Supporting Information

Three-component cascade carbopalladation/Heck cyclization/borylation: facile access to boryl-functionalized indenes

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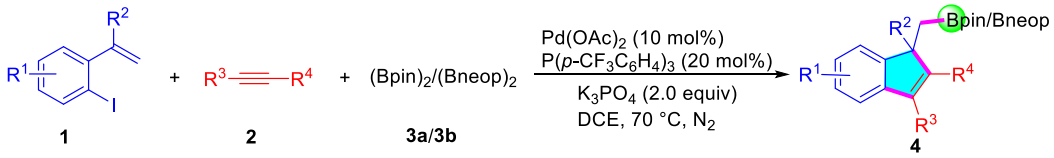
1. General Considerations

All reactions were carried out under N_2 atmosphere. Materials were obtained from commercial suppliers or prepared according to standard procedures unless otherwise noted. Solvents were purified and dried according to standard methods prior to use. For product purification by flash column chromatography, silica gel (200~300 mesh) and light petroleum ether (bp. 60~90) are used. ^{1}H NMR spectra were recorded on a Bruker advance III 400 MHz in $CDCl_3$ and $^{13}C\{^1H\}$ NMR spectra were recorded on 101 MHz in $CDCl_3$ using TMS as internal standard. Data for ^{1}H NMR are recorded as follows: chemical shift (δ, ppm), multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet or unresolved, br = broad singlet, dd = doublet of doublet, dt = triplet of doublets, ddd = doublet of doublet of doublets, coupling constant (s) in Hz, integration). Data for ^{13}C NMR is reported in terms of chemical shift (δ, ppm). IR spectra were recorded on a FT-IR spectrometer and only major peaks were reported in cm^{-1}. High-resolution mass spectral analysis (HRMS) data were measured on a Bruker Apex II.

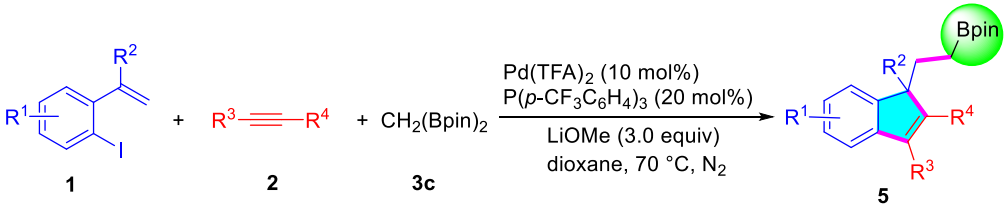
2. Preparation of Substrates

Substrates **1a-1l** were synthesized according to the known literature.[1-5] Substrates **2a-2n** were prepared from the coresponding ternal alkynes via Sonogashira coupling through the known literatures.[6-8] Substrates **3a-3c** were purchased commercially.

3. Experiment Procedure



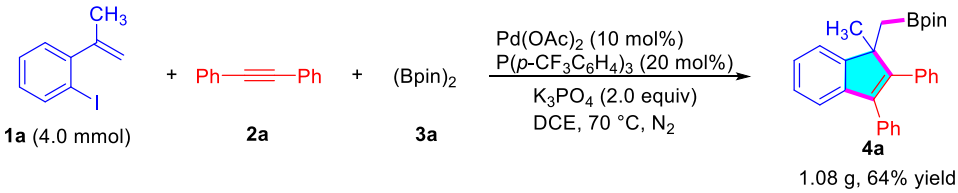
O-iodostyrenes **1** (0.2 mmol, 1.0 equiv), internal alkynes **2** (0.4 mmol, 2.0 equiv), boron reagent **3a** or **3b** (0.3 mmol, 1.5 equiv), $Pd(OAc)_2$ (10 mol%), P(*p*-$CF_3C_6H_4)_3$ (20 mol%), K_3PO_4 (0.4 mmol, 2.0 equiv) were added to a sealed tube, DCE (2.0 mL) were added via syringe. The mixture was flushed with N_2 and then heated at 70 ℃ in an oil bath about for 12 h until completion (monitored by TLC). After cooling at room temperature, the reaction mixture was filtered through celite. The solvent in the filtrate was evaporated under reduced pressure. The residue was purified through silica gel chromatography to afford the products **4**.



O-iodostyrenes **1** (0.2 mmol, 1.0 equiv), internal alkynes **2** (0.4 mmol, 2.0 equiv), *gem*-diborylmethane **3c** (0.4 mmol, 2.0 equiv), $Pd(TFA)_2$ (10 mol%), P(*p*-$CF_3C_6H_4)_3$ (20 mol%), LiOMe (0.6 mmol, 3.0 equiv) were added to a sealed tube, dioxane (0.5 mL) were added via syringe. The mixture was flushed with N_2 and then heated at 70 ℃ in an oil bath about for 12 h until completion (monitored by TLC). After cooling at room temperature, the reaction mixture was filtered through celite. The solvent in the filtrate was evaporated under reduced pressure. The

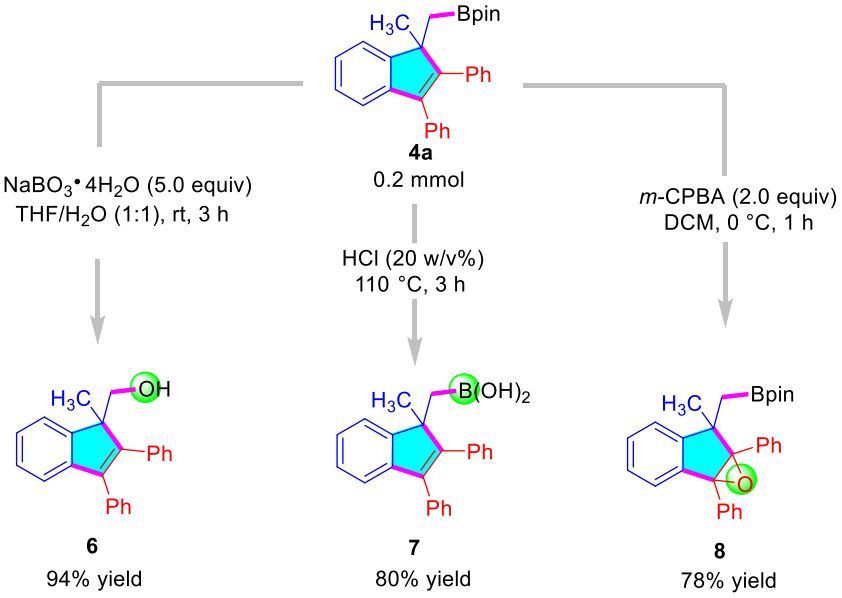
residue was purified through silica gel chromatography to afford the products **5**.

4. Gram-Scale Synthesis



O-iodostyrene **1a** (4.0 mmol, 0.98 g, 1.0 equiv), internal alkyne **2a** (8.0 mmol, 1.42 g, 2.0 equiv), boron reagent **3a** (6.0 mmol, 1.52 g, 1.5 equiv), $Pd(OAc)_2$ (10 mol%, 89.6 mg), $P(p\text{-}CF_3C_6H_4)_3$ (20 mol%, 373 mg), K_3PO_4 (8.0 mmol, 1.70 g, 2.0 equiv) were added to a sealed tube, DCE (40 mL) were added via syringe. The mixture was flushed with N_2 and then heated at 70 ℃ in an oil bath about for 12 h until completion (monitored by TLC). After cooling at room temperature, the reaction mixture was filtered through celite. The solvent in the filtrate was evaporated under reduced pressure. The residue was purified through silica gel chromatography (petroleum ether/ethyl acetate = 20:1~10:1, v/v) to afford the product **4a**.

5. Synthetic transformations of 4a



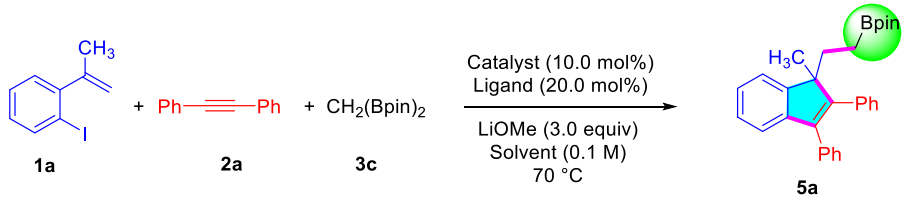
(1-methyl-2,3-diphenyl-1H-inden-1-yl)methanol (**6**) was synthesized according to the following procedure. A vial containing **4a** (1.0 equiv, 0.2 mmol, 84 mg) was charged with THF (1 mL) and H_2O (1 mL), then $NaBO_3$ $4H_2O$ (5.0 equiv, 1.0 mmol) was added in one portion. The reaction mixture was stirred at room temperature for 3 hours in open flask. The reaction was quenched with a saturated aqueous solution of NH_4Cl. The aqueous layer was extracted for three times with EtOAc and separated organic layer was washed with brine, dried over Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1~1:1, v/v) afforded **6** as a colorless solid (59 mg, 94% yield).

((1-methyl-2,3-diphenyl-1H-inden-1-yl)methyl)boronic acid (**7**) was synthesized according to

the following procedure. A mixture of **4a** (1.0 equiv, 0.2 mmol, 84 mg) in 4 mL 20% HCl (w/v) was stirred at 110 ℃ for 3 hours. After complete consumption of starting material **4a**, the crude material was extracted with diethylether twice, and the organic layer was washed with brine, dried over Na_2SO_4, filtered and concentrated. The residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 5:1~2:1, v/v) to afford **7** as a colorless solid (54 mg, 80% yield).

4,4,5,5-tetramethyl-2-((6-methyl-1a,6a-diphenyl-1a,6a-dihydro-6H-indeno[1,2-b]oxiren-6-yl)methyl)-1,3,2-dioxaborolane (**8**) was synthesized according to the following procedure. To a solution of **4a** (1.0 equiv, 0.2 mmol, 84 mg) in DCM (2.0 mL) was added *m*-CPBA (0.4 mmol, 69.0 mg, 2.0 equiv) at 0 ℃ under air. Then the reaction mixture was allowed to room temperature, and stirred for 1 h. The reaction mixture was filtered through Celite. The solvent in the filtrate was evaporated under reduced pressure, and the crude product was purified by flash chromatography (petroleum ether/ethyl acetate = 10:1, v/v) to afford the pure epoxide product **8** as a colorless solid (68 mg, 78% yield).

6. Optimization of the reaction conditions with $CH_2(Bpin)_2$[a]

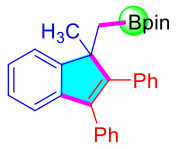


1a **2a** **3c** **5a**

Entry	Catalyst	Ligand	Solvent	Yield[b] (%)
1	$Pd(OAc)_2$	PPh_3	dioxane	21
2	$Pd_2(dba)_3$	PPh_3	dioxane	<10
3	$Pd(TFA)_2$	PPh_3	dioxane	39
4	$[Pd(C_3H_5)Cl]_2$	PPh_3	dioxane	32
5	$PdCl_2(PPh_3)_2$	PPh_3	dioxane	24
6	$Pd(OAc)_2$	PPh_3	MeCN	14
7	$Pd(TFA)_2$	PPh_3	DME	27
8	$Pd(TFA)_2$	PPh_3	DCE	36
9	$Pd(TFA)_2$	PPh_3	toluene	<10
10	$Pd(TFA)_2$	PCy_3	dioxane	0
11	$Pd(TFA)_2$	P(*p*-$MeOC_6H_5)_3$	dioxane	47
12	$Pd(TFA)_2$	P(2-furyl)$_3$	dioxane	49
13	$Pd(TFA)_2$	P(*p*-$CF_3OC_6H_5)_3$	dioxane	66
14	$Pd(TFA)_2$	P(*p*-$FC_6H_5)_3$	dioxane	50
15	$Pd(TFA)_2$	DPPB	dioxane	0
16	$Pd(TFA)_2$	DPEphos	dioxane	34
[c]17	$Pd(TFA)_2$	P(*p*-$CF_3OC_6H_5)_3$	dioxane	72
[d]18	$Pd(TFA)_2$	P(*p*-$CF_3OC_6H_5)_3$	dioxane	78

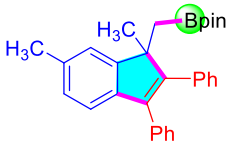
[a]Reaction conditions: **1a** (0.2 mmol), **2a** (0.4 mmol), **3c** (0.4 mmol), catalyst (10 mol %), ligand (20 mol %), LiOMe (0.6 mmol), solvent (2.0 mL, 0.1 M), 70 ℃, 12 h under N_2 conditions. [b]Isolated yields. [c]solvent (1.0 mL, 0.2 M), [d]solvent (0.5 mL, 0.4 M).

7. Spectra Data



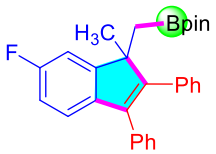
4a

4,4,5,5-tetramethyl-2-((1-methyl-2,3-diphenyl-1H-inden-1-yl)methyl)-1,3,2-dioxaborolane ***(4a)***: Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 20:1~10:1, v/v) affords the title compound as a colorless solid, Mp = 92-94 ℃, 61 mg, 72% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46-7.41 (m, 1H), 7.25-7.06 (m, 13H), 1.33 (d, *J* = 20.9 Hz, 5H), 0.86 (s, 12H). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 153.1, 152.7, 143.5, 138.1, 137.1, 135.6, 130.4, 129.6, 128.0, 127.9, 126.8, 126.7, 126.5, 125.2, 122.3, 120.3, 82.7, 52.8, 26.2, 24.7. IR(neat) 3430, 2976, 1507, 1377, 1239, 803, 531. HRMS (ESI-TOF) calcd for $C_{29}H_{32}BO_2$ $[M+H]^+$: 423.2490, found: 423.2492.



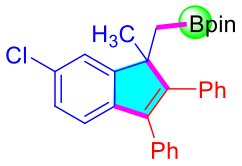
4b

2-((1,6-dimethyl-2,3-diphenyl-1H-inden-1-yl)methyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane ***(4b)***: Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 20:1~10:1, v/v) affords the title compound as a brown viscous oil, 56 mg, 64% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 (s, 1H), 7.23-7.09 (m, 11H), 6.96 (dd, *J* = 7.9, 1.6 Hz, 1H), 2.34 (s, 3H), 1.36 (s, 3H), 1.27-1.20 (m, 2H), 0.90 (d, *J* = 3.2 Hz, 12H). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 152.9, 152.3, 140.9, 137.2, 135.9, 134.8, 130.5, 129.6, 128.0, 127.9, 127.1, 126.68, 126.66, 123.3, 120.1, 82.7, 52.6, 26.1, 24.8, 24.7, 21.7. IR(neat) 3437, 2980, 1617, 1351, 1329, 1140, 969, 819, 698. HRMS (ESI-TOF) calcd for $C_{30}H_{34}BO_2$ $[M+H]^+$: 437.2646, found: 437.2646.



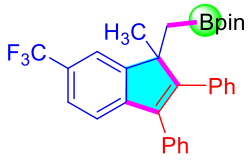
4c

2-((6-fluoro-1-methyl-2,3-diphenyl-1H-inden-1-yl)methyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolan e ***(4c)***: Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 20:1~10:1, v/v) affords the title compound as a colorless solid, Mp = 100-102 ℃, 61 mg, 69% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27-7.04 (m, 12H), 6.84 (ddd, *J* = 9.3, 8.3, 2.4 Hz, 1H), 1.37-1.25 (m, 5H), 0.93 (d, *J* = 2.1 Hz, 12H). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 161.9 (d, *J* = 244.1 Hz), 155.0 (d, *J* = 7.6 Hz), 152.9 (d, *J* = 4.3 Hz), 139.3 (d, *J* = 2.2 Hz), 137.2, 136.8, 135.4, 130.4, 129.5, 128.1, 128.0, 126.9 (d, *J* = 1.2 Hz), 121.0 (d, *J* = 8.6 Hz), 113.1 (d, *J* = 22.5 Hz), 110.2 (d, *J* = 23.1 Hz), 82.9, 52.9 (d, *J* = 2.1 Hz), 26.0, 24.8. ^{19}F NMR (376 MHz, $CDCl_3$) δ -117.76. IR(neat) 3442, 2974, 1596, 1476, 1333, 1139, 815, 702. HRMS (ESI-TOF) calcd for $C_{29}H_{31}FBO_2$ $[M+H]^+$: 441.2396, found: 441.2399.



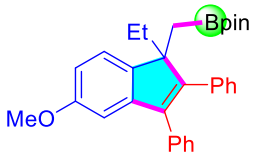
4d

2-((6-chloro-1-methyl-2,3-diphenyl-1H-inden-1-yl)methyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane ***(4d)***: Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 20:1~10:1, v/v) affords the title compound as a brown viscous oil, 53 mg, 58% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (t, *J* = 1.2 Hz, 1H), 7.19-7.09 (m, 12H), 1.38-1.23 (m, 5H), 0.94 (d, *J* = 2.7 Hz, 12H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 154.6, 153.7, 142.0, 137.3, 136.5, 135.1, 131.1, 130.3, 129.5, 128.2, 128.0, 127.0, 126.6, 123.0, 121.2, 82.9, 52.9, 25.7, 24.83, 24.76. IR(neat) 3439, 2971, 1651, 1398, 1127, 708, 620. HRMS (ESI-TOF) calcd for $C_{29}H_{31}ClBO_2$ $[M+H]^+$: 457.2100, found: 457.2102.



4e

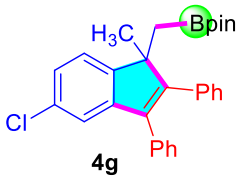
2-((6-((difluoro-l3-methyl)-l2-fluoranyl)-1-methyl-2,3-diphenyl-1H-inden-1-yl)methyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane ***(4e)***: Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 20:1~5:1, v/v) affords the title compound as a yellow oil, 65 mg, 66% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, *J* = 1.7 Hz, 1H), 7.41 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.28 (d, *J* = 8.0 Hz, 1H), 7.15 (tt, *J* = 8.3, 4.5 Hz, 10H), 1.39 (s, 3H), 1.23-1.17 (m, 2H), 0.91 (d, *J* = 2.7 Hz, 12H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 156.4, 153.2, 147.0 (d, *J* = 1.6 Hz), 137.4, 136.3, 135.3 (t, *J* = 6.4 Hz), 134.8, 130.1, 129.4, 128.2, 128.1, 127.3, 127.2 (d, *J* = 4.7 Hz), 127.0, 123.9 (dd, *J* = 7.8, 3.8 Hz), 120.3, 119.5 (dd, *J* = 7.6, 3.8 Hz), 83.0, 53.1, 25.4, 24.75, 24.74. ^{19}F NMR (376 MHz, $CDCl_3$) δ -61.22. IR(neat) 3422, 2978, 1798, 1613, 1533, 1330, 1105, 1063, 699. HRMS (ESI-TOF) calcd for $C_{30}H_{31}F_3BO_2$ $[M+H]^+$: 491.2364, found: 491.2360.



4f

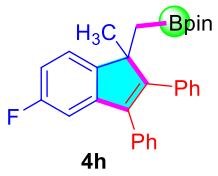
2-((1-ethyl-5-methoxy-2,3-diphenyl-1H-inden-1-yl)methyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane ***(4f)***: Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 20:1~5:1, v/v) affords the title compound as a colorless solid, Mp = 93-95 ℃, 69 mg, 74% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28-7.07 (m, 11H), 6.80-6.67 (m, 2H), 3.71 (s, 3H), 1.84 (ddp, *J* = 21.0, 14.2, 7.3 Hz, 2H), 1.32 (q, *J* = 14.7 Hz, 2H), 0.88 (s, 12H), 0.49 (t, *J* = 7.3 Hz, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 159.0, 151.6, 146.1, 143.0, 140.1, 137.2, 135.8, 130.1, 129.7, 128.1, 127.9, 126.8, 126.7, 122.8, 110.6, 106.1, 82.7, 56.6, 55.7, 32.2, 24.8, 8.8. IR(neat) 3421, 2974, 1604, 1479,

1358, 1324, 1141, 847, 702. HRMS (ESI-TOF) calcd for $C_{31}H_{36}BO_3$ $[M+H]^+$: 467.2752, found: 467.2752.



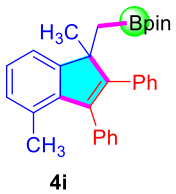
4g

2-((5-chloro-1-methyl-2,3-diphenyl-1H-inden-1-yl)methyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane ***(4g)***: Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 20:1~10:1, v/v) affords the title compound as a yellow viscous oil, 50 mg, 55% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (d, *J* = 7.9 Hz, 1H), 7.28-7.02 (m, 12H), 1.39-1.27 (m, 5H), 0.90 (d, *J* = 2.3 Hz, 12H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 154.8, 151.0, 145.4, 136.5, 134.9, 132.4, 130.2, 129.5, 128.2, 128.0, 127.1, 127.0, 125.0, 123.4, 120.5, 82.9, 52.6, 26.1, 24.8, 24.7. IR(neat) 3435, 2911, 1769, 1533, 1469, 1377, 1303, 1131, 896, 717. HRMS (ESI-TOF) calcd for $C_{29}H_{31}BClO_2$ $[M+H]^+$: 457.2100, found: 457.2104.



4h

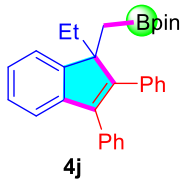
2-((5-fluoro-1-methyl-2,3-diphenyl-1H-inden-1-yl)methyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane ***(4h)***: Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 20:1~10:1, v/v) affords the title compound as a yellow solid, Mp = 110-112 ℃, 54 mg, 61% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (dd, *J* = 8.2, 5.1 Hz, 1H), 7.22-7.07 (m, 10H), 6.91 (dd, *J* = 9.5, 2.5 Hz, 1H), 6.87-6.81 (m, 1H), 1.31 (d, *J* = 17.1 Hz, 5H), 0.89 (d, *J* = 2.3 Hz, 12H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 162.6 (d, *J* = 242.4 Hz), 155.1, 148.0 (d, *J* = 2.4 Hz), 145.5 (d, *J* = 8.6 Hz), 137.5 (d, *J* = 3.0 Hz), 136.7, 135.1, 130.2, 129.4, 128.2, 128.0, 127.01, 126.98, 123.1 (d, *J* = 9.0 Hz), 111.6 (d, *J* = 22.8 Hz), 107.5 (d, *J* = 23.5 Hz), 82.8, 52.4, 26.3, 24.8, 24.7. ^{19}F NMR (376 MHz, $CDCl_3$) δ -117.01. IR(neat) 3435, 2976, 1612, 1469, 1329, 1138, 887, 732. HRMS (ESI-TOF) calcd for $C_{29}H_{31}FBO_2$ $[M+H]^+$: 441.2396, found: 441.2397.



4i

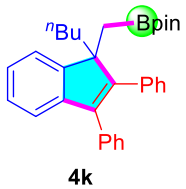
2-((1,4-dimethyl-2,3-diphenyl-1H-inden-1-yl)methyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane ***(4i)***: Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 20:1~10:1, v/v) affords the title compound as a yellow solid, Mp = 118-120 ℃, 52 mg, 60% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 (d, *J* = 7.4 Hz, 1H), 7.19-7.02 (m, 11H), 6.86 (d, *J* = 7.5 Hz, 1H), 1.78 (s, 3H), 1.34 (s, 3H), 1.28-1.18 (m, 2H), 0.92 (d, *J* = 9.2 Hz, 12H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ

154.0, 152.9, 139.7, 138.5, 136.9, 131.4, 130.3, 129.94, 129.90, 129.5, 127.60, 127.57, 127.56, 126.51, 126.47, 125.1, 120.0, 82.7, 52.0, 26.2, 24.8, 24.7, 20.2. IR(neat) 3441, 2968, 1599, 1436, 1352, 1324, 1147, 966, 845, 697. HRMS (ESI-TOF) calcd for $C_{30}H_{34}BO_2$ $[M+H]^+$: 437.2646, found: 437.2648.



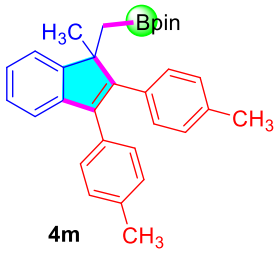
4j

2-((1-ethyl-2,3-diphenyl-1H-inden-1-yl)methyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane ***(4j)***: Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 20:1~10:1, v/v) affords the title compound as a pale yellow solid, Mp = 63-65 ℃, 66 mg, 76% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36-7.32 (m, 1H), 7.22-7.10 (m, 13H), 1.95-1.80 (m, 2H), 1.39-1.30 (m, 2H), 0.85 (s, 12H), 0.48 (t, *J* = 7.3 Hz, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 150.7, 150.2, 144.7, 140.3, 137.2, 135.9, 130.2, 129.7, 128.1, 127.9, 126.73, 126.70, 126.4, 125.2, 122.3, 120.1, 82.6, 57.2, 32.1, 24.7, 8.8. IR(neat) 3349, 2974, 1569, 1478, 1401, 1322, 1199, 1105, 942, 803. HRMS (ESI-TOF) calcd for $C_{30}H_{34}BO_2$ $[M+H]^+$: 437.2646, found: 437.2642.



4k

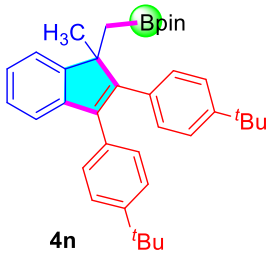
2-((1-butyl-2,3-diphenyl-1H-inden-1-yl)methyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane ***(4k)***: Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 20:1~10:1, v/v) affords the title compound as a yellow viscous oil, 73 mg, 79% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37-7.32 (m, 1H), 7.17 (dddd, *J* = 20.1, 14.0, 7.7, 3.8 Hz, 13H), 1.97-1.70 (m, 2H), 1.40-1.29 (m, 2H), 1.24 (s, 2H), 1.06 (td, *J* = 7.8, 3.5 Hz, 2H), 0.84 (s, 12H), 0.67 (t, *J* = 7.1 Hz, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 151.1, 150.6, 137.2, 135.9, 130.2, 129.7, 128.0, 127.9, 126.72, 126.69, 126.3, 125.1, 122.3, 120.1, 82.6, 56.7, 39.3, 26.2, 24.70, 24.69, 23.1, 14.1. IR(neat) 3430, 2977, 1608, 1544, 1408, 1322, 1274, 1132, 973, 866. HRMS (ESI-TOF) calcd for $C_{32}H_{38}BO_2$ $[M+H]^+$: 465.2959, found: 465.2960.



4m

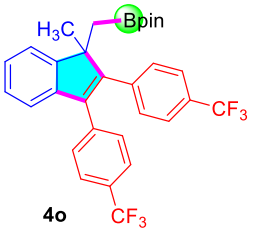
4,4,5,5-tetramethyl-2-((1-methyl-2,3-di-p-tolyl-1H-inden-1-yl)methyl)-1,3,2-dioxaborolane ***(4m)***: Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 20:1~10:1, v/v) affords the title compound as a colorless solid, Mp = 122-124 ℃, 67 mg, 74% yield. ^{1}H NMR

(400 MHz, $CDCl_3$) δ 7.46-7.41 (m, 1H), 7.24-7.19 (m, 1H), 7.17-6.88 (m, 10H), 2.23 (d, *J* = 4.2 Hz, 6H), 1.38-1.23 (m, 5H), 0.87 (s, 12H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 152.8, 152.7, 136.2, 134.1, 132.8, 130.2, 129.5, 128.8, 128.7, 126.4, 125.1, 122.3, 120.3, 82.7, 52.7, 26.2, 24.7, 21.42, 21.40. IR(neat) 3429, 2973, 1623, 1587, 1501, 1451, 1329, 1140, 950, 837. HRMS (ESI-TOF) calcd for $C_{31}H_{36}BO_2$ $[M+H]^+$: 451.2803, found: 451.2809.



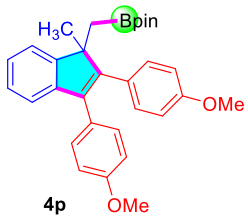
4n

*2-((2,3-bis(4-(tert-butyl)phenyl)-1-methyl-1H-inden-1-yl)methyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**4n**)*: Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 20:1~10:1, v/v) affords the title compound as a brown solid, Mp = 86-88 ℃, 76 mg, 71% yield. ^1H NMR (400 MHz, $CDCl_3$) δ 7.43 (dd, *J* = 5.8, 2.8 Hz, 1H), 7.24 (dd, *J* = 5.7, 2.9 Hz, 1H), 7.16 (dq, *J* = 13.8, 8.3 Hz, 10H), 1.34 (s, 3H), 1.22 (d, *J* = 4.6 Hz, 20H), 0.89 (s, 12H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 152.9, 152.8, 149.2, 143.8, 134.0, 132.7, 130.0, 129.2, 126.4, 125.0, 124.8, 124.7, 122.3, 120.4, 82.7, 52.8, 34.59, 34.55, 31.50, 31.48, 26.2, 24.79, 24.76. IR(neat) 3562, 2970, 1633, 1539, 1488, 1407, 1359, 1166, 910, 882. HRMS (ESI-TOF) calcd for $C_{37}H_{48}BO_2$ $[M+H]^+$: 535.3742, found: 535.3742.



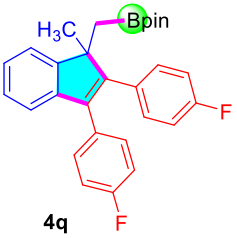
4o

*4,4,5,5-tetramethyl-2-((1-methyl-2,3-bis(4-(trifluoromethyl)phenyl)-1H-inden-1-yl)methyl)-1,3,2-dioxaborolane (**4o**)*: Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 20:1~5:1, v/v) affords the title compound as a brown solid, Mp = 133-135 ℃, 55 mg, 49% yield. ^1H NMR (400 MHz, $CDCl_3$) δ 7.51-7.42 (m, 5H), 7.32 (dd, *J* = 10.4, 8.1 Hz, 4H), 7.24-7.17 (m, 3H), 1.44-1.34 (m, 4H), 1.27 (d, *J* = 14.8 Hz, 1H), 0.85 (d, *J* = 2.8 Hz, 12H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 152.6, 152.4, 142.5, 140.5, 139.0, 138.0, 130.6, 129.8, 129.4 (d, *J* = 10.4 Hz), 129.0 (d, *J* = 10.4 Hz), 126.9, 126.1, 125.7 (d, *J* = 7.0 Hz), 125.3 (dd, *J* = 7.4, 3.6 Hz), 125.1 (dd, *J* = 7.5, 3.7 Hz), 123.0 (d, *J* = 7.0 Hz), 122.5, 120.3, 82.9, 53.3, 26.3, 24.73, 24.68. ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.45 (d, *J* = 2.6 Hz). IR(neat) 3547, 2988, 1607, 1533, 1473, 1321, 1109, 899, 766. HRMS (ESI-TOF) calcd for $C_{31}H_{30}F_6BO_2$ $[M+H]^+$: 559.2238, found: 559.2231.



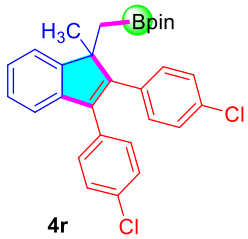
4p

*2-((2,3-bis(4-methoxyphenyl)-1-methyl-1H-inden-1-yl)methyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**4p**)*: Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 20:1~5:1, v/v) affords the title compound as a yellow solid, Mp = 119-121 ℃, 76 mg, 79% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (dd, *J* = 5.8, 2.8 Hz, 1H), 7.22 (dd, *J* = 5.7, 3.0 Hz, 1H), 7.17-7.01 (m, 6H), 6.78-6.69 (m, 4H), 3.71 (d, *J* = 3.5 Hz, 6H), 1.34 (s, 4H), 1.25 (d, *J* = 7.4 Hz, 1H), 0.87 (d, *J* = 3.1 Hz, 12H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 158.3, 158.2, 152.7, 152.2, 143.7, 137.4, 131.5, 130.7, 129.5, 128.2, 126.4, 125.1, 122.3, 120.2, 113.5, 113.4, 82.7, 55.2, 52.7, 26.3, 24.74, 24.73. IR(neat) 3441, 2962, 1594, 1501, 1351, 1241, 1143, 1032, 839. HRMS (ESI-TOF) calcd for $C_{31}H_{36}BO_4$ $[M+H]^+$: 483.2701, found: 483.2701.



4q

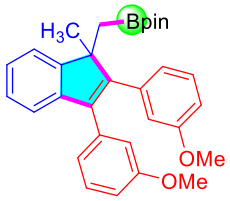
*2-((2,3-bis(4-fluorophenyl)-1-methyl-1H-inden-1-yl)methyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**4q**)*: Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 20:1~10:1, v/v) affords the title compound as a red solid, Mp = 139-141 ℃, 53 mg, 58% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46-7.41 (m, 1H), 7.16 (qd, *J* = 5.4, 2.1 Hz, 7H), 6.89 (td, *J* = 8.7, 5.7 Hz, 4H), 1.40-1.23 (m, 5H), 0.86 (d, *J* = 3.2 Hz, 12H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 163.2 (d, *J* = 22.6 Hz), 160.7 (d, *J* = 22.7 Hz), 152.5, 152.2, 143.1, 137.7, 132.7 (d, *J* = 3.3 Hz), 132.0 (d, *J* = 8.1 Hz), 131.4 (d, *J* = 3.3 Hz), 131.1 (d, *J* = 7.9 Hz), 126.7, 125.5, 122.4, 120.2, 115.2 (d, *J* = 21.3 Hz), 115.1 (d, *J* = 21.1 Hz), 82.8, 52.8, 26.2, 24.73, 24.70. ^{19}F NMR (376 MHz, $CDCl_3$) δ -115.27, -115.64. IR(neat) 3440, 2988, 1599, 1508, 1354, 1222, 838, 729. HRMS (ESI-TOF) calcd for $C_{29}H_{30}F_2O_2B$ $[M+H]^+$: 459.2301, found: 459.2302.



4r

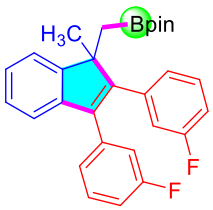
*2-((2,3-bis(4-chlorophenyl)-1-methyl-1H-inden-1-yl)methyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**4r**)*: Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 20:1~10:1, v/v) affords the title compound as a brown solid, Mp = 173-175 ℃, 55 mg, 56% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45-7.40 (m, 1H), 7.21-7.11 (m, 11H), 1.40-1.31 (m, 4H), 1.25 (d, *J* =

14.8 Hz, 1H), 0.84 (d, *J* = 3.5 Hz, 12H). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 152.5, 152.2, 142.8, 137.6, 135.2, 133.8, 133.0, 132.8, 131.7, 130.8, 128.5, 128.4, 126.7, 125.7, 122.4, 120.2, 82.8, 52.9, 26.2, 24.72, 24.68. IR(neat) 3434, 2968, 1566, 1478, 1353, 1327, 1146, 1086, 1015, 830. HRMS (ESI-TOF) calcd for $C_{29}H_{30}BCl_2O_2$ $[M+H]^+$: 491.1710, found: 491.1713.



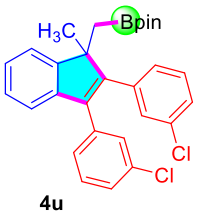
4s

*2-((2,3-bis(3-methoxyphenyl)-1-methyl-1H-inden-1-yl)methyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**4s**)*: Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 20:1~5:1, v/v) affords the title compound as a brown viscous oil, 67 mg, 70% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45-7.40 (m, 1H), 7.28-7.24 (m, 1H), 7.19-7.14 (m, 2H), 7.10 (td, *J* = 7.9, 2.6 Hz, 2H), 6.87-6.82 (m, 2H), 6.81-6.75 (m, 2H), 6.69 (ddd, *J* = 10.7, 8.1, 2.6 Hz, 2H), 3.63 (s, 3H), 3.58 (s, 3H), 1.34 (d, *J* = 15.1 Hz, 5H), 0.86 (d, *J* = 5.7 Hz, 12H). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 159.2, 159.1, 152.9, 152.6, 143.2, 138.5, 137.9, 137.0, 129.0, 128.8, 126.5, 125.3, 122.8, 122.3, 122.0, 120.4, 115.8, 114.6, 112.9, 112.6, 82.7, 55.2, 55.1, 52.9, 26.3, 24.75, 24.72. IR(neat) 3449, 2997, 1600, 1501, 1477, 1149, 1033, 901, 792. HRMS (ESI-TOF) calcd for $C_{31}H_{36}BO_4$ $[M+H]^+$: 483.2701, found: 483.2701.



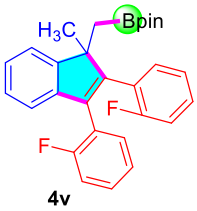
4t

*2-((2,3-bis(3-fluorophenyl)-1-methyl-1H-inden-1-yl)methyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**4t**)*: Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 20:1~10:1, v/v) affords the title compound as a red solid, Mp = 82-84 ℃, 60 mg, 66% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45-7.41 (m, 1H), 7.21-7.13 (m, 5H), 6.99-6.81 (m, 6H), 1.39 (d, *J* = 14.7 Hz, 1H), 1.35 (s, 3H), 1.27 (d, *J* = 14.8 Hz, 1H), 0.86 (d, *J* = 2.5 Hz, 12H). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 163.9 (d, *J* = 14.2 Hz), 161.4 (d, *J* = 14.3 Hz), 152.4, 152.3 (d, *J* = 2.0 Hz), 142.7, 139.0 (d, *J* = 8.0 Hz), 137.7 (d, *J* = 2.1 Hz), 137.6 (d, *J* = 8.0 Hz), 129.6 (d, *J* = 17.4 Hz), 129.5 (d, *J* = 17.5 Hz), 126.8, 126.1 (d, *J* = 2.9 Hz), 125.8, 125.2 (d, *J* = 2.9 Hz), 122.4, 120.3, 117.2 (d, *J* = 21.3 Hz), 116.3 (d, *J* = 21.6 Hz), 114.1 (d, *J* = 3.0 Hz), 113.9 (d, *J* = 3.0 Hz), 82.82, 52.98, 26.28, 24.71, 24.67. ^{19}F NMR (376 MHz, $CDCl_3$) δ -113.62 (d, *J* = 6.2 Hz). IR(neat) 3439, 2988, 1504, 1477, 1306, 1256, 1103, 973, 829, 664. HRMS (ESI-TOF) calcd for $C_{29}H_{30}F_2BO_2$ $[M+H]^+$: 459.2301, found: 459.2306.



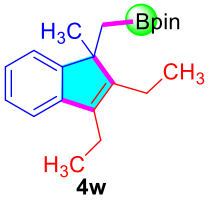
4u

*2-((2,3-bis(3-chlorophenyl)-1-methyl-1H-inden-1-yl)methyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**4u**)*: Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 20:1~10:1, v/v) affords the title compound as a brown solid, Mp = 114-116 ℃, 70 mg, 71% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44-7.39 (m, 1H), 7.23 (d, *J* = 2.0 Hz, 2H), 7.21-7.09 (m, 7H), 7.05 (tt, *J* = 6.4, 1.9 Hz, 2H), 1.42-1.23 (m, 5H), 0.86 (d, *J* = 1.9 Hz, 12H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 152.4, 152.2, 142.7, 138.5, 137.2, 134.0, 133.8, 130.1, 129.6, 129.4, 129.3, 128.7, 127.8, 127.3, 127.2, 126.8, 125.8, 122.4, 120.3, 82.8, 53.0, 26.2, 24.7, 24.6. IR(neat) 3398, 2960, 1539, 1464, 1355, 1231, 1148, 864, 539. HRMS (ESI-TOF) calcd for $C_{29}H_{30}BCl_2O_2$ $[M+H]^+$: 491.1710, found: 491.1712.



4v

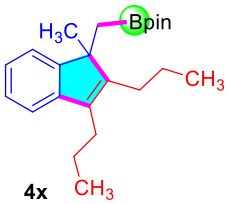
*2-((2,3-bis(2-fluorophenyl)-1-methyl-1H-inden-1-yl)methyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**4v**)*: Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 20:1~10:1, v/v) affords the title compound as a colorless solid, Mp = 105-107 ℃, 47 mg, 51% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52-7.45 (m, 1H), 7.35 (t, *J* = 7.4 Hz, 1H), 7.18-7.09 (m, 5H), 7.05-6.84 (m, 5H), 1.36 (d, *J* = 1.9 Hz, 3H), 1.32-1.11 (m, 2H), 0.92 (d, *J* = 7.3 Hz, 12H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 160.3 (d, *J* = 249.4 Hz), 152.6, 142.8, 135.5, 132.5, 131.6 (d, *J* = 4.0 Hz), 129.2, 129.1, 126.6, 125.5, 124.0, 123.8, 123.7 (d, *J* = 3.6 Hz), 123.6, 122.3, 120.6 (d, *J* = 2.1 Hz), 115.7, 115.5, 82.9, 53.7, 25.6, 24.74, 24.68. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -111.52. IR(neat) 3441, 2983, 1603, 1481, 1353, 1331, 1149, 759. HRMS (ESI-TOF) calcd for $C_{29}H_{30}F_2BO_2$ $[M+H]^+$: 459.2301, found: 459.2303.



4w

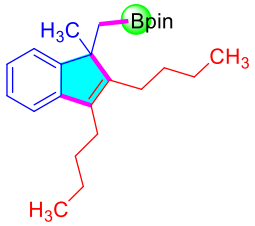
*2-((2,3-diethyl-1-methyl-1H-inden-1-yl)methyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**4w**)*: Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 20:1~10:1, v/v) affords the title compound as a brown viscous oil, 44 mg, 67% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (d, *J* = 7.3 Hz, 1H), 7.10 (d, *J* = 4.2 Hz, 2H), 7.05-7.00 (m, 1H), 2.42 (q, *J* = 7.6 Hz, 2H), 2.28 (ddt, *J* = 21.6, 14.6, 6.8 Hz, 2H), 1.25 (d, *J* = 15.8 Hz, 5H), 1.12-1.06 (m, 6H), 0.90 (d, *J* =

4.4 Hz, 12H). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 153.0, 152.3, 144.2, 136.1, 126.1, 123.9, 121.7, 118.2, 82.7, 51.6, 25.9, 24.74, 24.71, 18.8, 18.4, 14.9, 13.7. IR(neat) 3569, 2925, 1639, 1496, 1366, 1103, 1003, 856, 690. HRMS (ESI-TOF) calcd for $C_{21}H_{32}BO_2$ $[M+H]^+$: 327.2490, found: 327.2494.



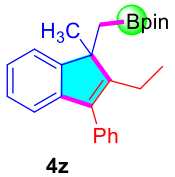
4x

4,4,5,5-tetramethyl-2-((1-methyl-2,3-dipropyl-1H-inden-1-yl)methyl)-1,3,2-dioxaborolane ***(4x)***: Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 20:1~10:1, v/v) affords the title compound as a brown viscous oil, 42 mg, 60% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (d, *J* = 7.3 Hz, 1H), 7.09 (td, *J* = 4.9, 4.0, 2.6 Hz, 2H), 7.04-6.99 (m, 1H), 2.42-2.31 (m, 2H), 2.27-2.15 (m, 2H), 1.50 (h, *J* = 7.8 Hz, 5H), 1.25 (d, *J* = 14.8 Hz, 5H), 0.95 (s, 2H), 0.92 (d, *J* = 5.2 Hz, 15H). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 153.0, 151.6, 144.4, 134.9, 126.1, 123.8, 121.7, 118.4, 82.7, 51.6, 28.2, 28.1, 26.0, 24.7, 23.5, 22.2, 15.2, 14.8. IR(neat) 3439, 2988, 1664, 1504, 1360, 1229, 1148, 969, 743. HRMS (ESI-TOF) calcd for $C_{23}H_{36}BO_2$ $[M+H]^+$: 355.2803, found: 355.2801.



