Supporting Information for

Paired electrocatalysis enabled oxidative coupling of styrenes with alkyl radicals

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Supporting Information

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1.General Information

1.1 Analytic Methods

^{1}H NMR, ^{13}C NMR data were obtained on Bruker Avance NEO 500 nuclear resonance spectrometers unless otherwise noted (^{1}H NMR 500 MHz, ^{13}C NMR 126 MHz, ^{19}F NMR 471 MHz) and Buker Avance NEO 400 MHz NMR spectrometer (^{1}H NMR 400 MHz, ^{13}C NMR 101 MHz, ^{19}F NMR 376 MHz). ^{1}H NMR chemical shifts (in ppm) were referenced to $CHCl_3$ (δ = 7.26 ppm) in $CDCl_3$, DMSO (δ = 2.50 ppm) in DMSO-d_6, MeOH (δ = 3.31 ppm) in CD_3OD, or as an internal standard. The data of ^{1}H NMR were reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet and br = broad), coupling constant (*J* values) in Hz and integration. ^{13}C-NMR spectra were obtained by the same NMR spectrometers and were calibrated with $CDCl_3$ (δ = 77.16 ppm), DMSO-d_6 (δ = 39.52 ppm), CD_3OD (49.00 ppm). Yields refer to products isolated after purification by preparative TLC (GF254, 10-50 μm, Yantai Xincheng Silicone Materials Co., LTD) unless otherwise stated. Flash chromatography was performed using 300-400 mesh silica gel with the indicated eluent according to standard techniques. Thin-layer chromatography (TLC) was conducted with silica gel 60 F_{254} pre-coated plates (0.25 mm) and visualized with UV and phosphomolybdic acid unless otherwise noted. HR-MS analyses were performed with Waters G2-XS/APGC (ESI) and Thermo Orbitrap Exploris GA10097 Orbitrap Exploris GC 240 (EI). GC-MS analyses were performed with SHIMADZU GCMS-QP2010 SE (EI) system.

1.2 Reagents

All commercially available compounds were purchased from Energy Chemical, Innochem, TCI, Adamas, Alfa-Aesar. All the solvents and all the other reagents were directly used from purchased without any further purification unless otherwise specified.

2. Experimental Section

2.1 Electrolysis Set-up and Materials

Electrolysis experiments were performed using the MESTEK DC power supply. Platinum plate (99.99%, 25 mm × 7.5 mm × 0.2 mm, or 30 mm × 30 mm × 0.3 mm for gram scale reaction) were purchased from OMIK Ectrochemistry. The Nickel plate was cut into 25 mm × 7.5 mm × 0.3 mm pieces before use and was clamped between electrode clips. The Nickel plate as cathode (30 mm × 30 mm × 0.3 mm) for gram scale reaction setup.

General procedures of oxidative coupling products of styrenes and THF

An oven-dried undivided cell as described above was equipped with a stir bar (Fig. S1). The cell was equipped with Platinum plate (25 mm × 7.5 mm × 0.2 mm) as the anode and Nickel plate (25 mm × 7.5 mm × 0.3 mm) as the cathode. To the cell was added with $LiClO_4$ (31.9 mg, 0.3 mmol, 0.1 M), styrene (20.8 mg, 0.2 mmol), 4,4'-dimethoxybenzophenone (38.8 mg, 0.16 mmol), TBAI (14.8 mg, 0.04 mmol) in 3 mL of THF at room temperature. The cell was sealed using a rubber septum and insert a thin needle into the stopper to prevent it from bursting open. The solution was then stirred at room temperature and electrolyzed under a constant current of 10.0 mA from DC power for 8 h under air atmosphere. The reaction mixture was extracted with water (ca. 20 mL). The aqueous layer was separated and extracted with EtOAc (3×15 mL), and the combined organic layers were washed with brine and dried over anhydrous Na_2SO_4. And the reaction mixture was concentrated under vacuum. The residue was purified by flash chromatography on silica gel (petroleum ether: ethyl acetate = 30:1) to give the desired product.

General procedures of oxidative coupling products of styrenes and p-methylphenols

An oven-dried undivided cell as described above was equipped with a stir bar (Fig. S1). The cell was equipped with Platinum plate (25 mm × 7.5 mm × 0.2 mm) as the anode and Ni foam (25 mm × 7.5 mm × 3 mm) as the cathode. To the cell was added with $LiClO_4$ (31.9 mg, 0.3 mmol, 0.1 M), butylated Hydroxytoluene (44.1 mg, 0.2 mmol), styrene (31.2 mg, 0.3 mmol), 4,4'-dimethoxybenzophenone (38.8 mg, 0.16 mmol), TBAI (14.8 mg, 0.04 mmol) in 3 mL of THF at room temperature. The cell was sealed using a rubber septum and insert a thin needle into the stopper to prevent it from bursting open. The solution was then stirred at room temperature and electrolyzed under a constant current of 10.0 mA from DC power for 8 h under air atmosphere. The reaction mixture was extracted with water (ca. 20 mL). The aqueous layer was separated and extracted with EtOAc (3×15 mL), and the combined organic layers were washed with brine and dried over anhydrous Na_2SO_4. And the reaction mixture was concentrated under vacuum. The residue was purified by flash chromatography on silica gel (petroleum ether) to give the desired product.

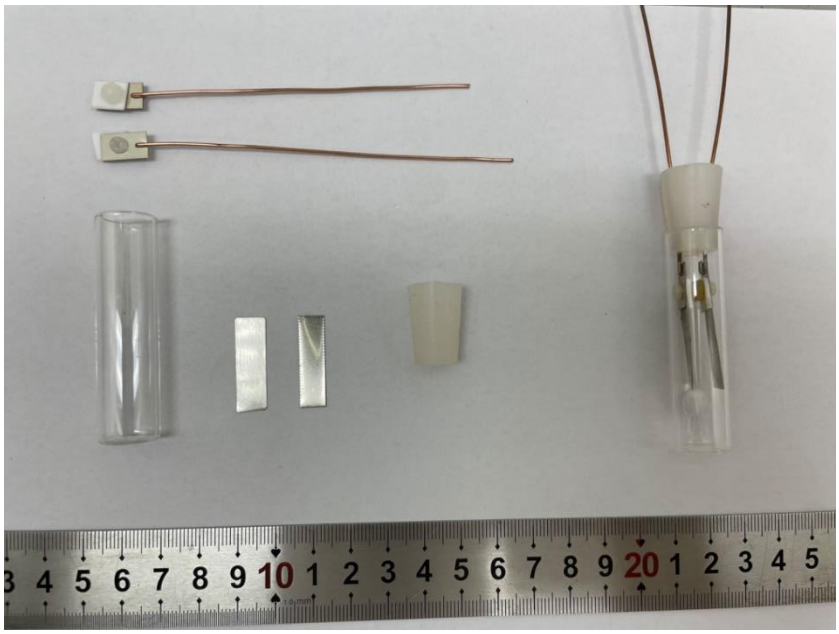


Figure S1: Electrolysis setups and materials used for undivided cell.

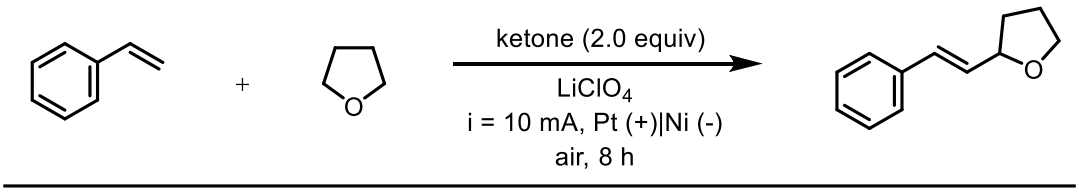
General procedure for the scale-up synthesis

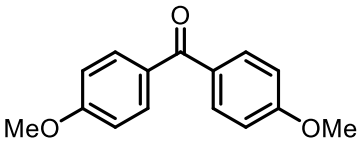
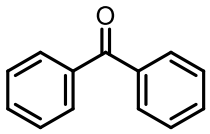
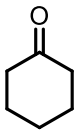
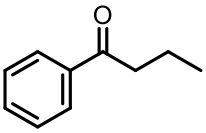
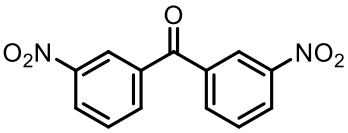
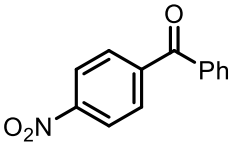
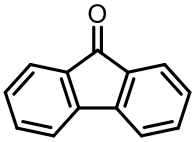
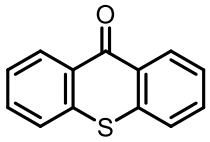
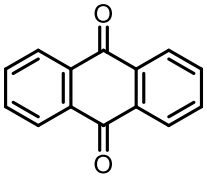
An oven-dried 100 mL undivided cell as described above (see Fig. S2) was equipped with a stir bar. The cell was equipped with Platinum plate (30 mm × 30 mm × 0.3 mm) as the anode and Ni foam (30 mm × 30 mm ×3 mm) as the cathode. To the cell was added with $LiClO_4$ (5.0 g), styrene (1.041 g, 10 mmol), 4,4'-dimethoxybenzophenone (1.45 g, 6 mmol), TBAI (0.74 g, 2 mmol) in 80 mL of THF at room temperature. The solution was then stirred at room temperature and electrolyzed under a constant current of 40.0 mA from DC power for 36 h under air atmosphere. The reaction mixture was extracted with water (ca. 60 mL). The aqueous layer was separated and extracted with EtOAc (3×25 mL), and the combined organic layers were washed with brine and dried over anhydrous Na_2SO_4. And the reaction mixture was concentrated under vacuum. The residue was purified by flash chromatography on silica gel (petroleum ether: ethyl acetate = 30:1) to give the desired product **4a** 0.8867 g (52% yield, yellow oil).

Figure S2: Gram scale-up setups

2.2 Optimization of Reaction Conditions

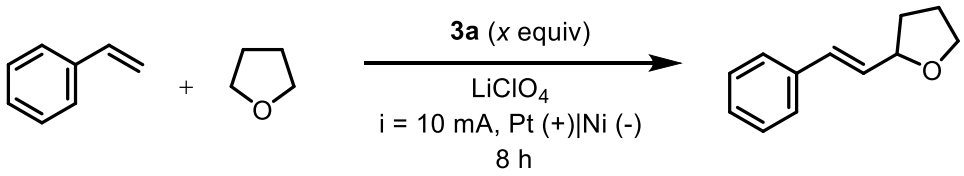
Table S1. Investigation of ketones[a]



		
3a 55% yield	**3b** 31% yield	**3c** 20% yield
		
3d 24% yield	**3e** 12% yield	**3f** trace
		
3g 29% yield	**3h** 44% yield	**3i** 50% yield

[a]Reaction conditions: undivided cell, Platinum plate (25 mm * 7.5 mm * 2 mm), Nickel plate (25 mm * 7.5 mm * 0.3 mm), constant current = 10 mA, $LiClO_4$(31.9 mg, 0.3 mmol, 0.1 M), Styrene (20.8 mg, 0.2 mmol), ketone (0.4 mmol) in THF (3.0 mL), r.t., 8 h. Isolated yield.

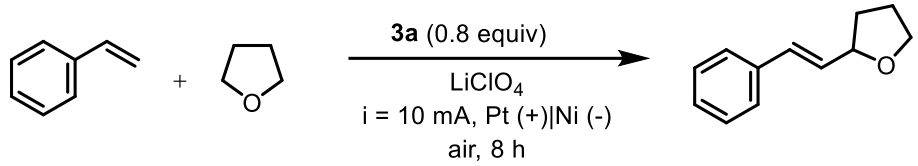
Table S2. Investigation of equivalents of 3a[a,b]



entry	**3a** (*x* equiv)	yield[a]
1	0.2	<5%
2	0.4	11%
3	0.6	47%
4	0.8	53%
5	1.0	38%
6	1.2	46%
7	1.5	45%

[a]Reaction conditions: undivided cell, Platinum plate (25 mm ∗ 7.5 mm ∗ 2 mm), Nickel plate (25 mm ∗ 7.5 mm ∗ 0.3 mm), constant current = 10 mA, $LiClO_4$(31.9 mg, 0.3 mmol, 0.1 M), Styrene (20.8 mg, 0.2 mmol), ketone in THF (3.0 mL), r.t., 8 h.
[b]Isolated yield.

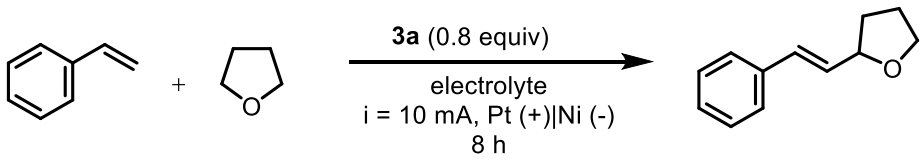
Table S3. Investigation of electrodes[a,b]



entry	deviation from the reaction conditions	yield[a]
1	Ni (+)|Pt (-)	N. D.
2	C cloth (+)|Ni (-)	N. D.
3	C felt (+)|Ni (-)	N. D.
4	Mg (+)|Ni (-)	N. D.
5	Ti (+)|Ni (-)	N. D.
6	Zn (+)|Ni (-)	N. D.
7	SS (+)|Ni (-)	N. D.
8	Pt (+)|Pt (-)	21%
9	Ni (+)|Ni (-)	N. D.

[a]Reaction conditions: undivided cell, constant current = 10 mA, $LiClO_4$(31.9 mg, 0.3 mmol, 0.1 M), Styrene (20.8 mg, 0.2 mmol), **3a** (0.16 mmol) in THF (3.0 mL), r.t., 8 h.
[b]Isolated yield.

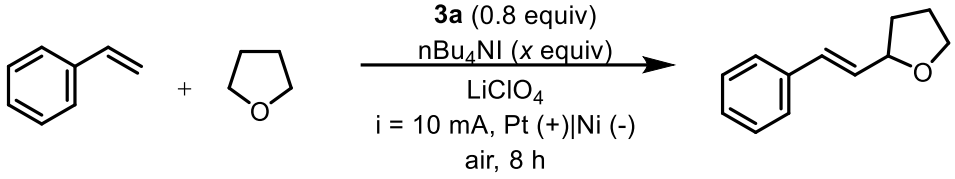
Table S4. Investigation of electrolytes[a,b]



entry	electrolyte	yield
1	$^{n}Bu_4NClO_4$	N. D.
2	$AgClO_4$	21%
3	$NaClO_4$	9%
4	$KClO_4$	N. D.
5	$Mg(ClO_4)_2$	N. D.

[a]Reaction conditions: undivided cell, Platinum plate (25 mm * 7.5 mm * 2 mm), Nickel plate (25 mm * 7.5 mm * 0.3 mm), constant current = 10 mA, electrolyte(0.1 M), Styrene (20.8 mg, 0.2 mmol), **3a** (0.16 mmol) in THF (3.0 mL), r.t., 8 h.
[b]Isolated yield.

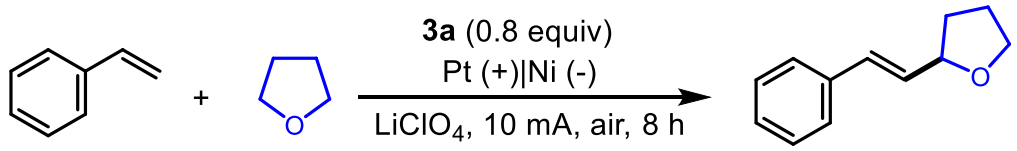
Table S5. Investigation of equivalents of TBAI[a,b]



entry	$^{n}Bu_4NI$ (*x* equiv)	yield
1	2.0	19%
2	1.5	40%
3	1.0	52%
4	0.5	65% (94%)[c]
5	3.5	N. D.
6	5	N. D.
7	0.4	63% (94%)[c]
8	0.3	63% (92%)[c]
9	0.2	70% (94%)[c]
10	0.1	65% (91%)[c]

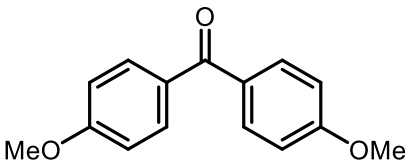
[a]Reaction conditions: undivided cell, Platinum plate (25 mm ∗ 7.5 mm ∗ 2 mm), Nickel plate (25 mm ∗ 7.5 mm ∗ 0.3 mm), constant current = 10 mA, $LiClO_4$(31.9 mg, 0.3 mmol, 0.1 M), Styrene (20.8 mg, 0.2 mmol), **3a** (0.16 mmol), TBAI in THF (3.0 mL), r.t., 8 h.
[b]Isolated yield.
[c]yield of **5a**

Table S6. Variations from standard conditions

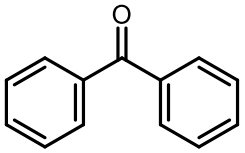


1a + **2** → **4a**

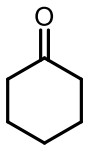
entry	deviation from the reaction conditions	yield[a,b]
1	none	53%
2	i = 5 mA	20%
3	i = 12 mA	34%
4	C (+)|Ni (-)	0%
5	$^{n}Bu_4NI$ (0.5 equiv)	65%
6	$^{n}Bu_4NI$ (0.5 equiv), under N_2	59%
7	$^{n}Bu_4NI$ (0.5 equiv), under O_2	24%
8	**$^{n}Bu_4NI$ (0.2 equiv)**	**70%**
9	2.0 equiv. **3a**	55%
10	2.0 equiv. **3b**	31%
11	2.0 equiv. **3c**	20%
12	no **3a**	14%
13	no current	0%



3a



3b

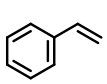


3c

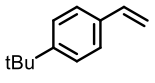
[a]Reaction conditions: undivided cell, Platinum plate (25 mm * 7.5 mm * 2 mm), Ni plate (25 mm * 7.5 mm * 0.3 mm), constant current = 10 mA, $LiClO_4$(31.9 mg, 0.3 mmol, 0.1 M), Styrene (20.8 mg, 0.2 mmol), **3a** (0.16 mmol), TBAI in THF (3.0 mL), r.t., 8 h.
[b]Isolated yield.

2.3 Preparation of Starting Materials

The substrates were prepared according to reports in the literature[1-10].



1a



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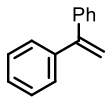

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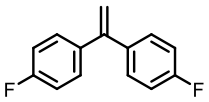

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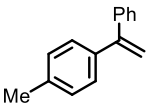

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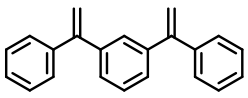

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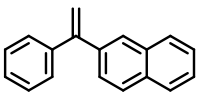

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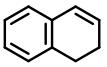

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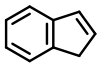

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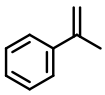

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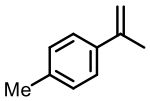

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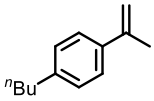

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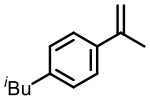

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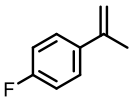

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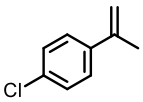

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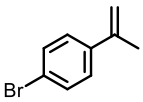
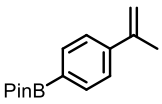


1p



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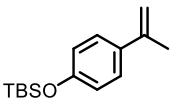

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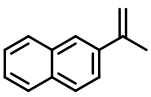

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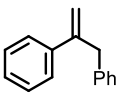

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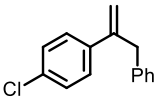
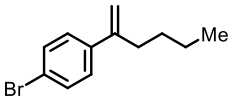


1u



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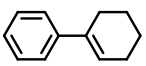
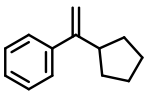
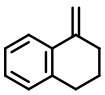


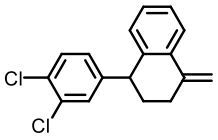
1w



1x



1y



1z

2.4 Mechanism Studies

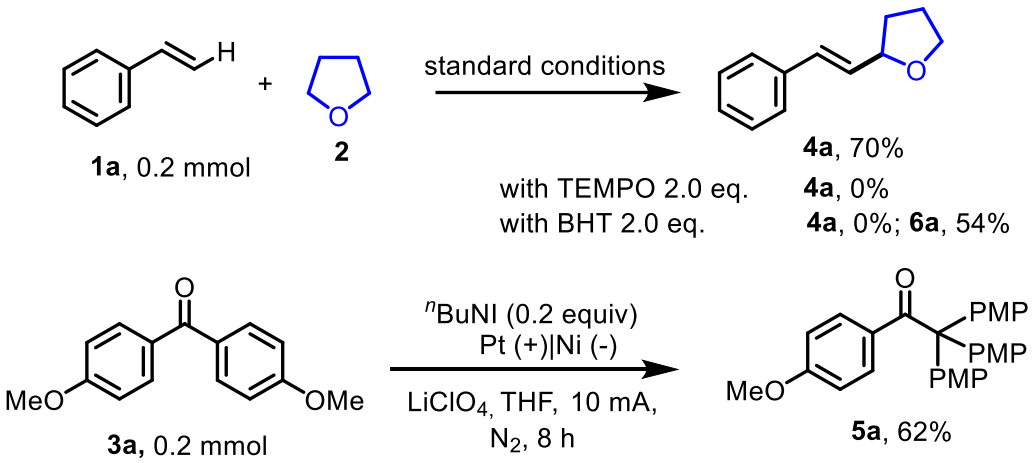


Figure S3 Mechanism Studies

2.5 Cyclic Voltammetry Studies

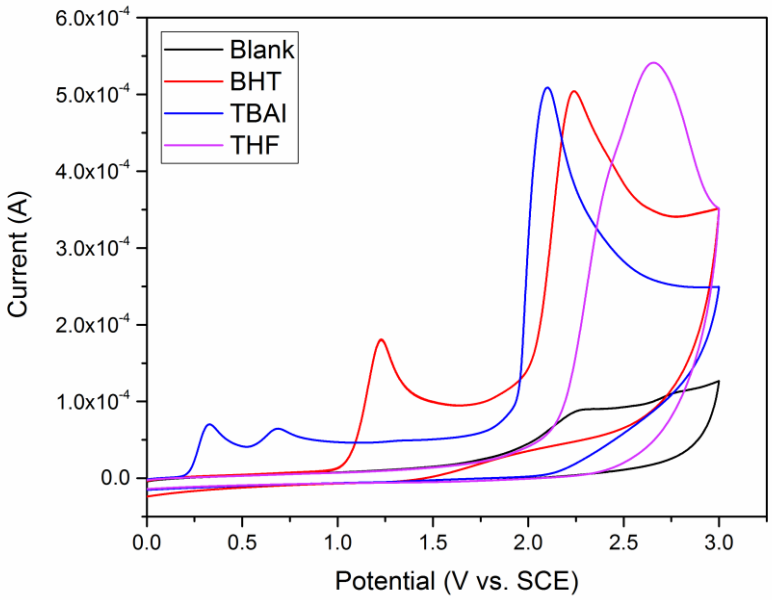


Figure S4 Cyclic voltammogram of substrates [3 mM] in [0.1 M] Et_4NBF_4 in CH_3CN. Scan rate: 100 mV/s.

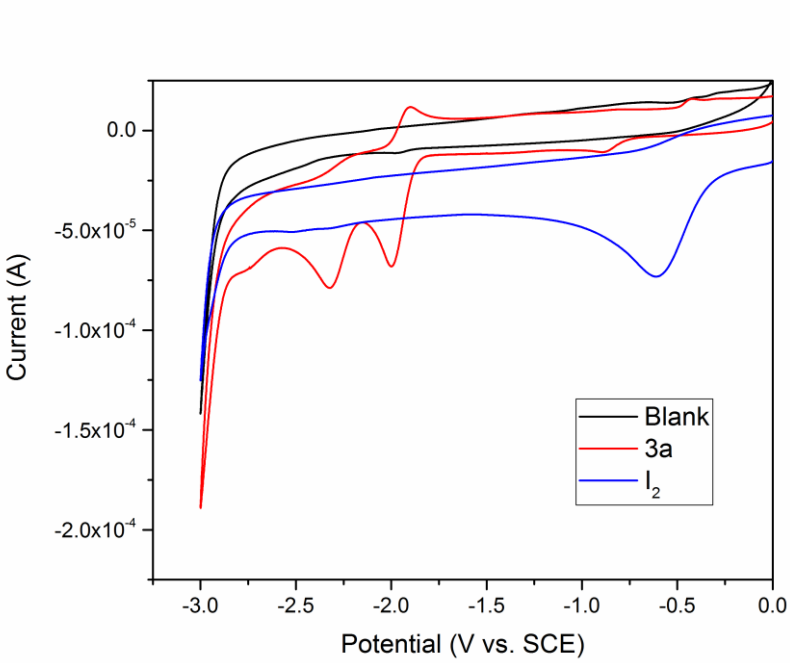


Figure S5 Cyclic voltammogram of substrates [3 mM] in [0.1 M] Et_4NBF_4 in DMF. Scan rate: 100 mV/s.

2.6 Gas chromatography analysis of electrolysis headspace

We have detected H_2 evolution at the cathode in model reaction by gas chromatography (GC) with a TCD detector.

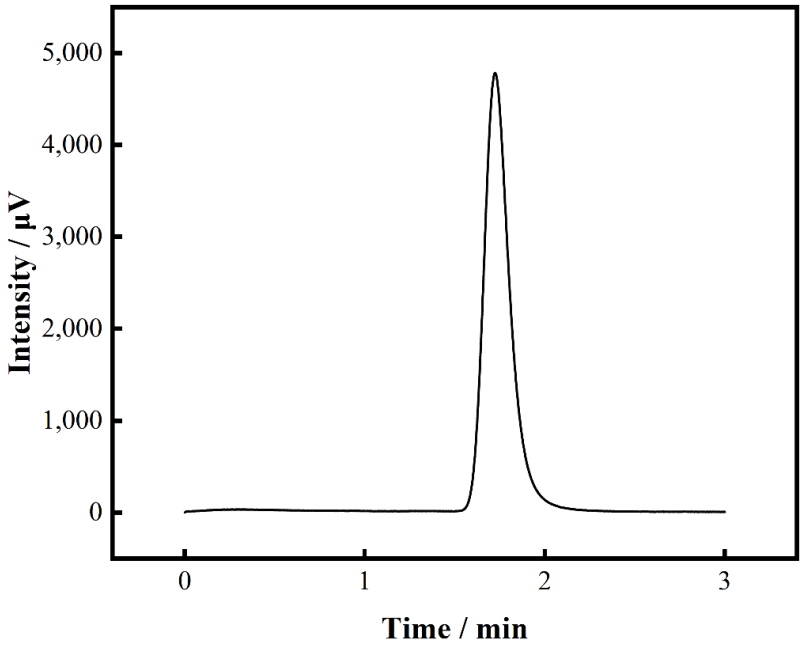


Figure S6: Gas chromatogram of the headspace of diamination reaction

2.7 Voltage monitoring of the reaction under standard conditions.

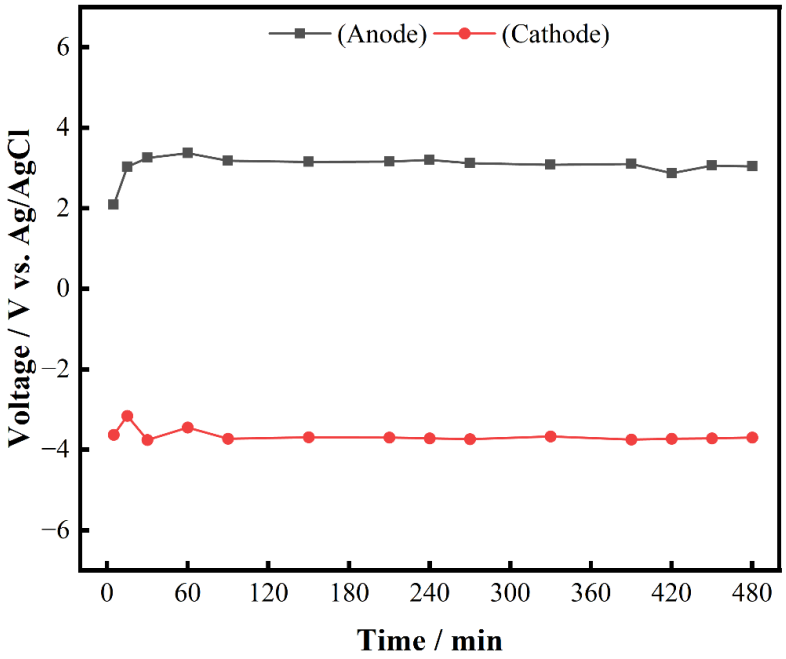
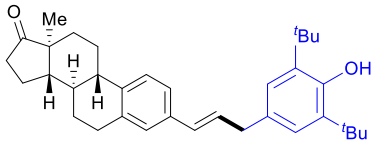


Figure S7: Voltage monitoring of the reaction under standard conditions

2.8 Anti-tumor Activity Test

Table S7 IC50 (μM) values for compound **7g** against cancer cell lines.

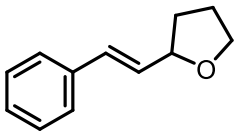


7g

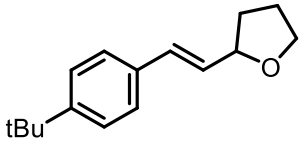
compound	A549	Huh7
7g	88.8±11.8	60.1±2.7

The 100 μL cell suspensions (8000-9000 cells/mL) was seeded in 96-well plates and incubated for 24 h. **7g** was dissolved in the Phosphate Buffered Saline (PBS) with 0.1% DMSO to give various concentrations (2.5, 5, 10, 20, and 40 μM respectively) to 96-well plates and control wells contained supplemented media with 0.1% DMSO. Continue incubating for 48 h at 37 ℃ in 5% CO_2 atmosphere and then the MTT solution (10 μL, 5 mg/mL) was added into each well and the cultures were incubated further for 4~6 h. After removal of the supernatant, formazan solution (100 μL) was added to dissolve the formazan crystals. The absorbance was read by enzyme labeling instrument with 570/630 nm double wavelength measurement. The cytotoxicity was estimated based on the percentage cell survival in a dose dependent manner relative to the negative control. The final IC50 (a drug concentration killing 50% cells) values were calculated by the Bliss method. All the tests were repeated in at least three independent experiments.

