Supplementary Information

Nickel-Catalyzed Stereospecific Reductive Cross-coupling of Vinyl Chlorosilanes with Axially Chiral Biaryl Electrophiles

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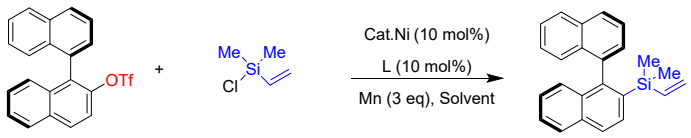
1. General Information

All chemicals were obtained from commercial sources and were used as received unless otherwise noted. All the reactions were carried out under argon atmosphere in a argon-filled glove box. The ^{1}H NMR spectra were recorded on a 400 MHz or 600 MHz NMR spectrometer. The ^{13}C NMR spectra were recorded at 101 MHz or 151 MHz. The ^{19}F NMR spectra were recorded at 376 MHz or 565 MHz. The ^{31}P NMR spectra were recorded at 243 MHz. Chemical shifts were expressed in parts per million (δ) downfield from the internal standard tetramethylsilane, and were reported as s (singlet), d (doublet), t (triplet), dd (doublet of doublet), dt (doublet of triplet), m (multiplet), brs (broad single), 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 glass back plates and visualized with UV light at 254 nm. Flash column chromatography was performed on silica gel.

2. General Synthetic Procedures

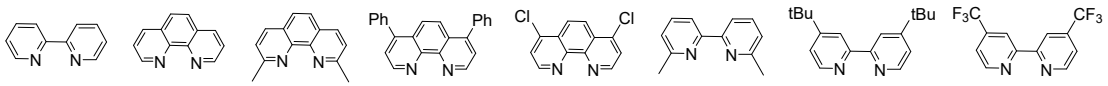
2.1 General procedure: The procedure was conducted in an argon-filled glove box. (DME)$NiCl_2$ (2.20 mg, 0.01 mmol), **L4** (3.33 mg, 0.01 mmol) and Mn (16.50 mg, 0.3 mmol, 3.0 eq) in DMA (1.0 mL) were charged sequentially into a 25 mL pressure tube under argon. The reaction mixture was stirred for 30 min at room temperature. Then **1a** (40.24 mg, 0.1 mmol) and **2a** (36.20 mg, 0.3 mmol) were added to the reaction mixture. The reaction tube was sealed and stirred at 30 °C. After the reaction was completed (12 h), the reaction mixture was filtered through a pad of celite, eluted with ethyl acetate, concentrated, and purified by silica gel chromatography to give the indicated product **3a**.

2.2 Supplementary Table 1, Optimization of reaction conditions of **1a** and **2a**[a].



1a **2a** **3a**

Entry	Cat.Ni	L	Solvent	T (°C)	Time (h)	Isolated yield (%) **3a**	ee (%) **3a**
1	$(DME)NiBr_2$	**L1**	Toluene	50	60h	NR	--
2	$(DME)NiBr_2$	**L1**	Dioxane	50	60h	16	94
3	$(DME)NiBr_2$	**L1**	THF	50	60h	NR	--
4	$(DME)NiBr_2$	**L1**	DMSO	50	60h	NR	--
5	$(DME)NiBr_2$	**L1**	DCE	50	60h	NR	--
6	$(DME)NiBr_2$	**L1**	CH_3CN	50	60h	NR	--
7	$(DME)NiBr_2$	**L1**	EtOH	50	60h	NR	--
8	$(DME)NiBr_2$	**L1**	DMF	50	60h	65	97
9	$(DME)NiBr_2$	**L1**	DMA	50	60h	83	97
10[b]	$(DME)NiBr_2$	**L1**	DMA	50	60h	16	97
11	$(DME)NiBr_2$	PPh_3	DMA	50	60h	NR	--
12	$(DME)NiBr_2$	BINAP	DMA	50	60h	NR	--
13	$(DME)NiBr_2$	**L2**	DMA	50	60h	89	97
14	$(DME)NiBr_2$	**L3**	DMA	50	60h	9	97
15	$(DME)NiBr_2$	**L4**	DMA	50	60h	97	97
16	$(DME)NiBr_2$	**L5**	DMA	50	60h	25	97
17	$(DME)NiBr_2$	**L6**	DMA	50	60h	17	97
18	$(DME)NiBr_2$	**L7**	DMA	50	60h	63	97
19	$(DME)NiBr_2$	**L8**	DMA	50	60h	88	97
20	$(DME)NiBr_2$	**L4**	DMA	30	60h	96	97
21	$(DME)NiCl_2$	**L4**	DMA	30	60h	99	97
22	$NiCl_2$	**L4**	DMA	30	60h	95	97
23	$Ni(cod)_2$	**L4**	DMA	30	60h	98	97
24	$Ni(acac)_2$	**L4**	DMA	30	60h	98	97
25	$(DME)NiCl_2$	**L4**	DMA	30	24h	99	97
26	$(DME)NiCl_2$	**L4**	DMA	30	12h	99	97
27	$(DME)NiCl_2$	**L4**	DMA	30	3h	99	97
28[c]	$(DME)NiCl_2$	**L4**	DMA	30	12h	55	97
29	--	**L4**	DMA	30	60h	NR	--

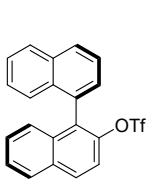


L1 **L2** **L3** **L4** **L5** **L6** **L7** **L8**

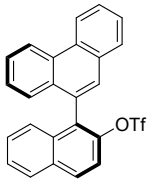
[a] Reaction conditions: **1a** (0.1 mmol), **2a** (0.3 mmol), [Ni] (10 mol%), **L** (10 mol%), Mn (3.0 eq) in solvent (1.0 mL), argon. Determined by HPLC analysis.[b] Zn instead of Mn.[c] $(DME)NiCl_2$ (5 mol%), **L4** (5 mol%).

2.3 Synthesis of Substrates and characterization of products

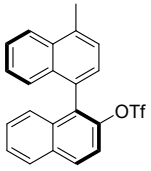
The starting materials aryl trifluoromethanesulfonates **1a**[1], **1b-1c**[2], **1d-1l**[3], **1m**[4], **1n-1q**[5], **1r**[6], **1s**[7], **1t**[8] were synthesized according to the literature procedure.



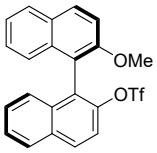
1a, 98% ee



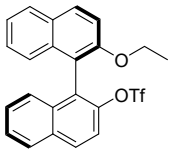
1b, 88% ee



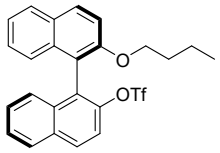
1c, 86% ee



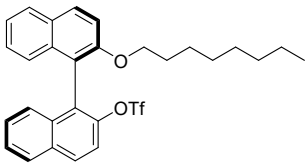
1d, 99% ee



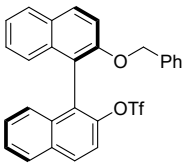
1e, 99% ee



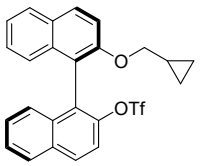
1f, 99% ee



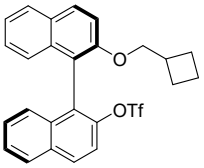
1g, 92% ee



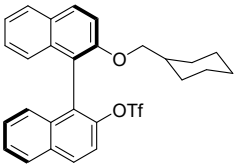
1h, 99% ee



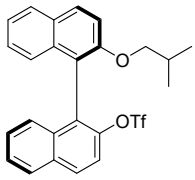
1i, 99% ee



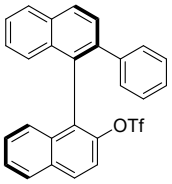
1j, 98% ee



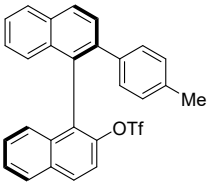
1k, 98% ee



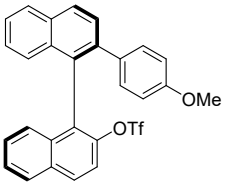
1l, 97% ee



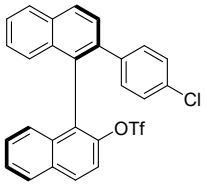
1m, 98% ee



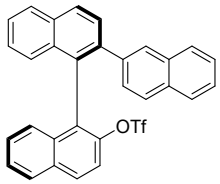
1n, 99% ee



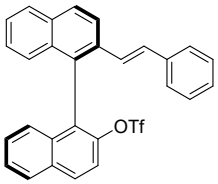
1o, 99% ee



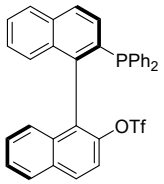
1p, 99% ee



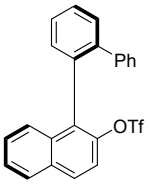
1q, 99% ee



1r, 97% ee

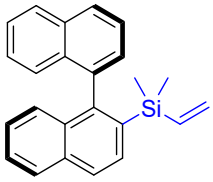


1s, 99% ee



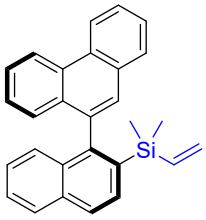
1t, 98% ee

The characterization data of axially chiral vinylsilanes are provided as follows:



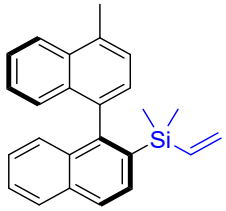
3a

3a, colorless oil. 33.85 mg, 99% yield, 97% ee, HPLC analysis on a Chiralcel OD-H column (hexane, flow rate 1.0 mL/min): t_R = 8.6 min (minor), t_R = 13.8 min (major). $[\alpha]_D^{19}$ = -22.9 (c 1.00, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 7.93 - 7.86 (m, 4H), 7.78 (d, *J* = 8.2 Hz, 1H), 7.56 - 7.52 (m, 1H), 7.42 (dd, *J* = 16.0, 6.8 Hz, 3H), 7.24 – 7.15 (m, 4H), 5.85 (dd, *J* = 20.0, 14.6 Hz, 1H), 5.68 (dd, *J* = 14.6, 3.8 Hz, 1H), 5.39 (dd, *J* = 20.0, 3.8 Hz, 1H), -0.18 (s, 3H), -0.22 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.3, 139.2, 138.8, 136.1, 134.1, 133.7, 133.4, 133.2, 131.2, 131.2, 128.8, 128.2, 128.1, 127.9, 127.1, 127.1, 126.9, 126.4, 126.0, 125.9, 125.2, -1.8, -1.9. HRMS (ESI, m/z): calcd for $C_{24}H_{22}NaSi^+$ $[M + Na]^+$: 361.1383, found 361.1386.



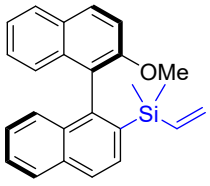
3b

3b, colorless oil. 38.09 mg, 98% yield, 87% ee, HPLC analysis on a Chiralcel OD-H column (hexane/isopropanol = 99/1, flow rate 1.0 mL/min): t_R = 4.4 min (major), t_R = 5.3 min (minor). $[\alpha]_D^{20}$ = 6.3 (c 1.00, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 8.78 (d, *J* = 8.2 Hz, 2H), 7.95 - 7.80 (m, 4H), 7.73 - 7.68 (m, 2H), 7.65 - 7.59 (m, 2H), 7.45 - 7.41 (m, 1H), 7.35 - 7.31 (m, 1H), 7.27 -7.22 (m, 2H), 7.19-7.15 (m, 1H), 5.88 (dd, *J* = 20.2, 14.6 Hz, 1H), 5.63 (dd, *J* = 14.6, 3.6 Hz, 1H), 5.34 (dd, *J* = 20.2, 3.6 Hz, 1H), -0.12 (s, 3H), -0.20 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.3, 138.8, 137.8, 136.3, 133.8, 133.4, 133.2, 131.5, 131.3, 131.2, 130.5, 130.2, 129.7, 128.8, 128.0, 127.9, 127.2, 127.0, 126.9, 126.7, 126.6, 126.4, 126.1, 122.8, -1.6, -1.9. HRMS (ESI, m/z): calcd for $C_{28}H_{25}Si^+$ $[M + H]^+$: 389.1720, found 389.1712.



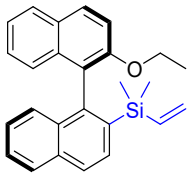
3c

3c, colorless oil. 35.25 mg, 99% yield, 86% ee, HPLC analysis on a Chiralcel OD-H column (hexane, flow rate 1.0 mL/min): t_R = 7.7 min (major), t_R = 11.9 min (minor). $[\alpha]_D^{20}$ = 17.5 (c 1.00, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, *J* = 8.6 Hz, 1H), 7.88 (dd, *J* = 13.0, 8.2 Hz, 2H), 7.77 (d, *J* = 8.2 Hz, 1H), 7.49-7.38 (m, 3H), 7.28 (d, *J* = 7.0 Hz, 1H), 7.22-7.17 (m, 4H), 5.87 (dd, *J* = 20.0, 14.6 Hz, 1H), 5.69 (dd, *J* = 14.6, 3.8 Hz, 1H), 5.41 (dd, *J* = 20.0, 3.8 Hz, 1H), 2.80 (s, 3H), -0.19 (s, 3H), -0.22 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.7, 139.0, 137.4, 136.2, 134.5, 134.2, 133.7, 133.4, 132.6, 131.3, 131.2, 128.5, 127.9, 127.8, 127.2, 126.8, 126.3, 126.0, 125.9, 125.7, 125.6, 124.3, 19.8, -1.7, -1.8. HRMS (ESI, m/z): calcd for $C_{25}H_{24}NaSi^+$ $[M + Na]^+$: 375.1539, found 375.1548.



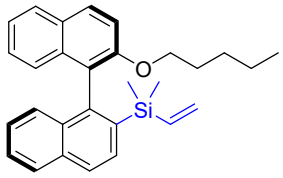
3d

3d, colorless oil. 36.81 mg, 99% yield, 98% ee, HPLC analysis on a Chiralcel OD-H column (hexane, flow rate 1.0 mL/min): t_R = 10.3 min (minor), t_R = 12.2 min (major). $[\alpha]_D^{19}$ = 8.4 (c 1.00, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 9.0 Hz, 1H), 7.92 – 7.79 (m, 4H), 7.44 - 7.40 (m, 1H), 7.36 (d, *J* = 9.0 Hz, 1H), 7.29 – 7.26 (m, 1H), 7.19 – 7.13 (m, 3H), 6.92 (d, *J* = 8.6 Hz, 1H), 5.80 (dd, *J* = 20.0, 14.6 Hz, 1H), 5.65 (dd, *J* = 14.6, 4.0 Hz, 1H), 5.35 (dd, *J* = 20.0, 4.0 Hz, 1H), 3.72 (s, 3H), -0.19 (s, 3H), -0.20 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.0, 141.6, 138.7, 136.6, 135.3, 134.0, 133.1, 131.5, 130.7, 129.7, 128.8, 128.0, 127.8, 126.7, 126.4, 126.4, 126.3, 126.0, 123.6, 123.5, 113.0, 55.8, -2.1, -2.2. HRMS (ESI, m/z): calcd for $C_{25}H_{24}NaOSi^+$ $[M + Na]^+$: 391.1489, found 391.1490.



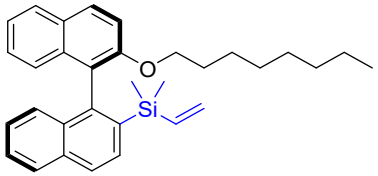
3e

3e, colorless oil. 38.21 mg, 99% yield, 99% ee, HPLC analysis on a Chiralcel OD-H column (hexane, flow rate 1.0 mL/min): t_R = 9.7 min (minor), t_R = 11.5 min (major). $[\alpha]_D^{20}$ = 13.6 (c 1.00, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 7.86 – 7.69 (m, 5H), 7.35 – 7.31 (m, 1H), 7.25 (d, *J* = 9.0 Hz, 1H), 7.18 (t, *J* = 7.2 Hz, 1H), 7.10 – 7.08 (m, 2H), 7.05 (t, *J* = 7.4 Hz, 1H), 6.84 (d, *J* = 8.4 Hz, 1H), 5.74 (dd, *J* = 20.0, 14.6 Hz, 1H), 5.57 (dd, *J* = 14.6, 3.8 Hz, 1H), 5.29 (dd, *J* = 20.0, 3.8 Hz, 1H), 3.91 (q, *J* = 7.0 Hz, 2H), 0.96 (t, *J* = 7.0 Hz, 3H), -0.26 (s, 3H), -0.28 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.4, 141.8, 138.8, 136.6, 135.4, 133.9, 133.1, 131.5, 130.7, 129.5, 128.8, 127.9, 127.7, 126.6, 126.5, 126.3, 126.2, 126.0, 125.8, 124.1, 123.5, 114.4, 64.2, 15.1, -2.2, -2.2. HRMS (ESI, m/z): calcd for $C_{26}H_{26}NaOSi^+$ $[M + Na]^+$: 405.1645, found 405.1646.



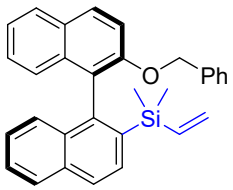
3f

3f, colorless oil. 42.46 mg, 99% yield, 99% ee, HPLC analysis on a Chiralcel OD-H column (hexane, flow rate 1.0 mL/min): t_R = 7.7 min (minor), t_R = 8.1 min (major). $[\alpha]_D^{21}$ = 19.2 (c 1.00, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 7.94 – 7.76 (m, 5H), 7.43 – 7.39 (m, 1H), 7.33 (d, *J* = 9.0 Hz, 1H), 7.29 – 7.25 (m, 1H), 7.18 – 7.13 (m, 3H), 6.98 (d, *J* = 8.4 Hz, 1H), 5.81 (dd, *J* = 20.0, 14.6 Hz, 1H), 5.65 (dd, *J* = 14.6, 4.0 Hz, 1H), 5.36 (dd, *J* = 20.0, 4.0 Hz, 1H), 3.96 – 3.82 (m, 2H), 1.42 – 1.34 (m, 2H), 1.00 - 0.94 (m, 2H), 0.91 - 0.85 (m, 2H), 0.60 (t, *J* = 7.2 Hz, 3H), -0.18 (s, 3H), -0.21 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.7, 141.7, 138.8, 136.5, 135.3, 134.0, 133.2, 131.4, 130.7, 129.5, 128.8, 127.8, 127.7, 126.5, 126.4, 126.2, 126.1, 126.0, 125.7, 124.4, 123.5, 114.6, 68.9, 29.1, 28.0, 22.2, 14.0, -2.1, -2.2. HRMS (ESI, m/z): calcd for $C_{29}H_{32}NaOSi^+$ $[M + Na]^+$: 447.2115, found 447.2119.



3g

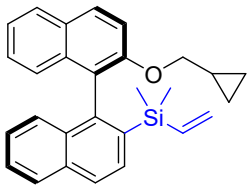
3g, colorless oil. 46.67 mg, 99% yield, 91% ee, HPLC analysis on a Chiralcel OD-H column (hexane, flow rate 1.0 mL/min): t_R = 8.1 min (minor), t_R = 8.8 min (major). $[\alpha]_D^{21}$ = 15.5 (c 1.00, $CHCl_3$). ^1H NMR (600 MHz, $CDCl_3$) δ 7.93 (d, *J* = 9.0 Hz, 1H), 7.87 (dd, *J* = 14.2, 8.2 Hz, 2H), 7.82 (d, *J* = 8.2 Hz, 1H), 7.77 (d, *J* = 8.2 Hz, 1H), 7.42 – 7.39 (m, 1H), 7.33 (d, *J* = 9.0 Hz, 1H), 7.27 (t, *J* = 7.4 Hz, 1H), 7.18 – 7.13 (m, 3H), 6.97 (d, *J* = 8.6 Hz, 1H), 5.81 (dd, *J* = 20.2, 14.6 Hz, 1H), 5.65 (dd, *J* = 14.6, 3.8 Hz, 1H), 5.36 (dd, *J* = 20.2, 3.8 Hz, 1H), 3.95 – 3.83 (m, 2H), 1.40 – 1.34 (m, 2H), 1.22 – 1.18 (m, 2H), 1.08 – 1.03 (m, 2H), 0.99 – 0.92 (m, 4H), 0.90 – 0.87 (m, 2H), 0.84 (t, *J* = 7.2 Hz, 3H), -0.18 (s, 3H), -0.21 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.7, 141.8, 138.9, 136.6, 135.3, 134.0, 133.2, 131.4, 130.7, 129.5, 128.9, 127.9, 127.8, 126.6, 126.5, 126.3, 126.1, 126.1, 125.7, 124.5, 123.5, 114.7, 68.9, 31.8, 29.4, 29.2, 29.1, 25.7, 22.8, 14.2, -2.1, -2.1. HRMS (ESI, m/z): calcd for $C_{32}H_{38}NaOSi^+$ $[M + Na]^+$: 489.2584, found 489.2592.



3h

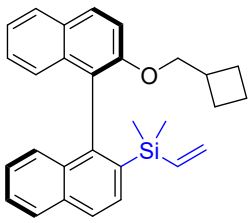
3h, colorless oil. 44.46 mg, 99% yield, 99% ee, HPLC analysis on a Chiralcel OD-H column (hexane, flow rate 1.0 mL/min): t_R = 22.1 min (minor), t_R = 25.1 min (major). $[\alpha]_D^{21}$ = 0.9 (c 1.00, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 7.93 – 7.88 (m, 3H), 7.82 - 7.80 (m, 2H), 7.45 – 7.41 (m, 1H), 7.35 – 7.27 (m, 2H), 7.23 – 7.12 (m, 6H), 7.03 – 7.00 (d, *J* = 8.4 Hz, 1H), 6.95 – 6.92 (m, 2H), 5.80 (dd, *J* = 20.0, 14.6 Hz, 1H), 5.63 (dd, *J* = 14.6, 4.0 Hz, 1H), 5.34 (dd, *J* = 20.0, 4.0 Hz, 1H), 5.06 – 5.00 (m, 2H), -0.18 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.2, 141.5, 138.7, 137.7, 136.7, 135.3, 134.0, 133.1, 131.5, 130.8, 129.6, 129.1, 128.3, 128.0, 127.8, 127.4, 126.7, 126.5, 126.4, 126.3, 126.1, 125.9, 124.8, 123.8,

115.0, 70.4, -2.1, -2.1. HRMS (ESI, m/z): calcd for $C_{31}H_{28}NaOSi^+$ [M + Na]$^+$: 467.1802, found 467.1807.



3i

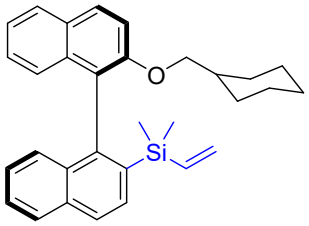
3i, colorless oil. 40.86 mg, 98% yield, 99% ee, HPLC analysis on a Chiralcel OD-H column (hexane, flow rate 1.0 mL/min): t_R = 11.7 min (minor), t_R = 12.6 min (major). $[\alpha]_D^{21}$ = 25.2 (c 1.00, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 – 7.77 (m, 5H), 7.43 – 7.39 (m, 1H), 7.33 (d, *J* = 9.0 Hz, 1H), 7.29 – 7.25 (m, 1H), 7.21 – 7.13 (m, 3H), 6.96 (d, *J* = 8.6 Hz, 1H), 5.83 (dd, *J* = 20.0, 14.6 Hz, 1H), 5.65 (dd, *J* = 14.6, 4.0 Hz, 1H), 5.37 (dd, *J* = 20.0, 4.0 Hz, 1H), 3.83 – 3.74 (m, 2H), 0.91 - 0.83 (m, 2H), 0.25 – 0.17 (m, 2H), 0.08 – 0.13 (m, 1H), -0.17 (s, 3H), -0.20 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.5, 141.7, 138.8, 136.6, 135.4, 134.0, 133.2, 131.4, 130.7, 129.4, 128.9, 127.9, 127.7, 126.6, 126.5, 126.3, 126.1, 126.0, 125.8, 124.7, 123.6, 115.1, 72.6, 10.5, 2.8, 2.7, -2.1, -2.2. HRMS (ESI, m/z): calcd for $C_{28}H_{28}NaOSi^+$ [M + Na]$^+$: 431.1802, found 431.1804.



3j

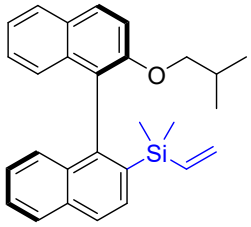
3j, colorless oil. 42.26 mg, 99% yield, 96% ee, HPLC analysis on a Chiralcel OD-H column (hexane, flow rate 1.0 mL/min): t_R = 8.9 min (minor), t_R = 9.7 min (major). $[\alpha]_D^{21}$ = 22.4 (c 1.00, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, *J* = 9.0 Hz, 1H), 7.86 (dd, *J* = 18.2, 8.6 Hz, 3H), 7.77 (d, *J* = 8.4 Hz, 1H), 7.43 – 7.39 (m, 1H), 7.34 – 7.26 (m, 2H), 7.19 – 7.15 (m, 3H), 7.02 (d, *J* = 8.4 Hz, 1H), 5.81 (dd, *J* = 20.0, 14.6 Hz, 1H), 5.65 (dd, *J* = 14.6, 4.0 Hz, 1H), 5.35 (dd, *J* = 20.0, 4.0 Hz, 1H), 3.91 - 3.87 (m, 1H), 3.81 – 3.77 (m, 1H), 2.38 – 2.35 (m, 1H), 1.67 – 1.32 (m, 6H), -0.18 (s, 3H), -0.21 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.7, 141.8, 138.8, 136.5, 135.3, 133.9, 133.2, 131.4, 130.7, 129.5, 128.9,

127.8, 127.7, 126.5, 126.4, 126.3, 126.1, 126.0, 125.7, 124.5, 123.5, 114.6, 72.1, 34.8, 24.1, 24.1, 18.2, -2.1, -2.2. HRMS (ESI, m/z): calcd for $C_{29}H_{30}NaOSi^+$ $[M + Na]^+$: 445.1958, found 445.1962.



3k

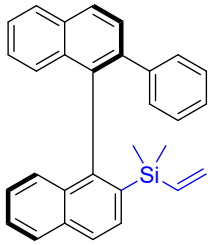
3k, colorless oil. 45.07 mg, 99% yield, 97% ee, HPLC analysis on a Chiralcel OD-H column (hexane, flow rate 1.0 mL/min): t_R = 7.5 min (minor), t_R = 8.2 min (major). $[\alpha]_D^{21}$ = 21.4 (c 1.00, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 7.93 – 7.76 (m, 5H), 7.42 – 7.38 (m, 1H), 7.32 – 7.25 (m, 2H), 7.19 – 7.13 (m, 3H), 7.01 (d, *J* = 8.6 Hz, 1H), 5.81 (dd, *J* = 20.0, 14.6 Hz, 1H), 5.64 (dd, *J* = 14.6, 4.0 Hz, 1H), 5.35 (dd, *J* = 20.0, 4.0 Hz, 1H), 3.74 – 3.63 (m, 2H), 1.43 – 1.41 (m, 1H), 1.36 – 1.22 (m, 4H), 0.99 – 0.85 (m, 4H), 0.61 – 0.53 (m, 2H), -0.18 (s, 3H), -0.21 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.8, 141.7, 138.8, 136.5, 135.2, 133.9, 133.2, 131.4, 130.7, 129.4, 128.8, 127.8, 127.7, 126.6, 126.4, 126.2, 126.1, 125.7, 124.5, 123.5, 114.8, 74.4, 37.7, 29.6, 29.4, 26.5, 25.7, 25.7, -2.1, -2.1. HRMS (ESI, m/z): calcd for $C_{31}H_{34}NaOSi^+$ $[M + Na]^+$: 473.2271, found 473.2276.



3l

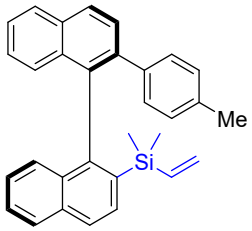
3l, colorless oil. 41.06 mg, 99% yield, 94% ee, HPLC analysis on a Chiralcel OD-H column (hexane, flow rate 1.0 mL/min): t_R = 8.2 min (minor), t_R = 8.9 min (major). $[\alpha]_D^{21}$ = 20.0 (c 1.00, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, *J* = 9.0 Hz, 1H), 7.89 – 7.82 (m, 3H), 7.77 (d, *J* = 8.2 Hz, 1H), 7.43 – 7.39 (m, 1H), 7.33 – 7.26 (m, 2H), 7.20 – 7.14 (m, 3H), 7.01 (d, *J* = 8.4 Hz, 1H), 5.80 (dd, *J* = 20.0, 14.6 Hz, 1H), 5.64 (dd, *J* = 14.6, 4.0 Hz, 1H), 5.35 (dd, *J* = 20.0, 4.0 Hz, 1H), 3.73 – 3.59 (m, 2H), 1.67 – 1.61 (m, 1H), 0.53 – 0.49 (m, 6H), -0.19 (s, 3H), -0.21 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.7, 141.8, 138.8, 136.5, 135.2, 133.9, 133.2, 131.3, 130.7, 129.5, 128.8, 127.8, 127.7, 126.5, 126.4, 126.2,

126.1, 126.0, 125.7, 124.4, 123.5, 114.5, 75.1, 28.4, 19.0, 18.9, -2.1, -2.2. HRMS (ESI, m/z): calcd for $C_{28}H_{30}NaOSi^+$ [M + Na]$^+$: 433.1958, found 433.1964.



3m

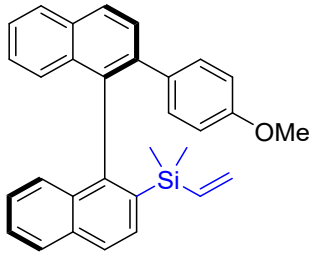
3m, colorless oil. 41.46 mg, 99% yield, 98% ee, HPLC analysis on a Chiralcel OD-H column (hexane, flow rate 1.0 mL/min): t_R = 16.0 min (minor), t_R = 17.9 min (major). $[\alpha]_D^{21}$ = 61.9 (c 1.00, $CHCl_3$). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.01 (d, *J* = 8.6 Hz, 1H), 7.91 (d, *J* = 8.2 Hz, 1H), 7.81 – 7.79 (m, 2H), 7.64 (d, *J* = 8.6 Hz, 1H), 7.59 (d, *J* = 8.4 Hz, 1H), 7.44 – 7.37 (m, 2H), 7.26 – 7.18 (m, 3H), 7.14 (d, *J* = 8.4 Hz, 1H), 7.05 – 7.03 (m, 2H), 7.01 – 6.96 (m, 3H), 5.64 – 5.59 (m, 2H), 5.30 – 5.24 (m, 1H), -0.30 (s, 3H), -0.34 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.2, 141.6, 138.9, 138.3, 136.9, 136.8, 134.5, 134.0, 133.3, 132.7, 131.4, 131.0, 129.6, 128.5, 128.3, 128.0, 127.9, 127.5, 127.2, 126.6, 126.5, 126.4, 126.2, 125.8, -2.1, -2.2. HRMS (ESI, m/z): calcd for $C_{30}H_{26}NaSi^+$ [M + Na]$^+$: 437.1696, found 437.1703.



3n

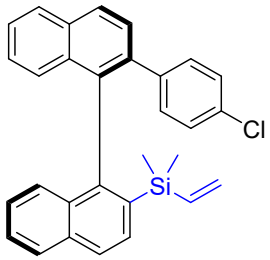
3n, colorless oil. 42.86 mg, 99% yield, 99% ee, HPLC analysis on a Chiralcel MD-H column (hexane/isopropanol = 99/1, flow rate 1.0 mL/min): t_R = 3.8 min (minor), t_R = 4.2 min (major). $[\alpha]_D^{23}$ = 57.6 (c 1.00, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 8.4 Hz, 1H), 7.90 (d, *J* = 8.2 Hz, 1H), 7.80 (d, *J* = 8.4 Hz, 2H), 7.62 (t, *J* = 8.8 Hz, 2H), 7.43 – 7.36 (m, 2H), 7.27 – 7.17 (m, 3H), 7.11 (d, *J* = 8.4 Hz, 1H), 6.94 (d, *J* = 8.2 Hz, 2H), 6.79 (d, *J* = 8.0 Hz, 2H), 5.68 – 5.58 (m, 2H), 5.32 – 5.24 (m, 1H), 2.14 (s, 3H), -0.30 (s, 3H), -0.34 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.4, 138.9, 138.6, 138.3, 136.9, 136.6, 136.1, 134.5, 133.9, 133.3, 132.5, 131.4, 131.0, 129.4, 128.6, 128.3, 128.2, 127.9, 127.8,

127.5, 127.2, 126.5, 126.3, 126.2, 125.7, 21.1, -2.1, -2.2. HRMS (ESI, m/z): calcd for $C_{31}H_{28}NaSi^+$ [M + Na]$^+$: 451.1852, found 451.1857.



3o

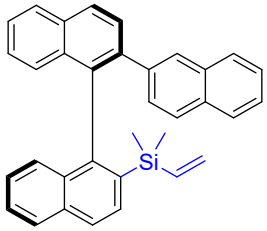
3o, colorless oil. 44.40 mg, 99% yield, 99% ee, HPLC analysis on a Chiralcel MD-H column (hexane/isopropanol = 99.5/0.5, flow rate 1.0 mL/min): t_R = 5.5 min (minor), t_R = 5.8 min (major). $[\alpha]_D^{23}$ = 63.1 (c 1.00, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 8.4 Hz, 1H), 7.90 (d, *J* = 8.2 Hz, 1H), 7.82 – 7.80 (m, 2H), 7.63 – 7.60 (m, 2H), 7.43 – 7.37 (m, 2H), 7.27 – 7.19 (m, 3H), 7.10 (d, *J* = 8.4 Hz, 1H), 6.97 (d, *J* = 8.6 Hz, 2H), 6.52 (d, *J* = 8.6 Hz, 2H), 5.67 – 5.60 (m, 2H), 5.32 – 5.25 (m, 1H), 3.62 (s, 3H), -0.30 (s, 3H), -0.34 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.3, 143.5, 138.6, 138.4, 136.9, 136.5, 134.6, 134.1, 134.0, 133.4, 132.5, 131.5, 131.0, 130.6, 128.6, 128.2, 128.0, 127.8, 127.4, 127.2, 126.6, 126.3, 126.2, 126.2, 125.6, 113.1, 55.2, -2.1, -2.2. HRMS (ESI, m/z): calcd for $C_{31}H_{32}NOSi^+$ [M + NH_4]$^+$: 462.2248, found 462.2250.



3p

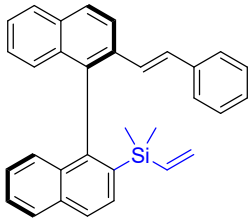
3p, colorless oil. 44.00 mg, 98% yield, 99% ee, HPLC analysis on a Chiralcel MD-H column (hexane/isopropanol = 99/1, flow rate 1.0 mL/min): t_R = 3.9 min (minor), t_R = 4.3 min (major). $[\alpha]_D^{24}$ = 64.0 (c 1.00, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, *J* = 8.6 Hz, 1H), 7.92 (d, *J* = 8.2 Hz, 1H), 7.82 (d, *J* = 8.4 Hz, 2H), 7.62 - 7.57 (m 2H), 7.47 – 7.38 (m, 2H), 7.24 – 7.19 (m, 3H), 7.13 (d, *J* = 8.6 Hz, 1H), 6.99 – 6.93 (m, 4H), 5.62 – 5.53 (m, 2H), 5.30 – 5.26 (m, 1H), -0.27 (s, 3H), -0.34 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.8, 140.1, 138.0, 137.7, 137.0, 134.4, 133.8, 133.3, 132.7, 132.6, 131.4,

131.2, 130.8, 128.5, 128.1, 128.0, 127.9, 127.7, 127.5, 127.0, 126.8, 126.5, 126.4, 126.3, 126.1, -2.1, -2.2. HRMS (ESI, m/z): calcd for $C_{30}H_{25}ClKSi^+$ $[M + K]^+$: 487.1046, found 487.1047.



3q

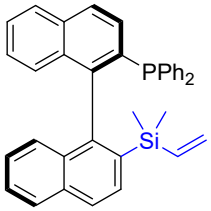
3q, colorless oil. 46.46 mg, 99% yield, 99% ee, HPLC analysis on a Chiralcel MD-H column (hexane/isopropanol = 99/1, flow rate 1.0 mL/min): t_R = 4.4 min (minor), t_R = 5.1 min (major). $[\alpha]_D^{24}$ = 82.3 (c 1.00, $CHCl_3$). ^1H NMR (600 MHz, $CDCl_3$) δ 8.05 (d, *J* = 8.6 Hz, 1H), 7.95 (d, *J* = 8.2 Hz, 1H), 7.81 – 7.71 (m, 3H), 7.61 (d, *J* = 7.6 Hz, 1H), 7.58 – 7.53 (m, 2H), 7.48 – 7.41 (m, 3H), 7.39 (t, *J* = 7.4 Hz, 1H), 7.35 – 7.29 (m, 3H), 7.26 – 7.22 (m, 2H), 7.20 – 7.16 (m, 2H), 5.68 – 5.52 (m, 2H), 5.26 (dd, *J* = 19.4, 4.4 Hz, 1H), -0.27 (s, 3H), -0.34 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.1, 139.1, 138.9, 138.2, 137.1, 137.0, 134.5, 133.9, 133.4, 132.9, 132.7, 131.9, 131.4, 131.1, 128.8, 128.7, 128.3, 128.1, 128.0, 127.9, 127.7, 127.5, 127.4, 127.2, 126.9, 126.7, 126.4, 126.3, 126.2, 125.9, 125.8, 125.7, -2.0, -2.1. HRMS (ESI, m/z): calcd for $C_{34}H_{28}NaSi^+$ $[M + Na]^+$: 487.1852, found 487.1859.



3r

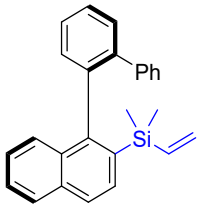
3r, colorless oil. 44.00 mg, 99% yield, 97% ee, HPLC analysis on a Chiralcel MD-H column (hexane/isopropanol = 99/1, flow rate 1.0 mL/min): t_R = 4.3 min (minor), t_R = 5.0 min (major). $[\alpha]_D^{15}$ = 43.5 (c 1.00, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 7.97 (q, *J* = 8.8 Hz, 3H), 7.92 – 7.87 (m, 1H), 7.86 – 7.82 (m, 1H), 7.45 – 7.36 (m, 2H), 7.20 – 7.09 (m, 10H), 7.01 (d, *J* = 8.4 Hz, 1H), 6.66 (d, *J* = 16.4 Hz, 1H), 5.77 (dd, *J* = 20.0, 14.6 Hz, 1H), 5.62 (dd, *J* = 14.6, 3.8 Hz, 1H), 5.35 (dd, *J* = 20.0, 3.8 Hz, 1H), -0.21 (s, 3H), -0.23 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.1, 138.2, 137.6, 137.6, 137.1, 134.7,

134.2, 133.8, 133.1, 132.9, 131.4, 131.1, 129.4, 128.6, 128.4, 127.9, 127.8, 127.7, 127.5, 127.0, 126.8, 126.6, 126.5, 126.4, 126.3, 125.9, 122.5, -2.2. HRMS (ESI, m/z): calcd for $C_{32}H_{28}NaSi^+$ $[M + Na]^+$: 463.1852, found 463.1860.



3s

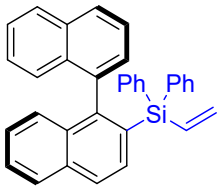
3s, colorless oil. 23.30 mg, 45% yield, 99% ee, HPLC analysis on a Chiralcel AD-H column (hexane/isopropanol = 99.5/0.5, flow rate 1.0 mL/min): t_R = 5.0 min (major), t_R = 6.9 min (minor). $[\alpha]_D^{25}$ = 6.4 (c 1.00, $CHCl_3$). ^1H NMR (600 MHz, $CDCl_3$) δ 7.92 (d, *J* = 8.2 Hz, 1H), 7.90 – 7.87 (m, 2H), 7.80 – 7.77 (m, 2H), 7.51 (dd, *J* = 8.6, 2.8 Hz, 1H), 7.47 -7.44 (m, 1H), 7.30 – 7.26 (m, 5H), 7.24 – 7.19 (m, 3H), 7.14 – 7.12 (m, 1H), 7.05 – 7.03 (m, 2H), 6.95 – 6.92 (m, 2H), 6.74 – 6.71 (m, 1H), 6.65 (d, *J* = 8.4 Hz, 1H), 5.73 (dd, *J* = 20.0, 14.6 Hz, 1H), 5.63 (dd, *J* = 14.6, 4.0 Hz, 1H), 5.37 (dd, *J* = 20.0, 4.0 Hz, 1H), -0.26 (s, 3H), -0.28 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 146.7 (d, *J* = 33.8 Hz), 143.8 (d, *J* = 8.5 Hz), 138.5, 138.1 (d, *J* = 14.3 Hz), 137.5 (d, *J* = 13.1 Hz), 136.5 (d, *J* = 2.3 Hz), 136.0 (d, *J* = 12.7 Hz), 134.4 (d, *J* = 6.7 Hz), 134.2, 134.1, 133.8, 133.7, 133.5, 133.4, 133.2 (d, *J* = 3.0 Hz), 131.2, 131.1, 130.1 (d, *J* = 1.5 Hz), 128.5, 128.4, 128.4, 128.3, 128.1, 128.0, 127.9, 127.8, 127.6 (d, *J* = 2.7), 127.6, 127.2, 127.0, 126.8, 126.4, 126.0, 125.4, -1.9, -2.0. ^{31}P NMR (243 MHz, $CDCl_3$) δ -15.83 (s). HRMS (ESI, m/z): calcd for $C_{36}H_{32}PSi^+$ $[M + H]^+$: 523.2005, found 523.2004.



3t

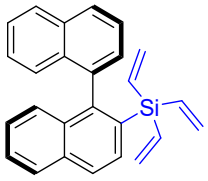
3t, colorless oil. 36.40 mg, 99% yield, 69% ee, HPLC analysis on a Chiralcel OD-H column (hexane/isopropanol = 99.5/0.5, flow rate 1.0 mL/min): t_R = 4.8 min (minor), t_R = 5.9 min (major). $[\alpha]_D^{26}$ = 16.7 (c 1.00, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, *J* = 8.0 Hz, 2H), 7.61 (d, *J* = 8.4 Hz,

1H), 7.55 – 7.52 (m, 2H), 7.44 – 7.32 (m, 4H), 7.27 – 7.23 (m, 1H), 7.06 – 7.03 (m, 2H), 6.99 – 6.95 (m, 3H), 5.95 (dd, *J* = 19.8, 14.6 Hz, 1H), 5.82 (dd, *J* = 14.6, 4.0 Hz, 1H), 5.53 (dd, *J* = 19.8, 4.0 Hz, 1H), -0.00 (s, 3H), -0.01 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.1, 141.8, 141.1, 140.0, 138.9, 135.3, 133.4, 132.7, 132.3, 131.5, 131.1, 130.1, 129.2, 128.3, 127.8, 127.6, 127.0, 126.9, 126.5, 126.4, 126.1, 125.8, -1.6, -2.0. HRMS (ESI, m/z): calcd for $C_{26}H_{25}Si^+$ $[M + H]^+$: 365.1720, found 365.1719.



3v

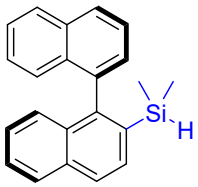
3v, white solid, m.p. 71 - 72 ℃. 43.00 mg, 93% yield, 96% ee, HPLC analysis on a Chiralcel MD-H column (hexane, flow rate 1.0 mL/min): t_R = 12.4 min (minor), t_R = 19.7 min (major). $[\alpha]_D^{17}$ = 6.0 (c 0.50, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (t, *J* = 7.4 Hz, 2H), 7.76 (d, *J* = 8.2 Hz, 2H), 7.69 (d, *J* = 8.4 Hz, 1H), 7.47 – 7.43 (m, 1H), 7.35 – 7.32 (m, 1H), 7.27 – 7.12 (m, 16H), 5.50 (dd, *J* = 13.0, 5.0 Hz, 1H), 5.27 – 5.11 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.8, 138.9, 136.0, 135.7, 135.0, 134.9, 134.0, 133.9, 133.4, 133.3, 133.2, 133.1, 132.9, 129.2, 129.1, 128.7, 128.2, 128.0, 127.6, 127.5, 127.3, 127.0, 126.7, 126.8, 126.1, 125.9, 125.6, 125.1. HRMS (ESI, m/z): calcd for $C_{34}H_{27}Si^+$ $[M + H]^+$: 463.1877, found 463.1863.



3w

3w, colorless oil. 34.50 mg, 95% yield, 98% ee, HPLC analysis on a Chiralcel MD-H column (hexane, flow rate 1.0 mL/min): t_R = 7.8 min (minor), t_R = 12.6 min (major). $[\alpha]_D^{17}$ = -8.4 (c 1.00, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 – 7.87 (m, 4H), 7.80 (d, *J* = 8.4 Hz, 1H), 7.49 – 7.35 (m, 4H), 7.23 – 7.19 (m, 3H), 7.14 (d, *J* = 8.4 Hz, 1H), 5.78 – 5.72 (m, 4H), 5.68 – 5.63 (m, 2H), 5.44 (dd, *J* = 19.6, 4.6 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.1, 139.3, 134.3, 134.2, 134.1, 133.9, 133.5, 133.3, 133.2,

132.0, 129.0, 128.2, 128.0, 127.9, 127.2, 127.1, 126.8, 126.6, 126.1, 126.0, 125.8, 125.0. HRMS (ESI, m/z): calcd for $C_{26}H_{22}NaSi^+$ $[M + Na]^+$: 363.1383, found 363.1385.

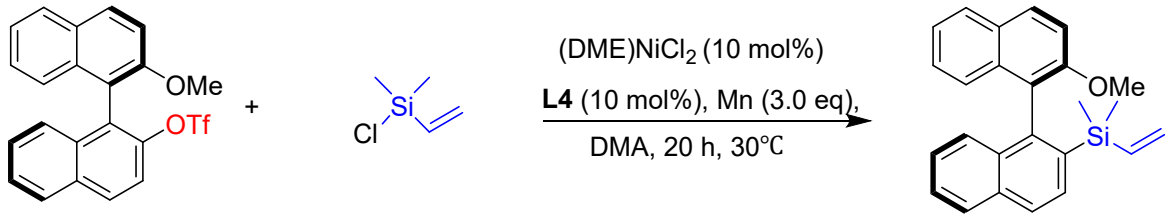


3x

3x, colorless oil. 31.24 mg, 99% yield, 96% ee, HPLC analysis on a Chiralcel OD-H column (hexane/isopropanol = 99.5/0.5, flow rate 1.0 mL/min): t_R = 4.9 min (minor), t_R = 5.5 min (major). $[\alpha]_D^{26}$ = -35.6 (c 1.00, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 8.06 -7.98 (m, 4H), 7.87 (d, *J* = 8.2 Hz, 1H), 7.69 – 7.65 (m, 1H), 7.54 – 7.51 (m, 3H), 7.36 – 7.26 (m, 4H), 4.06 - 4.02 (m, 1H), -0.01 (d, *J* = 3.8 Hz, 3H), -0.03 (d, *J* = 3.8 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.6, 138.7, 135.3, 133.9, 133.7, 133.5, 133.0, 131.0, 128.6, 128.2, 128.1, 128.0, 127.0, 127.0, 126.9, 126.4, 126.1, 126.0, 125.2, -2.9, -3.0. HRMS (ESI, m/z): calcd for $C_{22}H_{21}Si^+$ $[M + H]^+$: 313.1407, found 313.1431.

3. Synthetic Application

3.1. Scale-up reaction.

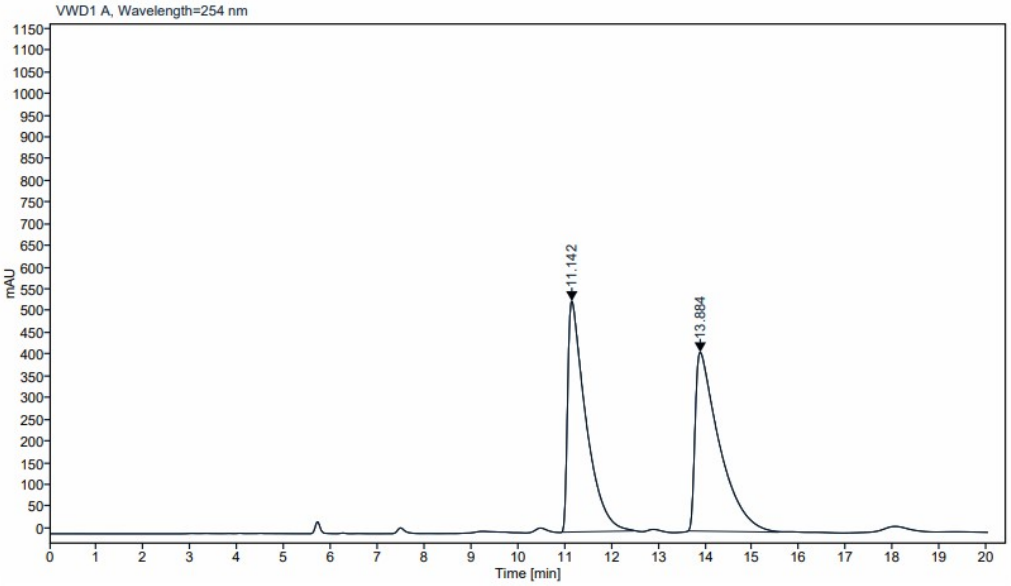


1d, 3.0 mmol
99% ee

2a

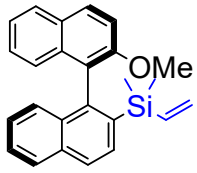
3d,
99% yield, 97% ee

This procedure was conducted in an argon-filled glove box. $(DME)NiCl_2$ (65.92 mg, 0.3 mmol), **L4** (99.72 mg, 0.3 mmol) and Mn (494.5 mg, 9.0 mmol) in DMA (30 mL) were charged sequentially into a 100 mL pressure tube under argon. The mixture was stirred for 30 min at room temperature. Then **1d** (1.298 g, 3.0 mmol, 1.0 equiv.) and **2a** (1.086 g, 9.0 mmol) were added to the reaction mixture. The reaction tube was sealed and stirred at 30 °C. After the reaction was completed (20 h), the reaction mixture was filtered through a pad of celite, eluted with ethyl acetate, concentrated, and purified by silica gel chromatography (PE:EA = 20:1) to give the indicated product **3d** (1.103 g, 99% yield, 97% ee). HPLC analysis on a Chiralcel OD-H column (hexane, flow rate 1.0 mL/min): t_R = 13.3 min (minor), t_R = 14.4 min (major). ^1H NMR (600 MHz, $CDCl_3$) δ 7.98 (d, *J* = 9.0 Hz, 1H), 7.90 (dd, *J* = 19.2, 8.2 Hz, 2H), 7.84 (d, *J* = 8.2 Hz, 1H), 7.80 (d, *J* = 8.4 Hz, 1H), 7.44 – 7.41 (m, 1H), 7.38 (d, *J* = 9.0 Hz, 1H), 7.30 – 7.27 (m, 1H), 7.22 – 7.14 (m, 3H), 6.92 (d, *J* = 8.6 Hz, 1H), 5.79 (dd, *J* = 20.2, 14.6 Hz, 1H), 5.65 (dd, *J* = 14.6, 3.8 Hz, 1H), 5.35 (dd, *J* = 20.2, 3.8 Hz, 1H), 3.74 (s, 3H), -0.19 (s, 3H), -0.20 (s, 3H).

