Supplementary Information

Rhodium(III)-Catalyzed Diverse [4+1] Annulation of Arenes with 1,3-Enynes via sp3/sp2 C-H Activation and 1,4-Rhodium Migration

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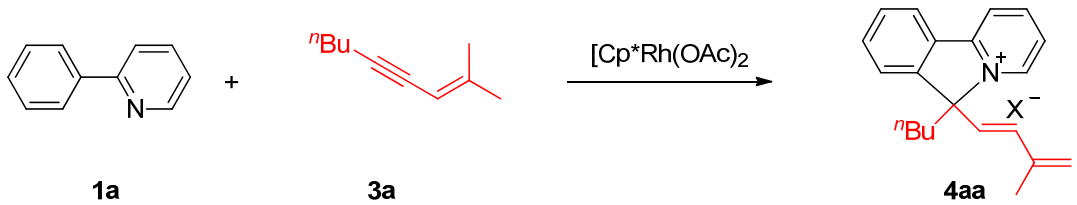
1, General Information

All chemicals were obtained from commercial sources and were used as received unless otherwise noted. All the reactions were carried out under nitrogen atmosphere using standard Schlenk technique except for the synthesis of product **4**. The ^{1}H NMR spectra were recorded on a 400 MHz or 600 MHz NMR spectrometer. The ^{13}C NMR spectra were recorded at 100 MHz or 150 MHz. The ^{19}F NMR spectra were recorded at 565 MHz. Chemical shifts were expressed in parts per million (δ) downfield from the internal standard tetramethylsilane, and were reported as s (singlet), d (doublet), t (triplet), dd (doublet of doublet), dt (doublet of triplet), m (multiplet), brs (broad singlet), etc. The residual solvent signals were used as references and the chemical shifts were converted to the TMS scale. High resolution mass spectra were obtained on an Agilent Q-TOF 6540 spectrometer. Column chromatography was performed on silica gel (300-400 mesh). Thin layer chromatography was performed on pre-coated glassback plates and visualized with UV light at 254 nm. Flash column chromatography was performed on silica gel. The 2-phenylpridines was purchased from commercial sources, and isoquinolones **2** were prepared by following a literature procedure.[1] The 1,3-enynes were prepared according to the literature report.[2] The 8-methylquinolines **6** were prepared according to the literature reports.[3] The oximes **8**[4] and ketimines **10** [5] were synthesized according to previously described methods.

2. Experimental procedure and characterization

2.1 Supplementary Table 1. Optimization Studies of Annulation of 1a with 3a [a]



1a **3a** **4aa**

Entry	Catalyst (mol %)	Solvent	Temp	Additive	Yield **4a**(%)[b]

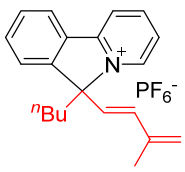
1	$Cp^*Rh(OAc)_2$	DCE	100	$Cu(OAc)_2$ (2.0 eq)	92
2	$Cp^*Rh(OAc)_2$	DCE	100	$Cu(OTf)_2$ (2.0 eq)	11
3	$Cp^*Rh(OAc)_2$	DCE	100	AgOAc (2.0 eq)	35
4	$Cp^*Rh(OAc)_2$	Dioxane	100	$Cu(OAc)_2$ (2.0 eq)	15
5	$Cp^*Rh(OAc)_2$	DME	100	$Cu(OAc)_2$ (2.0 eq)	--
6	$Cp^*Rh(OAc)_2$	EtOH	100	$Cu(OAc)_2$ (2.0 eq)	32
7	$Cp^*Rh(OAc)_2$	Toluene	100	$Cu(OAc)_2$ (2.0 eq)	10
8	$Cp^*Rh(OAc)_2$	CF_3CH_2OH	100	$Cu(OAc)_2$ (2.0 eq)	98
9 [c]	$Cp^*Rh(OAc)_2$	CF_3CH_2OH	100	$Cu(OAc)_2$ (0.5 eq)/air	92
10 [c,d]	$Cp^*Rh(OAc)_2$	CF_3CH_2OH	100	$Cu(OAc)_2$ (0.5 eq), air, KPF_6	92
11 [c]	$Cp^*Rh(OAc)_2$	CF_3CH_2OH	100	$Cu(OAc)_2$ (0.1 eq)/air	16
12[c,d]	$Cp^*Rh(OAc)_2$	CF_3CH_2OH	50	$Cu(OAc)_2$ (0.5 eq) air, KPF_6	95
13 [c]	$Cp^*Rh(OAc)_2$	CF_3CH_2OH	100	air	--
14	--	CF_3CH_2OH	100	$Cu(OAc)_2$ (2.0 eq)	--

[a]Reaction conditions: **1a** (0.2 mmol), **3a** (0.22 mmol), [$Cp^*Rh(OAc)_2$] (8 mol%), additive (0.2 equiv), Solvent (2.0 mL), [b]isolated yields. [c] under air in a 100 mL pressure tube. [d] KPF_6 (0.5 mmol).

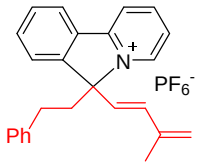
2.2 General procedure for Rhodium(III)-Catalyzed C-H Activation/annulation of 2-phenylpridines or isoquinolones with 1,3-enynes:

General procedure A: $Cp^*Rh(OAc)_2$ (6.0 mg, 0.016 mmol), $Cu(OAc)_2$ (20 mg, 0.1 mmol, 0.50 equiv), KPF_6 (92 mg, 0.5 mmol, 2.5 equiv) in CF_3CH_2OH (2.0 mL) were charged into a 25 mL pressure tube under air. The mixture was stirred for 10 min at

room temperature, followed by addition of a 2-phenylpridine or isoquinolone (0.200 mmol, 1.00 equiv) and 1,3-enyne (0.220 mmol, 1.10 equiv). The reaction tube was then placed in an oil bath at 50 °C. After the reaction was complete (12 h), the reaction vessel was removed from the oil bath and cooled to ambient temperature. The reaction mixture was filtered through a pad of celite eluting with DCM:MeOH = 10:1, concentrated, and purified by silica gel chromatography (DCM:MeOH = 20:1) to give the indicated product.

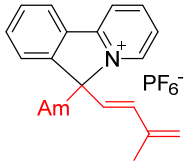


(*E*)-6-butyl-6-(3-methylbuta-1,3-dien-1-yl)-6H-pyrido[2,1-a]isoindol-5-ium hexafluorophosphate (**4aa**, 85.0 mg, 98%). ^{1}H NMR (400 MHz, CD_2Cl_2) δ 8.78 (d, *J* = 6.3 Hz, 1H), 8.64 – 8.57 (m, 1H), 8.42 (d, *J* = 8.2 Hz, 1H), 8.18 (d, *J* = 7.7 Hz, 1H), 8.05 – 8.00 (m, 1H), 7.88-7.82 (m, 1H), 7.77 (dt, *J* = 7.6, 3.8 Hz, 1H), 7.59 (d, *J* = 7.7 Hz, 1H), 6.47 (d, *J* = 15.8 Hz, 1H), 5.86 (d, *J* = 15.8 Hz, 1H), 5.21 (s, 1H), 5.13 (s, 1H), 2.70-2.54 (m, 2H), 1.84 (s, 3H), 1.25 – 1.13 (m, 2H), 0.72 (t, *J* = 7.4 Hz, 3H), 0.60 - 0.50 (m, 1H), 0.47 – 0.32 (m, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 151.8, 146.6, 144.7, 140.1, 139.7, 138.6, 134.2, 130.7, 129.7, 126.6, 125.1, 124.0, 123.6, 121.8, 120.8, 83.3, 38.3, 24.6, 21.8, 18.2, 13.6. ^{19}F NMR (376 MHz, Acetone-d_6) δ -71.92 (d, *J* = 708.9 Hz). ^{31}P NMR (162 MHz, Acetone-d_6) δ -110.24 – -166.77 (m). HRMS (ESI) calcd. for $C_{21}H_{24}N^+$ [M-PF_6]: 290.1903, found: 290.1903. HRMS (ESI) calcd. for $[PF_6]^-$: 144.9647, found: 144.9647.

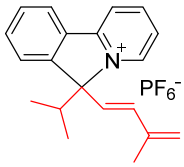


(*E*)-6-(3-methylbuta-1,3-dien-1-yl)-6-phenethyl-6H-pyrido[2,1-a]isoindol-5-ium hexafluorophosphate (**4ab**, 78.0 mg, 81%). ^{1}H NMR (600 MHz, CD_2Cl_2) δ 8.73 (d, *J* = 6.2 Hz, 1H), 8.48 (t, *J* = 7.8 Hz, 1H), 8.38 (d, *J* = 8.1 Hz, 1H), 8.22 (d, *J* = 7.7 Hz, 1H), 7.87 (t, *J* = 7.5 Hz, 1H), 7.84 – 7.77 (m, 2H), 7.64 (d, *J* = 7.7 Hz, 1H), 7.16 – 7.06 (m, 3H), 6.83 (d, *J* = 7.3 Hz, 2H), 6.44 (d, *J* = 15.8 Hz, 1H), 5.89 (d, *J* = 15.8 Hz, 1H), 5.18 (s, 1H), 5.10 (s, 1H), 3.07 – 2.91 (m, 2H), 2.22-2.17 (m, 1H), 1.82 (s, 3H), 1.86-1.78 (m, 1H). ^{13}C NMR (151 MHz, CD_2Cl_2) δ 152.3, 146.6, 144.3, 140.3, 139.2, 138.7, 138.4, 134.7, 131.0, 129.8, 128.7,

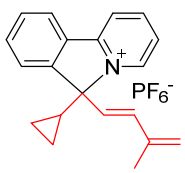
128.0, 126.6, 126.0, 125.0, 124.0, 123.9, 121.7, 120.8, 83.2, 39.1, 29.1, 17.9. HRMS (ESI) calcd. for $C_{25}H_{24}N^+$ [M-PF_6]: 338.1903, found: 338.1908. HRMS (ESI) calcd. for [PF_6]$^-$: 144.9647, found: 144.9656.



(*E*)-6-(3-methylbuta-1,3-dien-1-yl)-6-pentyl-6H-pyrido[2,1-a]isoindol-5-ium hexafluorophosphate (**4ac**, 88.0 mg, 98%). ^{1}H NMR (400 MHz, Acetone-d_6) δ 9.36 (d, *J* = 6.3 Hz, 1H), 8.91 – 8.79 (m, 2H), 8.53 – 8.45 (m, 1H), 8.21 (td, *J* = 6.3, 2.5 Hz, 1H), 7.88-7.81 (m, 3H), 6.63 (d, *J* = 15.9 Hz, 1H), 6.26 (d, *J* = 15.9 Hz, 1H), 5.16 (s, 1H), 5.13 (s, 1H), 2.86 – 2.69 (m, 2H), 1.82 (s, 3H), 1.17-1.07 (m, 4H), 0.69 (t, *J* = 7.2 Hz, 1H), 0.66 – 0.58 (m, 1H), 0.58 – 0.44 (m, 1H). ^{13}C NMR (151 MHz, CD_2Cl_2) δ 152.4, 146.5, 144.9, 140.3, 139.2, 138.5, 134.6, 130.8, 129.5, 126.3, 124.9, 123.9, 123.8, 121.5, 120.9, 83.4, 38.4, 30.9, 22.1, 22.1, 17.9, 13.5. HRMS (ESI) calcd. for $C_{22}H_{26}N^+$ [M-PF_6]: 304.2060, found: 304.2058. HRMS (ESI) calcd. for [PF_6]$^-$: 144.9647, found: 144.9647.

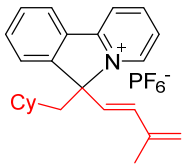


(*E*)-6-isopropyl-6-(3-methylbuta-1,3-dien-1-yl)-6H-pyrido[2,1-a]isoindol-5-ium hexafluorophosphate (**4ad**, 79.0 mg, 94%). ^{1}H NMR (600 MHz, CD_2Cl_2) δ 8.88 (d, *J* = 6.3 Hz, 1H), 8.51 (t, *J* = 7.8 Hz, 1H), 8.39 (d, *J* = 8.1 Hz, 1H), 8.18 (d, *J* = 7.7 Hz, 1H), 7.95 (t, *J* = 6.9 Hz, 1H), 7.80-7.70 (m, 2H), 7.60 (d, *J* = 7.6 Hz, 1H), 6.20 (d, *J* = 15.8 Hz, 1H), 6.11 (d, *J* = 15.8 Hz, 1H), 5.08 (s, 1H), 4.91 (s, 1H), 2.89 – 2.80 (m, 1H), 1.86 (s, 3H), 1.24 (d, *J* = 6.8 Hz, 3H), 0.19 (d, *J* = 6.6 Hz, 3H). ^{13}C NMR (151 MHz, CD_2Cl_2) δ 151.8, 146.1, 142.0, 140.4, 140.0, 139.2, 133.8, 130.8, 130.6, 126.2, 125.4, 124.4, 123.9, 121.5, 120.5, 86.8, 38.73, 18.0, 17.4, 15.1. HRMS (ESI) calcd. for $C_{20}H_{22}N^+$ [M-PF_6]: 276.1747, found: 276.1747. HRMS (ESI) calcd. for [PF_6]$^-$: 144.9647, found: 144.9648.

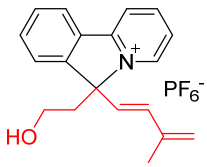


(*E*)-6-cyclopropyl-6-(3-methylbuta-1,3-dien-1-yl)-6H-pyrido[2,1-a]isoindol-5-ium hexafluorophosphate (**4ae**, 77.0 mg, 92%). ^{1}H NMR (400 MHz, Acetone-d_6) δ 9.49 (d, *J* = 6.3 Hz, 1H), 8.87 – 8.77 (m, 2H), 8.56 – 8.42 (m, 1H), 8.40 – 8.13 (m, 1H), 7.91-7.81 (m, 3H), 6.76 (d, *J* = 15.8

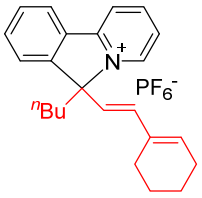
Hz, 1H), 6.19 (d, J = 15.8 Hz, 1H), 5.18 (s, 1H), 5.16 (s, 1H), 2.02-1.97 (m, 1H), 1.84 (s, 3H), 1.14-1.07 (m, 1H), 1.05 – 0.94 (m, 1H), 0.64 – 0.54 (m, 1H), 0.17-0.10 (m, 1H).^{13}C NMR (151 MHz, CD_2Cl_2) δ 151.4, 146.5, 143.0, 140.3, 140.1, 139.6, 134.0, 131.0, 129.7, 126.3, 124.9, 124.0, 122.3, 121.8, 120.8, 84.4, 19.0, 18.0, 3.5, 0.5. HRMS (ESI) calcd. for $C_{20}H_{20}N^+$ [M-PF_6]: 274.1590, found: 274.1575. HRMS (ESI) calcd. for [PF_6]$^-$: 144.9647, found: 144.9647.



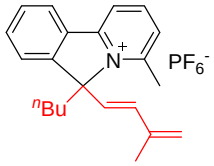
(*E*)-6-(cyclohexylmethyl)-6-(3-methylbuta-1,3-dien-1-yl)-6H-pyrido[2,1-a]isoindol-5-ium hexafluorophosphate (**4af**, 90.0 mg, 95%). ^{1}H NMR (400 MHz, Acetone-d_6) δ 9.45 (d, J = 6.3 Hz, 1H), 8.86 (dd, J = 5.7, 1.6 Hz, 2H), 8.50 (d, J = 7.7 Hz, 1H), 8.23 (td, J = 6.3, 2.5 Hz, 1H), 7.99 – 7.76 (m, 3H), 6.50 (d, J = 15.9 Hz, 1H), 6.26 (d, J = 15.9 Hz, 1H), 5.14 (s, 1H), 5.10 (s, 1H), 2.87-2.81 (m, 2H), 1.81 (s, 3H), 1.44 – 1.28 (m, 4H), 1.04 – 0.77 (m, 6H), 0.71-0.65 (m, 1H). ^{13}C NMR (151 MHz, Acetone-d6) δ 153.3, 147.7, 146.1, 141.4, 141.1, 137.0, 134.8, 131.3, 130.6, 128.3, 126.9, 125.1, 124.9, 122.2, 120.9, 83.6, 54.9, 45.1, 34.6, 34.0, 33.6, 26.2, 26.2, 18.3. HRMS (ESI) calcd. for $C_{24}H_{28}N^+$ [M-PF_6]: 330.2216, found: 330.2212. HRMS (ESI) calcd. for [PF_6]$^-$: 144.9647, found: 144.9648.



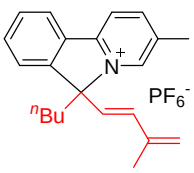
(E)-6-(2-hydroxyethyl)-6-(3-methylbuta-1,3-dien-1-yl)-6H-pyrido[2,1-a]isoindol-5-ium hexafluorophosphate (**4ag**, 51.0 mg, 61%). ^{1}H NMR (400 MHz, Acetone-d_6) δ 9.38 (dt, J = 6.3, 0.9 Hz, 1H), 8.77 (dd, J = 4.9, 0.9 Hz, 2H), 8.46 (dt, J = 7.7, 0.8 Hz, 1H), 8.21 – 8.07 (m, 1H), 7.89-7.81 (m, 3H), 6.60 (d, J = 15.9 Hz, 1H), 6.25 (d, J = 15.9 Hz, 1H), 5.16 (s, 1H), 5.13 (s, 1H), 3.53 (s, 1H), 3.51 – 3.42 (m, 1H), 3.21 – 3.12 (m, 1H), 3.02 (m, 2H), 1.82 (s, 3H). ^{13}C NMR (101 MHz, Acetone-d_6): δ153.3, 147.2, 145.6, 141.7, 141.5, 137.4, 134.7, 131.2, 127.7, 126.2, 124.8, 124.7, 121.6, 121.0, 82.9, 57.6, 40.2, 18.3. HRMS (ESI) calcd. for $C_{19}H_{20}NO^+$ [M-PF_6]: 278.1539, found: 278.1538. HRMS (ESI) calcd. for [PF_6]$^-$: 144.9647, found: 144.9647.



(E)-6-butyl-6-(2-(cyclohex-1-en-1-yl)vinyl)-6H-pyrido[2,1-a]isoindol-5-ium hexafluorophosphate (**4ai**, 84.0 mg, 88%). ^{1}H NMR (400 MHz, CD_2Cl_2) δ 8.80 (d, *J* = 6.2 Hz, 1H), 8.59 – 8.48 (m, 1H), 8.41 (d, *J* = 8.1 Hz, 1H), 8.14 (d, *J* = 7.7 Hz, 1H), 7.98-7.92 (m, 1H), 7.77-7.65 (m, 2H), 7.50 (d, *J* = 7.7 Hz, 1H), 6.27 (d, *J* = 15.8 Hz, 1H), 5.83 (t, *J* = 3.7 Hz, 1H), 5.69 (d, *J* = 15.7 Hz, 1H), 2.60 – 2.43 (m, 2H), 2.13 – 1.93 (m, 4H), 1.64 – 1.42 (m, 4H), 1.12 (q, *J* = 7.2 Hz, 3H), 0.63 (t, *J* = 7.4 Hz, 3H), 0.56 – 0.42 (m, 1H), 0.34-0.20 (m, 1H). ^{13}C NMR (151 MHz, CD_2Cl_2) δ 152.2, 146.3, 145.3, 139.5, 139.2, 135.6, 134.4, 134.2, 130.6, 129.5, 126.2, 123.8, 123.8, 120.8, 120.7, 83.8, 38.3, 26.1, 24.6, 24.2, 22.1, 22.0, 13.4. HRMS (ESI) calcd. for $C_{24}H_{28}N^+$ [M-PF_6]: 330.2216, found: 330.2209. HRMS (ESI) calcd. for [PF_6]$^-$: 144.9647, found: 144.9649.

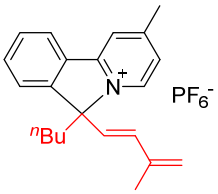


(E)-6-butyl-4-methyl-6-(3-methylbuta-1,3-dien-1-yl)-6H-pyrido[2,1-a]isoindol-5-ium hexafluorophosphate (**4ba**, 85.0 mg, 95%). ^{1}H NMR (400 MHz, CD_2Cl_2) δ 8.44 (t, *J* = 7.9 Hz, 1H), 8.30 (d, *J* = 7.6 Hz, 1H), 8.10-8.07 (m, 2H), 7.72 – 7.66 (m, 2H), 7.62 (td, *J* = 7.6, 1.0 Hz, 1H), 7.40 – 7.36 (m, 1H), 6.56 (d, *J* = 16.0 Hz, 1H), 5.66 (d, *J* = 16.1 Hz, 1H), 5.14 (s, 1H), 5.11 (s, 1H), 2.90 (s, 3H), 2.85-2.80 (m, 1H), 2.52-2.48 (m, 1H), 1.74 (s, 3H), 1.19 – 1.06 (m, 2H), 0.64 (t, *J* = 7.4 Hz, 3H), 0.42-0.35 (m, 2H). ^{13}C NMR (101 MHz, Acetone-d_6) δ 155.9, 154.9, 147.2, 146.9, 141.9, 137.7, 135.2, 131.3, 130.7, 129.6, 126.3, 124.2, 123.9, 120.6, 119.8, 86.4, 34.90, 24.9, 22.6, 20.5, 18.5, 13.8. HRMS (ESI) calcd. for $C_{22}H_{26}N^+$ [M-PF_6]: 304.2060, found: 304.2058. HRMS (ESI) calcd. for [PF_6]$^-$: 144.9647, found: 144.9651.

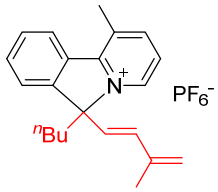


(*E*)-6-butyl-3-methyl-6-(3-methylbuta-1,3-dien-1-yl)-6H-pyrido[2,1-a]isoindol-5-ium hexafluorophosphate (**4ca**, 80.0 mg, 90%). ^{1}H NMR (400 MHz, CD_2Cl_2) δ 8.64 (d, *J* = 6.5 Hz, 1H), 8.17 (s, 1H), 8.14 – 8.05 (m, 1H), 7.75-7.64 (m, 3H), 7.48 (d, *J* = 7.6 Hz, 1H), 6.33 (d, *J* = 15.8 Hz, 1H), 5.81 (d, *J* = 15.8 Hz, 1H), 5.09 (s, 1H), 5.02 (s, 1H), 2.70 (s, 3H), 2.53 – 2.38 (m,

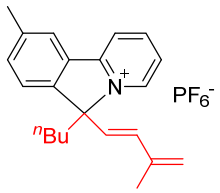
2H), 1.75 (s, 3H), 1.12 (q, J = 7.2 Hz, 2H), 0.63 (t, J = 7.3 Hz, 3H), 0.52 – 0.39 (m, 1H), 0.38 – 0.26 (m, 1H). ^{13}C NMR (101 MHz, CD_2Cl_2) δ 150.1, 147.6, 144.7, 140.6, 138.7, 138.3, 138.0, 134.0, 130.7, 129.8, 125.3, 123.8, 123.6, 121.4, 120.2, 83.4, 38.2, 24.6, 22.0, 18.5, 18.0, 13.5. HRMS (ESI) calcd. for $C_{22}H_{26}N^+$ [M-PF_6]: 304.2060, found: 304.2059. HRMS (ESI) calcd. for [PF_6]$^-$: 144.9647, found: 144.9647.



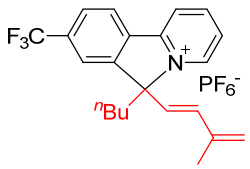
(*E*)-6-butyl-2-methyl-6-(3-methylbuta-1,3-dien-1-yl)-6H-pyrido[2,1-a]isoindol-5-ium hexafluorophosphate (**4da**, 83.0 mg, 93%). ^{1}H NMR (400 MHz, CD_2Cl_2) δ 8.64 (d, J = 6.5 Hz, 1H), 8.17 (s, 1H), 8.14 – 8.05 (m, 1H), 7.75-7.64 (m, 3H), 7.48 (d, J = 7.6 Hz, 1H), 6.33 (d, J = 15.8 Hz, 1H), 5.81 (d, J = 15.8 Hz, 1H), 5.09 (s, 1H), 5.02 (s, 1H), 2.70 (s, 3H), 2.53 – 2.38 (m, 2H), 1.75 (s, 3H), 1.12 (q, J = 7.2 Hz, 2H), 0.63 (t, J = 7.3 Hz, 3H), 0.52 – 0.39 (m, 1H), 0.38 – 0.26 (m, 1H). ^{13}C NMR (101 MHz, CD_2Cl_2) δ 160.6, 151.4, 144.8, 140.1, 137.7, 134.0, 130.3, 129.3, 126.9, 125.1, 123.5, 123.4, 121.0, 120.6, 82.1, 37.8, 24.2, 22.2, 21.7, 17.7, 13.1. HRMS (ESI) calcd. for $C_{22}H_{26}N^+$ [M-PF_6]: 304.2060, found: 304.2060. HRMS (ESI) calcd. for [PF_6]$^-$: 144.9647, found: 144.9648.



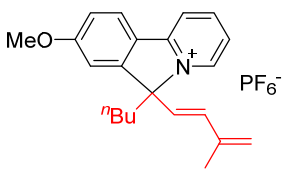
(*E*)-6-butyl-1-methyl-6-(3-methylbuta-1,3-dien-1-yl)-6H-pyrido[2,1-a]isoindol-5-ium hexafluorophosphate (**4ea**, 80.0 mg, 90%). ^{1}H NMR (400 MHz, CD_2Cl_2) δ 8.71 (d, J = 6.1 Hz, 1H), 8.32 (d, J = 7.7 Hz, 1H), 8.18 (d, J = 7.8 Hz, 1H), 7.90 (dd, J = 7.6, 6.3 Hz, 1H), 7.82-7.72 (m, 2H), 7.62 – 7.49 (m, 1H), 6.37 (d, J = 15.8 Hz, 1H), 5.82 (d, J = 15.8 Hz, 1H), 5.12 (s, 1H), 5.06 (s, 1H), 2.92 (s, 3H), 2.55-2.51 (m, 3H), 1.77 (s, 3H), 1.13 (q, J = 7.2 Hz, 2H), 0.64 (t, J = 7.4 Hz, 4H), 0.52 – 0.37 (m, 1H), 0.34 – 0.18 (m, 1H). ^{13}C NMR (151 MHz, CD_2Cl_2) δ 150.5, 147.8, 145.3, 140.4, 138.3, 137.0, 135.0, 133.9, 130.7, 130.5, 126.3, 125.5, 125.5, 123.8, 121.5, 82.4, 38.4, 24.4, 22.0, 19.6, 18.0, 13.4. HRMS (ESI) calcd. for $C_{22}H_{26}N^+$ [M-PF_6]: 304.2060, found: 304.2053. HRMS (ESI) calcd. for [PF_6]$^-$: 144.9647, found: 144.9647.



(*E*)-6-butyl-9-methyl-6-(3-methylbuta-1,3-dien-1-yl)-6H-pyrido[2,1-a]isoindol-5-ium hexafluorophosphate (**4fa**, 85.0 mg, 95%). ^{1}H NMR (400 MHz, Acetone-d$_6$) δ 9.47 (d, *J* = 6.1 Hz, 1H), 8.83 (d, *J* = 3.2 Hz, 2H), 8.33 (s, 1H), 8.22-8.18 (m, 1H), 7.74 (s, 2H), 6.59 (d, *J* = 15.9 Hz, 1H), 6.31 (d, *J* = 15.9 Hz, 1H), 5.16 (s, 1H), 5.12 (s, 1H), 2.87 – 2.79 (m, 2H), 2.57 (s, 3H), 1.83 (s, 3H), 1.22 (q, *J* = 7.4 Hz, 2H), 0.70 (t, *J* = 7.4 Hz, 3H), 0.67 – 0.57 (m, 1H), 0.55 – 0.42 (m, 1H). ^{13}C NMR (151 MHz, Acetone-d$_6$) δ153.4, 147.5, 143.3, 141.8, 141.6, 141.0, 137.7, 136.0, 131.1, 127.7, 127.1, 124.9, 124.4, 121.9, 120.9, 83.9, 38.2, 25.2, 22.6, 21.3, 18.4, 13.8. HRMS (ESI) calcd. for $C_{22}H_{26}N^{+}$ [M-PF_6]: 304.2060, found: 304.2051. HRMS (ESI) calcd. for [PF_6]$^{-}$: 144.9647, found: 144.9649.

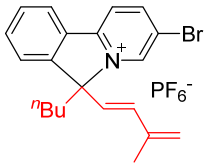


(*E*)-6-butyl-6-(3-methylbuta-1,3-dien-1-yl)-8-(trifluoromethyl)-6H-pyrido[2,1-a]isoindol-5-ium hexafluorophosphate (**4ga**, 86.0 mg, 86%). ^{1}H NMR (600 MHz, CD_2Cl_2) δ 8.89 (d, *J* = 6.1 Hz, 1H), 8.70 (t, *J* = 7.8 Hz, 1H), 8.60 (d, *J* = 8.1 Hz, 1H), 8.40 (d, *J* = 8.2 Hz, 1H), 8.14 (t, *J* = 6.8 Hz, 1H), 8.03 (d, *J* = 8.1 Hz, 1H), 7.84 (s, 1H), 6.53 (d, *J* = 15.8 Hz, 1H), 5.86 (d, *J* = 15.8 Hz, 1H), 5.24 (s, 1H), 5.18 (s, 1H), 2.70 – 2.58 (m, 2H), 1.84 (s, 3H), 1.24-1.20 (m, 2H), 0.72 (t, *J* = 7.3 Hz, 3H), 0.59 – 0.51 (m, 1H), 0.40-0.35 (m, 1H). ^{13}C NMR (151 MHz, CD_2Cl_2) δ 150.7, 147.1, 145.6, 140.2, 139.8, 139.4, 135.69 (q, *J* = 33.5 Hz), 132.8, 128.09 (q, *J* = 3.4 Hz), 127.6, 124.9, 123.9, 123.3 (q, *J* = 273.1 Hz), 122.2, 121.9, 120.71 (q, *J* = 3.9 Hz), 83.8, 38.0, 24.5, 21.9, 17.9, 13.3. ^{19}F NMR (565 MHz, CD_2Cl_2) δ -63.05 (s, 3F), -72.49 (d, *J* = 711.2 Hz, 6F). HRMS (ESI) calcd. for $C_{22}H_{23}F_3N^{+}$ [M-PF_6]: 358.1777, found: 358.1778. HRMS (ESI) calcd. for [PF_6]$^{-}$: 144.9647, found: 144.9648.

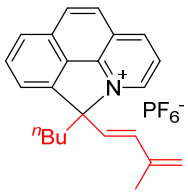


(*E*)-6-butyl-8-methoxy-6-(3-methylbuta-1,3-dien-1-yl)-6H-pyrido[2,1-a]isoindol-5-ium hexafluorophosphate (**4ha**, 77.0 mg, 83%). ^{1}H NMR (400 MHz, Acetone-d$_6$) δ 9.24 (d, *J* = 6.3 Hz, 1H), 8.76-8.68 (m, 2H), 8.38 (d, *J* = 8.7 Hz, 1H), 8.11 – 8.00 (m, 1H), 7.44 (d, *J* = 2.2 Hz, 1H), 7.36 (dd, *J* = 8.7, 2.3 Hz, 1H), 6.62 (d, *J* = 15.9 Hz, 1H), 6.24 (d, *J* = 15.9 Hz,

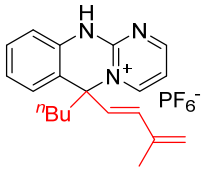
1H), 5.16 (s, 1H), 5.14 (s, 1H), 4.02 (s, 3H), 2.84 – 2.78 (m, 2H), 1.83 (s, 3H), 1.27 – 1.16 (m, 2H), 0.71 (t, J = 7.4 Hz, 3H), 0.69 – 0.59 (m, 1H), 0.56 – 0.43 (m, 1H).^{13}C NMR (151 MHz, CD_2Cl_2) δ 165.3, 152.7, 148.0, 146.0, 140.4, 138.6, 138.3, 125.5, 125.2, 124.4, 121.8, 121.5, 119.8, 117.3, 108.7, 82.6, 56.4, 38.1, 24.4, 22.0, 18.0, 13.4. HRMS (ESI) calcd. for $C_{22}H_{26}NO^+$ [M-PF_6]: 320.2009, found: 320.2009. HRMS (ESI) calcd. for [PF_6]$^-$: 144.9647, found: 144.9649.



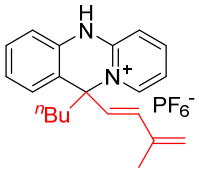
(E)-3-bromo-6-butyl-6-(3-methylbuta-1,3-dien-1-yl)-6H-pyrido[2,1-a]isoindol-5-ium hexafluorophosphate (**4ia**, 60.0 mg, 59%). ^{1}H NMR (400 MHz, Acetone-d_6) δ 9.73 (d, J = 1.4 Hz, 1H), 9.00 (d, J = 8.8 Hz, 1H), 8.83 (d, J = 8.7 Hz, 1H), 8.51 (d, J = 7.6 Hz, 1H), 8.02 – 7.92 (m, 1H), 7.92 – 7.77 (m, 2H), 6.70 (d, J = 15.9 Hz, 1H), 6.28 (d, J = 15.9 Hz, 1H), 5.18 (s, 1H), 5.15 (s, 1H), 2.90 – 2.87 (m, 2H), 1.83 (s, 3H), 1.26-1.21 (m, 2H), 0.72 (t, J = 7.4 Hz, 4H), 0.68 – 0.58 (m, 2H). ^{13}C NMR (101 MHz, Acetone-d_6) δ 152.6, 150.3, 146.0, 141.9, 141.6, 138.5, 135.4, 131.5, 130.4, 126.8, 125.1, 124.8, 122.9, 121.4, 121.3, 85.4, 38.1, 25.2, 22.6, 18.4, 13.8. HRMS (ESI) calcd. for $C_{21}H_{23}BrN^+$ [M-PF_6]: 368.1008, found: 368.1008. HRMS (ESI) calcd. for [PF_6]$^-$: 144.9647, found: 144.9647.



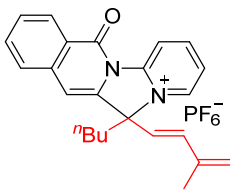
(*E*)-5-butyl-5-(3-methylbuta-1,3-dien-1-yl)-5H-isoindolo[7,1,2-hij]quinolin-4-ium hexafluorophosphate (**4ja**, 61.0 mg, 66%). ^{1}H NMR (400 MHz, Acetone-d_6) δ 9.85 (d, J = 5.8 Hz, 1H), 9.37 (d, J = 8.0 Hz, 1H), 8.55 – 8.46 (m, 2H), 8.40 (dd, J = 8.5, 2.9 Hz, 2H), 8.29 (t, J = 7.6 Hz, 1H), 8.20 (d, J = 7.2 Hz, 1H), 6.72 – 6.53 (m, 2H), 5.14 (s, 1H), 5.09 (s, 1H), 3.04 - 3.01 (m, 1H), 2.94 - 2.86 (m, 1H), 1.87 (s, 3H), 1.27 – 1.18 (m, 2H), 0.87 - 0.82 (m, 1H), 0.76-0.72 (m, 1H), 0.70 (t, J = 7.4 Hz, 3H).^{13}C NMR (101 MHz, Acetone-d_6) δ144.1, 143.1, 142.7, 141.6, 139.9, 138.5, 134.7, 132.2, 130.8, 127.5, 127.2, 127.0, 126.3, 126.1, 125.6, 123.6, 121.2, 90.8, 38.3, 25.8, 22.7, 18.4, 13.8. HRMS (ESI) calcd. for $C_{23}H_{24}N^+$ [M-PF_6]: 314.1903, found: 314.1897. HRMS (ESI) calcd. for [PF_6]$^-$: 144.9647, found: 144.9647.



(*E*)-6-butyl-6-(3-methylbuta-1,3-dien-1-yl)-6,11-dihydropyrimido[2,1-b]quinazolin-5-ium hexafluorophosphate (**4la**, 67.0 mg, 74%). ^{1}H NMR (400 MHz, Acetone-d_6) δ 8.9 (dd, *J* = 4.0, Hz, 1H), 8.69 (d, *J* = 6.8 Hz, 1H), 7.52 – 7.35 (m, 2H), 7.32 – 7.20 (m, 3H), 6.92 (d, *J* = 16.2 Hz, 1H), 6.42 (d, *J* = 16.2 Hz, 1H), 5.74 (br, 1H), 5.28 (s, 1H), 5.26 (s, 1H), 2.56 - 2.38 (m, 2H), 1.90 (s, 3H), 1.38 – 1.15 (m, 4H), 0.78 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, Acetone-d_6) δ 166.6, 151.2, 147.4, 141.5, 137.8, 133.8, 131.5, 130.4, 127.9, 126.4, 122.5, 121.1, 118.0, 114.3, 74.5, 42.7, 25.8, 22.7, 18.3, 13.8. HRMS (ESI) calcd. for $C_{20}H_{24}N_3^+$ [M-PF_6]: 306.1965, found: 306.1954. HRMS (ESI) calcd. for [PF_6]$^-$: 144.9647, found: 144.9647.

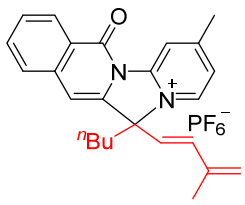


(E)-11-butyl-11-(3-methylbuta-1,3-dien-1-yl)-5,11-dihydropyrido[2,1-b]quinazolin-10-ium hexafluorophosphate (**4ka**, 64.0 mg, 71%). ^{1}H NMR (600 MHz, Acetone-d_6) δ 8.36 (d, J = 6.8 Hz, 1H), 8.11 (t, J = 7.7 Hz, 1H), 7.57 (d, J = 8.8 Hz, 1H), 7.41 – 7.37 (m, 1H), 7.33 – 7.20 (m, 4H), 6.91 (d, J = 16.2 Hz, 1H), 6.44 (d, J = 16.2 Hz, 1H), 5.28 (s, 1H), 5.26 (s, 1H), 2.60-2.55 (m, 1H), 2.44 – 2.35 (m, 1H), 1.90 (s, 3H), 1.30 – 1.23 (m, 2H), 1.19 – 1.13 (m, 1H), 1.09 – 0.99 (m, 1H), 0.75 (t, J = 7.3 Hz, 3H). ^{13}C NMR (151 MHz, Acetone-d_6) δ 148.7, 143.8, 141.4, 137.6, 137.2, 132.2, 132.0, 130.3, 128.2, 126.1, 121.7, 120.9, 117.8, 116.2, 116.0, 73.3, 42.7, 25.8, 22.6, 18.3, 13.7. HRMS (ESI) calcd. for $C_{21}H_{25}N_2^+$ [M-PF_6]: 305.2012, found: 305.2016. HRMS (ESI) calcd. for [PF_6]$^-$: 144.9647, found: 144.9647.

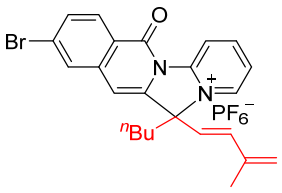


5aa, 95.0 mg, 95%. mp: 222-224 °C; ^{1}H NMR (600 MHz, CD_2Cl_2) δ 9.17 (d, *J* = 8.6 Hz, 1H), 8.82 (d, *J* = 5.6 Hz, 1H), 8.63 (t, *J* = 7.9 Hz, 1H), 8.53 (d, *J* = 8.0 Hz, 1H), 7.98 (t, *J* = 6.4 Hz, 1H), 7.89 (t, *J* = 7.5 Hz, 1H), 7.79 - 7.71 (m, 2H), 6.82 (s, 1H), 6.66 (d, *J* = 15.7 Hz, 1H), 6.07 (d, *J* = 15.7 Hz, 1H), 5.28 (s, 1H), 5.22 (s, 1H), 2.78 - 2.68 (m, 1H), 5.51-2.42 (m, 1H), 1.89 (s, 3H), 1.41 - 1.33 (d, *J* = 7.4 Hz, 4H), 1.10 - 1.06 (m, 1H), 0.78 (t, *J* = 7.3 Hz, 3H). 0.71 - 0.66 (m, 1H). ^{13}C NMR (151 MHz, CD_2Cl_2) δ 159.6,

149.0, 146.5, 140.1, 139.8, 137.9, 137.1, 135.4, 135.3, 129.2, 128.7, 127.8, 124.9, 124.7, 124.3, 122.7, 116.3, 105.7, 79.0, 39.9, 24.7, 21.9, 17.9, 13.3. HRMS (ESI) calcd. for $C_{24}H_{25}N_2O^+$ [M-PF_6]: 357.1961, found: 357.1953. HRMS (ESI) calcd. for [PF_6]$^-$: 144.9647, found: 144.9647.

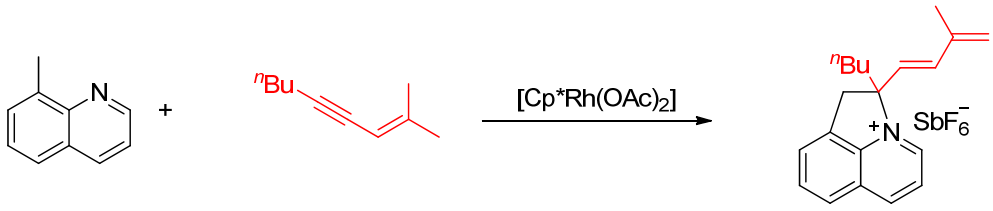


5ba, 93.0 mg, 92%. mp: 220-223 °C;^{1}H NMR (600 MHz, CD_2Cl_2) δ 8.89 (s, 1H), 8.45 (d, J = 6.3 Hz, 1H), 8.41 (d, J = 7.9 Hz, 1H).7.79 (t, *J* = 7.1 Hz, 1H), 7.73 – 7.51 (m, 2H), 6.75 (s, 1H), 6.52 (d, *J* = 15.8 Hz, 1H), 5.94 (d, *J* = 15.8 Hz, 1H), 5.16 (s, 1H), 5.12 (s, 1H), 2.70 (s, 3H), 2.53 (m, 1H), 2.37 (m, 1H), 1.79 (s, 3H), 1.22 (m, 2H), 1.03 – 0.88 (m, 1H), 0.69 (s, 3H), 0.65 – 0.52 (m, 1H). ^{13}C NMR (151 MHz, CD_2Cl_2) δ 164.2, 159.7, 146.1, 140.2, 139.1, 137.6, 136.4, 135.5, 135.3, 129.1, 128.6, 127.8, 125.7, 124.9, 124.7, 122.4, 116.1, 105.5, 78.0, 39.6, 24.8, 23.2, 21.9, 17.9, 13.4. HRMS (ESI) calcd. for $C_{25}H_{27}N_2O^+$ [M-PF_6]: 371.2118, found: 371.2112. HRMS (ESI) calcd. for [PF_6]$^-$: 144.9647, found: 144.9650.



5ca, 87.0 mg, 75%. mp: 232-234 °C;^{1}H NMR (400 MHz, CD_2Cl_2) δ 9.05 (d, *J* = 8.7 Hz, 1H), 8.65 (d, *J* = 6.1 Hz, 1H), 8.58 (t, *J* = 8.1 Hz, 1H), 8.26 (d, *J* = 8.6 Hz, 1H), 7.92 – 7.84 (m, 1H), 7.80 (d, *J* = 1.8 Hz, 1H), 7.69 (dd, *J* = 8.6, 1.8 Hz, 1H), 6.69 (s, 1H), 6.58 (d, *J* = 15.8 Hz, 1H), 5.98 (d, *J* = 15.8 Hz, 1H), 5.19 (s, 1H), 5.15 (s, 1H), 2.58 (m, 1H), 2.46 – 2.35 (m, 1H), 1.79 (s, 3H), 1.23 - 1.20 (m, 2H), 1.01 - 0.96 (m, 2H), 0.69 (t, *J* = 7.3 Hz, 3H), 0.61 – 0.52 (m, 1H). ^{13}C NMR (151 MHz, CD_2Cl_2) δ 159.1, 149.4, 146.4, 140.2, 139.7, 138.9, 137.7, 136.8, 132.3, 130.6, 130.4, 130.2, 124.8, 124.2, 123.7, 122.7, 116.5, 104.4, 79.0, 39.6, 24.7, 21.8, 17.9, 13.4. HRMS (ESI) calcd. for $C_{24}H_{24}BrN2O^+$ [M-PF_6]: 435.1067, found: 435.1067. HRMS (ESI) calcd. for [PF_6]$^-$: 144.9647, found: 144.9647.

2.3 Supplementary Table 2. Optimization Studies of Annulation of 6a with 3a [a]



6a **3a** **7aa**

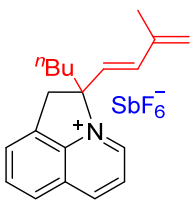
Entry	Solvent	T	Ag	additive	Yield (%)[b]
1	DCE	100	--	AgOAc (1.5 eq)	0
2	DCE	100	$AgSbF_6$ (1.0 eq)	--	0
3[c]	DCE	100	$AgSbF_6$ (1.0 eq)	AgOAc(1.5 eq)	64
4	DCE	100	$AgSbF_6$ (0.5 eq), $NaSbF_6$ (0.5 eq)	AgOAc (1.5 eq)	52
5	DCE	100	$AgSbF_6$ (1.0 eq)	AgOAc (1.5 eq)	82
6	DCE	100	$AgSbF_6$ (1.0 eq)	$Cu(OAc)_2$(2.0 eq)	60
7	THF	100	$AgSbF_6$ (1.0 eq)	AgOAc(1.0 eq)	50
8	DME	100	$AgSbF_6$ (1.0 eq)	AgOAc(1.5 eq)	77
9	Dioxane	100	$AgSbF_6$ (1.0 eq)	AgOAc(1.5 eq)	63
10	Toluene	100	$AgSbF_6$ (1.0 eq)	AgOAc(1.5 eq)	trace
11	CH_3CN	100	$AgSbF_6$ (1.0 eq)	AgOAc(1.5 eq)	12
12	CF_3CH_2OH	100	$AgSbF_6$ (1.0 eq)	AgOAc(1.5 eq)	20
13	DCE	100	$NaSbF_6$ (1.0 eq)	AgOAc(1.5 eq)	--
14	DCE	100	$Zn(OTf)_2$ (1.0 eq)	AgOAc(1.5 eq)	--

15	DCE	100	$AgBF_4$ (1.0 eq)	AgOAc(1.5 eq)	56
16	DCE	80	$AgSbF_6$ (1.0 eq)	AgOAc(1.5 eq)	72

[a]Reaction conditions: **6a** (0.2 mmol), **3a** (0.3 mmol), [Cp*Rh(OAc)$_2$] (8 mol%), solvent (2.0 mL), additive and oxidant. [b]isolated yields. [c] **3a** (0.2 mmol),

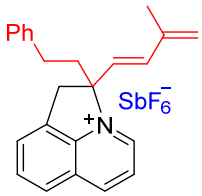
2.4 General procedure for Rhodium(III)-Catalyzed C-H Activation/annulation of 8-methylquinolines with 1,3-enynes:

General procedure B: [Cp*Rh(OAc)$_2$] (6.0 mg, 0.0016 mmol), AgOAc (50 mg, 0.30 mmol, 1.5 equiv), $AgSbF_6$ (68 mg, 0.2 mmol, 1.0 equiv) in DCE (2.0 mL) were charged into a tube under argon atmosphere in the dark. The mixture was stirred for 10 min at room temperature in the dark, followed by addition of 8-methylquinoline (0.20 mmol, 1.00 equiv) and 1,3-enyne (0.20 mmol, 1.00 equiv). The reaction tube was then placed into an oil bath at 100 °C. After the reaction was complete (24 h), the reaction vial was removed from the oil bath and cooled to ambient temperature. The reaction mixture was filtered through a pad of celite eluting with DCM:MeOH = 10:1 and was concentrated. Then the crude product was transferred to a tube with a magnetic stirring bar, followed by the addition with DCM (2.0 mL), water (2.0 mL) and $NaSbF_6$ (100 mg) at room temperature. After the reaction mixture was stirred for 10 min, the organic layers was separated and the water layers was extracted twice with DCM, The organic layers were evaporated and purified by silica gel chromatography (DCM : MeOH = 15:1) to give the indicated product.

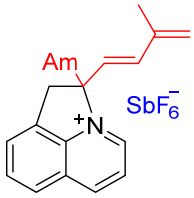


7aa, 84.0 mg, 82%. ^{1}H NMR (600 MHz, CD_2Cl_2) δ 10.06 (d, *J* = 5.5 Hz, 1H), 9.06 (d, *J* = 8.2 Hz, 1H), 8.50 – 8.35 (m, 1H), 8.15 (d, *J* = 8.1 Hz, 1H), 8.03 – 7.88 (m, 2H), 6.44 (d, *J* = 15.9 Hz, 1H), 6.23 (d, *J* = 15.9 Hz, 1H), 5.06 (s, 2H), 3.90 - 3.80 (m, 2H), 2.45-2.40 (m, 2H), 1.82 (s, 3H), 1.30 - 1.25 (m, 2H), 1.25-1.20 (m, 1H), 0.75 (t, *J* = 7.2 Hz, 3H), 0.73 – 0.64 (m, 1H). ^{13}C NMR (151 MHz, CD_2Cl_2) δ 144.1, 143.1, 140.7, 139.8, 136.3, 133.7, 132.3, 129.4, 128.9, 127.7, 125.6, 125.3, 120.4, 81.3, 39.8, 39.3, 25.5,

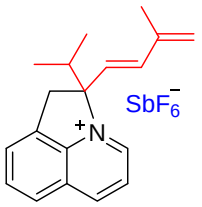
22.4, 18.3, 13.6. HRMS (ESI) calcd. for $C_{20}H_{24}N^+$ [M-SbF_6]: 278.1903, found: 278.1903. HRMS (ESI) calcd. for [SbF_6]$^-$: 234.8948, found: 234.8947.



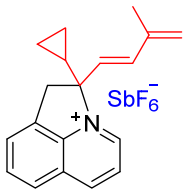
7ab, 69.0 mg, 62%. ^{1}H NMR (400 MHz, CD_2Cl_2) δ 10.19 (d, *J* = 5.7 Hz, 1H), 8.96 – 8.87 (m, 1H), 8.26 (dd, *J* = 8.3, 5.7 Hz, 1H), 8.11 (d, *J* = 8.2 Hz, 1H), 8.01-7.92 (m, 2H), 7.25 – 6.92 (m, 5H), 6.50 (d, *J* = 16.0 Hz, 1H), 6.33 (d, *J* = 16.0 Hz, 1H), 5.08 (s, 2H), 4.00 – 3.86 (m, 2H), 2.85 – 2.78 (m, 2H), 2.68 – 2.58 (m, 1H), 2.29 – 2.13 (m, 1H), 1.83 (s, 3H). ^{13}C NMR (151 MHz, CD_2Cl_2) δ 143.9, 143.5, 140.8, 139.7, 139.4, 136.5, 133.6, 132.3, 129.5, 128.8, 128.5, 128.3, 127.7, 126.4, 125.5, 125.3, 120.6, 81.1, 41.1, 39.1, 29.9, 18.4. HRMS (ESI) calcd. for $C_{24}H_{24}N^+$ [M-SbF_6]: 326.1903, found: 326.1903.



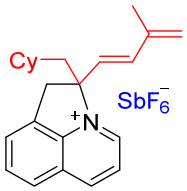
7ac, 82.0 mg, 78%. ^{1}H NMR (400 MHz, Acetone-d_6) δ 10.73 (d, *J* = 5.7 Hz, 1H), 9.43 (d, *J* = 8.3 Hz, 1H), 8.43 – 8.34 (m, 2H), 8.18 (d, *J* = 0.8 Hz, 1H), 8.07 (t, *J* = 4.1 Hz, 1H), 6.76 (d, *J* = 1.6 Hz, 2H), 5.16 (s, 1H), 5.09 (s, 1H), 4.20 (d, *J* = 18.0 Hz, 1H), 4.10 (d, *J* = 18.0 Hz, 1H), 2.74 – 2.57 (m, 2H), 1.90 (s, 3H), 1.39 – 1.17 (m, 5H), 0.97 – 0.85 (m, 1H), 0.78 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (151 MHz, Acetone-d_6) δ 145.2, 144.8, 142.3, 140.7, 136.5, 135.5, 132.9, 131.1, 130.2, 128.7, 126.1, 126.0, 120.1, 82.3, 40.6, 39.3, 32.2, 24.0, 23.0, 18.9, 14.2. HRMS (ESI) calcd. for $C_{21}H_{26}N^+$ [M-SbF_6]: 292.2060, found: 292.2058.



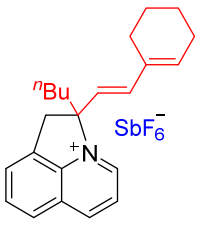
7ad, 52.0 mg, 52%. ^{1}H NMR (400 MHz, Acetone-d_6) δ 10.13 (s, 1H), 9.31 (d, *J* = 7.8 Hz, 1H), 8.41 (s, 1H), 8.35 (d, *J* = 8.2 Hz, 1H), 8.20 (d, *J* = 7.0 Hz, 1H), 8.17 – 8.04 (m, 1H), 6.72 (d, *J* = 16.0 Hz, 1H), 6.63 (d, *J* = 16.0 Hz, 1H), 5.11 (s, 2H), 4.22 – 4.01 (m, 2H), 3.18 (m, 1H), 1.91 (s, 3H), 1.21 (d, *J* = 6.6 Hz, 3H), 0.62 (d, *J* = 6.6 Hz, 3H). ^{13}C NMR (151 MHz, Acetone-d_6) δ145.5, 143.6, 141.9, 141.0, 137.5, 135.7, 133.3, 130.5, 130.4, 128.8, 126.0, 125.8, 120.5, 85.9, 37.6, 34.4, 18.7, 17.7, 16.0. HRMS (ESI) calcd. for $C_{19}H_{22}N^+$ [M-SbF_6]: 264.1747, found: 264.1732. HRMS (ESI) calcd. for [SbF_6]$^-$: 234.8948, found: 234.8948.



7ae, 60.0 mg, 61%. ^{1}H NMR (400 MHz, Acetone-d_6) δ 9.93 (d, *J* = 5.3 Hz, 1H), 9.31 (d, *J* = 8.2 Hz, 1H), 8.39 (dd, *J* = 7.6, 5.6 Hz, 1H), 8.34 (d, *J* = 8.2 Hz, 1H), 8.17 – 8.02 (m, 2H), 6.70 (d, *J* = 15.9 Hz, 1H), 6.38 (d, *J* = 15.9 Hz, 1H), 5.14 (s, 2H), 3.95 - 3.85 (m, 2H), 2.16 – 2.03 (m, 1H), 1.87 (s, 3H), 0.95-0.91 (m, 2H), 0.71 – 0.60 (m, 1H), 0.59 – 0.47 (m, 1H).^{13}C NMR (151 MHz, Acetone-d_6) δ145.3, 143.3, 141.7, 140.9, 137.2, 135.1, 133.1, 130.4, 128.9, 128.6, 125.9, 125.6, 120.6, 83.6, 38.7, 20.1, 18.6, 3.4, 1.2. HRMS (ESI) calcd. for $C_{19}H_{20}N^{+}$ [M-SbF_6]: 262.1590, found: 262.1590. HRMS (ESI) calcd. for [SbF_6]$^{-}$: 234.8948, found: 234.8948.

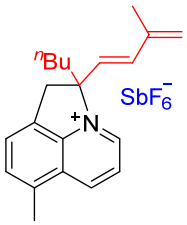


7af, 69.0 mg, 61%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.55 (d, *J* = 5.4 Hz, 1H), 9.08 (d, *J* = 8.2 Hz, 1H), 8.60 (dd, *J* = 8.0, 5.6 Hz, 1H), 8.26 – 8.14 (m, 1H), 8.08 – 7.92 (m, 2H), 6.43 (d, *J* = 15.9 Hz, 1H), 6.37 (d, *J* = 15.9 Hz, 1H), 5.12 (s, 1H), 5.08 (s, 1H), 4.18 – 3.71 (m, 2H), 2.66 (dd, *J* = 14.4, 5.1 Hz, 1H), 2.29 (dd, *J* = 14.4, 6.4 Hz, 1H), 1.91 (s, 3H), 1.62-1.26 (m, 3H), 1.41 – 0.92 (m, 8H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.5, 143.9, 140.7, 139.3, 136.3, 133.8, 132.4, 129.4, 129.2, 127.8, 126.4, 125.7, 121.1, 81.8, 47.9, 39.1, 34.8, 34.5, 34.2, 26.3, 26.2, 25.9, 18.9. HRMS (ESI) calcd. for $C_{23}H_{28}N^{+}$ [M-SbF_6]: 318.2216, found: 318.2216. HRMS (ESI) calcd. for [SbF_6]$^{-}$: 234.8948, found: 234.8950.

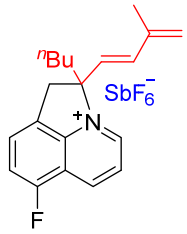


7ai, 91.0 mg, 83%. ^{1}H NMR (400 MHz, Acetone-d_6) δ 10.50 (d, *J* = 5.6 Hz, 1H), 9.43 (d, *J* = 8.2 Hz, 1H), 8.46 (dd, *J* = 8.3, 5.7 Hz, 1H), 8.40 (d, *J* = 8.3 Hz, 1H), 8.19 (d, *J* = 7.1 Hz, 1H), 8.08-8.05 (m, 1H), 6.65 (d, *J* = 16.0 Hz, 1H), 6.46 (d, *J* = 16.0 Hz, 1H), 5.93 (t, *J* = 4.0 Hz, 1H), 4.11 (dd, *J* = 56.3, 18.0 Hz, 2H), 2.77 – 2.52 (m, 2H), 2.11 – 2.03 (m, 2H), 1.61 – 1.47 (m, 4H), 1.40-1.32 (m, 3H), 0.97 – 0.88 (m, 1H), 0.81 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (151 MHz, Acetone-d_6) δ145.0, 144.2, 140.5, 137.3, 135.6, 135.3, 133.6, 132.8, 130.1, 128.5, 126.6, 126.0, 125.9, 82.3, 40.2, 39.4, 26.4, 26.3,

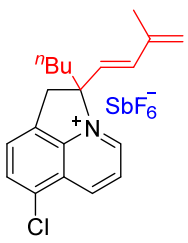
24.9, 23.0, 22.8, 14.0. HRMS (ESI) calcd. for $C_{23}H_{28}N^+$ [M-SbF_6]: 318.2216, found: 318.2216.



7ba, 75.0 mg, 72%. ^{1}H NMR (400 MHz, Acetone-d_6) δ 10.75 (d, *J* = 5.7 Hz, 1H), 9.41 (d, *J* = 8.4 Hz, 1H), 8.43 (dd, *J* = 8.4, 5.7 Hz, 1H), 8.06 (d, *J* = 7.3 Hz, 1H), 7.90 (d, *J* = 8.0 Hz, 1H), 6.74 (s, 2H), 5.15 (s, 1H), 5.09 (s, 1H), 4.10 (d, *J* = 17.8 Hz, 1H), 4.02 (d, *J* = 17.8 Hz, 1H), 2.87 (s, 3H), 2.72 – 2.59 (m, 2H), 1.90 (s, 3H), 1.43 – 1.30 (m, 3H), 0.93 – 0.86 (m, 1H), 0.82 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (151 MHz, CD_2Cl_2) δ 142.8, 141.3, 140.7, 140.3, 136.2, 134.5, 132.2, 131.2, 129.3, 129.1, 127.5, 125.1, 120.4, 81.4, 39.9, 38.9, 25.5, 22.4, 18.3, 17.6, 13.6. HRMS (ESI) calcd. for $C_{21}H_{26}N^+$ [M-SbF_6]: 292.2060, found: 292.2060.

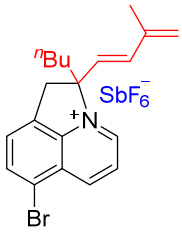


7ca, 64.0 mg, 60%. ^{1}H NMR (400 MHz, Acetone-d_6) δ 10.50 (s, 1H), 9.28 (d, *J* = 6.3 Hz, 1H), 8.53 (s, 1H), 8.18 (d, *J* = 3.7 Hz, 1H), 7.88 (dd, *J* = 10.4, 7.9 Hz, 1H), 6.76 (d, *J* = 16.0 Hz, 1H), 6.64 (d, *J* = 16.0 Hz, 1H), 5.16 (s, 1H), 5.12 (s, 1H), 4.15 - 4.05 (m, 2H), 2.74 – 2.55 (m, 2H), 1.89 (s, 3H), 1.38-1.21 (m, 3H), 1.01 – 0.88 (m, 1H), 0.83 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (151 MHz, Acetone-d_6) δ156.6 (d, *J* = 255.9 Hz), 145.8, 142.0, 141.3, 139.1, 136.7, 131.6 (d, *J* = 4.2 Hz), 130.7 (d, *J* = 7.9 Hz), 126.70, 120.4, 119.7 (d, *J* = 23.3 Hz), 117.07 (d, *J* = 20.0 Hz), 100.90, 83.8, 40.3, 39.3, 26.2, 23.1, 18.8, 14.1. HRMS (ESI) calcd. for $C_{20}H_{23}FN^+$ [M-SbF_6]: 296.1809, found: 296.1809. HRMS (ESI) calcd. for [SbF_6]$^-$: 234.8948, found: 234.8948.

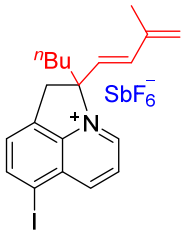


7da, 73.0 mg, 67%. ^{1}H NMR (400 MHz, Acetone-d_6) δ 10.85 (d, *J* = 5.6 Hz, 1H), 9.29 (d, *J* = 8.5Hz, 1H), 8.63 (dd, *J* = 8.5, 5.7 Hz, 1H), 8.21 (dt, *J* = 16.6, 7.1 Hz, 2H), 6.80 (d, *J* = 16.0 Hz, 1H), 6.73 (d, *J* = 16.0 Hz, 1H), 5.17 (s, 1H), 5.10 (s, 1H), 4.20 - 4.10 (m, 2H), 2.85 – 2.53 (m, 2H), 1.90 (s, 3H), 1.41 – 1.30 (m, 3H), 0.99 – 0.87 (m, 1H), 0.83 (t, *J* = 7.2 Hz, 3H).^{13}C NMR (151 MHz, Acetone-d_6) δ146.0, 142.1, 141.5, 136.7, 135.2, 132.6, 130.7, 130.6, 129.3, 127.4, 126.8, 120.2, 83.4, 40.4, 39.0, 26.3,

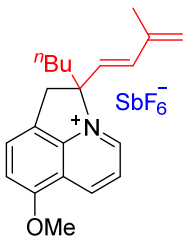
23.0, 18.8, 14.0. HRMS (ESI) calcd. for $C_{20}H_{23}ClN^+$ [M-SbF_6]: 312.1514, found: 312.1511.



7ea, 97.0 mg, 83%. ^{1}H NMR (600 MHz, CD_2Cl_2) δ 10.68 (d, *J* = 5.4 Hz, 1H), 8.95 (d, *J* = 8.4 Hz, 1H), 8.51 (dd, *J* = 8.1, 5.7 Hz, 1H), 8.12 (d, *J* = 7.6 Hz, 1H), 7.80 (d, *J* = 7.6 Hz, 1H), 6.46 (d, *J* = 15.9 Hz, 1H), 6.33 (d, *J* = 15.9 Hz, 1H), 5.08 (s, 1H), 5.07 (s, 1H), 3.82 - 3.70 (m, 2H), 2.62 – 2.39 (m, 2H), 1.83 (s, 3H), 1.35 – 1.26 (m, 2H), 1.22 - 1.18 (m, 2H), 0.75 (t, *J* = 7.1 Hz, 3H), 0.75 – 0.70 (m, 1H). ^{13}C NMR (151 MHz, CD_2Cl_2) δ 145.6, 142.7, 140.9, 140.3, 136.8, 135.4, 133.9, 129.8, 128.7, 127.6, 127.0, 120.7, 119.1, 82.5, 40.1, 38.7, 25.8, 22.5, 18.4, 13.7. HRMS (ESI) calcd. for $C_{20}H_{23}BrN^+$ [M-SbF_6]: 356.1008, found: 356.1008.

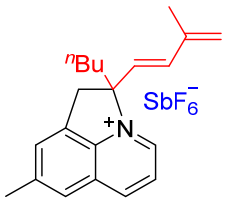


7fa, 98.0 mg, 78%. ^{1}H NMR (400 MHz, CD_2Cl_2) δ 10.17 (d, *J* = 5.6 Hz, 1H), 9.02 (d, *J* = 8.2 Hz, 1H), 8.41 (dd, *J* = 8.2, 5.7 Hz, 1H), 8.14 (dd, *J* = 7.2, 1.8 Hz, 1H), 8.03 – 7.82 (m, 2H), 6.45 (d, *J* = 15.9 Hz, 1H), 6.26 (d, *J* = 16.0 Hz, 1H), 5.09 (s, 1H), 5.07 (s, 1H), 3.90 - 3.80 (m, 2H), 2.59 – 2.34 (m, 2H), 1.84 (s, 3H), 1.36 – 1.16 (m, 2H), 1.15 – 1.01(m, 1H), 0.77 (t, *J* = 7.2 Hz, 3H), 0.75 – 0.70(m, 1H). ^{13}C NMR (151 MHz, CD_2Cl_2) δ 147.0, 144.8, 142.4, 140.8, 140.0, 136.6, 134.7, 130.6, 130.2, 128.7, 126.9, 120.6, 93.8, 82.0, 40.0, 38.8, 25.7, 22.4, 18.4, 13.6. HRMS (ESI) calcd. for C20H23IN+ [M-SbF_6]: 404.0870, found: 404.0870.

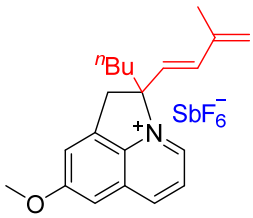


7ga, 57.0 mg, 53%. ^{1}H NMR (400 MHz, CD_2Cl_2) δ 9.89 (d, *J* = 5.6 Hz, 1H), 9.00 (d, *J* = 8.1 Hz, 1H), 8.32 – 8.18 (m, 1H), 7.84 (d, *J* = 8.0 Hz, 1H), 7.20 (d, *J* = 8.0 Hz, 1H), 6.40 (d, *J* = 15.9 Hz, 1H), 6.17 (d, *J* = 16.0 Hz, 1H), 5.07 (s, 1H), 5.05 (s, 1H), 4.04 (s, 3H), 3.81-3.71 (m, 2H), 2.41 – 2.30 (m, 2H), 1.81 (s, 3H), 1.31 – 1.24 (m, 2H), 1.24 - 1.21 (m, 1H), 0.79 – 0.72 (t, t, *J* = 7.2 Hz, 3H), 0.73 – 0.64 (m, 1H). ^{13}C NMR (151 MHz, CD_2Cl_2) δ 154.3, 143.6, 140.8, 140.6, 139.5, 136.1, 130.2, 129.1, 124.4, 124.1,

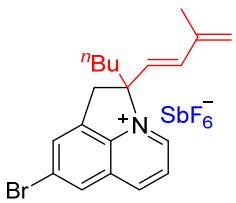
120.5, 120.3, 109.8, 82.1, 56.9, 39.9, 38.5, 25.6, 22.5, 18.4, 13.6. HRMS (ESI) calcd. for $C_{21}H_{26}NO^+$ [M-SbF_6]: 308.2009, found: 308.2009.



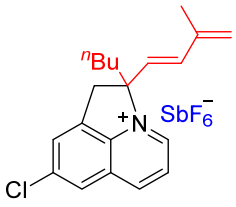
7ha, 85.0 mg, 81%. ^{1}H NMR (400 MHz, CD_2Cl_2) δ 9.89 (d, *J* = 5.6 Hz, 1H), 8.86 (d, *J* = 8.3 Hz, 1H), 8.31 (dd, *J* = 8.2, 5.6 Hz, 1H), 7.85 (s, 1H), 7.76 (d, *J* = 1.0 Hz, 1H), 6.40 (d, *J* = 16.0 Hz, 1H), 6.20 (d, *J* = 16.0 Hz, 1H), 5.07 (s, 1H), 5.05 (s, 1H), 3.89 – 3.70 (m, 2H), 2.61 (s, 3H), 2.44 – 2.31 (m, 2H), 1.80 (s, 3H), 1.28 - 1.25 (m, 2H), 1.19 - 1.12 (m, 1H), 0.75 (t, *J* = 7.2 Hz, 3H), 0.72 - 0.65 (m, 1H). ^{13}C NMR (151 MHz, CD_2Cl_2) δ 143.9, 142.9, 141.7, 140.7, 138.6, 136.1, 133.4, 131.5, 129.0, 127.6, 125.5, 123.9, 120.3, 81.3, 39.8, 39.1, 25.5, 22.4, 22.3, 18.3, 13.6. HRMS (ESI) calcd. for $C_{21}H_{26}N^+$ [M-SbF_6]: 292.2060, found: 292.2061.



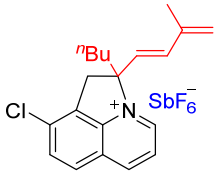
7ia, 87.0 mg, 80%. ^{1}H NMR (400 MHz, CD_2Cl_2) δ 9.57 (d, *J* = 5.6 Hz, 1H), 8.98 (d, *J* = 8.3 Hz, 1H), 8.31 (dd, *J* = 8.3, 5.7 Hz, 1H), 7.62 (d, *J* = 1.2 Hz, 1H), 7.53 (d, *J* = 1.2 Hz, 1H), 6.47 (d, *J* = 16.0 Hz, 1H), 6.21 (d, *J* = 16.0 Hz, 1H), 5.16 (s, 1H), 5.14 (s, 1H), 4.05 (s, 3H), 3.90-3.81 (m, 2H), 2.46-2.39 (m, 2H), 1.89 (s, 3H), 1.40 – 1.23 (m, 3H), 0.83 (t, *J* = 7.2 Hz, 3H), 0.80 – 0.69 (m, 1H). ^{13}C NMR (151 MHz, Acetone-d_6) δ163.6, 143.3, 142.2, 141.0, 137.1, 137.0, 136.4, 131.1, 130.1, 126.2, 123.1, 120.1, 104.4, 82.4, 57.3, 40.3, 39.1, 26.3, 23.1, 18.9, 14.1. HRMS (ESI) calcd. for C21H26NO+ [M-SbF_6]: 308.2009, found: 308.2007.



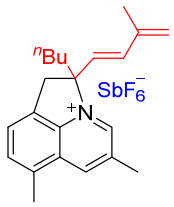
7ja, 93.0 mg, 79%. ^{1}H NMR (400 MHz, CD_2Cl_2) δ 10.31 (d, *J* = 5.1 Hz, 1H), 8.97 (d, *J* = 8.3 Hz, 1H), 8.46 (dd, *J* = 8.0, 5.6 Hz, 1H), 8.32 (s, 1H), 8.00 (s, 1H), 6.45 (d, *J* = 15.9 Hz, 1H), 6.27 (d, *J* = 15.9 Hz, 1H), 5.08 (s, 2H), 3.91 - 3.81 (m, 2H), 2.46-2.31 (m, 2H), 1.82 (s, 3H), 1.35 – 1.17 (m, 3H), 0.76 (t, *J* = 7.2 Hz, 3H), 0.73 – 0.66 (m, 1H). ^{13}C NMR (151 MHz, CD_2Cl_2) δ 144.1, 142.8, 140.8, 138.5, 136.7, 135.8, 132.8, 128.5, 128.3, 127.7, 127.1, 126.7, 120.7, 82.0, 39.9, 38.9, 25.7, 22.5, 18.4, 13.6. HRMS (ESI) calcd. for $C_{20}H_{23}BrN^+$ [M-SbF_6]: 356.1008, found: 356.1007.



7ka, 78.0 mg, 72%. ^{1}H NMR (400 MHz, Acetone-d_6) δ 10.62 (d, J = 5.6 Hz, 1H), 9.49 (d, J = 7.9 Hz, 1H), 8.55 (s, 1H), 8.50 (dd, J = 8.3, 5.7 Hz, 1H), 8.17 (s, 1H), 6.81 (d, J = 16.0 Hz, 1H), 6.70 (d, J = 16.0 Hz, 1H), 5.17 (s, 1H), 5.09 (s, 1H), 4.25 - 4.15 (m, 2H), 2.76 – 2.53 (m, 2H), 1.90 (s, 3H), 1.45 – 1.28 (m, 3H), 1.03 – 0.89 (m, 1H), 0.81 (t, J = 7.2 Hz, 3H). ^{13}C NMR (151 MHz, Acetone-d_6) δ144.8, 144.5, 142.1, 139.5, 138.0, 138.0, 136.7, 130.8, 130.6, 128.9, 127.2, 125.1, 120.2, 82.8, 40.2, 39.3, 26.2, 23.0, 18.8, 14.0. HRMS (ESI) calcd. for $C_{20}H_{23}ClN^{+}$ [M-SbF_6]: 312.1514, found: 312.1512.

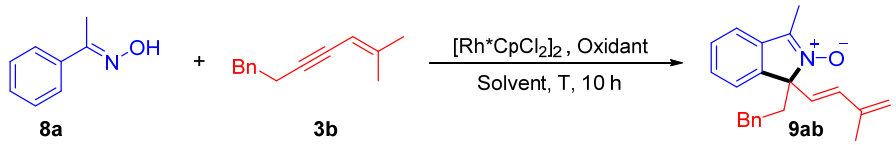


7la, 50.0 mg, 46%. ^{1}H NMR (400 MHz, CD_2Cl_2) δ 10.03 (d, J = 5.6 Hz, 1H), 9.10 (d, J = 8.2 Hz, 1H), 8.41 (dd, J = 8.3, 5.7 Hz, 1H), 8.22 (d, J = 8.9 Hz, 1H), 7.93 (d, J = 8.8 Hz, 1H), 6.52 (d, J = 15.9 Hz, 1H), 6.26 (d, J = 16.0 Hz, 1H), 5.19 (s, 1H), 5.17 (s, 1H), 3.92 - 3.82 (m, 1H), 2.59 – 2.36 (m, 2H), 1.90 (s, 3H), 1.42-1.38 (m, 2H), 1.30-1.22 (m, 1H), 0.86 (t, J = 7.2 Hz, 3H), 0.91-0.80 (m, 1H). ^{13}C NMR (151 MHz, CD_2Cl_2) δ 144.6, 144.4, 140.7, 140.1, 136.7, 135.6, 133.1, 131.4, 128.4, 127.5, 126.3, 125.9, 120.8, 81.7, 39.9, 38.8, 25.6, 22.4, 18.4, 13.6. HRMS (ESI) calcd. for $C_{20}H_{23}ClN^{+}$ [M-SbF_6]: 312.1514, found: 312.1514.



7ma, 56.0 mg, 52%. ^{1}H NMR (400 MHz, CD_2Cl_2) δ 8.91 (s, 1H), 8.69 (s, 1H), 7.73 (d, J = 7.2 Hz, 1H), 7.68 (d, J = 7.3Hz, 1H), 6.41 (d, J = 15.9 Hz, 1H), 5.99 (d, J = 16.0 Hz, 1H), 5.12 (s, 1H), 5.08 (s, 1H), 3.88 – 3.64 (m, 2H), 2.75 (s, 3H), 2.72 (s, 3H), 2.37 – 2.19 (m, 2H), 1.80 (s, 3H), 1.31 – 1.23 (m, 3H), 0.75 (t, J = 7.3 Hz, 3H), 0.65 – 0.54 (m, 1H). ^{13}C NMR (151 MHz, Acetone-d_6) δ 145.1, 142.4, 141.7, 139.7, 136.9, 136.4, 134.2, 132.7, 132.6, 131.4, 128.8, 127.8, 119.9, 82.3, 40.6, 38.8, 26.4, 23.1, 19.1, 19.0, 17.7, 14.2. HRMS (ESI) calcd. for $C_{22}H_{28}N^{+}$ [M-SbF_6]: 306.2216, found: 306.2210.

2.5 Supplementary Table 3. Optimization Studies of Annulation of 8a with 3b [a]

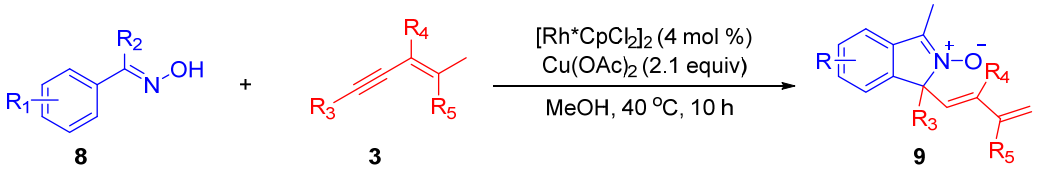


8a 3b 9ab

Entry	Solvent	oxidant	*t* (°C)	yield[b] (%)
1	MeOH	$Cu(OAc)_2$	60	78
2	EtOH	$Cu(OAc)_2$	60	74
3	DCE	$Cu(OAc)_2$	60	68
4	DMF	$Cu(OAc)_2$	60	76
5	DCM	$Cu(OAc)_2$	60	72
6	acetone	$Cu(OAc)_2$	60	58
7	MeOH	AgOAc	60	56
8	MeOH	$Cu(OAc)_2$	80	70
9	**MeOH**	**$Cu(OAc)_2$**	**40**	**88**
10	MeOH	$Cu(OAc)_2$	25	74
11	MeOH	-	40	trace
12[c]	MeOH	$Cu(OAc)_2$	40	-

[a]Reaction conditions: **8a** (0.2 mmol), **3b** (0.22 mmol), $[Cp^*RhCl_2]_2$ (4 mol %), oxidant (2.1 equiv), solvent (2 mL) under N_2 for 10 h. [b]Isolated yield. [c] No catalyst was used.

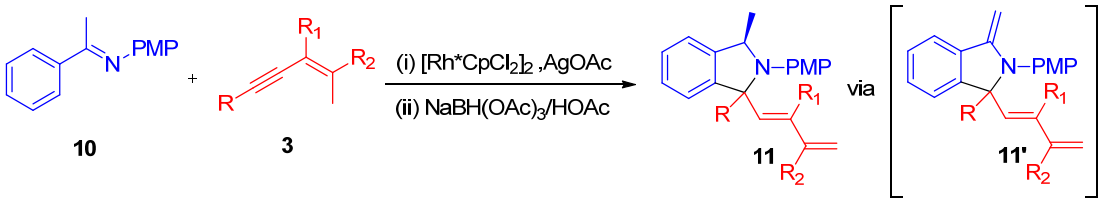
2.6 General procedure for Rhodium(III)-Catalyzed C-H Activation/annulation of oximes with 1,3-enynes:



8 3 9

General Procedure C: Oximes **8** (0.2 mmol), $[Cp^*RhCl_2]_2$ (4 mol%, 5.0 mg), $Cu(OAc)_2$ (0.42 mmol, 76.5 mg), and MeOH (2.0 mL) were charged into a pressure tube, then 1,3-enynes **3** (0.22 mmol) was subsequently added. The reaction mixture was stirred at 40 °C for 10 h under N_2 atmosphere. After cooled to room temperature, the solvent was removed under reduced pressure, the residue was purified by silica gel chromatography using PE/EA to afford compound **9**.

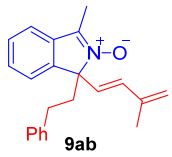
2.7 General Procedure for Rhodium(III)-Catalyzed C-H Activation/Annulation of Ketimines with 1,3-Enynes:



General Procedure D: Ketimine **10** (0.2 mmol), $[Cp^*RhCl_2]_2$ (4 mol%, 5.0 mg), AgOAc (0.42 mmol, 70.2 mg), and 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP) (2.0 mL) were charged into a pressure tube, then 1,3-enynes **3** (0.22 mmol) was subsequently added. The reaction mixture was stirred at 100 °C for 10 h under N_2 atmosphere. After cooled to room temperature, the solvent was removed under reduced pressure. Then, the residue [4] (if **11'**is exposed to air for a long time, it will decompose), without purified by silica gel chromatography, was directly dissolved in THF for the next transformation. The mixture was cooled to 0 °C and $NaBH(OAc)_3$ (0.5 mmol, 106.0 mg) was added to the solution. The mixture was stirred for 5 min before HOAc (4 mmol, 250 μL) was added dropwise. The mixture was warmed to room temperature and stirred for an additional 30 min. The reaction was quenched with NaOH solution to pH 9-10. The aqueous layer was extracted with EtOAc for three times, and the combined organic layers were washed with brine, dried over Na_2SO_4, filtered, and concentrated in vacuum. The residue was purified by silica gel chromatography to give the crude products **11**. The diastereomeric ratio was determined by ^1H NMR analysis of the crude products **11**. The pure products were obtained by washing the crude compound using *n*-pentane for two times.