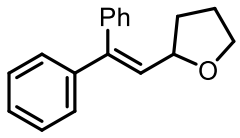
3. Characterization Data



(4a) 24.4mg, 70% yield, colorless oil. ^{1}H NMR (500 MHz, Chloroform-*d*): δ (ppm) = 7.42 – 7.35 (m, 2H), 7.34 – 7.28 (m, 2H), 7.25 – 7.19 (m, 1H), 6.58 (d, *J* = 15.9 Hz, 1H), 6.21 (dd, *J* = 15.9, 6.5 Hz, 1H), 4.58 – 4.35 (m, 1H), 4.11 – 3.91 (m, 1H), 3.89 – 3.79 (m, 1H), 2.21 – 2.06 (m, 1H), 2.02 – 1.90 (m, 2H), 1.77 – 1.67 (m, 1H). ^{13}C NMR (126 MHz, Chloroform-*d*): δ (ppm) = 136.87, 130.53, 130.47, 128.53, 128.53, 127.51, 126.48, 79.70, 68.21, 32.42, 25.94. These data are in accordance with the literature.[1]

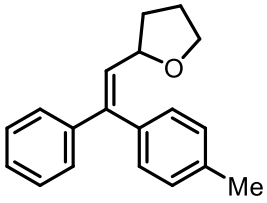


(4b) 25.3mg, 55% yield, colorless oil. ^{1}H NMR (500 MHz, Chloroform-*d*): δ (ppm) = 7.40 – 7.29 (m, 4H), 6.56 (d, *J* = 15.9 Hz, 1H), 6.16 (dd, *J* = 15.9, 6.6 Hz, 1H), 4.58 – 4.37 (m, 1H), 4.04 – 3.92 (m, 1H), 3.90 – 3.79 (m, 1H), 2.21 – 2.06 (m, 1H), 2.02 – 1.85 (m, 2H), 1.76 – 1.65 (m, 1H), 1.31 (s, 9H).. ^{13}C NMR (126 MHz, Chloroform-*d*): δ (ppm) = 150.60, 134.09, 130.23, 129.75, 126.18, 125.45, 79.81, 68.16, 34.57, 32.46, 31.30, 25.91. These data are in accordance with the literature.[3]

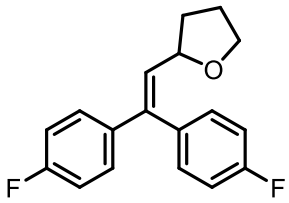


(4c) 36.5mg, 73% yield, colorless oil. ^{1}H NMR (500 MHz, Chloroform-*d*): δ (ppm) = 7.41 – 7.30 (m, 3H), 7.28 – 7.23 (m, 5H), 7.23 – 7.19 (m, 2H), 6.06 (d, *J* = 9.0 Hz, 1H), 4.36 – 4.20 (m, 1H), 4.05 – 3.88 (m, 1H), 3.84 – 3.67 (m, 1H), 2.12 – 1.94 (m, 2H), 1.92 – 1.82 (m, 1H), 1.82 – 1.69 (m, 1H).. ^{13}C NMR (126 MHz, Chloroform-*d*): δ (ppm) = 143.71, 142.01, 139.44, 129.99,

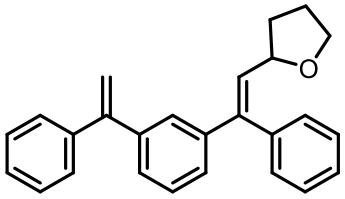
129.74, 128.12, 128.11, 127.63, 127.46, 127.36, 76.68, 68.13, 33.11, 26.46. These data are in accordance with the literature.[2]



(4d) 23.8mg, 45% yield, colorless oil. ^{1}H NMR (500 MHz, Chloroform-*d*): δ (ppm) = 7.39 – 7.29 (m, 1H), 7.28 – 7.22 (m, 3H), 7.23 – 7.05 (m, 5H), 6.08 – 5.99 (m, 1H), 4.40 – 4.17 (m, 1H), 4.02 – 3.88 (m, 1H), 3.79 – 3.68 (m, 1H), 2.38 (s, 3H), 2.32 (s, 1H), 2.09 – 1.95 (m, 2H), 1.90 – 1.81 (m, 1H), 1.79 – 1.69 (m, 1H). ^{13}C NMR (126 MHz, Chloroform-*d*): δ (ppm) = 143.75, 143.61, 142.26, 139.62, 139.20, 137.27, 137.05, 136.47, 129.98, 129.90, 129.51, 128.84, 128.79, 128.08, 128.06, 127.68, 127.52, 127.39, 127.28, 76.74, 68.09, 33.12, 26.46, 21.27, 21.11. These data are in accordance with the literature.[4]

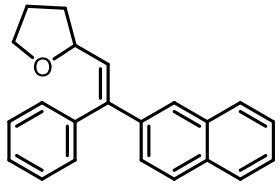


(4e) 28.6mg, 50% yield, colorless oil. ^{1}H NMR (500 MHz, Chloroform-*d*): δ (ppm) = 7.23 – 7.14 (m, 4H), 7.08 – 7.02 (m, 2H), 6.99 – 6.92 (m, 2H), 5.98 (d, *J* = 9.0 Hz, 1H), 4.43 – 4.14 (m, 1H), 4.07 – 3.88 (m, 1H), 3.78 – 3.70 (m, 1H), 2.10 – 1.96 (m, 2H), 1.94 – 1.83 (m, 1H), 1.78 – 1.66 (m, 1H). ^{13}C NMR (126 MHz, Chloroform-*d*) : δ (ppm) = 163.40, 163.23, 161.43, 161.27, 141.91, 138.00, 135.11, 131.60, 131.54, 129.92, 129.25, 129.19, 115.27, 115.14, 115.09, 114.97, 113.95, 76.52, 68.16, 33.06, 26.47. ^{19}F NMR (471 MHz, Chloroform-*d*): -114.52, -114.83. These data are in accordance with the literature.[4]

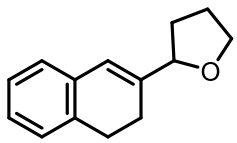


(4f) 28.8mg, 41% yield, colorless oil. ^{1}H NMR (500 MHz, Chloroform-*d*): δ (ppm) = 7.40 – 7.28 (m, 7H), 7.28 – 7.19 (m, 4H), 7.22 – 7.09 (m, 3H), 6.05 (dd, *J* = 9.0,

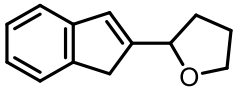
4.2 Hz, 1H), 5.59 – 5.30 (m, 2H), 4.43 – 4.22 (m, 1H), 4.05 – 3.89 (m, 1H), 3.77 – 3.68 (m, 1H), 2.17 – 1.82 (m, 3H), 1.79 – 1.62 (m, 1H).^{13}C NMR (126 MHz, Chloroform-*d*): δ (ppm) = 149.83, 143.33, 141.44, 139.24, 129.95, 129.93, 129.85, 129.40, 128.25, 128.17, 128.12, 128.09, 127.98, 127.75, 127.65, 127.47, 127.36, 127.20, 114.55, 113.87, 76.67, 68.13, 33.09, 33.05, 26.47. HRMS (ESI): $[M + H]^+$ Calcd. for $C_{26}H_{24}O$ 353.1900, Found: 353.1896.



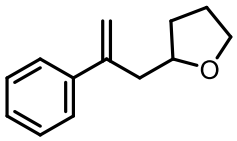
(4g) 37.2mg, 62% yield, colorless oil. ^{1}H NMR (500 MHz, Chloroform-*d*): δ (ppm) = 7.91 – 7.59 (m, 4H), 7.54 – 7.35 (m, 4H), 7.32 – 7.26 (m, 4H), 6.23 – 6.11 (m, 1H), 4.39 – 4.29 (m, 1H), 4.04 – 3.89 (m, 1H), 3.83 – 3.65 (m, 1H), 2.18 – 1.97 (m, 2H), 1.93 – 1.74 (m, 2H). ^{13}C NMR (126 MHz, Chloroform-*d*): δ (ppm) = 143.64, 141.86, 139.39, 136.94, 133.25, 133.11, 132.78, 132.65, 130.29, 130.15, 130.08, 128.84, 128.24, 128.18, 128.13, 127.71, 127.65, 127.54, 127.51, 127.47, 126.97, 126.18, 126.10, 126.07, 125.95, 125.54, 68.18, 68.13, 33.15, 26.50, 26.44. These data are in accordance with the literature.[5]



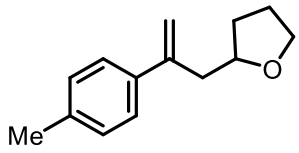
(4h) 14.8mg, 37% yield, colorless oil. ^{1}H NMR (500 MHz, Chloroform-*d*): δ (ppm) = 7.17 – 7.05 (m, 3H), 7.03 (d, *J* = 7.1 Hz, 1H), 6.45 (d, *J* = 1.5 Hz, 1H), 4.45 (t, *J* = 7.3 Hz, 1H), 4.08 – 3.94 (m, 1H), 3.94 – 3.82 (m, 1H), 2.83 (t, *J* = 8.1 Hz, 2H), 2.55 – 2.20 (m, 2H), 2.17 – 2.05 (m, 1H), 1.99 – 1.84 (m, 2H), 1.77 – 1.68 (m, 1H). ^{13}C NMR (126 MHz, Chloroform-*d*): 141.72, 135.13, 134.30, 129.74, 127.22, 126.64, 126.48, 126.02, 121.95, 113.85, 81.63, 68.61, 30.78, 28.08, 26.00, 23.37. These data are in accordance with the literature.[7]



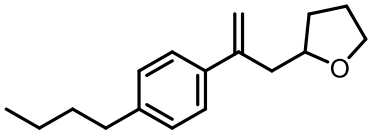
(4i) 23.1mg, 62% yield, colorless oil. ^{1}H NMR (500 MHz, Chloroform-*d*): δ (ppm) = 7.41 (d, *J* = 7.4 Hz, 1H), 7.31 (d, *J* = 7.4 Hz, 1H), 7.28 – 7.20 (m, 1H), 7.17 – 7.10 (m, 1H), 6.71 (s, 1H), 4.94 – 4.65 (m, 1H), 4.12 – 3.93 (m, 1H), 3.93 – 3.83 (m, 1H), 3.40 (s, 2H), 2.25 – 2.12 (m, 1H), 2.07 – 1.93 (m, 2H), 1.93 – 1.79 (m, 1H). ^{13}C NMR (126 MHz, Chloroform-*d*): 150.47, 144.72, 143.26, 126.72, 126.35, 124.30, 123.70, 120.70, 77.78, 68.24, 38.14, 32.18, 26.05. These data are in accordance with the literature.[6]



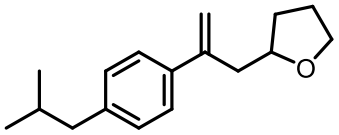
(4j) 13.2mg, 35% yield, colorless oil. ^{1}H NMR (500 MHz, Chloroform-*d*): δ (ppm) = 7.45 – 7.40 (m, 2H), 7.34 – 7.29 (m, 2H), 7.29 – 7.24 (m, 1H), 5.33 (d, *J* = 1.5 Hz, 1H), 5.15 (d, *J* = 1.4 Hz, 1H), 3.99 – 3.82 (m, 2H), 3.78 – 3.62 (m, 1H), 3.08 – 2.80 (m, 1H), 2.74 – 2.51 (m, 1H), 1.96 – 1.74 (m, 3H), 1.55 – 1.45 (m, 1H). ^{13}C NMR (126 MHz, Chloroform-*d*): 145.66, 141.08, 128.31, 127.46, 126.21, 114.27, 77.55, 67.84, 41.63, 31.14, 25.58. These data are in accordance with the literature.[1]



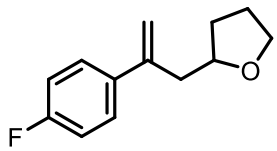
(4k) 22.6mg, 56% yield, colorless oil. ^{1}H NMR (500 MHz, Chloroform-*d*): δ (ppm) = 7.32 (d, *J* = 8.1 Hz, 2H), 7.17 – 6.93 (m, 2H), 5.31 (d, *J* = 1.6 Hz, 1H), 5.10 (d, *J* = 1.4 Hz, 1H), 4.04 – 3.81 (m, 2H), 3.72 – 3.60 (m, 1H), 3.04 – 2.77 (m, 1H), 2.69 – 2.51 (m, 1H), 2.34 (s, 3H), 2.00 – 1.78 (m, 3H), 1.53 – 1.41 (m, 1H). ^{13}C NMR (126 MHz, Chloroform-*d*): 145.41, 138.11, 137.22, 129.02, 126.07, 113.49, 77.60, 67.83, 41.62, 31.13, 25.58, 21.12. These data are in accordance with the literature.[7]



(4l) 23.9mg, 49% yield, colorless oil. ^{1}H NMR (500 MHz, Chloroform-*d*): δ (ppm) = 7.34 (d, *J* = 8.1 Hz, 2H), 7.16 – 7.09 (m, 2H), 5.31 (s, 1H), 5.10 (s, 1H), 4.07 – 3.83 (m, 2H), 3.79 – 3.65 (m, 1H), 2.87 (dd, *J* = 14.2, 6.3 Hz, 1H), 2.75 – 2.48 (m, 3H), 1.91 – 1.87 (m, 2H), 1.85 – 1.79 (m, 1H), 1.61 – 1.55 (m, 2H), 1.55 – 1.46 (m, 1H), 1.46 – 1.31 (m, 2H), 0.93 (t, *J* = 7.3 Hz, 3H).^{13}C NMR (126 MHz, Chloroform-*d*): 145.40, 142.27, 138.25, 128.35, 126.01, 113.44, 77.59, 67.83, 41.61, 35.30, 33.59, 31.13, 25.58, 22.41, 13.98. HRMS (ESI): $[M + H]^+$ Calcd. for $C_{17}H_{24}O$ 245.1900, Found: 245.1905.

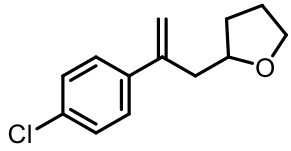


(4m) 21.5mg, 44% yield, colorless oil. ^{1}H NMR (500 MHz, Chloroform-*d*): δ (ppm) = 7.34 (d, *J* = 8.2 Hz, 2H), 7.09 (d, *J* = 8.3 Hz, 2H), 5.33 (d, *J* = 1.6 Hz, 1H), 5.11 (d, *J* = 1.5 Hz, 1H), 4.18 – 3.80 (m, 2H), 3.80 – 3.62 (m, 1H), 3.09 – 2.82 (m, 1H), 2.70 – 2.55 (m, 1H), 2.46 (d, *J* = 7.2 Hz, 2H), 2.03 – 1.79 (m, 4H), 1.57 – 1.45 (m, 1H), 0.90 (d, *J* = 6.6 Hz, 6H).^{13}C NMR (126 MHz, Chloroform-*d*): 145.39, 141.07, 138.26, 129.05, 125.85, 113.42, 77.61, 67.83, 45.08, 41.60, 31.13, 30.21, 25.58, 22.41. HRMS (ESI): $[M + H]^+$, Calcd. for $C_{17}H_{24}O$ 245.1900, Found: 245.1901.

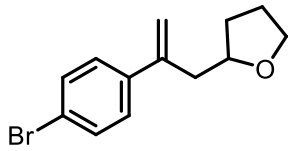


(4n) 14.8mg, 36% yield, colorless oil. ^{1}H NMR (500 MHz, Chloroform-*d*): δ (ppm) = 7.52 – 7.32 (m, 2H), 7.10 – 6.79 (m, 2H), 5.28 (s, 1H), 5.14 (s, 1H), 4.08 – 3.83 (m, 2H), 3.77 – 3.56 (m, 1H), 2.83 (dd, *J* = 14.4, 6.6 Hz, 1H), 2.58 (dd, *J* = 14.4, 6.7 Hz, 1H), 1.97 – 1.69 (m, 3H), 1.53 – 1.43 (m, 1H).^{13}C NMR (126 MHz, Chloroform-*d*): 163.29, 161.33, 144.68, 137.15, 137.13, 127.79 (d, *J* = 7.9 Hz), 115.20, 115.03, 114.22, 77.48, 67.86, 41.74, 31.16, 25.57.

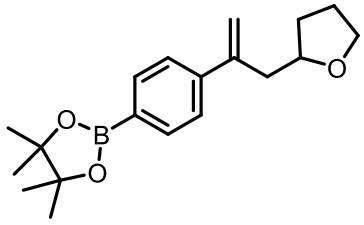
^{19}F NMR (471 MHz, Chloroform-*d*): -115.29. These data are in accordance with the literature.[8]



(4o) 33.7mg, 76% yield, colorless oil. ^{1}H NMR (500 MHz, Chloroform-*d*): δ (ppm) = 7.35 (d, *J* = 8.5 Hz, 2H), 7.32 – 7.12 (m, 2H), 5.32 (s, 1H), 5.17 (s, 1H), 4.18 – 3.82 (m, 2H), 3.77 – 3.46 (m, 1H), 3.08 – 2.67 (m, 1H), 2.67 – 2.46 (m, 1H), 2.01 – 1.85 (m, 2H), 1.85 – 1.76 (m, 1H), 1.61 – 1.39 (m, 1H). ^{13}C NMR (126 MHz, Chloroform-*d*): 144.59, 139.54, 133.24, 128.45, 127.53, 114.80, 77.45, 67.87, 41.52, 31.18, 25.57. These data are in accordance with the literature.[8]

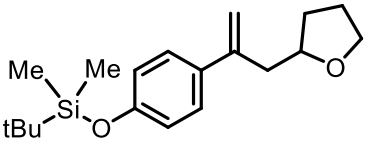


(4p) 41.5mg, 78% yield, colorless oil. ^{1}H NMR (500 MHz, Chloroform-*d*): δ (ppm) = 7.63 – 7.38 (m, 2H), 7.29 (d, *J* = 8.5 Hz, 2H), 5.33 (d, *J* = 1.3 Hz, 1H), 5.17 (d, *J* = 1.4 Hz, 1H), 4.06 – 3.79 (m, 2H), 3.77 – 3.58 (m, 1H), 3.03 – 2.74 (m, 1H), 2.65 – 2.42 (m, 1H), 2.01 – 1.79 (m, 2H), 1.84 – 1.72 (m, 1H), 1.58 – 1.43 (m, 1H). ^{13}C NMR (126 MHz, Chloroform-*d*): 144.65, 140.02, 131.41, 127.88, 121.40, 114.88, 77.45, 67.87, 41.47, 31.17, 25.57. These data are in accordance with the literature.[8]

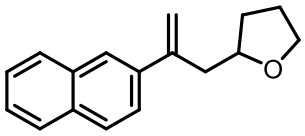


(4q) 44.6mg, 71% yield, yellow oil. ^{1}H NMR (500 MHz, Chloroform-*d*): δ (ppm) = 7.77 (d, *J* = 7.8 Hz, 2H), 7.42 (d, *J* = 8.1 Hz, 2H), 5.38 (d, *J* = 1.5 Hz, 1H), 5.18 (d, *J* = 1.5 Hz, 1H), 4.04 – 3.77 (m, 2H), 3.75 – 3.56 (m, 1H), 2.89 (dd, *J* = 14.3, 6.4 Hz, 1H), 2.60 (dd, *J* = 14.3, 7.0 Hz, 1H), 1.94 – 1.77 (m, 2H), 1.83 – 1.76 (m, 1H), 1.54 – 1.45 (m, 1H), 1.34 (s, 12H). ^{13}C NMR (126 MHz, Chloroform-*d*): 145.63,

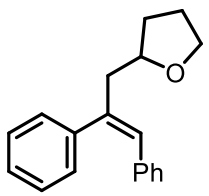
143.86, 134.83, 125.55, 114.98, 103.73, 100.68, 83.78, 77.53, 67.82, 41.45, 31.10, 25.56, 24.87, 24.26, 22.09. HRMS (ESI): $[M + H]^+$, Calcd. for $C_{19}H_{27}BO_3$ 315.2126, Found: 315.2122.



(4r) 38.8mg, 61% yield, colorless oil. ^{1}H NMR (500 MHz, Chloroform-*d*): δ (ppm) = 7.10 (d, *J* = 8.6 Hz, 2H), 6.58 (d, *J* = 8.6 Hz, 2H), 5.07 (d, *J* = 1.6 Hz, 1H), 4.86 (d, *J* = 1.4 Hz, 1H), 3.83 – 3.64 (m, 2H), 3.59 – 3.39 (m, 1H), 2.64 (dd, *J* = 14.3, 6.3 Hz, 1H), 2.35 (dd, *J* = 14.3, 7.0 Hz, 1H), 1.77 – 1.57 (m, 2H), 1.64 – 1.55 (m, 1H), 1.37 (s, 6H), 1.35 – 1.26 (m, 1H), 0.78 (s, 9H).^{13}C NMR (126 MHz, Chloroform-*d*): 155.23, 144.98, 133.97, 127.19, 119.78, 112.68, 77.64, 67.82, 41.65, 31.12, 25.69, 25.58, 18.22, -4.39. HRMS (ESI): $[M + H]^+$, Calcd. for $C_{19}H_{30}O_2Si$ 319.2088, Found: 319.2090.

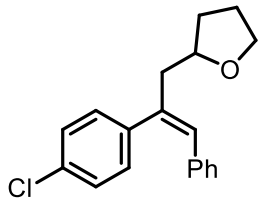


(4s) 33.8mg, 71% yield, colorless oil. ^{1}H NMR (500 MHz, Chloroform-*d*): δ (ppm) = 8.08 – 7.73 (m, 4H), 7.59 (dd, *J* = 8.6, 1.9 Hz, 1H), 7.57 – 7.38 (m, 2H), 5.49 (d, *J* = 1.4 Hz, 1H), 5.26 (d, *J* = 1.4 Hz, 1H), 4.13 – 3.96 (m, 1H), 3.96 – 3.83 (m, 1H), 3.83 – 3.58 (m, 1H), 3.01 (dd, *J* = 14.2, 6.4 Hz, 1H), 2.71 (dd, *J* = 14.5, 7.1 Hz, 1H), 2.12 – 1.74 (m, 2H), 1.84 – 1.71 (m, 1H), 1.56 – 1.51 (m, 1H). ^{13}C NMR (126 MHz, Chloroform-*d*): 145.45, 138.27, 133.36, 132.83, 128.19, 127.87, 127.54, 126.16, 125.87, 124.83, 124.70, 114.85, 77.61, 67.87, 41.64, 31.17, 25.59. These data are in accordance with the literature.[7]

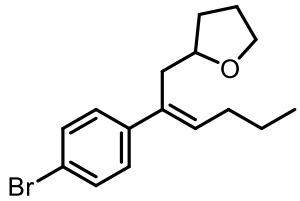


(4t) 29.6mg, 56% yield, colorless oil. ^{1}H NMR (500 MHz, Chloroform-*d*): δ (ppm) = 7.51 – 7.45 (m, 2H), 7.42 (d, *J* = 7.2 Hz, 2H), 7.39 – 7.33 (m, 4H), 7.32 – 7.21 (m, 2H), 6.77 (s, 1H), 3.93 –

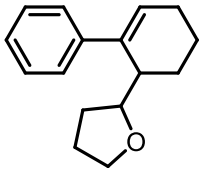
3.85 (m, 1H), 3.84 – 3.76 (m, 1H), 3.71 – 3.60 (m, 1H), 3.11 (dd, *J* = 14.0, 6.9 Hz, 1H), 2.84 (dd, *J* = 14.0, 6.6 Hz, 1H), 1.91 – 1.72 (m, 3H), 1.42 – 1.34 (m, 1H)..^{13}C NMR (126 MHz, Chloroform-*d*): 143.05, 139.97, 137.98, 130.39, 129.04, 128.40, 128.26, 127.26, 126.83, 126.67, 113.86, 77.74, 67.74, 36.08, 31.26, 25.69. These data are in accordance with the literature.[9]



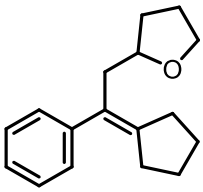
(4u) 31.6mg, 53% yield, colorless oil. ^{1}H NMR (500 MHz, Chloroform-*d*): δ (ppm) = 7.46 – 7.30 (m, 8H), 7.28 – 7.23 (m, 1H), 6.76 (s, 1H), 3.94 – 3.75 (m, 2H), 3.70 – 3.61 (m, 1H), 3.06 (dd, *J* = 14.1, 7.2 Hz, 1H), 2.81 (dd, *J* = 14.1, 6.3 Hz, 1H), 1.87 – 1.70 (m, 3H), 1.44 – 1.32 (m, 1H). ^{13}C NMR (126 MHz, Chloroform-*d*): 141.51, 138.89, 137.64, 132.99, 130.79, 129.74, 129.00, 128.52, 128.29, 128.13, 126.85, 77.61, 67.76, 36.03, 31.31, 25.66. These data are in accordance with the literature.[9]



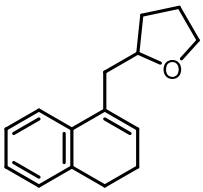
(4v) 27.7mg, 45% yield, colorless oil. ^{1}H NMR (500 MHz, Chloroform-*d*): δ (ppm) = 7.41 (d, *J* = 8.5 Hz, 2H), 7.22 (d, *J* = 8.5 Hz, 2H), 5.71 (t, *J* = 7.3 Hz, 1H), 3.90 – 3.73 (m, 2H), 3.73 – 3.60 (m, 1H), 2.85 (dd, *J* = 13.8, 6.1 Hz, 1H), 2.61 (dd, *J* = 13.8, 7.5 Hz, 1H), 2.20 (q, *J* = 7.4 Hz, 2H), 1.93 – 1.82 (m, 1H), 1.81 – 1.74 (m, 2H), 1.51 – 1.43 (m, 2H), 1.42 – 1.31 (m, 1H), 0.96 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*): 142.34, 136.05, 131.84, 131.26, 128.20, 120.39, 78.03, 67.70, 35.61, 31.01, 30.92, 25.62, 22.92, 13.96. HRMS (ESI): $[M + H]^+$, Calcd. for $C_{16}H_{21}BrO$ 309.0849, Found: 309.0856.



(4w) 14.6mg, 32% yield, colorless oil. ^{1}H NMR (500 MHz, Chloroform-*d*): δ (ppm) = 7.33 – 7.23 (m, 4H), 7.23 – 7.16 (m, 1H), 5.99 – 5.79 (m, 1H), 4.14 – 3.43 (m, 3H), 2.96 – 2.69 (m, 1H), 2.28 – 2.01 (m, 3H), 1.82 – 1.65 (m, 4H), 1.58 – 1.37 (m, 2H), 1.40 – 1.16 (m, 1H). ^{13}C NMR (126 MHz, Chloroform-*d*): 144.06, 143.25, 139.78, 139.63, 129.19, 128.78, 128.09, 128.08, 126.71, 126.40, 126.37, 126.31, 80.64, 80.55, 68.30, 67.42, 40.55, 39.44, 30.17, 26.20, 26.19, 26.14, 26.01, 24.45, 23.05, 20.60, 18.54. HRMS (ESI): [M + H]$^{+}$ Calcd. for $C_{16}H_{20}O$ 229.1587, Found: 229.1592.

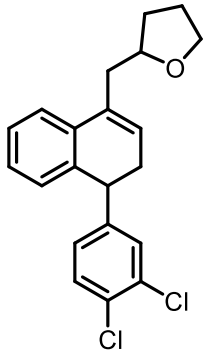


(4x) 34.9mg, 72% yield, colorless oil. ^{1}H NMR (500 MHz, Chloroform-*d*): δ (ppm) = 7.36 – 7.25 (m, 2H), 7.23 – 7.12 (m, 3H), 3.88 – 3.79 (m, 1H), 3.76 – 3.70 (m, 1H), 3.68 – 3.58 (m, 1H), 2.88 – 2.70 (m, 1H), 2.56 – 2.32 (m, 3H), 2.24 – 2.08 (m, 2H), 1.92 – 1.77 (m, 3H), 1.74 – 1.67 (m, 2H), 1.60 – 1.51 (m, 2H), 1.42 – 1.35 (m, 1H).^{13}C NMR (126 MHz, Chloroform-*d*): 143.57, 142.22, 128.71, 128.42, 127.95, 125.90, 78.09, 67.58, 41.05, 32.53, 31.04, 26.89, 26.41, 25.69. HRMS (ESI): [M + H]$^{+}$, Calcd. for $C_{17}H_{22}O$ 243.1743, Found: 243.1739.

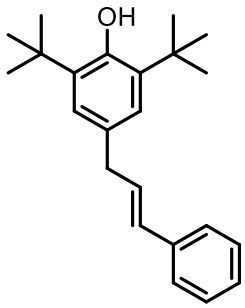


(4y) 26.9mg, 63% yield, colorless oil. ^{1}H NMR (500 MHz, Chloroform-*d*): δ (ppm) = 7.29 (d, *J* = 7.6 Hz, 1H), 7.21 – 7.16 (m, 1H), 7.18 – 7.03 (m, 2H), 5.94 (t, *J* = 4.5 Hz, 1H), 4.15 – 4.04 (m, 1H), 3.96 – 3.86 (m, 1H), 3.76 – 3.66 (m, 1H), 3.03 – 2.81 (m, 1H), 2.81 – 2.68 (m, 2H), 2.63 – 2.43 (m, 1H), 2.41 – 2.20 (m, 2H), 2.00 – 1.89 (m, 2H), 1.88 – 1.78 (m, 1H), 1.62 – 1.49 (m, 1H). ^{13}C NMR (126 MHz, Chloroform-*d*): 136.70, 134.80, 133.70,

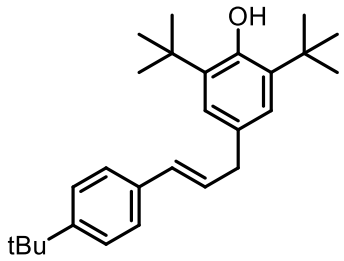
129.74, 127.62, 126.74, 126.70, 126.32, 122.74, 113.85, 77.69, 67.90, 38.98, 31.36, 28.36, 25.57, 23.16. These data are in accordance with the literature.[10]



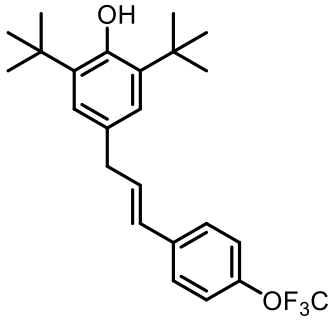
(4z) 56.6mg, 79% yield, colorless oil. ^{1}H NMR (500 MHz, Chloroform-*d*): δ (ppm) = 7.59 – 7.37 (m, 2H), 7.35 – 7.26 (m, 2H), 7.17 – 7.10 (m, 1H), 7.08 – 6.96 (m, 1H), 6.94 – 6.80 (m, 1H), 5.84 (m, 1H), 4.22 – 3.87 (m, 3H), 3.80 – 3.63 (m, 1H), 3.10 – 2.79 (m, 1H), 2.75 – 2.37 (m, 3H), 2.04 – 1.80 (m, 3H), 1.60 – 1.36 (m, 1H).^{13}C NMR (126 MHz, Chloroform-*d*): 144.77, 144.68, 137.66, 137.30, 134.60, 134.48, 132.26, 132.19, 131.92, 130.35, 130.25, 130.20, 130.17, 129.56, 128.41, 128.16, 127.91, 127.77, 127.42, 127.33, 127.30, 127.14, 126.71, 126.61, 126.04, 125.98, 125.86, 124.42, 124.40, 123.41, 123.35, 113.63, 77.58, 77.56, 67.92, 43.41, 42.93, 39.21, 38.84, 31.54, 31.46, 31.36, 31.32, 31.26, 25.66, 25.60, 25.57. HRMS (ESI): $[M + H]^+$ Calcd. for $C_{20}H_{20}Cl_2O$ 359.0964, Found: 359.0970.



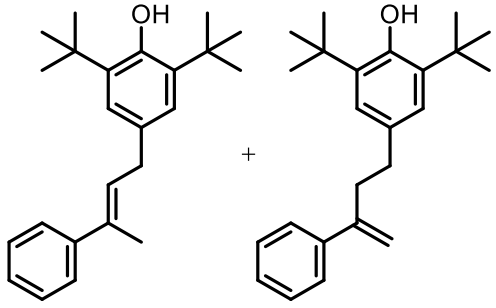
(7a) 41.2mg, 64% yield, yellow oil. ^{1}H NMR (500 MHz, Chloroform-*d*): δ (ppm) = 7.37 (d, *J* = 7.3 Hz, 2H), 7.29 (t, *J* = 7.6 Hz, 2H), 7.20 (t, *J* = 7.3 Hz, 1H), 7.04 (s, 2H), 6.51 – 6.43 (m, 1H), 6.41 – 6.29 (m, 1H), 5.08 (s, 1H), 3.47 (d, *J* = 6.8 Hz, 2H), 1.44 (s, 18H).^{13}C NMR (126 MHz, Chloroform-*d*): 152.17, 137.76, 135.95, 130.72, 130.41, 130.19, 128.48, 126.94, 126.14, 125.16, 39.42, 34.34, 30.33. HRMS (ESI): $[M + H]^+$ Calcd. for $C_{23}H_{30}O$ 323.2369, Found: 323.2375.



