 7.80 – 7.66 (m, 2H), 7.60 – 7.48 (m, 2H), 7.48 – 7.36 (m, 3H), 7.23 (dd, J = 8.7, 0.7 Hz, 2H), 6.43 – 6.31 (m, 1H), 6.25 (td, J = 3.4, 0.6 Hz, 1H), 2.99 – 2.88 (m, 2H), 2.66 – 2.54 (m, 2H), 2.35 (s, 3H), 1.31 (s, 12H).

¹³C NMR (75 MHz, CDCl₃) δ 199.8, 144.9, 136.7, 135.8, 132.8, 130.9, 130.6, 129.6, 128.4, 128.1, 127.5, 123.1, 116.2, 111.8, 83.5, 37.8, 25.0, 24.8, 21.6.

¹¹B NMR (96 MHz, CDCl₃) δ 30.6.

HRMS (EI): calcd for [M] C₂₈H₃₂BNO₅S 505.20888, found: 505.20969.

IR (ATR): 1681, 1596, 1348, 1172, 1141, 1088, 733, 689, 669, 586, 542 cm⁻¹.

1,2-Diphenyl-2-(1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclopropyl)ethan-1-one (4a)

The title compound was prepared from (cyclopropylidenemethyl)benzene (27 uL, 0.2 mmol) and iodobenzene (34 uL, 0.3 mmol), according to general borocarbonylation II (ring close). The crude residue was purified by flash chromatography (pentane/EA = 20:1, Rf = 0.36) to give the product as a white solid (44.9 mg, 62%). X-ray (single-crystal) colorless block crystals of X-ray diffraction quality were obtained by slow evaporation of saturated solution of **4a** in ethyl acetate/*n*-pentane (CCDC 2122869).

¹H NMR (300 MHz, CDCl₃) δ 7.77 – 7.69 (m, 2H), 7.31 – 7.24 (m, 1H), 7.21 – 7.14 (m, 2H), 7.13 – 7.08 (m, 2H), 7.04 (tt, J = 8.0, 1.7 Hz, 3H), 4.78 (s, 1H), 1.07 (s, 6H), 1.01 (s, 6H), 0.74 (ddd, J = 8.8, 5.9, 4.1 Hz, 1H), 0.40 (ddd, J = 8.8, 5.7, 3.7 Hz, 1H), 0.28 – 0.20 (m, 1H), 0.06 – -0.05 (m, 1H).

¹³C NMR (75 MHz, CDCl₃) δ 200.6, 137.3, 136.1, 132.1, 130.1, 128.7, 128.2, 128.1, 126.9, 83.1, 56.0, 24.7, 24.1, 6.5, 6.3.

¹¹B NMR (96 MHz, CDCl₃) δ 33.3.

HRMS (**EI**): calcd for [M] C₂₃H₂₇BO₃ 362.20478, found: 362.20569.

IR (ATR): 2977, 1677, 1409, 1314, 1244, 1219, 1135, 961, 845, 749, 710, 695, 684, 627 cm⁻¹.

Mp: 101-102 °C

1-(3,4-Dimethylphenyl)-2-phenyl-2-(1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclopropyl)ethan-1-one (4b)

The title compound was prepared from (cyclopropylidenemethyl)benzene (27 uL, 0.2 mmol) and 4-iodo-1,2-dimethylbenzene (42 uL, 0.3 mmol), according to general borocarbonylation II (ring close). The crude residue was purified by flash chromatography (pentane/EA = 20:1, Rf = 0.33) to give the product as a white solid (44.3 mg, 57%).

¹H NMR (300 MHz, CDCl₃) δ 7.66 (d, J = 1.9 Hz, 1H), 7.57 (dd, J = 8.0, 1.8 Hz, 1H), 7.26 – 7.19 (m, 2H), 7.19 – 7.11 (m, 3H), 7.04 (d, J = 8.0 Hz, 1H), 4.86 (s, 1H), 2.22 (s, 6H), 1.19 (s, 6H), 1.14 (s, 6H), 0.84 (ddd, J = 8.8, 5.9, 4.1 Hz, 1H), 0.51 (ddd, J = 8.8, 5.6, 3.7 Hz, 1H), 0.39 – 0.28 (m, 1H), 0.18 – 0.06 (m, 1H).

¹³C NMR (75 MHz, CDCl₃) δ 200.3, 141.5, 136.6, 136.4, 135.1, 130.1, 130.0, 129.4, 128.2, 126.8, 126.6, 83.1, 56.0, 24.7, 24.2, 19.9, 19.7, 6.6, 6.4.

¹¹**B NMR (96 MHz, CDCl₃)** δ 32.9.

HRMS (EI): calcd for [M] C₂₅H₃₁BO₃ 390.23608, found: 390.23642.

IR (**ATR**): 1671, 1406, 1316, 1241, 1134, 977, 965, 864, 704, 670 cm⁻¹.

Mp: 107-109 ℃

$2- Phenyl-2-(1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl) cyclopropyl)-1-(\textit{m-tolyl}) ethan-1-one \\ (4c)$

The title compound was prepared from (cyclopropylidenemethyl)benzene (27 uL, 0.2 mmol) and 1-iodo-3-methylbenzene (39 uL, 0.3 mmol), according to general borocarbonylation II (ring close). The crude residue was purified by flash chromatography (pentane/EA = 20:1, Rf = 0.36) to give the product as a white solid (53.7 mg, 71%).

¹H NMR (300 MHz, CDCl₃) δ 7.68 (ddt, J = 1.8, 1.4, 0.7 Hz, 1H), 7.66 – 7.58 (m, 1H), 7.27 – 7.11 (m, 7H), 4.87 (s, 1H), 2.31 (d, J = 0.6 Hz, 3H), 1.19 (s, 6H), 1.14 (s, 6H), 0.84 (ddd, J = 8.9, 5.9, 4.2 Hz, 1H), 0.51 (ddd, J = 8.8, 5.6, 3.7 Hz, 1H), 0.40 – 0.28 (m, 1H), 0.17 – 0.07 (m, 1H).

¹³C NMR (75 MHz, CDCl₃) δ 200.8, 137.8, 137.4, 136.3, 132.9, 130.1, 129.3, 128.2, 128.0, 126.9, 126.1, 83.2, 56.1, 24.8, 24.2, 21.3, 6.6, 6.4.

¹¹**B NMR (96 MHz, CDCl₃)** δ 33.0.

HRMS (EI): calcd for [M] C₂₄H₂₉BO₃ 376.22043, found: 376.22110.

IR (**ATR**): 2964, 2922, 1674, 1408, 1313, 1250, 1156, 1136, 964, 703, 679 cm⁻¹.

Mp: 100-101 °C

1-(4-(*tert*-Butyl)phenyl)-2-phenyl-2-(1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-vl)cyclopropyl)ethan-1-one (4d)

The title compound was prepared from (cyclopropylidenemethyl)benzene (27 uL, 0.2 mmol) and 1-(tert-butyl)-4-iodobenzene (53 uL, 0.3 mmol), according to general borocarbonylation II (ring close). The crude residue was purified by flash chromatography (pentane/EA = 20:1, Rf = 0.40) to give the product as a white solid (57.0 mg, 68%).

¹H NMR (400 MHz, CDCl₃) δ 7.84 – 7.74 (m, 2H), 7.34 – 7.29 (m, 2H), 7.27 – 7.21 (m, 2H), 7.20 – 7.12 (m, 3H), 4.84 (s, 1H), 1.27 (s, 9H), 1.19 (s, 6H), 1.13 (s, 6H), 0.83 (ddd, J = 8.8, 5.9, 4.2 Hz, 1H), 0.57 – 0.46 (m, 1H), 0.37 – 0.29 (m, 1H), 0.17 – 0.08 (m, 1H).

¹³C NMR (101 MHz, CDCl₃) δ 200.1, 155.6, 136.6, 134.6, 130.1, 128.8, 128.2, 126.8, 125.1, 83.1, 56.2, 34.9, 31.0, 24.7, 24.2, 6.6, 6.3.

¹¹**B NMR (128 MHz, CDCl₃)** δ 33.4.

HRMS (EI): calcd for [M] C₂₇H₃₅BO₃ 418.26738, found: 418.26713.

IR (**ATR**): 2961, 1689, 1410, 1326, 1138, 971, 962, 705, 669, 556 cm⁻¹.

Mp: 129-131 ℃

$1\hbox{-}(4\hbox{-}Methoxyphenyl)\hbox{-}2\hbox{-}phenyl\hbox{-}2\hbox{-}(1\hbox{-}(4,4,5,5\hbox{-}tetramethyl\hbox{-}1,3,2\hbox{-}dioxaborolan-2-dio$

yl)cyclopropyl)ethan-1-one (4e)

The title compound was prepared from (cyclopropylidenemethyl)benzene (27 uL, 0.2 mmol) and 1-iodo-4-methoxybenzene (70.2 mg, 0.3 mmol), according to general borocarbonylation II (ring close). The crude residue was purified by flash chromatography (pentane/EA = 15:1, Rf = 0.31) to give the product as a white solid (51.9 mg, 66%).

¹H NMR (300 MHz, CDCl₃) δ 7.87 – 7.80 (m, 2H), 7.26 – 7.20 (m, 2H), 7.20 – 7.10 (m, 3H), 6.84 – 6.72 (m, 2H), 4.83 (s, 1H), 3.79 (s, 3H), 1.19 (s, 6H), 1.13 (s, 6H), 0.83 (ddd, J = 8.8, 5.9, 4.1 Hz, 1H), 0.58 – 0.44 (m, 1H), 0.40 – 0.25 (m, 1H), 0.18 – 0.02 (m, 1H).

¹³C NMR (**75 MHz, CDCl**₃) δ 199.0, 162.7, 136.7, 131.1, 130.2, 130.1, 128.2, 126.8, 113.3, 83.1, 55.9, 55.3, 24.8, 24.1, 6.5, 6.3.

¹¹**B NMR (96 MHz, CDCl₃)** δ 30.3.

HRMS (EI): calcd for [M] C₂₄H₂₉BO₄ 392.21534, found: 392.21566.

IR (**ATR**): 1668, 1602, 1406, 1307, 1250, 1176, 1134, 1029, 709 cm⁻¹.

Mp: 113-114 ℃

1-(4-(Benzyloxy)phenyl)-2-phenyl-2-(1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclopropyl)ethan-1-one (4f)

The title compound was prepared from (cyclopropylidenemethyl)benzene (27 uL, 0.2 mmol) and 1-(benzyloxy)-4-iodobenzene (34 uL, 0.3 mmol), according to general borocarbonylation III (ring close). The crude residue was purified by flash chromatography (pentane/EA = 10:1, Rf = 0.20) to give the product as a colorless oil (58.9 mg, 82%).

¹H NMR (300 MHz, CDCl₃) δ 7.93 – 7.86 (m, 2H), 7.44 – 7.25 (m, 10H), 6.98 – 6.89 (m, 2H), 5.10 (s, 2H), 4.29 (d, J = 1.0 Hz, 1H), 4.20 (s, 1H), 1.01 – 0.92 (m, 1H), 0.89 – 0.79 (m, 1H), 0.72 – 0.62 (m, 1H), 0.54 (ddd, J = 10.6, 6.8, 5.2 Hz, 1H).

¹³C NMR (75 MHz, CDCl₃) δ 200.4, 162.8, 136.8, 136.0, 131.3, 129.2, 128.9, 128.8, 128.7, 128.3, 127.4, 127.4, 114.6, 70.1, 59.1, 57.3, 13.3, 11.4.

HRMS (EI): calcd for [M] C₂₄H₂₂O₃ 358.15635, found: 358.15654.

IR (**ATR**): 1657, 1595, 1250, 1217, 1164, 1010, 728, 696, 647, 513 cm⁻¹.

2-Phenyl-2-(1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclopropyl)-1-(4-(trifluoromethoxy)phenyl)ethan-1-one (4g)

The title compound was prepared from (cyclopropylidenemethyl)benzene (27 uL, 0.2 mmol) and 1-iodo-4-(trifluoromethoxy)benzene (45 uL, 0.3 mmol), according to general borocarbonylation II (ring close). The crude residue was purified by flash chromatography (pentane/EA = 20:1, Rf = 0.41) to give the product as a colorless solid (58.2 mg, 65%).

¹**H NMR** (300 MHz, CDCl₃) δ 7.93 – 7.84 (m, 2H), 7.30 – 7.17 (m, 3H), 7.16 – 7.07 (m, 4H), 4.86 (s, 1H), 1.19 (s, 6H), 1.13 (s, 6H), 0.87 (ddd, J = 8.9, 5.9, 4.2 Hz, 1H), 0.50 (ddd, J = 9.4, 5.7, 3.8 Hz, 1H), 0.41 – 0.28 (m, 1H), 0.15 – 0.03 (m, 1H).

¹³C NMR (75 MHz, CDCl₃) δ 199.2, 151.8, 135.6, 135.5, 130.7, 130.1, 128.4, 127.2, 120.2 (q, J = 258.5 Hz), 120.0, 83.3, 56.1, 24.8, 24.1, 6.5, 6.2.

¹¹B NMR (96 MHz, CDCl₃) δ 33.8.

¹⁹F NMR (282 MHz, CDCl₃) δ -57.6.

HRMS (EI): calcd for [M] C₂₄H₂₆BF₃O₄ 446.18708, found: 446.18792.

IR (ATR): 1680, 1410, 1321, 1256, 1210, 1168, 1133, 972, 961, 874, 841, 705, 671 cm⁻¹.

Mp: 122-124 ℃

2-Phenyl-2-(1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclopropyl)-1-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)ethan-1-one (4h)

The title compound was prepared from (cyclopropylidenemethyl)benzene (27 uL, 0.2 mmol) and 2-(4-iodophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (98.1 mg, 0.3 mmol), according to general borocarbonylation II (ring close). The crude residue was purified by flash chromatography (pentane/EA = 20:1, Rf = 0.20) to give the product as a white solid (45.8 mg, 47%).

¹H NMR (300 MHz, CDCl₃) δ 7.85 – 7.79 (m, 2H), 7.77 – 7.72 (m, 2H), 7.25 – 7.08 (m, 5H), 4.90 (s, 1H), 1.31 (s, 12H), 1.19 (s, 6H), 1.12 (s, 6H), 0.85 (ddd, J = 8.8, 5.9, 4.2 Hz, 1H), 0.50 (ddd, J = 8.9, 5.6, 3.7 Hz, 1H), 0.39 – 0.28 (m, 1H), 0.15 – 0.05 (m, 1H).

¹³C NMR (75 MHz, CDCl₃) δ 200.9, 139.3, 135.9, 134.5, 130.2, 128.2, 127.8, 126.9, 84.0, 83.2, 56.1, 24.8, 24.8, 24.8, 24.1, 6.5, 6.3.

¹¹B NMR (96 MHz, CDCl₃) δ 30.0.

HRMS (EI): calcd for [M] $C_{29}H_{38}B_2O_5$ 487.29362, found: 487.29403.

IR (ATR): 2980, 1678, 1398, 1380, 1362, 1315, 1133, 1092, 960, 708, 651 cm⁻¹.

Mp: 182-184 °C



1-(Naphthalen-1-yl)-2-phenyl-2-(1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclopropyl)ethan-1-one~(4i)

The title compound was prepared from (cyclopropylidenemethyl)benzene (27 uL, 0.2 mmol) and 1-iodonaphthalene (44 uL, 0.3 mmol), according to general borocarbonylation II (ring close). The crude residue was purified by flash chromatography (pentane/EA = 20:1, Rf = 0.36) to give the product as a colorless oil (38.8 mg, 47%).

¹H NMR (300 MHz, CDCl₃) δ 8.63 (ddt, J = 8.5, 1.5, 0.8 Hz, 1H), 7.86 – 7.76 (m, 3H), 7.54 (ddd, J = 8.5, 6.8, 1.6 Hz, 1H), 7.47 (ddd, J = 8.1, 6.8, 1.4 Hz, 1H), 7.38 – 7.31 (m, 1H), 7.23 – 7.08 (m, 5H), 4.95 (s, 1H), 1.23 (s, 6H), 1.15 (s, 6H), 0.98 – 0.90 (m, 1H), 0.62 – 0.46 (m, 2H), 0.18 – 0.07 (m, 1H).

¹³C NMR (75 MHz, CDCl₃) δ 204.5, 137.0, 135.8, 133.8, 131.6, 130.6, 130.2, 128.1, 127.4, 127.3, 126.9, 126.1, 126.1, 124.2, 83.3, 59.0, 24.8, 24.3, 7.1, 6.9.

¹¹**B NMR (96 MHz, CDCl₃)** δ 33.2.

HRMS (EI): calcd for [M] C₂₇H₂₉BO₃ 412.22043, found: 412.22118.

IR (**ATR**): 2975, 1669, 1449, 1405, 1388, 1371, 1316, 1226, 1132, 848, 777, 704, 671 cm⁻¹.

$1\hbox{-}(4\hbox{-}Chlorophenyl)\hbox{-}2\hbox{-}phenyl\hbox{-}2\hbox{-}(1\hbox{-}(4,4,5,5\hbox{-}tetramethyl\hbox{-}1,3,2\hbox{-}dioxaborolan-2-diox$

yl)cyclopropyl)ethan-1-one (4j)

The title compound was prepared from (cyclopropylidenemethyl)benzene (27 uL, 0.2 mmol) and 1-chloro-4-iodobenzene (71.4 mg, 0.3 mmol), according to general borocarbonylation II (ring close). The crude residue was purified by flash chromatography (pentane/EA = 20:1, Rf = 0.41) to give the product as a white solid (40.4 mg, 51%).

¹H NMR (400 MHz, CDCl₃) δ 7.83 – 7.75 (m, 2H), 7.32 – 7.16 (m, 5H), 7.13 – 7.07 (m, 2H), 4.85 (s, 1H), 1.19 (s, 6H), 1.13 (s, 6H), 0.86 (ddd, J = 8.8, 6.0, 4.3 Hz, 1H), 0.55 – 0.46 (m, 1H), 0.37 – 0.30 (m, 1H), 0.13 – 0.04 (m, 1H).

¹³C NMR (101 MHz, CDCl₃) δ 199.4, 138.5, 135.6, 135.6, 130.2, 130.1, 128.5, 128.4, 127.1, 83.2, 56.0, 24.8, 24.1, 6.5, 6.2.

¹¹B NMR (128 MHz, CDCl₃) δ 33.3.

HRMS (**EI**): calcd for [M] C₂₃H₂₆BClO₃ 396.16580, found: 396.16635.

IR (**ATR**): 1674, 1408, 1318, 1245, 1135, 1094, 961, 707, 676 cm⁻¹.

Mp: 132-134 °C

1-(4-Bromophenyl)-2-phenyl-2-(1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-

yl)cyclopropyl)ethan-1-one (4k)

The title compound was prepared from (cyclopropylidenemethyl)benzene (27 uL, 0.2 mmol) and 1-bromo-4-iodobenzene (84.5 mg, 0.3 mmol), according to general borocarbonylation II (ring close). The crude residue was purified by flash chromatography (pentane/EA = 20:1, Rf = 0.38) to give the product as a white solid (51.9 mg, 59%).

¹H NMR (300 MHz, CDCl₃) δ 7.73 – 7.67 (m, 2H), 7.49 – 7.39 (m, 2H), 7.29 – 7.15 (m, 3H), 7.13 – 7.06 (m, 2H), 4.84 (s, 1H), 1.19 (s, 6H), 1.12 (s, 6H), 0.86 (ddd, J = 8.8, 5.9, 4.2 Hz, 1H), 0.59 – 0.41 (m, 1H), 0.38 – 0.28 (m, 1H), 0.13 – 0.03 (m, 1H).

¹³C NMR (75 MHz, CDCl₃) δ 199.6, 136.0, 135.6, 131.5, 130.4, 130.1, 128.4, 127.2, 127.1, 83.3, 56.0, 24.8, 24.1, 6.5, 6.2.

¹¹**B NMR (96 MHz, CDCl₃)** δ 33.2.

HRMS (**EI**): calcd for [M] C₂₃H₂₆BBrO₃ 441.11687, found: 441.11713.

IR (**ATR**): 1675, 1407, 1318, 1245, 1135, 962, 751, 708 cm⁻¹.

Mp: 139-141 ℃

1-(3,4-Dichlorophenyl)-2-phenyl-2-(1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclopropyl)ethan-1-one~(4l)

The title compound was prepared from (cyclopropylidenemethyl)benzene (27 uL, 0.2 mmol) and 1,2-dichloro-4-iodobenzene (81.9 uL, 0.3 mmol), according to general borocarbonylation II (ring close). The crude residue was purified by flash chromatography (pentane/EA = 20:1, Rf = 0.41) to give the product as a colorless oil (38.7 mg, 45%).

¹H NMR (300 MHz, CDCl₃) δ 7.97 (d, J = 2.0 Hz, 1H), 7.65 (dd, J = 8.4, 2.1 Hz, 1H), 7.40 (d, J = 8.3 Hz, 1H), 7.34 – 7.19 (m, 3H), 7.11 (dd, J = 7.9, 1.7 Hz, 2H), 4.85 (s, 1H), 1.22 (s, 6H), 1.15 (s, 6H), 0.89 (ddd, J = 8.8, 5.9, 4.2 Hz, 1H), 0.59 – 0.44 (m, 1H), 0.42 – 0.31 (m, 1H), 0.09 (ddd, J = 8.7, 5.9, 3.8 Hz, 1H).

¹³C NMR (75 MHz, CDCl₃) δ 198.5, 136.9, 136.6, 135.1, 132.8, 130.7, 130.3, 130.1, 128.5, 127.8, 127.3, 83.4, 56.0, 24.8, 24.1, 6.5, 6.2.

¹¹B NMR (96 MHz, CDCl₃) δ 33.6.

HRMS (**EI**): calcd for [M] C₂₃H₂₅BCl₂O₃ 432.12388, found: 432.12456.

IR (ATR): 1680, 1406, 1318, 1205, 1134, 979, 965, 847, 733, 704, 668 cm⁻¹.

2-Phenyl-2-(1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclopropyl)-1-(3-(trifluoromethyl)phenyl)ethan-1-one (4m)

The title compound was prepared from (cyclopropylidenemethyl)benzene (27 uL, 0.2 mmol) and 1-iodo-3-(trifluoromethyl)benzene (43 uL, 0.3 mmol), according to general borocarbonylation II (ring close). The crude residue was purified by flash chromatography (pentane/EA = 20:1, Rf = 0.37) to give the product as a colorless oil (52.8 mg, 61%).

¹H NMR (300 MHz, CDCl₃) δ 8.13 (dt, J = 1.8, 1.1 Hz, 1H), 7.97 (dddd, J = 7.9, 1.7, 1.1, 0.6 Hz, 1H), 7.66 (dddd, J = 7.8, 1.9, 1.2, 0.6 Hz, 1H), 7.43 (tt, J = 7.9, 0.7 Hz, 1H), 7.30 – 7.16 (m, 3H), 7.15 – 7.09 (m, 2H), 4.89 (s, 1H), 1.19 (s, 6H), 1.13 (s, 6H), 0.88 (ddd, J = 8.8, 5.9, 4.2 Hz, 1H), 0.59 – 0.46 (m, 1H), 0.43 – 0.33 (m, 1H), 0.09 (ddd, J = 8.7, 5.9, 3.7 Hz, 1H).

¹³C NMR (75 MHz, CDCl₃) δ 199.5, 138.0, 135.2, 131.8, 131.2 (q, J = 33.0 Hz), 130.1, 128.8, 128.5 (q, J = 3.7 Hz), 128.5, 127.3, 125.6 (q, J = 3.7 Hz), 123.7 (q, J = 272.8 Hz), 83.4, 56.2, 24.8, 24.1, 6.6, 6.4.

¹¹**B NMR (96 MHz, CDCl₃)** δ 32.9.

¹⁹F NMR (282 MHz, CDCl₃) δ -62.9.

HRMS (**EI**): calcd for [M] C₂₄H₂₆BF₃O₃ 429.19579, found: 429.19489.

IR (ATR): 1689, 1406, 1329, 1202, 1166, 1126, 1071, 692, 670 cm⁻¹.

1-(1-Methyl-1H-indol-5-yl)-2-phenyl-2-(1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclopropyl)ethan-1-one (4n)

The title compound was prepared from (cyclopropylidenemethyl)benzene (27 uL, 0.2 mmol) and 5-iodo-1-methyl-1H-indole (76.8 mg, 0.3 mmol), according to general borocarbonylation III (ring close). The crude residue was purified by flash chromatography (pentane/EA = 10:1, Rf = 0.20) to give the product as a colorless oil (48.3 mg, 79%).

¹H NMR (300 MHz, CDCl₃) δ 8.22 (d, J = 1.1 Hz, 1H), 7.85 (dd, J = 8.8, 1.7 Hz, 1H), 7.40 – 7.35 (m, 2H), 7.35 – 7.26 (m, 3H), 7.26 – 7.20 (m, 1H), 7.07 (d, J = 3.2 Hz, 1H), 6.53 (dd, J = 3.2, 0.9 Hz, 1H), 4.49 (s, 1H), 4.32 (s, 1H), 3.77 (s, 3H), 1.01 – 0.91 (m, 1H), 0.83 (ddd, J = 10.3, 6.5, 5.5 Hz, 1H), 0.76 – 0.62 (m, 1H), 0.55 (ddd, J = 10.3, 6.5, 4.8 Hz, 1H).

¹³C NMR (75 MHz, CDCl₃) δ 202.1, 139.2, 137.3, 130.5, 129.0, 128.7, 128.2, 127.9, 127.3, 124.0, 122.5, 109.2, 103.2, 59.0, 57.6, 33.0, 13.4, 11.5.

HRMS (**EI**): calcd for [M] C₂₀H₁₉NO₂ 305.14103, found: 305.14076.

IR (ATR): 1648, 1600, 1340, 1249, 1146, 1097, 714, 700, 586, 424 cm⁻¹.

1-(4-((1H-Indol-1-yl)methyl)phenyl)-2-phenyl-2-(1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclopropyl)ethan-1-one (4o)

The title compound was prepared from (cyclopropylidenemethyl)benzene (27 uL, 0.2 mmol) and 1-(4-iodobenzyl)-1*H*-indole (100 mg, 0.3 mmol), according to general borocarbonylation III (ring close).

The crude residue was purified by flash chromatography (pentane/EA = 10:1, Rf = 0.25) to give the product as a colorless oil (48.0 mg, 63%).

¹H NMR (300 MHz, CDCl₃) δ 7.91 – 7.84 (m, 1H), 7.82 – 7.76 (m, 1H), 7.74 – 7.70 (m, 1H), 7.43 – 7.21 (m, 10H), 7.15 (d, J = 3.1 Hz, 1H), 6.68 (d, J = 3.2 Hz, 1H), 5.39 (s, 2H), 4.19 (s, 1H), 4.11 (d, J = 0.9 Hz, 1H), 1.06 – 0.96 (m, 1H), 0.94 – 0.84 (m, 1H), 0.74 – 0.63 (m, 1H), 0.55 (ddd, J = 10.5, 6.4, 4.8 Hz, 1H).

¹³C NMR (75 MHz, CDCl₃) δ 201.3, 138.2, 136.4, 136.0, 131.4, 129.1, 129.0, 128.9, 128.1, 128.0, 127.5, 127.1, 121.9, 121.1, 119.7, 109.4, 102.2, 59.7, 57.0, 49.6, 13.1, 11.4.

HRMS (EI): calcd for [M] C₂₆H₂₃NO₂ 381.17233, found: 381.17237.

IR (**ATR**): 1668, 1461, 1254, 1184, 728, 698, 658, 512, 460, 425 cm⁻¹.

Ethyl 2-methyl-2-(4-(2-phenyl-2-(1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclopropyl)acetyl)phenoxy)propanoate (4p)

The title compound was prepared from (cyclopropylidenemethyl)benzene (27 uL, 0.2 mmol) and ethyl 2-(4-iodophenoxy)-2-methylpropanoate (100 mg, 0.3 mmol), according to general borocarbonylation II (ring close). The crude residue was purified by flash chromatography (pentane/EA = 15:1, Rf = 0.26) to give the product as a colorless oil (51.1 mg, 52%).

¹H NMR (300 MHz, CDCl₃) δ 7.79 – 7.71 (m, 2H), 7.26 – 7.09 (m, 5H), 6.75 – 6.61 (m, 2H), 4.80 (s, 1H), 4.17 (qd, J = 7.2, 0.9 Hz, 2H), 1.59 (s, 3H), 1.59 (s, 3H), 1.18 (s, 6H), 1.15 (t, J = 7.2 Hz, 3H), 1.12 (s, 6H), 0.84 – 0.76 (m, 1H), 0.50 (ddd, J = 9.0, 5.7, 3.8 Hz, 1H), 0.39 – 0.27 (m, 1H), 0.17 – 0.04 (m, 1H).

¹³C NMR (75 MHz, CDCl₃) δ 199.1, 173.8, 158.9, 136.6, 130.8, 130.6, 130.1, 128.2, 126.8, 117.0, 83.1, 79.1, 61.6, 55.9, 25.4, 25.3, 24.7, 24.1, 13.9, 6.5, 6.3.

¹¹**B NMR (96 MHz, CDCl₃)** δ 34.4.

HRMS (**EI**): calcd for [M] C₂₉H₃₇BO₆ 492.26777, found: 492.26874.

IR (ATR): 1731, 1671, 1594, 1413, 1221, 1172, 1136, 1113, 708, 621 cm⁻¹.

1-(4-((((1R,2S,5R)-2-Isopropyl-5-methylcyclohexyl)oxy)methyl)phenyl)-2-phenyl-2-(1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclopropyl)ethan-1-one (4q)

The title compound was prepared from (cyclopropylidenemethyl)benzene (27 uL, 0.2 mmol) and 1-iodo-4-((((1R,2S,5R)-2-isopropyl-5-methylcyclohexyl)oxy)methyl)benzene (111.0 mg, 0.3 mmol), according to general borocarbonylation III (ring close). The crude residue was purified by flash chromatography (pentane/EA = 10:1, Rf = 0.20) to give the product as a colorless oil (54.2 mg, 65%).

¹H NMR (300 MHz, CDCl₃) δ 7.90 – 7.80 (m, 2H), 7.38 – 7.27 (m, 6H), 7.26 – 7.21 (m, 1H), 4.64 (dd, J = 12.4, 2.0 Hz, 1H), 4.37 (dd, J = 12.4, 2.0 Hz, 1H), 4.24 (s, 1H), 4.12 (d, J = 1.0 Hz, 1H), 3.14 (tdd, J = 10.5, 4.3, 1.7 Hz, 1H), 2.24 (dtt, J = 10.5, 6.8, 3.2 Hz, 1H), 2.17 – 2.07 (m, 1H), 1.70 – 1.57 (m, 2H), 1.38 – 1.26 (m, 2H), 0.93 (t, J = 6.1 Hz, 5H), 0.88 (dd, J = 7.1, 2.7 Hz, 5H), 0.83 – 0.76 (m, 1H), 0.73 – 0.61 (m, 4H), 0.51 (ddd, J = 10.3, 6.5, 4.8 Hz, 1H).

¹³C NMR (75 MHz, CDCl₃) δ 201.5, 145.2, 136.4, 129.1, 129.0, 128.8, 127.5, 127.4, 79.3, 69.6, 59.5, 57.2, 48.2, 40.2, 34.5, 31.5, 25.6, 23.2, 22.3, 21.0, 16.1, 13.2, 11.5.

HRMS (**EI**): calcd for [M] C₂₈H₃₆O₃ 420.26590, found: 420.26494.

IR (ATR): 2951, 2920, 2866, 1668, 1255, 1215, 1087, 1013, 729, 699, 590, 507 cm⁻¹.

$1-Phenyl-2-(1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclopropyl)-2-(m-tolyl)ethan-1-one \\ (4r)$

The title compound was prepared from 1-(cyclopropylidenemethyl)-3-methylbenzene (32 uL, 0.2 mmol) and iodobenzene (34 uL, 0.3 mmol), according to general borocarbonylation II (ring close). The crude residue was purified by flash chromatography (pentane/EA = 20:1, Rf = 0.35) to give the product as a colorless oil (40.0 mg, 53%).

¹H NMR (300 MHz, CDCl₃) δ 7.95 – 7.78 (m, 2H), 7.45 – 7.37 (m, 1H), 7.32 (ddt, J = 8.3, 6.8, 1.3 Hz, 2H), 7.16 – 7.10 (m, 1H), 7.02 – 6.89 (m, 3H), 4.84 (s, 1H), 2.27 (d, J = 0.6 Hz, 3H), 0.85 (ddd, J = 8.8, 5.9, 4.1 Hz, 1H), 0.50 (ddd, J = 8.8, 5.7, 3.7 Hz, 1H), 0.42 – 0.30 (m, 1H), 0.19 – 0.04 (m, 1H). ¹³C NMR (75 MHz, CDCl₃) δ 200.7, 137.7, 137.4, 135.9, 132.1, 130.7, 128.8, 128.1, 128.1, 127.7, 127.3, 83.1, 56.1, 24.8, 24.2, 21.4, 6.6, 6.4.

¹¹B NMR (96 MHz, CDCl₃) δ 33.5.

HRMS (EI): calcd for [M] C₂₄H₂₉BO₃ 376.22043, found: 376.22116.

IR (**ATR**): 1677, 1405, 1306, 1131, 960, 849, 751, 715, 698 cm⁻¹.

yl)cyclopropyl)ethan-1-one (4s)

The title compound was prepared from (cyclopropylidenemethyl)-4-isobutylbenzene (37.2 mg, 0.2 mmol) and iodobenzene (34 uL, 0.3 mmol), according to general borocarbonylation II (ring close). The crude residue was purified by flash chromatography (pentane/EA = 20:1, Rf = 0.36) to give the product as a colorless oil (37.9 mg, 45%).

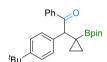
¹H NMR (300 MHz, CDCl₃) δ 7.89 – 7.80 (m, 2H), 7.45 – 7.36 (m, 1H), 7.34 – 7.27 (m, 2H), 7.06 – 6.97 (m, 4H), 4.88 (s, 1H), 2.38 (d, J = 7.2 Hz, 2H), 1.79 (hept, J = 6.6 Hz, 1H), 1.19 (s, 6H), 1.13 (s, 6H), 0.84 (dd, J = 6.6, 0.6 Hz, 7H), 0.48 (ddd, J = 8.8, 5.7, 3.6 Hz, 1H), 0.39 – 0.30 (m, 1H), 0.17 – 0.06 (m, 1H).

¹³C NMR (75 MHz, CDCl₃) δ 200.8, 140.3, 137.4, 133.1, 132.0, 129.9, 129.0, 128.8, 128.1, 83.2, 55.6, 45.0, 30.1, 24.8, 24.1, 22.3, 6.5, 6.1.

¹¹**B NMR (96 MHz, CDCl₃)** δ 33.6.

HRMS (EI): calcd for [M] C₂₇H₃₅BO₃ 418.26738, found: 418.26821.

IR (ATR): 1681, 1405, 1314, 1213, 1132, 960, 845, 689, 670 cm⁻¹.



2-(4-(tert-Butyl)phenyl)-1-phenyl-2-(1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclopropyl)ethan-1-one (4t)

The title compound was prepared from 1-(tert-butyl)-4-(cyclopropylidenemethyl)benzene (40 uL, 0.2 mmol) and iodobenzene (34 uL, 0.3 mmol), according to general borocarbonylation II (ring close). The crude residue was purified by flash chromatography (pentane/EA = 20:1, Rf = 0.36) to give the product as a colorless oil (37.0 mg, 44%).

¹H NMR (300 MHz, CDCl₃) δ 7.92 – 7.81 (m, 2H), 7.45 – 7.38 (m, 1H), 7.35 – 7.28 (m, 2H), 7.26 – 7.20 (m, 2H), 7.09 – 7.01 (m, 2H), 4.90 (s, 1H), 1.25 (s, 9H), 1.19 (s, 6H), 1.13 (s, 6H), 0.85 (ddd, J = 8.7, 6.0, 4.1 Hz, 1H), 0.54 – 0.44 (m, 1H), 0.41 – 0.30 (m, 1H), 0.17 – 0.06 (m, 1H).

