Supporting Information for:

Cobalt-Catalyzed Cyclization/Hydroboration of 1,6-Diynes with Pinacolborane

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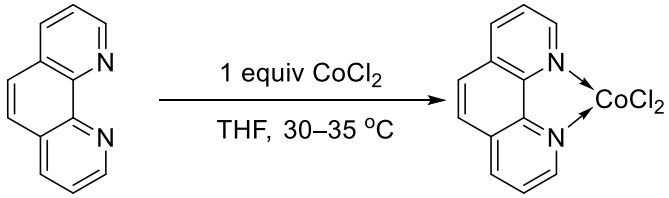
1. General Information

Unless otherwise noted, all manipulations were carried out using standard Schlenk and glovebox techniques. Cobalt(II) chloride (99.99%) was purchased from Sigma-Aldrich and used as received. Anhydrous solvents were purified and dried following standard procedures.[1] All commercially available reagents were used as received. Liquid diynes were dried over CaH_2 and distilled prior to use and solid diynes were recrystallized and dried under vacuum. TLC analysis was performed on pre-coated, glass-backed silica gel plates and visualized with UV light. Flash column chromatography was performed on silica gel (200-300 mesh). Melting points were measured on a RY-I apparatus and uncorrected. The NMR spectra were recorded on a Bruker 400 AV spectrometers at 400 MHz (^{1}H NMR), 101 MHz (^{13}C NMR), 128 MHz (^{11}B NMR). Chemical shifts for protons are quoted in parts per million downfield from tetramethylsilane and are referenced to the solvent peak (for $CDCl_3$, ^{1}H NMR: 7.26 ppm, ^{13}C NMR: 77.16 ppm). Abbreviations are used in the description of NMR data as follows: chemical shift (δ, ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constant (*J*, Hz). The high-resolution mass spectra (HRMS) were recorded on an IonSpec FT-ICR mass spectrometer and Waters GCT Premier mass spectrometer.

2. Synthesis of L1.$CoCl_2$



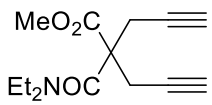
L1 **L1**.$CoCl_2$

In an argon-filled glovebox, a Schlenk flask (50 mL) was charged with 1,10-phenanthrolines **L1** (2 mmol), $CoCl_2$ (2 mmol) and dry THF (20 mL). The reaction mixture was stirred at 70 °C for 24 h. The solvent was partially removed under vacuum (about 5 mL left), then dry *n*-hexane (15 mL) was added, and solids precipitated. The product was collected by filtration, washed with 20 mL *n*-hexane, and dried under vacuum to get the desired complex **L1**.$CoCl_2$ (558 mg, 90% yield) as a blue solid. Decomposition temperature >320 °C. ^{1}H NMR (400 MHz, acetonitrile-d3) δ 1.27-1.16 (m), 0.84-0.76 (m). IR (neat) 3550w, 3475s, 3415s, 3237w, 1639w, 1620m, 1580w, 1423m, 1343w, 1265m, 1140w, 1102w, 858m, 730s, 620w cm^{-1}. UV/VIS (acetonitrile) 589 nm, 683 nm. Elemental Analysis Calcd for $C_{12}H_8N_2Cl_2Co$: C, 46.49; H, 2.60; N, 9.04; Found: C, 46.35; H, 2.50; N, 9.07.

3. Preparation of Diynes

Diynes **1a-1h**,[2] **1n-1p**,[2] **1j**,[3] **1k**,[3] **1l**,[3] **1i**,[4] **1t**,[5] **1r-1s**[6] were prepared according to known procedures. The analytical data of new diynes were listed as following.

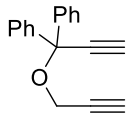
Methyl-2-(diethylcarbamoyl)-2-(prop-2-yn-1-yl)pent-4-ynoate (1f)



Compound **1f** was prepared from methyl 3-(diethylamino)-3-oxopropanoate according to literature procedure[2] as a white solid (2.4 g, 76%). The flash chromatography was performed with petroleum ether/ethyl acetate, PE/EA (10:1~5:1,

v/v) as the eluent. m.p.: 52-54 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.78 (s, 3H), 3.37 (s, 2H), 3.25 (s, 2H), 3.12-2.93 (m, 4H), 2.04 (t, *J* = 2.6 Hz, 2H), 1.13 (t, *J* = 6.9 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.68, 165.99, 78.74, 72.01, 55.74, 53.01, 41.16, 24.21, 13.49, 12.41. HRMS (EI) Calcd for $[C_{14}H_{19}NO_3, M]^+$: 249.1365; Found: 249.1359.

(1-(Prop-2-yn-1-yloxy)prop-2-yne-1,1-diyl)dibenzene (1r)



Compound **1r** was prepared from 1,1-diphenylprop-2-yn-1-ol according to literature procedure[6] as a slight yellow solid (4.7 g, 95%). The flash chromatography was performed with PE/EA (30:1~10:1, v/v) as the eluent. m.p.: 67-69 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61-7.53 (m, 4H), 7.36-7.24 (m, 6H), 4.18 (d, *J* = 2.4 Hz, 2H), 2.91 (s, 1H), 2.40 (t, *J* = 2.4 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.30, 128.39, 128.11, 126.77, 82.44, 80.67, 80.13, 78.58, 74.02, 53.44. HRMS (EI) Calcd for $[C_{18}H_{14}O, M]^+$: 246.1045; Found: 246.0991.

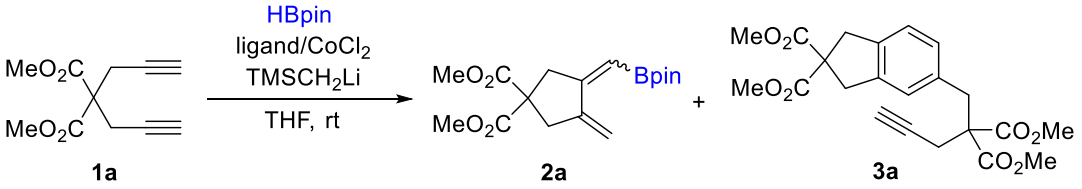
4. Additional Evaluations of Reaction Conditions

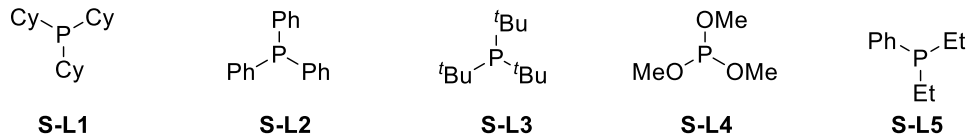
Method A (used in situ prepared cobalt catalysts): In an argon-filled glovebox, a vial (10 mL) was charged with ligand (0.015 mmol), metal salt (0.015 mmol), anhydrous THF (1 mL). The reaction mixture was stirred at room temperature for 2 hours. Then diynes (0.5 mmol), HBpin (0.5 mmol), and $TMSCH_2Li$ (0.7 M in THF, 43 μL, 0.03 mmol, 6 mol %) was added sequentially. After stirring for 12 hours at rt, the vial was removed from the glovebox and the reaction mixture was filtered over silica gel deactivated with 2% NEt_3 in hexanes using ethyl acetate as eluant. The combined organic phases were concentrated by rotary evaporation, and determined the yield, conversion, and *Z*/*E* ratio of **2a** by ^{1}H NMR.

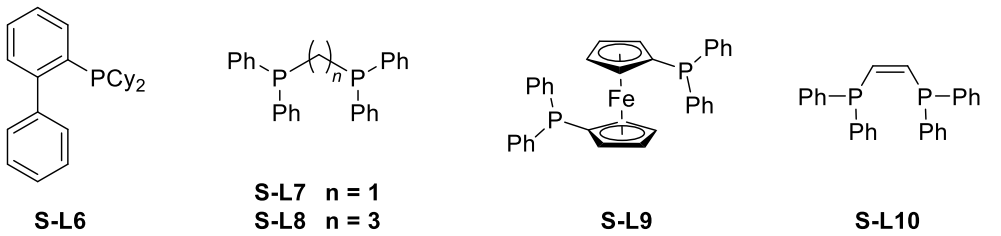
Method B (used pre-prepared L1.$CoCl_2$): In an argon-filled glovebox, a vial (10 mL) was charged with diynes (0.5 mmol), HBpin (0.5 mmol), anhydrous solvent (1

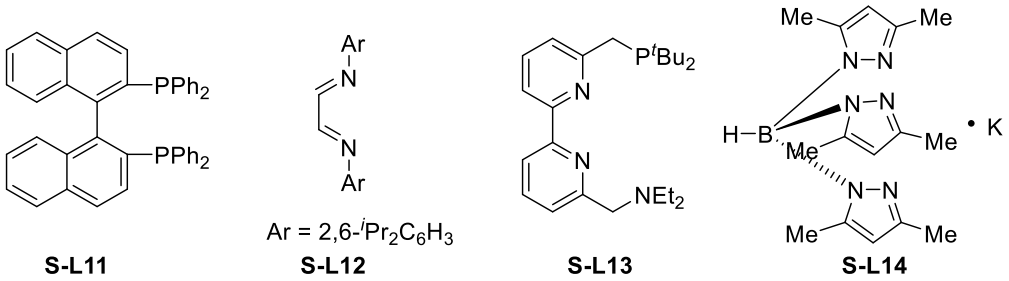
mL) and complex **L1.**$CoCl_2$ (0.015 mmol). The reaction mixture was stirred at room temperature for 1 minutes, then additive (0.03 mmol, 6 mol %) was added. After stirring for 12 hours at rt, the vial was removed from the glovebox and the reaction mixture was filtered over silica gel deactivated with 2% NEt_3 using ethyl acetate as eluant. The combined organic phases were concentrated by rotary evaporation, and determined the product yield, conversion, and *Z*/*E* ratio of **2a** by ^{1}H NMR.

Table S1. Evaluation of Ligands [a]







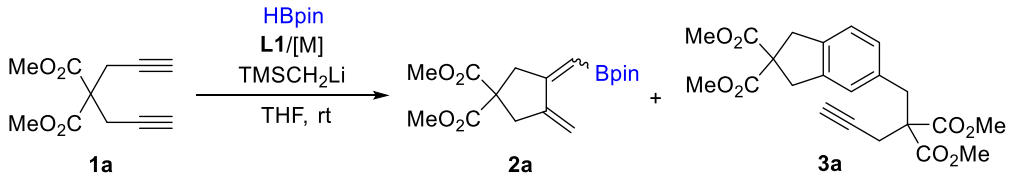


entry	ligand	conv. (%)[b]	yield **2a** (%)[b]	yield **3a** (%)[b]	*Z*/*E*[b]
1[c]	**S-L1**	> 95	11	36	55:45
2[c]	**S-L2**	> 95	21	12	86:14
3[c]	**S-L3**	> 95	7	26	>95:5
4[c]	**S-L4**	48	trace	13	NA[d]
5[c]	**S-L5**	71	0	9	NA[d]

6[c]	**S-L6**	91	trace	18	NA[d]
7	**S-L7**	66	7	6	71:29
8	**S-L8**	> 95	18	26	83:17
9	**S-L9**	> 95	28	12	>95:5
10	**S-L10**	63	trace	10	NA[d]
11	**S-L11**	> 95	14	40	71:29
12	**S-L12**	70	trace	17	NA[d]
13	**S-L13**	53	7	6	57:43
14	**S-L14**	10	0	5	NA[d]

[a] Typical procedure for the reaction according to method A. [b] Determined by ^{1}H NMR analysis using 1,3,5-trimethoxybenzene as an internal standard. [c] Used 0.03 mmol ligand. [d] Not analyzed.

Table S2. Evaluation of Metal Salts [a]

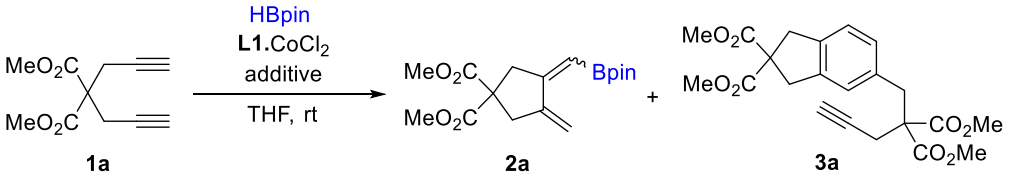


1a 2a 3a

entry	[M]	conv. (%)[b]	yield **2a** (%)[b]	yield **3a** (%)[b]	*Z*/*E*[b]
1	CoF_2	31	trace	trace	NA[d]
2	$CoBr_2$	> 95	28	9	>95:5
3[c]	$Co(acac)_2$	> 95	39	6	>95:5
4	$CrCl_2$	23	0	36	NA[d]
5	$MnCl_2$	20	0	0	NA[d]
6	$FeCl_2$	> 95	0	35	NA[d]
7	$CuCl_2$	<5	0	0	NA[d]
8	$NiCl_2$	> 95	0	trace	NA[d]
9	$ZnCl_2$	24	0	0	NA[d]

[a] Typical procedure for the reaction according to method A. [b] Determined by ^{1}H NMR analysis using 1,3,5-trimethoxybenzene as an internal standard. [c] No additive. [d] Not analyzed.

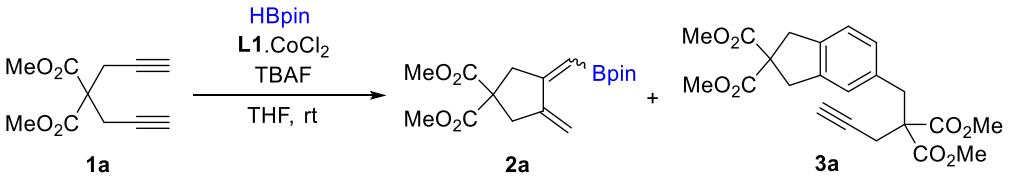
Table S3. Evaluation of Additives [a]



entry	additive	conv. (%)[b]	yield **2a** (%)[b]	yield **3a** (%)[b]	*Z*/*E*[b]
1	EtMgBr	> 95	trace	36	NA[c]
2	Zn	<5	0	0	NA[c]
3	$LiAlH_4$	> 95	17	9	94:6
4	$NaHBEt_3$	> 95	8	17	>95:5
5	Me_2Zn	77	12	15	75:25
6	KHMDS	> 95	59	8	>95:5
7	CsF	> 95	50	8	>95:5
8	KF	> 95	trace	10	NA[c]
9	ZnF_2	70	trace	10	NA[c]
10	TBAT	> 95	27	9	>95:5

[a] Typical procedure for the reaction according to method B. [b] Determined by ^{1}H NMR analysis using 1,3,5-trimethoxybenzene as an internal standard. [c] Not analyzed.

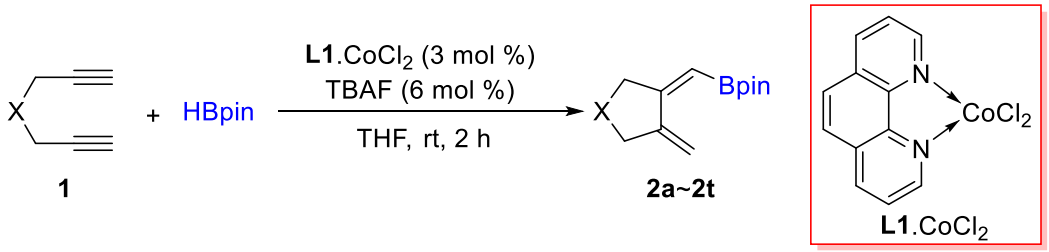
Table S4. Evaluation of Solvents [a]



entry	solvent	conv. (%)[b]	yield **2a** (%)[b]	yield **3a** (%)[b]	*Z*/*E*[b]
1	Hexane	36	15	5	>95:5
2	Toluene	> 95	27	13	>95:5
3	Diethyl ether	52	19	8	>95:5
4	Dioxane	78	60	9	>95:5
5	Acetonitrile	29	trace	6	NA[c]
6	Chlorobenzene	> 95	74	15	>95:5
7	Trifluorotoluene	57	36	5	>95:5
8	Fluorobenzene	> 95	73	14	>95:5
9	2-Methyl-THF	83	52	10	>95:5

[a] Typical procedure for the reaction according to method B. [b] Determined by ^{1}H NMR analysis using 1,3,5-trimethoxybenzene as an internal standard. [c] Not analyzed.

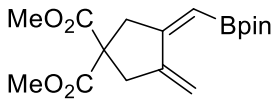
5. Typical Procedure for Cobalt-Catalyzed Cyclization/Hydroboration of 1,6-Diynes with HBpin



In an argon-filled glovebox, a vial (10 mL) was charged with diynes (0.5 mmol), HBpin (0.5 mmol), anhydrous THF (5 mL) and complex **L1**.$CoCl_2$ (0.015 mmol). The reaction mixture was stirred at room temperature (25~35 ^oC) for 1 minutes, then TBAF (1 M in THF, 30 μL, 0.03 mmol, 6 mol %) was added. After stirring for 2 hours at rt, the vial was removed from the glovebox and the reaction mixture was concentrated by rotary evaporation. The product was isolated by column chromatography over silica gel deactivated with 2% NEt_3 in hexanes.

6. Analytical Data of Products

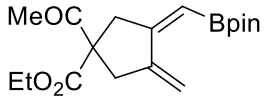
Dimethyl(*Z*)-3-methylene-4-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl ene)cyclopentane-1,1-dicarboxylate (2a)



Compound **2a** was prepared according to typical procedure as a yellow oily liquid (139 mg, 83%). The flash chromatography was performed with PE/EA (30:1~10:1, v/v) as the eluent. ^1H NMR (400 MHz, $CDCl_3$) δ 6.18 (s, 1H), 5.36 (s, 1H), 5.20 (s, 1H), 3.72 (s, 6H), 3.12 (s, 2H), 3.08 (s, 2H), 1.28 (s, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.59, 156.16, 143.87, 113.35, 83.30, 56.94, 52.83, 45.36, 42.70, 24.87. ^{11}B NMR (128 MHz, $CDCl_3$) δ 29.42. HRMS (ESI) Calcd for [$C_{17}H_{25}BNaO_6$, M + Na]$^+$: 359.1642; Found: 359.1640. The relative configuration of compound **2a** was

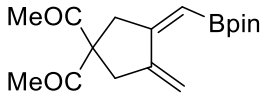
determined from 2D-NOE spectroscopy. The correlation from H_a and H_d, H_a and H_e, H_a and H_f, H_c and H_e, H_b and H_d, H_c and H_f based on 2D-NOE experiment also determines the vinylboronate fragment with a *Z*-configuration.

Ethyl (*Z*)-1-acetyl-3-methylene-4-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl) methylene)cyclopentane-1-carboxylate (2b)



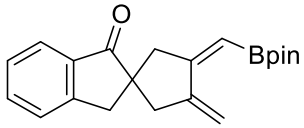
Compound **2b** was prepared according to typical procedure as a yellow oily liquid (140 mg, 84%). The flash chromatography was performed with PE/EA (30:1~10:1, v/v) as the eluent. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.15 (s, 1H), 5.35 (s, 1H), 5.19 (s, 1H), 4.19 (q, *J* = 7.1 Hz, 2H), 3.13-2.94 (m, 4H), 2.17 (s, 3H), 1.27 (s, 12H), 1.24 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 203.26, 171.90, 156.48, 144.08, 113.35, 83.34, 63.35, 61.75, 44.04, 41.41, 26.40, 24.89, 14.07. ^{11}B NMR (128 MHz, $CDCl_3$) δ 29.29. HRMS (ESI) Calcd for $[C_{18}H_{27}BNaO_5, M + Na]^+$: 357.1849; Found: 357.1848.

(*Z*)-1,1'-(3-methylene-4-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methylene) cyclopentane-1,1-diyl)bis(ethan-1-one) (2c)



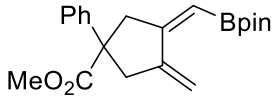
Compound **2c** was prepared according to typical procedure as a yellow oily liquid (109 mg, 72%). The flash chromatography was performed with PE/EA (30:1~10:1, v/v) as the eluent. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.07 (s, 1H), 5.31 (s, 1H), 5.13 (s, 1H), 2.98 (s, 2H), 2.93 (s, 2H), 2.05 (s, 6H), 1.20 (s, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 205.08, 156.17, 143.95, 113.58, 83.36, 71.05, 42.96, 40.31, 26.70, 24.86. ^{11}B NMR (128 MHz, $CDCl_3$) δ 29.58. HRMS (ESI) Calcd for $[C_{17}H_{25}BNaO_4, M + Na]^+$: 327.1744; Found: 327.1743.

(*Z*)-3-methylene-4-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methylene)spiro[cyclopentane-1,2'-inden]-1'(*3'H*)-one (2d)



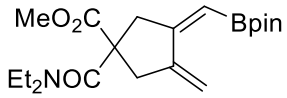
Compound **2d** was prepared according to typical procedure as a yellow oily liquid (118 mg, 70%). The flash chromatography was performed with PE/EA (30:1~10:1, v/v) as the eluent. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 7.6 Hz, 1H), 7.59 (td, *J* = 7.5, 1.1 Hz, 1H), 7.42 (d, *J* = 7.7 Hz, 1H), 7.37 (t, *J* = 7.5 Hz, 1H), 6.26 (d, *J* = 2.8 Hz, 1H), 5.38 (s, 1H), 5.20 (s, 1H), 3.10 (dd, *J* = 16.1, 2.6 Hz, 1H), 3.01 (m, 3H), 2.35 (d, *J* = 4.3 Hz, 1H), 2.31 (d, *J* = 1.6 Hz, 1H), 1.31 (s, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 208.70, 158.50, 152.60, 146.03, 136.36, 135.01, 127.53, 126.69, 124.15, 112.76, 83.37, 53.70, 49.95, 46.78, 41.27, 24.92. ^{11}B NMR (128 MHz, $CDCl_3$) δ 29.79. HRMS (EI): Caculated for $[C_{21}H_{25}BO_3, M]^+$: 336.1897, found: 336.1888.

Methyl-(*Z*)-3-methylene-1-phenyl-4-((4,4,5,5-tetramethyl-1,3,2–dioxaborolan-2-yl)methylene)cyclopentane-1-carboxylate (2e)



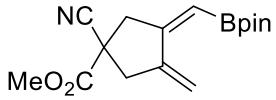
Compound **2e** was prepared according to typical procedure as a yellow oily liquid (138 mg, 78%). The flash chromatography was performed with PE/EA (30:1~10:1, v/v) as the eluent. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37-7.26 (m, 4H), 7.26-7.20 (m, 1H), 6.21 (s, 1H), 5.42 (s, 1H), 5.24 (s, 1H), 3.59 (s, 3H), 3.55-3.39 (m, 2H), 2.96 (dd, *J* = 16.4, 1.8 Hz, 1H), 2.89 (d, *J* = 15.0 Hz, 1H), 1.28 (s, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.29, 157.45, 144.94, 141.98, 128.52, 127.16, 126.67, 113.21, 83.33, 54.75, 52.60, 48.15, 45.40, 24.93. ^{11}B NMR (128 MHz, $CDCl_3$) δ 29.31. HRMS (ESI) Calcd for $[C_{21}H_{27}BNaO_4, M + Na]^+$: 377.1900; Found: 377.1920.

Methyl-(*Z*)-1-(diethylcarbamoyl)-3-methylene-4-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methylene)cyclopentane-1-carboxylate (2f)



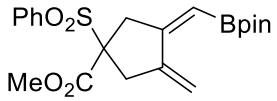
Compound **2f** was prepared according to typical procedure as a yellow oily liquid (139 mg, 74%). The flash chromatography was performed with PE/EA (30:1~10:1, v/v) as the eluent. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.16 (s, 1H), 5.33 (s, 1H), 5.18 (s, 1H), 3.71 (d, *J* = 1.6 Hz 3H), 3.35 (q, *J* = 6.8 Hz, 2H), 3.23-3.12 (m, 4H), 3.12-2.98 (m, 2H), 1.27 (d, *J* = 1.6 Hz, 12H), 1.09 (q, *J* = 6.6 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.77, 168.61, 156.86, 144.09, 112.82, 83.11, 56.16, 52.53, 46.18, 43.59, 40.86, 40.04, 24.78, 13.32, 12.15. ^{11}B NMR (128 MHz, $CDCl_3$) δ 30.96. HRMS (ESI) Calcd for $[C_{20}H_{32}BNNaO_5, M + Na]^+$: 400.2271; Found: 400.2268.

Methyl-(*Z*)-1-cyano-3-methylene-4-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methylene)cyclopentane-1-carboxylate (2g)



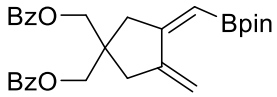
Compound **2g** was prepared as yellow oily liquid (85 mg, 56%) according to typical procedure but adding the diyne after the generation of active catalysts. The flash chromatography was performed with PE/EA (30:1~10:1, v/v) as the eluent. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.32 (s, 1H), 5.43 (s, 1H), 5.30 (s, 1H), 3.83 (s, 3H), 3.27-3.12 (m, 2H), 3.10-3.00 (m, 2H), 1.29 (s, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.74, 153.24, 141.65, 119.65, 115.27, 83.66, 53.92, 47.37, 44.96, 24.95. ^{11}B NMR (128 MHz, $CDCl_3$) δ 29.32. HRMS (ESI) Calcd for $[C_{16}H_{22}BNNaO_4, M + Na]^+$: 326.1540; Found: 326.1538.

Methyl-(*Z*)-3-methylene-1-(phenylsulfonyl)-4-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methylene)cyclopentane-1-carboxylate (2h)



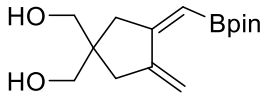
Compound **2h** was prepared according to typical procedure as a yellow oily liquid (121 mg, 58%). The flash chromatography was performed with PE/EA (30:1~10:1, v/v) as the eluent. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85-7.80 (m, 2H), 7.73-7.65 (m, 1H), 7.56 (t, *J* = 7.8 Hz, 2H), 6.19 (s, 1H), 5.35 (s, 1H), 5.19 (s, 1H), 3.65 (s, 3H), 3.44-3.27 (m, 2H), 3.24-3.10 (m, 2H), 1.27 (s, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.13, 154.27, 142.36, 136.51, 134.43, 129.90, 129.02, 114.34, 83.55, 75.34, 53.57, 42.75, 40.52, 24.97. ^{11}B NMR (128 MHz, $CDCl_3$) δ 29.16. HRMS (ESI) Calcd for $[C_{21}H_{27}BSNaO_6$, M + Na$]^+$: 441.1519; Found: 441.1518.

(*Z*)-(3-methylene-4-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methylene)cyclopentane-1,1-diyl)bis(methylene) dibenzoate (2i)



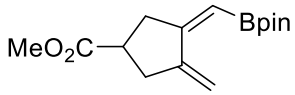
Compound **2i** was prepared according to typical procedure as a colorless oily liquid (194 mg, 80%). The flash chromatography was performed with PE/EA (30:1~10:1, v/v) as the eluent. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05-8.00 (m, 4H), 7.58-7.52 (m, 2H), 7.42 (t, *J* = 7.7 Hz, 4H), 6.22 (s, 1H), 5.40 (s, 1H), 5.22 (s, 1H), 4.39-4.30 (m, 4H), 2.72 (d, *J* = 1.7 Hz, 2H), 2.67 (s, 2H), 1.29 (s, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.42, 157.50, 144.99, 133.13, 129.97, 129.65, 128.47, 113.69, 83.36, 67.21, 44.29, 43.05, 41.22, 24.92. ^{11}B NMR 29.19. HRMS (ESI) Calcd for $[C_{29}H_{33}BNaO_6$, M + Na$]^+$: 511.2268; Found: 511.2265.

(*Z*)-(3-methylene-4-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methylene)cyclopentane-1,1-diyl)dimethanol (2j)



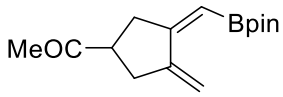
Compound **2j** was prepared as a yellow oily liquid (118 mg, 85%) according to typical procedure but adding the diyne after the generation of active catalyst. The flash chromatography was performed with PE/EA (10:1~3:1, v/v) as the eluent. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.07 (s, 1H), 5.31 (s, 1H), 5.14 (s, 1H), 3.58 (d, *J* = 4.1 Hz, 4H), 3.37 (s, 2H), 2.43-2.37 (m, 4H), 1.28 (s, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.98, 146.03, 112.91, 83.36, 68.61, 44.88, 43.86, 40.54, 24.89. ^{11}B NMR (128 MHz, $CDCl_3$) δ 30.44. HRMS (ESI) Calcd for $[C_{15}H_{25}BNaO_4, M + Na]^+$: 303.1744; Found: 303.1741.

Methyl-(*Z*)-3-methylene-4-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl) methylene)cyclopentane-1-carboxylate (2k)



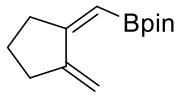
Compound **2k** was prepared according to typical procedure as a yellow oily liquid (90 mg, 65%). The flash chromatography was performed with PE/EA (30:1~10:1, v/v) as the eluent. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.12 (s, 1H), 5.35 (s, 1H), 5.17 (s, 1H), 3.68 (d, *J* = 2.0 Hz, 3H), 2.88-2.71 (m, 5H), 1.29 (s, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.35, 158.29, 145.75, 112.33, 83.35, 51.90, 41.84, 41.10, 38.72, 24.92. ^{11}B NMR (128 MHz, $CDCl_3$) δ 29.64. HRMS (EI) Calcd for $[C_{15}H_{23}BO_4, M]^+$: 278.1689; Found: 278.1684.

(*Z*)-1-(3-methylene-4-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methylene)cyclopentyl)ethan-1-one (2l)



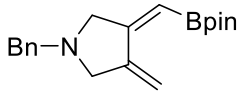
Compound **2l** was prepared according to typical procedure as a yellow oily liquid (52 mg, 40%). The flash chromatography was performed with PE/EA (30:1~10:1, v/v) as the eluent. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.10 (s, 1H), 5.35 (s, 1H), 5.17 (s, 1H), 3.04-2.88 (m, 1H), 2.79-2.63 (m, 4H), 2.17 (s, 3H), 1.29 (s, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 209.52, 158.50, 145.92, 112.38, 83.37, 49.34, 40.82, 37.77, 28.77, 24.93. ^{11}B NMR (128 MHz, $CDCl_3$) δ 29.63. HRMS (EI) Calcd for $[C_{15}H_{23}BO_3, M]^+$: 262.1740; Found: 262.1735.

(*Z*)-4,4,5,5-tetramethyl-2-((2-methylenecyclopentylidene)methyl)-1,3,2-dioxaborolane (2m)



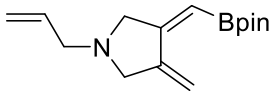
Compound **2m** was prepared according to typical procedure as a yellow oily liquid (49 mg, 45%). The flash chromatography was performed with PE/EA (100:1~50:1, v/v) as the eluent. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.06 (s, 1H), 5.32 (s, 1H), 5.13 (s, 1H), 2.55-2.43 (m, 4H), 1.64 (p, J = 7.2 Hz, 2H), 1.29 (s, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.40, 148.30, 111.06, 83.21, 39.15, 35.74, 24.96, 23.67. ^{11}B NMR (128 MHz, $CDCl_3$) δ 29.91. HRMS (ESI) Calcd for $[C_{13}H_{22}BO_2, M + H]^+$: 221.1713; Found: 221.1819.

(*E*)-1-benzyl-3-methylene-4-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methylene)pyrrolidine (2n)



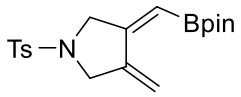
Compound **2n** was prepared according to typical procedure as a yellow oily liquid (114 mg, 73%). The flash chromatography was performed with PE/EA (20:1~5:1, v/v) as the eluent. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36-7.28 (m, 4H), 7.29-7.23 (m, 1H), 6.31 (s, 1H), 5.30 (s, 1H), 5.16 (s, 1H), 3.60 (s, 2H), 3.36 (d, *J* = 1.9 Hz, 2H), 3.33 (t, *J* = 1.9 Hz, 2H), 1.27 (s, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.64, 144.17, 138.64, 128.85, 128.34, 127.13, 111.51, 83.35, 64.28, 61.53, 60.53, 24.92. ^{11}B NMR (128 MHz, $CDCl_3$) δ 29.31. HRMS (ESI) Calcd for $[C_{19}H_{27}BNO_2, M + H]^+$: 312.2135; Found: 312.2133.

(*E*)-1-allyl-3-methylene-4-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methylene)pyrrolidine (2o)



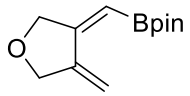
Compound **2o** was prepared according to typical procedure as a yellow oily liquid (112 mg, 86%). The flash chromatography was performed with PE/EA (20:1~5:1, v/v) as the eluent. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.30 (s, 1H), 5.96- 5.81 (m, 1H), 5.31 (s, 1H), 5.24-5.16 (m, 2H), 5.11 (d, *J* = 10.2 Hz, 1H), 3.35 (s, 2H), 3.33 (s, 2H), 3.08 (d, *J* = 6.4 Hz, 2H), 1.28 (s, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.53, 144.06, 135.51, 117.26, 111.47, 83.36, 64.09, 61.43, 59.16, 24.91. ^{11}B NMR (128 MHz, $CDCl_3$) δ 29.62. HRMS (ESI) Calcd for $[C_{15}H_{25}BNO_2, M + H]^+$: 262.1978; Found: 262.2351.

(*E*)-3-methylene-4-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methylene)-1-tosylpyrrolidine (2p)



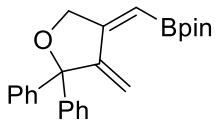
Compound **2p** was prepared according to typical procedure as a yellow oily liquid (99 mg, 53%). The flash chromatography was performed with PE/EA (20:1~5:1, v/v) as the eluent. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, *J* = 8.2 Hz, 2H), 7.34 (d, *J* = 8.0 Hz, 2H), 6.27 (t, *J* = 2.0 Hz, 1H), 5.32 (s, 1H), 5.21 (s, 1H), 4.02-3.96 (m, 4H), 2.44 (s, 3H), 1.27 (s, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.02, 143.93, 140.51, 129.78, 128.05, 113.35, 83.71, 56.38, 54.41, 24.88, 21.62. ^{11}B NMR (128 MHz, $CDCl_3$) δ 29.77. HRMS (ESI) Calcd for $[C_{19}H_{26}BNNaO_4S$, M + Na$]^+$: 398.1573; Found: 398.1573.

(*E*)-4,4,5,5-tetramethyl-2-((4-methylenedihydrofuran-3(*2H*)-ylidene)methyl)-1,3,2-dioxaborolane (2q)



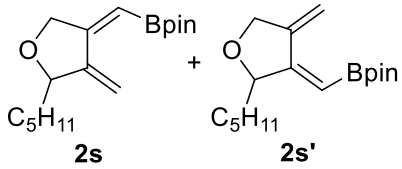
Compound **2q** was prepared according to typical procedure as a yellow oily liquid (90 mg, 81%). The flash chromatography was performed with PE/EA (30:1~10:1, v/v) as the eluent. m.p.: 48.5-52 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.39 (t, *J* = 2.3 Hz, 1H), 5.35-5.30 (m, 1H), 5.25-5.20 (m, 1H), 4.50 (t, *J* = 2.0 Hz, 2H), 4.47 (d, *J* = 2.0 Hz, 2H), 1.31 (s, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.02, 143.66, 110.62, 83.59, 76.18, 74.40, 24.97. ^{11}B NMR (128 MHz, $CDCl_3$) δ 29.79. HRMS (ESI) Calcd for $[C_{12}H_{19}BNaO_3$, M + Na$]^+$: 245.1325; Found: 245.1323.

(*E*)-4,4,5,5-tetramethyl-2-((4-methylene-5,5-diphenyldihydrofuran-3(*2H*)-ylidene)methyl)-1,3,2-dioxaborolane (2r)



Compound **2r** was prepared according to typical procedure as a yellow oily liquid (138 mg, 74%). The flash chromatography was performed with PE/EA (30:1~10:1, v/v) as the eluent. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37-7.24 (m, 10H), 6.71 (s, 1H), 5.28 (s, 1H), 4.93 (s, 1H), 4.43 (s, 2H), 1.28 (s, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.66, 149.65, 143.42, 128.04, 127.96, 127.51, 116.13, 92.40, 83.52, 71.96, 25.00. ^{11}B NMR (128 MHz, $CDCl_3$) δ 29.59. HRMS (ESI) Calcd for [$C_{24}H_{27}BNaO_3$, M + Na]$^{+}$:397.1951; Found: 397.1950.