(7b) 43.1mg, 57% yield, yellow oil. ^{1}H NMR (500 MHz, Chloroform-*d*): δ (ppm) = 7.37 – 7.29 (m, 4H), 7.03 (s, 2H), 6.50 – 6.41 (m, 1H), 6.36 – 6.24 (m, 1H), 5.08 (s, 1H), 3.46 (d, *J* = 7.0 Hz, 2H), 1.43 (s, 18H), 1.31 (s, 9H).^{13}C NMR (126 MHz, Chloroform-*d*): 150.11, 135.90, 135.01, 130.91, 130.16, 129.37, 125.84, 125.40, 125.15, 77.28, 77.03, 76.77, 39.44, 34.33, 31.32, 30.33. HRMS (ESI): $[M + H]^+$ Calcd. for $C_{27}H_{38}O$ 379.2995, Found: 379.3001.

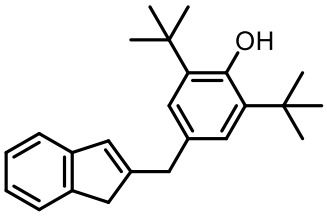


(7c) 44.7mg, 55% yield, yellow oil. ^{1}H NMR (500 MHz, Chloroform-*d*): δ (ppm) = 7.37 (d, *J* = 8.7 Hz, 2H), 7.18 – 7.10 (m, 2H), 7.02 (s, 2H), 6.44 (d, *J* = 15.8 Hz, 1H), 6.41 – 6.24 (m, 1H), 5.10 (s, 1H), 3.46 (dd, *J* = 6.8, 1.3 Hz, 2H), 1.44 (s, 18H). ^{13}C NMR (126 MHz, Chloroform-*d*) : 152.25, 136.53, 136.02, 131.36, 130.37, 128.94, 127.28, 125.15, 121.04, 39.38, 34.35, 30.31. ^{19}F NMR (471 MHz, Chloroform-*d*): -57.88. HRMS (ESI): $[M + H]^+$ Calcd. for $C_{24}H_{29}F_3O_2$ 407.2192, Found: 407.2197.

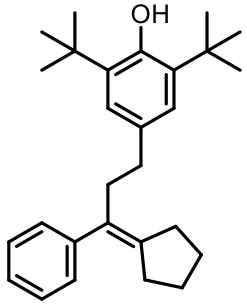


(7d) 35.6mg, 53% yield, yellow oil. ^{1}H NMR (500 MHz, Chloroform-*d*): δ (ppm) = 7.45 – 7.38 (m, 4H), 7.37 – 7.18 (m, 7H), 7.04 (s, 2H), 6.97 (s, 2H), 6.05 – 5.86 (m, 1H), 5.30 (d, *J* = 1.4 Hz, 1H), 5.10 (d, *J* = 1.4 Hz, 1H), 5.06 (s, 1H), 5.04 (s, 1H), 3.52 – 3.42 (m, 2H), 2.86 – 2.75 (m, 2H), 2.74 – 2.66 (m, 2H), 2.18 – 2.05 (m, 3H), 1.43 (d, *J* = 2.7 Hz, 36H). ^{13}C NMR (126 MHz, Chloroform-*d*): 152.01, 151.87, 148.36, 143.92, 141.38,

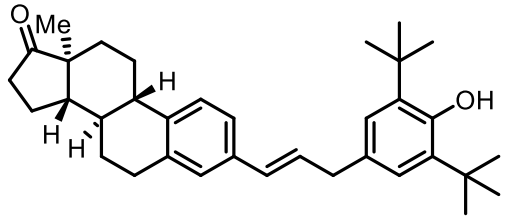
135.93, 135.71, 135.13, 132.55, 131.45, 128.32, 128.19, 127.70, 127.37, 126.62, 126.17, 125.77, 124.96, 124.87, 112.34, 37.49, 34.83, 34.67, 34.35, 34.33, 30.37, 30.34, 16.01. HRMS (ESI): $[M + H]^+$, Calcd. for $C_{24}H_{32}O$ 337.2526, Found: 337.2533.



(7e) 46.8mg, 70% yield, yellow oil. ^{1}H NMR (500 MHz, Chloroform-*d*): δ (ppm) = 7.35 (d, *J* = 7.4 Hz, 1H), 7.26 (t, *J* = 7.1 Hz, 1H), 7.20 (t, *J* = 7.4 Hz, 1H), 7.14 – 7.06 (m, 1H), 7.02 (s, 2H), 6.48 (s, 1H), 5.07 (s, 1H), 3.71 (s, 2H), 3.29 (s, 2H), 1.43 (s, 18H). ^{13}C NMR (126 MHz, Chloroform-*d*): 152.14, 150.43, 145.60, 143.51, 135.90, 130.60, 127.14, 126.23, 125.37, 123.69, 123.48, 120.12, 40.95, 37.98, 34.33, 30.38. HRMS (ESI): $[M + H]^+$, Calcd. for $C_{24}H_{30}O$ 335.2369, Found: 335.2372.

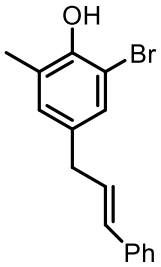


(7f) 39.8mg, 51% yield, yellow oil. ^{1}H NMR (500 MHz, Chloroform-*d*): δ (ppm) = 7.35 – 7.26 (m, 2H), 7.23 – 7.17 (m, 3H), 6.93 (s, 2H), 5.00 (s, 1H), 2.65 (t, *J* = 7.8 Hz, 2H), 2.54 – 2.46 (m, 2H), 2.21 (t, *J* = 7.2 Hz, 2H), 2.13 (t, *J* = 7.0 Hz, 2H), 1.68 – 1.59 (m, 2H), 1.56 – 1.48 (m, 2H), 1.42 (s, 18H).^{13}C NMR (126 MHz, Chloroform-*d*): 151.70, 143.72, 140.77, 135.52, 132.99, 131.14, 128.54, 128.23, 128.02, 127.92, 125.82, 124.94, 124.91, 123.80, 37.25, 34.28, 34.12, 32.50, 30.52, 30.39, 27.00, 26.45. HRMS (ESI): $[M + H]^+$, Calcd. for $C_{28}H_{38}O$ 391.2995, Found: 391.2997.

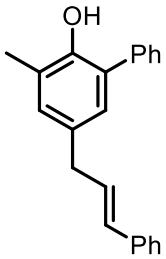


(7g) 42.8mg, 43% yield, yellow oil. ^{1}H NMR (500 MHz, Chloroform-*d*): δ (ppm) = 7.23 (d, *J* = 8.1 Hz, 1H), 7.19 – 7.14 (m, 1H), 7.11 (s, 1H), 7.03 (s, 2H), 6.41 (d, *J* = 15.7 Hz, 1H), 6.36 – 6.24 (m, 1H), 5.08 (s, 1H),

3.98 – 3.79 (m, 1H), 3.74 – 3.69 (m, 2H), 3.45 (d, *J* = 6.8 Hz, 2H), 2.95 – 2.83 (m, 1H), 2.62 – 2.46 (m, 1H), 2.45 – 2.37 (m, 1H), 2.30 (d, *J* = 6.6 Hz, 1H), 2.01 – 1.94 (m, 2H), 1.86 (t, *J* = 5.7 Hz, 1H), 1.56 – 1.47 (m, 4H), 1.43 (s, 18H), 1.30 (d, *J* = 2.9 Hz, 1H), 0.91 (s, 3H).^{13}C NMR (126 MHz, Chloroform-*d*): 152.15, 138.60, 136.50, 135.91, 135.39, 130.85, 130.04, 129.59, 126.78, 125.50, 125.17, 123.60, 77.29, 77.03, 76.78, 50.51, 48.02, 44.44, 39.46, 38.21, 35.89, 34.34, 31.61, 30.40, 30.33, 29.41, 26.54, 25.74, 21.61, 14.22, 13.86. HRMS (ESI): $[M + H]^+$, Calcd. for $C_{35}H_{46}O_2$ 499.3571, Found: 499.3574.

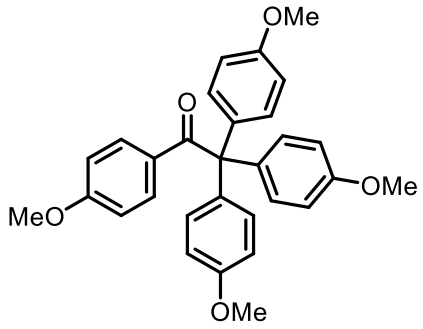


(7h) 33.2mg, 55% yield, yellow oil. ^{1}H NMR (500 MHz, Chloroform-*d*): δ (ppm) = 7.39 – 7.33 (m, 2H), 7.33 – 7.27 (m, 2H), 7.25 – 7.18 (m, 1H), 7.16 (d, *J* = 2.1 Hz, 1H), 6.95 – 6.86 (m, 1H), 6.49 – 6.38 (m, 1H), 6.35 – 6.18 (m, 1H), 5.45 (s, 1H), 3.69 – 3.25 (m, 2H), 2.27 (s, 3H).^{13}C NMR (126 MHz, Chloroform-*d*): 148.77, 137.32, 133.10, 131.20, 130.76, 129.12, 128.90, 128.55, 127.24, 126.17, 125.74, 110.01, 38.19, 16.68. HRMS (ESI): $[M + H]^+$, Calcd. for $C_{16}H_{15}BrO$ 303.0379, Found: 303.0384.



(7i) 27.6mg, 46% yield, yellow oil. ^{1}H NMR (500 MHz, Chloroform-*d*): δ (ppm) =7.53 – 7.42 (m, 4H), 7.40 – 7.34 (m, 3H), 7.32 – 7.27 (m, 2H), 7.23 – 7.11 (m, 1H), 7.02 (d, *J* = 2.3 Hz, 1H), 6.94 (d, *J* = 2.3 Hz, 1H), 6.57 – 6.42 (m, 1H), 6.42 – 6.31 (m, 1H), 5.17 (s, 1H), 3.48 (dd, *J* = 6.9, 1.3 Hz, 2H), 2.29 (s, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*): 148.99, 137.54, 137.43, 131.74, 130.73, 129.67, 129.33, 129.16, 128.50, 127.84, 127.77, 127.06,

126.15, 38.61, 16.23. HRMS (ESI): $[M + H]^+$, Calcd. for $C_{22}H_{20}O$ 301.1587, Found: 301.1591.



(5a) White solid. ^{1}H NMR (500 MHz, Chloroform-*d*): δ (ppm) = 7.68 (d, *J* = 9.1 Hz, 2H), 7.10 (d, *J* = 8.9 Hz, 6H), 6.77 (d, *J* = 8.9 Hz, 6H), 6.65 (d, *J* = 9.0 Hz, 2H), 3.76 (s, 9H), 3.75 (s, 3H).^{13}C NMR (126 MHz, Chloroform-*d*): 197.81, 162.05, 157.89, 136.09, 133.55, 131.76, 130.19, 113.05, 112.82, 68.89, 55.28, 55.17. HRMS (ESI): $[M + H]^+$, Calcd. for $C_{30}H_{28}O_5$ 469.2010, Found: 469.2013.

4. References

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[2] L. Chen, K. Jiang, G. Zeng and B. Yin, *Org. Lett.*, **2022**, *24*, 9071−9075.

[3] Z.-Q. Song, Z. Liu, Q.-C. Gan, T. Lei, C.-H. Tung and L.-Z. Wu, *Org. Lett.*, **2020**, *22*, 832−836.

[4] C. Pan, H. Zhang, C. Zhu, *Tetrahedron Letters* **2016**, *57*, 595-598.

[5] D.-L. Kong, *Org. Biomol. Chem.*, **2016**, *14*, 2210-2217.

[6] S. Xu, Y. Ping, W. Li, H. Guo, M. Wang, W. Kong, *J. Am. Chem. Soc.*, **2023**, *145*, 5231 – 5241.

[7] D. Liu, C. Liu, H. Li and A. Lei, *Chem. Commun.*, **2014**, *50*, 3623-3626.

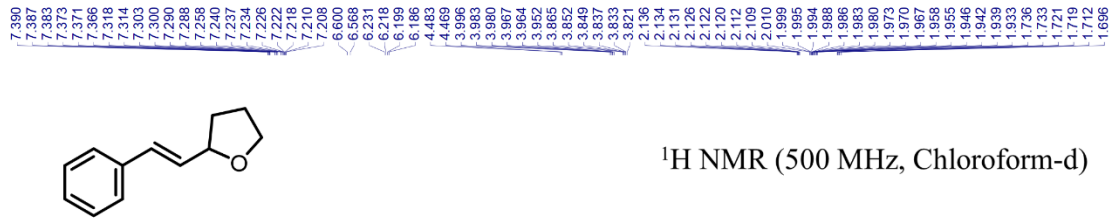
[8] M. S. Ahmad, Z. Shafiq, K. Meguellati, *Tetrahedron* **2022**, *110*, 132704.

[9] Franz-Lucas et al., *Angew. Chem., Int. Ed.*, **2023**, 62, e202304084

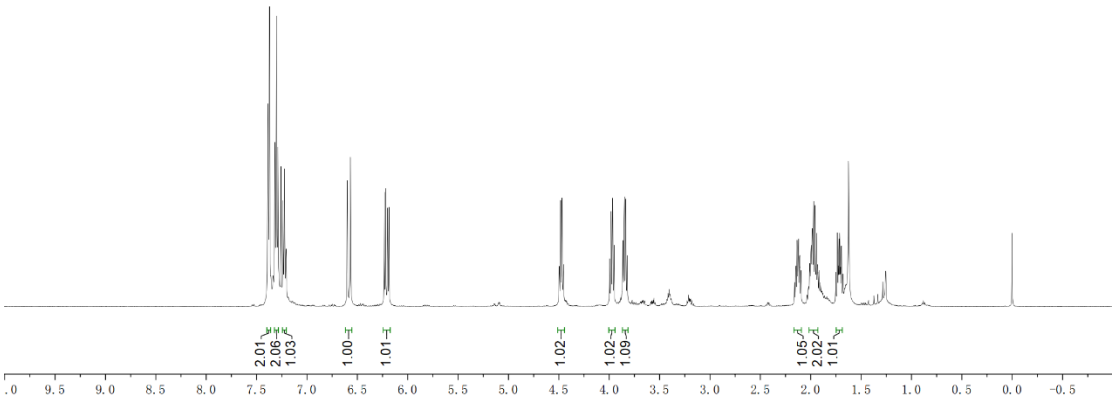
[10] C.-Y. Huang, J. Li, W. Liu, C.-J. Li, *Chem. Sci.*, **2019**, *10*, 5018-5024.

5. NMR Spectra of Products

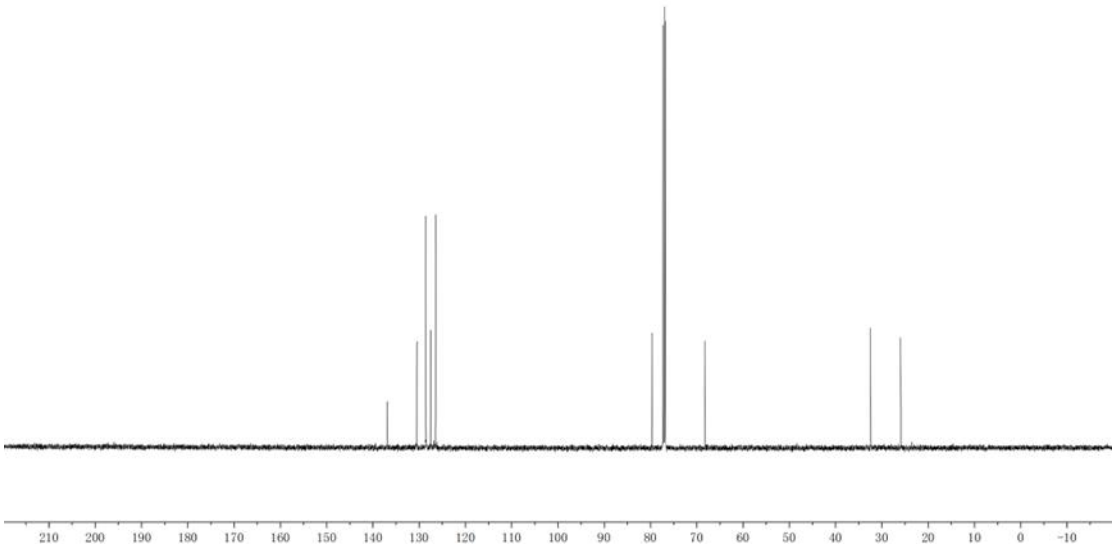
Compound **4a**



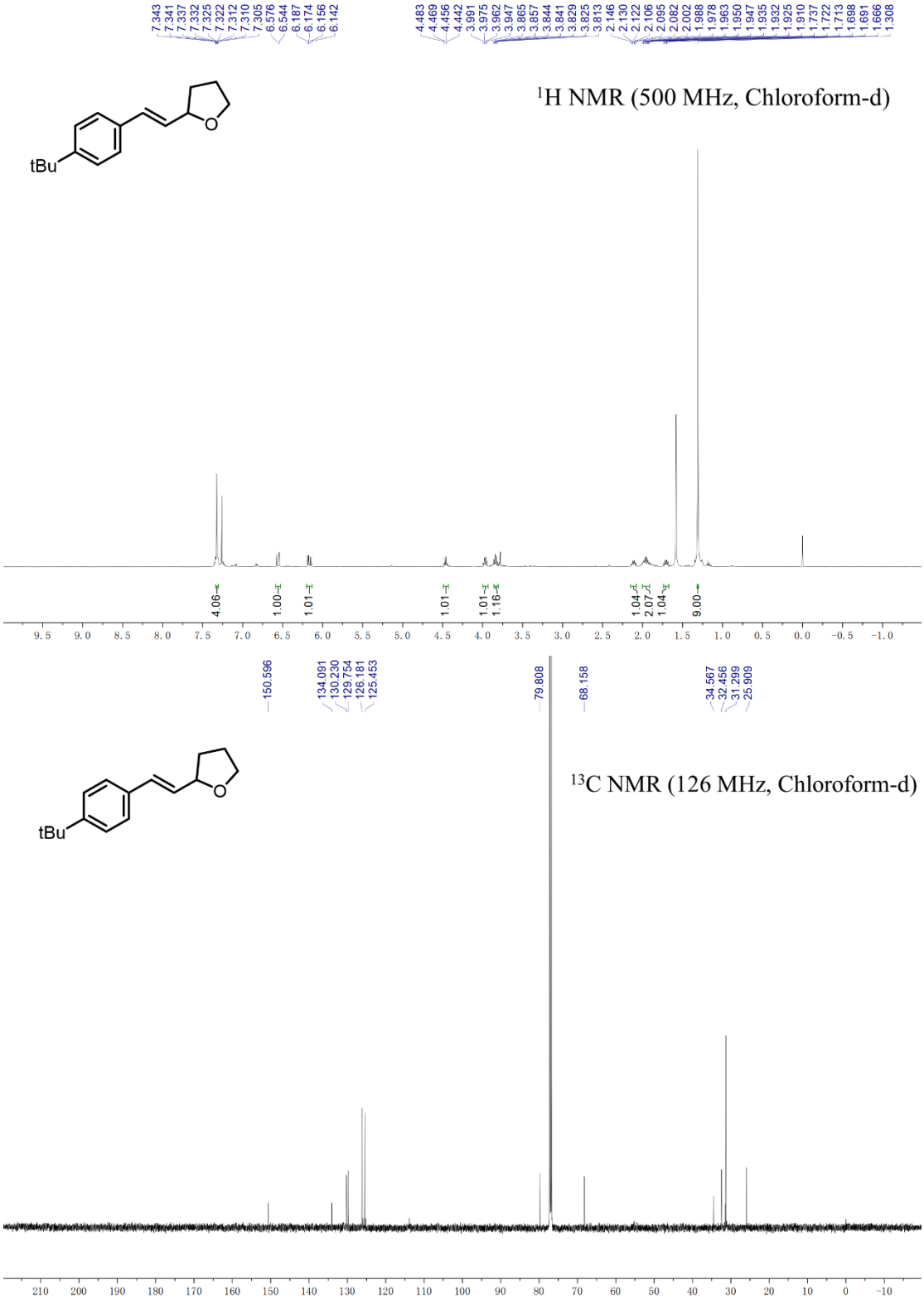
^{1}H NMR (500 MHz, Chloroform-d)



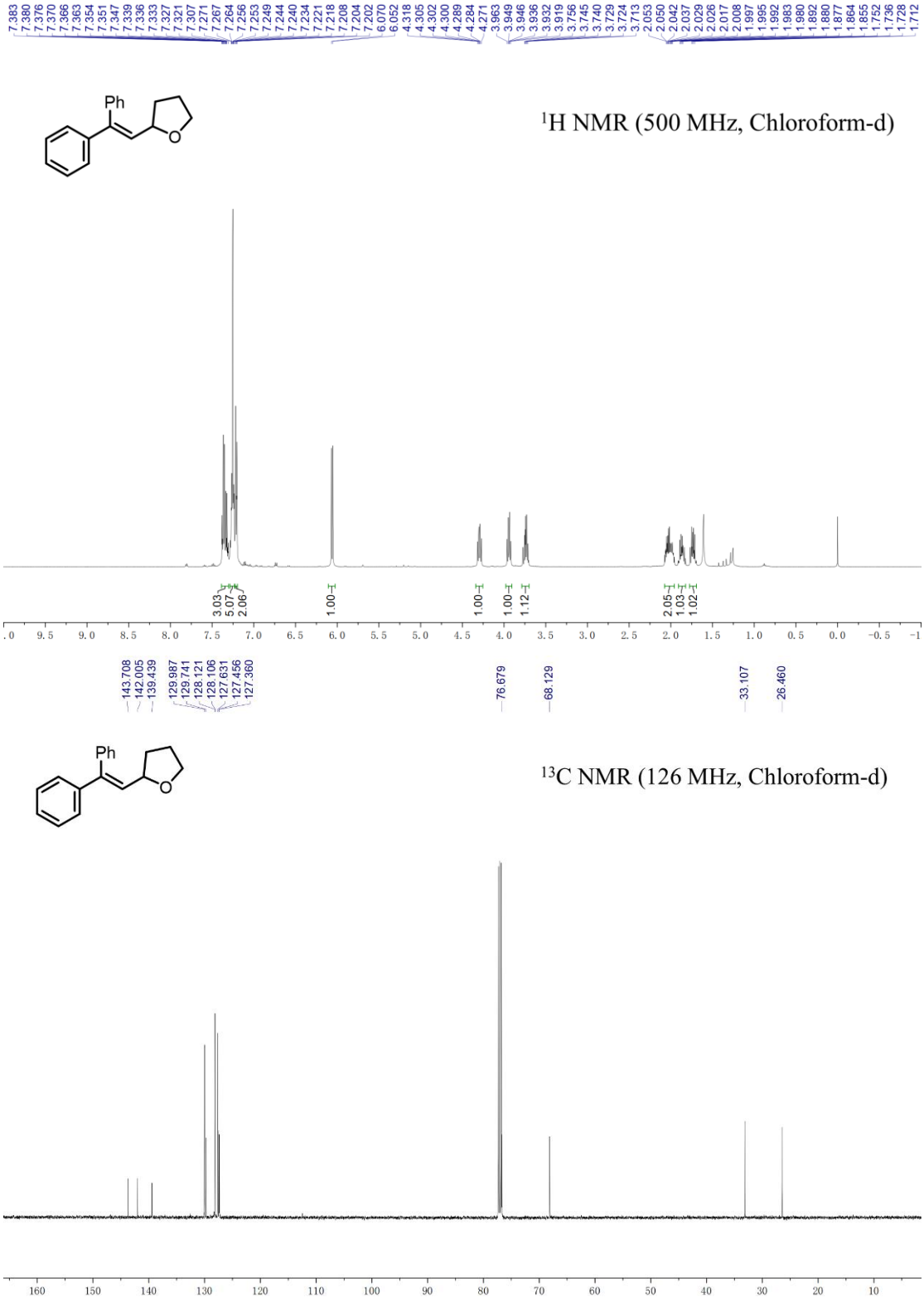
^{13}C NMR (126 MHz, Chloroform-d)



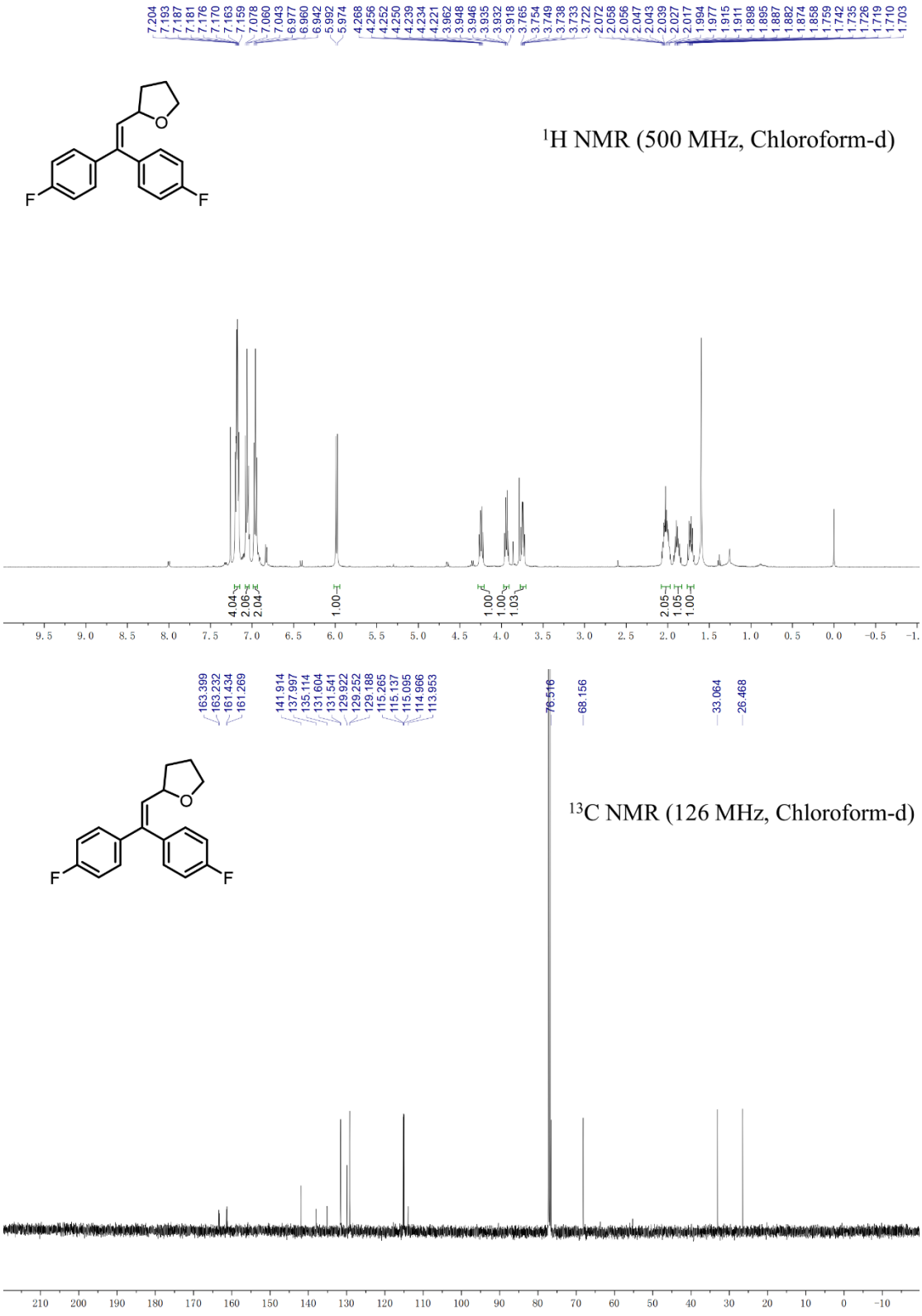
Compound **4b**

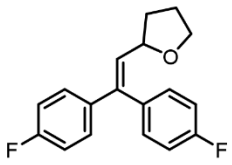

7.343
7.341
7.337
7.332
7.325
7.322
7.312
7.310
7.305
6.576
6.544
6.187
6.174
6.156
6.142
4.483
4.469
4.456
4.442
3.991
3.975
3.962
3.947
3.865
3.857
3.844
3.841
3.829
3.825
3.813
2.146
2.130
2.122
2.106
2.095
2.082
2.002
1.988
1.978
1.963
1.950
1.947
1.935
1.932
1.925
1.910
1.737
1.722
1.713
1.698
1.691
1.666
1.308
tBu
^{1}H NMR (500 MHz, Chloroform-d)
4.06
1.00
1.01
1.01
1.01
1.16
1.04
2.07
1.04
9.00
150.596
134.091
130.230
129.754
126.181
125.453
79.808
68.158
34.567
32.456
31.299
25.909
tBu
^{13}C NMR (126 MHz, Chloroform-d)

