
Rhodium-Catalyzed Construction of Boron-Based Point and Axially Chirality via Asymmetric Annulation of Alkynylboron Reagents

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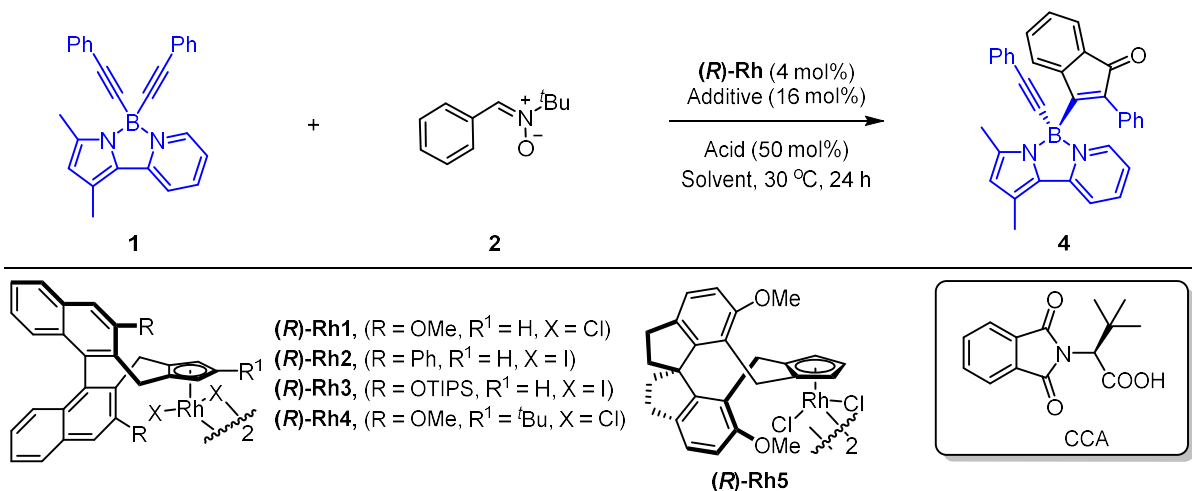
1. General Information

Commercially available chemicals were obtained from Adamas, Acros Organics, Aldrich Chemical Co., Alfa Aesar, and TCI and used as received unless otherwise noted. All air- and moisture-sensitive manipulations were carried out with standard Schlenk techniques under nitrogen or in a glove box under argon. The ^1H NMR spectra were recorded on 600 MHz NMR spectrometer. The ^{13}C NMR spectra were recorded at 150 MHz. The ^{11}B NMR spectra were recorded at 193 MHz. The ^{19}F NMR spectra were recorded at 376 MHz. The ^{31}P NMR spectra were recorded at 243 MHz. Chemical shifts were expressed in parts per million (δ) downfield from the internal standard tetramethylsilane (TMS), and were reported as s (singlet), d (doublet), t (triplet), dd (doublets of doublet), and m (multiplet). The residual solvent signals were used as references and the chemical shifts were converted to the TMS scale (CDCl_3 : $\delta \text{H} = 7.26 \text{ ppm}$, $\delta \text{C} = 77.16 \text{ ppm}$). The coupling constants J were given in Hz. High resolution mass spectra (HRMS) were obtained via ESI mode by using a MicroTOF mass spectrometer. Column chromatography was performed on silica gel 200-300 mesh. The enantiomeric excess (ee) of the products were determined by high-performance liquid chromatography (HPLC) with a chiral stationary phase in comparison with the authentic racemate sample with n -hexane and i -PrOH as solvents. All the chiral stationary phases including Chiralcel IE, IA, IB, IC used in this study were purchased from Daicel Chiral Technologies. Optical rotations were reported as follows: $[\alpha]_{\text{D}}^{\text{T}} = (c: \text{g}/100\text{mL}, \text{in } \text{CHCl}_3)$.

Chiral rhodium catalysts,^[1] aromatic substrates,^[2] and alkynyl boron substrates^[3] were prepared according to published procedures.

2. Experimental Section

2.1 Tables of the Optimization of Reaction Conditions of Synthesis of 4.

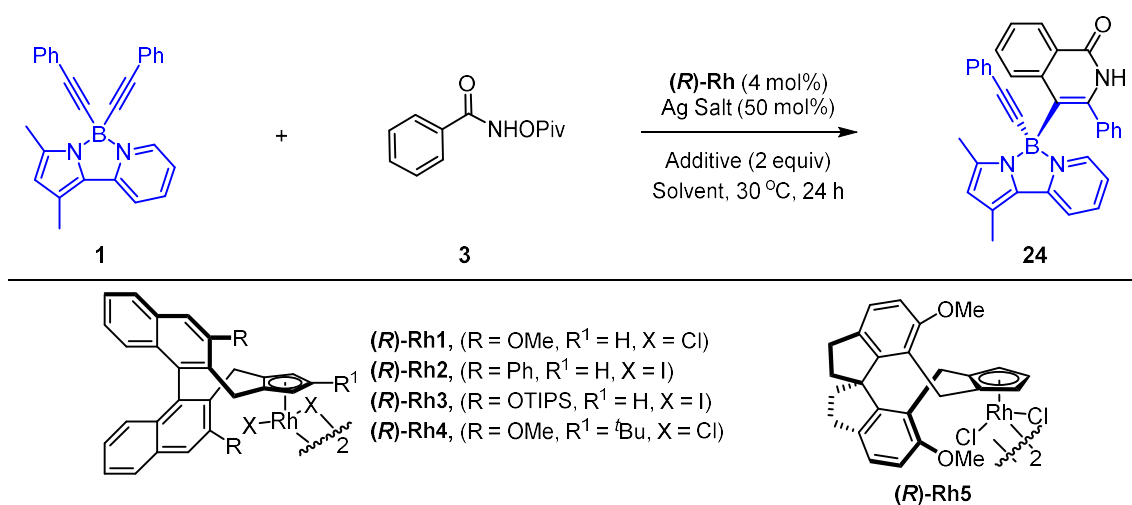


Entry	Cat.	Additive	Acid	Solvent	Yield (%)	ee (%)
1	(R)-Rh1	AgSbF ₆	HOPiv	DCM	35	19
2	(R)-Rh2	AgSbF ₆	HOPiv	DCM	33	39
3	(R)-Rh3	AgSbF ₆	HOPiv	DCM	42	37
4	(R)-Rh4	AgSbF ₆	HOPiv	DCM	28	21
5	(R)-Rh5	AgSbF ₆	HOPiv	DCM	15	<5
6	(R)-Rh3	AgSbF ₆	HOPiv	toluene	45	72
7	(R)-Rh3	AgSbF ₆	HOPiv	PhCl	50	67
8	(R)-Rh3	AgSbF ₆	HOPiv	THF	40	50
9	(R)-Rh3	AgSbF ₆	HOPiv	MeOH	Trace	-
10	(R)-Rh3	AgSbF ₆	HOAc	toluene	42	75
11	(R)-Rh3	AgSbF ₆	MesCOOH	toluene	40	75
12	(R)-Rh3	AgSbF ₆	CyCOOH	toluene	45	74
13	(R)-Rh3	AgOTf	HOAc	toluene	56	84
14	(R)-Rh3	AgBF ₄	HOAc	toluene	52	86
15	(R)-Rh3	AgPF ₆	HOAc	toluene	43	83
16	(R)-Rh3	AgNTf ₂	HOAc	toluene	50	78
17	(R)-Rh3	AgOAc	HOAc	toluene	N.D.	-
18	(R)-Rh3	-	HOAc	toluene	N.D.	-
19	(R)-Rh3	AgBF ₄	HOPiv	toluene	32	86

20	(R)-Rh3	AgBF ₄	MesCOOH	toluene	48	88
21 ^[b]	(R)-Rh3	AgBF ₄	(<i>rac</i>)-CCA	toluene	65	90
22 ^[b]	(R)-Rh3	AgBF ₄	CCA	toluene	70	90
23 ^[b,c]	(R)-Rh3	AgBF ₄	CCA	toluene	78	94

[a] **Reaction conditions A:** **1** (0.12 mmol), **2** (0.10 mmol), **(R)-Rh** (4 mol%), Additive (16 mol%) and Acid (0.20 mmol) in Solvent (2 mL), 30 °C, 24 h, isolated yield. The ee was determined by HPLC analysis using a chiral stationary phase. [b] CCA (50 mol%) was used. [c] 0 °C, 48 h. N.D. = not detected.

2.2 Tables of the Optimization of Reaction Conditions of Synthesis of **24**.

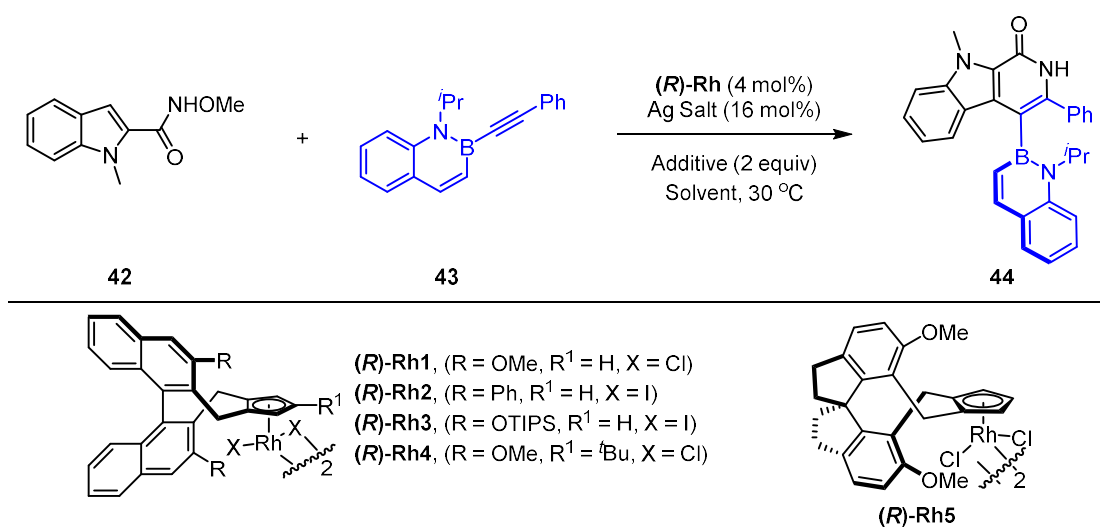


Entry	Cat.	Ag Salt	Additive	Solvent	Yield (%)	ee (%)
1	(R)-Rh1	AgOAc		toluene	31	25
2	(R)-Rh2	AgOAc	-	toluene	<10	23
3	(R)-Rh3	AgOAc	-	toluene	38	90
4	(R)-Rh4	AgOAc	-	toluene	21	20
5	(R)-Rh5	AgOAc	-	toluene	25	-60
6	(R)-Rh3	AgOAc	-	PhCl	29	89
7	(R)-Rh3	AgOAc	-	DCM	12	81
8	(R)-Rh3	AgOAc	-	MeOH	Trace	-
9	(R)-Rh3	AgOAc	-	THF	Trace	-
10	(R)-Rh3	AgOAc	HOPiv	toluene	35	91
11	(R)-Rh3	AgOAc	NaOAc	toluene	40	94
12	(R)-Rh3	AgOAc	Zn(OAc) ₂	toluene	51	90
13	(R)-Rh3	AgOAc	CsOAc	toluene	35	94

14	(<i>R</i>)-Rh3	Ag ₂ CO ₃	Zn(OAc) ₂	toluene	26	94
15	(<i>R</i>)-Rh3	AgF	Zn(OAc) ₂	toluene	29	90
16	(<i>R</i>)-Rh3	Ag ₂ O	Zn(OAc) ₂	toluene	41	91
17	(<i>R</i>)-Rh3	PhCOOAg	Zn(OAc) ₂	toluene	56	93
18	(<i>R</i>)-Rh3	AgOPiv	Zn(OAc) ₂	toluene	39	92
19	(<i>R</i>)-Rh3	PhCOOAg	HOPiv	toluene	36	90
20	(<i>R</i>)-Rh3	PhCOOAg	HOAc	toluene	70	92
21	(<i>R</i>)-Rh3	PhCOOAg	NaOAc	toluene	29	94
22	(<i>R</i>)-Rh3	PhCOOAg	Zn(OTf) ₂	toluene	Trace	-
23 ^b	(<i>R</i>)-Rh3	PhCOOAg	HOAc	toluene	80	91

[a] **Reaction conditions B:** **1** (0.12 mmol), **3** (0.10 mmol), (*R*)-Rh (4 mol%), Ag Salt (50 mol%) and Additive (0.20 mmol) in Solvent (2 mL), 30 °C, 24 h, isolated yield. The ee was determined by HPLC analysis using a chiral stationary phase. [b] 40 °C.

2.3 Tables of the Optimization of Reaction Conditions of Synthesis of 44.



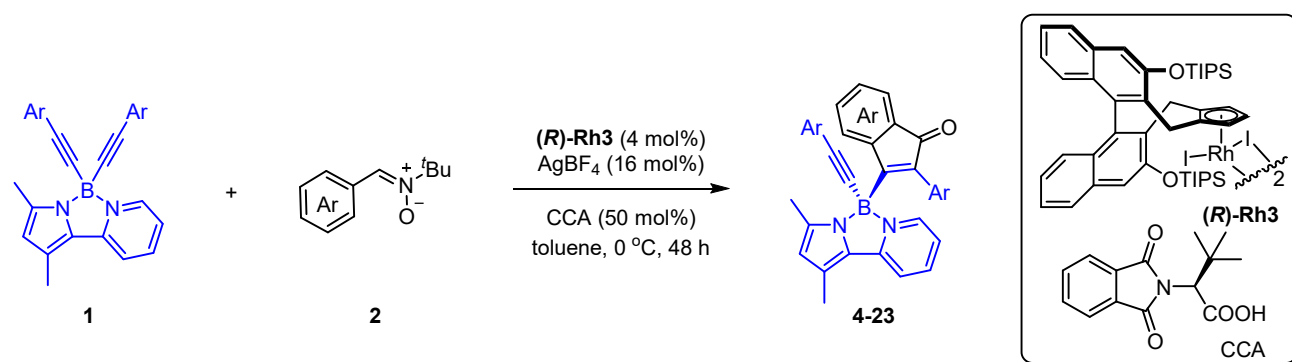
Entry	Cat.	Ag Salt	Additive	Solvent	Yield (%)	ee (%)
1	(<i>R</i>)-Rh1	-	NaOAc	TFE	32	20
2	(<i>R</i>)-Rh1	-	CsOAc	TFE	38	13
3	(<i>R</i>)-Rh1	-	Zn(OAc) ₂	TFE	30	37
4	(<i>R</i>)-Rh1	-	Fe(OAc) ₂	TFE	18	30
5	(<i>R</i>)-Rh1	-	Zn(OAc) ₂	DCE	35	56
6	(<i>R</i>)-Rh1	-	Zn(OAc) ₂	toluene	29	64
7	(<i>R</i>)-Rh1	-	Zn(OAc) ₂	PhOMe	36	69

8	(<i>R</i>)-Rh1	-	Zn(OAc) ₂	THF	15	62
9	(<i>R</i>)-Rh1	-	Zn(OAc) ₂	CH ₃ CN	29	44
10	(<i>R</i>)-Rh2	-	Zn(OAc) ₂	PhOMe	25	39
11	(<i>R</i>)-Rh3	-	Zn(OAc) ₂	PhOMe	Trace	-
12	(<i>R</i>)-Rh4	-	Zn(OAc) ₂	PhOMe	43	83
13	(<i>R</i>)-Rh5	-	Zn(OAc) ₂	PhOMe	19	-42
14	(<i>R</i>)-Rh4	-	Zn(OAc) ₂	DCM	18	81
15	(<i>R</i>)-Rh4	-	Zn(OAc) ₂	THF	11	78
16	(<i>R</i>)-Rh4	-	Zn(OAc) ₂	MeOH	<10	67
17	(<i>R</i>)-Rh4	-	Zn(OAc) ₂	EA	52	87
18	(<i>R</i>)-Rh4	AgOAc	Zn(OAc) ₂	EA	26	79
19	(<i>R</i>)-Rh4	AgSbF ₆	Zn(OAc) ₂	EA	62	94
20 ^b	(<i>R</i>)-Rh4	AgSbF ₆	Zn(OAc) ₂	EA	58	98
21 ^c	(<i>R</i>)-Rh4	AgSbF ₆	Zn(OAc) ₂	EA	70	96

[a] **Reaction conditions C:** **42** (0.15 mmol), **43** (0.10 mmol), (*R*)-Rh (4 mol%), Ag Salt (16 mol%) and Additive (0.20 mmol) in Solvent (2 mL), 30 °C, 24 h, isolated yield. The ee was determined by HPLC analysis using a chiral stationary phase. [b] 20 °C. [c] 40 °C.

2.4 Typical General Procedure for the Asymmetric Catalysis

General procedure for the synthesis of 4-23.

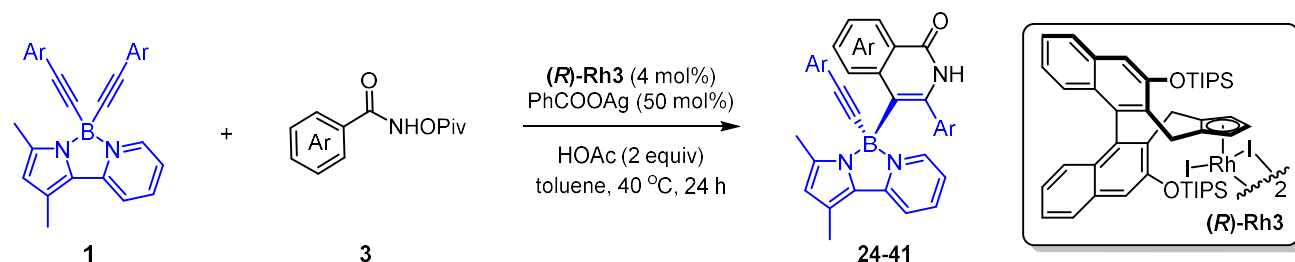


A screw-cap vial (8 mL) was charged with *N,N*-chelated tetracoordinate arylboron-diyne **1** (0.12 mmol, 1.2 equiv), (*R*)-Rh3 (4 mol%), AgBF₄ (16 mol%) and CCA (50 mol%) in toluene (2 mL). The resulted mixture was kept at 0 °C for 15 min, to which was added nitrone **2** (0.10 mmol, 1.0 equiv). The reaction was maintained at 0 °C for 48 h. The reaction mixture was evaporated under vacuum and the residue was purified by preparative TLC to give the corresponding products **4-23**.

A similar synthetic procedure was followed for synthesis of racemic product except that [Cp*RhCl₂]₂

(4 mol %), AgSbF₆ (16 mol%) and HOPiv (1.0 equiv) was used in DCM at 50 °C for 24 h.

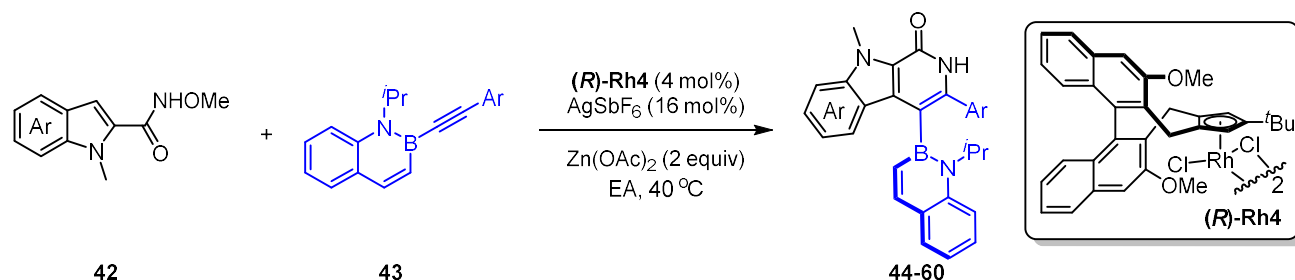
General procedure for the synthesis of 24-41.



A screw-cap vial (8 mL) was charged with *N,N*-chelated tetracoordinate arylboron-diyne **1** (0.12 mmol, 1.2 equiv), benzamide **3** (0.10 mmol, 1.0 equiv), **(R)-Rh3** (4 mol%), PhCOOAg (50 mol%) and HOAc (0.20 mmol, 2.0 equiv) in toluene (2 mL) and the reaction mixture was stirred at 40 °C for 24 h. The reaction mixture was evaporated under vacuum and the residue was purified by preparative TLC to give the corresponding products **24-41**.

A similar synthetic procedure was followed for synthesis of racemic product except that [Cp*RhCl₂]₂ (4 mol %), AgOAc (40 mol%) and HOPiv (1.0 equiv) was used in DCM at 50 °C for 24 h.

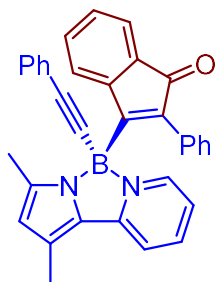
General procedure for the synthesis of 44-60.



A screw-cap vial (8 mL) was charged with BN-alkyne **43** (0.10 mmol, 1.0 equiv), indolecarboxamide **42** (0.15 mmol, 1.5 equiv), **(R)-Rh4** (4 mol%), AgSbF₆ (16 mol%) and Zn(OAc)₂ (0.20 mmol, 2.0 equiv) in EA (2 mL) and the reaction mixture was stirred at 40 °C for 24 h under N₂. The reaction mixture was evaporated under vacuum and the residue was purified by preparative TLC to give the corresponding products **44-60**.

A similar synthetic procedure was followed for synthesis of racemic product except that [Cp*RhCl₂]₂ (4 mol %) and NaOAc (1.0 equiv) was used in DCE at 60 °C for 24 h.

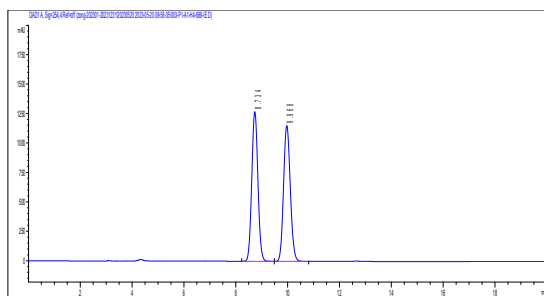
3. Characterization Data and HPLC Chromatograms



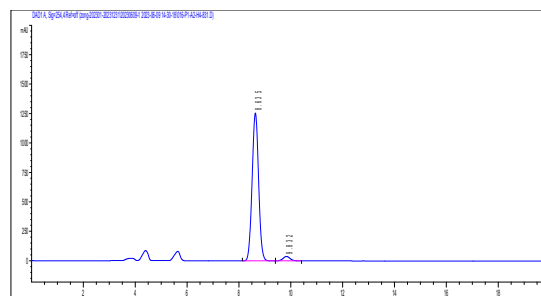
(*R*)-3-(1,3-dimethyl-5-(phenylethynyl)-5*H*-5λ⁴,6λ⁴-pyrrolo[1',2':3,4][1,3,2]diazaborolo[1,5-*a*]pyridin-5-yl)-2-phenyl-1*H*-inden-1-one (4)

The title compound was isolated as a yellow solid (38.1 mg, 78%). **¹H NMR (600 MHz, CDCl₃)** δ 8.24 (s, br, 1H), 8.06 – 8.00 (m, 1H), 7.51 – 7.45 (m, 2H), 7.43 – 7.38 (m, 1H), 7.36 – 7.32 (m, 2H), 7.26 – 7.23 (m, 3H), 7.22 – 7.18 (m, 1H), 7.06 – 7.01 (m, 2H), 7.00 – 6.95 (m, 2H), 6.75 – 6.70 (m, 1H), 6.55 (d, *J* = 7.4 Hz, 2H), 5.83 (s, 1H), 2.29 (s, 3H), 2.28 (s, 3H). **¹³C NMR (150 MHz, CDCl₃)** δ 199.1, 150.4, 149.8, 143.5, 141.8, 140.7, 137.1, 133.9, 133.0, 131.6, 130.8, 129.3, 128.2, 127.7, 127.6, 127.1, 126.7, 124.8, 124.5, 122.6, 122.3, 116.9, 115.8, 115.6, 99.0, 14.1, 12.2. **¹¹B NMR (193 MHz, CDCl₃)** δ -4.73. **HRMS (ESI):** calcd. for C₃₄H₂₅BN₂NaO⁺ [*M*+Na]⁺: 511.1952, found: 511.1946. [*α*]_D²⁰ = -212 (*c* = 0.1, CHCl₃).

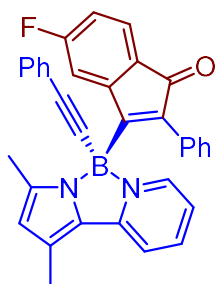
HPLC analysis: Daicel Chiralpak IE column (hexane: 2-propanol = 85:15, *v* = 1.0 mL/min, 40 °C, 254 nm); *tr* (major) = 8.635 min, *tr* (minor) = 9.832 min, 94% ee.



No.	Time	Area	Area (%)
1	8.734	20837.7	50.06
2	9.968	20788.1	49.94



No.	Time	Area	Area (%)
1	8.635	21786.6	96.87
2	9.832	703.1	3.13

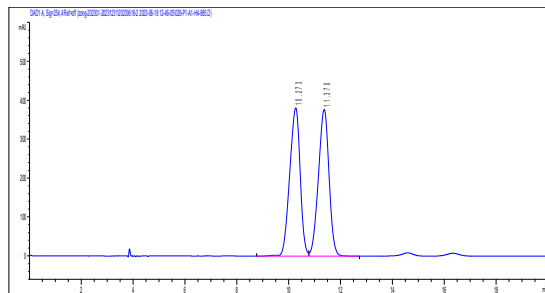


(*R*)-3-(1,3-dimethyl-5-(phenylethynyl)-5*H*-5λ⁴,6λ⁴-pyrrolo[1',2':3,4][1,3,2]diazaborolo[1,5-*a*]pyridin-5-yl)-5-fluoro-2-phenyl-1*H*-inden-1-one (5)

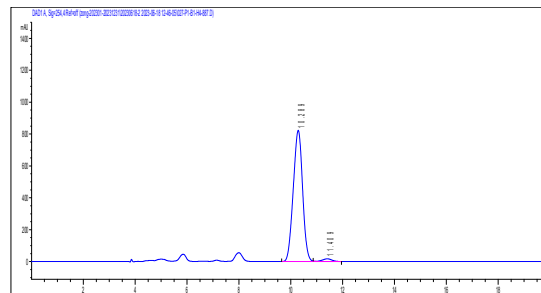
The title compound was isolated as a yellow solid (37.4 mg, 74%). **¹H NMR (600 MHz, CDCl₃)** δ 8.03 (s, br, 1H), 8.00 – 7.97 (m, 1H), 7.50 – 7.46 (m, 1H), 7.44 – 7.40 (m, 1H), 7.37 – 7.31 (m, 2H), 7.25 – 7.21 (m, 3H), 7.06 – 7.00 (m, 2H), 6.96 (t, *J* = 7.5 Hz, 2H), 6.85 – 6.81 (m, 1H), 6.74 – 6.70 (m, 1H), 6.51 (d, *J* = 7.2 Hz, 2H), 5.82 (s, 1H), 2.27 (s, 3H), 2.26 (s, 3H). **¹³C NMR (150 MHz, CDCl₃)** δ 197.3, 166.9 (d, *J*_{C-F} = 251.9 Hz), 166.1, 153.8 (d, *J*_{C-F} = 10.0 Hz), 149.9, 144.9, 141.7, 140.8, 137.1, 132.7, 131.6, 129.2, 128.2, 127.8, 127.6,

127.2, 126.9, 126.7 (d, J_{C-F} = 2.8 Hz), 124.5, 123.8, 123.7, 122.8, 117.0, 115.9, 115.7, 113.4 (d, J_{C-F} = 25.8 Hz), 113.1 (d, J_{C-F} = 23.2 Hz), 99.3, 14.1, 12.1. **^{11}B NMR (193 MHz, CDCl_3)** δ -5.04. **^{19}F NMR (376 MHz, CDCl_3)** δ -104.31. **HRMS (APCI)**: calcd. for $\text{C}_{34}\text{H}_{25}\text{BFN}_2\text{O}^+$ $[\text{M}+\text{H}]^+$: 507.2038, found : 507.2031. $[\alpha]_{\text{D}}^{20}$ = -210 (c = 0.1, CHCl_3).

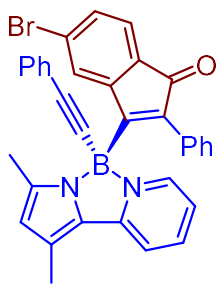
HPLC analysis: Daicel Chiralpak IE column (hexane: 2-propanol = 90:10, v = 0.8 mL/min, 40 °C, 254 nm); tr (major) = 10.289 min, tr (minor) = 11.409 min, 96% ee.



No.	Time	Area	Area (%)
1	10.273	10717.2	49.94
2	11.370	10741.0	50.06



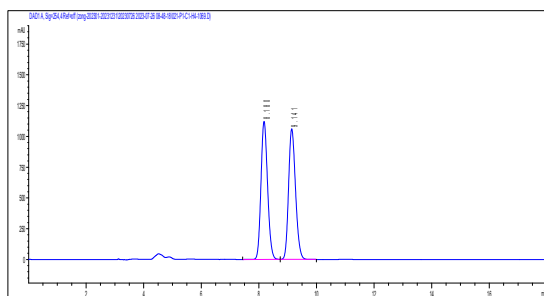
No.	Time	Area	Area (%)
1	10.289	20534.2	98.02
2	11.409	414.9	1.98



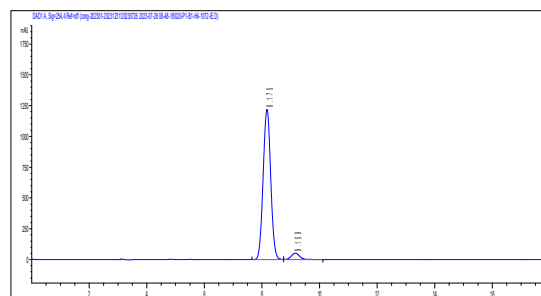
(*R*)-5-bromo-3-(1,3-dimethyl-5-(phenylethynyl)-5*H*-5 λ^4 ,6 λ^4 -pyrrolo[1',2':3,4][1,3,2]diazaborolo[1,5-*a*]pyridin-5-yl)-2-phenyl-1*H*-inden-1-one (6)

The title compound was isolated as a yellow solid (39.6 mg, 70%). **^1H NMR (600 MHz, CDCl_3)** δ 8.58 (s, br, 1H), 7.98 (dt, J = 6.0, 1.2 Hz, 1H), 7.51 – 7.46 (m, 1H), 7.43 – 7.38 (m, 2H), 7.36 (dd, J = 7.5, 1.6 Hz, 1H), 7.30 (d, J = 7.5 Hz, 1H), 7.25 – 7.22 (m, 3H), 7.05 – 6.99 (m, 2H), 6.95 (t, J = 7.6 Hz, 2H), 6.75 – 6.69 (m, 1H), 6.46 (d, J = 7.4 Hz, 2H), 5.81 (s, 1H), 2.26 (s, 3H), 2.24 (s, 3H). **^{13}C NMR (150 MHz, CDCl_3)** δ 197.8, 152.4, 149.9, 144.4, 141.7, 140.8, 137.1, 132.5, 131.8, 130.3, 129.4, 129.2, 128.7, 128.24, 128.22, 127.9, 127.6, 127.2, 127.0, 124.5, 123.3, 122.8, 117.0, 115.9, 115.7, 99.5, 14.1, 12.1. **^{11}B NMR (193 MHz, CDCl_3)** δ -5.09. **HRMS (APCI)**: calcd. for $\text{C}_{34}\text{H}_{25}\text{BBrN}_2\text{O}^+$ $[\text{M}+\text{H}]^+$: 567.1238, found : 567.1230. $[\alpha]_{\text{D}}^{20}$ = -162 (c = 0.1, CHCl_3).

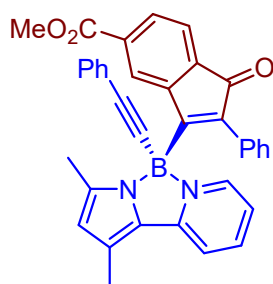
HPLC analysis: Daicel Chiralpak IE column (hexane: 2-propanol = 90:10, v = 1.0 mL/min, 40 °C, 254 nm); tr (major) = 8.175 min, tr (minor) = 9.159 min, 91% ee.



No.	Time	Area	Area (%)
1	8.180	17816.8	50.09
2	9.141	17751.9	49.91



No.	Time	Area	Area (%)
1	8.175	22270.1	95.62
2	9.159	1021.4	4.38



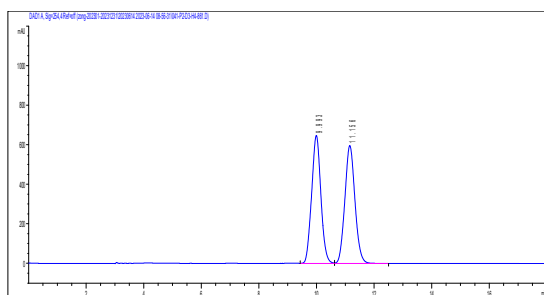
(R)-methyl 3-(1,3-dimethyl-5-(phenylethynyl)-5H-5λ⁴,6λ⁴-pyrrolo [1',2':3,4][1,3,2]diazaborolo[1,5-a]pyridin-5-yl)-1-oxo-2-phenyl-1H-indene-5-carboxylate (7)

The title compound was isolated as a yellow solid (30.1 mg, 55%). ¹H NMR (600 MHz, CDCl₃) δ 9.04 (s, br, 1H), 8.04 – 8.00 (m, 1H), 7.97 (dd, *J* = 7.4,

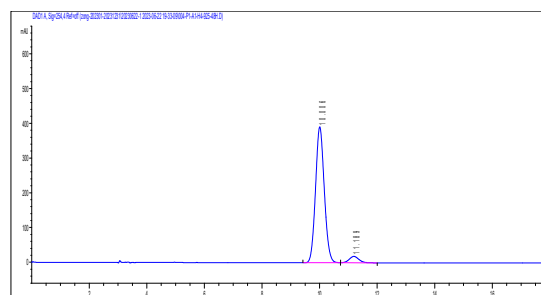
1.4 Hz, 1H), 7.53 – 7.49 (m, 2H), 7.45 – 7.42 (m, 2H), 7.26 – 7.22 (m, 3H), 7.07 – 7.01 (m, 2H), 6.97 (t, *J* = 7.5 Hz, 2H), 6.76 – 6.72 (m, 1H), 6.51 (d, *J* = 7.5 Hz, 2H), 5.82 (s, 1H), 3.85 (s, 3H), 2.28 (s, 3H), 2.27 (s, 3H). ¹³C NMR (150 MHz, CDCl₃) δ 198.2, 166.9, 150.4, 149.9, 144.2, 141.7, 140.8, 137.1, 135.0, 134.3, 132.6, 131.9, 130.3, 129.2, 128.1, 127.71, 127.68, 127.2, 126.9, 125.1, 124.6, 122.8, 121.8, 117.0, 115.9, 115.7, 99.6, 52.3, 14.1, 12.1. ¹¹B NMR (193 MHz, CDCl₃) δ -5.01. HRMS

(APCI): calcd. for C₃₆H₂₈BN₂O₃⁺ [M+H]⁺: 547.2187, found: 547.2177. [α]_D²⁰ = -194 (c = 0.1, CHCl₃).

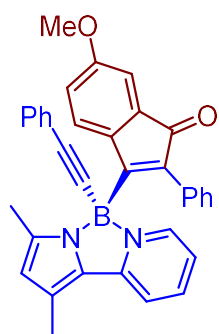
HPLC analysis: Daicel Chiralpak IE column (hexane: 2-propanol = 85:15, v = 1.0 mL/min, 40 °C, 254 nm); tr (major) = 10.006 min, tr (minor) = 11.189 min, 91% ee.



No.	Time	Area	Area (%)
1	9.993	14430.8	49.90
2	11.156	14486.9	50.10



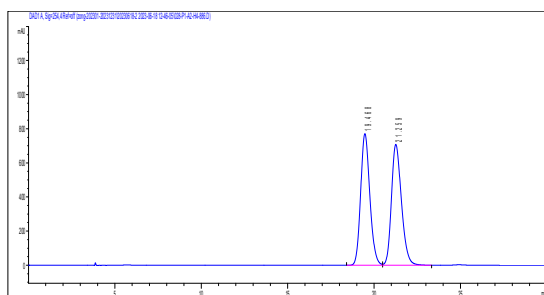
No.	Time	Area	Area (%)
1	10.006	8256.8	95.25
2	11.189	414.8	4.75



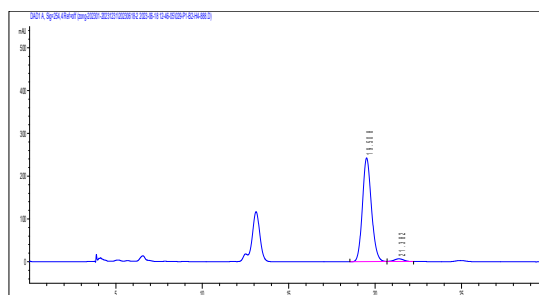
(R)-3-(1,3-dimethyl-5-(phenylethynyl)-5H-5λ⁴,6λ⁴-pyrrolo[1',2':3,4][1,3,2]diazaborolo[1,5-a]pyridin-5-yl)-6-methoxy-2-phenyl-1H-inden-1-one (8)

The title compound was isolated as a yellow solid (37.8 mg, 73%). ¹H NMR (600 MHz, CDCl₃) δ 8.10 (s, br, 1H), 8.03 (d, *J* = 5.9 Hz, 1H), 7.52 – 7.47 (m, 1H), 7.37 – 7.31 (m, 2H), 7.25 (q, *J* = 2.9 Hz, 3H), 7.08 (d, *J* = 2.6 Hz, 1H), 7.06 – 7.00 (m, 2H), 6.97 (t, *J* = 7.5 Hz, 2H), 6.85 (dd, *J* = 8.1, 2.6 Hz, 1H), 6.72 (t, *J* = 6.6 Hz, 1H), 6.54 (d, *J* = 7.3 Hz, 2H), 5.83 (s, 1H), 3.84 (s, 3H), 2.29 (s, 3H), 2.28 (s, 3H). ¹³C NMR (150 MHz, CDCl₃) δ 198.7, 160.0, 149.8, 142.4, 142.2, 141.7, 140.7, 137.1, 133.1, 132.9, 131.6, 129.3, 128.1, 127.6, 127.1, 126.6, 125.3, 124.8, 122.5, 116.9, 116.8, 115.8, 115.5, 109.8, 98.9, 55.8, 14.0, 12.1. ¹¹B NMR (193 MHz, CDCl₃) δ -5.22. HRMS (APCI): calcd. for C₃₅H₂₈BN₂O₂⁺ [M+H]⁺ : 519.2238, found : 519.2227. [α]_D²⁰ = -142 (c = 0.1, CHCl₃).

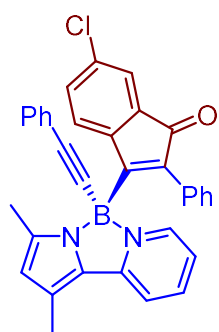
HPLC analysis: Daicel Chiralpak IE column (hexane: 2-propanol = 90:10, v = 0.8 mL/min, 40 °C, 254 nm); tr (major) = 19.508 min, tr (minor) = 21.382 min, 95% ee.



No.	Time	Area	Area (%)
1	19.468	28521.6	49.92
2	21.259	28614.1	50.08



No.	Time	Area	Area (%)
1	19.508	8785.1	97.50
2	21.382	225.0	2.50

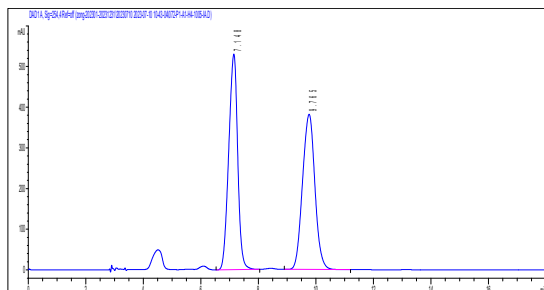


(R)-6-chloro-3-(1,3-dimethyl-5-(phenylethynyl)-5H-5λ⁴,6λ⁴-pyrrolo[1',2':3,4][1,3,2]diazaborolo[1,5-a]pyridin-5-yl)-2-phenyl-1H-inden-1-one (9)

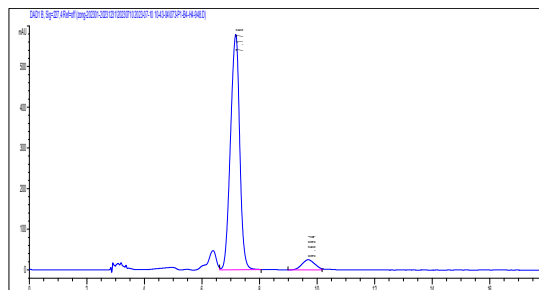
The title compound was isolated as a yellow solid (30.3 mg, 58%). ¹H NMR (600 MHz, CDCl₃) δ 8.16 (s, br, 1H), 7.98 (dt, *J* = 6.0, 1.2 Hz, 1H), 7.51 – 7.46 (m, 1H), 7.40 (d, *J* = 2.1 Hz, 1H), 7.35 (dd, *J* = 7.9, 2.1 Hz, 1H), 7.33 – 7.28 (m, 2H), 7.25 – 7.22 (m, 3H), 7.06 – 7.01 (m, 2H), 6.96 (t, *J* = 7.5 Hz, 2H), 6.75 – 6.67 (m, 1H), 6.52 (d, *J* = 7.4 Hz, 2H), 5.83 (s, 1H), 2.27 (s, 3H), 2.26 (s, 3H). ¹³C NMR (150 MHz, CDCl₃) δ 197.7, 149.9, 148.5, 141.7, 140.8, 137.1, 133.7, 133.0, 132.57, 132.55, 131.6, 129.3, 128.2, 127.8, 127.6, 127.2, 127.0, 125.5, 124.6, 122.8, 117.0, 115.9, 115.7, 99.2, 14.1, 12.2. ¹¹B NMR (193 MHz, CDCl₃)

δ -5.12. **HRMS (APCI)**: calcd. for $C_{34}H_{25}BClN_2O^+$ $[M+H]^+$: 523.1743, found : 523.1738. $[\alpha]_D^{20} = -208$ ($c = 0.1$, $CHCl_3$).

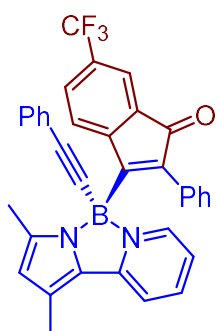
HPLC analysis: Daicel Chiralpak IA column (hexane: 2-propanol = 95:5, $v = 1.0$ mL/min, 40 °C, 254 nm); tr (major) = 7.176 min, tr (minor) = 9.694 min, 90% ee.



No.	Time	Area	Area (%)
1	7.148	11475.6	50.11
2	9.765	11426.2	49.89



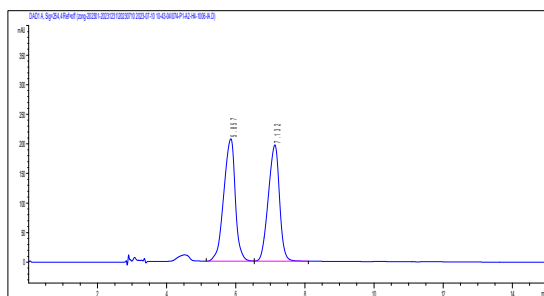
No.	Time	Area	Area (%)
1	7.176	12842.0	94.88
2	9.694	693.1	5.12



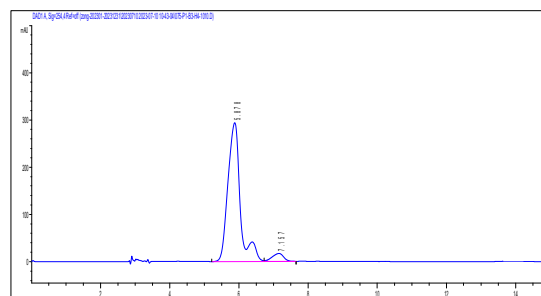
(R)-3-(1,3-dimethyl-5-(phenylethynyl)-5H-5 λ ⁴,6 λ ⁴-pyrrolo[1',2':3,4][1,3,2]diazaborolo[1,5-a]pyridin-5-yl)-2-phenyl-6-(trifluoromethyl)-1H-inden-1-one (10)

The title compound was isolated as a yellow solid (25.6 mg, 46%). **¹H NMR (600 MHz, CDCl₃)** δ 8.35 (s, br, 1H), 7.98 (dt, $J = 6.0, 1.2$ Hz, 1H), 7.71 – 7.65 (m, 2H), 7.52 – 7.48 (m, 1H), 7.34 – 7.30 (m, 2H), 7.25 – 7.24 (m, 3H), 7.08 – 7.02 (m, 2H), 6.99 (t, $J = 7.5$ Hz, 2H), 6.75 – 6.71 (m, 1H), 6.54 (d, $J = 7.4$ Hz, 2H), 5.85 (s, 1H), 2.28 (s, 3H), 2.27 (s, 3H). **¹³C NMR (150 MHz, CDCl₃)** δ 197.4, 153.8, 149.9, 145.4, 141.6, 140.9, 137.1, 132.3, 131.6, 131.3, 131.1 (q, $J_{C-F} = 3.7$ Hz), 129.9 (q, $J_{C-F} = 32.8$ Hz), 129.2, 128.3, 127.9, 127.6, 127.3, 127.2, 124.5, 124.3, 124.2 (q, $J_{C-F} = 272.2$ Hz), 122.9, 118.9 (q, $J_{C-F} = 3.4$ Hz), 117.1, 115.9, 115.8, 99.4, 14.1, 12.2. **¹¹B NMR (193 MHz, CDCl₃)** δ -4.91. **¹⁹F NMR (376 MHz, CDCl₃)** δ -62.53. **HRMS (APCI)**: calcd. for $C_{35}H_{24}BF_3N_2O^+$ $[M+H]^+$: 557.2007, found : 557.2002. $[\alpha]_D^{20} = -210$ ($c = 0.1$, $CHCl_3$).

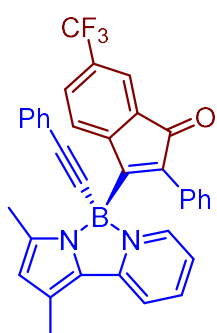
HPLC analysis: Daicel Chiralpak IA column (hexane: 2-propanol = 95:5, $v = 1.0$ mL/min, 40 °C, 254 nm); tr (major) = 5.878 min, tr (minor) = 7.157 min, 90% ee.



No.	Time	Area	Area (%)
1	5.857	4799.7	52.05
2	7.132	4421.4	47.95



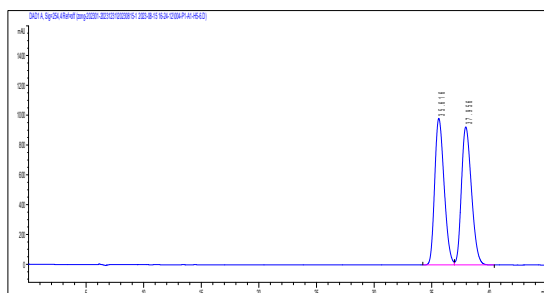
No.	Time	Area	Area (%)
1	5.878	7291.5	95.00
2	7.157	384.4	5.00



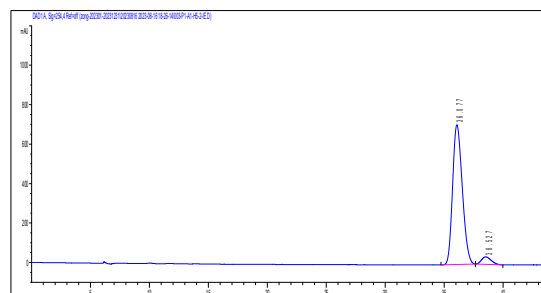
(R)-methyl 3-(1,3-dimethyl-5-(phenylethynyl)-5H-5λ⁴,6λ⁴-pyrrolo[1',2':3,4][1,3,2]diazaborolo[1,5-a]pyridin-5-yl)-1-oxo-2-phenyl-1H-indene-6-carboxylate (11)

The title compound was isolated as a yellow solid (28.4 mg, 52%). **¹H NMR (600 MHz, CDCl₃)** δ 8.37 (s, br, 1H), 8.18 – 8.14 (m, 1H), 8.11 – 8.06 (m, 1H), 7.98 (d, *J* = 6.0 Hz, 1H), 7.47 (t, *J* = 7.8 Hz, 1H), 7.36 – 7.30 (m, 2H), 7.26 – 7.21 (m, 3H), 7.06 – 7.00 (m, 2H), 6.97 (t, *J* = 7.5 Hz, 2H), 6.70 (t, *J* = 6.6 Hz, 1H), 6.53 (d, *J* = 7.5 Hz, 2H), 5.83 (s, 1H), 3.91 (s, 3H), 2.27 (s, 3H), 2.26 (s, 3H). **¹³C NMR (150 MHz, CDCl₃)** δ 197.7, 166.6, 155.1, 149.8, 145.7, 141.6, 140.9, 137.0, 135.9, 132.4, 131.6, 130.9, 129.6, 129.2, 128.2, 127.8, 127.6, 127.14, 127.05, 124.5, 124.3, 122.8, 122.7, 117.0, 115.9, 115.7, 99.3, 52.2, 14.0, 12.1. **¹¹B NMR (193 MHz, CDCl₃)** δ -4.92. **HRMS (APCI):** calcd. for C₃₆H₂₈BN₂O₃⁺ [M+H]⁺ : 547.2187, found : 547.2181. **[α]_D²⁰** = -170 (c = 0.1, CHCl₃).

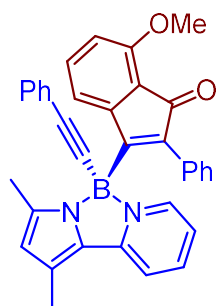
HPLC analysis: Daicel Chiralpak IE column (hexane: 2-propanol = 85:15, v = 0.5 mL/min, 40 °C, 254 nm); tr (major) = 36.077 min, tr (minor) = 38.527 min, 90% ee.



No.	Time	Area	Area (%)
1	35.616	55960.6	49.91
2	37.956	56163.2	50.09



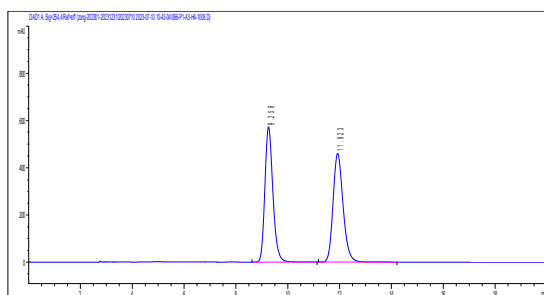
No.	Time	Area	Area (%)
1	36.077	40385.0	94.92
2	38.527	2161.3	5.08



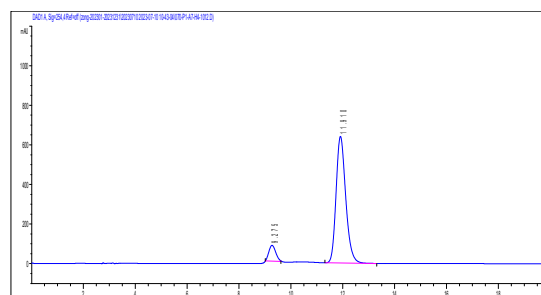
(R)-3-(1,3-dimethyl-5-(phenylethynyl)-5H-5λ⁴,6λ⁴-pyrrolo[1',2':3,4][1,3,2]diazaborolo[1,5-a]pyridin-5-yl)-7-methoxy-2-phenyl-1H-inden-1-one (12)

The title compound was isolated as a yellow solid (29.5 mg, 57%). ¹H NMR (600 MHz, CDCl₃) δ 8.02 (d, *J* = 5.9 Hz, 1H), 7.94 (s, br, 1H), 7.51 – 7.45 (m, 1H), 7.38 (t, *J* = 7.9 Hz, 1H), 7.35 – 7.30 (m, 2H), 7.25 – 7.20 (m, 3H), 7.06 – 6.98 (m, 2H), 6.94 (t, *J* = 7.5 Hz, 2H), 6.81 (d, *J* = 8.6 Hz, 1H), 6.71 (t, *J* = 6.6 Hz, 1H), 6.52 (d, *J* = 7.4 Hz, 2H), 5.81 (s, 1H), 3.94 (s, 3H), 2.28 (s, 3H), 2.27 (s, 3H). ¹³C NMR (150 MHz, CDCl₃) δ 196.8, 156.4, 152.8, 149.7, 144.0, 141.7, 140.6, 137.0, 135.7, 133.1, 131.6, 129.4, 128.1, 127.6, 127.5, 126.9, 126.5, 124.8, 122.4, 118.0, 116.9, 115.8, 115.7, 115.4, 113.1, 98.7, 56.0, 13.9, 12.1. ¹¹B NMR (193 MHz, CDCl₃) δ -4.89. HRMS (APCI): calcd. for C₃₅H₂₈BN₂O₂⁺ [M+H]⁺ : 519.2238, found : 519.2236. [α]_D²⁰ = -160 (c = 0.1, CHCl₃).

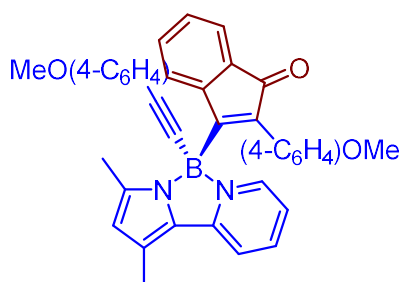
HPLC analysis: Daicel Chiralpak IA column (hexane: 2-propanol = 85:15, v = 1.0 mL/min, 40 °C, 254 nm); tr (major) = 9.275 min, tr (minor) = 11.910 min, 85% ee.



No.	Time	Area	Area (%)
1	9.258	12366.8	50.05
2	11.923	12344.7	49.95



No.	Time	Area	Area (%)
1	9.275	1338.9	7.51
2	11.910	16489.4	92.49



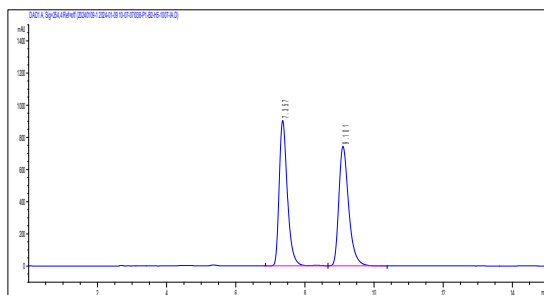
(R)-2-(4-methoxyphenyl)-3-(5-((4-methoxyphenyl) ethynyl)-1,3-dimethyl-5H-5λ⁴,6λ⁴-pyrrolo[1',2':3,4][1,3,2]diazaborolo[1,5-a]pyridin-5-yl)-1H-inden-1-one (13)

The title compound was isolated as a yellow solid (37.3 mg, 68%).

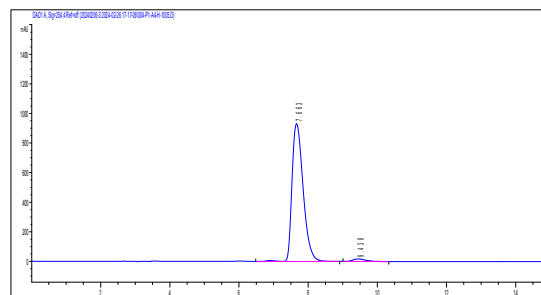
¹H NMR (600 MHz, CDCl₃) δ 8.08 (s, br, 1H), 7.94 (d, *J* = 5.9 Hz, 1H), 7.47 – 7.41 (m, 1H), 7.35 (d, *J* = 7.0 Hz, 1H), 7.29 (t, *J* = 7.7 Hz, 1H), 7.20 – 7.14 (m, 2H), 7.08 (t, *J* = 7.4 Hz, 1H), 7.01 (d, *J* = 8.4 Hz, 1H), 6.68 (d, *J* = 8.4 Hz, 2H), 6.64 (t, *J* = 6.6 Hz, 1H), 6.49 – 6.33 (m, 4H), 5.74 (s, 1H), 3.69 (s, 3H), 3.62 (s, 3H), 2.21 (s, 3H), 2.18 (s, 3H). ¹³C NMR (150 MHz, CDCl₃) δ 199.5, 159.1, 158.6, 150.5, 149.8, 143.0, 141.8, 140.7, 137.1, 133.9, 133.3, 133.0, 130.9,

130.6, 127.6, 127.5, 125.5, 124.4, 122.5, 122.2, 117.1, 116.9, 115.8, 115.5, 113.8, 112.7, 98.8, 55.4, 55.3, 14.0, 12.2. **¹¹B NMR (193 MHz, CDCl₃)** δ -4.72. **HRMS (APCI)**: calcd. for C₃₆H₃₀BN₂O₃⁺ [M+H]⁺ : 549.2344, found : 549.2330. [α]_D²⁰ = -202 (c = 0.1, CHCl₃).

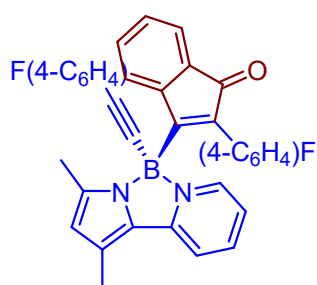
HPLC analysis: Daicel Chiralpak IA column (hexane: 2-propanol = 80:20, v = 1.0 mL/min, 40 °C, 254 nm); tr (major) = 7.663 min, tr (minor) = 9.438 min, 96% ee.



No.	Time	Area	Area (%)
1	7.357	14828.1	50.13
2	9.101	14751.0	49.87



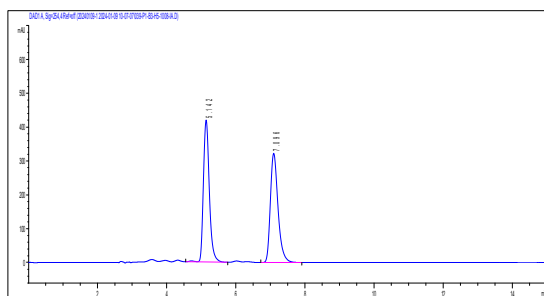
No.	Time	Area	Area (%)
1	7.663	20698	97.93
2	9.438	436.6	2.07



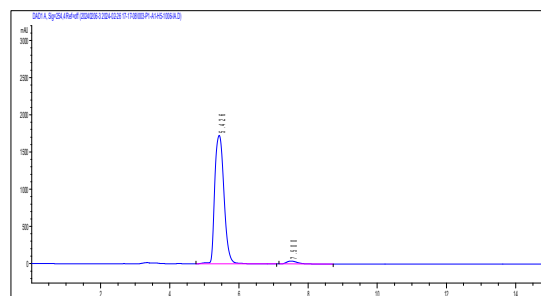
(*R*)-2-(4-fluorophenyl)-3-(5-((4-fluorophenyl)ethynyl)-1,3-dimethyl-5*H*-5 λ ⁴,6 λ ⁴-pyrrolo[1',2':3,4][1,3,2]diazaborolo[1,5-*a*]pyridin-5-yl)-1*H*-inden-1-one (14)

The title compound was isolated as a yellow solid (47.2 mg, 90%). **¹H NMR (600 MHz, CDCl₃)** δ 8.14 (s, br, 1H), 8.04 (d, *J* = 5.9 Hz, 1H), 7.63 – 7.54 (m, 1H), 7.46 (d, *J* = 7.0 Hz, 1H), 7.40 (t, *J* = 7.7 Hz, 1H), 7.34 – 7.26 (m, 2H), 7.21 (t, *J* = 7.4 Hz, 1H), 7.14 (d, *J* = 8.4 Hz, 1H), 6.98 – 6.89 (m, 2H), 6.78 (t, *J* = 6.6 Hz, 1H), 6.69 (t, *J* = 8.6 Hz, 2H), 6.55 (s, 2H), 5.84 (s, 1H), 2.30 (s, 3H), 2.26 (s, 3H). **¹³C NMR (150 MHz, CDCl₃)** δ 198.9, 162.9 (d, *J*_{C-F} = 28.1 Hz), 161.3 (d, *J*_{C-F} = 25.4 Hz), 150.0, 149.7, 142.4, 141.7, 140.9, 137.2, 133.9, 133.4 (d, *J*_{C-F} = 8.1 Hz), 131.0 (d, *J*_{C-F} = 8.1 Hz), 130.7, 128.9 (d, *J*_{C-F} = 3.4 Hz), 127.8, 127.5, 124.3, 122.9, 122.4, 120.7 (d, *J*_{C-F} = 3.5 Hz), 117.1, 115.8, 115.7, 115.4, 115.3, 114.0 (d, *J*_{C-F} = 21.4 Hz), 98.0, 14.0, 12.1. **¹¹B NMR (193 MHz, CDCl₃)** δ -4.91. **¹⁹F NMR (376 MHz, CDCl₃)** δ -111.76, -115.51. **HRMS (APCI)**: calcd. for C₃₄H₂₄BF₂N₂O⁺ [M+H]⁺ : 525.1944, found : 525.1938. [α]_D²⁰ = -178 (c = 0.1, CHCl₃).

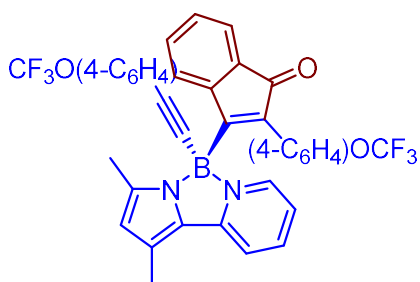
HPLC analysis: Daicel Chiralpak IA column (hexane: 2-propanol = 80:20, v = 1.0 mL/min, 40 °C, 254 nm); tr (major) = 5.426 min, tr (minor) = 7.500 min, 95% ee.



No.	Time	Area	Area (%)
1	5.142	5020.1	50.25
2	7.096	4969.6	49.75



No.	Time	Area	Area (%)
1	5.426	32075.5	97.47
2	7.500	833.5	2.53

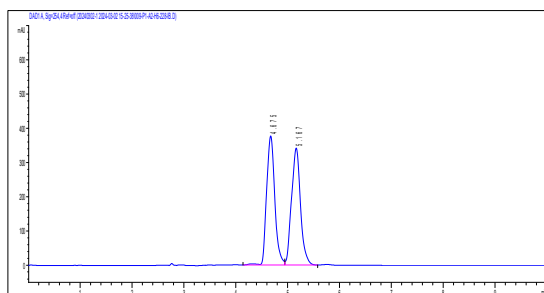


(*R*)-3-(1,3-dimethyl-5-((4-(trifluoromethoxy)phenyl)ethynyl)-5*H*-5λ⁴,6λ⁴-pyrrolo[1',2':3,4][1,3,2]diazaborolo[1,5-*a*]pyridin-5-yl)-2-(4-(trifluoromethoxy)phenyl)-1*H*-inden-1-one (15)

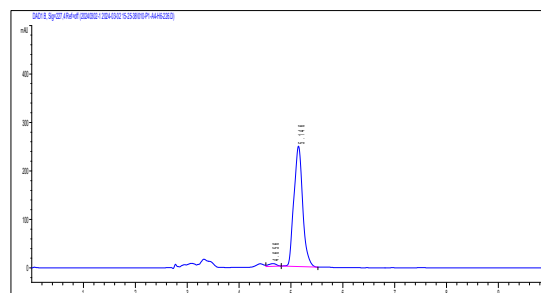
The title compound was isolated as a yellow solid (29.5 mg, 45%).

¹H NMR (600 MHz, CDCl₃) δ 8.21 (s, br, 1H), 8.03 (dt, *J* = 6.1, 1.2 Hz, 1H), 7.58 – 7.52 (m, 1H), 7.48 – 7.45 (m, 1H), 7.45 – 7.39 (m, 1H), 7.35 (d, *J* = 8.3 Hz, 2H), 7.24 – 7.20 (m, 1H), 7.12 – 7.06 (m, 3H), 6.84 (d, *J* = 8.1 Hz, 2H), 6.80 – 6.74 (m, 1H), 6.55 (d, *J* = 4.9 Hz, 2H), 5.82 (s, 1H), 2.28 (s, 3H), 2.25 (s, 3H). **¹³C NMR (150 MHz, CDCl₃)** δ 198.6, 150.0, 149.8, 148.6, 148.2, 142.1, 141.7, 141.1, 137.3, 134.1, 133.4, 133.1, 131.9, 130.8, 130.7, 128.1, 127.5, 124.5, 123.4, 123.2, 122.6, 121.44, 121.37, 120.9, 119.8, 119.74, 119.67, 117.1, 115.9, 97.7, 14.0, 12.0. **¹¹B NMR (193 MHz, CDCl₃)** δ -5.14. **¹⁹F NMR (376 MHz, CDCl₃)** δ -57.54, -57.73. **HRMS (APCI):** calcd. for C₃₆H₂₄BF₆N₂O₃⁺ [M+H]⁺: 657.1779, found: 657.1756. **[α]_D²⁰** = -116 (c = 0.1, CHCl₃).

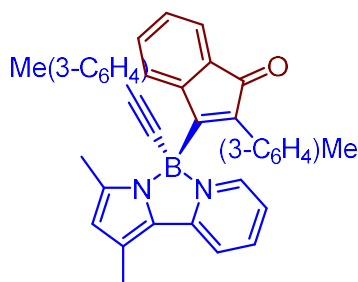
HPLC analysis: Daicel Chiralpak IB column (hexane: 2-propanol = 85:15, v = 1.0 mL/min, 40 °C, 254 nm); tr (major) = 4.656 min, tr (minor) = 5.146 min, 96% ee.



No.	Time	Area	Area (%)
1	4.675	4135.7	50.08
2	5.167	4122.5	49.92



No.	Time	Area	Area (%)
1	4.656	58.8	1.96
2	5.146	2932.8	98.04



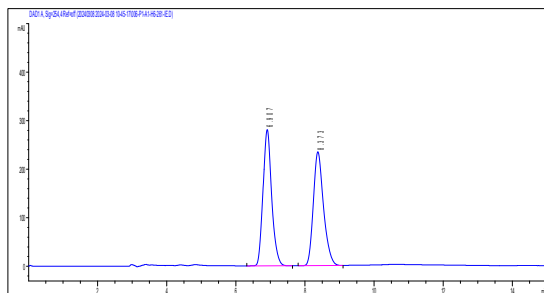
(*R*)-3-(1,3-dimethyl-5-(*m*-tolylethynyl)-5*H*-5λ⁴,6λ⁴-pyrrolo[1',2':3,4][1,3,2]diazaborolo[1,5-*a*]pyridin-5-yl)-2-(*m*-tolyl)-1*H*-inden-1-one (16)

The title compound was isolated as a yellow solid (33.5 mg, 65%). ¹H

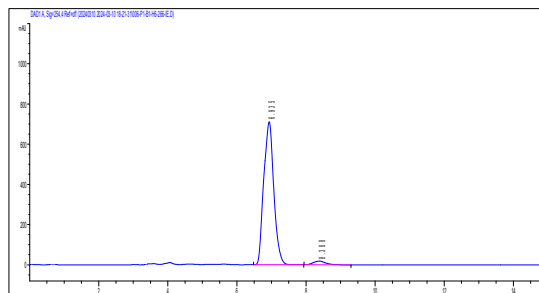
NMR (600 MHz, CDCl₃) δ 8.34 (s, br, 1H), 8.01 (d, *J* = 5.9 Hz, 1H),

7.52 – 7.45 (m, 2H), 7.42 (t, *J* = 7.6 Hz, 1H), 7.23 – 7.11 (m, 4H), 7.09 – 7.03 (m, 2H), 6.90 (t, *J* = 7.5 Hz, 1H), 6.84 (d, *J* = 7.5 Hz, 1H), 6.70 (t, *J* = 6.6 Hz, 1H), 6.46 (d, *J* = 7.4 Hz, 1H), 6.25 (s, 1H), 5.85 (s, 1H), 2.30 (s, 3H), 2.29 (s, 3H), 2.29 (s, 3H), 2.09 (s, 3H). ¹³C **NMR (150 MHz, CDCl₃)** δ 199.2, 150.5, 149.8, 143.4, 141.8, 140.5, 137.8, 137.1, 136.4, 133.8, 133.0, 132.3, 130.9, 129.8, 128.7, 128.5, 128.1, 127.6, 127.5, 127.0, 126.3, 124.64, 124.60, 122.3, 122.2, 116.8, 115.52, 115.46, 99.1, 21.3, 14.1, 12.2. ¹¹B **NMR (193 MHz, CDCl₃)** δ -5.34. **HRMS (APCI):** calcd. for C₃₆H₃₀BN₂O⁺ [M+H]⁺ : 517.2446, found : 517.2439. [α]_D²⁰ = -264 (c = 0.1, CHCl₃).

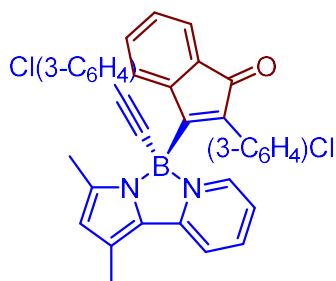
HPLC analysis: Daicel Chiralpak IE column (hexane: 2-propanol = 80:20, v = 1.0 mL/min, 40 °C, 254 nm); tr (major) = 6.935 min, tr (minor) = 8.388 min, 94% ee.



No.	Time	Area	Area (%)
1	6.907	4872.6	50.25
2	8.373	4824.5	49.75



No.	Time	Area	Area (%)
1	6.935	14314.9	96.98
2	8.388	445.7	3.02



(*R*)-2-(3-chlorophenyl)-3-(5-((3-chlorophenyl)ethynyl)-1,3-dimethyl-5*H*-5λ⁴,6λ⁴-pyrrolo[1',2':3,4][1,3,2]diazaborolo[1,5-*a*]pyridin-5-yl)-1*H*-inden-1-one (17)

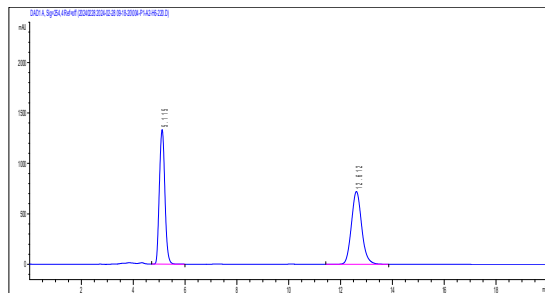
The title compound was isolated as a yellow solid (34.5 mg, 62%). ¹H

NMR (600 MHz, CDCl₃) δ 8.21 (s, br, 1H), 8.02 (d, *J* = 5.9 Hz, 1H), 7.58

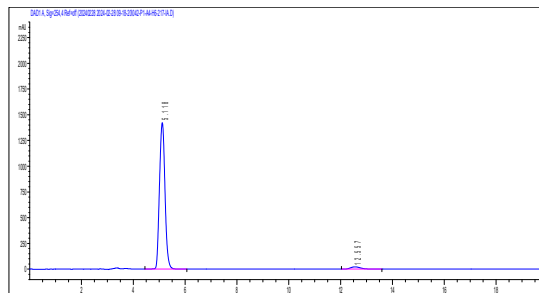
(t, *J* = 7.9 Hz, 1H), 7.47 (d, *J* = 7.1 Hz, 1H), 7.43 (t, *J* = 7.6 Hz, 1H), 7.31 (s, 1H), 7.25 – 7.14 (m, 5H), 7.06 – 6.93 (m, 2H), 6.77 (t, *J* = 6.6 Hz, 1H), 6.64 (d, *J* = 7.4 Hz, 1H), 6.39 (s, 1H), 5.81 (s, 1H), 2.32 (s, 3H), 2.24 (s, 3H). ¹³C **NMR (150 MHz, CDCl₃)** δ 198.4, 149.9, 149.8, 141.6, 141.0, 137.3, 134.8,

134.02, 133.98, 133.1, 131.5, 130.7, 129.7, 129.4, 129.2, 128.3, 128.1, 128.0, 127.6, 127.5, 127.0, 126.3, 124.6, 123.4, 122.5, 117.1, 115.94, 115.86, 97.7, 14.1, 12.3. **¹¹B NMR (193 MHz, CDCl₃)** δ -5.21. **HRMS (APCI)**: calcd. for C₃₄H₂₄BCl₂N₂O⁺ [M+H]⁺ : 557.1353, found : 557.1340. [α]_D²⁰ = -160 (c = 0.1, CHCl₃).

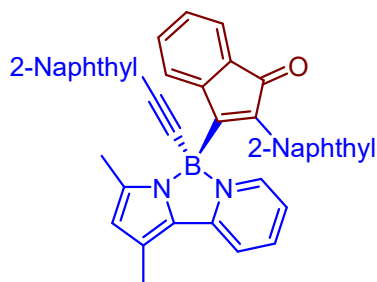
HPLC analysis: Daicel Chiralpak IA column (hexane: 2-propanol = 85:15, v = 1.0 mL/min, 40 °C, 254 nm); tr (major) = 5.118 min, tr (minor) = 12.557 min, 94% ee.



No.	Time	Area	Area (%)
1	5.115	19660.3	49.69
2	12.612	19909.1	50.31



No.	Time	Area	Area (%)
1	5.118	20999.7	97.15
2	12.557	617.1	2.85

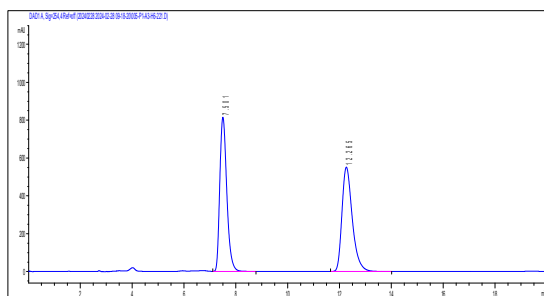


(*R*)-3-(1,3-dimethyl-5-(naphthalen-2-ylethynyl)-5*H*-5λ⁴,6λ⁴-pyrrolo[1',2':3,4][1,3,2]diazaborolo[1,5-*a*]pyridin-5-yl)-2-(naphthalen-2-yl)-1*H*-inden-1-one (18)

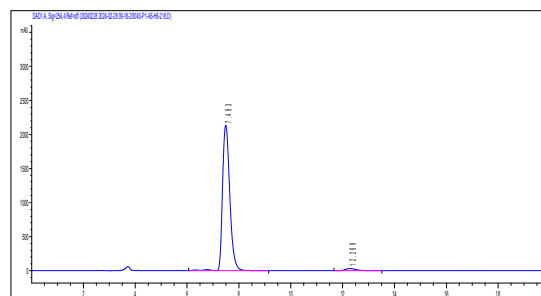
The title compound was isolated as a yellow solid (42.3 mg, 72%). **¹H**

NMR (600 MHz, CDCl₃) δ 8.34 (s, br, 1H), 8.02 (d, *J* = 5.9 Hz, 1H), 7.80 – 7.71 (m, 2H), 7.70 – 7.61 (m, 3H), 7.53 – 7.40 (m, 6H), 7.39 – 7.28 (m, 3H), 7.22 (t, *J* = 7.4 Hz, 2H), 6.92 (d, *J* = 8.3 Hz, 1H), 6.84 (s, 1H), 6.76 – 6.65 (m, 1H), 6.62 (t, *J* = 6.7 Hz, 1H), 5.82 (s, 1H), 2.36 (s, 3H), 2.11 (s, 3H). **¹³C NMR (150 MHz, CDCl₃)** δ 199.2, 150.5, 149.8, 143.5, 141.6, 140.3, 137.2, 134.0, 133.0, 132.8, 132.6, 132.5, 131.2, 130.9, 130.8, 128.7, 128.6, 128.1, 127.80, 127.75, 127.7, 127.6, 127.5, 127.3, 126.44, 126.39, 126.36, 125.6, 125.5, 124.7, 122.8, 122.3, 122.0, 117.0, 115.7, 115.4, 99.3, 14.2, 12.2. **¹¹B NMR (193 MHz, CDCl₃)** δ -4.68. **HRMS (APCI)**: calcd. for C₄₂H₃₀BN₂O⁺ [M+H]⁺ : 589.2446, found : 589.2439. [α]_D²⁰ = -210 (c = 0.1, CHCl₃).

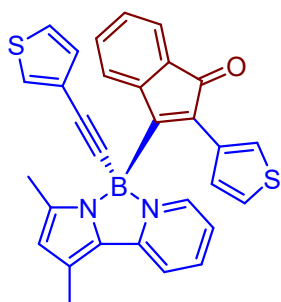
HPLC analysis: Daicel Chiralpak IA column (hexane: 2-propanol = 85:15, v = 1.0 mL/min, 40 °C, 254 nm); tr (major) = 7.493 min, tr (minor) = 12.289 min, 96% ee.



No.	Time	Area	Area (%)
1	7.501	15248.3	49.89
2	12.265	15316.-	50.11



No.	Time	Area	Area (%)
1	7.493	41521.3	97.98
2	12.289	857.0	2.02

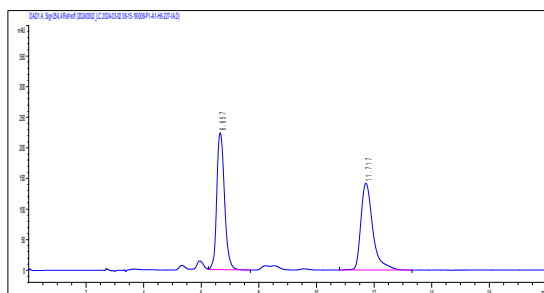


(R)-3-(1,3-dimethyl-5-(thiophen-3-ylethynyl)-5H-5λ⁴,6λ⁴-

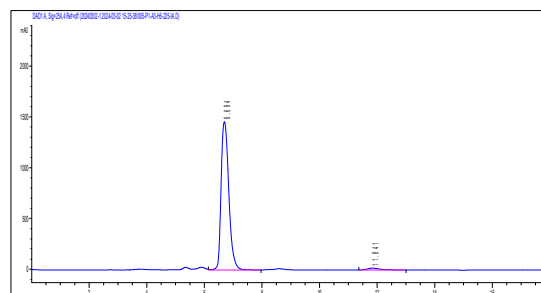
pyrrolo[1',2':3,4][1,3,2]diazaborolo[1,5-a]pyridin-5-yl)-2-(thiophen-3-yl)-1H-inden-1-one (19)

The title compound was isolated as a yellow solid (43.0 mg, 86%). ¹H NMR (600 MHz, CDCl₃) δ 8.16 (s, br, 1H), 8.01 (d, *J* = 5.8 Hz, 1H), 7.58 (t, *J* = 7.8 Hz, 1H), 7.45 (d, *J* = 7.0 Hz, 1H), 7.39 (t, *J* = 7.6 Hz, 1H), 7.31 (d, *J* = 2.9 Hz, 1H), 7.22 – 7.14 (m, 3H), 7.03 (d, *J* = 5.0 Hz, 1H), 6.97 – 6.91 (m, 1H), 6.75 (t, *J* = 6.6 Hz, 1H), 6.45 (d, *J* = 28.3 Hz, 2H), 5.88 (s, 1H), 2.33 (s, 3H), 2.27 (s, 3H). ¹³C NMR (150 MHz, CDCl₃) δ 199.0, 150.4, 149.7, 141.7, 140.9, 138.5, 137.2, 133.9, 132.8, 130.8, 130.1, 128.8, 128.0, 127.6, 127.5, 124.9, 124.5, 124.3, 123.9, 123.6, 122.7, 122.2, 117.0, 115.9, 115.6, 93.7, 14.0, 12.2. ¹¹B NMR (193 MHz, CDCl₃) δ -5.01. HRMS (APCI): calcd. for C₃₀H₂₂BN₂OS₂⁺ [M+H]⁺ : 501.1261, found : 501.1261. [α]_D²⁰ = -222 (c = 0.1, CHCl₃).

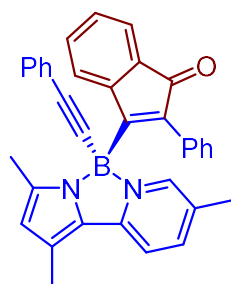
HPLC analysis: Daicel Chiralpak IA column (hexane: 2-propanol = 85:15, v = 1.0 mL/min, 40 °C, 254 nm); tr (major) = 6.694 min, tr (minor) = 11.841 min, 96% ee.



No.	Time	Area	Area (%)
1	6.657	4167.9	50.39
2	11.717	4103.0	49.61



No.	Time	Area	Area (%)
1	6.694	27038.2	98.17
2	11.841	504.8	1.83



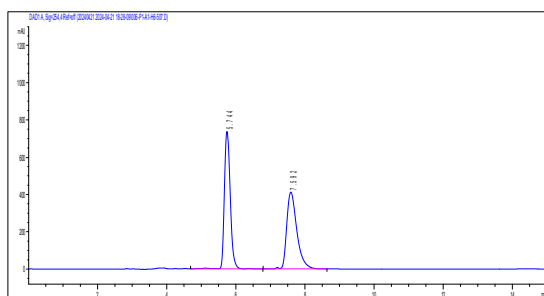
(R)-2-phenyl-3-(1,3,8-trimethyl-5-(phenylethynyl)-5H-5λ⁴,6λ⁴-

pyrrolo[1',2':3,4][1,3,2]diazaborolo[1,5-a]pyridin-5-yl)-1H-inden-1-one (20)

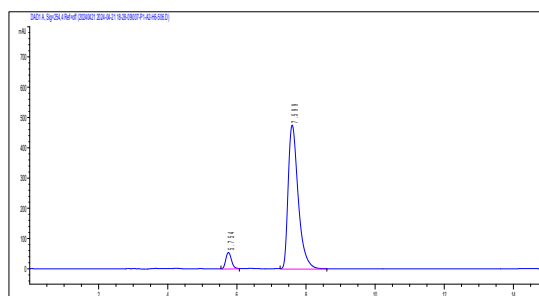
The title compound was isolated as a yellow solid (31.1 mg, 62%). ¹H NMR (600 MHz, CDCl₃) δ 8.25 (s, br, 1H), 7.80 (s, 1H), 7.48 – 7.45 (m, 1H), 7.43 – 7.38 (m, 1H), 7.37 – 7.29 (m, 3H), 7.26 – 7.22 (m, 3H), 7.20 (t, *J* = 7.4 Hz, 1H), 7.05 – 6.94

(m, 4H), 6.56 (d, *J* = 7.3 Hz, 2H), 5.82 (s, 1H), 2.29 (s, 3H), 2.28 (s, 3H), 2.16 (s, 3H). ¹³C NMR (150 MHz, CDCl₃) δ 199.2, 150.5, 147.9, 143.2, 142.2, 141.0, 136.3, 133.9, 133.2, 131.7, 130.9, 129.3, 128.2, 127.7, 127.64, 127.61, 127.2, 127.1, 126.7, 124.9, 124.7, 122.2, 121.3, 115.5, 115.1, 98.9, 18.0, 14.2, 12.1. ¹¹B NMR (193 MHz, CDCl₃) δ -4.70. HRMS (APCI): calcd. for C₃₅H₂₈BN₂O⁺ [M+H]⁺ : 503.2289, found : 503.2285. [α]_D²⁰ = -208 (c = 0.1, CHCl₃).

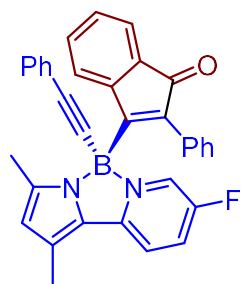
HPLC analysis: Daicel Chiralpak IB column (hexane: 2-propanol = 85:15, v = 1.0 mL/min, 40 °C, 254 nm); tr (major) = 7.599 min, tr (minor) = 5.754 min, 90% ee.



No.	Time	Area	Area (%)
1	5.744	8638.0	50.702
2	7.592	8398.8	49.298



No.	Time	Area	Area (%)
1	5.754	532.2	5.22
2	7.599	9664.0	94.78



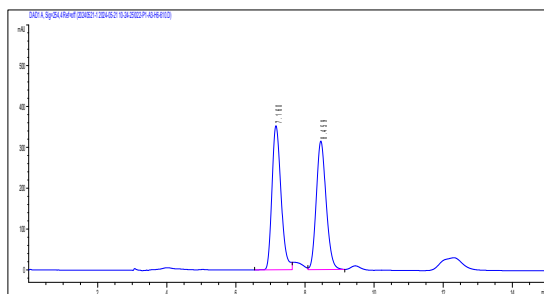
(R)-3-(8-fluoro-1,3-dimethyl-5-(phenylethynyl)-5H-5λ⁴,6λ⁴-pyrrolo[1',2':3,4][1,3,2]diazaborolo[1,5-a]pyridin-5-yl)-2-phenyl-1H-inden-1-one (21)

The title compound was isolated as a yellow solid (30.4 mg, 62%). ¹H NMR (600 MHz, CDCl₃) δ 8.26 (s, br, 1H), 7.89 (t, *J* = 2.6 Hz, 1H), 7.46 (d, *J* = 7.0 Hz, 1H), 7.43 – 7.38 (m, 1H), 7.37 – 7.32 (m, 2H), 7.31 – 7.23 (m, 4H), 7.20 (t, *J* = 7.4 Hz,

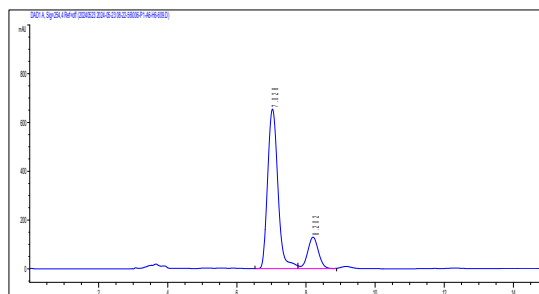
1H), 7.07 – 7.02 (m, 1H), 7.02 – 6.91 (m, 3H), 6.54 (d, *J* = 7.4 Hz, 2H), 5.84 (s, 1H), 2.29 (s, 3H), 2.26 (s, 3H). ¹³C NMR (150 MHz, CDCl₃) δ 198.9, 155.9, 154.3, 150.3, 147.4, 143.4, 137.5, 133.9, 133.1, 131.7, 130.7, 129.9, 129.8, 129.72, 129.69, 129.4, 128.2, 127.9, 127.8, 127.3, 127.1, 126.9, 124.6, 124.5, 122.4, 122.2, 116.51, 116.47, 115.5, 99.4, 14.2, 12.1. ¹¹B NMR (193 MHz, CDCl₃) δ -4.48. ¹⁹F NMR (376 MHz, CDCl₃) δ -133.11. HRMS (APCI): calcd. for C₃₄H₂₅BFN₂O⁺ [M+H]⁺ : 507.2038,

found : 507.2034. $[\alpha]_D^{20} = -182$ (c = 0.1, CHCl₃).

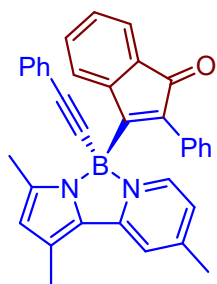
HPLC analysis: Daicel Chiralpak IE column (hexane: 2-propanol = 85:15, v = 1.0 mL/min, 40 °C, 254 nm); tr (major) = 7.028 min, tr (minor) = 8.202 min, 65% ee.



No.	Time	Area	Area (%)
1	7.160	6464.1	50.96
2	8.459	6220.7	49.04



No.	Time	Area	Area (%)
1	7.028	13581.7	82.78
2	8.202	2824.5	17.22



(R)-2-phenyl-3-(1,3,9-trimethyl-5-(phenylethynyl)-5H-5λ⁴,6λ⁴-

pyrrolo[1',2':3,4][1,3,2]diazaborolo[1,5-a]pyridin-5-yl)-1H-inden-1-one (22)

The title compound was isolated as a yellow solid (34.2 mg, 68%). **¹H NMR (600**

MHz, CDCl₃) δ 8.21 (s, br, 1H), 7.89 (d, *J* = 6.1 Hz, 1H), 7.46 (d, *J* = 7.0 Hz, 1H),

7.40 (t, *J* = 7.5 Hz, 1H), 7.36 – 7.31 (m, 2H), 7.26 – 7.22 (m, 3H), 7.19 (t, *J* = 7.4

Hz, 1H), 7.05 (t, *J* = 7.4 Hz, 1H), 6.98 (t, *J* = 7.5 Hz, 2H), 6.83 (s, 1H), 6.62 – 6.48 (m, 3H), 5.82 (s,

1H), 2.29 (s, 3H), 2.28 (s, 3H), 2.28 (s, 3H). **¹³C NMR (150 MHz, CDCl₃)** δ 199.2, 153.2, 150.4,

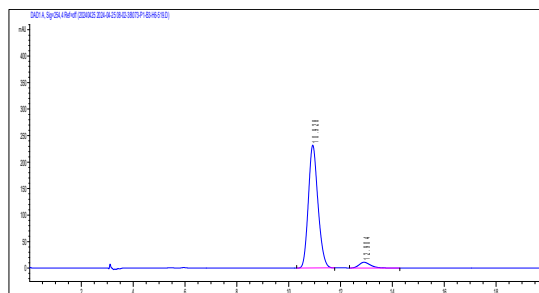
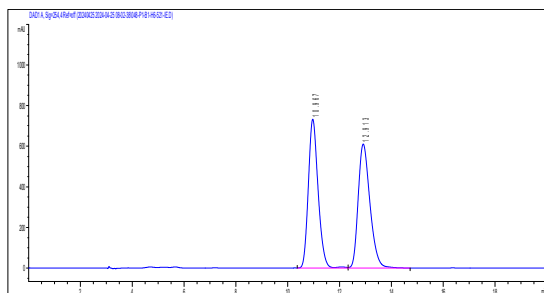
149.5, 143.3, 140.9, 136.6, 133.9, 133.1, 131.6, 130.9, 129.4, 128.1, 127.61, 127.57, 127.4, 127.0, 126.5,

124.9, 124.5, 122.2, 122.0, 118.7, 115.8, 115.3, 98.9, 21.9, 14.0, 12.2. **¹¹B NMR (193 MHz, CDCl₃)**

δ -4.93. **HRMS (APCI):** calcd. for C₃₅H₂₈BN₂O⁺ [M+H]⁺ : 503.2289, found : 503.2286. $[\alpha]_D^{20} = -190$

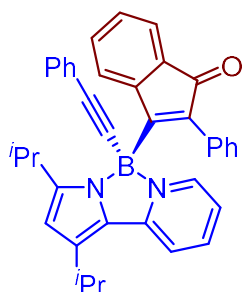
(c = 0.1, CHCl₃).

HPLC analysis: Daicel Chiralpak IE column (hexane: 2-propanol = 90:10, v = 1.0 mL/min, 40 °C, 254 nm); tr (major) = 10.928 min, tr (minor) = 12.904 min, 90% ee.



No.	Time	Area	Area (%)
1	10.967	19131.2	49.88
2	12.913	19220.8	50.12

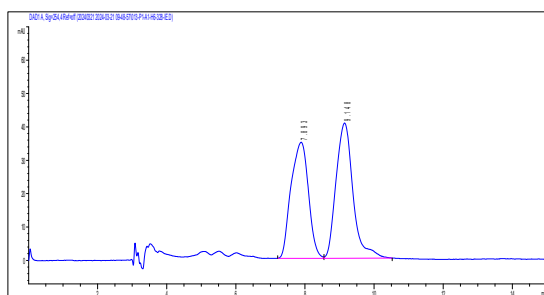
No.	Time	Area	Area (%)
1	10.928	5971.7	94.84
2	12.904	338.4	5.16



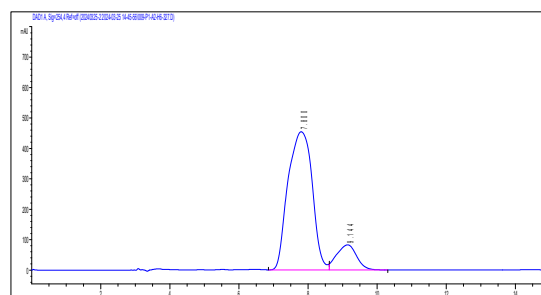
(R)-3-(1,3-diisopropyl-5-(phenylethynyl)-5H-5λ⁴,6λ⁴-pyrrolo[1',2':3,4][1,3,2] diazaborolo[1,5-a]pyridin-5-yl)-2-phenyl-1H-inden-1-one (23)

The title compound was isolated as a yellow solid (35.9 mg, 66%). ¹H NMR (600 MHz, CDCl₃) δ 8.16 (s, br, 1H), 8.01 (d, *J* = 5.9 Hz, 1H), 7.50 – 7.43 (m, 2H), 7.41 – 7.28 (m, 3H), 7.26 – 7.21 (m, 3H), 7.19 (t, *J* = 7.4 Hz, 1H), 7.08 – 6.93 (m, 4H), 6.71 (t, *J* = 6.6 Hz, 1H), 6.58 (s, 2H), 6.03 (s, 1H), 3.16 – 3.01 (m, 2H), 1.41 (d, *J* = 6.9 Hz, 3H), 1.35 (d, *J* = 6.8 Hz, 3H), 1.32 (d, *J* = 6.9 Hz, 3H), 1.14 (d, *J* = 6.8 Hz, 3H). ¹³C NMR (150 MHz, CDCl₃) δ 199.2, 150.3, 149.6, 148.6, 141.7, 140.6, 135.7, 133.9, 133.2, 132.0, 131.5, 130.7, 129.4, 128.8, 128.4, 128.1, 127.6, 127.3, 126.8, 125.6, 124.9, 124.3, 122.2, 116.8, 116.0, 107.3, 99.1, 28.4, 26.5, 24.1, 23.8, 23.7, 22.9. ¹¹B NMR (193 MHz, CDCl₃) δ -5.45. HRMS (APCI): calcd. for C₃₈H₃₄BN₂O⁺ [M+H]⁺ : 545.2759, found : 545.2754. [α]_D²⁰ = -168 (c = 0.1, CHCl₃).

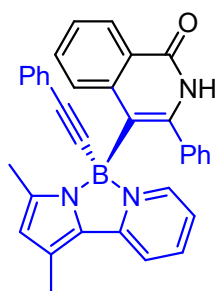
HPLC analysis: Daicel Chiralpak IE column (hexane: 2-propanol = 90:10, v = 1.0 mL/min, 40 °C, 254 nm); tr (major) = 7.800 min, tr (minor) = 9.144 min, 74% ee.



No.	Time	Area	Area (%)
1	7.893	1215.9	46.91
2	9.148	1376.2	53.09



No.	Time	Area	Area (%)
1	7.800	22182.6	87.09
2	9.144	3287.6	12.91

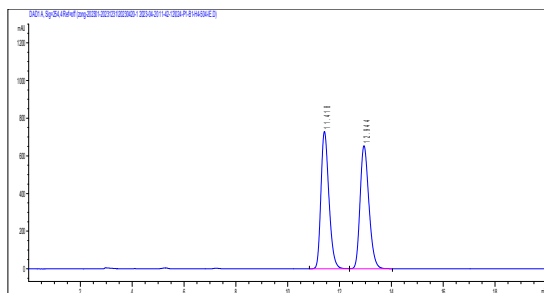


(R)-4-(1,3-dimethyl-5-(phenylethynyl)-5H-5λ⁴,6λ⁴-pyrrolo[1',2':3,4][1,3,2]diazaborolo[1,5-a]pyridin-5-yl)-3-phenylisoquinolin-1(2H)-one (24)

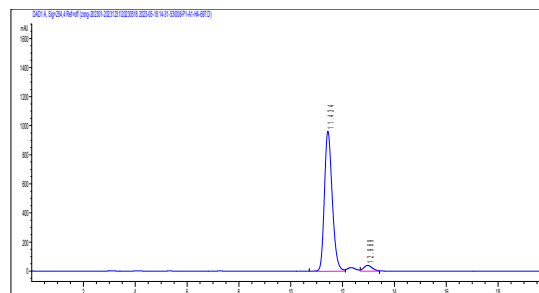
The title compound was isolated as a yellow solid (40.2 mg, 80%). ¹H NMR (600 MHz, CDCl₃) δ 9.79 (s, br, 1H), 8.68 (s, 1H), 8.49 (d, *J* = 7.7 Hz, 1H), 8.01 (d, *J* = 5.9 Hz, 1H), 7.83 – 7.67 (m, 1H), 7.63 – 7.33 (m, 3H), 7.33 – 7.27 (m, 1H), 7.23 –

7.14 (m, 3H), 7.08 (t, $J = 7.5$ Hz, 1H), 7.04 – 6.80 (m, 3H), 6.79 (t, $J = 6.6$ Hz, 1H), 6.63 (s, 1H), 6.32 (s, 1H), 5.83 (s, 1H), 2.26 (s, 3H), 2.16 (s, 3H). ^{13}C NMR (150 MHz, CDCl_3) δ 162.8, 149.3, 141.5, 140.2, 136.8, 131.6, 131.5, 129.5, 129.3, 128.7, 128.1, 128.0, 127.70, 127.67, 127.64, 127.59, 127.5, 127.5, 127.2, 126.2, 125.8, 125.6, 125.1, 122.5, 117.0, 115.8, 115.6, 99.0, 14.1, 12.2. ^{11}B NMR (193 MHz, CDCl_3) δ -3.62. HRMS (APCI): calcd. for $\text{C}_{34}\text{H}_{27}\text{BN}_3\text{O}^+$ $[\text{M}+\text{H}]^+$: 504.2242, found : 504.2242. $[\alpha]_{\text{D}}^{20} = -314$ ($c = 0.1$, CHCl_3).

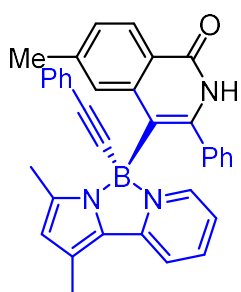
HPLC analysis: Daicel Chiralpak IE column (hexane: 2-propanol = 75:25, $v = 1.0$ mL/min, 40 °C, 254 nm); tr (major) = 11.434 min, tr (minor) = 12.969 min, 91% ee.



No.	Time	Area	Area (%)
1	11.418	15548.1	50.08
2	12.944	15496.7	49.92



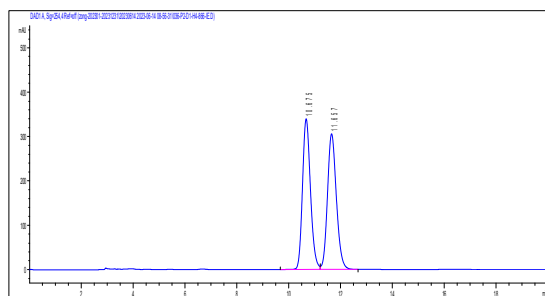
No.	Time	Area	Area (%)
1	11.434	20228.9	95.70
2	12.969	908.3	4.30



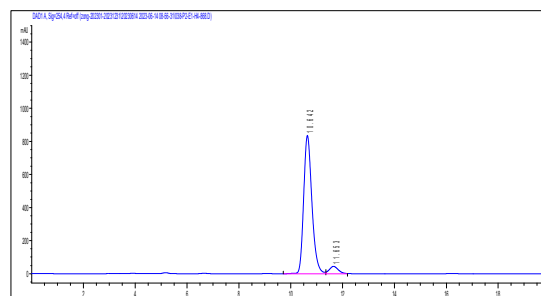
(R)-4-(1,3-dimethyl-5-(phenylethynyl)-5H-5 λ ⁴,6 λ ⁴-pyrrolo[1',2':3,4][1,3,2]diazaborolo[1,5-a]pyridin-5-yl)-6-methyl-3-phenylisoquinolin-1(2H)-one (25)

The title compound was isolated as a yellow solid (38.3 mg, 74%). ^1H NMR (600 MHz, CDCl_3) δ 9.63 (s, br, 1H), 8.45 – 8.26 (m, 2H), 8.02 (d, $J = 5.9$ Hz, 1H), 7.52 – 7.40 (m, 1H), 7.40 – 7.24 (m, 3H), 7.23 – 7.13 (m, 3H), 7.07 (t, $J = 7.4$ Hz, 1H), 7.03 – 6.72 (m, 4H), 6.59 (s, 1H), 6.34 (s, 1H), 5.82 (s, 1H), 2.52 (s, 3H), 2.26 (s, 3H), 2.15 (s, 3H). ^{13}C NMR (150 MHz, CDCl_3) δ 162.6, 149.4, 144.3, 143.5, 141.8, 141.6, 140.1, 136.8, 131.5, 129.5, 128.0, 127.7, 127.6, 127.3, 127.12, 125.2, 123.4, 122.5, 117.0, 115.7, 115.6, 99.1, 22.5, 14.0, 12.1. ^{11}B NMR (193 MHz, CDCl_3) δ -3.56. HRMS (APCI): calcd. for $\text{C}_{35}\text{H}_{29}\text{BN}_3\text{O}^+$ $[\text{M}+\text{H}]^+$: 518.2398, found : 518.2393. $[\alpha]_{\text{D}}^{20} = -356$ ($c = 0.1$, CHCl_3).

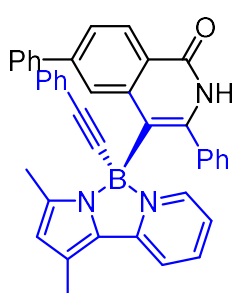
HPLC analysis: Daicel Chiralpak IE column (hexane: 2-propanol = 70:30, $v = 1.0$ mL/min, 40 °C, 254 nm); tr (major) = 10.642 min, tr (minor) = 11.653 min, 90% ee.



No.	Time	Area	Area (%)
1	10.675	7274.7	49.91
2	11.657	7301.5	50.09

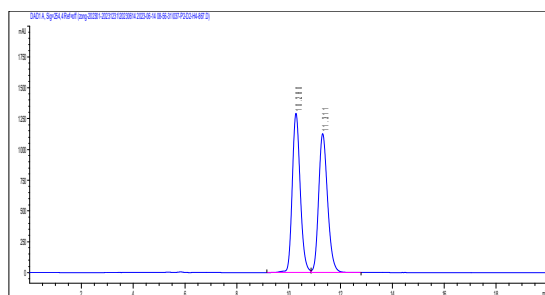


No.	Time	Area	Area (%)
1	10.642	18440.2	94.86
2	11.653	1000.1	5.14

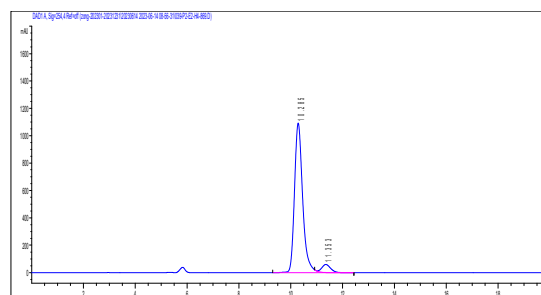


(R)-4-(1,3-dimethyl-5-(phenylethynyl)-5H-5λ⁴,6λ⁴-pyrrolo[1',2':3,4][1,3,2]diazaborolo[1,5-a]pyridin-5-yl)-3,6-diphenylisoquinolin-1(2H)-one (26)

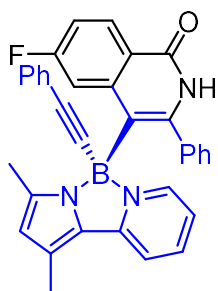
The title compound was isolated as a yellow solid (40.5 mg, 70%). **¹H NMR (600 MHz, CDCl₃)** δ 10.14 (s, 1H), 8.73 – 8.37 (m, 2H), 8.06 (d, J = 5.9 Hz, 1H), 7.88 – 7.62 (m, 3H), 7.52 – 7.40 (m, 1H), 7.36 – 7.27 (m, 2H), 7.26 – 7.21 (m, 1H), 7.21 – 7.02 (m, 6H), 7.02 – 6.86 (m, 2H), 6.81 (t, J = 6.6 Hz, 2H), 6.58 (s, 1H), 6.36 (s, 1H), 5.82 (s, 1H), 2.29 (s, 3H), 2.12 (s, 3H). **¹³C NMR (150 MHz, CDCl₃)** δ 162.6, 149.4, 144.5, 144.3, 141.5, 141.0, 140.1, 137.0, 136.7, 131.6, 129.4, 128.9, 128.3, 128.2, 128.0, 127.9, 127.8, 127.7, 127.3, 124.8, 124.5, 122.5, 117.0, 115.8, 115.6, 99.4, 14.2, 12.2. **¹¹B NMR (193 MHz, CDCl₃)** δ -3.03. **HRMS (APCI):** calcd. for C₄₀H₃₁BN₃O⁺ [M+H]⁺: 580.2555, found: 580.2550. **[α]_D²⁰** = -280 (c = 0.1, CHCl₃). **HPLC analysis:** Daicel Chiralpak IE column (hexane: 2-propanol = 70:30, v = 1.0 mL/min, 40 °C, 254 nm); tr (major) = 10.285 min, tr (minor) = 11.353 min, 90% ee.



No.	Time	Area	Area (%)
1	10.280	27602.9	50.47
2	11.311	27091.0	49.53



No.	Time	Area	Area (%)
1	10.285	23895.9	94.76
2	11.353	1156	5.24

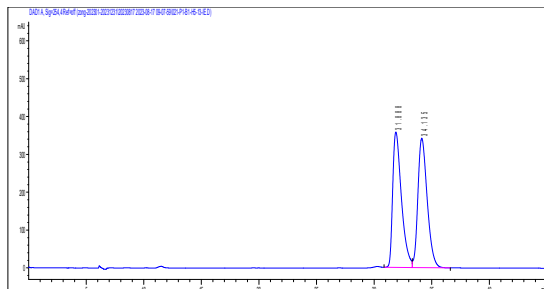


(R)-4-(1,3-dimethyl-5-(phenylethynyl)-5H-5λ⁴,6λ⁴-

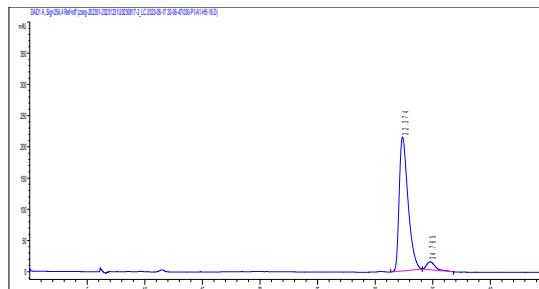
pyrrolo[1',2':3,4][1,3,2]diazaborolo[1,5-a]pyridin-5-yl)-6-fluoro-3-phenylisoquinolin-1(2H)-one (27)

The title compound was isolated as a yellow solid (32.8 mg, 63%). **¹H NMR (600 MHz, CDCl₃)** δ 9.63 (s, br, 1H), 8.81 – 8.59 (m, 1H), 8.45 (t, *J* = 7.8 Hz, 1H), 7.99 (d, *J* = 5.9 Hz, 1H), 7.45 (s, 1H), 7.40 – 7.26 (m, 2H), 7.25 – 7.14 (m, 4H), 7.09 – 7.07 (m, 1H), 7.02 – 6.87 (m, 2H), 6.80 (t, *J* = 6.7 Hz, 2H), 6.59 (s, 1H), 6.30 (s, 1H), 5.83 (s, 1H), 2.25 (s, 3H), 2.14 (s, 3H). **¹³C NMR (150 MHz, CDCl₃)** δ 164.9 (d, *J*_{C-F} = 248.8 Hz), 161.9, 149.2, 141.3, 140.1, 136.6, 131.3, 130.0, 129.9, 129.8 (d, *J*_{C-F} = 9.0 Hz), 129.6, 129.3, 128.0, 127.6, 127.4, 124.7, 122.5, 122.3, 117.0, 115.7, 115.6 (d, *J*_{C-F} = 2.8 Hz), 115.54, 115.48 (d, *J*_{C-F} = 2.6 Hz), 114.3, 114.1, 99.4, 13.9, 12.0. **¹¹B NMR (193 MHz, CDCl₃)** δ -3.76. **¹⁹F NMR (376 MHz, CDCl₃)** δ -106.39, -107.43. **HRMS (APCI)**: calcd. for C₃₄H₂₆BFN₃O⁺ [M+H]⁺ : 522.2147, found : 522.2146. [α]_D²⁰ = -316 (c = 0.1, CHCl₃).

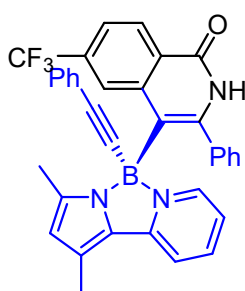
HPLC analysis: Daicel Chiralpak IE column (hexane: 2-propanol = 85:15, v = 0.5 mL/min, 40 °C, 254 nm); tr (major) = 32.374 min, tr (minor) = 34.765 min, 90% ee.



No.	Time	Area	Area (%)
1	31.888	18852.6	49.51
2	34.135	19229.8	50.49



No.	Time	Area	Area (%)
1	32.374	11411.3	94.83
2	34.765	647.4	5.17



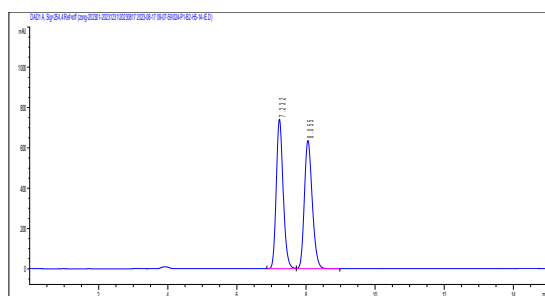
(R)-4-(1,3-dimethyl-5-(phenylethynyl)-5H-5λ⁴,6λ⁴-

pyrrolo[1',2':3,4][1,3,2]diazaborolo[1,5-a]pyridin-5-yl)-3-phenyl-6-(trifluoromethyl)isoquinolin-1(2H)-one (28)

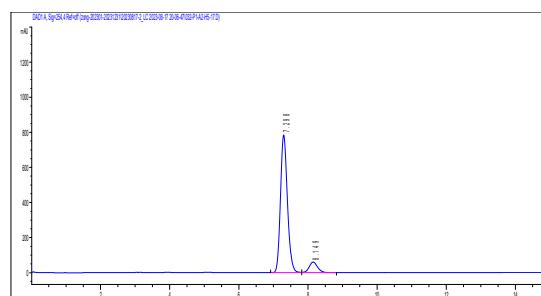
The title compound was isolated as a yellow solid (38.8 mg, 68%). **¹H NMR (600 MHz, CDCl₃)** δ 10.23 (s, 1H), 9.41 (s, 1H), 8.52 (d, *J* = 8.3 Hz, 1H), 7.98 (d, *J* = 6.2 Hz, 1H), 7.78 – 7.58 (m, 1H), 7.54 – 7.26 (m, 3H), 7.24 – 7.14 (m, 3H), 7.11 (t, *J* = 7.6 Hz, 1H), 7.02 – 6.84 (m, 2H), 6.80 (t, *J* = 6.7 Hz, 2H), 6.66 (s, 1H), 6.27 (s, 1H), 5.86

(s, 1H), 2.25 (s, 3H), 2.15 (s, 3H). **¹³C NMR (150 MHz, CDCl₃)** δ 162.2, 149.4, 145.7, 143.6, 141.3, 140.3, 136.5 (q, J_{C-F} = 21.7 Hz), 133.0, 131.5, 129.6, 129.1 (d, J_{C-F} = 263.5 Hz), 128.1, 128.0, 127.9, 127.8, 127.6, 127.5, 127.1, 125.3 (d, J_{C-F} = 7.0 Hz), 124.6, 123.5, 122.7, 121.6, 117.1, 115.84, 115.77, 99.8, 14.0, 12.1. **¹¹B NMR (193 MHz, CDCl₃)** δ -3.57. **¹⁹F NMR (376 MHz, CDCl₃)** δ -62.23, -62.80. **HRMS (APCI)**: calcd. for C₃₅H₂₆BF₃N₃O⁺ [M+H]⁺ : 572.2116, found : 572.2110. **[α]_D²⁰** = -266 (c = 0.1, CHCl₃).

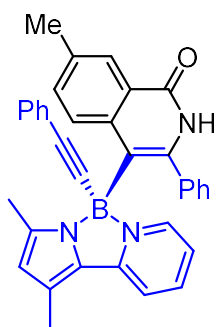
HPLC analysis: Daicel Chiralpak IE column (hexane: 2-propanol = 80:20, v = 1.0 mL/min, 40 °C, 254 nm); tr (major) = 7.298 min, tr (minor) = 8.149 min, 84% ee.



No.	Time	Area	Area (%)
1	7.232	10243.9	50.35
2	8.055	10101.6	49.65



No.	Time	Area	Area (%)
1	7.298	10915.0	91.73
2	8.149	1023.0	8.27

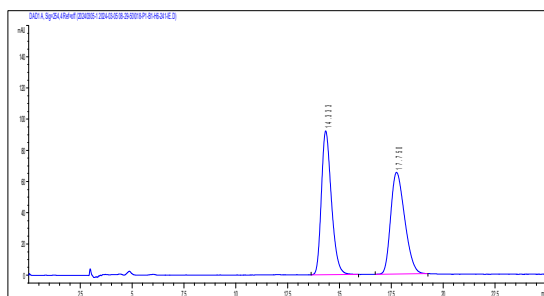


(R)-4-(1,3-dimethyl-5-(phenylethynyl)-5H-5 λ ⁴,6 λ ⁴-

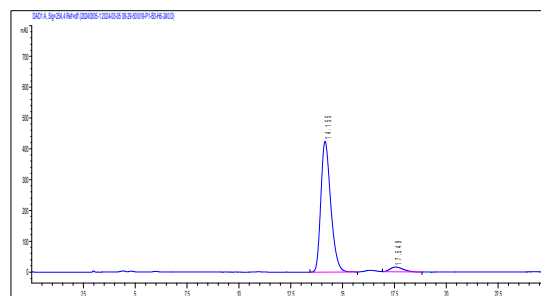
pyrrolo[1',2':3,4][1,3,2]diazaborolo[1,5-a]pyridin-5-yl)-7-methyl-3-phenylisoquinolin-1(2H)-one (29)

The title compound was isolated as a yellow solid (36.7 mg, 71%). **¹H NMR (600 MHz, CDCl₃)** δ 9.70 (s, br, 1H), 8.52 (s, 1H), 8.30 (s, 1H), 8.00 (d, J = 5.9 Hz, 1H), 7.70 – 7.52 (m, 1H), 7.52 – 7.26 (m, 3H), 7.26 – 7.10 (m, 4H), 7.07 (t, J = 7.4 Hz, 1H), 7.00 – 6.85 (m, 2H), 6.78 (t, J = 6.6 Hz, 1H), 6.62 (s, 1H), 6.32 (s, 1H), 5.82 (s, 1H), 2.52 (s, 3H), 2.24 (s, 3H), 2.16 (s, 3H). **¹³C NMR (150 MHz, CDCl₃)** δ 162.7, 149.3, 141.5, 141.0, 140.1, 136.8, 135.7, 133.2, 131.5, 130.0, 129.6, 128.0, 127.7, 127.6, 127.3, 126.8, 125.5, 125.2, 122.5, 117.0, 115.7, 115.5, 99.0, 21.3, 14.0, 12.2. **¹¹B NMR (193 MHz, CDCl₃)** δ -3.46. **HRMS (APCI)**: calcd. for C₃₅H₂₉BN₃O⁺ [M+H]⁺ : 518.2398, found : 518.2391. **[α]_D²⁰** = -278 (c = 0.1, CHCl₃).

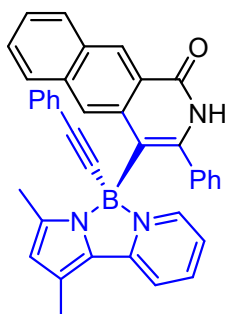
HPLC analysis: Daicel Chiralpak IE column (hexane: 2-propanol = 80:20, v = 1.0 mL/min, 40 °C, 254 nm); tr (major) = 14.155 min, tr (minor) = 17.549 min, 91% ee.



No.	Time	Area	Area (%)
1	14.333	3100.5	50.29
2	17.750	3065.3	49.71



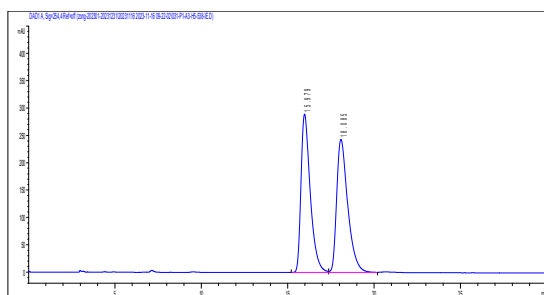
No.	Time	Area	Area (%)
1	14.155	14082.9	95.47
2	17.549	668.2	4.53



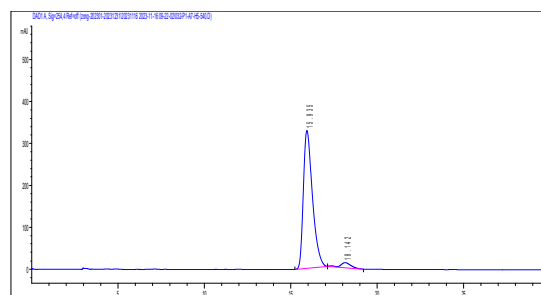
(*R*)-4-(1,3-dimethyl-5-(phenylethynyl)-5*H*-5 λ^4 ,6 λ^4 -pyrrolo[1',2':3,4][1,3,2]diazaborolo[1,5-*a*]pyridin-5-yl)-3-phenylbenzo[glisoquinolin-1(2*H*)-one (30)

The title compound was isolated as a yellow solid (37.1 mg, 67%). **¹H NMR (600 MHz, CDCl₃)** δ 10.38 (s, br, 1H), 9.11 (s, 1H), 8.29 (s, 1H), 8.15 – 7.84 (m, 3H), 7.65 – 7.26 (m, 5H), 7.24 – 7.13 (m, 3H), 7.10 (t, *J* = 7.5 Hz, 1H), 7.07 – 6.80 (m, 3H), 6.79 (t, *J* = 6.6 Hz, 1H), 6.65 (s, 1H), 6.38 (s, 1H), 5.85 (s, 1H), 2.29 (s, 3H), 2.18 (s, 3H). **¹³C NMR (150 MHz, CDCl₃)** δ 163.3, 149.4, 141.6, 140.2, 135.4, 131.6, 131.0, 129.6, 129.5, 129.1, 128.7, 128.07, 127.74, 127.68, 127.6, 127.4, 125.9, 125.2, 124.6, 122.5, 117.0, 115.8, 115.6, 99.4, 14.1, 12.2. **¹¹B NMR (193 MHz, CDCl₃)** δ -3.01. **HRMS (APCI):** calcd. for C₃₈H₂₉BN₃O⁺ [M+H]⁺: 554.2398, found: 554.2390. [α]_D²⁰ = -294 (c = 0.1, CHCl₃).

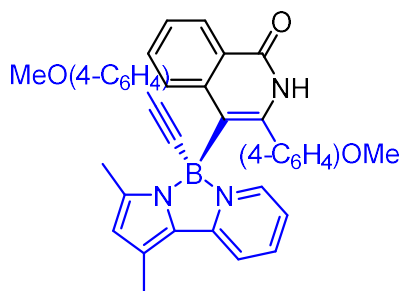
HPLC analysis: Daicel Chiralpak IE column (hexane: 2-propanol = 80:20, *v* = 1.0 mL/min, 40 °C, 254 nm); tr (major) = 15.935 min, tr (minor) = 18.142 min, 92% ee.



No.	Time	Area	Area (%)
1	15.979	10742.0	49.81
2	18.085	10824.3	50.19



No.	Time	Area	Area (%)
1	15.935	11952.0	96.04
2	18.142	492.6	3.96



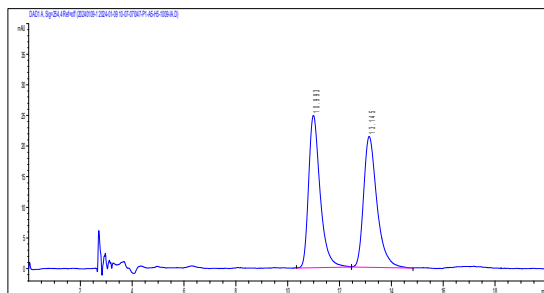
(R)-3-(4-methoxyphenyl)-4-(5-((4-methoxyphenyl)ethynyl)-1,3-dimethyl-5H-5λ⁴,6λ⁴-pyrrolo[1',2':3,4][1,3,2]diazaborolo[1,5-a]pyridin-5-yl)isoquinolin-1(2H)-one (31)

The title compound was isolated as a yellow solid (32.1 mg, 57%).

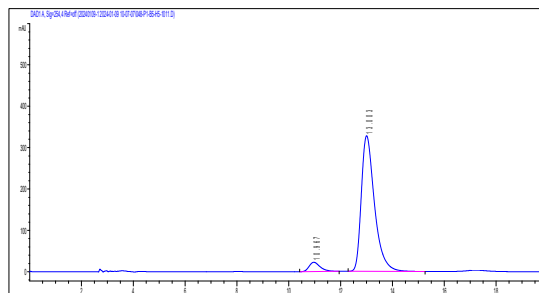
¹H NMR (600 MHz, CDCl₃) δ 9.76 (s, 1H), 8.47 (d, *J* = 8.1 Hz, 1H), 8.34 (s, 1H), 8.00 (d, *J* = 5.9 Hz, 1H), 7.84 – 7.60 (m, 1H), 7.48 (s,

2H), 7.26 – 7.06 (m, 2H), 6.98 – 6.82 (m, 1H), 6.79 (t, *J* = 6.6 Hz, 1H), 6.72 (d, *J* = 8.3 Hz, 2H), 6.64 – 6.34 (m, 3H), 6.24 (s, 1H), 5.84 (s, 1H), 3.75 (s, 3H), 3.71 (s, 3H), 2.24 (s, 3H), 2.20 (s, 3H). **¹³C NMR (150 MHz, CDCl₃)** δ 162.7, 159.1, 159.0, 149.4, 141.6, 140.1, 136.8, 132.8, 131.5, 130.9, 130.1, 127.6, 127.2, 125.73, 125.66, 122.3, 117.6, 117.0, 115.7, 115.5, 113.9, 113.7, 112.4, 98.8, 55.4, 55.3, 14.1, 12.3. **¹¹B NMR (193 MHz, CDCl₃)** δ -3.38. **HRMS (APCI):** calcd. for C₃₆H₃₁BN₃O₃⁺ [M+H]⁺: 564.2453, found: 564.2438. [α]_D²⁰ = -286 (c = 0.1, CHCl₃).

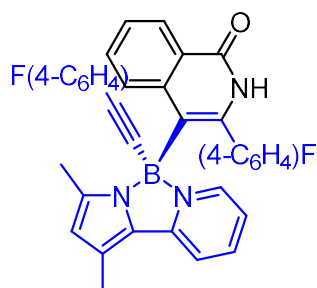
HPLC analysis: Daicel Chiralpak IA column (hexane: 2-propanol = 85:15, v = 1.0 mL/min, 40 °C, 254 nm); tr (major) = 13.003 min, tr (minor) = 10.967 min, 90% ee.



No.	Time	Area	Area (%)
1	10.993	770.2	50.18
2	13.145	764.7	49.82



No.	Time	Area	Area (%)
1	10.967	660.8	5.19
2	13.003	11597.5	94.81



(R)-3-(4-fluorophenyl)-4-(5-((4-fluorophenyl)ethynyl)-1,3-dimethyl-5H-5λ⁴,6λ⁴-pyrrolo[1',2':3,4][1,3,2]diazaborolo[1,5-a]pyridin-5-yl)isoquinolin-1(2H)-one (32)

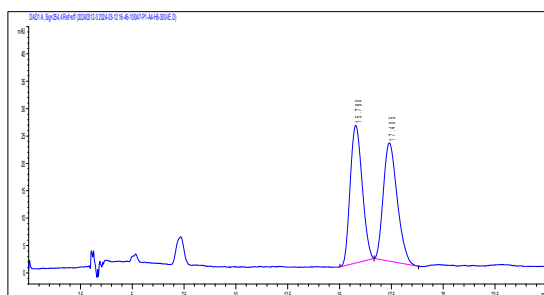
The title compound was isolated as a yellow solid (37.7 mg, 70%).

