Supporting Information

Base-Mediated Synthesis of Aryl Enol Ethers from Allylic Alcohols and Arylsulfonium Salts

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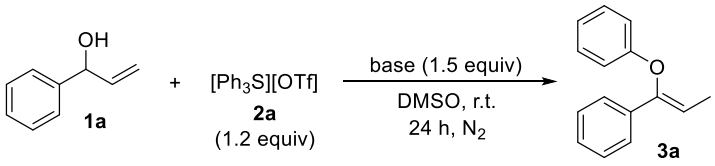
1. General information

All reactions were carried out under a nitrogen atmosphere. Unless otherwise specified, NMR spectra were recorded in $CDCl_3$ on a 500 MHz (for ^1H), 471 MHz (for ^{19}F), and 126 MHz (for ^{13}C) spectrometer. All chemical shifts were reported in ppm relative to TMS (0 ppm for ^1H NMR) or $PhCF_3$ (-63.5 ppm for ^{19}F NMR) as an internal or external standard. The HPLC experiments were conducted on a Wufeng LC-100 II instrument (column: Shodex, C18, 5 μm, 4.6 × 250 mm), and the yields of product were determined by using the corresponding pure compound as an external standard. The coupling constants were reported in Hertz (Hz). The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, brs = broad singlet, dd = doublet of doublets, td = triplet of doublets, dm = doublet of multiplets, and tm = triplet of multiplets. Melting points of solid products were measured and uncorrected. MS experiments were performed on a TOF-Q ESI instrument. Dibenzo[*b*,*d*]thiophene 5-oxide (DBTO),[1] thianthrene 5-oxide (TTO),[2] phenoxathiine 10-oxide,[3] 10-methyl-10*H*-phenothiazine 5-oxide,[4] and aryl sulfonium salts[5,6] were prepared according to the literature. Allylic alcohols were prepared according to the literature.[7] Solvents were dried before use according to the literature. Other reagents used in the reactions were all purchased from the commercial sources and used without further purification. Reactions that require heating employed oil bath as the heat source.

2. Screening of the optimal reaction conditions for the base-mediated synthesis of aryl enol ether

Table S1. Transition-metal-free synthesis of aryl enol ether (**3a**) from **1a** and **2a** in the presence of different bases.[a]

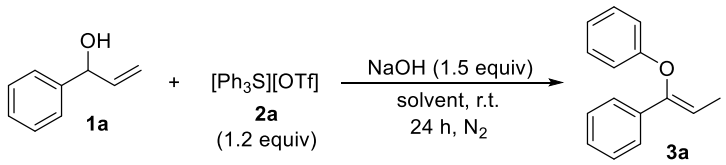


Entry	Base	Yield (**3a**, %)
1	K_2HPO_4	0
2	K_3PO_4	7
3	**NaOH**	**89**

4	KOH	84
5	*t*-BuOK	55
6	NaH	68
7	$NaHCO_3$	trace
8	Na_2CO_3	0
9	K_2CO_3	0
10	LiOH	10
11	CsOH	87
12	Cs_2CO_3	19
13	DBU	trace
14	Et_3N	trace
15 [b]	NaOH	78

[a] Reaction conditions: **1a** (0.1 mmol), **2a** (0.12 mmol), base (0.15 mmol), DMSO (1 mL), room temperature, N_2, and 24 h. The yields were determined by HPLC using pure **3a** as an external standard (t_R = 10.5 min, λ_{max} = 252 nm, water / methanol = 20 / 80 (v / v)). [b] The reaction was run under an air atmosphere.

Table S2. NaOH-mediated synthesis of **3a** from **1a** and **2a** in different solvents.[a]

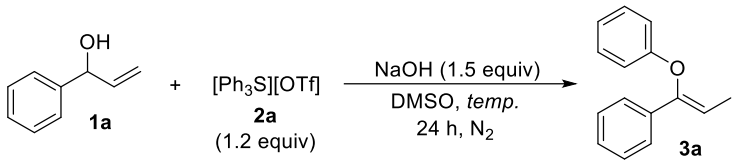


Entry	Solvent	Yield (**3a**, %)
1	**DMSO**	**89**
2	DMF	38
3	THF	trace
4	MeCN	trace
5	1,4-dioxane	trace
6	DMAc	47
7	DG	13
8	*n*-hexane	trace
9	acetone	13

[a] Reaction conditions: **1a** (0.1 mmol), **2a** (0.12 mmol), NaOH (0.15 mmol), solvent (1

mL), room temperature, N_2, and 24 h. The yields were determined by HPLC using pure **3a** as an external standard (t_R = 10.5 min, λ_{max} = 252 nm, water / methanol = 20 / 80 (v / v)).

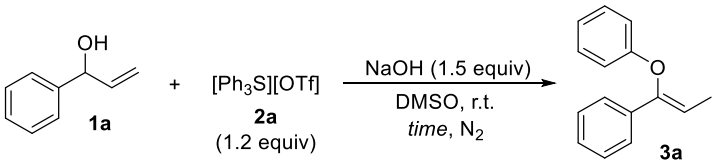
Table S3. NaOH-mediated synthesis of **3a** from **1a** and **2a** at different temperatures.[a]



Entry	Temperature (^oC)	Yield (**3a**, %)
1	**r.t.**	**89**
2	40	92
3	60	91
4	80	94

[a] Reaction conditions: **1a** (0.1 mmol), **2a** (0.12 mmol), NaOH (0.15 mmol), DMSO (1 mL), room temperature to 80 ^{o}C, N_2, and 24 h. The yields were determined by HPLC using pure **3a** as an external standard (t_R = 10.5 min, λ_{max} = 252 nm, water / methanol = 20 / 80 (v / v)).

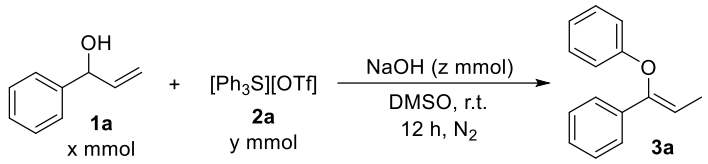
Table S4. NaOH-mediated synthesis of **3a** from **1a** and **2a** in different times.[a]



Entry	Time (h)	Yield (**3a**, %)
1	3	83
2	6	92
3	**12**	**91**
4	24	89

[a] Reaction conditions: **1a** (0.1 mmol), **2a** (0.12 mmol), NaOH (0.15 mmol), DMSO (1 mL), room temperature, N_2, and 3-24 h. The yields were determined by HPLC using pure **3a** as an external standard (t_R = 10.5 min, λ_{max} = 252 nm, water / methanol = 20 / 80 (v / v)).

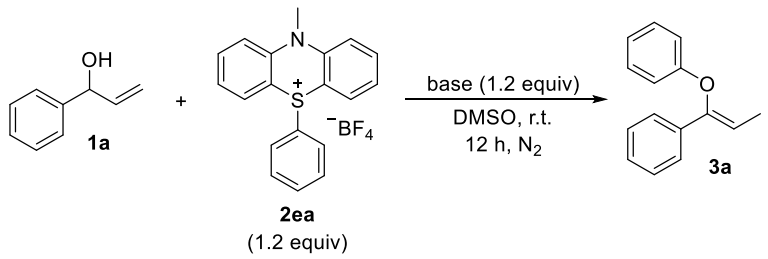
Table S5. NaOH-mediated synthesis of **3a** from **1a** and **2a** using different reactant molar ratios.[a]



Entry	x : y : z	Yield (**3a**, %)
1	1:1.2:1.5	91
2	**1:1.2:1.2**	**87**
3	1:1:1	64

[a] Reaction conditions: **1a** (0.1 mmol), **2a** (0.12 or 0.1 mmol), NaOH (0.12 or 0.15 mmol), DMSO (1 mL), room temperature, N_2, and 12 h. The yields were determined by HPLC using pure **3a** as an external standard (t_R = 10.5 min, λ_{max} = 252 nm, water / methanol = 20 / 80 (v / v)).

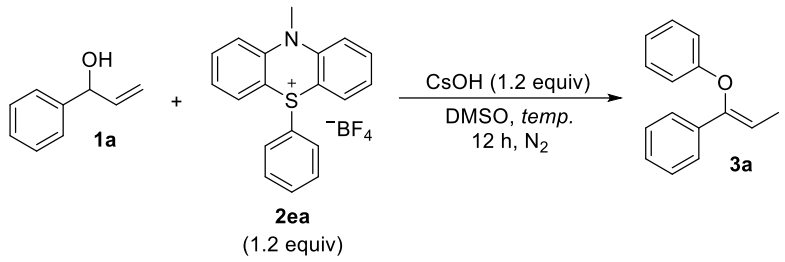
Table S6. Base-mediated synthesis of **3a** from **1a** and **2ea** with different bases.[a]



Entry	Base	Yield (**3a**, %)
1	NaOH	72
2	KOH	66
3	**CsOH**	**76**
4	Cs_2CO_3	9
5	*t*-BuOK	63
6	NaH	66

[a] Reaction conditions: **1a** (0.1 mmol), **2ea** (0.12 mmol), base (0.12 mmol), DMSO (1 mL), room temperature, N_2, and 12 h. The yields were determined by HPLC using pure **3a** as an external standard (t_R = 10.5 min, λ_{max} = 252 nm, water / methanol = 20 / 80 (v / v).

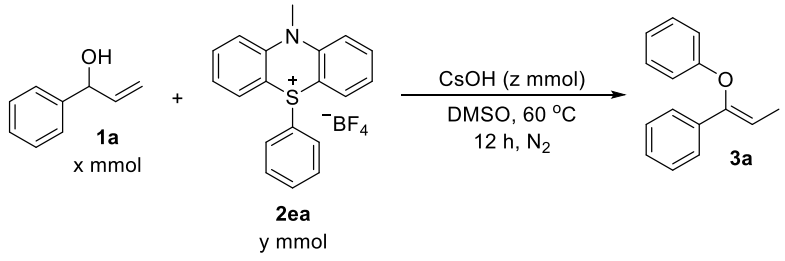
Table S7. Base-mediated synthesis of **3a** from **1a** and **2ea** at different temperatures.[a]



Entry	Temperature (^{o}C)	Yield (**3a**, %)
1	40	77
2	**60**	**79**
3	80	62
4	100	62

[a] Reaction conditions: **1a** (0.1 mmol), **2ea** (0.12 mmol), CsOH (0.12 mmol), DMSO (1 mL), 40-100 ^{o}C, N_2, and 12 h. The yields were determined by HPLC using pure **3a** as an external standard (t_R = 10.5 min, λ_{max} = 252 nm, water / methanol = 20 / 80 (v / v).

Table S8. Base-mediated synthesis of **3a** from **1a** and **2ea** using different reactant molar ratios.[a]



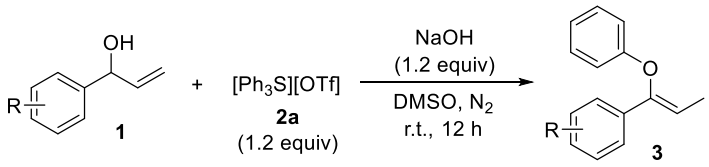
Entry	x : y : z	Yield (**3a**, %)
1	1:1.2:1.2	79, 81[b]
2	1:1.2:1.5	83, 86 [b]
3	1:1.5:1.5	81, 82[b]
4	1:1.5:2	79, 80[b]
5	1:2:2	75, 79[b]

[a] Reaction conditions: **1a** (0.1 mmol), **2ea** (0.12, 0.15, or 0.2 mmol), CsOH (0.12,

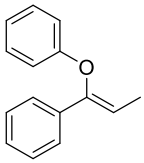
0.15, or 0.2 mmol), DMSO (1 mL), 60 °C, N_2, and 12 h. The yields were determined by HPLC using pure **3a** as an external standard (t_R = 10.5 min, λ_{max} = 252 nm, water / methanol = 20 / 80 (v / v). [b] The reaction was run at 60 °C for 24 h.