Compound **4c**



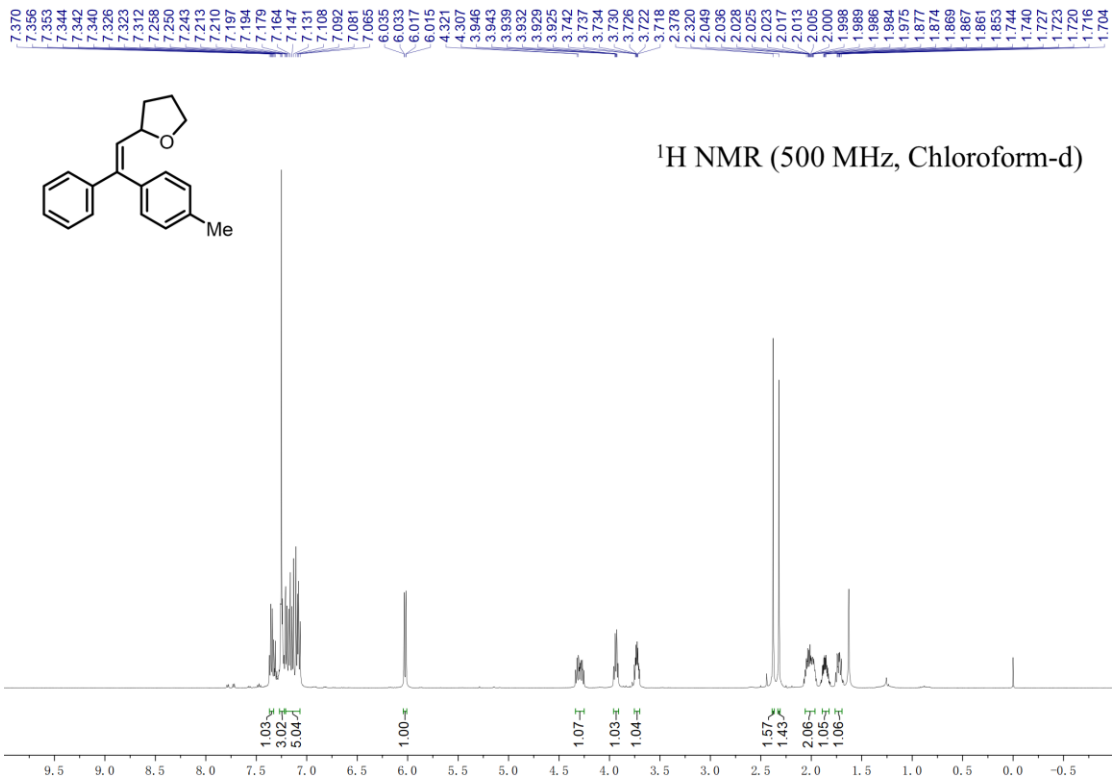
Compound **4d**

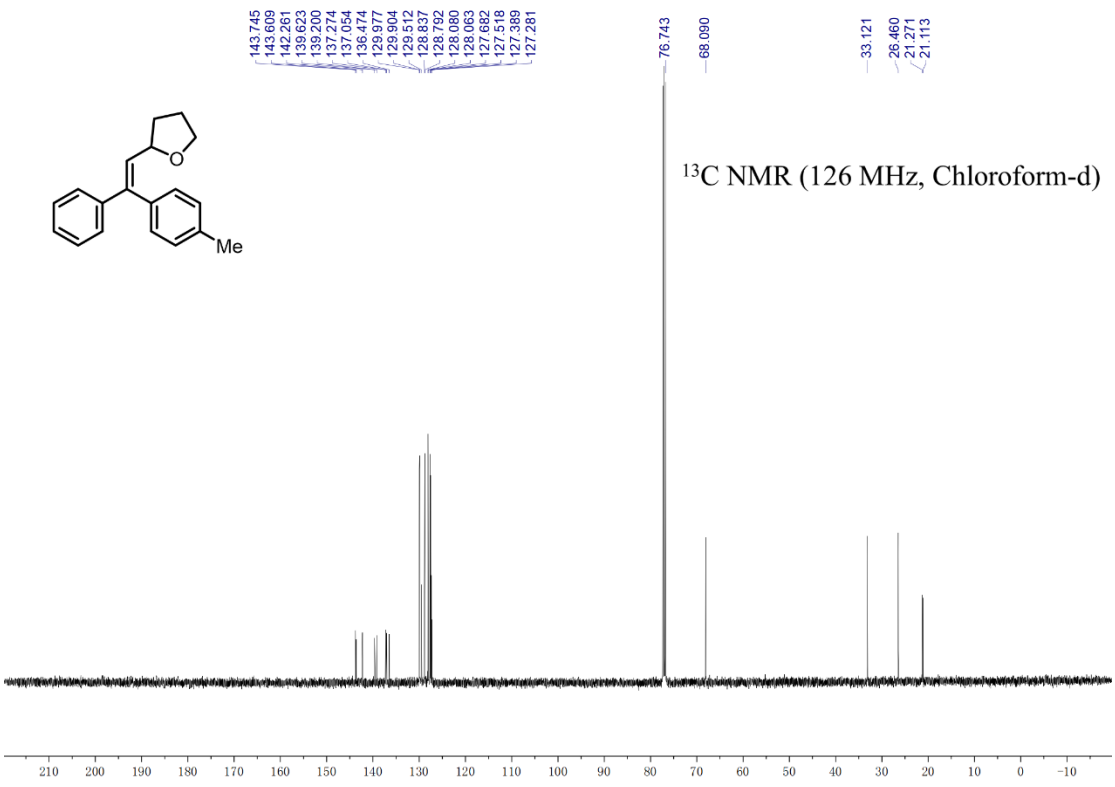

7.204 7.193 7.187 7.181 7.176 7.170 7.163 7.159 7.078 7.060 7.043 6.977 6.960 6.942 5.992 5.974 4.268 4.256 4.252 4.250 4.239 4.234 4.221 3.962 3.948 3.946 3.935 3.932 3.918 3.765 3.754 3.749 3.738 3.733 3.722 2.072 2.058 2.056 2.047 2.043 2.039 2.027 2.017 1.994 1.977 1.915 1.911 1.898 1.895 1.887 1.882 1.874 1.858 1.759 1.742 1.735 1.726 1.719 1.710 1.703
F
O
F
^{1}H NMR (500 MHz, Chloroform-d)
4.04 2.06 2.04 1.00 1.00 1.00 1.03 2.05 1.05 1.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5
163.399 163.232 161.434 161.269 141.914 137.997 135.114 131.604 131.541 129.922 129.252 129.188 115.265 115.137 115.095 114.966 113.953 76.516 68.156 33.064 26.468
F
O
F
^{13}C NMR (126 MHz, Chloroform-d)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10



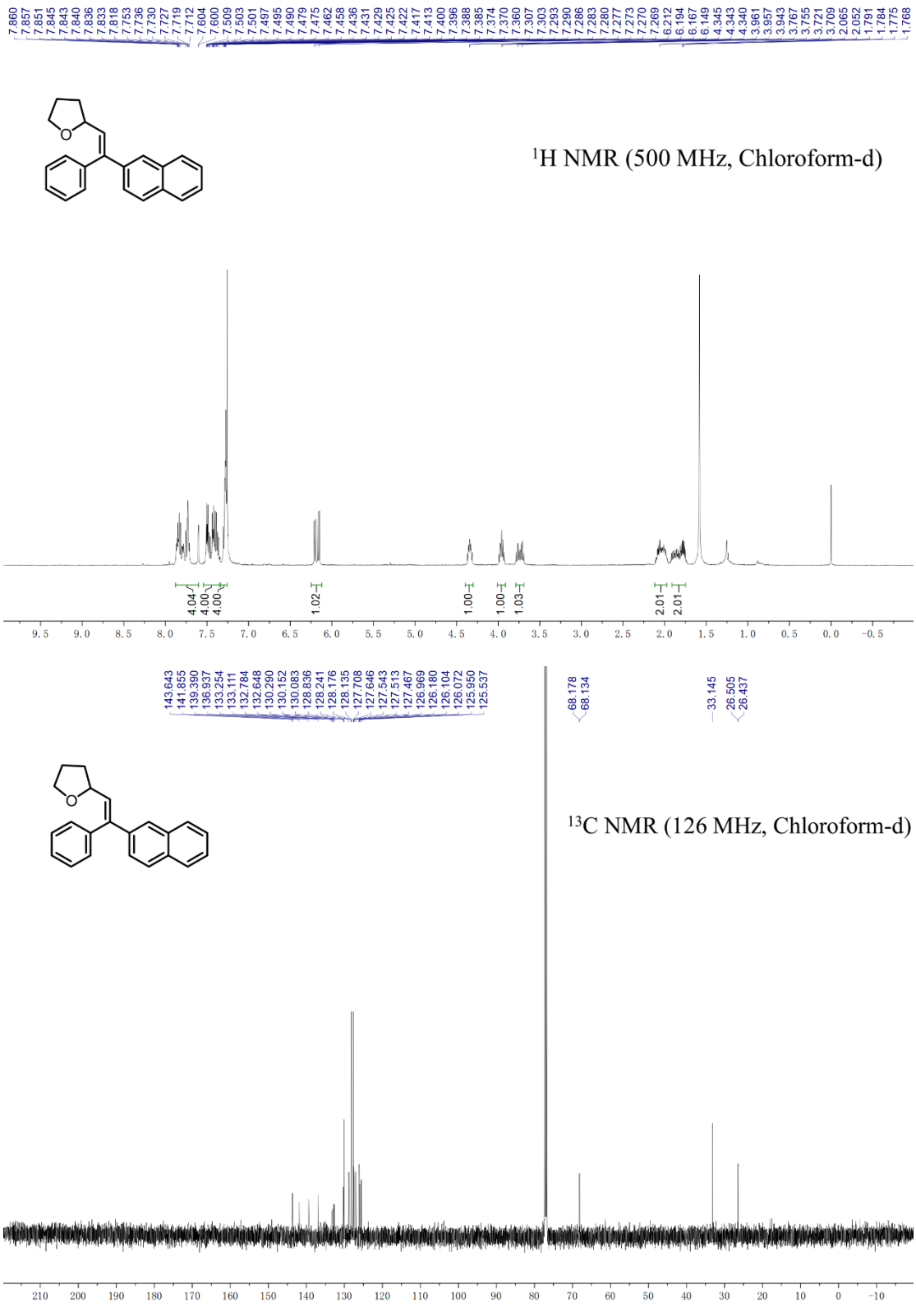
^{19}F NMR (471 MHz, Chloroform-d)

Compound **4e**

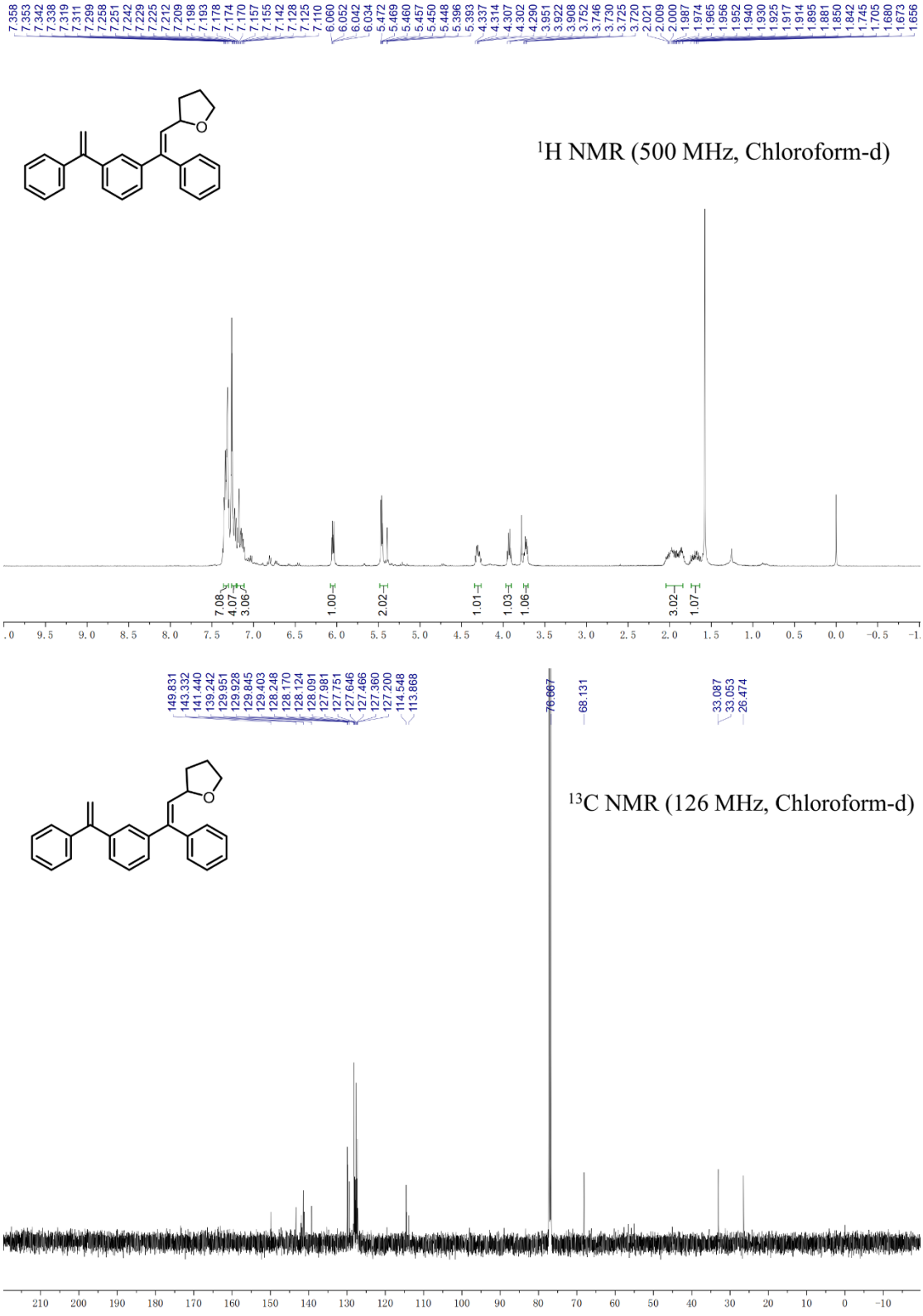




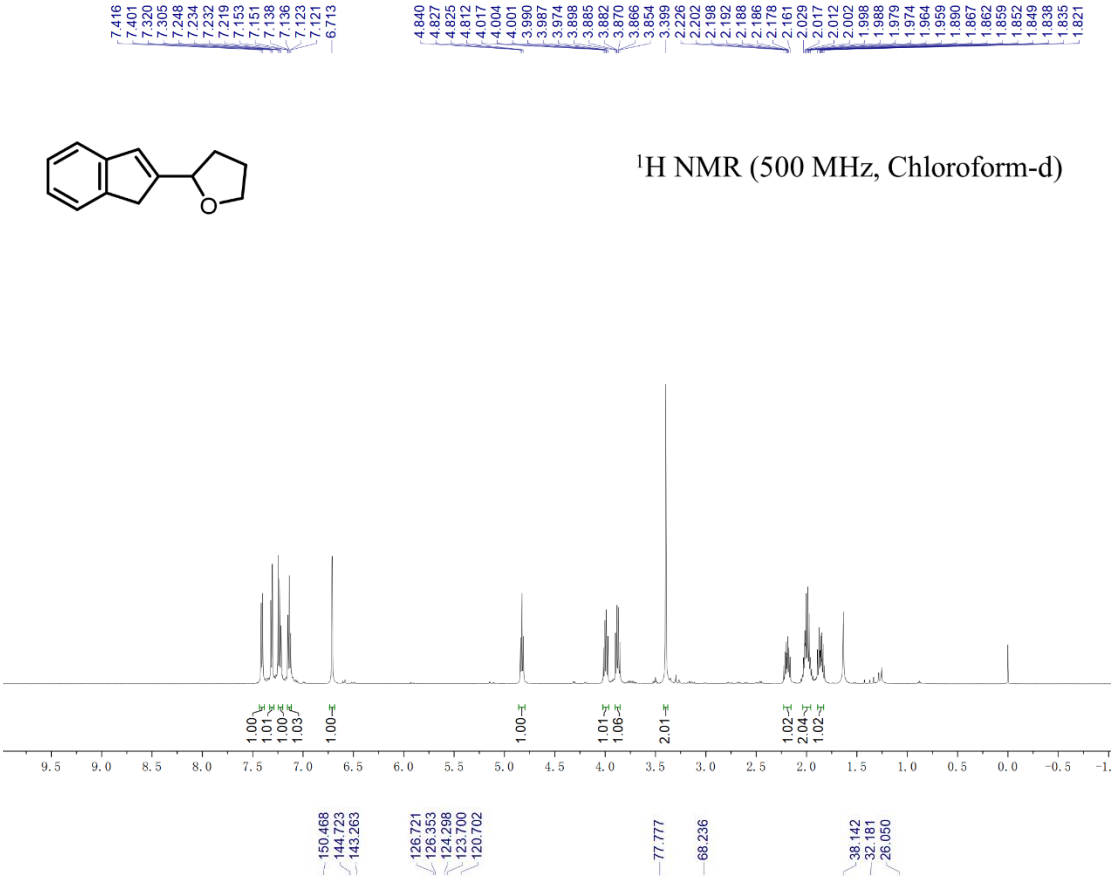
Compound **4f**


7.860
7.857
7.851
7.845
7.843
7.840
7.836
7.833
7.818
7.753
7.736
7.730
7.727
7.719
7.712
7.604
7.600
7.509
7.503
7.501
7.497
7.495
7.490
7.479
7.475
7.462
7.458
7.436
7.431
7.429
7.425
7.422
7.417
7.413
7.400
7.396
7.388
7.385
7.374
7.370
7.360
7.307
7.303
7.293
7.290
7.286
7.283
7.280
7.277
7.273
7.270
7.269
6.212
6.194
6.167
6.149
4.345
4.343
4.340
3.961
3.957
3.943
3.767
3.755
3.721
3.709
2.065
2.052
1.791
1.784
1.775
1.768
O
^{1}H NMR (500 MHz, Chloroform-d)
4.04
4.00
4.00
1.02
1.00
1.00
1.03
2.01
2.01
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
143.643
141.855
139.390
136.937
133.254
133.111
132.784
132.648
130.290
130.152
130.083
128.836
128.241
128.176
128.135
127.708
127.646
127.543
127.513
127.467
126.969
126.180
126.104
126.072
125.950
125.537
68.178
68.134
33.145
26.505
26.437
O
^{13}C NMR (126 MHz, Chloroform-d)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

Compound **4g**


7.358
7.353
7.342
7.338
7.319
7.311
7.299
7.258
7.251
7.242
7.229
7.225
7.212
7.209
7.198
7.193
7.178
7.174
7.170
7.157
7.155
7.142
7.128
7.125
7.110
6.060
6.052
6.042
6.034
5.472
5.469
5.460
5.457
5.450
5.448
5.396
5.393
4.337
4.314
4.307
4.302
4.290
3.951
3.922
3.908
3.752
3.746
3.730
3.725
3.720
2.021
2.009
2.000
1.987
1.974
1.965
1.956
1.952
1.940
1.930
1.925
1.917
1.914
1.895
1.881
1.850
1.842
1.745
1.705
1.680
1.673
1.656
O
^{1}H NMR (500 MHz, Chloroform-d)
7.08
4.07
3.06
1.00
2.02
1.01
1.03
1.06
3.02
1.07
149.831
143.332
141.440
139.242
129.951
129.928
129.845
129.403
128.248
128.170
128.124
128.091
127.981
127.751
127.646
127.466
127.360
127.200
114.548
113.868
76.667
68.131
33.087
33.053
26.474
O
^{13}C NMR (126 MHz, Chloroform-d)

Compound **4h**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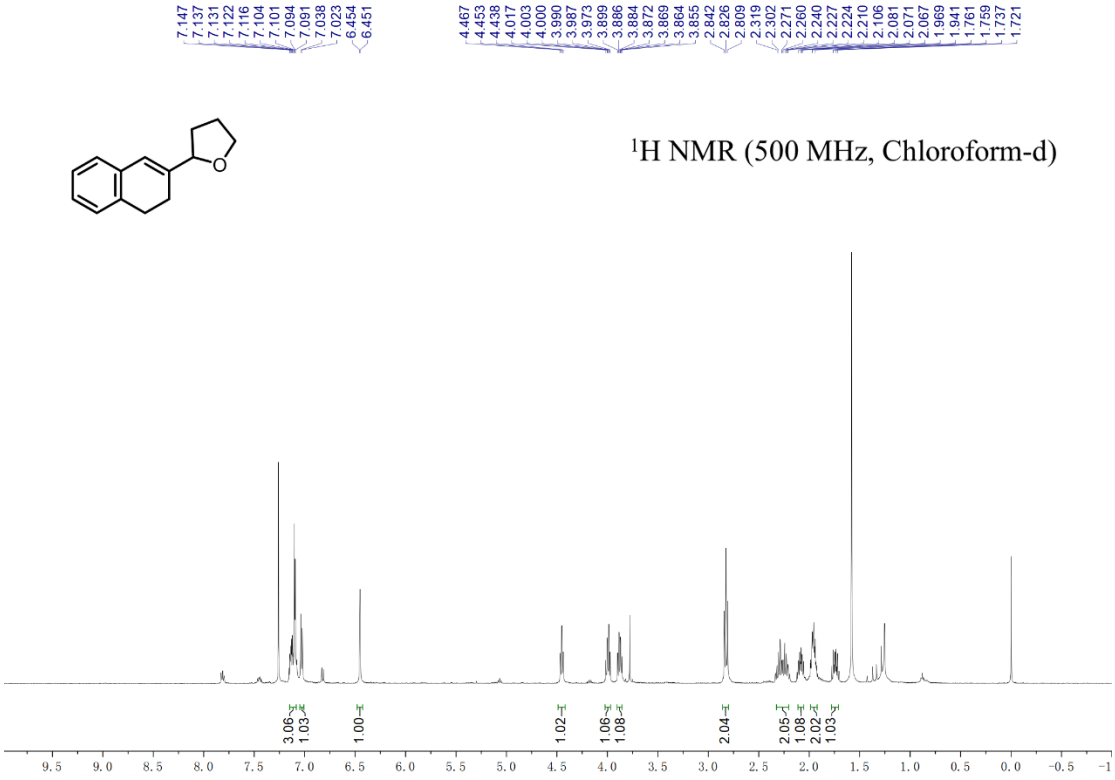
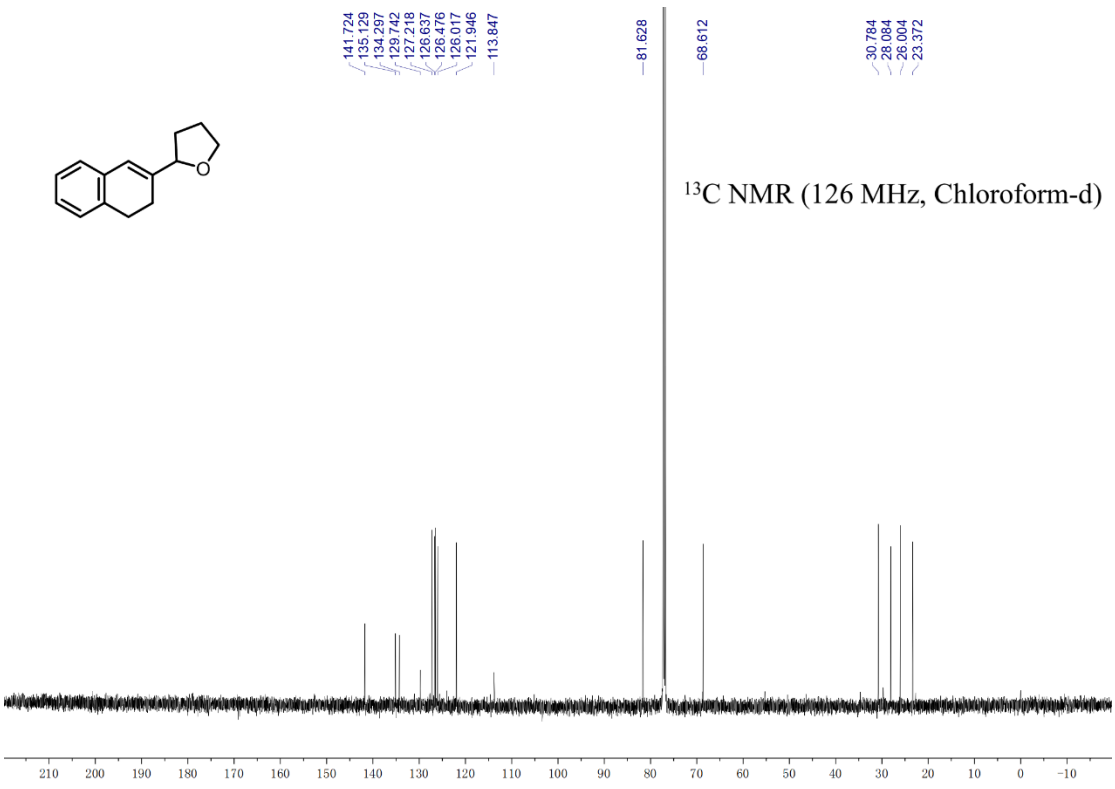
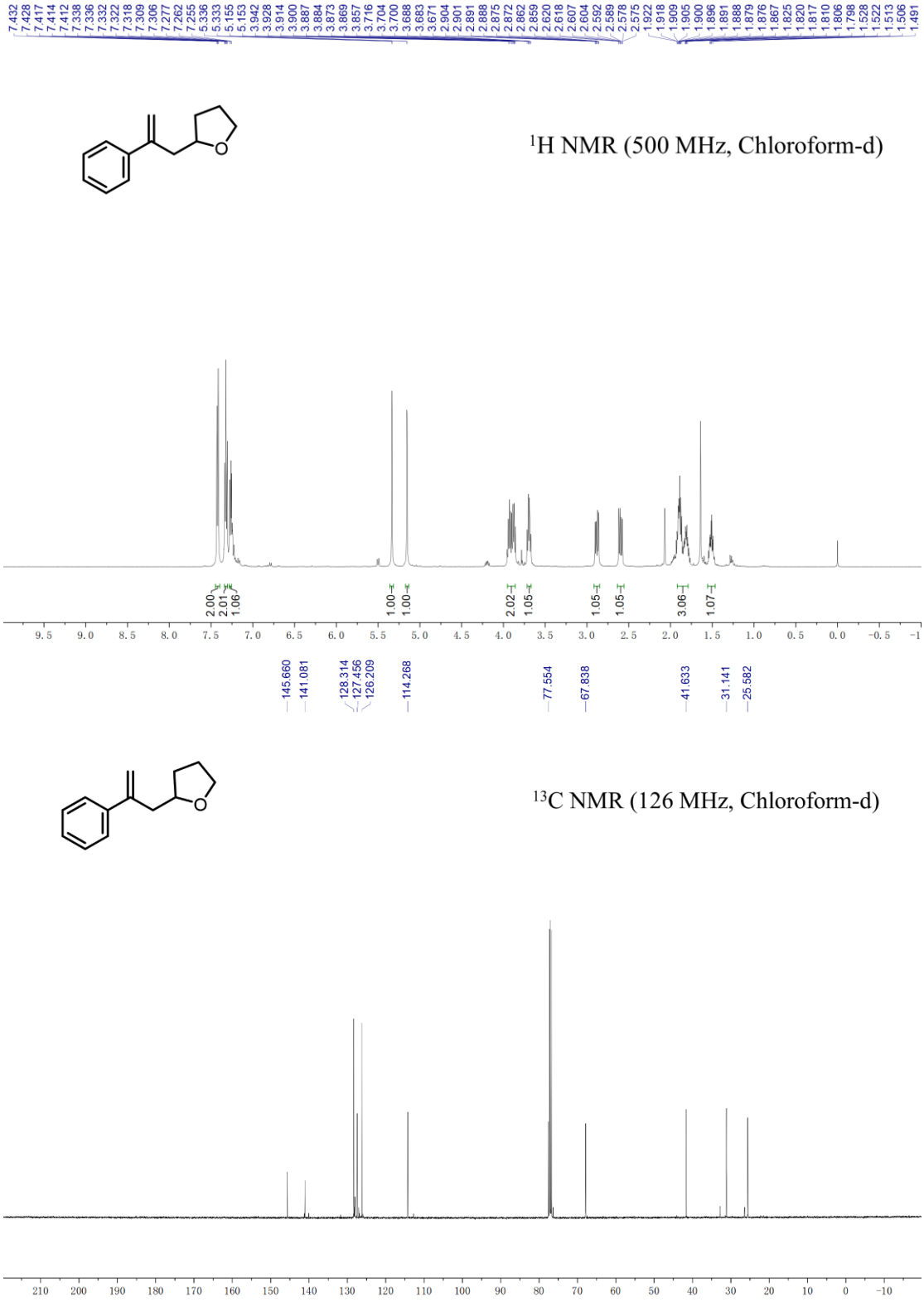
7.401
7.320
7.305
7.248
7.234
7.232
7.219
7.153
7.151
7.138
7.136
7.123
7.121
6.713
4.840
4.827
4.825
4.812
4.017
4.004
4.001
3.990
3.987
3.974
3.898
3.885
3.882
3.870
3.866
3.854
3.399
2.226
2.202
2.198
2.192
2.188
2.186
2.178
2.161
2.029
2.017
2.012
2.002
1.998
1.988
1.979
1.974
1.964
1.959
1.890
1.867
1.862
1.859
1.852
1.849
1.838
1.835
1.821
1H NMR (500 MHz, Chloroform-d)
1.00
1.01
1.00
1.03
1.00
1.00
1.01
1.08
2.01
1.02
2.04
1.02
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5 −1.
150.468
144.723
143.263
126.721
126.353
124.298
123.700
120.702
77.777
68.236
38.142
32.181
26.050
13C NMR (126 MHz, Chloroform-d)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10

Compound **4i**

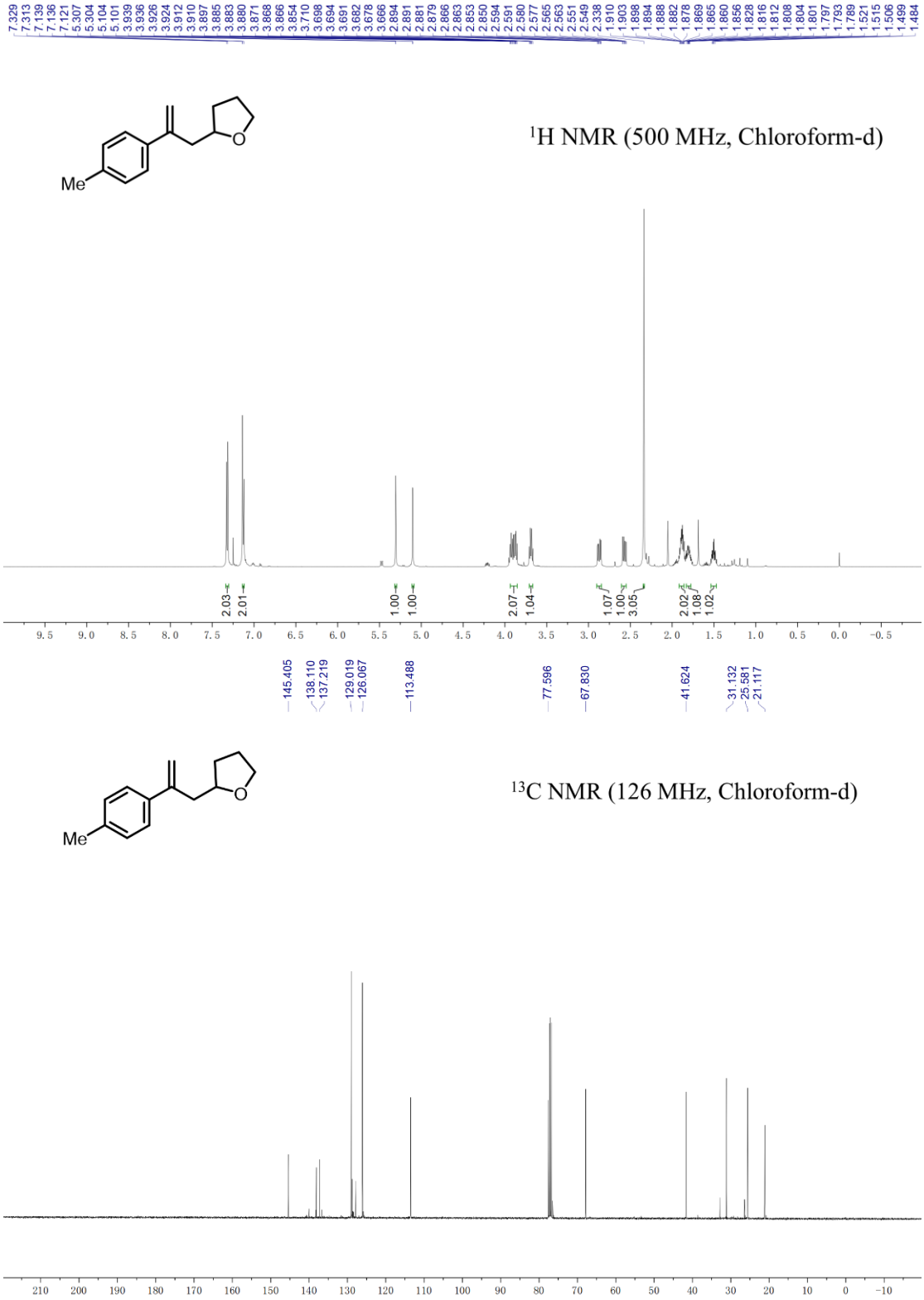

7.147
7.137
7.131
7.122
7.116
7.104
7.101
7.094
7.091
7.038
7.023
6.454
6.451
4.467
4.453
4.438
4.017
4.003
4.000
3.990
3.987
3.973
3.899
3.886
3.884
3.872
3.869
3.864
3.855
2.842
2.826
2.809
2.319
2.302
2.271
2.260
2.240
2.227
2.224
2.210
2.106
2.081
2.071
2.067
1.969
1.941
1.761
1.759
1.737
1.721
[1]H NMR (500 MHz, Chloroform-d)
3.06
1.03
1.00
1.02
1.06
1.08
2.04
2.05
1.08
2.02
1.03