¹H NMR (600 MHz, CDCl₃) δ 9.74 (s, br, 1H), 9.51 (s, 1H), 8.47 (d, *J* = 8.0 Hz, 1H), 8.00 (d, *J* = 6.0 Hz, 1H), 7.87 – 7.61 (m, 1H), 7.60 – 7.47 (m, 2H), 7.39 (t,

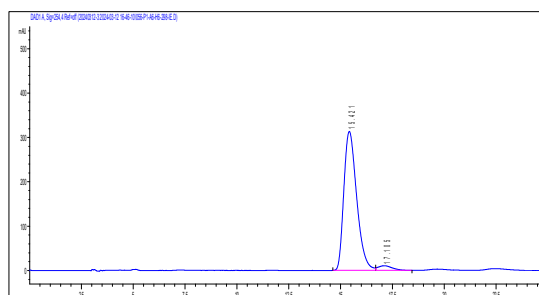
J = 7.6 Hz, 1H), 7.25 (s, 1H), 7.03 – 6.84 (m, 3H), 6.82 (t, *J* = 6.6 Hz, 1H), 6.79 – 6.46 (m, 3H), 6.31 (s, 1H), 5.85 (s, 1H), 2.23 (s, 3H), 2.21 (s, 3H). **¹³C NMR (150 MHz, CDCl₃)** δ 170.9, 163.2, 162.0

(d, J_{C-F} = 247.6 Hz), 149.4, 141.5, 140.4, 136.9, 133.23, 133.17, 132.9, 131.7, 130.8, 130.0, 129.6, 128.3, 127.5, 127.3, 126.0, 125.5, 122.9, 121.1 (d, J_{C-F} = 3.3 Hz), 117.1, 115.3 (d, J_{C-F} = 21.6 Hz), 114.7, 114.5, 114.4, 98.1, 14.0, 12.1. **^{11}B NMR (193 MHz, CDCl_3)** δ -4.00. **^{19}F NMR (376 MHz, CDCl_3)** δ -112.20, -113.83. **HRMS (APCI)**: calcd. for $\text{C}_{34}\text{H}_{25}\text{BF}_2\text{N}_3\text{O}^+$ $[\text{M}+\text{H}]^+$: 540.2053, found : 540.2040. $[\alpha]_{\text{D}}^{20}$ = -292 (c = 0.1, CHCl_3).

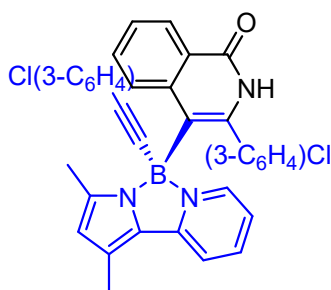
HPLC analysis: Daicel Chiralpak IE column (hexane: 2-propanol = 85:15, v = 1.0 mL/min, 40 °C, 254 nm); tr (major) = 15.421 min, tr (minor) = 17.105 min, 93% ee.



No.	Time	Area	Area (%)
1	15.780	1014.6	50.15
2	17.405	1008.7	49.85



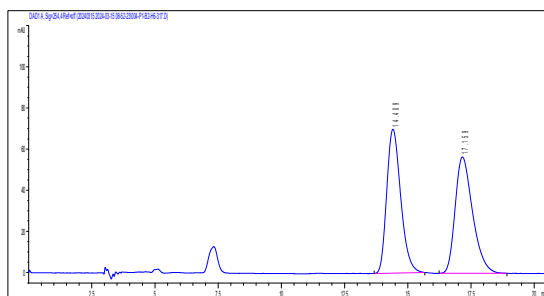
No.	Time	Area	Area (%)
1	15.421	13499.7	96.39
2	17.105	506.3	3.61



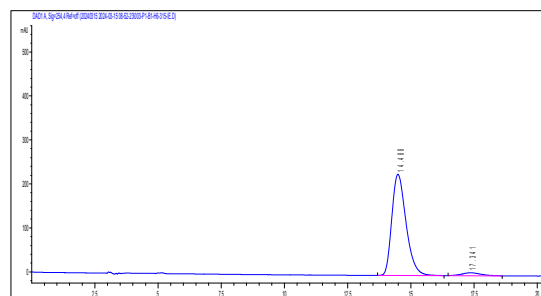
(*R*)-3-(3-chlorophenyl)-4-(5-((3-chlorophenyl)ethynyl)-1,3-dimethyl-5H-5 λ ⁴,6 λ ⁴-pyrrolo[1',2':3,4][1,3,2]diazaborolo[1,5-*a*]pyridin-5-yl)isoquinolin-1(2*H*)-one (33)

The title compound was isolated as a yellow solid (36.0 mg, 63%, 1.2:1 dr). **^1H NMR (600 MHz, CDCl_3)** δ 9.69 (s, 1H), 9.43 – 9.06 (m, 1H), 8.54 – 8.32 (m, 1H), 8.12 – 7.60 (m, 3H), 7.58 – 7.35 (m, 2H), 7.22 – 7.04 (m, 4H), 7.02 – 6.72 (m, 3H), 6.66 – 6.16 (m, 2H), 5.73 (s, 1H), 2.31 – 2.19 (m, 3H), 2.19 – 2.08 (m, 3H). **^{13}C NMR (150 MHz, CDCl_3)** δ 162.79, 162.76, 149.3, 149.2, 141.4, 141.3, 140.4, 140.3, 136.9, 133.8, 133.7, 132.8, 131.6, 131.2, 129.9, 129.5, 129.2, 128.9, 128.6, 128.2, 127.6, 127.4, 127.3, 126.6, 125.62, 125.57, 123.3, 122.7, 117.2, 116.9, 116.1, 115.9, 115.8, 115.6, 14.0, 13.8, 12.2, 12.0. **^{11}B NMR (193 MHz, CDCl_3)** δ -3.42. **HRMS (APCI)**: calcd. for $\text{C}_{34}\text{H}_{25}\text{BCl}_2\text{N}_3\text{O}^+$ $[\text{M}+\text{H}]^+$: 572.1462, found : 572.1455. $[\alpha]_{\text{D}}^{20}$ = -182 (c = 0.1, CHCl_3).

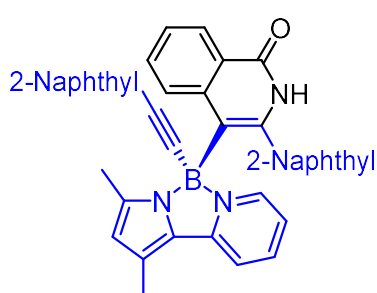
HPLC analysis: Daicel Chiralpak IE column (hexane: 2-propanol = 85:15, v = 1.0 mL/min, 40 °C, 254 nm); tr (major) = 14.488 min, tr (minor) = 17.341 min, 93% ee.



No.	Time	Area	Area (%)
1	14.409	2691.2	49.78
2	17.159	2715.3	50.22



No.	Time	Area	Area (%)
1	14.488	8988.1	96.31
2	17.341	344.2	3.69

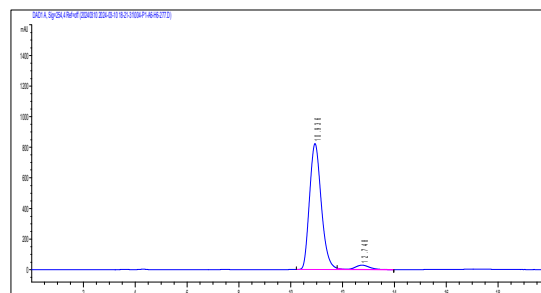
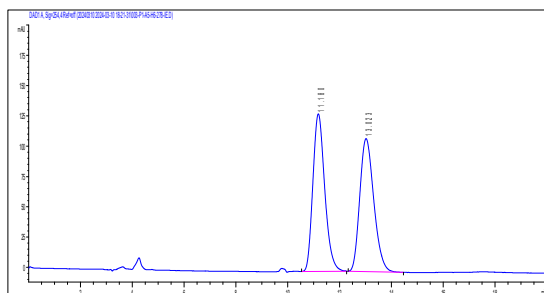


(*R*)-4-(1,3-dimethyl-5-(naphthalen-2-ylethynyl)-5*H*-5 λ^4 ,6 λ^4 -pyrrolo[1',2':3,4][1,3,2]diazaborolo[1,5-*a*]pyridin-5-yl)-3-(naphthalen-2-yl)isoquinolin-1(2*H*)-one (34)

The title compound was isolated as a yellow solid (39.8 mg, 66%, 1.8:1 dr). ¹H NMR (600 MHz, CDCl₃) δ 9.86 (s, br, 1H), 9.37 – 8.91 (m, 1H), 8.54 (d, *J* = 8.0 Hz, 1H), 8.27 – 7.96 (m, 1H), 7.93 – 7.62 (m, 6H),

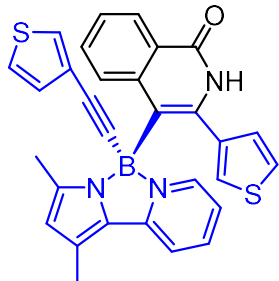
7.57 – 7.30 (m, 9H), 7.04 – 6.65 (m, 3H), 6.26 (s, 1H), 5.93 (s, 1H), 2.51 – 2.19 (m, 3H), 1.91 – 1.59 (m, 3H). ¹³C NMR (150 MHz, CDCl₃) δ 170.6, 169.6, 163.0, 162.8, 149.13, 149.12, 144.0, 143.5, 141.6, 141.42, 140.1, 139.7, 136.8, 133.0, 132.4, 132.3, 131.9, 131.6, 131.5, 130.8, 130.7, 129.9, 129.8, 128.7, 128.6, 128.1, 127.6, 127.53, 127.46, 127.4, 127.3, 127.1, 126.4, 126.3, 126.2, 126.1, 125.8, 125.6, 125.5, 124.9, 124.8, 122.9, 122.7, 122.3, 117.0, 116.7, 115.6, 115.1, 99.5, 99.2, 77.3, 14.3, 13.9, 12.1, 11.6. ¹¹B NMR (193 MHz, CDCl₃) δ -4.20. HRMS (APCI): calcd. for C₄₂H₃₁BN₃O⁺ [M+H]⁺ : 604.2555, found : 604.2549. [α]_D²⁰ = -282 (c = 0.1, CHCl₃).

HPLC analysis: Daicel Chiralpak IE column (hexane: 2-propanol = 60:40, v = 1.0 mL/min, 40 °C, 254 nm); tr (major) = 10.936 min, tr (minor) = 12.748 min, 92% ee.



No.	Time	Area	Area (%)
1	11.180	4141.4	50.09
2	13.023	4126.6	49.91

No.	Time	Area	Area (%)
1	10.936	25970.7	96.02
2	12.748	1077.0	3.98

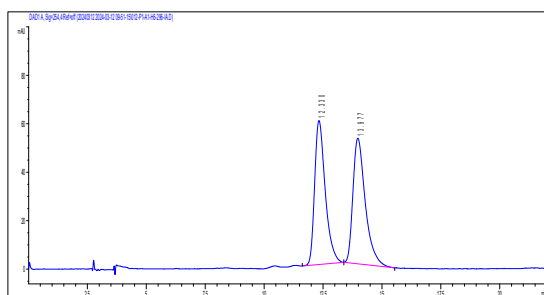


(R)-4-(1,3-dimethyl-5-(thiophen-3-ylethynyl)-5H-5λ⁴,6λ⁴-

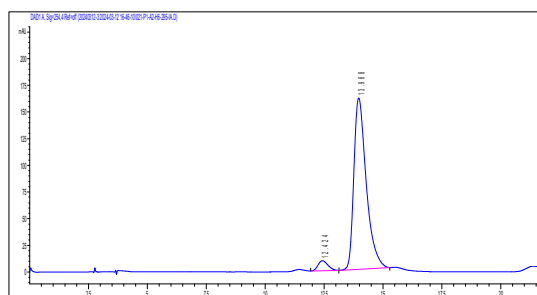
pyrrolo[1',2':3,4][1,3,2]diazaborolo[1,5-a]pyridin-5-yl)-3-(thiophen-3-yl)isoquinolin-1(2H)-one (35)

The title compound was isolated as a yellow solid (35.0 mg, 68%). ¹H NMR (600 MHz, CDCl₃) δ 9.68 (s, br, 1H), 8.88 – 8.66 (m, 1H), 8.46 (d, *J* = 7.9 Hz, 1H), 7.96 (d, *J* = 6.0 Hz, 1H), 7.83 – 7.60 (m, 1H), 7.60 – 7.40 (m, 2H), 7.25 – 7.09 (m, 2H), 7.08 – 6.83 (m, 3H), 6.79 (t, *J* = 6.6 Hz, 1H), 6.39 (s, 1H), 6.17 (s, 1H), 5.87 (s, 1H), 2.25 (s, 6H). ¹³C NMR (150 MHz, CDCl₃) δ 162.8, 149.3, 143.3, 141.3, 140.2, 136.7, 131.4, 130.1, 129.5, 127.6, 127.5, 127.2, 125.9, 125.8, 125.1, 125.0, 124.7, 124.3, 122.7, 117.1, 115.9, 115.5, 93.8, 14.0, 12.3. ¹¹B NMR (193 MHz, CDCl₃) δ -3.27. HRMS (APCI): calcd. for C₃₀H₂₃BN₃OS₂⁺ [M+H]⁺: 516.1370, found: 516.1367. [α]_D²⁰ = -352 (c = 0.1, CHCl₃).

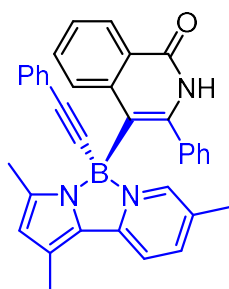
HPLC analysis: Daicel Chiralpak IA column (hexane: 2-propanol = 90:10, v = 1.0 mL/min, 40 °C, 254 nm); tr (major) = 13.968 min, tr (minor) = 12.424 min, 91% ee.



No.	Time	Area	Area (%)
1	12.330	1865.4	49.65
2	13.977	1891.6	50.35



No.	Time	Area	Area (%)
1	12.424	276.1	4.49
2	13.968	5877.7	95.51



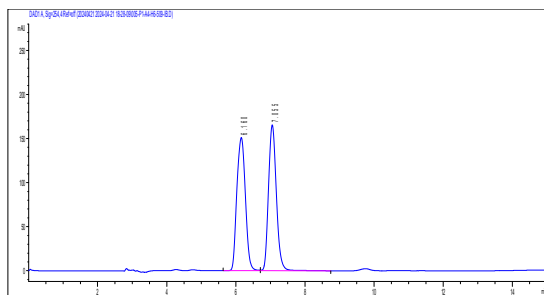
(R)-3-phenyl-4-(1,3,8-trimethyl-5-(phenylethynyl)-5H-5λ⁴,6λ⁴-

pyrrolo[1',2':3,4][1,3,2]diazaborolo[1,5-a]pyridin-5-yl)isoquinolin-1(2H)-one (36)

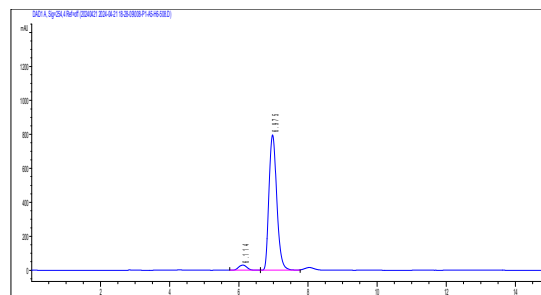
The title compound was isolated as a yellow solid (34.6 mg, 67%). ¹H NMR (600 MHz, CDCl₃) δ 9.79 (s, br, 1H), 8.76 – 8.54 (m, 1H), 8.47 (d, *J* = 8.0 Hz, 1H),

7.84 (s, 1H), 7.82 – 7.64 (m, 1H), 7.56 – 7.46 (m, 1H), 7.35 – 7.13 (m, 6H), 7.08 (t, $J = 7.5$ Hz, 1H), 6.93 (s, 2H), 6.77 (s, 1H), 6.61 (s, 1H), 6.35 (s, 1H), 5.81 (s, 1H), 2.25 (s, 3H), 2.23 (s, 3H), 2.15 (s, 3H). **^{13}C NMR (150 MHz, CDCl_3)** δ 162.6, 147.5, 143.5, 141.6, 140.6, 135.9, 131.5, 129.6, 128.6, 128.0, 127.6, 127.53, 127.46, 127.3, 127.2, 127.1, 125.72, 125.70, 125.2, 121.2, 115.4, 115.0, 98.9, 18.0, 14.0, 12.1. **^{11}B NMR (193 MHz, CDCl_3)** δ -3.37. **HRMS (APCI):** calcd. for $\text{C}_{35}\text{H}_{29}\text{BN}_3\text{O}^+$ $[\text{M}+\text{H}]^+$: 518.2398, found : 518.2395. $[\alpha]_{\text{D}}^{20} = -248$ ($c = 0.1$, CHCl_3).

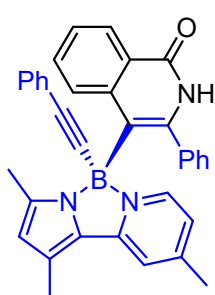
HPLC analysis: Daicel Chiralpak IB column (hexane: 2-propanol = 85:15, $v = 1.0$ mL/min, 40 °C, 254 nm); tr (major) = 6.975 min, tr (minor) = 6.114 min, 92% ee.



No.	Time	Area	Area (%)
1	6.160	2598.9	49.75
2	7.055	2624.5	50.25



No.	Time	Area	Area (%)
1	6.114	506.4	3.91
2	6.975	12462.8	96.09



(*R*)-3-phenyl-4-(1,3,9-trimethyl-5-(phenylethynyl)-5*H*-5 λ^4 ,6 λ^4 -

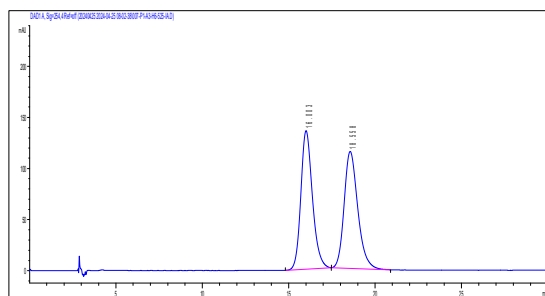
pyrrolo[1',2':3,4][1,3,2]diazaborolo[1,5-*a*]pyridin-5-yl)isoquinolin-1(2*H*)-one

(37)

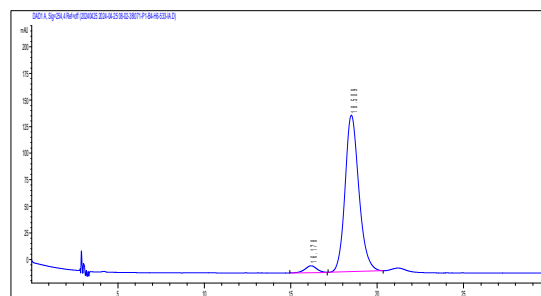
The title compound was isolated as a yellow solid (33.6 mg, 65%). **^1H NMR (600 MHz, CDCl_3)** δ 9.78 (s, br, 1H), 8.63 – 8.29 (m, 2H), 7.87 (d, $J = 6.1$ Hz, 1H), 7.80 – 7.64 (m, 1H), 7.56 – 7.26 (m, 3H), 7.23 – 7.13 (m, 3H), 7.08 (t, $J = 7.5$ Hz, 1H),

7.02 – 6.79 (m, 2H), 6.76 – 6.45 (m, 3H), 6.31 (s, 1H), 5.82 (s, 1H), 2.28 (s, 3H), 2.25 (s, 3H), 2.17 (s, 3H). **^{13}C NMR (150 MHz, CDCl_3)** δ 162.6, 152.5, 149.1, 143.5, 140.7, 136.3, 131.5, 129.6, 128.6, 128.0, 127.6, 127.5, 127.34, 127.26, 127.1, 125.7, 125.2, 121.9, 118.7, 115.7, 115.3, 98.9, 21.8, 14.0, 12.2. **^{11}B NMR (193 MHz, CDCl_3)** δ -4.23. **HRMS (APCI):** calcd. for $\text{C}_{35}\text{H}_{29}\text{BN}_3\text{O}^+$ $[\text{M}+\text{H}]^+$: 518.2398, found : 518.2393. $[\alpha]_{\text{D}}^{20} = -336$ ($c = 0.1$, CHCl_3).

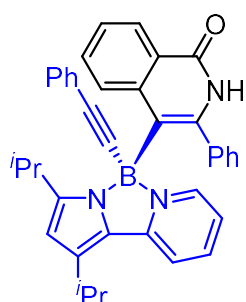
HPLC analysis: Daicel Chiralpak IA column (hexane: 2-propanol = 95:5, $v = 1.0$ mL/min, 40 °C, 254 nm); tr (major) = 18.509 min, tr (minor) = 16.178 min, 93% ee.



No.	Time	Area	Area (%)
1	16.003	6328.4	50.15
2	18.558	6289.3	49.85



No.	Time	Area	Area (%)
1	16.178	299.9	3.54
2	18.509	8166.6	96.46



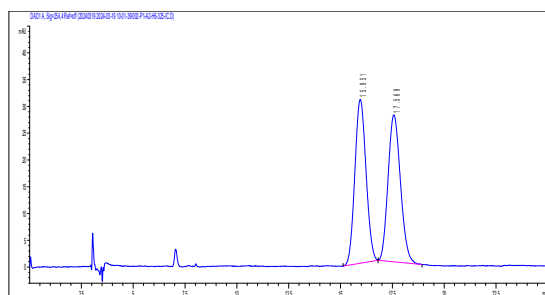
(*R*)-4-(1,3-diisopropyl-5-(phenylethynyl)-5*H*-5λ⁴,6λ⁴-pyrrolo[1',2':3,4][1,3,2]diazaborolo[1,5-*a*]pyridin-5-yl)-3-phenylisoquinolin-1(2*H*)-one (38)

The title compound was isolated as a yellow solid (24.0 mg, 43%). ¹H NMR (600 MHz, CDCl₃) δ 9.82 (s, 1H), 9.10 (s, 1H), 8.52 (s, 1H), 8.05 – 7.64 (m, 3H), 7.59 – 7.28 (m, 5H), 7.24 – 7.15 (m, 2H), 7.06 (t, *J* = 7.5 Hz, 1H), 6.97 – 6.64 (m, 4H),

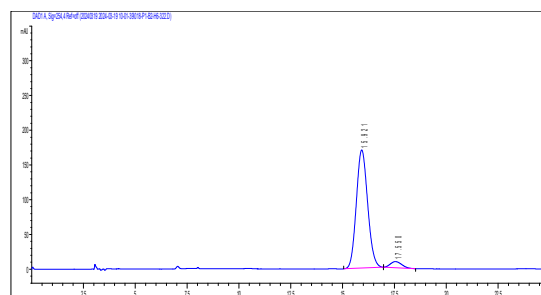
6.21 (s, 1H), 6.01 (s, 1H), 3.24 – 2.64 (m, 2H), 1.40 (s, 3H), 1.31 (s, 3H), 1.26 (s, 3H), 1.09 (s, 3H). ¹³C NMR (150 MHz, CDCl₃) δ 163.1, 149.0, 141.3, 139.9, 132.8, 132.0, 131.5, 131.2, 130.0, 129.6,

128.6, 128.2, 128.0, 127.8, 127.4, 127.3, 127.0, 125.8, 125.3, 125.1, 116.7, 115.8, 107.0, 98.8, 27.9, 27.2, 26.4, 23.8, 23.3, 22.6. ¹¹B NMR (193 MHz, CDCl₃) δ -4.11. HRMS (APCI): calcd. for C₃₈H₃₅BN₃O⁺ [M+H]⁺: 560.2868, found: 560.2864. [α]_D²⁰ = -298 (c = 0.1, CHCl₃).

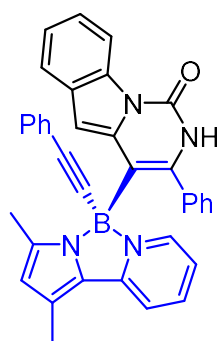
HPLC analysis: Daicel Chiralpak IC column (hexane: 2-propanol = 90:10, v = 1.0 mL/min, 40 °C, 254 nm); tr (major) = 15.921 min, tr (minor) = 17.550 min, 90% ee.



No.	Time	Area	Area (%)
1	15.951	1146.0	50.11
2	17.569	1140.9	49.89



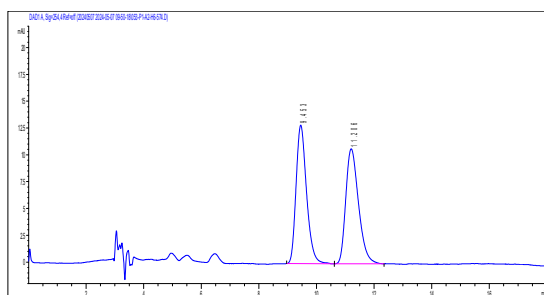
No.	Time	Area	Area (%)
1	15.921	6467.7	95.08
2	17.550	334.7	4.92



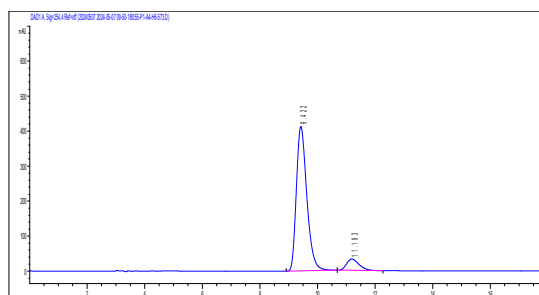
(*R*)-4-(1,3-dimethyl-5-(phenylethynyl)-5*H*-5 λ^4 ,6 λ^4 -pyrrolo[1',2':3,4][1,3,2]diazaborolo[1,5-*a*]pyridin-5-yl)-3-phenylpyrimido[1,6-*a*]indol-1(2*H*)-one (39)

The title compound was isolated as a yellow solid (39.0 mg, 72%). **¹H NMR (600 MHz, CDCl₃)** δ 8.69 – 8.43 (m, 2H), 8.33 – 7.97 (m, 2H), 7.76 – 7.27 (m, 7H), 7.26 – 7.10 (m, 4H), 7.10 – 6.82 (m, 3H), 6.79 (t, *J* = 6.6 Hz, 1H), 6.72 – 6.37 (m, 1H), 5.80 (s, 1H), 2.27 (s, 3H), 2.17 (s, 3H). **¹³C NMR (150 MHz, CDCl₃)** δ 170.4, 149.5, 148.8, 141.5, 140.4, 137.1, 133.3, 132.4, 131.6, 131.2, 130.2, 129.2, 128.4, 128.1, 127.7, 127.5, 127.4, 125.1, 123.5, 122.4, 122.0, 119.7, 116.9, 116.3, 115.7, 115.5, 98.2, 13.8, 12.1. **¹¹B NMR (193 MHz, CDCl₃)** δ -4.76. **HRMS (APCI):** calcd. for C₃₆H₂₈BN₄O⁺ [*M*+*H*]⁺ : 543.2351, found : 543.2345. [α]_D²⁰ = -72 (c = 0.1, CHCl₃).

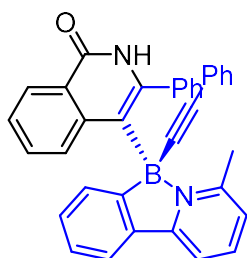
HPLC analysis: Daicel Chiralpak IE column (hexane: 2-propanol = 85:15, v = 1.0 mL/min, 40 °C, 254 nm); tr (major) = 9.422 min, tr (minor) = 11.193 min, 83% ee.



No.	Time	Area	Area (%)
1	9.453	327.5	49.81
2	11.206	330.1	50.19



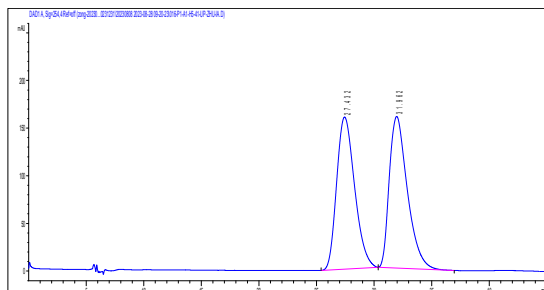
No.	Time	Area	Area (%)
1	9.422	10395.9	91.50
2	11.193	965.2	8.50



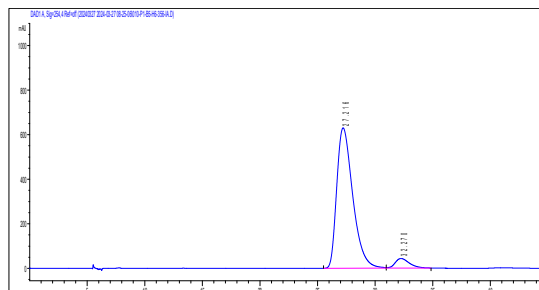
(*R*)-4-(4-methyl-6-(phenylethynyl)-6*H*-5 λ^4 ,6 λ^4 -benzo[3,4][1,2]azaborolo[1,5-*a*]pyridin-6-yl)-3-phenylisoquinolin-1(2*H*)-one (40)

The title compound was isolated as a yellow solid (34.0 mg, 68%). **¹H NMR (600 MHz, CDCl₃)** δ 9.73 (d, *J* = 8.3 Hz, 1H), 8.51 (d, *J* = 7.7 Hz, 1H), 8.24 (s, 1H), 7.91 – 7.88 (m, 1H), 7.87 – 7.83 (m, 1H), 7.64 (d, *J* = 7.6 Hz, 1H), 7.59 – 7.50 (m, 2H), 7.44 (t, *J* = 7.3 Hz, 1H), 7.38 – 7.33 (m, 2H), 7.24 – 7.19 (m, 2H), 7.18 – 7.11 (m, 3H), 7.01 – 6.94 (m, 3H), 6.81 (d, *J* = 7.6 Hz, 1H), 6.67 – 6.57 (m, 1H), 6.10 (d, *J* = 7.5 Hz, 1H), 2.73 (s, 3H). **¹³C NMR (150 MHz, CDCl₃)** δ 162.7, 158.8, 156.6, 143.0, 140.6, 138.8, 137.4, 136.5, 131.5, 131.22, 131.20, 130.7, 129.98, 129.95, 128.23, 128.20, 128.0, 127.6, 127.3, 127.1, 126.9, 126.7, 126.3,

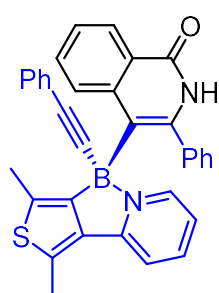
126.2, 125.9, 125.7, 123.9, 121.9, 115.4, 98.7, 22.1. **¹¹B NMR (193 MHz, CDCl₃)** δ -3.28. **HRMS (APCI)**: calcd. for C₃₅H₂₆BN₂O⁺ [M+H]⁺: 501.2133, found: 501.2128. **[α]_D²⁰** = -446 (c = 0.1, CHCl₃). **HPLC analysis**: Daicel Chiralpak IA column (hexane: 2-propanol = 90:10, v = 0.5 mL/min, 40 °C, 254 nm); tr (major) = 27.216 min, tr (minor) = 32.270 min, 89% ee.



No.	Time	Area	Area (%)
1	27.432	17308.3	49.93
2	31.962	17357.3	50.07



No.	Time	Area	Area (%)
1	27.216	60869.8	94.27
2	32.270	3700.4	5.73

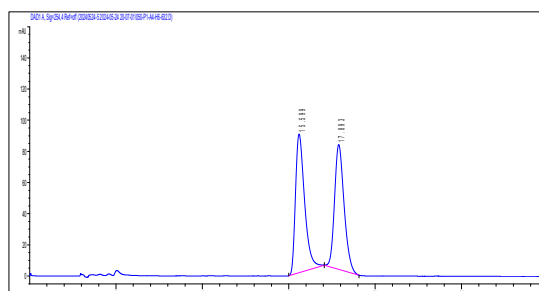
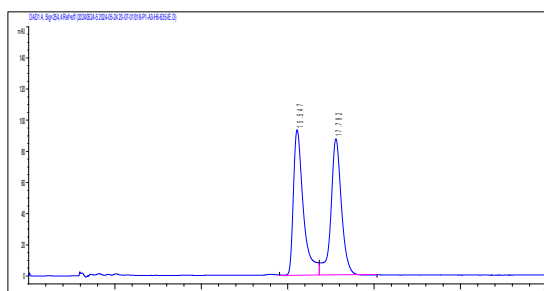


(R)-4-(1,3-dimethyl-4-(phenylethynyl)-4H-5λ⁴,6λ⁴-

thieno[3',4':3,4][1,2]azaborolo[1,5-a]pyridin-4-yl)-3-phenylisoquinolin-1(2H)-one (41)

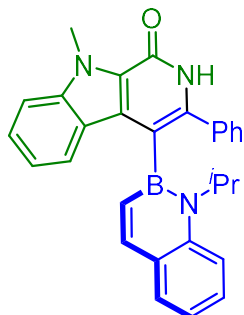
The title compound was isolated as a yellow solid (27.1 mg, 52%). **¹H NMR (600 MHz, CDCl₃)** δ 9.59 (s, br, 1H), 8.48 (d, *J* = 8.0 Hz, 1H), 8.42 – 8.21 (m, 2H), 7.74 (t, *J* = 7.8 Hz, 1H), 7.65 (t, *J* = 7.8 Hz, 1H), 7.50 (t, *J* = 7.5 Hz, 1H), 7.29 – 7.05 (m, 7H), 7.01 (t, *J* = 7.5 Hz, 1H), 6.92 – 6.77 (m, 2H), 6.70 – 6.43 (m, 2H), 2.50 (s, 3H), 2.39 (s, 3H). **¹³C NMR (150 MHz, CDCl₃)** δ 162.7, 153.1, 144.7, 143.7, 141.6, 140.4, 138.8, 137.9, 135.6, 132.1, 131.3, 131.2, 130.1, 128.0, 127.5, 127.1, 126.9, 125.8, 125.74, 125.72, 121.0, 119.0, 99.4, 15.2, 14.0. **¹¹B NMR (193 MHz, CDCl₃)** δ -6.06. **HRMS (APCI)**: calcd. for C₃₄H₂₆BN₂OS⁺ [M+H]⁺: 521.1853, found: 521.1847. **[α]_D²⁰** = 0 (c = 0.1, CHCl₃).

HPLC analysis: Daicel Chiralpak IE column (hexane: 2-propanol = 75:25, v = 1.0 mL/min, 40 °C, 254 nm); tr (major) = 15.599 min, tr (minor) = 17.893 min, <5% ee.



No.	Time	Area	Area (%)
1	15.547	3755.8	50.52
2	17.792	3679.1	49.48

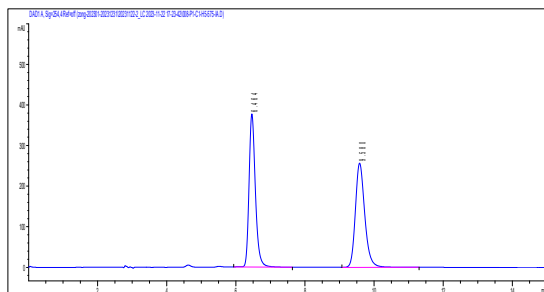
No.	Time	Area	Area (%)
1	15.599	3266.1	51.42
2	17.893	3085.5	48.58



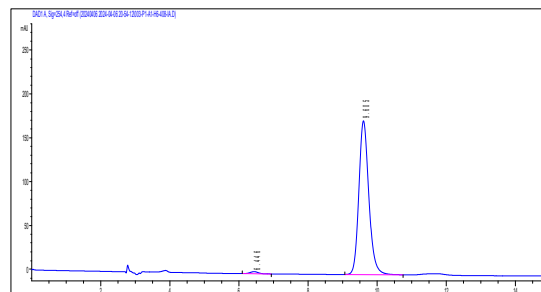
(R)-4-(1-isopropylbenzo[e][1,2]azaborinin-2(1H)-yl)-9-methyl-3-phenyl-2,9-dihydro-1H-pyrido[3,4-b]indol-1-one (44)

The title compound was isolated as a white solid (31.1 mg, 70%). ¹H NMR (600 MHz, CDCl₃) δ 10.37 (s, 1H), 8.03 (d, *J* = 11.1 Hz, 1H), 7.81 – 7.69 (m, 2H), 7.55 – 7.48 (m, 2H), 7.47 – 7.40 (m, 2H), 7.40 – 7.34 (m, 1H), 7.26 – 7.17 (m, 4H), 7.07 (d, *J* = 11.1 Hz, 1H), 7.04 (d, *J* = 8.1 Hz, 1H), 6.91 – 6.81 (m, 1H), 4.89 – 4.75 (m, 1H), 4.35 (s, 3H), 1.25 (d, *J* = 7.6 Hz, 3H), 0.93 (d, *J* = 7.2 Hz, 3H). ¹³C NMR (150 MHz, CDCl₃) δ 157.4, 144.5, 141.4, 140.4, 137.2, 135.9, 132.8, 131.3, 128.74, 128.69, 128.5, 128.3, 127.4, 126.5, 126.2, 123.32, 123.30, 120.7, 119.7, 119.0, 109.9, 52.4, 31.5, 21.6. ¹¹B NMR (193 MHz, CDCl₃) δ 38.83. HRMS (APCI): calcd. for C₂₉H₂₇BN₃O⁺ [M+H]⁺: 444.2242, found: 444.2255. [α]_D²⁰ = +64 (c = 0.1, CHCl₃).

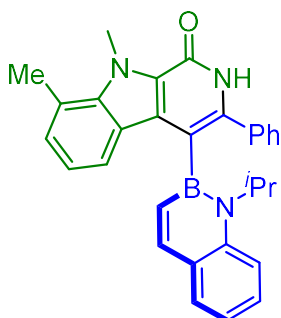
HPLC analysis: Daicel Chiralpak IA column (hexane: 2-propanol = 90:10, v = 1.0 mL/min, 40 °C, 254 nm); tr (major) = 9.605 min, tr (minor) = 6.446 min, 98% ee.



No.	Time	Area	Area (%)
1	6.464	4804.1	49.77
2	9.580	4847.8	50.23



No.	Time	Area	Area (%)
1	6.446	40.3	1.13
2	9.605	3511.8	98.87

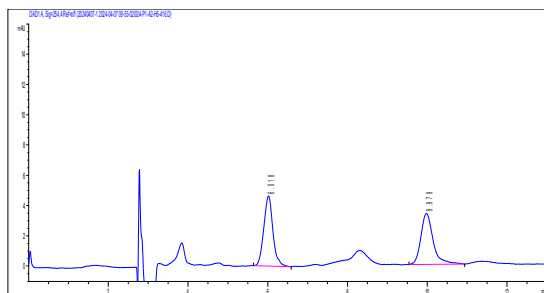


(R)-4-(1-isopropylbenzo[e][1,2]azaborinin-2(1H)-yl)-8,9-dimethyl-3-phenyl-2,9-dihydro-1H-pyrido[3,4-b]indol-1-one (45)

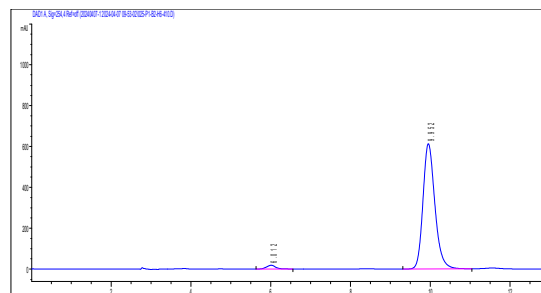
The title compound was isolated as a white solid (28.3 mg, 62%). ¹H NMR (600 MHz, CDCl₃) δ 10.58 (s, br, 1H), 8.02 (d, *J* = 11.2 Hz, 1H), 7.81 – 7.70 (m, 2H), 7.55 – 7.48 (m, 2H), 7.47 – 7.41 (m, 1H), 7.27 – 7.17 (m, 4H), 7.10

– 7.02 (m, 2H), 6.94 – 6.84 (m, 1H), 6.71 (t, $J = 7.6$ Hz, 1H), 4.89 – 4.76 (m, 1H), 4.69 (s, 3H), 2.85 (s, 3H), 1.27 (d, $J = 7.7$ Hz, 4H), 0.94 (d, $J = 7.6$ Hz, 3H). ^{13}C NMR (150 MHz, CDCl_3) δ 157.5, 157.4, 144.4, 140.7, 140.4, 137.2, 136.0, 133.1, 131.2, 129.4, 128.81, 128.80, 128.7, 128.62, 128.59, 128.2, 127.3, 126.5, 124.3, 122.1, 121.3, 120.7, 119.7, 119.0, 114.3, 52.4, 34.6, 21.5, 21.0, 20.8. ^{11}B NMR (193 MHz, CDCl_3) δ 39.08. HRMS (APCI): calcd. for $\text{C}_{30}\text{H}_{29}\text{BN}_3\text{O}^+$ $[\text{M}+\text{H}]^+$: 458.2398, found : 458.2394. $[\alpha]_{\text{D}}^{20} = +98$ ($c = 0.1$, CHCl_3).

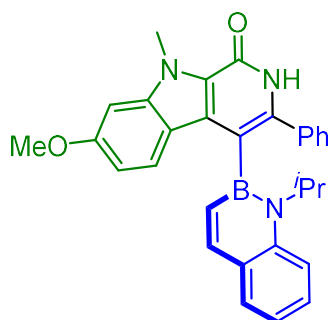
HPLC analysis: Daicel Chiralpak IA column (hexane: 2-propanol = 90:10, $v = 1.0$ mL/min, 40 °C, 254 nm); tr (major) = 9.952 min, tr (minor) = 6.012 min, 96% ee.



No.	Time	Area	Area (%)
1	6.018	73.4	50.58
2	9.979	71.7	49.42



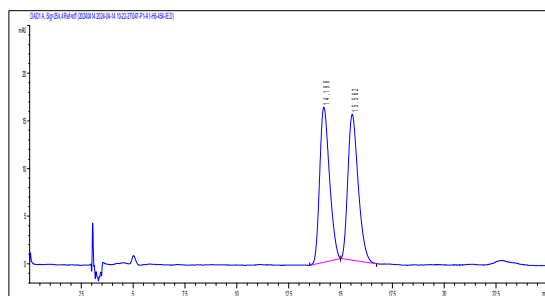
No.	Time	Area	Area (%)
1	6.012	289.8	2.23
2	9.952	12699.6	97.77



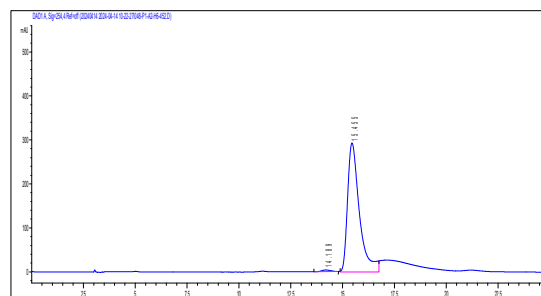
(R)-4-(1-isopropylbenzo[e][1,2]azaborinin-2(1H)-yl)-7-methoxy-9-methyl-3-phenyl-2,9-dihydro-1H-pyrido[3,4-b]indol-1-one (46)

The title compound was isolated as a white solid (28.9 mg, 61%). ^1H NMR (600 MHz, CDCl_3) δ 10.16 (s, br, 1H), 8.03 (d, $J = 11.1$ Hz, 1H), 7.80 – 7.71 (m, 2H), 7.52 – 7.47 (m, 2H), 7.46 – 7.41 (m, 1H), 7.26 – 7.15 (m, 4H), 7.06 (d, $J = 11.1$ Hz, 1H), 6.89 (d, $J = 8.9$ Hz, 1H), 6.80 (d, $J = 2.2$ Hz, 1H), 6.51 (dd, $J = 8.9, 2.3$ Hz, 1H), 4.87 – 4.72 (m, 1H), 4.31 (s, 3H), 3.85 (s, 3H), 1.26 (d, $J = 7.2$ Hz, 3H), 0.93 (d, $J = 7.2$ Hz, 3H). ^{13}C NMR (150 MHz, CDCl_3) δ 159.6, 156.8, 144.5, 142.7, 140.2, 137.1, 136.0, 131.1, 129.0, 128.8, 128.6, 128.5, 128.1, 127.3, 126.2, 125.5, 124.0, 120.6, 118.9, 117.3, 110.0, 92.2, 55.5, 52.2, 31.4, 21.4, 20.9. ^{11}B NMR (193 MHz, CDCl_3) δ 38.42. HRMS (APCI): calcd. for $\text{C}_{30}\text{H}_{29}\text{BN}_3\text{O}_2^+$ $[\text{M}+\text{H}]^+$: 474.2347, found : 474.2347. $[\alpha]_{\text{D}}^{20} = +82$ ($c = 0.1$, CHCl_3).

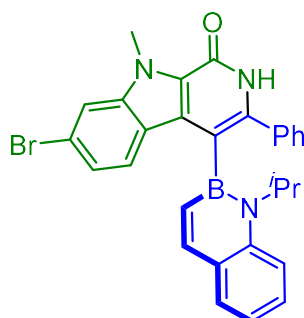
HPLC analysis: Daicel Chiralpak IE column (hexane: 2-propanol = 85:15, $v = 1.0$ mL/min, 40 °C, 254 nm); tr (major) = 15.455 min, tr (minor) = 14.189 min, 98% ee.



No.	Time	Area	Area (%)
1	14.196	537.8	50.26
2	15.562	532.2	49.74



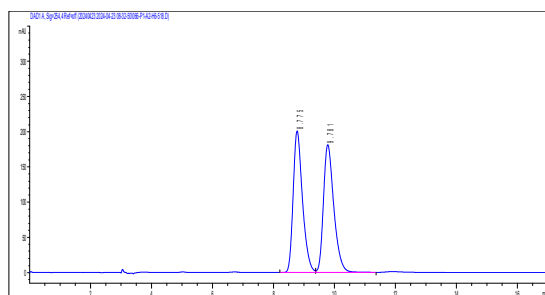
No.	Time	Area	Area (%)
1	14.189	119.2	1.01
2	15.455	11651.2	98.99



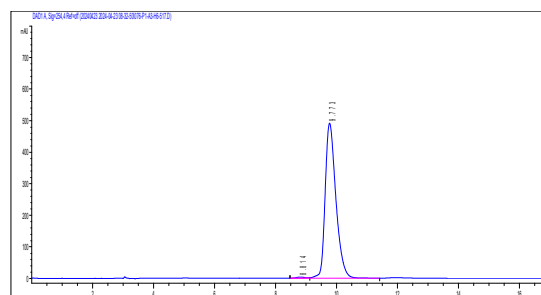
(R)-7-bromo-4-(1-isopropylbenzo[e][1,2]azaborinin-2(1H)-yl)-9-methyl-3-phenyl-2,9-dihydro-1H-pyrido[3,4-b]indol-1-one (47)

The title compound was isolated as a white solid (32.3 mg, 62%). ¹H NMR (600 MHz, CDCl₃) δ 10.81 – 10.52 (m, 1H), 8.03 (d, *J* = 11.1 Hz, 1H), 7.79 – 7.70 (m, 2H), 7.59 – 7.54 (m, 1H), 7.54 – 7.47 (m, 2H), 7.46 – 7.41 (m, 1H), 7.26 – 7.17 (m, 4H), 7.03 (d, *J* = 11.1 Hz, 1H), 6.95 (dd, *J* = 8.6, 1.7 Hz, 1H), 6.86 (d, *J* = 8.6 Hz, 1H), 4.85 – 4.72 (m, 1H), 4.29 (s, 3H), 1.25 (d, *J* = 7.2 Hz, 3H), 0.92 (d, *J* = 7.2 Hz, 3H). ¹³C NMR (150 MHz, CDCl₃) δ 157.3, 144.8, 142.1, 140.3, 137.0, 136.6, 131.3, 128.74, 128.69, 128.4, 127.5, 126.5, 124.5, 123.2, 122.2, 120.9, 120.6, 119.0, 113.0, 52.4, 31.6, 21.6, 21.0. ¹¹B NMR (193 MHz, CDCl₃) δ 39.09. HRMS (APCI): calcd. for C₂₉H₂₆BBBrN₃O⁺ [M+H]⁺ : 522.1347, found : 522.1342. [α]_D²⁰ = +118 (c = 0.1, CHCl₃).

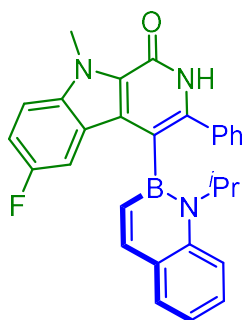
HPLC analysis: Daicel Chiralpak IE column (hexane: 2-propanol = 85:15, v = 1.0 mL/min, 40 °C, 254 nm); tr (major) = 9.773 min, tr (minor) = 8.814 min, 99% ee.



No.	Time	Area	Area (%)
1	8.775	4266.6	49.85
2	9.781	4292.8	50.15



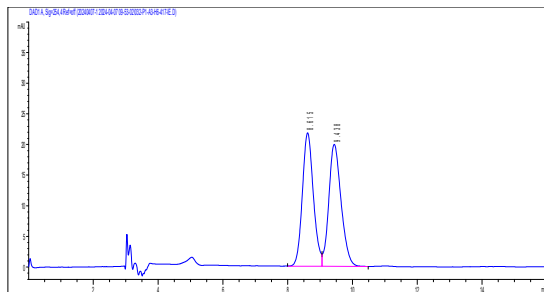
No.	Time	Area	Area (%)
1	8.814	64.0	0.53
2	9.773	11990.8	99.47



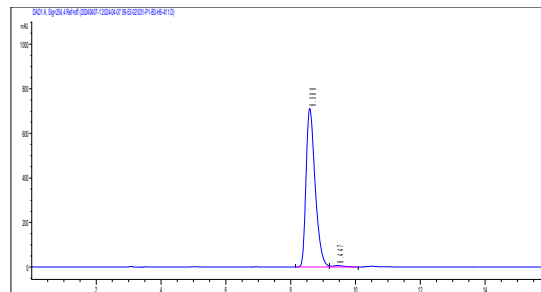
(*R*)-6-fluoro-4-(1-isopropylbenzo[*e*][1,2]azaborinin-2(1*H*)-yl)-9-methyl-3-phenyl-2,9-dihydro-1*H*-pyrido[3,4-*b*]indol-1-one (48)

The title compound was isolated as a white solid (31.3 mg, 68%). ¹H NMR (600 MHz, CDCl₃) δ 10.90 – 10.53 (m, 1H), 8.05 (d, *J* = 11.2 Hz, 1H), 7.77 (dd, *J* = 7.8, 1.7 Hz, 1H), 7.73 (d, *J* = 8.7 Hz, 1H), 7.55 – 7.48 (m, 2H), 7.46 – 7.41 (m, 1H), 7.35 (dd, *J* = 9.0, 4.2 Hz, 1H), 7.26 – 7.17 (m, 4H), 7.14 (td, *J* = 9.0, 2.5 Hz, 1H), 7.05 (d, *J* = 11.1 Hz, 1H), 6.71 (dd, *J* = 9.7, 1.5 Hz, 1H), 4.84 – 4.73 (m, 1H), 4.33 (s, 3H), 1.28 (d, *J* = 7.2 Hz, 3H), 0.92 (d, *J* = 7.2 Hz, 3H). ¹³C NMR (150 MHz, CDCl₃) δ 157.5, 157.2 (d, *J*_{C-F} = 236.2 Hz), 144.9, 140.3, 138.0, 137.1, 135.9, 131.4, 128.81, 128.79 (d, *J*_{C-F} = 4.0 Hz), 128.75, 128.69, 128.66, 128.65, 128.3, 128.0 (d, *J*_{C-F} = 4.2 Hz), 127.5, 127.4, 123.4 (d, *J*_{C-F} = 9.7 Hz), 120.9, 118.9, 115.2, 115.1, 110.74, 110.67, 108.1, 107.9, 52.4, 31.7, 21.6, 21.1. ¹¹B NMR (193 MHz, CDCl₃) δ 38.91. ¹⁹F NMR (376 MHz, CDCl₃) δ -122.88. HRMS (APCI): calcd. for C₂₉H₂₆BFN₃O⁺ [M+H]⁺ : 462.2147, found : 462.2146. [α]_D²⁰ = +108 (c = 0.1, CHCl₃).

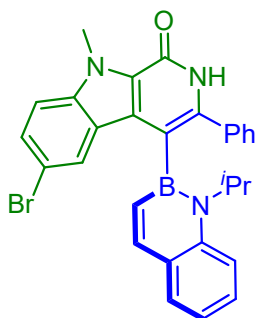
HPLC analysis: Daicel Chiralpak IE column (hexane: 2-propanol = 85:15, v = 1.0 mL/min, 40 °C, 254 nm); tr (major) = 8.588 min, tr (minor) = 9.447 min, 98% ee.



No.	Time	Area	Area (%)
1	8.615	514.6	49.54
2	9.438	524.1	50.46



No.	Time	Area	Area (%)
1	8.588	13895.9	98.81
2	9.447	167.6	1.19



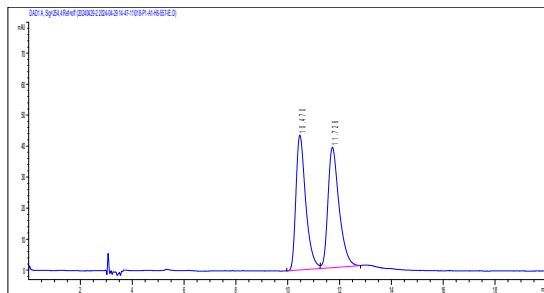
(*R*)-6-bromo-4-(1-isopropylbenzo[*e*][1,2]azaborinin-2(1*H*)-yl)-9-methyl-3-phenyl-2,9-dihydro-1*H*-pyrido[3,4-*b*]indol-1-one (49)

The title compound was isolated as a white solid (36.5 mg, 70%). ¹H NMR (600 MHz, CDCl₃) δ 10.60 (s, 1H), 8.06 (d, *J* = 11.2 Hz, 1H), 7.78 (dd, *J* = 7.9, 1.7 Hz, 1H), 7.73 (d, *J* = 8.7 Hz, 1H), 7.53 – 7.47 (m, 2H), 7.47 – 7.41 (m, 2H), 7.29 (d, *J* = 8.8 Hz, 1H), 7.25 – 7.19 (m, 4H), 7.17 – 7.14 (m, 1H), 7.03 (d, *J* = 11.2 Hz, 1H), 4.82 – 4.72 (m, 1H), 4.31 (s, 3H), 1.28 (d, *J* = 7.2 Hz, 3H), 0.94 (d, *J* = 7.2 Hz, 3H). ¹³C NMR (150 MHz, CDCl₃) δ 157.5, 157.2 (d, *J*_{C-F} = 236.2 Hz), 144.9, 140.3, 138.0, 137.1, 135.9, 131.4, 128.81, 128.79 (d, *J*_{C-F} = 4.0 Hz), 128.75, 128.69, 128.66, 128.65, 128.3, 128.0 (d, *J*_{C-F} = 4.2 Hz), 127.5, 127.4, 123.4 (d, *J*_{C-F} = 9.7 Hz), 120.9, 118.9, 115.2, 115.1, 110.74, 110.67, 108.1, 107.9, 52.4, 31.7, 21.6, 21.1. ¹¹B NMR (193 MHz, CDCl₃) δ 38.91. ¹⁹F NMR (376 MHz, CDCl₃) δ -122.88. HRMS (APCI): calcd. for C₂₉H₂₆BFN₃O⁺ [M+H]⁺ : 462.2147, found : 462.2146. [α]_D²⁰ = +108 (c = 0.1, CHCl₃).

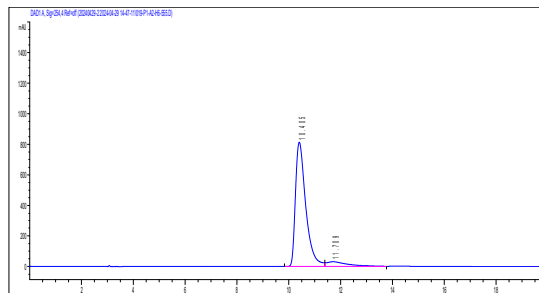
HPLC analysis: Daicel Chiralpak IE column (hexane: 2-propanol = 85:15, v = 1.0 mL/min, 40 °C, 254 nm); tr (major) = 8.588 min, tr (minor) = 9.447 min, 98% ee.

NMR (150 MHz, CDCl₃) δ 157.3, 144.9, 140.0, 137.0, 136.4, 131.4, 129.4, 128.73, 128.69, 128.66, 128.4, 127.6, 127.5, 126.8, 125.7, 124.9, 120.9, 112.6, 111.4, 52.4, 31.7, 21.7, 21.2. **¹¹B NMR (193 MHz, CDCl₃)** δ 40.55. **HRMS (APCI)**: calcd. for C₂₉H₂₆BBrN₃O⁺ [M+H]⁺ : 522.1347, found : 522.1348. $[\alpha]_D^{20}$ = +56 (c = 0.1, CHCl₃).

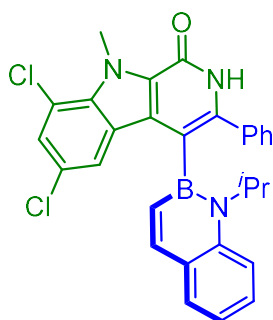
HPLC analysis: Daicel Chiralpak IE column (hexane: 2-propanol = 90:10, v = 1.0 mL/min, 40 °C, 254 nm); tr (major) = 10.405 min, tr (minor) = 11.709 min, 88% ee.



No.	Time	Area	Area (%)
1	10.470	1140.1	49.53
2	11.726	1161.5	50.47



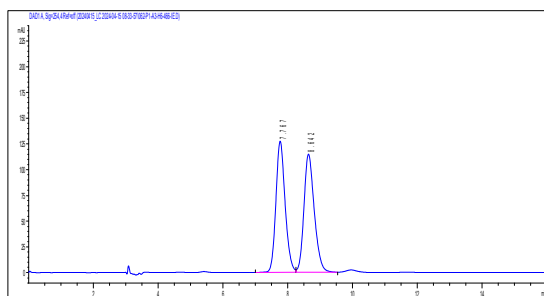
No.	Time	Area	Area (%)
1	10.405	22450.0	93.75
2	11.709	1498.7	6.25



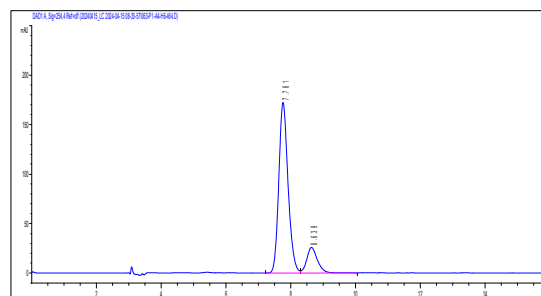
(R)-6,8-dichloro-4-(1-isopropylbenzo[e][1,2]azaborinin-2(1H)-yl)-9-methyl-3-phenyl-2,9-dihydro-1H-pyrido[3,4-b]indol-1-one (50)

The title compound was isolated as a white solid (24.5 mg, 48%). **¹H NMR (600 MHz, CDCl₃)** δ 10.48 (s, 1H), 8.05 (d, *J* = 11.2 Hz, 1H), 7.77 (dd, *J* = 7.8, 1.7 Hz, 1H), 7.72 (d, *J* = 8.7 Hz, 1H), 7.52 – 7.39 (m, 3H), 7.29 (d, *J* = 1.9 Hz, 1H), 7.26 – 7.18 (m, 4H), 6.99 (d, *J* = 11.2 Hz, 1H), 6.91 (d, *J* = 1.9 Hz, 1H), 4.81 – 4.72 (m, 1H), 4.73 (s, 3H), 1.27 (d, *J* = 7.2 Hz, 3H), 0.93 (d, *J* = 7.2 Hz, 3H). **¹³C NMR (150 MHz, CDCl₃)** δ 157.2, 145.0, 137.0, 136.7, 135.5, 131.4, 128.8, 128.7, 128.6, 128.1, 127.92, 127.86, 127.6, 126.9, 124.7, 121.3, 121.0, 118.9, 118.3, 52.5, 34.8, 21.6, 21.2. **¹¹B NMR (193 MHz, CDCl₃)** δ 35.86. **HRMS (APCI)**: calcd. for C₂₉H₂₅BCl₂N₃O⁺ [M+H]⁺ : 512.1462, found : 512.1460. $[\alpha]_D^{20}$ = +64 (c = 0.1, CHCl₃).

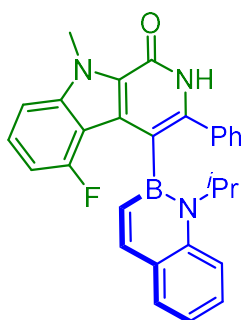
HPLC analysis: Daicel Chiralpak IE column (hexane: 2-propanol = 90:10, v = 1.0 mL/min, 40 °C, 254 nm); tr (major) = 7.761 min, tr (minor) = 8.639 min, 71% ee.



No.	Time	Area	Area (%)
1	7.767	2525.5	49.79
2	8.642	2546.6	50.21



No.	Time	Area	Area (%)
1	7.761	3419.1	85.40
2	8.639	584.6	14.60

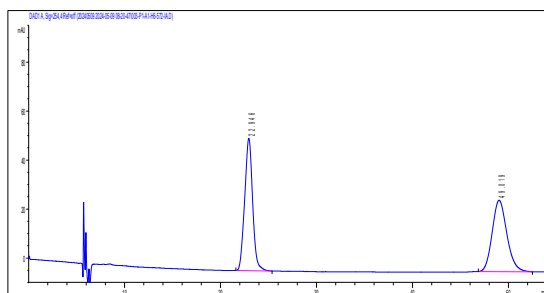


(R)-5-fluoro-4-(1-isopropylbenzo[e][1,2]azaborinin-2(1H)-yl)-9-methyl-3-phenyl-2,9-dihydro-1H-pyrido[3,4-b]indol-1-one (51)

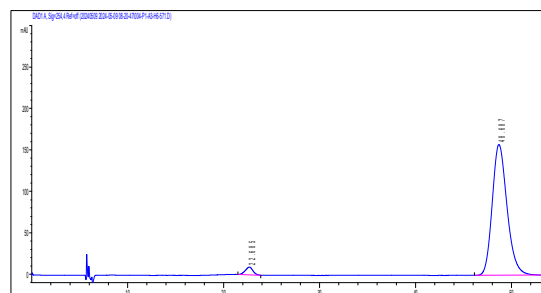
The title compound was isolated as a white solid (20.8 mg, 45%). **¹H NMR (600 MHz, CDCl₃)** δ 10.37 (s, 1H), 7.90 (d, J = 11.2 Hz, 1H), 7.73 – 7.65 (m, 2H), 7.48 – 7.42 (m, 2H), 7.42 – 7.36 (m, 1H), 7.37 – 7.30 (m, 1H), 7.25 – 7.15 (m, 5H), 6.94 (d, J = 11.1 Hz, 1H), 6.60 (dd, J = 10.8, 7.7 Hz, 1H), 4.88 – 4.78 (m, 1H), 4.36 (s, 3H), 1.36 (d, J = 7.1 Hz, 3H), 0.99 (d, J = 7.1 Hz, 3H). **¹³C NMR (150 MHz, CDCl₃)** δ

157.5 (d, J_{C-F} = 253.1 Hz), 156.9, 143.6 (d, J_{C-F} = 10.0 Hz), 143.1, 140.3, 137.3, 136.6, 131.0, 129.2, 128.7, 128.5, 128.3, 127.3 (d, J_{C-F} = 8.2 Hz), 127.0, 126.3, 120.2, 118.7, 112.0, 105.9 (d, J = 3.3 Hz), 105.6, 105.5, 52.1, 32.1, 21.3, 21.2. **¹¹B NMR (193 MHz, CDCl₃)** δ 38.73. **¹⁹F NMR (376 MHz, CDCl₃)** δ -109.18. **HRMS (ESI):** calcd. for C₂₉H₂₅BFN₃NaO⁺ [M+Na]⁺: 484.1967, found: 484.1971. **$[\alpha]_D^{20}$** = +112 (c = 0.1, CHCl₃).

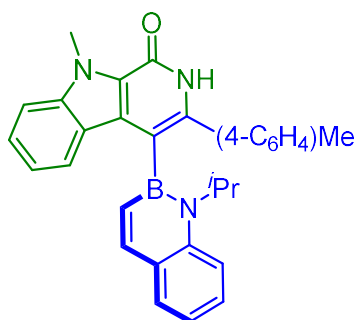
HPLC analysis: Daicel Chiralpak IA column (hexane: 2-propanol = 95:5, v = 0.5 mL/min, 40 °C, 254 nm); tr (major) = 48.687 min, tr (minor) = 22.685 min, 94% ee.



No.	Time	Area	Area (%)
1	22.946	3120.5	50.23
2	49.019	3091.7	49.77

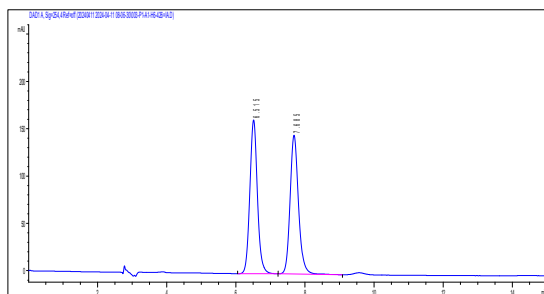


No.	Time	Area	Area (%)
1	22.685	511.7	2.93
2	48.687	16927.1	97.07

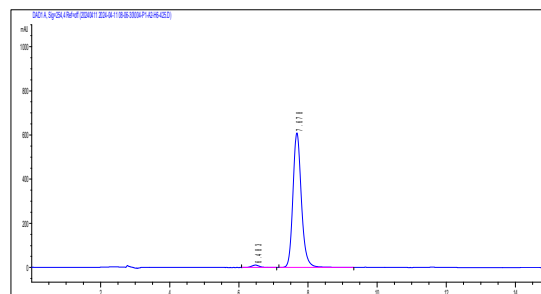


(*R*)-4-(1-isopropylbenzo[*e*][1,2]azaborinin-2(1*H*)-yl)-9-methyl-3-(*p*-tolyl)-2,9-dihydro-1*H*-pyrido[3,4-*b*]indol-1-one (52)

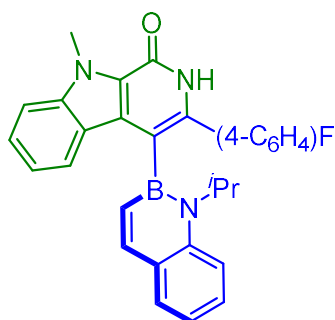
The title compound was isolated as a white solid (32.9 mg, 72%). ¹H NMR (600 MHz, CDCl₃) δ 10.07 (s, 1H), 8.03 (d, *J* = 11.2 Hz, 1H), 7.81 – 7.72 (m, 2H), 7.47 – 7.40 (m, 2H), 7.40 – 7.33 (m, 3H), 7.26 – 7.22 (m, 1H), 7.10 – 6.99 (m, 4H), 6.89 – 6.82 (m, 1H), 4.88 – 4.77 (m, 1H), 4.36 (s, 3H), 2.24 (s, 3H), 1.25 (d, *J* = 7.2 Hz, 3H), 0.96 (d, *J* = 7.3 Hz, 3H). ¹³C NMR (150 MHz, CDCl₃) δ 157.3, 144.5, 141.4, 138.2, 136.0, 134.4, 131.3, 129.4, 128.8, 128.6, 128.5, 127.3, 126.4, 126.1, 123.3, 120.7, 119.7, 109.8, 52.5, 31.5, 21.6, 21.2. ¹¹B NMR (193 MHz, CDCl₃) δ 39.39. HRMS (APCI): calcd. for C₃₀H₂₉BN₃O⁺ [M+H]⁺: 458.2398, found: 458.2402. [α]_D²⁰ = +76 (c = 0.1, CHCl₃). HPLC analysis: Daicel Chiralpak IA column (hexane: 2-propanol = 90:10, v = 1.0 mL/min, 40 °C, 254 nm); tr (major) = 7.678 min, tr (minor) = 6.483 min, 97% ee.



No.	Time	Area	Area (%)
1	6.515	2475.5	49.94
2	7.685	2481.9	50.06



No.	Time	Area	Area (%)
1	6.483	168.9	1.61
2	7.678	10301.5	98.39

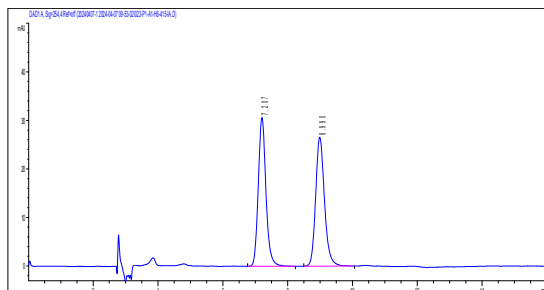


(*R*)-3-(4-fluorophenyl)-4-(1-isopropylbenzo[*e*][1,2]azaborinin-2(1*H*)-yl)-9-methyl-2,9-dihydro-1*H*-pyrido[3,4-*b*]indol-1-one (53)

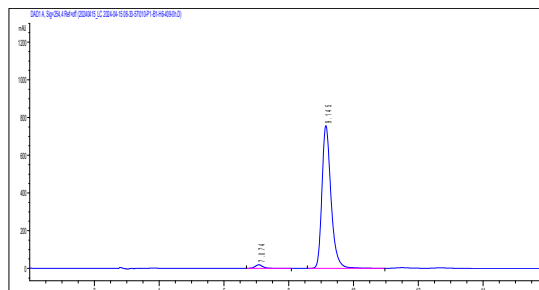
The title compound was isolated as a white solid (27.7 mg, 60%). ¹H NMR (600 MHz, CDCl₃) δ 11.31 (s, 1H), 8.06 (d, *J* = 11.1 Hz, 1H), 7.83 – 7.75 (m, 2H), 7.60 – 7.53 (m, 2H), 7.50 – 7.43 (m, 2H), 7.42 – 7.38 (m, 1H), 7.28 (t, *J* = 7.4 Hz, 1H), 7.09 – 7.03 (m, 2H), 6.96 (t, *J* = 8.6 Hz, 2H), 6.92 – 6.85 (m, 1H), 4.90 – 4.79 (m, 1H), 4.34 (s, 3H), 1.29 (d, *J* = 7.2 Hz, 3H), 1.02 (d, *J* = 7.2 Hz, 3H). ¹³C NMR (150 MHz, CDCl₃) δ 162.6 (d, *J*_{C-F} = 248.5 Hz), 157.6, 144.7, 141.5, 140.4, 135.1, 133.3 (d, *J*_{C-F} = 3.0 Hz), 131.3, 130.9, 130.8, 128.7, 128.5, 127.5, 126.6, 126.1, 123.3, 123.2, 120.9, 119.8, 119.0 (d, *J*_{C-F} = 8.9 Hz), 115.6, 115.4, 109.9, 52.4, 31.5, 21.6, 21.3. ¹¹B NMR (193 MHz, CDCl₃)

δ 39.35. **^{19}F NMR (376 MHz, CDCl_3)** δ -113.18. **HRMS (APCI)**: calcd. for $\text{C}_{29}\text{H}_{26}\text{BFN}_3\text{O}^+$ $[\text{M}+\text{H}]^+$: 462.2147, found: 462.2142. $[\alpha]_{\text{D}}^{20} = +28$ ($c = 0.1$, CHCl_3).

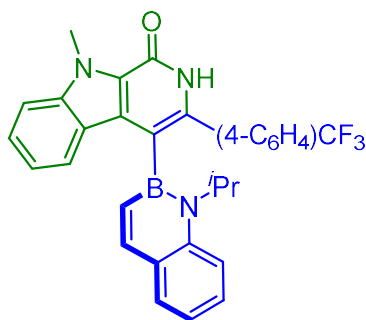
HPLC analysis: Daicel Chiralpak IA column (hexane: 2-propanol = 90:10, $v = 1.0$ mL/min, 40°C , 254 nm); tr (major) = 9.145 min, tr (minor) = 7.074 min, 96% ee.



No.	Time	Area	Area (%)
1	7.207	505.0	50.05
2	8.990	504.0	49.95



No.	Time	Area	Area (%)
1	7.074	302.6	2.02
2	9.145	14713.8	97.98

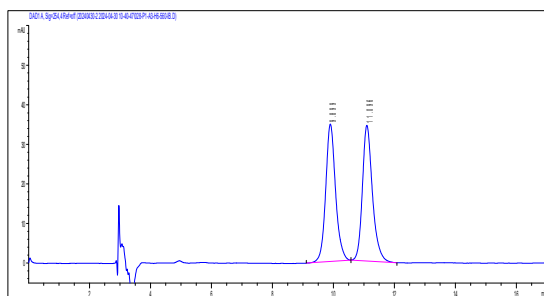


(*R*)-4-(1-isopropylbenzo[*e*][1,2]azaborinin-2(1*H*)-yl)-9-methyl-3-(4-(trifluoromethyl)phenyl)-2,9-dihydro-1*H*-pyrido[3,4-*b*]indol-1-one (54)

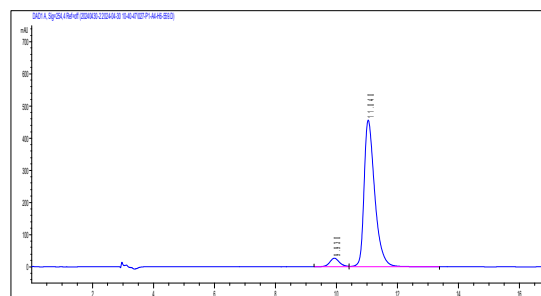
The title compound was isolated as a white solid (21.5 mg, 42%). **^1H NMR (600 MHz, CDCl_3)** δ 11.78 (s, 1H), 8.08 (d, $J = 11.1$ Hz, 1H), 7.83 – 7.80 (m, 1H), 7.79 – 7.76 (m, 1H), 7.76 – 7.70 (m, 2H), 7.57 –

7.51 (m, 2H), 7.51 – 7.47 (m, 1H), 7.47 – 7.43 (m, 1H), 7.43 – 7.39 (m, 1H), 7.30 (t, $J = 7.4$ Hz, 1H), 7.09 – 7.00 (m, 2H), 6.93 – 6.88 (m, 1H), 4.91 – 4.76 (m, 1H), 4.28 (s, 3H), 1.29 (d, $J = 6.9$ Hz, 3H), 1.00 (d, $J = 7.2$ Hz, 3H). **^{13}C NMR (150 MHz, CDCl_3)** δ 157.8, 145.0, 141.5, 140.6, 140.3, 134.5, 131.4, 130.1, 129.4, 128.7, 127.7, 127.4 (q, $J = 296.4$ Hz), 126.7, 125.43, 125.41, 125.38, 125.36, 123.3, 123.22, 123.19, 121.0, 120.0, 119.0 (q, $J = 6.9$ Hz), 110.0, 52.6, 31.4, 21.6, 21.2. **^{11}B NMR (193 MHz, CDCl_3)** δ 39.12. **^{19}F NMR (376 MHz, CDCl_3)** δ -62.48. **HRMS (APCI)**: calcd. for $\text{C}_{30}\text{H}_{26}\text{BF}_3\text{N}_3\text{O}^+$ $[\text{M}+\text{H}]^+$: 512.2116, found: 512.2101. $[\alpha]_{\text{D}}^{20} = +100$ ($c = 0.1$, CHCl_3).

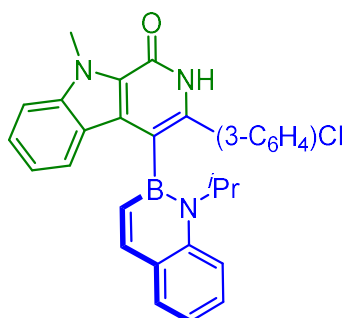
HPLC analysis: Daicel Chiralpak IB column (hexane: 2-propanol = 95:5, $v = 1.0$ mL/min, 40°C , 254 nm); tr (major) = 11.040 min, tr (minor) = 9.930 min, 90% ee.



No.	Time	Area	Area (%)
1	9.899	780.6	49.81
2	11.096	786.6	50.19



No.	Time	Area	Area (%)
1	9.930	606.3	5.19
2	11.040	11075.0	94.81

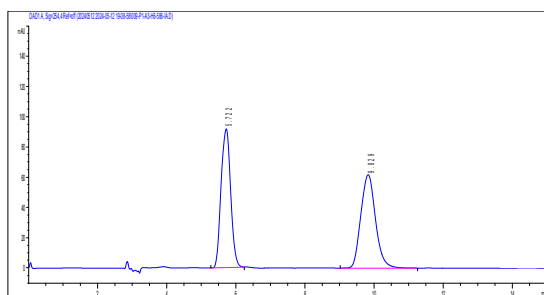


(R)-3-(3-chlorophenyl)-4-(1-isopropylbenzo[e][1,2]azaborinin-

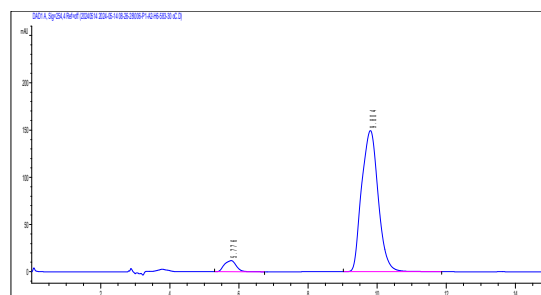
2(1H)-yl)-9-methyl-2,9-dihydro-1H-pyrido[3,4-b]indol-1-one (55)

The title compound was isolated as a white solid (26.7 mg, 56%). ¹H NMR (600 MHz, CDCl₃) δ 11.20 (s, 1H), 8.10 – 8.02 (m, 1H), 7.83 – 7.73 (m, 2H), 7.67 – 7.61 (m, 1H), 7.50 – 7.43 (m, 2H), 7.42 – 7.35 (m, 2H), 7.28 (t, *J* = 7.8 Hz, 1H), 7.21 – 7.17 (m, 1H), 7.12 (td, *J* = 7.9, 2.7 Hz, 1H), 7.09 – 7.00 (m, 2H), 6.89 (t, *J* = 7.5 Hz, 1H), 4.86 – 4.76 (m, 1H), 4.36 (s, 3H), 1.29 (d, *J* = 7.4 Hz, 3H), 1.03 (d, *J* = 7.2 Hz, 3H). ¹³C NMR (150 MHz, CDCl₃) δ 157.6, 144.8, 141.5, 140.4, 138.9, 134.6, 134.4, 131.4, 129.8, 129.0, 128.8, 128.4, 128.2, 127.5, 127.2, 126.6, 126.3, 123.3, 123.2, 120.9, 119.9, 110.0, 52.5, 31.6, 21.6, 21.3. ¹¹B NMR (193 MHz, CDCl₃) δ 39.09. HRMS (APCI): calcd. for C₂₉H₂₆BClN₃O⁺ [M+H]⁺: 478.1852, found: 478.1841. [α]_D²⁰ = +26 (c = 0.1, CHCl₃).

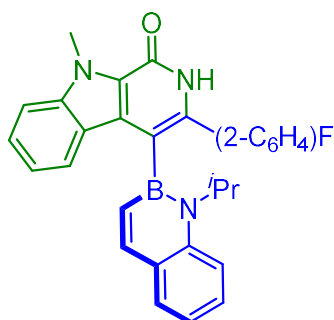
HPLC analysis: Daicel Chiralpak IA column (hexane: 2-propanol = 90:10, v = 1.0 mL/min, 40 °C, 254 nm); tr (major) = 9.804 min, tr (minor) = 5.776 min, 90% ee.



No.	Time	Area	Area (%)
1	5.722	1763.7	49.30
2	9.829	1814.0	50.70



No.	Time	Area	Area (%)
1	5.776	284.5	5.22
2	9.804	4957.5	94.78

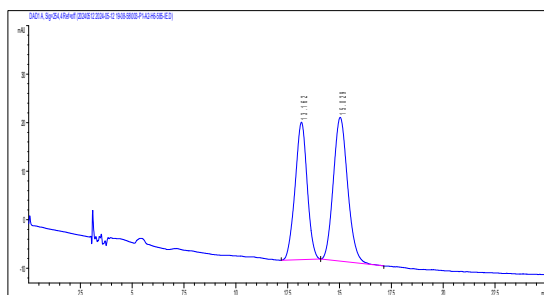


(R)-3-(2-fluorophenyl)-4-(1-isopropylbenzo[e][1,2]azaborinin-2(1H)-yl)-9-methyl-2,9-dihydro-1H-pyrido[3,4-b]indol-1-one (56)

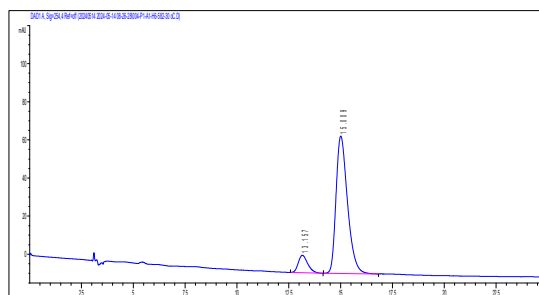
The title compound was isolated as a white solid (21.2 mg, 46%). ¹H NMR (600 MHz, CDCl₃) δ 10.54 (s, 1H), 8.02 (d, *J* = 11.2 Hz, 1H), 7.81 – 7.72 (m, 2H), 7.48 – 7.41 (m, 2H), 7.41 – 7.34 (m, 2H), 7.26 – 7.19 (m, 2H), 7.11 – 7.07 (m, 1H), 7.06 – 6.99 (m, 2H), 6.93 (t, *J* = 7.6 Hz, 1H),

6.90 – 6.85 (m, 1H), 4.93 (p, *J* = 7.1 Hz, 1H), 4.32 (s, 3H), 1.32 (d, *J* = 7.0 Hz, 3H), 1.14 (d, *J* = 7.0 Hz, 3H). ¹³C NMR (150 MHz, CDCl₃) δ 160.2 (d, *J*_{C-F} = 248.6 Hz), 157.1, 144.6, 141.2, 140.3, 132.3 (d, *J*_{C-F} = 2.4 Hz), 131.2, 130.6, 130.5, 130.4, 128.7, 128.1, 127.4, 126.4, 124.7 (d, *J*_{C-F} = 14.8 Hz), 124.21, 124.19, 123.3, 123.1, 120.8, 119.8, 119.0, 116.0, 115.9, 109.9, 52.5, 31.5, 21.6, 21.5. ¹¹B NMR (193 MHz, CDCl₃) δ 39.07. ¹⁹F NMR (376 MHz, CDCl₃) δ -114.11. HRMS (APCI): calcd. for C₂₉H₂₆BFN₃O⁺ [M+H]⁺: 462.2147, found: 462.2139. [α]_D²⁰ = +88 (c = 0.1, CHCl₃).

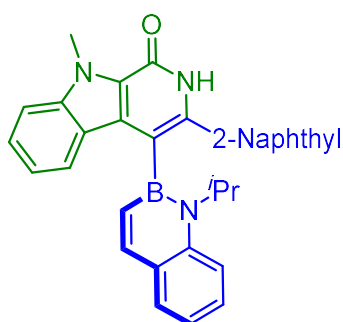
HPLC analysis: Daicel Chiralpak IE column (hexane: 2-propanol = 90:10, v = 1.0 mL/min, 40 °C, 254 nm); tr (major) = 15.009 min, tr (minor) = 13.157 min, 81% ee.



No.	Time	Area	Area (%)
1	13.162	1297.4	47.57
2	15.029	1429.7	52.43



No.	Time	Area	Area (%)
1	13.157	289.5	9.45
2	15.009	2775.4	90.55



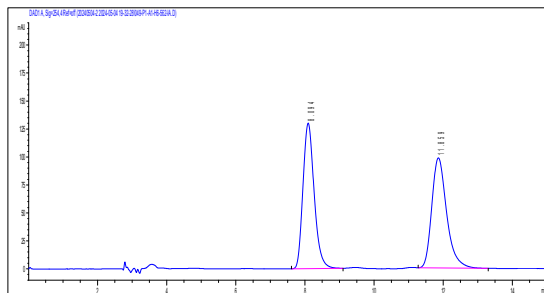
(R)-4-(1-isopropylbenzo[e][1,2]azaborinin-2(1H)-yl)-9-methyl-3-(naphthalen-2-yl)-2,9-dihydro-1H-pyrido[3,4-b]indol-1-one (57)

The title compound was isolated as a white solid (24.7 mg, 50%). ¹H NMR (600 MHz, CDCl₃) δ 11.14 (s, br, 1H), 8.17 – 8.05 (m, 2H), 7.79 (d, *J* = 7.9 Hz, 1H), 7.77 – 7.61 (m, 5H), 7.47 – 7.37 (m, 5H), 7.26 – 7.22 (m, 1H), 7.16 (d, *J* = 11.1 Hz, 1H), 7.09 (d, *J* = 8.1 Hz, 1H), 6.93 – 6.84

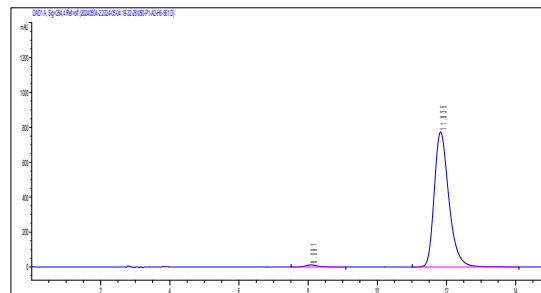
(m, 1H), 4.98 – 4.84 (m, 1H), 4.26 (s, 3H), 1.28 (d, *J* = 7.4 Hz, 3H), 0.88 (d, *J* = 7.3 Hz, 3H). ¹³C NMR (150 MHz, CDCl₃) δ 157.7, 144.6, 141.4, 136.0, 134.6, 133.2, 132.8, 131.3, 128.7, 128.6, 128.4,

128.24, 128.21, 127.7, 127.4, 126.54, 126.50, 126.45, 126.4, 126.3, 123.4, 123.3, 120.7, 119.7, 118.9, 109.9, 52.4, 31.5, 21.6, 21.2. **¹¹B NMR (193 MHz, CDCl₃)** δ 35.97. **HRMS (APCI)**: calcd. for C₃₃H₂₉BN₃O⁺ [M+H]⁺: 494.2398, found : 494.2386. **[α]_D²⁰** = -64 (c = 0.1, CHCl₃).

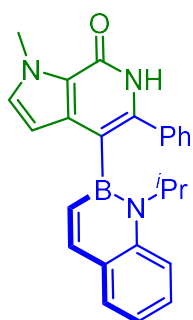
HPLC analysis: Daicel Chiralpak IA column (hexane: 2-propanol = 90:10, v = 1.0 mL/min, 40 °C, 254 nm); tr (major) = 11.835 min, tr (minor) = 8.091 min, 98% ee.



No.	Time	Area	Area (%)
1	8.094	2918.0	49.89
2	11.859	2930.6	50.11



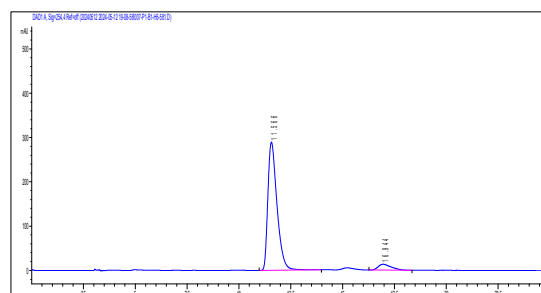
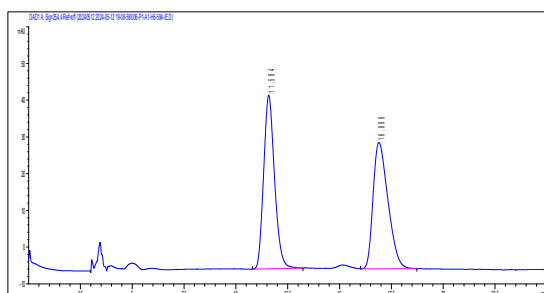
No.	Time	Area	Area (%)
1	8.091	266.1	1.16
2	11.835	22684.2	98.84



(R)-4-(1-isopropylbenzo[e][1,2]azaborinin-2(1H)-yl)-1-methyl-5-phenyl-1,6-dihydro-7H-pyrrolo[2,3-c]pyridin-7-one (58)

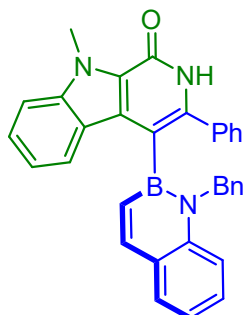
The title compound was isolated as a white solid (21.6 mg, 55%). **¹H NMR (600 MHz, CDCl₃)** δ 9.39 (s, 1H), 7.95 (d, *J* = 11.2 Hz, 1H), 7.74 (d, *J* = 8.7 Hz, 1H), 7.71 – 7.67 (m, 1H), 7.46 – 7.36 (m, 3H), 7.26 – 7.13 (m, 4H), 6.96 (d, *J* = 2.7 Hz, 1H), 6.88 (d, *J* = 11.2 Hz, 1H), 5.98 (d, *J* = 2.7 Hz, 1H), 4.88 – 4.76 (m, 1H), 4.20 (s, 3H), 1.44 (d, *J* = 7.2 Hz, 3H), 1.01 (d, *J* = 7.2 Hz, 3H). **¹³C NMR (150 MHz, CDCl₃)** δ 156.6, 144.6, 140.5, 137.5, 136.6, 136.2, 132.7, 131.5, 131.1, 128.8, 128.6, 128.34, 128.28, 127.2, 121.8, 120.5, 118.8, 104.2, 52.0, 36.0, 22.1, 21.0. **¹¹B NMR (193 MHz, CDCl₃)** δ 37.80. **HRMS (APCI)**: calcd. for C₂₅H₂₅BN₃O⁺ [M+H]⁺: 394.2085, found : 394.2078. **[α]_D²⁰** = +10 (c = 0.1, CHCl₃).

HPLC analysis: Daicel Chiralpak IE column (hexane: 2-propanol = 85:15, v = 1.0 mL/min, 40 °C, 254 nm); tr (major) = 11.566 min, tr (minor) = 16.944 min, 88% ee.



No.	Time	Area	Area (%)
1	11.584	1726.7	50.14
2	16.899	1716.8	49.86

No.	Time	Area	Area (%)
1	11.566	8837.8	93.79
2	16.944	585.9	6.21

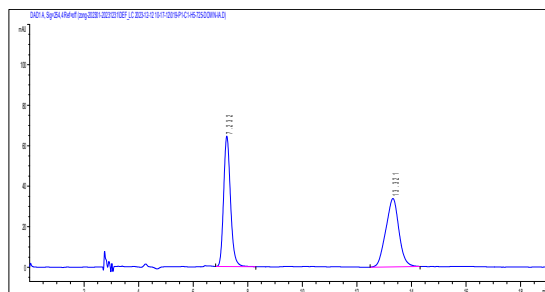


(R)-4-(1-benzylbenzo[e][1,2]azaborinin-2(1H)-yl)-9-methyl-3-phenyl-2,9-dihydro-1H-pyrido[3,4-b]indol-1-one (59)

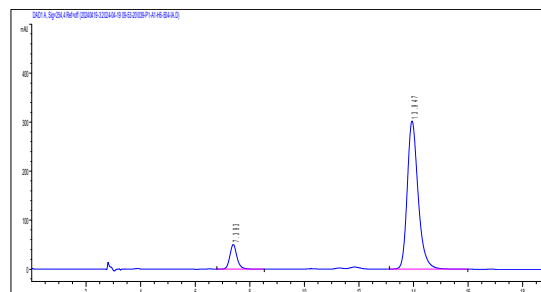
The title compound was isolated as a white solid (30.5 mg, 62%). ¹H NMR (600 MHz, CDCl₃) δ 10.28 (s, 1H), 8.14 (d, *J* = 11.3 Hz, 1H), 7.82 – 7.74 (m, 1H), 7.46 – 7.40 (m, 2H), 7.37 – 7.30 (m, 3H), 7.26 – 7.15 (m, 7H), 7.01 – 6.97 (m, 1H), 6.96 – 6.90 (m, 3H), 6.60 (d, *J* = 7.3 Hz, 2H), 5.15 – 5.01 (m, 2H), 4.31 (s, 3H).

¹³C NMR (150 MHz, CDCl₃) δ 157.1, 144.7, 141.34, 141.30, 137.9, 137.3, 137.0, 132.7, 130.4, 128.8, 128.7, 128.5, 128.4, 128.3, 128.2, 128.1, 127.4, 126.4, 126.2, 126.0, 125.8, 125.6, 123.0, 122.7, 121.3, 119.8, 117.4, 109.9, 52.2, 31.4. ¹¹B NMR (193 MHz, CDCl₃) δ 37.62. HRMS (APCI): calcd. for C₃₃H₂₇BN₃O⁺ [M+H]⁺: 492.2242, found: 492.2234. [α]_D²⁰ = +136 (c = 0.1, CHCl₃).

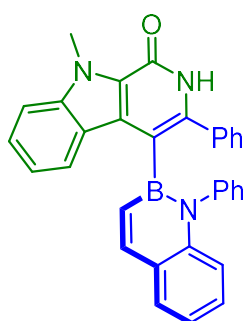
HPLC analysis: Daicel Chiralpak IA column (hexane: 2-propanol = 90:10, v = 1.0 mL/min, 40 °C, 254 nm); tr (major) = 13.947 min, tr (minor) = 7.393 min, 80% ee.



No.	Time	Area	Area (%)
1	7.232	1126.1	49.95
2	13.321	1128.1	50.05



No.	Time	Area	Area (%)
1	7.393	911.9	9.82
2	13.947	8376.9	90.18

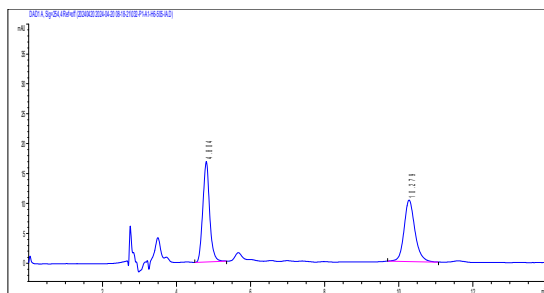


(R)-9-methyl-3-phenyl-4-(1-phenylbenzo[e][1,2]azaborinin-2(1H)-yl)-2,9-dihydro-1H-pyrido[3,4-b]indol-1-one (60)

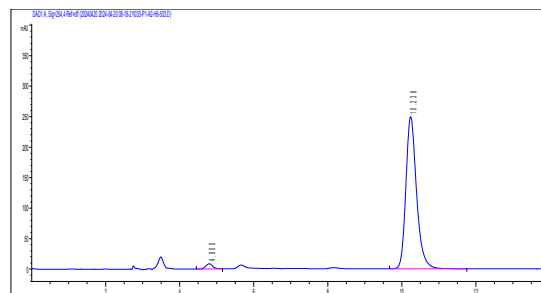
The title compound was isolated as a white solid (28.6 mg, 60%, 1.6:1 dr). ¹H NMR (600 MHz, CDCl₃) δ 10.13 – 9.75 (m, 1H), 8.32 – 8.20 (m, 1H), 7.86 – 7.64 (m, 1H), 7.55 – 7.42 (m, 2H), 7.42 – 7.26 (m, 8H), 7.25 – 7.19 (m, 1H), 7.15 – 6.96 (m, 3H), 6.95 – 6.54 (m, 3H), 5.88 – 5.73 (m, 1H), 4.27 – 4.17 (m, 3H).

¹³C NMR (150 MHz, CDCl₃) δ 157.1, 156.9, 144.7, 144.5, 143.1, 142.9, 142.8, 142.3, 141.3, 140.9, 138.1, 137.1, 136.3, 131.2, 129.9, 129.7, 129.7, 129.62, 129.60, 128.98, 128.96, 128.95, 128.8, 128.42, 128.40, 128.31, 128.28, 128.2, 128.1, 128.0, 127.8, 127.7, 127.5, 127.2, 126.7, 126.31, 126.26, 126.21, 126.16, 126.1, 125.7, 124.8, 124.4, 123.3, 123.2, 123.1, 122.4, 121.7, 121.6, 121.4, 121.3, 119.7, 119.5, 117.8, 117.6, 109.8, 109.7, 31.2, 31.1. **¹¹B NMR (193 MHz, CDCl₃)** δ 35.10. **HRMS (APCI):** calcd. for C₃₂H₂₅BN₃O⁺ [M+H]⁺ : 478.2085, found : 478.2057. [α]_D²⁰ = +64 (c = 0.1, CHCl₃).

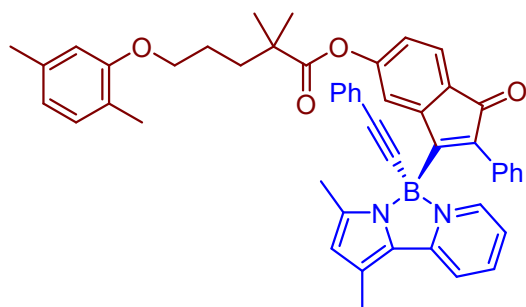
HPLC analysis: Daicel Chiralpak IA column (hexane: 2-propanol = 85:15, v = 1.0 mL/min, 40 °C, 254 nm); tr (major) = 10.238 min, tr (minor) = 4.800 min, 96% ee.



No.	Time	Area	Area (%)
1	4.804	214.2	50.64
2	10.279	208.9	49.36



No.	Time	Area	Area (%)
1	4.800	110.2	2.16
2	10.238	4984.2	97.84



(R)-3-(1,3-dimethyl-5-(phenylethynyl)-5H-5λ⁴,6λ⁴-pyrrolo[1',2':3,4][1,3,2]diazaborolo[1,5-a]pyridin-5-yl)-1-oxo-2-phenyl-1H-inden-5-yl 5-(2,5-dimethylphenoxy)-2,2-dimethylpentanoate (61)

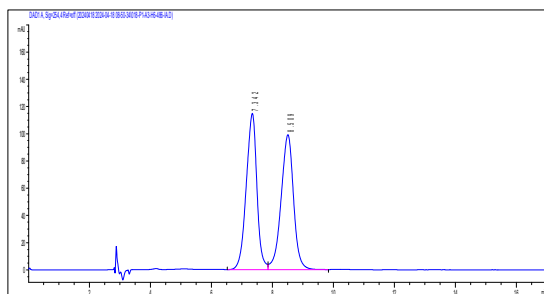
The title compound was isolated as a yellow solid (40.5 mg, 55%). **¹H NMR (600 MHz, CDCl₃)** δ 8.19 – 7.86 (m, 2H),

7.52 – 7.48 (m, 1H), 7.45 (d, *J* = 7.6 Hz, 1H), 7.38 – 7.31 (m, 2H), 7.25 – 7.17 (m, 3H), 7.11 – 7.00 (m, 3H), 6.97 (t, *J* = 7.5 Hz, 2H), 6.87 – 6.80 (m, 1H), 6.77 – 6.71 (m, 1H), 6.68 (d, *J* = 7.5 Hz, 1H), 6.60 (s, 1H), 6.57 – 6.45 (m, 2H), 5.81 (s, 1H), 3.87 (t, *J* = 5.7 Hz, 2H), 2.32 (s, 3H), 2.28 (s, 3H), 2.26 (s, 3H), 2.18 (s, 3H), 1.86 – 1.74 (m, 4H), 1.30 (s, 6H). **¹³C NMR (150 MHz, CDCl₃)** δ 197.7, 176.0, 157.0, 155.8, 152.4, 149.8, 144.5, 141.7, 140.8, 137.2, 136.6, 132.8, 131.7, 130.5, 129.2, 128.1, 127.7, 127.6, 127.1, 126.8, 124.6, 123.7, 123.1, 122.6, 120.9, 119.8, 119.1, 117.1, 115.8, 115.6, 112.1, 99.3, 67.8, 42.6, 37.1, 25.3, 25.19, 25.17, 21.6, 15.9, 14.0, 12.1. **¹¹B NMR (193 MHz, CDCl₃)** δ -5.36.

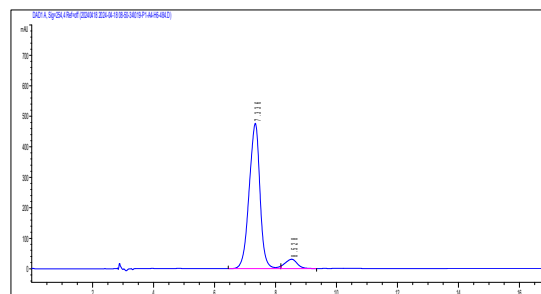
HRMS (APCI): calcd. for C₄₉H₄₆BN₂O₄⁺ [M+H]⁺ : 737.3545, found : 737.3535. [α]_D²⁰ = -180 (c =

0.1, CHCl₃).

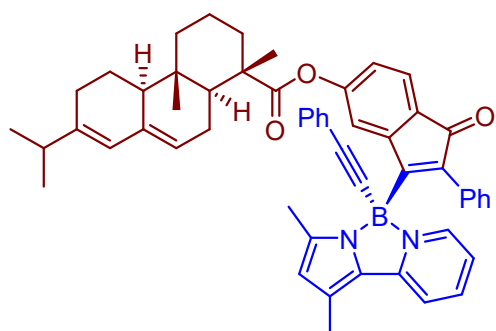
HPLC analysis: Daicel Chiralpak IA column (hexane: 2-propanol = 95:5, $v = 1.0$ mL/min, 40 °C, 254 nm); t_r (major) = 7.336 min, t_r (minor) = 8.528 min, 87% ee.



No.	Time	Area	Area (%)
1	7.342	2790.7	49.81
2	8.509	2812.0	50.19

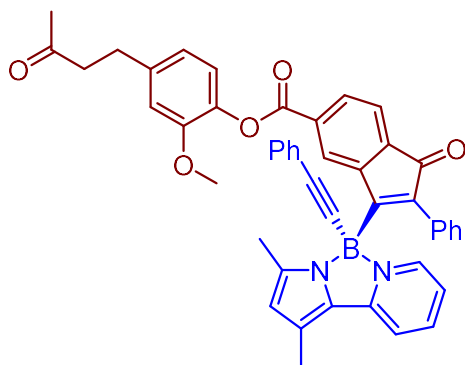


No.	Time	Area	Area (%)
1	7.336	11742.9	93.38
2	8.528	832.0	6.62



3-(1,3-dimethyl-5-(phenylethynyl)-5*H*-5 λ^4 ,6 λ^4 -pyrrolo[1',2':3,4][1,3,2]diazaborolo[1,5-*a*]pyridin-5-yl)-1-oxo-2-phenyl-1*H*-inden-5-yl (1*S*,4*aS*,4*bS*,10*aS*)-7-isopropyl-1,4*a*-dimethyl-1,2,3,4,4*a*,4*b*,5,6,10,10*a*-decahydrophenanthrene-1-carboxylate (62)

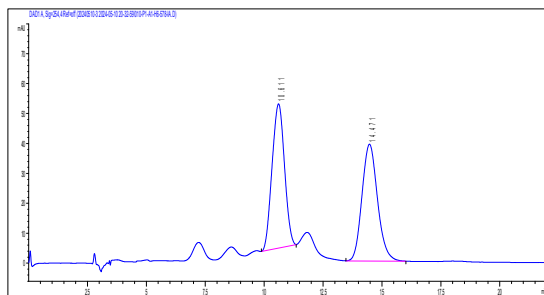
The title compound was isolated as a yellow solid (30.0 mg, 38%). **¹H NMR (600 MHz, CDCl₃)** δ 8.11 – 7.77 (m, 2H), 7.54 – 7.47 (m, 1H), 7.44 (d, $J = 7.7$ Hz, 1H), 7.38 – 7.29 (m, 2H), 7.25 – 7.17 (m, 3H), 7.08 – 6.99 (m, 2H), 6.99 – 6.90 (m, 2H), 6.85 – 6.78 (m, 1H), 6.75 (t, $J = 6.6$ Hz, 1H), 6.60 – 6.38 (m, 2H), 5.80 (d, $J = 21.0$ Hz, 2H), 5.34 – 5.24 (m, 1H), 2.27 (s, 3H), 2.26 (s, 3H), 2.23 – 2.19 (m, 1H), 2.11 (t, $J = 4.3$ Hz, 2H), 2.05 – 1.93 (m, 2H), 1.93 – 1.77 (m, 4H), 1.72 – 1.52 (m, 4H), 1.33 (s, 3H), 1.25 – 1.11 (m, 2H), 1.03 (t, $J = 6.3$ Hz, 6H), 0.85 (s, 3H). **¹³C NMR (150 MHz, CDCl₃)** δ 197.7, 176.8, 156.0, 152.3, 149.8, 145.5, 144.4, 141.8, 140.8, 137.2, 135.6, 132.8, 131.79, 131.75, 129.2, 128.1, 128.0, 127.7, 127.6, 127.1, 126.8, 124.6, 123.0, 122.6, 122.5, 120.7, 119.8, 119.2, 117.0, 115.8, 115.6, 99.3, 51.0, 47.0, 45.0, 38.3, 37.3, 35.0, 34.7, 27.6, 25.9, 22.6, 21.6, 21.0, 18.2, 17.2, 14.2, 14.0, 12.2. **¹¹B NMR (193 MHz, CDCl₃)** δ -5.15. **HRMS (APCI):** calcd. for C₅₄H₅₄BN₂O₃⁺ [$M+H$]⁺: 789.4222, found: 789.4225. $[\alpha]_D^{20} = -64$ ($c = 0.1$, CHCl₃). >20:1 dr determined by ¹H NMR.



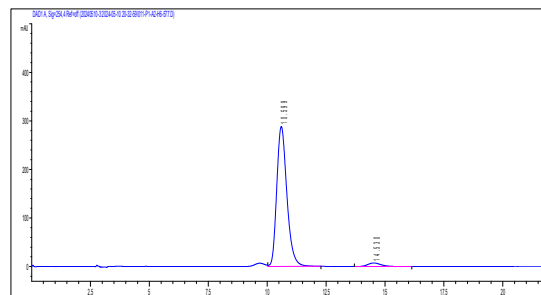
(*R*)-2-methoxy-4-(3-oxobutyl)phenyl 3-(1,3-dimethyl-5-(phenylethynyl)-5*H*-5 λ ⁴,6 λ ⁴-pyrrolo[1',2':3,4][1,3,2]diazaborolo[1,5-*a*]pyridin-5-yl)-1-oxo-2-phenyl-1*H*-indene-5-carboxylate (63)

The title compound was isolated as a yellow solid (27.6 mg, 39%). ¹H NMR (600 MHz, CDCl₃) δ 9.19 (s, br, 1H), 8.11 (dd, J = 7.3, 1.4 Hz, 1H), 8.04 (d, J = 5.7 Hz, 1H), 7.56 (d, J = 7.4 Hz, 1H), 7.54 – 7.48 (m, 1H), 7.38 – 7.31 (m, 2H), 7.15 – 7.09 (m, 1H), 7.08 – 7.03 (m, 2H), 7.03 – 6.93 (m, 5H), 6.87 – 6.83 (m, 1H), 6.81 – 6.77 (m, 1H), 6.77 – 6.72 (m, 1H), 6.54 (d, J = 7.4 Hz, 2H), 5.80 (s, 1H), 3.76 (s, 3H), 2.93 (t, J = 7.5 Hz, 2H), 2.81 (t, J = 7.5 Hz, 2H), 2.29 (s, 3H), 2.24 (s, 3H), 2.18 (s, 3H). ¹³C NMR (150 MHz, CDCl₃) δ 207.8, 198.2, 164.7, 151.2, 150.5, 149.9, 144.1, 141.7, 140.8, 140.2, 138.4, 137.2, 134.7, 134.3, 132.5, 131.8, 131.1, 129.2, 127.9, 127.7, 127.5, 127.2, 127.0, 125.6, 124.4, 122.9, 122.8, 121.8, 120.5, 117.0, 115.9, 115.7, 113.0, 99.6, 56.0, 45.3, 30.3, 29.8, 14.1, 12.1. ¹¹B NMR (193 MHz, CDCl₃) δ -4.63. HRMS (APCI): calcd. for C₄₆H₃₈BN₂O₅⁺ [M+H]⁺ : 709.2868, found : 709.2854. [α]_D²⁰ = -160 (c = 0.1, CHCl₃).

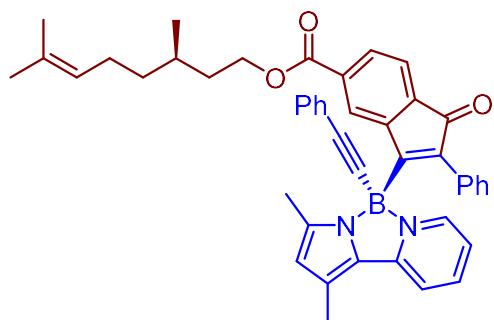
HPLC analysis: Daicel Chiralpak IA column (hexane: 2-propanol = 85:15, v = 1.0 mL/min, 40 °C, 254 nm); tr (major) = 10.599 min, tr (minor) = 14.530 min, 93% ee.



No.	Time	Area	Area (%)
1	10.611	1765.9	49.69
2	14.471	1787.9	50.31



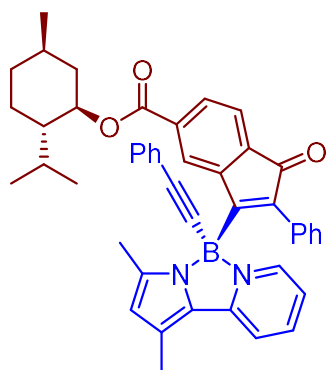
No.	Time	Area	Area (%)
1	10.599	8630.2	96.69
2	14.530	295.7	3.31



(R)-3,7-dimethyloct-6-en-1-yl 3-(1,3-dimethyl-5-(phenylethynyl)-5H-5 λ^4 ,6 λ^4 -pyrrolo[1',2':3,4][1,3,2]diazaborolo[1,5-a]pyridin-5-yl)-1-oxo-2-phenyl-1H-indene-5-carboxylate (64)

The title compound was isolated as a yellow solid (24.2 mg, 36%). ^1H NMR (600 MHz, CDCl_3) δ 9.02 (s, br, 1H), 8.01 (d, J = 5.9 Hz, 1H), 7.98 – 7.92 (m, 1H), 7.54 – 7.47 (m, 2H), 7.45 – 7.38 (m, 2H), 7.25 – 7.18 (m, 3H), 7.08 – 7.01 (m, 2H), 6.97 (t, J = 7.5 Hz, 2H), 6.72 (t, J = 6.6 Hz, 1H), 6.52 (d, J = 7.5 Hz, 2H), 5.81 (s, 1H), 5.13 – 5.02 (m, 1H), 4.38 – 4.22 (m, 2H), 2.28 (s, 3H), 2.27 (s, 3H), 2.03 – 1.91 (m, 2H), 1.68 (s, 3H), 1.67 – 1.62 (m, 1H), 1.59 – 1.52 (m, 3H), 1.46 – 1.39 (m, 1H), 1.36 – 1.28 (m, 2H), 1.21 – 1.14 (m, 1H), 0.92 (d, J = 6.7 Hz, 3H). ^{13}C NMR (150 MHz, CDCl_3) δ 198.3, 166.5, 150.4, 149.9, 143.9, 141.8, 140.8, 137.2, 135.4, 134.3, 132.6, 131.9, 131.5, 130.2, 129.2, 128.1, 127.73, 127.69, 127.2, 127.0, 125.2, 124.7, 124.6, 122.8, 121.8, 117.0, 115.9, 115.7, 99.6, 64.0, 37.2, 35.5, 29.8, 25.9, 25.5, 19.6, 17.8, 14.1, 12.2. ^{11}B NMR (193 MHz, CDCl_3) δ -5.06. HRMS (APCI): calcd. for $\text{C}_{45}\text{H}_{44}\text{BN}_2\text{O}_3^+$ $[\text{M}+\text{H}]^+$: 671.3440, found: 671.3438. $[\alpha]_{\text{D}}^{20}$ = -92 (c = 0.1, CHCl_3).

>20:1 dr determined by ^1H NMR.

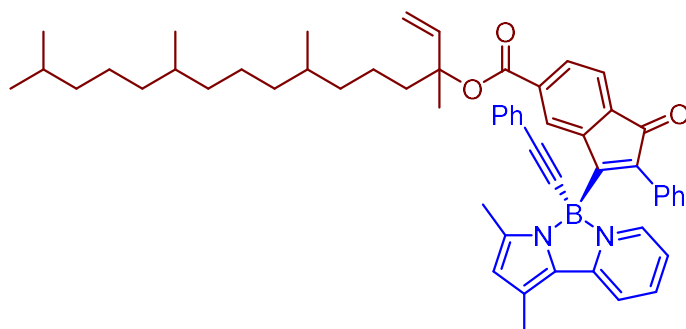


(1R,2S,5R)-2-isopropyl-5-methylcyclohexyl 3-(1,3-dimethyl-5-(phenylethynyl)-5H-5 λ^4 ,6 λ^4 -pyrrolo[1',2':3,4][1,3,2]diazaborolo[1,5-a]pyridin-5-yl)-1-oxo-2-phenyl-1H-indene-5-carboxylate (65)

The title compound was isolated as a yellow solid (28.2 mg, 42%). ^1H NMR (600 MHz, CDCl_3) δ 8.98 (s, br, 1H), 8.09 (d, J = 6.0 Hz, 1H), 7.98 – 7.91 (m, 1H), 7.61 – 7.56 (m, 1H), 7.51 (d, J = 7.4 Hz, 1H), 7.43 – 7.37 (m, 2H), 7.25 – 7.19 (m, 3H), 7.15 (d, J = 8.4 Hz, 1H), 7.06 (t, J = 7.4 Hz, 1H), 6.99 (t, J = 7.5 Hz, 2H), 6.77 (t, J = 6.6 Hz, 1H), 6.57 (d, J = 7.4 Hz, 2H), 5.69 (s, 1H), 4.92 (td, J = 10.9, 4.4 Hz, 1H), 2.26 (s, 3H), 2.20 (s, 3H), 2.11 – 2.04 (m, 1H), 1.93 – 1.86 (m, 1H), 1.72 – 1.63 (m, 2H), 1.56 – 1.49 (m, 1H), 1.37 – 1.27 (m, 2H), 1.14 – 1.06 (m, 1H), 0.99 – 0.95 (m, 1H), 0.92 (d, J = 6.5 Hz, 3H), 0.85 (d, J = 6.9 Hz, 3H), 0.79 (d, J = 6.9 Hz, 3H). ^{13}C NMR (150 MHz, CDCl_3) δ 198.4, 165.9, 150.3, 149.8, 143.9, 141.7, 140.9, 137.4, 135.8, 134.3, 132.5, 132.0, 130.1, 129.1, 128.1, 127.7, 127.1, 126.9, 125.1, 124.7, 122.9, 121.8, 116.9, 115.9, 115.8, 99.6, 75.3, 47.0, 40.9, 34.3, 31.6, 26.9, 23.9, 22.2, 20.8,

16.9, 13.9, 12.2. **¹¹B NMR (193 MHz, CDCl₃)** δ -5.06. **HRMS (APCI):** calcd. for C₄₅H₄₄BN₂O₃⁺ [M+H]⁺ : 671.3440, found : 671.3433. [α]_D²⁰ = -52 (c = 0.1, CHCl₃).

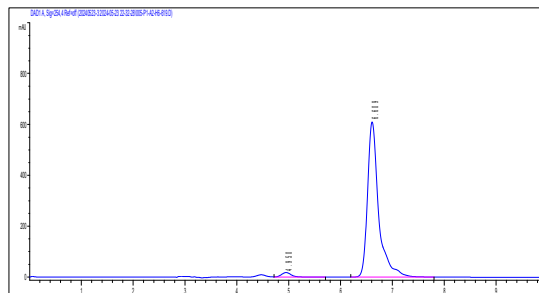
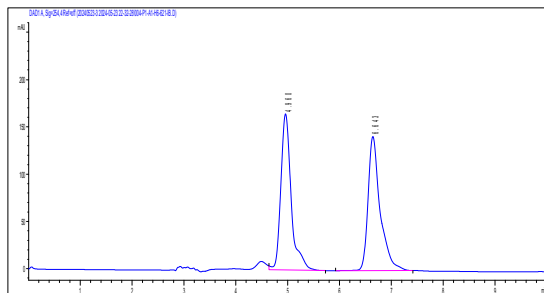
>20:1 dr determined by ¹H NMR.



(R)-3,7,11,15-tetramethylhexadec-1-en-3-yl 3-(1,3-dimethyl-5-(phenylethynyl)-5H-5 λ ⁴,6 λ ⁴-pyrrolo[1',2':3,4][1,3,2]diazaborolo[1,5-a]pyridin-5-yl)-1-oxo-2-phenyl-1H-indene-5-carboxylate (66)

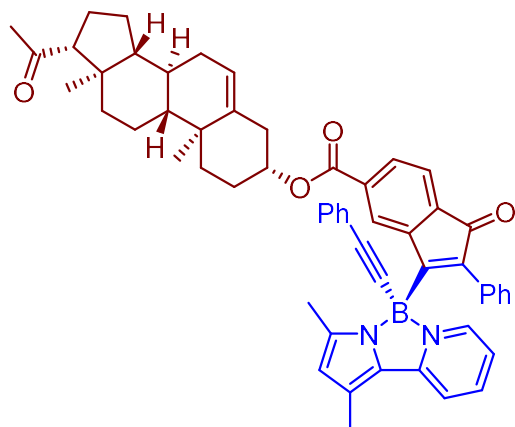
The title compound was isolated as a yellow solid (27.6 mg, 34%). **¹H NMR (600 MHz, CDCl₃)** δ 9.07 (s, br, 1H), 8.00 (d, *J* = 6.1 Hz, 1H), 7.92 (d, *J* = 7.4 Hz, 1H), 7.53 – 7.47 (m, 2H), 7.44 – 7.38 (m, 2H), 7.25 – 7.18 (m, 3H), 7.09 – 7.01 (m, 2H), 7.00 – 6.93 (m, 2H), 6.69 (t, *J* = 6.6 Hz, 1H), 6.58 – 6.48 (m, 2H), 6.12 – 5.97 (m, 1H), 5.80 (s, 1H), 5.21 (dd, *J* = 17.5, 8.8 Hz, 1H), 5.14 (t, *J* = 10.8 Hz, 1H), 2.29 (s, 3H), 2.27 (s, 3H), 1.88 – 1.67 (m, 3H), 1.60 (s, 1H), 1.57 – 1.47 (m, 2H), 1.39 – 1.30 (m, 5H), 1.25 – 1.18 (m, 6H), 1.17 – 1.10 (m, 3H), 1.08 – 1.01 (m, 4H), 0.87 (s, 3H), 0.86 (s, 3H), 0.84 (d, *J* = 6.5 Hz, 3H), 0.82 (d, *J* = 6.6 Hz, 3H). **¹³C NMR (150 MHz, CDCl₃)** δ 198.3, 165.1, 150.5, 149.9, 143.5, 141.9, 141.8, 140.8, 137.2, 136.6, 136.5, 134.1, 132.5, 132.0, 129.9, 129.2, 128.1, 128.0, 127.7, 127.2, 127.0, 125.4, 124.6, 122.7, 121.7, 117.0, 115.9, 115.8, 113.5, 113.4, 99.5, 84.33, 84.29, 40.4, 40.3, 39.5, 37.61, 37.57, 37.54, 37.48, 37.44, 37.39, 33.0, 32.8, 28.1, 24.97, 24.95, 24.6, 23.6, 23.5, 22.9, 22.8, 21.3, 19.9, 19.82, 19.77, 19.7, 14.2, 12.2. **¹¹B NMR (193 MHz, CDCl₃)** δ -5.17. **HRMS (APCI):** calcd. for C₅₅H₆₄BN₂O₃⁺ [M+H]⁺ : 811.5005, found : 811.4990. [α]_D²⁰ = -36 (c = 0.1, CHCl₃).

HPLC analysis: Daicel Chiralpak IB column (hexane: 2-propanol = 90:10, v = 1.0 mL/min, 40 °C, 254 nm); tr (major) = 6.609 min, tr (minor) = 4.950 min, 95% ee.



No.	Time	Area	Area (%)
1	4.960	2303.2	50.03
2	6.643	2300.4	49.97

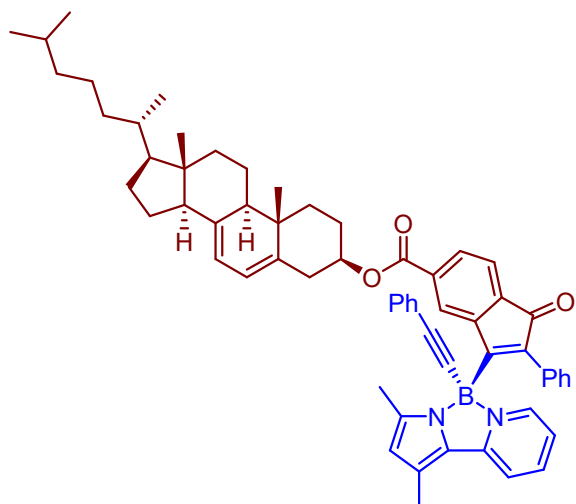
No.	Time	Area	Area (%)
1	4.950	232.0	2.48
2	6.609	9112.9	97.52



(3R,8R,9R,10S,13R,14R,17R)-17-acetyl-10,13-dimethyl-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-3-yl 3-(1,3-dimethyl-5-(phenylethynyl)-5H-5λ⁴,6λ⁴-pyrrolo[1',2':3,4][1,3,2]diazaborolo[1,5-a]pyridin-5-yl)-1-oxo-2-phenyl-1H-indene-5-carboxylate (67)

The title compound was isolated as a yellow solid (22.4 mg, 27%). ¹H NMR (600 MHz, CDCl₃) δ 8.96 (s, br, 1H), 8.00

(d, *J* = 6.0 Hz, 1H), 7.95 (d, *J* = 7.4 Hz, 1H), 7.55 – 7.48 (m, 2H), 7.42 – 7.36 (m, 2H), 7.25 – 7.17 (m, 3H), 7.09 – 7.02 (m, 2H), 7.00 – 6.93 (m, 2H), 6.71 (t, *J* = 6.6 Hz, 1H), 6.55 (d, *J* = 7.4 Hz, 2H), 5.81 (s, 1H), 5.44 – 5.36 (m, 1H), 4.86 – 4.76 (m, 1H), 2.58 – 2.52 (m, 1H), 2.41 – 2.36 (m, 1H), 2.28 (s, 3H), 2.27 (s, 3H), 2.24 – 2.16 (m, 2H), 2.14 (s, 3H), 2.08 – 2.01 (m, 2H), 1.89 – 1.82 (m, 2H), 1.76 – 1.63 (m, 4H), 1.56 – 1.45 (m, 5H), 1.21 – 1.15 (m, 2H), 1.08 – 1.02 (m, 1H), 0.97 (s, 3H), 0.65 (s, 3H). ¹³C NMR (150 MHz, CDCl₃) δ 209.7, 198.3, 165.9, 150.4, 149.9, 143.8, 141.8, 140.8, 139.8, 137.2, 135.7, 134.2, 132.6, 131.9, 130.2, 129.2, 128.1, 127.71, 127.70, 127.2, 127.0, 125.2, 124.6, 122.8, 122.6, 121.7, 121.5, 117.0, 115.9, 115.8, 99.5, 74.9, 71.9, 63.8, 57.0, 50.1, 44.1, 39.0, 38.2, 37.2, 36.8, 32.0, 31.7, 27.8, 24.6, 23.0, 21.2, 19.6, 14.2, 13.4, 12.2. ¹¹B NMR (193 MHz, CDCl₃) δ -4.82. HRMS (APCI): calcd. for C₅₆H₅₆BN₂O₄⁺ [M+H]⁺: 831.4328, found: 831.4323. [α]_D²⁰ = -84 (c = 0.1, CHCl₃). >20:1 dr determined by ¹H NMR.