¹³C NMR (**75 MHz, CDCl₃**) δ 200.9, 149.7, 137.5, 132.6, 132.0, 129.7, 128.8, 128.1, 125.1, 83.2, 55.3, 34.3, 31.3, 24.8, 24.1, 6.6, 6.2.

¹¹B NMR (96 MHz, CDCl₃) δ 32.9.

HRMS (**EI**): calcd for [M] C₂₇H₃₅BO₃ 418.26738, found: 418.26794.

IR (ATR): 1685, 1405, 1314, 1215, 1133, 1111, 962, 847, 716, 688, 671, 653, 605 cm⁻¹.

2-(4-Methoxyphenyl)-1-phenyl-2-(1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-

yl)cyclopropyl)ethan-1-one (4u)

The title compound was prepared from 1-(cyclopropylidenemethyl)-4-methoxybenzene (32.0 mg, 0.2 mmol) and iodobenzene (34 uL, 0.3 mmol), according to general borocarbonylation II (ring close). The crude residue was purified by flash chromatography (pentane/EA = 20:1, Rf = 0.21) to give the product as a colorless oil (42.4 mg, 54%).

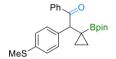
¹H NMR (300 MHz, CDCl₃) δ 7.88 – 7.80 (m, 2H), 7.45 – 7.37 (m, 1H), 7.34 – 7.27 (m, 2H), 7.08 – 7.02 (m, 2H), 6.80 – 6.74 (m, 2H), 4.84 (s, 1H), 3.74 (s, 3H), 1.19 (s, 6H), 1.13 (s, 6H), 0.84 (ddd, J = 8.9, 5.9, 4.2 Hz, 1H), 0.59 – 0.42 (m, 1H), 0.38 – 0.28 (m, 1H), 0.16 – 0.05 (m, 1H).

¹³C NMR (101 MHz, CDCl₃) δ 200.8, 158.5, 137.4, 132.1, 131.2, 128.8, 128.1, 128.0, 113.7, 83.1, 55.3, 55.1, 24.8, 24.1, 6.4, 6.2.

¹¹**B NMR (128 MHz, CDCl₃)** δ 33.1.

HRMS (EI): calcd for [M] C₂₄H₂₉BO₄ 392.21534, found: 392,21754.

IR (ATR): 1679, 1509, 1403, 1302, 1251, 1229, 1130, 1031, 841, 761, 698, 680, 669 cm⁻¹.



$\hbox{2-}(4-(Methylthio)phenyl)-1-phenyl-2-(1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-dioxaborol$

yl)cyclopropyl)ethan-1-one (4v)

The title compound was prepared from (4-(cyclopropylidenemethyl)phenyl)(methyl)sulfane (35.2 mg, 0.2 mmol) and iodobenzene (34 uL, 0.3 mmol), according to general borocarbonylation II (ring close). The crude residue was purified by flash chromatography (pentane/EA = 20:1, Rf = 0.21) to give the product as a colorless oil (47.8 mg, 59%).

¹H NMR (300 MHz, CDCl₃) δ 7.88 – 7.80 (m, 2H), 7.45 – 7.38 (m, 1H), 7.32 (ddt, J = 8.3, 6.8, 1.2 Hz, 2H), 7.15 – 7.03 (m, 4H), 4.82 (s, 1H), 2.42 (s, 3H), 1.19 (s, 6H), 1.13 (s, 6H), 0.84 (ddd, J = 8.8, 5.9, 4.2 Hz, 1H), 0.58 – 0.47 (m, 1H), 0.41 – 0.29 (m, 1H), 0.17 – 0.05 (m, 1H).

¹³C NMR (75 MHz, CDCl₃) δ 200.5, 137.2, 137.0, 132.9, 132.2, 130.5, 128.8, 128.2, 126.2, 83.2, 55.6, 24.7, 24.2, 15.5, 6.6, 6.4.

¹¹B NMR (96 MHz, CDCl₃) δ 33.1.

HRMS (**EI**): calcd for [M] C₂₄H₂₉BO₃S 408.19250, found: 408.19333.

IR (**ATR**): 2974, 1678, 1398, 1308, 1216, 1130, 960, 841, 713, 678 cm⁻¹.

$\hbox{2-}(3,5-Dimethoxyphenyl)-1-phenyl-2-(1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-1-1-quality)-1-phenyl-2-(1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-1-quality)-1-phenyl-2-(1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-1-quality)-1-phenyl-2-(1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-1-quality)-1-phenyl-2-(1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-1-quality)-1-phenyl-2-(1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-1-quality)-1-phenyl-2-(1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-1-quality)-1-phenyl-2-(1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-1-quality)-1-phenyl-2-(1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-1-quality)-1-phenyl-2-(1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-1-quality)-1-phenyl-2-(1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-1-quality)-1-phenyl-2-(1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-1-quality)-1-phenyl-2-(1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-1-quality)-1-phenyl-2-(1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-quality)-1-quality$

yl)cyclopropyl)ethan-1-one (4w)

The title compound was prepared from 1-(cyclopropylidenemethyl)-3,5-dimethoxybenzene (38 uL, 0.2 mmol) and iodobenzene (34 uL, 0.3 mmol), according to general borocarbonylation II (ring close). The crude residue was purified by flash chromatography (pentane/EA = 20:1, Rf = 0.16) to give the product as a colorless oil (58.5 mg, 70%).

¹H NMR (300 MHz, CDCl₃) δ 7.92 – 7.80 (m, 2H), 7.46 – 7.39 (m, 1H), 7.36 – 7.28 (m, 2H), 6.32 (d, J = 2.2 Hz, 2H), 6.31 – 6.26 (m, 1H), 4.71 (s, 1H), 3.71 (s, 6H), 1.20 (s, 6H), 1.14 (s, 6H), 0.84 (ddd, J = 8.8, 6.0, 4.0 Hz, 1H), 0.59 – 0.51 (m, 1H), 0.50 – 0.41 (m, 1H), 0.25 – 0.15 (m, 1H).

¹³C NMR (75 MHz, CDCl₃) δ 200.4, 160.4, 138.5, 137.3, 132.2, 128.7, 128.2, 108.3, 99.0, 83.1, 56.9, 55.2, 25.0, 24.7, 24.2, 7.1, 7.1.

¹¹B NMR (96 MHz, CDCl₃) δ 32.2.

HRMS (EI): calcd for [M] C₂₅H₃₁BO₅ 422.22591, found: 422.22701.

IR (ATR): 1681, 1593, 1404, 1314, 1203, 1131, 1060, 848, 688 cm⁻¹.

2-(Benzo[d][1,3]dioxol-5-yl)-1-phenyl-2-(1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclopropyl)ethan-1-one (4x)

The title compound was prepared from 5-(cyclopropylidenemethyl)benzo[d][1,3]dioxole (31 uL, 0.2 mmol) and iodobenzene (34 uL, 0.3 mmol), according to general borocarbonylation II (ring close). The crude residue was purified by flash chromatography (pentane/EA = 20:1, Rf = 0.21) to give the product as a colorless oil (49.6 mg, 61%).

¹H NMR (300 MHz, CDCl₃) δ 7.89 – 7.83 (m, 2H), 7.47 – 7.39 (m, 1H), 7.33 (ddt, J = 8.3, 6.8, 1.2 Hz, 2H), 6.71 – 6.65 (m, 2H), 6.59 (dd, J = 8.0, 1.8 Hz, 1H), 5.91 – 5.86 (m, 2H), 4.77 (s, 1H), 1.19 (s, 6H), 1.13 (s, 6H), 0.85 (ddd, J = 8.8, 5.9, 4.1 Hz, 1H), 0.53 (ddd, J = 8.8, 5.6, 3.6 Hz, 1H), 0.46 – 0.30 (m, 1H), 0.21 – 0.12 (m, 1H).

¹³C NMR (101 MHz, CDCl₃) δ 200.5, 147.5, 146.5, 137.3, 132.2, 129.8, 128.8, 128.2, 123.5, 110.4, 108.1, 100.9, 83.2, 55.8, 24.7, 24.2, 6.7, 6.6.

¹¹**B NMR (128 MHz, CDCl₃)** δ 32.9.

HRMS (EI): calcd for [M] C₂₄H₂₇BO₅ 406.19461, found: 406.19576.

IR (ATR): 1676, 1486, 1401, 1306, 1242, 1230, 1131, 1038, 931, 850, 699, 659 cm⁻¹.

2-(6-Methoxynaphthalen-2-yl)-1-phenyl-2-(1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclopropyl)ethan-1-one (4y)

The title compound was prepared from 2-(cyclopropylidenemethyl)-6-methoxynaphthalene (42.0 mg, 0.2 mmol) and iodobenzene (34 uL, 0.3 mmol), according to general borocarbonylation II (ring close). The crude residue was purified by flash chromatography (pentane/EA = 20:1, Rf = 0.16) to give the product as a colorless oil (61.7 mg, 70%).

¹H NMR (300 MHz, CDCl₃) δ 7.91 – 7.85 (m, 2H), 7.63 (dd, J = 8.9, 4.3 Hz, 2H), 7.51 (d, J = 2.0 Hz, 1H), 7.42 – 7.34 (m, 1H), 7.32 – 7.27 (m, 2H), 7.26 – 7.24 (m, 1H), 7.13 – 7.04 (m, 2H), 5.00 (s, 1H), 3.88 (s, 3H), 1.20 (s, 6H), 1.14 (s, 6H), 0.87 (ddd, J = 8.7, 5.9, 4.1 Hz, 1H), 0.57 – 0.46 (m, 1H), 0.45 – 0.35 (m, 1H), 0.19 – 0.08 (m, 1H).

¹³C NMR (101 MHz, CDCl₃) δ 200.7, 157.6, 137.4, 133.5, 132.1, 131.3, 129.3, 128.8, 128.8, 128.7, 128.2, 126.8, 118.8, 105.4, 83.2, 56.1, 55.3, 24.8, 24.2, 6.7, 6.4.

¹¹B NMR (128 MHz, CDCl₃) δ 33.9.

HRMS (EI): calcd for [M] C₂₈H₃₁BO₄ 442.23099, found: 442.23141.

IR (ATR): 1680, 1604, 1405, 1390, 1314, 1258, 1222, 1204, 1163, 1133, 1028, 847, 679 cm⁻¹.

$\hbox{$2$-(4-Fluorophenyl)-1-phenyl-2-(1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclopropyl)ethan-1-one (4z)}$

The title compound was prepared from 1-(cyclopropylidenemethyl)-3-fluorobenzene (28 uL, 0.2 mmol) and iodobenzene (34 uL, 0.3 mmol), according to general borocarbonylation II (ring close). The crude residue was purified by flash chromatography (pentane/EA = 20:1, Rf = 0.36) to give the product as a colorless oil (68.0 mg, 89%).

¹H NMR (300 MHz, CDCl₃) δ 7.92 – 7.74 (m, 2H), 7.48 – 7.41 (m, 1H), 7.38 – 7.30 (m, 2H), 7.21 (td, J = 7.9, 6.1 Hz, 1H), 7.02 – 6.82 (m, 3H), 4.80 (s, 1H), 1.18 (s, 6H), 1.13 (s, 6H), 0.85 (ddd, J = 8.9, 5.9, 4.2 Hz, 1H), 0.66 – 0.55 (m, 1H), 0.44 – 0.32 (m, 1H), 0.25 – 0.15 (m, 1H).

¹³C NMR (75 MHz, CDCl₃) δ 200.0, 162.6 (d, J = 245.7 Hz), 139.2 (d, J = 7.1 Hz), 137.1, 132.4, 129.6 (d, J = 8.4 Hz), 128.7, 128.3, 125.7 (d, J = 3.0 Hz), 116.9 (d, J = 21.9 Hz), 113.9 (d, J = 21.2 Hz), 83.3, 56.0, 56.0, 24.7, 24.2, 7.1.

¹¹B NMR (96 MHz, CDCl₃) δ 32.7.

¹⁹F NMR (282 MHz, CDCl₃) δ -112.98 (td, J = 9.2, 5.3 Hz).

HRMS (EI): calcd for [M] C₂₃H₂₆BFO₃ 380.19536, found: 380.19634.

IR (**ATR**): 1682, 1445, 1404, 1390, 1317, 1206, 1138, 1129, 961, 851, 737, 690 cm⁻¹.

2-(4-Fluorophenyl)-1-phenyl-2-(1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-

yl)cyclopropyl)ethan-1-one (4aa)

The title compound was prepared from 1-(cyclopropylidenemethyl)-4-fluorobenzene (28 uL, 0.2 mmol) and iodobenzene (34 uL, 0.3 mmol), according to general borocarbonylation II (ring close). The crude residue was purified by flash chromatography (pentane/EA = 20:1, Rf = 0.36) to give the product as a colorless oil (43.0 mg, 57%).

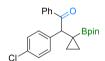
¹H NMR (300 MHz, CDCl₃) δ 7.92 – 7.76 (m, 2H), 7.47 – 7.40 (m, 1H), 7.33 (ddt, J = 8.3, 6.8, 1.2 Hz, 2H), 7.18 – 7.09 (m, 2H), 6.99 – 6.87 (m, 2H), 4.82 (s, 1H), 1.18 (s, 6H), 1.13 (s, 6H), 0.84 (ddd, J = 8.8, 5.8, 4.2 Hz, 1H), 0.57 (ddd, J = 8.9, 5.6, 3.8 Hz, 1H), 0.38 – 0.28 (m, 1H), 0.20 – 0.09 (m, 1H). ¹³C NMR (75 MHz, CDCl₃) δ 200.4, 161.9 (d, J = 245.7 Hz), 137.2, 132.3, 132.3 (d, J = 3.4 Hz), 131.5 (d, J = 7.7 Hz), 128.8, 128.2, 115.2 (d, J = 21.2 Hz), 83.2, 55.4, 24.7, 24.2, 6.8, 6.7.

¹¹**B NMR (96 MHz, CDCl₃)** δ 33.4.

¹⁹F NMR (282 MHz, CDCl₃) δ -115.68 (ddd, J = 13.7, 8.4, 5.0 Hz).

HRMS (EI): calcd for [M] C₂₃H₂₆BFO₃ 380.19536, found: 380.19647.

IR (**ATR**): 1674, 1504, 1406, 1311, 1218, 1131, 844, 763, 696, 680, 609 cm⁻¹.



2-(4-Chlorophenyl)-1-phenyl-2-(1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclopropyl)ethan-1-one (4bb)

The title compound was prepared from 1-chloro-4-(cyclopropylidenemethyl)benzene (32.8 mg, 0.2 mmol) and iodobenzene (34 uL, 0.3 mmol), according to general borocarbonylation II (ring close). The crude residue was purified by flash chromatography (pentane/EA = 20:1, Rf = 0.36) to give the product as a colorless oil (34.5 mg, 44%).

¹H NMR (300 MHz, CDCl₃) δ 7.90 – 7.75 (m, 2H), 7.49 – 7.40 (m, 1H), 7.37 – 7.30 (m, 2H), 7.25 – 7.18 (m, 2H), 7.15 – 7.08 (m, 2H), 4.78 (s, 1H), 1.18 (s, 6H), 1.13 (s, 6H), 0.84 (ddd, J = 8.8, 5.9, 4.3 Hz, 1H), 0.64 – 0.53 (m, 1H), 0.39 – 0.28 (m, 1H), 0.20 – 0.09 (m, 1H).

¹³C NMR (**75 MHz, CDC1**₃) δ 200.2, 137.1, 135.2, 132.9, 132.4, 131.3, 128.8, 128.5, 128.3, 83.2, 55.6, 24.7, 24.2, 6.9, 6.9.

¹¹**B NMR (96 MHz, CDCl₃)** δ 32.5.

HRMS (**EI**): calcd for [M] C₂₃H₂₆BClO₃ 395.16944, found: 395.16836.

IR (ATR): 1685, 1401, 1314, 1232, 1216, 1132, 961, 816, 715, 690, 680, 670, 644 cm⁻¹.

2-(Benzo[b]thiophen-3-yl)-1-phenyl-2-(1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclopropyl)ethan-1-one (4cc)

The title compound was prepared from 3-(cyclopropylidenemethyl)benzo[b]thiophene (37.2 mg, 0.2 mmol) and iodobenzene (34 uL, 0.3 mmol), according to general borocarbonylation II (ring close). The crude residue was purified by flash chromatography (pentane/EA = 20:1, Rf = 0.21) to give the product as a colorless oil (49.7 mg, 60%).

¹H NMR (300 MHz, CDCl₃) δ 7.93 (d, J = 7.9 Hz, 1H), 7.88 – 7.79 (m, 3H), 7.48 – 7.36 (m, 3H), 7.35 – 7.26 (m, 2H), 7.11 (s, 1H), 5.42 (s, 1H), 1.20 (s, 6H), 1.16 (s, 6H), 0.93 – 0.85 (m, 1H), 0.58 – 0.46 (m, 2H), 0.08 – -0.03 (m, 1H).

¹³C NMR (75 MHz, CDCl₃) δ 199.9, 140.2, 138.9, 137.1, 132.3, 130.6, 128.4, 128.3, 125.8, 124.4, 124.3, 123.0, 121.5, 83.3, 48.3, 24.8, 24.2, 7.8, 7.1.

¹¹B NMR (96 MHz, CDCl₃) δ 33.1.

HRMS (EI): calcd for [M] C₂₅H₂₇BO₃S 418.17685, found: 418.17801.

IR (**ATR**): 1677, 1405, 1312, 1216, 1133, 959, 847, 755, 732, 721, 694, 672, 659 cm⁻¹.

2-(4-Morpholinophenyl)-1-phenyl-2-(1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclopropyl)ethan-1-one (4dd)

The title compound was prepared from 4-(4-(cyclopropylidenemethyl)phenyl)morpholine (43.0 mg, 0.2 mmol) and iodobenzene (34 uL, 0.3 mmol), according to general borocarbonylation III (ring close). The crude residue was purified by flash chromatography (pentane/EA = 3:1, Rf = 0.20) to give the product as a red oil (47.7 mg, 70%).

¹H NMR (300 MHz, CDCl₃) δ 7.91 – 7.85 (m, 2H), 7.51 – 7.44 (m, 1H), 7.40 – 7.32 (m, 2H), 7.22 – 7.15 (m, 2H), 6.88 – 6.82 (m, 2H), 4.22 (s, 1H), 4.06 (s, 1H), 3.84 – 3.79 (m, 4H), 3.14 – 3.10 (m, 4H), 0.96 – 0.87 (m, 1H), 0.85 – 0.75 (m, 1H), 0.67 – 0.58 (m, 1H), 0.48 (ddd, J = 10.2, 6.4, 4.7 Hz, 1H). ¹³C NMR (75 MHz, CDCl₃) δ 201.9, 150.4, 136.2, 133.2, 129.8, 128.9, 128.5, 127.3, 115.8, 66.8, 58.7, 57.2, 48.9, 12.9, 11.4.

HRMS (**EI**): calcd for [M] C₂₁H₂₃NO₃ 337.16725, found: 337.16803.

IR (**ATR**): 1667, 1514, 1447, 1236, 1214, 1175, 1116, 924, 785, 733, 689, 658, 551 cm⁻¹.

6. Derivatization of γ -vinylboryl ketone 3a and β -cyclopropylboryl ketone 4a

6.1 Procedure of oxidation²

1,5-Diphenylpentane-1,4-dione (5a)

The title compound was synthesized according to the following procedure: To the boration product **3a** (36.2 mg, 0.1 mmol) in THF (2.0 mL) and water (2.0 mL) was added NaBO₃·4H₂O (76.5 mg. 5 equiv). The reaction mixture was stirred vigorously for 6 h at room temperature. The reaction mixture was quenched with water and then extracted with ethyl acetate (5 mL). The combined organic layers were washed with brine (15 mL), dried over Na₂SO₄ and concentrated. The crude product was purified by column chromatography on silica gel to afford the corresponding product **5a** as a colorless oil (24.2 mg, 96%).

¹H NMR (300 MHz, CDCl₃) δ 8.03 – 7.92 (m, 2H), 7.62 – 7.54 (m, 1H), 7.51 – 7.43 (m, 2H), 7.41 – 7.34 (m, 2H), 7.33 – 7.25 (m, 3H), 3.85 (s, 2H), 3.33 – 3.23 (m, 2H), 2.92 (dd, J = 6.9, 5.7 Hz, 2H). ¹³C NMR (75 MHz, CDCl₃) δ 207.0, 198.5, 136.6, 134.2, 133.1, 129.5, 128.7, 128.5, 128.0, 127.0, 50.2, 35.6, 32.5.

IR (**ATR**): 1712, 1681, 1448, 1351, 1212, 761, 734, 689 cm⁻¹.

6.2 Procedure of iodination³

(E)-4-Iodo-1,5-diphenylpent-4-en-1-one (5b)

The title compound was synthesized according to the following procedure: To a solution of **3a** (36.2 mg, 0.1 mmol) in THF (1.0 mL) was added 0.1 mL of NaOH (aq. 3M, 0.3 mmol). After stirring for 10 minutes at room temperature, 0.1 mL of solution of I2 (2M, 0.2 mmol) in THF was added into the reaction mixture, and the resulting mixture was stirred for another 1 h. The mixture was then quenched with saturated aqueous Na₂S₂O₄ (5.0 mL) and extracted with diethyl ether for three times. The combined organic layers were washed with saturated aqueous NHCO₃ solution and brine, then dried over Na₂SO₄. The volatiles were removed under reduced pressure and the residue was purified by column chromatography on silica gel to afford the corresponding product **5b** as a colorless oil (21.0 mg, 58%).

¹**H NMR** (300 MHz, CDCl₃) δ 8.03 – 7.94 (m, 2H), 7.62 – 7.54 (m, 1H), 7.51 – 7.43 (m, 2H), 7.39 – 7.26 (m, 4H), 7.21 (ddd, J = 7.2, 1.9, 1.1 Hz, 2H), 3.36 – 3.25 (m, 2H), 3.10 – 2.96 (m, 2H).

¹³C NMR (75 MHz, CDCl₃) δ 198.0, 141.9, 137.3, 136.5, 133.3, 128.7, 128.6, 128.1, 128.0, 127.5, 106.5, 39.2, 34.1.

IR (**ATR**): 2953, 2921, 1683, 1447, 1272, 1202, 1182, 1079, 1030, 968, 741, 688, 650 cm⁻¹.

6.3 Procedure of Suzuki-Miyaura coupling⁴

$$\begin{array}{c} \text{Ph} \\ + \text{ Ph-Br} \\ \\ \text{Ph} \\ \\ \textbf{3a} \end{array} \\ \begin{array}{c} \text{Pd(PPh_3)_4 (10 \text{ mol\%})} \\ \\ \text{K}_2\text{CO}_3 (1.5 \text{ equiv.})} \\ \\ \text{DMF/H}_2\text{O (7:4), 80 °C, 5 h} \\ \\ \textbf{5c, 68\%} \end{array}$$

(E)-1,4,5-Triphenylpent-4-en-1-one (5c)

The title compound was synthesized according to the following procedure: To a 5 mL Schlenk flask charged with a magnetic stirring bar, were added the 3a (72.4 mg, 0.2 mmol), PhBr (37.2 mg, 0.24 mmol), Pd(PPh₃)₄ (23.1 mg, 10 mol%), K₂CO₃ (41.7 mg, 0.3 mmol), DMF (0.7 mL) and H₂O (0.4 mL). The flask was sealed with a PTFE septum and allowed to react at 80 °C for 5 h. The reaction mixture was quenched with water and then extracted with ethyl acetate (5 mL) and concentrated. The crude product was purified by column chromatography on silica gel to afford the corresponding product 5c as a colorless oil (42.2 mg, 68%).

¹H NMR (300 MHz, CDCl₃) δ 7.91 – 7.85 (m, 2H), 7.59 – 7.52 (m, 3H), 7.47 – 7.26 (m, 10H), 6.86 (s, 1H), 3.28 – 3.18 (m, 2H), 3.15 – 3.06 (m, 2H).

¹³C NMR (75 MHz, CDCl₃) δ 199.3, 142.1, 141.4, 137.8, 136.6, 133.0, 129.2, 128.6, 128.6, 128.5, 128.4, 128.0, 127.5, 126.8, 126.6, 37.6, 24.7.

IR (**ATR**): 1681, 1595, 1447, 1267, 1201, 968, 757, 741, 733, 696, 689, 655, 643, 506 cm⁻¹.

6.4 Procedure of protodeboronation⁵

(Z)-1,5-Diphenylpent-4-en-1-one (5d)

The title compound was synthesized according to the following procedure: To a 5 mL Schlenk flask charged with a magnetic stirring bar, were added the **3a** (36.2 mg, 0.1 mmol), KHF2 (23.4 mg, 0.3 mmol) and HOAc (2 mL) under air. Then the reaction was allowed to stir at room temperature for 6 h. The reaction mixture was quenched with saturated NaHCO₃ solution slowly and resulting mixture was extracted with ethyl acetate (5 mL). The combined organic layers were washed with brine and dried over anhydrous Na₂SO₄. The volatiles were removed under reduced pressure and the residue was

purified by column chromatography on silica gel to afford the corresponding product **5d** as a colorless oil (19.6 mg, 83%).

¹H NMR (300 MHz, CDCl₃) δ 8.00 – 7.93 (m, 2H), 7.59 – 7.53 (m, 1H), 7.49 – 7.42 (m, 2H), 7.38 – 7.29 (m, 4H), 7.26 – 7.19 (m, 1H), 6.49 (dt, J = 11.6, 1.9 Hz, 1H), 5.72 (dt, J = 11.6, 7.3 Hz, 1H), 3.12 (t, J = 7.5 Hz, 2H), 2.79 (qd, J = 7.6, 2.1 Hz, 2H).

¹³C NMR (75 MHz, CDCl₃) δ 199.3, 137.3, 136.8, 133.0, 130.9, 130.0, 128.7, 128.6, 128.2, 128.0, 126.7, 38.6, 23.2.

IR (**ATR**): 1682, 1447, 1202, 1179, 967, 767, 745, 688, 655 cm⁻¹.

6.5 Procedure of oxidation²

2-(1-Hydroxycyclopropyl)-1,2-diphenylethan-1-one (6a)

The title compound was synthesized according to the following procedure: To the boration product **4a** (72.4 mg, 0.2 mmol) in THF (3.0 mL) and water (3.0 mL) was added NaBO₃·4H₂O (153.0 mg. 5 equiv). The reaction mixture was stirred vigorously for 6 h at room temperature. The reaction mixture was quenched with water and then extracted with ethyl acetate (5 mL). The combined organic layers were washed with brine (15 mL), dried over Na₂SO₄ and concentrated. The crude product was purified by column chromatography on silica gel to afford the corresponding product **6a** as a colorless oil (50.3 mg, 99%).

¹H NMR (300 MHz, CDCl₃) δ 8.01 – 7.85 (m, 2H), 7.56 – 7.48 (m, 1H), 7.43 – 7.25 (m, 7H), 4.29 (s, 1H), 4.15 (d, J = 1.0 Hz, 1H), 0.98 (ddd, J = 10.6, 6.4, 4.9 Hz, 1H), 0.90 – 0.80 (m, 1H), 0.69 (dddd, J = 10.3, 6.3, 5.5, 1.0 Hz, 1H), 0.55 (ddd, J = 10.3, 6.5, 4.8 Hz, 1H).

¹³C NMR (**75 MHz, CDCl₃**) δ 201.8, 136.3, 136.1, 133.4, 129.0, 128.9, 128.9, 128.6, 127.5, 59.5, 57.2, 13.2, 11.5.

IR (**ATR**): 1682, 1655, 1449, 1249, 1212, 1198, 1013, 759, 736, 700, 692, 681, 658, 545 cm⁻¹.

6.6 Procedure of reduction

1,2-Diphenyl-2-(1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclopropyl)ethan-1-ol (6b)

The title compound was synthesized according to the following procedure: To the boration product **4a** (36.2 mg, 0.2 mmol) in MeOH (3.0 mL) was added NaBH₄ (38.0 mg. 5 equiv). The reaction mixture was stirred vigorously for 0.5 h at room temperature. The reaction mixture was quenched with water

and then extracted with ethyl acetate (5 mL). The combined organic layers were washed with brine (15 mL), dried over Na₂SO₄ and concentrated. The crude product was purified by column chromatography on silica gel to afford the corresponding product **6b** as a colorless oil (27.9 mg, 77%).

¹H NMR (300 MHz, CDCl₃) δ 7.42 (dt, J = 8.1, 1.5 Hz, 4H), 7.36 – 7.21 (m, 6H), 5.57 (dd, J = 7.7, 1.8 Hz, 1H), 2.81 (d, J = 1.8 Hz, 1H), 1.85 (d, J = 7.7 Hz, 1H), 1.31 (s, 6H), 1.28 (s, 6H), 0.74 – 0.65 (m, 1H), 0.51 – 0.41 (m, 1H), 0.28 (ddd, J = 9.6, 5.9, 3.8 Hz, 1H), 0.00 (ddd, J = 8.4, 5.8, 3.8 Hz, 1H). ¹³C NMR (75 MHz, CDCl₃) δ 143.8, 142.5, 129.2, 128.1, 127.8, 127.1, 126.9, 126.5, 83.5, 76.0, 64.1, 25.0, 24.2, 16.2, 11.6.

¹¹**B NMR (96 MHz, CDCl₃)** δ 33.0.

6.7 Procedure of condensation

(Z)-N'-(1,2-Diphenyl-2-(1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclopropyl)ethylidene)-4-methylbenzenesulfonohydrazide (6c)

The title compound was synthesized according to the following procedure: To the boration product **4a** (72.4 mg, 0.2 mmol) in MeOH (2.0 mL) was added Na₂SO₄ (56.8 mg, 2.0 equiv.) and TsNHNH₂ (56.0 mg, 1.5 equiv.). The reaction mixture was stirred vigorously for 12 h at room temperature. After the **4a** was consumed completely, the crude product was purified by column chromatography on silica gel to afford the corresponding product **6c** as a white solid (48.9 mg, 77%).

¹H NMR (300 MHz, CDCl₃) δ 7.99 – 7.86 (m, 2H), 7.38 (dt, J = 8.0, 0.6 Hz, 2H), 7.33 – 7.26 (m, 4H), 7.13 – 7.04 (m, 2H), 6.93 – 6.84 (m, 2H), 6.75 (dd, J = 8.3, 1.5 Hz, 2H), 4.05 (s, 1H), 2.50 (s, 3H), 1.22 (s, 6H), 1.14 (s, 6H), 0.92 – 0.85 (m, 1H), 0.43 – 0.26 (m, 2H), -0.13 – -0.25 (m, 1H).

¹³C NMR (75 MHz, CDCl₃) δ 159.9, 143.8, 135.9, 135.6, 134.2, 130.4, 129.4, 129.2, 129.1, 128.6, 128.0, 127.6, 126.8, 83.2, 55.0, 25.2, 24.1, 21.6, 7.1, 6.7.

¹¹**B NMR (96 MHz, CDCl₃)** δ 33.5.

6.8 Procedure for trifluoroborate preparation

Ph Bpin
$$\frac{\text{KHF}_2}{\text{MeOH}}$$
 Ph $\frac{\text{BF}_3\text{K}}{\text{BF}_3\text{K}}$

1,2-Diphenyl-2-(1-(trifluoro-l4-boraneyl)cyclopropyl)ethan-1-one, potassium salt (6d)

The title compound was synthesized according to the following procedure: To the boration product 4a (72.4 mg, 0.2 mmol) in MeOH (5.0 mL) and H₂O (0.4 mL) was added KHF₂ (140.0 mg, 4.5 M). The reaction mixture was stirred vigorously for 3 h at room temperature. The resulting slurry was stirred

concentrated, then placed under high vacuum. The dried solids were triturated with hot acetone and filtered to remove inorganic salts. The resulting filtrate was concentrated to a minimal volume and Et2O was added to afford 6d as a white solid (45.6 mg, 67%).

¹H NMR (300 MHz, d_6 -Acetone) δ 8.04 – 7.99 (m, 2H), 7.47 – 7.35 (m, 3H), 7.31 (ddd, J = 8.2, 1.7, 0.9 Hz, 2H), 7.24 – 7.18 (m, 2H), 7.15 – 7.08 (m, 1H), 5.18 (s, 1H), 0.46 – 0.35 (m, 1H), 0.14 (dd, J = 7.3, 1.8 Hz, 2H), -0.35 – 0.47 (m, 1H).

¹³C NMR (75 MHz, *d*₆-Acetone) δ 203.7, 140.3, 140.2, 132.7, 131.1, 129.4, 129.0, 128.4, 126.8, 55.4, 5.7, 4.9.

¹¹B NMR (96 MHz, d_6 -Acetone) δ 4.3.

IR (**ATR**): 1676, 1228, 1043, 1006, 972, 752, 700, 685, 649, 537, 482 cm⁻¹.

7. References

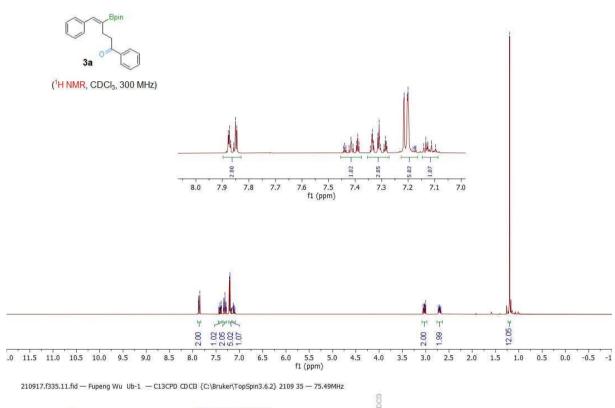
- [1] Y. Wang, M. E. Muratore, Z. Rong, A. M. Echavarren, Angew. Chem., Int. Ed. 2014, 53, 14022.
- [2] J.-E. Lee, J. Yun, Angew. Chem. Int. Ed. 2008, 47, 145.
- [3] C. Wu, S. Ge, Chem. Sci. 2020, 11, 2783.
- [4] K. Endo, M. Hirokami, T. Shibata, T. J. Org. Chem. 2010, 75, 3469.
- [5] M. Xiong, X. Xie, Y. Liu, Org. Lett. 2017, 19, 3398.