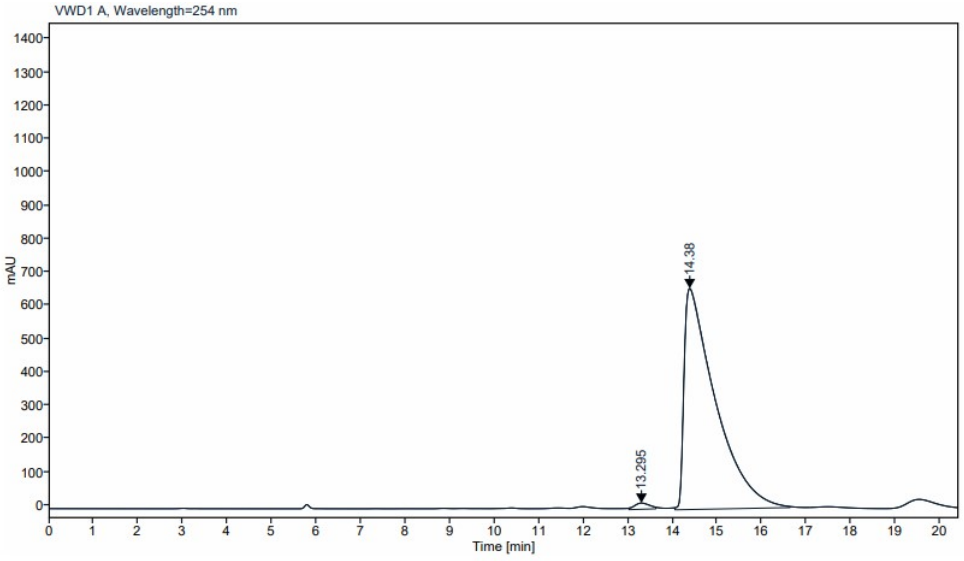


Results

No.	RT[min]	Area	Height	Relative Height %	Relative Area %
	11.142	14303.3682	531.2927	56.36	49.23
	13.884	14751.6621	411.3700	43.64	50.77
SUM	25.026	29055.0303	942.6627	100.00	100.00



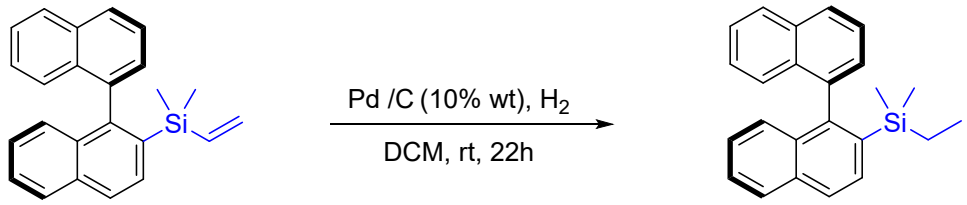
3d



Results

No.	RT[min]	Area	Height	Relative Height %	Relative Area %
	13.295	441.2271	18.7074	2.74	1.34
	14.380	32398.0703	663.6711	97.26	98.66
SUM	27.675	32839.2975	682.3785	100.00	100.00

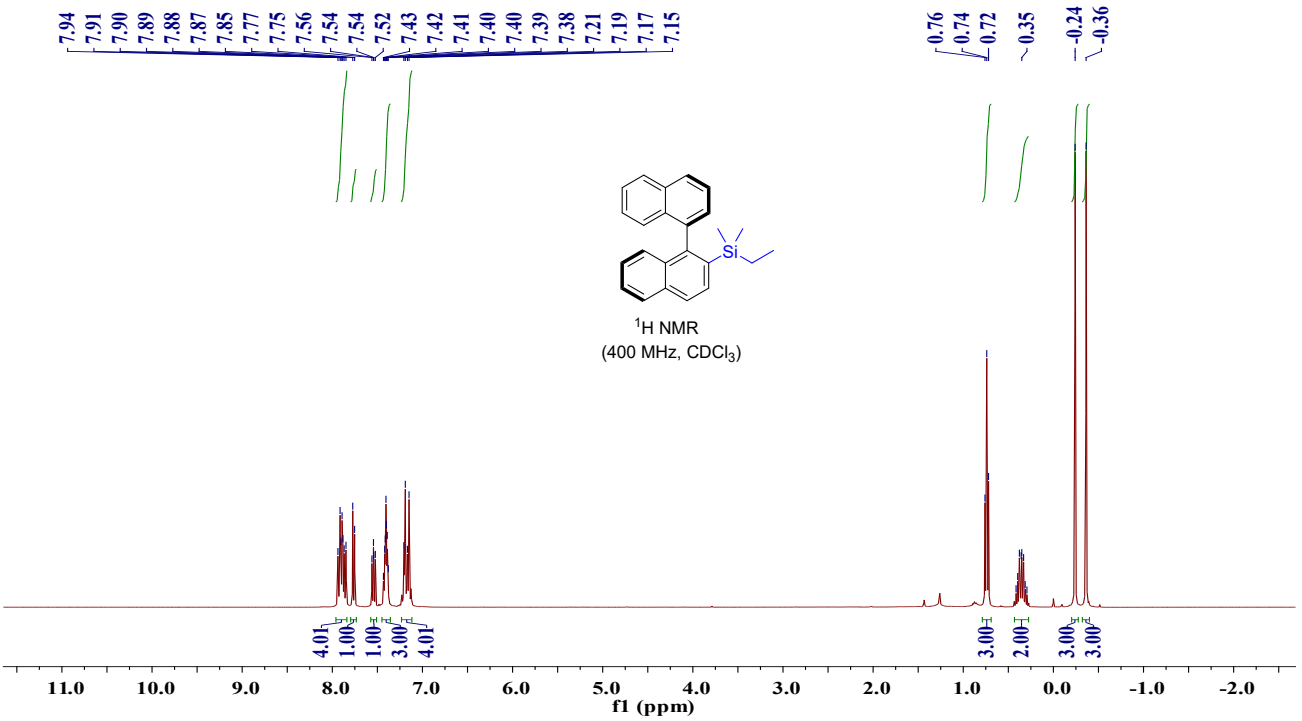
3.2. Derivatization Reactions.



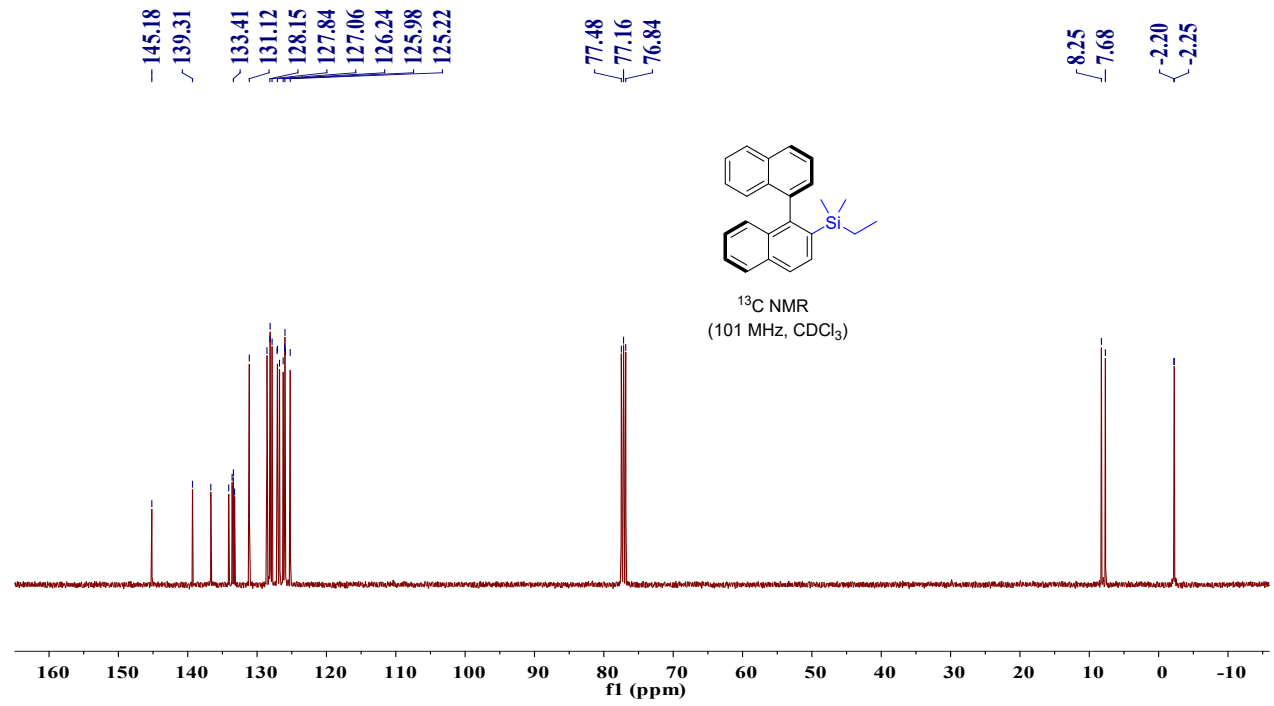
3a
97% ee

4
99% yield, 97% ee

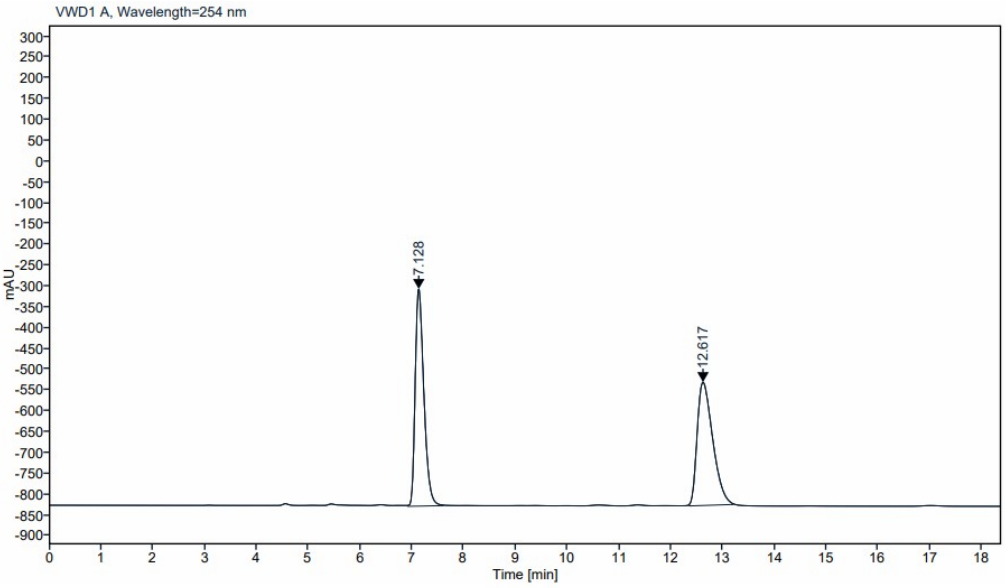
3a (67.71 mg, 0.2 mmol) and DCM (4.0 mL) were added to a flame dried schlenk tube under hydrogen, the Pd/C (21.20 mg, 10% wt) was added and stirred at room temperature. After stirred for 22 h, the reaction mixture was filtered through a pad of celite eluting with ethyl acetate. The crude mixture was concentrated and purified by silica gel chromatography (PE) to give the product **4** (68.10 mg, 99% yield, 97% ee). HPLC analysis on a Chiralcel MD-H column (hexane, flow rate 1.0 mL/min): t_R = 7.5 min (minor), t_R = 12.6 min (major). $[\alpha]_D^{20}$ = -24.6 (c 1.00, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 7.94 – 7.85 (m, 4H), 7.76 (d, *J* = 8.4 Hz, 1H), 7.54 (dd, *J* = 8.2, 7.0 Hz, 1H), 7.43 – 7.38 (m, 3H), 7.23 – 7.13 (m, 4H), 0.74 (t, *J* = 7.8 Hz, 3H), 0.41 – 0.29 (m, 2H), -0.24 (s, 3H), -0.36 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.2, 139.3, 136.7, 134.1, 133.6, 133.4, 133.3, 131.1, 128.6, 128.2, 128.1, 127.8, 127.1, 127.0, 126.8, 126.2, 126.0, 126.0, 125.9, 125.2, 8.3, 7.7, -2.2, -2.3. HRMS (ESI, m/z): calcd for $C_{24}H_{25}Si^+$ [M + H]$^+$: 341.1720, found 341.1734.



^{1}H NMR
(400 MHz, $CDCl_3$)

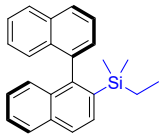


^{13}C NMR
(101 MHz, $CDCl_3$)

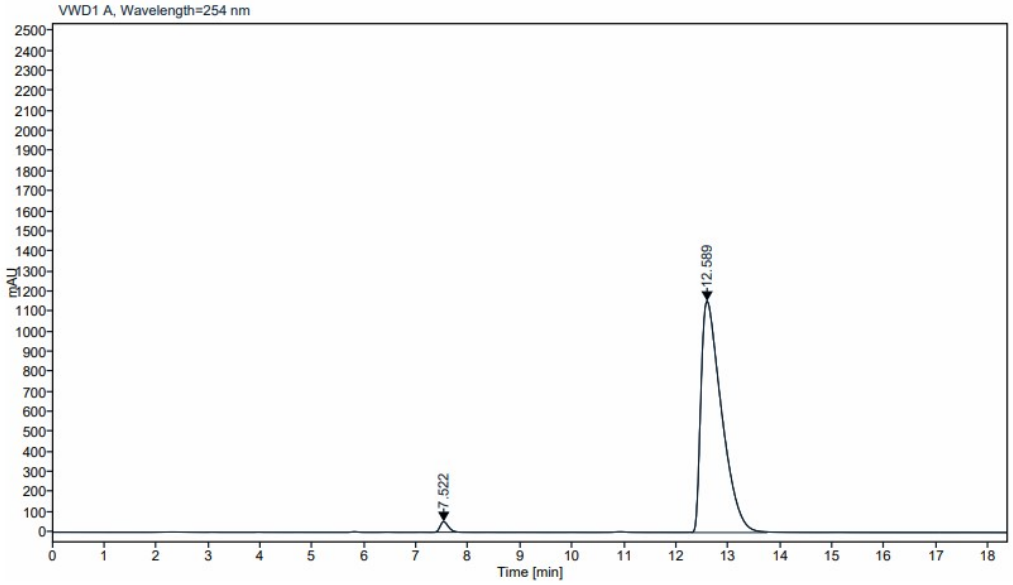


Results

No.	RT[min]	Area	Height	Relative Height %	Relative Area %
	7.128	6071.3252	521.4600	63.77	49.59
	12.617	6170.6973	296.1962	36.23	50.41
SUM	19.745	12242.0225	817.6562	100.00	100.00

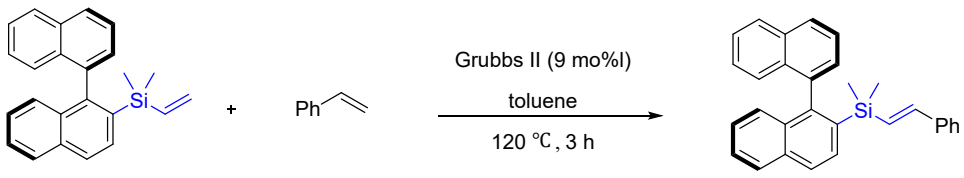


4



Results

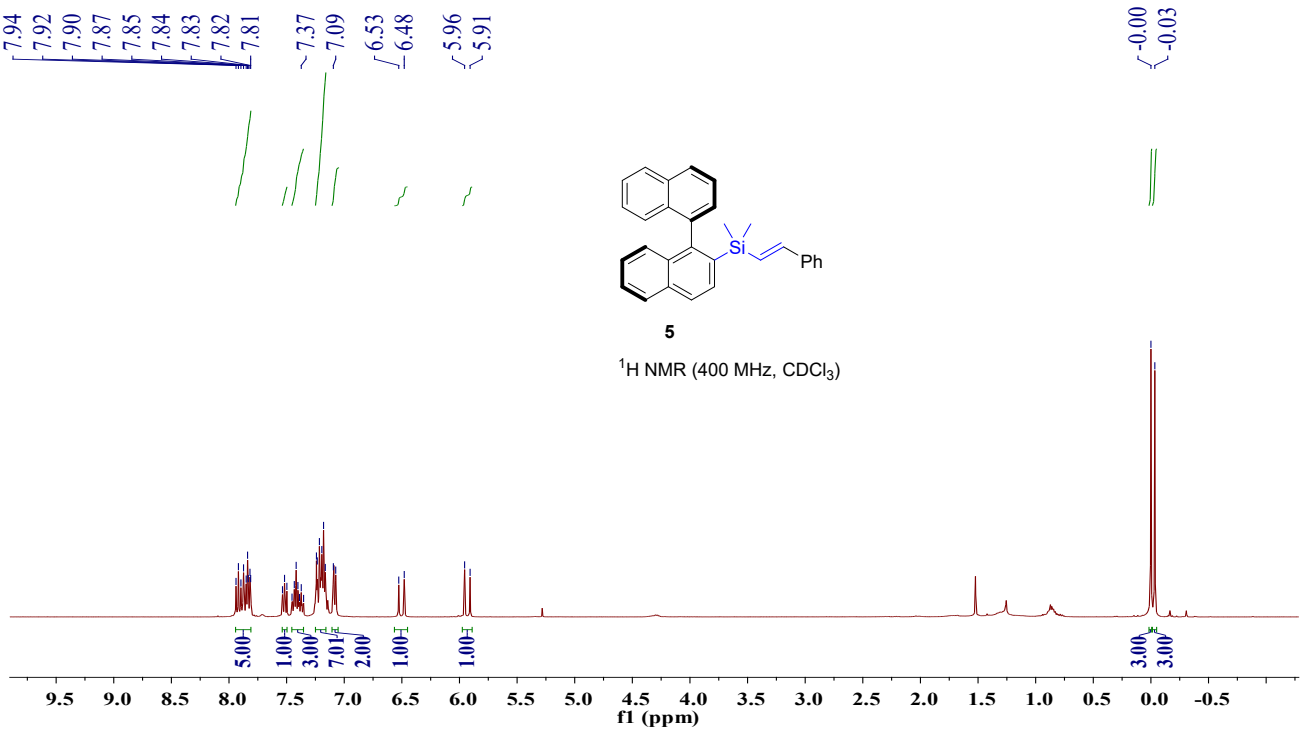
No.	RT[min]	Area	Height	Relative Height %	Relative Area %
	7.522	572.5878	52.1798	4.33	1.77
	12.589	31811.5664	1154.1949	95.67	98.23
SUM	20.111	32384.1542	1206.3747	100.00	100.00



3a
97% ee

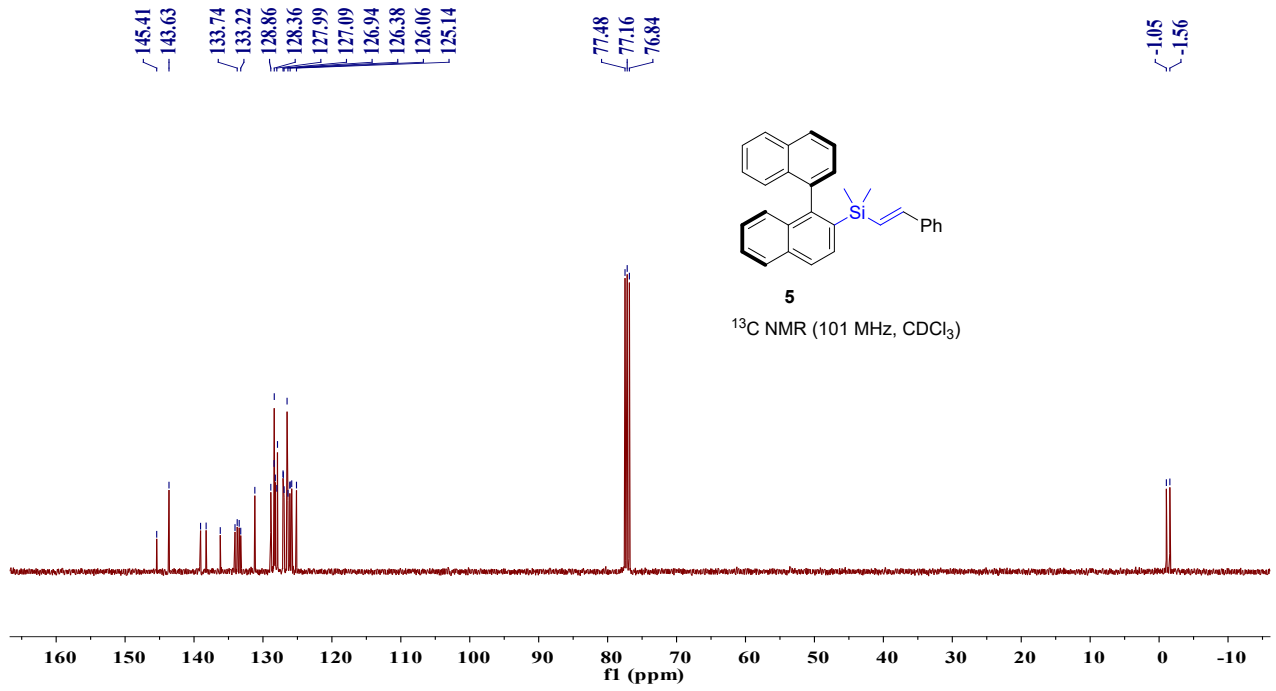
5
89% yield, 96% ee

3a (33.86 mg, 0.1 mmol, 1.0 equiv) , styrene(104.15 mg, 1.0 mmol, 10.0 equiv), Grubbs II (7.64 mg, 0.9 mol%) and toluene (0.5 mL) were added to a flame dried schlenk tube under argon, then stirred at 120℃. After stirred for 3 h, the reaction mixture was filtered through a pad of celite eluting with ethyl acetate. The crude mixture was concentrated and purified by silica gel chromatography (PE) to give the product **5** (36.80 mg, 89% yield, 96% ee). HPLC analysis on a Chiralcel MD-H column (hexane, flow rate 1.0 mL/min): t_R = 15.1 min (minor), t_R = 27.9 min (major). $[\alpha]_D^{21}$ = 8.4 (c 1.00, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 7.94 – 7.81 (m, 5H), 7.54 – 7.50 (m, 1H), 7.43 -7.35 (m, 3H), 7.24 – 7.16 (m, 7H), 7.09 – 7.07 (m, 2H), 6.50 (d, *J* = 19.1 Hz, 1H), 5.93 (d, *J* = 19.1 Hz, 1H), -0.00 (s, 3H), -0.03 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.4, 143.6, 139.1, 138.2, 136.2, 134.1, 133.7, 133.5, 133.2, 131.2, 128.9, 128.4, 128.4, 128.2, 128.0, 127.9, 127.1, 127.0, 126.9, 126.5, 126.4, 126.1, 126.0, 125.8, 125.1, -1.1, -1.6. HRMS (ESI, m/z): calcd for $C_{30}H_{26}NaSi^+$ $[M + Na]^+$: 437.1696, found 437.1705.



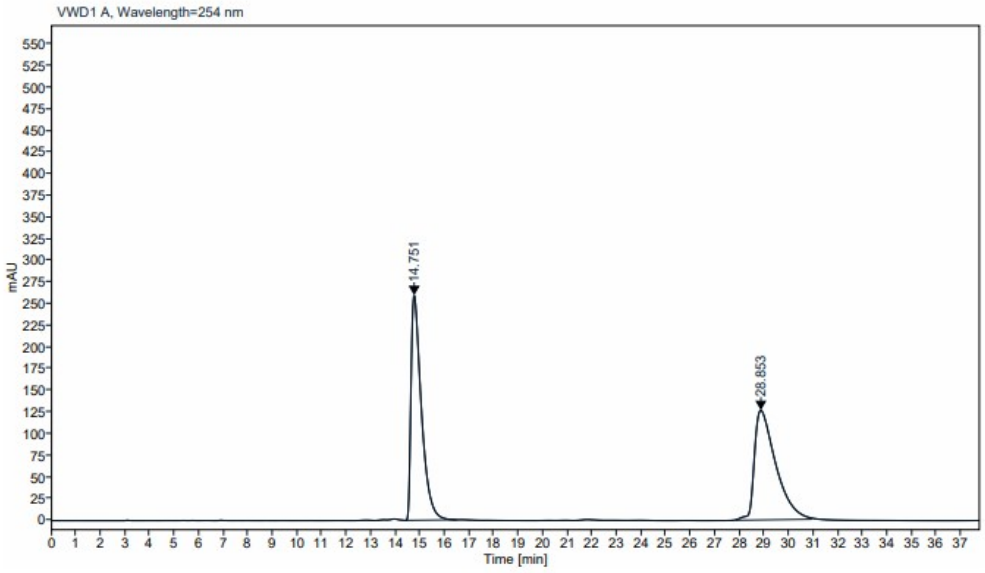
5

^{1}H NMR (400 MHz, $CDCl_3$)



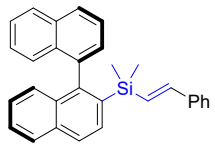
5

^{13}C NMR (101 MHz, $CDCl_3$)

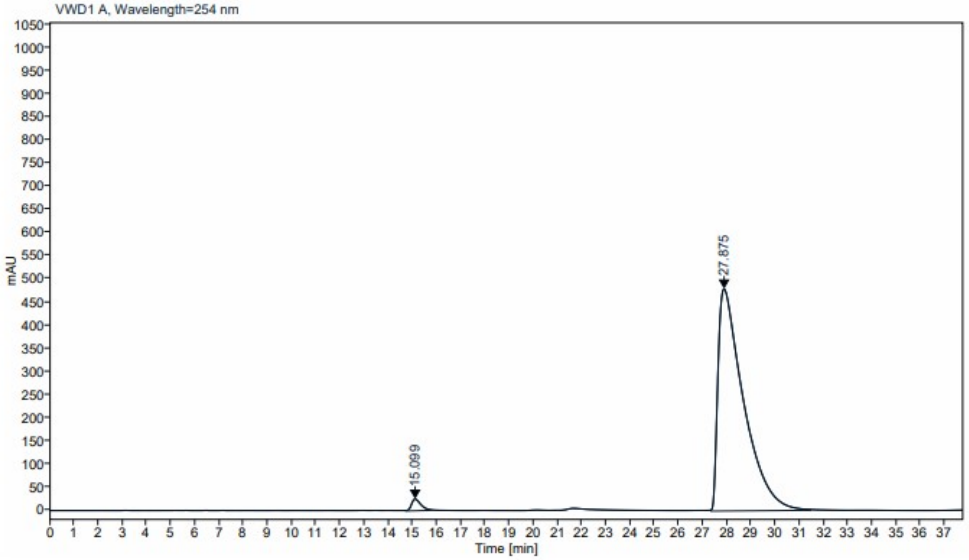


Results

No.	RT[min]	Area	Height	Relative Height %	Relative Area %
	14.751	7631.9165	259.7105	67.23	49.94
	28.853	7650.7178	126.5722	32.77	50.06
SUM	43.604	15282.6343	386.2827	100.00	100.00



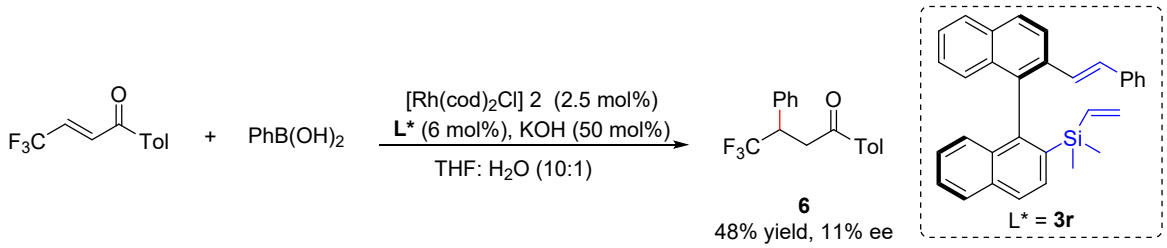
5



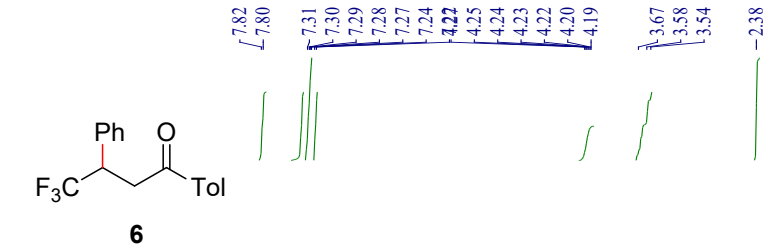
Results

No.	RT[min]	Area	Height	Relative Height %	Relative Area %
	15.099	677.7655	25.1042	4.98	1.89
	27.875	35184.8125	479.4846	95.02	98.11
SUM	42.973	35862.5780	504.5888	100.00	100.00

3.3. Application of chiral alkene ligands.



The procedure was conducted in an argon-filled glove box. $[Rh(cod)_2Cl]_2$ (2.47 mg) and **3r** (5.3 mg) in THF (1.0 mL) were charged into a 25 mL pressure tube under argon. The mixture was stirred for 30 min at 60 °C. Then enone (42.84 mg, 0.2 mmol, 1.0 equiv), $PhB(OH)_2$ (29.27 mg, 0.24 mmol, 1.2 equiv) and KOH (5.62 mg, 10 mol%) in H_2O (0.1 mL) were added to the reaction mixture sequentially. The reaction tube was sealed and stirred at -30 °C. After the reaction was completed (48 h), the reaction mixture was filtered through a pad of celite, eluted with ethyl acetate, concentrated, and purified by silica gel chromatography (PE:DCM = 10:1) to give the indicated product **6 (**28.1 mg, 48% yield, 11% ee), HPLC analysis on a Chiralcel OD-H column (hexane/isopropanol = 95/5, flow rate 1.0 mL/min), t_R = 4.7 min (major), t_R = 5.3 min (minor).^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, *J* = 8.2 Hz, 2H), 7.38 (d, *J* = 7.2 Hz, 2H), 7.31 – 7.27 (m, 3H), 7.23 (d, *J* = 8.0 Hz, 2H), 4.29 – 4.19 (m, 1H), 3.69 – 3.53 (m, 2H), 2.38 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 195.0, 144.6, 134.8, 134.0, 129.9, 129.5, 129.2, 128.8, 128.4, 128.3, 127.2 (q, *J* = 279.5 Hz), 45.0 (q, *J* = 27.3 Hz), 38.2, 21.7. ^{19}F NMR (376 MHz, $CDCl_3$) δ -69.57 (d, *J* = 9.7 Hz, 3F). HRMS (ESI, m/z): calcd for $C_{17}H_{16}F_3O^+$ $[M + H]^+$: 293.1148, found 293.1150.



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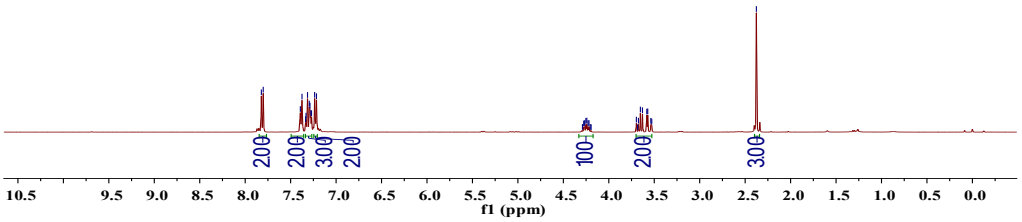
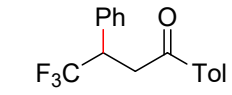
^{1}H NMR (400 MHz, $CDCl_3$)





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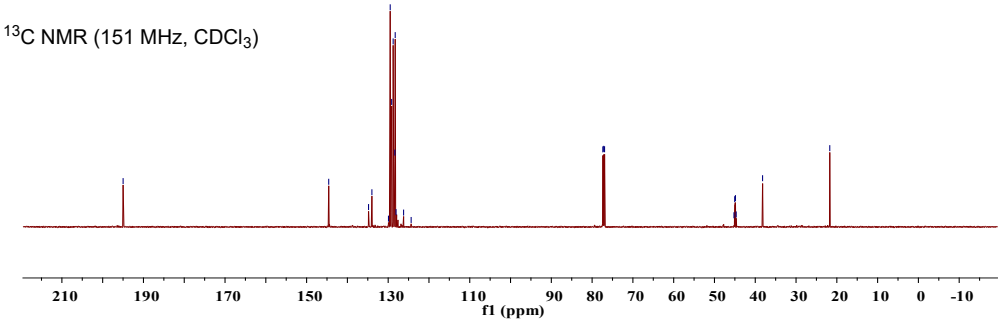
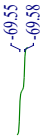
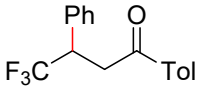
^{13}C NMR (151 MHz, $CDCl_3$)

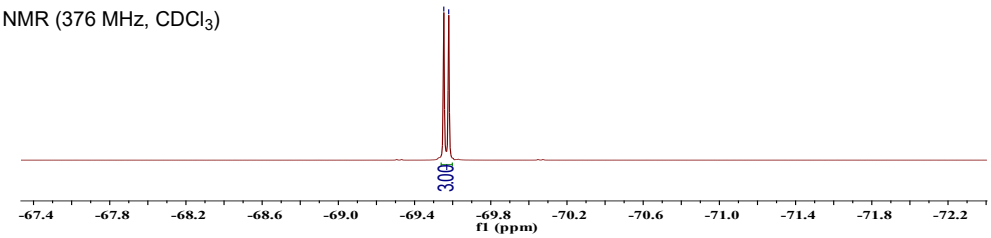


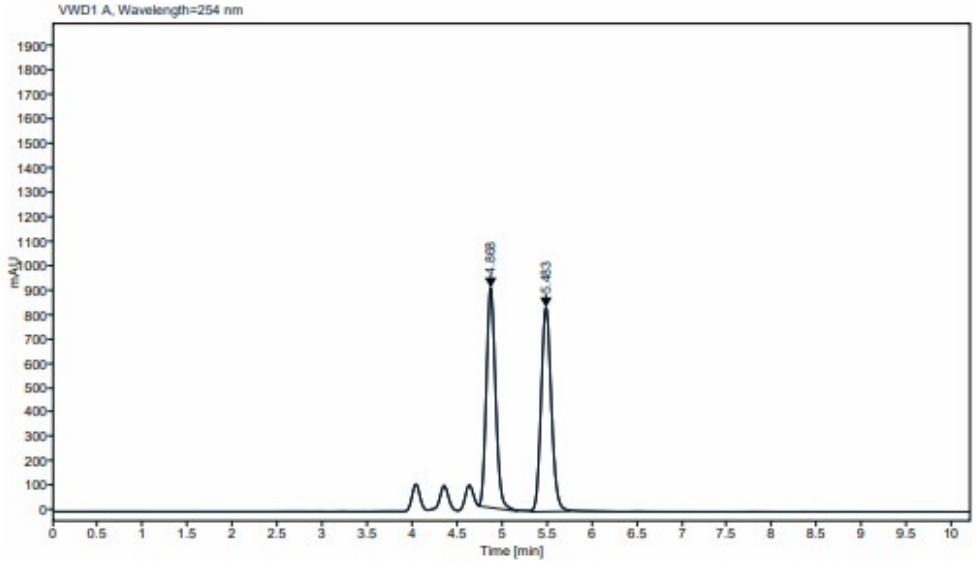




6

^{19}F NMR (376 MHz, $CDCl_3$)





Results

No.	RT[min]	Area	Height	Relative Height %	Relative Area %
	4.868	6427.4795	901.7827	51.84	49.18
	5.483	6642.4634	837.7372	48.16	50.82
SUM	10.351	13069.9429	1739.5199	100.00	100.00

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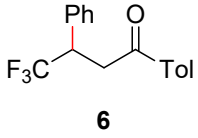

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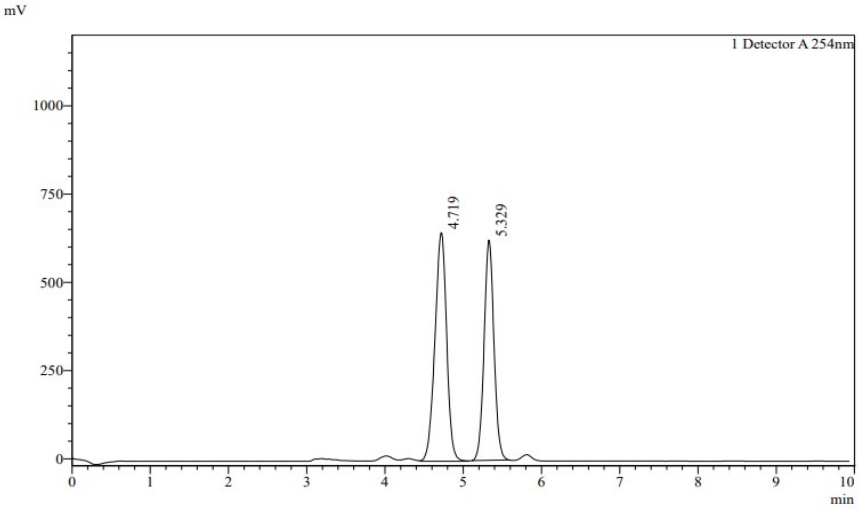
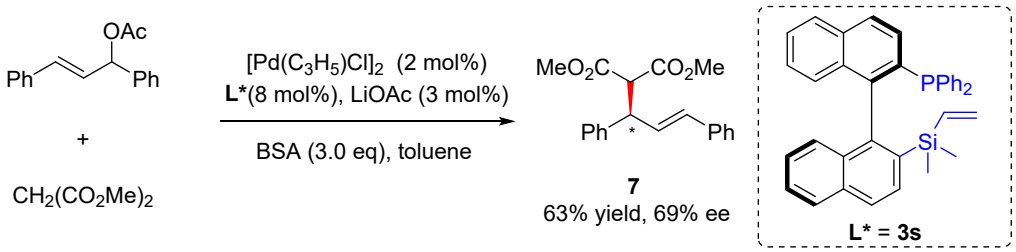


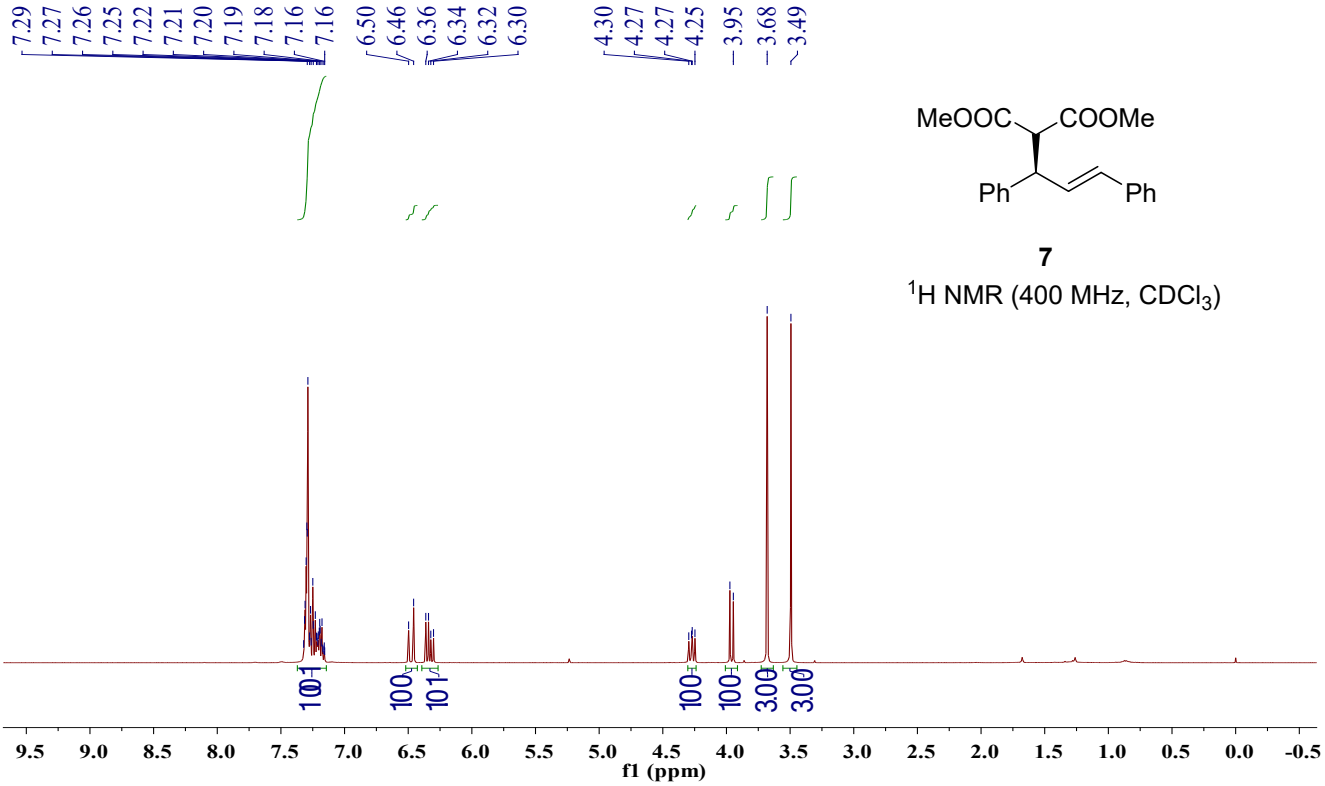
<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Area%
1	4.719	6739566	647141	55.238	55.238
2	5.329	5461293	623850	44.762	44.762
Total		12200859	1270991		100.000



A mixture of $[PdCl(C_3H_5)]_2$ (1.83 mg, 2.0 mol%), the chiral ligand **3s** (11.50 mg, 8.0 mol%, 99% ee) in toluene (0.5 mL) was stirred at 30 °C for 30 min under nitrogen atmosphere. Then allylic substrate (63.10 mg, 0.25 mmol, 1.0 equiv) and toluene (0.5 mL) were added and stirred for another 30 minutes. Subsequently, $CH_2(CO_2Me)$ (99.08 mg, 0.75 mmol, 3.0 equiv), bis(trimethylsllyl)acetamide (152.27 mg, 0.75 mmol, 3.0 equiv) and lithium acetate (0.50 mg, 3.0 mol%) were added. The mixture was stirred at 60 °C for three hours. At the end of the reaction, the saturated ammonium chloride solution (two drops) was added to quench the reaction. The mixture was diluted with ethyl acetate, filtered, and concentrated under the reduced pressure. The crude residue was purified by flash column chromatography on silica gel using hexanes/ethyl acetate (20:1) as eluent to give the corresponding product 7 (51.0 mg, 63% yield, 69% ee), HPLC analysis on a Chiralcel AD-H column (hexane/isopropanol = 95/5, flow rate 1.0 mL/min): t_R = 13.9 min (major), t_R = 19.2 min (minor). $[\alpha]_D^{26}$ = 3.0 (c 0.50, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.16 (m, 10H), 6.48 (d, *J* = 15.8 Hz, 1H), 6.33 (dd, *J* = 15.8, 8.6 Hz, 1H), 4.27 (dd, *J* = 10.8, 8.6 Hz, 1H), 3.96 (d, *J* = 10.8 Hz, 1H), 3.68 (s, 3H), 3.49 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.2, 167.8, 140.2, 136.9, 131.9, 129.2, 128.8, 128.5, 127.9, 127.6, 127.2, 126.4, 57.7, 52.7, 52.5, 49.3. HRMS (ESI, m/z): calcd for $C_{20}H_{20}O_4Na^+$ $[M + Na]^+$: 347.1254, found 347.1253.



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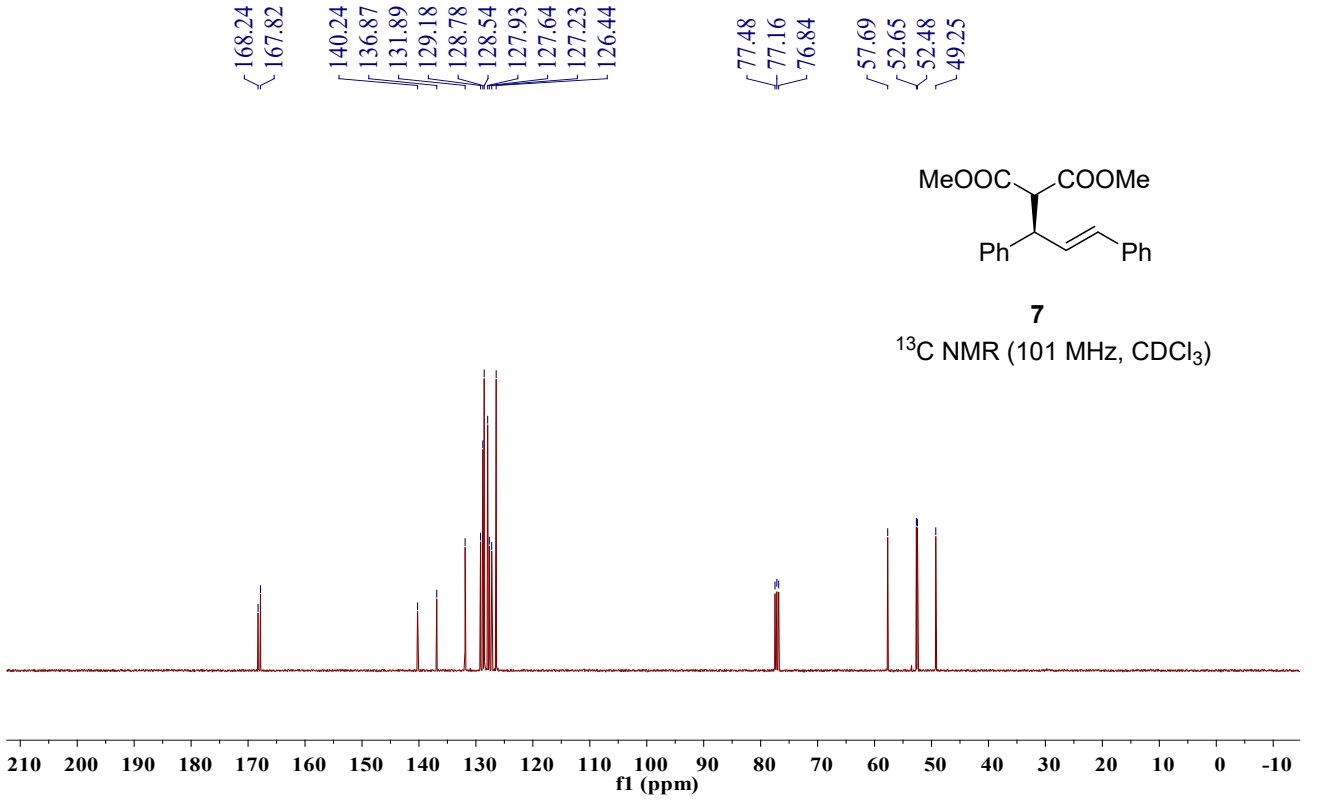
^{1}H NMR (400 MHz, $CDCl_3$)



7

^{13}C NMR (101 MHz, $CDCl_3$)

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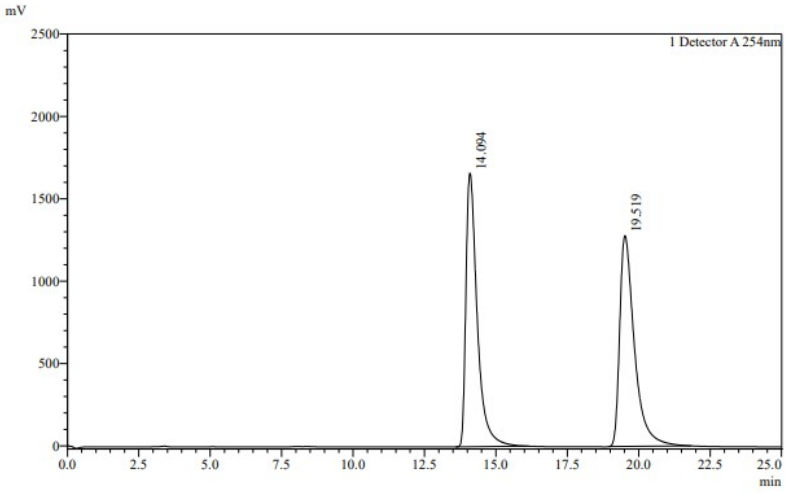

<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Area%
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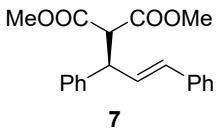

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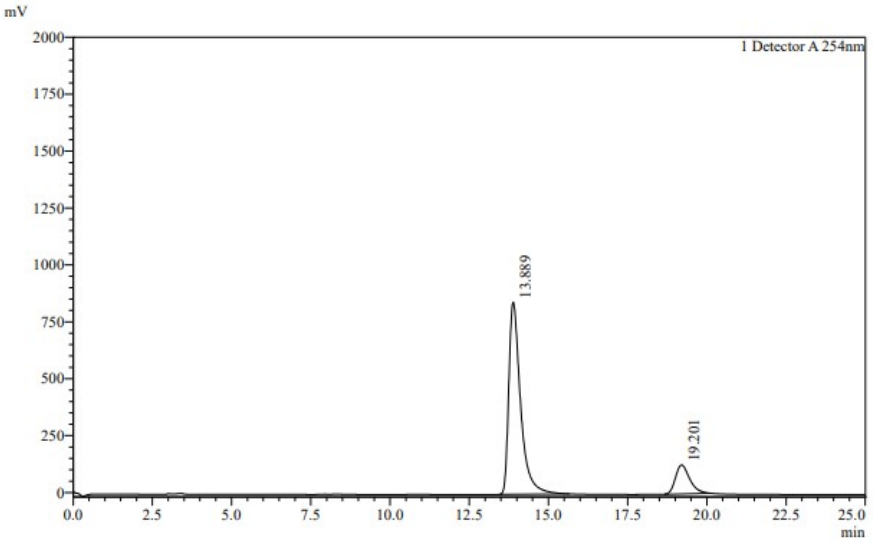

<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Area%
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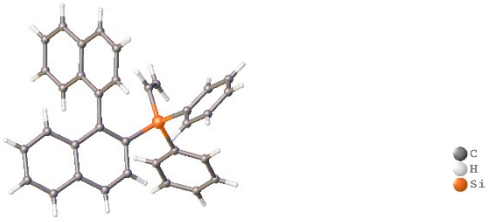
2	19.201	3977116	127230	15.403	15.403
Total		25820946	971191		100.000

4. X-Ray Crystallographic Data

Crystal structure details for 3v (CCDC 2387787). Thermal ellipsoids are shown at 50 % probability level (two molecules in each unit). Single crystals suitable for X-ray diffraction were obtained by slow evaporation of CH_2Cl_2 solution of **3v**.