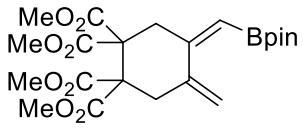
(*E*)-4,4,5,5-tetramethyl-2-((4-methylene-5-pentyldihydrofuran-3(*2H*)-ylidene)methyl)-1,3,2-dioxaborolane (2s) & (*E*)-4,4,5,5-tetramethyl-2-((4-methylene-2-pentyldihydrofuran-3(*2H*)-ylidene)methyl)-1,3,2-dioxaborolane (2s')



Compound **2s** and **2s'** were prepared according to typical procedure as yellow oily liquid (105 mg, 72%). The flash chromatography was performed with PE/EA (40:1~20:1, v/v) as the eluent. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.42 (d, J = 2.0 Hz, 1H), 6.32 (s, 0.63H), 5.29 (s, 1H), 5.24 (s, 0.73H), 5.19 (s, 0.77H), 5.12 (s, 1H), 4.52-4.36 (m, 5.54H), 1.71-1.62 (m, 2.87H), 1.48 (m, 3.69H), 1.30 (m, 36.41H), 0.89 (m, 9.31H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.48, 157.01, 147.41, 144.54, 110.67, 110.33, 84.98, 83.61, 83.57, 83.51, 74.10, 72.07, 34.96, 32.04, 31.99, 25.16, 25.11,

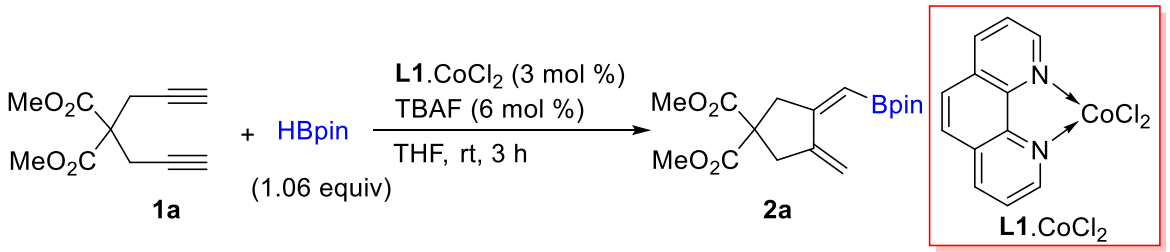
24.96, 24.70, 22.75, 22.70, 14.19. ^{11}B NMR (128 MHz, $CDCl_3$) δ 30.84, 22.67. HRMS (EI) Calcd for [$C_{17}H_{29}BO_3$, M]$^+$: 292.2210; Found: 292.2204.

Tetramethyl (*Z*)-4-methylene-5-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methylene)cyclohexane-1,1,2,2-tetracarboxylate (2t)



Compound **2t** was prepared according to typical procedure as a yellow oily liquid (151 mg, 65%). The flash chromatography was performed with PE/EA (10:1~5:1, v/v) as the eluent. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.17-5.10 (m, 2H), 4.88 (s, 1H), 3.79-3.72 (m, 12H), 3.07 (s, 2H), 3.04 (s, 2H) 1.22 (s, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.95, 153.62, 141.41, 115.22, 82.91, 59.99, 52.93, 41.79, 38.66, 24.66. ^{11}B NMR (128 MHz, $CDCl_3$) δ 30.41. HRMS (ESI) Calcd for [$C_{22}H_{31}BNaO_{10}$, M + Na]$^+$: 489.1908; Found: 489.1907.

7. Gram-Scale Experiment

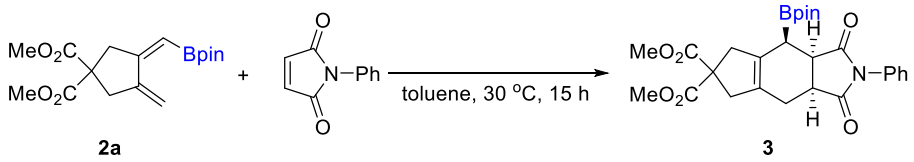


The pre-catalyst **L1**.$CoCl_2$ (46.5 mg, 0.15 mmol, 3 mol %) was introduced into an oven-dried 100 mL Schlenk flask in an argon-filled glovebox. After THF (40 mL), HBpin (678 mg, 5.3 mmol) and TBAF (1M in THF, 300 μL, 0.30 mmol, 6 mol %) were introduced into the Schlenk flask, and the mixture was stirred at room temperature for 1 minutes The diyne **1a** (1.04 g, 5.0 mmol) diluted in THF (10 mL) was then added dropwise and the resulting solution stirred at rt for 3 h The reaction

mixture was concentrated by rotating evaporation and purified by a flash column chromatography on silica gel using PE/EA (30:1~10:1, v/v) as the eluent to give 1.34 g (4.0 mmol, 80% yield) of **2a** as a yellow oily liquid.

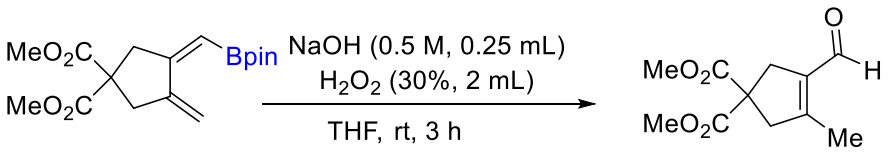
8. Transformations of Product 2a

8.1 Synthesis of Dimethyl 1,3-dioxo-2-phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2,3,3a,4,5,7,8,8a-octahydrocyclopenta[*f*]isoindole-6,6(*1H*)-dicarboxylate (3)



Compound **3** was prepared according to the reported procedure:[7] Under argon atmosphere, a mixture of compound **2a** (0.49 mmol, 0.165 g) and N-phenylmaleimid (0.74 mmol, 1.5 equiv) in toluene (2.5 mL) was stirred for 15 h at 30 ℃. The resulted mixture was concentrated under vacuum and the residue was purified by column chromatography using PE/EA (10:1~3:1, v/v) as the eluent to give 0.167g (0.33 mmol, 67% yield) of **3** as a yellow oily liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49-7.40 (m, 2H), 7.35 (t, *J* = 7.0 Hz, 1H), 7.26-7.20 (m, 2H), 3.71 (s, 3H), 3.65 (s, 3H), 3.40 (m, 2H), 3.16-2.85 (m, 4H), 2.67-2.54 (m, 2H), 2.50-2.40 (m, 1H), 1.26-1.18 (m, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 179.66, 179.39, 172.32, 172.21, 132.24, 132.14, 129.57, 129.02, 128.47, 126.57, 84.09, 57.86, 52.79, 43.66, 40.76, 39.53, 24.81, 24.73, 24.58, 24.23. ^{11}B NMR (128 MHz, $CDCl_3$) δ 30.30. HRMS (ESI) Calcd for $[C_{27}H_{32}BNNaO_8, M + Na]^+$: 532.2119; Found: 532.2118. The relative configuration of compound **3** was determined by 2D-NOE spectroscopy. The correlation from H_a and H_c, H_b and H_d, based on 2D-NOE experiment determines the H_a and H_c, H_b and H_d with a *cis*-configuration.

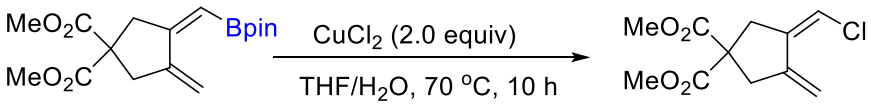
8.2 Synthesis of Dimethyl 3-formyl-4-methylcyclopent-3-ene-1,1-dicarboxylate (4)



2a **4**

Compound **4** was prepared according to the reported procedure:[8] To a solution of **2a** (0.53 mmol, 0.178 g) in THF (1 mL), aqueous 0.5 M NaOH (0.25 mL) and 30% aq. H_2O_2 (2.0 mL) was successively added via syringe at 0 °C. The resulted mixture was stirred at room temperature for 3 hours. Then saturated aqueous $Na_2S_2O_3$ was added dropwise. The mixture was diluted with H_2O and extracted with DCM. The combined organic layer was dried over $MgSO_4$ and concentrated in vacuo. The residue was purified by column chromatography on silica gel with PE/EA (10:1, v/v) as the eluent to give 0.113 g (0.5 mmol, 95% yield) of **4** as a colorless oily liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.93 (s, 1H), 3.75 (s, 6H), 3.24 (s, 4H), 2.16 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 187.25, 171.89, 157.72, 135.08, 56.68, 53.20, 47.78, 38.43, 13.98. HRMS (ESI) Calcd for $[C_{11}H_{14}NaO_5, M + Na]^+$: 249.0739; Found:249.0737.

8.3 Synthesis of Dimethyl (*Z*)-3-(chloromethylene)-4-methylenecyclopentane-1,1-dicarboxylate (5)

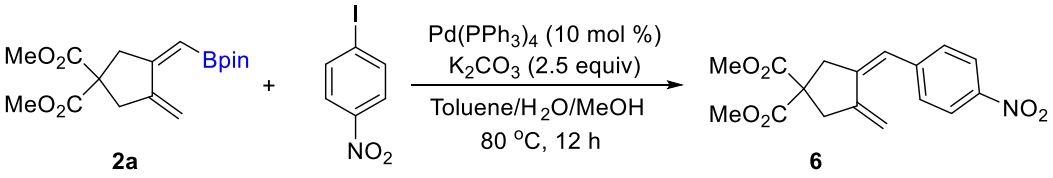


2a **5**

Compound **5** was prepared according to the reported procedure:[9] Under argon atmosphere, a solution of **2a** (0.45 mmol, 0.151 g) and $CuCl_2$ (0.90 mmol, 2.0 equiv) in THF (0.5 mL) and H_2O (0.5 mL) was stirred for 10 h at 70 °C. The resulting mixture was extracted with EA (10 mL) and the organic layer was dried over $MgSO_4$. After filtration and evaporation of all volatiles, the residue was purified on silica gel with PE/EA (20:1, v/v) as the eluent to give 0.0850 g (0.35 mmol, 78% yield) of **5** as a colorless oily liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.13 (s, 2H), 5.37 (s, 1H), 3.74

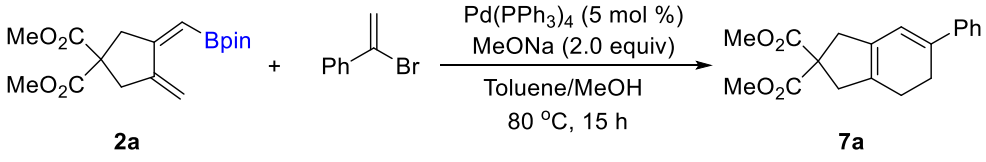
(s, 6H), 3.11 (s, 2H), 3.07 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.15, 141.67, 135.88, 114.76, 112.53, 57.65, 53.07, 42.89, 41.69. HRMS (ESI) Calcd for $[C_{11}H_{13}ClNaO_4, M + Na]^+$: 267.0400; Found:267.0398.

8.4 Synthesis of Dimethyl (*Z*)-3-methylene-4-(4-nitrobenzylidene)cyclopentane-1,1-dicarboxylate (6)



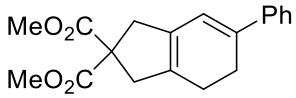
To a flame-dried sealed tube charged with a magnetic stir bar, $Pd(PPh_3)_4$ (0.061mmol, 0.071 g), compound **2a** (0.61 mmol dissolved in 3 ml of toluene), K_2CO_3 (1.53 mmol, 0.21 g, dissolved in 1 mL H_2O and 1 mL MeOH), and *p*-nitroiodobenzene (1.22 mmol, 0.304 g) was added under an inert atmosphere. The reaction tube was sealed and heated at 80 ℃. After 12 hours, the reaction mixture was cooled to ambient temperature, diluted with ether, filtered through a pad of celite, and concentrated in vacuo. The crude material was purified on silica gel with PE/EA (30:1~10:1, v/v) as the eluent to give 0.123 g (0.37 mmol, 60% yield) of **6** as a yellow oily liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (d, *J* = 8.3 Hz, 2H), 7.54 (d, *J* = 8.3 Hz, 2H), 6.47 (s, 1H), 5.13 (s, 1H), 5.02 (s, 1H), 3.77 (s, 6H), 3.19 (s, 2H), 3.10 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.55, 146.53, 144.64, 142.22, 140.44, 129.54, 123.84, 122.73, 112.85, 56.99, 53.13, 43.14, 42.70. HRMS (ESI) Calcd for $[C_{17}H_{17}NNaO_6, M + Na]^+$: 354.0954; Found: 354.0953.The relative configuration of compound **6** was determined from 2D-NOE spectroscopy. The correlation from H_a and H_c, H_b and H_d, H_d and H_f, H_e and H_f based on 2D-NOE experiment determines the aryl alkene fragment with a *Z*-configuration.

8.5 Synthesis of Cyclohexadienes (7)



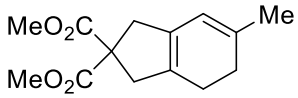
To a flame-dried sealed tube charged with a magnetic stir bar, $Pd(PPh_3)_4$ (0.024 mmol, 0.028 g), compound **2a** (0.48 mmol, 0.162 g dissolved in 4 ml toluene), NaOMe (0.97 mmol, 0.052 g, in 1 ml MeOH), and the vinyl bromide (0.97 mmol, 0.177 g) were added under an inert atmosphere. The reaction tube was sealed and heated at 80 ℃. After 15 hours, the reaction mixture was cooled to ambient temperature, diluted with ether, filtered through a pad of celite, and concentrated in vacuo. The crude material was purified on silica gel with PE/EA (30:1~10:1, v/v) as the eluent to give 0.108 g (0.35 mmol, 72% yield) of **7a** as a yellow solid.

Dimethyl 6-phenyl-1,3,4,5-tetrahydro-*2H*-indene-2,2-dicarboxylate (7a)



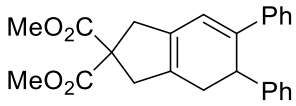
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (m, 2H), 7.34-7.27 (m, 2H), 7.24-7.17 (m, 1H), 6.24 (s, 1H), 3.74 (s, 6H), 3.16-3.08 (m, 4H), 2.69 (t, *J* = 9.8 Hz, 2H), 2.32 (t, *J* = 9.6 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.72, 141.09, 135.94, 132.50, 131.31, 128.40, 126.99, 125.05, 119.04, 58.67, 52.92, 43.30, 41.53, 26.48, 23.82. HRMS (ESI) Calcd for $[C_{19}H_{20}NaO_4, M + Na]^+$: 335.1259; Found: 335.1260.

Dimethyl 6-methyl-1,3,4,5-tetrahydro-*2H*-indene-2,2-dicarboxylate (7b)



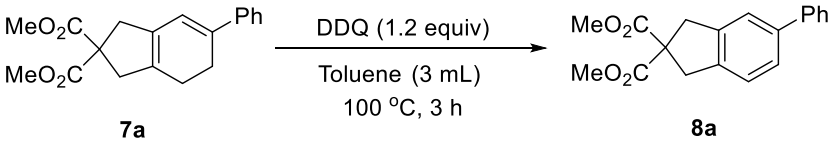
The reaction tube was heated at 100 ℃. The crude material was purified on silica gel with PE/EA (30:1~10:1, v/v) as the eluent to give 104 mg (0.416 mmol, 51% yield) of **7b** as a colorless oily liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.59 (s, 1H), 3.73 (s, 6H), 3.00 (s, 4H), 2.18 (s, 4H), 1.77 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.84, 135.36, 130.51, 128.83, 117.32, 58.56, 52.83, 43.22, 41.54, 29.05, 23.44, 23.16. HRMS (EI) Calcd for $[C_{14}H_{18}O_4, M]^+$: 250.1205; Found: 250.1201.

Dimethyl 5,6-diphenyl-1,3,4,5-tetrahydro-*2H*-indene-2,2-dicarboxylate (7c)



The crude material was purified on silica gel with PE/EA (30:1~10:1, v/v) as the eluent to give 120 mg (0.31 mmol, 64% yield) of **7c** as a yellow oily liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37-7.10 (m, 10H), 6.57 (s, 1H), 4.03 (d, *J* = 8.7 Hz, 1H), 3.73 (s, 3H), 3.66 (s, 3H), 3.27 (d, *J* = 16.0 Hz, 1H), 3.18-2.99 (m, 2H), 2.90 (m, 2H), 2.38 (d, *J* = 17.3 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.65, 172.45, 143.30, 140.39, 137.86, 131.41, 130.89, 128.58, 128.36, 127.45, 127.07, 126.51, 125.60, 120.57, 58.97, 52.96, 52.88, 43.25, 42.57, 41.32, 33.52. HRMS (ESI) Calcd for [$C_{25}H_{24}NaO_4$, M + Na]$^{+}$: 411.1572; Found: 411.1571.

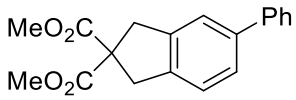
8.6 Synthesis of Multisubstituted Benzenes (8)



7a **8a**

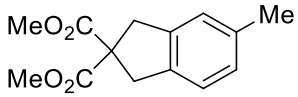
Compound **8a** was prepared according to the reported procedure:[10] To a flame-dried tube charged with a magnetic stir bar, compound **7a** (0.27 mmol, 0.084 g) and DDQ (0.32 mmol, 0.073 g dissolved in 3 ml toluene) were added under an argon atmosphere. The reaction tube was sealed and heated at 100 ℃ for 3 h. A colorless precipitate of 2,3-dichloro-5,6-dicyanohydroquinone was observed. After cooling to room temperature, the precipitate was removed by filtration, and the filtrate was concentrated in vacuo. The crude material was purified on silica gel with PE/EA (30:1~10:1, v/v) as the eluent to give 0.076 g (0.25 mmol, 92% yield) of **8a** as a yellow oily liquid.

Dimethyl 5-phenyl-1,3-dihydro-*2H*-indene-2,2-dicarboxylate (8a)



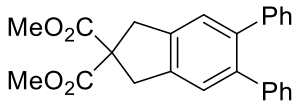
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58-7.51 (m, 2H), 7.39 (m, 4H), 7.31 (m, 1H), 7.25 (d, *J* = 7.6 Hz, 1H), 3.75 (m, 6H), 3.65 (s, 2H), 3.63 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.15, 141.30, 140.64, 140.46, 139.08, 128.78, 127.20, 126.28, 124.57, 123.10, 60.55, 53.09, 40.67, 40.40. HRMS (EI) Calcd for $[C_{19}H_{18}O_4, M]^+$: 310.1205; Found: 310.1201.

Dimethyl 5-methyl-1,3-dihydro-*2H*-indene-2,2-dicarboxylate (8b)



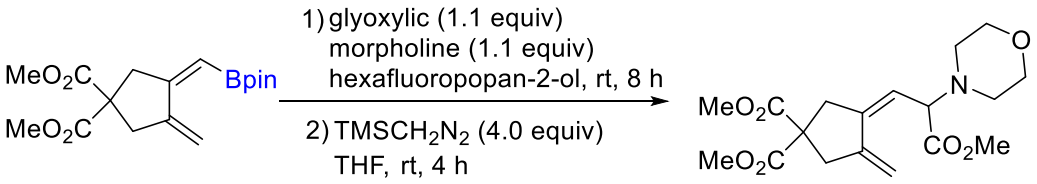
The crude material was purified on silica gel with PE/EA (30:1~10:1, v/v) as the eluent to give 50 mg (0.206 mmol, 86% yield) of **8b** as a colorless oily liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.07 (d, *J* = 7.6 Hz, 1H), 7.01 (s, 1H), 6.97 (d, *J* = 7.6 Hz, 1H), 3.74 (s, 6H), 3.55 (s, 4H), 2.30 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.27, 140.06, 136.87, 136.73, 127.88, 124.97, 124.01, 60.59, 53.05, 40.59, 40.32, 21.36. HRMS (ESI) Calcd for $[C_{14}H_{17}O_4, M + H]^+$: 249.1127; Found: 249.1125.

Dimethyl 5,6-diphenyl-1,3-dihydro-*2H*-indene-2,2-dicarboxylate (8c)



The crude material was purified on silica gel with PE/EA (30:1~10:1, v/v) as the eluent to give 80 mg (0.207 mmol, 71% yield) of **8c** as a colorless oily liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 (s, 2H), 7.29-7.11 (m, 10H), 3.85 (s, 6H), 3.77 (s, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.18, 141.69, 139.78, 139.35, 129.99, 127.89, 126.40, 60.56, 53.15, 40.51. HRMS (ESI) Calcd for $[C_{25}H_{22}NaO_4, M + Na]^+$: 409.1416; Found: 409.1415.

8.7 Synthesis of Dimethyl-(*Z*)-3-(3-methoxy-2-morpholino-3-oxopropylidene)-4-methylenecyclopentane-1,1-dicarboxylate (9)

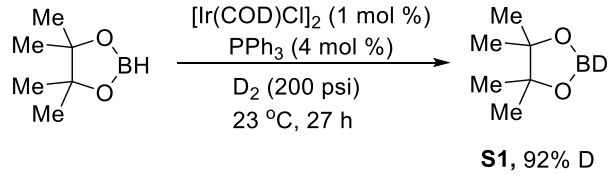


2a **9**

Compound **9** was prepared according to the reported procedure:[11] Glyoxylic acid monohydrate (0.56 mmol, 0.052 g) and morpholine (0.56 mmol, 0.049 g) were added to a stirred solution of **2a** (0.51 mmol) in hexafluoropropan-2-ol (5 mL) under an argon atmosphere at room temperature. The reaction mixture was stirred for 8 h. The solvent was removed under reduced pressure to give a residue that was directly used for the further esterification reaction. To a solution of the crude acid in THF (5 mL) at 0 °C was added a solution of $TMSCH_2N_2$ (1.03 mL, 2M) in THF until the persistence of yellow color. After 4 h, the solvent was evaporated, and the resulting residue was purified on silica gel with PE/EA (5:1~3:1, v/v) as the eluent to give 0.136 g (0.37 mmol, 72% yield) of **9** as a yellow oily liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.59 (s, 1H), 5.54 (d, *J* = 9.2 Hz, 1H), 5.25 (s, 1H), 4.07 (d, *J* = 9.3 Hz, 1H), 3.80-3.67 (m, 13H), 3.17-2.99 (m, 4H), 2.60-2.51 (m, 2H), 2.51-2.41 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.49, 171.35, 170.92, 142.69, 142.33, 120.87, 113.80, 67.38, 66.81, 57.03, 52.90, 52.02, 51.00, 42.56, 41.90. HRMS (ESI) Calcd for $[C_{18}H_{25}NNaO_7, M + Na]^+$: 390.1529; Found:390.1526.

9. Mechanistic Experiments

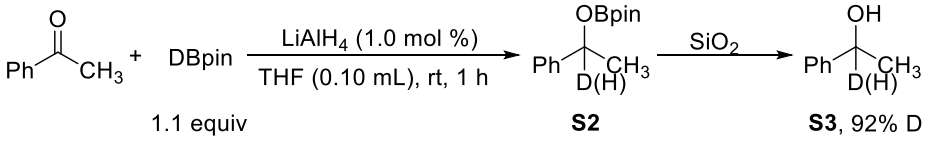
9.1 Synthesis of Pinacolborane-d1 (S1)



S1, 92% D

The title compound **S1** was prepared according to previously published procedure:[12] $[Ir(COD)Cl]_2$ (134 mg, 0.20 mmol, 0.0097 equiv) and PPh_3 (210 mg, 0.80 mmol, 0.039 equiv) were charged in a vial and pinacolborane (2.65 g, 3.00 mL, 20.70 mmol, 1.00 equiv) was added. The vial was carefully sealed in a pressure reactor and removed from the inert atmosphere box. The reactor was purged once with D_2 then pressurized to 200 psi and stirred at 23 ℃ for 12 h. The reactor was vented and repressurized to 150 psi, stirred for 15 h at 23 ℃, vented and brought into the inert atmosphere box. The reaction mixture was under reduced pressure to give a colorless oily liquid (2.68 g). ^{1}H NMR (400MHz, C_6D_6): δ 1.04 (s, 12H). ^{13}C NMR (101 MHz, C_6D_6): δ 83.20, 25.02. ^{11}B NMR (128 MHz, C_6D_6): δ 29.90-27.15 (broad m).

9.2 Determine the Amount of 2H-incorporation

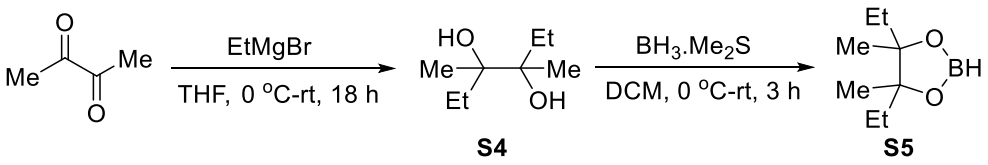


S2 **S3**, 92% D

The title compound **S3** was prepared according to previously published procedure:[13] Acetophenone (0.06 g, 0.5 mmol), DBpin (0.071 g, 0.55 mmol) and THF (0.10 mL) were added at room temperature to a flask containing a solution of $LiAlH_4$ (2.0 μL, 1 M in THF) and stirred for 1 h. The mixture was diluted with CH_2Cl_2 and hydrolyzed to the corresponding alcohol adding SiO_2 gel. The residue was purified on silica gel with PE/EA (10:1~5:1, v/v) as the eluent to give 0.605 g (0.49 mmol, 98% yield) of **S3** as a yellow oily liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38-7.20 (m, 5H), 4.83 (q, *J* = 6.1 Hz, 0.08H), 2.31 (s, 1H), 1.44 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.85,

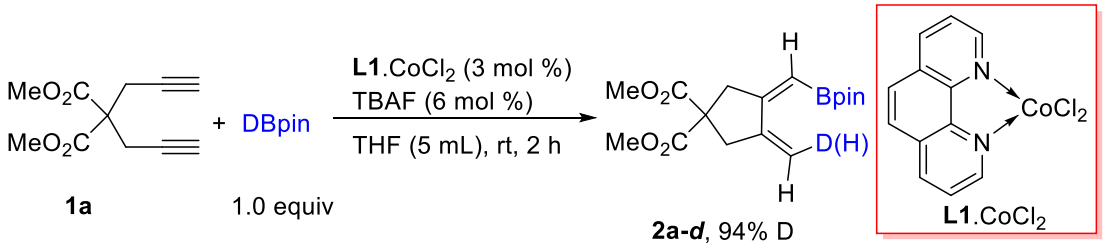
128.54, 127.49, 125.47, 70.40, 69.98 (t, $J_{C\text{-}D}$ = 22.1 Hz), 25.07.

9.3 Synthesis of 4,5-Diethyl-4,5-dimethyl-1,3,2-dioxaborolane (S5)



The compound **S4**[14] and **S5**[15] was prepared according to previously published method. **S5** was a new compound. Colourless oily liquid, b.p.: 45-46 °C (11 mm Hg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.71 (m, 2H), 1.49 (m, 2H), 1.22 (s, 3H), 1.20 (s, 3H), 1.02-0.95 (m, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 86.01, 85.93, 29.93, 29.07, 21.31, 20.50, 8.70, 8.63. ^{11}B NMR (128 MHz, $CDCl_3$) δ 28.16 (d, J = 171.9 Hz). HRMS (EI) Calcd for $[C_8H_{17}BO_2, M]^+$: 156.1322; Found: 156.1316.

9.4 Deuterium Labeling Experiment

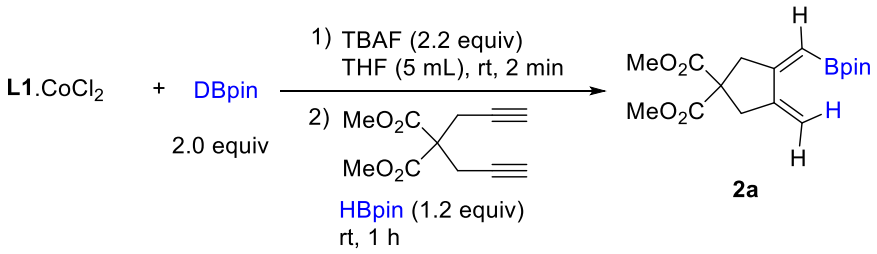


In an argon-filled glovebox, a vial (10 mL) was charged with **1a** (0.5 mmol), DBpin (0.5 mmol), anhydrous THF (5 mL) and complex **L1**.$CoCl_2$ (0.015 mmol). The reaction mixture was stirred at room temperature (25~35 °C) for 1 minute, then TBAF (1 M in THF, 30 μL, 0.03 mmol, 6 mol %) was added. After stirring for 2 hours at rt, the vial was removed from the glovebox and the reaction mixture was concentrated by rotary evaporation. The product was isolated by column chromatography over silica gel deactivated with 2% NEt_3 in hexanes and with PE/EA (30:1~10:1, v/v) as the eluent to give 0.126 g (0.37 mmol, 75% yield) of **2a-*d*** as a yellow oily liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.20-6.15 (m, 0.06H), 5.36 (s, 1H), 5.19 (s, 1H), 3.72 (s, 6H), 3.12 (d, J = 1.7 Hz, 2H), 3.07 (d, J = 1.8 Hz, 2H), 1.28 (s, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.53, 156.11, 143.68, 113.07 (t, $J_{C\text{-}D}$ = 24.6 Hz), 83.24, 56.85,

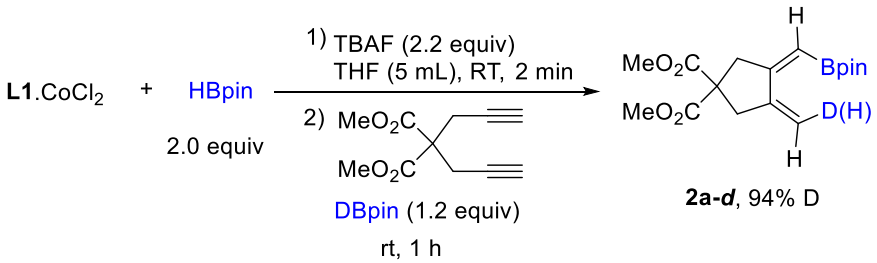
52.79, 45.30, 42.58, 24.80. ^{11}B NMR (128 MHz, $CDCl_3$) δ 28.84. HRMS (EI) Calcd for [$C_{17}H_{24}DBO_6$, M]$^+$: 337.1807; Found: 337.1801.

The relative configuration of compound **2a-*d*** was determined from 2D-NOE spectroscopy. The correlation from H_a and H_d, H_a and H_e, H_c and H_e, H_b and H_d, based on 2D-NOE experiment determines the deuterated vinyl fragment with a *Z*-configuration.

9.5 Stoichiometric Reactions

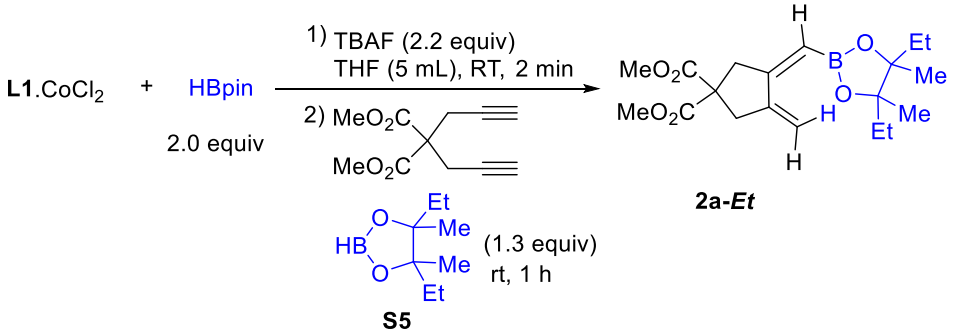


In an argon-filled glovebox, a vial (25 mL) was charged with complex **L1**.$CoCl_2$ (0.5 mmol, 0.155 g), DBpin (1.0 mmol, 0.129 g), anhydrous THF (5 mL) and TBAF(1 M in THF, 1.1 mL, 1.1 mmol, 2.2 equiv). The reaction mixture was stirred at room temperature (25~35 ^{o}C) for 2 minutes, then **1a** (0.5 mmol, 0.104 g) and HBpin (0.6 mmol, 0.077 g) was added. After stirring for 1 hour at rt, the vial was removed from the glovebox and the reaction mixture was concentrated by rotary evaporation. The product was isolated by column chromatography over silica gel deactivated with 2% NEt_3 in hexanes and with PE/EA (30:1~10:1, v/v) as the eluent to give 0.104 g (0.31 mmol, 62% yield) of **2a** as a yellow oily liquid. No deuterium atoms were observed in product **2a**.

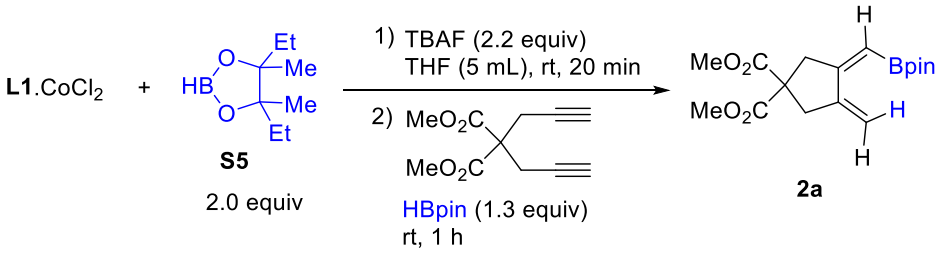


In an argon-filled glovebox, a vial (25 mL) was charged with complex **L1**.$CoCl_2$ (0.5 mmol, 0.155 g), HBpin (1.0 mmol, 0.128 g), anhydrous THF (5 mL) and TBAF (1 M in THF, 1.1 mL, 1.1 mmol, 2.2 equiv). The reaction mixture was stirred at room

temperature (25~35 °C) for 2 minutes, then **1a** (0.5 mmol, 0.104 g) and DBpin (0.6 mmol, 0.077 g) was added. After stirring for 1 hour at rt, the vial was removed from the glovebox and the reaction mixture was concentrated by rotary evaporation. The product was isolated by column chromatography over silica gel deactivated with 2% NEt_3 in hexanes and with PE/EA (30:1~10:1, v/v) as the eluent to give 0.082 g (0.24 mmol, 49% yield) of **2a-*d*** as a yellow oily liquid. The degree of deuteration of the product **2a-*d*** was 94%.



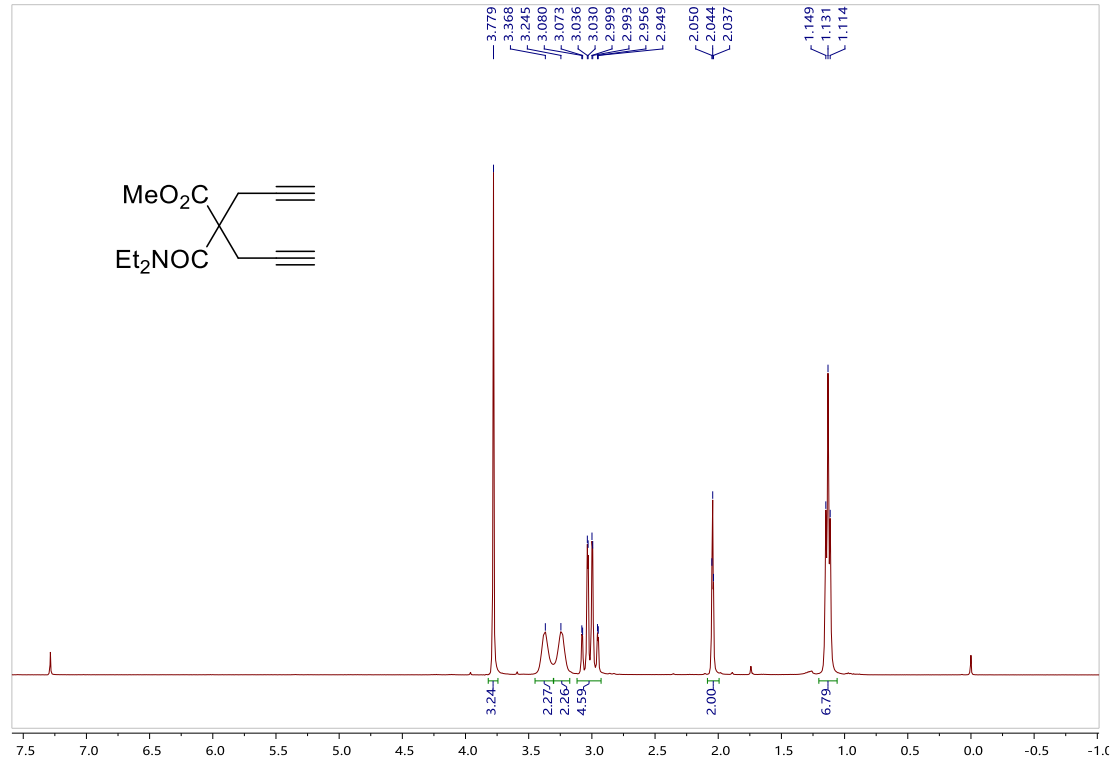
In an argon-filled glovebox, a vial (25 mL) was charged with complex **L1**.$CoCl_2$ (0.3 mmol, 0.093 g), HBpin (0.6 mmol, 0.077 g), anhydrous THF (5 mL) and TBAF (1 M in THF, 0.66 mL, 0.66 mmol, 2.2 equiv). The reaction mixture was stirred at room temperature (25~35 °C) for 2 minutes, then **1a** (0.3 mmol, 0.062 g) and **S5** (0.39 mmol, 0.062 g) was added. After stirring for 1 hour at rt, the vial was removed from the glovebox and the reaction mixture was concentrated by rotary evaporation. The product was isolated by column chromatography over silica gel deactivated with 2% NEt_3 in hexanes and with PE/EA (30:1~10:1, v/v) as the eluent to give 0.044 g (0.12 mmol, 40% yield) of **2a-*Et*** as a yellow oily liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.27 (s, 1H), 5.37 (s, 1H), 5.21 (s, 1H), 3.72 (s, 6H), 3.13 (d, *J* = 1.2 Hz, 2H), 3.10-3.06 (m, 2H), 1.82-1.66 (m, 2H), 1.55-1.42 (m, 2H), 1.22 (s, 3H), 1.20 (s, 3H), 1.02-0.94 (m, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.58, 156.27, 143.78, 113.51, 85.89, 85.80, 56.89, 52.80, 45.42, 42.73, 29.73, 28.91, 21.12, 20.37, 8.70, 8.61. ^{11}B NMR (128 MHz, $CDCl_3$) δ 31.20. HRMS (ESI) Calcd for $[C_{19}H_{30}BO_6, M + H]^+$: 365.2135; Found: 365.2142.