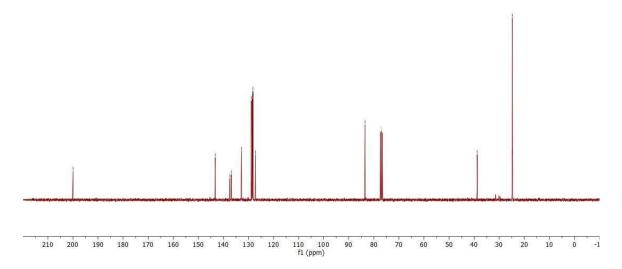
8. NMR Spectra of the γ -vinylboryl ketones, β -cyclopropylboryl ketones and BCPs

8.1 NMR spectra of the γ -vinylboryl ketones and β -cyclopropylboryl ketones

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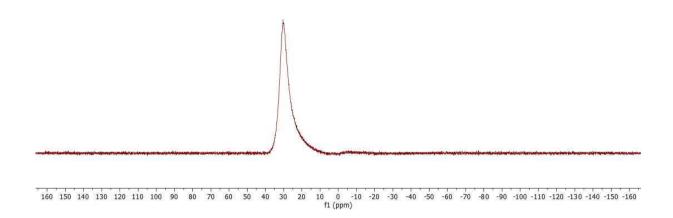
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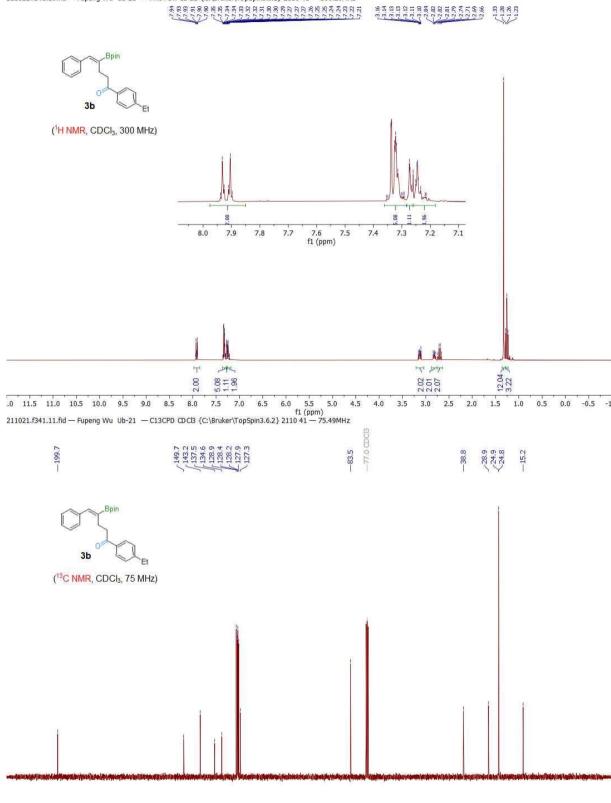




210917.f335.12.fid — Fupeng Wu Ub-1 — 118 CDCl3 {C:\Bruker\TopSpin3.6.2} 2109 35 — 96.32MHz $\stackrel{\Omega}{\sim}$

(11B NMR, CDCI₃, 96 MHz)





110 100 f1 (ppm)

210 200

190 180 170

160

150

140

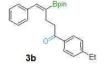
130 120

30

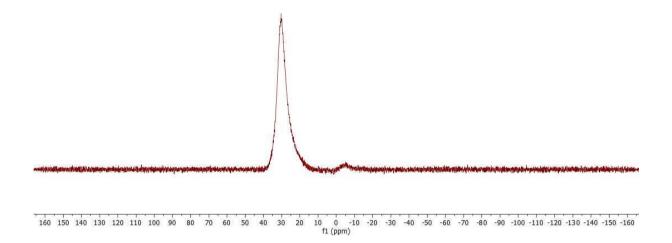
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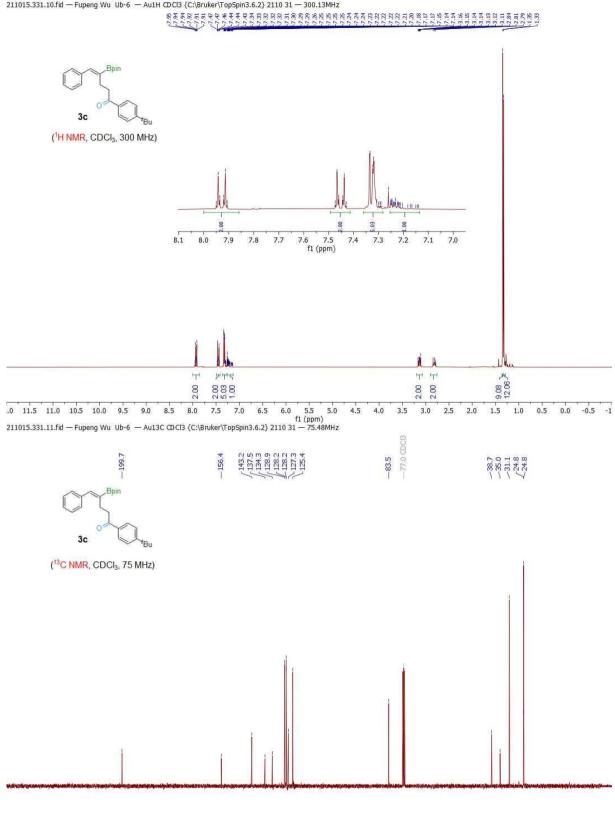
-10 -2

211021.f341.12.fid — Fupeng Wu Ub-21 — 11B CDCl3 {C:\Bruker\TopSpin3.6.2} 2110 41 — 96.32MHz



(11B NMR, CDCl₃, 96 MHz)

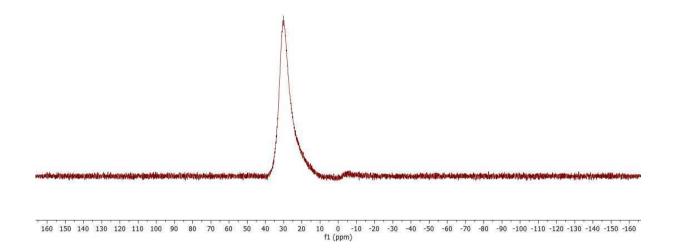


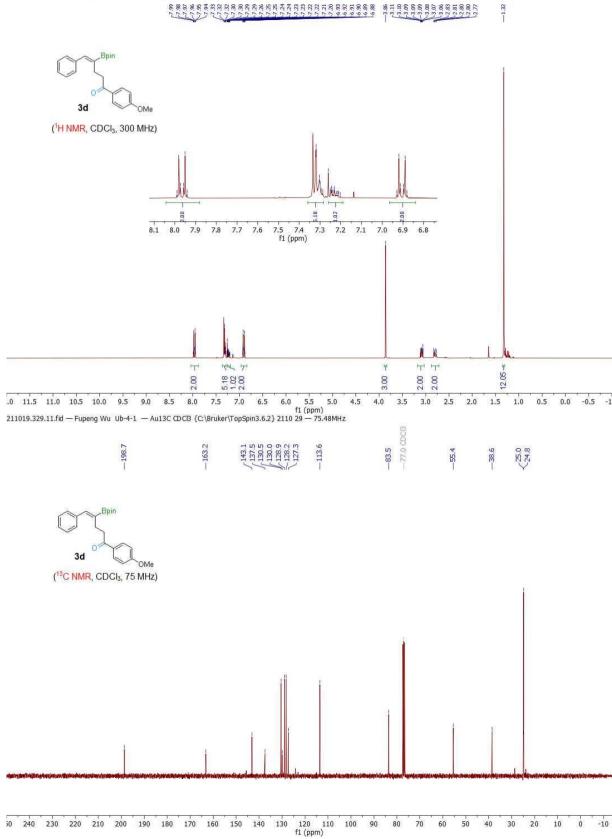


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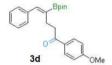
211015.331.12.fid — Fupeng Wu Ub-6 — Au11B CDCl3 {C:\Bruker\TopSpin3.6.2} 2110 31 — 96.29MHz $\stackrel{\text{Cl}}{\otimes}$

(11B NMR, CDCI₃, 96 MHz)

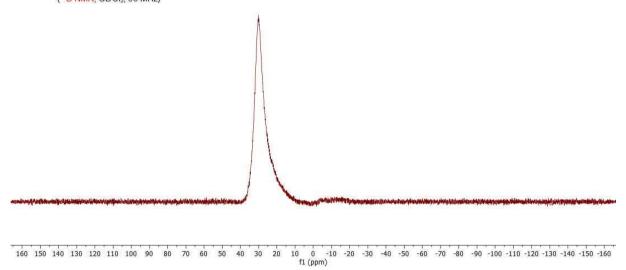


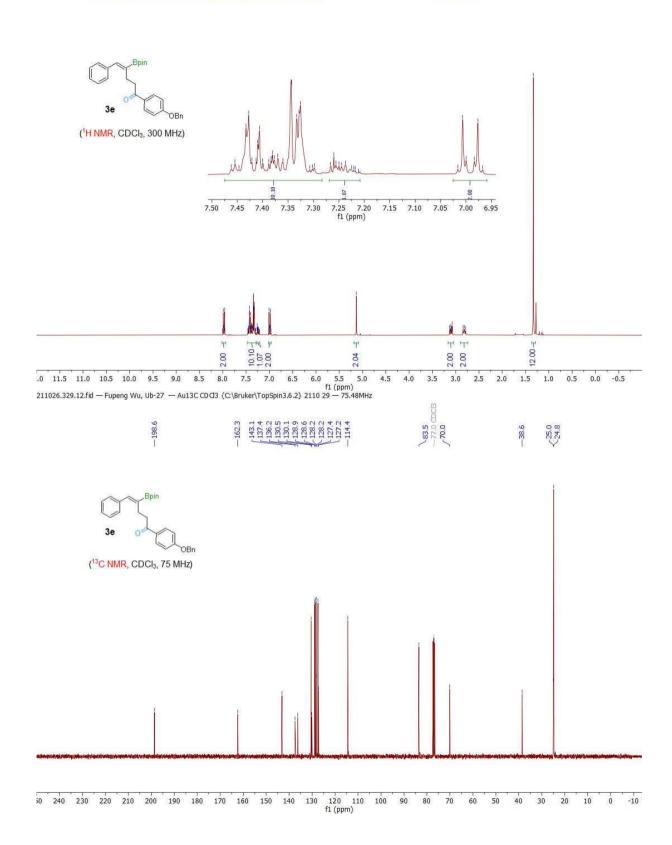






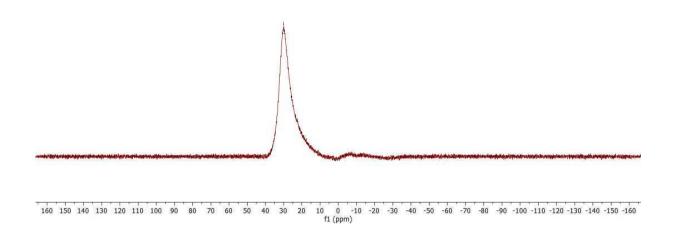
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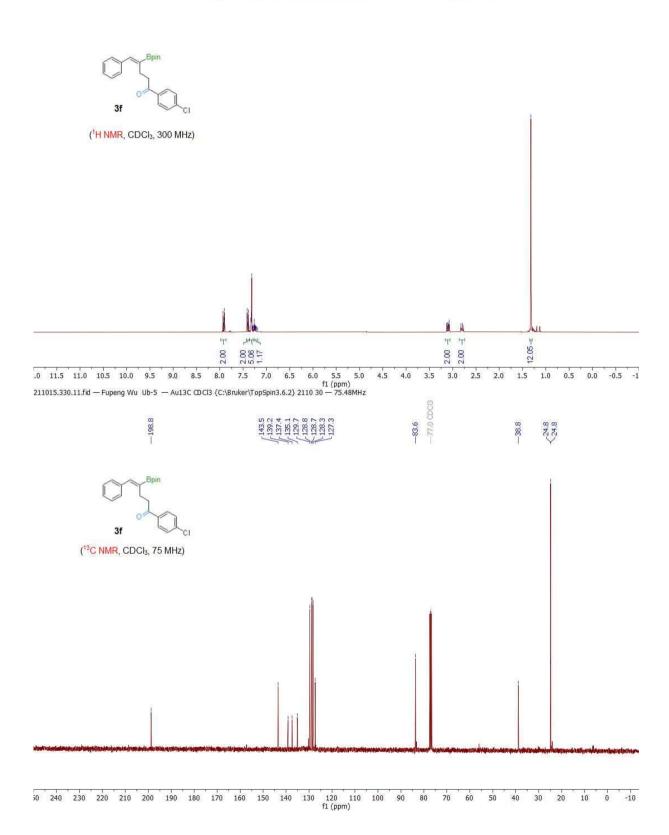




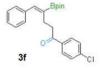
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(11B NMR, CDCl₃, 96 MHz)

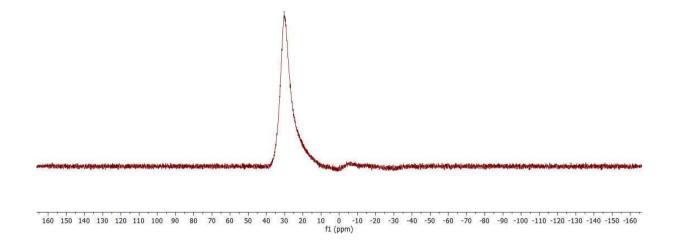


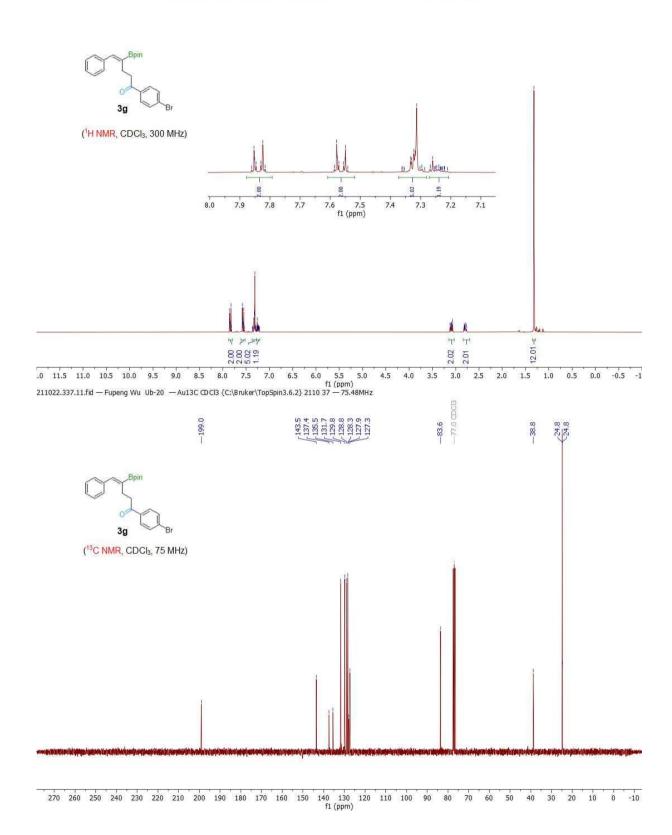


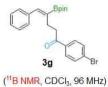
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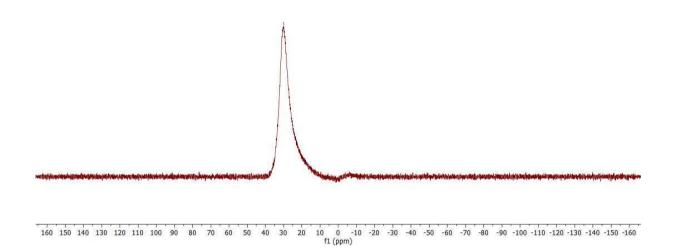


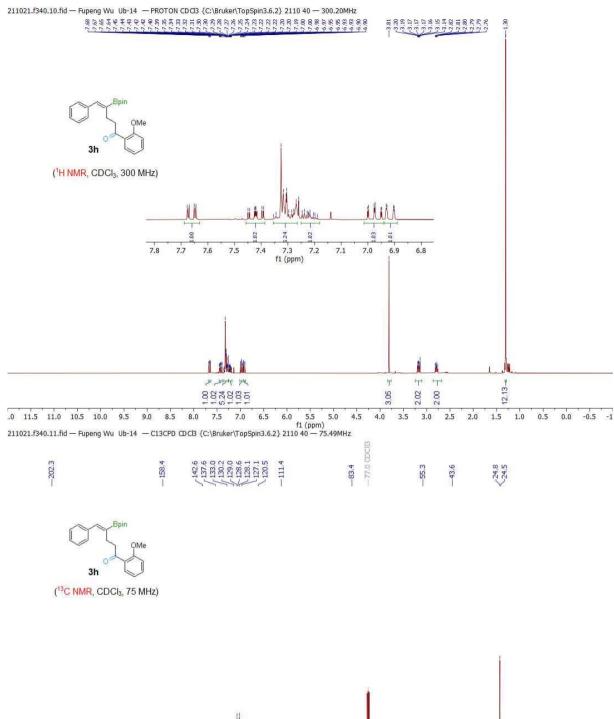
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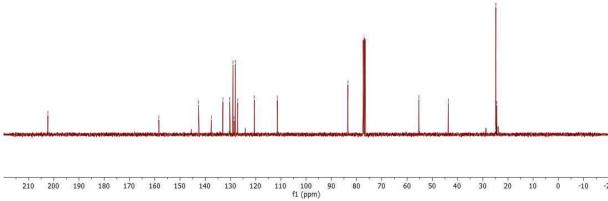






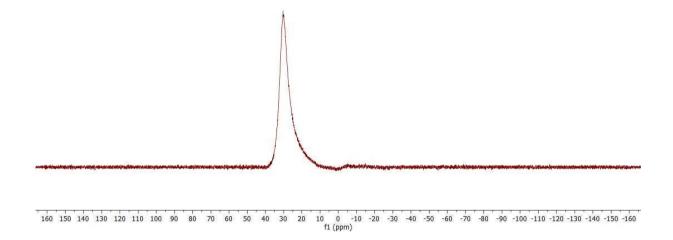




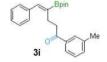


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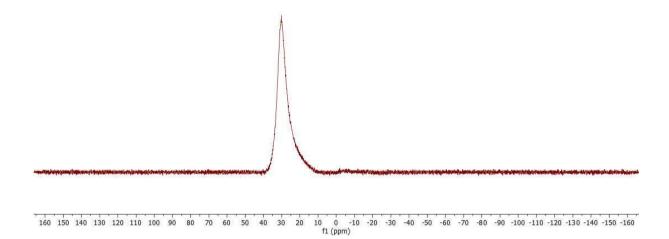
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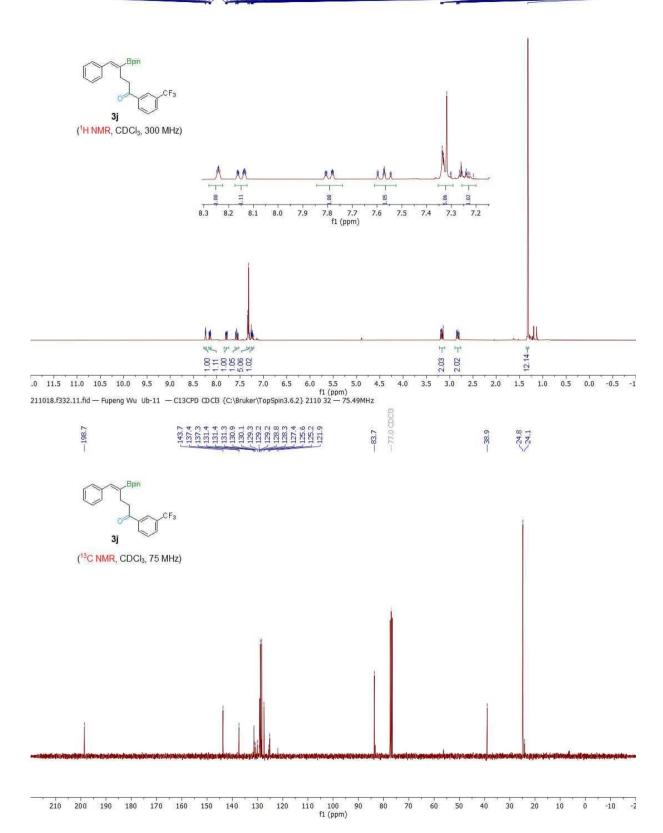


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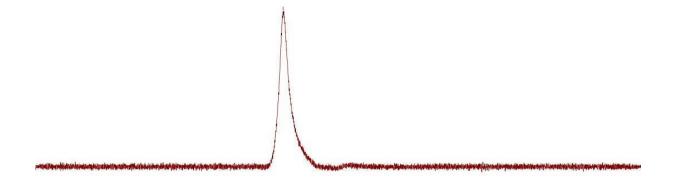


(11B NMR, CDCI₃, 96 MHz)









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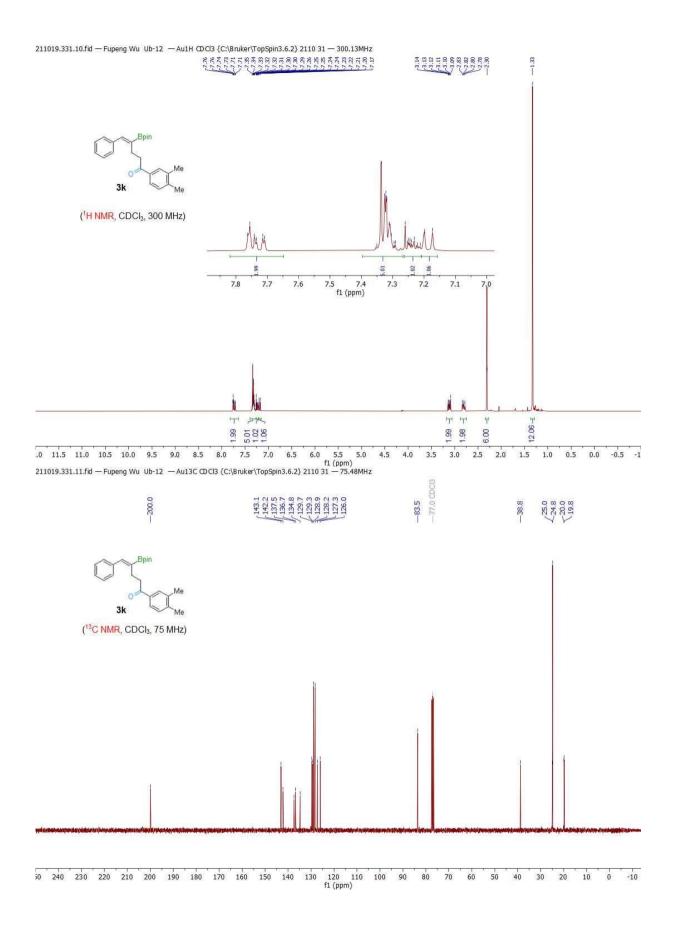
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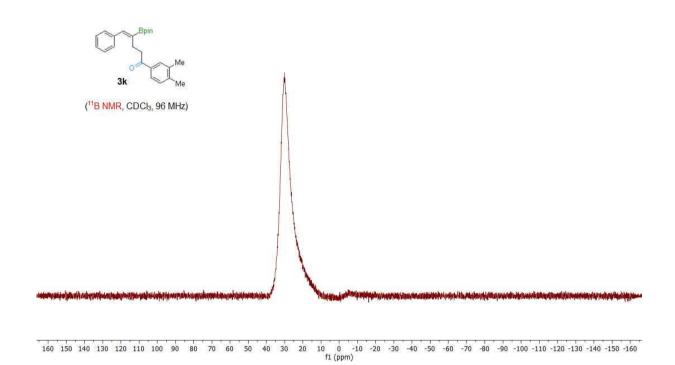


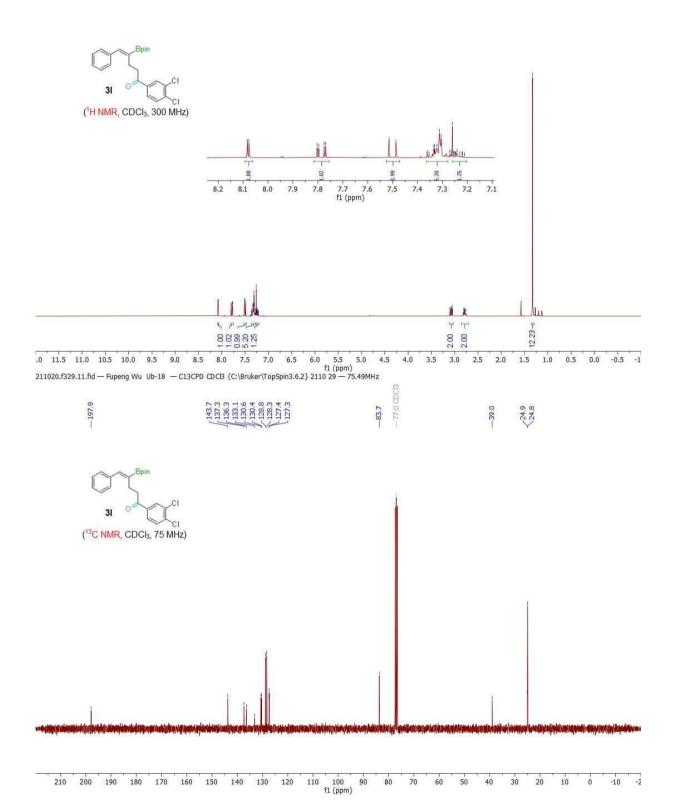
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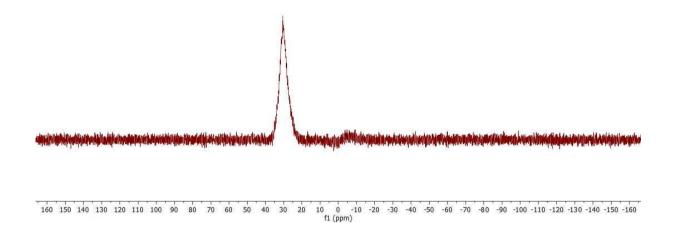


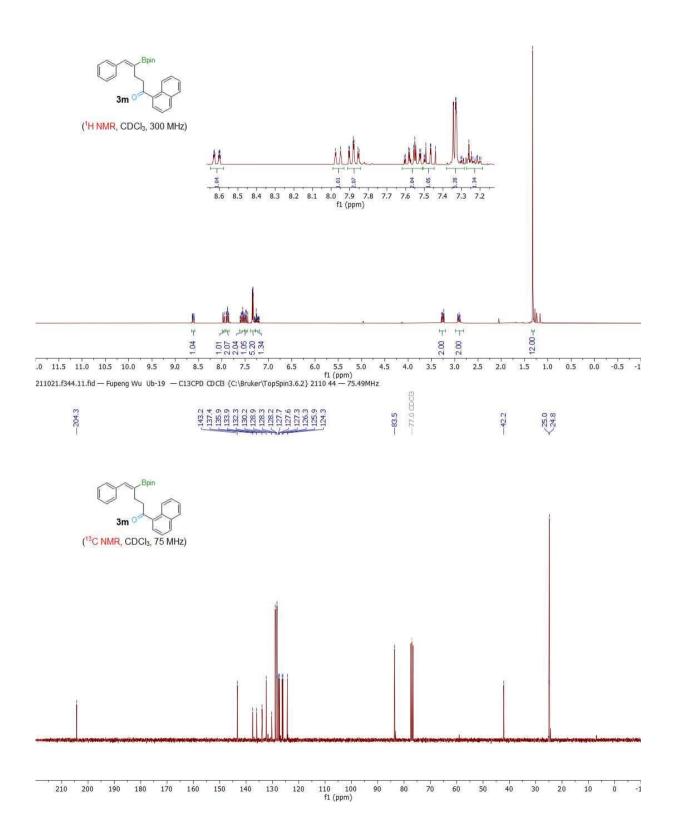




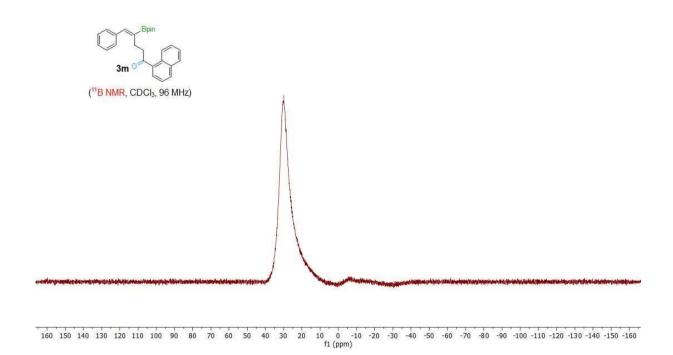


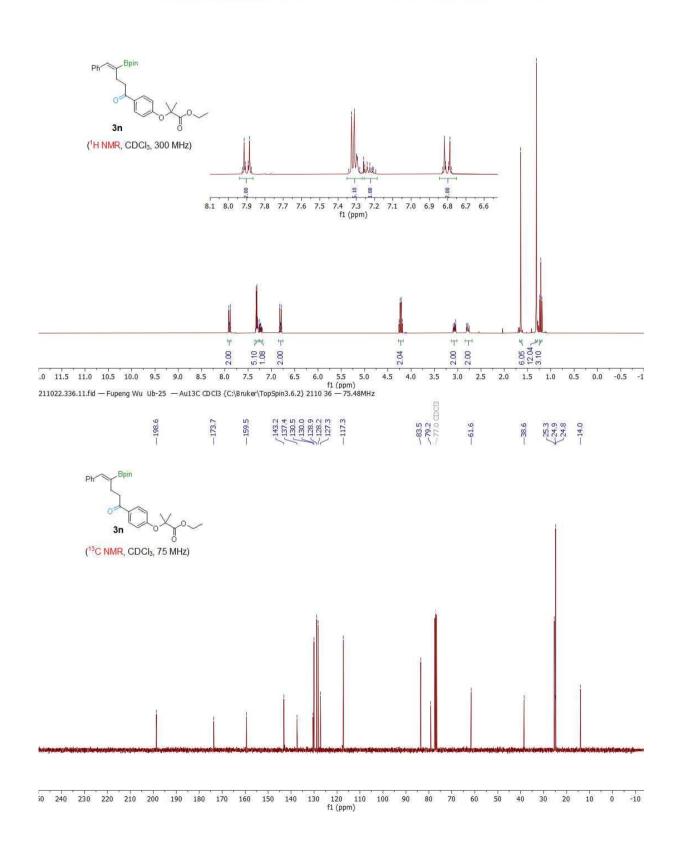
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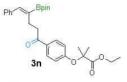




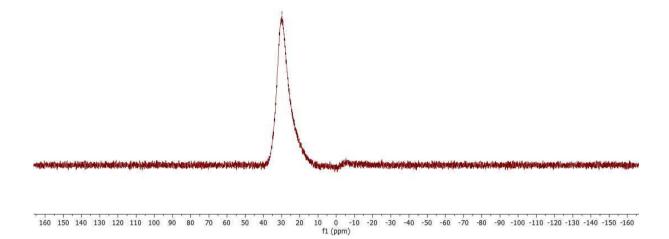


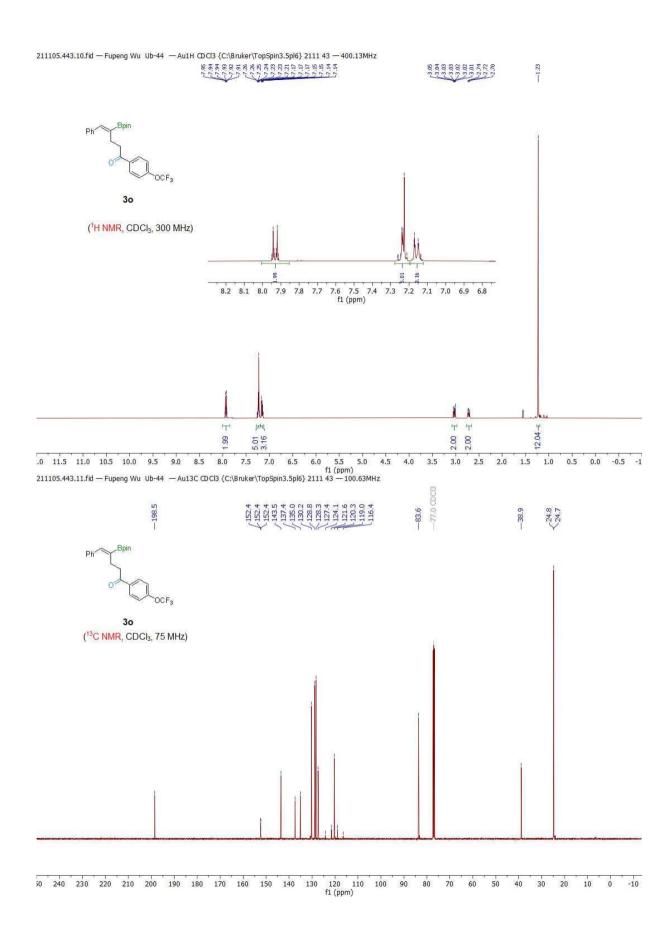






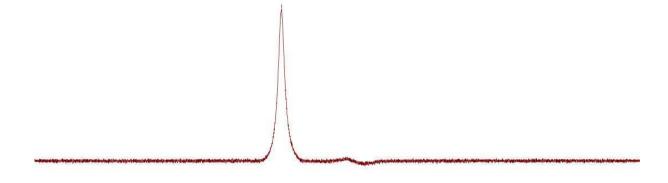
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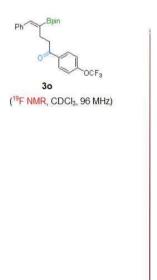




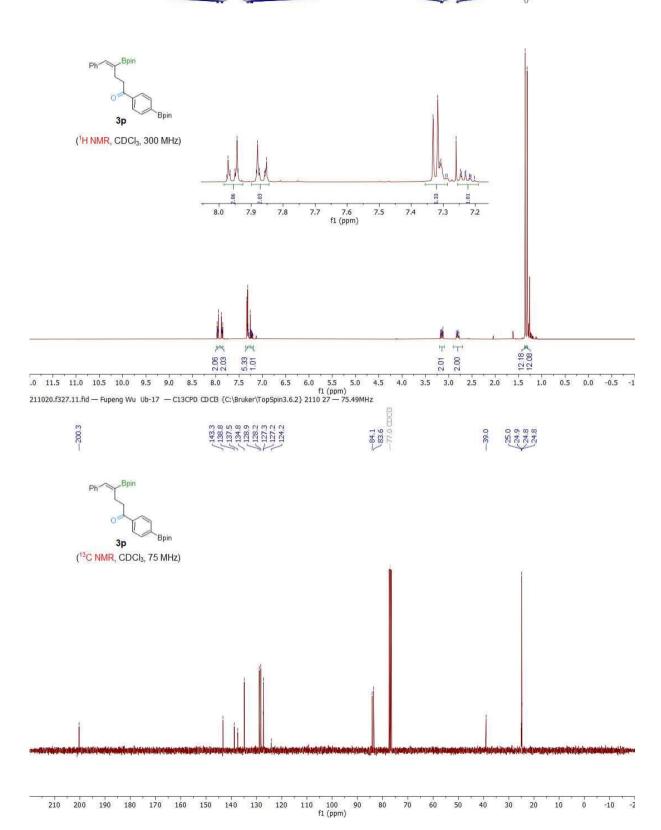


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--57.6

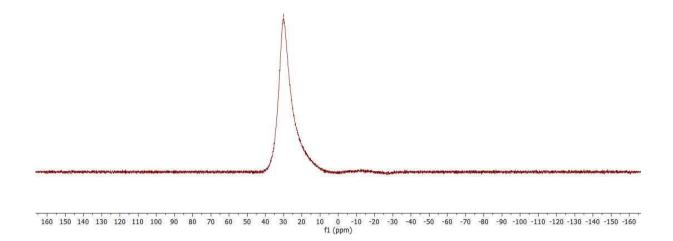


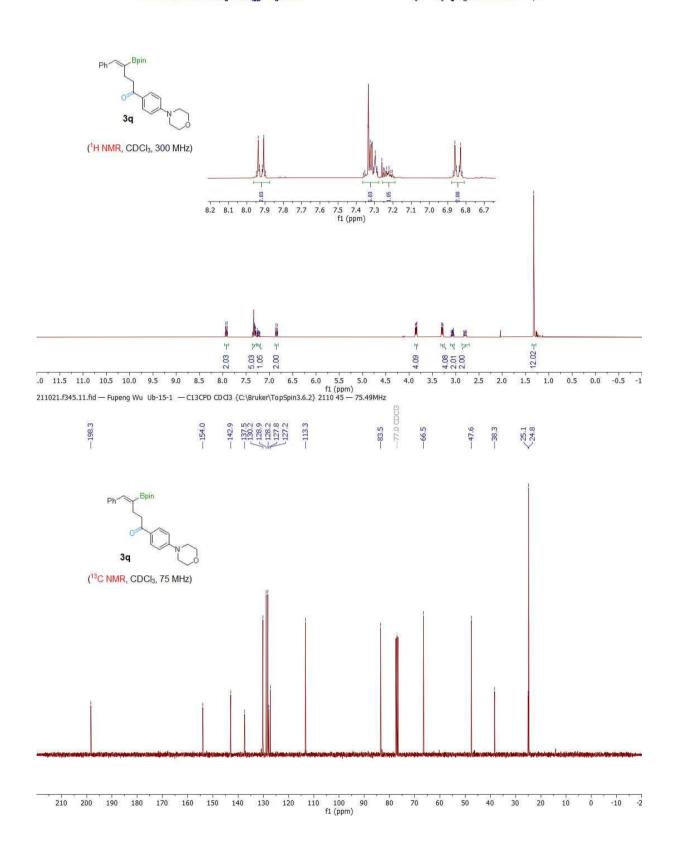
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 fl (ppm)