(*E*)-3-methyl-1-(3-methylbuta-1, 3-dien-1-yl)-1-phenethyl-1*H*-isoindole 2-oxide (9ab).

Following the general procedure C, purified by column chromatography on silica gel (PE/EA = 6/1; PE/EA = 4/1, $R_f \approx 0.13$) to deliver the desired product as a pale-yellow solid (55.7 mg, 88% yield).

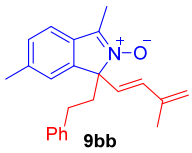


9ab

^{1}H NMR (400 MHz, acetone-d_6) δ 7.56 - 7.40 (m, 4H), 7.25 - 7.17 (m, 2H), 7.17 - 7.10 (m, 1H), 7.10 - 7.00 (m, 2H), 6.39 (d, J = 16.0 Hz, 1H), 5.95 (d, J = 16.0 Hz, 1H), 4.99 (d, J = 13.9 Hz, 2H), 2.61 - 2.50 (m, 1H), 2.45 - 2.30 (m, 1H), 2.32 (s, 3H), 2.17 (ddd, J = 13.0 , 4.8 Hz, 1H), 1.91 (ddd, J = 12.6 , 4.6 Hz, 1H), 1.80 (s, 3H). ^{13}C NMR (101 MHz, acetone-d_6) δ 141.2, 141.0, 140.0, 139.5, 136.0, 133.8, 128.6, 128.5, 128.3, 128.2, 127.2, 125.9, 122.2, 119.0, 117.7, 82.7, 38.1, 29.3, 17.7, 8.2. **HRMS** $[M + H]^+$ calcd for $C_{22}H_{24}NO$ 318.1852, found 318.1849.

(*E*)-3,6-dimethyl-1-(3-methylbuta-1,3-dien-1-yl)-1-phenethyl-1*H*-isoindole 2-oxide (9bb).

Following the general procedure C, purified by column chromatography on silica gel (PE/EA = 4/1; PE/EA = 2/1, $R_f \approx 0.15$) to deliver the desired product as yellow liquid (63.5 mg, 96% yield).

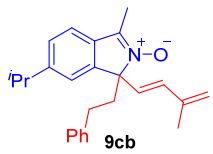


9bb

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 - 7.26 (m, 1H), 7.25 - 7.17 (m, 3H), 7.16 - 7.08 (m, 2H), 7.08 - 7.03 (m, 2H), 6.32 (d, J = 16.0 Hz, 1H), 5.86 (d, J = 16.0 Hz, 1H), 4.98 (d, J = 17.9 Hz, 2H), 2.78 - 2.65 (m, 1H), 2.45 (s, 3H), 2.39 (s, 3H), 2.36 - 2.24 (m, 2H), 1.97 - 1.84 (m, 1H), 1.82 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 141.1, 140.8, 140.4, 138.4, 134.9, 132.9, 129.4, 129.1, 128.4, 128.3, 127.5, 126.0, 122.9, 119.3, 118.5, 82.8, 37.9, 29.4, 21.9, 18.5, 9.5. **HRMS** $[M + H]^+$ calcd for $C_{23}H_{26}NO$ 332.2009, found 332.2007.

(*E*)-6-isopropyl-3-methyl-1-(3-methylbuta-1,3-dien-1-yl)-1-phenethyl-1*H*-isoindole 2-oxide (9cb).

Following the general procedure C, purified by column chromatography on silica gel (PE/EA = 4/1; PE/EA = 2/1, $R_f \approx 0.32$) to deliver the desired product as a colorless oil (44.3 mg, 62% yield).

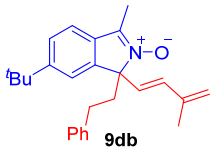


9cb

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 - 7.27 (m, 2H), 7.24 - 7.17 (m, 2H), 7.17 - 7.08 (m, 2H), 7.07 - 6.98 (m, 2H), 6.31 (d, J = 16.0 Hz, 1H), 5.88 (d, J = 16.0 Hz, 1H), 5.00 (s, 1H), 4.94 (s, 1H), 3.08 - 2.94 (m, 1H), 2.80 - 2.65 (m, 1H), 2.39 (s, 3H), 2.36 - 2.24 (m, 2H), 1.95 - 1.85 (m, 1H), 1.82 (s, 3H), 1.31 (d, J = 6.9 Hz, 6H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 149.5, 145.8, 141.2, 140.9, 140.3, 135.0, 133.3, 128.4, 128.3, 127.5, 126.7, 126.0, 120.5, 119.4, 118.5, 82.9, 38.0, 34.4, 29.5, 24.2, 24.1, 18.5, 9.4. **HRMS** $[M + H]^+$ calcd for $C_{25}H_{30}NO$ 360.2322, found 360.2324.

(*E*)-6-(tert-butyl)-3-methyl-1-(3-methylbuta-1,3-dien-1-yl)-1-phenethyl-1*H*-isoindole 2-oxide (9db).

Following the general procedure C, purified by column chromatography on silica gel (PE/EA = 4/1; PE/EA = 1/2, $R_f \approx 0.47$) to deliver the desired product as a colorless oil (42.8 mg, 57% yield).

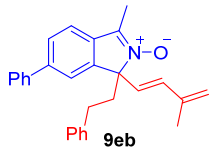


9db

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (dd, J = 8.0, 1.8 Hz, 1H), 7.35 - 7.29 (m, 2H), 7.23 - 7.16 (m, 2H), 7.15 - 7.09 (m, 1H), 7.06 - 7.00 (m, 2H), 6.30 (d, J = 16.0 Hz, 1H), 5.89 (d, J = 16.0 Hz, 1H), 5.00 (s, 1H), 4.93 (s, 1H), 2.80 - 2.66 (m, 1H), 2.39 (s, 3H), 2.35 - 2.66 (m, 2H), 1.95 - 1.85 (m, 1H), 1.8 (s, 3H), 1.38 (s, 9H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 151.8, 142.1, 141.2, 140.9, 140.0, 135.0, 132.9, 128.3 (two overlapping signals), 127.5, 126.0, 125.6, 119.4, 119.1, 118.5, 83.1, 38.1, 35.2, 31.5, 29.5, 18.4, 9.4. **HRMS** $[M + H]^+$ calcd for $C_{26}H_{32}NO$ 374.2478, found 374.2482.

(*E*)-3-methyl-1-(3-methylbuta-1,3-dien-1-yl)-1-phenethyl-6-phenyl-1*H*-isoindole 2-oxide (9eb).

Following the general procedure C, purification by column chromatography on silica gel (PE/EA = 6/1; PE/EA = 4/1, $R_f \approx 0.15$) to deliver the desired product as colorless oil (36.6 mg, 47% yield).

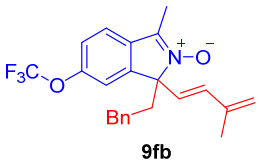


9eb

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (dd, J = 7.9, 1.6 Hz, 1H), 7.64 - 7.59 (m, 2H), 7.53 - 7.43 (m, 4H), 7.43 - 7.36 (m, 1H), 7.23 - 7.16 (m, 2H), 7.16 – 7.09 (m, 1H), 7.08 - 7.01 (m, 2H), 6.37 (d, J = 16.0 Hz, 1H), 5.90 (d, J = 16.0 Hz, 1H), 5.01 (s, 1H), 4.96 (s, 1H), 2.83 - 2.69 (m, 1H), 2.43 (s, 3H), 2.39 - 2.29 (m, 2H), 2.05 - 1.92 (m, 1H), 1.82 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 147.8, 141.6, 141.1, 141.0, 140.7, 140.4, 135.2, 134.7, 129.0, 128.4, 128.3, 127.9, 127.7, 127.4, 127.2, 126.0, 120.8, 119.7, 118.8, 83.2, 38.1, 29.5, 18.5, 9.5. **HRMS** $[M + H]^+$ calcd for $C_{28}H_{28}NO$ 394.2165, found 394.2163.

(*E*)-3-methyl-1-(3-methylbuta-1,3-dien-1-yl)-1-phenethyl-6-(trifluoromethoxy)-1*H*-isoindole 2-oxide (9fb).

Following the general procedure C, purification by column chromatography on silica gel (PE/EA = 4/1; PE/EA = 2/1, $R_f \approx 0.23$) to deliver the desired product as a light yellow oil (68.9 mg, 86% yield).

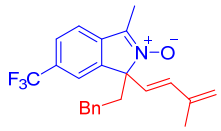


9fb

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (d, J = 8.3 Hz, 1H), 7.34 - 7.28 (m, 1H), 7.24 - 7.10 (m, 4H), 7.06 - 7.00 (m, 2H), 6.28 (d, J = 16.0 Hz, 1H), 5.85 (d, J = 16.0 Hz, 1H), 5.03 (s, 1H), 4.97 (s, 1H), 2.82 - 2.63(m, 1H), 2.38 (s, 3H), 2.36 - 2.25 (m, 2H), 1.98 - 1.86 (m, 1H), 1.81 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 149.0, 141.6, 140.8, 140.5, 140.3, 135.5, 134.4, 128.4, 128.3, 126.5, 126.2, 121.7, 121.6, 120.2, 119.2, 115.8, 83.2, 38.1, 29.5, 18.4, 9.3. **^{19}F NMR (376 MHz, $CDCl_3$)** δ -58.0. **HRMS** $[M + H]^+$ calcd for $C_{23}H_{23}F_3NO_2$ 402.1675, found 402.1679.

(*E*)-3-methyl-1-(3-methylbuta-1,3-dien-1-yl)-1-phenethyl-6-(trifluoromethyl)-1*H*-isoindole 2-oxide (9gb).

Following the general procedure C, purification by column chromatography on silica gel (PE/EA = 6/1; PE/EA = 2/1, $R_f \approx 0.29$) to deliver the desired product as a white solid (67.6 mg, 88% yield).

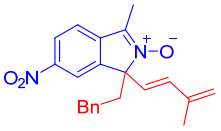


9gb

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 - 7.65 (m, 1H), 7.52 - 7.43 (m, 2H), 7.23 - 7.16 (m, 2H), 7.16 - 7.09 (m, 1H), 7.06 - 6.97 (m, 2H), 6.29 (d, J = 16.0 Hz, 1H), 5.82 (d, J = 16.0 Hz, 1H), 5.05 (s, 1H), 4.98 (s, 1H), 2.82 - 2.68 (m, 1H), 2.41 (s, 3H), 2.39 - 2.23 (m, 2H), 1.96 - 1.85 (m, 1H), 1.82 (d, J = 0.5 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** 140.7, 140.3, 140.2, 139.1, 138.4, 135.6, 129.6 (q, J = 32.5 Hz), 128.4, 128.3, 126.4, 126.2, 126.1 (q, J = 3.9 Hz), 124.1 (q, J = 270.7 Hz), 119.4, 119.3, 118.6 (q, J = 2.8 Hz), 83.5, 37.8, 29.4, 18.4, 9.4. **^{19}F NMR (376 MHz, $CDCl_3$)** δ -61.9. **HRMS** $[M + H]^+$ calcd for $C_{23}H_{23}F_3NO$ 386.1726, found 386.1728.

(*E*)-3-methyl-1-(3-methylbuta-1,3-dien-1-yl)-6-nitro-1-phenethyl-1*H*-isoindole 2-oxide (9hb).

Following the general procedure C, purification by column chromatography on silica gel (PE/EA = 6/1; PE/EA = 4/1, $R_f \approx 0.14$) delivered the desired product as yellow oil (71.0 mg, 98% yield).

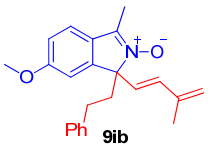


9hb

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.32 (dd, J = 8.4, 2.1 Hz, 1H), 8.08 (d, J = 1.9 Hz, 1H), 7.48 (d, J = 8.4 Hz, 1H), 7.21 - 7.14 (m, 2H), 7.14 - 7.08 (m, 1H), 7.02 - 6.95 (m, 2H), 6.30 (d, J = 16.0 Hz, 1H), 5.80 (d, J = 16.0 Hz, 1H), 5.06 (s, 1H), 5.00 (s, 1H), 2.82 - 2.70 (m, 1H), 2.50 - 2.38 (m, 1H), 2.42 (s,3H), 2.37 - 2.26 (m, 1H), 2.00 - 1.88 (m, 1H), 1.81 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 147.1, 141.7, 140.6, 140.5, 140.5, 139.8, 135.9, 128.4, 128.2, 126.2, 125.9, 125.0, 119.8, 119.2, 117.4, 83.9, 37.8, 29.5, 18.3, 9.4. **HRMS** $[M + H]^+$ calcd for $C_{22}H_{23}N_2O_3$ 363.1703, found 363.1700.

(*E*)-6-methoxy-3-methyl-1-(3-methylbuta-1,3-dien-1-yl)-1-phenethyl-1*H*-isoindol e 2-oxide (9ib).

Following the general procedure C, purified by column chromatography on silica gel (PE/EA = 6/1; PE/EA = 4/1, $R_f \approx 0.12$) to deliver the desired product as colorless oil (22.5 mg, 32% yield).

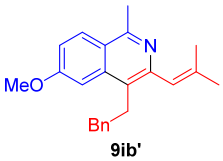


9ib

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (d, J = 8.4 Hz, 1H), 7.24 - 7.17 (m, 2H), 7.17 - 7.10 (m, 1H), 7.09 - 7.02 (m, 2H), 6.96 (dd, J = 8.4, 2.3 Hz, 1H), 6.86 (d, J = 2.3 Hz, 1H), 6.32 (d, J = 16.0 Hz, 1H), 5.87 (d, J = 16.0 Hz, 1H), 5.00 (s, 1H), 4.96 (s, 1H), 3.87 (s, 3H), 2.82 - 2.66 (m, 1H), 2.39 (s, 3H), 2.36 - 2.21 (m, 2H), 1.96 - 1.85 (m, 1H), 1.82 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 160.4, 142.4, 142.2, 141.1, 140.8, 135.0, 128.4, 128.3, 128.1, 127.3, 126.0, 120.6, 118.7, 113.6, 109.4, 82.6, 55.7, 38.0, 29.4, 18.4, 9.5. **HRMS** [M + H]$^+$ calcd for $C_{23}H_{26}NO_2$ 348.1958, found 348.1961.

6-Methoxy-1-methyl-3-(2-methylprop-1-en-1-yl)-4-phenethylisoquinoline (9ib').

Following the general procedure C, purification by column chromatography on silica gel (PE/EA = 6/1; PE/EA = 4/1, $R_f \approx 0.29$) to deliver the desired product as colorless oil (6.8 mg, 10% yield).

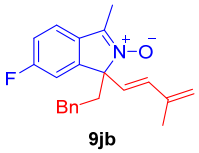


9ib'

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, J = 9.1 Hz, 1H), 7.30 - 7.23 (m, 3H), 7.23 - 7.11 (m, 4H), 7.06 (d, J = 2.5 Hz, 1H), 6.18 (s, 1H), 3.89 (s, 3H), 3.17 - 3.07 (m, 2H), 3.03 - 2.95(m, 2H), 2.92 (s, 3H), 2.02 (d, J = 1.2 Hz, 3H), 1.40 (d, J = 0.8 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 160.3, 155.9, 151.7, 142.6, 138.3, 137.5, 128.5, 128.2, 127.6, 125.7, 124.7, 121.4, 120.1, 117.9, 103.7, 55.3, 38.1, 35.8, 25.4, 22.3, 19.7. **HRMS** [M + H]$^+$ calcd for $C_{23}H_{26}NO$ 332.2009, found 332.2012.

(*E*)-6-fluoro-3-methyl-1-(3-methylbuta-1,3-dien-1-yl)-1-phenethyl-1*H*-isoindole 2-oxide (9jb).

Following the general procedure C, purification by column chromatography on silica gel (PE/EA = 4/1; PE/EA = 1/1, $R_f \approx 0.40$) to deliver the desired product as a colorless oil (53.0 mg, 79% yield).



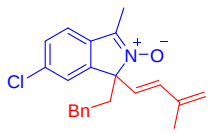
9jb

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (dd, J = 8.3, 4.8 Hz, 1H), 7.24 - 7.18 (m, 2H), 7.18 - 7.10 (m, 2H), 7.10 - 7.00 (m, 3H), 6.29 (d, J = 16.0 Hz, 1H), 5.85 (d, J = 16.0 Hz, 1H), 5.03 (s, 1H), 4.97 (s, 1H), 2.80 - 2.64 (m, 1H), 2.38 (s, 3H), 2.35 - 2.21 (m, 2H), 1.97 - 1.84 (m,

1H), 1.81 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 163.1 (d, J = 247.8 Hz), 142.2 (d, J = 8.4 Hz), 141.2, 140.9, 140.4, 135.3, 131.6 (d, J = 2.7 Hz), 128.4, 128.3, 126.7, 126.1, 120.7 (d, J = 8.4 Hz), 119.1, 115.9 (d, J = 23.0Hz), 110.5 (d, J = 24.7 Hz), 83.0 (d, J = 2.2 Hz), 38.0, 29.4, 18.4, 9.4. **^{19}F NMR (376 MHz, $CDCl_3$)** δ -112.1. **HRMS** $[M + H]^+$ calcd for $C_{22}H_{23}FNO$ 336.1758, found 336.1756.

(*E*)-6-chloro-3-methyl-1-(3-methylbuta-1,3-dien-1-yl)-1-phenethyl-1*H*-isoindole 2-oxide (9kb).

Following the general procedure C, purified by column chromatography on silica gel (PE/EA = 4/1; PE/EA = 2/1, $R_f \approx 0.13$) to deliver the desired product as yellow oil (62.4 mg, 89% yield).

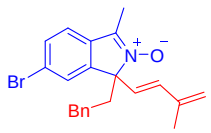


9kb

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (dd, J = 8.1, 1.7 Hz, 1H), 7.41 (d, J = 1.6 Hz, 1H), 7.25 - 7.17 (m, 3H), 7.17 - 7.10 (m, 1H), 7.09 - 7.02 (m, 2H), 6.30 (d, J = 16.0 Hz, 1H), 5.81 (d, J = 16.0 Hz, 1H), 5.03 (s, 1H), 4.99 (s, 1H), 2.80 - 2.64 (m, 1H), 2.37 (s, 3H), 2.34 - 2.20 (m, 2H), 2.01 - 1.86 (m, 1H), 1.81 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 141.7, 141.0, 140.8, 140.3, 135.4, 134.6, 131.9, 128.4, 128.3, 126.7, 126.1, 125.4, 122.1, 120.5, 119.2, 83.0, 37.8, 29.4, 18.4, 9.3. **HRMS** $[M + H]^+$ calcd for $C_{22}H_{23}ClNO$ 352.1463, found 352.1460.

(*E*)-6- bromo -3-methyl-1-(3-methylbuta-1,3-dien-1-yl)-1-phenethyl-1*H*-isoindole 2-oxide (9lb).

Following the general procedure C, purification by column chromatography on silica gel (PE/EA = 6/1; PE/EA = 4/1, $R_f \approx 0.06$) to deliver the desired product as yellow oil (64.5 mg, 82% yield).



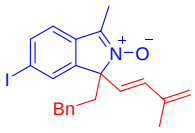
9lb

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (dd, J = 8.1, 1.7 Hz, 1H), 7.41 (d, J = 1.6 Hz, 1H), 7.25 - 7.18 (m, 3H), 7.17 - 7.10 (m, 1H), 7.08 - 7.00 (m, 2H), 6.30 (d, J = 16.0 Hz, 1H), 5.81 (d, J = 16.0 Hz, 1H), 5.03 (s, 1H), 4.99 (s, 1H), 2.80 - 2.64(m, 1H), 2.37 (s, 3H), 2.34 - 2.23 (m, 2H), 2.00 - 1.85 (m, 1H), 1.81 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 141.7, 141.0,

140.8, 140.3, 135.4, 134.6, 131.9, 128.4, 128.3, 126.7, 126.1, 125.4, 122.1, 120.5, 119.2, 83.0, 37.8, 29.4, 18.4, 9.3. **HRMS** $[M + H]^+$ calcd for $C_{22}H_{23}BrNO$ 396.0958, found 396.0952.

(*E*)-6- iodo -3-methyl-1-(3-methylbuta-1,3-dien-1-yl)-1-phenethyl-1*H*-isoindole 2-oxide (9mb).

Following the general procedure C, purified by column chromatography on silica gel (PE/EA = 6/1; PE/EA = 4/1, $R_f \approx 0.05$) to deliver the desired product as a pale yellow foam (54.3 mg, 61% yield).

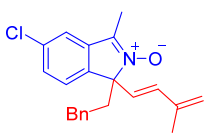


9mb

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (dd, J = 8.0, 1.2 Hz, 1H), 7.58 (s, 1H), 7.21 (t, J = 7.2 Hz, 2H), 7.18 - 7.08 (m, 2H), 7.08 - 7.00 (m, 2H), 6.29 (d, J = 16.0 Hz, 1H), 5.79 (d, J = 16.0 Hz, 1H), 5.04 (s, 1H), 4.99 (s, 1H), 2.78 - 2.63 (m, 1H), 2.37 (s, 3H), 2.33 - 2.22 (m, 2H), 1.97 - 1.87 (m, 1H), 1.81 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 141.8, 141.1, 140.9, 140.3, 137.8, 135.4, 135.2, 131.0, 128.4, 128.3, 126.7, 126.2, 120.7, 119.1, 93.2, 82.9, 37.7, 29.4, 18.4, 9.3. **HRMS** $[M + H]^+$ calcd for $C_{22}H_{23}INO$ 444.0819, found 444.0821.

(*E*)-5-chloro-3-methyl-1-(3-methylbuta-1,3-dien-1-yl)-1-phenethyl-1*H*-isoindole 2-oxide (9nb).

Following the general procedure C, purified by column chromatography on silica gel (PE/EA = 6/1; PE/EA = 4/1, $R_f \approx 0.19$) to deliver the desired product as pale yellow oil (38.5 mg, 55% yield).

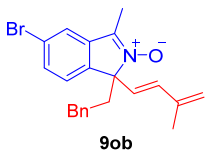


9nb

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (d, J = 1.8 Hz, 1H), 7.37 - 7.34 (m, 1H), 7.25 - 7.17 (m, 3H), 7.17 - 7.11 (m, 1H),7.08 - 6.97 (m, 2H), 6.26 (d, J = 16.0 Hz, 1H), 5.84 (d, J = 16.0 Hz, 1H), 5.02 (s, 1H), 4.95 (s, 1H), 2.78 - 2.62 (m, 1H), 2.36 (s, 3H), 2.33 - 2.21 (m, 2H), 1.98 - 1.86 (m, 1H), 1.81 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 140.9, 140.8, 140.4, 137.9, 137.4, 135.3, 134.8, 128.4, 128.3, 127.6, 126.9, 126.1, 123.2, 119.6, 119.0, 83.1, 38.1, 29.5, 18.4, 9.3. **HRMS** $[M + H]^+$ calcd for $C_{22}H_{23}ClNO$ 352.1463, found 352.1460.

(*E*)-5-bromo-3-methyl-1-(3-methylbuta-1,3-dien-1-yl)-1-phenethyl-1*H*-isoindole 2-oxide (9ob).

Following the general procedure C, purification by column chromatography on silica gel (PE/EA = 6/1; PE/EA = 4/1, $R_f \approx 0.19$) to deliver the desired product as a pale yellow oil (38.5 mg, 55% yield).

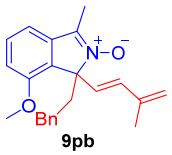


9ob

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (d, J = 1.7 Hz, 1H), 7.53 - 7.49 (m, 1H), 7.24 - 7.18 (m, 2H), 7.17 - 7.10 (m, 2H), 7.08 - 6.98 (m, 2H), 6.26 (d, J = 16.0 Hz, 1H), 5.83 (d, J = 16.0 Hz, 1H), 5.02 (s, 1H), 4.95 (s, 1H), 2.76 - 2.63 (m, 1H), 2.36 (s, 3H), 2.33 - 2.21 (m, 2H), 1.97 - 1.85 (m, 1H), 1.81 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 140.9, 140.5, 140.4, 138.4, 137.7, 135.3, 130.4, 128.4, 128.3, 126.8, 126.1, 123.6, 122.7, 122.5, 119.0, 83.2, 38.0, 29.4, 18.4, 9.3. **HRMS** $[M + H]^+$ calcd for $C_{22}H_{23}BrNO$ 396.0958, found 396.0960.

(*E*)-7-methoxy-3-methyl-1-(3-methylbuta-1,3-dien-1-yl)-1-phenethyl-1*H*-isoindol e 2-oxide (9pb).

Following the general procedure C, purification by column chromatography on silica gel (PE/EA = 6/1; PE/EA = 4/1, $R_f \approx 0.19$) to deliver the desired product as colorless oil (18.8 mg, 28% yield).

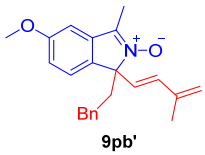


9pb

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (t, J = 7.9 Hz, 1H), 7.17 (t, J = 7.3 Hz, 2H), 7.13 - 7.07 (m, 1H), 7.05 - 6.97 (m, 3H), 6.88 (d, J = 8.4 Hz, 1H), 6.27 (d, J = 15.9 Hz, 1H), 5.89 (d, J = 15.9 Hz, 1H), 4.96 (s, 1H), 4.92 (s, 1H), 3.85 (s, 3H), 2.77 - 2.59 (m, 2H), 2.37 (s, 3H), 2.30 - 2.15 (m, 1H), 1.92 - 1.81 (m, 1H), 1.81 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 153.8, 141.8, 141.4, 141.1, 136.8, 134.2, 130.2, 128.4, 128.1, 126.6, 126.3, 125.7, 118.0, 112.2, 110.8, 83.9, 55.5, 35.2, 29.9, 18.5, 9.5. **HRMS** $[M + H]^+$ calcd for $C_{23}H_{26}NO_2$ 348.1958, found 348.1951.

(*E*)-5-methoxy-3-methyl-1-(3-methylbuta-1,3-dien-1-yl)-1-phenethyl-1*H*-isoindol e 2-oxide (9pb').

Following the general procedure C, purification by column chromatography on silica gel (PE/EA = 6/1; PE/EA = 4/1, $R_f \approx 0.21$) to deliver the desired product as colorless oil (18.8 mg, 18% yield).

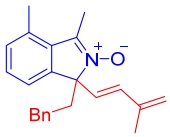


9pb'

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (dd, J = 8.1, 1.8 Hz, 1H), 7.33 - 7.27 (m, 1H), 7.27 (d, J = 1.8 Hz, 1H), 7.23 - 7.16 (m, 2H), 7.16 - 7.10 (m, 1H), 7.08 - 7.00 (m, 2H), 6.30 (d, J = 16.0 Hz, 1H), 5.82 (d, J = 16.0 Hz, 1H), 5.03 (s, 1H), 4.99 (s, 1H), 2.79 - 2.64 (m, 1H), 2.37 (s, 3H), 2.35 - 2.23 (m, 2H), 2.00 - 1.86 (m, 1H), 1.81 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 141.5, 141.1, 140.8, 140.3, 135.4, 134.2, 134.1, 129.1, 128.4, 128.3, 126.7, 126.1, 122.7, 120.3, 119.2, 83.0, 37.9, 29.4, 18.4, 9.4. **HRMS** $[M + H]^+$ calcd for $C_{23}H_{26}NO_2$ 348.1958, found 348.1951.

(*E*)-3,4-dimethyl-1-(3-methylbuta-1,3-dien-1-yl)-1-phenethyl-1*H*-isoindole 2-oxide (9qb).

Following the general procedure C, purification by column chromatography on silica gel (PE/EA = 6/1; PE/EA = 4/1, $R_f \approx 0.19$) to deliver the desired product as a colorless oil (43.2 mg, 65% yield).

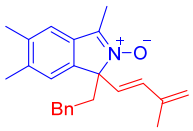


9qb

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (t, J = 7.6 Hz, 1H), 7.25 - 7.16 (m, 3H), 7.16 - 7.10 (m, 2H), 7.08 - 7.02(m, 2H), 6.29 (d, J = 16.0 Hz, 1H), 5.86 (d, J = 16.0 Hz, 1H), 4.99 (s, 1H), 4.94 (s, 1H), 2.80 - 2.66 (m, 1H), 2.60 (s, 3H), 2.58 (s, 3H), 2.34 - 2.19 (m, 2H), 1.94 - 1.80 (m, 1H), 1.80 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 143.0, 141.1, 140.8, 140.5, 134.8, 133.5, 131.2, 131.2, 128.4, 128.3, 127.9, 127.7, 126.0, 119.9, 118.5, 81.9, 38.2, 29.4, 19.8, 18.4, 12.5. **HRMS** $[M + H]^+$ calcd for $C_{23}H_{26}NO$ 332.2009, found 332.2007.

(*E*)-3,5,6-trimethyl-1-(3-methylbuta-1,3-dien-1-yl)-1-phenethyl-1*H*-isoindole 2-oxide (9rb).

Following the general procedure C, purification by column chromatography on silica gel (PE/EA = 6/1; PE/EA = 4/1, $R_f \approx 0.17$) to deliver the desired product as a colorless oil (58.7 mg, 85% yield).

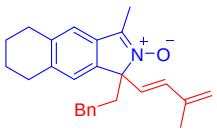


9rb

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 - 7.17 (m, 2H), 7.16 (s, 1H), 7.15 - 7.09 (m, 1H), 7.09 - 7.01 (m, 3H), 6.31 (d, J = 16.0 Hz, 1H), 5.86 (d, J = 16.0 Hz, 1H), 4.99 (s, 1H), 4.95 (s, 1H), 2.77 - 2.61 (m, 1H), 2.37 (s, 3H), 2.35 (s, 6H) 2.32 - 2.23 (m, 2H), 1.96 - 1.86 (m, 1H), 1.81 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 142.0, 141.2, 141.0, 137.8, 137.2, 136.8, 134.8, 133.4, 128.4, 128.3, 127.8, 125.9, 123.4, 120.6, 118.4, 82.7, 38.0, 29.4, 20.3, 20.1, 18.5, 9.4. **HRMS** $[M + H]^+$ calcd for $C_{24}H_{28}NO$ 346.2165, found 346.2165.

(*E*)-3-methyl-1-(3-methylbuta-1,3-dien-1-yl)-1-phenethyl-5,6,7,8-tetrahydro-1*H*-benzo[f]isoindole 2-oxide (9sb).

Following the general procedure C, purification by column chromatography on silica gel (PE/EA = 6/1; PE/EA = 4/1, $R_f \approx 0.19$) to deliver the desired product as a white solid (48.9 mg, 66% yield).

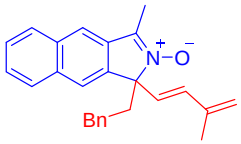


9sb

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20 (t, J = 7.3 Hz, 2H), 7.16 - 7.08 (m, 1H), 7.08 - 7.01 (m, 3H), 6.95 (s, 1H), 6.33 (d, J = 16.0 Hz, 1H), 5.86 (d, J = 16.0 Hz, 1H), 4.99 (s, 2H), 4.96 (s, 1H), 2.94 - 2.76 (m, 4H), 2.75 - 2.61 (m, 1H), 2.37 (s, 3H), 2.35 - 2.22 (m, 2H), 1.99 - 1.90 (m, 1H), 1.85 (q, J = 6.1 Hz, 4H), 1.81 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 142.0, 141.2, 141.0, 137.7, 137.5, 137.4, 134.7, 133.0, 128.4, 128.2, 127.9, 125.9, 122.9, 120.0, 118.3, 82.6, 38.0, 29.9, 29.7, 29.5, 23.0, 23.0, 18.5, 9.4. **HRMS** $[M + H]^+$ calcd for $C_{26}H_{30}NO$ 372.2322, found 372.2319.

(*E*)-3-methyl-1-(3-methylbuta-1,3-dien-1-yl)-1-phenethyl-1*H*-benzo[f]isoindole 2-oxide (9tb).

Following the general procedure C, purification by column chromatography on silica gel (PE/EA = 6/1; PE/EA = 2/1, $R_f \approx 0.25$) to deliver the desired product as a pale yellow solid (55.4 mg, 75% yield).



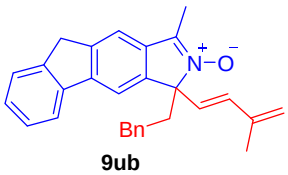
9tb

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (dd, J = 9.7, 4.6 Hz, 2H), 7.79 (s, 1H), 7.70 (s, 1H), 7.59 - 7.49 (m, 2H), 7.18 (t, J = 7.5 Hz,

2H), 7.14 - 7.07 (m, 1H), 7.07 - 7.01 (m, 2H), 6.38 (d, J = 16.0 Hz, 1H), 5.98 (d, J = 16.0 Hz, 1H), 5.00 (s, 1H), 4.94 (s, 1H), 2.90 - 2.72 (m, 1H), 2.49 (s, 3H), 2.45 - 2.29 (m, 2H), 2.02 - 1.90 (m, 1H), 1.83 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 142.1, 141.1, 140.7, 137.2, 135.1, 133.9, 133.6, 133.0, 128.5, 128.4 (overlapping), 128.3, 127.8, 126.9, 126.6, 126.0, 121.3, 118.8, 118.2, 82.6, 38.5, 29.5, 18.5, 9.5. **HRMS** $[M + H]^+$ calcd for $C_{26}H_{26}NO$ 368.2009, found 368.2004.

(*E*)-1-methyl-3-(3-methylbuta-1,3-dien-1-yl)-3-phenethyl-3,9-dihydroindeno[1,2-f]isoindole 2-oxide (9ub).

Following the general procedure C, purification by column chromatography on silica gel (PE/EA = 6/1; PE/EA = 4/1, $R_f \approx 0.07$) to deliver the desired product as a white solid (44.5 mg, 55% yield).

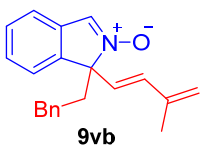


9ub

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, J = 7.6 Hz, 1H), 7.68 (s, 1H), 7.62 - 7.54 (m, 2H), 7.43 (t, J = 7.1 Hz, 1H), 7.36 (td, J = 7.4, 1.1 Hz, 1H), 7.23 - 7.15 (m, 2H), 7.14 - 7.02 (m, 3H), 6.38 (d, J = 16.0 Hz, 1H), 5.93 (d, J = 16.0 Hz, 1H), 5.00 (s, 1H), 4.95 (s, 1H), 3.98 (s, 2H), 2. 87 - 2.73 (m, 1H), 2.44 (s, 3H), 2.41 - 2.27 (m, 2H), 1.99 - 1.89 (m, 1H), 1.83 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 144.0, 143.4, 142.1, 142.0, 141.1, 141.0, 140.8, 139.3, 135.1, 134.5, 128.4, 128.3, 127.8, 127.3, 127.1, 126.0, 125.2, 120.1, 118.7, 116.2, 113.8, 82.7, 38.2, 37.0, 29.5, 18.5, 9.5. **HRMS** $[M + H]^+$ calcd for $C_{29}H_{28}NO$ 406.2165, found 406.2162.

(*E*)-1-(3-methylbuta-1,3-dien-1-yl)-1-phenethyl-1*H*-isoindole 2-oxide (9vb).

Following the general procedure C, purification by column chromatography on silica gel (PE/EA = 6/1; PE/EA = 4/1, $R_f \approx 0.20$) to deliver the desired product as a light yellow oil (30.2 mg, 50% yield).



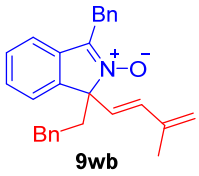
9vb

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (s, 1H), 7.44 - 7.38 (m, 3H), 7.33 - 7.27 (m, 1H), 7.24 - 7.18 (m, 2H), 7.18 - 7.11 (m, 1H), 7.10 - 7.03 (m, 2H), 6.32 (d, J = 16.0 Hz, 1H), 5.86 (d, J = 16.0 Hz, 1H), 5.02 (s, 1H), 4.96 (s, 1H), 2.67 (td, J = 11.6, 3.5 Hz, 1H), 2.45 - 2.26 (m, 2H), 1.94 (td,

J = 12.9, 3.0 Hz, 1H), 1.81 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 140.9, 140.8, 140.6, 135.4, 133.9, 133.0, 128.8, 128.4, 128.4, 127.8, 126.9, 126.1, 122.4, 120.5, 119.0, 84.4, 38.2, 29.4, 18.4. **HRMS** $[M + H]^+$ calcd for $C_{21}H_{22}NO$ 304.1696, found 304.1696.

(*E*)-3-benzyl-1-(3-methylbuta-1,3-dien-1-yl)-1-phenethyl-1*H*-isoindole 2-oxide (9wb).

Following the general procedure C, purification by column chromatography on silica gel (PE/EA = 6/1; PE/EA = 2/1, $R_f \approx 0.47$) to deliver the desired product as a colorless oil (67.0 mg, 85% yield).

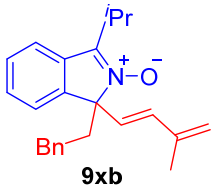


9wb

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 - 7.15 (m, 11H), 7.15 - 7.08 (m, 1H), 7.06 - 6.97 (m, 2H), 6.30 (d, J = 16.0 Hz, 1H), 5.89 (d, J = 16.0 Hz, 1H), 5.00 (s, 1H), 4.93 (s, 1H), 4.33 (d, J = 15.2 Hz, 1H), 4.14 (d, J = 15.2 Hz, 1H), 2.73 (td, J = 13.0, 4.1 Hz, 1H), 2.39 - 2.16 (m, 2H), 1.90 - 1.77 (m, 1H), 1.82 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 143.4, 141.1, 140.8, 140.1, 135.9, 135.1, 135.0, 129.0, 128.8, 128.6, 128.4, 128.4, 127.6, 127.4, 127.0, 126.0, 122.2, 120.0, 118.7, 83.1, 38.4, 30.2, 29.4, 18.5. **HRMS** $[M + H]^+$ calcd for $C_{28}H_{28}NO$ 394.2165, found 394.2127.

(*E*)-3-isopropyl-1-(3-methylbuta-1,3-dien-1-yl)-1-phenethyl-1*H*-isoindole 2-oxide (9xb).

Following the general procedure C, purification by column chromatography on silica gel (PE/EA = 6/1; PE/EA = 4/1, $R_f \approx 0.42$) to deliver the desired product as a colorless oil (37.3 mg, 54% yield).



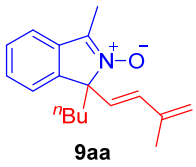
9xb

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 - 7.54 (m, 1H), 7.44 - 7.35 (m, 2H), 7.33 - 7.27(m, 1H), 7.24 - 7.16 (m, 2H), 7.16 - 7.09 (m, 1H), 7.08 - 7.01 (m, 2H), 6.32 (d, J = 16.0 Hz, 1H), 5.86 (d, J = 16.0 Hz, 1H), 5.00 (s, 1H), 4.95 (s, 1H), 3.73 (hept, J = 7.1 Hz, 1H), 2.79 - 2.62 (m, 1H), 2.36 - 2.19 (m, 2H), 1.90 - 1.73 (m, 4H), 1.50 - 1.40 (m, 6H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 149.0, 141.2, 140.9, 140.4, 134.9, 134.4, 128.4, 128.4, 128.4,

127.6, 127.4, 126.0, 122.3, 120.3, 118.5, 82.4, 38.5, 29.2, 25.1, 18.9, 18.6, 18.5. **HRMS** $[M + H]^+$ calcd for $C_{24}H_{28}NO$ 346.2165, found 346.2164.

(*E*)-1-butyl-3-methyl-1-(3-methylbuta-1,3-dien-1-yl)-1*H*-isoindole 2-oxide (9aa).

Following the general procedure C, purification by column chromatography on silica gel (PE/EA = 6/1; PE/EA = 4/1, $R_f \approx 0.11$) to deliver the desired product as a yellow oil (6.5 mg, 12% yield).

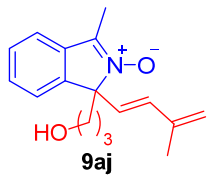


9aa

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 - 7.33 (m, 3H), 7.31 - 7.23 (m, 1H), 6.27 (d, J = 16.0 Hz, 1H), 5.88 (d, J = 16.0 Hz, 1H), 5.00 (s, 1H), 4.95 (s, 1H), 2.47 - 2.23 (m, 4H), 2.05 (td, J = 12.4, 4.1 Hz, 1H), 1.83 (s, 3H), 1.38 - 1.14 (m, 3H), 0.99 - 0.86 (m, 1H), 0.78 (t, J = 7.4 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 141.4, 141.2, 140.4, 135.5, 134.7, 128.4, 127.8, 127.6, 122.2, 119.3, 118.4, 83.2, 36.3, 25.1, 22.5, 18.5, 13.8, 9.3. **HRMS** $[M + H]^+$ calcd for $C_{18}H_{24}NO$ 270.1852, found 270.1858.

(*E*)-1-(3-hydroxypropyl)-3-methyl-1-(3-methylbuta-1,3-dien-1-yl)-1*H*-isoindole 2-oxide (9aj).

Following the general procedure C, purification by column chromatography on silica gel (PE/EA = 6/1 then DCM/MeOH = 100/1; PE/EA = 2/1, $R_f \approx 0.10$) to deliver the desired product as a yellow oil (44.3 mg, 82% yield).

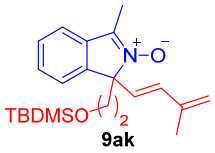


9aj

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 - 7.35 (m, 3H), 7.31 - 7.26 (m, 1H), 6.28 (d, J = 16.0 Hz, 1H), 5.86 (d, J = 16.0 Hz, 1H), 5.01 (s, 1H), 4.95 (s, 1H), 3.58 - 3.41 (m, 2H), 2.95 - 2.54(brs, 1H), 2.54 - 2.42 (m, 1H), 2.37 (s, 3H), 2.25 - 2.11 (m, 1H), 1.82 (s, 3H), 1.17 - 0.94 (m, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 142.8, 141.0, 140.3, 135.2, 134.9, 128.6, 128.1, 127.4, 122.2, 119.6, 118.6, 83.1, 61.9, 32.5, 26.3, 18.4, 9.4. **HRMS** $[M + H]^+$ calcd for $C_{17}H_{22}NO_2$ 272.1645, found 272.1650.

(*E*)-1-(2-((tert-butyldimethylsilyl)oxy)ethyl)-3-methyl-1-(3-methylbuta-1,3-dien-1-yl)-1*H*-isoindole 2-oxide (9ak).

Following the general procedure C, purified by column chromatography on silica gel (PE/EA = 6/1; PE/EA = 4/1, $R_f \approx 0.29$) to deliver the desired product as a light yellow oil (61.9 mg, 83% yield).

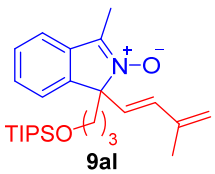


9ak

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 - 7.39 (m, 4H), 6.37 (d, J = 16.0 Hz, 1H), 5.98 (d, J = 16.0 Hz, 1H), 5.11 (s, 1H), 5.06 (s, 1H), 3.67 - 3.53 (m, 1H), 3.40 - 3.28(m, 1H), 2.73 - 2.61 (m, 1H), 2.55 - 2.41 (m, 4H), 1.93 (s, 3H), 0.87 (s, 9H), 0.0 (s, 3H), -0.05 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 141.9, 141.0, 140.4, 134.9, 134.7, 128.4, 127.8, 127.5, 122.8, 119.5, 118.6, 81.8, 58.4, 38.7, 25.8, 18.4, 18.1, 9.4, -5.6, -5.6. **HRMS** $[M + H]^+$ calcd for $C_{22}H_{34}NO_2Si$ 372.2353, found 372.2344.

(*E*)-3-methyl-1-(3-methylbuta-1,3-dien-1-yl)-1-(3-((triisopropylsilyl)oxy)propyl)-1*H*-isoindole 2-oxide (9al).

Following the general procedure C, purification by column chromatography on silica gel (PE/EA = 6/1; PE/EA = 4/1, $R_f \approx 0.18$) to deliver the desired product as a light yellow oil (76.2 mg, 89% yield).

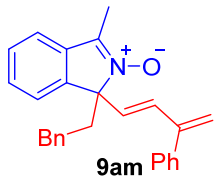


9al

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 - 7.32 (m, 3H), 7.31 - 7.23 (m, 1H), 6.28 (d, J = 16.0 Hz, 1H), 5.89 (d, J = 16.0 Hz, 1H), 5.00 (s, 1H), 4.94 (s, 1H), 3.68 - 3.46 (m, 2H), 2.36 (s, 3H), 2.33 - 2.16 (m, 2H), 1.83 (s, 3H), 1.30 - 0.82 (m, 23H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 141.3, 141.2, 140.2, 135.5, 134.8, 128.5, 127.7, 127.6, 122.3, 119.2, 118.4, 83.1, 62.7, 32.9, 26.6, 18.4, 18.0, 11.9, 9.3. **HRMS** $[M + H]^+$ calcd for $C_{26}H_{42}NO_2Si$ 428.2979, found 428.2979.

(*E*)-3-methyl-1-phenethyl-1-(3-phenylbuta-1,3-dien-1-yl)-1*H*-isoindole 2-oxide (9am).

Following the general procedure C, purification by column chromatography on silica gel (PE/EA = 6/1; PE/EA = 4/1, $R_f \approx 0.17$) to deliver the desired product as a colorless oil (58.9 mg, 78% yield).

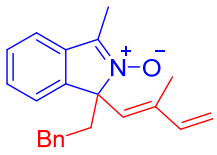


9am

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 - 7.36 (m, 3H), 7.35 - 7.16 (m, 8H), 7.15 - 7.09 (m, 1H), 7.07 - 7.00 (m, 2H), 6.50 (d, J = 16.0 Hz, 1H), 5.88 (d, J = 16.0 Hz, 1H), 5.26 (d, J = 0.7 Hz, 1H), 5.18 (d, J = 1.6 Hz, 1H), 2.75 - 2.62 (m, 1H), 2.38 (s, 3H), 2.33 - 2.22 (m, 2H), 1.96 - 1.82 (m, 1H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 146.8, 141.8, 140.7, 139.9, 139.5, 135.6, 133.5, 130.5, 128.7, 128.4, 128.3, 128.3, 128.2, 127.9, 127.6, 126.0, 122.0, 119.4, 118.7, 83.1, 38.1, 29.4, 9.4. **HRMS** $[M + H]^+$ calcd for $C_{27}H_{26}NO$ 380.2009, found 380.2008.

(*E*)-3-methyl-1-(2-methylbuta-1,3-dien-1-yl)-1-phenethyl-1*H*-isoindole 2-oxide (9an).

Following the general procedure C, purification by column chromatography on silica gel (PE/EA = 6/1; PE/EA = 4/1, $R_f \approx 0.18$) to deliver the desired product as a yellow oil (58.9 mg, 14% yield).

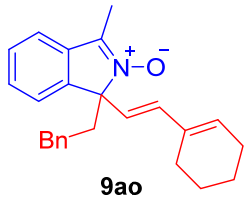


9an

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 - 7.33 (m, 3H), 7.25 - 7.16 (m, 3H), 7.16 - 7.09 (m, 1H), 7.03 (d, J = 7.1 Hz, 2H), 6.35 (dd, J = 17.3, 10.7 Hz, 1H), 5.69 (s, 1H), 5.15 (d, J = 17.3 Hz, 1H), 5.05 (d, J = 10.7 Hz, 1H), 2.71 (td, J = 12.7, 4.7 Hz, 1H), 2.50 - 2.30 (m, 4H), 2.30 - 2.19 (m, 1H), 1.86 (td, J = 12.7, 3.8 Hz, 1H), 1.16 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 142.2, 141.9, 141.0, 140.8, 140.6, 135.8, 128.4, 128.4, 128.3, 128.2, 126.0, 123.8, 121.6, 119.1, 114.2, 81.7, 41.7, 28.8, 11.7. **HRMS** $[M + H]^+$ calcd for $C_{22}H_{24}NO$ 318.1852, found 318.1852.

(*E*)-1-(2-(cyclohex-1-en-1-yl)vinyl)-3-methyl-1-phenethyl-1*H*-isoindole 2-oxide (9ao).

Following the general procedure C, purification by column chromatography on silica gel (PE/EA = 6/1; PE/EA = 4/1, $R_f \approx 0.17$) to deliver the desired product as a colorless oil (58.9 mg, 78% yield).

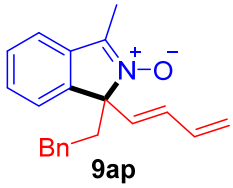


9ao

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 - 7.35 (m, 3H), 7.33 - 7.27 (m, 1H), 7.24 - 7.16 (m, 2H), 7.14 - 7.09 (m, 1H), 7.09 - 6.99 (m, 2H), 6.19 (d, J = 16.0 Hz, 1H), 5.76 (d, J = 16.0 Hz, 1H), 5.71 (t, J = 3.6 Hz, 1H), 2.76 - 2.60 (m, 1H), 2.38 (s, 3H), 2.35 - 2.23 (m, 2H), 2.14 - 2.02 (m, 4H), 1.97 - 1.83 (m, 1H), 1.68 - 1.49 (m, 4H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 146.8, 141.8, 140.7, 139.9, 139.5, 135.6, 133.5, 130.5, 128.7, 128.4, 128.3, 128.3, 128.2, 127.9, 127.6, 126.0, 122.0, 119.4, 118.7, 83.1, 38.1, 29.4, 9.4. **HRMS** $[M + H]^+$ calcd for $C_{25}H_{28}NO$ 358.2165, found 358.2169.

(*E*)-1-(buta-1,3-dien-1-yl)-3-methyl-1-phenethyl-1*H*-isoindole 2-oxide (9ap).

Following the general procedure C, purification by column chromatography on silica gel (PE/EA = 6/1; PE/EA = 4/1, $R_f \approx 0.20$) to deliver the desired product as a colorless oil (28.1 mg, 46% yield).

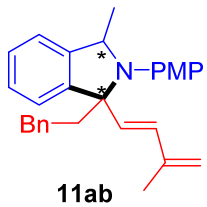


9ap

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 - 7.36 (m, 3H), 7.35 - 7.28 (m, 1H), 7.24 - 7.16 (m, 2H), 7.16 - 7.09 (m, 1H), 7.04 (d, J = 7.0 Hz, 2H), 6.40 - 6.15 (m, 2H), 5.95 (d, J = 15.1 Hz, 1H), 5.25 - 5.06 (m, 2H), 2.75 - 2.62 (m, 1H), 2.39 (s, 3H), 2.34 - 2.22 (m, 2H), 1.95 - 1.84 (m, 1H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 141.8, 140.7, 139.7, 135.9, 135.6, 133.0, 131.2, 128.7, 128.4, 128.3, 127.9, 126.0, 122.1, 119.5, 119.3, 82.9, 37.9, 29.4, 9.3. **HRMS** $[M + H]^+$ calcd for $C_{21}H_{22}NO$ 304.1696, found 304.1695.

(*E*)-2-(4-methoxyphenyl)-3-methyl-1-(3-methylbuta-1,3-dien-1-yl)-1-phenethyliso indoline (11ab).

Following the general procedure D, the title compound was obtained in 74% yield as a white solid after chromatography on silica gel (PE/EA = 100/1; PE/EA = 50/1, $R_f \approx$ 0.46), 60.2 mg. The diastereomeric ratio, as determined by ^{1}H NMR analysis of the crude mixture, was found to be 2:1.



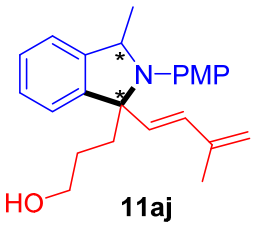
11ab

Major: ^{1}H NMR (400 MHz, Acetone) δ 7.41 - 7.32 (m, 3H), 7.30 - 7.20 (m, 2H), 7.15 (d, J = 7.5 Hz, 2H), 7.10 - 7.00 (m, 3H),

6.92 - 6.82 (m, 2H), 6.67 (d, J = 6.9 Hz, 1H), 6.18 (d, J = 16.1 Hz, 1H), 5.70 (d, J = 16.2 Hz, 1H), 5.16 (q, J = 6.1 Hz, 1H), 4.84 (s, 2H), 3.77 - 3.70 (m, 3H), 2.92 - 2.75 (m, 1H), 2.64 - 2.41 (m, 2H), 1.81 - 1.67 (m, 1H), 1.60 (s, 3H), 1.50 (d, J = 6.1 Hz, 3H). **^{13}C NMR (101 MHz, Acetone)** δ 153.5, 143.3, 142.7, 142.1, 141.7, 138.7, 135.8, 131.1, 128.3, 128.1, 127.7, 127.5, 125.6, 122.6, 121.9, 120.6, 115.7, 114.2, 73.4, 59.2, 54.7, 40.3, 31.0, 19.7, 17.9. **Minor: ^{1}H NMR (400 MHz, Acetone)** δ 7.41 - 7.32 (m, 3H), 7.30 - 7.20 (m, 2H), 7.10 - 7.00 (m, 3H), 6.92 - 6.82 (m, 2H), 6.92 - 6.82 (m, 2H), 6.67 (d, J = 6.9 Hz, 1H), 6.46 (d, J = 16.0 Hz, 1H), 6.16 (d, J = 16.2 Hz, 1H), 5.32 (q, J = 6.0 Hz, 1H) , 4.97 (d, J = 5.3 Hz, 2H), 3.77 - 3.70 (m, 3H), 2.92 - 2.75 (m, 1H), 2.29 (td, J = 12.6, 4.6 Hz, 1H), 2.22 - 2.08 (m, 2H), 1.85 (s, 3H) , 1.56 (d, J = 6.0 Hz, 3H). **^{13}C NMR (101 MHz, Acetone)** δ 151.9, 144.0, 143.1, 142.1, 141.8, 138.7, 138.3, 130.6, 128.3, 128.0, 127.7, 127.5, 125.5, 122.3, 122.0, 116.7, 115.9, 114.3, 73.4, 59.4, 54.9, 37.8, 26.6, 20.6, 18.1. **HRMS** $[M + H]^+$ calcd for $C_{29}H_{32}NO$ 410.2478, found 410.2485.

(*E*)-3-(2-(4-methoxyphenyl)-3-methyl-1-(3-methylbuta-1,3-dien-1-yl)isoindolin-1-yl)propan-1-ol (11aj).

Following the general procedure D, the title compound was obtained in 88% yield as a colorless oil after chromatography on silica gel (PE/EA = 8/1; PE/EA = 4/1, $R_f \approx$ 0.63), 64.2 mg. The diastereomeric ratio, as determined by ^{1}H NMR analysis of the crude mixture, was found to be 3:1.



11aj

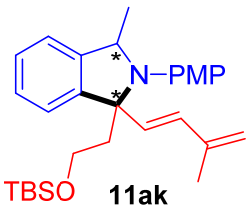
Major: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 - 7.18 (m, 3H), 7.11 - 7.03 (m, 1H), 6.98 - 6.88 (m, 2H), 6.87 - 6.78 (m, 2H), 6.14 - 5.99 (m, 1H), 5.56 (d, J = 16.2 Hz, 1H), 5.07 - 4.94 (m, 2H), 4.86 (d, J = 5.8 Hz, 1H), 3.76 (s, 3H), 3.67 - 3.51 (m, 1H), 2.40 - 2.26 (m, 1H), 2.24 - 2.12 (m, 1H), 2.06 - 1.88 (m, 2H), 1.80 - 1.67 (m, 1H), 1.61 (s, 3H), 1.44 (d, J = 6.1 Hz, 3H), 1.30 - 1.13 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 153.2, 143.0, 142.9, 141.8, 138.5, 136.0, 131.2, 127.5, 127.4, 122.8, 121.8, 120.5, 116.1, 114.2, 73.4, 63.1, 59.5, 55.6, 34.6, 28.0, 19.7, 18.7.

Minor: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 - 7.18 (m, 3H), 7.11 - 7.03 (m, 1H), 6.98 - 6.88 (m, 2H), 6.87 - 6.78 (m, 2H), 6.41 (d, J = 16.1 Hz, 1H), 6.14 - 5.99 (m, 1H), 5.14 (q, J = 6.0 Hz, 1H), 5.07 - 4.94 (m,2H), 3.76 (s, 3H), 3.34 - 3.18 (m, 2H), 2.72 - 2.55 (m, 1H), 2.06 - 1.88 (m, 2H), 1.84 (s, 3H), 1.80 - 1.67 (m, 1H), 1.54 (d, J = 6.0 Hz, 3H), 1.30 - 1.13 (m, 1H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 151.4, 143.8, 142.1, 138.8, 138.6, 130.4, 127.6, 127.5, 123.2, 122.4, 121.9, 116.4, 116.4, 114.5, 73.1, 62.7, 59.5, 55.6, 31.4, 26.3, 21.1, 18.8. **HRMS** $[M + H]^+$ calcd for $C_{33}H_{50}NO_2Si$ 364.2271, found 364.2276.

(*E*)-1-(2-((tert-butyldimethylsilyl)oxy)ethyl)-2-(4-methoxyphenyl)-3-methyl-1-(3-methylbuta-1,3-dien-1-yl)isoindoline (11ak).

Following the general procedure D, the title compound was obtained in 71% yield as a colorless oil after chromatography on silica gel (PE/EA = 200/1; PE/EA = 100/1, R_f ≈ 0.69), 66.2 mg. The diastereomeric ratio, as determined by ^{1}H NMR analysis of the crude mixture, was found to be 2.6:1.



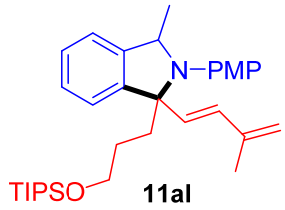
11ak

Major: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 - 7.31 (m, 2H), 7.31 - 7.25 (m, 1H), 7.21 - 7.16 (m, 1H), 7.03 - 6.94 (m, 2H) , 6.94 - 6.86 (m, 2H), 6.22 (d, J = 16.2 Hz, 1H), 5.61 (d, J = 16.2 Hz, 1H), 5.17 - 5.02 (m, 2H), 4.95 (s, 1H), 3.83 (m, 3H), 3.47 - 3.34 (m, 1H), 2.76 - 2.62 (m, 2H) , 2.52 - 2.38 (m, 1H), 1.68 (s, 3H), 1.50 (d, J = 6.1 Hz, 3H) , 0.87 (s, 9H), -0.00 (s, 6H),. **^{13}C NMR (101 MHz, $CDCl_3$)** δ 152.8, 143.1, 142.5, 141.9, 138.7, 135.9, 131.1, 127.5, 127.4, 122.9, 121.7, 119.5, 116.1, 114.2, 71.9, 60.6, 59.2, 55.6, 40.8, 26.0, 25.9, 20.0, 18.67, -5.3, -5.5. **Minor**: **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.38 - 7.31 (m, 2H), 7.31 - 7.25 (m, 1H), 7.21 - 7.16 (m, 1H), 7.03 - 6.94 (m, 2H), 6.94 - 6.86 (m, 2H), 6.49 (d, J = 16.1 Hz, 1H), 6.09 (d, J = 16.1 Hz, 1H) 5.17 - 5.02 (m, 2H), 5.17 - 5.02 (m, 1H), 3.83 (m, 3H), 3.30 - 3.19 (m, 1H), 3.00 - 2.83 (m, 2H), 2.36 - 2.25 (m, 1H), 1.92 (s, 3H), 1.60 (d, J = 6.0 Hz, 3H), 0.75 (s, 9H), -0.23 (d, J = 6.2 Hz, 6H) .**^{13}C NMR (101 MHz, $CDCl_3$)** 151.9, 143.4, 141.5, 138.9, 138.8, 130.3, 127.6, 127.6, 123.2, 122.6, 121.8, 116.5, 116.5, 114.8, 71.6, 59.1, 58.7, 55.9,

38.3,21.0, 18.9, 18.3, 18.2, -5.3, -5.7. **HRMS** $[M + H]^+$ calcd for $C_{29}H_{42}NO_2Si$ 464.2979, found 464.2976.

(*E*)-2-(4-methoxyphenyl)-3-methyl-1-(3-methylbuta-1,3-dien-1-yl)-1-(3-((triisopropylsilyl)oxy)propyl)isoindoline (11al).

Following the general procedure D, the title compound was obtained in 85% yield as a white solid after chromatography on silica gel (PE/EA = 100/1; PE/EA = 100/1, $R_f \approx 0.63$), 87.7 mg. The diastereomeric ratio, as determined by ^1H NMR analysis of the crude mixture, was found to be 3:1.



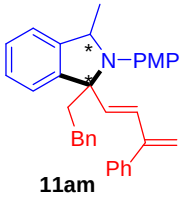
11al

Major: ^1H NMR (400 MHz, $CDCl_3$) δ 7.23 - 7.11 (m, 3H), 7.01 - 6.96 (m, 4H), 6.87 - 6.80 (m, 2H), 6.77 - 6.70 (m, 2H), 6.01 (d, J = 16.2 Hz, 1H), 5.52 (d, J = 16.2 Hz, 1H) , 4.97 (q, J = 6.1 Hz, 1H) , 4.77 (d, J = 3.7 Hz, 2H) , 3.69 (s, 3H) , 2.37 - 2.23 (m, 1H), 2.18 - 2.03 (m, 1H) , 1.73 - 1.61 (m, 1H) , 1.58 - 1.50 (m, 3H) , 1.37 (d, J = 6.1 Hz, 3H) , 1.04 - 0.89 (m, 19H) , 0.89 - 0.78 (m, 5H) . **^{13}C NMR (101 MHz, $CDCl_3$)** δ 152.8, 143.4, 142.9, 142.0, 138.9, 136.4, 131.0, 127.3, 122.9, 121.7, 120.0, 116.4, 115.8, 114.2, 73.4, 63.5, 59.2, 55.6, 34.7, 28.1, 20.0, 18.7, 18.1, 12.0 . **Minor: ^1H NMR (400 MHz, $CDCl_3$)** δ 7.23 - 7.11 (m, 3H) , 7.01 - 6.96 (m, 4H), 6.87 - 6.80 (m, 2H), 6.77 - 6.70 (m, 2H) , 6.32 (d, J = 16.1 Hz, 1H) , 5.99 (d, J = 16.1 Hz, 1H) , 5.05 (q, J = 6.0 Hz, 1H) , 4.90 (s, 2H) , 3.67 (s, 3H) , 2.67 - 2.58 (m, 1H) , 2.58 - 2.47 (m, 1H) , 1.98 - 1.86 (m, 1H) , 1.78 (s, 3H) , 1.46 (d, J = 6.0 Hz, 3H) , 1.04 - 0.89 (m, 19H) , 0.89 - 0.78 (m, 5H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 149.9, 144.1, 142.1, 142.0, 139.0, 130.3, 127.5, 127.4, 123.1, 122.5, 121.8, 116.4, 116.2, 113.4, 73.3, 63.2, 59.4, 55.6, 31.8, 26.4, 21.0, 18.9, 17.9, 11.9. **HRMS** $[M + H]^+$ calcd for $C_{33}H_{50}NO_2Si$ 520.3605, found 520.3605.

(*E*)-2-(4-methoxyphenyl)-3-methyl-1-phenethyl-1-(3-phenylbuta-1,3-dien-1-yl)isoindoline (11am).

Following the general procedure D, the title compound was obtained in 69% yield as a yellow oil after chromatography on silica gel (PE/EA = 100/1; PE/EA = 100/1, $R_f \approx$

0.35), 65.3 mg. The diastereomeric ratio, as determined by ^{1}H NMR analysis of the crude mixture, was found to be 1.7:1.

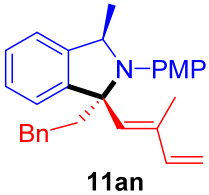


11am

Major: ^{1}H NMR (400 MHz, $CDCl_3$) 7.37 - 7.19 (m, 6H), 7.18 - 6.95 (m, 9H), 6.94 - 6.85 (m, 2H), 6.73 - 6.63 (m, 1H), 6.26 (d, *J* = 16.2 Hz, 1H), 5.64 (d, *J* = 16.2 Hz, 1H), 5.31 - 4.96 (m, 3H), 3.80 (s, 3H), 2.63 (td, *J* = 13.5, 4.5 Hz, 1H), 2.39 (td, *J* = 13.7, 4.3 Hz, 1H), 2.21 - 2.08 (m, 2H), 1.51 (d, *J* = 6.1 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** *δ* 153.0, 147.6, 143.0, 142.9, 142.8, 141.2, 139.4, 139.2, 129.8, 128.5, 128.4, 128.2, 128.0, 127.6, 127.6, 127.4, 125.7, 122.5, 121.9, 119.6, 116.6, 114.5, 74.0, 59.2, 55.8, 41.1, 31.0, 20.2. **Minor: ^{1}H NMR (400 MHz, $CDCl_3$)** 7.37 - 7.19 (m, 6H), 7.18 - 6.95 (m, 9H), 6.94 - 6.85 (m, 2H), 6.73 - 6.63 (m, 1H), 6.54 (d, *J* = 16.0 Hz, 1H), 6.08 (d, *J* = 16.0 Hz, 1H), 5.31 - 4.96 (m, 3H), 3.80 (s, 3H), 2.94 - 2.77 (m, 2H), 2.07 - 1.98 (m, 1H), 1.74 (td, *J* = 12.6, 3.9 Hz, 1H), 1.54 (d, *J* = 6.0 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** *δ* 151.7, 147.6, 143.7, 142.2, 142.1, 140.3, 140.0, 138.9, 129.4, 128.2, 128.2, 128.1, 128.0, 127.8, 127.6, 127.5,125.6, 122.2, 122.1,119.6, 116.0, 114.7,73.5, 59.6, 55.8, 38.2, 29.4, 21.1. **HRMS** $[M + H]^+$ calcd for $C_{34}H_{34}NO$ 472.2635, found 472.2635.

(1S,3R)-2-(4-methoxyphenyl)-3-methyl-1-((*E*)-2-methylbuta-1,3-dien-1-yl)-1-phenethylisoindoline (11an).

Following the general procedure D, the title compound was obtained in 87% yield as a white solid after chromatography on silica gel (PE/EA = 100/1; PE, $R_f \approx 0.44$), 71.2 mg. The diastereomeric ratio, as determined by ^{1}H NMR analysis of the crude mixture, was found > 25:1.



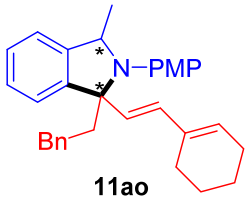
11an

^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.40 - 7.21 (m, 3H), 7.17 - 6.96 (m, 6H), 6.87 (d, *J* = 8.9 Hz, 2H), 6.67 (d, *J* = 7.1 Hz, 2H), 6.44 (dd, *J* = 17.3, 10.7 Hz, 1H), 5.93 (s, 1H), 5.24 - 5.19 (m, 2H), 4.99 (d, *J* = 10.7 Hz, 1H), 3.79 (s, 3H), 2.68 (td, *J* = 13.0, 3.6 Hz, 1H), 2.09 (td, *J* = 12.6, 3.7 Hz, 1H), 1.98 (td, *J* = 12.9, 3.6 Hz, 1H), 1.81 (td, *J* = 12.6, 3.6 Hz, 1H), 1.60 (d, *J* = 6.0 Hz, 3H), 1.53 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) *δ* 152.6, 152.2,

144.8, 142.4, 142.3, 142.1, 139.0, 138.4, 137.5, 128.1, 127.7, 127.3, 125.5, 122.3, 121.6, 118.0, 114.5, 111.9, 71.9, 59.4, 55.7, 43.1, 29.2, 19.0, 11.8. **HRMS** $[M + H]^+$ calcd for $C_{29}H_{32}NO$ 410.2478, found 410.2481.

(*E*)-1-(2-(cyclohex-1-en-1-yl)vinyl)-2-(4-methoxyphenyl)-3-methyl-1-phenethyliso indoline (11ao).

Following the general procedure D, the title compound was obtained in 65% yield as a white solid after chromatography on silica gel (hexane; hexane, $R_f \approx 0.11$), 62.2 mg. The diastereomeric ratio, as determined by ^1H NMR analysis of the crude mixture, was found to be 1.5:1.

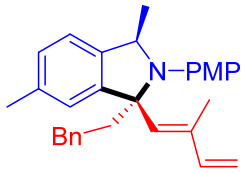


11ao

Major: ^1H NMR (400 MHz, $CDCl_3$) δ 7.37 - 7.20 (m, 4H) , 7.20 - 6.97 (m, 5H) , 6.97 - 6.90 (m, 1H) , 6.90 - 6.81 (m, 2H) , 6.02 (d, J = 16.3 Hz, 1H), 5.60 (s, 1H) , 5.50 (d, J = 16.2 Hz, 1H) , 5.10 (q, J = 5.9 Hz, 1H) , 3.91 - 3.67 (m, 3H) , 2.60 (td, J = 13.5, 4.4 Hz, 1H) , 2.37 (td, J = 13.4, 4.1 Hz, 1H) , 2.26 - 1.96 (m, 4H) , 1.85 (s, 1H) , 1.73 (td, J = 12.7, 3.9 Hz, 1H) , 1.68 - 1.42 (m, 6H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 152.5, 143.6, 143.0, 142.4, 139.1, 135.5, 134.4, 131.9, 129.1, 128.5, 128.2, 127.7, 127.4, 125.7, 122.7, 121.8, 119.2, 114.3, 73.7, 59.3, 55.6, 40.8, 31.2, 25.9, 24.4, 22.6, 22.5, 20.2. **Minor: ^1H NMR (400 MHz, $CDCl_3$)** δ 7.37 - 7.20 (m, 4H) , 7.20 - 6.97 (m, 5H) , 6.90 - 6.81 (m, 2H), 6.68 (d, J = 7.1 Hz, 1H) , 6.26 (d, J = 16.2 Hz, 1H) , 5.93 (d, J = 16.2 Hz, 1H) , 5.70 (s, 1H) , 5.21 (q, J = 5.8 Hz, 1H) , 3.91 - 3.67 (m, 3H) , 2.91 - 2.72 (m, 2H) , 2.26 - 1.96 (m, 4H) , 1.85 (s, 1H) , 1.68 - 1.42 (m, 1H) , 1.68 - 1.42 (m, 6H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 151.5, 144.2, 142.9, 142.1, 139.1, 135.5, 132.0, 131.1, 129.4, 128.4, 128.2, 127.7, 127.5, 125.5, 122.4, 121.9, 116.5, 114.6, 73.5, 59.5, 55.8, 38.1, 29.5, 26.0, 24.7, 22.4, 22.4, 21.1. **HRMS** $[M + H]^+$ calcd for $C_{32}H_{36}NO_2$ 450.2791, found 450.2790

(1S,3R)-2-(4-methoxyphenyl)-3,6-dimethyl-1-((*E*)-2-methylbuta-1,3-dien-1-yl)-1-phenethylisoindoline (11bn).

Following the general procedure D, the title compound was obtained in 70% yield as a white solid, after chromatography on silica gel (PE/EA = 100/1; PE/EA = 100/1, R_f ≈ 0.55), 69.0 mg. The diastereomeric ratio, as determined by ^{1}H NMR analysis of the crude mixture, was found to be 25:1.

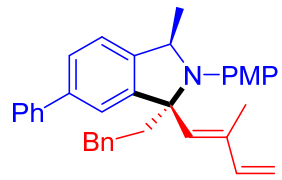


11bn

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18 - 6.98 (m, 7H), 6.87 (t, J = 8.3 Hz, 3H), 6.68 (d, J = 7.2 Hz, 2H), 6.45 (dd, J = 17.3, 10.7 Hz, 1H), 5.92 (s, 1H), 5.20 - 5.08 (m, 2H), 4.99 (d, J = 10.7 Hz, 1H), 3.79 (s, 3H), 2.69 (td, J = 13.0, 3.7 Hz, 1H), 2.37 (s, 3H), 2.07 (td, J = 12.5, 3.7 Hz, 1H), 1.97 (td, J = 12.8, 3.8 Hz 1H), 1.82 (td, J = 12.5, 3.6 Hz, 1H), 1.58 (d, J = 6.0 Hz, 3H), 1.55 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 152.1, 144.8, 142.4, 142.2, 139.5, 139.2, 138.6, 137.3, 137.2, 128.3, 128.1, 128.1, 125.5, 122.7, 121.2, 117.9, 114.5, 111.8, 71.9, 59.2, 55.7, 42.9, 29.2, 21.6, 19.1, 11.8. **HRMS** $[M + H]^+$ calcd for $C_{30}H_{34}NO$ 424.2635, found 424.2636.

(1S,3R)-2-(4-methoxyphenyl)-3-methyl-1-((*E*)-2-methylbuta-1,3-dien-1-yl)-1-phenethyl-6-phenylisoindoline (11cn).

Following the general procedure D, the title compound was obtained in 70% yield as a white solid, after chromatography on silica gel (PE/EA = 100/1; PE/EA = 50/1, R_f ≈ 0.57), 70.2 mg. The diastereomeric ratio, as determined by ^{1}H NMR analysis of the crude mixture, was found > 25:1.

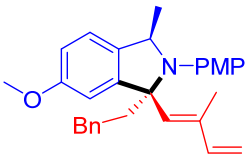


11cn

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 - 7.46 (m, 3H), 7.37 (t, J = 7.6 Hz, 2H), 7.32 - 7.21 (m, 3H), 7.05 - 6.91 (m, 5H), 6.85 - 6.76 (m, 2H), 6.61 (d, J = 7.0 Hz, 2H), 6.38 (dd, J = 17.3, 10.7 Hz, 1H), 5.89 (s, 1H), 5.20 - 5.08 (m, 2H), 4.92 (d, J = 10.7 Hz, 1H), 3.72 (s, 3H), 2.64 (td, J = 12.9, 3.7 Hz, 1H), 2.07 (td, J = 12.4, 3.6 Hz, 1H), 2.02 - 1.91 (m, 1H), 1.83 (m, J = 12.7, 3.2 Hz, 1H), 1.56 (d, J = 6.1 Hz, 3H), 1.49 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 152.3, 145.6, 142.3, 142.0, 141.6, 141.2, 141.0, 139.0, 138.3, 137.7, 128.8, 128.2, 128.1, 127.3, 127.2, 126.6, 125.5, 121.9, 121.0, 118.1, 114.5, 112.1, 72.0, 59.2, 55.7, 43.1, 29.3, 19.0, 11.9. **HRMS** $[M + H]^+$ calcd for $C_{35}H_{36}NO$ 486.2791, found 486.2795.

(1S,3R)-6-methoxy-2-(4-methoxyphenyl)-3-methyl-1-((*E*)-2-methylbuta-1,3-dien-1-yl)-1-phenethylisoindoline (11dn).

Following the general procedure D, the title compound was obtained in 74% yield as a white solid, after chromatography on silica gel (PE/EA = 100/1; PE/EA = 50/1, $R_f \approx$ 0.43), 66.7 mg. The diastereomeric ratio, as determined by ^{1}H NMR analysis of the crude mixture, was found > 25:1.

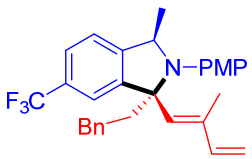


11dn

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19 (d, J = 8.3 Hz, 1H), 7.15 - 6.99 (m, 5H), 6.95 - 6.84 (m, 3H), 6.70 (d, J = 7.0 Hz, 2H), 6.64 (d, J = 2.0 Hz, 1H), 6.46 (dd, J = 17.3, 10.7 Hz, 1H), 5.92 (s, 1H), 5.25 - 5.07 (m, 2H), 5.01 (d, J = 10.7 Hz, 1H), 3.84 (s, 3H), 3.81 (s, 3H), 2.71 (td, J = 13.0, 3.8 Hz, 1H), 2.11 (td, J = 12.5, 3.6 Hz, 1H), 1.98 (td, J = 13.0, 3.7 Hz, 1H), 1.86 (td, J = 12.5, 3.6 Hz, 1H), 1.63 - 1.52 (m, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 159.8, 152.2, 146.2, 142.3, 142.1, 139.1, 138.2, 137.7, 134.7, 128.1, 125.5, 122.3, 118.0, 114.5, 113.5, 112.0, 107.5, 72.0, 59.0, 55.7, 55.5, 43.0, 29.2, 19.2, 11.8. **HRMS** $[M + H]^+$ calcd for $C_{30}H_{34}NO_2$ 440.2584, found 440.2582.

(1S,3R)-2-(4-methoxyphenyl)-3-methyl-1-((*E*)-2-methylbuta-1,3-dien-1-yl)-1-phenethyl-6-(trifluoromethyl)isoindoline (11en).

Following the general procedure D, the title compound was obtained in 50% yield as a white solid, after chromatography on silica gel (PE/EA = 100/1; PE/EA = 50/1, $R_f \approx$ 0.44), 47.2 mg. The diastereomeric ratio, as determined by ^{1}H NMR analysis of the crude mixture, was found > 25:1.



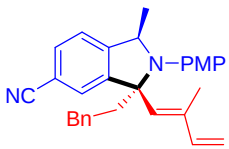
11en

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, J = 7.8 Hz, 1H), 7.39 (d, J = 7.9 Hz 1H), 7.35 (s, 1H), 7.15 - 6.99 (m, 5H), 6.93 - 6.83 (m, 2H), 6.74 - 6.60 (m, 2H), 6.45 (dd, J = 17.3, 10.8 Hz, 1H), 5.92 (s, 1H), 5.29 - 5.14 (m, 2H), 5.04 (d, J = 10.7 Hz, 1H), 3.80 (s, 3H), 2.68 (td, J = 13.3, 4.1 Hz, 1H), 2.11 (td, J = 12.5, 3.9 Hz, 1H), 2.00 (td, J = 13.4, 4.0 Hz , 1H), 1.80 (td, J = 12.6, 4.0 Hz, 1H), 1.62 (d, J = 6.2 Hz, 3H), 1.51 (d, J = 0.9 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 152.7, 146.3, 145.8, 141.9, 141.5,

138.4, 138.3, 137.4, 130.4 (q, J = 32.0 Hz), 128.2, 128.0, 125.7, 125.7, 124.7 (q, J = 3.6 Hz), 122.2 (q, J = 280.0 Hz), 119.4 (q, J = 3.6 Hz), 118.4, 114.5, 112.6, 71.9, 59.2, 55.7, 42.9, 29.3, 18.8, 11.9. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -61.8. **HRMS** $[M + H]^+$ calcd for $C_{30}H_{31}F_3NO$ 478.2352, found 478.2355.

(1R,3S)-2-(4-methoxyphenyl)-1-methyl-3-((*E*)-2-methylbuta-1,3-dien-1-yl)-3-phenethylisoindoline-5-carbonitrile (11fn).

Following the general procedure D, the title compound was obtained in 74% yield as a white solid, after chromatography on silica gel (PE/EA = 100/1; PE/EA = 20/1, $R_f \approx$ 0.33), 60.1 mg. The diastereomeric ratio, as determined by ^{1}H NMR analysis of the crude mixture, was found to be > 20:1.

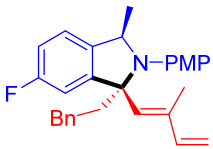


11fn

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (dd, J = 7.9, 1.3 Hz, 1H), 7.46 - 7.35 (m, 2H), 7.18 - 6.97 (m, 5H), 6.95 - 6.83 (m, 2H), 6.73 - 6.62 (m, 2H), 6.44 (dd, J = 17.2, 10.8 Hz, 1H), 5.89 (s, 1H), 5.27 - 5.15 (m, 2H), 5.06 (d, J = 10.7 Hz, 1H), 3.80 (s, 3H), 2.64 (td, J = 13.6, 4.3 Hz, 1H), 2.12 (td, J = 12.7, 6.3 Hz, 1H), 2.01 - 1.90 (m, 1H), 1.80 (td, J = 12.6, 4.3 Hz, 1H), 1.61 (d, J = 6.2 Hz, 3H), 1.50 (d, J = 0.9 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 152.9, 147.7, 146.4, 141.6, 141.2, 138.7, 138.1, 137.0, 131.5, 128.3, 128.0, 126.4, 125.8, 122.7, 119.0, 118.6, 114.6, 113.0, 111.7, 71.8, 59.4, 55.7, 42.9, 29.3, 18.6, 12.0. **HRMS** $[M + H]^+$ calcd for $C_{30}H_{31}N_2O$ 435.2431, found 435.2429.