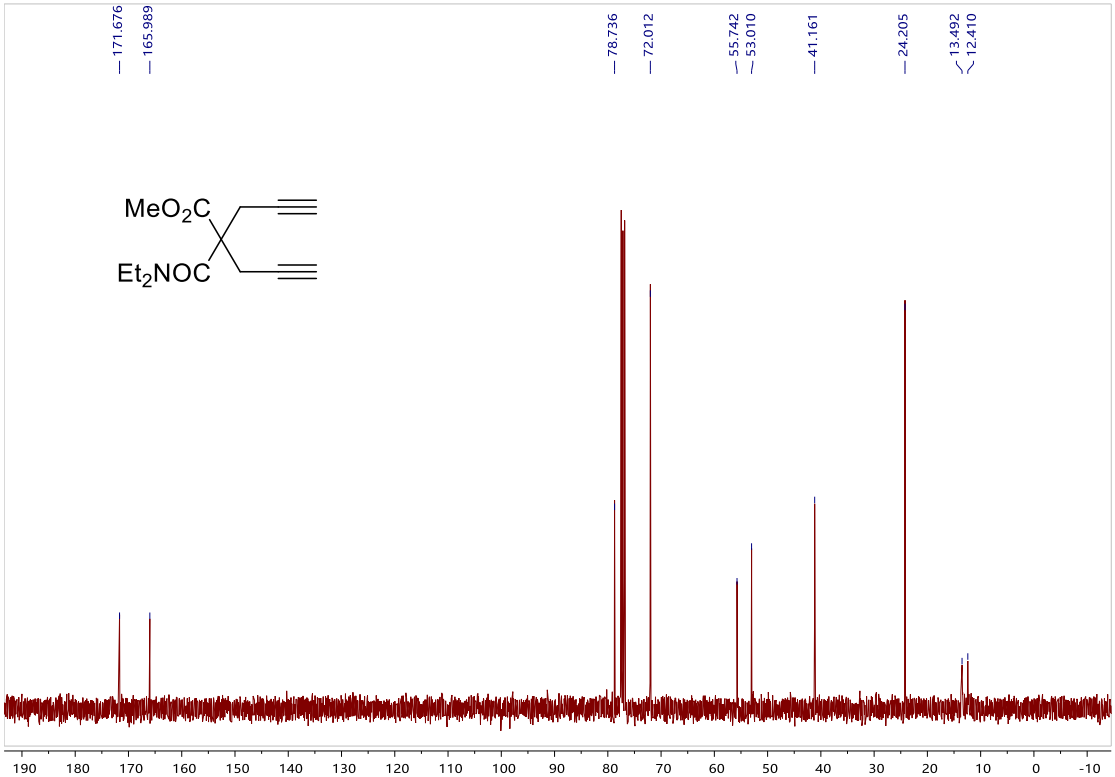


In an argon-filled glovebox, a vial (25 mL) was charged with complex **L1**.$CoCl_2$ (0.3 mmol, 0.093 g), **S5** (0.6 mmol, 0.095 g), anhydrous THF (5 mL) and TBAF (1 M in THF, 0.66 mL, 0.66 mmol, 2.2 equiv). The reaction mixture was stirred at room temperature (25~35 ^oC) for 20 minutes, then **1a** (0.3 mmol, 0.062 g) and HBpin (0.39 mmol, 0.05 g) was added. After stirring for 1 hour at rt, the vial was removed from the glovebox and the reaction mixture was concentrated by rotary evaporation. The product was isolated by column chromatography over silica gel deactivated with 2% NEt_3 in hexanes and with PE/EA (30:1-10:1, v/v) as the eluent to give 0.030 g (0.09 mmol, 30% yield) of **2a** as a yellow oily liquid.

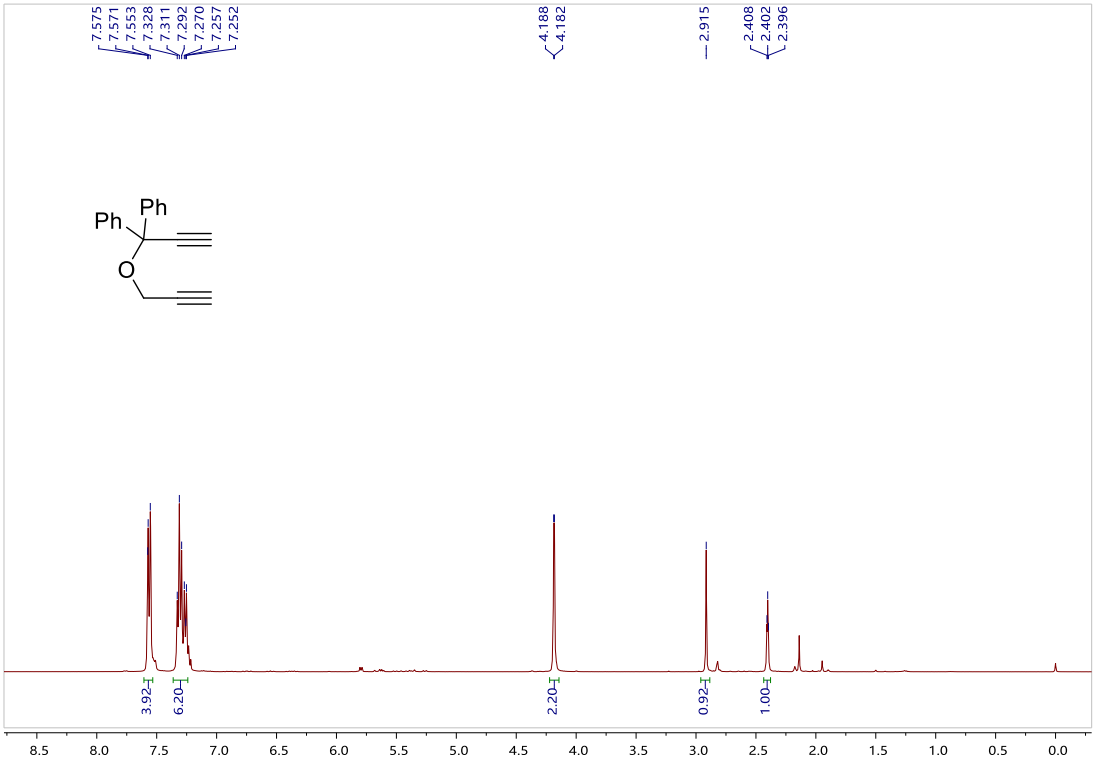
10. NMR Spectra for New Compounds

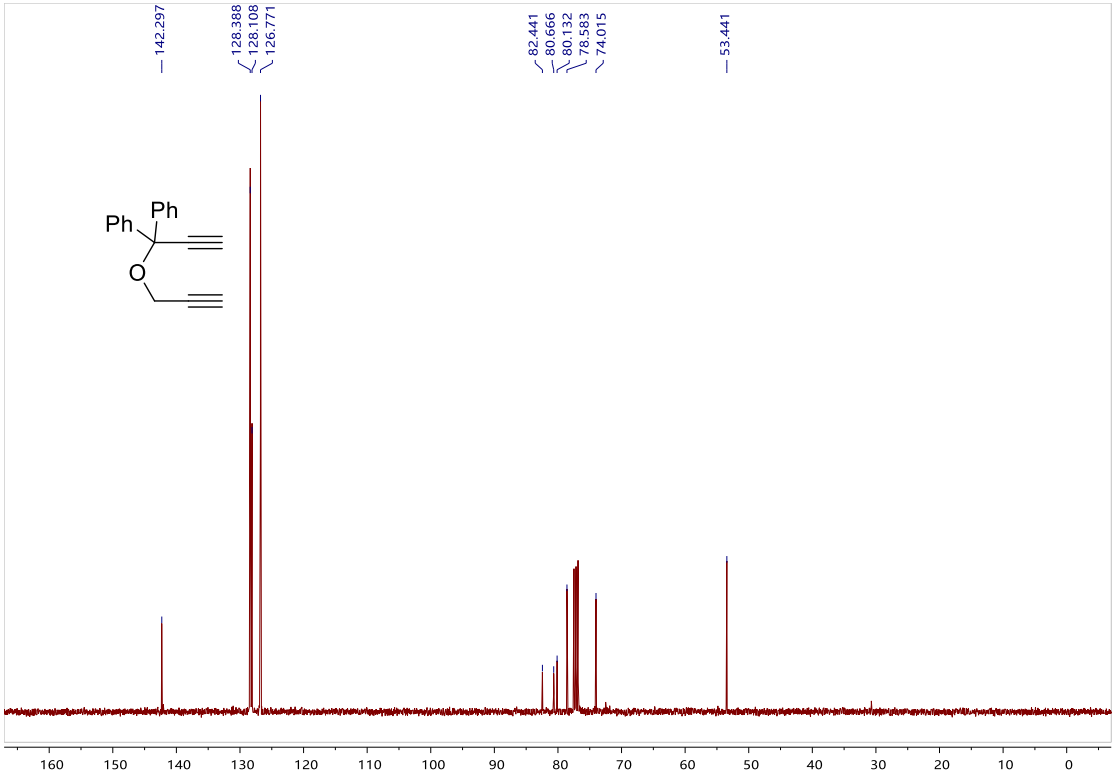
Methyl-2-(diethylcarbamoyl)-2-(prop-2-yn-1-yl)pent-4-ynoate (1f)



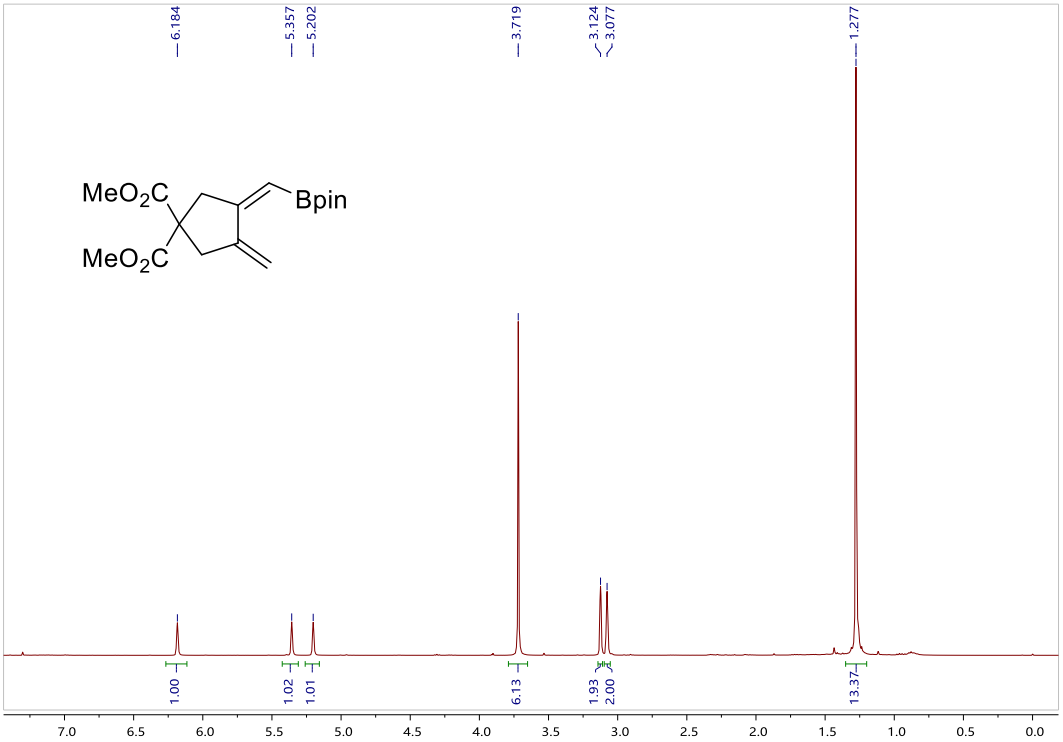


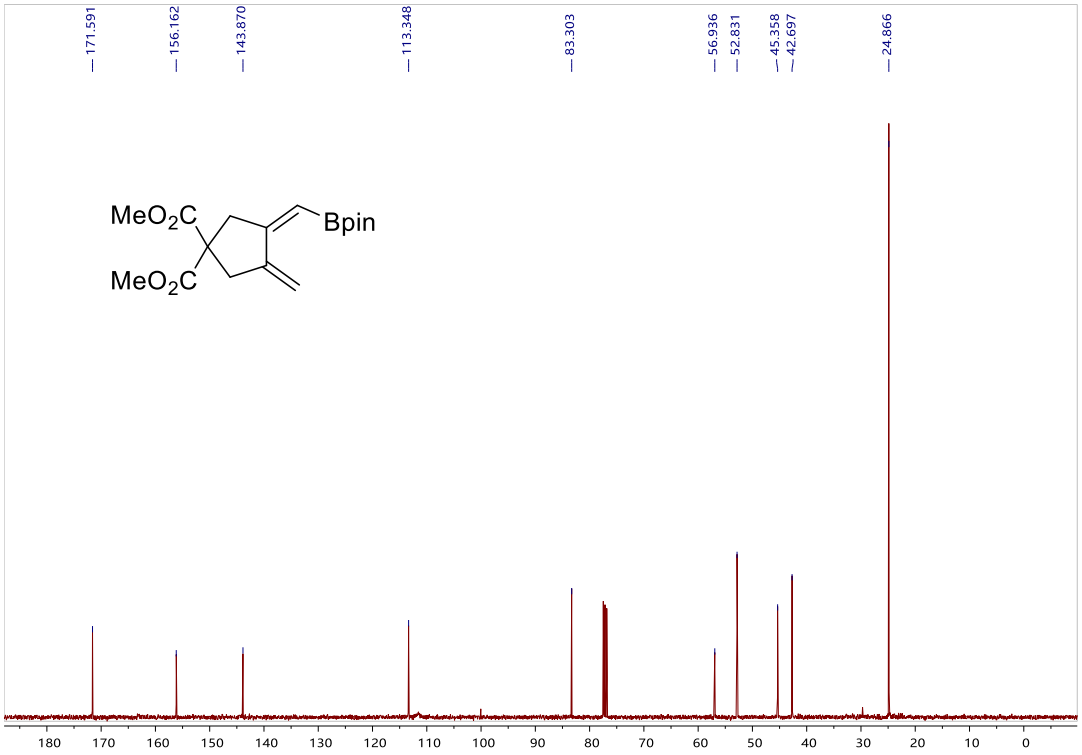
(1-(prop-2-yn-1-yloxy)prop-2-yne-1,1-diyl)dibenzene (1r)

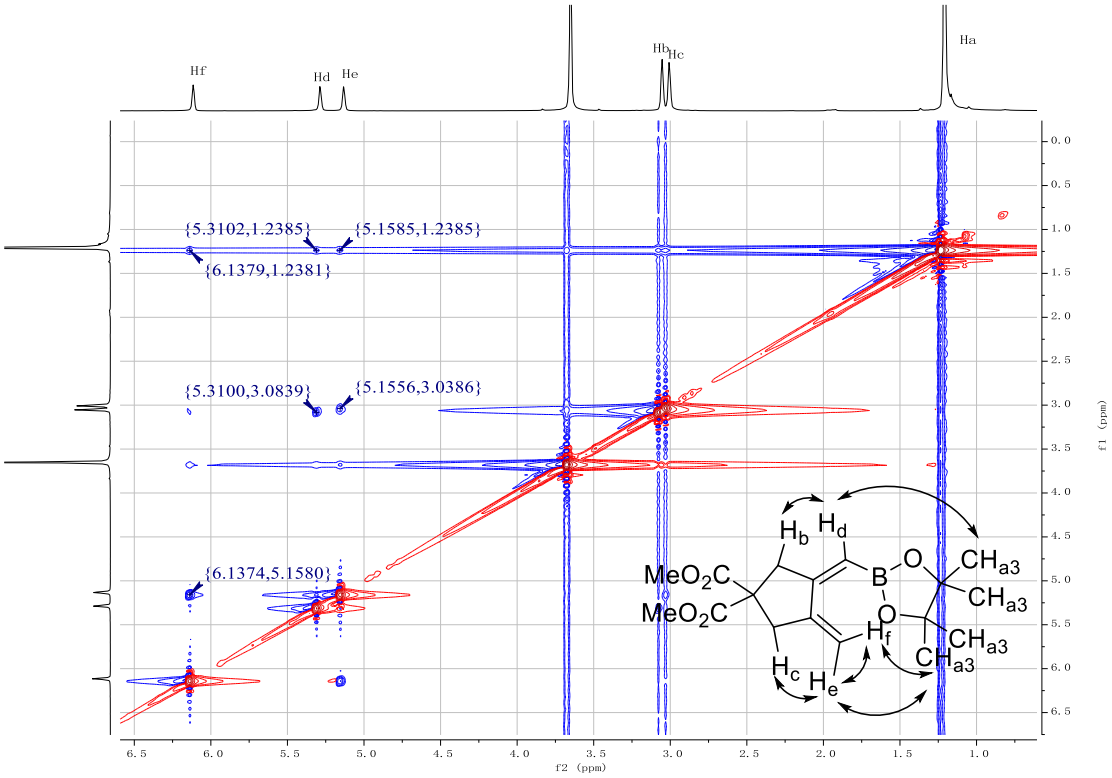




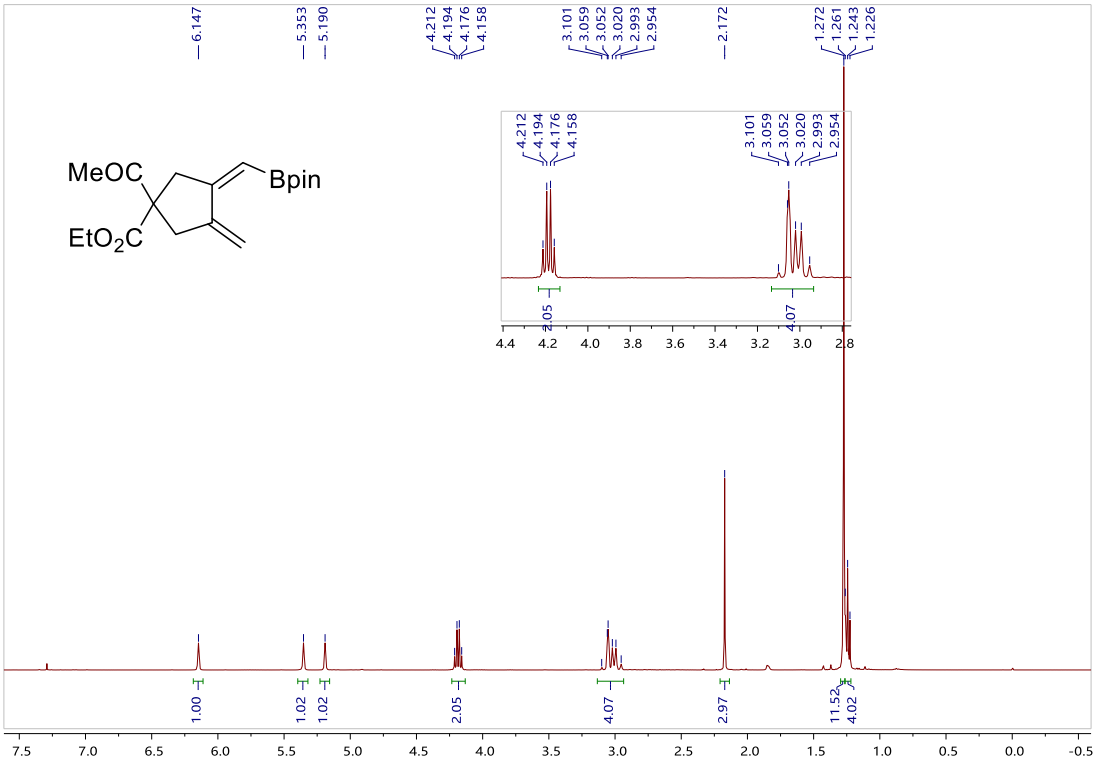
Dimethyl(*Z*)-3-methylene-4-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl ene)cyclopentane-1,1-dicarboxylate (2a)

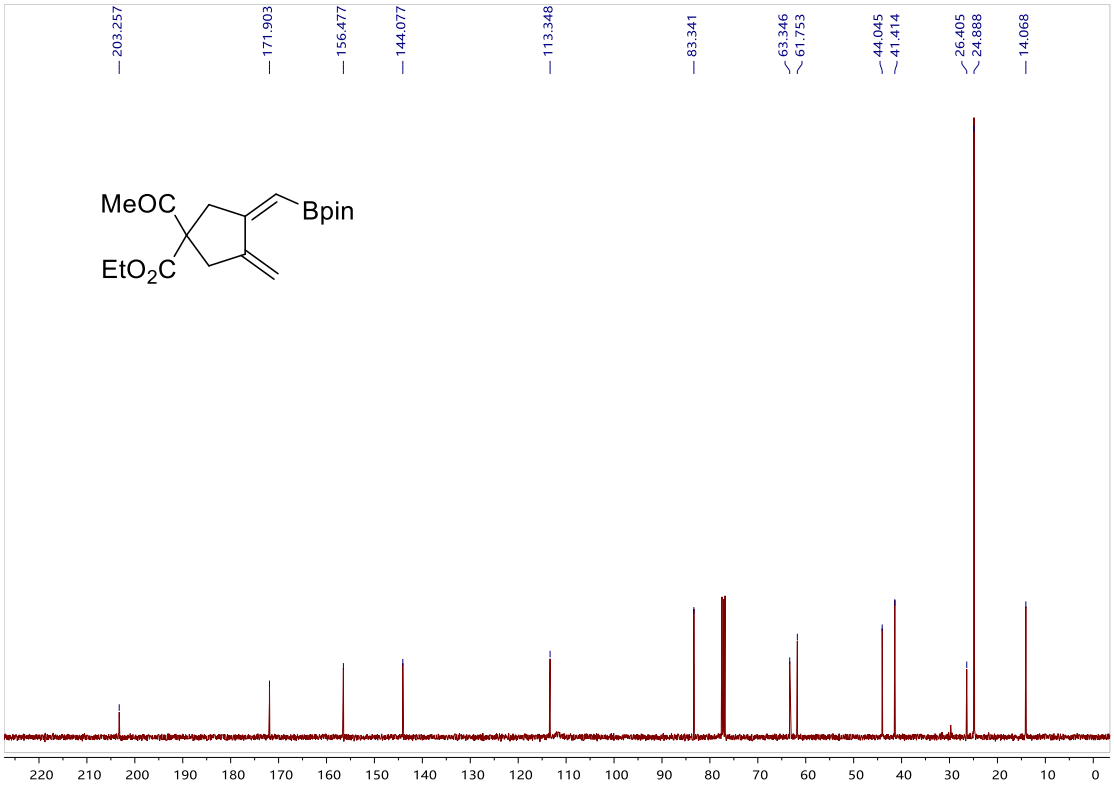




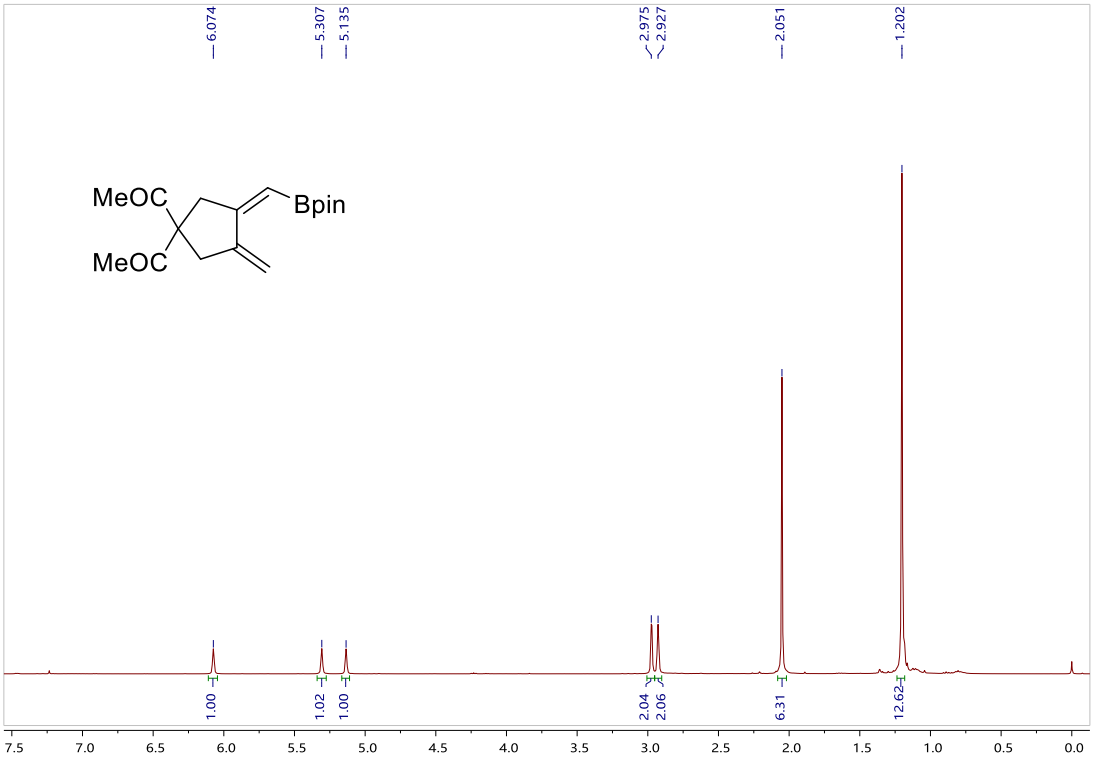

Hf
Hd
He
Hb
Hc
Ha
{5.3102,1.2385}
{5.1585,1.2385}
{6.1379,1.2381}
{5.3100,3.0839}
{5.1556,3.0386}
{6.1374,5.1580}
f2 (ppm)
f1 (ppm)
MeO2C
MeO2C
Hb
Hd
B
O
CHa3
CHa3
O
Hf
CHa3
CHa3
Hc
He

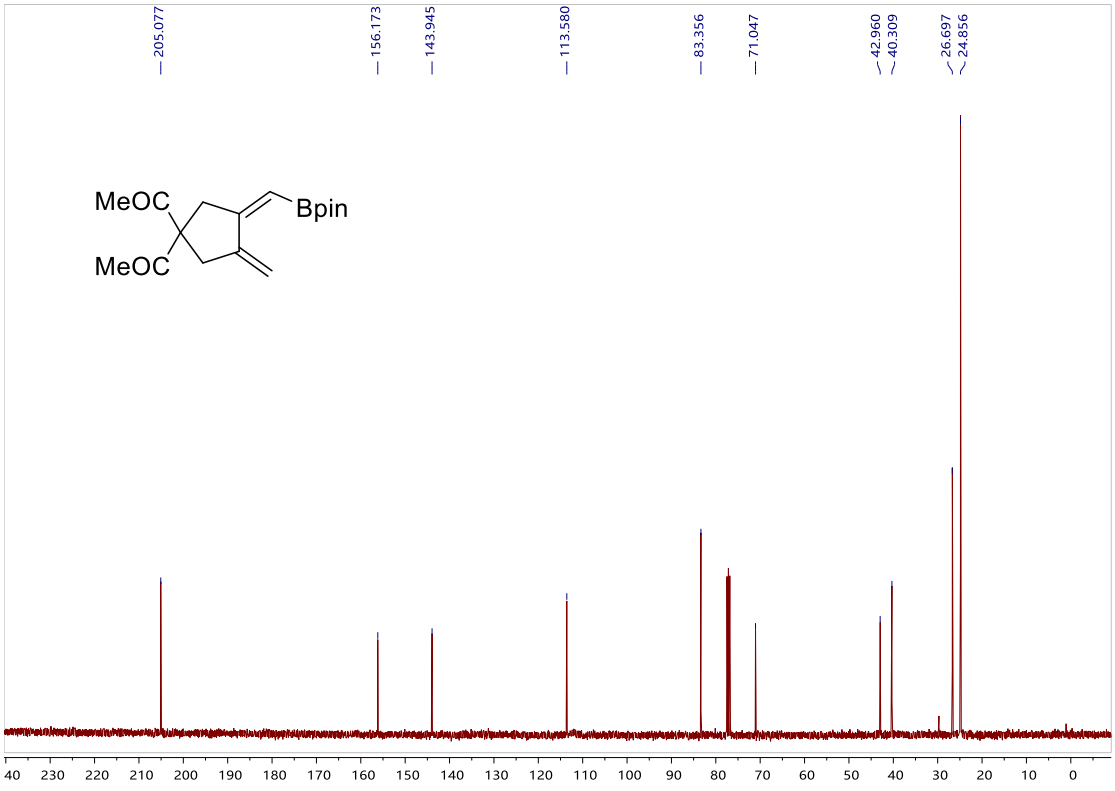
Ethyl (*Z*)-1-acetyl-3-methylene-4-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl) methylene)cyclopentane-1-carboxylate (2b)



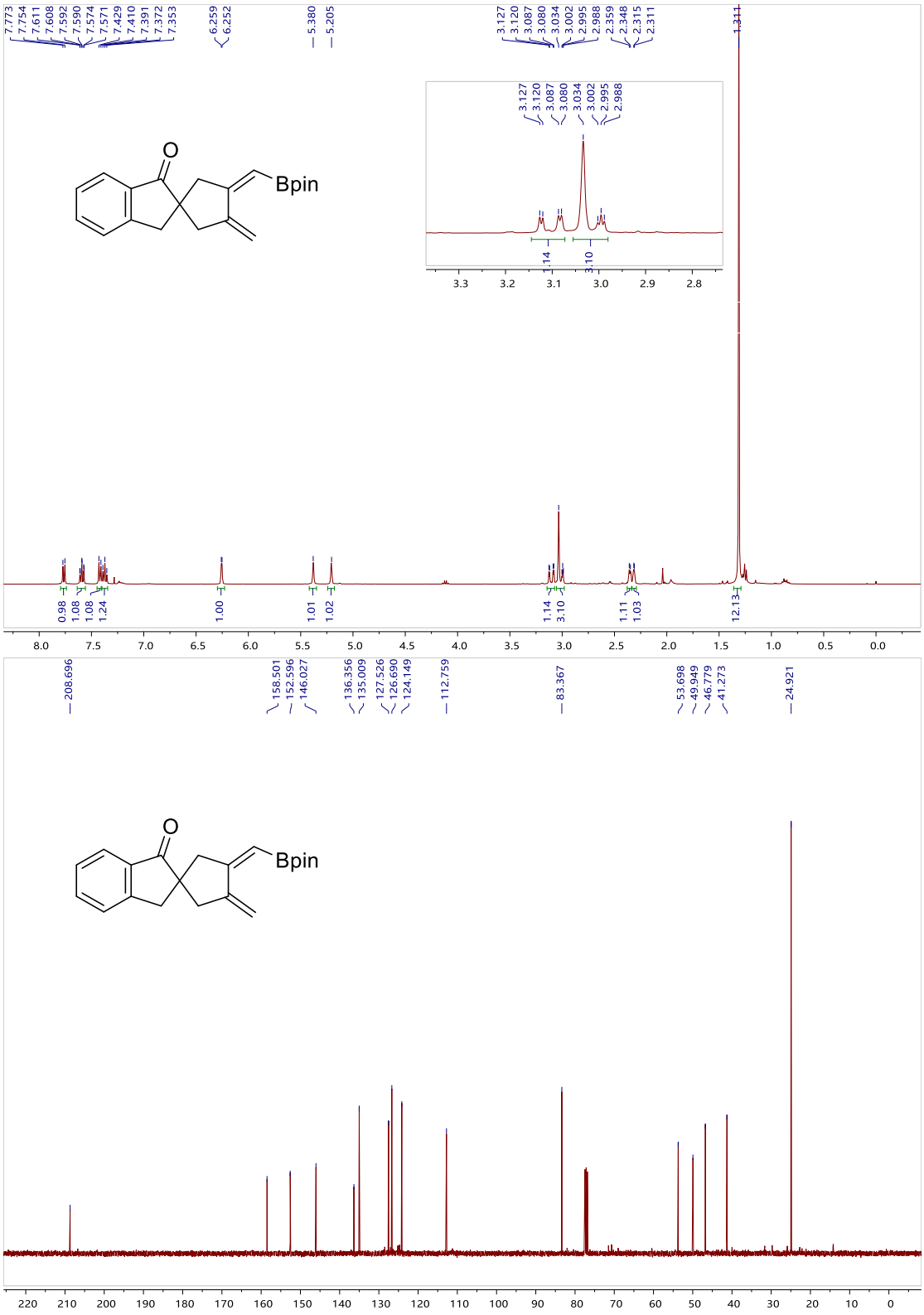


(*Z*)-1,1'-(3-methylene-4-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methylene) cyclopentane-1,1-diyl)bis(ethan-1-one) (2c)