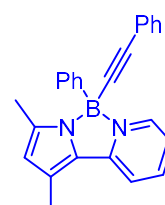
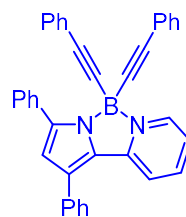
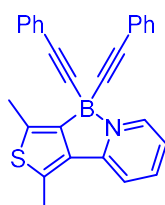
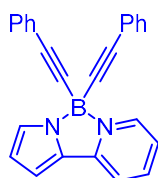
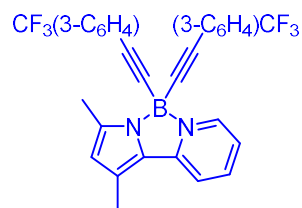
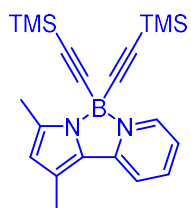
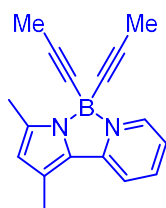
(3R,9R,10S,13S,14S,17S)-10,13-dimethyl-17-((S)-6-methylheptan-2-yl)-2,3,4,9,10,11,12,13,14,15, 16,17-dodecahydro-1H-cyclopenta[*a*] phenanthrene-3-yl 3-(1,3-dimethyl-5-(phenylethynyl)-5*H*-5 λ^4 ,6 λ^4 -pyrrolo[1',2':3,4][1,3,2]diazaborolo[1,5-*a*]pyridin-5-yl)-1-oxo-2-phenyl-1*H*-indene-5-carboxylate (68)

The title compound was isolated as a yellow solid (24.3 mg, 27%). ¹H NMR (600 MHz, CDCl₃) δ 8.97 (s, br, 1H), 8.01 (d, *J* = 6.0 Hz, 1H), 7.99 – 7.92 (m, 1H), 7.57

– 7.46 (m, 2H), 7.43 – 7.37 (m, 2H), 7.25 – 7.17 (m, 3H), 7.10 – 7.02 (m, 2H), 7.01 – 6.92 (m, 2H), 6.72 (t, *J* = 6.6 Hz, 1H), 6.54 (d, *J* = 7.6 Hz, 2H), 5.81 (s, 1H), 5.62 – 5.53 (m, 1H), 5.44 – 5.38 (m, 1H), 4.95 – 4.85 (m, 1H), 2.58 – 2.49 (m, 1H), 2.37 – 2.31 (m, 1H), 2.28 (s, 3H), 2.27 (s, 3H), 2.13 – 2.08 (m, 1H), 2.03 – 1.99 (m, 1H), 1.97 – 1.84 (m, 4H), 1.76 – 1.56 (m, 5H), 1.46 – 1.30 (m, 8H), 1.18 – 1.09 (m, 3H), 1.04 – 1.00 (m, 1H), 0.95 (d, *J* = 6.5 Hz, 3H), 0.91 (s, 3H), 0.88 (d, *J* = 2.8 Hz, 3H), 0.87 (d, *J* = 2.9 Hz, 3H), 0.64 (s, 3H). ¹³C NMR (150 MHz, CDCl₃) δ 198.3, 165.9, 150.4, 149.9, 143.9, 141.8, 140.8, 138.7, 137.2, 135.7, 134.2, 132.6, 131.9, 130.2, 129.2, 128.1, 127.8, 127.7, 127.2, 127.0, 125.2, 124.6, 122.8, 121.7, 120.4, 117.0, 116.5, 115.9, 115.8, 99.5, 73.9, 56.1, 54.6, 46.2, 43.1, 39.7, 39.3, 38.2, 37.3, 36.8, 36.31, 36.28, 28.3, 28.20, 28.17, 24.1, 23.2, 23.0, 22.7, 21.2, 19.0, 16.5, 14.2, 12.2, 12.0. ¹¹B NMR (193 MHz, CDCl₃) δ -5.33. HRMS (APCI): calcd. for C₆₂H₆₈BN₂O₃⁺ [M+H]⁺ : 899.5318, found : 899.5311. [α]_D²⁰ = -96 (c = 0.1, CHCl₃).

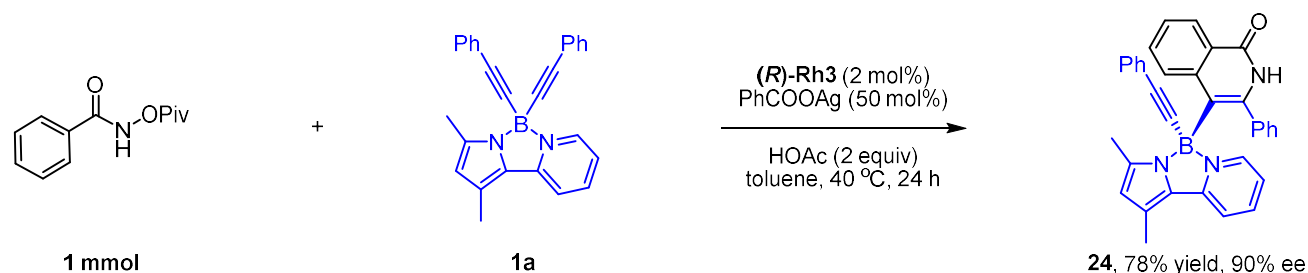
>20:1 dr determined by ¹H NMR.

4. Unsuccessful Examples for Alkynes



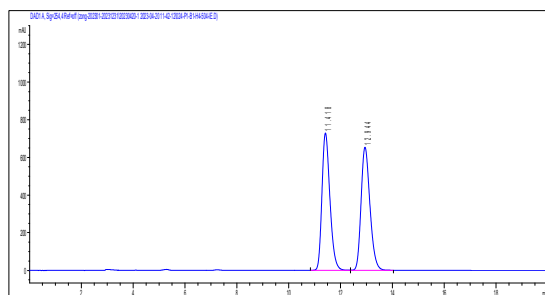
5. Synthetic applications

1 mmol-scale synthesis of **24**.

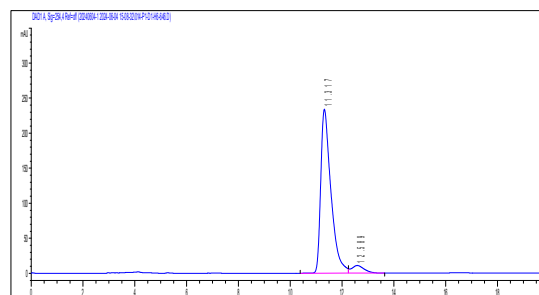


A tube (15 mL) was charged with alkyne **1a** (1.2 mmol, 1.2 equiv), benzamide **3** (1.0 mmol, 1.0 equiv), *(R)*-Rh3 (2 mol%), PhCOOAg (50 mol%) and HOAc (2.0 mmol, 2.0 equiv) in toluene (2 mL) and the reaction mixture was stirred at 40 °C for 24 h. The reaction mixture was evaporated under vacuum and the residue was purified by preparative TLC to give the corresponding products **24** as a yellow solid (392.3 mg, 78% yield, 90% ee).

HPLC analysis: Daicel Chiralpak IE column (hexane: 2-propanol = 75:25, $v = 1.0$ mL/min, 40 °C, 254 nm); tr (major) = 11.317 min, tr (minor) = 12.589 min, 90% ee.

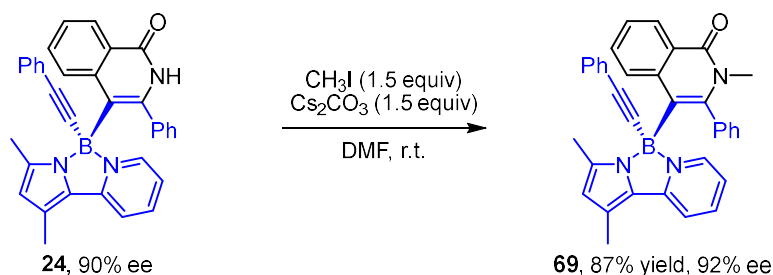


No.	Time	Area	Area (%)
1	11.418	15548.1	50.08
2	12.944	15496.7	49.92



No.	Time	Area	Area (%)
1	11.317	6422.3	95.05
2	12.589	334.4	4.95

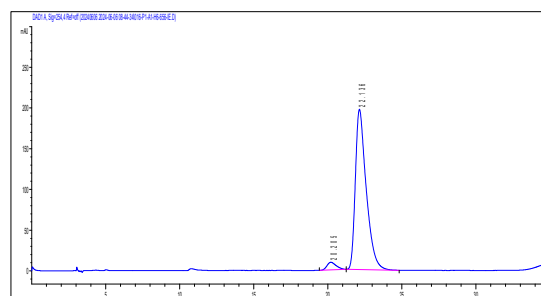
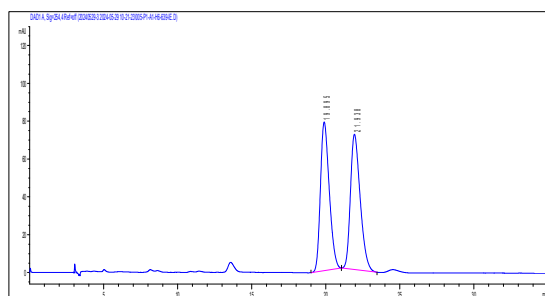
Transformations and Synthetic Applications



A screw-cap vial (8 mL) was charged with **24** (0.1 mmol, 50.3 mg) and Cs_2CO_3 (0.15 mmol, 48.9 mg) in DMF (2 mL), then CH_3I (0.5 mmol, 126.9 mg) was added to the reaction mixture dropwise, the reaction mixture was allowed to stir at room temperature for overnight. After the completion of the reaction as indicated by TLC, water was added to quench the reaction. The product was extracted by ethyl acetate, washed with brine, dried over anhydrous Na_2SO_4 , evaporated the solvent under vacuum, and purified by silica gel column chromatography to afford the product **69** as a yellow solid (45.0 mg, 87% yield, 92% ee).

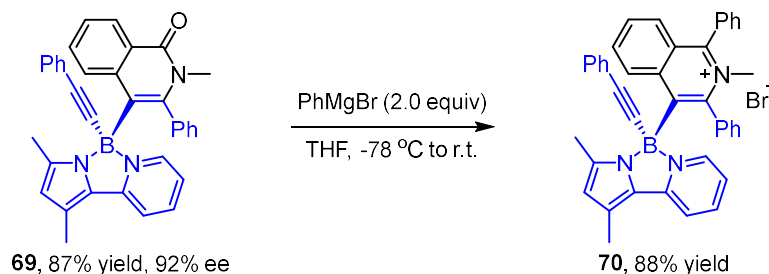
(R)-4-(1,3-dimethyl-5-(phenylethynyl)-5*H*-5λ⁴,6λ⁴-pyrrolo[1',2':3,4][1,3,2]diazaborolo[1,5-*a*]pyridin-5-yl)-2-methyl-3-phenylisoquinolin-1(2*H*)-one (69)
¹H NMR (600 MHz, CDCl_3) δ 9.87 (s, 1H), 8.57 (d, J = 8.1 Hz, 1H), 8.00 (d, J = 5.9 Hz, 1H), 7.84 – 7.63 (m, 1H), 7.59 – 7.41 (m, 2H), 7.38 – 7.27 (m, 2H), 7.25 – 7.12 (m, 3H), 7.05 (t, J = 7.5 Hz, 1H), 6.99 – 6.87 (m, 1H), 6.86 – 6.65 (m, 3H), 6.53 – 6.14 (m, 2H), 5.81 (s, 1H), 2.97 (s, 3H), 2.23 (s, 3H), 2.08 (s, 3H). ¹³C NMR (150 MHz, CDCl_3) δ 163.5, 149.1, 141.4, 139.8, 136.4, 135.9, 131.4, 130.7, 129.7, 129.3, 128.04, 127.95, 127.5, 127.4, 127.3, 126.2, 125.8, 125.7, 125.3, 122.2, 116.9, 116.1, 115.3, 98.9, 34.1, 13.9, 12.1. ¹¹B NMR (193 MHz, CDCl_3) δ -3.66. HRMS (APCI): calcd. for $\text{C}_{35}\text{H}_{29}\text{BN}_3\text{O}^+$ $[\text{M}+\text{H}]^+$: 518.2398, found: 518.2392. $[\alpha]_{\text{D}}^{20}$ = -212 (c = 0.1, CHCl_3).

HPLC analysis: Daicel Chiralpak IE column (hexane: 2-propanol = 85:15, v = 1.0 mL/min, 40 °C, 254 nm); tr (major) = 22.136 min, tr (minor) = 20.205 min, 92% ee.

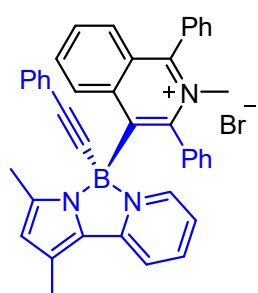


No.	Time	Area	Area (%)
1	19.895	3256.2	49.85
2	21.938	3275.8	50.15

No.	Time	Area	Area (%)
1	20.205	413.2	3.95
2	22.136	10053.2	96.05

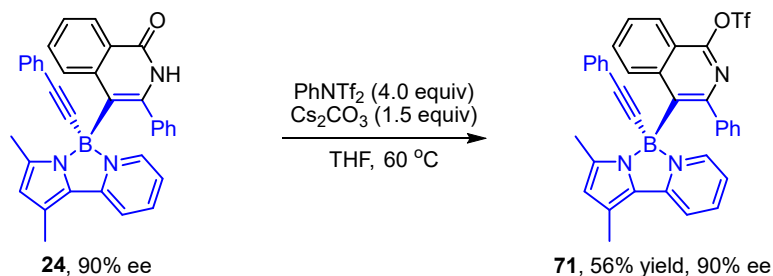


A screw-cap vial (8 mL) was charged with **69** (0.1 mmol, 51.7 mg) and THF (2 mL) was stirred at -78 °C for 10 min. Then PhMgBr (0.2 mmol, 0.2 mL, 1 M) was added and the reaction was allowed to room temperature and stirred for 12 h. The mixture was quenched with 10 mL saturate NH₄Cl solution and the resulting mixture was extracted with EA (3 × 5 mL). The organic layers were combined, dried over anhydrous Na₂SO₄ and then concentrated under reduced pressure. The residue was purified by silica gel column chromatography to afford the product **70** as a yellow solid (57.8 mg, 88% yield).^[4]

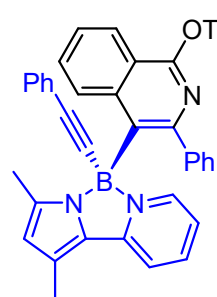


4-(1,3-dimethyl-5-(phenylethynyl)-5H-5λ⁴,6λ⁴-pyrrolo[1',2':3,4][1,3,2]diazaborolo[1,5-a]pyridin-5-yl)-2-methyl-1,3-diphenylisoquinolin-2-ium bromide (70**)**

¹H NMR (600 MHz, CDCl₃) δ 10.48 (d, *J* = 8.8 Hz, 1H), 8.68 – 8.39 (m, 2H), 8.15 – 8.00 (m, 1H), 7.87 – 7.72 (m, 4H), 7.70 – 7.62 (m, 2H), 7.61 – 7.53 (m, 1H), 7.47 – 7.31 (m, 4H), 7.26 – 7.13 (m, 4H), 7.03 – 6.90 (m, 2H), 6.84 (d, *J* = 8.3 Hz, 1H), 6.44 – 6.11 (m, 1H), 5.94 (s, 1H), 3.61 (s, 3H), 2.35 (s, 3H), 2.18 (s, 3H). ¹³C NMR (150 MHz, CDCl₃) δ 159.3, 150.2, 148.1, 144.0, 143.6, 140.5, 135.1, 133.5, 133.0, 131.8, 131.4, 131.0, 130.9, 130.7, 130.4, 130.2, 130.1, 129.7, 129.2, 128.6, 128.5, 128.4, 128.2, 128.1, 127.7, 127.6, 127.5, 127.0, 125.9, 124.6, 122.0, 119.3, 115.7, 115.4, 100.1, 46.3, 14.3, 12.0. ¹¹B NMR (193 MHz, CDCl₃) δ -4.06. HRMS (APCI): calcd. for C₄₁H₃₃BN₃⁺ [M-Br]⁺: 578.2762, found: 578.2769. [α]_D²⁰ = -182 (c = 0.1, CHCl₃).



A screw-cap vial (8 mL) was charged with **24** (0.1 mmol, 50.3 mg), Cs₂CO₃ (0.15 mmol, 48.9 mg) PhNTf₂ (0.4 mmol, 142.8 mg) and THF (2 mL). The resulted mixture was stirred at 60 °C for 12 h. After the reaction was completed, the solvent was removed under reduced pressure. Then the residue was purified by silica gel column chromatography to afford the product **71** as a yellow solid (35.6 mg, 56% yield, 90% ee).

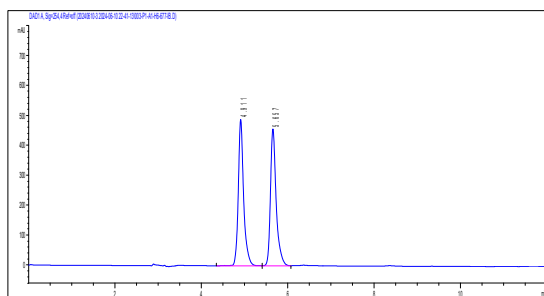


(R)-4-(1,3-dimethyl-5-(phenylethynyl)-5H-5λ⁴,6λ⁴-

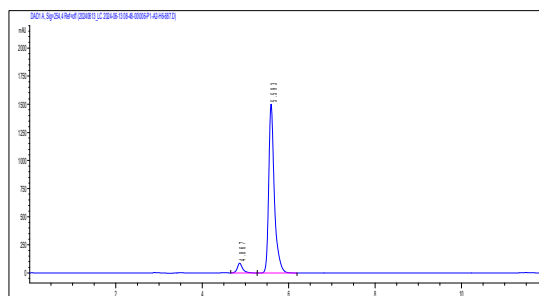
pyrrolo[1',2':3,4][1,3,2]diazaborolo[1,5-a]pyridin-5-yl)-3-phenylisoquinolin-1-yl trifluoromethanesulfonate (71**)**

¹H NMR (600 MHz, CDCl₃) δ 10.02 (s, 1H), 8.22 (d, *J* = 8.3 Hz, 1H), 7.92 – 7.86 (m, 1H), 7.80 (d, *J* = 6.0 Hz, 1H), 7.75 (t, *J* = 7.6 Hz, 1H), 7.42 (t, *J* = 7.8 Hz, 1H), 7.33 – 7.28 (m, 2H), 7.25 – 7.19 (m, 3H), 7.06 – 7.01 (m, 1H), 6.98 – 6.67 (m, 5H), 6.23 (s, 1H), 5.92 (s, 1H), 2.29 (s, 3H), 2.23 (s, 3H). ¹³C NMR (150 MHz, CDCl₃) δ 156.0, 151.8, 149.7, 146.2, 141.7, 141.2, 140.3, 136.6, 131.5, 130.3, 129.9, 129.2, 128.14, 128.11, 127.7, 127.6, 126.4, 124.9, 122.9, 122.6, 118.8 (q, *J* = 320.7 Hz), 118.7, 117.2, 115.93, 115.85, 99.2, 14.3, 12.2. ¹¹B NMR (193 MHz, CDCl₃) δ -3.36. ¹⁹F NMR (376 MHz, CDCl₃) δ -72.46. HRMS (APCI): calcd. for C₃₅H₂₆BF₃N₃O₃S⁺ [M+H]⁺ : 636.1735, found : 636.1747. [α]_D²⁰ = -392 (c = 0.1, CHCl₃).

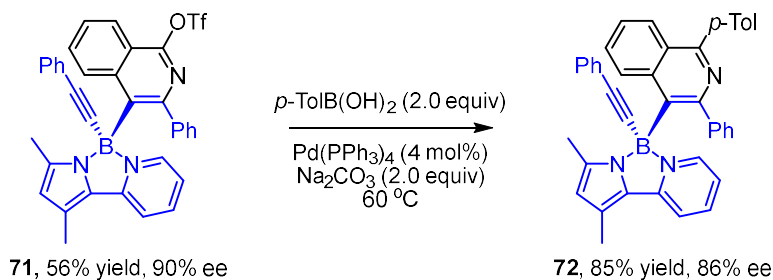
HPLC analysis: Daicel Chiralpak IB column (hexane: 2-propanol = 90:10, v = 1.0 mL/min, 40 °C, 254 nm); tr (major) = 5.593 min, tr (minor) = 4.867 min, 90% ee.



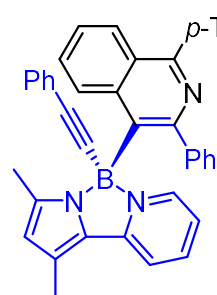
No.	Time	Area	Area (%)
1	4.911	4213.9	50.20
2	5.657	4180.9	49.80



No.	Time	Area	Area (%)
1	4.867	732.8	5.12
2	5.593	13571.8	94.88



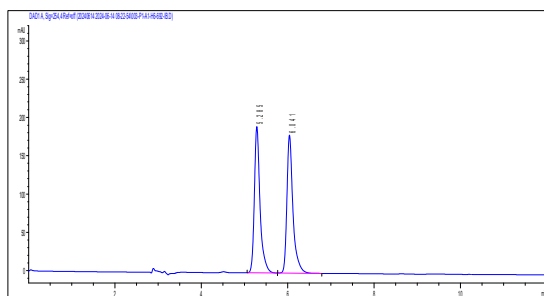
A scew-cap vial (8 mL) was charged with **71** (0.1 mmol, 63.5 mg), Pd(PPh₃)₄ (4 mol%, 4.6 mg), Na₂CO₃ (0.2 mmol, 21.2 mg) and toluene:EtOH:H₂O (2 mL, 10 : 1 : 1). *p*-tolylboronic acid (0.2 mmol, 27.2 mg) was then added and the mixture was stirred at 60 °C for 12 h. The solvent was evaporated under vacuum and the residue was purified by flash column chromatography to afford the product **72** as a yellow solid (49.1 mg, 85% yield, 86% ee).



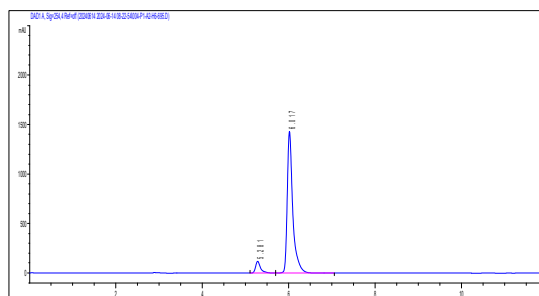
(R)-1,3-dimethyl-5-(3-phenyl-1-(*p*-tolyl)isoquinolin-4-yl)-5-(phenylethynyl)-5H-5λ⁴,6λ⁴-pyrrolo[1',2':3,4][1,3,2]diazaborolo[1,5-*a*]pyridine (72**)**

¹H NMR (600 MHz, CDCl₃) δ 10.15 – 9.82 (m, 1H), 8.18 (d, *J* = 8.4 Hz, 1H), 7.89 (d, *J* = 6.0 Hz, 1H), 7.82 – 7.75 (m, 1H), 7.72 – 7.64 (m, 2H), 7.54 (t, *J* = 7.6 Hz, 1H), 7.42 (t, *J* = 7.8 Hz, 1H), 7.38 – 7.33 (m, 2H), 7.33 – 7.28 (m, 2H), 7.26 – 7.16 (m, 3H), 7.00 (t, *J* = 7.5 Hz, 1H), 6.96 – 6.75 (m, 4H), 6.77 – 6.73 (m, 1H), 6.37 (s, 1H), 5.91 (s, 1H), 2.45 (s, 3H), 2.34 (s, 3H), 2.22 (s, 3H). ¹³C NMR (150 MHz, CDCl₃) δ 158.5, 158.0, 149.6, 143.8, 143.3, 141.3, 140.0, 138.3, 137.2, 136.6, 131.5, 130.6, 129.9, 129.3, 128.9, 128.2, 128.1, 128.0, 127.7, 127.3, 126.9, 125.64, 125.57, 125.4, 125.3, 122.4, 117.0, 115.9, 115.6, 98.8, 21.5, 14.4, 12.2. ¹¹B NMR (193 MHz, CDCl₃) δ -3.29. HRMS (APCI): calcd. for C₄₁H₃₃BN₃⁺ [M+H]⁺ : 578.2762, found : 578.2764 [α]_D²⁰ = -274 (c = 0.1, CHCl₃).

HPLC analysis: Daicel Chiralpak IB column (hexane: 2-propanol = 90:10, v = 1.0 mL/min, 40 °C, 254 nm); tr (major) = 6.017 min, tr (minor) = 5.281 min, 86% ee.



No.	Time	Area	Area (%)
1	5.285	1743.6	49.91
2	6.041	1749.7	50.09



No.	Time	Area	Area (%)
1	5.281	939.3	6.87
2	6.017	12744.0	93.13

6. Photophysical properties

Table S1. Photophysical properties of selected compounds (1×10^{-5} M in DCM)

Compound	$\lambda_{\text{abs}}^{[a]}$ (nm)	$\epsilon^{[b]}$ ($\text{M}^{-1}\text{cm}^{-1}$)	$\lambda_{\text{em}}^{[c]}$ (nm)	$\Delta\lambda^{[d]}$ (nm)	$\phi^{[e]}$ (DCM)	$\lambda_{\text{mon}}^{[f]}$ (nm)	τ (Percentage) ^[g]
44	360	10400	411	51	0.24	411	1.42 ns (100 %)
49	351	10600	422	71	0.10	422	0.69 ns (100 %)
57	363	19900	433	70	0.30	433	0.91 ns (39 %) 1.52 ns (61 %)
60	361	15000	412	51	0.11	412	0.68 ns (53 %) 2.31 ns (47 %)

[a] Absorption maxima in dichloromethane. [b] The maximum molar absorption coefficient in dichloromethane. [c] Fluorescent emission maxima in dichloromethane. [d] Stokes shift in dichloromethane. [e] Absolute quantum yields in dichloromethane. (Measured by quantum efficiency measurement system (C9920-02G)). [f] The fluorescence decays monitoring wavelength. [g] Observed lifetime in dichloromethane.

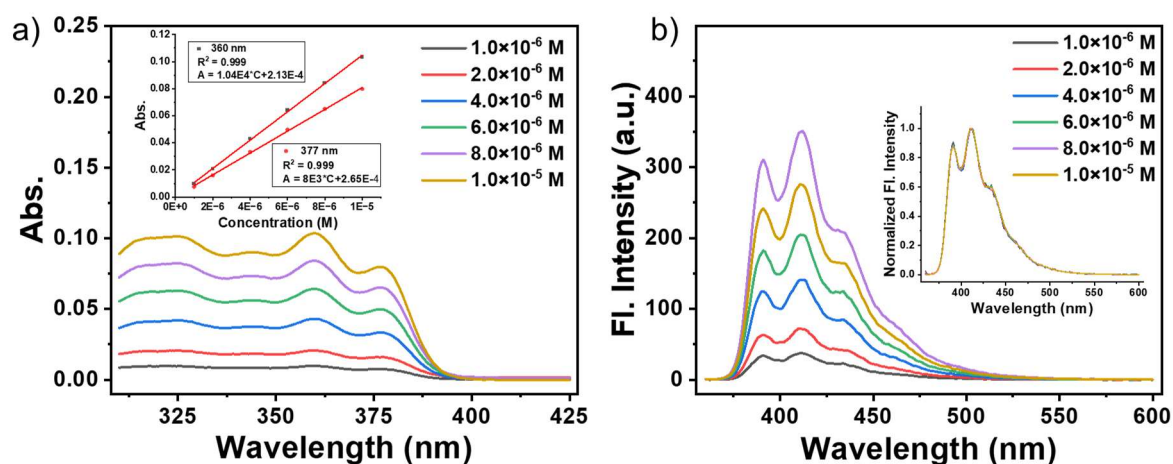


Figure S1. Concentration effect of **44** on UV-vis absorption spectra (a) and fluorescence spectra (b) in dichloromethane. The interior illustration are linear fits of absorption intensity to concentration and normalized fluorescence spectra. $\lambda_{\text{ex}} = 350$ nm, monitoring wavelength: 360 nm and 377 nm.

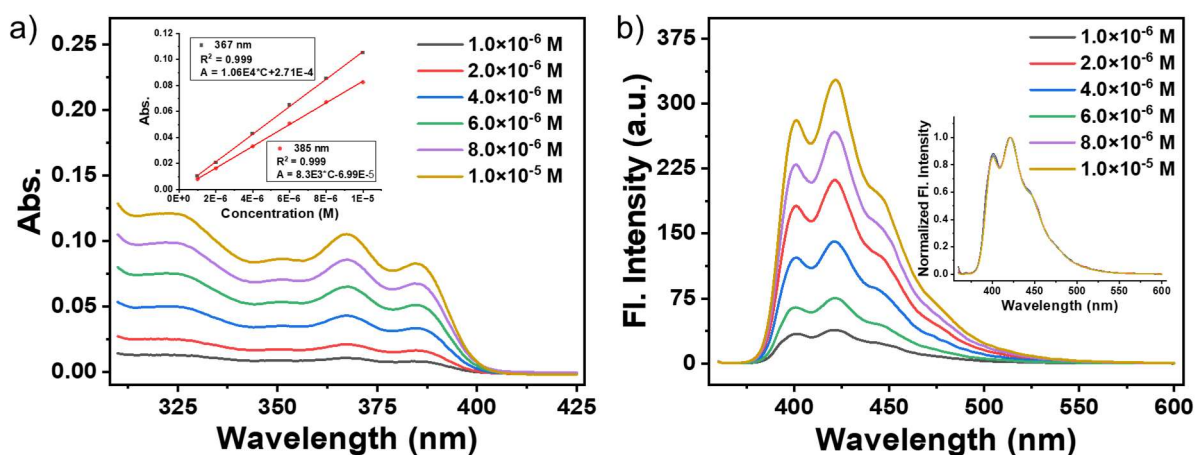


Figure S2. Concentration effect of **49** on UV-vis absorption spectra (a) and fluorescence spectra (b) in dichloromethane. The interior illustration are linear fits of absorption intensity to concentration and normalized fluorescence spectra. $\lambda_{\text{ex}} = 350$ nm, monitoring wavelength: 367 nm and 385 nm.

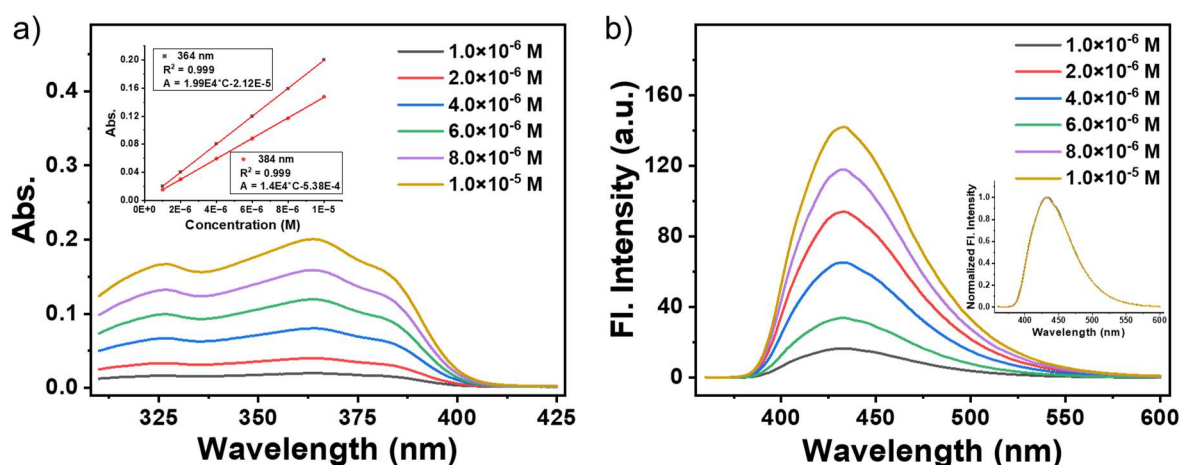


Figure S3. Concentration effect of **57** on UV-vis absorption spectra (a) and fluorescence spectra (b) in dichloromethane. The interior illustration are linear fits of absorption intensity to concentration and normalized fluorescence spectra. $\lambda_{\text{ex}} = 350$ nm, monitoring wavelength: 364 nm and 384 nm.

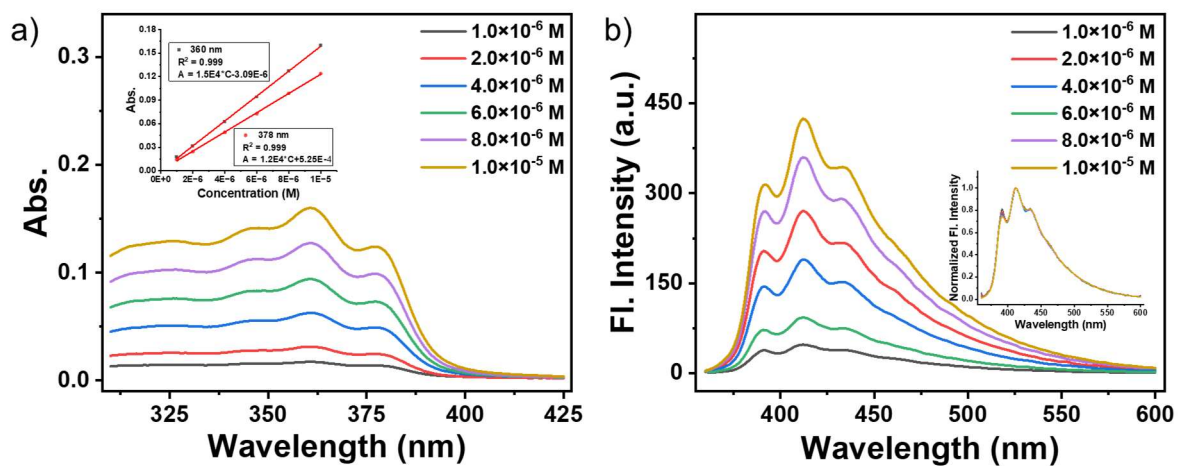
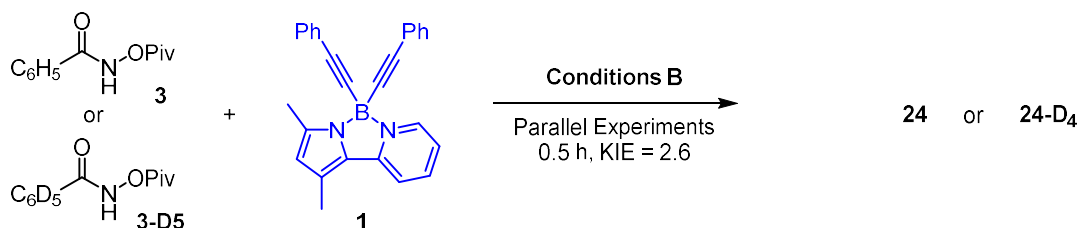


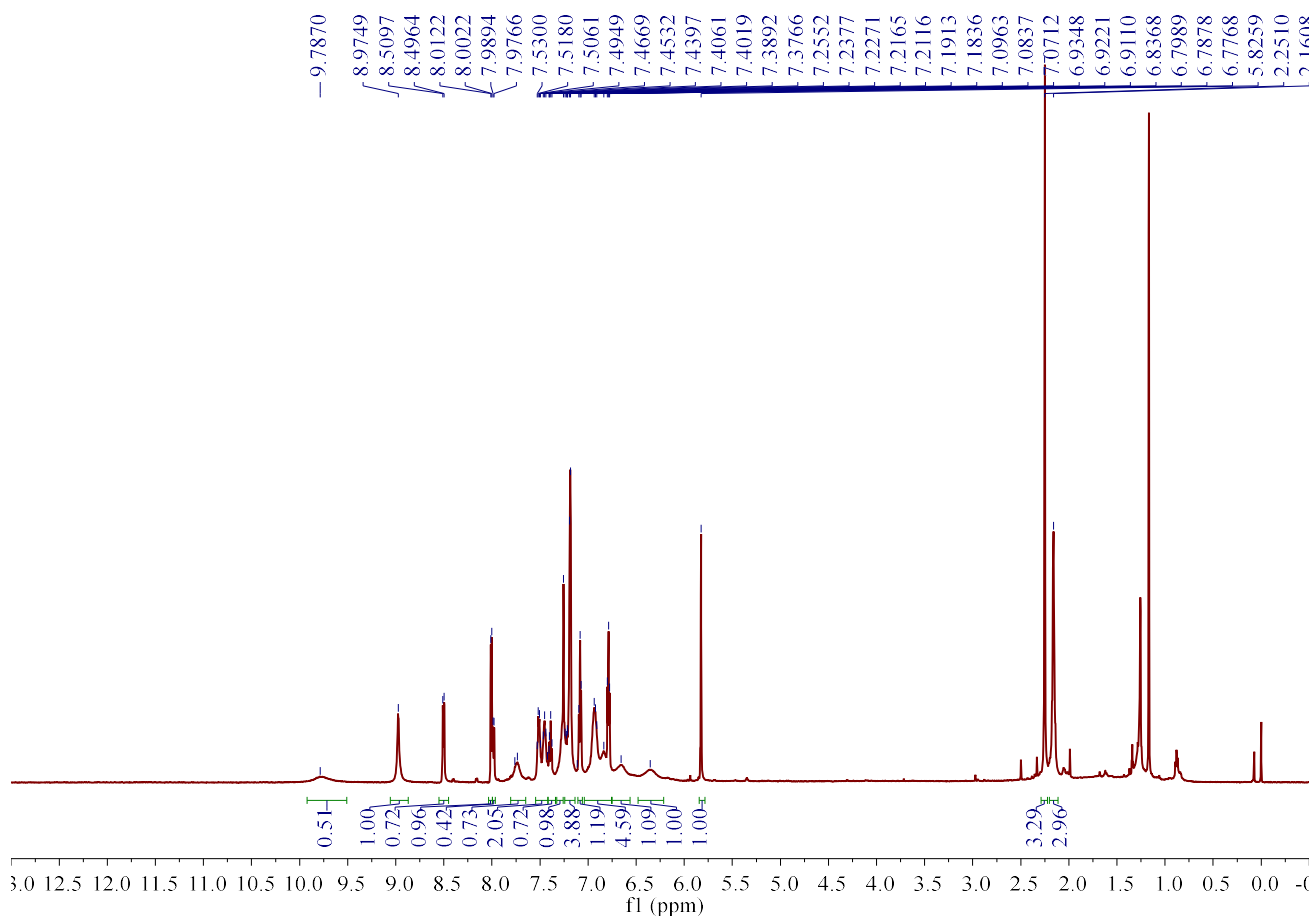
Figure S4. Concentration effect of **60** on UV-vis absorption spectra (a) and fluorescence spectra (b) in dichloromethane. The interior illustration are linear fits of absorption intensity to concentration and normalized fluorescence spectra. $\lambda_{\text{ex}} = 350$ nm, monitoring wavelength: 360 nm and 378 nm.

7. Mechanistic Studies

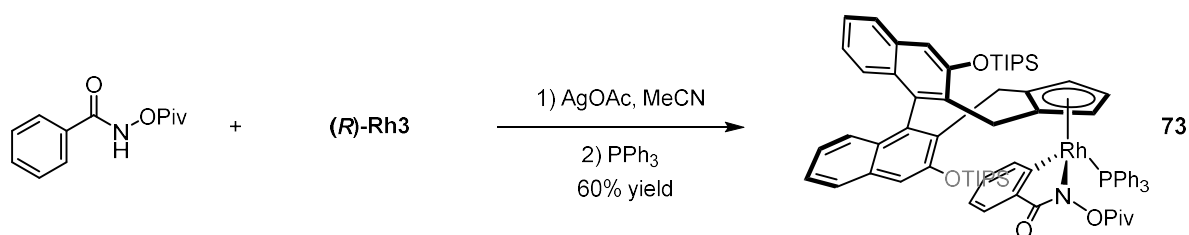
7.1 Parallel Experiments for KIE



Two screw-cap vials (8 mL) each was charged with dialkynyl tetracoordinate boron substrate **1** (0.12 mmol, 1.2 equiv), (**R**)-**Rh3** (4 mol%), PhCOOAg (50 mol%) and HOAc (0.20 mmol, 2.0 equiv) in toluene (2 mL), to which was added benzamide **3** (0.10 mmol, 1.0 equiv) and **3-D5** (0.10 mmol, 1.0 equiv) and the reaction mixture was stirred at 40 °C for 0.5 h. The two mixtures were combined and were rapidly evaporated under reduced pressure separately. The purification was performed by flash column chromatography on silica gel to afford the products. The KIE value was determined to be $k_H/k_D = 2.6$ on the basis of ^1H NMR analysis.

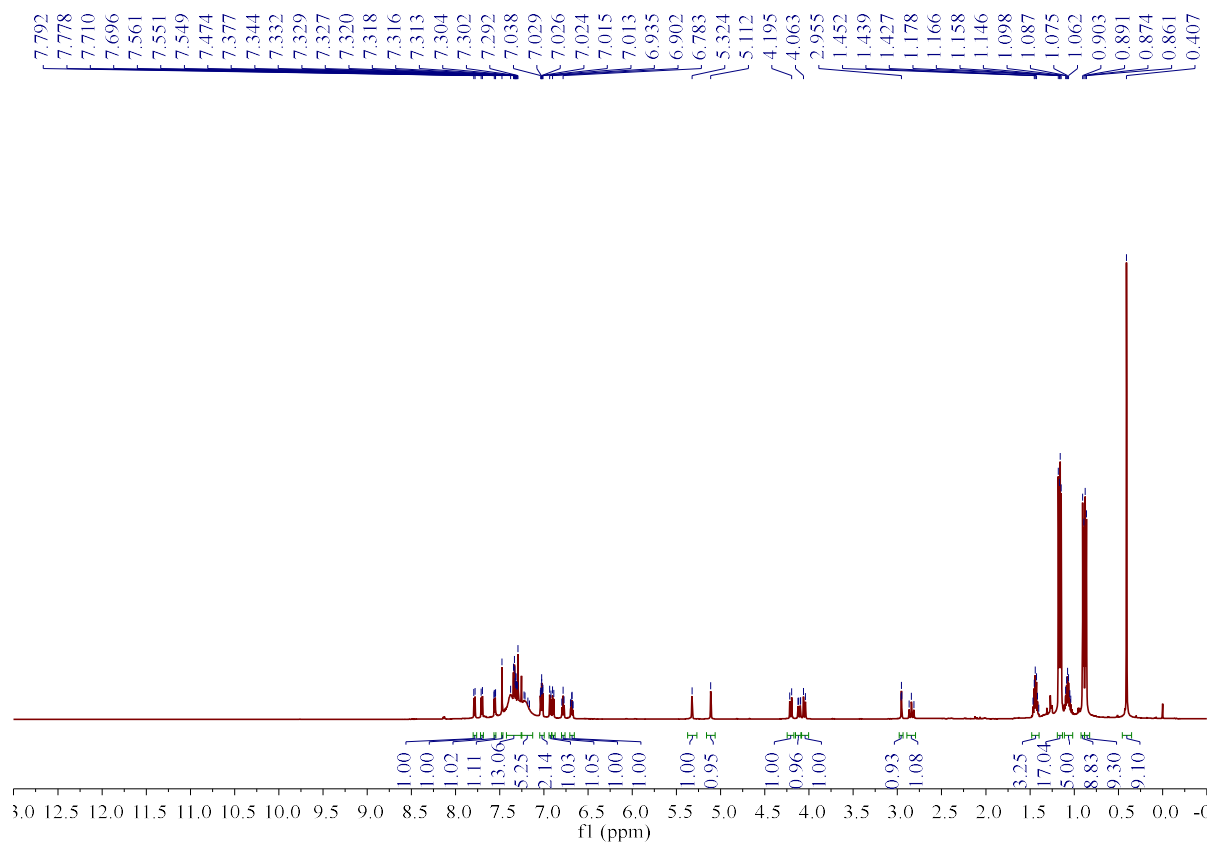


7.2 Synthesis of Rhodium complexes **73**.

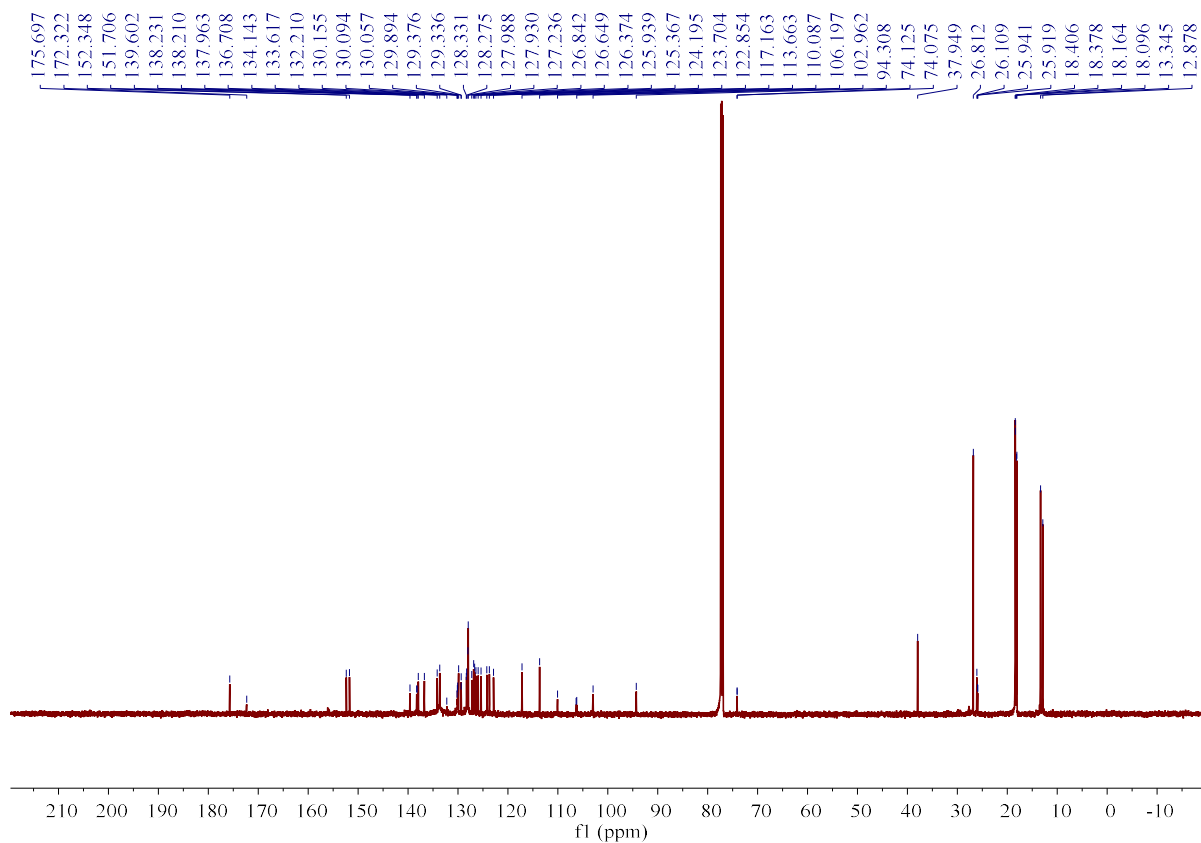


A mixture of *N*-(pivaloyloxy)benzamide (22.1 mg, 0.1 mmol, 2.0 equiv), (*R*)-**Rh3** compound (104.4 mg, 0.05 mmol) and silver acetate (33.4 mg, 0.2 mmol, 4.0 equiv) in acetonitrile (5 mL) was stirred for 30 min at room temperature under N₂ atmosphere. Another portion of triphenylphosphine (26.2 mg, 0.1 mmol, 2.0 equiv) was added and the mixture was allowed to stir for additional 50 min at room temperature. The resulting crude mixture was filtered through PTFE syringe filter washing with acetonitrile (10 mL) and concentrated under reduced pressure. **73** was purified by deactivated silica gel chromatography (by flushing with hexane-ethyl acetate-triethylaminen = 1 : 1 : 0.4 solution). Product **73** was isolated in 60% yield as a yellow solid.

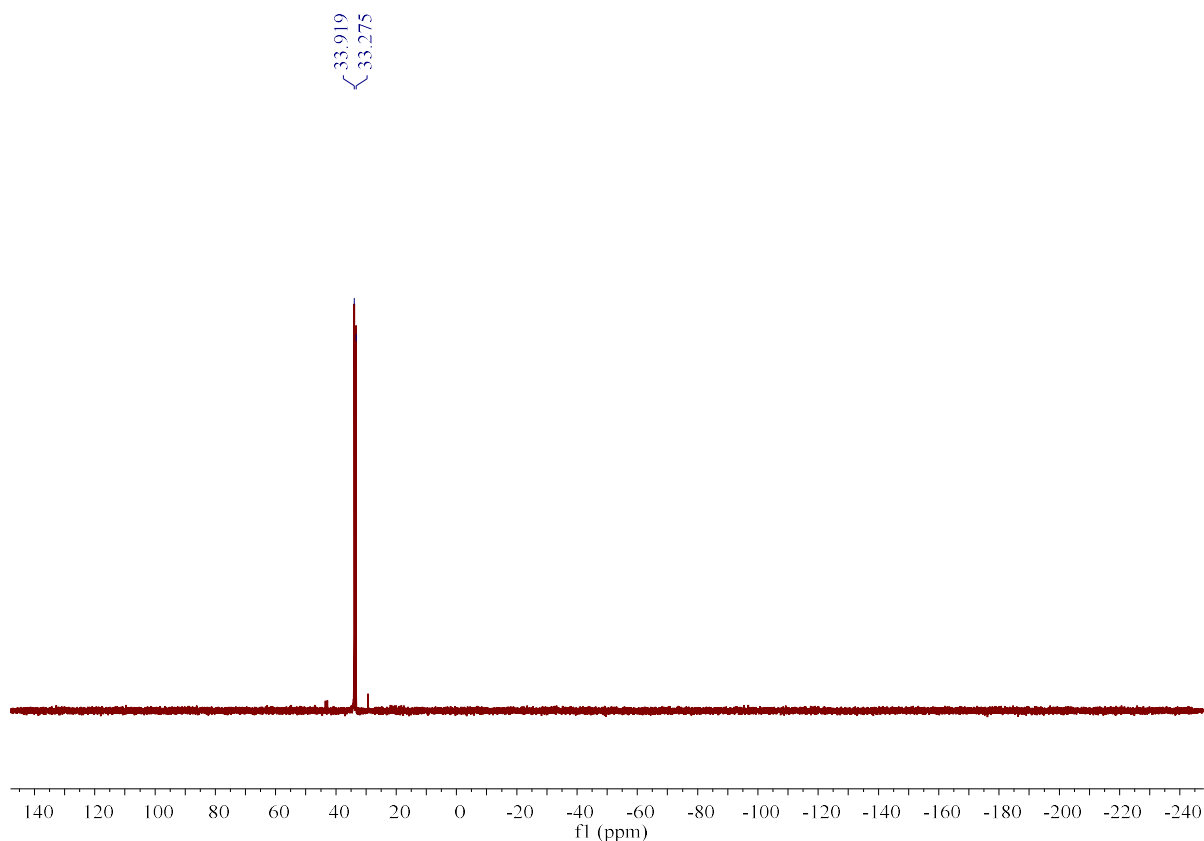
¹H NMR (600 MHz, CDCl₃) δ 7.78 (d, J = 8.2 Hz, 1H), 7.70 (d, J = 8.3 Hz, 1H), 7.56 (dd, J = 7.4, 1.6 Hz, 1H), 7.47 (s, 1H), 7.43 – 7.26 (m, 13H), 7.25 – 7.07 (m, 5H), 7.05 – 7.00 (m, 2H), 6.93 (d, J = 8.4 Hz, 1H), 6.90 (d, J = 8.5 Hz, 1H), 6.78 (t, J = 7.3 Hz, 1H), 6.71 – 6.66 (m, 1H), 5.32 (s, 1H), 5.11 (s, 1H), 4.21 (d, J = 13.1 Hz, 1H), 4.11 (dd, J = 15.3, 2.2 Hz, 1H), 4.05 (d, J = 13.1 Hz, 1H), 2.95 (t, J = 2.4 Hz, 1H), 2.84 (t, J = 15.7 Hz, 1H), 1.48 – 1.40 (m, 3H), 1.20 – 1.12 (m, 17H), 1.12 – 1.03 (m, 5H), 0.90 (d, J = 7.5 Hz, 9H), 0.87 (d, J = 7.5 Hz, 9H), 0.41 (s, 9H). **¹³C NMR (150 MHz, CDCl₃)** δ 175.7, 172.3, 152.4, 151.7, 139.6, 138.2 (d, J = 3.3 Hz), 138.0, 136.7, 134.1, 133.6, 130.2, 130.1, 129.9, 129.4, 129.3, 128.33, 128.27, 128.0, 127.9, 127.2, 126.8, 126.7, 126.4, 125.9, 125.4, 124.2, 123.7, 122.9, 117.2, 113.7, 110.1, 106.3 (d, J = 18.8 Hz), 103.0 (d, J = 3.3 Hz), 94.3, 74.1, 38.0, 26.8, 26.1, 25.9 (d, J = 3.5 Hz), 18.41, 18.38, 18.2, 18.1, 13.3, 12.9. **³¹P NMR (243 MHz, CDCl₃)** δ 33.60 (d, J = 156.5 Hz). **HRMS (ESI)**: calcd. for C₇₅H₈₇NNaO₅PRhSi₂⁺ [M+Na]⁺: 1294.4808, found: 1294.4815.



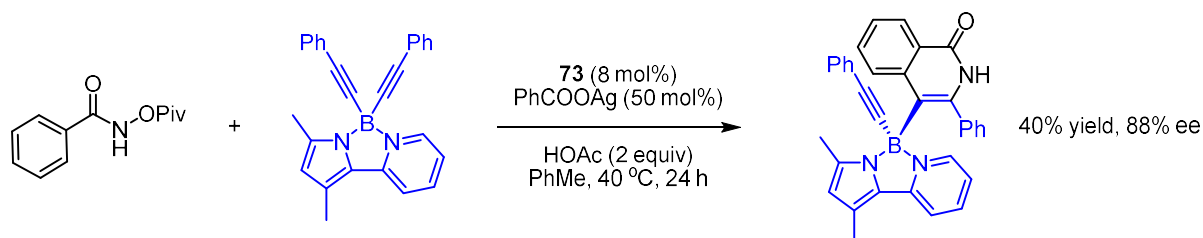
¹H NMR (600 MHz, CDCl₃) spectrum of 73.



¹³C NMR (150 MHz, CDCl₃) spectrum of 73.

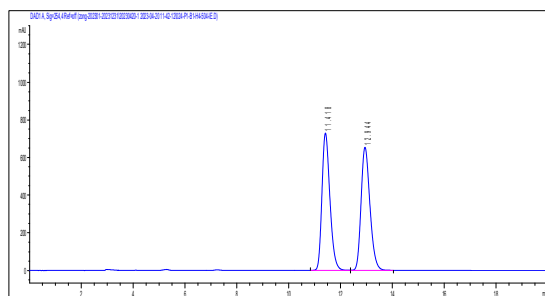


^{31}P NMR (243 MHz, CDCl_3) spectrum of **73.**

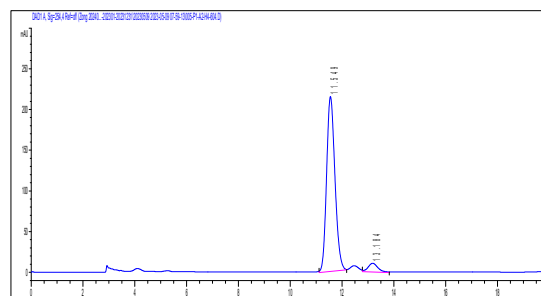


A screw-cap vial (8 mL) was charged with dialkynyl tetracoordinate boron substrate **1** (0.12 mmol, 1.2 equiv), benzamide **3** (0.10 mmol, 1.0 equiv), **73** (8 mol%), PhCOOAg (50 mol%) and HOAc (0.20 mmol, 2.0 equiv) in toluene (2 mL) and the reaction mixture was stirred at 40 °C for 24 h. The reaction mixture was evaporated under vacuum and the residue was purified by preparative TLC to give the corresponding products **24** (20.2 mg, 40%, 88% ee).

HPLC analysis: Daicel Chiralpak IE column (hexane: 2-propanol = 75:25, $v = 1.0$ mL/min, 40 °C, 254 nm); t_r (major) = 11.317 min, t_r (minor) = 12.589 min, 88% ee.



No.	Time	Area	Area (%)
1	11.418	15548.1	50.08
2	12.944	15496.7	49.92



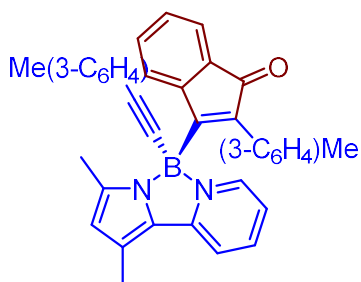
No.	Time	Area	Area (%)
1	11.549	4821	94.22
2	13.184	296.1	5.78

7.3 Rotational Barrier for Products 16, 24 and 53.

The enantiomerisation barrier, corresponding to the barrier to rotation for the following atropisomers, was obtained by kinetic of racemisation of an enantiomer. The slope of the first order kinetic line gives the racemisation constant ($k_{\text{racemisation}} = 2 \times k_{\text{enantiomerisation}}$). Eyring equation gives the enantiomerisation barrier ($\Delta G^{\ddagger}_{\text{enantiomerization}}$) from enantiomerisation constant ($k_{\text{enantiomerisation}}$), $R = 8.31451 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$, $h = 6.62608 \times 10^{-34} \text{ Js}$ and $k_B = 1.38066 \times 10^{-23} \text{ J/K}$. Reactions were conducted at 1 mg/mL concentration. Enantiomeric excess values were determined by HPLC.

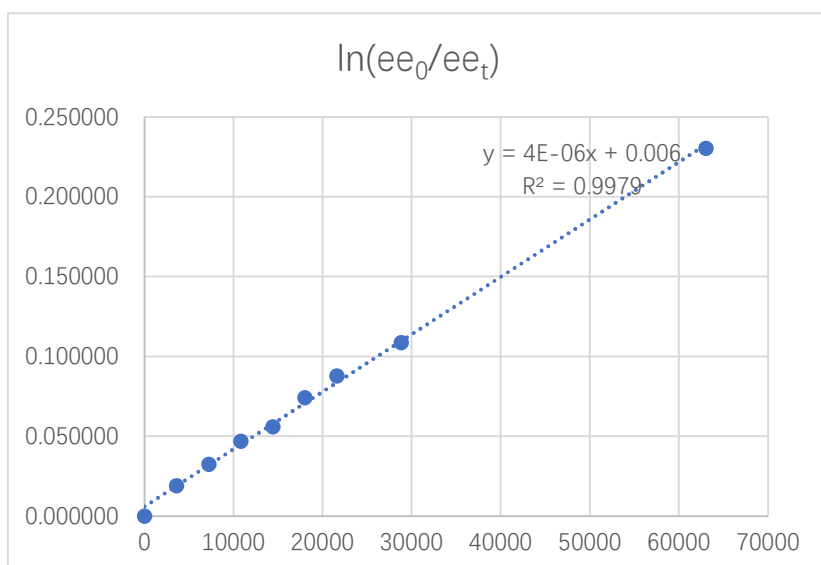
$$\Delta G^{\ddagger}_{\text{enantiomerization}} = RT \times \ln \frac{k_B \times T}{h \times k_{\text{enantiomerisation}}}$$

Racemization of **16** in toluene at 100 °C.



16. $\Delta G^\ddagger = 31.7 \text{ kcal/mol}$ (100 °C, toluene)

T(s)	ee	ln (ee ₀ /ee _t)
0	94.4	0.000000
3600	92.7	0.019136
7200	91.4	0.032610
10800	90.1	0.047045
14400	89.3	0.055963
18000	87.7	0.074271
21600	86.5	0.087820
28800	84.7	0.108731
63000	75.0	0.230610



$$k_{\text{racemization}} (100 \text{ }^\circ\text{C}) = 4.0 \times 10^{-6} \text{ s}^{-1}$$

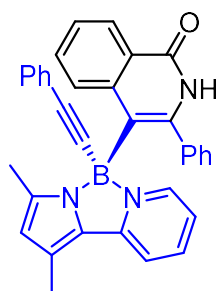
$$k_{\text{enantiomerization}} (100 \text{ }^\circ\text{C}) = 2 \times 10^{-6} \text{ s}^{-1}$$

$$\text{Employing the Eyring equation: } \Delta G^\ddagger = RT \ln\left(\frac{k_B \times T}{k_{\text{ent}} \times h}\right)$$

$$\Delta G^\ddagger = 8.314 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} \times 373.15 \text{ K} \times \ln\left(\frac{1.381 \times 10^{-23} \text{ J} \cdot \text{K}^{-1} \times 373.15 \text{ K}}{2.0 \times 10^{-6} \text{ s}^{-1} \times 6.626 \times 10^{-34} \text{ J} \cdot \text{s}}\right)$$

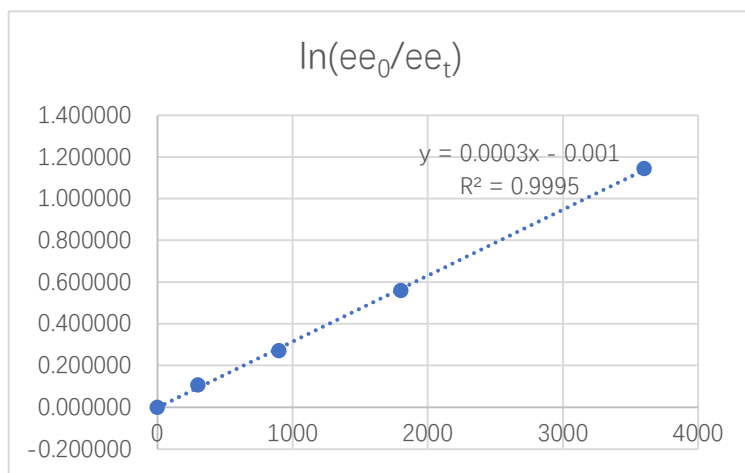
$$\Delta G^\ddagger = 132.8 \text{ kJ} \cdot \text{mol}^{-1} = 31.7 \text{ kcal} \cdot \text{mol}^{-1}$$

Racemization of **24** in toluene at 100 °C.



24. $\Delta G^\ddagger = 28.5 \text{ kcal/mol}$ (100 °C, toluene)

T(s)	ee	ln (ee ₀ /ee _t)
0	89.0	0.000000
300	79.9	0.107299
900	67.8	0.271365
1800	50.8	0.560178
3600	28.3	1.143800



$$k_{\text{racemization}} (100\text{ °C}) = 3.0 \times 10^{-4} \text{ s}^{-1}$$

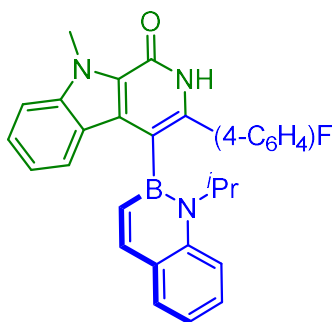
$$k_{\text{enantiomerization}} (100\text{ °C}) = 1.5 \times 10^{-4} \text{ s}^{-1}$$

$$\text{Employing the Eyring equation: } \Delta G^\ddagger = RT \ln\left(\frac{k_B \times T}{k_{\text{ent}} \times h}\right)$$

$$\Delta G^\ddagger = 8.314 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} \times 373.15 \text{ K} \times \ln\left(\frac{1.381 \times 10^{-23} \text{ J} \cdot \text{K}^{-1} \times 373.15 \text{ K}}{1.5 \times 10^{-4} \text{ s}^{-1} \times 6.626 \times 10^{-34} \text{ J} \cdot \text{s}}\right)$$

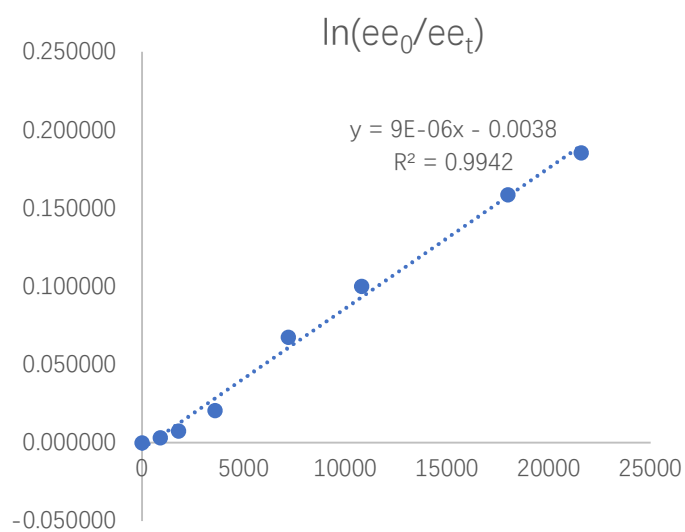
$$\Delta G^\ddagger = 119.4 \text{ kJ} \cdot \text{mol}^{-1} = 28.5 \text{ kcal} \cdot \text{mol}^{-1}$$

Racemization of **53** in toluene at 100 °C.



53. $\Delta G^\ddagger = 31.1$ kcal/mol (100 °C, toluene)

T(s)	ee	ln (ee ₀ /ee _t)
0	93.4	0.000000
900	93.1	0.003217
1800	92.7	0.007523
3600	91.5	0.020552
7200	87.3	0.067541
10800	84.5	0.100140
18000	79.7	0.158622
21600	77.6	0.185324



$$k_{\text{racemization}} (100\text{ }^\circ\text{C}) = 9.0 \times 10^{-6} \text{ s}^{-1}$$

$$k_{\text{enantiomerization}} (100\text{ }^\circ\text{C}) = 4.5 \times 10^{-6} \text{ s}^{-1}$$

Employing the Eyring equation: $\Delta G^\ddagger = RT \ln\left(\frac{k_B \times T}{k_{\text{ent}} \times h}\right)$

$$\Delta G^\ddagger = 8.314 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} \times 373.15 \text{ K} \times \ln\left(\frac{1.381 \times 10^{-2} \text{ J} \cdot \text{K}^{-1} \times 373.15}{4.5 \times 10^{-6} \text{ s}^{-1} \times 6.626 \times 10^{-34} \text{ J} \cdot \text{s}}\right)$$

$$\Delta G^\ddagger = 130.28 \text{ kJ} \cdot \text{mol}^{-1} = 31.1 \text{ kcal} \cdot \text{mol}^{-1}$$

8. X-Ray Crystallographic Data

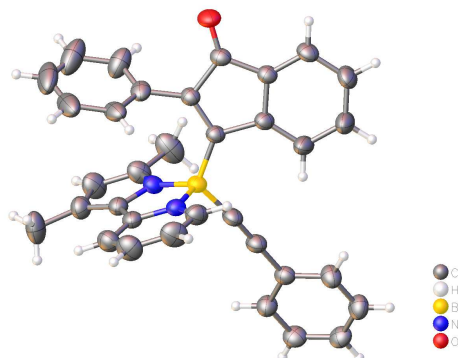


Table 1 Crystal data and structure refinement for 4 (CCDC 2410668).

Identification code	4
$C_{34}H_{25}BN_2O$	$C_{34}H_{25}BN_2O$
488.37	488.37
248.00	248.00
orthorhombic	orthorhombic
$P2_12_12_1$	$P2_12_12_1$
8.8066(3)	8.8066(3)
12.9199(4)	12.9199(4)
23.7613(8)	23.7613(8)
90	90
90	90
90	90
2703.57(15)	2703.57(15)
4	4
1.200	1.200
0.557	0.557
1024.0	1024.0
$0.32 \times 0.2 \times 0.1$	$0.32 \times 0.2 \times 0.1$
$CuK\alpha$ ($\lambda = 1.54178$)	$CuK\alpha$ ($\lambda = 1.54178$)
7.44 to 136.834	7.44 to 136.834
$-10 \leq h \leq 10, -15 \leq k \leq 15, -28 \leq l \leq 28$	$-10 \leq h \leq 10, -15 \leq k \leq 15, -28 \leq l \leq 28$
41242	41242
4970 [$R_{int} = 0.0535, R_{sigma} = 0.0219$]	4970 [$R_{int} = 0.0535, R_{sigma} = 0.0219$]
4970/0/345	4970/0/345
1.043	1.043
$R_1 = 0.0320, wR_2 = 0.0827$	$R_1 = 0.0320, wR_2 = 0.0827$
$R_1 = 0.0348, wR_2 = 0.0855$	$R_1 = 0.0348, wR_2 = 0.0855$
0.31/-0.14	0.31/-0.14
0.02(9)	0.02(9)

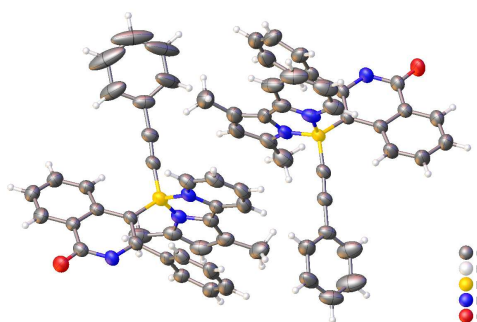


Table 2 Crystal data and structure refinement for 24 (CCDC 2410665).

Identification code	24
Empirical formula	C ₆₈ H ₅₀ B ₂ N ₆ O ₂
Formula weight	1004.76
Temperature/K	153.00
Crystal system	triclinic
Space group	P1
a/Å	9.7361(13)
b/Å	10.7220(15)
c/Å	13.5115(18)
α/°	92.461(6)
β/°	93.848(5)
γ/°	105.447(6)
Volume/Å ³	1353.7(3)
Z	1
ρ _{calc} /cm ³	1.232
μ/mm ⁻¹	0.582
F(000)	526.0
Crystal size/mm ³	0.5 × 0.4 × 0.3
Radiation	CuKα (λ = 1.54178)
2θ range for data collection/°	6.57 to 149.016
Index ranges	-12 ≤ h ≤ 12, -13 ≤ k ≤ 13, -16 ≤ l ≤ 16
Reflections collected	39542
Independent reflections	10415 [R _{int} = 0.0539, R _{sigma} = 0.0454]
Data/restraints/parameters	10415/3/707
Goodness-of-fit on F ²	1.049
Final R indexes [I ≥ 2σ (I)]	R ₁ = 0.0700, wR ₂ = 0.1959
Final R indexes [all data]	R ₁ = 0.0782, wR ₂ = 0.2093
Largest diff. peak/hole / e Å ⁻³	0.81/-0.21
Flack parameter	0.11(16)

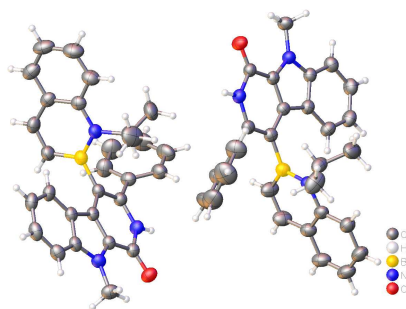


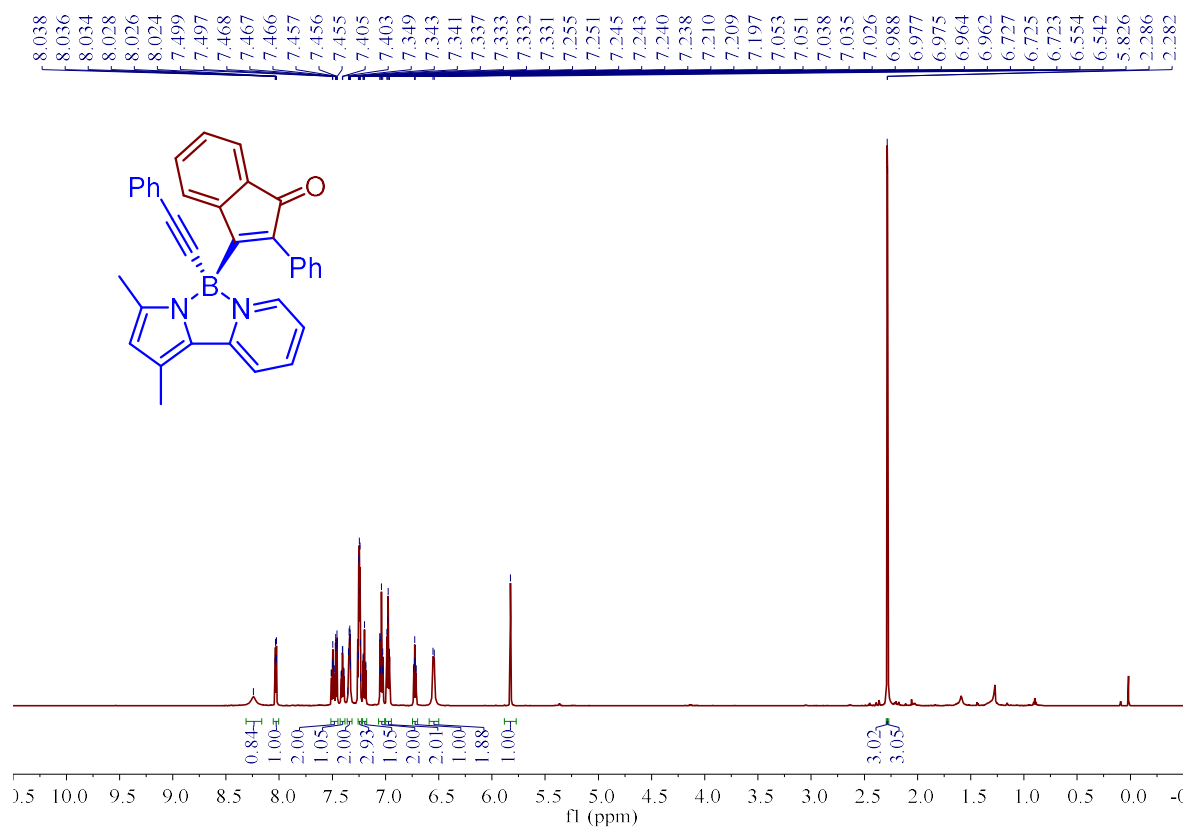
Table 3 Crystal data and structure refinement for compound 44 (CCDC 2410664).

Identification code	44
Empirical formula	C ₅₈ H ₅₂ B ₂ N ₆ O ₂
Formula weight	886.67
Temperature/K	200.00
Crystal system	orthorhombic
Space group	P2 ₁ 2 ₁ 2 ₁
a/Å	9.0688(2)
b/Å	16.1207(4)
c/Å	32.3718(8)
α/°	90
β/°	90
γ/°	90
Volume/Å ³	4732.6(2)
Z	4
ρ _{calc} /cm ³	1.244
μ/mm ⁻¹	0.590
F(000)	1872.0
Crystal size/mm ³	0.3 × 0.2 × 0.1
Radiation	CuKα (λ = 1.54178)
2θ range for data collection/°	5.46 to 136.566
Index ranges	-10 ≤ h ≤ 10, -19 ≤ k ≤ 19, -38 ≤ l ≤ 38
Reflections collected	77954
Independent reflections	8660 [R _{int} = 0.0527, R _{sigma} = 0.0221]
Data/restraints/parameters	8660/0/627
Goodness-of-fit on F ²	1.053
Final R indexes [I ≥ 2σ (I)]	R ₁ = 0.0343, wR ₂ = 0.0859
Final R indexes [all data]	R ₁ = 0.0382, wR ₂ = 0.0893
Largest diff. peak/hole / e Å ⁻³	0.14/-0.14
Flack parameter	0.14(8)

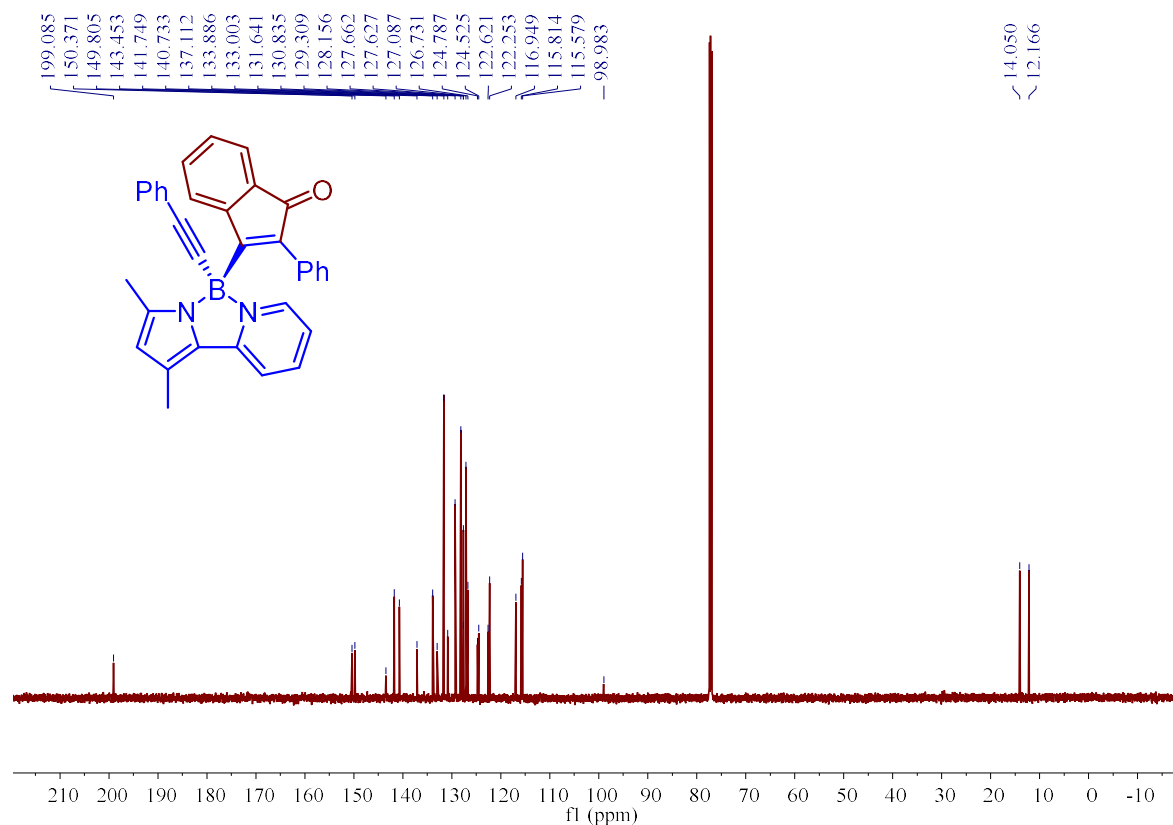
9. References

- [1] (a) B. Ye, N. Cramer. *J. Am. Chem. Soc.* **2013**, *135*, 636. (b) N. Zheng, W. Cui, C. Zheng, S. You. *J. Am. Chem. Soc.* **2016**, *138*, 5242.
- [2] (a) F. Wang, Z. Qi, Y. Zhao, S. Zhai, G. Zheng, R. Mi, Z. Huang, X. Zhu, X. He, X. Li. *Angew. Chem., Int. Ed.* **2020**, *59*, 13288–13294. (b) F. Wang, J. Jing, Y. Zhao, X. Zhu, X.-P. Zhang, L. Zhao, P. Hu, W.-Q. Deng, X. Li. *Angew. Chem., Int. Ed.* **2021**, *60*, 16628–16633. (c) 66) X. Zhu, R. Mi, J. Yin, F. Wang, X. Li. *Chem. Sci.* **2023**, *14*, 7999–8005.
- [3] (a) B. Zu, Y. Guo, C. He. *J. Am. Chem. Soc.* **2021**, *143*, 16302–16310. (b) 57) H. Wang, B. Qiao, J. Zhu, H. Guo, Z. Zhang, K. Yang, S.-J. Li, Y. Lan, Q. Song. *Chem.* **2024**, *10*, 317–329.
- [4] J. Selby, M. Holzapfel, B. K. Lombe, D. Schmidt, A.-M. Krause, F. Würthner, G. Bringmann, C. Lambert. *J. Org. Chem.* **2020**, *85*, 12227–12242.

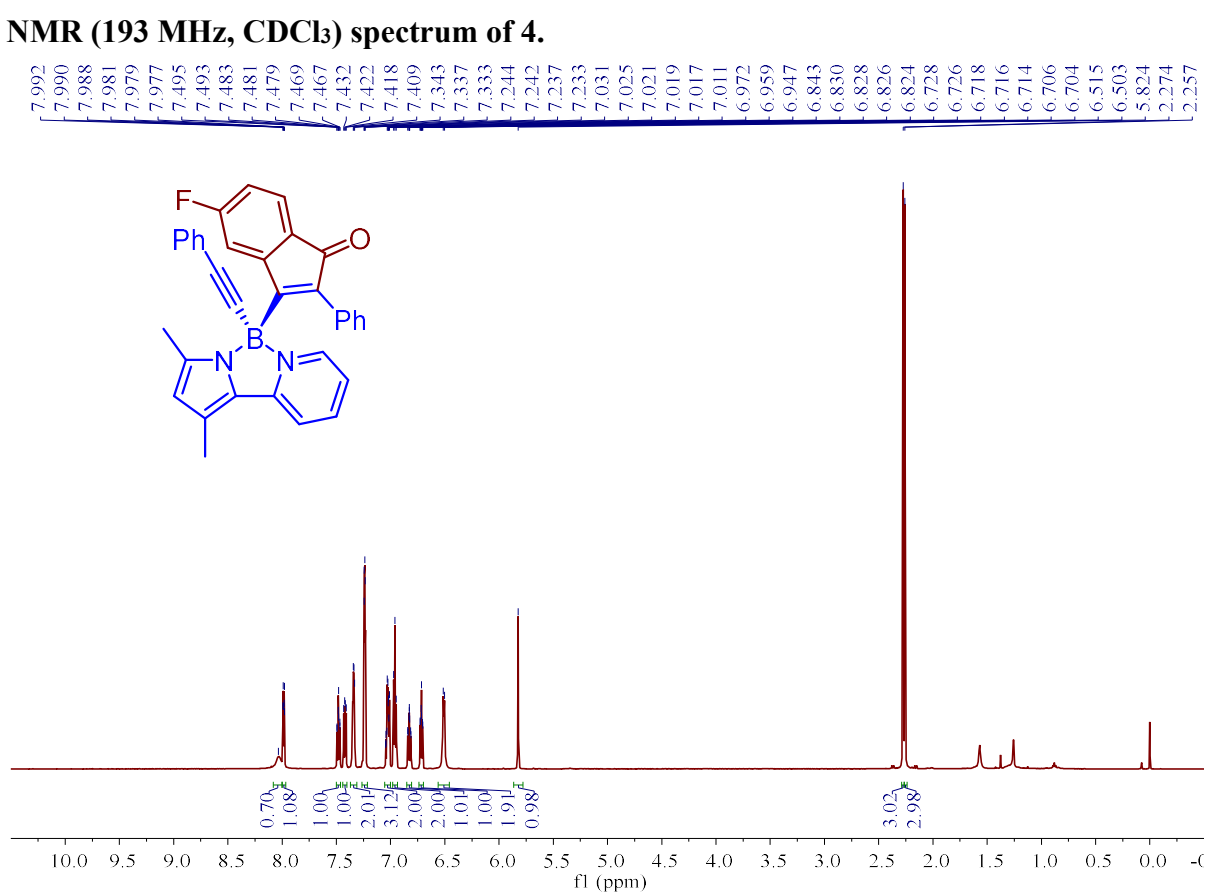
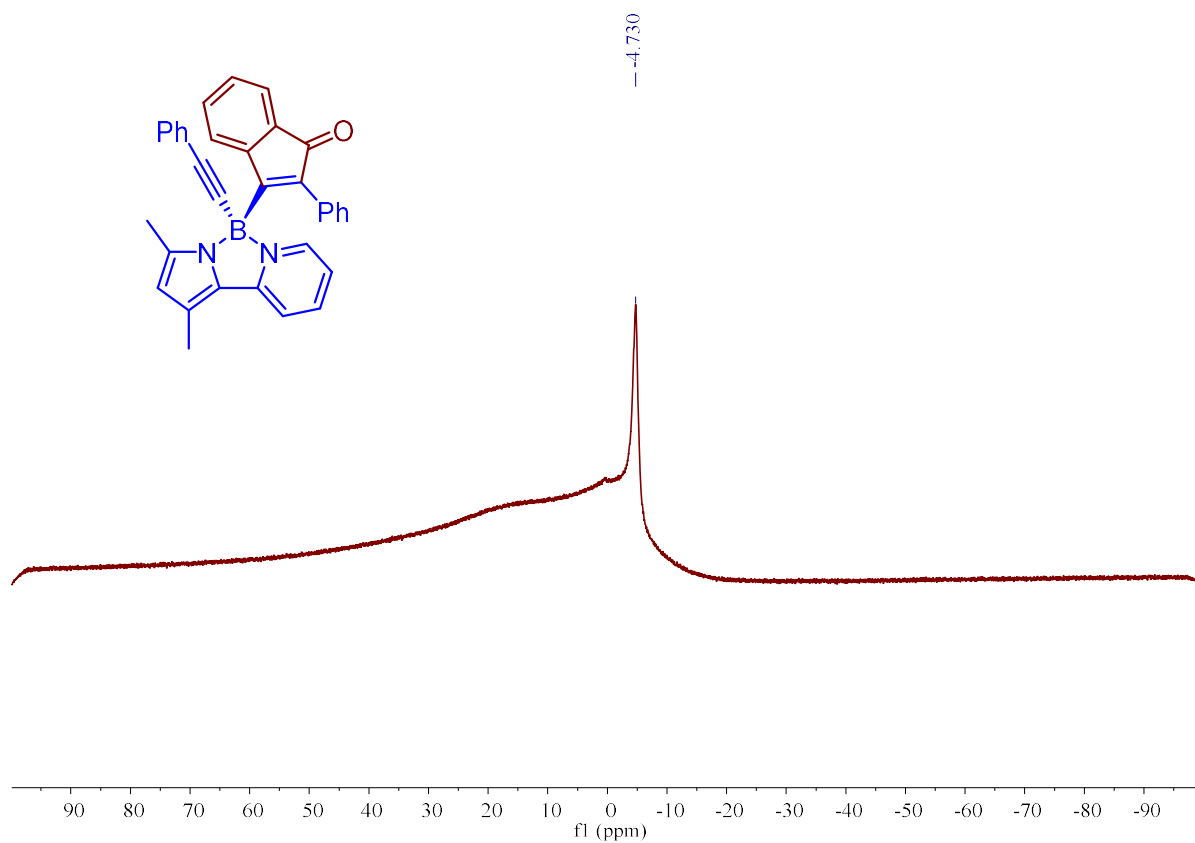
10. NMR Spectra

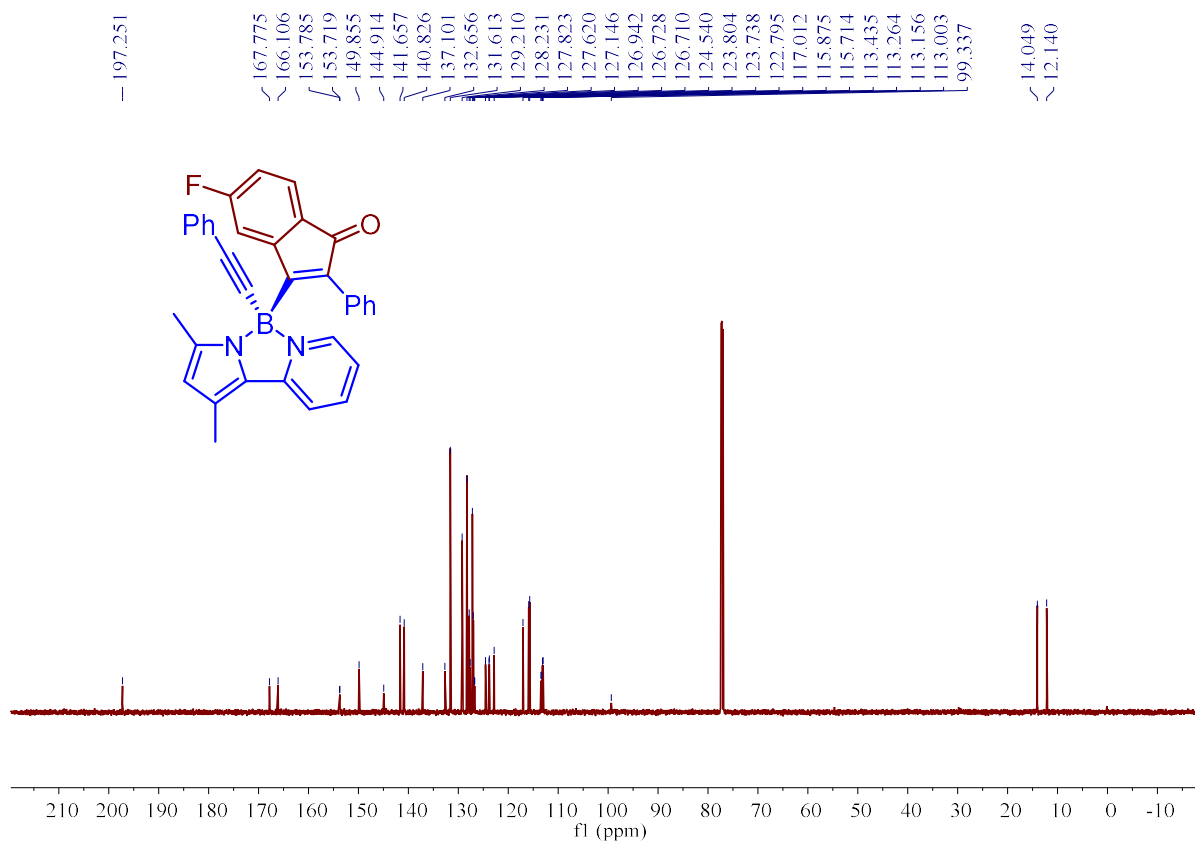


¹H NMR (600 MHz, CDCl₃) spectrum of 4.

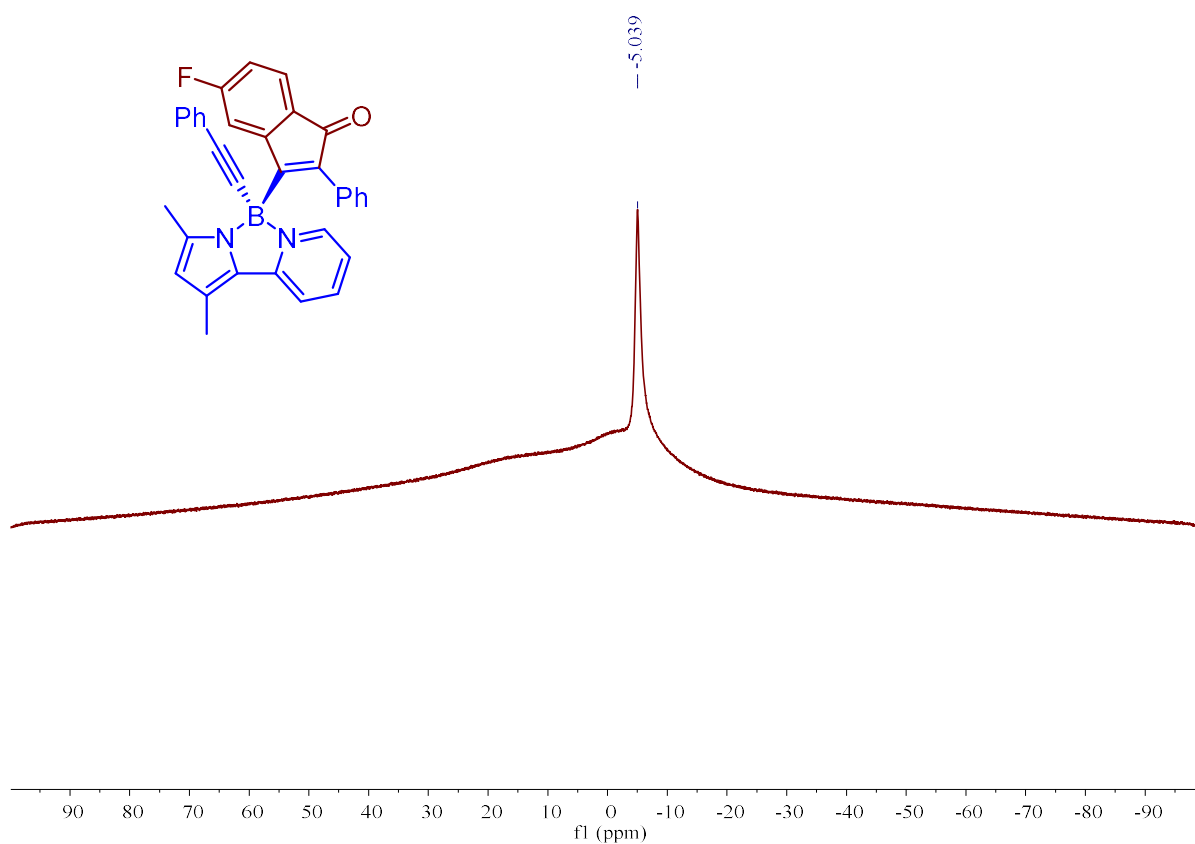


¹³C NMR (150 MHz, CDCl₃) spectrum of 4.

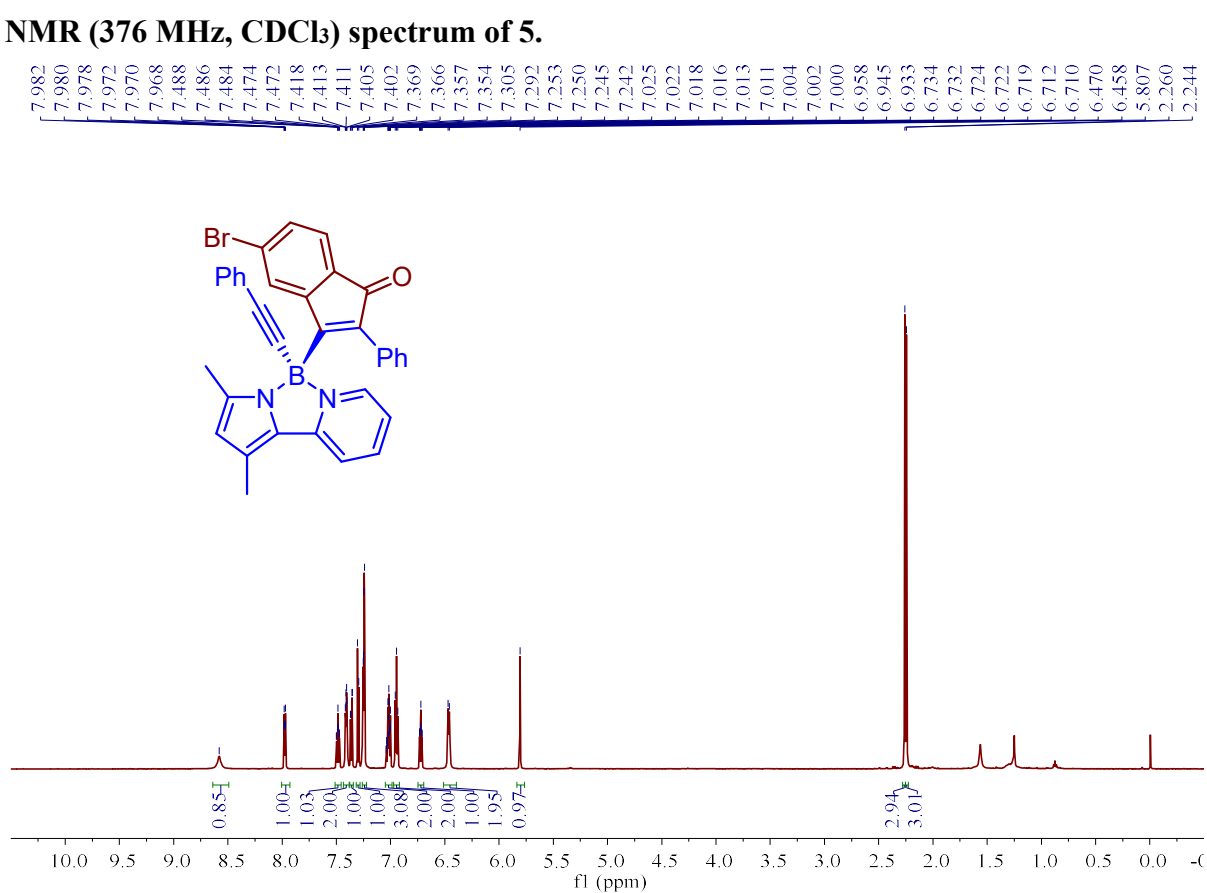
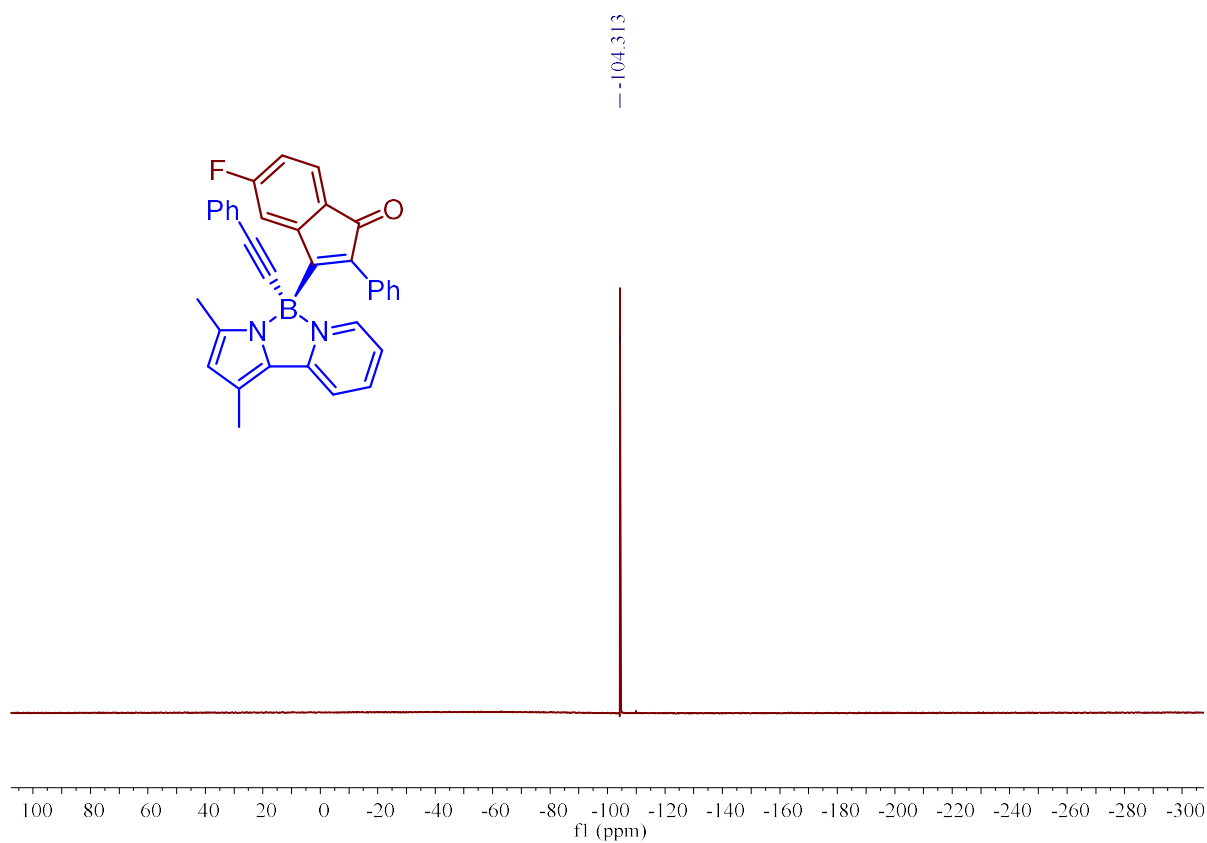


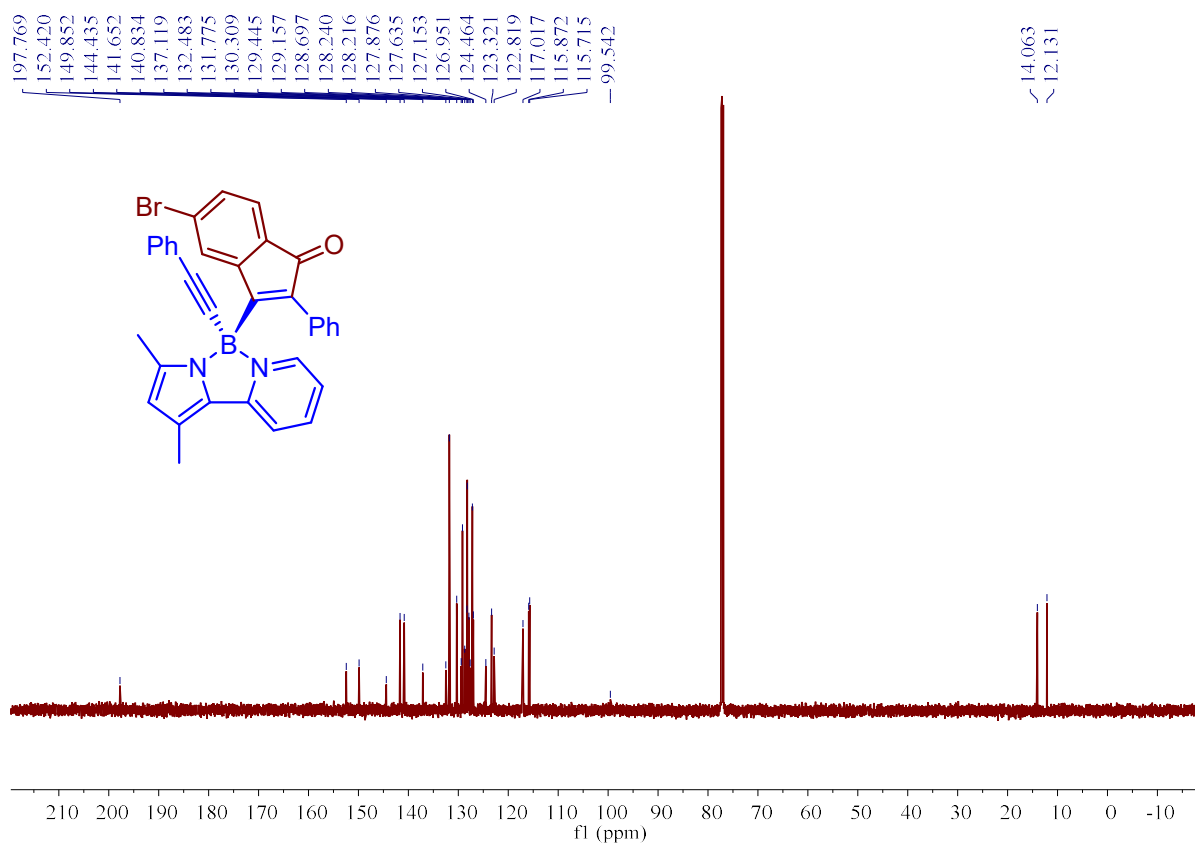


¹³C NMR (150 MHz, CDCl₃) spectrum of 5.

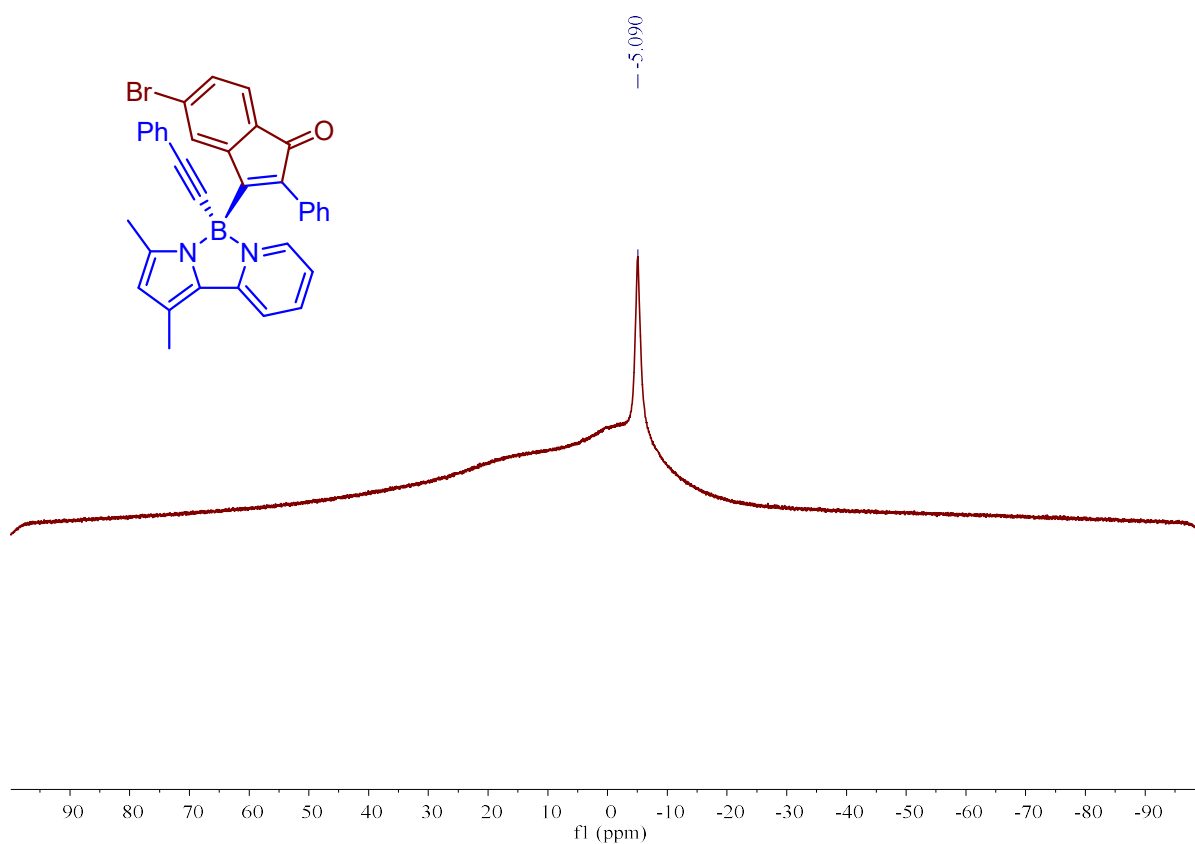


¹¹B NMR (193 MHz, CDCl₃) spectrum of 5.

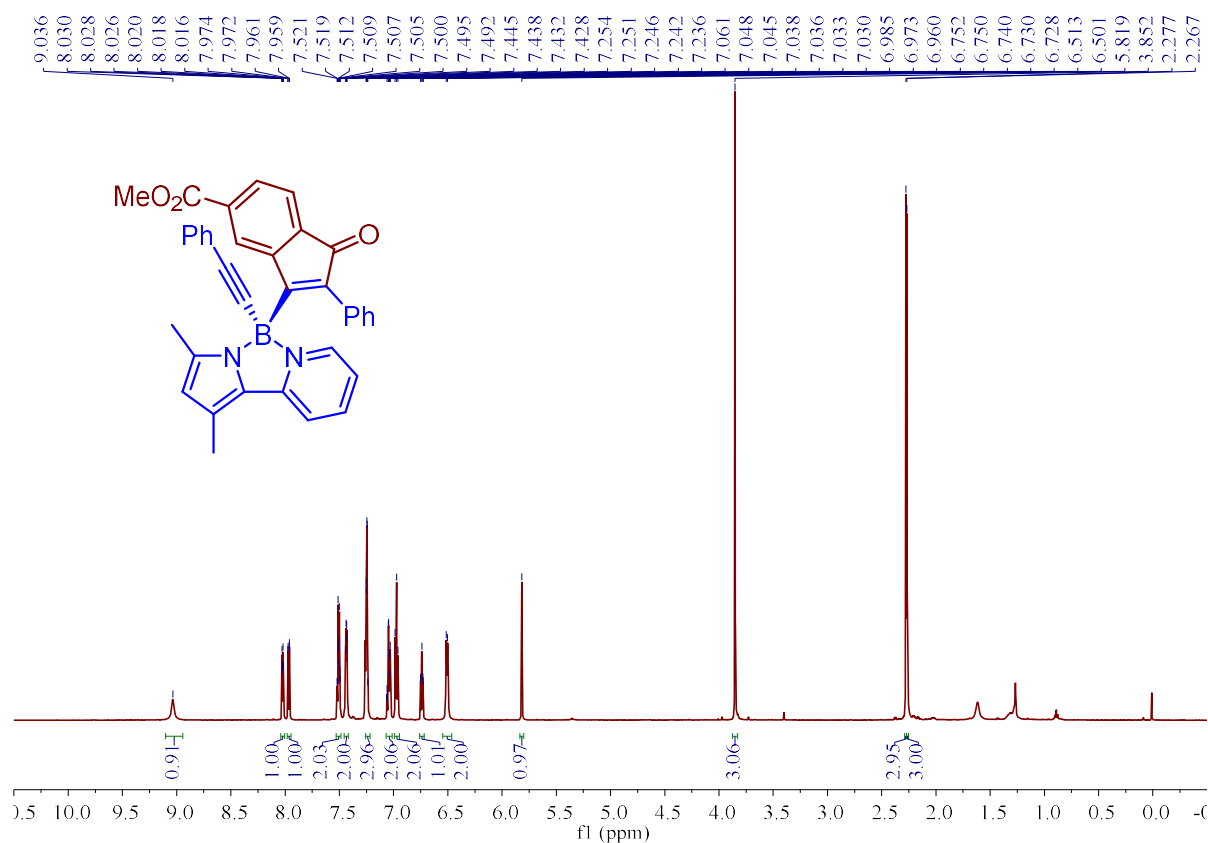




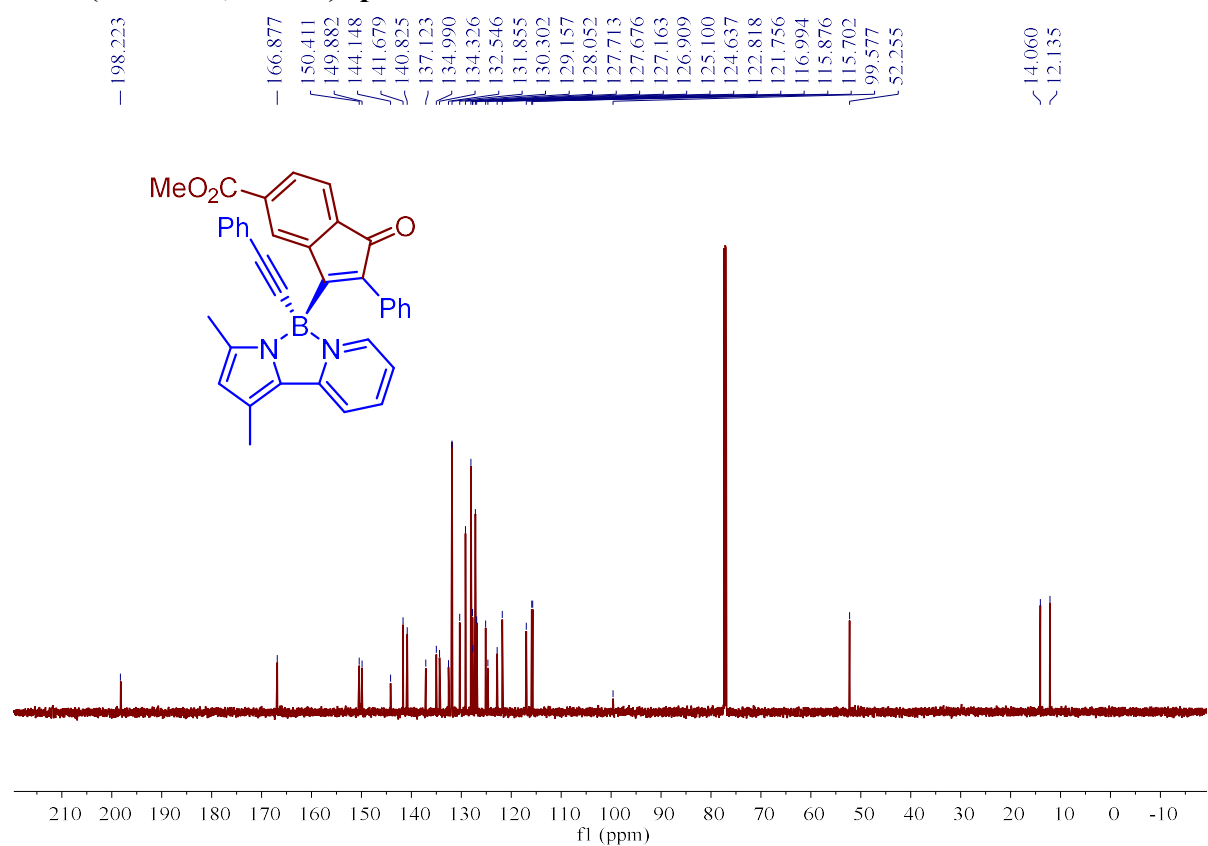
¹³C NMR (150 MHz, CDCl₃) spectrum of 6.



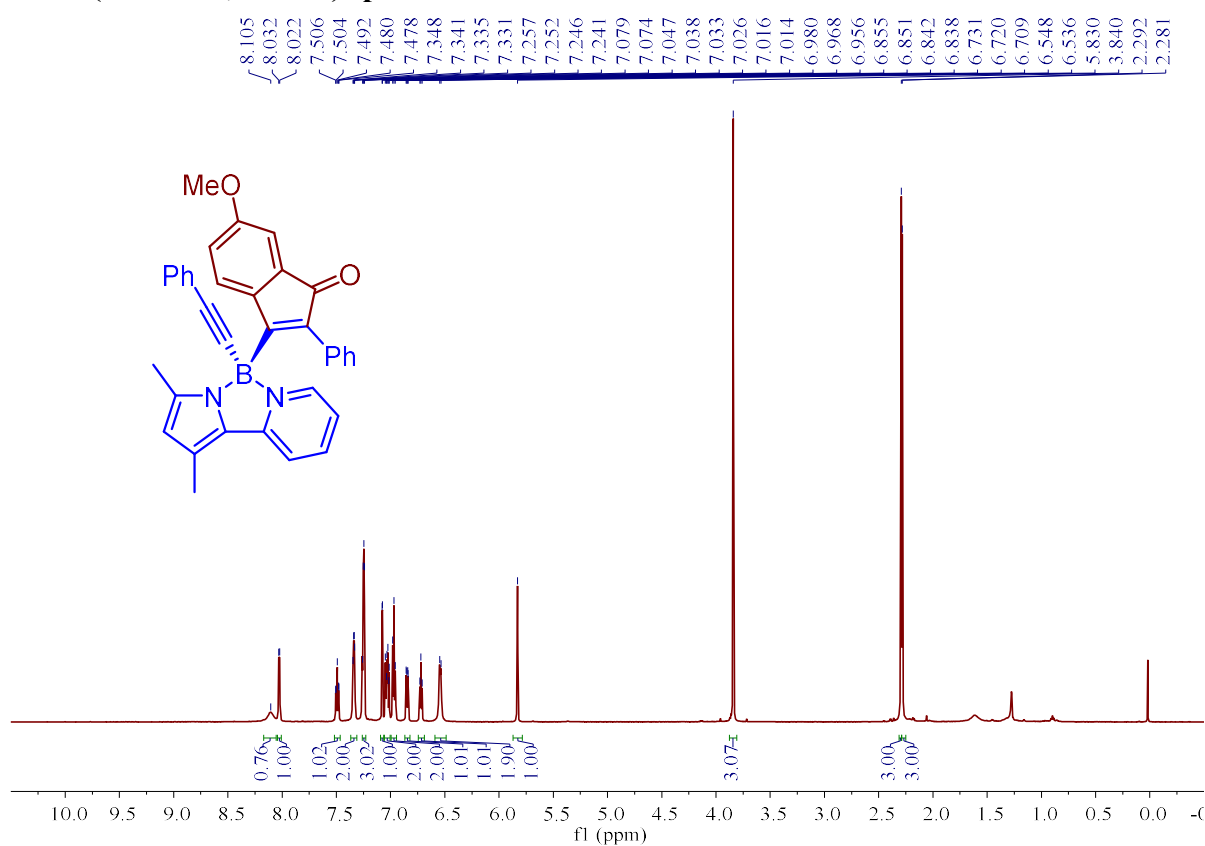
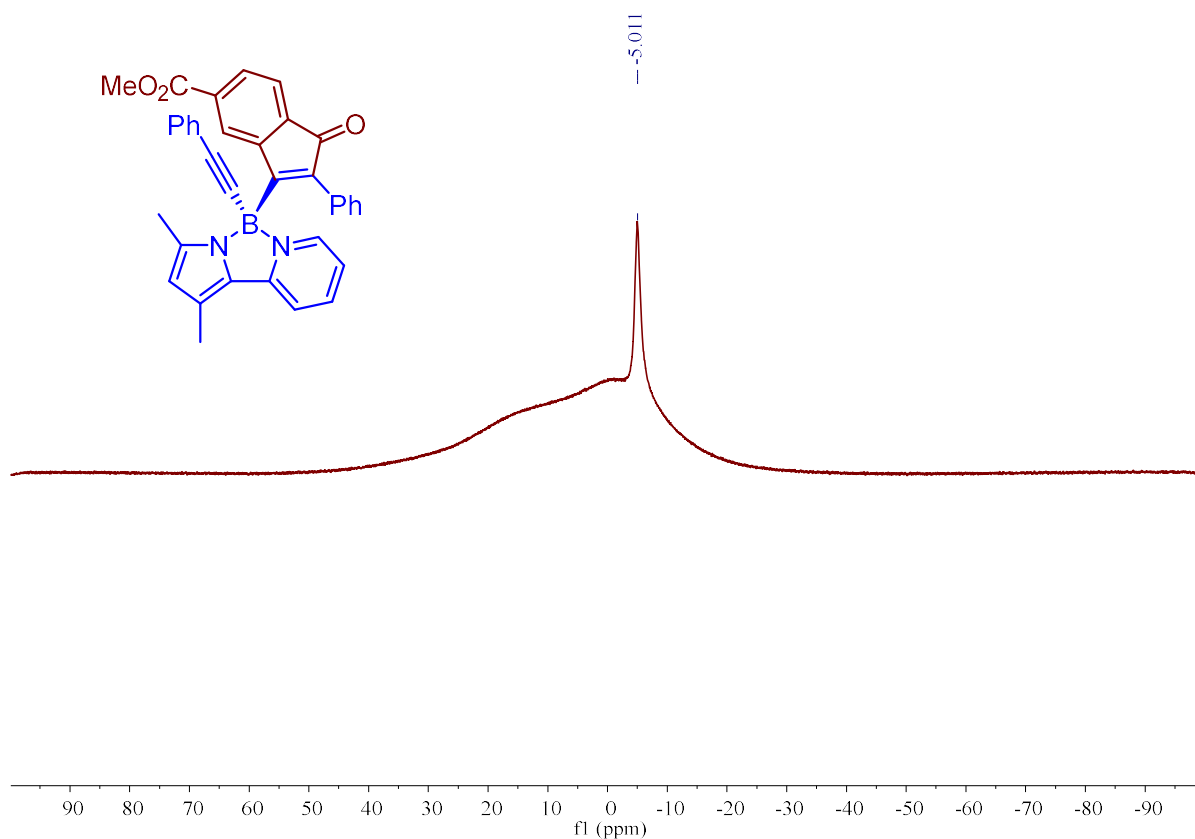
¹¹B NMR (193 MHz, CDCl₃) spectrum of 6.

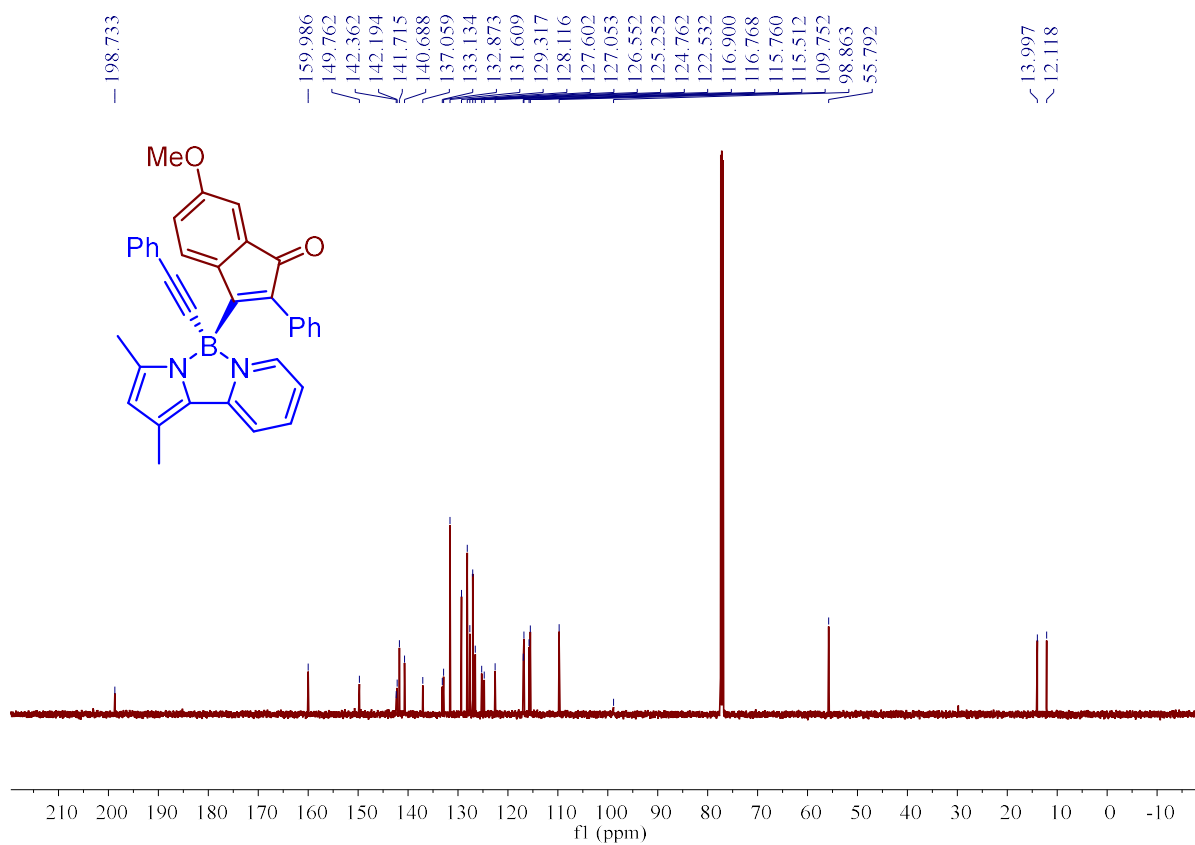


¹H NMR (600 MHz, CDCl₃) spectrum of 7.