Table 1 Crystal data and structure refinement for 3v.

Identification code	**3v**
Empirical formula	$C_{34}H_{26}Si$
Formula weight	462.64
Temperature/K	293(2)
Crystal system	monoclinic
Space group	$P2_1$
a/Å	14.5996(2)
b/Å	9.42640(10)
c/Å	18.8989(2)
α/°	90
β/°	94.4420(10)
γ/°	90
Volume/Å^3	2593.09(5)
Z	4
ρ_{calc}g/cm^3	1.185
μ/mm^{-1}	0.932
F(000)	976.0
Crystal size/mm^3	0.3 × 0.12 × 0.06
Radiation	CuKα (λ = 1.54178)
2Θ range for data collection/°	7.382 to 133.176
Index ranges	-15 ≤ h ≤ 17, -11 ≤ k ≤ 11, -22 ≤ l ≤ 22
Reflections collected	43685
Independent reflections	9145 [R_{int} = 0.1162, R_{sigma} = 0.0603]
Data/restraints/parameters	9145/1/631
Goodness-of-fit on F^2	1.054
Final R indexes [I>=2σ (I)]	R_1 = 0.0583, wR_2 = 0.1551
Final R indexes [all data]	R_1 = 0.0631, wR_2 = 0.1596
Largest diff. peak/hole / e Å^{-3}	0.53/-0.24
Flack parameter	0.03(3)



5. Supplementary References

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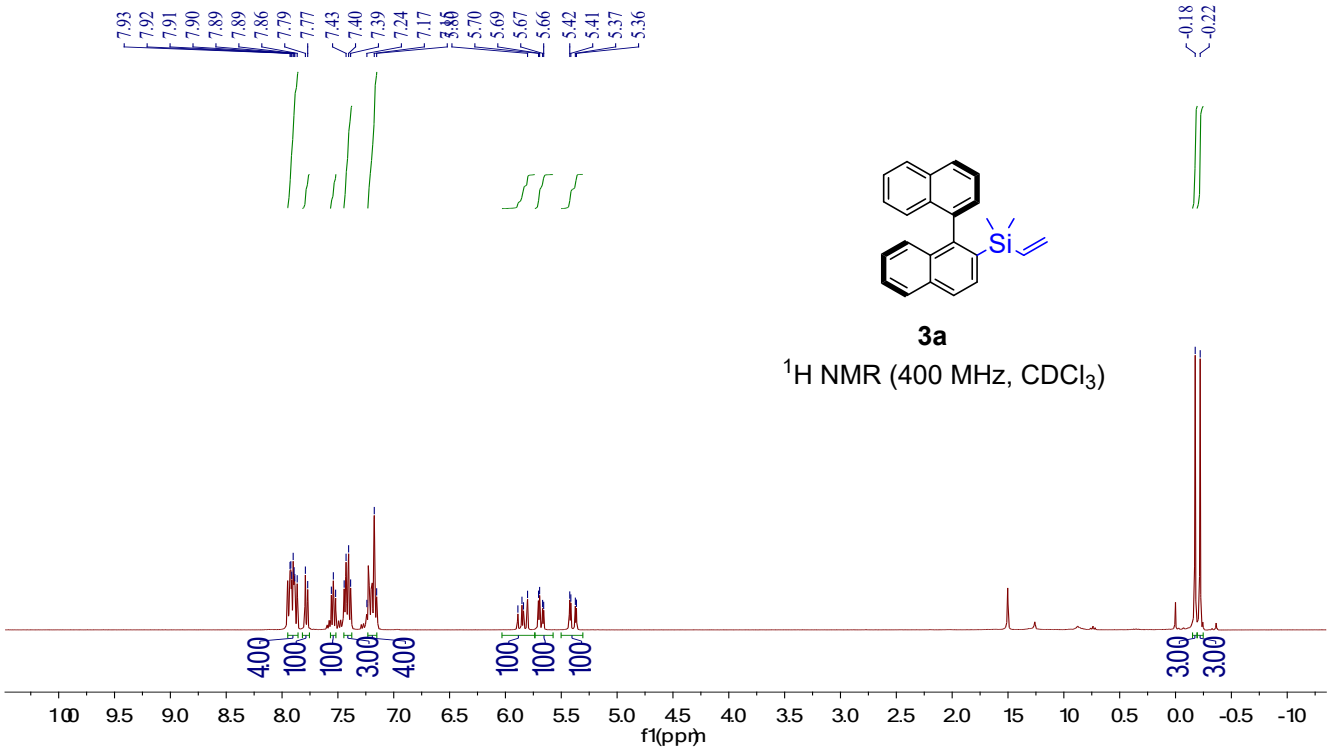
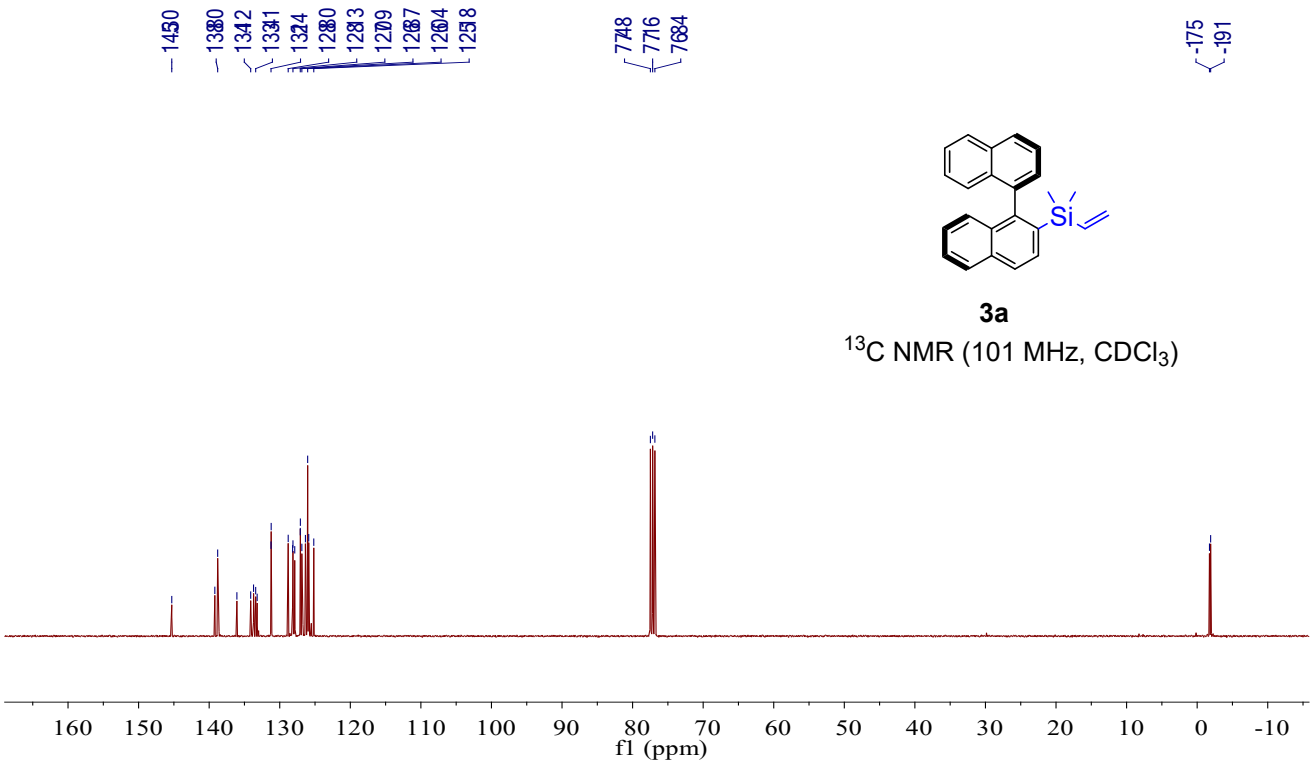
[8] Y. M. Yang, C. H. Wu, J. H. Xing, X. W. Dou, Developing Biarylhemiboronic Esters for Biaryl Atropisomer Synthesis via Dynamic Kinetic Atroposelective Suzuki−Miyaura Cross-Coupling, *J. Am. Chem. Soc.,* **2024**, *146*, 6283−6293.

6. NMR Spectra and HPLC Spectra



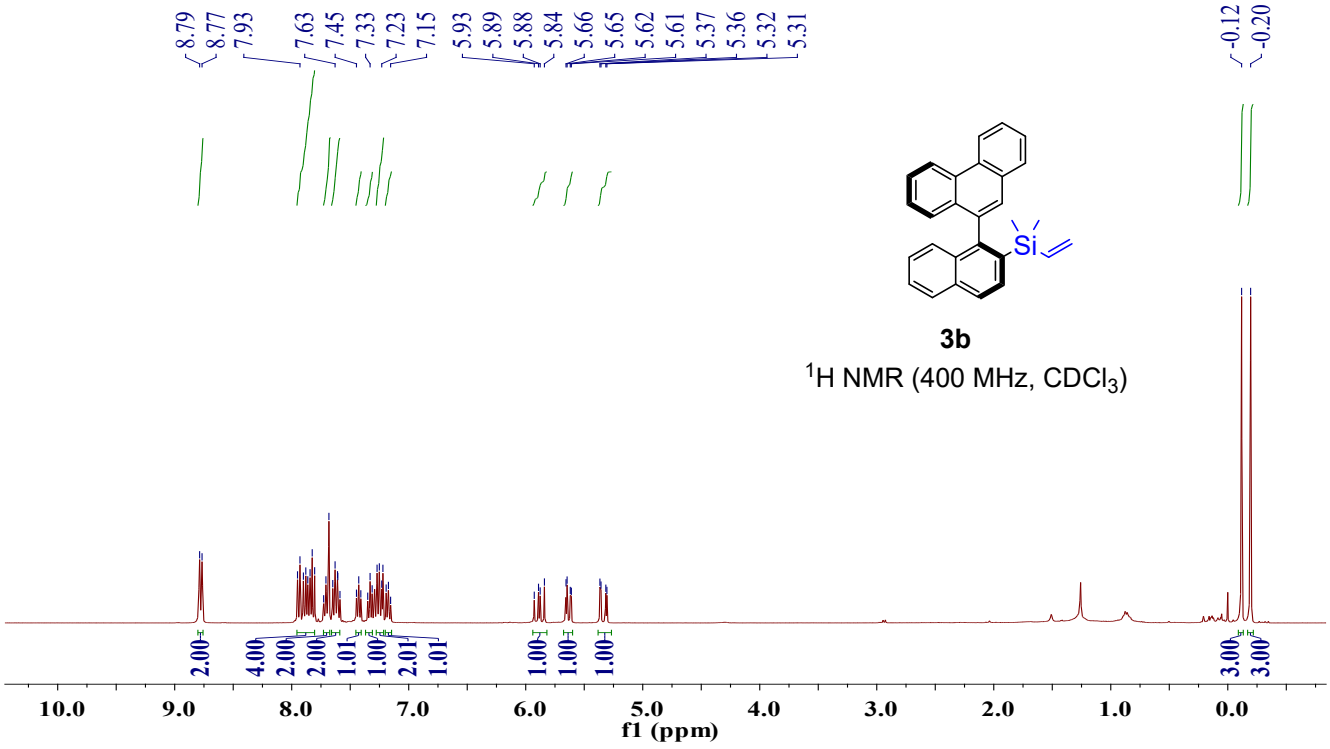
3a

^{1}H NMR (400 MHz, $CDCl_3$)



3a

^{13}C NMR (101 MHz, $CDCl_3$)



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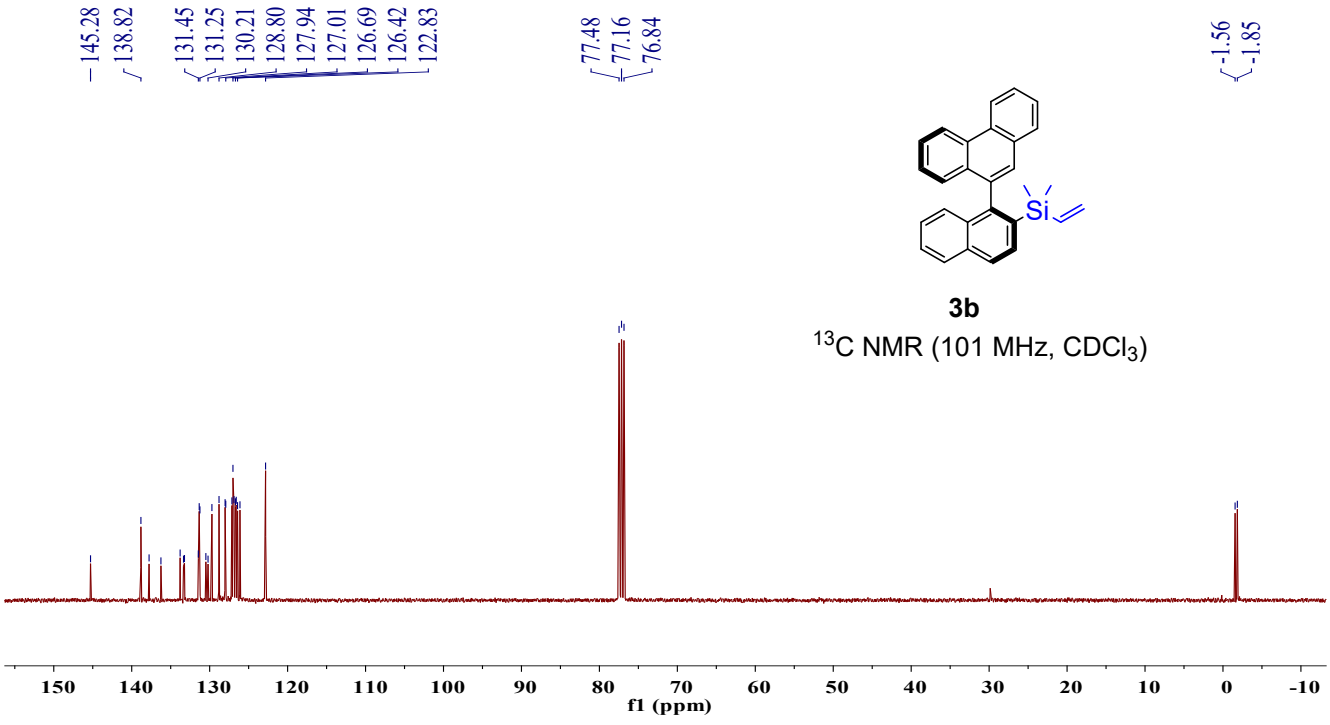

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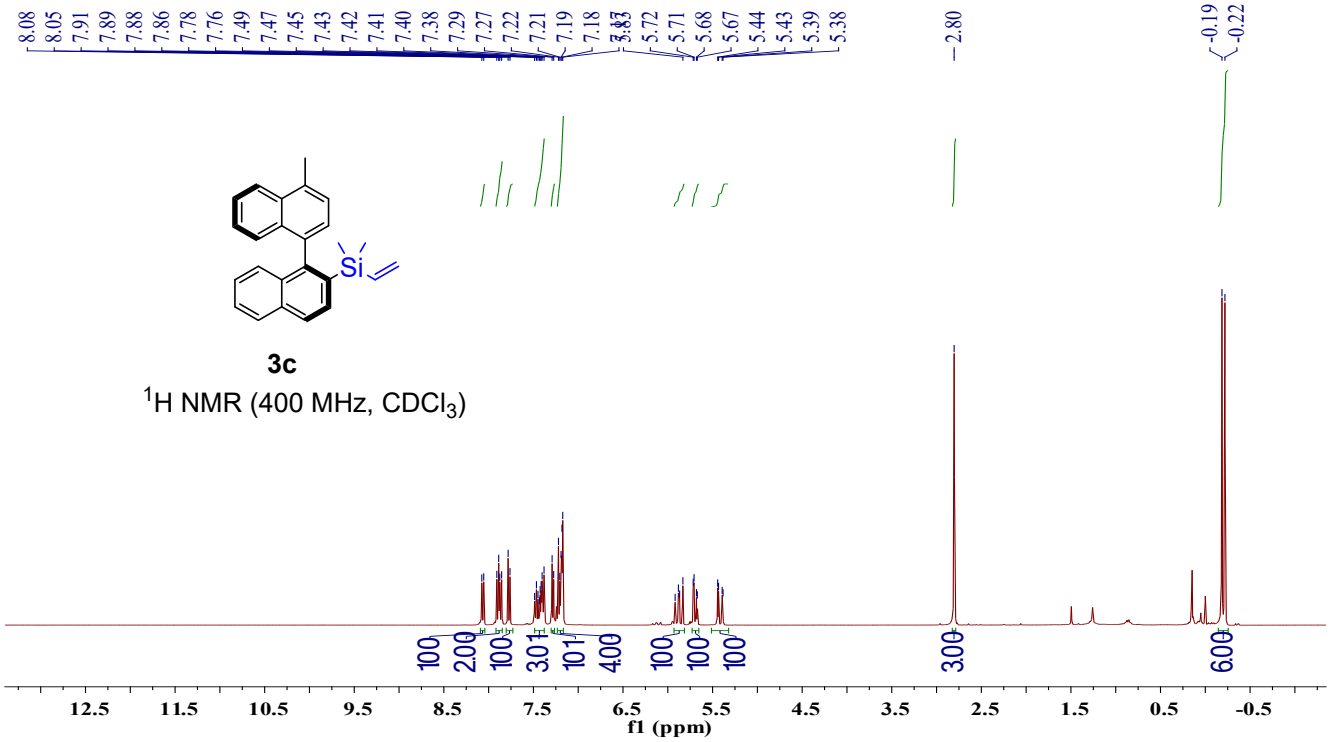

3c

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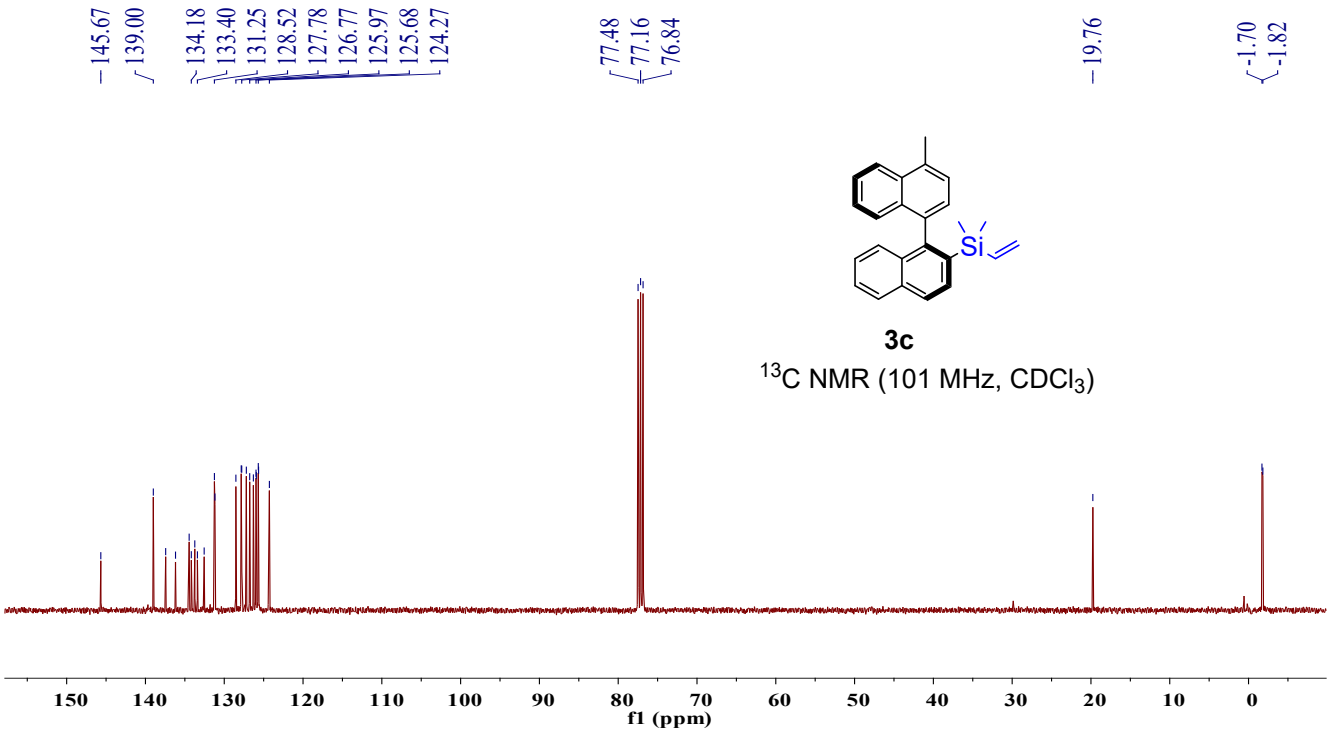

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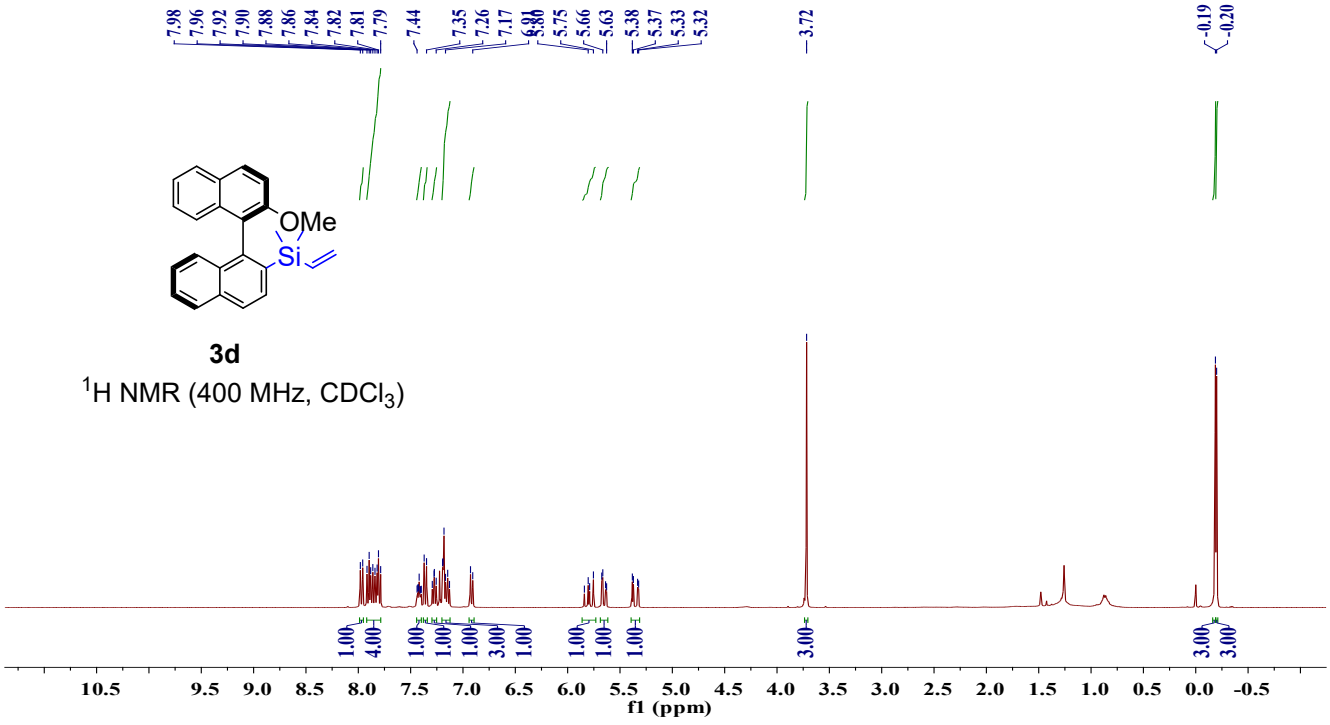

3d

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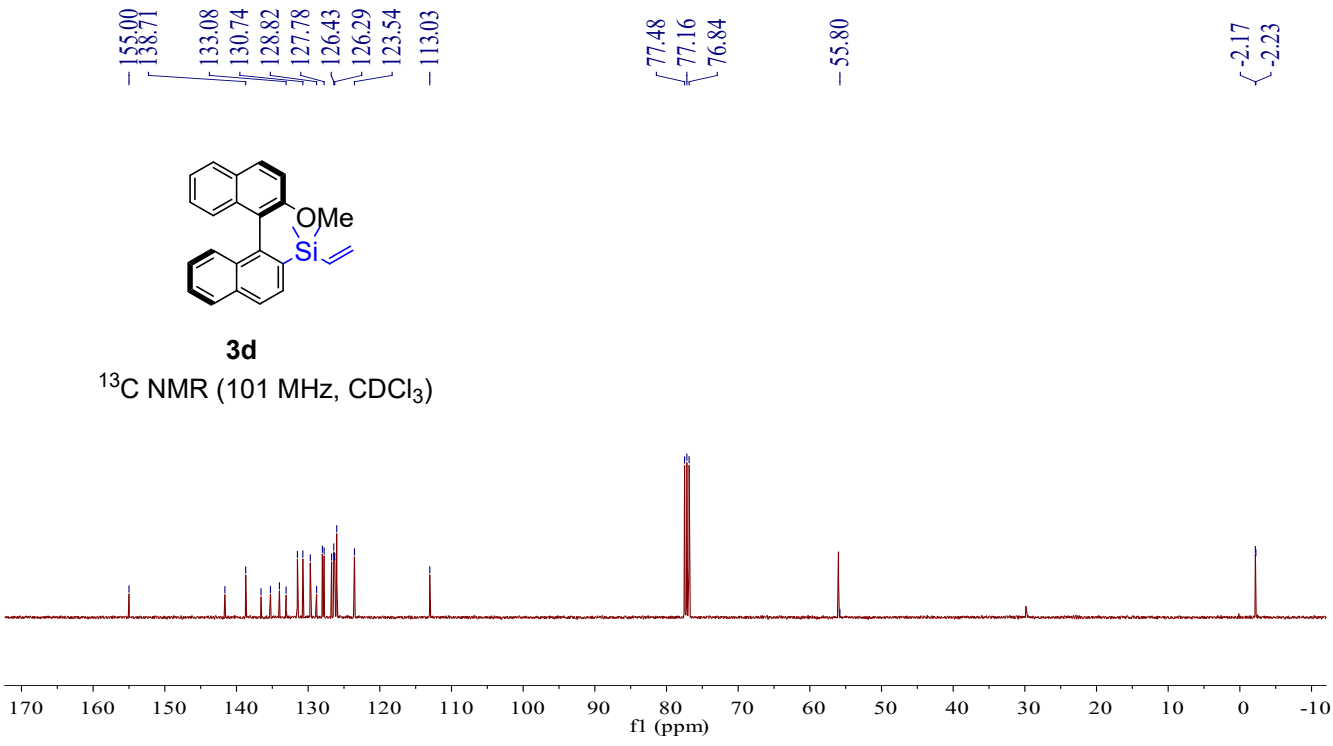

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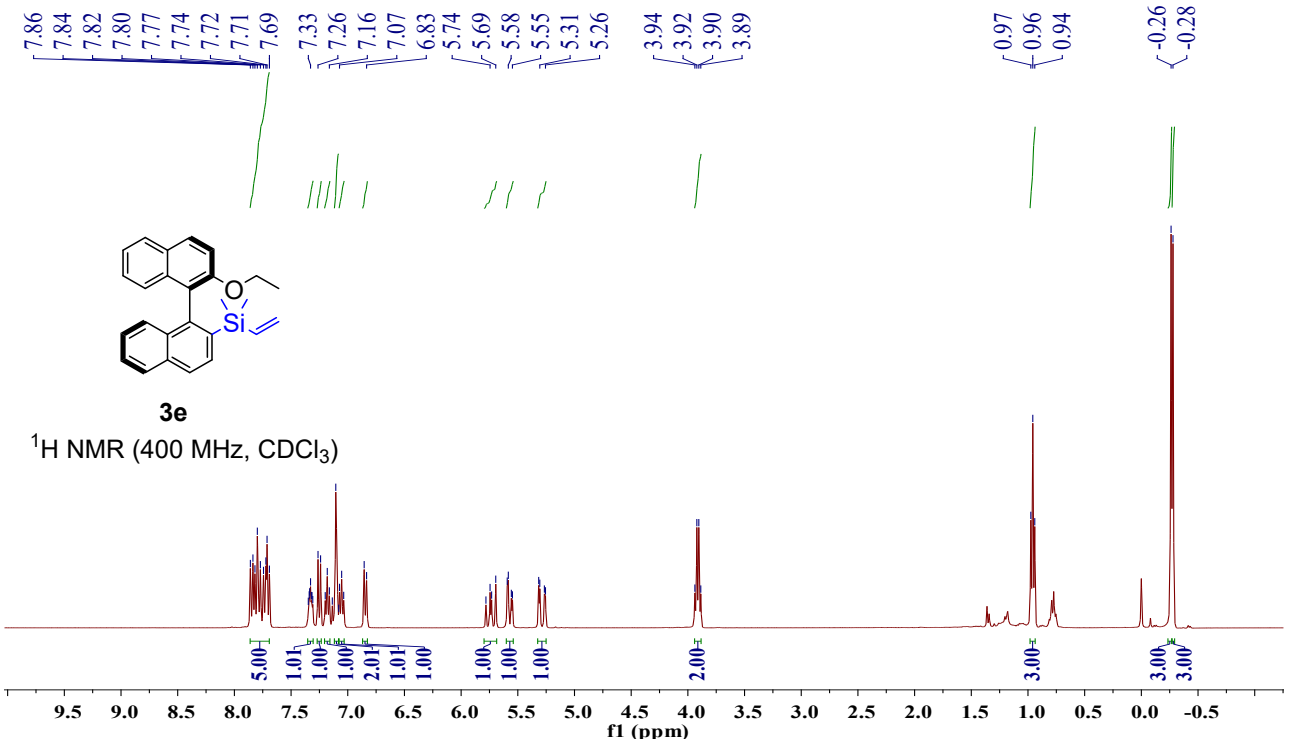

3e

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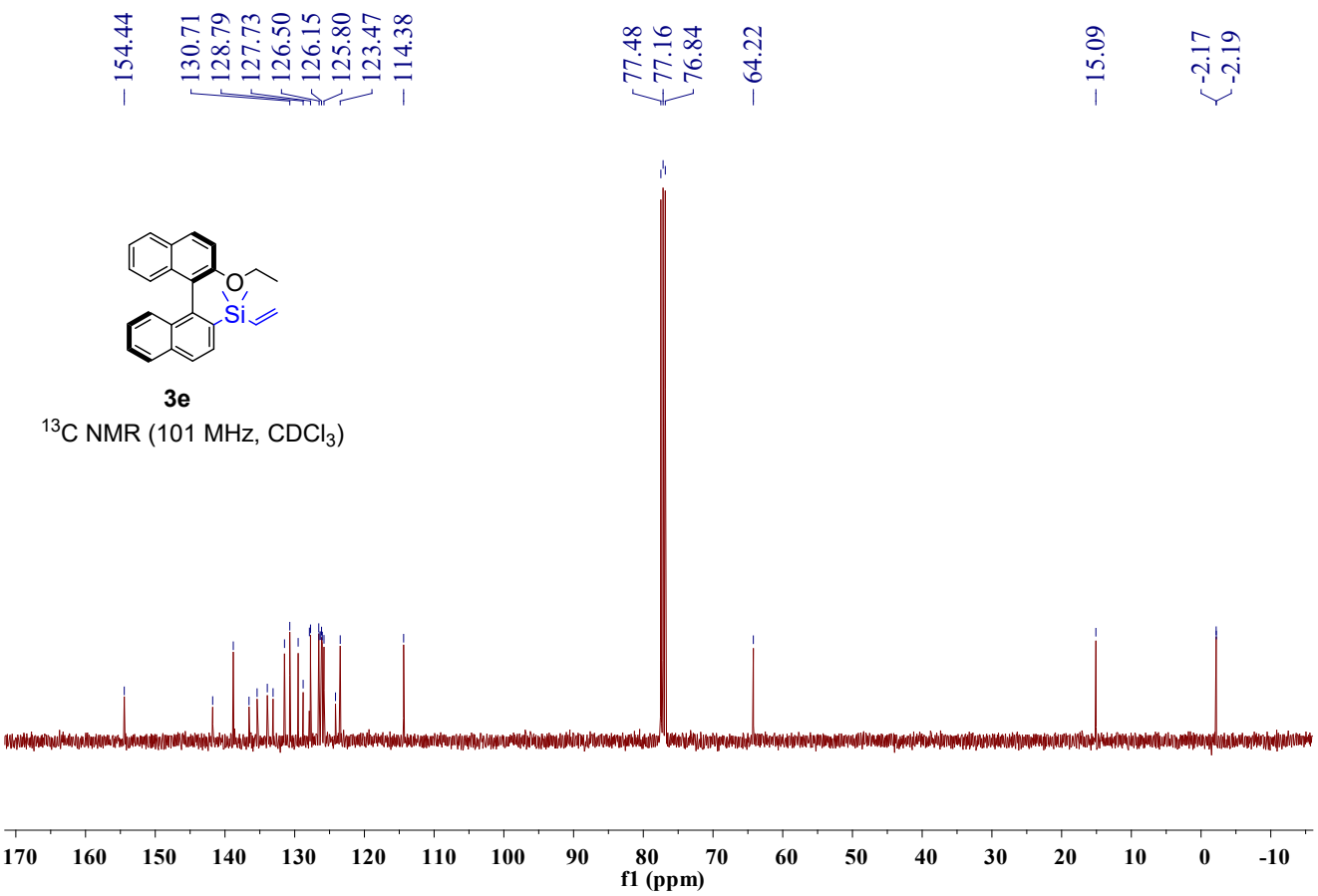

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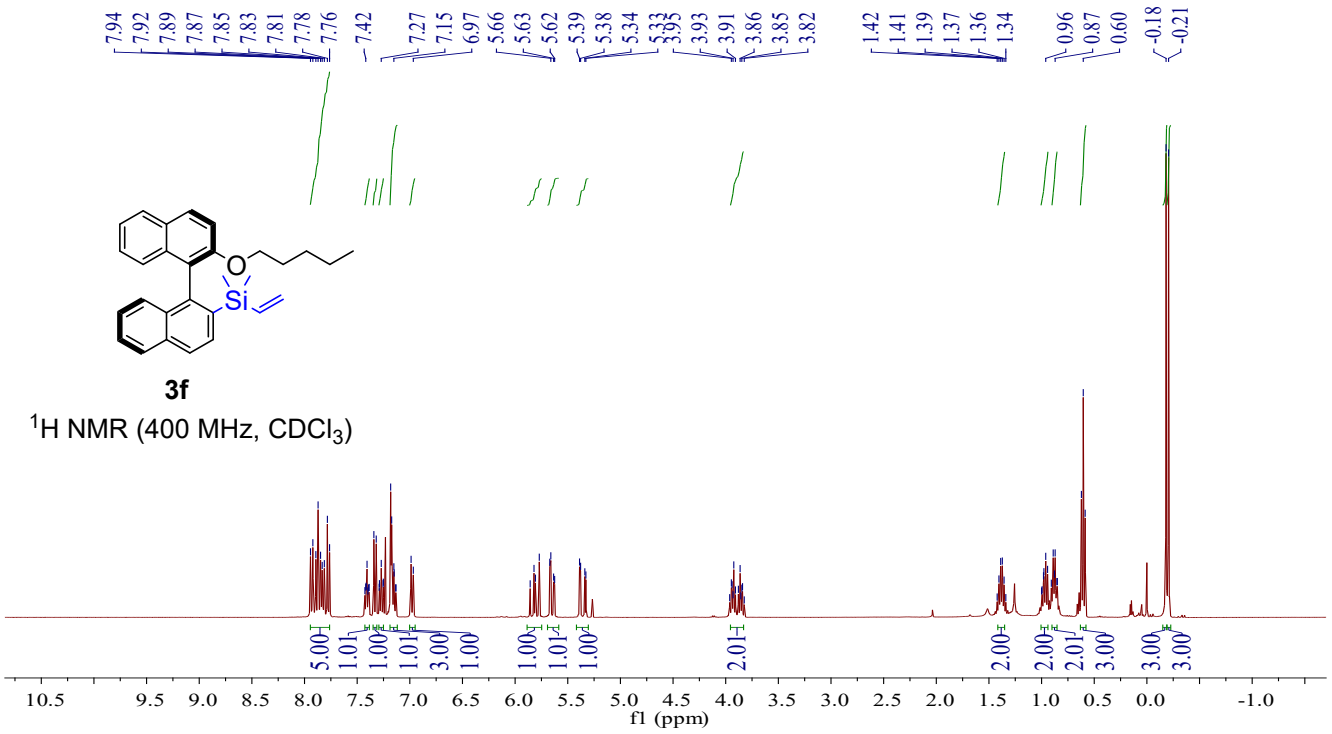

3f

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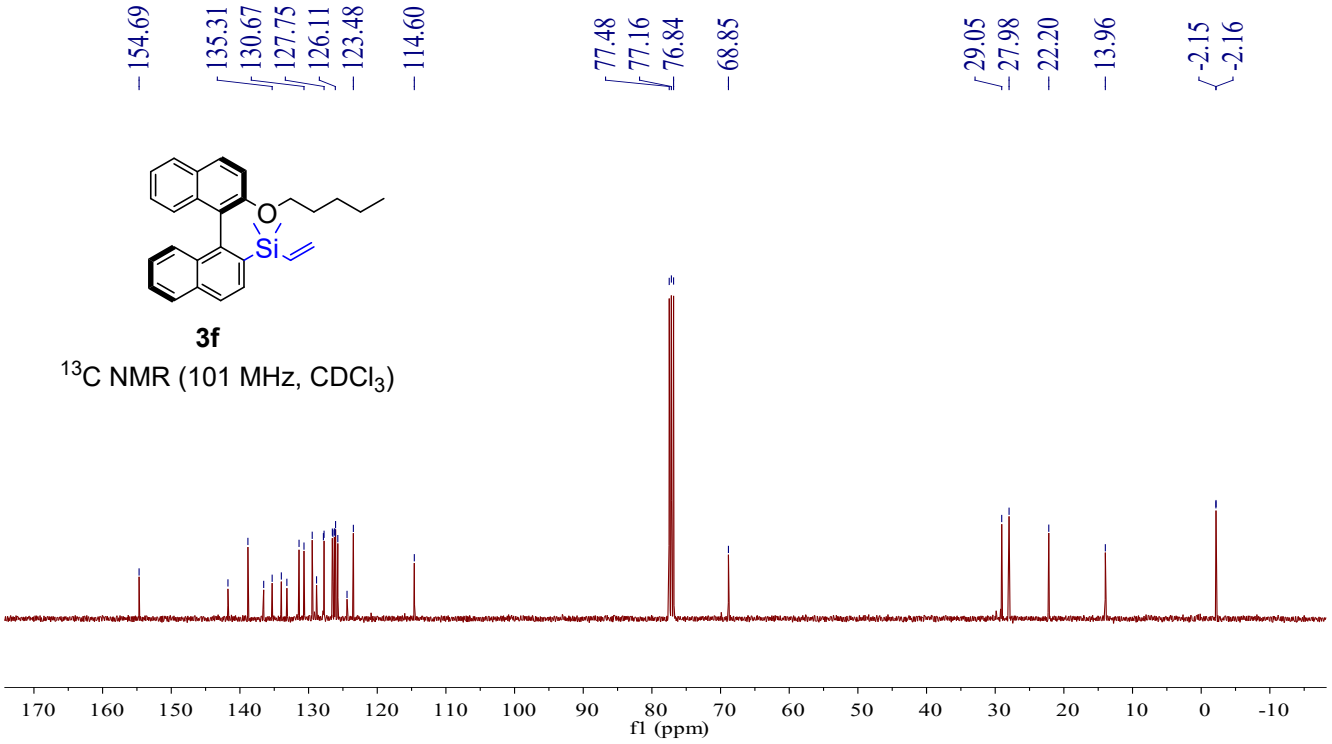

3f

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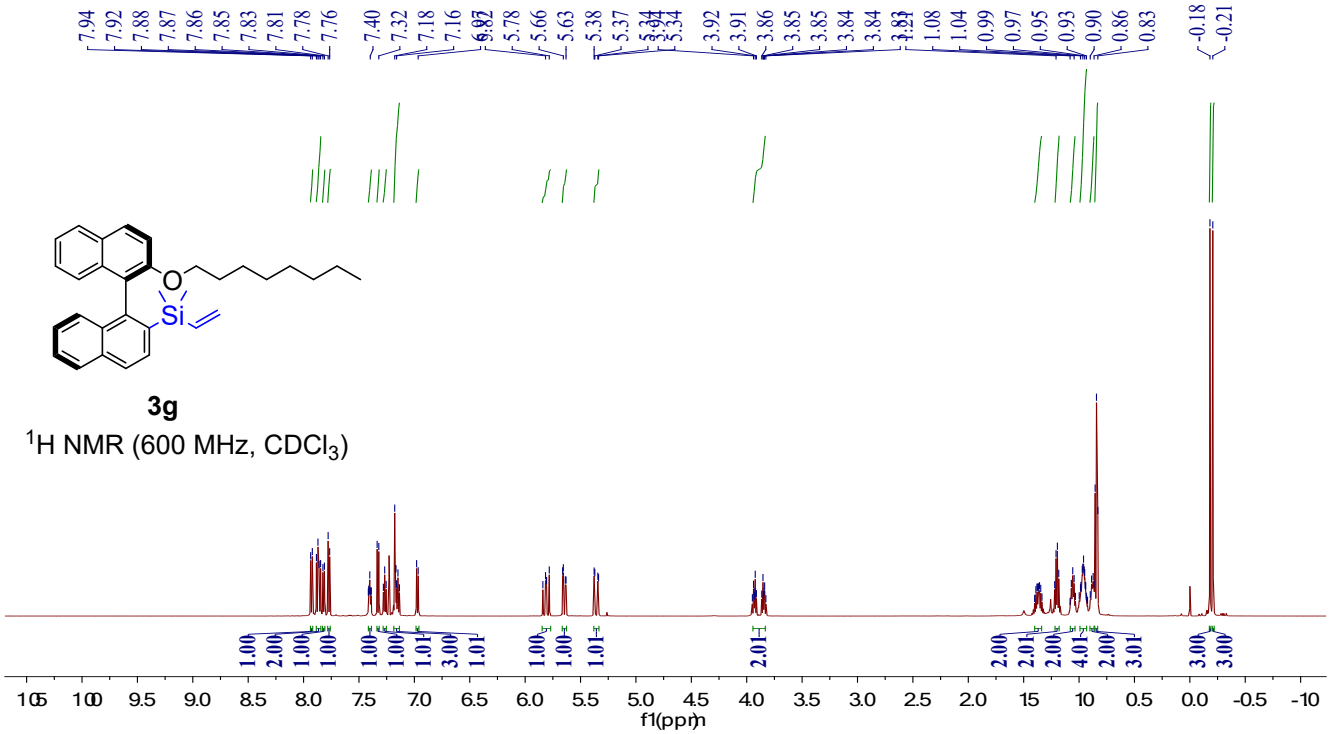

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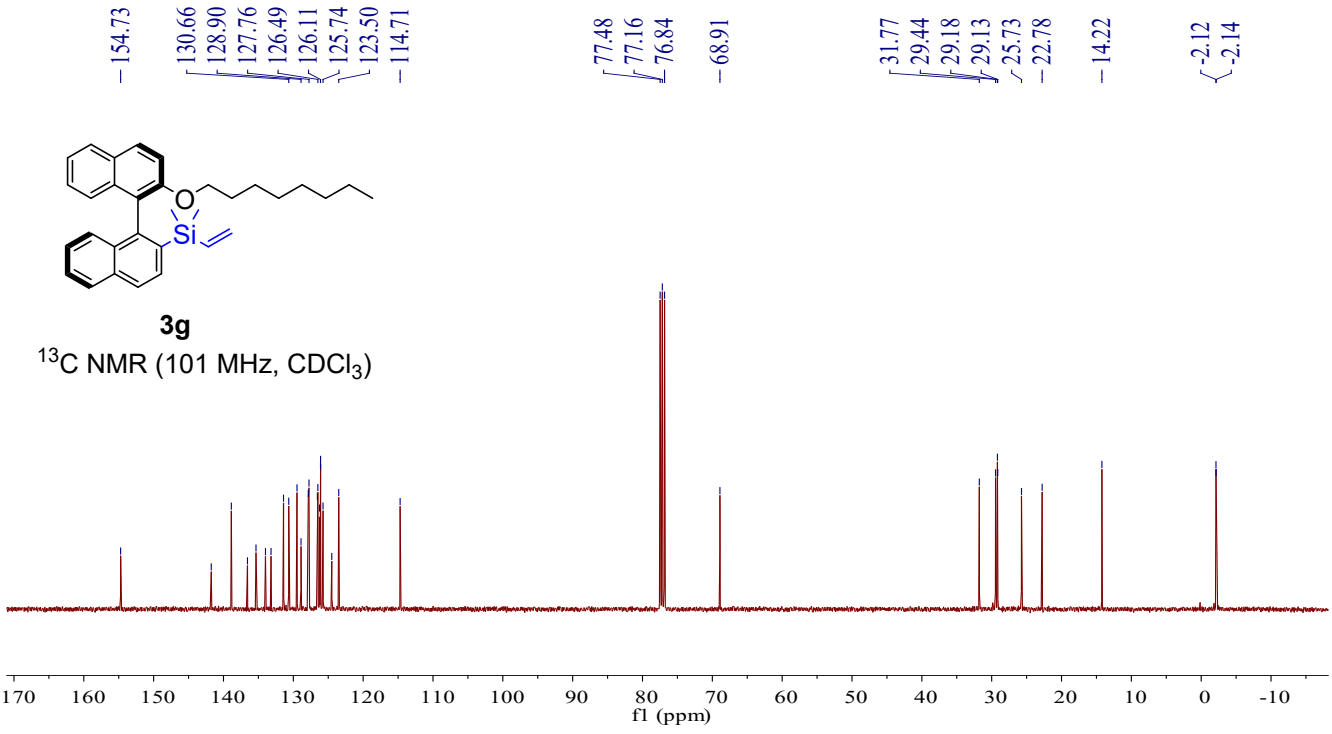
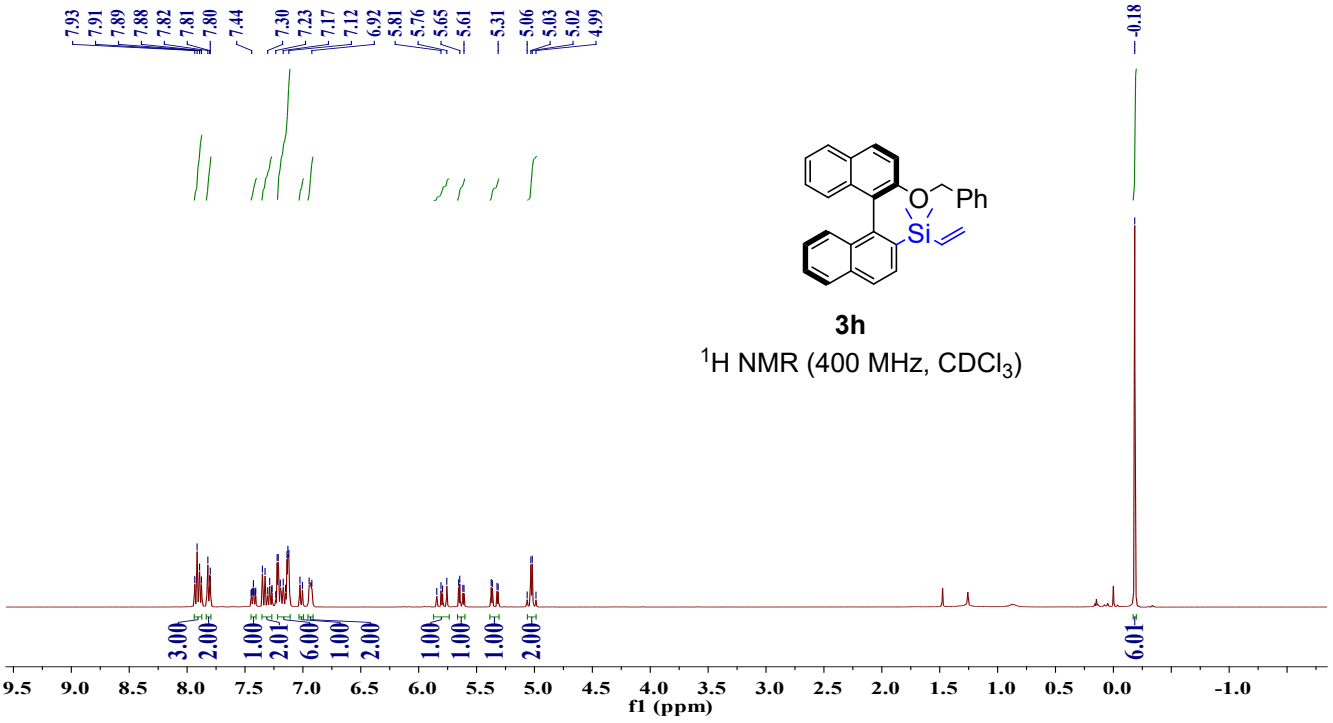