(1S,3R)-6-fluoro-2-(4-methoxyphenyl)-3-methyl-1-((*E*)-2-methylbuta-1,3-dien-1-yl)-1-phenethylisoindoline (11gn).

Following the general procedure D, the title compound was obtained in 71% yield as a white solid after chromatography on silica gel (PE/EA = 100/1; PE/EA = 50/1, $R_f \approx$ 0.59), 62.2 mg. The diastereomeric ratio, as determined by ^{1}H NMR analysis of the crude mixture, was found to be 20:1.



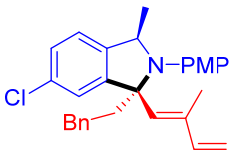
11gn

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 - 7.18 (m, 1H), 7.15 - 6.98 (m, 6H), 6.92 - 6.83(m, 2H), 6.80 (dd, J = 8.7, 2.1 Hz, 1H), 6.68 (d, J =

7.0 Hz, 2H), 6.43 (dd, *J* = 17.3, 10.7 Hz, 1H), 5.88 (s, 1H), 5.23 - 5.09 (m, 2H), 5.02 (d, *J* = 10.7 Hz, 1H), 3.79 (s, 3H), 2.66 (td, *J* = 13.2, 4.1 Hz, 1H), 2.11 (td, *J* = 12.5, 3.9 Hz, 1H), 2.00 - 1.88 (m, 1H), 1.83 (td, *J* = 12.7, 4.0 Hz, 1H), 1.58 (d, *J* = 6.1 Hz, 3H), 1.54 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 162.9 (d, *J* = 242.7 Hz), 152.4, 146.9 (d, *J* = 7.7 Hz), 142.0, 141.7, 138.8, 138.1, 137.9, 137.7, 128.2, 128.1, 125.6, 122.9 (d, *J* = 8.7 Hz), 118.2, 114.8, 114.5, 112.4, 109.3 (d, *J* = 22.9 Hz), 71.8 (d, *J* = 2.3 Hz), 58.9, 55.7, 43.0, 29.3, 19.1, 11.8. **HRMS** $[M + H]^+$ calcd for $C_{29}H_{31}FNO$ 428.2384, found 428.2381.

(1S,3R)-6-chloro-2-(4-methoxyphenyl)-3-methyl-1-((*E*)-2-methylbuta-1,3-dien-1-yl)-1-phenethylisoindoline (11hn).

Following the general procedure D, the title compound was obtained in 73% yield as a white solid after chromatography on silica gel (PE/EA = 100/1; PE/EA = 50/1, $R_f \approx$ 0.33), 66.9 mg. The diastereomeric ratio, as determined by ^{1}H NMR analysis of the crude mixture, was found to be 20:1.



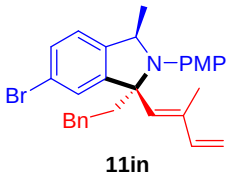
11hn

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 (dd, *J* = 8.1, 1.9 Hz, 1H), 7.23 - 7.18 (m, 1H), 7.14 - 6.97 (m, 6H), 6.91 - 6.83 (m, 2H), 6.75 - 6.63 (m, 2H), 6.44 (dd, *J* = 17.3, 10.8 Hz, 1H), 5.88 (s, 1H), 5.23 - 5.09 (m, 2H), 5.03 (d, *J* = 10.7 Hz, 1H), 3.79 (s, 3H), 2.66 (td, *J* = 13.1, 4.1 Hz, 1H), 2.10 (td, *J* = 12.5, 4.0 Hz, 1H), 1.94 (td, *J* = 13.5, 4.2 Hz, 1H), 1.83 (td, *J* = 12.6, 4.1 Hz, 1H), 1.58 (d, *J* = 6.1 Hz, 3H), 1.54 (d, *J* = 0.9 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 152.5, 146.8, 142.0, 141.7, 140.9, 138.6, 138.1, 137.6, 133.4, 128.2, 128.1, 127.7, 125.6, 122.9, 122.5, 118.2, 114.5, 112.5, 71.8, 59.0, 55.7, 43.0, 29.2, 18.9, 11.9. **HRMS** $[M + H]^+$ calcd for $C_{29}H_{31}ClNO$ 444.2089, found 444.2087.

(1S,3R)-6-bromo-2-(4-methoxyphenyl)-3-methyl-1-((E)-2-methylbuta-1,3-dien-1-yl)-1-phenethylisoindoline (11in).

Following the general procedure D, the title compound was obtained in 76% yield as a pale yellow solid after chromatography on silica gel (PE/EA = 100/1; PE/EA = 50/1,

$R_f \approx 0.59$), 74.3 mg. The diastereomeric ratio, as determined by ^{1}H NMR analysis of the crude mixture, was found > 25:1.

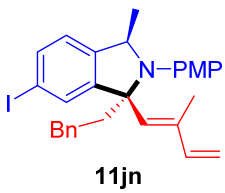


11in

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (dd, J = 8.1, 1.8 Hz, 1H), 7.23 (d, J = 1.7 Hz, 1H), 7.15 (d, J = 8.1 Hz, 1H), 7.13 - 6.98 (m, 5H), 6.90 - 6.83 (m, 2H), 6.72 - 6.64 (m, 2H), 6.44 (dd, J = 17.3, 10.9 Hz, 1H), 5.87 (s, 1H), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (dd, J = 8.1, 1.8 Hz, 1H), 7.23 (d, J = 1.7 Hz, 1H), 7.15 (d, J = 8.1 Hz, 1H), 7.06 (m, 5H), 6.86 (m, 2H), 6.69 (m, 2H), 6.44 (dd, J = 17.3, 10.9 Hz, 1H), 5.87 (s, 1H), 5.19 (d, J = 17.4 Hz, 1H), 5.12 (q, J = 6.0 Hz, 1H), 5.03 (d, J = 10.7 Hz, 1H), 3.79 (s, 3H), 2.66 (td, J = 13.0, 4.1 Hz, 1H), 2.10 (td, J = 12.5, 4.0 Hz, 1H), 2.00 - 1.89 (m, 1H), 1.83 (td, J = 12.6, 4.1 Hz, 1H), 1.58 (d, J = 6.1 Hz, 3H), 1.54 (d, J = 1.0 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 152.5, 147.1, 142.0, 141.6, 141.4, 138.6, 138.1, 137.6, 130.6, 128.2, 128.1, 125.7, 125.5, 123.3, 121.4, 118.2, 114.5, 112.5, 71.8, 59.1, 55.7, 43.0, 29.2, 18.8, 11.9. **HRMS** $[M + H]^+$ calcd for $C_{29}H_{31}BrNO$ 488.1584, found 488.1586.

(1S,3R)-6-iodo-2-(4-methoxyphenyl)-3-methyl-1-((E)-2-methylbuta-1,3-dien-1-yl) -1-phenethylisoindoline (11jn)

Following the general procedure D, the title compound was obtained in 62% yield as a white solid after chromatography on silica gel (PE/EA = 100/1; PE/EA = 100/1, R_f ≈ 0.46), 66.4 mg. The diastereomeric ratio, as determined by ^{1}H NMR analysis of the crude mixture, was found > 25:1.



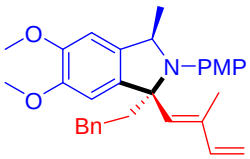
11jn

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (dd, J = 8.0, 1.6 Hz, 1H), 7.43 (d, J = 1.5 Hz, 1H), 7.16 - 6.97 (m, 6H), 6.92 - 6.83 (m, 2H), 6.73 - 6.65 (m, 2H), 6.44 (dd, J = 17.3, 11.0 Hz, 1H), 5.87 (s, 1H), 5.19 (d, J = 17.4 Hz, 1H), 5.12 (q, J = 6.0 Hz, 1H), 5.03 (d, J = 10.7 Hz, 1H), 3.80 (s, 3H), 2.66 (td, J = 13.2, 4.1 Hz, 1H), 2.10 (td, J = 12.5, 4.1 Hz, 1H), 2.00 - 1.88 (m, 1H), 1.84 (td, J = 12.6, 4.2 Hz, 1H), 1.58 (d, J = 6.1 Hz, 3H), 1.55 (d, J = 1.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 152.5, 147.3, 142.1, 142.0, 141.7, 138.5, 138.1, 137.6, 136.4, 131.4, 128.2, 128.1, 125.6, 123.7, 118.2, 114.5,

112.5, 92.7, 71.6, 59.1, 55.7, 42.9, 29.2, 18.8, 11.9. **HRMS** $[M + H]^+$ calcd for $C_{29}H_{31}INO$ 536.1445, found 536.1449.

(1S,3R)-5,6-dimethoxy-2-(4-methoxyphenyl)-3-methyl-1-((E)-2-methylbuta-1,3-dien-1-yl)-1-phenethylisoindoline (11kn).

Following the general procedure D, the title compound was obtained in 58% yield as a white solid after chromatography on silica gel (PE/EA = 100/1; PE/EA = 20/1, $R_f \approx$ 0.16), 54.4 mg. The diastereomeric ratio, as determined by ^{1}H NMR analysis of the crude mixture, was found to be 20:1.

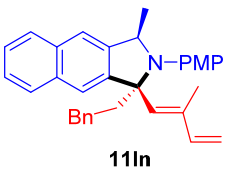


11kn

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.15 - 6.97 (m, 5H), 6.93 - 6.83 (m, 2H), 6.76 (s, 1H), 6.68 (d, J = 6.9 Hz, 2H), 6.57 (s, 1H), 6.44 (dd, J = 17.3, 10.7 Hz, 1H), 5.89 (s, 1H), 5.24 - 5.07 (m, 2H), 4.99 (d, J = 10.7 Hz, 1H), 3.95 (s, 3H), 3.88 (s, 3H), 3.79 (s, 3H), 2.69 (td, J = 13.1, 4.1 Hz, 1H), 2.12 - 2.01 (m, 1H), 2.00 - 1.88 (m, 1H), 1.81 (td, J = 12.6, 3.9 Hz, 1H), 1.62 - 1.51 (m, 6H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 152.1, 149.4, 149.0, 142.3, 142.1, 139.1, 138.2, 137.6, 136.2, 134.0, 128.1 (overlapped), 125.5, 117.8, 114.5, 111.9, 105.0, 104.3, 71.9, 59.4, 56.3, 56.1, 55.7, 43.1, 29.2, 19.0, 11.7. **HRMS** $[M + H]^+$ calcd for $C_{31}H_{36}NO_3$ 470.2690, found 470.2697.

(1S,3R)-2-(4-methoxyphenyl)-3-methyl-1-((E)-2-methylbuta-1,3-dien-1-yl)-1-phenethyl-2,3-dihydro-1H-benzo[f]isoindole (11ln).

Following the general procedure D, the title compound was obtained in 68% yield as a white solid after chromatography on silica gel (PE/EA = 100/1; PE/EA = 100/1, R_f ≈ 0.3), 62.1 mg. The diastereomeric ratio, as determined by ^{1}H NMR analysis of the crude mixture, was found to be > 20:1.



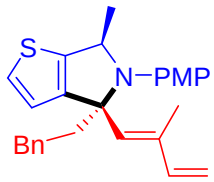
11ln

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 - 7.81 (m, 2H), 7.73 (s, 1H), 7.56 (s, 1H), 7.51 - 7.41 (m, 2H), 7.16 - 6.97 (m, 5H), 6.94 - 6.84 (m, 2H), 6.73 - 6.60 (m, 2H), 6.49 (dd, J = 17.3, 10.9 Hz, 1H), 6.05 (s, 1H), 5.32 (q, J = 6.0 Hz, 1H), 5.14 (d, J = 17.4 Hz, 1H), 5.00 (d, J = 10.8 Hz, 1H), 3.80 (s, 3H), 2.72 (td, J = 11.3, 3.0 Hz, 1H), 2.23 - 2.04 (m, 2H), 1.86 (td, J

= 12.9, 3.8 Hz, 1H), 1.70 (d, *J* = 6.1 Hz, 3H), 1.48 (d, *J* = 1.0 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 152.5, 144.7, 142.1, 142.0, 142.0, 139.0, 138.9, 137.7, 133.6, 133.4, 128.2, 128.1, 128.1, 127.8, 125.5, 125.5, 125.4, 120.8, 120.1, 118.7, 114.5, 112.1, 71.5, 58.9, 55.7, 43.6, 29.4, 19.5, 12.2. **HRMS** $[M + H]^+$ calcd for $C_{33}H_{34}NO$ 460.2635, found 460.2631.

(4S,6R)-5-(4-methoxyphenyl)-6-methyl-4-((E)-2-methylbuta-1,3-dien-1-yl)-4-phenethyl-5,6-dihydro-4H-thieno[2,3-c]pyrrole (11mn).

Following the general procedure D, the title compound was obtained in 42% yield as a white solid after chromatography on silica gel (PE/EA = 100/1; PE/EA = 100/1, R_f ≈ 0.28), 34.8 mg. The diastereomeric ratio, as determined by ^{1}H NMR analysis of the crude mixture, was found to be > 20:1.

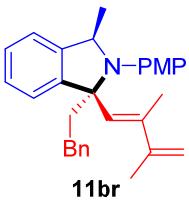


11mn

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 (dd, *J* = 4.9, 0.8 Hz, 1H), 7.15 - 7.02 (m, 3H), 7.00 - 6.93 (m, 2H), 6.88 - 6.81 (m, 2H), 6.77 - 6.67 (m, 3H), 6.42 (dd, *J* = 17.3, 11.1 Hz, 1H), 5.84 (s, 1H), 5.25 (q, *J* = 6.0 Hz, 1H), 5.17 (d, *J* = 17.4 Hz, 1H), 5.00 (d, *J* = 10.7 Hz, 1H), 3.79 (s, 3H), 2.62 - 2.51 (m, 1H), 2.22 - 2.09 (m, 1H), 2.05 - 1.90(m, 2H), 1.63 (d, *J* = 1.1 Hz, 3H), 1.59 (d, *J* = 6.1 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 152.2, 146.6, 142.3, 142.0, 141.0, 139.2, 137.6, 136.9, 128.2, 128.2 (two overlapping signals), 125.5, 120.2, 117.5, 114.5, 112.0, 70.5, 57.8, 55.7, 42.1, 29.5, 19.6, 11.4. **HRMS** $[M + H]^+$ calcd for $C_{27}H_{30}NOS$ 416.2043, found 416.2043.

(1S,3R)-1-((*E*)-2,3-dimethylbuta-1,3-dien-1-yl)-2-(4-methoxyphenyl)-3-methyl-1-phenethylisoindoline (11br).

Following the general procedure D, the title compound was obtained in 62% yield as a white solid after chromatography on silica gel (PE/EA = 100/1; PE/EA = 100/1, R_f ≈ 0.44), 52.4 mg. The diastereomeric ratio, as determined by ^{1}H NMR analysis of the crude mixture, was found to be > 20:1.

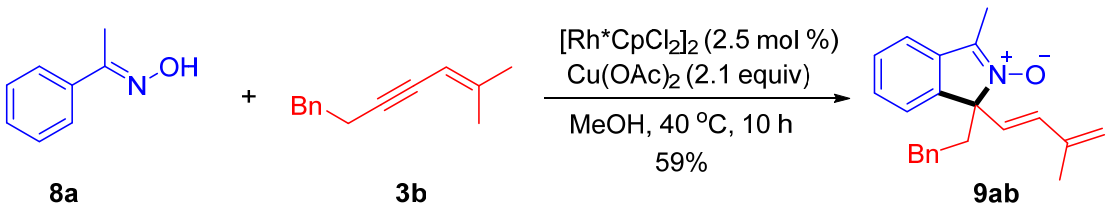


11br

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 - 7.26 (m, 3H), 7.15 - 6.99 (m, 6H), 6.91 - 6.83 (m, 2H), 6.68 (d, J = 6.8 Hz, 2H), 6.02 (s, 1H), 5.18 (q, J = 6.2 Hz, 1H), 5.03 (s, 1H), 4.91 (s, 1H), 3.80 (s, 3H), 2.70 (td, J = 12.7, 4.0 Hz, 1H), 2.10 (td, J = 12.7, 4.0 Hz, 1H), 2.15 - 1.92 (m, 4H), 1.82 (td, J = 12.6, 3.8 Hz, 1H), 1.60 (d, J = 6.1 Hz, 3H), 1.58 - 1.52 (m, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 152.2, 145.5, 145.1, 142.4, 142.2, 139.1, 133.3, 128.1, 128.1 (overlapped), 127.7, 127.2, 125.5, 122.3, 121.5, 118.0, 114.5, 112.1, 71.9, 59.4, 55.7, 43.8, 29.3, 21.3, 18.8, 13.9. **HRMS** $[M + H]^+$ calcd for $C_{30}H_{34}NO$ 424.2635, found 424.2631.

3. Derivatization of 9ab

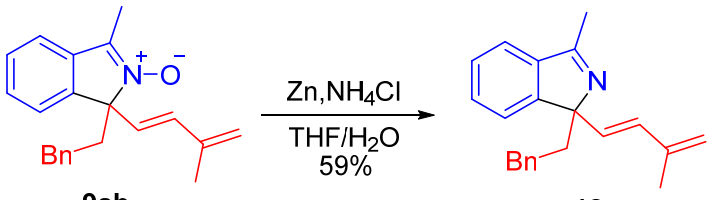
3.1 Gram-scale synthesis



8a **3b** **9ab**

Oximes **8a** (4.0 mmol), $[Rh^*CpCl_2]_2$ (2.5 mol %, 61.8 mg), $Cu(OAc)_2$ (8.4 mmol, 1528.8 mg), and MeOH (20.0 mL) were charged into a pressure tube, then 1,3-enynes **3b** (4.4 mmol, 809.6 mg) was subsequently added. The reaction mixture was stirred at 40 °C for 10 h under the protection of N_2 atmosphere. After cooled to room temperature, the solvent was removed under reduced pressure, and the residue was purified by silica gel chromatography using PE/EA to afford compound **9ab** (748.1 mg, 59%).

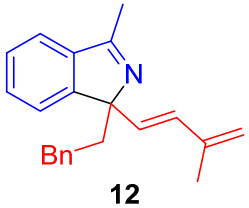
3.2 Deoxygenation of 9ab



9ab **12**

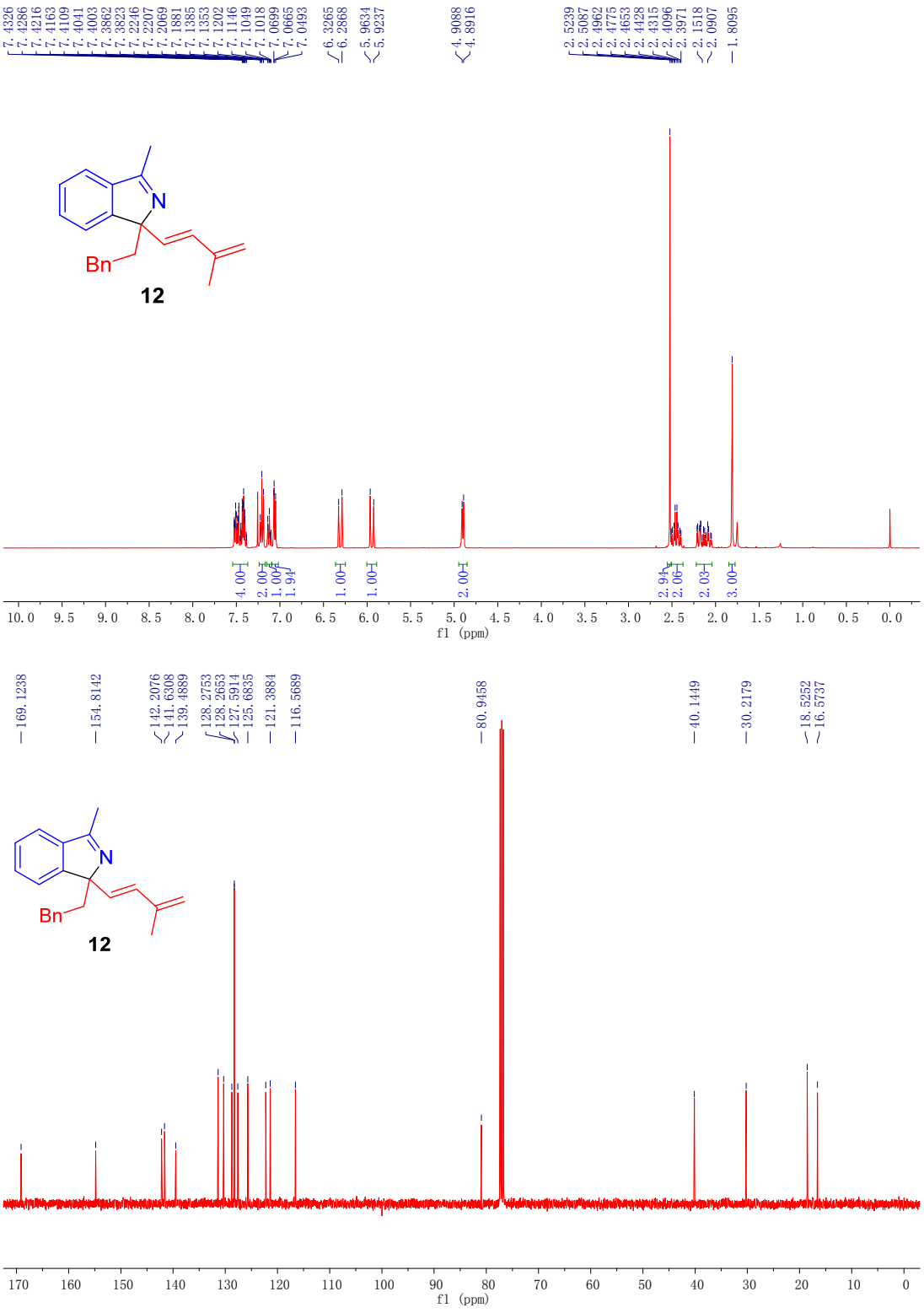
To a solution of **9ab** (47.5 mg, 0.15 mmol) in THF (2 mL) were added a 30% aqueous solution of NH_4Cl (2 mL) and zinc dust (58.5 mg, 0.9 mmol) sequentially. The reaction mixture was stirred at room temperature and monitored by TLC. After full conversion, the mixture was diluted with water (10 mL), and extracted with EtOAc (10 mL x 3). The organic extracts were dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel to give the deoxygenated product **12** (**Supplementary Fig. 1**).

(*E*)-3-methyl-1-(3-methylbuta-1,3-dien-1-yl)-1-phenethyl-1*H*-isoindole (12).



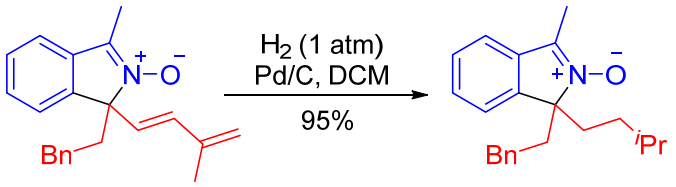
12

Purified by column chromatography on silica gel (PE/EA = 6/1; PE/EA = 4/1, $R_f \approx 0.66$) to deliver the desired product as pale yellow oil (26.6 mg, 59% yield). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.54 - 7.37 (m, 4H), 7.24 - 7.17 (m, 2H), 7.16 - 7.09 (m, 1H), 7.09 - 7.01 (m, 2H), 6.31 (d, J = 15.9 Hz, 1H), 5.94 (d, J = 15.9 Hz, 1H), 4.95 - 4.85 (m, 2H), 2.52 (s, 3H), 2.51 - 2.38 (m, 2H), 2.23 - 2.03 (m, 2H), 1.81 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 169.1, 154.8, 142.2, 141.6, 139.5, 131.4, 130.3, 128.7, 128.3, 128.3, 127.6, 125.7, 122.3, 121.4, 116.6, 81.0, 40.1, 30.2, 18.5, 16.6. **HRMS** $[M + H]^+$ calcd for $C_{22}H_{24}N$: 302.1903, found 302.1904.



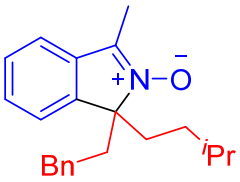
Supplementary Figure 1. ^{1}H NMR and ^{13}CNMR Spectra of 12.

3.3 Hydrogenation of 9ab



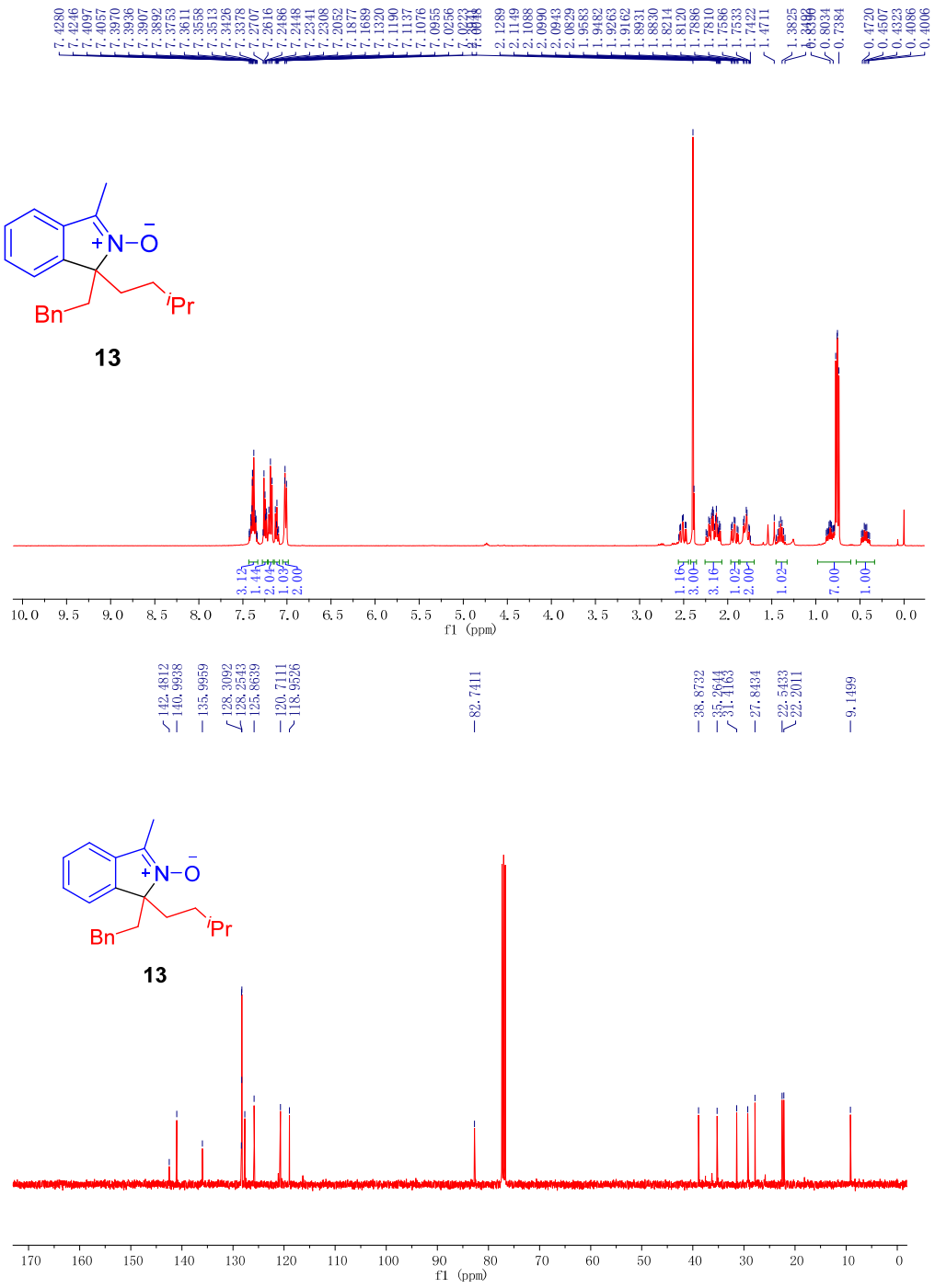
9ab **13**

To a solution of **9ab** (31.7 mg, 0.10 mmol) in DCM (2 mL) were added Pd/C (10 w/w%, 10.6 mg). The reaction mixture was stirred at room temperature and kept under 1 atm of H_2 atmosphere for 20 h. Then, the mixture was diluted with water (10 mL), and extracted with EtOAc (10 mL x 3). The organic extracts were dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel to give the hydrogenated product **13** (**Supplementary Fig. 2**).



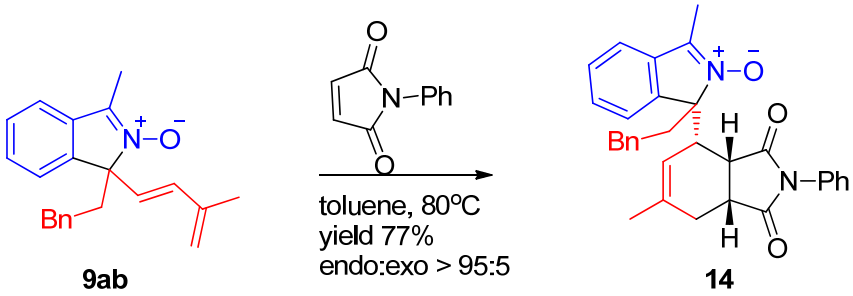
13

1-isopentyl-3-methyl-1-phenethyl-1*H*-isoindole 2-oxide (13). Purified by column chromatography on silica gel (PE/EA = 6/1then DCM/MeOH = 100/1; PE/EA = 2/1, $R_f \approx 0.04$) to deliver the desired product as white solid (30.5 mg, 95% yield). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.44 - 7.33 (m, 3H), 7.29 - 7.22 (m, 1H), 7.22 - 7.15 (m, 2H), 7.15 - 7.08 (m, 1H), 7.05 - 6.98 (m, 2H), 2.51 (td, J = 11.6, 3.0 Hz, 1H), 2.44 - 2.36 (m, 3H), 2.28 - 2.06 (m, 3H), 1.98 - 1.87 (m, 1H), 1.87 - 1.70 (m, 2H), 1.50 - 1.33 (m, 1H), 1.00 - 0.61 (m, 7H), 0.54 - 0.36 (m, 1H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 142.5, 141.0, 136.0, 128.4, 128.3, 128.3, 128.3, 127.7, 125.9, 120.7, 119.0, 82.7, 38.9, 35.3, 31.4, 29.2, 27.8, 22.5, 22.2, 9.2. **HRMS [M + H]$^+$** calcd for $C_{22}H_{28}NO^+$: 322.2165, found 322.2157.

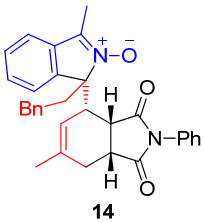


Supplementary Figure 2. ^{1}H NMR and ^{13}CNMR Spectra of 13

3.4 Diels−Alder reaction of 9ab

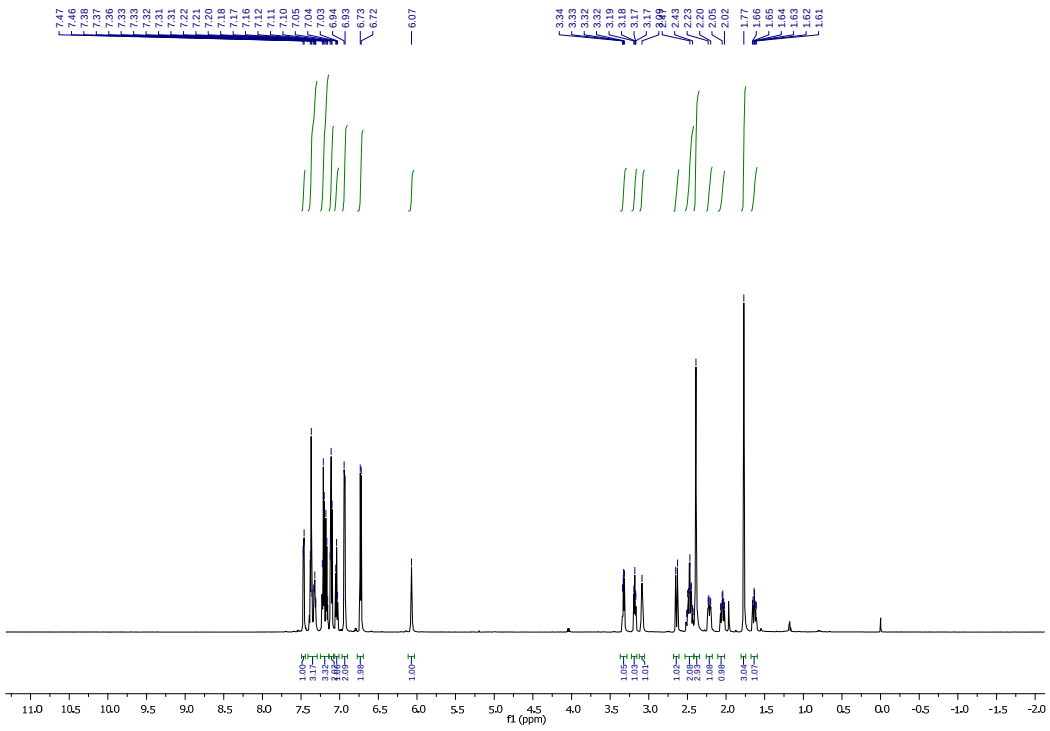


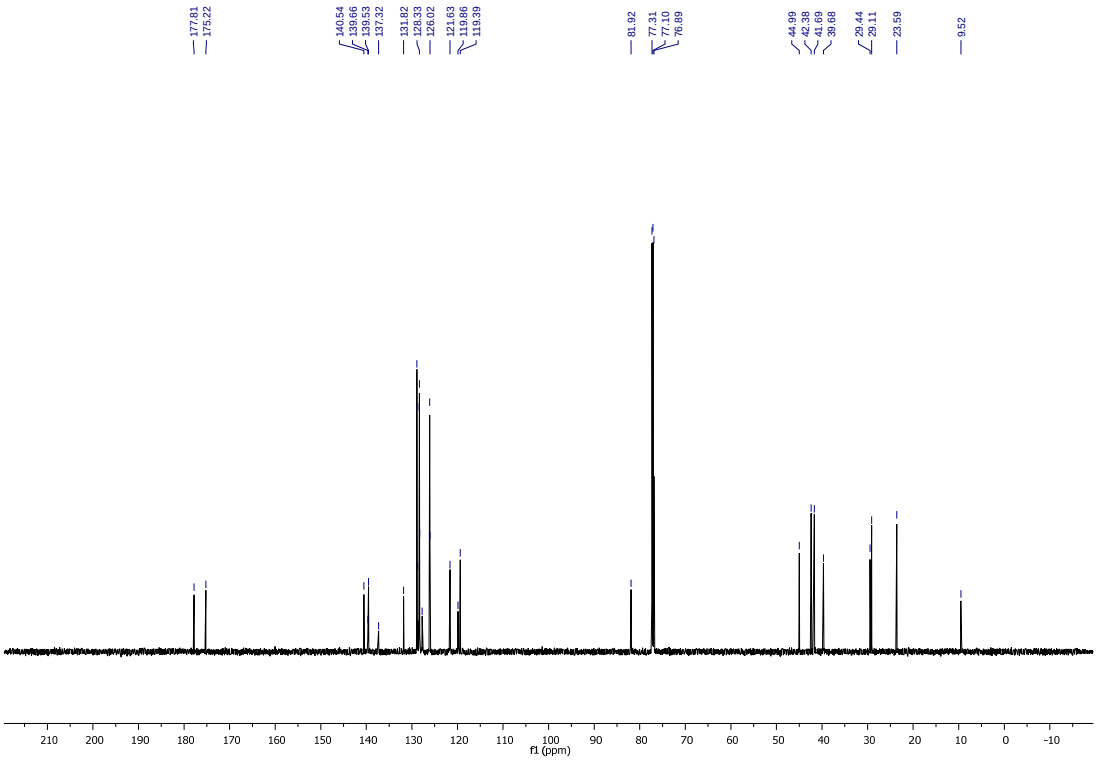
To a solution of **9ab** (154 mg, 0.5 mmol) in Toluene (4 mL) were added N-phenylmaleimide (104 mg, 0.6 mmol). The reaction mixture was stirred at 80 ^{o}C for 24h under the protection of N_2 atmosphere. After cooled to room temperature, the solvent was removed under reduced pressure, and the residue was purified by silica gel chromatography using PE/EA to afford compound **14** as a purple solid (158 mg, 77%) (**Supplementary Fig. 3**).

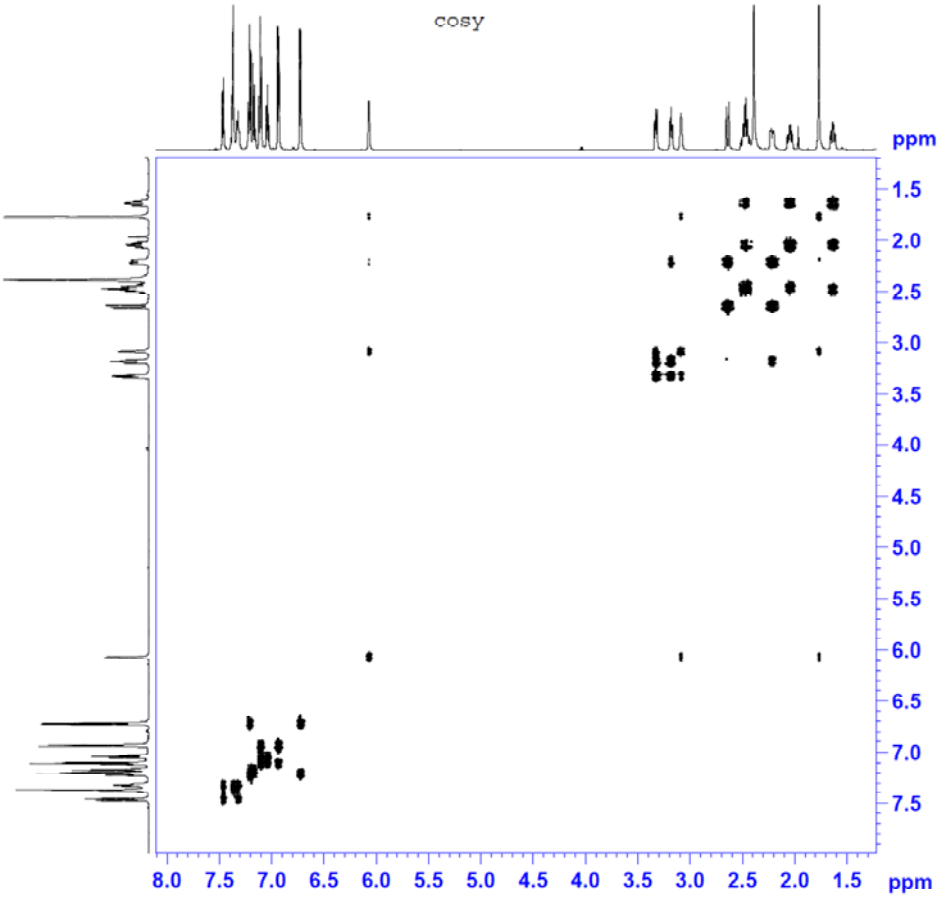


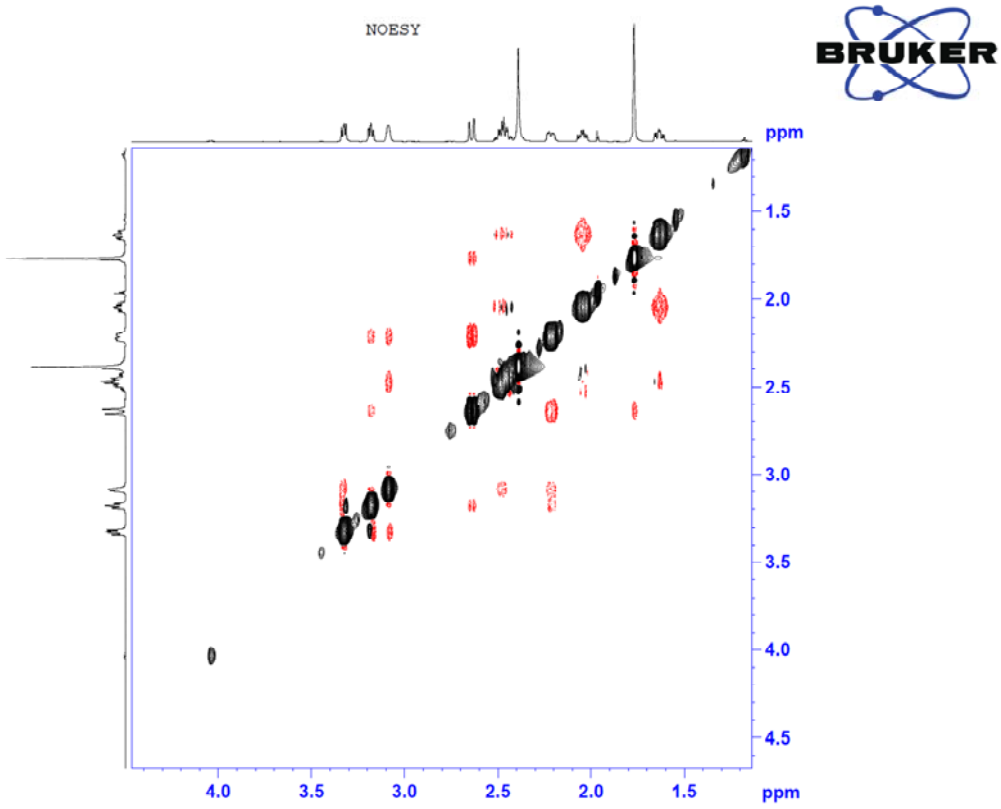
14

mp: 78-80 ^{o}C; ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.47 (d, *J* = 7.4 Hz,, 1H), 7.40-7.30 (m, 3H), 7.25 – 7.14 (m, 3H), 7.11 (t, *J* = 7.5 Hz,, 2H), 7.04 (t, *J* = 7.3 Hz, 1H), 6.94 (d, *J* = 7.4 Hz, 2H), 6.73 (d, *J* = 7.6 Hz, 2H), 6.07 (s, 1H), 3.33 (dd, *J* = 8.7, 5.9 Hz, 1H), 3.18 (dd, *J* = 11.0, 4.1 Hz, 1H), 3.09 (s, 1H), 2.64 (d, *J* = 14.5 Hz, 1H), 2.53 – 2.42 (m, 2H), 2.39 (s, 3H), 2.22 (dd, *J* = 14.8, 5.8 Hz, 1H), 2.05 (td, *J* = 12.6, 5.8 Hz, 1H), 1.77 (s, 3H), 1.63 (td, *J* = 12.9, 4.8 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 177.8, 175.2, 140.5, 139.7, 139.5, 137.3, 131.8, 128.9, 128.7, 128.4, 128.3, 128.3, 127.7, 126.1, 126.0, 121.6, 119.9, 119.4, 81.9, 45.0, 42.4, 41.7, 39.7, 29.4, 29.1, 23.6, 9.5. **HRMS [M + H]$^{+}$** calcd for $C_{32}H_{31}N_2O_3$: 491.2335, found:491.2330.



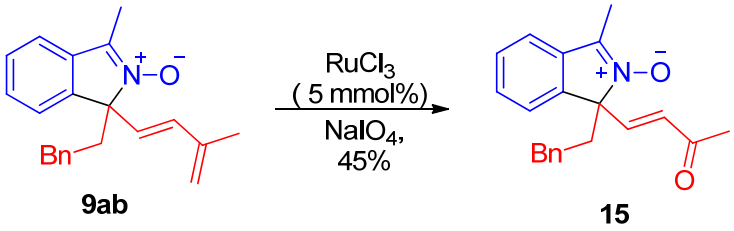

177.81
175.22
140.54
139.66
139.53
137.32
131.82
128.33
126.02
121.63
119.86
119.39
81.92
77.31
77.10
76.89
44.99
42.38
41.69
39.68
29.44
29.11
23.59
9.52
f1 (ppm)


cosy
ppm
ppm

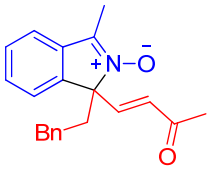


Supplementary Figure 3. ^{1}H NMR , ^{13}CNMR COSY and Noesy Spectra of 14

3.5 Oxidation of 9ab

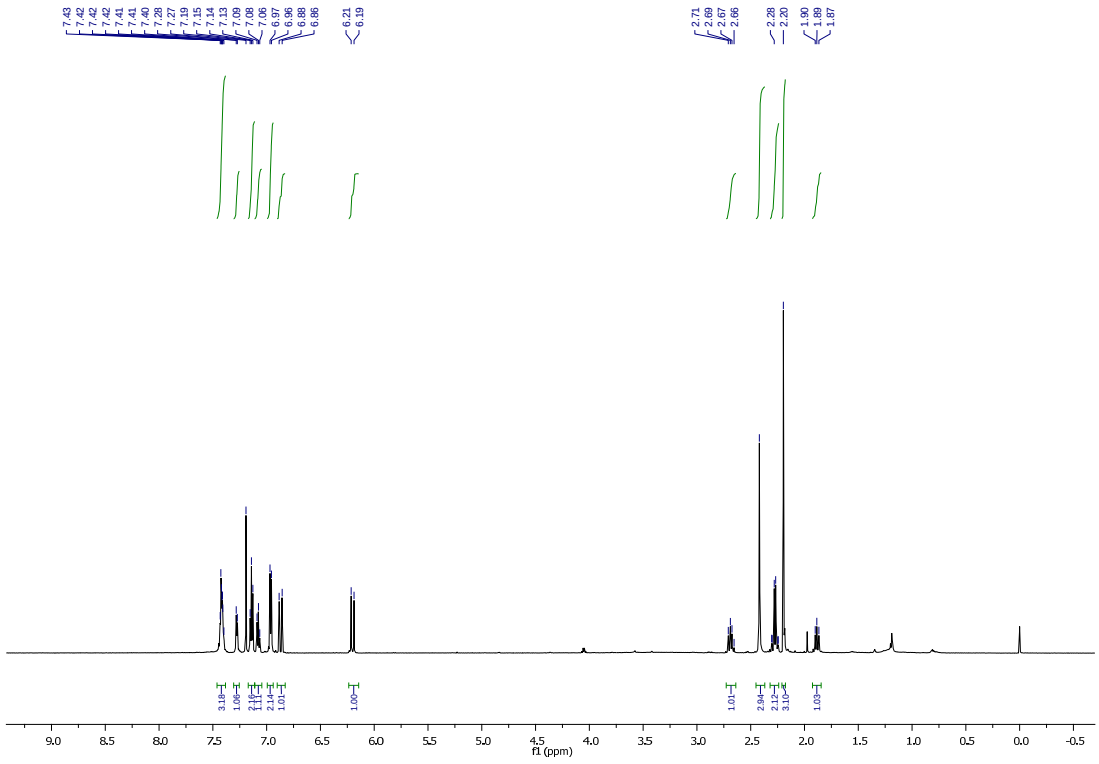


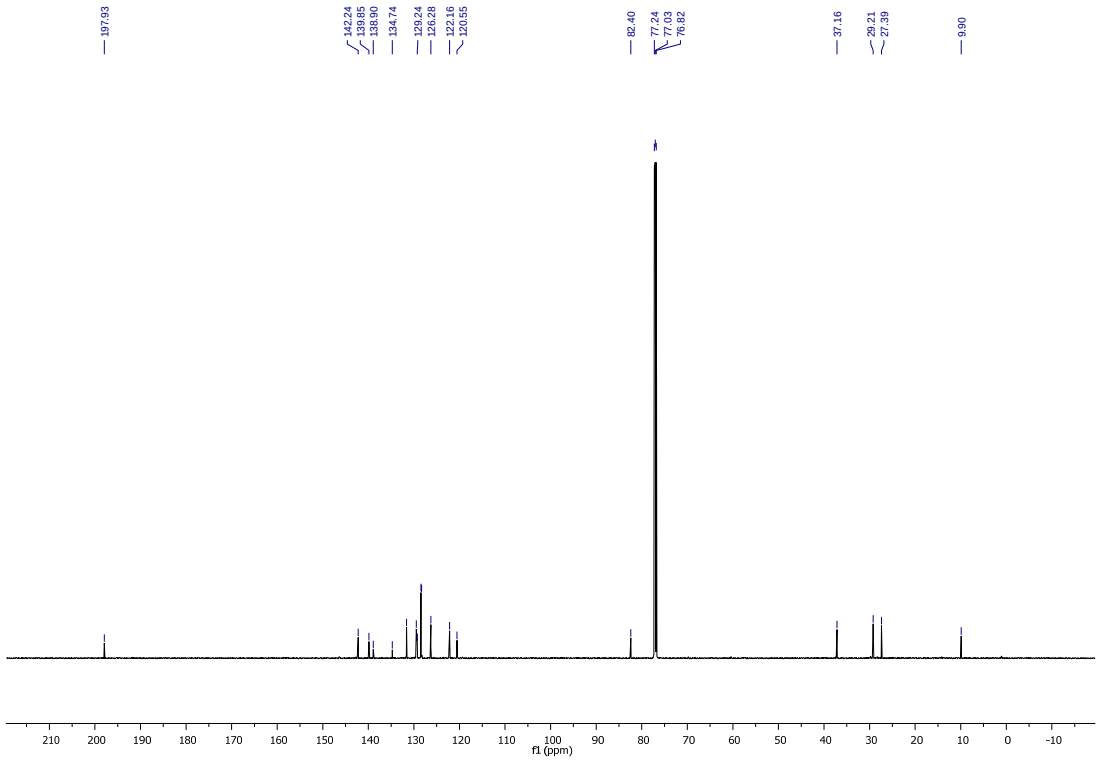
9ab (31 mg, 0.1 mmol,) and $RuCl_3$ (1.0 mg, 0.005 mmol,) were added to mixed solvent ($MeCN/H_2O$ 3 mL/0.5 mL) in a 25 mL round-bottom flask and the mixutre was stirred at room temperature for 0.5 h. $NaIO_4$ (42.8 mg, 0.2 mmol) was then added into the flask in one portion and the resulting mixture was stirred at 70 ^{o}C under air atmosphere for 2 h. Fianlly, the mixture was evaporatedand purified by chromatography (PE:EA=1:1) to give pure product 15 as a purple oil (15 mg, 45% yield) (**Supplementary Fig. 4**).



15

^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.47 – 7.39 (m, 2H), 7.29-7.27 (m, 1H), 7.14 (t, *J* = 7.5 Hz, 2H), 7.08 (t, *J* = 7.2 Hz, 2H), 6.96 (d, *J* = 7.6 Hz, 2H), 6.87 (d, *J* = 16.3 Hz, 1H), 6.20 (d, *J* = 16.3 Hz, 1H), 2.71-2.65 (m, 1H), 2.42 (s, 3H), 2.32 – 2.24 (m, 2H), 2.19 (s, 3H), 1.93 – 1.85 (m, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 198.0, 142.5, 139.9, 138.7, 135.0, 131.6, 129.4, 128.9, 128.4, 128.3, 126.3, 122.1, 120.3, 82.4, 37.2, 29.2, 27.4, 9.7. **HRMS [M + H]$^{+}$** calcd for$C_{21}H_{22}NO_2$: 320.1651, found : 320.1647.

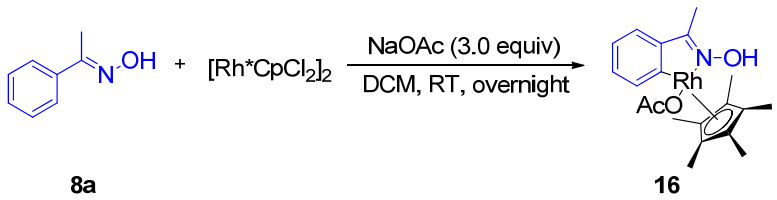




Supplementary Figure 4. ^{1}H NMR and ^{13}CNMR of 15

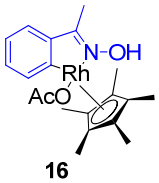
4. Mechanistic Studies

4.1 Procedure for the synthesis of cyclometalated Rh(III) complex 16



8a **16**

$[Cp^*RhCl_2]_2$ (0.25 mmol, 154.5 mg), Acetophenone Oxime **8a** (0.5 mmol, 67.5 mg) and sodium acetate (1.5 mmol, 3.0 equiv, 123 mg) in DCM (10 mL) were added to a schlenk tube under N_2 protected. Then, the mixture was stirred at room temperature for overnight. The solution was filtered through Celite and evaporated to dryness. The product was crystallized from DCM/hexane to give **16** (75.9 mg, 35%) as pale-yellow crystals (**Supplementary Fig. 5**).

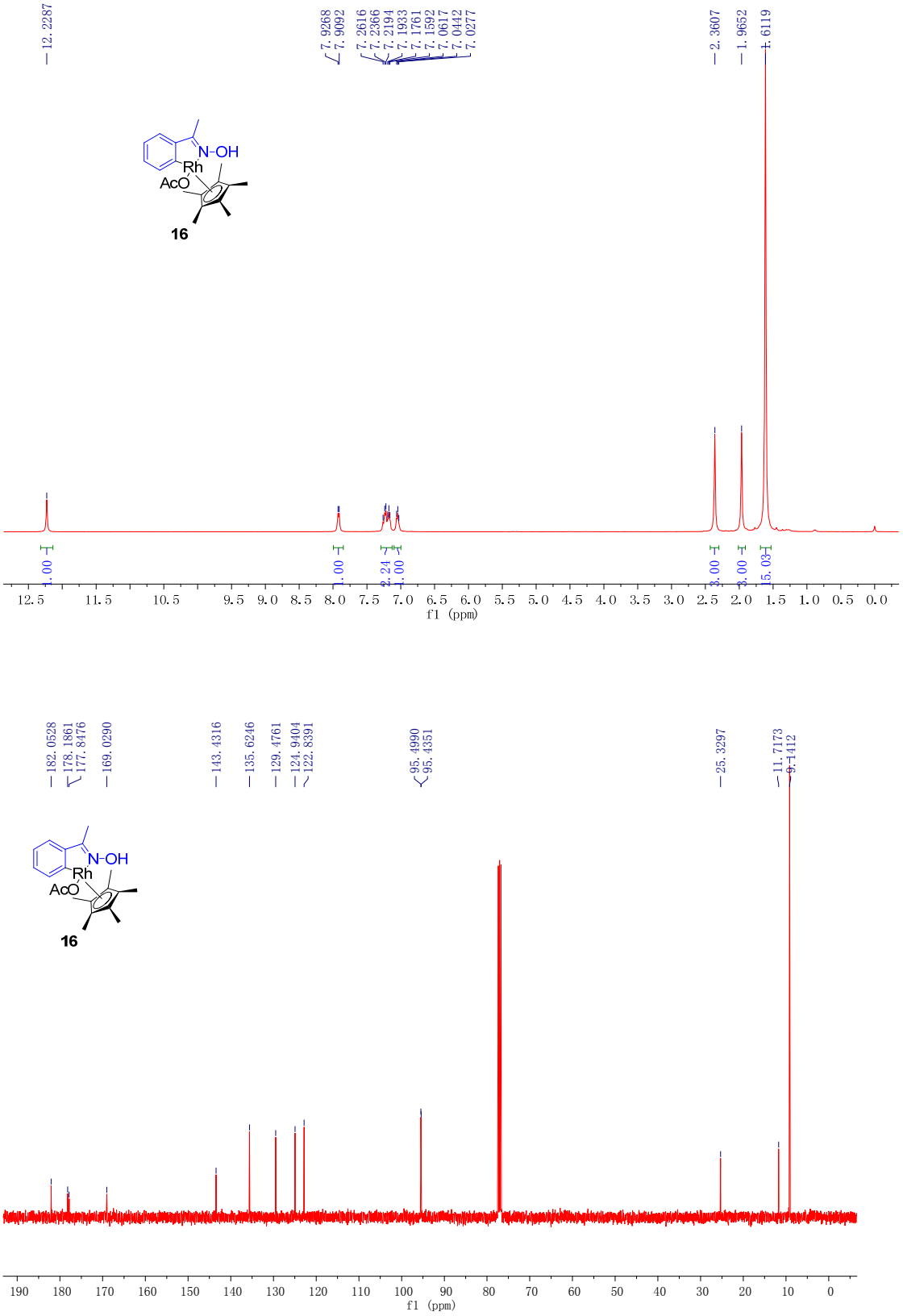


16

^{1}H NMR (400 MHz, $CDCl_3$) δ 12.23 (s, 1H), 7.92 (d, J = 7.0 Hz, 1H), 7.30 - 7.13 (m, 2H), 7.04 (t, J = 6.8 Hz, 1H), 2.36 (s, 3H), 1.97 (s, 3H), 1.61 (s, 15H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 182.1, 178.0 (d, J = 33.9

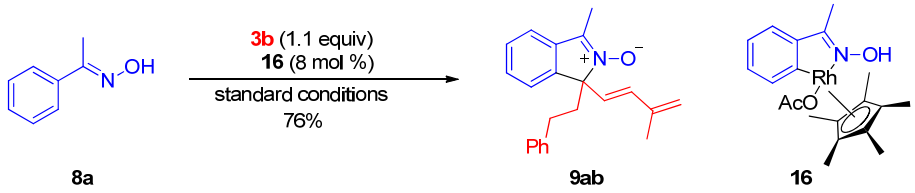
Hz), 169.0, 143.4, 135.6, 129.5, 124.9, 122.8, 95.5 (d, J = 6.4 Hz), 25.3, 11.7, 9.1.

HRMS (ESI): calcd for $C_{20}H_{26}NO_3Rh$ ([M-OAc])$^+$ 372.0835, found 372.0832.



Supplementary Figure 5. ^{1}H NMR and ^{13}CNMR of 16

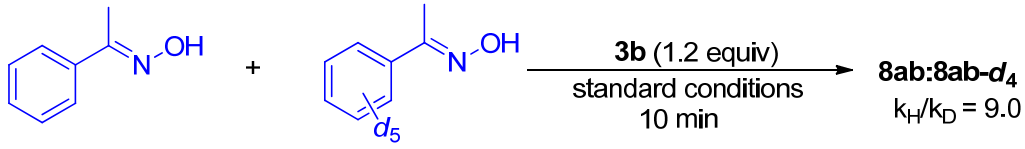
4. 2 Catalytic reaction of cyclometalated complex 16



8a **9ab** **16**

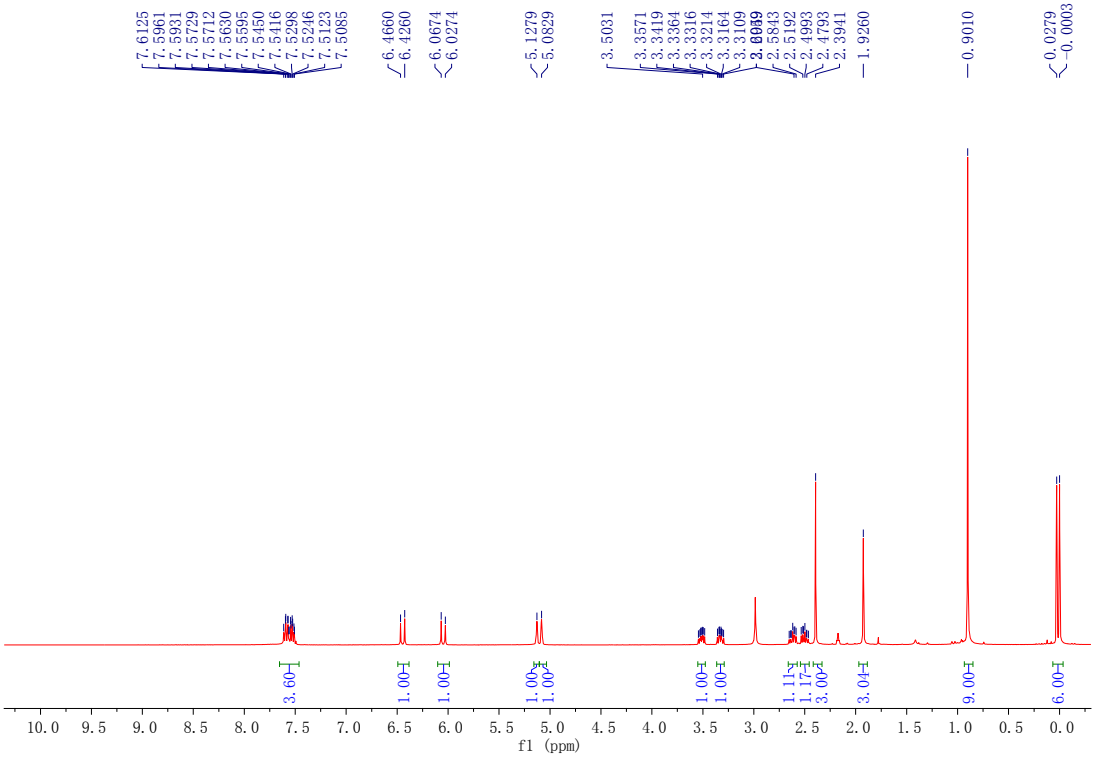
Acetophenone Oxime **8a** (0.2 mmol, 27.0 mg), 1,3-enyne **3b** (0.22 mmol, 40.5 mg), complex **16** (8 mol %, 6.9 mg) and methanol (2.0 mL) were charged into a pressure tube under N_2 atmosphere. The reaction mixture was stirred at 40 ^oC for 10 h. The solvent was removed under reduced pressure and the residue was purified by silica gel (PE/EA = 6/1) to yield product **9ab** (48.4 mg, 76%).

4. 3 Kinetic isotope effect experiment

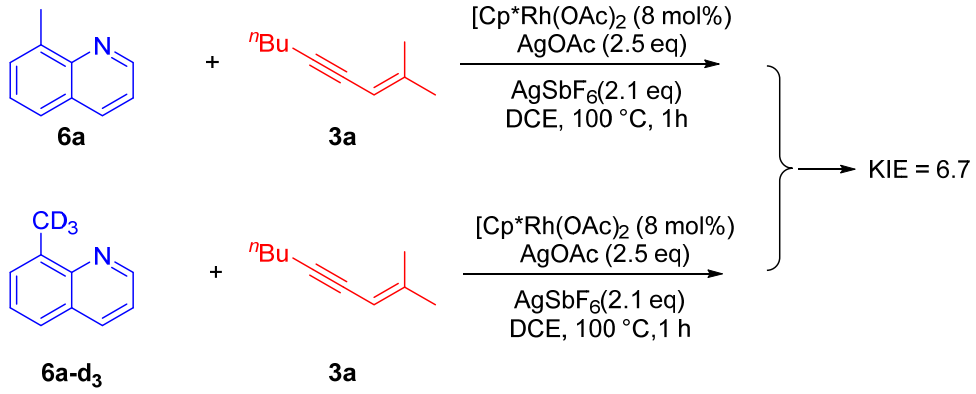


8a, 0.2mmol **8a-*d*$_5$**, 0.2mmol

A mixture of **8a** (0.2 mmol, 27.0 mg), **8a-*d*$_5$** (0.2 mmol, 28.0 mg), $[Rh^*CpCl_2]_2$ (0.008 mmol, 5.0 mg), $Cu(OAc)_2$ were dissolved in MeOH (2 mL) and **3b** (0.22 mmol, 40.5 mg) was then added. The mixture was stirred for 10 min at 40 ^oC under N_2 atmosphere. After that, the reaction was quenched in an ice bath. The solvent was removed under vacuum and the residue was purified by silica gel chromatography using ethyl acetate/petroleum ether (6:1) to afford product **8ab** and **8ab-*d*$_4$** as a pale yellow liquid (21.1 mg, 28% yield). The KIE value was determined to be k_H/k_D = 9.0 on the basis of ^1H NMR analysis (**Supplementary Fig. 6**).

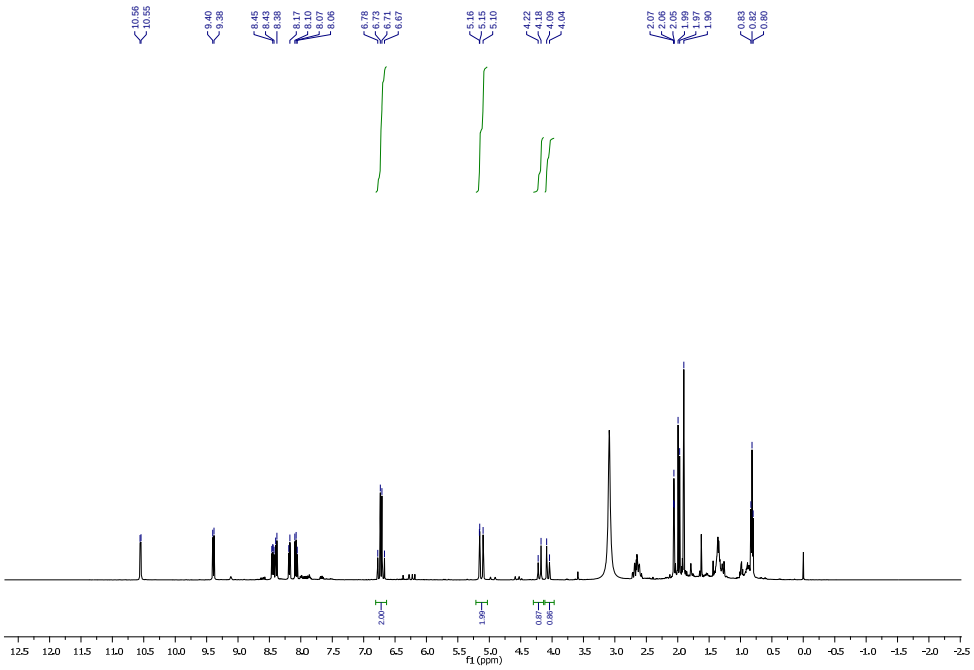


Supplementary Figure 6 . ^{1}H NMR of KIE value 8a and 8a-d5



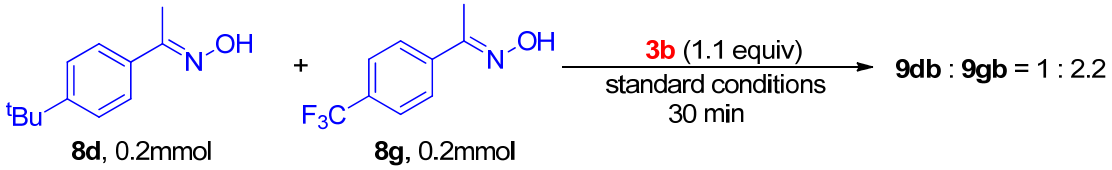
Two pressure tubes were separately charged with **6a** (0.2 mmol) and **6a-*d*$_5$** (0.2 mmol), and to each tube was added Cp*Rh(OAc)$_2$ (6.0 mg, 0.0016 mmol), AgOAc (50 mg, 0.30 mmol, 1.5 equiv), $AgSbF_6$ (68 mg, 0.2 mmol, 1.0 equiv) in DCE (2.0 mL) were charged into a 25 mL pressure tube under argon atmosphere . The mixture was stirred for 10 min at room temperature in the dark, followed by addition of **3a** (41 mg). The reaction tube was then placed in an oil bath at 100 °C for 30 min. After that, the reaction vial was removed from the oil bath and cooled to ambient temperature The two mixtures were rapidly combined and filtered through a pad of celite eluting with

DCM : MeOH = 10:1, concentrated, and purified by silica gel chromatography (DCM : MeOH = 20:1) to give the indicated mixed products. KIE value of k_H/k_D = 0.87/0.13 = 6.7 was determined by ^{1}H NMR analysis (**Supplementary Fig.7**). [4]

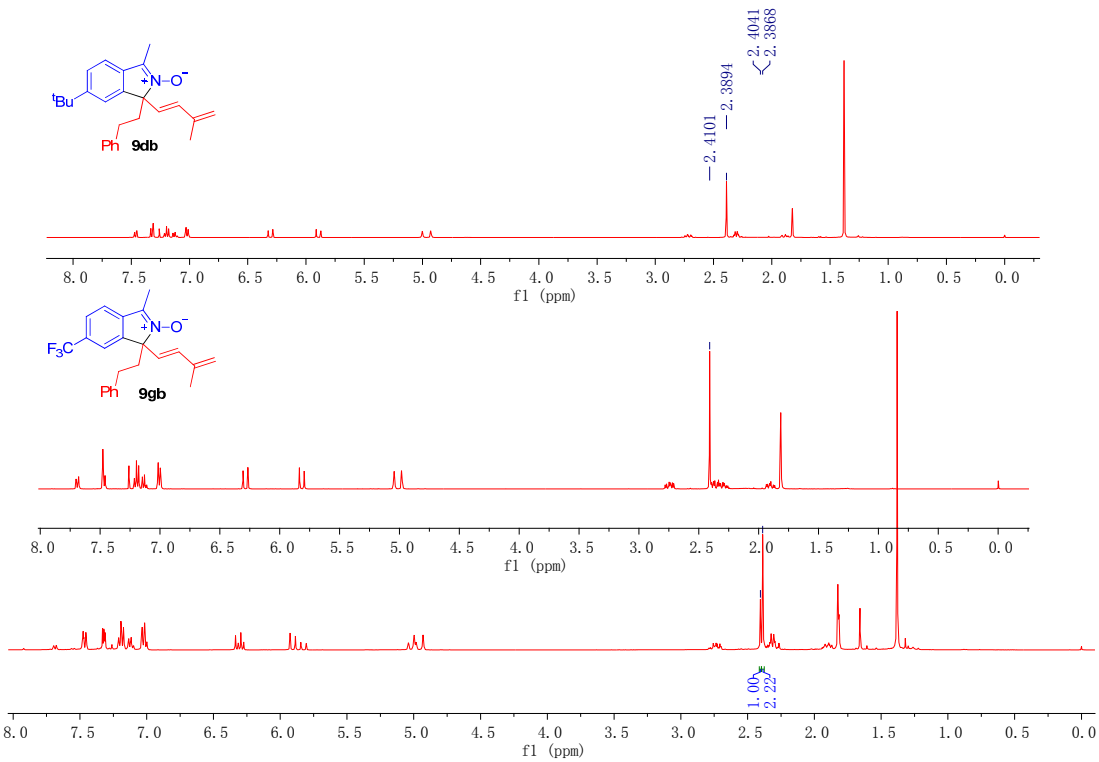


Supplementary Figure 7. ^{1}H NMR of KIE value 6a and 6a-d3

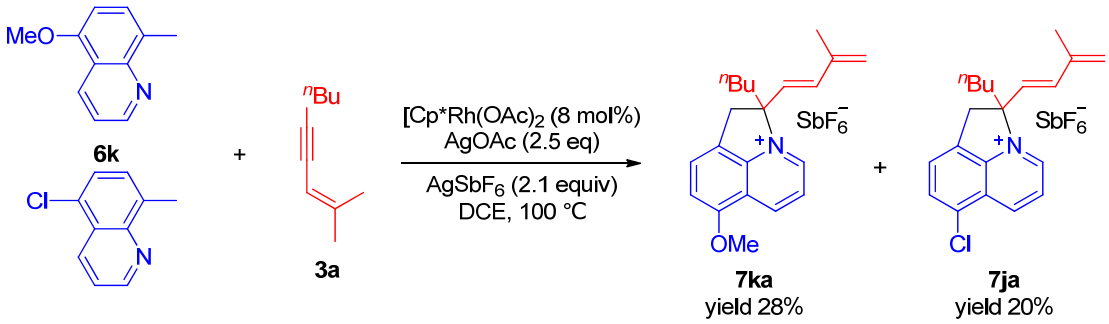
Competitive Experiments.



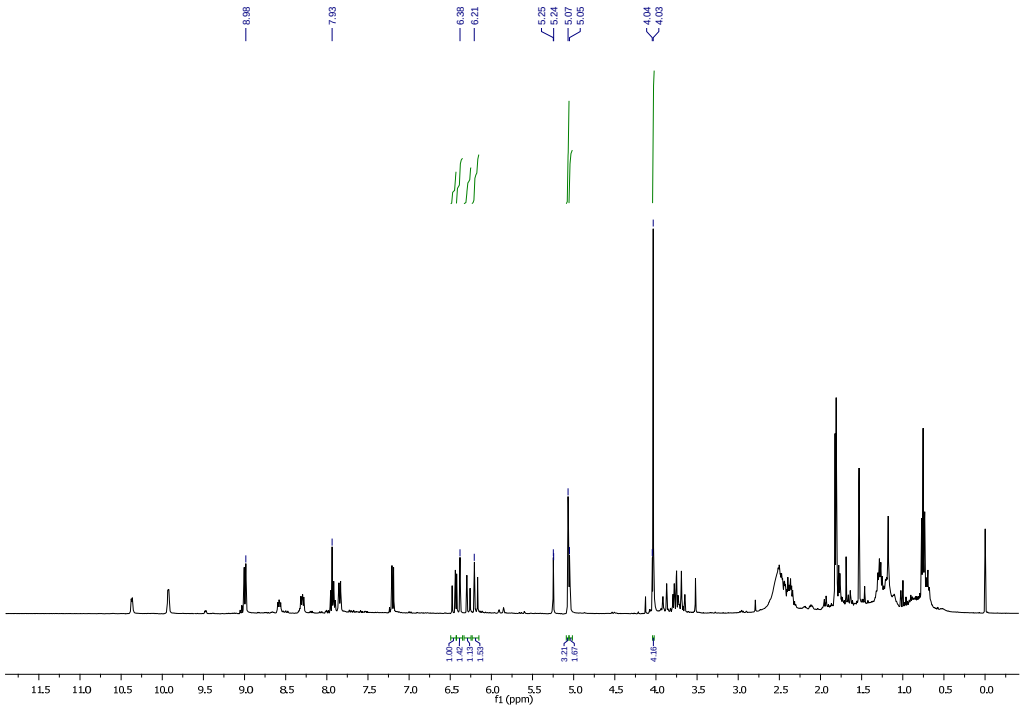
A mixture of **8d** (0.2 mmol, 38.2 mg), **8g** (0.2 mmol, 40.6 mg), [Rh*CpCl$_2$]$_2$ (0.008 mmol, 5.0 mg), Cu(OAc)$_2$ (0.42 mmol, 76.5 mg) were dissolved in MeOH (2.0 mL) and **3b** (0.22 mmol, 40.5 mg) was then added. The mixture was stirred for 30 min at 40 ^{o}C under N$_2$ protected. After that, the solvent was removed under vacuum and the residue was purified by silica gel chromatography using ethyl acetate/petroleum ether (8:1) to afford product **9db** and **9gb** as a yellow oil (22.4 mg), which were characterized by ^{1}H NMR spectroscopy. (**Supplementary Fig. 8**).



Supplementary Figure 8. ^{1}H NMR Spectra of Competitive Experiment of 1o and 1n.

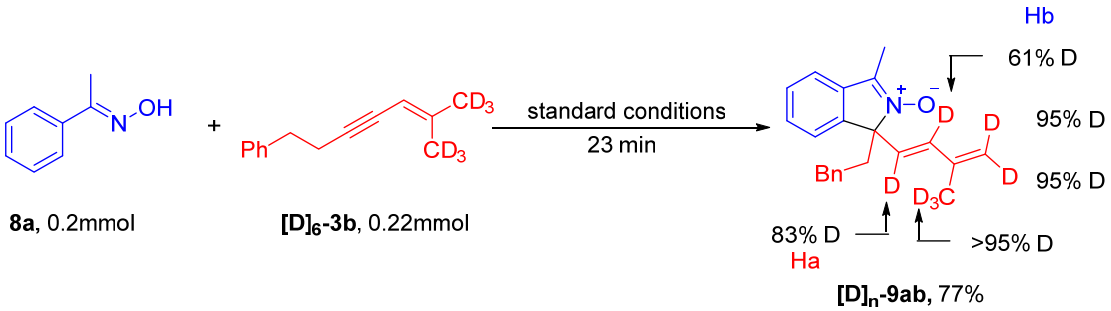


$Cp^*Rh(OAc)_2$ (6.0 mg, 0.0016 mmol), AgOAc (50 mg, 0.30 mmol, 1.5 equiv), $AgSbF_6$ (68 mg, 0.2 mmol, 1.0 equiv) in DCE (2.0 mL) were charged into a 25 mL pressure tube under argon atmosphere . The mixture was stirred for 10 min at room temperature in the dark, followed by addition of **6k** (0.200 mmol, 1.00 equiv), **6j** (0.200 mmol, 1.00 equiv) and **3a** (0.40 mmol). The reaction tube was then placed in an oil bath at 100 °C for 24 h, the reaction vial was removed from the oil bath and cooled to ambient temperature. The reaction mixture was filtered through a pad of celite eluting with DCM : MeOH = 10:1, concentrated, and purified by silica gel chromatography (DCM : MeOH = 15:1) to give the afford the product mixture. The yield ratio (**7ka**/**7ja**) was determined by ^{1}H NMR analysis (**Supplementary Fig. 9**).



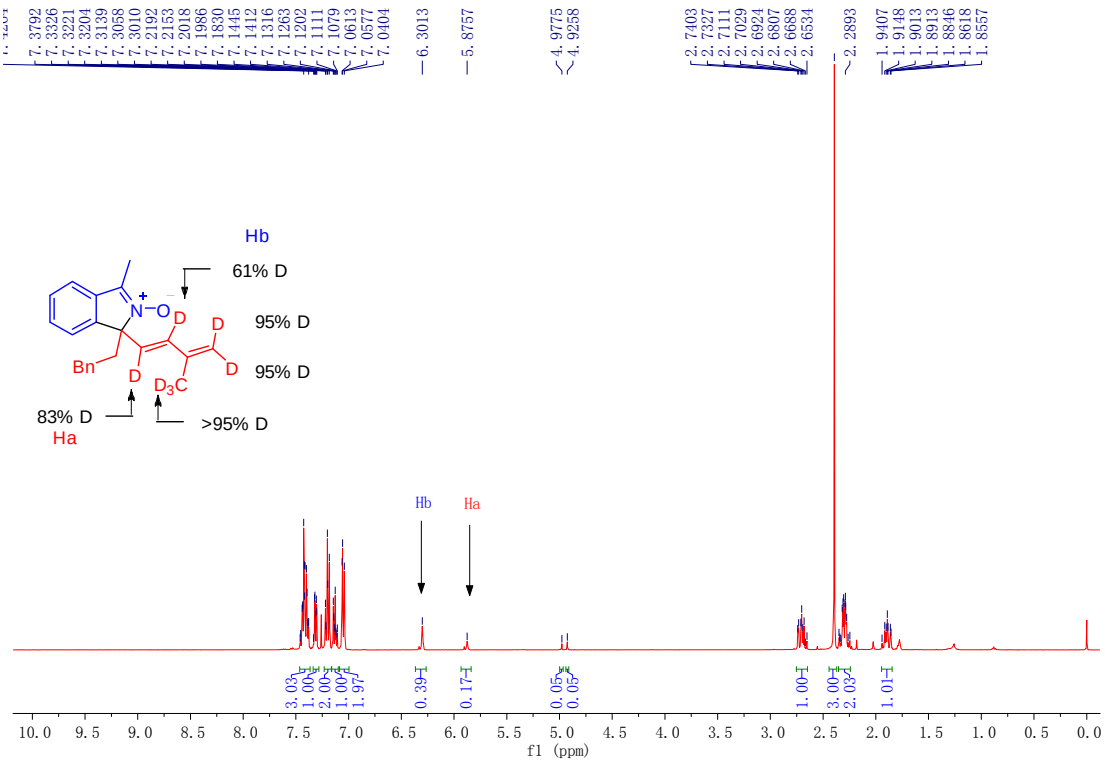
Supplementary Figure 9. ^{1}H NMR Spectra of Competitive Experiment.