3. Based-mediated synthesis of phenyl enol ethers (3) from diverse allylic alcohols (1) with [Ph_3S][OTf] (2a)

General procedure: In a nitrogen-filled glovebox, a sealed tube was charge with **1** (0.1 or 0.2 mmol), triphenylsulfonium triflate (**2a**, 49.5 or 99 mg, 0.12 or 0.24 mmol), NaOH (4.8 or 9.6 mg, 0.12 or 0.24 mmol) or *t*-BuOK (13.5 mg, 0.12 mmol), and DMSO (1.0 or 2.0 mL) with vigorous stirring. The mixture was reacted at room temperature or 60 °C for 12 or 24 h, cooled to room temperature, diluted with water (30 mL), and extracted with ethyl acetate (3 × 20 mL). The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated to dryness under reduced pressure. The residue was purified by flash column chromatography on silica gel using a mixture of petroleum ether (PE) and ethyl acetate (EA) as eluents to give the desired product (**3**).

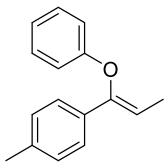


(*Z*)-(1-Phenoxyprop-1-en-1-yl)benzene (**3a**)[8]



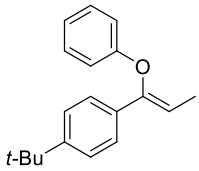
White solid (36.6 mg, 87%, eluents: PE), *Z*/*E* = 50/1. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.50 (d, *J* = 7.5 Hz, 2.04H), 7.29 (t, *J* = 7.5, 2.04H), 7.26-7.23 (m, 3.06H), 6.98 (d, *J* = 8.1 Hz, 2.04H), 6.95 (t, *J* = 7.4 Hz, 1.02H), 5.95 (q, *J* = 6.9 Hz, 1H), 5.49 (q, *J* = 7.5 Hz, 0.02H), 1.87 (d, *J* = 7.3 Hz, 0.06H), 1.77 (d, *J* = 7.0 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 157.3, 149.7, 135.6, 129.5, 128.4, 127.7, 125.1, 121.3, 115.4, 112.4, 11.4.

(*Z*)-1-Methyl-4-(1-phenoxyprop-1-en-1-yl)benzene (**3b**)



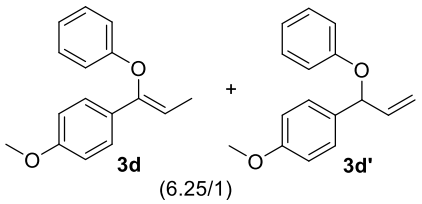
Colorless oil (18.4 mg, 82%, eluents: PE), *Z*/*E* = 25/1. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37 (d, *J* = 8.1 Hz, 2.08H), 7.23 (t, *J* = 7.9 Hz, 2.08H), 7.08 (d, *J* = 8.1 Hz, 2.08H), 6.96 (d, *J* = 8.2 Hz, 2.08H), 6.93 (t, *J* = 7.5 Hz, 1.04H), 5.89 (q, *J* = 6.9 Hz, 1H), 5.45 (q, *J* = 7.3 Hz, 0.04H), 2.33 (s, 0.12H), 2.30 (s, 3H), 1.86 (d, *J* = 7.4 Hz, 0.12H), 1.75 (d, *J* = 7.0 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 157.4, 149.6, 137.6, 132.7, 129.5, 129.2, 125.1, 121.3, 115.4, 111.5, 21.2, 11.4. IR (KBr): 3029. 2919, 2858, 1661, 1596, 1512, 1490, 1455, 1314, 1267, 1220, 1186, 1164, 1074, 1028, 1014, 969, 888, 825, 793, 752, 690 cm^{-1}. HRMS-ESI (m/z) calcd. for $[C_{16}H_{17}O]^+$ ($[M + H]^+$): 225.1274; found: 225.1270.

(*Z*)-1-(*Tert*-butyl)-4-(1-phenoxyprop-1-en-1-yl)benzene (**3c**)



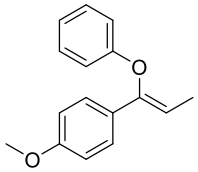
White solid (17.6 mg, 66%, eluents: PE/EA = 40/1), *Z*/*E* = 25/1. M.p.: 87-89 ºC. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40 (d, *J* = 8.5 Hz, 2.08H), 7.29 (d, *J* = 8.5 Hz, 2.08H), 7.23 (t, *J* = 8.0 Hz, 2.08H), 6.97 (d, *J* = 8.1 Hz, 2.08H), 6.93 (t, *J* = 7.3 Hz, 1.04H), 5.90 (q, *J* = 7.0 Hz, 1H), 5.42 (q, *J* = 7.4 Hz, 0.04H), 1.86 (d, *J* = 7.3 Hz, 0.12H), 1.74 (d, *J* = 7.0 Hz, 3H), 1.28 (s, 9.36H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 157.4, 150.8, 149.6, 132.7, 129.5, 125.3, 124.8, 121.2, 115.3, 111.6, 34.5, 31.2, 11.4. IR (KBr): 3034, 2962, 2934, 2866, 1661, 1596, 1488, 1457, 1408, 1364, 1315, 1304, 1270, 1219, 1163, 1118, 1073, 1029, 1012, 966, 886, 847, 832, 811, 777, 750, 699 cm^{-1}. HRMS-ESI (m/z) calcd. for $[C_{19}H_{23}O]^+$ ($[M + H]^+$): 267.1743; found: 267.1738.

A mixture of (Z)-1-methoxy-4-(1-phenoxyprop-1-en-1-yl)benzene (**3d**) and 1-methoxy-4-(1-phenoxyallyl)benzene (**3d'**)[9]



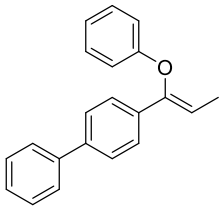
White solid (25.1 mg, 52%, eluents: PE/EA = 40/1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.43 (d, *J* = 8.8 Hz, 2H), 7.36 (d, *J* = 8.6 Hz, 0.32H), 7.26 (t, *J* = 8.0 Hz, 2.32H), 6.99-6.95 (m, 3.32H), 6.94-6.91 (m, 0.48H), 6.83 (d, *J* = 8.8 Hz, 2H), 6.16-6.09 (m, 0.16H), 5.82 (q, *J* = 6.9 Hz, 1H), 5.63 (d, *J* = 5.7 Hz, 0.16H), 5.35 (d, *J* = 17.2 Hz, 0.16H), 5.27 (d, *J* = 10.4 Hz, 0.16H), 3.82 (s, 0.48H), 3.79 (s, 3H), 1.76 (d, *J* = 6.9 Hz, 3H).

(*Z*)-1-Methoxy-4-(1-phenoxyprop-1-en-1-yl)benzene (**3d**)



White solid (43.3 mg, 90%, eluents: PE/EA = 40/1), *Z*/*E* = 25/1. M.p.: 76-78 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.43 (d, *J* = 8.7 Hz, 2.08H), 7.24 (t, *J* = 7.9 Hz, 2.08H), 6.98 (d, *J* = 7.9 Hz, 2.08H), 6.94 (t, *J* = 7.4 Hz, 1.04H), 6.82 (d, *J* = 8.7 Hz, 2.08H), 5.81 (q, *J* = 6.9 Hz, 1H), 5.43 (q, *J* = 7.3 Hz, 0.04H), 3.80 (s, 0.12H), 3.77 (s, 3H), 1.86 (d, *J* = 7.4 Hz, 0.12H), 1.75 (d, *J* = 6.9 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.4, 157.4, 149.4, 129.5, 128.3, 126.5, 121.3, 115.4, 113.9, 110.4, 55.2, 11.3. IR (KBr): 3060, 3038, 2962, 2932, 2911, 2859, 2836, 1658, 1610, 1594, 1573, 1513, 1489, 1479, 1453, 1315, 1290, 1265, 1247, 1213, 1178, 1162, 1115, 1075, 1030, 968, 834, 790, 753, 691 cm^{-1}. HRMS-ESI (m/z) calcd. for $[C_{16}H_{17}O]^+$ ($[M + H]^+$): 241.1223; found: 241.1217.

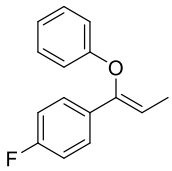
(*Z*)-4-(1-Phenoxyprop-1-en-1-yl)-1,1'-biphenyl (**3e**)



White solid (17.8 mg, 62%, eluents: PE/EA = 40/1), *Z*/*E* = 13/1. M.p.: 129-131 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.57-7.54 (m, 4.32H), 7.51 (d, *J* = 8.3 Hz, 2.16H), 7.41 (t, *J* = 7.6 Hz, 2.16H), 7.32 (t, *J* = 7.4 Hz, 1.08H), 7.27-7.24 (m, 2.16H), 7.0 (d, *J* = 8.5 Hz, 2.16H), 6.95 (t, *J* = 7.3 Hz, 1.08H), 6.02 (q, *J* = 7.0 Hz, 1H), 5.51 (q, *J* = 7.2 Hz, 0.08H), 1.91 (d, *J* = 7.4 Hz, 0.24H), 1.78 (d, *J* = 7.0 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 157.3, 149.4, 140.6, 140.5, 134.5, 129.6, 128.8, 127.3, 127.1, 126.9, 125.5, 121.4, 115.4, 112.5, 11.5. IR (KBr): 3054, 3028, 2962, 2912, 2853, 1651, 1596, 1488,

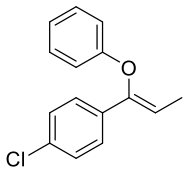
1449, 1405, 1261, 1225, 1166, 1158, 1075, 1028, 1012, 969, 879, 841, 813, 760, 748, 686 cm^{-1}. HRMS-ESI (m/z) calcd. for $[C_{21}H_{19}O]^+$ ($[M + H]^+$): 287.1430; found: 287.1425.

(*Z*)-1-Fluoro-4-(1-phenoxyprop-1-en-1-yl)benzene (**3f**)



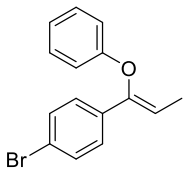
Light yellow oil (20.1 mg, 88%, eluents: PE/EA = 40/1), *Z*/*E* = 50/1. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44 (dd, *J* = 8.8 Hz, 5.4 Hz, 2.04H), 7.24 (t, *J* = 8.0 Hz, 2.04H), 6.98-6.93 (m, 5.10H), 5.85 (q, *J* = 7.0 Hz, 1H), 5.45 (q, *J* = 7.5 Hz, 0.02H), 1.83 (d, *J* = 7.4 Hz, 0.06H), 1.75 (d, *J* = 7.0 Hz, 3H). ^{19}F NMR (471 MHz, $CDCl_3$) δ -144.2 (m, 1F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 162.4 (d, *J* = 247.8 Hz), 157.1, 148.8, 131.7 (d, *J* = 3.2 Hz), 129.6, 126.9 (d, *J* = 8.1 Hz), 121.5, 115.4, 115.3 (d, *J* = 21.7 Hz), 112.1 (d, *J* = 1.5 Hz), 11.4. IR (KBr): 3043, 2980, 2939, 1689, 1596, 1507, 1489, 1407, 1353, 1262, 1221, 1157, 1073, 1027, 1014, 954, 848, 800, 754, 692 cm^{-1}. HRMS-ESI (m/z) calcd. for $[C_{15}H_{14}FO]^+$ ($[M + H]^+$): 229.1023; found: 229.1019.

(*Z*)-1-Chloro-4-(1-phenoxyprop-1-en-1-yl)benzene (**3g**)



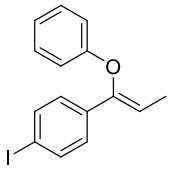
Colorless oil (42.0 mg, 90%, eluents: PE), *Z*/*E* = 100/1. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42(d, *J* = 8.6 Hz, 2.02H), 7.27-7.23 (m, 4.04H), 6.98-6.94 (m, 3.03H), 5.93 (q, *J* = 7.0 Hz, 1H), 5.49 (q, *J* = 7.3 Hz, 0.01H), 1.84 (d, *J* = 7.4 Hz, 0.03H), 1.77 (d, *J* = 7.0 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 157.0, 148.7, 134.1, 133.6, 129.6, 128.6, 126.4, 121.6, 115.3, 113.1, 11.4. IR (KBr): 3040, 2963, 1596, 1489, 1402, 1261, 1217, 1093, 1027, 971, 838, 799, 750, 689 cm^{-1}. HRMS-ESI (m/z) calcd. for $[C_{15}H_{14}ClO]^+$ ($[M + H]^+$): 245.0728; found: 245.0724.