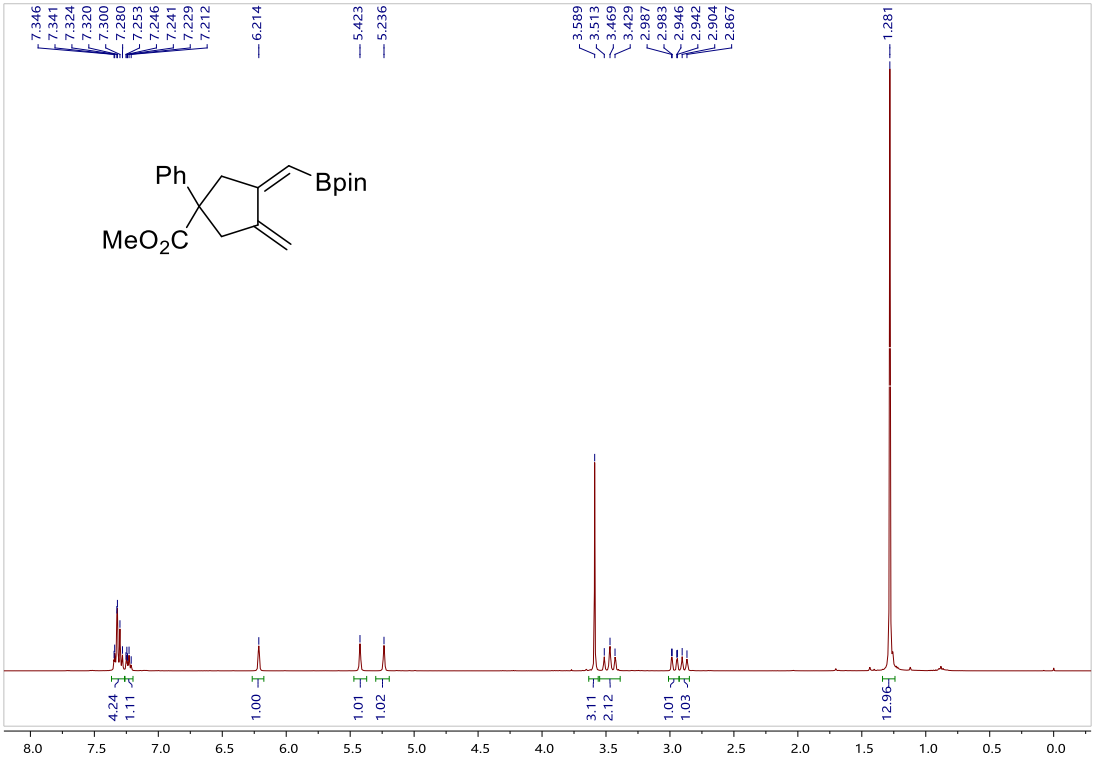


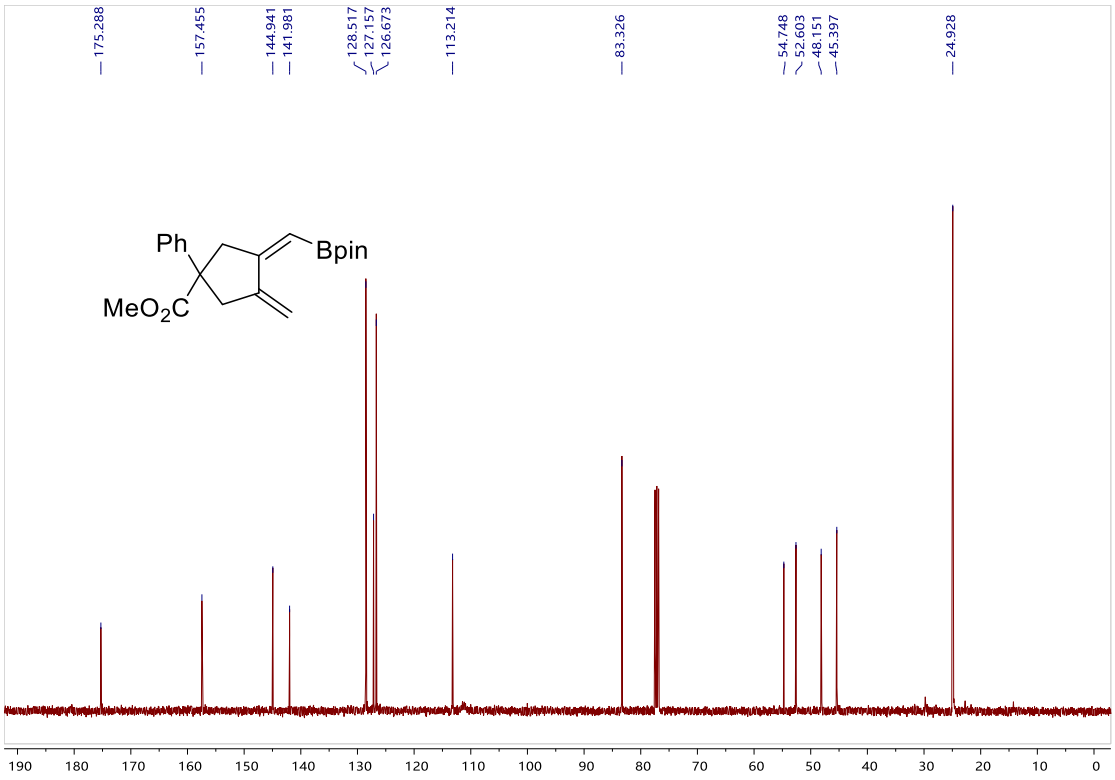


(*Z*)-3-methylene-4-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methylene)spiro[cyclopentane-1,2'-inden]-1'(*3'H*)-one (2d)

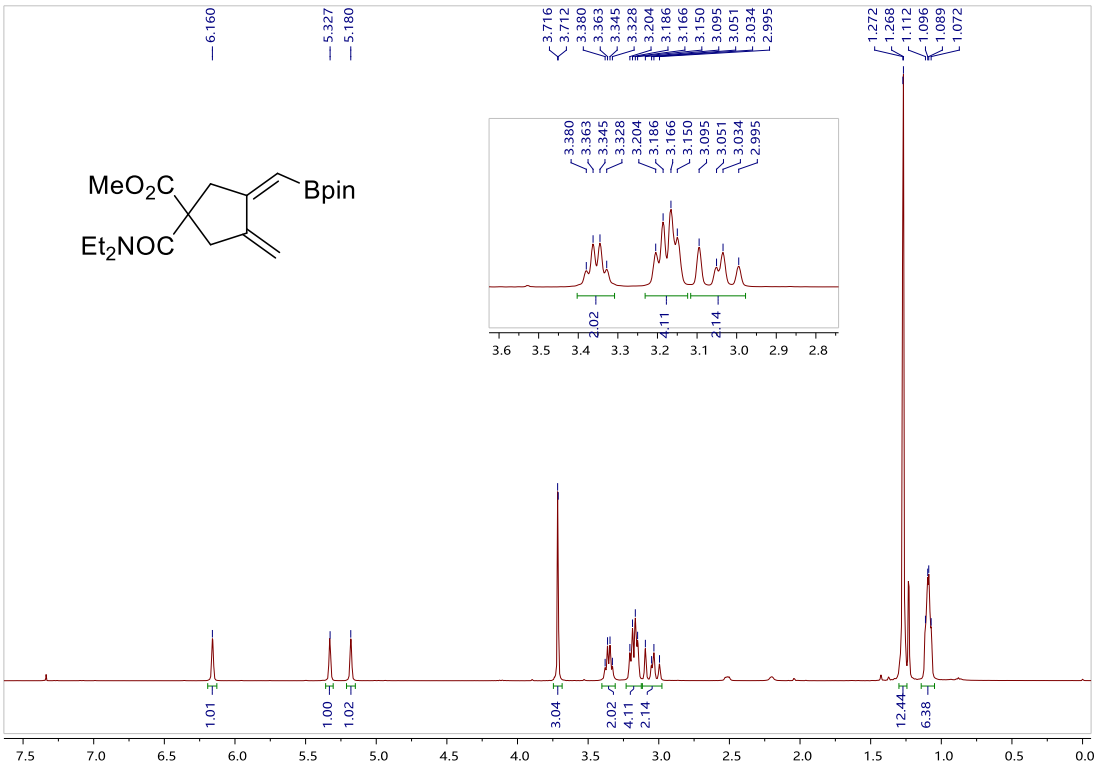


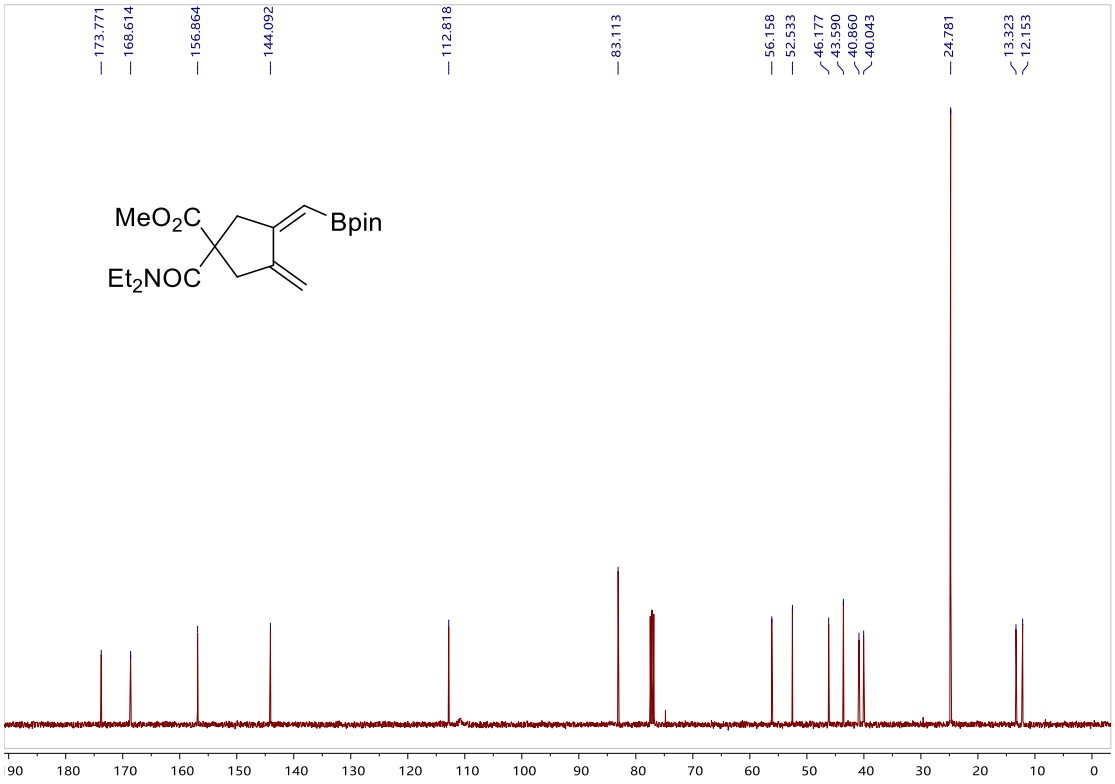
Methyl-(*Z*)-3-methylene-1-phenyl-4-((4,4,5,5-tetramethyl-1,3,2–dioxaborolan -2-yl)methylene)cyclopentane-1-carboxylate (2e)



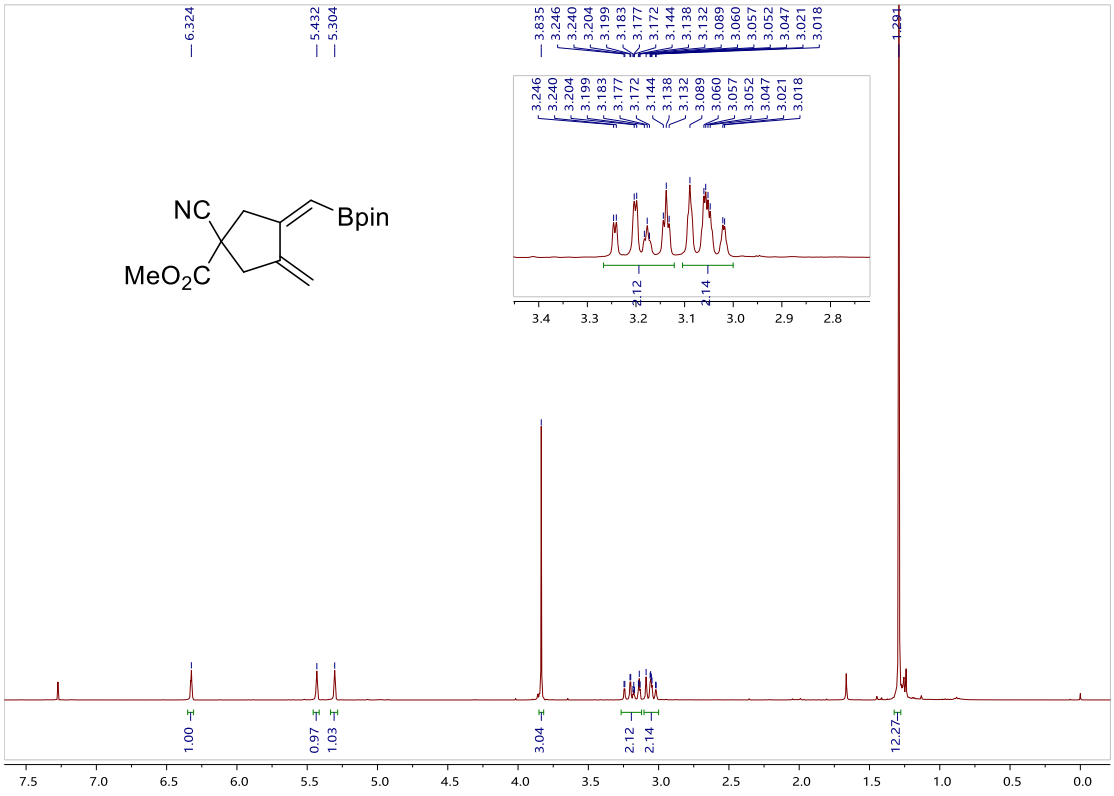


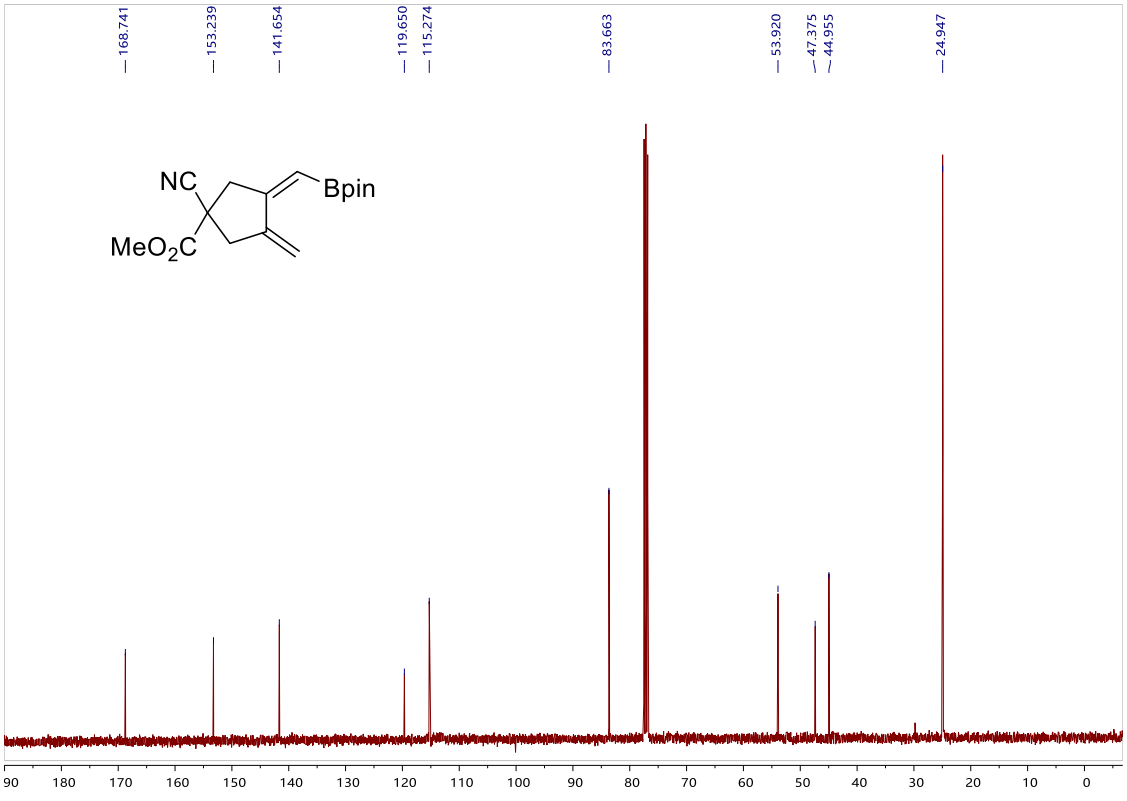
Methyl-(*Z*)-1-(diethylcarbamoyl)-3-methylene-4-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methylene)cyclopentane-1-carboxylate (2f)



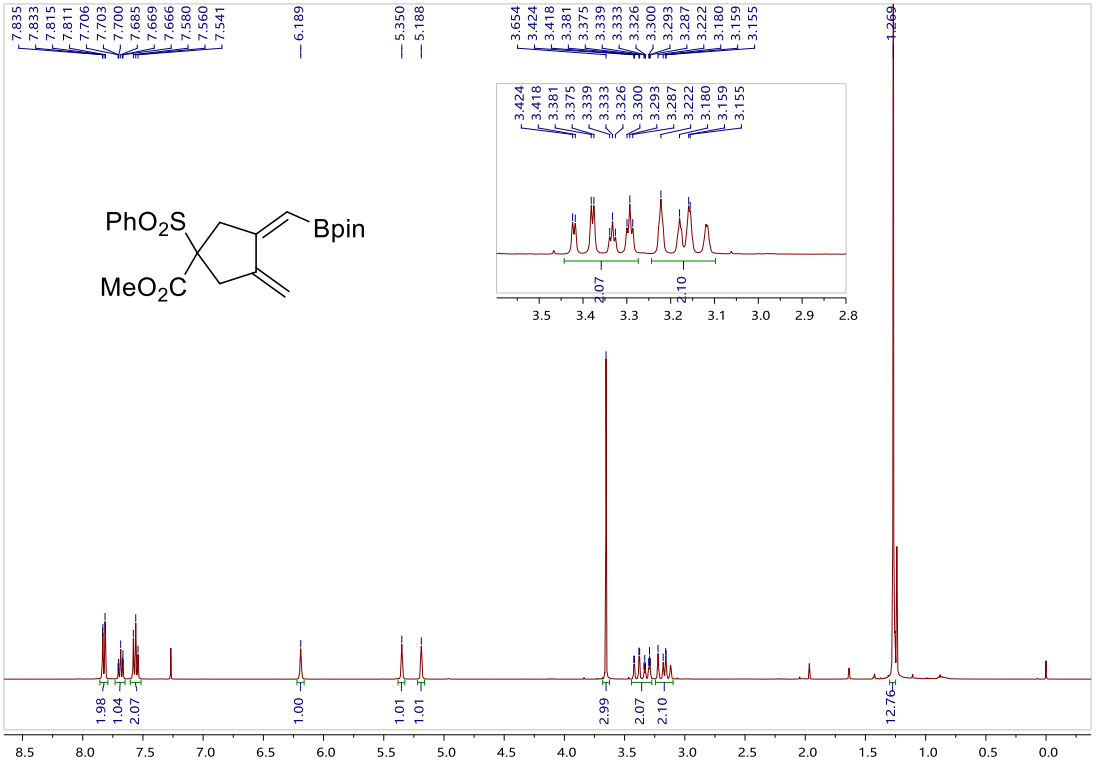


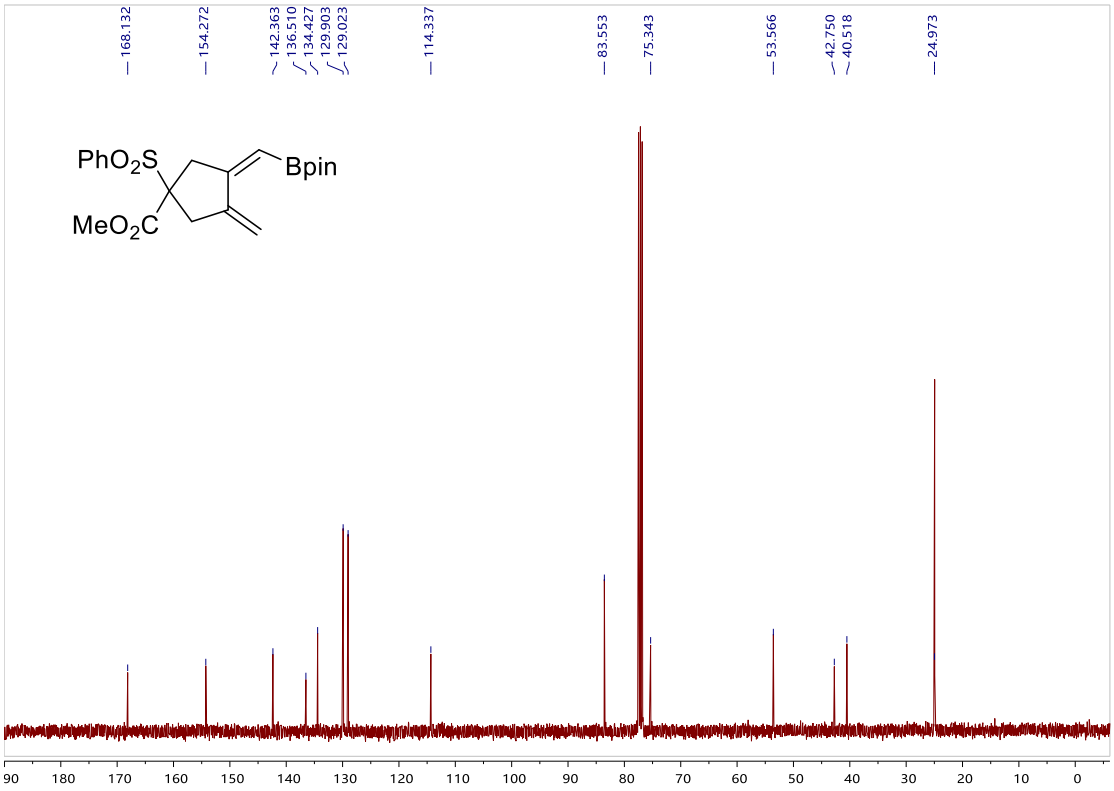
Methyl-(*Z*)-1-cyano-3-methylene-4-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan -2-yl)methylene)cyclopentane-1-carboxylate (2g)



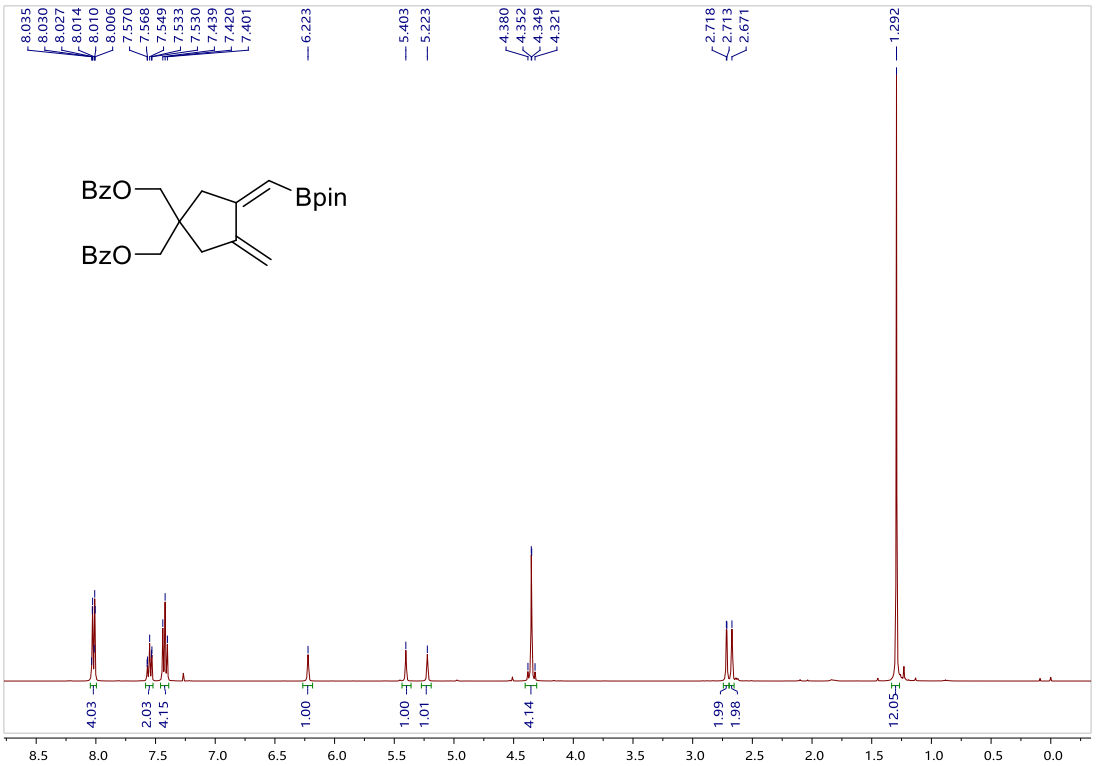


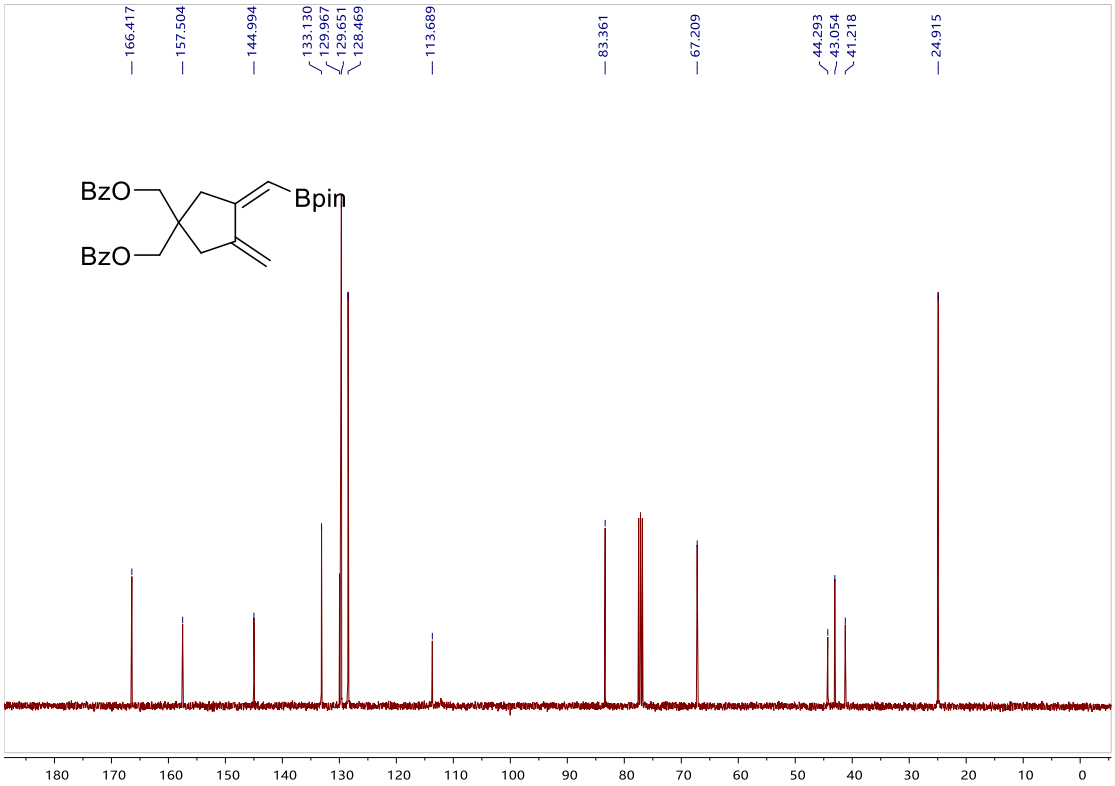
Methyl-(*Z*)-3-methylene-1-(phenylsulfonyl)-4-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methylene)cyclopentane-1-carboxylate (2h)



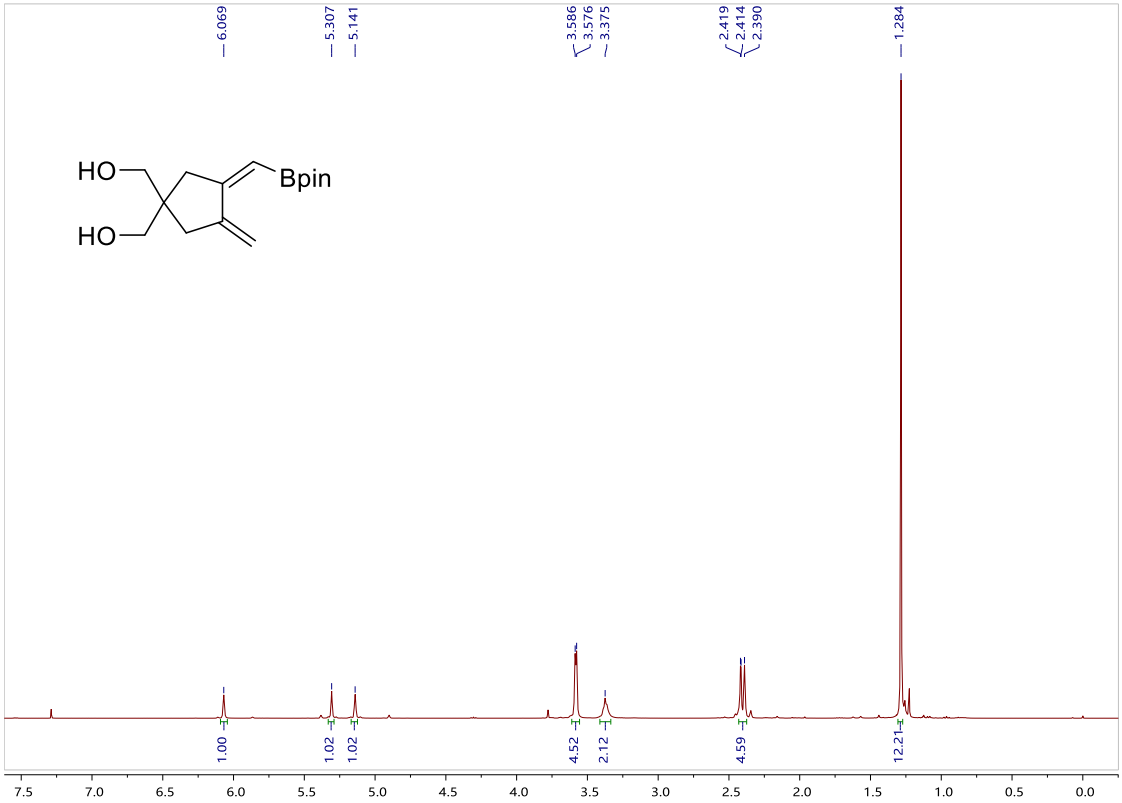


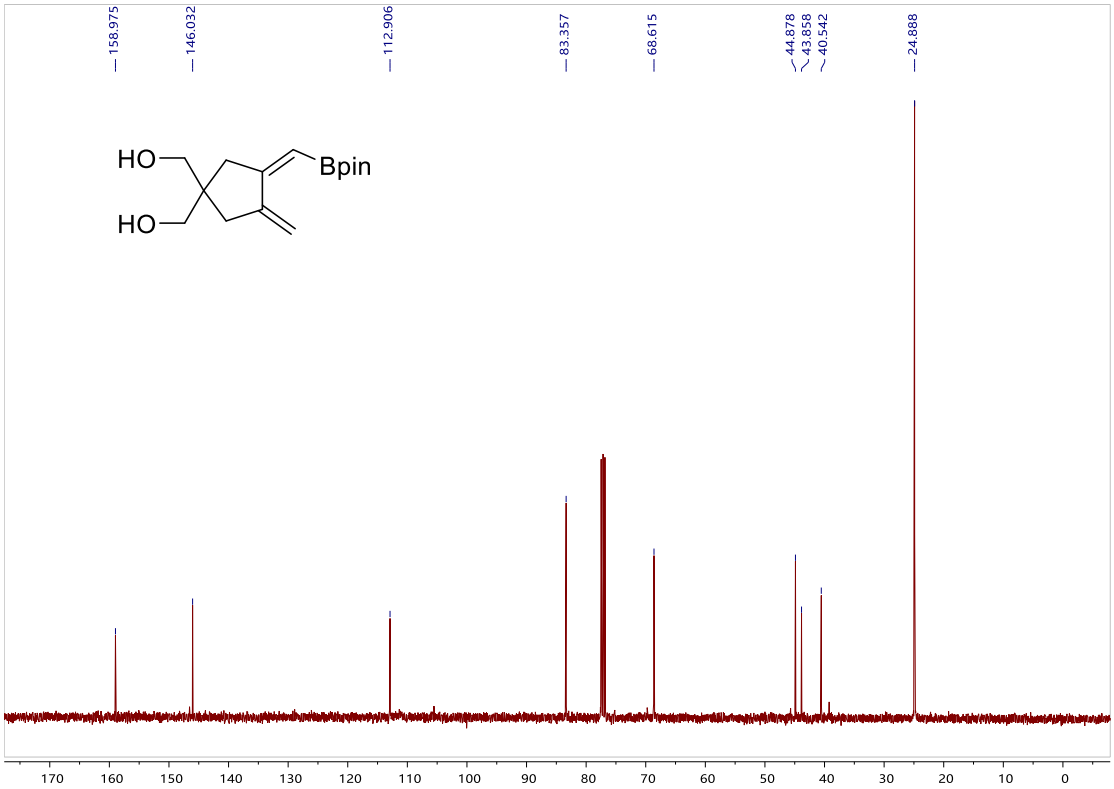
(*Z*)-(3-methylene-4-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methylene)cyclopentane-1,1-diyl)bis(methylene) dibenzoate (2i)



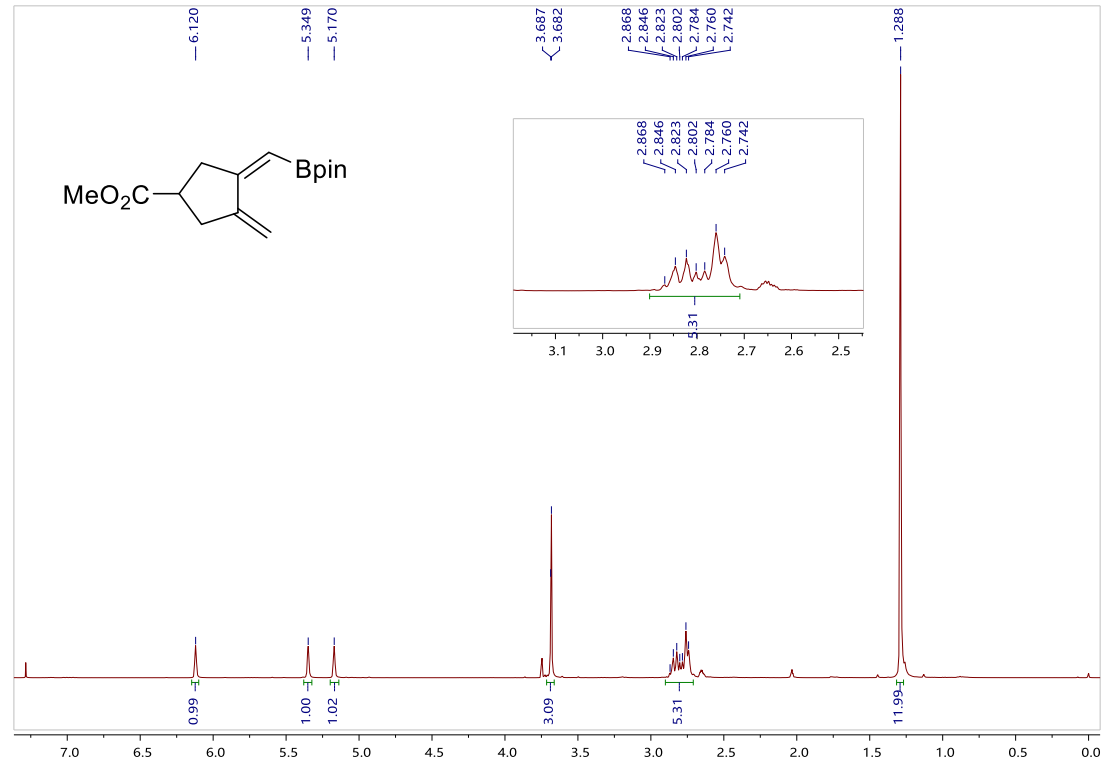


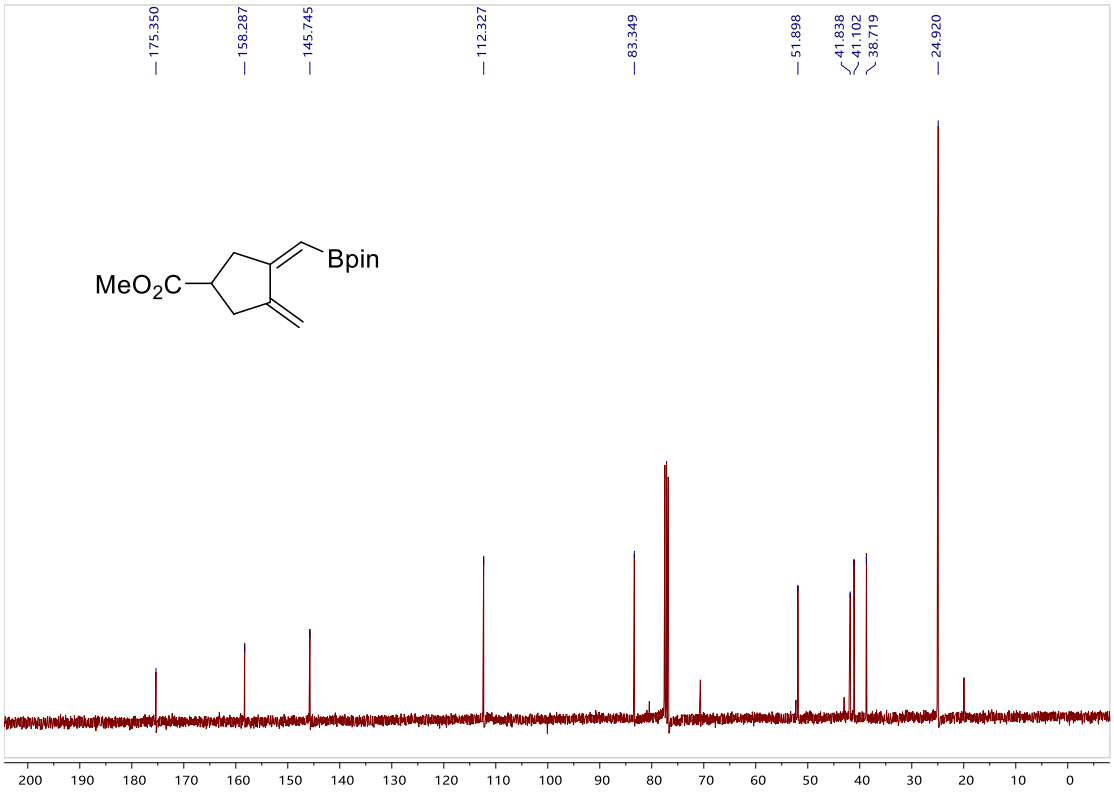
(*Z*)-(3-methylene-4-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methylene)cyclopentane-1,1-diyl)dimethanol (2j)