3g

^{13}C NMR (101 MHz, $CDCl_3$)



3h

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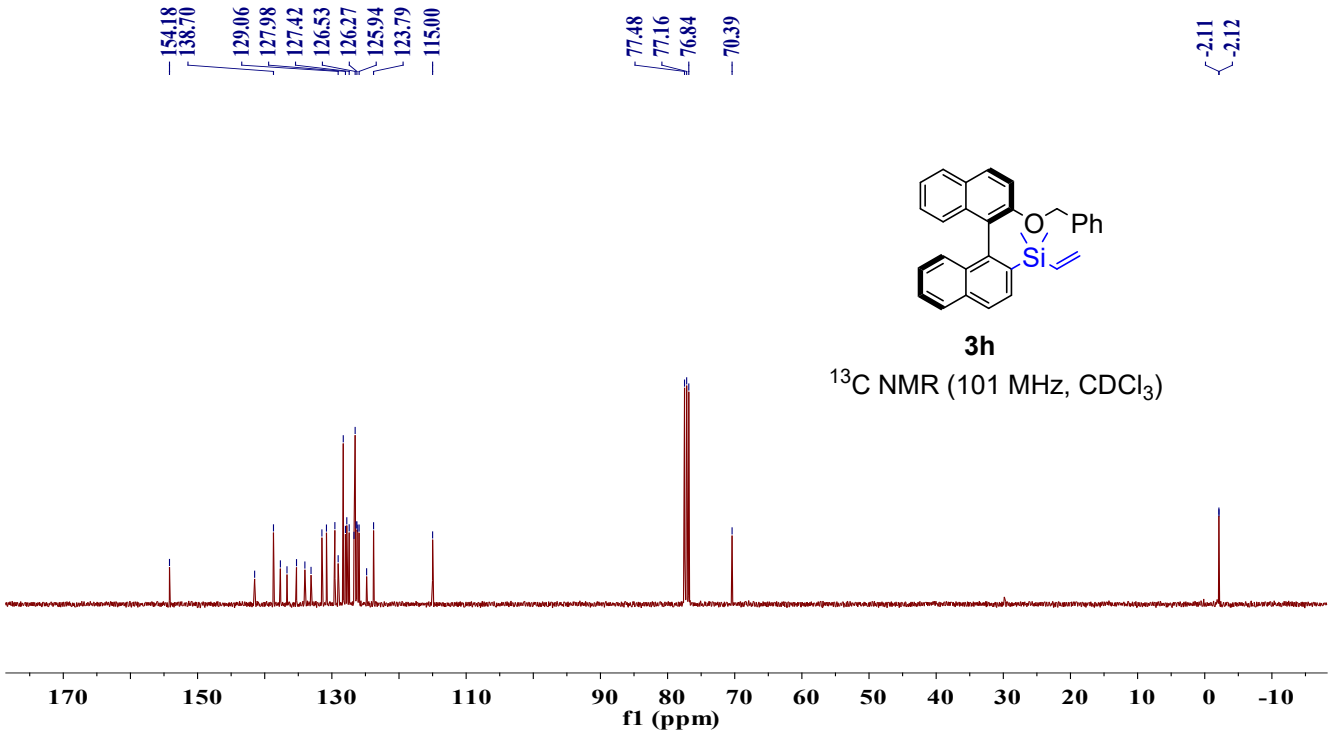

3h

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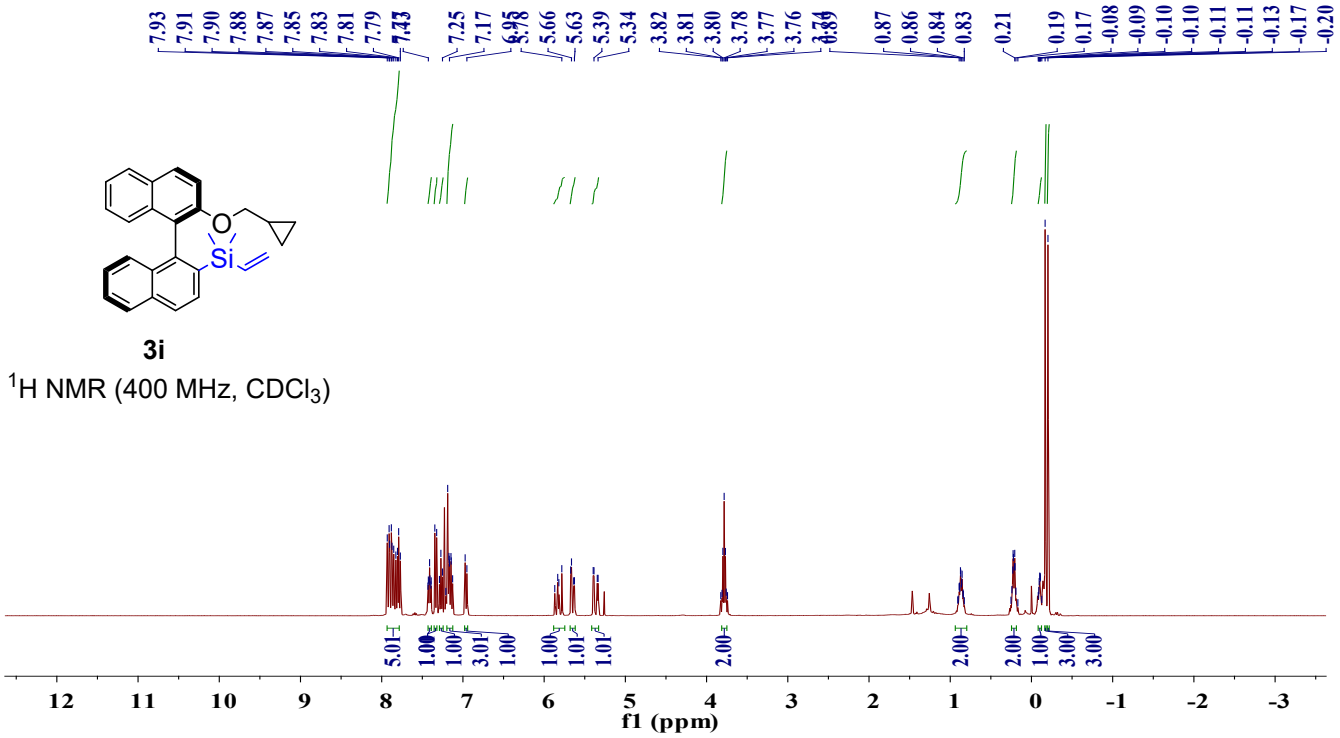

3i

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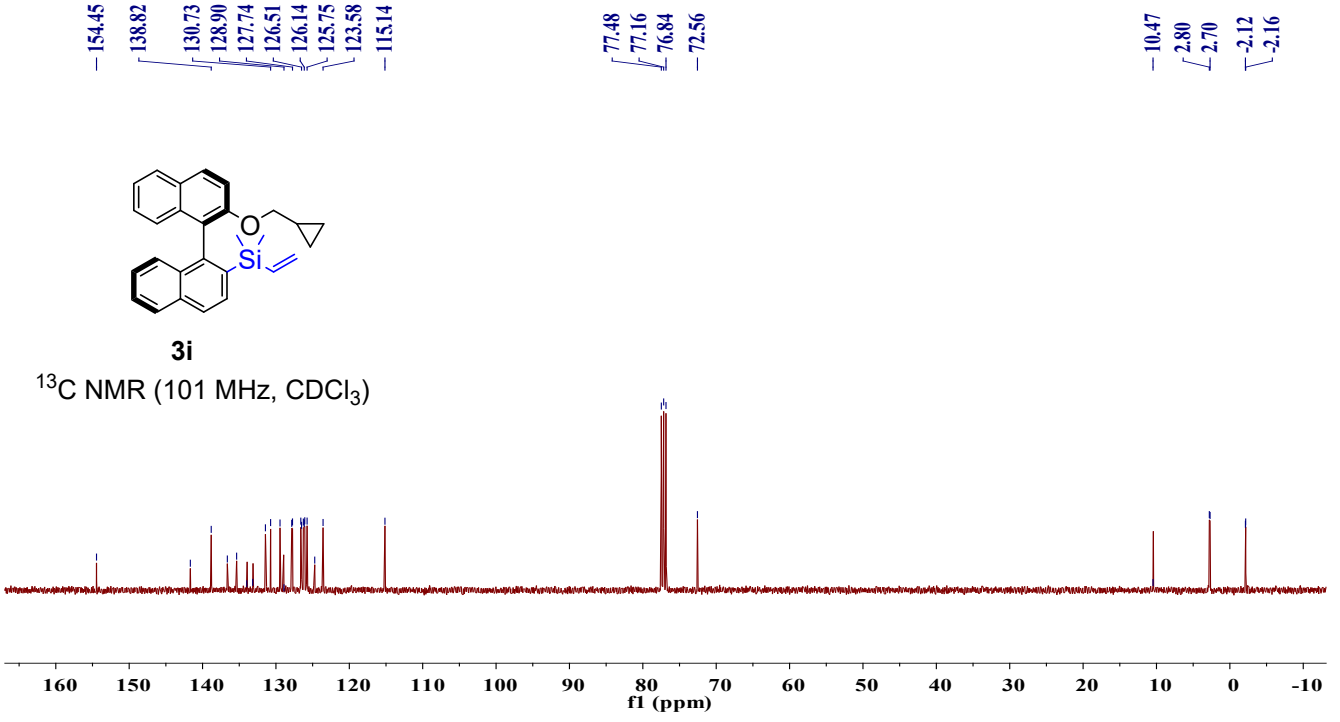

3i

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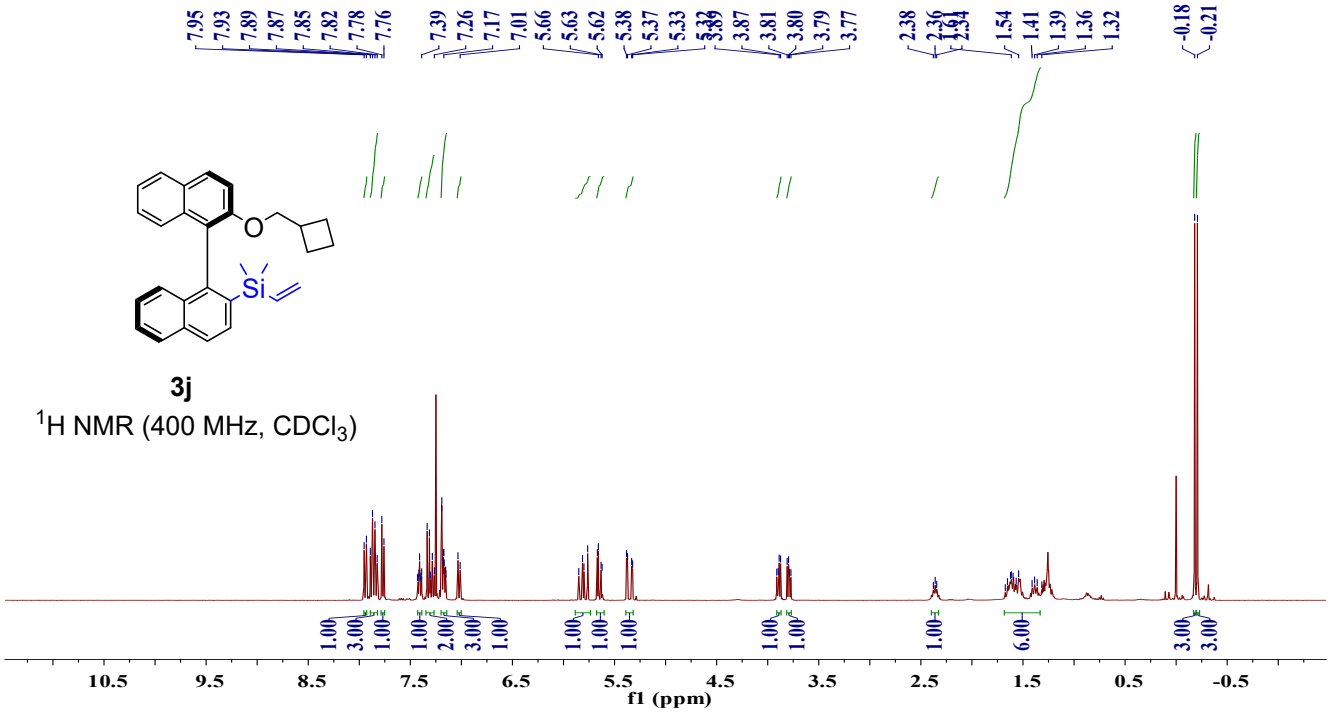
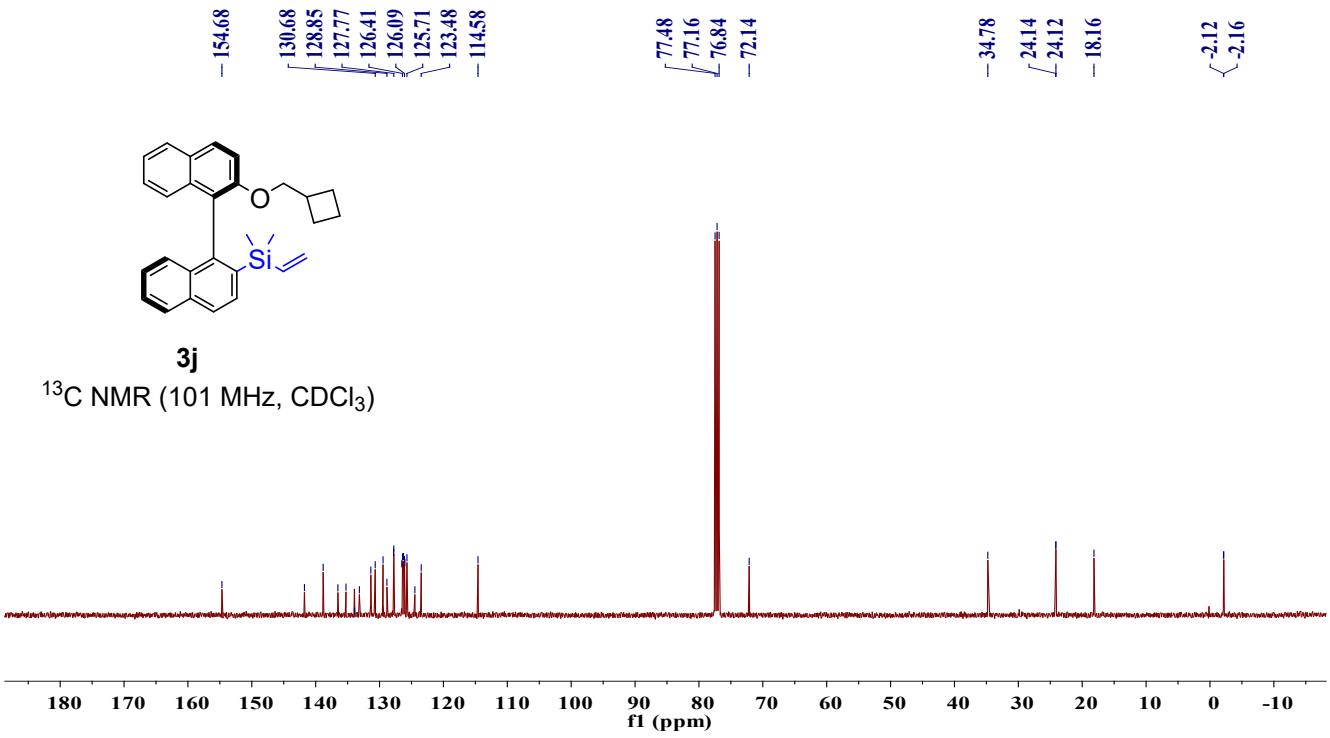


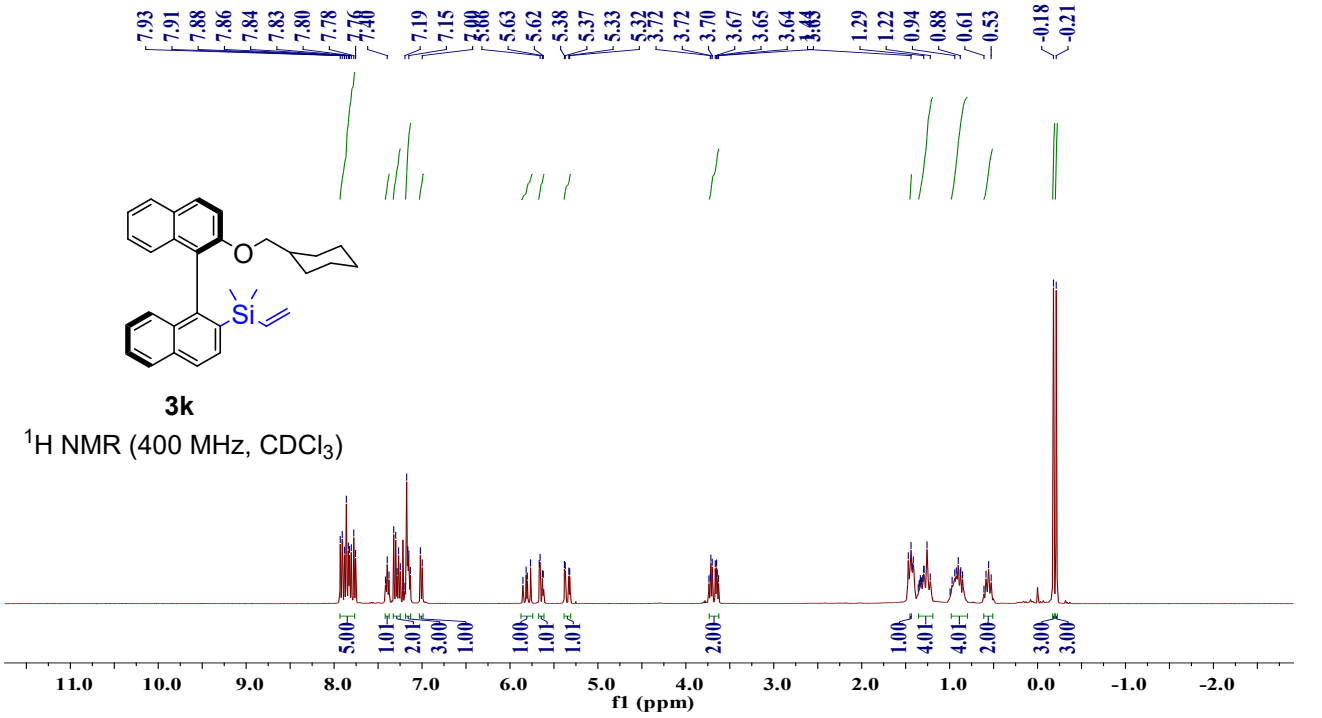
3j

^{1}H NMR (400 MHz, $CDCl_3$)



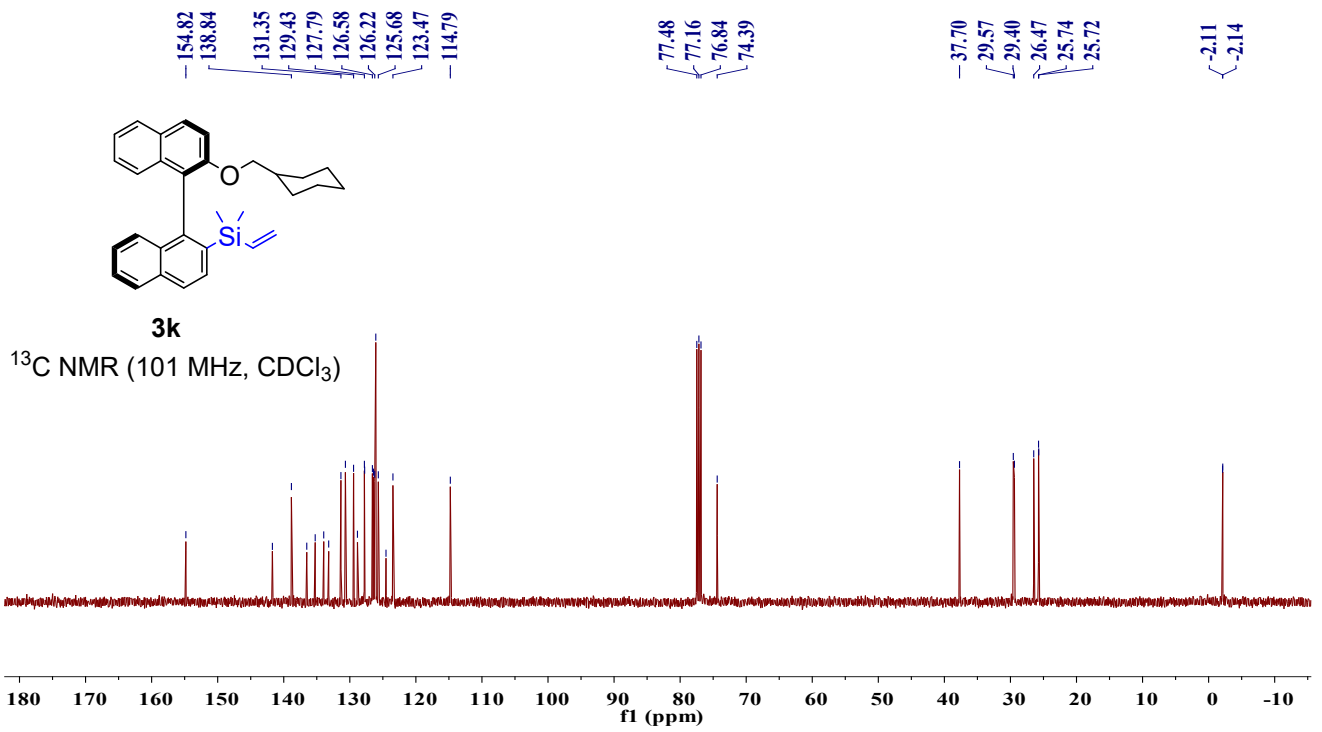
3j

^{13}C NMR (101 MHz, $CDCl_3$)



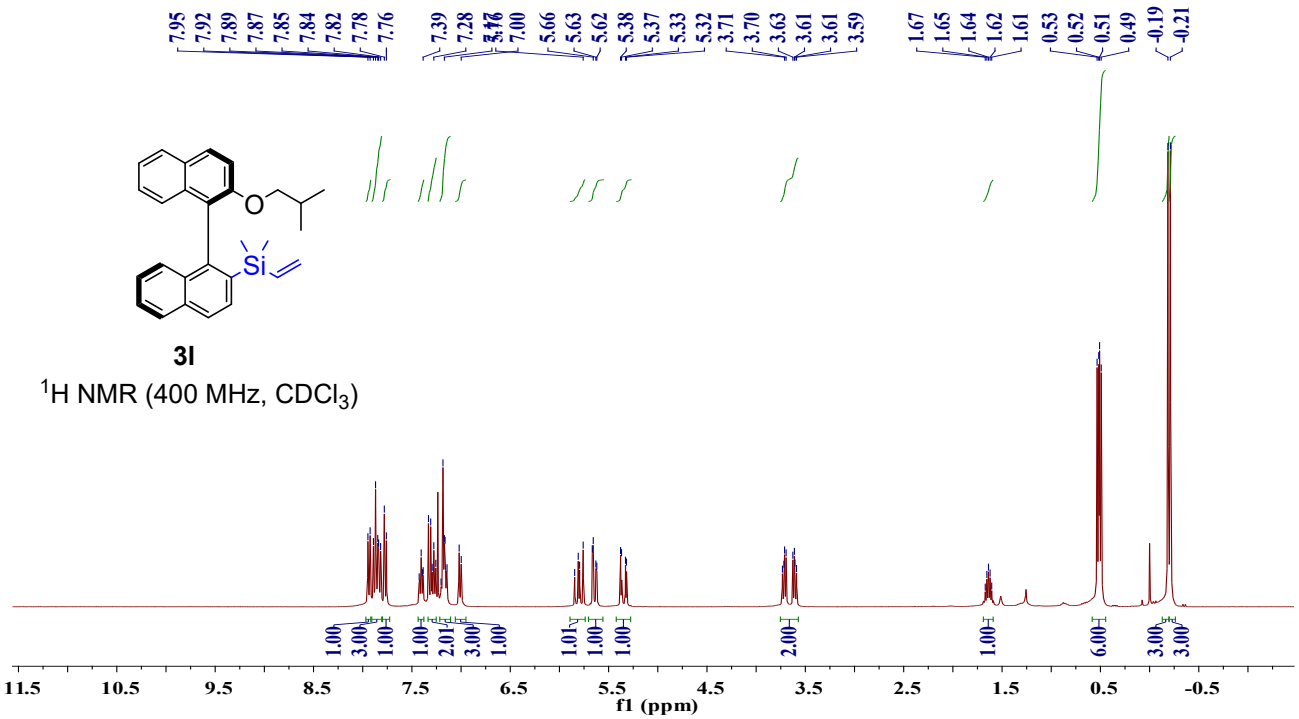
3k

^{1}H NMR (400 MHz, $CDCl_3$)



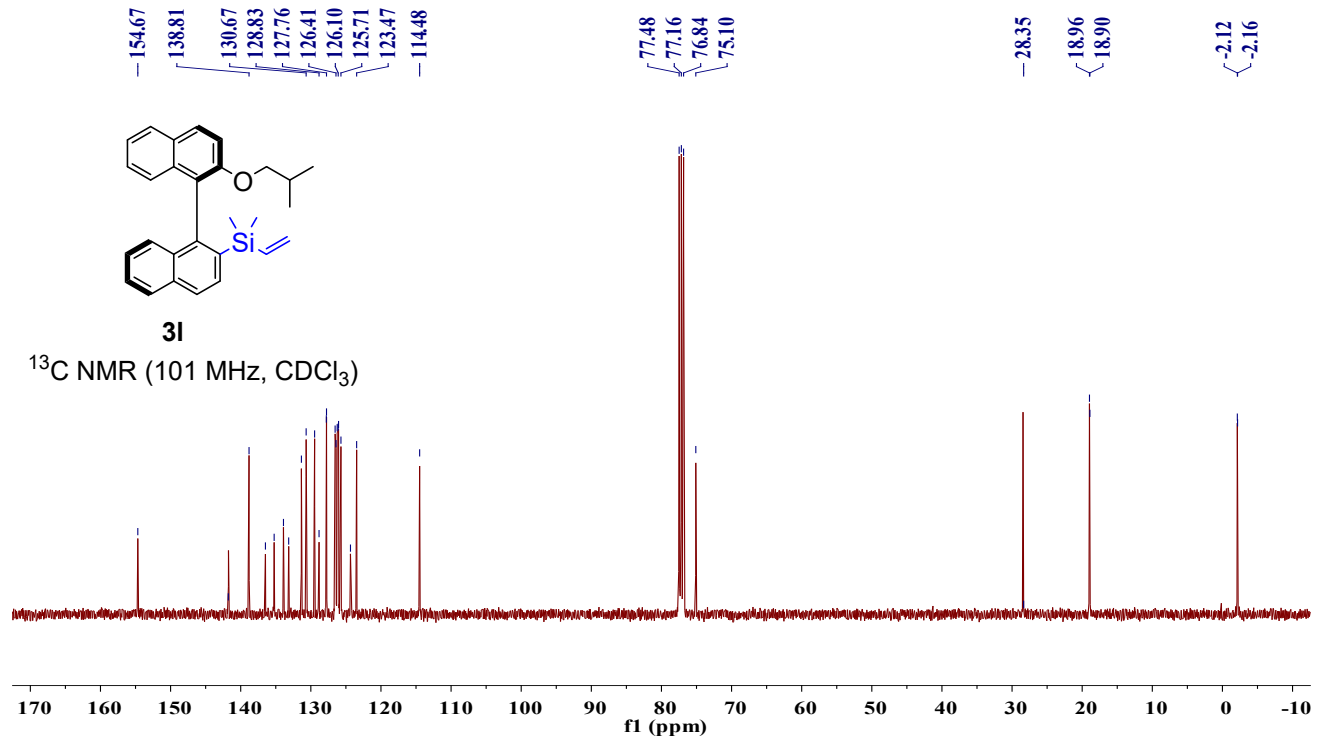
3k

^{13}C NMR (101 MHz, $CDCl_3$)



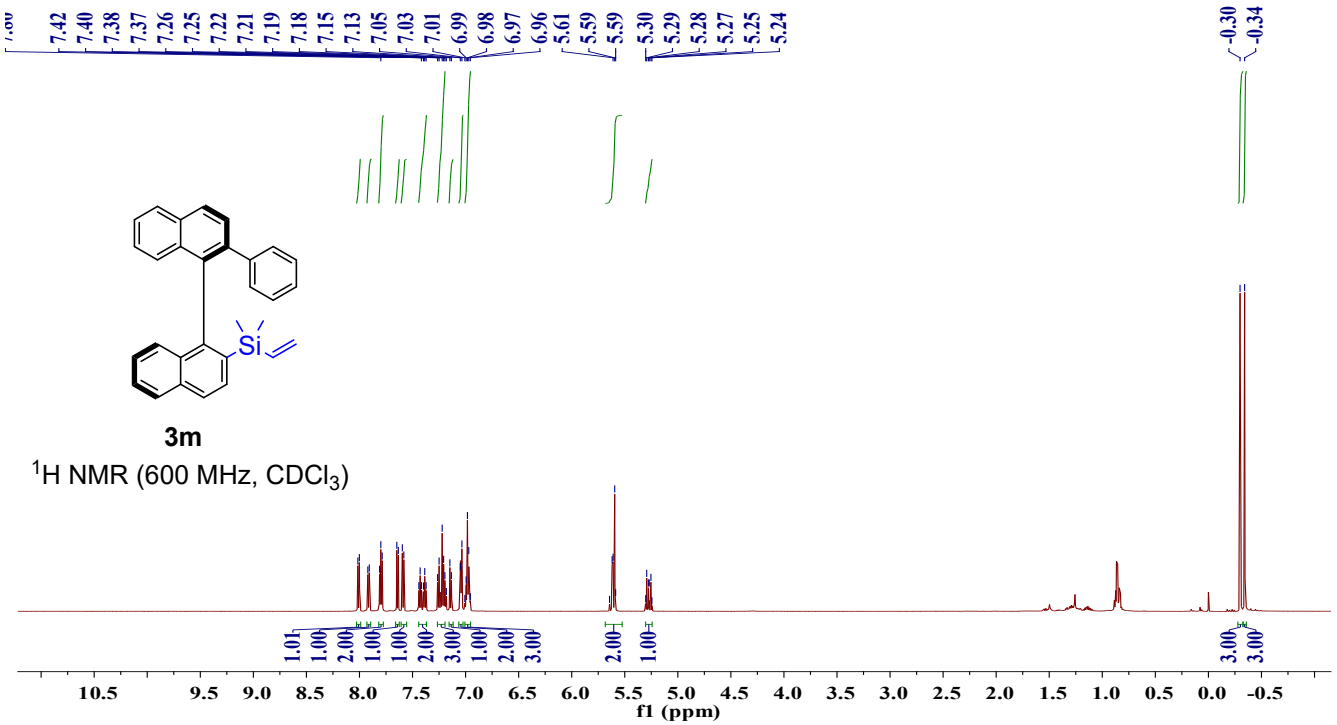
3l

^{1}H NMR (400 MHz, $CDCl_3$)



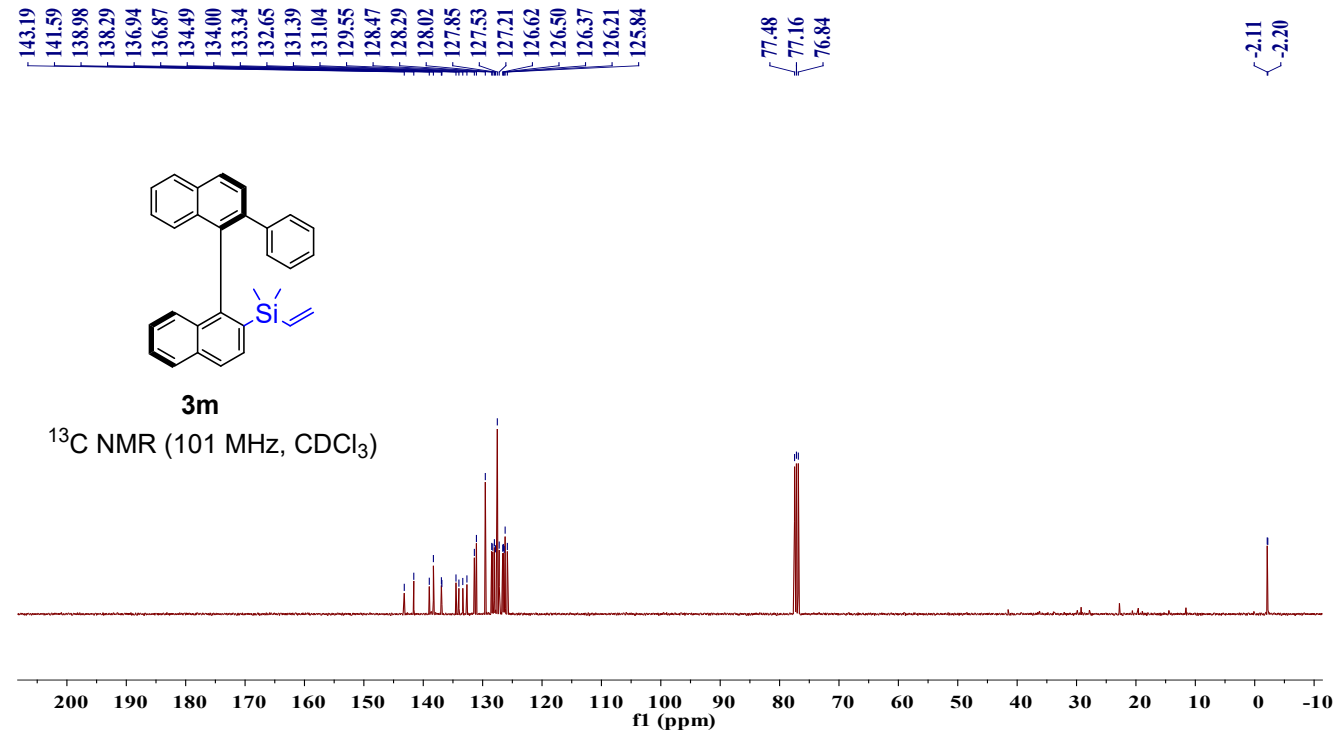
3l

^{13}C NMR (101 MHz, $CDCl_3$)



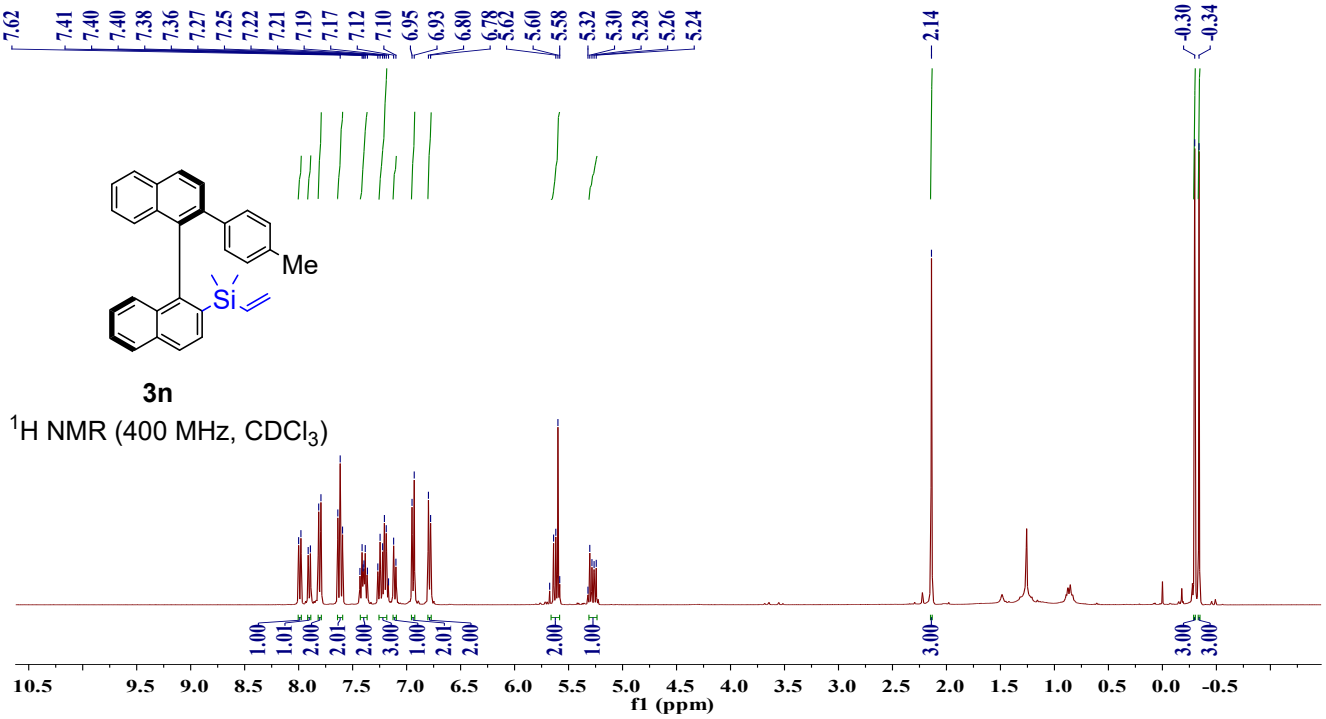
3m

^{1}H NMR (600 MHz, $CDCl_3$)



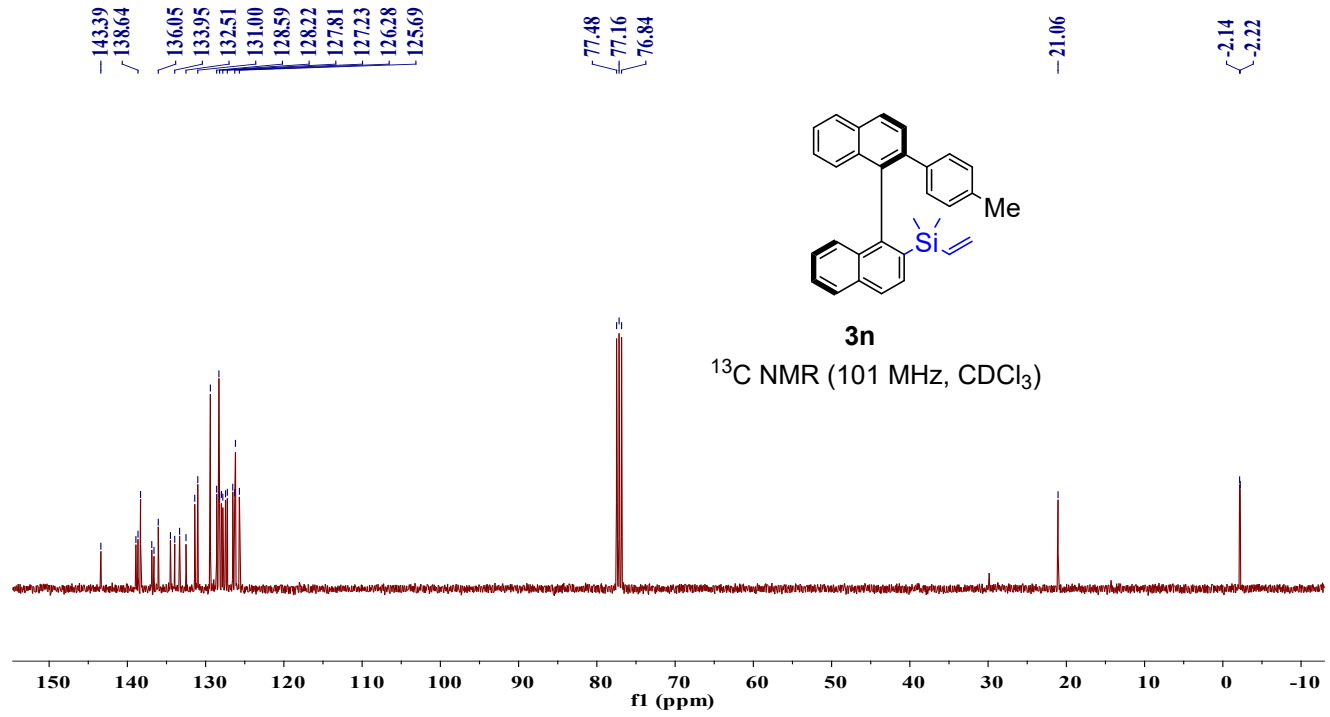
3m

^{13}C NMR (101 MHz, $CDCl_3$)



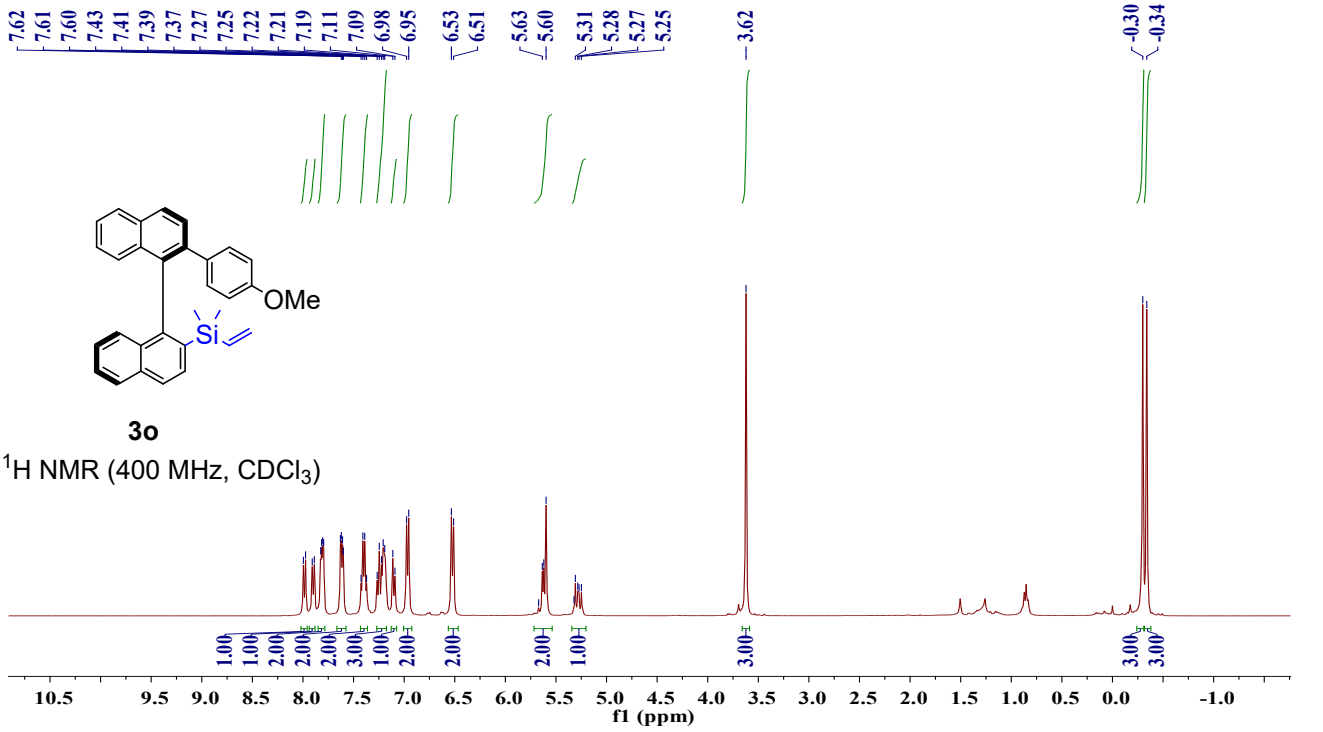
3n

^{1}H NMR (400 MHz, $CDCl_3$)



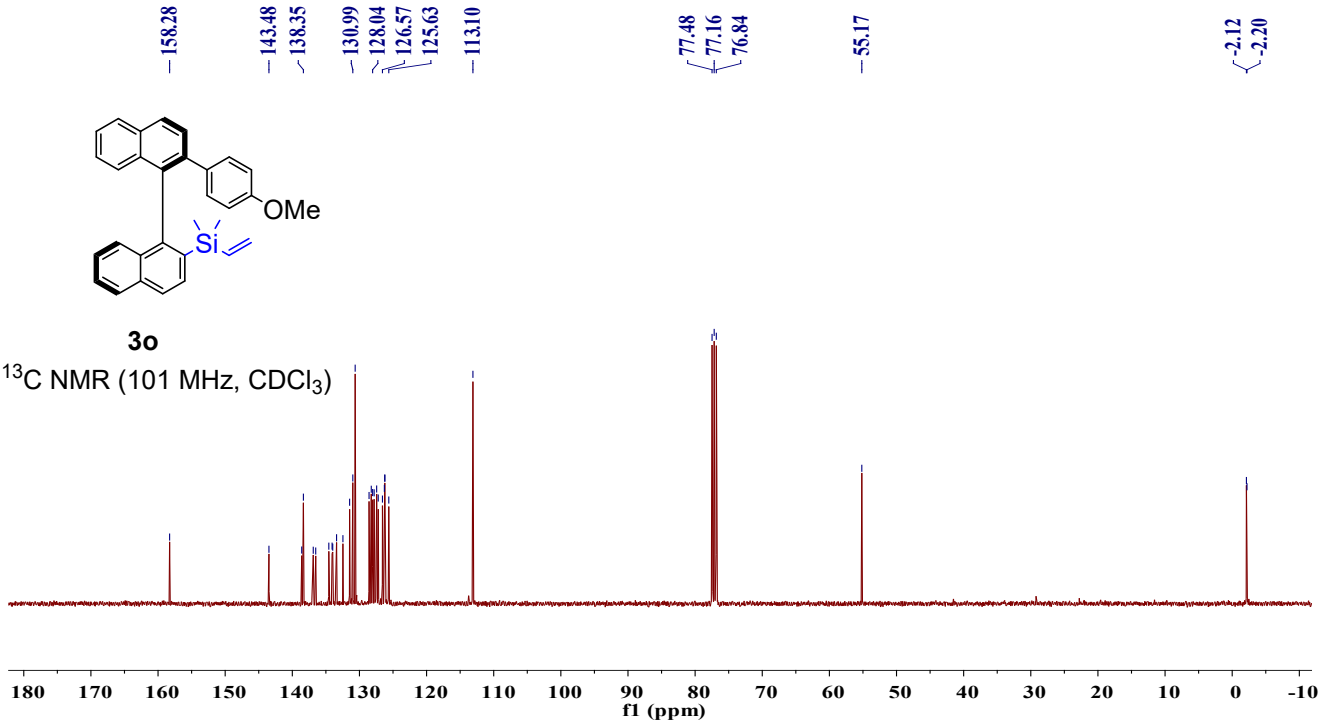
3n

^{13}C NMR (101 MHz, $CDCl_3$)



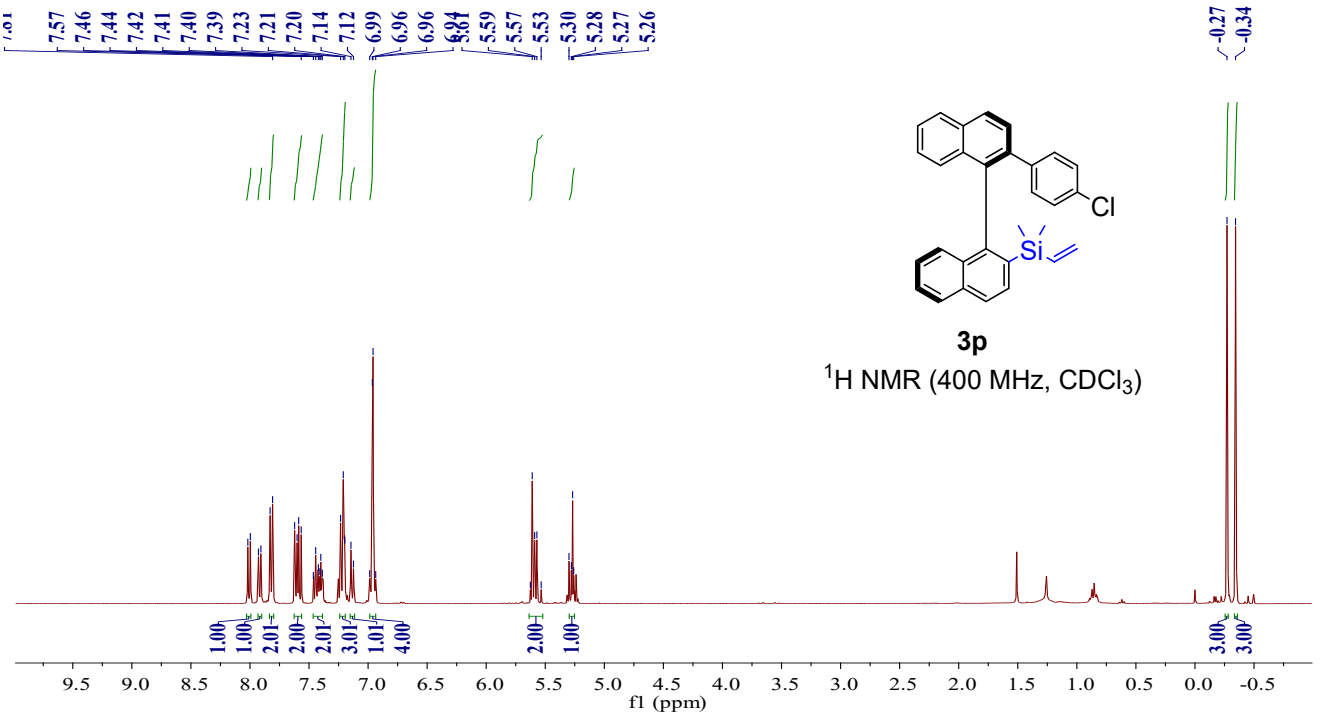
3o

^{1}H NMR (400 MHz, $CDCl_3$)