(*Z*)-1-Bromo-4-(1-phenoxyprop-1-en-1-yl)benzene (**3h**)



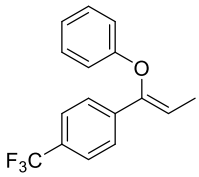
White solid (43.0 mg, 74%, eluents: PE), *Z*/*E* = 100/1. M.p.: 57-59 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39 (d, *J* = 8.8 Hz, 2.02H), 7.34 (d, *J* = 8.5 Hz, 2.02H), 7.26-7.22 (m, 2.02H), 6.96-6.92 (m, 3.03H), 5.93 (q, *J* = 7.0 Hz, 1H), 5.49 (q, *J* = 7.4 Hz, 0.01H), 1.83 (d, *J* = 7.4 Hz, 0.03H), 1.75 (d, *J* = 7.0 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 156.0, 147.8, 133.6, 130.6, 128.6, 125.7, 120.7, 120.6, 114.3, 112.1, 10.4. IR (KBr): 3072, 3037, 2962, 2922, 2855, 1657, 1594, 1487, 1454, 1397, 1311, 1261, 1220, 1185, 1158, 1112, 1072, 1025, 1007, 968, 885, 827, 810, 772, 748, 713 cm^{-1}. HRMS-ESI (m/z) calcd. for $[C_{15}H_{14}BrO]^+$ ($[M + H]^+$): 289.0223; found: 289.0217.

(*Z*)-1-Iodo-4-(1-phenoxyprop-1-en-1-yl)benzene (**3i**)



White solid (23.5 mg, 70%, eluents: PE), *Z*/*E* = 33/1. M.p.: 73-75 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.64 (d, *J* = 8.5Hz, 2.06H), 7.30-7.24 (m, 4.12H), 7.0-6.96 (m, 3.09H), 5.99 (q, *J* = 6.9 Hz, 1H), 5.49 (q, *J* = 7.4 Hz, 0.03H), 1.84 (d, *J* = 7.4 Hz, 0.09H), 1.79 (d, *J* = 7.0 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 157.0, 148.9, 137.6, 135.2, 129.6, 126.9, 121.6, 115.3, 113.2, 93.3, 11.4. IR (KBr): 3063, 3039, 2963, 2914, 2852, 1660, 1591, 1488, 1394, 1311, 1294, 1262, 1216, 1169, 1103, 1074, 1059, 1026, 1003, 967, 813, 749, 691 cm^{-1}. HRMS-ESI (m/z) calcd. for $[C_{15}H_{14}IO]^+$ ($[M + H]^+$): 337.0084; found: 337.0077.

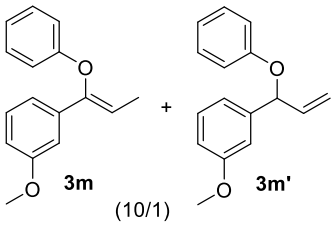
(*Z*)-1-(1-Phenoxyprop-1-en-1-yl)-4-(trifluoromethyl)benzene (**3j**)



Colorless oil (11.7 mg, 21%, eluents: PE). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.58 (d, *J* = 8.3 Hz, 2H), 7.52 (d, *J* = 8.3 Hz, 2H), 7.23 (d, *J* = 8.4 Hz, 2H), 6.97-6.93 (m, 3H), 6.06 (q, *J* = 7.0 Hz, 1H), 1.79 (d, *J* = 7.0 Hz, 3H). ^{19}F NMR (471 MHz, $CDCl_3$) δ -

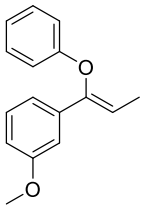
62.7 (s, 3F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 156.9, 148.6, 139.1, 129.7 (q, *J* = 32.2 Hz), 129.7, 125.5 (q, *J* = 3.8 Hz), 125.3, 124.1 (q, *J* = 272 Hz), 121.8, 115.3, 115.0, 11.5. IR (KBr): 3063, 3043, 2921, 2858, 1659, 1618, 1596, 1490, 1411, 1328, 1287, 1264, 1218, 1166, 1125, 1070, 1029, 1015, 970, 850, 819, 787, 750, 733, 691 cm^{-1}. HRMS-ESI (m/z) calcd. for $[C_{16}H_{14}F_3O]^+$ ($[M + H]^+$): 279.0991; found: 279.0986.

A mixture of (*Z*)-1-methoxy-3-(1-phenoxyprop-1-en-1-yl)benzene (**3m**) and 1-methoxy-3-(1-phenoxyallyl)benzene (**3m'**)[10]



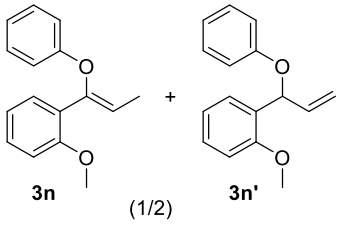
Colorless oil (42.8 mg, 89%, eluents: PE/EA = 40/1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.26-7.18 (m, 3.30H), 7.10 (d, *J* = 7.8 Hz, 1.10H), 7.03 (s, 1.10H), 6.98-6.93 (m, 3.30H), 6.78 (dd, *J* = 7.9 Hz, 2.1 Hz, 1.10H), 6.14-6.07 (m, 0.10H), 5.95 (q, *J* = 7.0 Hz, 1H), 5.62 (d, *J* = 5.8 Hz, 0.10H), 5.37 (d, *J* = 17.2 Hz, 0.10H), 5.27 (d, *J* = 10.4 Hz, 0.10H), 3.81 (s, 0.30H), 3.76 (s, 3H), 1.77 (d, *J* = 7.0 Hz, 3H).

(*Z*)-1-Methoxy-3-(1-phenoxyprop-1-en-1-yl)benzene (**3m**)



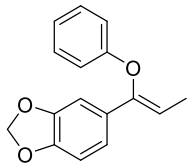
Colorless oil (43.7 mg, 91%, eluents: PE/EA = 40/1). *Z*/*E* = 25/1. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.26-7.19 (m, 3.09H), 7.11 (d, *J* = 7.8 Hz, 1.03H), 7.04 (s, 1.03H), 6.99-6.93 (m, 3.09H), 6.79 (dd, *J* = 8.1 Hz, 1.8 Hz, 1.03H), 5.95 (q, *J* = 7.0 Hz, 1H), 5.49 (q, *J* = 7.4 Hz, 0.03H), 3.79 (s, 0.09H), 3.76 (s, 3H), 1.88 (d, *J* = 7.4 Hz, 0.09H), 1.77 (d, *J* = 7.0 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.7, 157.3, 149.6, 137.1, 129.5, 129.4, 121.4, 117.8, 115.4, 113.3, 112.7, 110.9, 55.2, 11.4. IR (KBr): 3057, 3039, 3001, 2937, 2914, 2856, 2834, 1661, 1596, 1489, 1464, 1431, 1304, 1287, 1217, 1164, 1113, 1074, 1051, 1028, 985, 875, 780, 753, 690 cm^{-1}. HRMS-ESI (m/z) calcd. for $[C_{16}H_{17}O_2]^+$ ($[M + H]^+$): 241.1223; found: 241.1219.

A mixture of (*Z*)-1-methoxy-2-(1-phenoxyprop-1-en-1-yl)benzene (**3n**) and 1-methoxy-2-(1-phenoxyallyl)benzene (**3n'**)[9]



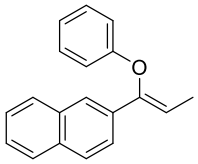
Colorless oil (38.9 mg, 81%, eluents: PE/EA = 40/1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.43 (dd, *J* = 7.6 Hz, 1.3 Hz, 1H), 7.38 (dd, *J* = 7.7 Hz, 1.4 Hz, 0.5H), 7.25-7.14 (m, 4.5H), 6.96-6.82 (m, 7.5H), 6.13-6.02 (m, 2.5H), 5.34 (dm, *J* = 17.0 Hz, 1H), 5.18 (dm, *J* = 9.4 Hz, 1H), 3.86 (s, 3H), 3.84 (s, 1.5H), 1.77 (d, *J* = 7.0 Hz, 1.5H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.0, 157.3, 157.2, 156.2, 146.3, 137.3, 129.3, 129.3, 128.9, 128.8, 128.7, 128.6, 127.2, 124.6, 121.2, 121.1, 120.7, 120.5, 116.5, 115.9, 115.8, 115.4, 111.2, 110.6, 74.0, 55.6, 55.5, 11.6. IR (KBr): 3066, 3038, 3008, 2938, 2837, 1643, 1597, 1492, 1464, 1437, 1339, 1289, 1239, 1165, 1097, 1028, 990, 929, 838, 752, 691 cm^{-1}. HRMS-ESI (m/z) calcd. for $[C_{16}H_{16}NaO_2]^+$ ($[M + Na]^+$): 263.1043; found: 263.1053.

(*Z*)-5-(1-Phenoxyprop-1-en-1-yl)benzo[*d*][1,3]dioxole (**3o**)



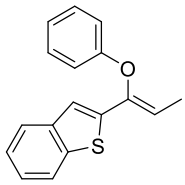
Colorless oil (20.0 mg, 79%, eluents: 20/1), *Z*/*E* = 20/1. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.25-7.21 (m, 2.1H), 6.98-6.91 (m, 5.25H), 6.70 (d, *J* = 8.3 Hz, 1.05H), 5.91 (s, 2H), 5.93 (s, 0.1H), 5.76 (q, *J* = 7.0 Hz, 1H), 5.41 (q, *J* = 7.3 Hz, 0.05H), 1.83 (d, *J* = 7.3 Hz, 0.15H), 1.72 (d, *J* = 6.9 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 157.2, 149.3, 147.8, 147.4, 130.0, 129.5, 121.4, 119.2, 115.4, 111.1, 108.2, 105.7, 101.1, 11.4. IR (KBr): 2895, 1659, 1596, 1490, 1443, 1350, 1296, 1251, 1171, 1096, 1040, 988, 936, 865, 811, 753, 691 cm^{-1}. HRMS-ESI (m/z) calcd. for $[C_{16}H_{15}O_3]^+$ ($[M + H]^+$): 255.1016; found: 255.1012.

(*Z*)-2-(1-Phenoxyprop-1-en-1-yl)naphthalene (**3p**)



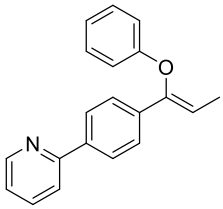
White solid (20.3 mg, 78%, eluents: PE/EA = 40/1), *Z*/*E* = 50/1. M.p.: 81-83 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.9 (s, 1.02H), 7.78-7.75 (m, 3.06H), 7.65 (dd, *J* = 8.7 Hz, 1.6 Hz, 1.02H), 7.43-7.41 (m, 2.04H), 7.24 (t, *J* = 8.0 Hz, 2.04H), 7.02 (d, *J* = 8.0 Hz, 2.04H), 6.94 (t, *J* = 7.3 Hz, 1.02H), 6.09 (q, *J* = 7.0 Hz, 1H), 5.59 (q, *J* = 7.4 Hz, 0.02H), 1.94 (d, *J* = 7.4 Hz, 0.06H), 1.82 (d, *J* = 7.0 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 157.4, 149.8, 133.3, 133.0, 132.9, 129.6, 128.3, 128.1, 127.5, 126.2, 126.0, 124.1, 123.1, 121.4, 115.4, 113.0, 11.6. IR (KBr): 3056, 3038, 2931, 2912, 2853, 1650, 1595, 1489, 1350, 1302, 1219, 1192, 1164, 1131, 1073, 1026, 1012, 967, 896, 866, 816, 798, 760, 687 cm^{-1}. HRMS-ESI (m/z) calcd. for $[C_{19}H_{17}O]^+$ ($[M + H]^+$): 261.1274; found: 261.1270.