141.724
135.129
134.297
129.742
127.218
126.637
126.476
126.017
121.946
113.847
81.628
68.612
30.784
28.084
26.004
23.372
[13]C NMR (126 MHz, Chloroform-d)

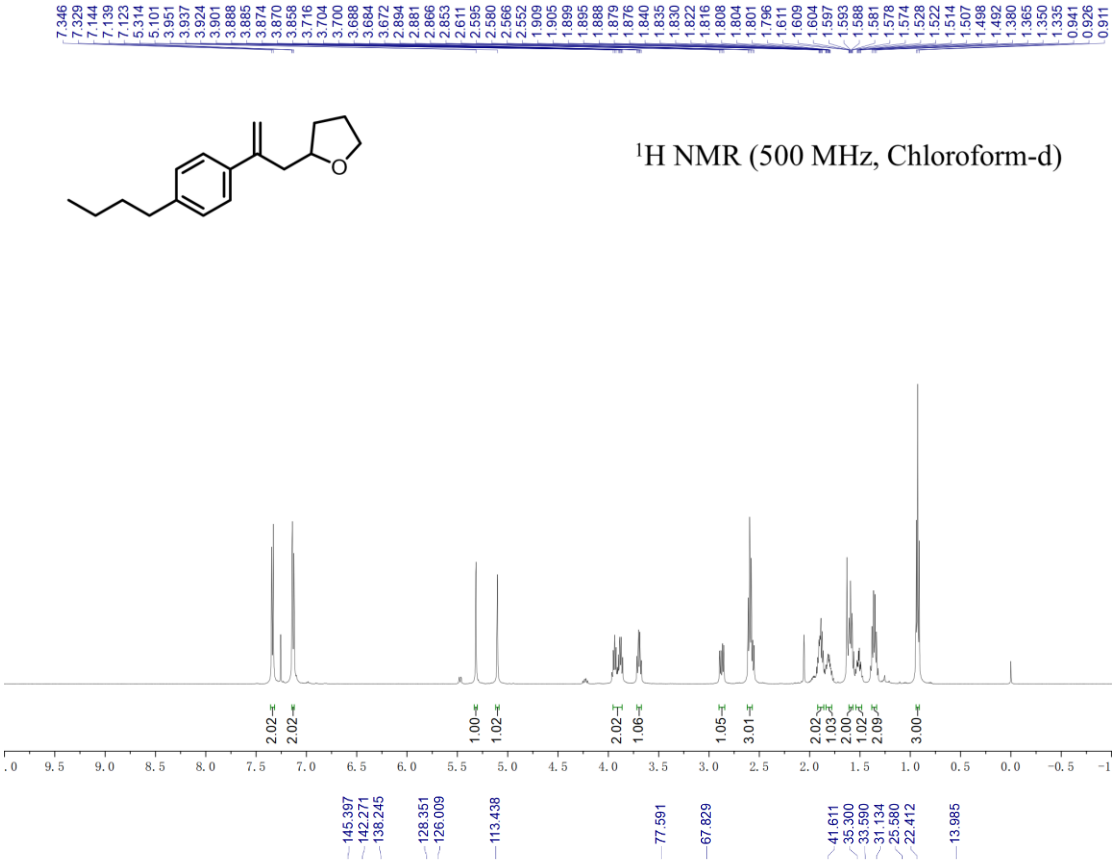
Compound **4j**

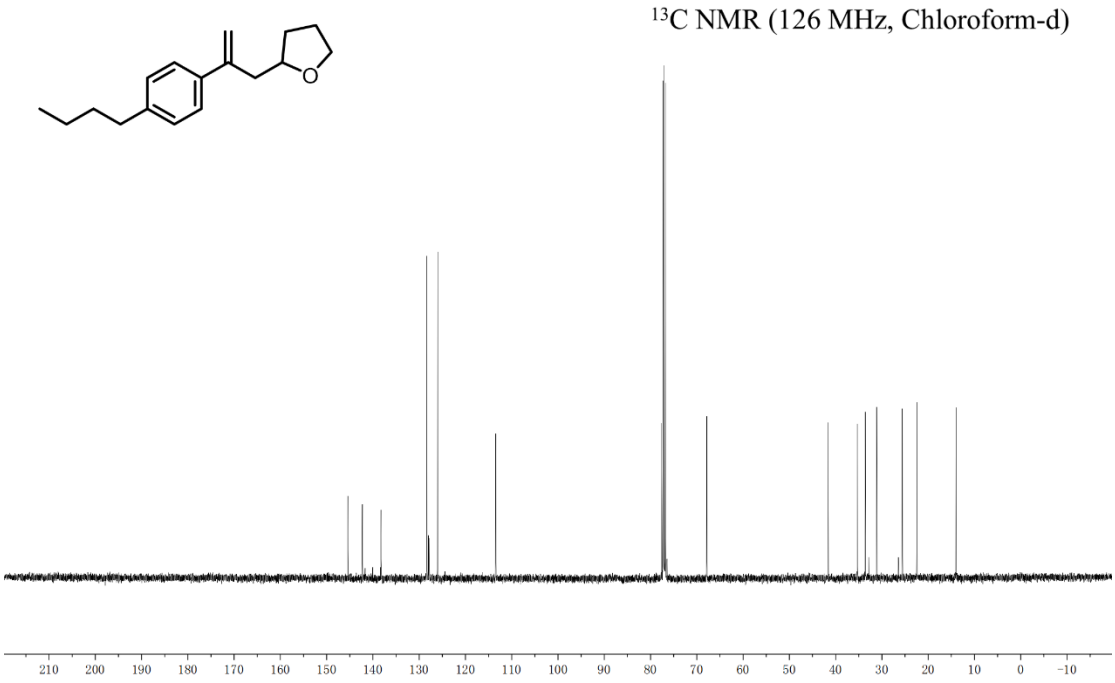

7.432 7.428 7.417 7.414 7.412 7.338 7.336 7.332 7.322 7.318 7.309 7.306 7.277 7.262 7.255 5.336 5.333 5.155 5.153 3.942 3.928 3.914 3.900 3.887 3.884 3.873 3.869 3.857 3.716 3.704 3.700 3.688 3.683 3.671 2.904 2.901 2.891 2.888 2.875 2.872 2.862 2.859 2.620 2.618 2.607 2.604 2.592 2.589 2.578 2.575 1.922 1.918 1.909 1.905 1.900 1.896 1.891 1.888 1.879 1.876 1.867 1.825 1.820 1.817 1.810 1.806 1.798 1.528 1.522 1.513 1.506 1.491
1H NMR (500 MHz, Chloroform-d)
2.00 2.01 1.06 1.00 1.00 2.02 1.05 1.05 1.05 3.06 1.07
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
145.660 141.081 128.314 127.456 126.209 114.268 77.554 67.838 41.633 31.141 25.582
13C NMR (126 MHz, Chloroform-d)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

Compound **4k**

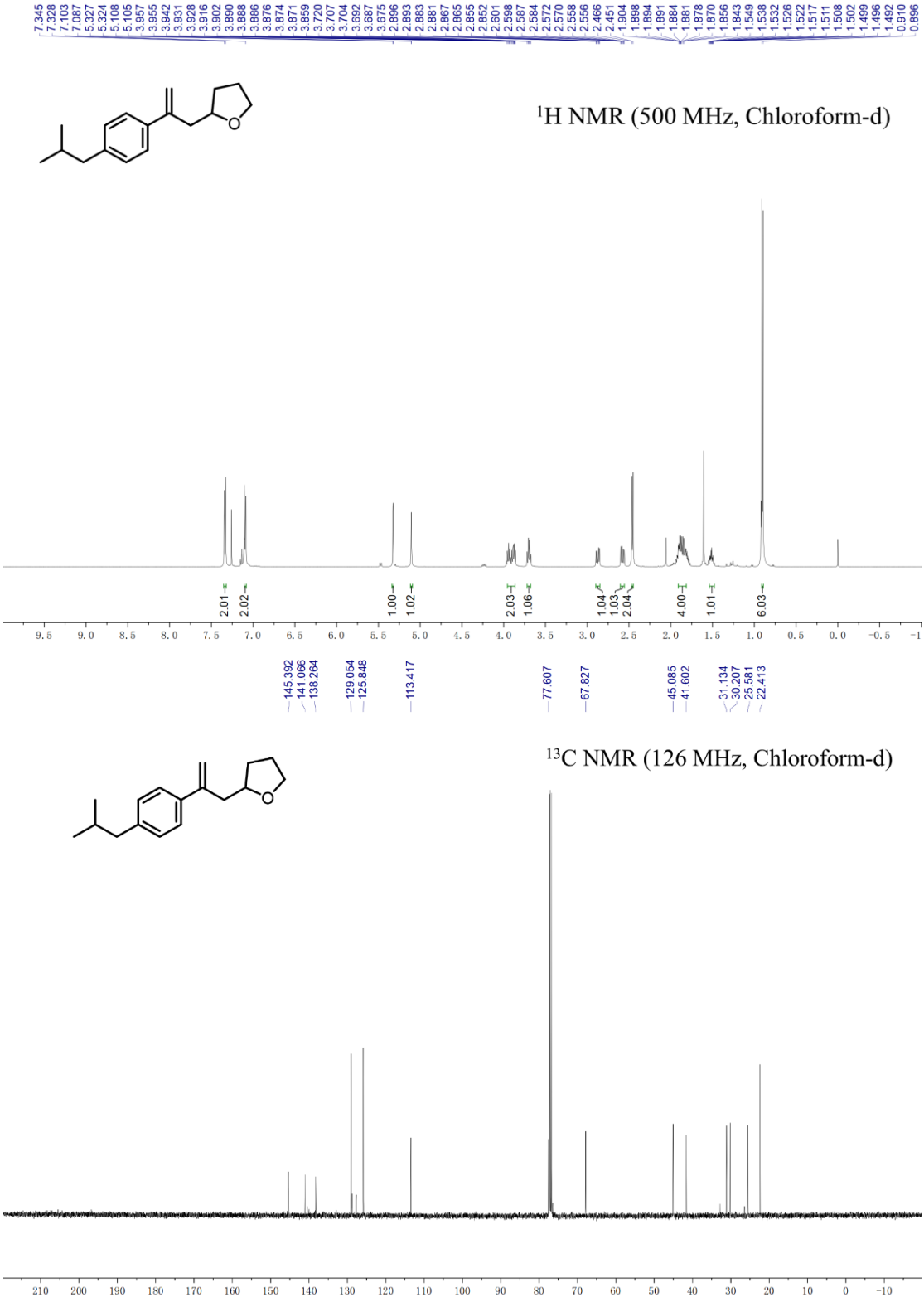

7.329
7.313
7.139
7.136
7.121
5.307
5.304
5.104
5.101
3.939
3.936
3.926
3.924
3.912
3.910
3.897
3.885
3.883
3.880
3.871
3.868
3.866
3.854
3.710
3.698
3.694
3.691
3.682
3.678
3.666
2.894
2.891
2.881
2.879
2.866
2.863
2.853
2.850
2.594
2.591
2.580
2.577
2.565
2.563
2.551
2.549
2.338
1.910
1.903
1.898
1.894
1.888
1.882
1.878
1.869
1.865
1.860
1.856
1.828
1.816
1.812
1.808
1.804
1.801
1.797
1.793
1.789
1.521
1.515
1.506
1.499
1.484
Me
O
^{1}H NMR (500 MHz, Chloroform-d)
2.03
2.01
1.00
1.00
2.07
1.04
1.07
1.00
3.05
2.02
1.08
1.02
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
145.405
138.110
137.219
129.019
126.067
113.488
77.596
67.830
41.624
31.132
25.581
21.117
Me
O
^{13}C NMR (126 MHz, Chloroform-d)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

Compound **4l**

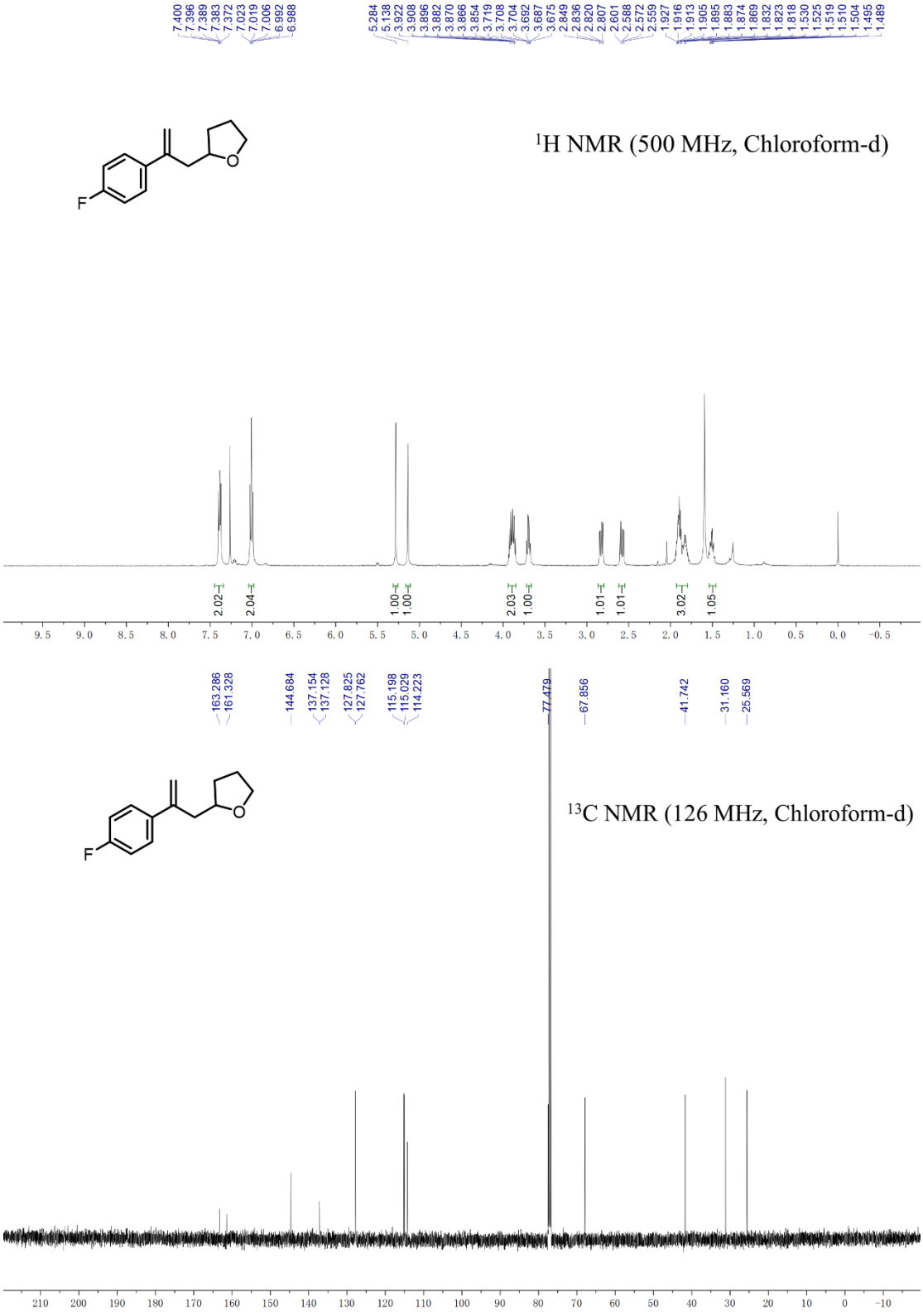

7.346
7.329
7.144
7.139
7.123
5.314
5.101
3.951
3.937
3.924
3.901
3.888
3.885
3.874
3.870
3.858
3.716
3.704
3.700
3.688
3.684
3.672
2.894
2.881
2.866
2.853
2.611
2.595
2.580
2.566
2.552
1.909
1.905
1.899
1.895
1.888
1.879
1.876
1.840
1.835
1.830
1.822
1.816
1.808
1.804
1.801
1.796
1.611
1.609
1.604
1.597
1.593
1.588
1.581
1.578
1.574
1.528
1.522
1.514
1.507
1.498
1.492
1.380
1.365
1.350
1.335
0.941
0.926
0.911
O
^{1}H NMR (500 MHz, Chloroform-d)
2.02
2.02
1.00
1.02
2.02
1.06
1.05
3.01
2.02
1.03
2.00
1.02
2.09
3.00

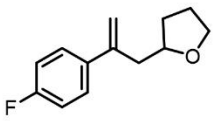

145.397
142.271
138.245
128.351
126.009
113.438
77.591
67.829
41.611
35.300
33.590
31.134
25.580
22.412
13.985
O
^{13}C NMR (126 MHz, Chloroform-d)

Compound **4m**


7.345
7.328
7.103
7.087
5.327
5.324
5.108
5.105
3.957
3.955
3.942
3.931
3.928
3.916
3.902
3.890
3.888
3.886
3.876
3.874
3.871
3.859
3.720
3.707
3.704
3.692
3.687
3.675
2.896
2.893
2.883
2.881
2.867
2.865
2.855
2.852
2.601
2.598
2.587
2.584
2.572
2.570
2.558
2.556
2.466
2.451
1.904
1.898
1.894
1.891
1.884
1.881
1.878
1.870
1.856
1.843
1.549
1.538
1.532
1.526
1.522
1.517
1.511
1.508
1.502
1.499
1.496
1.492
0.910
0.896
1H NMR (500 MHz, Chloroform-d)
2.01
2.02
1.00
1.02
2.03
1.06
1.04
1.03
2.04
4.00
1.01
6.03
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5 −1
145.392
141.066
138.264
129.054
125.848
113.417
77.607
67.827
45.085
41.602
31.134
30.207
25.581
22.413
13C NMR (126 MHz, Chloroform-d)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10

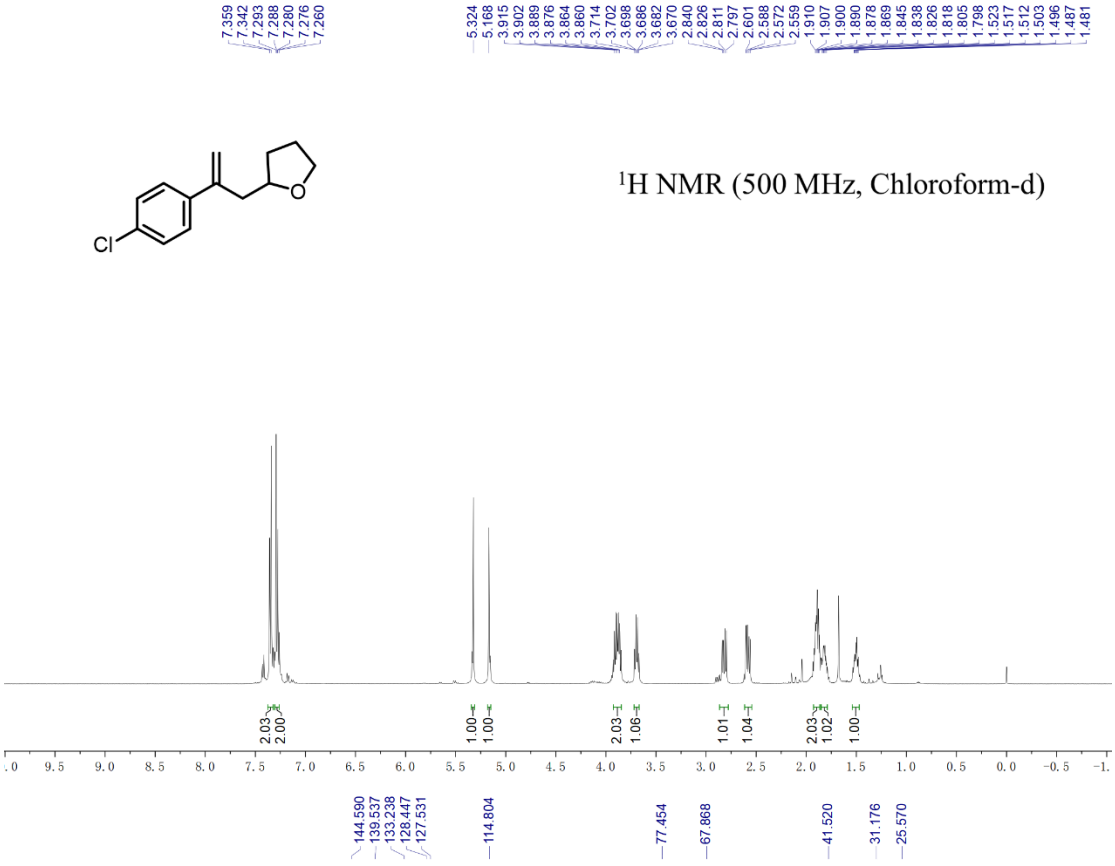
Compound **4n**


7.400
7.396
7.389
7.383
7.372
7.023
7.019
7.006
6.992
6.988
5.284
5.138
3.922
3.908
3.896
3.882
3.870
3.866
3.854
3.719
3.708
3.704
3.692
3.687
3.675
2.849
2.836
2.820
2.807
2.601
2.588
2.572
2.559
1.927
1.916
1.913
1.905
1.895
1.883
1.874
1.869
1.832
1.823
1.818
1.530
1.525
1.519
1.510
1.504
1.495
1.489
F
O
[1]H NMR (500 MHz, Chloroform-d)
2.02
2.04
1.00
1.00
2.03
1.00
1.01
1.01
3.02
1.05
163.286
161.328
144.684
137.154
137.128
127.825
127.762
115.198
115.029
114.223
77.479
67.856
41.742
31.160
25.569
F
O
[13]C NMR (126 MHz, Chloroform-d)

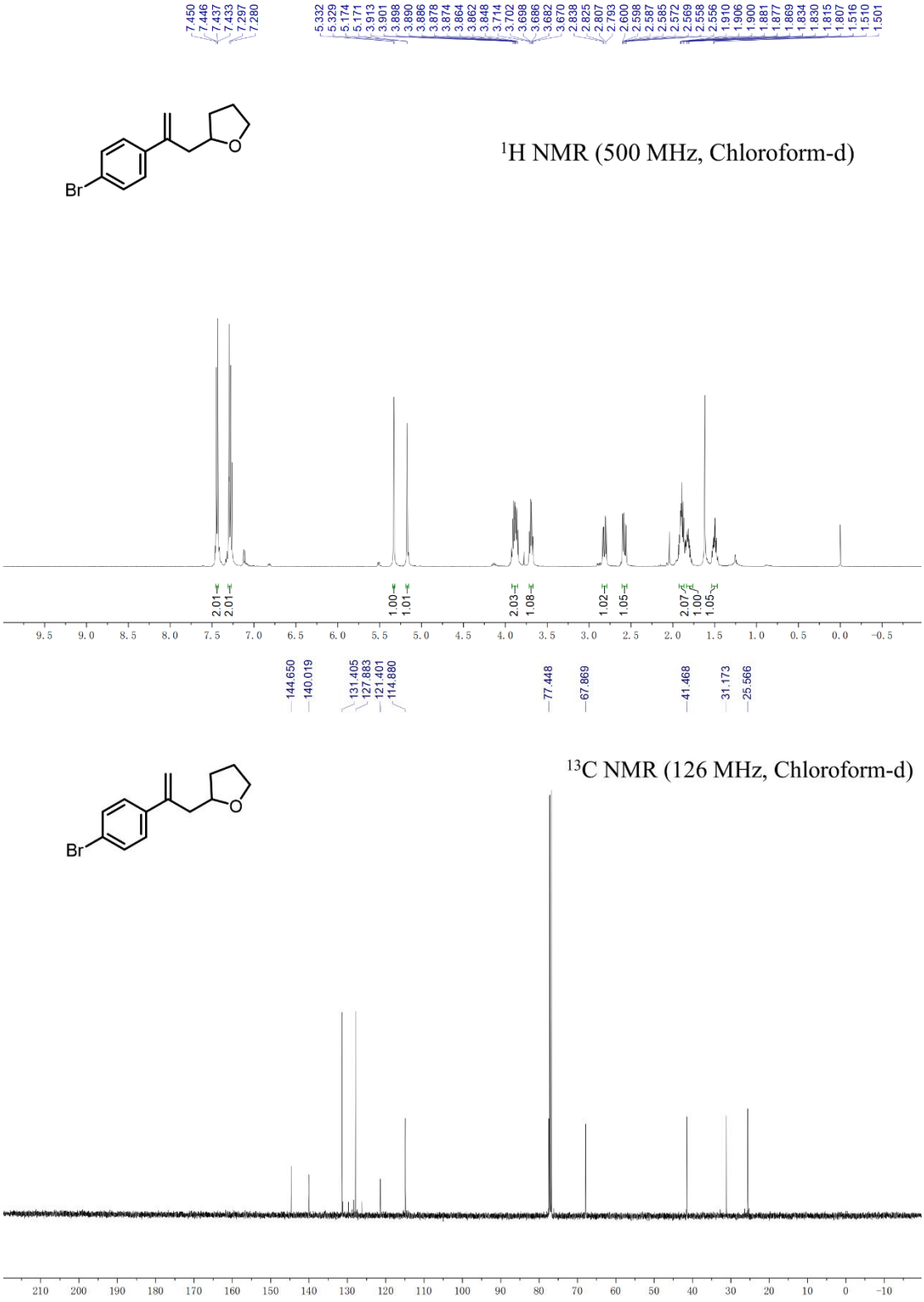


^{19}F NMR (471 MHz, Chloroform-d)

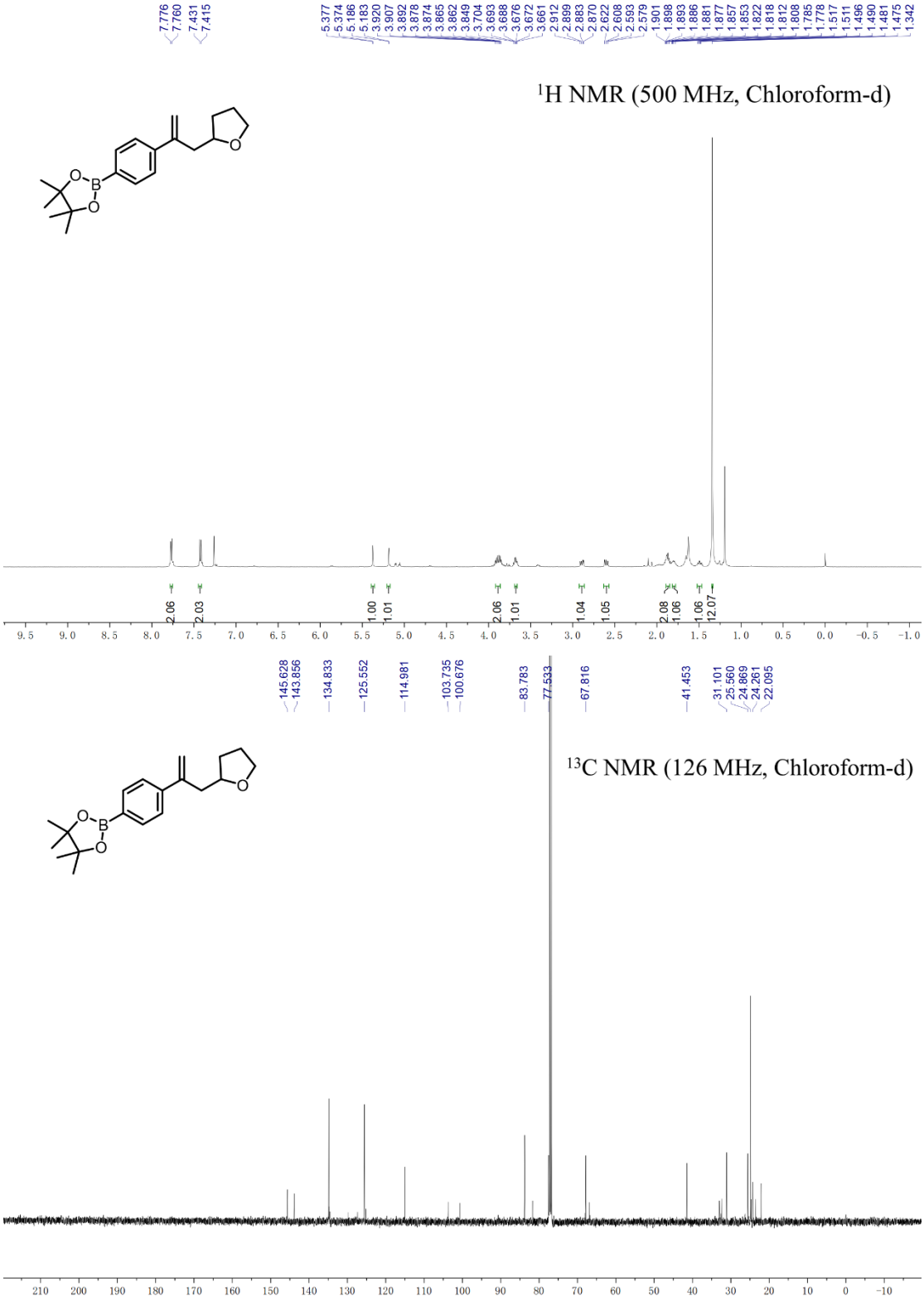
Compound **4o**


7.359
7.342
7.293
7.288
7.280
7.276
7.260
5.324
5.168
3.915
3.902
3.889
3.876
3.864
3.860
3.714
3.702
3.698
3.686
3.682
3.670
2.840
2.826
2.811
2.797
2.601
2.588
2.572
2.559
1.910
1.907
1.900
1.890
1.878
1.869
1.845
1.838
1.826
1.818
1.805
1.798
1.523
1.517
1.512
1.503
1.496
1.487
1.481
Cl
O
[1]H NMR (500 MHz, Chloroform-d)
2.03
2.00
1.00
1.00
2.03
1.06
1.01
1.04
2.03
1.02
1.00
144.590
139.537
133.238
128.447
127.531
114.804
77.454
67.868
41.520
31.176
25.570
Cl
O
[13]C NMR (126 MHz, Chloroform-d)