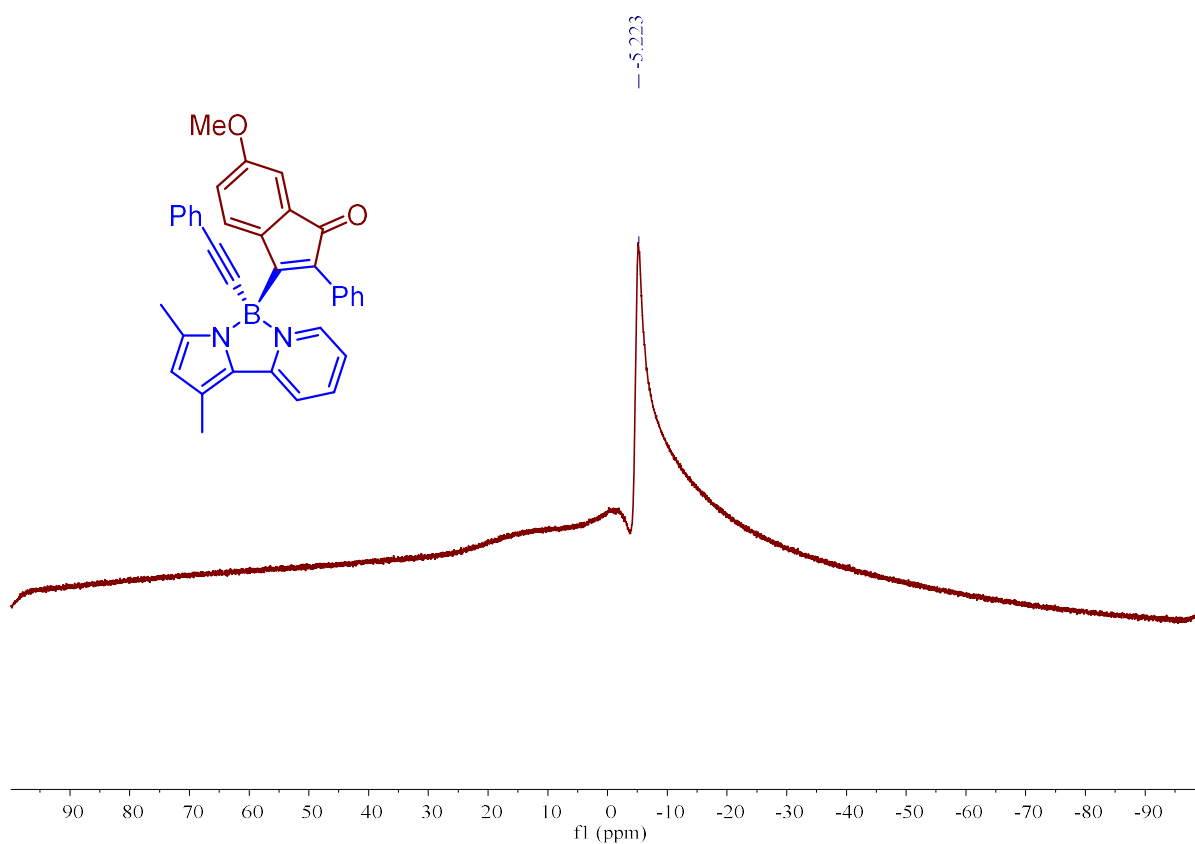


¹³C NMR (150 MHz, CDCl₃) spectrum of 7.

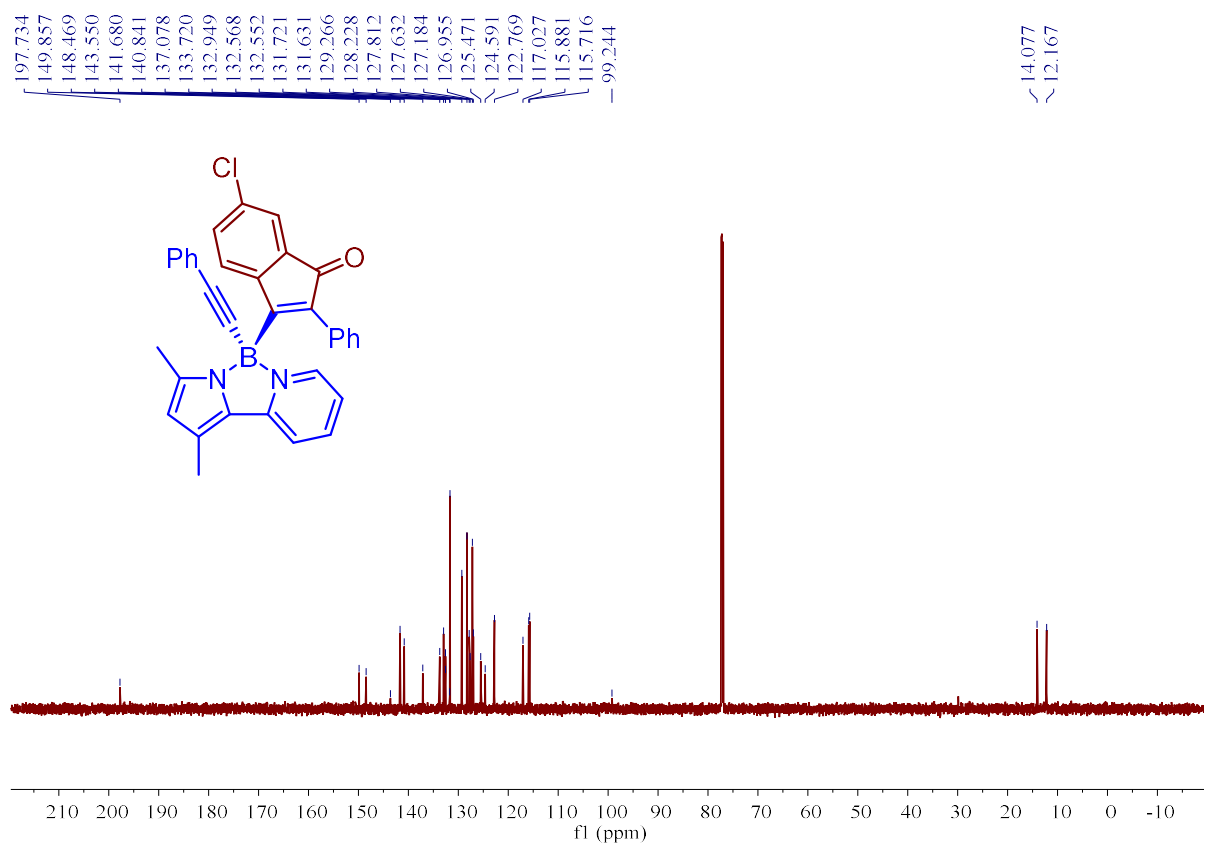
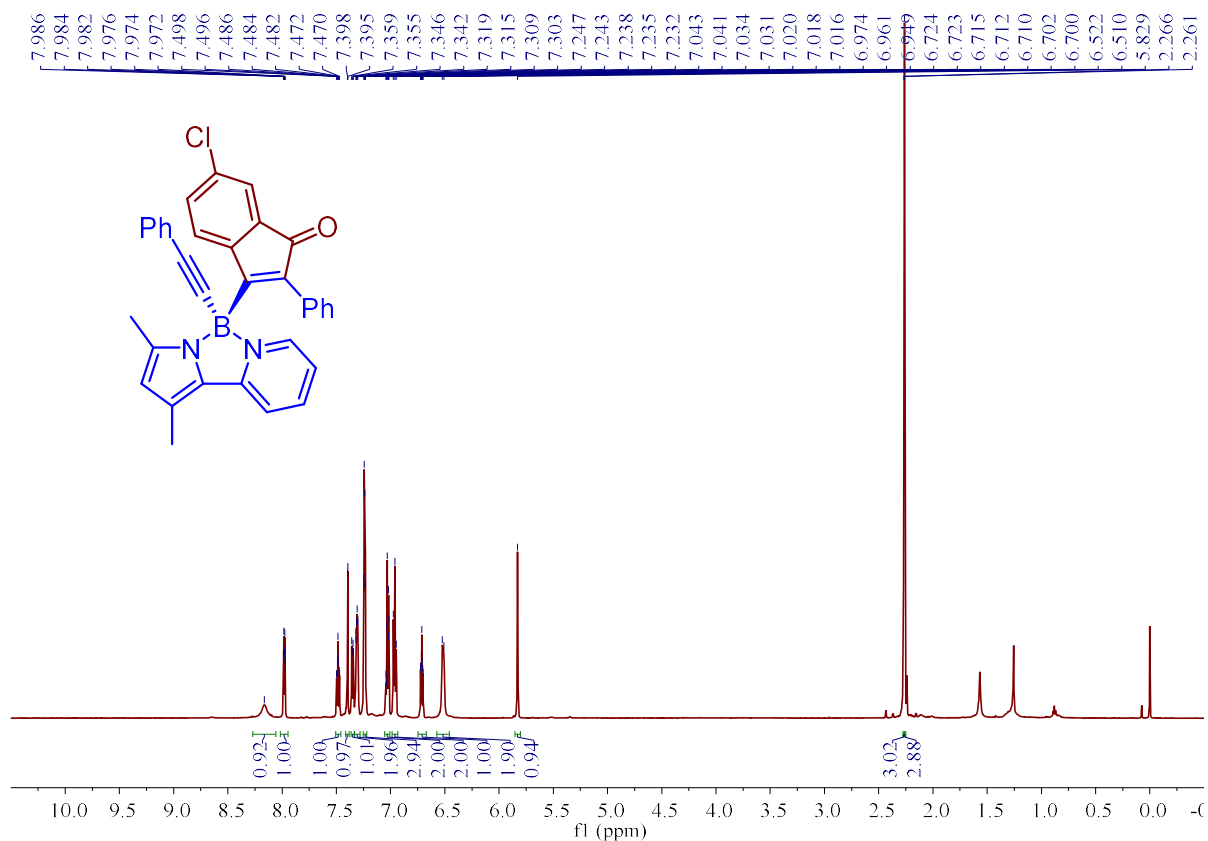


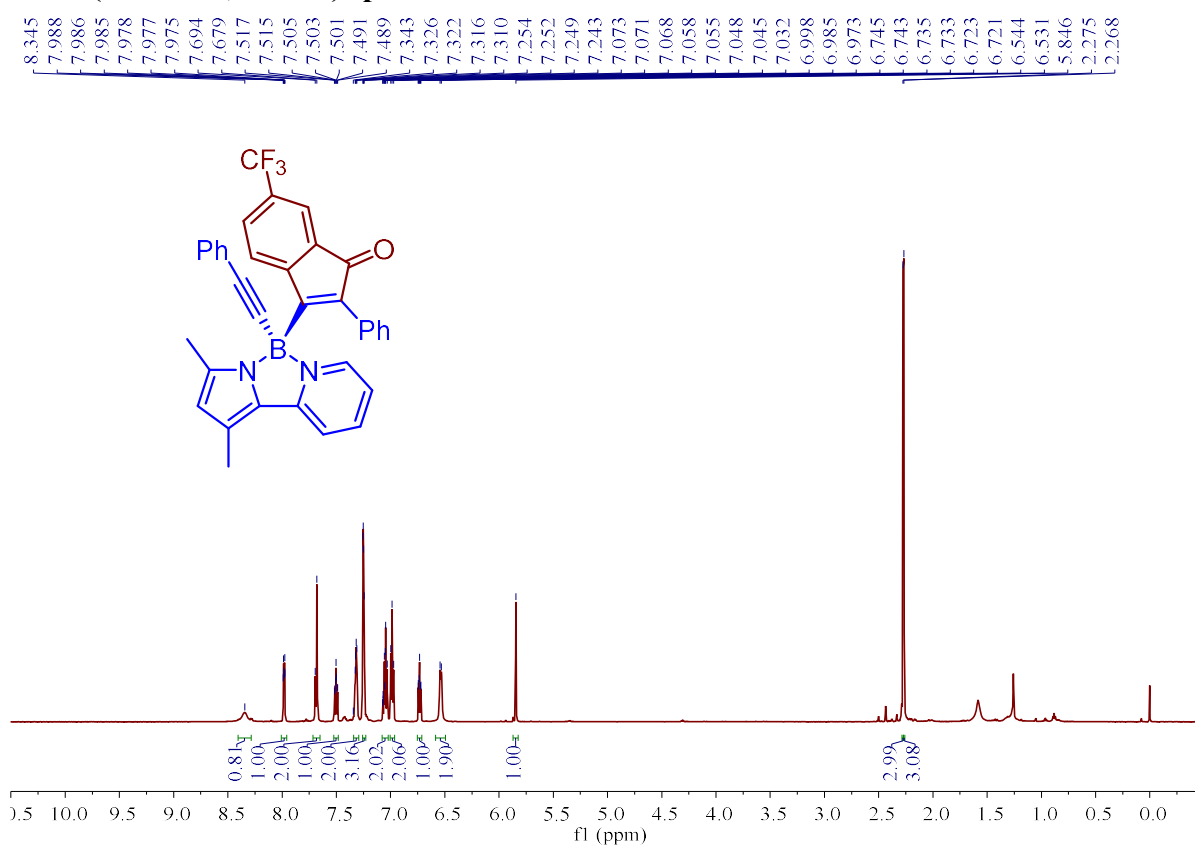
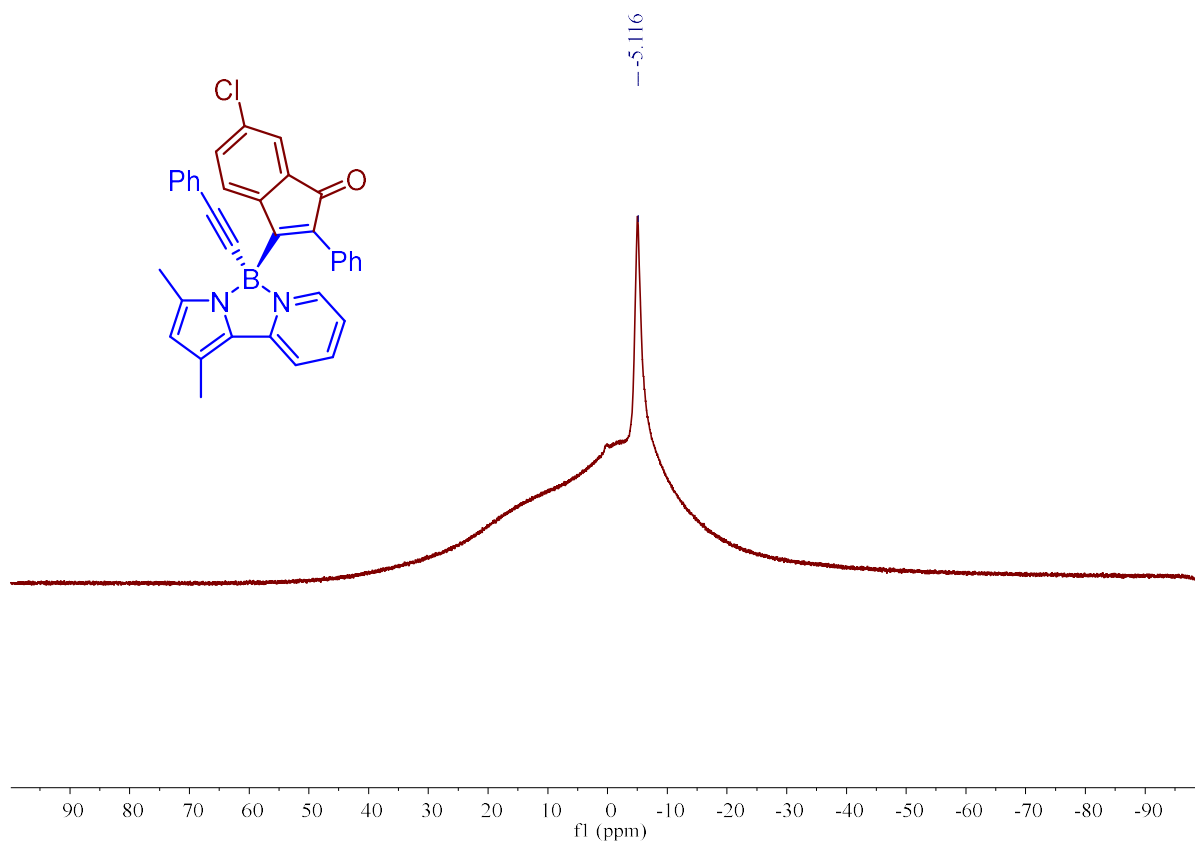


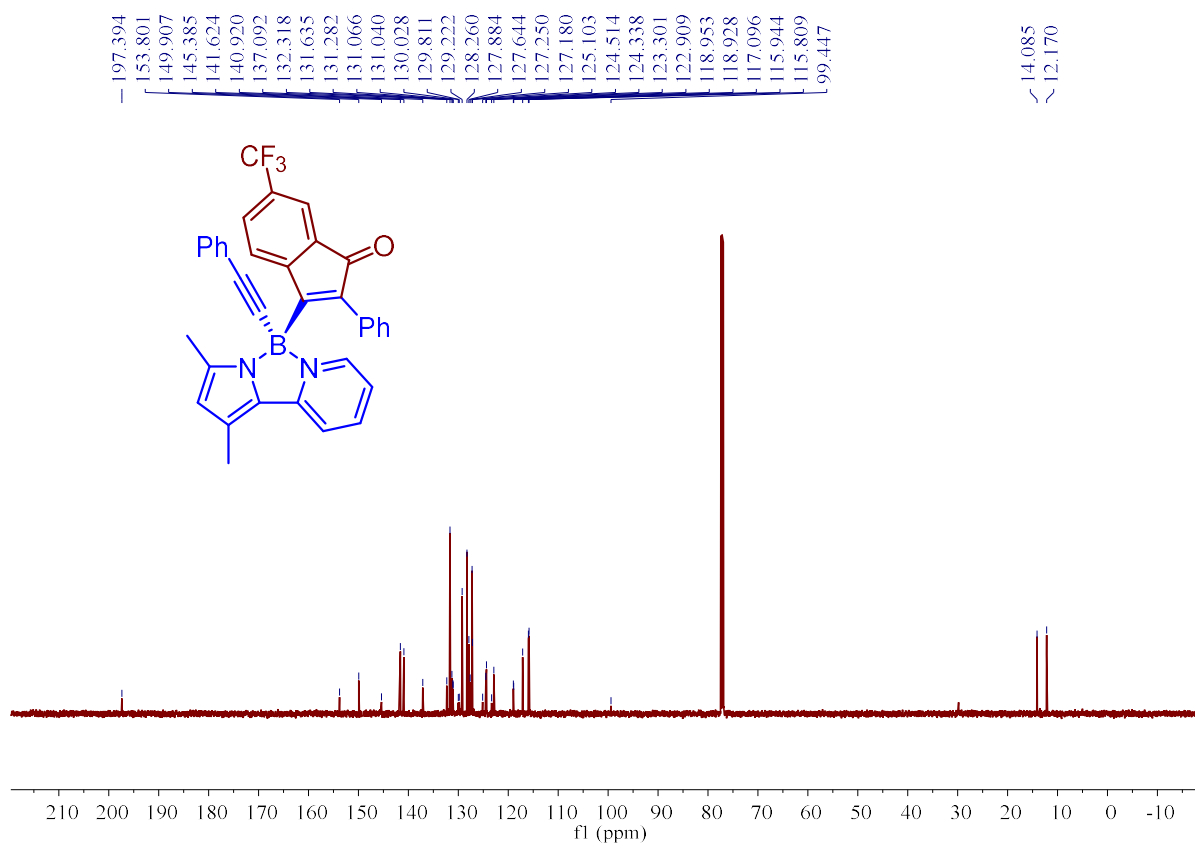
¹³C NMR (150 MHz, CDCl₃) spectrum of 8.



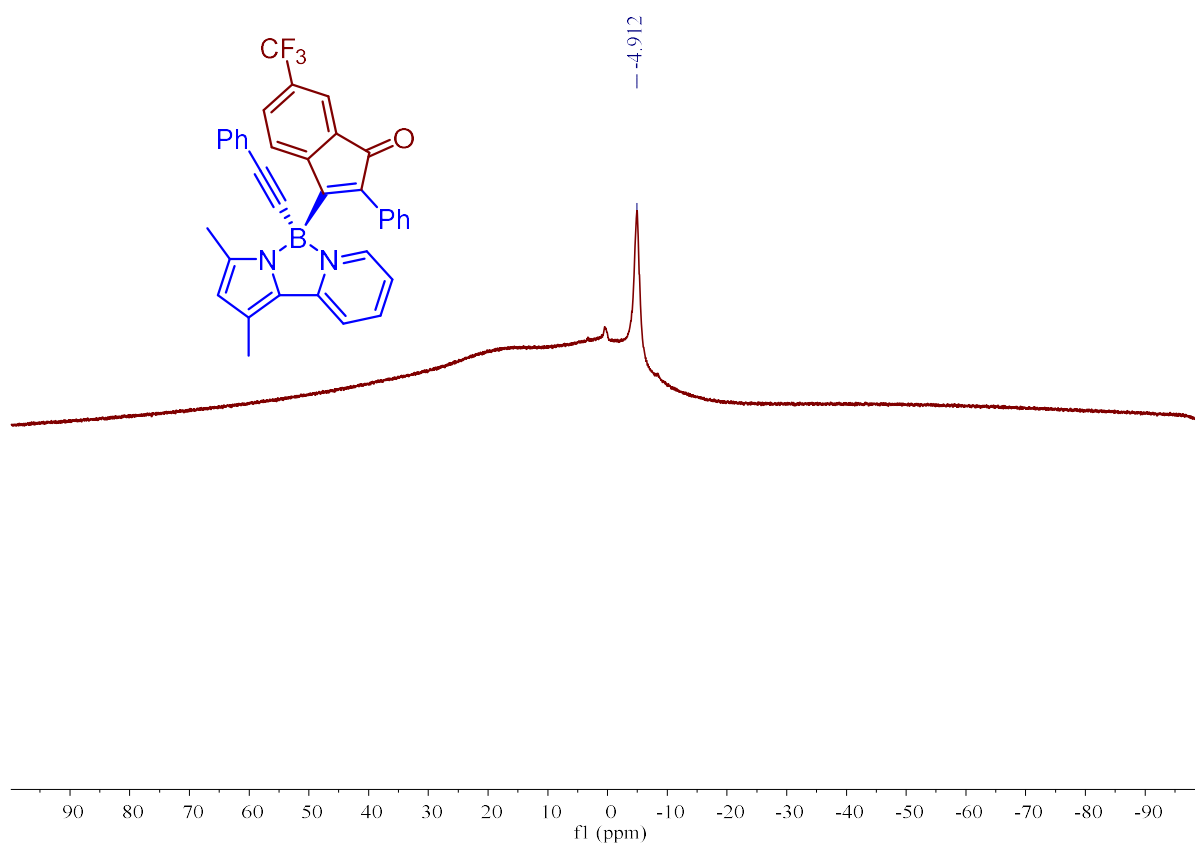
¹¹B NMR (193 MHz, CDCl₃) spectrum of 8.



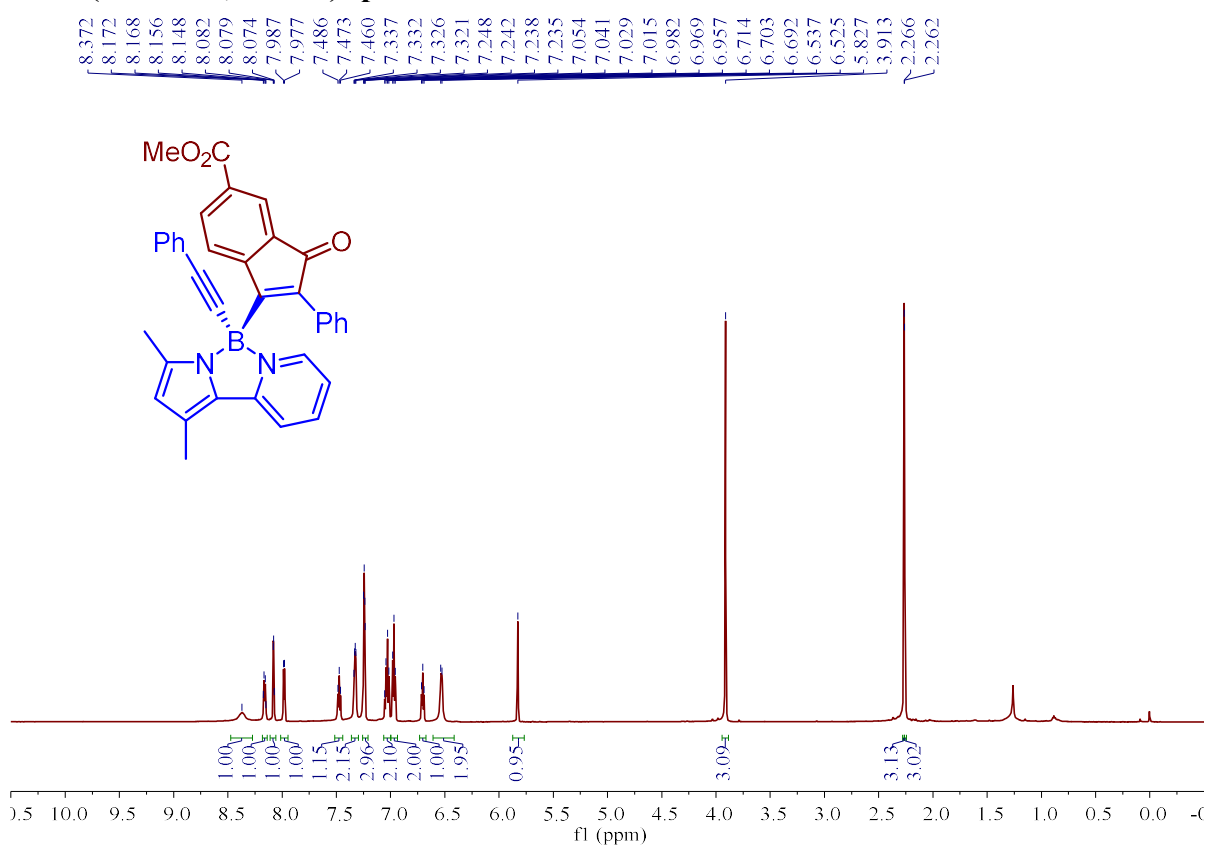
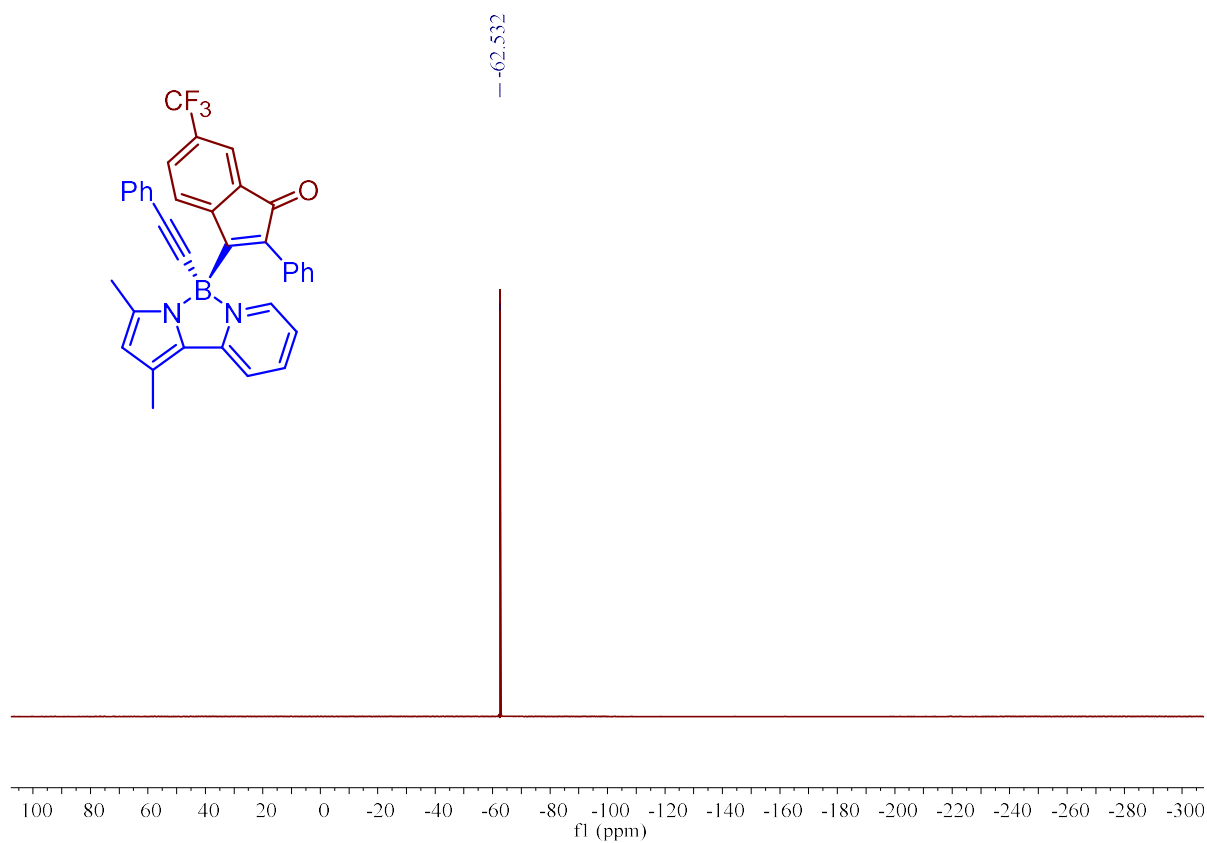


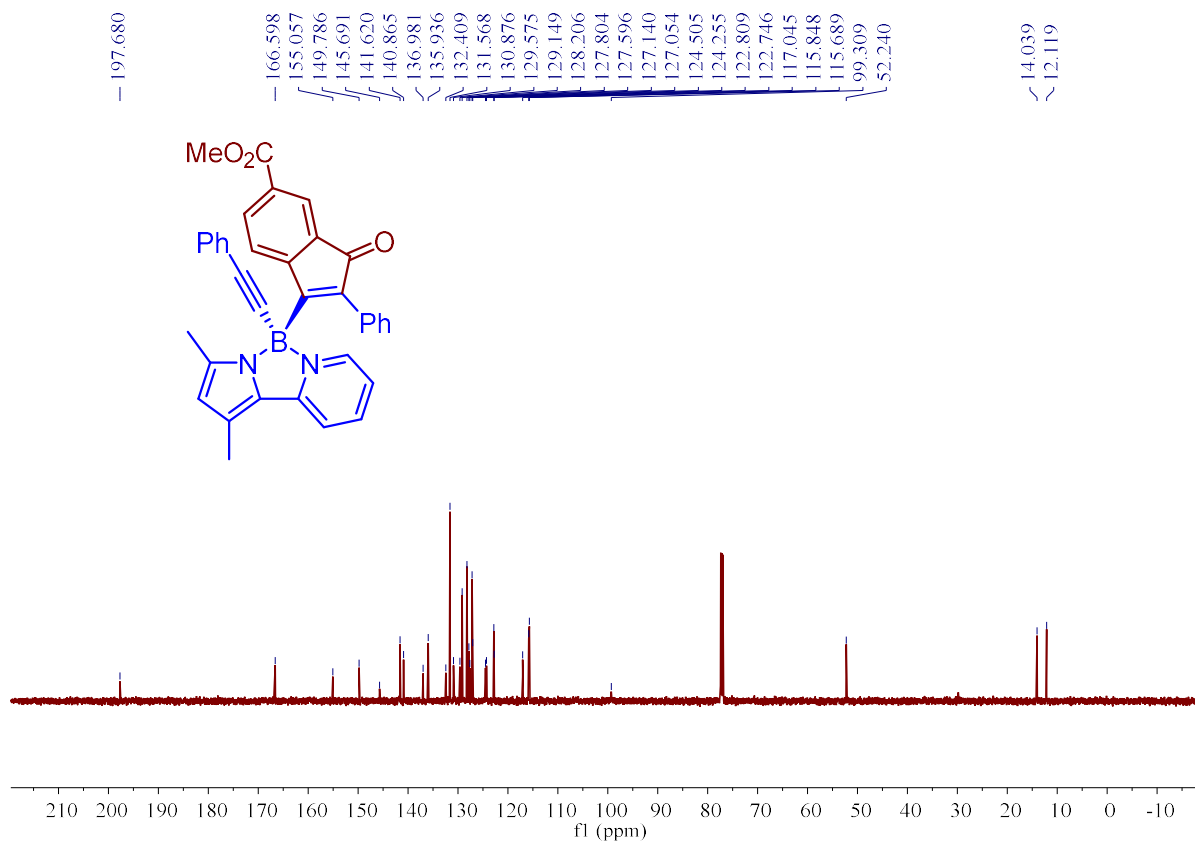


¹³C NMR (150 MHz, CDCl₃) spectrum of 10.

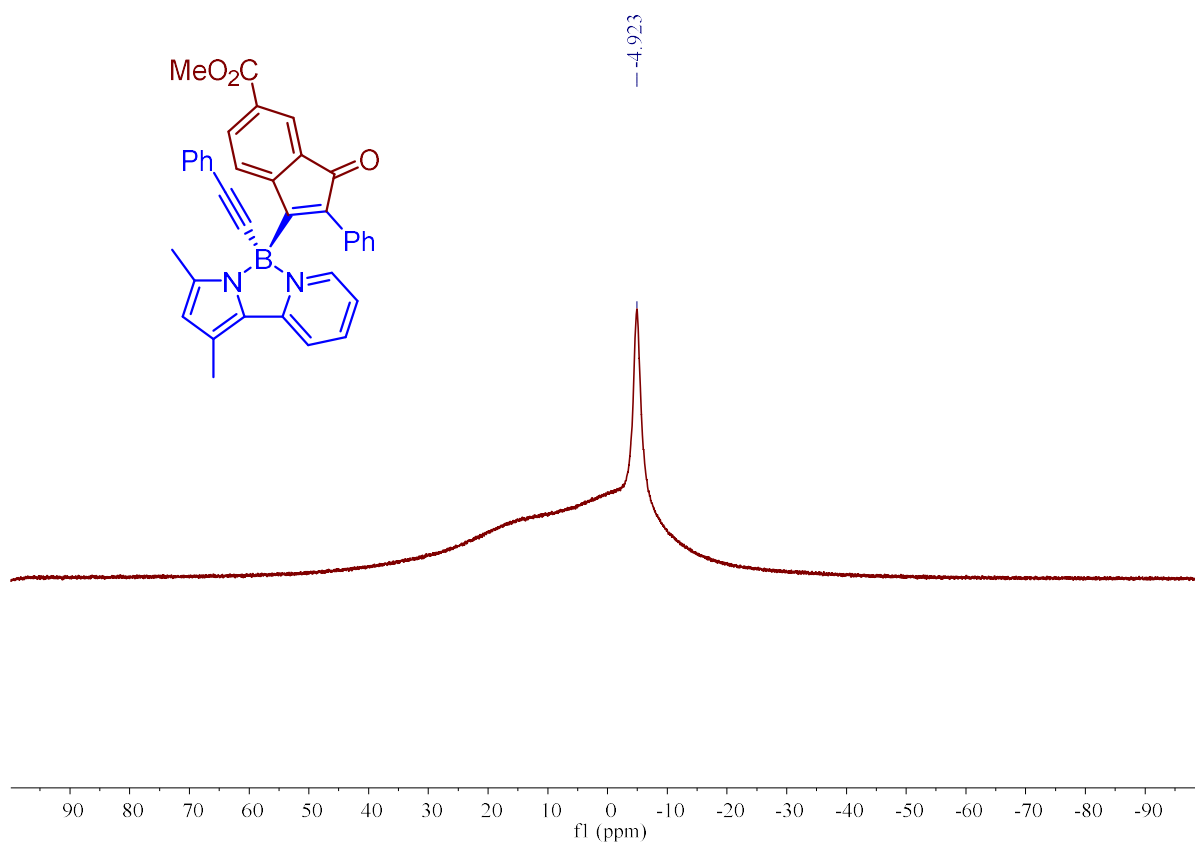


¹¹B NMR (193 MHz, CDCl₃) spectrum of 10.

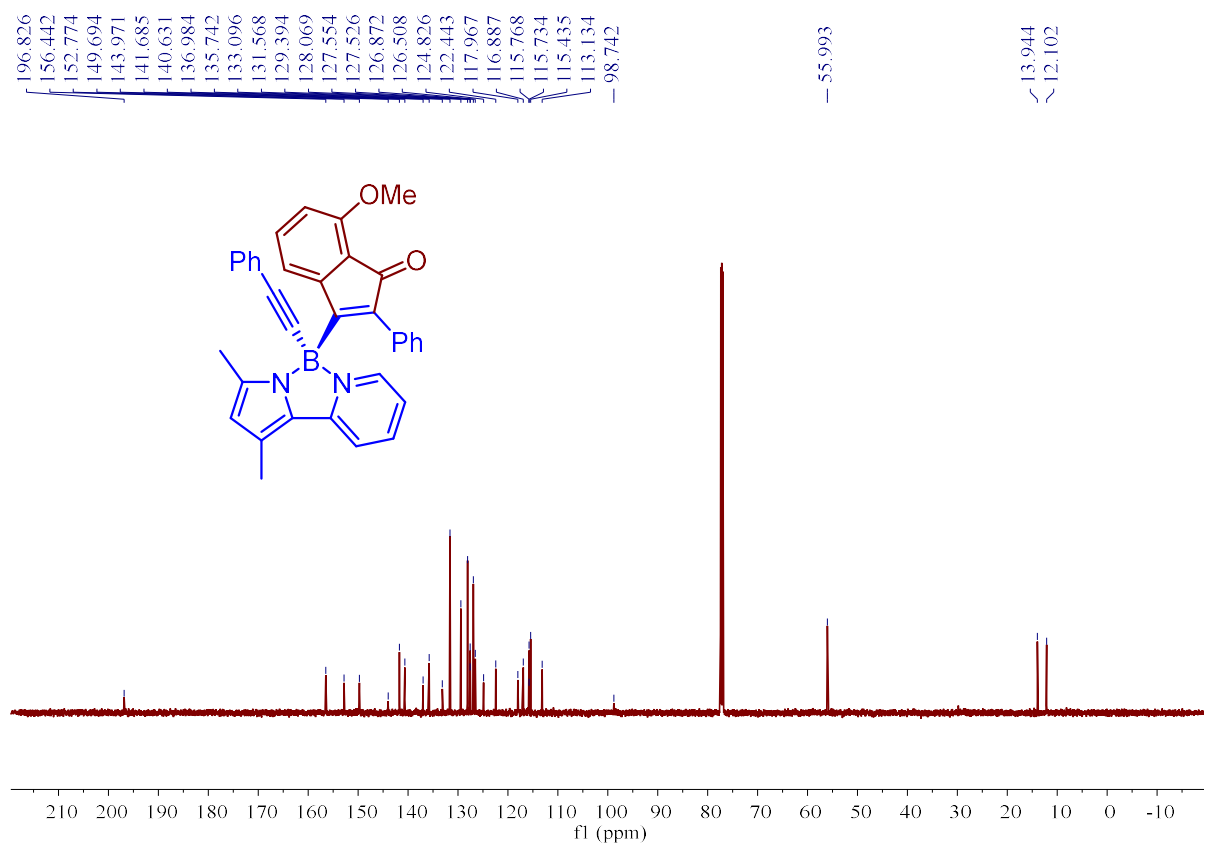
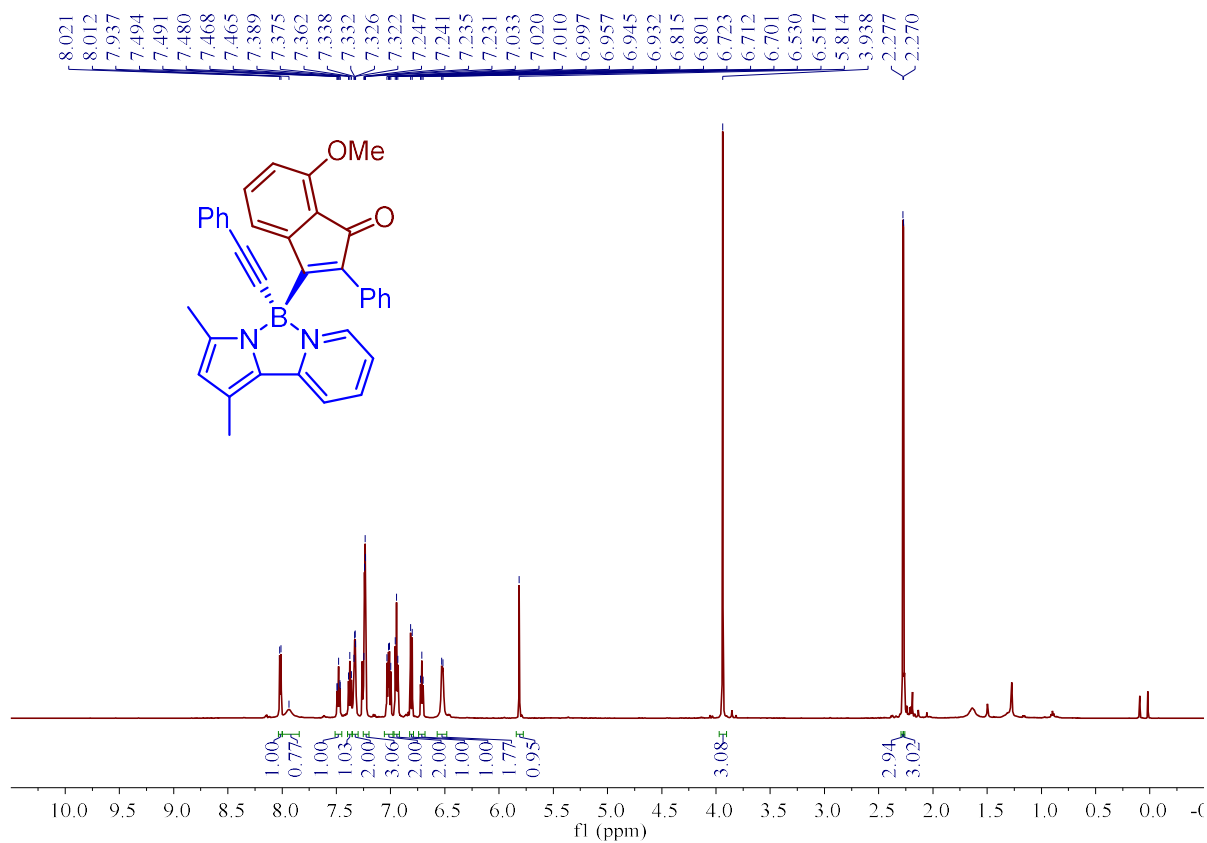


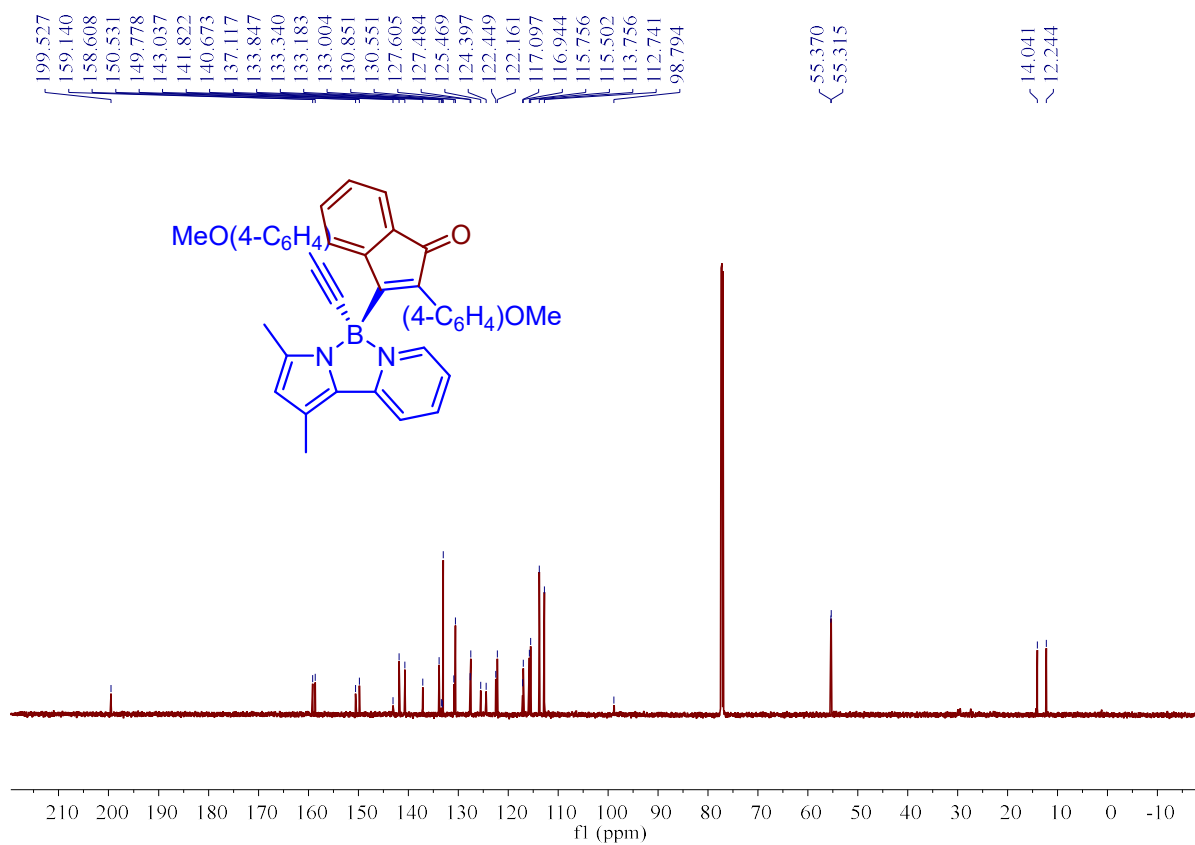


¹³C NMR (150 MHz, CDCl₃) spectrum of 11.

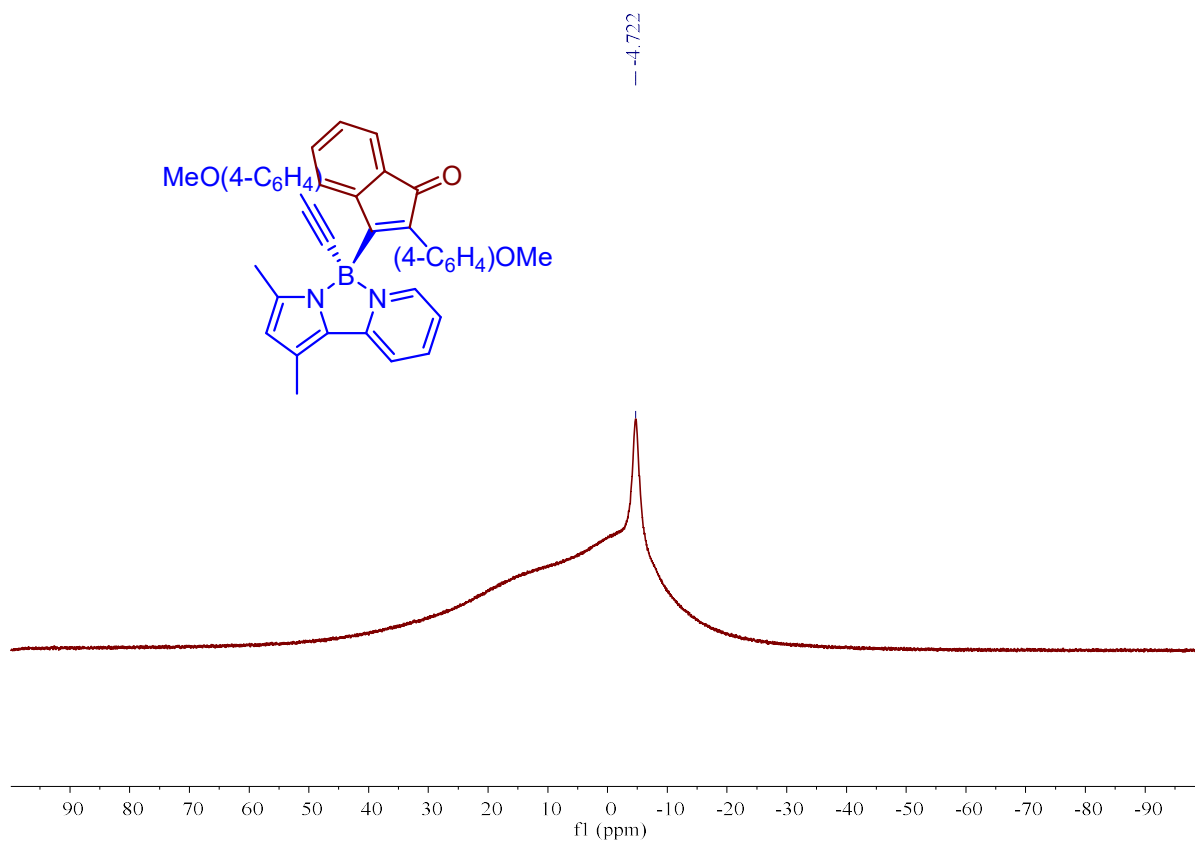


¹¹B NMR (193 MHz, CDCl₃) spectrum of 11.

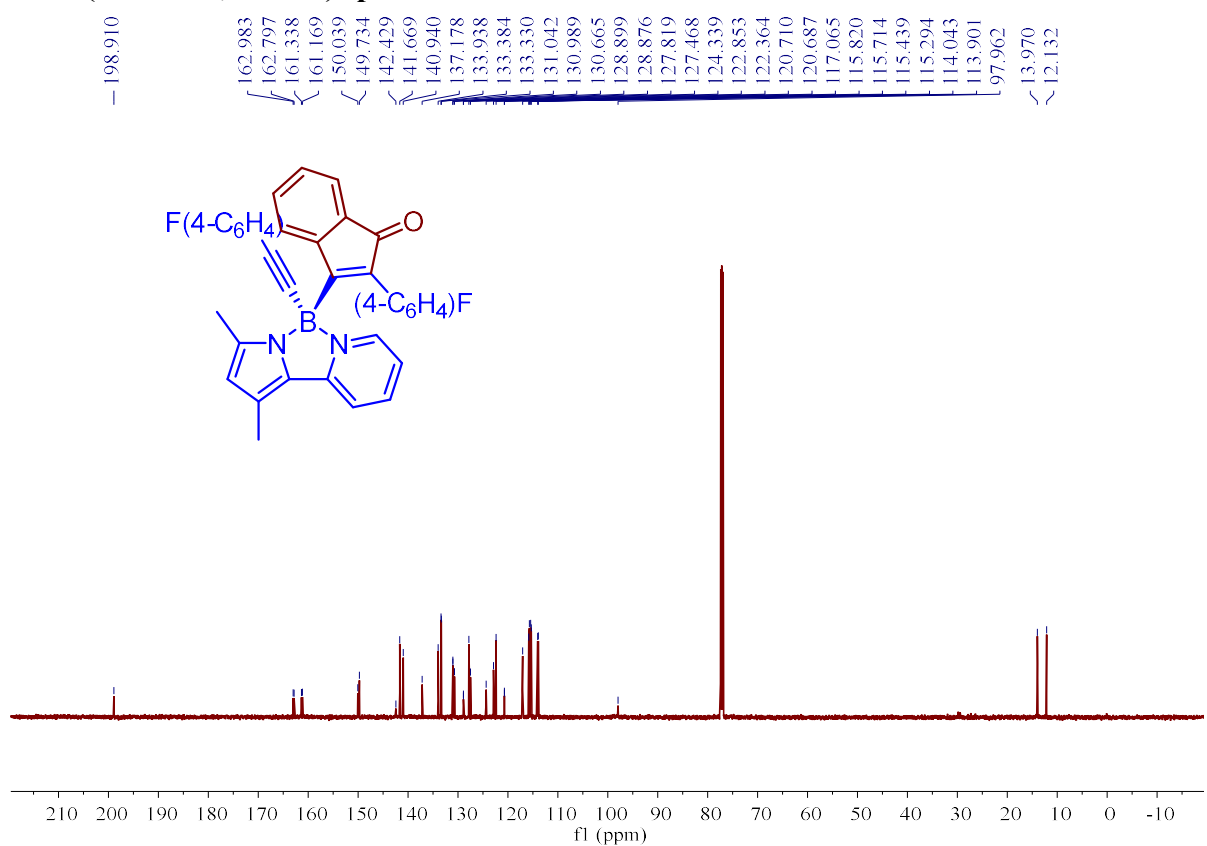
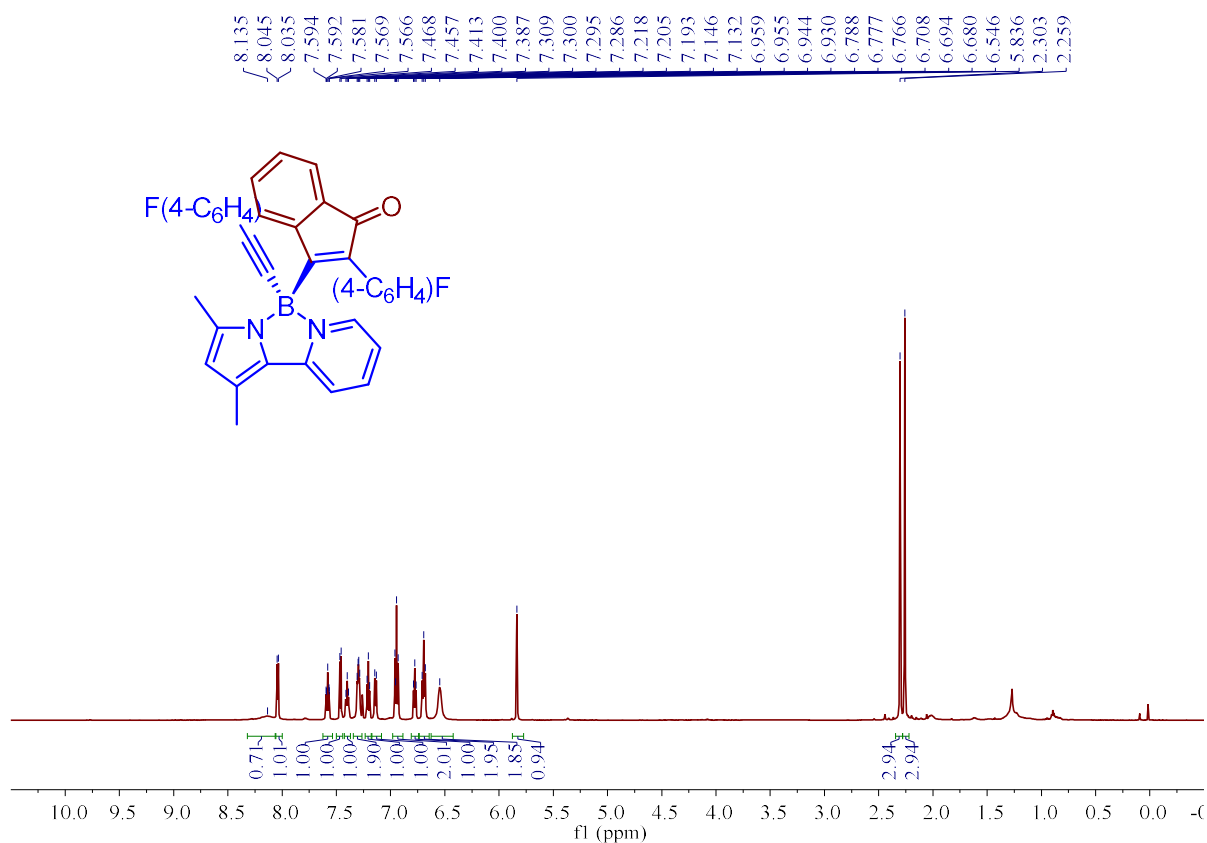


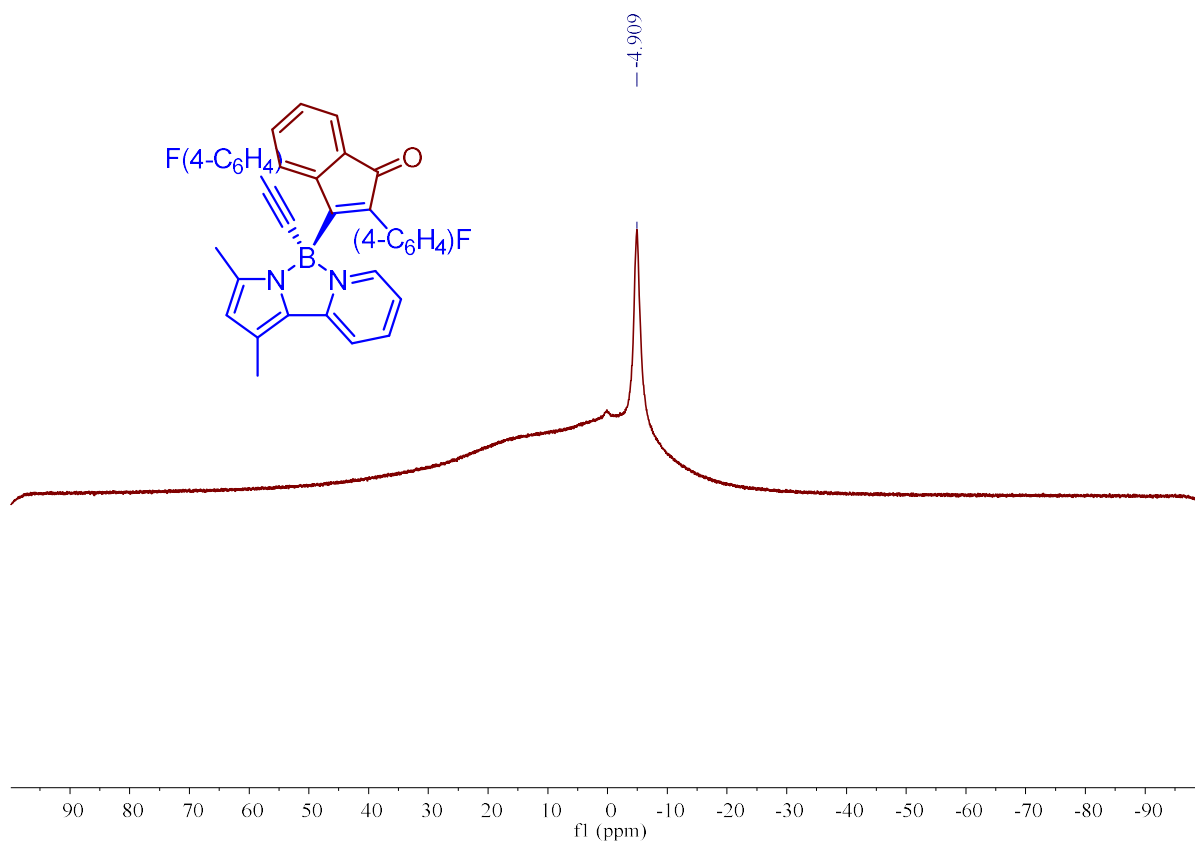


¹³C NMR (150 MHz, CDCl₃) spectrum of 13.

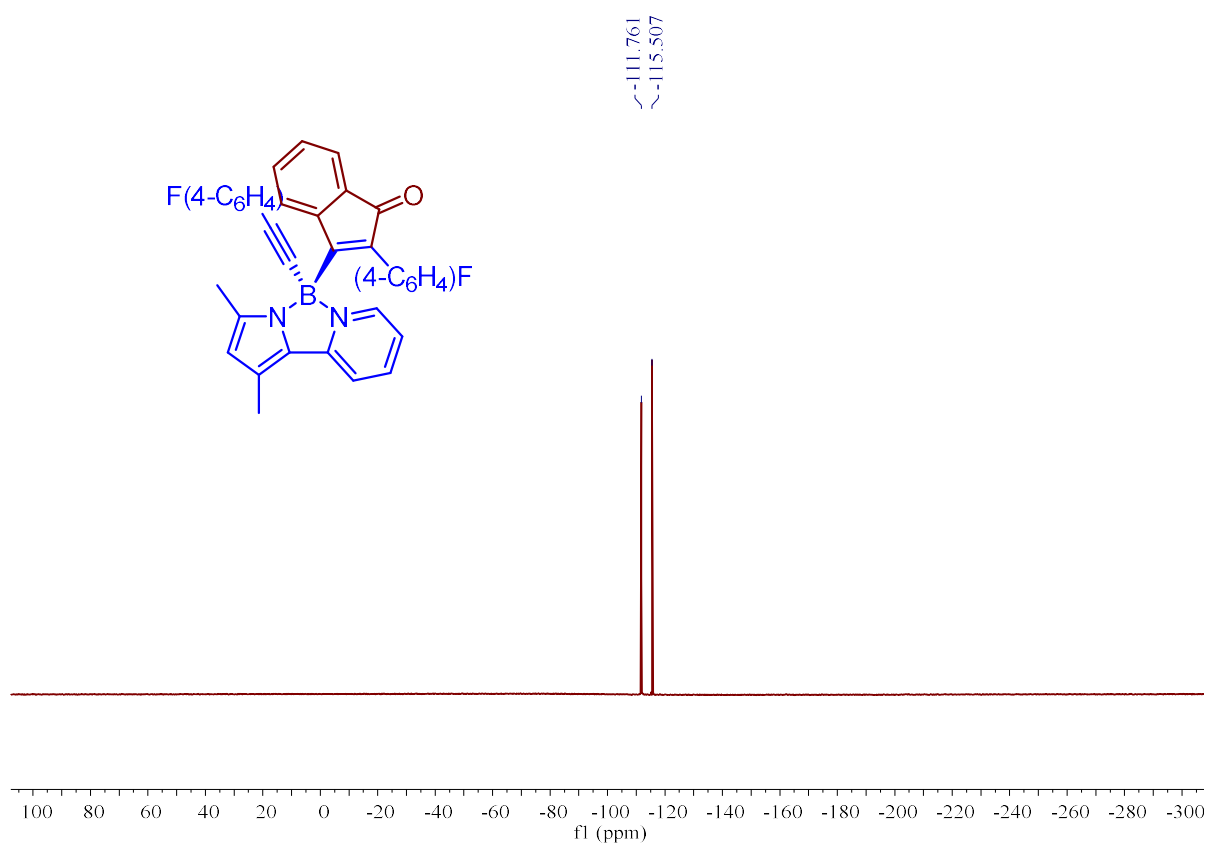


¹¹B NMR (193 MHz, CDCl₃) spectrum of 13.

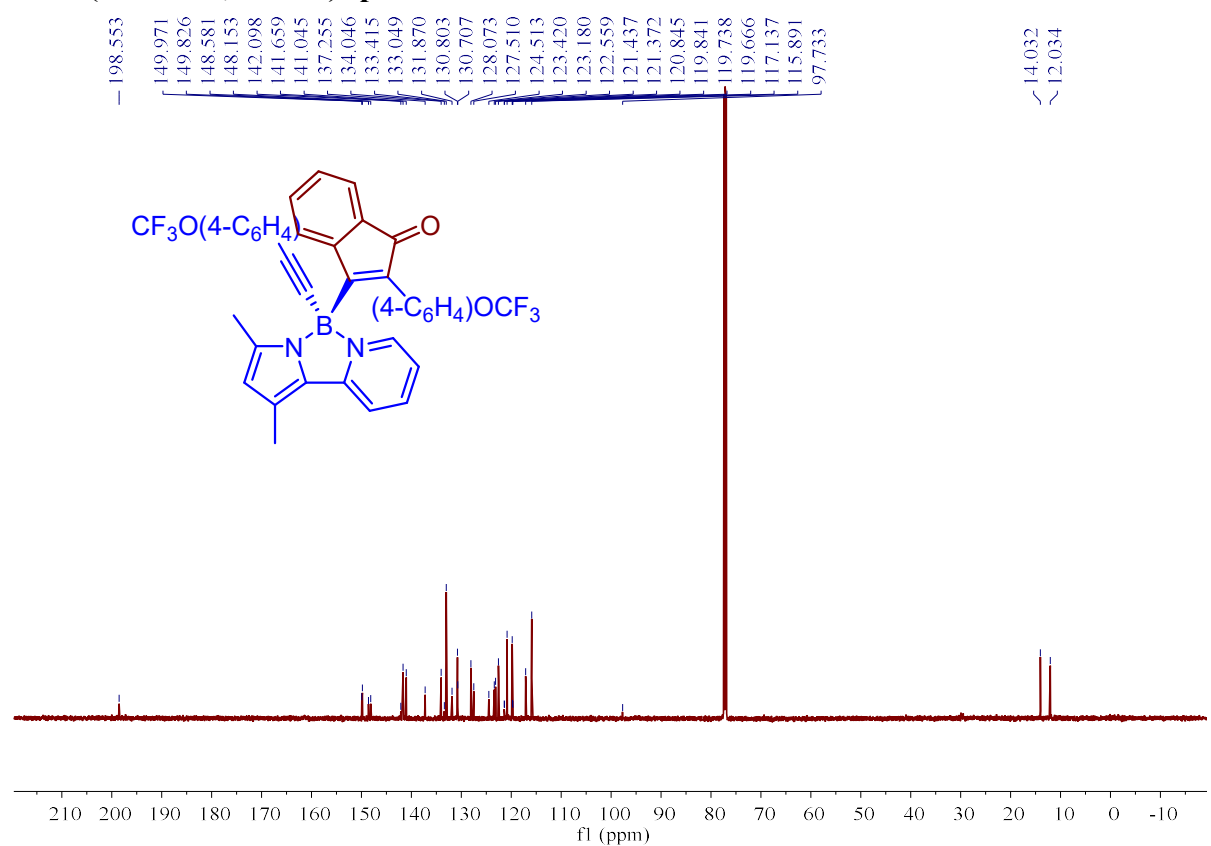
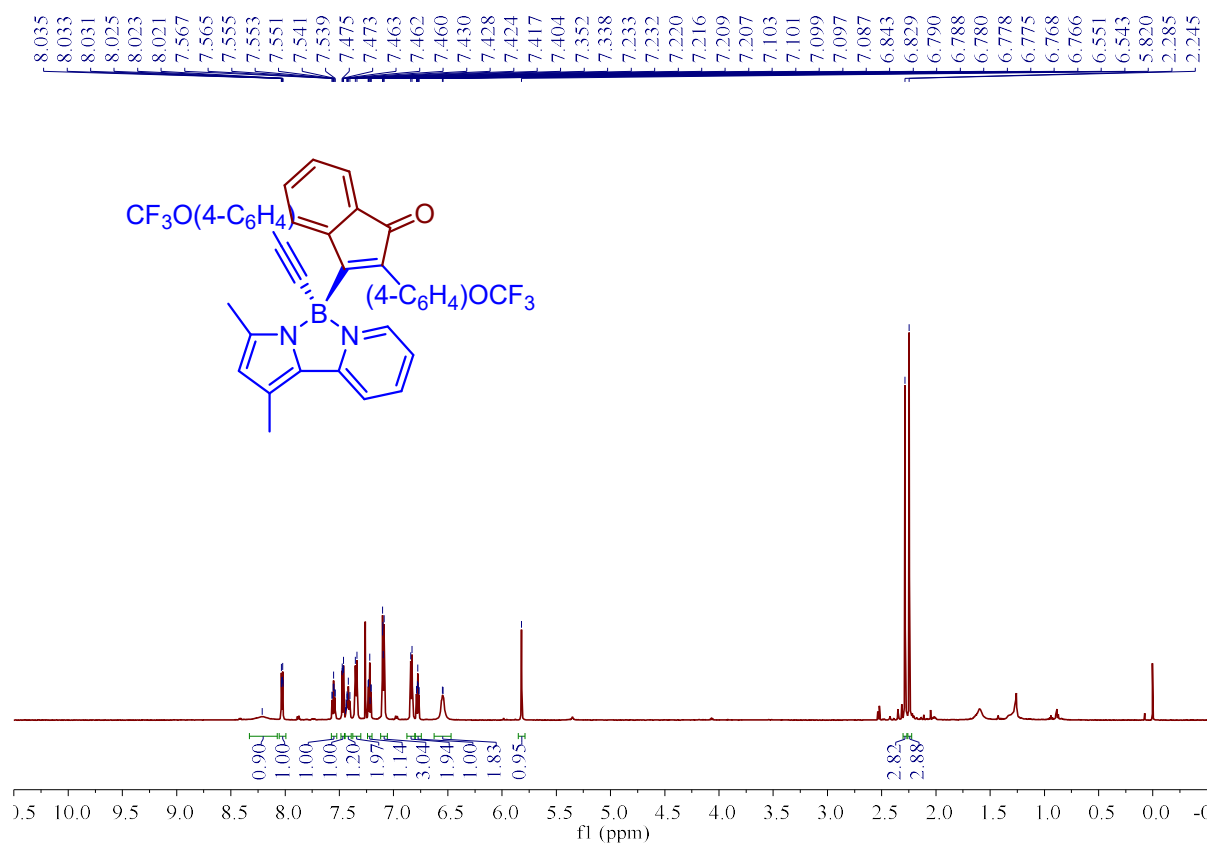


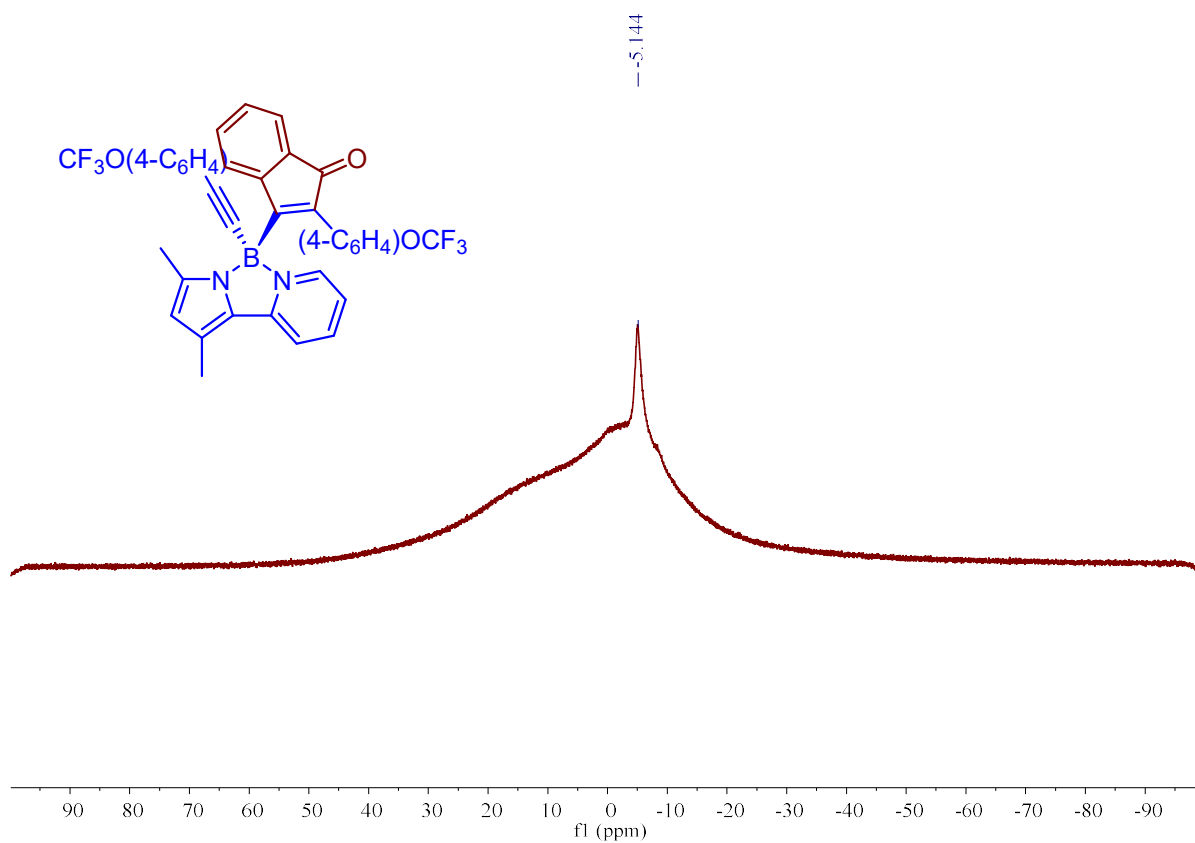


¹¹B NMR (193 MHz, CDCl₃) spectrum of 14.

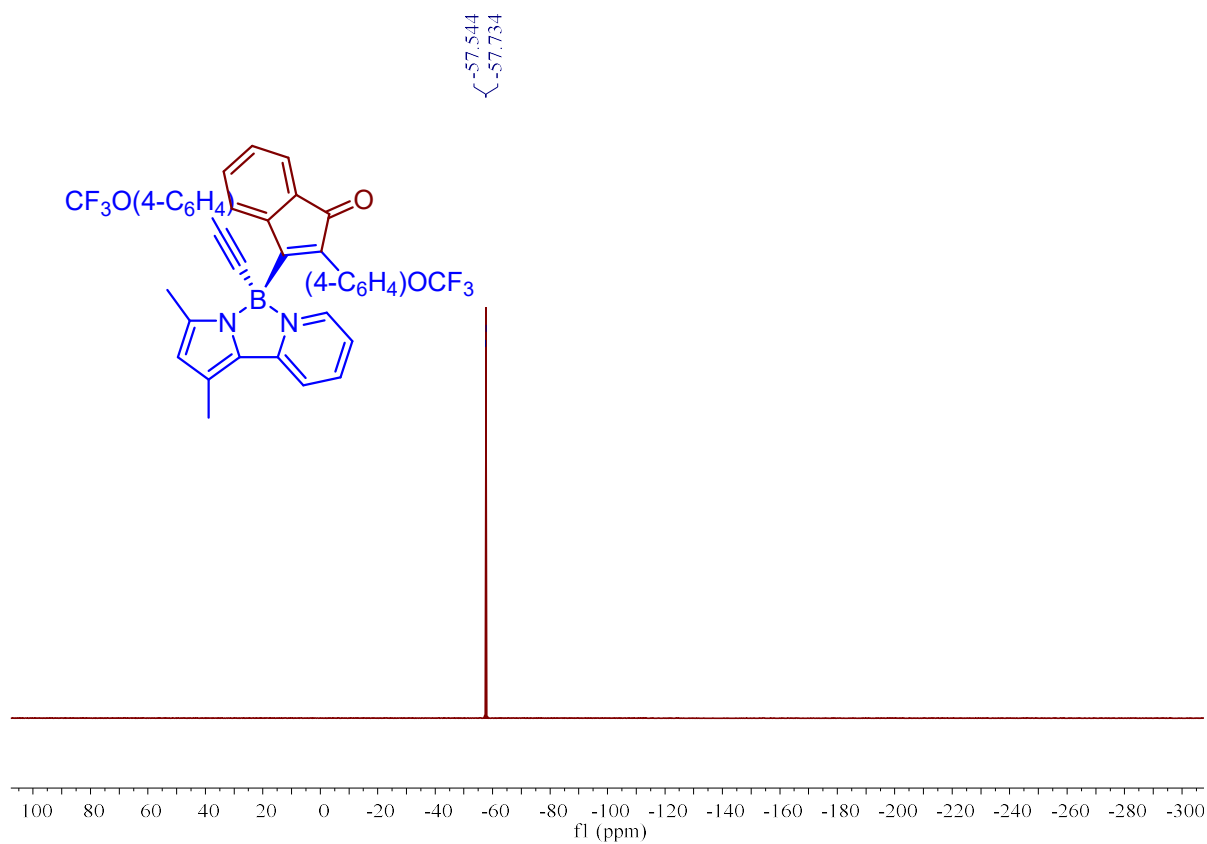


¹⁹F NMR (376 MHz, CDCl₃) spectrum of 14.

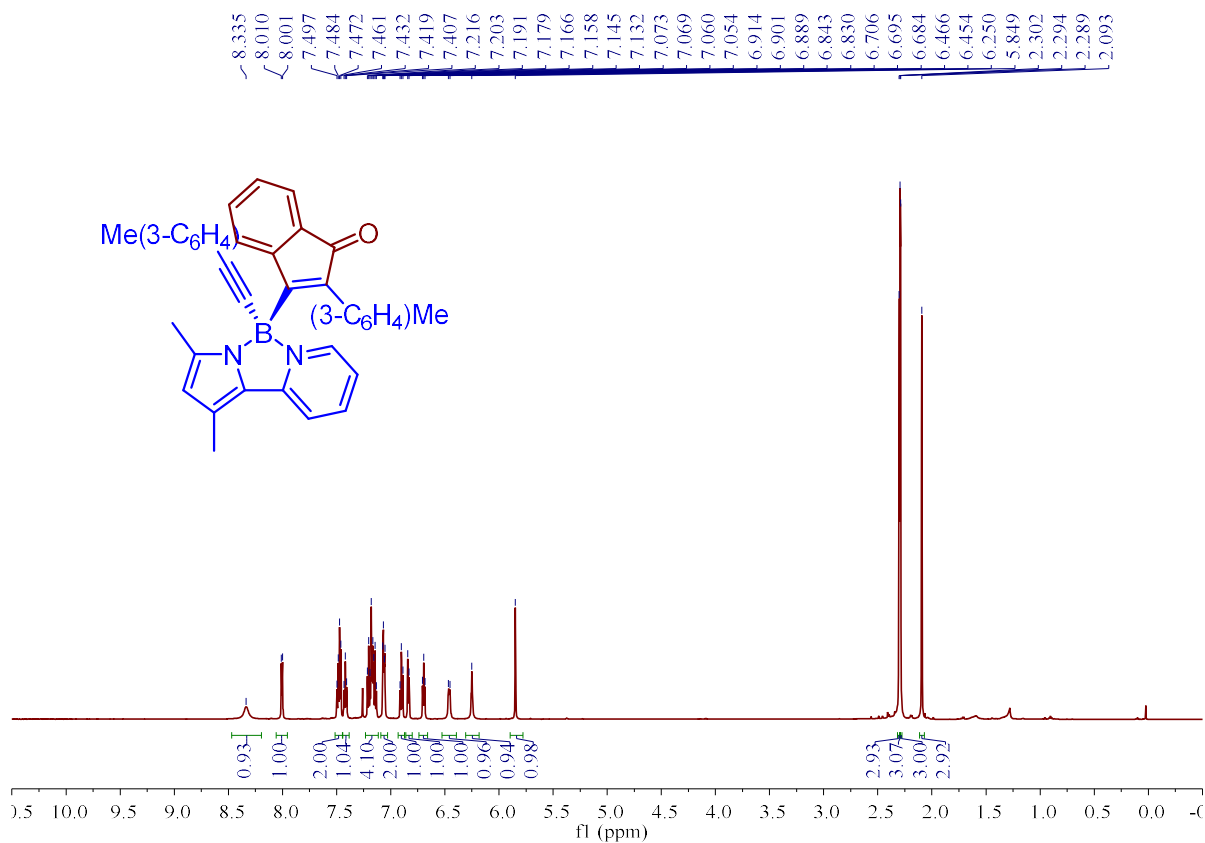




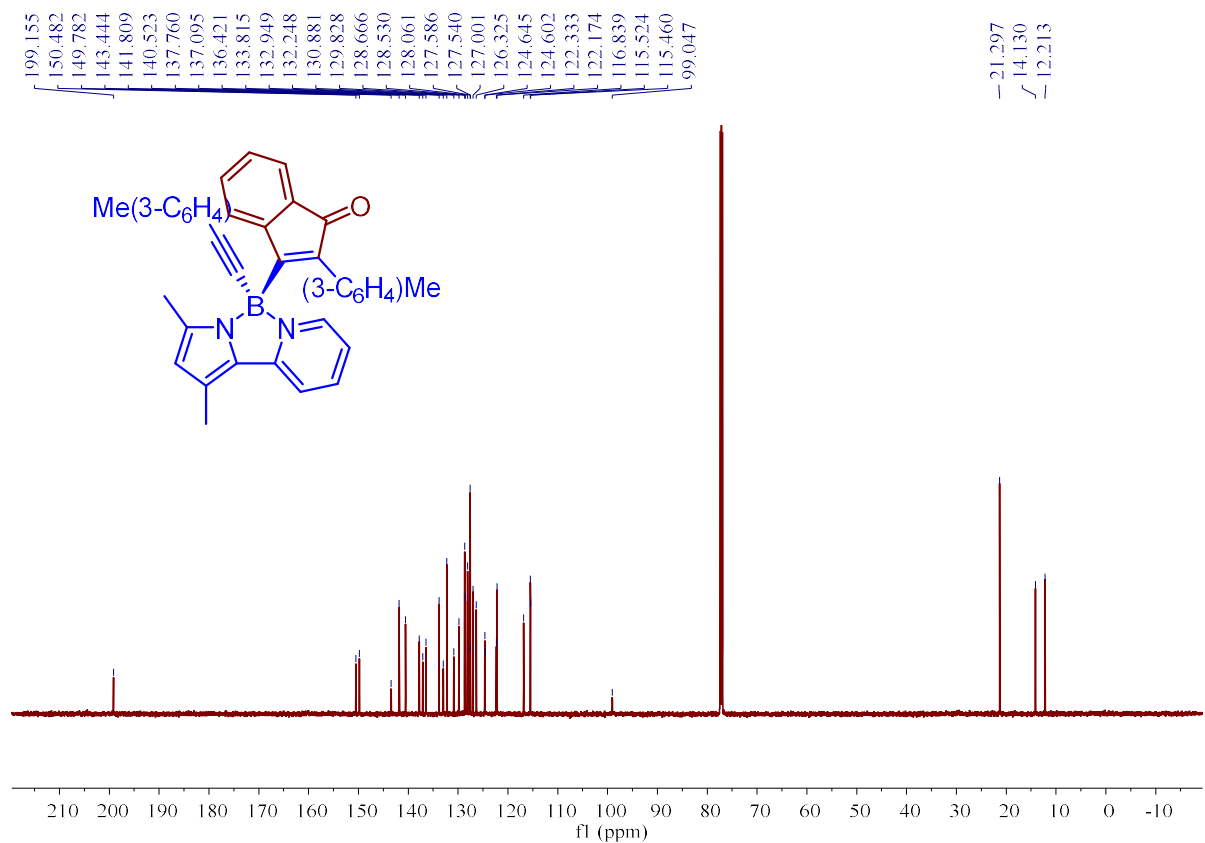
^{11}B NMR (193 MHz, CDCl_3) spectrum of 15.



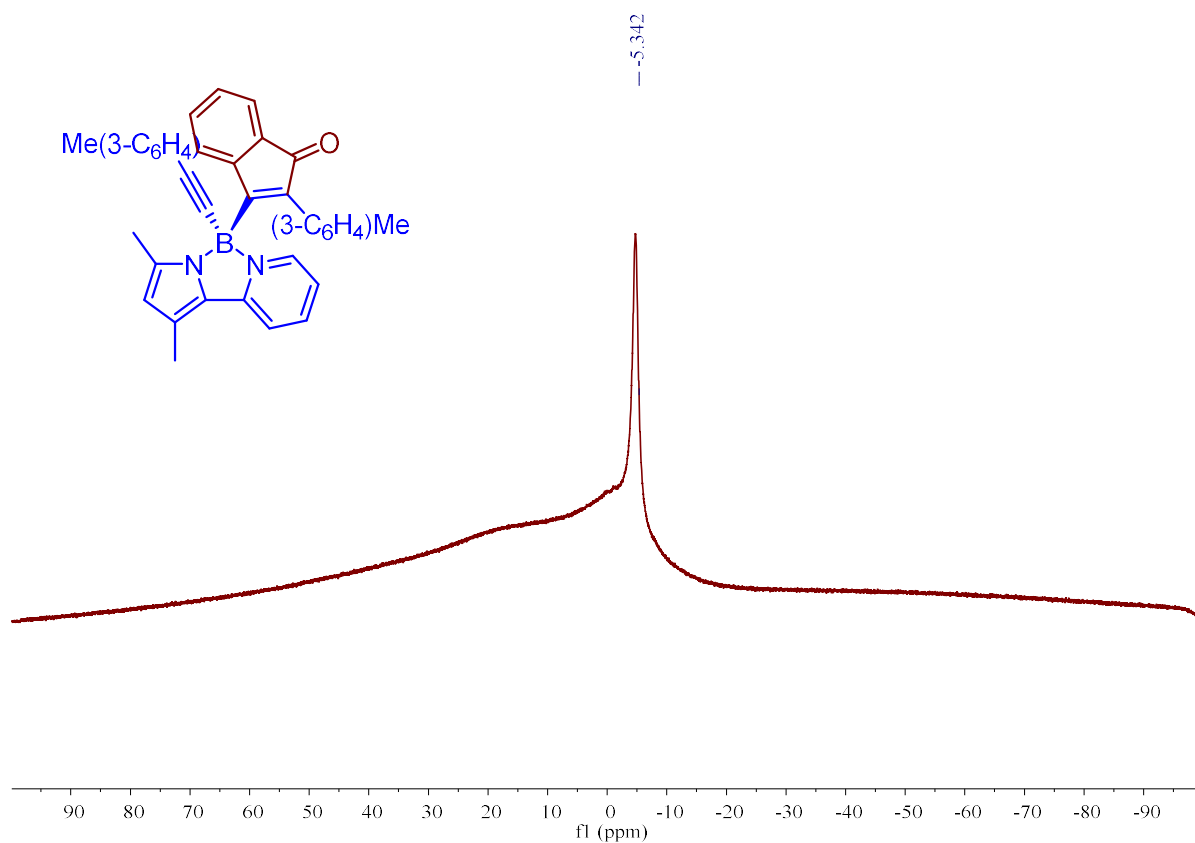
^{19}F NMR (376 MHz, CDCl_3) spectrum of 15.



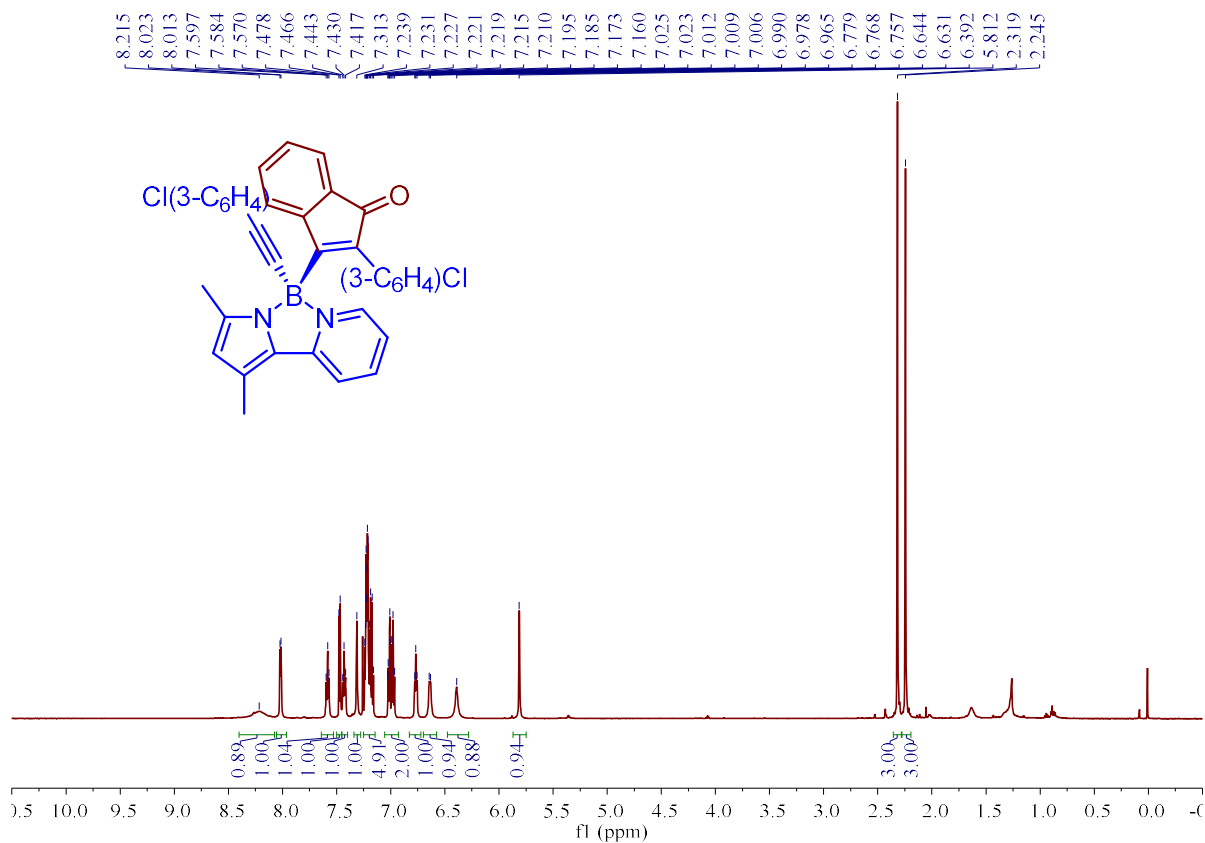
¹H NMR (600 MHz, CDCl₃) spectrum of 16.



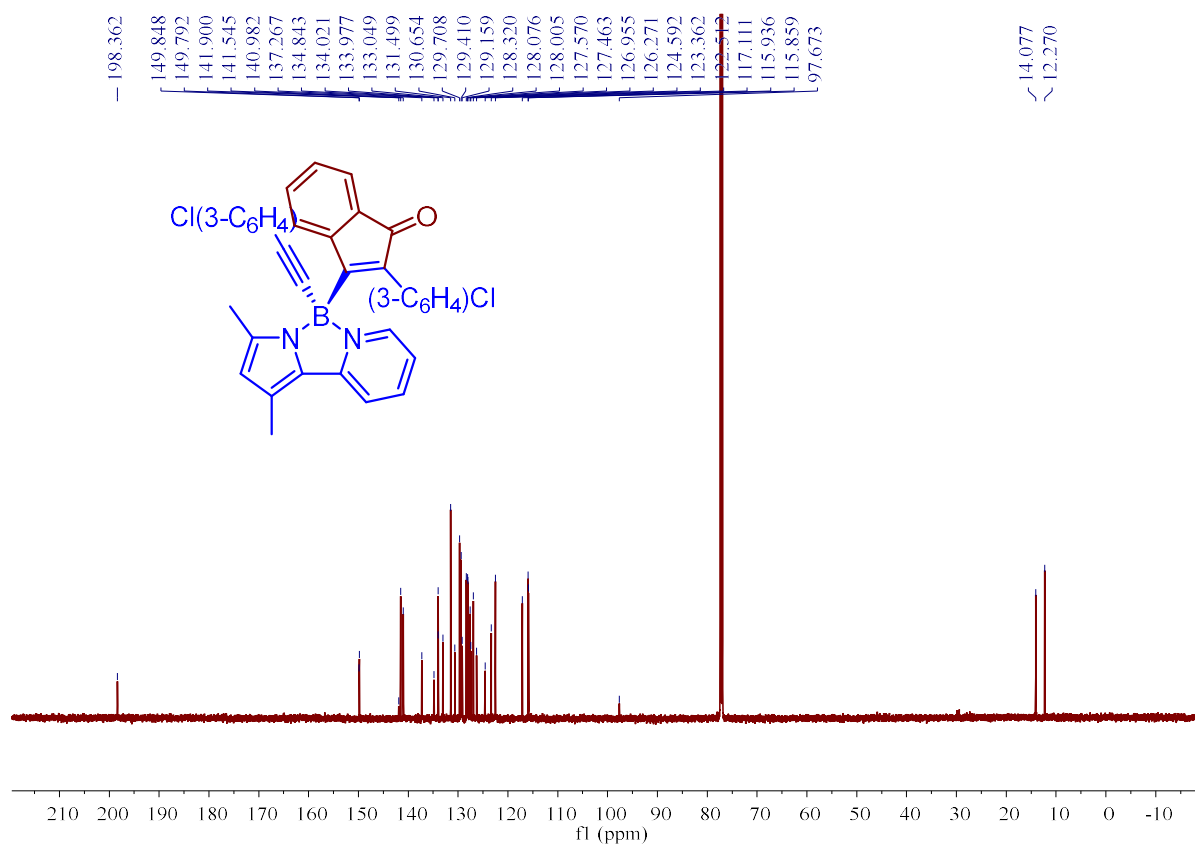
¹³C NMR (150 MHz, CDCl₃) spectrum of 16.



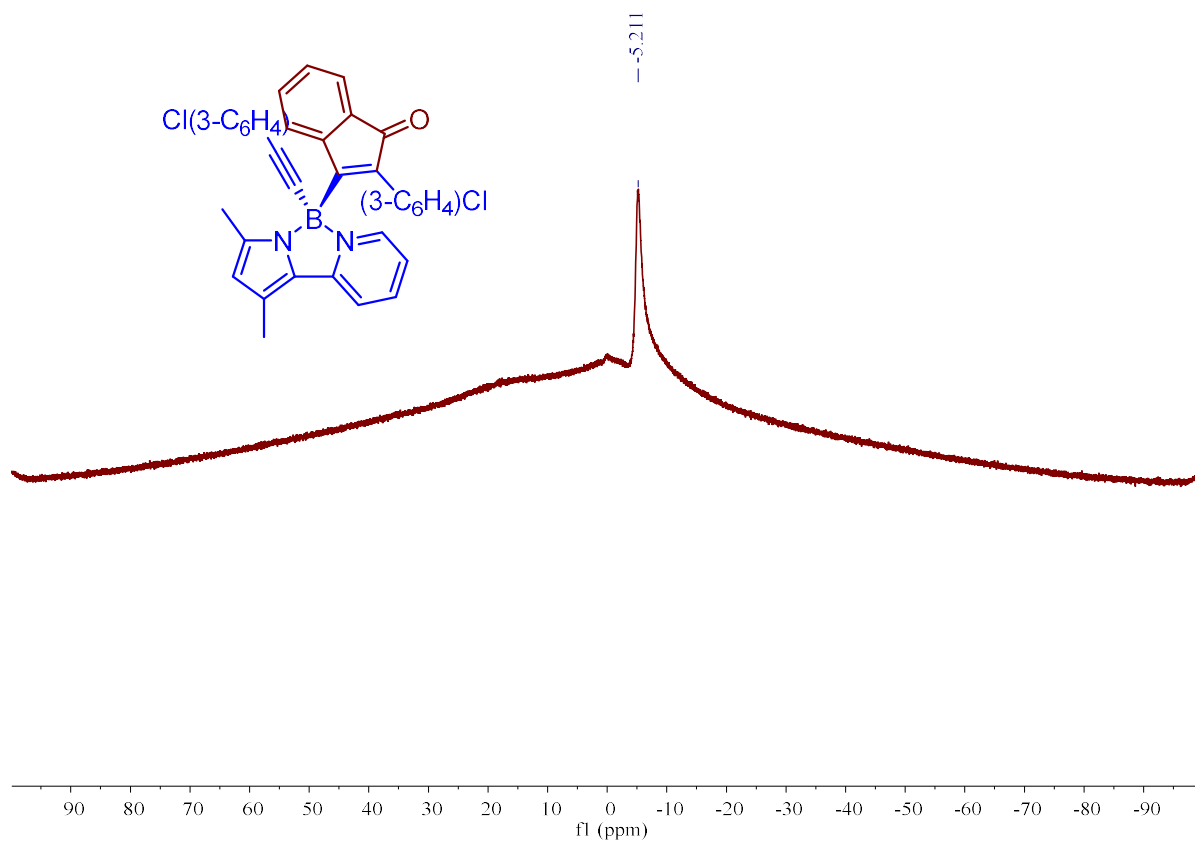
^{11}B NMR (193 MHz, CDCl_3) spectrum of 16.



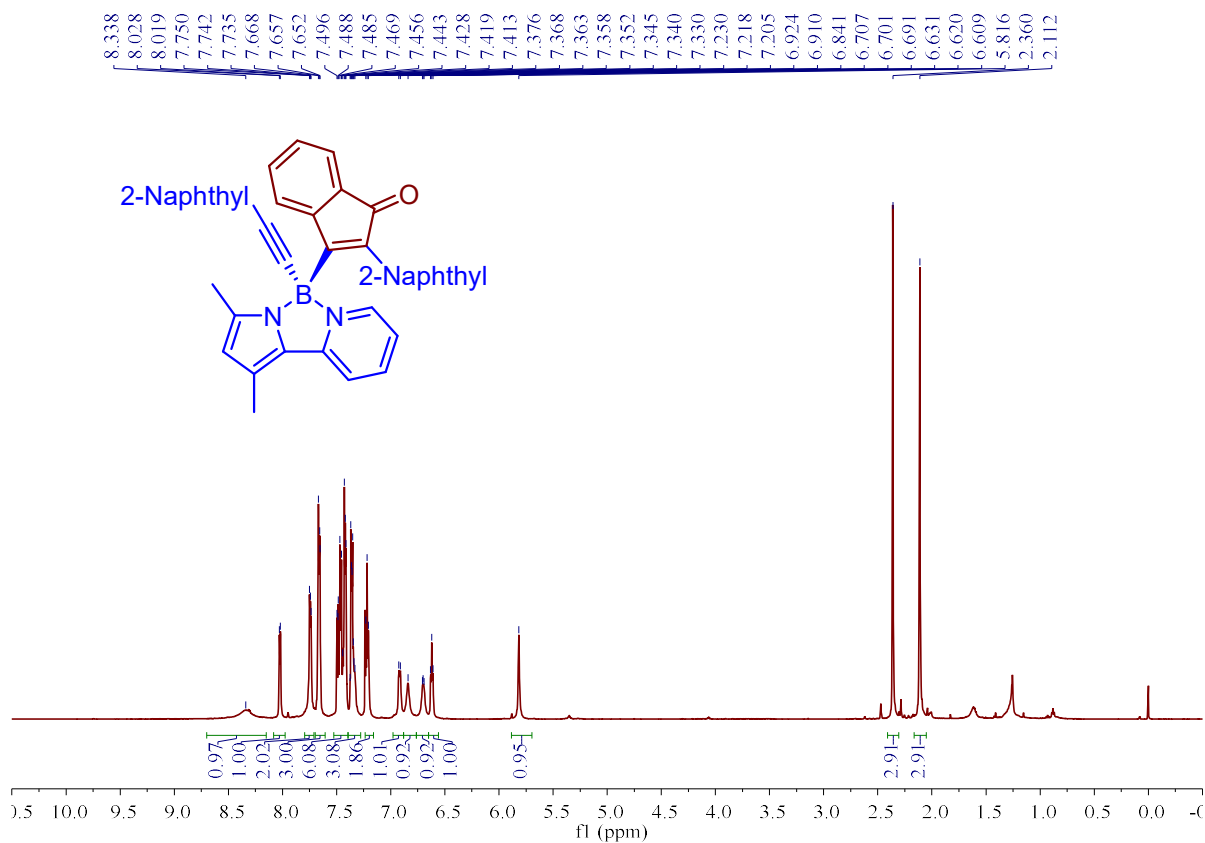
^1H NMR (600 MHz, CDCl_3) spectrum of 17.



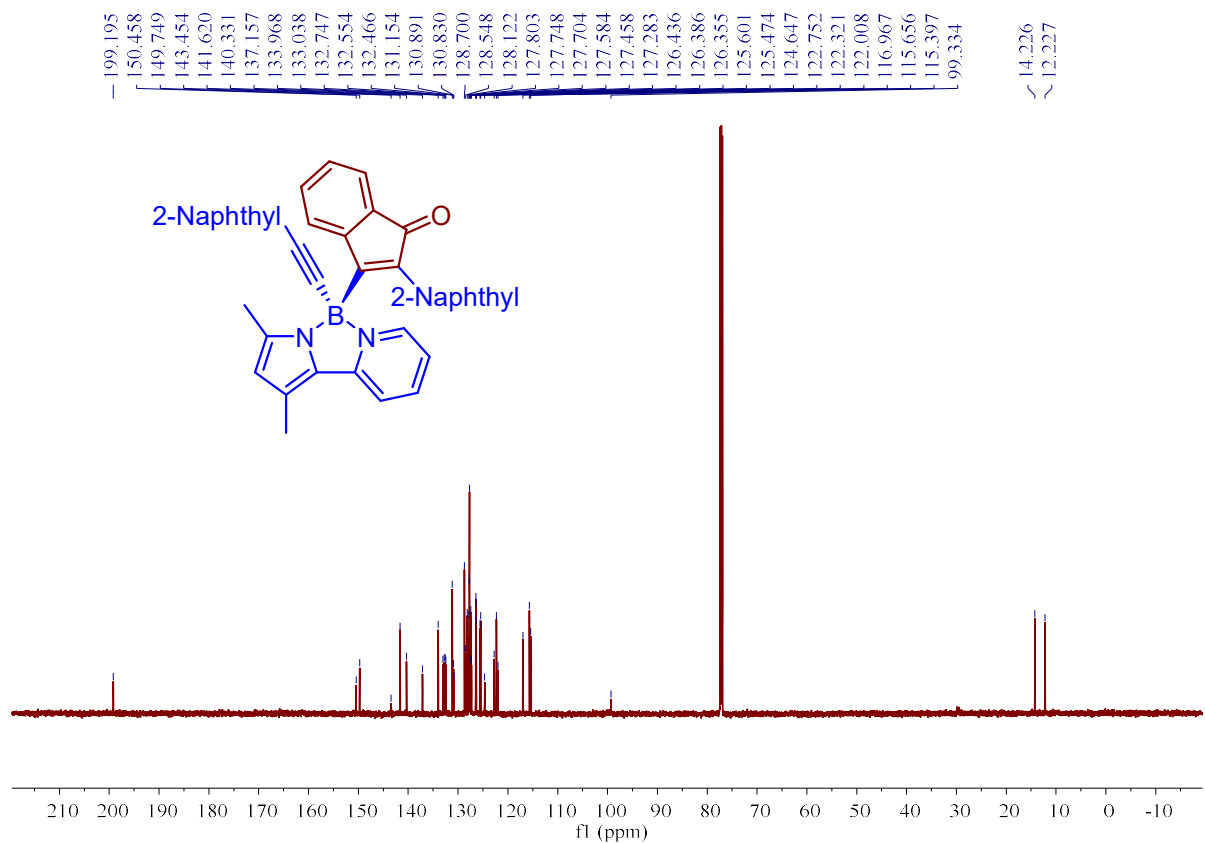
¹³C NMR (150 MHz, CDCl₃) spectrum of 17.



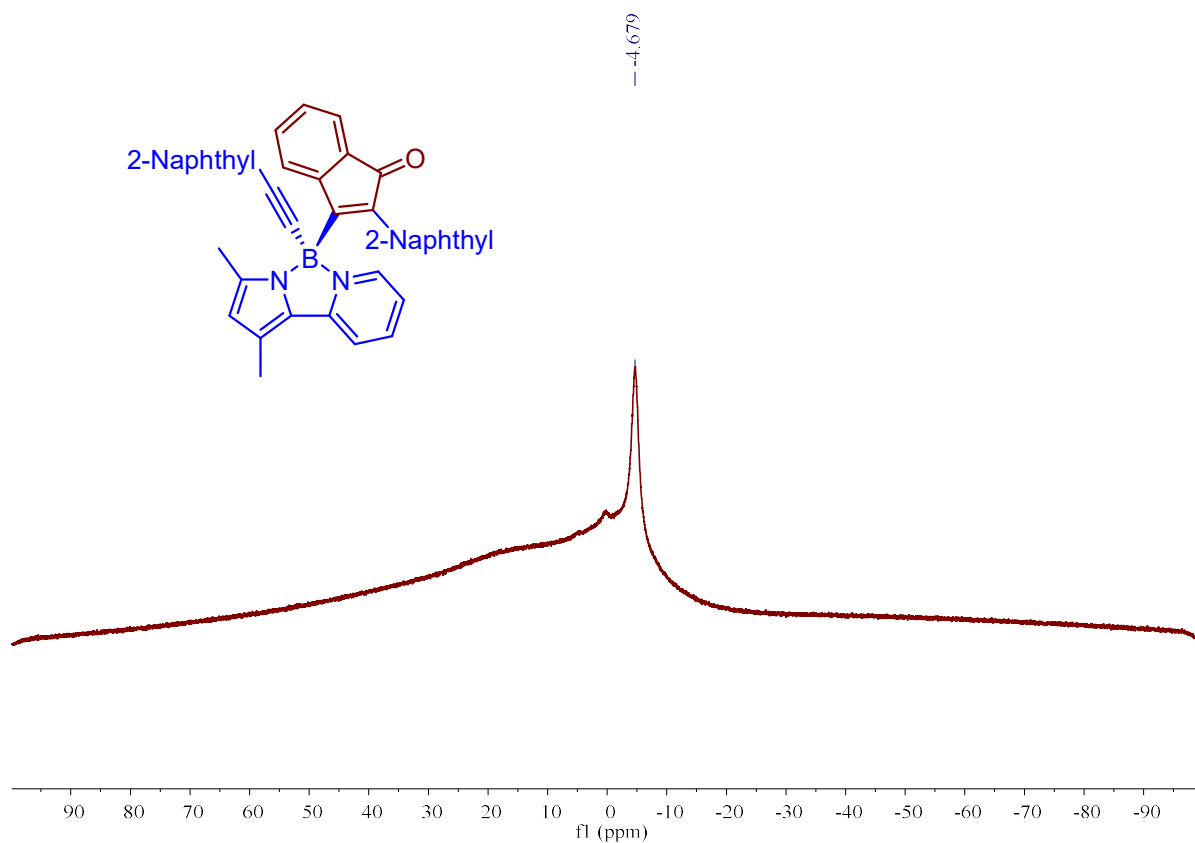
¹¹B NMR (193 MHz, CDCl₃) spectrum of 17.



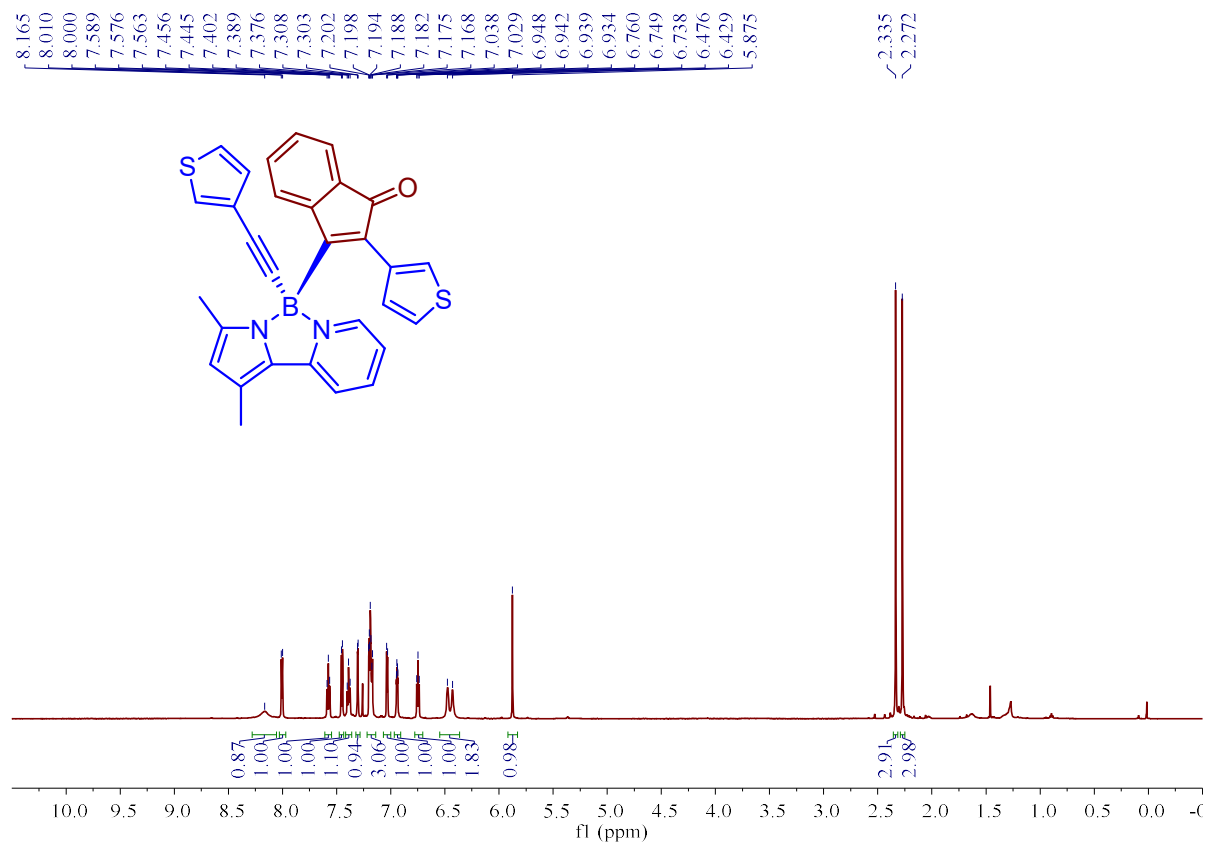
¹H NMR (600 MHz, CDCl₃) spectrum of 18.



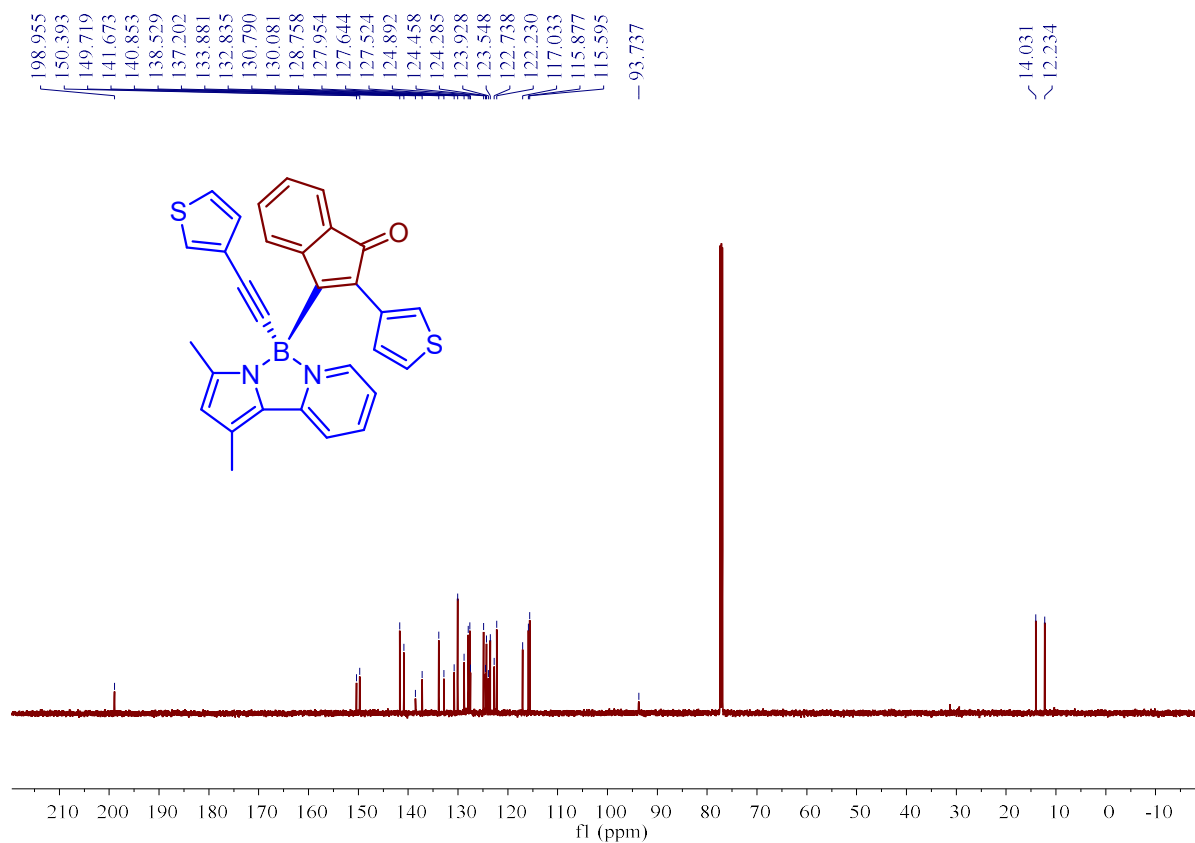
¹³C NMR (150 MHz, CDCl₃) spectrum of 18.



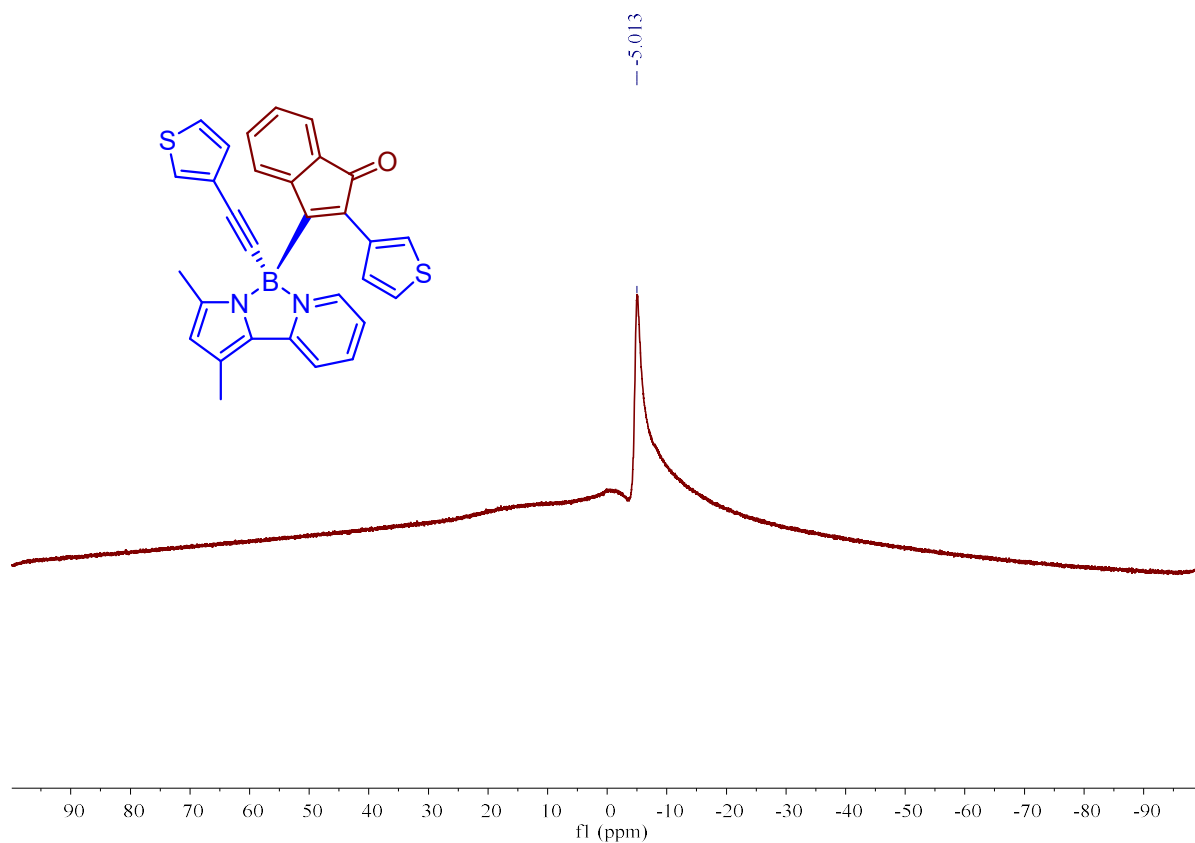
^{11}B NMR (193 MHz, CDCl_3) spectrum of 18.



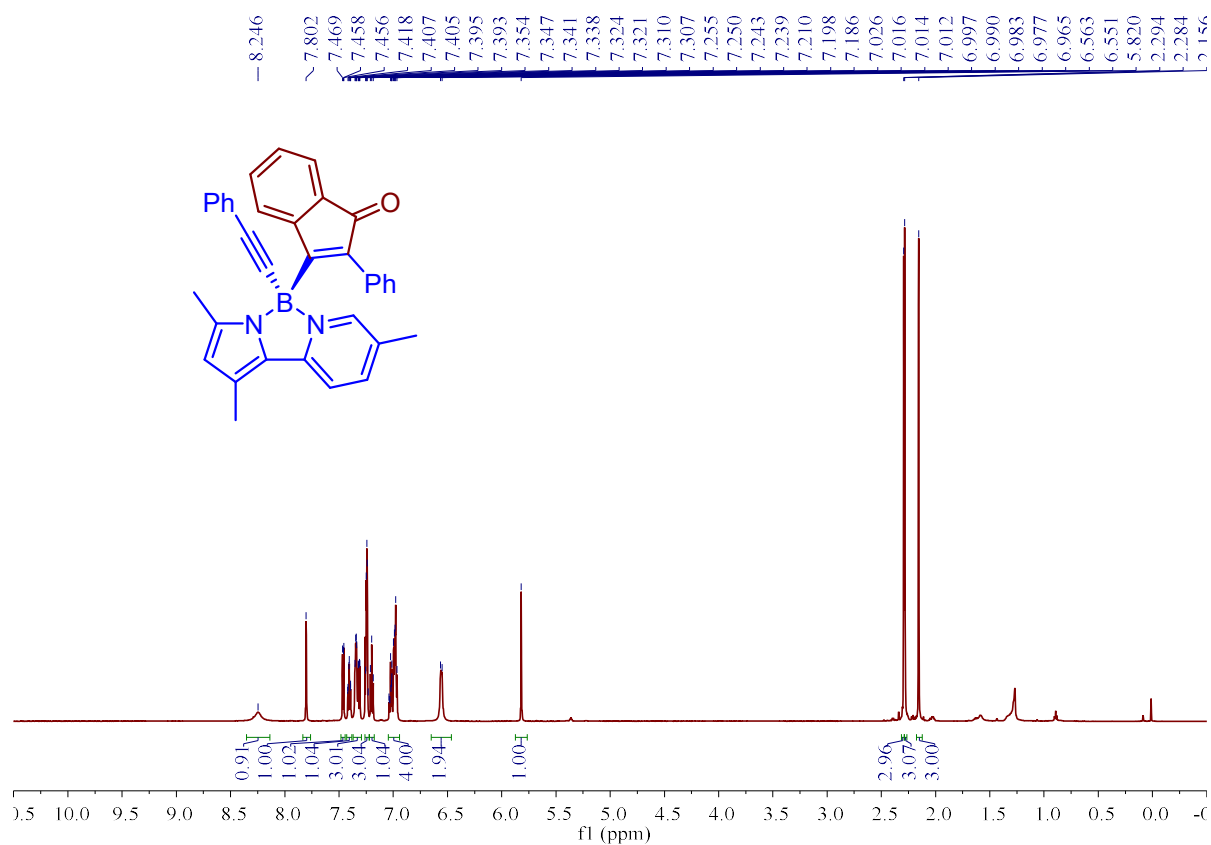
^1H NMR (600 MHz, CDCl_3) spectrum of 19.



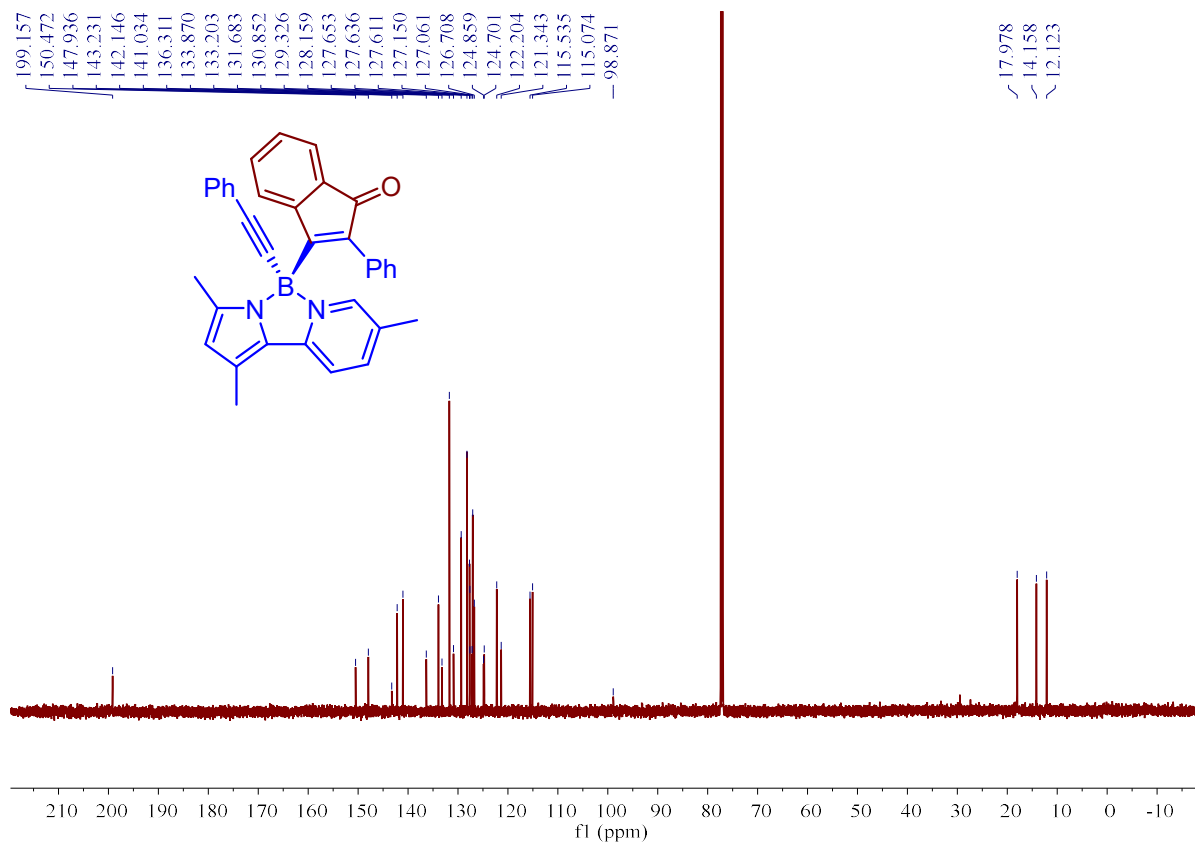
^{13}C NMR (150 MHz, CDCl_3) spectrum of 19.



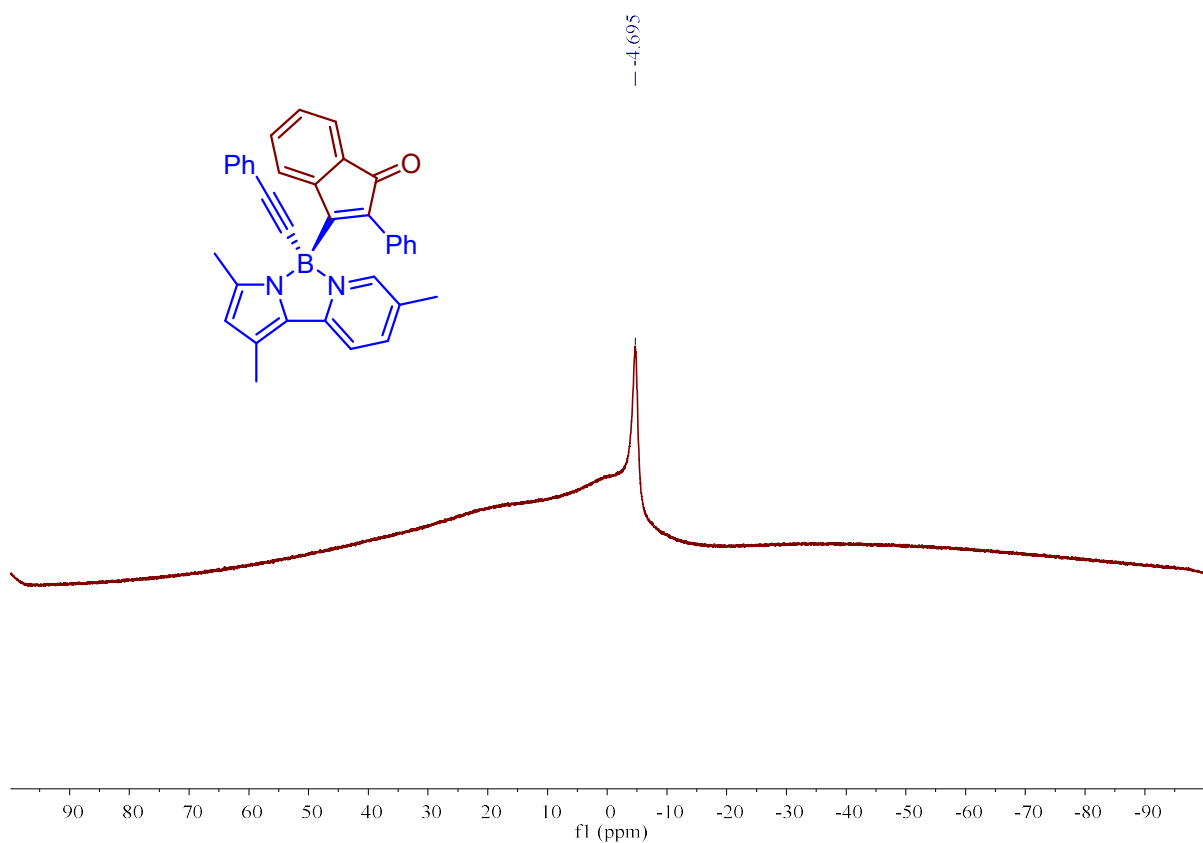
^{11}B NMR (193 MHz, CDCl_3) spectrum of 19.