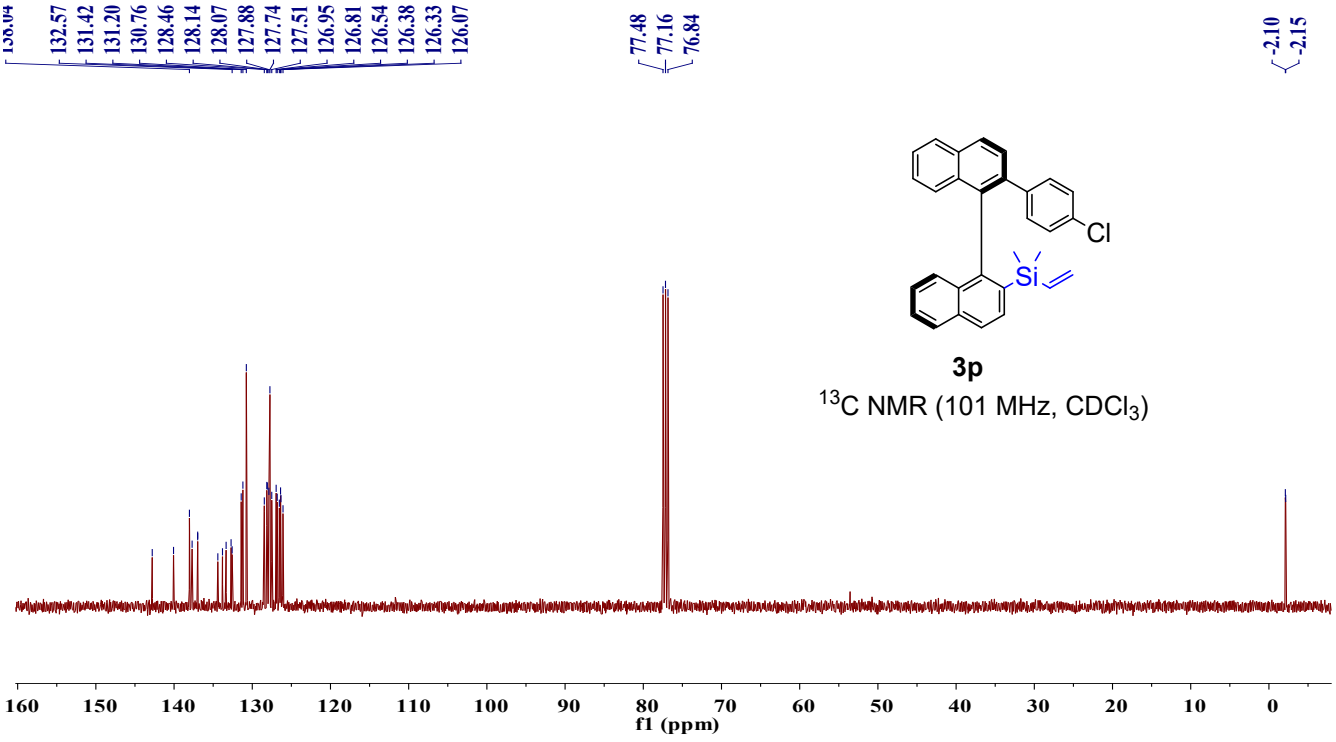
3o

^{13}C NMR (101 MHz, $CDCl_3$)



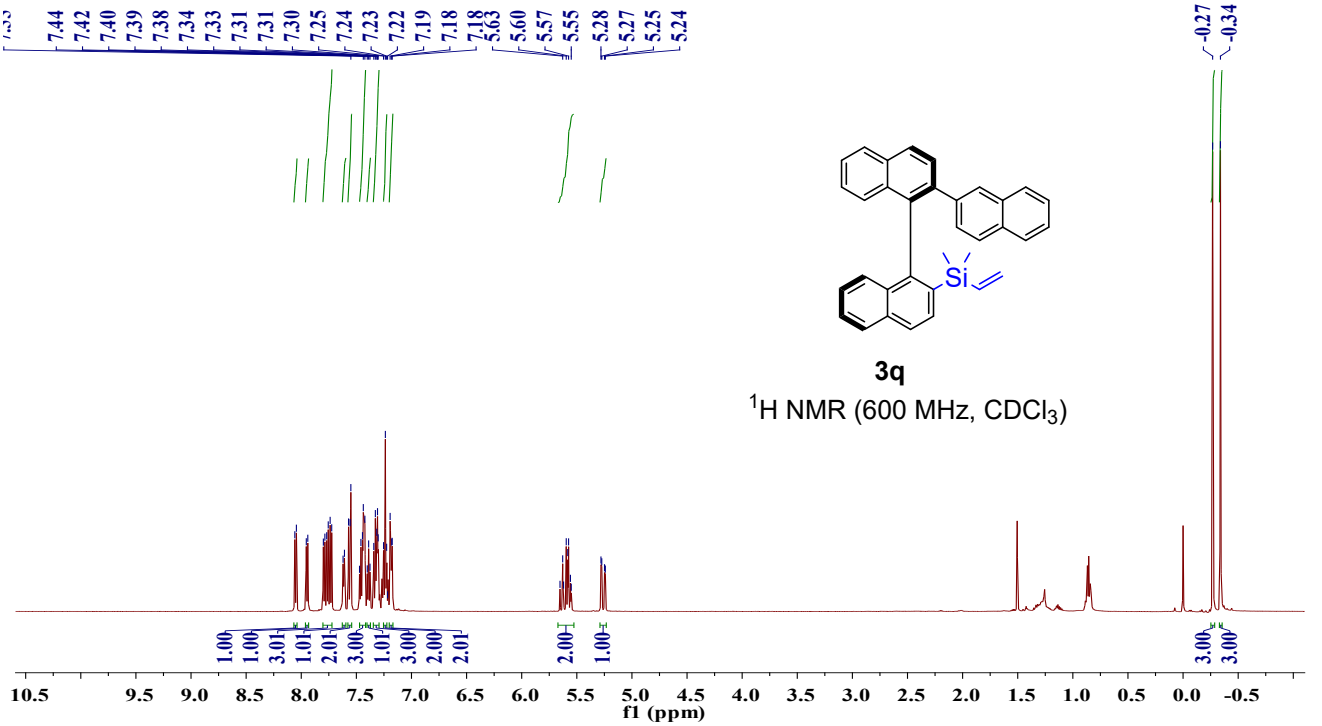
3p

^{1}H NMR (400 MHz, $CDCl_3$)



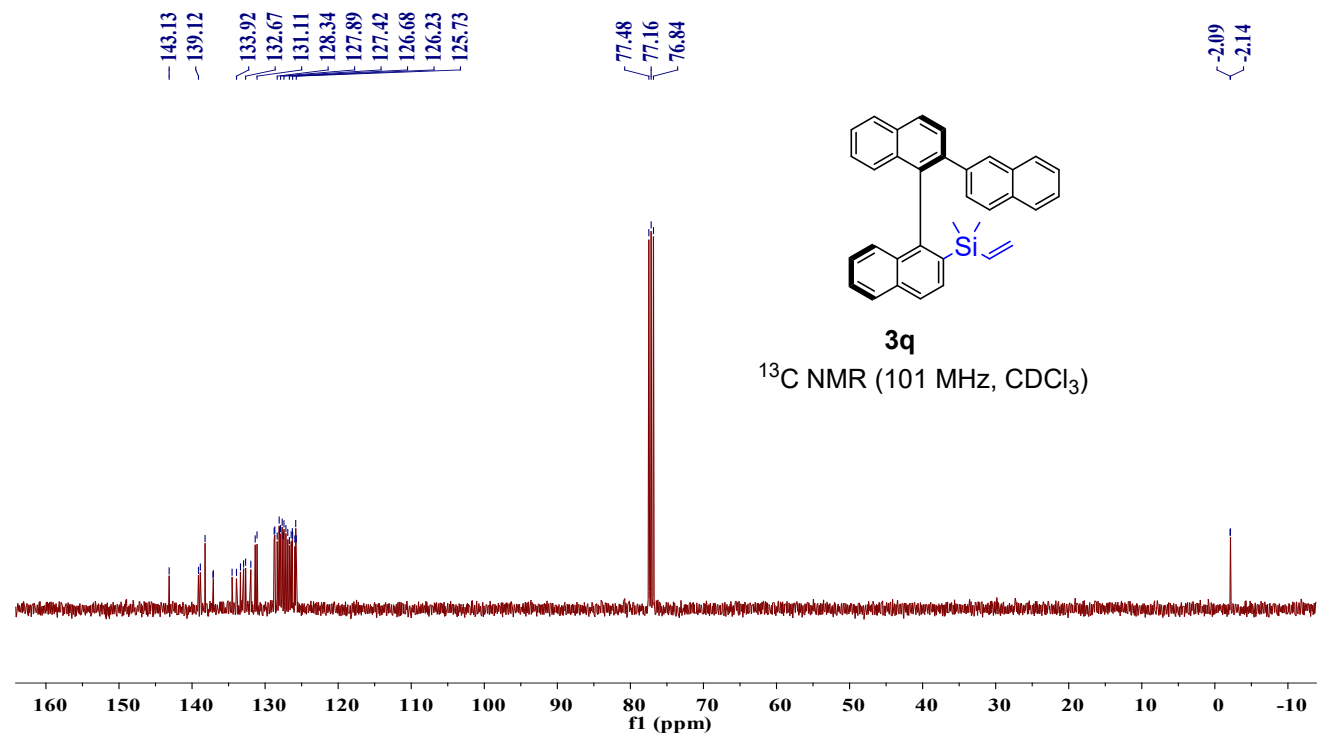
3p

^{13}C NMR (101 MHz, $CDCl_3$)



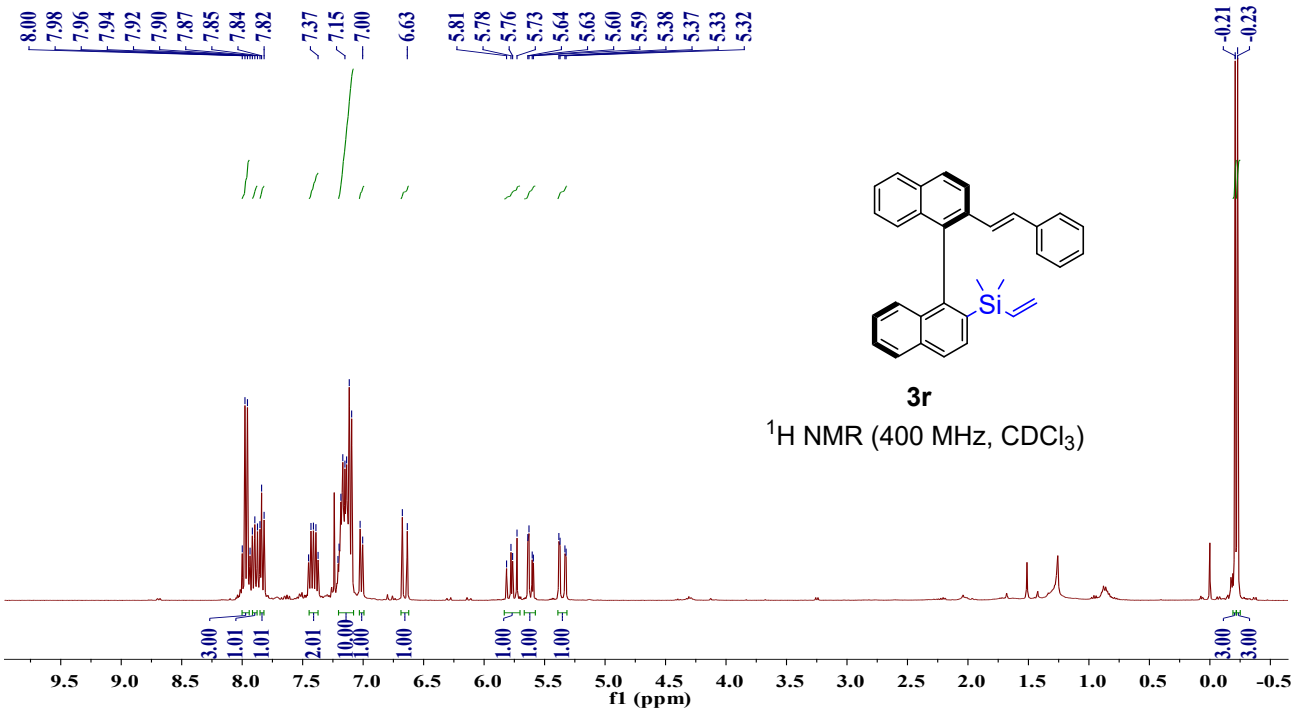
3q

^{1}H NMR (600 MHz, $CDCl_3$)



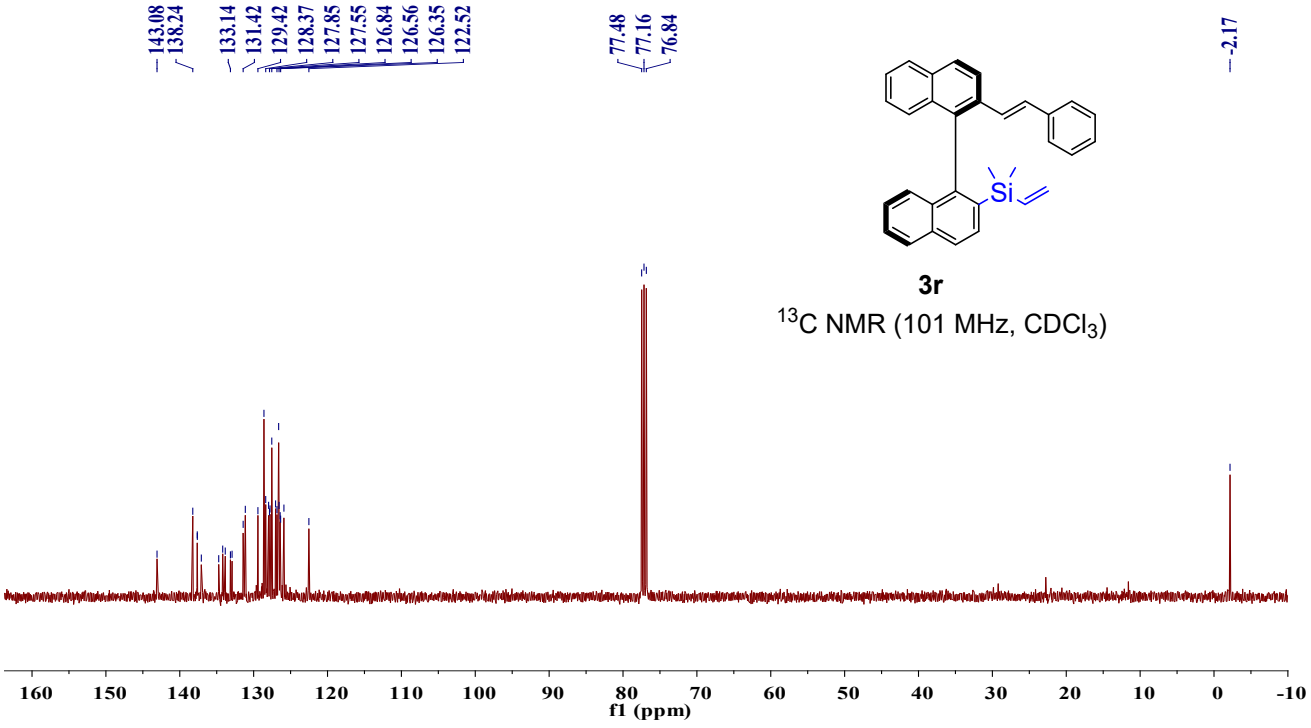
3q

^{13}C NMR (101 MHz, $CDCl_3$)



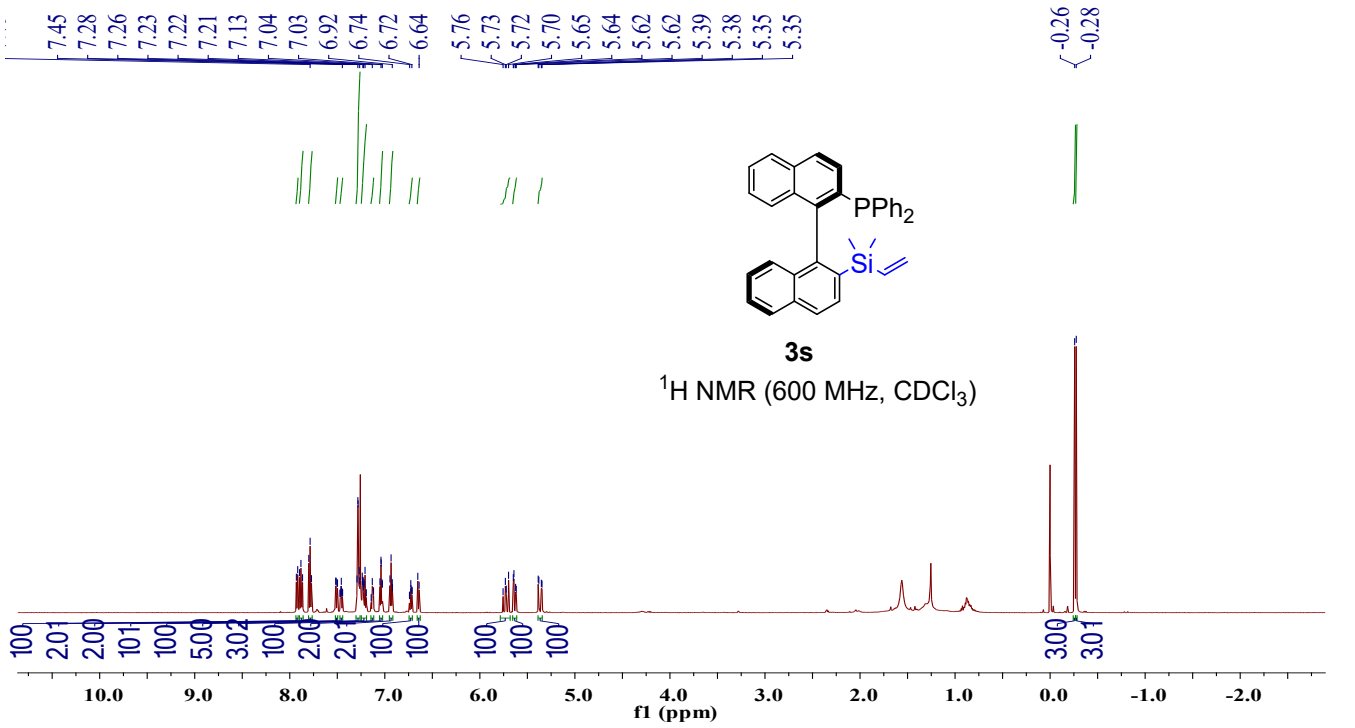
3r

^{1}H NMR (400 MHz, $CDCl_3$)



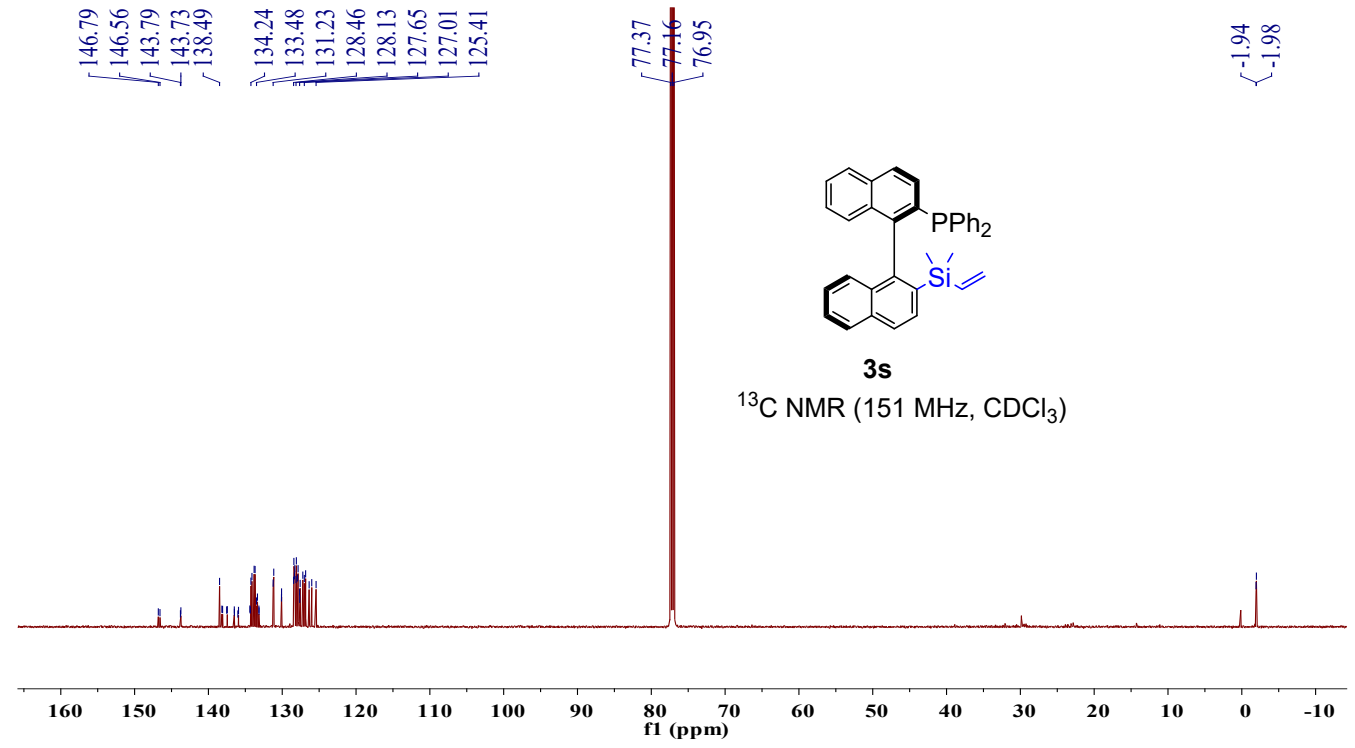
3r

^{13}C NMR (101 MHz, $CDCl_3$)



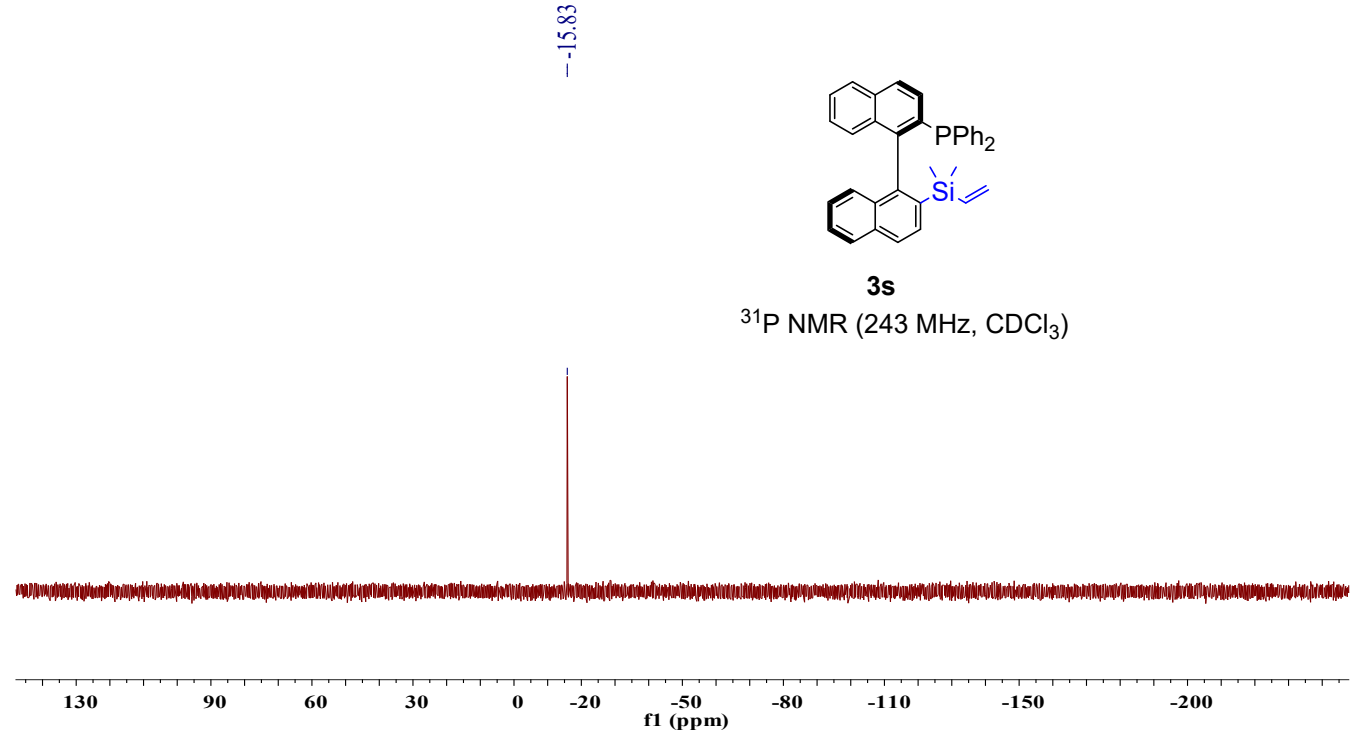
3s

^{1}H NMR (600 MHz, $CDCl_3$)



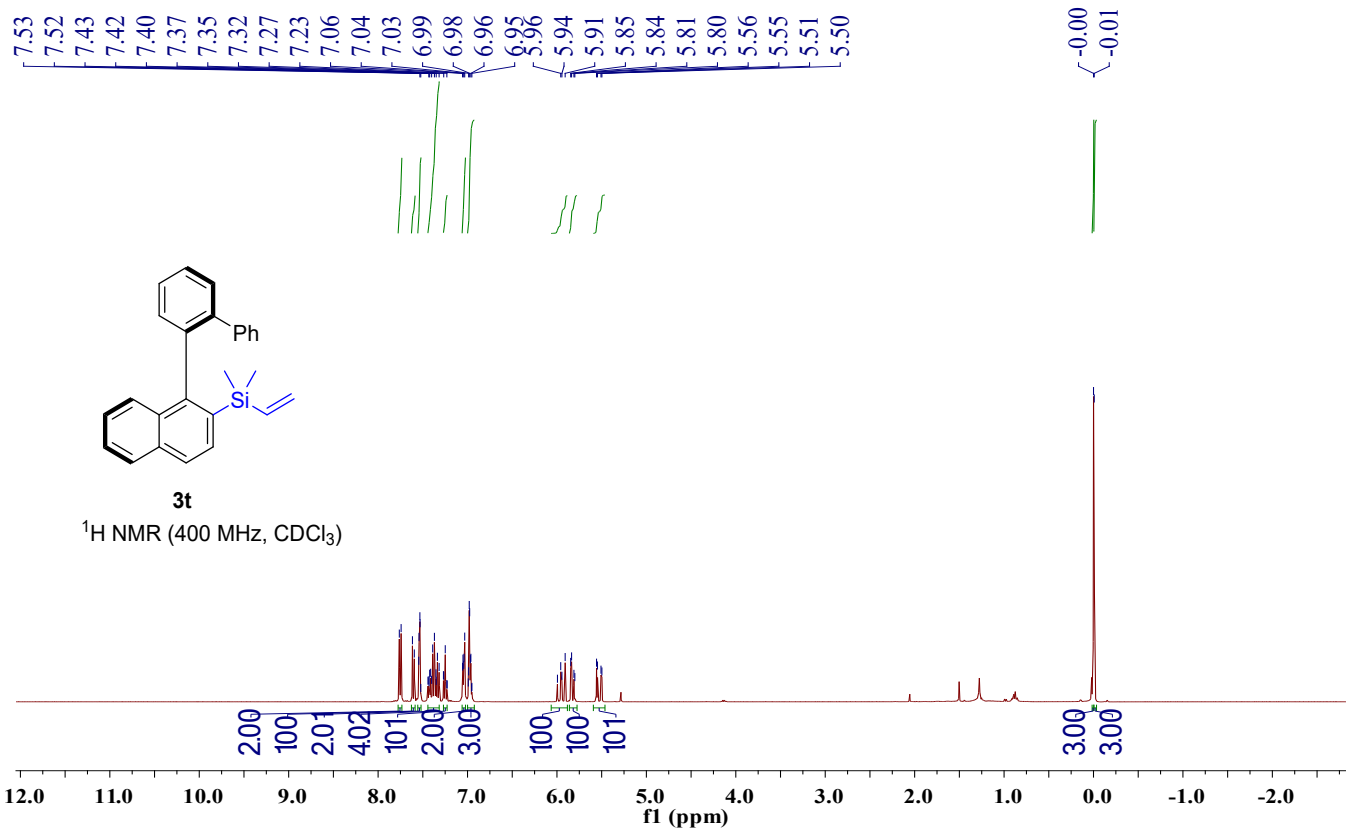
3s

^{13}C NMR (151 MHz, $CDCl_3$)



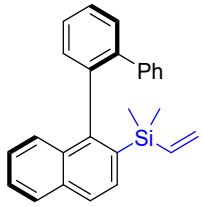
3s

^{31}P NMR (243 MHz, $CDCl_3$)



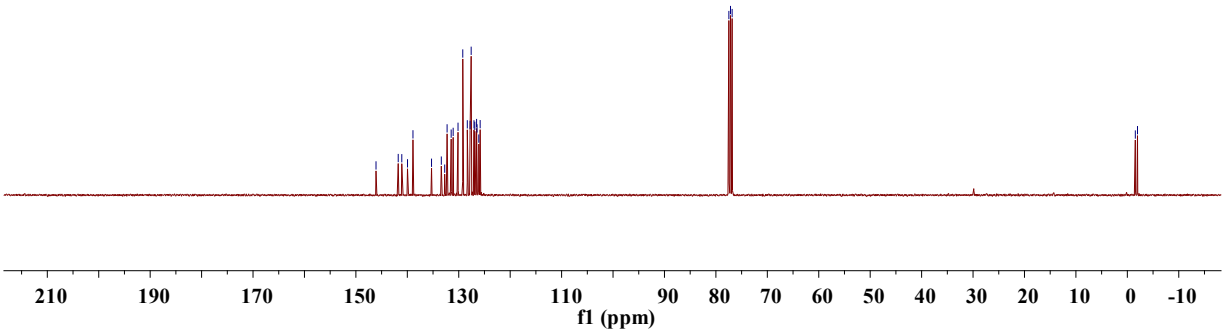
3t

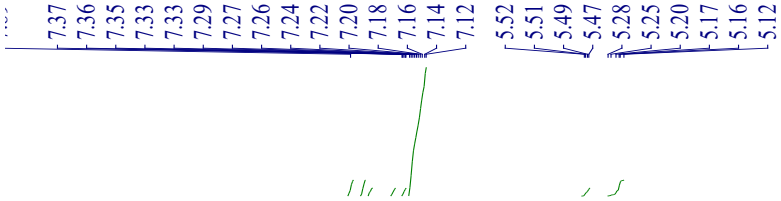
^{1}H NMR (400 MHz, $CDCl_3$)

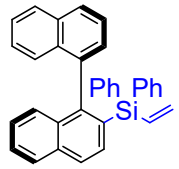


3t

^{13}C NMR (101 MHz, $CDCl_3$)

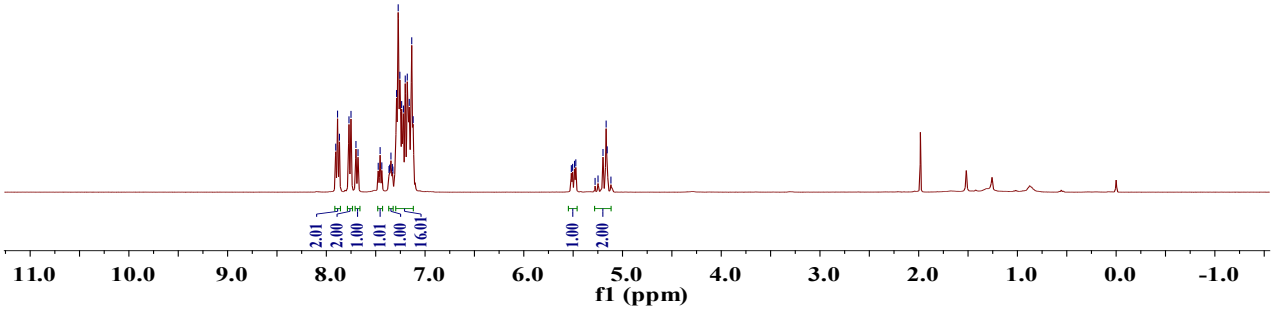


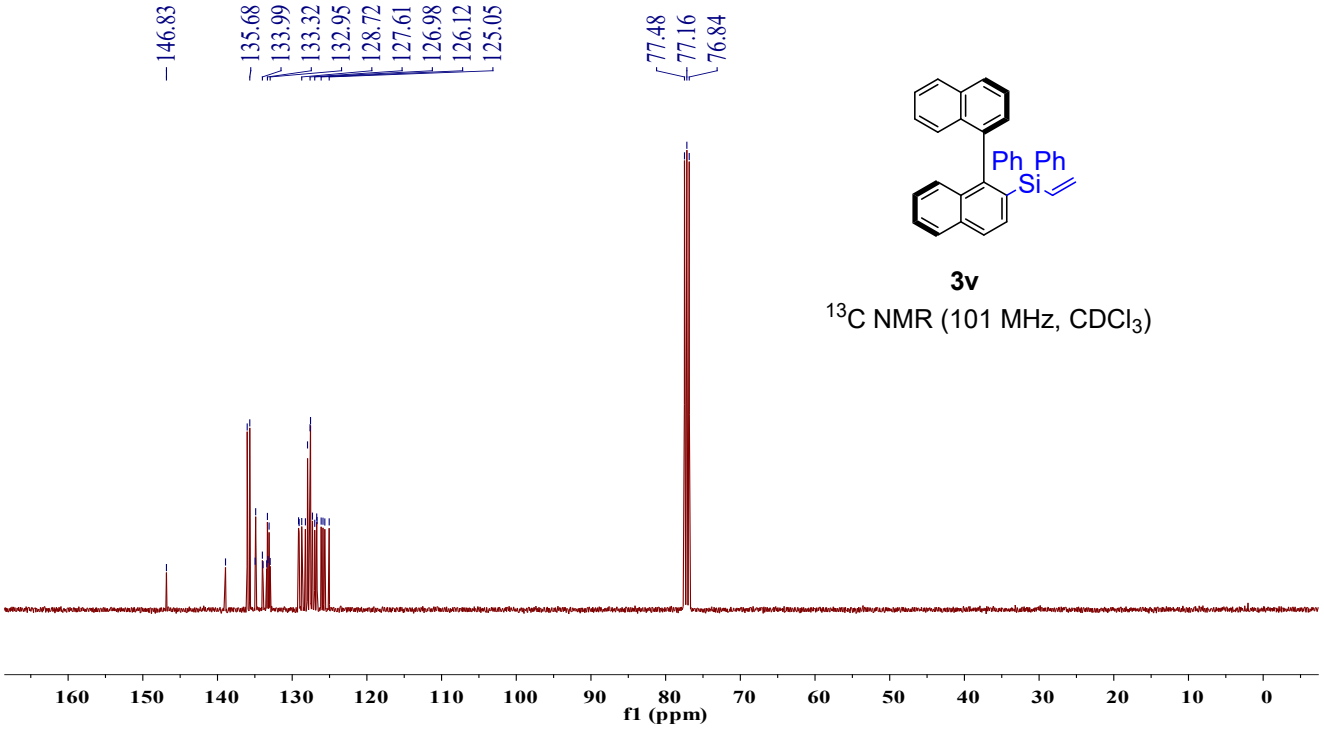




3v

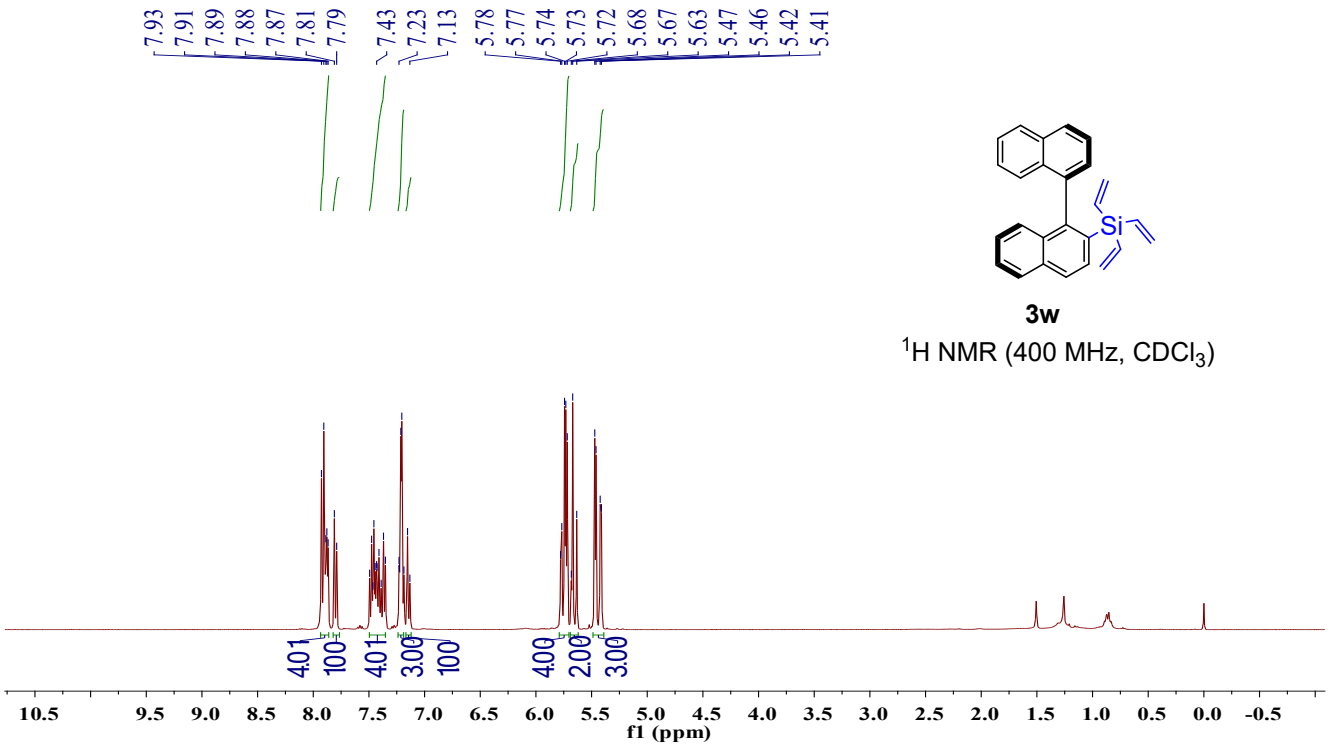
^{1}H NMR (400 MHz, $CDCl_3$)





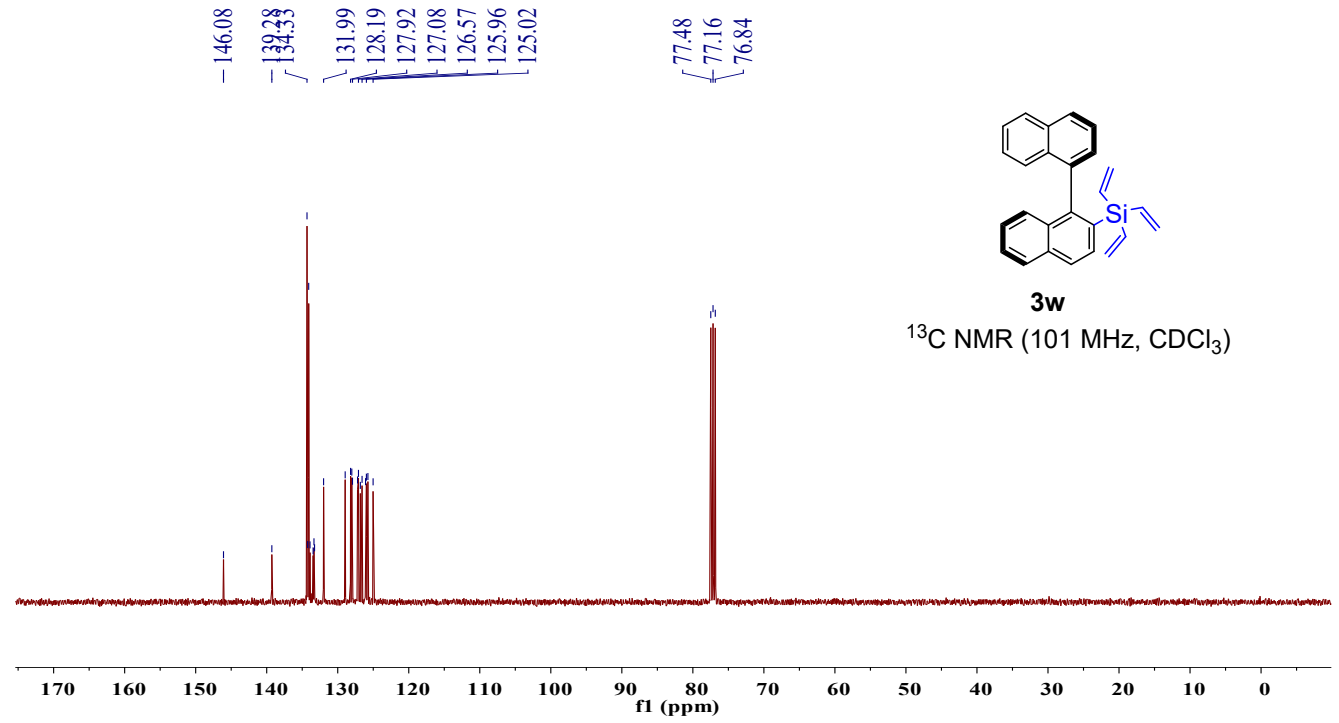
3v

^{13}C NMR (101 MHz, $CDCl_3$)



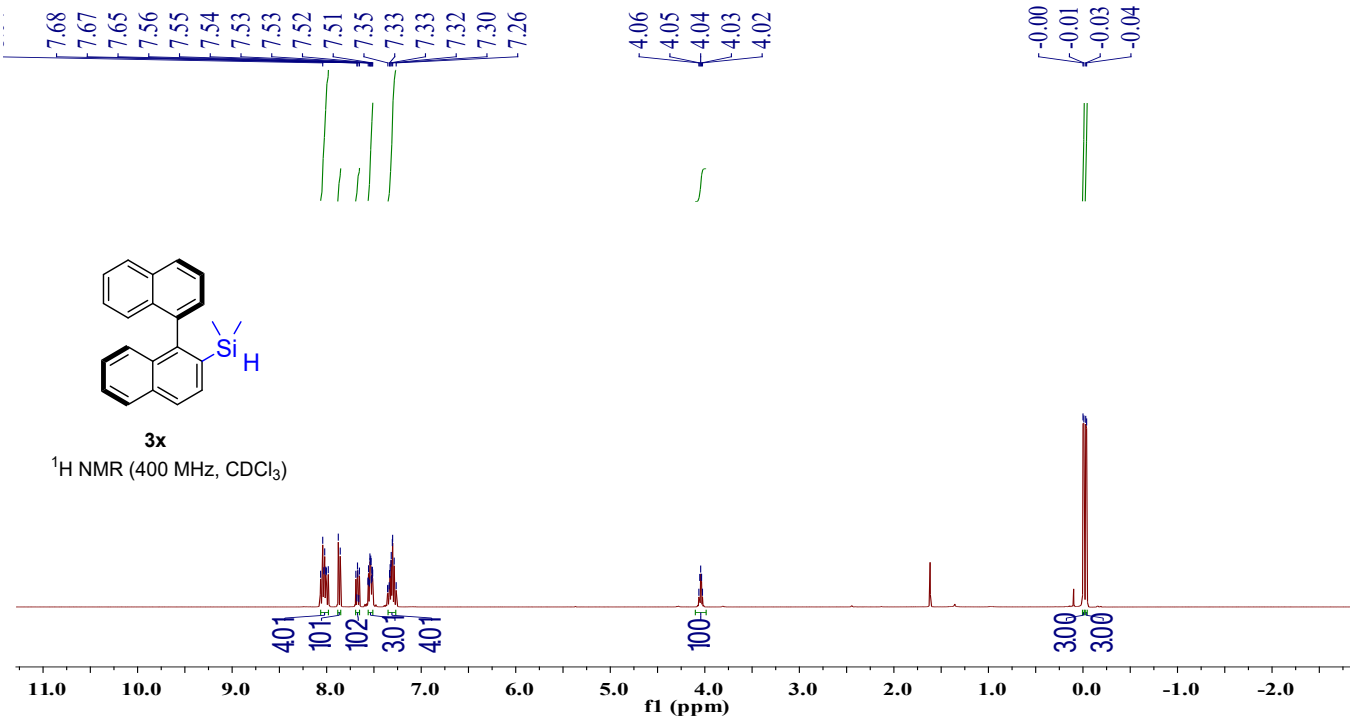
3w

^{1}H NMR (400 MHz, $CDCl_3$)



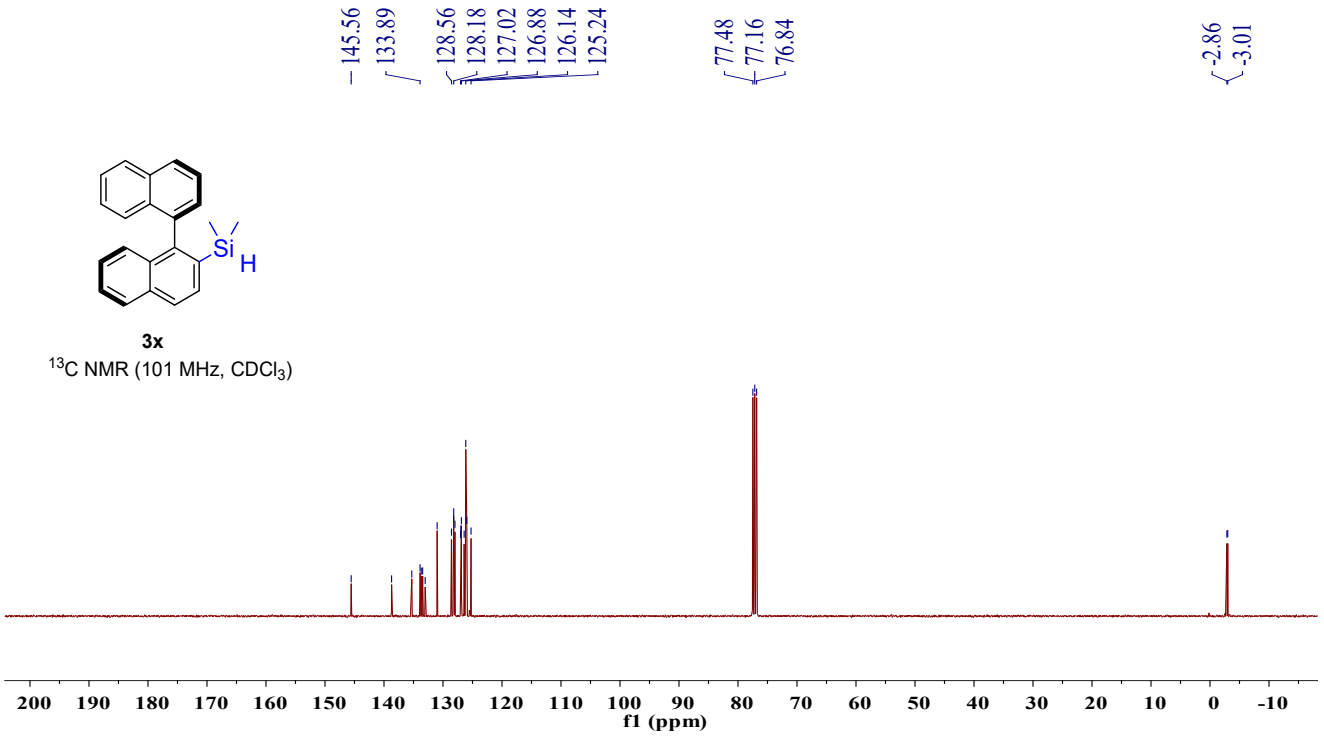
3w

^{13}C NMR (101 MHz, $CDCl_3$)



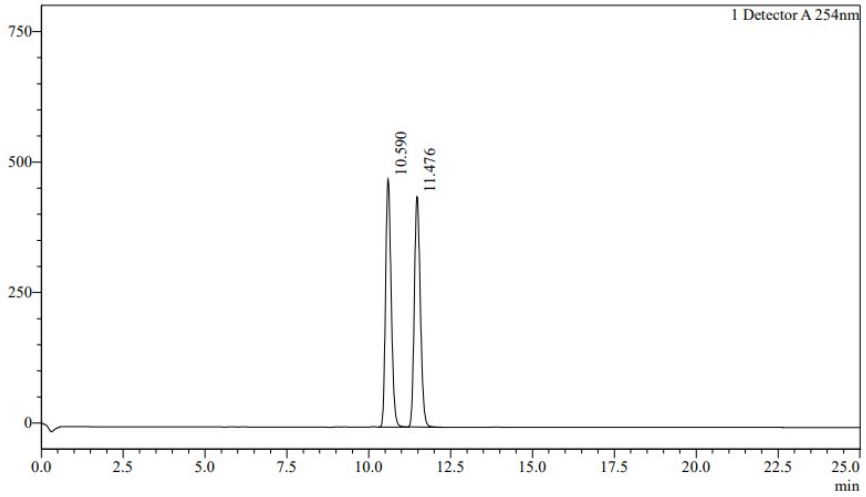
3x

^{1}H NMR (400 MHz, $CDCl_3$)



3x

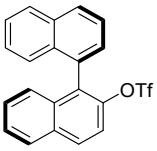
^{13}C NMR (101 MHz, $CDCl_3$)