(*Z*)-2-(1-Phenoxyprop-1-en-1-yl)benzo[*b*]thiophene (**3q**)



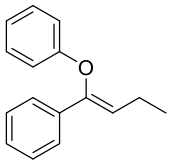
White solid (17.6 mg, 33%, eluents: PE/EA = 40/1), *Z*/*E* = 33/1. M.p.: 72-74 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.73-7.72 (m, 1.02H), 7.61-7.59 (m, 1.02H), 7.29-7.26 (m, 4.08H), 7.16 (s, 1.02H), 7.04 (d, *J* = 7.9 Hz, 2.04H), 6.98 (t, *J* = 7.3 Hz, 1.02H), 5.96 (q, *J* = 7.0 Hz, 1H), 5.62 (q, *J* = 7.7 Hz, 0.02H), 1.94 (d, *J* = 7.5 Hz, 0.06H), 1.77 (d, *J* = 7.0 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 157.2, 145.3, 140.0, 139.3, 138.9, 129.6, 124.6, 124.4, 123.7, 122.0, 121.8, 120.7, 115.1, 115.0, 11.4. IR (KBr): 3061, 3026, 2962, 2924, 2853, 1650, 1595, 1521, 1489, 1455, 1433, 1380, 1331, 1314, 1298, 1261, 1217, 1165, 1150, 1096, 1074, 1025, 1010, 946, 863, 798, 752, 725, 687 cm^{-1}. HRMS-ESI (m/z) calcd. for $[C_{17}H_{15}OS]^+$ ($[M + H]^+$): 267.0838; found: 267.0833.

(*Z*)-2-(4-(1-Phenoxyprop-1-en-1-yl)phenyl)pyridine (**3r**)



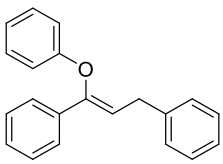
White solid (26.1 mg, 91%, eluents: PE/EA = 5/1), *Z*/*E* = 33/1. M.p.: 108-110 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.66 (d, *J* = 4.9 Hz, 1.03H), 7.91 (d, *J* = 8.5 Hz, 2.06H), 7.73-7.76 (m, 2.06H), 7.58 (d, *J* = 8.5 Hz, 2.06H), 7.24 (t, *J* = 8.0 Hz, 2.06H), 7.21-7.19 (m, 1.03H), 6.98 (d, *J* = 8.2 Hz, 2.06H), 6.94 (t, *J* = 7.4 Hz, 1.03H), 6.03 (q, *J* = 7.0 Hz, 1H), 5.55 (q, *J* = 7.5 Hz, 0.03H), 1.91 (d, *J* = 7.4 Hz, 0.09H), 1.79 (d, *J* = 7.0 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 157.3, 156.9, 149.7, 149.4, 138.7, 136.7, 136.1, 129.5, 127.0, 125.5, 122.1, 121.4, 120.4, 115.4, 113.1, 11.5. IR (KBr): 3053, 3009, 2977, 2913, 2853, 1652, 1585, 1490, 1465, 1434, 1405, 1317, 1292, 1256, 1218, 1195, 1167, 1151, 1115, 1096, 1060, 1027, 966, 884, 841, 772, 752, 686 cm^{-1}. HRMS-ESI (m/z) calcd. for $[C_{20}H_{18}NO]^+$ ($[M + H]^+$): 288.1383; found: 288.1378.

(*Z*)-(1-Phenoxybut-1-en-1-yl)benzene (**3s**)[8]



Colorless oil (23.8 mg, 53%, eluents: PE). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.48 (d, *J* = 7.8 Hz, 2H), 7.27 (t, *J* = 7.4 Hz, 2H), 7.24-7.21 (m, 3H), 6.96 (d, *J* = 8.3 Hz, 2H), 6.92 (t, *J* = 7.5 Hz, 1H), 5.86 (t, *J* = 7.3 Hz, 1H), 2.22 (m, 2H), 1.04 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 157.5, 148.4, 135.5, 129.5, 128.4, 127.8, 125.2, 121.3, 119.7, 115.4, 19.3, 13.8.

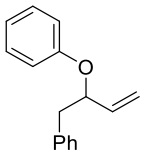
(*Z*)-(1-Phenoxyprop-1-ene-1,3-diyl)dibenzene (**3t**)



Colorless oil (16.2 mg, 28%, eluents: PE/EA = 40/1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.50 (d, *J* = 7.3 Hz, 2H), 7.29-7.18 (m, 10H), 6.99 (d, *J* = 7.9 Hz, 2H), 6.94 (t, *J* = 7.3 Hz, 1H), 6.01 (t, *J* = 7.4 Hz, 1H), 3.56 (d, *J* = 7.4 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 157.4, 149.3, 140.4, 135.2, 129.6, 128.5, 128.5, 128.4, 128.1, 126.1, 125.5,

121.6, 116.6, 115.7, 32.3. IR (KBr): 3061, 3027, 2963, 2851, 1655, 1594, 1490, 1453, 1332, 1278, 1217, 1165, 1091, 1063, 1025, 1006, 992, 889, 868, 753, 691 cm^{-1}. HRMS-ESI (m/z) calcd. for $[C_{21}H_{19}O]^+$ ($[M + H]^+$): 287.1430; found: 287.1423.

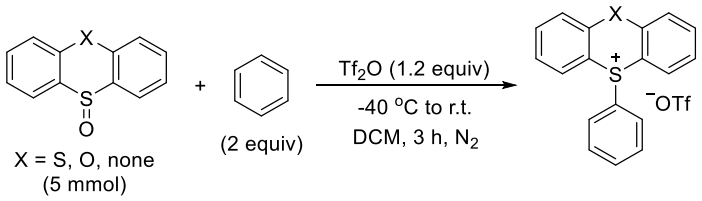
(2-Phenoxybut-3-en-1-yl)benzene (**3u'**)[11]



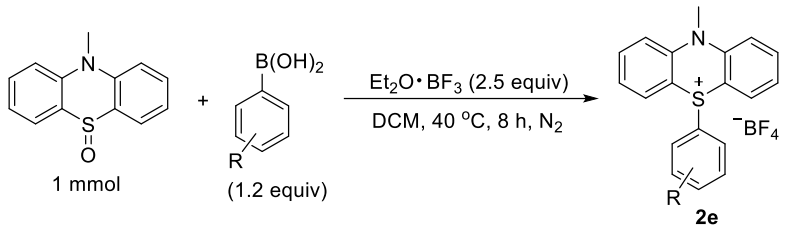
Colorless oil (23.3 mg, 52%, eluents: PE/EA = 40/1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.32-7.29 (m, 4H), 7.26-7.23 (m, 3H), 6.94-6.89 (m, 3H), 5.90 (m, 1H), 5.23 (d, *J* = 17.0 Hz, 1H), 5.21 (d, *J* = 10.4 Hz, 1H), 4.83 (q, *J* = 6.2 Hz, 1H), 3.16 (dd, *J* = 13.8 Hz, 7.1 Hz, 1H), 2.97 (dd, *J* = 13.8 Hz, 5.9 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.2, 137.7, 137.4, 129.7, 129.3, 128.2, 126.4, 120.9, 116.8, 116.2, 79.9, 42.2.

4. Base-mediated synthesis of aryl enol ethers from 1-phenylprop-2-en-1-ol (1a) with different arylsulfonium salts

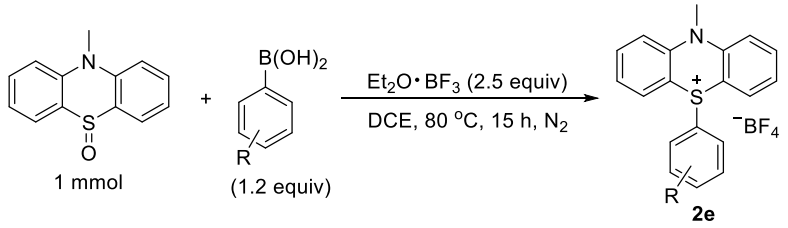
4.1. Procedures for the synthesis of arylsulfonium salts.



Procedure A:[12] Under a N_2 atmosphere, Tf_2O (1.0 mL, 6 mmol) was added to a mixture of benzene (0.781 g, 10 mmol), sulfoxide (5 mmol), and DCM (20 mL) at -40 ^{o}C with stirring. The mixture was reacted at room temperature for 3 h and neutralized by a saturated aqueous $NaHCO_3$ solution. The DCM layer was collected. The aqueous solution was extracted with DCM (3 × 20 mL). The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated to dryness under reduced pressure. The residue was crystallized from a mixture of DCM / *tert*-butyl methyl ether = 1/20 (v/v) to afford the desired product (**2b**-**d**).



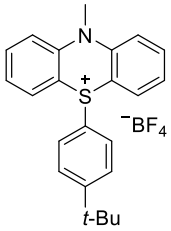
Procedure B:[4] Under a N_2 atmosphere, a flask was charged with $Et_2O{\bullet}BF_3$ (0.34 mL, 2.5 mmol), 10-methyl-10*H*-phenothiazine 5-oxide (229 mg, 1 mmol), aryl boronic acid (1.2 mmol), and DCM (10 mL) with stirring. The mixture was reacted at 40 °C for 8 h. Then, 2-(bis(2-hydroxyethyl)amino)-2-(hydroxymethyl)propane-1,3-diol (Bis-Tris, 2.1 g, 10 mmol) and a saturated aqueous $NaBF_4$ solution (10 mL) were added to the DCM solution. After shaking for at least 5 min, the DCM layer was collected. The aqueous solution was extracted with DCM (3 × 15 mL). The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated to dryness under reduced pressure. The residue was crystallized from a mixture of DCM / *tert*-butyl methyl ether = 1/20 (v/v) to afford the desired arylsulfonium salts (**2ea-ec**, **2ei**, and **2ek-eo**).



Procedure C:[4] Under a N_2 atmosphere, a flask was charged with 10-methyl-10*H*-phenothiazine 5-oxide (229 mg, 1 mmol), aryl boronic acid (1.2 mmol), $Et_2O{\bullet}BF_3$ (0.34 mL, 2.5 mmol), and DCE (10 mL) with stirring. The mixture was reacted at 80 °C for 15 h, quenched by moisture, concentrated under reduced pressure, and diluted with DCM (10 mL). Then, Bis-Tris (2.1 g, 10 mmol) and a saturated aqueous $NaBF_4$ solution (10 mL) were added to the DCM solution. After shaking for at least 5 min, the DCM layer was collected. The aqueous layer was extracted with DCM (3 × 15 mL). The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated to dryness under reduced pressure. The residue was crystallized from a mixture of DCM / *tert*-butyl methyl ether = 1/20 (v/v) to afford the desired arylsulfonium salts (**2ed-eh** and **2ej**).

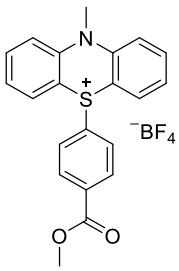
5-(4-(*Tert*-butyl)phenyl)-10-methyl-5,10-dihydrophenothiazin-5-ium tetrafluoroborate

(**2ec**)



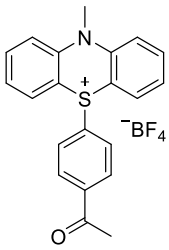
Light yellow solid (370.7 mg, 86%). M.p.: 280-282 ºC. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.09 (d, *J* = 7.9 Hz, 2H), 7.79 (t, *J* = 7.9 Hz, 2H), 7.53 (d, *J* = 8.5 Hz, 2H), 7.43 (d, *J* = 8.7 Hz, 2H), 7.37 (t, *J* = 7.6 Hz, 2H), 7.20 (d, *J* = 8.7 Hz, 2H), 3.71 (s, 3H), 1.19 (s, 9H). ^{19}F NMR (471 MHz, $CDCl_3$) δ -151.7 (brs), -151.7 (brs). ^{13}C NMR (126 MHz, $CDCl_3$) δ 157.5, 143.2, 136.0, 132.2, 128.3, 127.2, 125.7, 124.7, 117.6, 105.2, 36.0, 35.2, 30.8. IR (KBr): 3065, 2965, 2907, 2871, 1583, 1465, 1400, 1353, 1301, 1259, 1177, 1054, 877, 836, 768 cm^{-1}. HRMS-ESI (m/z) calcd. for $[C_{23}H_{24}NS]^{+}$ ($[M]^{+}$): 346.1624; found: 346.1619.