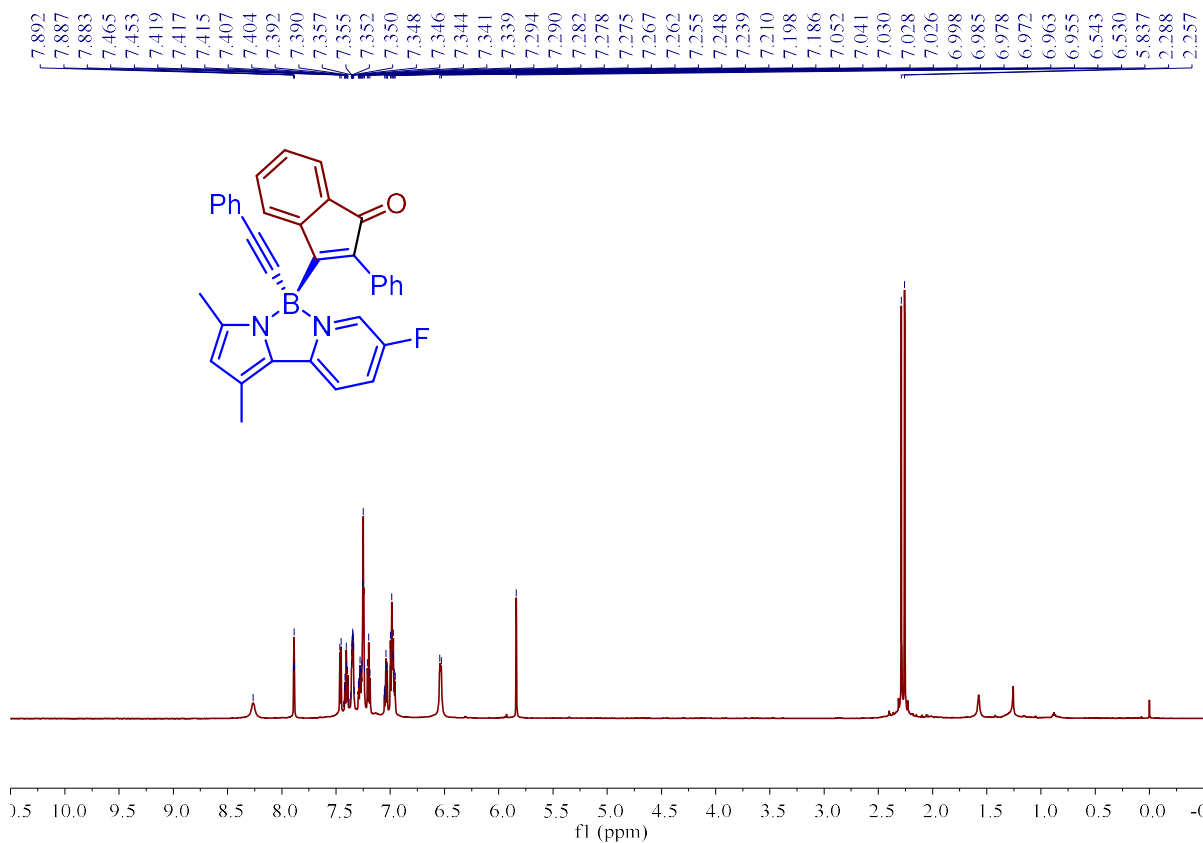
¹H NMR (600 MHz, CDCl₃) spectrum of 20.



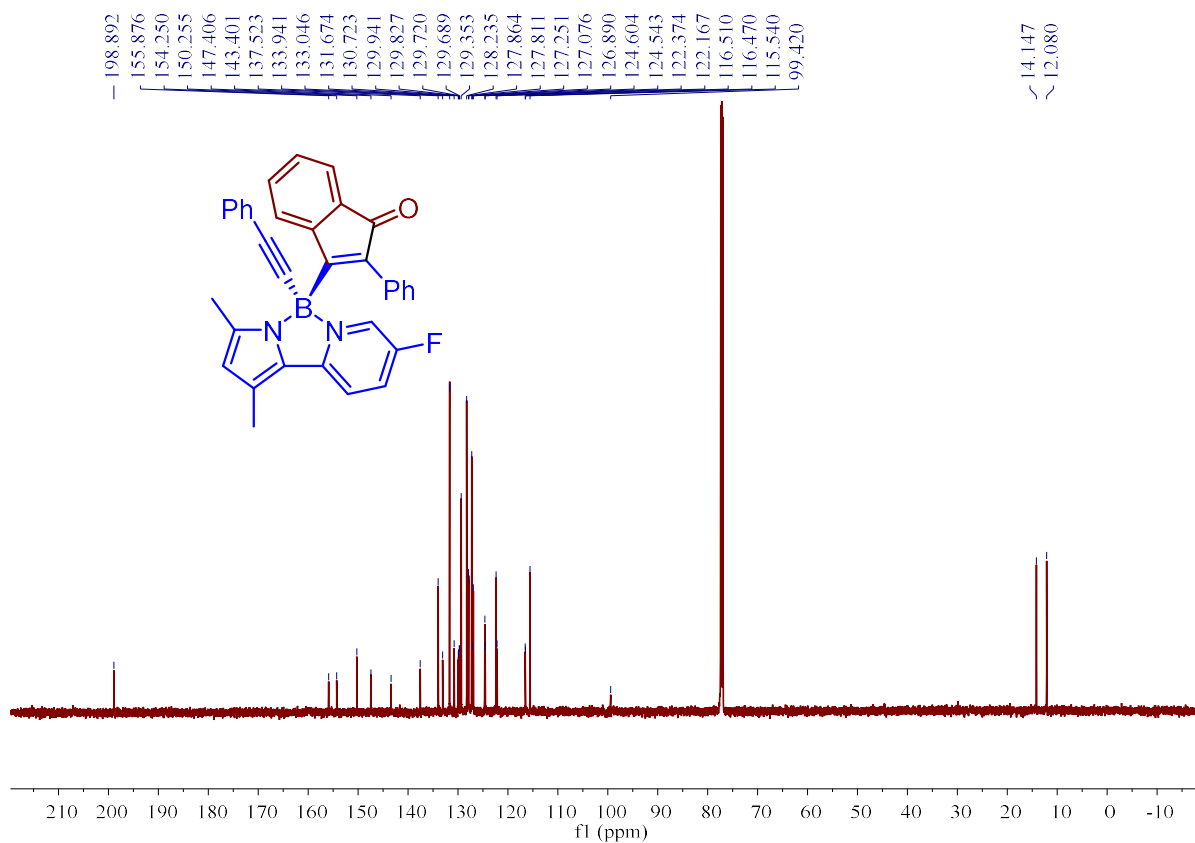
¹³C NMR (150 MHz, CDCl₃) spectrum of 20.



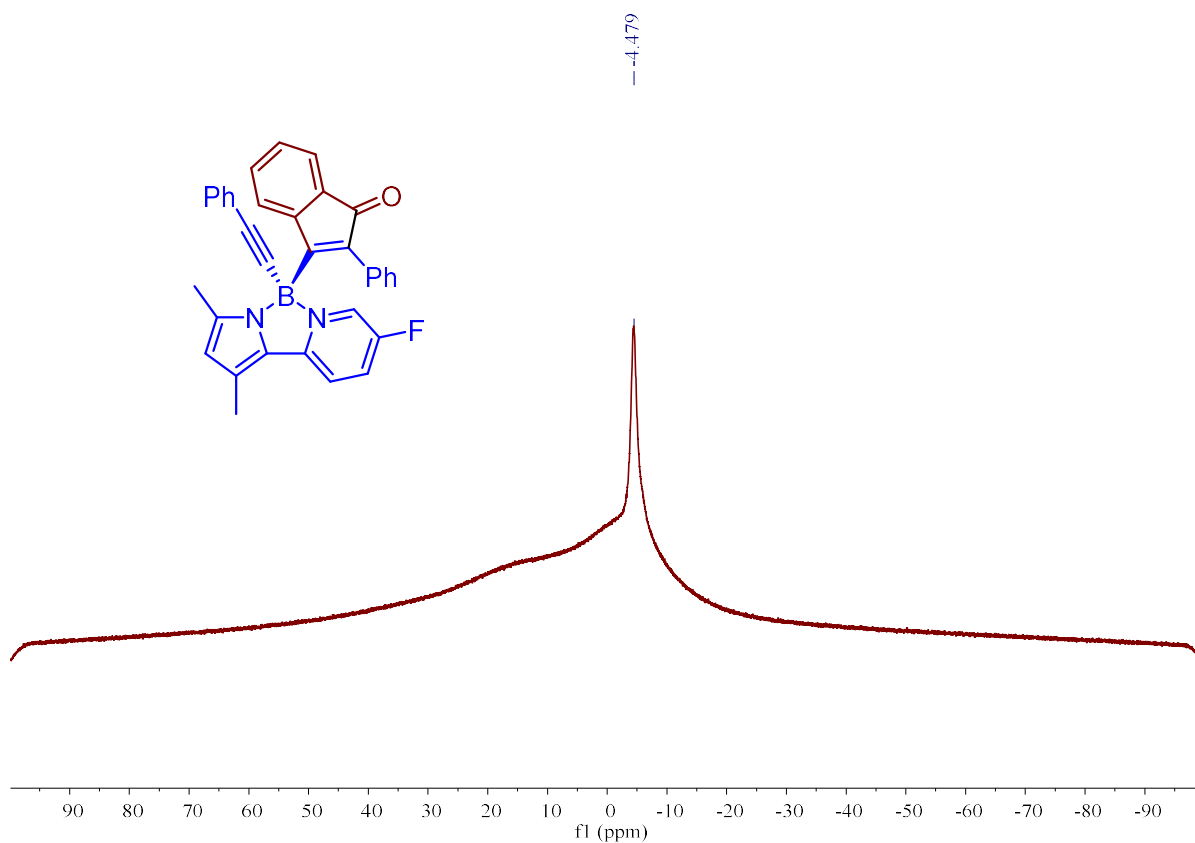
^{11}B NMR (193 MHz, CDCl_3) spectrum of 20.



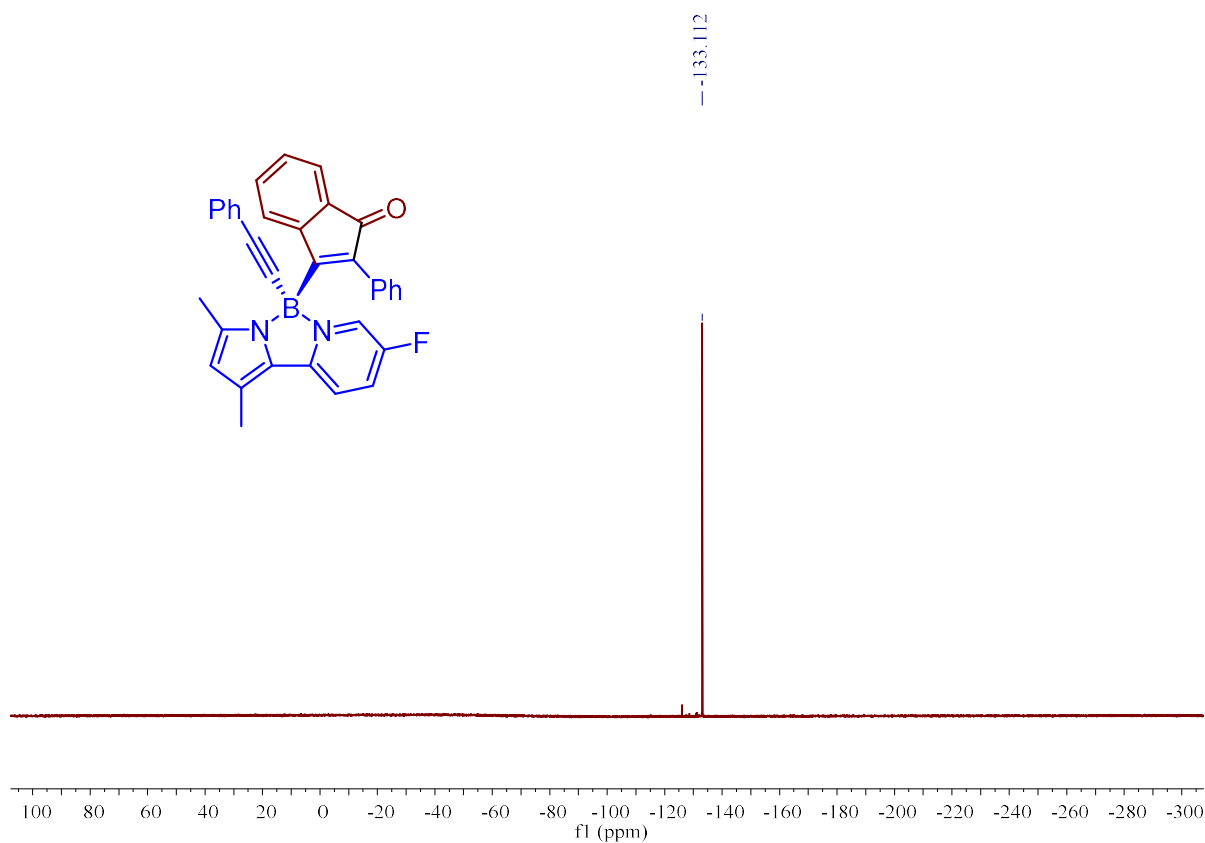
^1H NMR (600 MHz, CDCl_3) spectrum of 21.



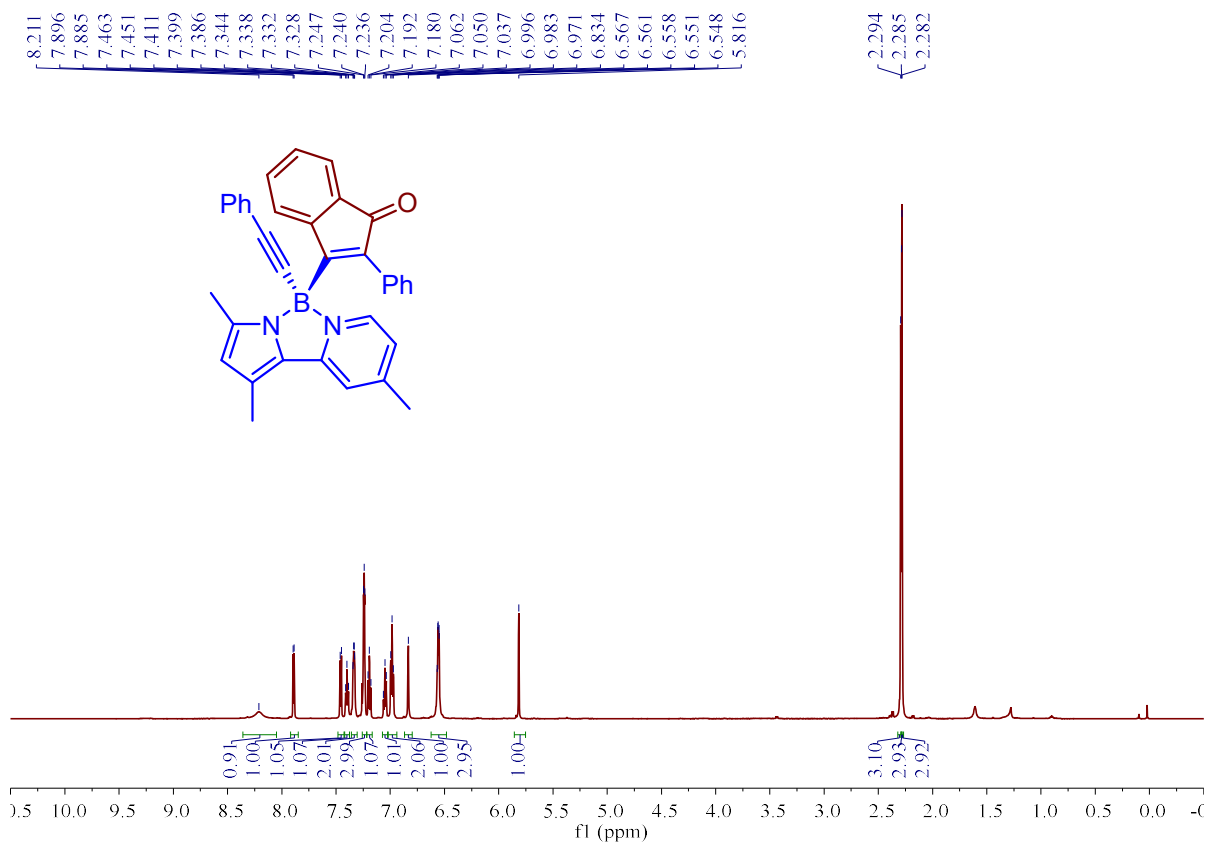
¹³C NMR (150 MHz, CDCl₃) spectrum of 21.



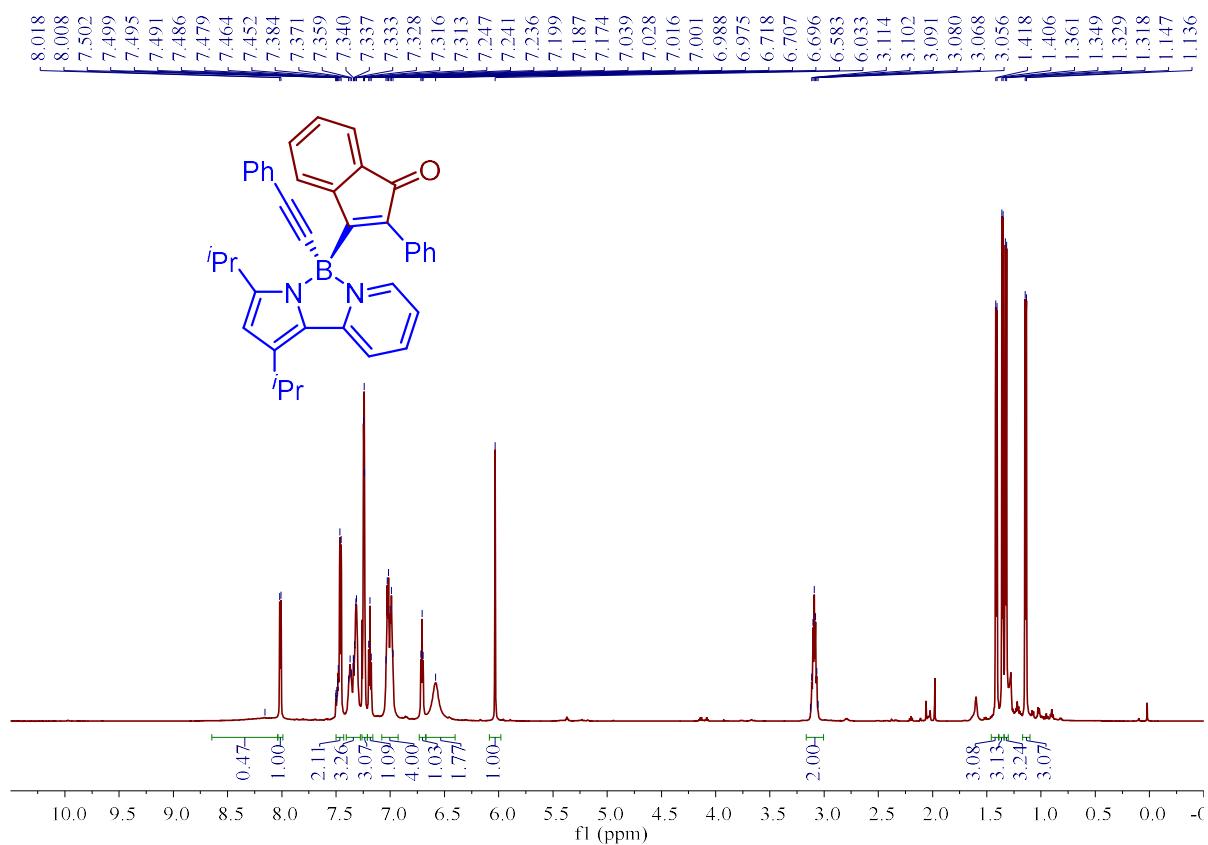
¹¹B NMR (193 MHz, CDCl₃) spectrum of 21.



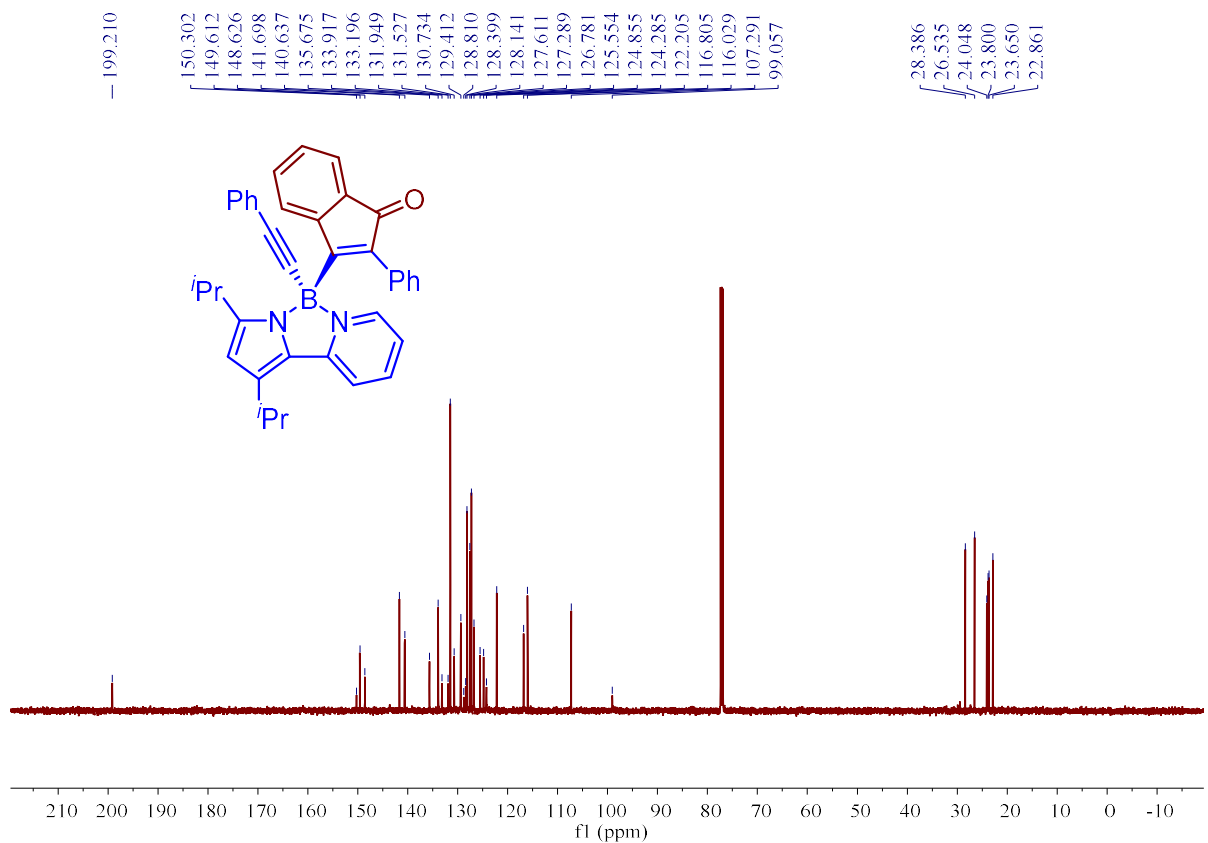
¹⁹F NMR (376 MHz, CDCl₃) spectrum of 21.



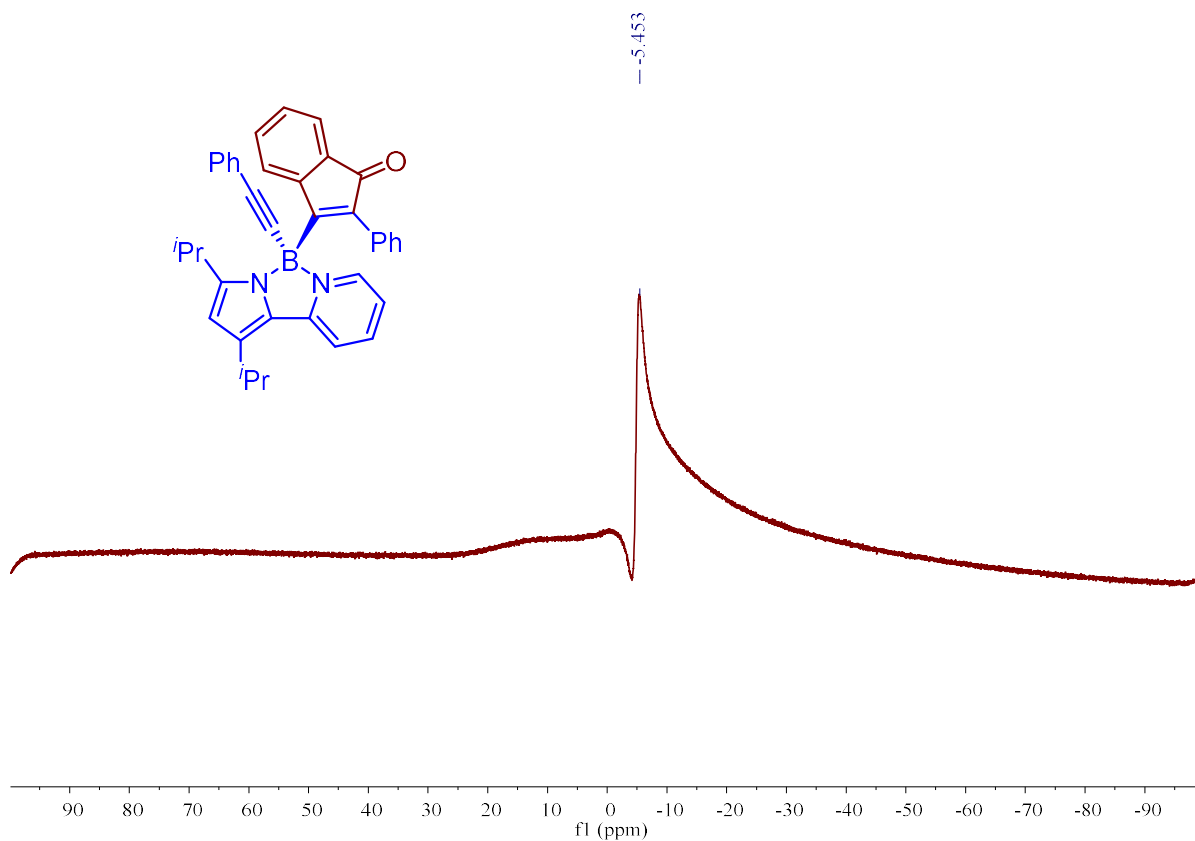
¹H NMR (600 MHz, CDCl₃) spectrum of 22.



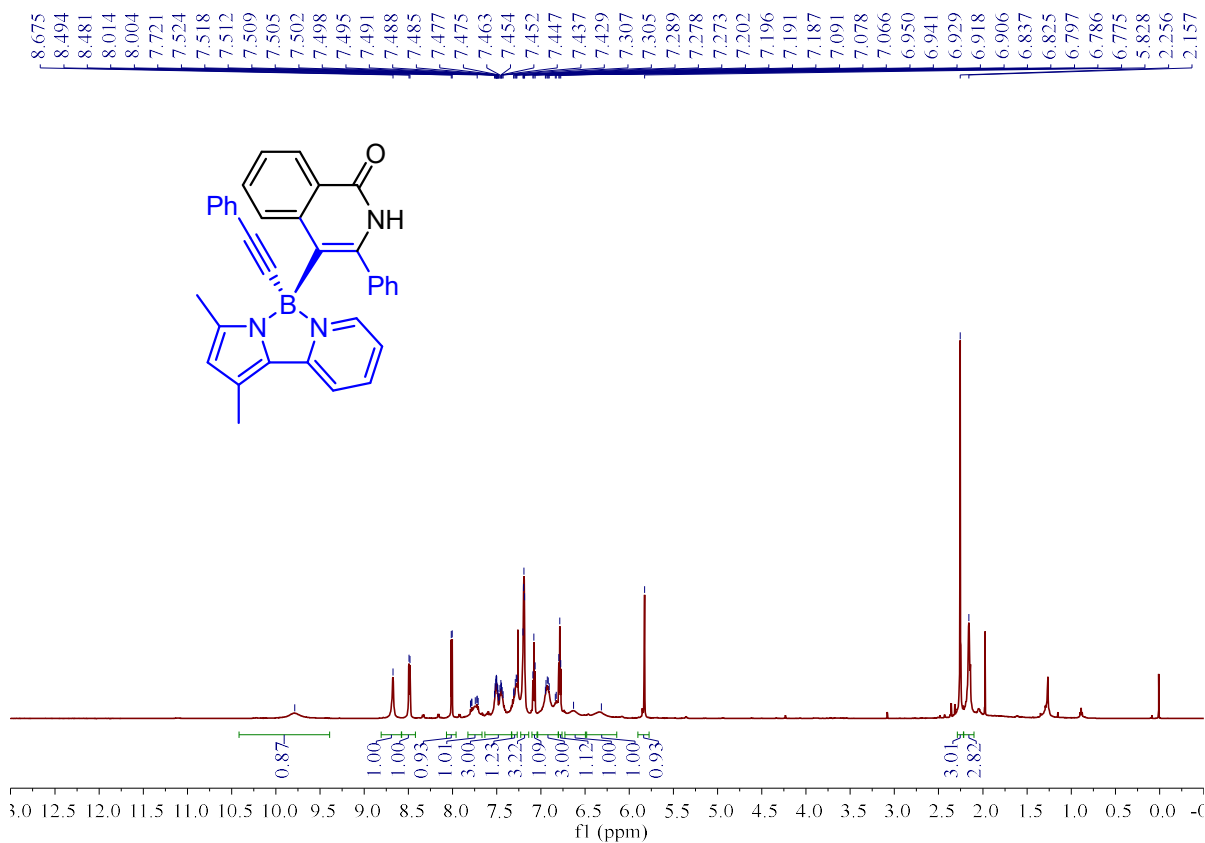
¹H NMR (600 MHz, CDCl₃) spectrum of 23.



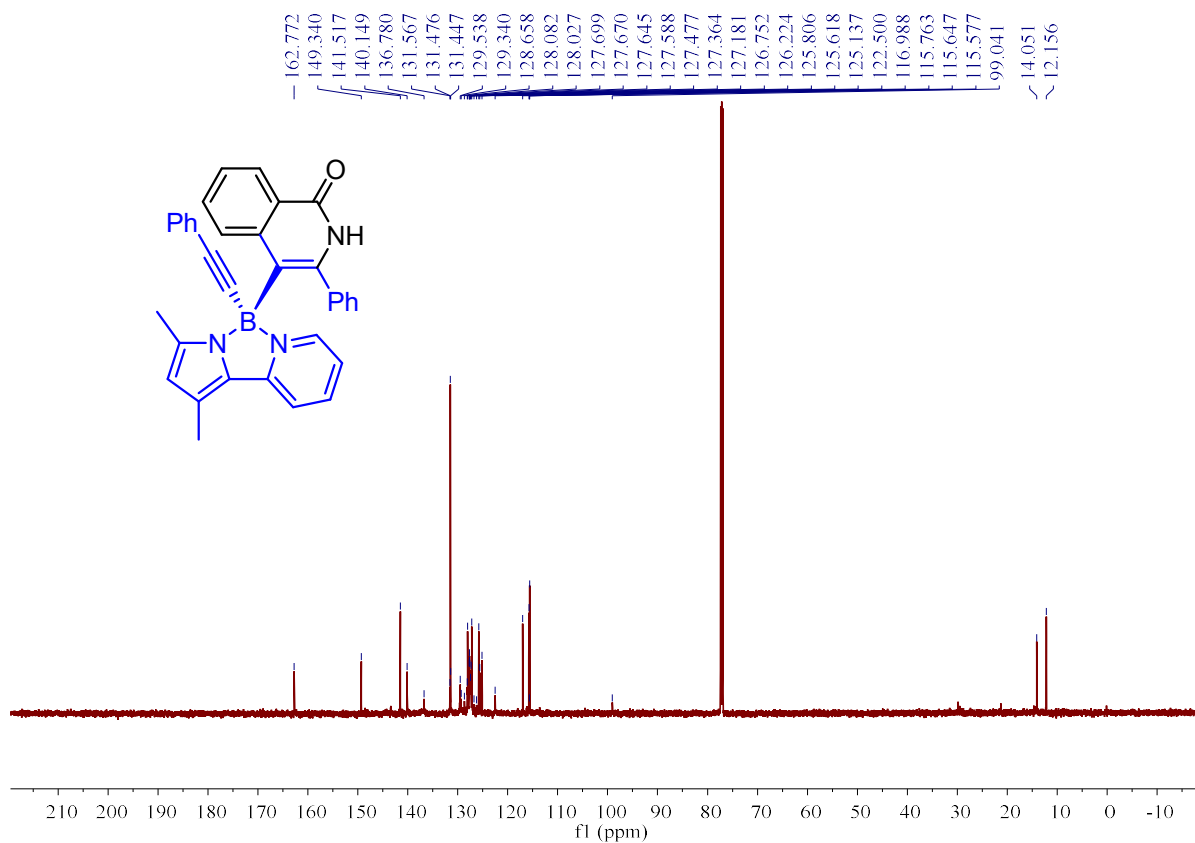
¹³C NMR (150 MHz, CDCl₃) spectrum of 23.



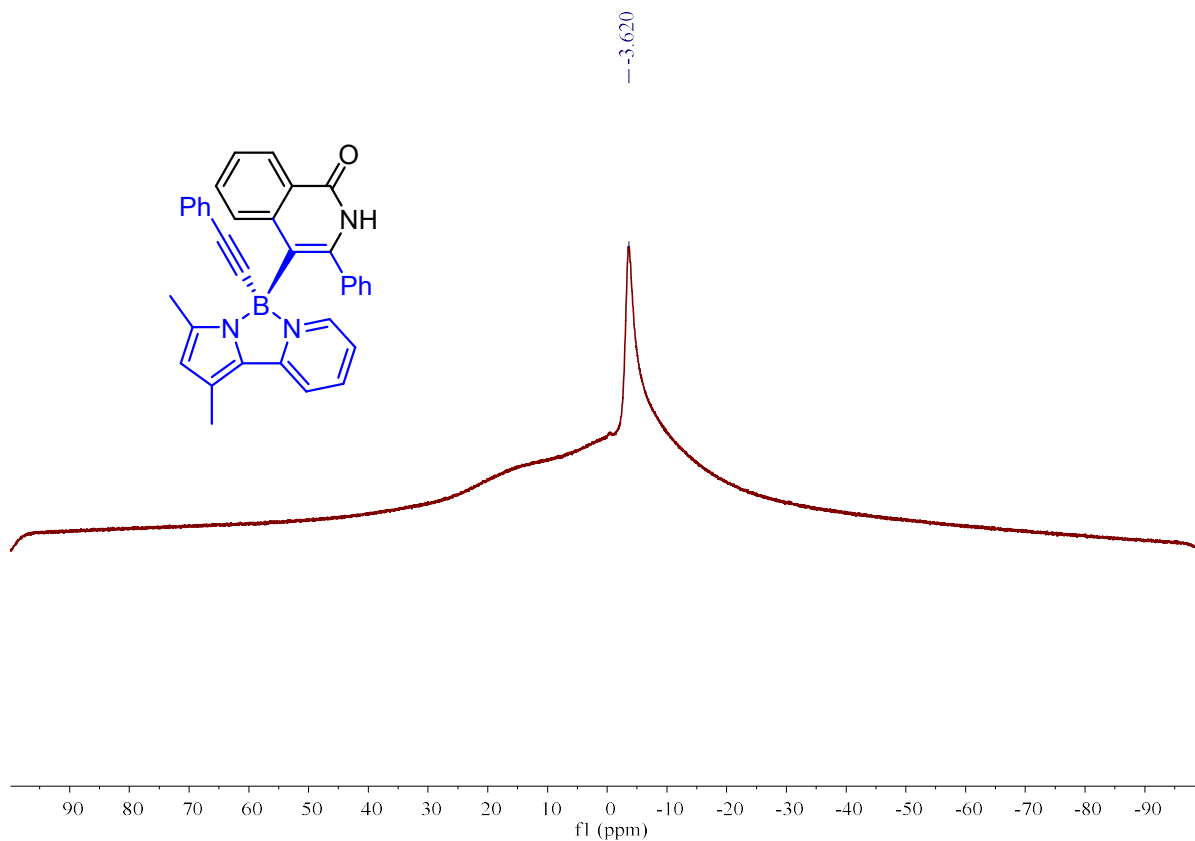
^{11}B NMR (193 MHz, CDCl_3) spectrum of 23.



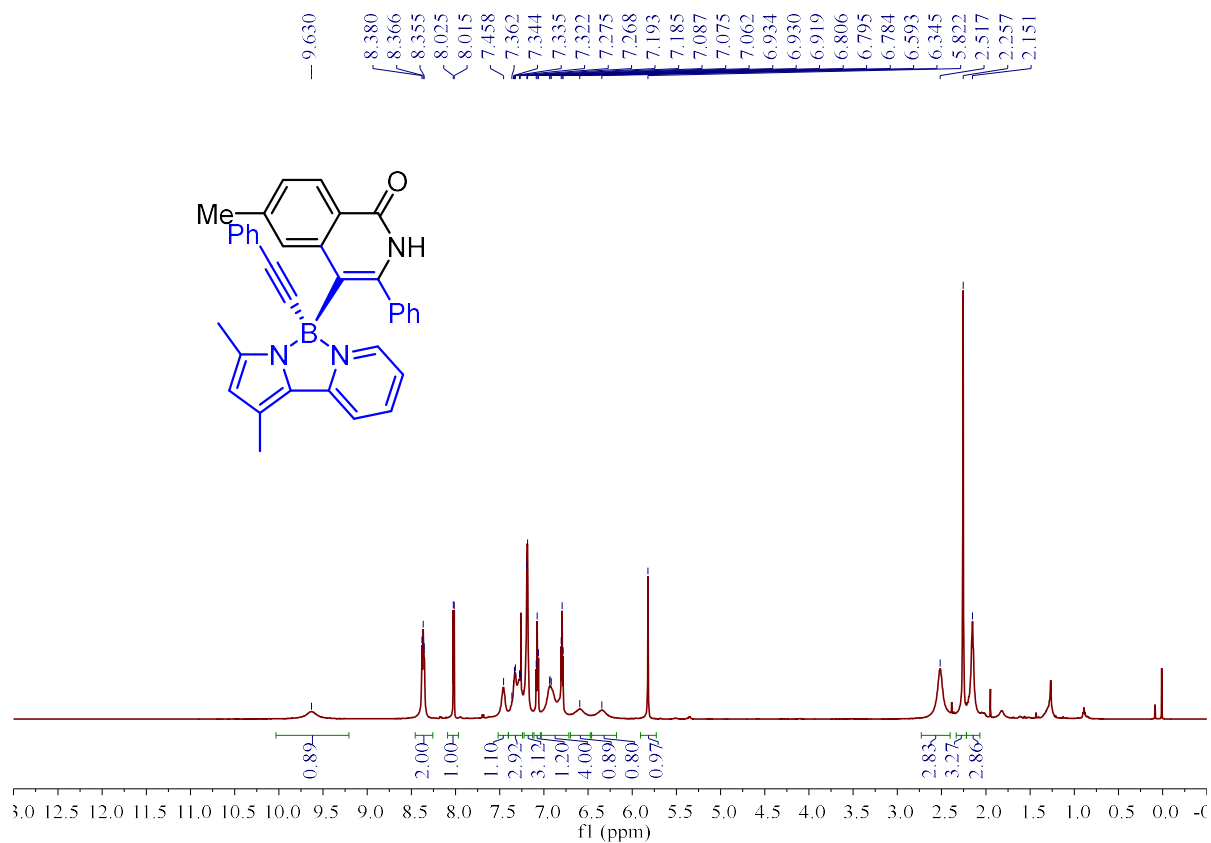
^1H NMR (600 MHz, CDCl_3) spectrum of 24.



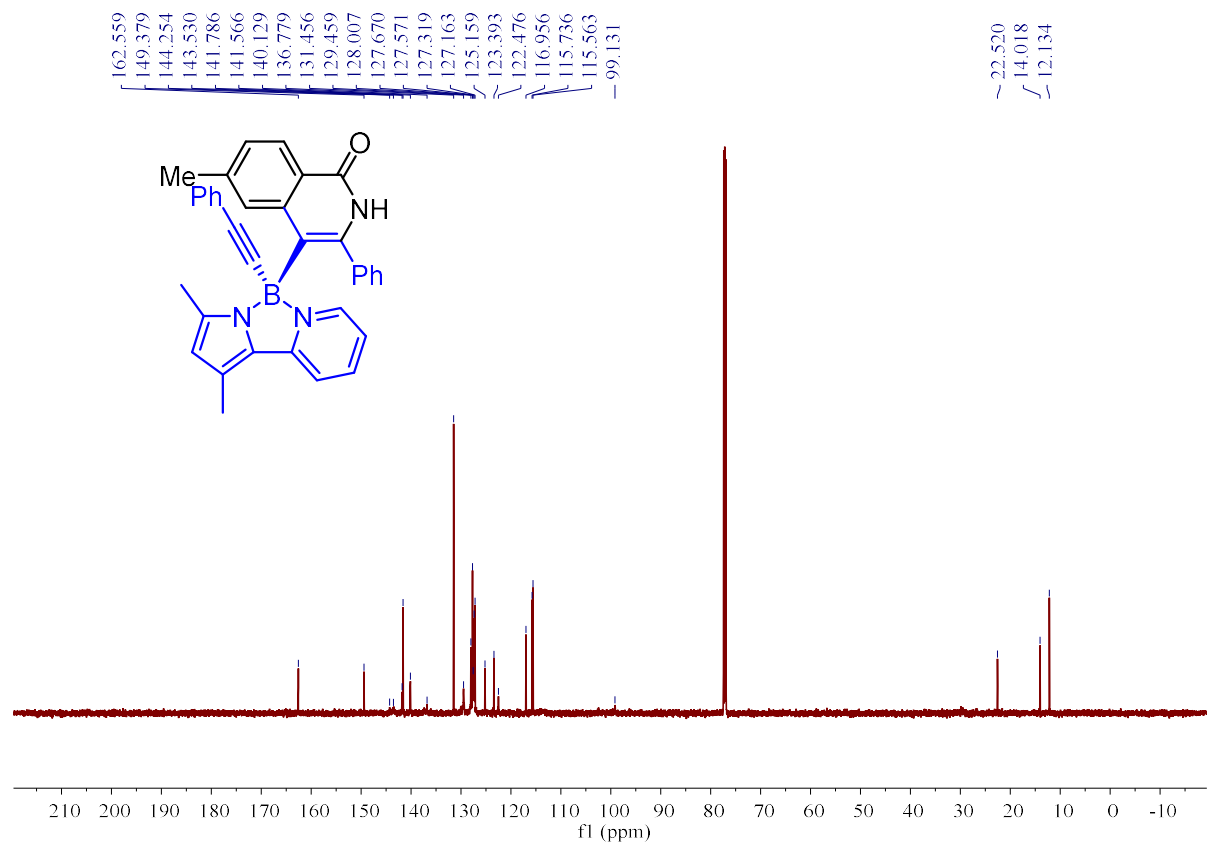
¹³C NMR (150 MHz, CDCl₃) spectrum of 24.



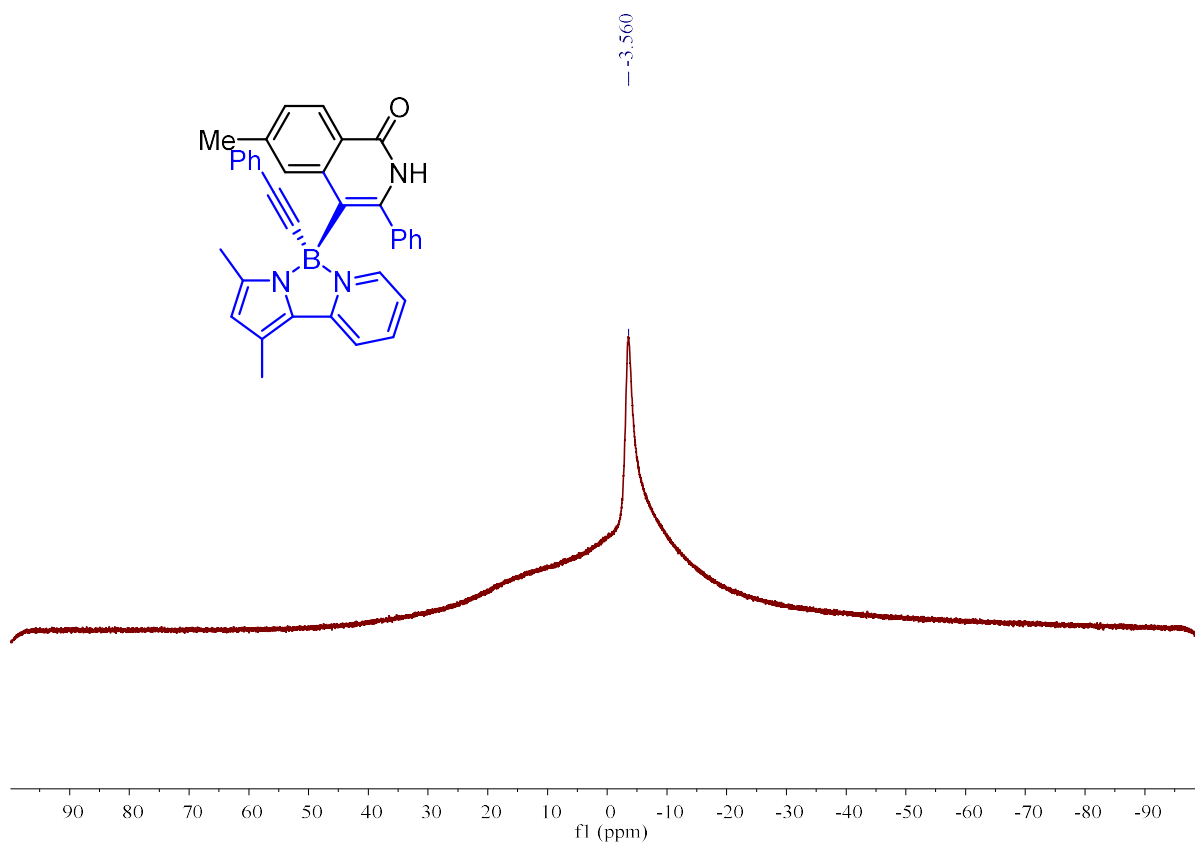
¹¹B NMR (193 MHz, CDCl₃) spectrum of 24.



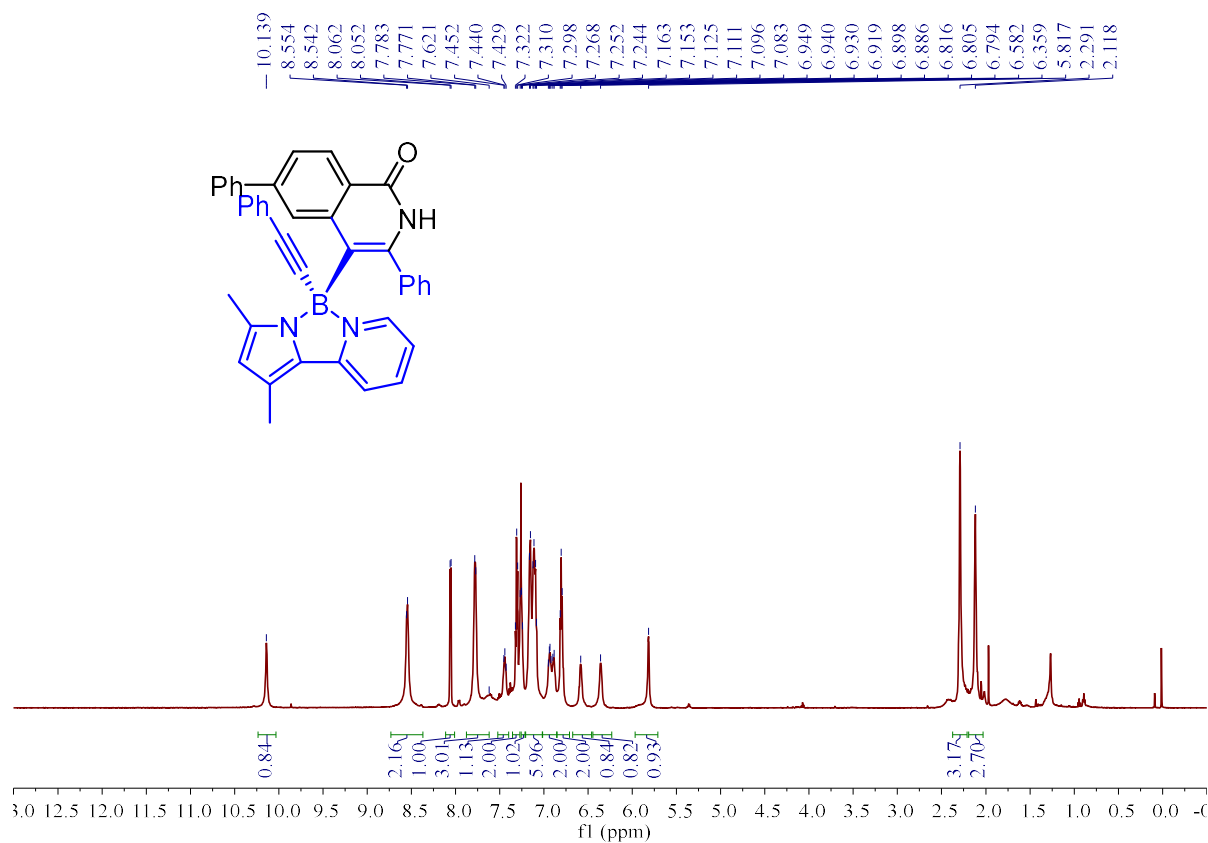
¹H NMR (600 MHz, CDCl₃) spectrum of 25.



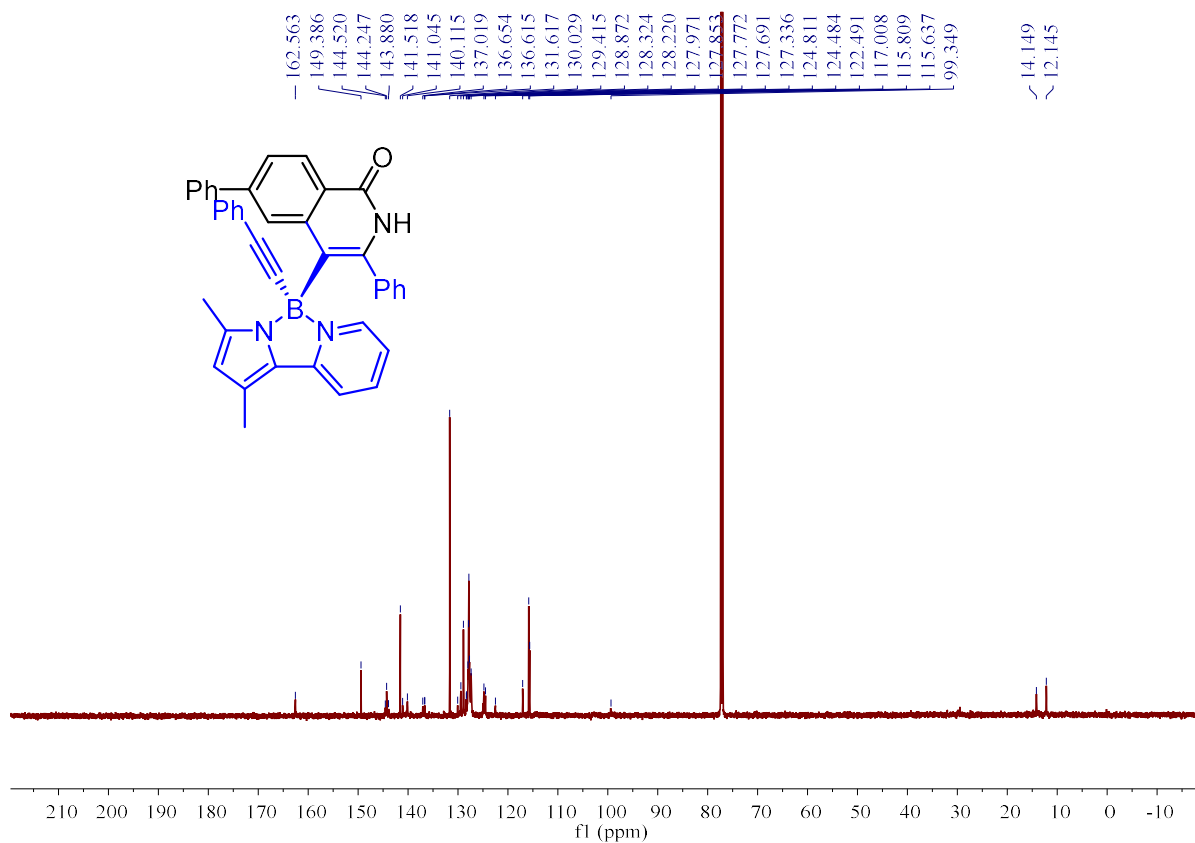
¹³C NMR (150 MHz, CDCl₃) spectrum of 25.



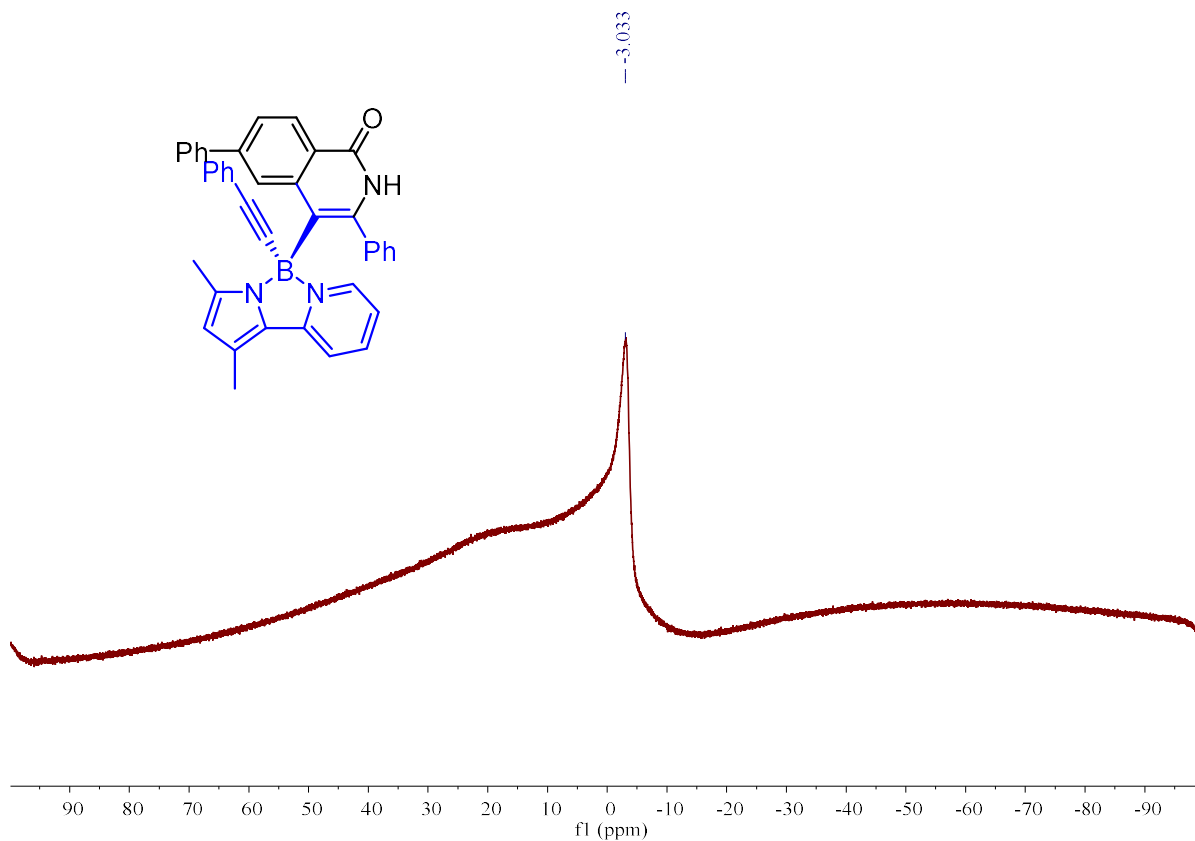
^{11}B NMR (193 MHz, CDCl_3) spectrum of 25.



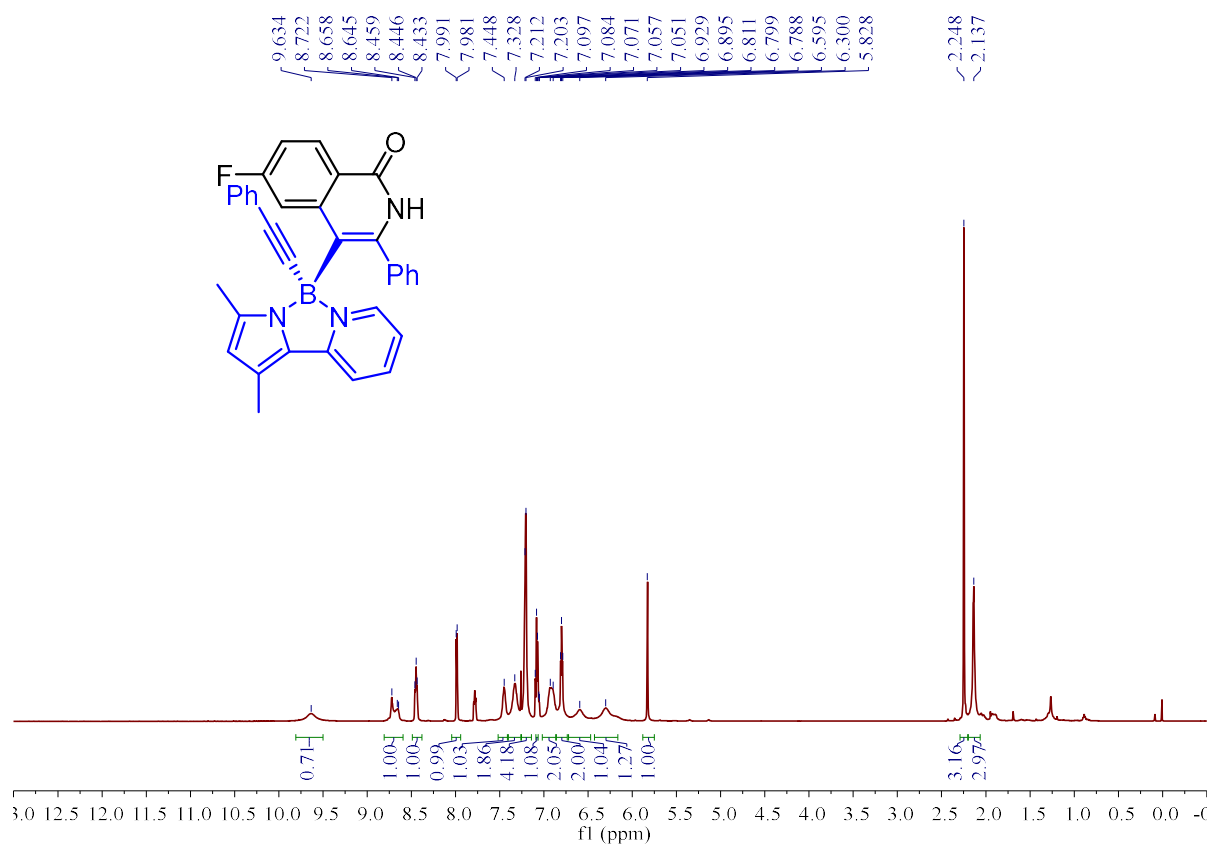
^1H NMR (600 MHz, CDCl_3) spectrum of 26.



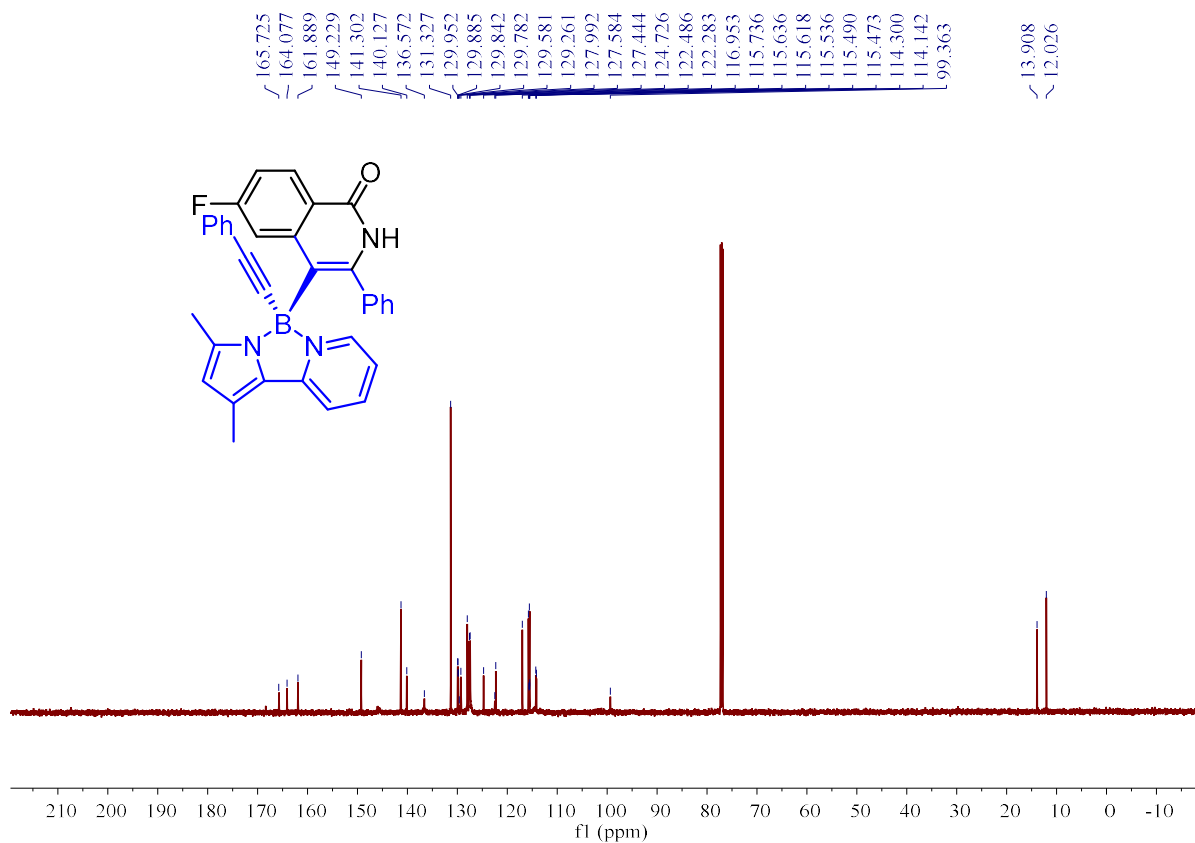
¹³C NMR (150 MHz, CDCl₃) spectrum of 26.



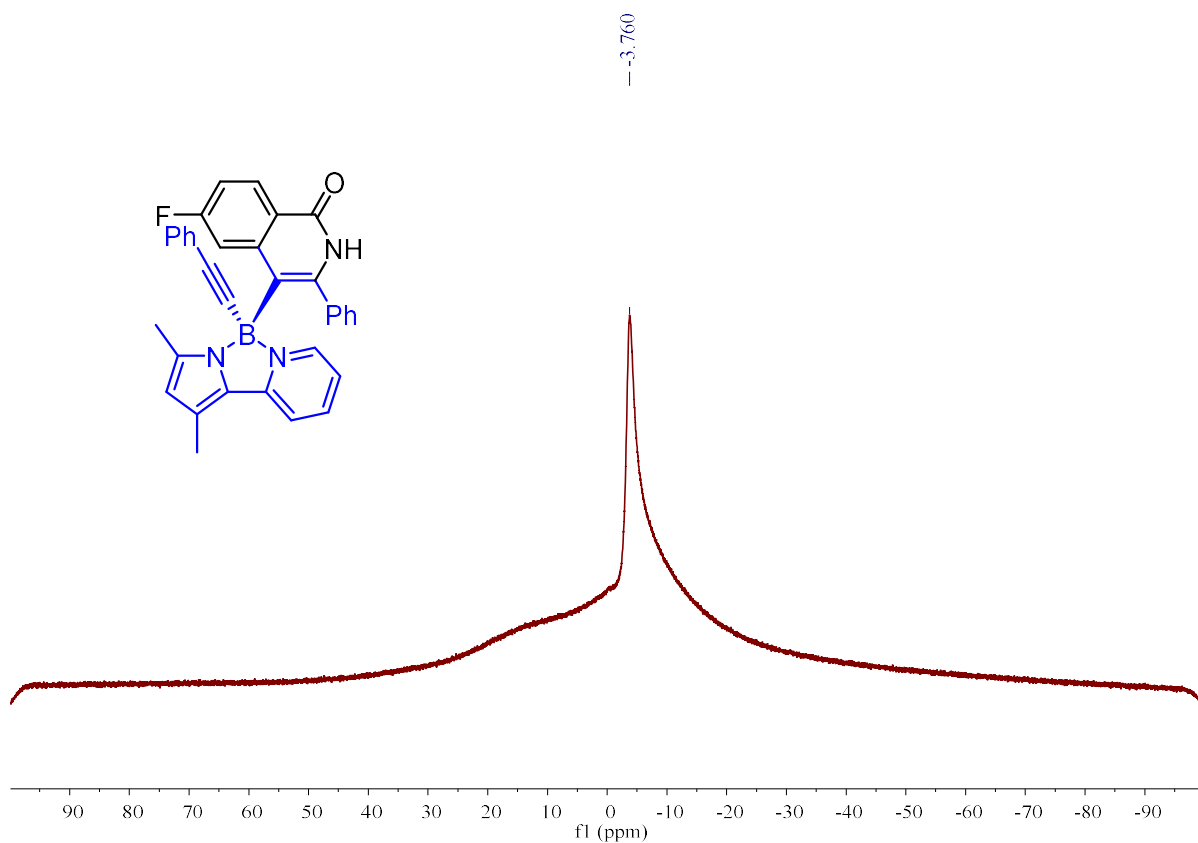
¹¹B NMR (193 MHz, CDCl₃) spectrum of 26.



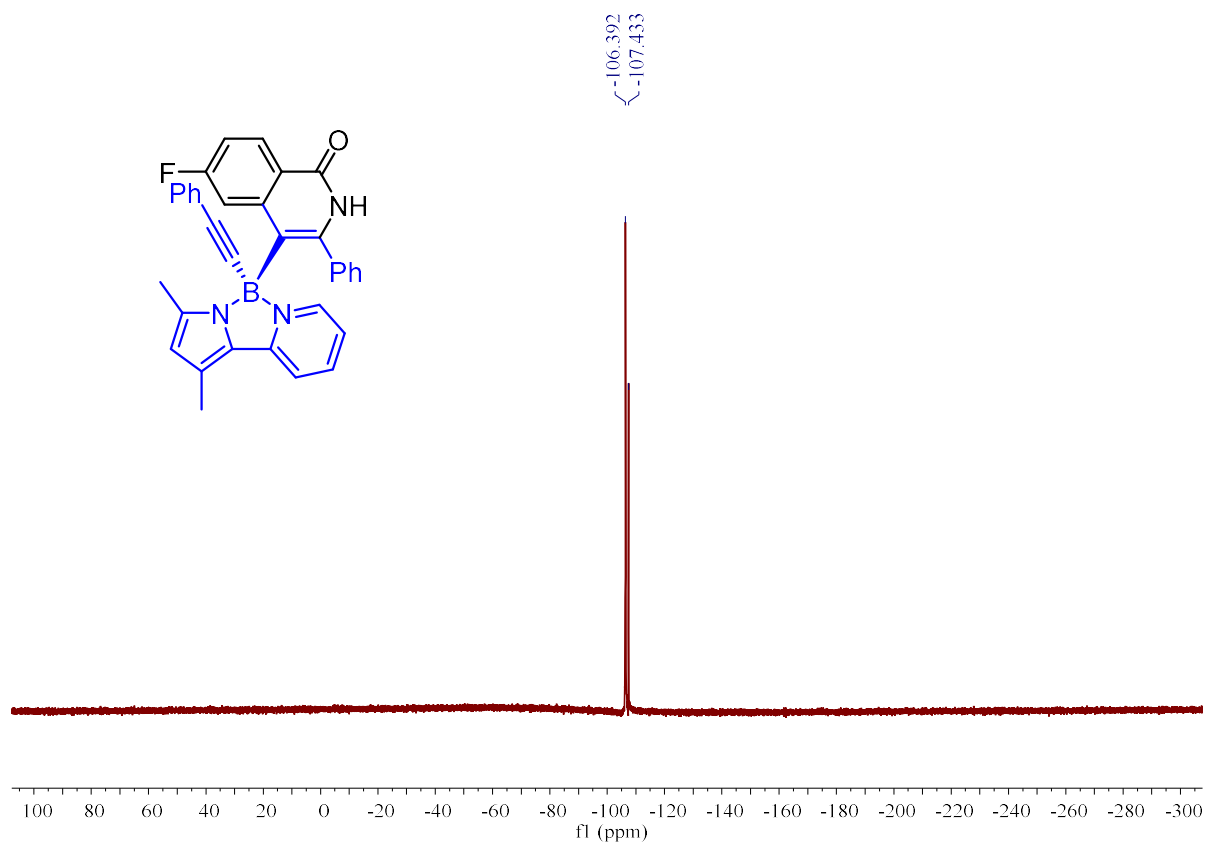
¹H NMR (600 MHz, CDCl₃) spectrum of 27.



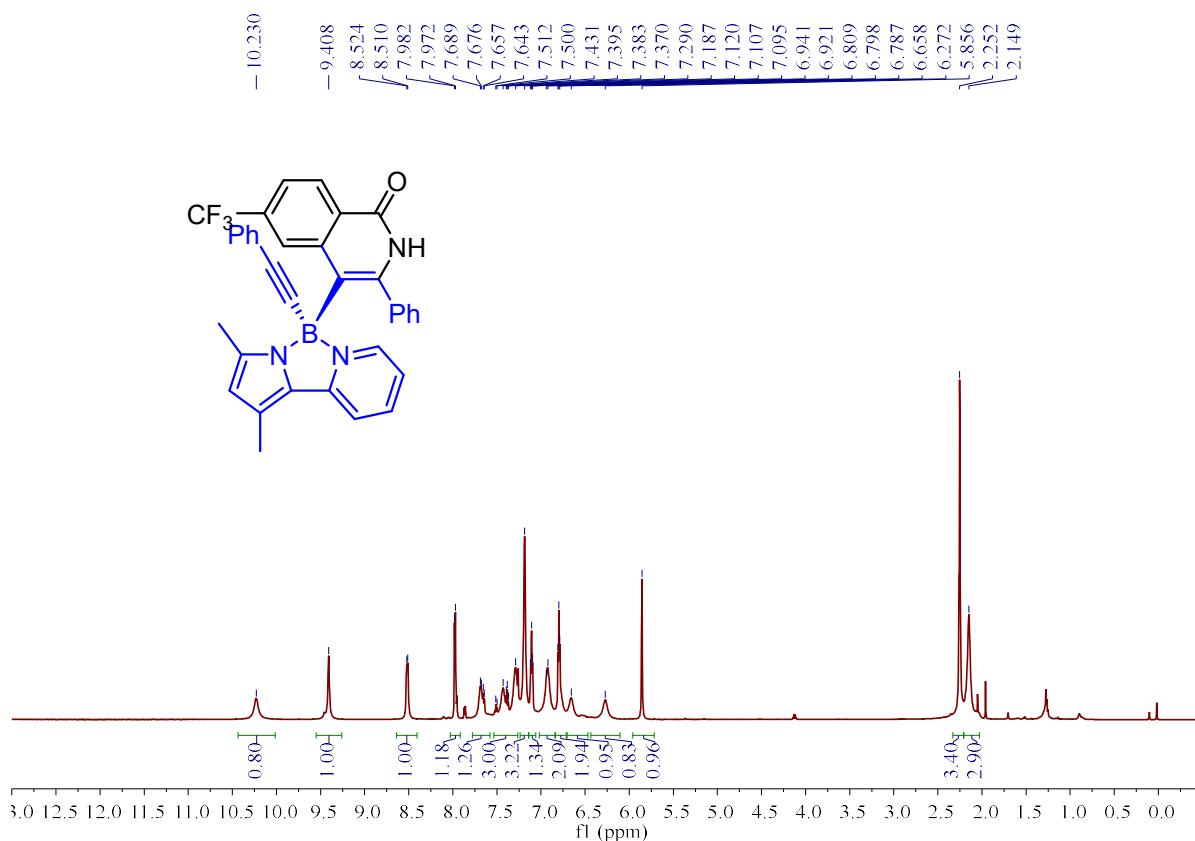
¹³C NMR (150 MHz, CDCl₃) spectrum of 27.



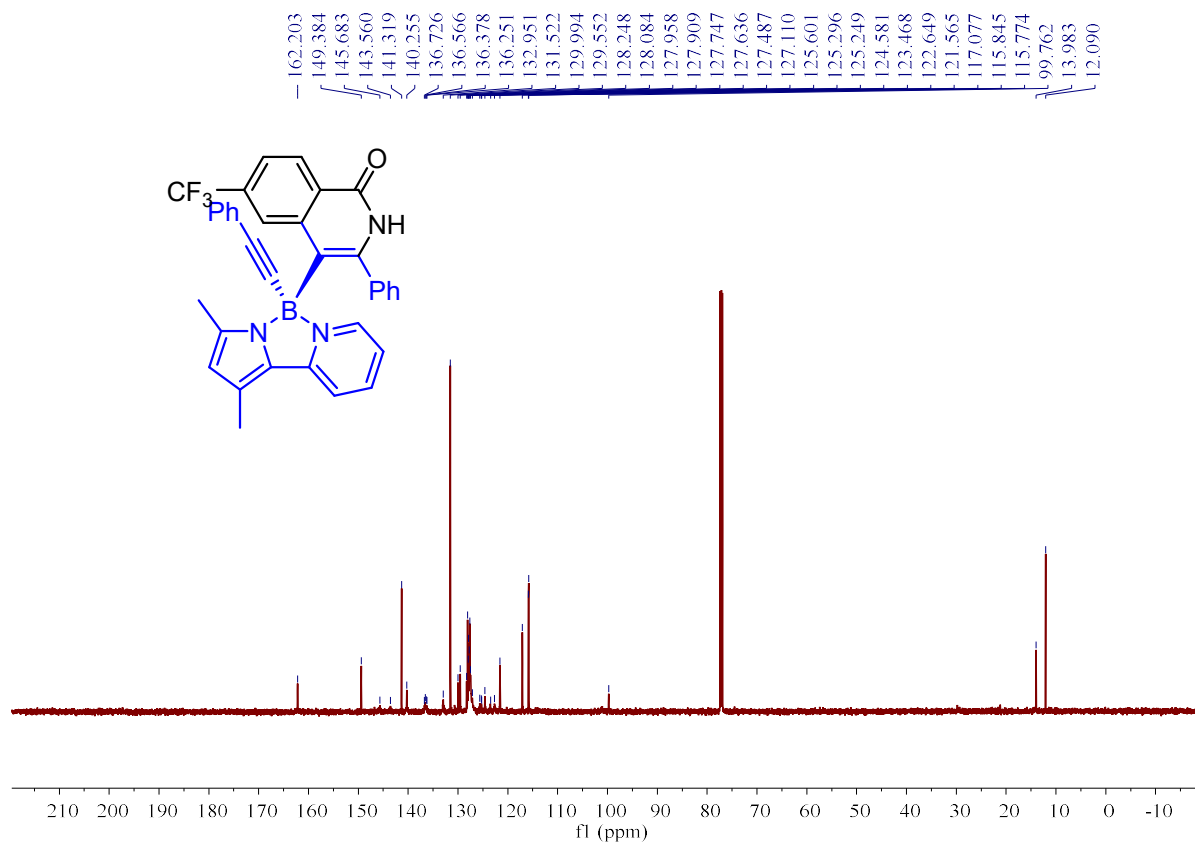
¹¹B NMR (193 MHz, CDCl₃) spectrum of 27.



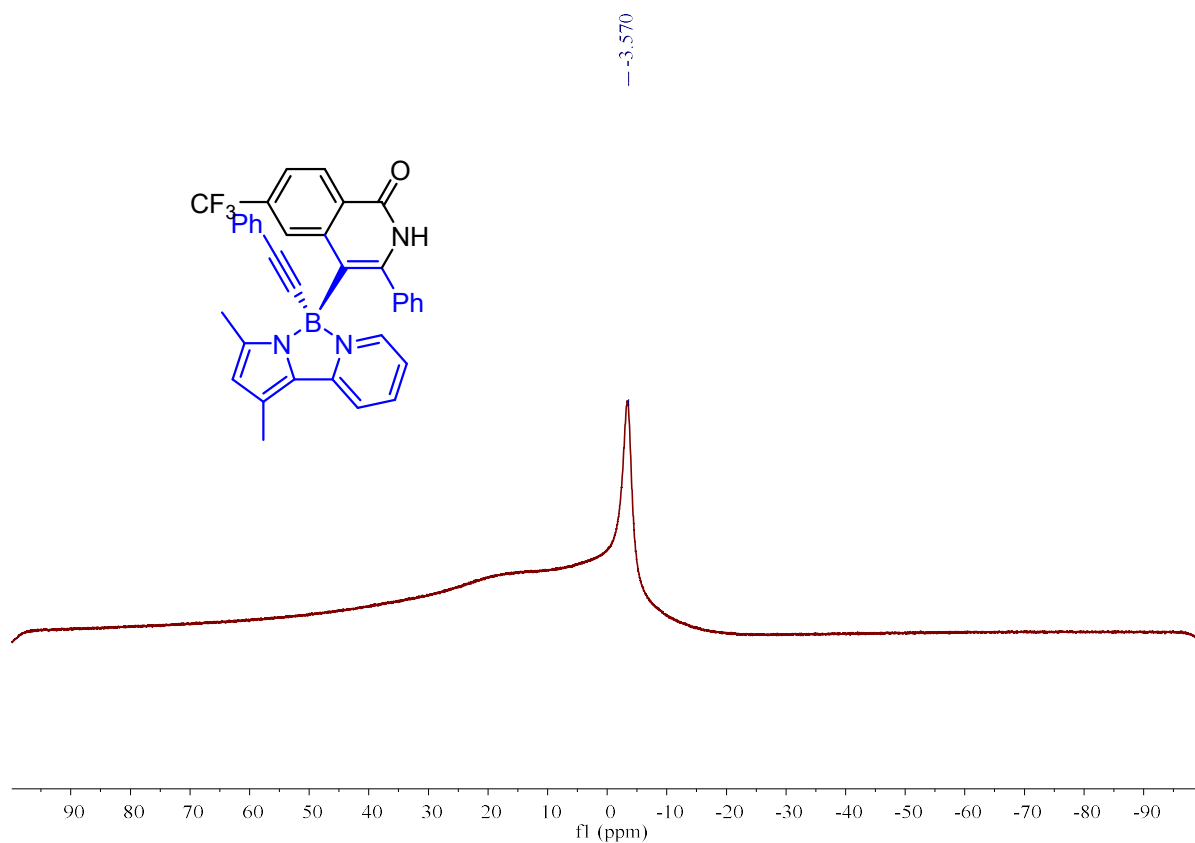
¹⁹F NMR (376 MHz, CDCl₃) spectrum of 27.



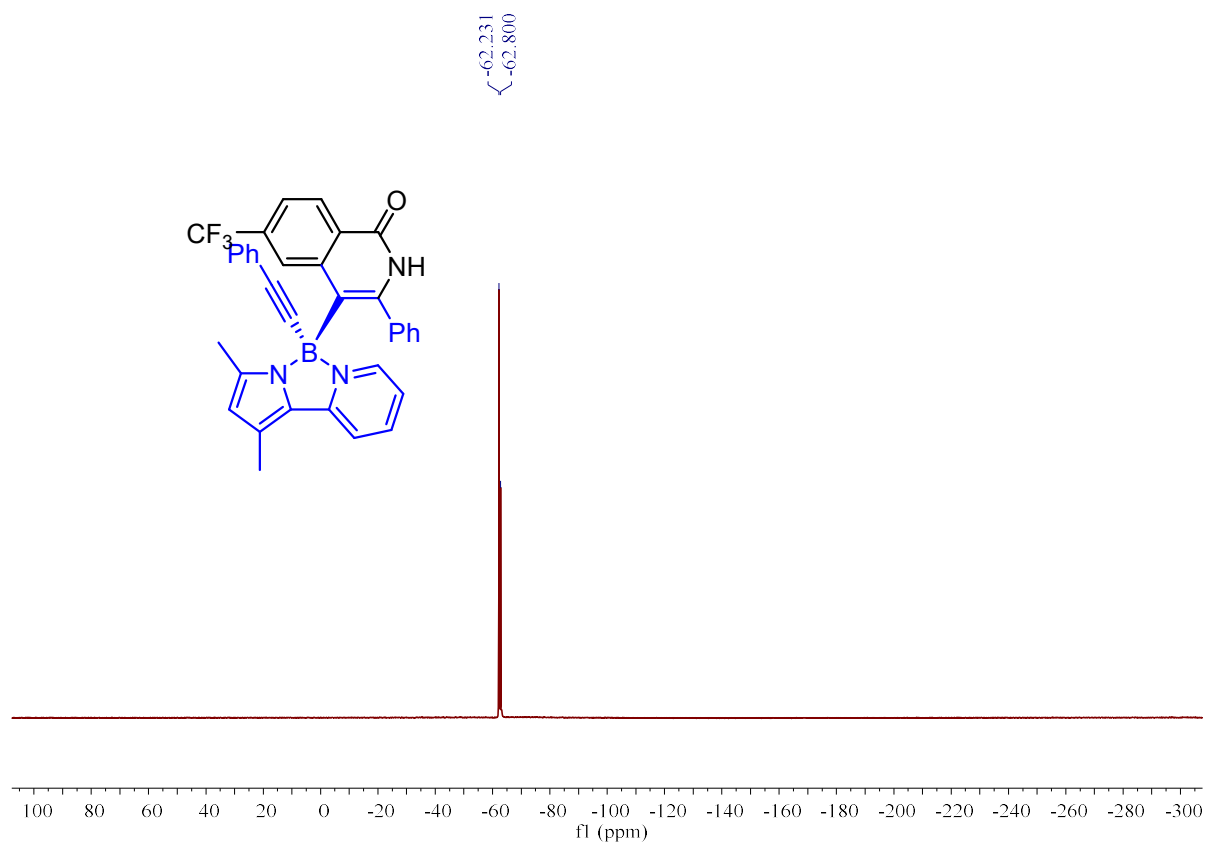
¹H NMR (600 MHz, CDCl₃) spectrum of 28.



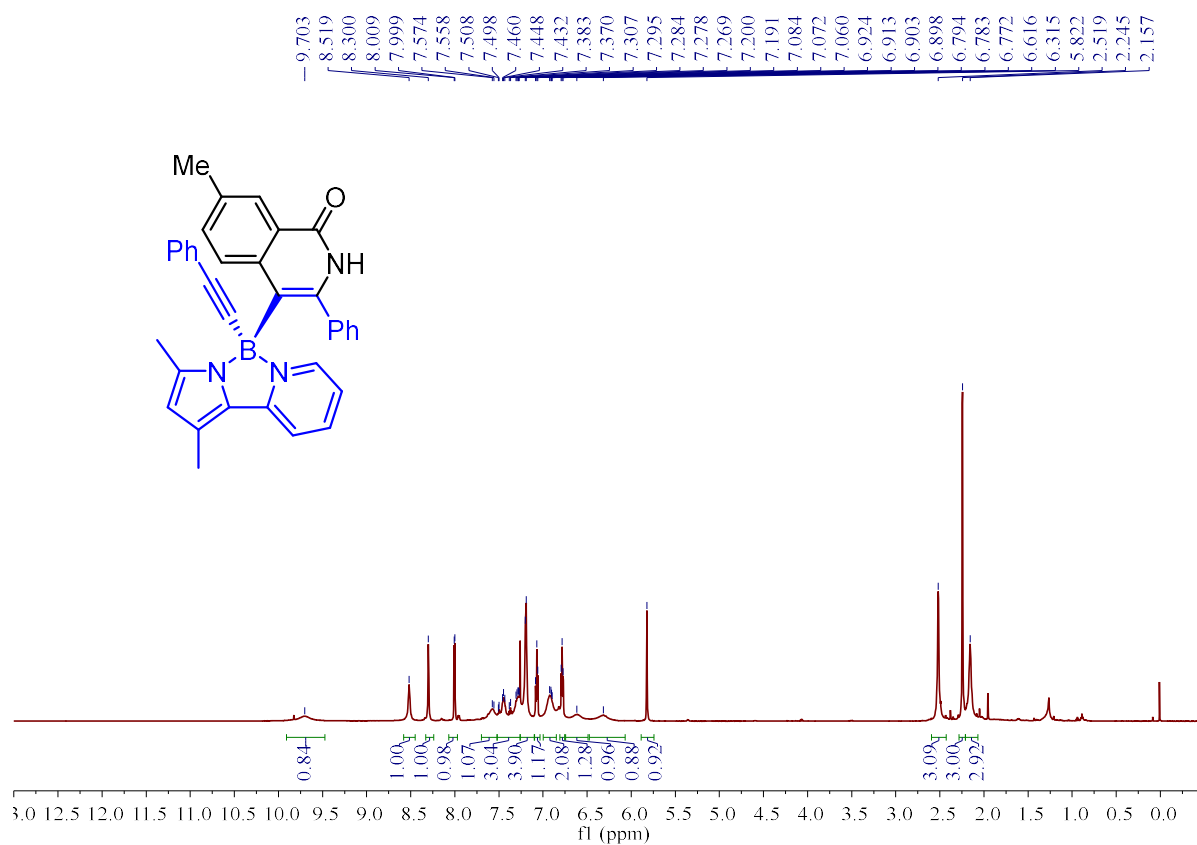
¹³C NMR (150 MHz, CDCl₃) spectrum of 28.



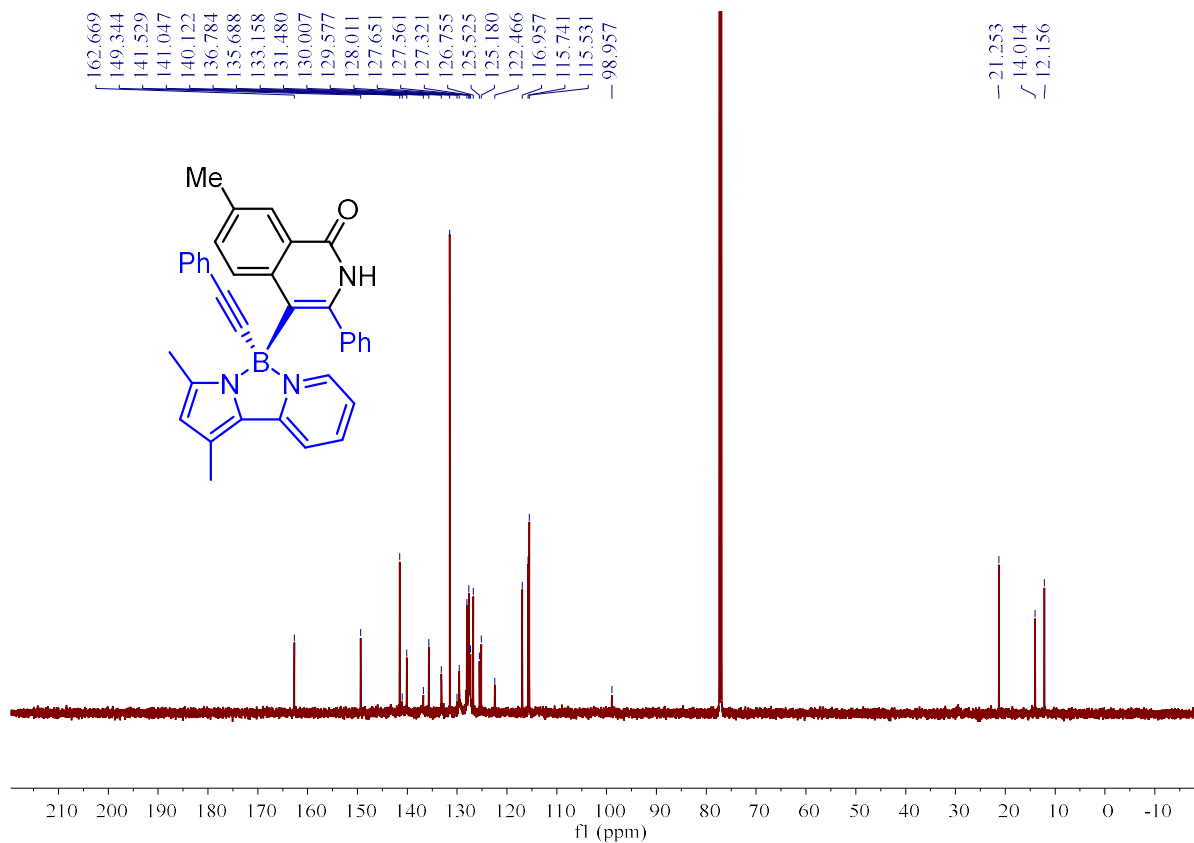
¹¹B NMR (193 MHz, CDCl₃) spectrum of 28.



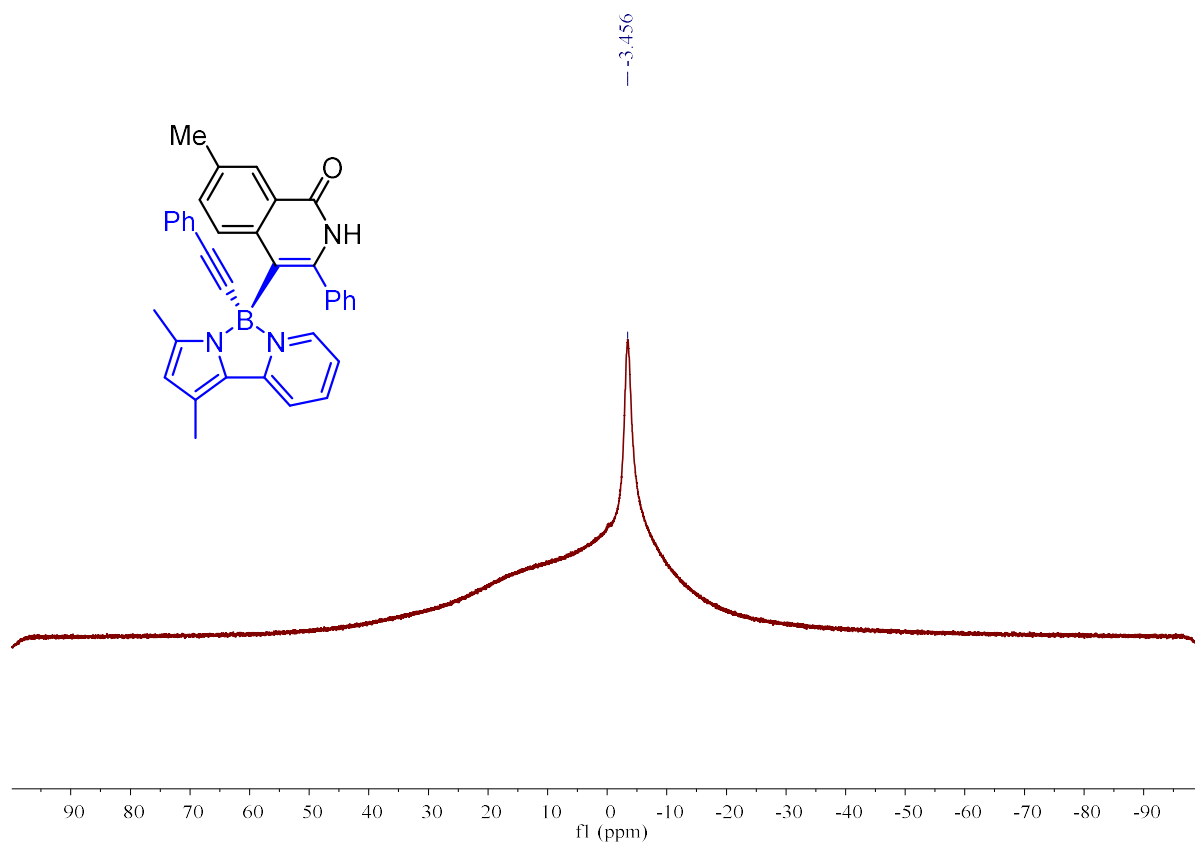
¹⁹F NMR (376 MHz, CDCl₃) spectrum of 28.



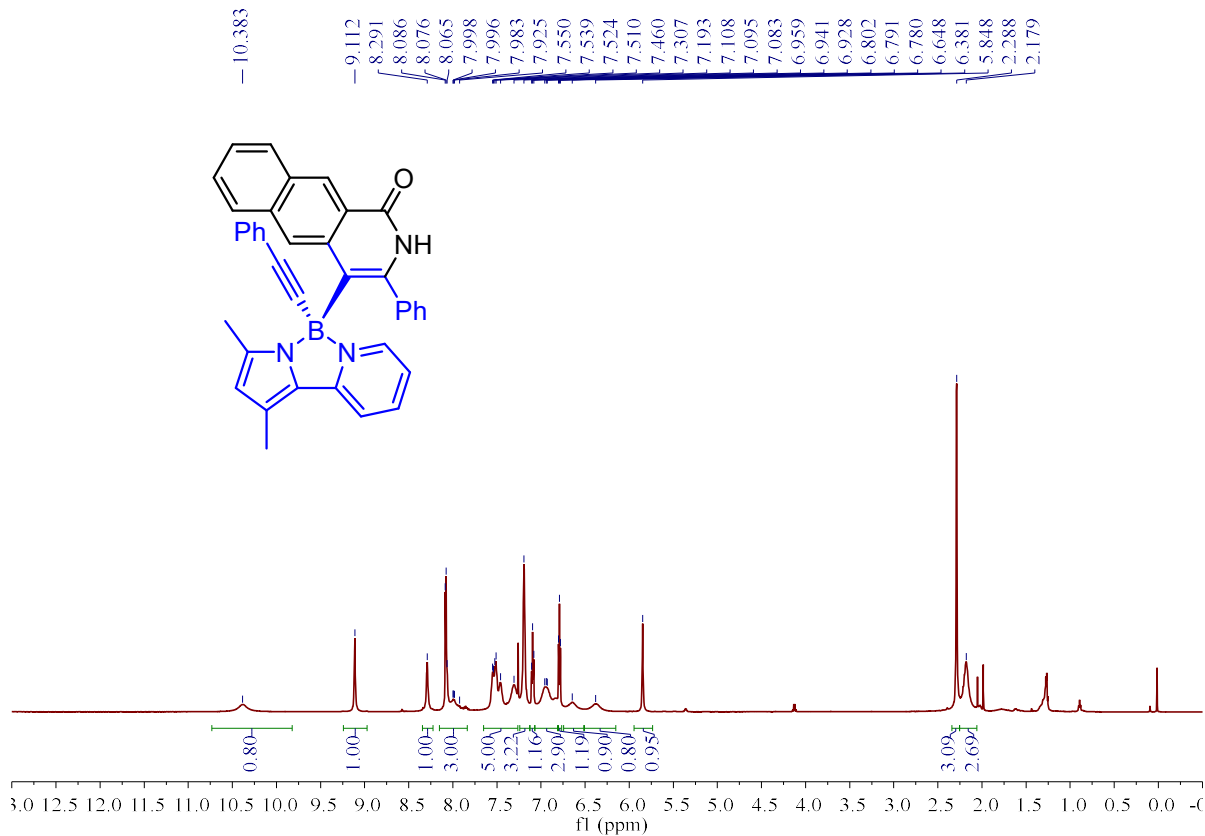
¹H NMR (600 MHz, CDCl₃) spectrum of 29.



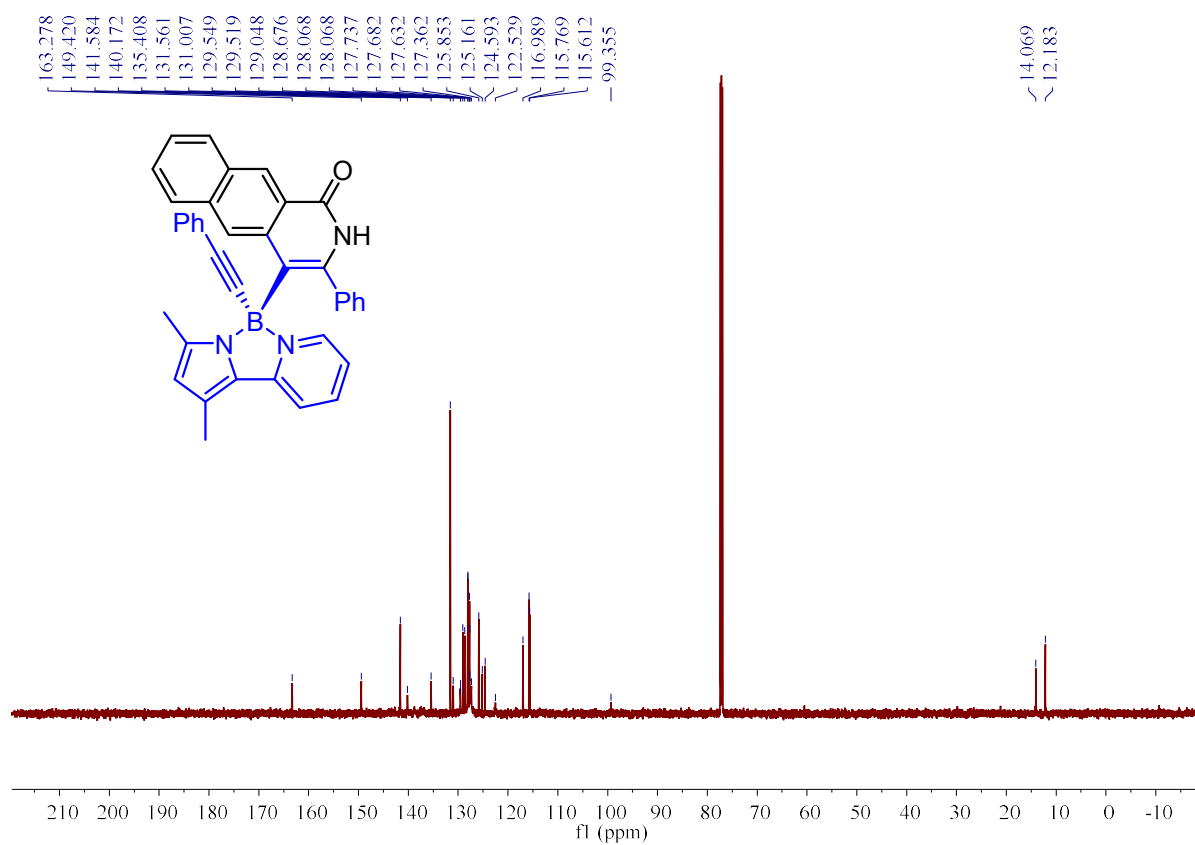
¹³C NMR (150 MHz, CDCl₃) spectrum of 29.



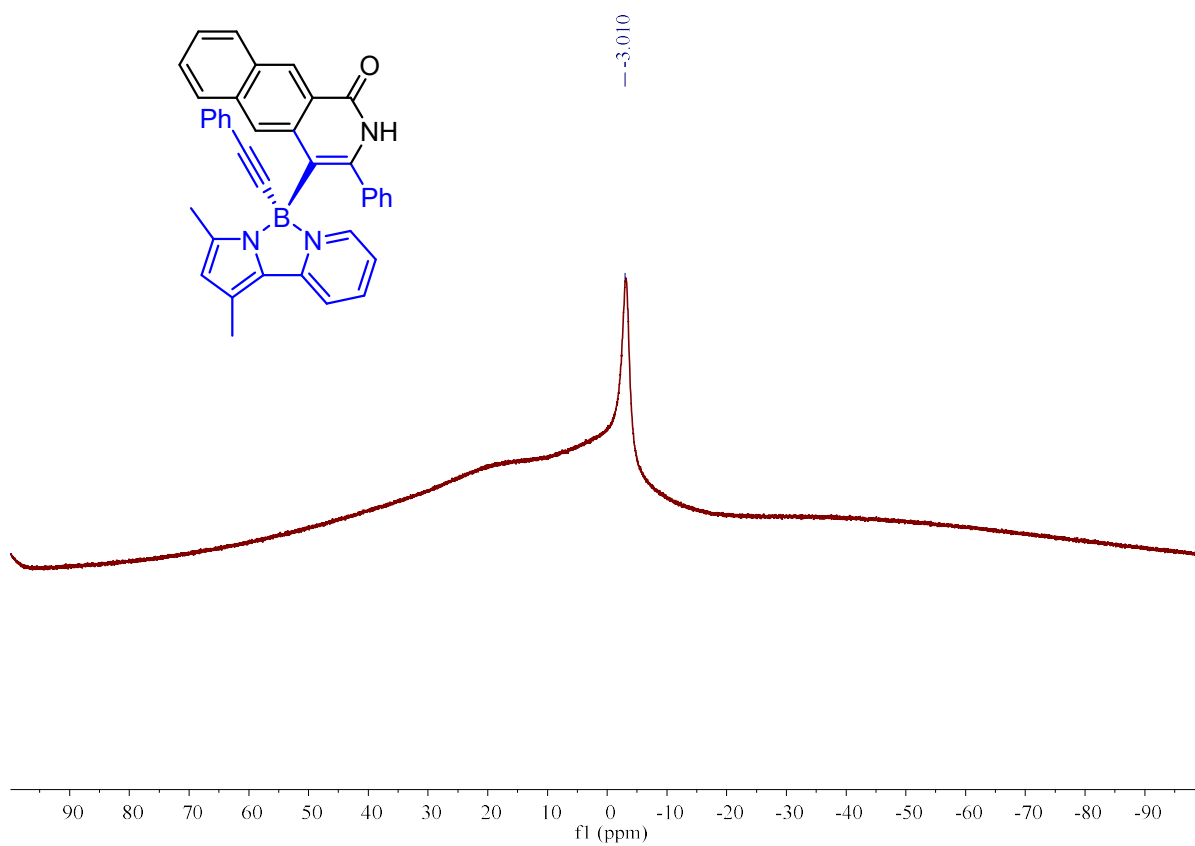
^{11}B NMR (193 MHz, CDCl_3) spectrum of **29**.



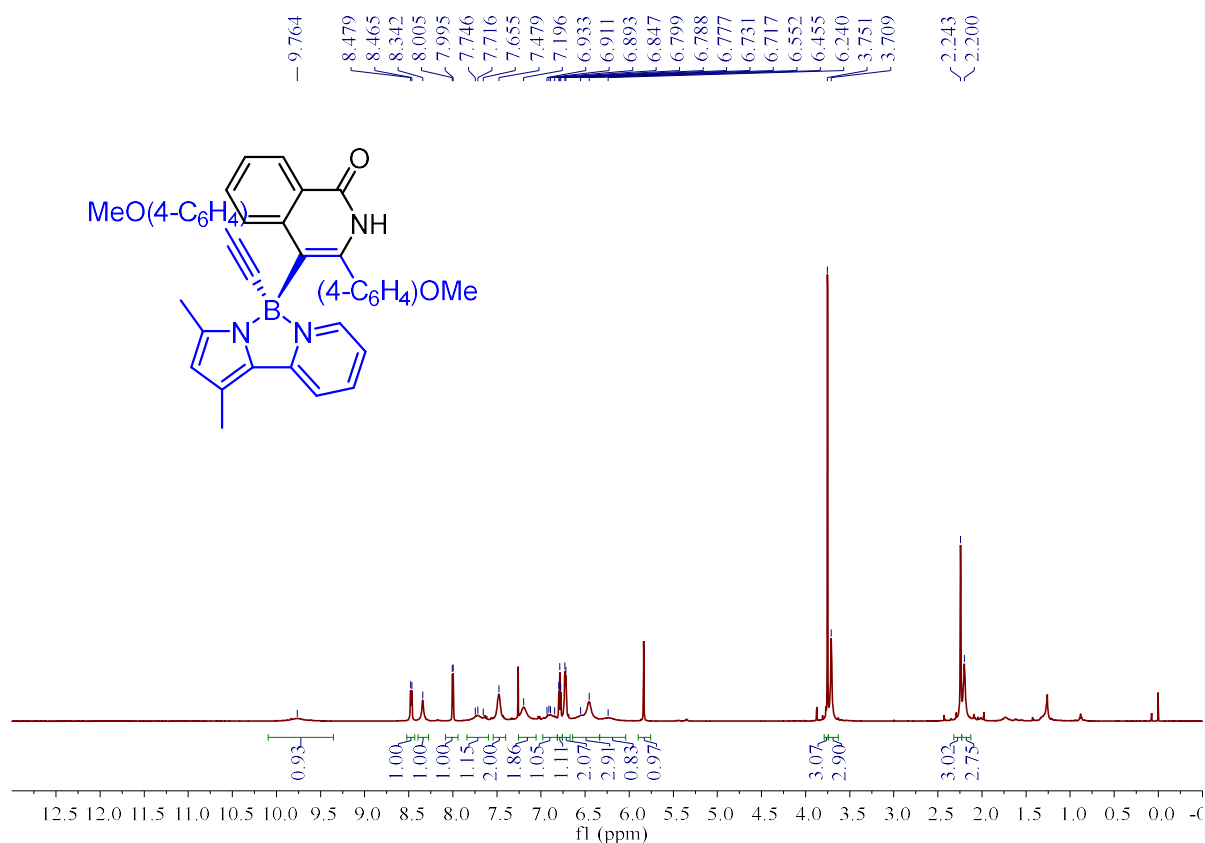
^1H NMR (600 MHz, CDCl_3) spectrum of **30**.



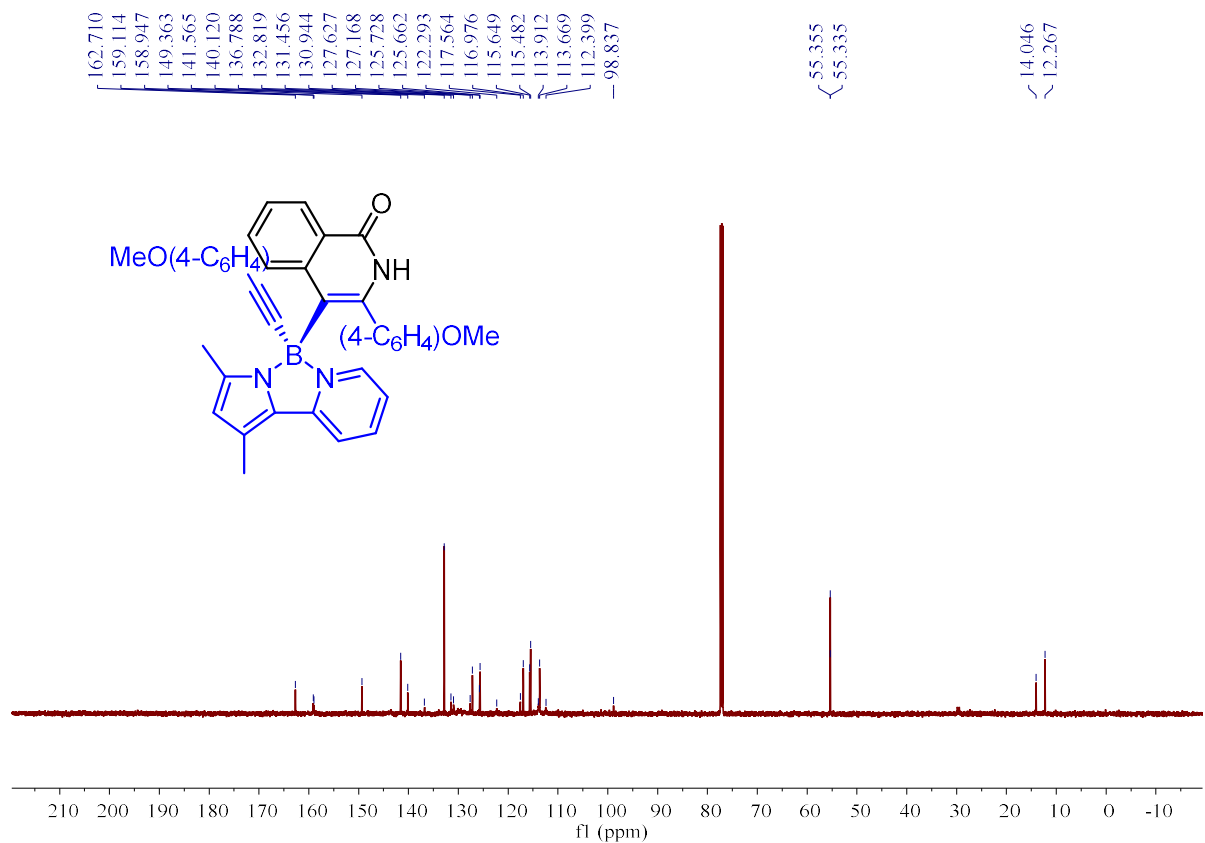
¹³C NMR (150 MHz, CDCl₃) spectrum of 30.



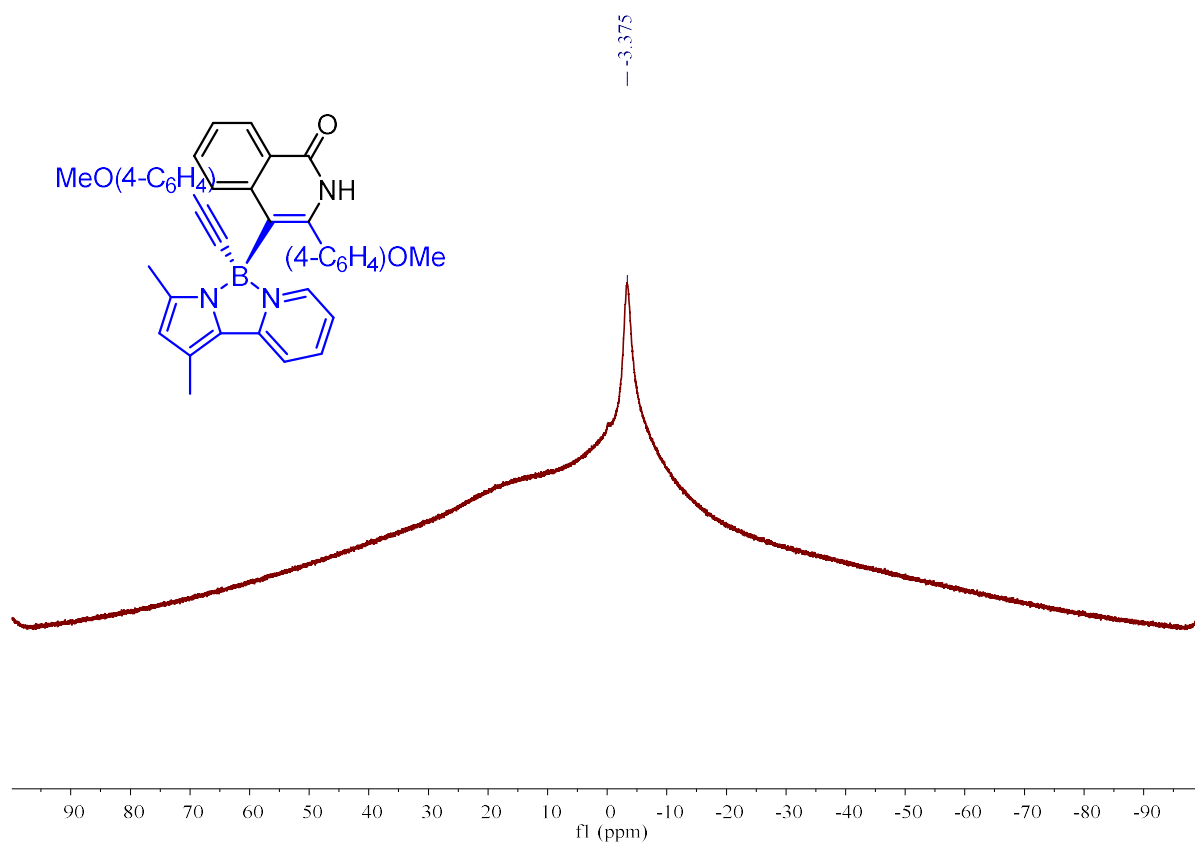
¹¹B NMR (193 MHz, CDCl₃) spectrum of 30.



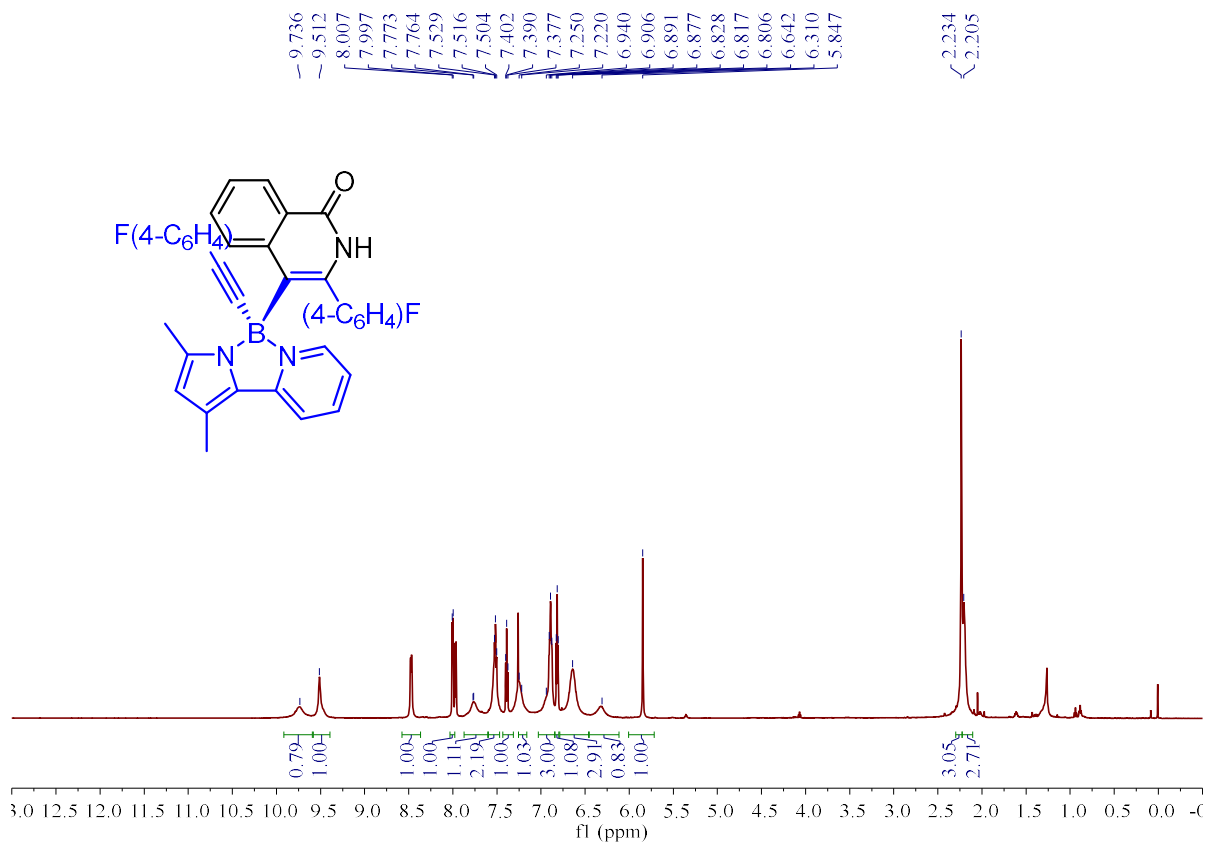
¹H NMR (600 MHz, CDCl₃) spectrum of 31.



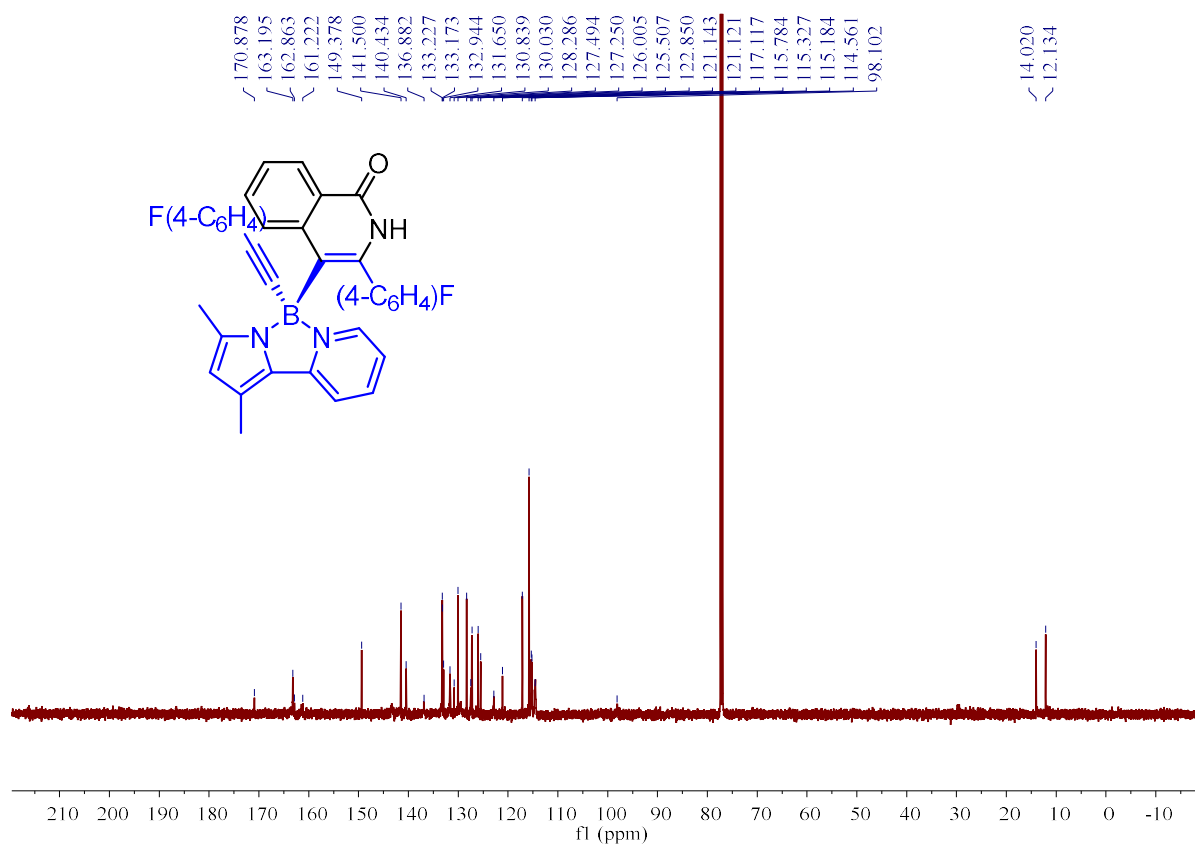
¹³C NMR (150 MHz, CDCl₃) spectrum of 31.



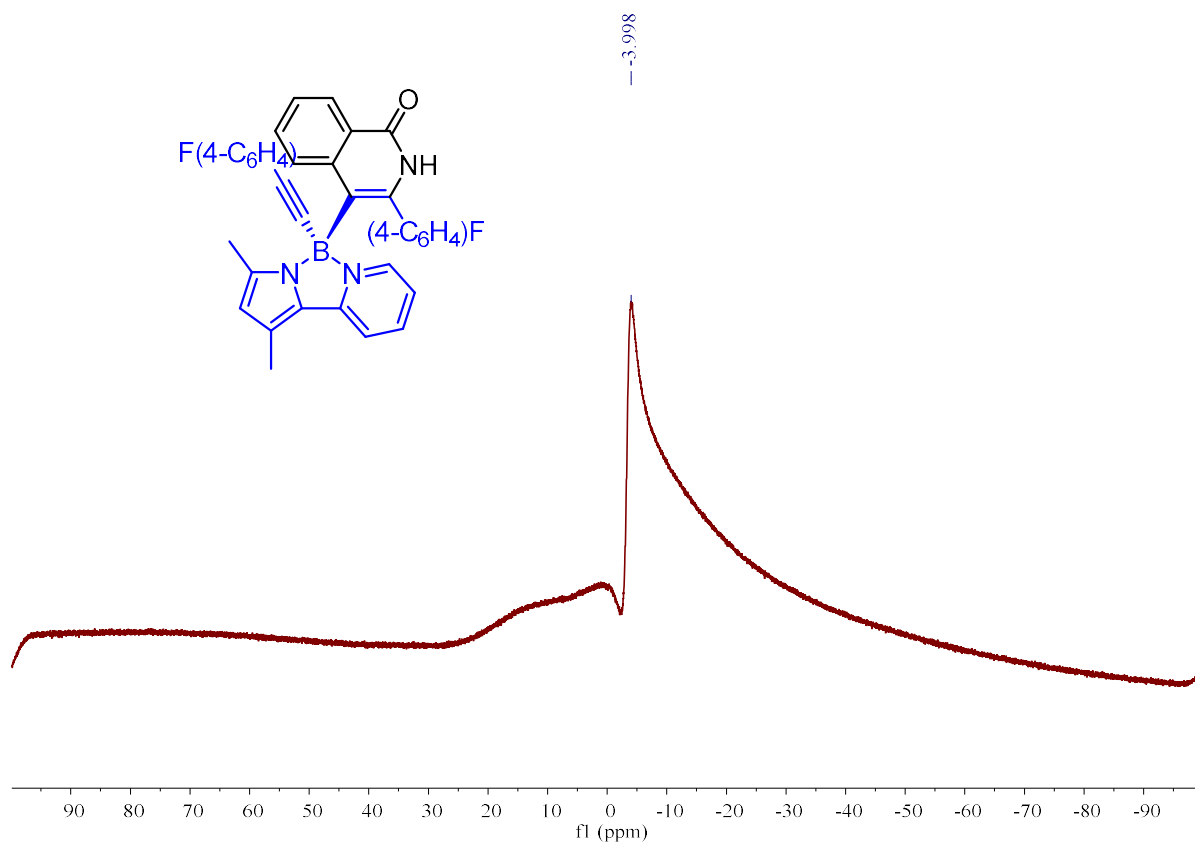
^{11}B NMR (193 MHz, CDCl_3) spectrum of 31.