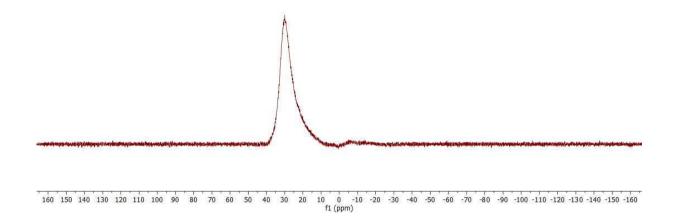


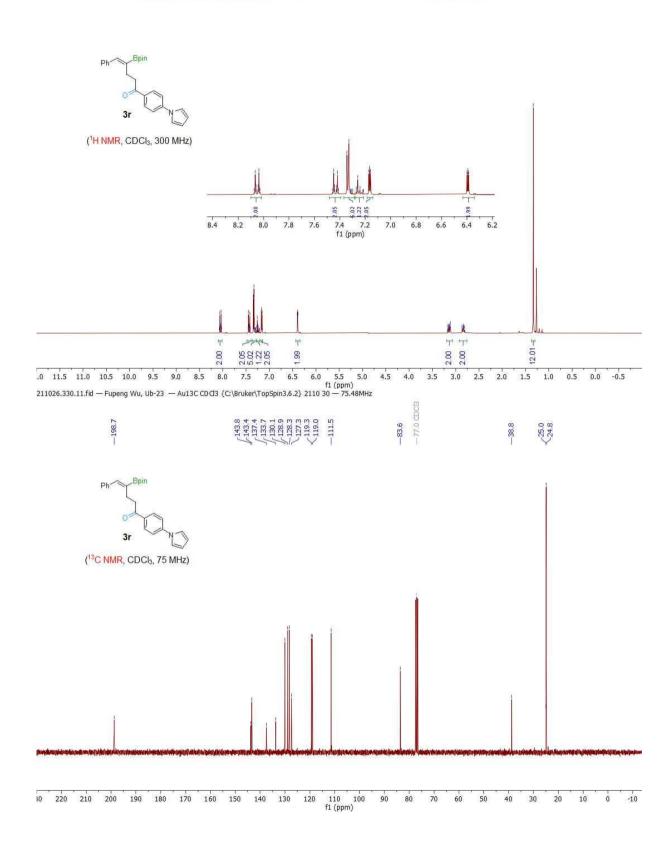


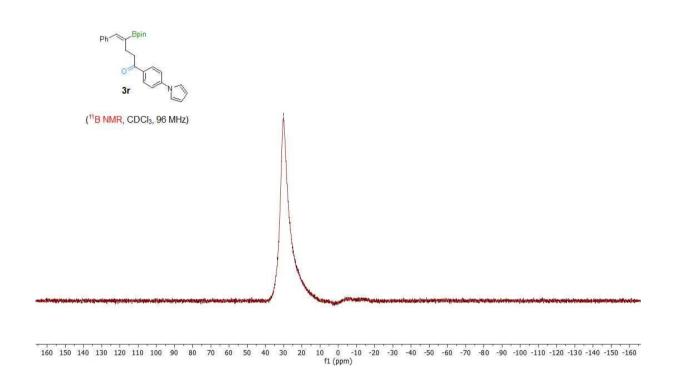


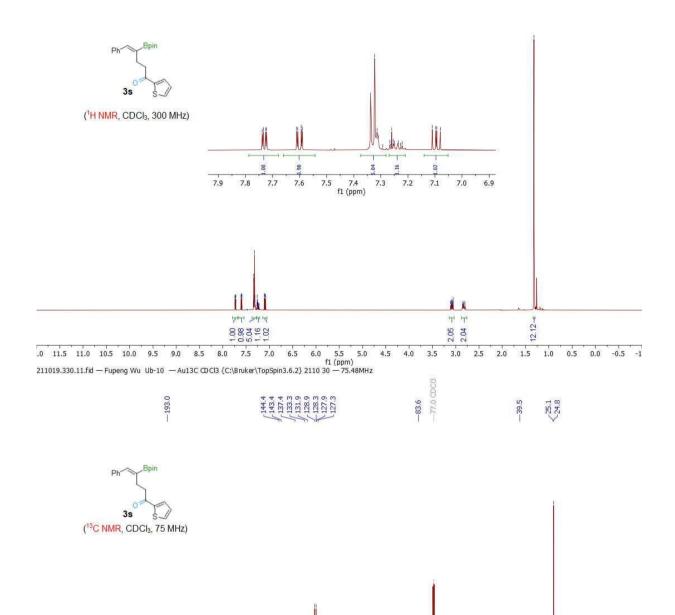
211021.f345.12.fid — Fupeng Wu Ub-15-1 — 118 CDCl3 {C:\Bruker\TopSpin3.6.2} 2110 45 — 96.32MHz $\stackrel{\bigcirc}{\text{S}}$

(11B NMR, CDCl₃, 96 MHz)





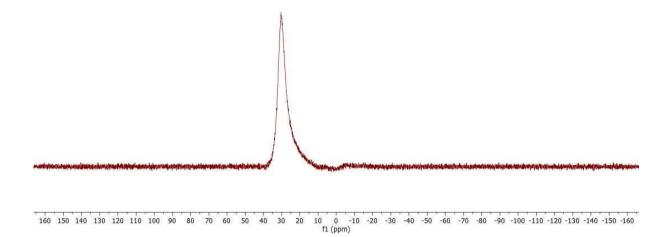


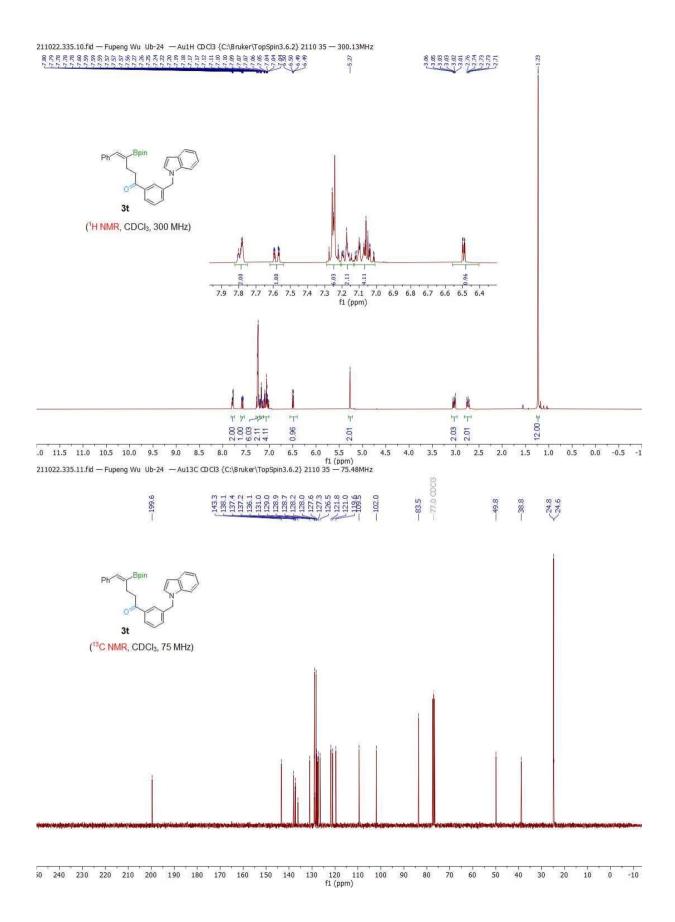


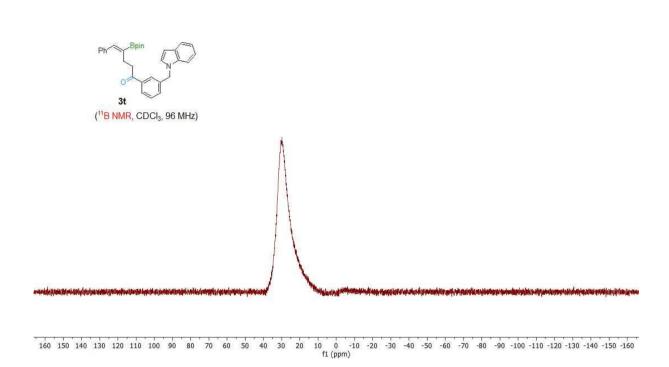
i0 240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 fl (ppm)

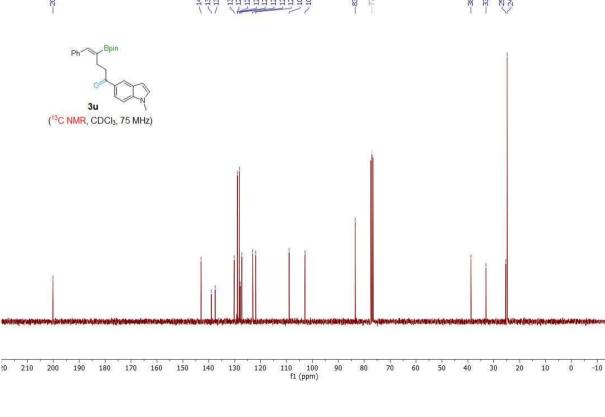


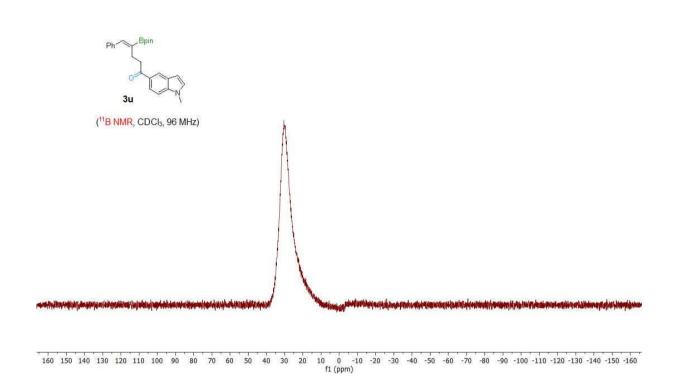
(11B NMR, CDCI₃, 96 MHz)

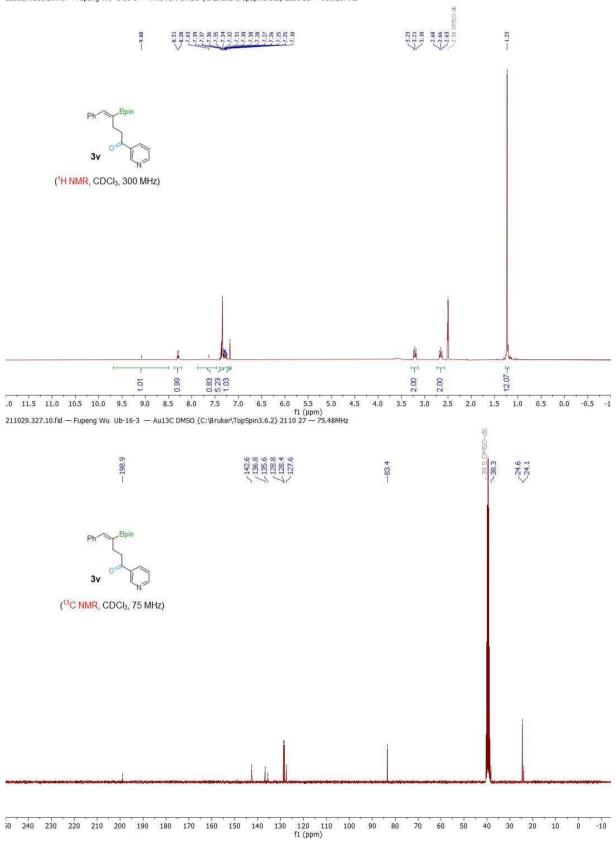


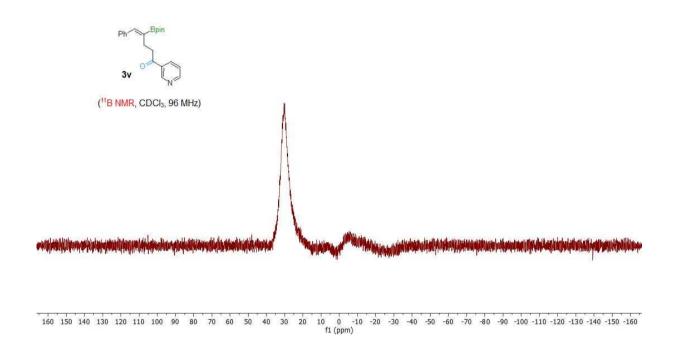


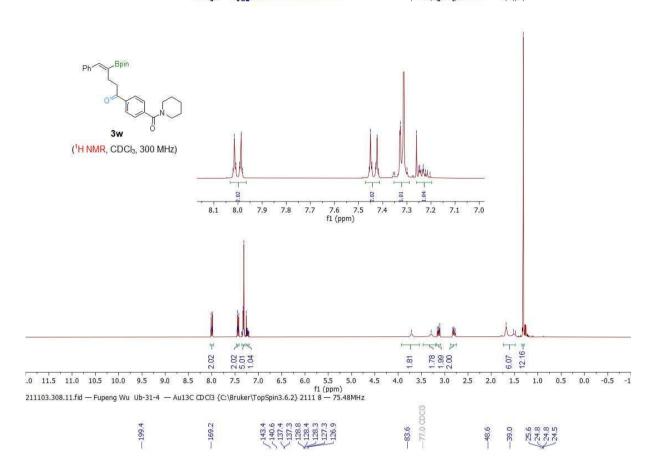


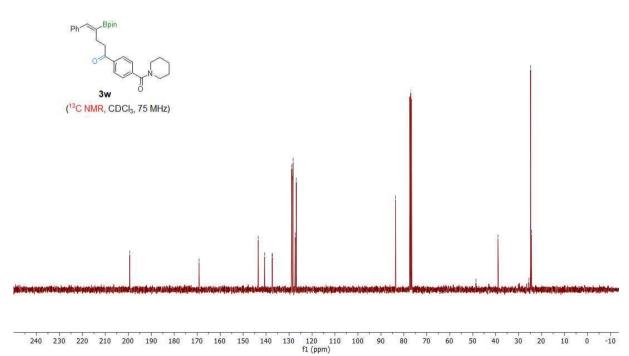


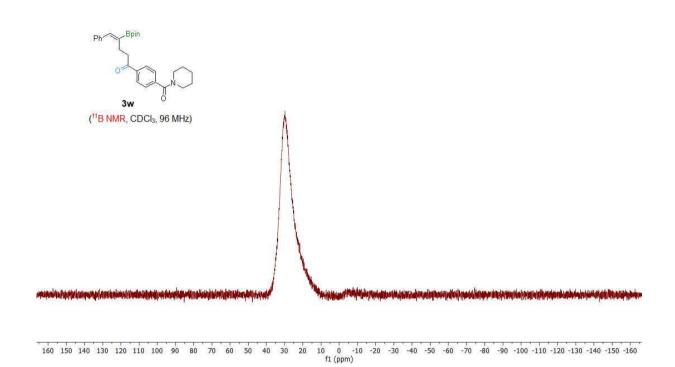


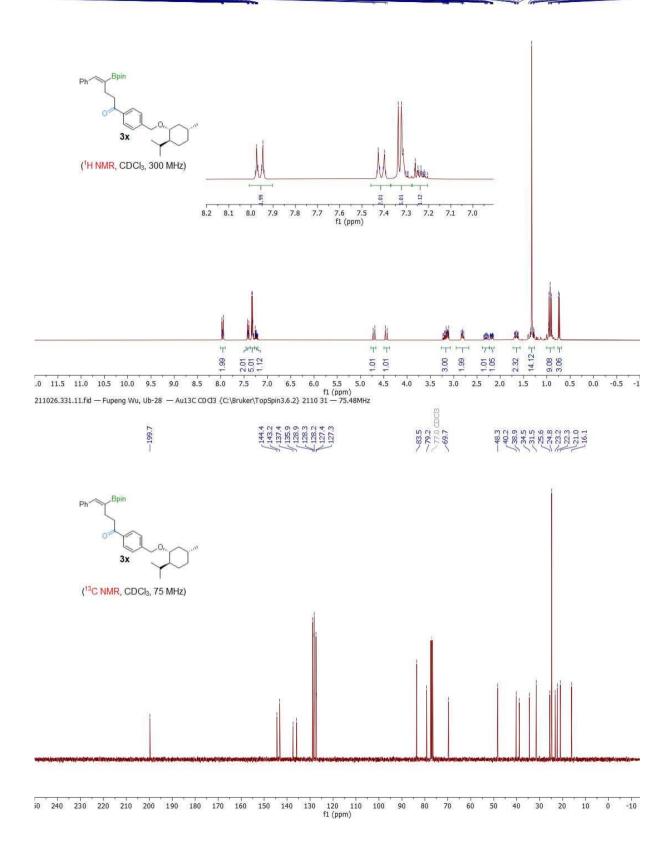


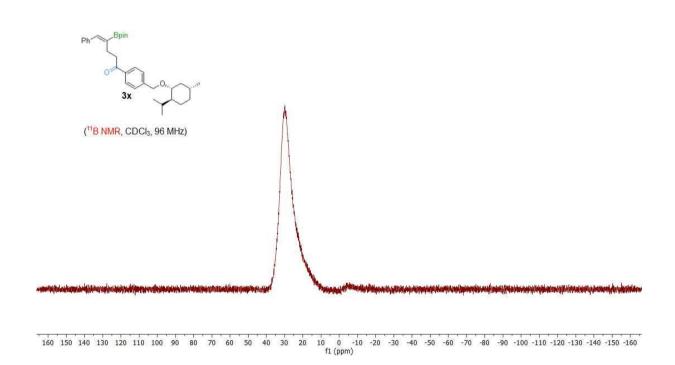


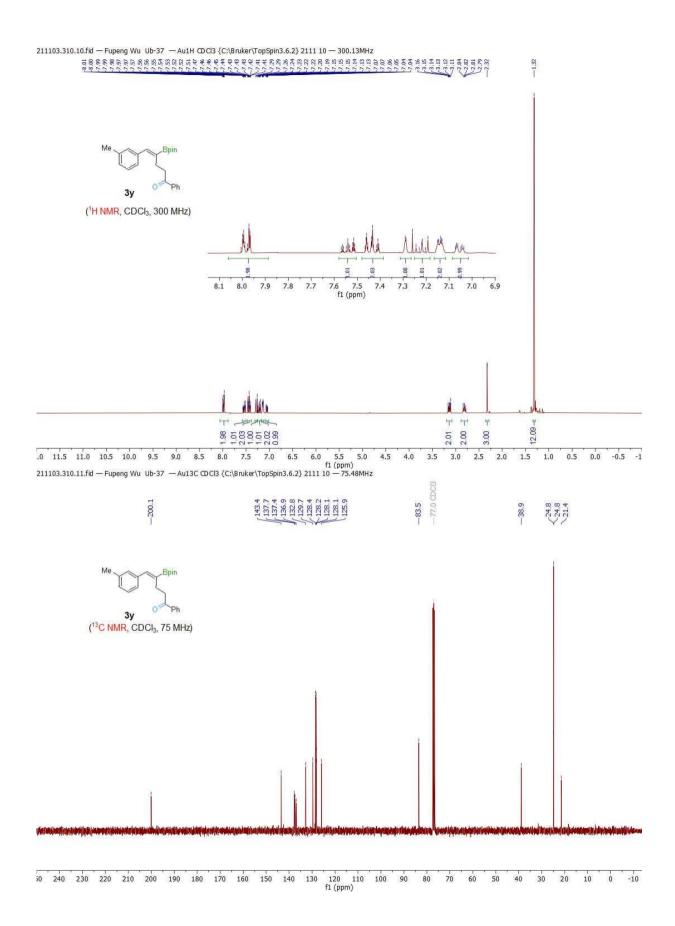




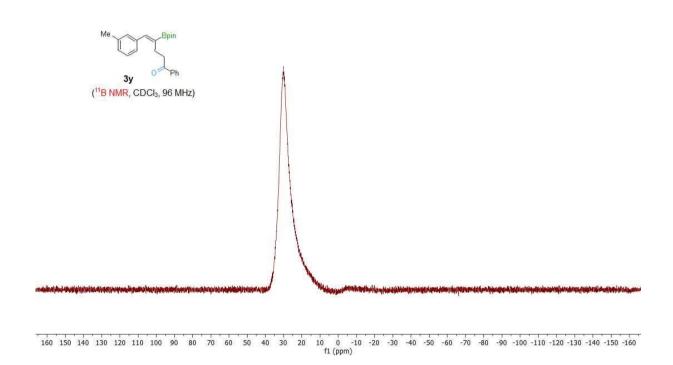


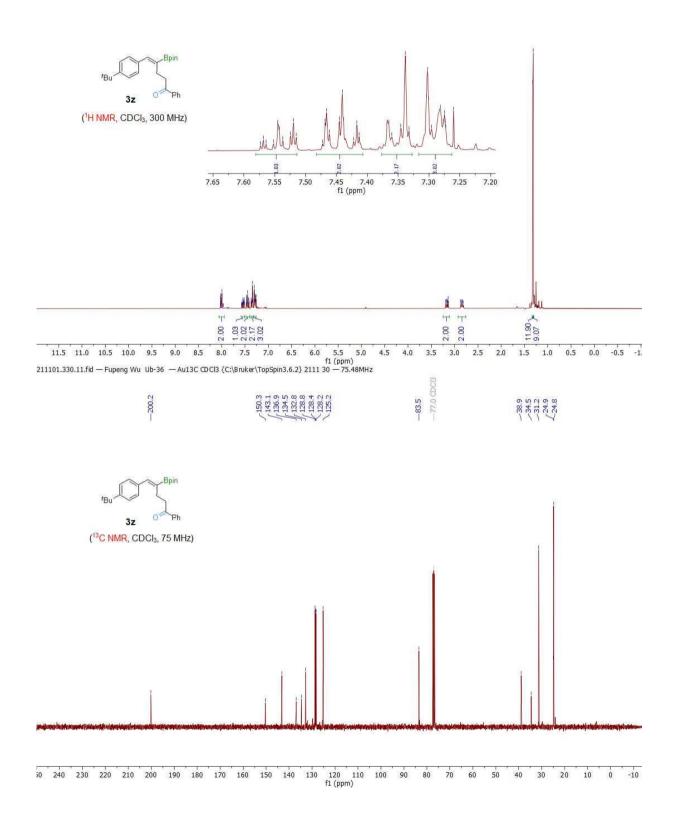








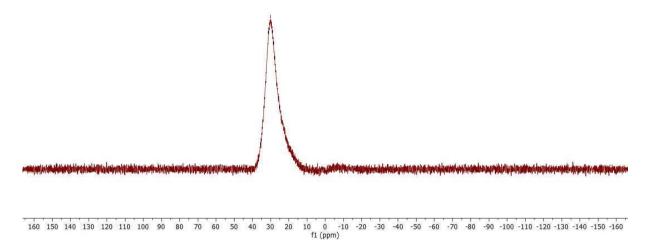


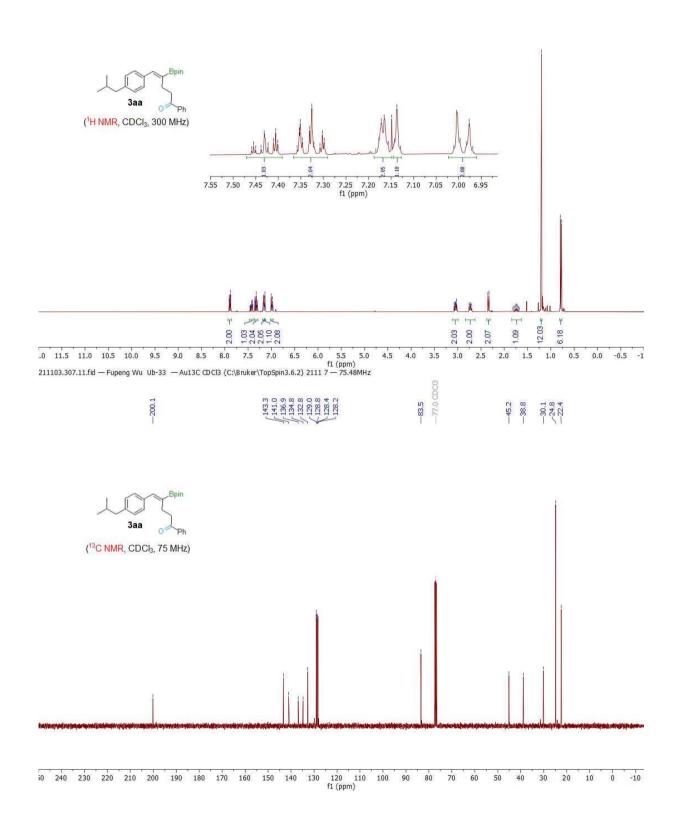


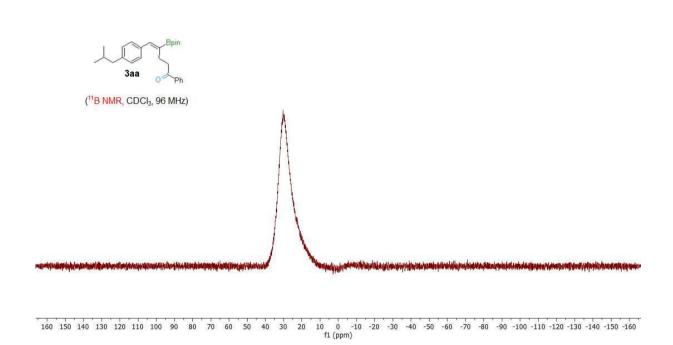


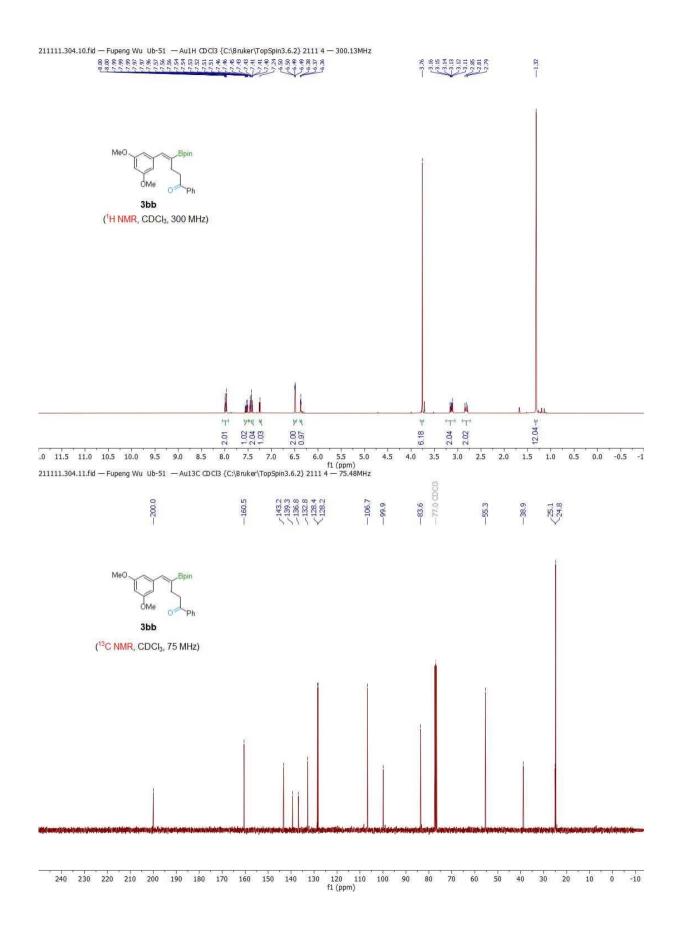


(11B NMR, CDCI₃, 96 MHz)



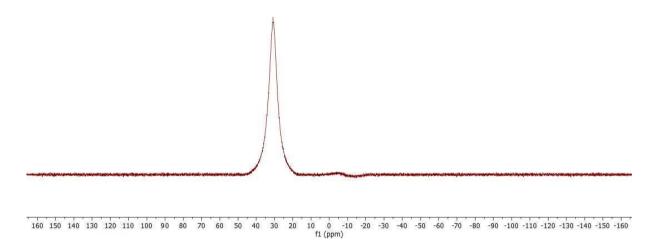


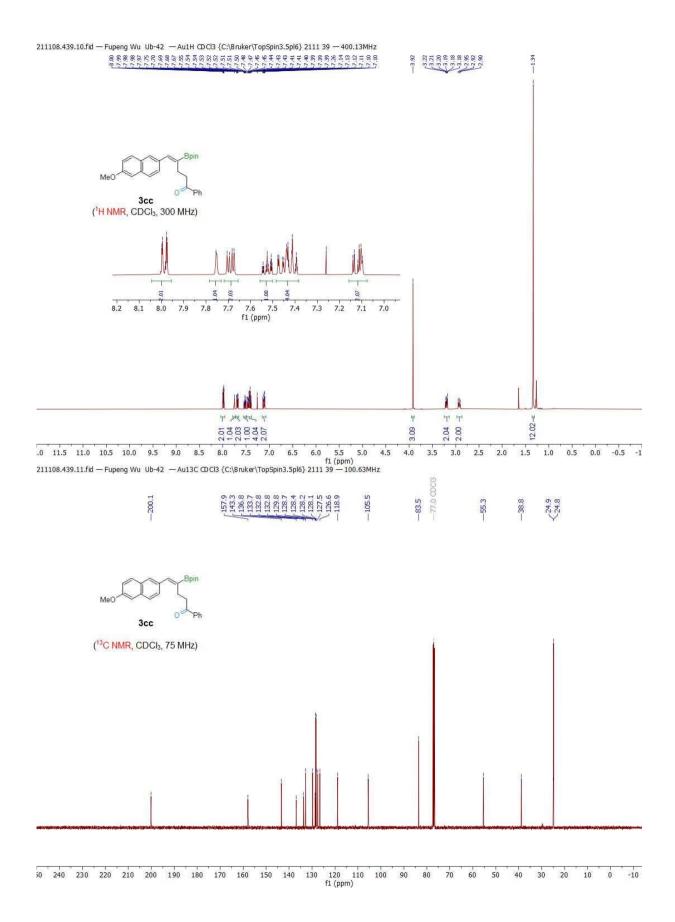


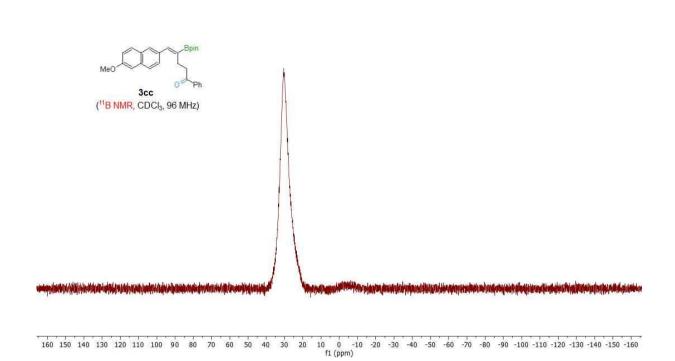


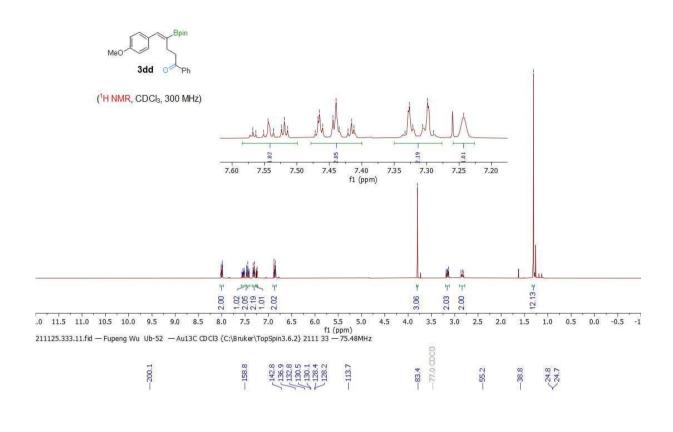


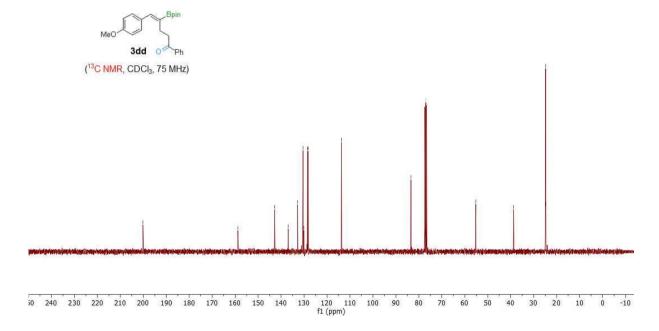


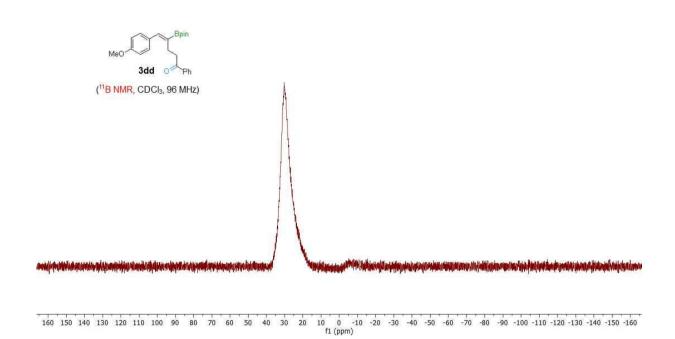








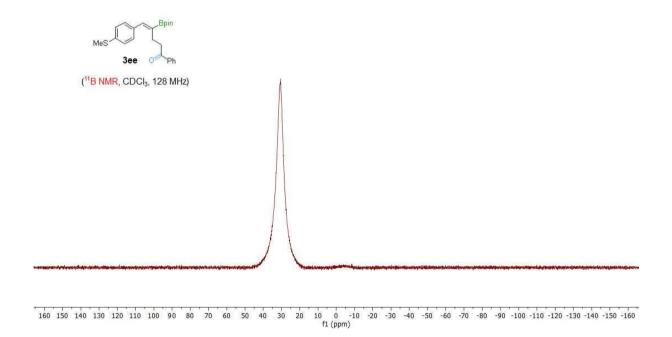


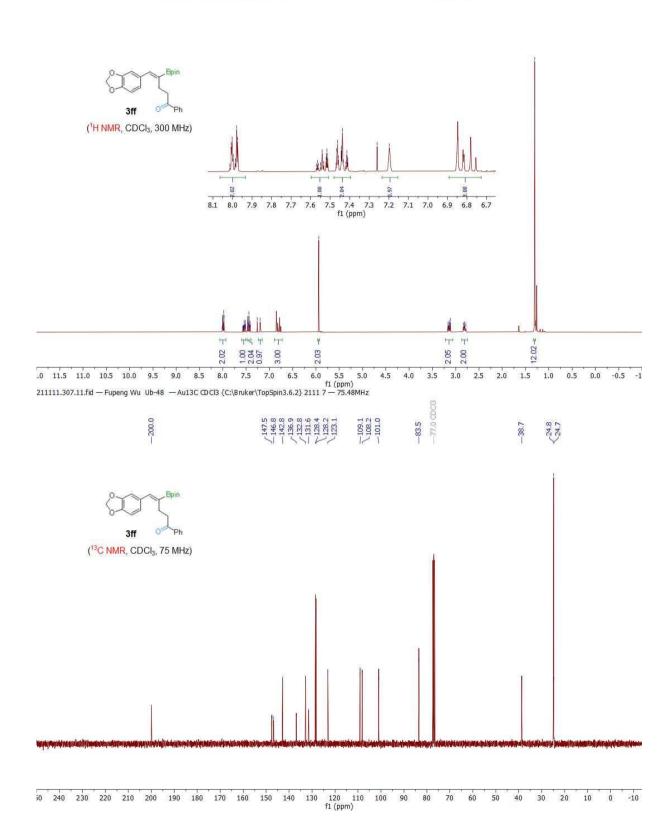


90 80

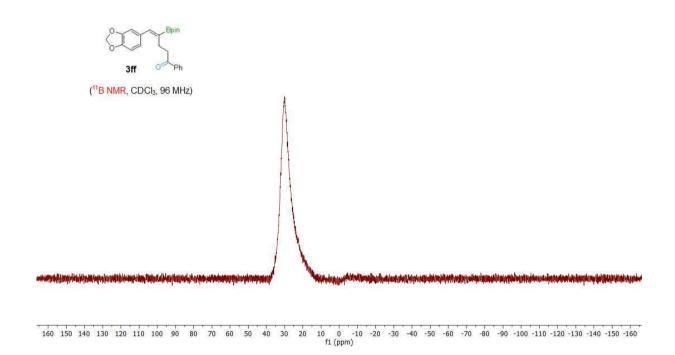
i0 240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 fl (ppm)