4.6 Reaction with Deuterio-enyne $[D]_6$-3b



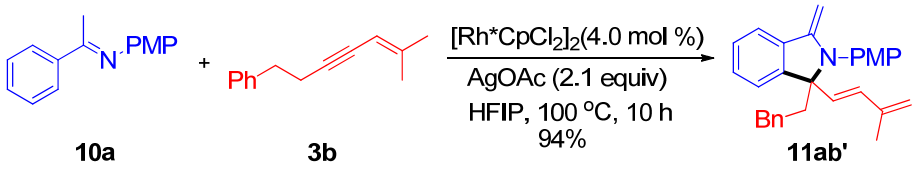
8a, 0.2mmol **$[D]_6$-3b**, 0.22mmol **$[D]_n$-9ab**, 77%

A mixture of **8a** (0.2 mmol, 27.0 mg), $[Rh^*CpCl_2]_2$ (0.008 mmol, 5.0 mg), $Cu(OAc)_2$ (0.42 mmol, 76.5 mg) were dissolved in MeOH (2.0 mL) and **$[D]_6$-3b** (0.22 mmol, 42.0 mg) (0.22 mmol, 40.5 mg) was then added. The mixture was stirred for 4 h at 40 ^oC under N_2 protected. After that, the solvent was removed under vacuum and the residue was purified by silica gel chromatography using ethyl acetate/petroleum ether (8:1) to afford product **$[D]_n$-9ab** as colorless oil (49.4 mg, 77% yield), which were characterized by ^{1}H NMR spectroscopy (**Supplementary Fig. 10**).

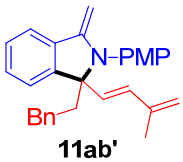


Supplementary Figure 10. ^{1}H NMR of $[D]_n$-9ab.

4.7 Procedure for the Separation of Intermediate

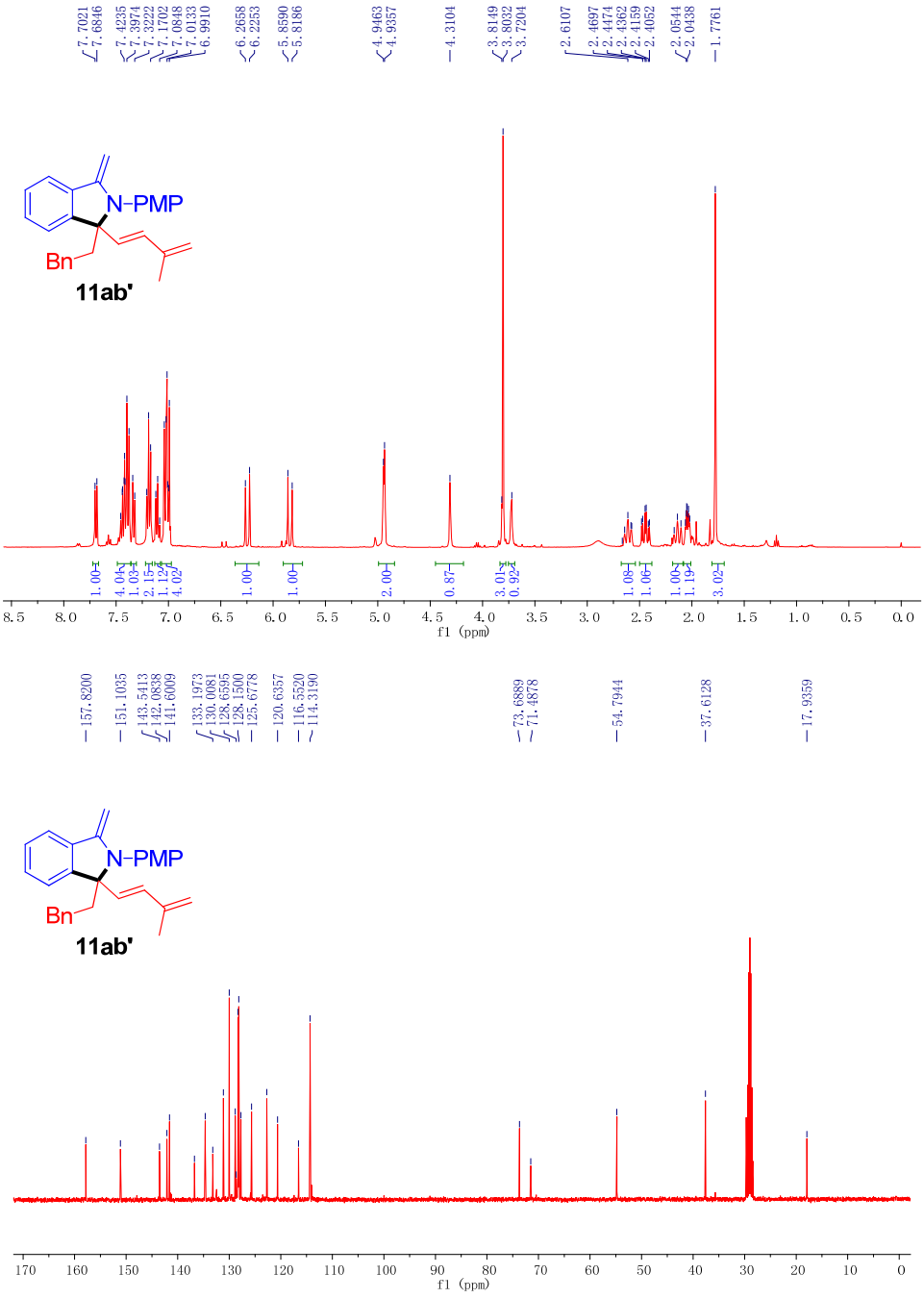


(*E*)-N-(4-methoxyphenyl)-1-phenylethan-1-imine **10a** (0.2 mmol, 45.0 mg), $[Cp^*RhCl_2]_2$ (0.25 mmol, 154.5 mg), AgOAc (2.1 equiv, 70.2 mg) were dissolved into HFIP (2 mL), then 1,3-enyne **3b** (0.22 mmol, 40.2 mg) was added at the N_2 protected. Then, the mixture was stirred at 100 °C for 10 h. The reaction was cooled to room temperature and the solvent quickly removed under vacuum and the residue was carefully purified by silica gel chromatography using DCM/MeOH (100/1). The product **11ab'** was delivered as colorless oil (76.5 mg, 94%). After placed at air for several minutes, the product quickly turned red(**Supplementary Fig. 11**).



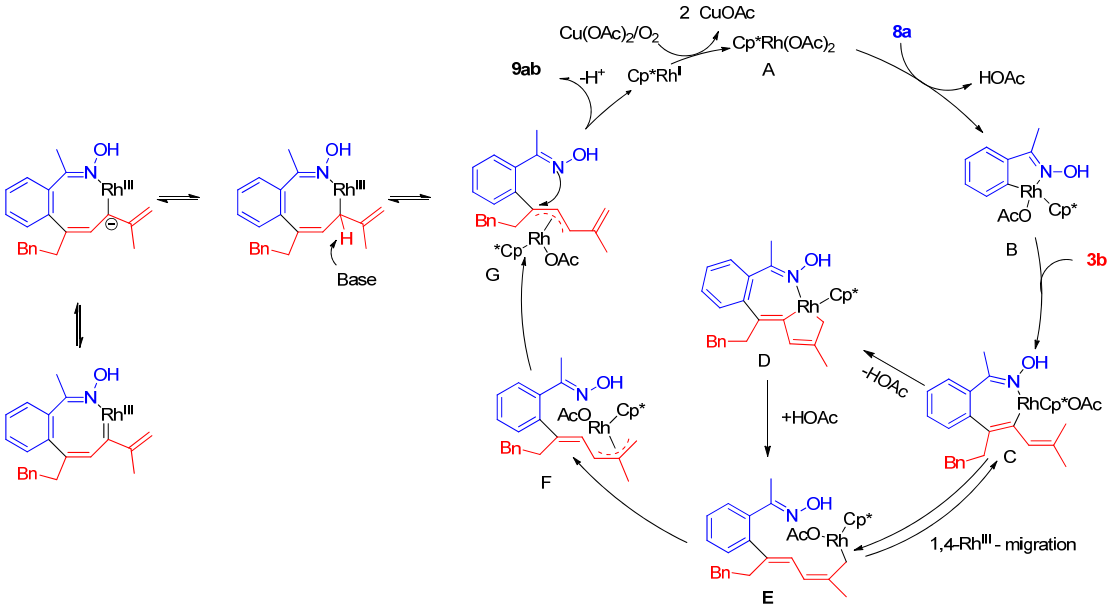
^{1}H NMR (400 MHz, Acetone) δ 7.69 (d, J = 7.0 Hz, 1H), 7.49 - 7.36 (m, 4H), 7.35 - 7.31 (m, 1H), 7.19 (t, J = 7.4 Hz, 2H), 7.14 - 7.07 (m,

1H), 7.06 - 6.97 (m, 4H), 6.25 (d, J = 16.2 Hz, 1H), 5.84 (d, J = 16.2 Hz, 1H), 4.94 (d, J = 4.3 Hz, 2H), 4.31 (s, 1H), 3.81 (d, J = 4.7 Hz, 3H), 3.72 (s, 1H), 2.69 - 2.54 (m, 1H), 2.44 (td, J = 13.4, 4.5 Hz, 1H), 2.19 - 2.08 (m, 1H), 2.08 - 2.00 (m, 1H), 1.78 (s, 3H). **^{13}C NMR** (101 MHz, Acetone) δ 157.8, 151.1, 143.5, 142.1, 141.6, 136.7, 134.7, 133.2, 131.2, 130.0, 128.9, 128.7, 128.3, 128.2, 127.7, 125.7, 122.7, 120.6, 116.6, 114.3, 73.7, 71.5, 54.8, 37.6, 17.9. **HRMS (ESI)**: calcd for $C_{29}H_{30}NO$ 408.2322, found 408.2321.



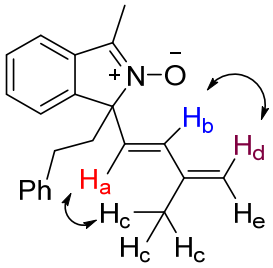
Supplementary Figure 11. ^{1}H NMR and ^{13}CNMR of 11ab'

4.7. Alternative Mechanism

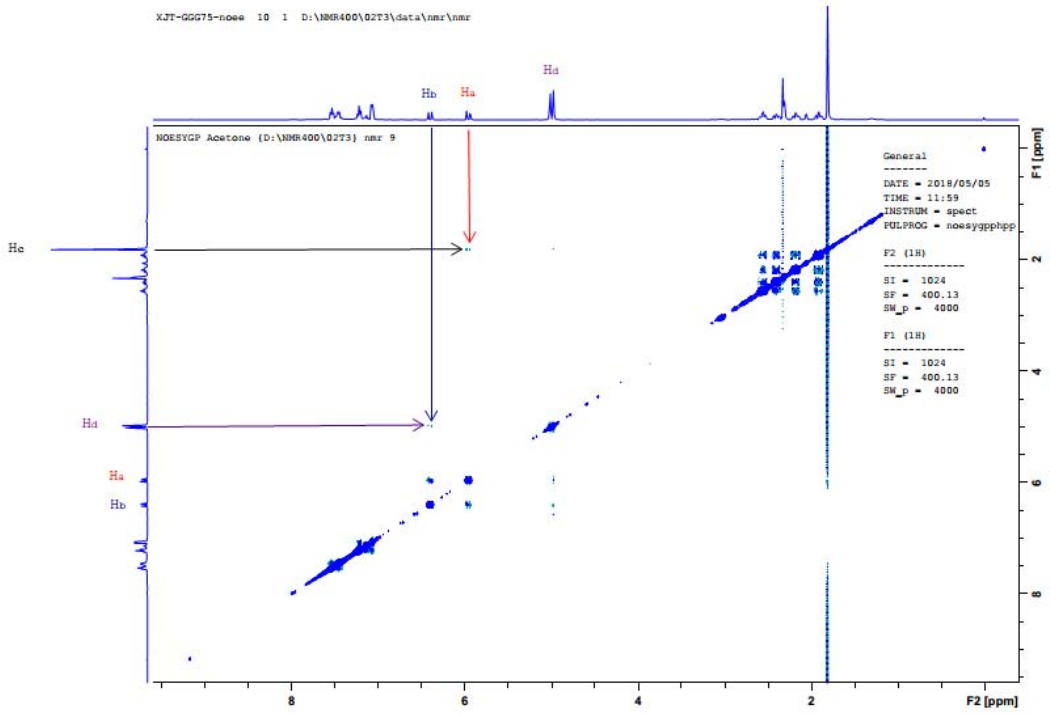


Supplementary Figure 12. Alternative Mechanism for partial deuteration at the H_b

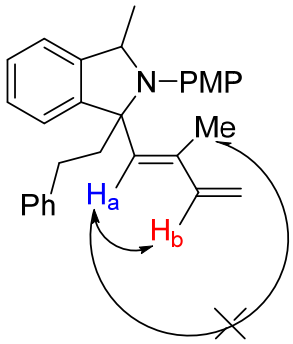
4.8 NOE of 9ab and 11an



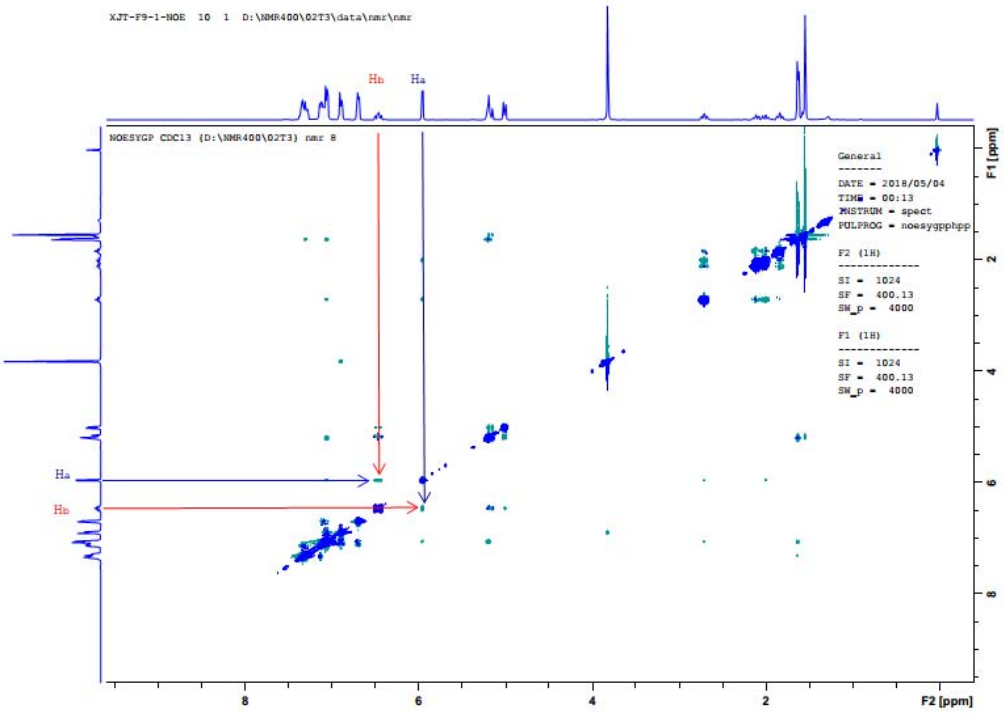
9ab



Supplementary Figure 13. NOESY of 9ab

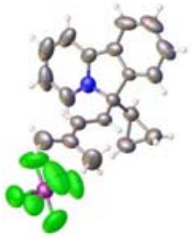


11an



Supplementary Figure 14. NOESY of 11an

5. X-Ray Crystallographic Data of 4ae

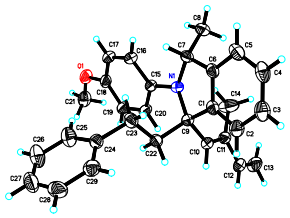


Crystal data and structure refinement for 4ae.

Empirical formula	$C_{20}H_{20}F_6NP$
Formula weight	419.34
Temperature/K	296.6(4)
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	8.90880(10)
b/Å	16.7762(3)
c/Å	13.3993(2)
α/°	90
β/°	101.0040(10)
γ/°	90
Volume/Å^3	1965.78(5)
Z	4
ρ_{calc}g/cm^3	1.417
μ/mm^{-1}	1.801
F(000)	864.0
Crystal size/mm^3	0.38 × 0.25 × 0.18
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	8.542 to 144.59
Index ranges	$-10 \le h \le 9$, $-20 \le k \le 16$, $-16 \le l \le 13$
Reflections collected	15460
Independent reflections	3818 [R_{int} = 0.0321, R_{sigma} = 0.0225]
Data/restraints/parameters	3818/0/262
Goodness-of-fit on F^2	1.061
Final R indexes [I>=2σ (I)]	R_1 = 0.0720, wR_2 = 0.2063
Final R indexes [all data]	R_1 = 0.0801, wR_2 = 0.2161
Largest diff. peak/hole / e Å^{-3}	0.54/-0.50

Supplementary Figure 15. X-Ray Crystallographic Data of 4ae

X-Ray Crystallographic Data of 11an



Crystal data and structure refinement for **11an.**		
Identification code	**11an**	
Empirical formula	$C_{29}H_{31}NO$	
Formula weight	409.55	
Temperature	296(2) K	
Wavelength	1.54178 Å	
Crystal system	Monoclinic	
Space group	P 21/c	
Unit cell dimensions	a = 10.6917(2) Å	α= 90°
	b = 22.9933(5) Å	β= 112.2200(10)°.
	c = 10.4658(2) Å	γ = 90°.
Volume	2381.82(8) $Å^3$	
Z	4	
Density (calculated)	1.142 Mg/m^3	
Absorption coefficient	0.521 mm^{-1}	
F(000)	880	
Crystal size	0.180 x 0.150 x 0.100 mm^3	
Theta range for data collection	5.393 to 64.998°.	
Index ranges	-12<=h<=12, -27<=k<=27, -10<=l<=12	
Reflections collected	25467	
Independent reflections	4014 [R(int) = 0.1030]	
Completeness to theta = 67.679°	93.0%	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7533 and 0.3215	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4014 / 0 / 292	
Goodness-of-fit on F^2	1.063	
Final R indices [I>2sigma(I)]	R1 = 0.0750, wR2 = 0.1954	
R indices (all data)	R1 = 0.0889, wR2 = 0.2129	
Extinction coefficient	0.026(3)	
Largest diff. peak and hole	0.236 and -0.277 $e.Å^{-3}$	

Supplementary Figure 16. X-Ray Crystallographic Data of 11an

6. References

1. (a) Sughara, M.; Ukita, T. *Chem. Pharm. Bull.* **1997**, *45*, 719. (b) Dasa, D.; Samantaa, R.; *Adv. Synth. Catal.* **2018**, *360*, 379.

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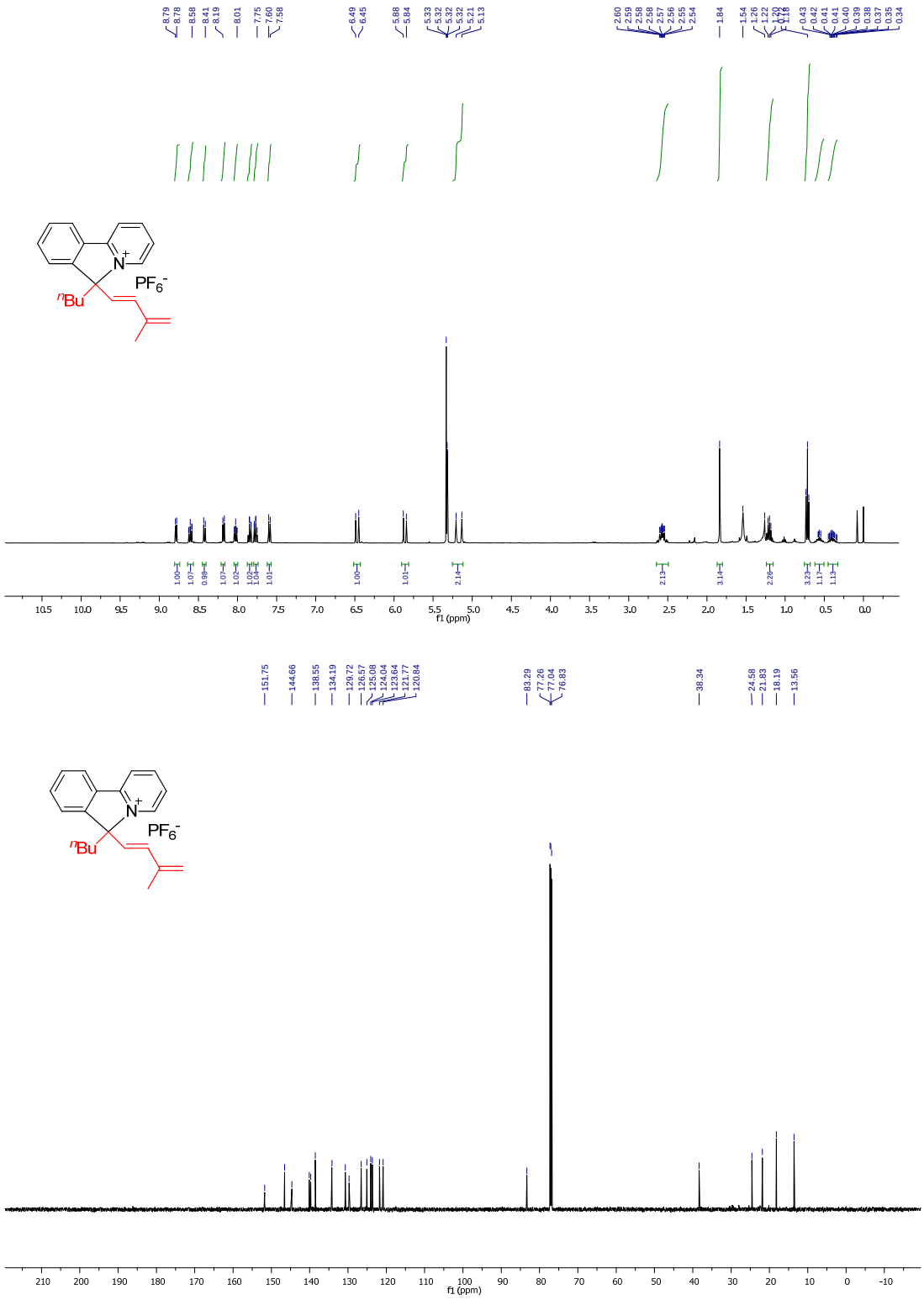
3. (a) Murchu, C. O. *Synthesis.* **1989**, 880. (b) Evans, P.; Hogg, P.; Grigg, R.; Nurnabi, M.; Hinsley, J.; Sridharan, V.; Suganthan, S.; Korn, S.; Collard, S.; Muir, J. E. *Tetrahedron.* **2005**, *61*, 9696. (c) Lu, B.; Li, C.-Q.; Zhang, L.-M. *J. Am. Chem. Soc.* **2010**, *132*, 14070. (d) Zhang, Y. C.; Wang, M.; Li, P. H.; Wang, L. *Org. Lett.* **2012**, *14*, 2206.

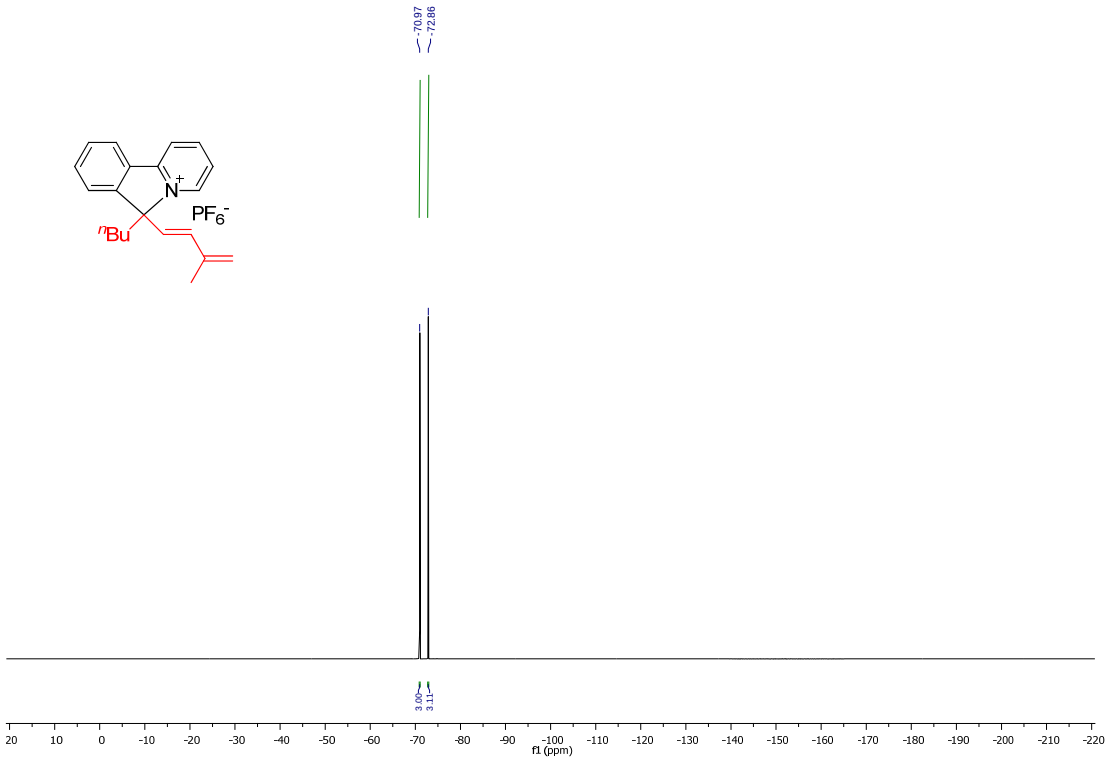
4. Zhang, G.; Wen, X.; Wang, Y.; Mo, W.; Ding, C. *J. Org. Chem.* **2011**, *76*, 4665.

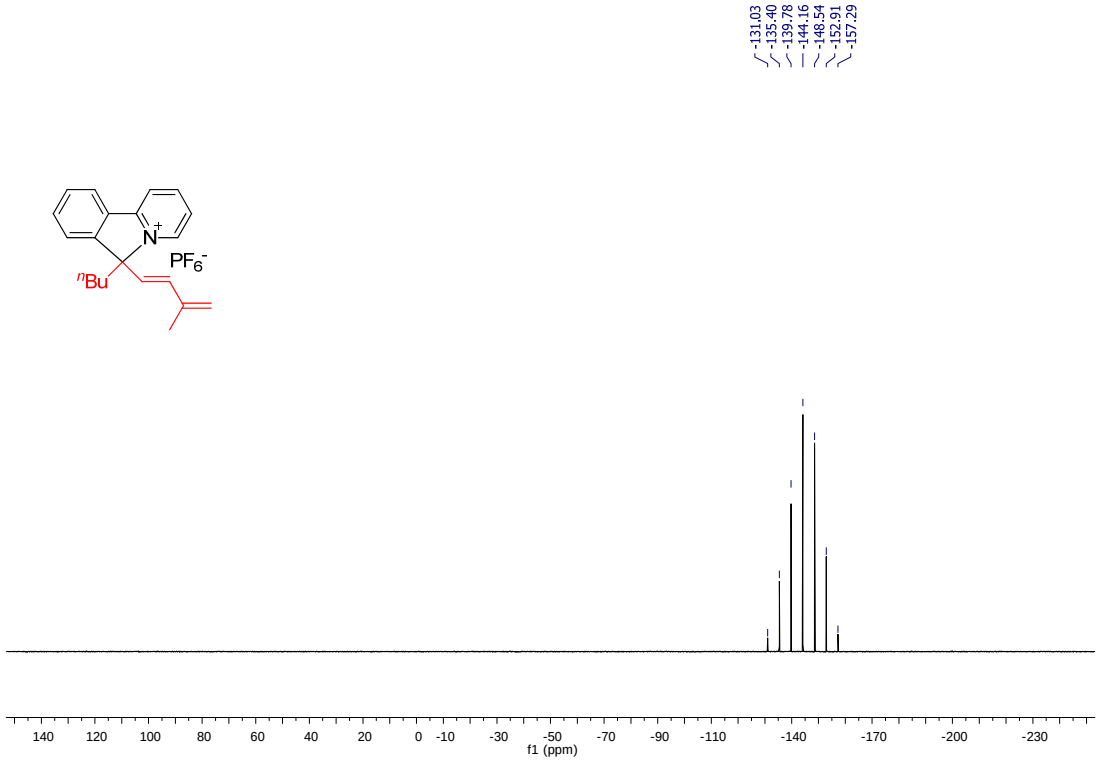
5. (a) Ackermann. L, *Org. Lett.* **2005**, *7*, 3123; (b) Liu. W, Zell. D, John. M, Ackermann. L. *Angew. Chem. Int. Ed.* **2015**, *54*, 4092; (c) Ghattas. G, Chen. D, Pan. F, Klankermayer. J. *Dalton Trans.* **2012**, *41*, 9026.

7. NMR Spectra

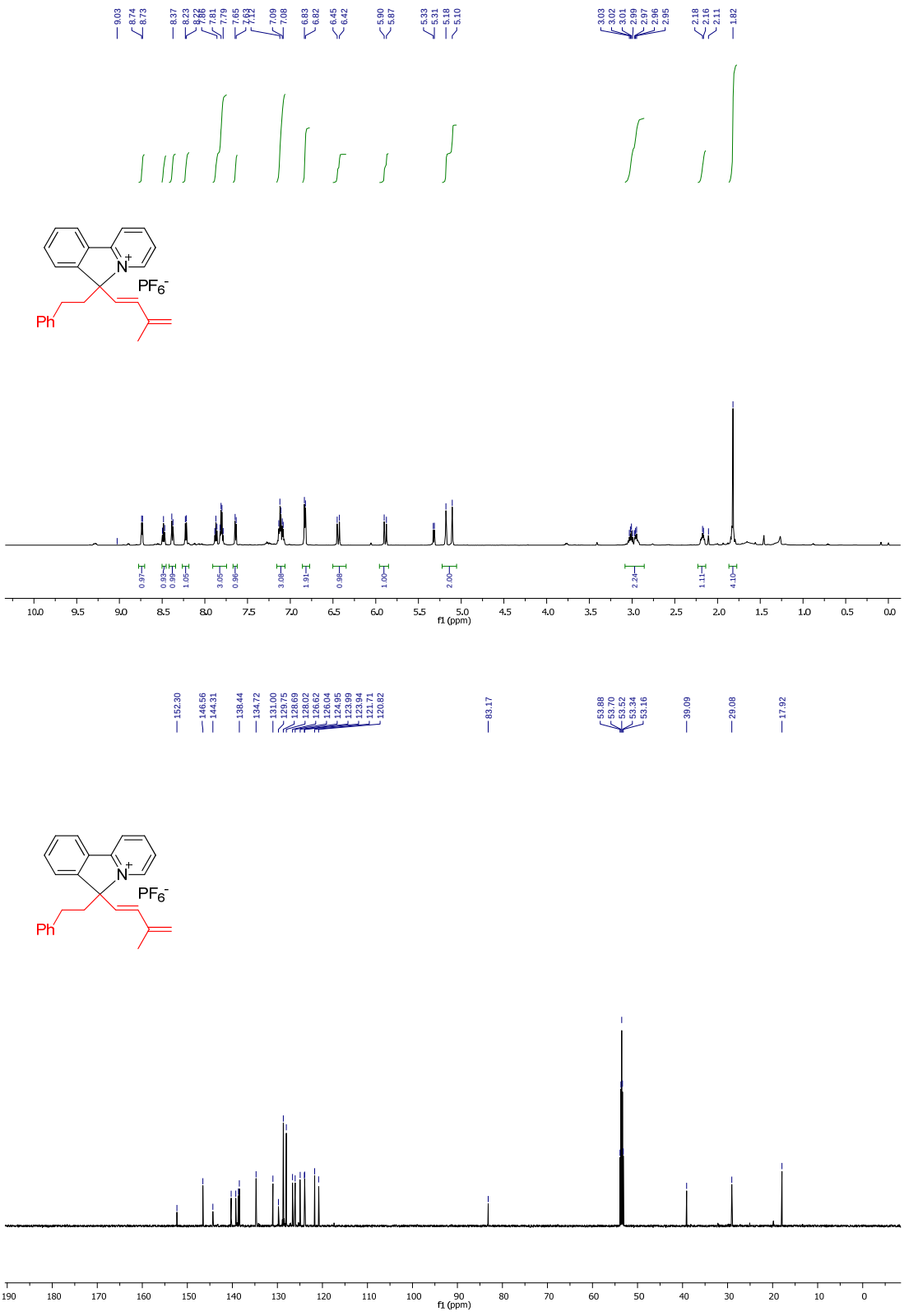


Supplementary Figure 17. ^{1}H NMR and ^{13}C NMR of **4aa**

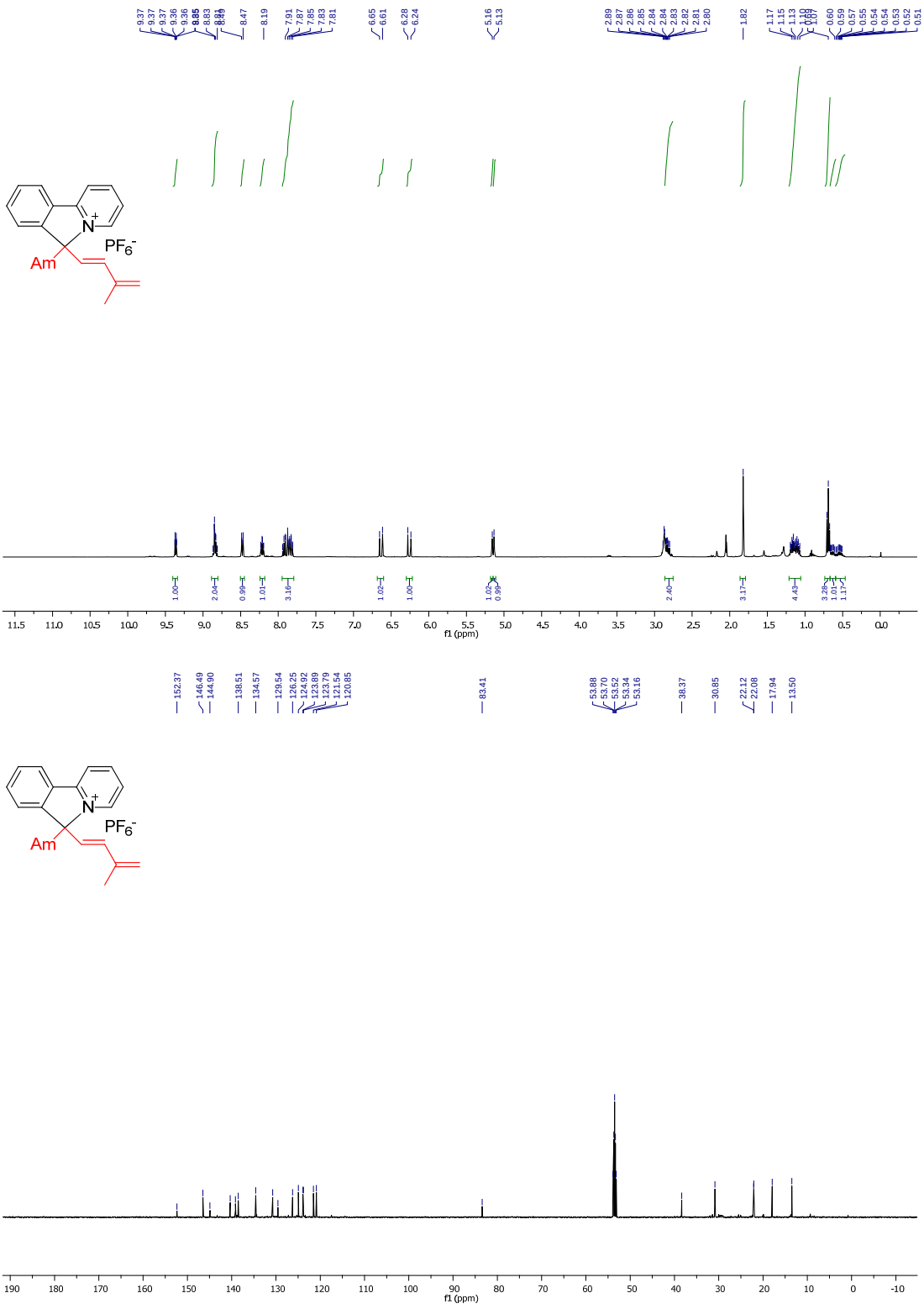




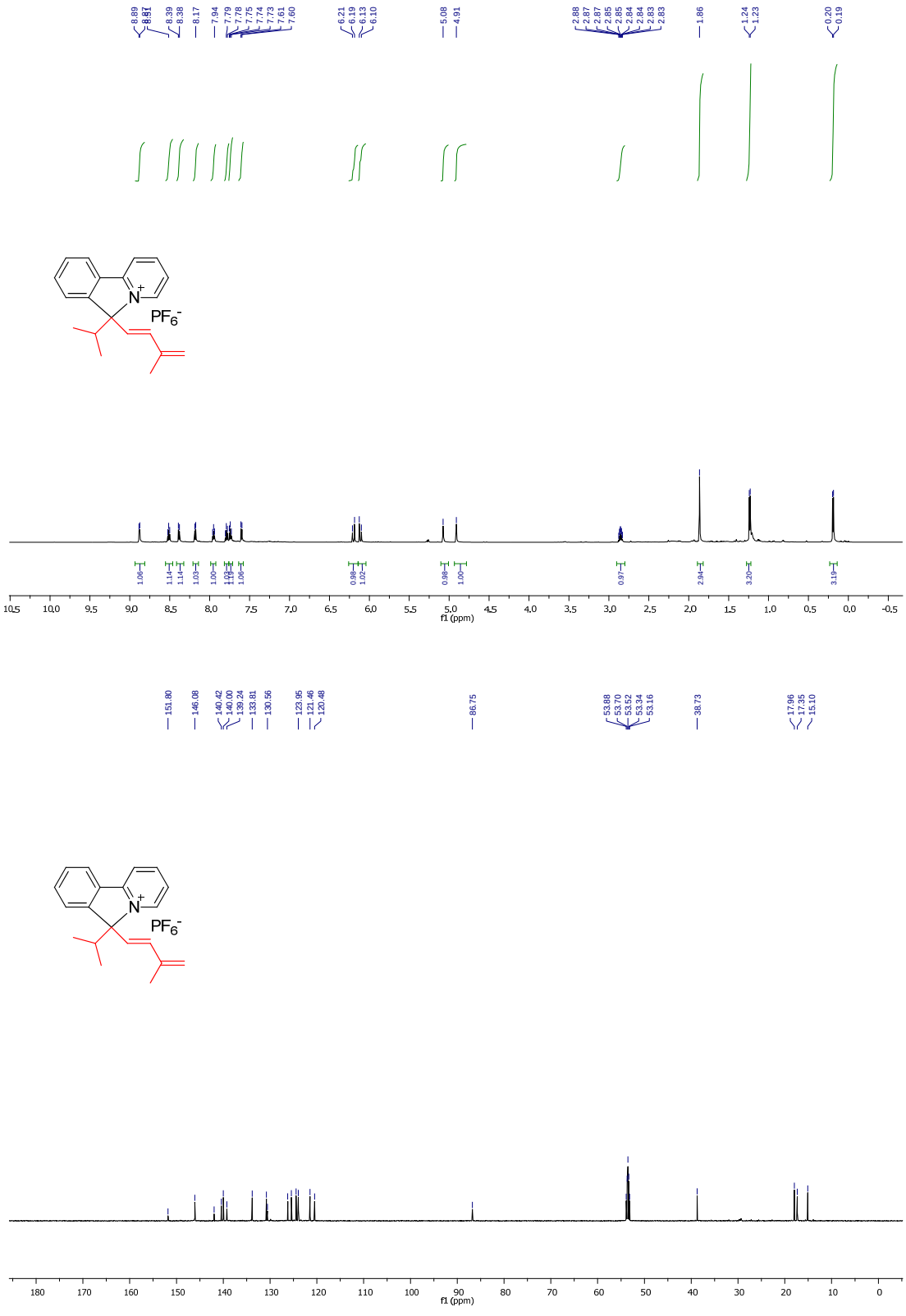
Supplementary Figure 18. ^{19}F NMR and ^{31}P NMR of **4aa**



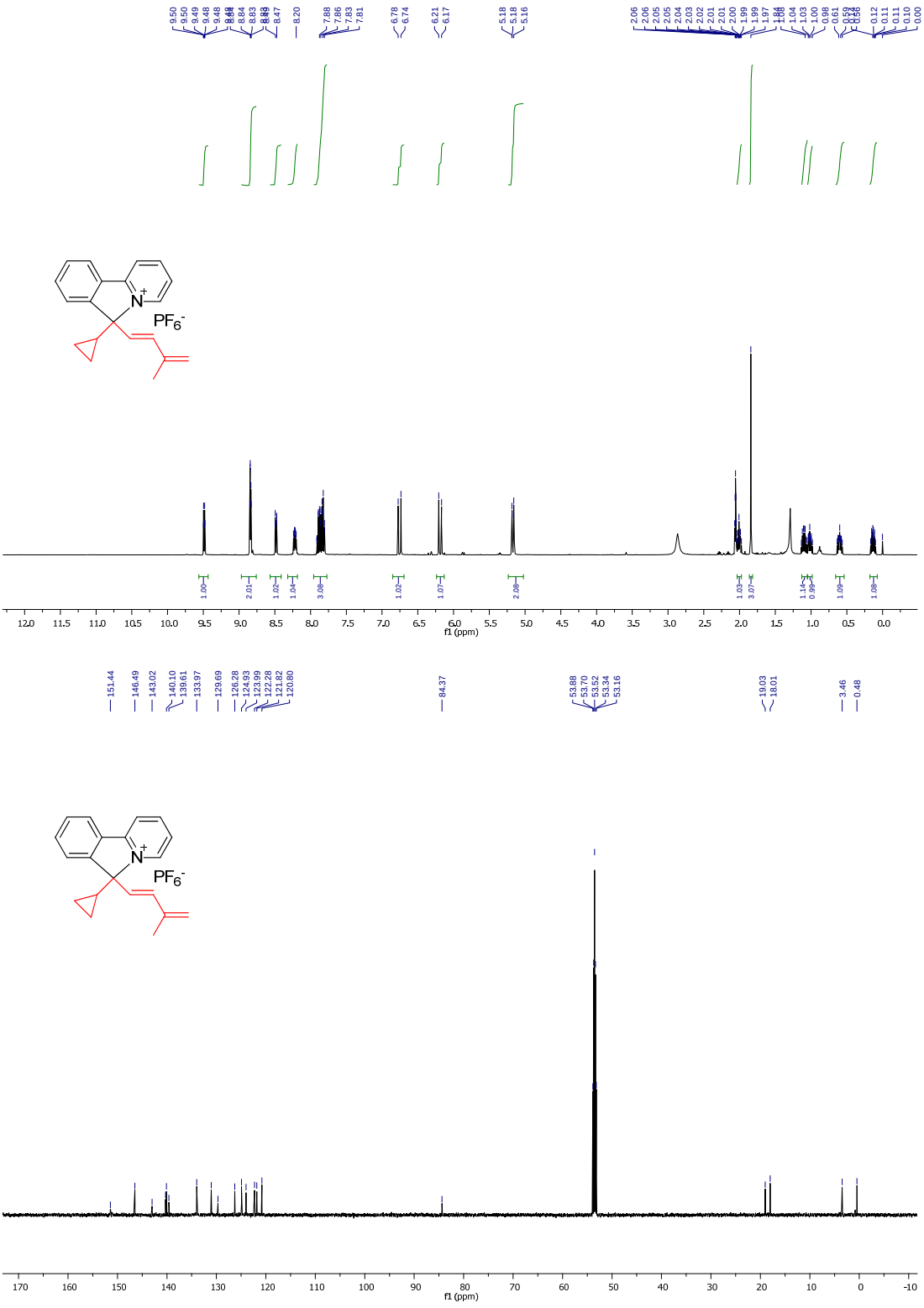
Supplementary Figure 19. ^{1}H NMR and ^{13}C NMR of **4ab**



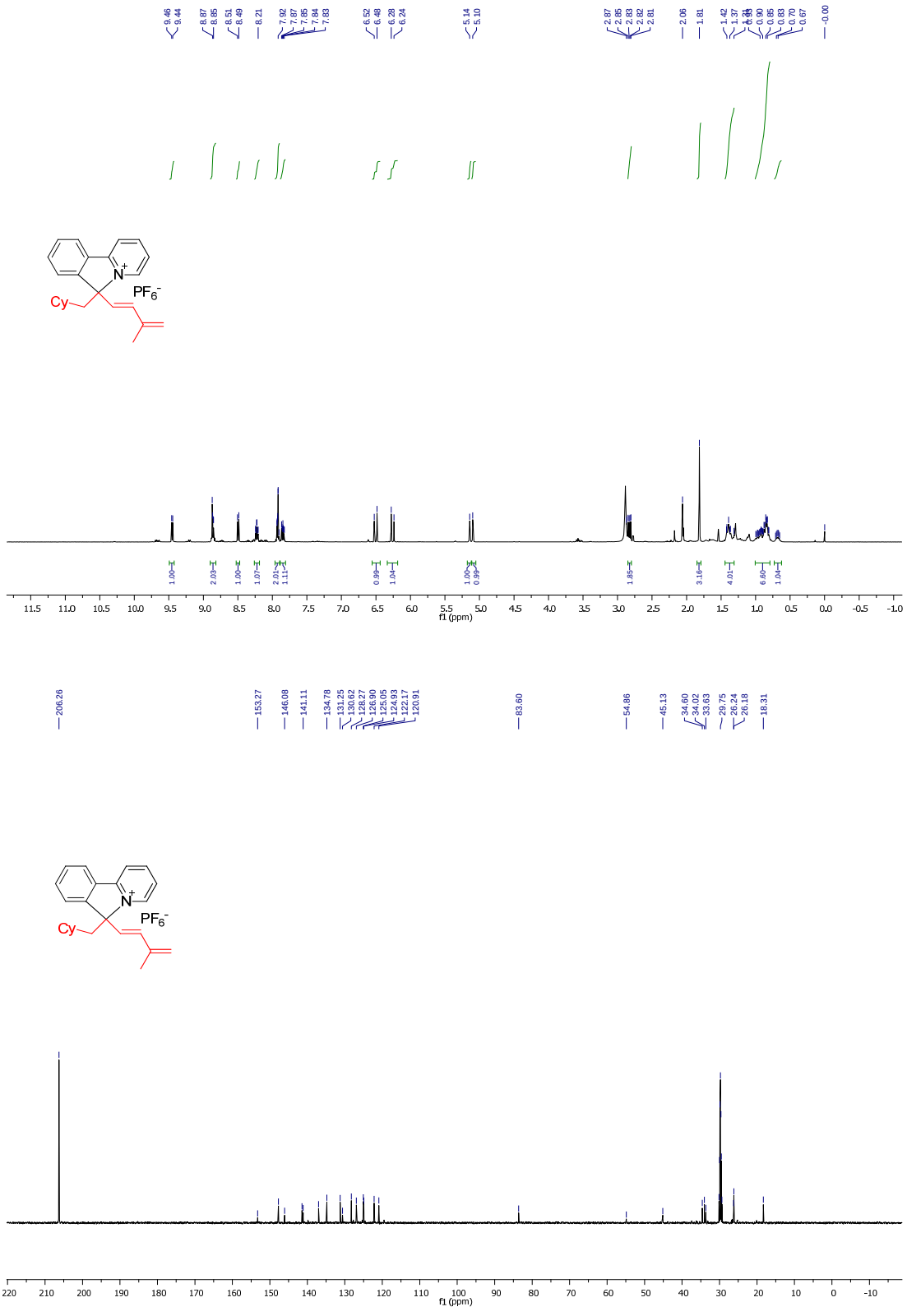
Supplementary Figure 20. ^{1}H NMR and ^{13}C NMR of **4ac**



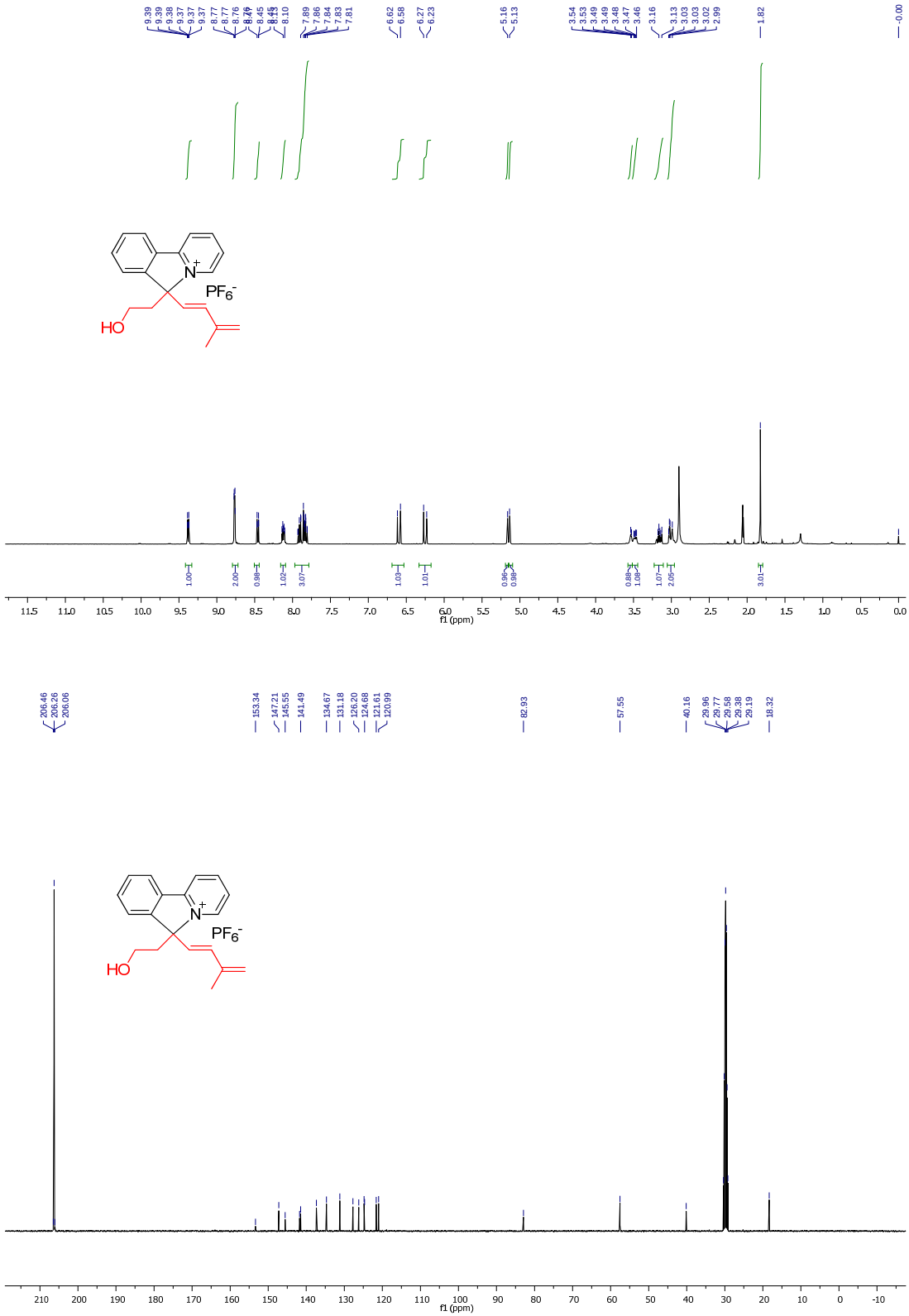
Supplementary Figure 21. ^{1}H NMR and ^{13}C NMR of **4ad**



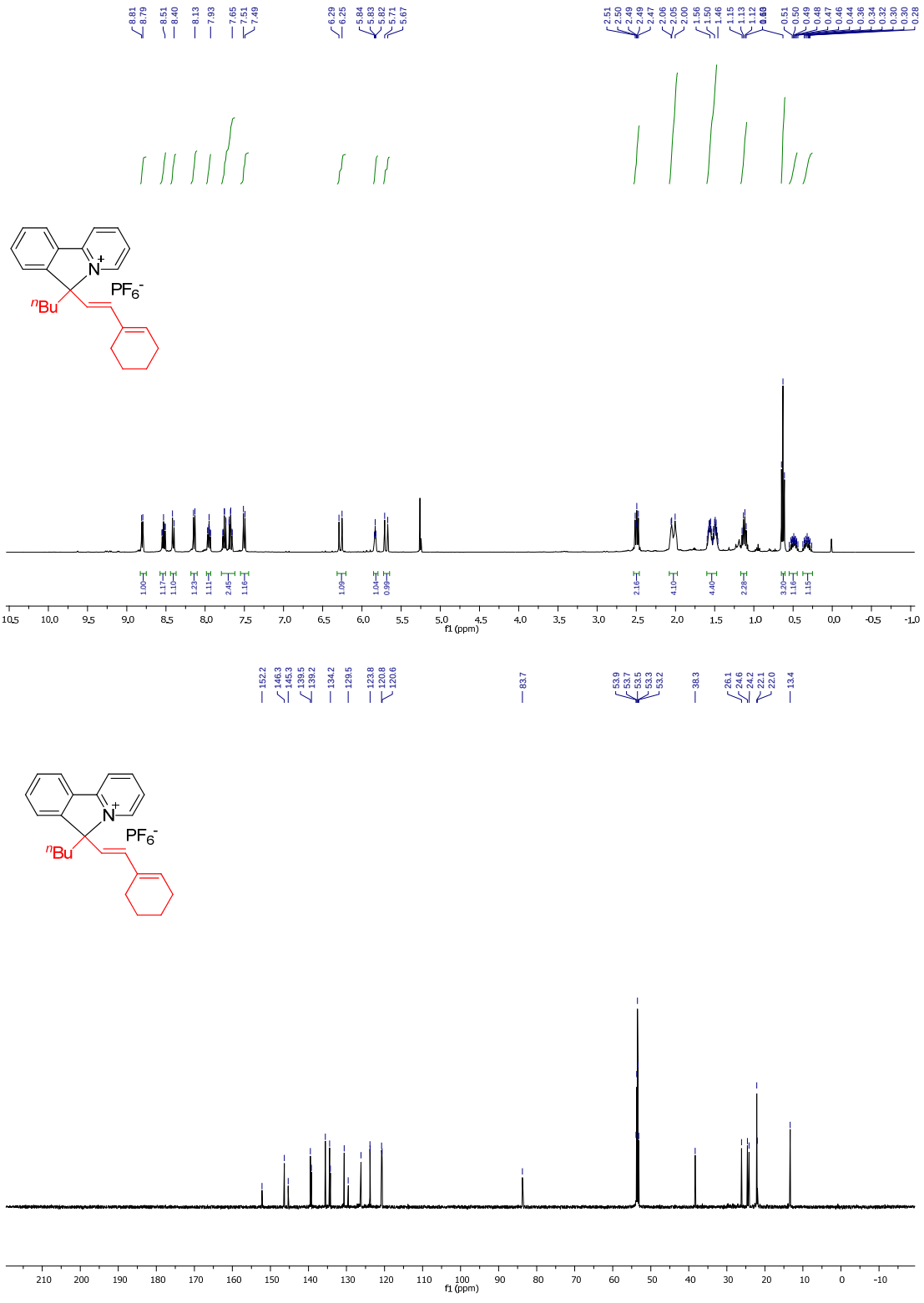
Supplementary Figure 22. ^{1}H NMR and ^{13}C NMR of **4ae**



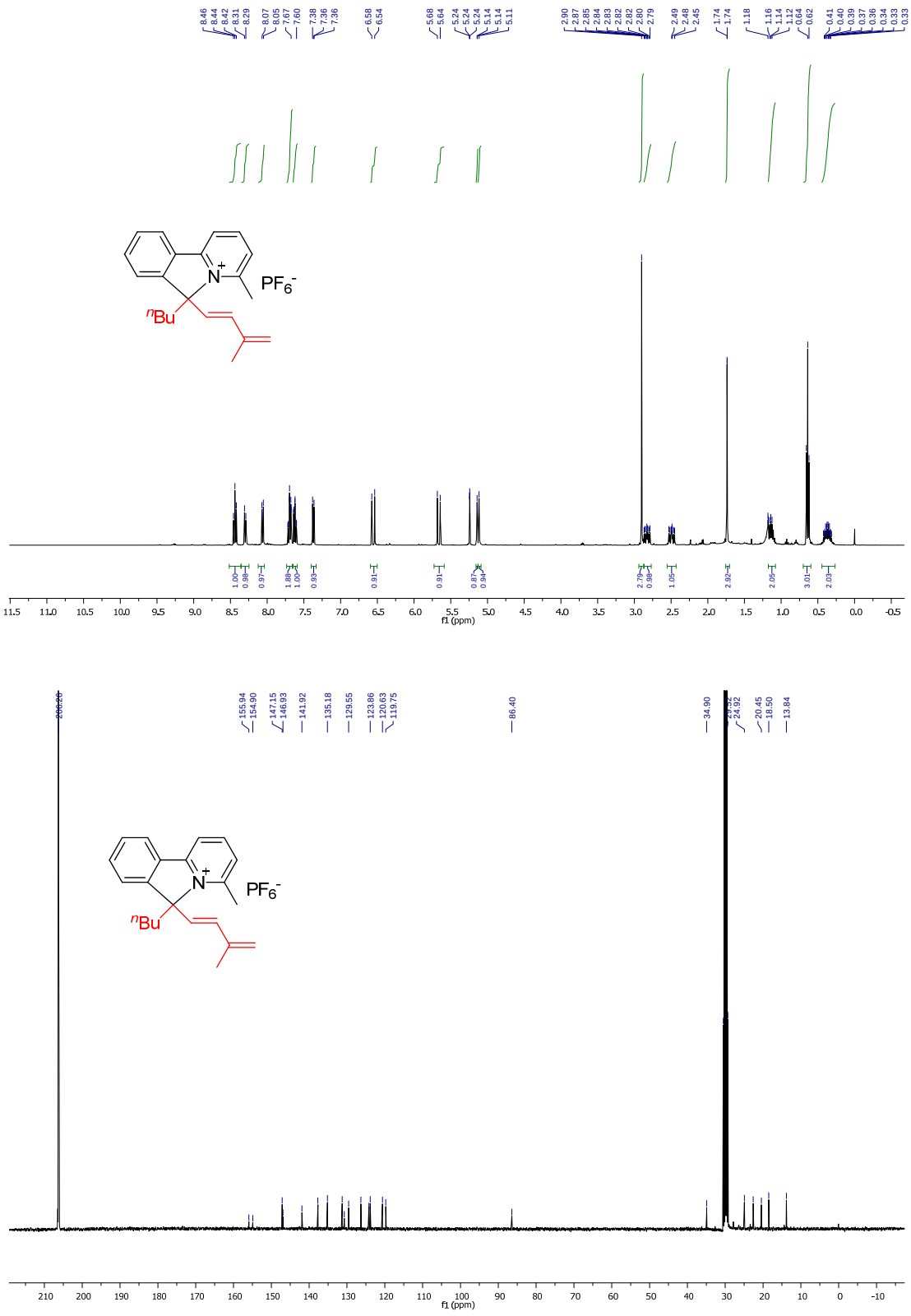
Supplementary Figure23. ^{1}H NMR and ^{13}C NMR of **4af**



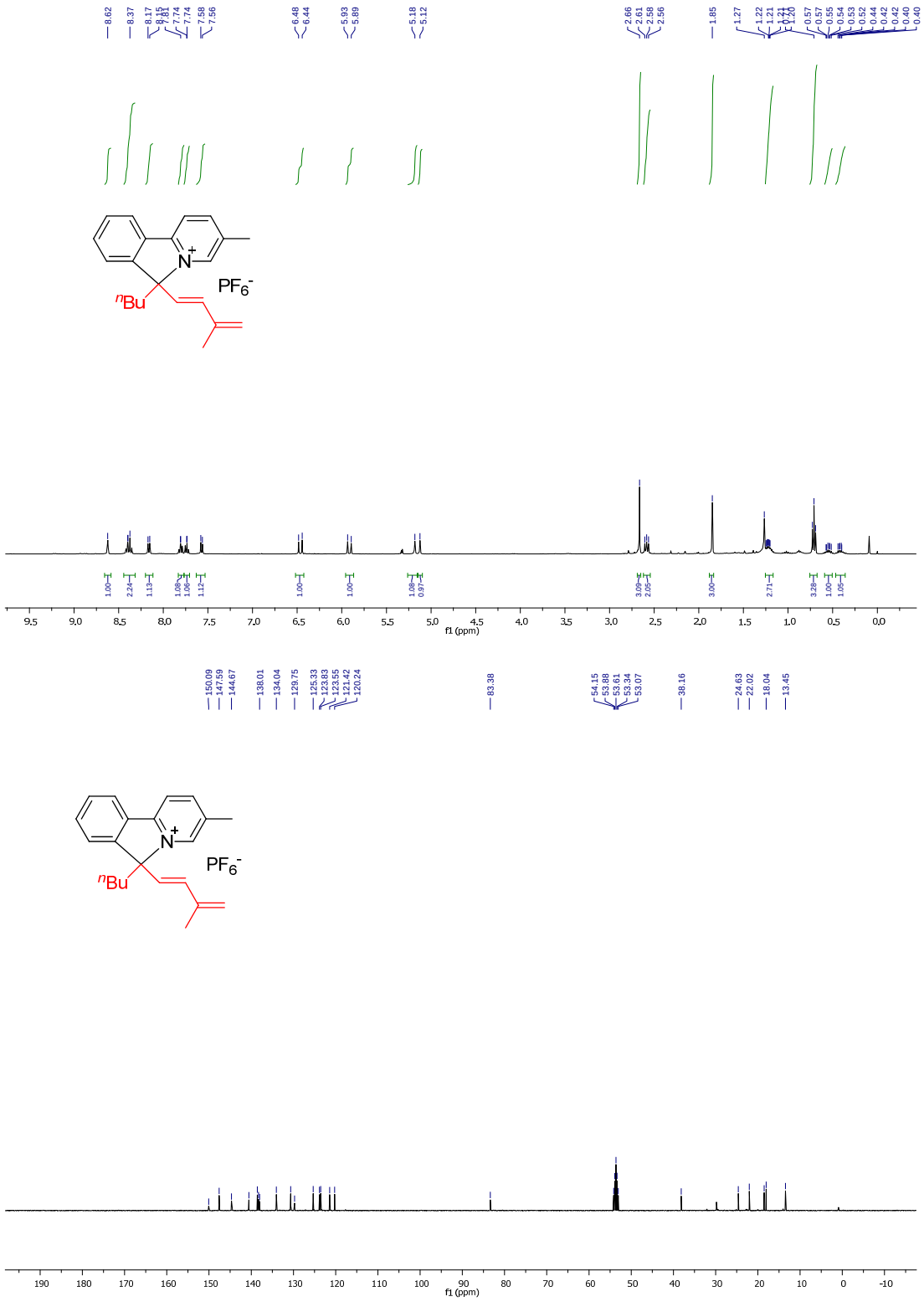
Supplementary Figure 24. ^{1}H NMR and ^{13}C NMR of **4ag**



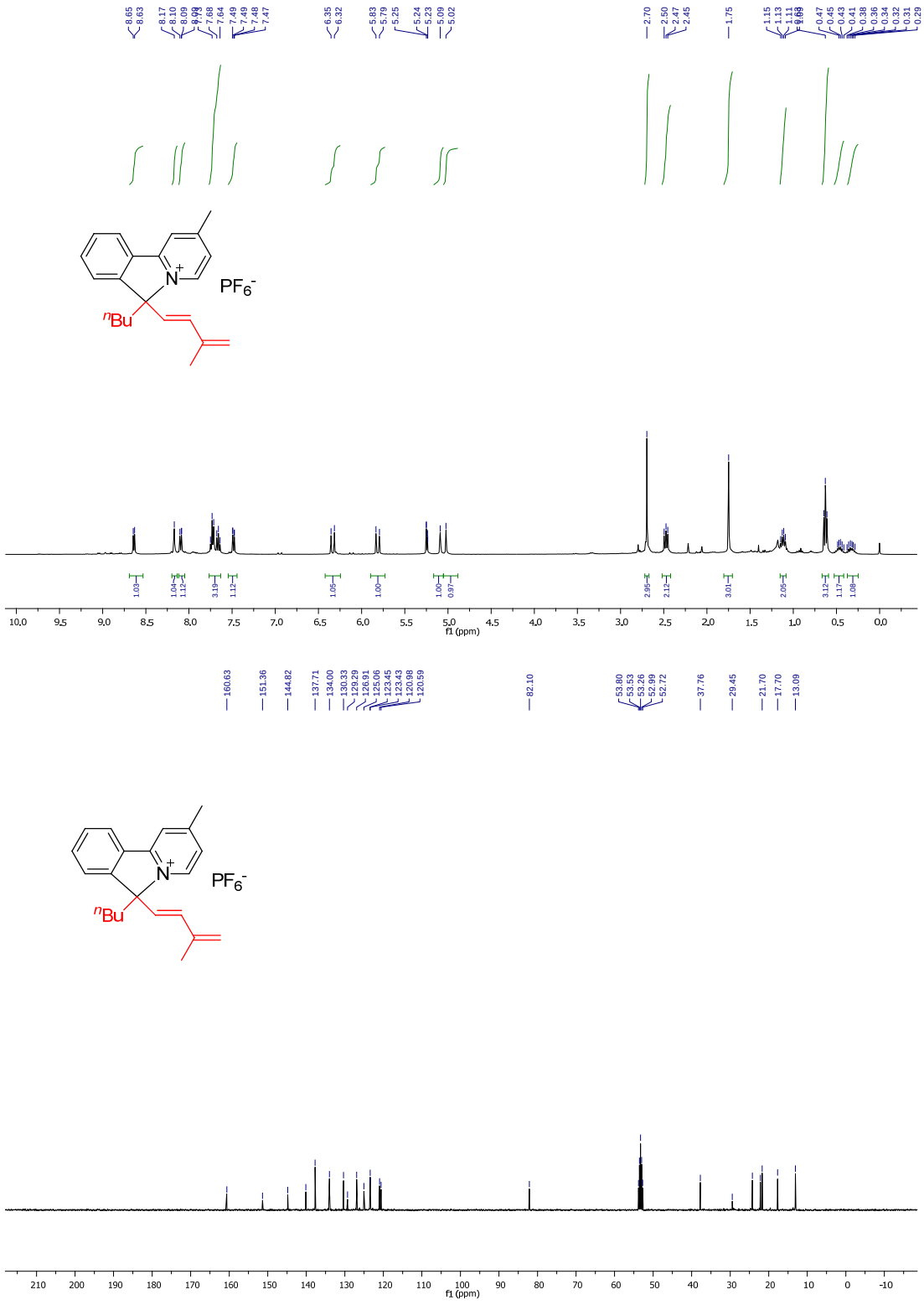
Supplementary Figure 25. ^{1}H NMR and ^{13}C NMR of **4ai**



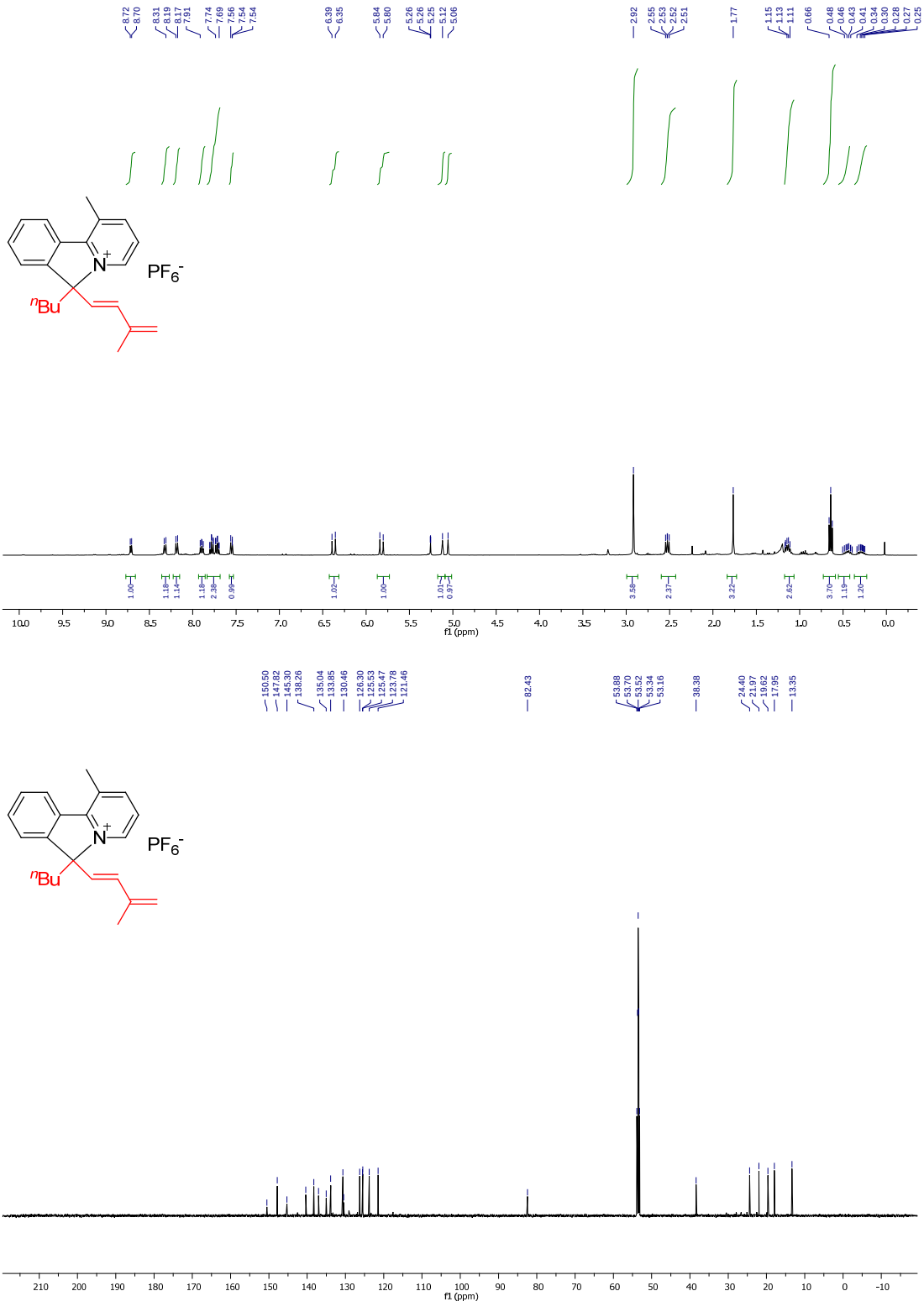
Supplementary Figure 26. ^{1}H NMR and ^{13}C NMR of **4ba**



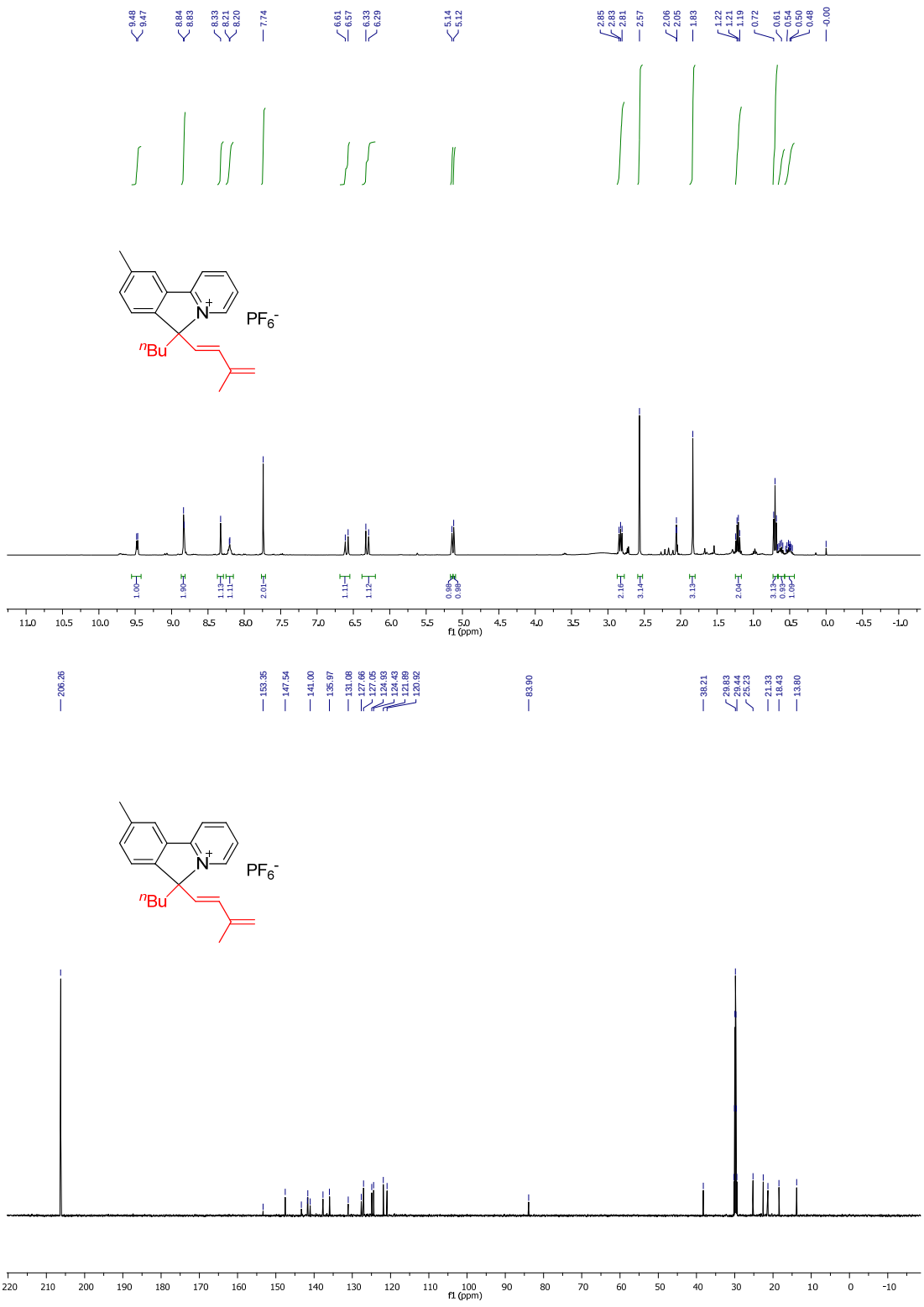
Supplementary Figure 27. ^{1}H NMR and ^{13}C NMR of **4ca**



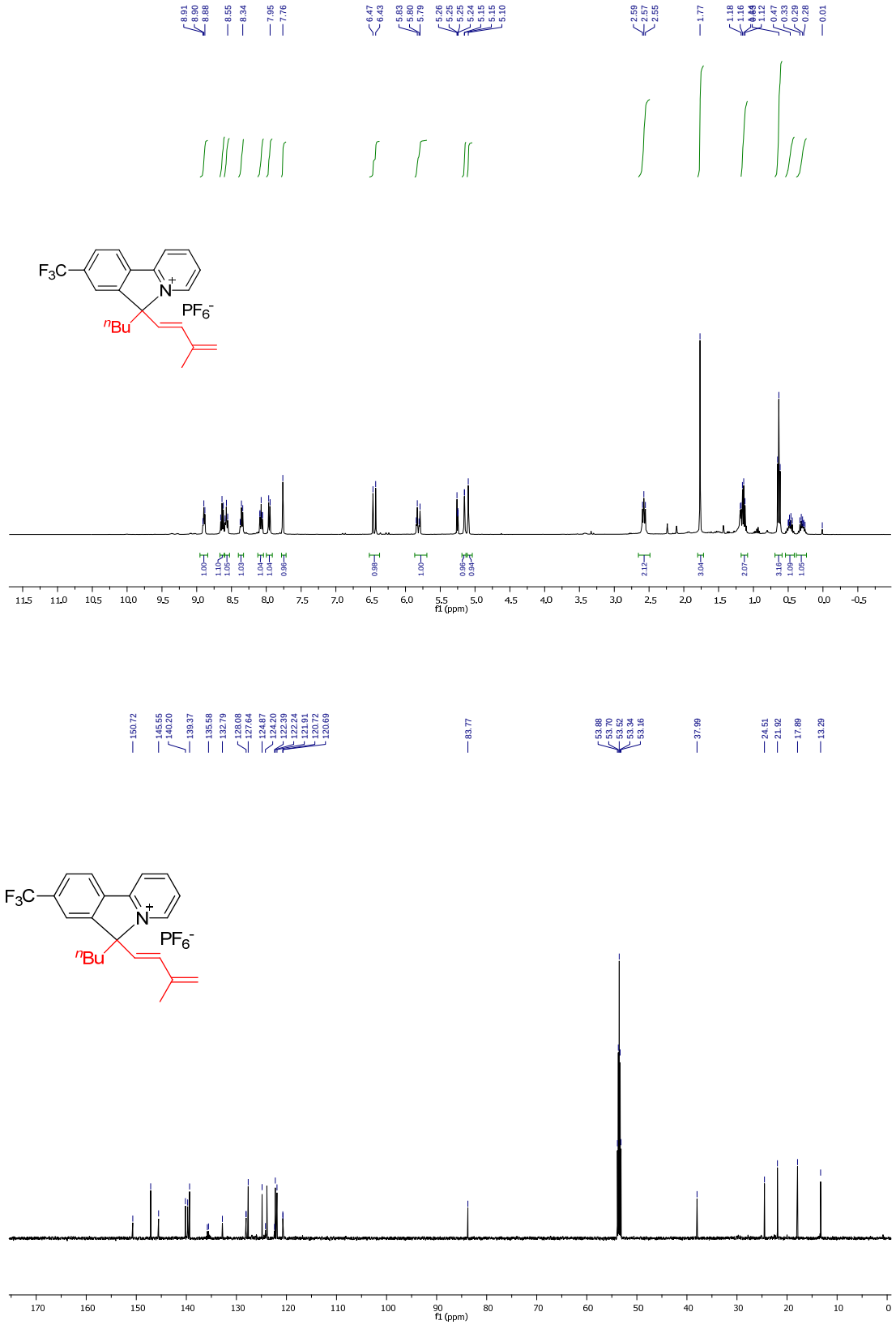
Supplementary Figure 28. ^{1}H NMR and ^{13}C NMR of **4da**



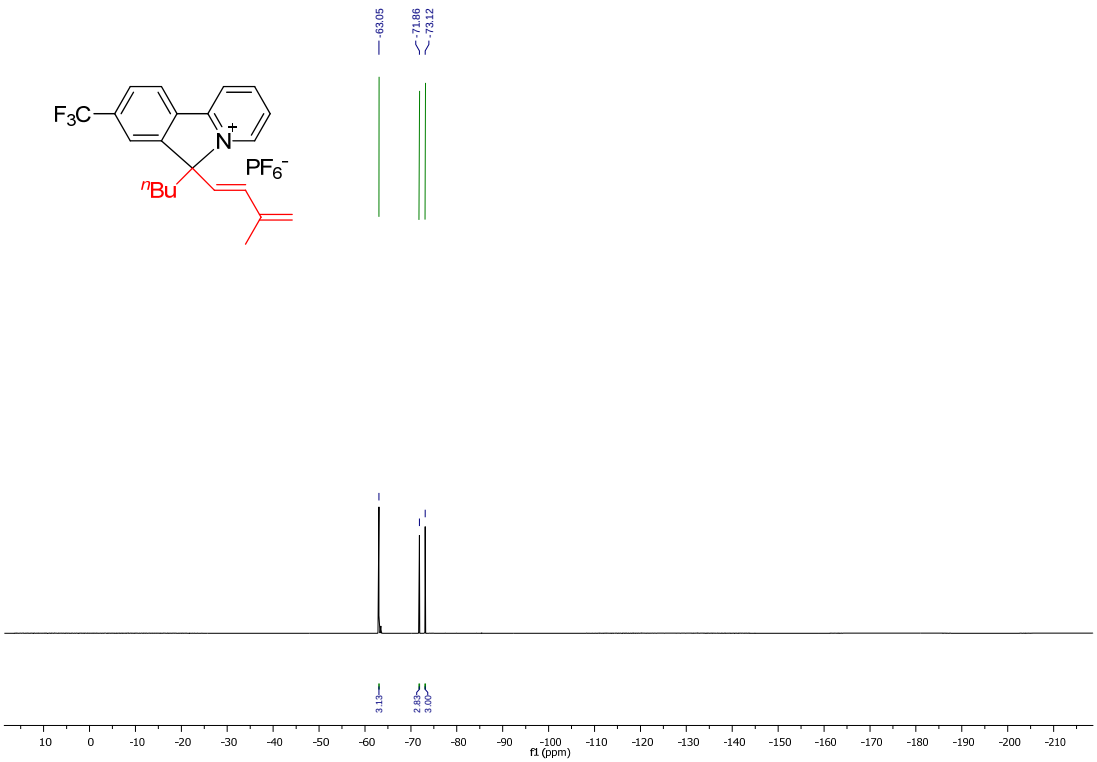
Supplementary Figure 29. ^{1}H NMR and ^{13}C NMR of **4ea**