5-(4-(Methoxycarbonyl)phenyl)-10-methyl-5,10-dihydrophenothiazin-5-ium tetrafluoroborate (**2eg**)



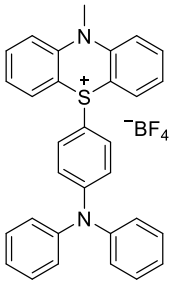
Grey solid (233.8 mg, 54%). M.p.: 229-231 ºC. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.35 (d, *J* = 8.0 Hz, 2H), 8.05 (d, *J* = 8.4 Hz, 2H), 7.87 (t, *J* = 7.9 Hz, 2H), 7.52 (t, *J* = 7.6 Hz, 2H), 7.48 (d, *J* = 8.5 Hz, 2H), 7.28 (d, *J* = 7.1 Hz, 2H), 3.90 (s, 3H), 3.66 (s, 3H). ^{19}F NMR (471 MHz, CD_3CN) δ -151.5 (brs), -151.6 (brs). ^{13}C NMR (126 MHz, CD_3CN) δ 165.1, 143.4, 136.1, 134.2, 134.0, 132.3, 131.1, 127.3, 124.5, 118.1, 104.4, 52.4, 35.7. IR (KBr): 3102, 3077, 2959, 2929, 2851, 1722, 1580, 1463, 1439, 1397, 1351, 1292, 1262, 1154, 1088, 1052, 1009, 956, 878, 756, 684 cm^{-1}. HRMS-ESI (m/z) calcd. for $[C_{21}H_{18}NO_2S]^{+}$ ($[M]^{+}$): 348.1053; found: 348.1046.

5-(4-Acetylphenyl)-10-methyl-5,10-dihydrophenothiazin-5-ium tetrafluoroborate (**2eh**)



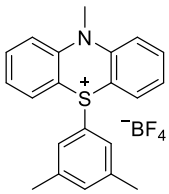
Yellow solid (272.4 mg, 65%). M.p.: 177-179 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.31 (d, *J* = 7.8 Hz, 2H), 7.91 (d, *J* = 8.5 Hz, 2H), 7.82 (t, *J* = 8.1 Hz, 2H), 7.47-7.43 (m, 4H), 7.30 (d, *J* = 8.5 Hz, 2H), 3.63 (s, 3H), 2.51 (s, 3H). ^{19}F NMR (471 MHz, $CDCl_3$) δ -151.0 (brs), -151.1 (brs). ^{13}C NMR (126 MHz, $CDCl_3$) δ 196.4, 143.2, 140.1, 136.2, 133.6, 132.9, 130.2, 127.5, 125.0, 117.3, 104.9, 35.9, 26.7. IR (KBr): 3114, 3068, 2926, 2855, 1686, 1582, 1463, 1395, 1348, 1260, 1141, 1057, 1005, 959, 831, 762 cm^{-1}. HRMS-ESI (m/z) calcd. for $[C_{21}H_{18}NOS]^+$ ($[M]^+$): 332.1104; found: 332.1098.

5-(4-(Diphenylamino)phenyl)-10-methyl-5,10-dihydrophenothiazin-5-ium tetrafluoroborate (**2ej**)



Yellowish solid (283.2 mg, 52%). M.p.: 180-182 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.00 (d, *J* = 7.9 Hz, 2H), 7.74 (t, *J* = 7.9 Hz, 2H), 7.50 (d, *J* = 8.5 Hz, 2H), 7.31 (t, *J* = 7.6 Hz, 2H), 7.26 (t, *J* = 7.7 Hz, 4H), 7.13-7.09 (m, 4H), 7.03 (d, *J* = 7.5 Hz, 4H), 6.82 (d, *J* = 9.1 Hz, 2H), 3.71 (s, 3H). ^{19}F NMR (471 MHz, $CDCl_3$) δ -151.8 (brs), -151.9 (brs). ^{13}C NMR (126 MHz, $CDCl_3$) δ 152.7, 145.2, 143.0, 135.7, 131.9, 130.0, 129.3, 126.5, 125.9, 124.6, 120.1, 117.5, 116.9, 106.4, 36.0. IR (KBr): 3063, 3034, 2927, 1577, 1491, 1466, 1334, 1299, 1261, 1196, 1141, 1061, 878, 820, 755, 700 cm^{-1}. HRMS-ESI (m/z) calcd. for $[C_{31}H_{25}N_2S]^+$ ($[M]^+$): 457.1733; found: 457.1726.

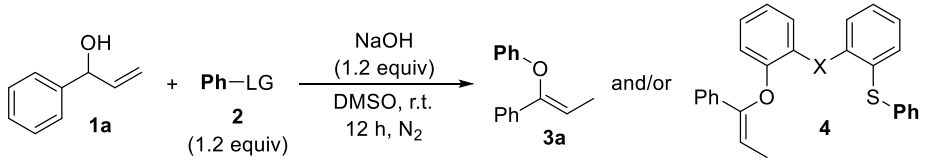
5-(3,5-Dimethylphenyl)-10-methyl-5,10-dihydrophenothiazin-5-ium tetrafluoroborate (**2en**)



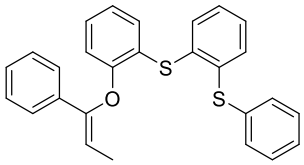
Light yellow solid (364.7 mg, 90%). M.p.: 272-274 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.12 (dd, *J* = 7.9 Hz, 1.1 Hz, 2H), 7.81 (t, *J* = 7.9 Hz, 2H), 7.52 (d, *J* = 8.4 Hz, 2H), 7.41 (t, *J* = 7.4 Hz, 2H), 7.09 (s, 1H), 6.78 (s, 2H), 3.70 (s, 3H), 2.23 (s, 6H). ^{19}F NMR (471 MHz, $CDCl_3$) δ -151.8 (brs), -151.8 (brs). ^{13}C NMR (126 MHz, $CDCl_3$) δ 143.2, 141.4, 136.0, 135.1, 132.4, 128.8, 124.8, 124.4, 117.4, 105.2, 35.9, 21.3. IR (KBr): 3070, 3049, 2922, 1606, 1584, 1467, 1356, 1303, 1259, 1182, 1067, 942, 877, 766, 677 cm^{-1}. HRMS-ESI (m/z) calcd. for $[C_{21}H_{20}NS]^+$ ($[M]^+$): 318.1311; found: 318.1305.

4.2. General procedure for the base-mediated synthesis of aryl enol ethers from 1a with different types of aryl transfer reagents (2).

In a nitrogen-filled glovebox, a sealed tube was charge with **1a** (13.4 mg, 0.1 mmol), aryl transfer regent (**2**, 0.12 mmol), NaOH (4.8 mg, 0.12 mmol), and DMSO (1 mL) with vigorous stirring. The mixture was reacted at room temperature for 12 h. The yields of **3a** were determined by HPLC using the pure **3a** as an external standard (t_R = 10.5 min, λ_{max} = 252 nm, water / methanol = 20 / 80 (v / v). Product **4** was isolated by the flash column chromatography on silica gel using a mixture of petroleum ether (PE) and ethyl acetate (EA) as eluents.



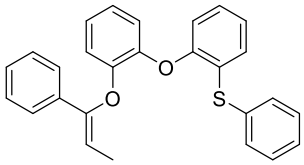
(*Z*)-Phenyl(2-((2-((1-phenylprop-1-en-1-yl)oxy)phenyl)thio)phenyl)sulfane (**4a**)



Light yellow oil (17.9 mg, 42%, eluents: PE/EA = 40/1), *Z*/*E* = 25/1. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42 (d, *J* = 6.6 Hz, 2.08H), 7.39 (d, *J* = 7.4 Hz, 2.08H), 7.29-7.26 (m, 3.12H), 7.23-7.21 (m, 6.24H), 7.15 (td, *J* = 6.9 Hz, 1.9 Hz, 2.08H), 7.11 (tm, *J* = 7.9

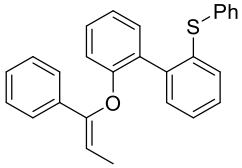
Hz, 1.04H), 6.91 (t, *J* = 7.4 Hz, 1.04H), 6.80 (d, *J* = 8.1 Hz Hz, 1.04H), 5.91 (q, *J* = 6.9 Hz, 1H), 5.40 (q, *J* = 7.4 Hz, 0.04H), 1.84 (d, *J* = 7.4 Hz, 0.12H), 1.67 (d, *J* = 7.0 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 156.0, 149.8, 137.7, 137.0, 135.1, 135.1, 133.6, 132.2, 131.3, 131.3, 129.2, 129.2, 128.4, 127.8, 127.6, 127.3, 127.1, 125.2, 122.2, 122.0, 114.1, 112.6, 11.3. IR (KBr): 3056, 2963, 2921, 2854, 1660, 1573, 1468, 1442, 1261, 1226, 1157, 1099, 1035, 1015, 802, 749, 691 cm^{-1}. HRMS-ESI (m/z) calcd. for $[C_{27}H_{23}OS_2]^+$ ($[M + H]^+$): 427.1185; found: 427.1180.

(*Z*)-Phenyl(2-(2-((1-phenylprop-1-en-1-yl)oxy)phenoxy)phenyl)sulfane (**4b**)



Light yellow oil (14.0 mg, 34%, eluents: PE/EA = 40/1), *Z*/*E* = 33/1. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44-7.40 (m, 4.12H), 7.27-7.24 (m, 4.12H), 7.22-7.19 (m, 4.12H), 7.00 (t, *J* = 7.5 Hz, 1.03H), 6.96 (dd, *J* = 7.8 Hz, 1.5 Hz, 1.03H), 6.93 (td, *J* = 7.1 Hz, 1.5 Hz, 1.03H), 6.89-6.86 (m, 2.06H), 6.83 (dd, *J* = 8.0 Hz, 1.3 Hz, 1.03H), 5.85 (q, *J* = 6.9 Hz, 1H), 5.29 (q, *J* = 7.4 Hz, 0.03H), 1.77 (d, *J* = 7.4 Hz, 0.09H), 1.67 (d, *J* = 6.9 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 156.3, 149.7, 148.4, 144.7, 135.3, 135.0, 132.8, 131.4, 129.0, 128.3, 127.8, 126.9, 125.9, 125.3, 124.7, 123.3, 121.8, 121.2, 117.0, 115.6, 112.5, 11.3. IR (KBr): 3060, 2923, 2855, 1663, 1574, 1492, 1468, 1440, 1304, 1260, 1214, 1188, 1157, 1108, 1063, 1014, 931, 796, 748, 692 cm^{-1}. HRMS-ESI (m/z) calcd. for $[C_{27}H_{23}O_2S]^+$ ($[M + H]^+$): 411.1413; found: 411.1405.

(*Z*)-Phenyl(2'-((1-phenylprop-1-en-1-yl)oxy)-[1,1'-biphenyl]-2-yl)sulfane (**4c**)



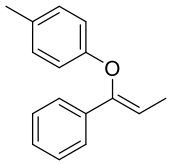
Light yellow oil (31.6 mg, 80%, eluents: PE/EA = 40/1), *Z*/*E* = 25/1. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45 (d, *J* = 6.7 Hz, 2.08H), 7.43 (d, *J* = 7.4 Hz, 1.04H), 7.36 (d, *J* = 7.1 Hz, 2.08H), 7.34-7.31 (m, 2.08H), 7.29-7.27 (m, 3.12H), 7.23-7.17 (m, 6.24H), 6.98 (t, *J* = 7.4 Hz, 1.04H), 6.85 (d, *J* = 8.3 Hz, 1.04H), 5.91 (q, *J* = 6.9 Hz, 1H), 5.25 (q, *J* = 7.4 Hz, 0.04H), 1.74 (d, *J* = 6.9 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 154.1, 149.7, 139.8, 136.7, 136.2, 135.5, 131.8, 131.4, 130.9, 130.7, 129.4, 129.1, 128.3,

128.2, 127.7, 127.0, 126.4, 125.1, 120.9, 113.4, 112.4, 11.5. IR (KBr): 3057, 3024, 2916, 2854, 1659, 1581, 1493, 1462, 1442, 1316, 1262, 1214, 1158, 1117, 1072, 1016, 967, 909, 817, 742, 692 cm^{-1}. HRMS-ESI (m/z) calcd. for $[C_{27}H_{23}OS]^+$ ($[M + H]^+$): 395.1464; found: 395.1457.