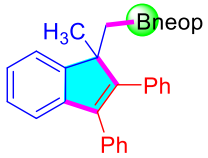
4y

2-((2,3-dibutyl-1-methyl-1H-inden-1-yl)methyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane ***(4y)***: Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 20:1~10:1, v/v) affords the title compound as a brown viscous oil, 40 mg, 52% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (d, *J* = 7.3 Hz, 1H), 7.10 (d, *J* = 6.2 Hz, 2H), 7.04-7.01 (m, 1H), 2.42-2.32 (m, 2H), 2.26-2.15 (m, 2H), 1.48-1.33 (m, 8H), 1.23 (s, 3H), 1.17 (d, *J* = 7.6 Hz, 2H), 0.92-0.86 (m, 18H). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 152.9, 151.6, 144.4, 134.9, 126.1, 123.8, 121.7, 118.3, 82.7, 51.5, 32.5, 31.2, 25.9, 25.63, 25.61, 24.73, 24.71, 23.8, 23.3, 14.3, 14.2. IR(neat) 3440, 2963, 1586, 1433, 1369, 1222, 1174, 960, 651. HRMS (ESI-TOF) calcd for $C_{25}H_{40}BO_2$ $[M+H]^+$: 383.3116, found: 383.3118.



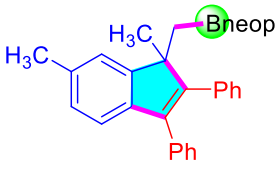
4z

2-((2-ethyl-1-methyl-3-phenyl-1H-inden-1-yl)methyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane ***(4z)***: Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 20:1~10:1, v/v) affords the title compound as a pale red solid, Mp = 97-99 ℃, 47 mg, 63% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (d, *J* = 7.3 Hz, 1H), 7.35-7.29 (m, 2H), 7.29-7.20 (m, 4H), 7.18-7.08 (m, 2H), 2.36-2.18 (m, 2H), 1.27 (s, 3H), 1.20 (d, *J* = 15.1 Hz, 2H), 1.03 (t, *J* = 7.5 Hz, 3H), 0.88 (d, *J* = 5.5 Hz, 12H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 153.0, 151.4, 143.6, 138.5, 137.4, 130.1, 128.1, 126.9, 126.4, 124.7, 122.2, 119.2, 82.7, 52.2, 25.9, 24.7, 19.3, 13.9. IR(neat) 3401, 2898, 1647, 1556, 1433, 1399, 1311, 1186, 951, 887, 563. HRMS (ESI-TOF) calcd for $C_{25}H_{32}BO_2$ $[M+H]^+$: 375.2490, found: 375.2493.



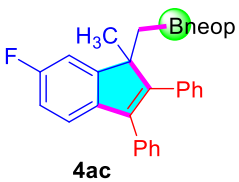
4aa

5,5-dimethyl-2-((1-methyl-2,3-diphenyl-1H-inden-1-yl)methyl)-1,3,2-dioxaborinane ***(4aa)***: Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 20:1~10:1, v/v) affords the title compound as a brown solid, Mp = 97-99 ℃, 52 mg, 64% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43-7.38 (m, 1H), 7.25-7.08 (m, 13H), 3.26 (s, 4H), 1.36 (s, 3H), 1.26 (s, 2H), 0.55 (s, 6H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 153.6, 153.3, 143.3, 137.7, 137.2, 135.8, 130.4, 129.6, 128.1, 127.8, 126.7, 126.4, 125.2, 122.2, 120.4, 71.8, 53.2, 31.6, 31.4, 30.3, 26.1, 21.7. IR(neat) 3462, 2977, 1603, 1466, 1368, 1103, 872, 697, 533. HRMS (ESI-TOF) calcd for $C_{28}H_{30}BO_2$ $[M+H]^+$: 409.2333, found: 409.2335.



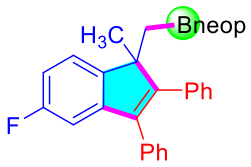
4ab

2-((1,6-dimethyl-2,3-diphenyl-1H-inden-1-yl)methyl)-5,5-dimethyl-1,3,2-dioxaborinane ***(4ab)***: Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 20:1~10:1, v/v) affords the title compound as a pale red solid, Mp = 99-101 ℃, 59 mg, 70% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 (d, *J* = 1.7 Hz, 1H), 7.19-7.07 (m, 11H), 6.94 (dd, *J* = 7.7, 1.5 Hz, 1H), 3.27 (s, 4H), 2.34 (s, 3H), 1.36 (s, 3H), 1.22 (d, *J* = 8.5 Hz, 2H), 0.57 (s, 6H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 153.7, 152.7, 140.7, 137.5, 137.4, 136.0, 134.8, 130.5, 129.6, 128.0, 127.8, 127.0, 126.61, 126.59, 123.1, 120.1, 71.8, 53.0, 31.4, 26.1, 21.8, 21.7. IR(neat) 3470, 2932, 1600, 1798, 1360, 1113, 982, 814, 697. HRMS (ESI-TOF) calcd for $C_{29}H_{32}BO_2$ $[M+H]^+$: 423.2490, found: 423.2493.



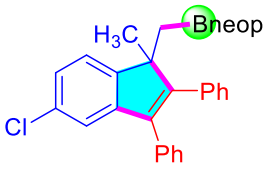
4ac

(S)-2-((6-fluoro-1-methyl-2,3-diphenyl-1H-inden-1-yl)methyl)-5,5-dimethyl-1,3,2-dioxaborinane ***(4ac)***: Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 20:1~10:1, v/v) affords the title compound as a brown solid, Mp = 100-102 ℃, 66 mg, 77% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20-7.09 (m, 12H), 6.82 (ddd, *J* = 10.7, 8.5, 2.4 Hz, 1H), 3.29 (s, 4H), 1.35 (s, 3H), 1.22 (d, *J* = 4.9 Hz, 2H), 0.60 (s, 6H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 161.9 (d, *J* = 243.9 Hz), 155.7 (d, *J* = 7.5 Hz), 153.3 (d, *J* = 4.1 Hz), 139.1 (d, *J* = 2.2 Hz), 137.0, 135.6, 130.4, 129.5, 128.1, 127.9, 126.8 (d, *J* = 4.6 Hz), 121.0 (d, *J* = 8.5 Hz), 112.9 (d, *J* = 22.8 Hz), 110.1 (d, *J* = 23.1 Hz), 71.9, 53.2, 53.2, 31.4, 26.0, 21.7. ^{19}F NMR (376 MHz, $CDCl_3$) δ -117.83. IR(neat) 3364, 2899, 1703, 1655, 1432, 1308, 1211, 1106, 977, 838. HRMS (ESI-TOF) calcd for $C_{28}H_{29}FBO_2$ $[M+H]^+$: 427.2239, found: 427.2242.



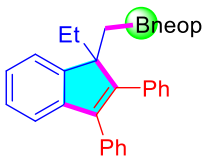
4ad

2-((5-fluoro-1-methyl-2,3-diphenyl-1H-inden-1-yl)methyl)-5,5-dimethyl-1,3,2-dioxaborinane ***(4ad)***: Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 20:1~10:1, v/v) affords the title compound as a brown solid, Mp = 123-125 ℃, 52 mg, 61% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (dd, *J* = 8.1, 5.2 Hz, 1H), 7.32-7.15 (m, 10H), 7.00-6.88 (m, 2H), 3.35 (s, 4H), 1.41 (s, 3H), 1.32 (d, *J* = 9.1 Hz, 2H), 0.66 (d, *J* = 0.9 Hz, 6H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 162.4 (d, *J* = 242.0 Hz), 155.6, 148.7 (d, *J* = 2.3 Hz), 145.3 (d, *J* = 8.7 Hz), 137.2 (d, *J* = 3.0 Hz), 136.9, 135.2, 130.2, 129.4, 128.2, 127.9, 127.0 (d, *J* = 4.7 Hz), 123.0 (d, *J* = 9.0 Hz), 111.6 (d, *J* = 22.8 Hz), 107.5 (d, *J* = 23.3 Hz), 71.9, 52.8, 31.4, 26.3, 21.7. ^{19}F NMR (376 MHz, $CDCl_3$) δ -117.34. IR(neat) 3430, 2966, 1674, 1467, 1382, 1030, 841, 679, 593. HRMS (ESI-TOF) calcd for $C_{28}H_{29}FBO_2$ $[M+H]^+$: 427.2239, found: 427.2239.



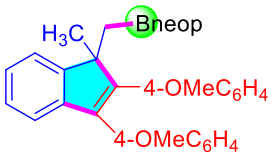
4ae

2-((5-chloro-1-methyl-2,3-diphenyl-1H-inden-1-yl)methyl)-5,5-dimethyl-1,3,2-dioxaborinane ***(4ae)***: Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 20:1~10:1, v/v) affords the title compound as a brown solid, Mp = 101-103 ℃, 648 mg, 54% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (d, *J* = 7.9 Hz, 1H), 7.29-7.16 (m, 12H), 3.36 (s, 4H), 1.41 (s, 3H), 1.31 (d, *J* = 7.6 Hz, 2H), 0.66 (d, *J* = 0.9 Hz, 6H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 155.2, 151.7, 145.3, 137.1, 136.7, 135.1, 132.2, 130.2, 129.5, 128.3, 127.9, 127.01, 126.96, 125.0, 123.2, 120.5, 71.9, 53.0, 31.4, 26.1, 21.6. IR(neat) 3411, 2964, 1605, 1477, 1392, 1240, 1169, 1008, 944, 802. HRMS (ESI-TOF) calcd for $C_{28}H_{29}ClBO_2$ $[M+H]^+$: 443.1944, found: 443.1947.



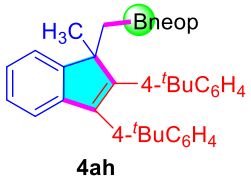
4af

2-((1-ethyl-2,3-diphenyl-1H-inden-1-yl)methyl)-5,5-dimethyl-1,3,2-dioxaborinane ***(4af)***: Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 20:1~10:1, v/v) affords the title compound as a brown viscous oil, 56 mg, 66% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (dd, *J* = 6.5, 1.7 Hz, 1H), 7.28-7.16 (m, 13H), 3.31 (s, 4H), 2.06-1.87 (m, 2H), 1.43-1.30 (m, 2H), 0.60 (s, 6H), 0.52 (t, *J* = 7.3 Hz, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 151.4, 150.6, 144.6, 140.0, 137.4, 136.1, 130.2, 129.7, 128.1, 127.9, 126.7, 126.6, 126.2, 125.1, 122.1, 120.1, 71.8, 57.6, 32.1, 31.3, 21.7, 8.7. IR(neat) 3365, 2903, 1677, 1546, 1339, 1286, 1135, 1091, 879, 667. HRMS (ESI-TOF) calcd for $C_{29}H_{32}BO_2$ $[M+H]^+$: 423.2490, found: 423.2497.



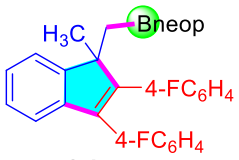
4ag

2-((2,3-bis(4-methoxyphenyl)-1-methyl-1H-inden-1-yl)methyl)-5,5-dimethyl-1,3,2-dioxaborinane ***(4ag)***: Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 20:1~10:1, v/v) affords the title compound as a brown viscous oil, 67 mg, 72% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (dd, *J* = 6.7, 1.8 Hz, 1H), 7.29 (dd, *J* = 6.9, 1.9 Hz, 1H), 7.24-7.14 (m, 6H), 6.80 (d, *J* = 8.5 Hz, 4H), 3.77 (s, 6H), 3.33 (s, 4H), 1.41 (s, 3H), 1.31 (d, *J* = 3.8 Hz, 2H), 0.62 (s, 6H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 158.3, 158.2, 153.4, 152.6, 143.6, 137.1, 131.5, 130.7, 129.7, 128.3, 126.3, 125.0, 122.1, 120.2, 113.6, 113.3, 71.8, 55.21, 55.18, 53.0, 31.3, 26.2, 21.7. IR(neat) 3401, 2973, 1505, 1496, 1387, 1266, 1164, 1100, 927, 843, 566. HRMS (ESI-TOF) calcd for $C_{30}H_{34}BO_4$ $[M+H]^+$: 469.2545, found: 469.2549.



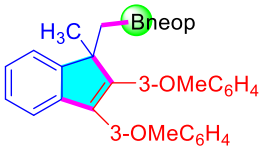
4ah

2-((2,3-bis(4-(tert-butyl)phenyl)-1-methyl-1H-inden-1-yl)methyl)-5,5-dimethyl-1,3,2-dioxaborinane ***(4ah)***: Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 20:1~10:1, v/v) affords the title compound as a brown viscous oil, 72 mg, 69% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47-7.44 (m, 1H), 7.33-7.30 (m, 1H), 7.27-7.24 (m, 4H), 7.19 (dd, *J* = 8.4, 2.0 Hz, 6H), 3.32 (s, 4H), 1.43 (s, 3H), 1.34-1.32 (m, 2H), 1.29 (d, *J* = 1.4 Hz, 18H), 0.65 (s, 6H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 153.6, 153.3, 149.2, 149.1, 143.7, 134.2, 130.0, 129.3, 126.2, 124.9, 124.9, 124.6, 122.1, 120.5, 71.8, 53.2, 34.59, 34.55, 31.51, 31.49, 31.4, 26.1, 21.8. IR(neat) 3406, 2962, 1635, 1486, 1381, 1199, 1154, 857, 591. HRMS (ESI-TOF) calcd for $C_{36}H_{46}BO_2$ $[M+H]^+$: 521.3585, found: 521.3587.



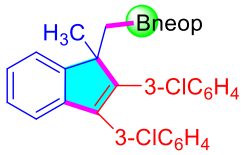
4ai

2-((2,3-bis(4-fluorophenyl)-1-methyl-1H-inden-1-yl)methyl)-5,5-dimethyl-1,3,2-dioxaborinane ***(4ai)***: Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 20:1~10:1, v/v) affords the title compound as a red solid, Mp = 125-127 ℃, 51 mg, 57% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51-7.45 (m, 1H), 7.26-7.14 (m, 7H), 6.95 (t, *J* = 8.6 Hz, 4H), 3.33 (s, 4H), 1.40 (s, 3H), 1.31 (s, 2H), 0.61 (s, 6H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 163.0 (d, *J* = 18.6 Hz), 160.6 (d, *J* = 18.8 Hz), 153.1, 152.7, 143.0, 137.3, 132.9 (d, *J* = 3.6 Hz), 132.0 (d, *J* = 7.9 Hz), 131.5 (d, *J* = 3.3 Hz), 131.1 (d, *J* = 7.9 Hz), 126.5, 125.5, 122.3, 120.2, 115.2 (d, *J* = 24.7 Hz), 114.9 (d, *J* = 24.6 Hz), 71.9, 53.2, 31.4, 26.2, 21.6. ^{19}F NMR (376 MHz, $CDCl_3$) δ -115.31, -115.70. IR(neat) 3449, 2966, 1632, 1347, 1244, 1036, 849, 792. HRMS (ESI-TOF) calcd for $C_{28}H_{28}BF_2O_2$ $[M+H]^+$: 445.2145, found: 445.2142.



4aj

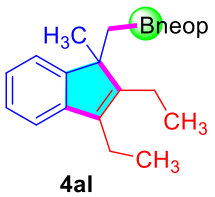
2-((2,3-bis(3-methoxyphenyl)-1-methyl-1H-inden-1-yl)methyl)-5,5-dimethyl-1,3,2-dioxaborinane ***(4aj)***: Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 20:1~10:1, v/v) affords the title compound as a red viscous oil, 63 mg, 67% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50-7.44 (m, 1H), 7.33 (dd, *J* = 7.0, 1.7 Hz, 1H), 7.26-7.15 (m, 4H), 6.93-6.80 (m, 4H), 6.75 (dddd, *J* = 8.0, 3.9, 2.6, 1.0 Hz, 2H), 3.70 (s, 3H), 3.66 (s, 3H), 3.34 (s, 4H), 1.44 (s, 3H), 1.35 (d, *J* = 10.0 Hz, 2H), 0.62 (s, 6H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 159.3, 159.1, 153.4, 153.3, 143.1, 138.7, 137.8, 137.2, 129.0, 128.8, 126.4, 125.2, 122.9, 122.2, 122.0, 120.5, 116.1, 114.8, 112.8, 112.3, 71.8, 55.2, 53.2, 31.4, 26.3, 21.7. IR(neat) 3439, 2993, 1677, 1458, 1329, 1102, 997, 870, 559. HRMS (ESI-TOF) calcd for $C_{30}H_{34}BO_4$ $[M+H]^+$: 469.2545, found: 469.2548.



4ak

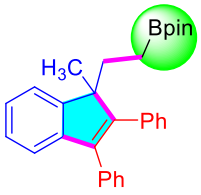
2-((2,3-bis(3-chlorophenyl)-1-methyl-1H-inden-1-yl)methyl)-5,5-dimethyl-1,3,2-dioxaborinane ***(4ak)***: Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 20:1~10:1, v/v) affords the title compound as a red viscous oil, 50 mg, 53% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42-7.38 (m, 1H), 7.24-7.10 (m, 9H), 7.02 (ddt, *J* = 8.8, 4.4, 1.6 Hz, 2H), 3.27 (d, *J* = 1.7 Hz, 4H), 1.34 (s, 3H), 1.25 (d, *J* = 6.5 Hz, 2H), 0.54 (s, 6H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 153.0, 152.8, 142.5, 138.7, 137.4, 137.3, 134.0, 133.8, 130.0, 129.6, 129.4, 129.3, 128.8, 127.9, 127.23, 127.21, 126.6, 125.8, 122.3, 120.3, 71.9, 53.4, 31.4, 26.2, 21.6. IR(neat) 3448, 2956, 1577, 1501, 1237,

1156, 992, 827, 729. HRMS (ESI-TOF) calcd for $C_{28}H_{28}BCl_2O_2$ $[M+H]^+$: 477.1554, found: 477.1554.



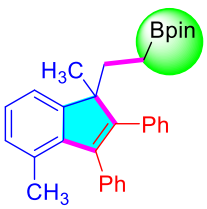
4al

2-((2,3-diethyl-1-methyl-1H-inden-1-yl)methyl)-5,5-dimethyl-1,3,2-dioxaborinane ***(4al)***: Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 20:1~10:1, v/v) affords the title compound as a red viscous oil, 34 mg, 55% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (d, *J* = 7.2 Hz, 1H), 7.22-7.14 (m, 2H), 7.14-7.07 (m, 1H), 3.33 (s, 4H), 2.53-2.26 (m, 4H), 1.28 (d, *J* = 10.0 Hz, 5H), 1.15 (td, *J* = 7.6, 5.7 Hz, 6H), 0.69 (s, 6H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 153.3, 152.8, 144.1, 135.7, 126.0, 123.8, 121.6, 118.2, 71.7, 51.9, 31.4, 25.9, 21.8, 18.7, 18.5, 14.9, 13.8. IR(neat) 3448, 2962, 1499, 1423, 1356, 1232, 1164, 1147, 984, 816. HRMS (ESI-TOF) calcd for $C_{20}H_{30}BO_2$ $[M+H]^+$: 313.2333, found: 313.2337.



5a

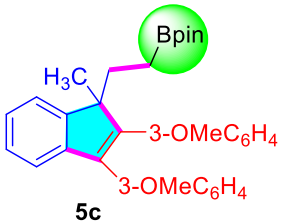
4,4,5,5-tetramethyl-2-(2-(1-methyl-2,3-diphenyl-1H-inden-1-yl)ethyl)-1,3,2-dioxaborolane ***(5a)***: Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 20:1~10:1, v/v) affords the title compound as a pale yellow oil, 68 mg, 78% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39-7.10 (m, 14H), 2.08-1.90 (m, 2H), 1.41 (s, 3H), 1.18 (d, *J* = 7.4 Hz, 12H), 0.59 (ddd, *J* = 16.7, 12.2, 4.6 Hz, 1H), 0.24 (ddd, *J* = 16.9, 12.2, 5.4 Hz, 1H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 151.3, 150.5, 140.3, 136.9, 135.4, 129.8, 129.7, 128.14, 128.09, 126.93, 126.86, 126.5, 125.5, 121.9, 120.5, 83.0, 56.4, 31.8, 25.0, 24.8, 23.9. IR(neat) 3477, 2976, 2309, 1574, 1366, 1279, 1063, 856, 563. HRMS (ESI-TOF) calcd for $C_{30}H_{34}BO_2$ $[M+H]^+$: 437.2646, found: 437.2647.



5b

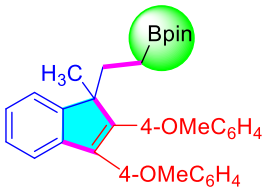
(S)-2-(2-(1,4-dimethyl-2,3-diphenyl-1H-inden-1-yl)ethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane ***(5b)***: Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 20:1~10:1, v/v) affords the title compound as a brown solid, Mp = 132-134 ℃, 56 mg, 62% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.15-7.03 (m, 10H), 7.01-6.95 (m, 2H), 6.87 (d, *J* = 7.4 Hz, 1H),

1.95-1.77 (m, 5H), 1.30 (s, 3H), 1.12 (d, *J* = 7.5 Hz, 12H), 0.56 (ddd, *J* = 16.6, 12.5, 4.3 Hz, 1H), 0.20 (ddd, *J* = 16.3, 12.5, 5.2 Hz, 1H). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 151.5, 151.4, 142.1, 138.3, 136.7, 131.7, 130.4, 129.9, 129.7, 129.6, 127.74, 127.70, 126.63, 126.59, 125.4, 119.6, 83.0, 55.7, 31.7, 25.0, 24.9, 24.0, 20.3. IR(neat) 3436, 3980, 1603, 1321, 1143, 846, 758, 699. HRMS (ESI-TOF) calcd for $C_{31}H_{36}BO_2$ $[M+H]^+$: 451.2803, found: 451.2806.



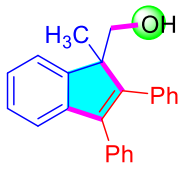
5c

*2-(2-(2,3-bis(3-methoxyphenyl)-1-methyl-1H-inden-1-yl)ethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**5c**)*: Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 20:1~10:1, v/v) affords the title compound as a pale yellow oil, 79 mg, 80% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30-7.25 (m, 2H), 7.19-7.15 (m, 2H), 7.13-7.06 (m, 2H), 6.81 (dd, *J* = 7.6, 1.4 Hz, 1H), 6.76-6.73 (m, 1H), 6.68 (td, *J* = 7.3, 6.3, 2.0 Hz, 3H), 6.63-6.59 (m, 1H), 3.60 (d, *J* = 5.4 Hz, 6H), 1.93 (ddd, *J* = 10.7, 5.6, 3.7 Hz, 2H), 1.33 (s, 3H), 1.10 (d, *J* = 6.7 Hz, 12H), 0.51 (ddd, *J* = 16.5, 10.9, 5.7 Hz, 1H), 0.16 (ddd, *J* = 17.0, 11.1, 6.7 Hz, 1H). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 159.4, 159.3, 151.3, 150.3, 129.2, 129.1, 126.6, 125.6, 122.2, 122.2, 121.9, 120.6, 114.9, 114.8, 113.1, 112.8, 83.0, 56.4, 55.3, 55.2, 31.9, 25.0, 24.9, 24.0. IR(neat) 3463, 2869, 2300, 1603, 1477, 1289, 1143, 980, 693. HRMS (ESI-TOF) calcd for $C_{32}H_{38}BO_4$ $[M+H]^+$: 497.2858, found: 497.2864.



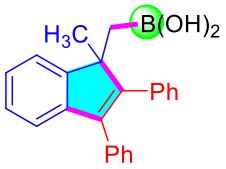
5d

*2-(2-(2,3-bis(4-methoxyphenyl)-1-methyl-1H-inden-1-yl)ethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**5d**)*: Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 20:1~10:1, v/v) affords the title compound as a red solid, Mp = 133-135 ℃, 81 mg, 82% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (ddd, *J* = 16.3, 5.9, 3.3 Hz, 2H), 7.25 (ddd, *J* = 13.7, 8.0, 3.1 Hz, 4H), 7.11 (d, *J* = 8.6 Hz, 2H), 6.88-6.81 (m, 4H), 3.82 (s, 6H), 2.10-1.94 (m, 2H), 1.43 (s, 3H), 1.22 (d, *J* = 7.1 Hz, 12H), 0.60 (ddd, *J* = 16.7, 12.3, 4.6 Hz, 1H), 0.25 (ddd, *J* = 16.9, 12.2, 5.3 Hz, 1H). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 158.37, 158.35, 151.3, 149.4, 144.5, 130.9, 130.8, 129.3, 127.9, 126.4, 125.3, 121.7, 120.3, 113.60, 113.56, 83.0, 56.1, 55.21, 55.19, 31.9, 25.0, 24.8, 24.0. IR(neat) 3437, 2961, 1603, 1479, 1352, 1260, 1106, 901, 829, 566. HRMS (ESI-TOF) calcd for $C_{32}H_{38}BO_4$ $[M+H]^+$: 497.2858, found: 497.2864.



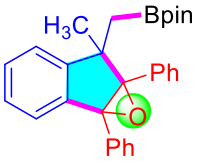
6

(1-methyl-2,3-diphenyl-1H-inden-1-yl)methanol ***(6)***: Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 5:1~2:1, v/v) affords the title compound as a colorless solid, Mp = 117-119 ℃, 59 mg, 94% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40-7.37 (m, 1H), 7.33-7.29 (m, 1H), 7.24-7.14 (m, 10H), 7.11 (td, *J* = 4.4, 2.3 Hz, 2H), 3.87 (d, *J* = 10.9 Hz, 1H), 3.71 (d, *J* = 10.9 Hz, 1H), 1.29 (s, 3H).^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 149.5, 148.9, 144.5, 140.6, 136.3, 134.8, 129.8, 129.6, 128.4, 128.2, 127.5, 127.3, 127.2, 125.8, 122.1, 121.1, 67.5, 57.6, 19.3. IR(neat) 3564, 2929, 1632, 1440, 1036, 761, 573. HRMS (ESI-TOF) calcd for $C_{23}H_{21}O$ $[M+H]^+$: 313.1587, found: 313.1589.



7

((1-methyl-2,3-diphenyl-1H-inden-1-yl)methyl)boronic acid ***(7)***: Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1~1:1, v/v) affords the title compound as a colorless solid, Mp = 120-122 ℃, 54 mg, 80% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43-7.38 (m, 1H), 7.36-7.32 (m, 1H), 7.28-7.24 (m, 2H), 7.22-7.14 (m, 8H), 7.10 (dd, *J* = 7.7, 1.9 Hz, 2H), 3.91 (d, *J* = 2.9 Hz, 2H), 1.56 (d, *J* = 16.1 Hz, 1H), 1.48 (d, *J* = 16.1 Hz, 1H), 1.37 (s, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 153.1, 152.3, 142.8, 138.9, 136.1, 134.6, 129.8, 129.5, 128.34, 128.30, 127.5, 127.33, 127.31, 126.5, 122.0, 121.6, 52.9, 27.3. IR(neat) 3540, 3389, 1595, 1400, 1326, 1072, 763, 701, 572. HRMS (ESI-TOF) calcd for $C_{23}H_{22}BO_2$ $[M+H]^+$: 341.1707, found: 341.1709.

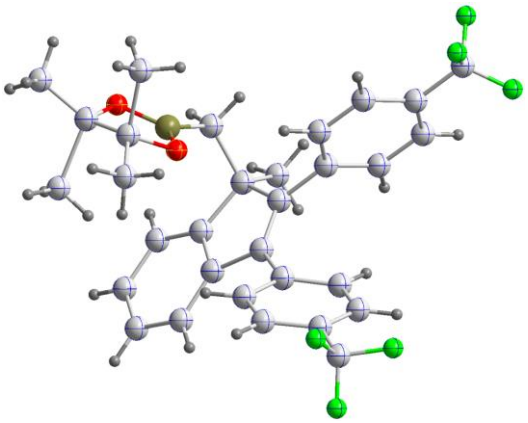


8

4,4,5,5-tetramethyl-2-((6-methyl-1a,6a-diphenyl-1a,6a-dihydro-6H-indeno[1,2-b]oxiren-6-yl)methyl)-1,3,2-dioxaborolane ***(8)***: Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 20:1~10:1, v/v) affords the title compound as a colorless solid, Mp = 134-136 ℃, 68 mg, 78% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (dd, *J* = 7.4, 1.4 Hz, 1H), 7.33 (td, *J* = 7.5, 1.4 Hz, 1H), 7.29-7.20 (m, 9H), 7.16 (dd, *J* = 8.0, 1.8 Hz, 2H), 7.10 (dd, *J* = 7.6, 1.4 Hz, 1H), 1.52 (d, *J* = 15.8 Hz, 1H), 1.32 (d, *J* = 15.8 Hz, 1H), 1.20 (s, 3H), 1.15 (s, 6H), 1.00 (s, 6H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 147.0, 144.1, 143.1, 129.7, 129.0, 128.4, 128.2, 128.0, 127.6,

127.2, 127.1, 126.8, 123.4, 83.4, 67.6, 51.5, 29.2, 24.9, 24.5. IR(neat) 3478, 2975, 1755, 1444, 1361, 1326, 1133, 884, 795, 703. HRMS (ESI-TOF) calcd for $C_{29}H_{32}BO_3$ $[M+H]^+$: 439.2439, found: 439.2440.

8. Crystallographic data of 4o and 4i'



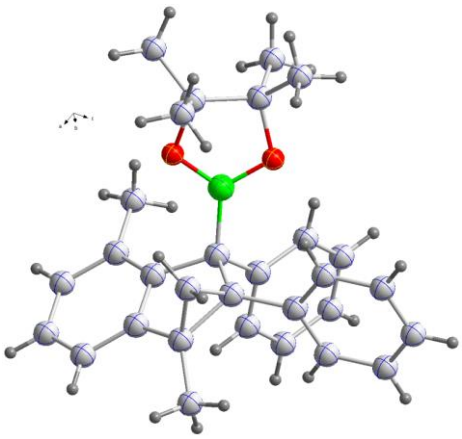
Structure of 4o CCDC: 2353045

Datablock:

Bond precision:	C-C = 0.0098 A		Wavelength = 0.71073
Cell:	a = 8.649(7)	b=13.234(7)	c=13.312(8)
	alpha=107.837(10)	beta=95.839(10)	gamma=96.840(7)
Temperature:	296 K		
	Calculated		Reported
Volume	1424.7(16)		1424.7(16)
Space group	p -1		p -1
Hall group	-p 1		-p 1
Moiety formula	C30 H26 B F6 O2 CH3		
Sum formula	C31 H29 B F6 O2		C31 H29 B F6 O2
Mr	558.35		558.38
Dx,g cm-3	1.302		1.302
Z	2		2
Mu (mm-1)	0.106		0.106
F000	580.0		580.0
F000'	580.39		
h,k,lmax	10,15,15		10,15,15
Nref	5022		4947
Tmin,Tmax			
Tmin'			

Correction method = Not given

Data completeness = 0.985	Theta (max) = 24.998
R (reflections) = 0.1046(3146)	wR2 (reflections) = 0.2669(4947)
S = 1.001	Npar = 366



Structure of 4i' CCDC: 2353044

Datablock:

Bond precision:	C-C = 0.0043 A		Wavelength = 0.71073
Cell:	a = 9.248(3)	b=12.097(4)	c=22.961(8)
	alpha=90	beta=100.211(6)	gamma=90
Temperature:	296 K		
	Calculated		Reported
Volume	2528.0(15)		2528.0(15)
Space group	p 21/n		p 21/n
Hall group	-p 2yn		-p 2yn
Moiety formula	C30 H33 B O2		?
Sum formula	C30 H33 B O2		C30 H33 B O2
Mr	436.37		436.37
Dx,g cm-3	1.147		1.147
Z	4		4
Mu (mm-1)	0.069		0.069
F000	936.0		936.0
F000'	936.37		
h,k,lmax	10,14,27		10,14,27
Nref	4442		4430
Tmin,Tmax			
Tmin'			

Correction method = Not given

Data completeness = 0.997	Theta (max) = 24.999
R (reflections) = 0.0752(3535)	wR2 (reflections) = 0.2784(4430)
S = 1.049	Npar = 304

9. References

(1) Tripathi, C. B.; Mukherjee, S. *Angew. Chem. Int. Ed.* **2013**, *52*, 8450.
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(5) Lou, Z.; Zhang, S.; Chen, C.; Pang, X.; Li, M.; Wen, L. *Adv. Synth. Catal.* **2014**, *356*, 153.
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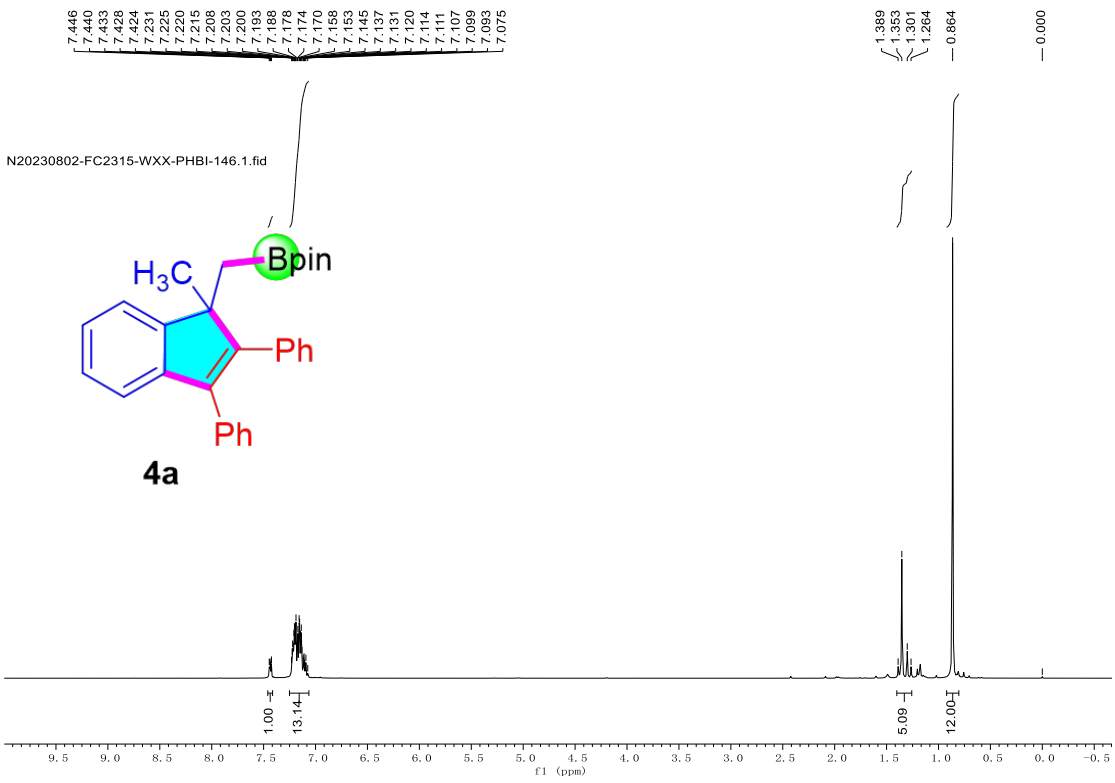
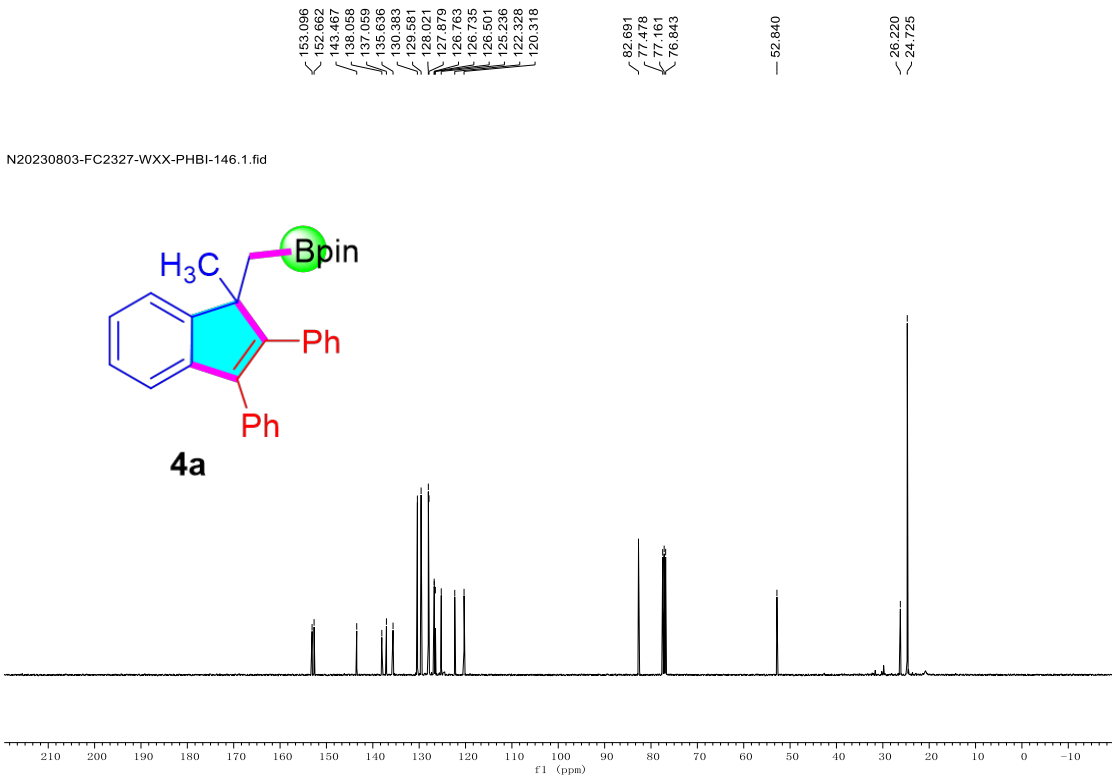
(7) Schmidt, B.; Berger, R.; Kelling, A.; Schilde, U. *Chem. Eur. J.* **2011**, *17*, 7032.
(8) Lee, D.-H.; Kwon, Y.-J.; Jin, M.-J. *Adv. Synth. Catal.* **2011**, *353*, 3090.