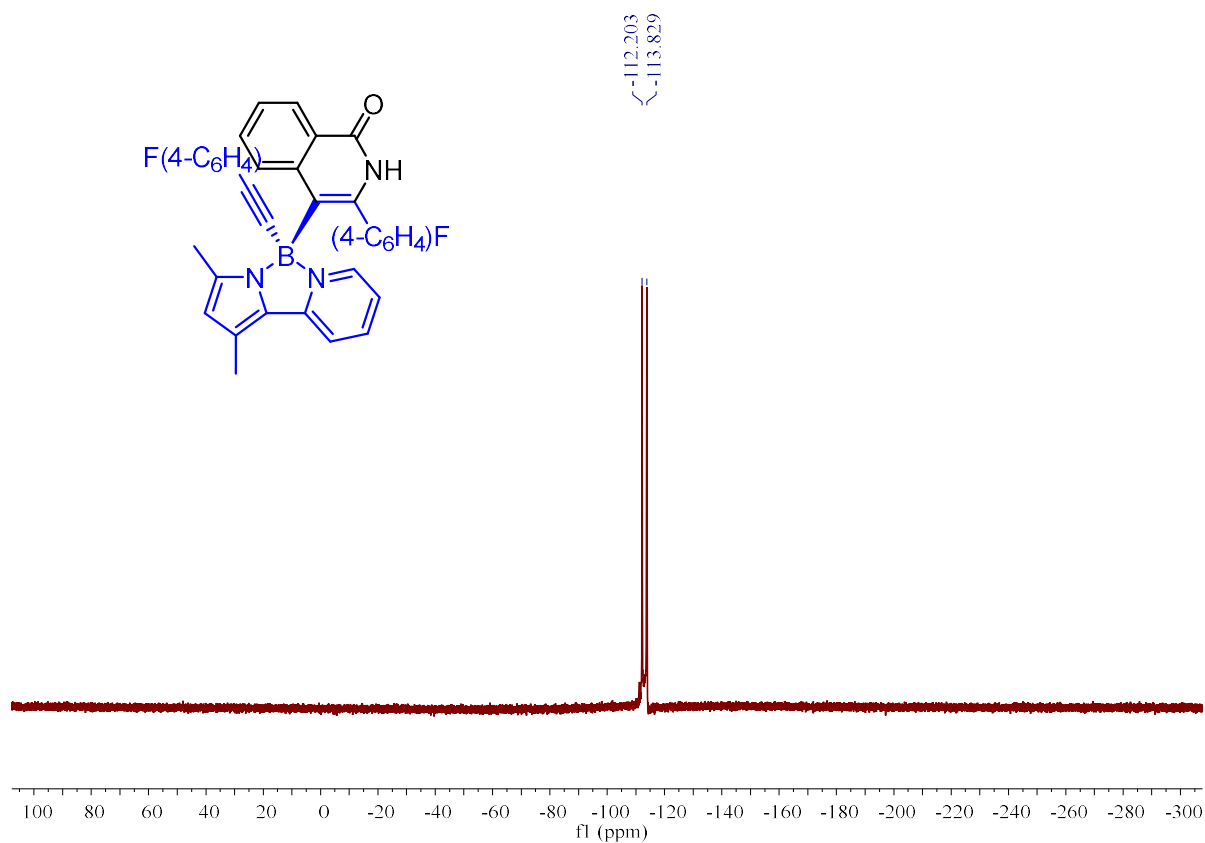
^1H NMR (600 MHz, CDCl_3) spectrum of 32.



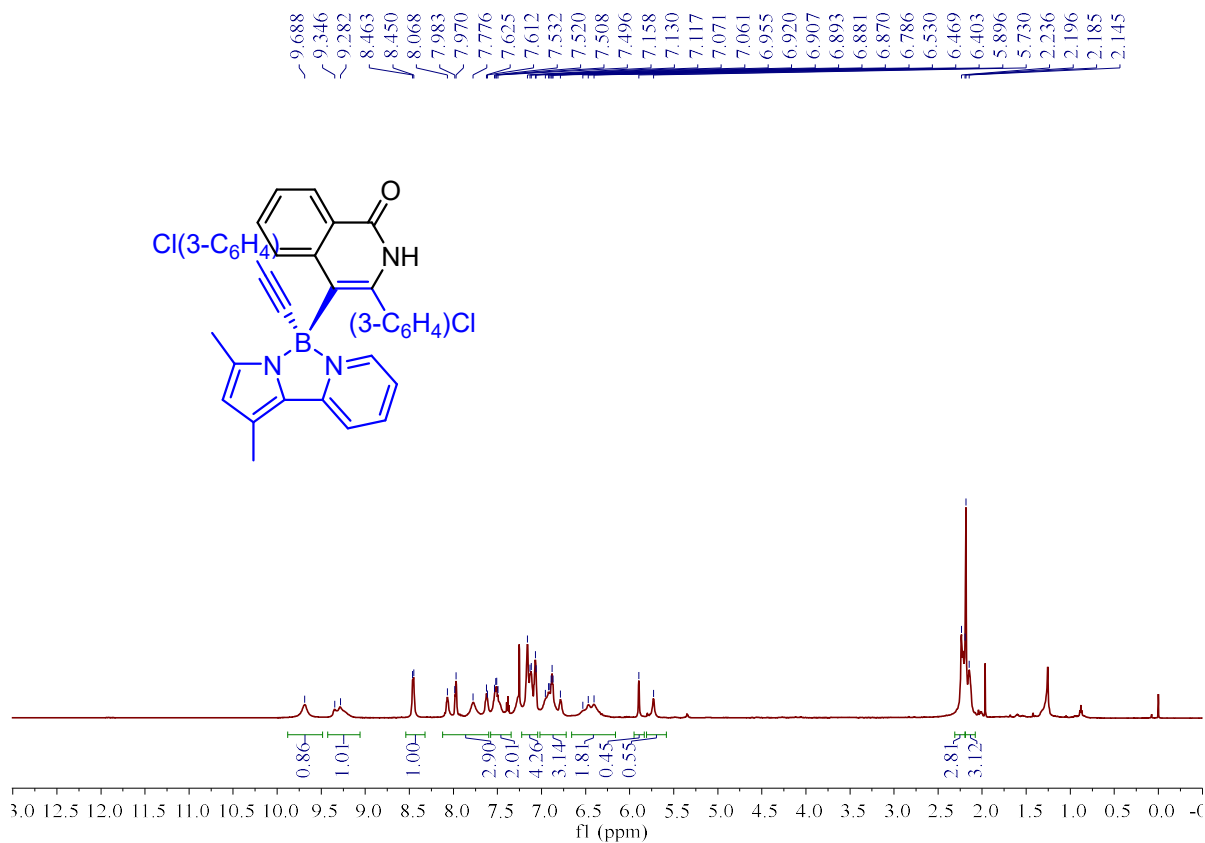
¹³C NMR (150 MHz, CDCl₃) spectrum of 32.



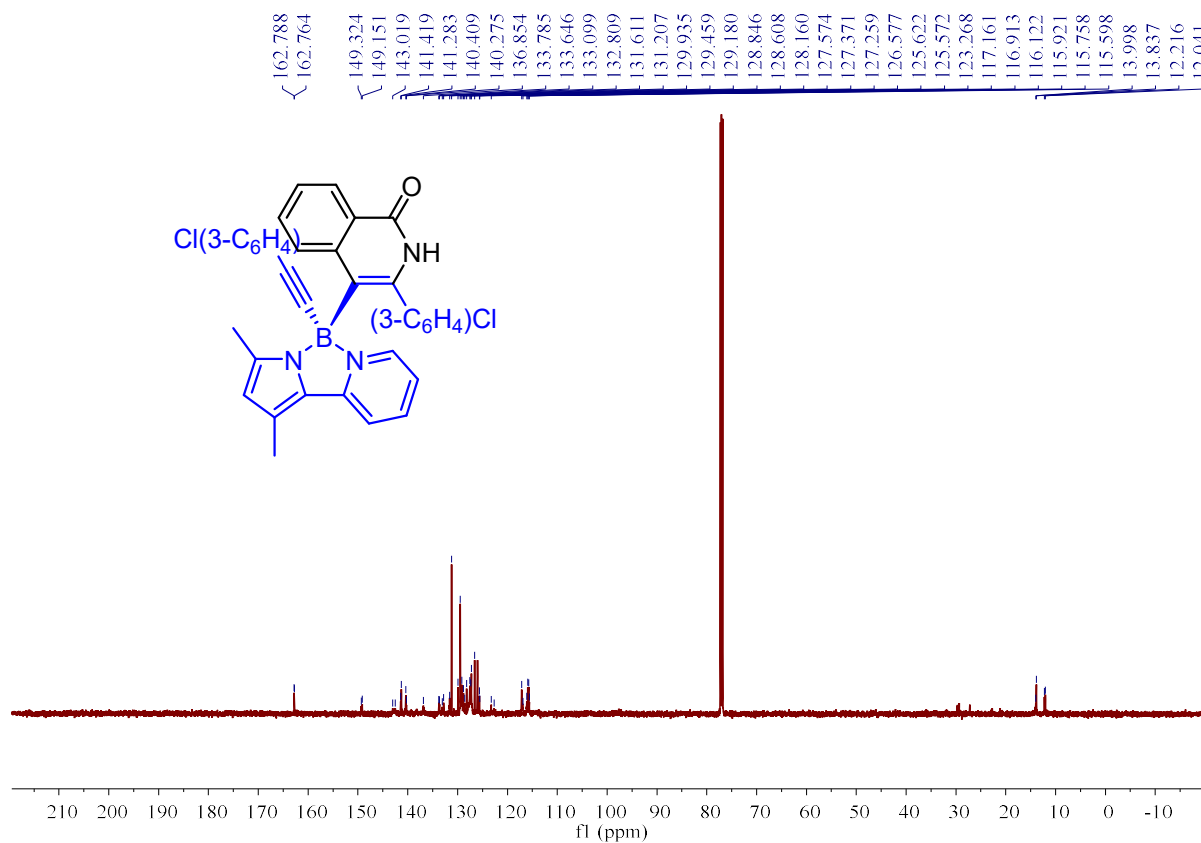
¹¹B NMR (193 MHz, CDCl₃) spectrum of 32.



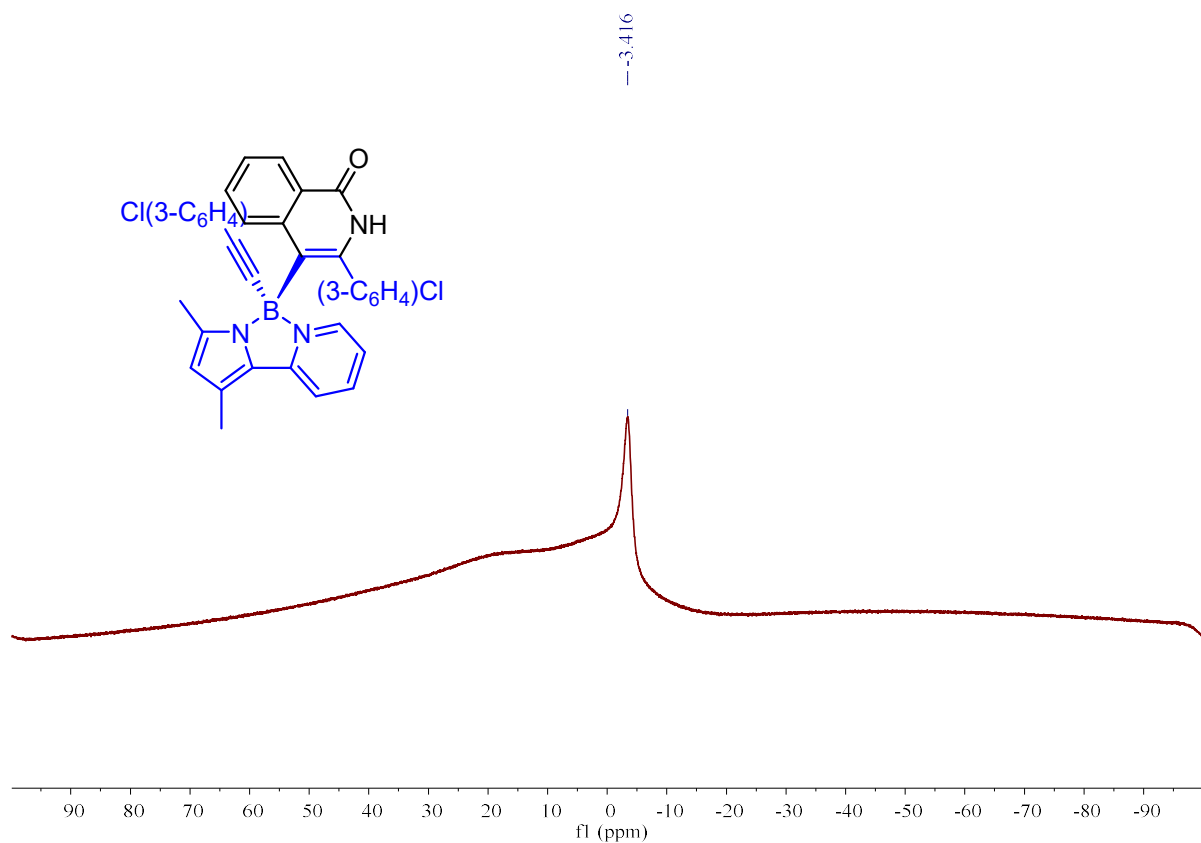
^{19}F NMR (376 MHz, CDCl_3) spectrum of 32.



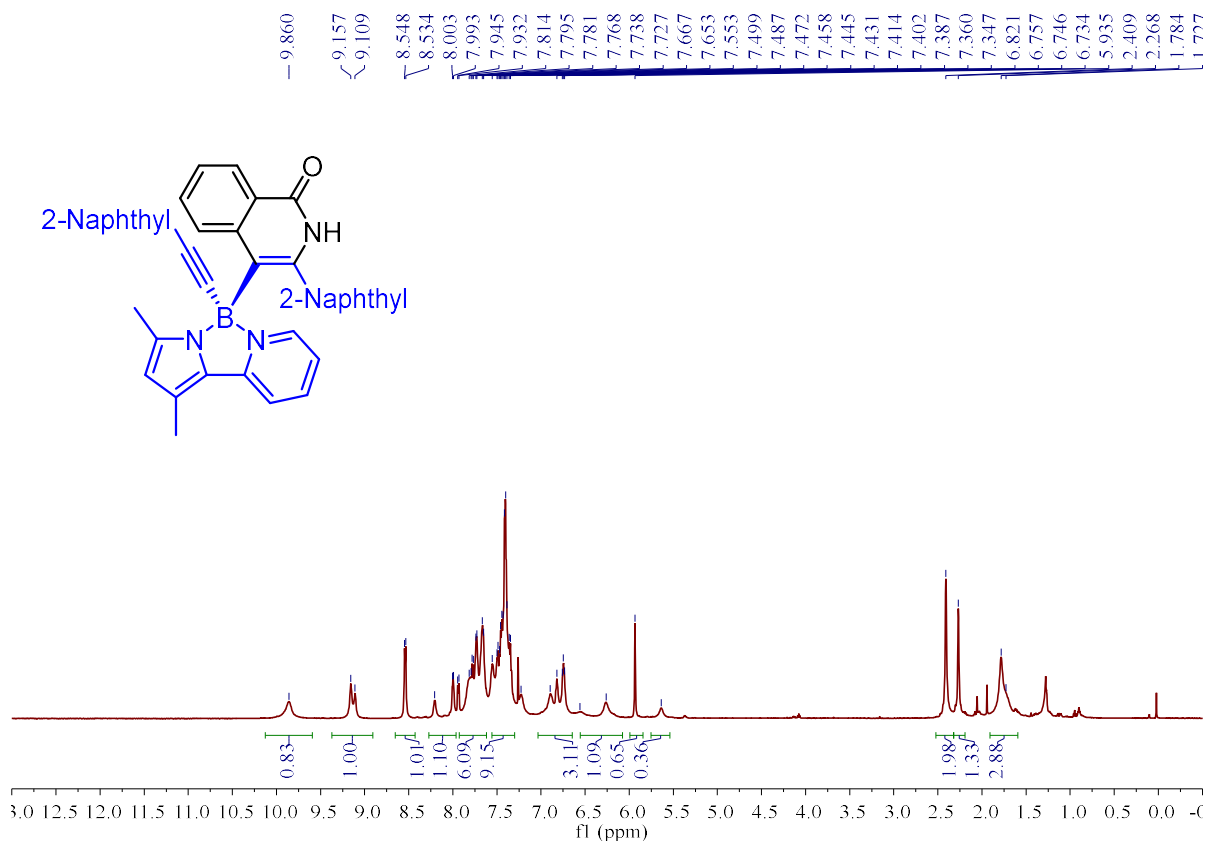
^1H NMR (600 MHz, CDCl_3) spectrum of 33.



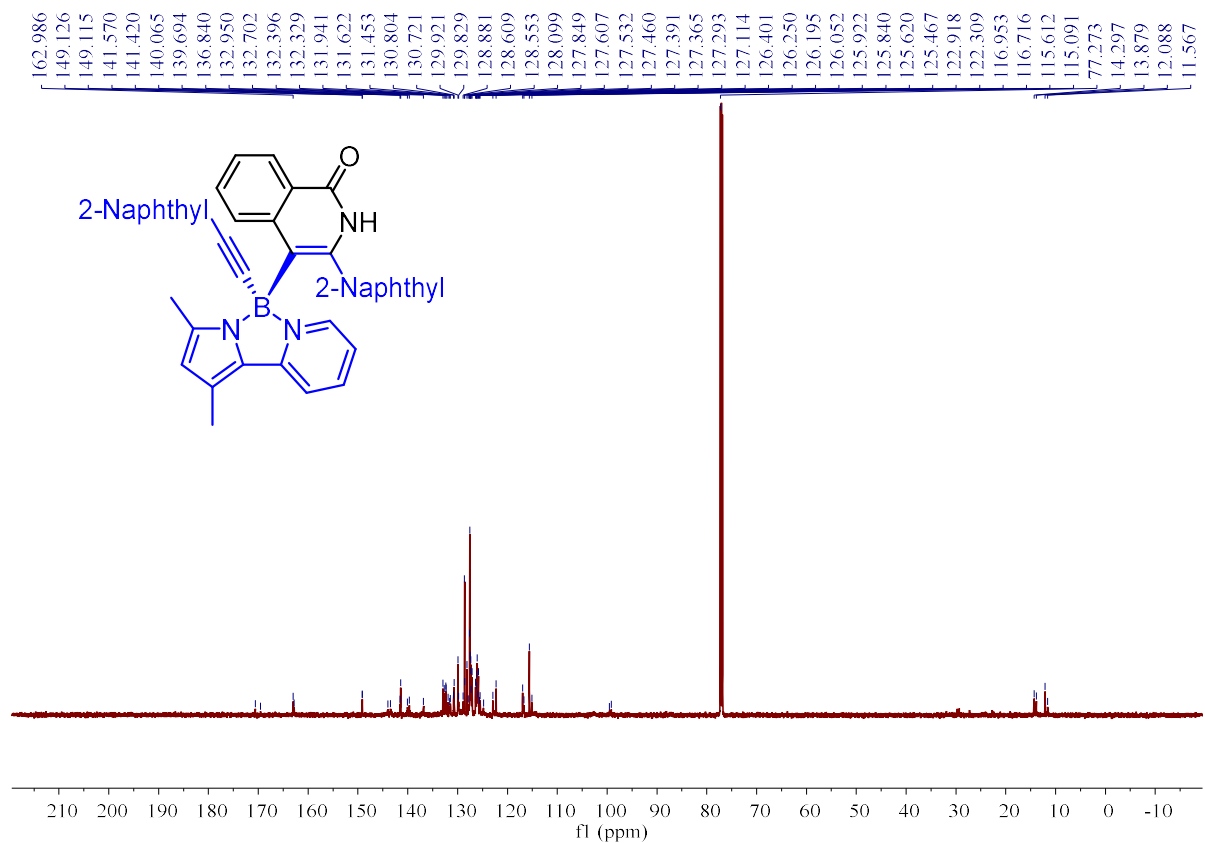
¹³C NMR (150 MHz, CDCl₃) spectrum of 33.



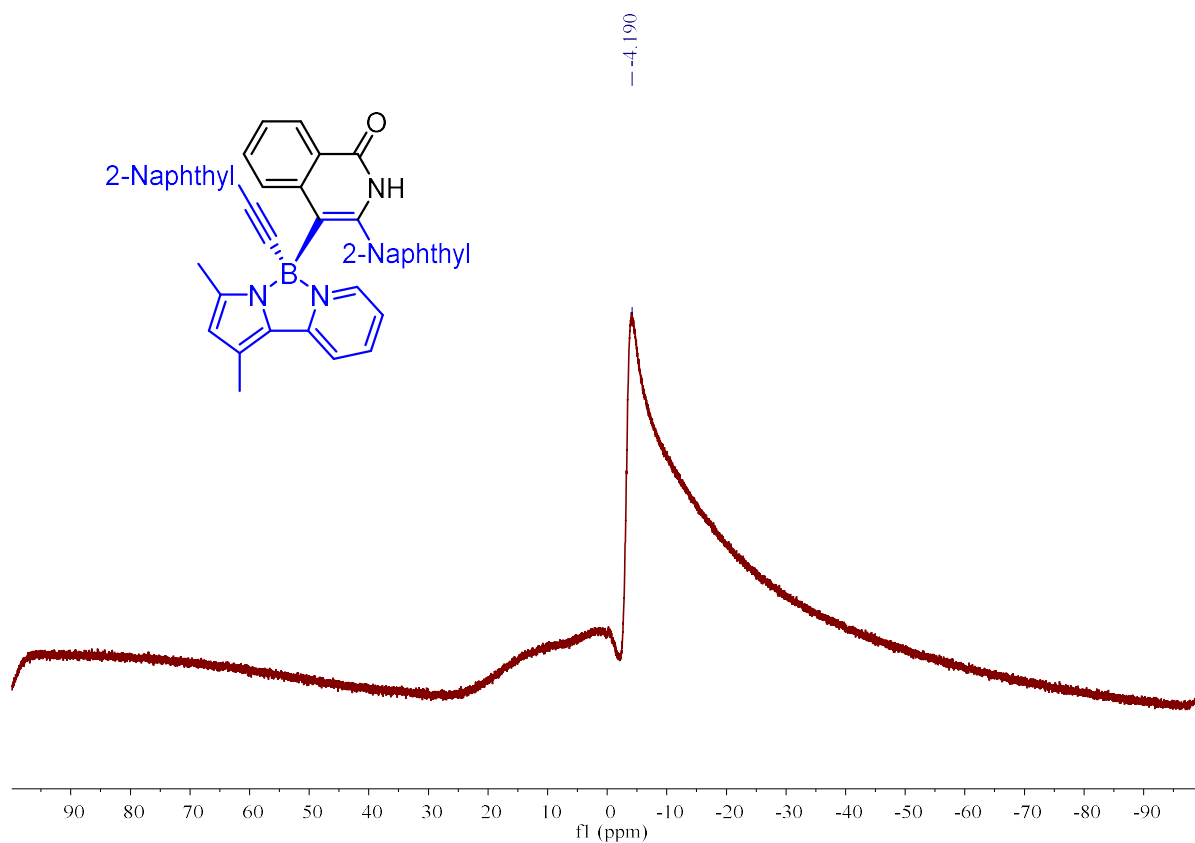
¹¹B NMR (193 MHz, CDCl₃) spectrum of 33.



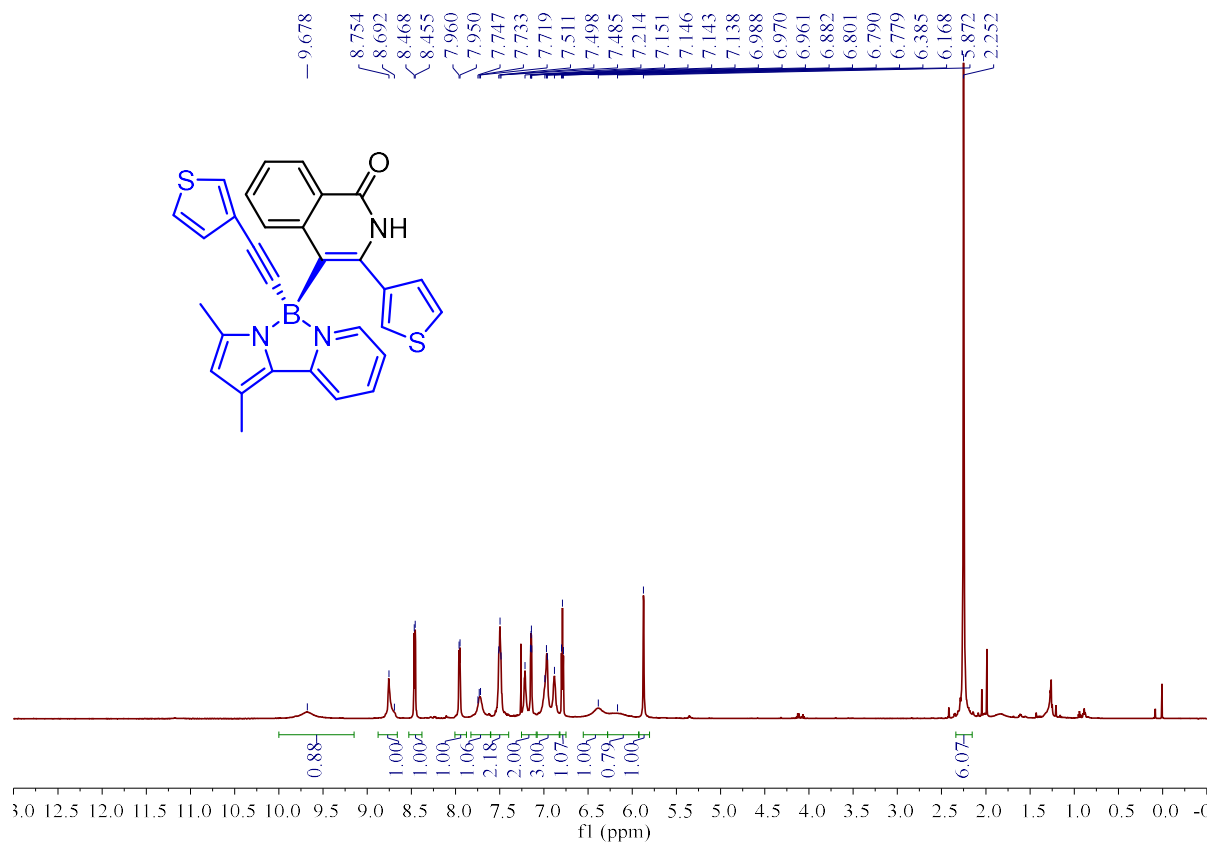
¹H NMR (600 MHz, CDCl₃) spectrum of 34.



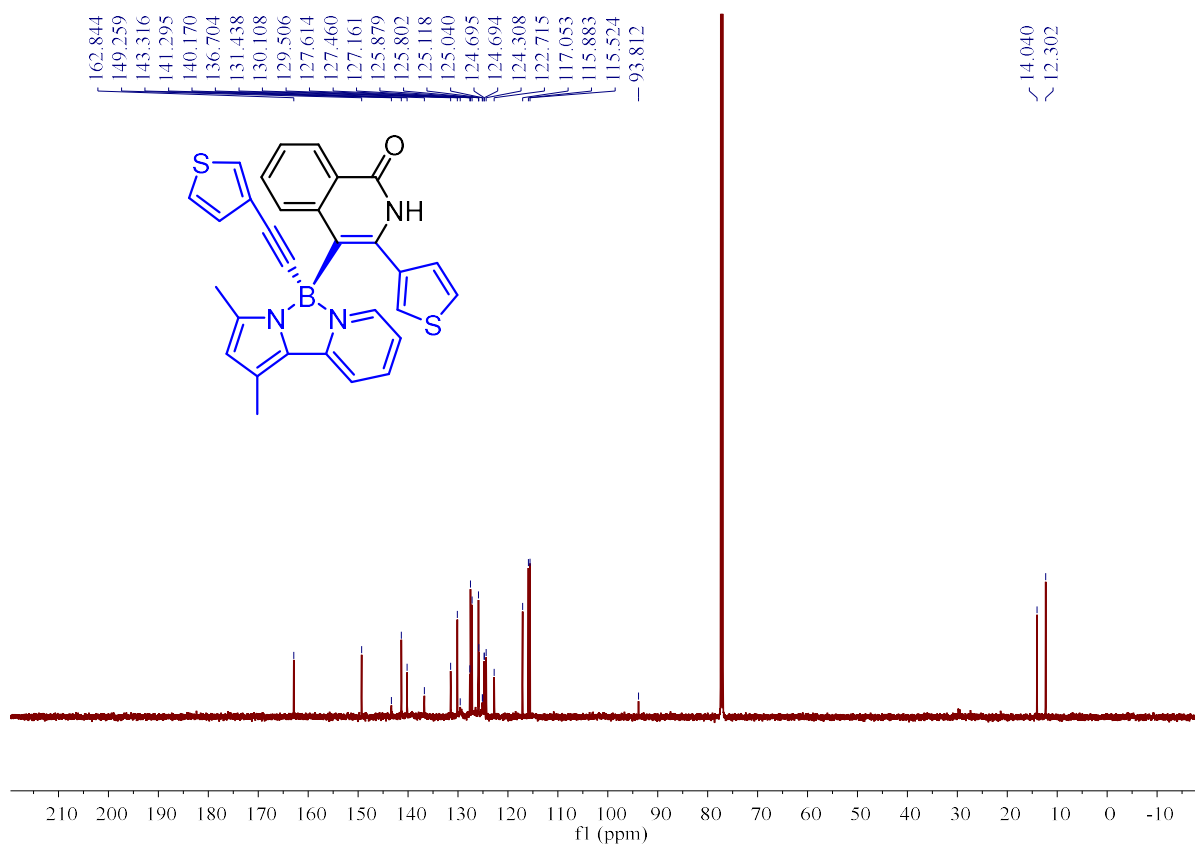
¹³C NMR (150 MHz, CDCl₃) spectrum of 34.



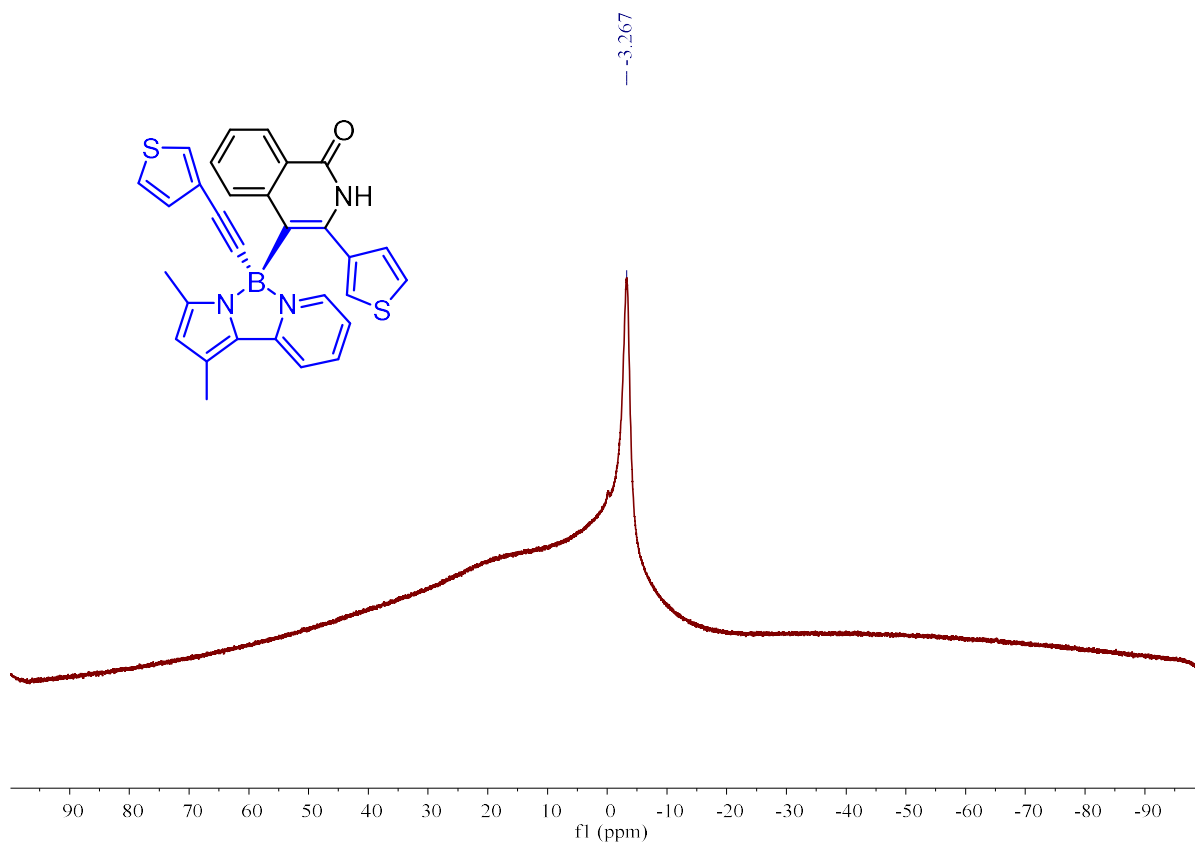
^{11}B NMR (193 MHz, CDCl_3) spectrum of 34.



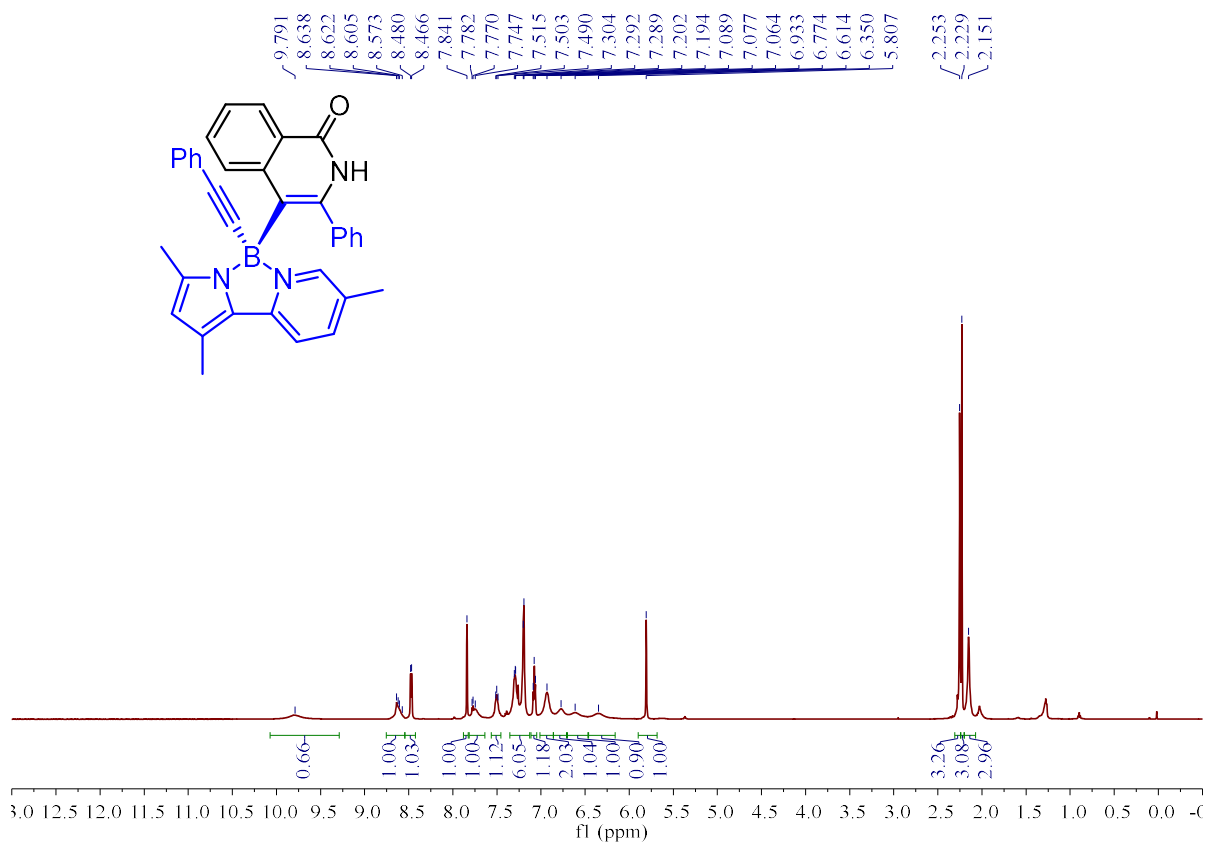
^1H NMR (600 MHz, CDCl_3) spectrum of 35.



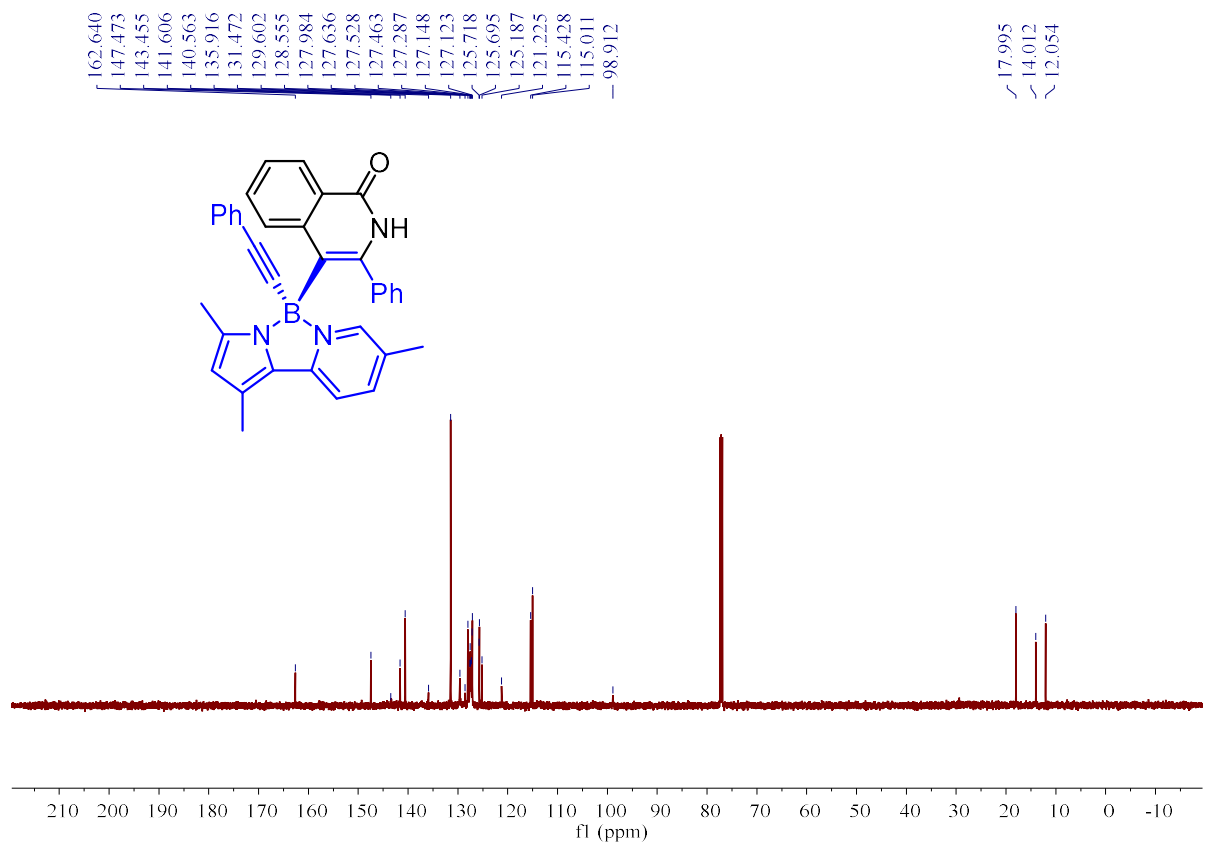
¹³C NMR (150 MHz, CDCl₃) spectrum of 35.



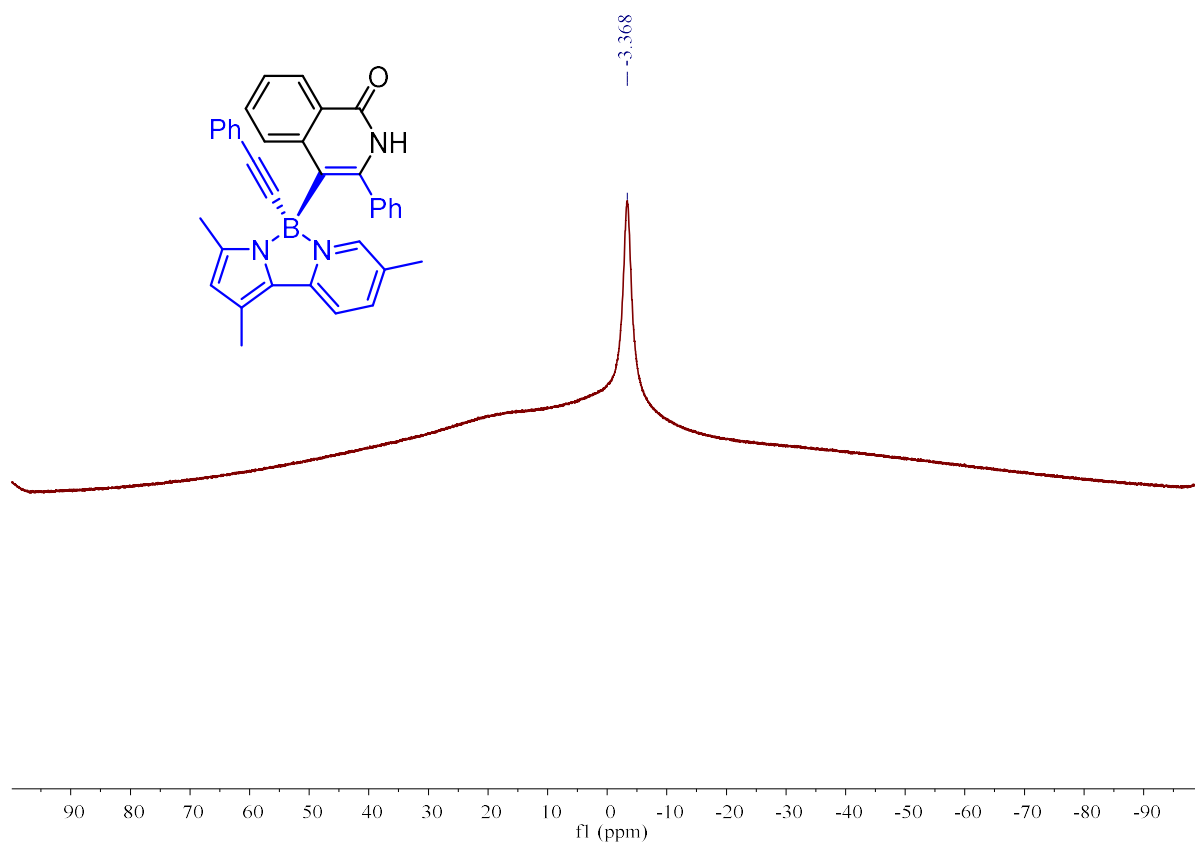
¹¹B NMR (193 MHz, CDCl₃) spectrum of 35.



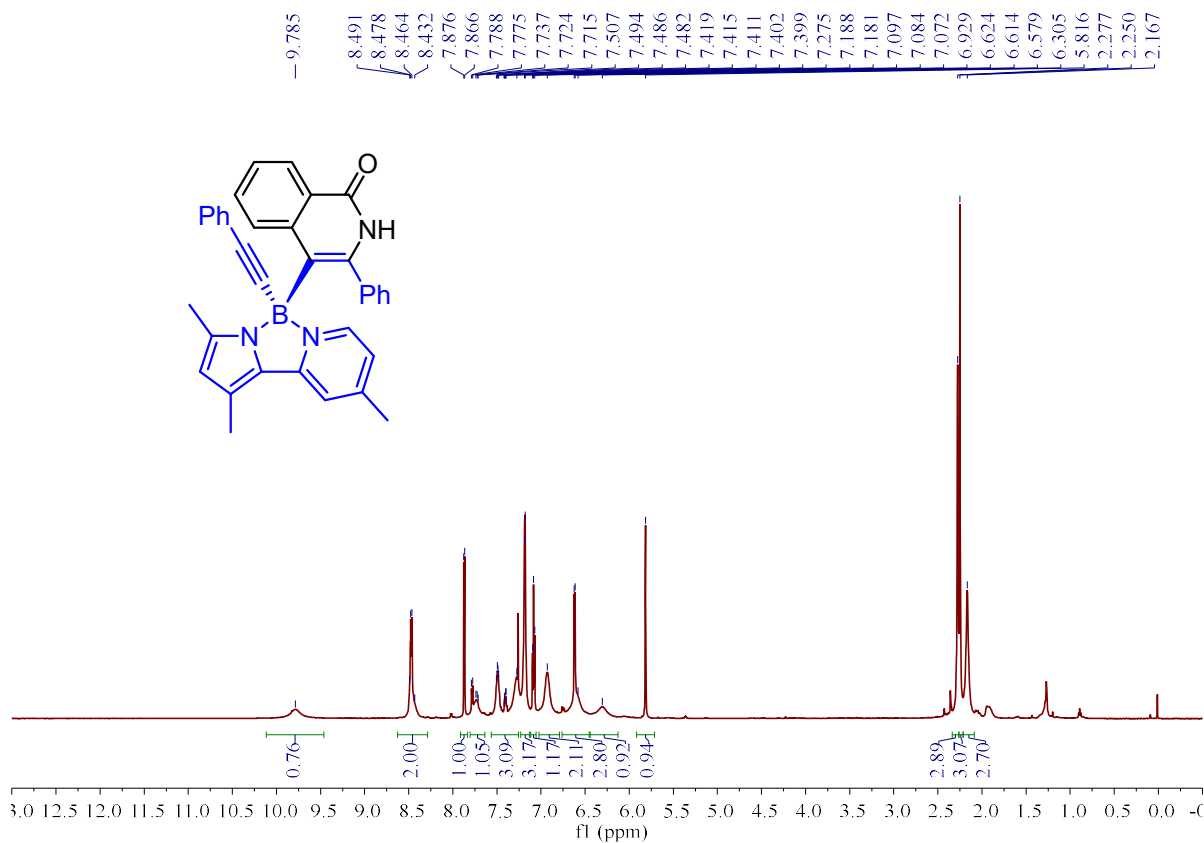
¹H NMR (600 MHz, CDCl₃) spectrum of 36.



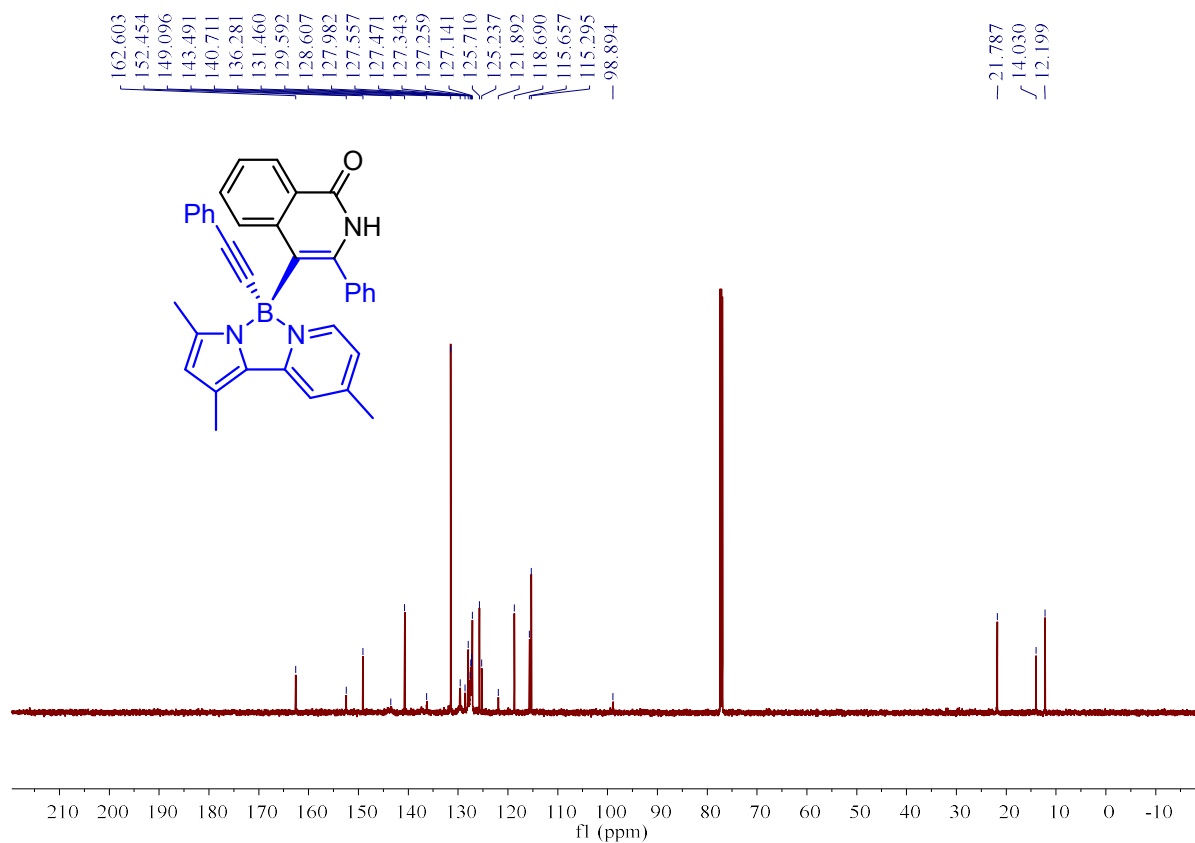
¹³C NMR (150 MHz, CDCl₃) spectrum of 36.



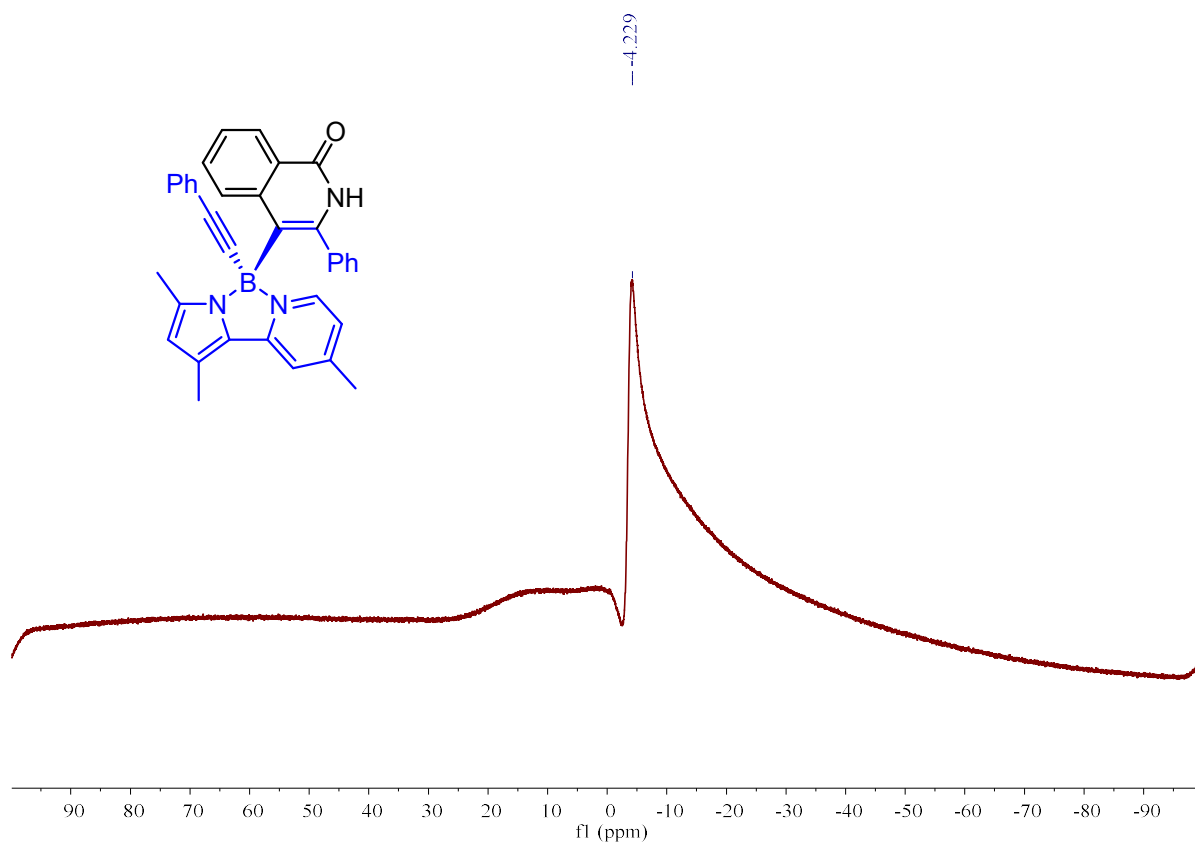
^{11}B NMR (193 MHz, CDCl_3) spectrum of 36.



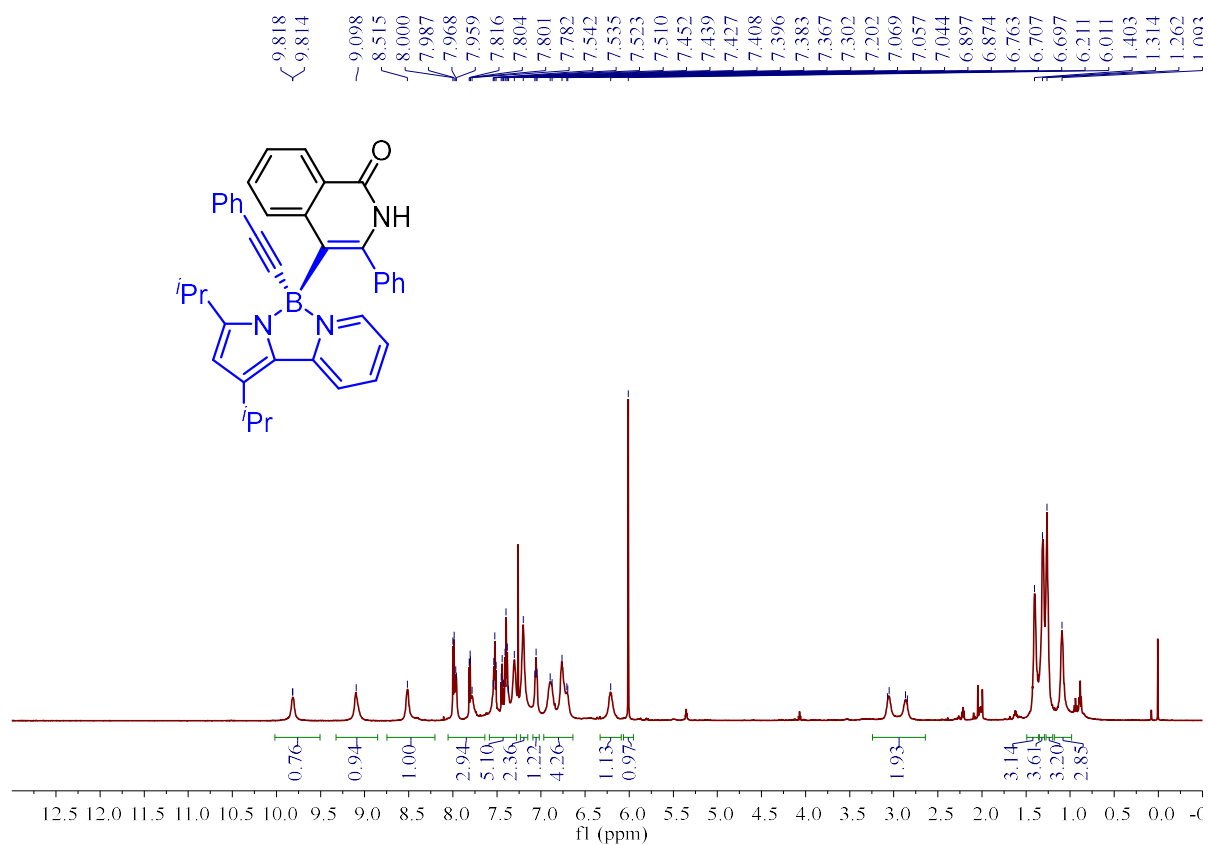
^1H NMR (600 MHz, CDCl_3) spectrum of 37.



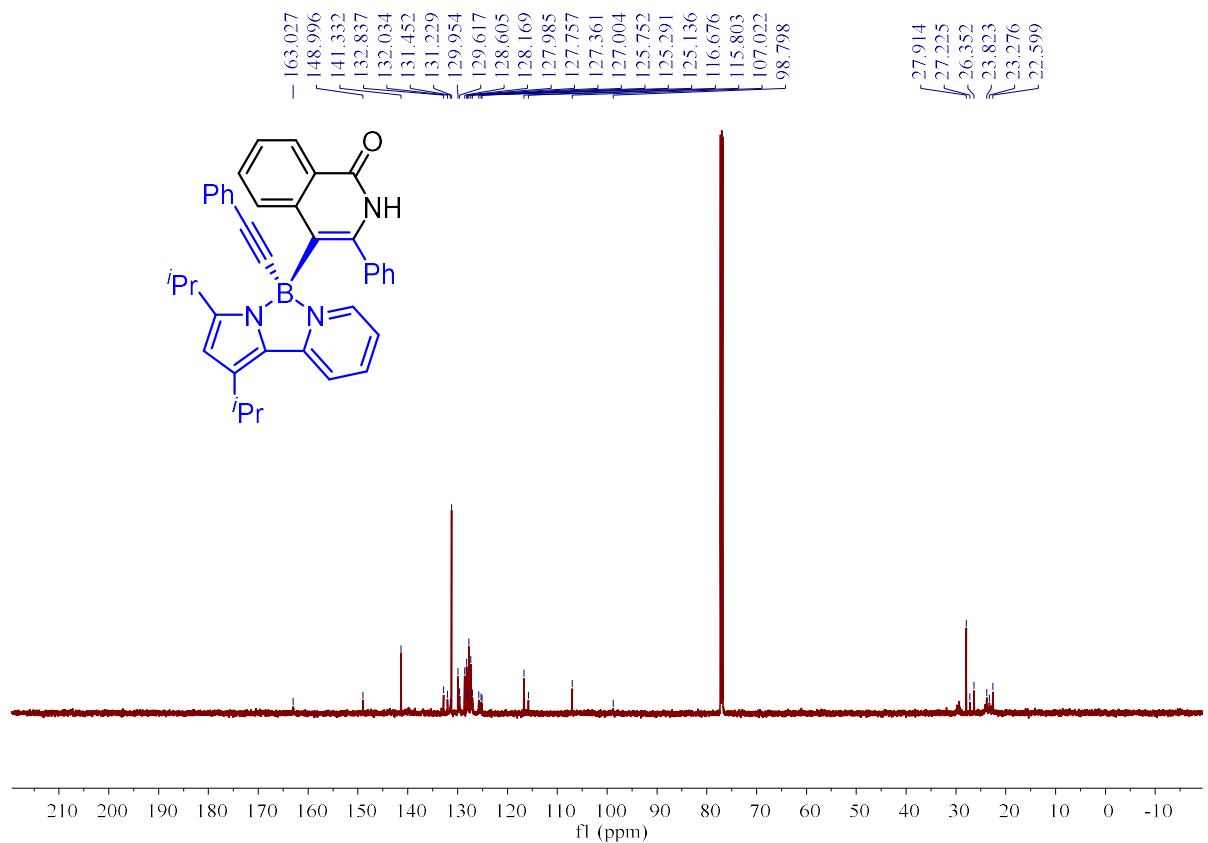
¹³C NMR (150 MHz, CDCl₃) spectrum of 37.



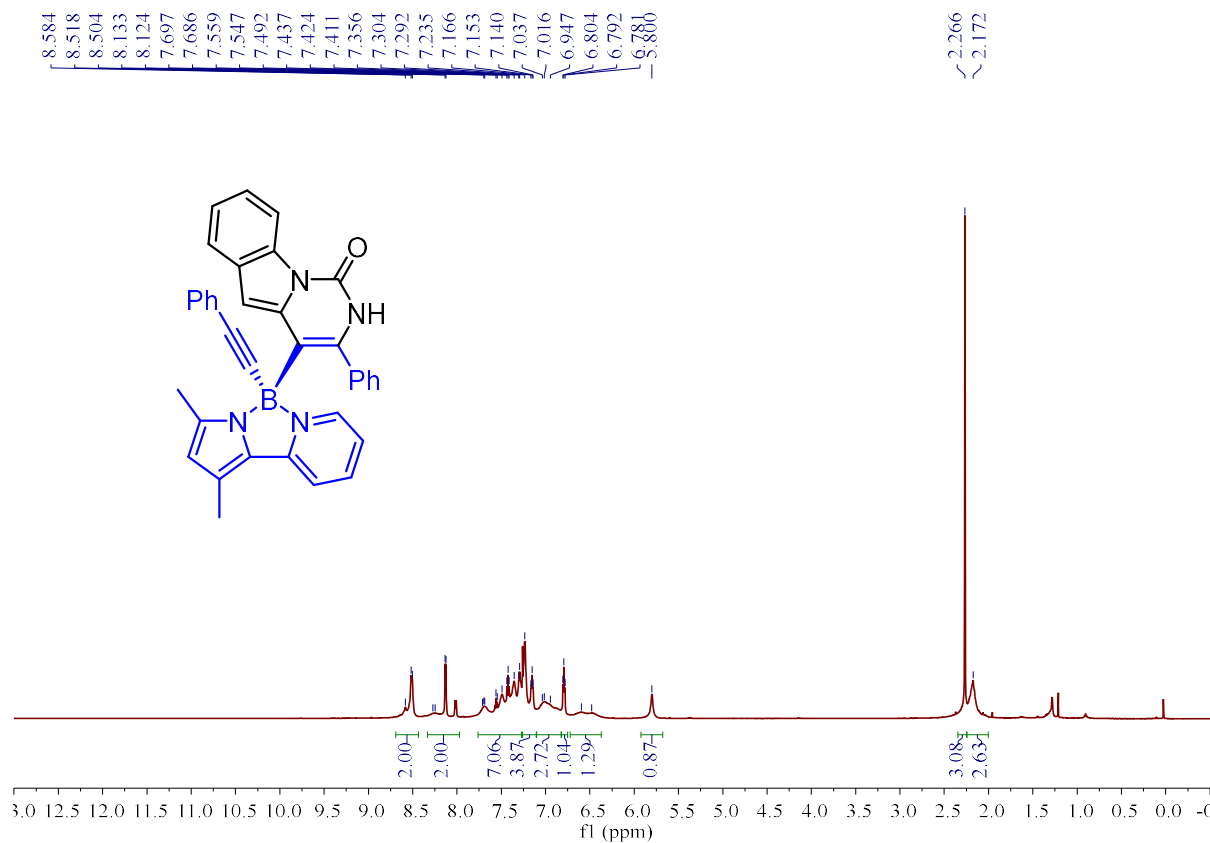
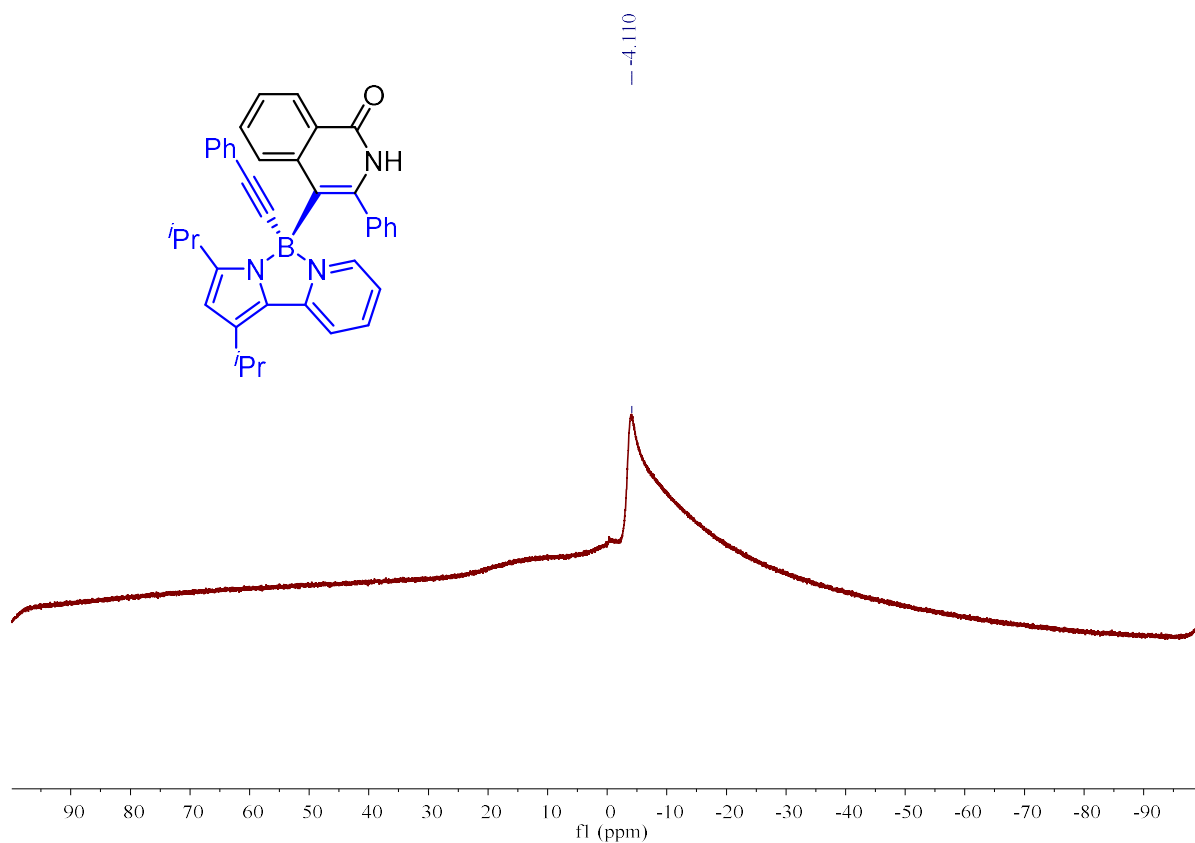
¹¹B NMR (193 MHz, CDCl₃) spectrum of 37.

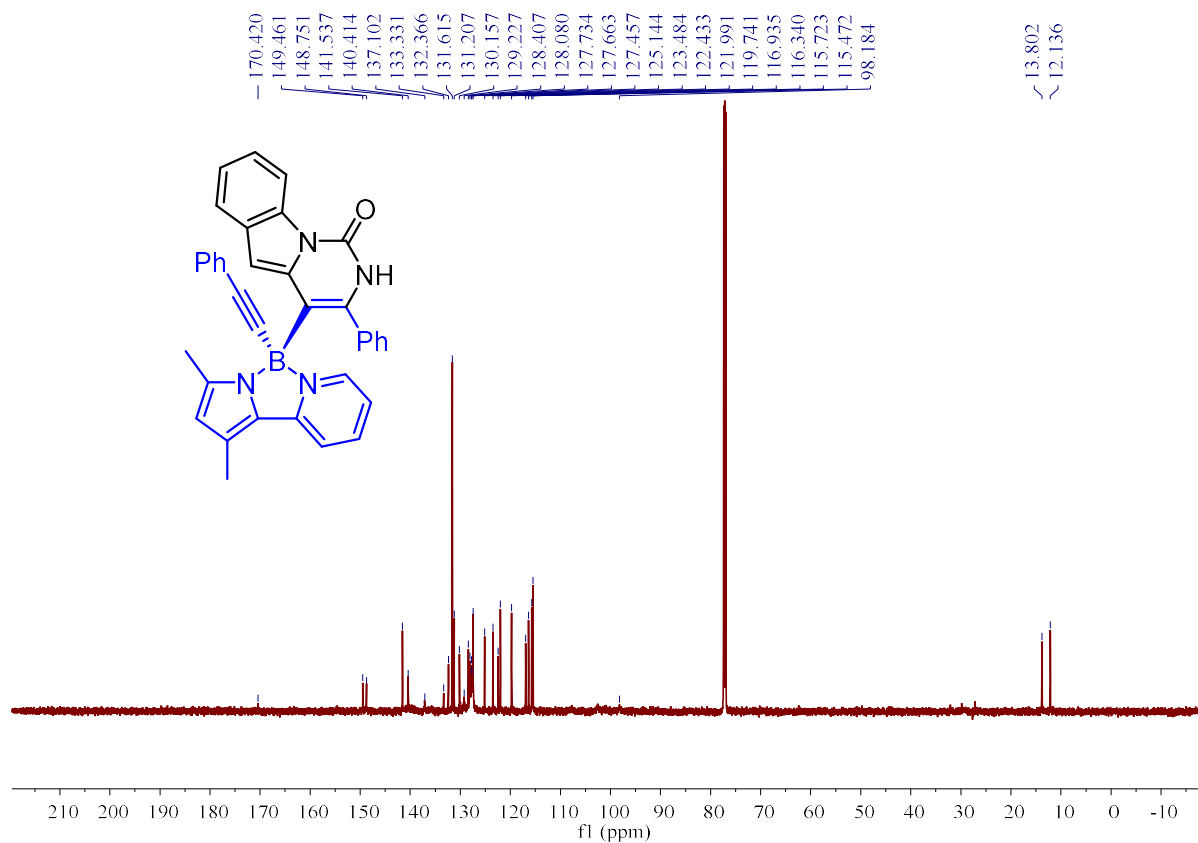


¹H NMR (600 MHz, CDCl₃) spectrum of 38.

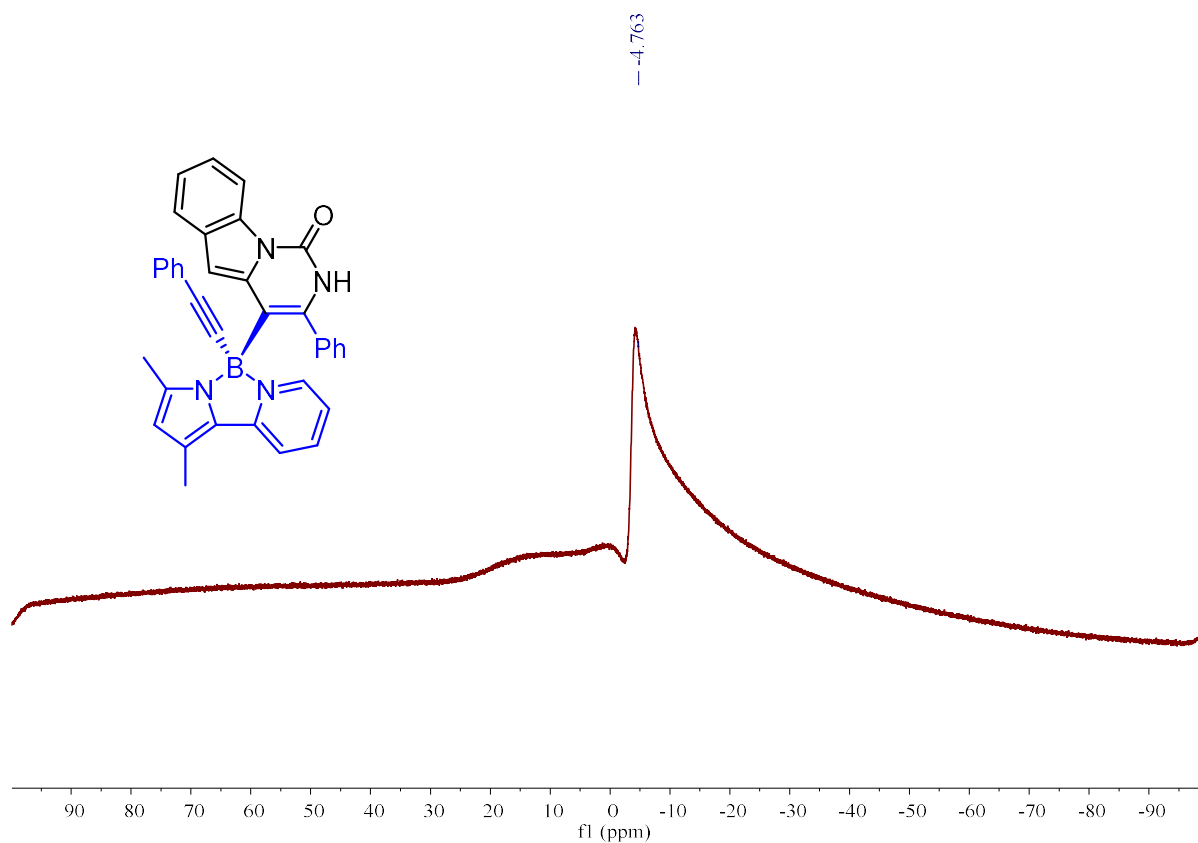


¹³C NMR (150 MHz, CDCl₃) spectrum of 38.

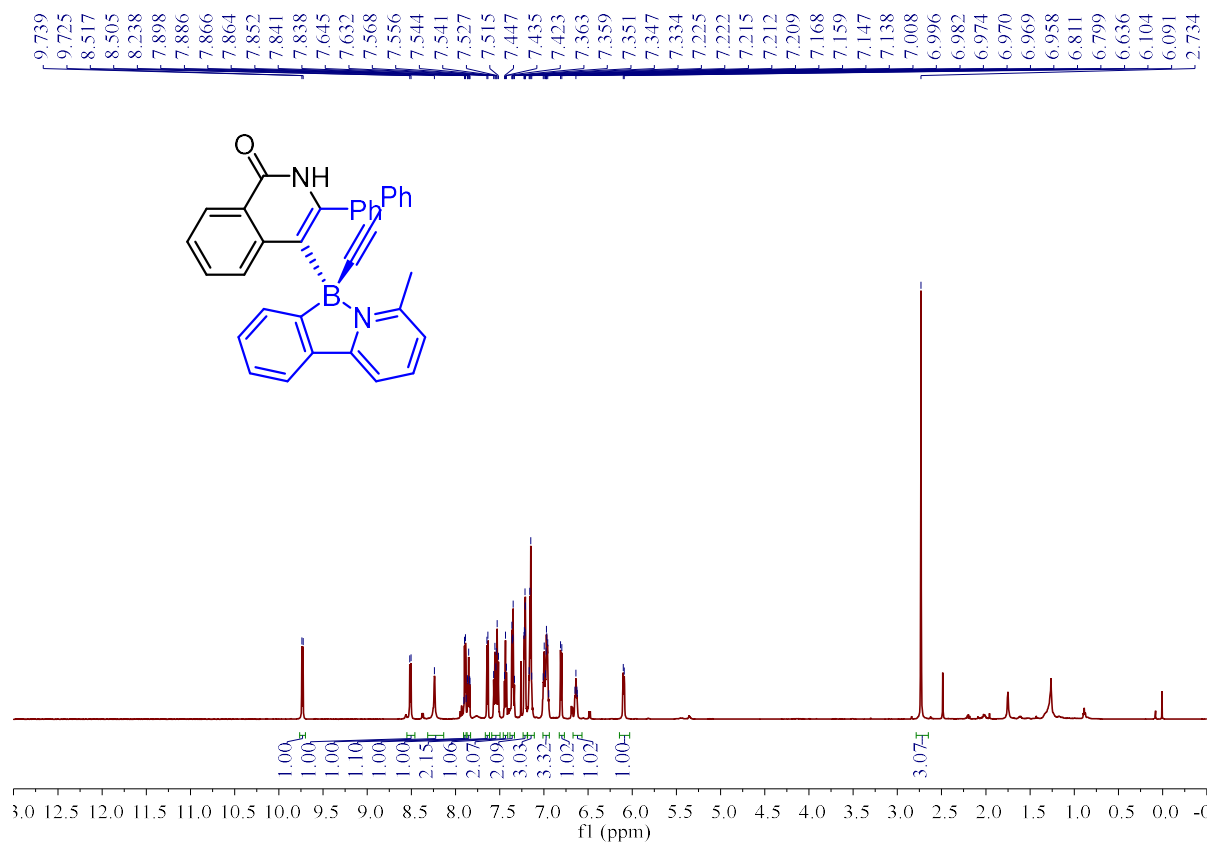




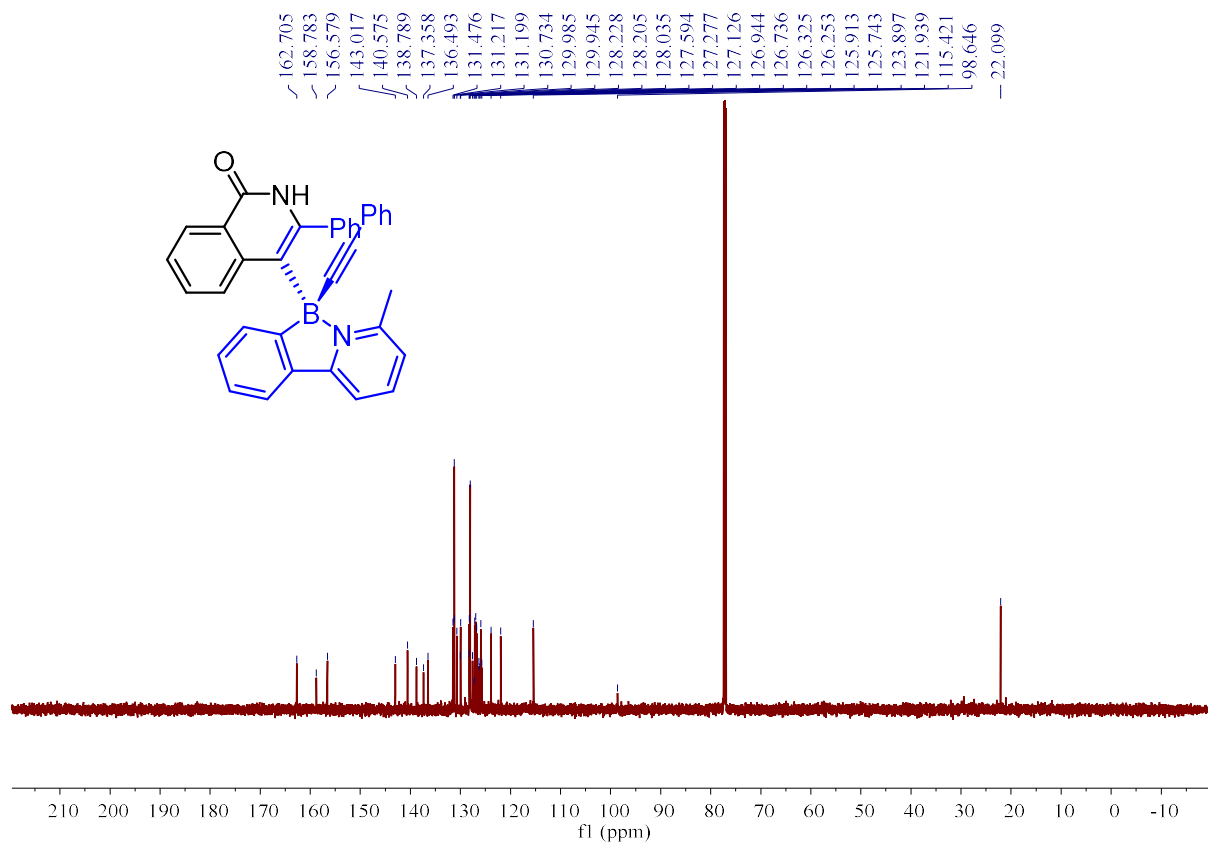
¹³C NMR (150 MHz, CDCl₃) spectrum of 39.



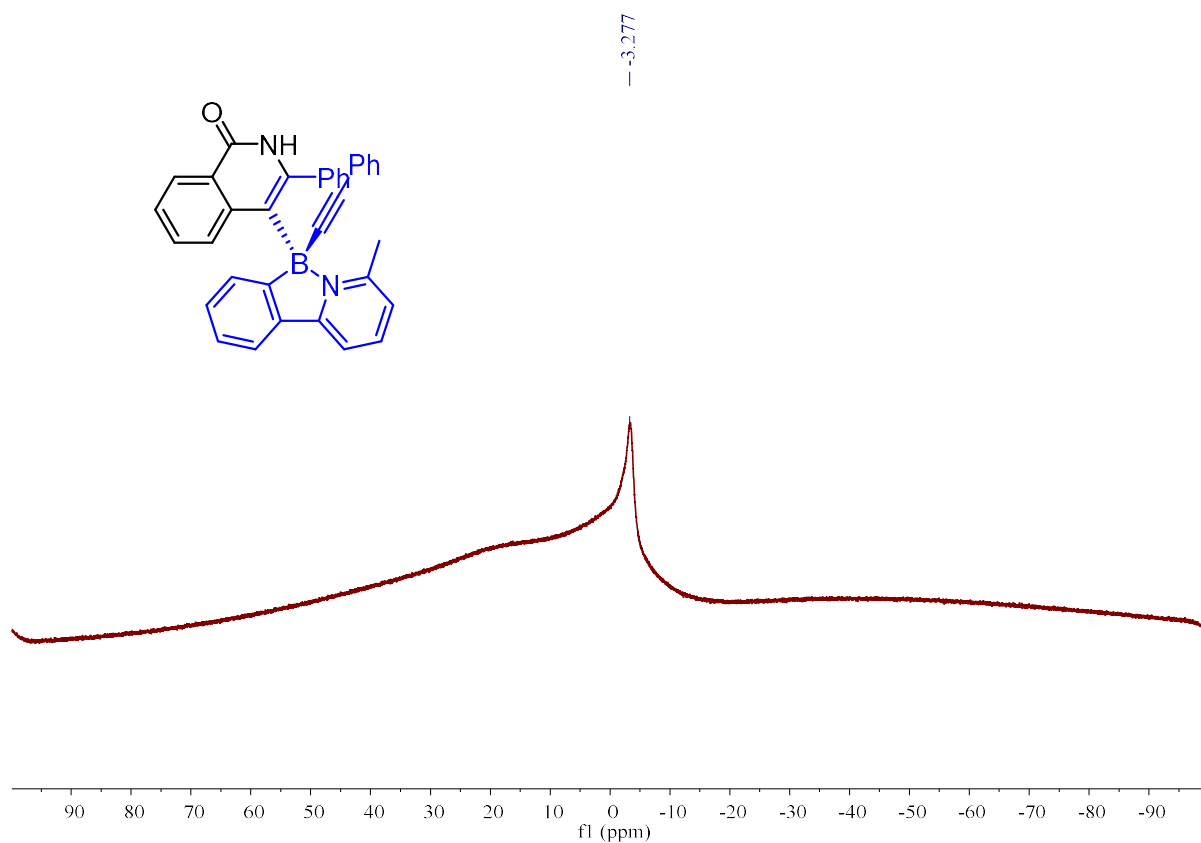
¹¹B NMR (193 MHz, CDCl₃) spectrum of 39.



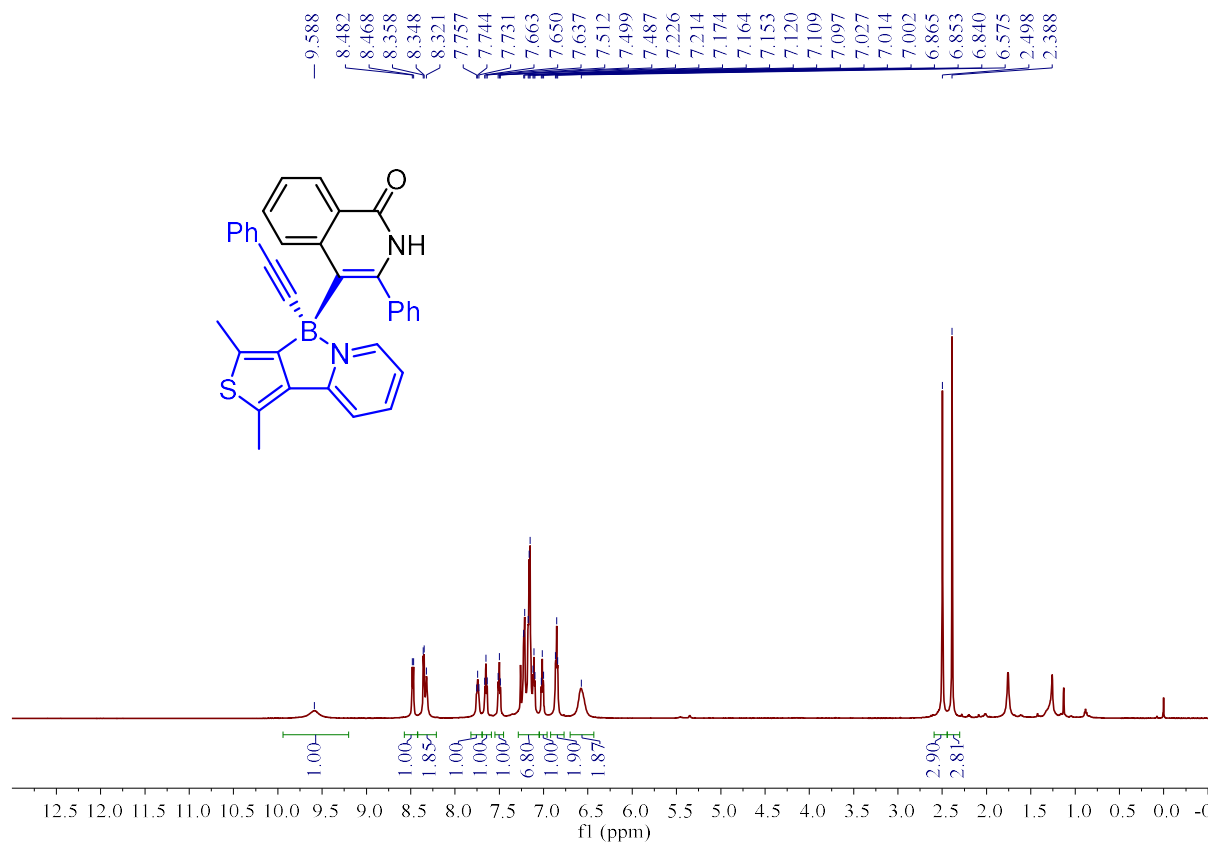
¹H NMR (600 MHz, CDCl₃) spectrum of 40.



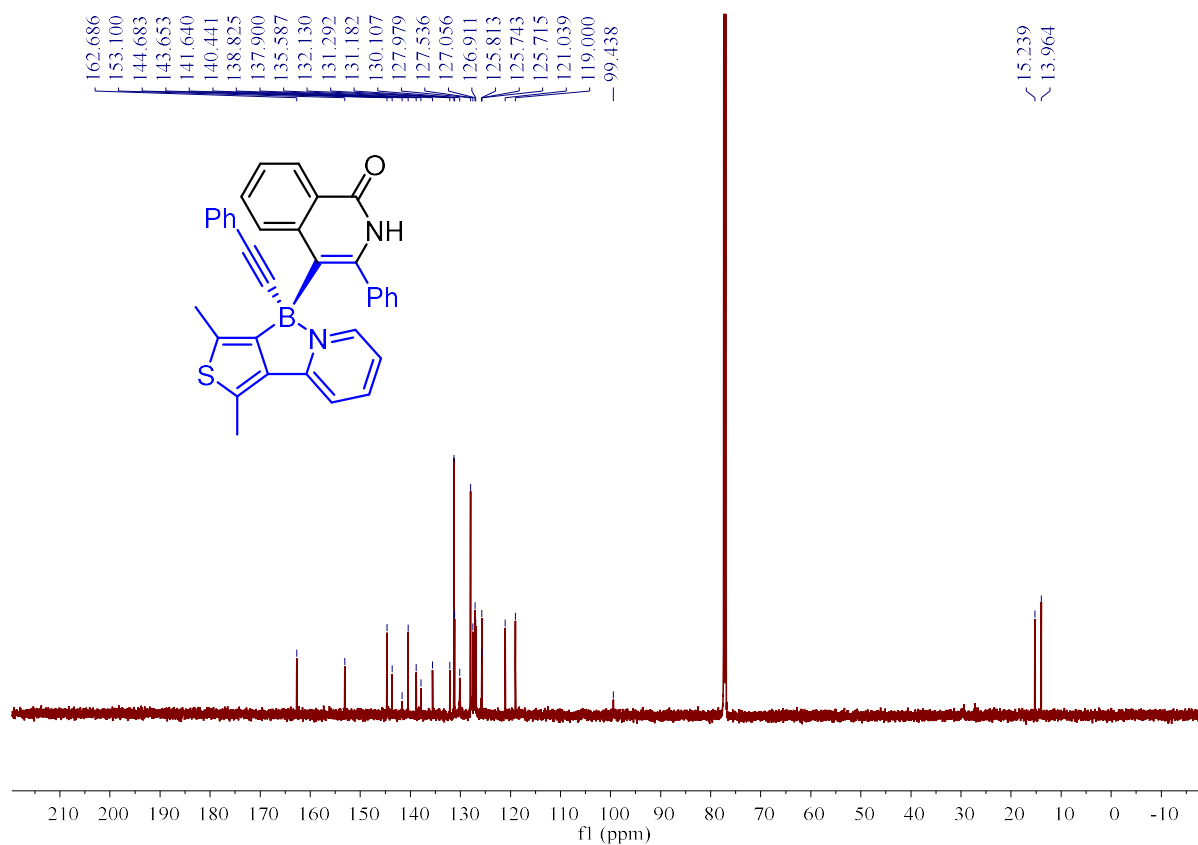
¹³C NMR (150 MHz, CDCl₃) spectrum of 40.



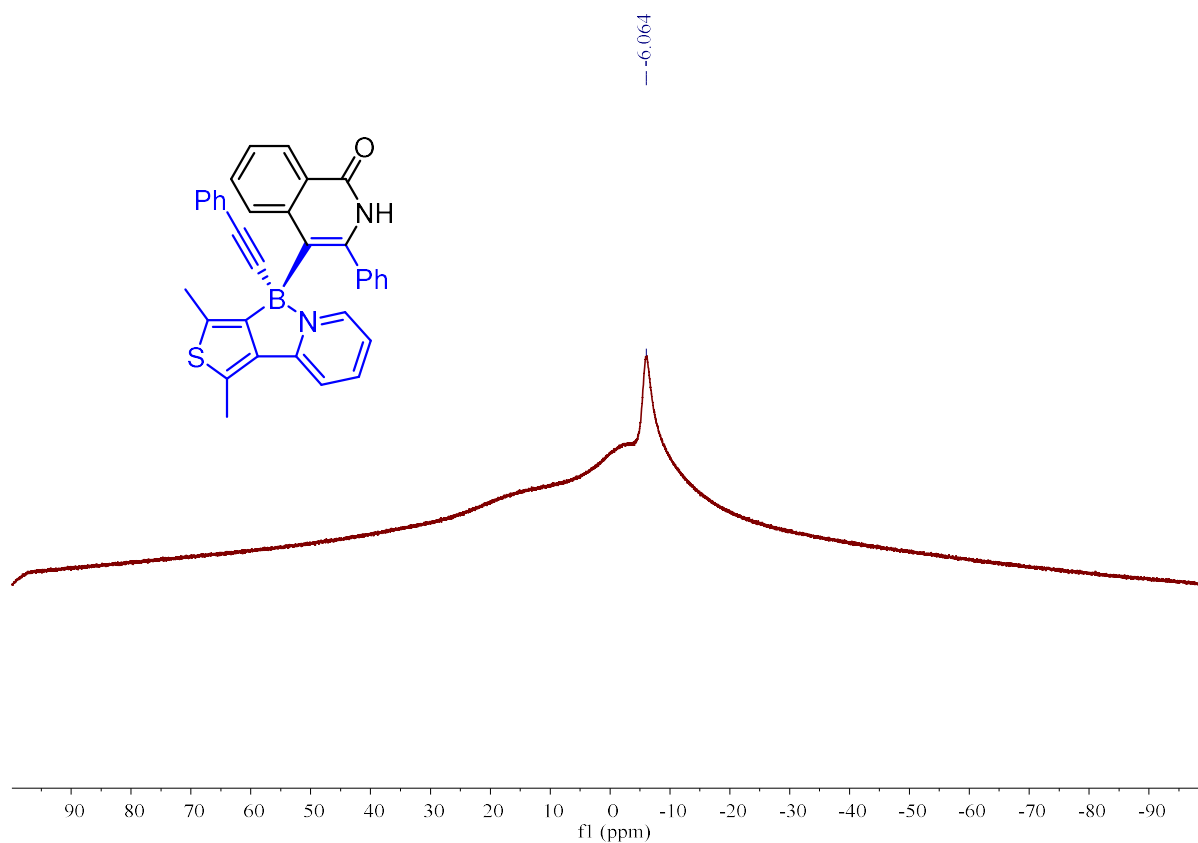
^{11}B NMR (193 MHz, CDCl_3) spectrum of 40.



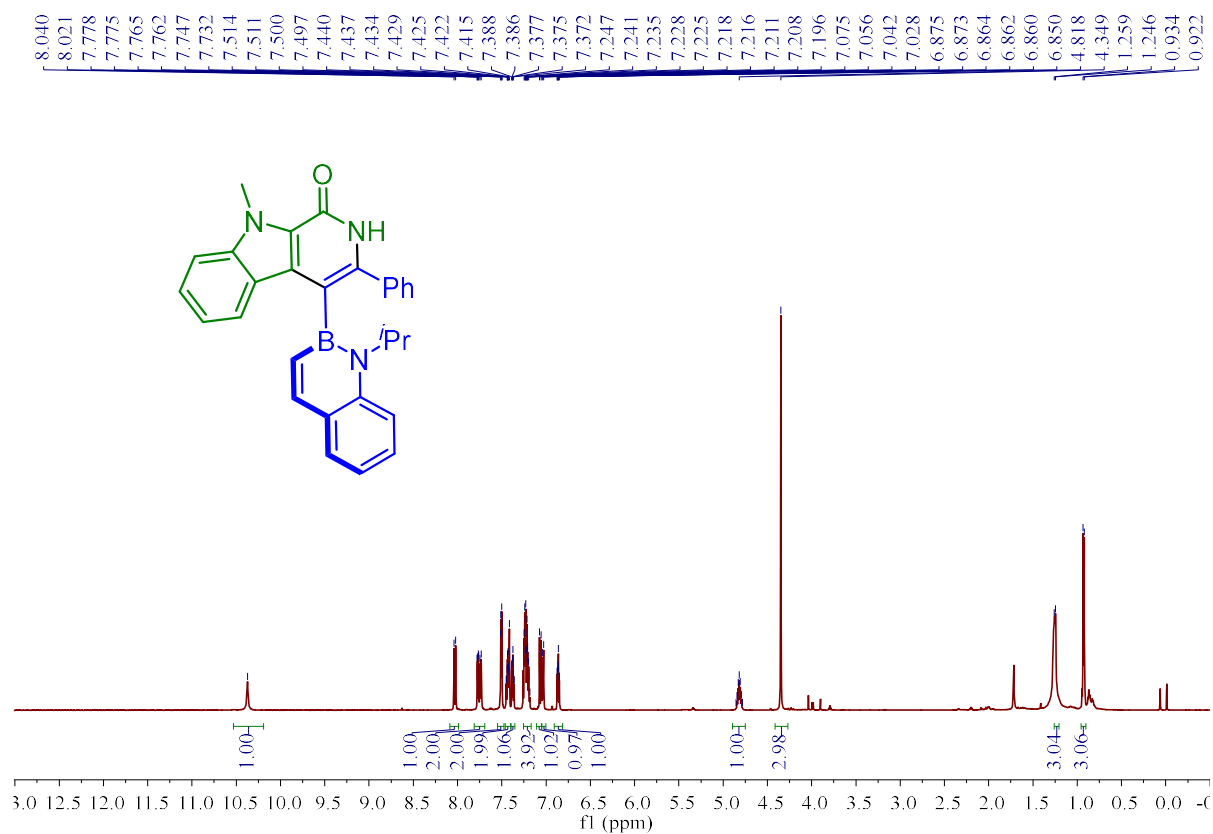
^1H NMR (600 MHz, CDCl_3) spectrum of 41.



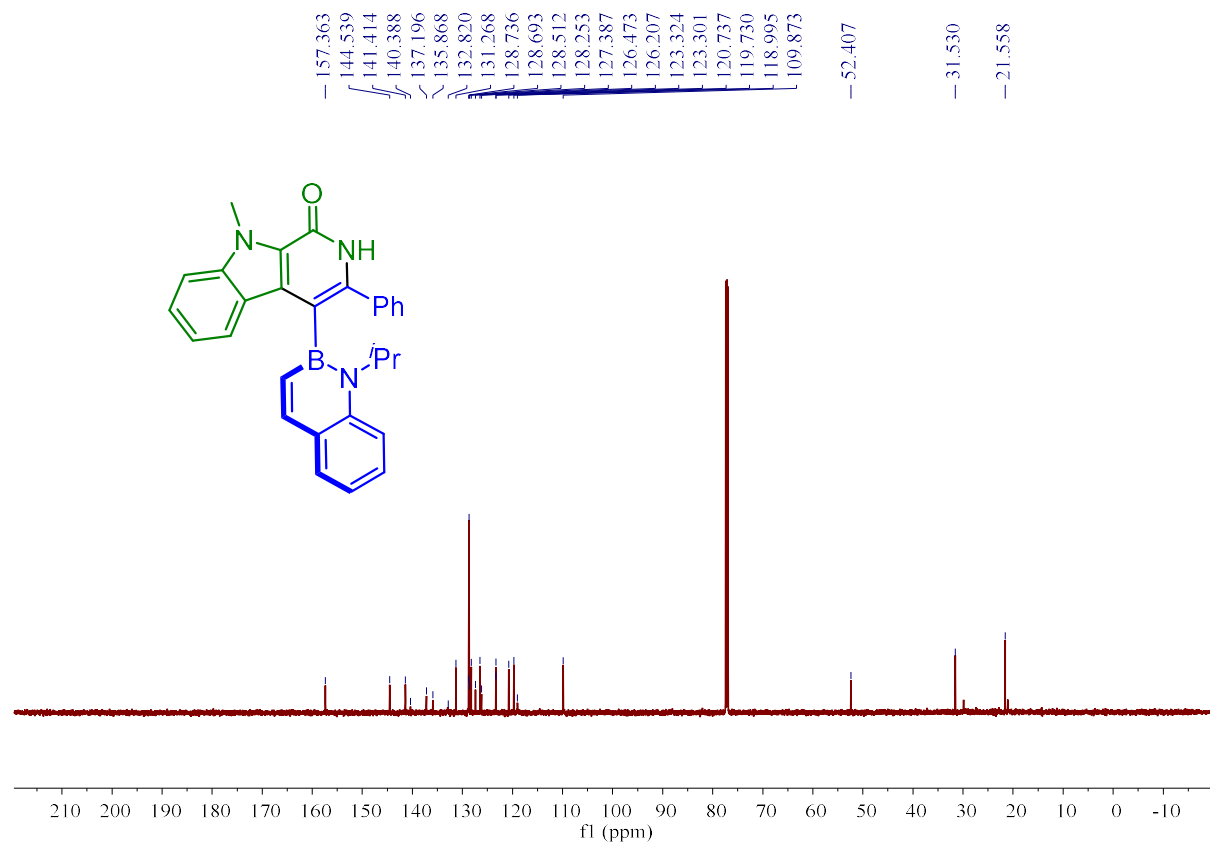
¹³C NMR (150 MHz, CDCl₃) spectrum of 41.



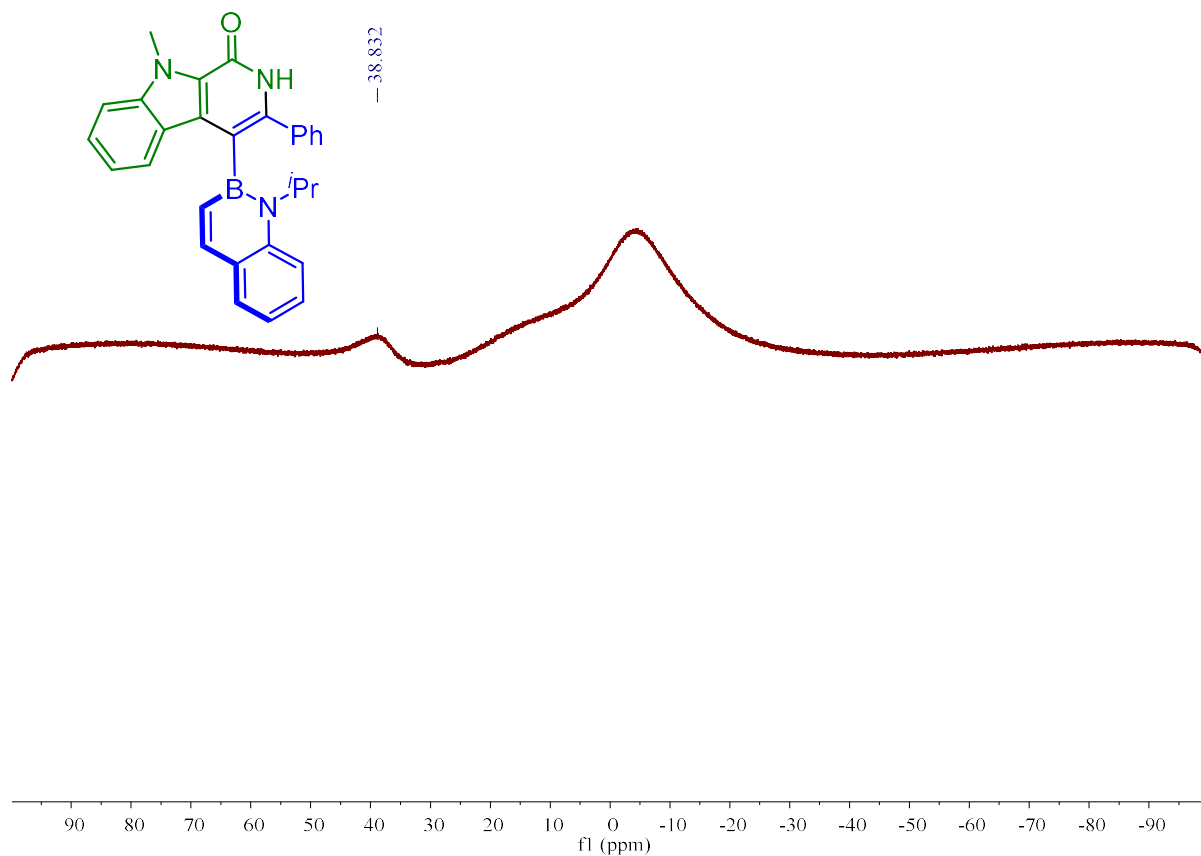
¹¹B NMR (193 MHz, CDCl₃) spectrum of 41.



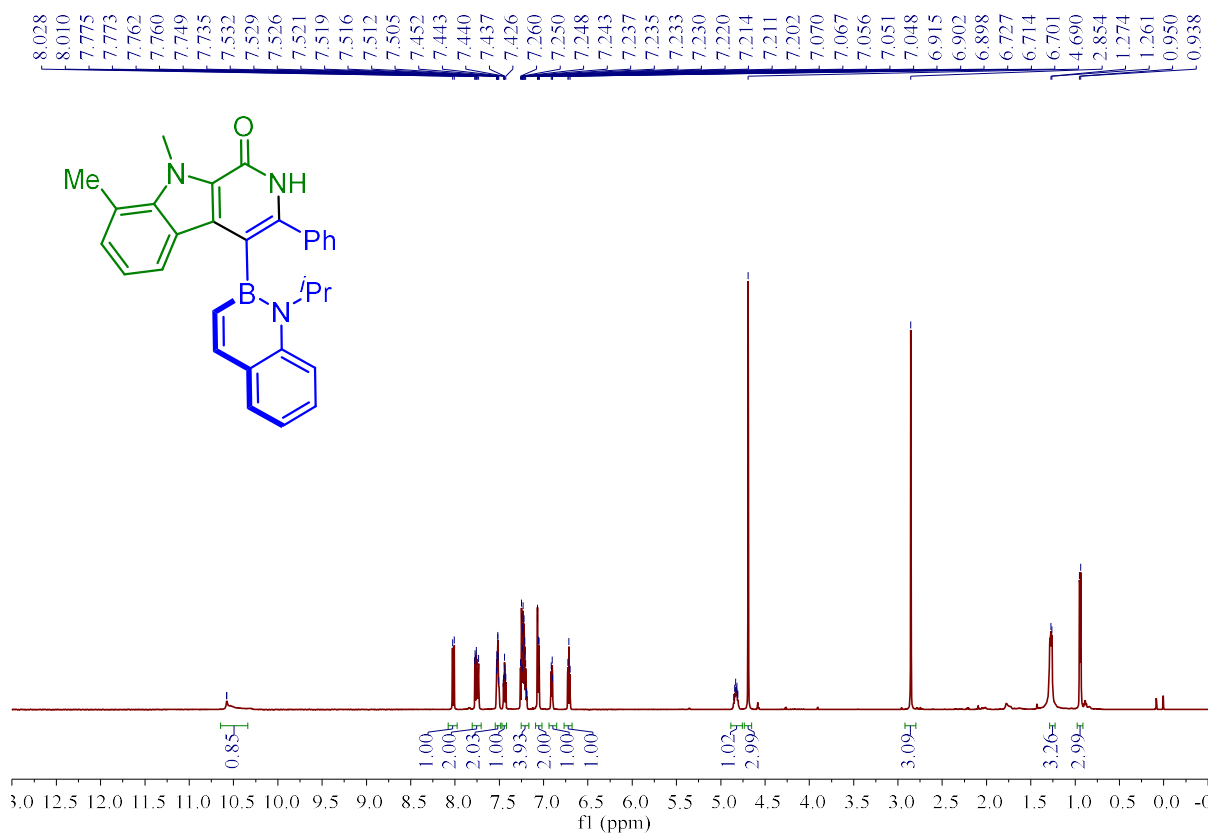
¹H NMR (600 MHz, CDCl₃) spectrum of 44.



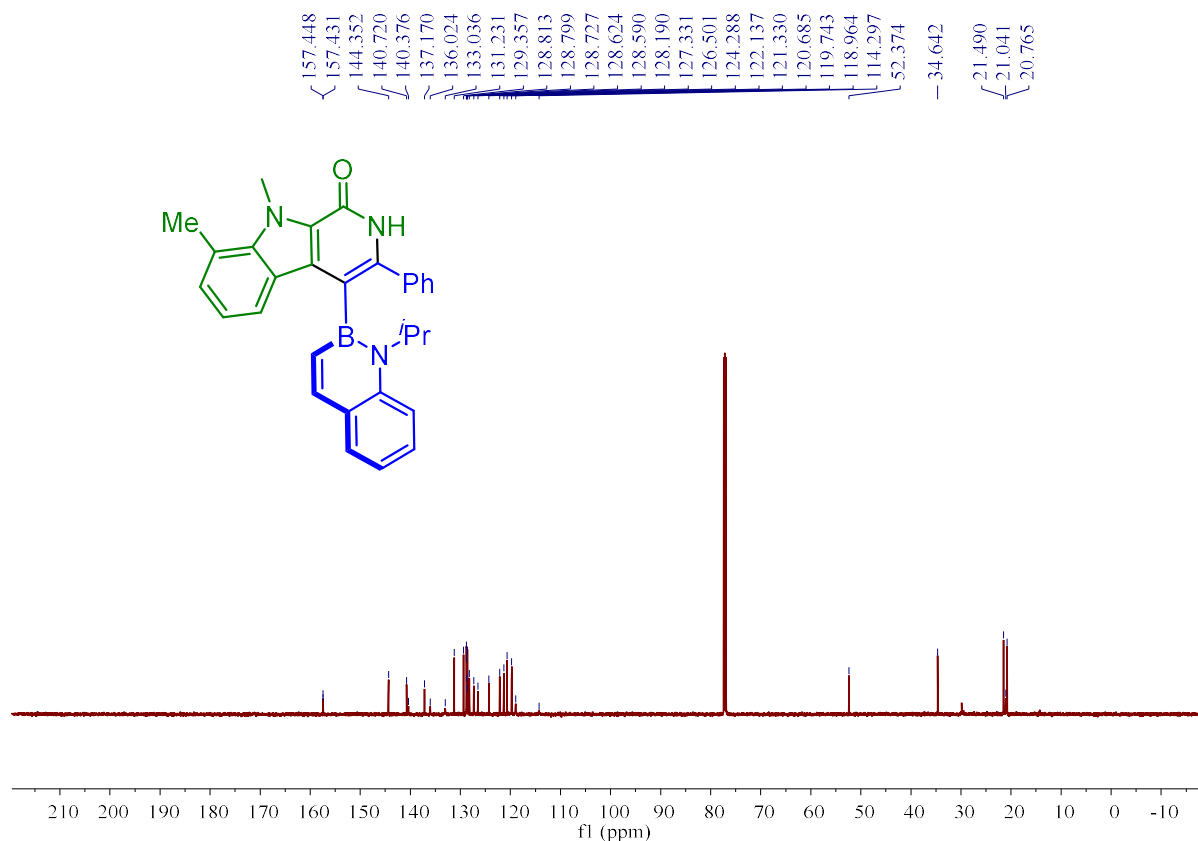
¹³C NMR (150 MHz, CDCl₃) spectrum of 44.



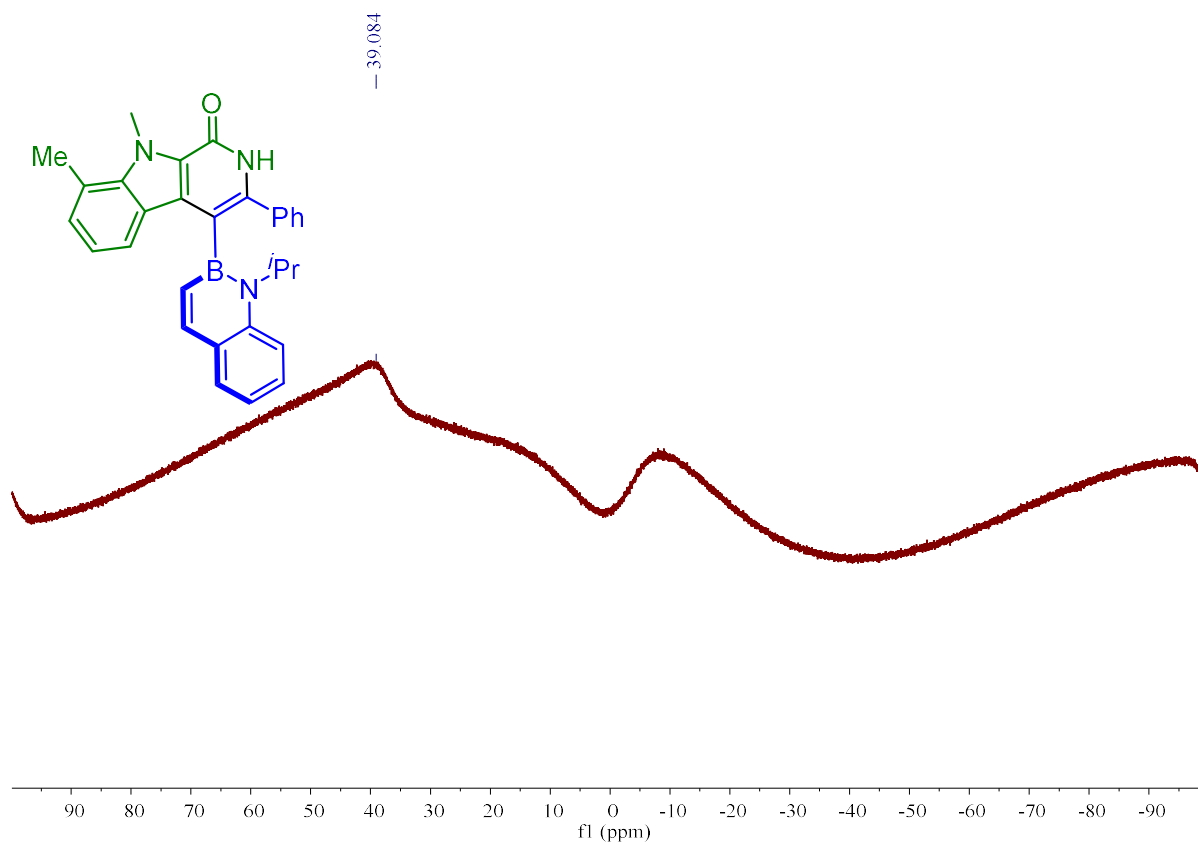
^{11}B NMR (193 MHz, CDCl_3) spectrum of 44.



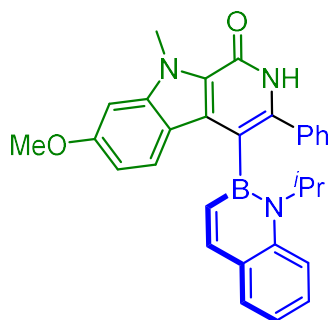
^1H NMR (600 MHz, CDCl_3) spectrum of 45.



¹³C NMR (150 MHz, CDCl₃) spectrum of 45.



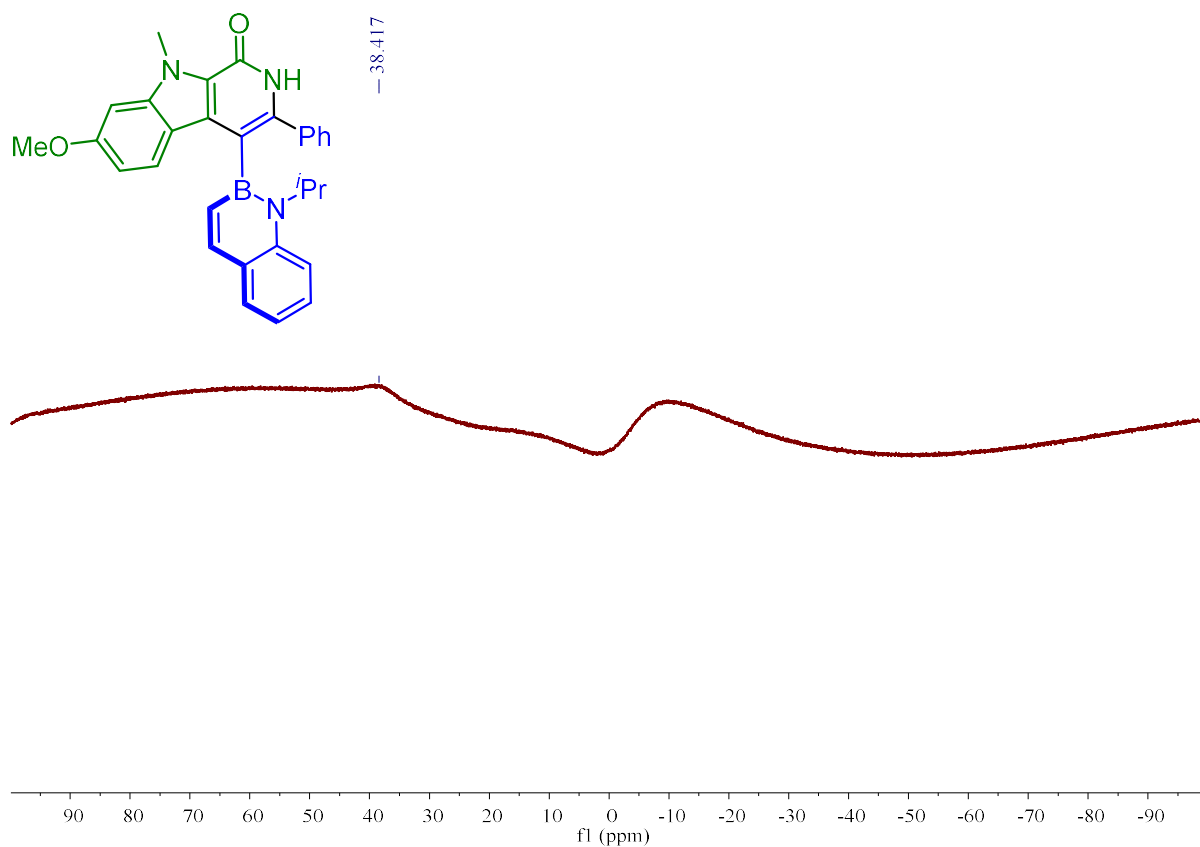
¹¹B NMR (193 MHz, CDCl₃) spectrum of 45.



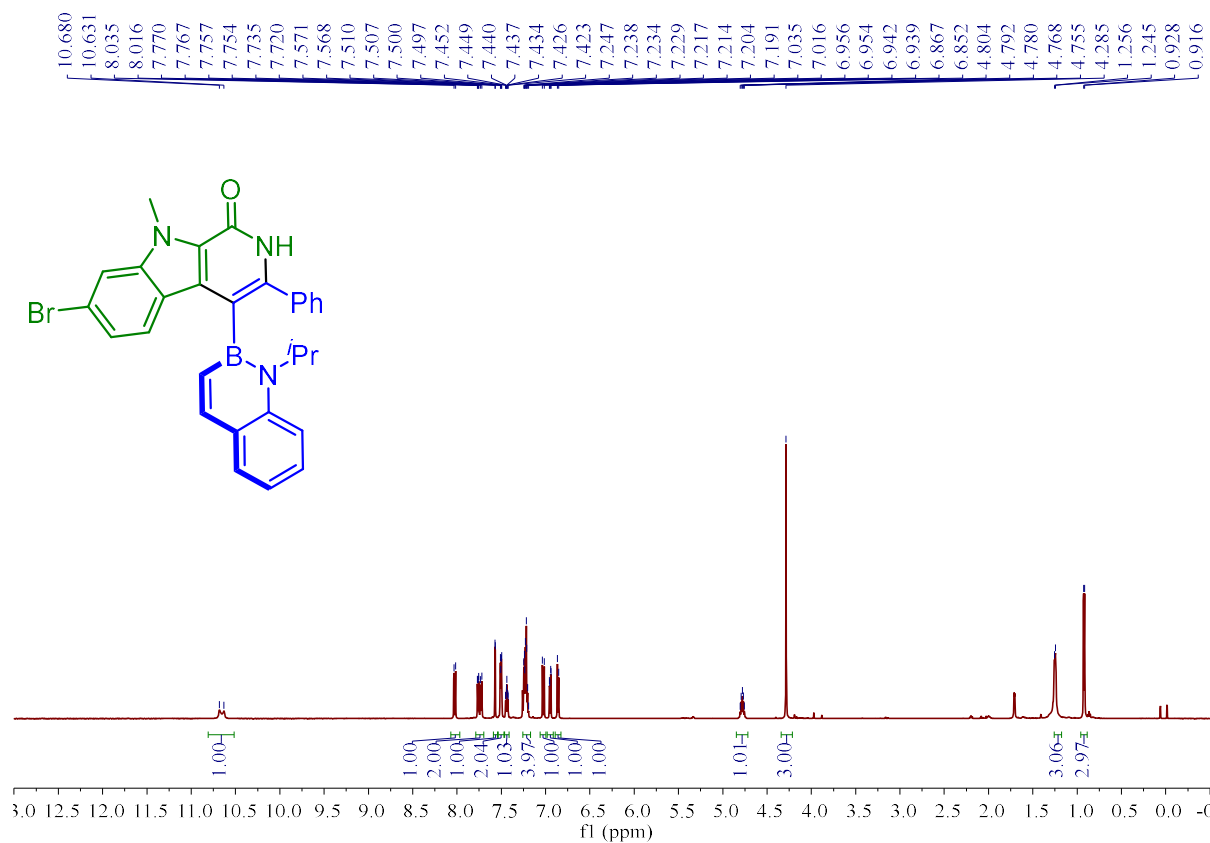
Chemical structure of compound 10 is shown above the ^{13}C NMR spectrum. The spectrum displays peaks corresponding to the structure, with the following chemical shifts (ppm) labeled on the right:

- 159.548
- 156.768
- 144.445
- 142.706
- 140.244
- 137.125
- 135.958
- 131.130
- 129.032
- 128.836
- 128.568
- 128.474
- 128.447
- 128.100
- 127.253
- 126.205
- 125.539
- 124.002
- 120.599
- 118.848
- 117.274
- 110.022
- 92.228
- 55.483
- 52.232
- 31.418
- 21.443
- 20.894

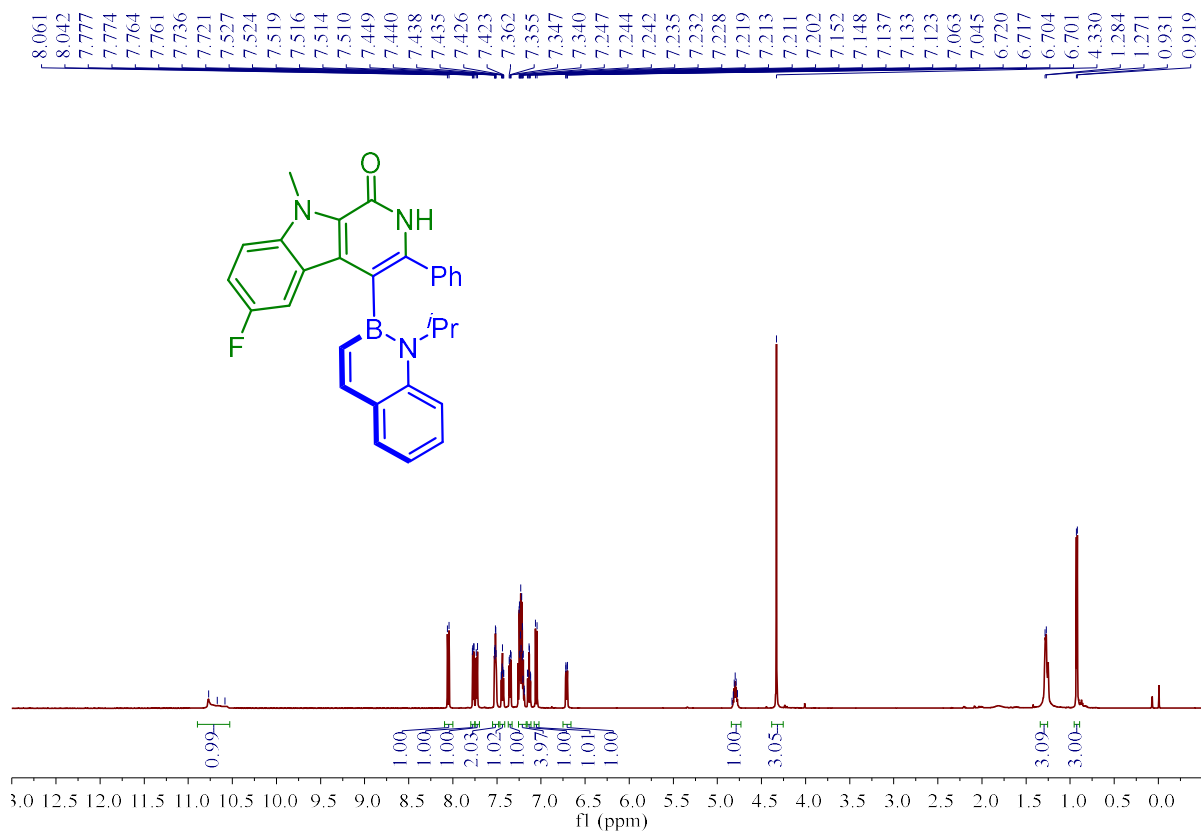
^{13}C NMR (150 MHz, CDCl_3) spectrum of 46.