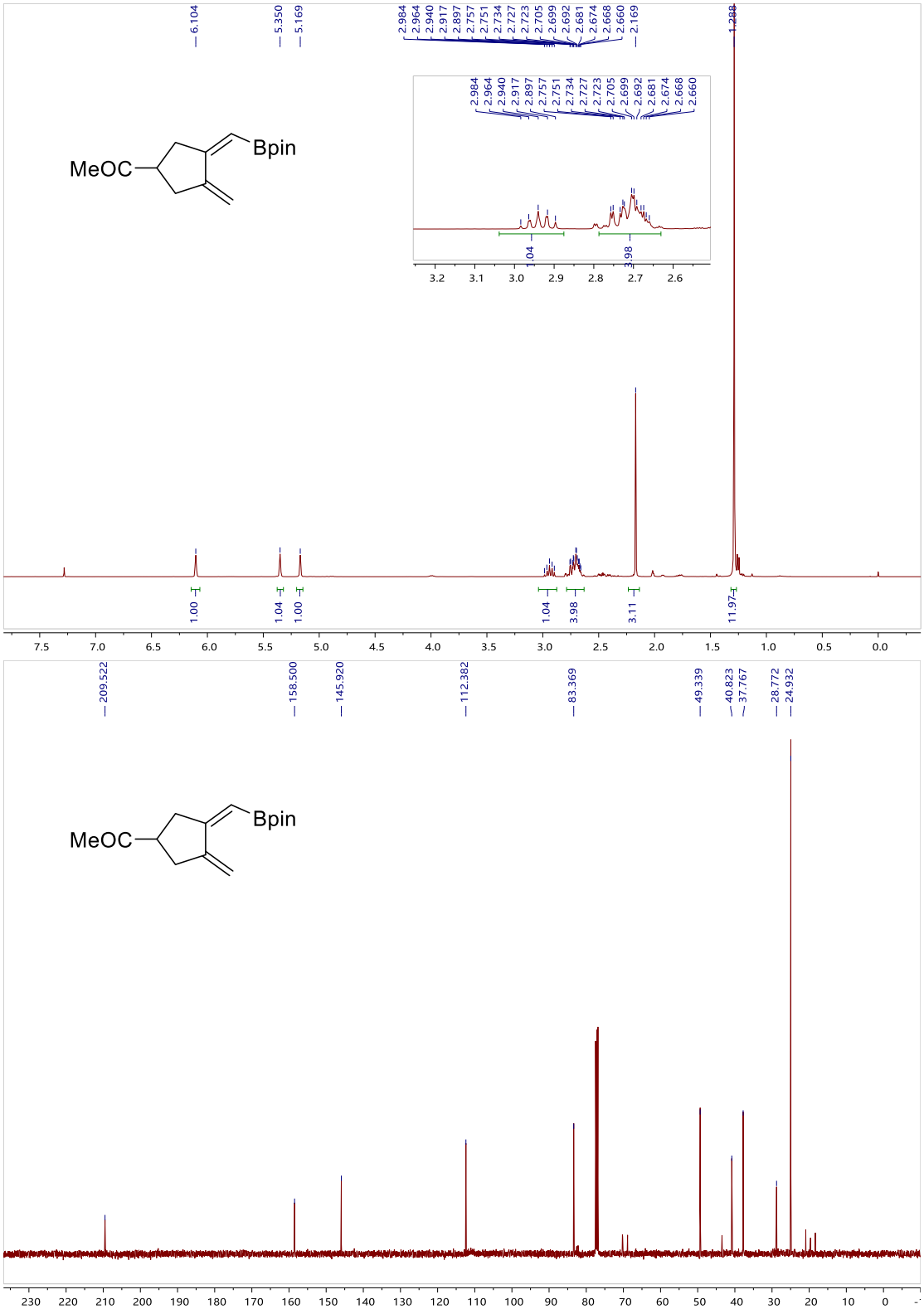


Methyl-(*Z*)-3-methylene-4-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl) methylene)cyclopentane-1-carboxylate (2k)

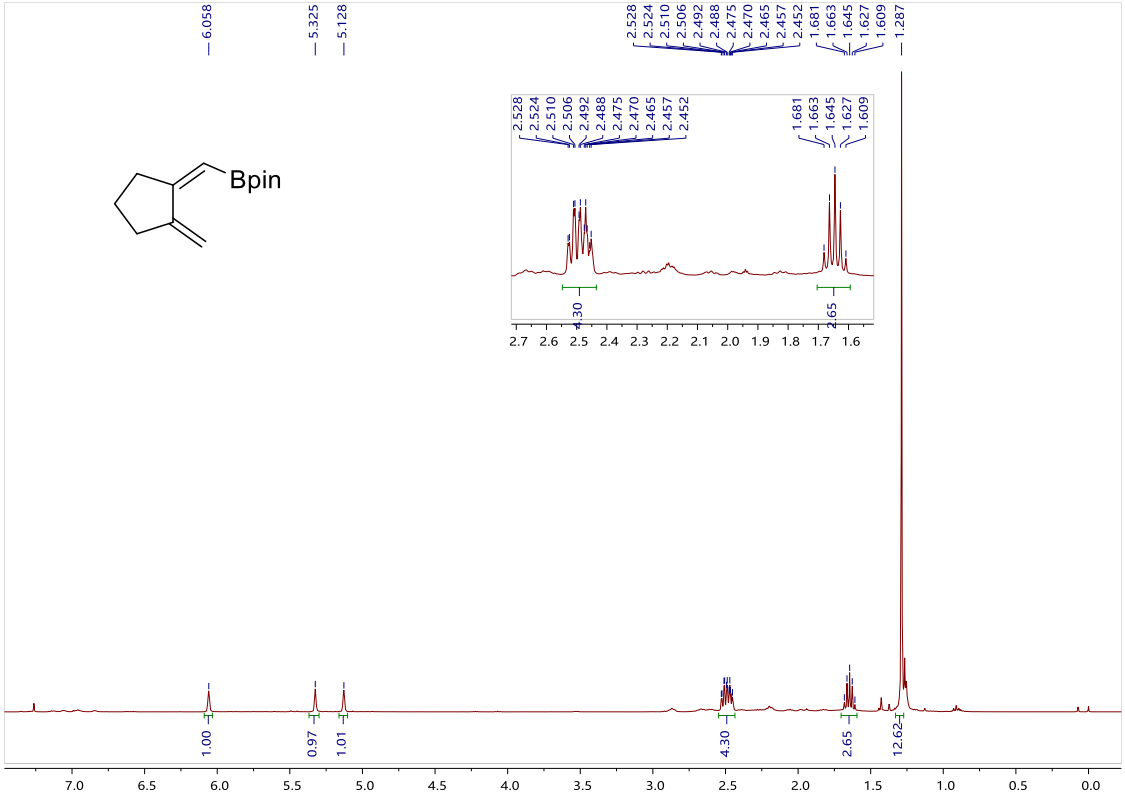


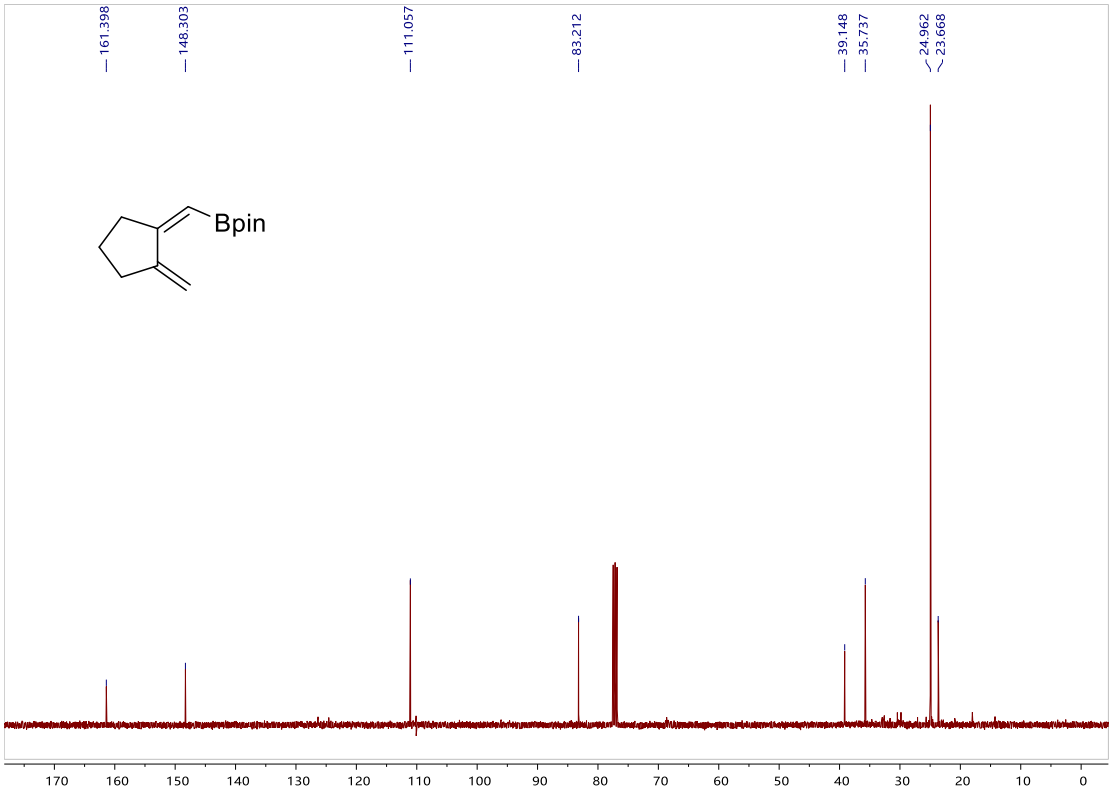


(*Z*)-1-(3-methylene-4-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methylene)cyclopentyl)ethan-1-one (2l)

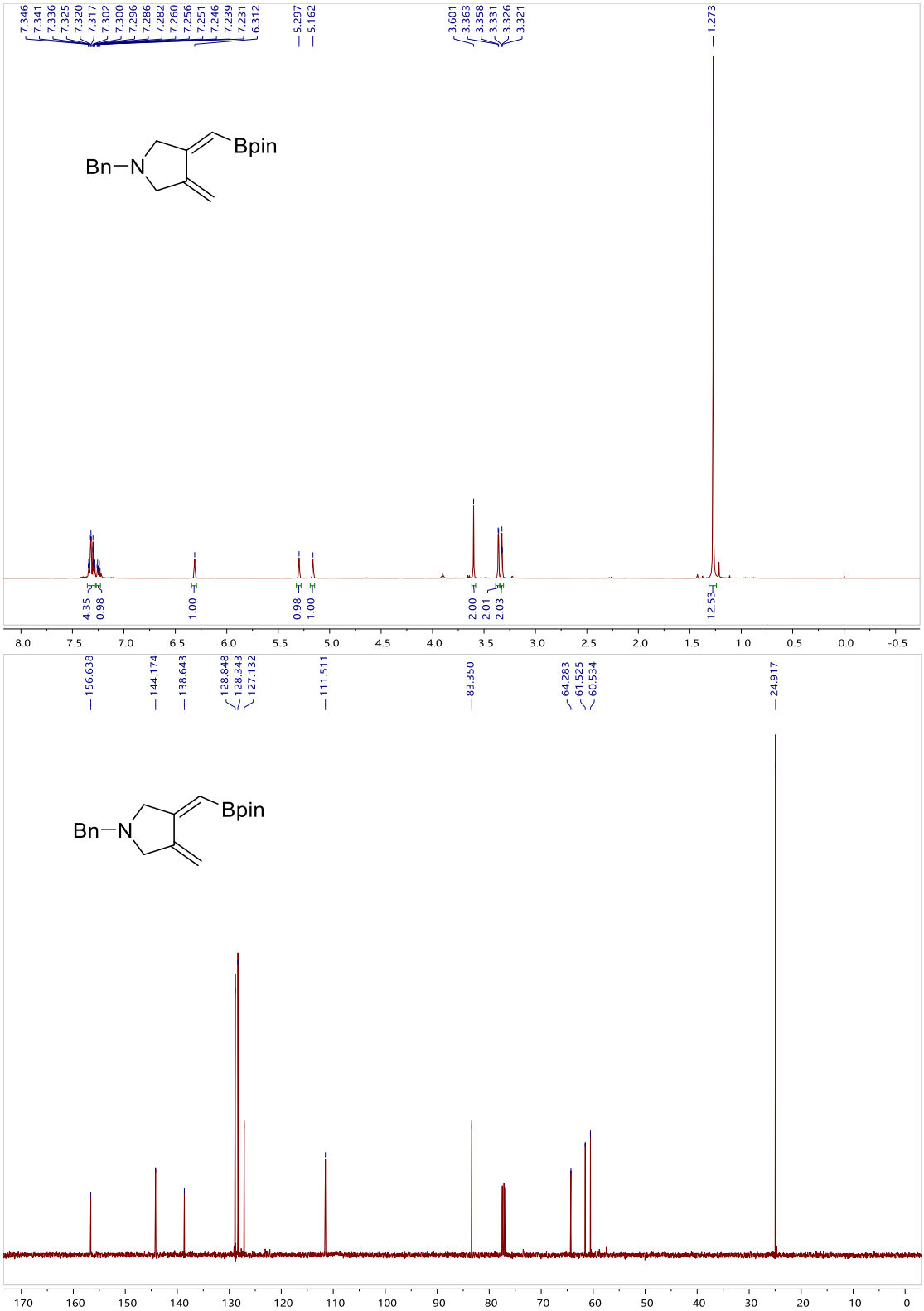


(*Z*)-4,4,5,5-tetramethyl-2-((2-methylenecyclopentylidene)methyl)-1,3,2-dioxaborolane (2m)

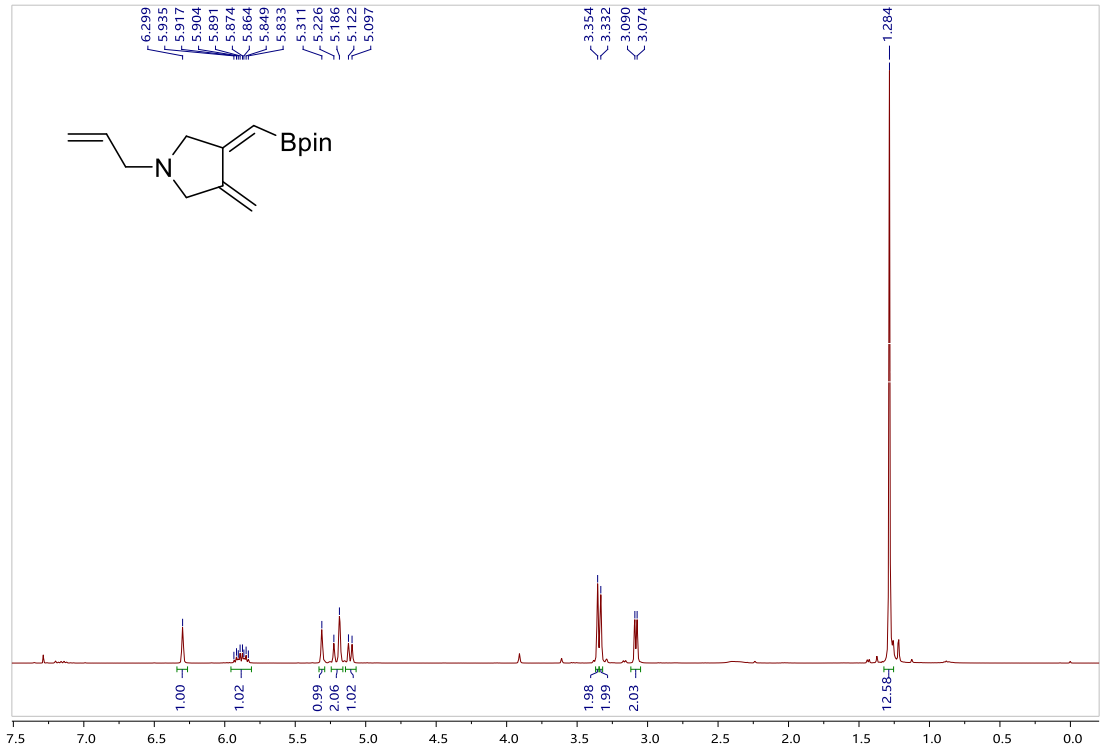


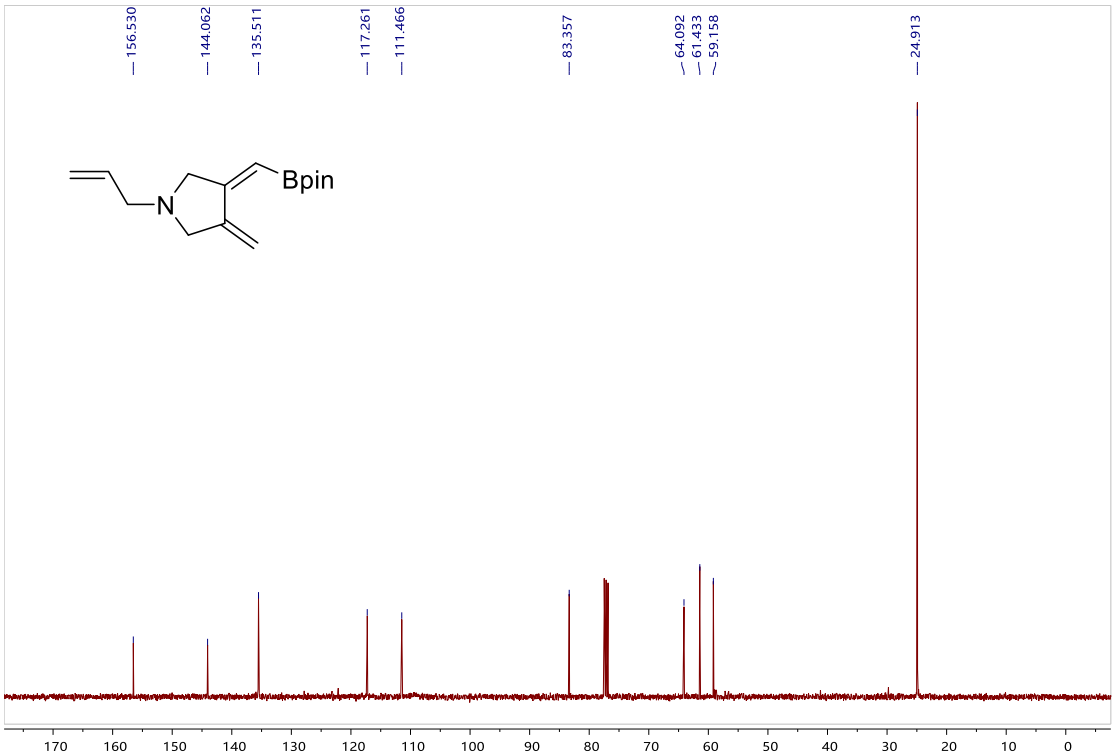


(*E*)-1-benzyl-3-methylene-4-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl ene)pyrrolidine (2n)

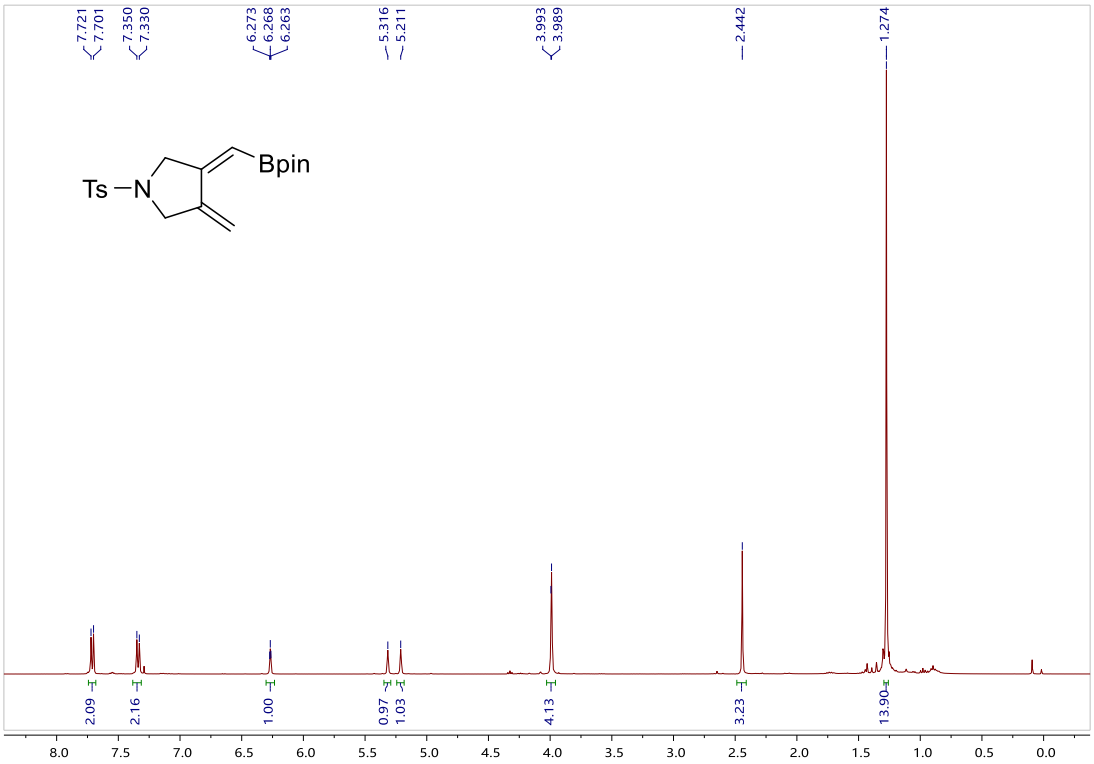


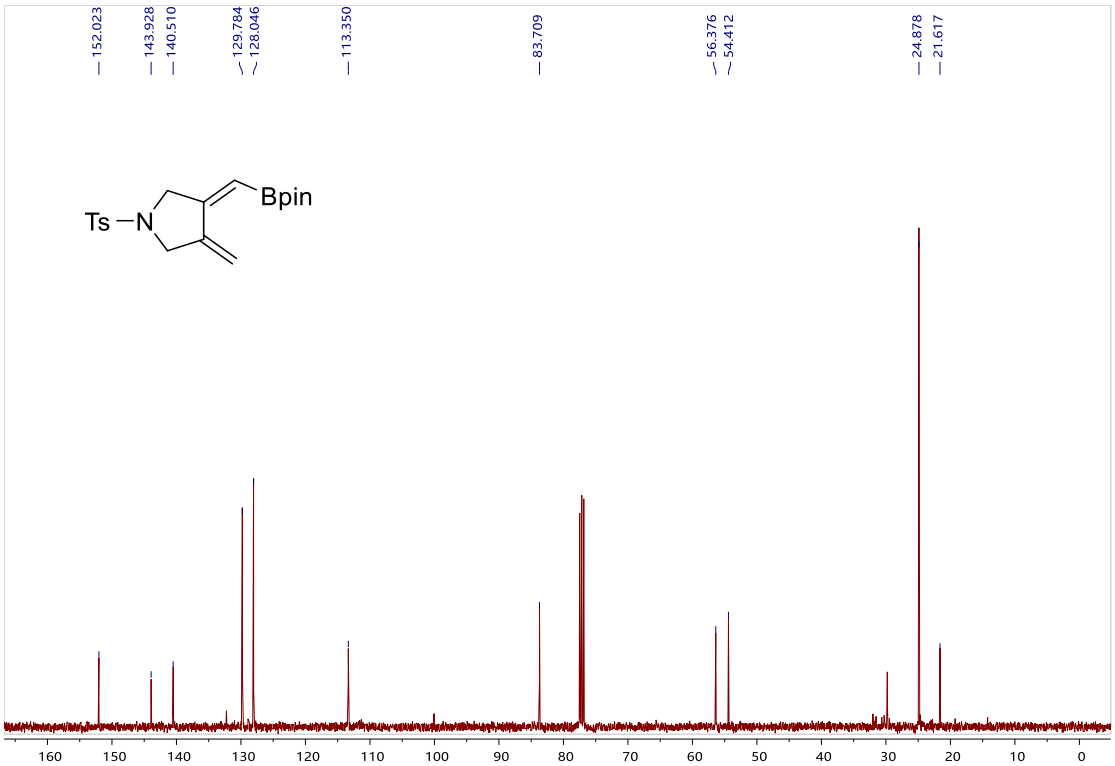
(*E*)-1-allyl-3-methylene-4-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methylene)pyrrolidine (2o)



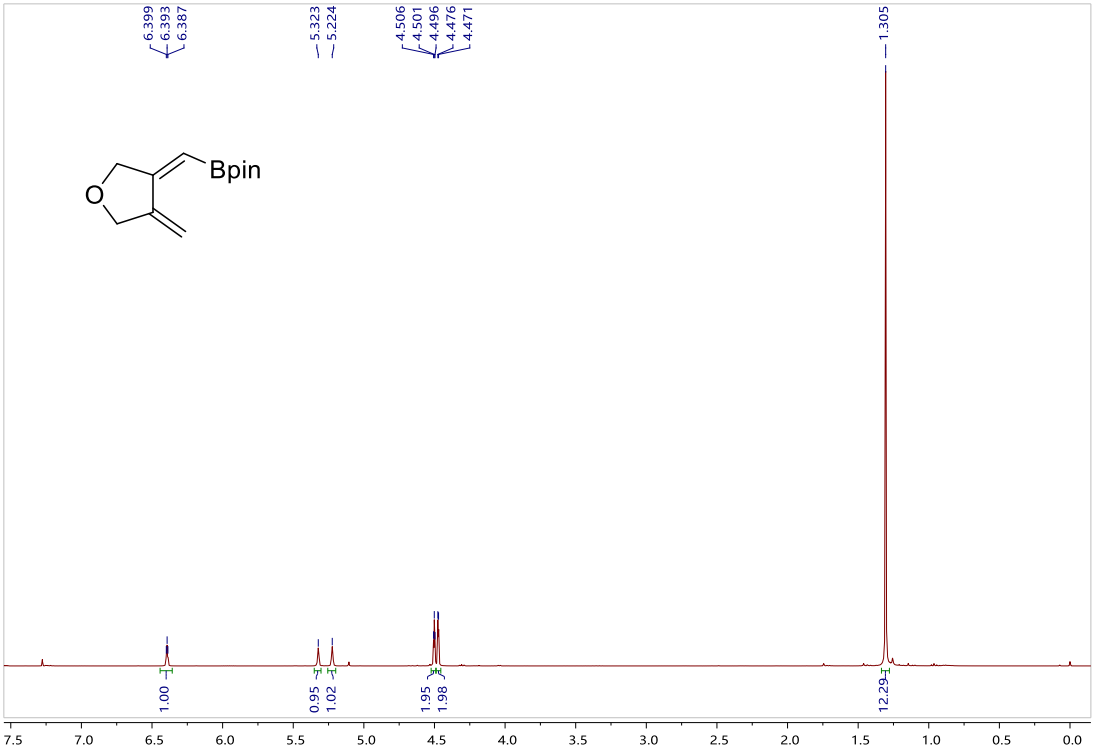


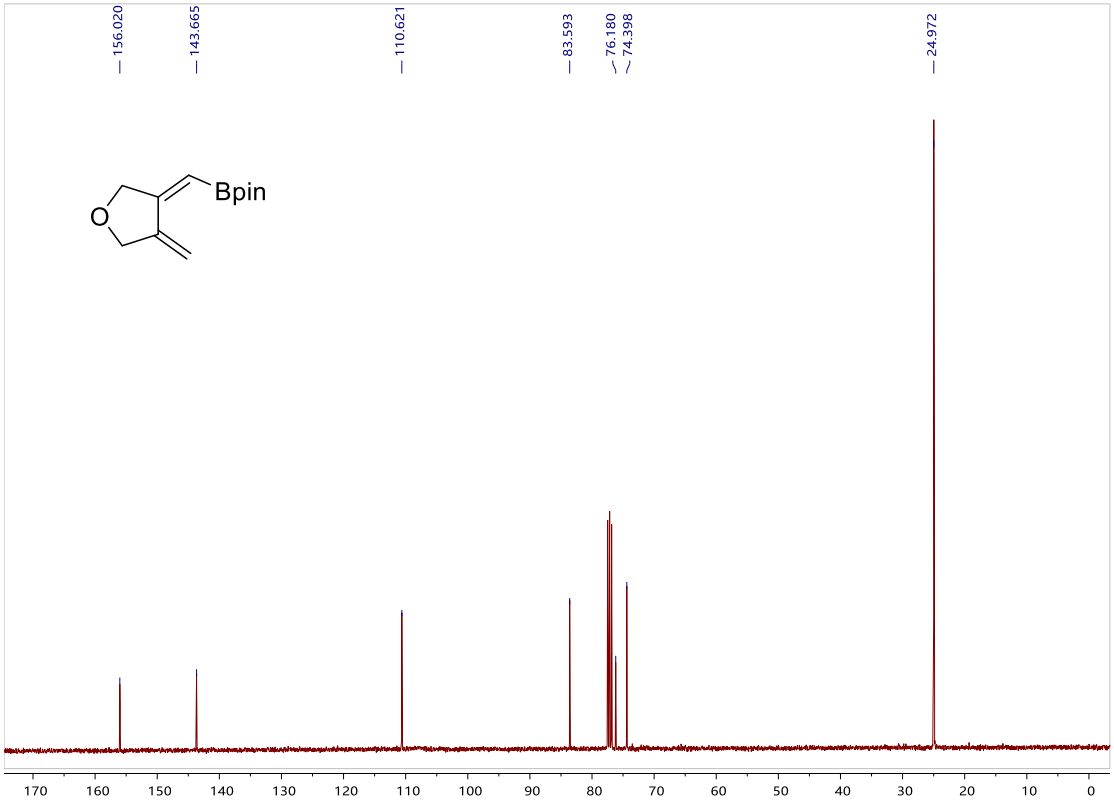
(*E*)-3-methylene-4-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methylene)-1-tosylpyrrolidine (2p)



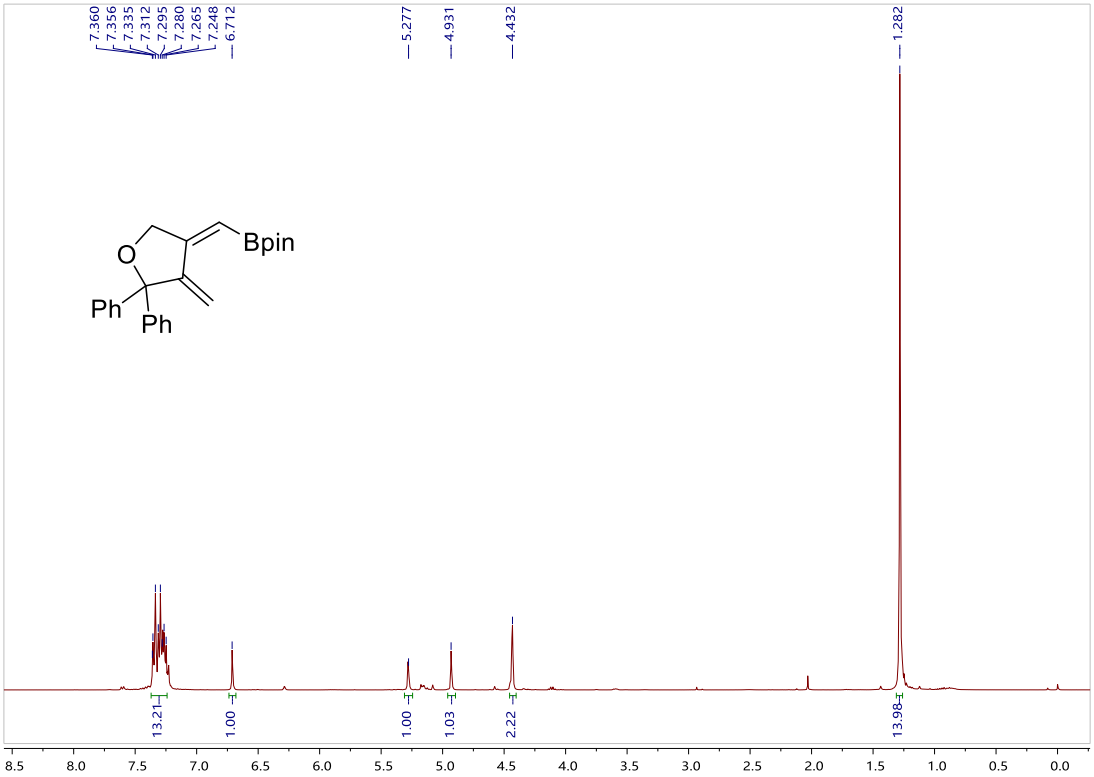


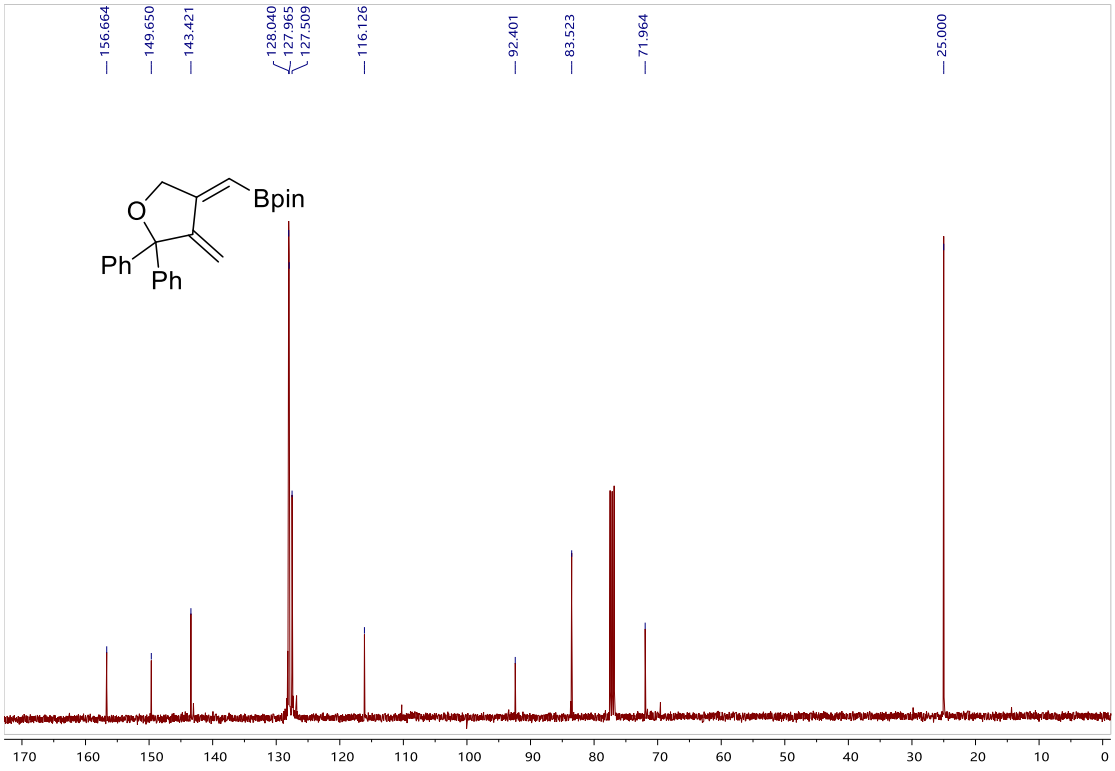
(*E*)-4,4,5,5-tetramethyl-2-((4-methylenedihydrofuran-3(*2H*)-ylidene)methyl)-1,3,2-dioxaborolane (2q)