10. NMR Spectra

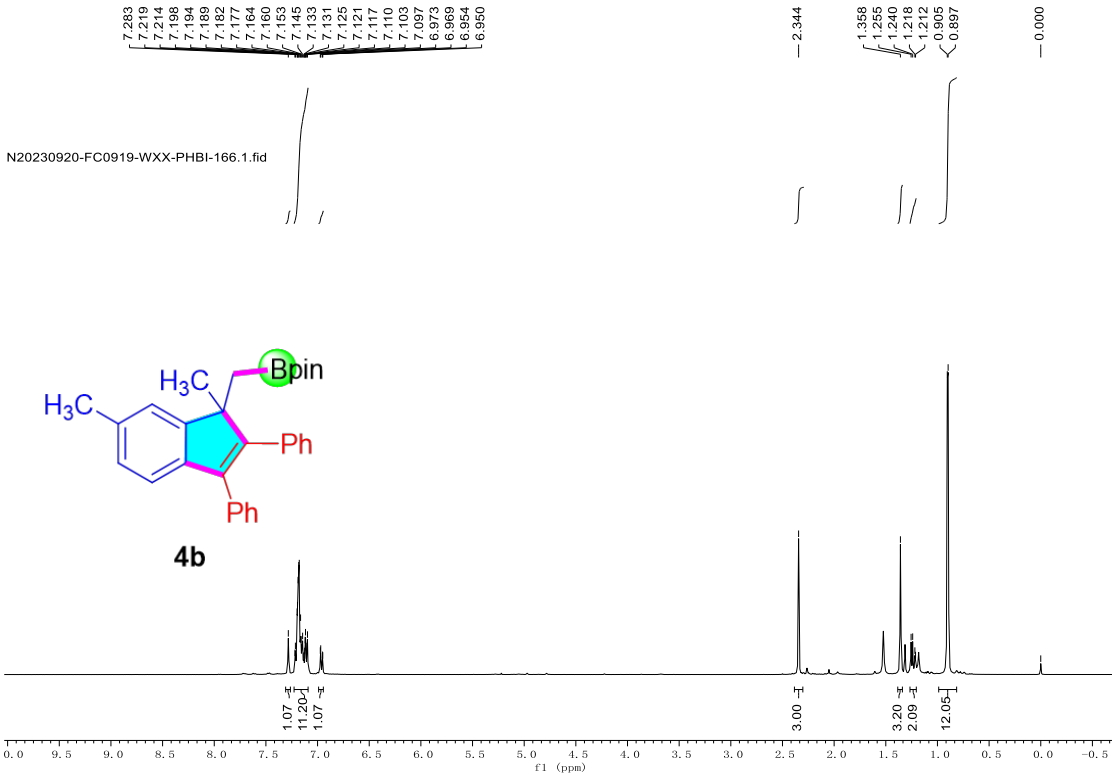
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of **4a**



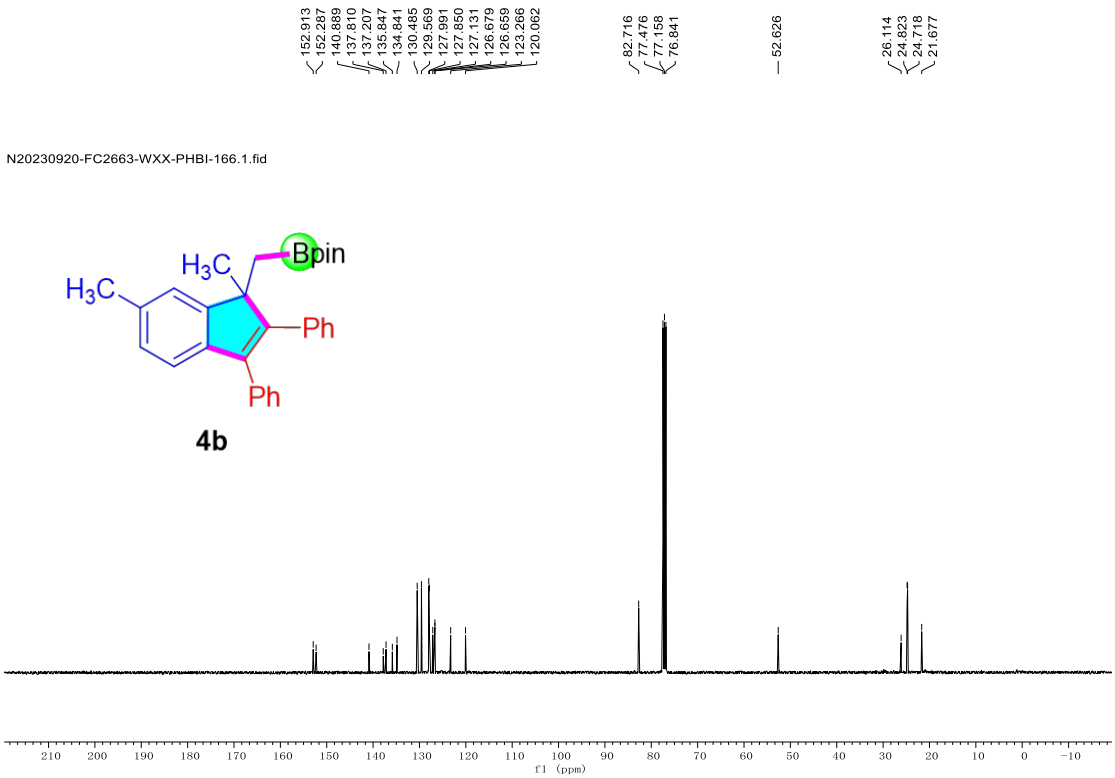
^{13}C{1H} NMR (101 MHz, $CDCl_3$) Spectrum of **4a**



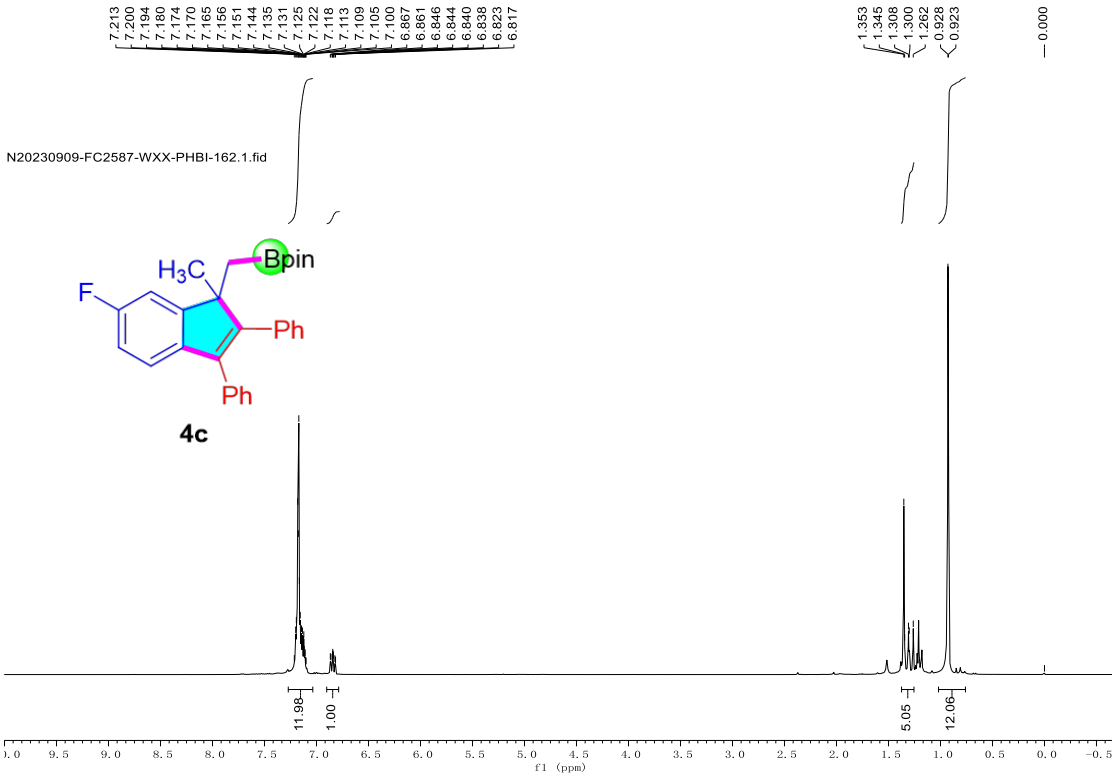
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of **4b**



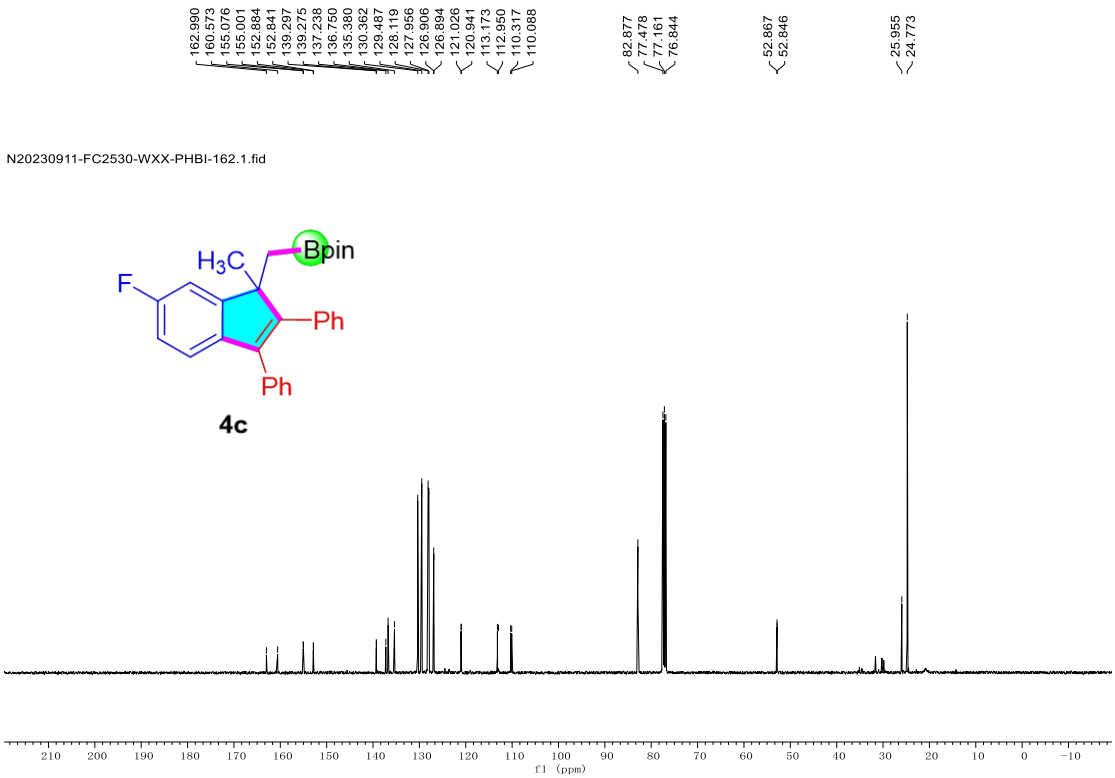
^{13}C{1H} NMR (101 MHz, $CDCl_3$) Spectrum of **4b**



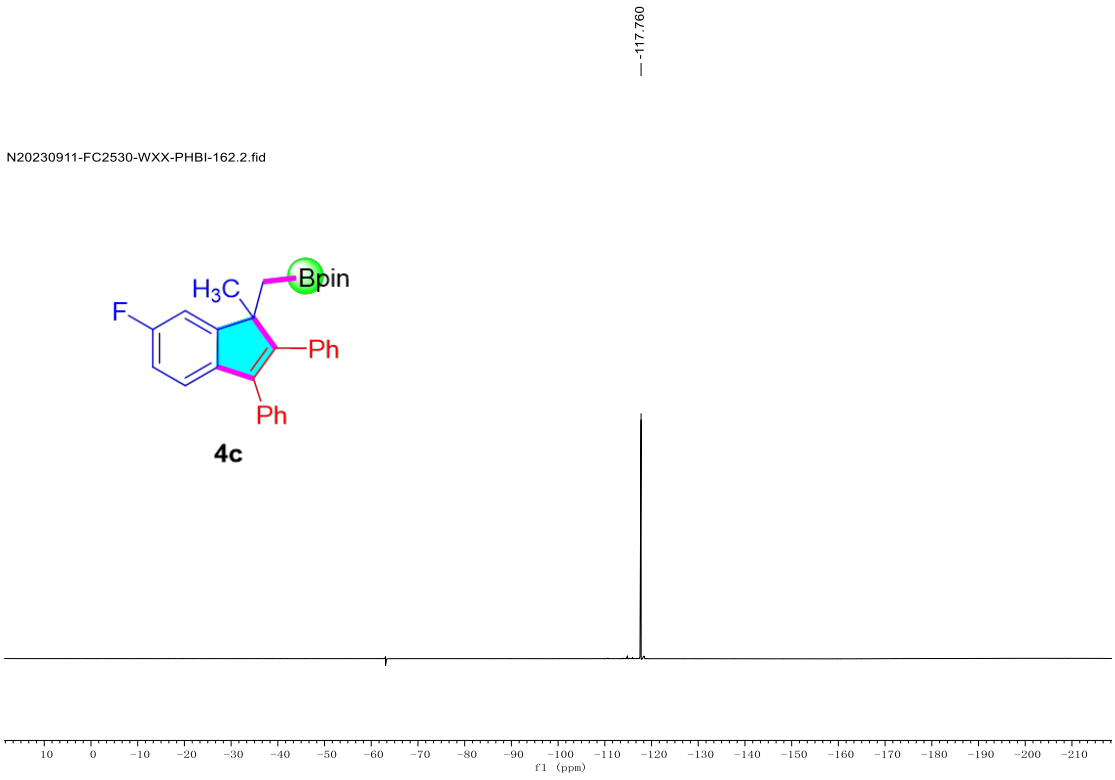
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of **4c**



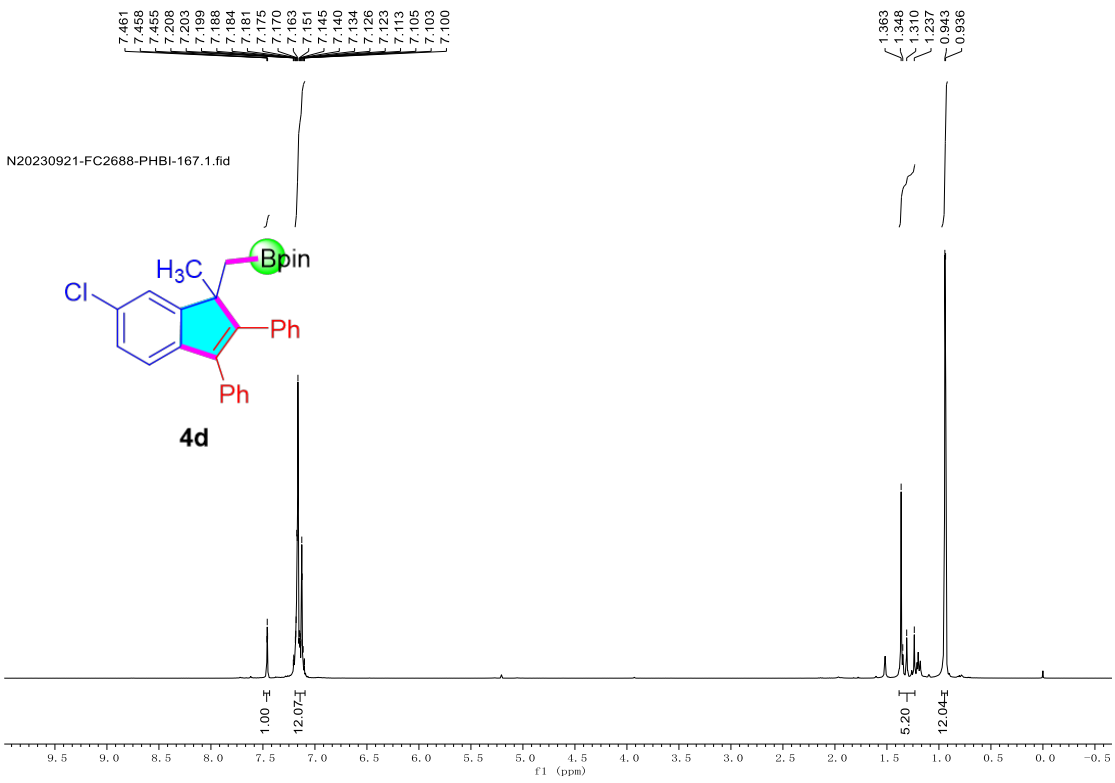
^{13}C{1H} NMR (101 MHz, $CDCl_3$) Spectrum of **4c**



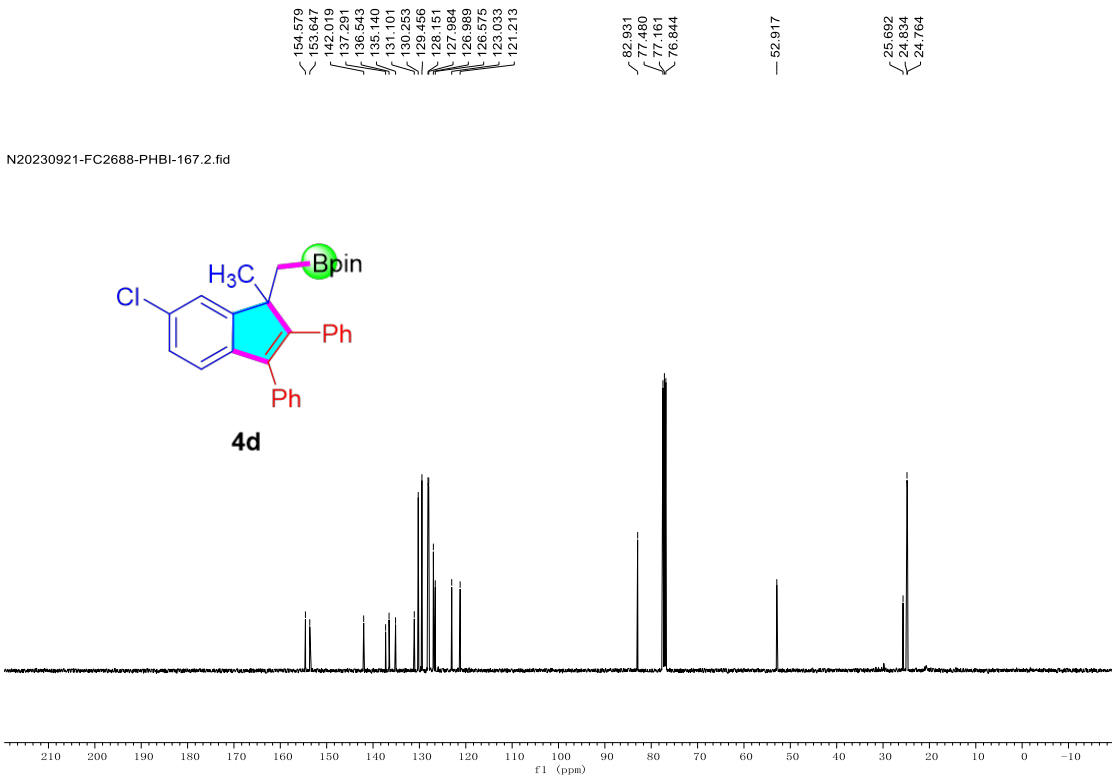
^{19}F NMR (376 MHz, $CDCl_3$) Spectrum of **4c**



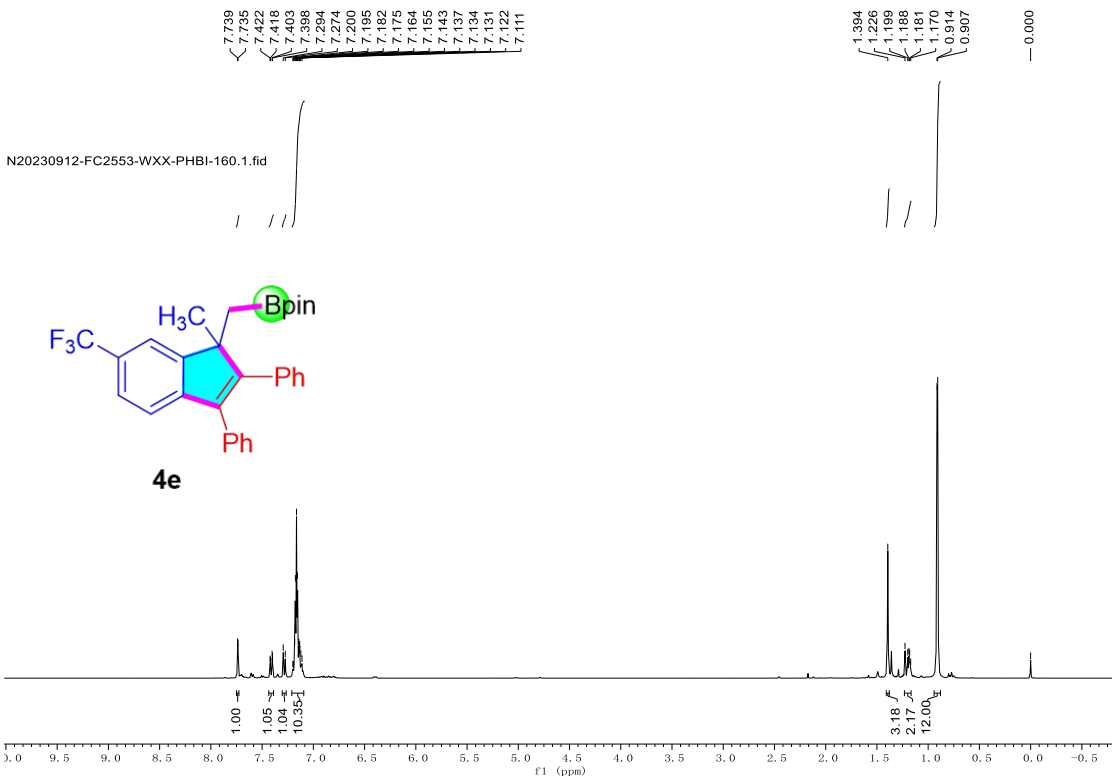
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of **4d**



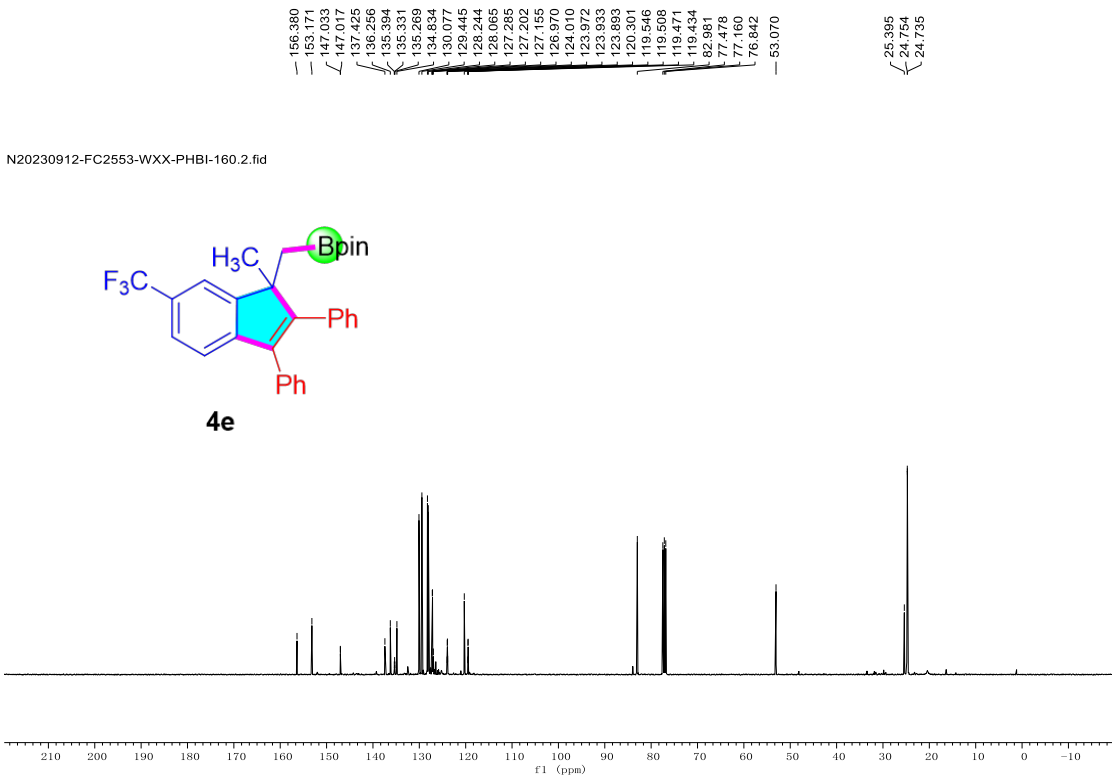
^{13}C{1H} NMR (101 MHz, $CDCl_3$) Spectrum of **4d**



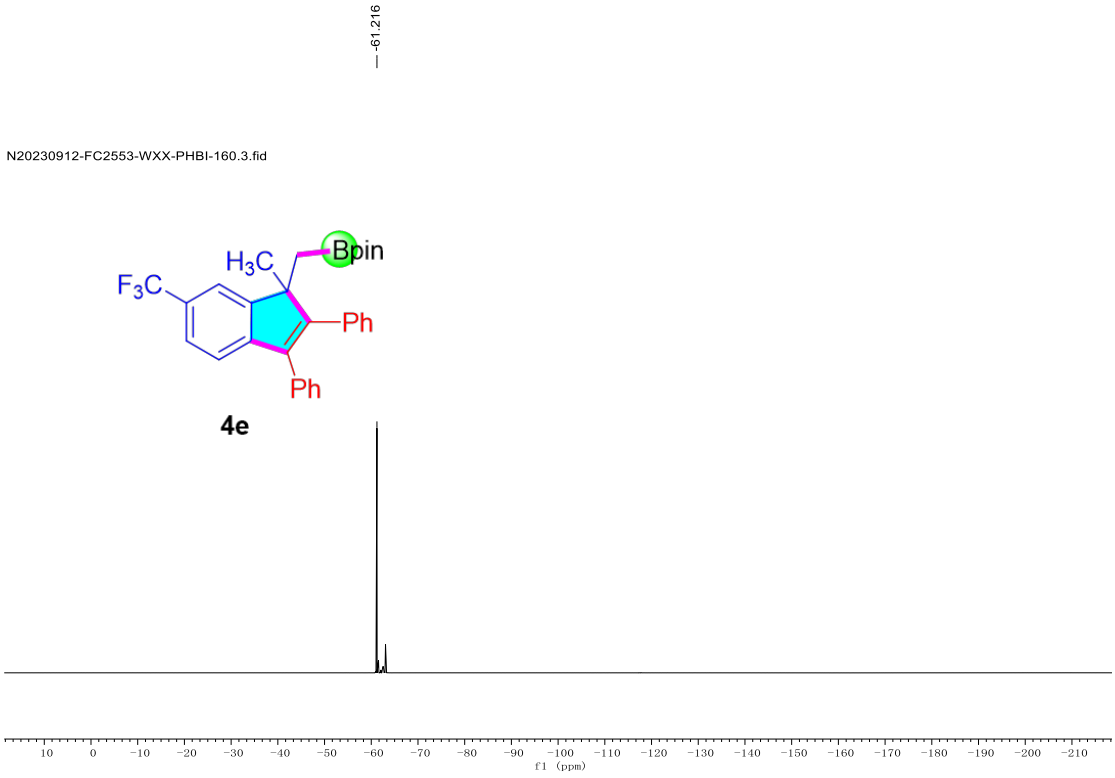
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of **4e**



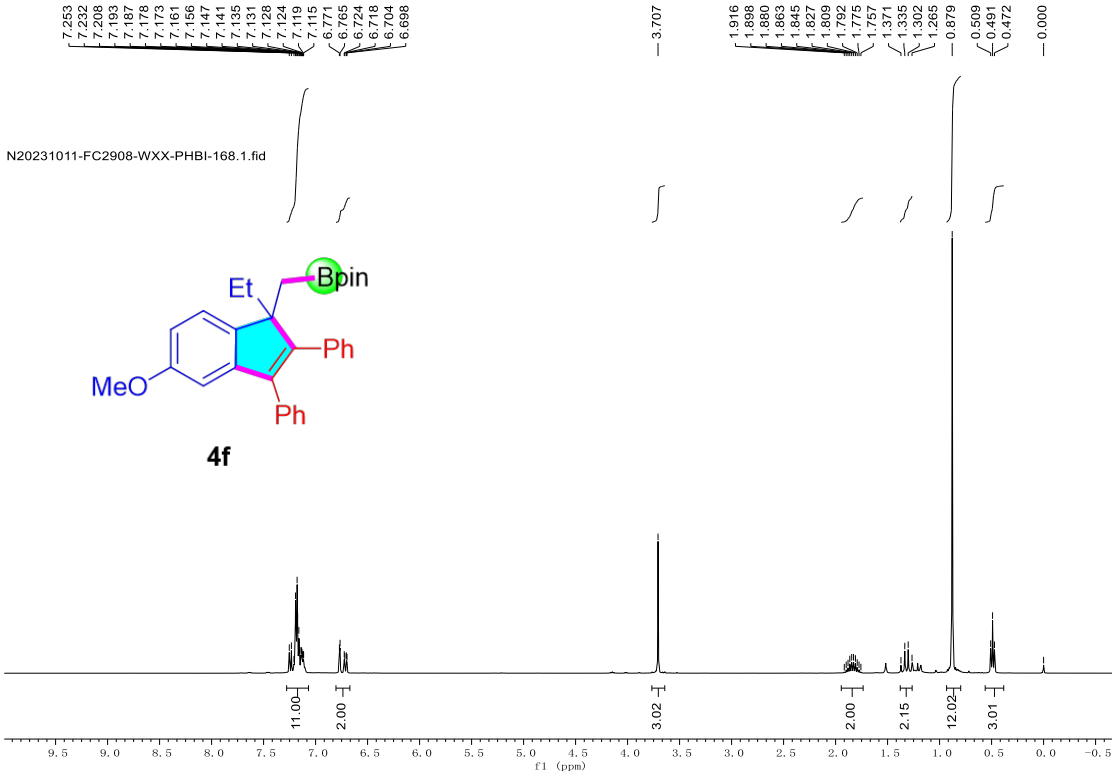
^{13}C{1H} NMR (101 MHz, $CDCl_3$) Spectrum of **4e**



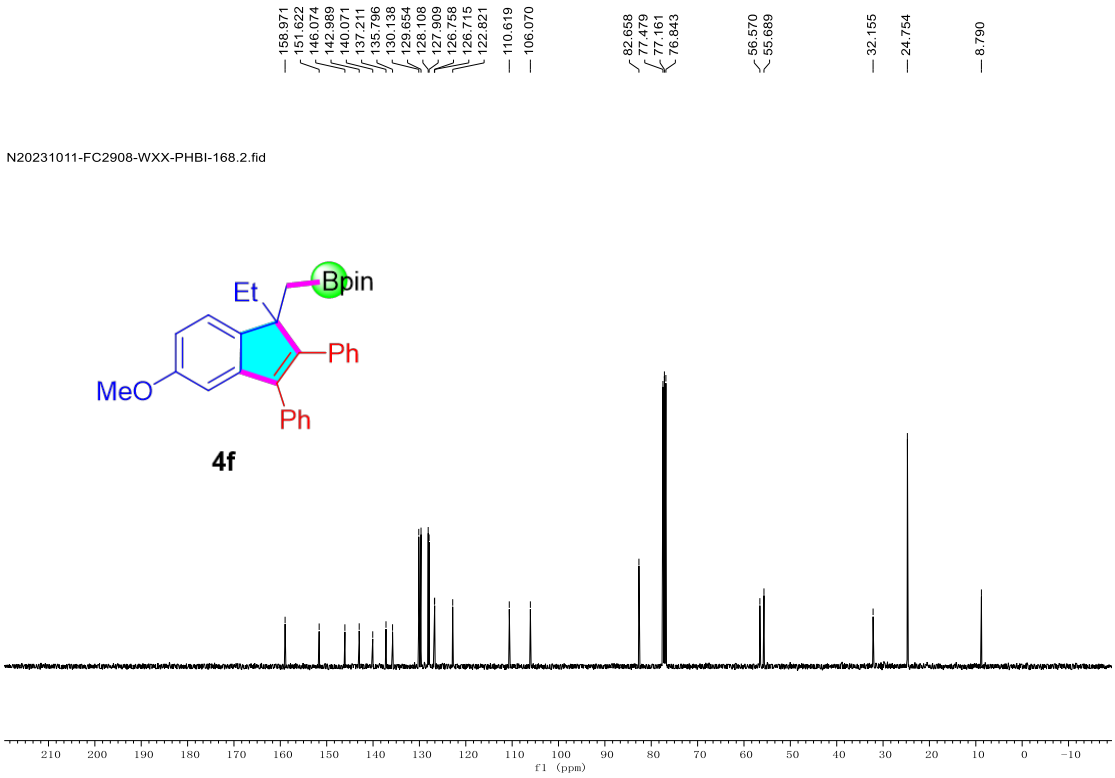
^{19}F NMR (376 MHz, $CDCl_3$) Spectrum of **4e**



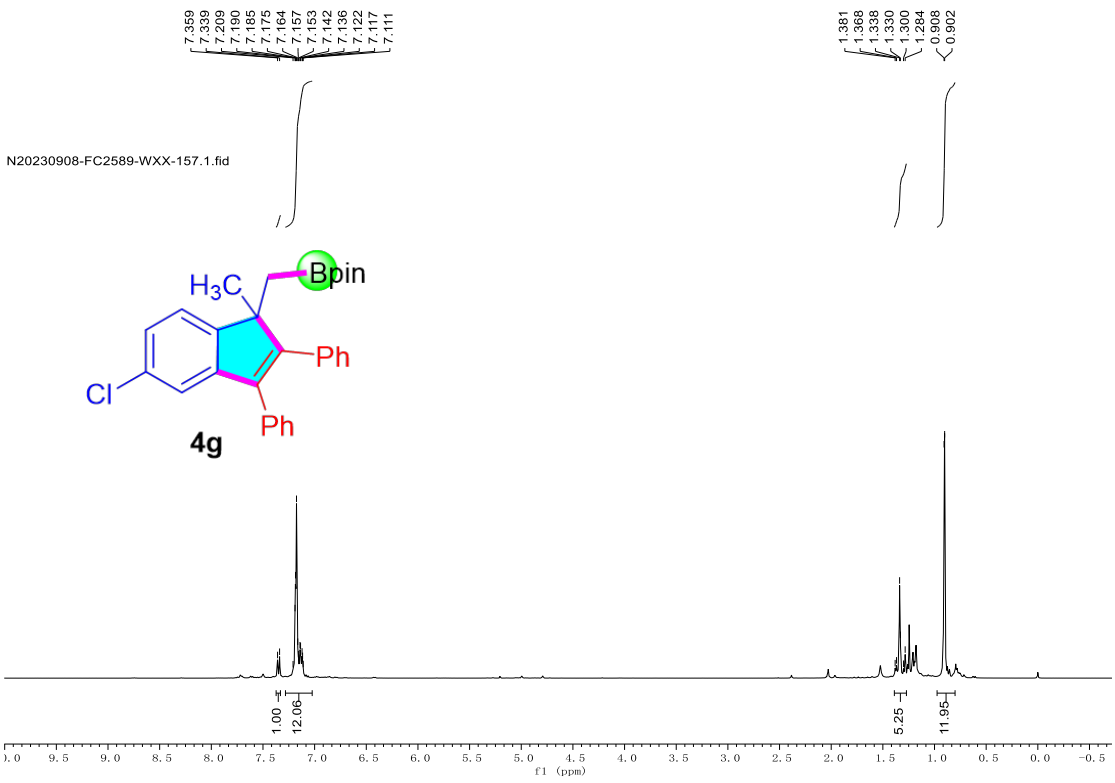
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of **4f**



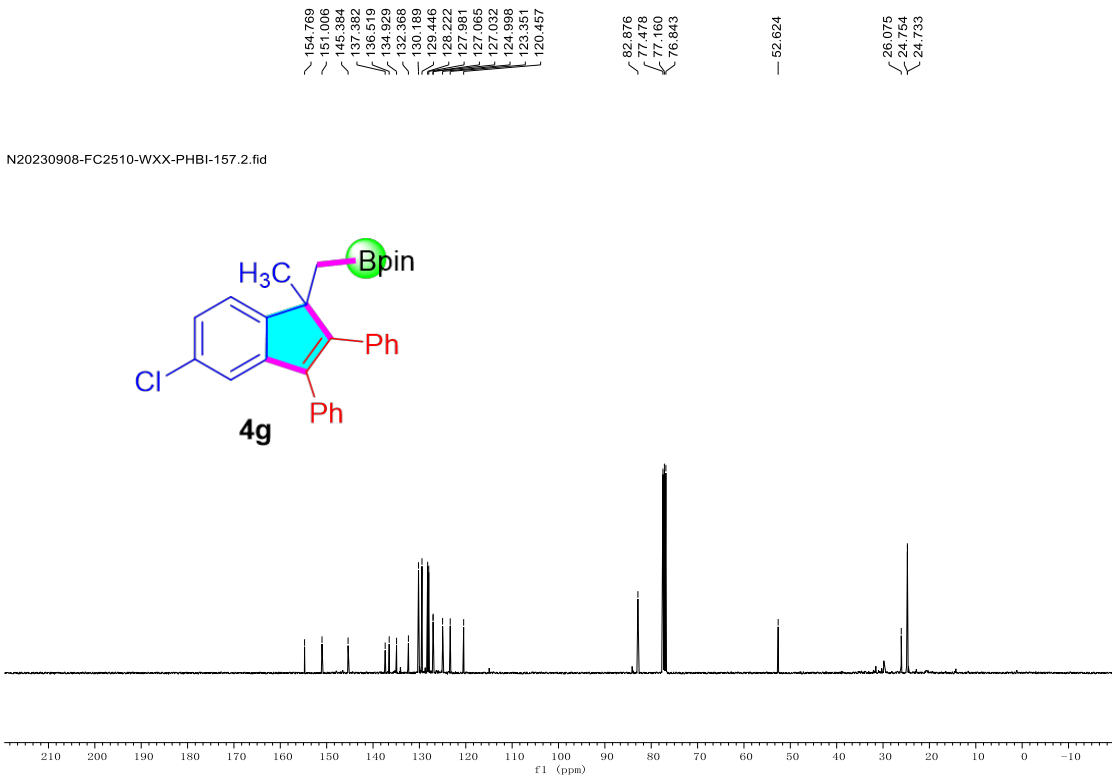
^{13}C{1H} NMR (101 MHz, $CDCl_3$) Spectrum of **4f**



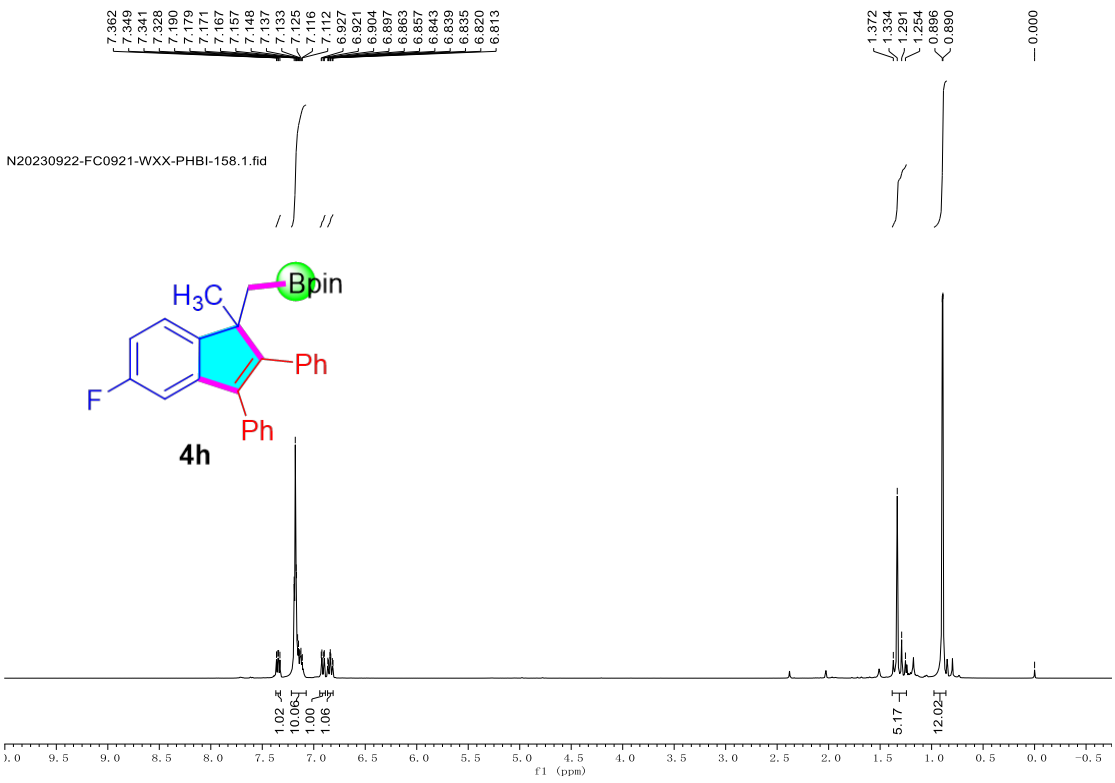
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of **4g**



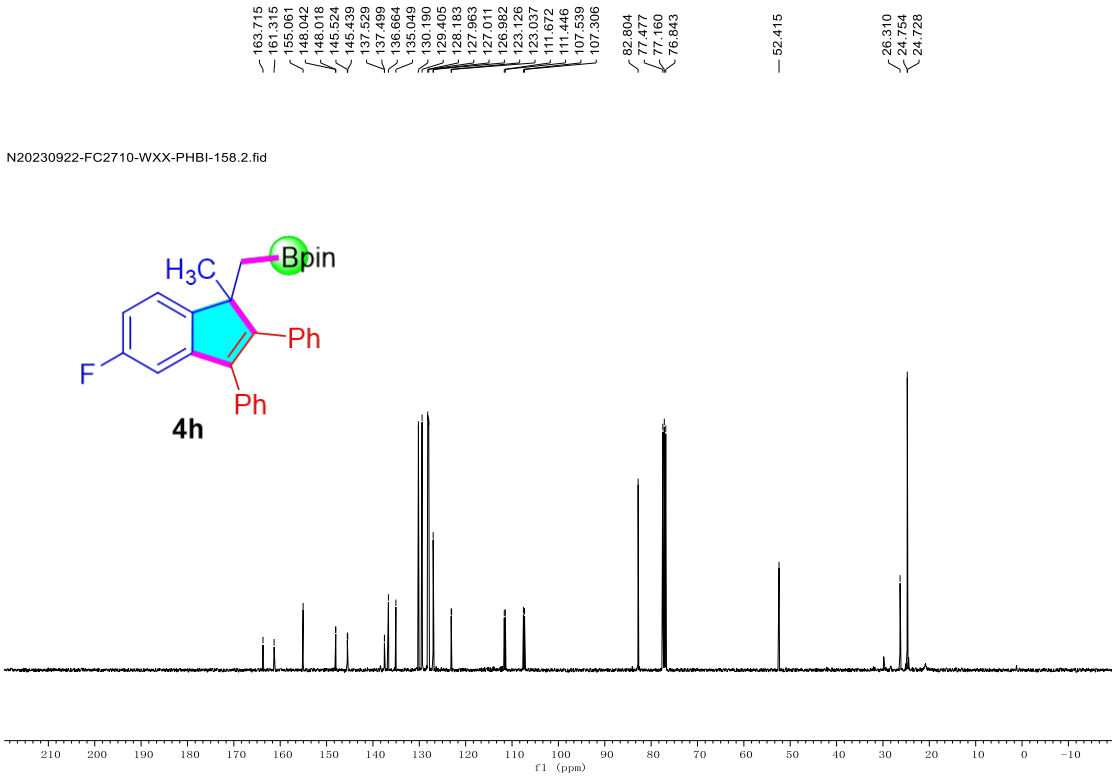
^{13}C{1H} NMR (101 MHz, $CDCl_3$) Spectrum of **4g**



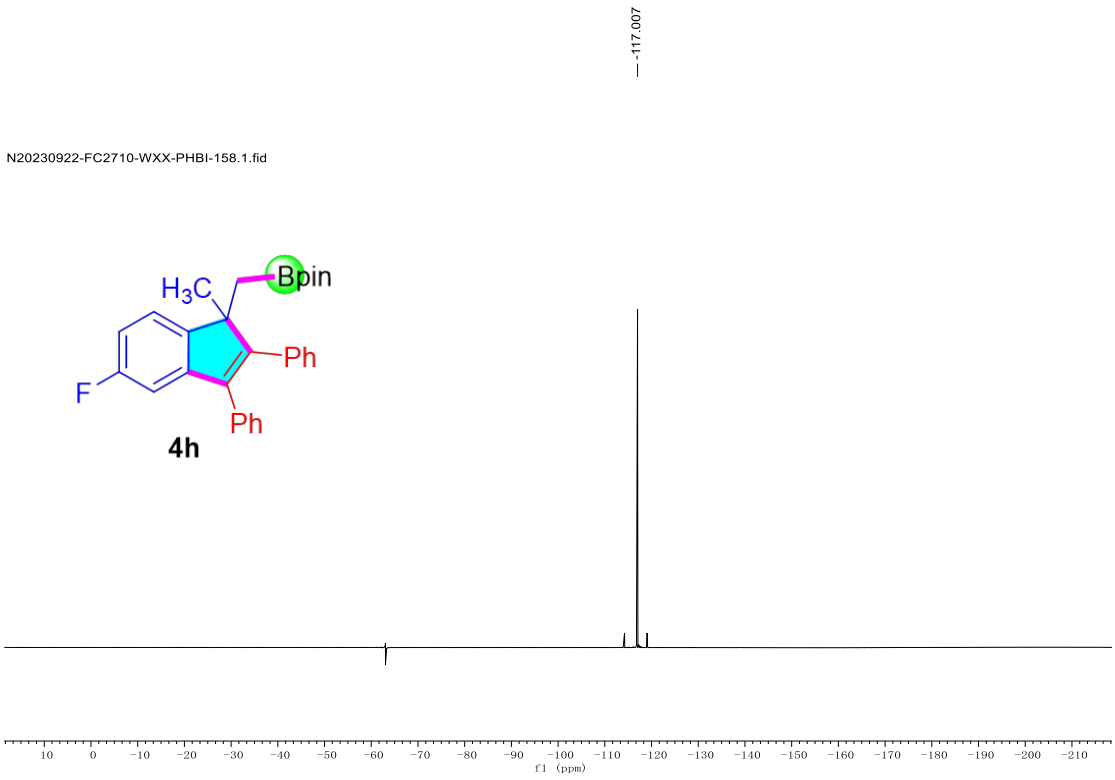
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of **4h**