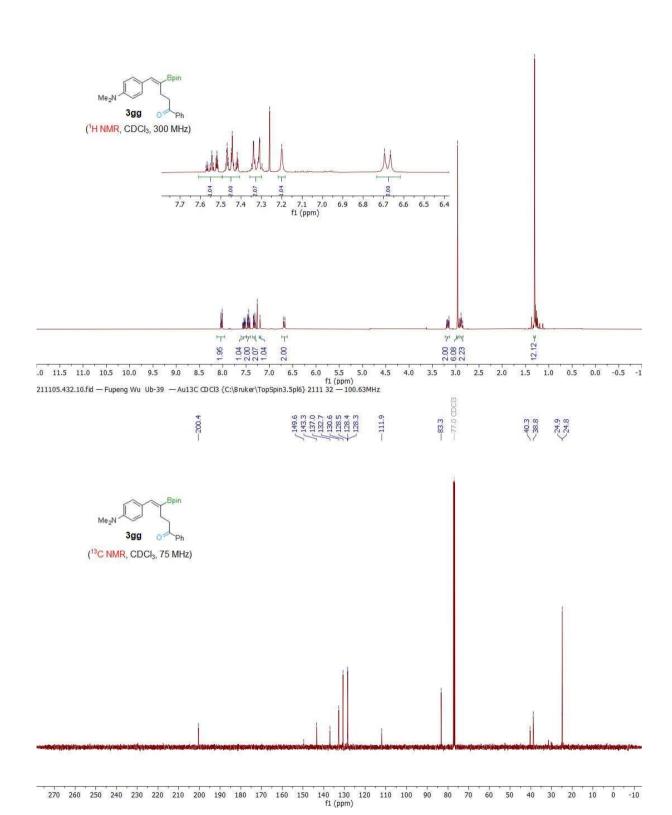








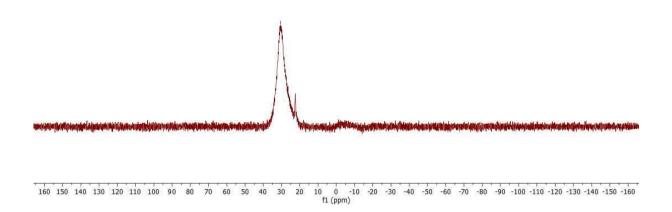




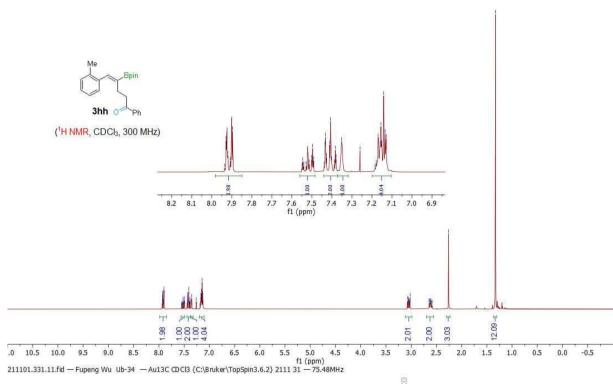
211105.432.11.fid — Fupeng Wu Ub-39 — Au11B CDCl3 {C:\Bruker\TopSpin3.5pl6} 2111 32 — 128.38MHz



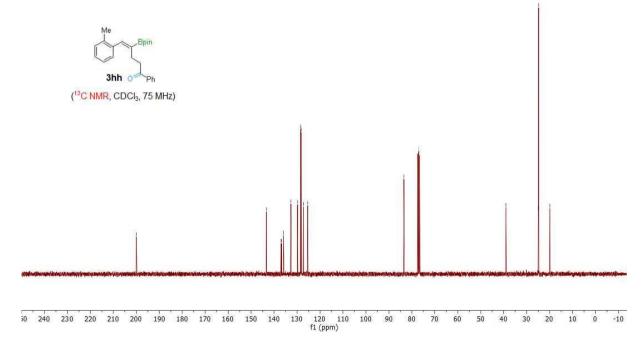
(11B NMR, CDCI3, 96 MHz)



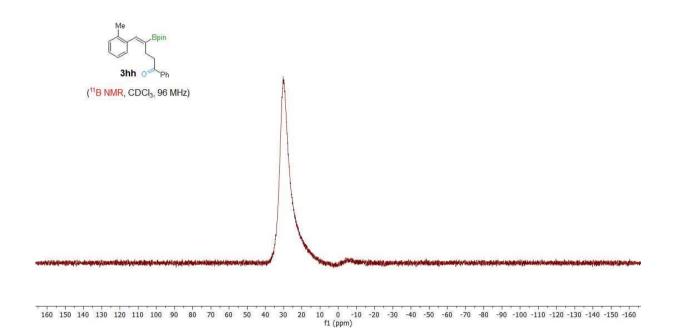


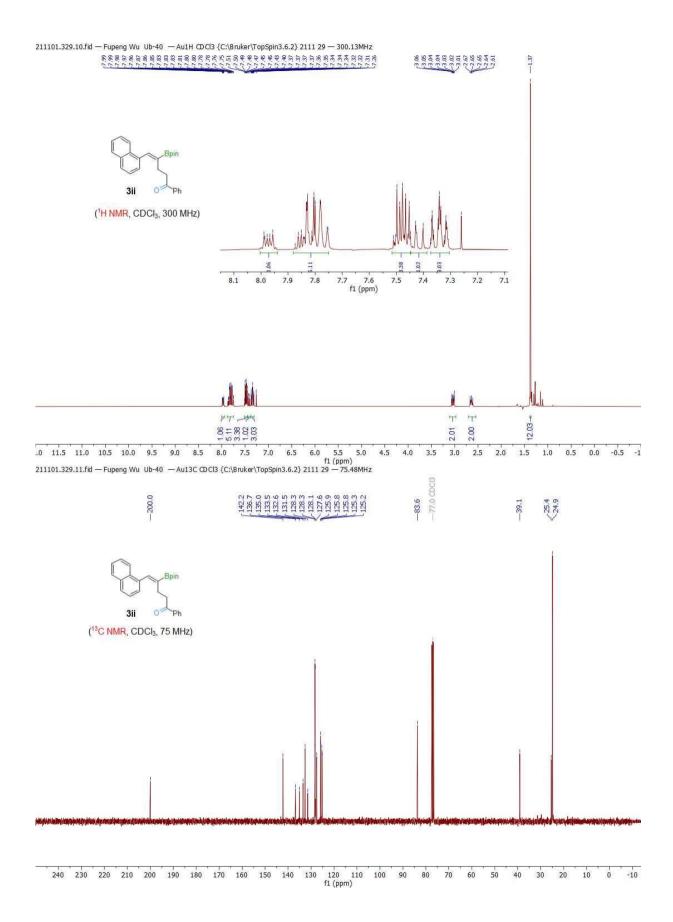


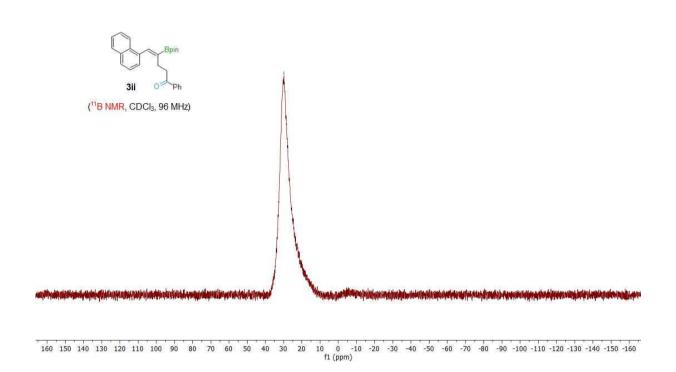


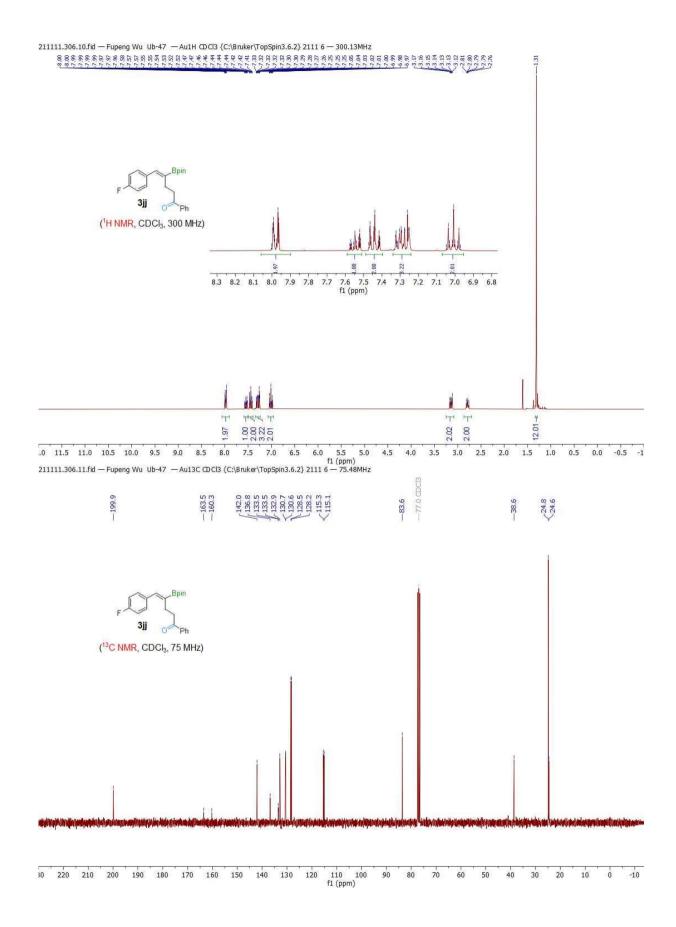




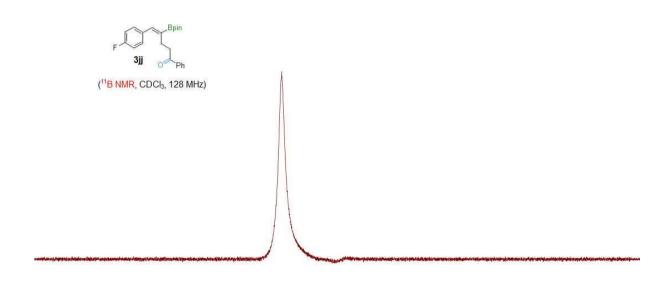












160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 f1 (ppm)
211111.306.12.fid — Fupeng Wu Ub-47 — Au19F CDCI3 {C:\Bruker\TopSpin3.6.2} 2111 6 — 282.39MHz

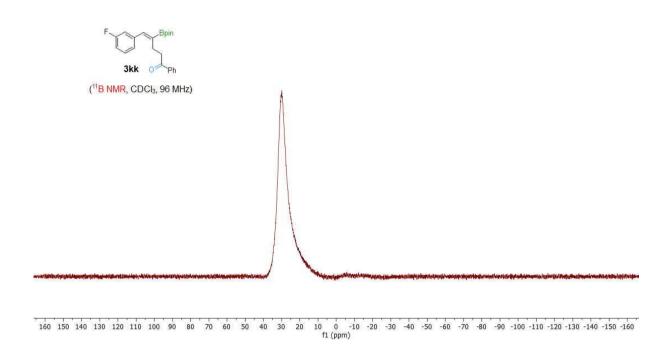


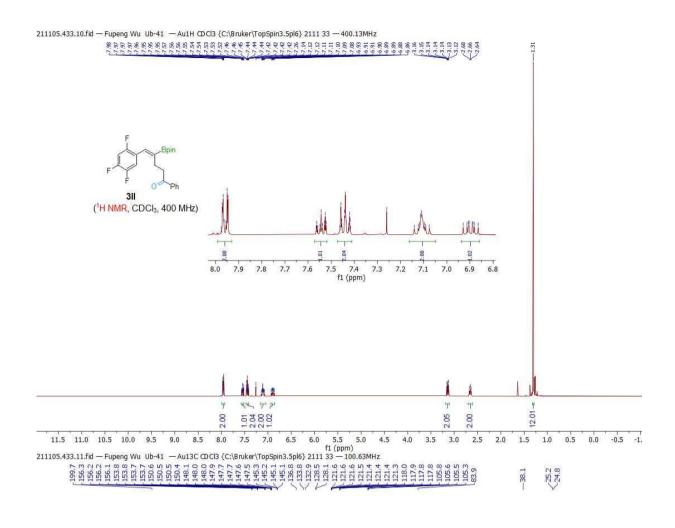
(19F NMR, CDCI₃, 282 MHz)

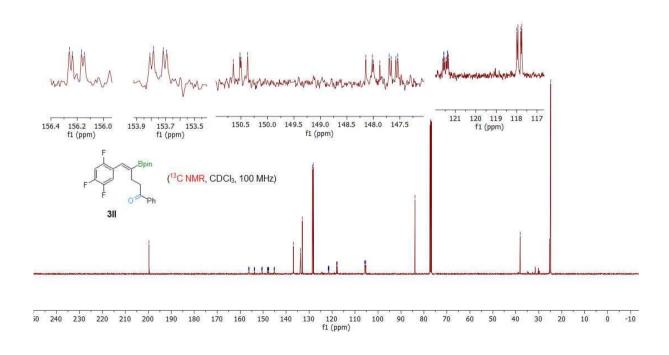
120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 f1 (ppm)

60

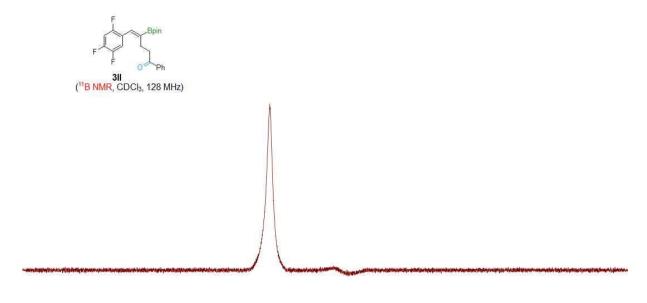
240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 fl (ppm)





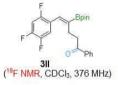


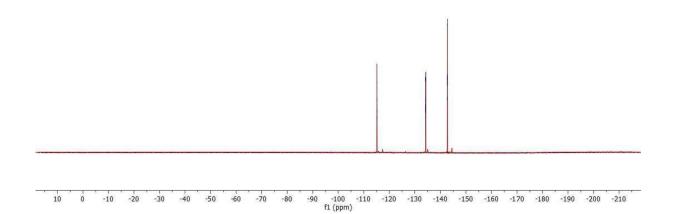


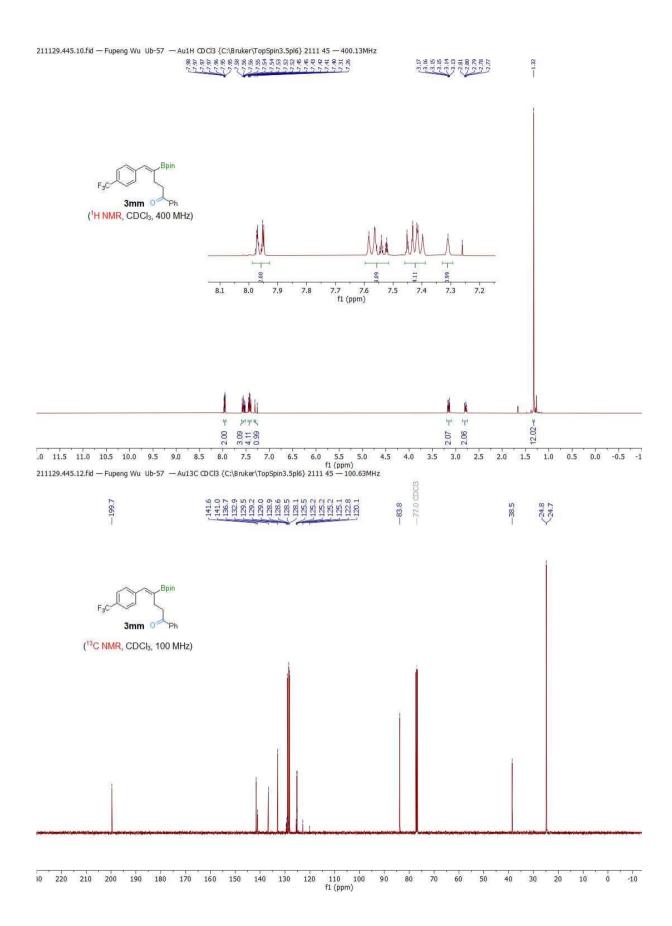


160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 f1 (ppm)
211105.433.13.fid — Fupeng Wu Ub-41 — F19 CDCl3 {C:\Bruker\TopSpin3.5pl6} 2111 33 — 376.46MHz

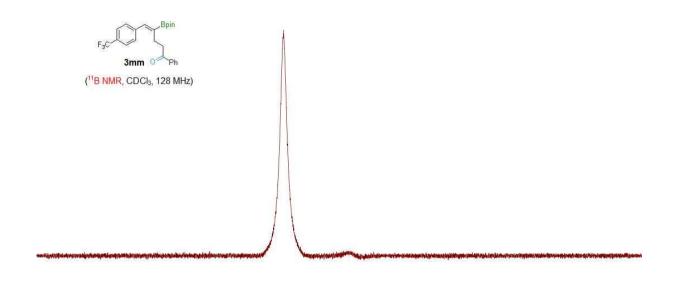








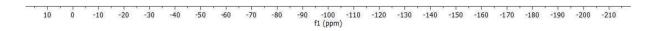


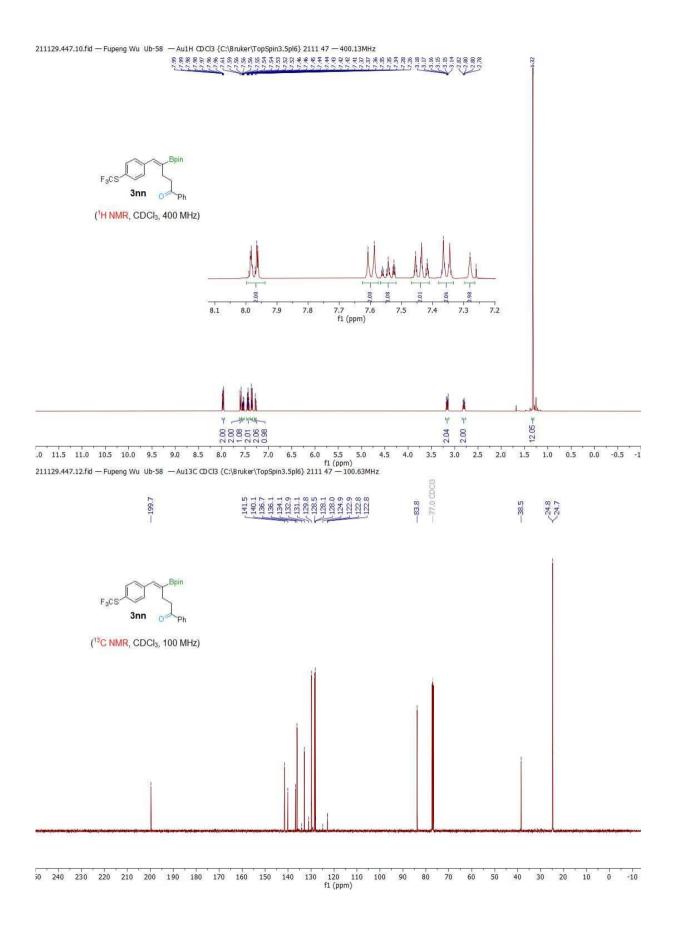


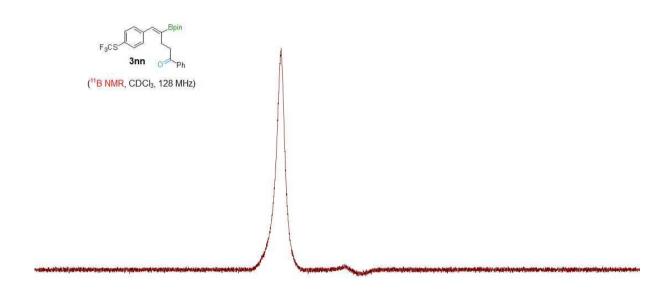
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 f1 (ppm)
211129,445,13,fld — Fupeng Wu Ub-57 — F19 CDCl3 {C:\Bruker\TopSpin3.5pl6} 2111 45 — 376.46MHz



(19F NMR, CDCl₃, 376 MHz)





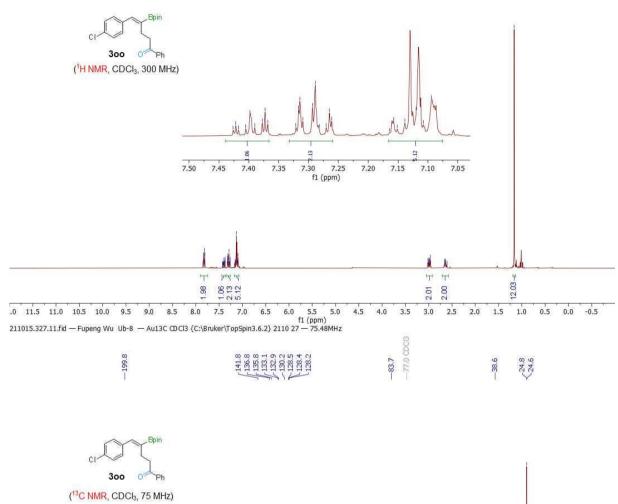


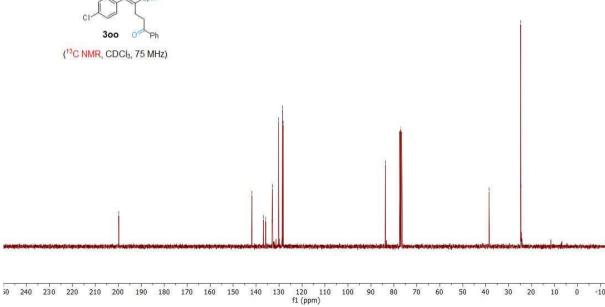
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 f1 (ppm)
211129.447,13.fld — Fupeng Wu Ub-58 — F19 CDCl3 {C:\Bruker\TopSpin3.5pl6} 2111 47 — 376.46MHz

F₃CS 3nn OPh

(19F NMR, CDCl₃, 376 MHz)

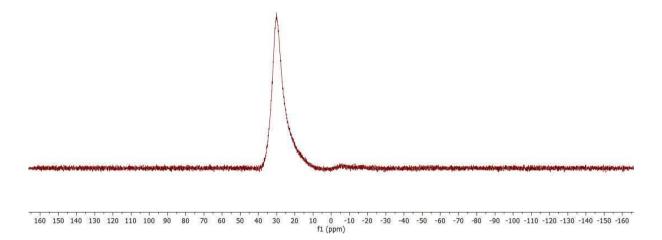
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 f1 (ppm)

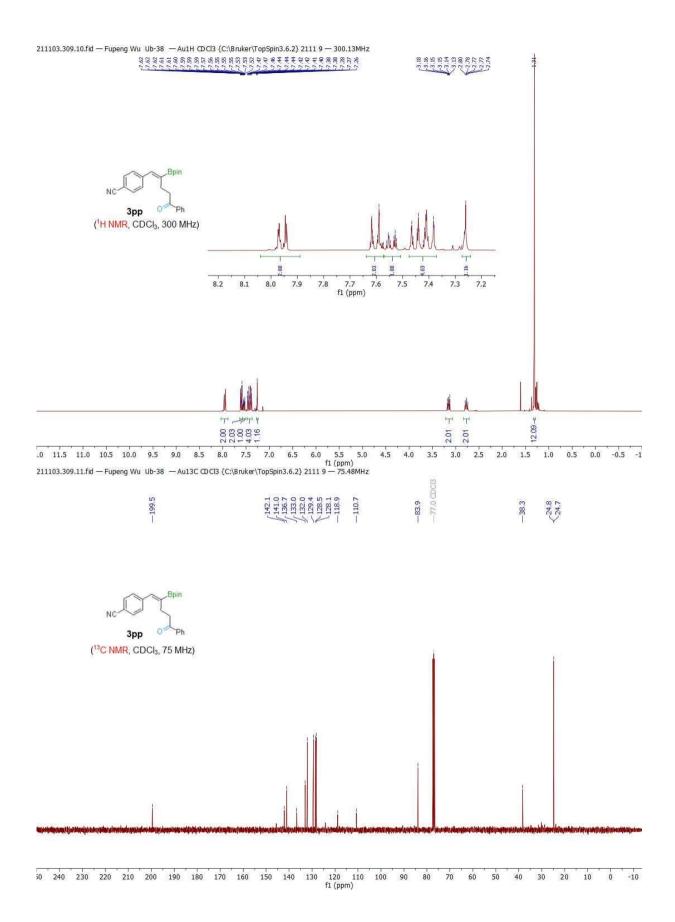


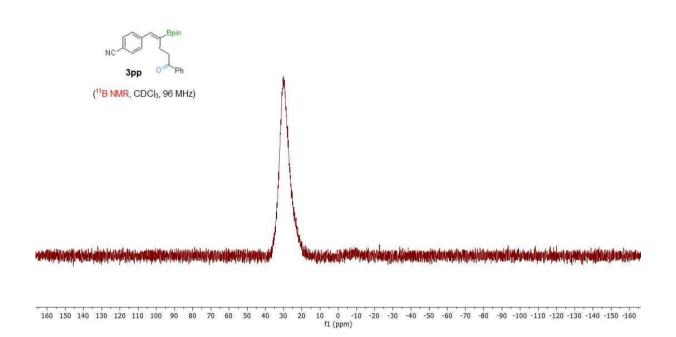


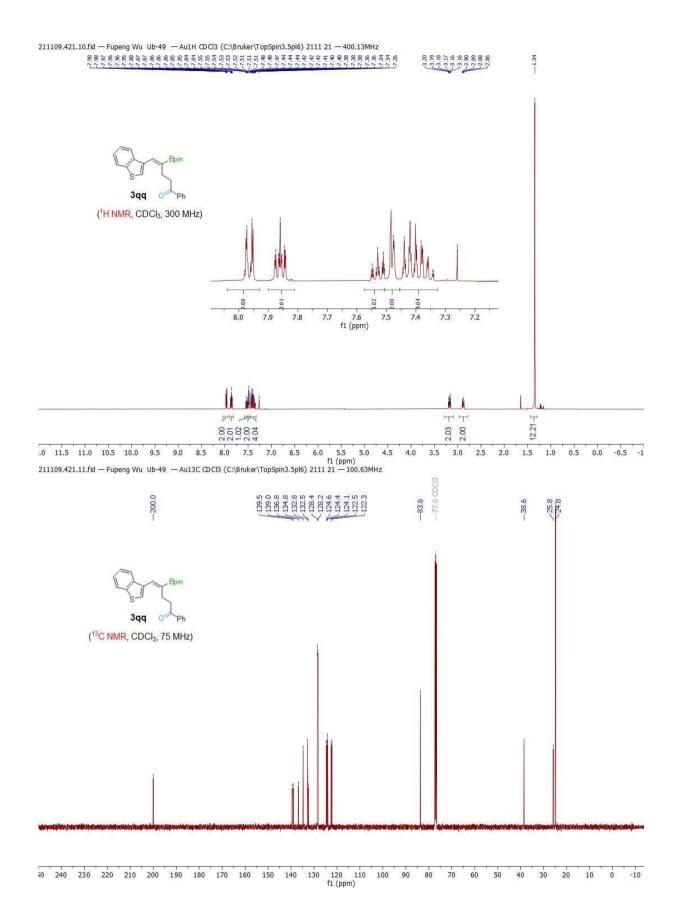


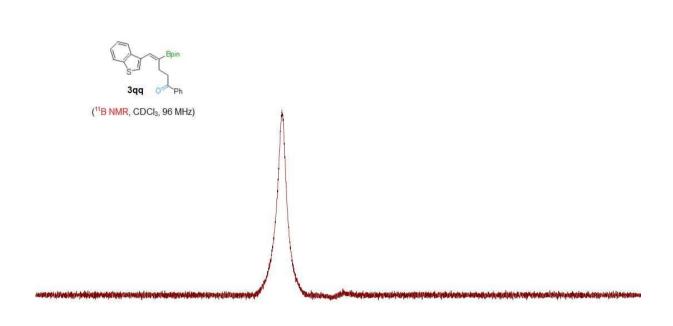
(11B NMR, CDCl₃, 96 MHz)



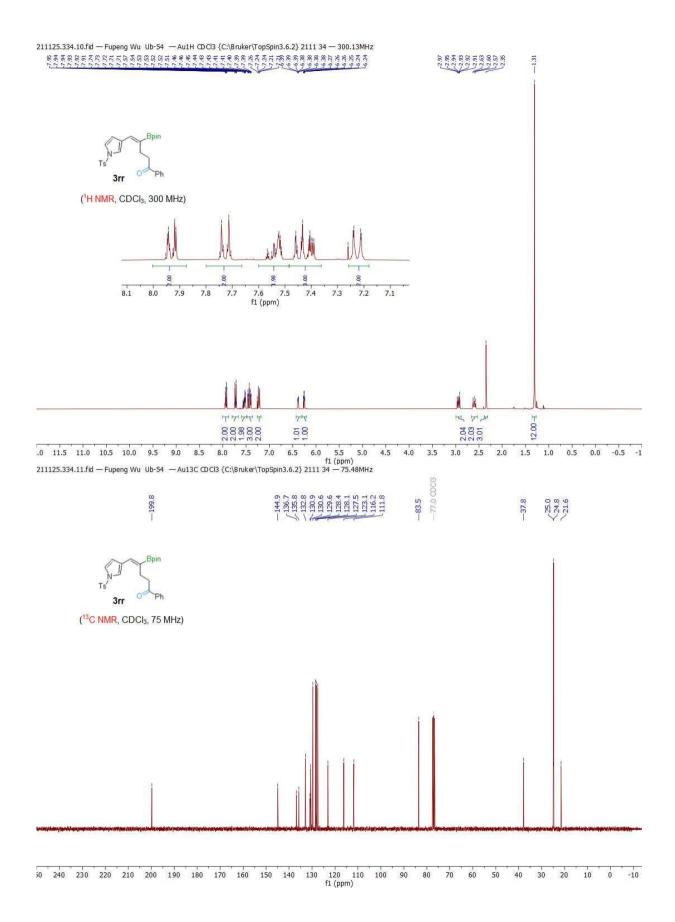


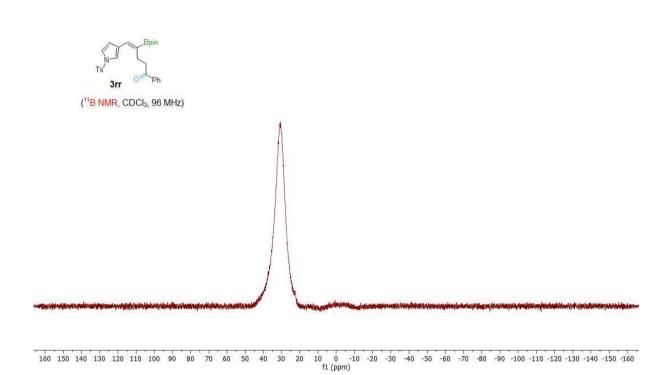




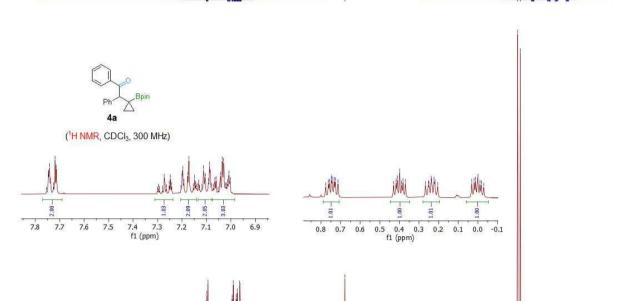


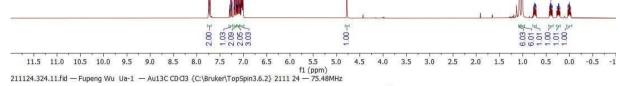
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 fi (ppm)



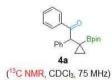


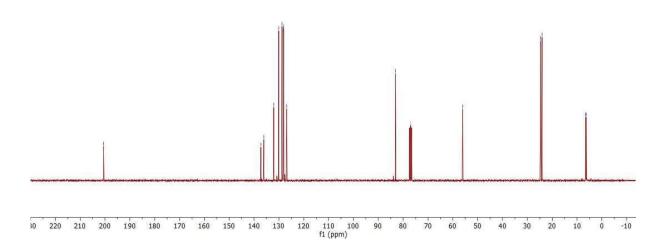




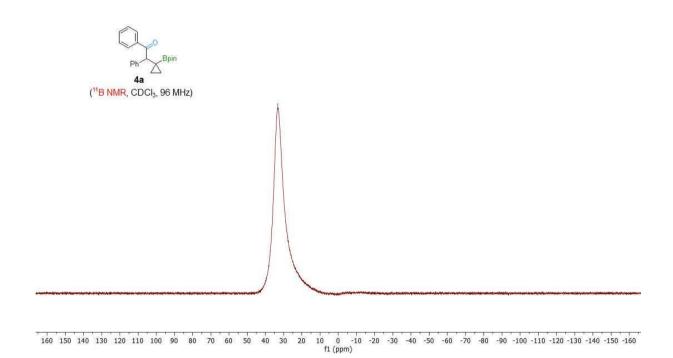


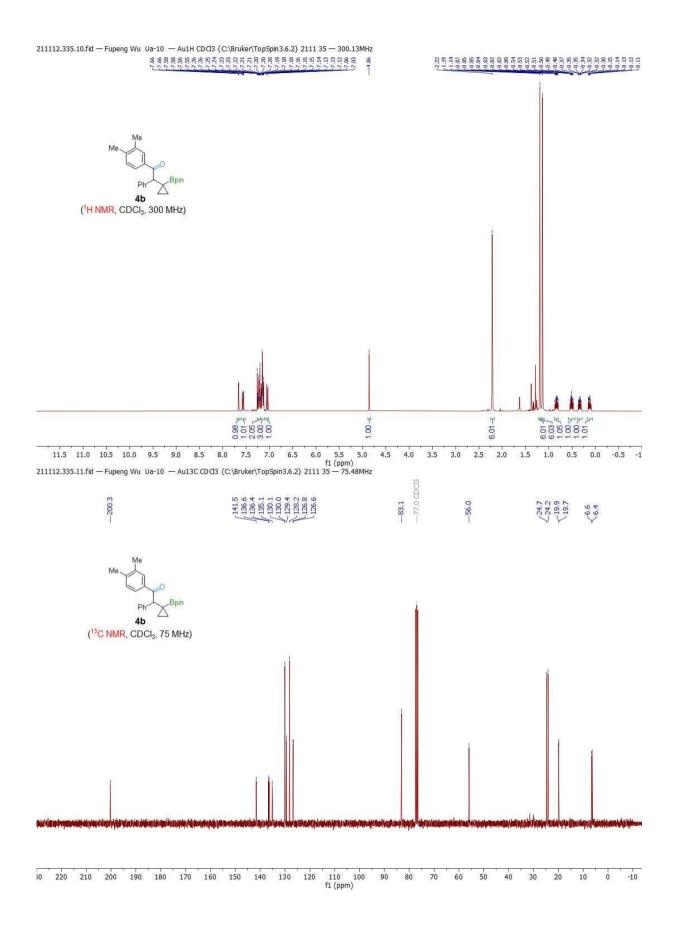
137.3 137.3 137.3 130.1 128.1 128.1 128.2 128.1 128.9 128.9 128.9 128.9 128.9 128.9 128.9 128.9 128.9 128.9 128.7 128.9 128.9 128.9 128.9 128.9 128.9 128.9 128.9 128.7 128.9 12