4.3. General procedure for the base-mediated synthesis of aryl enol ethers from 1a with different aryl phenothiazinium salts (2e).

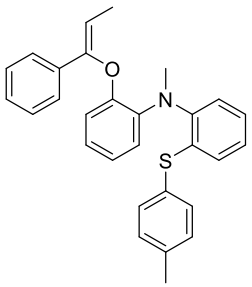
In a nitrogen-filled glovebox, a sealed tube was charge with **1a** (13.4 or 26.8 mg, 0.1 or 0.2 mmol), aryl phenothiazinium salt (**2e**, 0.12 or 0.24 mmol), NaOH (4.8 or 9.6 mg, 0.12 or 0.24 mmol) or CsOH (22.5 or 45 mg, 0.15 or 0.3 mmol) and DMSO (1 or 2 mL) with vigorous stirring. The mixture was reacted at room temperature or 60 ^oC for 12 or 24 h, cooled to room temperature, diluted with water (30 mL), and extracted with ethyl acetate (3 × 20 mL). The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated to dryness under reduced pressure. The residue was purified by flash column chromatography on silica gel using a mixture of petroleum ether (PE) and ethyl acetate (EA) as eluents to give the desired product (**5**).

(*Z*)-1-Methyl-4-((1-phenylprop-1-en-1-yl)oxy)benzene (**5a**)



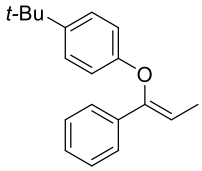
Light yellow oil (20.7 mg, 46%, eluents: PE/EA = 40/1), *Z*/*E* = 100/1. ^1H NMR (500 MHz, $CDCl_3$) δ 7.47 (d, *J* = 7.4 Hz, 2.02H), 7.27 (t, *J* = 7.7 Hz, 2.02H), 7.21 (t, *J* = 7.3 Hz, 1.01H), 7.02 (d, *J* = 8.2 Hz, 2.02H), 6.85 (d, *J* = 8.5 Hz, 2.02H), 5.91 (q, *J* = 7.0 Hz, 1H), 5.40 (q, *J* = 7.4 Hz, 0.01H), 2.25 (s, 3H), 2.13 (s, 0.03H), 1.83 (d, *J* = 7.4 Hz, 0.03H), 1.76 (d, *J* = 7.0 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 155.2, 149.8, 135.7, 130.5, 130.0, 128.4, 127.7, 125.2, 115.1, 112.2, 20.5, 11.4. IR (KBr): 3057, 3031, 2920, 2858, 1660, 1610, 1506, 1446, 1317, 1285, 1263, 1220, 1167, 1105, 1018, 968, 815, 774, 732, 692 cm^{-1}. HRMS-ESI (m/z) calcd. for $[C_{16}H_{17}O]^+$ ($[M + H]^+$): 225.1274; found: 225.1269.

(*Z*)-*N*-Methyl-2-((1-phenylprop-1-en-1-yl)oxy)-*N*-(2-(*p*-tolylthio)phenyl)aniline (**4d**)



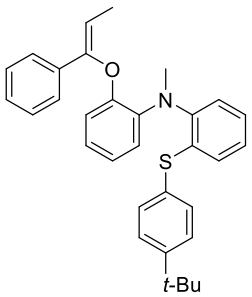
Colorless oil (18.4 mg, 21%, eluents: PE/EA = 40/1), *Z*/*E* = 10/1. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42-7.40 (m, 2.2H), 7.31 (d, *J* = 8.0 Hz, 2.2H), 7.16-7.15 (m, 3.3H), 7.12-7.09 (m, 4.4H), 6.98 (dd, *J* = 7.8 Hz, 1.4 Hz, 1.1H), 6.93 (tm, *J* = 7.9 Hz, 1.1H), 6.89-6.84 (m, 2.2H), 6.79 (tm, *J* = 7.9 Hz, 1.1H), 6.67 (dd, *J* = 8.0 Hz, 1.2 Hz, 1.1H), 5.82 (q, *J* = 6.9 Hz, 1H), 5.20 (q, *J* = 7.3 Hz, 0.1H), 3.38 (s, 3H), 3.29 (s, 0.3H), 2.34 (s, 0.3H), 2.33 (s, 3H), 1.74 (d, *J* = 7.4 Hz, 0.3H), 1.56 (d, *J* = 6.7 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 149.6, 149.6, 148.9, 139.3, 137.7, 135.6, 135.3, 133.9, 131.1, 130.0, 129.4, 128.2, 127.6, 126.0, 125.3, 124.4, 123.5, 122.6, 121.2, 120.9, 113.9, 112.2, 41.0, 21.1, 11.2. IR (KBr): 3057, 3026, 2920, 2854, 2802, 1659, 1580, 1494, 1471, 1445, 1317, 1260, 1216, 1122, 1104, 1051, 1016, 968, 874, 811, 747, 693 cm^{-1}. HRMS-ESI (m/z) calcd. for $[C_{29}H_{28}NOS]^+$ ($[M + H]^+$): 438.1886; found: 438.1894.

(*Z*)-1-(*Tert*-butyl)-4-((1-phenylprop-1-en-1-yl)oxy)benzene (**5b**)



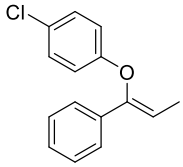
Colorless oil (18.1 mg, 34%, eluents: PE/EA = 40/1), *Z*/*E* = 50/1. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.46 (d, *J* = 7.4 Hz, 2.04H), 7.24 (d, *J* = 8.5 Hz, 2.04H), 7.21-7.17 (m, 3.06H), 6.85 (d, *J* = 8.5 Hz, 2.04H), 5.89 (q, *J* = 6.9 Hz, 1H), 1.81 (d, *J* = 7.3 Hz, 0.06H), 1.73 (d, *J* = 7.0 Hz, 3H), 1.36 (s, 0.18H), 1.24 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 155.0, 149.8, 143.9, 135.8, 128.4, 127.7, 126.3, 125.2, 114.7, 112.3, 34.1, 31.5, 11.4. IR (KBr): 3057, 3034, 2914, 2855, 1661, 1582, 1479, 1446, 1398, 1315, 1276, 1264, 1226, 1167, 1109, 1057, 1014, 1003, 968, 913, 820, 748, 692 cm^{-1}. HRMS-ESI (m/z) calcd. for $[C_{19}H_{23}O]^+$ ($[M + H]^+$): 267.1743; found: 267.1739.

(*Z*)-2-((4-(*Tert*-butyl)phenyl)thio)-*N*-methyl-*N*-(2-((1-phenylprop-1-en-1-yl)oxy)phenyl)aniline (**4e**)



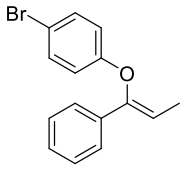
Colorless oil (30.7 mg, 32%, eluents: PE/EA = 40/1), *Z*/*E* = 50/1. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41-7.39 (m, 2.04), 7.33 (d, *J* = 8.6 Hz, 2.04H), 7.30 (d, *J* = 8.6 Hz, 2.04H), 7.17-7.16 (m, 3.06H), 7.13 (m, 2.04H), 6.99 (dd, *J* = 7.8 Hz, 1.2 Hz, 1.02H), 6.95 (m, 2.04H), 6.86 (td, *J* = 7.7 Hz, 1.1 Hz, 1.02H), 6.79 (tm, *J* = 7.9 Hz, 1.02H), 6.67 (dd, *J* = 8.0 Hz, 1.1 Hz, 1.02H), 5.82 (q, *J* = 6.9 Hz, 1H), 5.22 (q, *J* = 7.4 Hz, 0.02H), 3.39 (s, 3H), 3.31 (s, 0.06H), 1.76 (d, *J* = 7.4 Hz, 0.06H), 1.56 (d, *J* = 7.0 Hz, 3H), 1.31 (s, 9H), 1.28 (s, 0.18H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 150.7, 149.6, 149.6, 149.1, 139.3, 135.6, 134.9, 133.2, 131.2, 129.8, 128.2, 127.6, 126.2, 125.2, 124.4, 123.6, 122.6, 121.2, 120.8, 113.9, 112.2, 41.2, 34.6, 31.3, 11.2. IR (KBr): 3059, 2963, 2870, 2805, 1688, 1582, 1493, 1471, 1362, 1351, 1268, 1221, 1181, 1118, 1046, 1027, 1014, 951, 831, 814, 746, 691 cm^{-1}. HRMS-ESI (m/z) calcd. for $[C_{32}H_{34}NOS]^+$ ($[M + H]^+$): 480.2356; found: 480.2362.

(*Z*)-1-Chloro-4-((1-phenylprop-1-en-1-yl)oxy)benzene (**5c**)



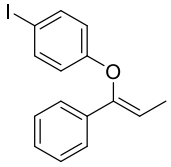
Light yellow oil (18.4 mg, 75%, eluents: PE/EA = 40/1), *Z*/*E* = 100/1. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44 (d, *J* = 7.2 Hz, 2.02H), 7.28 (t, *J* = 7.4 Hz, 2.02H), 7.23 (t, *J* = 7.2 Hz, 1.01H), 7.18 (d, *J* = 8.9 Hz, 2.02H), 6.89 (d, *J* = 8.9 Hz, 2.02H), 5.93 (q, *J* = 7.0 Hz, 1H), 5.49 (q, *J* = 7.4 Hz, 0.01H), 1.85 (d, *J* = 7.5 Hz, 0.03H), 1.74 (d, *J* = 7.0 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 155.9, 149.6, 135.1, 129.5, 128.5, 128.0, 126.3, 125.1, 116.7, 112.6, 11.3. IR (KBr): 3058, 3036, 2962, 2916, 2857, 1661, 1593, 1486, 1446, 1316, 1280, 1263, 1229, 1162, 1091, 1016, 969, 825, 753, 699 cm^{-1}. HRMS-ESI (m/z) calcd. for $[C_{15}H_{14}ClO]^+$ ($[M + H]^+$): 245.0728; found: 245.0723.

(*Z*)-1-Bromo-4-((1-phenylprop-1-en-1-yl)oxy)benzene (**5d**)



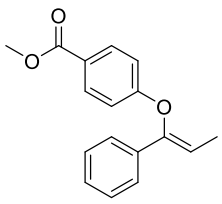
Colorless oil (22.8 mg, 79%, eluents: PE/EA = 40/1), *Z*/*E* = 50/1. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44 (d, *J* = 7.7 Hz, 2.04H), 7.32 (d, *J* = 8.5 Hz, 2.04H), 7.28 (t, *J* = 7.4 Hz, 2.04H), 7.23 (t, *J* = 7.1 Hz, 1.02H), 6.84 (d, *J* = 8.5 Hz, 2.04H), 5.94 (q, *J* = 7.0 Hz, 1H), 5.50 (q, *J* = 7.4 Hz, 0.02H), 1.86 (d, *J* = 7.3 Hz, 0.06H), 1.74 (d, *J* = 7.0 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 156.4, 149.5, 135.0, 132.4, 128.5, 128.0, 125.1, 117.2, 113.6, 112.7, 11.4. IR (KBr): 3059, 3035, 2919, 2855, 1662, 1588, 1483, 1446, 1316, 1263, 1228, 1164, 1099, 1070, 1015, 969, 824, 751, 695 cm^{-1}. HRMS-ESI (m/z) calcd. for $[C_{15}H_{14}BrO]^+$ ($[M + H]^+$): 289.0223; found: 289.0216.