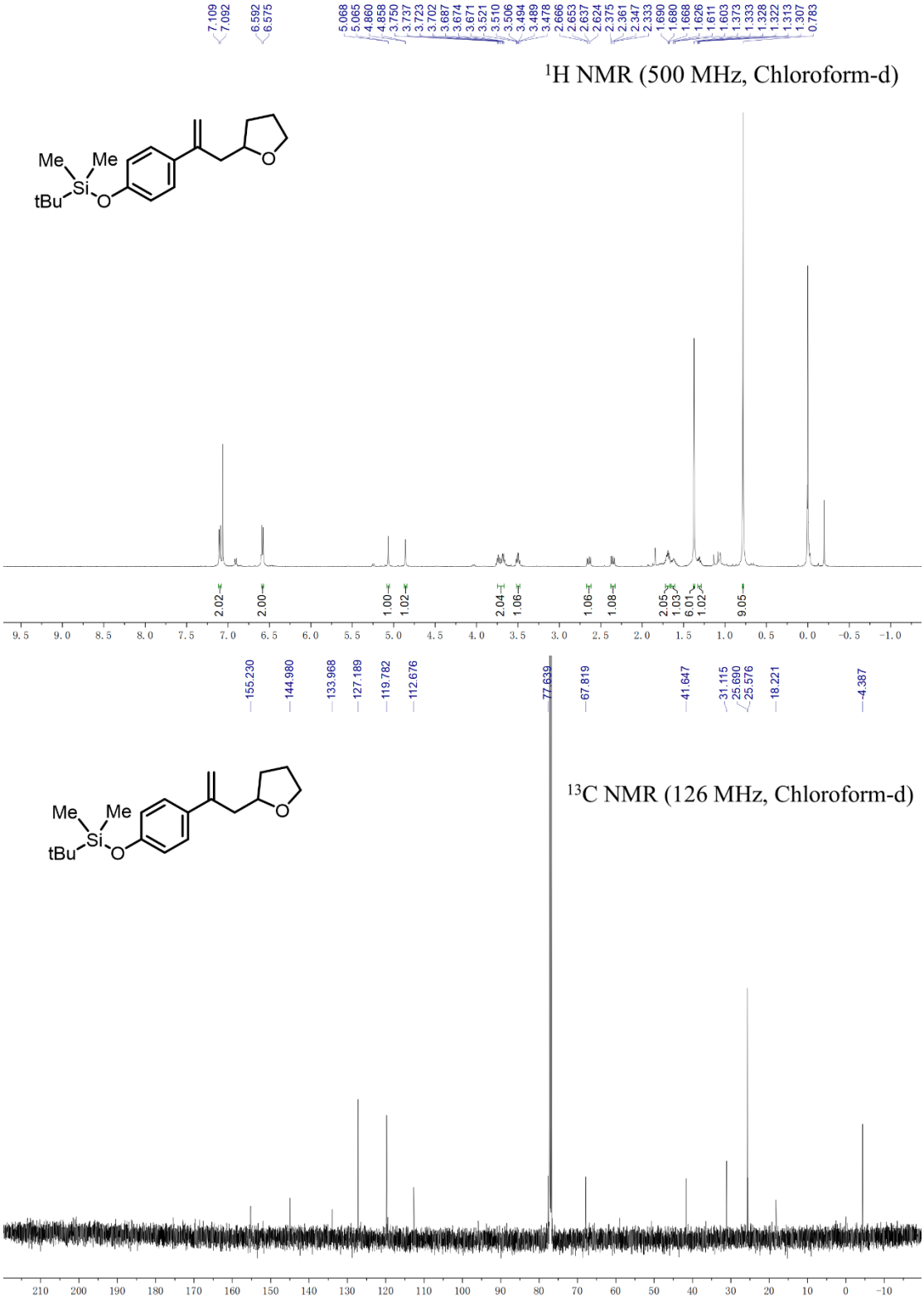
Compound **4p**


7.450
7.446
7.437
7.433
7.297
7.280
5.332
5.329
5.174
5.171
3.913
3.901
3.898
3.890
3.886
3.878
3.874
3.864
3.862
3.848
3.714
3.702
3.698
3.686
3.682
3.670
2.838
2.825
2.807
2.793
2.600
2.598
2.587
2.585
2.572
2.569
2.558
2.556
1.910
1.906
1.900
1.881
1.877
1.869
1.834
1.830
1.815
1.807
1.516
1.510
1.501
Br
^{1}H NMR (500 MHz, Chloroform-d)
2.01
2.01
1.00
1.01
2.03
1.08
1.02
1.05
2.07
1.00
1.05
144.650
140.019
131.405
127.883
121.401
114.880
77.448
67.869
41.468
31.173
25.566
Br
^{13}C NMR (126 MHz, Chloroform-d)

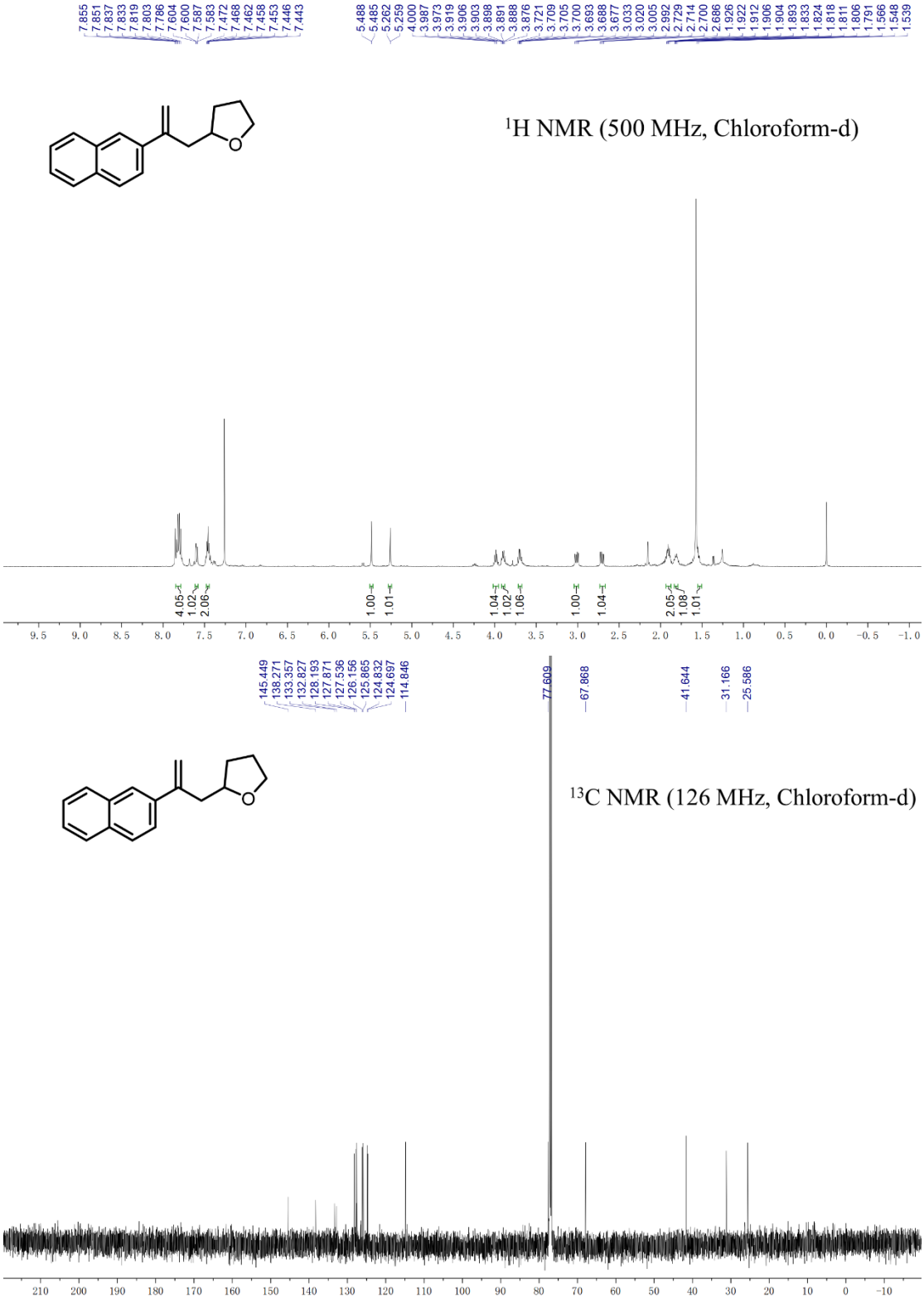
Compound **4q**


7.776
7.760
7.431
7.415
5.377
5.374
5.186
5.183
3.920
3.907
3.892
3.878
3.874
3.865
3.862
3.849
3.704
3.693
3.688
3.676
3.672
3.661
2.912
2.899
2.883
2.870
2.622
2.608
2.593
2.579
1.901
1.898
1.893
1.886
1.881
1.877
1.857
1.853
1.822
1.818
1.812
1.808
1.785
1.778
1.517
1.511
1.496
1.490
1.481
1.475
1.342
[1]H NMR (500 MHz, Chloroform-d)
2.06
2.03
1.00
1.01
2.06
1.01
1.04
1.05
2.08
1.06
1.06
12.07
145.628
143.856
134.833
125.552
114.981
103.735
100.676
83.783
77.533
67.816
41.453
31.101
25.560
24.869
24.261
22.095
[13]C NMR (126 MHz, Chloroform-d)

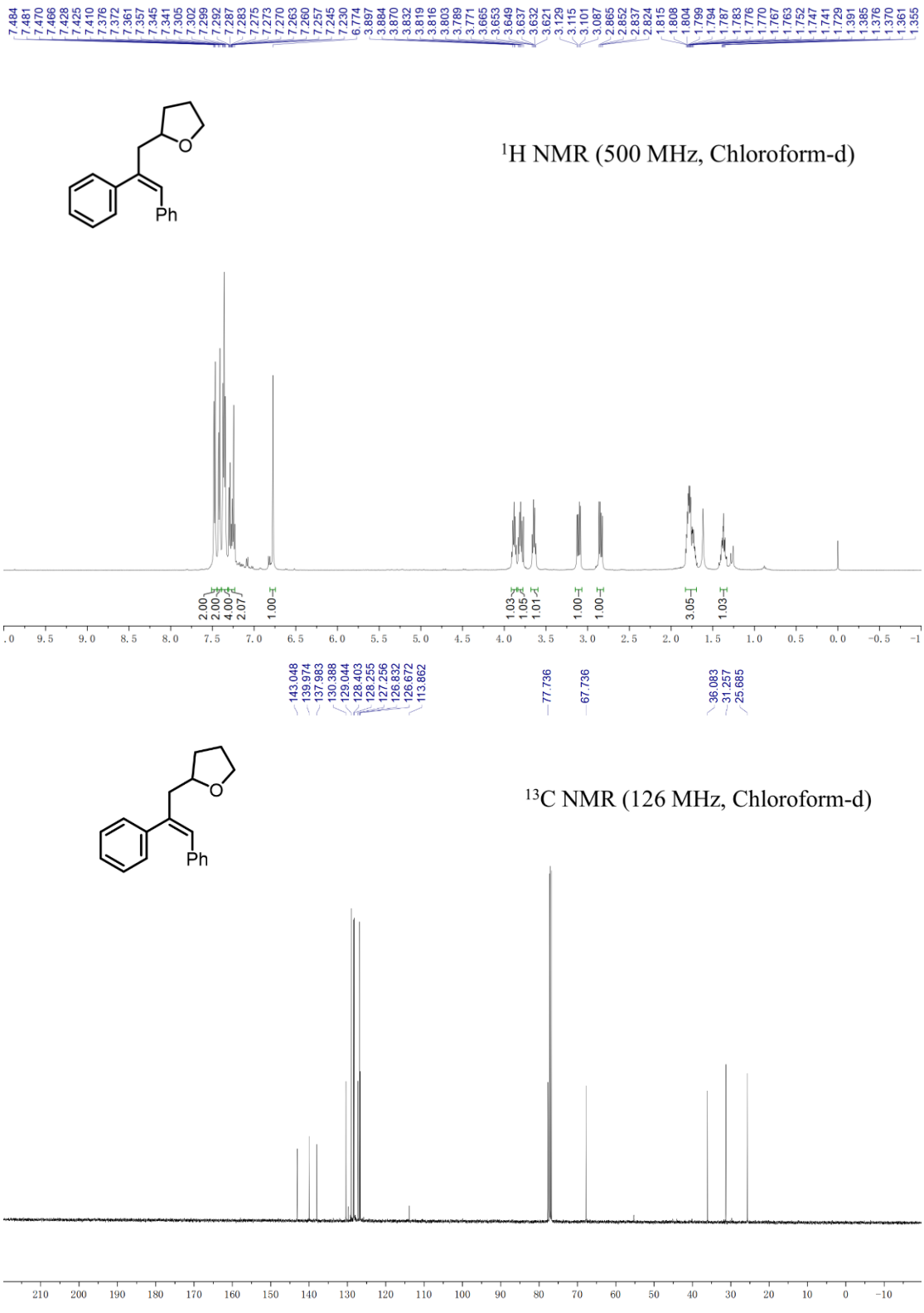
Compound **4r**


7.109
7.092
6.592
6.575
5.068
5.065
4.860
4.858
3.750
3.737
3.723
3.702
3.687
3.674
3.671
3.521
3.510
3.506
3.494
3.489
3.478
2.666
2.653
2.637
2.624
2.375
2.361
2.347
2.333
1.690
1.680
1.668
1.626
1.611
1.603
1.373
1.333
1.328
1.322
1.313
1.307
0.783
Me
Me
tBu
Si
O
O
1H NMR (500 MHz, Chloroform-d)
2.02
2.00
1.00
1.02
2.04
1.06
1.06
1.08
2.05
1.03
6.01
1.02
9.05
155.230
144.980
133.968
127.189
119.782
112.676
77.639
67.819
41.647
31.115
25.690
25.576
18.221
-4.387
13C NMR (126 MHz, Chloroform-d)

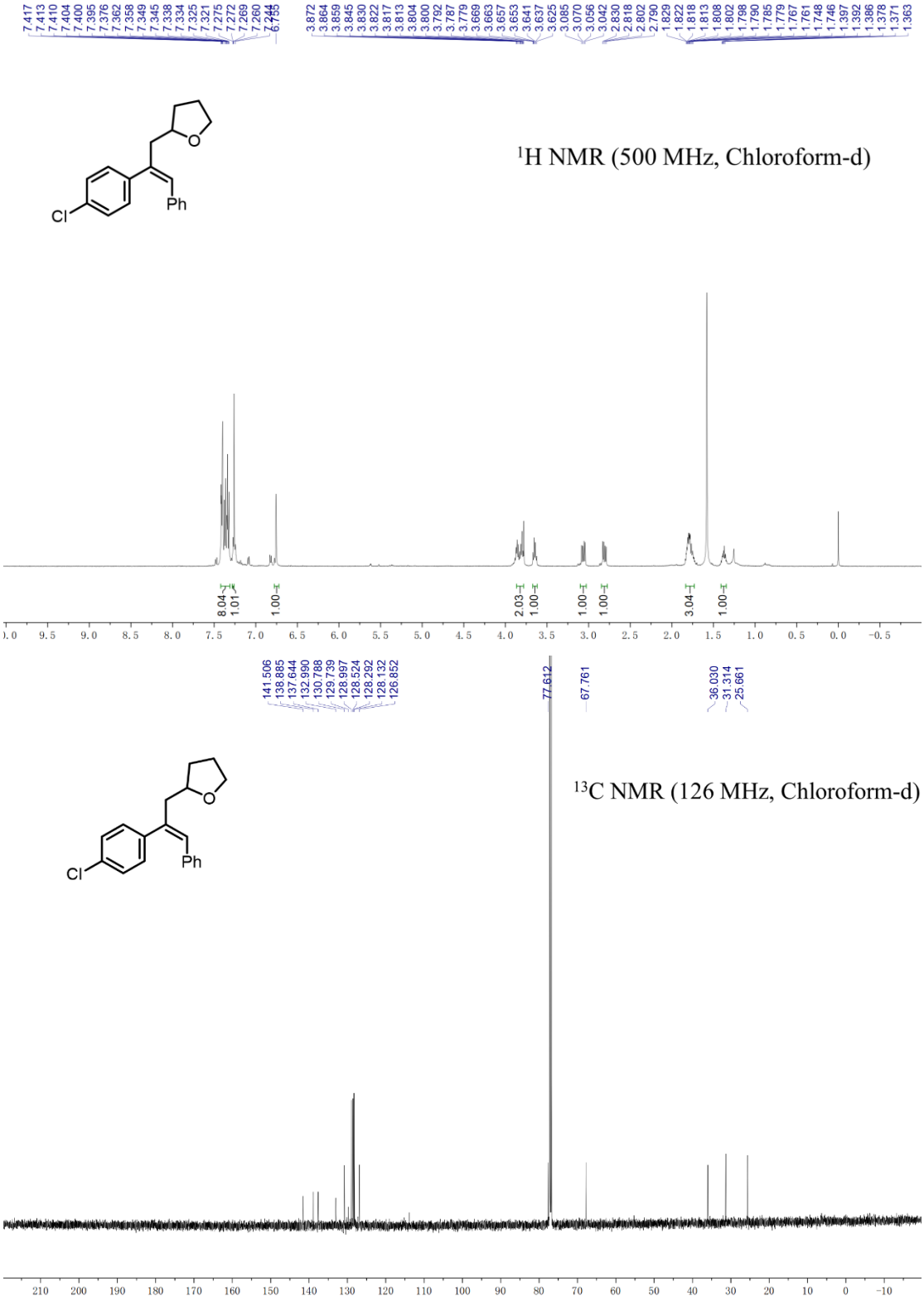
Compound **4s**


7.855
7.851
7.837
7.833
7.819
7.803
7.786
7.604
7.600
7.587
7.583
7.472
7.468
7.462
7.458
7.453
7.446
7.443
5.488
5.485
5.262
5.259
4.000
3.987
3.973
3.919
3.906
3.903
3.898
3.891
3.888
3.876
3.721
3.709
3.705
3.700
3.693
3.688
3.677
3.033
3.020
3.005
2.992
2.729
2.714
2.700
2.686
1.926
1.922
1.912
1.906
1.904
1.893
1.833
1.824
1.818
1.811
1.806
1.791
1.566
1.548
1.539
1H NMR (500 MHz, Chloroform-d)
4.05
1.02
2.06
1.00
1.01
1.04
1.02
1.06
1.00
1.04
2.05
1.08
1.01
145.449
138.271
133.357
132.827
128.193
127.871
127.536
126.156
125.865
124.832
124.697
114.846
77.609
67.868
41.644
31.166
25.586
13C NMR (126 MHz, Chloroform-d)

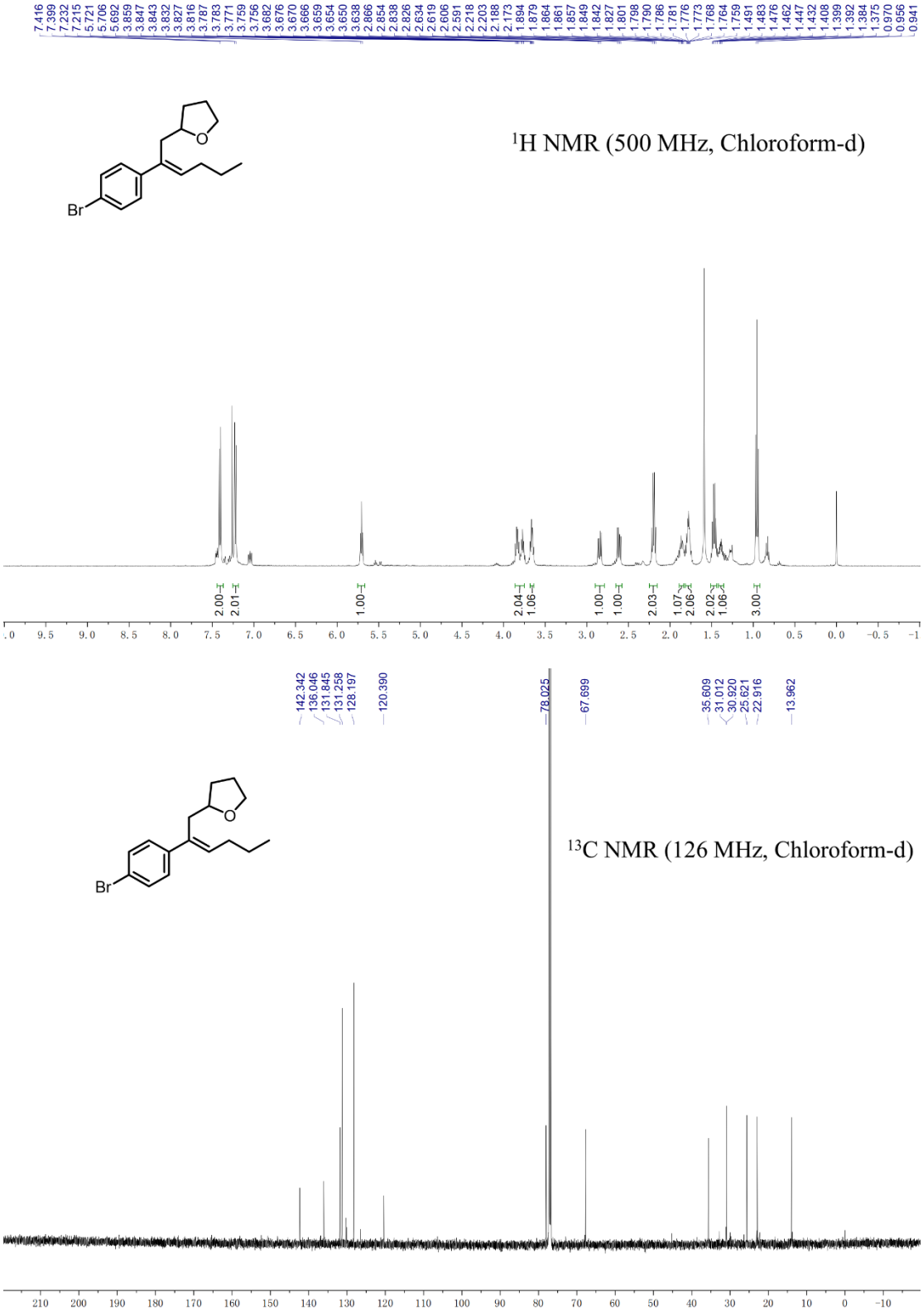
Compound **4t**


7.484 7.481 7.470 7.466 7.428 7.425 7.410 7.376 7.372 7.361 7.357 7.345 7.341 7.305 7.302 7.299 7.292 7.287 7.283 7.275 7.273 7.270 7.263 7.260 7.257 7.245 7.230 6.774 3.897 3.884 3.870 3.832 3.819 3.816 3.803 3.789 3.771 3.665 3.653 3.649 3.637 3.632 3.621 3.129 3.115 3.101 3.087 2.865 2.852 2.837 2.824 1.815 1.808 1.804 1.799 1.794 1.787 1.783 1.776 1.770 1.767 1.763 1.752 1.747 1.741 1.729 1.391 1.385 1.376 1.370 1.361 1.355
O
Ph
1H NMR (500 MHz, Chloroform-d)
2.00 2.00 4.00 2.07 1.00 1.03 1.05 1.01 1.00 1.00 3.05 1.03
143.048 139.974 137.983 130.388 129.044 128.403 128.255 127.256 126.832 126.672 113.862 77.736 67.736 36.083 31.257 25.685
13C NMR (126 MHz, Chloroform-d)

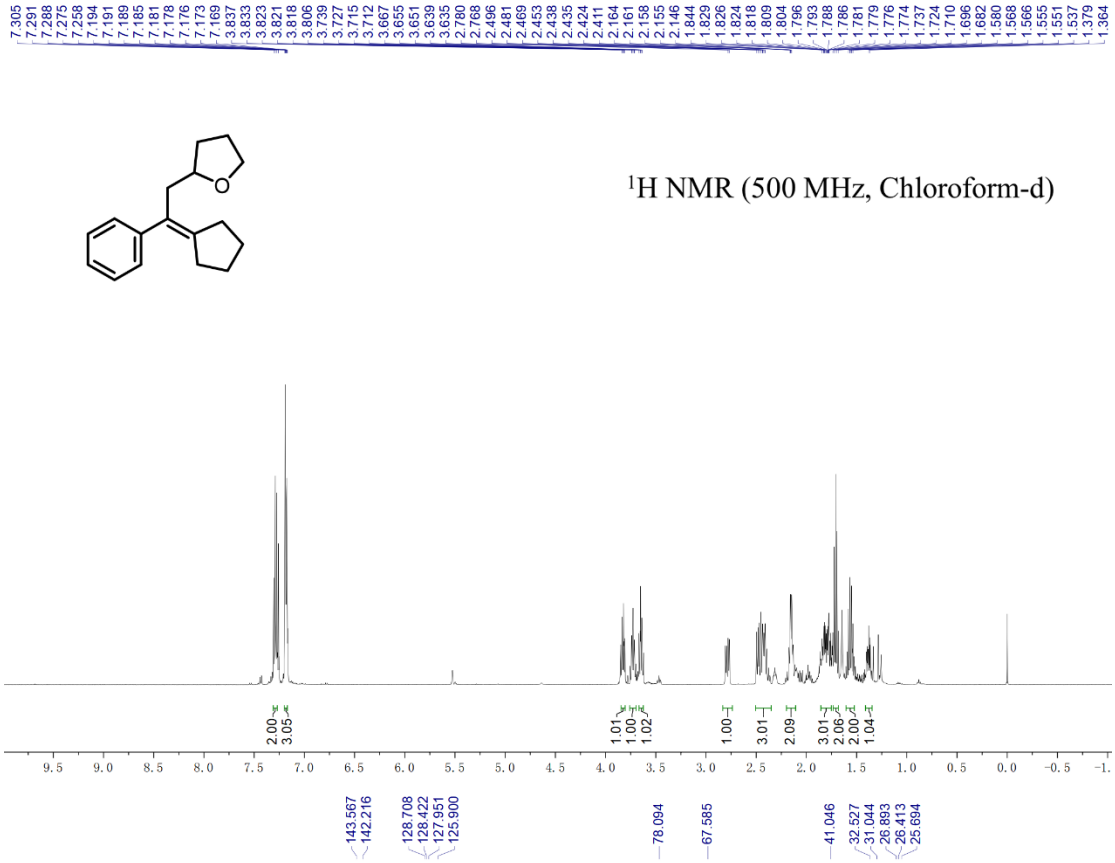
Compound **4u**


7.417
7.413
7.410
7.404
7.400
7.395
7.376
7.362
7.358
7.349
7.345
7.338
7.334
7.325
7.321
7.275
7.272
7.266
7.260
7.244
6.755
3.872
3.864
3.859
3.845
3.830
3.822
3.817
3.813
3.804
3.800
3.792
3.787
3.779
3.669
3.663
3.657
3.653
3.641
3.637
3.625
3.085
3.070
3.056
3.042
2.830
2.818
2.802
2.790
1.829
1.822
1.818
1.813
1.808
1.802
1.798
1.790
1.785
1.779
1.767
1.761
1.748
1.746
1.397
1.392
1.386
1.378
1.371
1.363
Cl
Ph
1H NMR (500 MHz, Chloroform-d)
8.04
1.01
1.00
2.03
1.00
1.00
1.00
3.04
1.00
141.506
138.885
137.644
132.990
130.788
129.739
128.997
128.524
128.292
128.132
126.852
77.612
67.761
36.030
31.314
25.661
Cl
Ph
13C NMR (126 MHz, Chloroform-d)

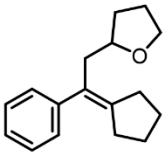
Compound **4v**


7.416
7.399
7.232
7.215
5.721
5.706
5.692
3.859
3.847
3.843
3.832
3.827
3.816
3.787
3.783
3.771
3.759
3.756
3.682
3.676
3.670
3.666
3.659
3.654
3.650
3.638
2.866
2.854
2.838
2.826
2.634
2.619
2.606
2.591
2.218
2.203
2.188
2.173
1.894
1.879
1.864
1.861
1.857
1.849
1.842
1.827
1.801
1.798
1.790
1.786
1.781
1.776
1.773
1.768
1.764
1.759
1.491
1.483
1.476
1.462
1.447
1.432
1.408
1.399
1.392
1.384
1.375
0.970
0.956
0.941
Br
1H NMR (500 MHz, Chloroform-d)
2.00
2.01
1.00
2.04
1.06
1.00
1.00
2.03
1.07
2.06
2.02
1.06
3.00
142.342
136.046
131.845
131.258
128.197
120.390
78.025
67.699
35.609
31.012
30.920
25.621
22.916
13.962
Br
13C NMR (126 MHz, Chloroform-d)

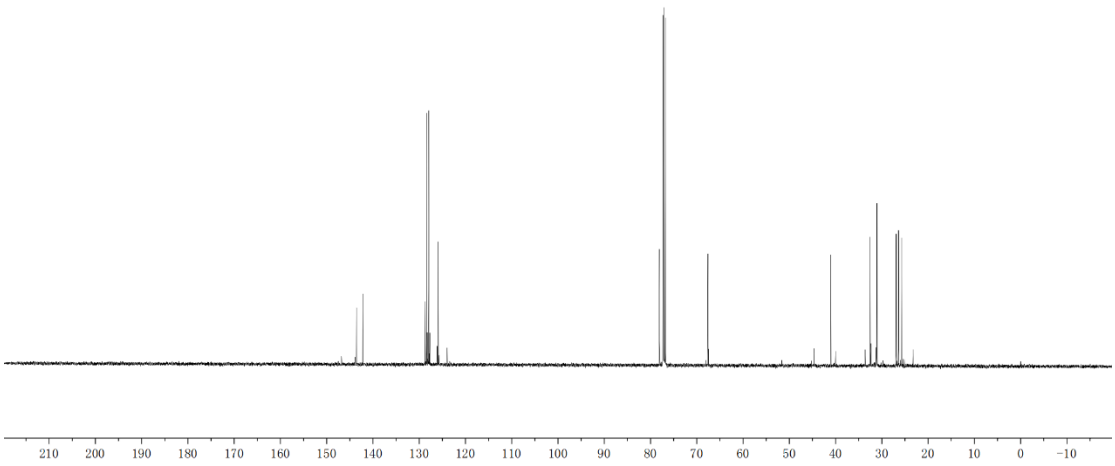
Compound **4w**



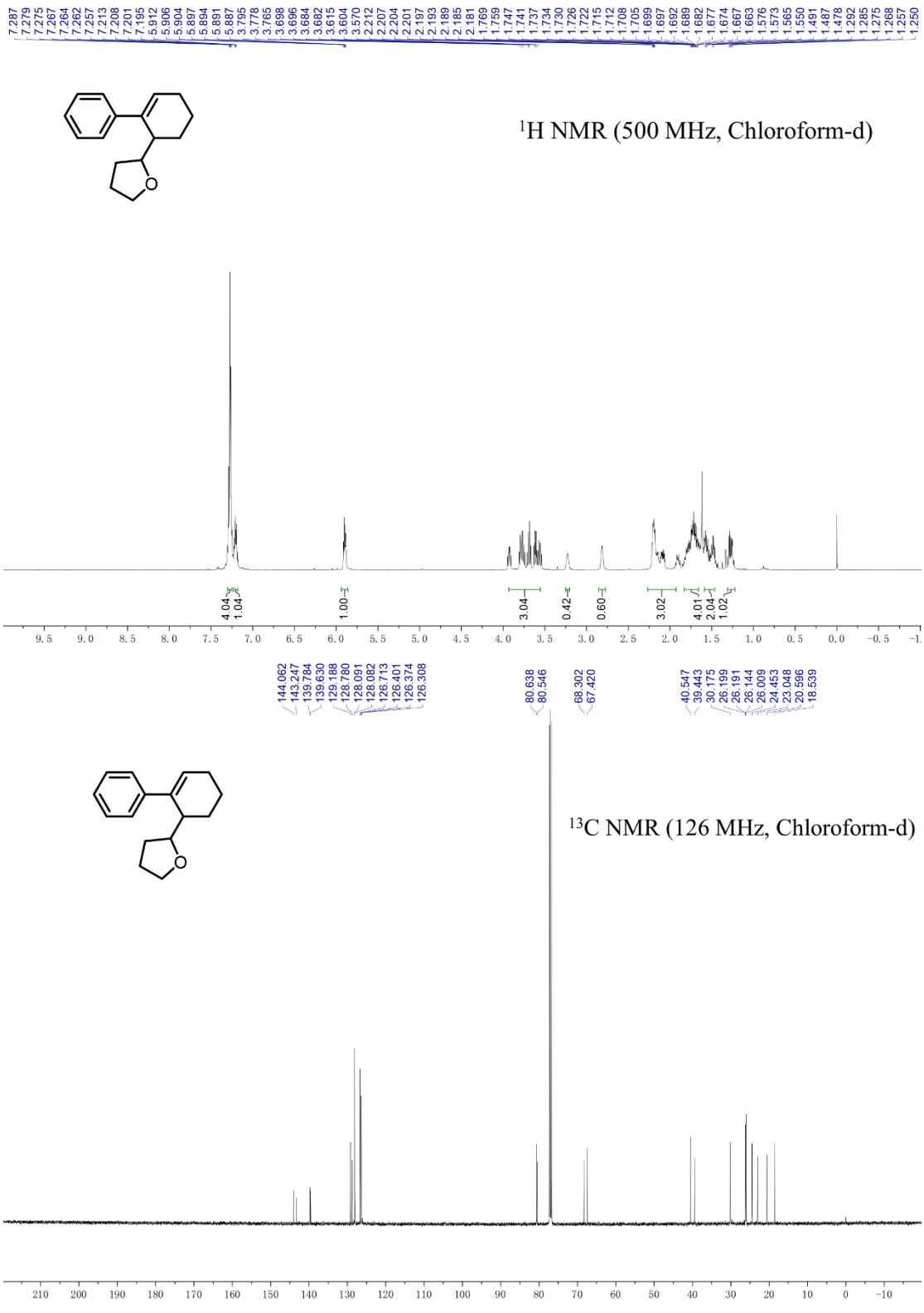
^{1}H NMR (500 MHz, Chloroform-d)