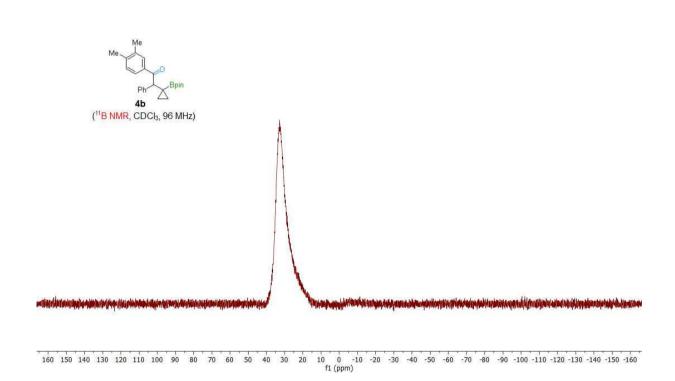


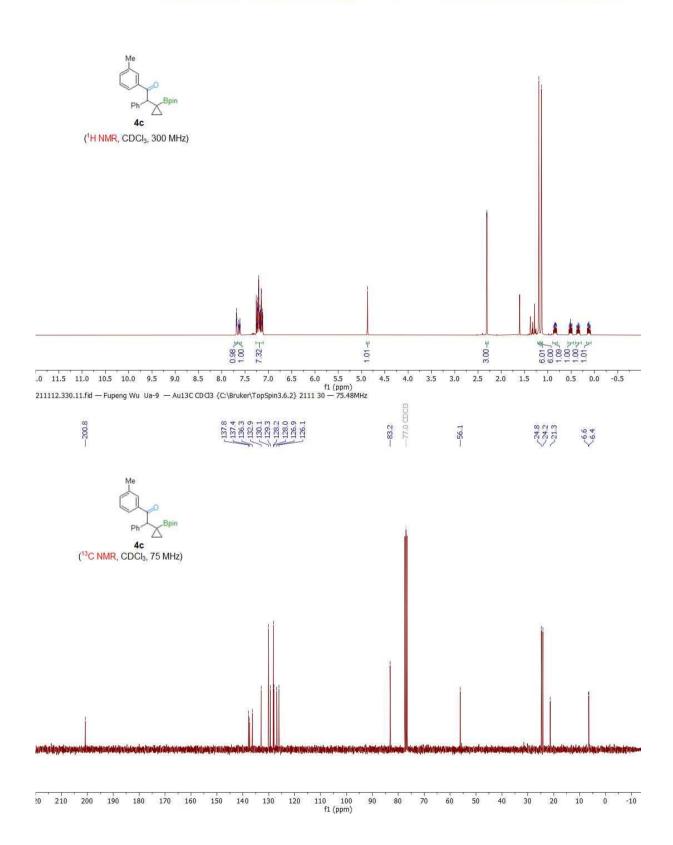


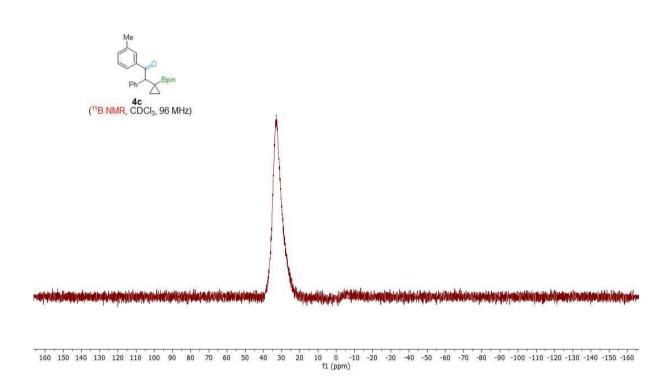


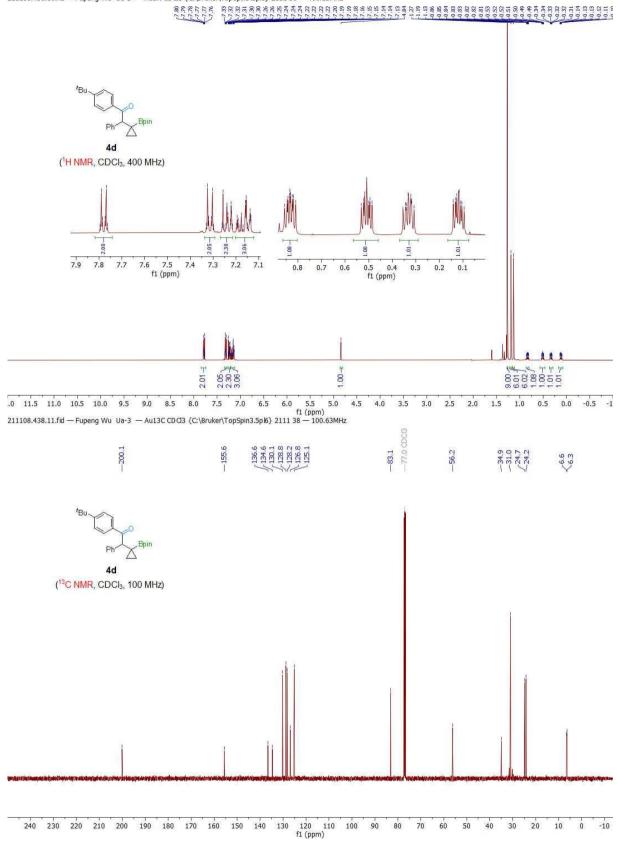




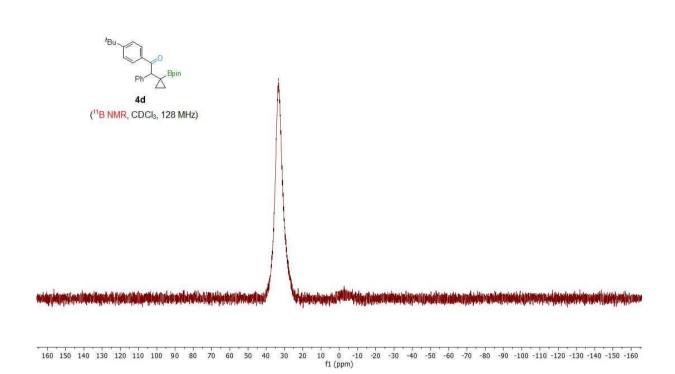


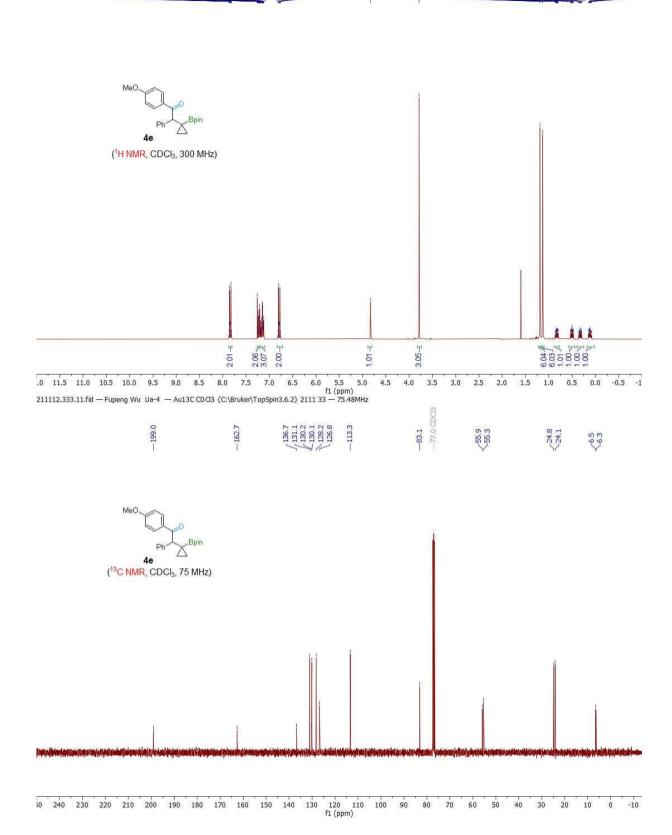


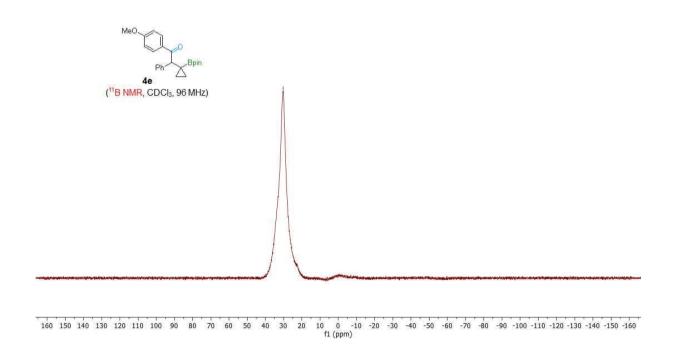


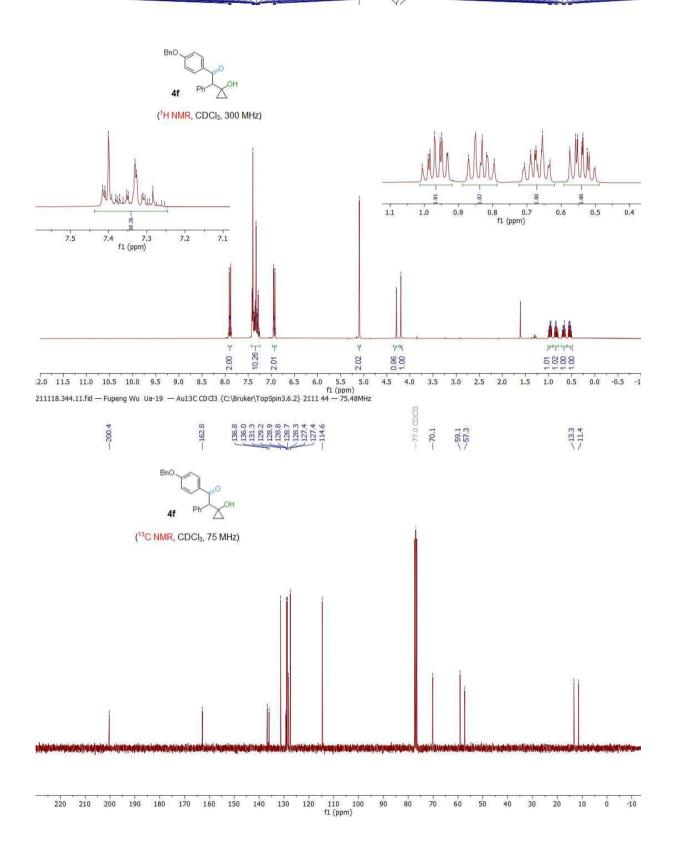


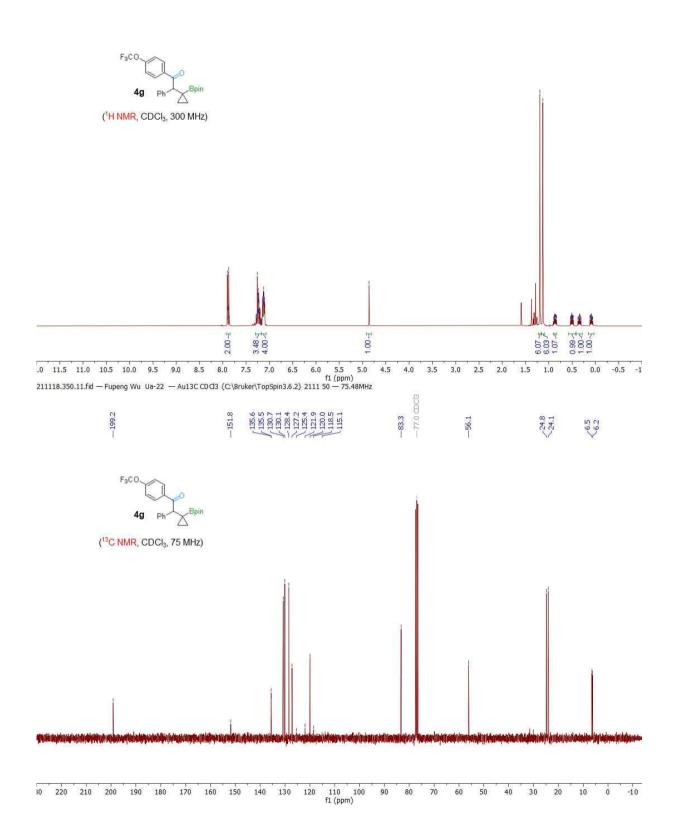






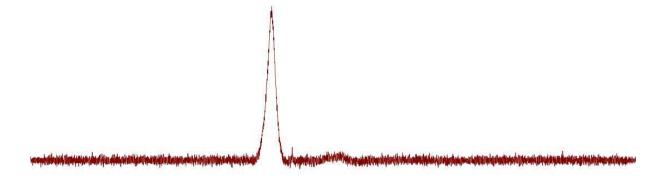








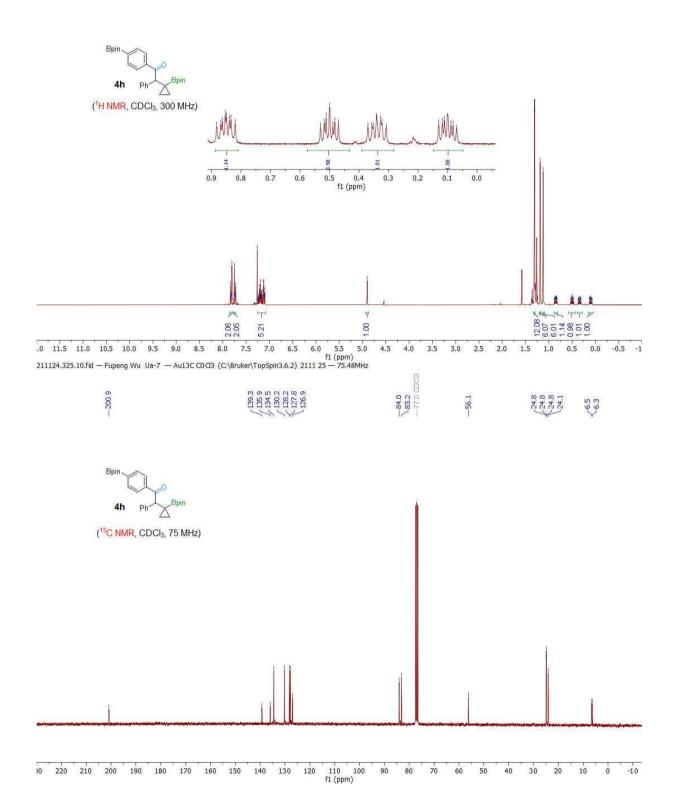
(11B NMR, CDCI₃, 96 MHz)

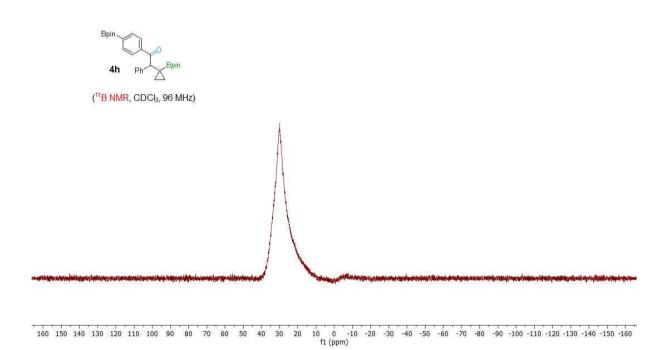


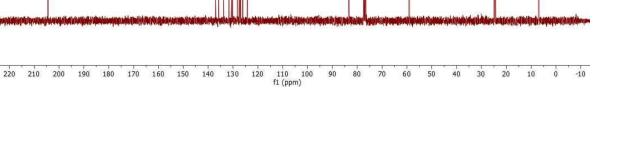
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 f1 (ppm)
211118.350,10,fld — Fupeng Wu Ua-22 — Au19F CDCI3 {C:\Bruken\TopSpin3.6.2} 2111 50 — 282,39MHz

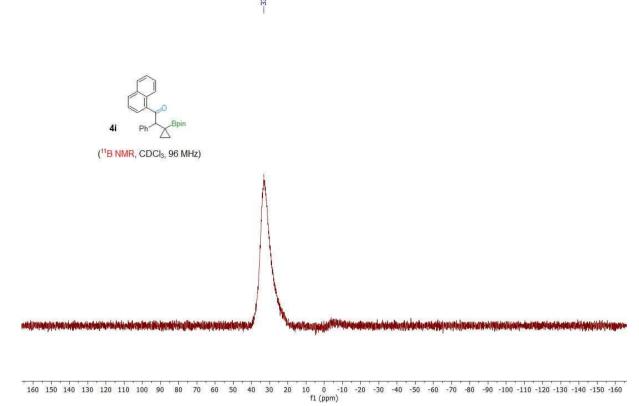
(19 F NMR, CDCI₃, 282 MHz)

120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 f1 (ppm)

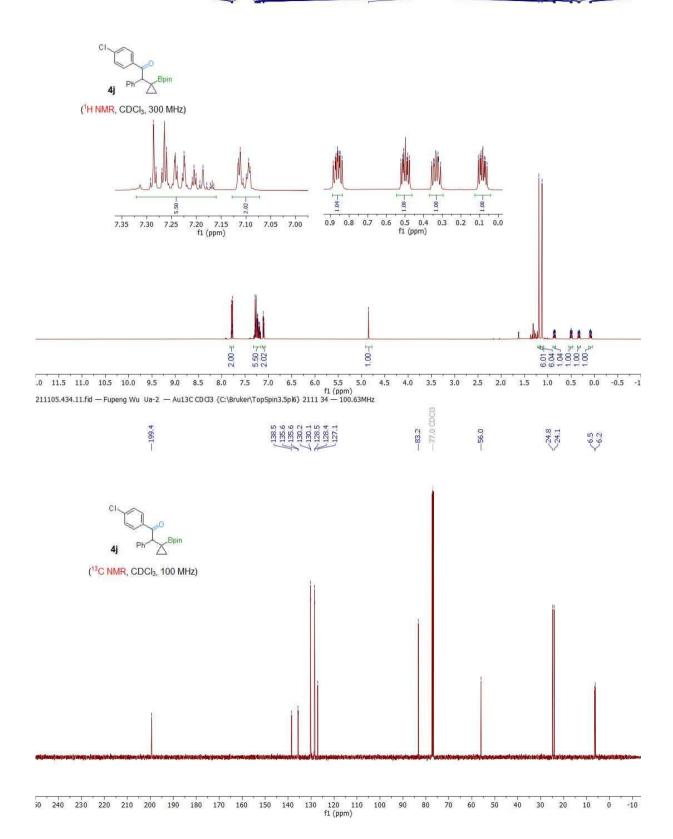




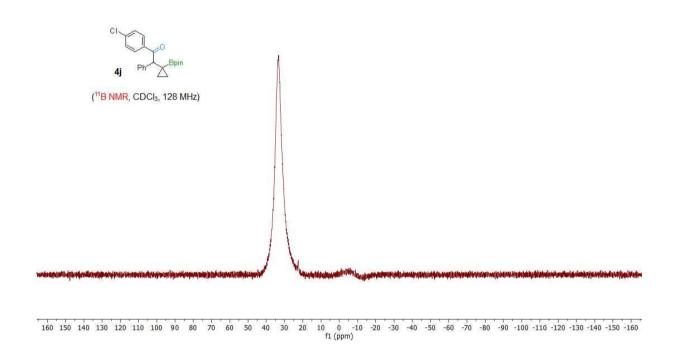


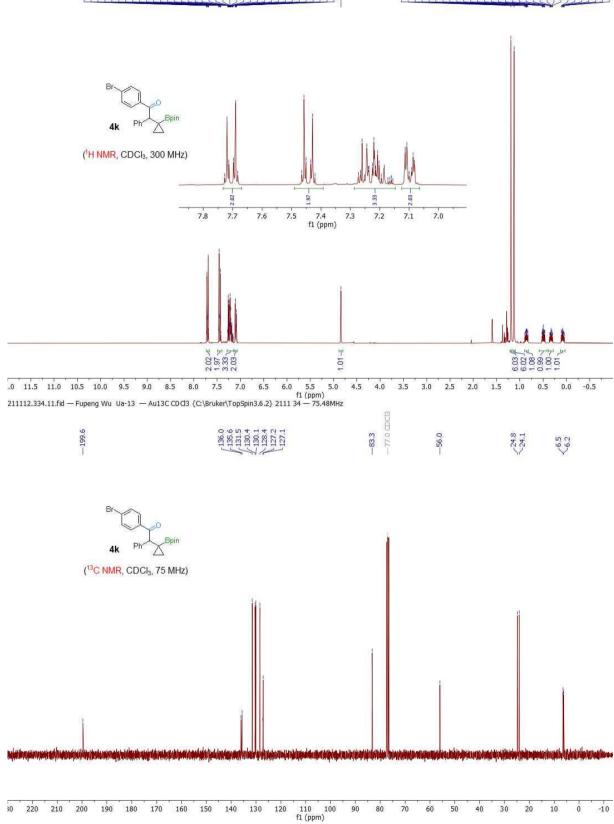




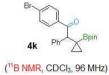


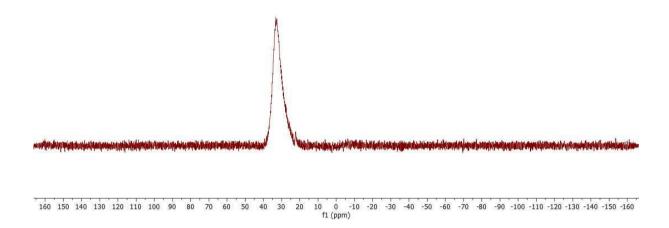




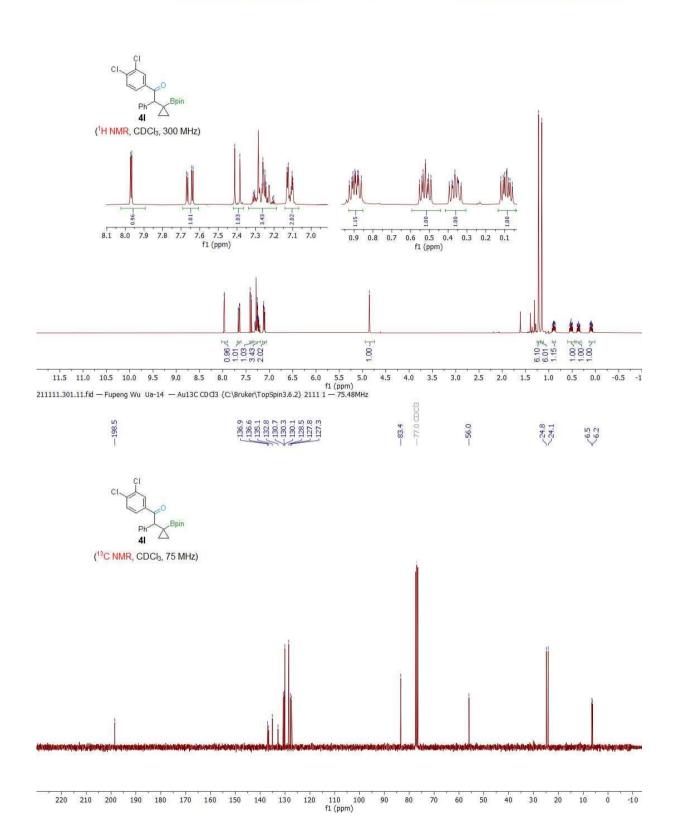


211112.334.12.fid — Fupeng Wu Ua-13 — Au118 CDCl3 {C:\Bruker\TopSpin3.6.2} 2111 34 — 96.29MHz $^{\rm Cl}_{\rm B}$



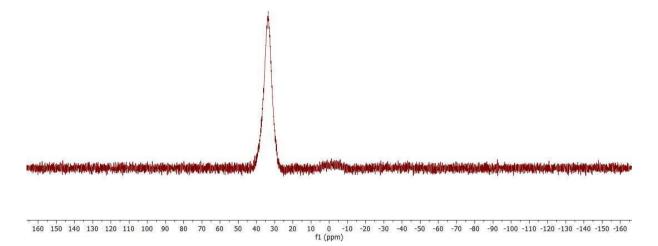


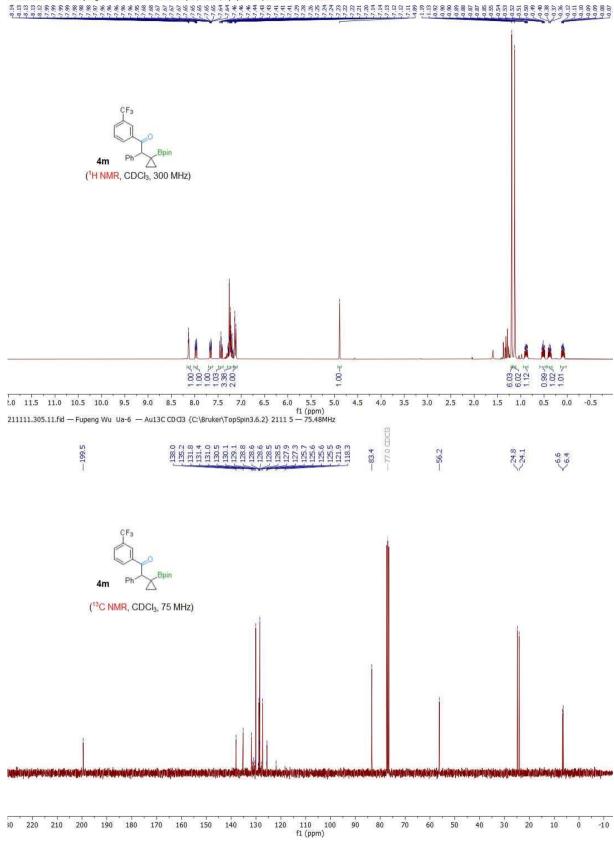


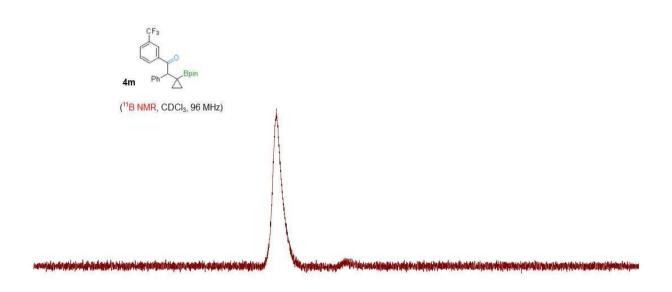




(11B NMR, CDCI₃, 96 MHz)



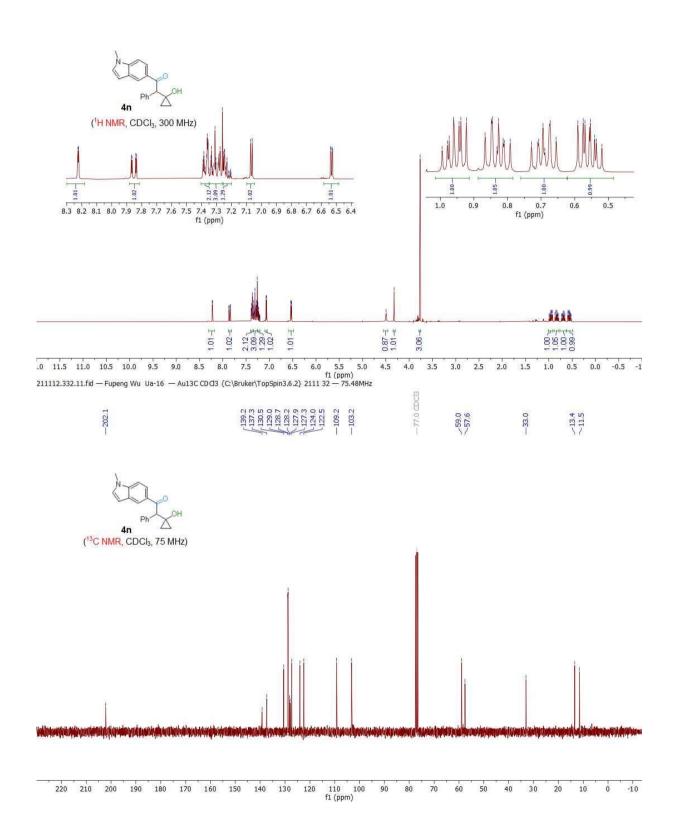


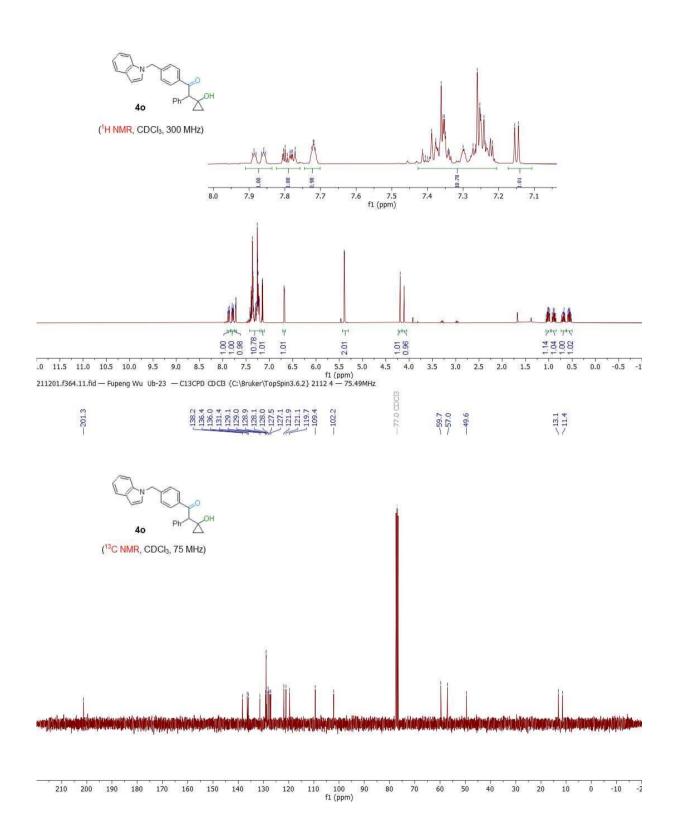


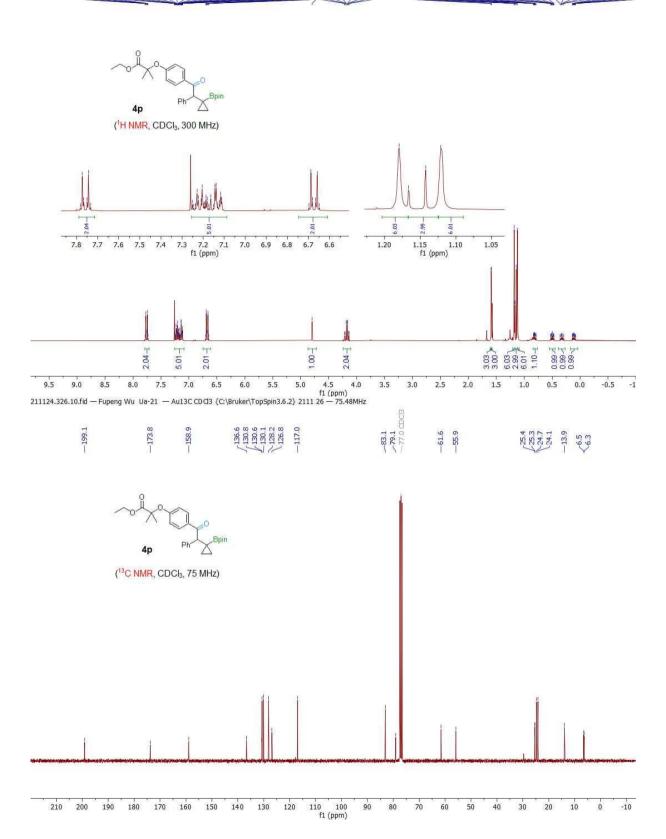
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 f1 (ppm)
211111.305.13.fid — Fupeng Wu Ua-6 — Au19F CDCl3 {C:\Bruker\TopSpin3.6.2} 2111 5 — 282.39MHz

(19F NMR, CDCI₃, 282 MHz)

120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 f1 (ppm)

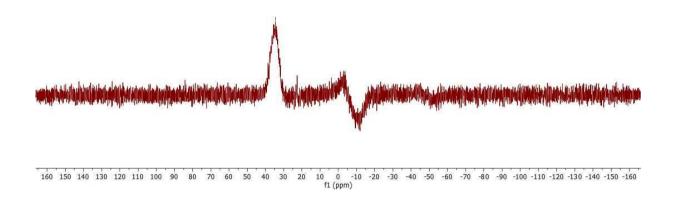


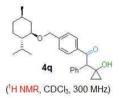


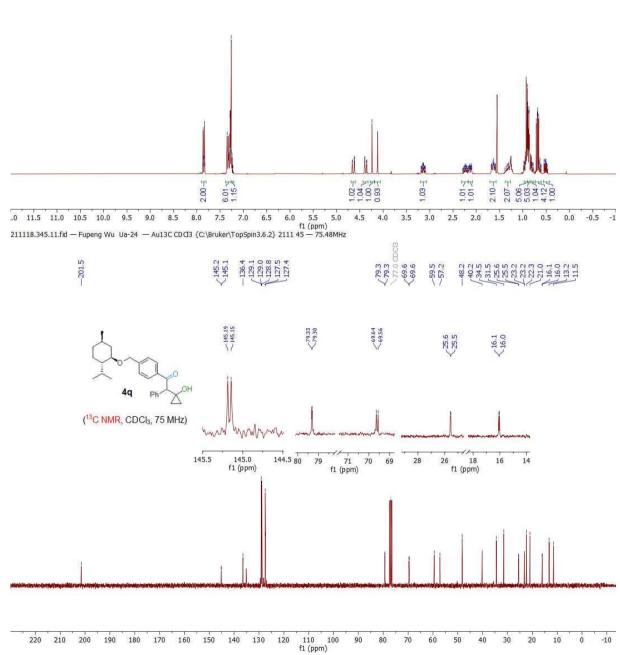


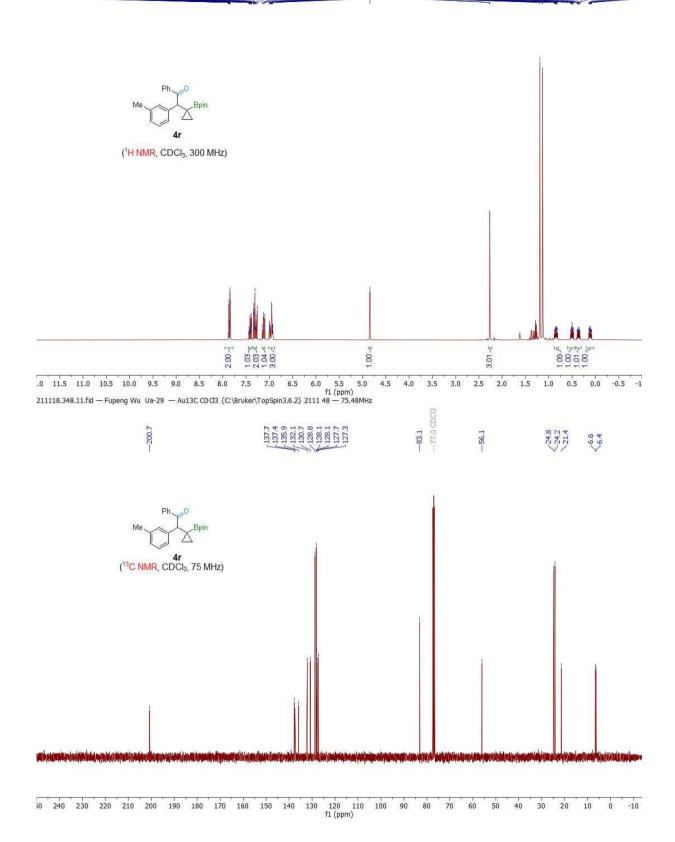
211126.f355.10.fid — Fupeng Wu Ua-21 — 11B CDCl3 {C:\Bruker\TopSpin3.6.2} 2111 55 — 96.32MHz $\stackrel{4:}{\Xi}$