(*Z*)-1-Iodo-4-((1-phenylprop-1-en-1-yl)oxy)benzene (**5e**)



Colorless oil (55.8 mg, 83%, eluents: PE/EA = 40/1), *Z*/*E* = 25/1. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.53 (d, *J* = 8.9 Hz, 2.08H), 7.47 (d, *J* = 7.2 Hz, 2.08H), 7.32-7.24 (m, 3.12H). 6.77 (d, *J* = 8.8 Hz, 2.08H), 5.96 (q, *J* = 7.0 Hz, 1H), 5.54 (q, *J* = 7.4 Hz, 0.04H), 1.89 (d, *J* = 7.4 Hz, 0.12H), 1.77 (d, *J* = 7.0 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 157.3, 149.5, 138.4, 138.3, 135.1, 128.5, 128.0, 125.1, 117.8, 112.7, 11.4. IR (KBr): 3056, 3035, 2961, 2913, 2857, 1661, 1582, 1508, 1479, 1446, 1398, 1315, 1264, 1227, 1167, 1111, 1057, 1015, 968, 913, 821, 785, 750, 694 cm^{-1}. HRMS-ESI (m/z) calcd. for $[C_{15}H_{14}IO]^+$ ($[M + H]^+$): 337.0084; found: 337.0075.

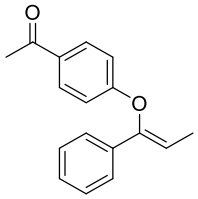
Methyl (*Z*)-4-((1-phenylprop-1-en-1-yl)oxy)benzoate (**5f**)



Yellow oil (11.5 mg, 43%, eluents: PE/EA = 40/1), *Z*/*E* = 33/1. ^{1}H NMR (500 MHz,

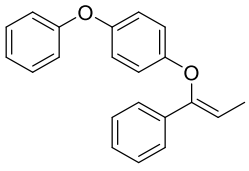
$CDCl_3$) δ 7.94 (d, *J* = 8.9 Hz, 2.06H), 7.45 (d, *J* = 7.5 Hz, 2.06H), 7.30-7.22 (m, 3.09H), 6.98 (d, *J* = 8.9 Hz, 2.06H), 5.98 (q, *J* = 7.0 Hz, 1H), 5.61 (q, *J* = 7.4 Hz, 0.03H), 3.86 (s, 3H), 3.85 (s, 0.09H), 1.90 (d, *J* = 7.4 Hz, 0.09H), 1.74 (d, *J* = 7.0 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.7, 161.2, 149.4, 134.9, 131.7, 128.5, 128.1, 124.9, 123.5, 115.1, 112.7, 51.8, 11.4. IR (KBr): 3058, 3035, 2951, 2923, 2856, 1720, 1664, 1605, 1505, 1435, 1315, 1278, 1237, 1190, 1162, 1111, 1014, 969, 850, 804, 769, 749, 695 cm^{-1}. HRMS-ESI (m/z) calcd. for $[C_{17}H_{17}O_3]^+$ ($[M + H]^+$): 269.1172; found: 269.1168.

(*Z*)-1-(4-((1-Phenylprop-1-en-1-yl)oxy)phenyl)ethan-1-one (**5g**)



Yellow oil (20.9 mg, 83%, eluents: PE/EA = 40/1), *Z*/*E* = 25/1. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.88 (d, *J* = 8.9 Hz, 2.08H), 7.45 (d, *J* = 7.3 Hz, 2.08H), 7.30-7.23 (m, 3.12H), 7.00 (d, *J* = 8.8 Hz, 2H), 5.99 (q, *J* = 7.0 Hz, 1H), 5.63 (q, *J* = 7.4 Hz, 0.04H), 2.52 (s, 3H), 2.50 (s, 0.12H), 1.91 (d, *J* = 7.4 Hz, 0.12H), 1.75 (d, *J* = 7.0 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 196.6, 161.3, 149.3, 134.8, 131.1, 130.7, 128.6, 128.1, 124.9, 115.2, 112.8, 26.3, 11.4. IR (KBr): 3060, 3007, 2920, 2855, 1674, 1597, 1580, 1500, 1447, 1416, 1355, 1318, 1269, 1225, 1165, 1108, 1008, 954, 843, 788, 759, 710 cm^{-1}. HRMS-ESI (m/z) calcd. for $[C_{17}H_{17}O_2]^+$ ($[M + H]^+$): 253.1223; found: 253.1218.

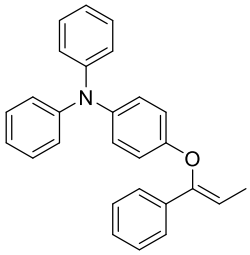
(*Z*)-1-Phenoxy-4-((1-phenylprop-1-en-1-yl)oxy)benzene (**5h**)



Colorless oil (33.3 mg, 55%, PE/EA = 40/1), *Z*/*E* = 25/1. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.49 (d, *J* = 7.4 Hz, 2.08H), 7.31-7.27 (m, 4.16H), 7.24 (t, *J* = 7.3 Hz, 1.04H), 7.04 (t, *J* = 7.4 Hz, 1.04H), 6.95-6.89 (m, 6.24H), 5.92 (q, *J* = 7.0 Hz, 1H), 5.43 (q, *J* = 7.3 Hz, 0.04H), 1.85 (d, *J* = 7.4 Hz, 0.12H), 1.79 (d, *J* = 7.0 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.2, 153.4, 150.9, 150.0, 135.5, 129.6, 128.4, 127.8, 125.2, 122.6, 120.5, 117.9, 116.3, 112.4, 11.4. IR (KBr): 3058, 2925, 2855, 1662, 1589, 1488, 1446, 1316,

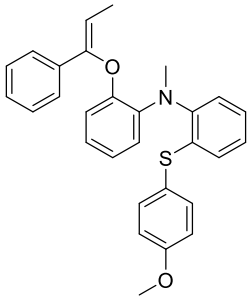
1246, 1211, 1194, 1098, 1084, 1017, 847, 834, 754, 692 cm^{-1}. HRMS-ESI (m/z) calcd. for $[C_{21}H_{19}O_2]^+$ ($[M + H]^+$): 303.1380; found: 303.1374.

(*Z*)-*N*,*N*-Diphenyl-4-((1-phenylprop-1-en-1-yl)oxy)aniline (**5i**)



Colorless oil (34.7 mg, 46%, eluents: PE/EA = 10/1), *Z*/*E* = 33/1. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.50 (d, *J* = 7.6 Hz, 2.06H), 7.31 (t, *J* = 7.4 Hz, 2.06H), 7.26 (m, 1.03H), 7.20 (t, *J* = 7.8 Hz, 4.12H), 7.02 (d, *J* = 7.9 Hz, 4.12H), 6.99 (d, *J* = 8.9 Hz, 2.06H), 6.94 (t, *J* = 7.3 Hz, 2.06H), 6.87 (d, *J* = 8.8 Hz, 2.06H), 5.92 (q, *J* = 6.9 Hz, 1H), 5.45 (q, *J* = 7.4 Hz, 0.03H), 1.85 (d, *J* = 7.4 Hz, 0.09H), 1.79 (d, *J* = 7.0 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 153.6, 149.9, 148.1, 141.4, 135.7, 129.1, 128.4, 127.8, 126.8, 125.2, 123.2, 122.0, 116.2, 112.4, 11.5. IR (KBr): 3058, 3036, 2917, 2855, 1660, 1588, 1500, 1446, 1314, 1276, 1217, 1161, 1104, 1075, 1016, 967, 914, 830, 751, 695 cm^{-1}. HRMS-ESI (m/z) calcd. for $[C_{27}H_{23}NNaO]^+$ ($[M + Na]^+$): 400.1672; found: 400.1679.

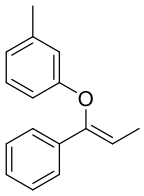
(*Z*)-2-((4-Methoxyphenyl)thio)-*N*-methyl-*N*-(2-((1-phenylprop-1-en-1-yl)oxy)phenyl) aniline (**4g**)



White solid (42.6 mg, 47%, eluents: PE/EA = 40/1), *Z*/*E* = 33/1. M.p.: 73-75 ºC. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.43 (m, 2.06H), 7.38 (d, *J* = 8.6 Hz, 2.06H), 7.20-7.16 (m, 3.09H), 7.12-7.07 (m, 2.06H), 6.99 (dd, *J* = 7.8 Hz, 1.2 Hz, 1.03H), 6.92 (t, *J* = 7.4 Hz, 1.03H), 6.89-6.85 (m, 3.09H), 6.81-6.77 (m, 2.06H), 6.68 (dd, *J* = 8.0 Hz, 1.1 Hz, 1.03H), 5.83 (q, *J* = 7.0 Hz, 1H), 5.21 (q, *J* = 7.4 Hz, 0.03H), 3.81 (s, 3H), 3.79 (s, 0.09H), 3.38 (s, 3H), 3.30 (s, 0.09H), 1.75 (d, *J* = 7.4 Hz, 0.09H), 1.57 (d, *J* = 7.1 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.9, 149.6, 149.6, 148.2, 139.3, 136.5, 136.5,

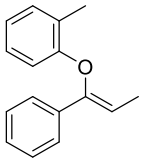
135.6, 128.2, 128.1, 127.6, 125.6, 125.3, 124.5, 124.5, 123.5, 122.6, 121.2, 120.7, 114.9, 113.9, 112.2, 55.3, 41.0, 11.2. IR (KBr): 3059, 2938, 2908, 2837, 2805, 1687, 1593, 1494, 1470, 1446, 1350, 1287, 1248, 1220, 1174, 1103, 1030, 952, 873, 830, 747, 691 cm^{-1}. HRMS-ESI (m/z) calcd. for $[C_{29}H_{28}NO_2S]^+$ ($[M + H]^+$): 454.1835; found: 454.1828.

(*Z*)-1-Methyl-3-((1-phenylprop-1-en-1-yl)oxy)benzene (**5k**)



Colorless oil (30.1 mg, 67%, eluents: PE/EA = 40/1), *Z*/*E* = 50/1. ^1H NMR (500 MHz, $CDCl_3$) δ 7.50 (d, *J* = 7.4 Hz, 2.04H), 7.29 (t, *J* = 7.4 Hz, 2.04H), 7.24 (t, *J* = 7.3 Hz, 1.02H), 7.12 (t, *J* = 7.8 Hz, 1.02H), 6.83 (s, 1.02H), 6.77 (d, *J* = 7.8 Hz, 2.04H), 5.95 (q, *J* = 7.0 Hz, 1H), 5.47 (q, *J* = 7.3 Hz, 0.02H), 2.43 (s, 0.06H), 2.31 (s, 3H), 1.87 (d, *J* = 7.4 Hz, 0.06H), 1.78 (d, *J* = 7.0 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 157.3, 149.7, 139.6, 135.7, 129.2, 128.4, 127.7, 125.1, 122.2, 116.1, 112.3, 21.5, 11.4. IR (KBr): 3055, 3034, 2917, 2858, 1661, 1610, 1588, 1488, 1445, 1317, 1253, 1150, 1025, 968, 916, 856, 817, 772, 735, 690 cm^{-1}. HRMS-ESI (m/z) calcd. for $[C_{16}H_{17}O]^+$ ($[M + H]^+$): 225.1274; found: 225.1272.