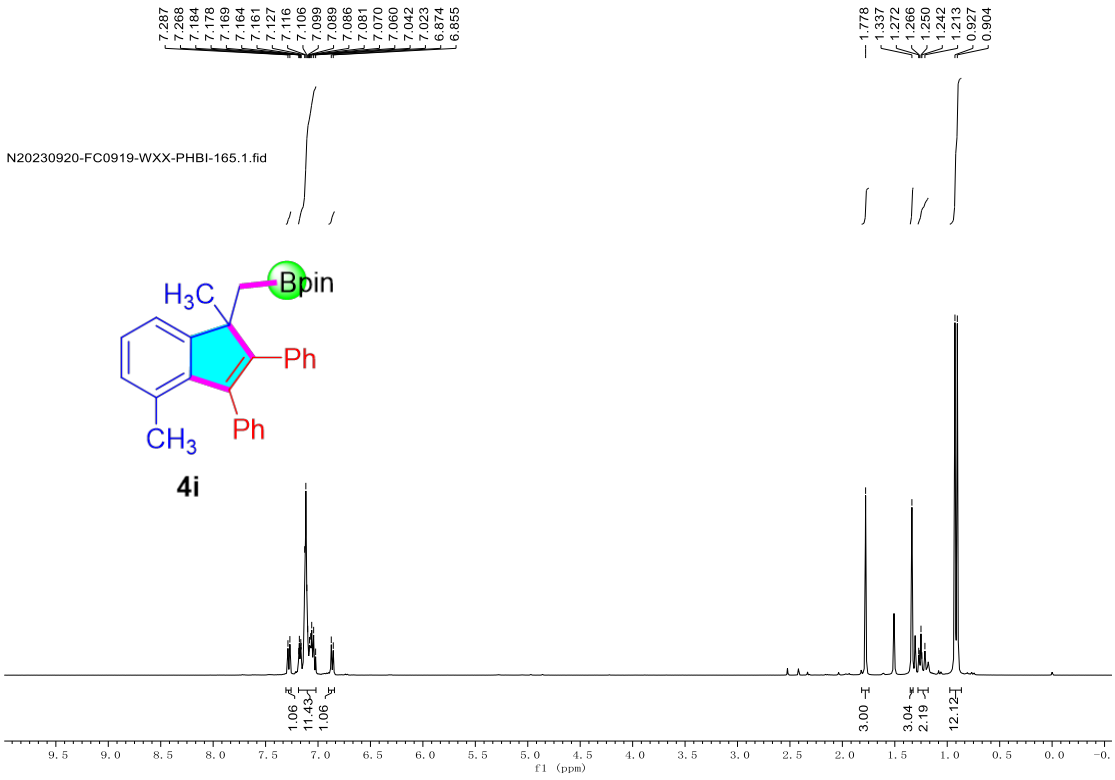
^{13}C{1H} NMR (101 MHz, $CDCl_3$) Spectrum of **4h**



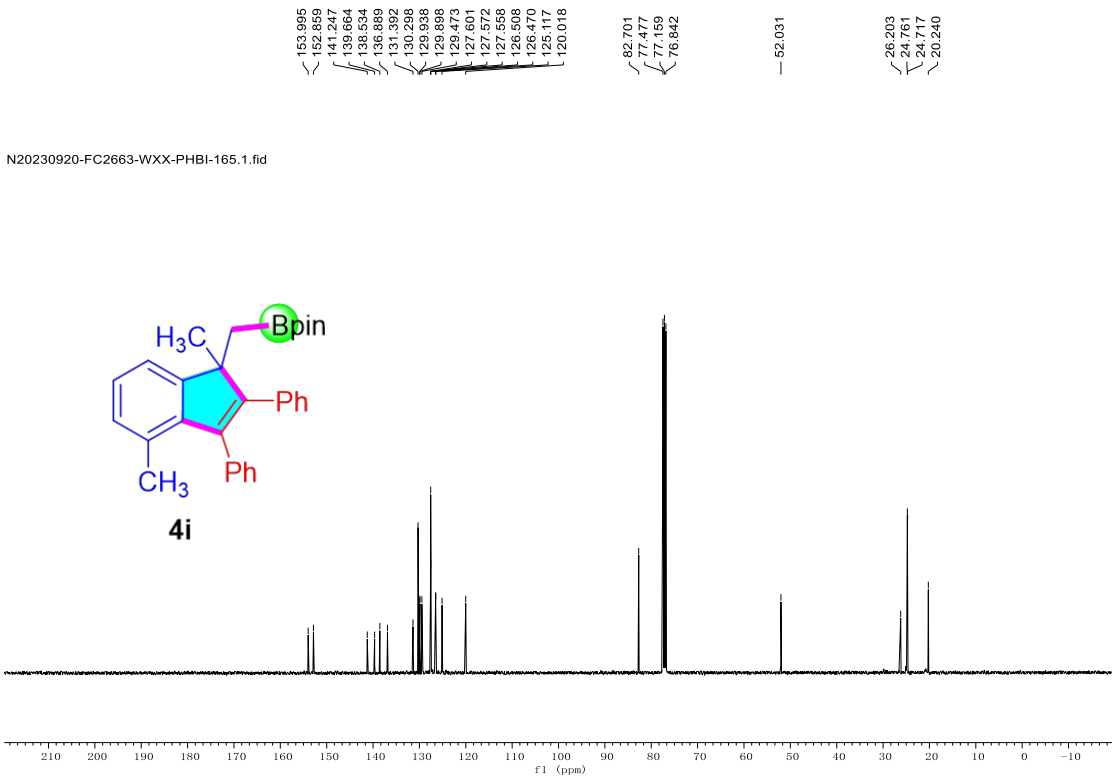
^{19}F NMR (376 MHz, $CDCl_3$) Spectrum of **4h**



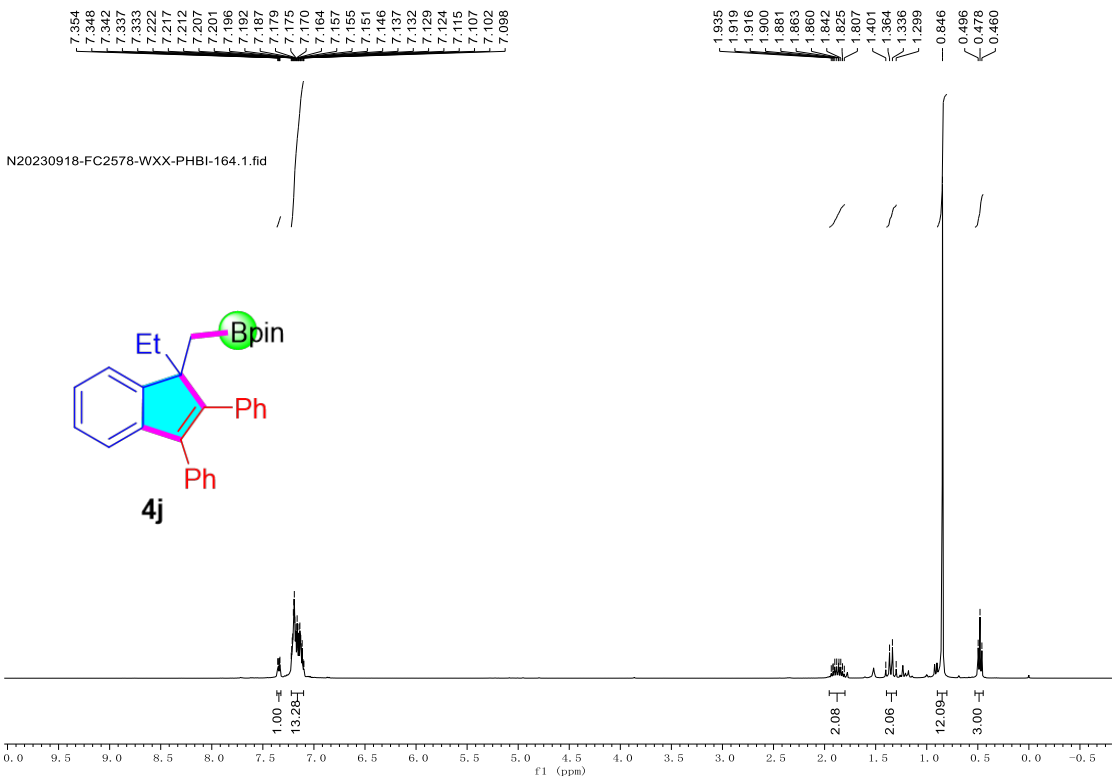
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of **4i**



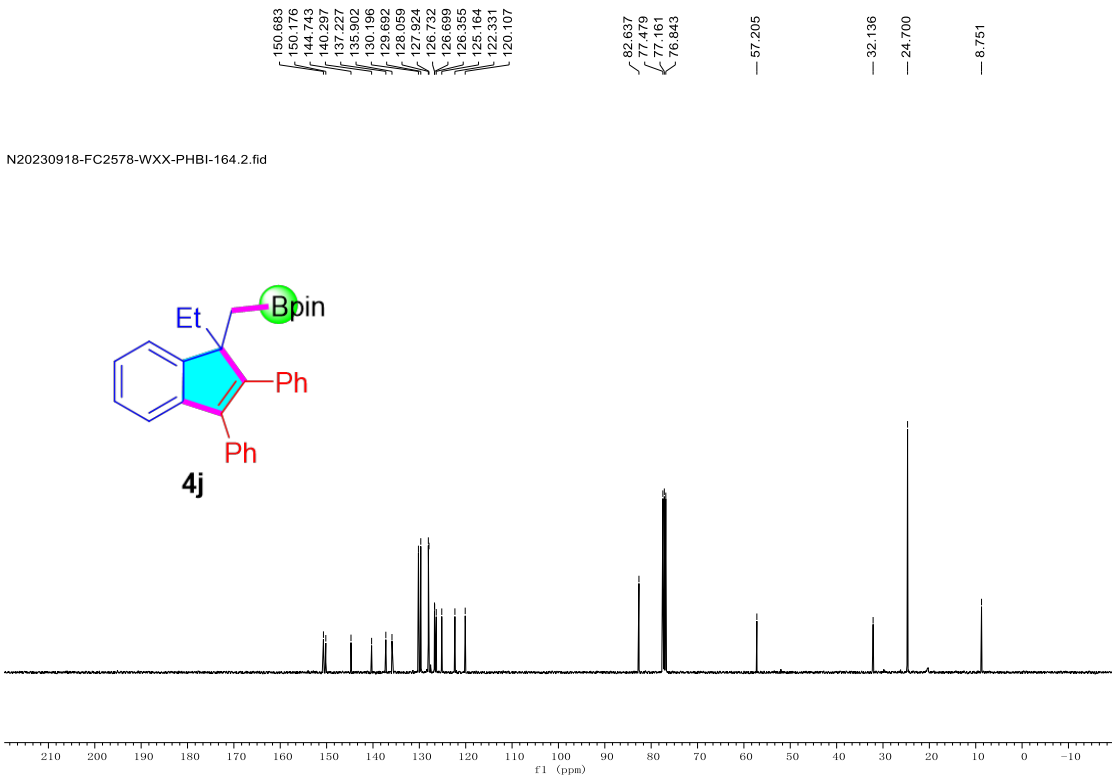
^{13}C{1H} NMR (101 MHz, $CDCl_3$) Spectrum of **4i**



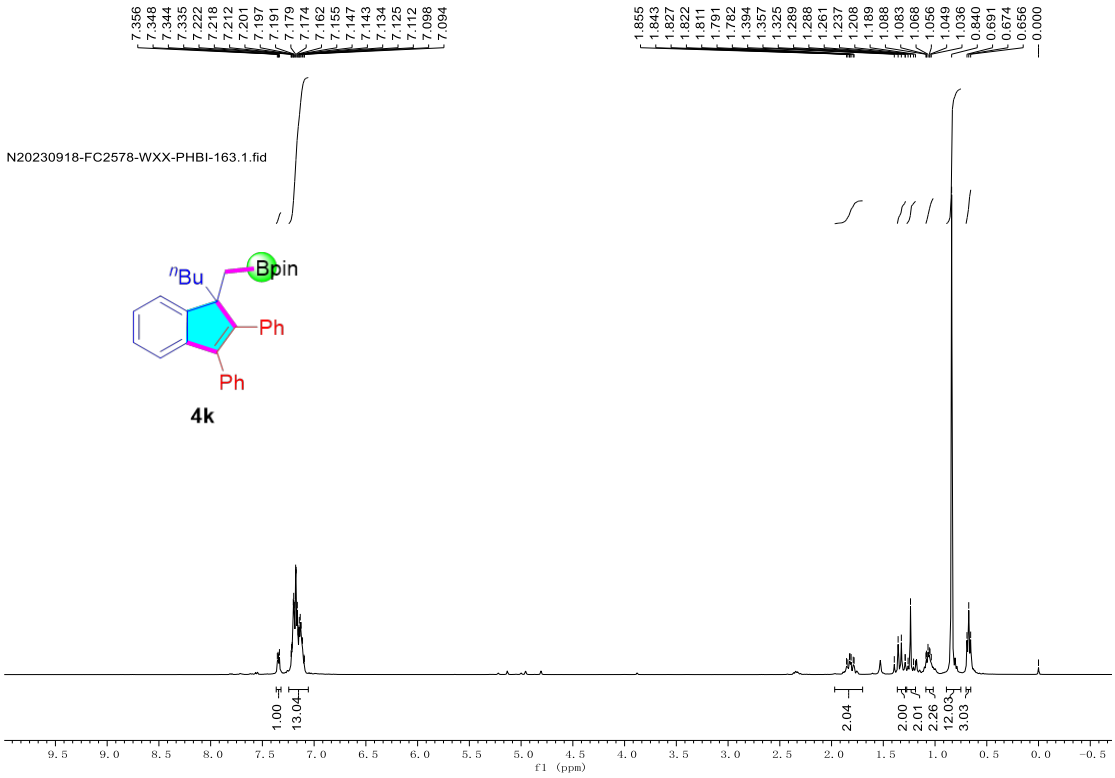
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of **4j**



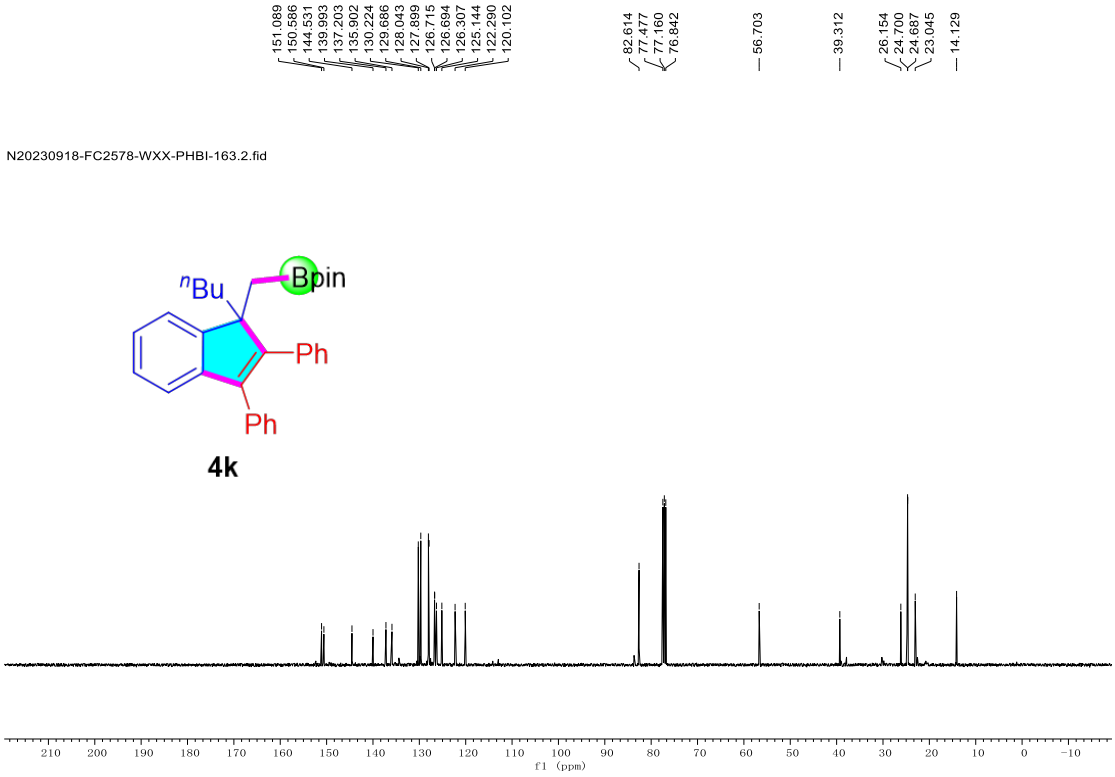
^{13}C{1H} NMR (101 MHz, $CDCl_3$) Spectrum of **4j**



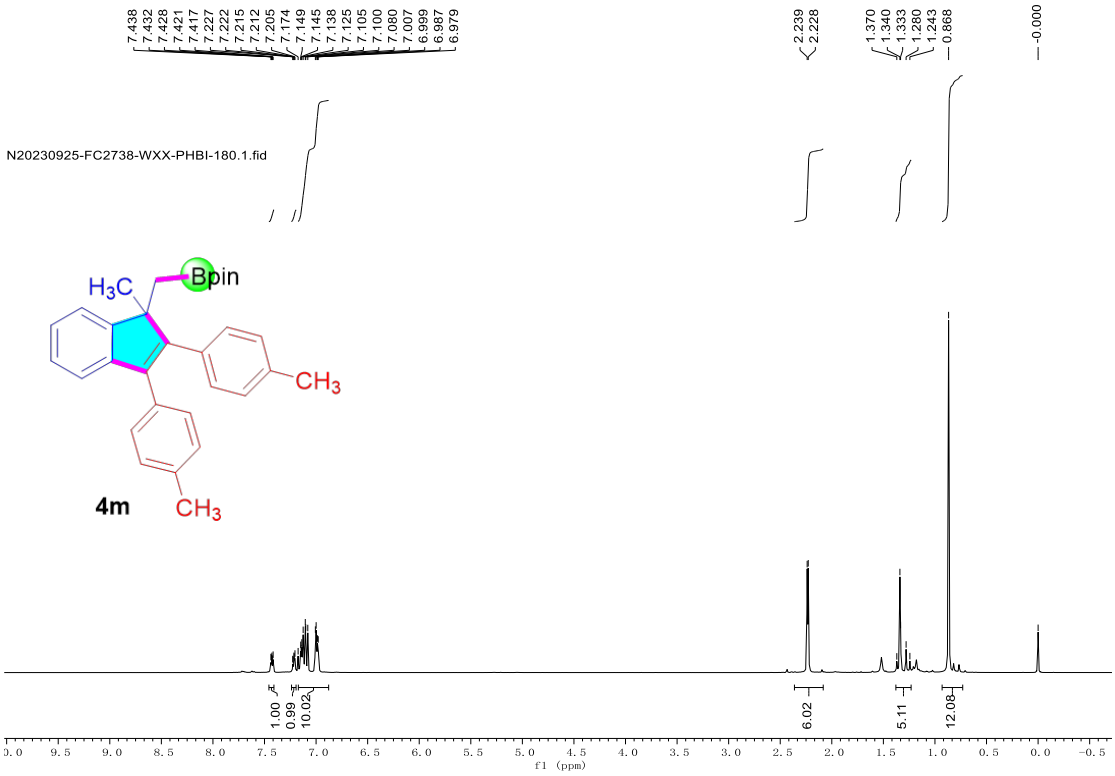
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of **4k**



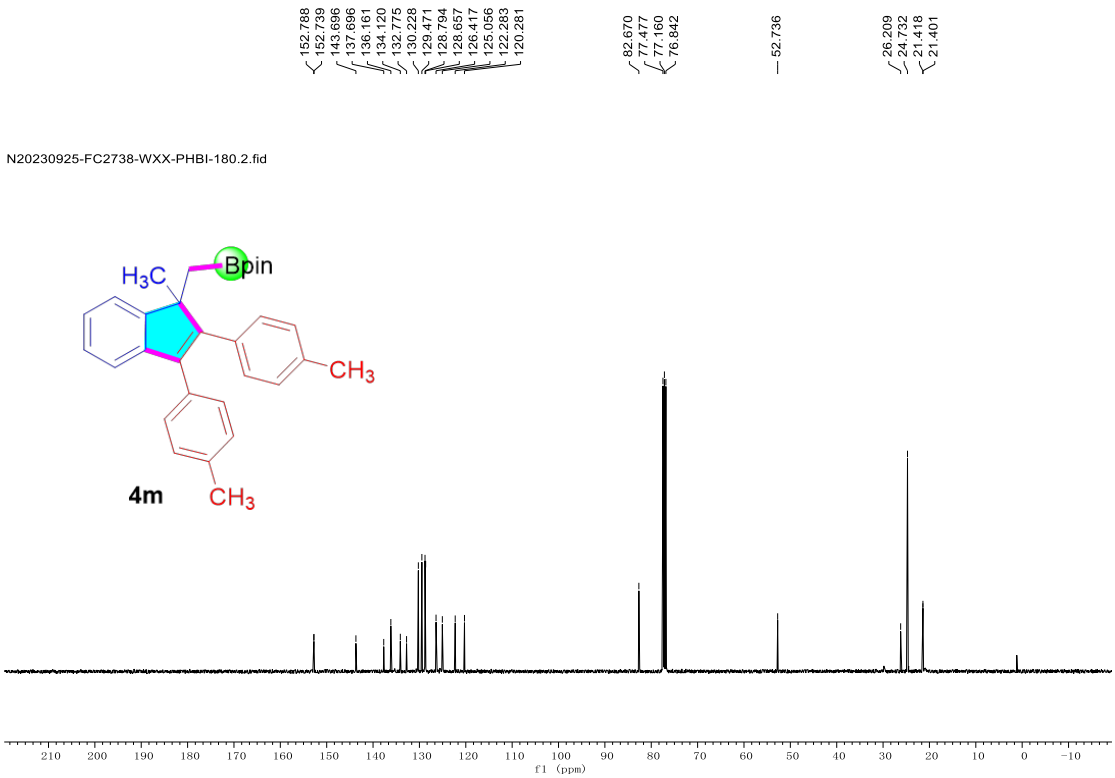
^{13}C{1H} NMR (101 MHz, $CDCl_3$) Spectrum of **4k**



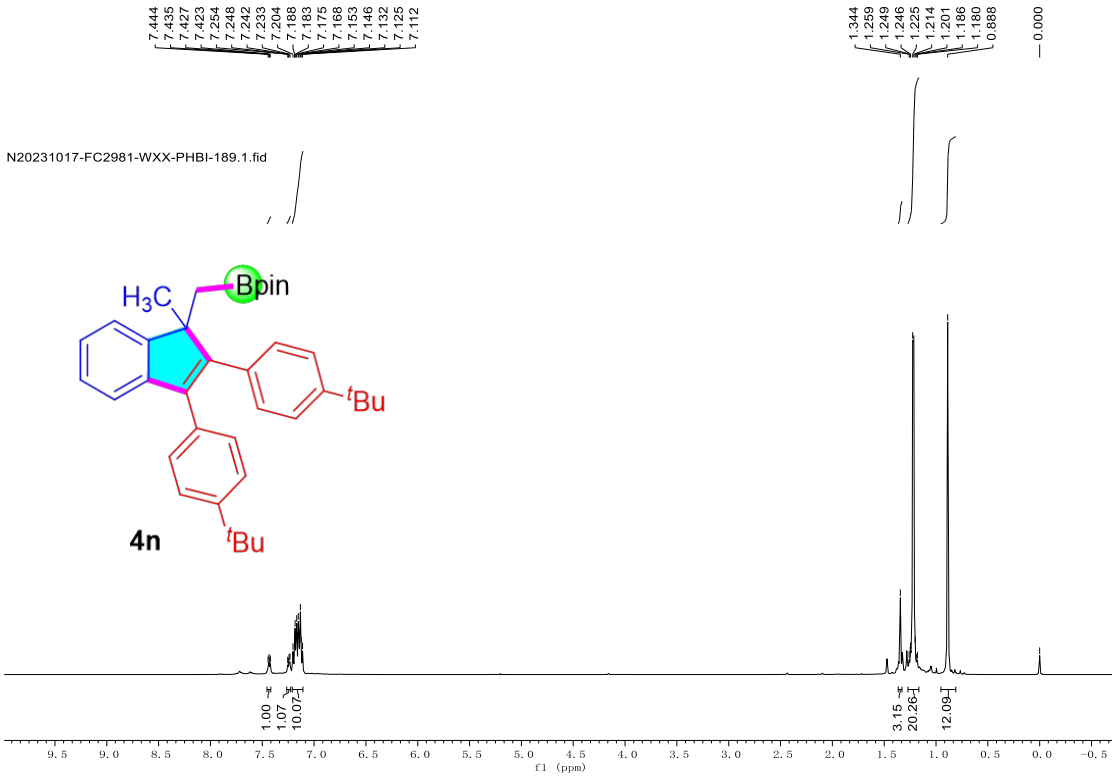
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of **4m**



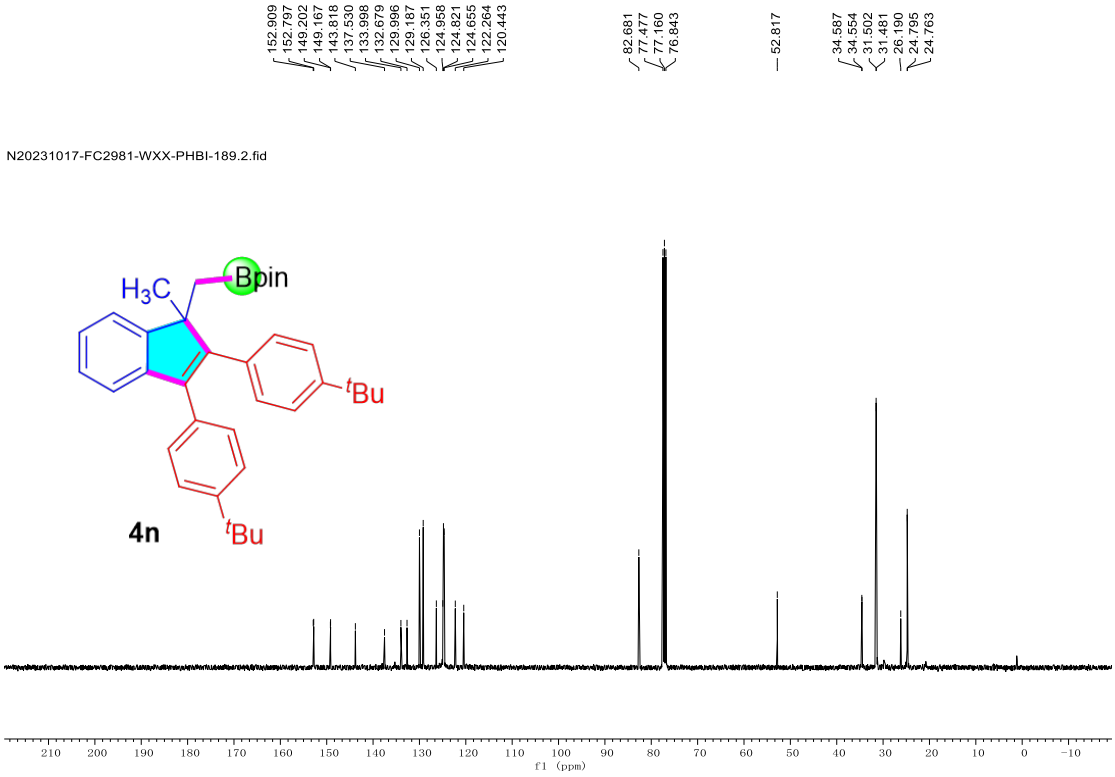
^{13}C{1H} NMR (101 MHz, $CDCl_3$) Spectrum of **4m**



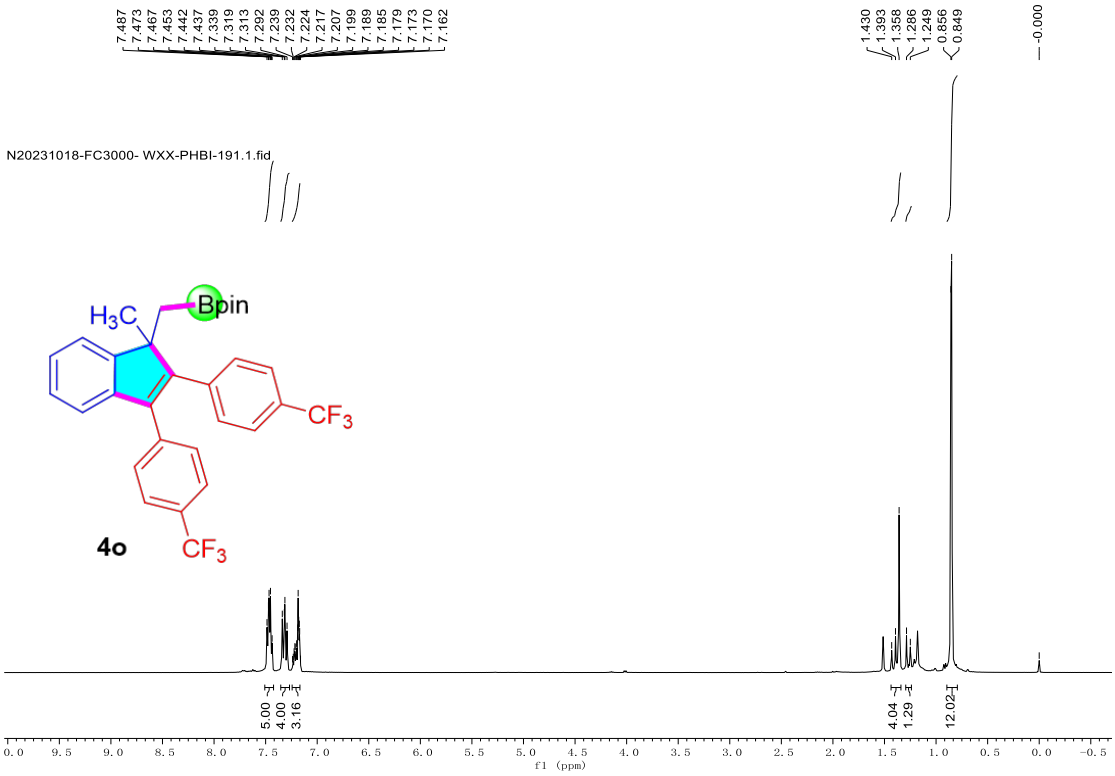
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of **4n**



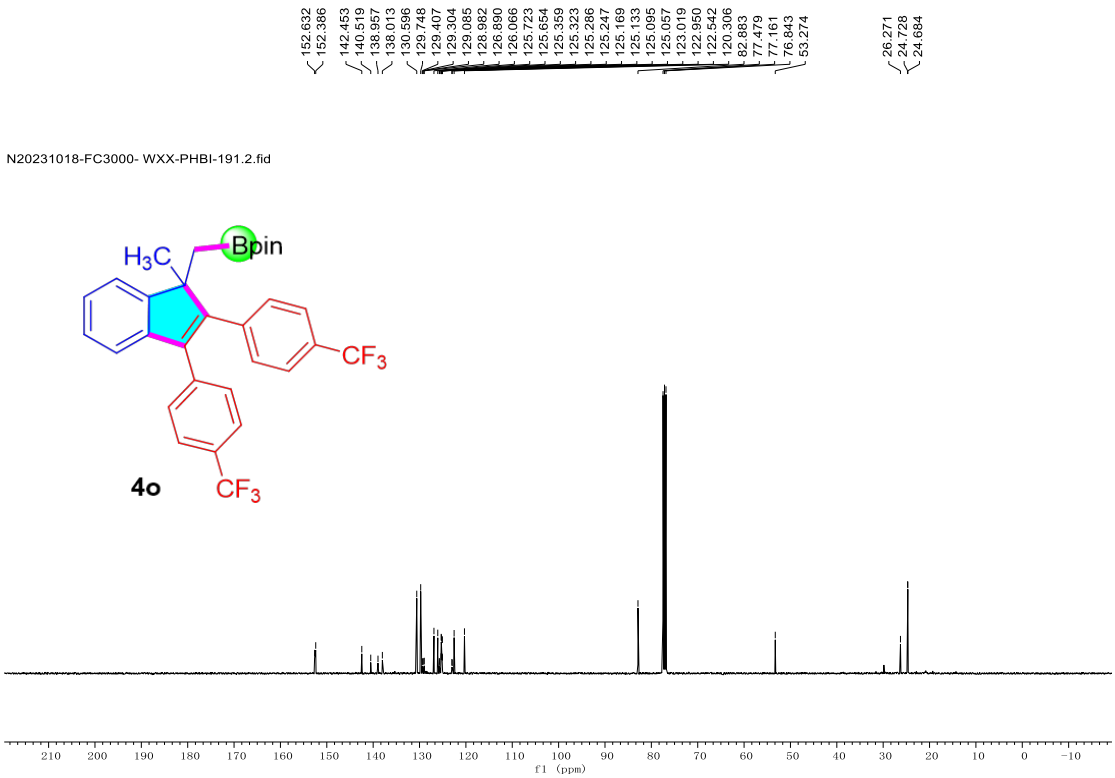
^{13}C{1H} NMR (101 MHz, $CDCl_3$) Spectrum of **4n**



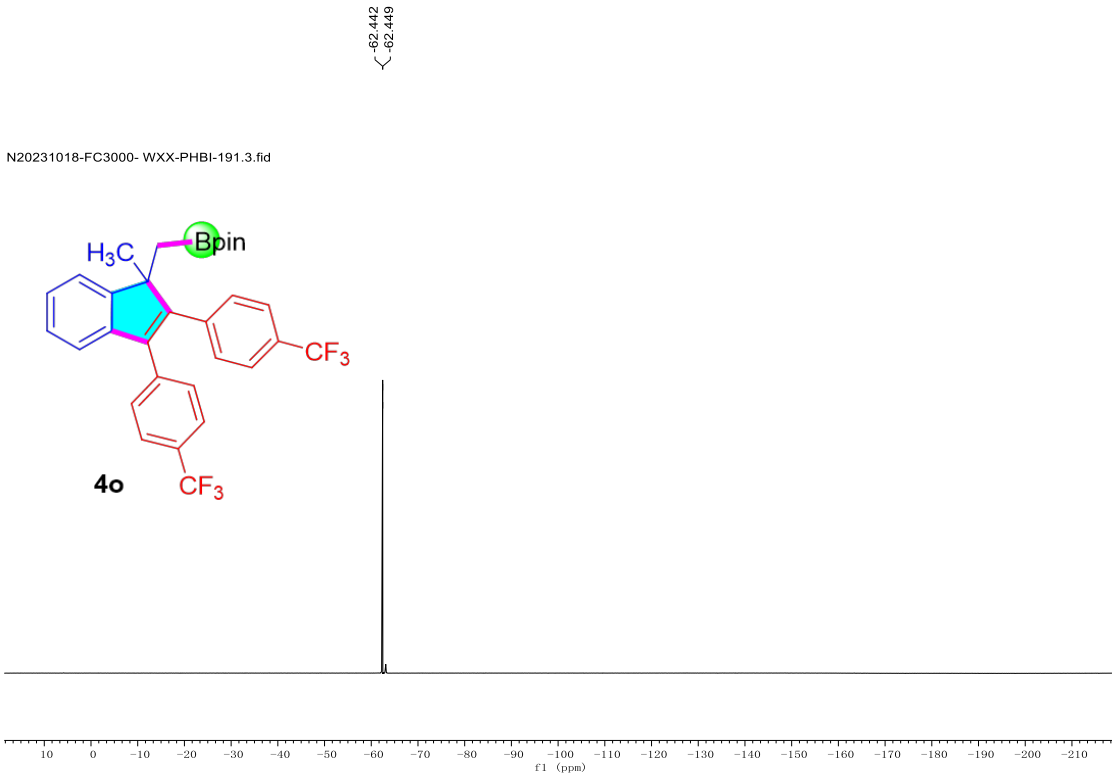
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of **4o**



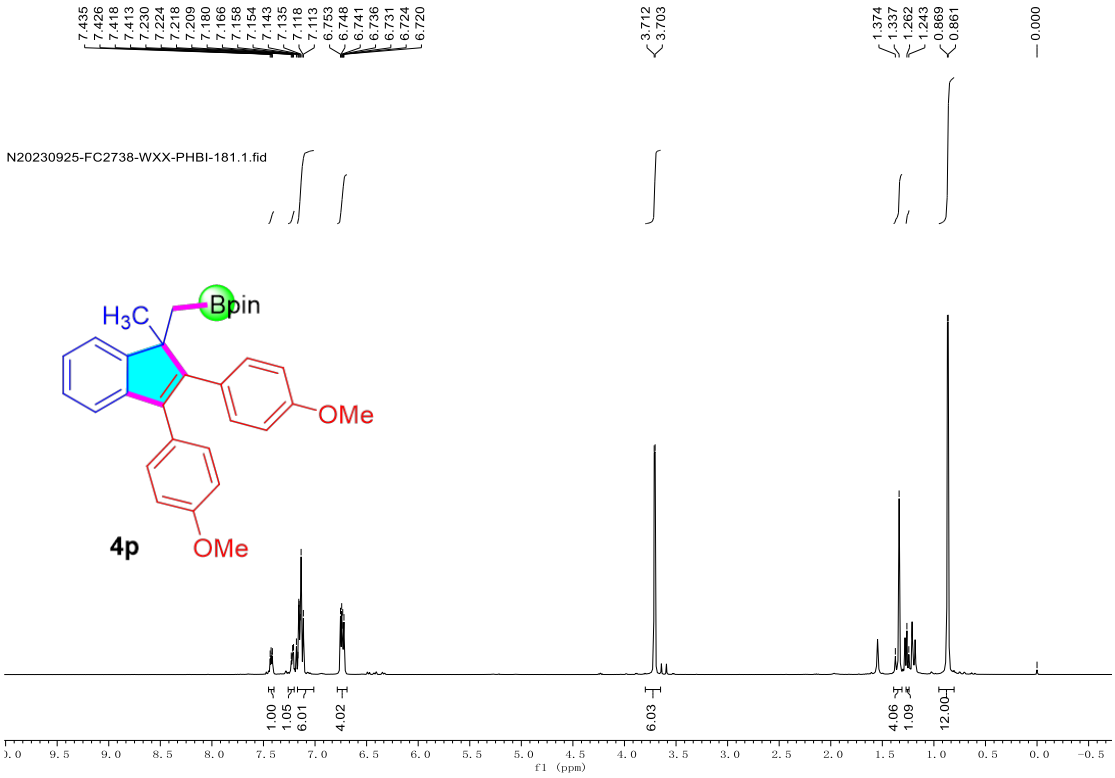
^{13}C{1H} NMR (101 MHz, $CDCl_3$) Spectrum of **4o**



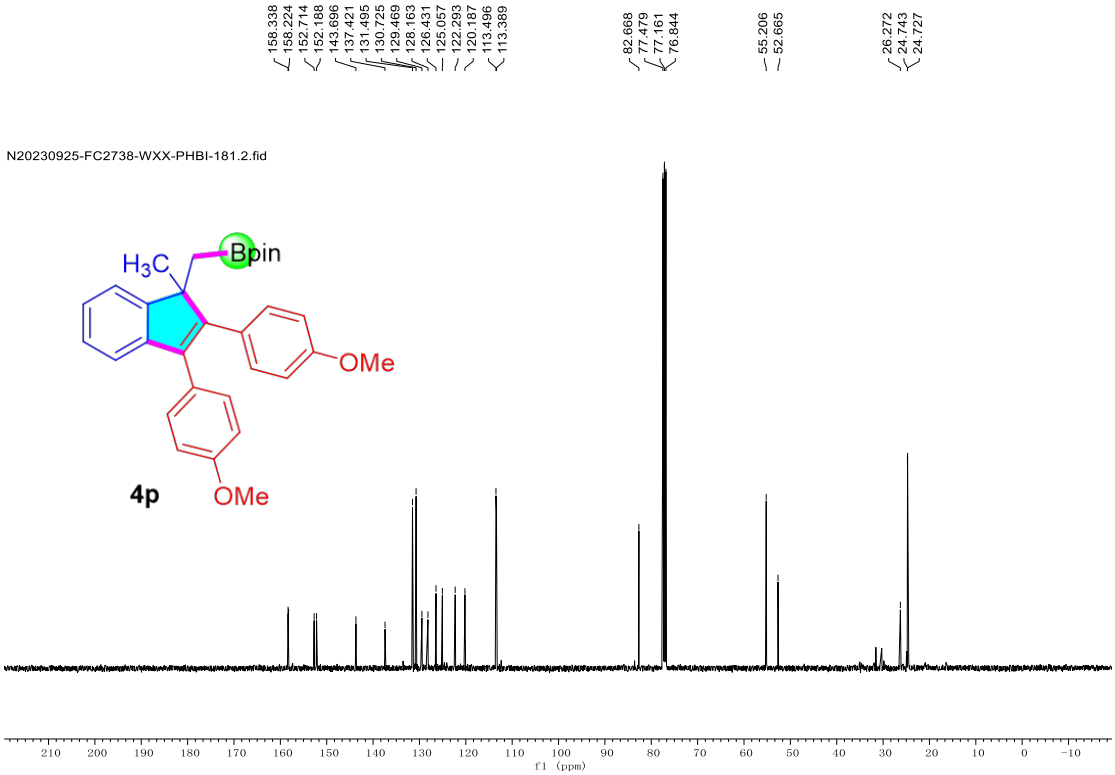
^{19}F NMR (376 MHz, $CDCl_3$) Spectrum of **4o**



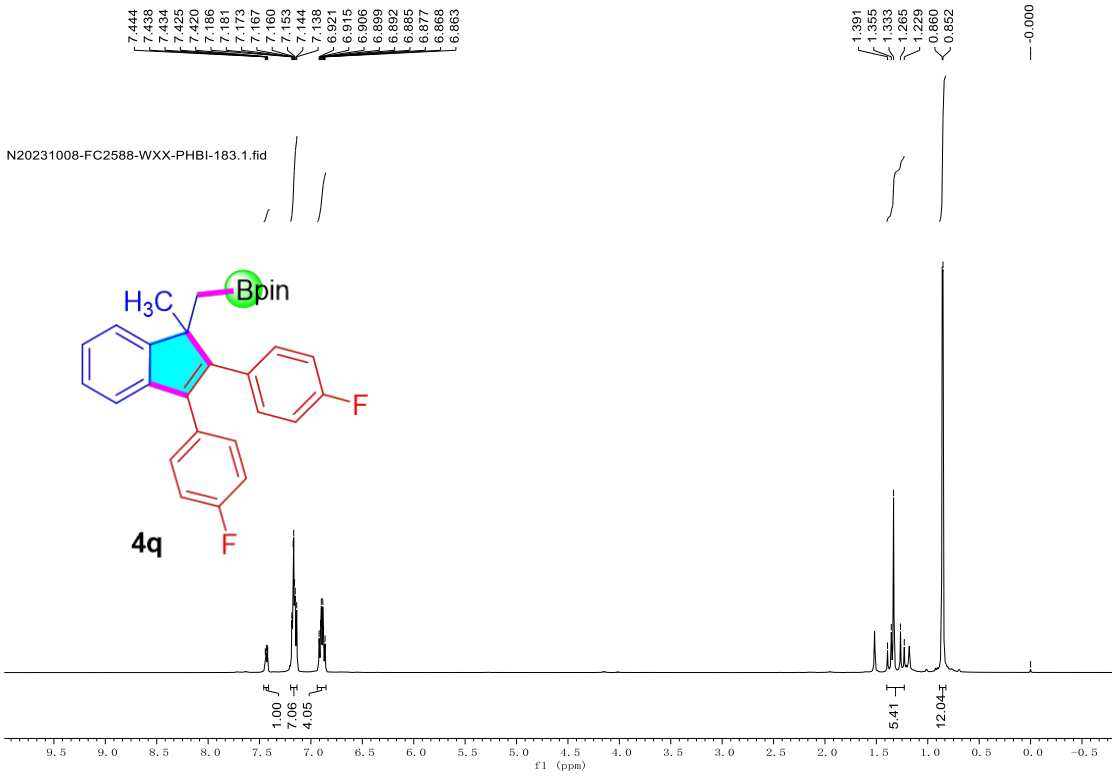
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of **4p**