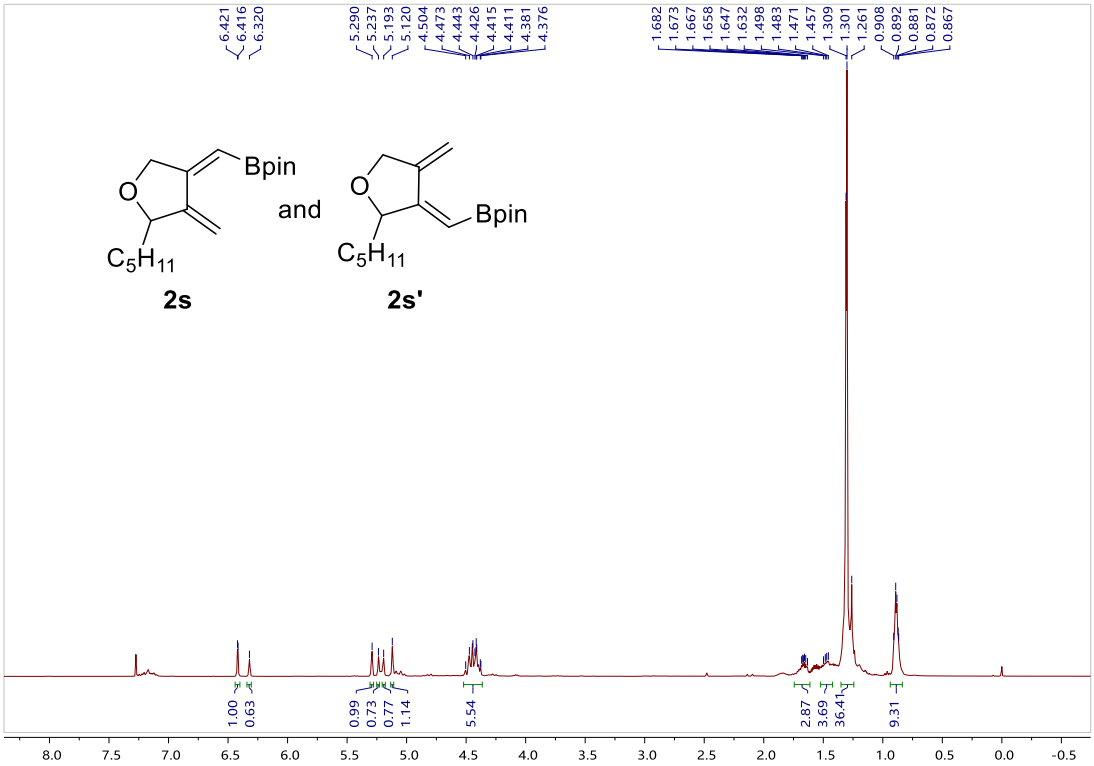


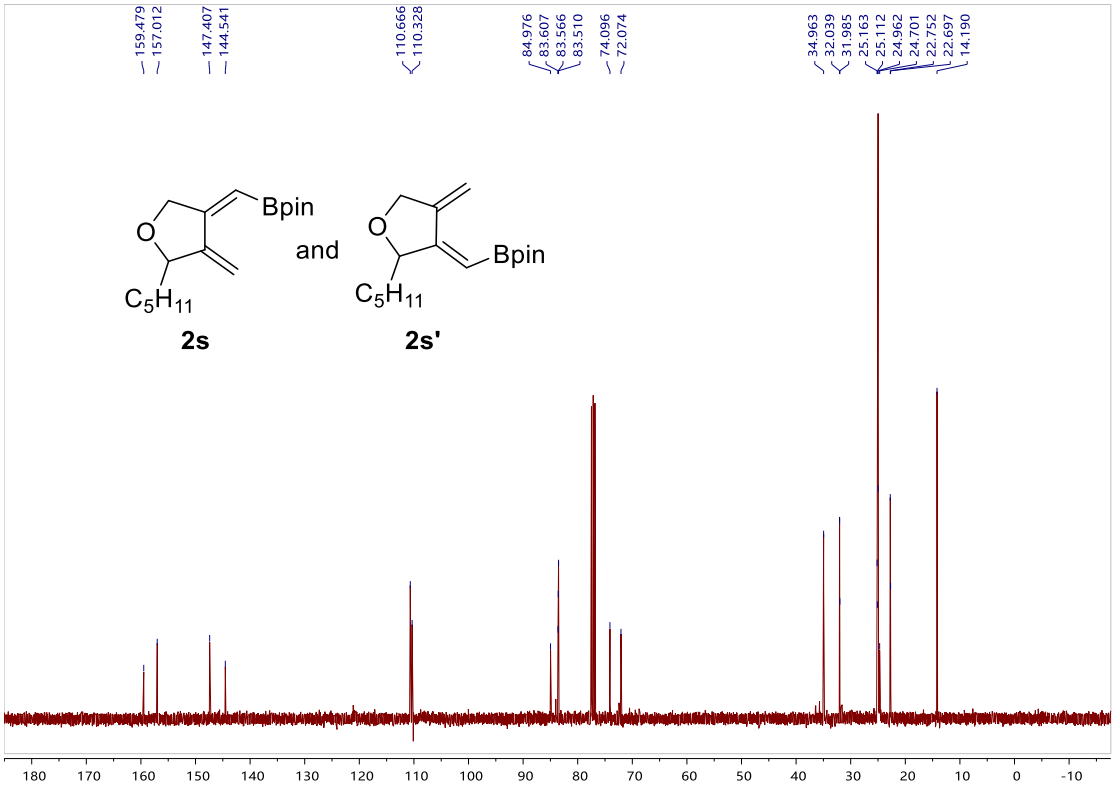
(*E*)-4,4,5,5-tetramethyl-2-((4-methylene-5,5-diphenyldihydrofuran-3(*2H*)-ylidene)methyl)-1,3,2-dioxaborolane (2r)





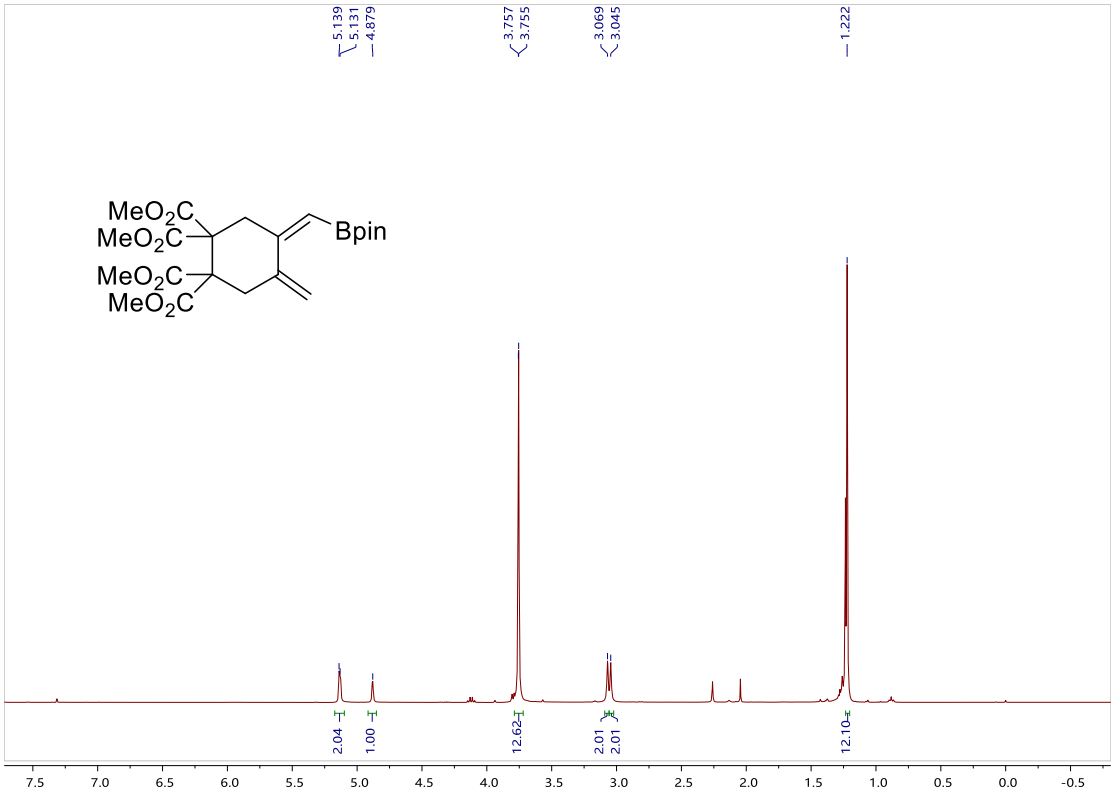
(*E*)-4,4,5,5-tetramethyl-2-((4-methylene-5-pentyldihydrofuran-3(*2H*)-ylidene)methyl)-1,3,2-dioxaborolane (2s) & (*E*)-4,4,5,5-tetramethyl-2-((4-methylene-2-pentyldihydrofuran-3(*2H*)ylidene)methyl)-1,3,2-dioxaborolane (2s')

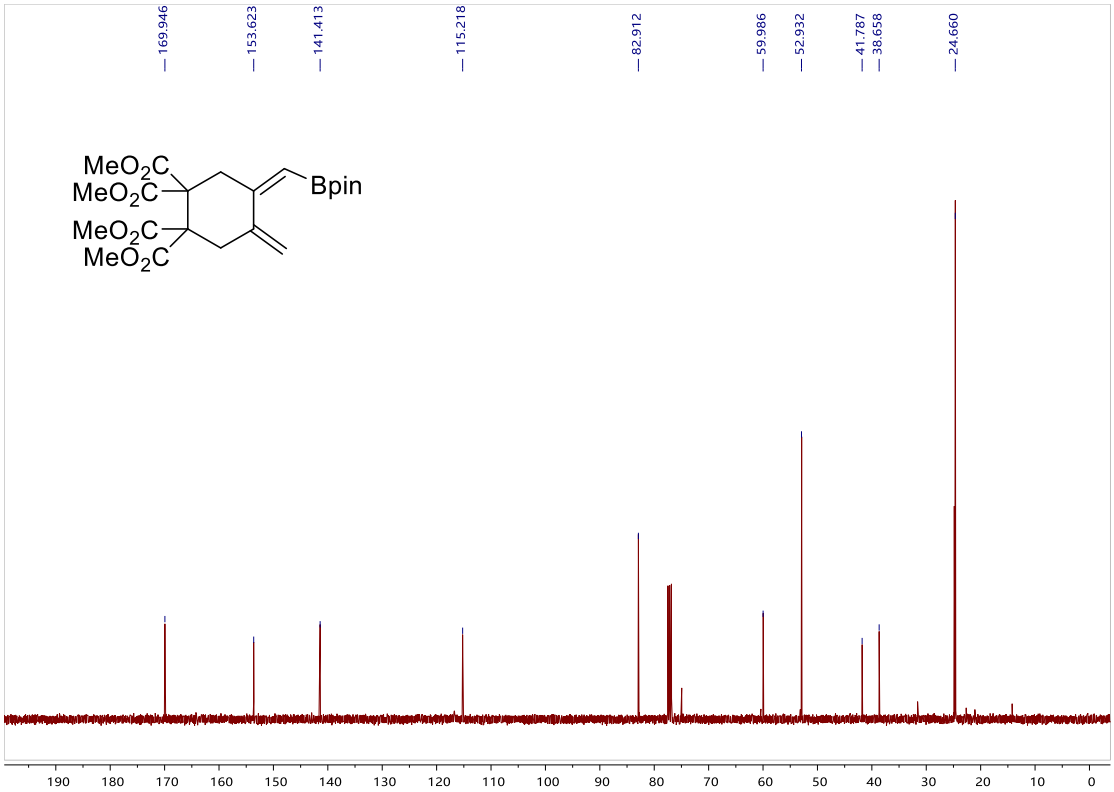




Tetramethyl

(*Z*)-4-methylene-5-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methylene)cyclohexane-1,1,2,2-tetracarboxylate (2t)

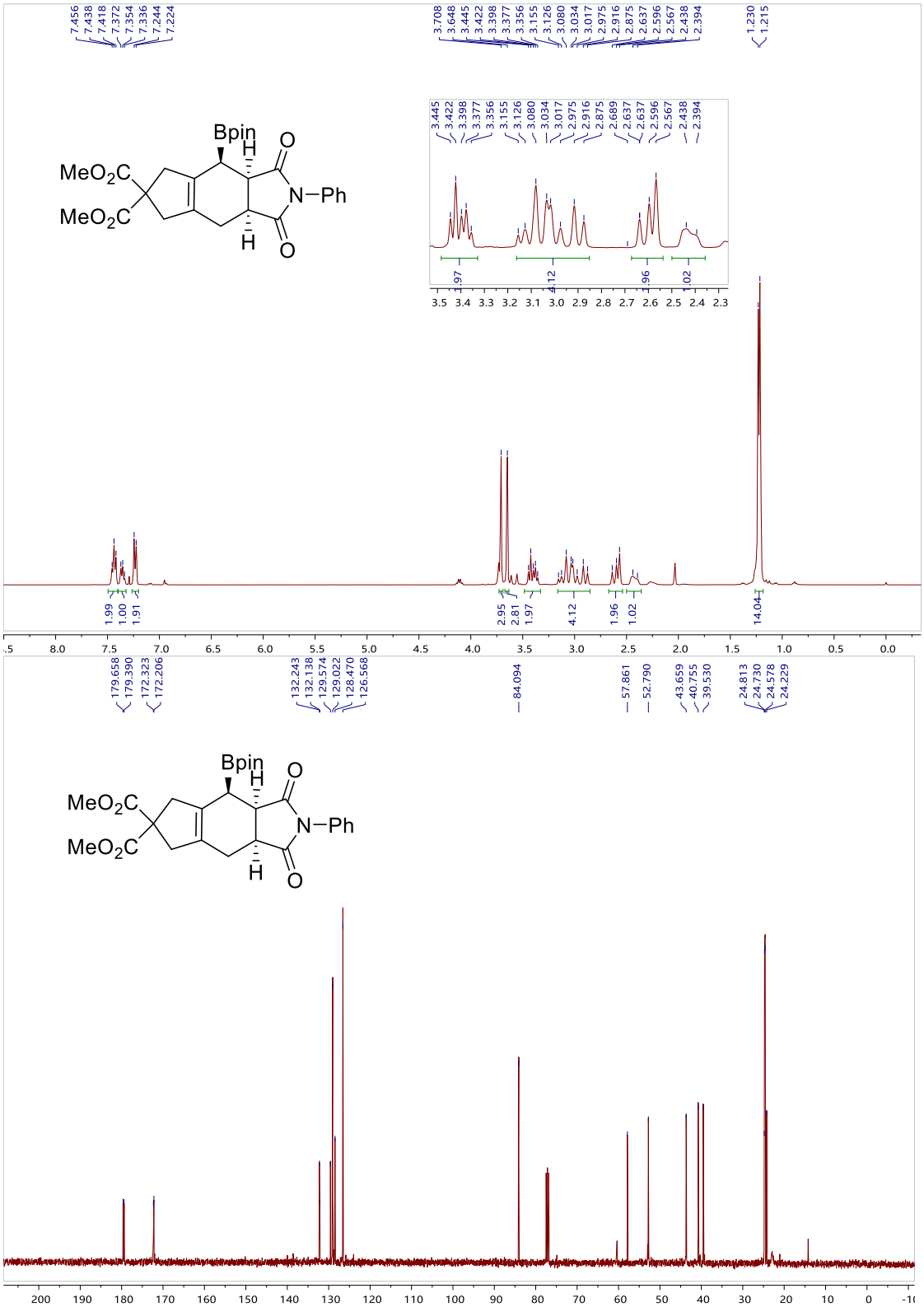


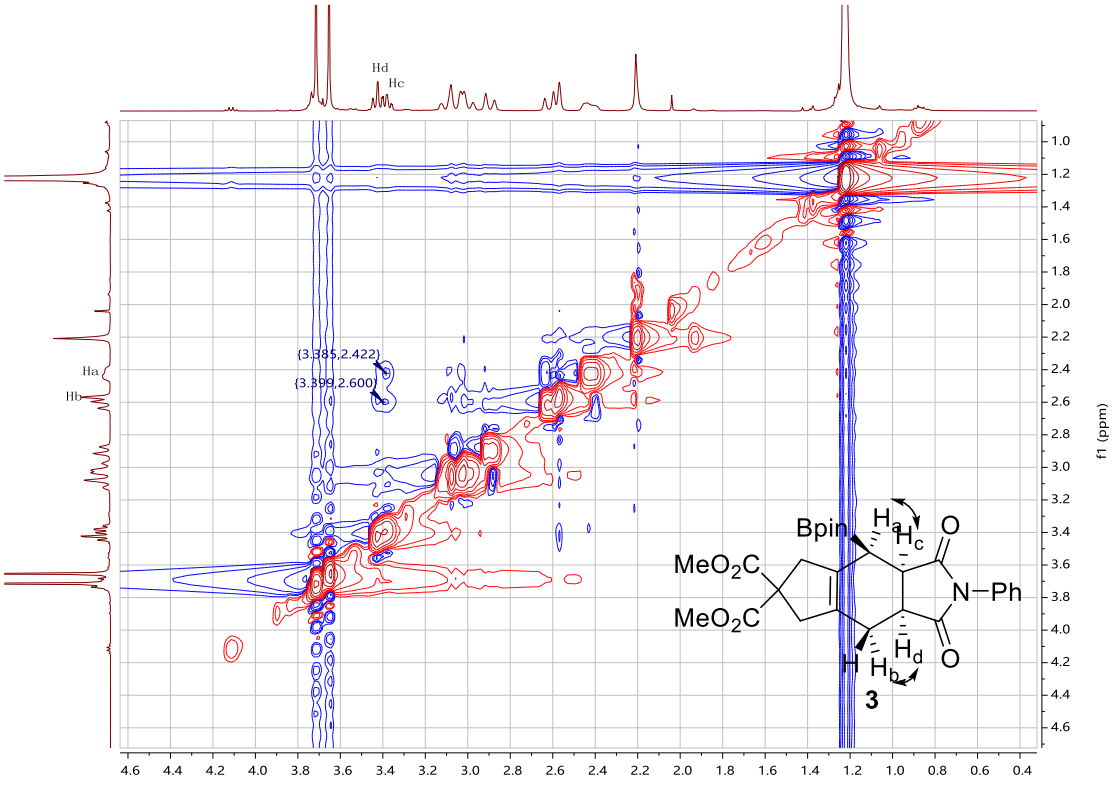


Dimethyl

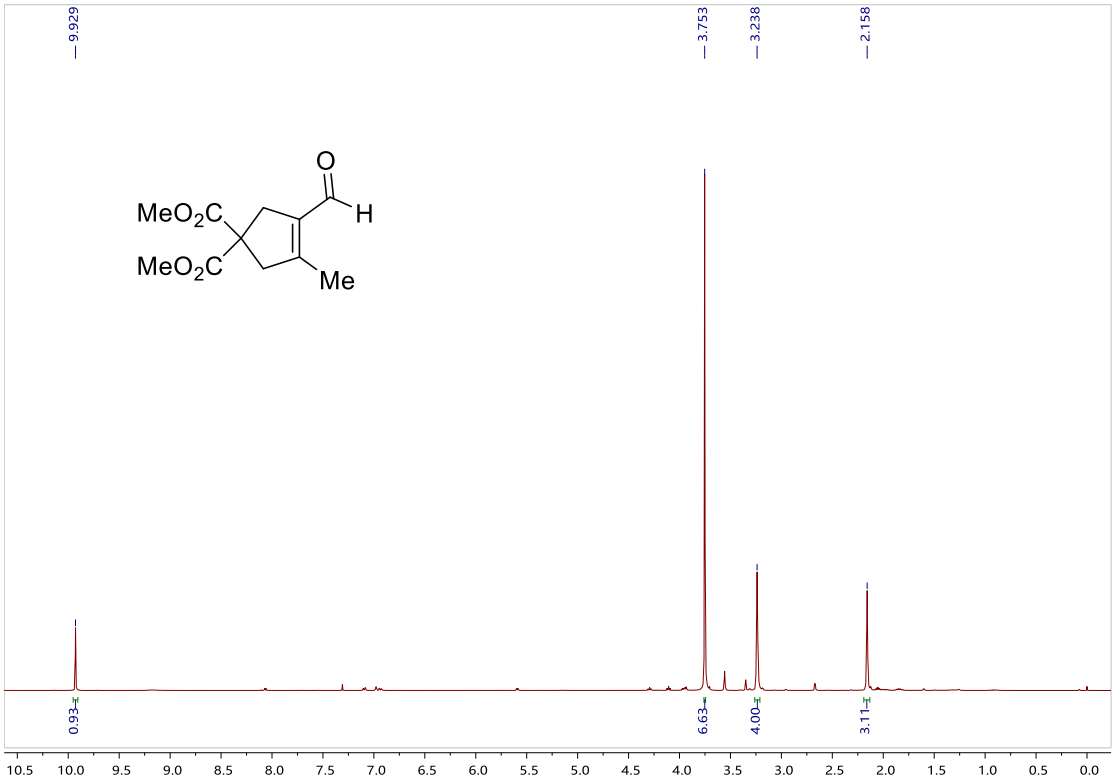
1,3-dioxo-2-phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2,3,3a,4,5,7,8,

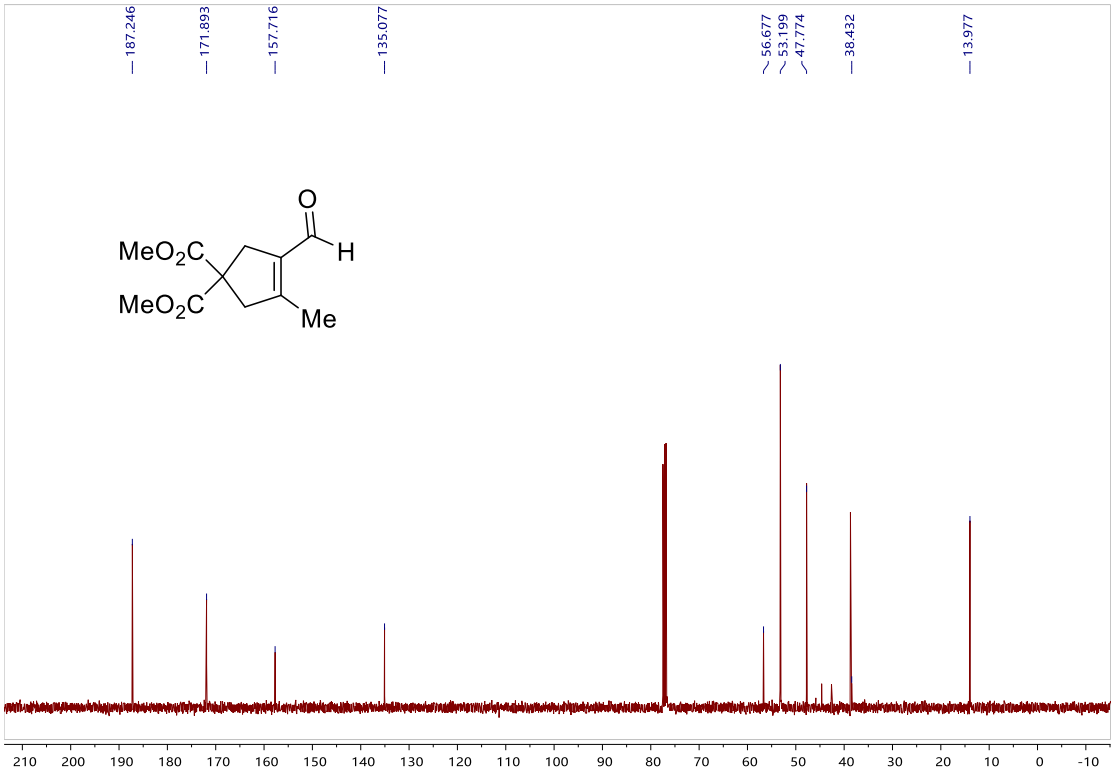
8a-octahydrocyclopenta[*f*]isoindole-6,6(*1H*)-dicarboxylate (3)



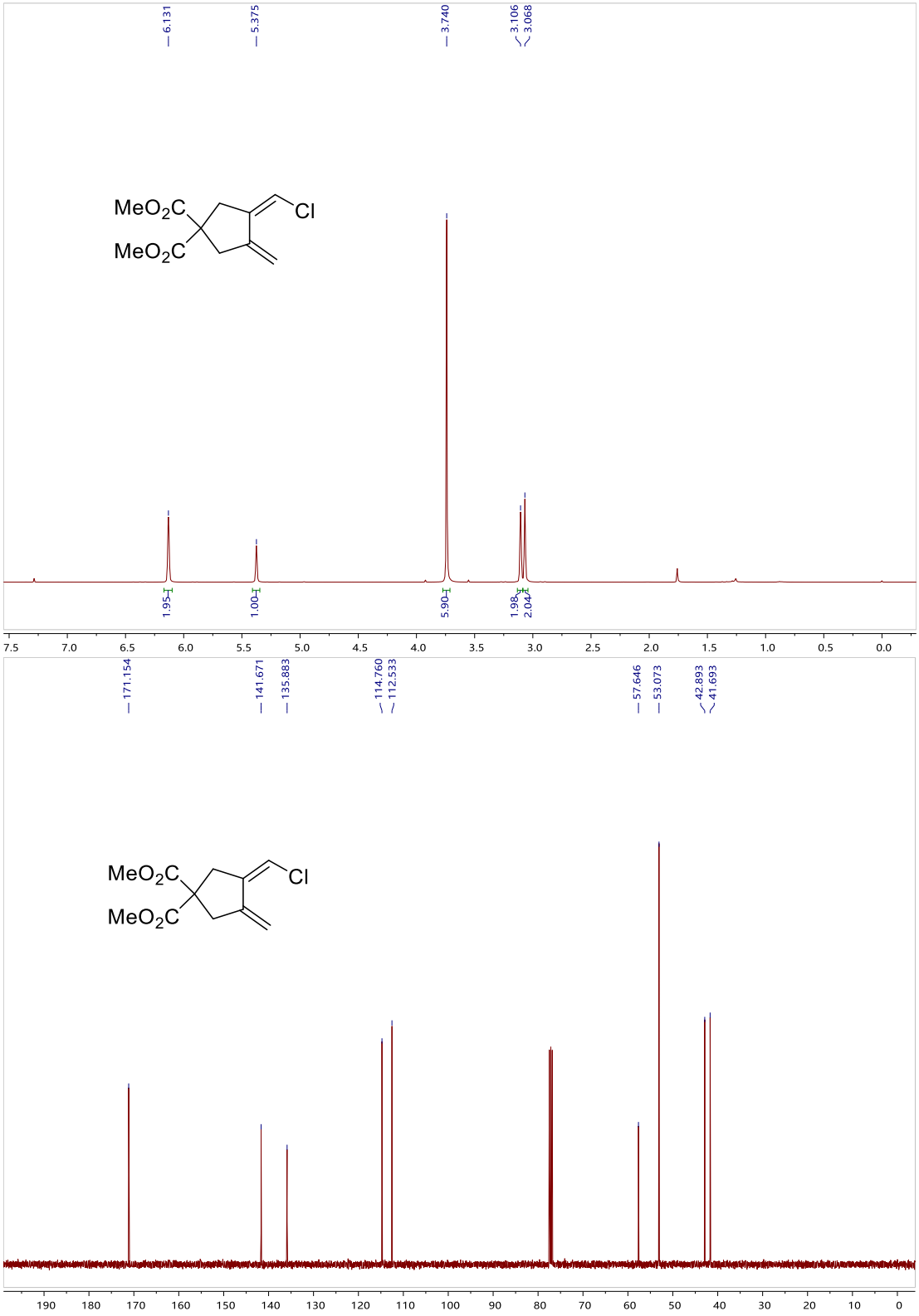

Hd
Hc
Ha
Hb
(3.385,2.422)
(3.399,2.600)
f1 (ppm)
Bpin
Ha
Hc
O
MeO2C
MeO2C
N–Ph
H
Hb
Hd
O
3

Dimethyl 3-formyl-4-methylcyclopent-3-ene-1,1-dicarboxylate (4)

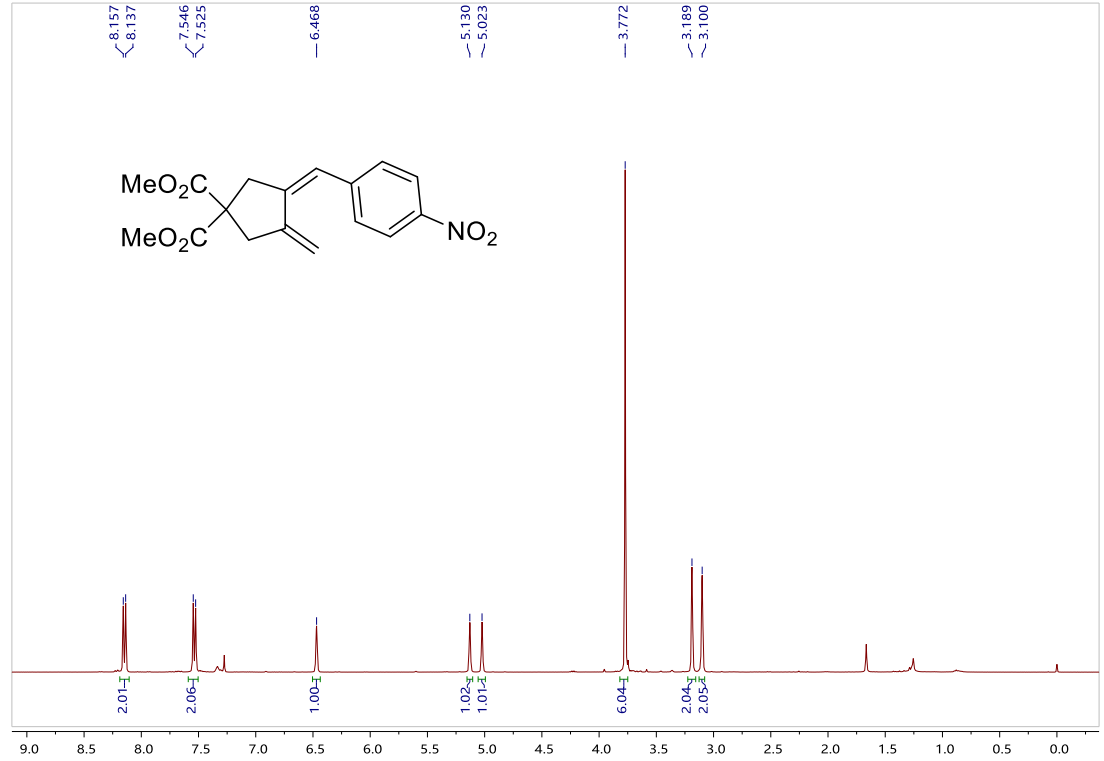


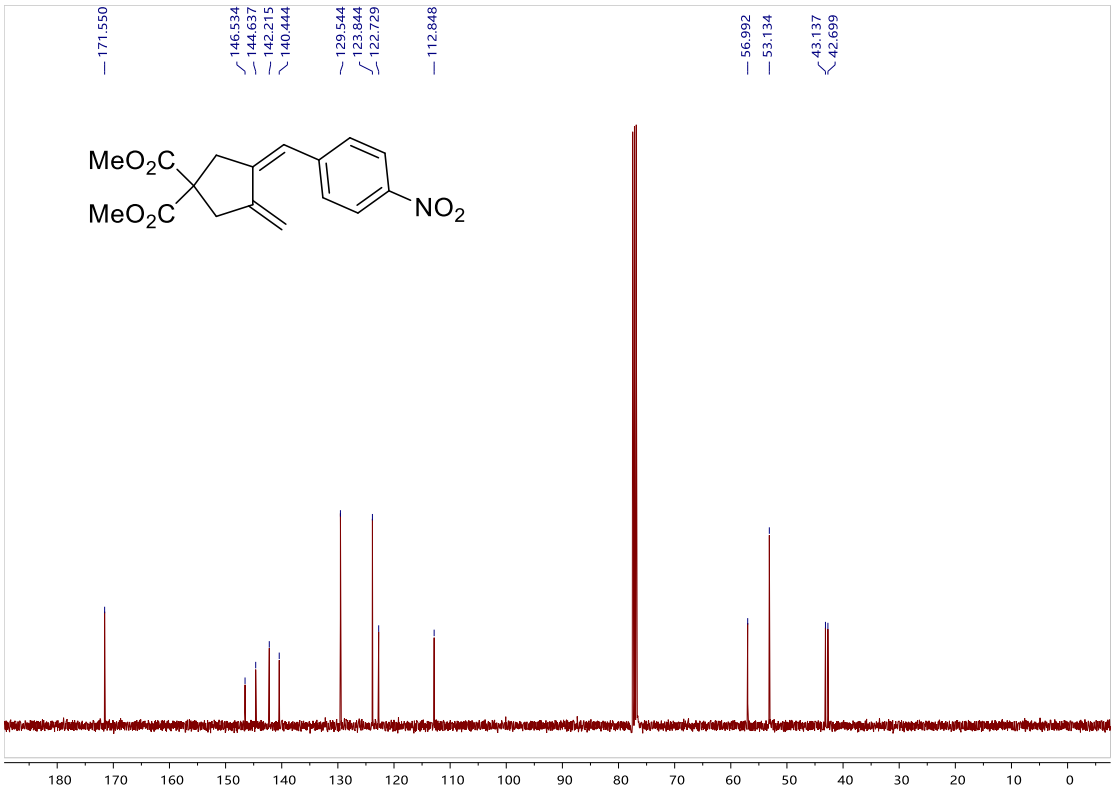


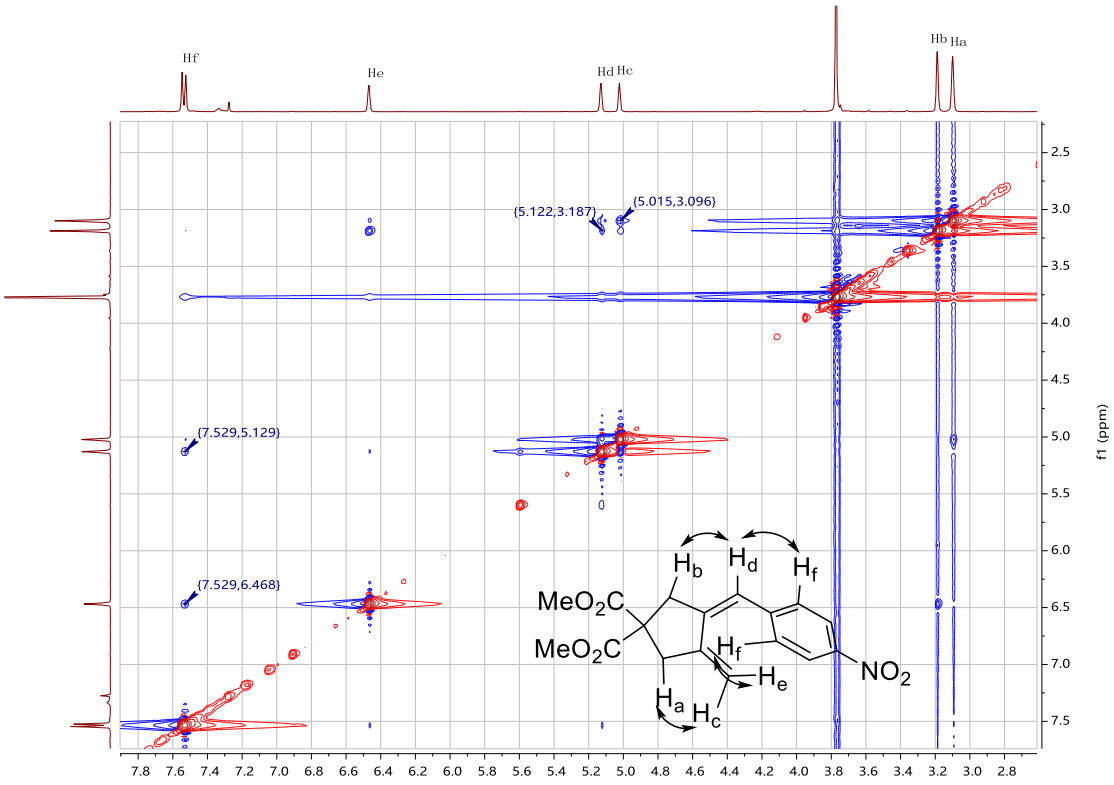
Dimethyl (*Z*)-3-(chloromethylene)-4-methylenecyclopentane-1,1-dicarboxylate (5)