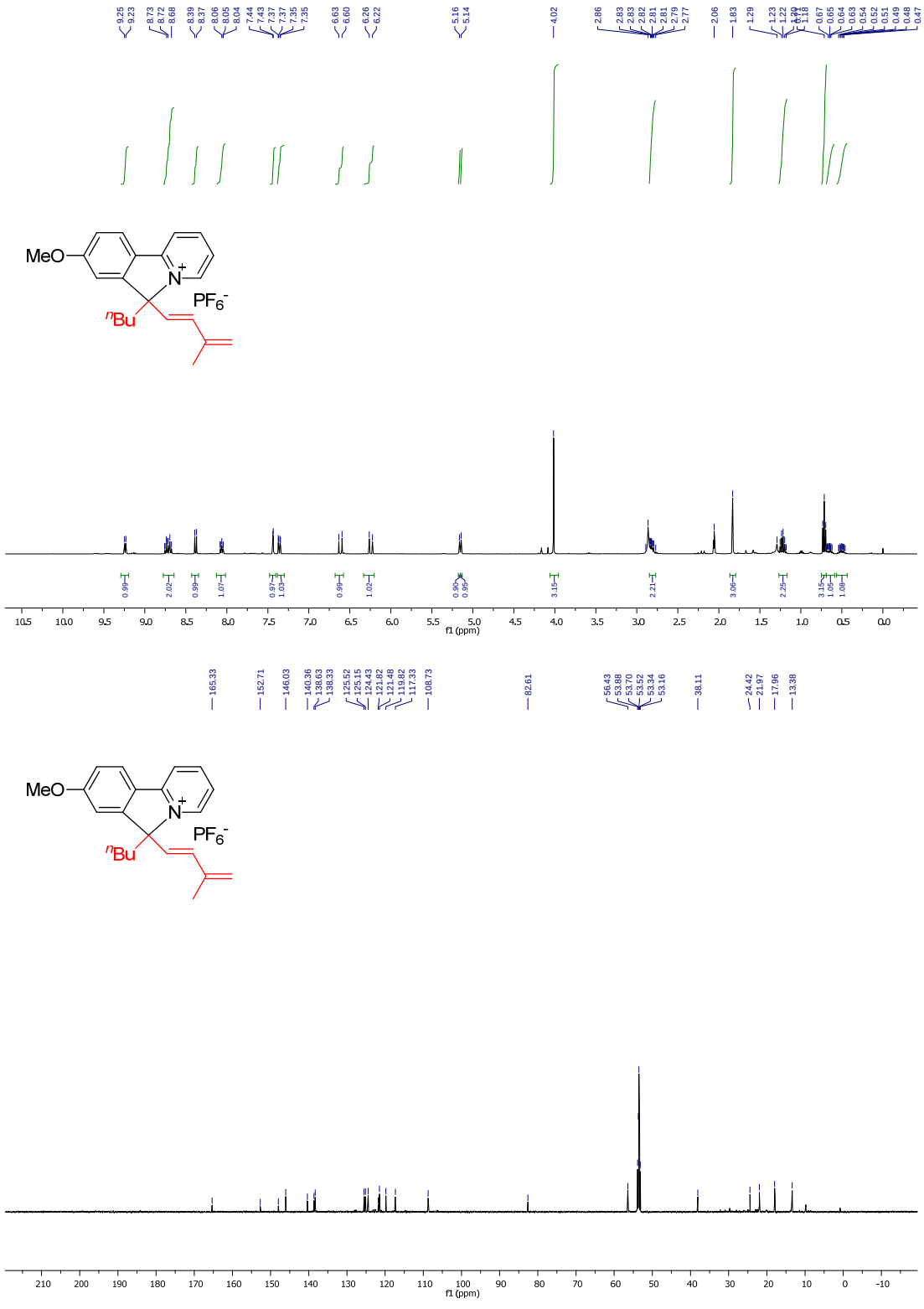
Supplementary Figure 30. ^{1}H NMR and ^{13}C NMR of **4ea**



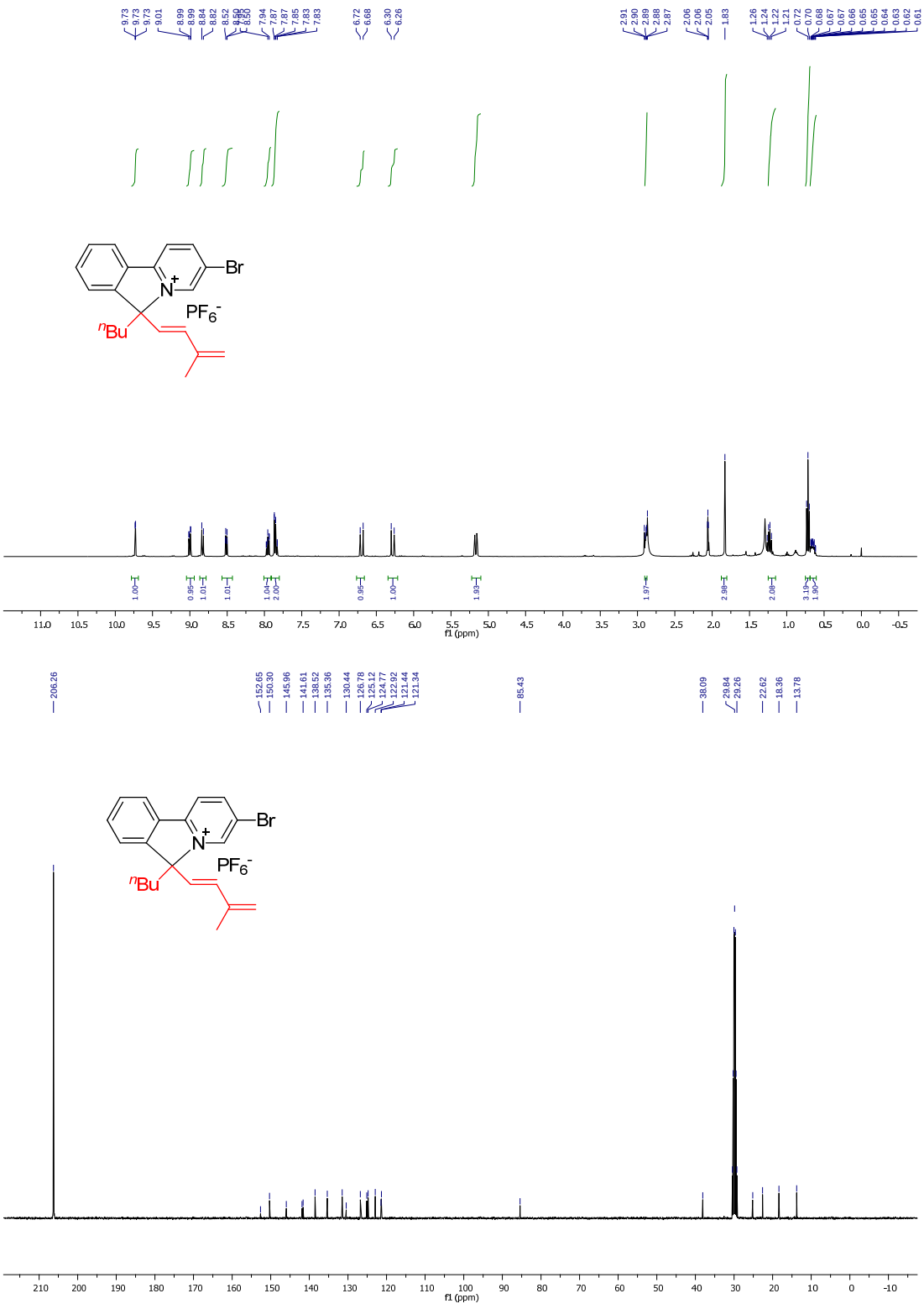
Supplementary Figure 31. ^{1}H NMR and ^{13}C NMR of **4ga**



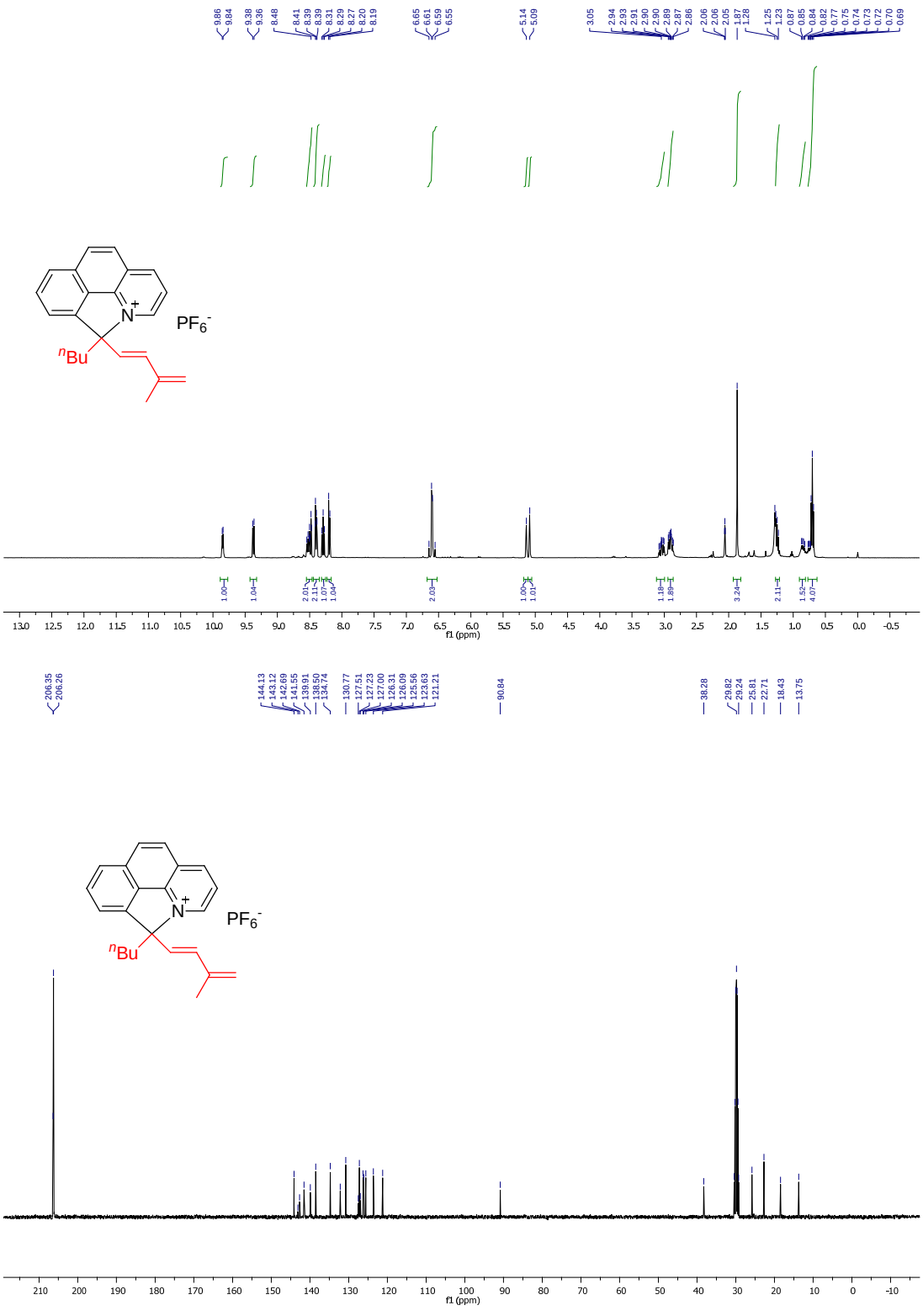
Supplementary Figure 32. ^{19}F NMR of **4ga**



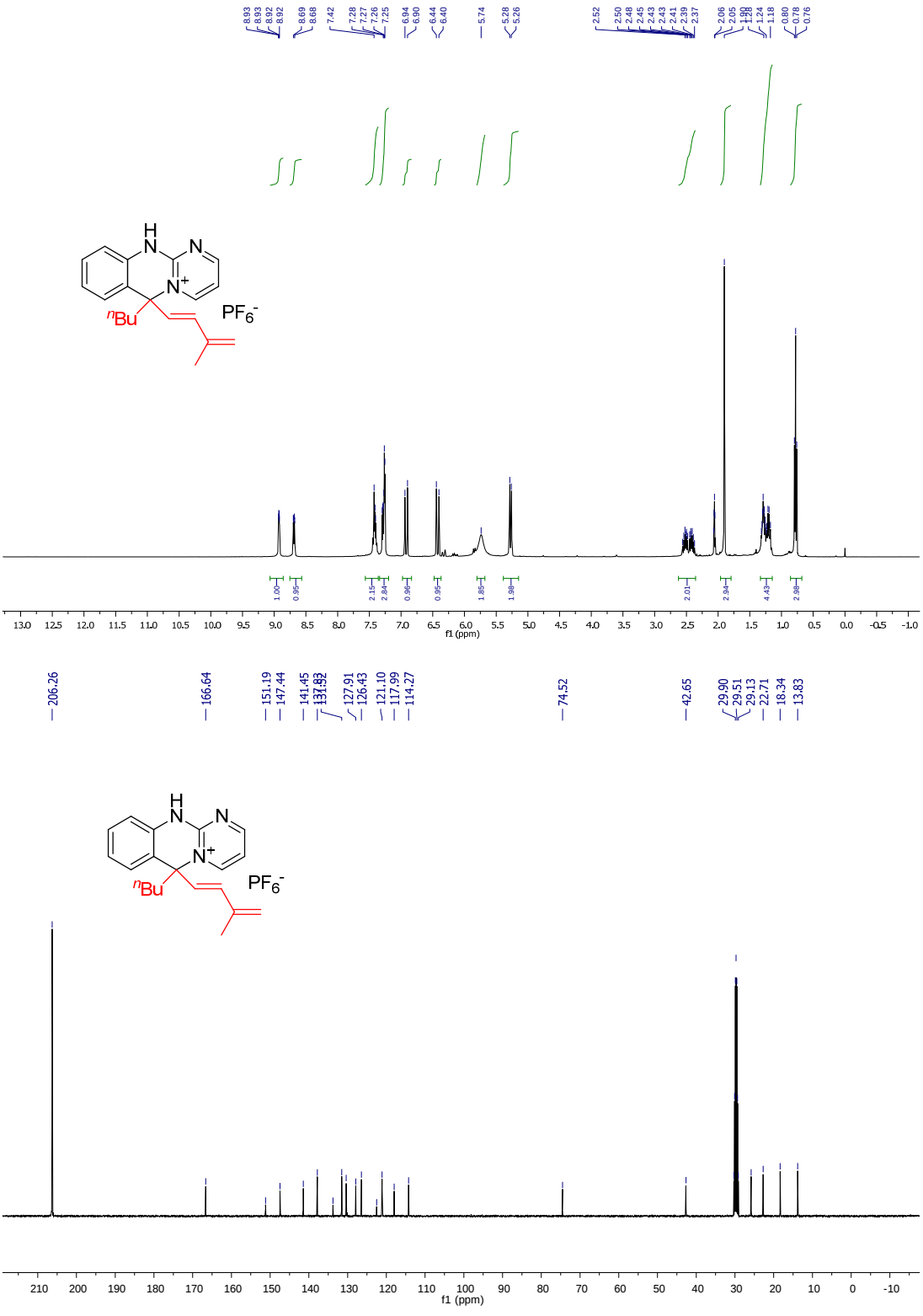
Supplementary Figure 33. ^{1}H NMR and ^{13}C NMR of **4ha**



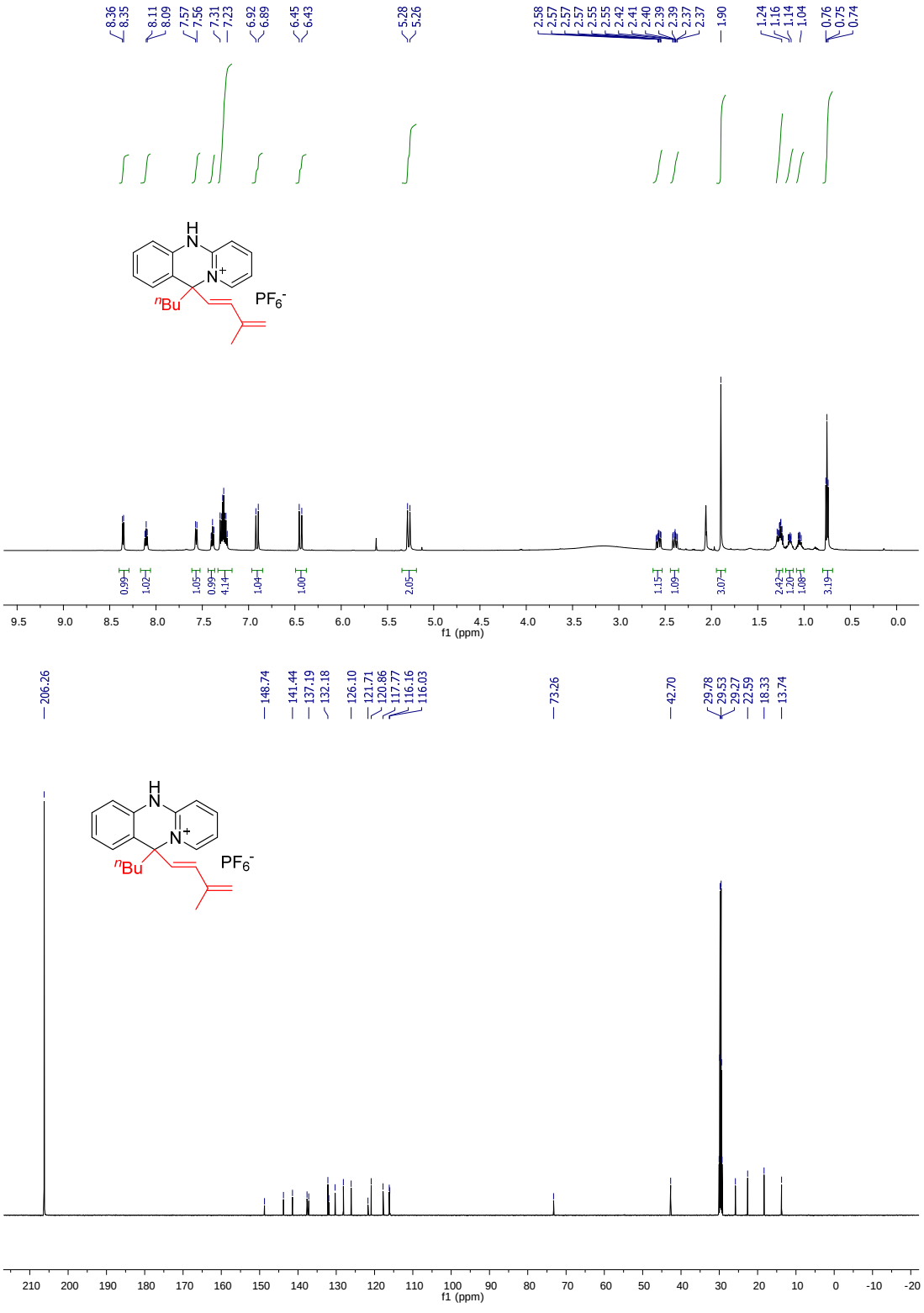
Supplementary Figure 34. ^{1}H NMR and ^{13}C NMR of **4ia**



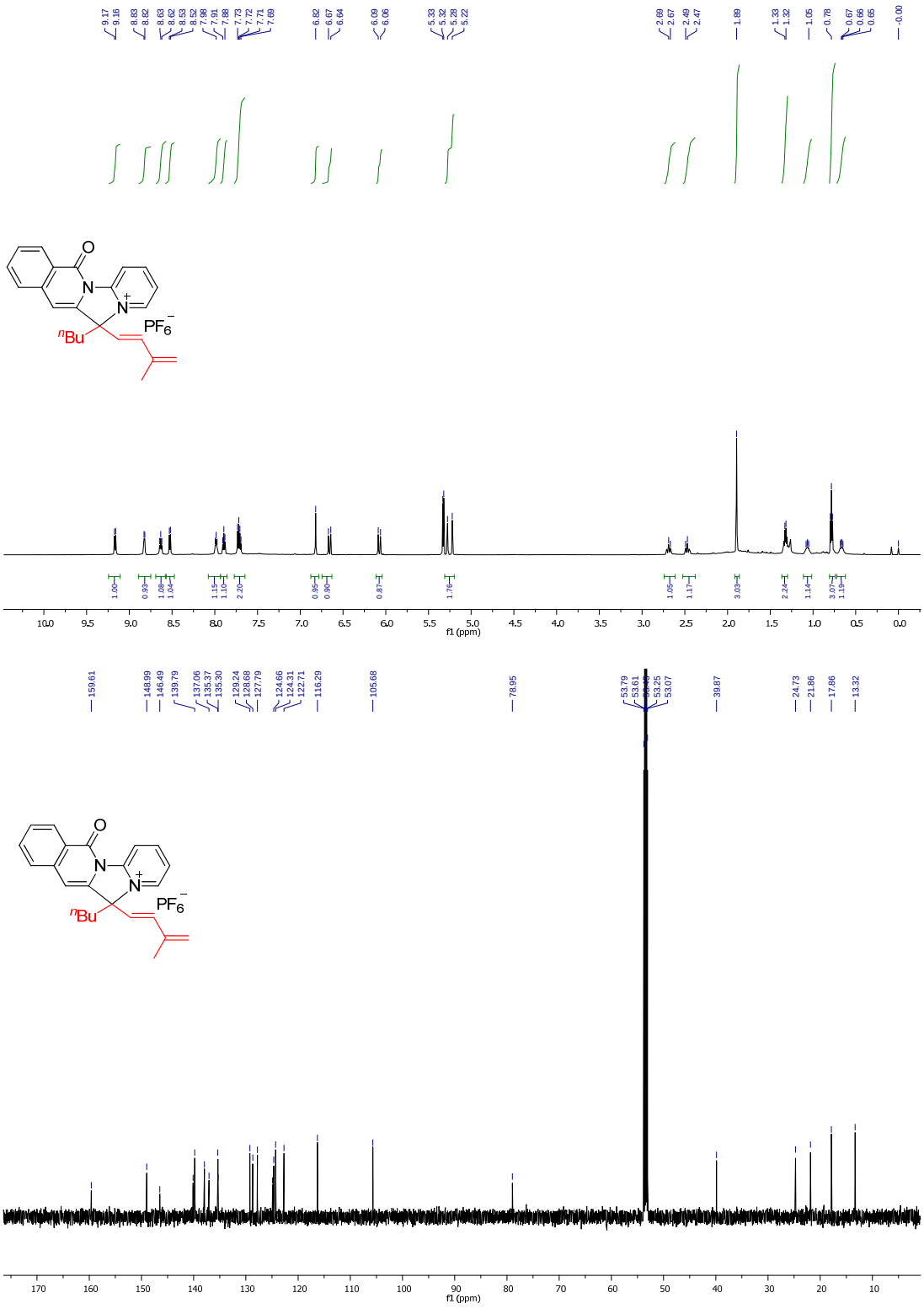
Supplementary Figure 35. ^{1}H NMR and ^{13}C NMR of **4ja**



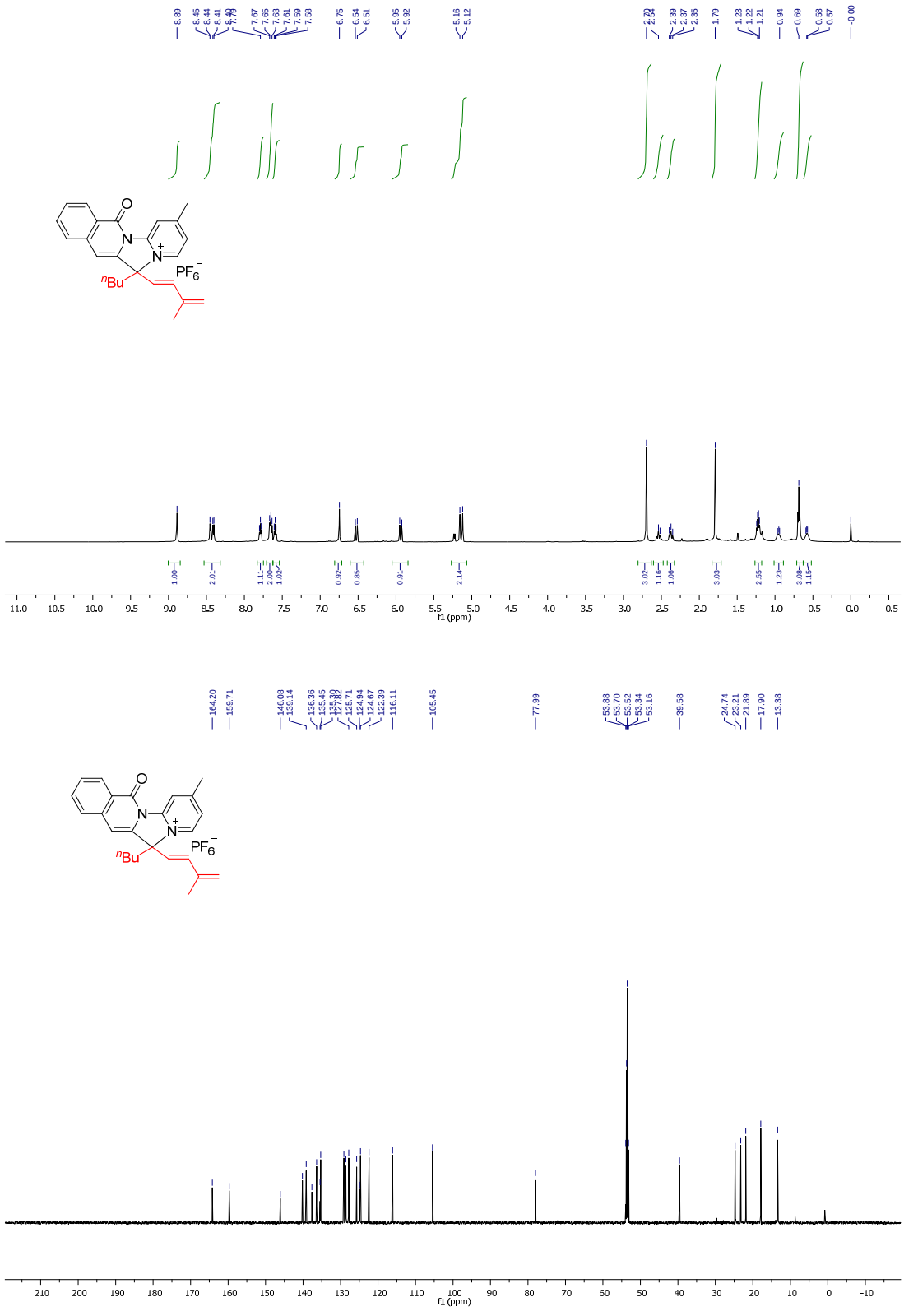
Supplementary Figure 36. ^{1}H NMR and ^{13}C NMR of **4la**



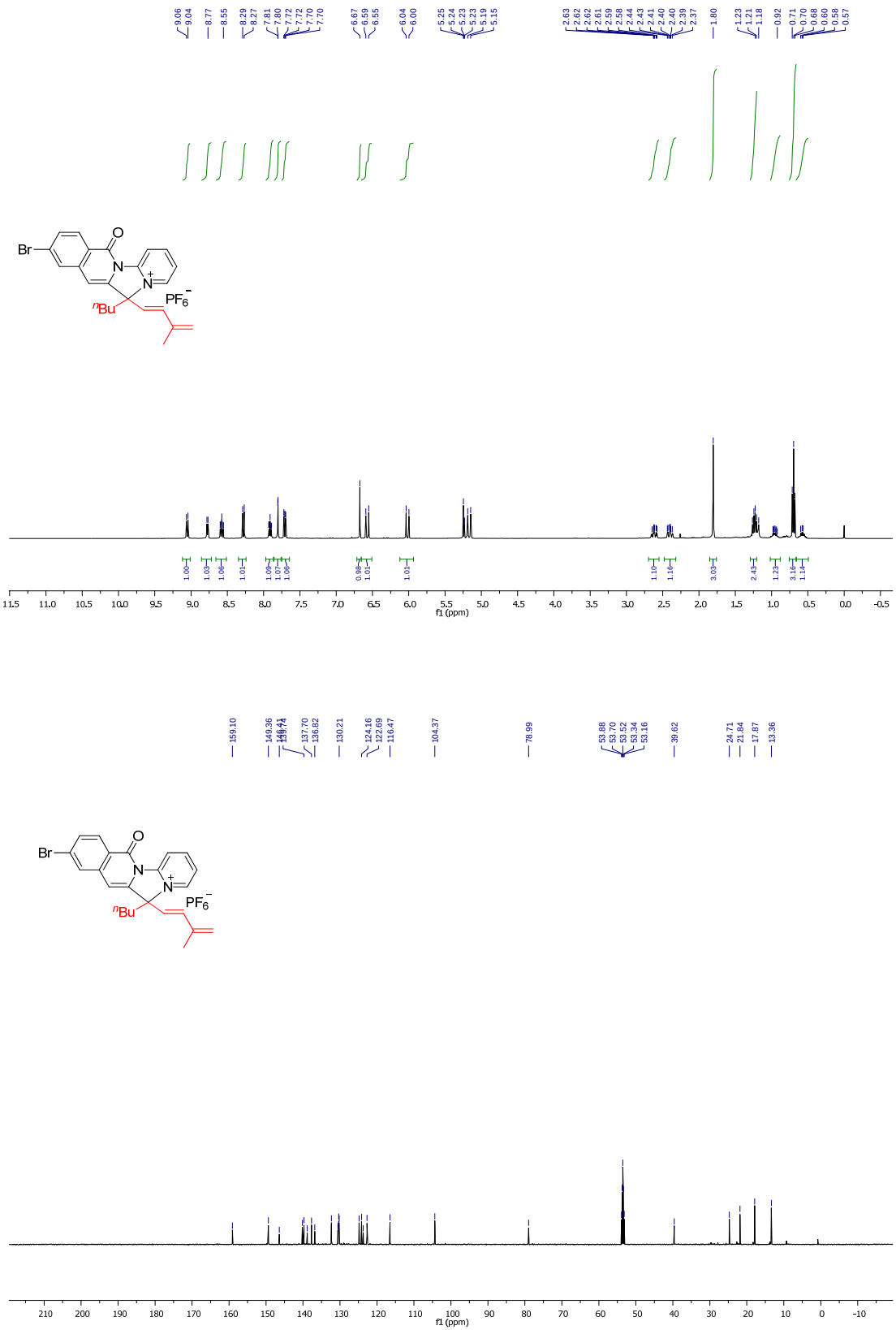
Supplementary Figure 37. ^{1}H NMR and ^{13}C NMR of **4ka**



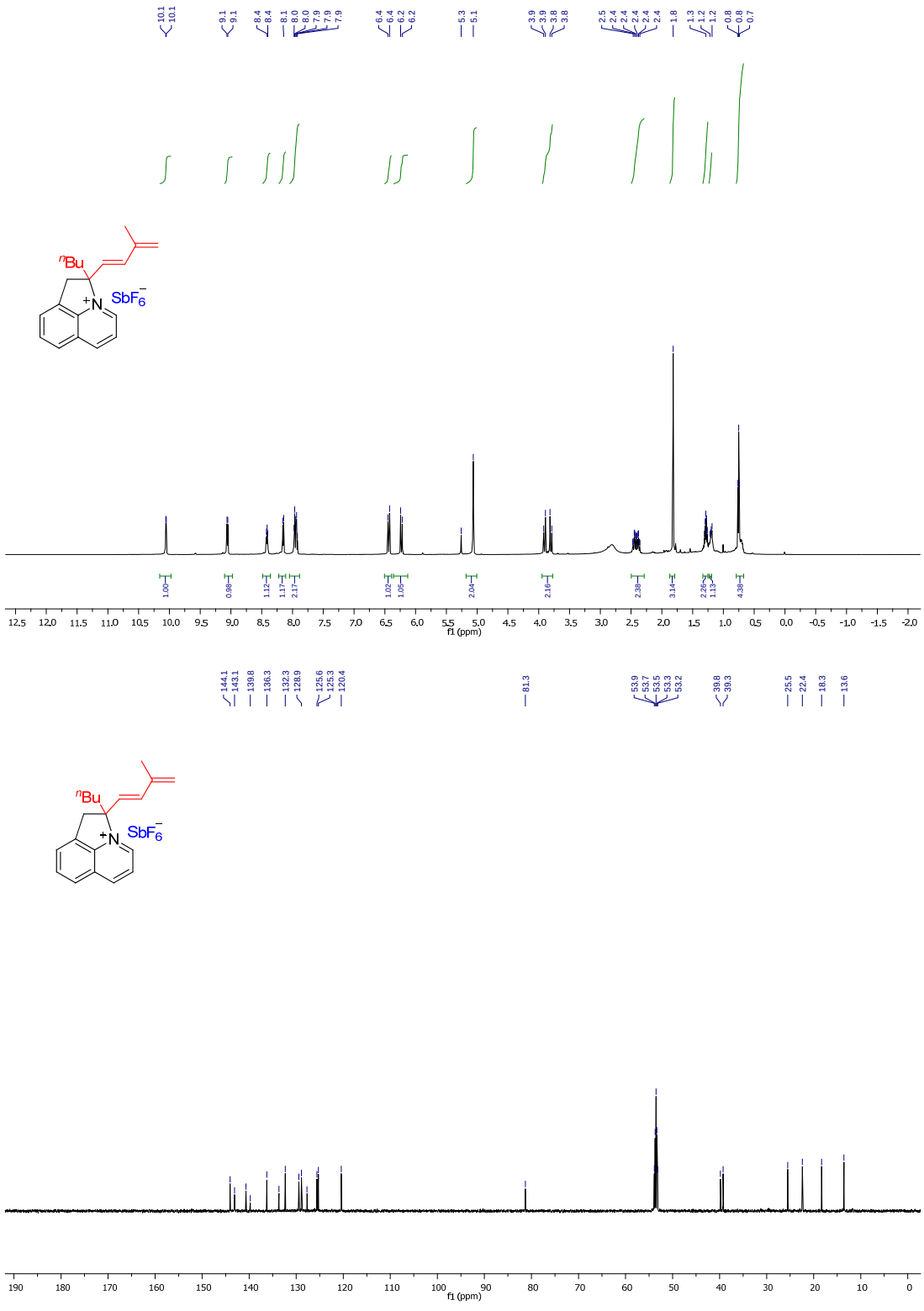
Supplementary Figure 38. ^{1}H NMR and ^{13}C NMR of **5aa**



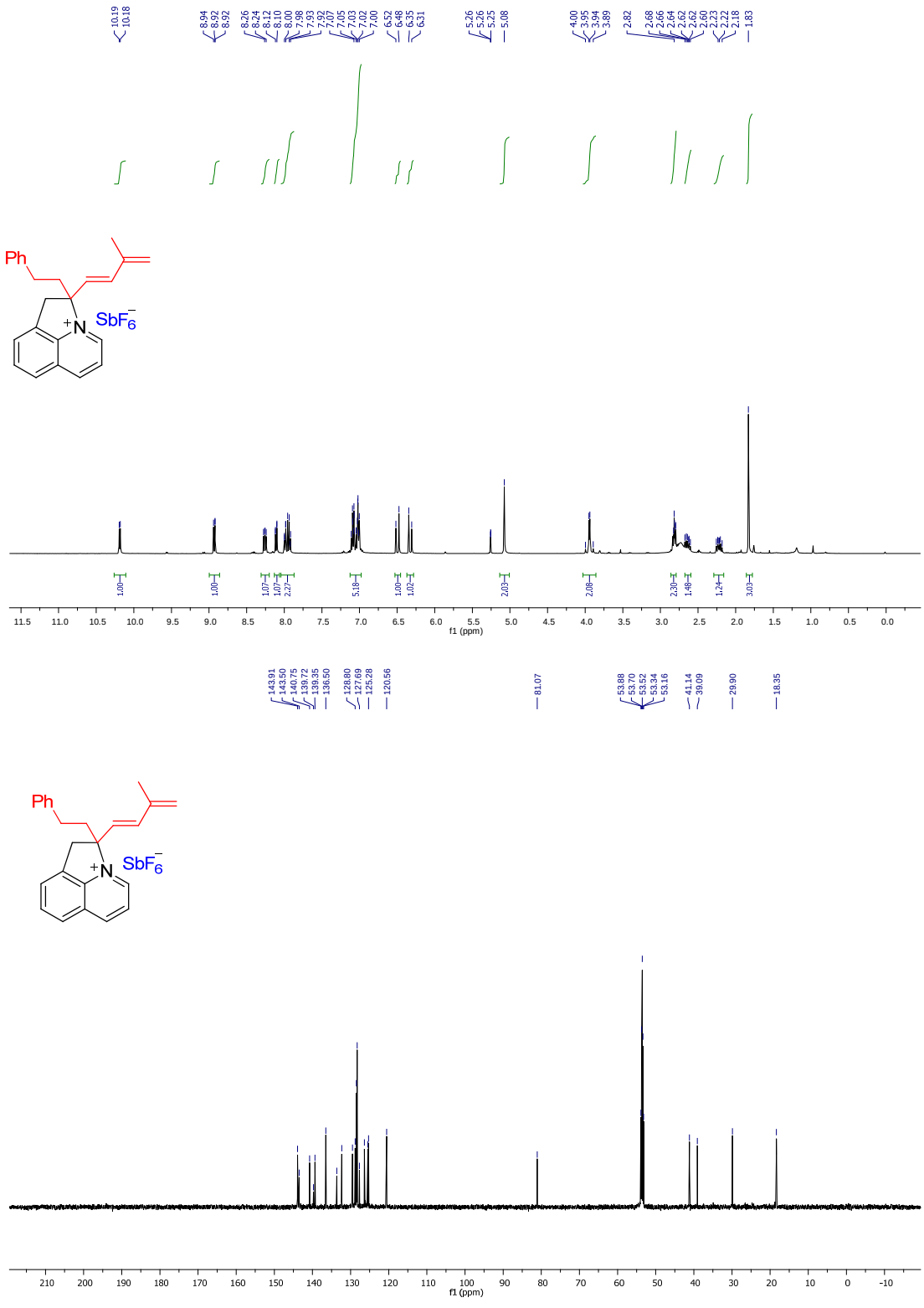
Supplementary Figure 39. ^{1}H NMR and ^{13}C NMR of **5ba**



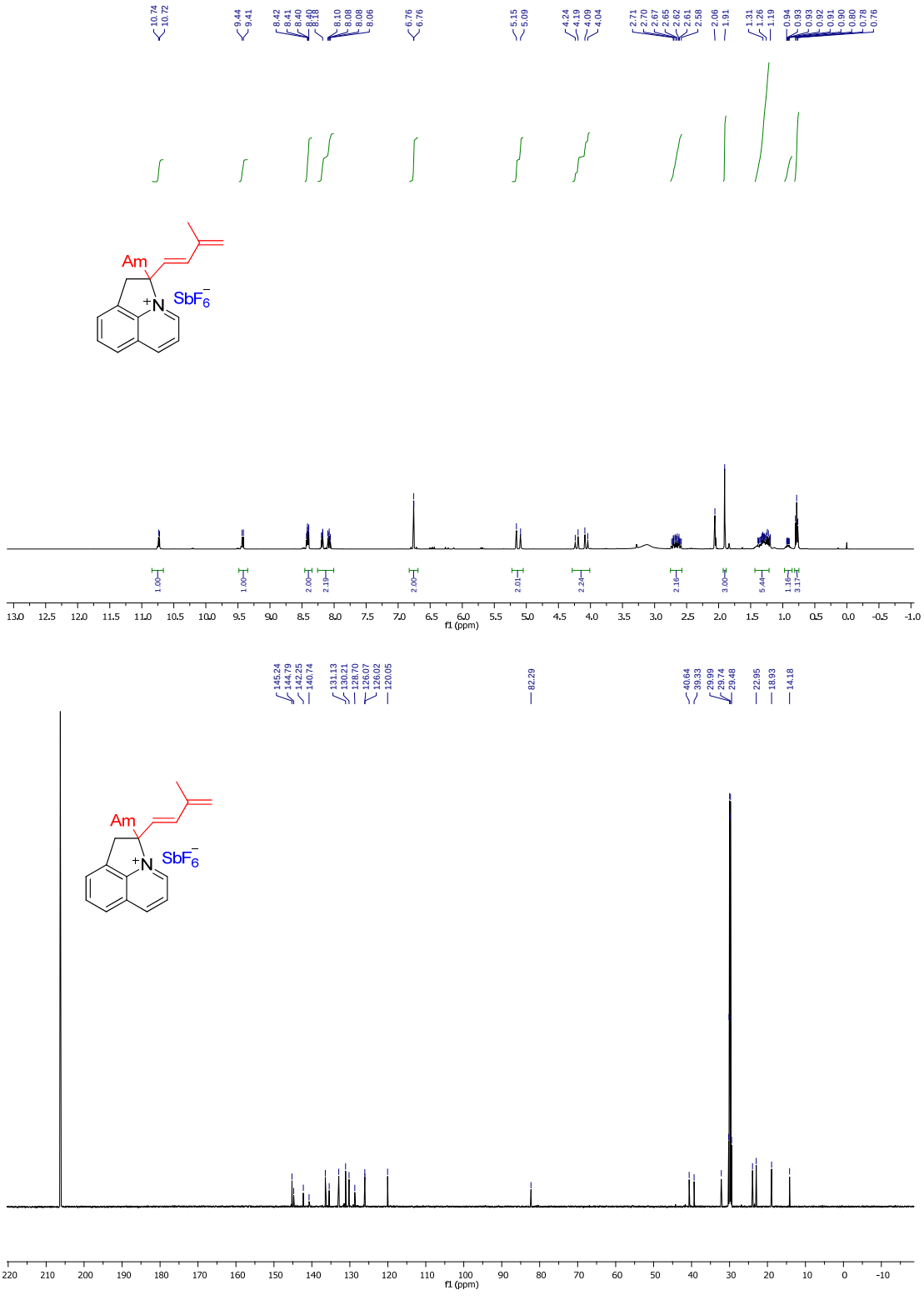
Supplementary Figure 40. ^{1}H NMR and ^{13}C NMR of **5ca**



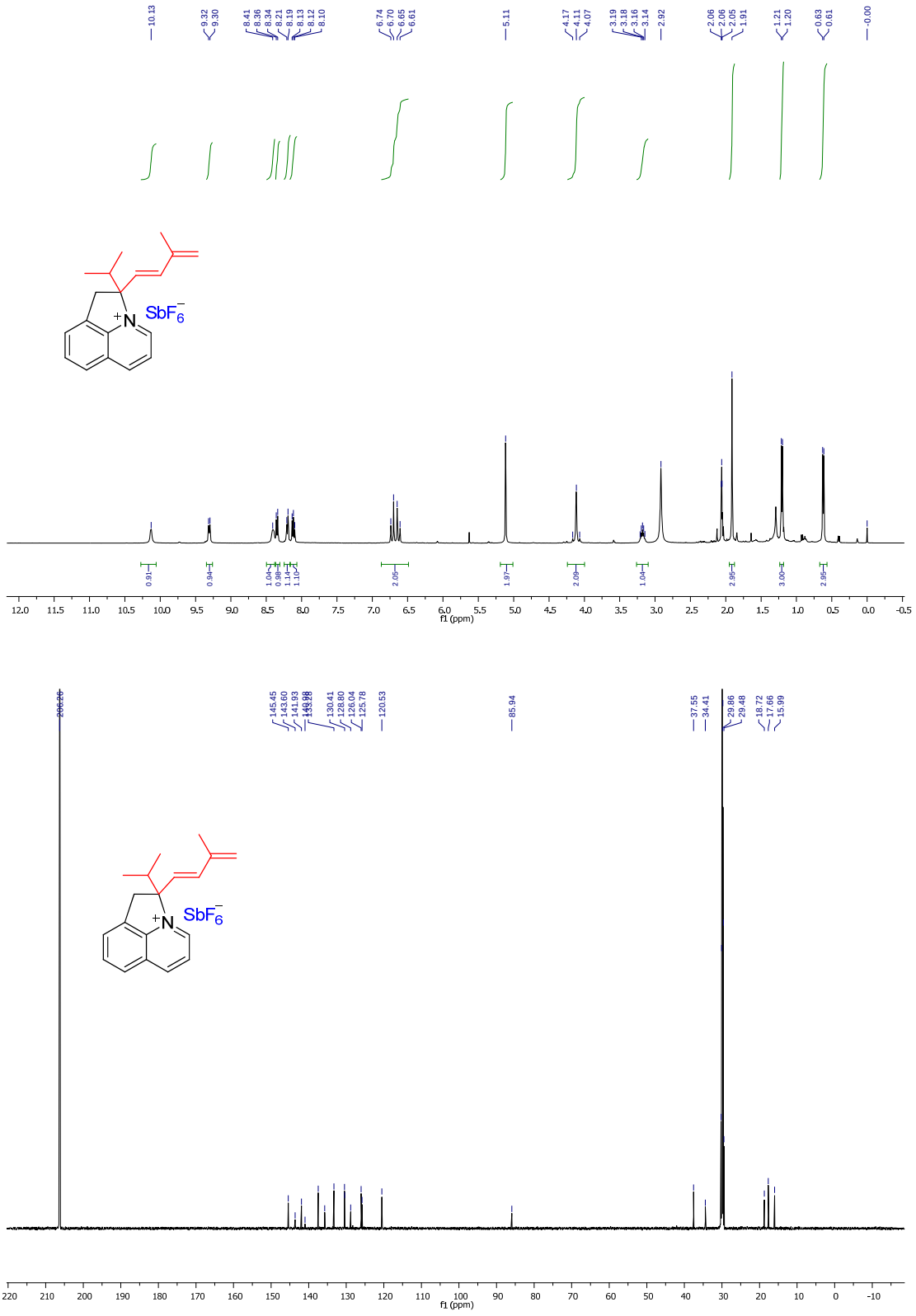
Supplementary Figure 41. ^{1}H NMR and ^{13}C NMR of **7aa**



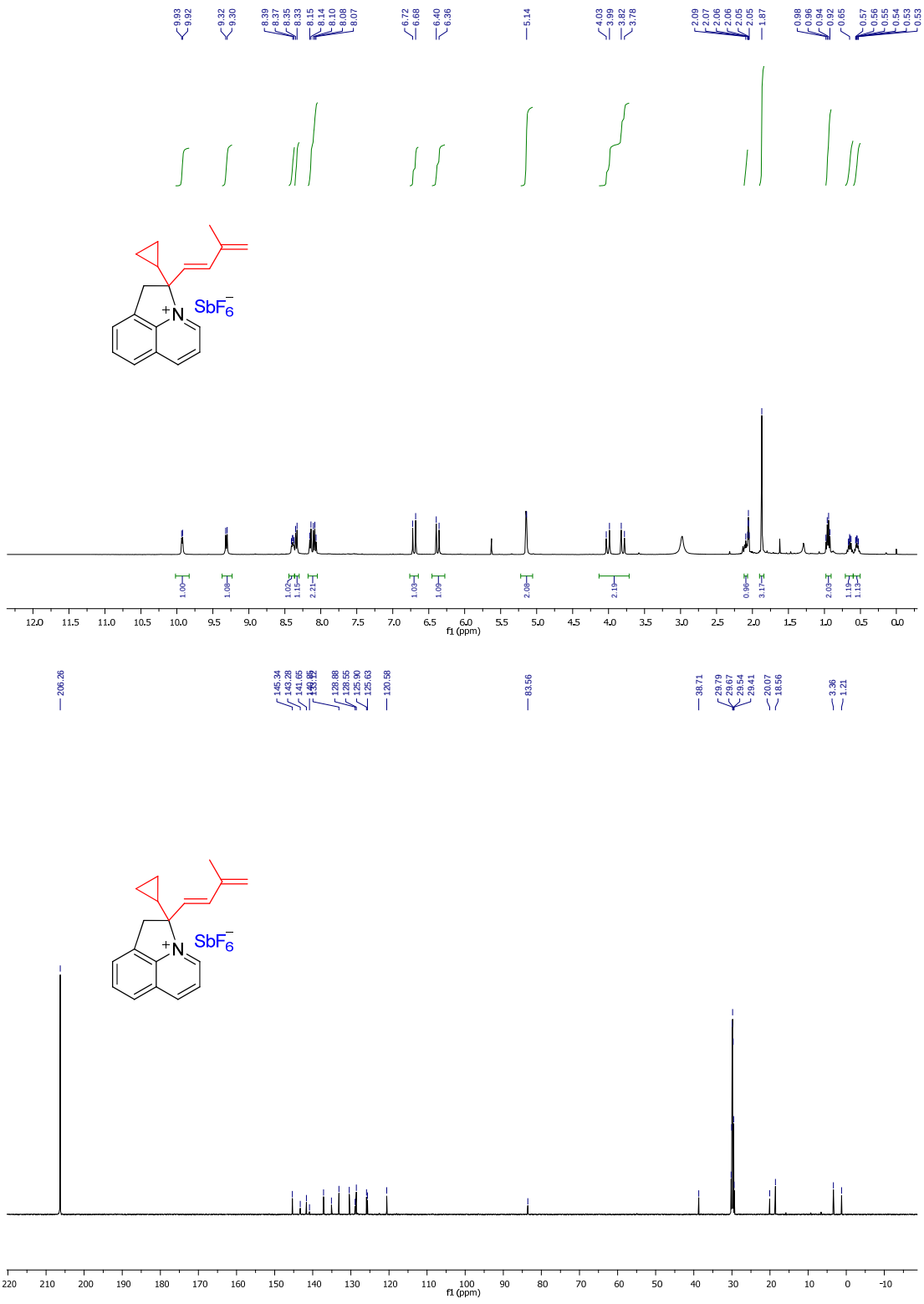
Supplementary Figure 42. ^{1}H NMR and ^{13}C NMR of **7ab**



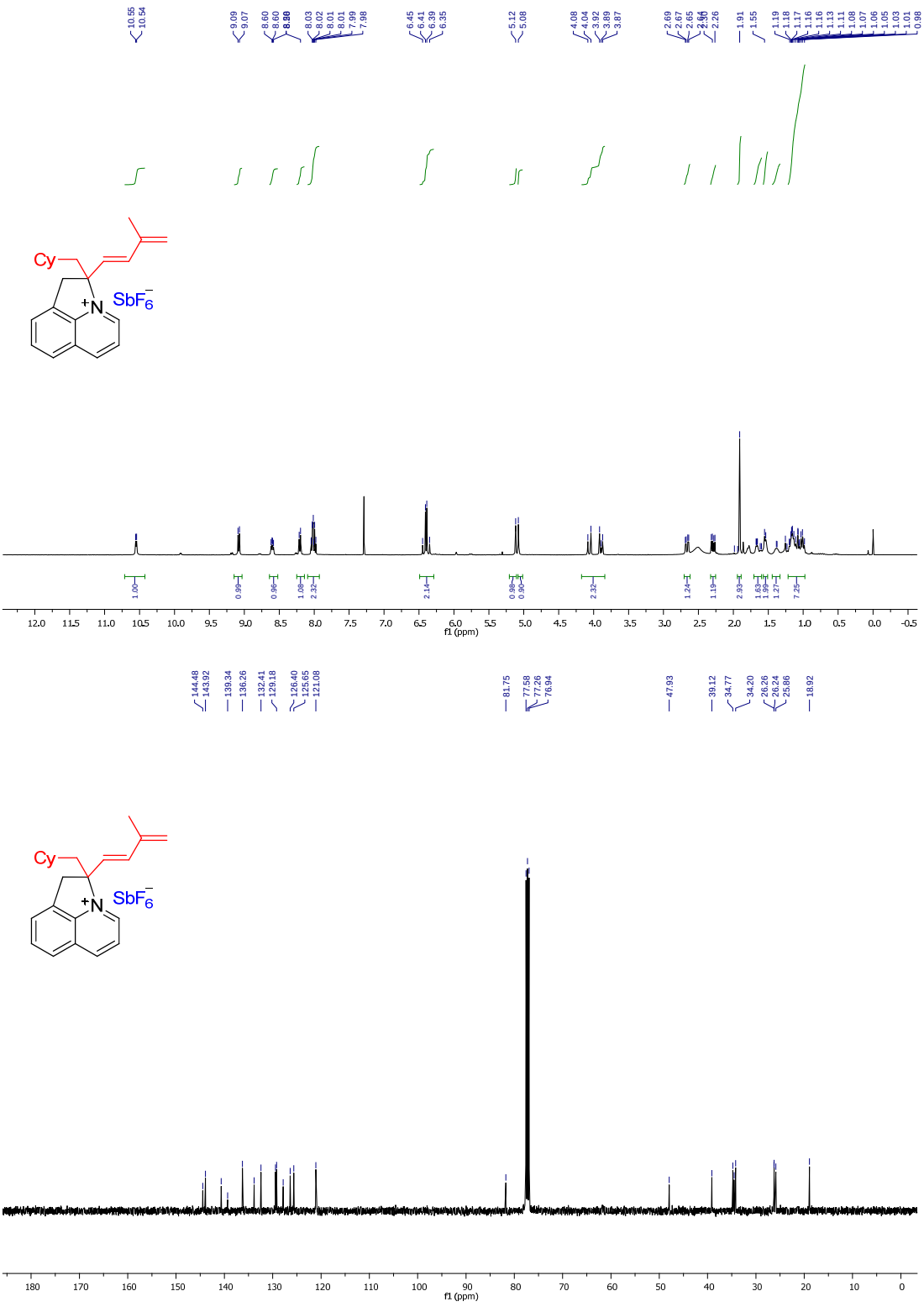
Supplementary Figure 43. ^{1}H NMR and ^{13}C NMR of **7ac**



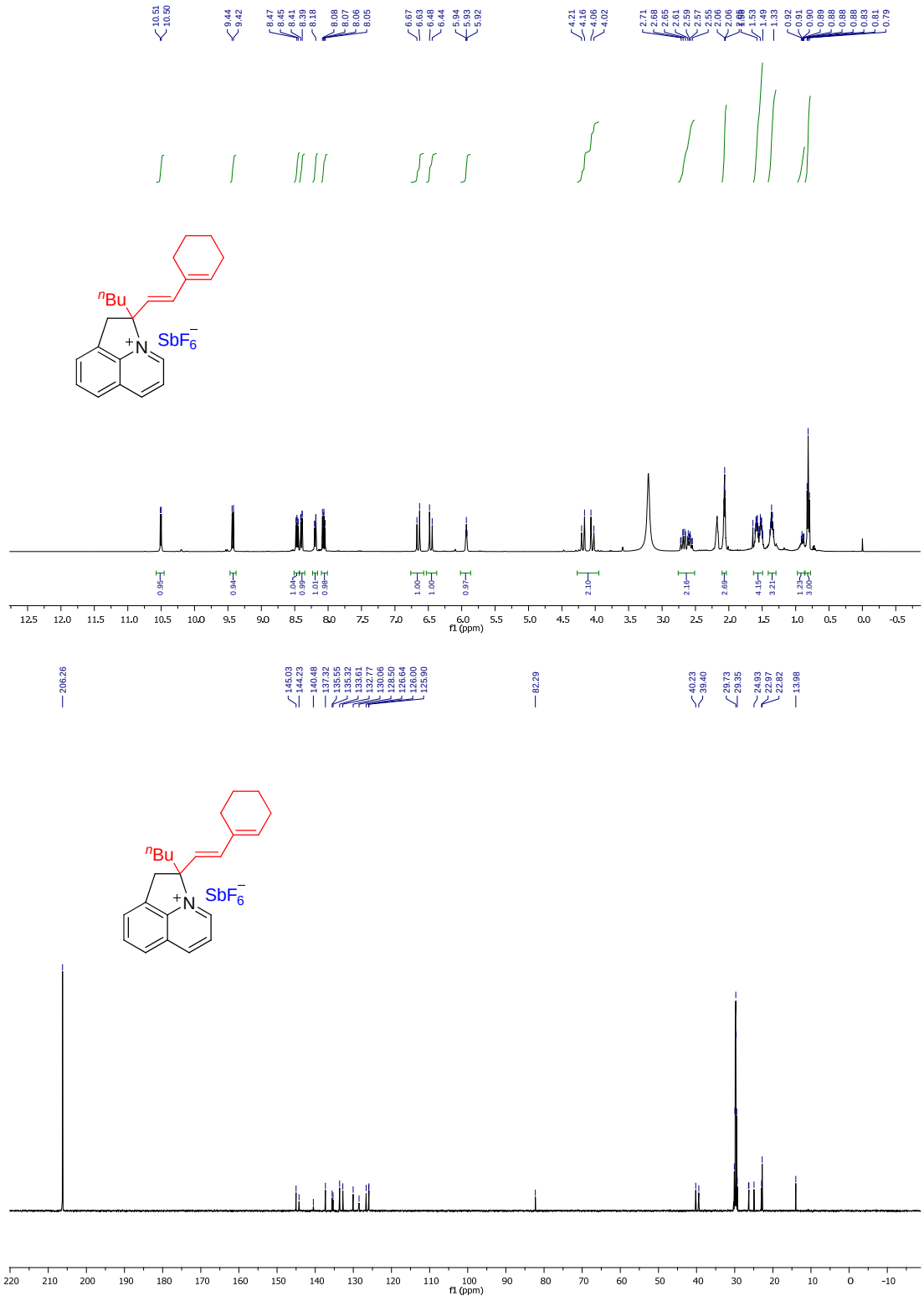
Supplementary Figure 44. ^{1}H NMR and ^{13}C NMR of **7ad**



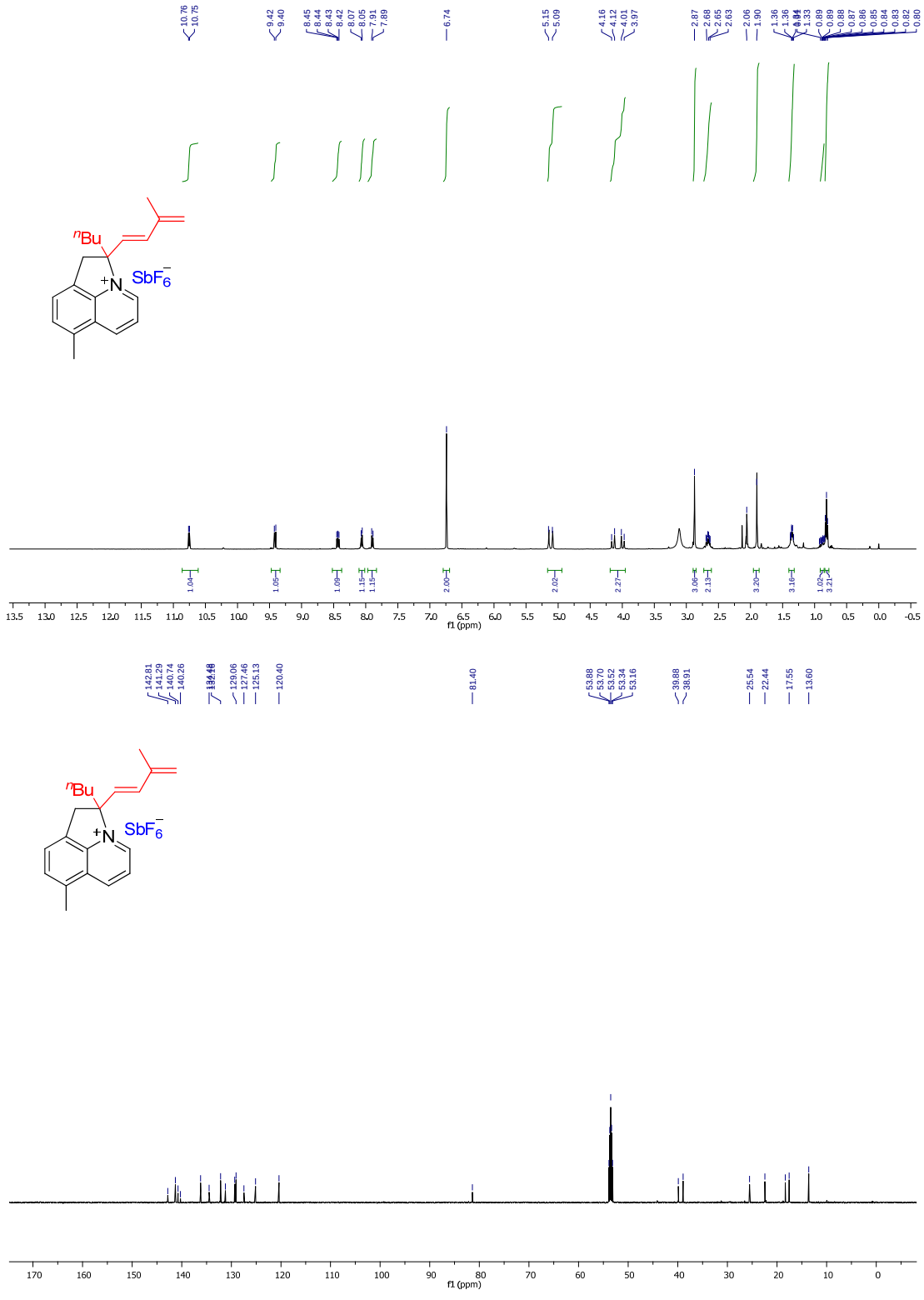
Supplementary Figure 45. ^{1}H NMR and ^{13}C NMR of **7ae**



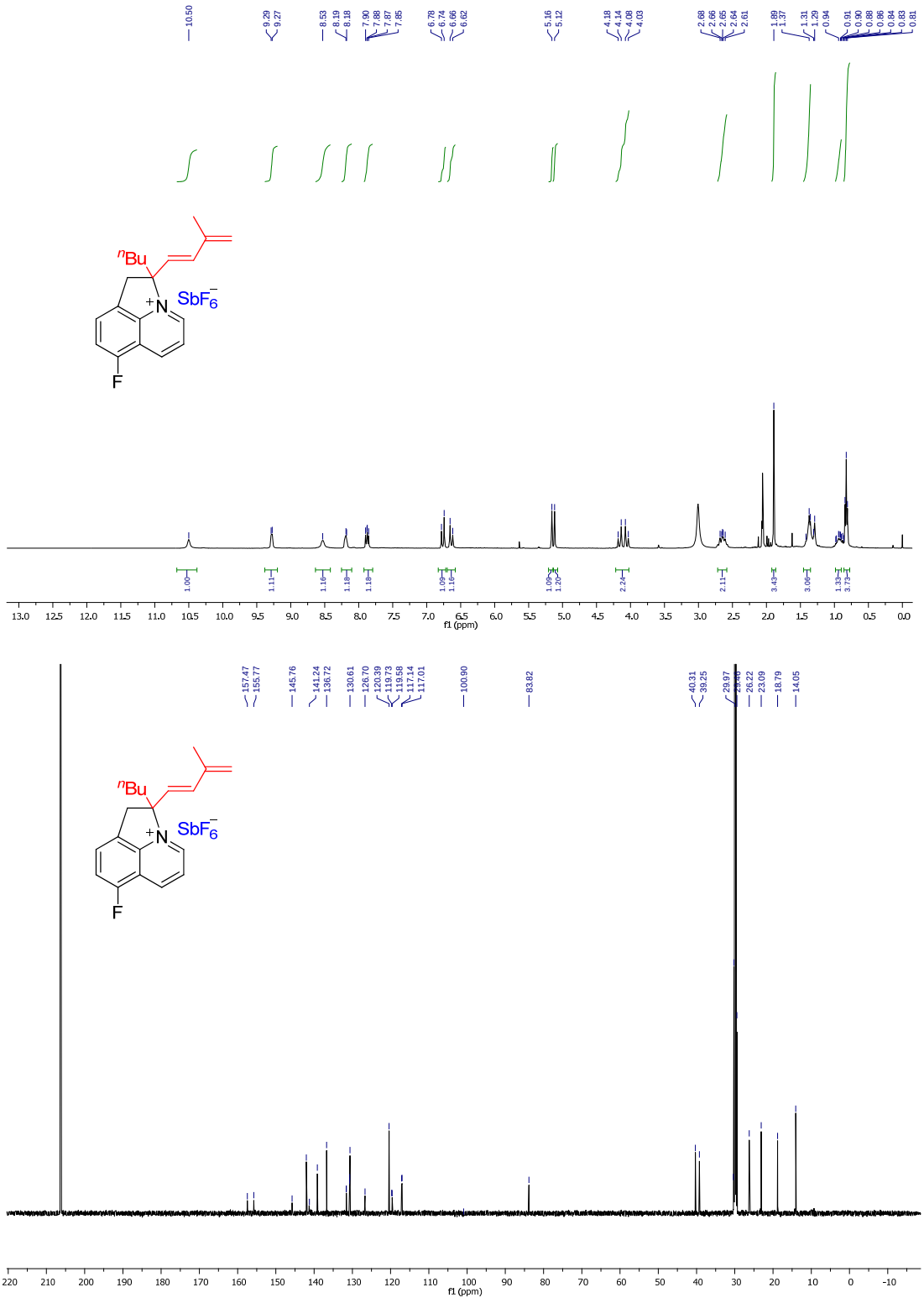
Supplementary Figure 46. ^{1}H NMR and ^{13}C NMR of **7af**



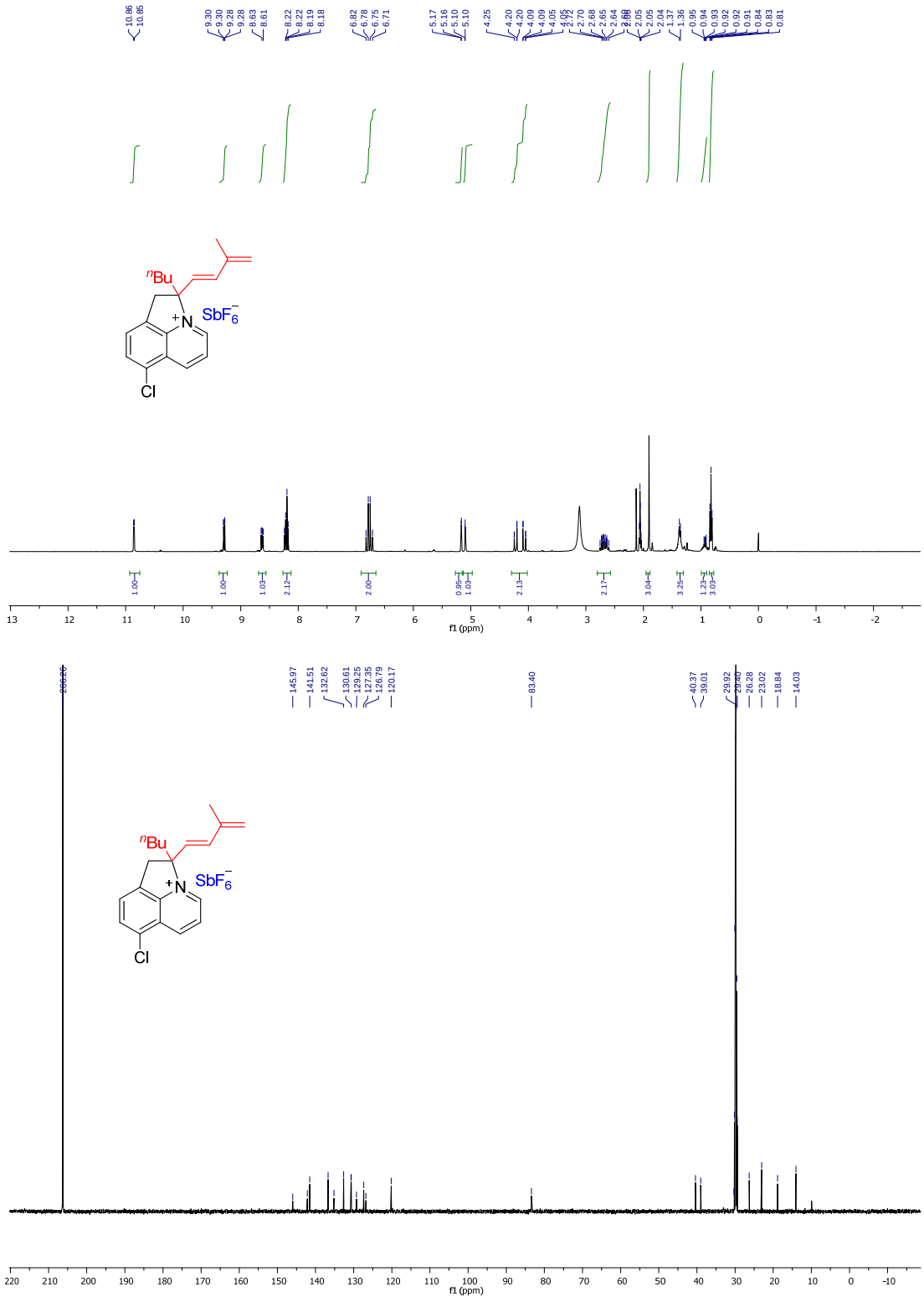
Supplementary Figure 47. ^{1}H NMR and ^{13}C NMR of **7ai**



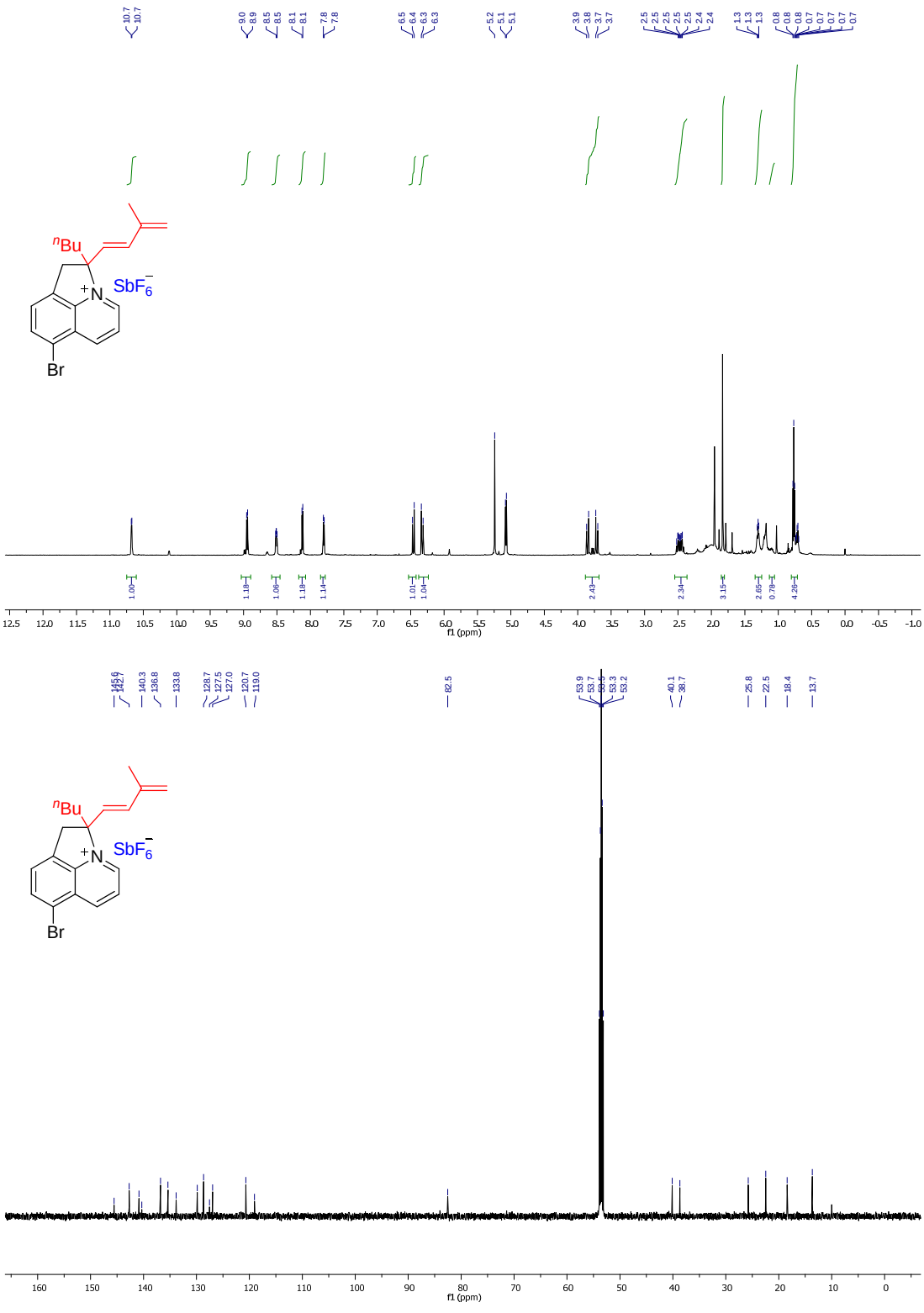
Supplementary Figure 48. ^{1}H NMR and ^{13}C NMR of **7ba**



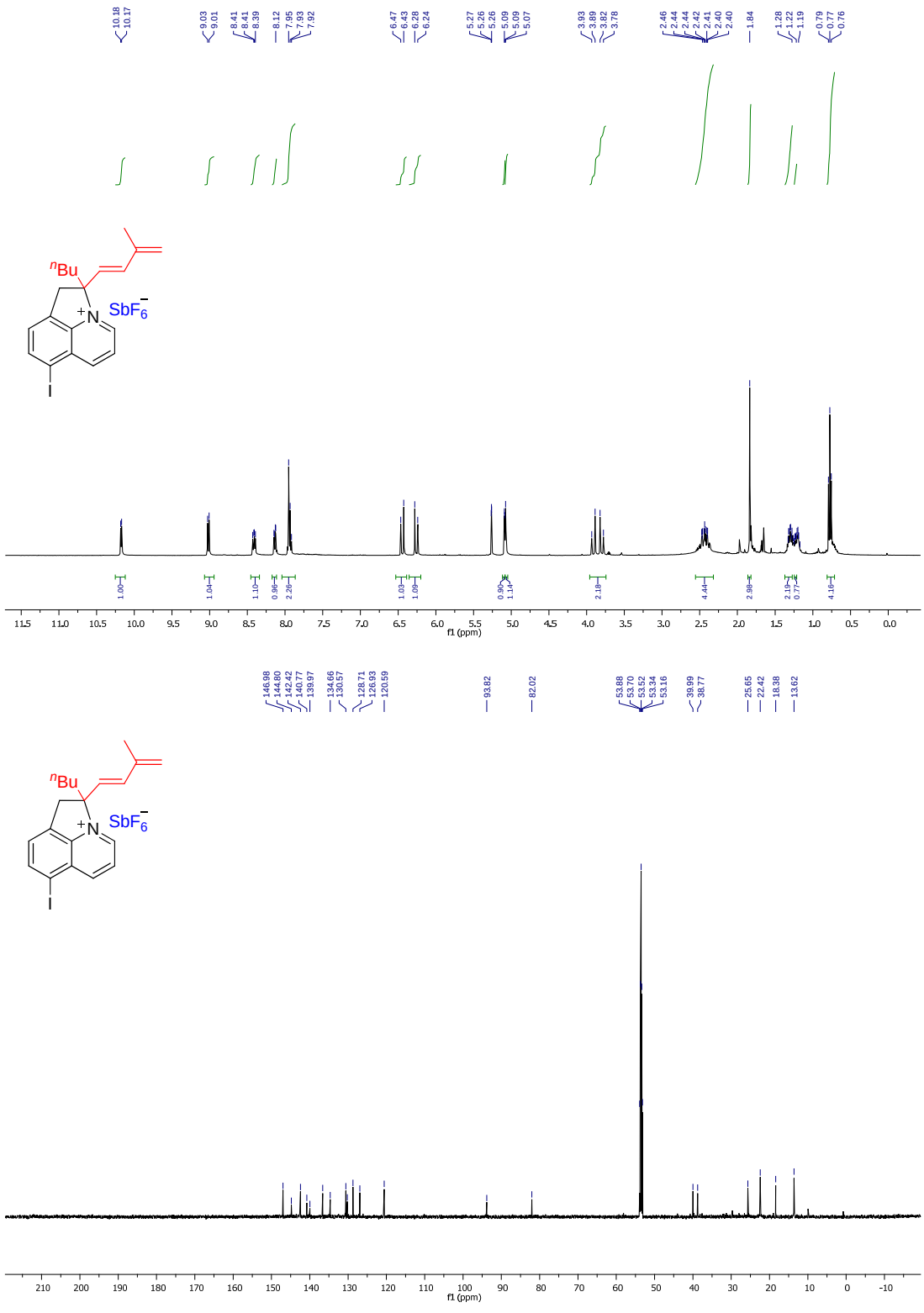
Supplementary Figure 49. ^{1}H NMR and ^{13}C NMR of **7ca**



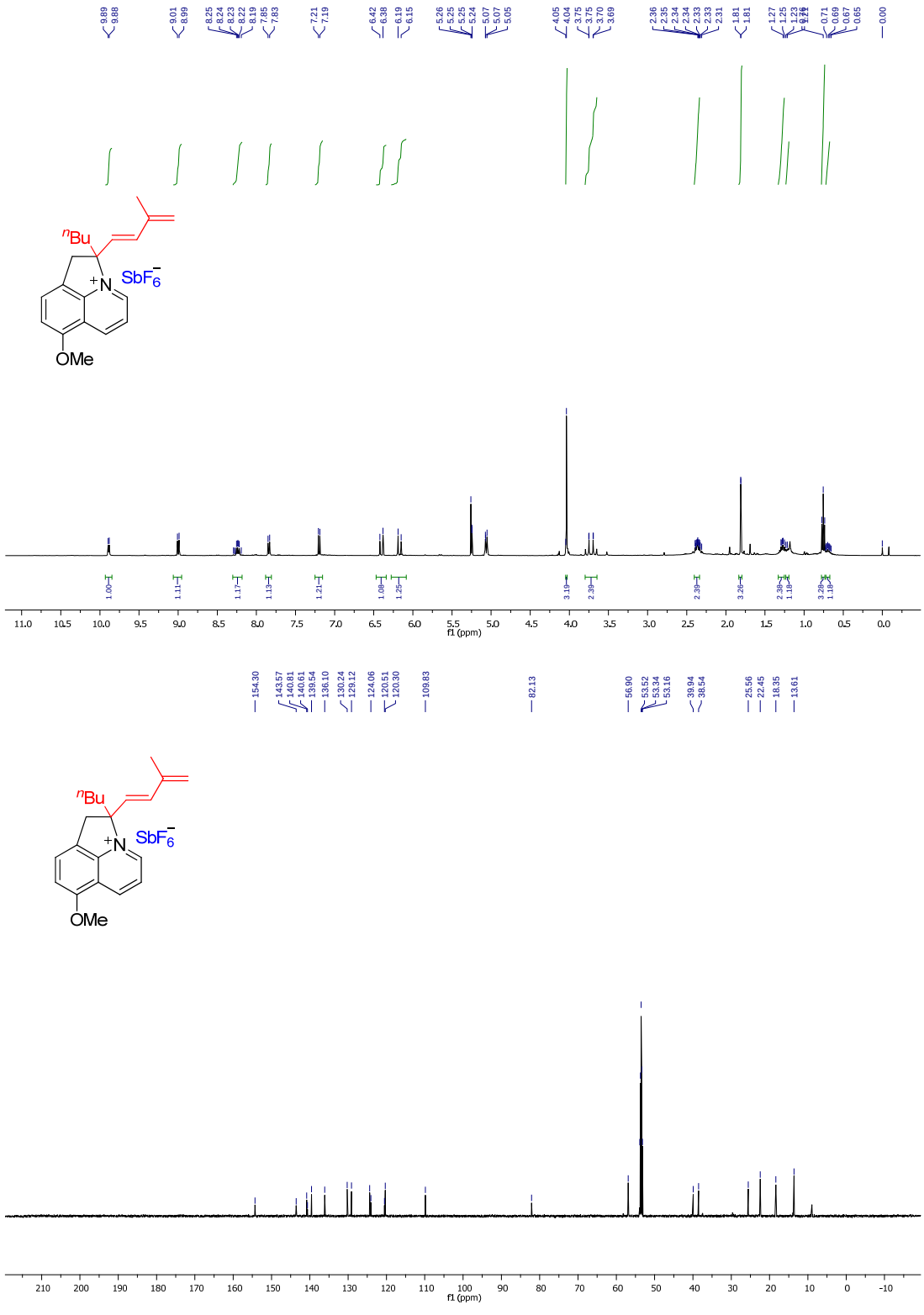
Supplementary Figure 50. ^{1}H NMR and ^{13}C NMR of **7da**