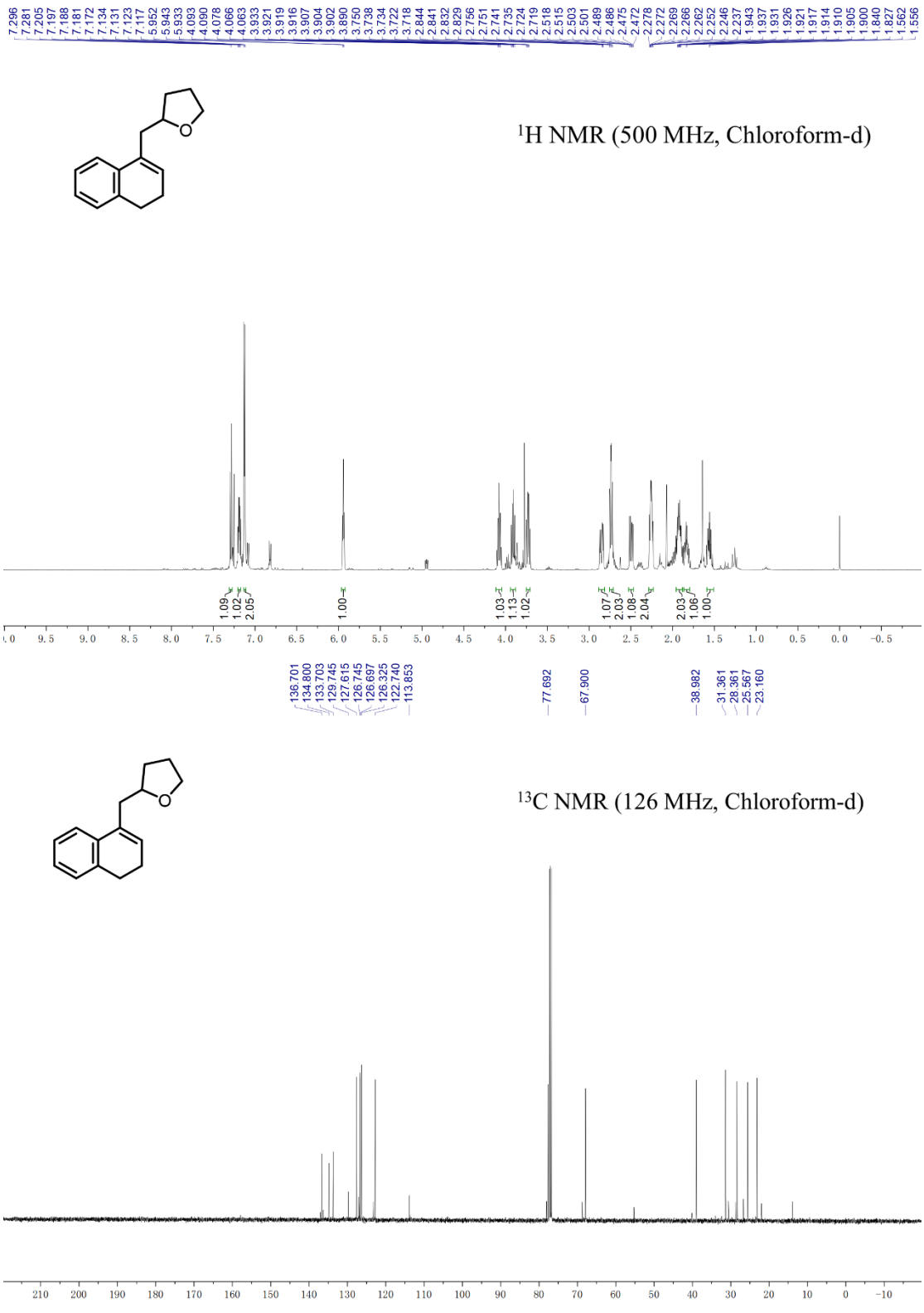
^{13}C NMR (126 MHz, Chloroform-d)



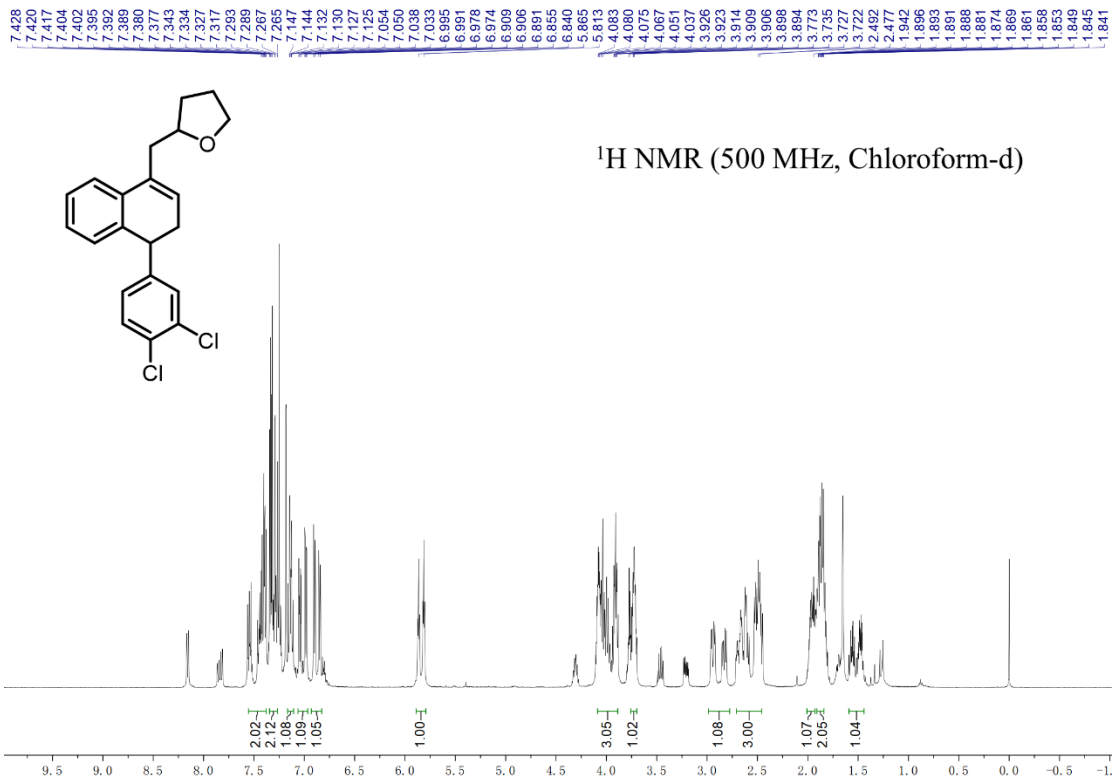
Compound **4x**

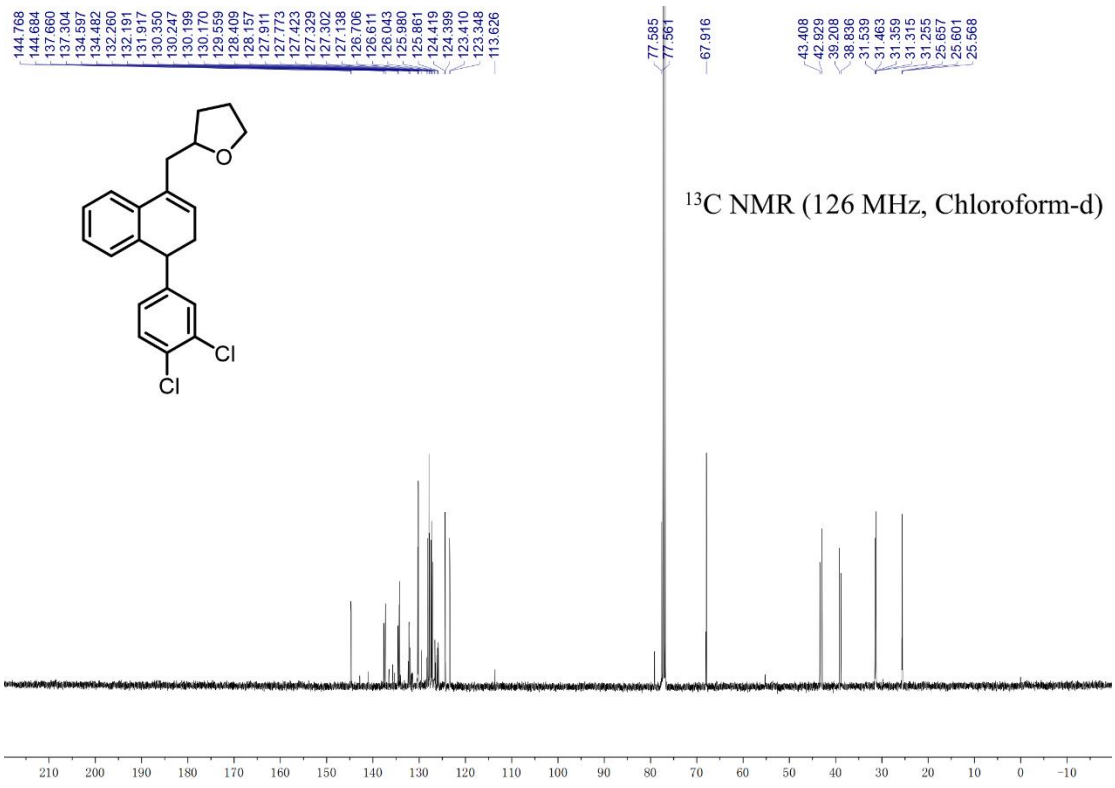

7.287
7.279
7.275
7.267
7.264
7.262
7.257
7.213
7.208
7.201
7.195
5.912
5.906
5.904
5.897
5.894
5.891
5.887
3.795
3.778
3.765
3.698
3.696
3.684
3.682
3.615
3.604
3.570
2.212
2.207
2.204
2.201
2.197
2.193
2.189
2.185
2.181
1.769
1.759
1.747
1.741
1.737
1.734
1.730
1.726
1.722
1.715
1.712
1.708
1.705
1.699
1.697
1.692
1.689
1.682
1.677
1.674
1.667
1.663
1.576
1.573
1.565
1.550
1.491
1.487
1.478
1.292
1.285
1.275
1.268
1.257
1.250
^{1}H NMR (500 MHz, Chloroform-d)
4.04
1.04
1.00
3.04
0.42
0.60
3.02
4.01
2.04
1.02
144.062
143.247
139.784
139.630
129.188
128.780
128.091
128.082
126.713
126.401
126.374
126.308
80.638
80.546
68.302
67.420
40.547
39.443
30.175
26.199
26.191
26.144
26.009
24.453
23.048
20.596
18.539
^{13}C NMR (126 MHz, Chloroform-d)

Compound **4y**

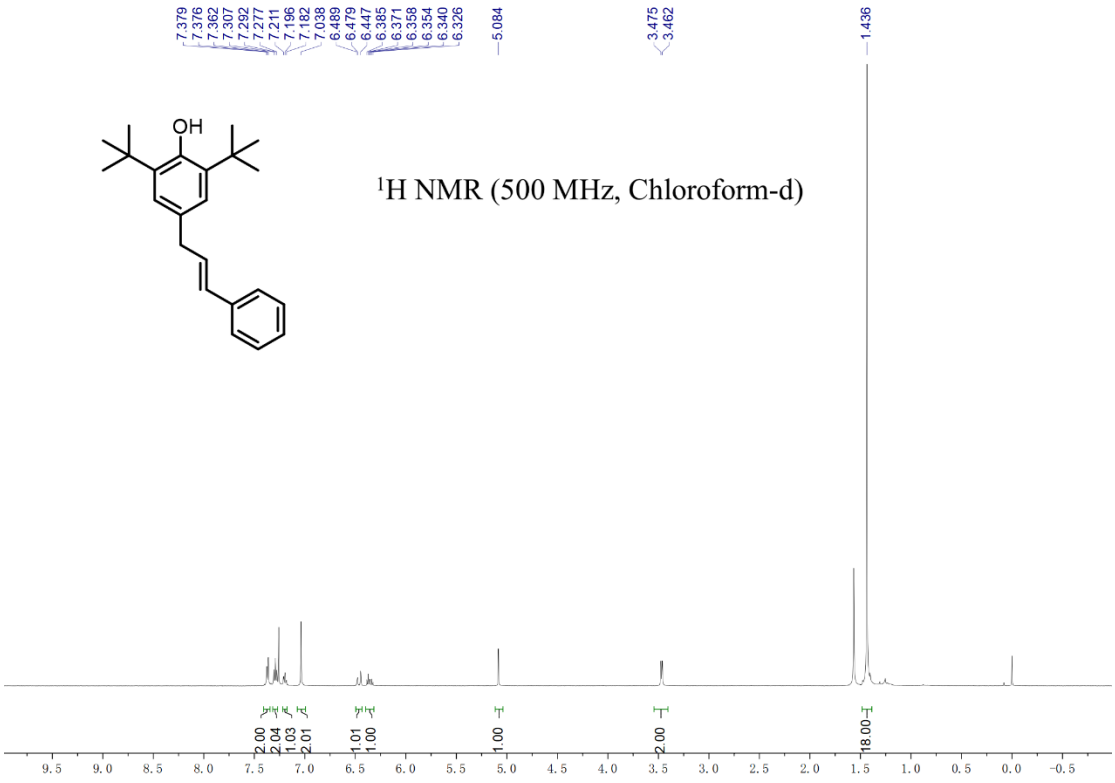

7.296 7.281 7.205 7.197 7.188 7.181 7.172 7.134 7.131 7.123 7.117 5.952 5.943 5.933 4.093 4.090 4.078 4.066 4.063 3.933 3.921 3.919 3.916 3.907 3.904 3.902 3.890 3.750 3.738 3.734 3.722 3.718 2.844 2.841 2.832 2.829 2.756 2.751 2.741 2.735 2.724 2.719 2.518 2.515 2.503 2.501 2.489 2.486 2.475 2.472 2.278 2.272 2.269 2.266 2.262 2.252 2.246 2.237 1.943 1.937 1.931 1.926 1.921 1.917 1.914 1.910 1.905 1.900 1.840 1.827 1.562 1.556
1H NMR (500 MHz, Chloroform-d)
1.09 1.02 2.05 1.00 1.03 1.13 1.02 1.07 2.03 1.08 2.04 2.03 1.06 1.00
136.701 134.800 133.703 129.745 127.615 126.745 126.697 126.325 122.740 113.853 77.692 67.900 38.982 31.361 28.361 25.567 23.160
13C NMR (126 MHz, Chloroform-d)

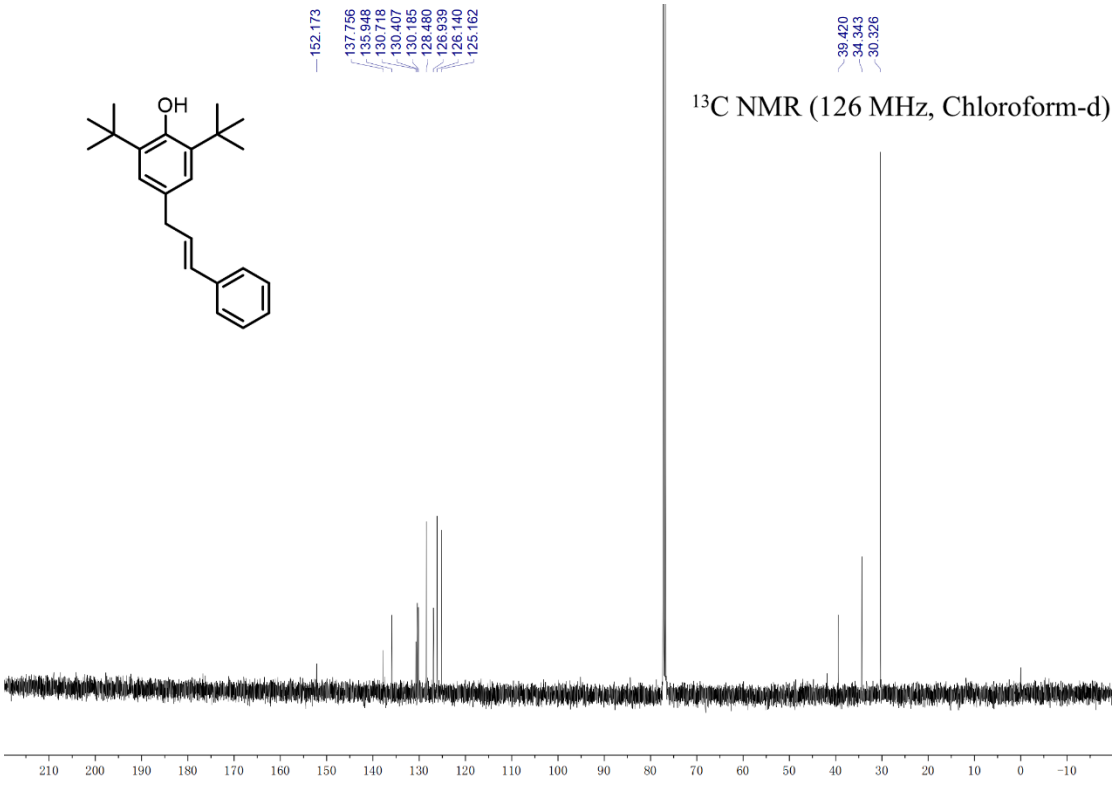
Compound **4z**


7.428 7.420 7.417 7.404 7.402 7.395 7.392 7.389 7.380 7.377 7.343 7.334 7.327 7.317 7.293 7.289 7.267 7.265 7.147 7.144 7.132 7.130 7.127 7.125 7.054 7.050 7.038 7.033 6.995 6.991 6.978 6.974 6.909 6.906 6.891 6.855 6.840 5.865 5.813 4.083 4.080 4.075 4.067 4.051 4.037 3.926 3.923 3.914 3.909 3.906 3.898 3.894 3.773 3.735 3.727 3.722 2.492 2.477 1.942 1.896 1.893 1.891 1.888 1.881 1.874 1.869 1.861 1.858 1.853 1.849 1.845 1.841
^{1}H NMR (500 MHz, Chloroform-d)
Cl
Cl
2.02 2.12 1.08 1.09 1.05 1.00 3.05 1.02 1.08 3.00 1.07 2.05 1.04
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5 −1.

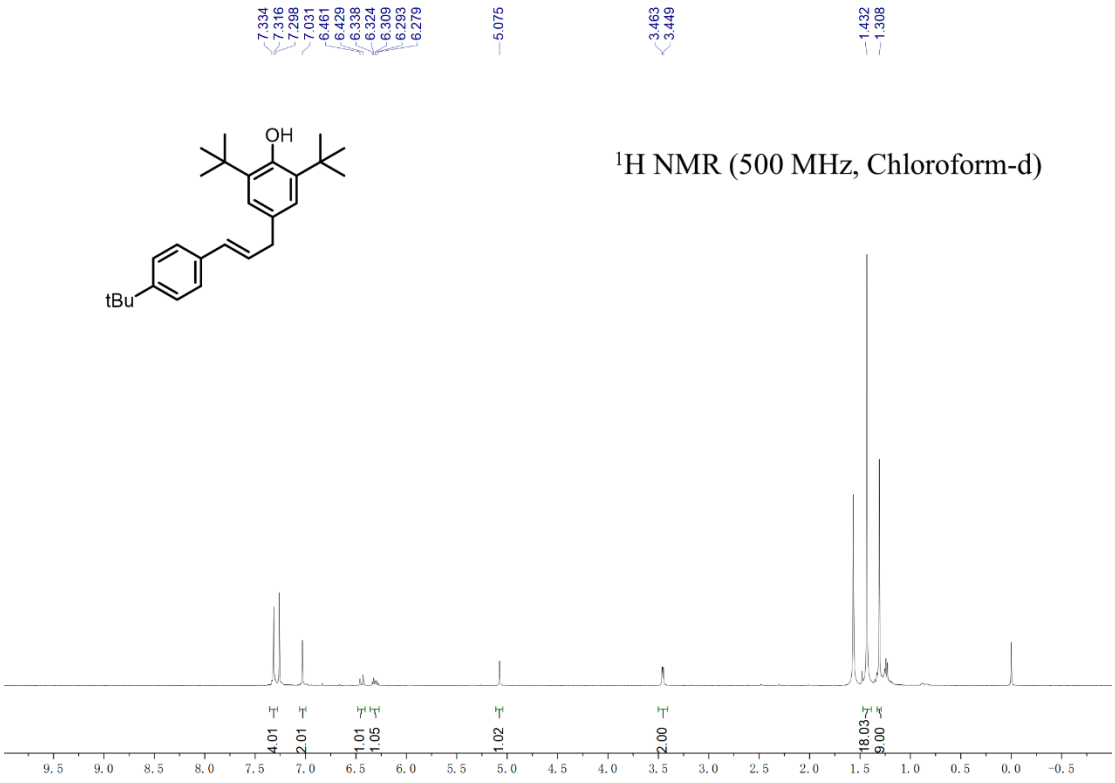

144.768 144.684 137.660 137.304 134.597 134.482 132.260 132.191 131.917 130.350 130.247 130.199 130.170 129.559 128.409 128.157 127.911 127.773 127.423 127.329 127.302 127.138 126.706 126.611 126.043 125.980 125.861 124.419 124.399 123.410 123.348 113.626
77.585 77.561 67.916
43.408 42.929 39.208 38.836 31.539 31.463 31.359 31.315 31.255 25.657 25.601 25.568
^{13}C NMR (126 MHz, Chloroform-d)
Cl
Cl
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10

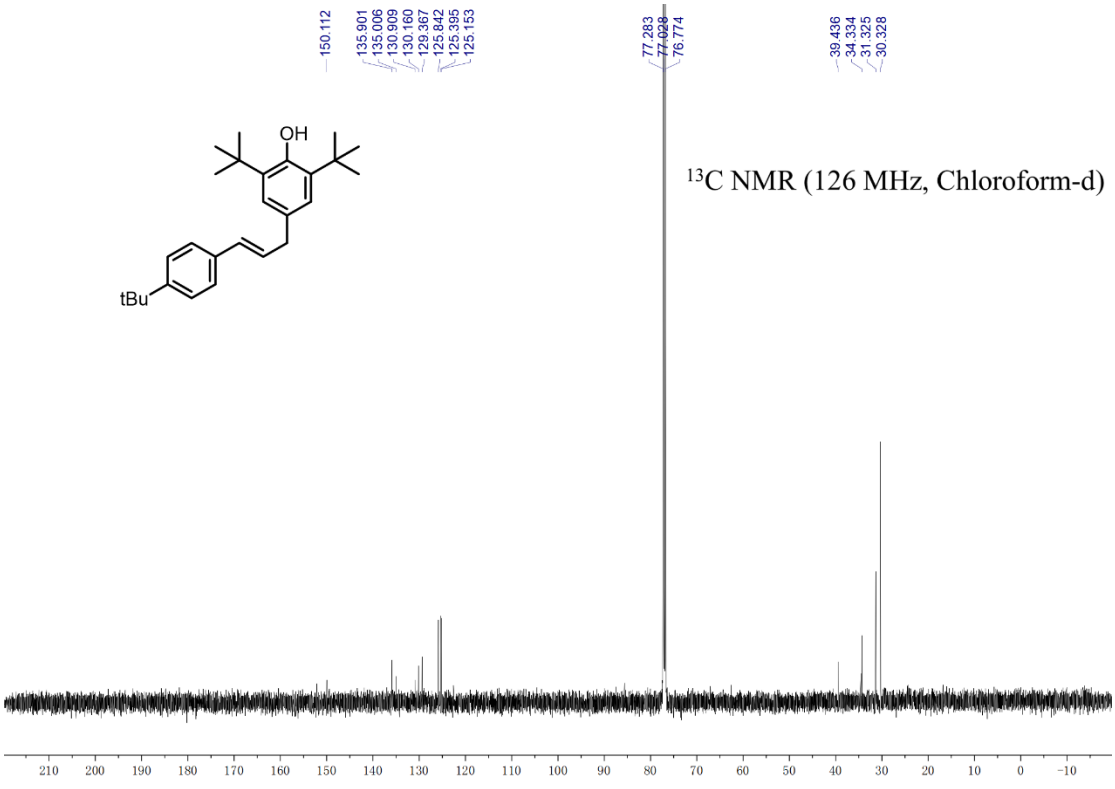
Compound **7a**


7.379
7.376
7.362
7.307
7.292
7.277
7.211
7.196
7.182
7.038
6.489
6.479
6.447
6.385
6.371
6.358
6.354
6.340
6.326
5.084
3.475
3.462
1.436
OH
^{1}H NMR (500 MHz, Chloroform-d)
2.00
2.04
1.03
2.01
1.01
1.00
1.00
2.00
18.00

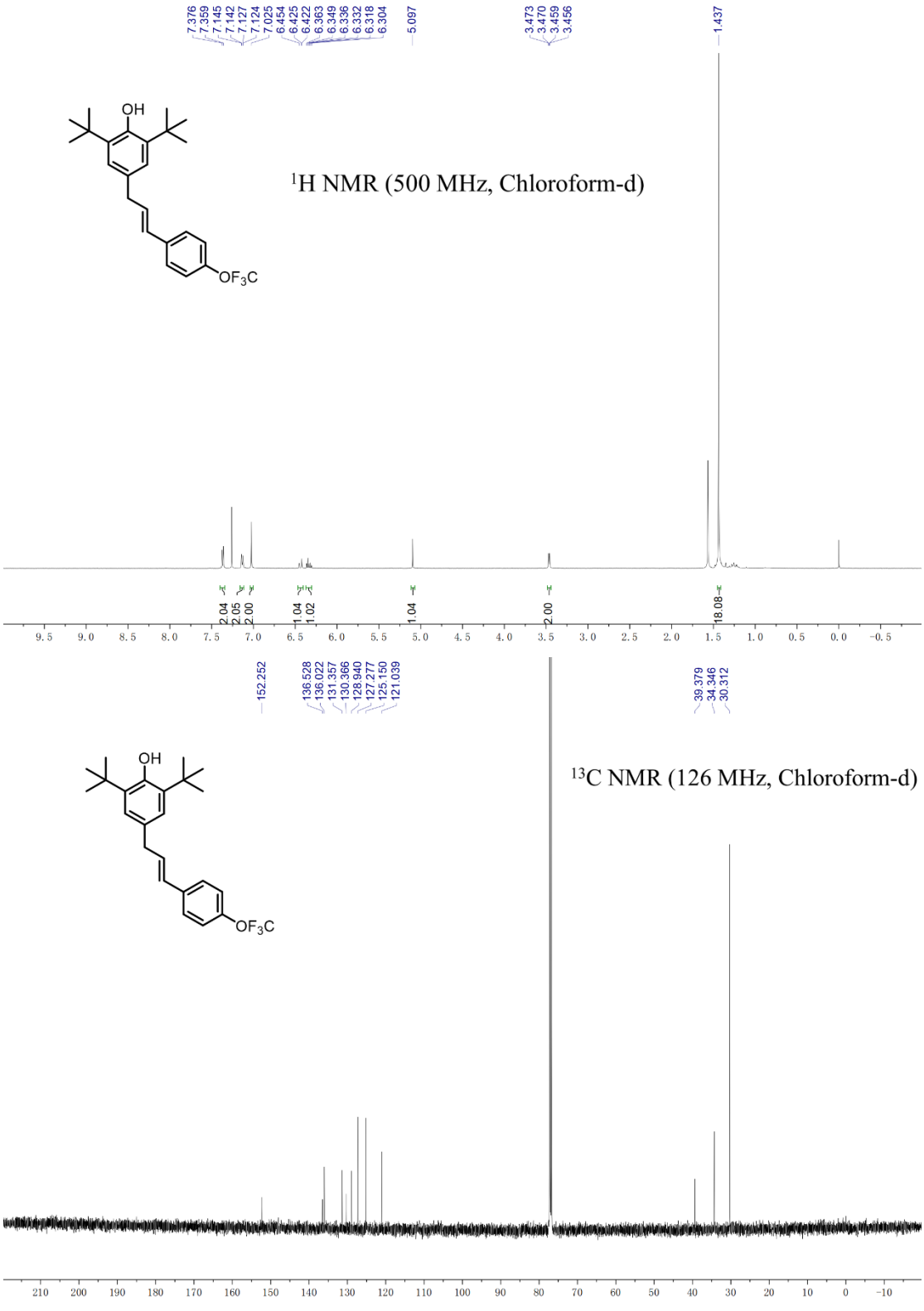

152.173
137.756
135.948
130.718
130.407
130.185
128.480
126.939
126.140
125.162
39.420
34.343
30.326
OH
^{13}C NMR (126 MHz, Chloroform-d)

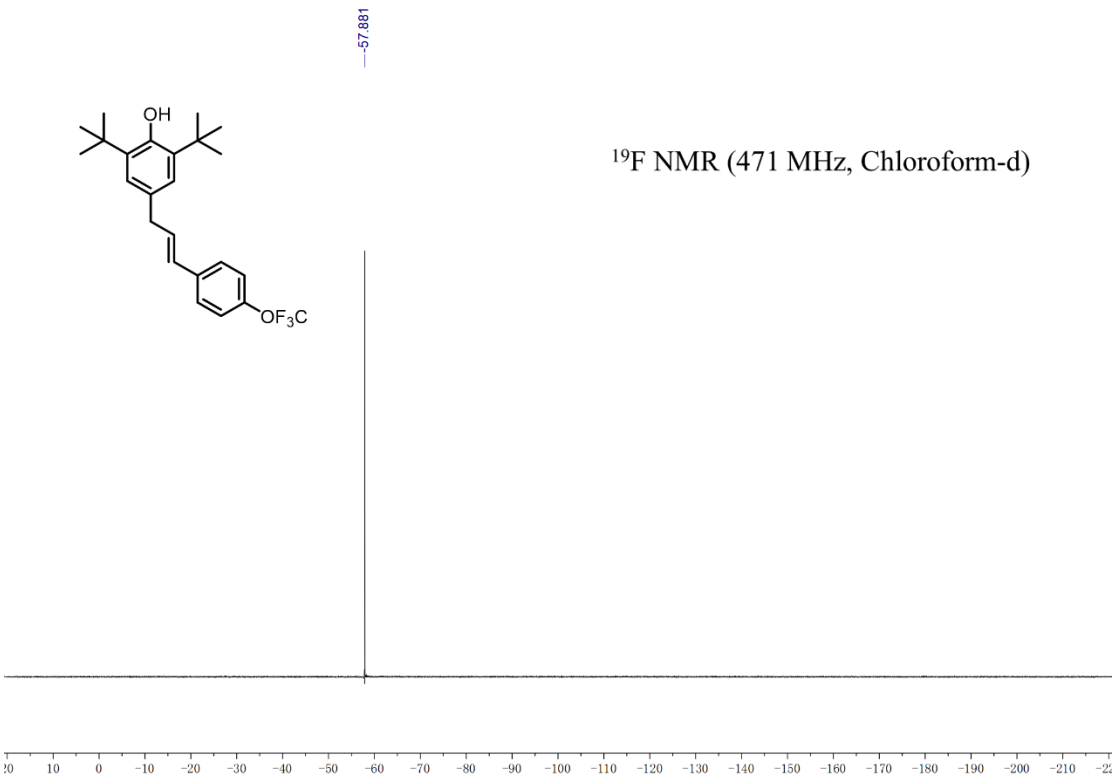
Compound **7b**


7.334
7.316
7.298
7.031
6.461
6.429
6.338
6.324
6.309
6.293
6.279
5.075
3.463
3.449
1.432
1.308
OH
tBu
^{1}H NMR (500 MHz, Chloroform-d)
4.01
2.01
1.01
1.05
1.02
2.00
18.03
9.00