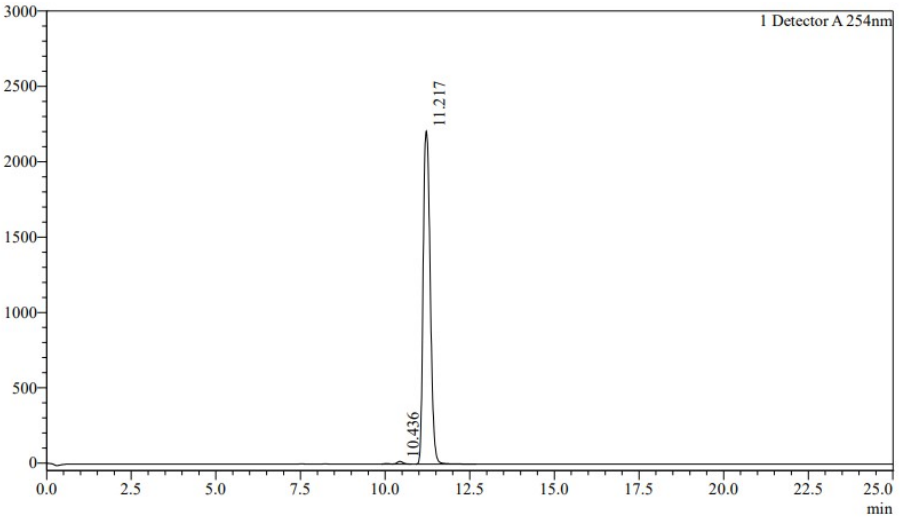
<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Area%
1	10.590	5637089	474701	50.008	50.008
2	11.476	5635228	440878	49.992	49.992
Total		11272317	915580		100.000



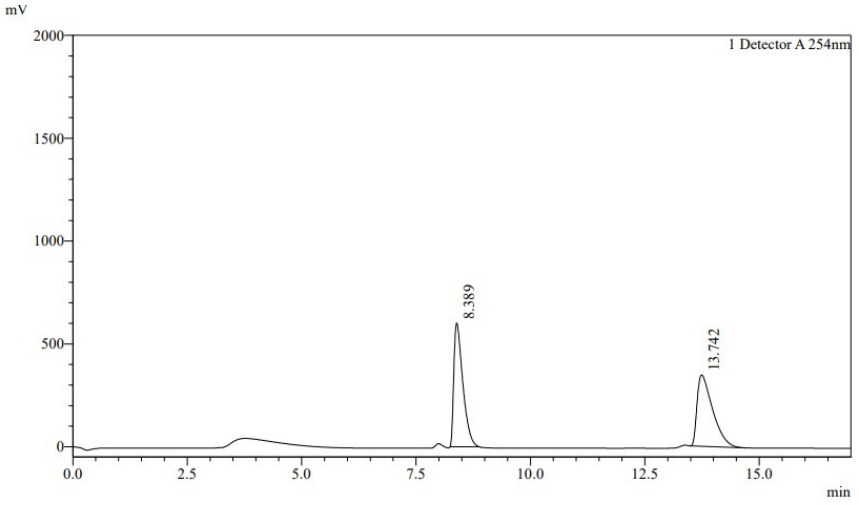
1a



<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Area%
1	10.436	231035	17412	0.719	0.719
2	11.217	31923901	2209612	99.281	99.281
Total		32154937	2227024		100.000

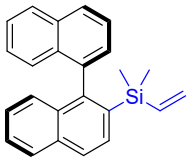


<Peak Table>

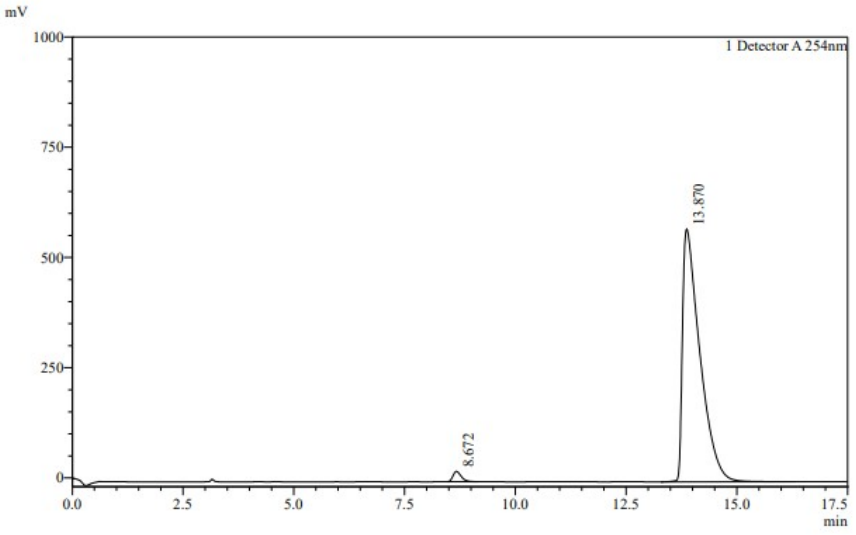
Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Area%
1	8.389	8251641	601208	50.199	50.199
2	13.742	8186282	347278	49.801	49.801
Total		16437924	948486		100.000

<Chromatogram>



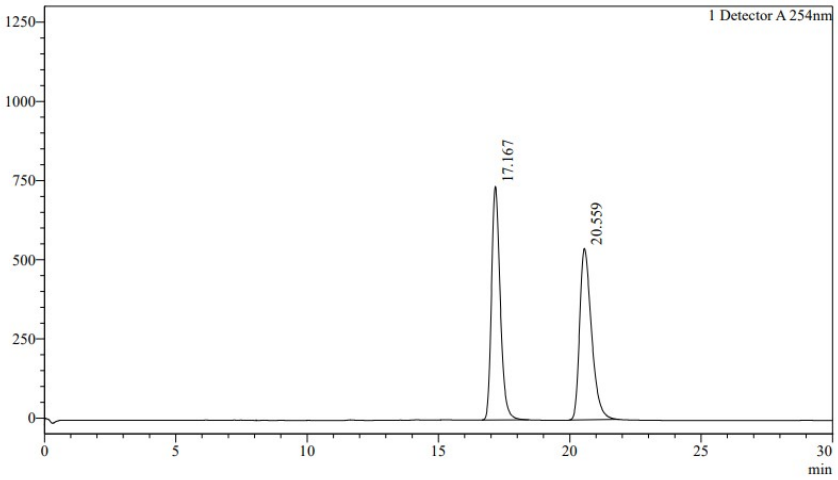
3a



<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Area%
1	8.672	297418	23239	1.864	1.864
2	13.870	15658340	573361	98.136	98.136
Total		15955758	596600		100.000

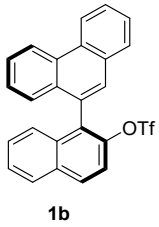


<Peak Table>

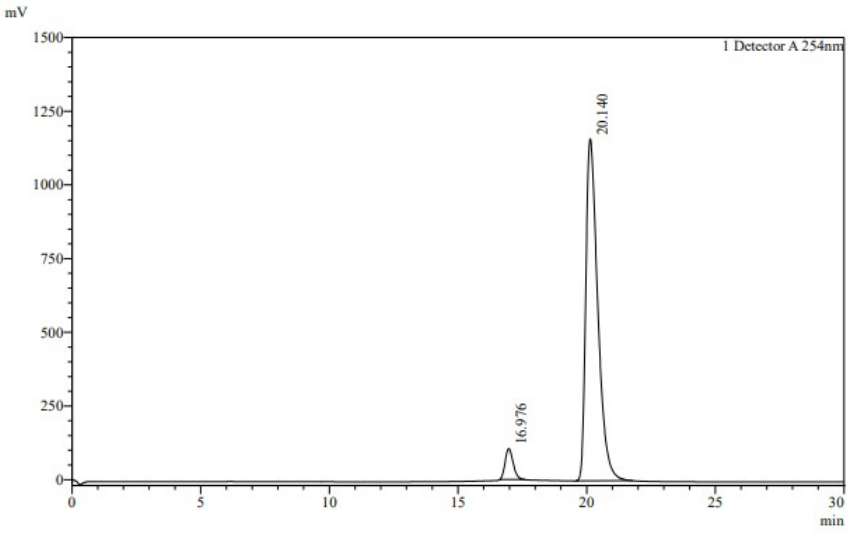
Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Area%
1	17.167	17008258	736791	50.051	50.051
2	20.559	16973509	540945	49.949	49.949
Total		33981767	1277736		100.000

<Chromatogram>



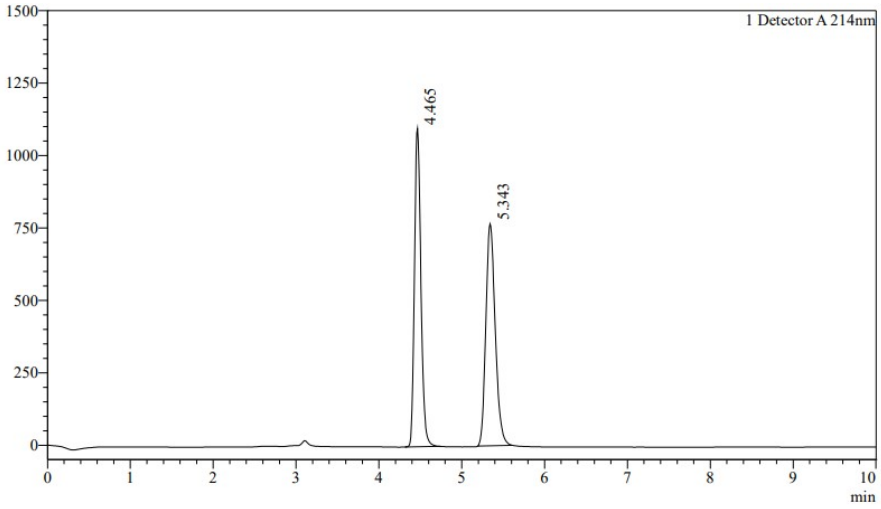
1b



<Peak Table>

Detector A 254nm

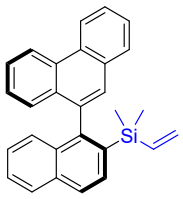
Peak#	Ret. Time	Area	Height	Conc.	Area%
1	16.976	2257219	104321	5.688	5.688
2	20.140	37423623	1159767	94.312	94.312
Total		39680842	1264088		100.000



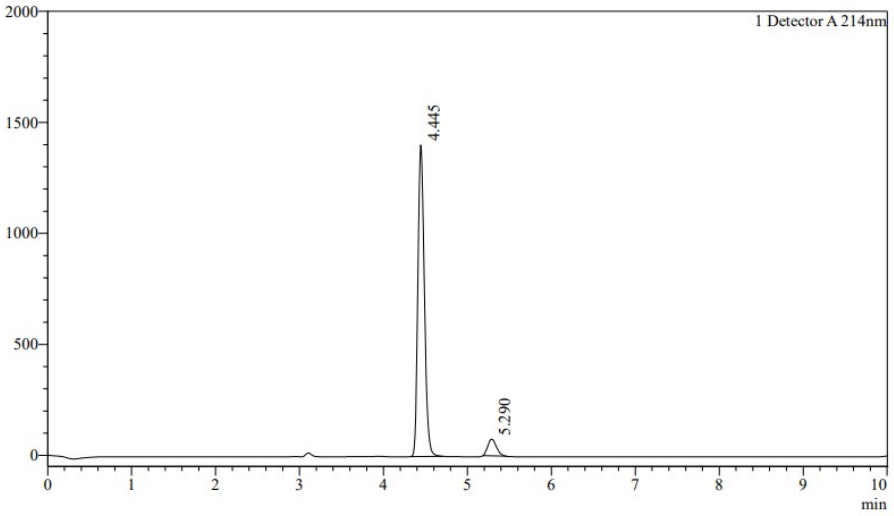
<Peak Table>

Detector A 214nm

Peak#	Ret. Time	Area	Height	Conc.	Area%
1	4.465	5962870	1099248	49.709	49.709
2	5.343	6032724	765972	50.291	50.291
Total		11995594	1865220		100.000



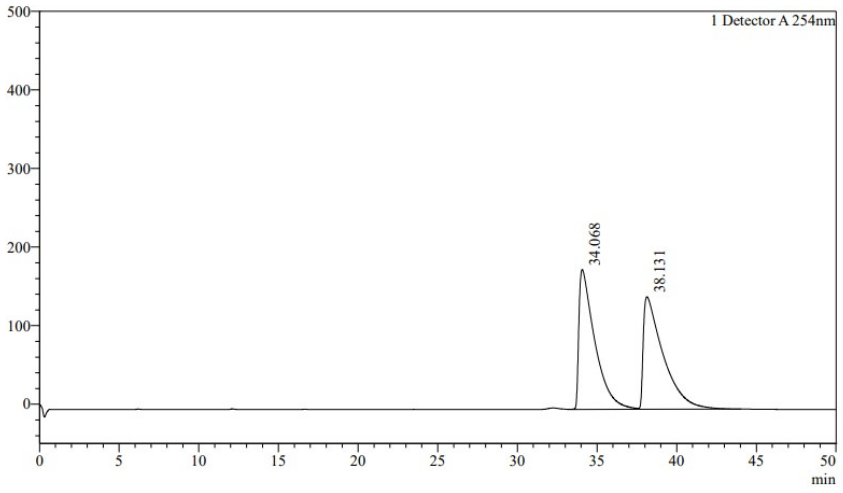
3b



<Peak Table>

Detector A 214nm

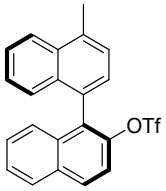
Peak#	Ret. Time	Area	Height	Conc.	Area%
1	4.445	7525936	1401439	93.289	93.289
2	5.290	541390	75284	6.711	6.711
Total		8067326	1476723		100.000



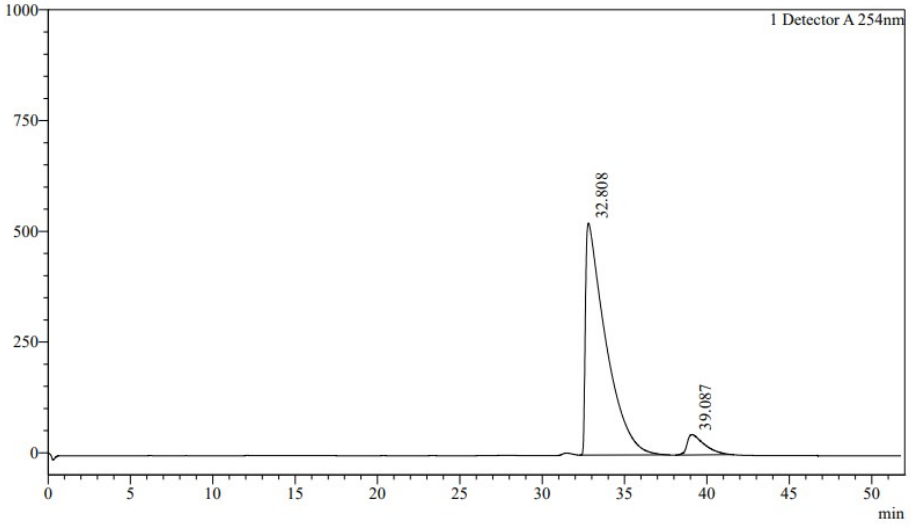
<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Area%
1	34.068	12401867	177919	49.889	49.889
2	38.131	12457138	143186	50.111	50.111
Total		24859006	321106		100.000



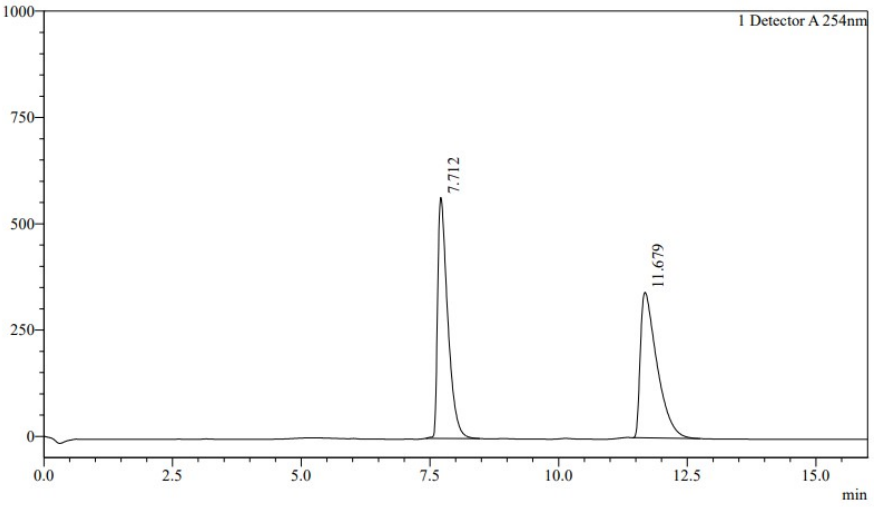
1c



<Peak Table>

Detector A 254nm

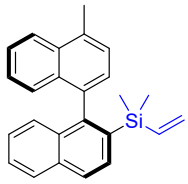
Peak#	Ret. Time	Area	Height	Conc.	Area%
1	32.808	44843884	523632	92.971	92.971
2	39.087	3390566	46159	7.029	7.029
Total		48234450	569791		100.000



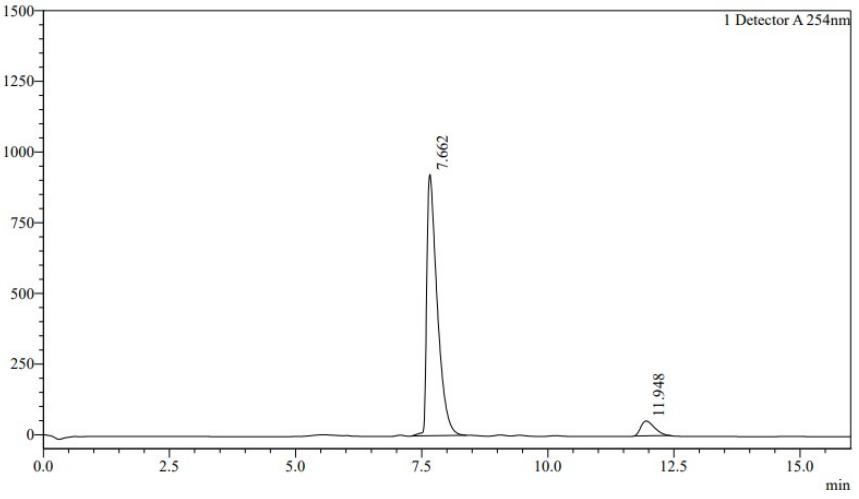
<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Area%
1	7.712	7727049	566085	50.120	50.120
2	11.679	7690175	341796	49.880	49.880
Total		15417224	907881		100.000



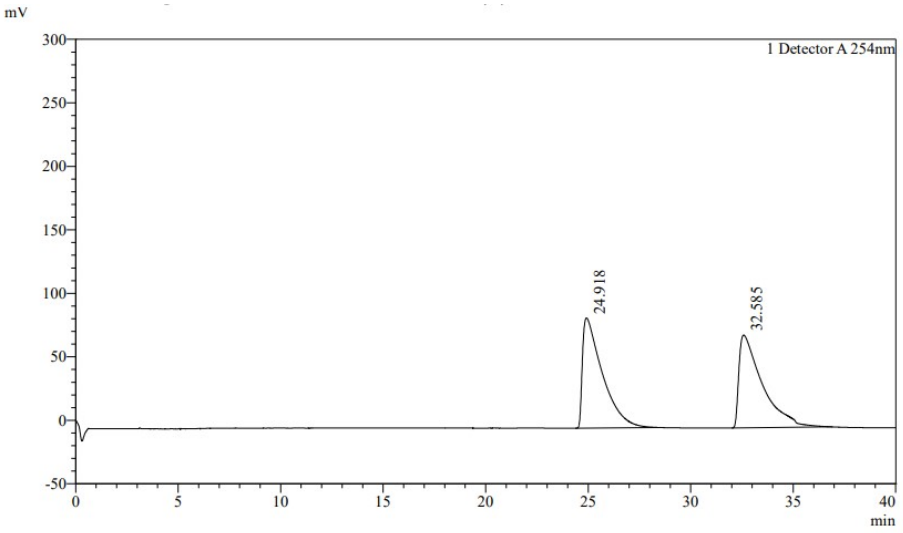
3c



<Peak Table>

Detector A 254nm

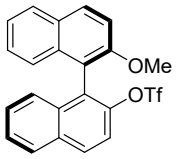
Peak#	Ret. Time	Area	Height	Conc.	Area%
1	7.662	13365496	924156	93.036	93.036
2	11.948	1000431	52789	6.964	6.964
Total		14365927	976945		100.000



<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Area%
1	24.918	5850278	86756	50.218	50.218
2	32.585	5799489	73038	49.782	49.782
Total		11649767	159794		100.000



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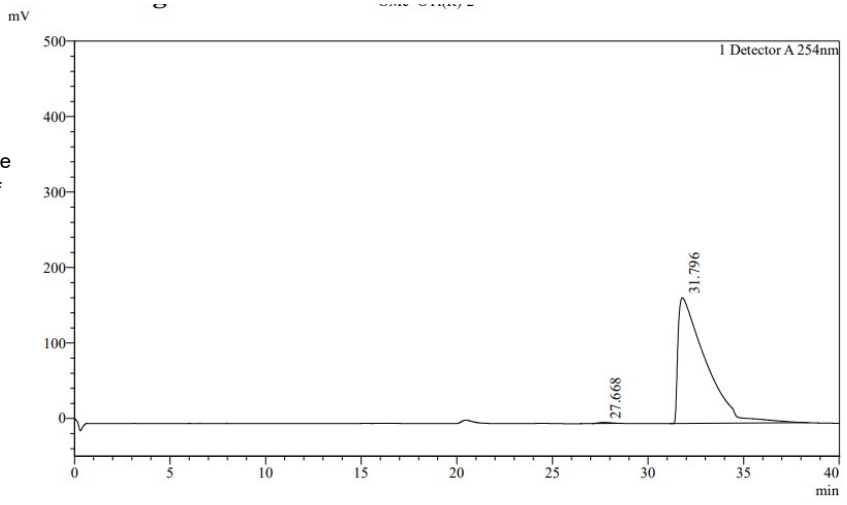
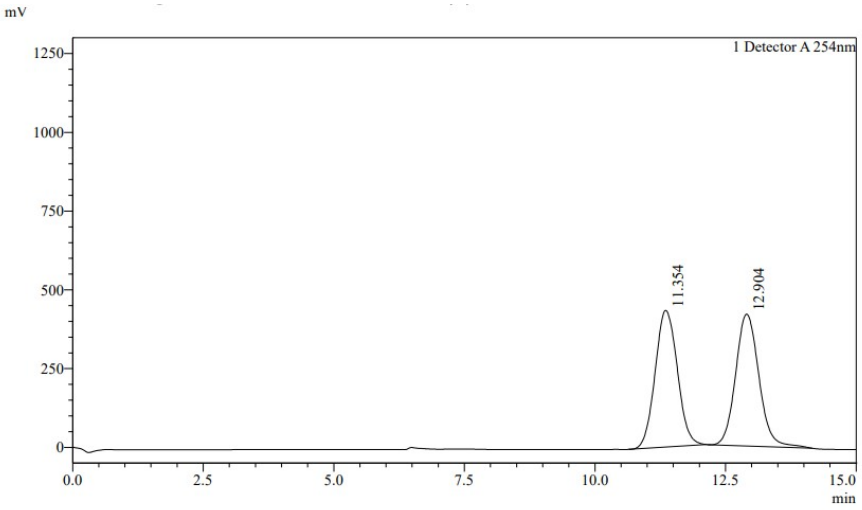


<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Area%
1	27.668	61288	1334	0.364	0.364
2	31.796	16754773	166736	99.636	99.636
Total		16816061	168070		100.000

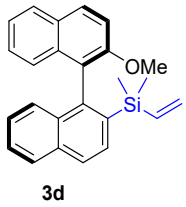


<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Area%
1	11.354	12854298	433692	49.728	49.728
2	12.904	12994989	418424	50.272	50.272
Total		25849287	852116		100.000

<Chromatogram>



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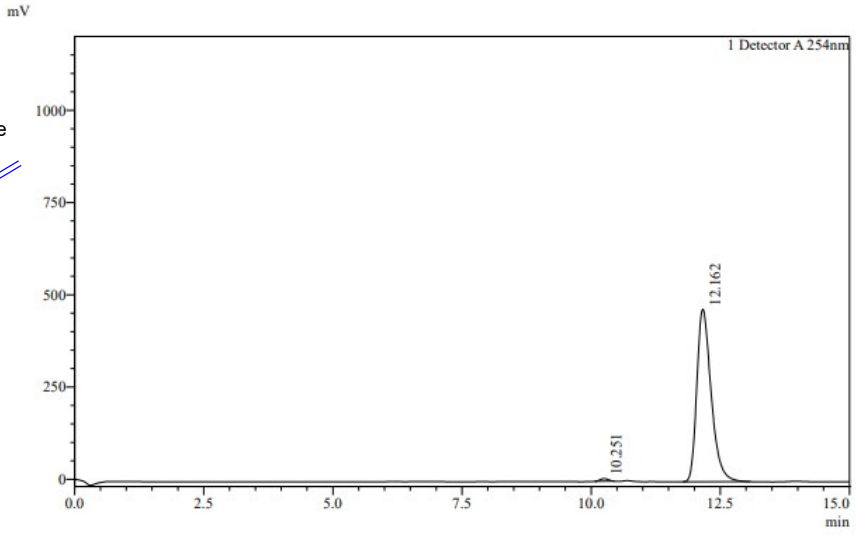
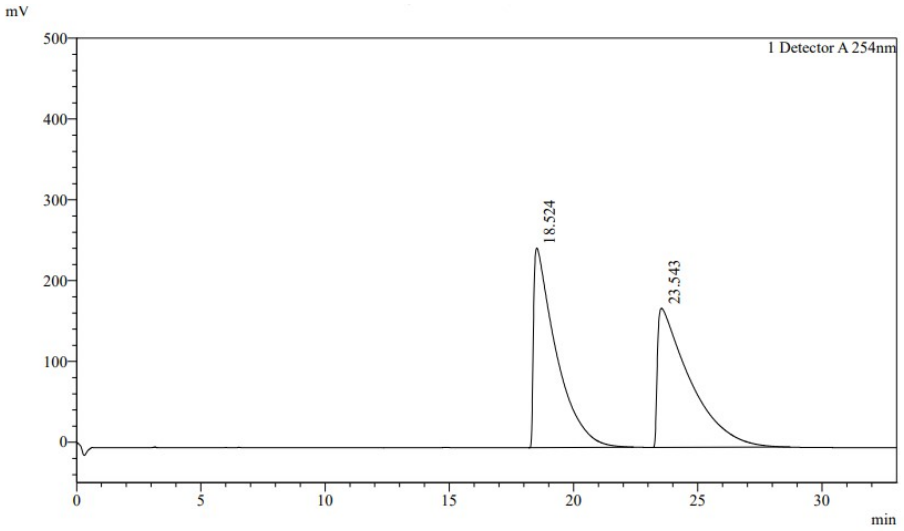


<Peak Table>

Detector A 254nm

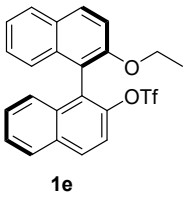
Peak#	Ret. Time	Area	Height	Conc.	Area%
1	10.251	75119	6875	0.824	0.824
2	12.162	9038812	467393	99.176	99.176
Total		9113931	474268		100.000



<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Area%
1	18.524	15588258	247228	49.890	49.890
2	23.543	15657306	172059	50.110	50.110
Total		31245564	419288		100.000



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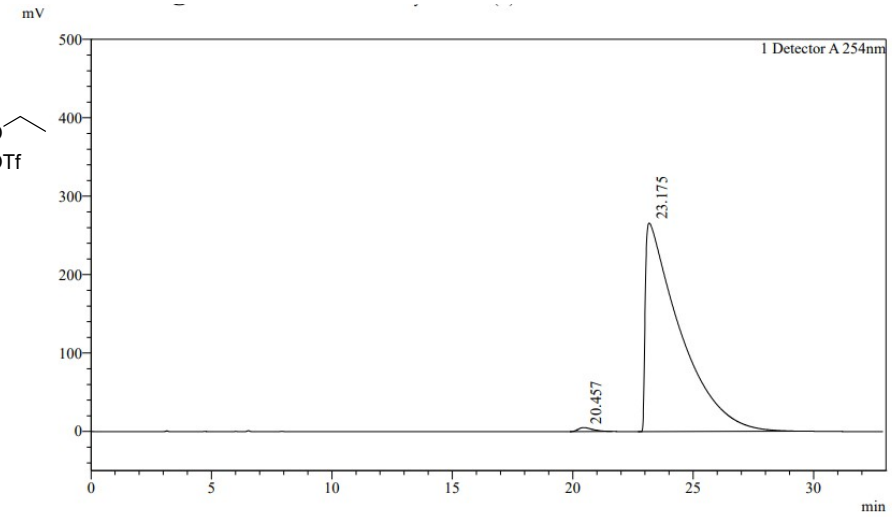
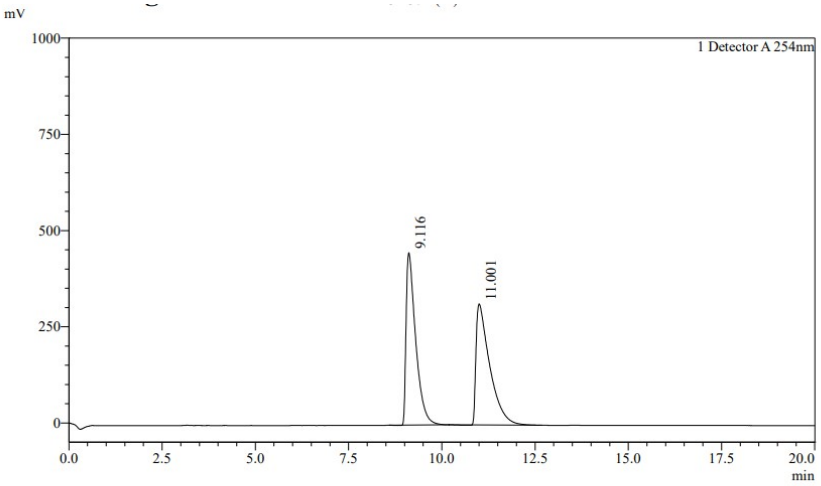


<Peak Table>

Detector A 254nm

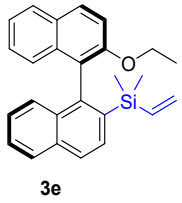
Peak#	Ret. Time	Area	Height	Conc.	Area%
1	20.457	208725	5086	0.778	0.778
2	23.175	26611282	265902	99.222	99.222
Total		26820007	270988		100.000



<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Area%
1	9.116	7990304	447605	49.797	49.797
2	11.001	8055411	314582	50.203	50.203
Total		16045714	762186		100.000



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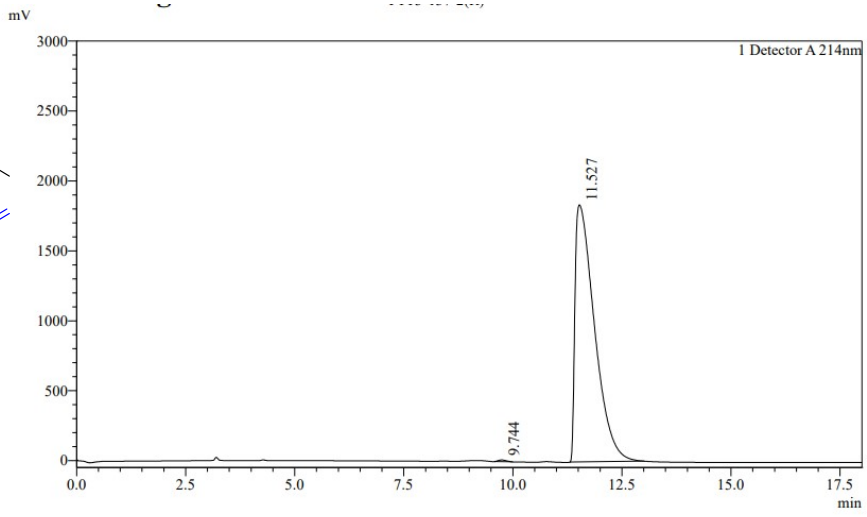
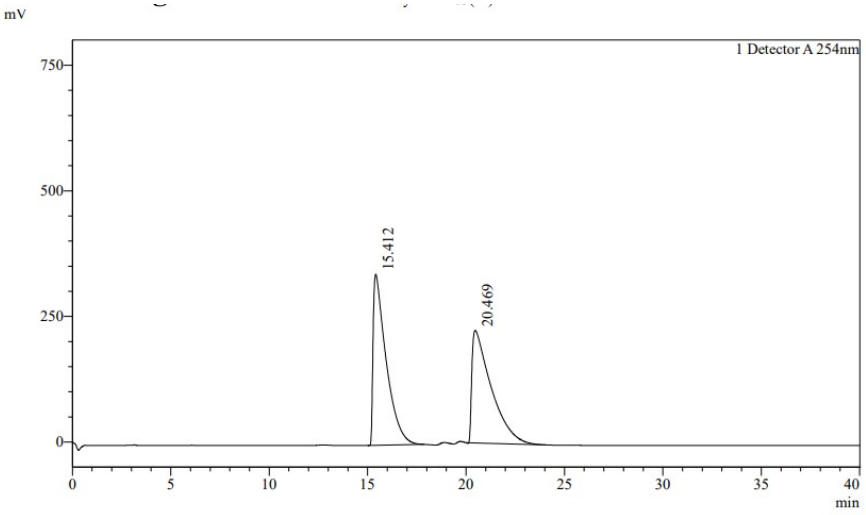


<Peak Table>

Detector A 214nm

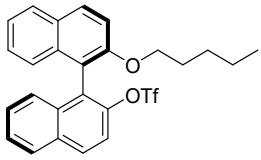
Peak#	Ret. Time	Area	Height	Conc.	Area%
1	9.744	156293	12171	0.273	0.273
2	11.527	57142253	1837967	99.727	99.727
Total		57298546	1850138		100.000



<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Area%
1	15.412	15705105	340274	50.615	50.615
2	20.469	15323490	224326	49.385	49.385
Total		31028595	564599		100.000



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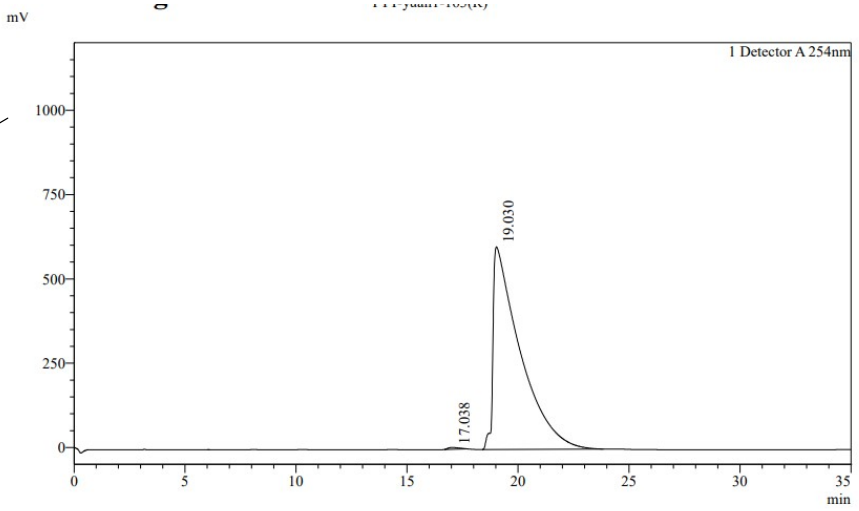
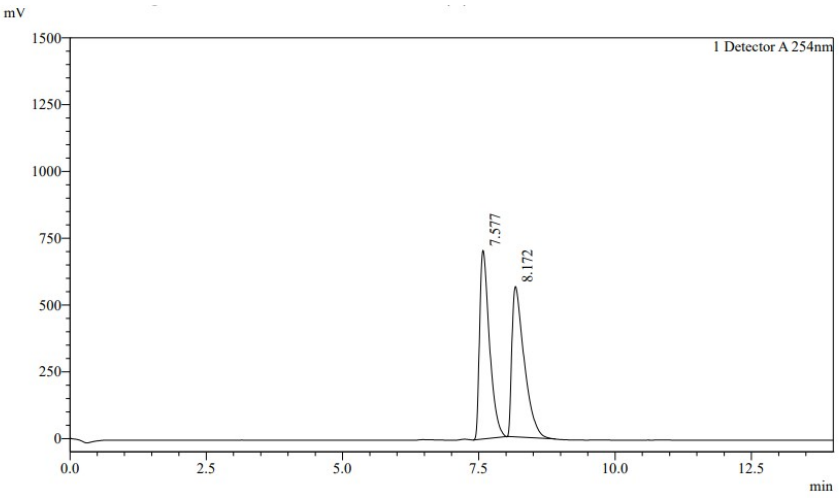


<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Area%
1	17.038	186841	5491	0.364	0.364
2	19.030	51113822	600894	99.636	99.636
Total		51300664	606385		100.000

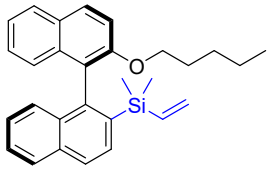


<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Area%
1	7.577	8858971	705829	50.033	50.033
2	8.172	8847284	562846	49.967	49.967
Total		17706256	1268674		100.000

<Chromatogram>



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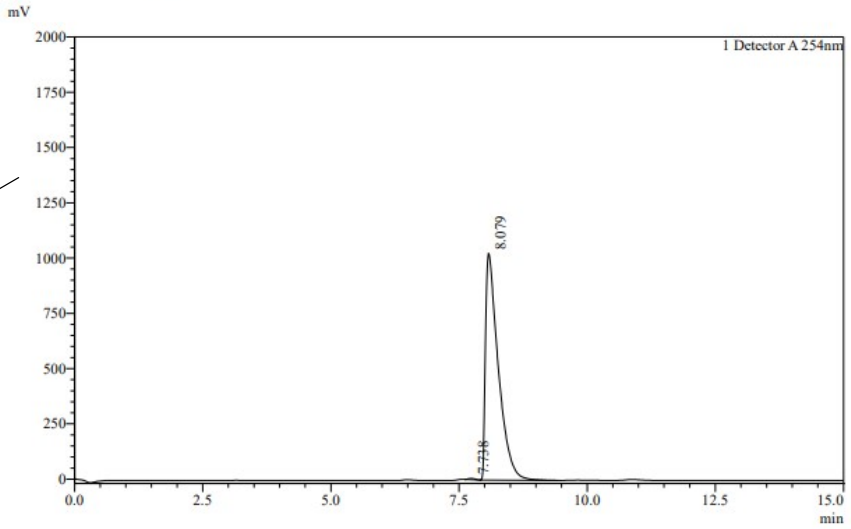
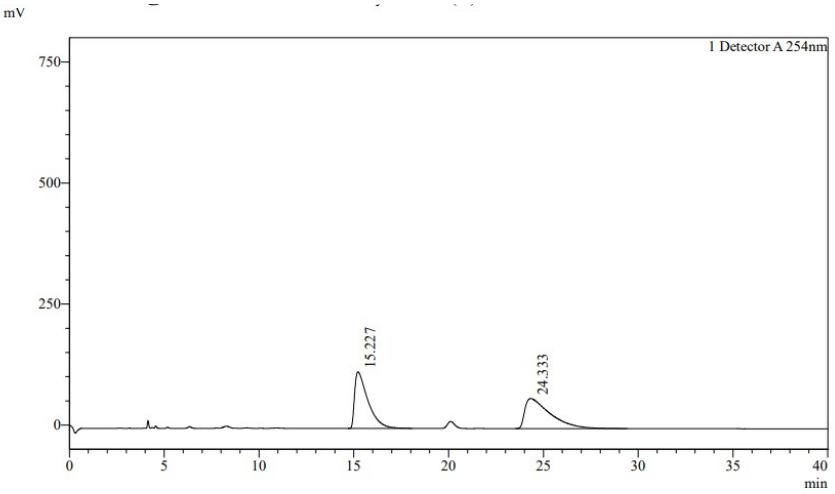


<Peak Table>

Detector A 254nm

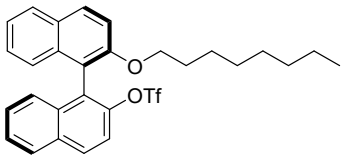
Peak#	Ret. Time	Area	Height	Conc.	Area%
1	7.738	52910	5861	0.296	0.296
2	8.079	17835566	1025289	99.704	99.704
Total		17888476	1031150		100.000



<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Area%
1	15.227	5714370	116913	49.810	49.810
2	24.333	5757882	62053	50.190	50.190
Total		11472252	178966		100.000



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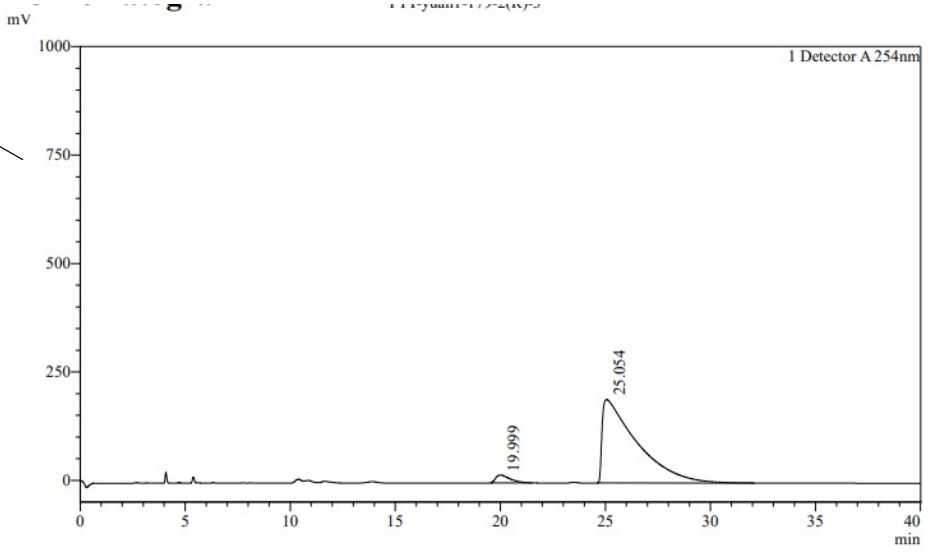
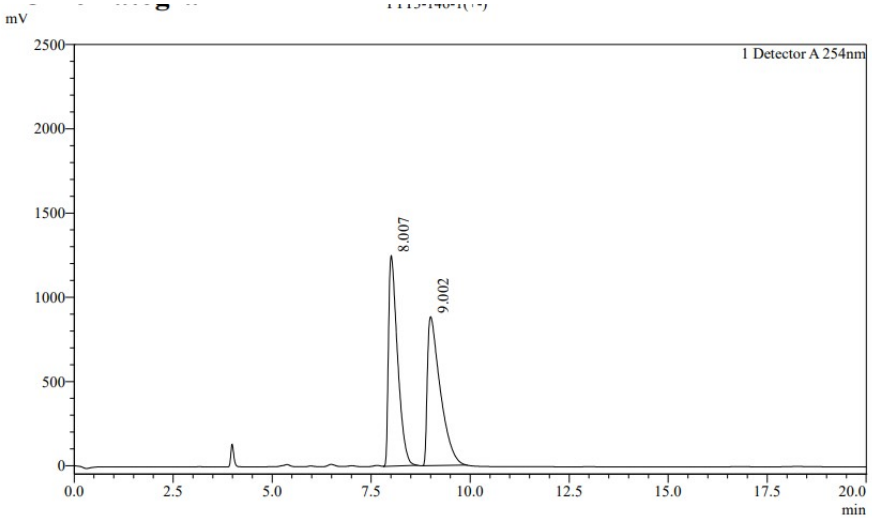


<Peak Table>

Detector A 254nm

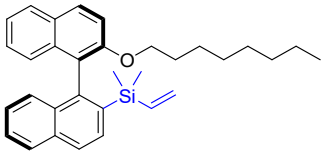
Peak#	Ret. Time	Area	Height	Conc.	Area%
1	19.999	841309	18003	3.667	3.667
2	25.054	22098638	192464	96.333	96.333
Total		22939947	210467		100.000



<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Area%
1	8.007	19875428	1248705	49.776	49.776
2	9.002	20054140	884582	50.224	50.224
Total		39929568	2133288		100.000



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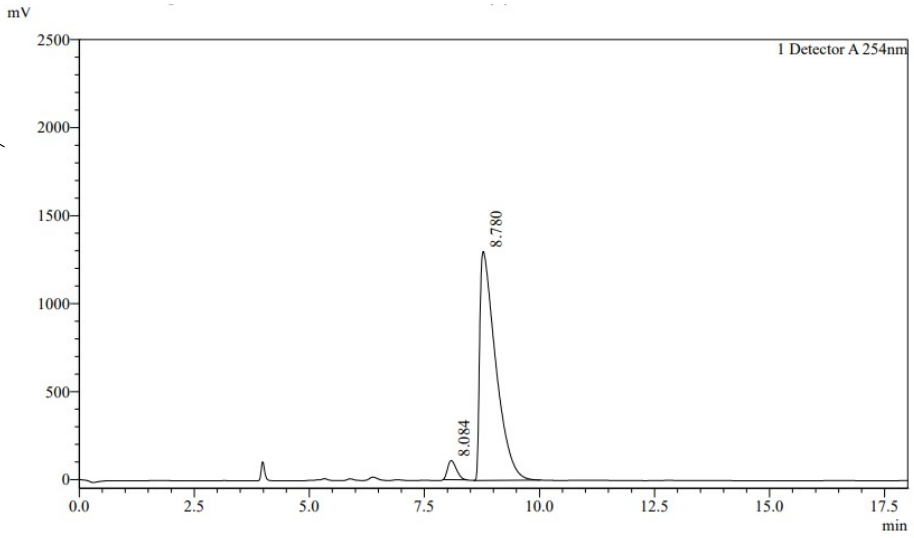
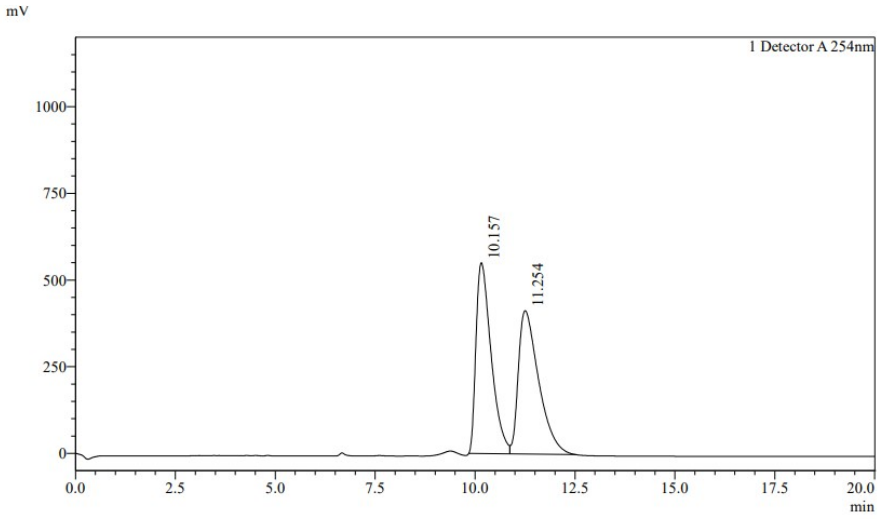


<Peak Table>

Detector A 254nm

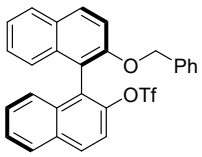
Peak#	Ret. Time	Area	Height	Conc.	Area%
1	8.084	1456034	109098	4.417	4.417
2	8.780	31511114	1301419	95.583	95.583
Total		32967148	1410517		100.000



<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Area%
1	10.157	14512057	550356	49.745	49.745
2	11.254	14660887	413423	50.255	50.255
Total		29172944	963778		100.000



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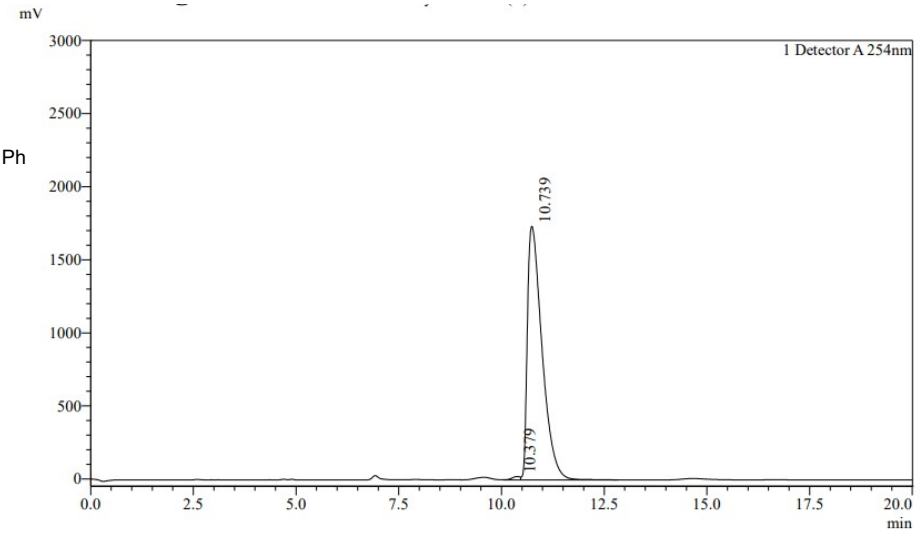
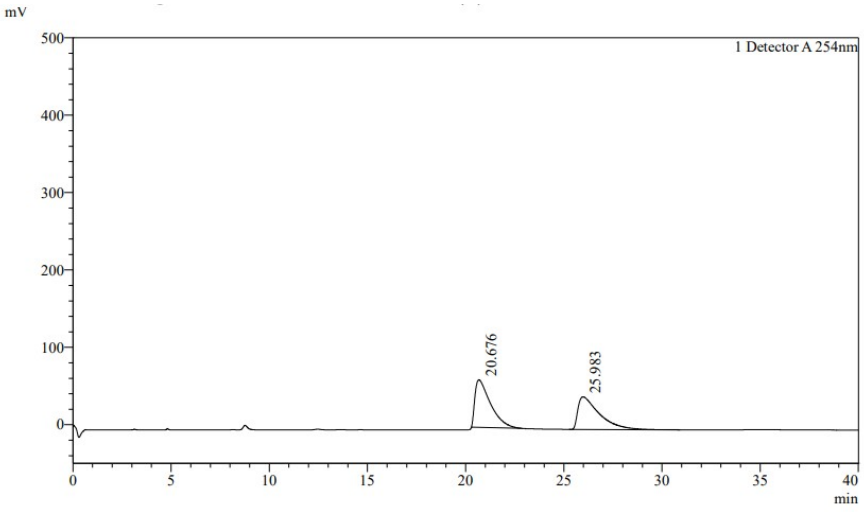