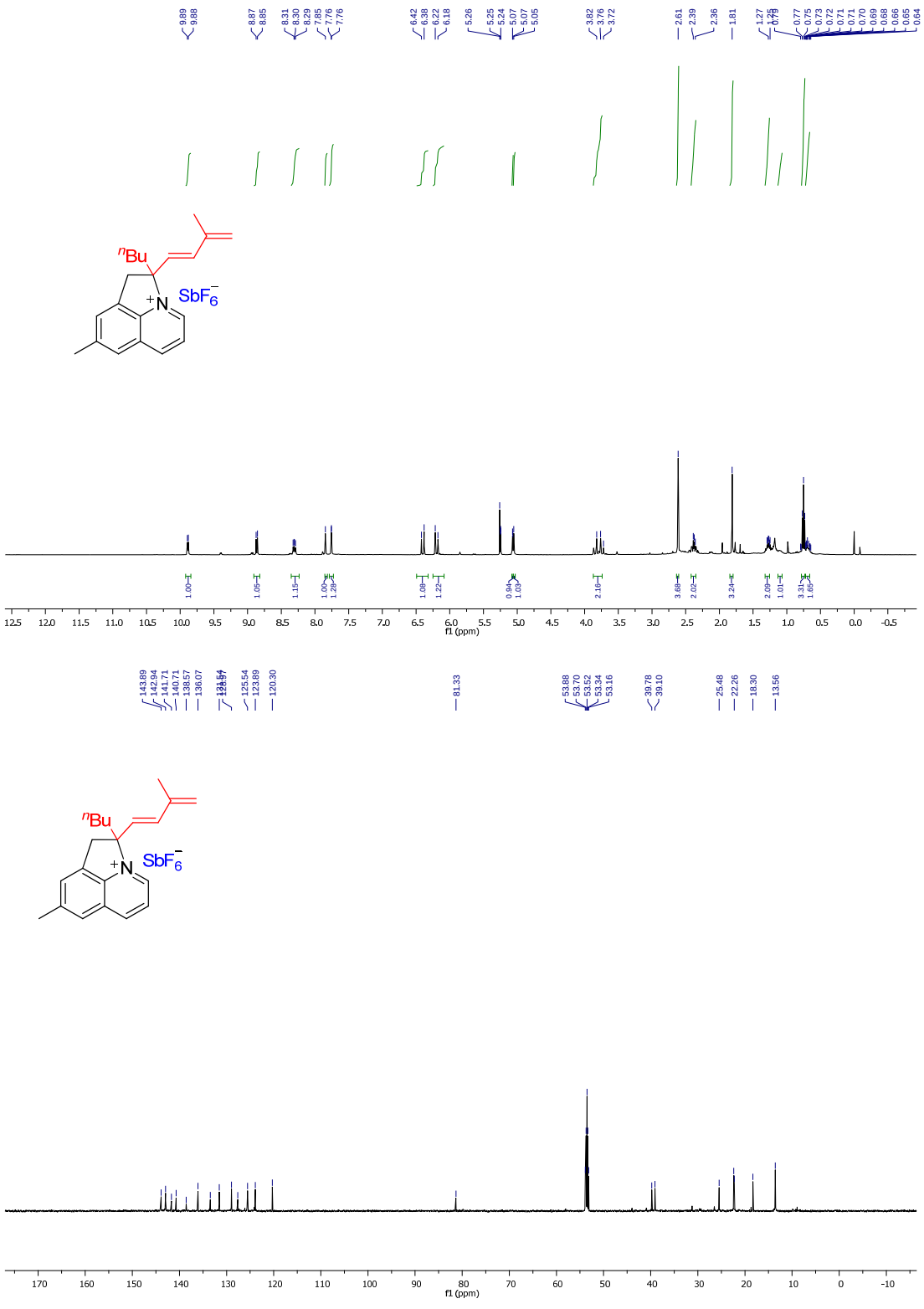
Supplementary Figure 51. ^{1}H NMR and ^{13}C NMR of **7ea**



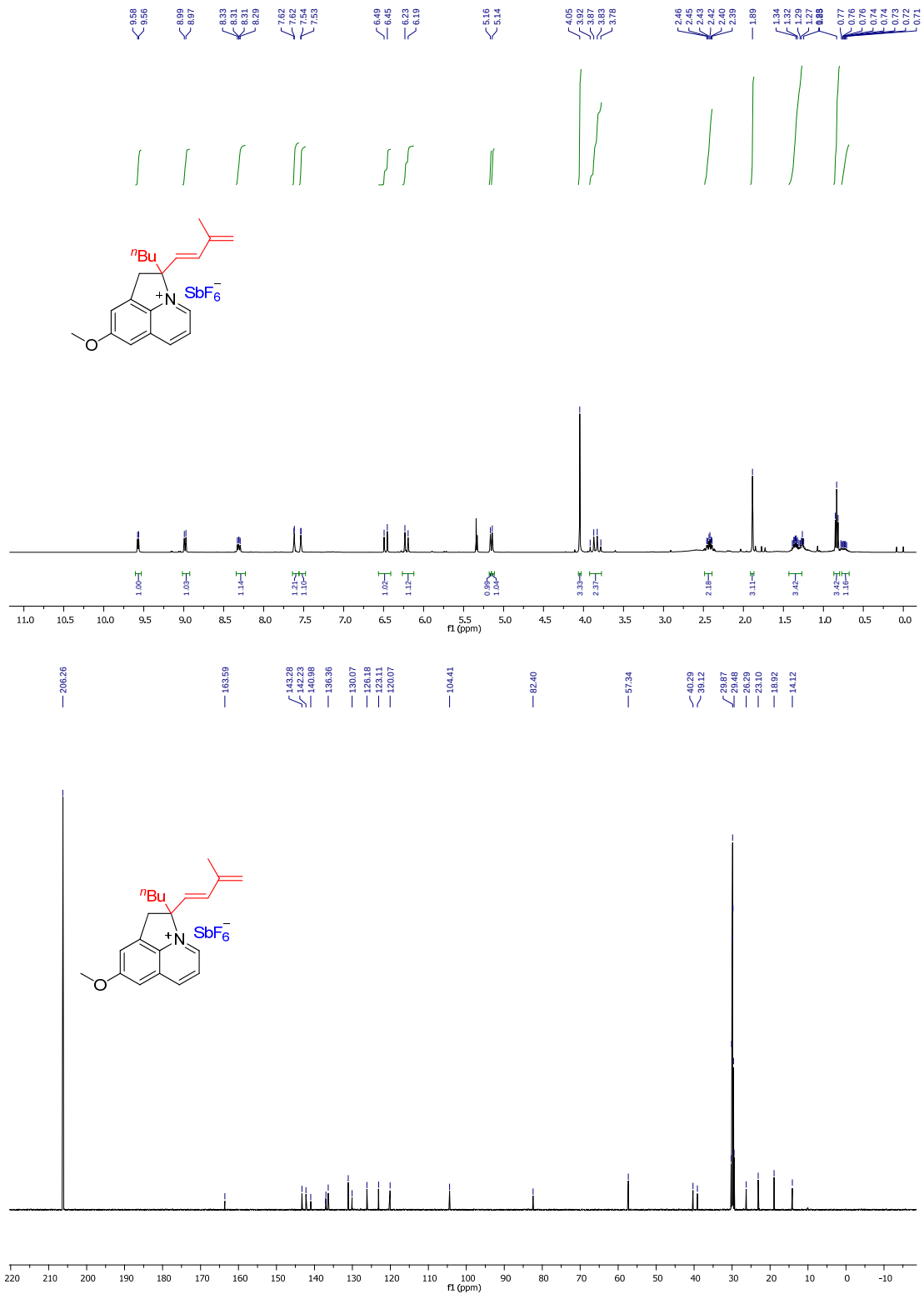
Supplementary Figure 52. ^{1}H NMR and ^{13}C NMR of **7fa**



Supplementary Figure 53. ^{1}H NMR and ^{13}C NMR of **7ga**

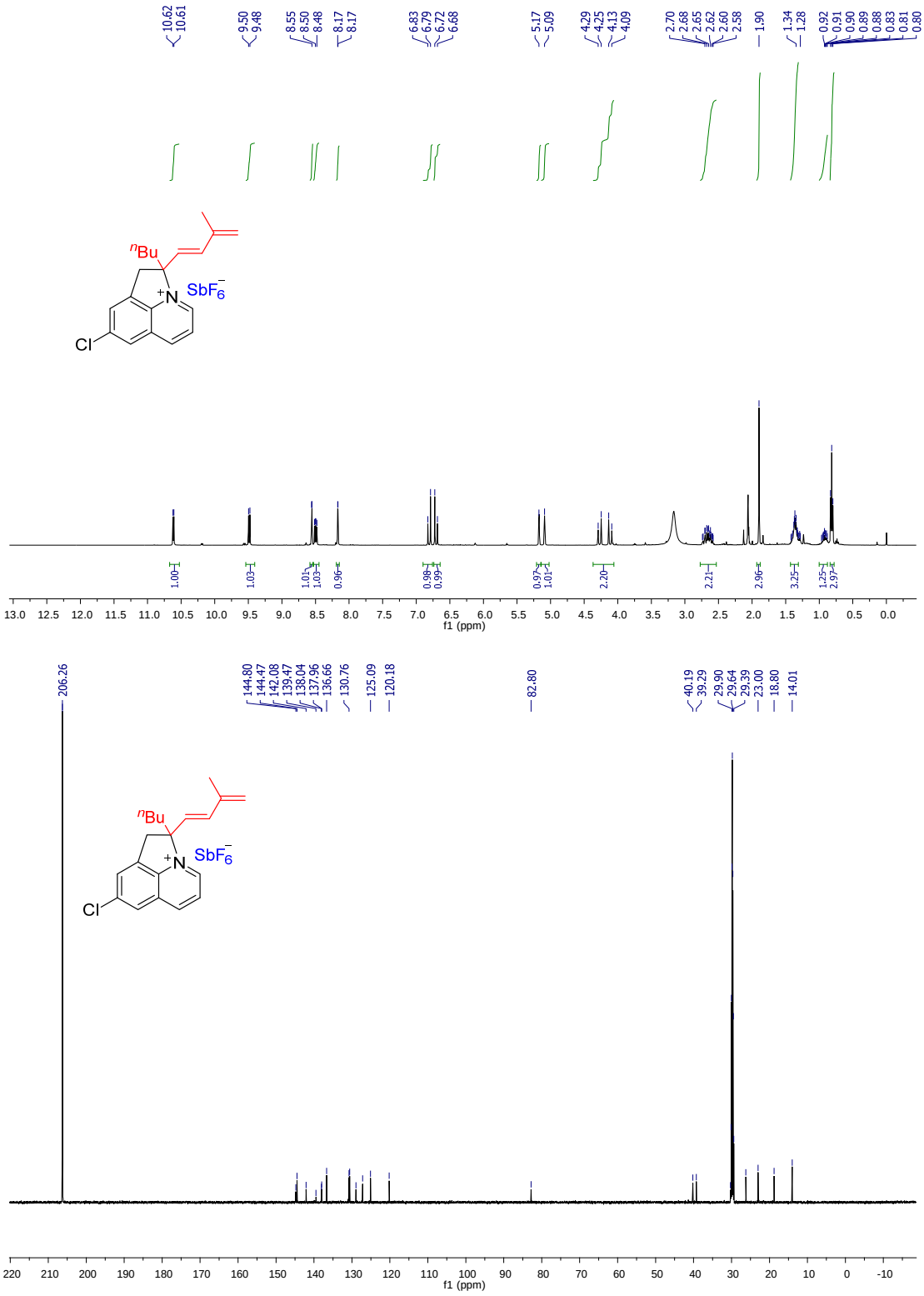


Supplementary Figure 54. ^{1}H NMR and ^{13}C NMR of **7ha**

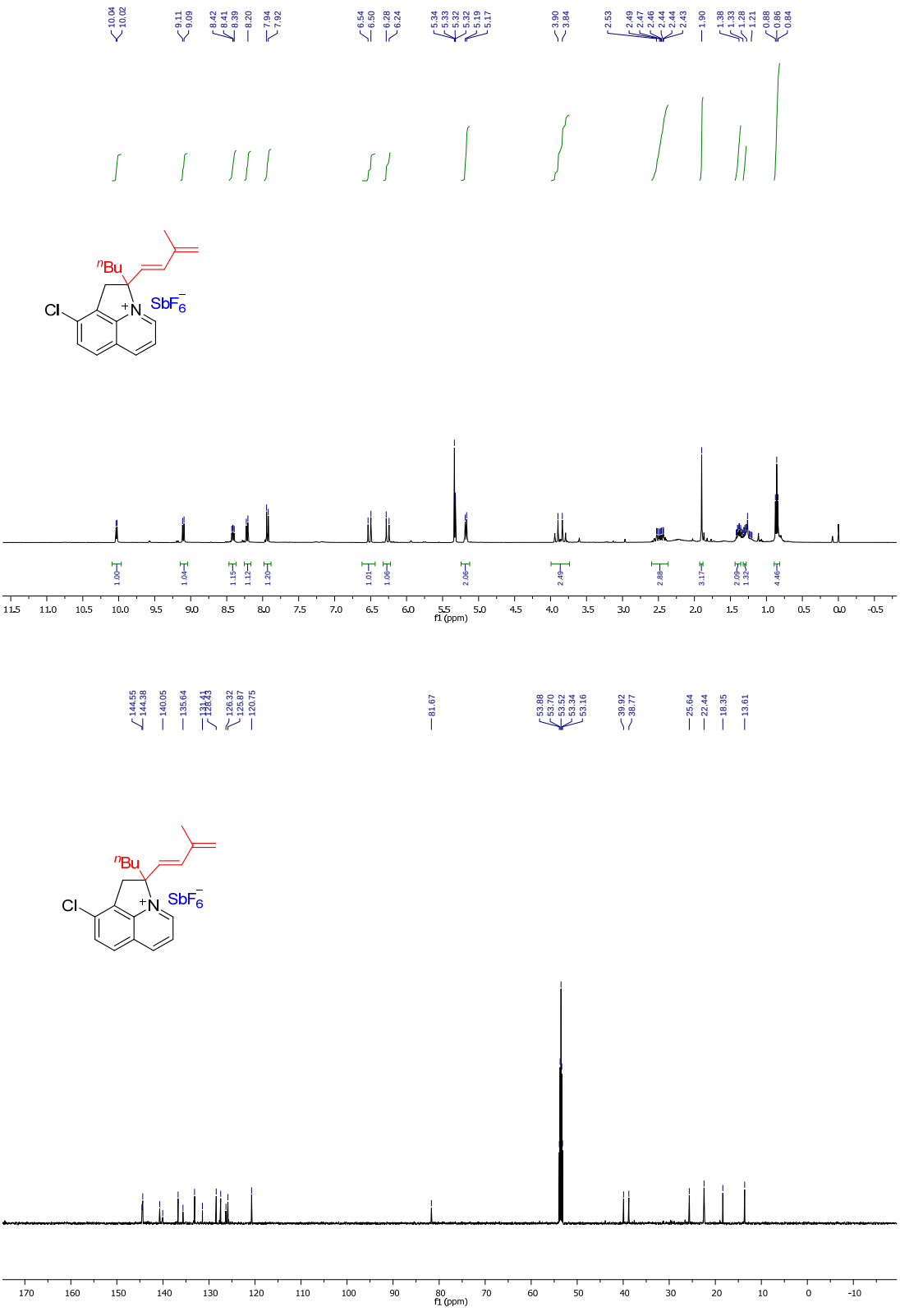


Supplementary Figure 55. ^{1}H NMR and ^{13}C NMR of **7ia**

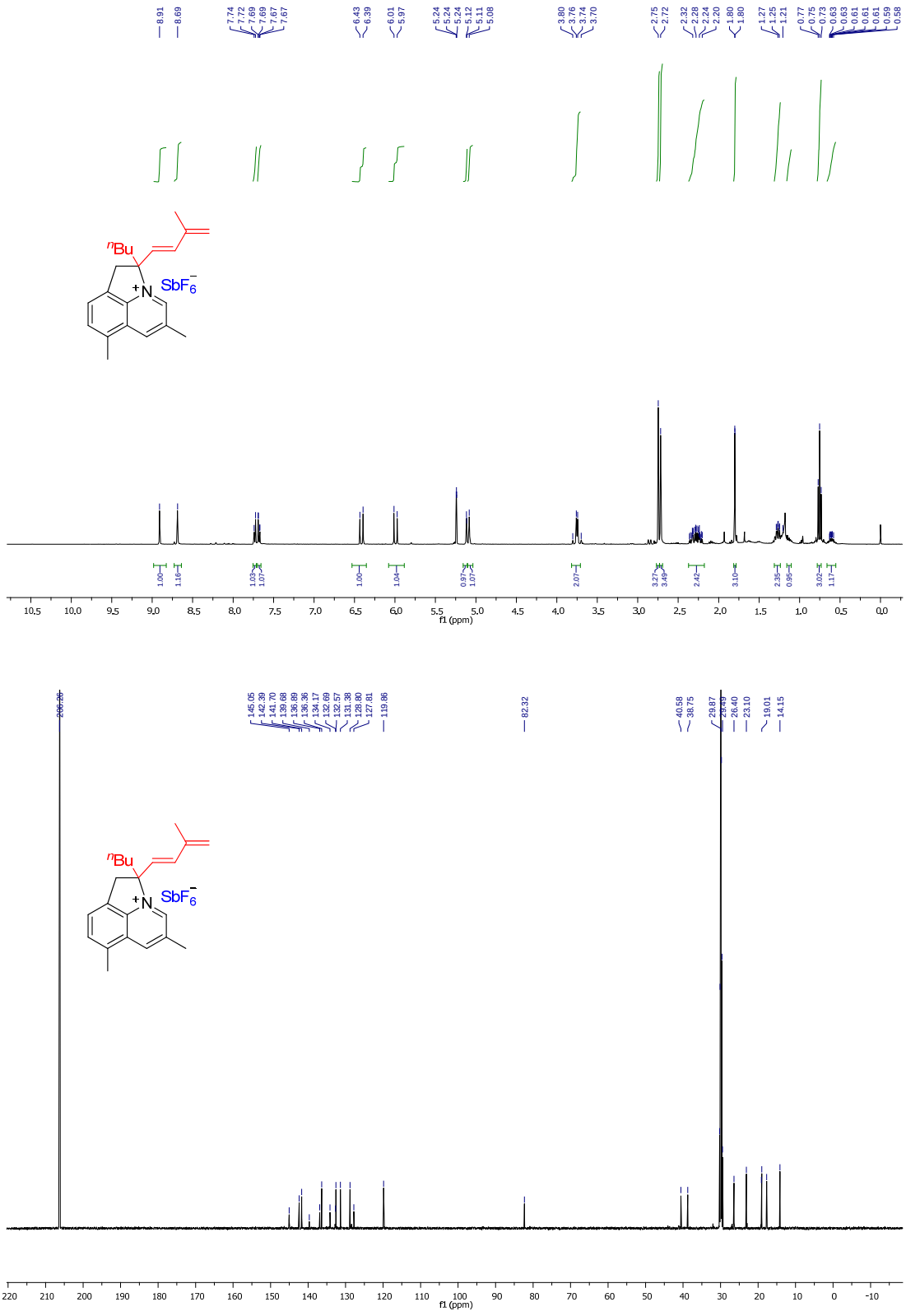
Supplementary Figure 56. ^{1}H NMR and ^{13}C NMR of **7ja**



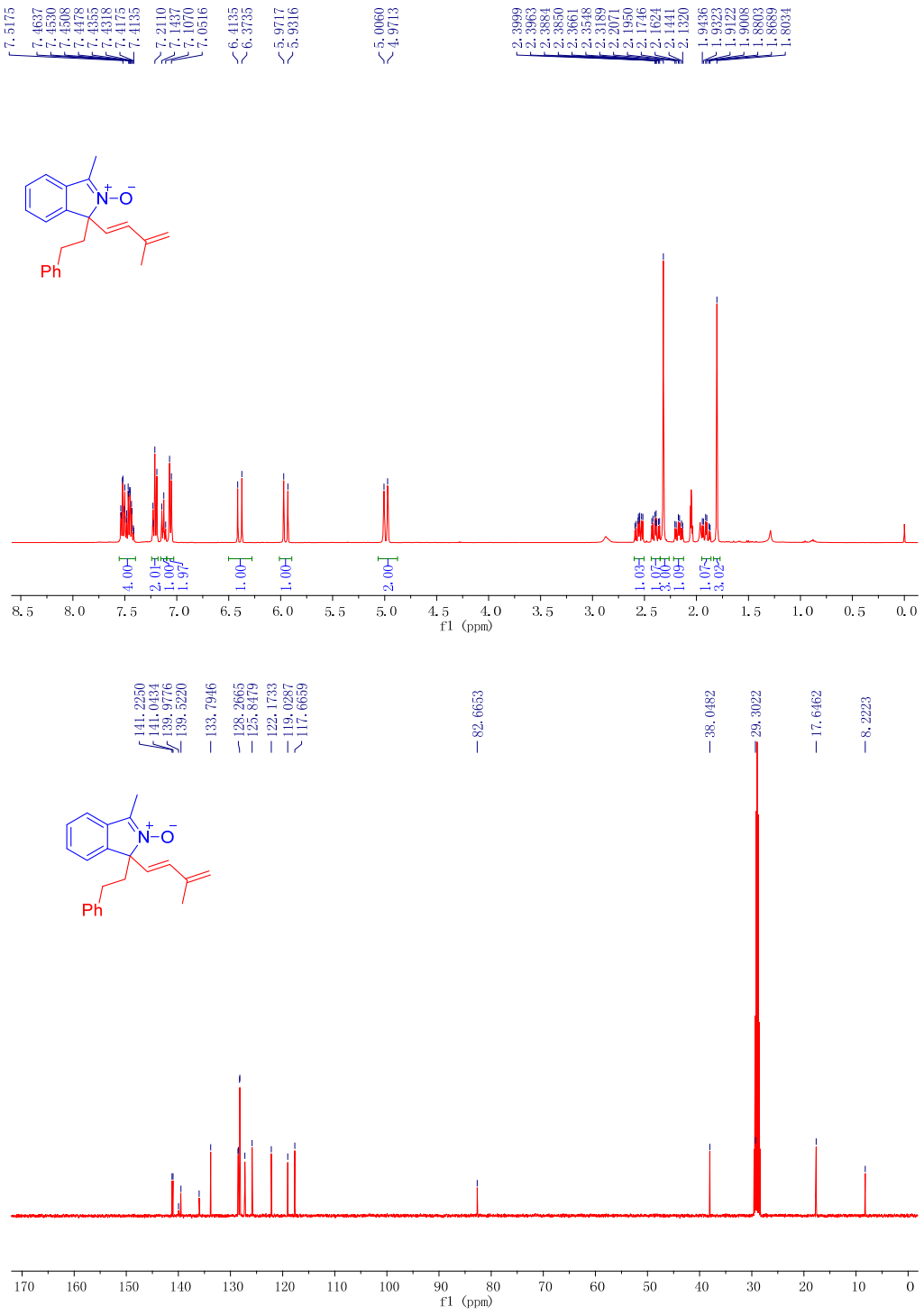
Supplementary Figure 57. ^{1}H NMR and ^{13}C NMR of **7ka**



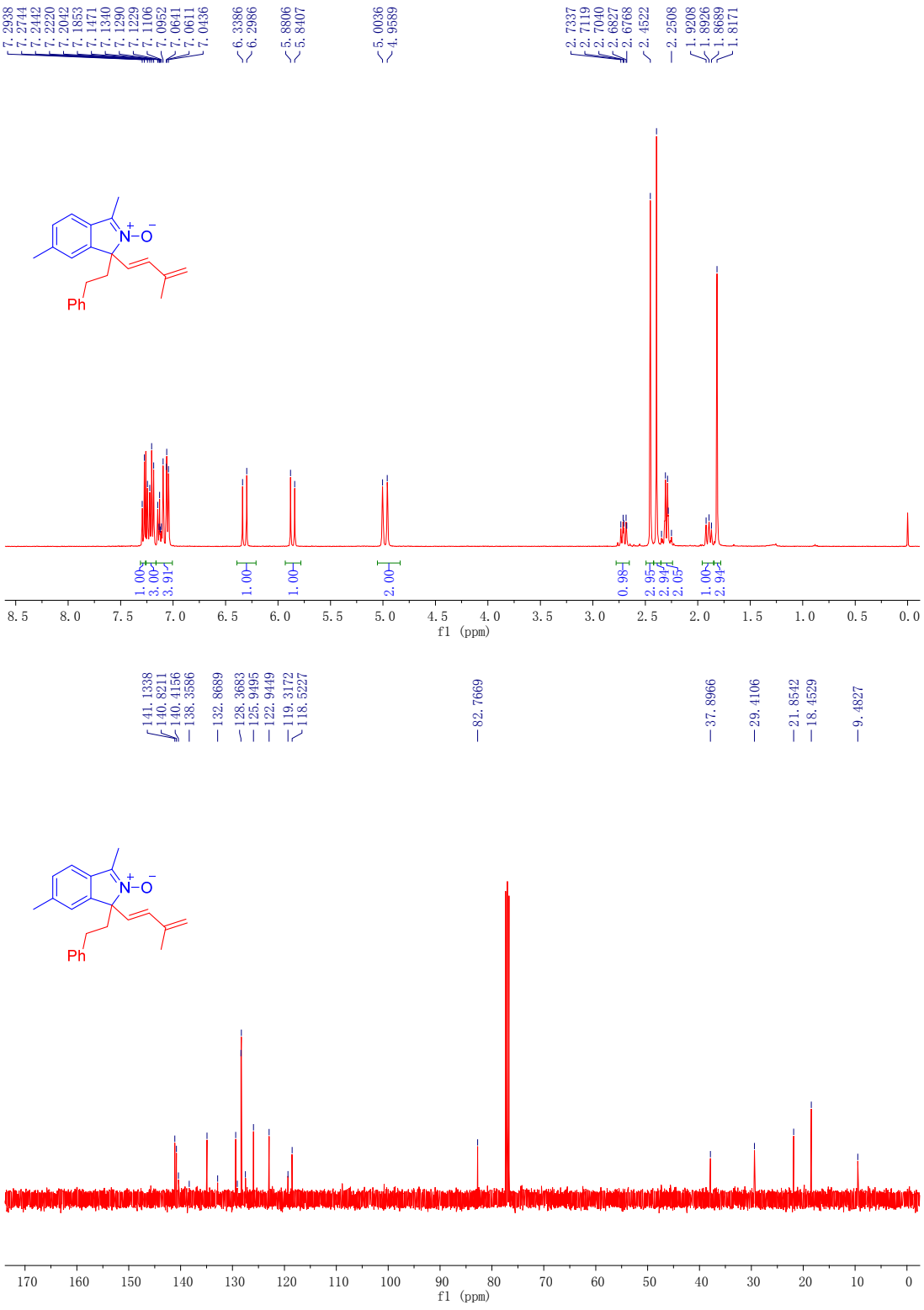
Supplementary Figure 58. ^{1}H NMR and ^{13}C NMR of **7la**



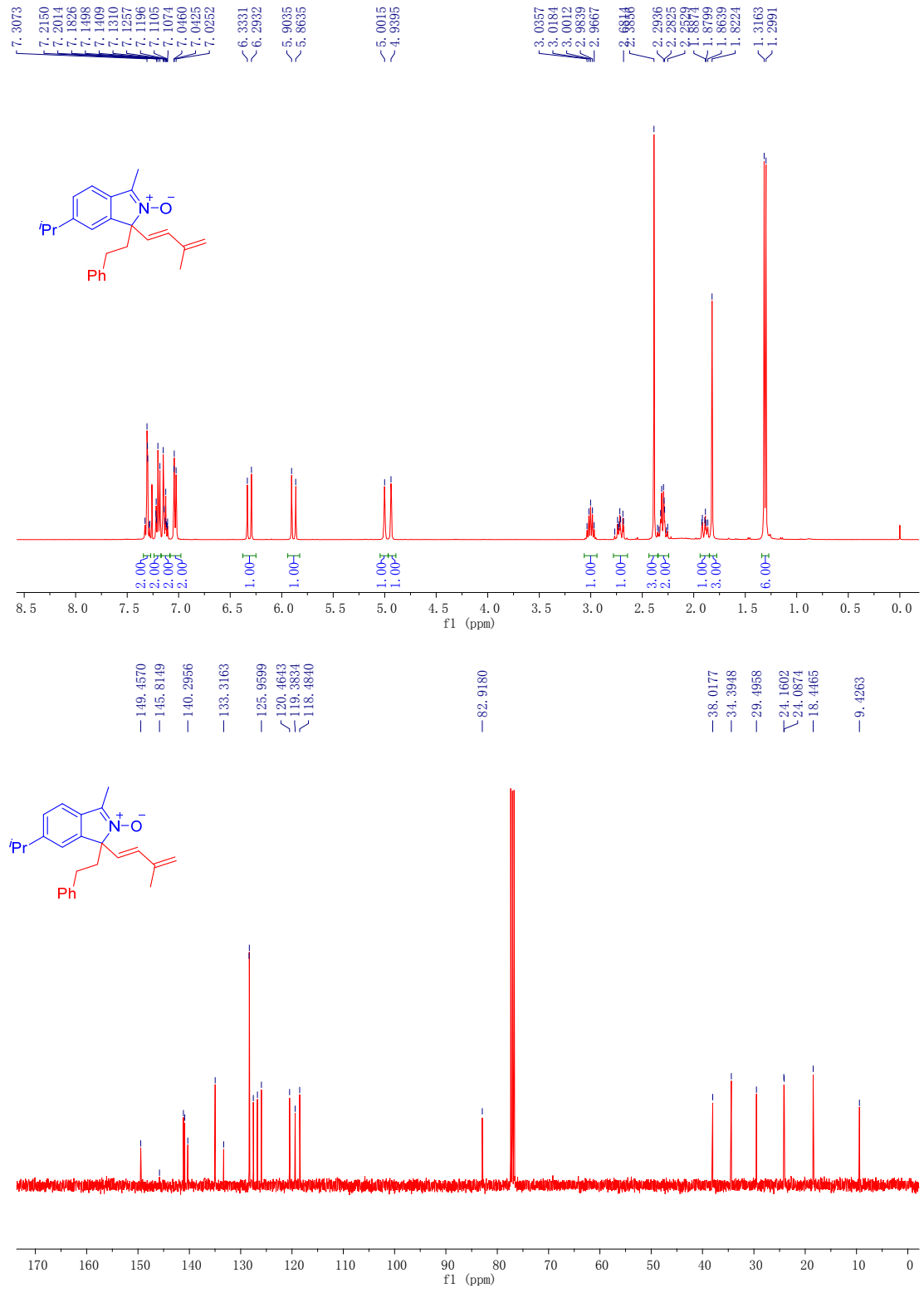
Supplementary Figure 59. ^{1}H NMR and ^{13}C NMR of **7ma**



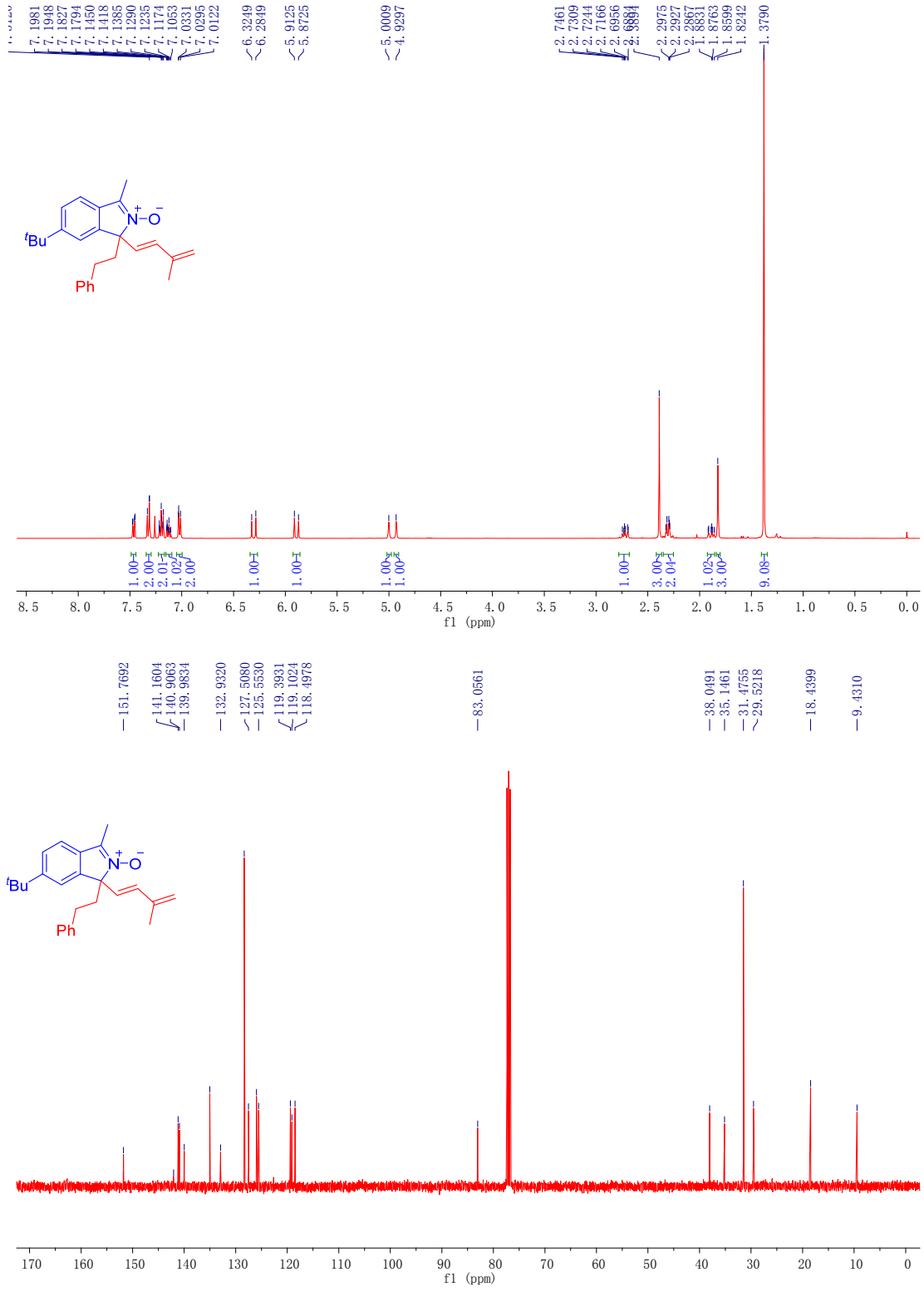
Supplementary Figure 60. ^{1}H NMR and ^{13}C NMR of **9ab**



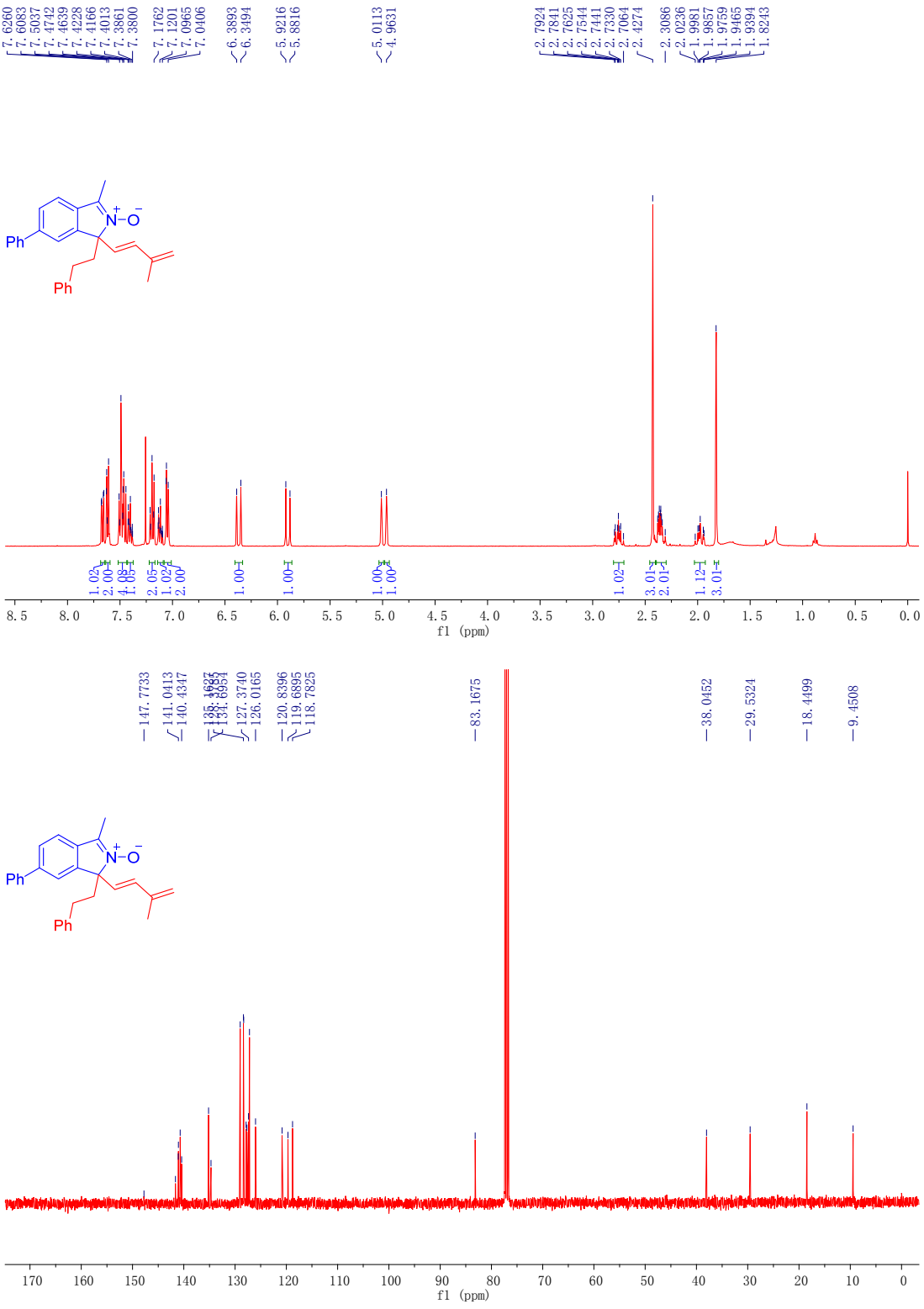
Supplementary Figure 61. ^{1}H NMR and ^{13}C NMR of **9bb**



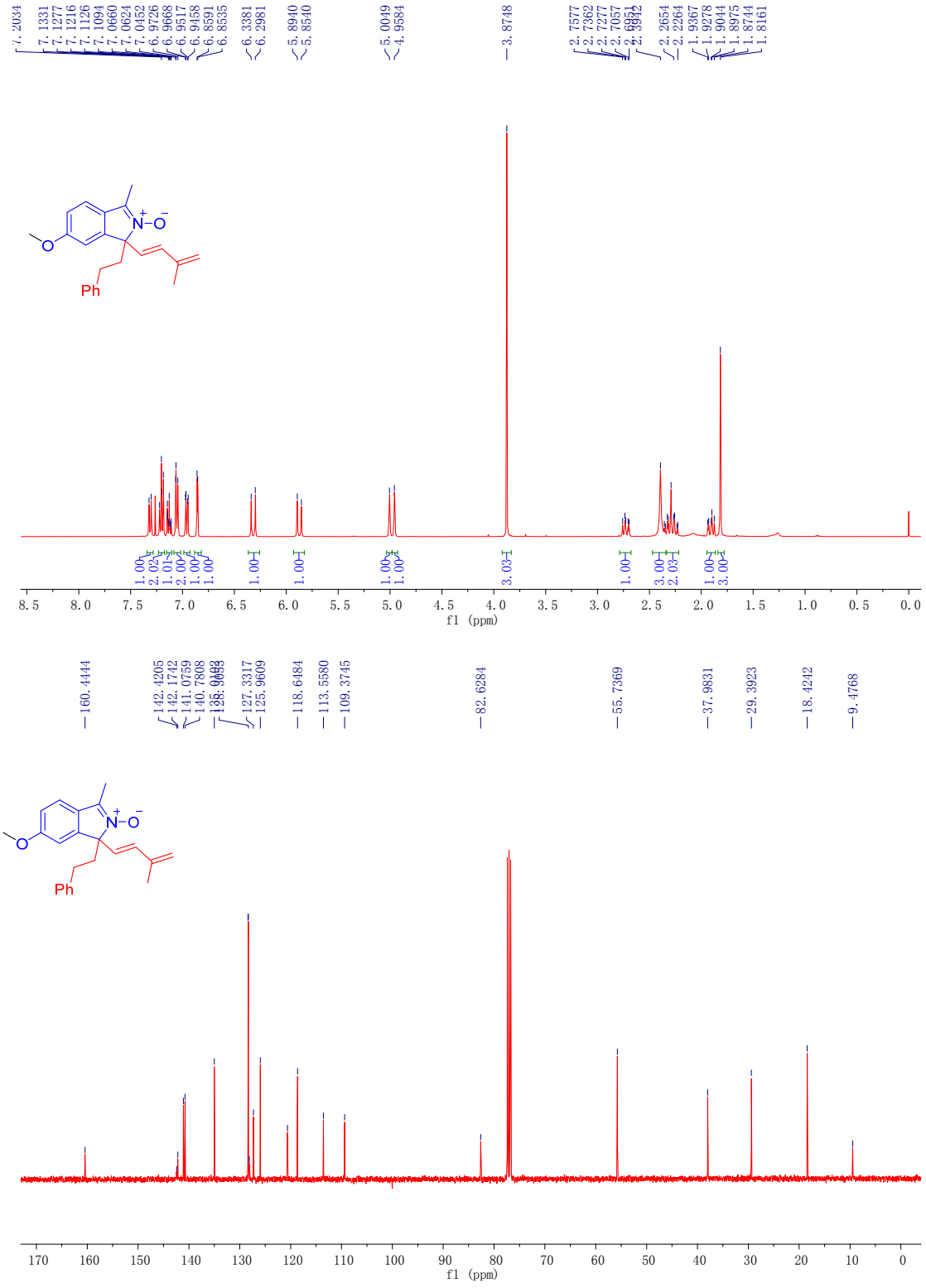
Supplementary Figure 62. ^{1}H NMR and ^{13}C NMR of **9cb**



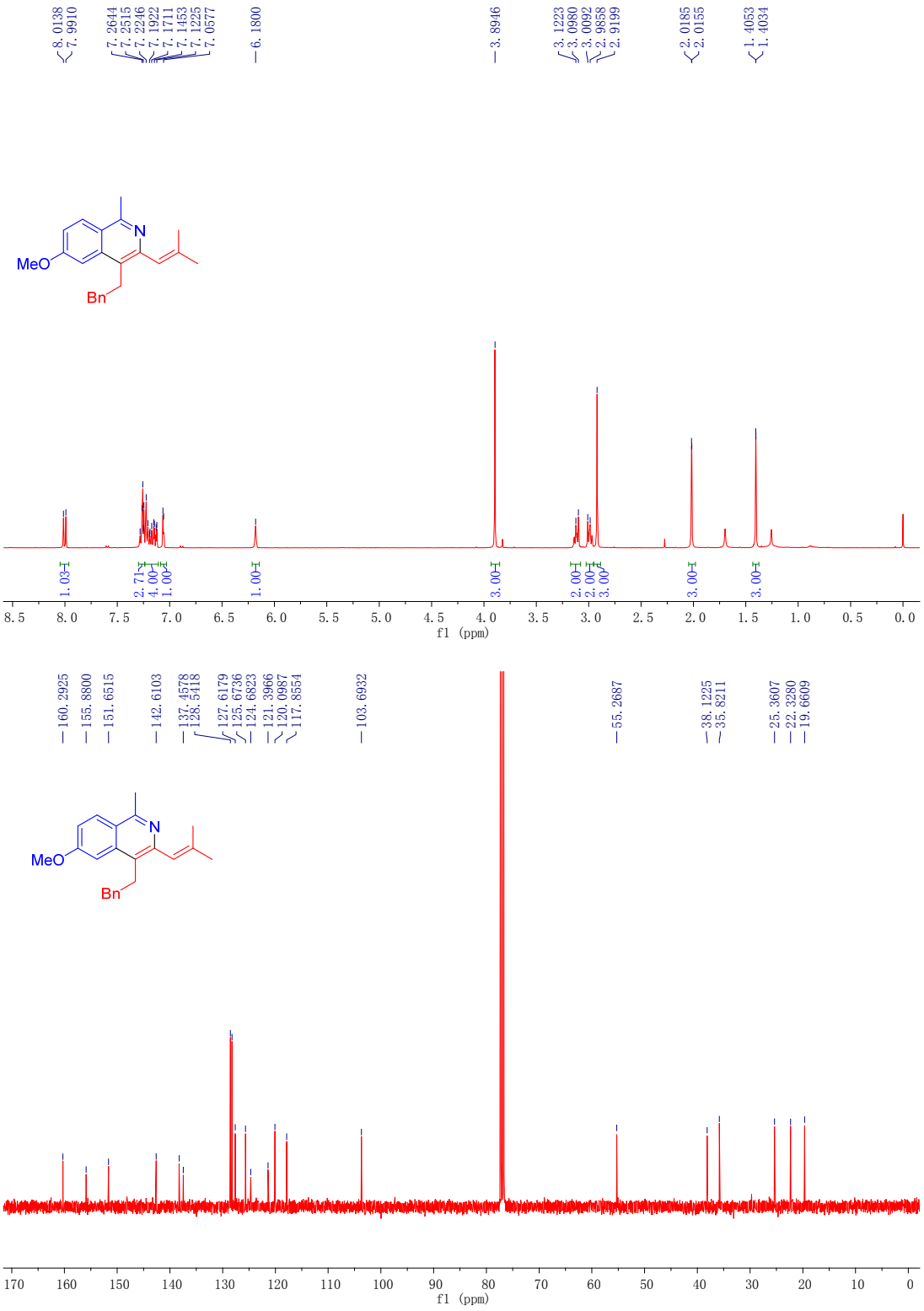
Supplementary Figure 63. ^{1}H NMR and ^{13}C NMR of **9db**



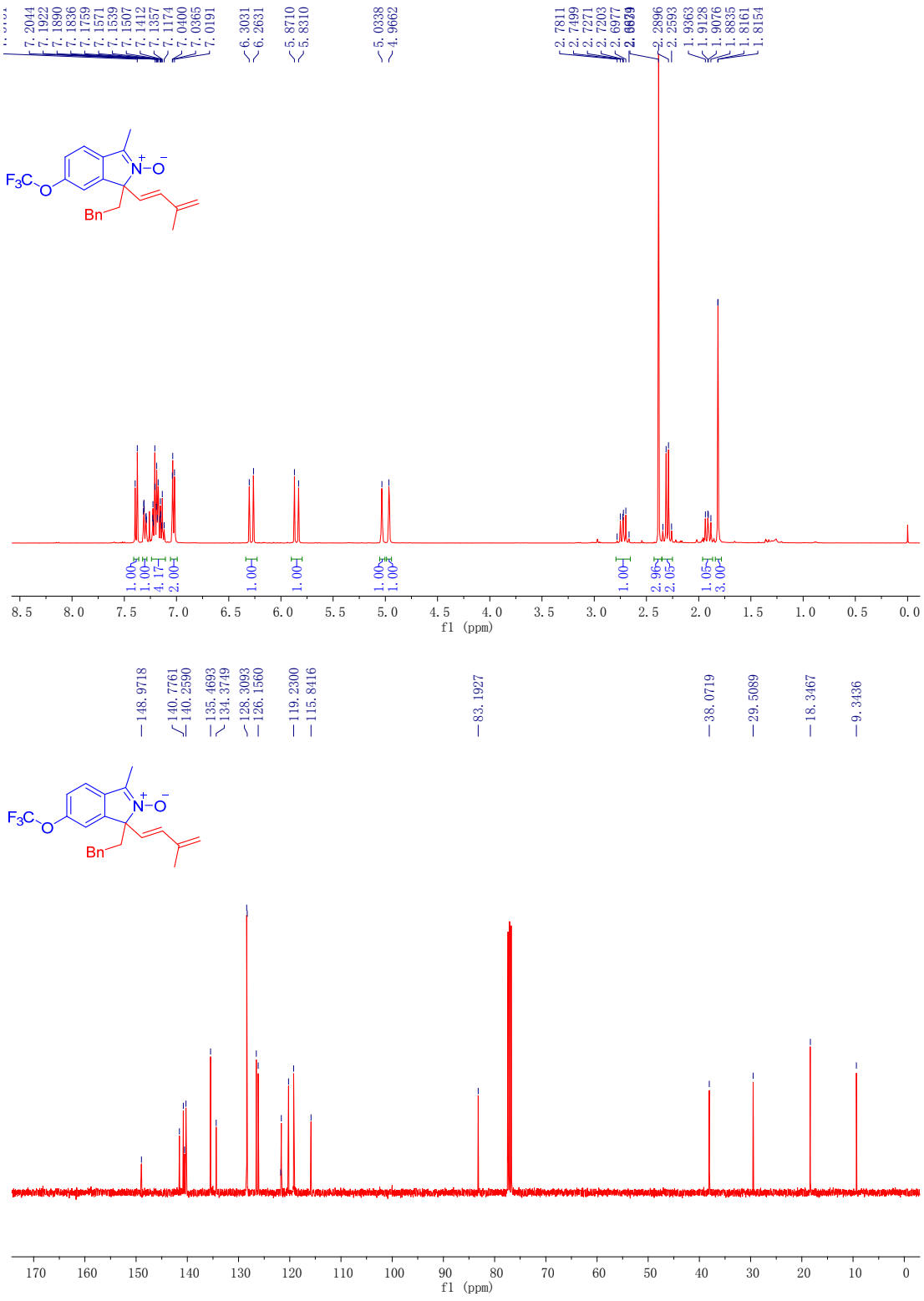
Supplementary Figure 64. ^{1}H NMR and ^{13}C NMR of **9eb**



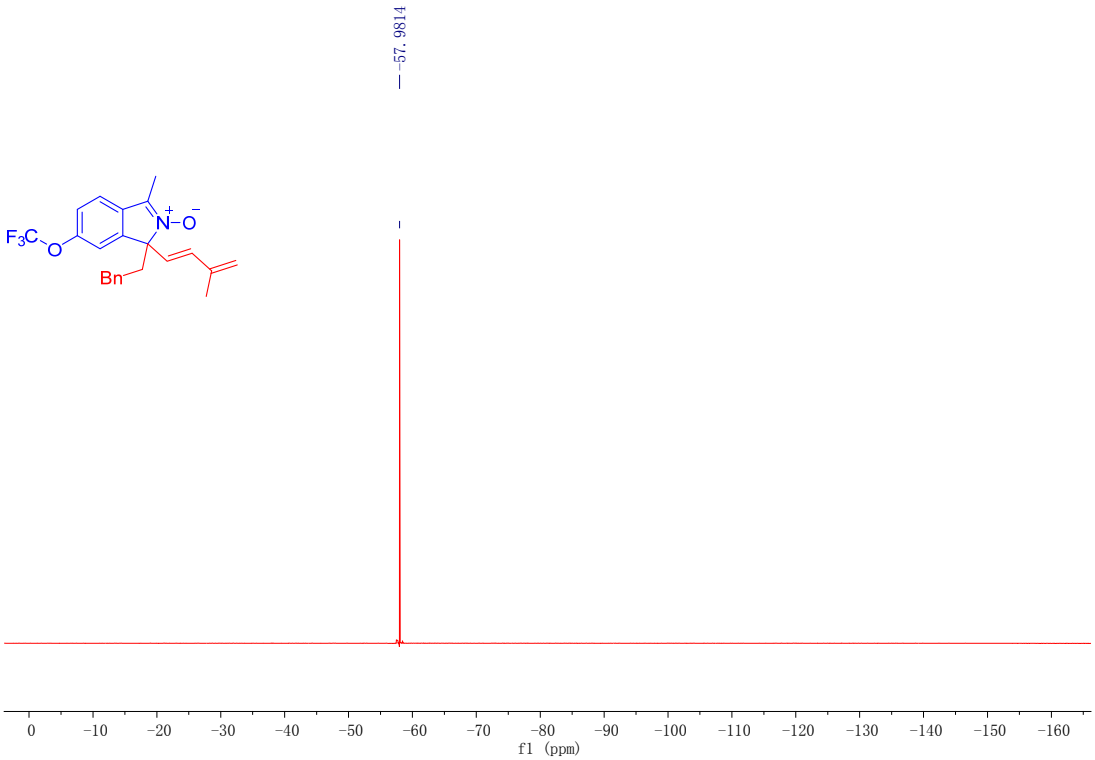
Supplementary Figure 65. ^{1}H NMR and ^{13}C NMR of **9ib**



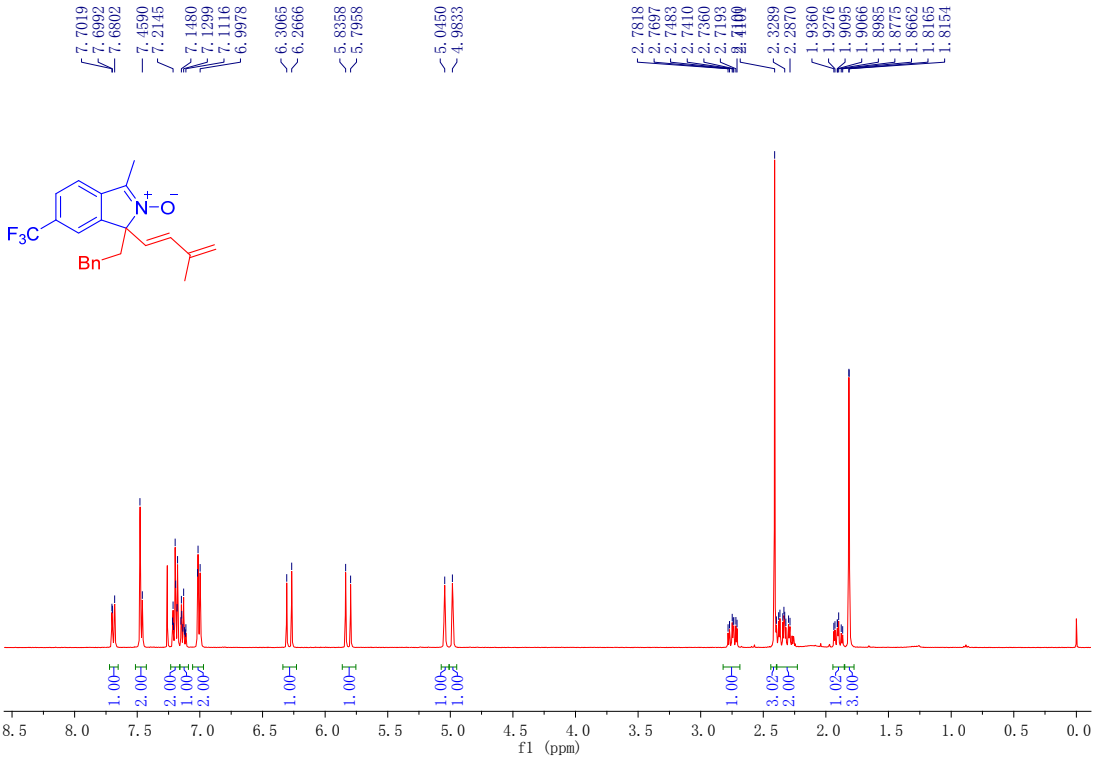
Supplementary Figure 66. ^{1}H NMR and ^{13}C NMR of **9ib'**



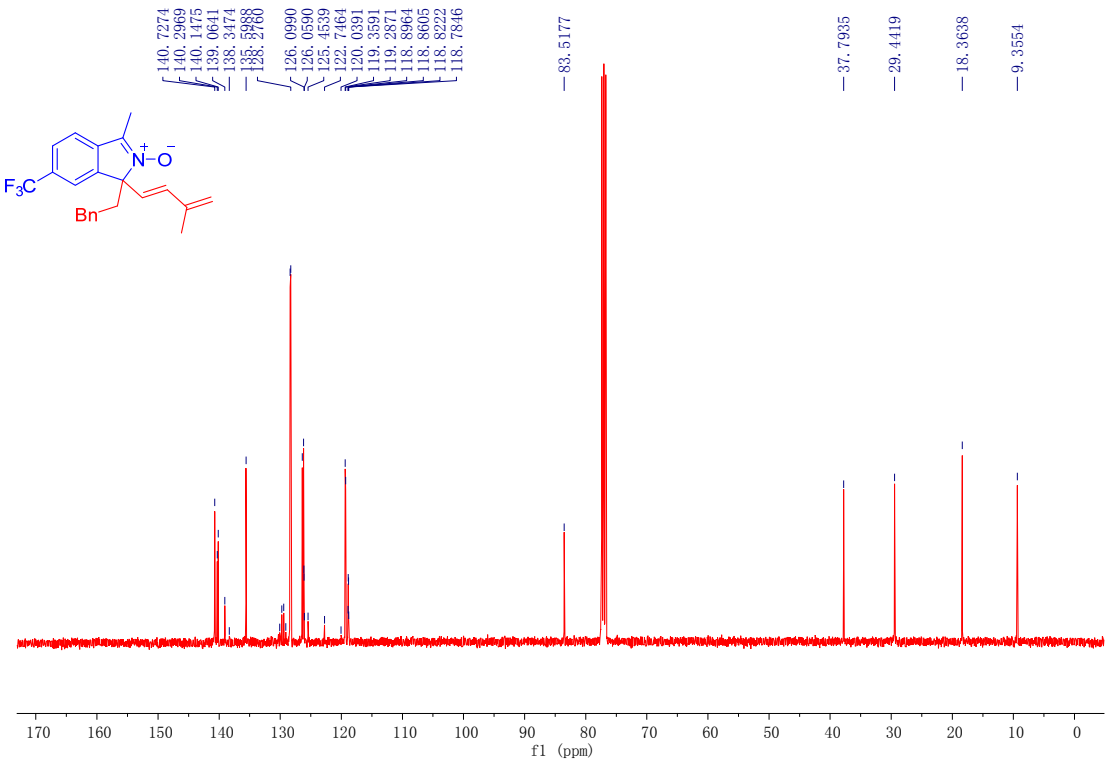
Supplementary Figure 67. ^{1}H NMR and ^{13}C NMR of **9fb**



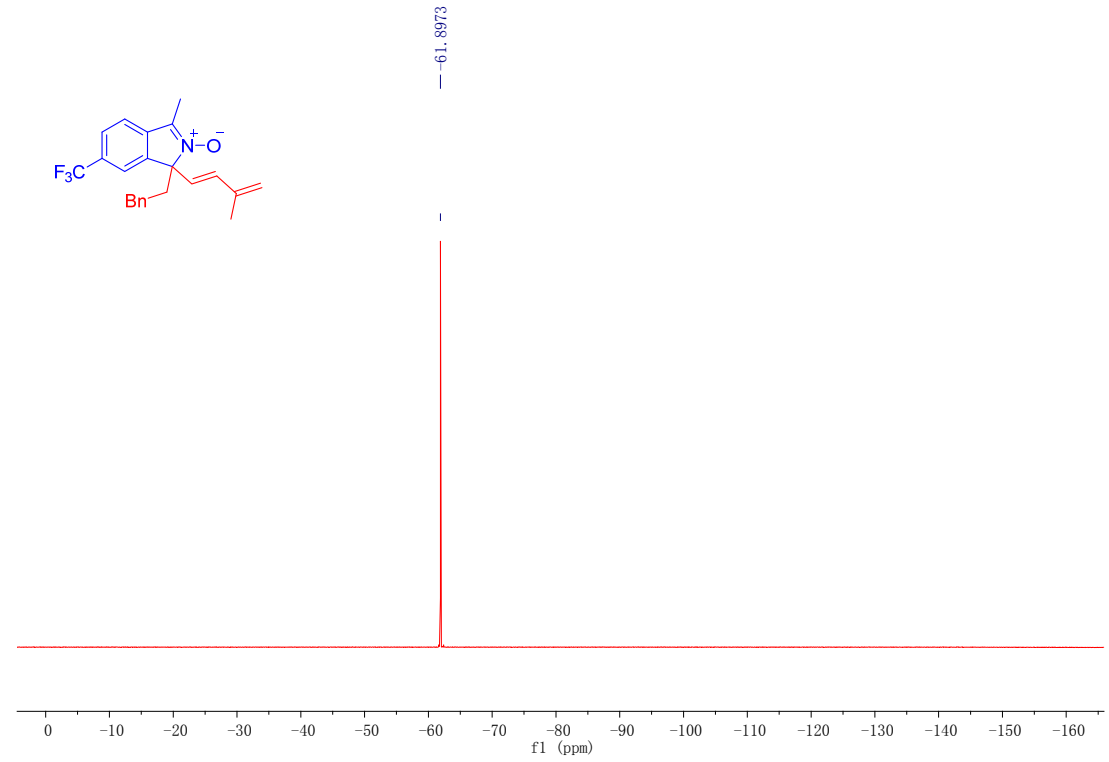
Supplementary Figure 68. ^{19}F NMR of **9fb**



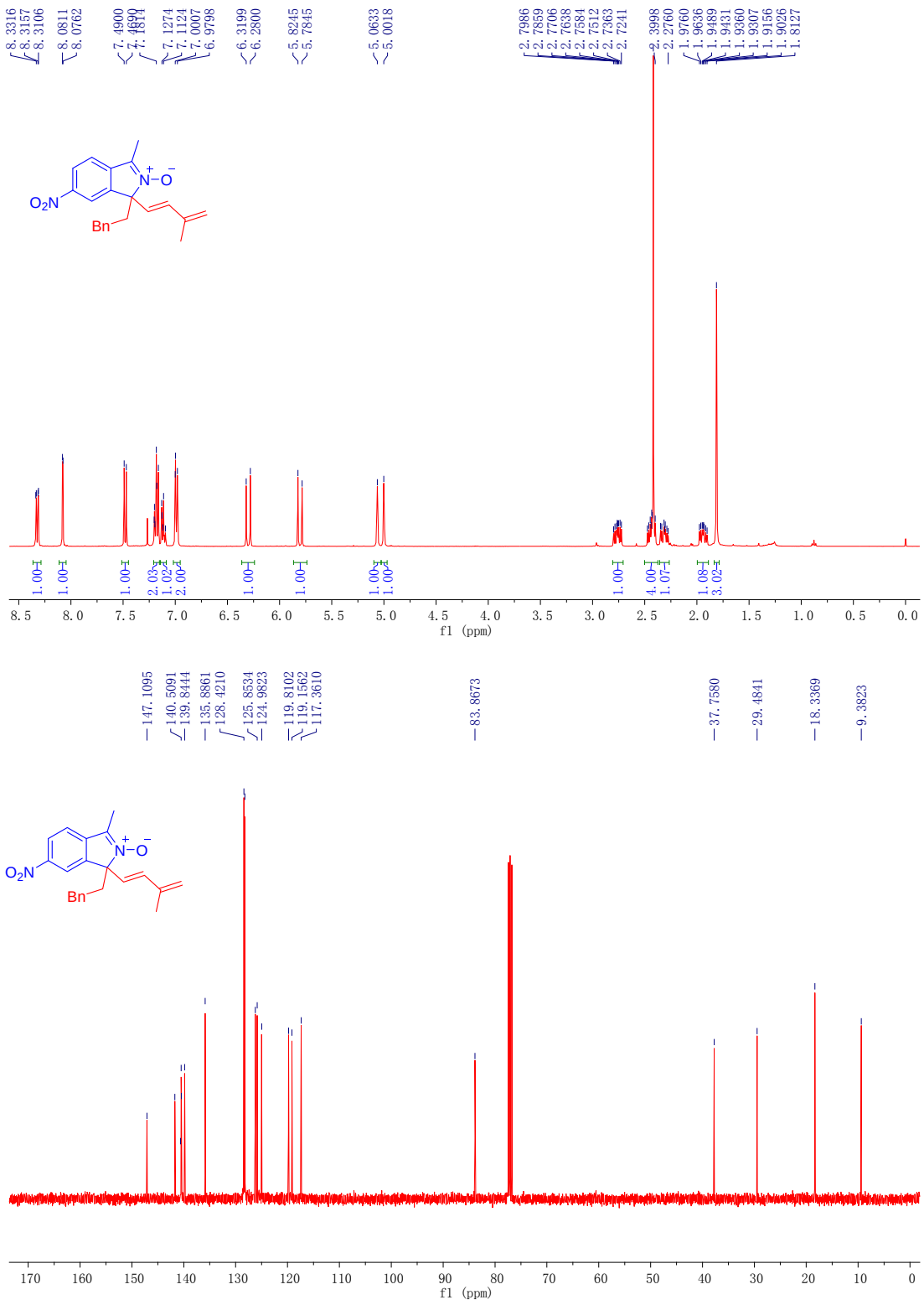
Supplementary Figure 69. ^{1}H NMR of **9gb**



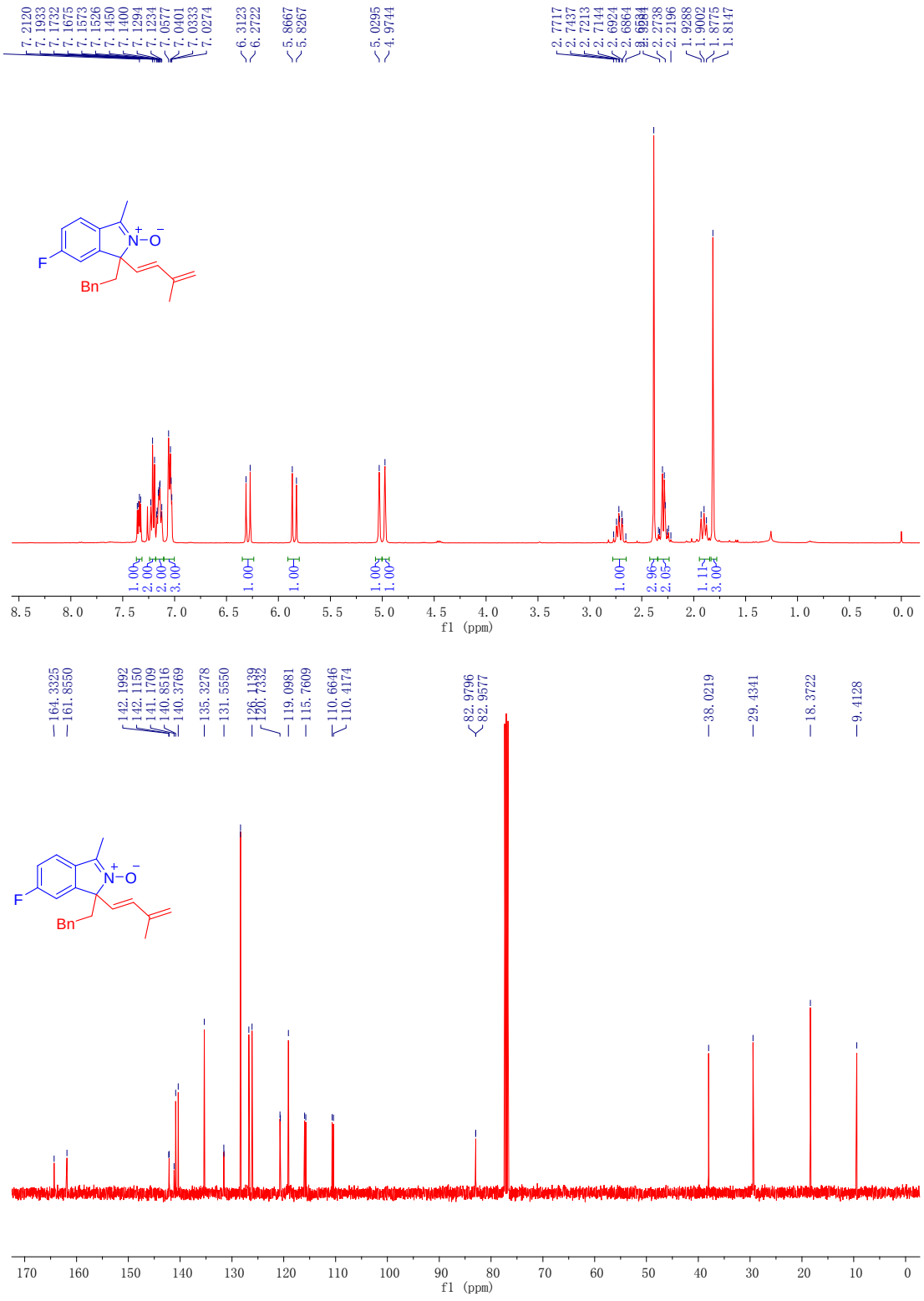
Supplementary Figure 70. ^{13}C NMR of **9gb**



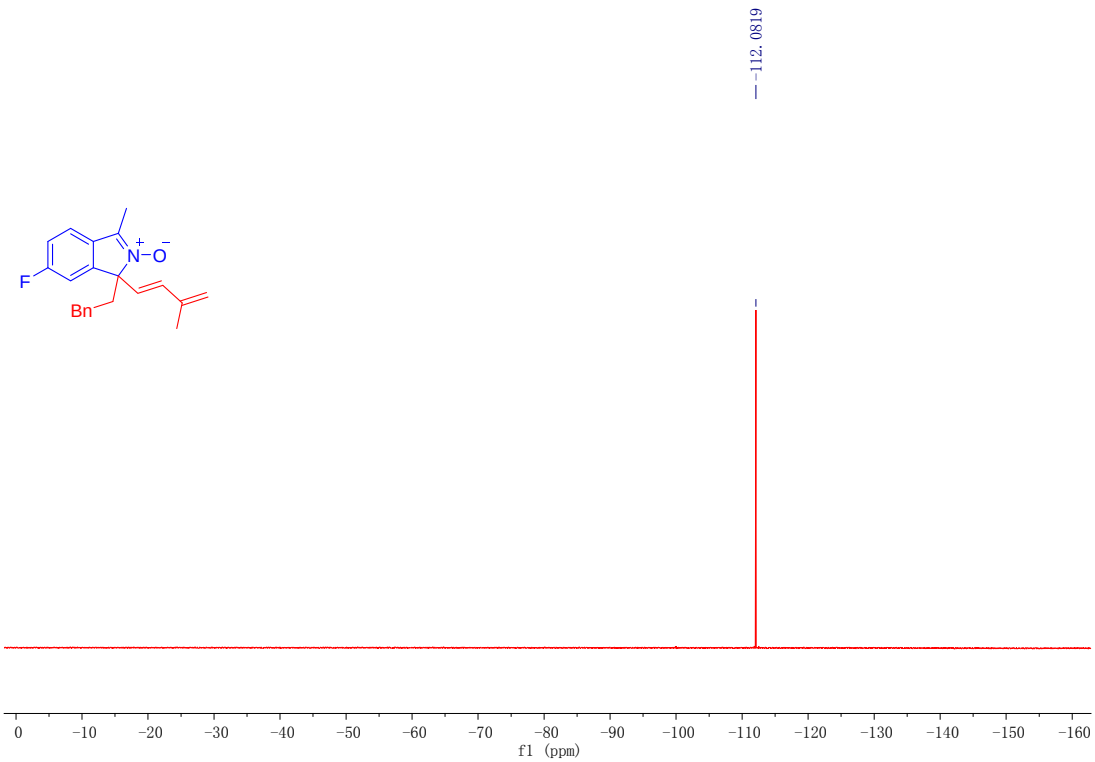
Supplementary Figure 71. ^{19}F NMR of **9gb**



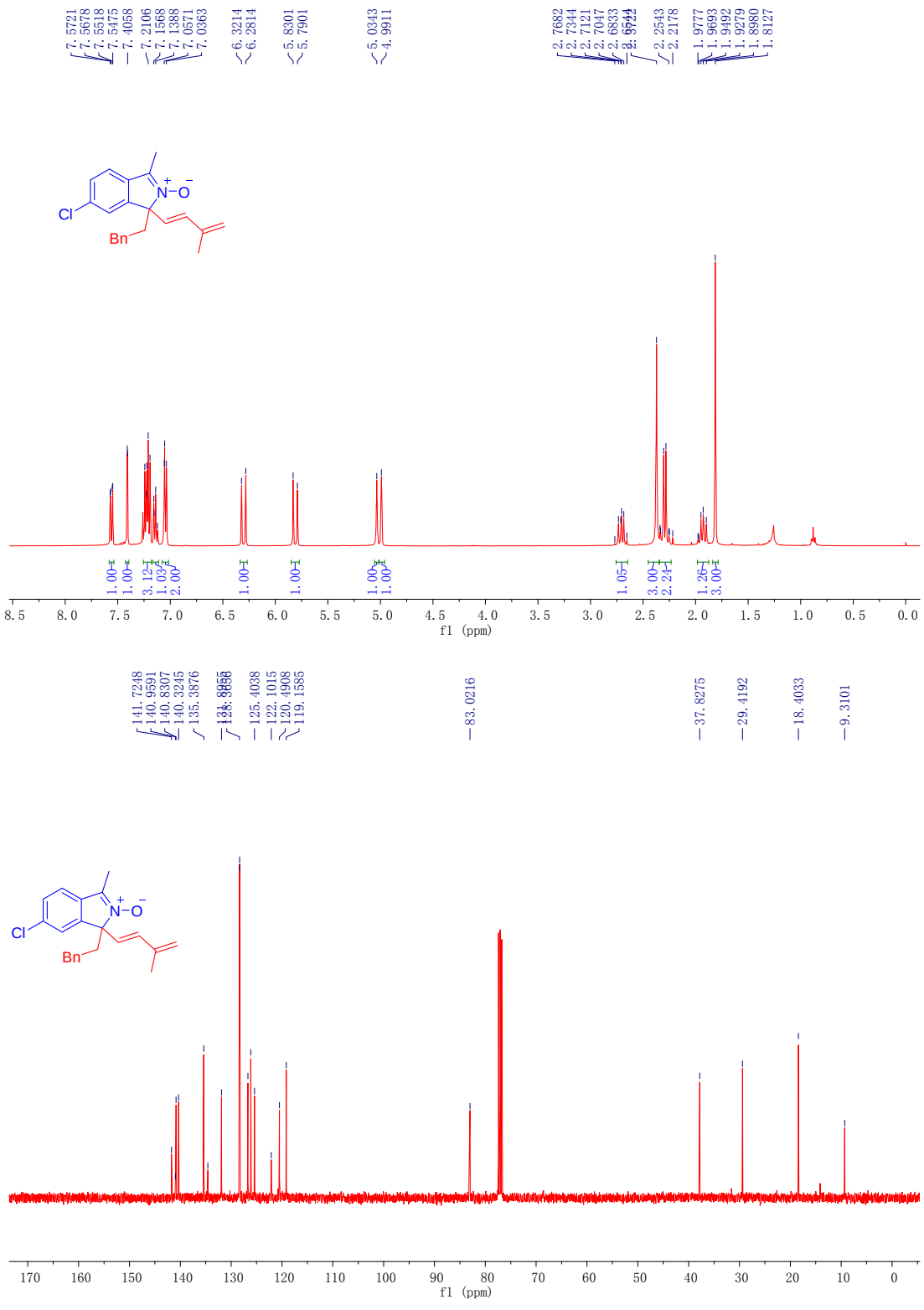
Supplementary Figure 72. ^{1}H NMR and ^{13}C NMR of **9hb**



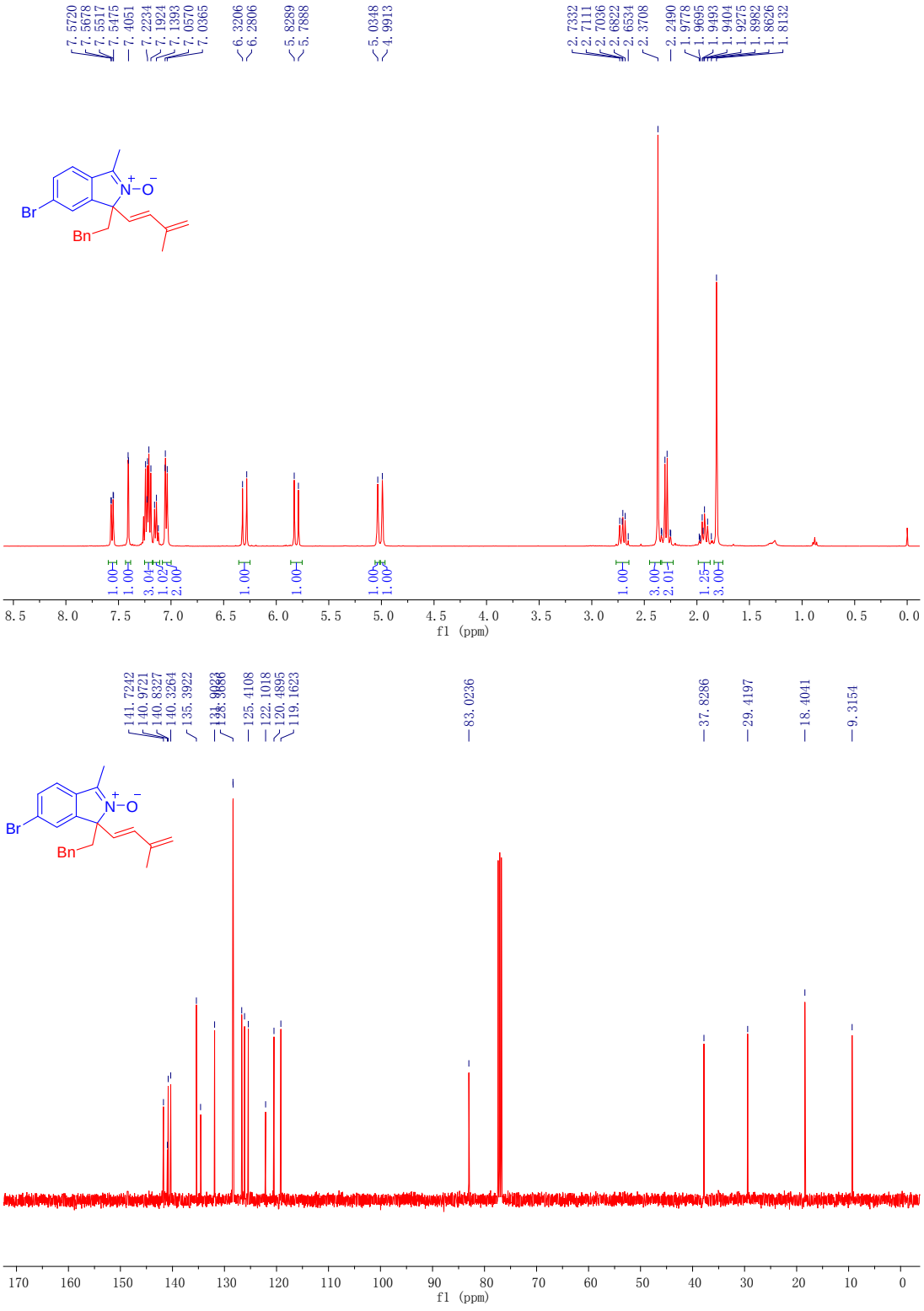
Supplementary Figure 73. ^{1}H NMR and ^{13}C NMR of **9jb**