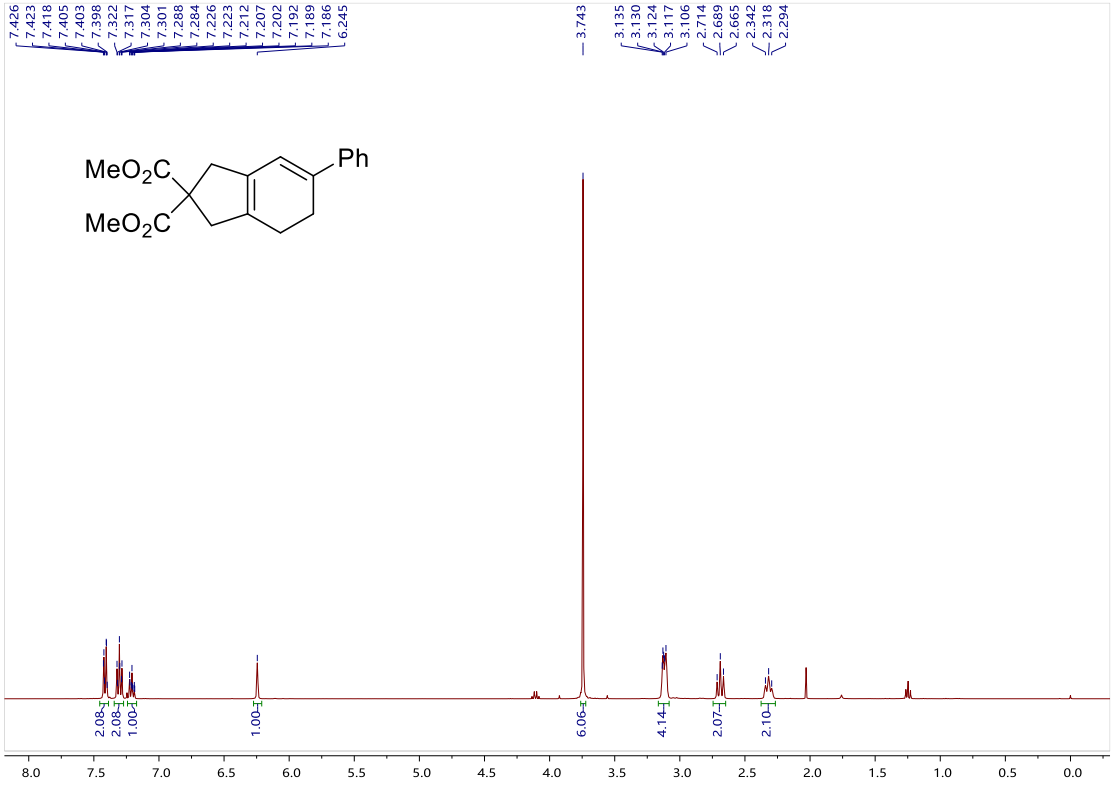
Dimethyl (*Z*)-3-methylene-4-(4-nitrobenzylidene)cyclopentane-1,1-dicarboxylate (6)

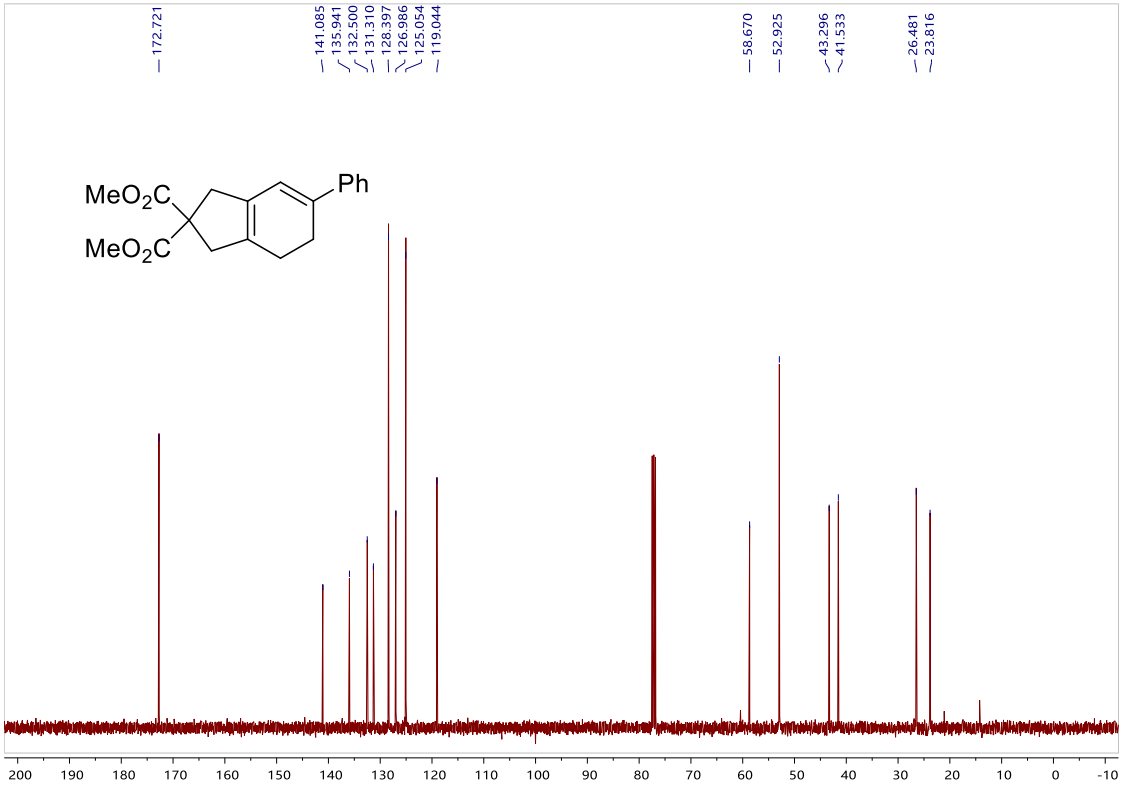




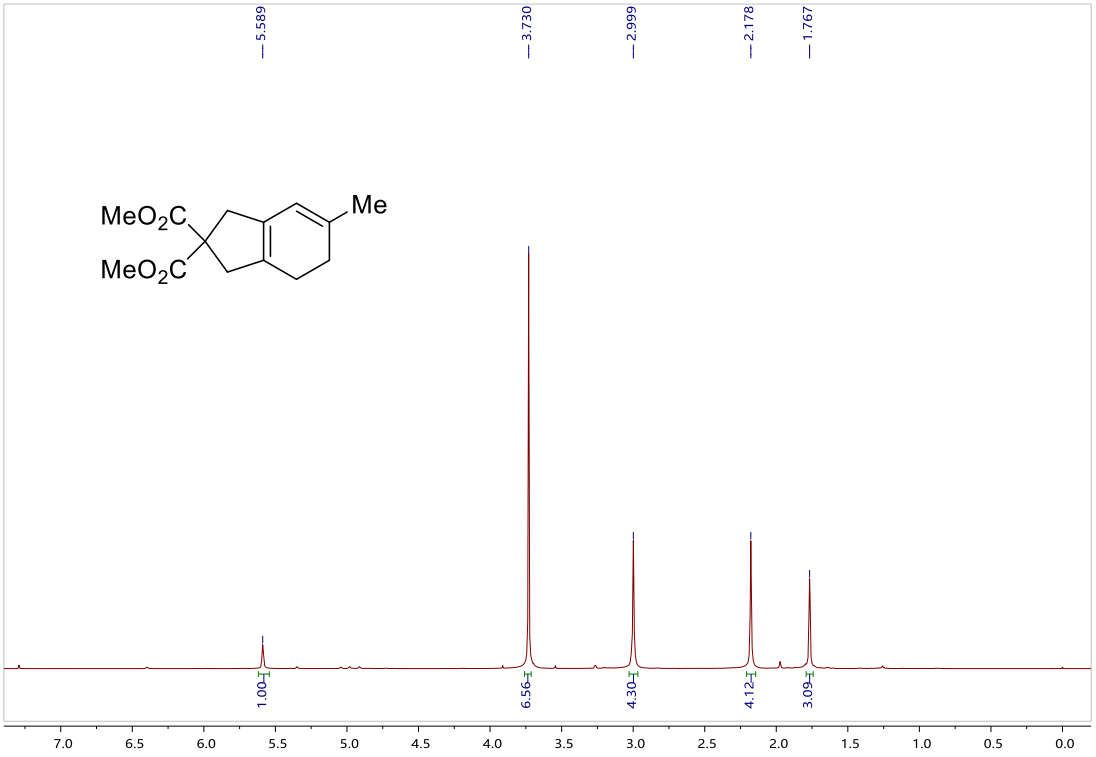

Hf
He
Hd Hc
Hb Ha
{5.122,3.187}
{5.015,3.096}
{7.529,5.129}
{7.529,6.468}
f1 (ppm)
MeO2C
MeO2C
NO2
Hb
Hd
Hf
Hf
He
Ha
Hc

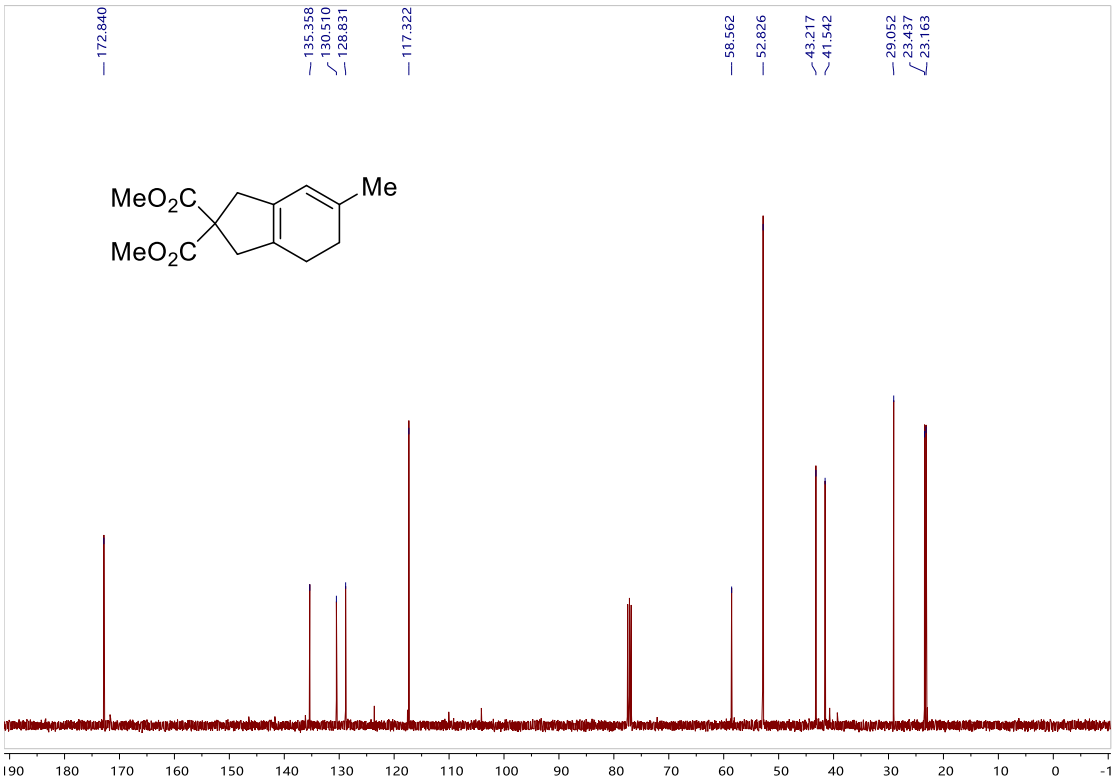
Dimethyl 6-phenyl-1,3,4,5-tetrahydro-2*H*-indene-2,2-dicarboxylate (7a)



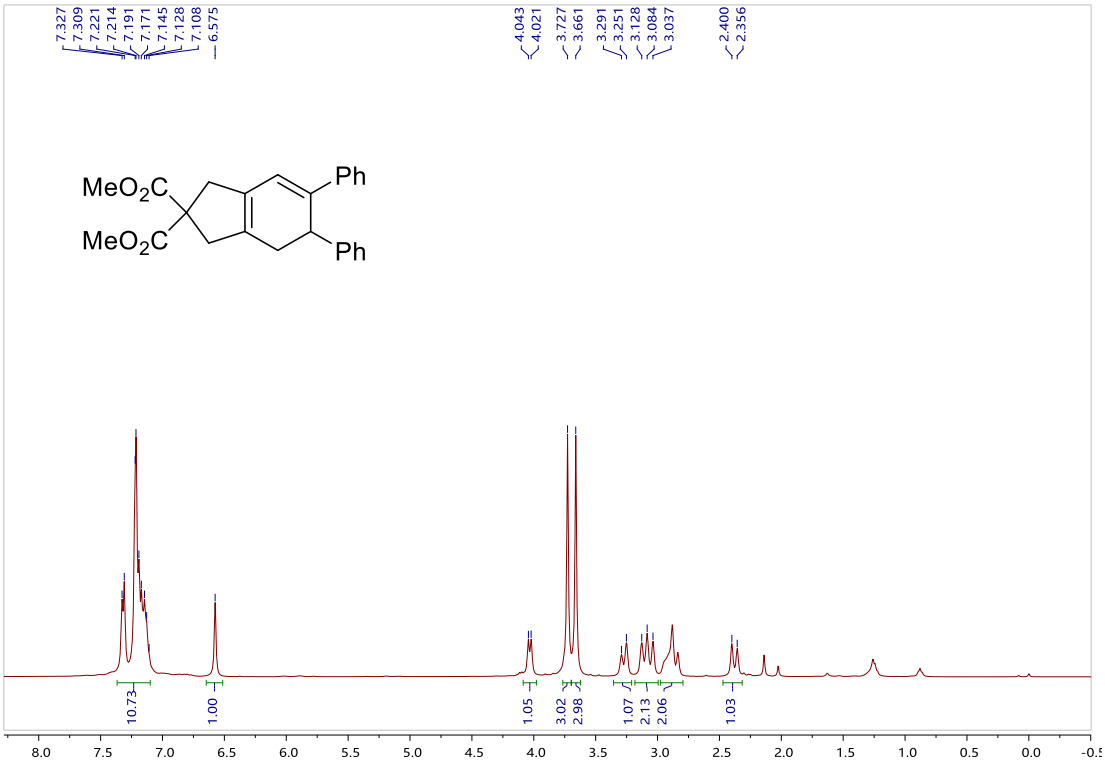


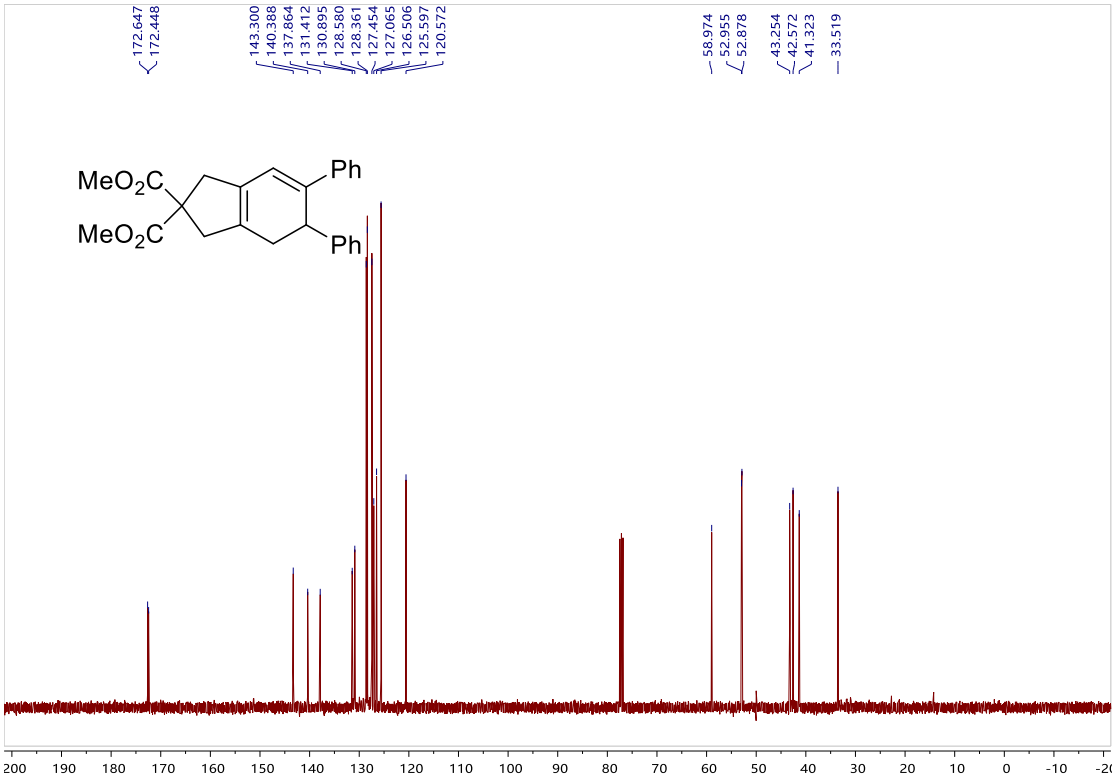
Dimethyl 6-methyl-1,3,4,5-tetrahydro-*2H*-indene-2,2-dicarboxylate (7b)



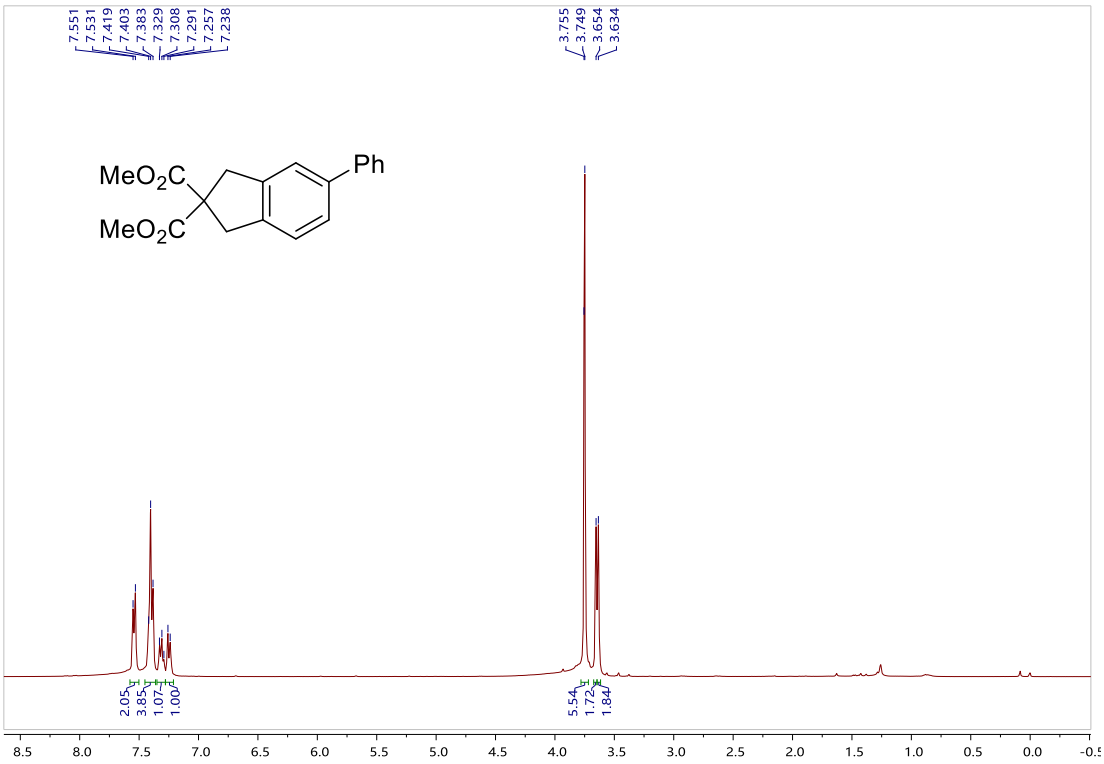


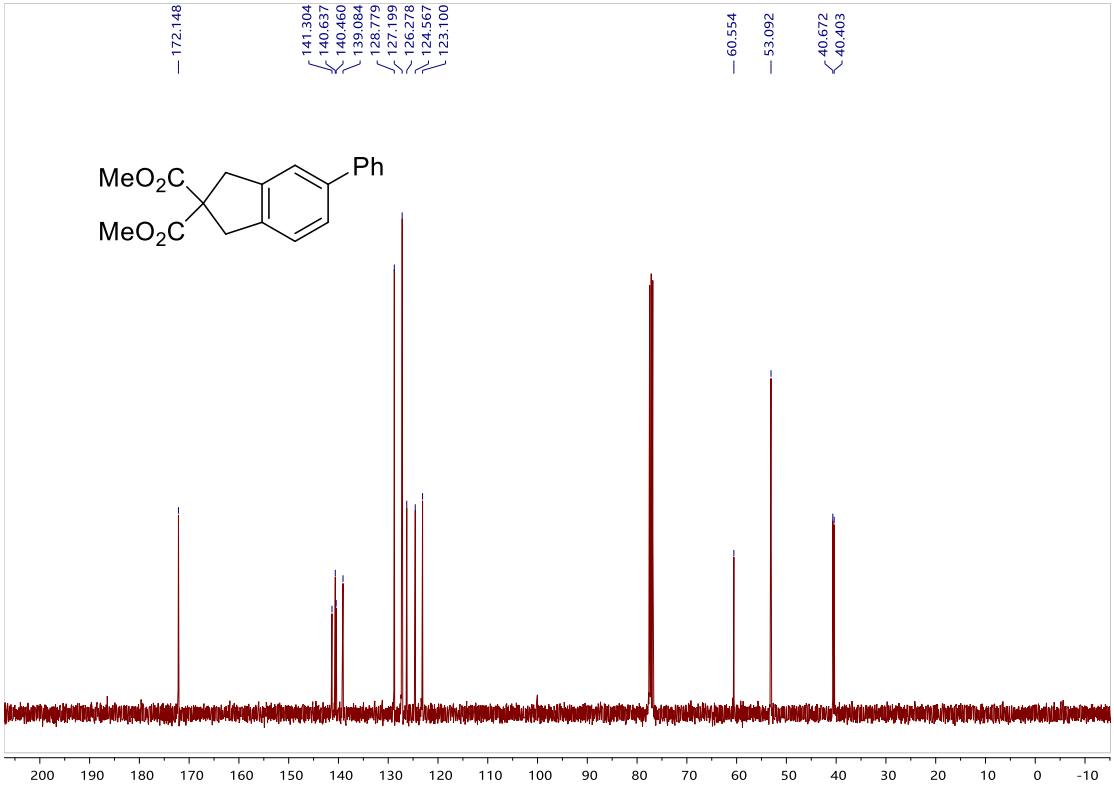
Dimethyl 5,6-diphenyl-1,3,4,5-tetrahydro-*2H*-indene-2,2-dicarboxylate (7c)



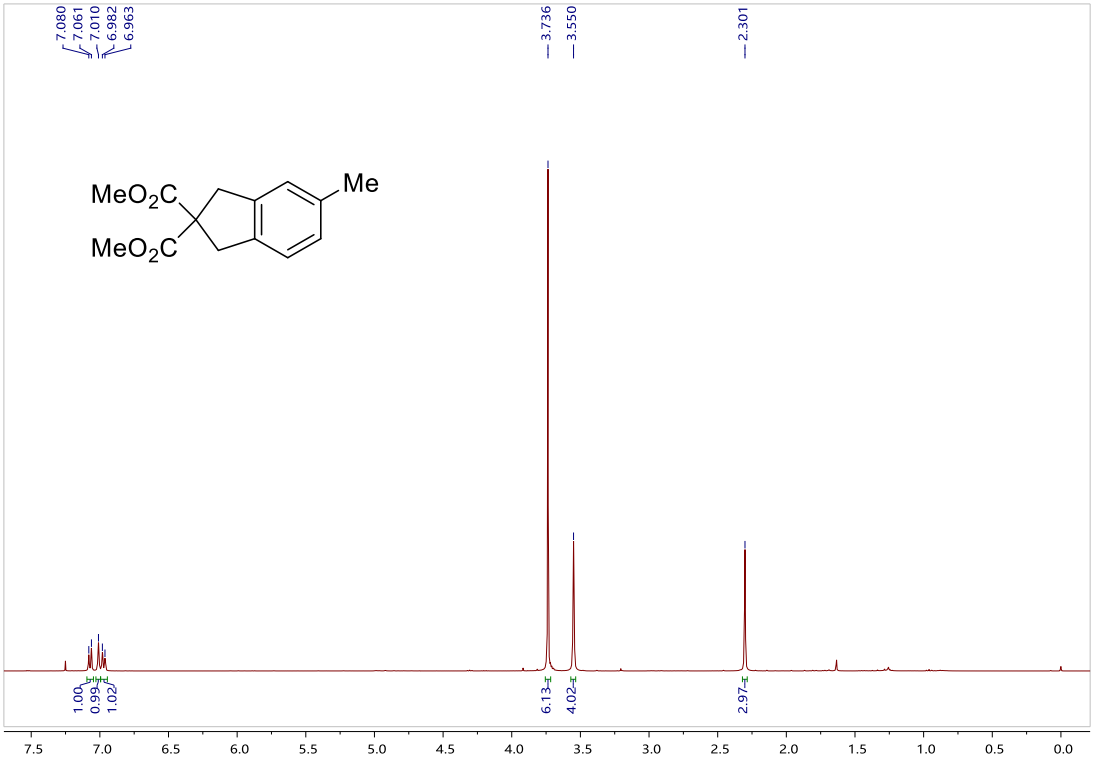


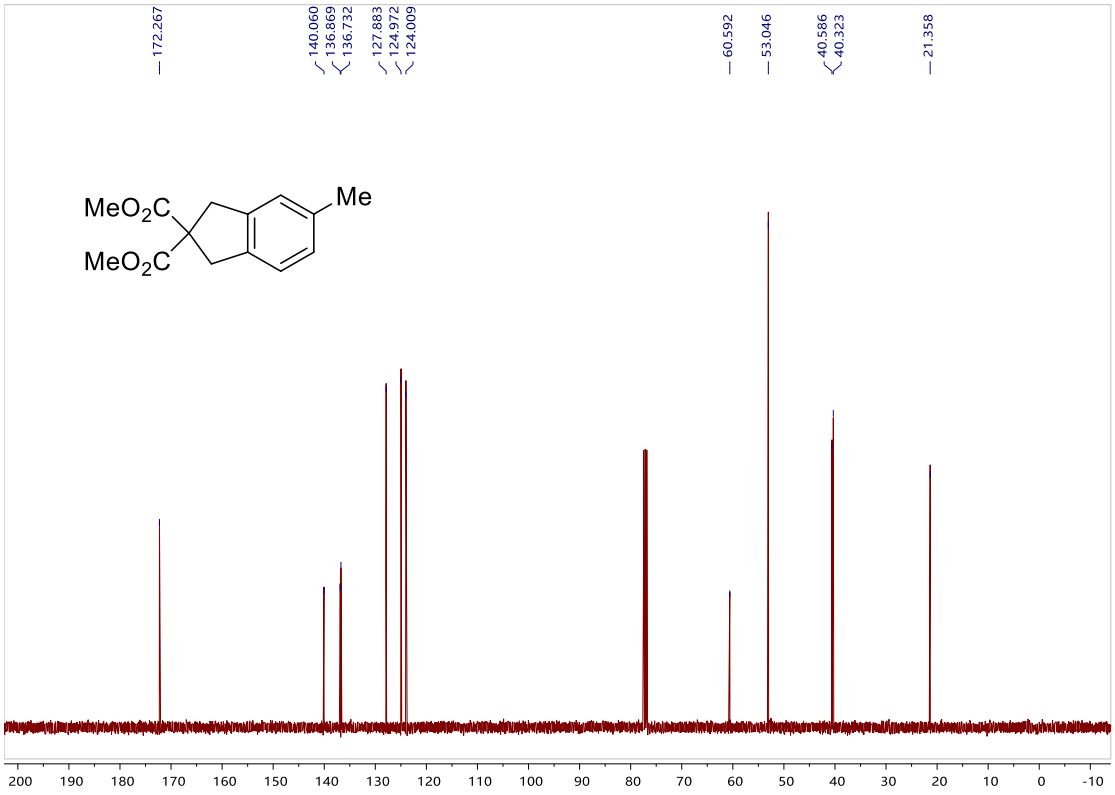
Dimethyl 5-phenyl-1,3-dihydro-2*H*-indene-2,2-dicarboxylate (8a)



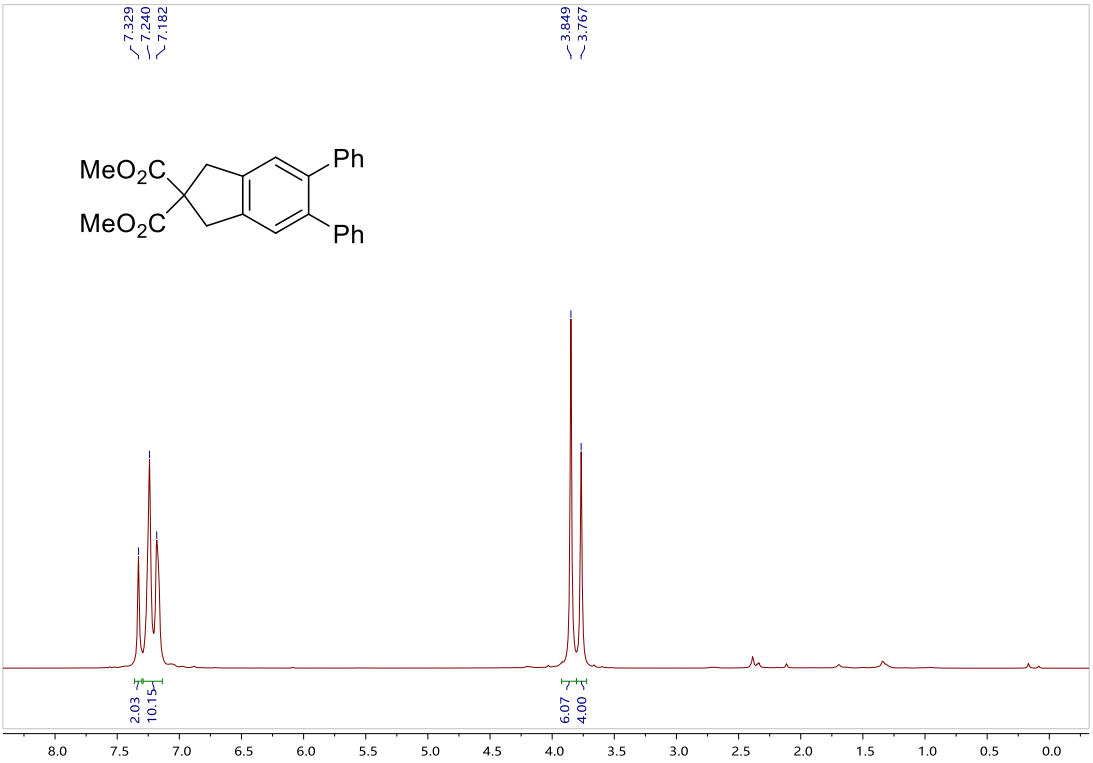


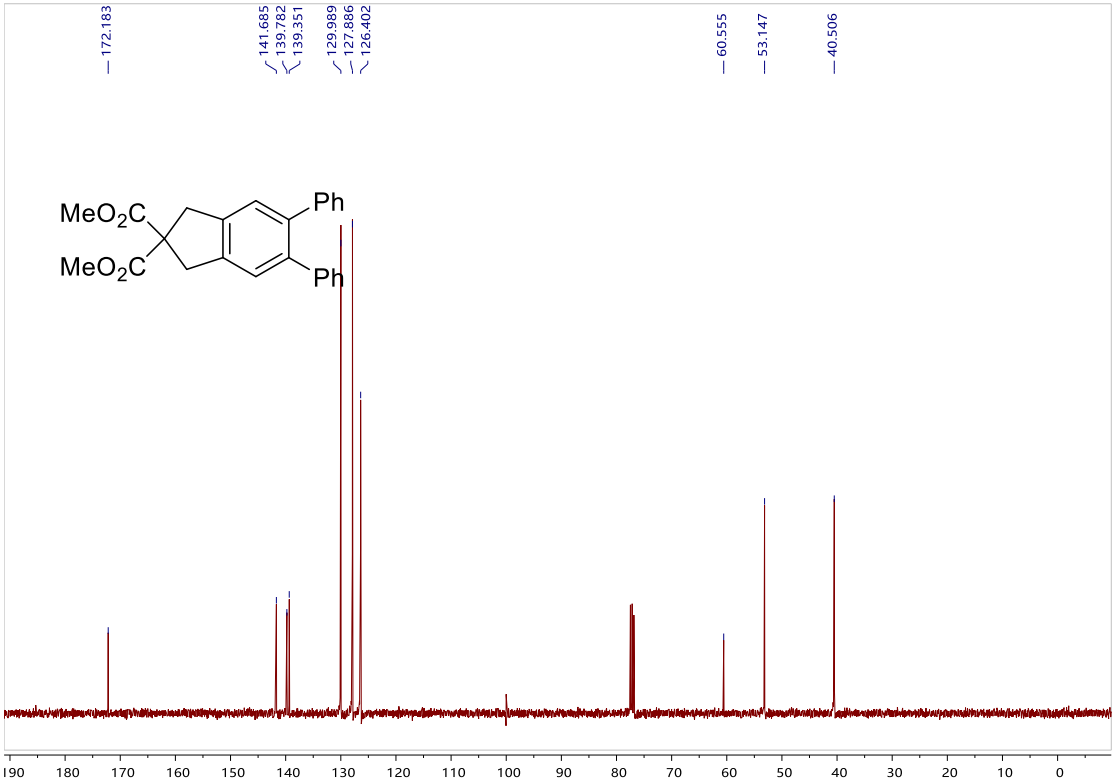
Dimethyl 5-methyl-1,3-dihydro-*2H*-indene-2,2-dicarboxylate (8b)





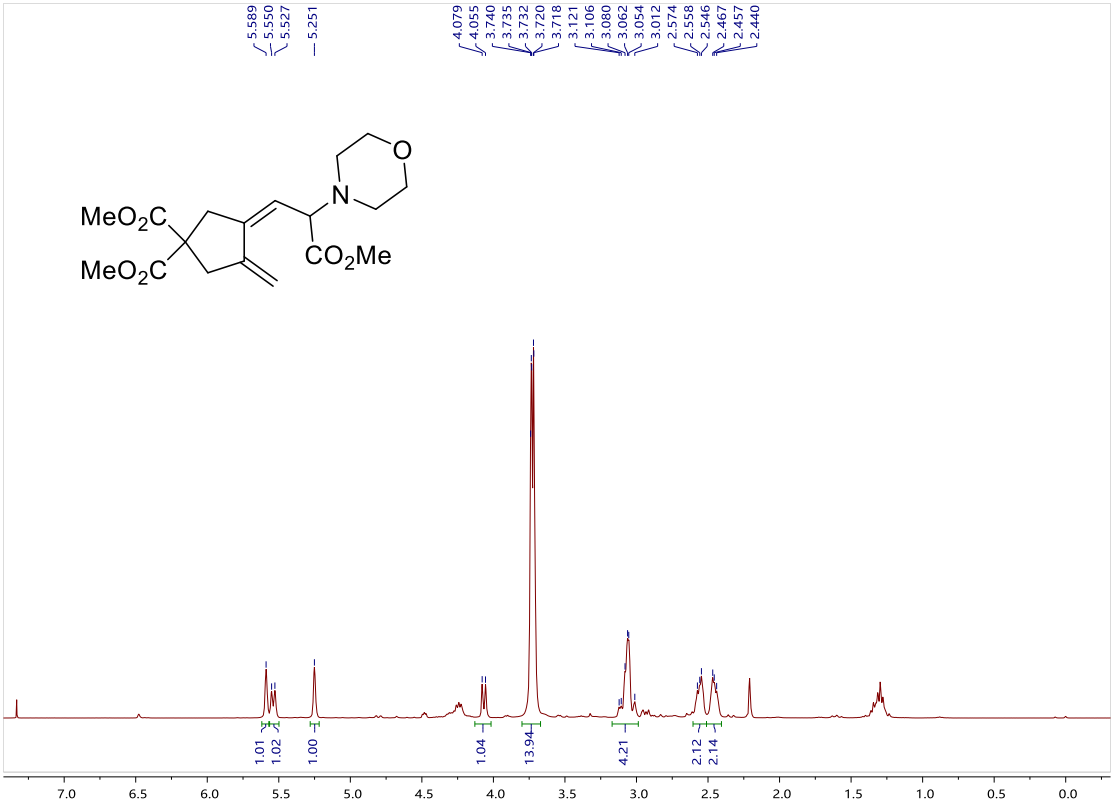
Dimethyl 5,6-diphenyl-1,3-dihydro-*2H*-indene-2,2-dicarboxylate (8c)