<Peak Table>

Detector A 254nm

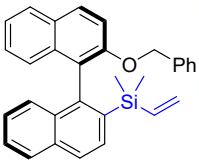
Peak#	Ret. Time	Area	Height	Conc.	Area%
1	10.379	309099	22820	0.712	0.712
2	10.739	43114816	1735052	99.288	99.288
Total		43423916	1757872		100.000



<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Area%
1	20.676	3381921	61464	51.289	51.289
2	25.983	3211939	42249	48.711	48.711
Total		6593860	103714		100.000



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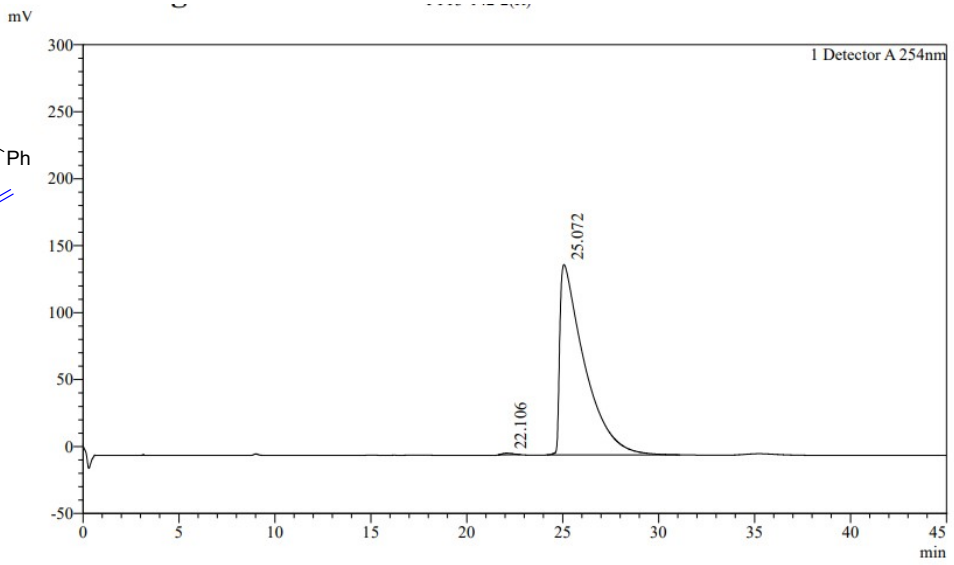
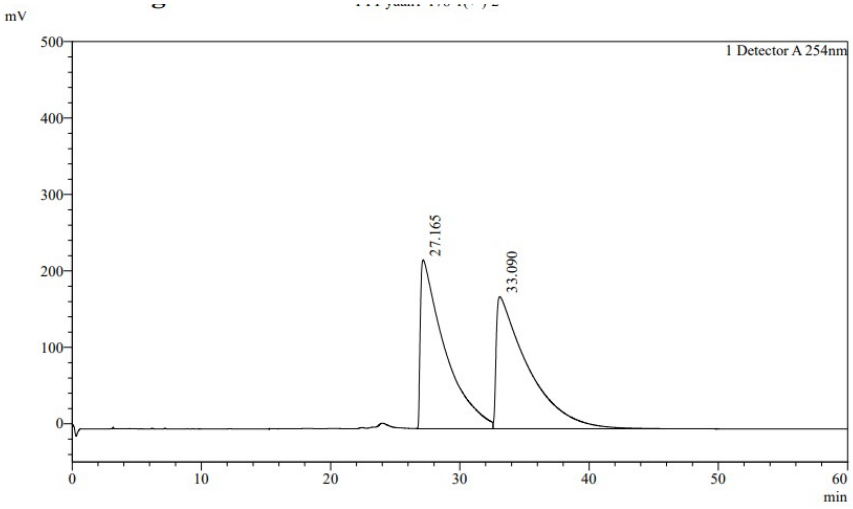


<Peak Table>

Detector A 254nm

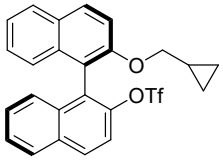
Peak#	Ret. Time	Area	Height	Conc.	Area%
1	22.106	46583	1203	0.366	0.366
2	25.072	12671073	142107	99.634	99.634
Total		12717656	143309		100.000



<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Area%
1	27.165	29045854	220914	49.728	49.728
2	33.090	29364079	172696	50.272	50.272
Total		58409932	393610		100.000



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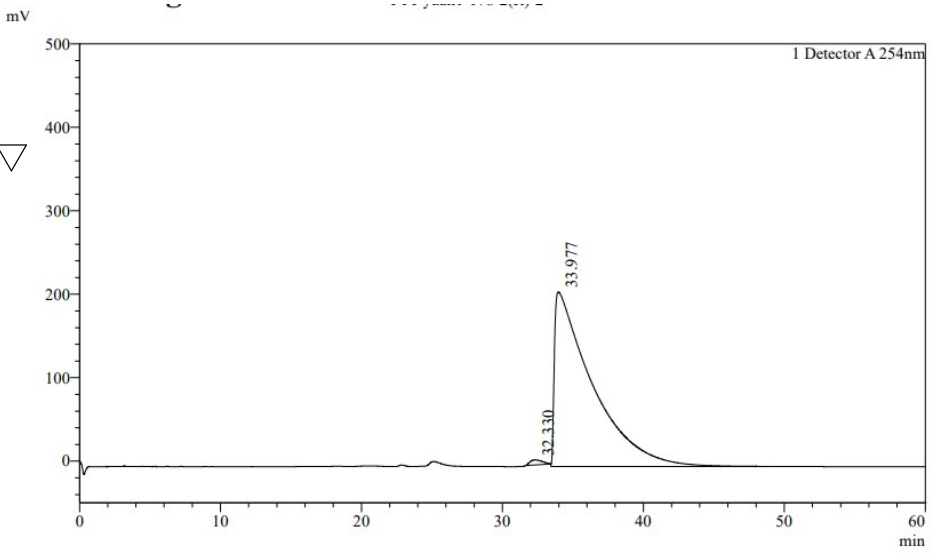
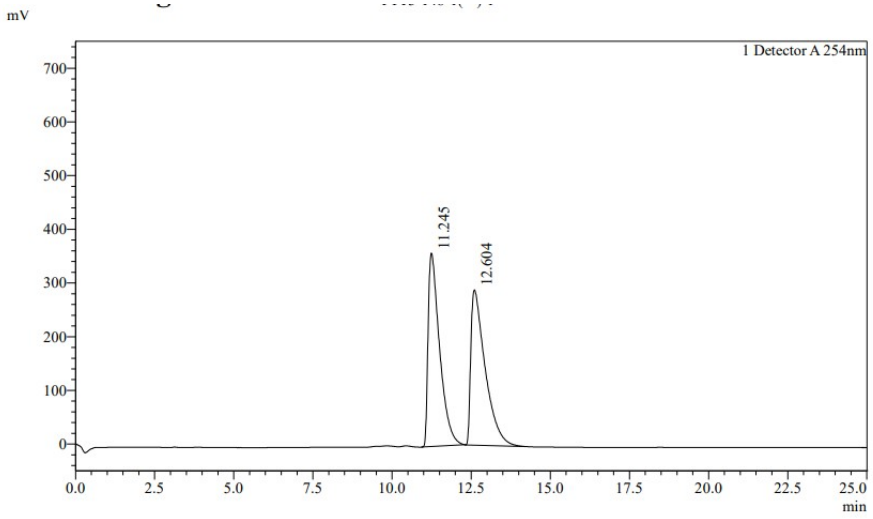


<Peak Table>

Detector A 254nm

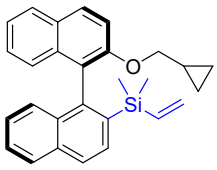
Peak#	Ret. Time	Area	Height	Conc.	Area%
1	32.330	370766	6057	0.940	0.940
2	33.977	39056588	209206	99.060	99.060
Total		39427354	215263		100.000



<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Area%
1	11.245	9098770	360110	49.965	49.965
2	12.604	9111696	289073	50.035	50.035
Total		18210466	649182		100.000



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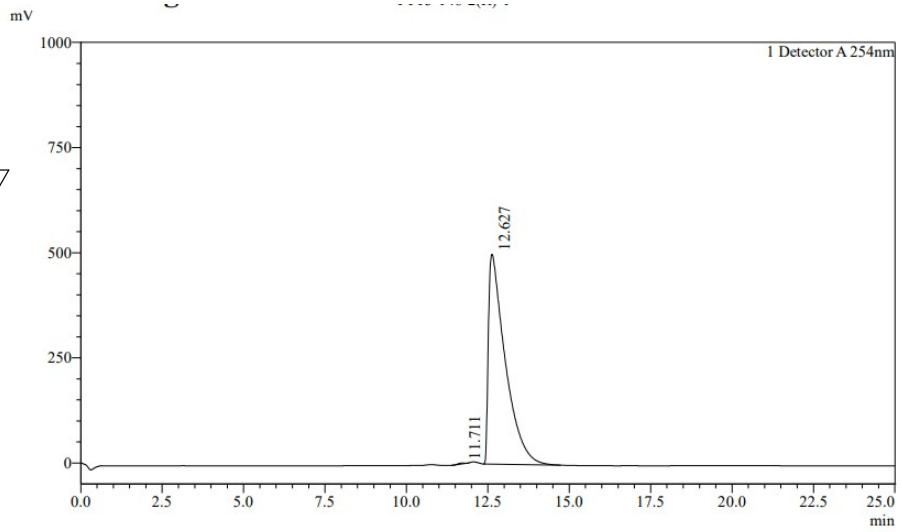
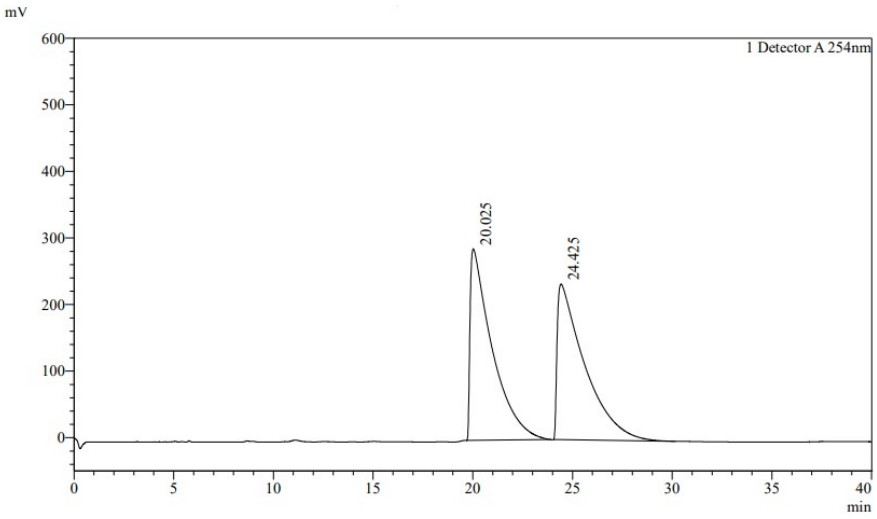


<Peak Table>

Detector A 254nm

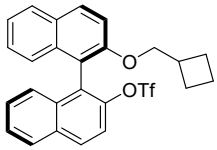
Peak#	Ret. Time	Area	Height	Conc.	Area%
1	11.711	28262	2142	0.157	0.157
2	12.627	17995454	499317	99.843	99.843
Total		18023716	501459		100.000



<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Area%
1	20.025	21987841	287803	49.667	49.667
2	24.425	22282990	233702	50.333	50.333
Total		44270832	521505		100.000



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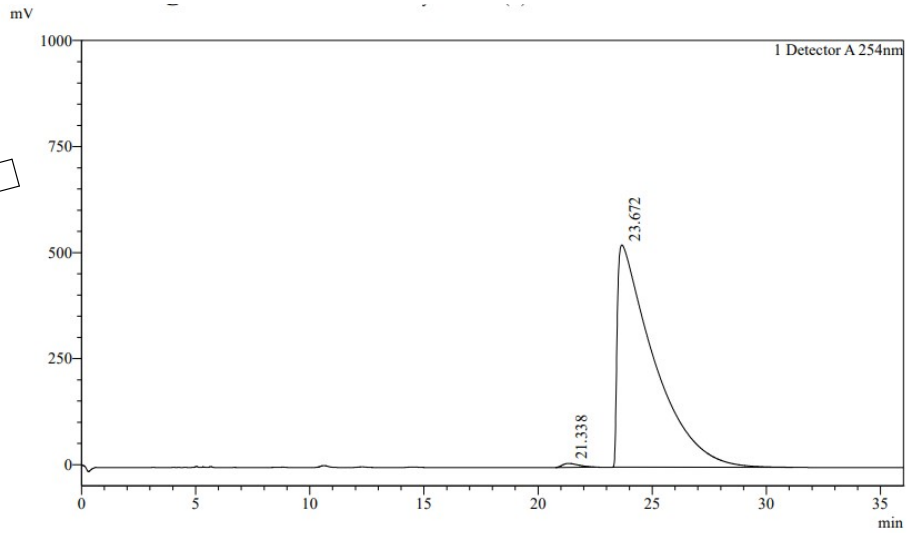
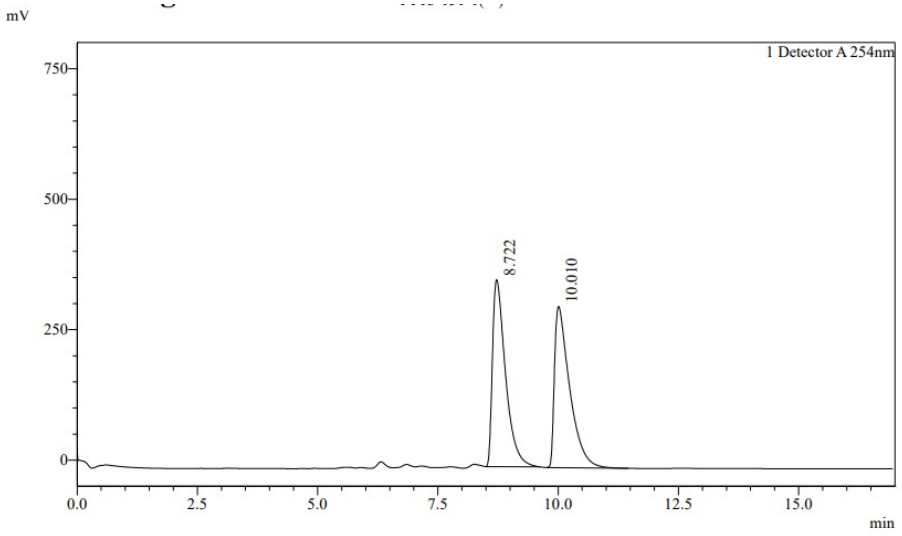


<Peak Table>

Detector A 254nm

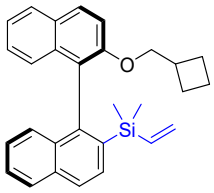
Peak#	Ret. Time	Area	Height	Conc.	Area%
1	21.338	450224	9231	0.768	0.768
2	23.672	58136365	523712	99.232	99.232
Total		58586589	532943		100.000



<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Area%
1	8.722	6759782	358294	49.890	49.890
2	10.010	6789493	308707	50.110	50.110
Total		13549276	667000		100.000



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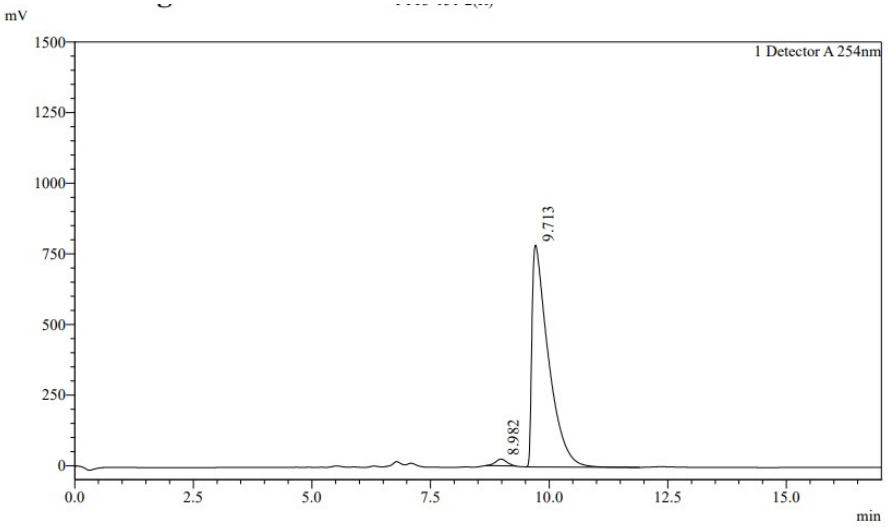
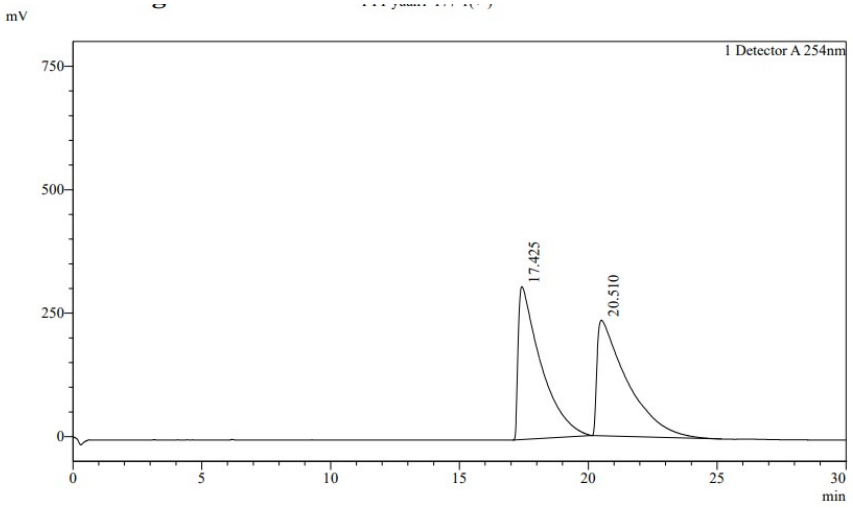


<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Area%
1	8.982	399982	23891	2.066	2.066
2	9.713	18960579	784823	97.934	97.934
Total		19360561	808713		100.000

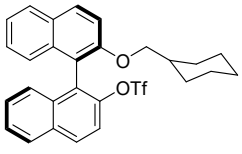


<Peak Table>

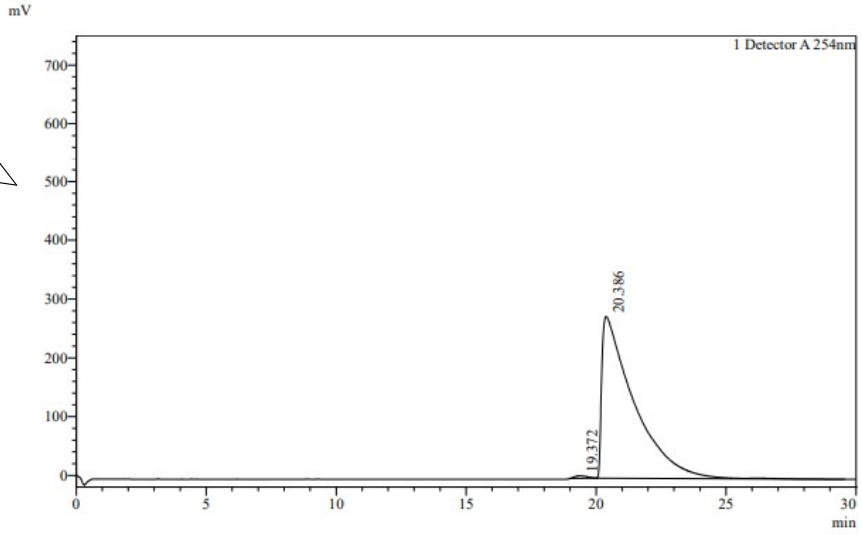
Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Area%
1	17.425	19051941	309500	50.038	50.038
2	20.510	19023004	234064	49.962	49.962
Total		38074944	543564		100.000

<Chromatogram>



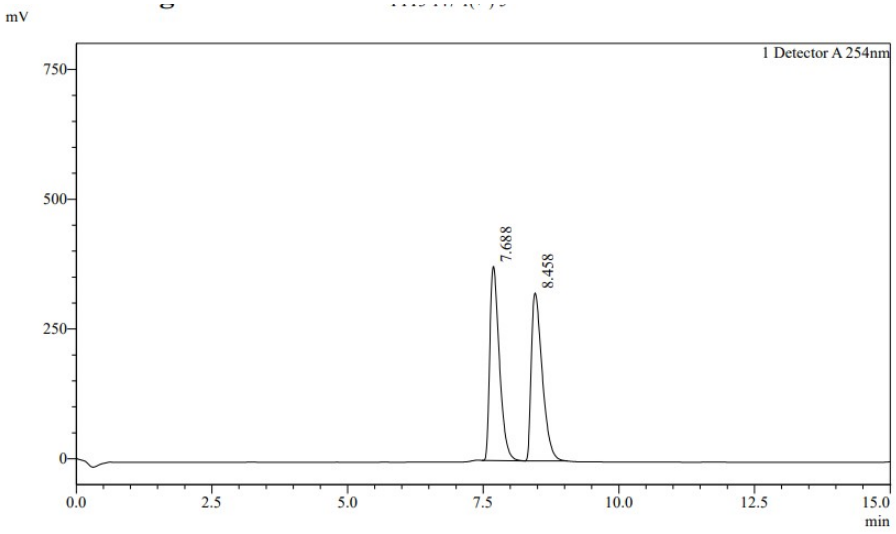
1k



<Peak Table>

Detector A 254nm

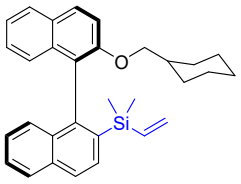
Peak#	Ret. Time	Area	Height	Conc.	Area%
1	19.372	143047	4164	0.602	0.602
2	20.386	23609077	274886	99.398	99.398
Total		23752124	279049		100.000



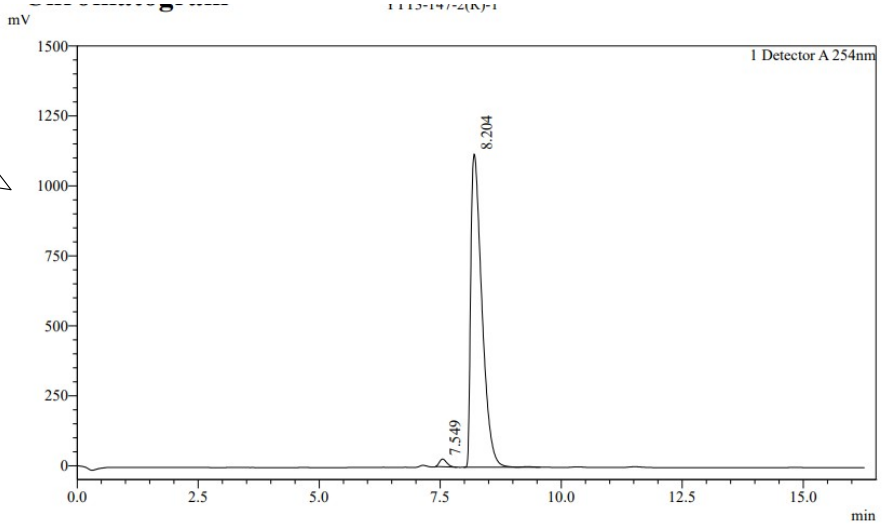
<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Area%
1	7.688	4587241	373666	50.251	50.251
2	8.458	4541356	323239	49.749	49.749
Total		9128597	696905		100.000



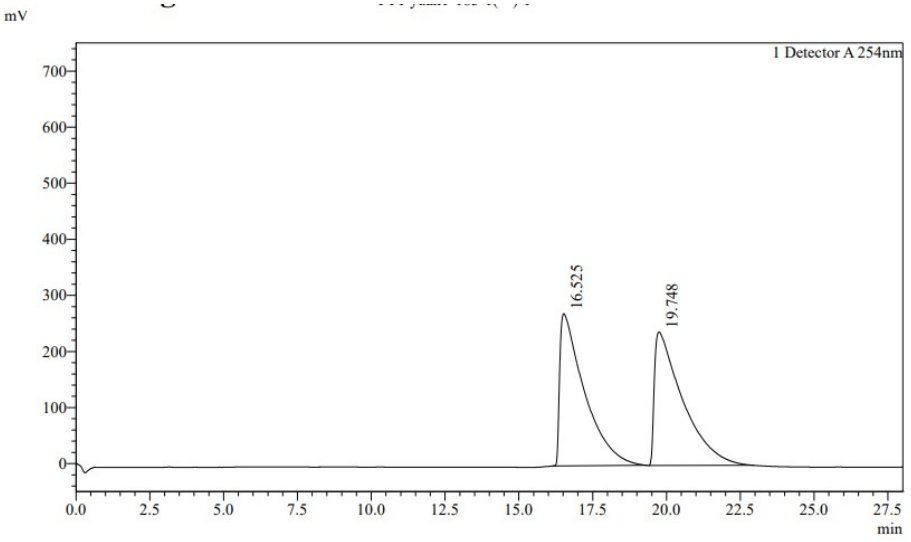
3k



<Peak Table>

Detector A 254nm

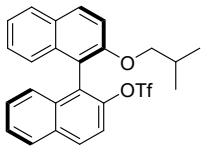
Peak#	Ret. Time	Area	Height	Conc.	Area%
1	7.549	292917	27960	1.609	1.609
2	8.204	17907717	1118838	98.391	98.391
Total		18200633	1146798		100.000



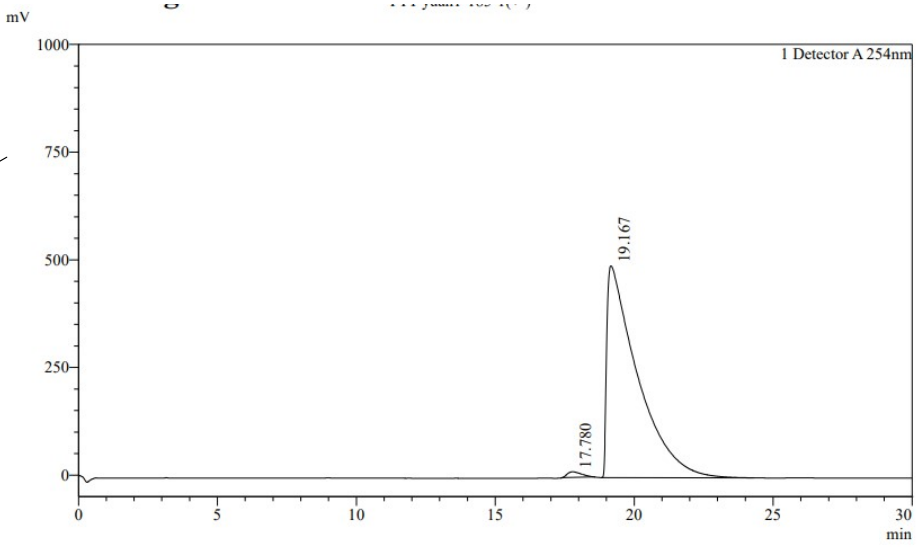
<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Area%
1	16.525	15772575	271375	49.885	49.885
2	19.748	15845127	237843	50.115	50.115
Total		31617702	509218		100.000



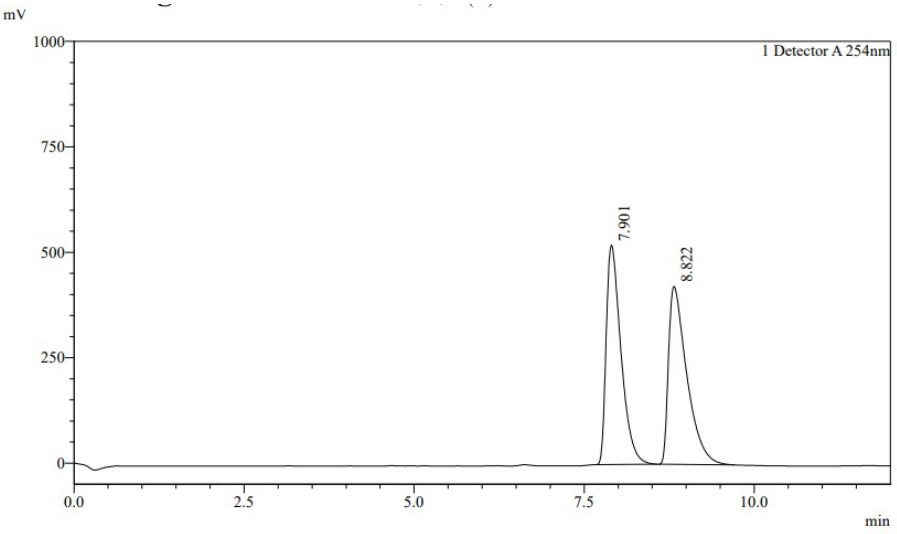
1l



<Peak Table>

Detector A 254nm

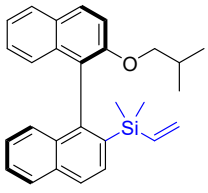
Peak#	Ret. Time	Area	Height	Conc.	Area%
1	17.780	469181	13166	1.227	1.227
2	19.167	37781128	491638	98.773	98.773
Total		38250308	504804		100.000



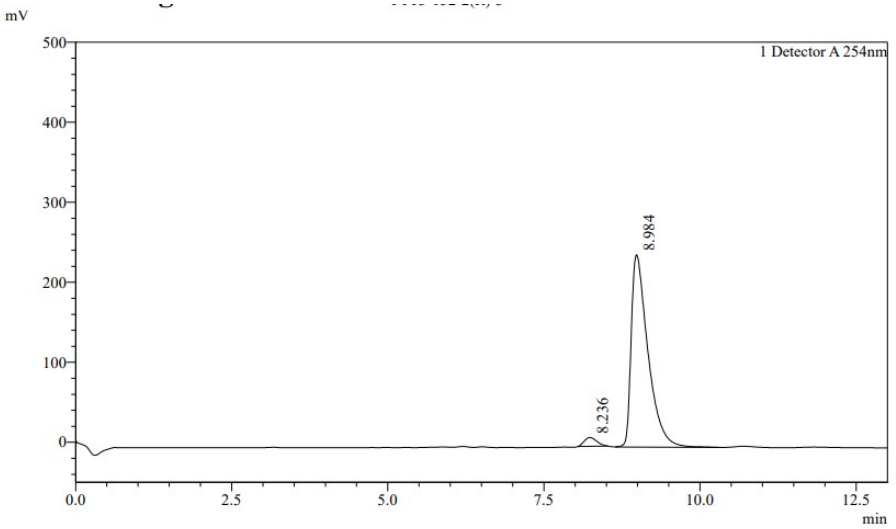
<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Area%
1	7.901	7864073	520026	49.832	49.832
2	8.822	7917031	421660	50.168	50.168
Total		15781104	941687		100.000



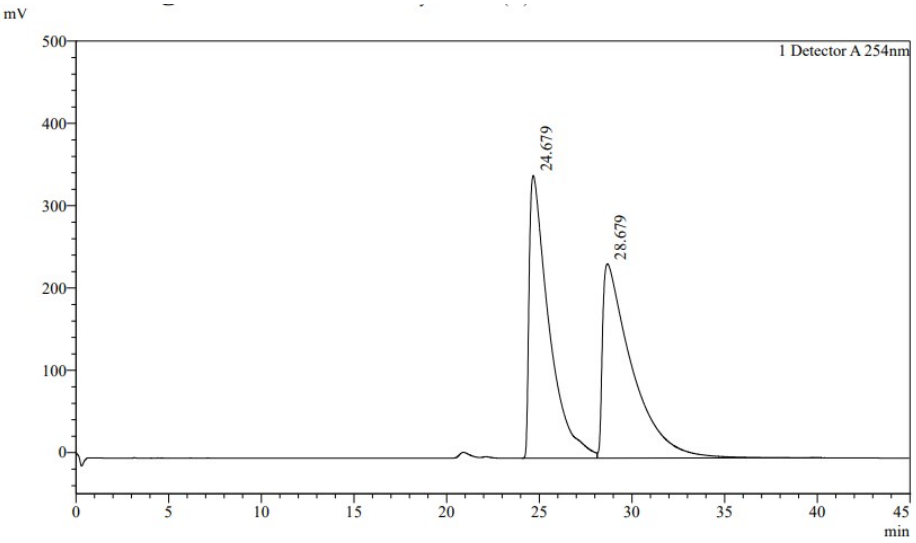
3l



<Peak Table>

Detector A 254nm

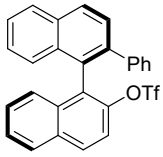
Peak#	Ret. Time	Area	Height	Conc.	Area%
1	8.236	152583	11079	3.300	3.300
2	8.984	4471526	240335	96.700	96.700
Total		4624109	251414		100.000



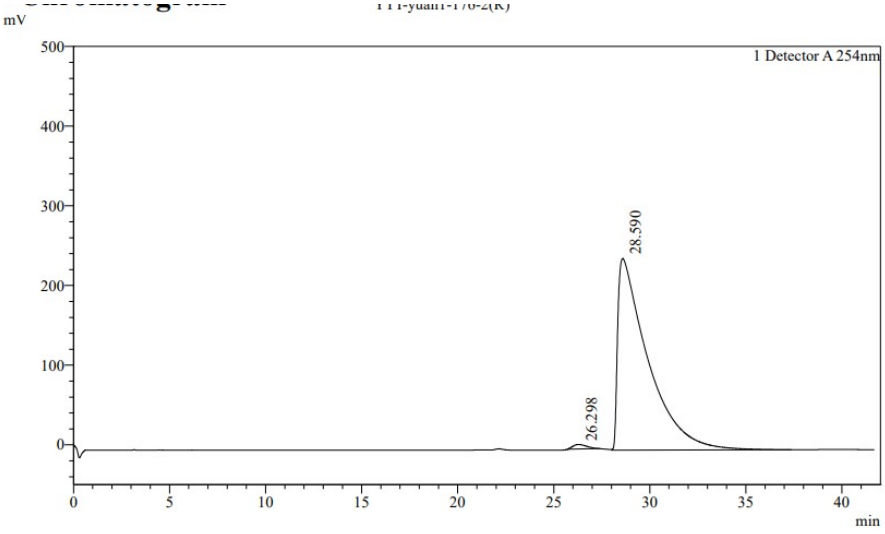
<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Area%
1	24.679	25427305	343403	49.509	49.509
2	28.679	25932121	235915	50.491	50.491
Total		51359426	579318		100.000



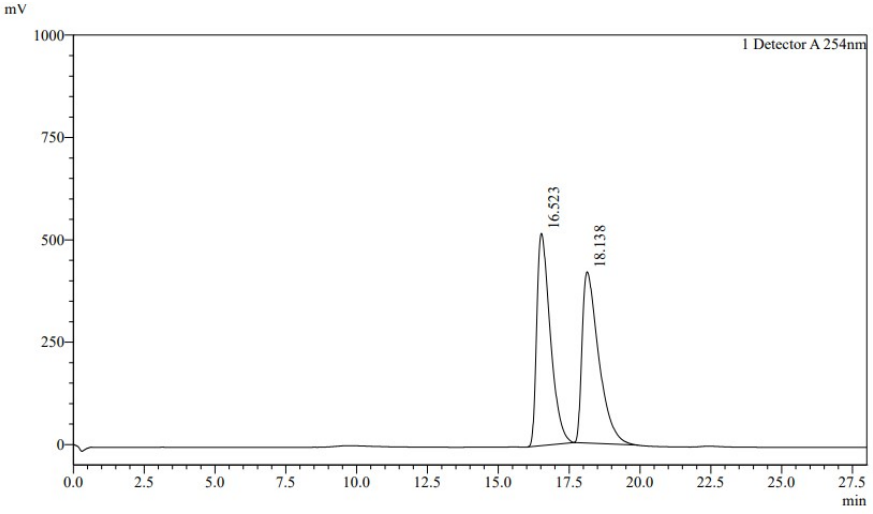
1m



<Peak Table>

Detector A 254nm

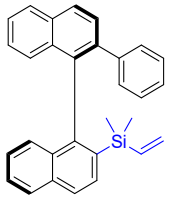
Peak#	Ret. Time	Area	Height	Conc.	Area%
1	26.298	294950	5760	1.111	1.111
2	28.590	26248162	240254	98.889	98.889
Total		26543112	246014		100.000



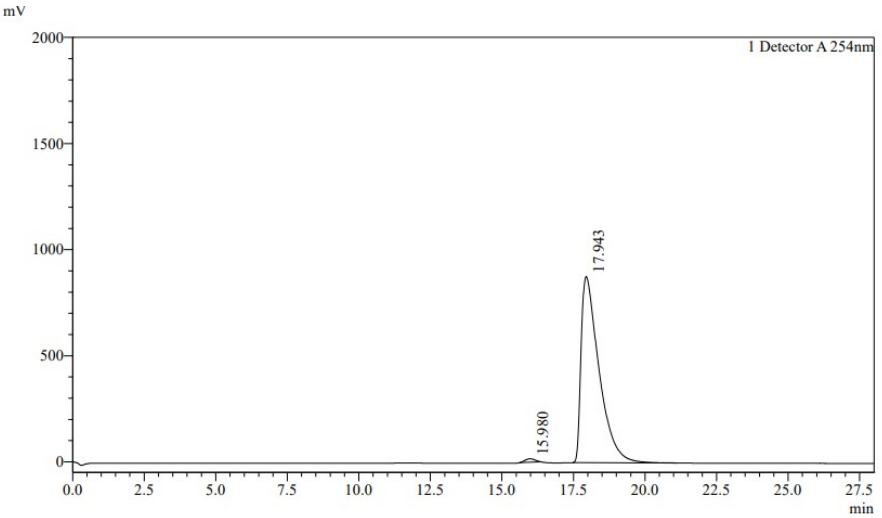
<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Area%
1	16.523	17267397	518368	50.211	50.211
2	18.138	17122158	417951	49.789	49.789
Total		34389555	936320		100.000



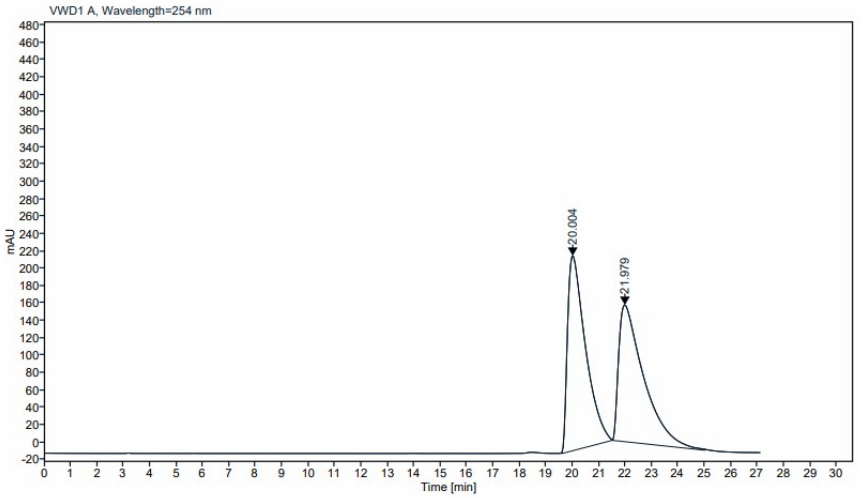
3m



<Peak Table>

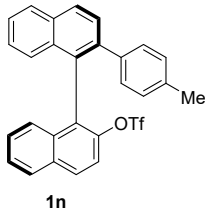
Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Area%
1	15.980	399028	16423	1.032	1.032
2	17.943	38253670	876748	98.968	98.968
Total		38652697	893171		100.000

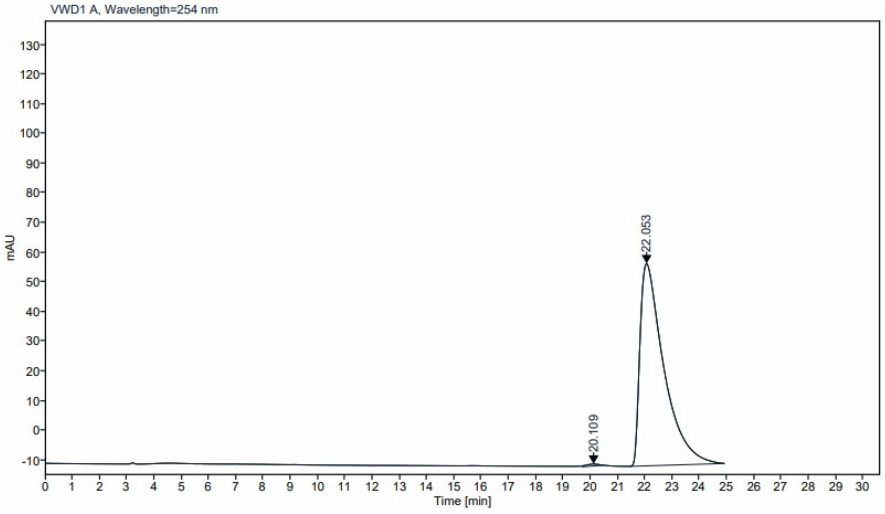


Results

No.	RT[min]	Area	Height	Relative Height %	Relative Area %
	20.004	10604.5146	224.1636	58.78	50.70
	21.979	10312.3926	157.2047	41.22	49.30
SUM	41.983	20916.9072	381.3683	100.00	100.00

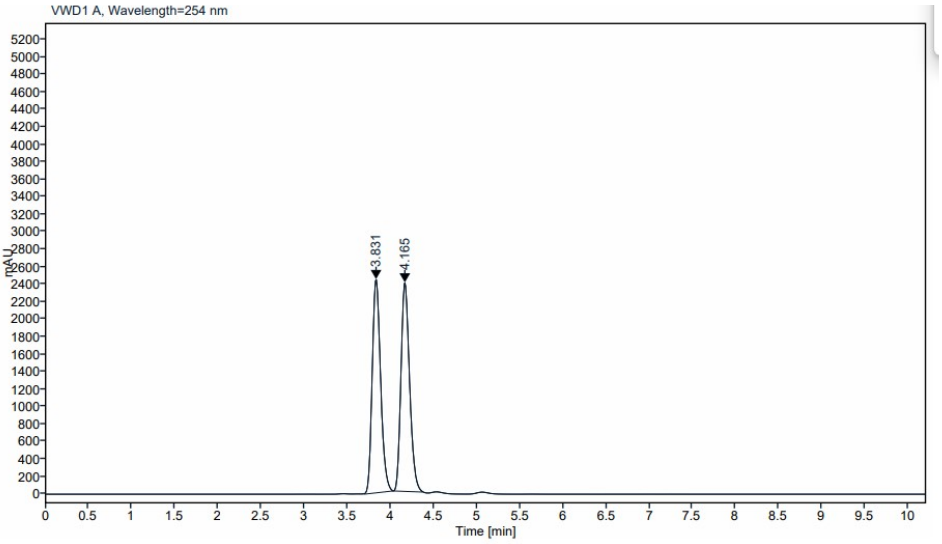


1n



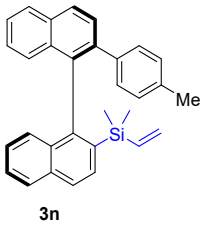
Results

No.	RT[min]	Area	Height	Relative Height %	Relative Area %
	20.109	21.2083	0.6436	0.94	0.51
	22.053	4140.4175	68.1227	99.06	99.49
SUM	42.163	4161.6258	68.7663	100.00	100.00



Results

No.	RT[min]	Area	Height	Height %	Relative Area %
	3.831	16502.2617	2444.6929	50.56	49.84
	4.165	16611.5059	2390.1685	49.44	50.16
SUM	7.996	33113.7676	4834.8613	100.00	100.00



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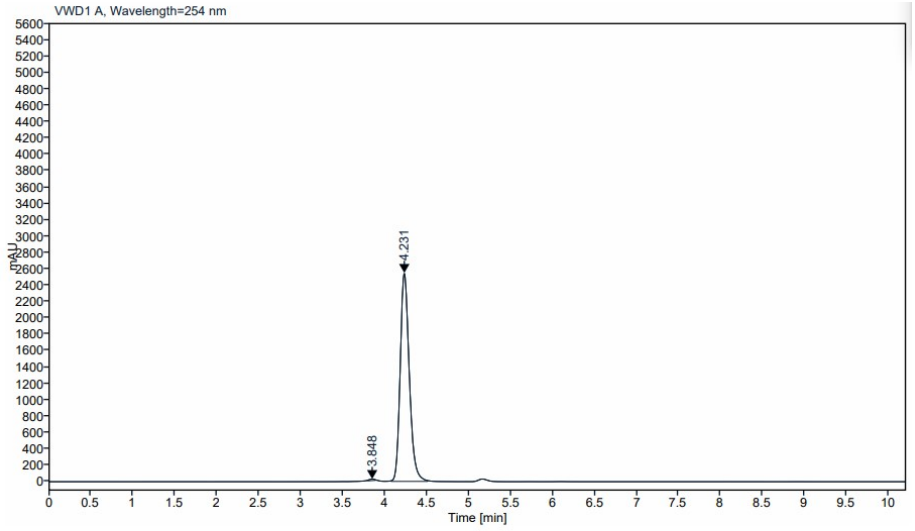
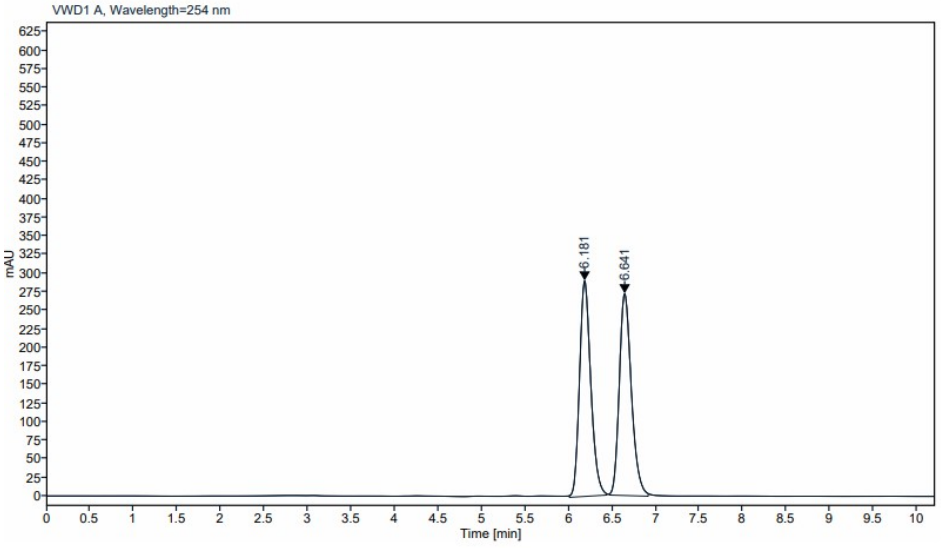


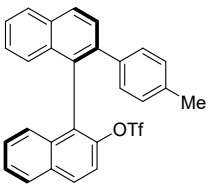
Results

No.	RT[min]	Area	Height	Relative Height %	Relative Area %
	3.848	75.7742	17.8290	0.69	0.39
	4.231	19180.8496	2549.3303	99.31	99.61
SUM	8.079	19256.6238	2567.1593	100.00	100.00

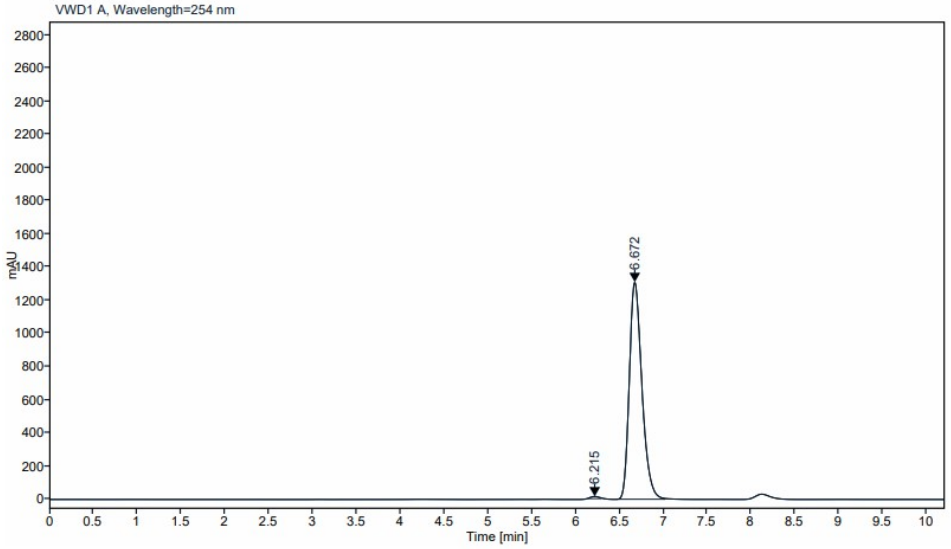


Results

No.	RT[min]	Area	Height	Relative Height %	Relative Area %
	6.181	2618.4912	290.5511	51.65	49.88
	6.641	2631.2188	272.0381	48.35	50.12
SUM	12.821	5249.7100	562.5891	100.00	100.00

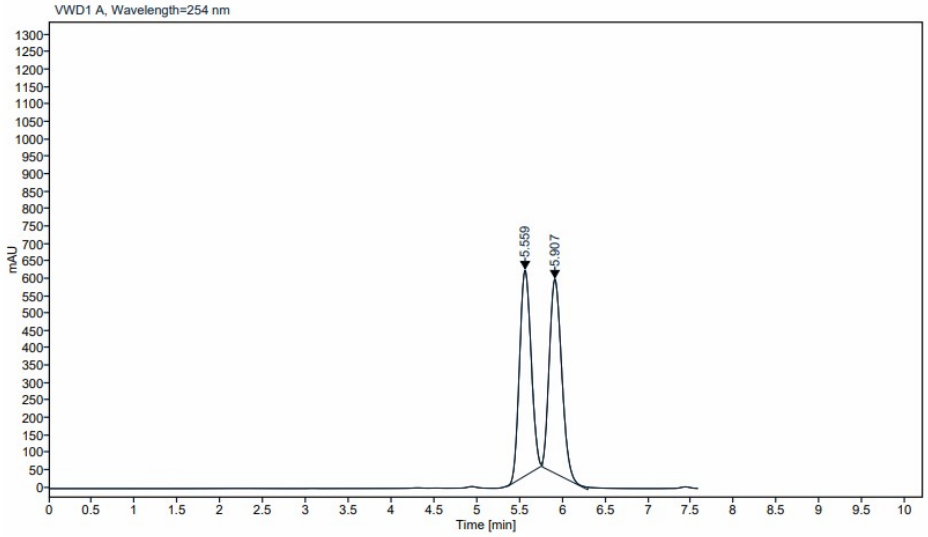


1o



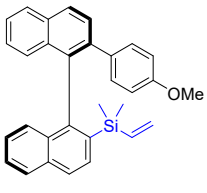
Results

No.	RT[min]	Area	Height	Relative Height %	Relative Area %
	6.215	78.4706	12.8130	0.97	0.60
	6.672	13058.7480	1309.6860	99.03	99.40
SUM	12.886	13137.2187	1322.4990	100.00	100.00