(11B NMR, CDCl₃, 96 MHz)



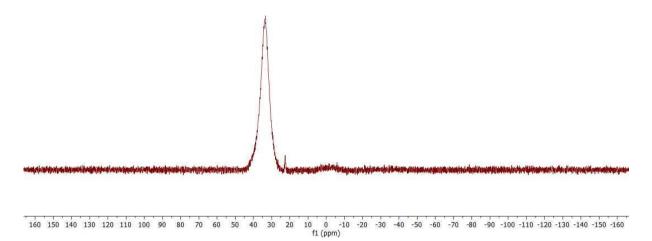


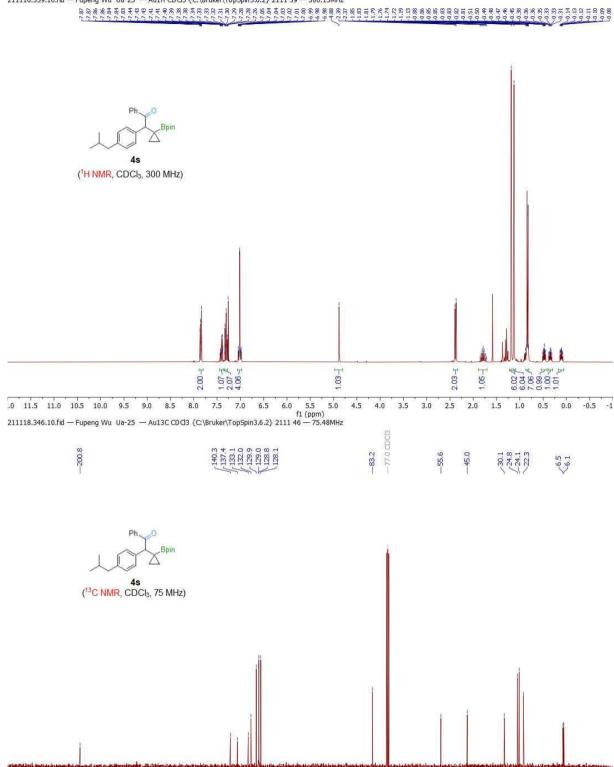












110 100 f1 (ppm)

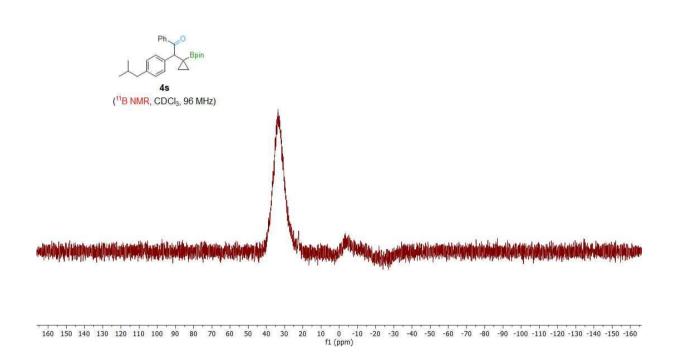
140 130

220 210 200

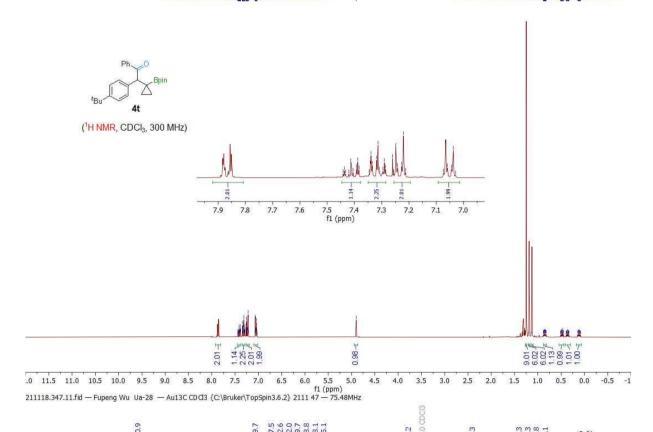
190 180

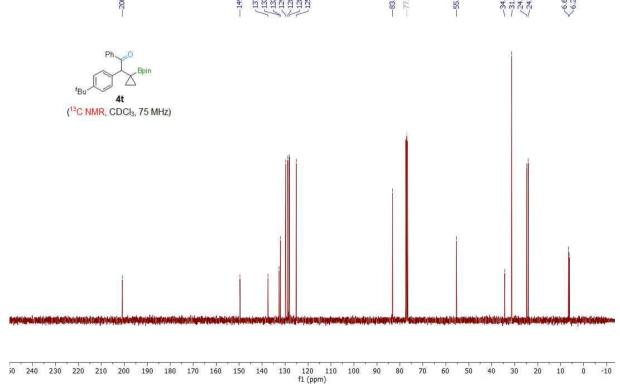
170 160 150





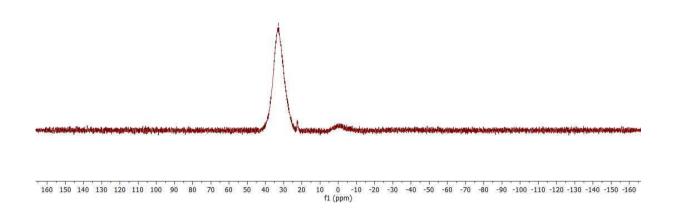




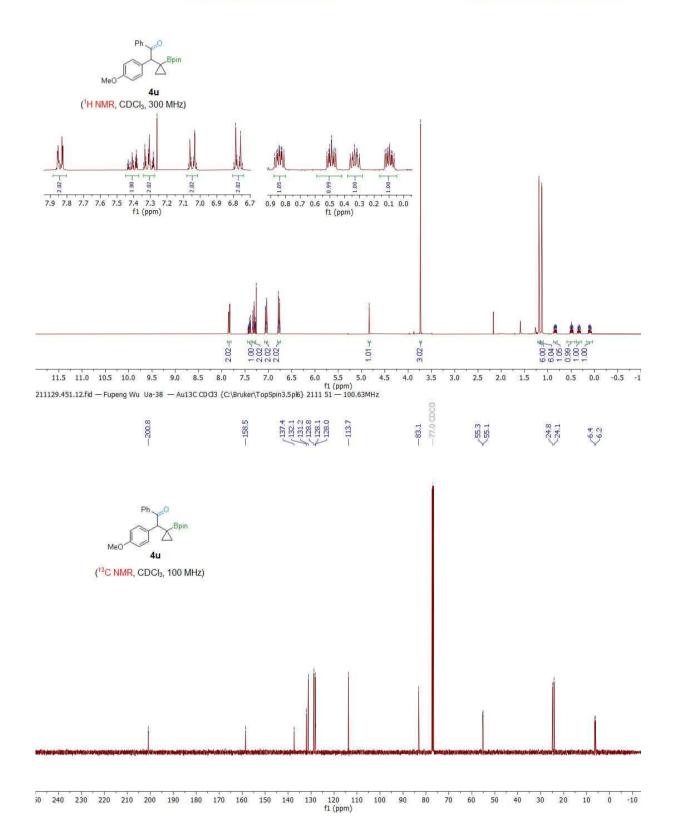




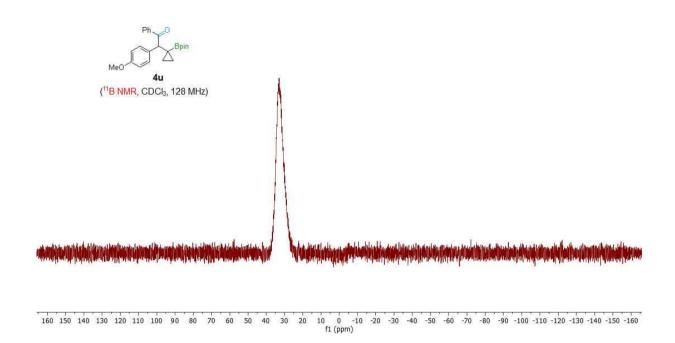


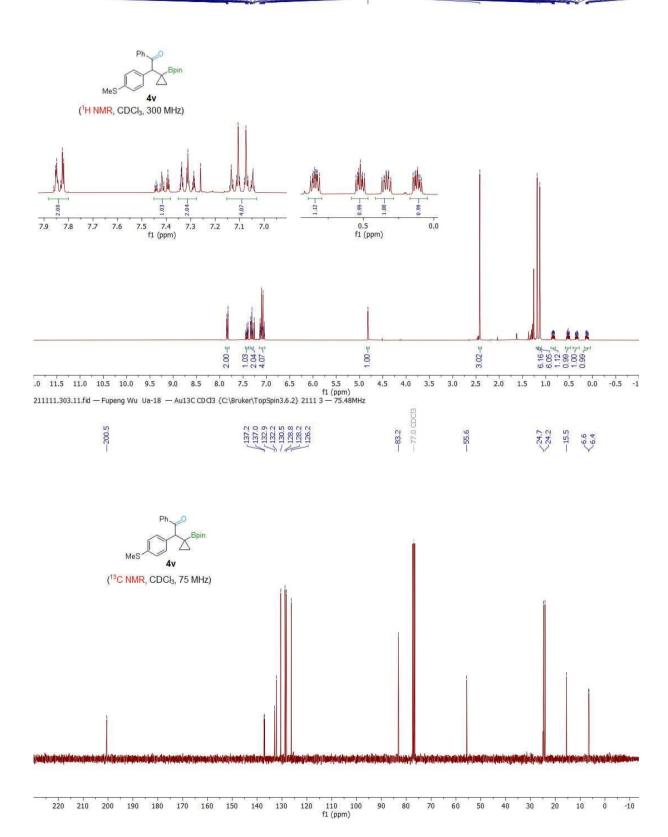




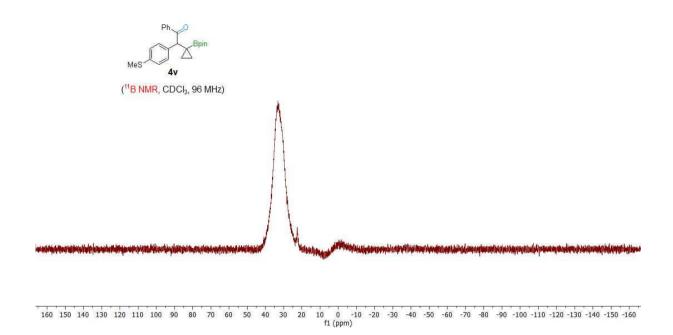












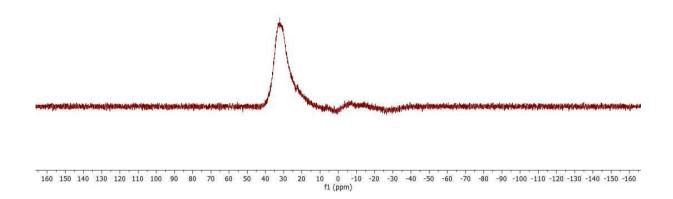
110 100 f1 (ppm)

140 130 120

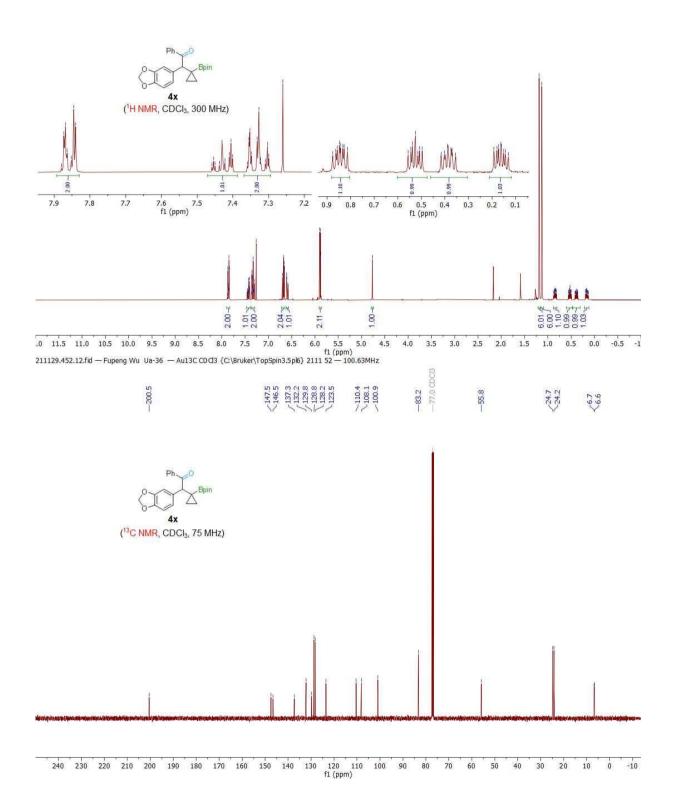
170 160 150

211125.338.12.fid — Fupeng Wu Ua-31 — Au118 CD Cl3 {C:\Bruker\TopSpin3.6.2} 2111 38 — 96.29MHz $^{\circ}$

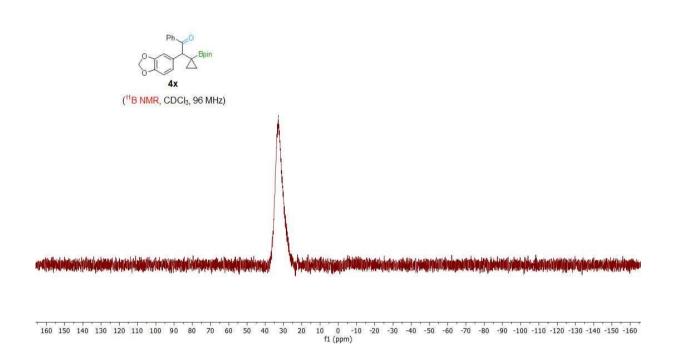
(11B NMR, CDCl₃, 96 MHz)



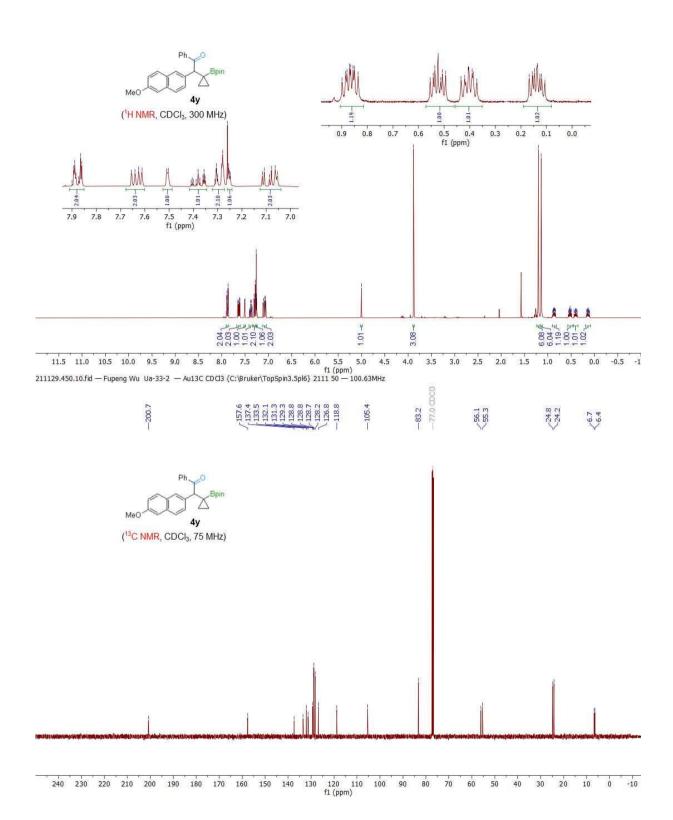




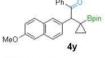






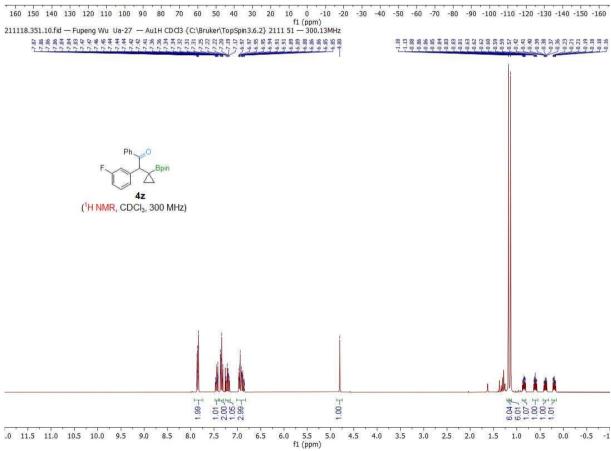






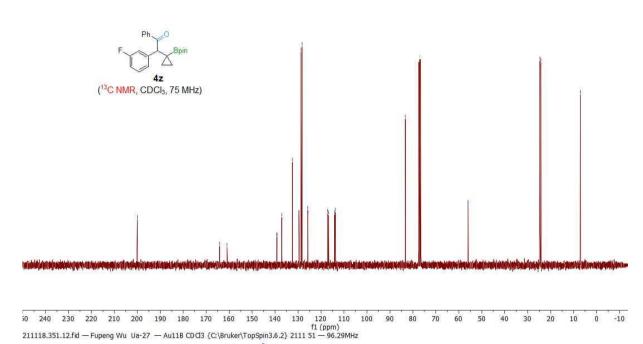
(11B NMR, CDCl₃, 96 MHz)



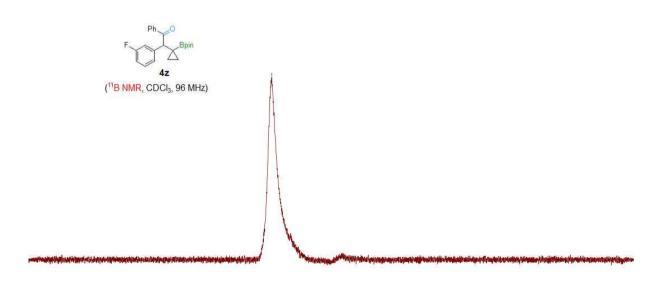


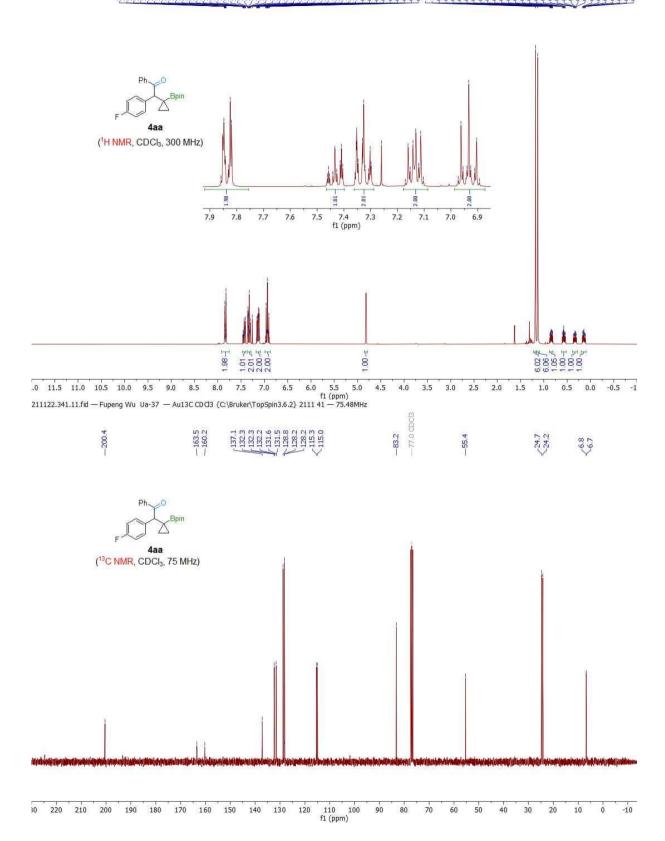




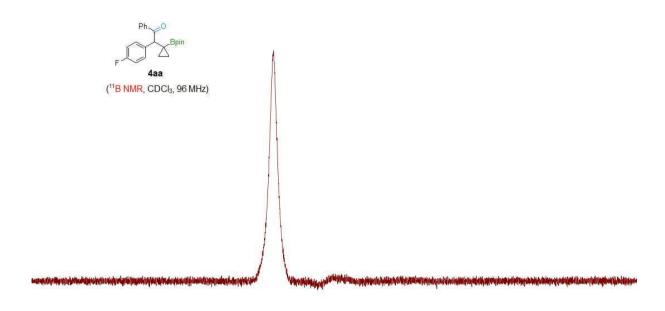








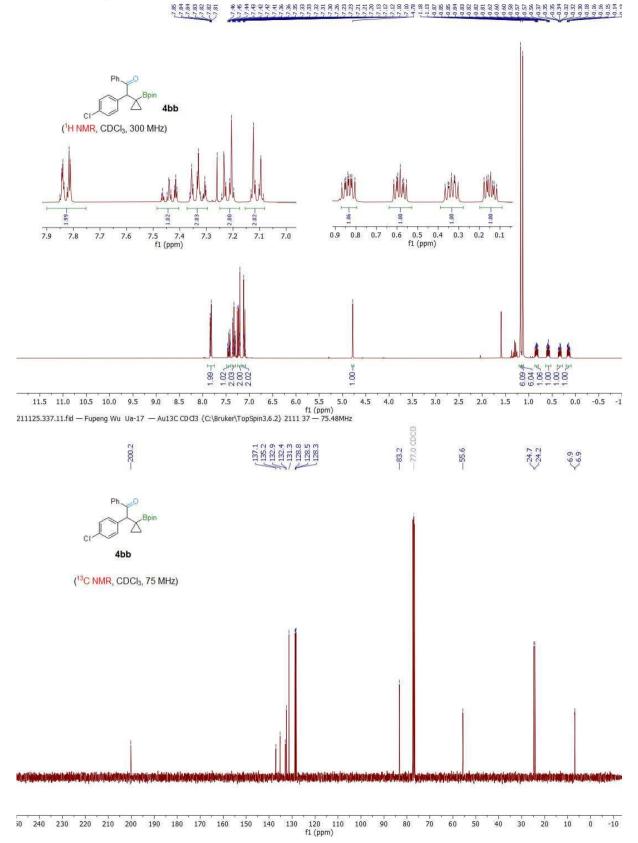




160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 f1 (ppm)
211122.341.13.fid — Fupeng Wu Ua-37 — Au19F CDCI3 {C:\Bruker\TopSpin3.6.2} 2111 41 — 282.39MHz

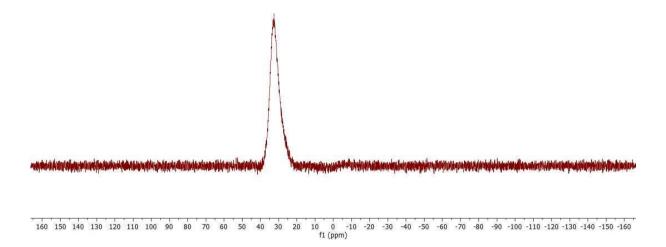
(19F NMR, CDCI₃, 282 MHz)

120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 f1 (ppm)

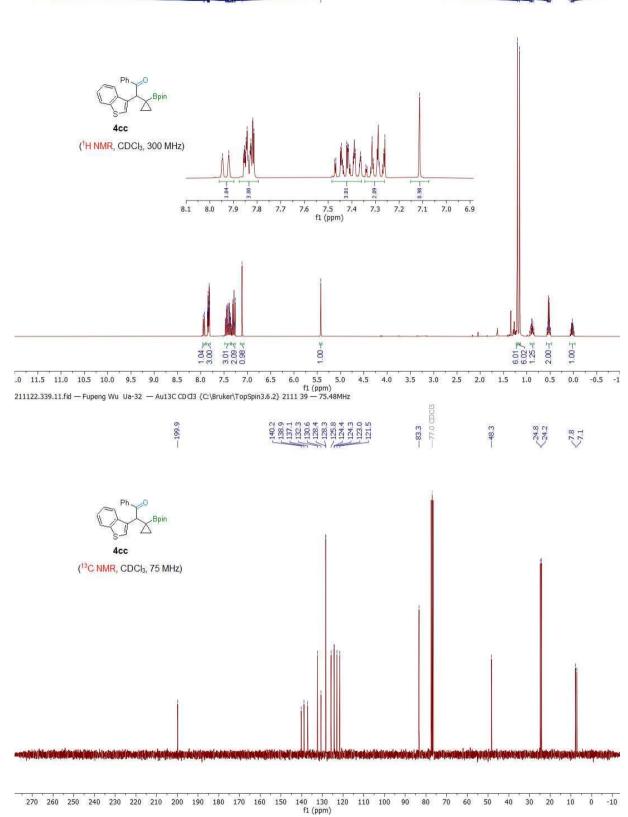


211125.337.12.fid — Fupeng Wu Ua-17 — Au118 CD Cl3 {C:\Bruker\TopSpin3.6.2} 2111 37 — 96.29MHz $^{\text{LY}}_{\text{Cl}}$

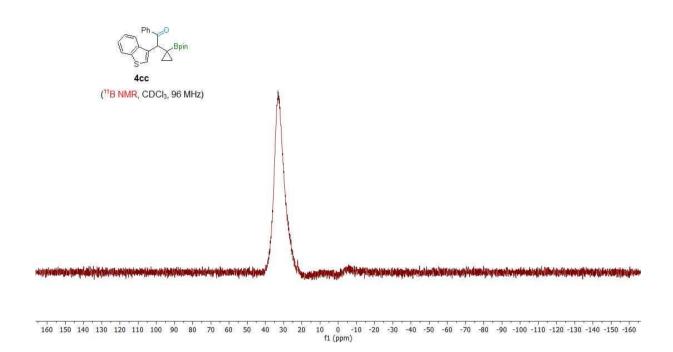
(11B NMR, CDCI₃, 96 MHz)