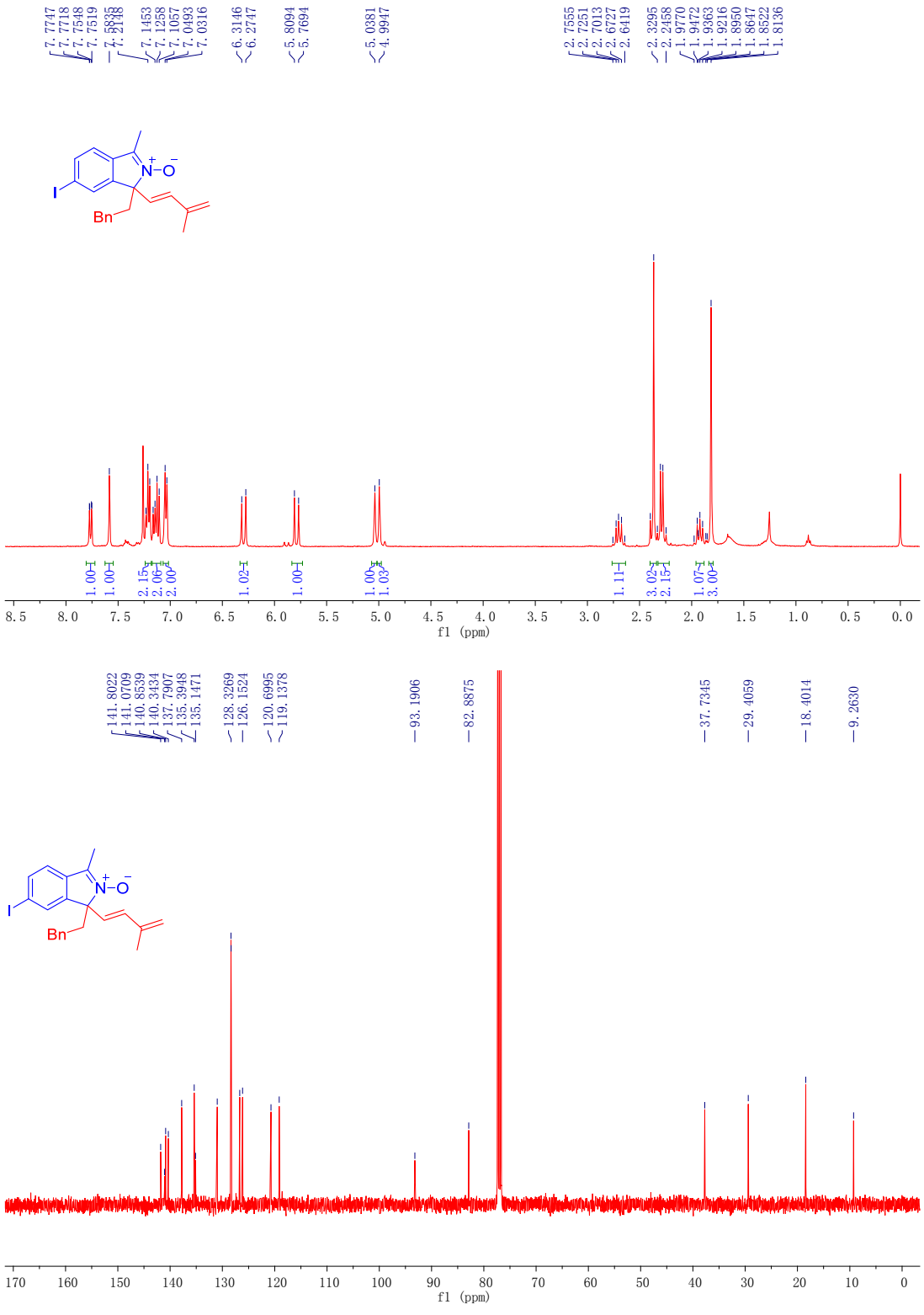
Supplementary Figure 74. ^{19}F NMR of **9jb**



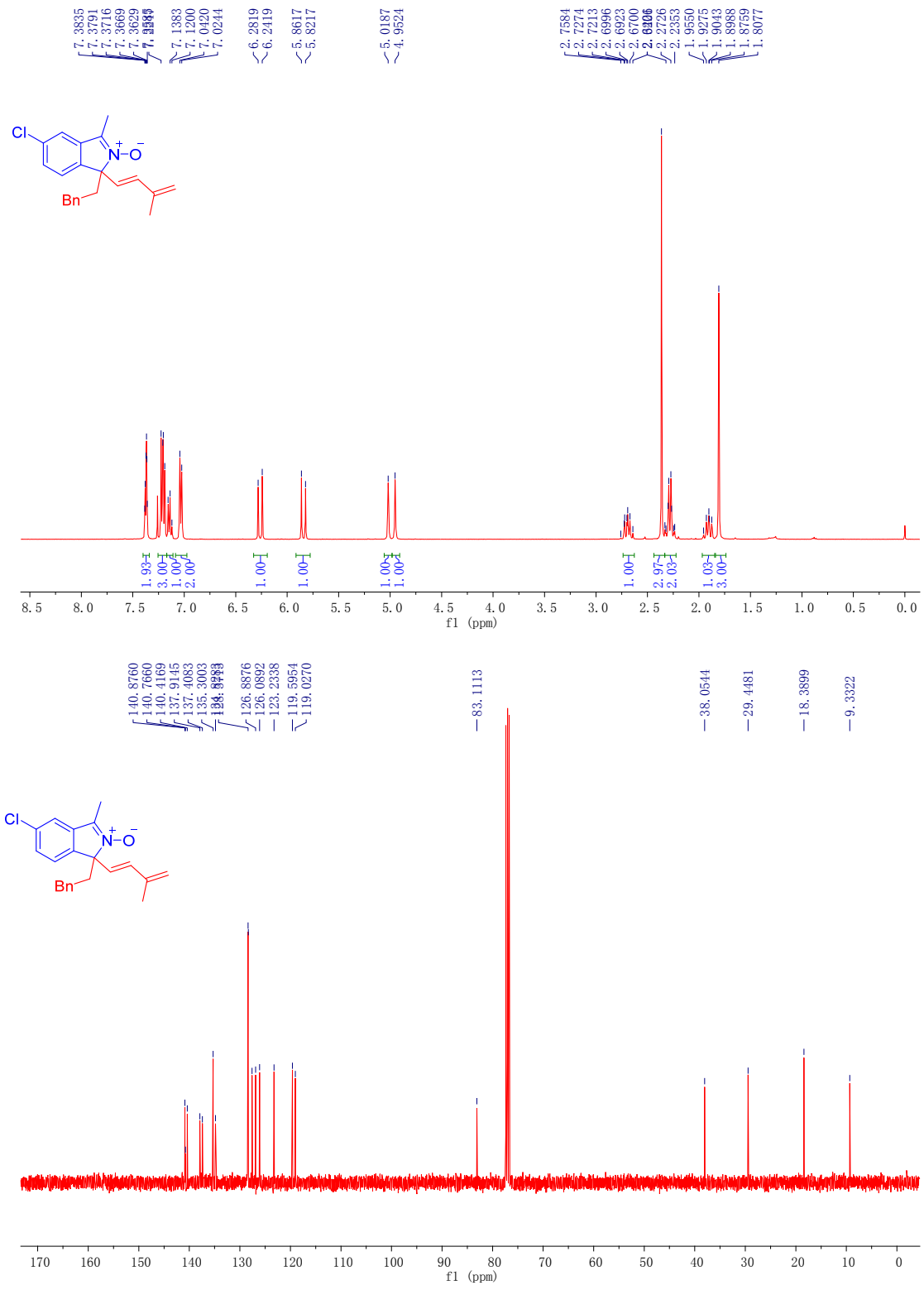
Supplementary Figure 75. ^{1}H NMR and ^{13}C NMR of **9kb**



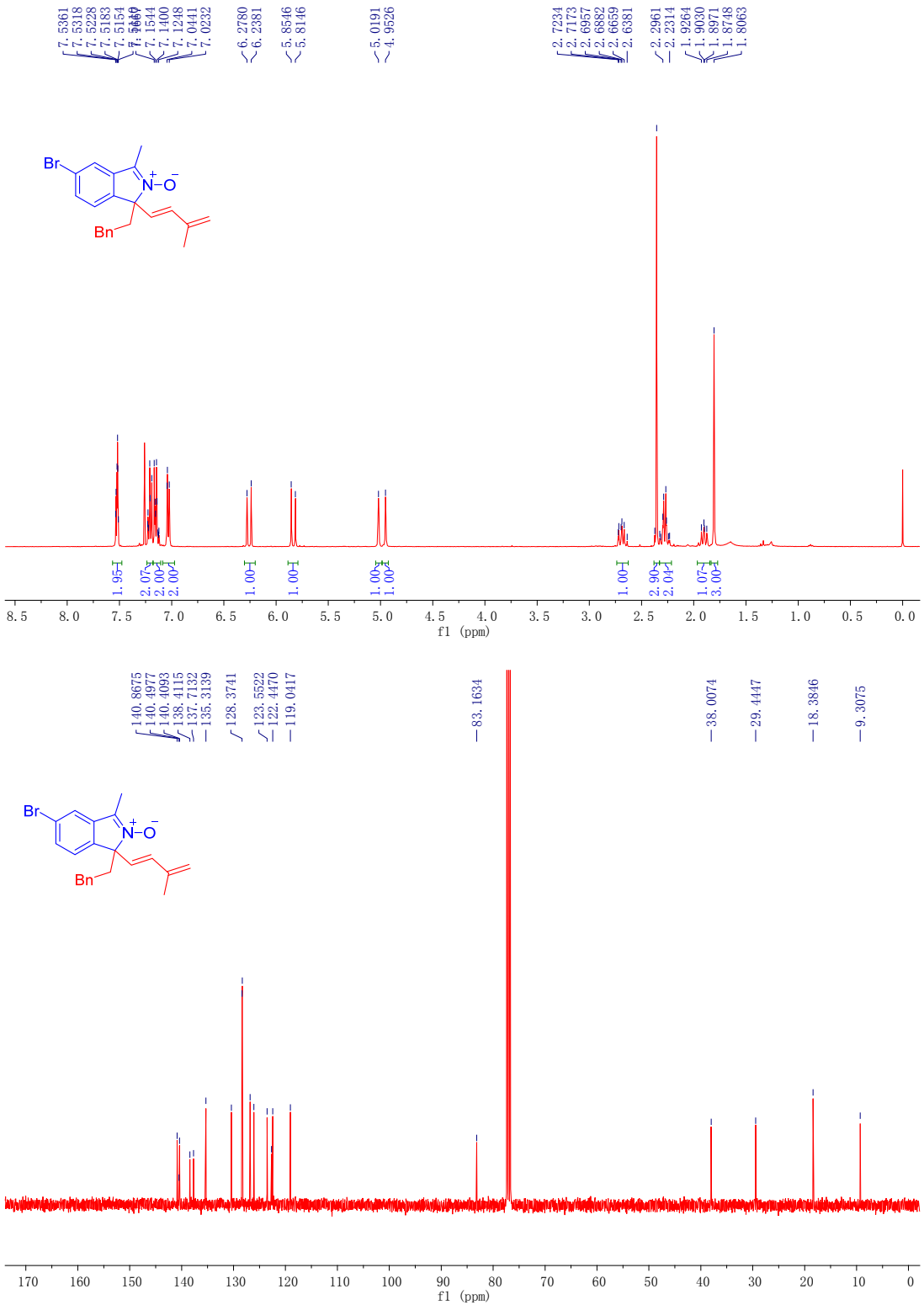
Supplementary Figure 76. ^{1}H NMR and ^{13}C NMR of **9lb**



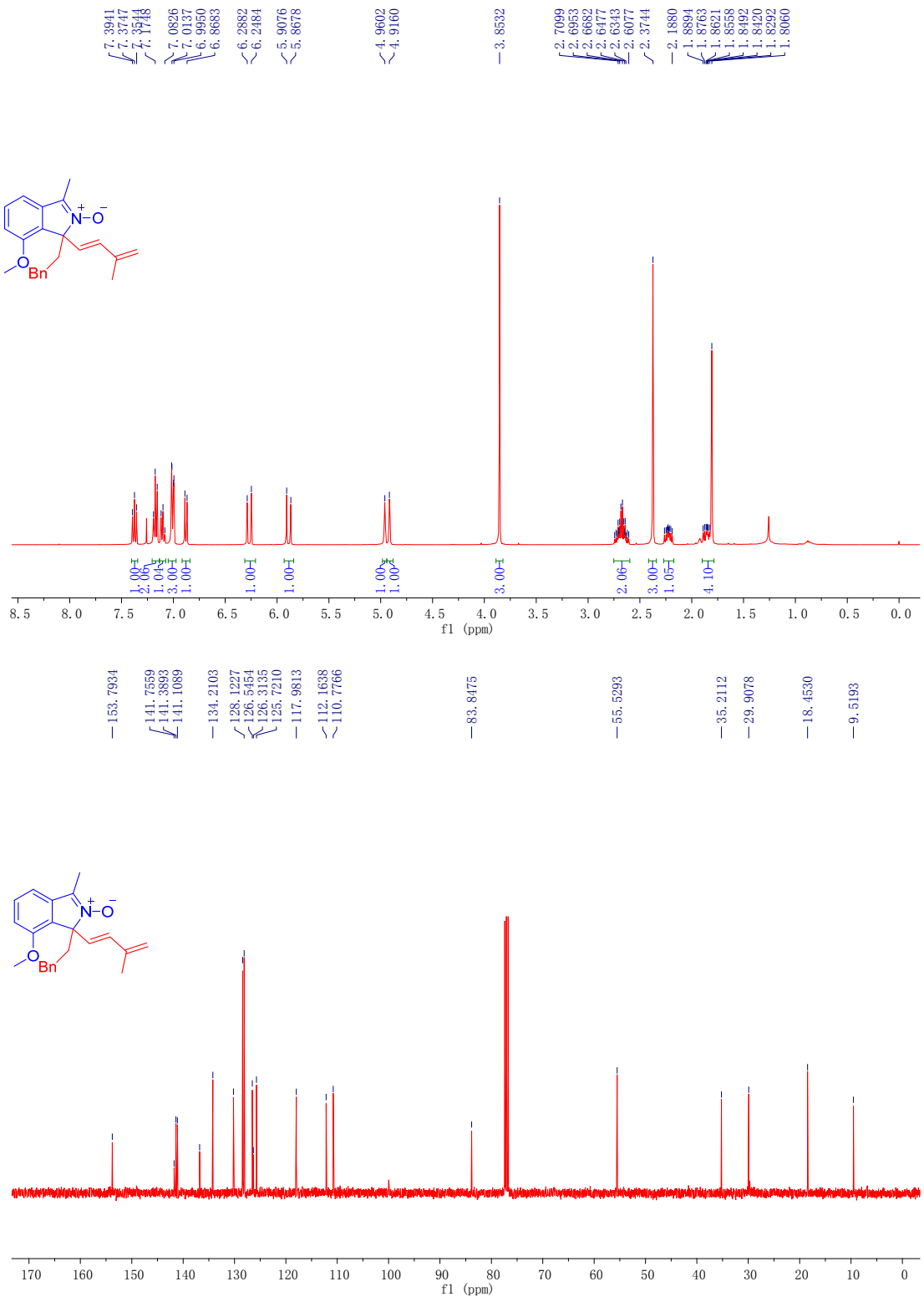
Supplementary Figure 77. ^{1}H NMR and ^{13}C NMR of **9mb**



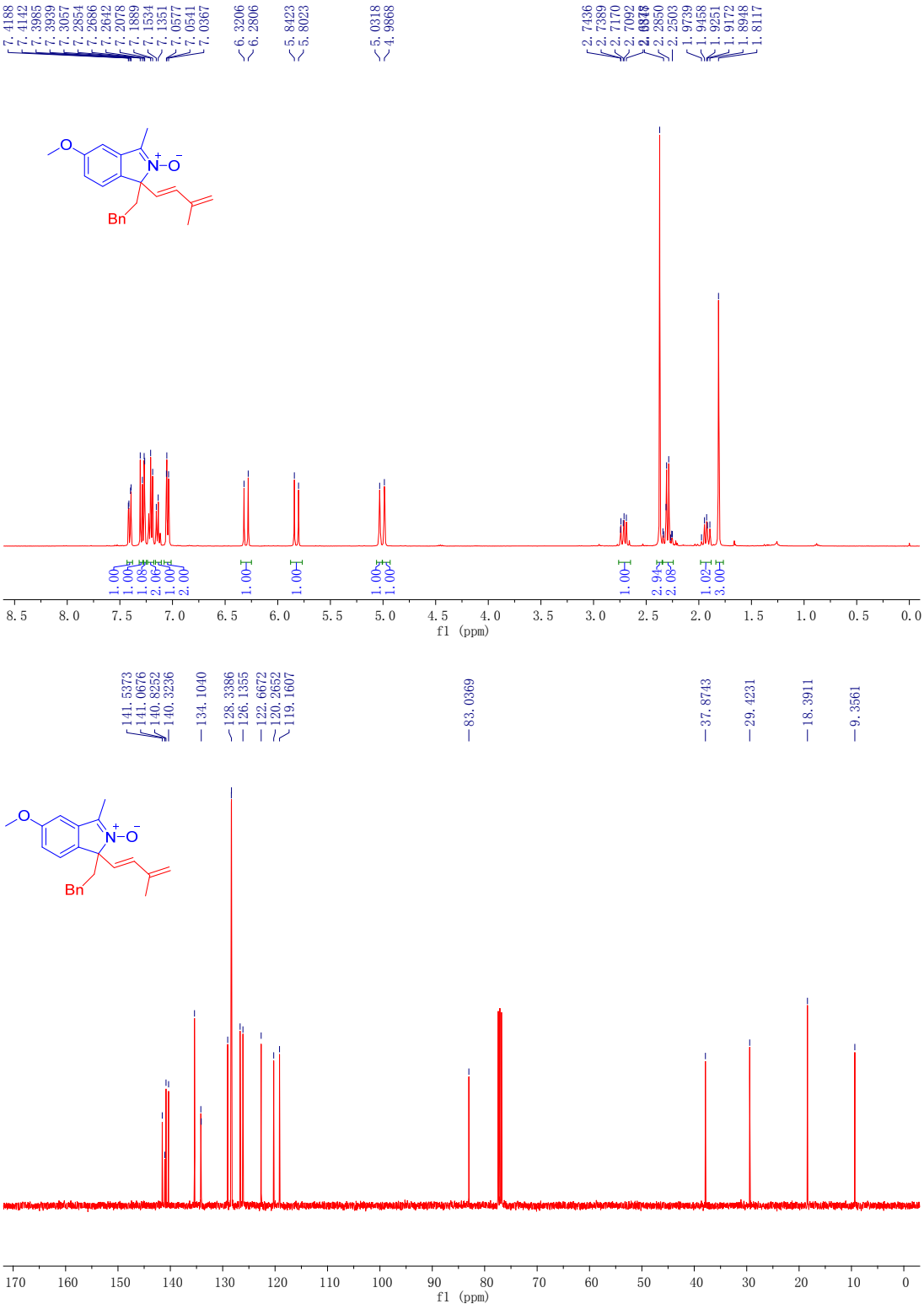
Supplementary Figure 78. ^{1}H NMR and ^{13}C NMR of **9nb**



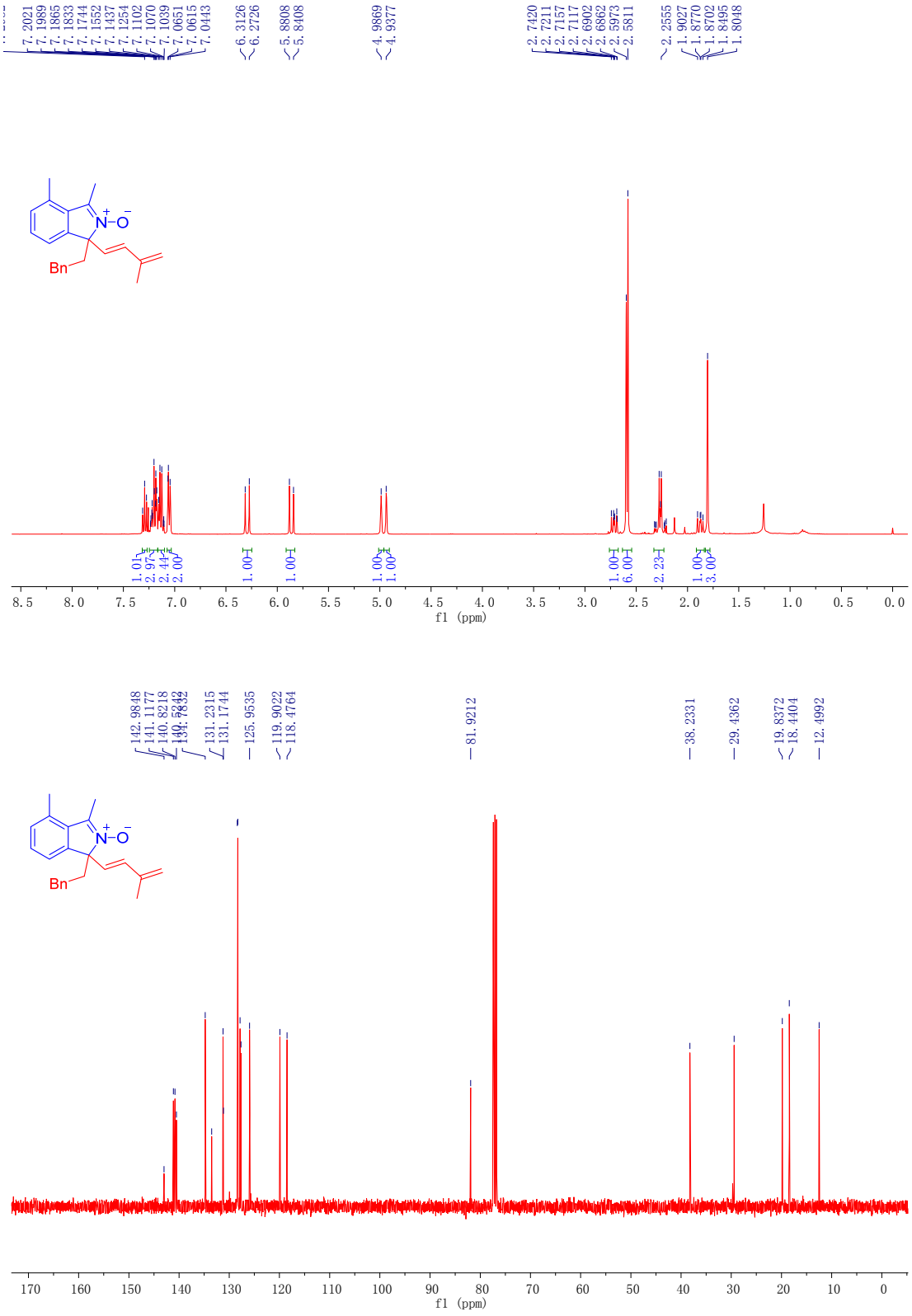
Supplementary Figure 79. ^{1}H NMR and ^{13}C NMR of **9ob**



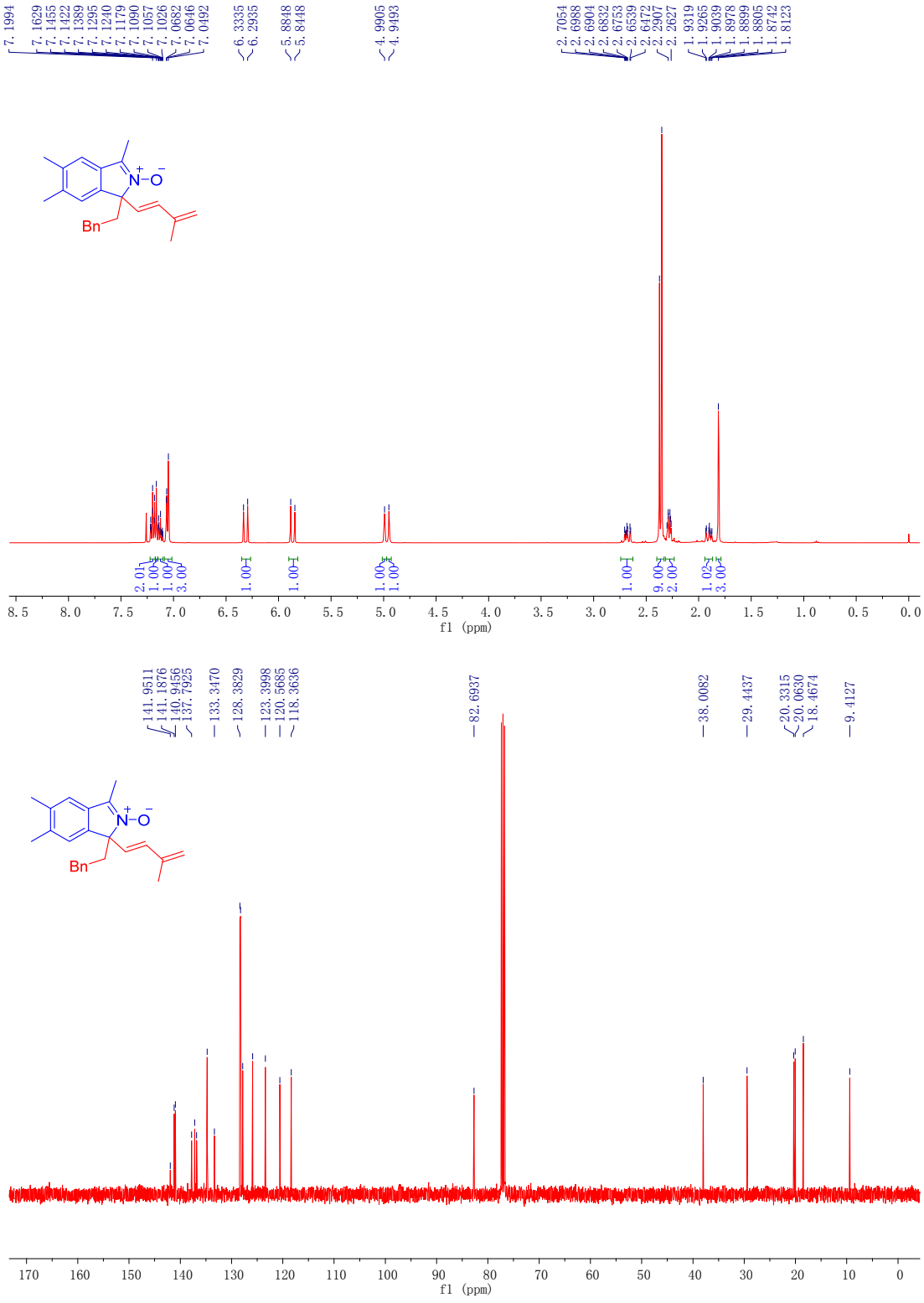
Supplementary Figure 80. ^{1}H NMR and ^{13}C NMR of **9pb**



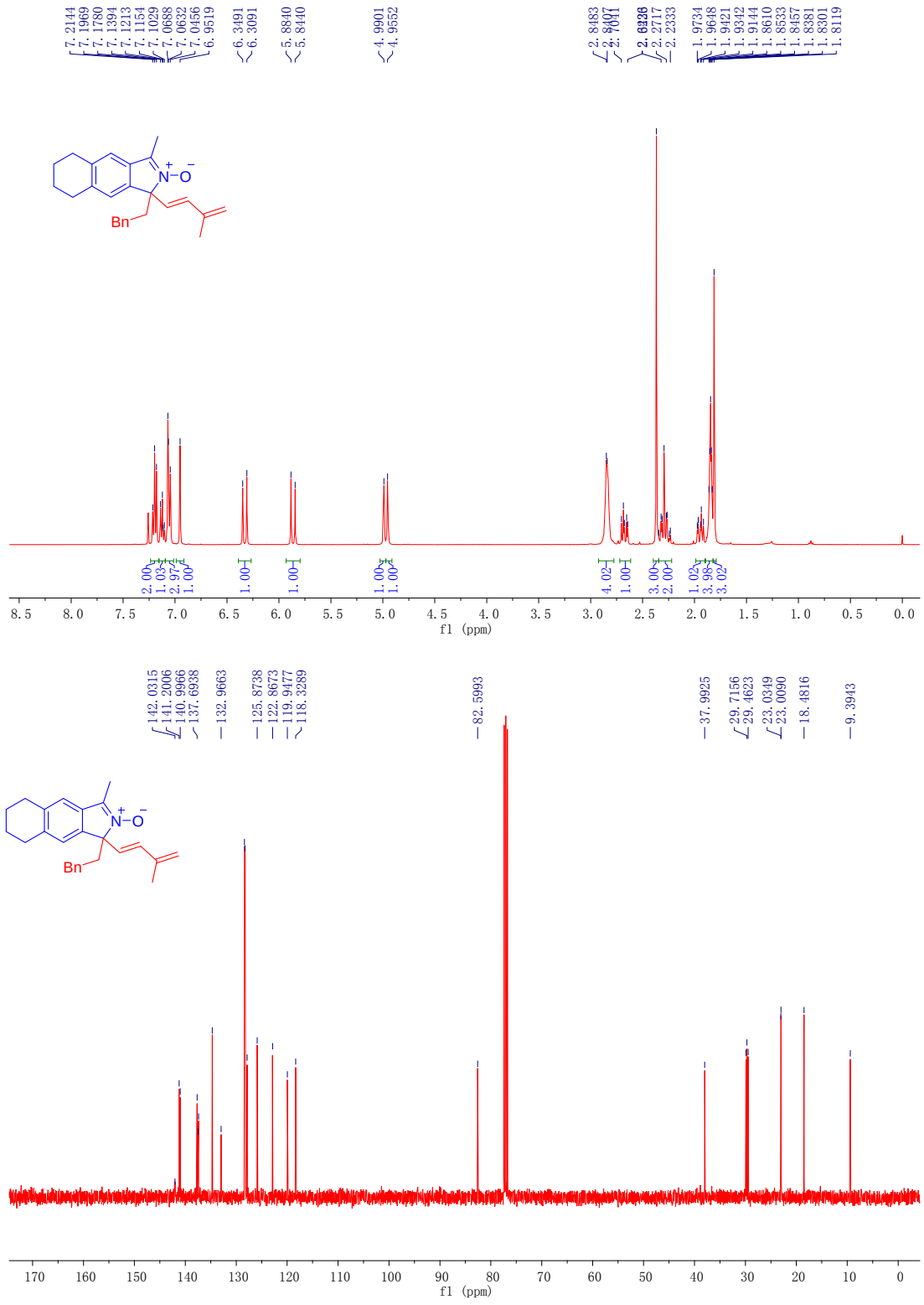
Supplementary Figure 81. ^{1}H NMR and ^{13}C NMR of **9pb'**



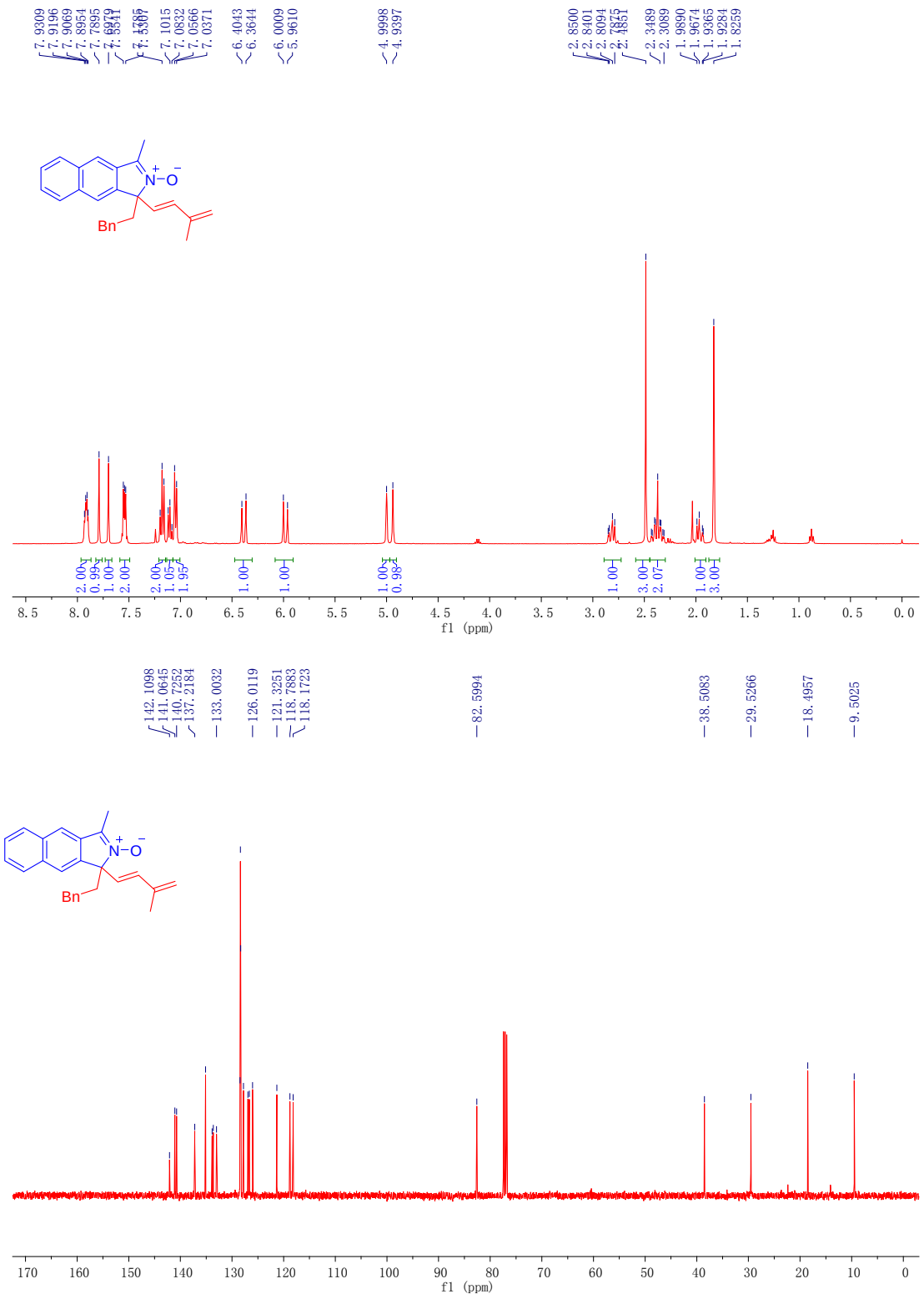
Supplementary Figure 82. ^{1}H NMR and ^{13}C NMR of **9qb**



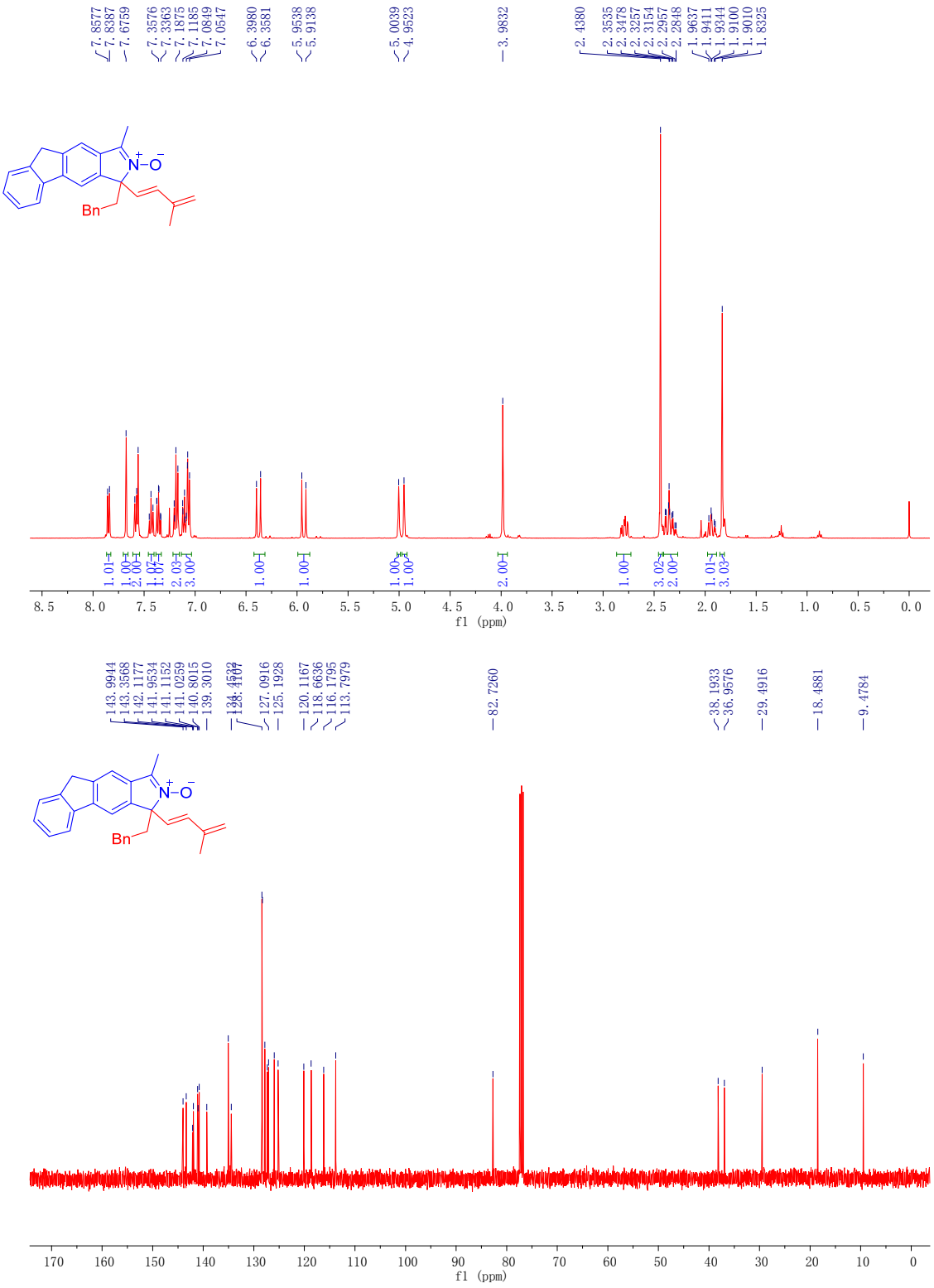
Supplementary Figure 83. ^{1}H NMR and ^{13}C NMR of **9rb**



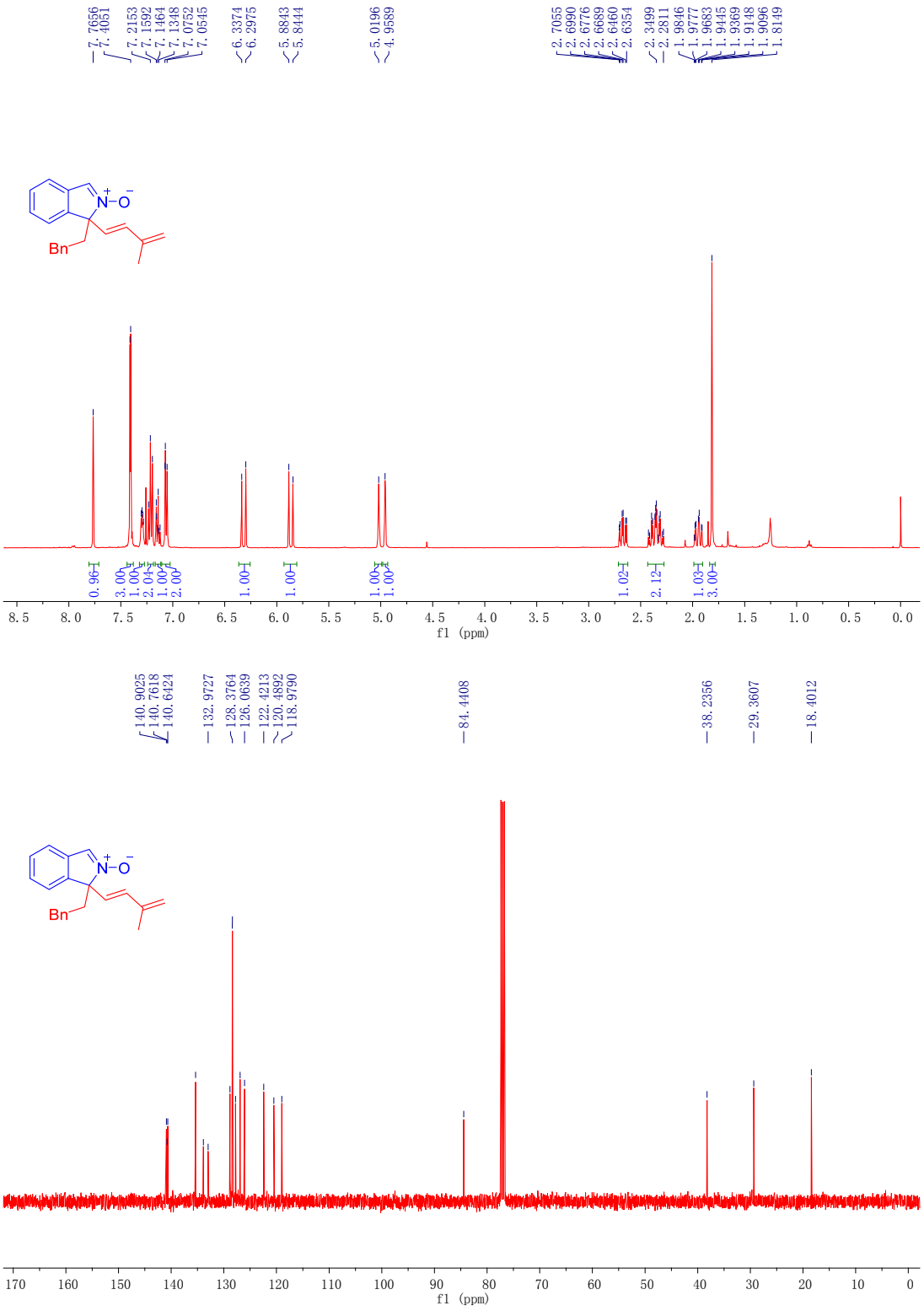
Supplementary Figure 84. ^{1}H NMR and ^{13}C NMR of **9sb**



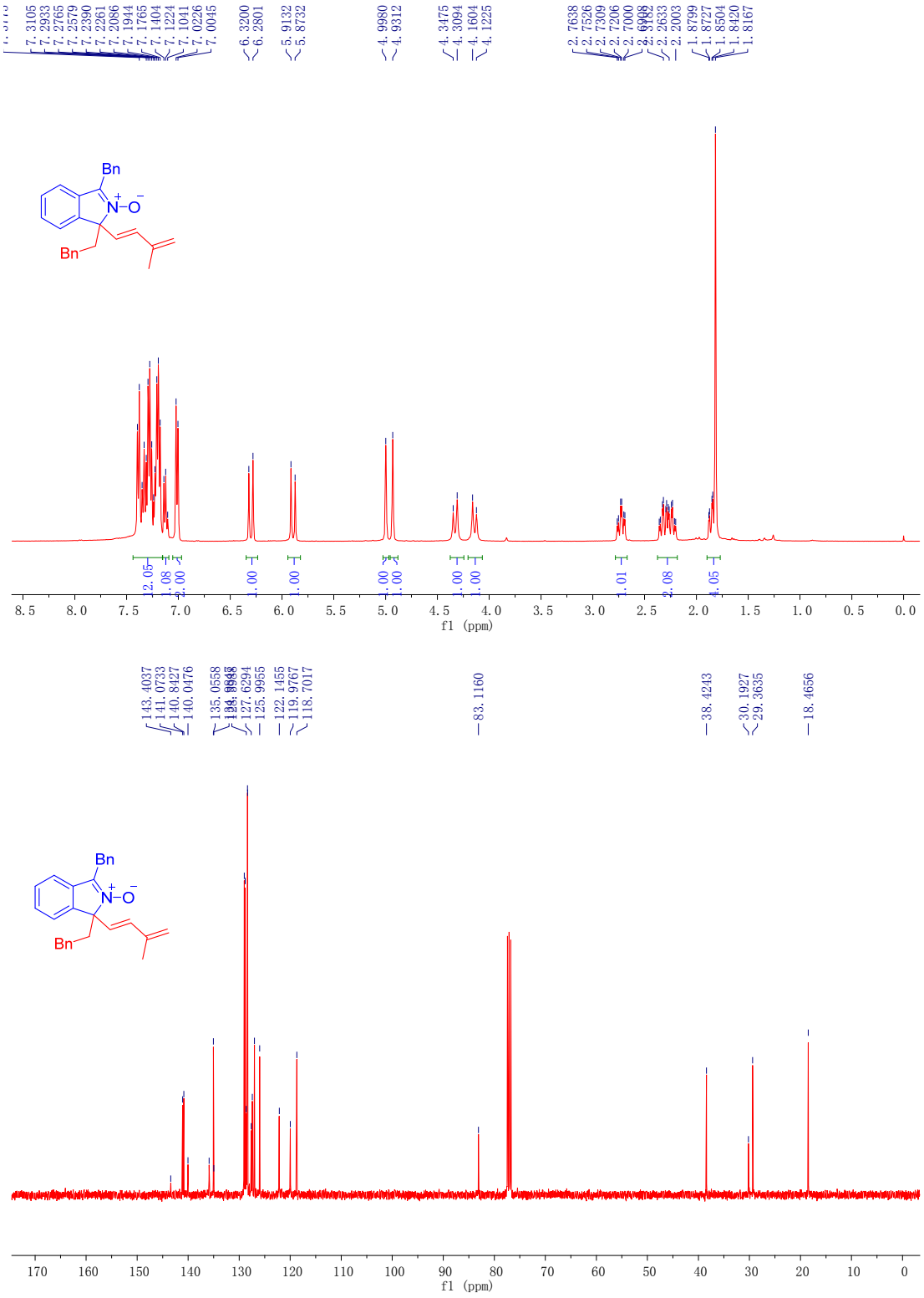
Supplementary Figure 85. ^{1}H NMR and ^{13}C NMR of **9tb**



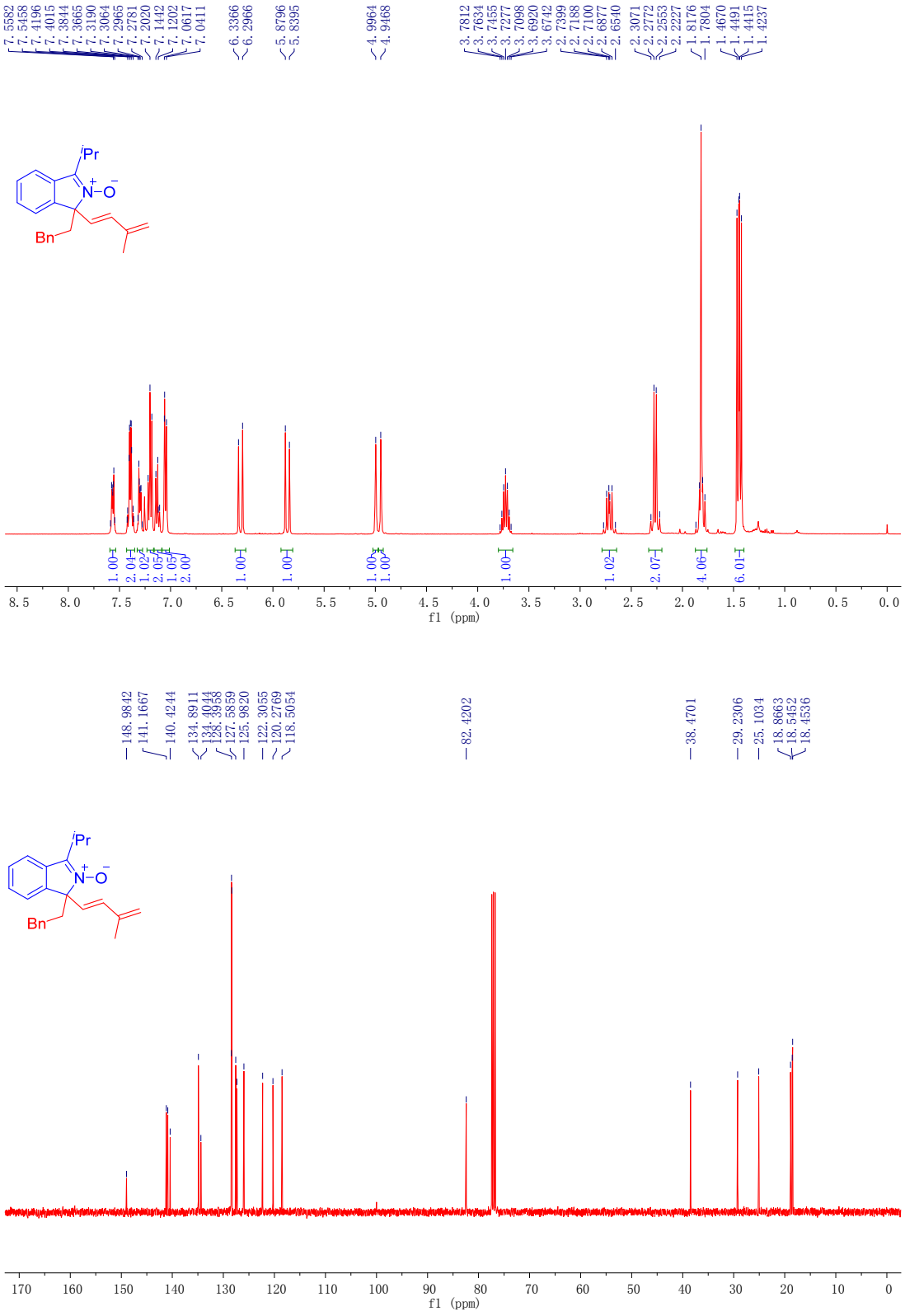
Supplementary Figure 86. ^{1}H NMR and ^{13}C NMR of **9ub**



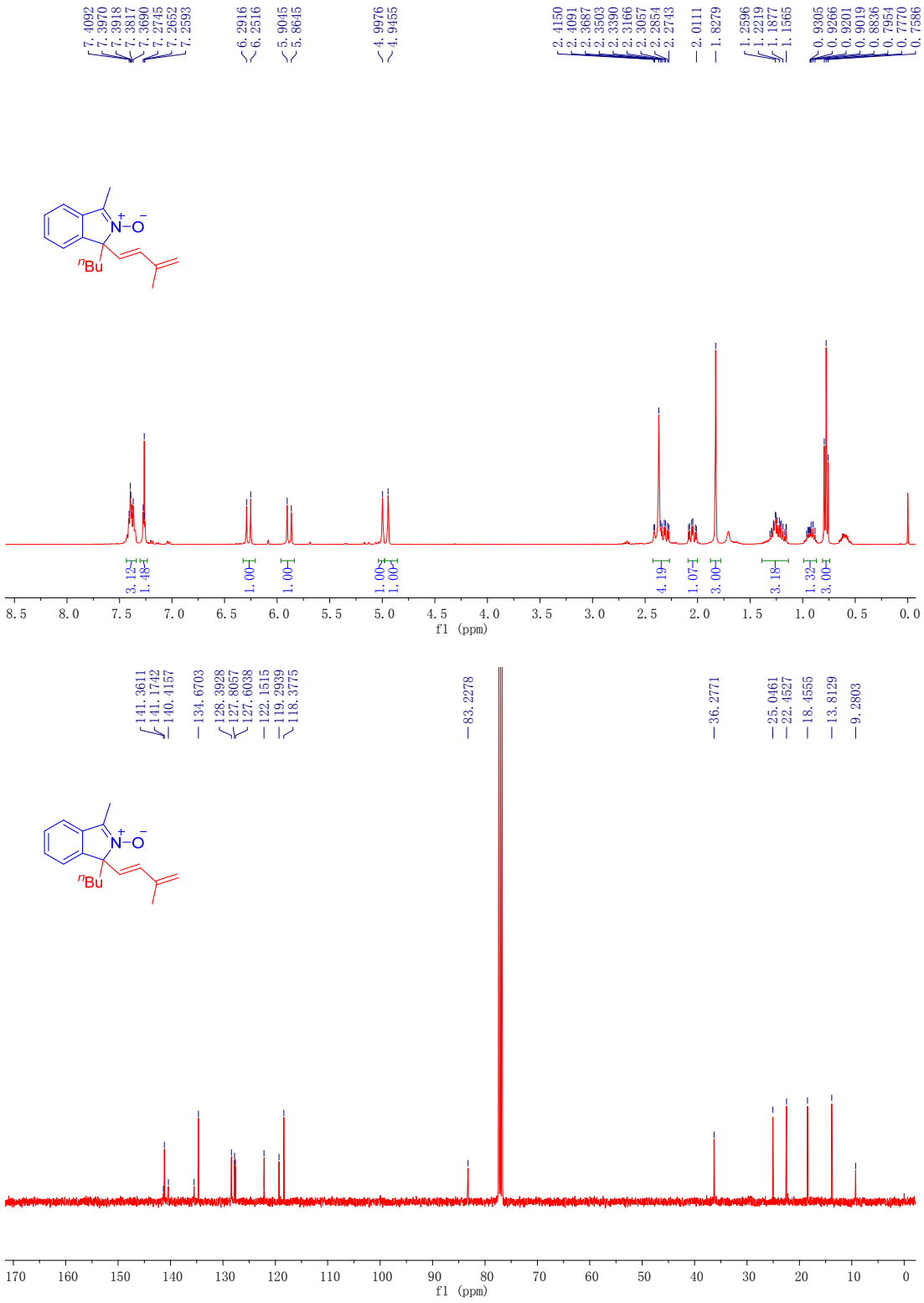
Supplementary Figure 87. ^{1}H NMR and ^{13}C NMR of **9vb**



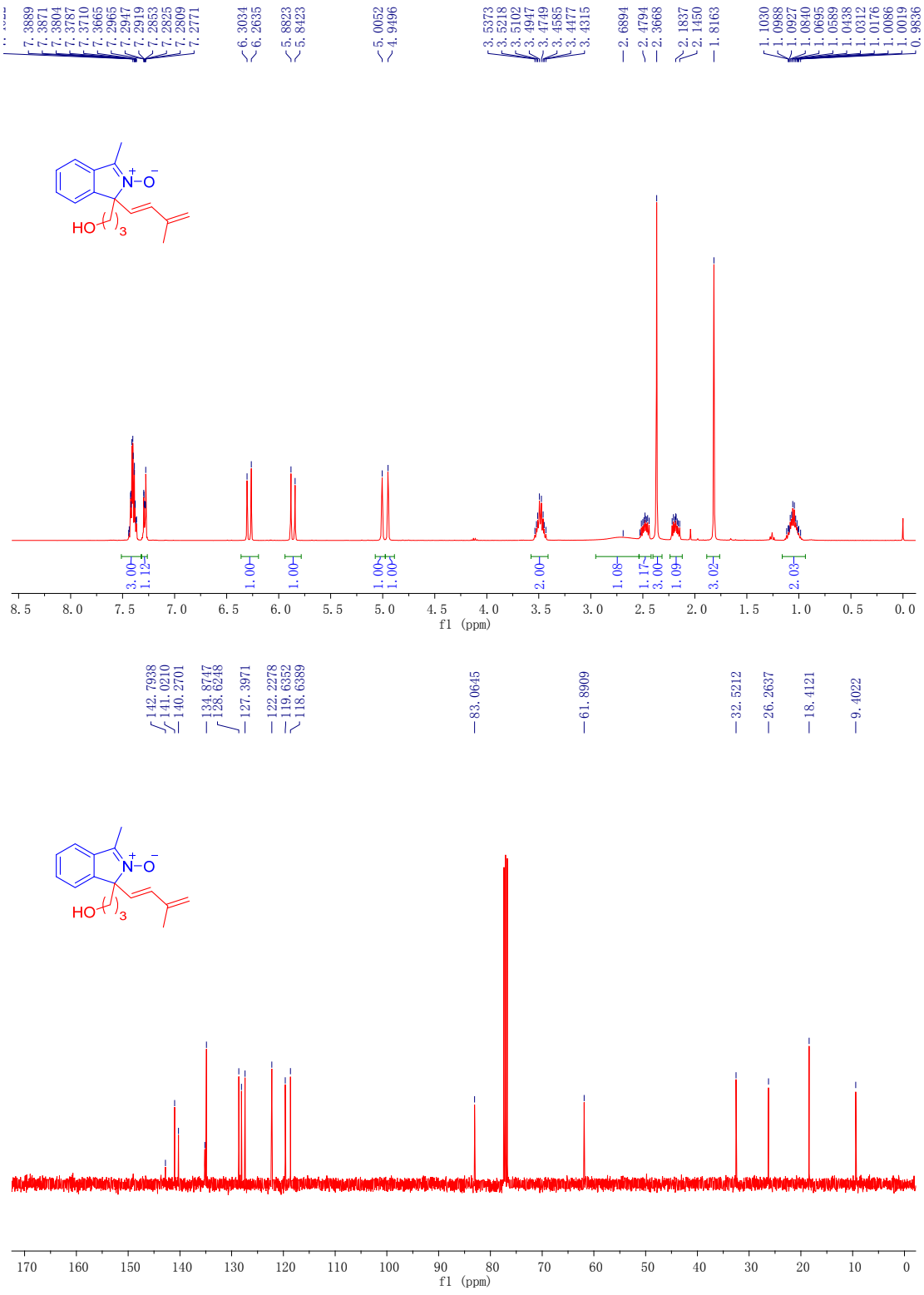
Supplementary Figure 88. ^{1}H NMR and ^{13}C NMR of **9wb**



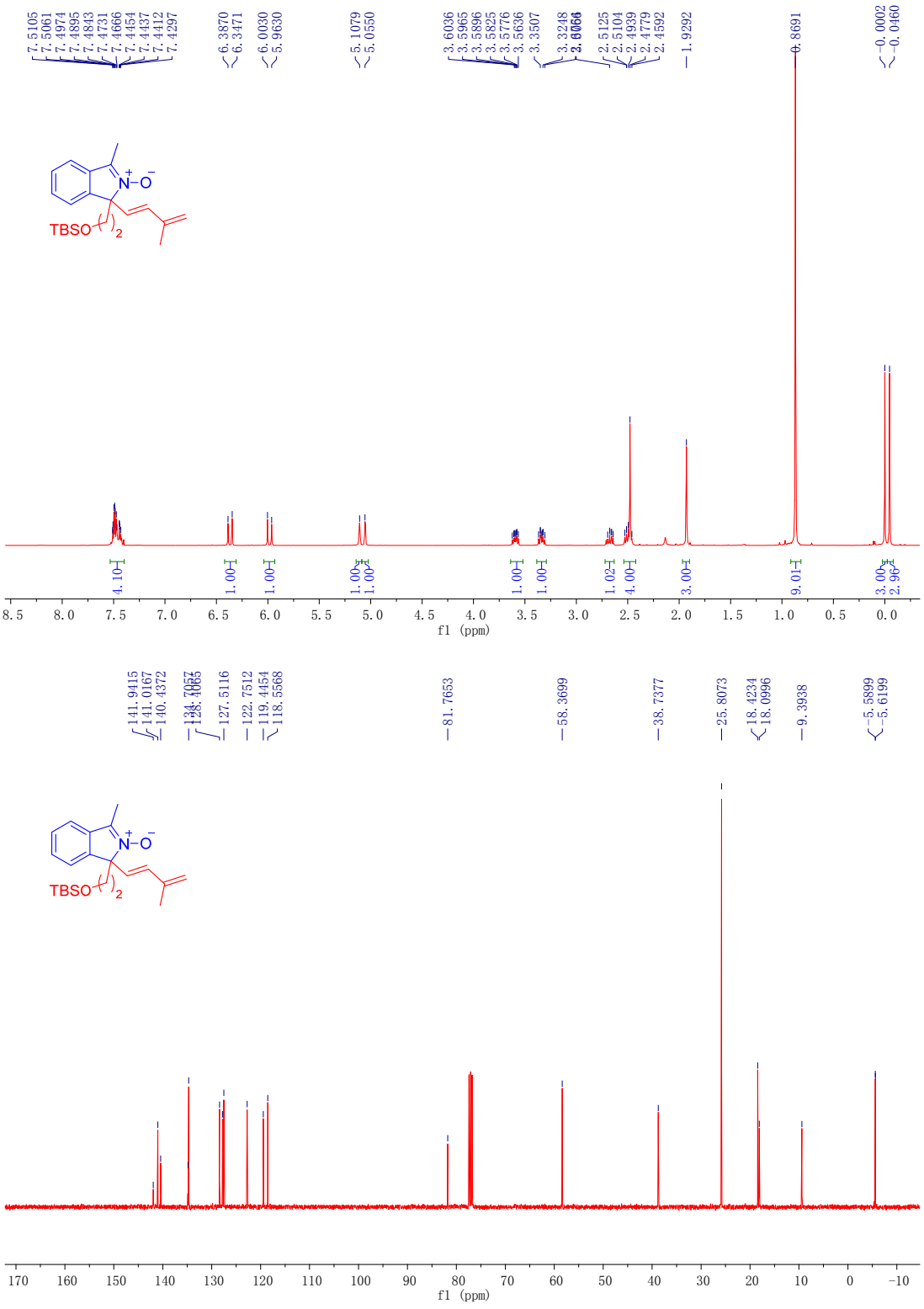
Supplementary Figure 89. ^{1}H NMR and ^{13}C NMR of **9xb**



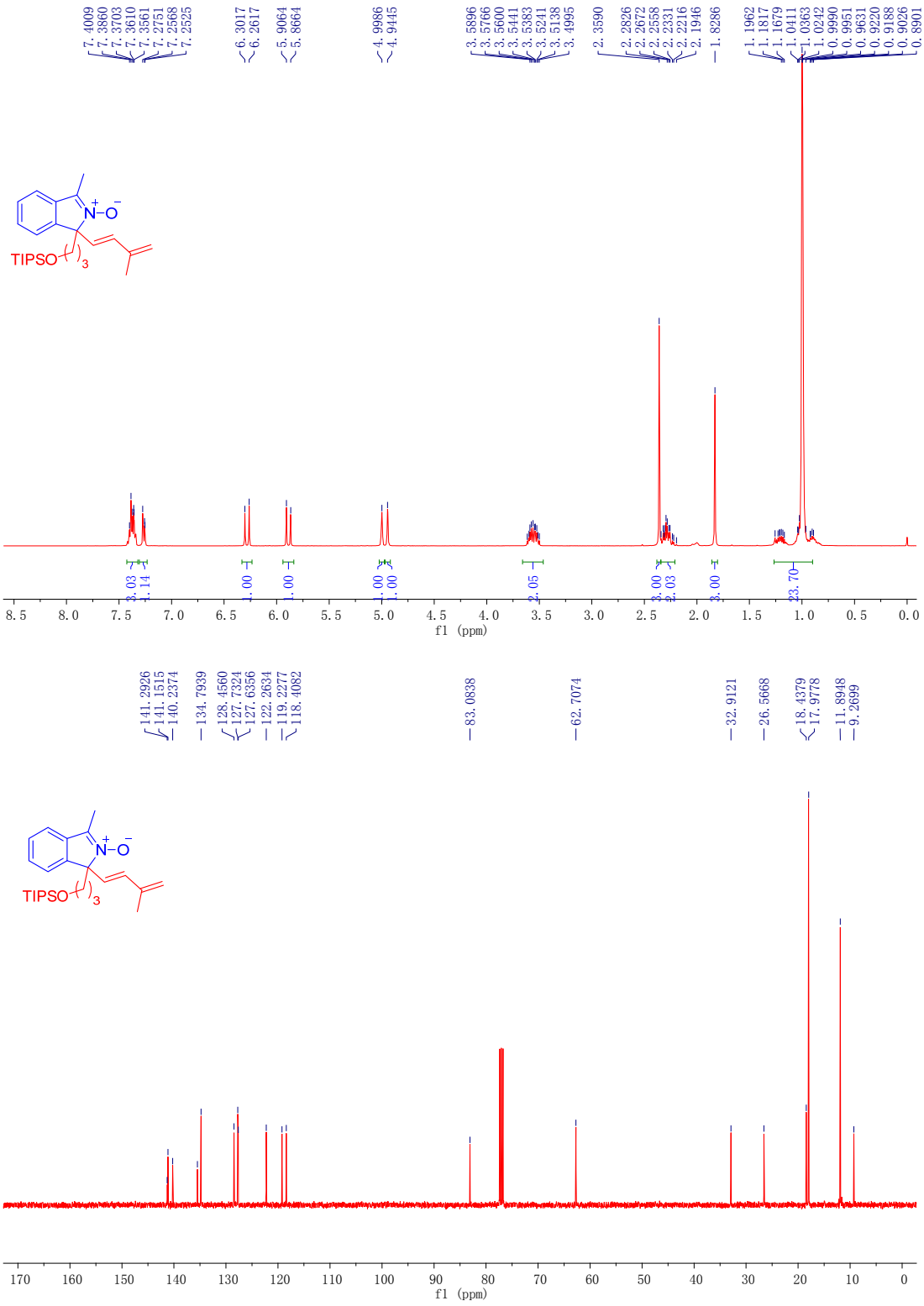
Supplementary Figure 90. ^{1}H NMR and ^{13}C NMR of **9aa**



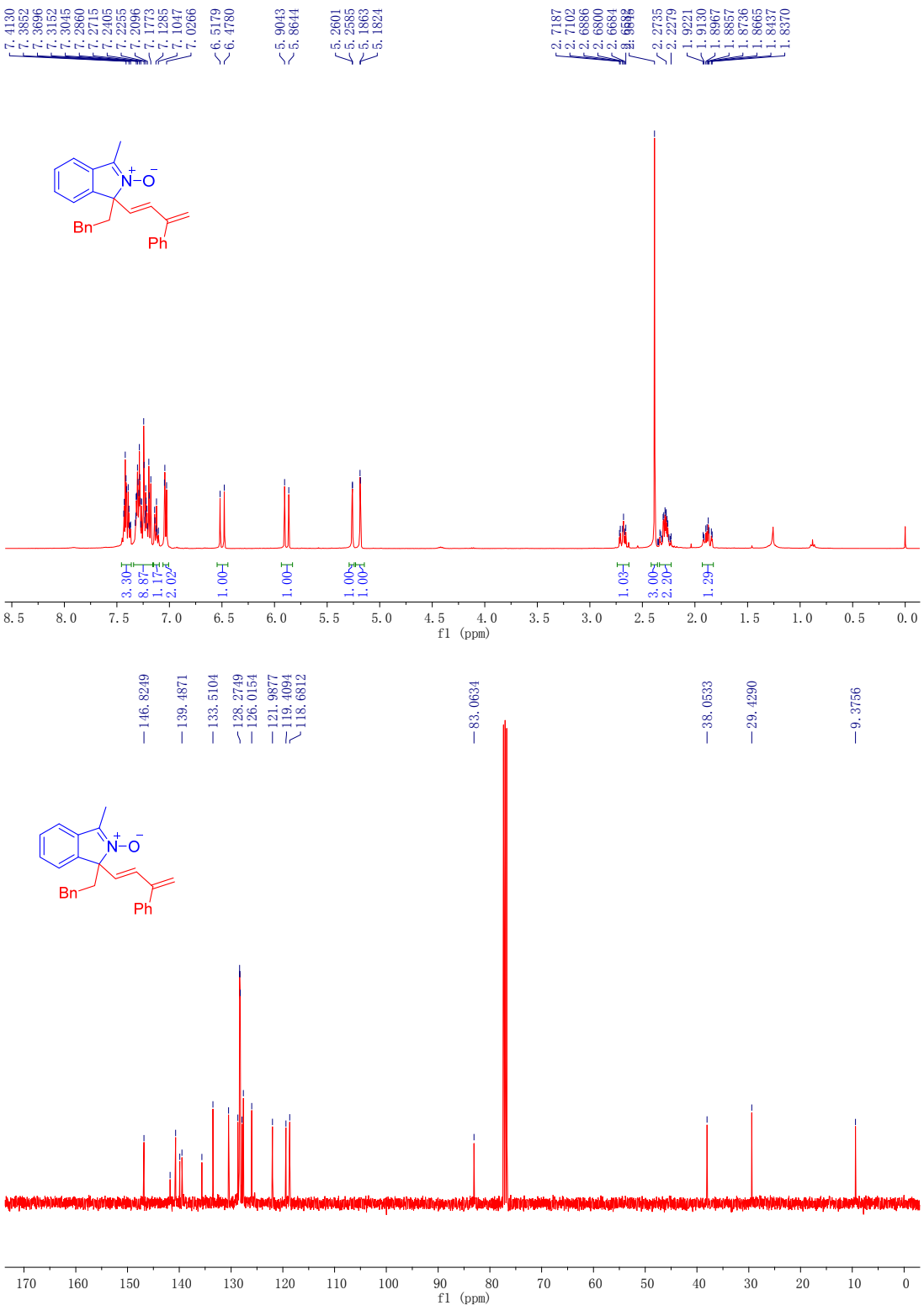
Supplementary Figure 91. ^{1}H NMR and ^{13}C NMR of **9aj**



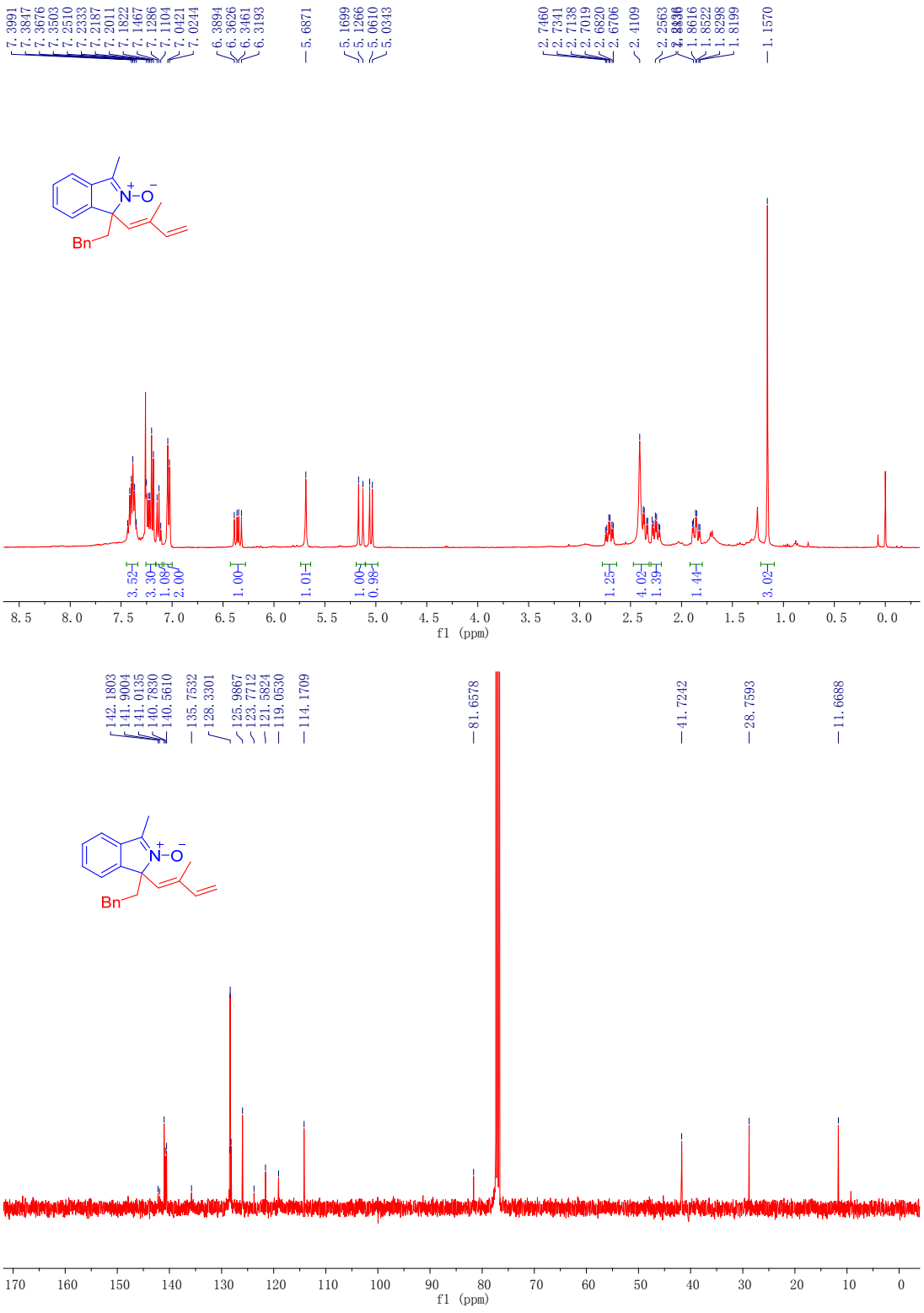
Supplementary Figure 92. ^{1}H NMR and ^{13}C NMR of **9ak**



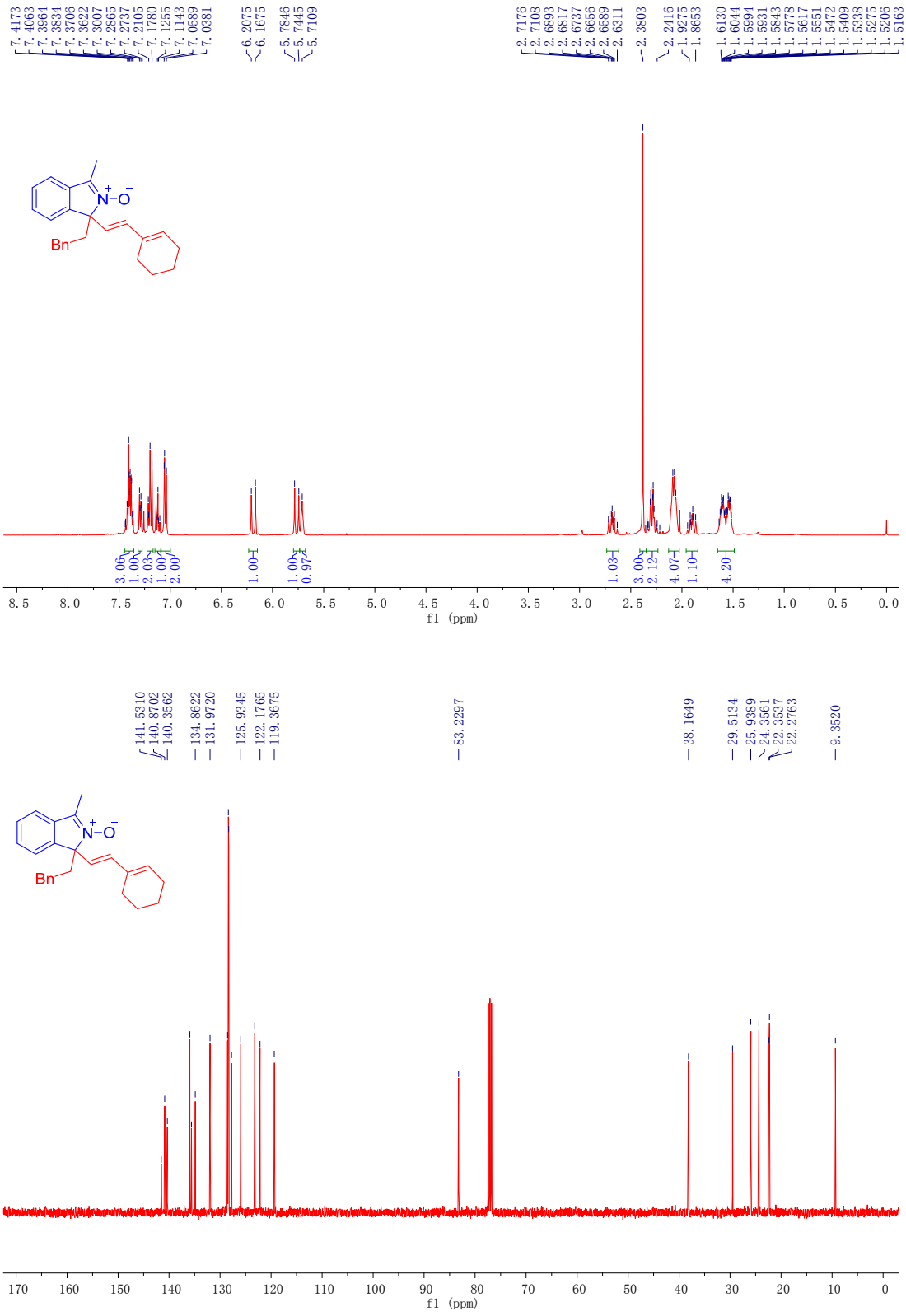
Supplementary Figure 93. ^{1}H NMR and ^{13}C NMR of **9al**



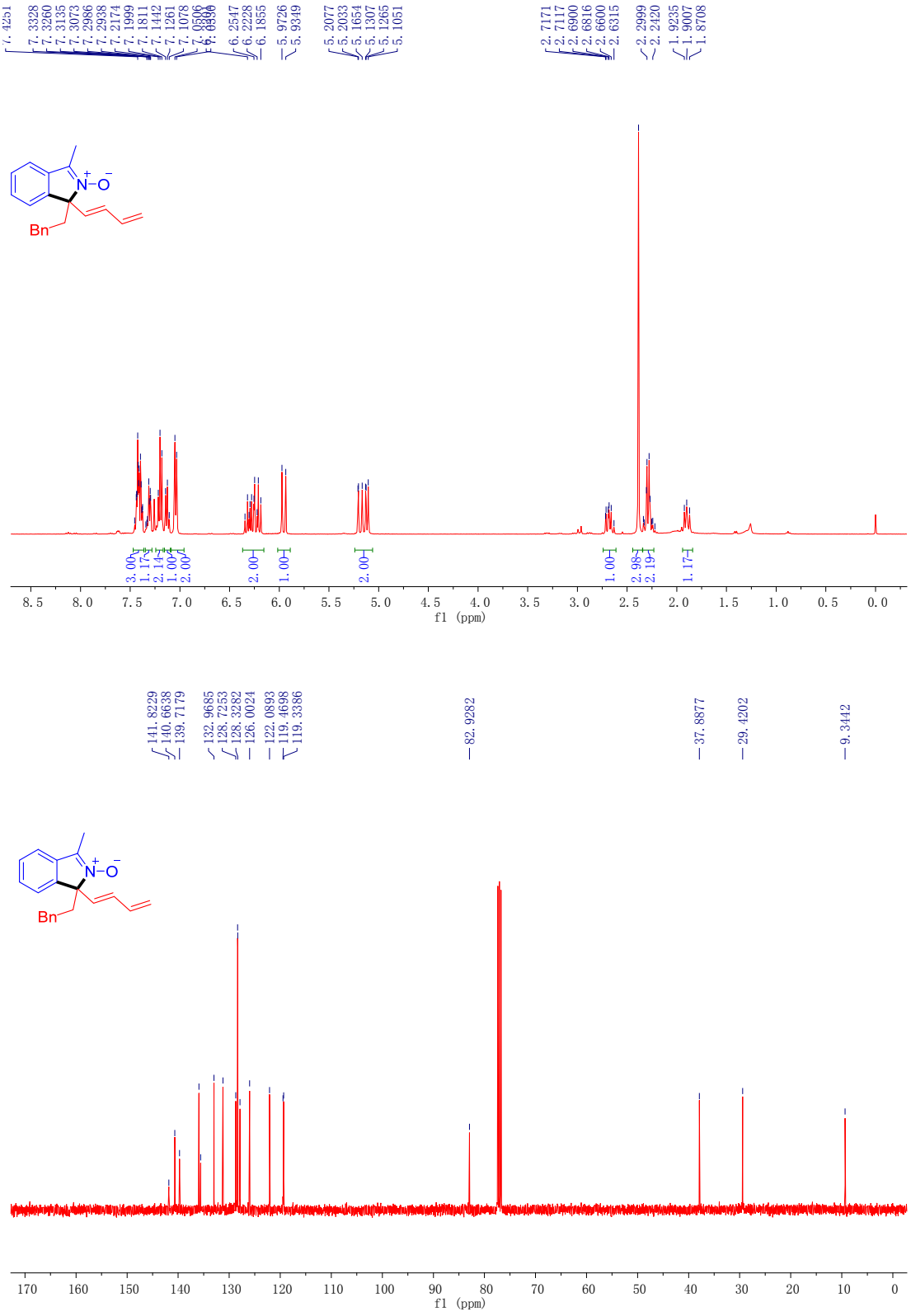
Supplementary Figure 94. ^{1}H NMR and ^{13}C NMR of **9am**