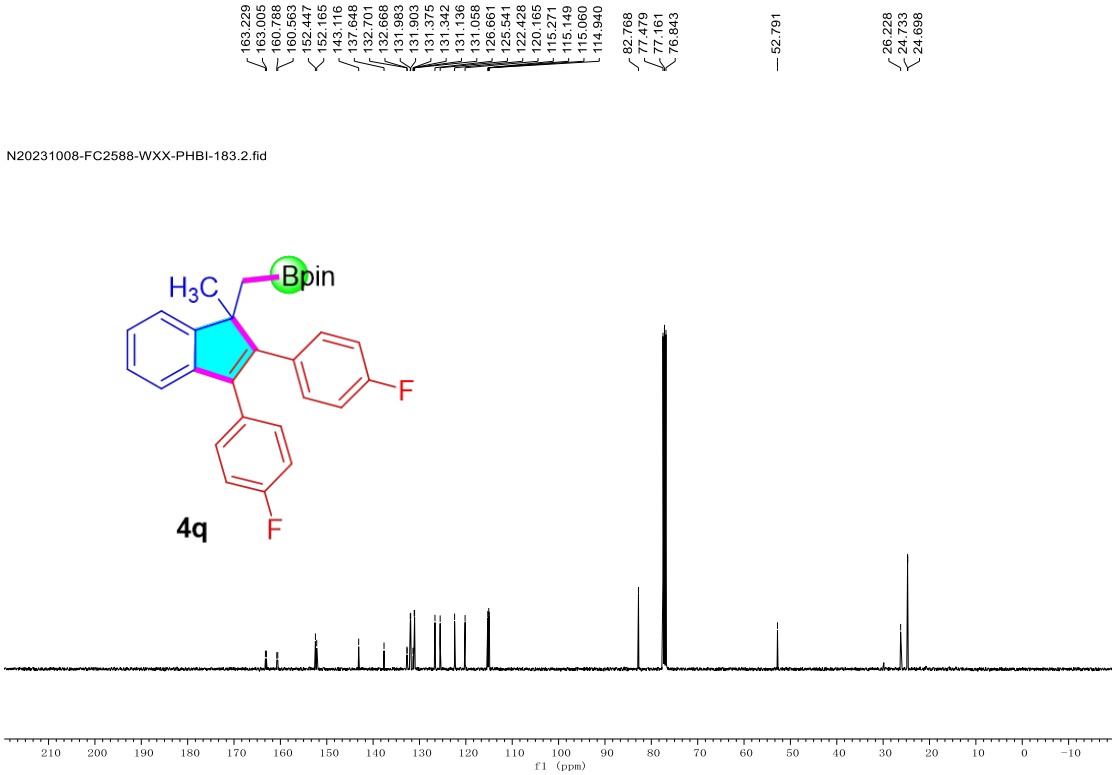
^{13}C{1H} NMR (101 MHz, $CDCl_3$) Spectrum of **4p**



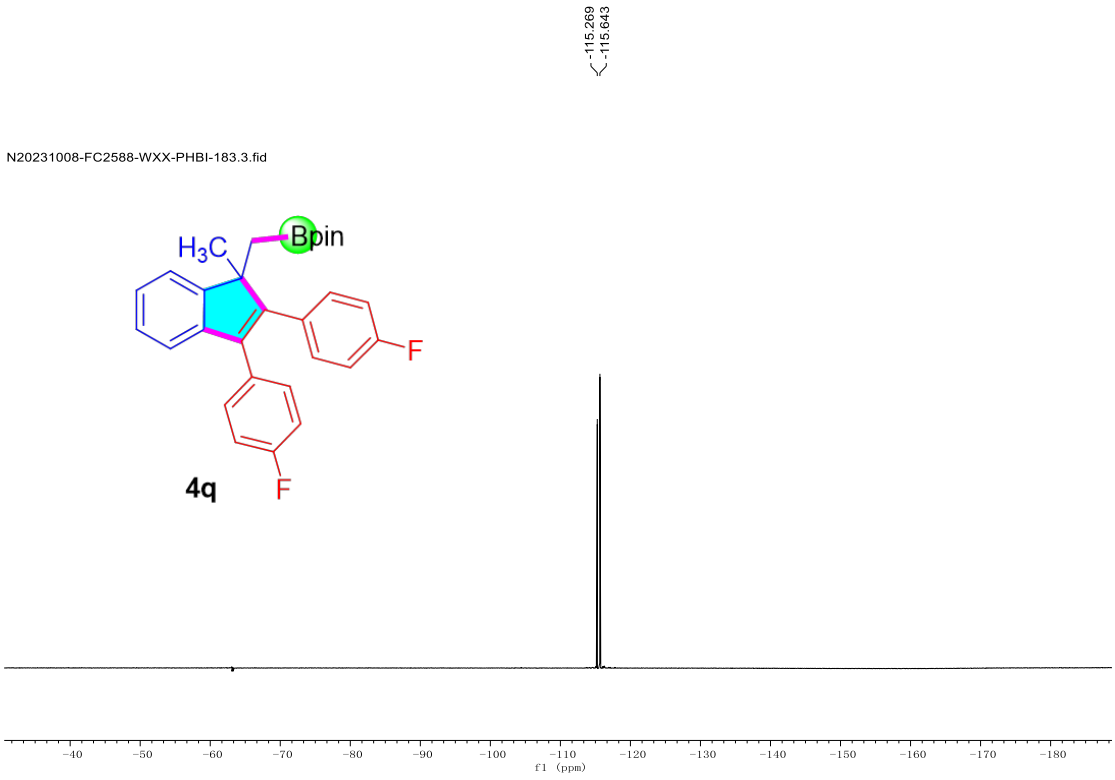
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of **4q**



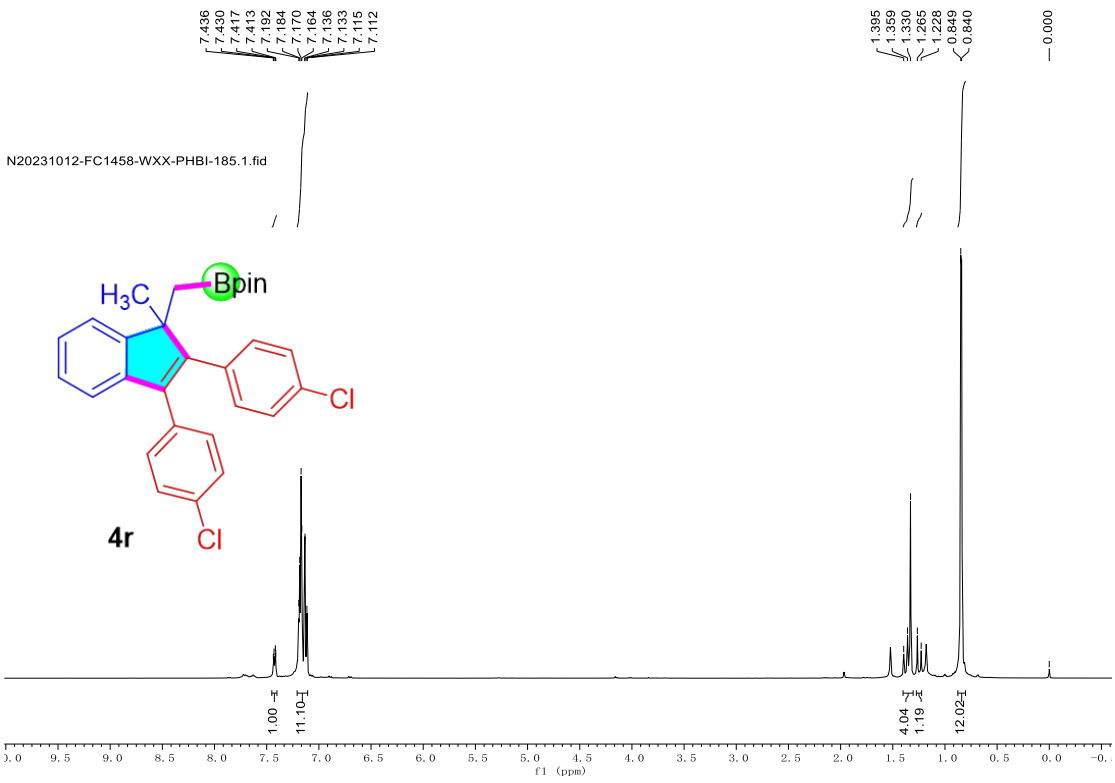
^{13}C{1H} NMR (101 MHz, $CDCl_3$) Spectrum of **4q**



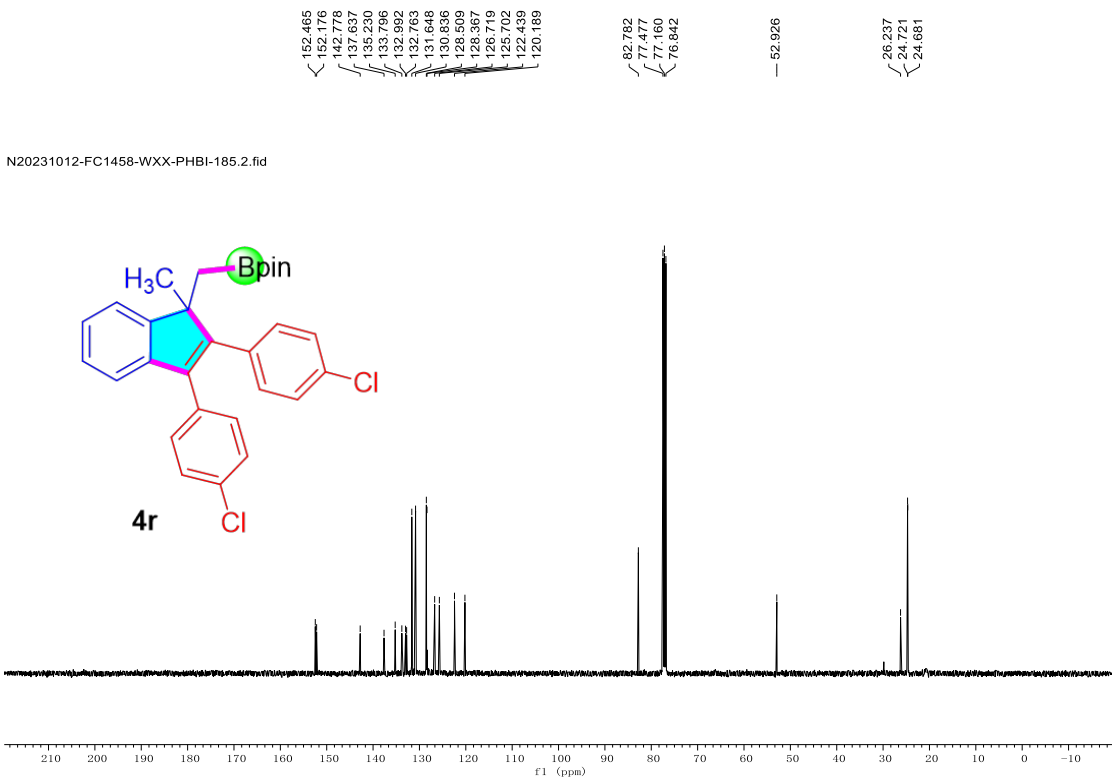
^{19}F NMR (376 MHz, $CDCl_3$) Spectrum of **4q**



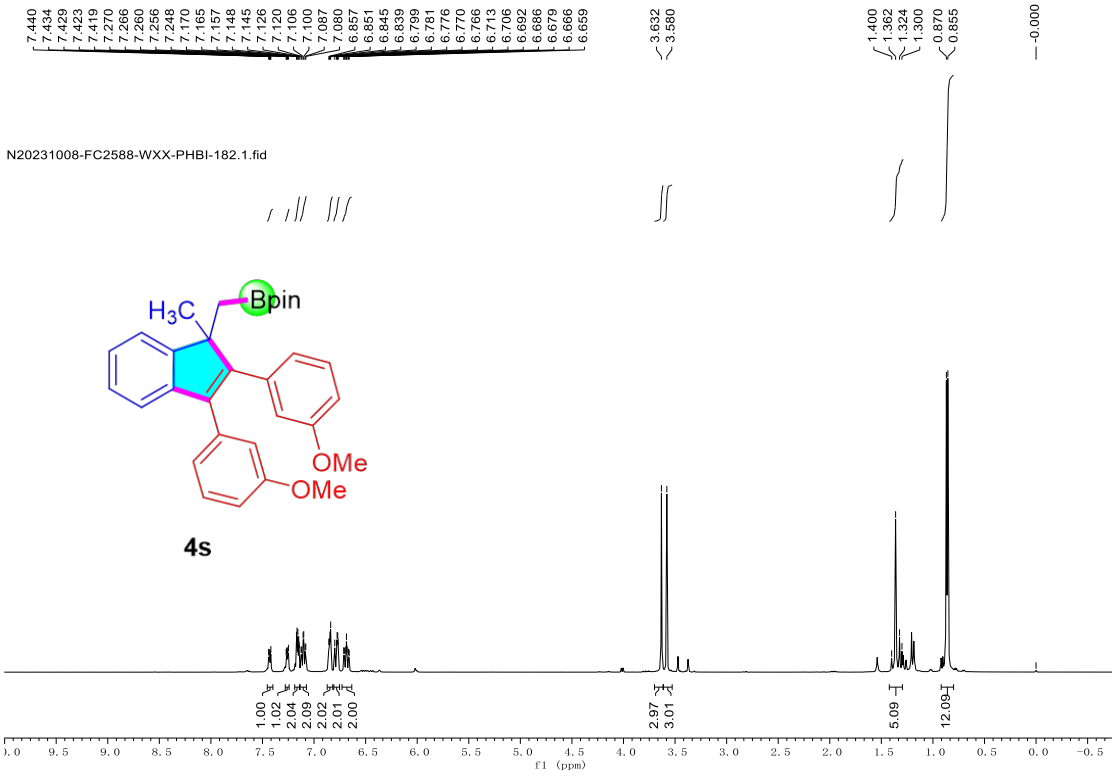
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of **4r**



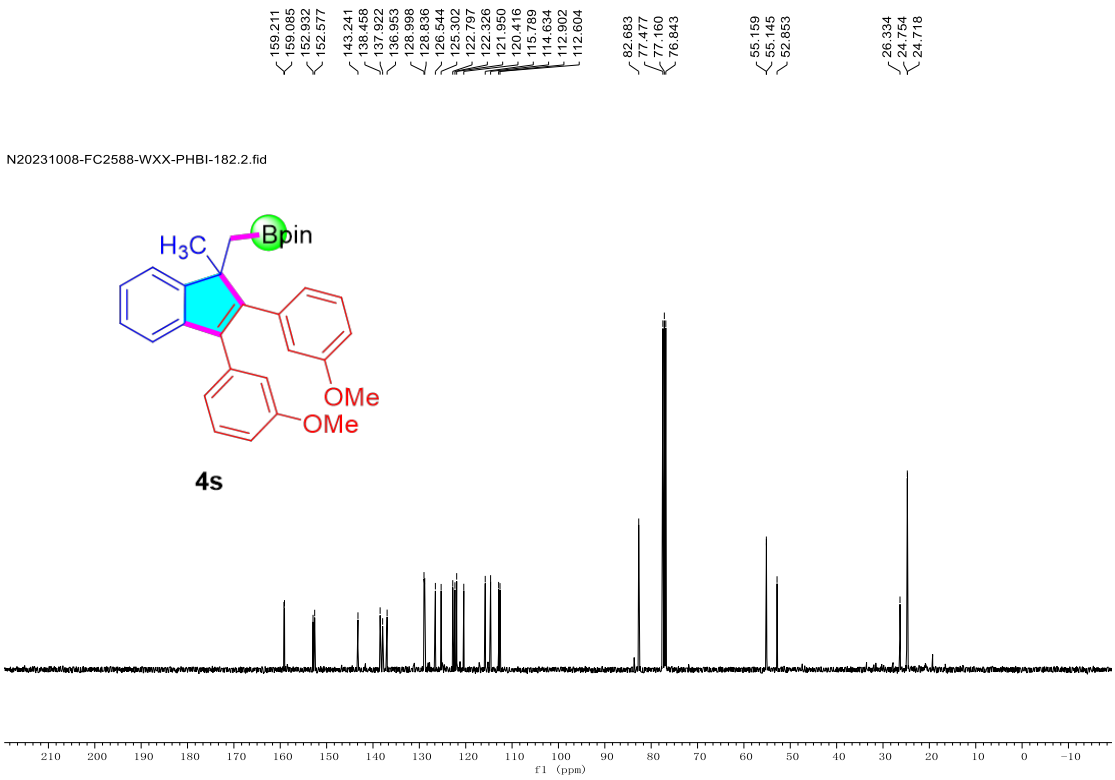
^{13}C{1H} NMR (101 MHz, $CDCl_3$) Spectrum of **4r**



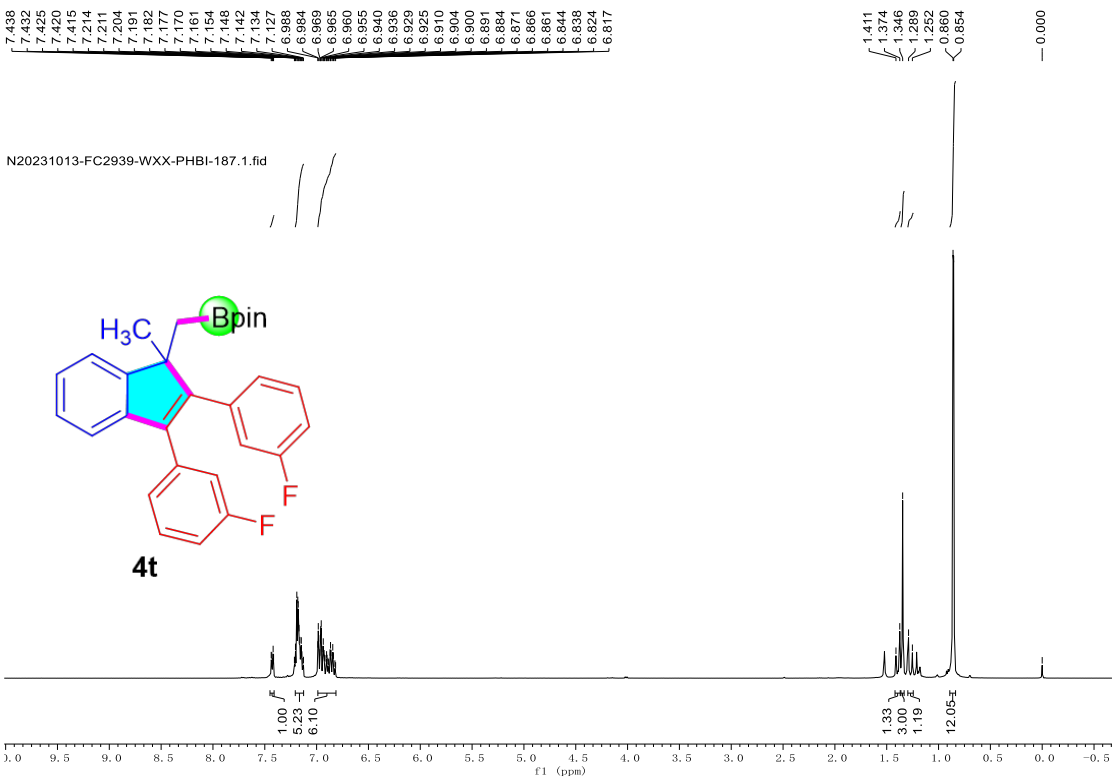
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of **4s**



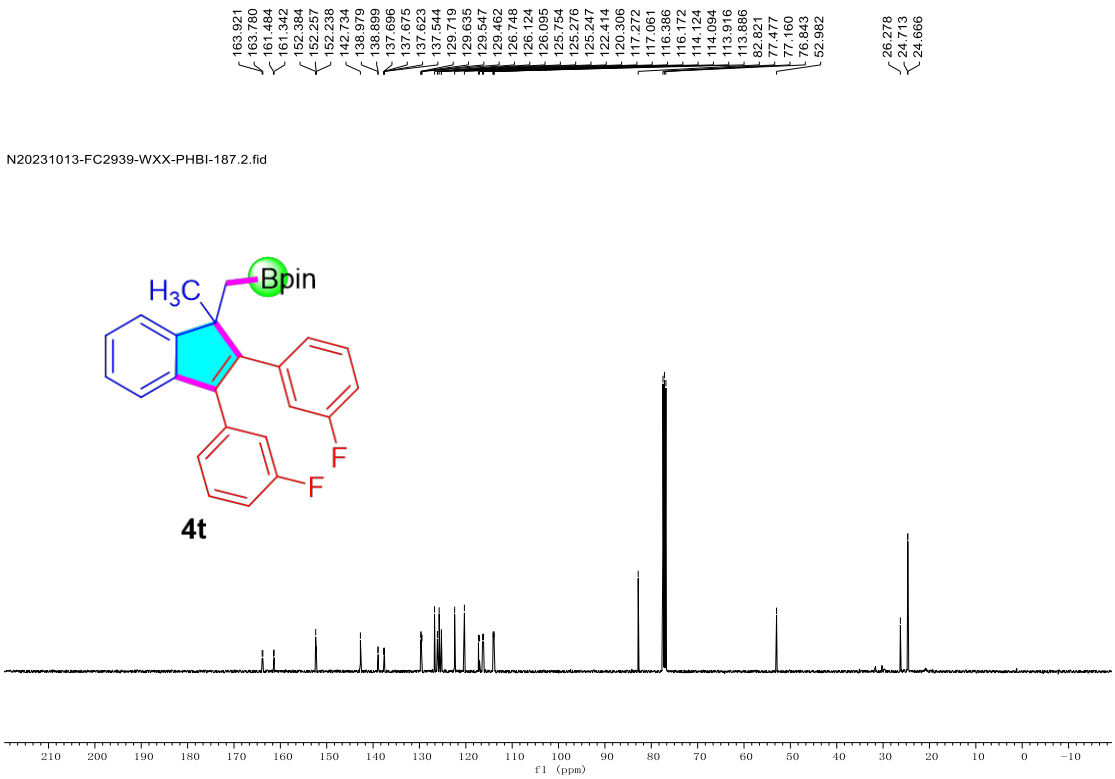
^{13}C{1H} NMR (101 MHz, $CDCl_3$) Spectrum of **4s**



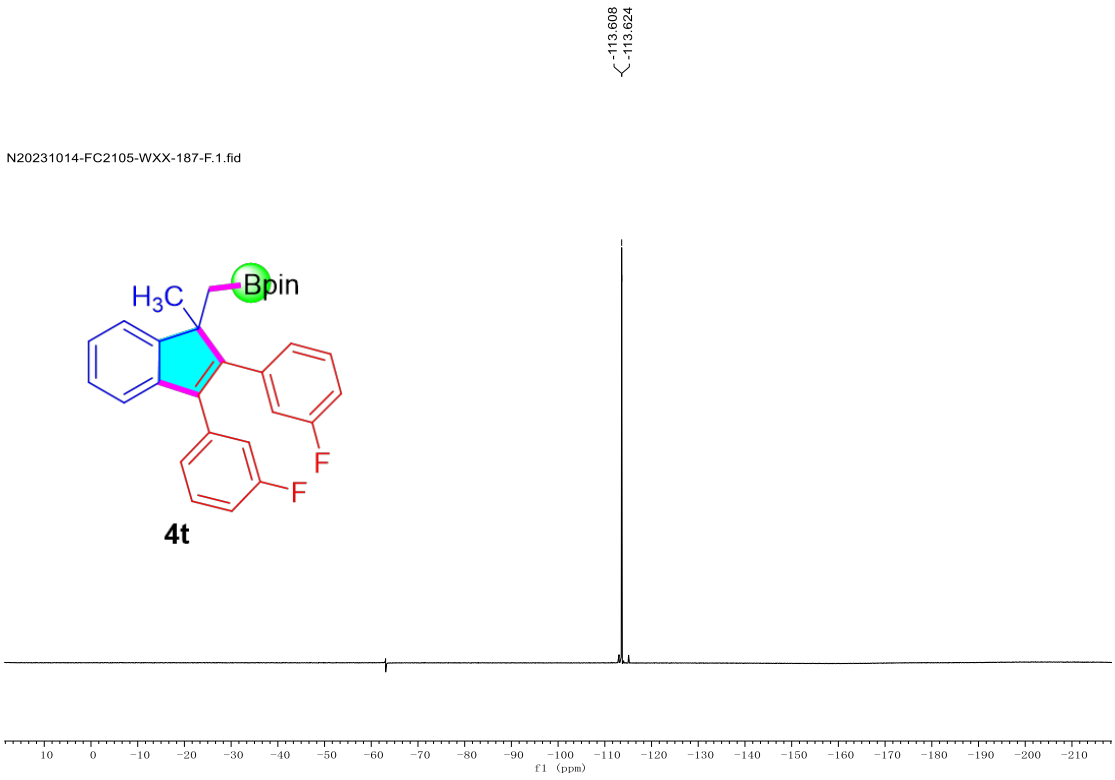
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of **4t**



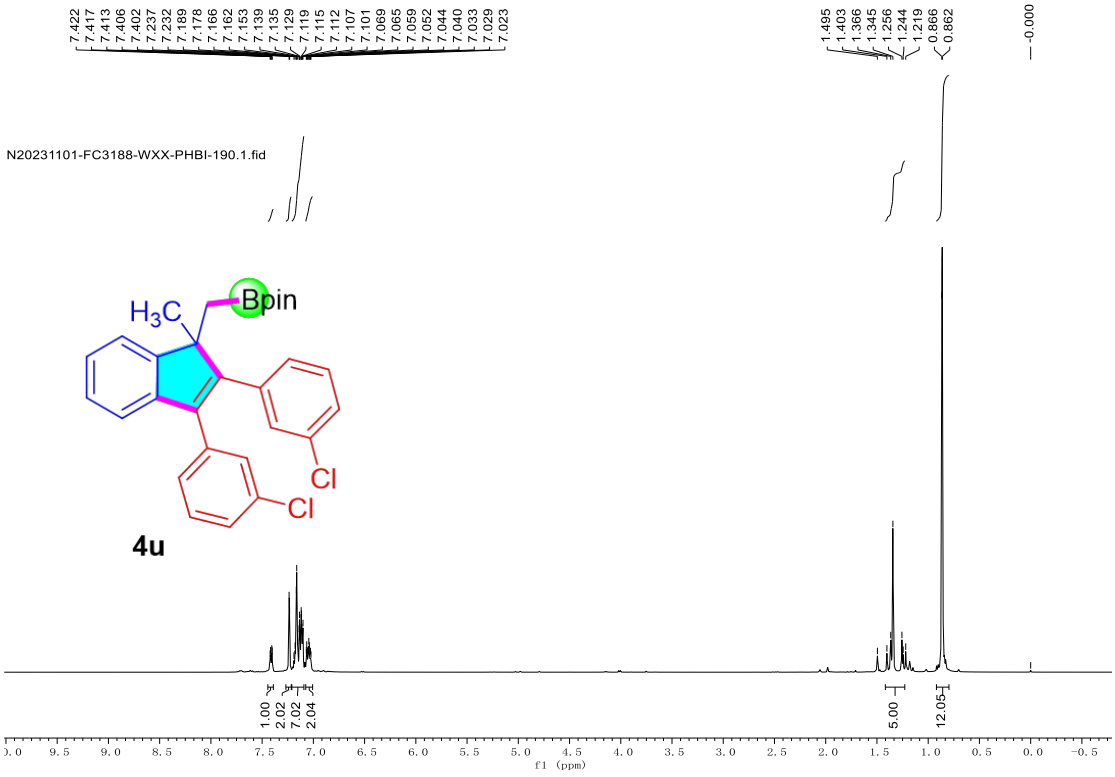
^{13}C{1H} NMR (101 MHz, $CDCl_3$) Spectrum of **4t**



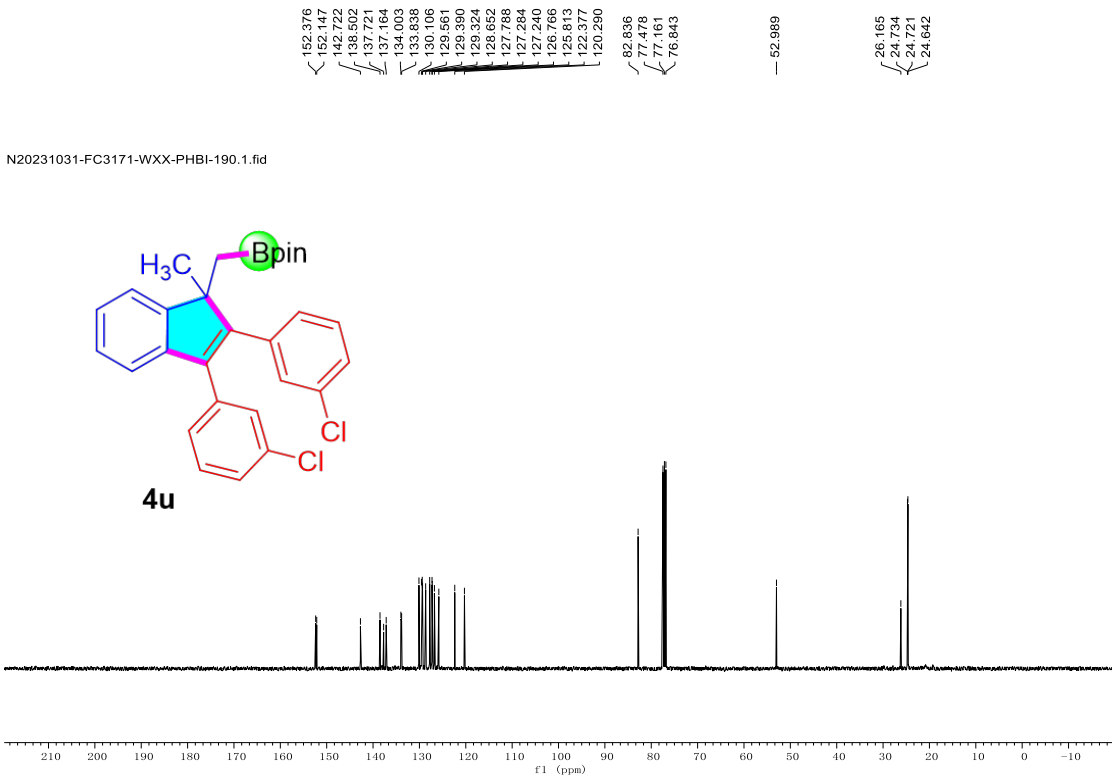
^{19}F NMR (376 MHz, $CDCl_3$) Spectrum of **4t**



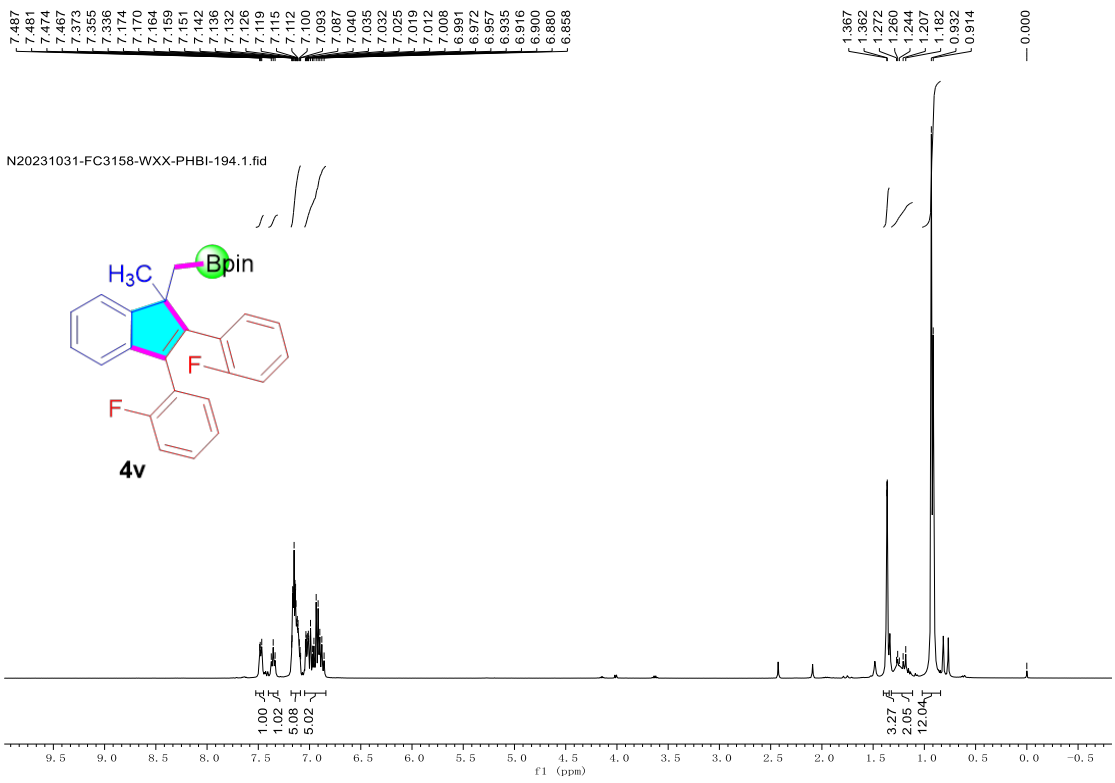
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of **4u**



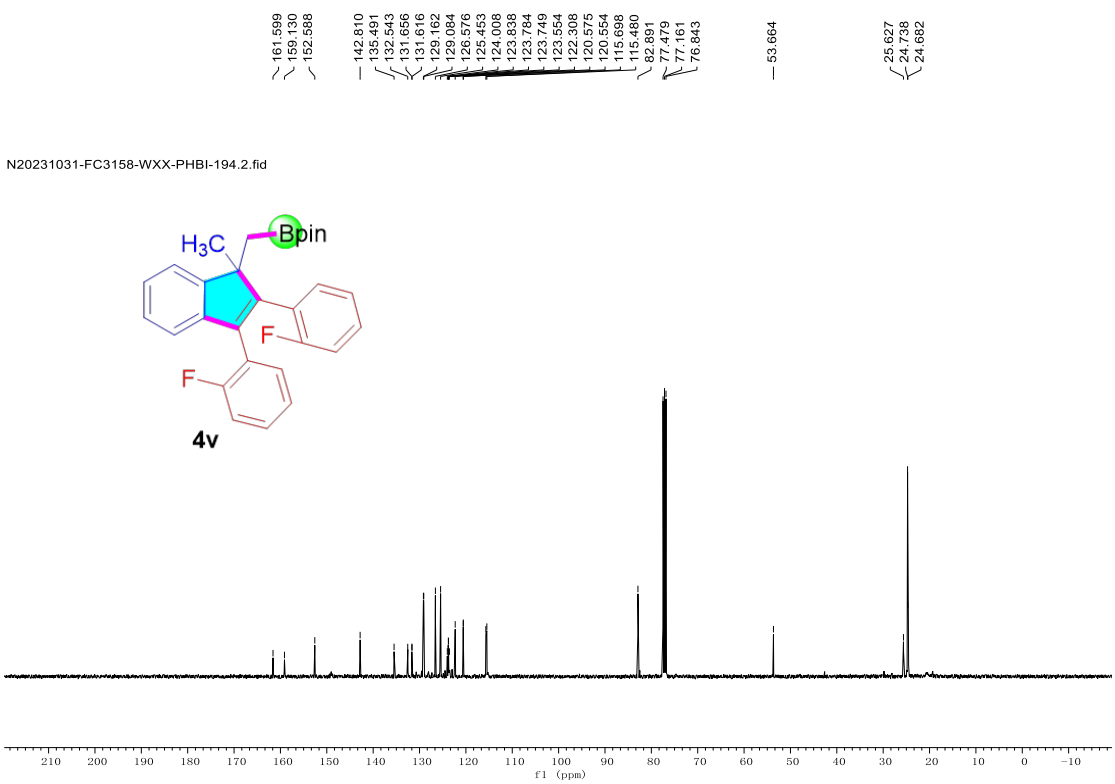
^{13}C{1H} NMR (101 MHz, $CDCl_3$) Spectrum of **4u**



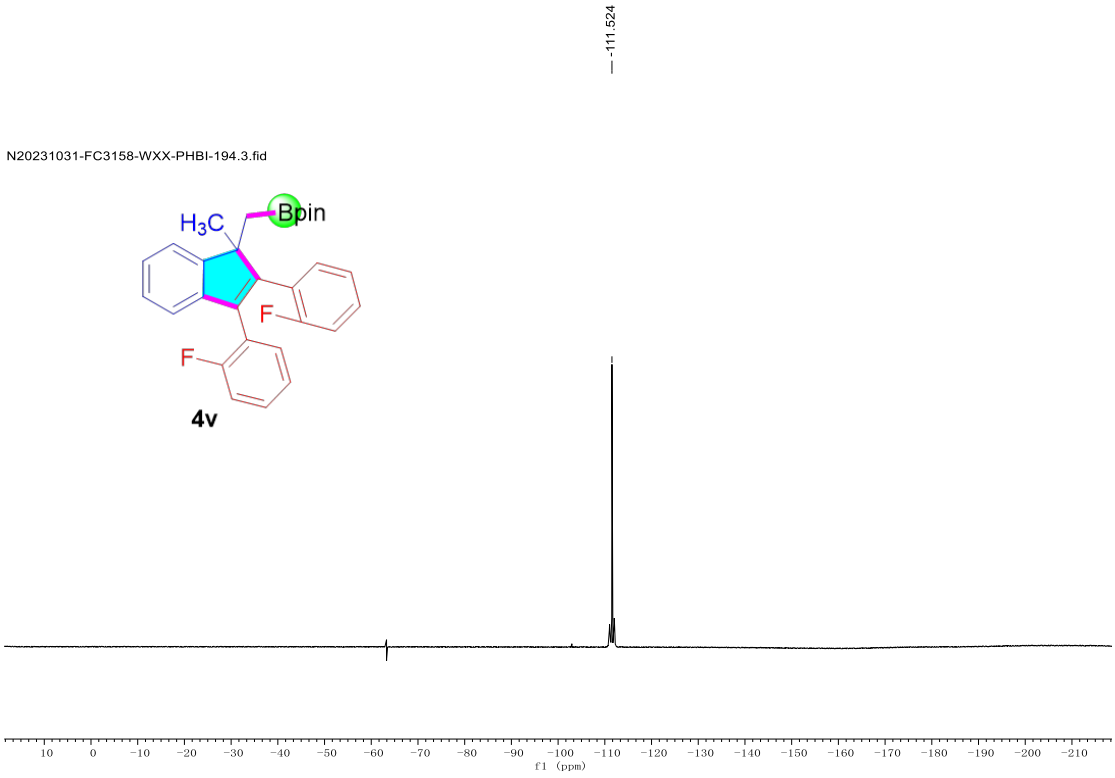
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of **4v**



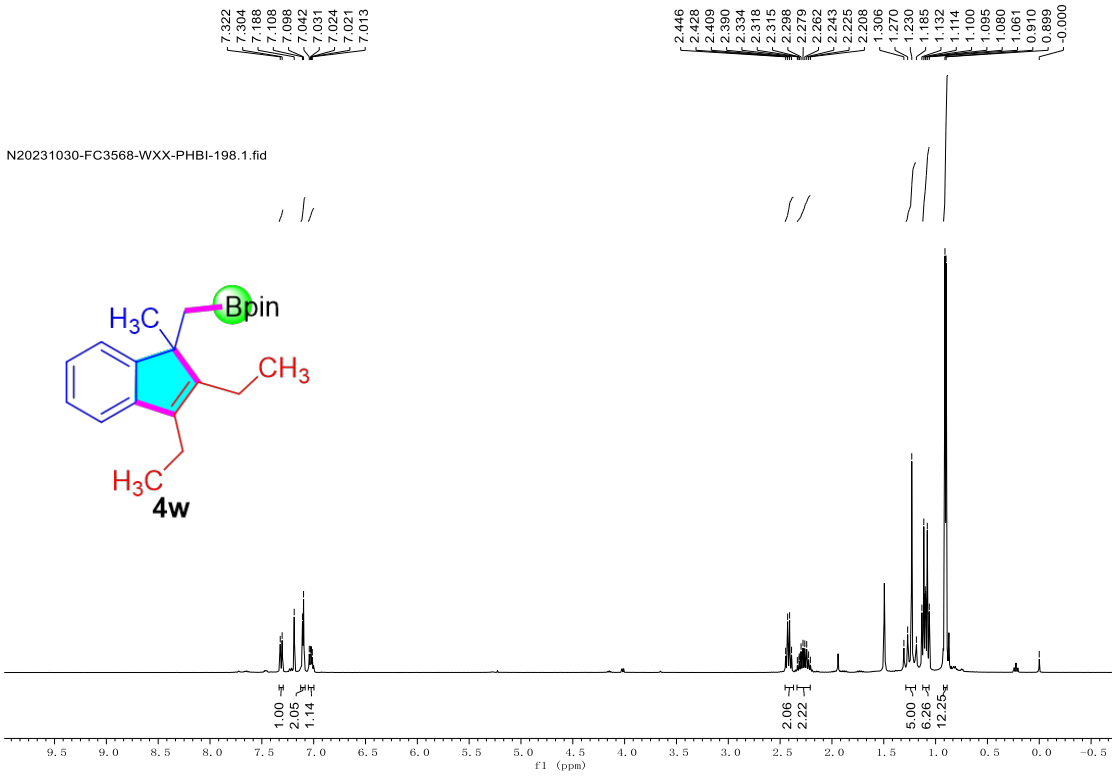
^{13}C{1H} NMR (101 MHz, $CDCl_3$) Spectrum of **4v**