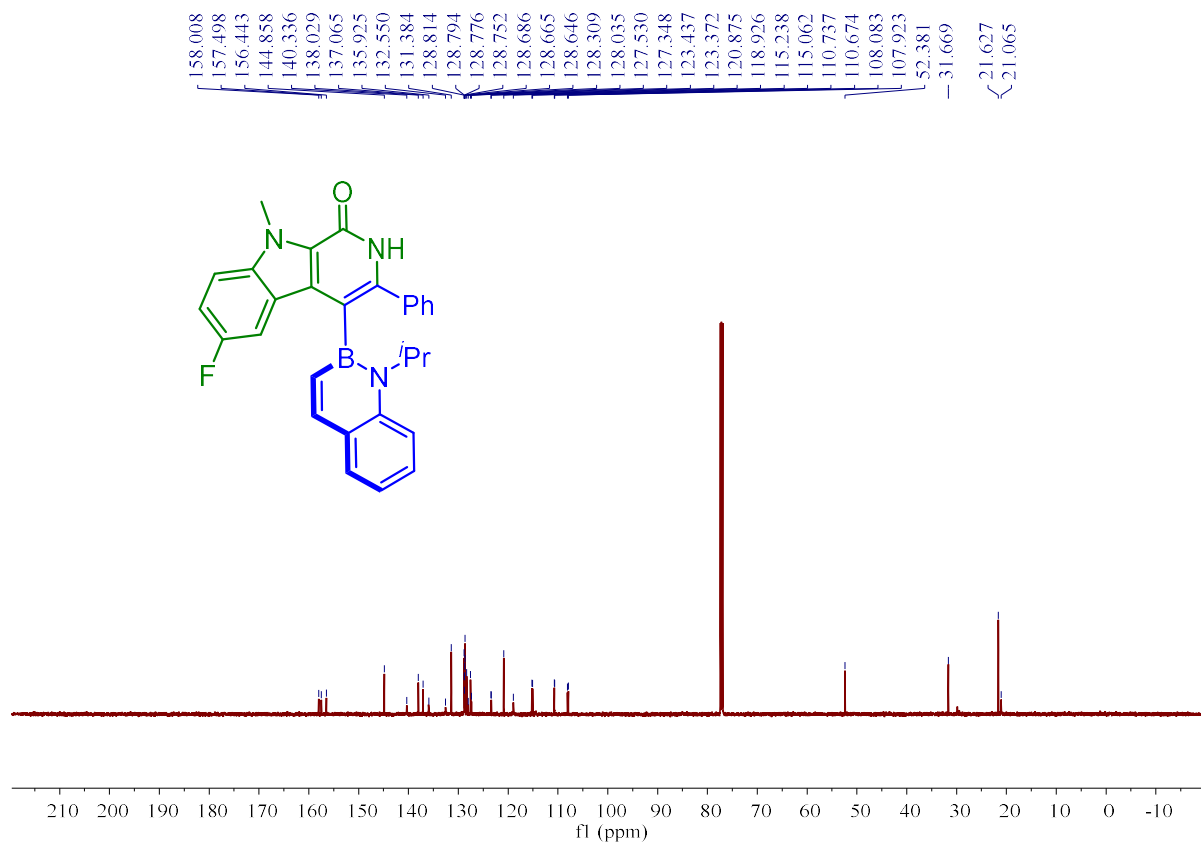
^{11}B NMR (193 MHz, CDCl_3) spectrum of 46.



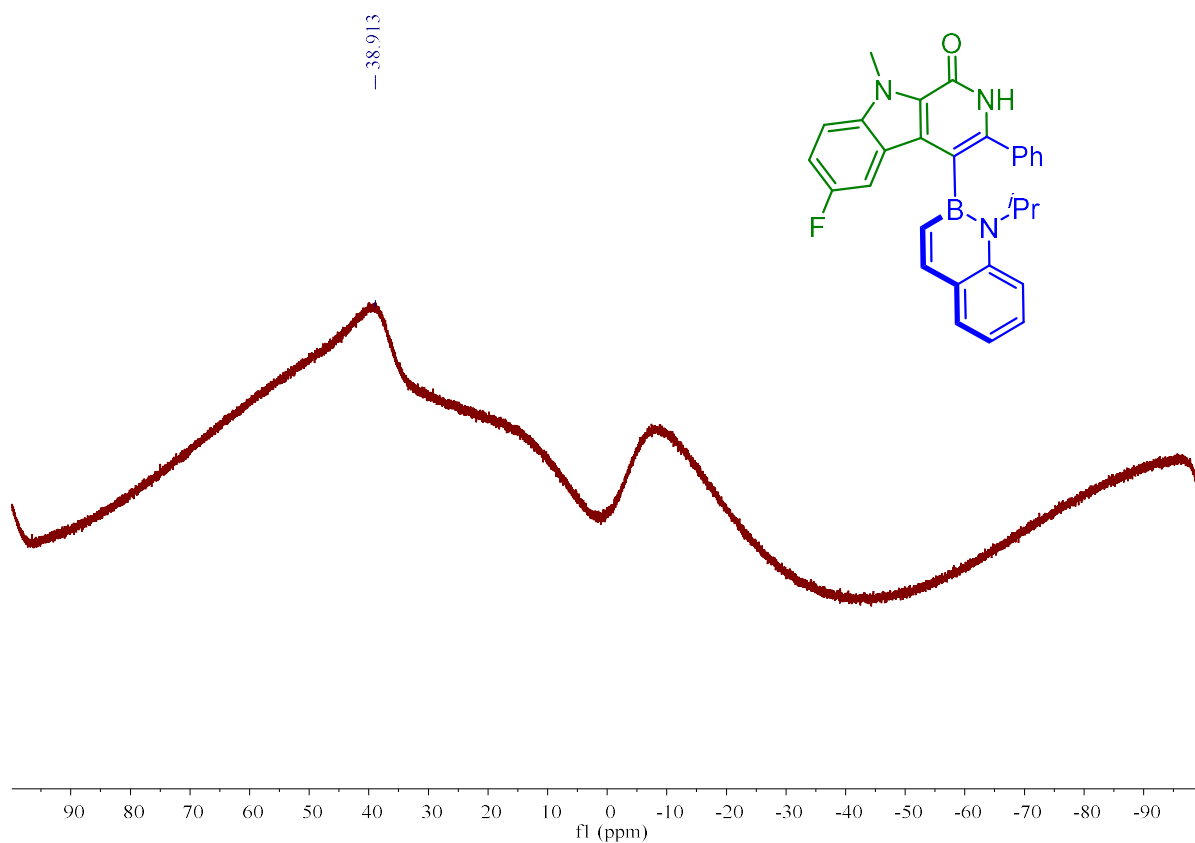
^1H NMR (600 MHz, CDCl_3) spectrum of 47.



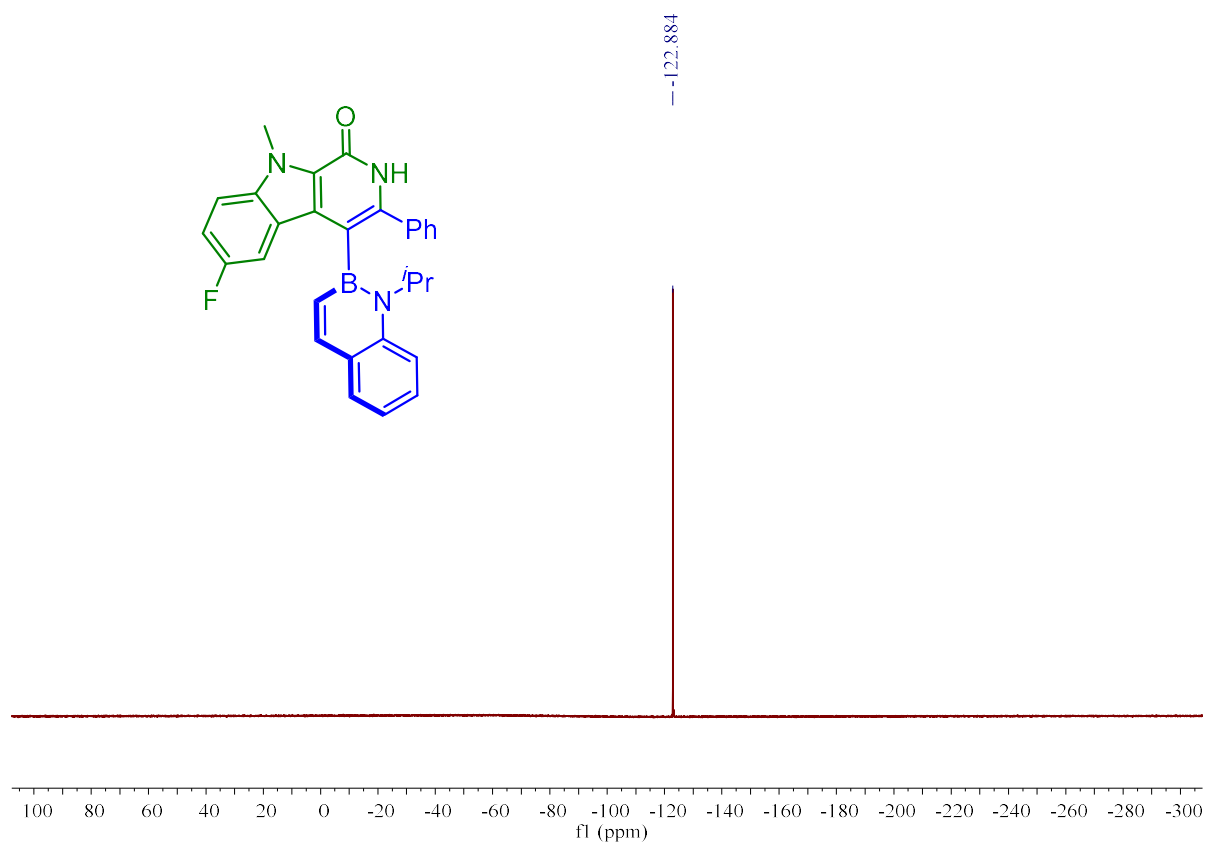
¹H NMR (600 MHz, CDCl₃) spectrum of 48.



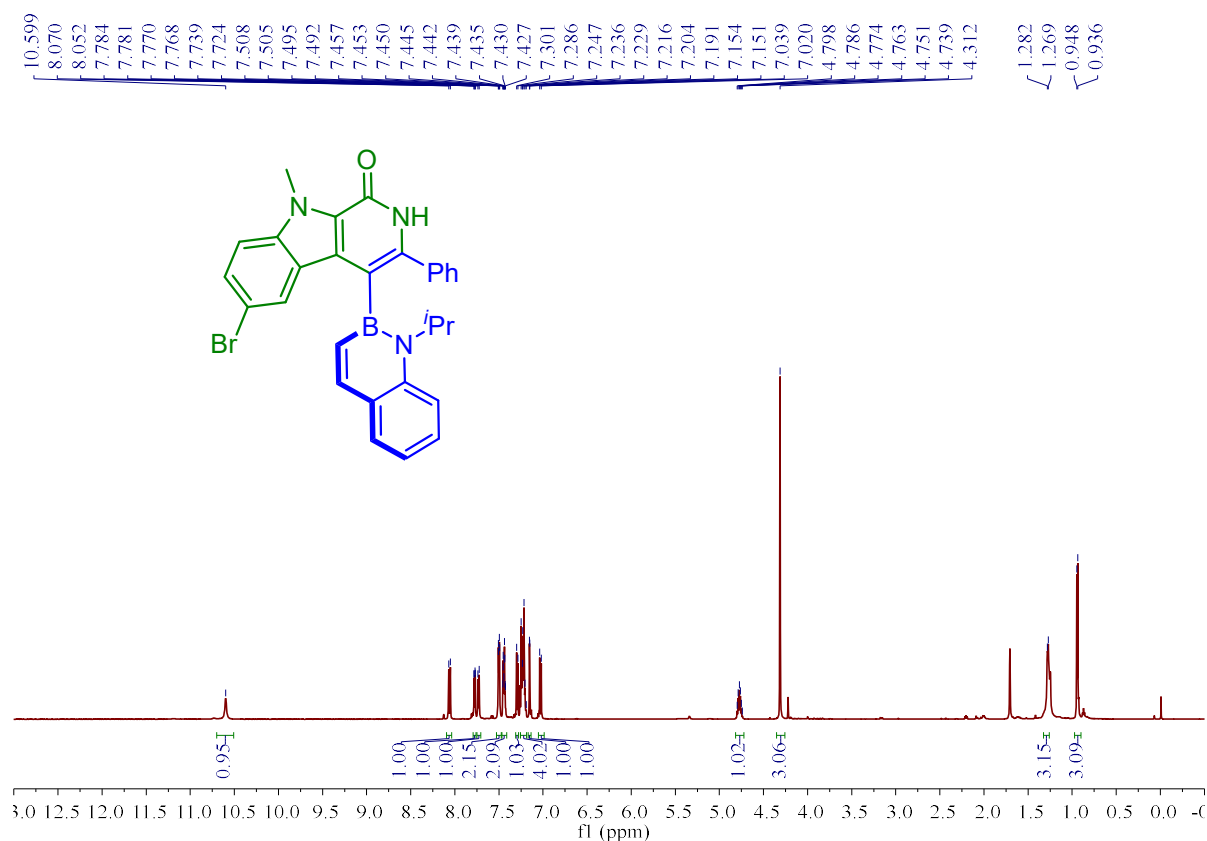
¹³C NMR (150 MHz, CDCl₃) spectrum of 48.



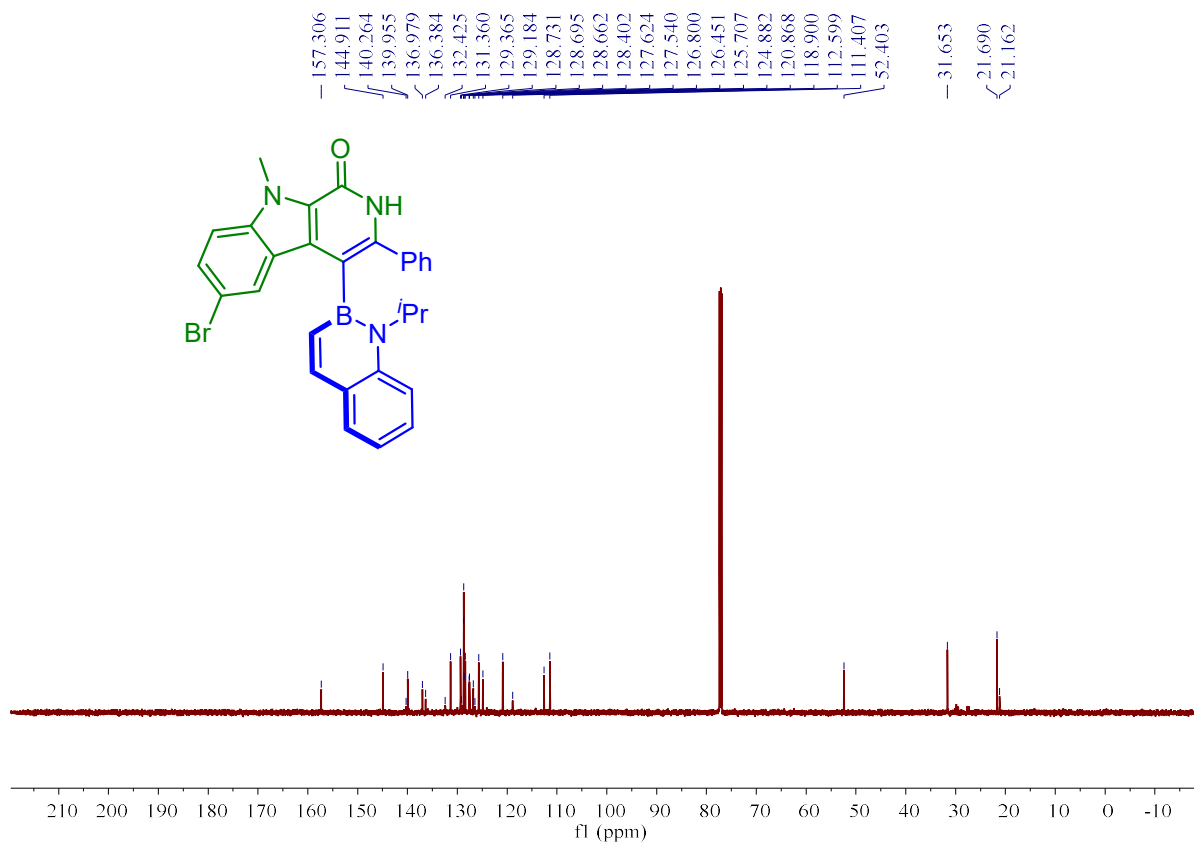
¹¹B NMR (193 MHz, CDCl₃) spectrum of 48.



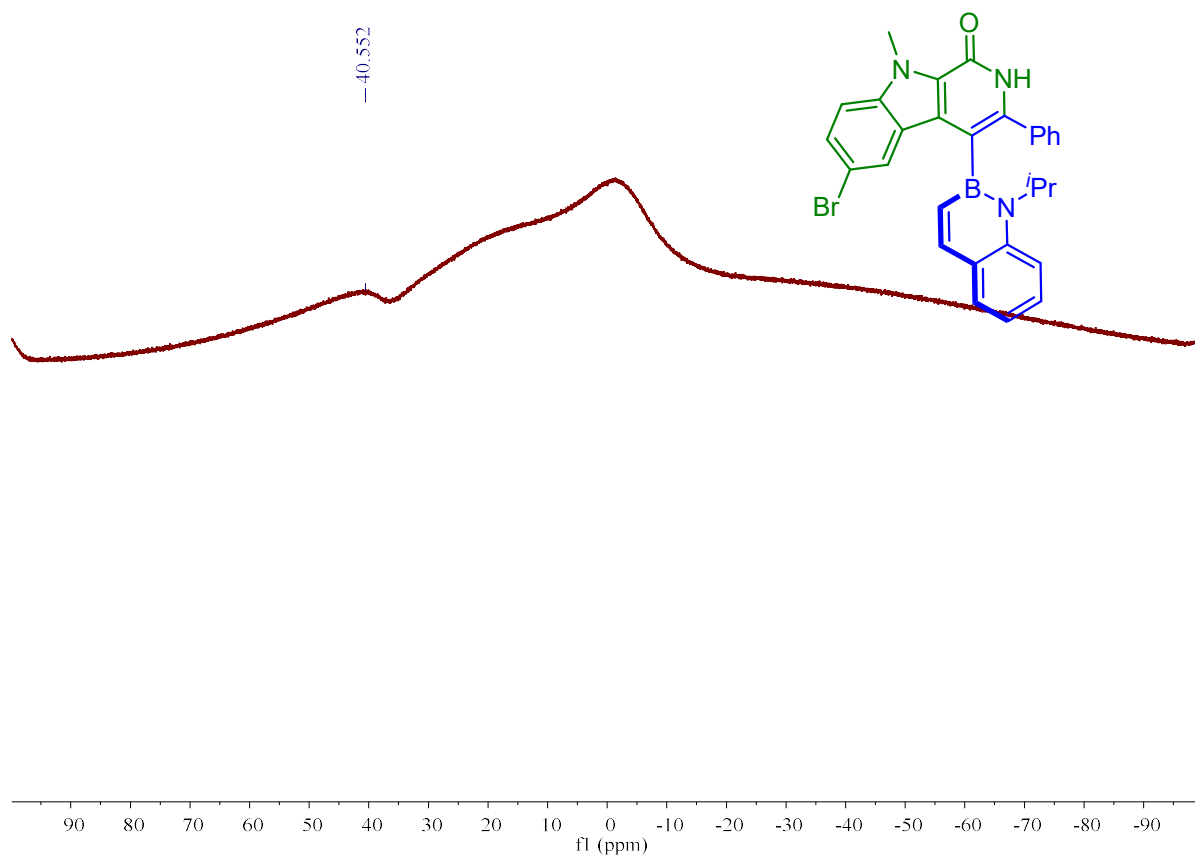
¹⁹F NMR (376 MHz, CDCl₃) spectrum of 48.



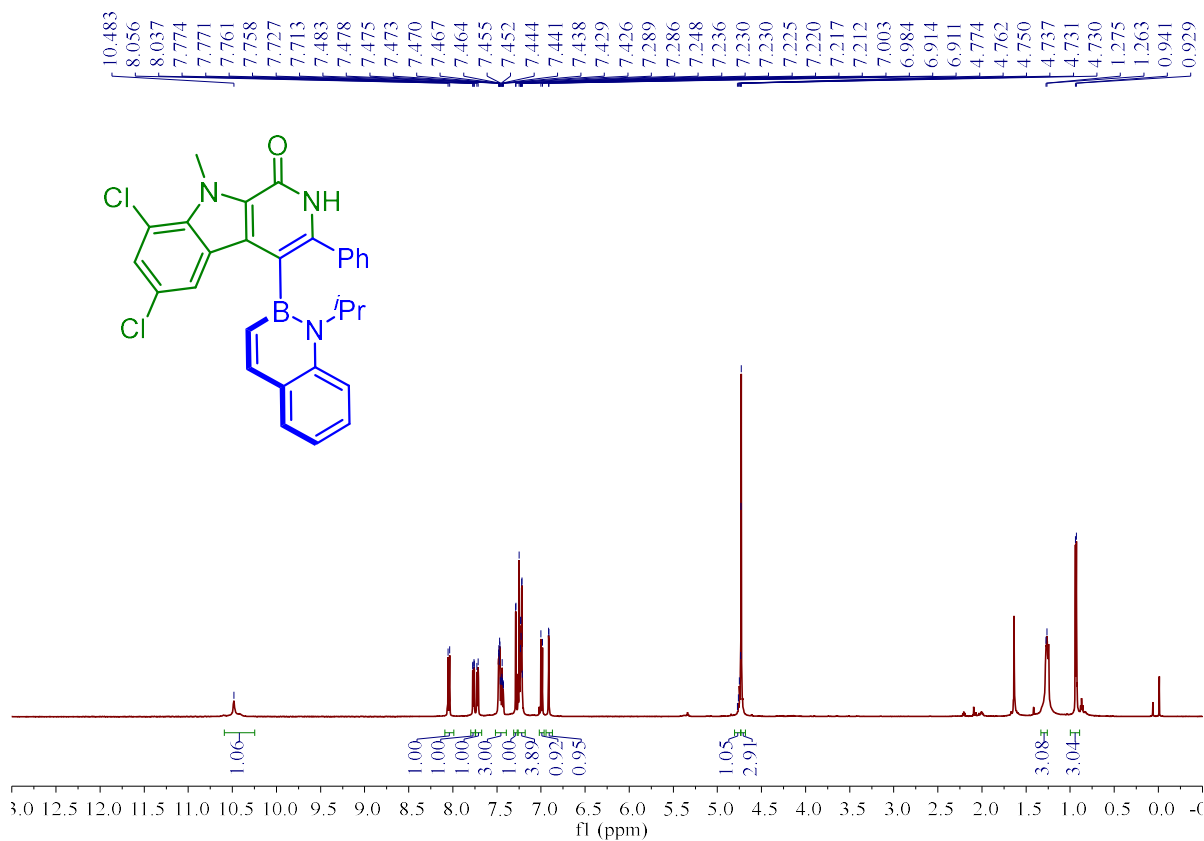
¹H NMR (600 MHz, CDCl₃) spectrum of 49.



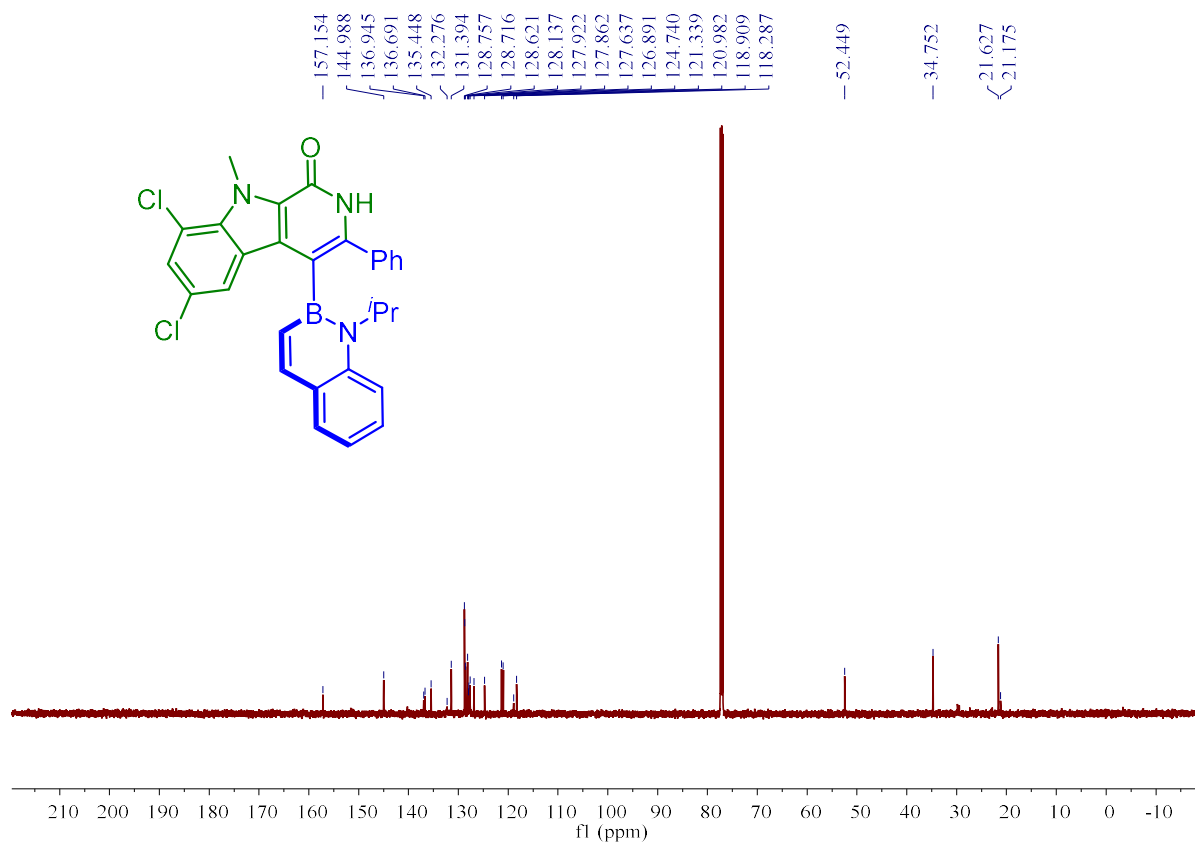
¹³C NMR (150 MHz, CDCl₃) spectrum of 49.



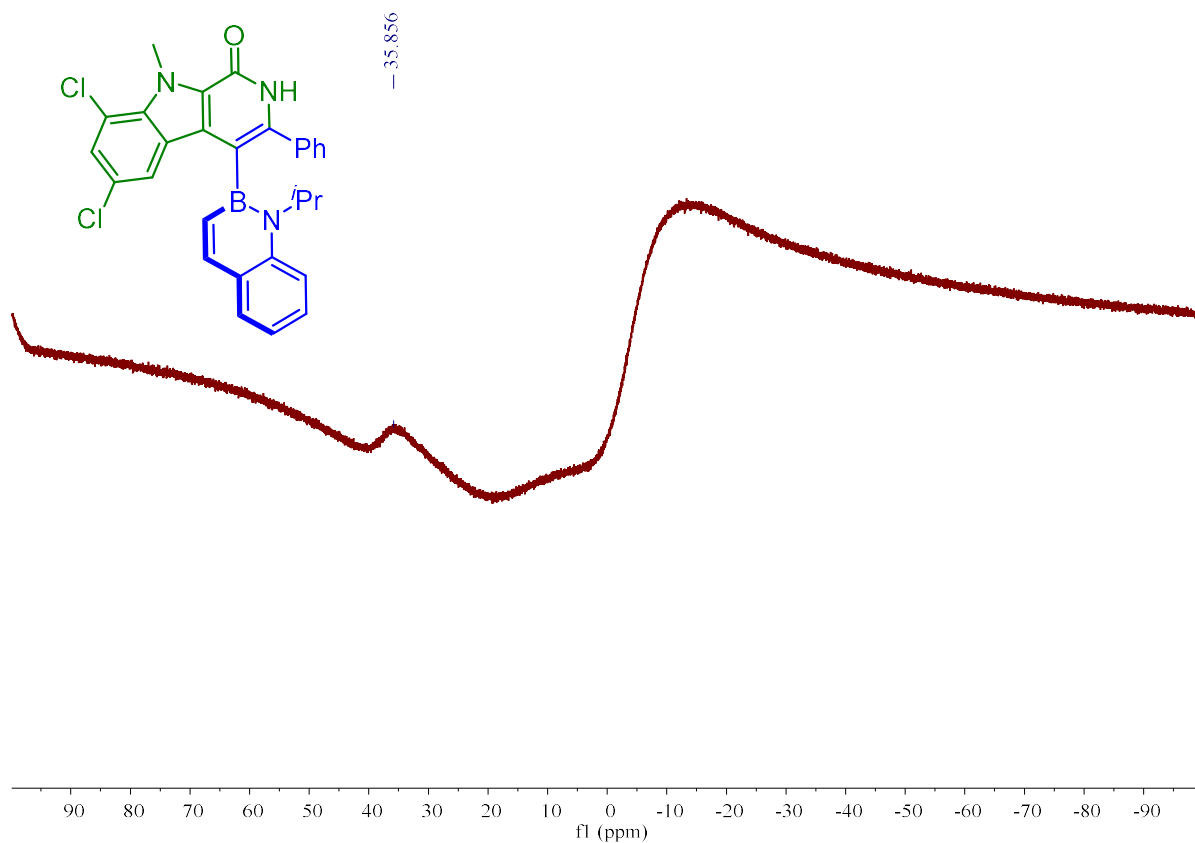
^{11}B NMR (193 MHz, CDCl_3) spectrum of 49.



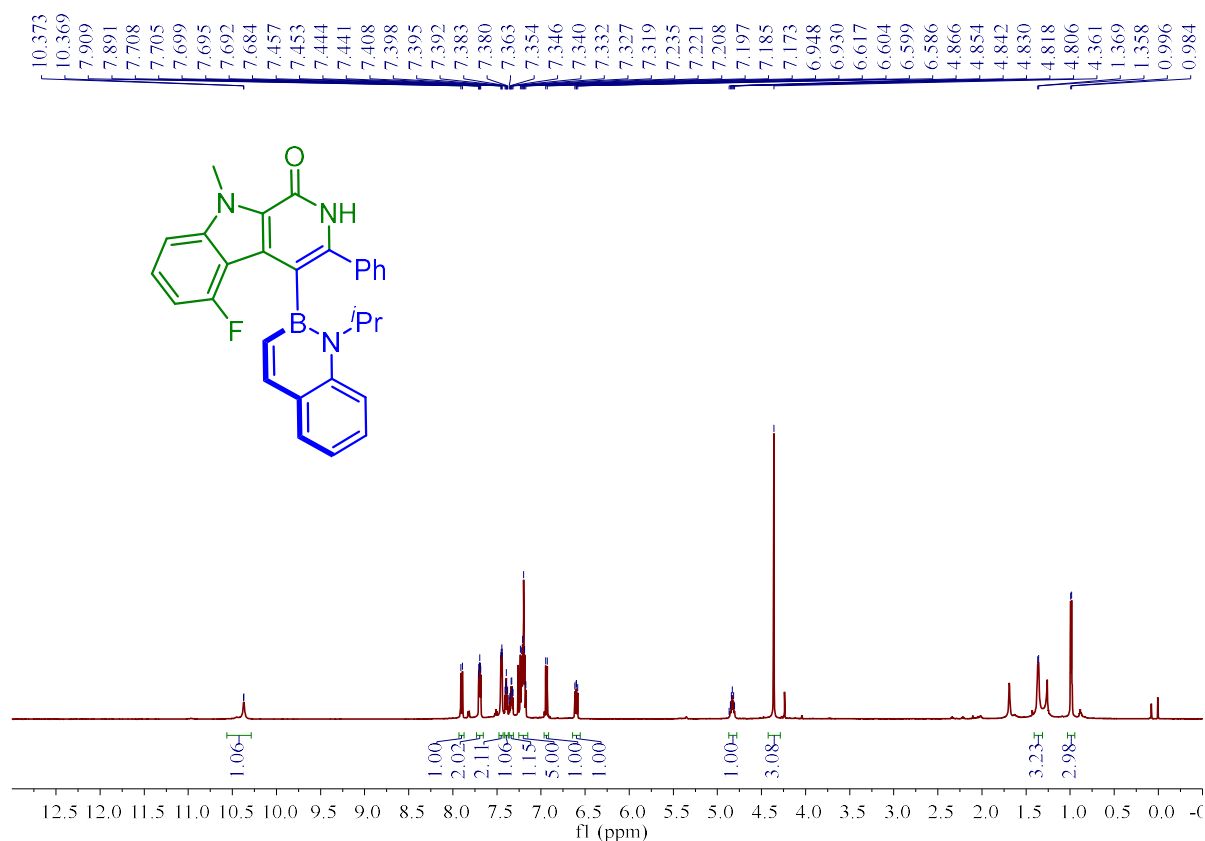
^1H NMR (600 MHz, CDCl_3) spectrum of 50.



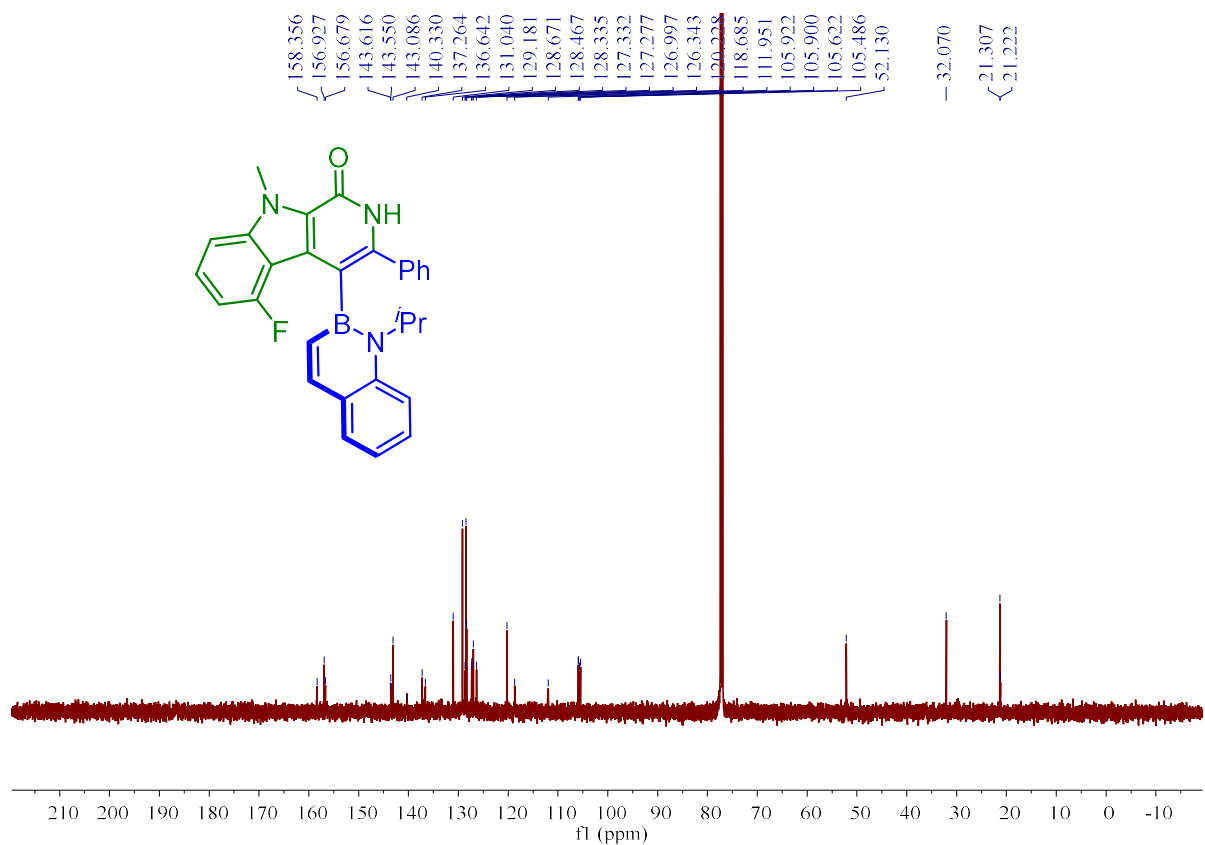
¹³C NMR (150 MHz, CDCl₃) spectrum of 50.



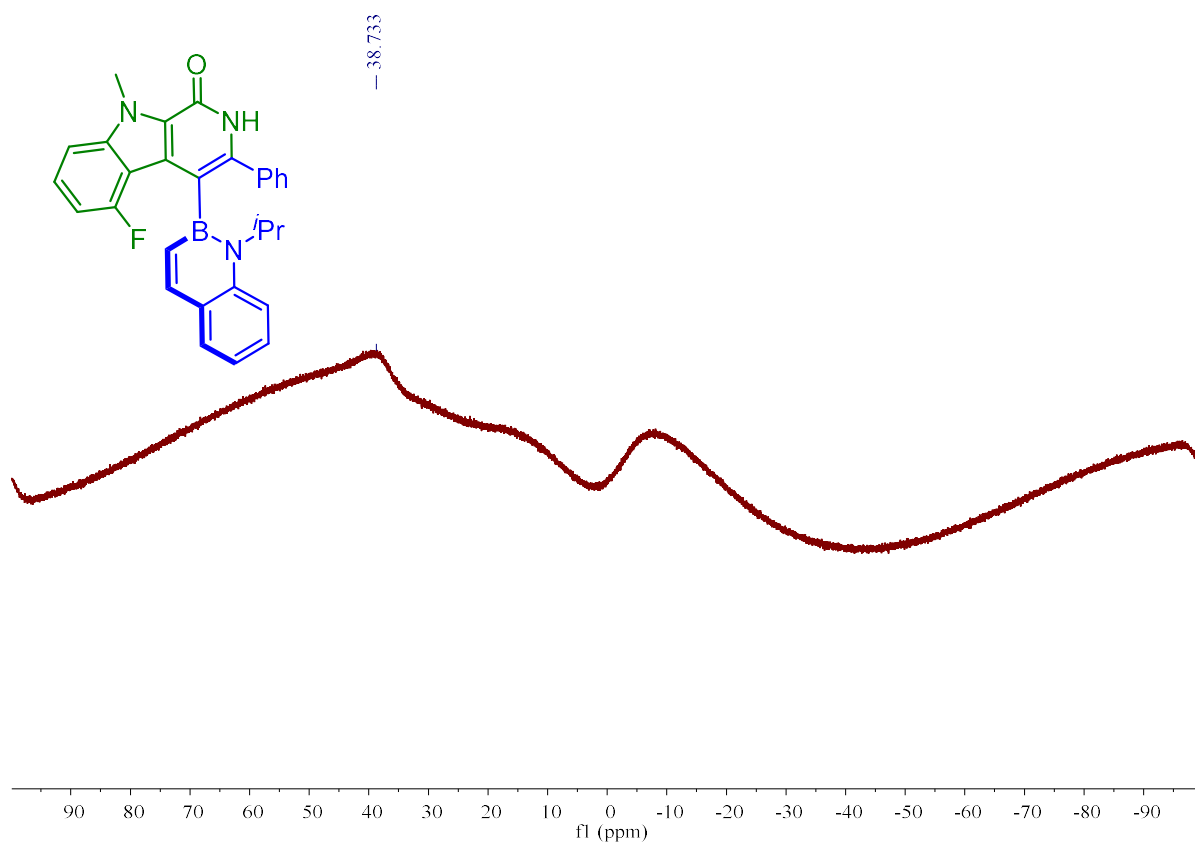
¹¹B NMR (193 MHz, CDCl₃) spectrum of 50.



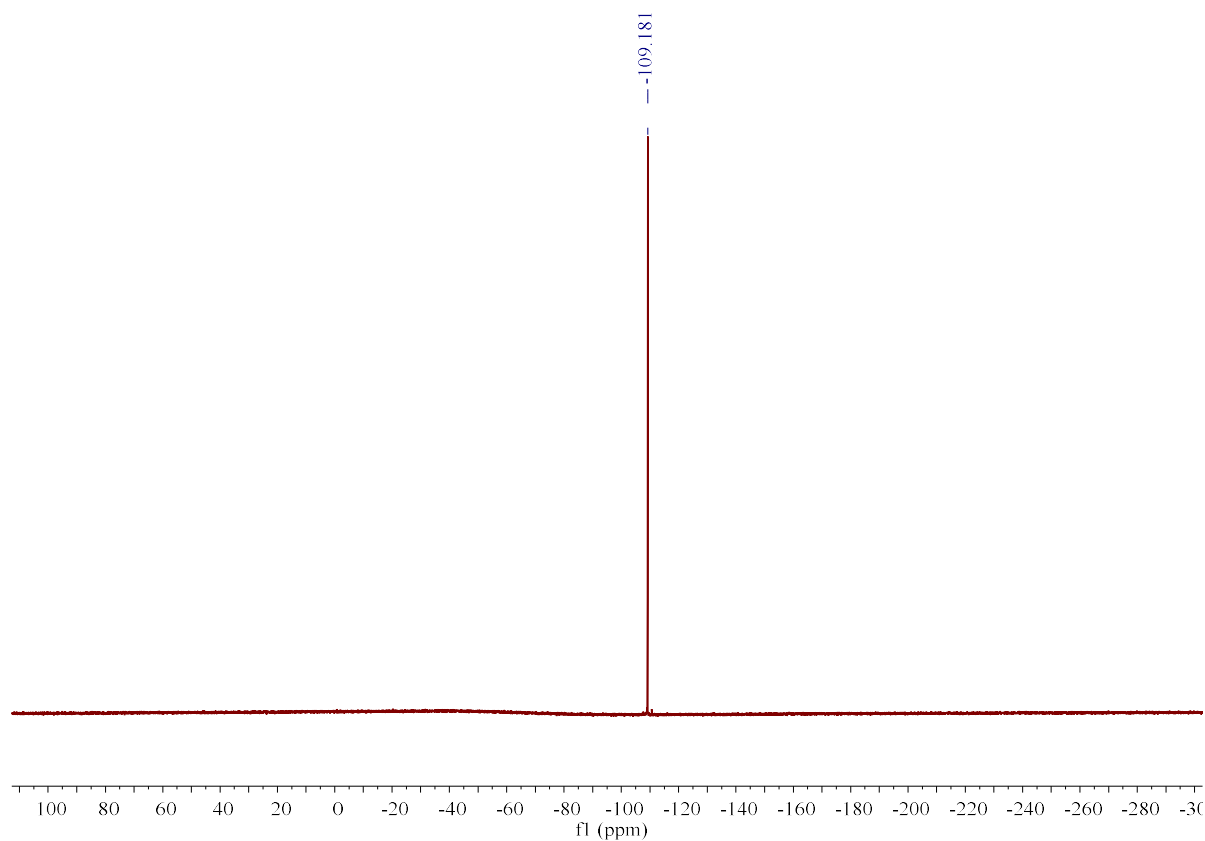
¹H NMR (600 MHz, CDCl₃) spectrum of 51.



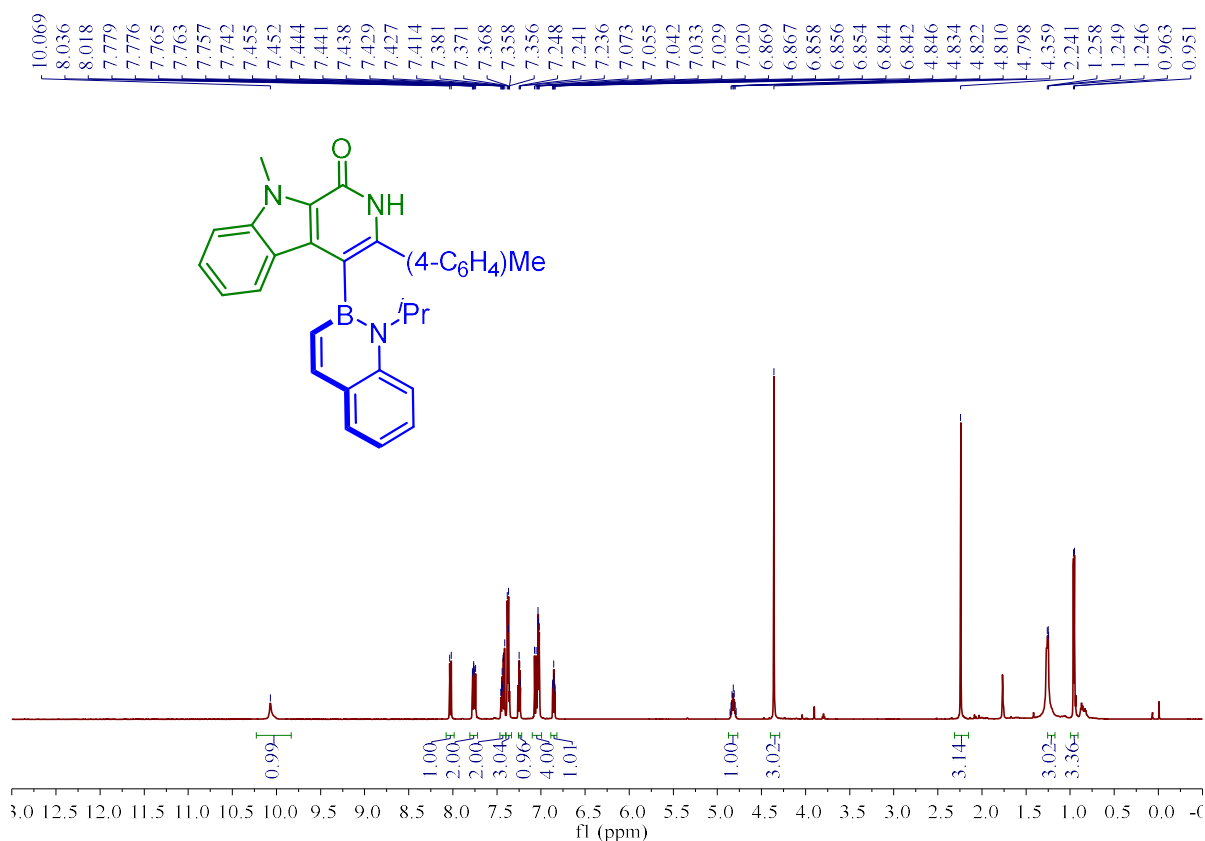
¹³C NMR (150 MHz, CDCl₃) spectrum of 51.



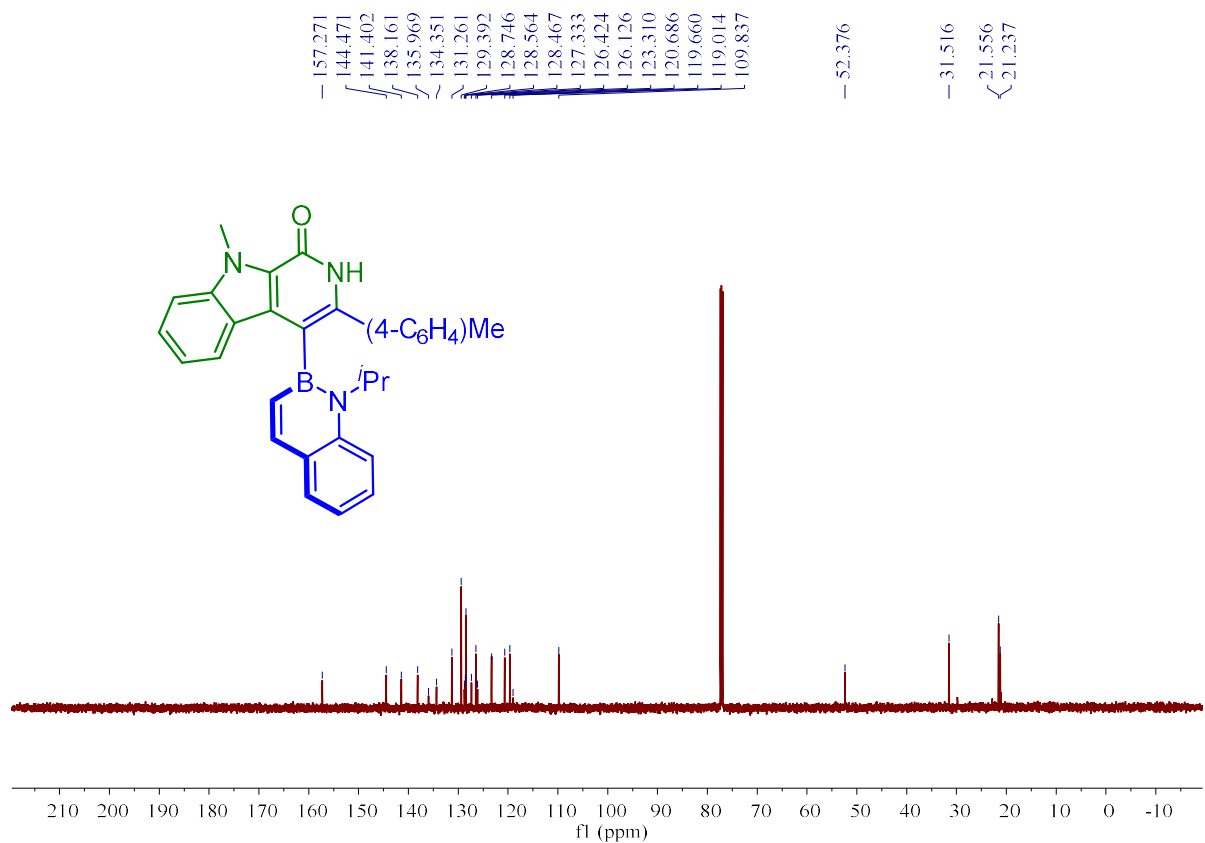
^{11}B NMR (193 MHz, CDCl_3) spectrum of 51.



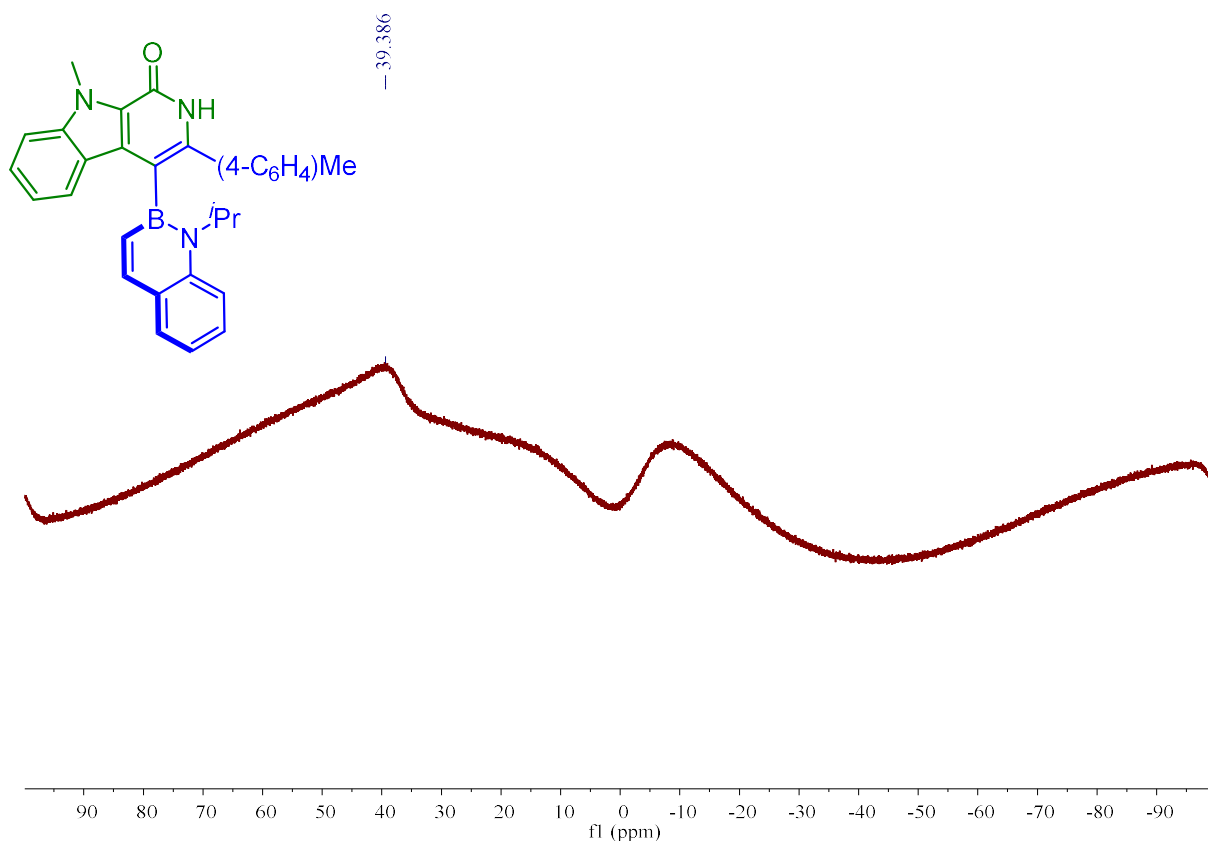
^{19}F NMR (376 MHz, CDCl_3) spectrum of 51.



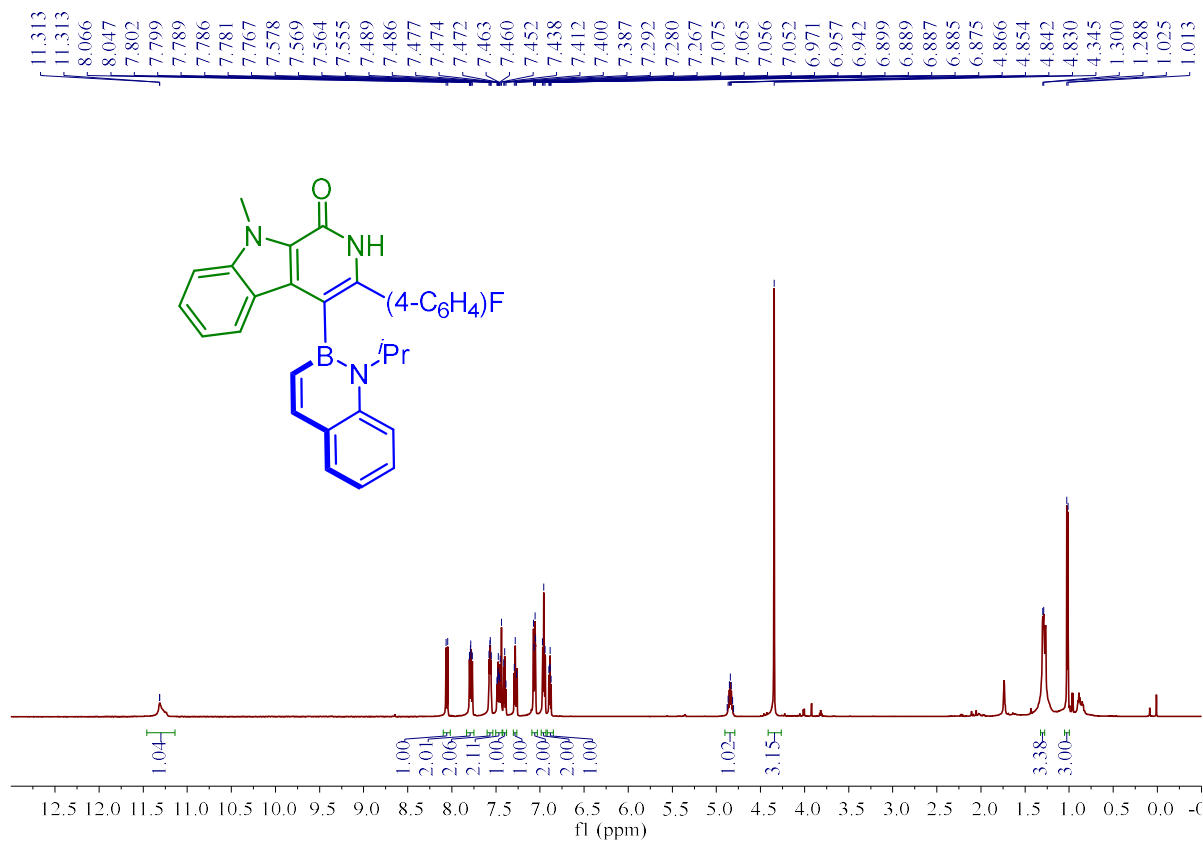
¹H NMR (600 MHz, CDCl₃) spectrum of 52.



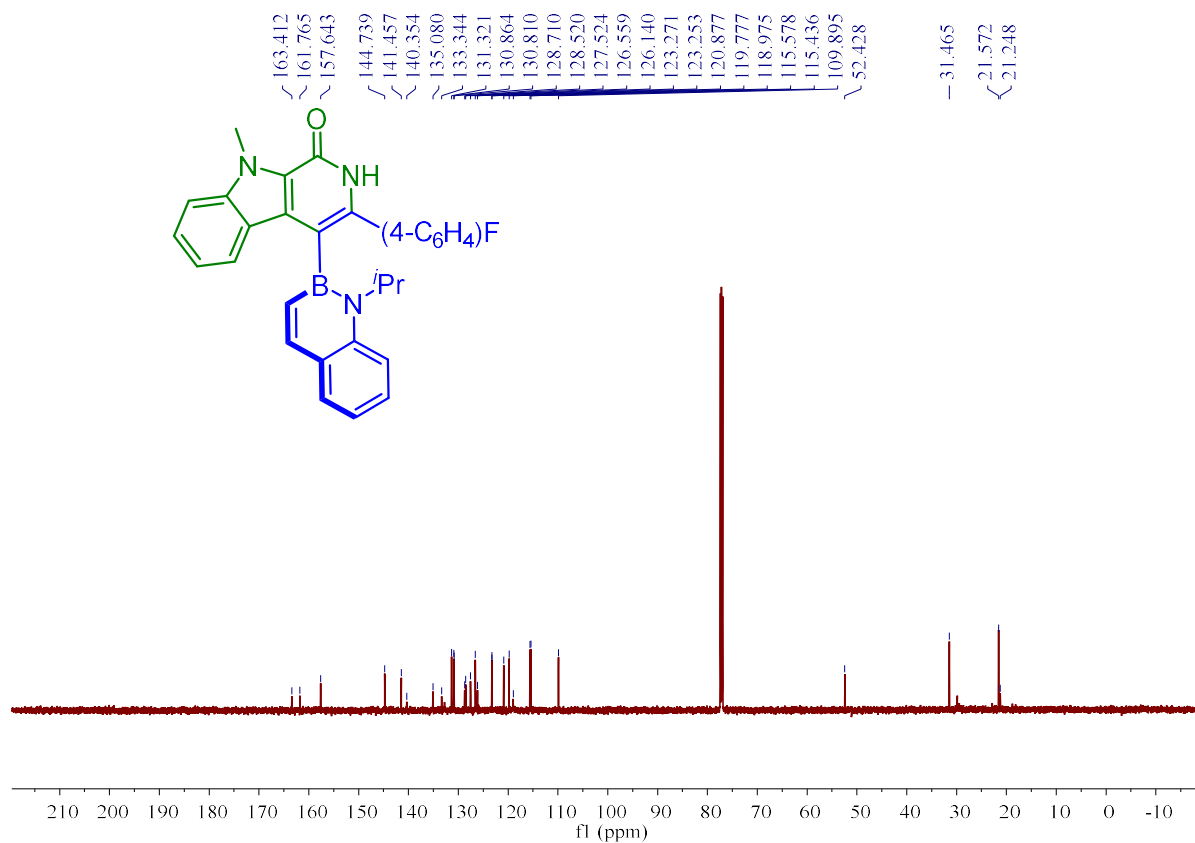
¹³C NMR (150 MHz, CDCl₃) spectrum of 52.



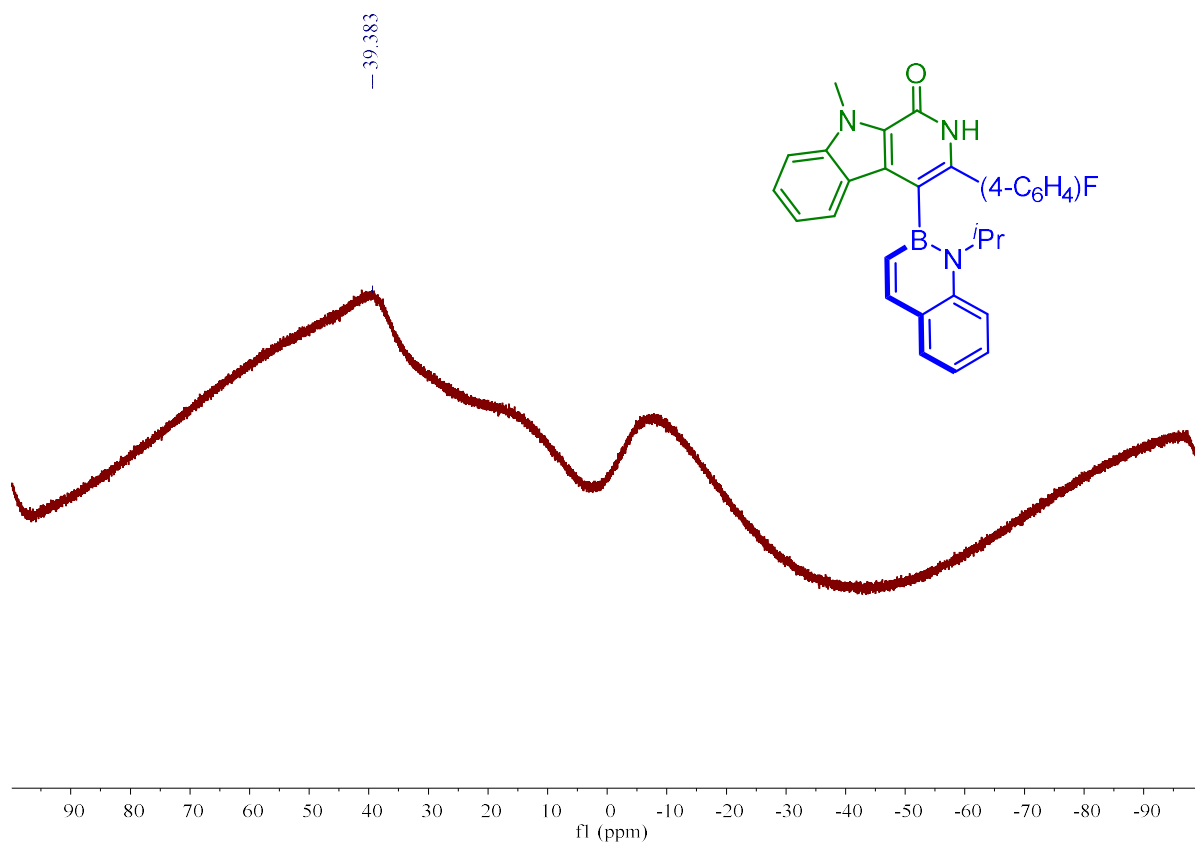
^{11}B NMR (193 MHz, CDCl_3) spectrum of 52.



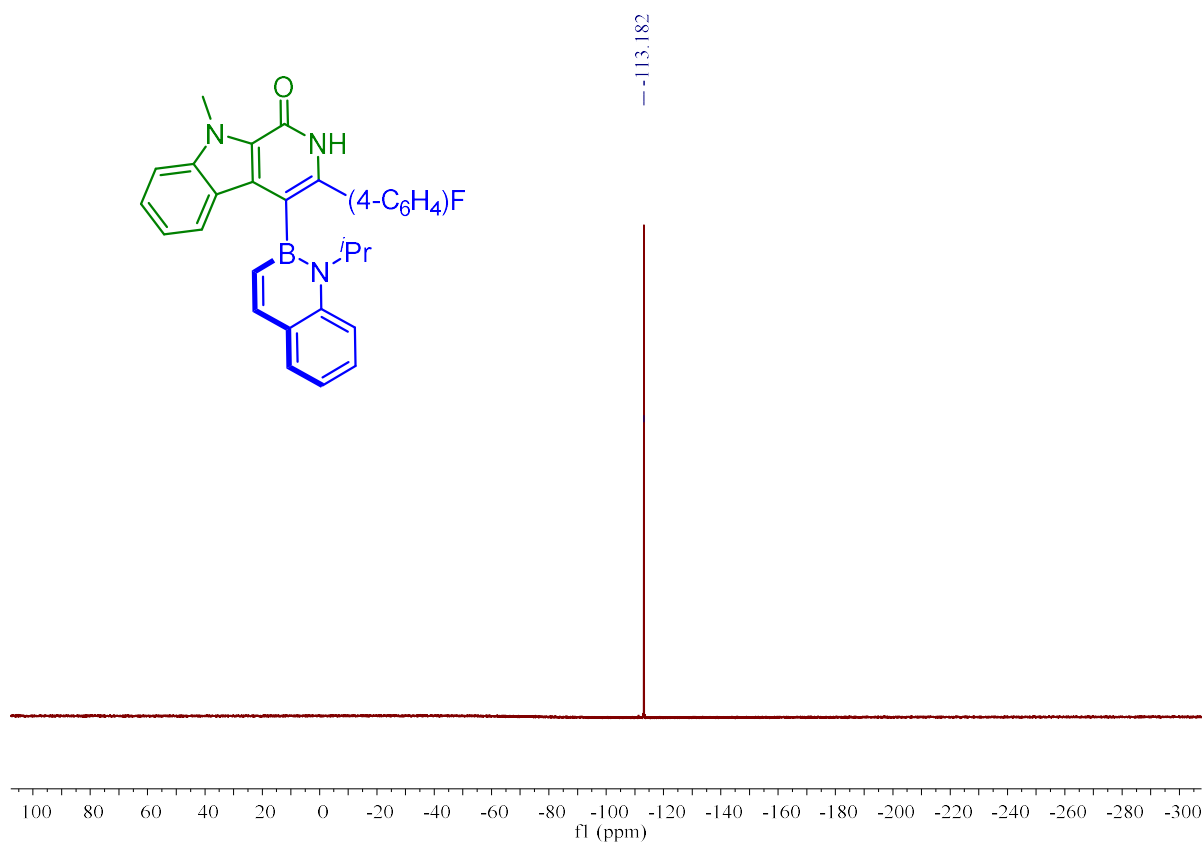
^1H NMR (600 MHz, CDCl_3) spectrum of 53.



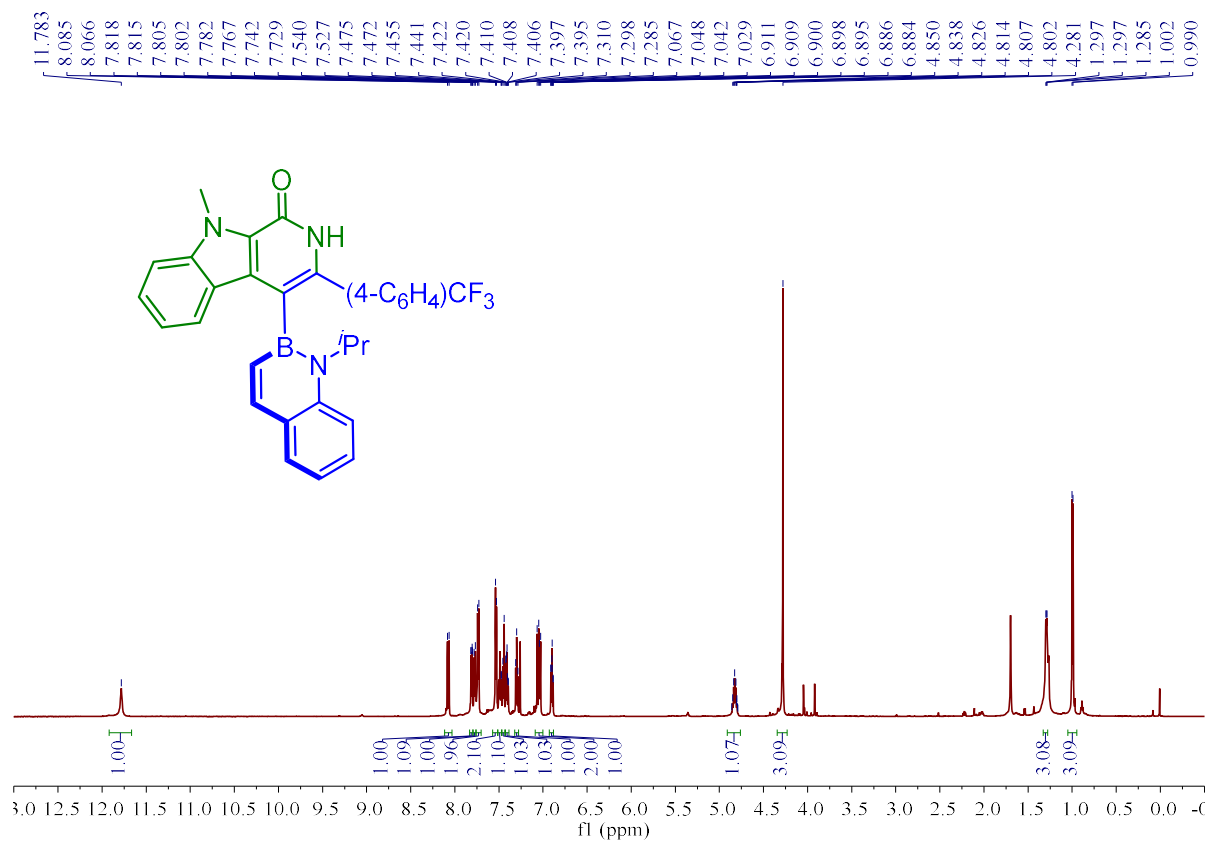
¹³C NMR (150 MHz, CDCl₃) spectrum of 53.



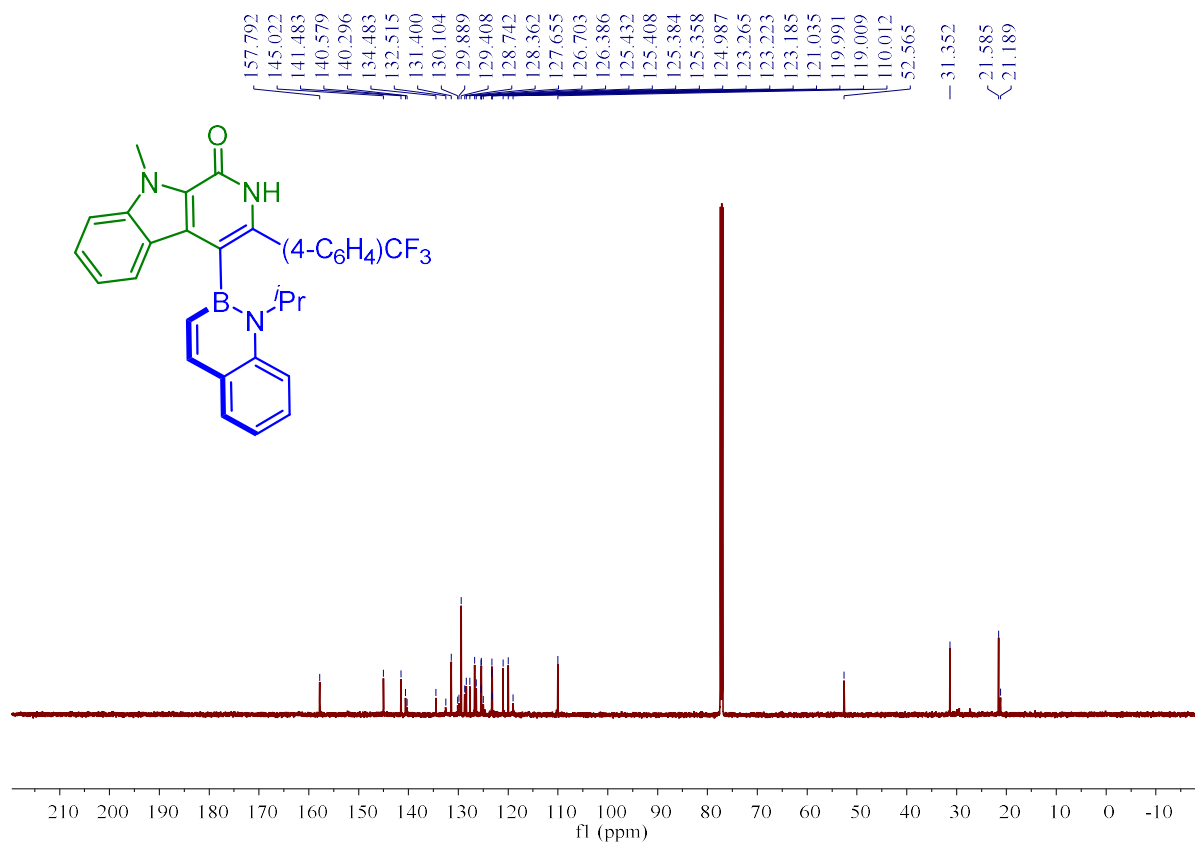
¹¹B NMR (193 MHz, CDCl₃) spectrum of 53.



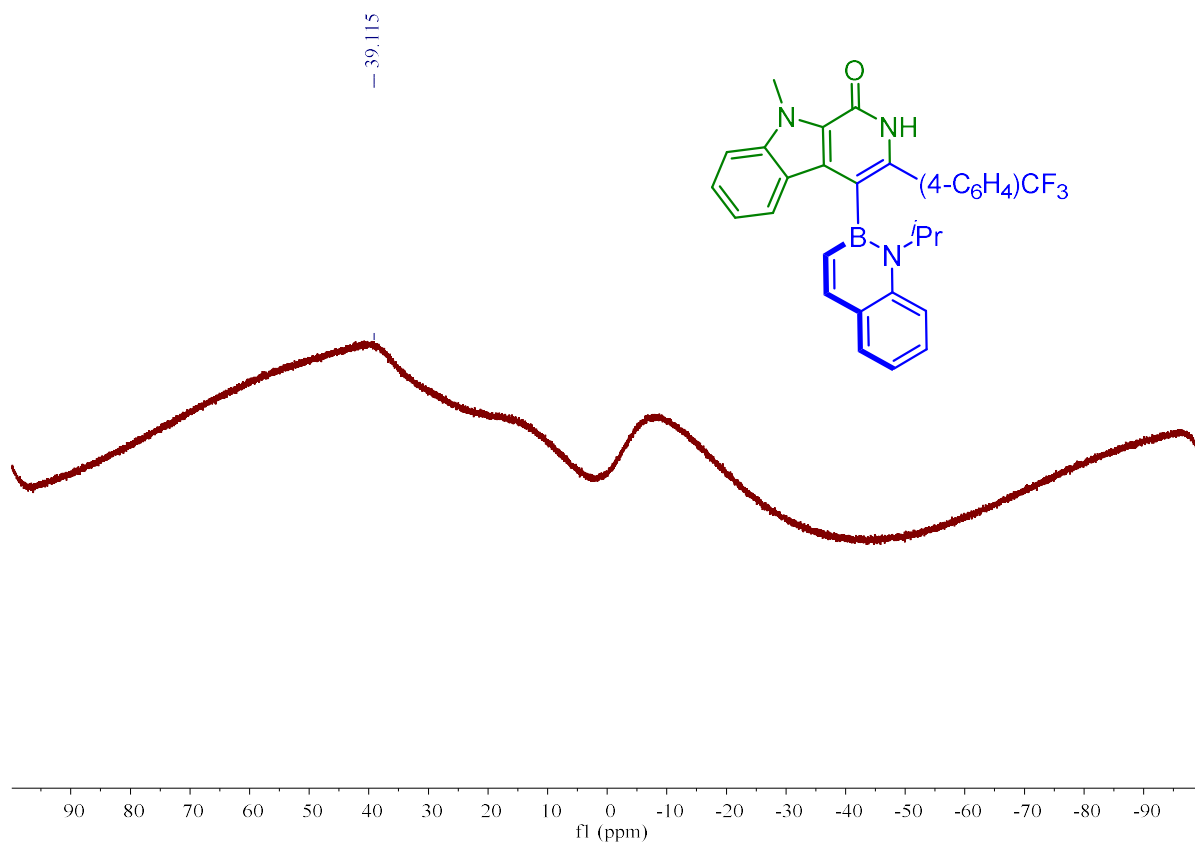
^{19}F NMR (376 MHz, CDCl_3) spectrum of 53.



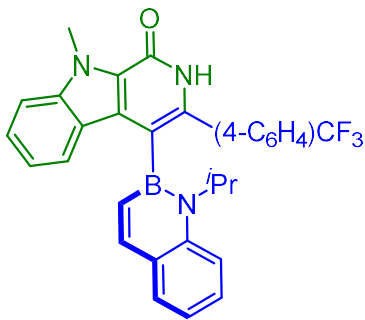
^1H NMR (600 MHz, CDCl_3) spectrum of 54.



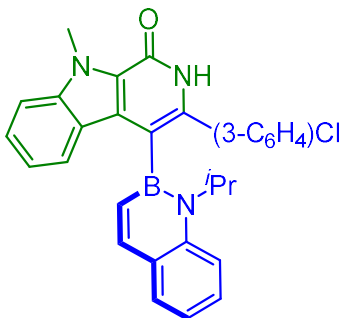
¹³C NMR (150 MHz, CDCl₃) spectrum of 54.



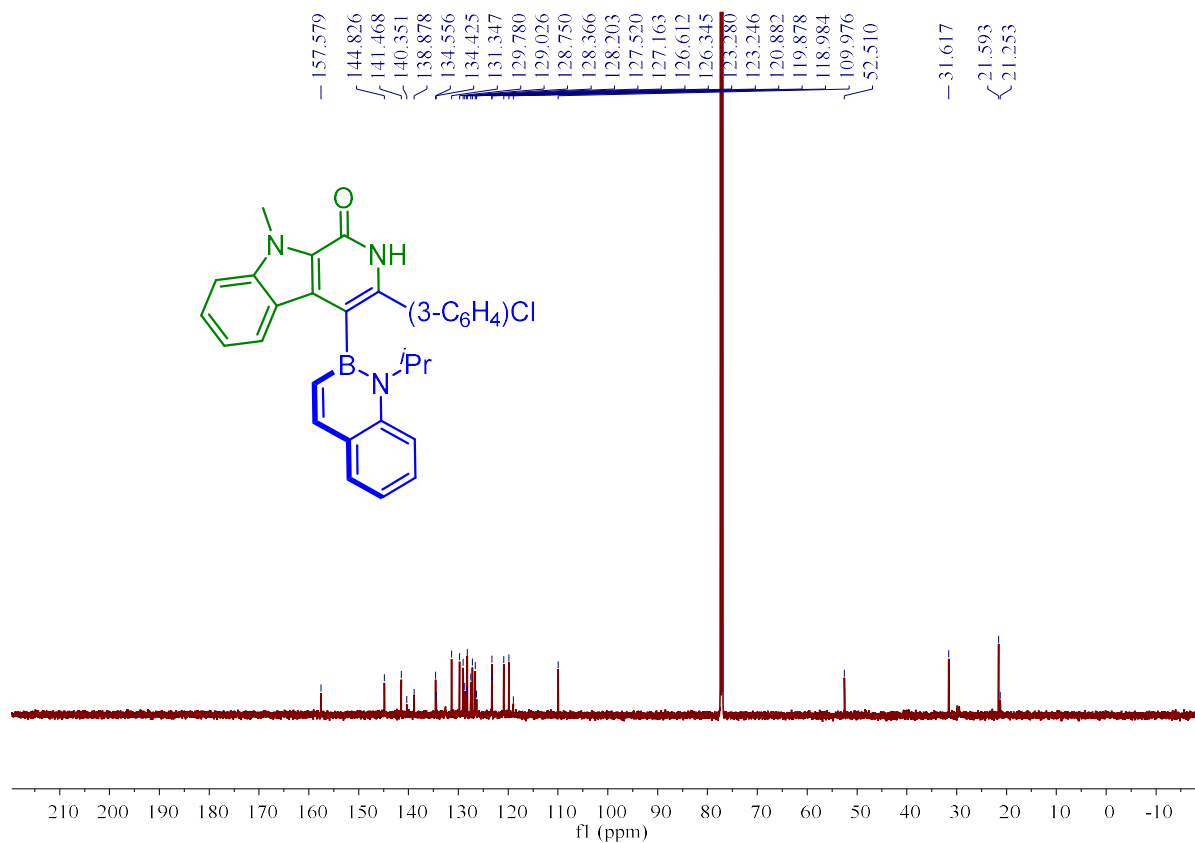
¹¹B NMR (193 MHz, CDCl₃) spectrum of 54.



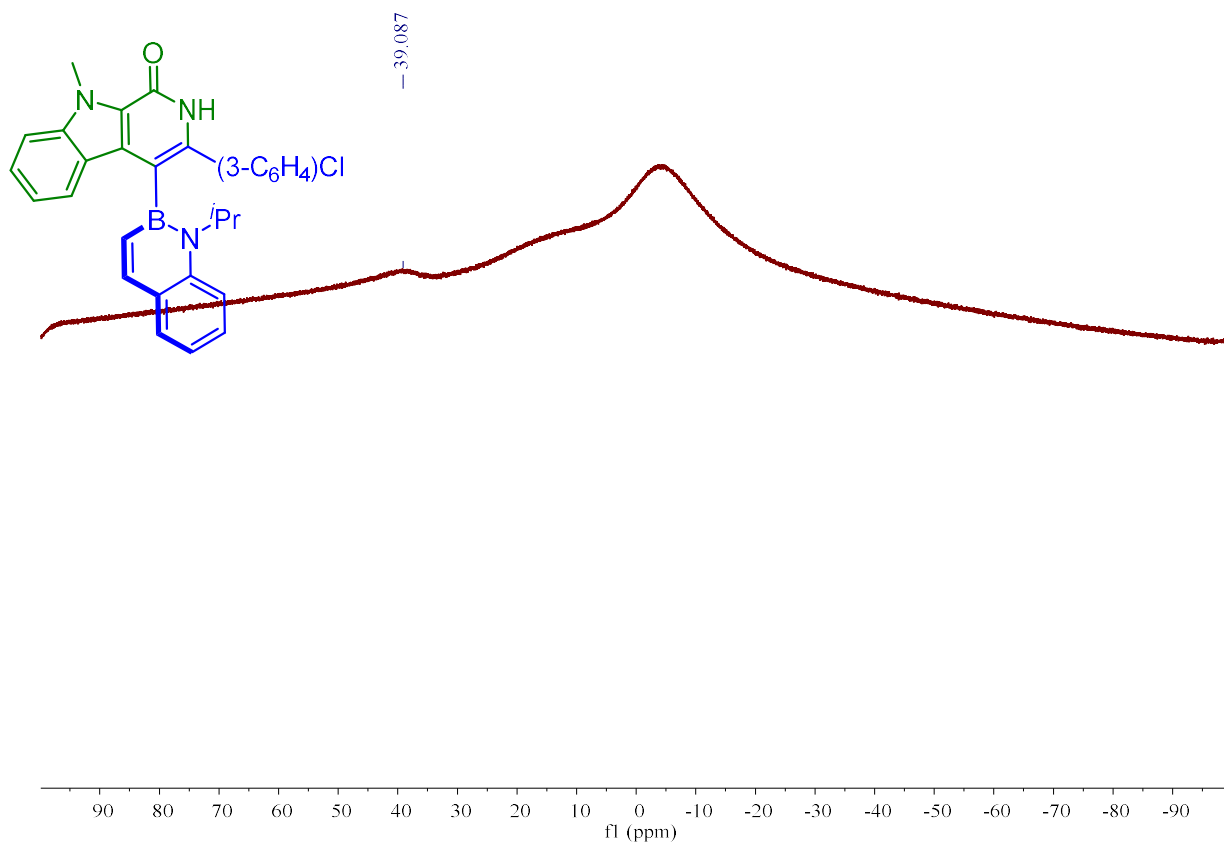
8.066	8.049	7.800	7.797	7.787	7.784	7.778	7.764	7.649	7.646	7.643	7.484	7.478	7.475	7.470	7.467	7.458	7.455	7.449	7.439	7.435	7.412	7.410	7.400	7.398	7.396	7.387	7.385	7.376	7.374	7.288	7.276	7.262	7.187	7.176	7.127	7.122	7.052	7.050	7.048	7.034	6.899	6.888	4.812	4.355	4.292	1.279	1.104	1.029
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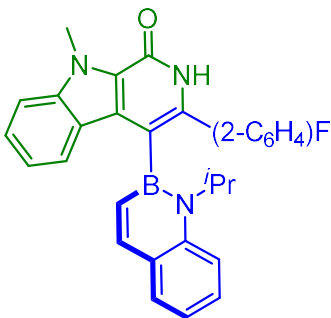
S154



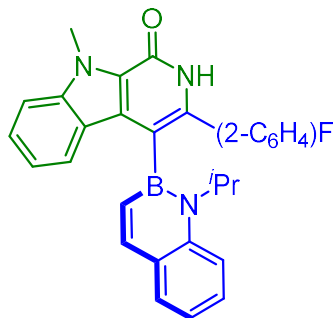
¹³C NMR (150 MHz, CDCl₃) spectrum of 55.



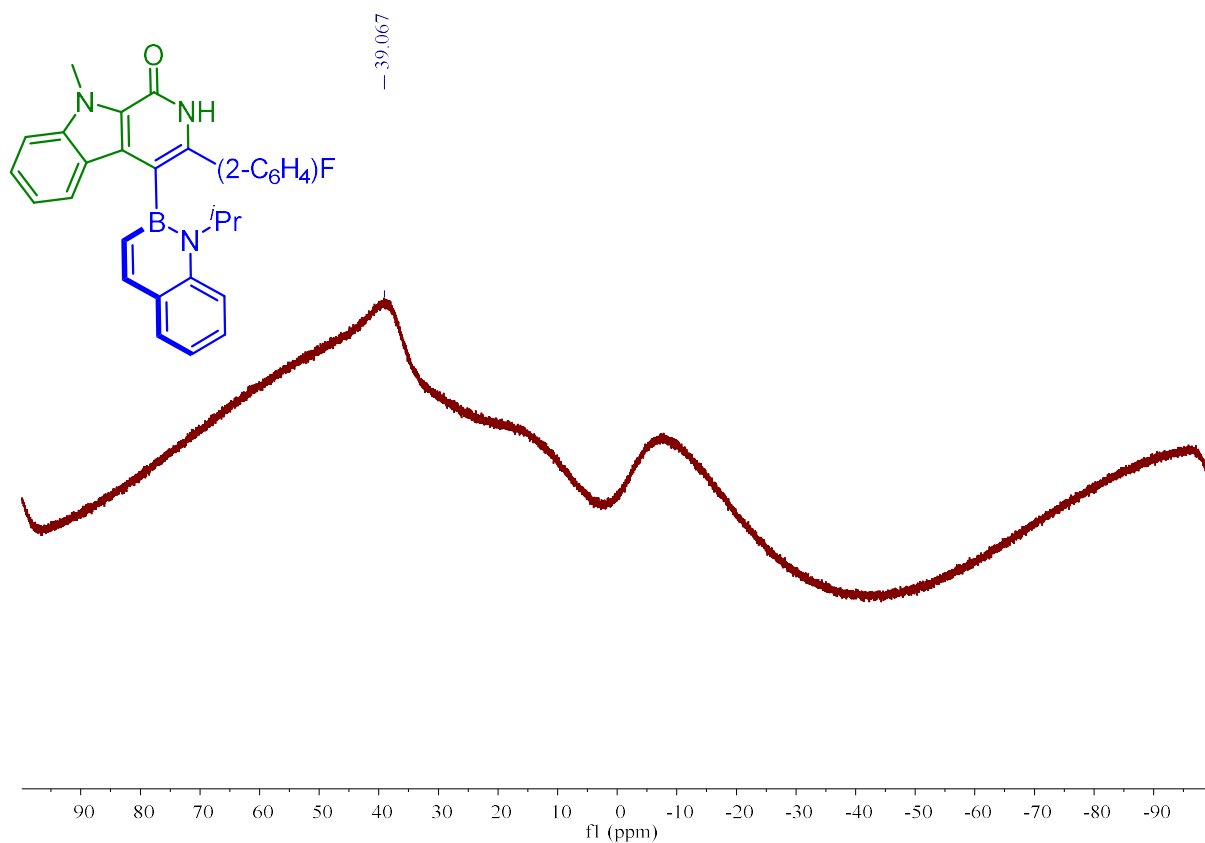
¹¹B NMR (193 MHz, CDCl₃) spectrum of 55.



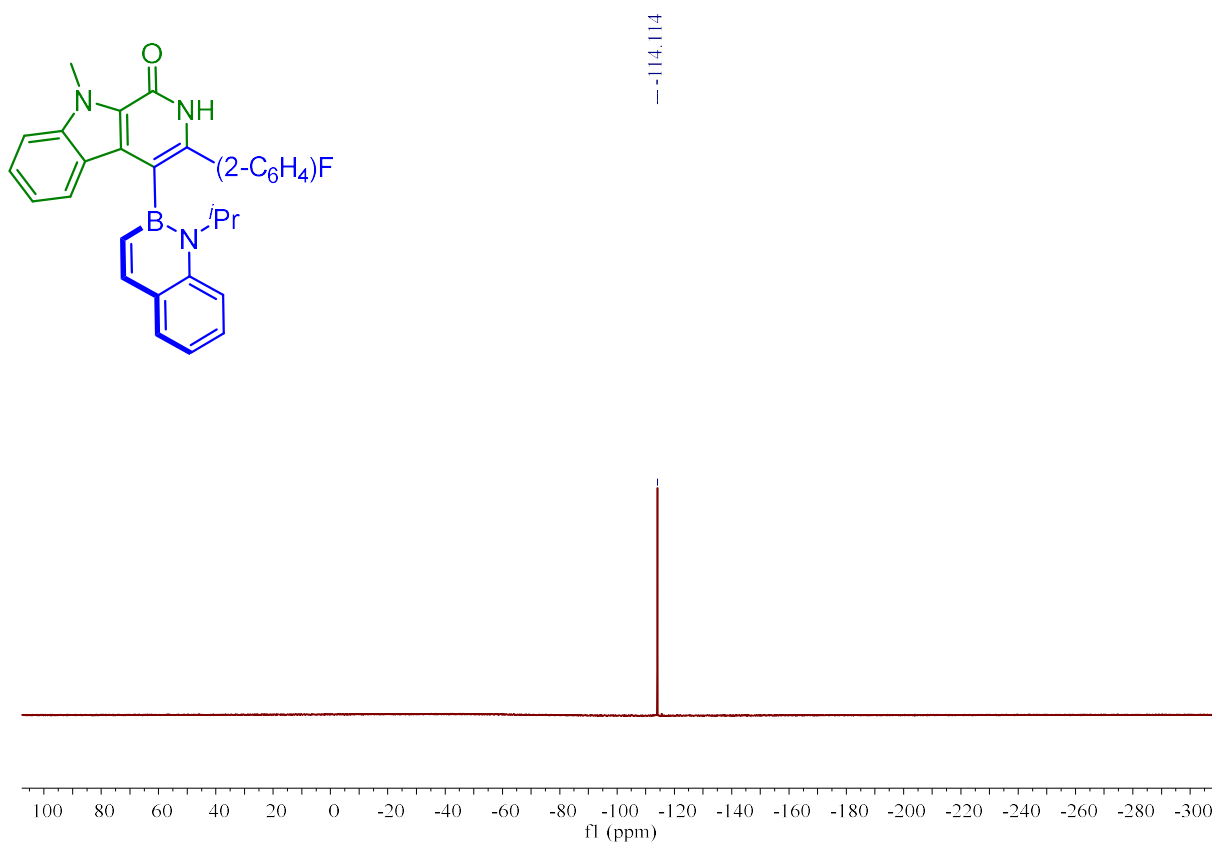
161.040	132.661	132.699	131.233	130.584	130.531	130.441	128.740	127.351	126.438	124.704	124.607	124.211	124.189	123.263	123.085	120.765	119.798	119.032	116.044	115.899	109.889	52.450	31.487	21.603	21.51
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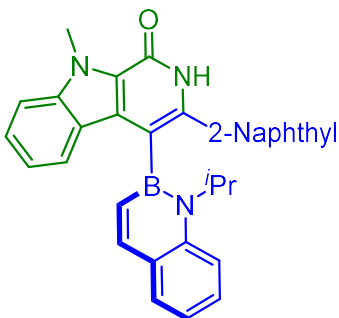
S156



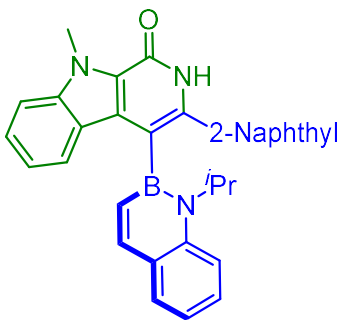
^{11}B NMR (193 MHz, CDCl_3) spectrum of 56.



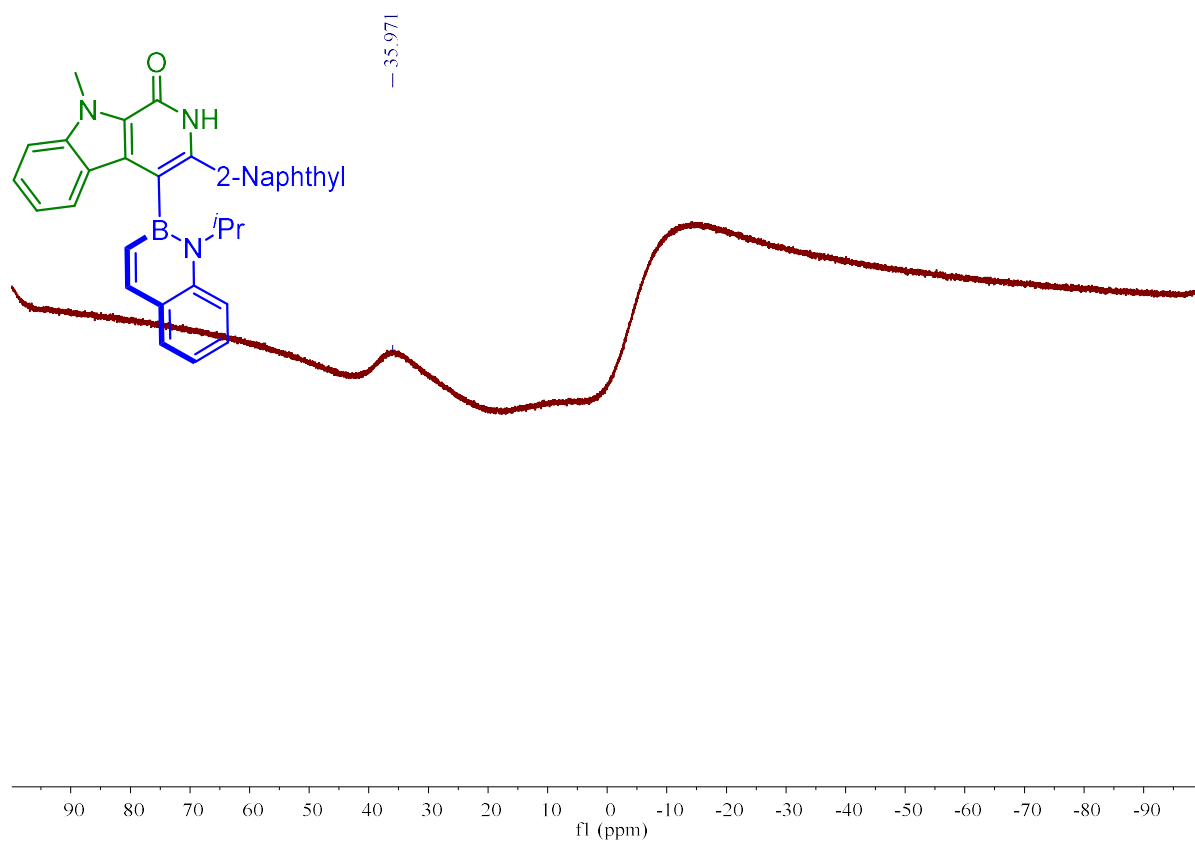
^{19}F NMR (376 MHz, CDCl_3) spectrum of 56.



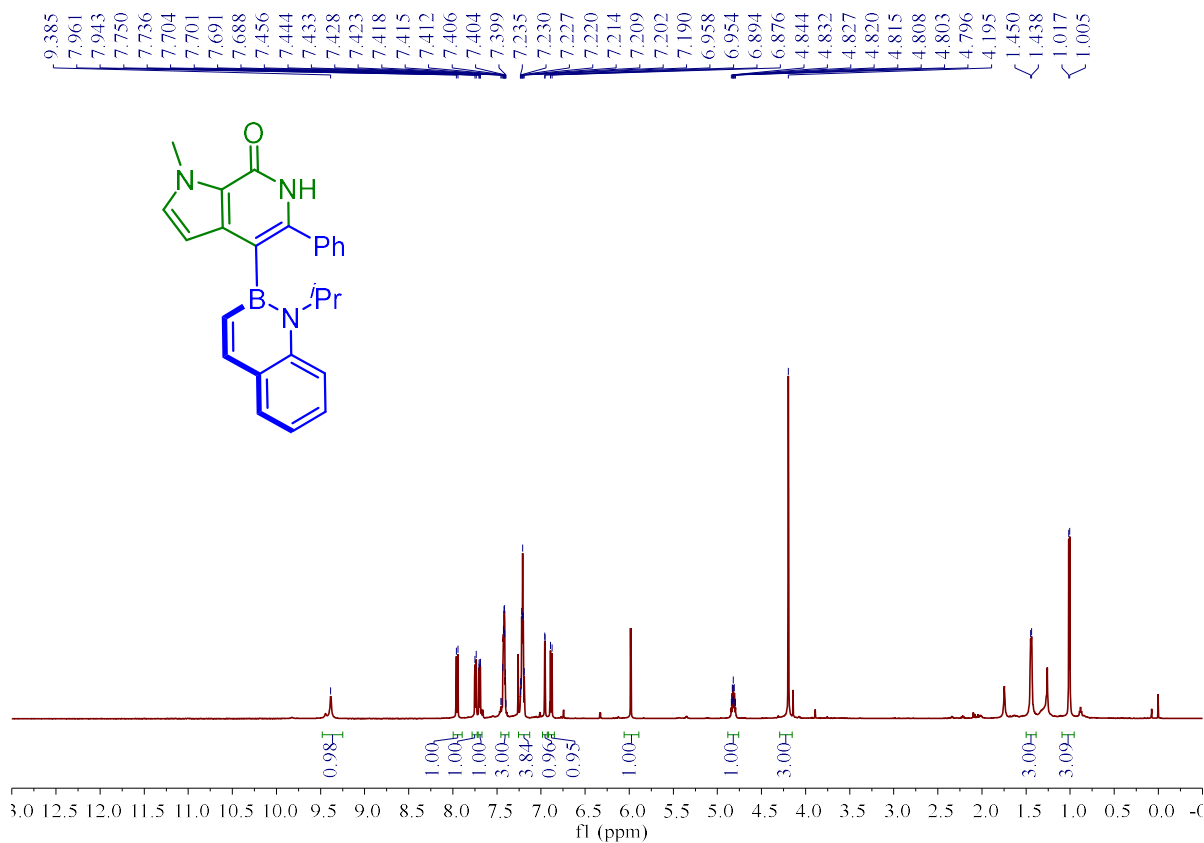
Chemical structure of the compound is shown, featuring a 2-Naphthyl group attached to a boron atom, which is also bonded to a nitrogen atom (N-Pr) and a carbonyl group (C=O). The structure is labeled with "2-Naphthyl" and "N-Pr".



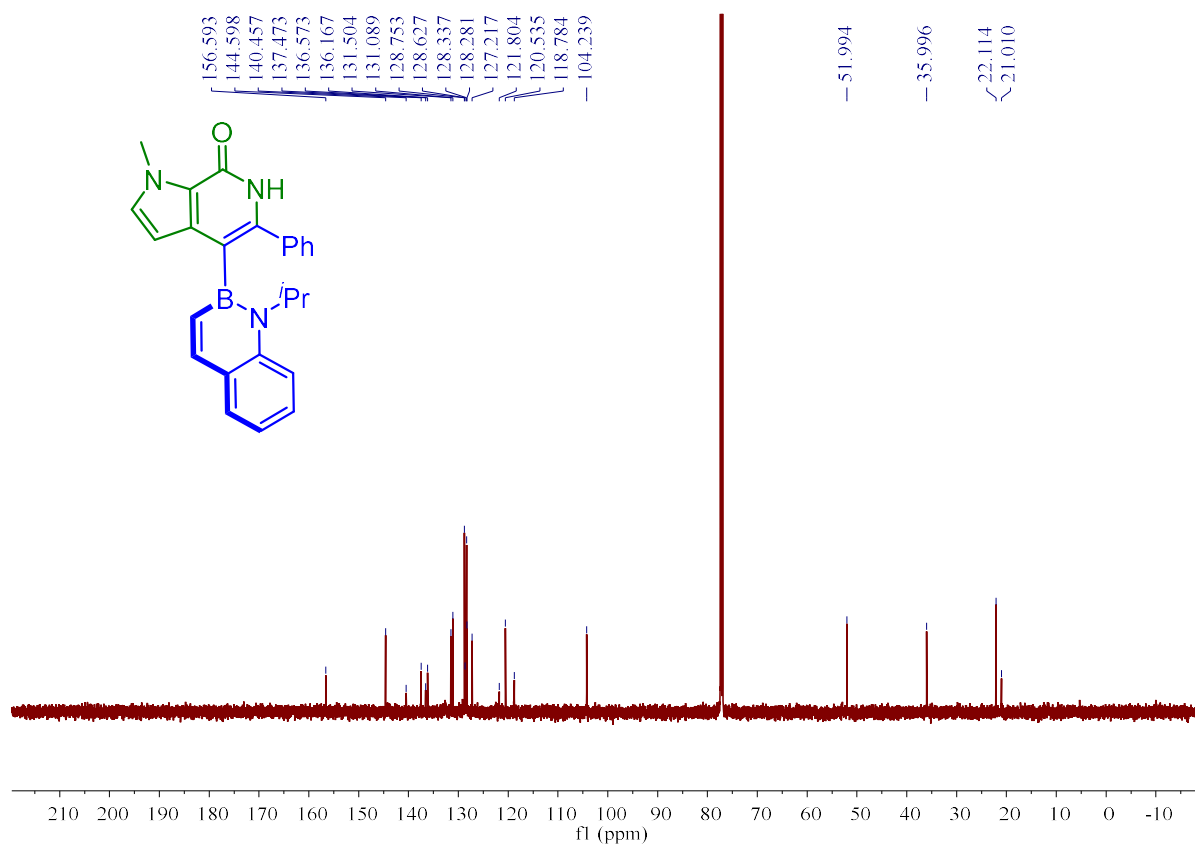
S158



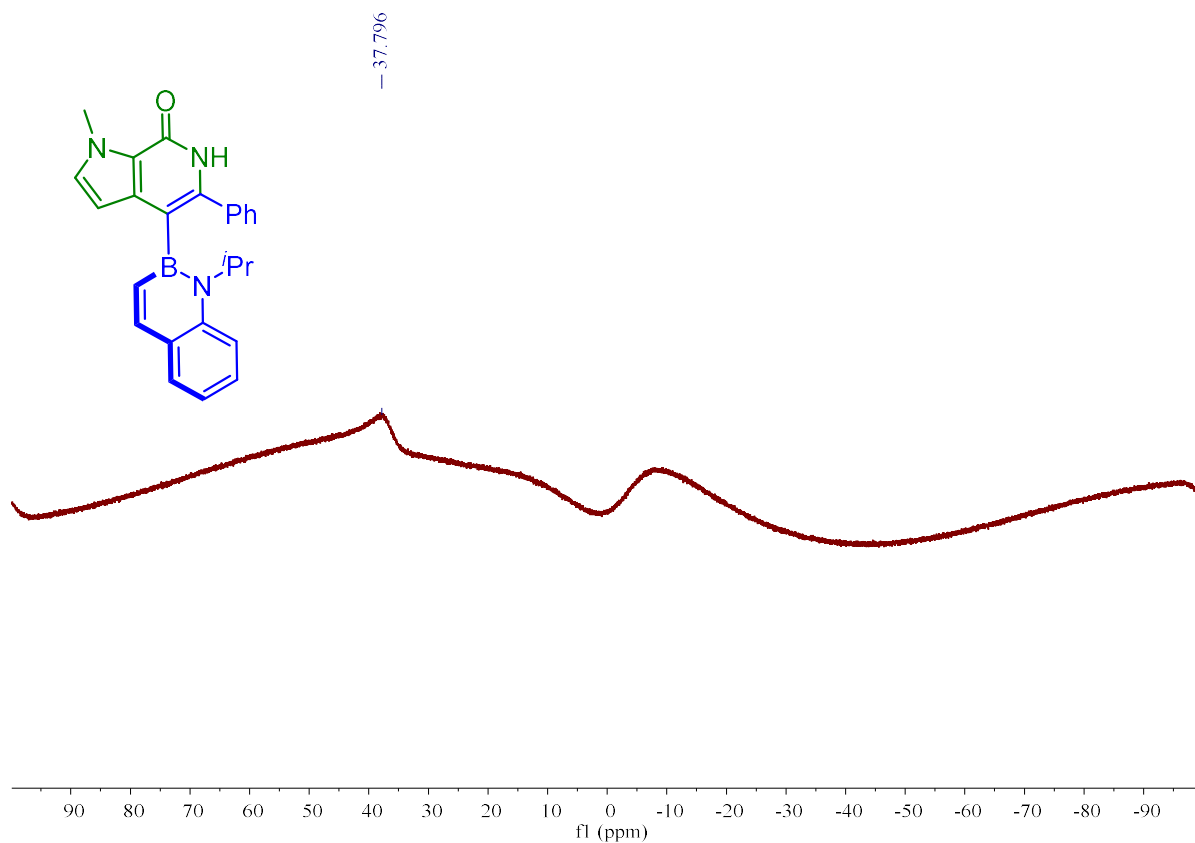
^{11}B NMR (193 MHz, CDCl_3) spectrum of 57.



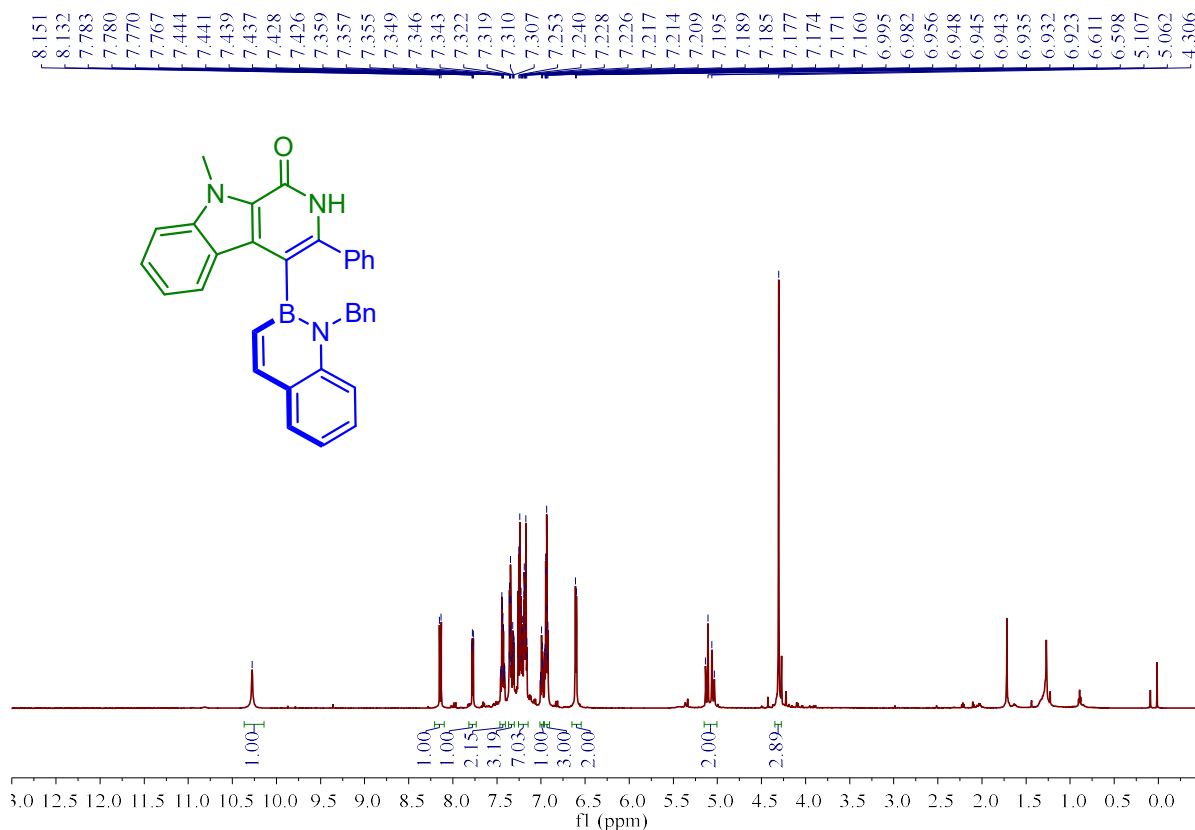
^1H NMR (600 MHz, CDCl_3) spectrum of 58.



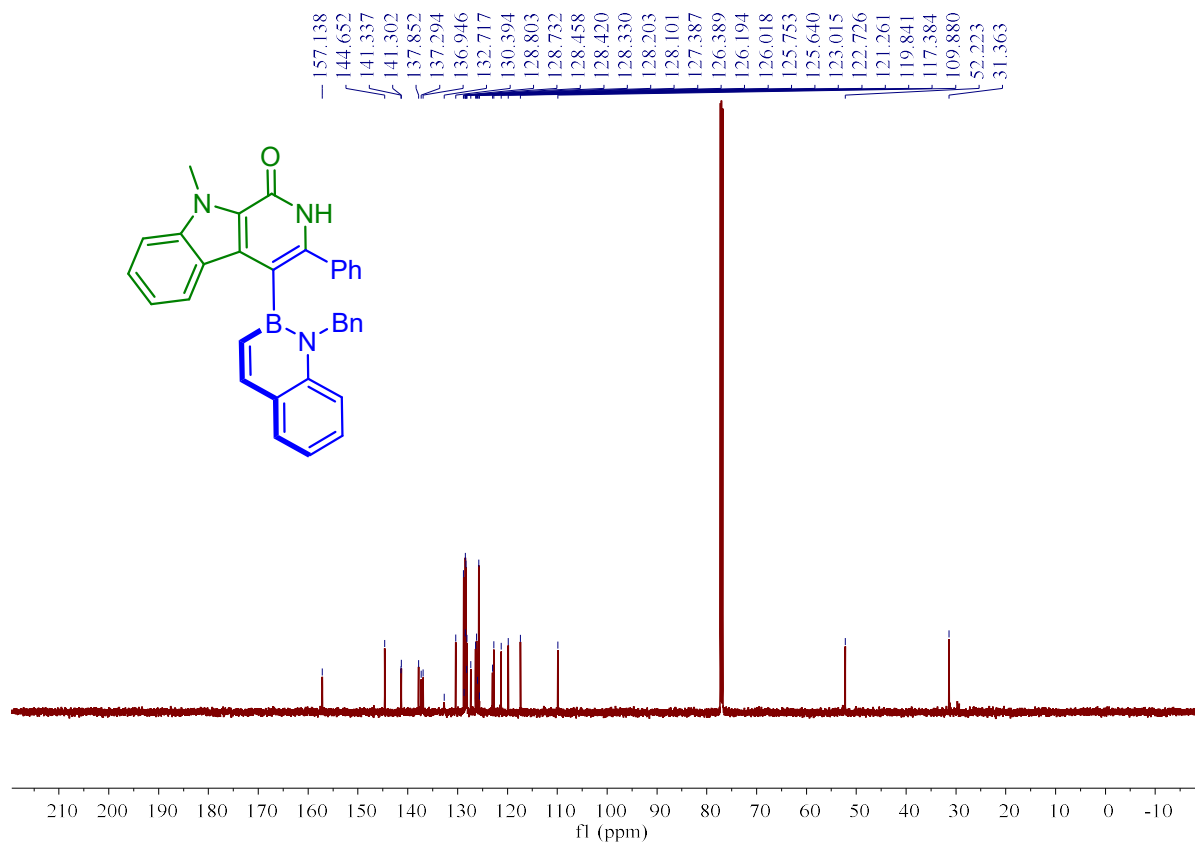
^{13}C NMR (150 MHz, CDCl_3) spectrum of 58.



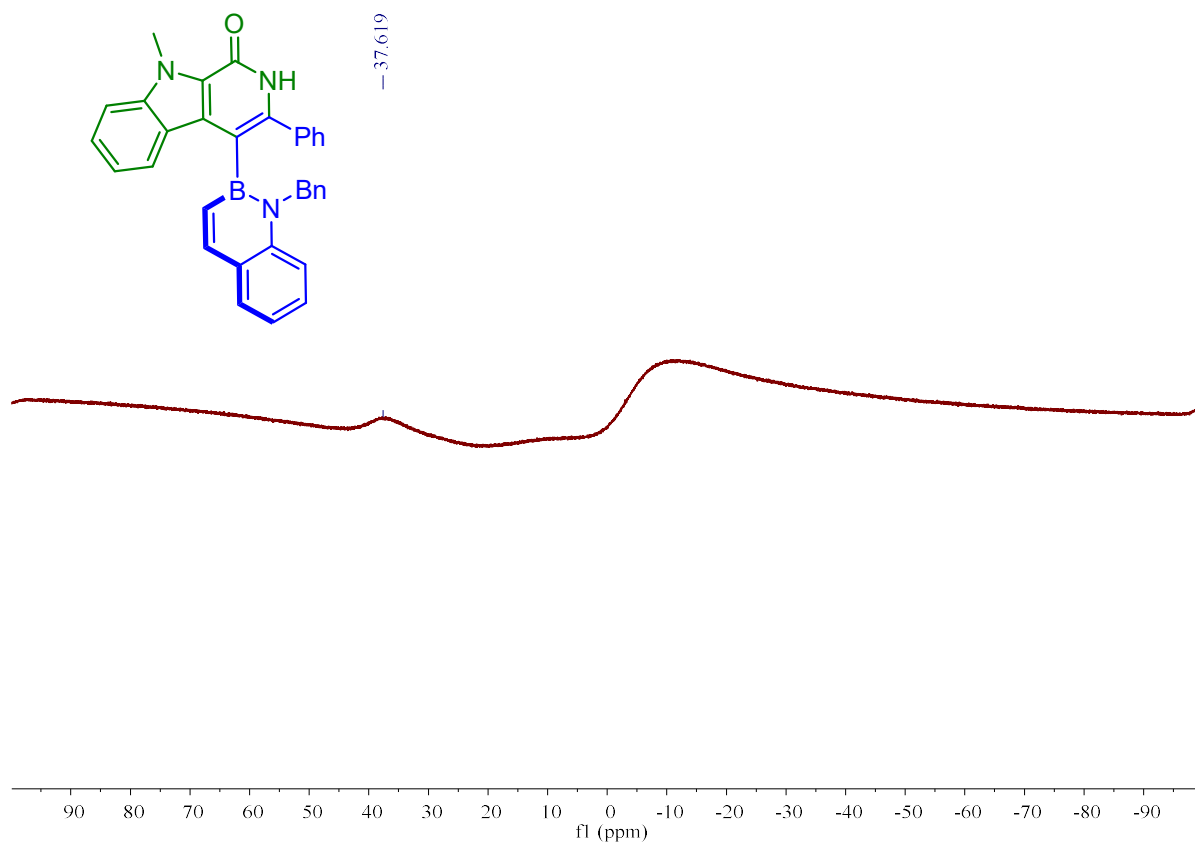
^{11}B NMR (193 MHz, CDCl_3) spectrum of 58.



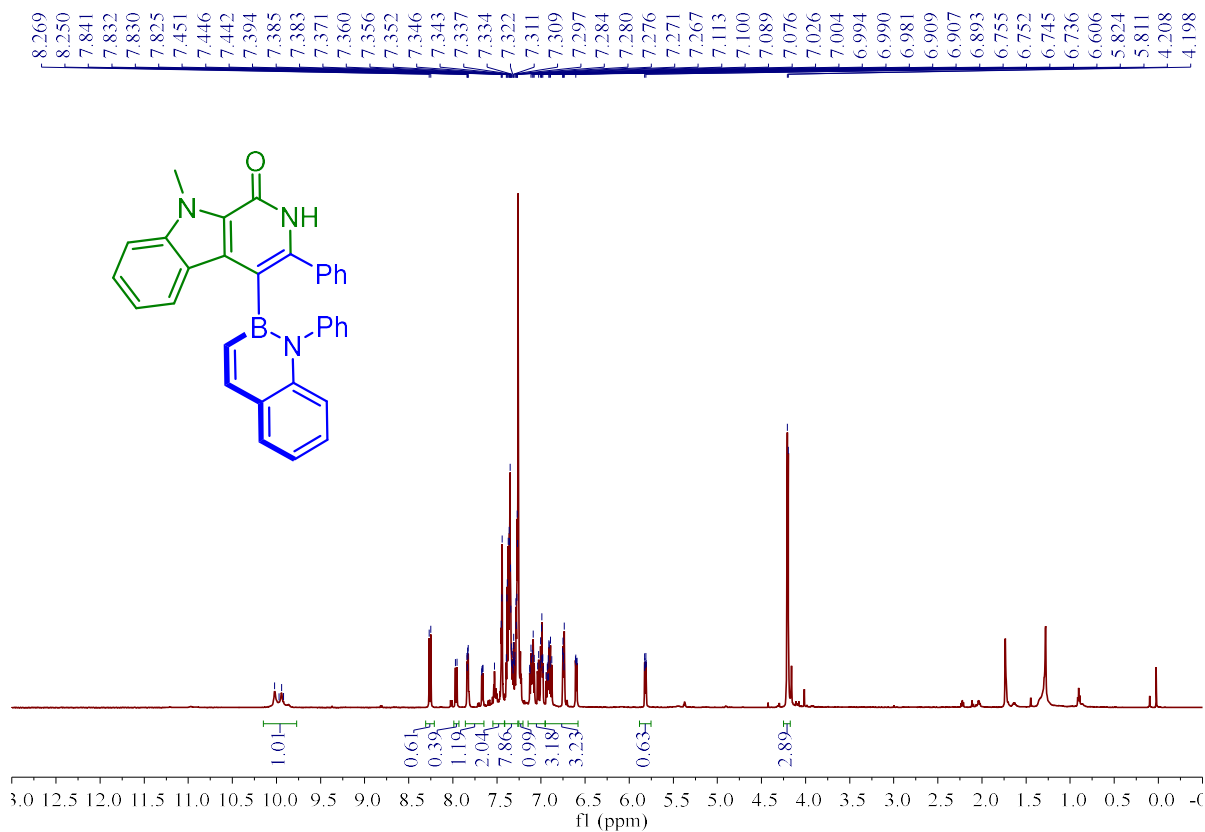
¹H NMR (600 MHz, CDCl₃) spectrum of 59.



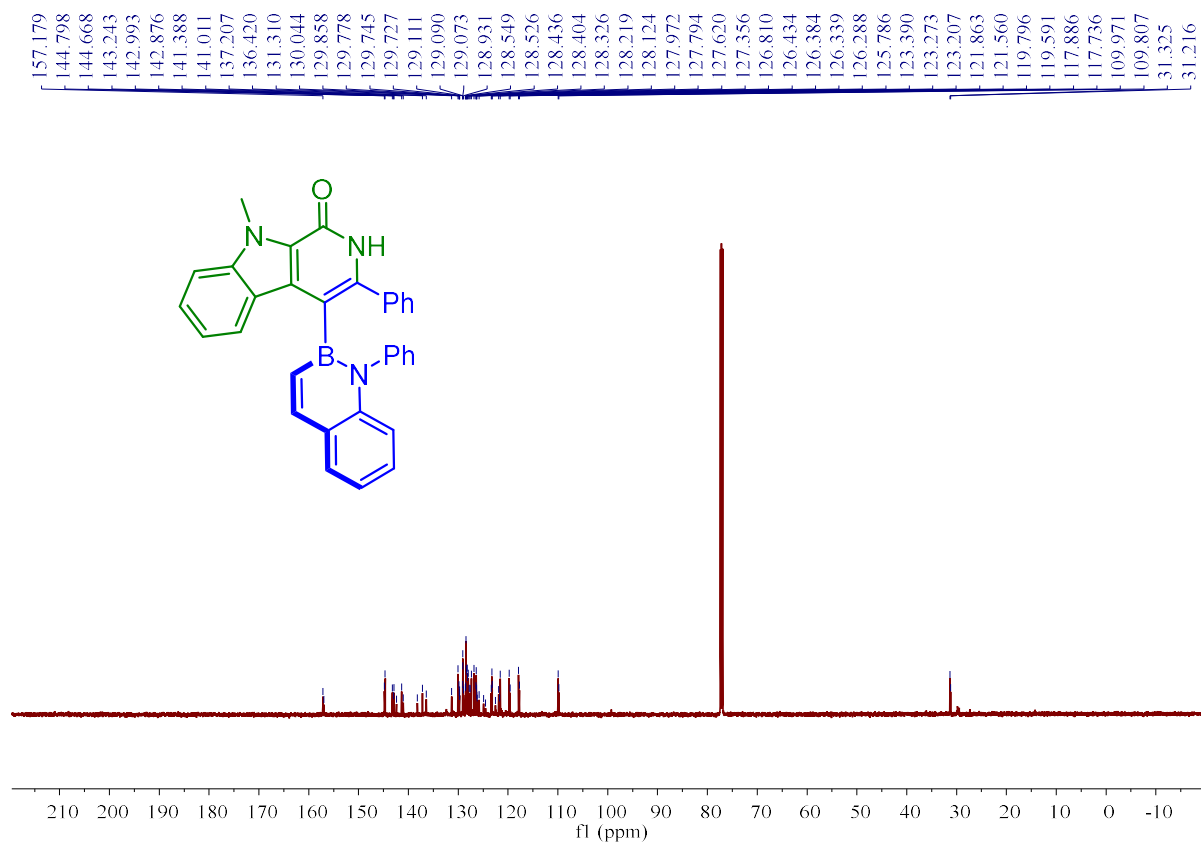
¹³C NMR (150 MHz, CDCl₃) spectrum of 59.



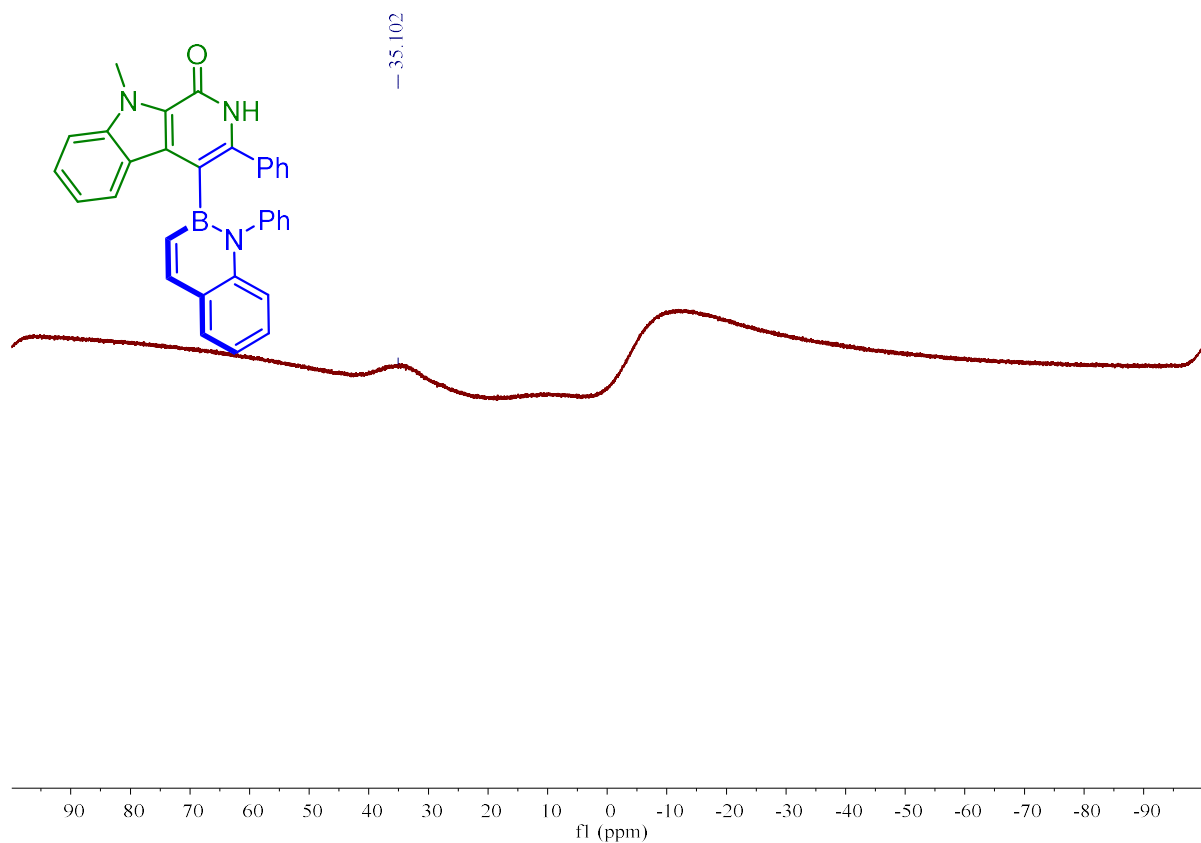
^{11}B NMR (193 MHz, CDCl_3) spectrum of 59.