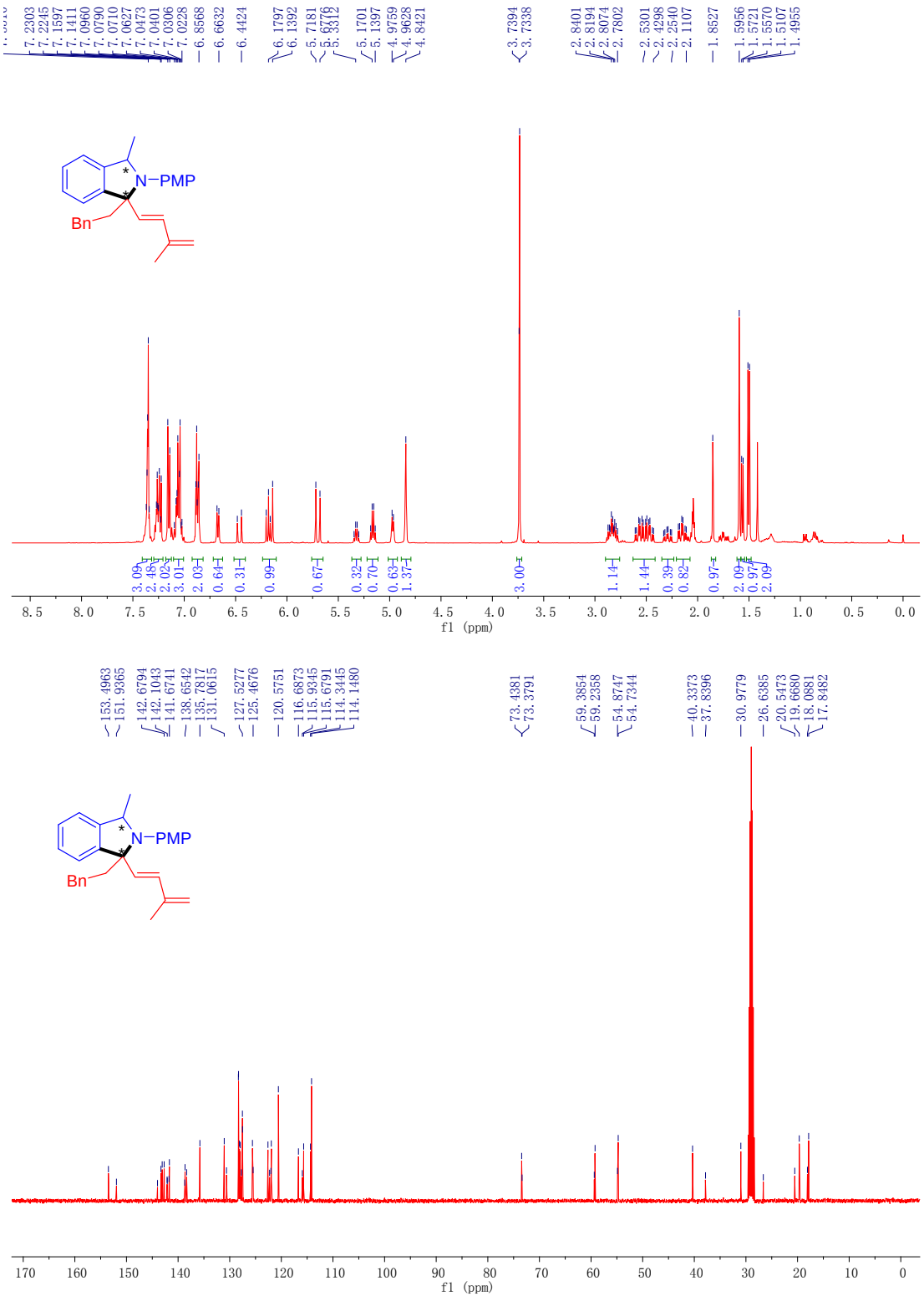
Supplementary Figure 95. ^{1}H NMR and ^{13}C NMR of **9an**



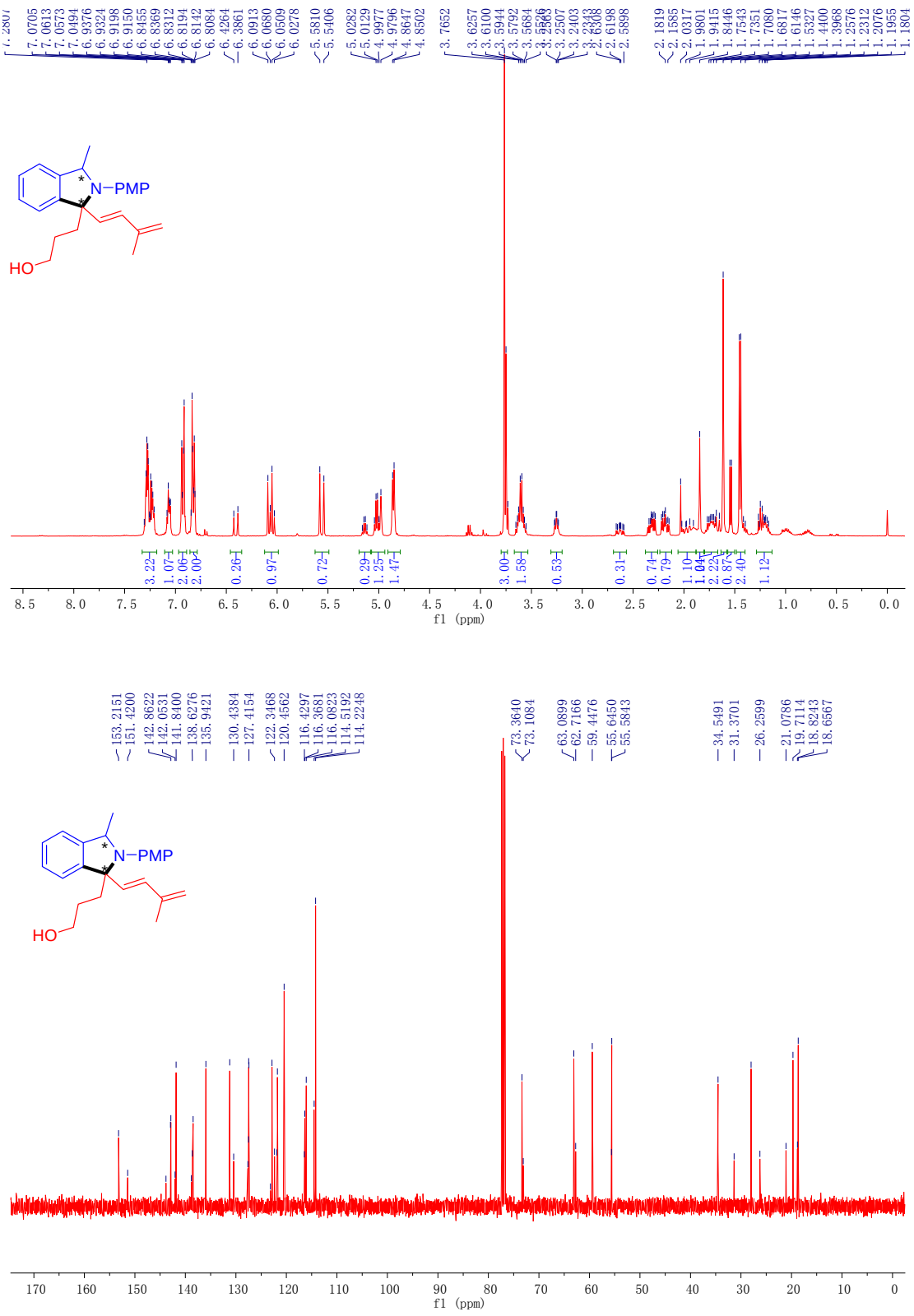
Supplementary Figure 96. ^{1}H NMR and ^{13}C NMR of **9ao**



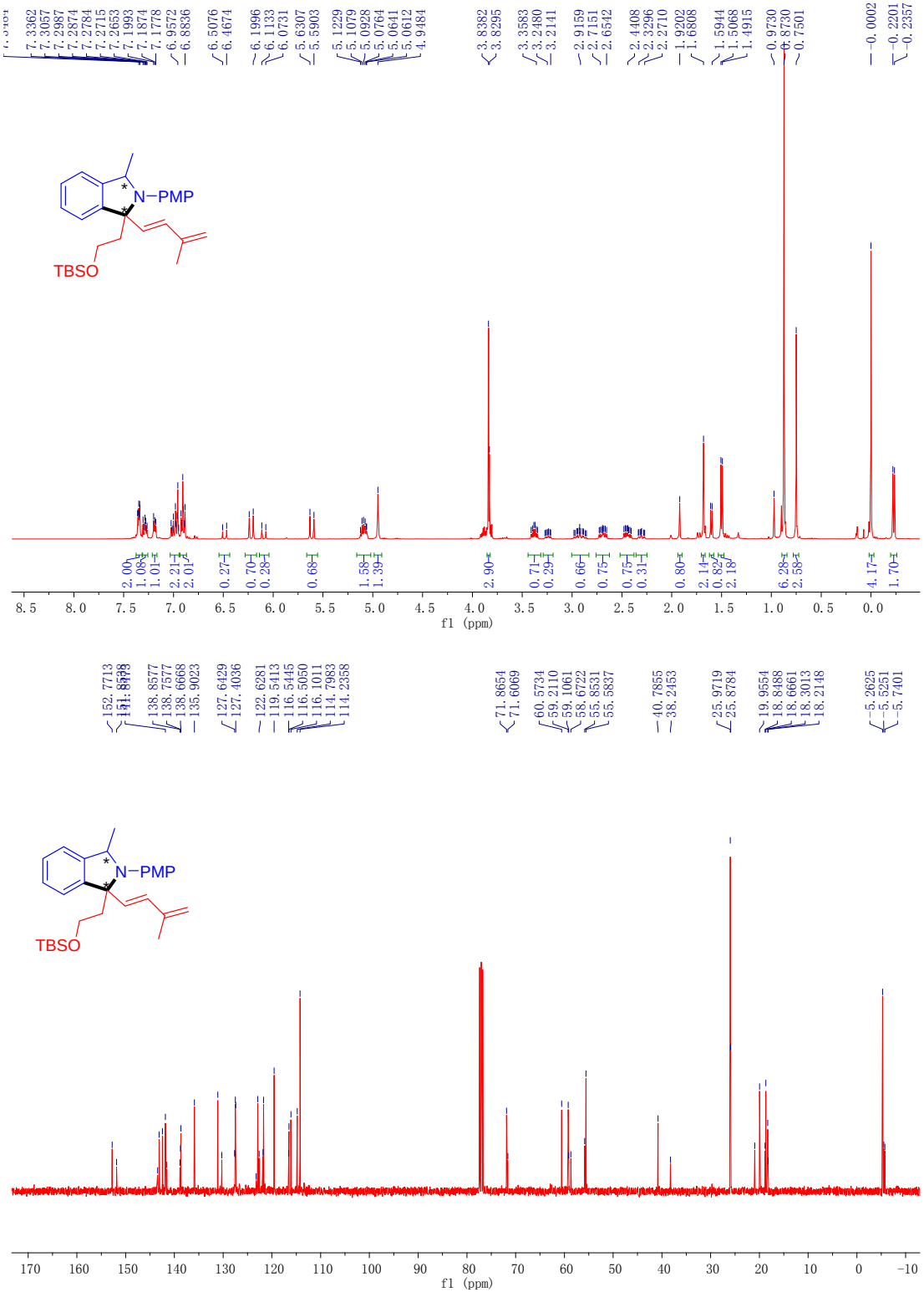
Supplementary Figure 97. ^{1}H NMR and ^{13}C NMR of **9ap**



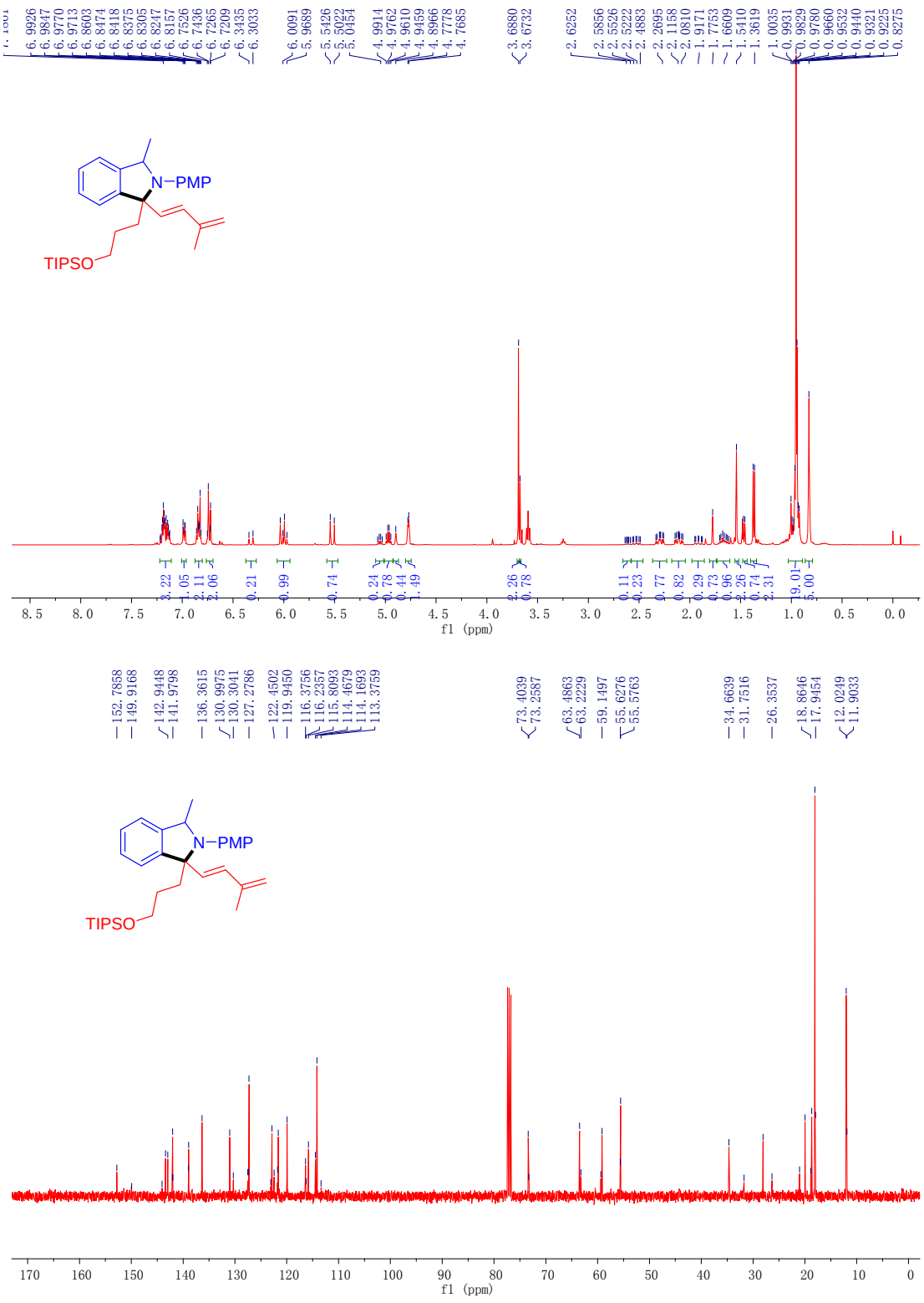
Supplementary Figure 98. ^{1}H NMR and ^{13}C NMR of **11ab**



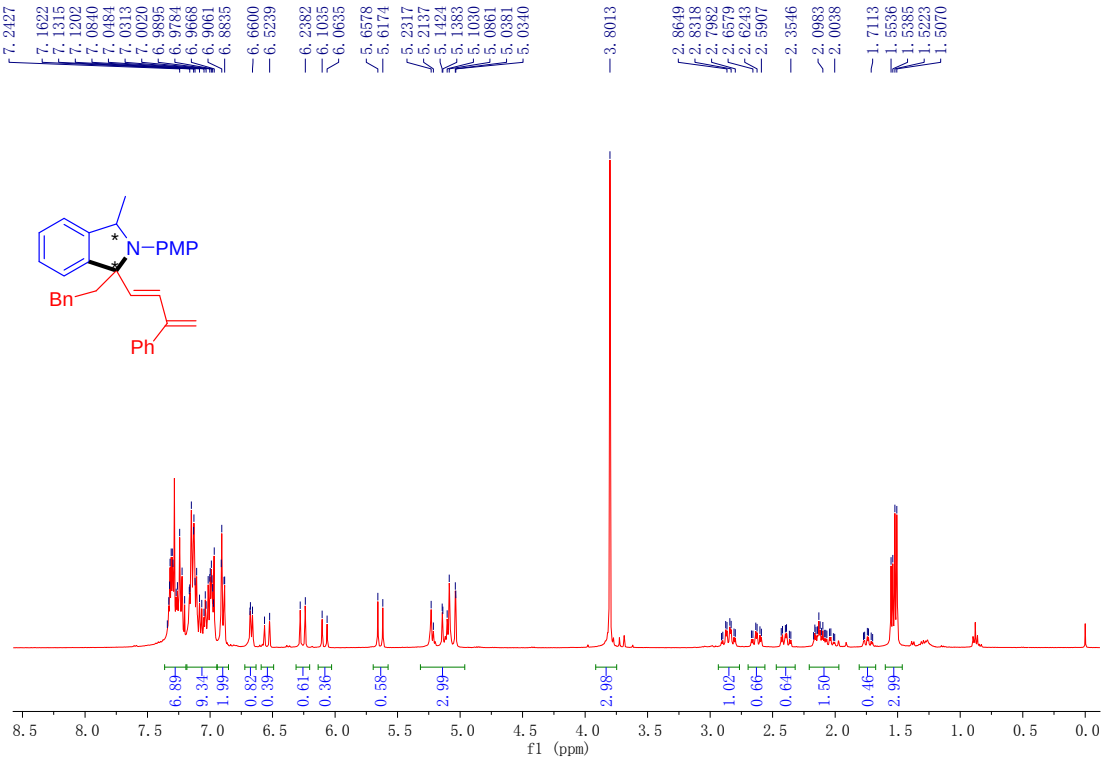
Supplementary Figure 99. ^{1}H NMR and ^{13}C NMR of **11aj**



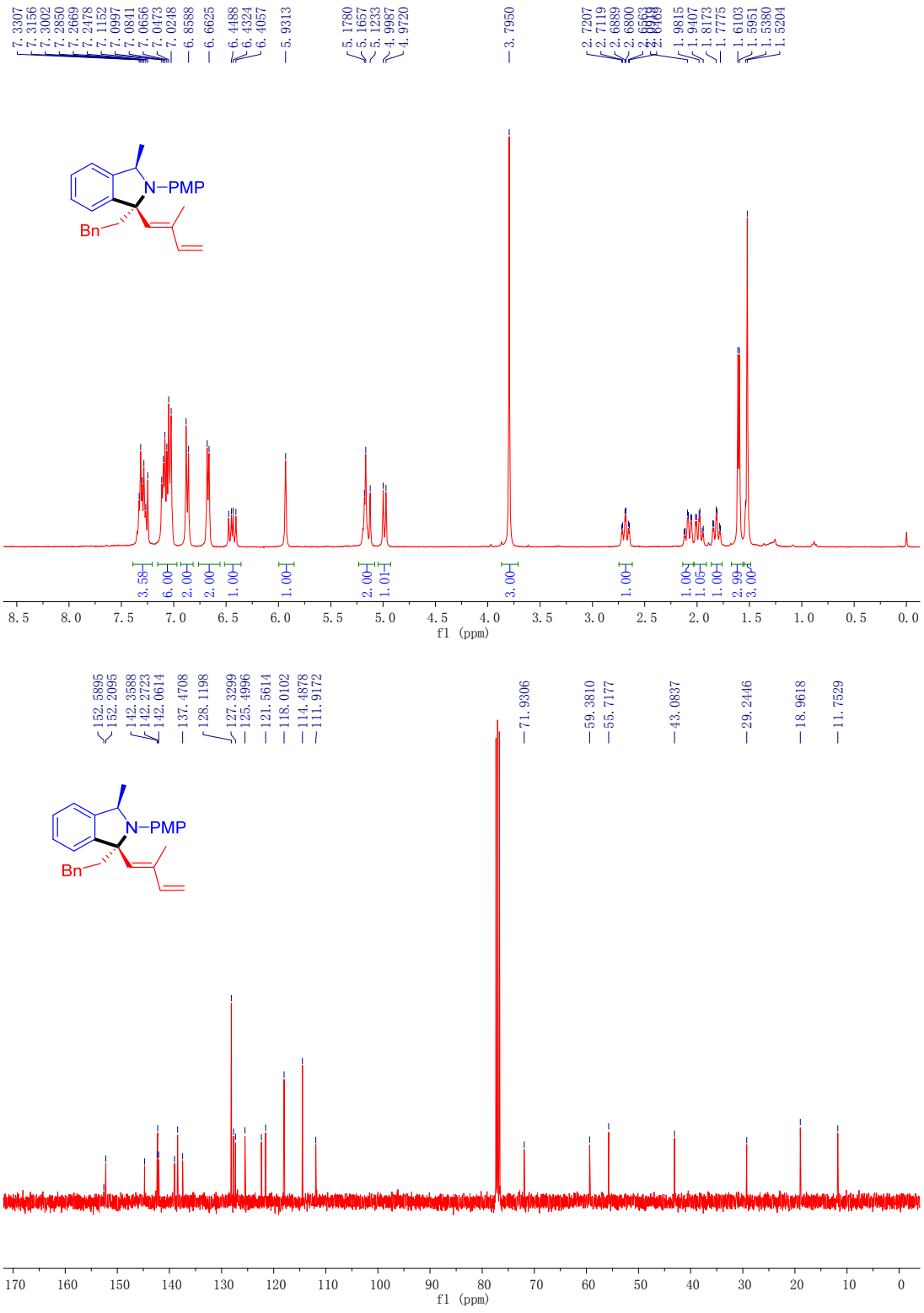
Supplementary Figure 100. ^{1}H NMR and ^{13}C NMR of **11ak**



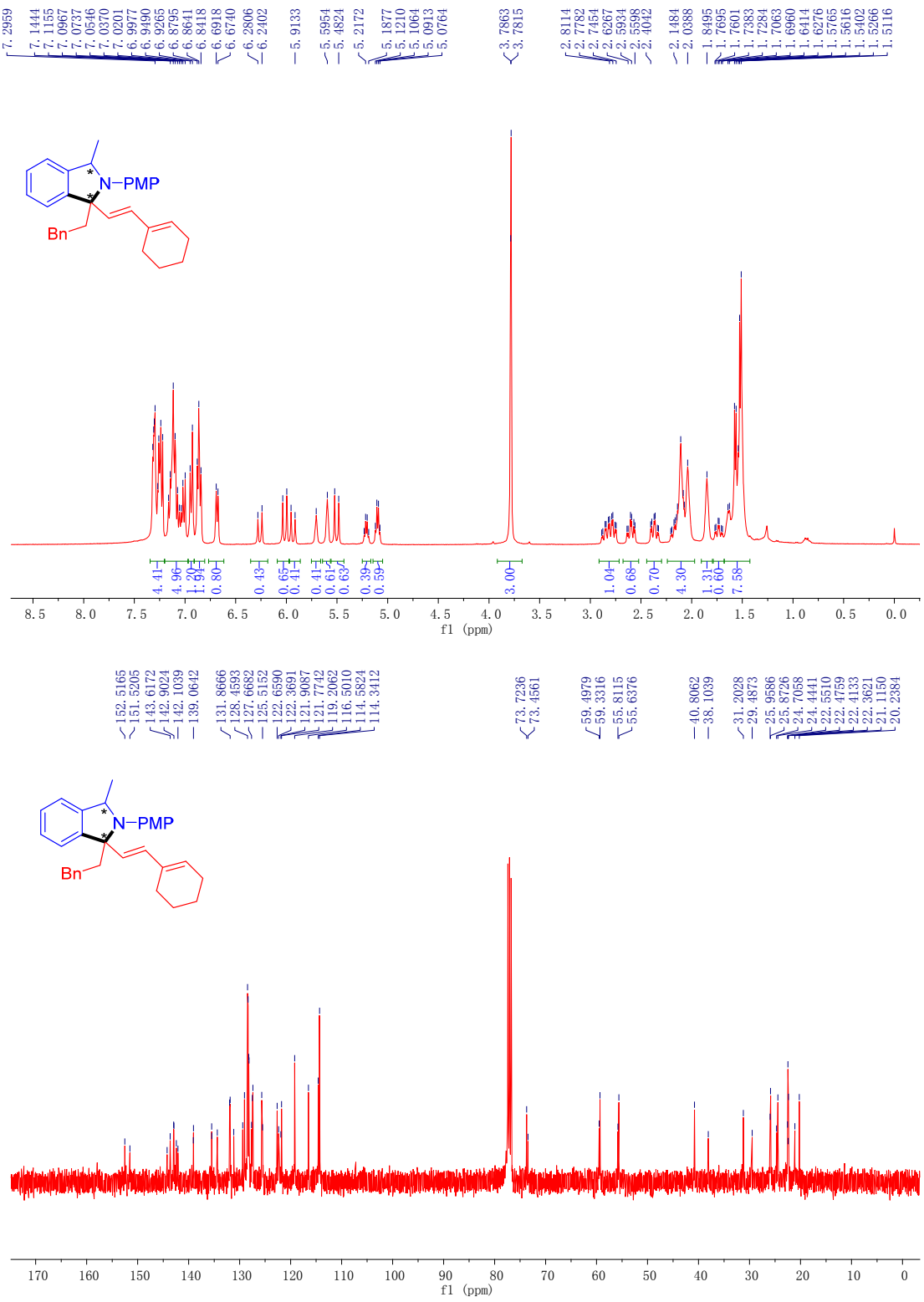
Supplementary Figure 101. ^{1}H NMR and ^{13}C NMR of **11al**



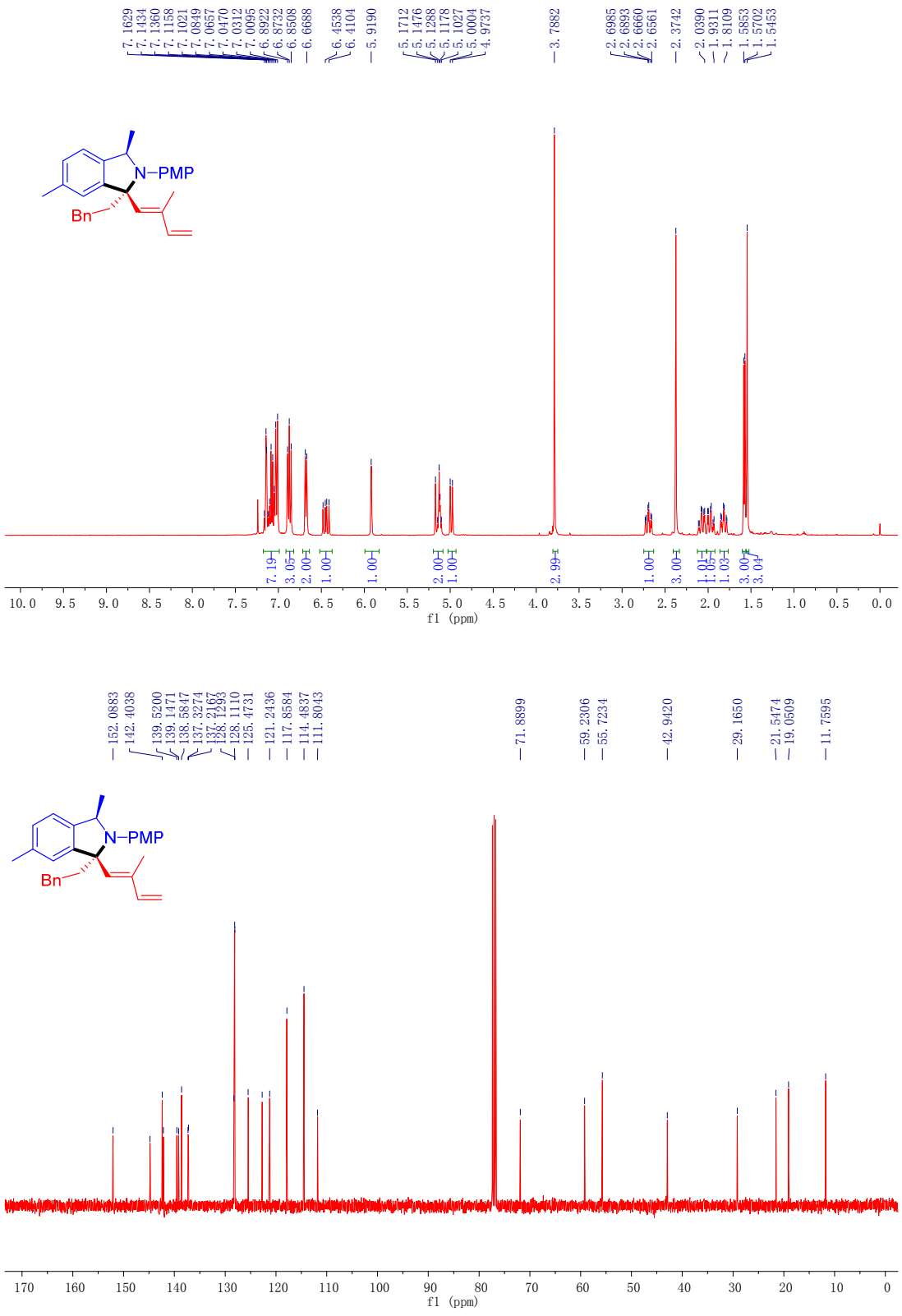
Supplementary Figure 102. ^{1}H NMR of **11am**



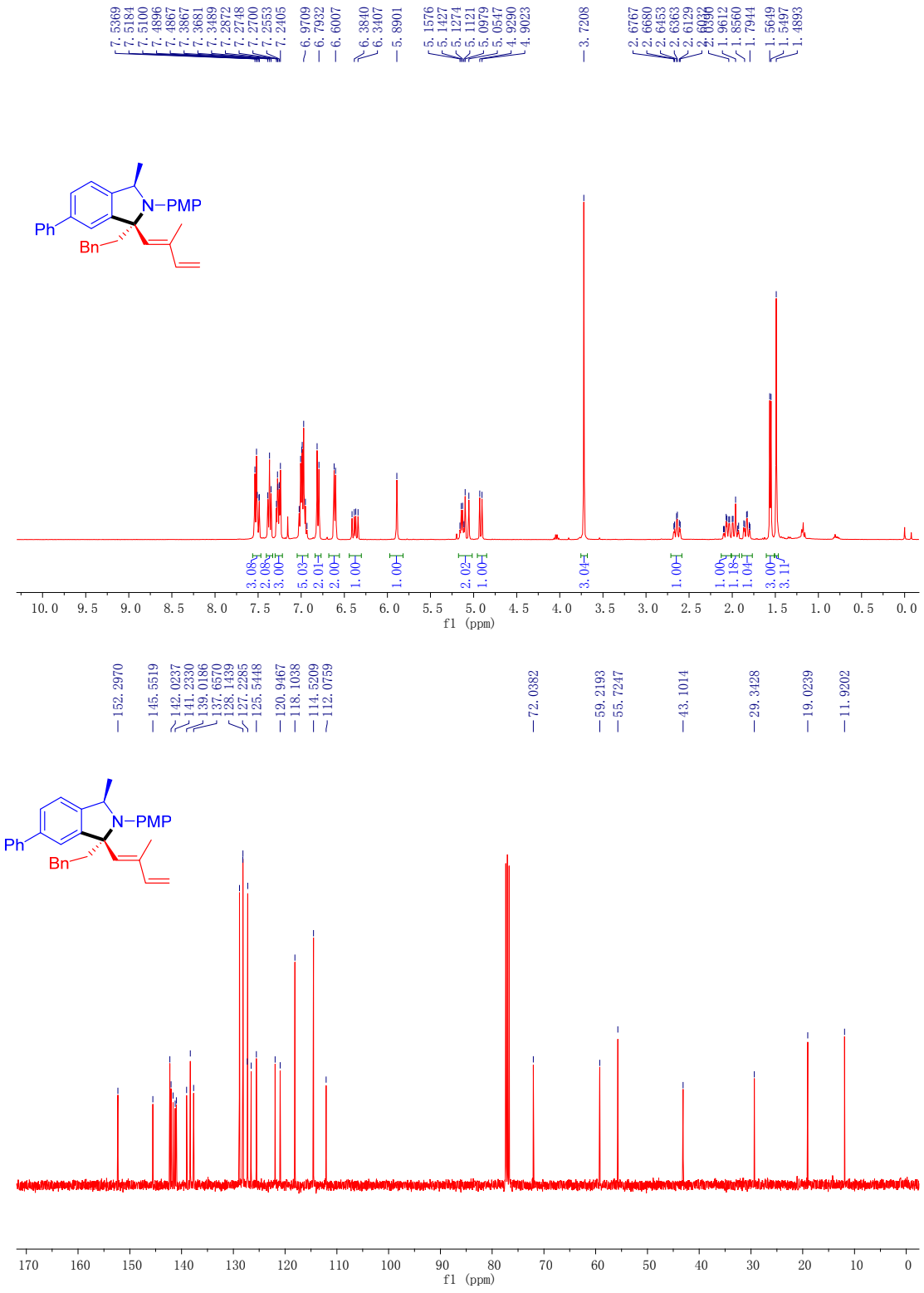
Supplementary Figure 103. ^{1}H NMR and ^{13}C NMR of **11an**



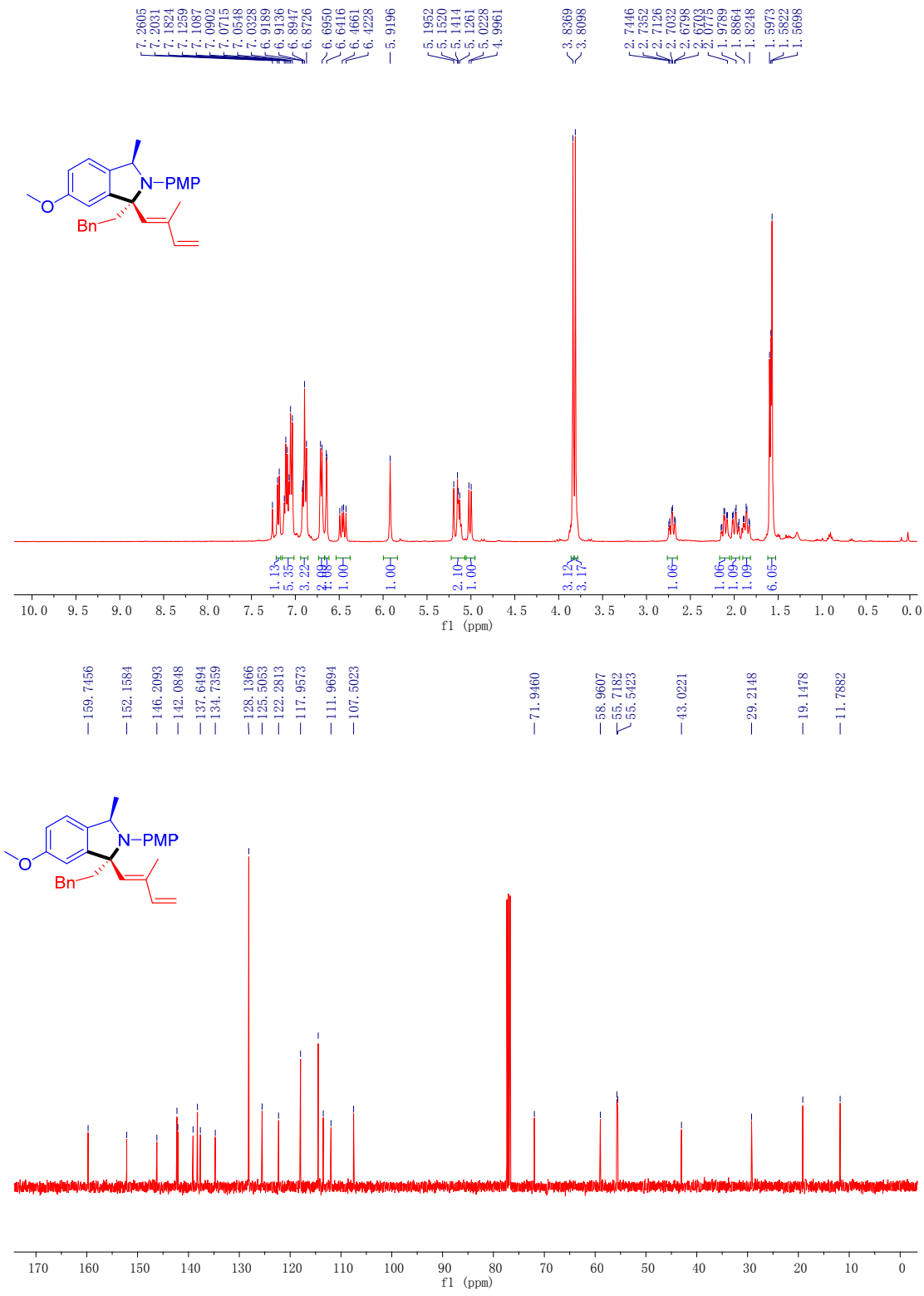
Supplementary Figure 104. ^{1}H NMR and ^{13}C NMR of **11ao**



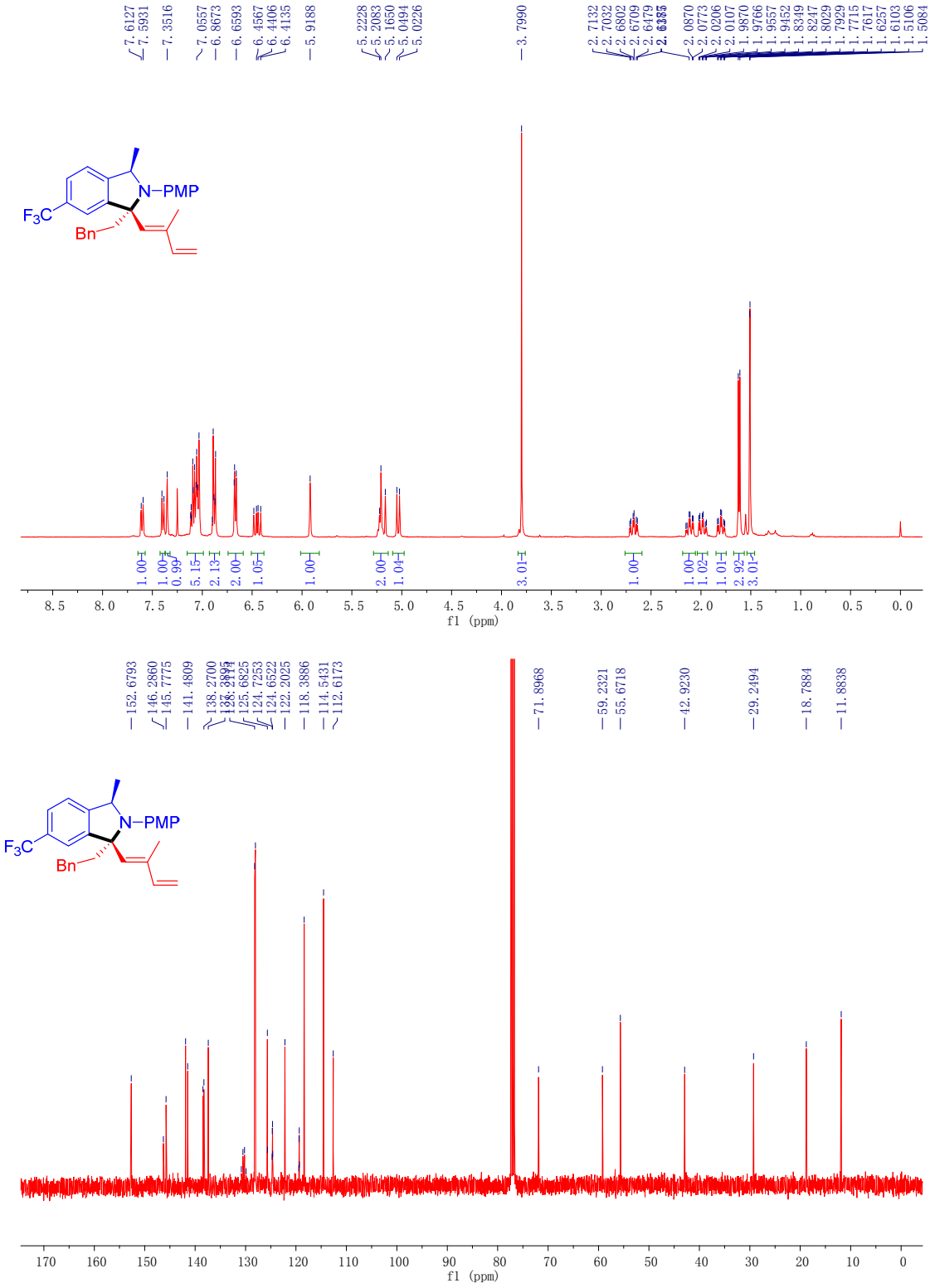
Supplementary Figure 105. ^{1}H NMR and ^{13}C NMR of **11bn**



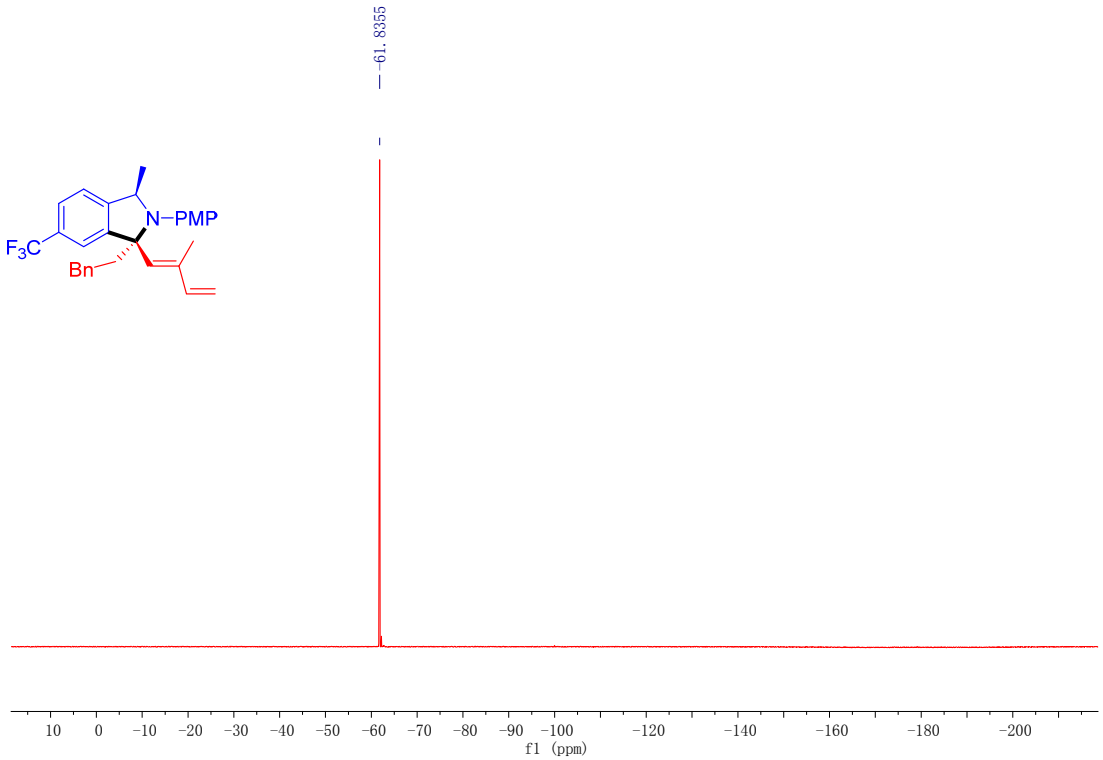
Supplementary Figure 106. ^{1}H NMR and ^{13}C NMR of **11cn**



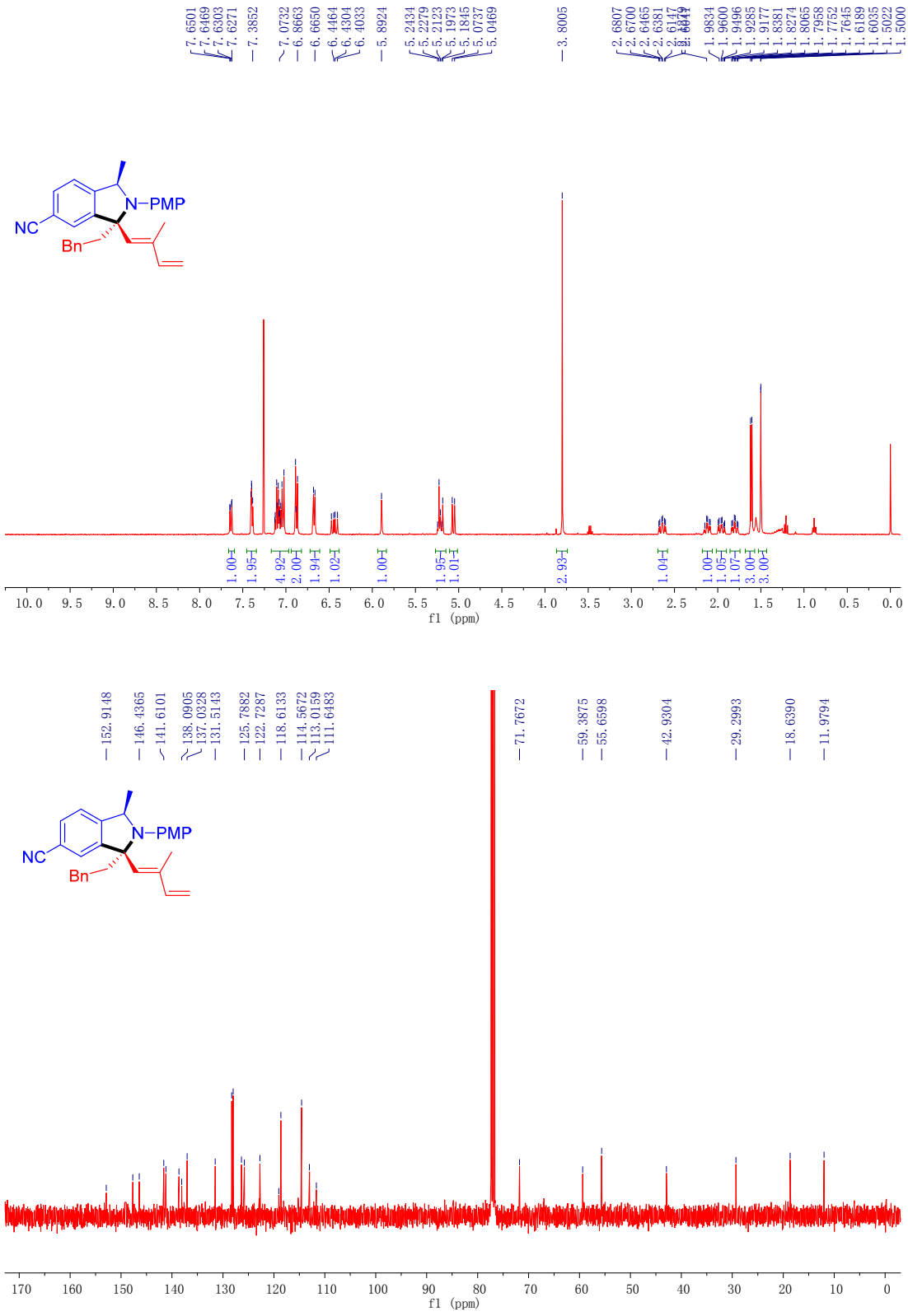
Supplementary Figure 107. ^{1}H NMR and ^{13}C NMR of **11dn**



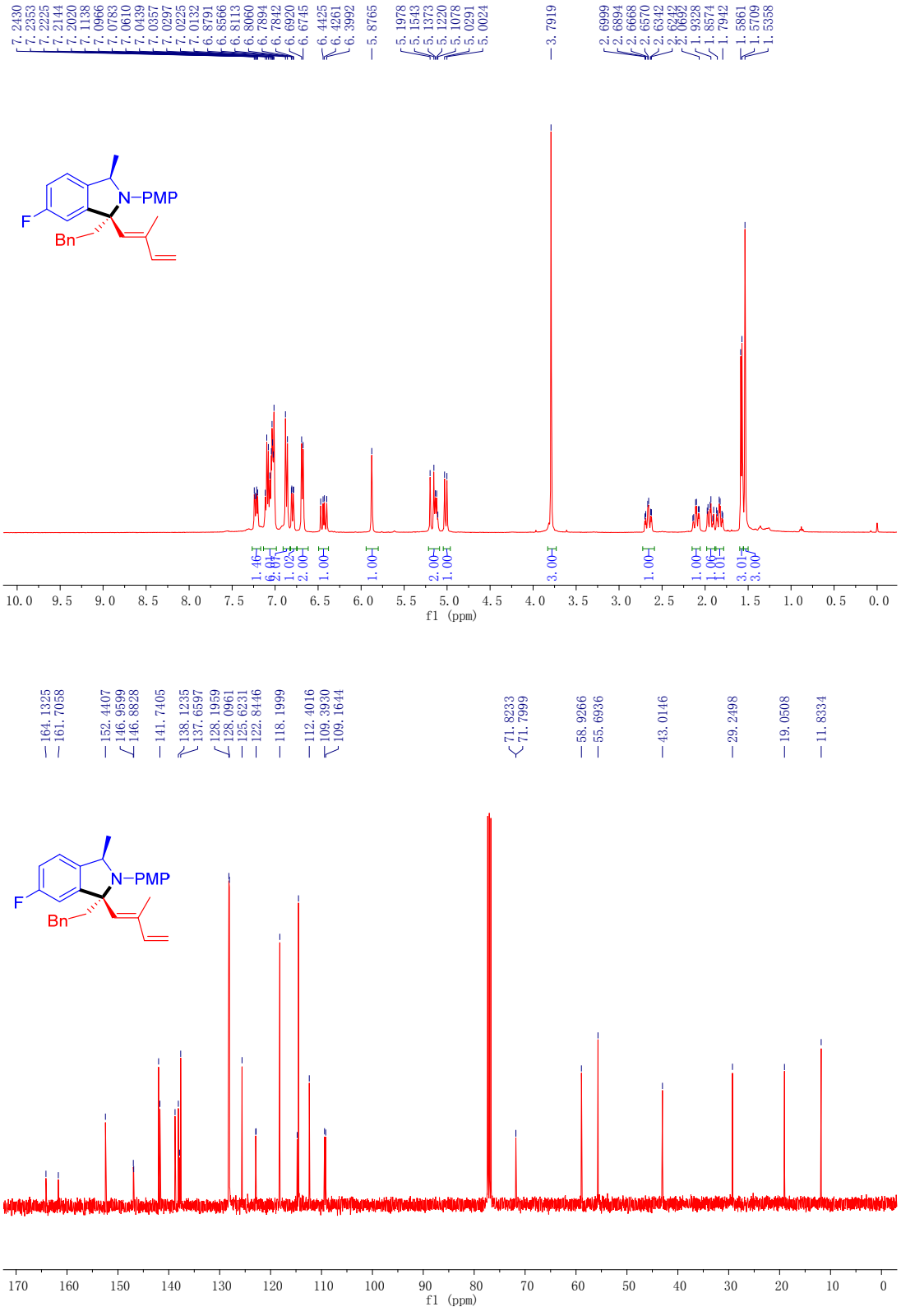
Supplementary Figure 108. ^{1}H NMR and ^{13}C NMR of **11en**



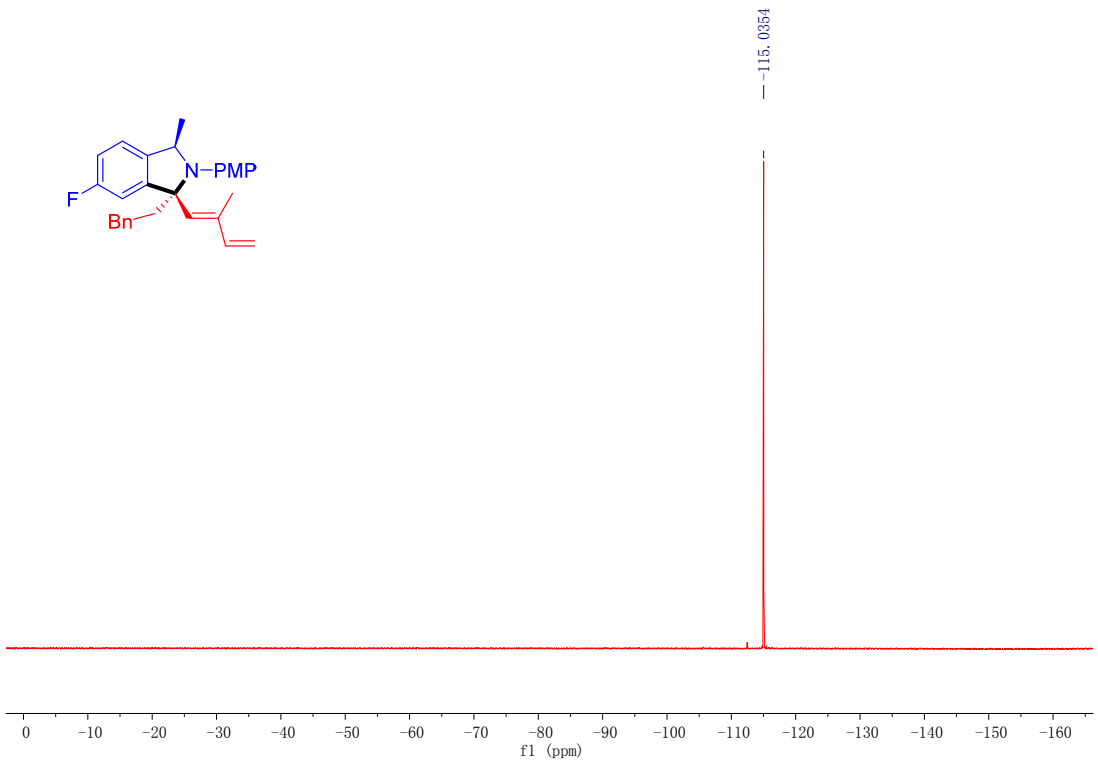
Supplementary Figure 109. ^{19}F NMR of **11en**



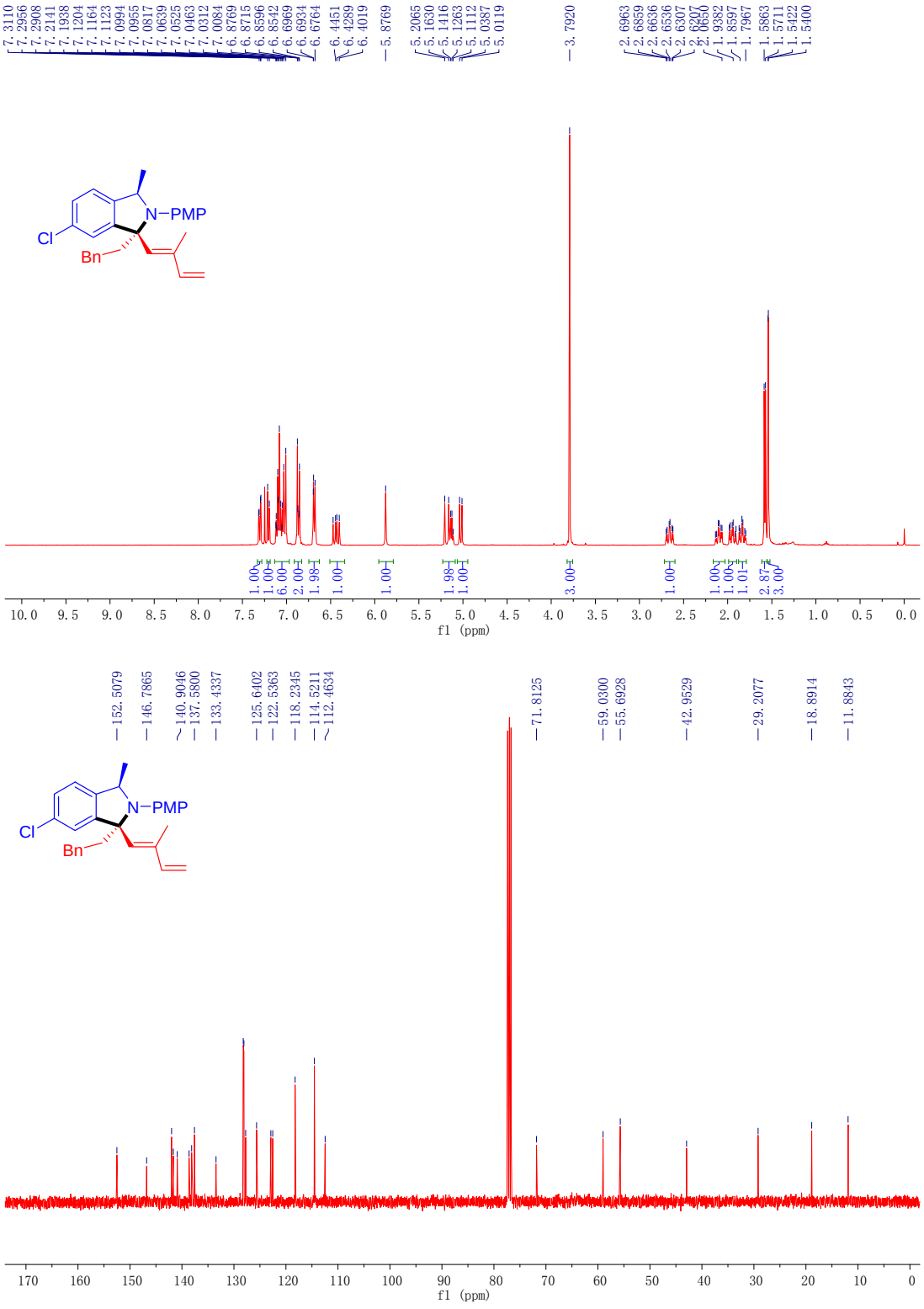
Supplementary Figure 110. ^{1}H NMR and ^{13}C NMR of **11fn**



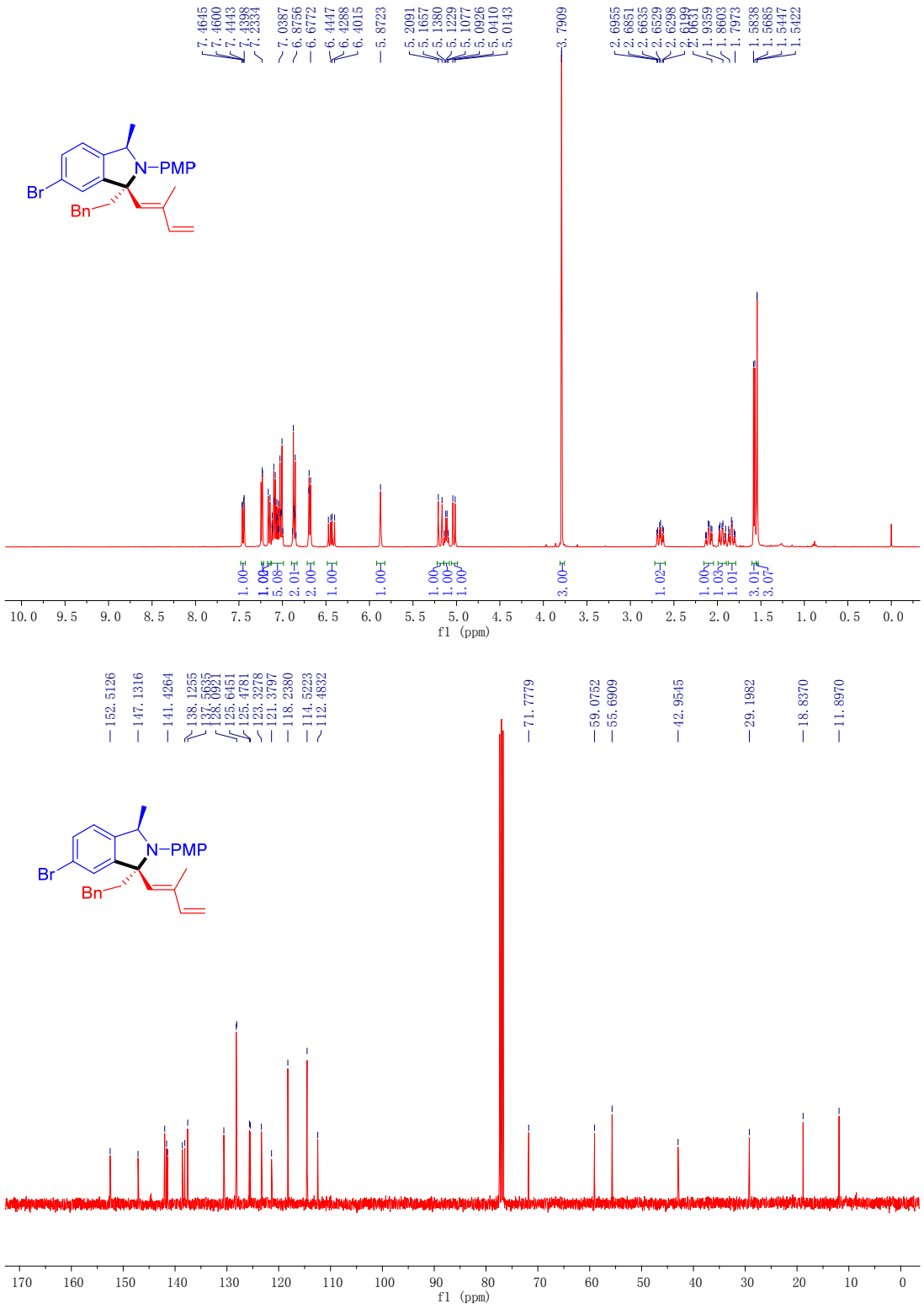
Supplementary Figure 111. ^{1}H NMR and ^{13}C NMR of **11gn**



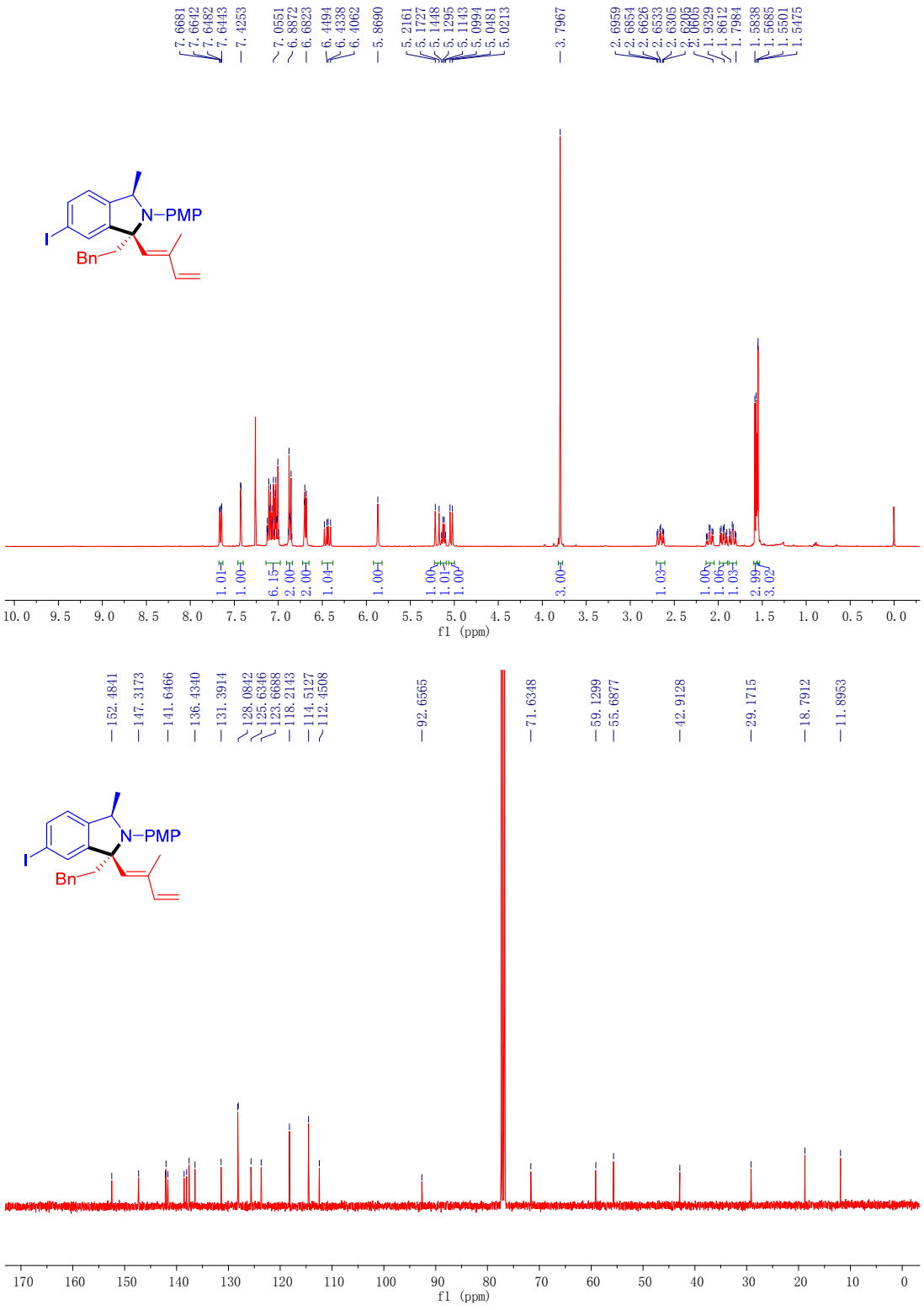
Supplementary Figure 112. ^{19}F NMR of **11gn**



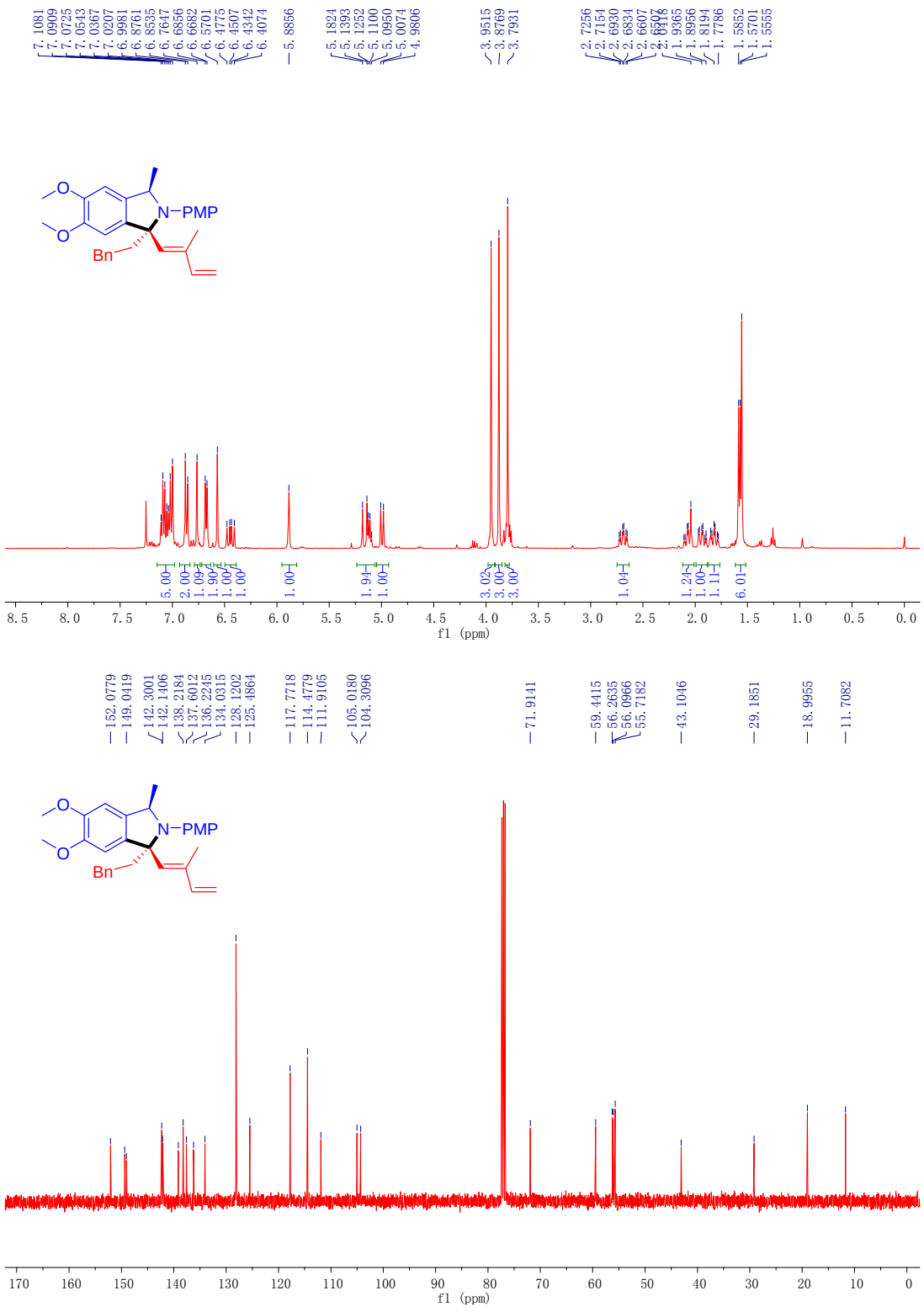
Supplementary Figure 113. ^{1}H NMR and ^{13}C NMR of **11hn**



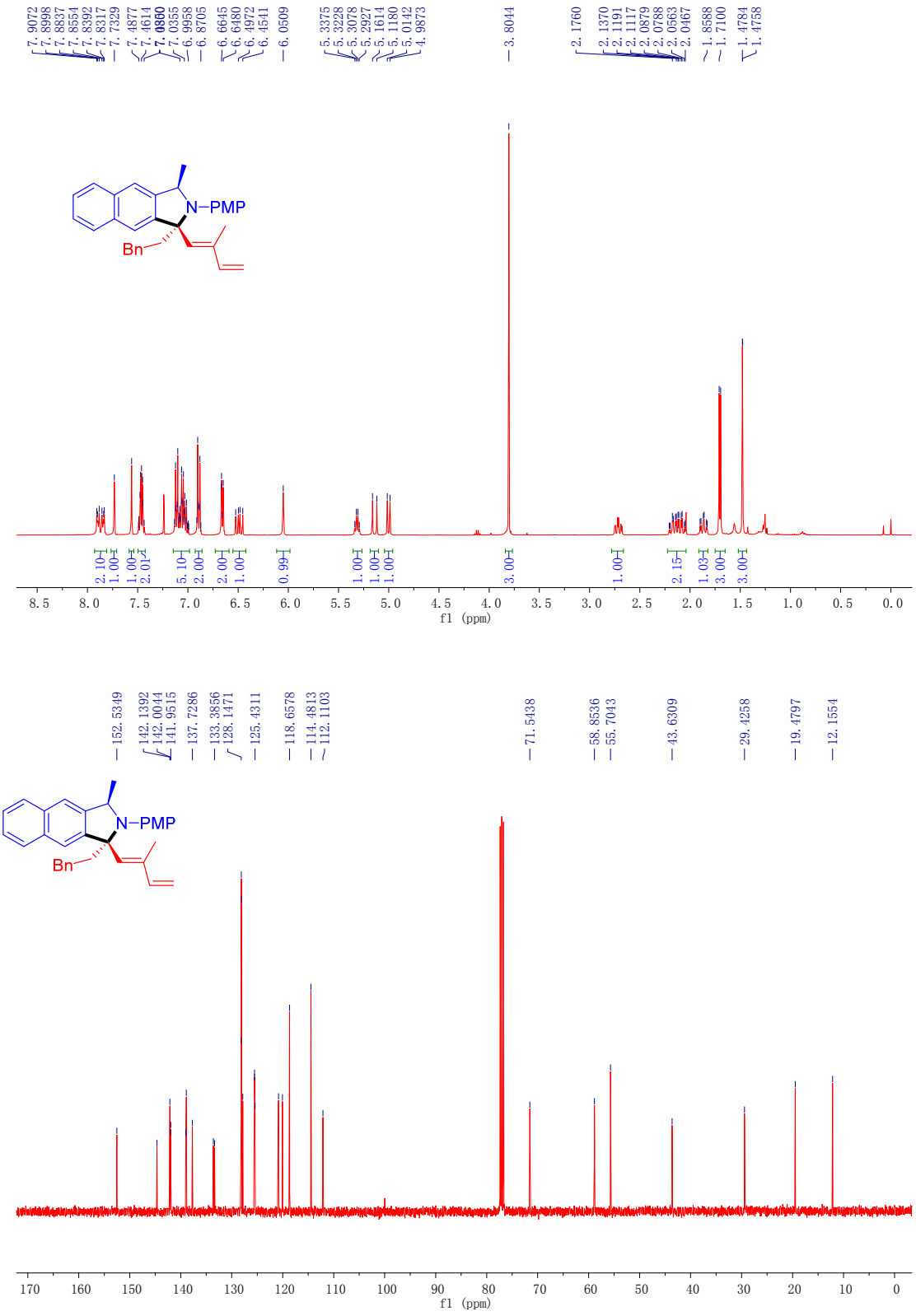
Supplementary Figure 114. ^{1}H NMR and ^{13}C NMR of **11in**



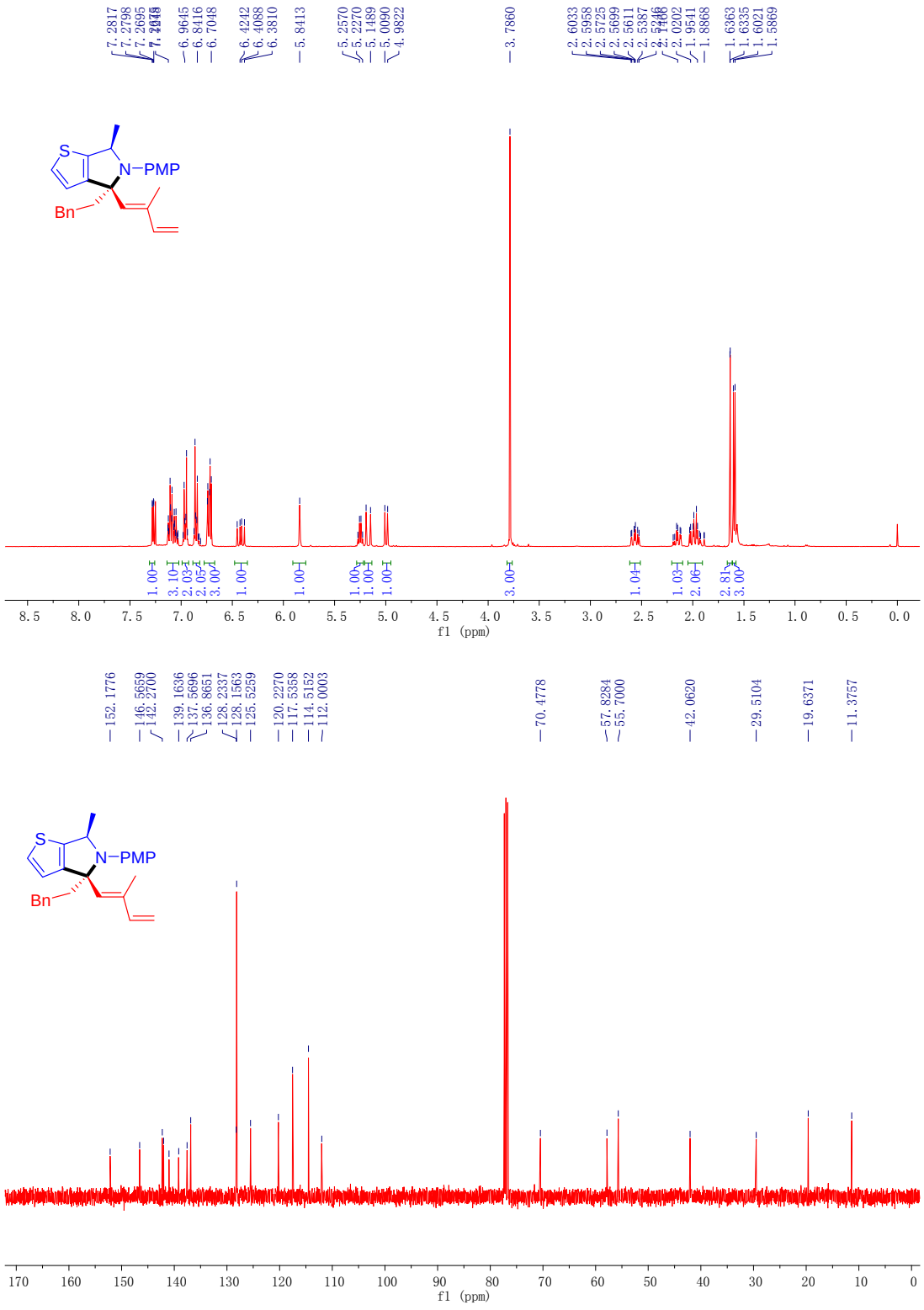
Supplementary Figure 115. ^{1}H NMR and ^{13}C NMR of **11jn**



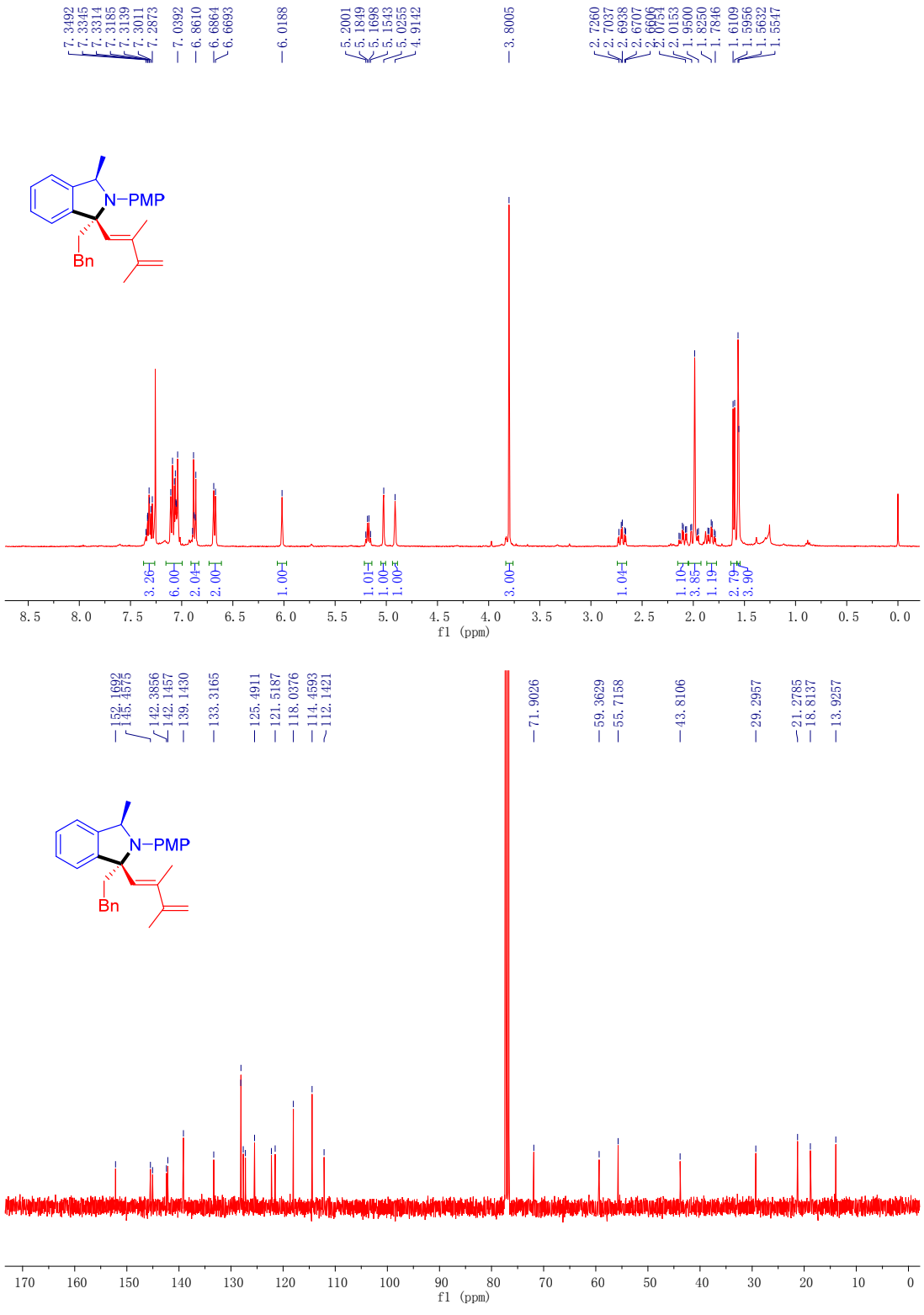
Supplementary Figure 116. ^{1}H NMR and ^{13}C NMR of **11kn**



Supplementary Figure 117. ^{1}H NMR and ^{13}C NMR of **11ln**



Supplementary Figure 118. ^{1}H NMR and ^{13}C NMR of **11mn**



Supplementary Figure 119. ^{1}H NMR and ^{13}C NMR of **11br**