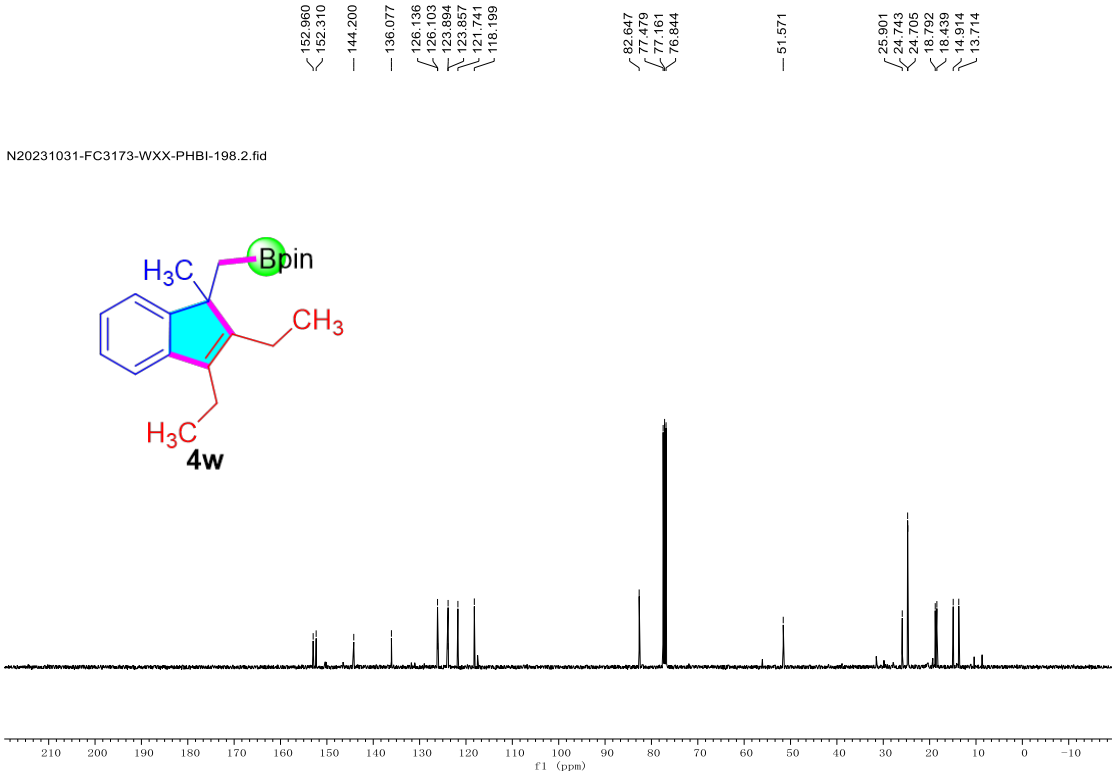
^{19}F NMR (376 MHz, $CDCl_3$) Spectrum of **4v**



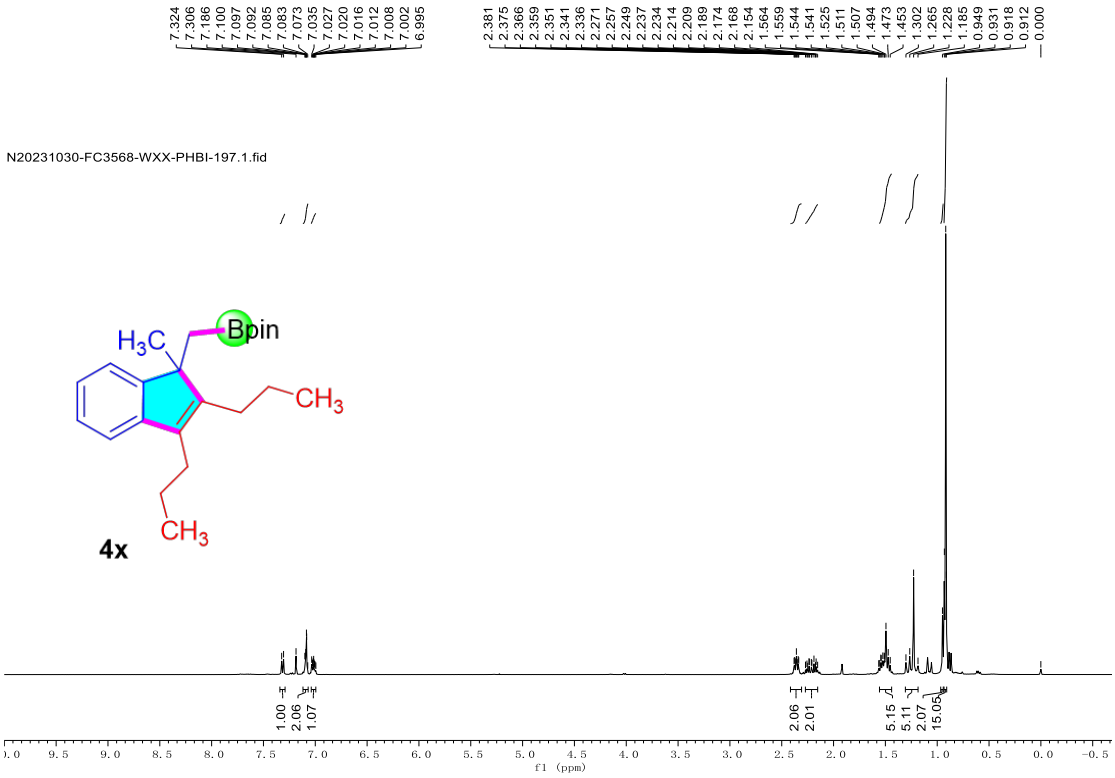
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of **4w**



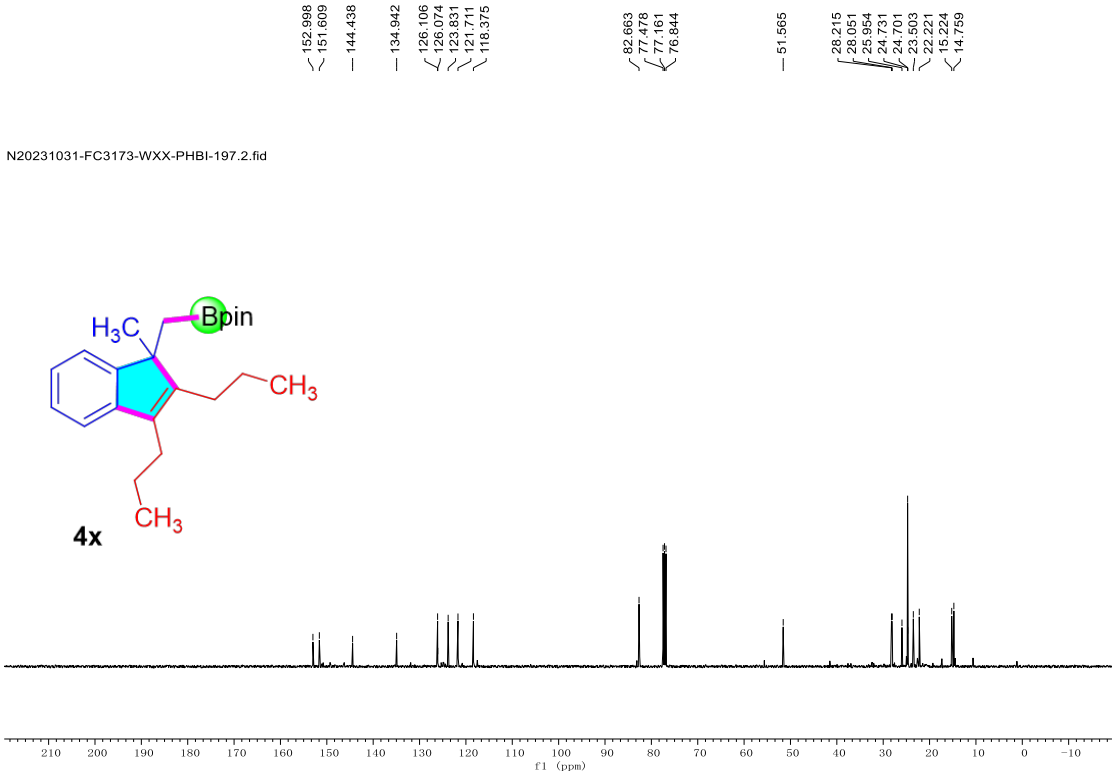
^{13}C{1H} NMR (101 MHz, $CDCl_3$) Spectrum of **4w**



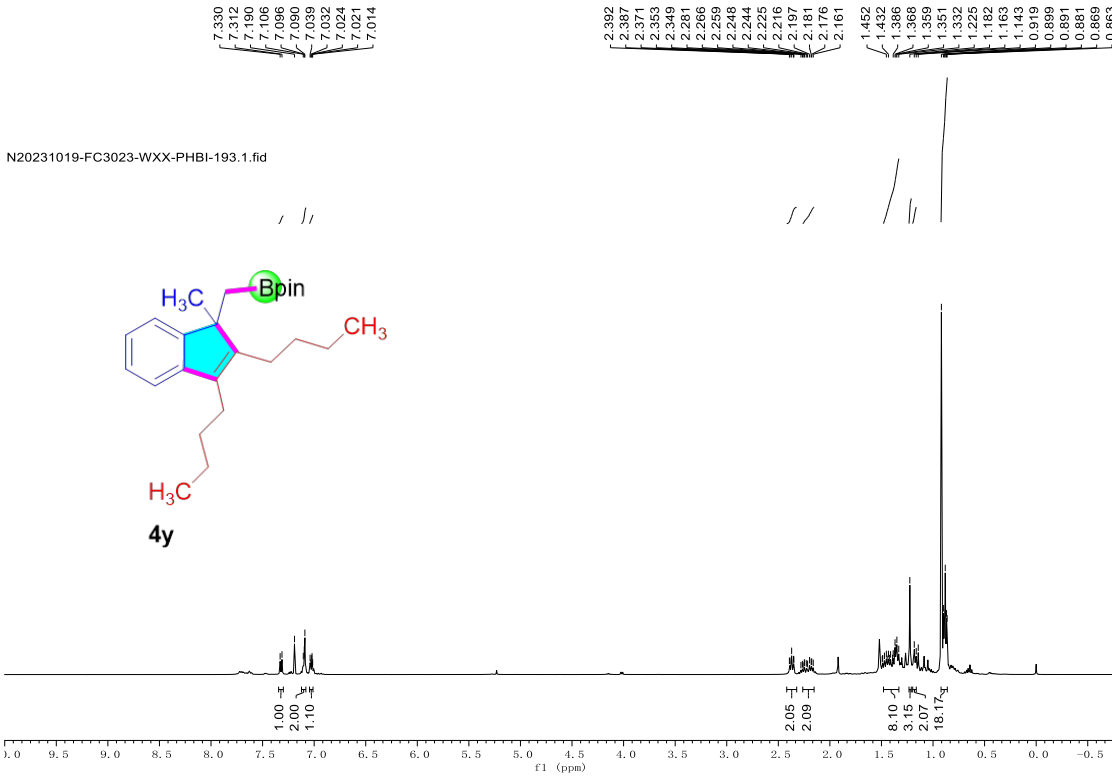
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of **4x**



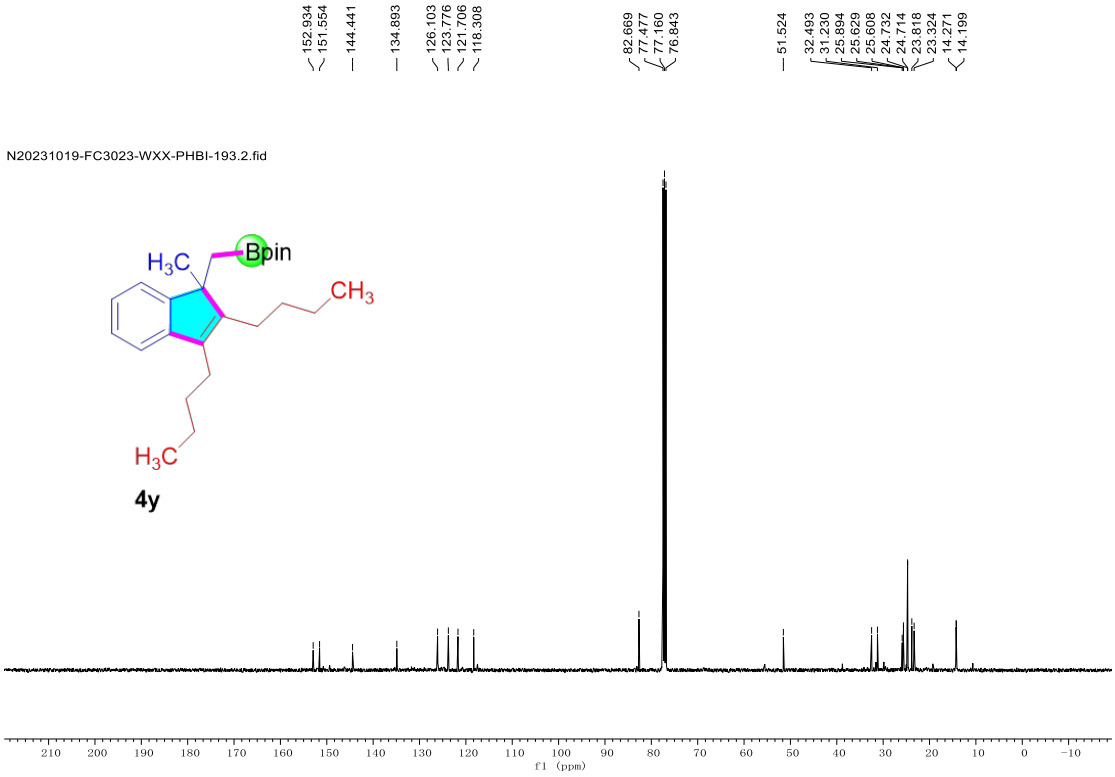
^{13}C{1H} NMR (101 MHz, $CDCl_3$) Spectrum of **4x**



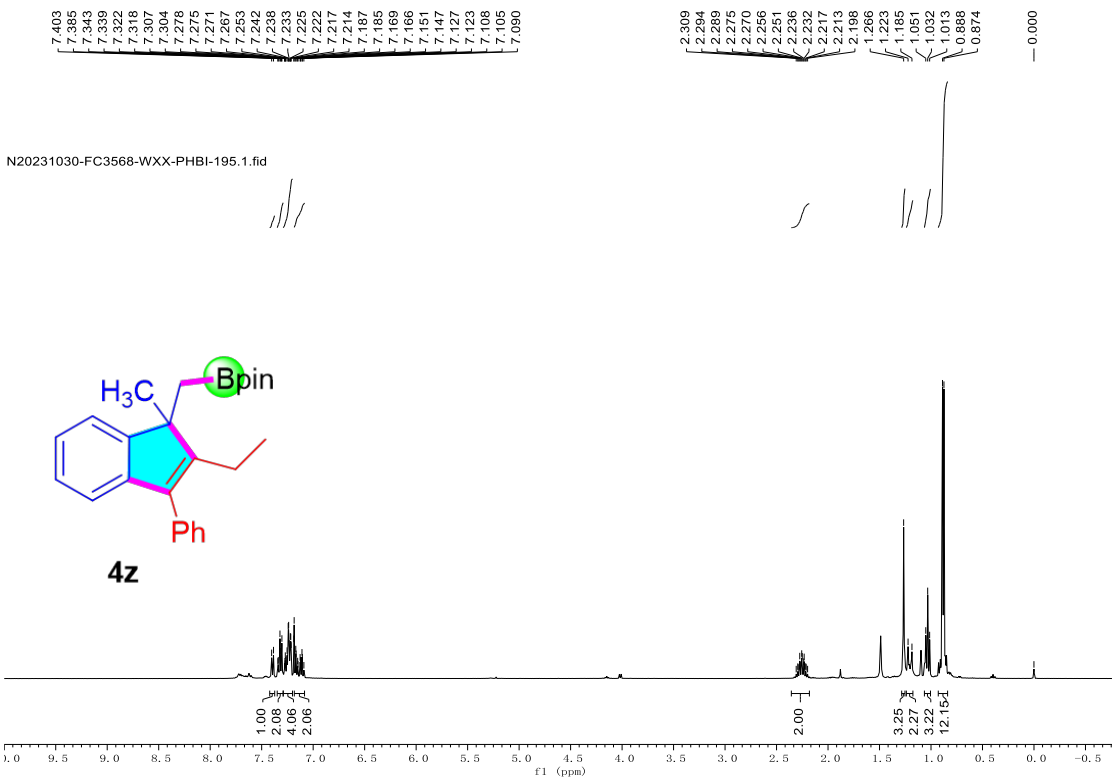
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of **4y**



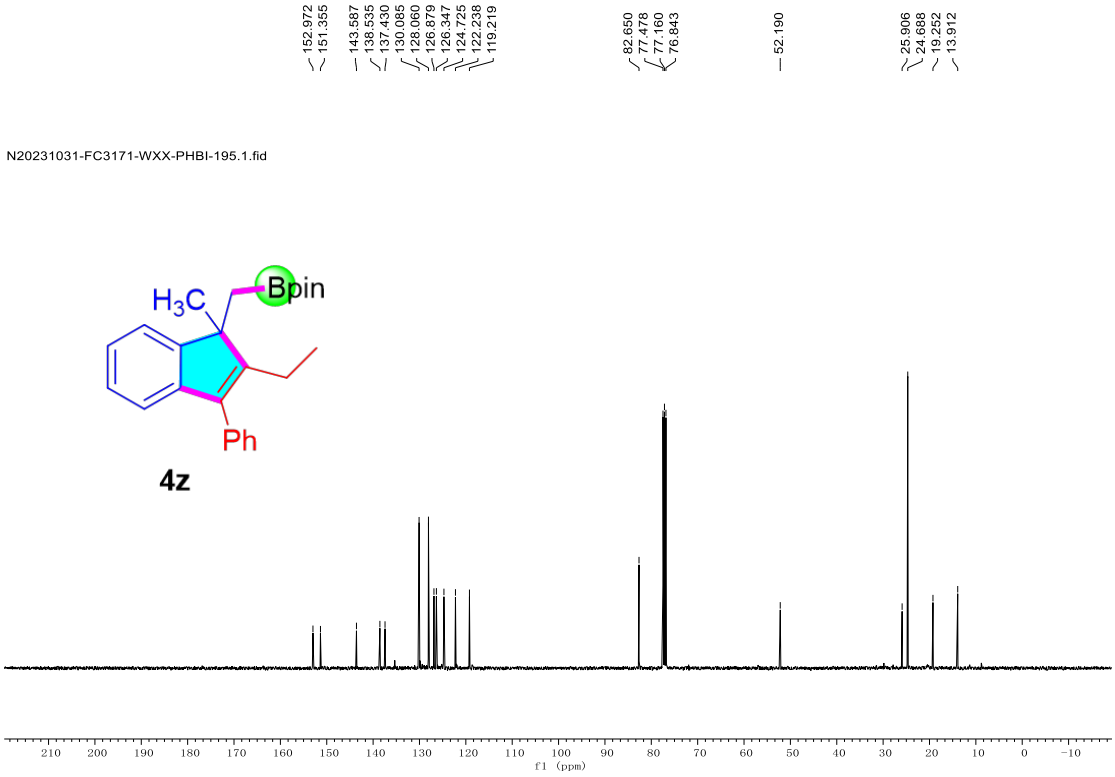
^{13}C{1H} NMR (101 MHz, $CDCl_3$) Spectrum of **4y**



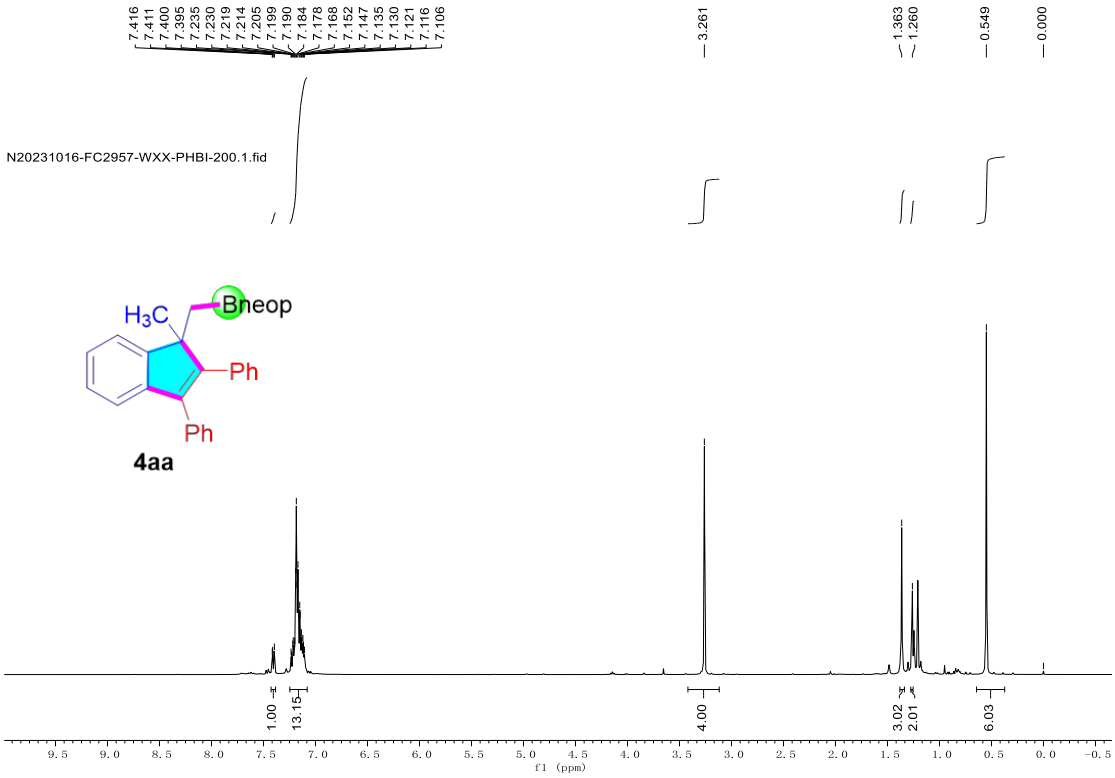
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of **4z**



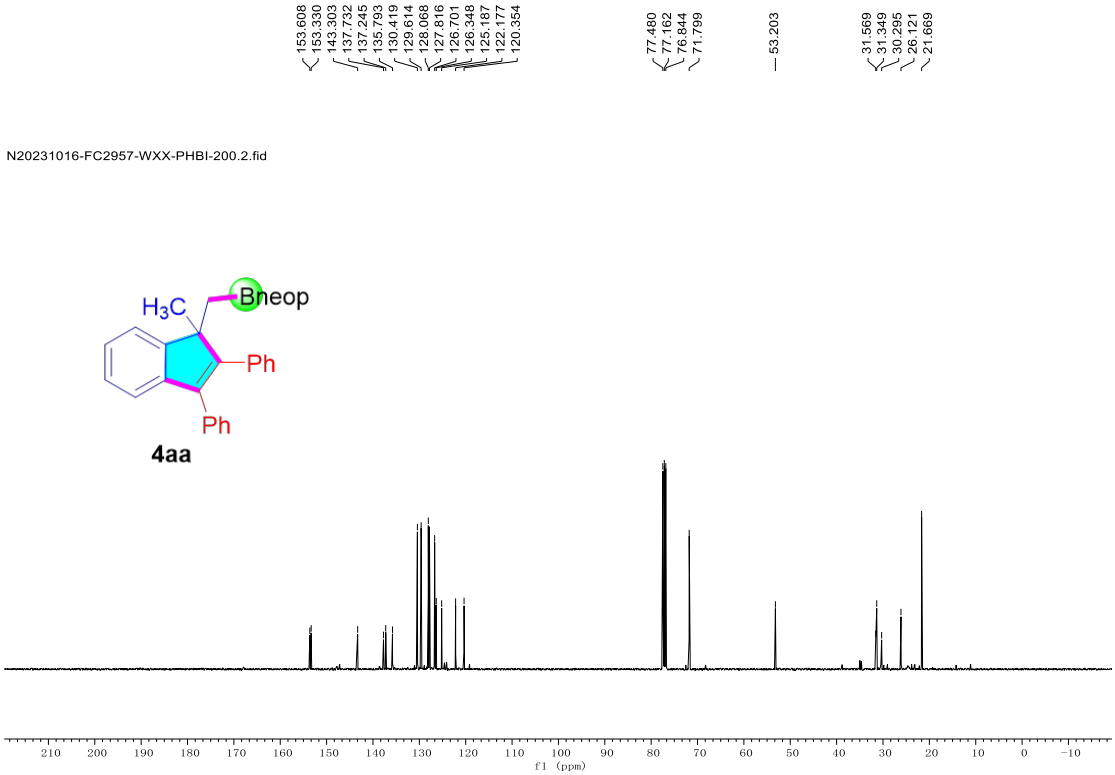
^{13}C{1H} NMR (101 MHz, $CDCl_3$) Spectrum of **4z**



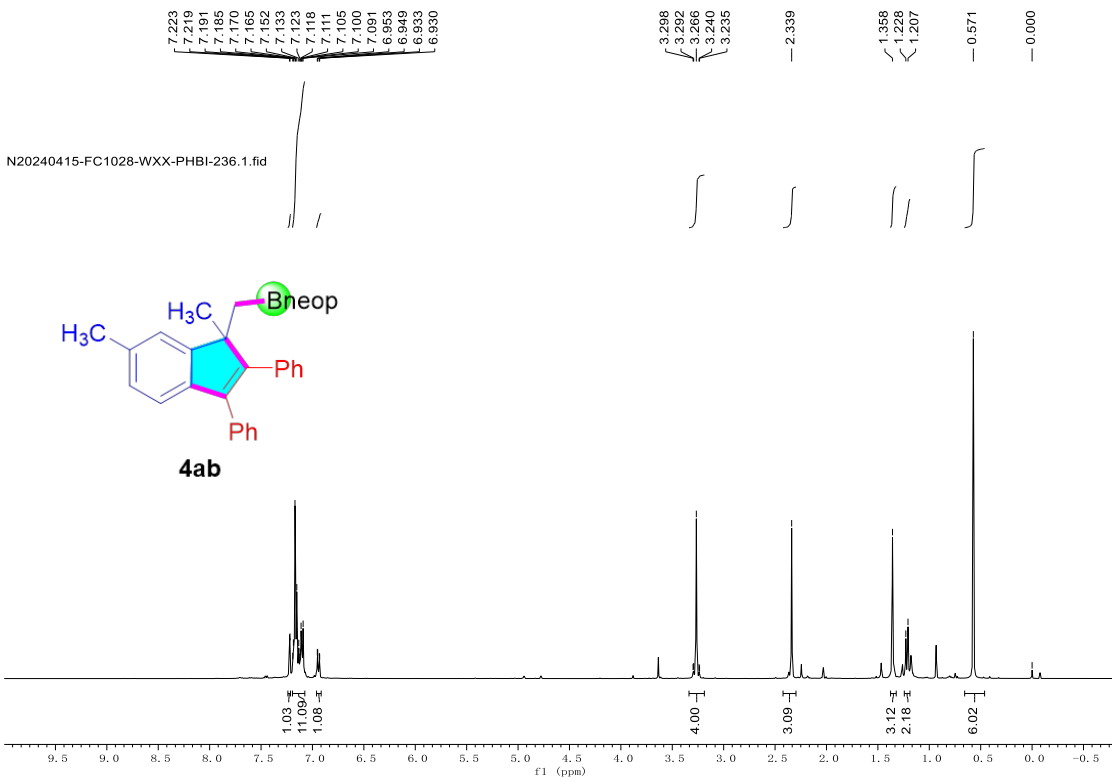
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of **4aa**



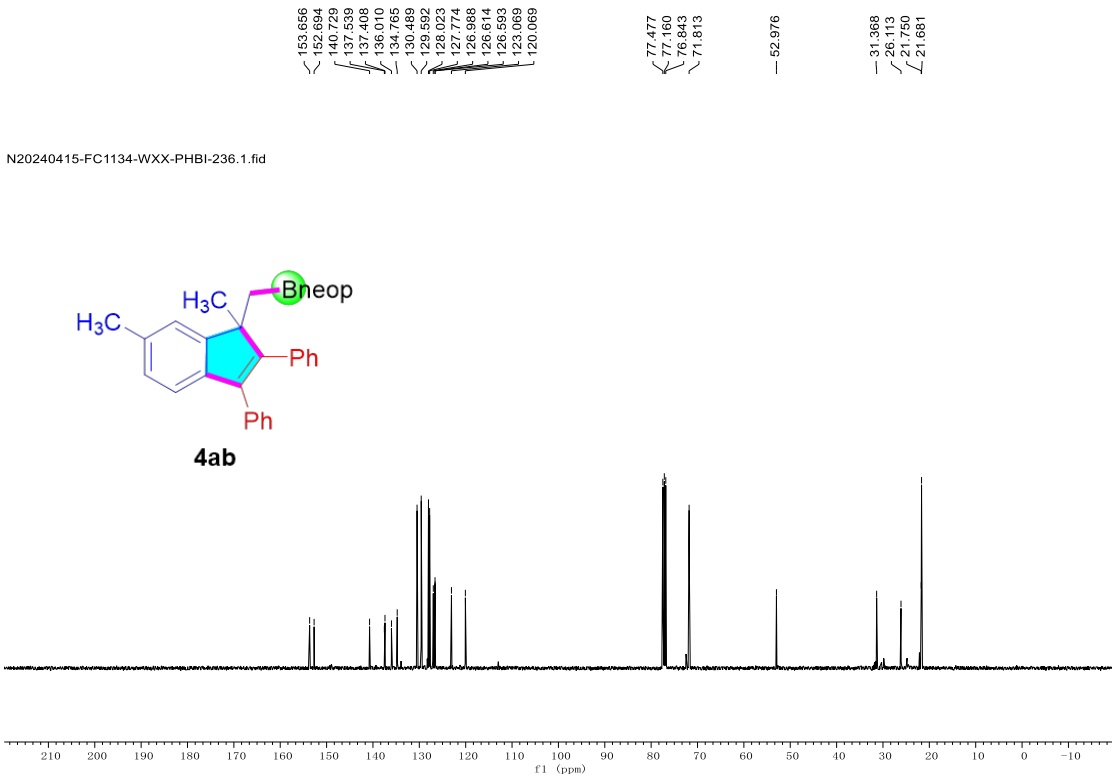
^{13}C{1H} NMR (101 MHz, $CDCl_3$) Spectrum of **4aa**



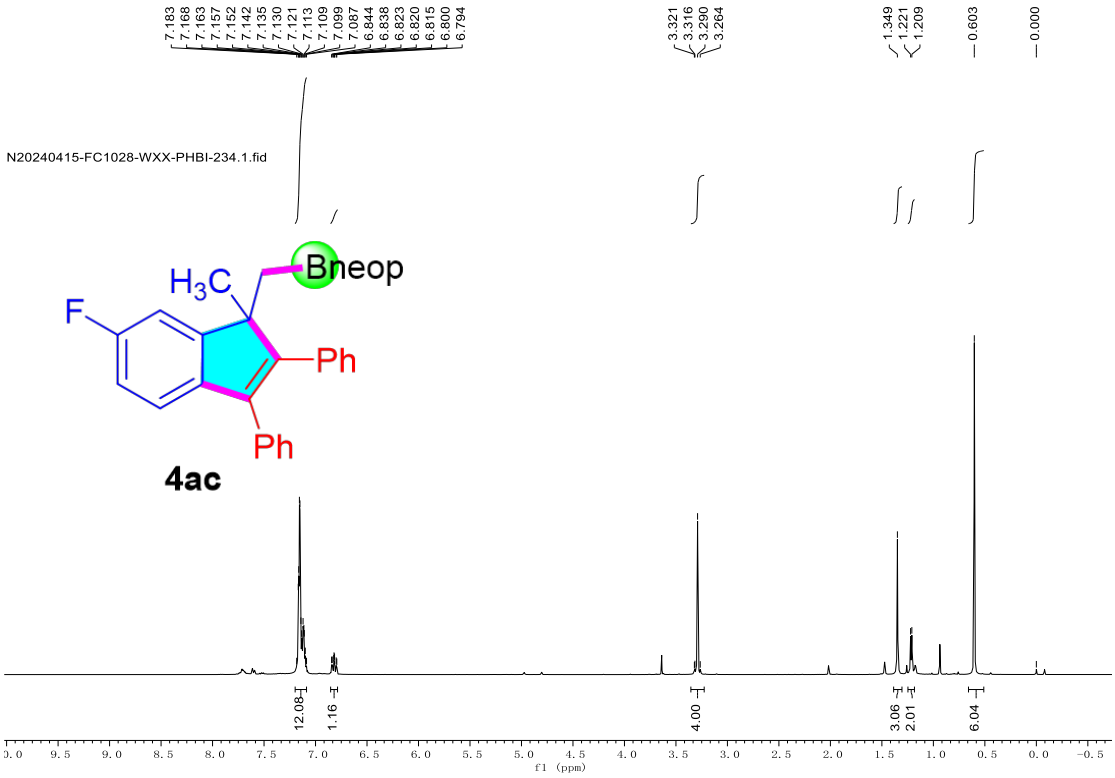
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of **4ab**



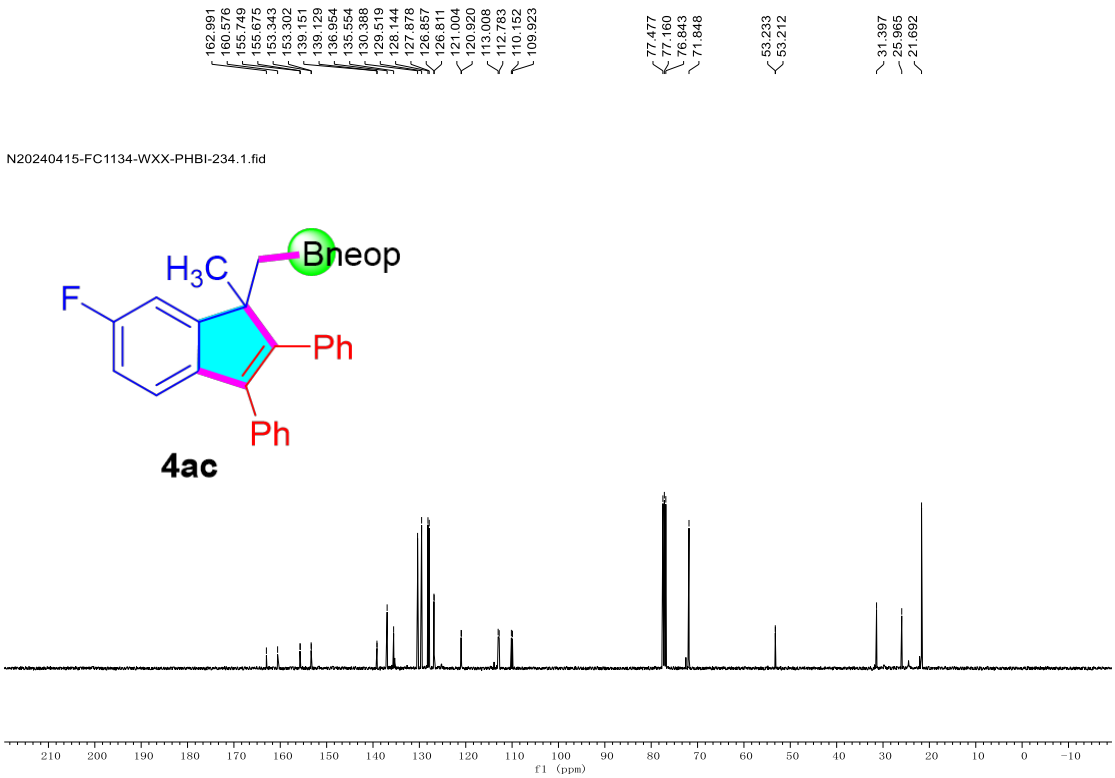
^{13}C{1H} NMR (101 MHz, $CDCl_3$) Spectrum of **4ab**



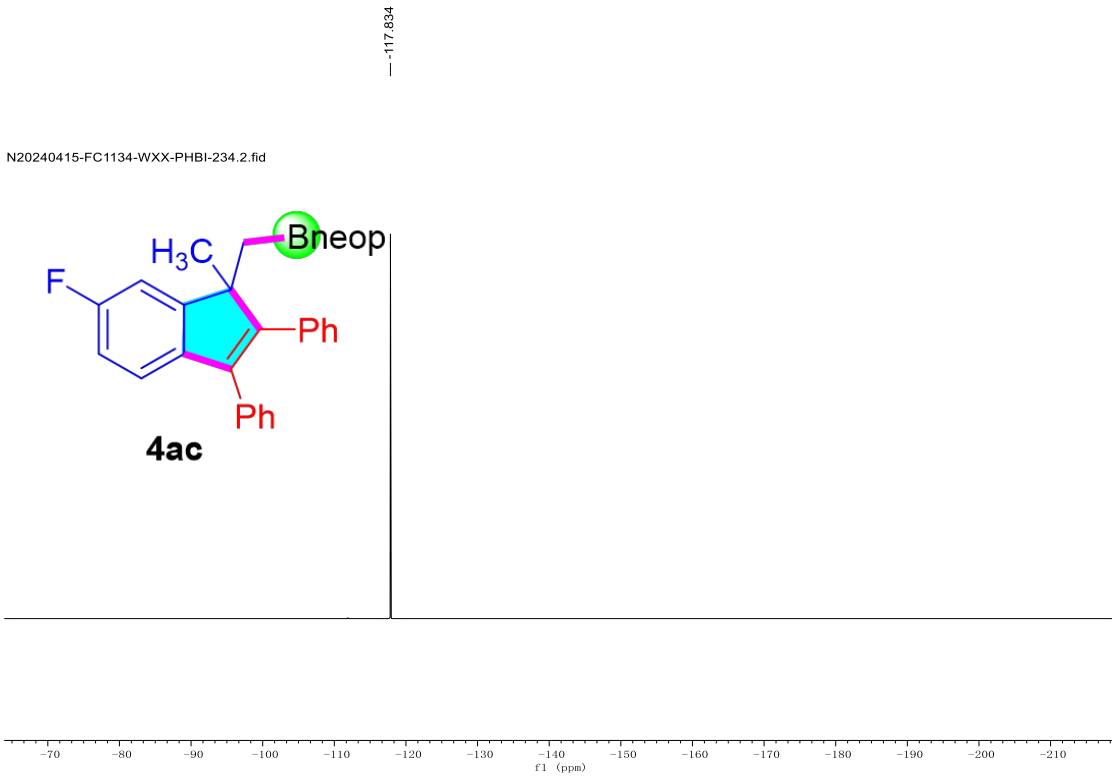
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of **4ac**



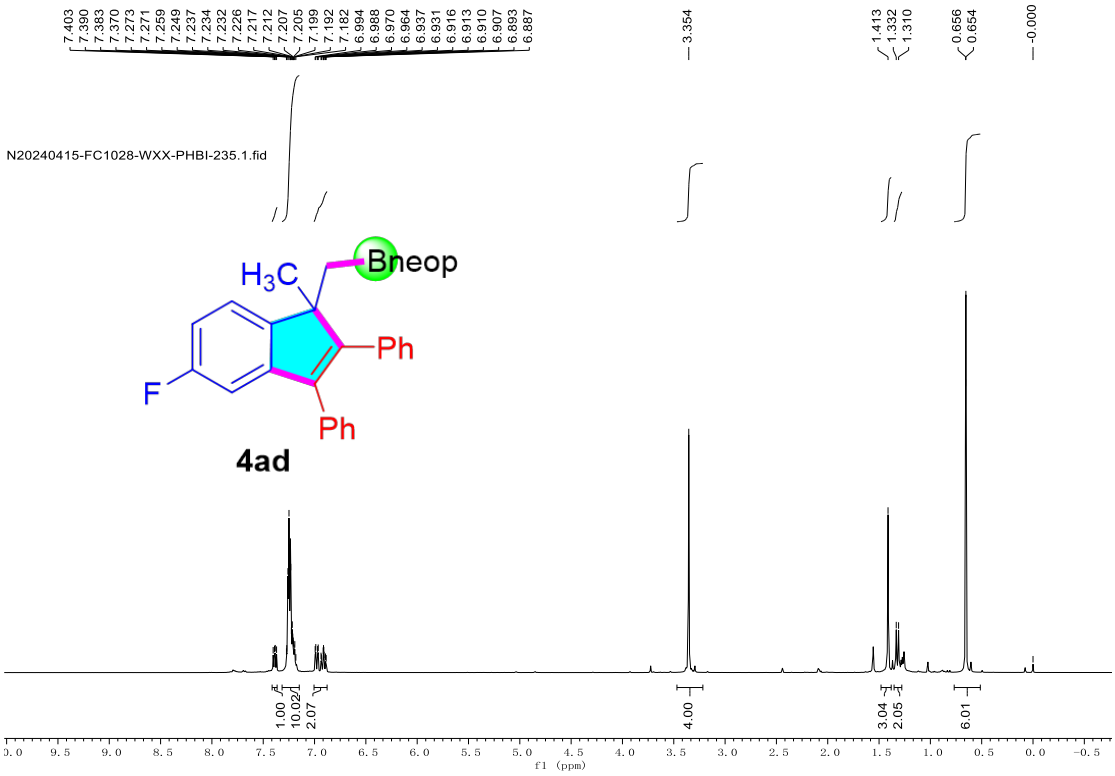
^{13}C{1H} NMR (101 MHz, $CDCl_3$) Spectrum of **4ac**



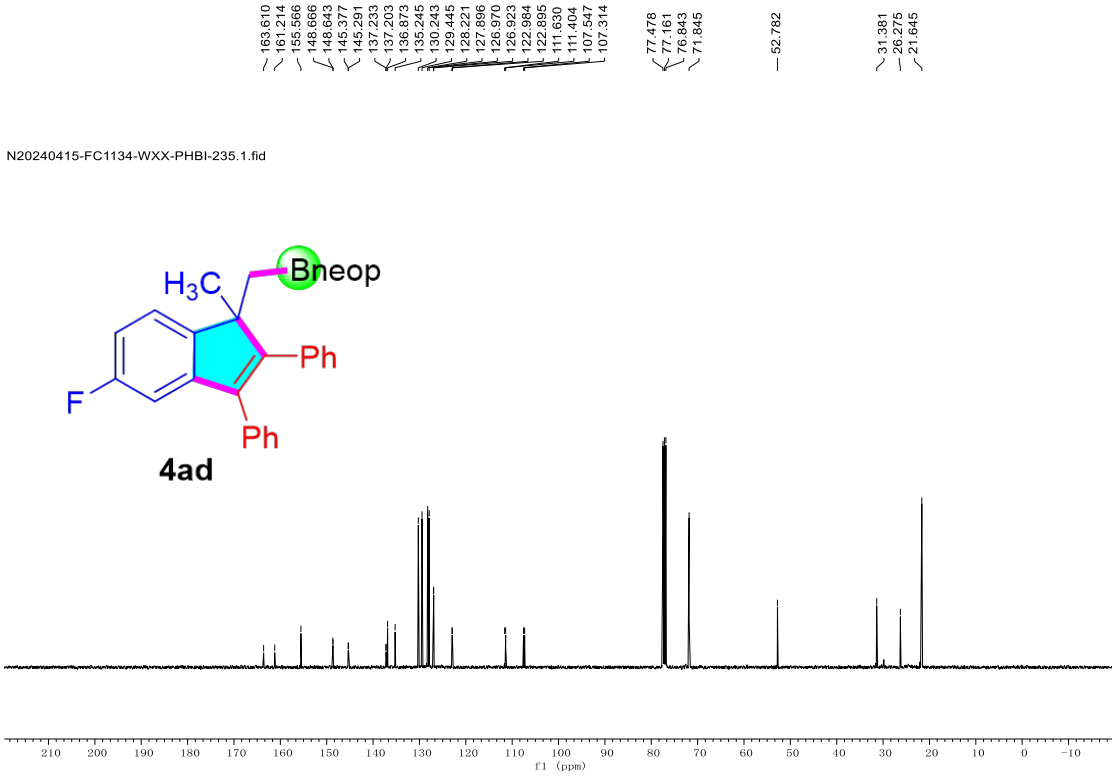
^{19}F NMR (376 MHz, $CDCl_3$) Spectrum of **4ac**