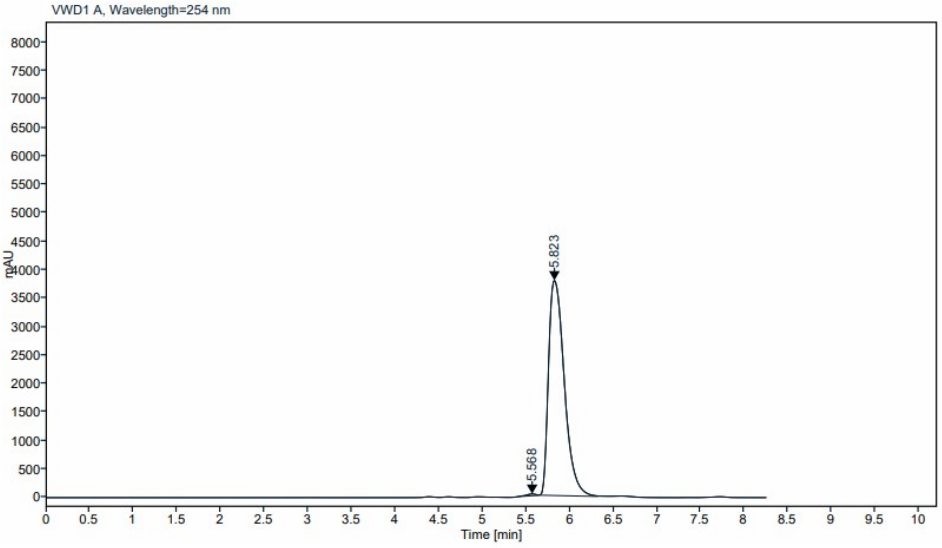


Results

No.	RT[min]	Area	Height	Relative Height %	Relative Area %
	5.559	5557.3530	591.0151	51.46	49.69
	5.907	5626.6729	557.5571	48.54	50.31
SUM	11.466	11184.0259	1148.5722	100.00	100.00

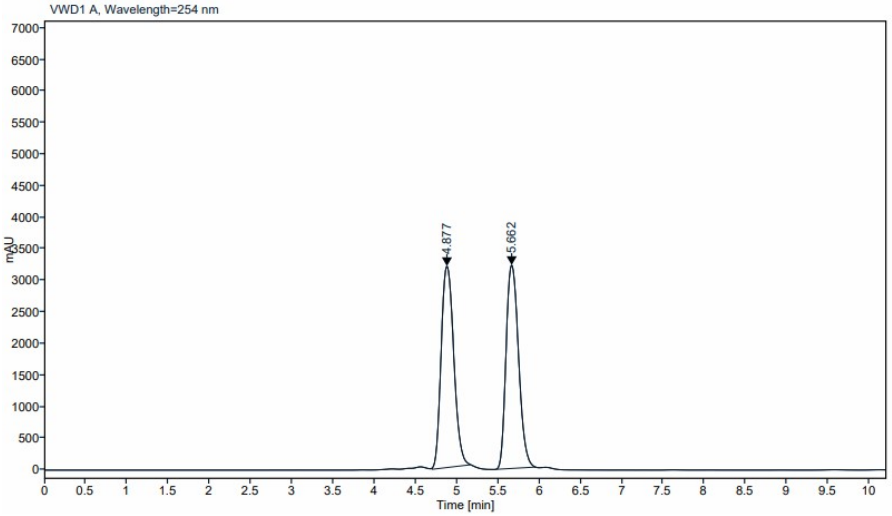


3o



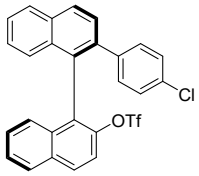
Results

No.	RT[min]	Area	Height	Relative Height %	Relative Area %
	5.568	233.3791	32.6100	0.86	0.49
	5.823	47431.0977	3780.0911	99.14	99.51
SUM	11.391	47664.4768	3812.7010	100.00	100.00

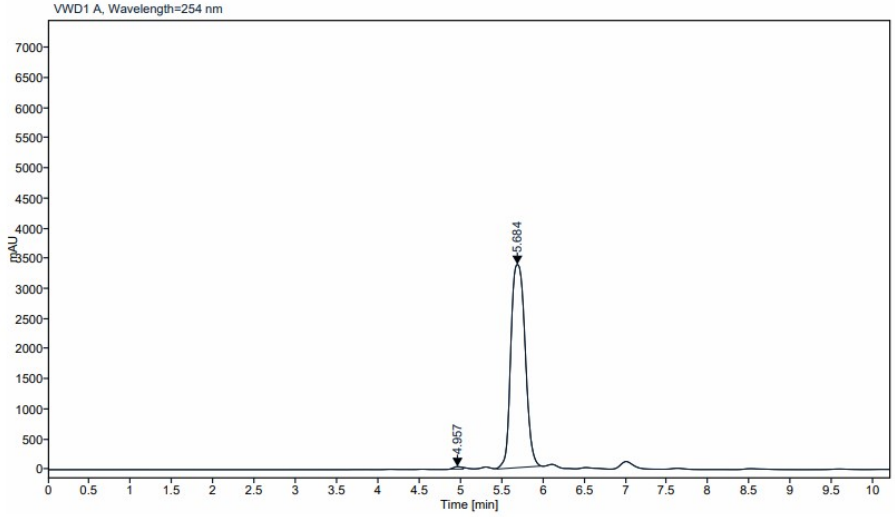


Results

No.	RT[min]	Area	Height	Relative Height %	Relative Area %
	4.877	33916.2656	3189.6772	49.76	49.99
	5.662	33923.0703	3220.5688	50.24	50.01
SUM	10.539	67839.3359	6410.2461	100.00	100.00

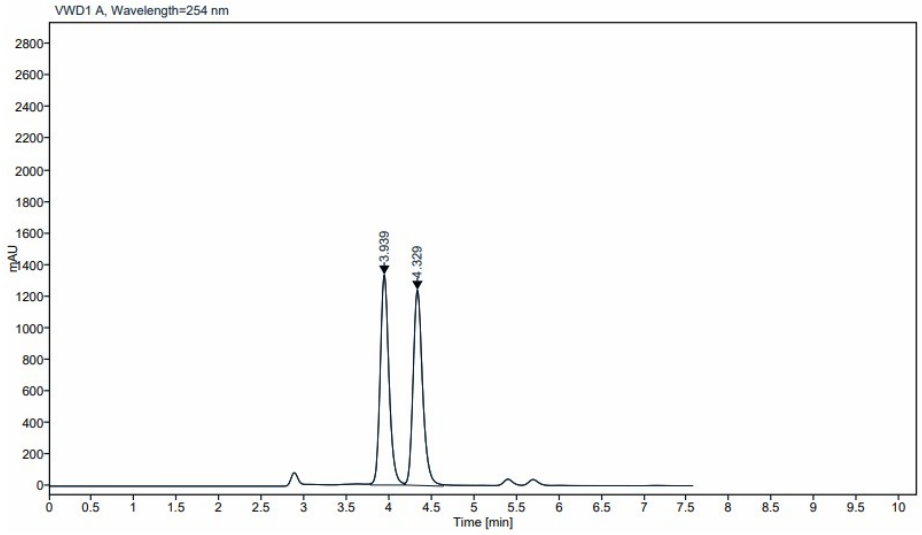


1p



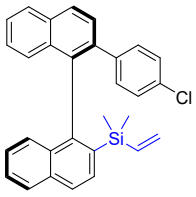
Results

No.	RT[min]	Area	Height	Relative Height %	Relative Area %
	4.957	270.3477	40.5305	1.19	0.66
	5.684	40648.3633	3374.9700	98.81	99.34
SUM	10.641	40918.7110	3415.5005	100.00	100.00

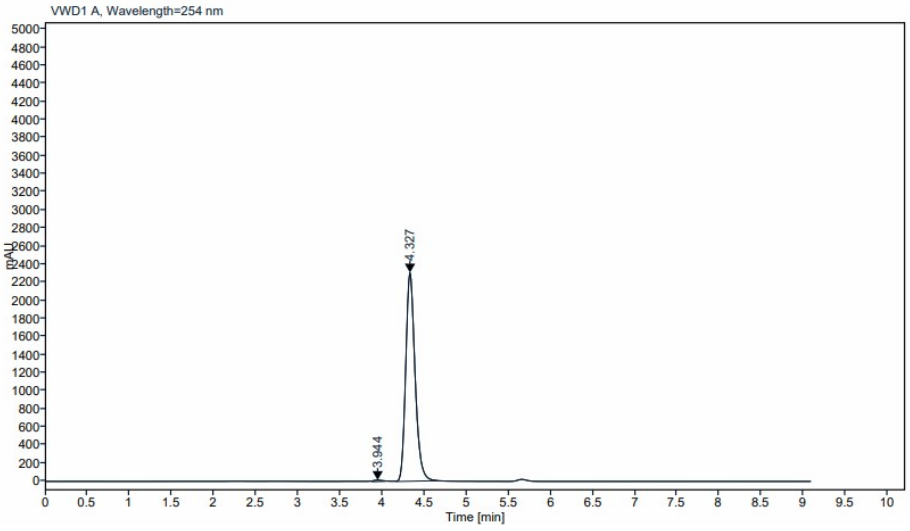


Results

No.	RT[min]	Area	Height	Relative Height %	Relative Area %
	3.939	9606.0117	1335.9635	51.85	49.86
	4.329	9660.1992	1240.4542	48.15	50.14
SUM	8.268	19266.2109	2576.4177	100.00	100.00

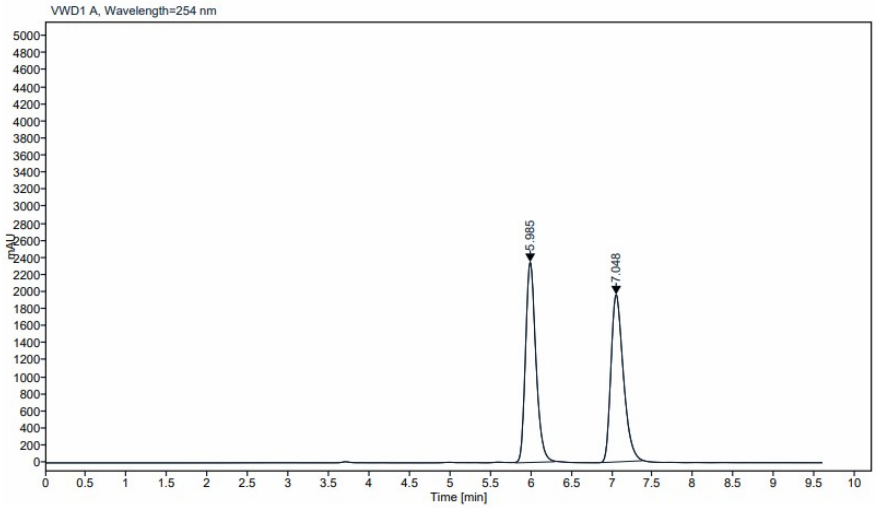


3p



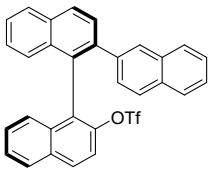
Results

No.	RT[min]	Area	Height	Relative Height %	Relative Area %
	3.944	107.8018	15.4704	0.67	0.60
	4.327	17790.1094	2306.8118	99.33	99.40
SUM	8.271	17897.9112	2322.2822	100.00	100.00

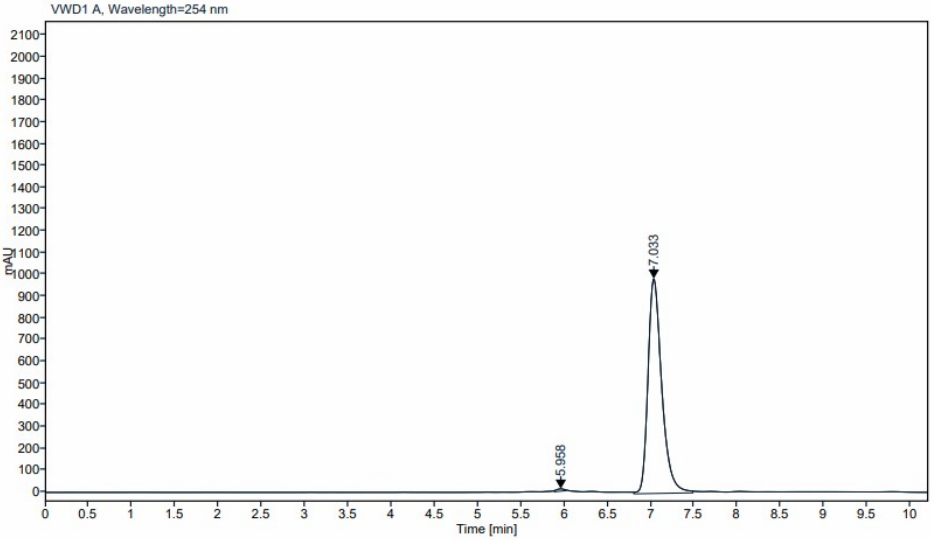


Results

No.	RT[min]	Area	Height	Relative Height %	Relative Area %
	5.985	20883.8809	2347.8438	54.47	49.94
	7.048	20930.1621	1962.7592	45.53	50.06
SUM	13.033	41814.0430	4310.6029	100.00	100.00

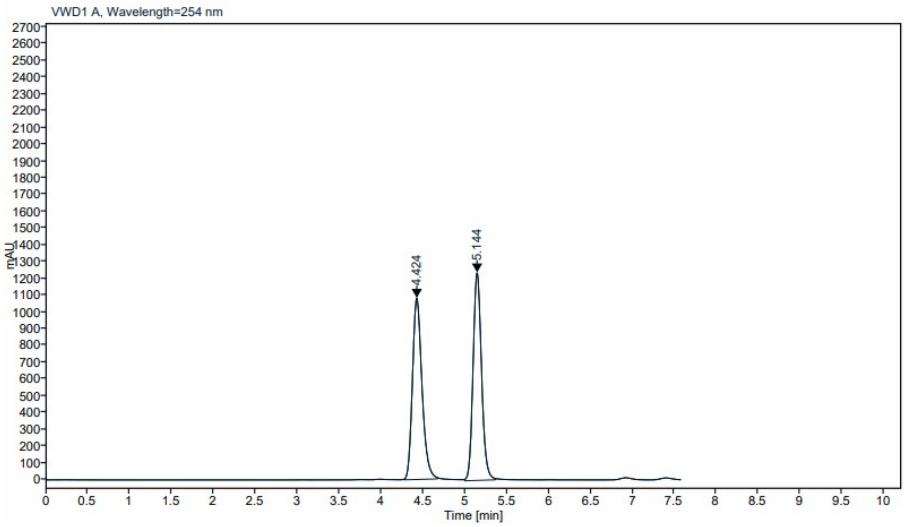


1q



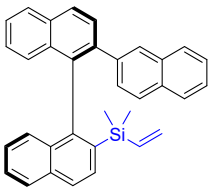
Results

No.	RT[min]	Area	Height	Relative Height %	Relative Area %
	5.958	66.7539	10.8133	1.08	0.61
	7.033	10912.7168	987.5244	98.92	99.39
SUM	12.991	10979.4707	998.3377	100.00	100.00

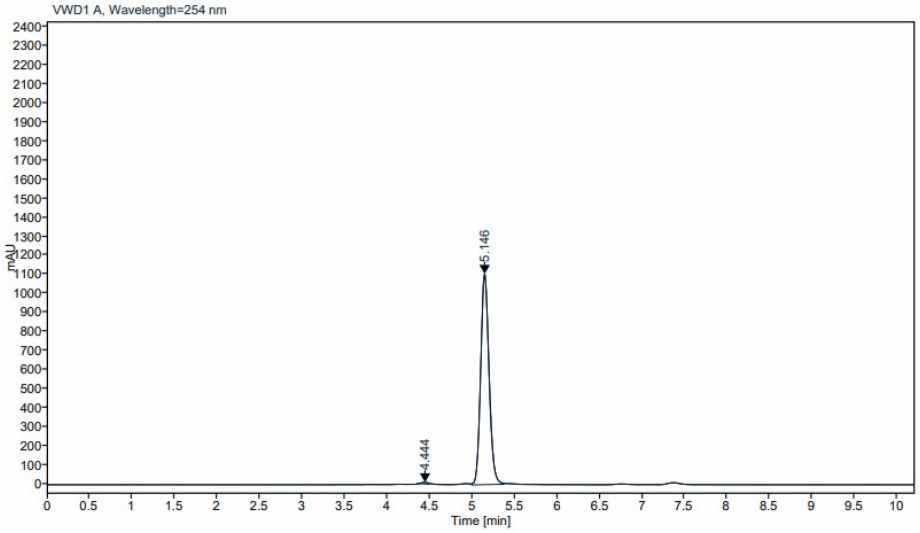


Results

No.	RT[min]	Area	Height	Relative Height %	Relative Area %
	4.424	8564.3818	1083.6571	46.62	49.63
	5.144	8690.7979	1240.7925	53.38	50.37
SUM	9.568	17255.1797	2324.4496	100.00	100.00

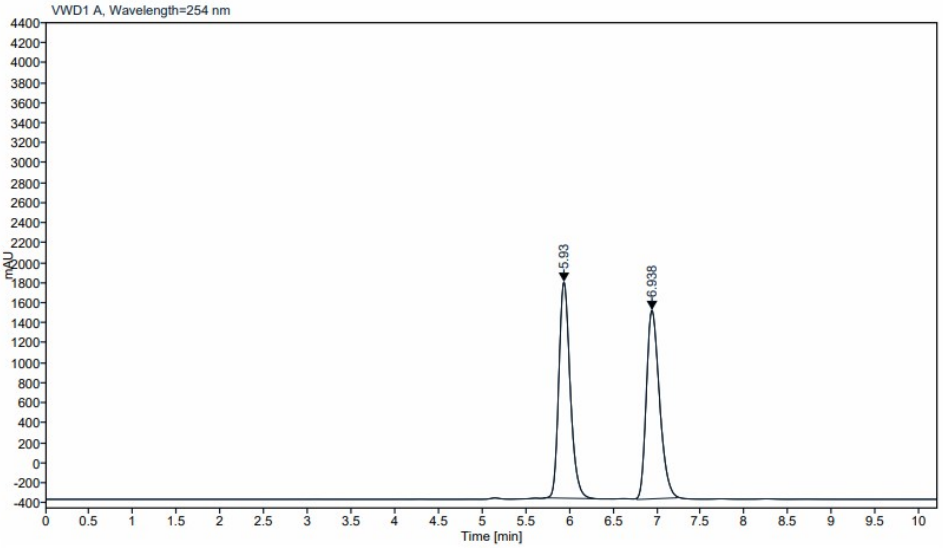


3q



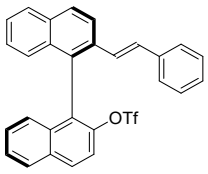
Results

No.	RT[min]	Area	Height	Relative Height %	Relative Area %
	4.444	41.8848	8.1755	0.73	0.55
	5.146	7585.3687	1104.9607	99.27	99.45
SUM	9.590	7627.2534	1113.1362	100.00	100.00

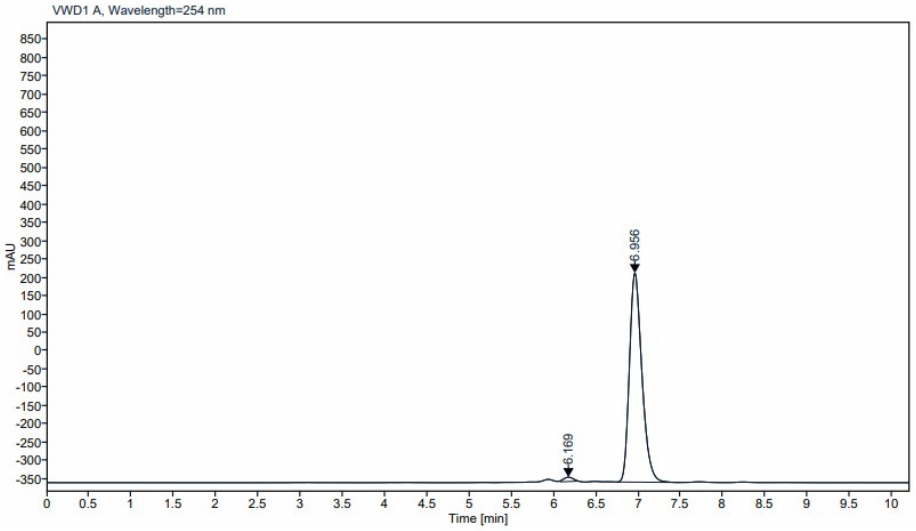


Results

No.	RT[min]	Area	Height	Relative Height %	Relative Area %
	5.930	19525.3047	2161.5571	53.40	49.75
	6.938	19720.4688	1886.6270	46.60	50.25
SUM	12.868	39245.7734	4048.1841	100.00	100.00

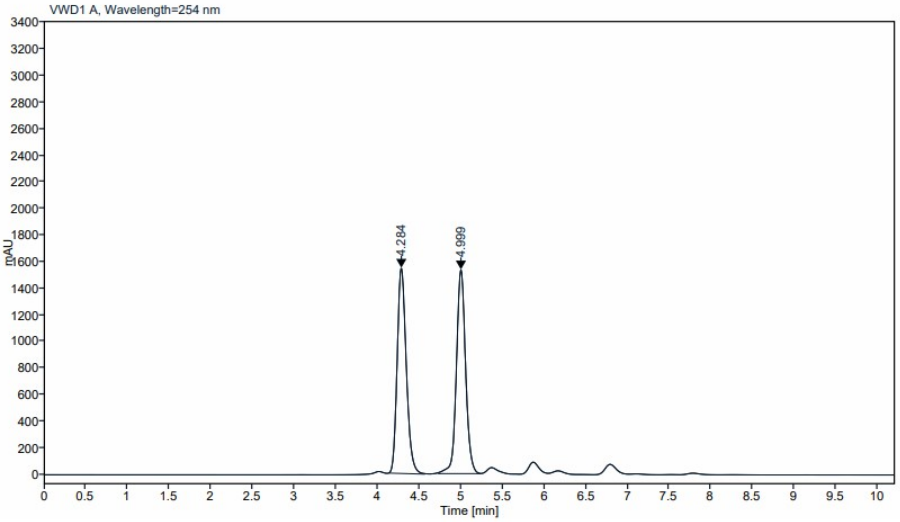


1r



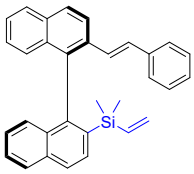
Results

No.	RT[min]	Area	Height	Relative Height %	Relative Area %
	6.169	91.9719	11.9383	2.05	1.54
	6.956	5867.6118	570.5962	97.95	98.46
SUM	13.125	5959.5837	582.5345	100.00	100.00

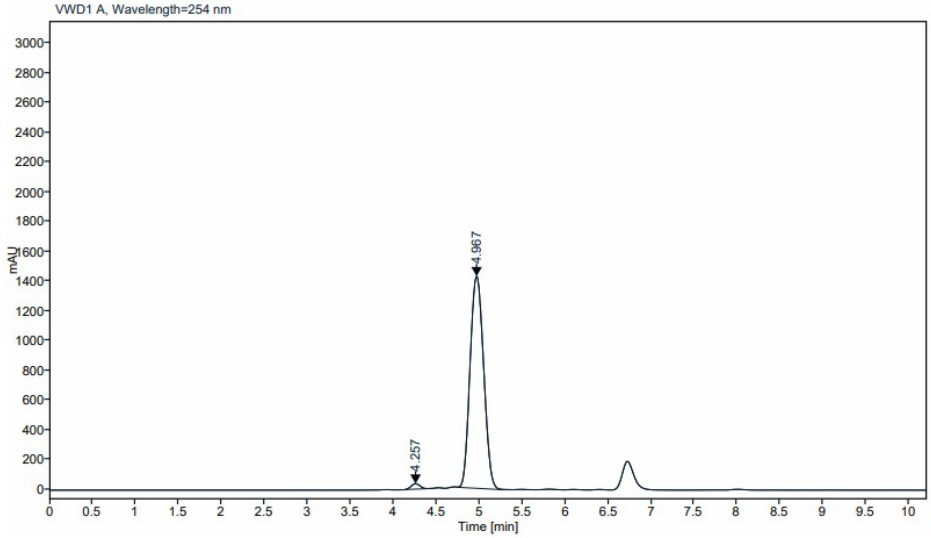


Results

No.	RT[min]	Area	Height	Relative Height %	Relative Area %
	4.284	11728.9375	1547.1804	50.19	49.97
	4.999	11744.6738	1535.4314	49.81	50.03
SUM	9.283	23473.6113	3082.6118	100.00	100.00



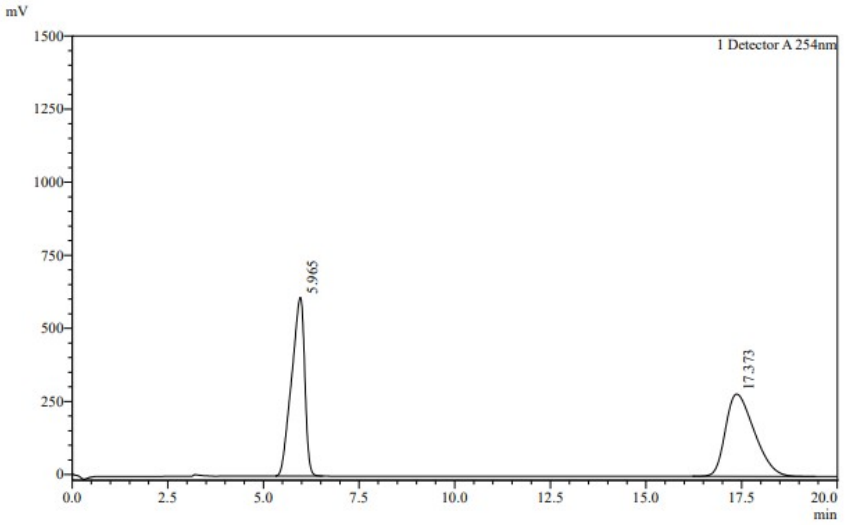
3r



Results

No.	RT[min]	Area	Height	Relative Height %	Relative Area %
	4.257	258.1785	36.5465	2.50	1.62
	4.967	15704.0313	1427.2317	97.50	98.38
SUM	9.224	15962.2097	1463.7782	100.00	100.00

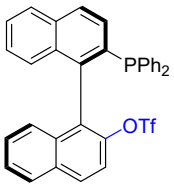
<Chromatogram>



<Peak Table>

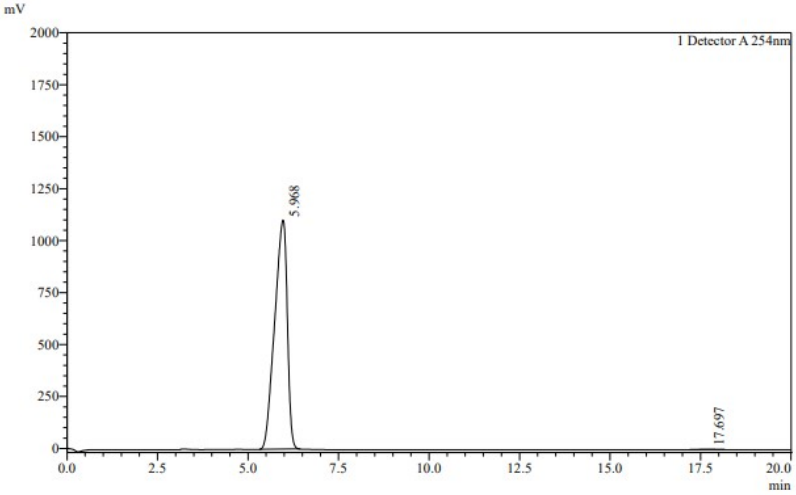
Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Area%
1	5.965	14575580	610976	49.686	49.686
2	17.373	14760062	281383	50.314	50.314
Total		29335641	892359		100.000



1s

<Chromatogram>

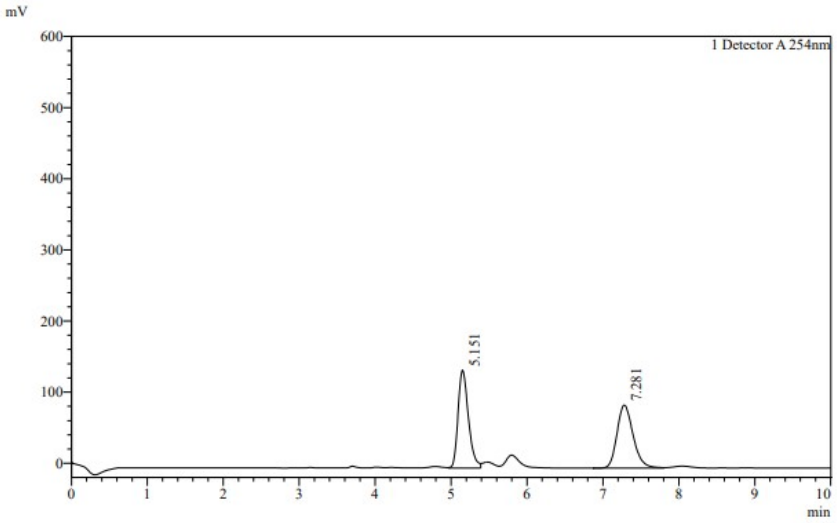


<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Area%
1	5.968	26666130	1102150	99.815	99.815
2	17.697	49482	1486	0.185	0.185
Total		26715612	1103636		100.000

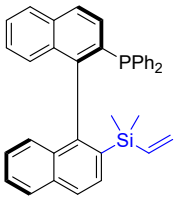
<Chromatogram>



<Peak Table>

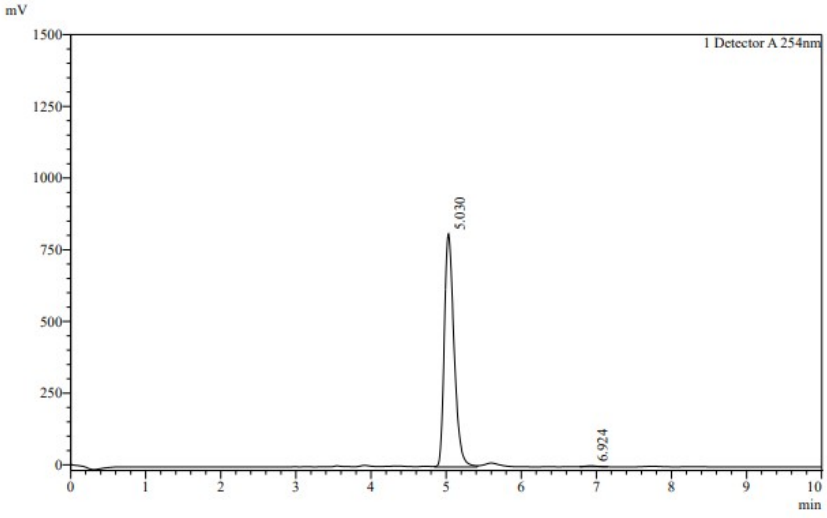
Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Area%
1	5.151	1307041	137594	49.950	49.950
2	7.281	1309660	88506	50.050	50.050
Total		2616702	226100		100.000



3s

<Chromatogram>

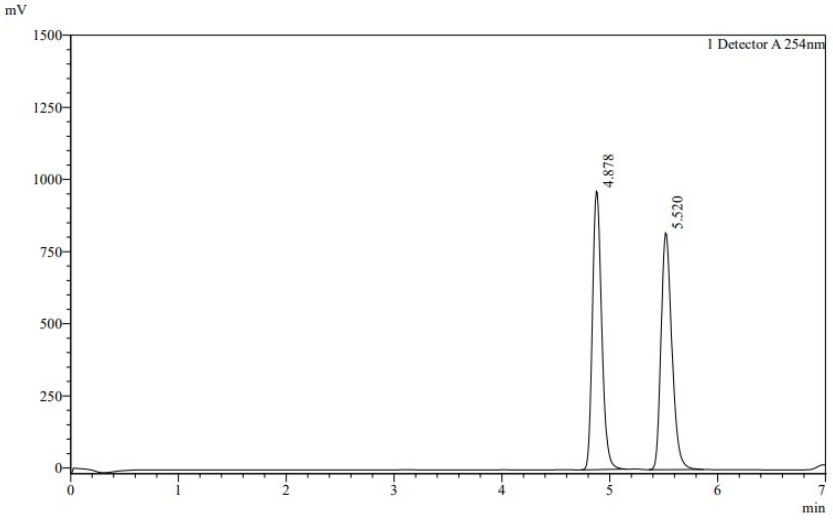


<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Area%
1	5.030	7352804	813011	99.588	99.588
2	6.924	30442	2880	0.412	0.412
Total		7383247	815892		100.000

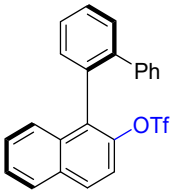
<Chromatogram>



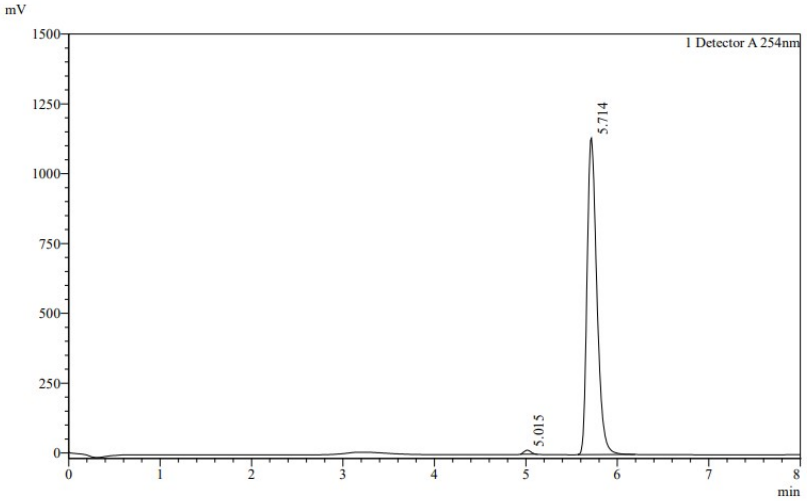
<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Area%
1	4.878	5744048	964240	49.986	49.986
2	5.520	5747179	819944	50.014	50.014
Total		11491226	1784184		100.000



1t

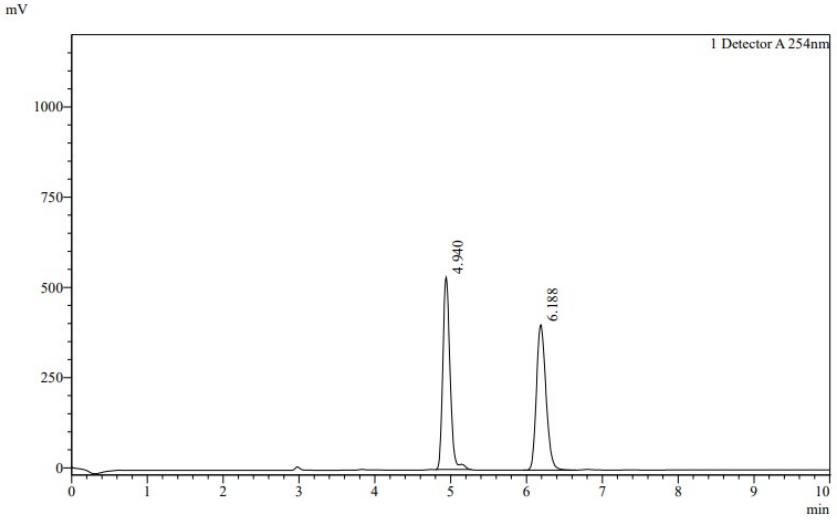


<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Area%
1	5.015	73809	14291	0.869	0.869
2	5.714	8415884	1132590	99.131	99.131
Total		8489693	1146881		100.000

<Chromatogram>

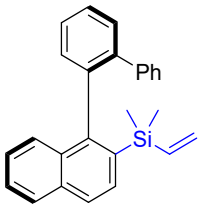


<Peak Table>

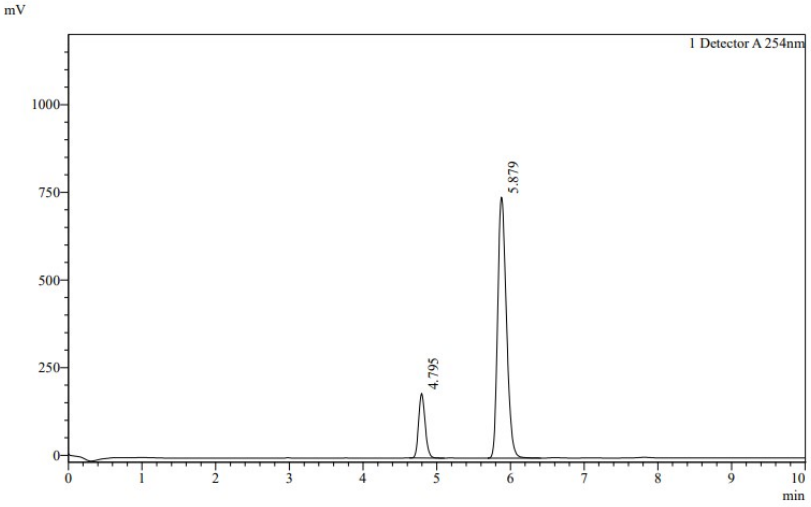
Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Area%
1	4.940	3534561	532792	50.054	50.054
2	6.188	3526968	402748	49.946	49.946
Total		7061529	935540		100.000

<Chromatogram>



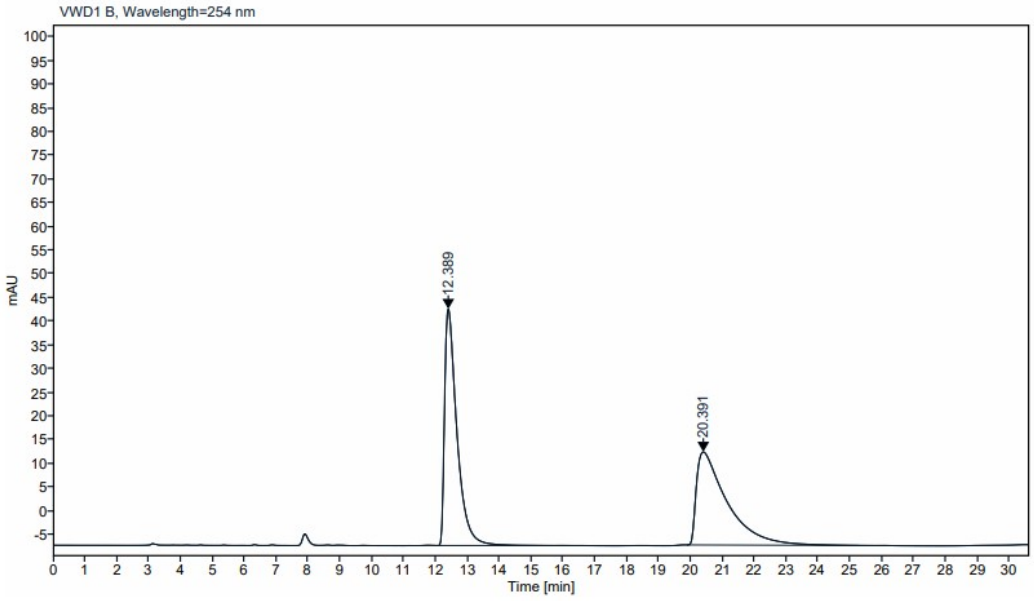
3t



<Peak Table>

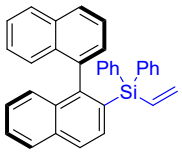
Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Area%
1	4.795	1137451	183975	15.630	15.630
2	5.879	6140056	743584	84.370	84.370
Total		7277507	927559		100.000

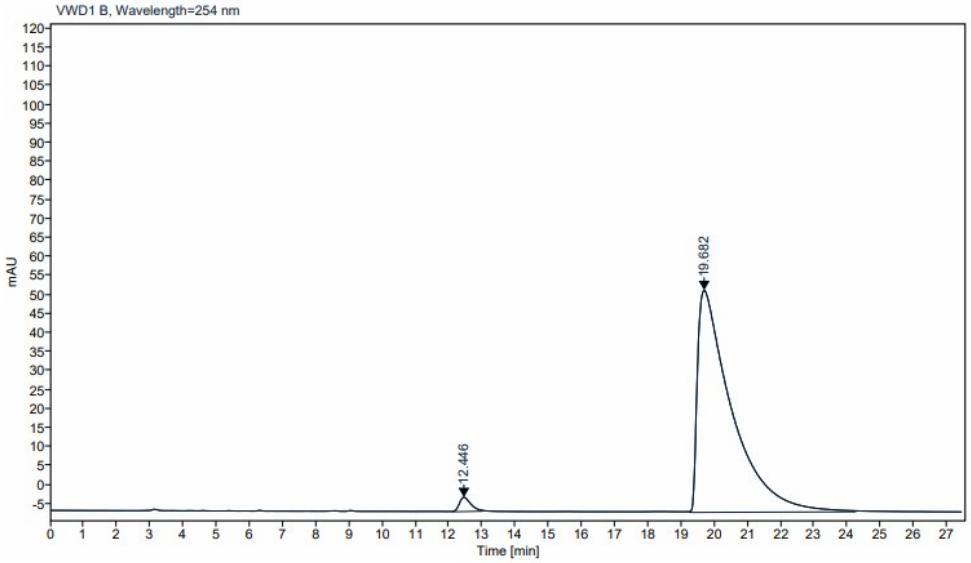


Results

No.	RT[min]	Area	Height	Relative Height %	Relative Area %
	12.389	1341.6210	49.8848	71.78	50.56
	20.391	1311.7988	19.6132	28.22	49.44
SUM	32.779	2653.4198	69.4980	100.00	100.00

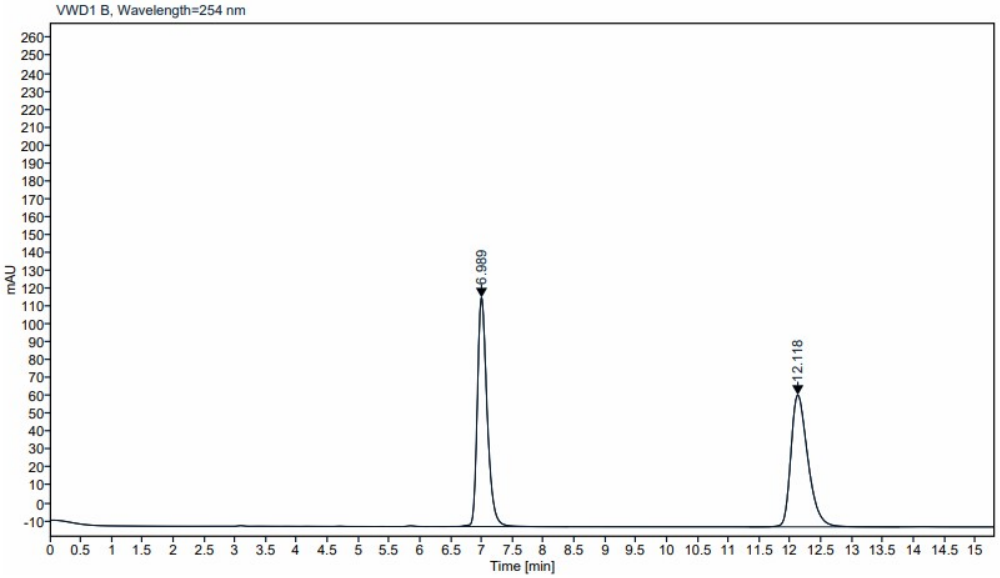


3v



Results

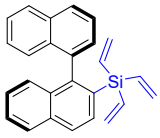
No.	RT[min]	Area	Height	Relative Height %	Relative Area %
	12.446	90.2758	3.7501	6.03	2.11
	19.682	4179.4590	58.4201	93.97	97.89
SUM	32.128	4269.7348	62.1702	100.00	100.00



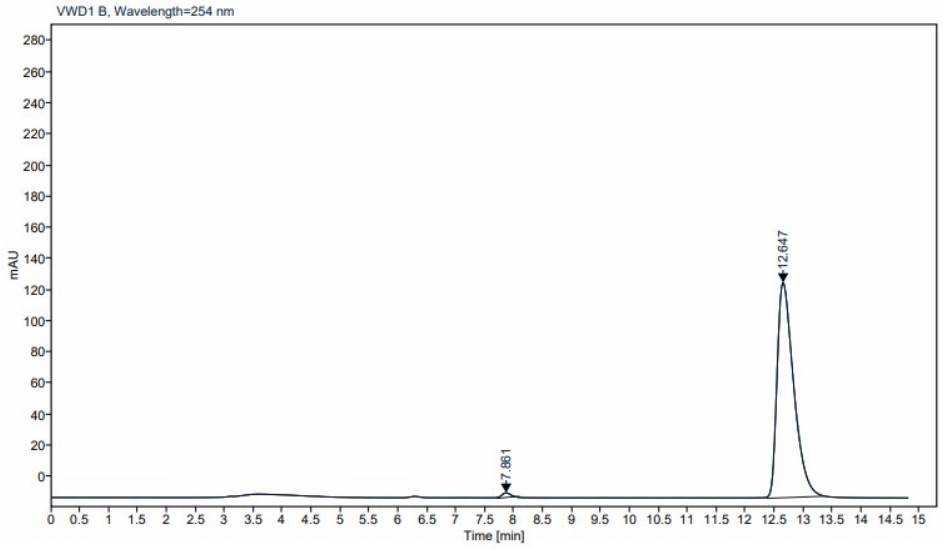
Results

No.	RT[min]	Area	Height	Relative Height %	Relative Area %
	6.989	1408.8342	127.8256	63.46	49.92
	12.118	1413.5310	73.6089	36.54	50.08
SUM	19.107	2822.3652	201.4345	100.00	100.00

截图(Alt + A)

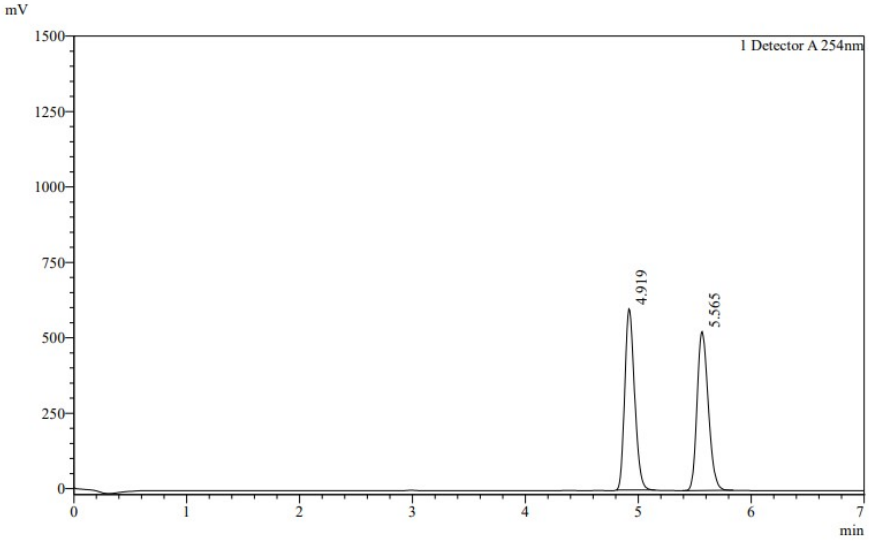


3w



Results

No.	RT[min]	Area	Height	Relative Height %	Relative Area %
	7.861	30.3597	2.9986	2.12	1.09
	12.647	2752.3108	138.2171	97.88	98.91
SUM	20.507	2782.6705	141.2156	100.00	100.00

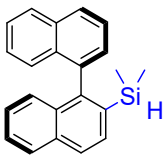


<Peak Table>

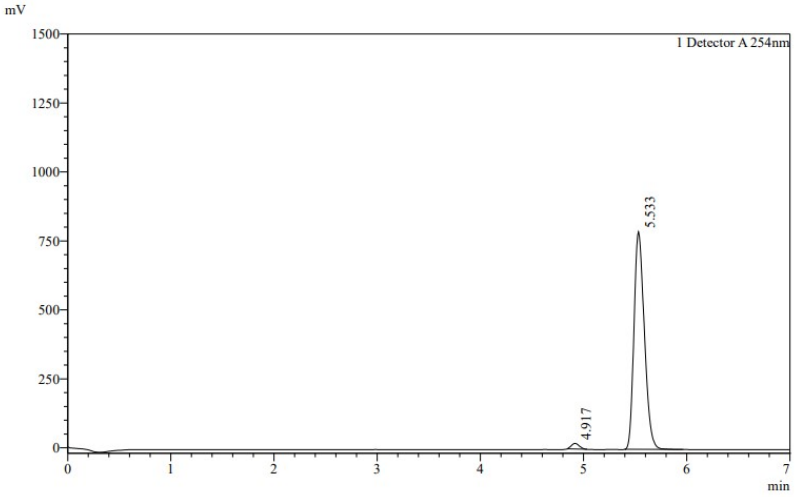
Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Area%
1	4.919	3635918	600077	50.008	50.008
2	5.565	3634753	525954	49.992	49.992
Total		7270671	1126031		100.000

<Chromatogram>



3x



<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Area%
1	4.917	109467	20468	1.942	1.942
2	5.533	5528061	788212	98.058	98.058
Total		5637527	808680		100.000