150.112
135.901
135.006
130.909
130.160
129.367
125.842
125.395
125.153
77.283
77.028
76.774
39.436
34.334
31.325
30.328
OH
tBu
^{13}C NMR (126 MHz, Chloroform-d)

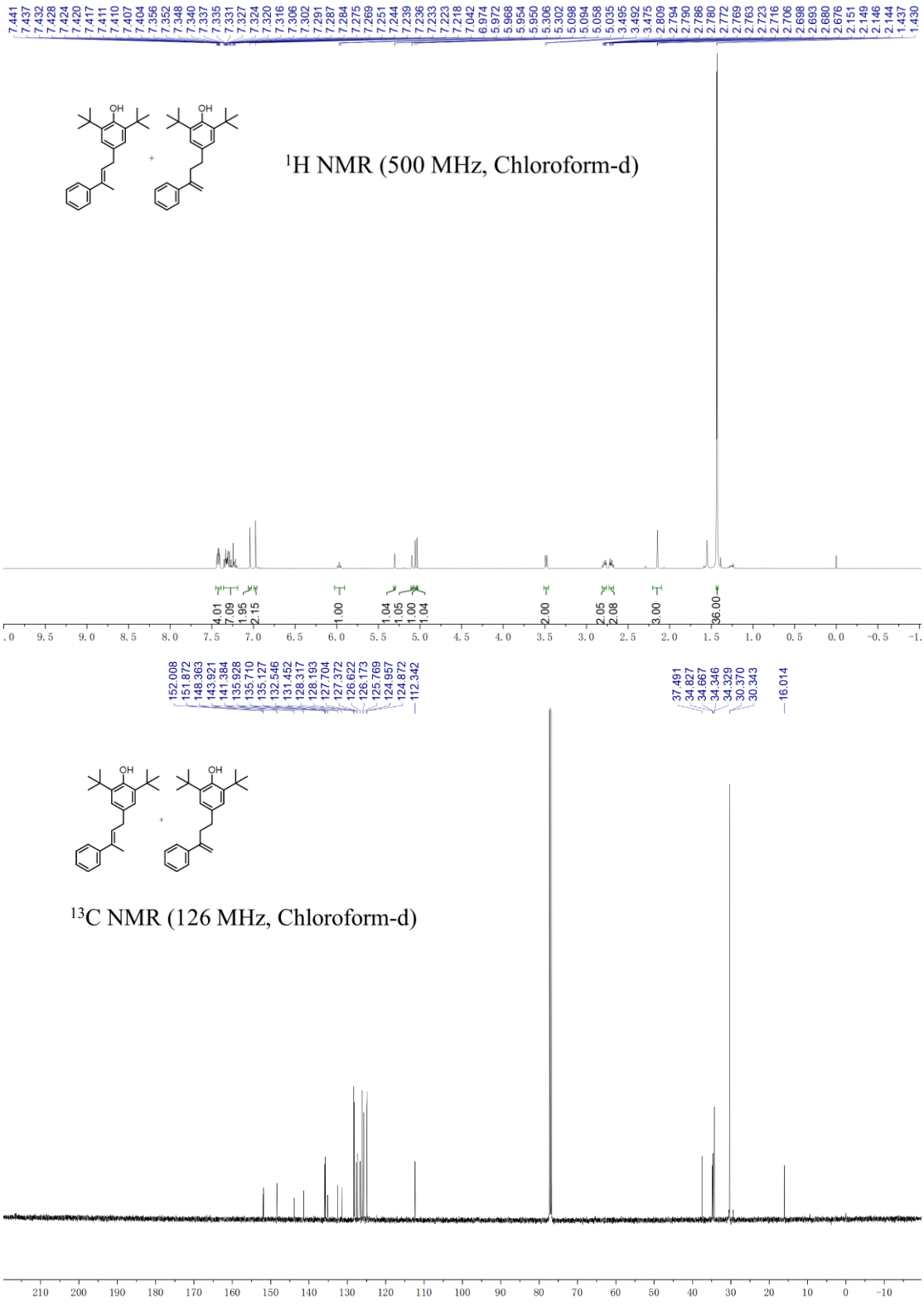
Compound **7c**


7.376
7.359
7.145
7.142
7.127
7.124
7.025
6.454
6.425
6.422
6.363
6.349
6.336
6.332
6.318
6.304
5.097
3.473
3.470
3.459
3.456
1.437
OH
OF3C
1H NMR (500 MHz, Chloroform-d)
2.04
2.05
2.00
1.04
1.02
1.04
2.00
18.08
152.252
136.528
136.022
131.357
130.366
128.940
127.277
125.150
121.039
39.379
34.346
30.312
OH
OF3C
13C NMR (126 MHz, Chloroform-d)

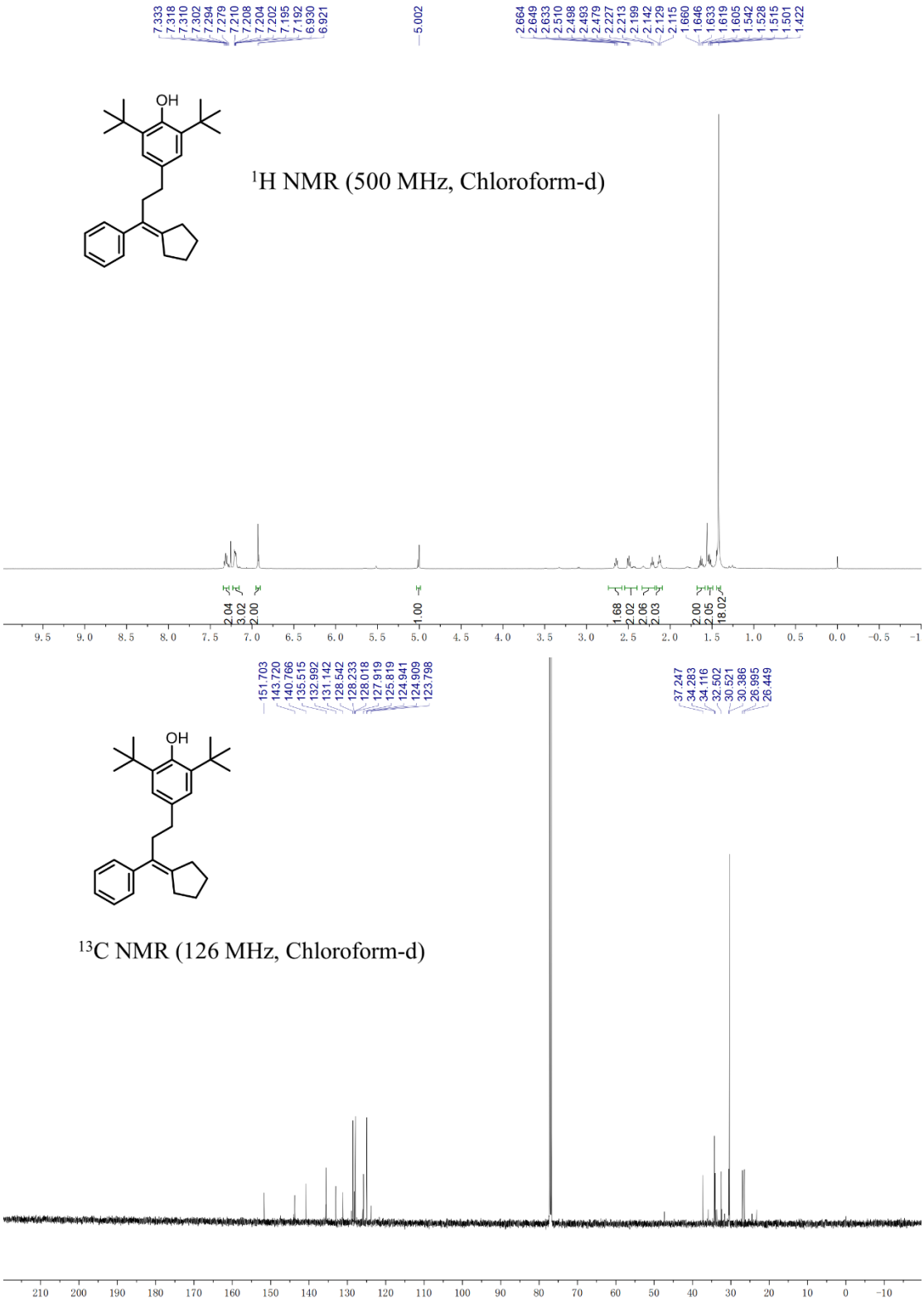


^{19}F NMR (471 MHz, Chloroform-d)

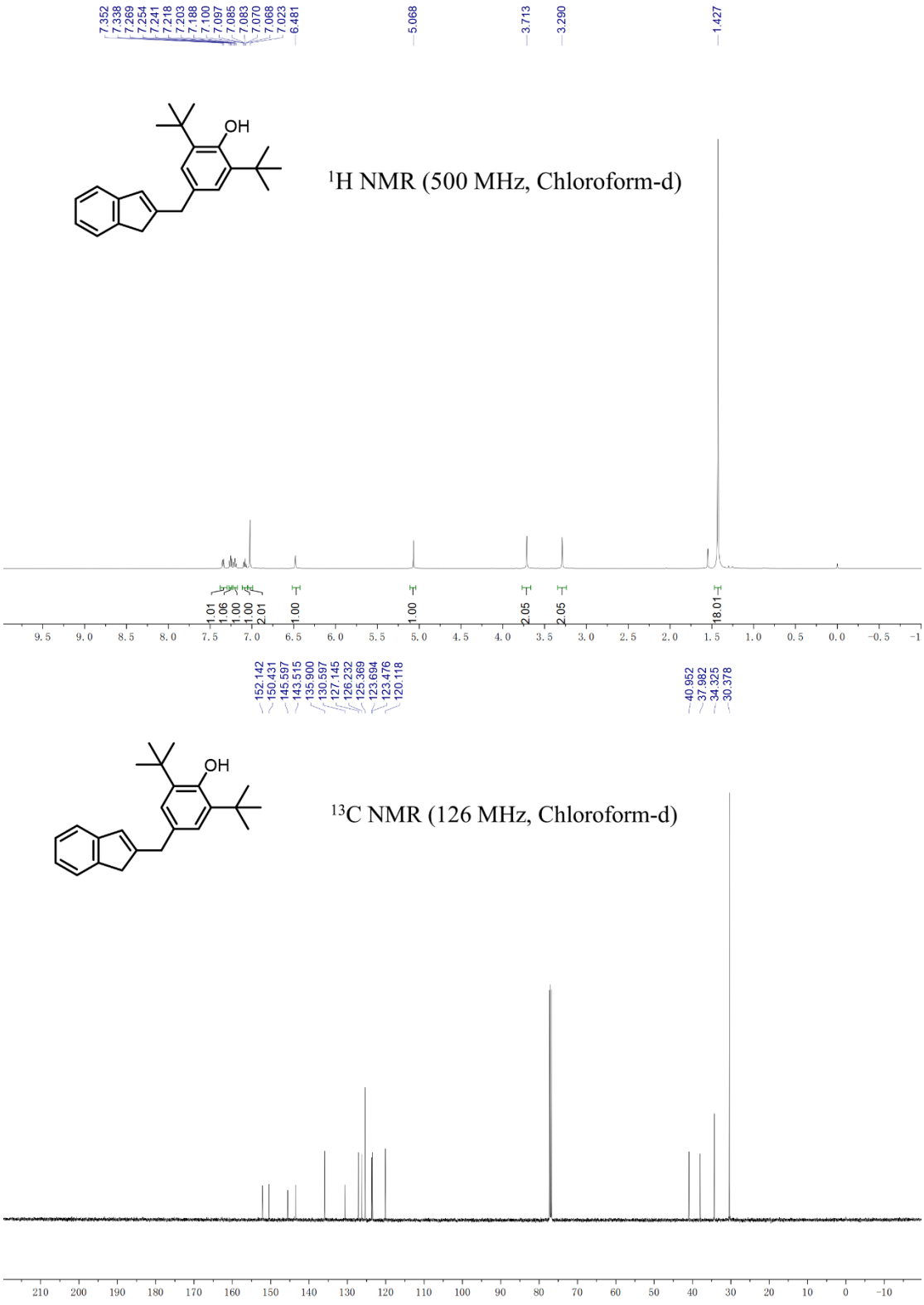
Compounds **7d** and **7d′**



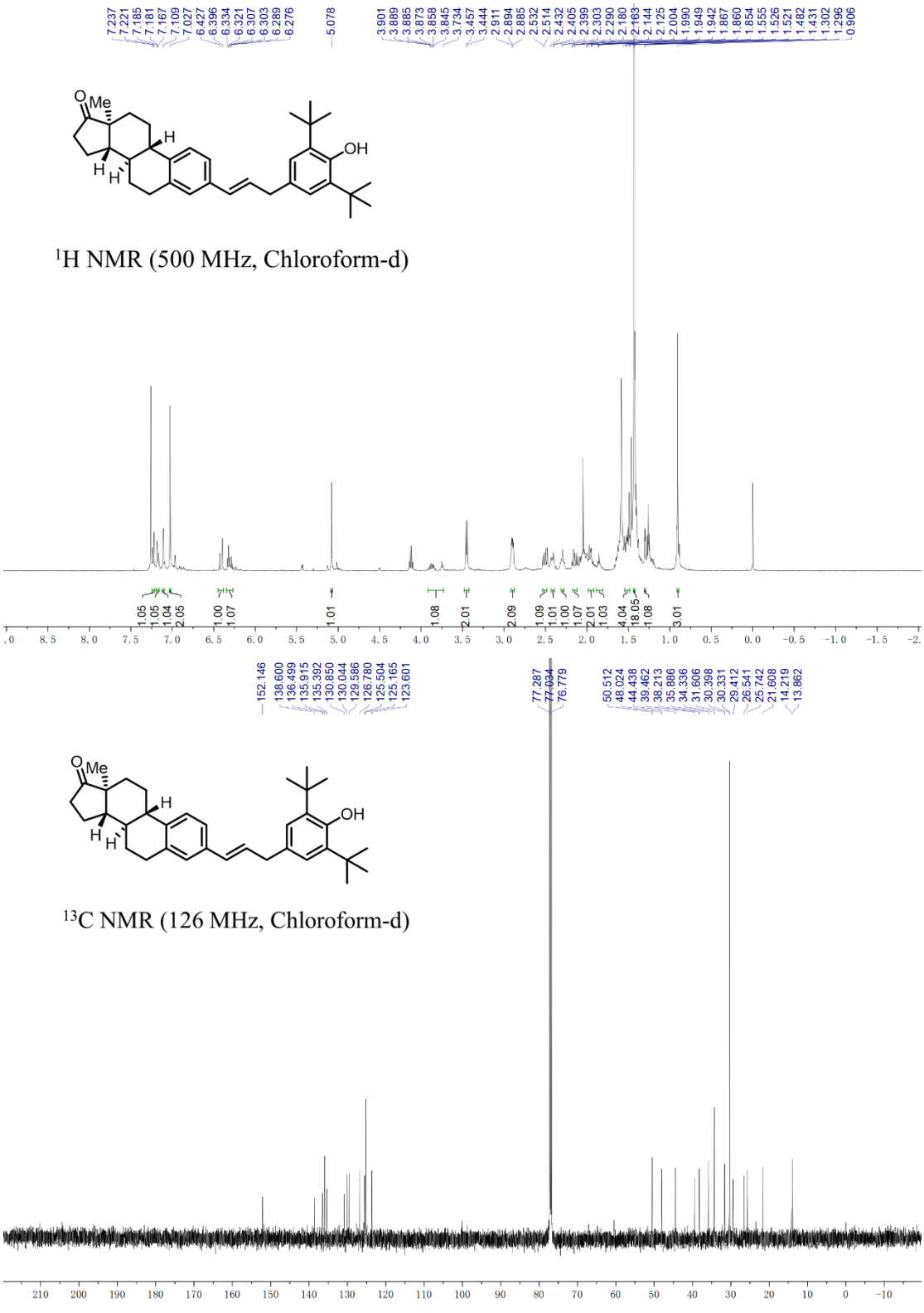
Compound **7e**


7.333
7.318
7.310
7.302
7.294
7.279
7.210
7.208
7.204
7.202
7.195
7.192
6.930
6.921
5.002
2.664
2.649
2.633
2.510
2.498
2.493
2.479
2.227
2.213
2.199
2.142
2.129
2.115
1.660
1.646
1.633
1.619
1.605
1.542
1.528
1.515
1.501
1.422
OH
[1]H NMR (500 MHz, Chloroform-d)
2.04
3.02
2.00
1.00
1.68
2.02
2.06
2.03
2.00
2.05
18.02
151.703
143.720
140.766
135.515
132.992
131.142
128.542
128.233
128.018
127.919
125.819
124.941
124.909
123.798
37.247
34.283
34.116
32.502
30.521
30.386
26.995
26.449
OH
[13]C NMR (126 MHz, Chloroform-d)

Compound **7f**


7.352
7.338
7.269
7.254
7.241
7.218
7.203
7.188
7.100
7.097
7.085
7.083
7.070
7.068
7.023
6.481
5.068
3.713
3.290
1.427
OH
^{1}H NMR (500 MHz, Chloroform-d)
1.01
1.06
1.00
1.00
2.01
1.00
1.00
2.05
2.05
18.01
152.142
150.431
145.597
143.515
135.900
130.597
127.145
126.232
125.369
123.694
123.476
120.118
40.952
37.982
34.325
30.378
OH
^{13}C NMR (126 MHz, Chloroform-d)

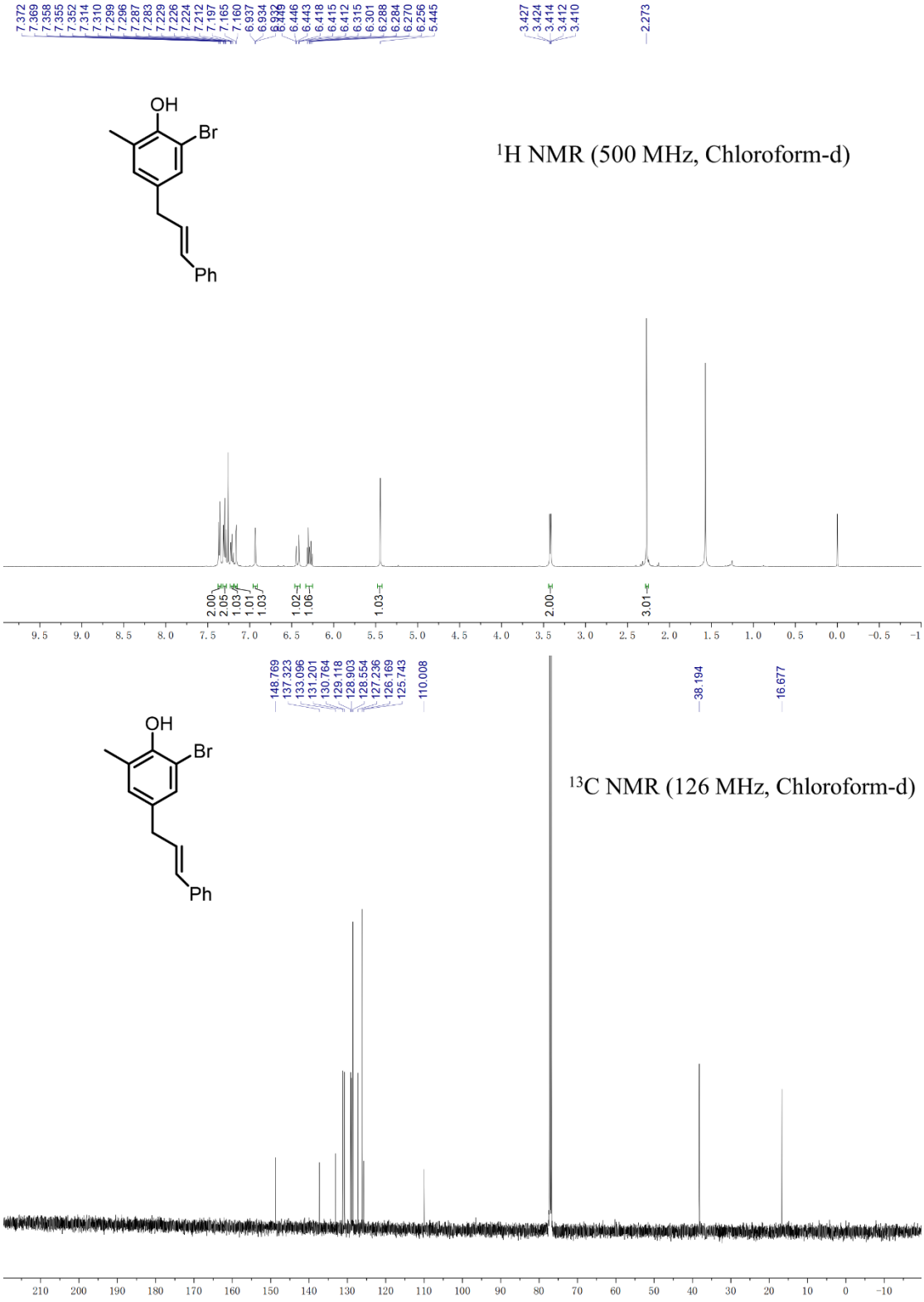
Compound **7g**



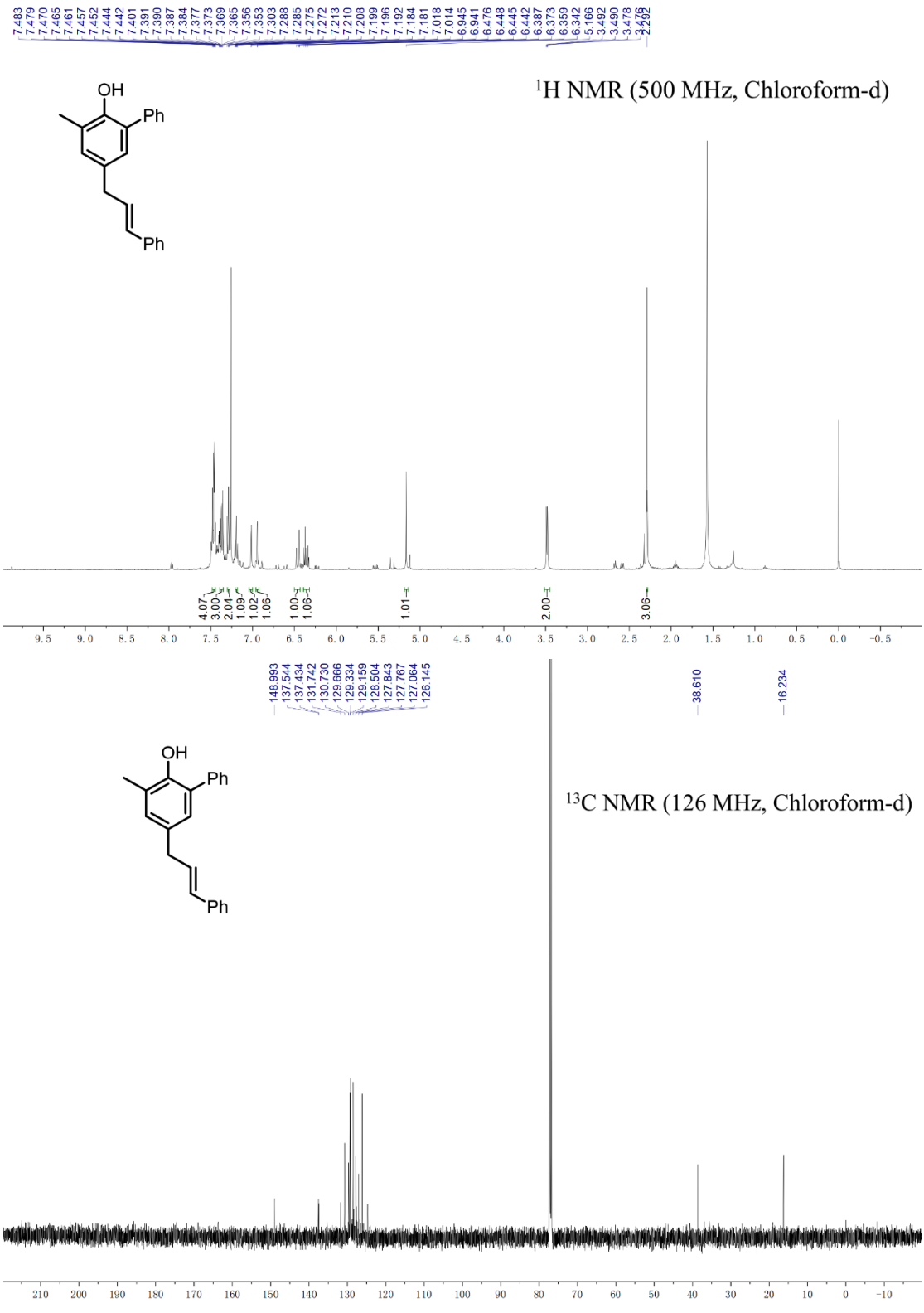
^{1}H NMR (500 MHz, Chloroform-d)

^{13}C NMR (126 MHz, Chloroform-d)

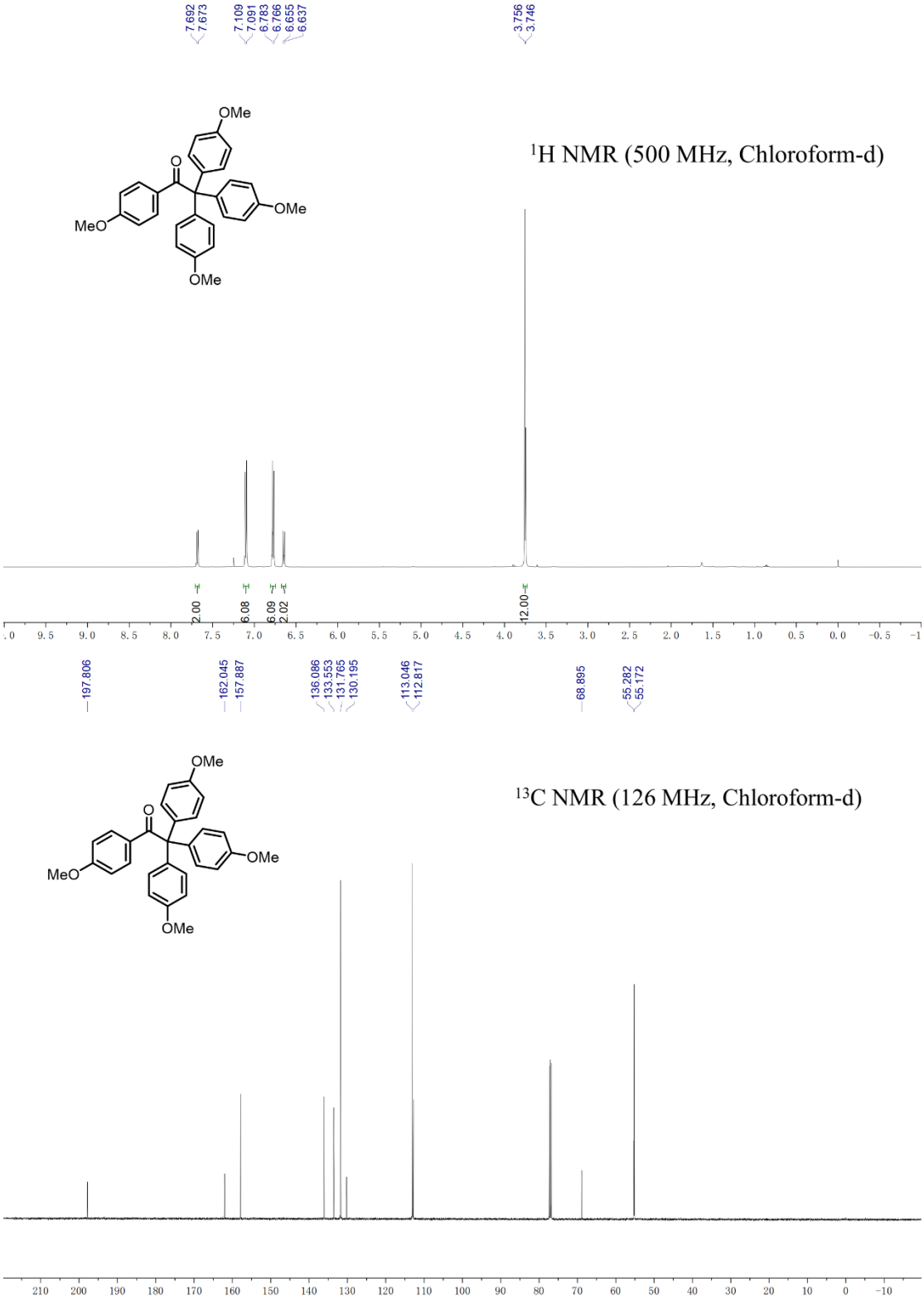
Compound **7h**


7.372
7.369
7.358
7.355
7.352
7.314
7.310
7.299
7.296
7.287
7.283
7.229
7.226
7.224
7.212
7.197
7.165
7.160
6.937
6.934
6.446
6.443
6.418
6.415
6.412
6.315
6.301
6.288
6.284
6.270
6.256
5.445
3.427
3.424
3.414
3.412
3.410
2.273
OH
Br
Ph
1H NMR (500 MHz, Chloroform-d)
2.00
2.05
1.03
1.01
1.03
1.02
1.06
1.03
2.00
3.01
148.769
137.323
133.096
131.201
130.764
129.118
128.903
128.554
127.236
126.169
125.743
110.008
38.194
16.677
13C NMR (126 MHz, Chloroform-d)

Compound **7i**


7.483
7.479
7.470
7.465
7.461
7.457
7.452
7.444
7.442
7.401
7.391
7.390
7.387
7.384
7.377
7.373
7.369
7.365
7.356
7.353
7.303
7.288
7.285
7.275
7.272
7.213
7.210
7.208
7.199
7.196
7.192
7.184
7.181
7.018
7.014
6.945
6.941
6.476
6.448
6.445
6.442
6.387
6.373
6.359
6.342
5.166
3.492
3.490
3.478
OH
Ph
Ph
1H NMR (500 MHz, Chloroform-d)
4.07
3.00
2.04
1.09
1.02
1.06
1.00
1.06
1.01
2.00
3.06
148.993
137.544
137.434
131.742
130.730
129.666
129.334
129.159
128.504
127.843
127.767
127.064
126.145
38.610
16.234
OH
Ph
Ph
13C NMR (126 MHz, Chloroform-d)

Compound **5a**


7.692
7.673
7.109
7.091
6.783
6.766
6.655
6.637
3.756
3.746
OMe
MeO
OMe
OMe
O
^{1}H NMR (500 MHz, Chloroform-d)
2.00
6.08
6.09
2.02
12.00
197.806
162.045
157.887
136.086
133.553
131.765
130.195
113.046
112.817
68.895
55.282
55.172
^{13}C NMR (126 MHz, Chloroform-d)