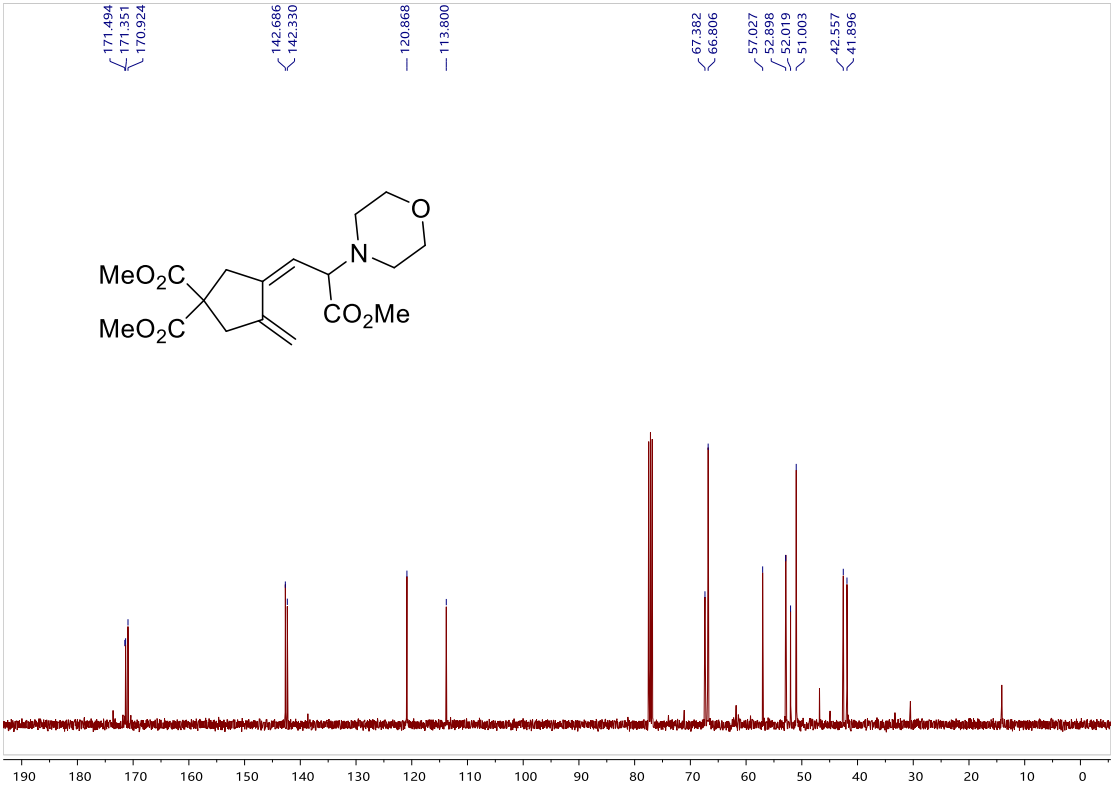




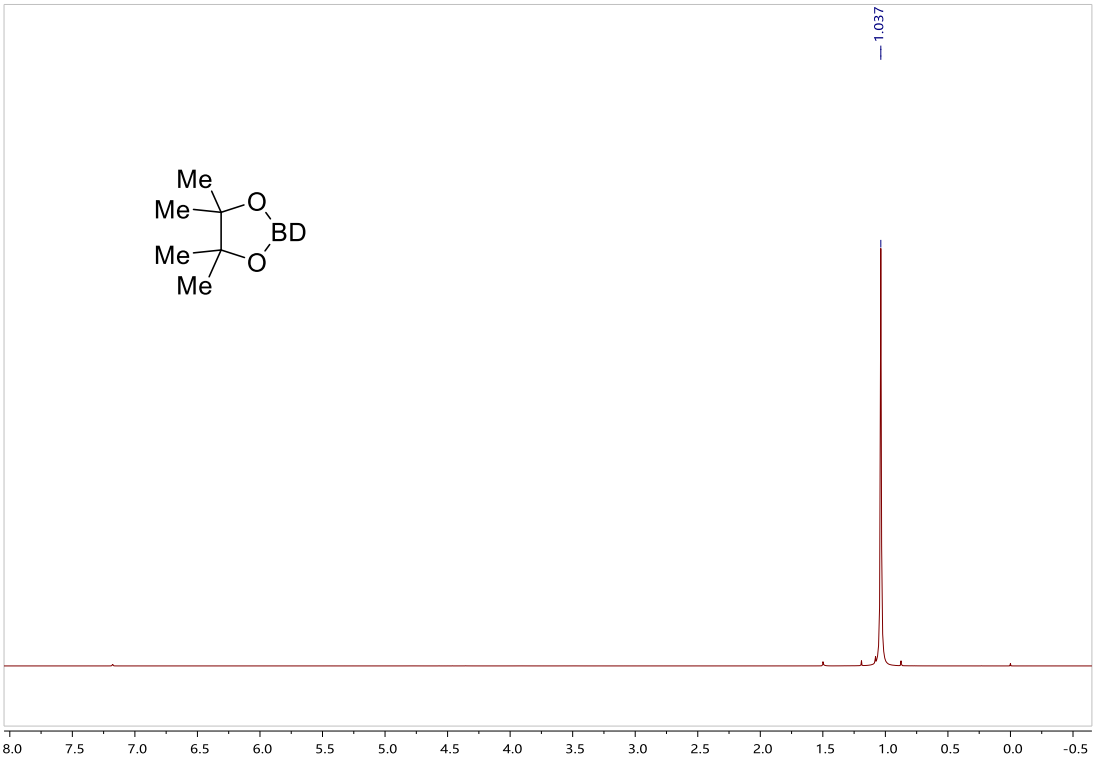
Dimethyl

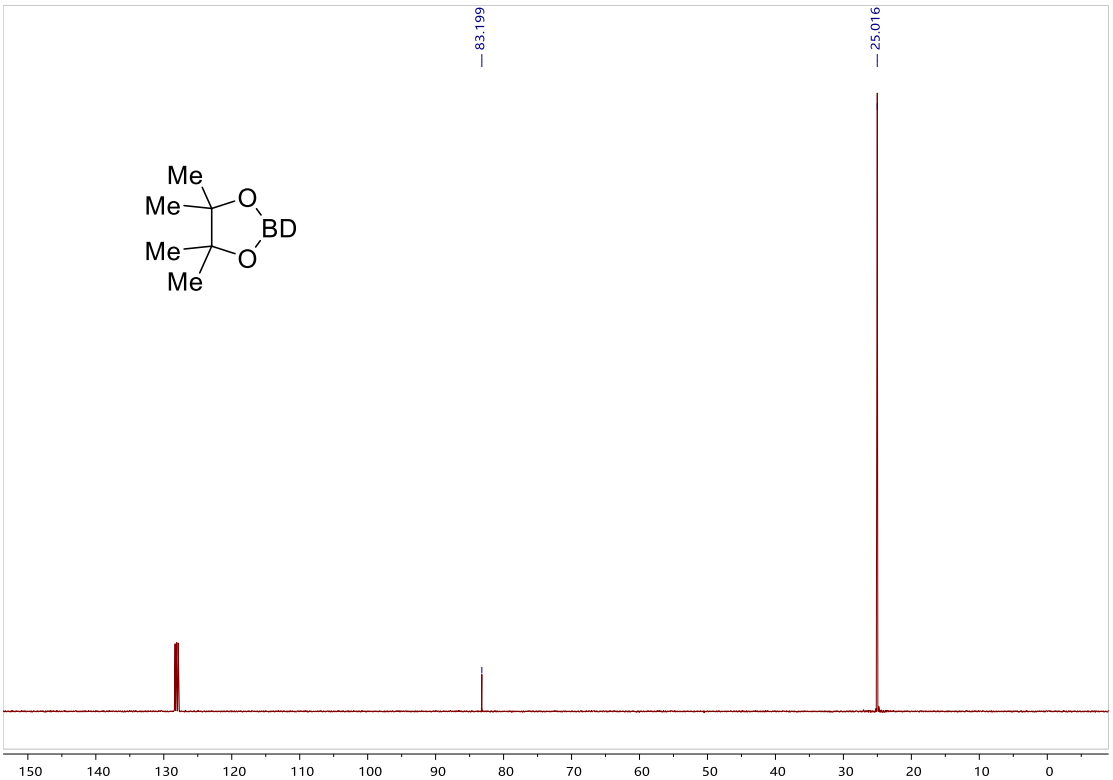
(*Z*)-3-(3-methoxy-2-morpholino-3-oxopropylidene)-4-methylenecyclopentane-1,1-dicarboxylate (9)



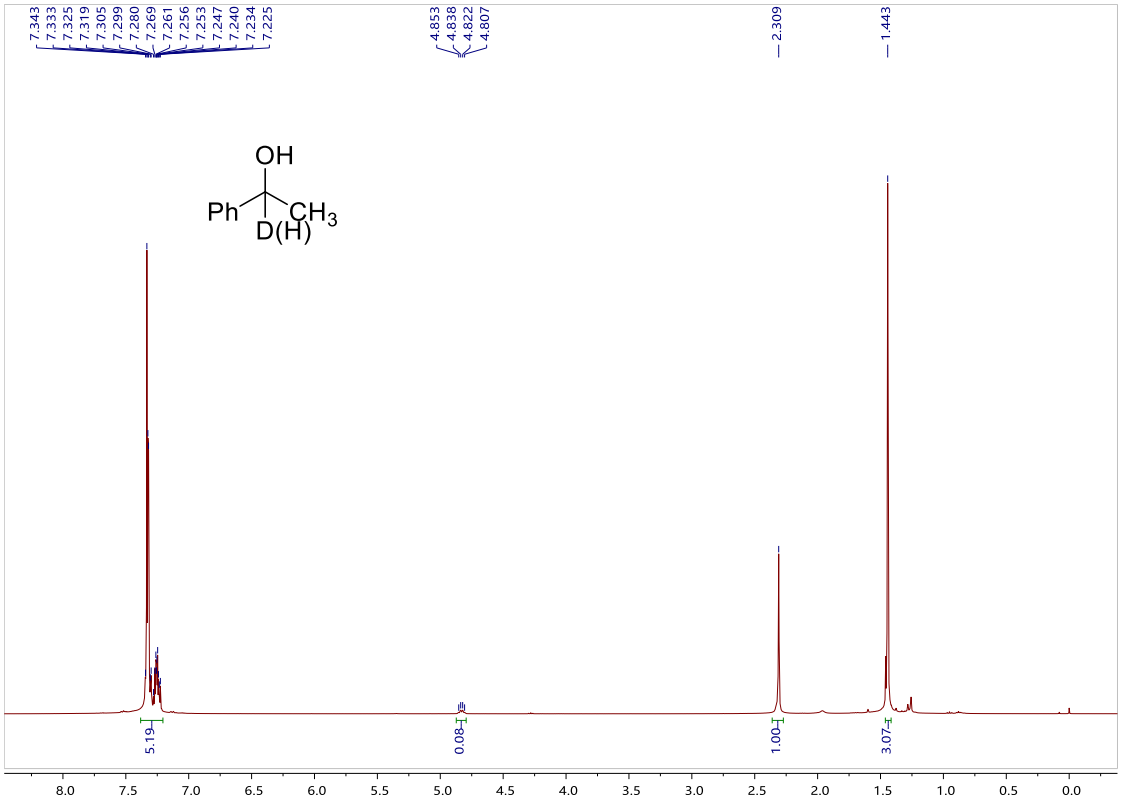


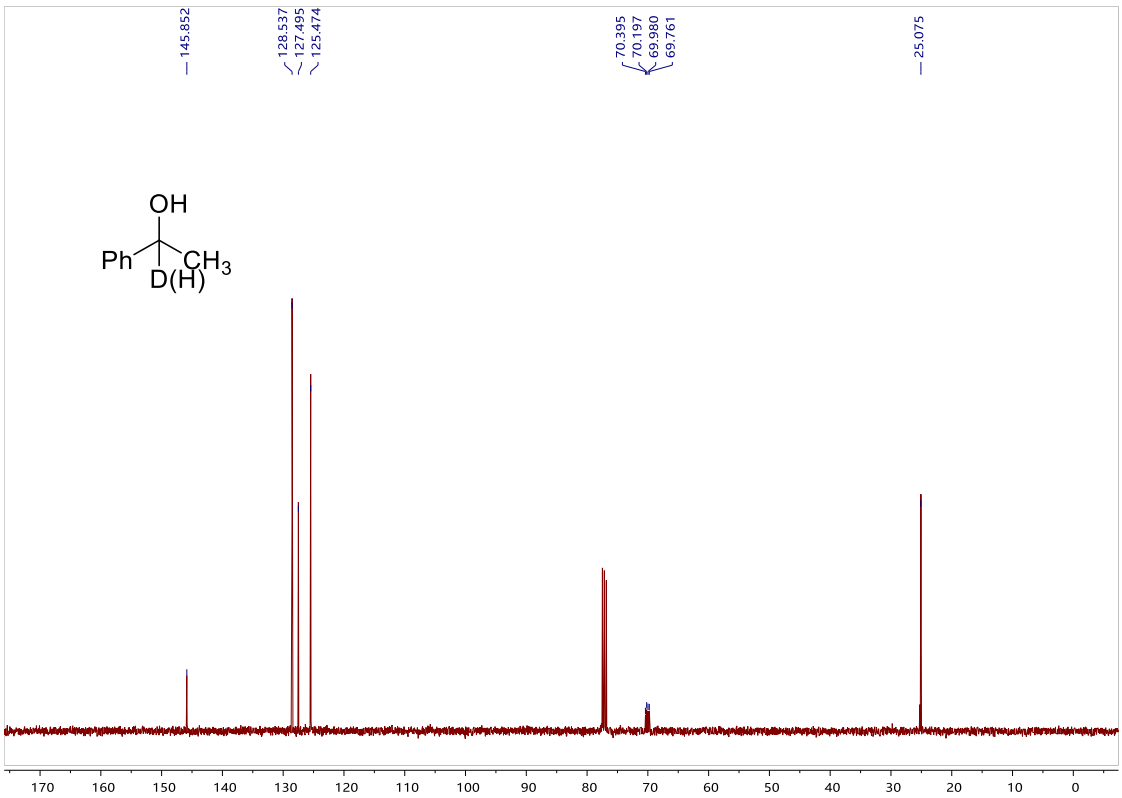
Pinacolborane-d1 (S1)



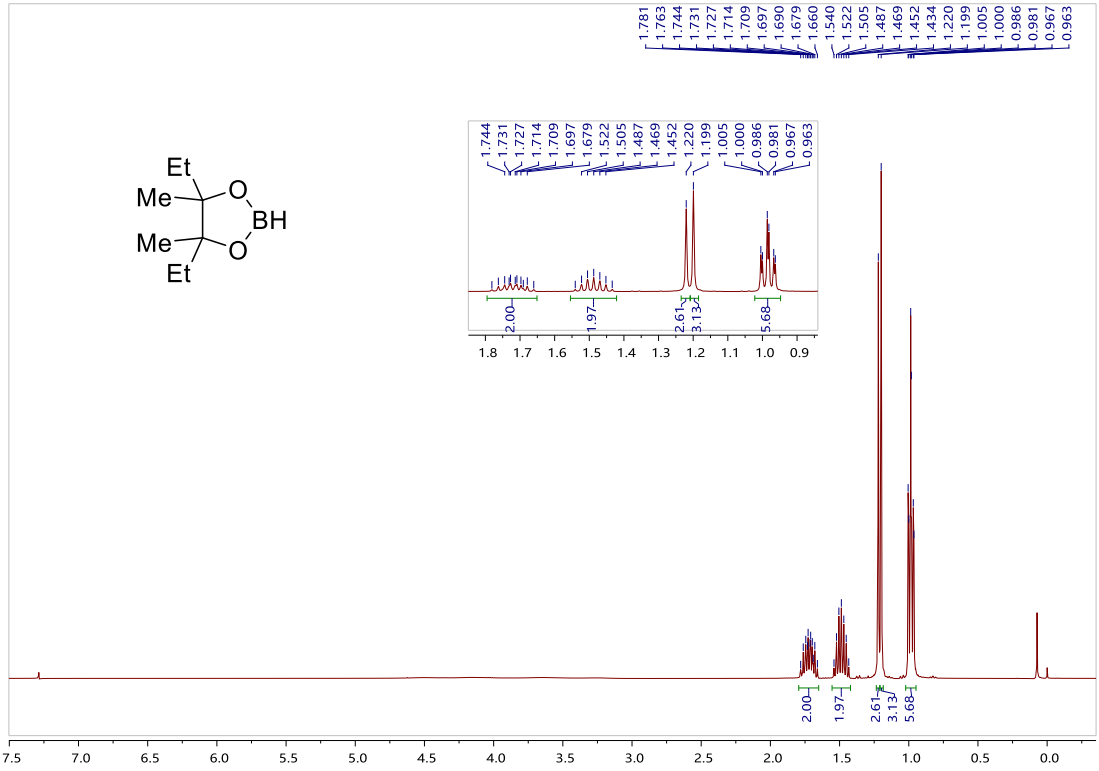


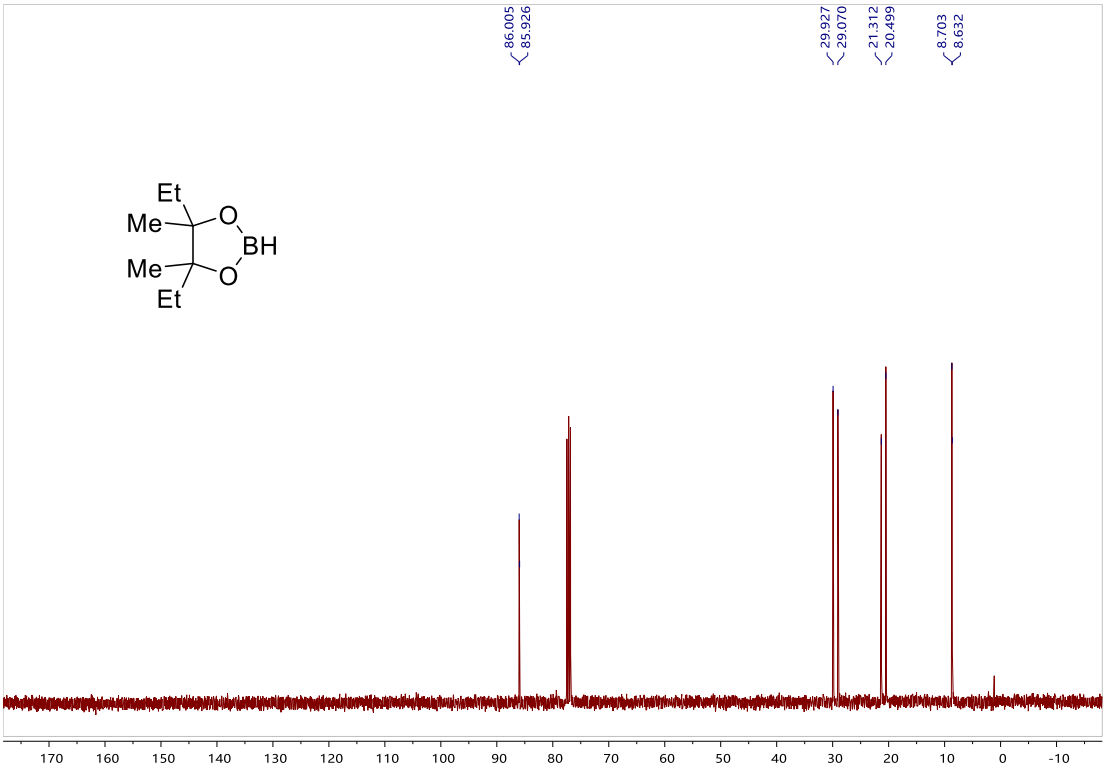
1-Phenylethan-1-*d*-1-ol (S3)

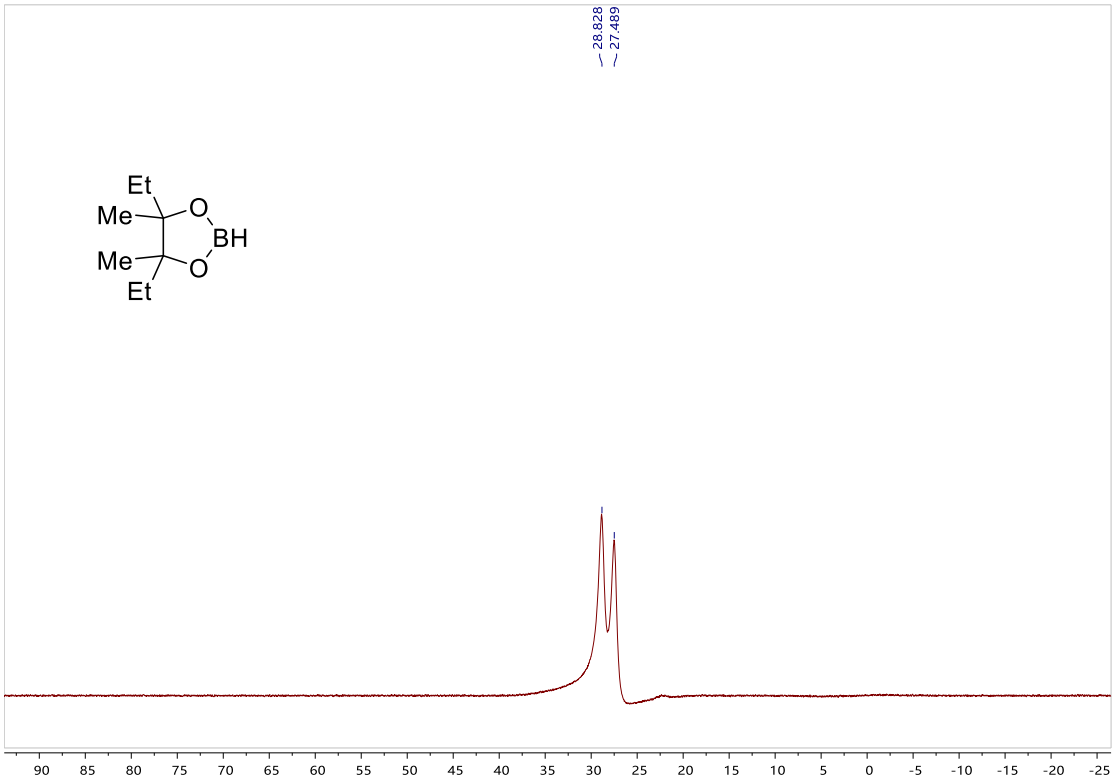




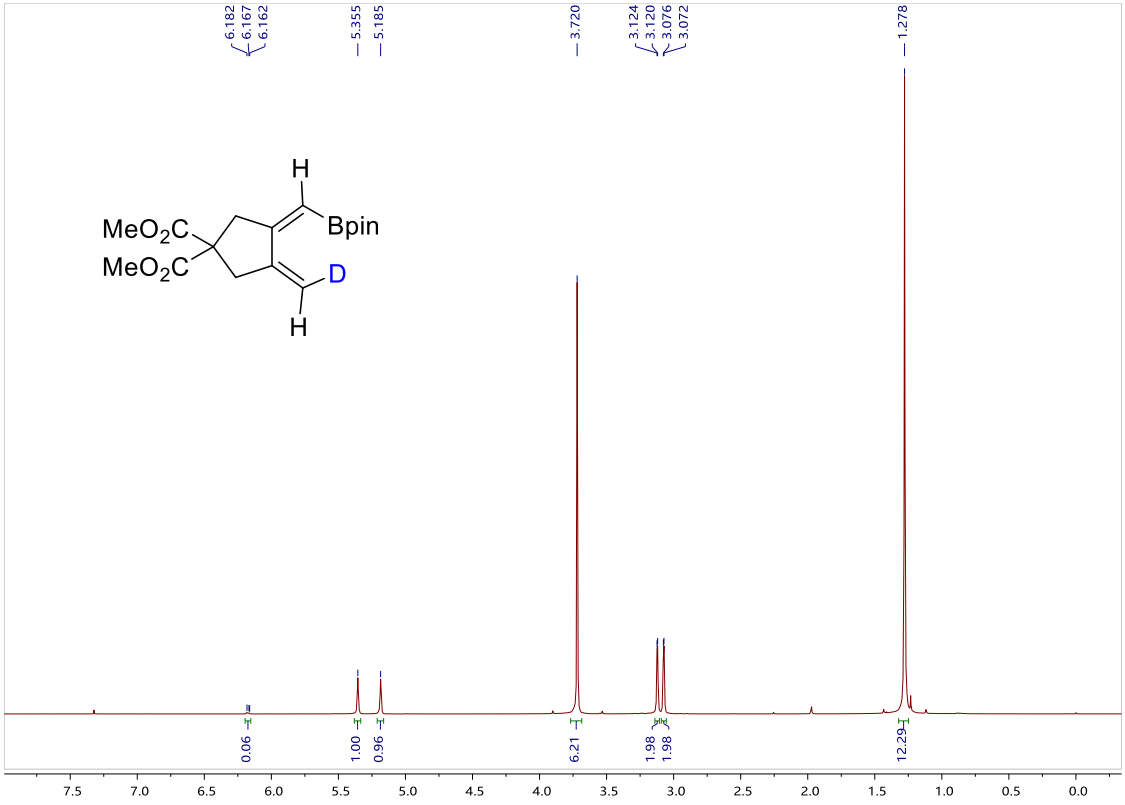
4,5-Diethyl-4,5-dimethyl-1,3,2-dioxaborolane (S5)

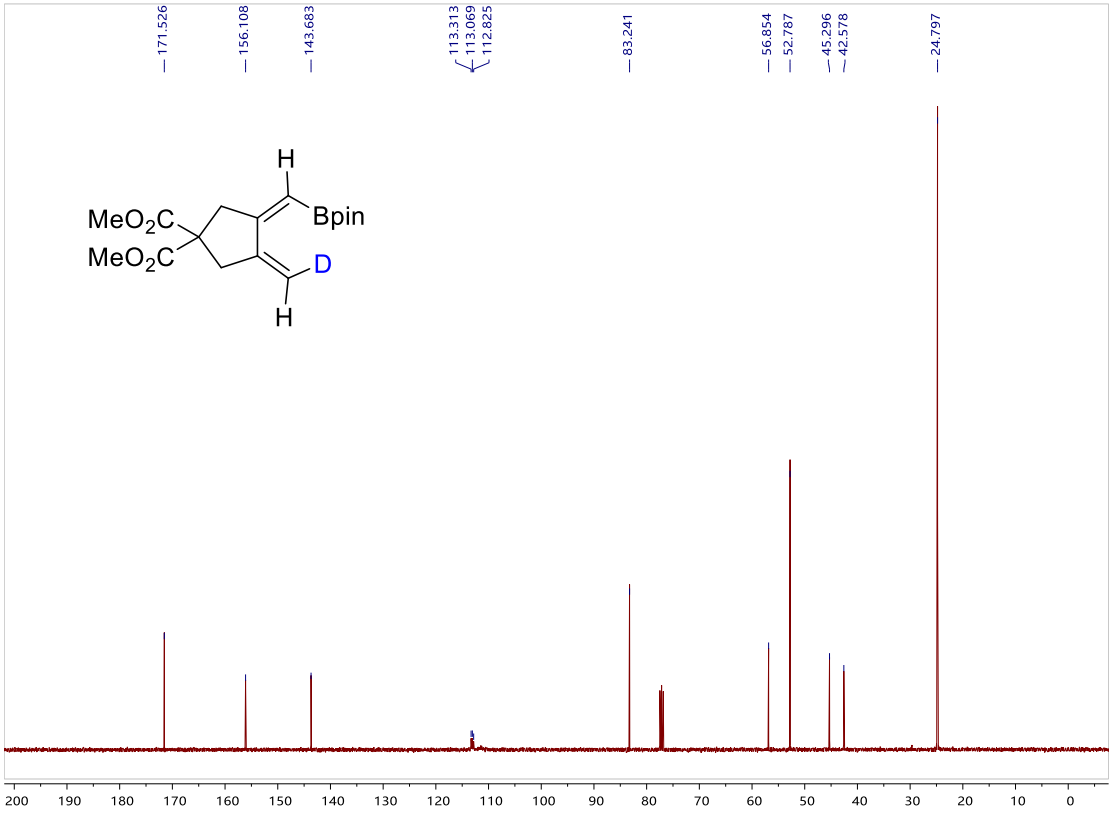


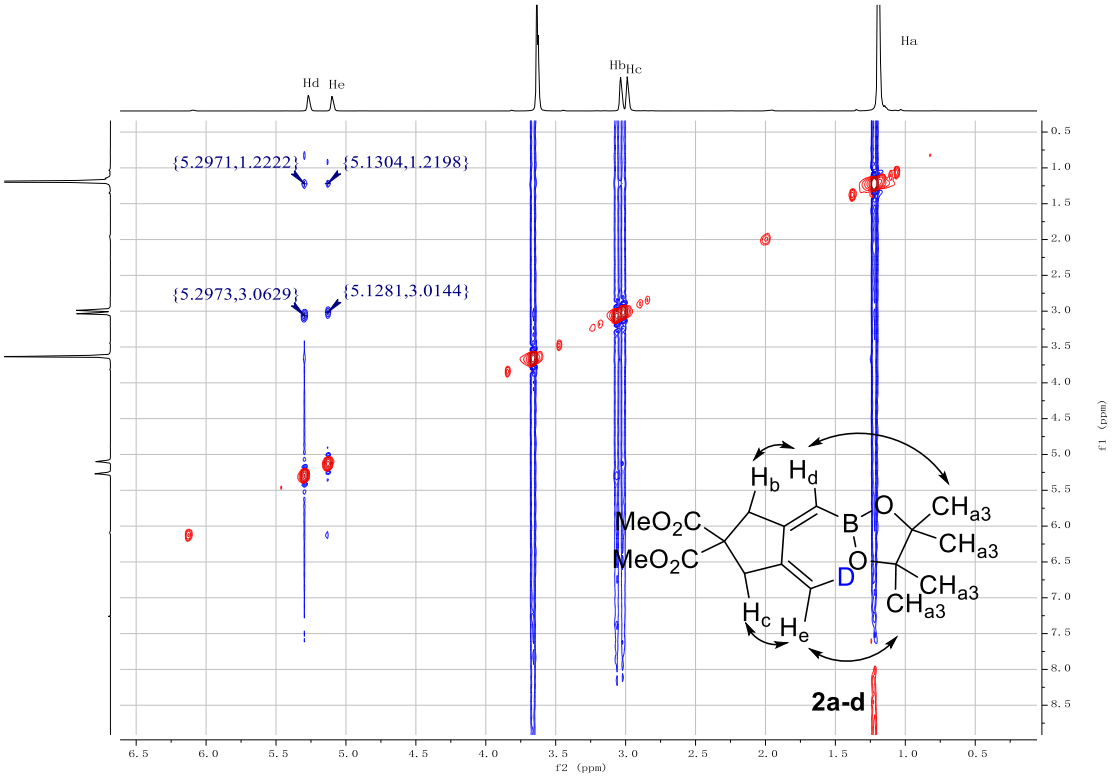



28.828
27.489
Et
Me
O
BH
Me
O
Et
90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0 -5 -10 -15 -20 -25

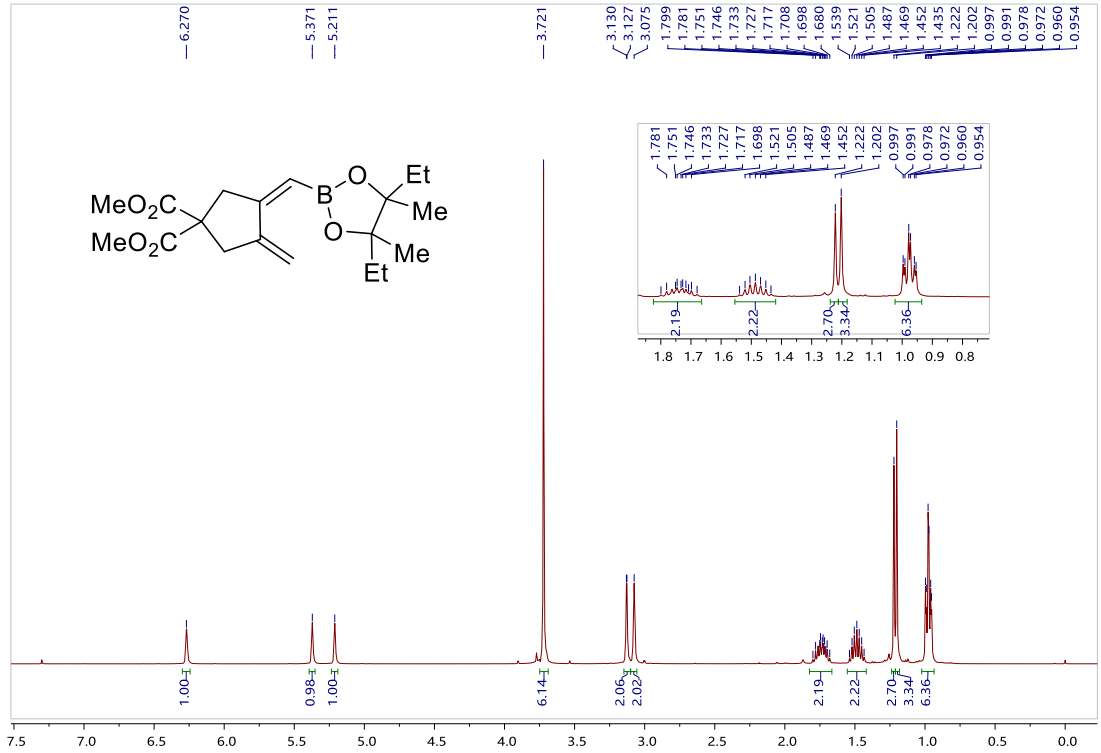
Dimethyl (3*Z*,4*Z*)-3-(methylene-d)-4-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methylene)cyclopentane-1,1-dicarboxylate (2a-*d*)

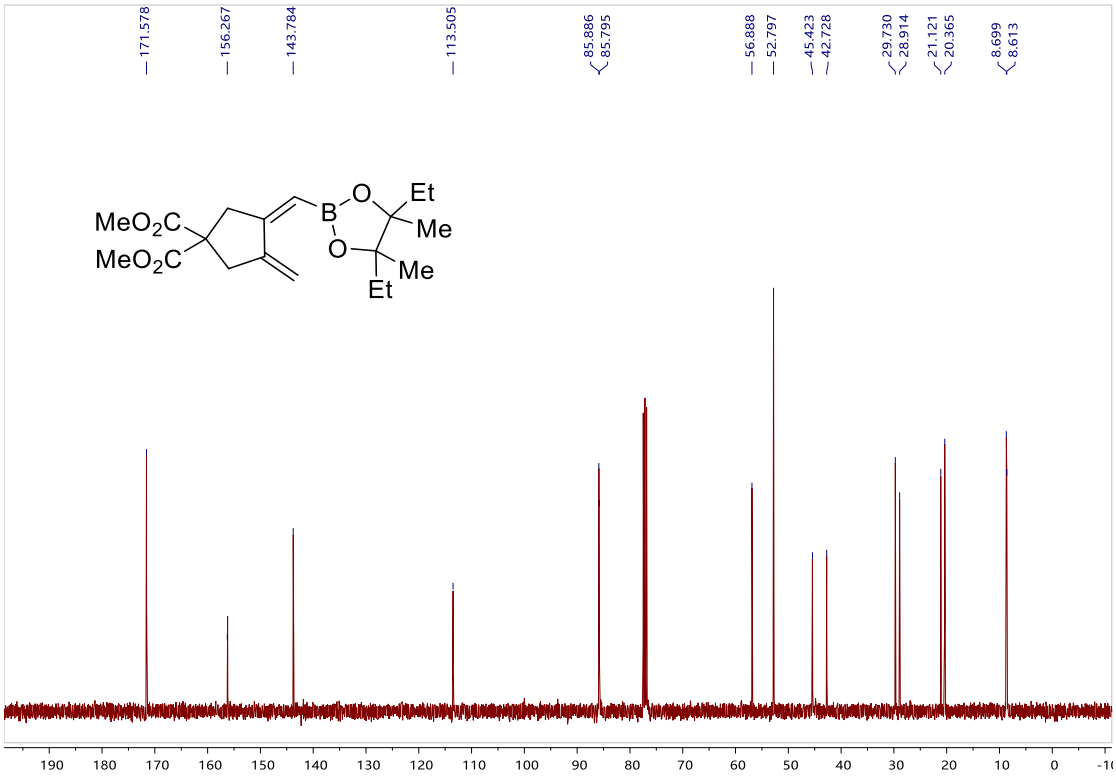





Hd
He
Hb
Hc
Ha
{5.2971,1.2222}
{5.1304,1.2198}
{5.2973,3.0629}
{5.1281,3.0144}
Hb
Hd
MeO2C
MeO2C
B
O
O
D
CHa3
CHa3
CHa3
CHa3
Hc
He
2a-d
f2 (ppm)
f1 (ppm)

Dimethyl
(*Z*)-3-((4,5-diethyl-4,5-dimethyl-1,3,2-dioxaborolan-2-yl)methylene)-4-methylene cyclopentane-1,1-dicarboxylate (2a-*Et*)





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