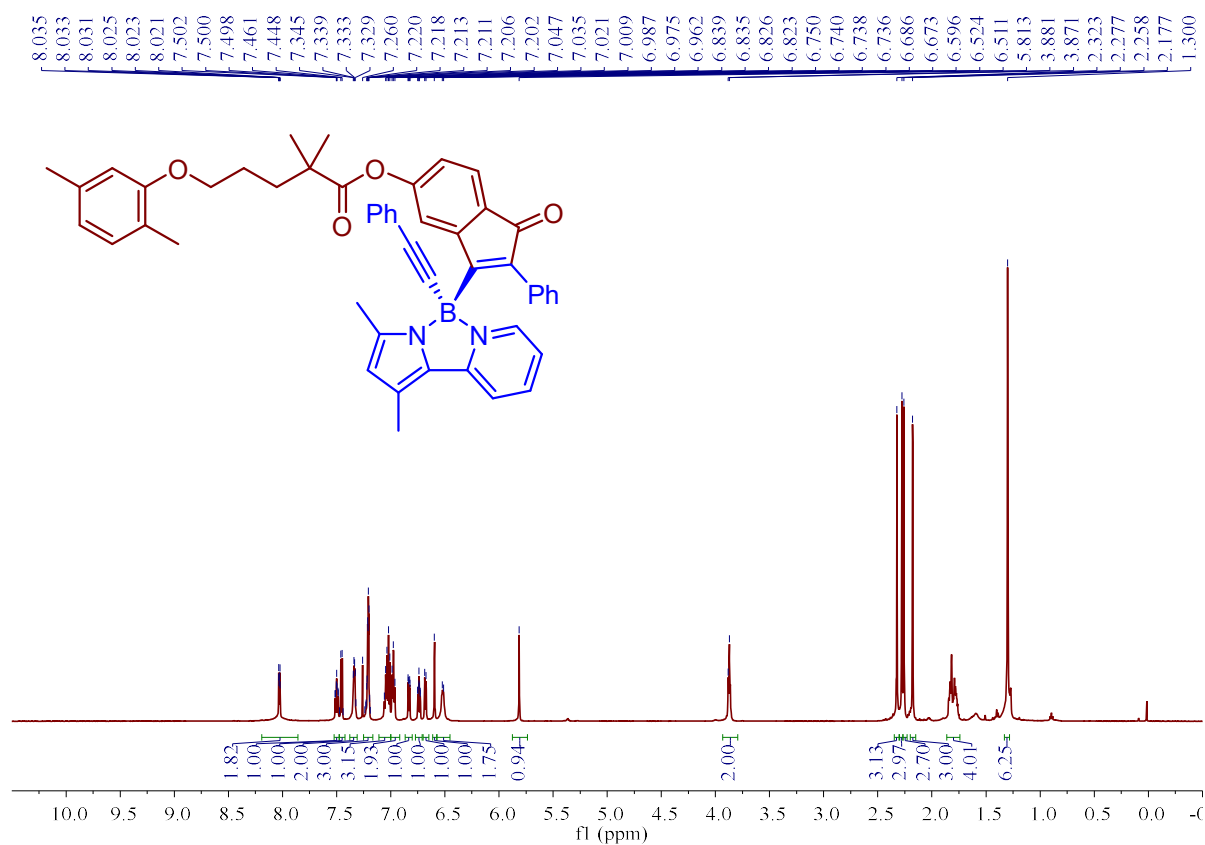
^1H NMR (600 MHz, CDCl_3) spectrum of 60.



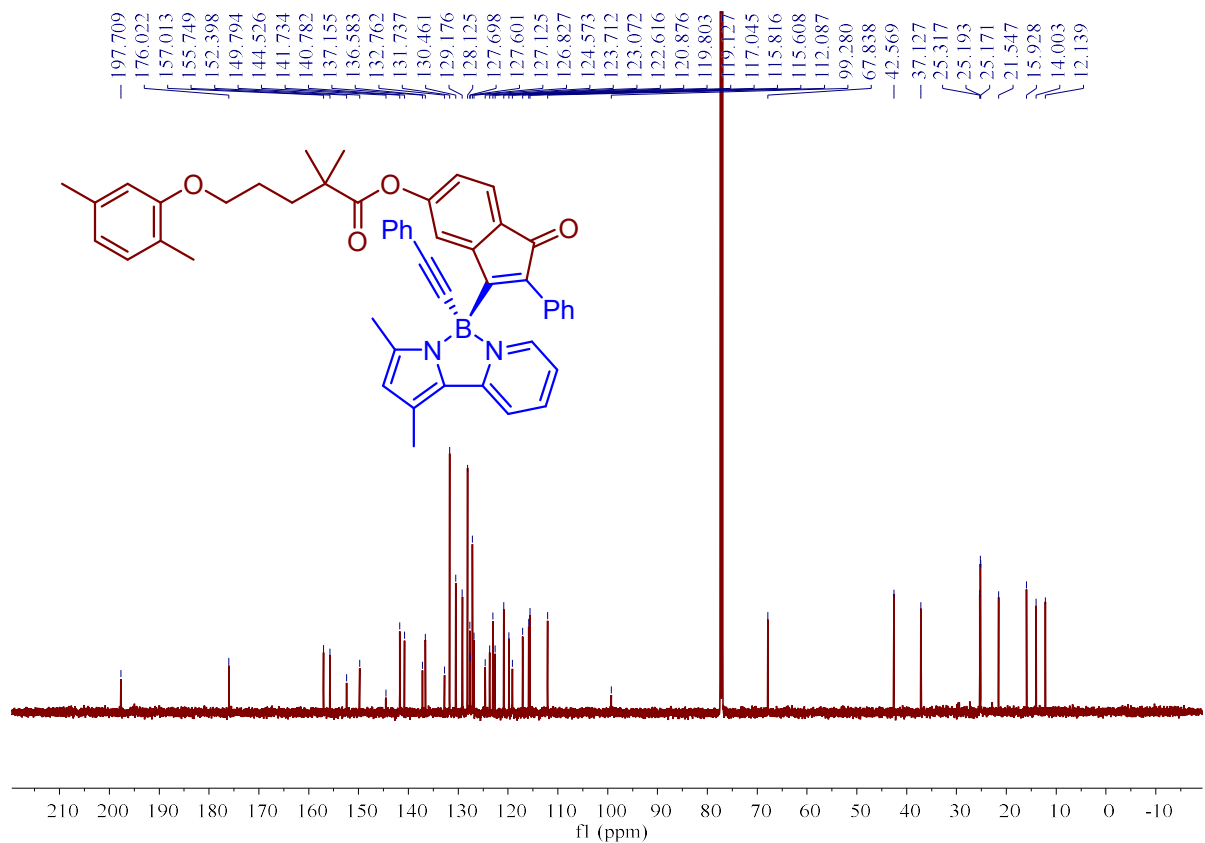
¹³C NMR (150 MHz, CDCl₃) spectrum of 60.



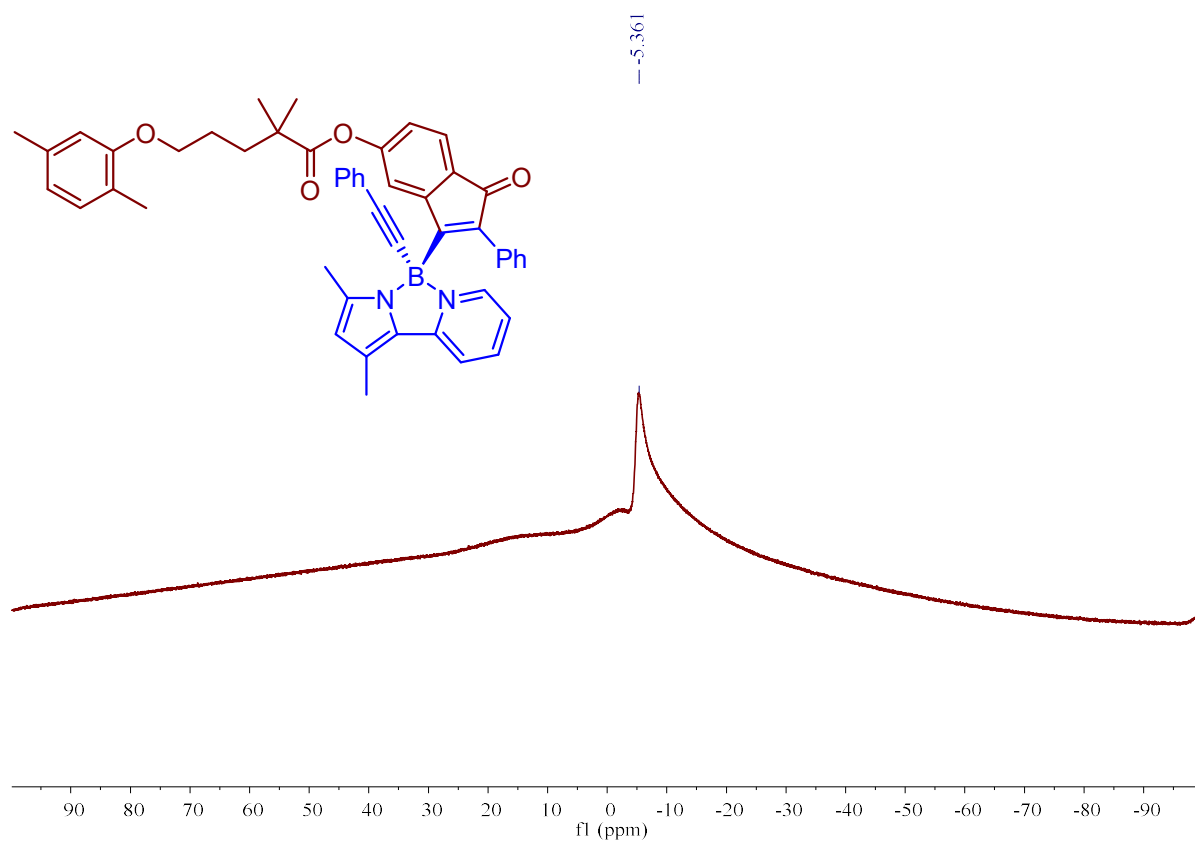
¹¹B NMR (193 MHz, CDCl₃) spectrum of 60.



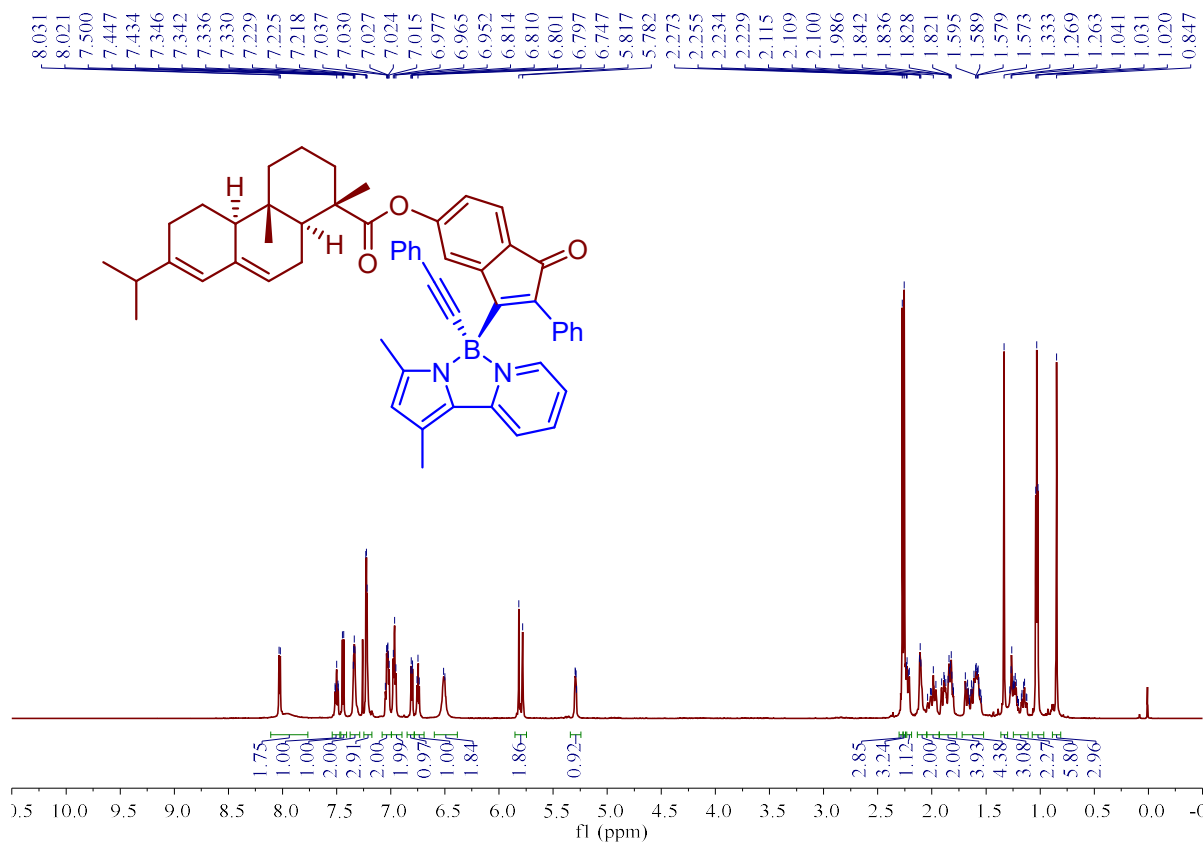
¹H NMR (600 MHz, CDCl₃) spectrum of 61.



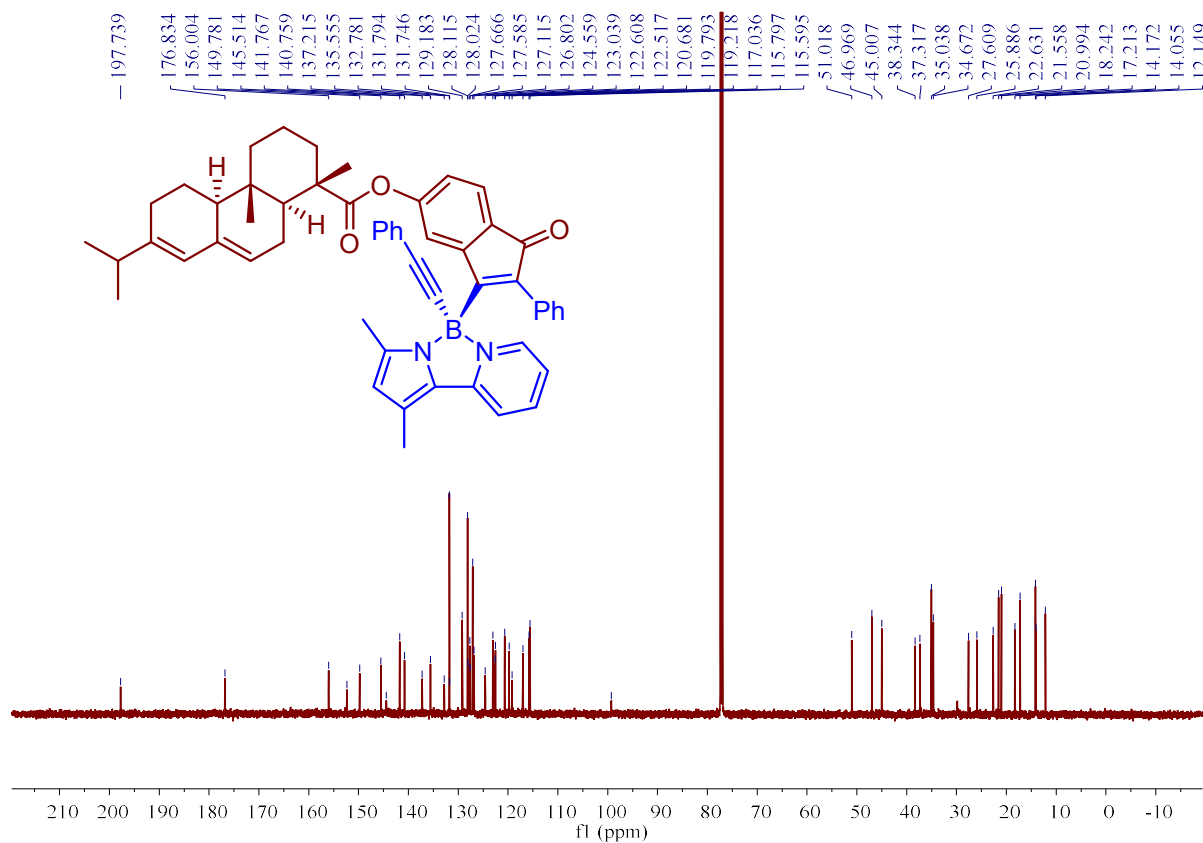
¹³C NMR (150 MHz, CDCl₃) spectrum of 61.



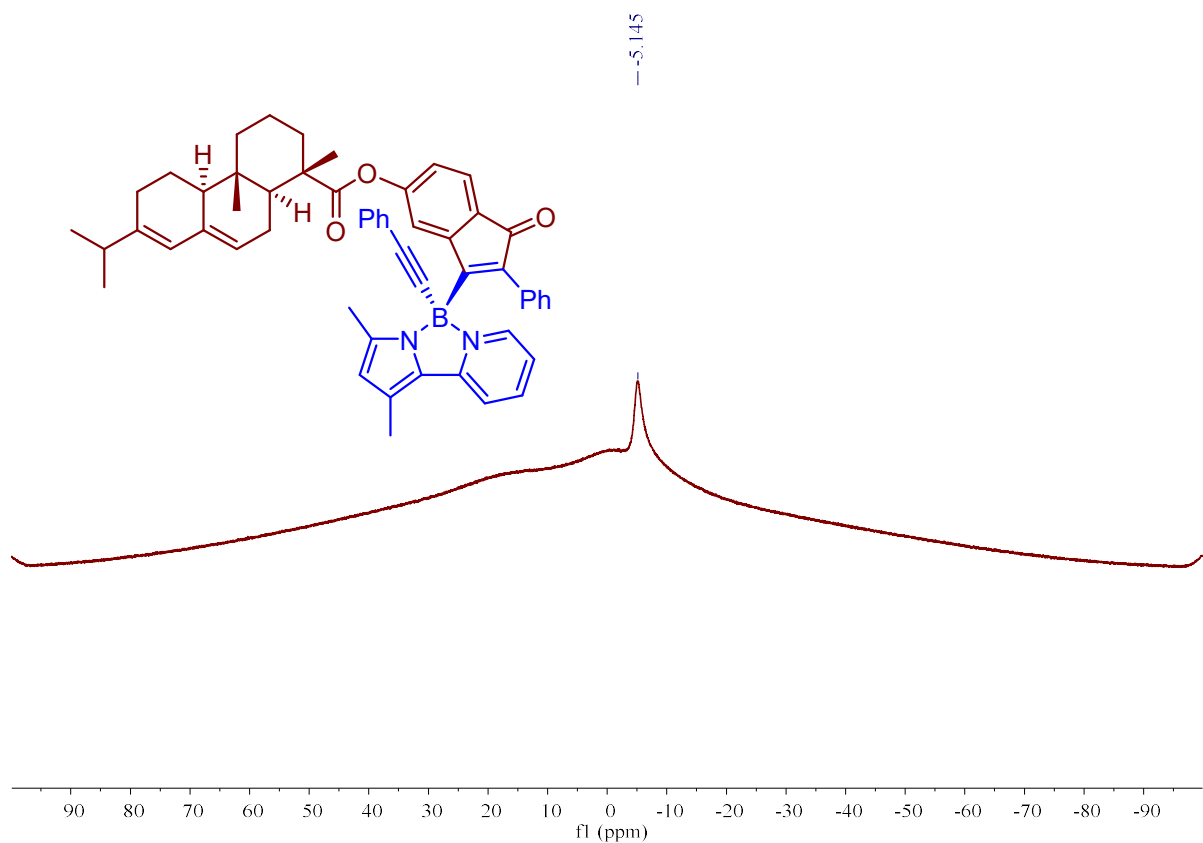
^{11}B NMR (193 MHz, CDCl_3) spectrum of 61.



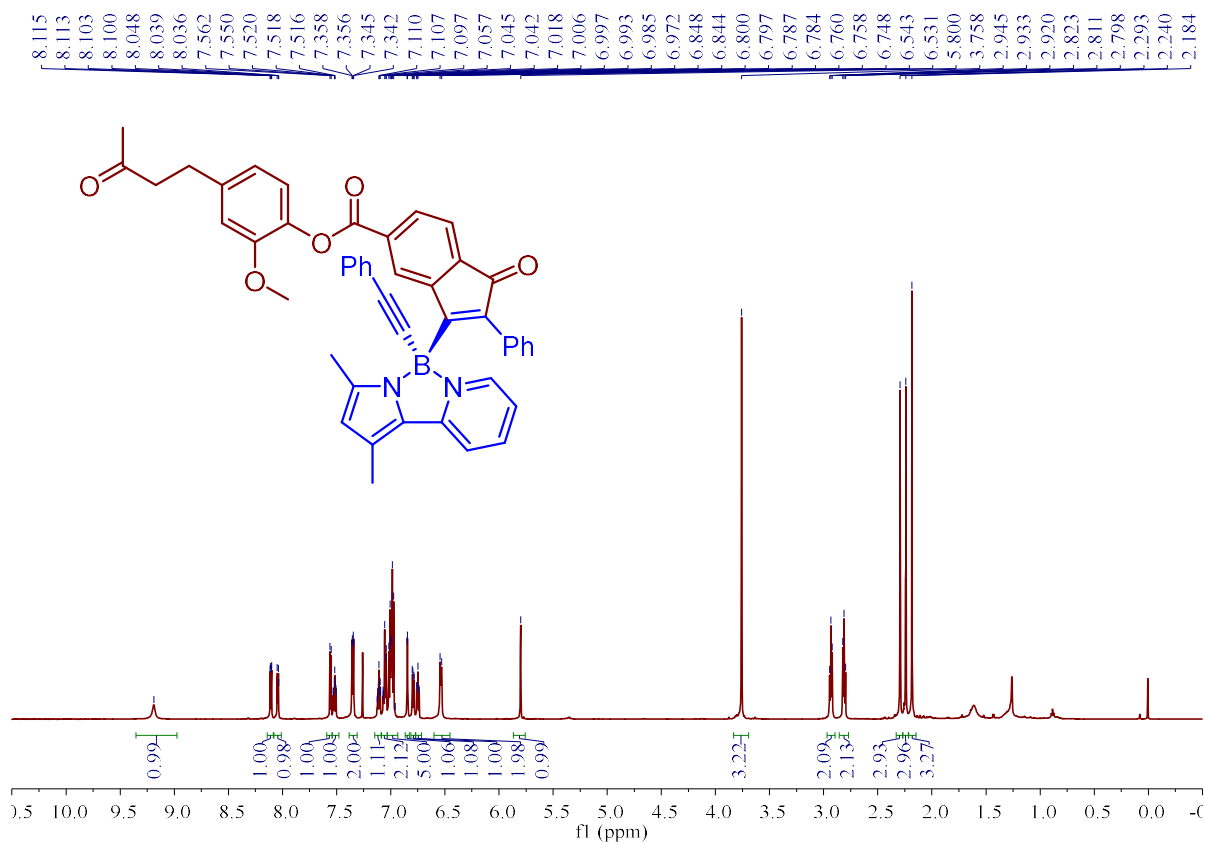
^1H NMR (600 MHz, CDCl_3) spectrum of 62.



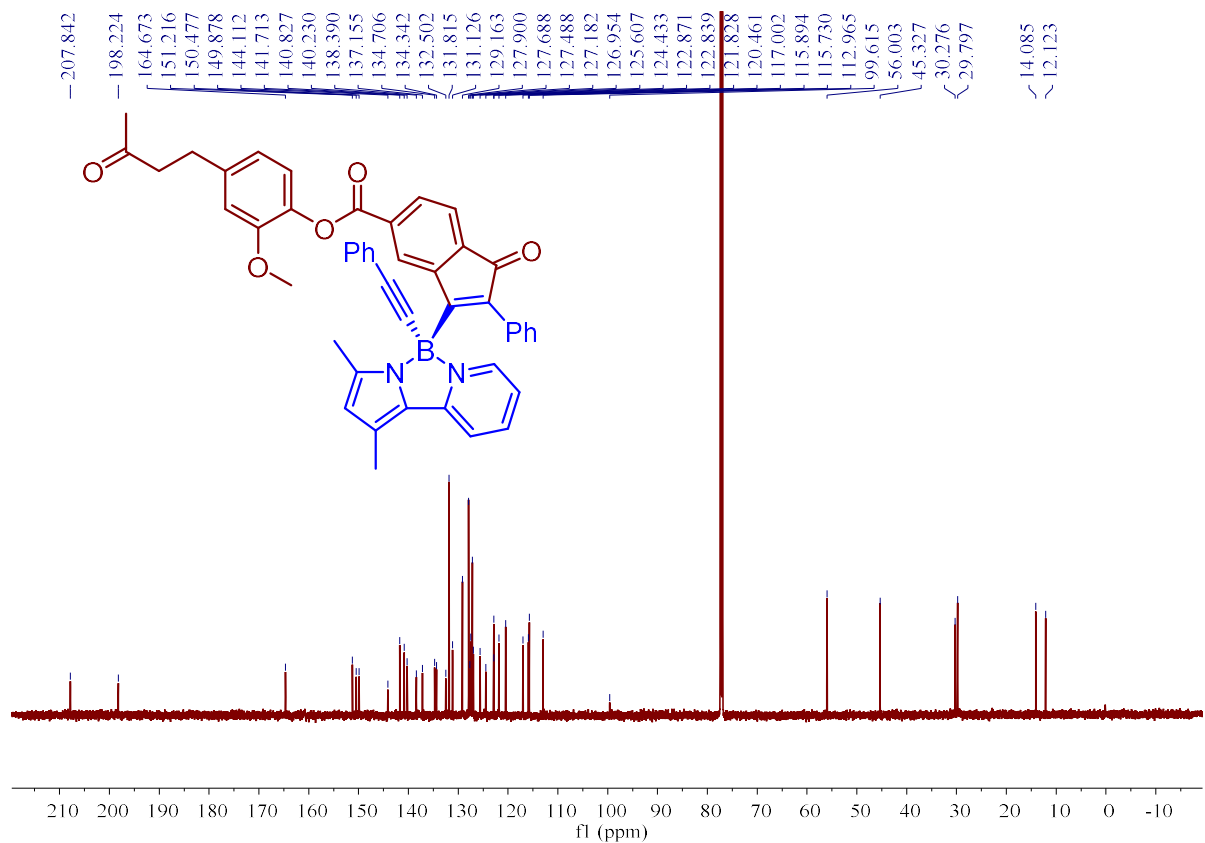
^{13}C NMR (150 MHz, CDCl_3) spectrum of 62.



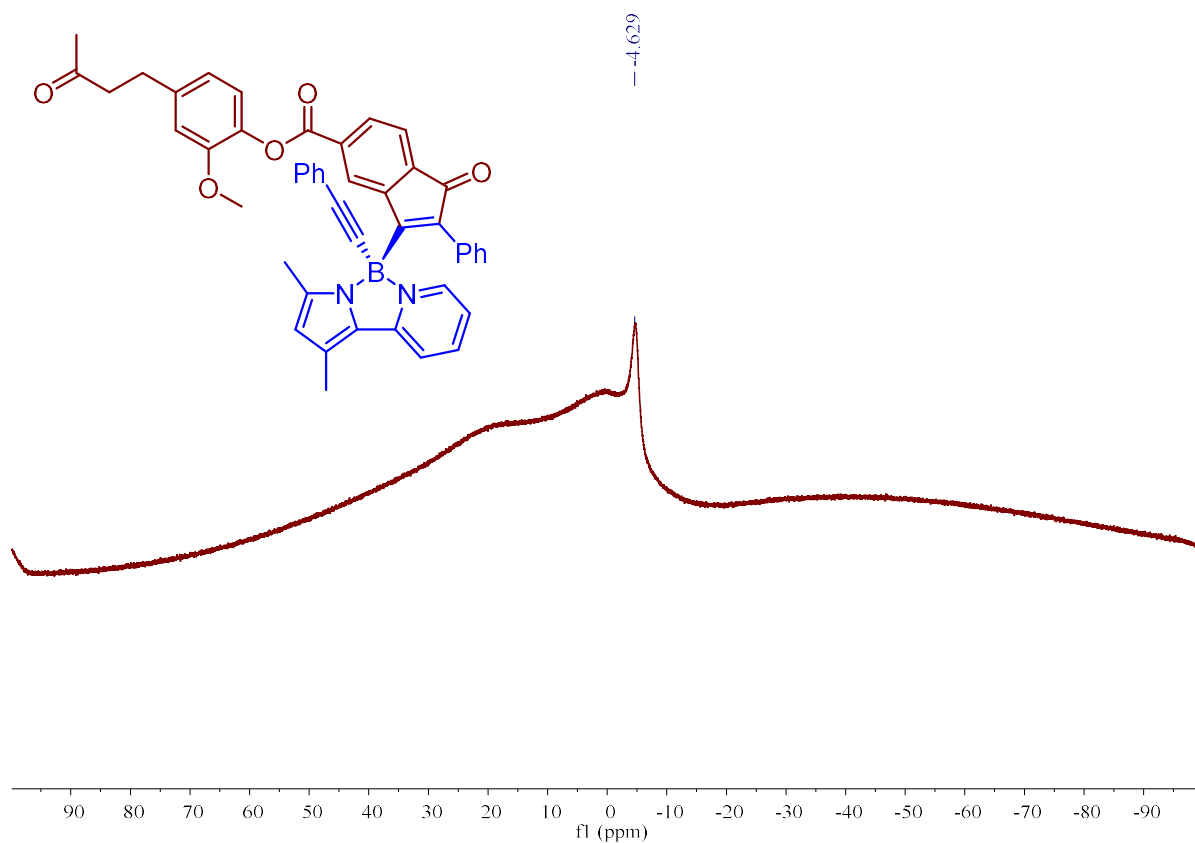
^{11}B NMR (193 MHz, CDCl_3) spectrum of 62.



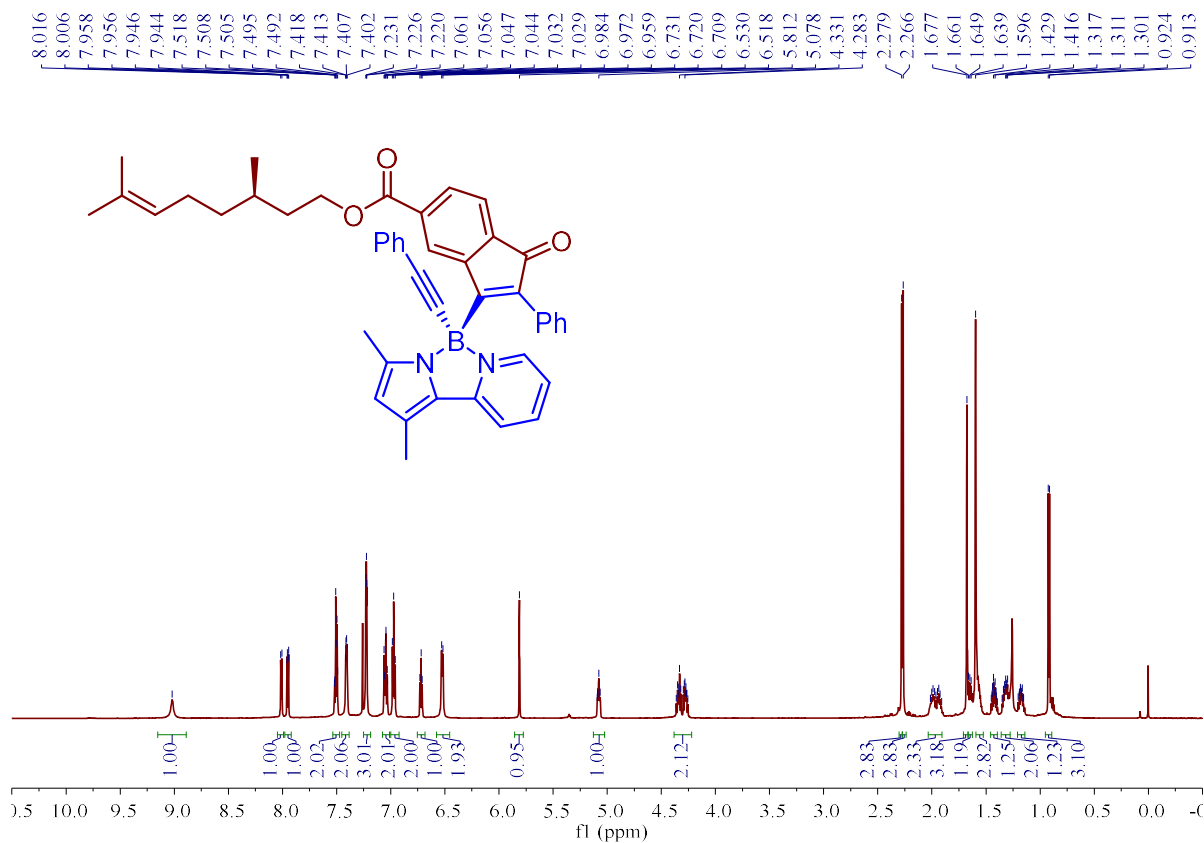
¹H NMR (600 MHz, CDCl₃) spectrum of 63.



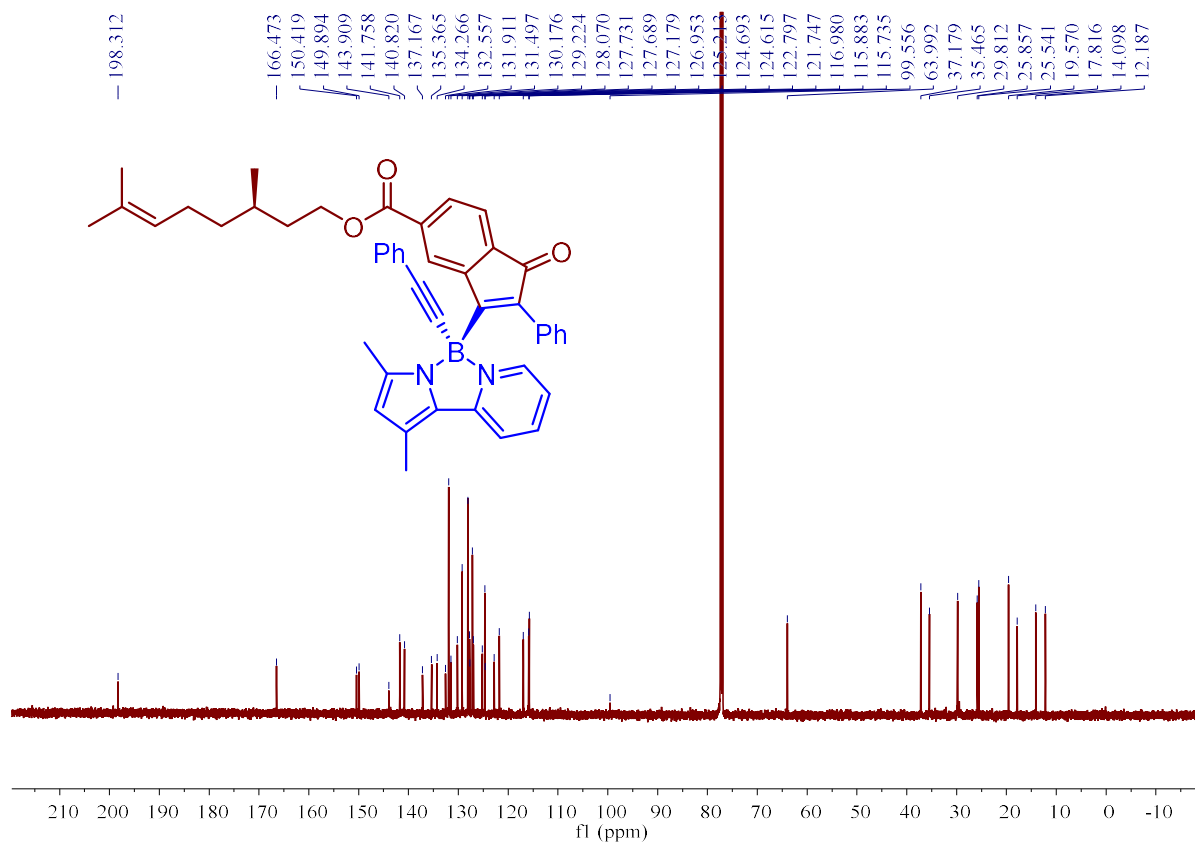
¹³C NMR (150 MHz, CDCl₃) spectrum of 63.



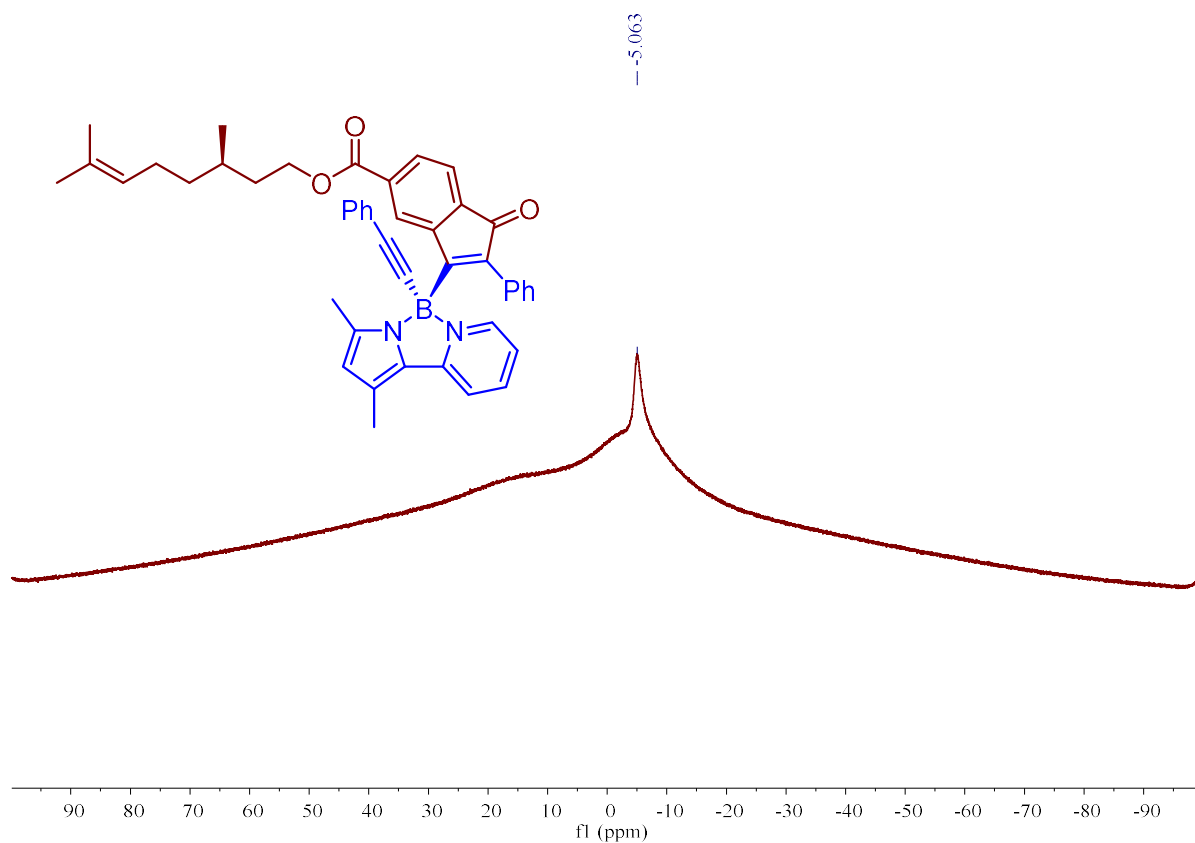
^{11}B NMR (193 MHz, CDCl_3) spectrum of 63.



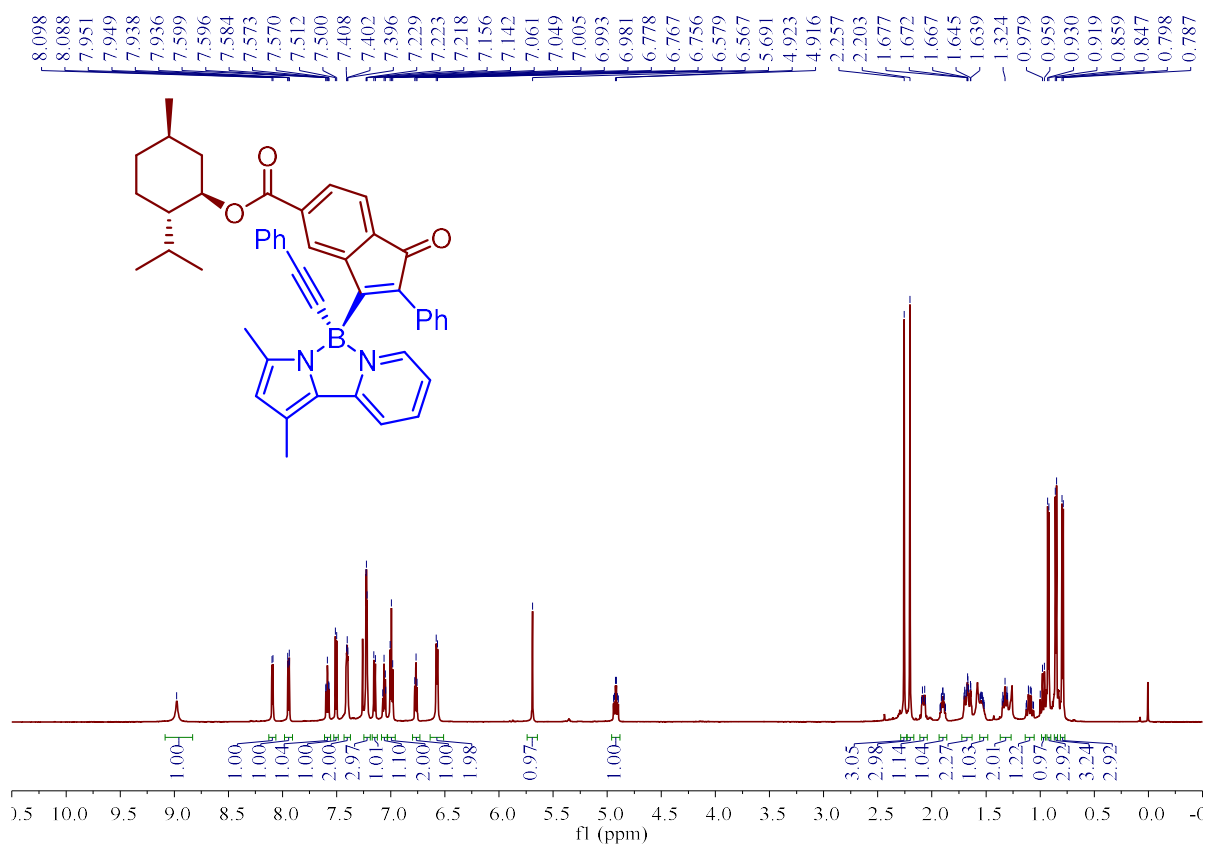
^1H NMR (600 MHz, CDCl_3) spectrum of 64.



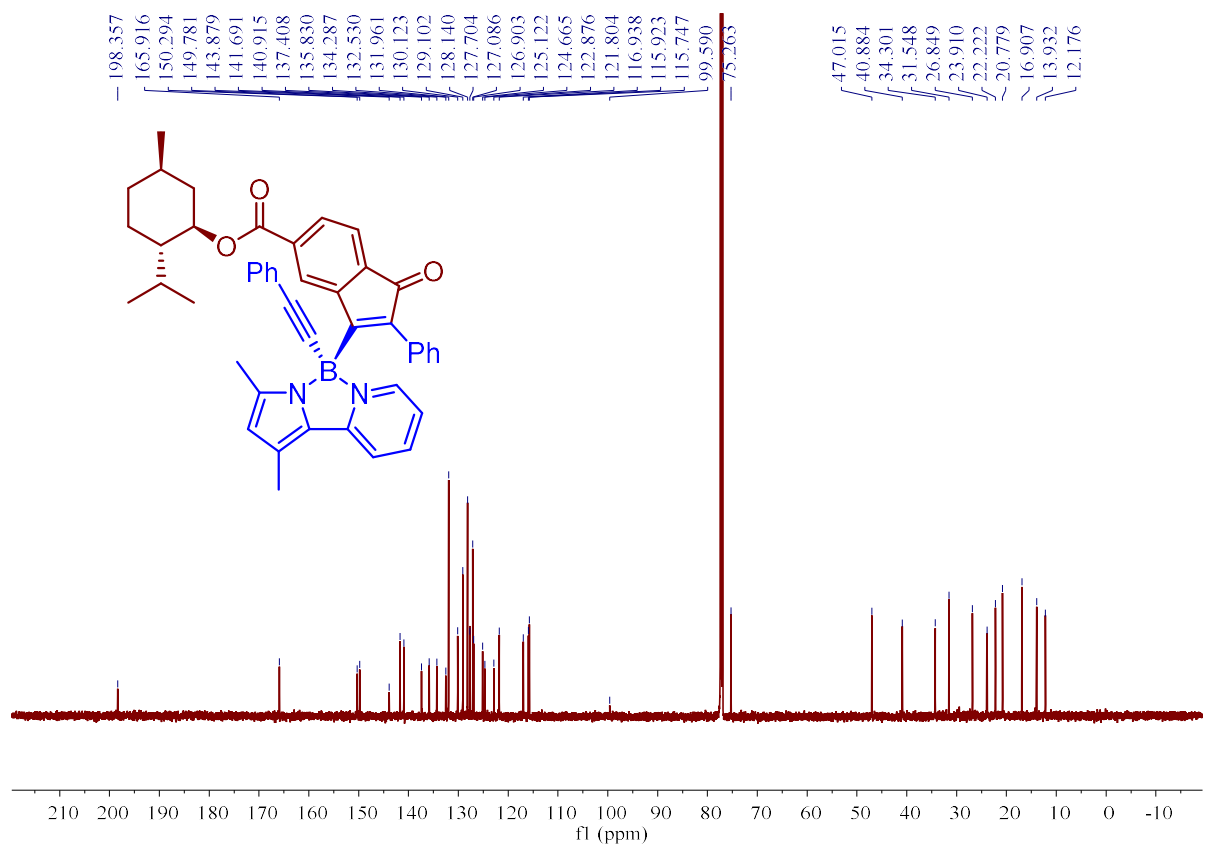
^{13}C NMR (150 MHz, CDCl_3) spectrum of 64.



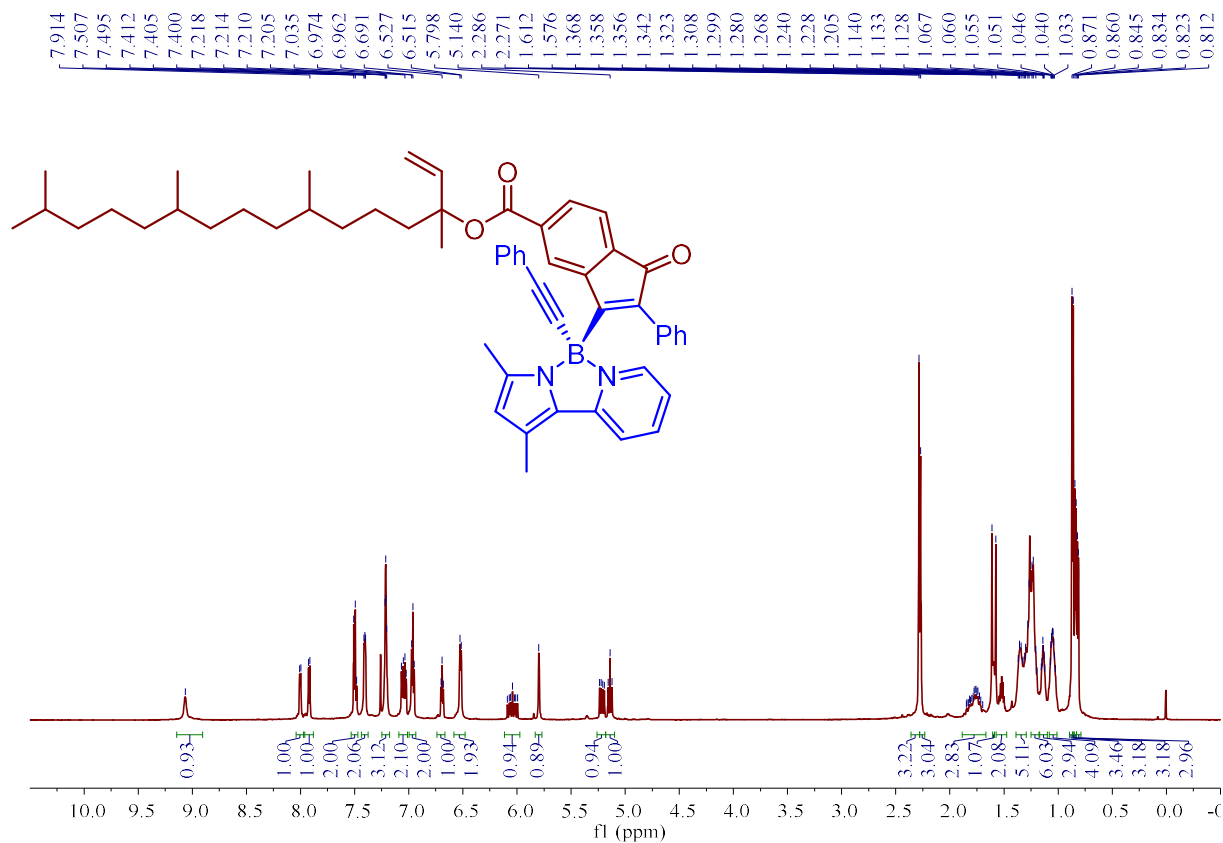
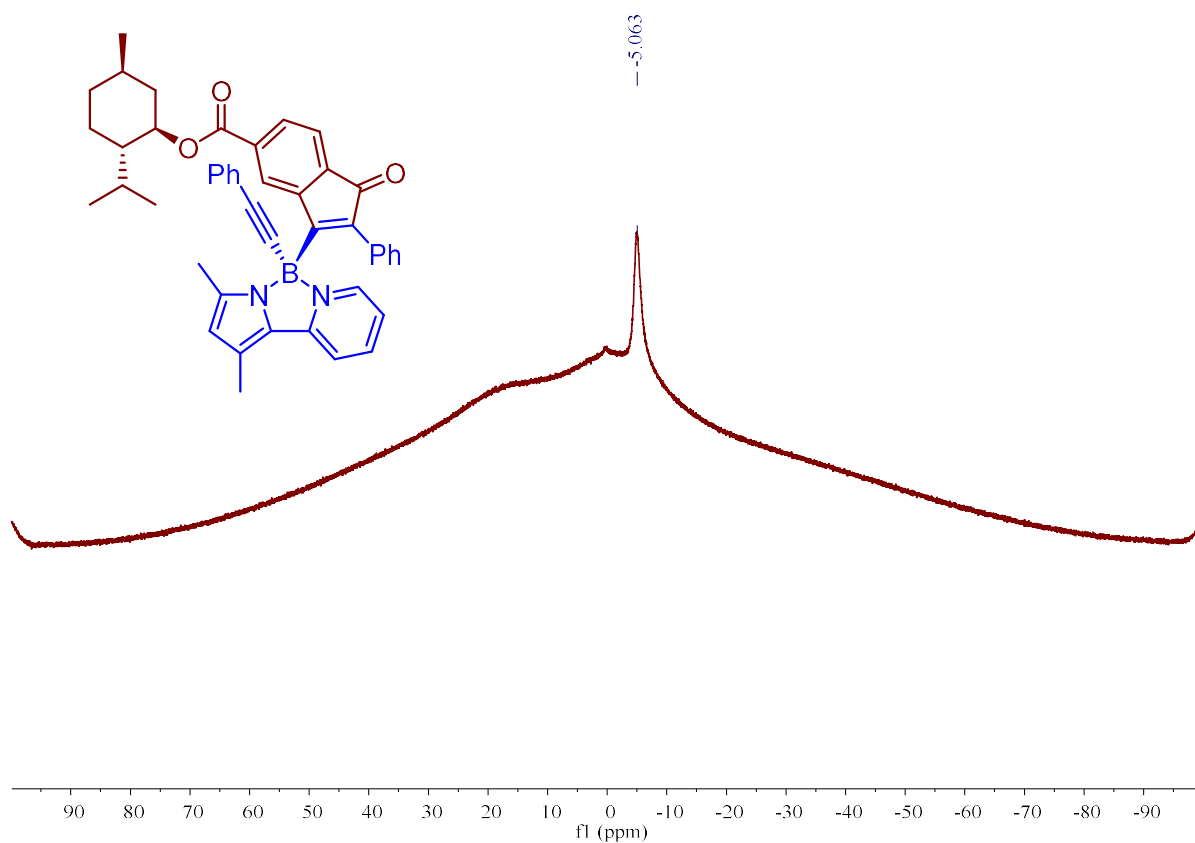
^{11}B NMR (193 MHz, CDCl_3) spectrum of 64.



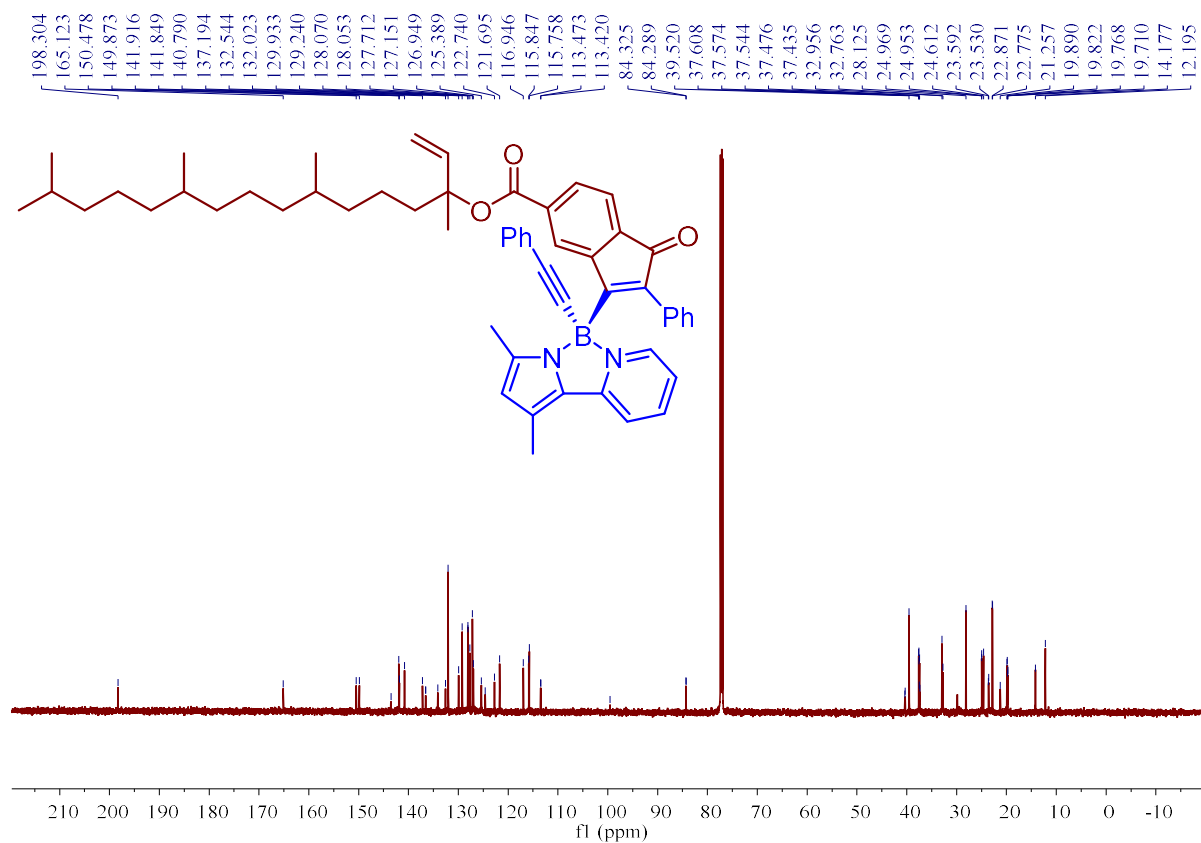
¹H NMR (600 MHz, CDCl₃) spectrum of 65.



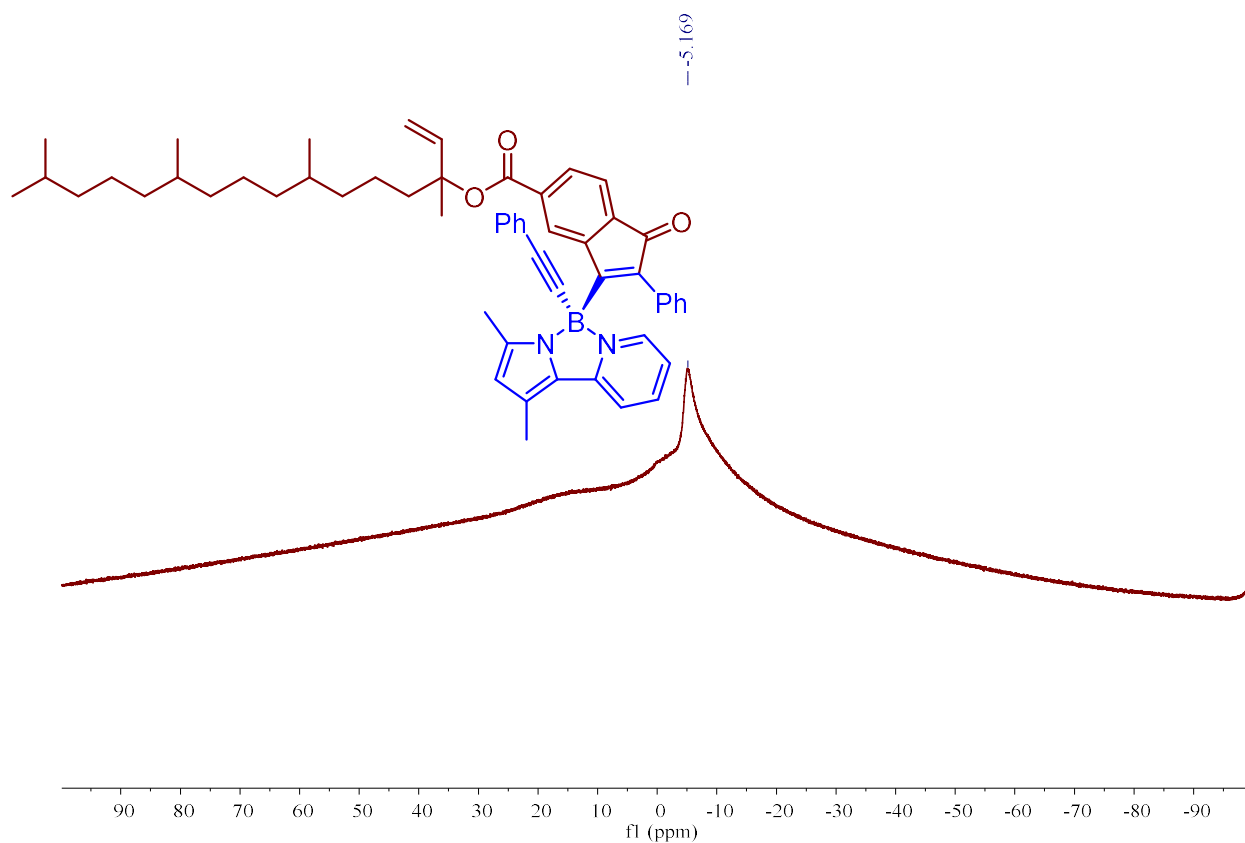
¹³C NMR (150 MHz, CDCl₃) spectrum of 65.



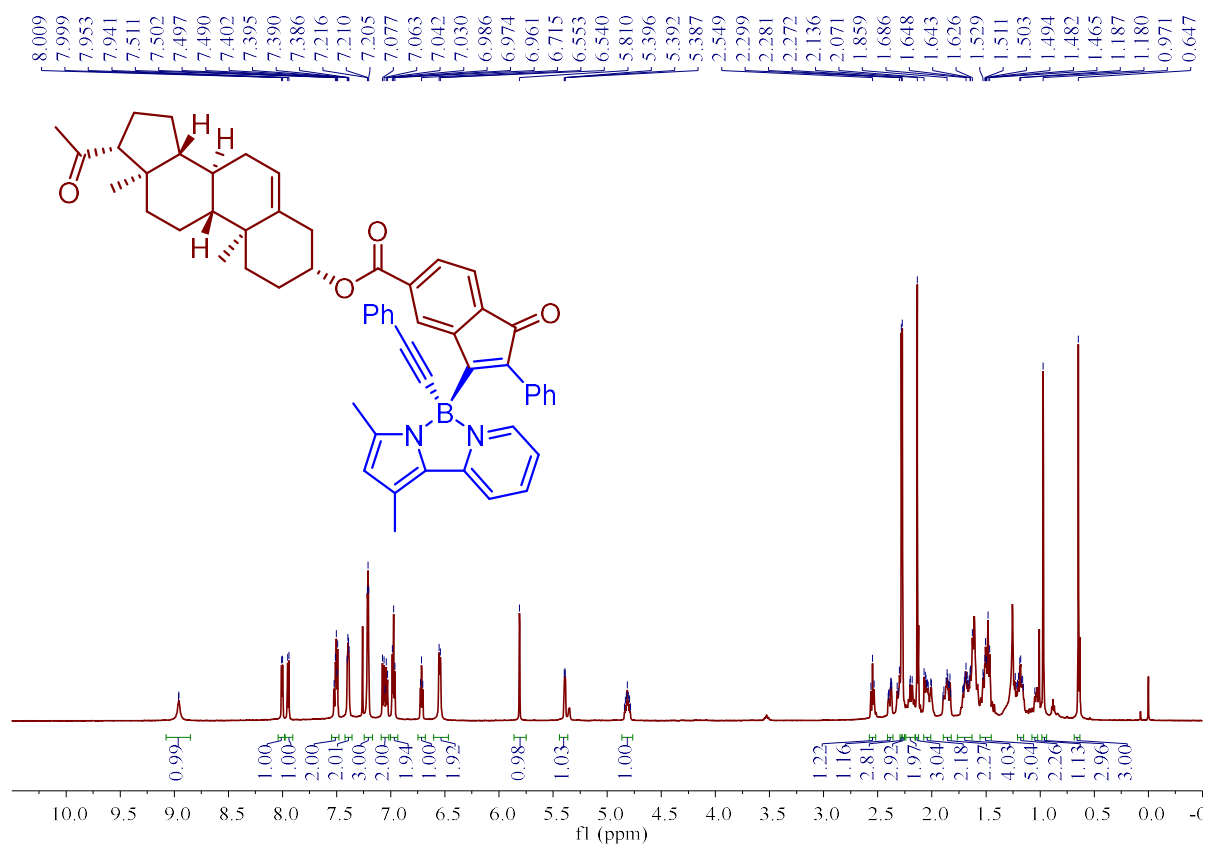
¹H NMR (600 MHz, CDCl₃) spectrum of 66.



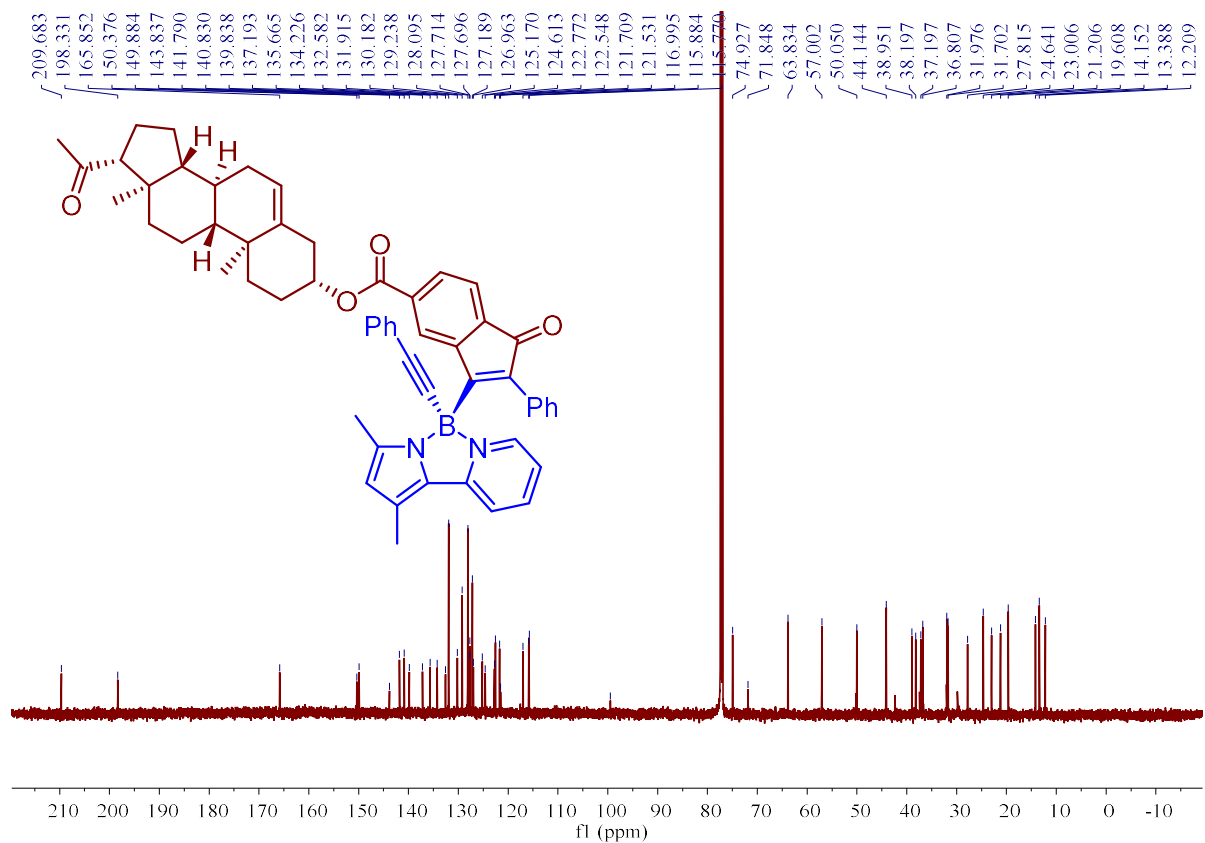
^{13}C NMR (150 MHz, CDCl_3) spectrum of 66.



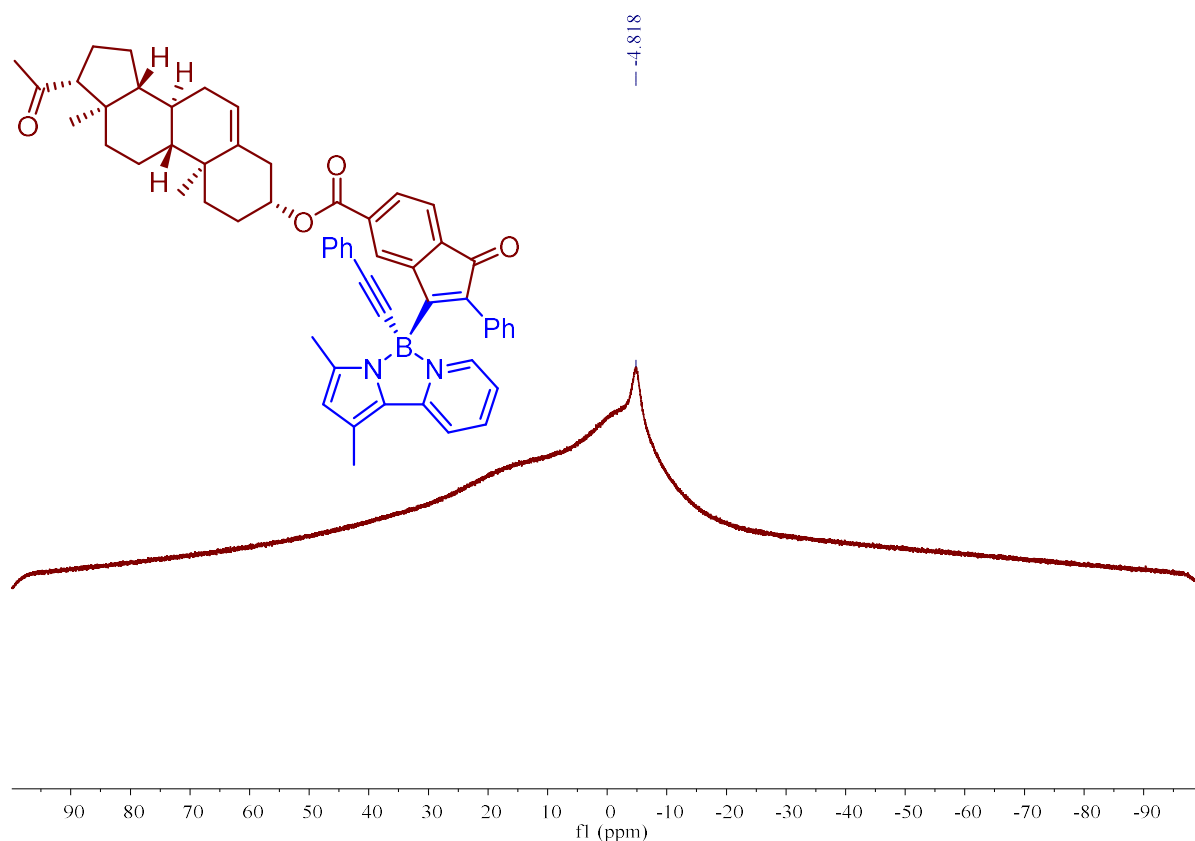
^{11}B NMR (193 MHz, CDCl_3) spectrum of 66.



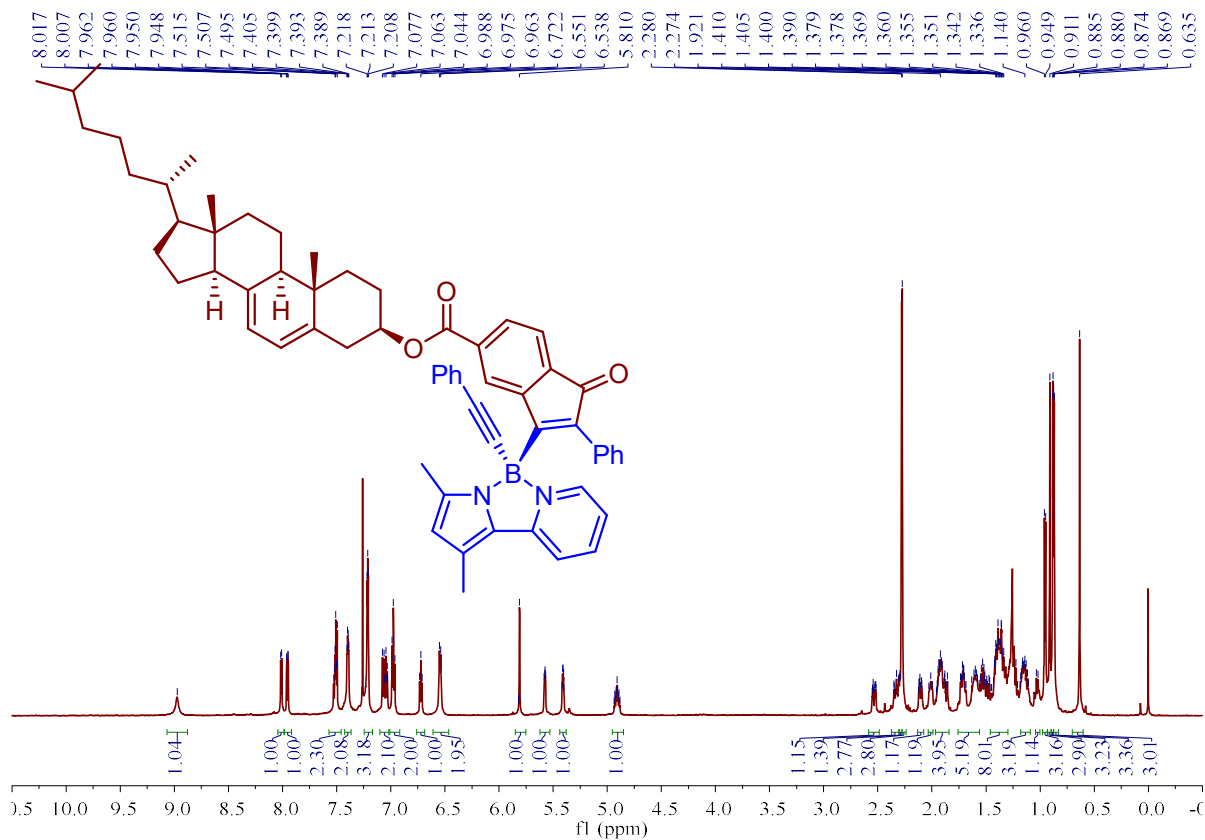
¹H NMR (600 MHz, CDCl₃) spectrum of 67.



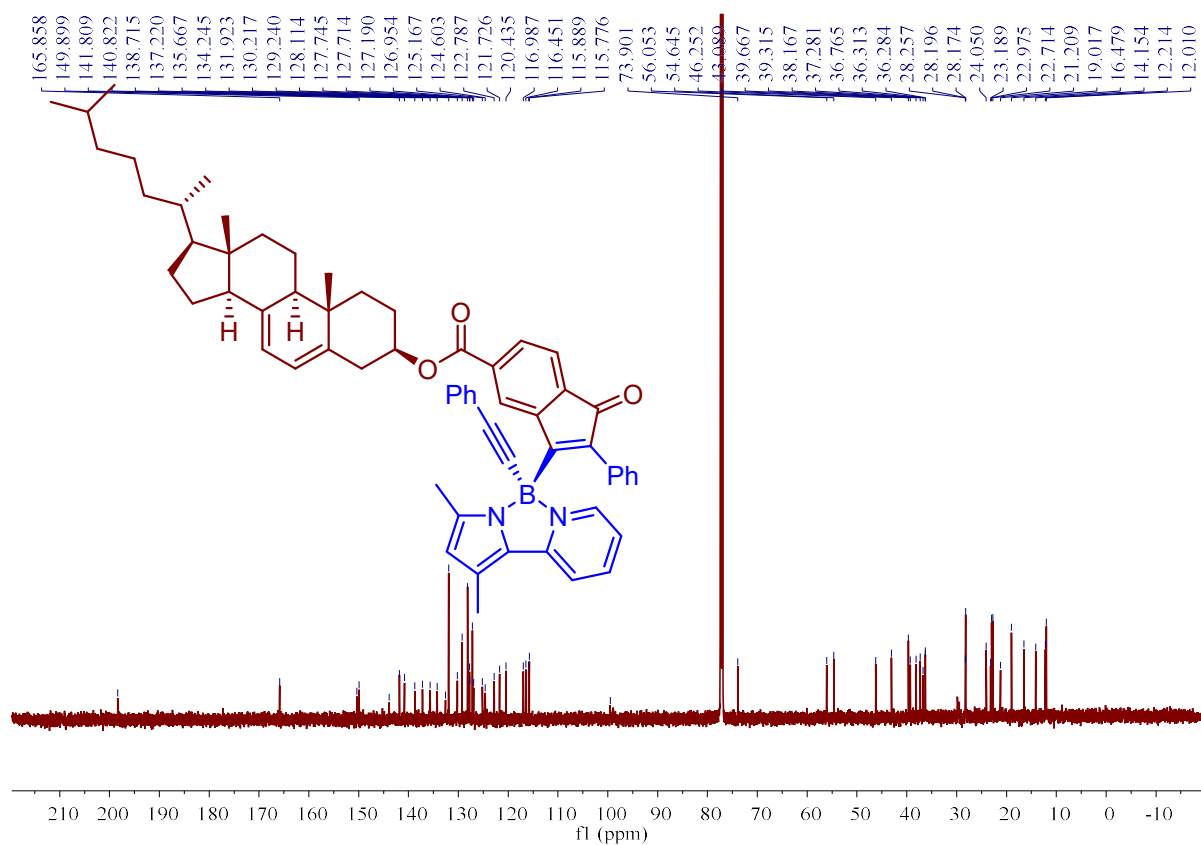
¹³C NMR (150 MHz, CDCl₃) spectrum of 67.



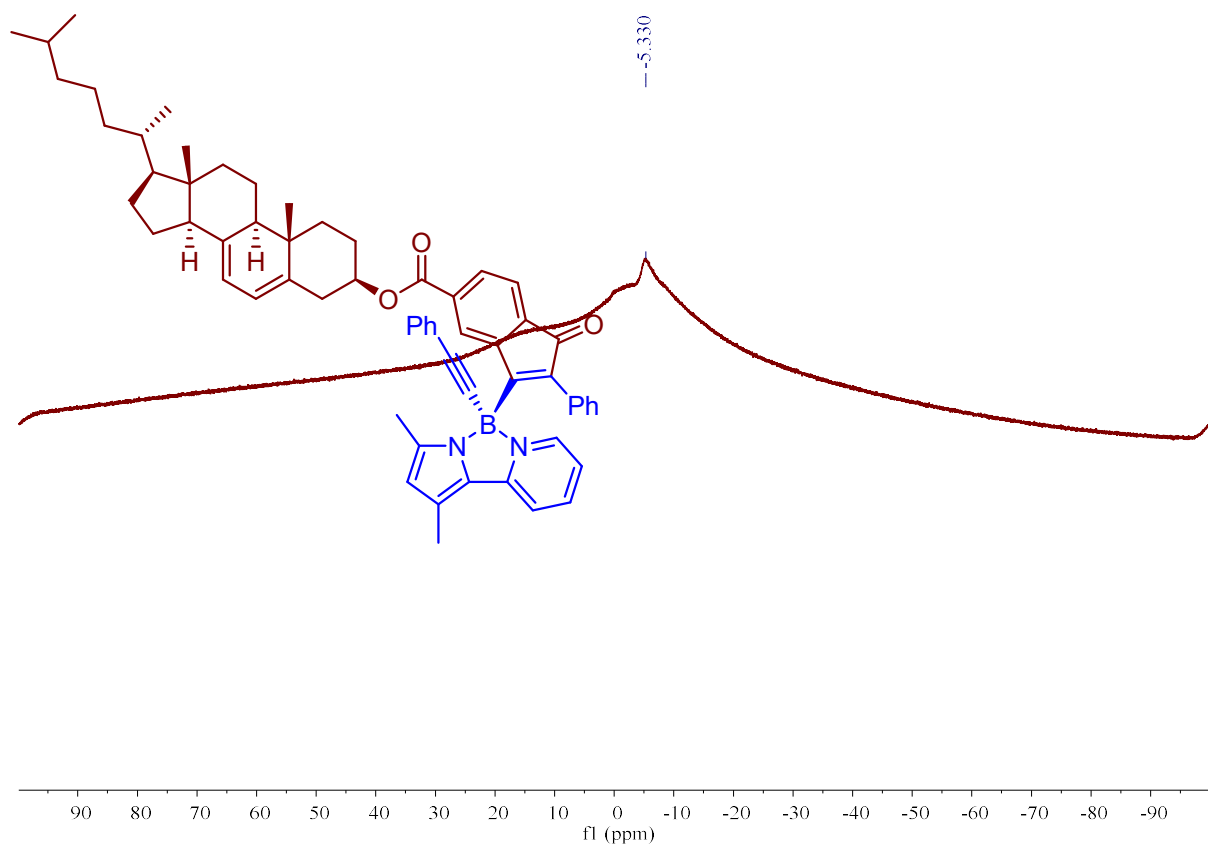
^{11}B NMR (193 MHz, CDCl_3) spectrum of 67.



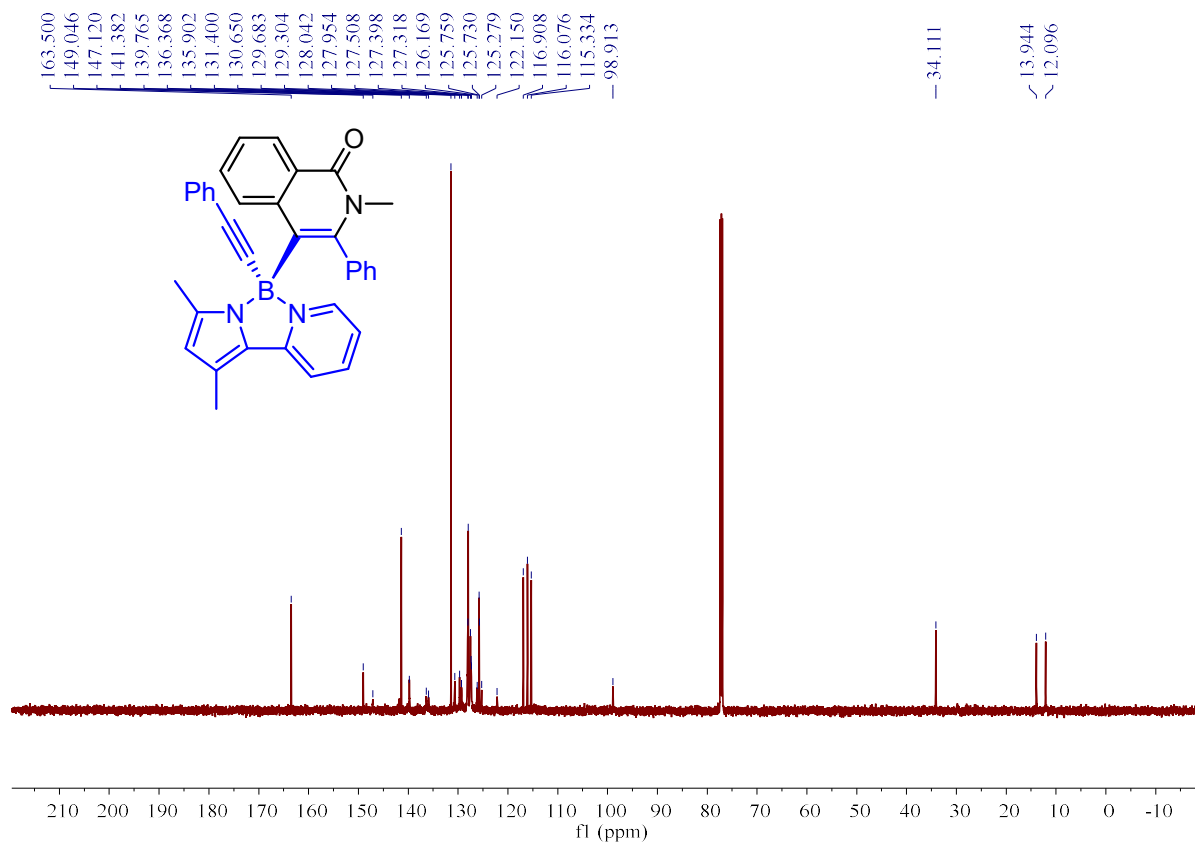
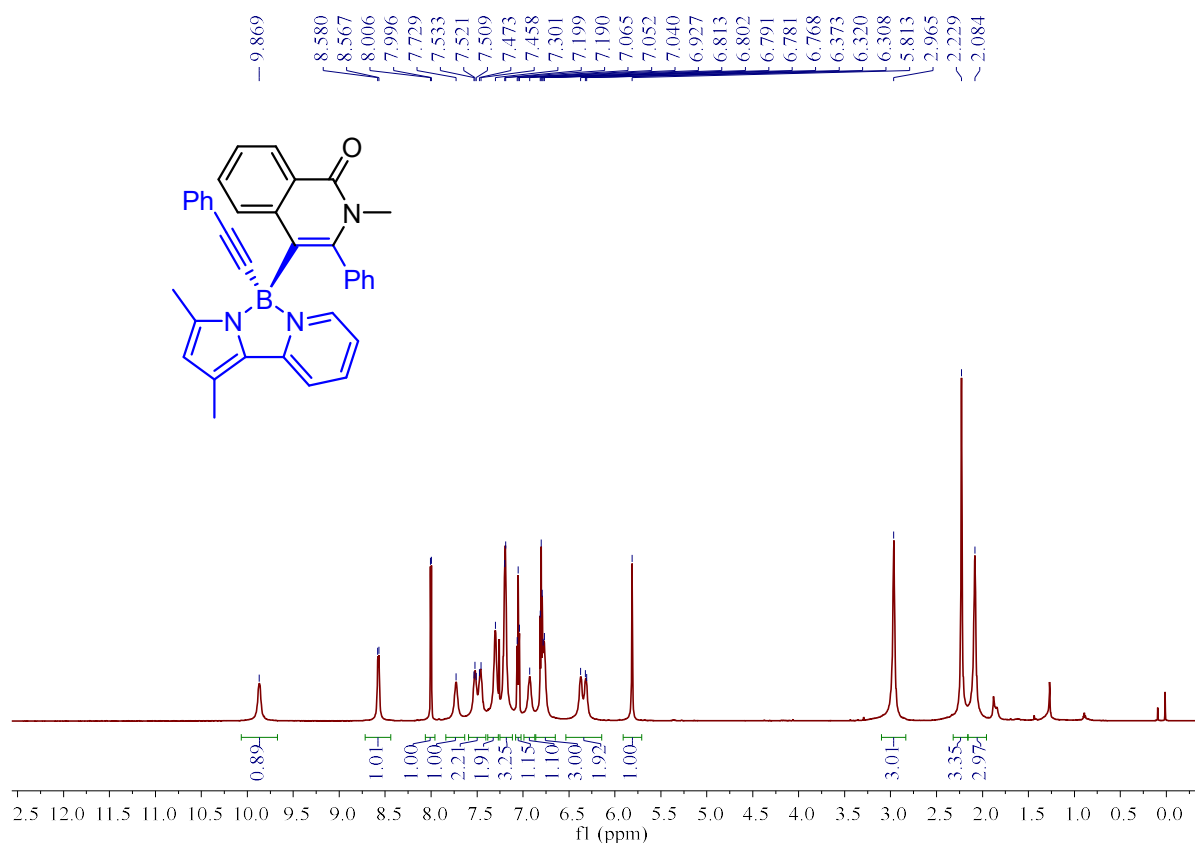
^1H NMR (600 MHz, CDCl_3) spectrum of 68.

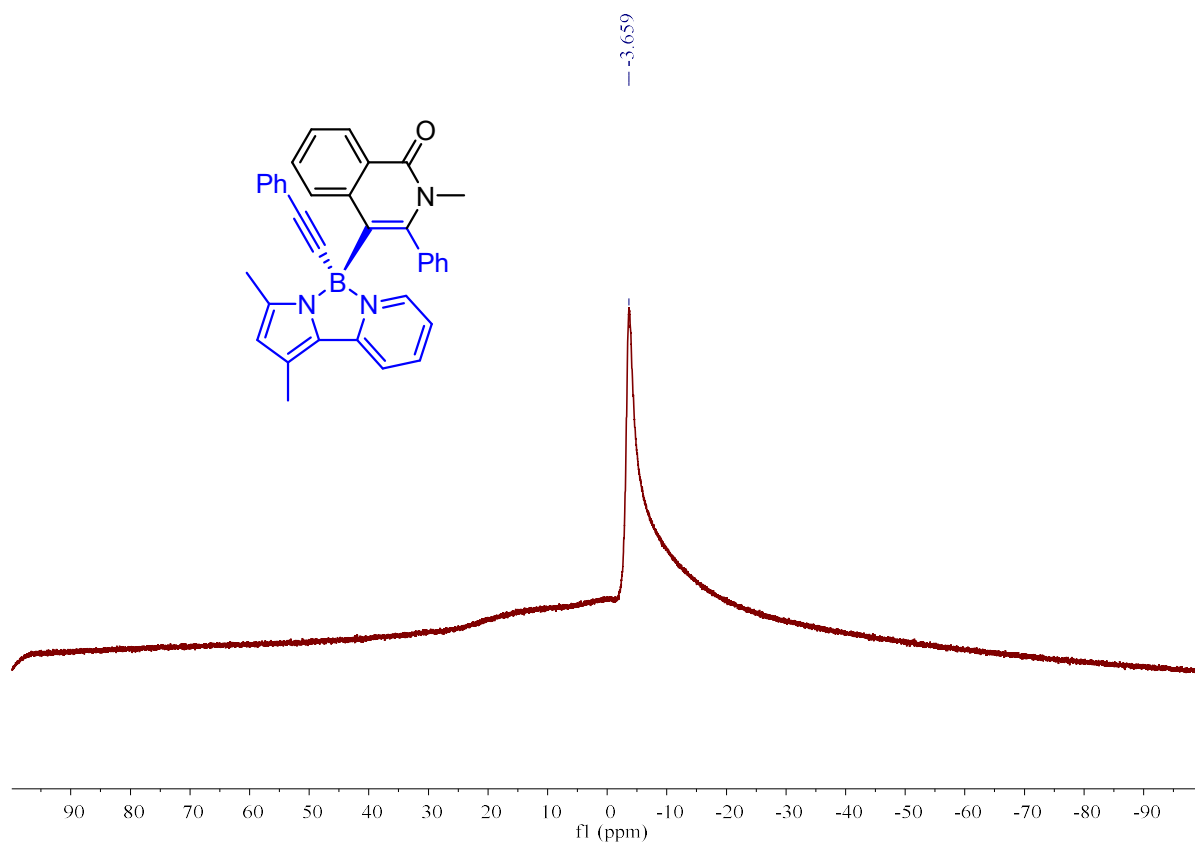


^{13}C NMR (150 MHz, CDCl_3) spectrum of 68.

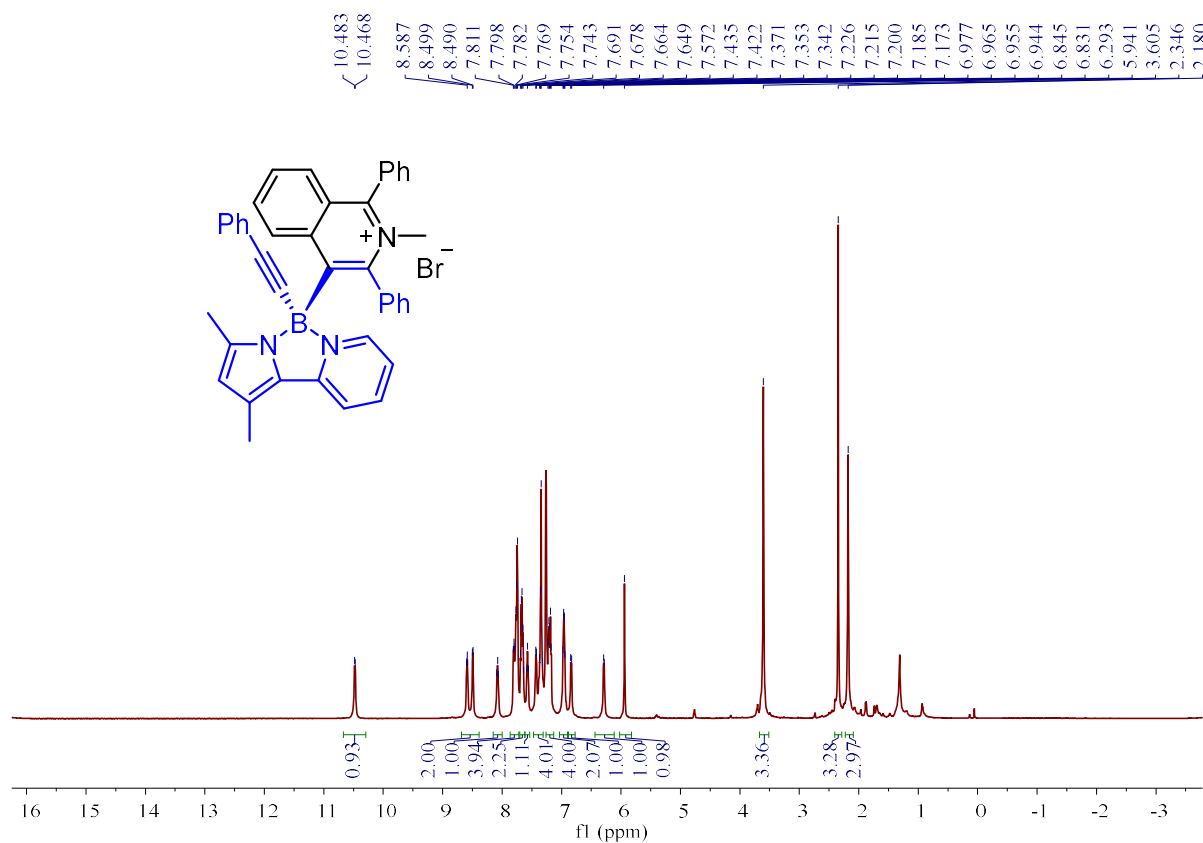


^{11}B NMR (193 MHz, CDCl_3) spectrum of 68.

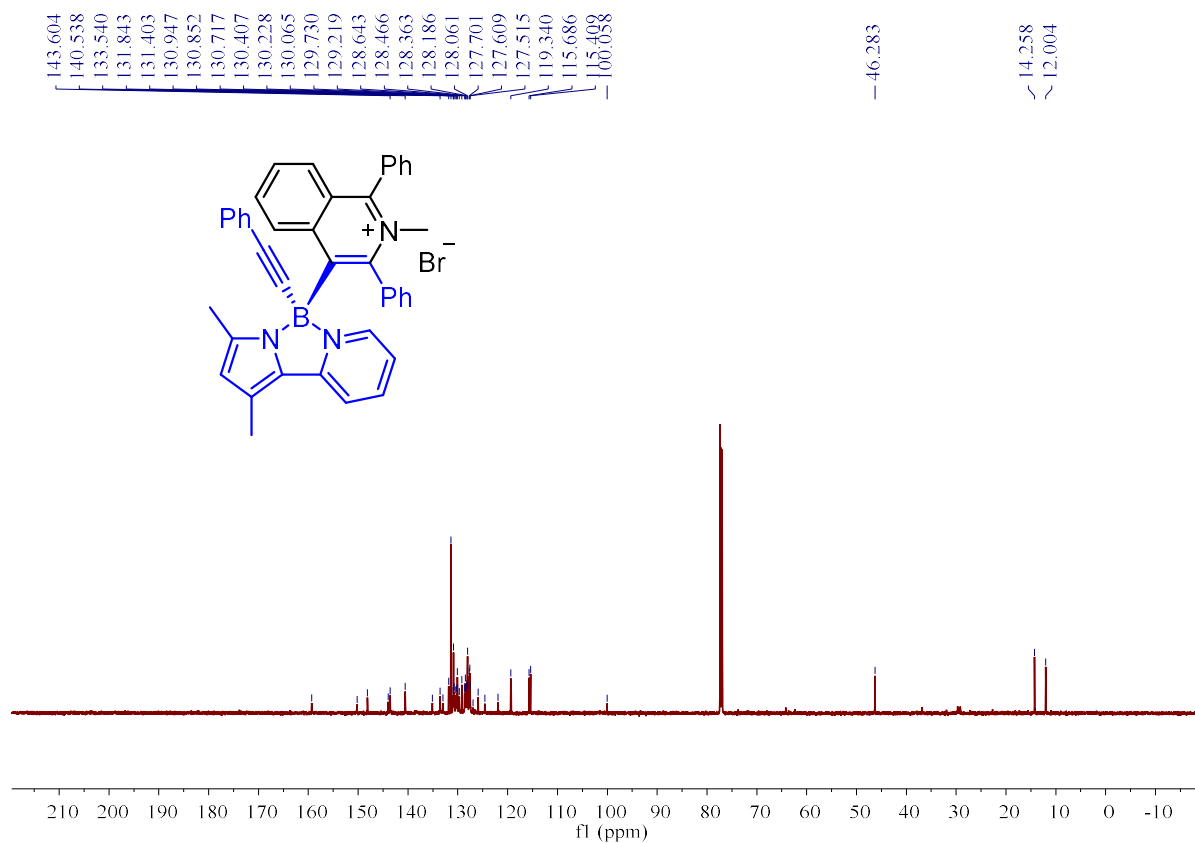




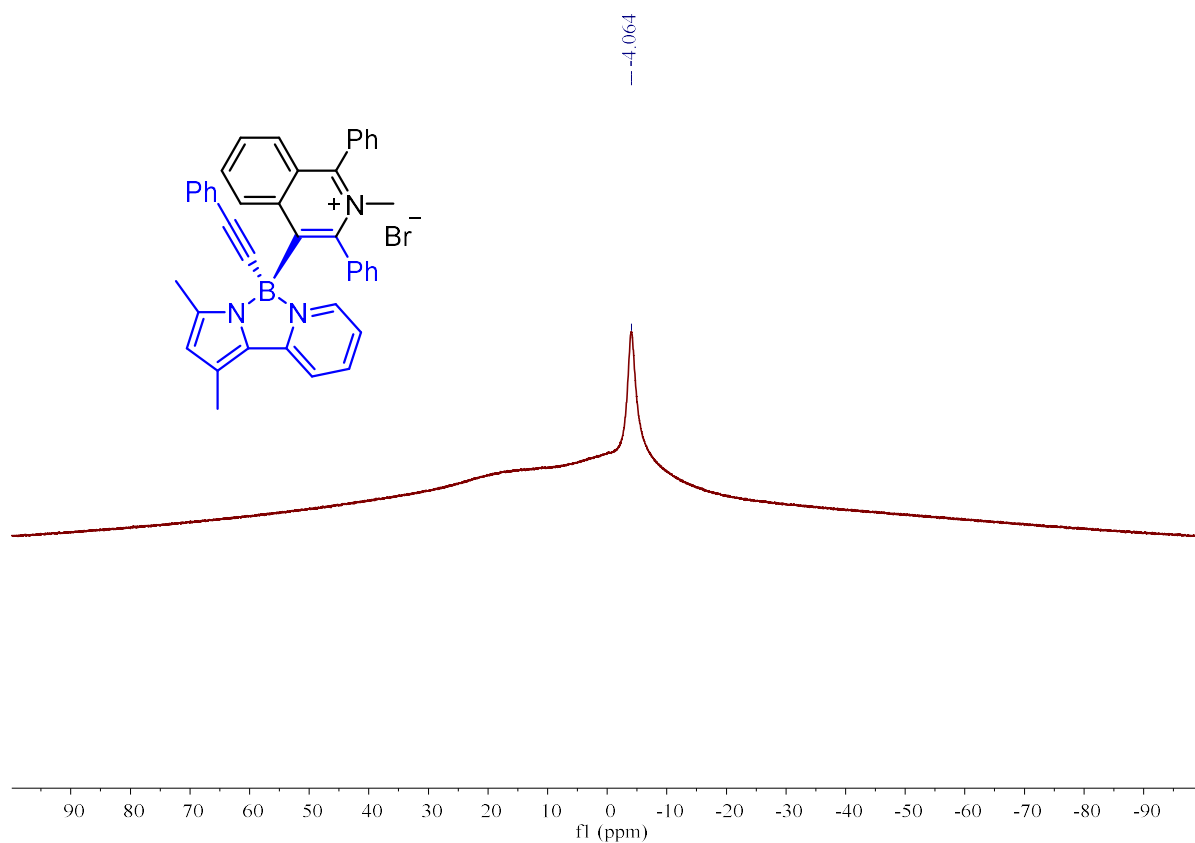
^{11}B NMR (193 MHz, CDCl_3) spectrum of 69.



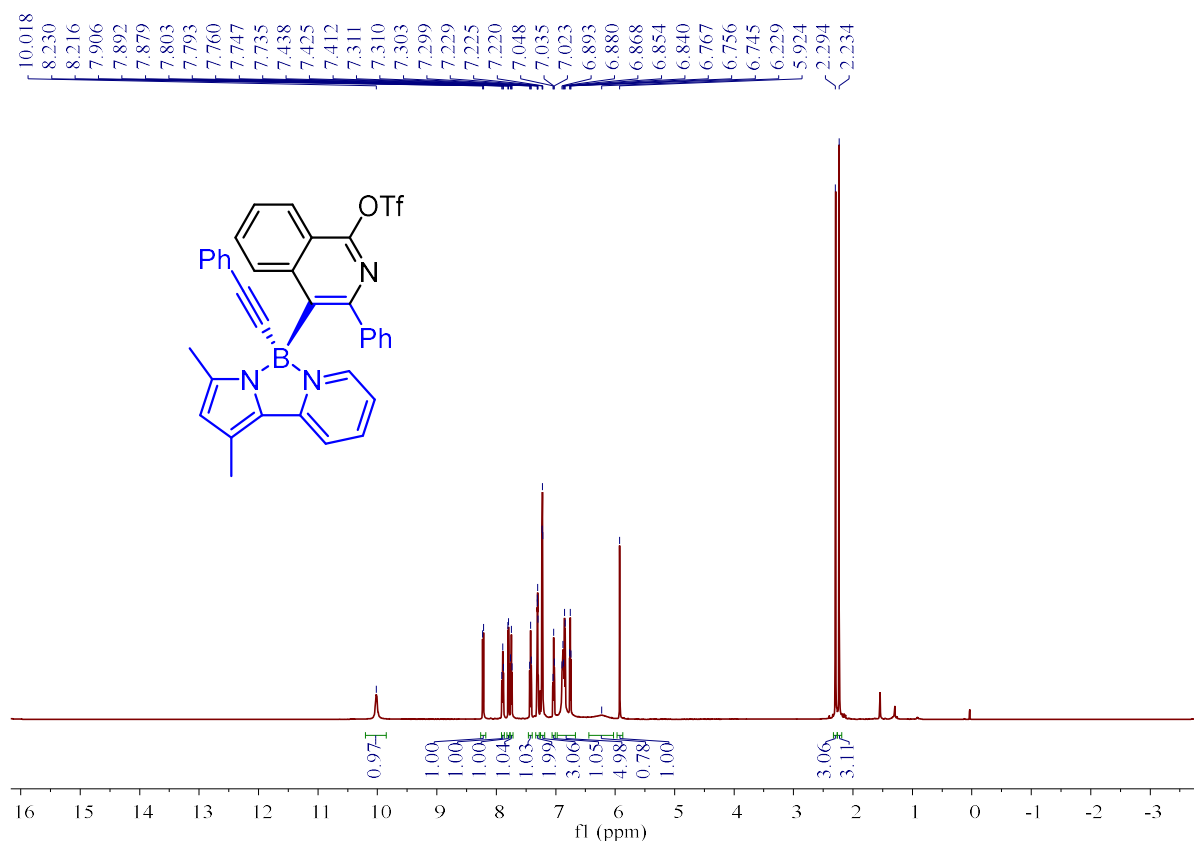
^1H NMR (600 MHz, CDCl_3) spectrum of 70.



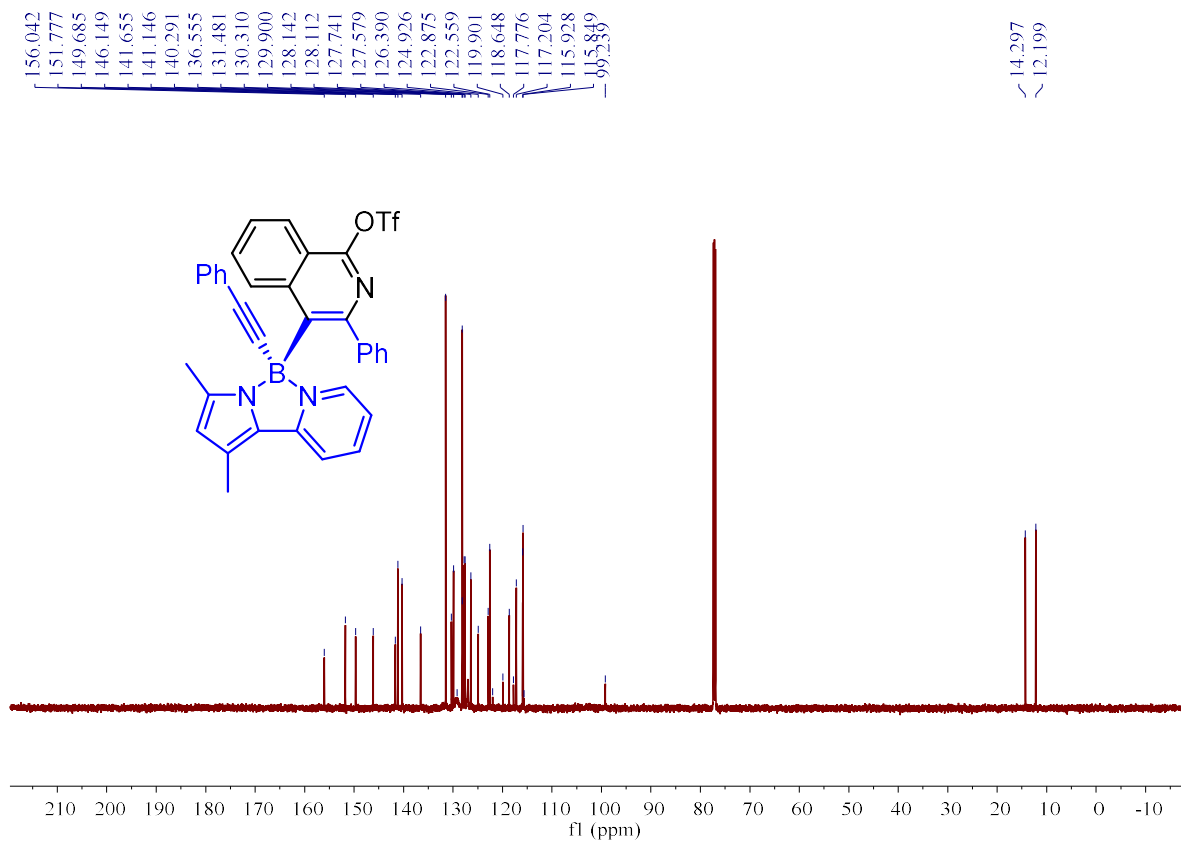
¹³C NMR (150 MHz, CDCl₃) spectrum of 70.



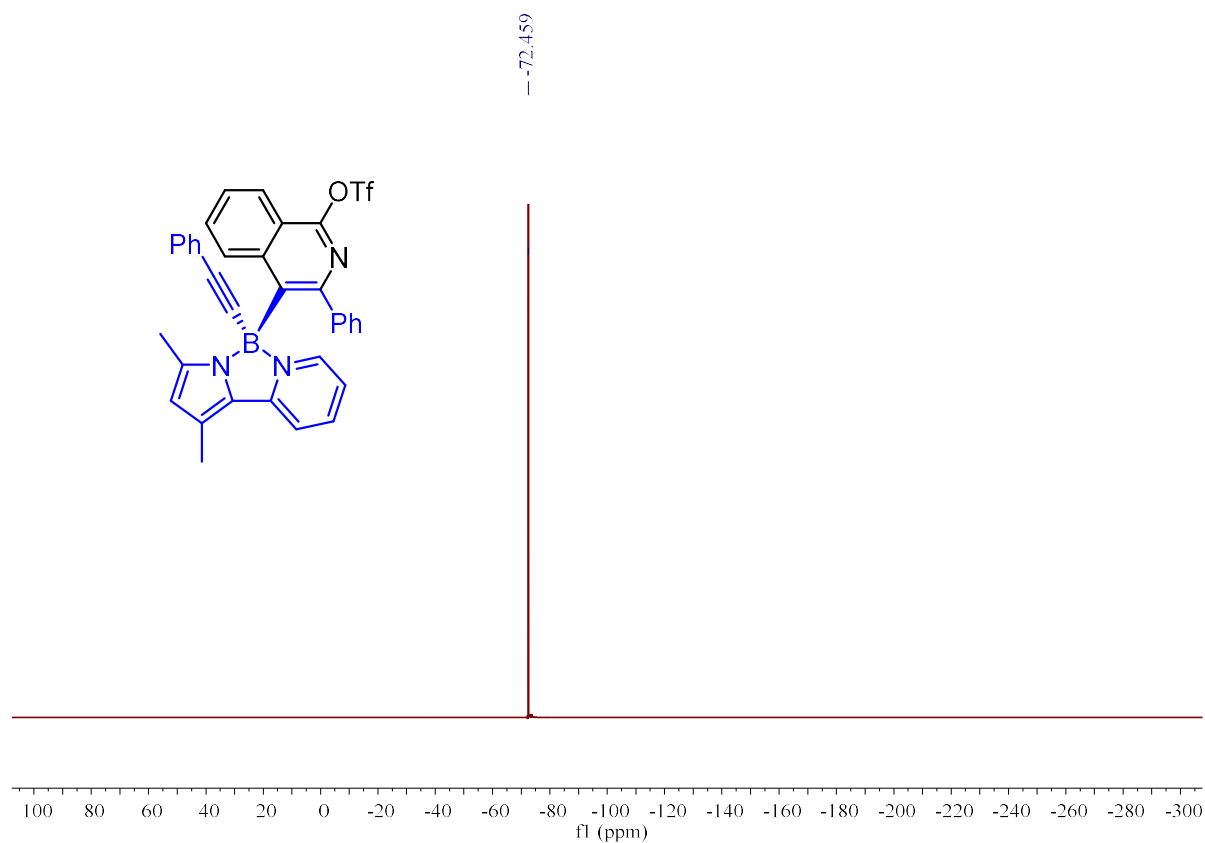
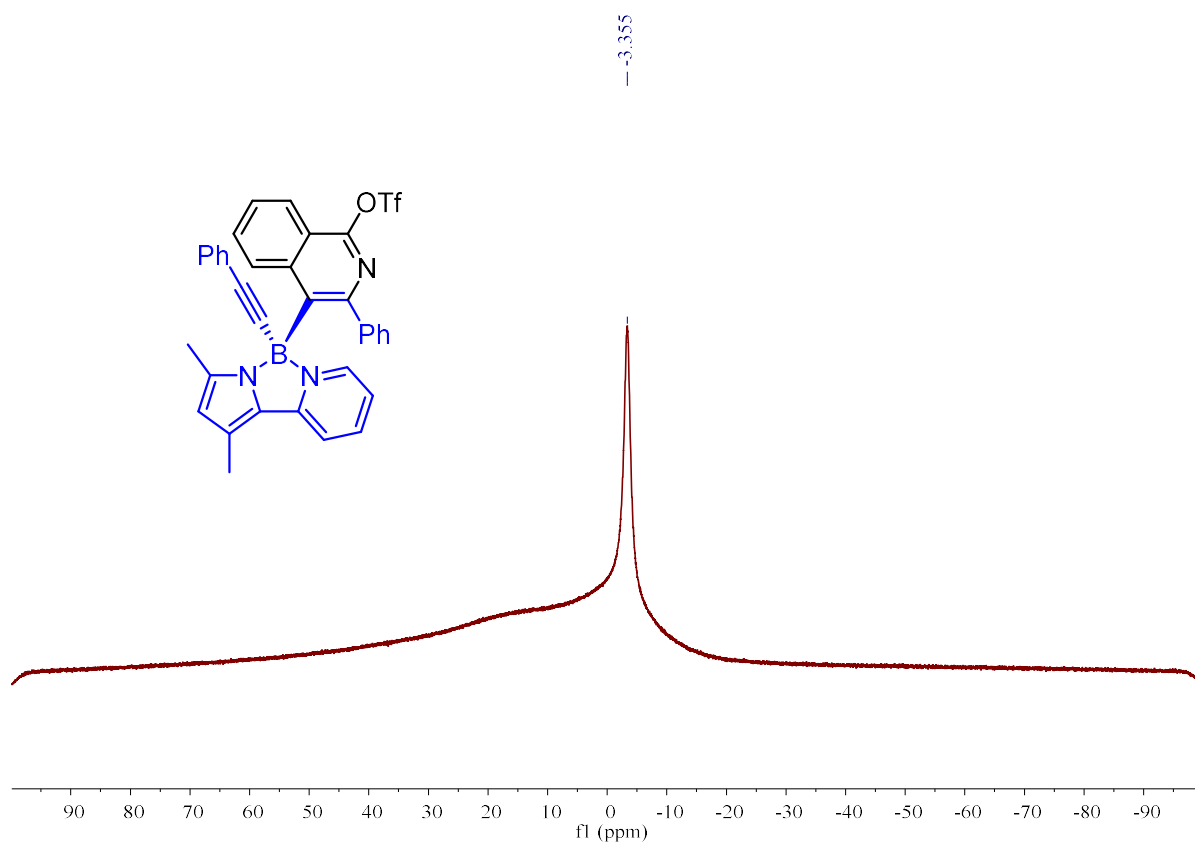
¹¹B NMR (193 MHz, CDCl₃) spectrum of 70.

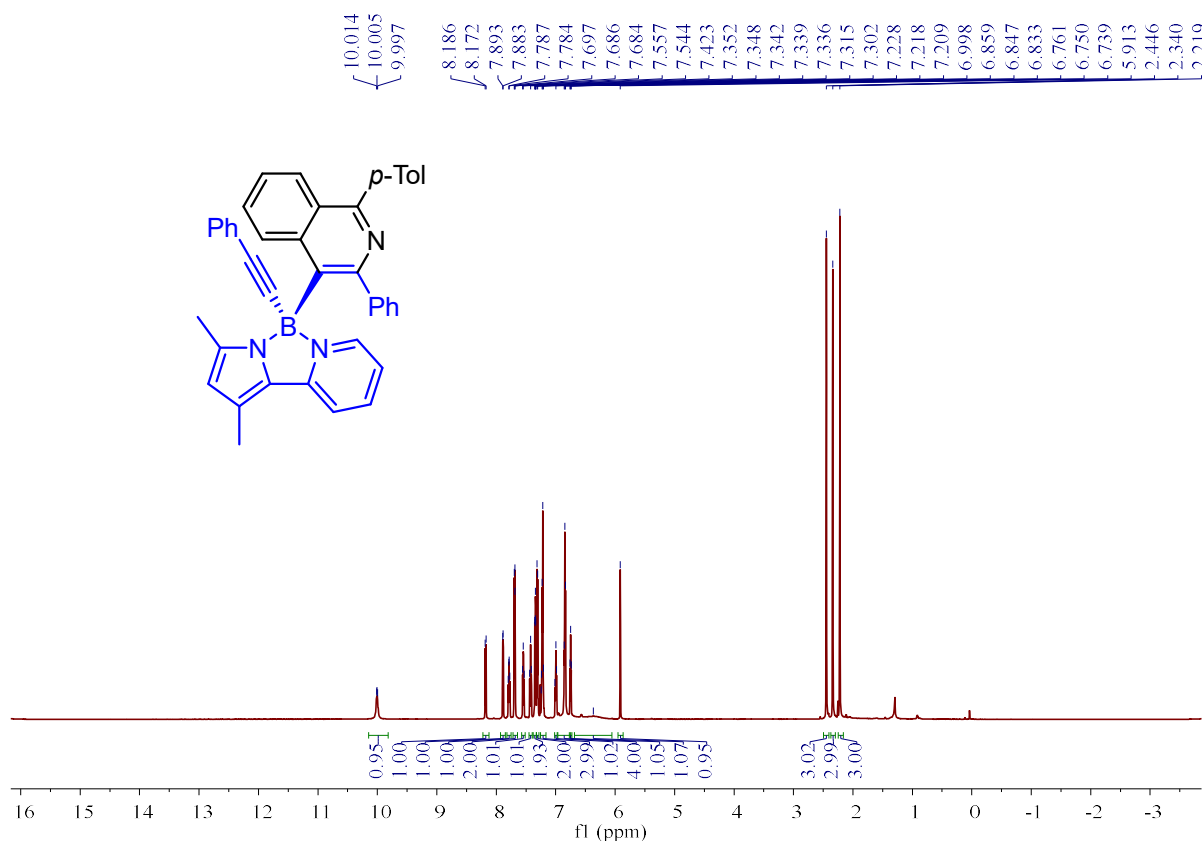


¹H NMR (600 MHz, CDCl₃) spectrum of 71.

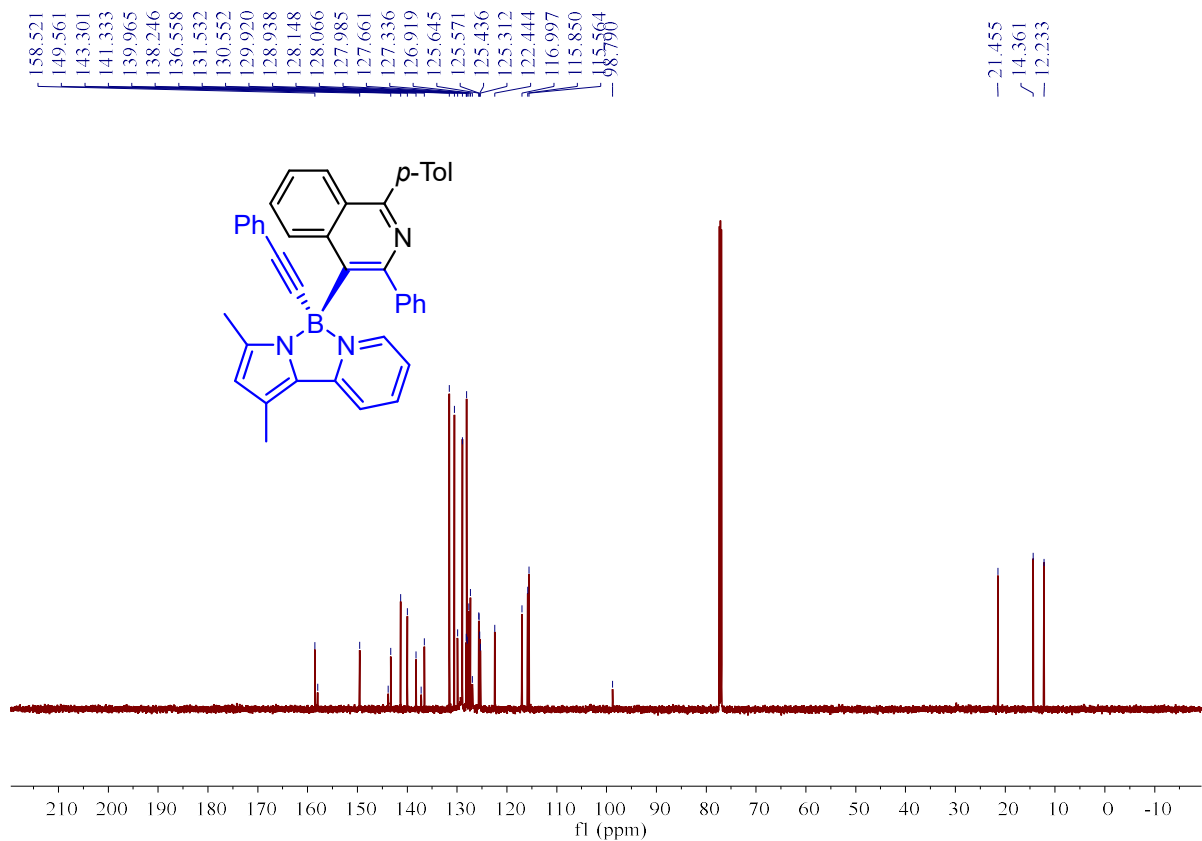


¹³C NMR (150 MHz, CDCl₃) spectrum of 71.

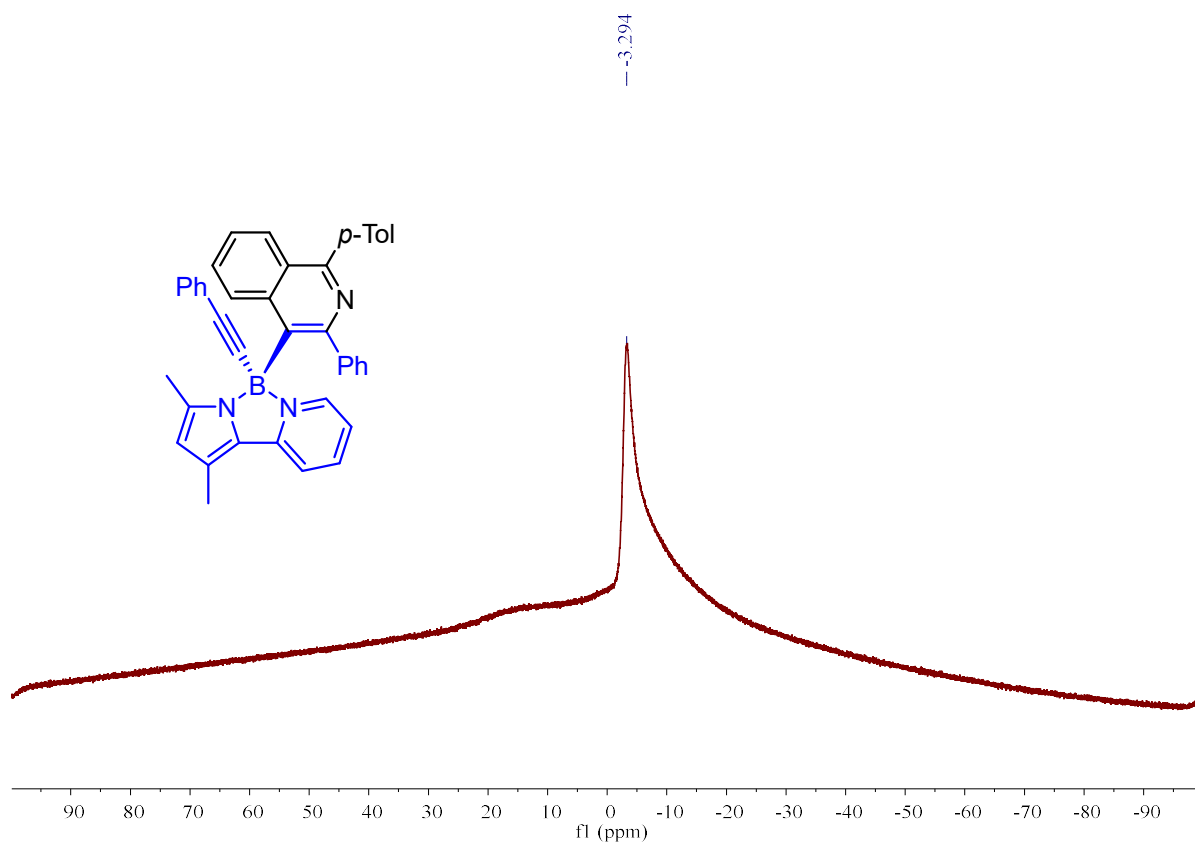




¹H NMR (600 MHz, CDCl₃) spectrum of 72.



¹³C NMR (150 MHz, CDCl₃) spectrum of 72.



^{11}B NMR (193 MHz, CDCl_3) spectrum of 72.