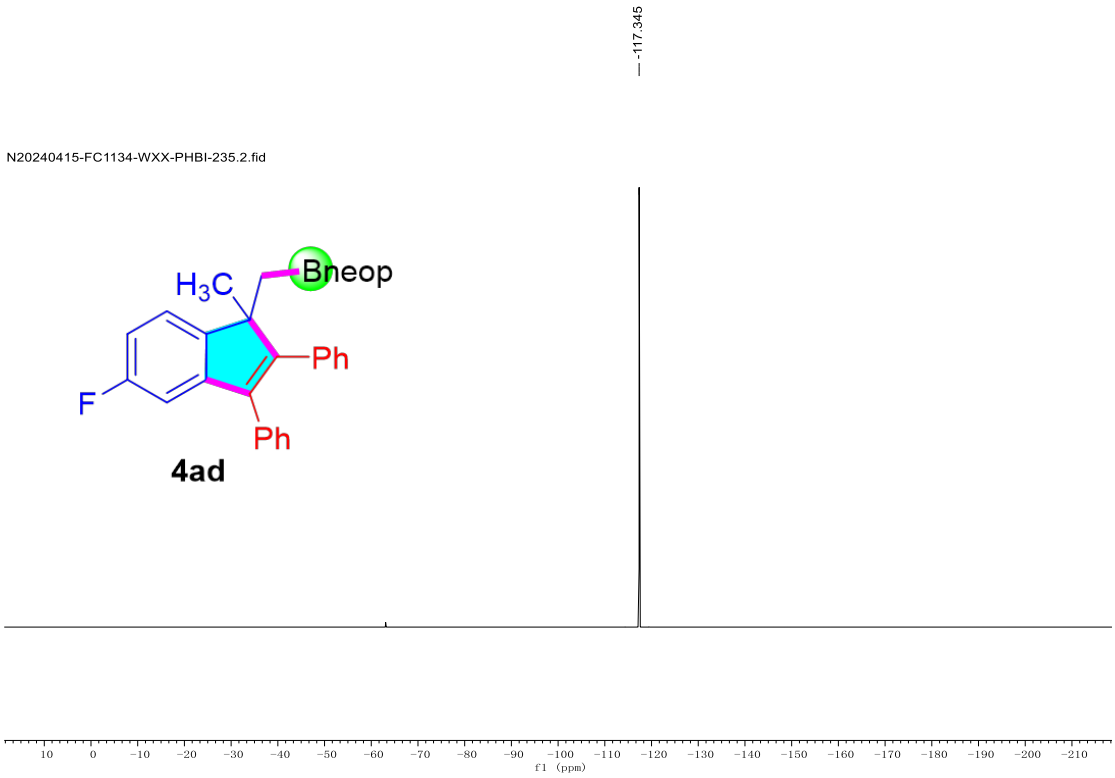
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of **4ad**



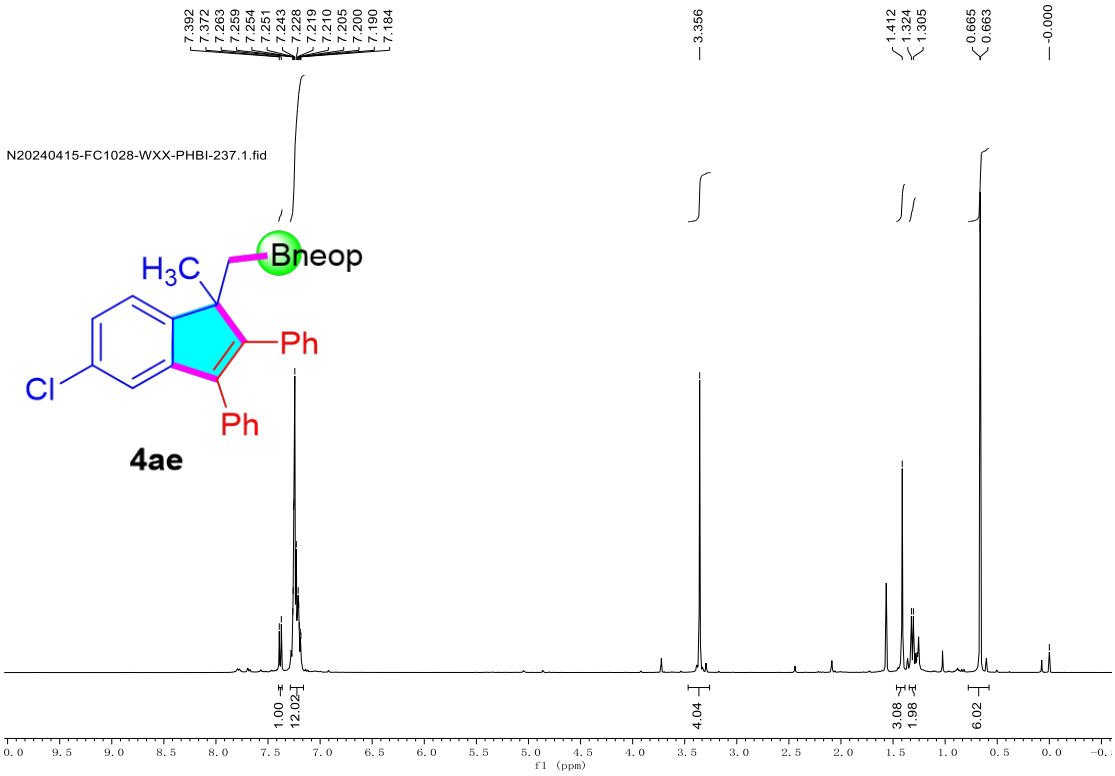
^{13}C{1H} NMR (101 MHz, $CDCl_3$) Spectrum of **4ad**



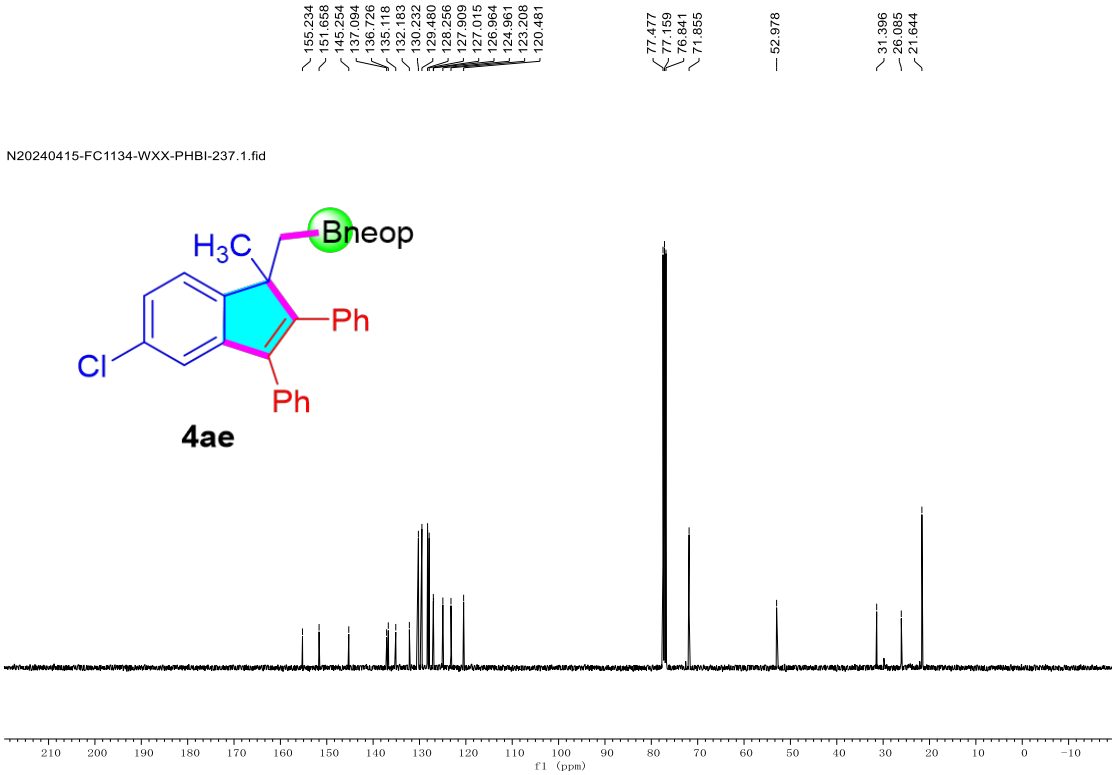
^{19}F NMR (376 MHz, $CDCl_3$) Spectrum of **4ad**



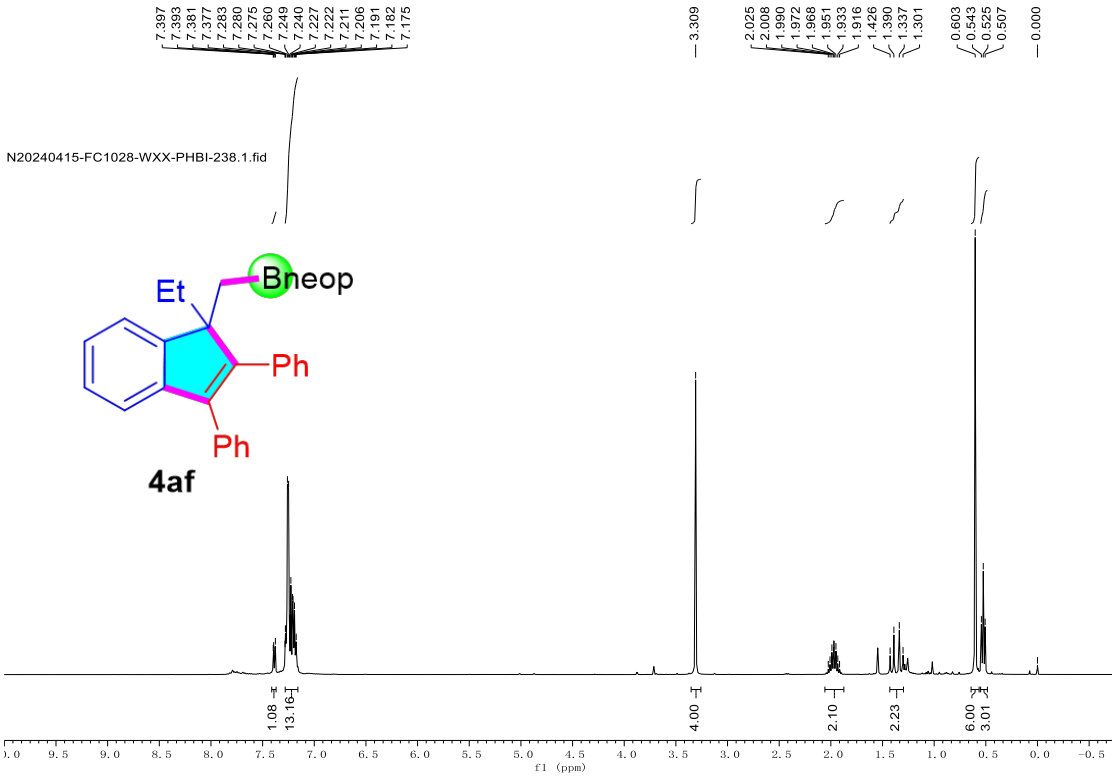
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of **4ae**



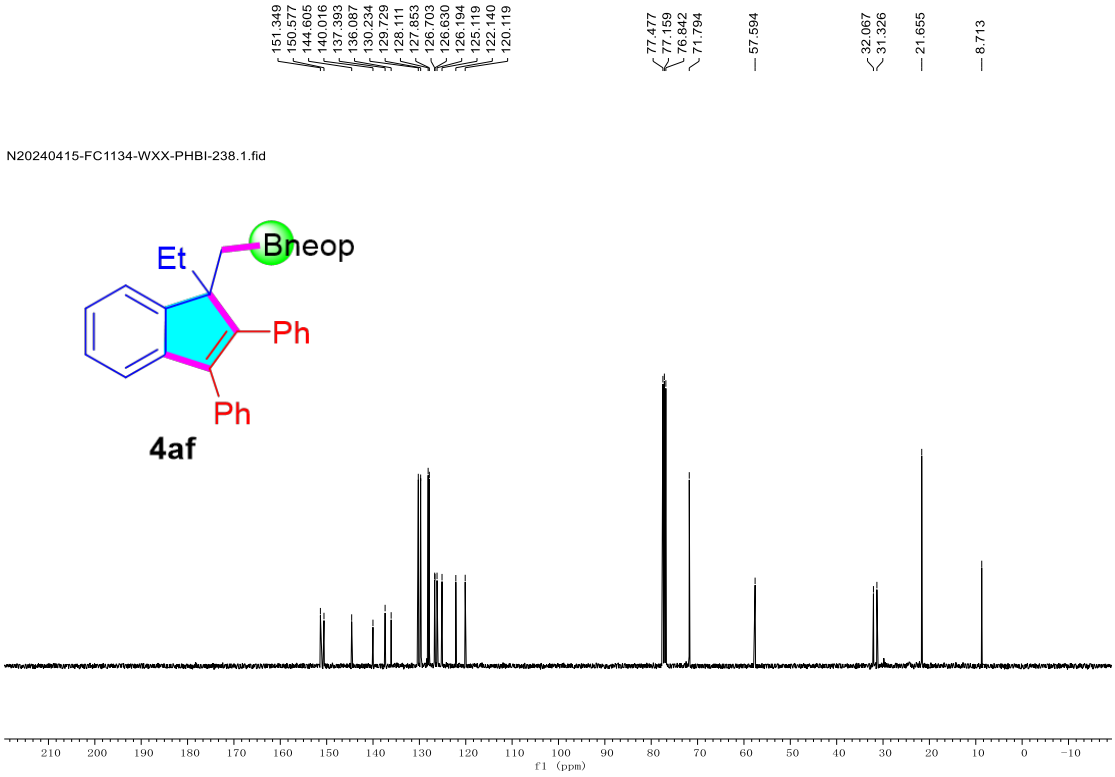
^{13}C{1H} NMR (101 MHz, $CDCl_3$) Spectrum of **4ae**



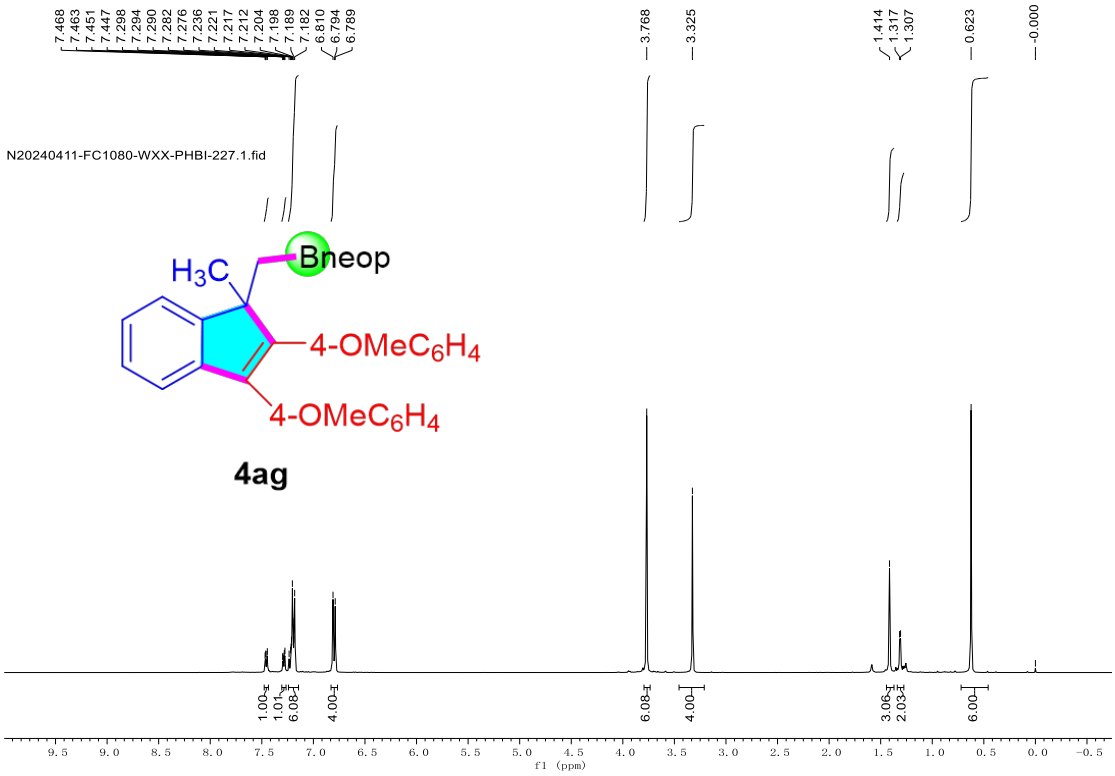
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of **4af**



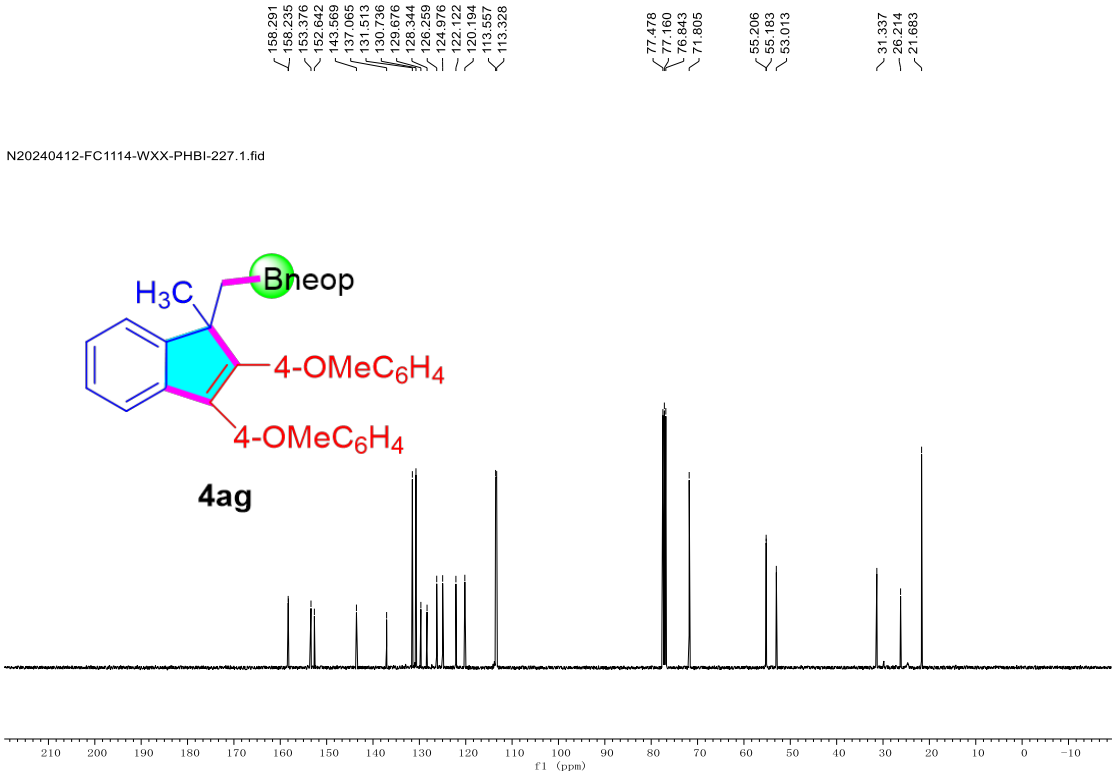
^{13}C{1H} NMR (101 MHz, $CDCl_3$) Spectrum of **4af**



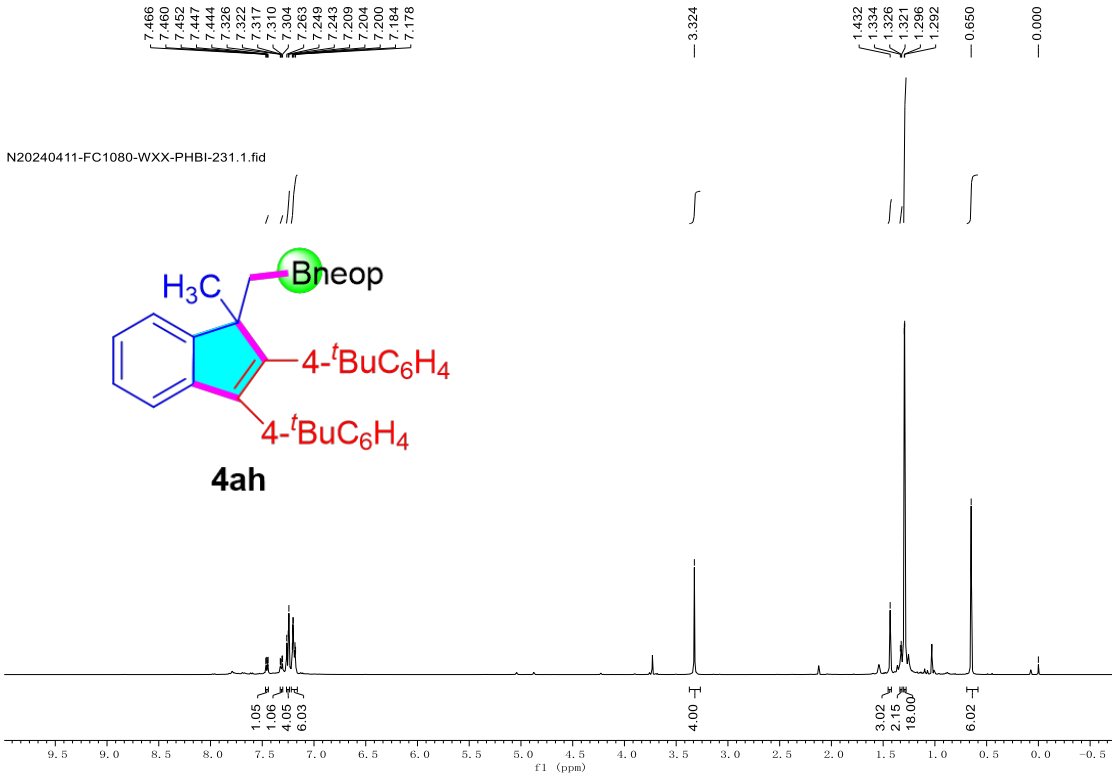
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of **4ag**



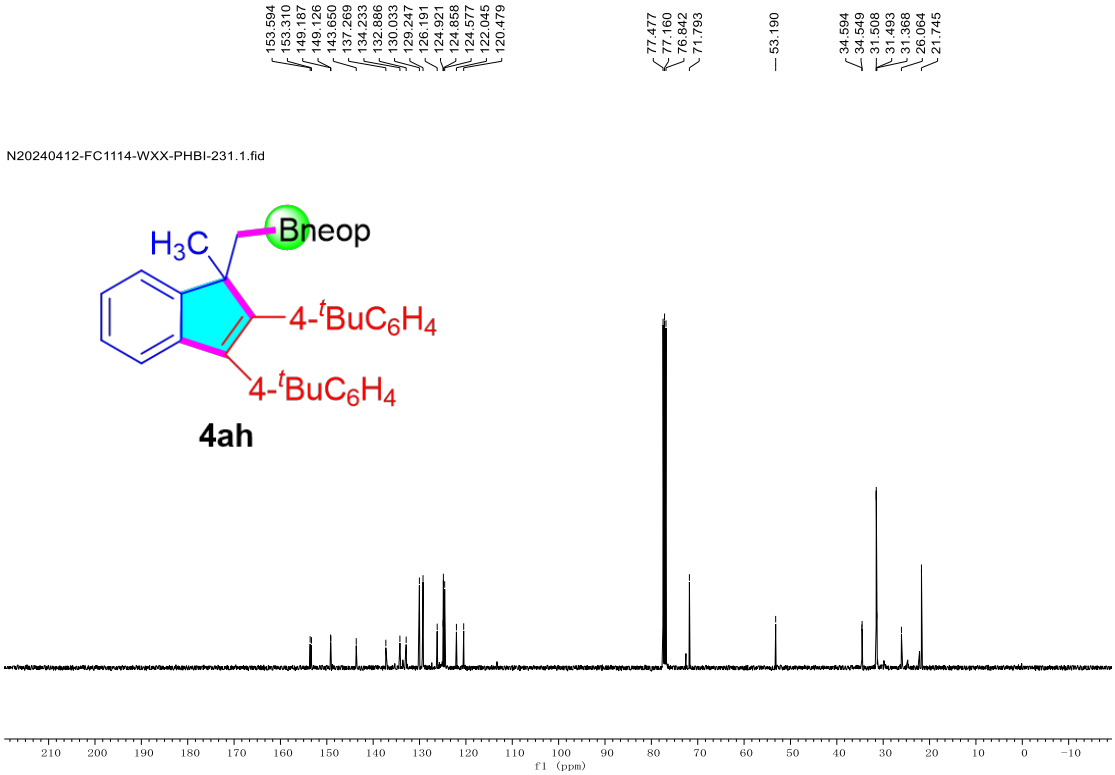
^{13}C{1H} NMR (101 MHz, $CDCl_3$) Spectrum of **4ag**



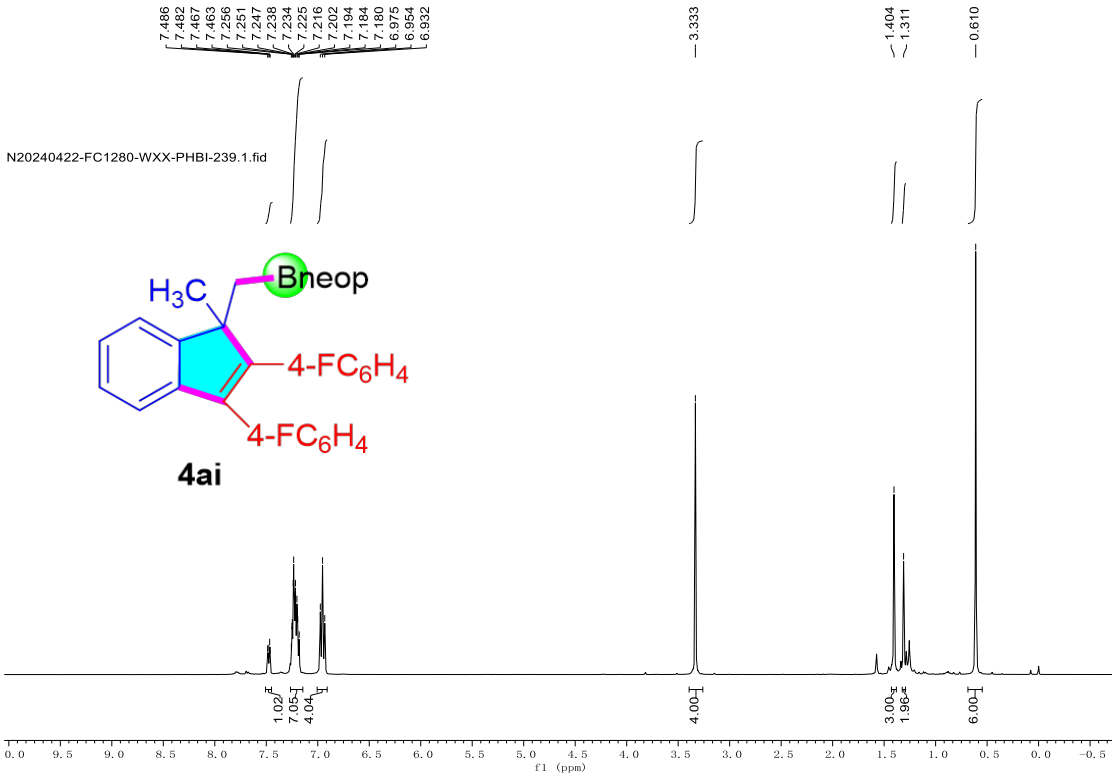
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of **4ah**



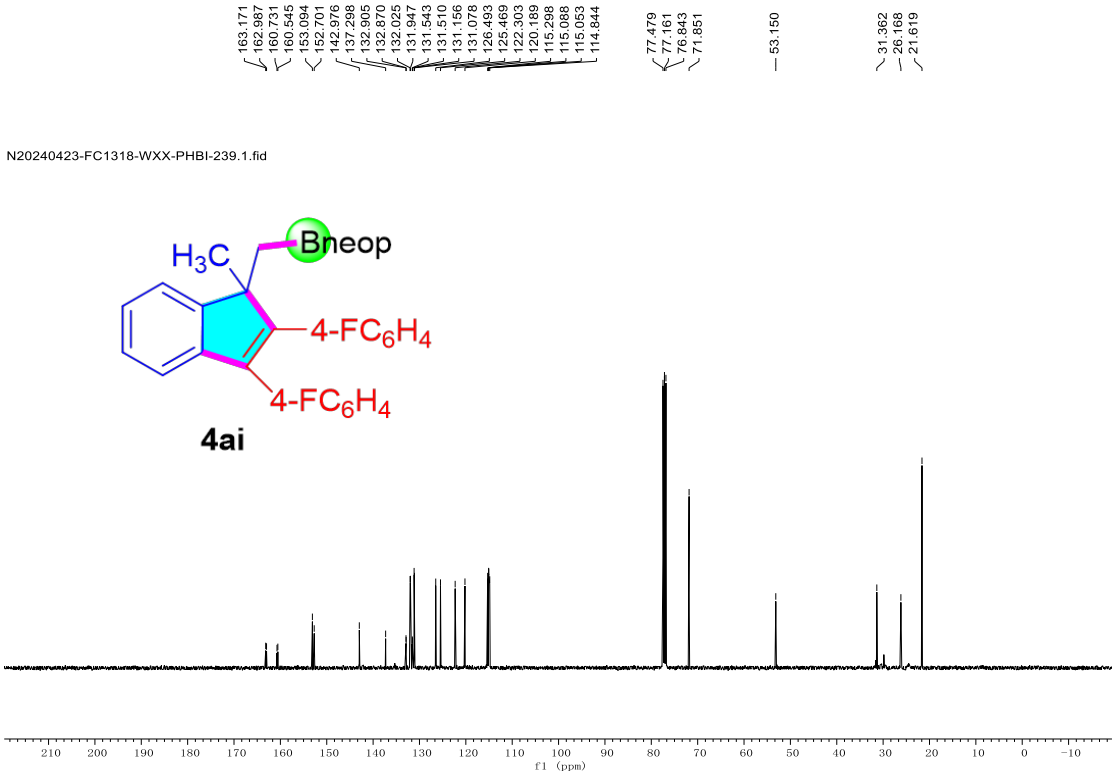
^{13}C{1H} NMR (101 MHz, $CDCl_3$) Spectrum of **4ah**



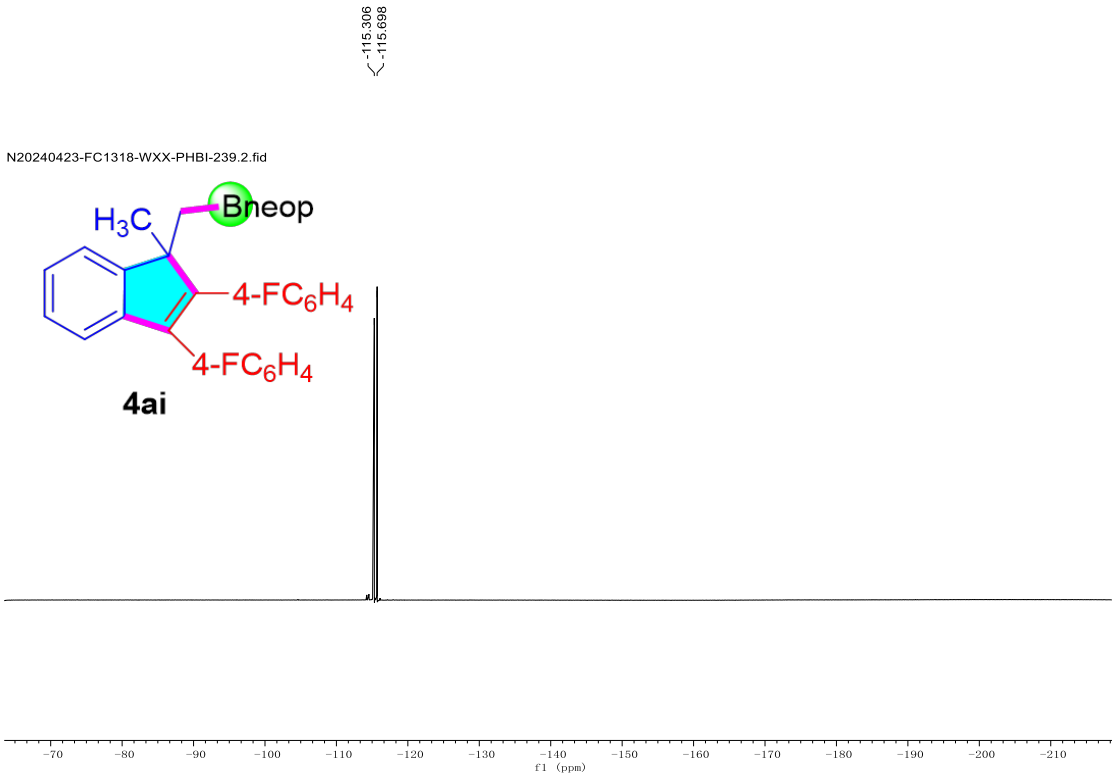
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of **4ai**



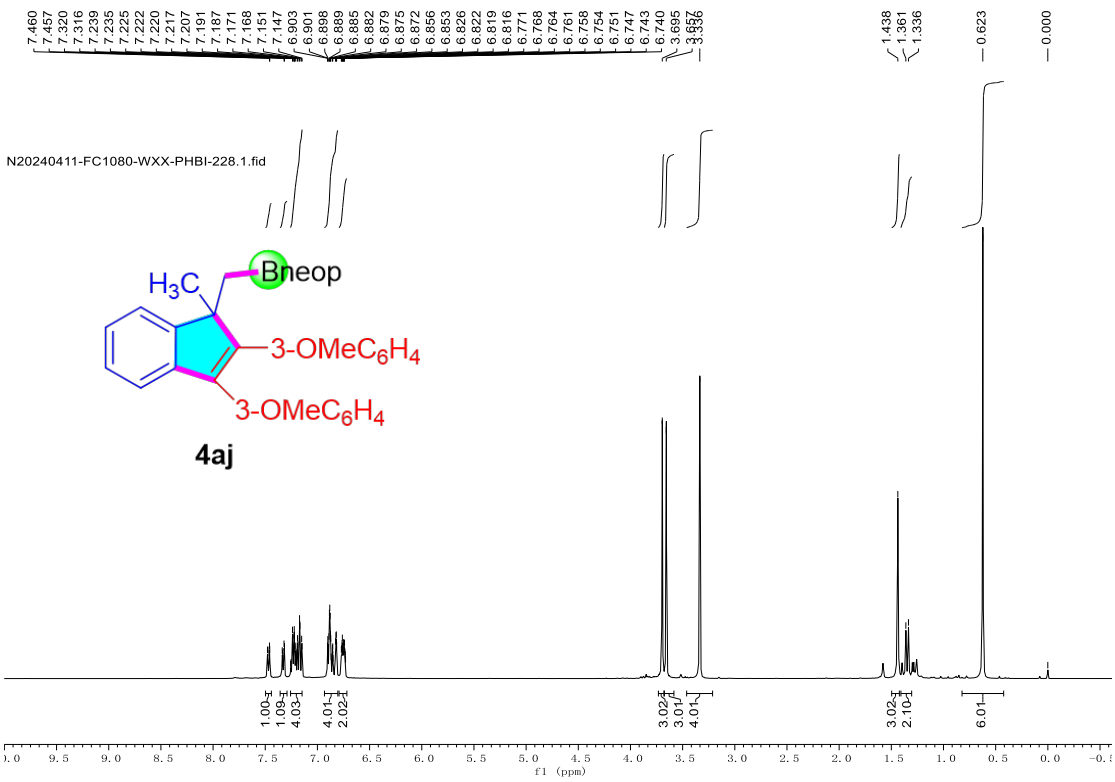
^{13}C{1H} NMR (101 MHz, $CDCl_3$) Spectrum of **4ai**



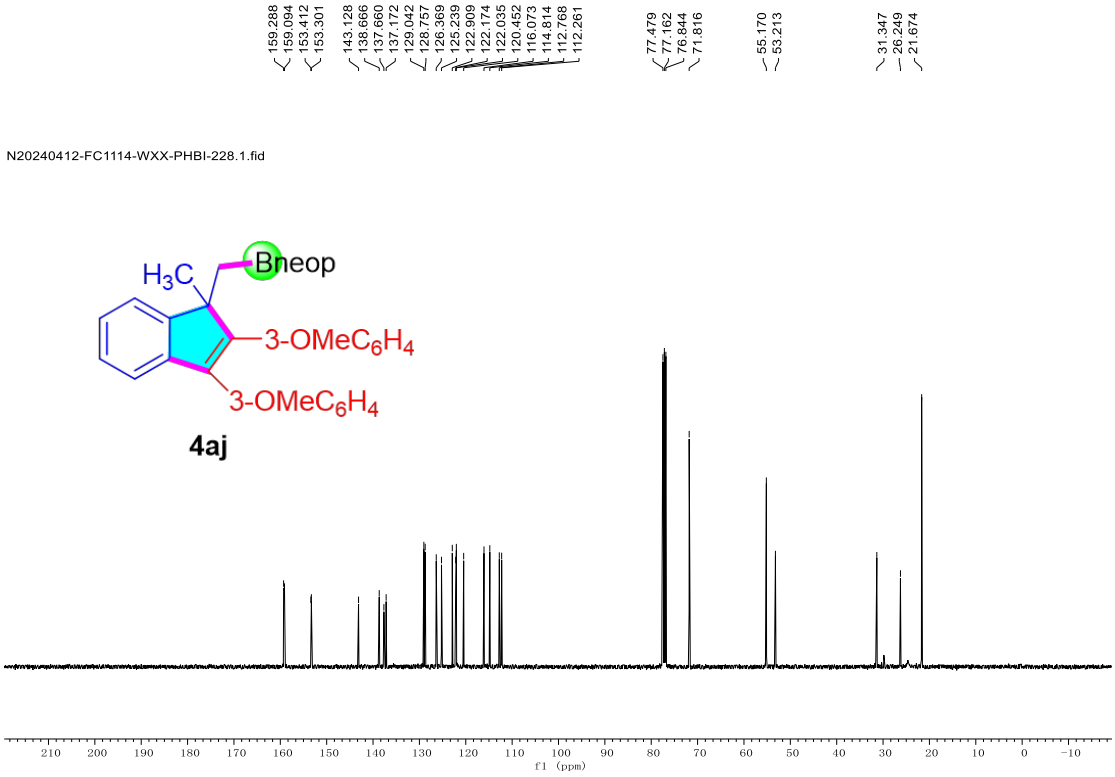
^{19}F NMR (376 MHz, $CDCl_3$) Spectrum of **4ai**



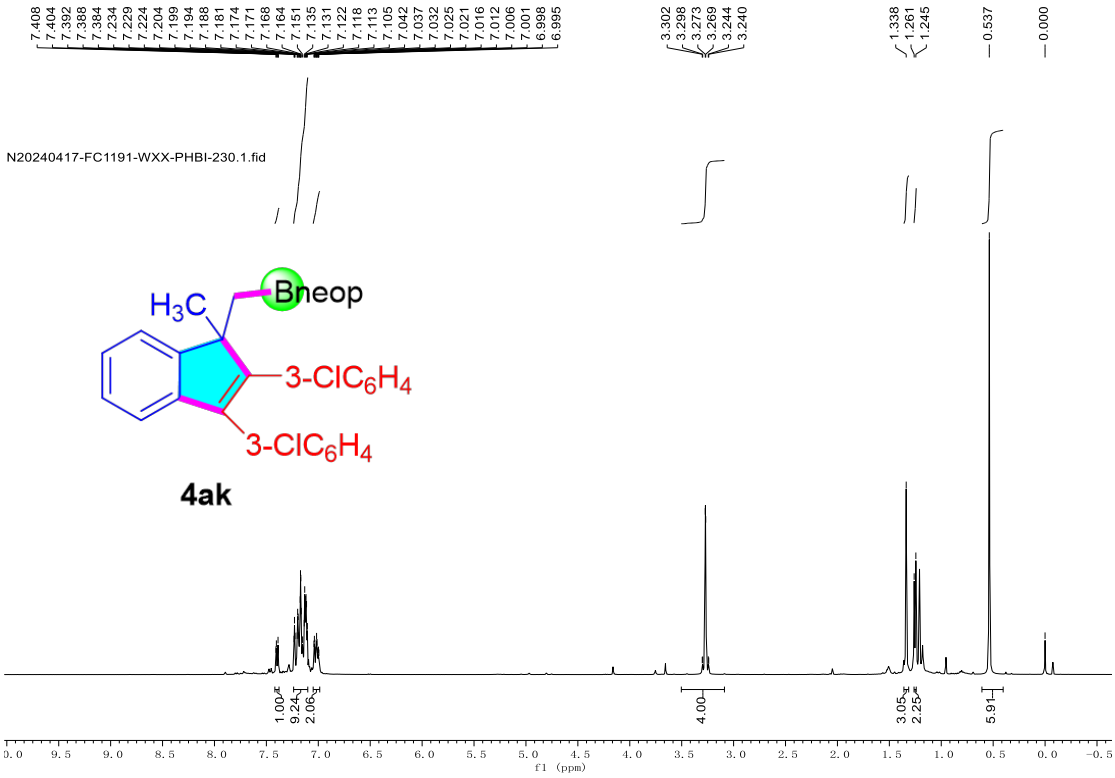
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of **4aj**