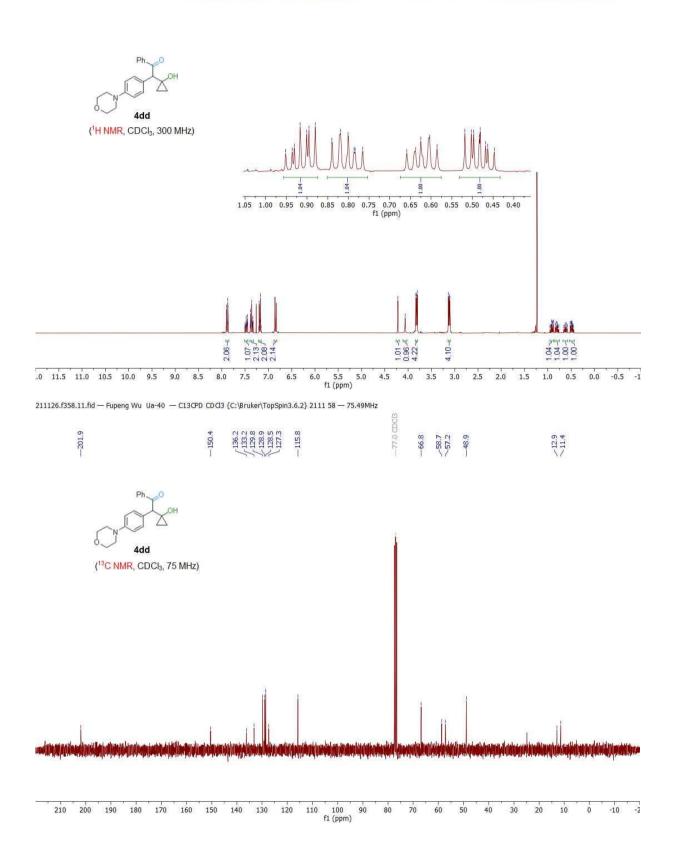


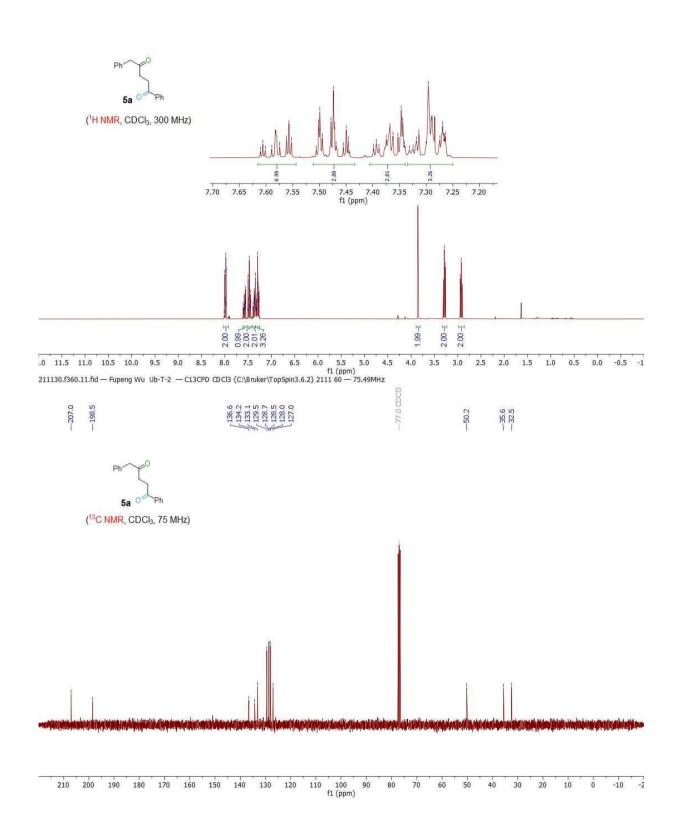


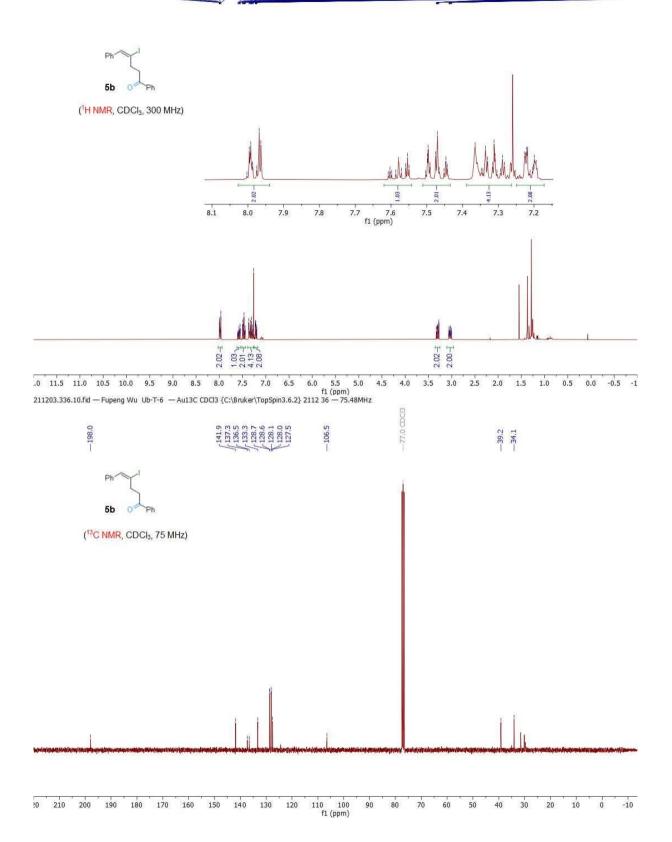


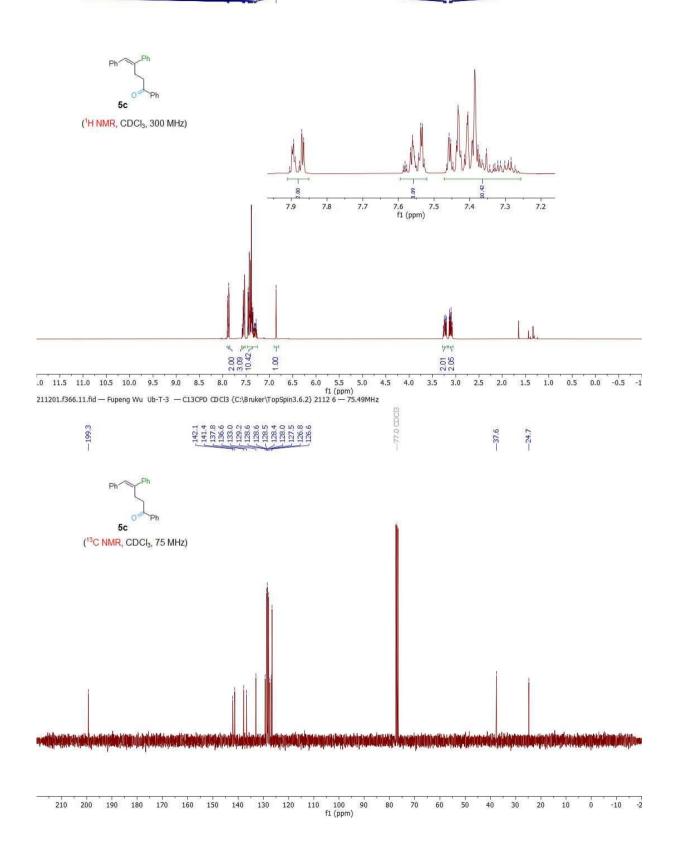


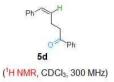


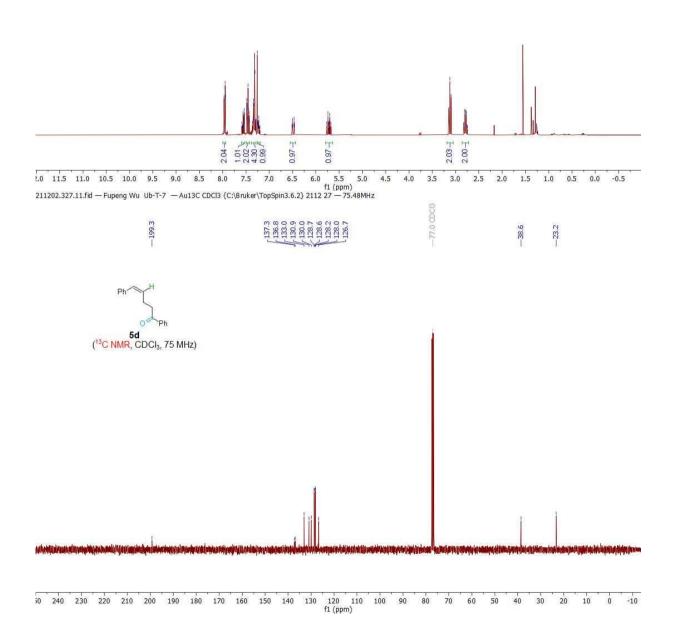


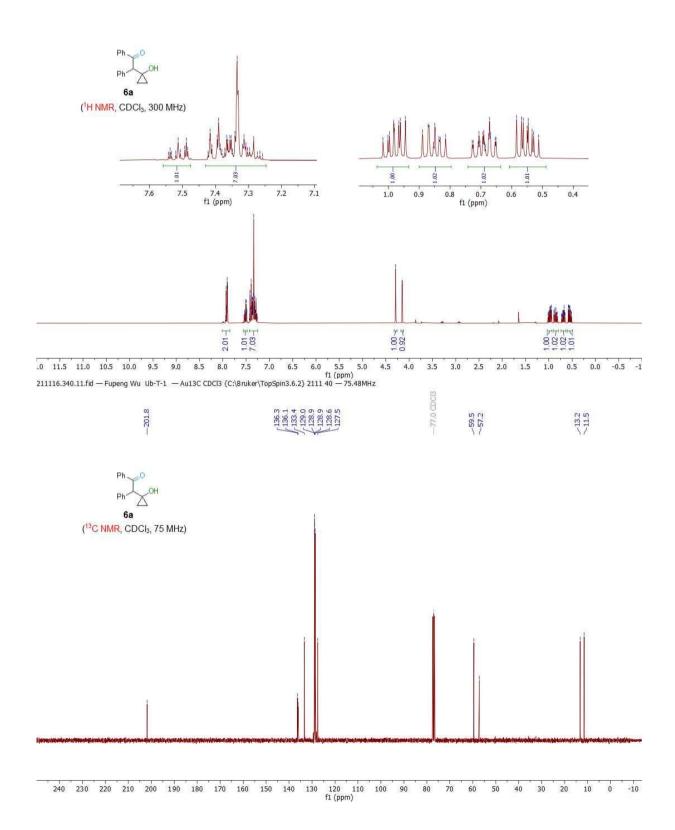


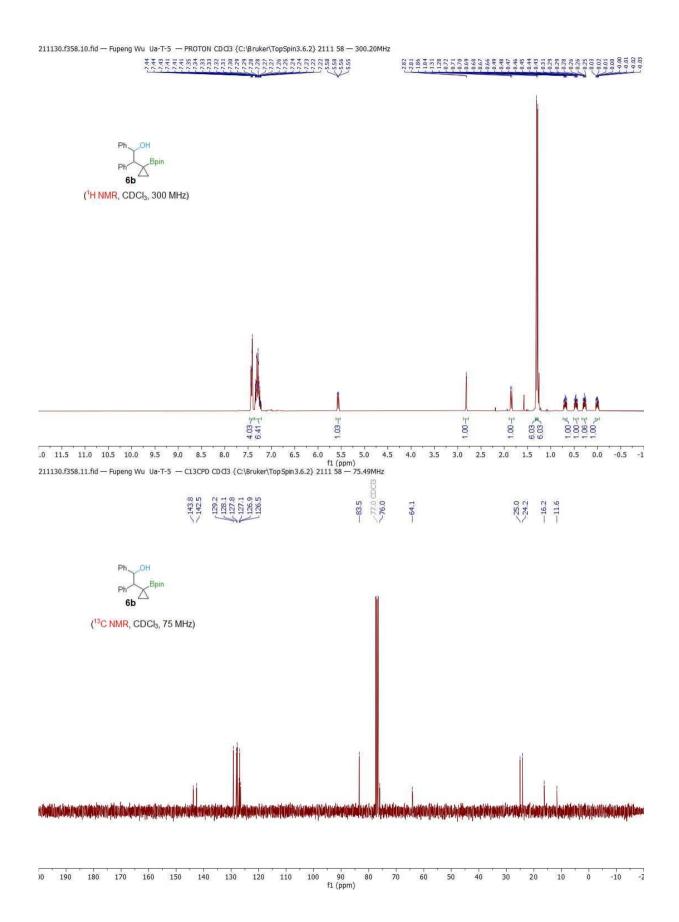






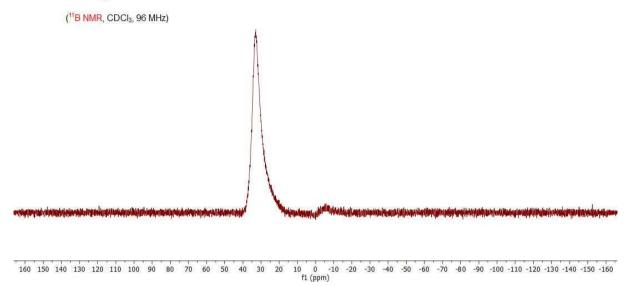




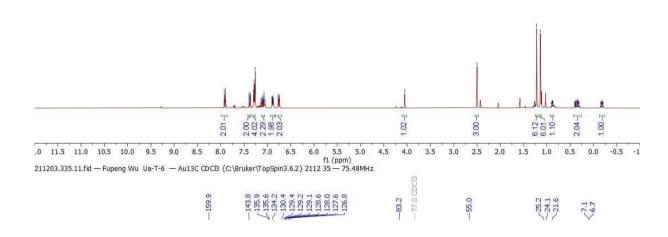






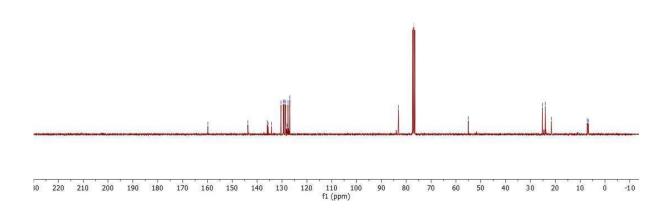




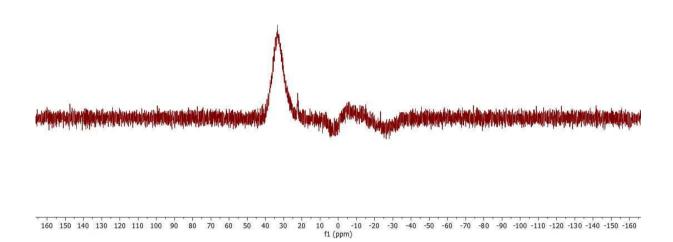


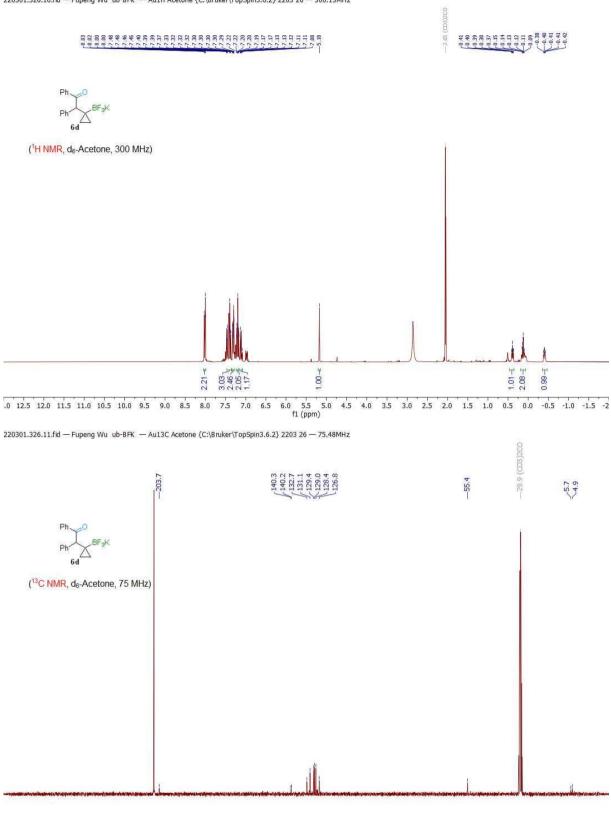
Ph NNHTs

(13C NMR, CDCl₃, 75 MHz)







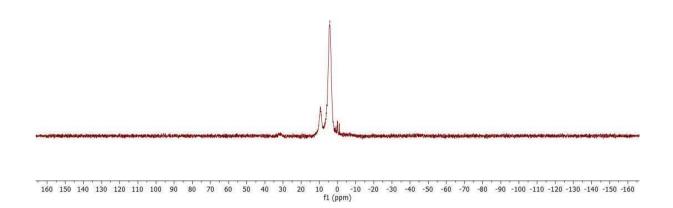


270 260 250 240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 fl (ppm)

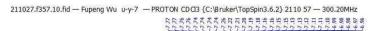
220301.326.12.fid — Fupeng Wu $\,$ ub-BFK $\,$ — Au11B Acetone {C:\Bruker\TopSpin3.6.2} 2203 26 — 96.29MHz



(11B NMR, d₆-Acetone, 96 MHz)

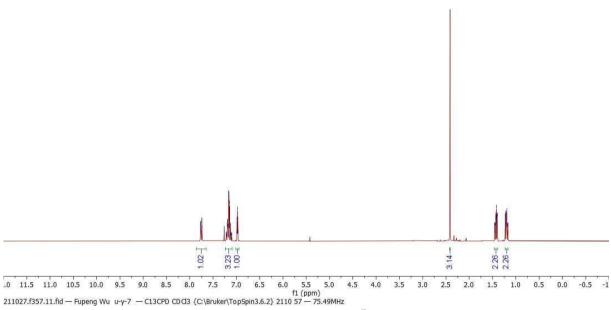


8.2 NMR spectra of the BCPs





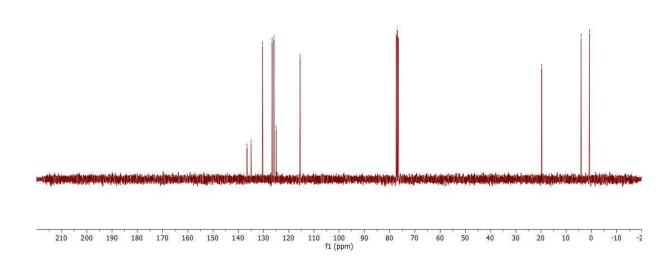


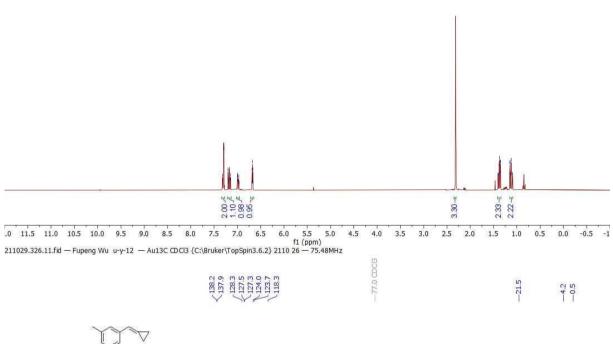


-77.0 CDCI3

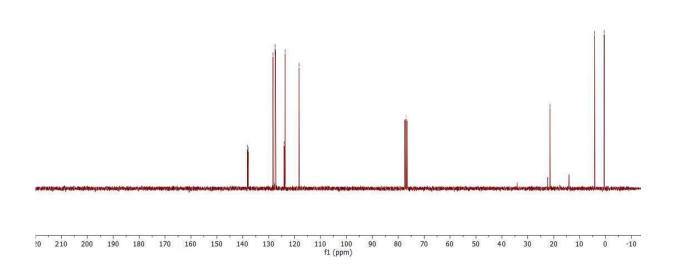
-4.1



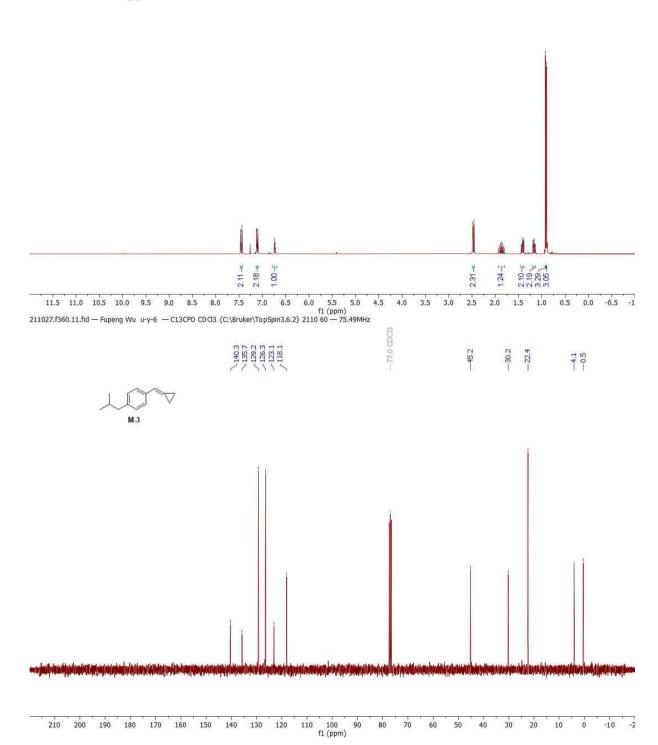




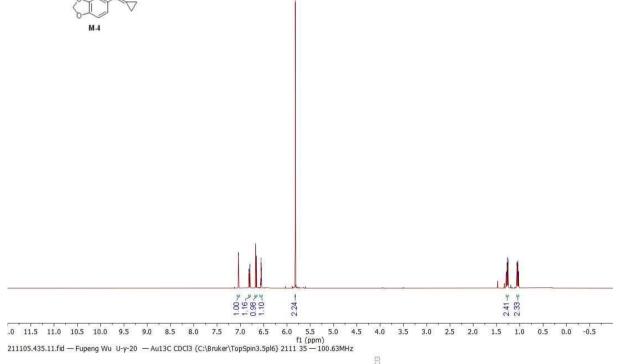


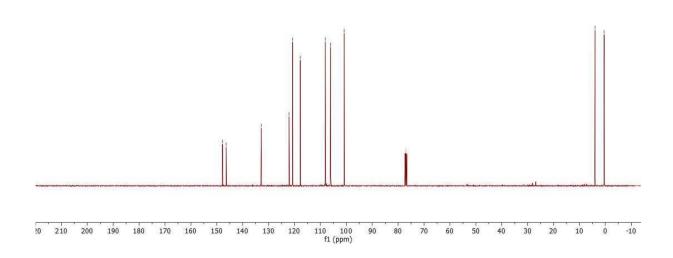


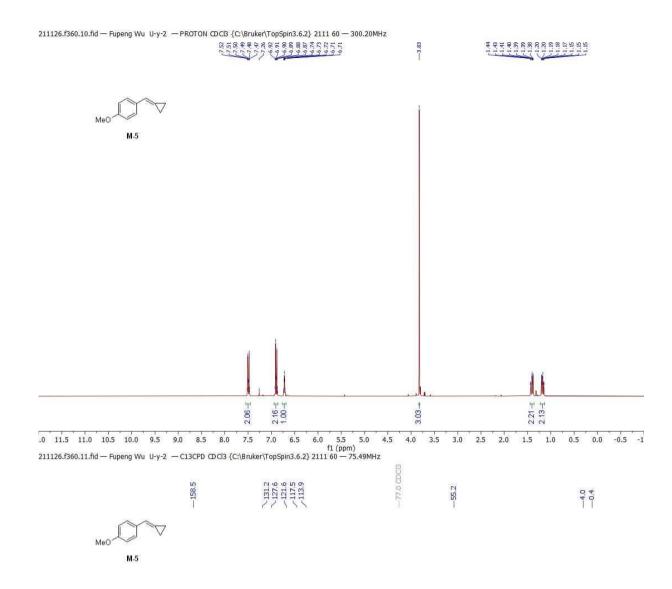


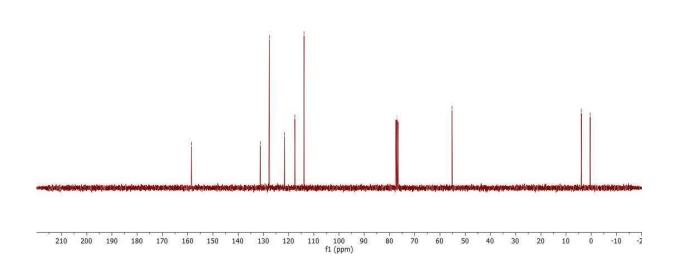


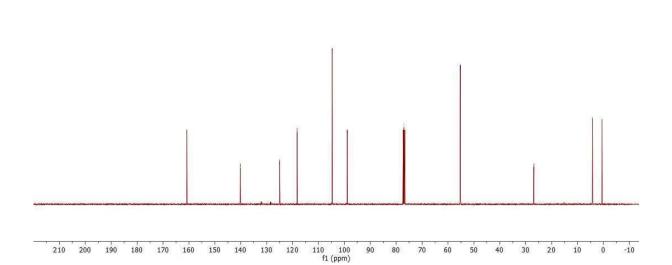




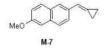


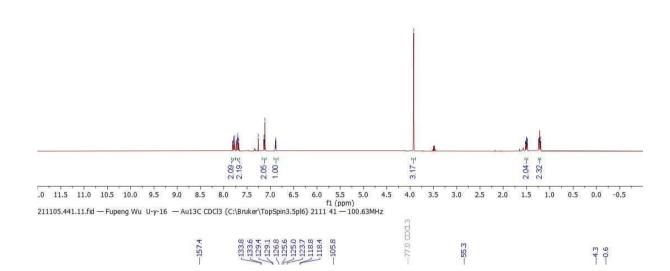


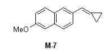


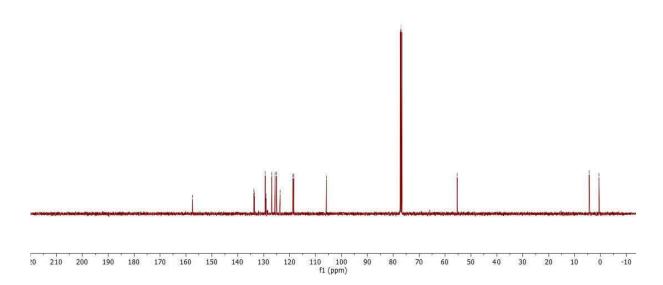


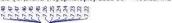
M-6





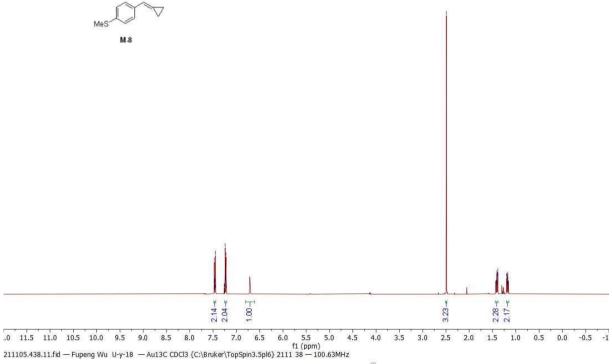




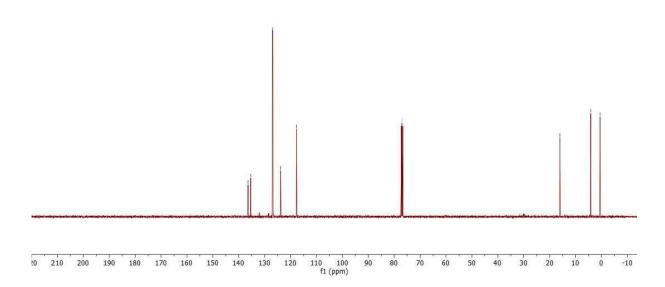




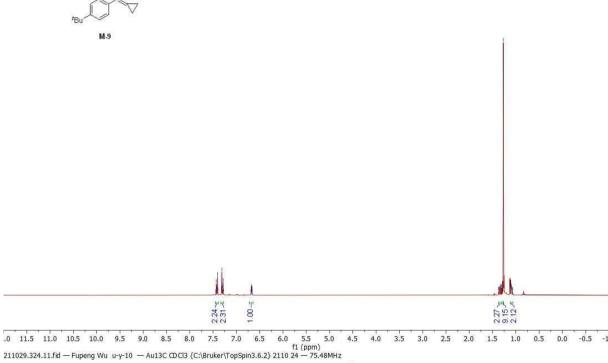


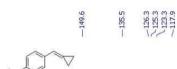


-77.0 CDCI3

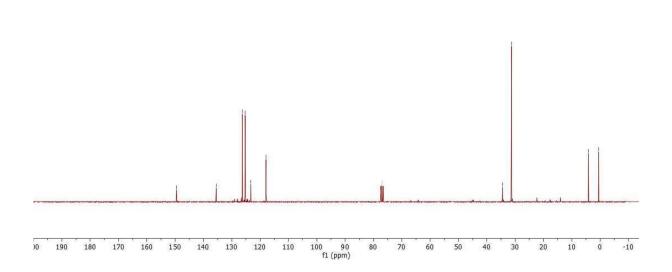




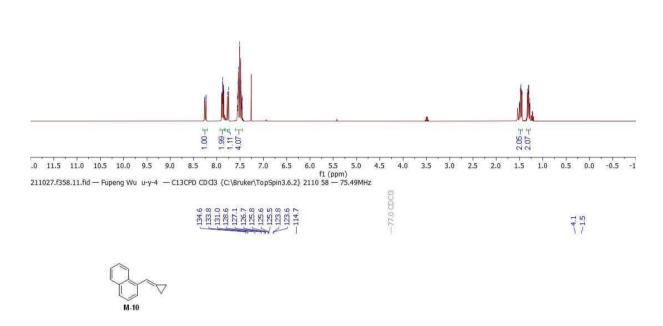


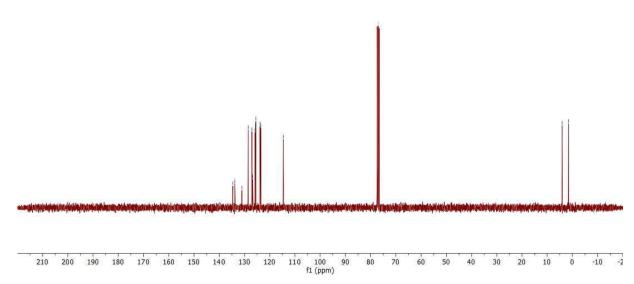


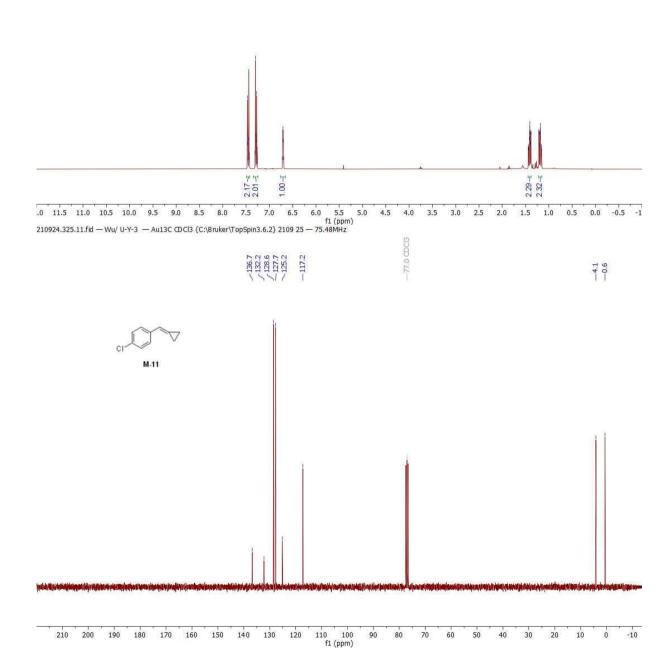




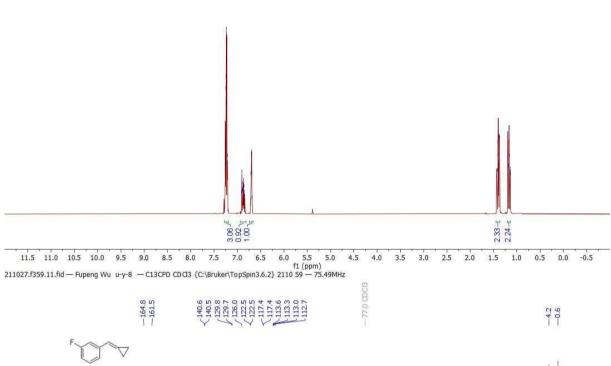


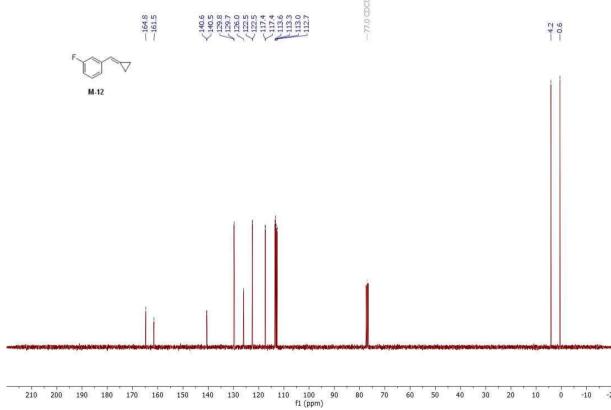


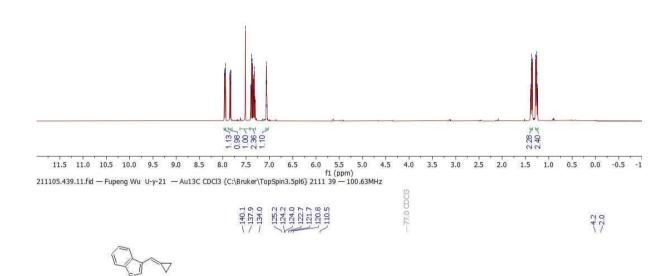


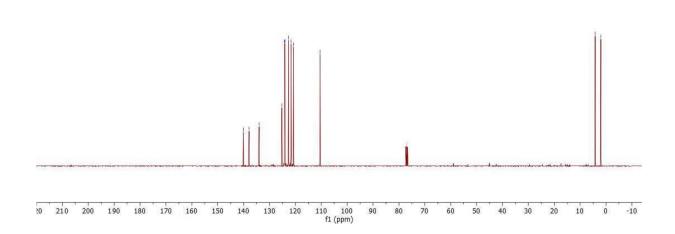


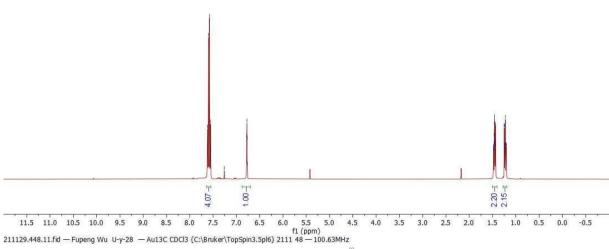






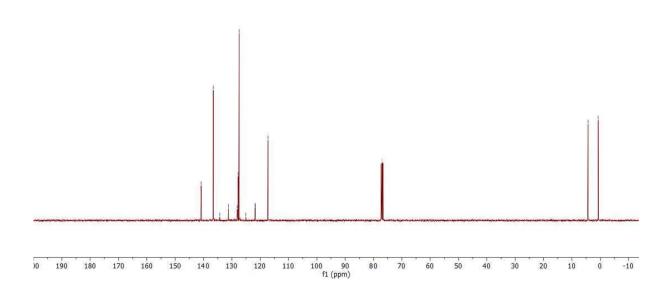




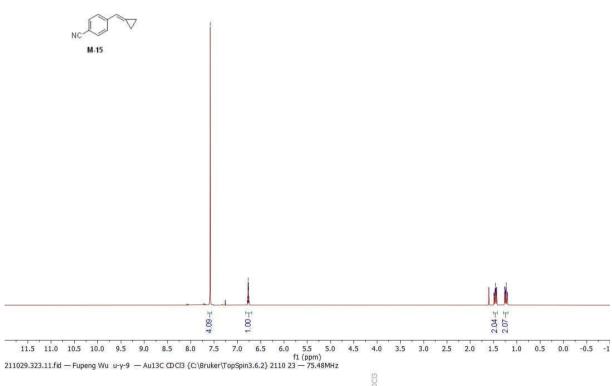


140.9 138.5 131.2 121.8 127.8 127.8 121.8 121.8 117.3

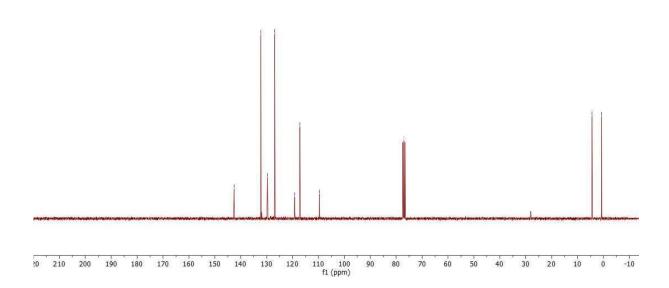
-4.3



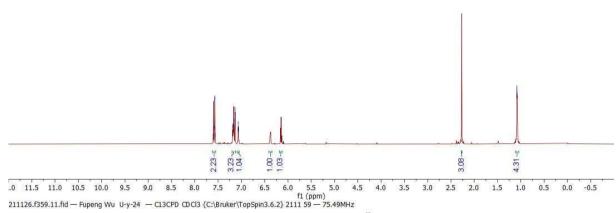








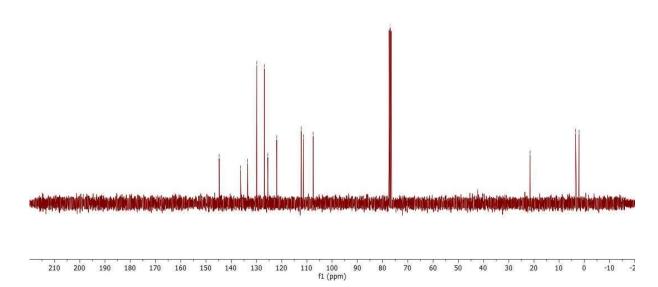




44.8 33.6 22.9 22.0 22.0 22.0 07.5 7.0 CDCB

3.5





9. Crystallographic reports for the x-ray structures

3a

checkCIF/PLATON report

Structure factors have been supplied for datablock(s) AX2220

THIS REPORT IS FOR GUIDANCE ONLY. IF USED AS PART OF A REVIEW PROCEDURE FOR PUBLICATION, IT SHOULD NOT REPLACE THE EXPERTISE OF AN EXPERIENCED CRYSTALLOGRAPHIC REFEREE.

Datablock: AX2220

Bond precision:	C-C = 0.0018 A	Wavelength=0.71073			
Cell:	a=12.4943(10) b	=9.9586(7)	c=16.7620(13)		
	alpha=90 b	eta=95.6616(15)	gamma=90		
Temperature:	150 K				
	Calculated	Reported			
Volume	2075.5(3)	2075.5(3)			
Space group	P 21/n	P 21/n			
Hall group	-P 2yn	-P 2yn			
Moiety formula	C23 H27 B O3	?			
Sum formula	C23 H27 B O3	C23 H27 B	03		
Mr	362.26	362.25			
Dx,g cm-3	1.159	1.159			
Z	4	4			
Mu (mm-1)	0.074	0.074			
F000	776.0	776.0			
F000'	776.34				
	17,13,23	17,13,22			
Nref	5612	5596			
	0.981,0.994	0.960,0.99	0		
Tmin'	0.964				
Correction method= # Reported T Limits: Tmin=0.960 Tmax=0.990 AbsCorr = MULTI-SCAN					
Data completenes	ss= 0.997	Theta(max) = 29.204			
R(reflections)=	0.0452(4098)		wR2(reflections) = 0.1209(5596)		
S = 1.032	Npar= 24	8			

The following ALERTS were generated. Each ALERT has the format test-name_ALERT_alert-type_alert-level.

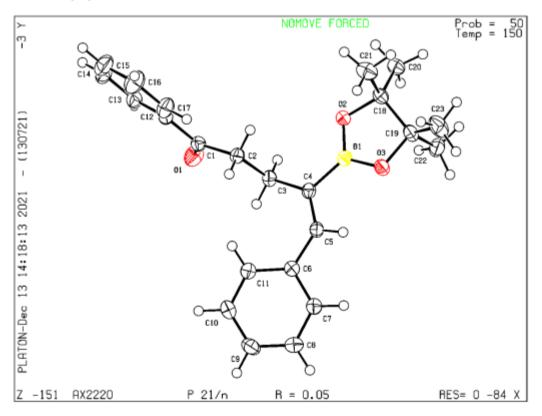
Click on the hyperlinks for more details of the test.

```
Alert level G
```

```
O ALERT level A - Most likely a serious problem - resolve or explain
O ALERT level B - A potentially serious problem, consider carefully
O ALERT level C - Check. Ensure it is not caused by an omission or oversight
ALERT level G - General information/check it is not something unexpected

2 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
3 ALERT type 2 Indicator that the structure model may be wrong or deficient
1 ALERT type 3 Indicator that the structure quality may be low
1 ALERT type 4 Improvement, methodology, query or suggestion
O ALERT type 5 Informative message, check
```

Datablock AX2220 - ellipsoid plot



checkCIF/PLATON report

Structure factors have been supplied for datablock(s) AX2232

THIS REPORT IS FOR GUIDANCE ONLY. IF USED AS PART OF A REVIEW PROCEDURE FOR PUBLICATION, IT SHOULD NOT REPLACE THE EXPERTISE OF AN EXPERIENCED CRYSTALLOGRAPHIC REFEREE.

Datablock: AX2232

Bond precision:	C-C = 0.0029 A	Wavelength=0.71073	
Cell:	a=12.9120(13) alpha=90	b=10.1397(10) beta=90	c=15.5970(16) gamma=90
Temperature:	150 K	Deca-30	gamma-30
	Calculated	Reported	
Volume	2042.0(4)	2042.0(4)	
Space group	P n a 21	P n a 21	
Hall group	P 2c -2n	P 2c -2n	
Moiety formula	C23 H27 B O3	?	
Sum formula	C23 H27 B O3	C23 H27 E	3 03
Mr	362.26	362.25	
Dx,g cm-3	1.178	1.178	
Z	4	4	
Mu (mm-1)	0.076	0.076	
F000	776.0	776.0	
F000'	776.34		
h,k,lmax	17,13,21	17,13,21	
	5518[2854]	5505	
,	0.978,0.993	0.980,0.9	990
Tmin'	0.978		
Correction metho AbsCorr = MULTI-	od= # Reported T List- -SCAN	mits: Tmin=0.980 Tm	max=0.990
Data completenes	ss= 1.93/1.00	Theta(max) = 29.17	8
R(reflections)=	0.0375(4869)		wR2 (reflections) = 0.0945(5505)
S = 1.050	Npar= 24	18	

The following ALERTS were generated. Each ALERT has the format test-name_ALERT_alert-type_alert-level.

Click on the hyperlinks for more details of the test.

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Alert level G
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                                                                       0.400 Report
PLAT066_ALERT_1_G Predicted and Reported Tmin&Tmax Range Identical
                                                                           ? Check
PLAT395_ALERT_2_G Deviating X-O-Y
                                     Angle From 120 for O2
                                                                       105.9 Degree
PLAT395_ALERT_2_G Deviating X-O-Y
                                     Angle From 120 for O3
                                                                       107.0 Degree
PLAT792_ALERT_1_G Model has Chirality at C2
                                                    (Polar SPGR)
                                                                          S Verify
PLAT883_ALERT_1_G No Info/Value for _atom_sites_solution_primary .
                                                                      Please Do !
PLAT978_ALERT_2_G Number C-C Bonds with Positive Residual Density.
                                                                          13 Info
```

```
O ALERT level A - Most likely a serious problem - resolve or explain
O ALERT level B - A potentially serious problem, consider carefully
O ALERT level C - Check. Ensure it is not caused by an omission or oversight
ALERT level G - General information/check it is not something unexpected

ALERT type 1 CIF construction/syntax error, inconsistent or missing data
ALERT type 2 Indicator that the structure model may be wrong or deficient
ALERT type 3 Indicator that the structure quality may be low
ALERT type 4 Improvement, methodology, query or suggestion
O ALERT type 5 Informative message, check
```

Datablock AX2232 - ellipsoid plot