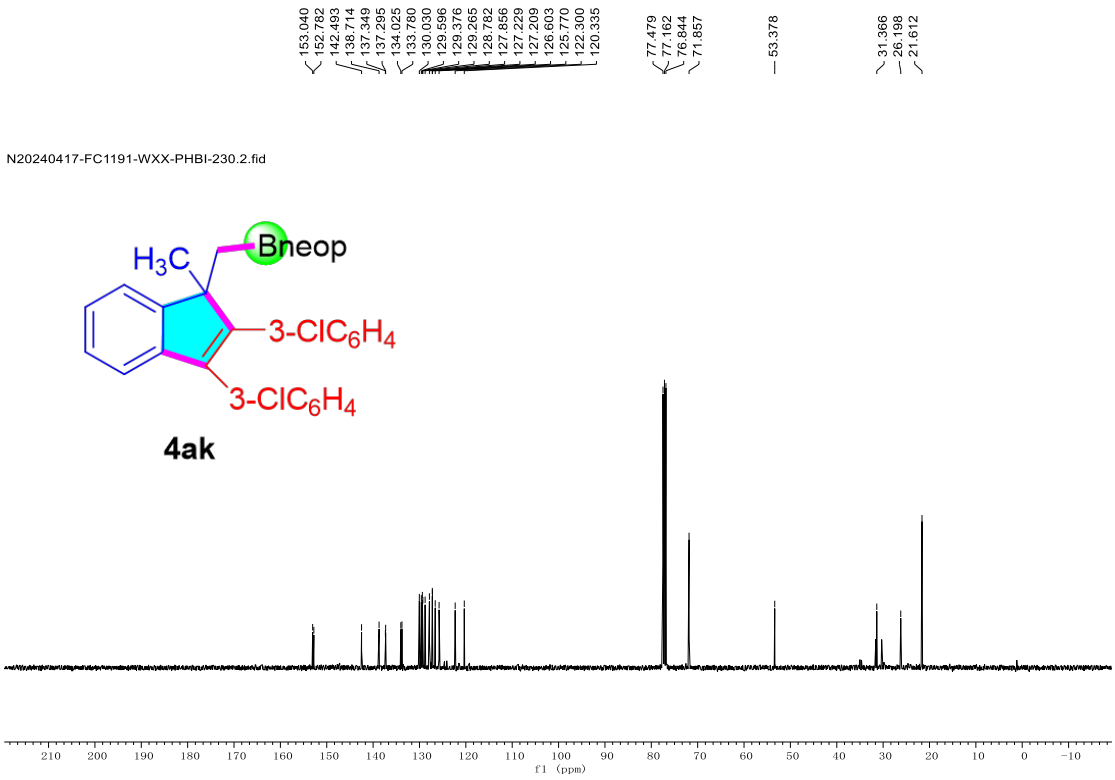
^{13}C{1H} NMR (101 MHz, $CDCl_3$) Spectrum of **4aj**



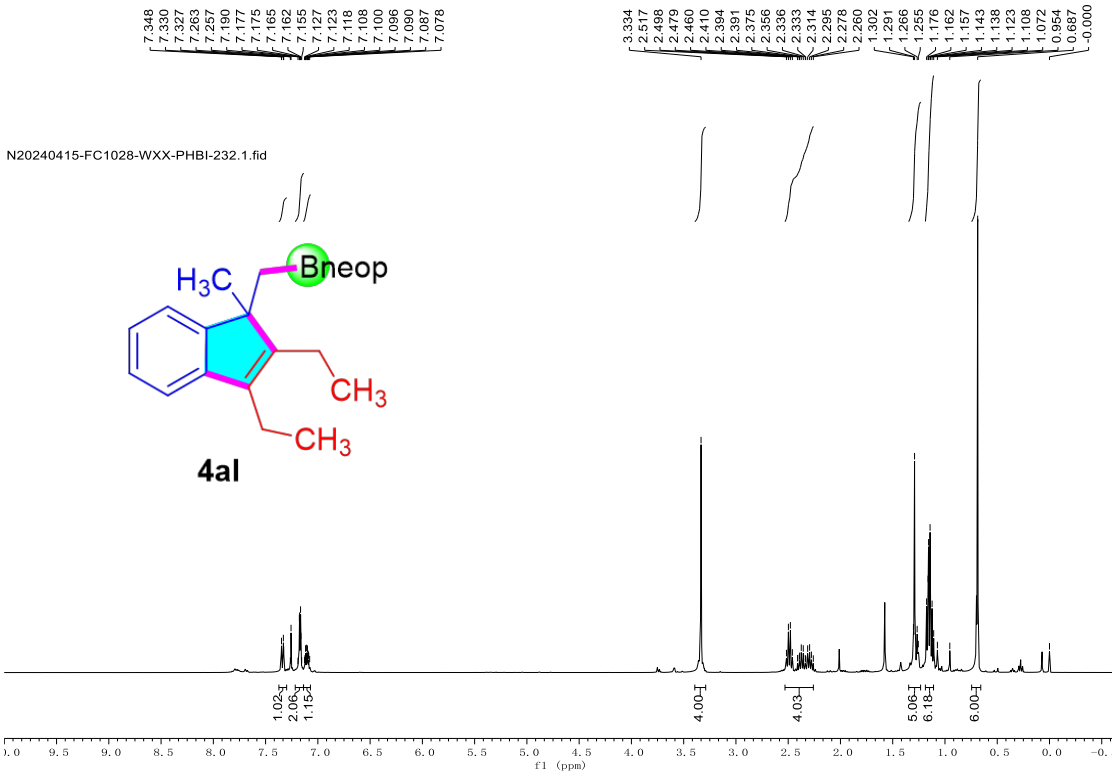
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of **4ak**



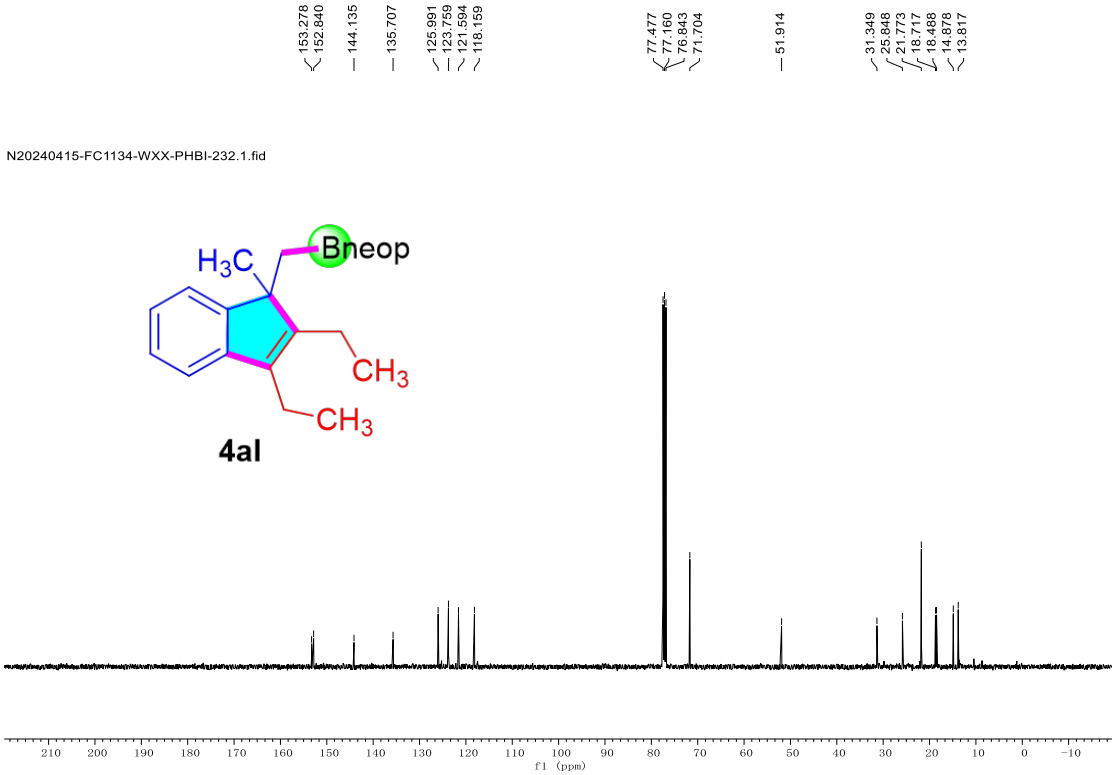
^{13}C{1H} NMR (101 MHz, $CDCl_3$) Spectrum of **4ak**



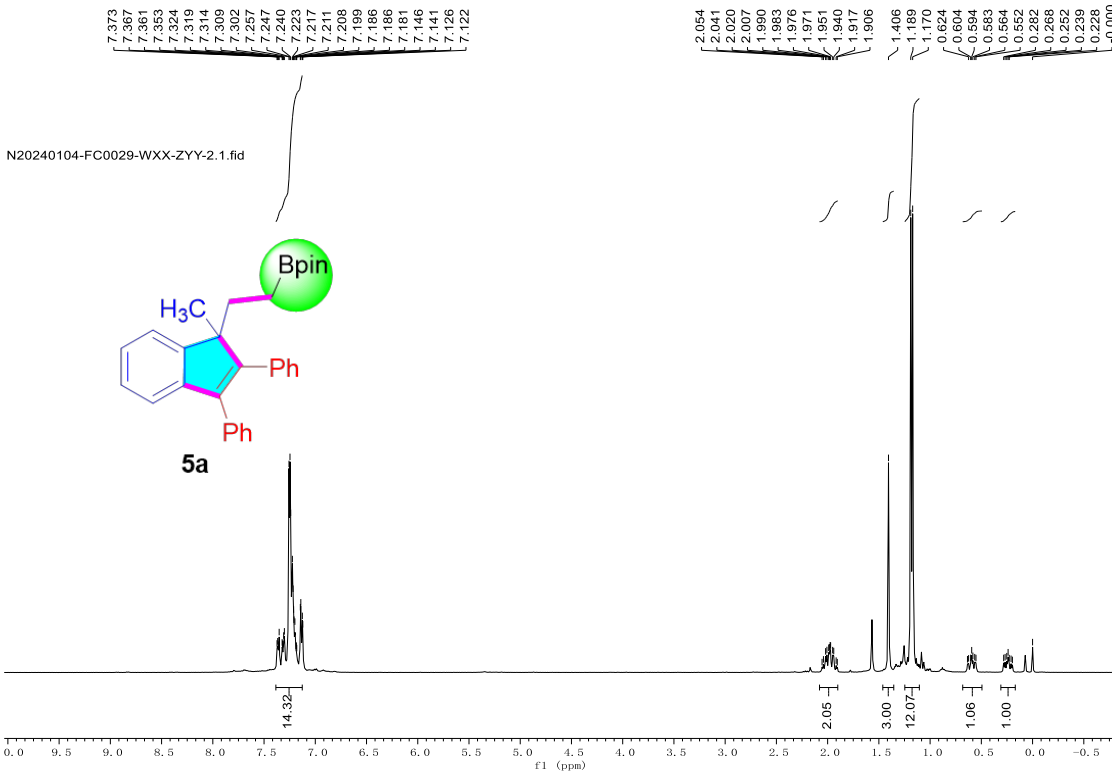
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of **4al**



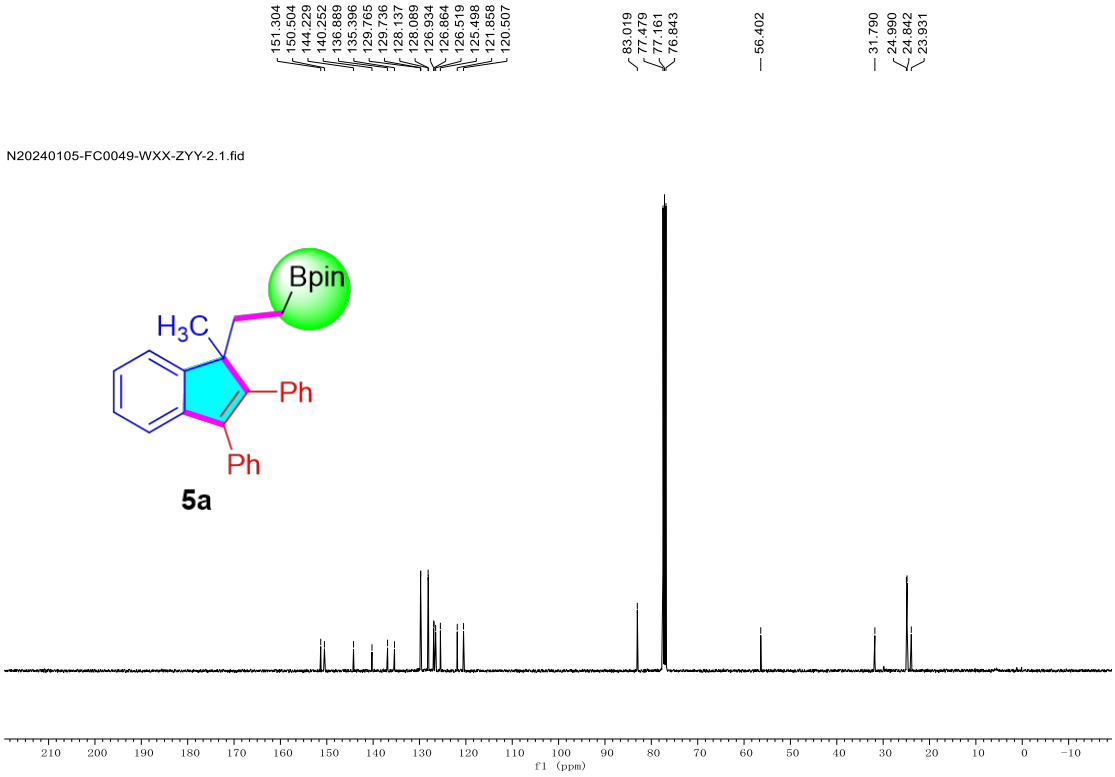
^{13}C{1H} NMR (101 MHz, $CDCl_3$) Spectrum of **4al**



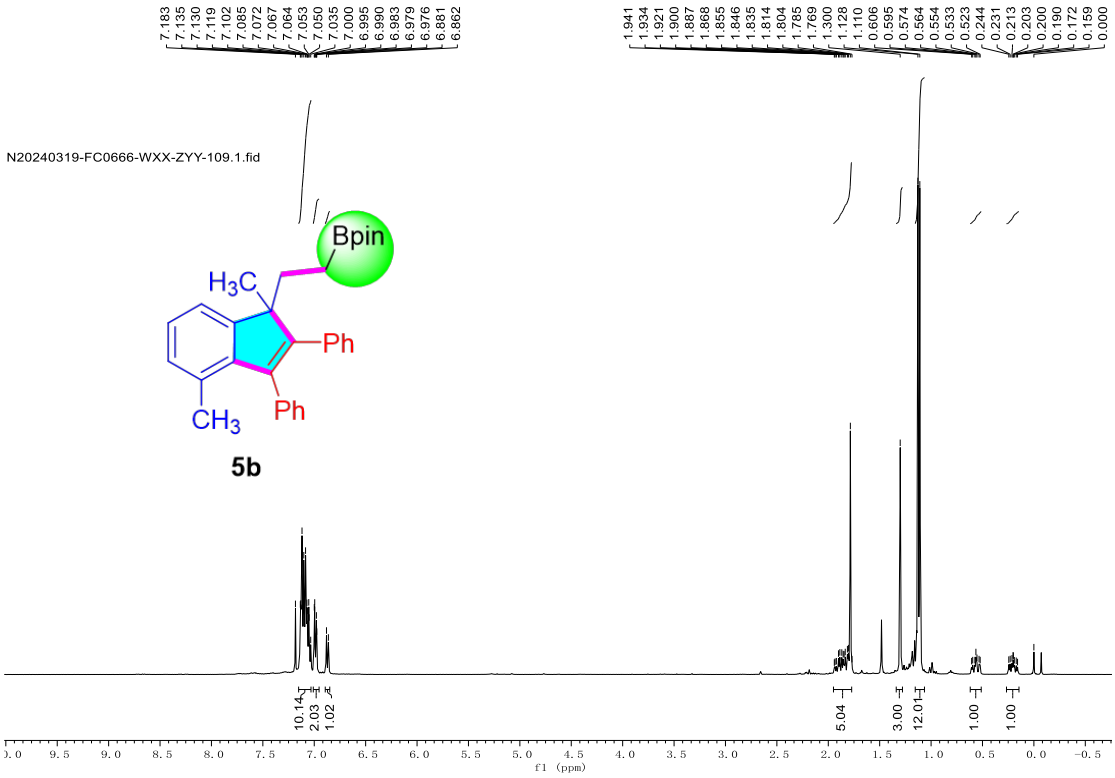
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of **5a**



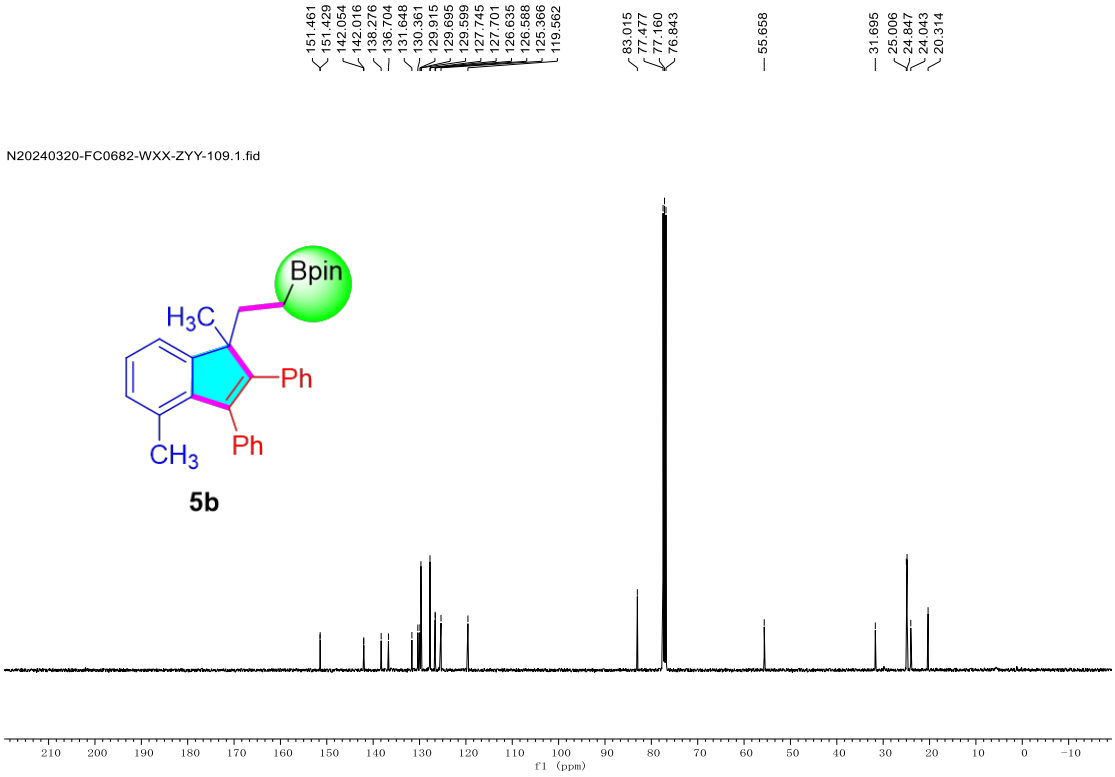
^{13}C{1H} NMR (101 MHz, $CDCl_3$) Spectrum of **5a**



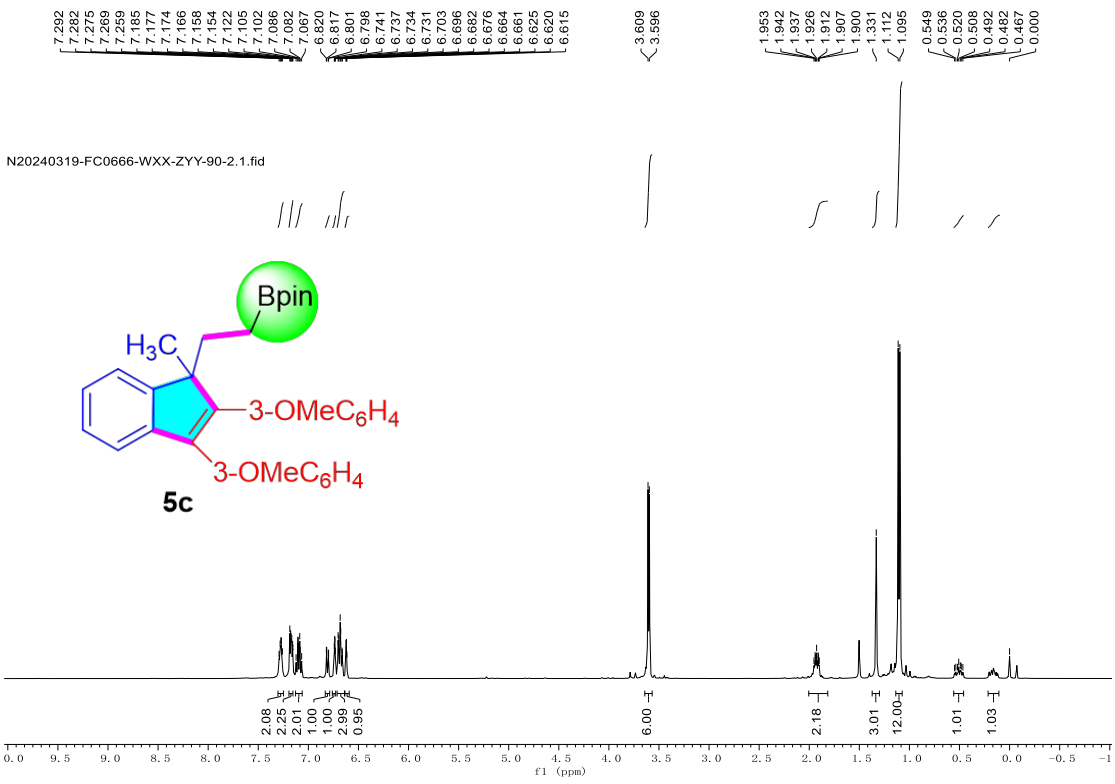
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of **5b**



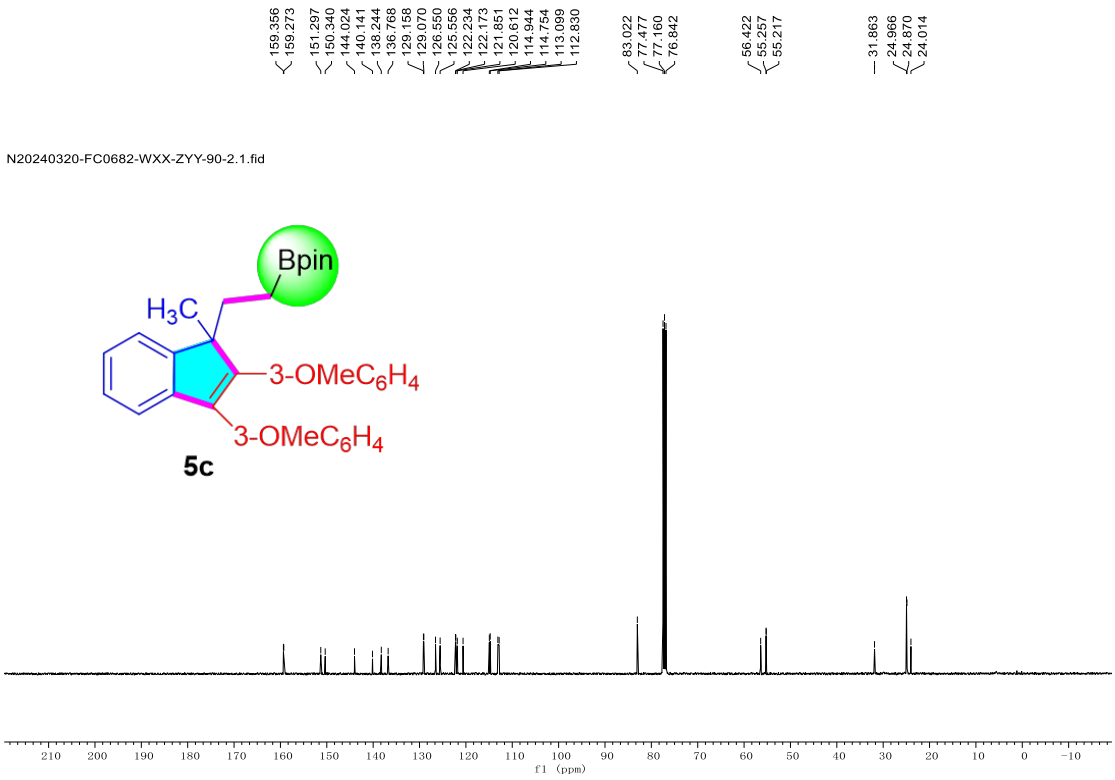
^{13}C{1H} NMR (101 MHz, $CDCl_3$) Spectrum of **5b**



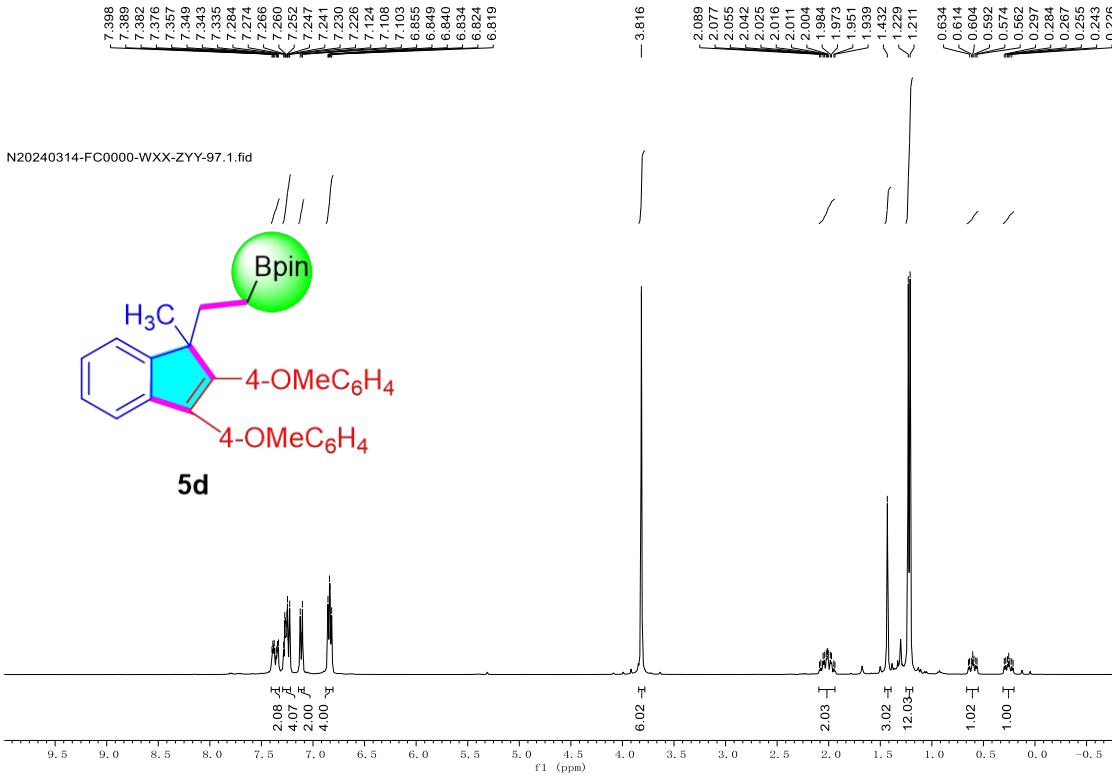
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of **5c**



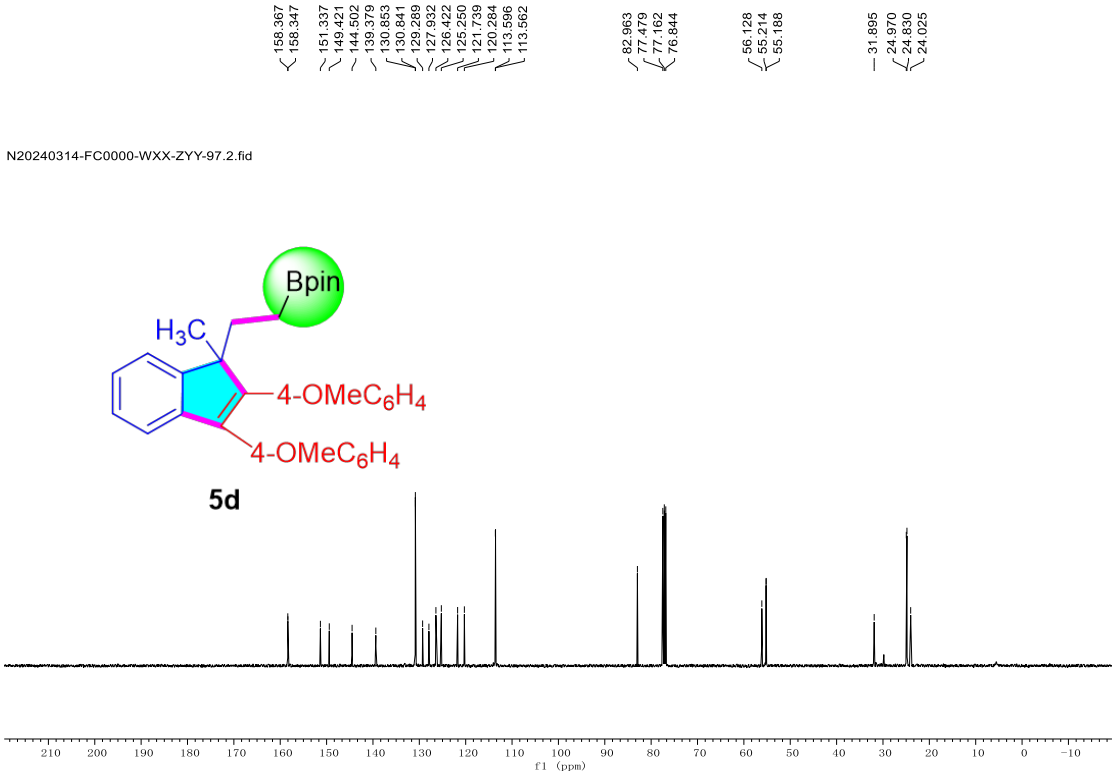
^{13}C{1H} NMR (101 MHz, $CDCl_3$) Spectrum of **5c**



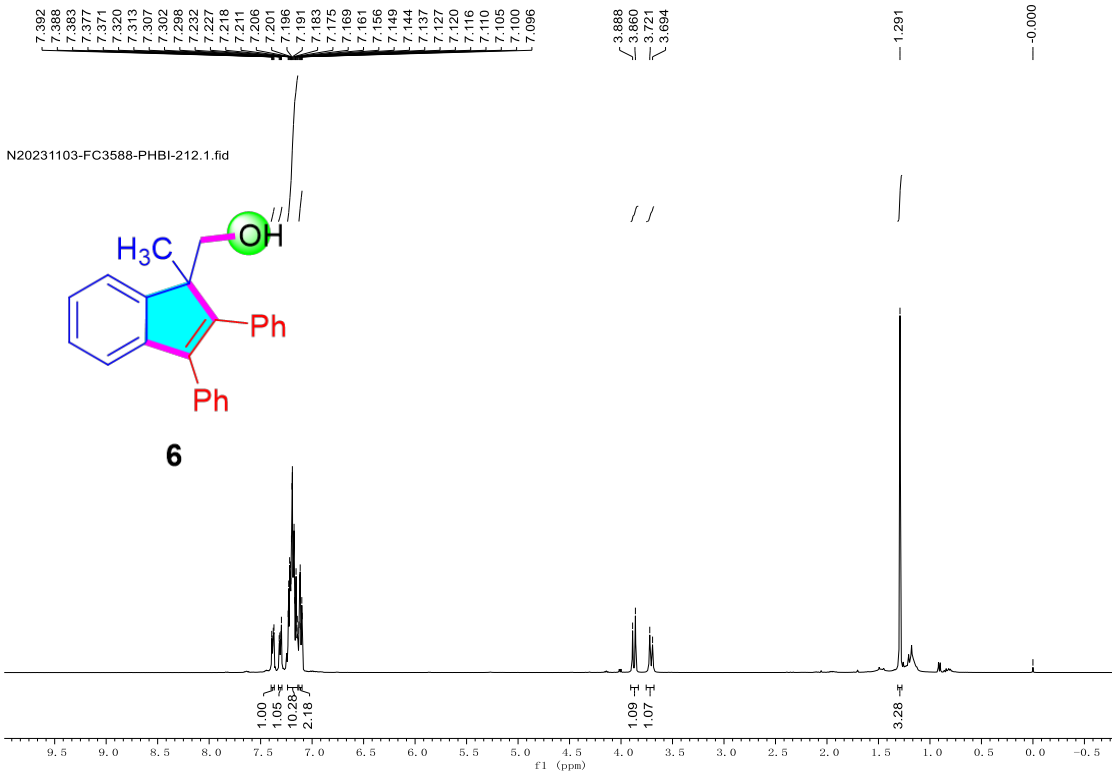
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of **5d**



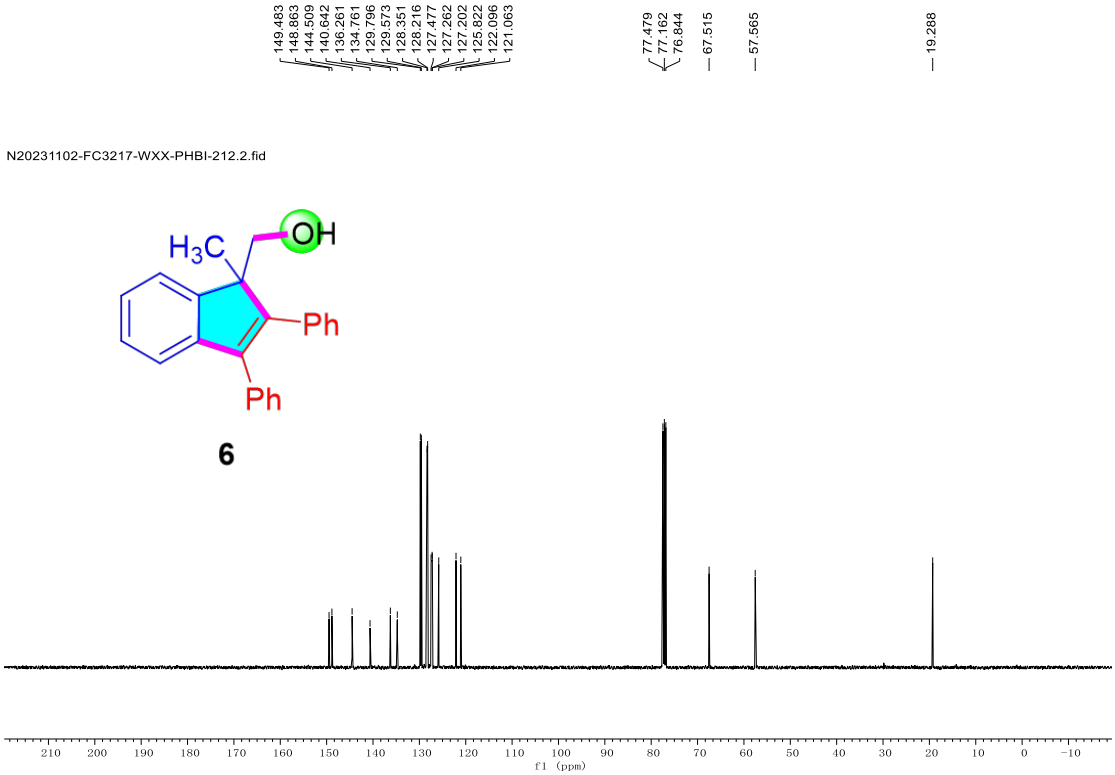
^{13}C{1H} NMR (101 MHz, $CDCl_3$) Spectrum of **5d**



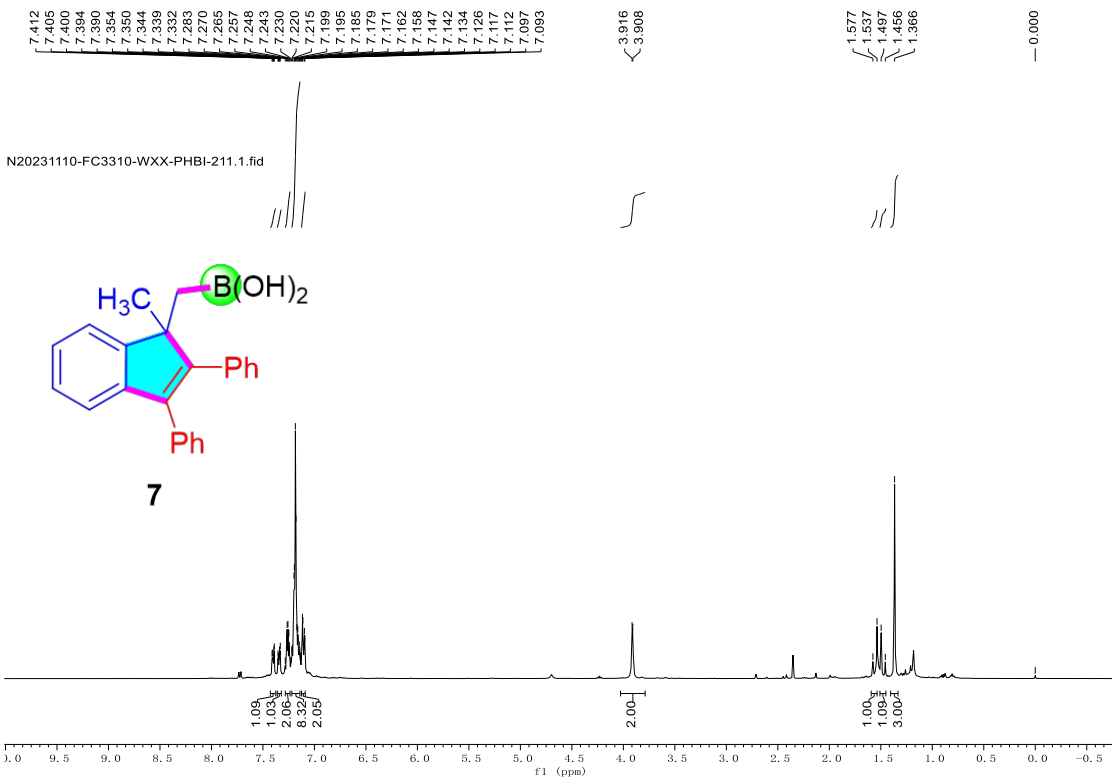
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of **6**



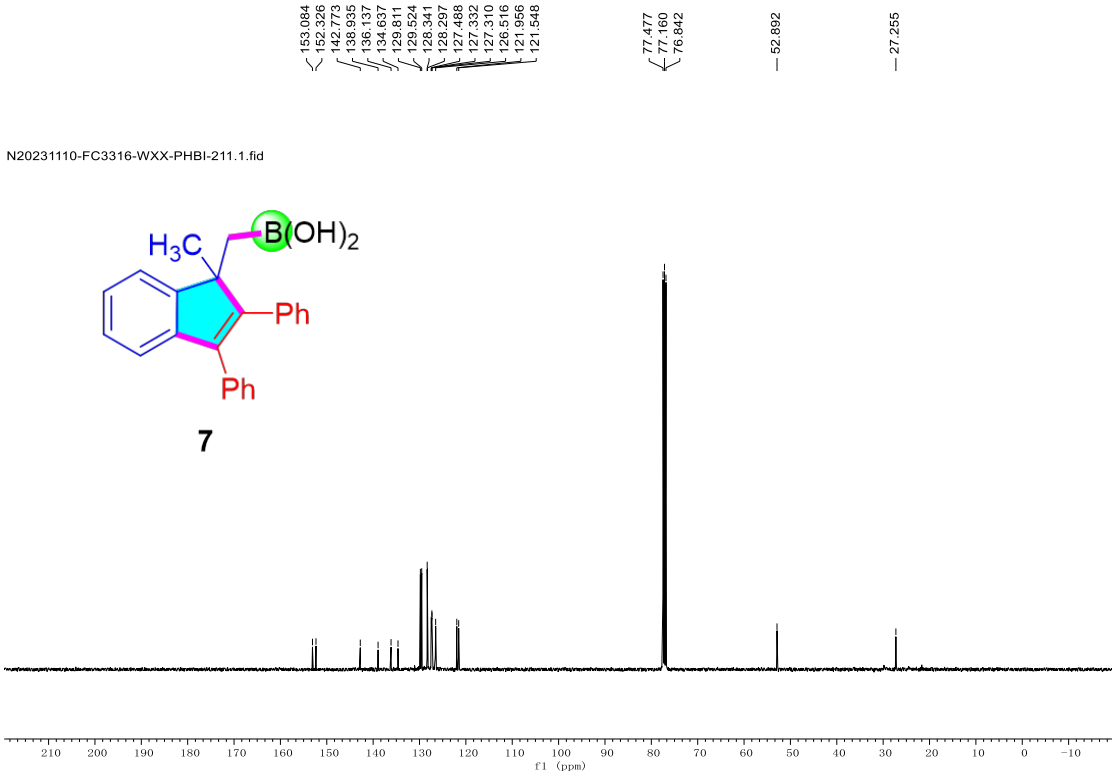
^{13}C{1H} NMR (101 MHz, $CDCl_3$) Spectrum of **6**



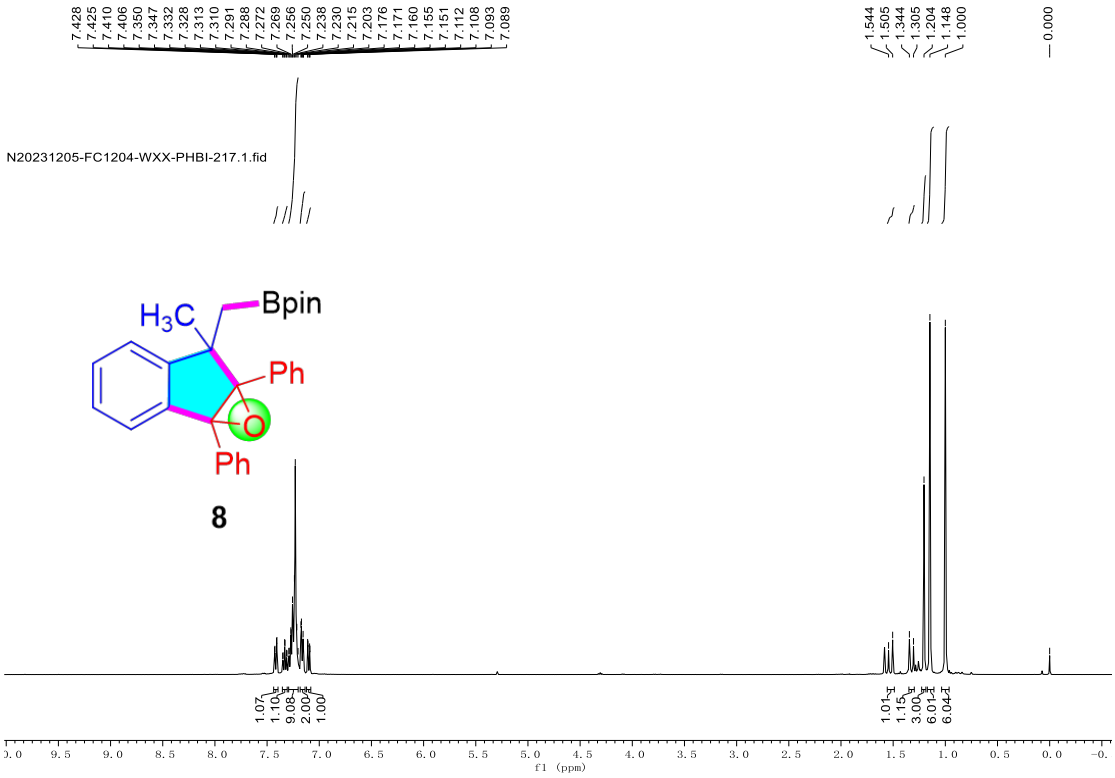
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of **7**



^{13}C{1H} NMR (101 MHz, $CDCl_3$) Spectrum of **7**



^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of **8**



^{13}C{1H} NMR (101 MHz, $CDCl_3$) Spectrum of **8**