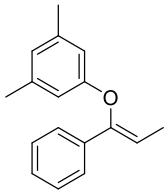
(*Z*)-1-Methyl-2-((1-phenylprop-1-en-1-yl)oxy)benzene (**5l**)



Colorless oil (21.0 mg, 47%, eluents: PE/EA = 40/1), *Z*/*E* = 50/1. ^1H NMR (500 MHz, $CDCl_3$) δ 7.47 (d, *J* = 7.3 Hz, 2.04H), 7.29 (t, *J* = 7.4 Hz, 2.04H), 7.25-7.19 (m, 2.04H), 6.99 (t, *J* = 7.7 Hz, 1.02H), 6.89 (t, *J* = 7.3 Hz, 1.02H), 6.70 (d, *J* = 8.1 Hz, 1.02H), 5.95 (q, *J* = 6.9 Hz, 1H), 5.18 (q, *J* = 7.3 Hz, 0.02H), 2.46 (s, 3H), 2.34 (s, 0.06H), 1.82 (d, *J* = 7.3 Hz, 0.06H), 1.75 (d, *J* = 6.9 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 155.3, 150.0, 135.7, 130.9, 128.4, 127.8, 126.7, 126.1, 125.0, 121.1, 112.9, 112.1, 16.3, 11.3. IR (KBr): 3057, 3029, 2921, 2856, 1660, 1589, 1490, 1445, 1317, 1262, 1229, 1186, 1151, 1118, 1018, 968, 876, 815, 745, 693 cm^{-1}. HRMS-ESI (m/z)

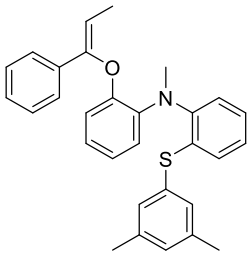
calcd. for $[C_{16}H_{17}O]^+$ ([M + H]$^+$): 225.1274; found: 225.1272.

(*Z*)-1,3-Dimethyl-5-((1-phenylprop-1-en-1-yl)oxy)benzene (**5m**)



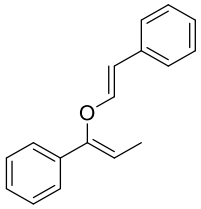
Colorless oil (37.2 mg, 78%, eluents: PE/EA = 40/1), *Z*/*E* = 50/1. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.50 (d, *J* = 7.4 Hz, 2.04H), 7.29 (t, *J* = 7.5 Hz, 2.04H), 7.23 (t, *J* = 7.3 Hz, 1.02H), 6.60 (m, 3.06H), 5.94 (q, *J* = 6.9 Hz, 1H), 5.44 (q, *J* = 7.3 Hz, 0.02H), 2.38 (s, 0.12H), 2.25 (s, 6H), 1.87 (d, *J* = 7.4 Hz, 0.06H), 1.75 (d, *J* = 7.0 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 157.3, 149.6, 139.3, 135.8, 128.4, 127.7, 125.1, 123.2, 113.0, 112.2, 21.4, 11.5. IR (KBr): 3055, 3035, 2917, 2857, 1660, 1614, 1593, 1492, 1470, 1446, 1377, 1313, 1292, 1263, 1144, 1054, 1032, 995, 969, 835, 762, 702 cm^{-1}. HRMS-ESI (m/z) calcd. for $[C_{17}H_{19}O]^+$ ([M + H]$^+$): 239.1430; found: 239.1426.

(*Z*)-2-((3,5-Dimethylphenyl)thio)-*N*-methyl-*N*-(2-((1-phenylprop-1-en-1-yl)oxy)phenyl)aniline (**4j**)



Colorless oil (5.4 mg, 6%, eluents: PE/EA = 40/1), *Z*/*E* = 11/1. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40-7.38 (m, 2.18H), 7.18-7.12 (m, 5.45H), 7.02 (s, 2.18H), 6.99-6.94 (m, 3.27H), 6.87-6.84 (m, 2.18H), 6.78 (t, *J* = 7.9 Hz, 1.09H), 6.66 (dd, *J* = 8.0 Hz, 1.1 Hz, 1.09H), 5.82 (q, *J* = 6.9 Hz, 1H), 5.20 (q, *J* = 7.4 Hz, 0.09H), 3.37 (s, 3H), 3.29 (s, 0.27H), 2.24 (s, 0.54H), 2.22 (s, 6H), 1.75 (d, *J* = 7.4 Hz, 0.27H), 1.55 (d, *J* = 6.9 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 149.6, 149.6, 149.3, 139.3, 138.7, 135.6, 134.8, 134.4, 131.0, 130.2, 129.3, 128.2, 127.5, 126.3, 125.2, 124.4, 123.6, 122.6, 121.2, 120.8, 113.9, 112.2, 41.2, 21.0, 11.2. IR (KBr): 3057, 3032, 2917, 2855, 2802, 1660, 1598, 1579, 1495, 1471, 1445, 1317, 1261, 1215, 1123, 1104, 1051, 1016, 968, 874, 811, 747, 692 cm^{-1}. HRMS-ESI (m/z) calcd. for $[C_{30}H_{30}NOS]^+$ ([M + H]$^+$): 452.2043; found: 452.2046.

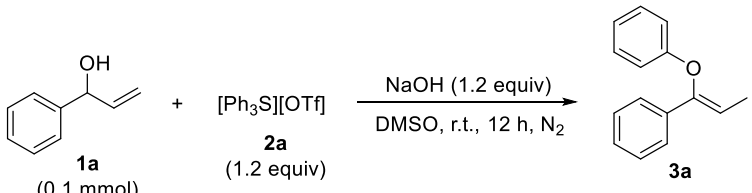
((*E*)-2-(((*Z*)-1-Phenylprop-1-en-1-yl)oxy)vinyl)benzene (**5n**)



Colorless oil (11.3 mg, 24%, eluents: PE). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.49 (d, *J* = 7.4 Hz, 2H), 7.33 (t, *J* = 7.5 Hz, 2H), 7.27 (t, *J* = 7.4 Hz, 1H), 7.23 (t, *J* = 7.3 Hz, 2H), 7.18 (d, *J* = 7.2 Hz, 2H), 7.12 (t, *J* = 7.1 Hz, 1H), 6.99 (d, *J* = 12.7 Hz, 1H), 6.06 (d, *J* = 12.7 Hz, 1H), 5.76 (q, *J* = 6.9 Hz, 1H), 1.83 (d, *J* = 7.0 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 151.4, 146.1, 135.8, 135.4, 128.5, 128.4, 127.9, 125.9, 125.3, 125.2, 110.9, 109.0, 11.3. IR (KBr): 3061, 3034, 2927, 2855, 1728, 1698, 1648, 1599, 1494, 1449, 1316, 1265, 1212, 1132, 1072, 1028, 971, 927, 752, 698 cm^{-1}. HRMS-ESI (m/z) calcd. for $[C_{17}H_{17}O]^+$ ($[M + H]^+$): 237.1274; found: 237.1269.

5. The control experiments for mechanistic insights.

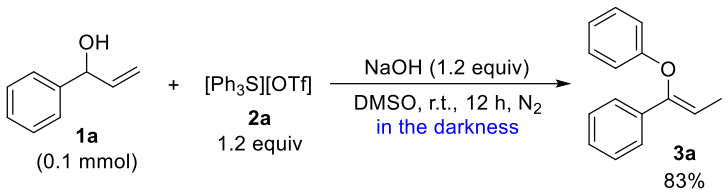
5.1. Reaction of 1a with 2a and NaOH under the standard conditions in the presence of different radical traps.



Additive	HPLC yield
none	89%
TEMPO (2 equiv)	62%
1,1-diphenylethylene (2 equiv)	65%

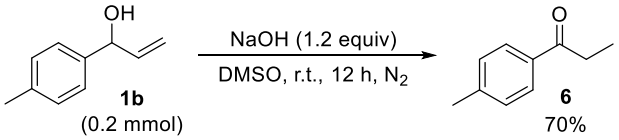
In a nitrogen-filled glovebox, a sealed tube was charge with **1a** (13.4 mg, 0.1 mmol), **2a** (49.5 mg, 0.12 mmol), NaOH (4.8 mg, 0.12 mmol), DMSO (1 mL), and a radical trap (0.2 mmol) with vigorous stirring. The mixture was reacted at room temperature for 12 h. The yields of **3a** were determined by HPLC using pure **3a** as an external standard (t_R = 10.5 min, λ_{max} = 252 nm, water / methanol = 20 / 80 (v / v).

5.2. The standard reaction of 1a, 2a and NaOH in the darkness.



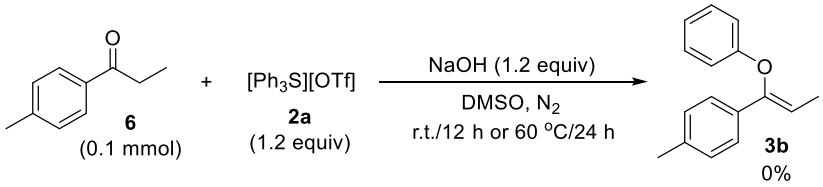
In a nitrogen-filled glovebox, a sealed tube was charge with **1a** (13.4 mg, 0.1 mmol), **2a** (49.5 mg, 0.12 mmol), NaOH (4.8 mg, 0.12 mmol), and DMSO (1 mL) with vigorous stirring. The sealed tube was fully wrapped with tin foil. The mixture was reacted at room temperature for 12 h. The yields of **3a** were determined by HPLC using pure **3a** as an external standard (t_R = 10.5 min, λ_{max} = 252 nm, water / methanol = 20 / 80 (v / v).

5.3. Reaction of 1b with NaOH in DMSO without using arylsulfonium salt under the standard conditions.



In a nitrogen-filled glovebox, a sealed tube was charge with **1b** (29.6 mg, 0.2 mmol), NaOH (9.6 mg, 0.24 mmol), and DMSO (2 mL) with vigorous stirring. The mixture was reacted at room temperature for 12 h, diluted with water (30 mL), and extracted with ethyl acetate (3 × 20 mL). The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated to dryness under reduced pressure. The residue was purified by flash column chromatography on silica gel using a mixture of petroleum ether and ethyl acetate (40/1, v/v) as eluents to give 1-(*p*-tolyl)propan-1-one (**6**)[13] as a yellow oil (20.7 mg, 50%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.87 (d, *J* = 8.0 Hz, 2H), 7.25 (d, *J* = 8.4 Hz, 2H), 2.97 (q, *J* = 7.3 Hz, 2H), 2.41 (s, 3H), 1.22 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 200.5, 143.5, 134.6, 129.2, 128.1, 31.6, 21.6, 8.3.

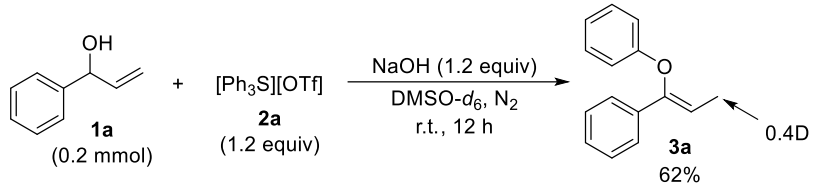
5.4. Reaction of 6 with 2a and NaOH in DMSO under the standard conditions.



In a nitrogen-filled glovebox, a sealed tube was charge with **6** (14.8 mg, 0.1 mmol),

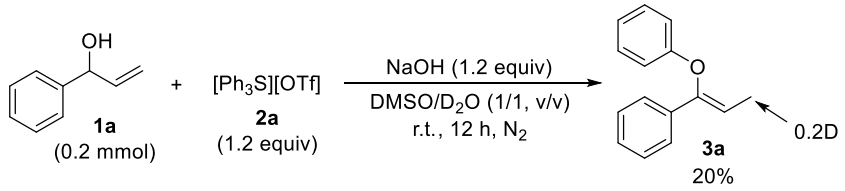
2a (49.5 mg, 0.12 mmol), NaOH (4.8 mg, 0.12 mmol), and DMSO (1 mL) with vigorous stirring. The mixture was reacted at room temperature for 12 h or at 60 °C for 24 h. Finally, no desired product (**3b**) was detected.

5.5. The standard reaction of 1a, 2a and NaOH in DMSO-d_6.



In a nitrogen-filled glovebox, a sealed tube was charge with **1a** (26.8 mg, 0.2 mmol), **2a** (99 mg, 0.24 mmol), NaOH (9.6 mg, 0.24 mmol), and DMSO-d_6 (2 mL) with vigorous stirring. The mixture was reacted at room temperature for 12 h, diluted with water (30 mL), and extracted with ethyl acetate (3 × 20 mL). The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated to dryness under reduced pressure. The residue was purified by flash column chromatography on silica gel using petroleum ether as eluents to give the partially deuterated **3a** (26.1 mg, 62%) as a white solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.49 (d, *J* = 7.5 Hz, 2H), 7.28 (t, *J* = 7.4 Hz, 2H), 7.25-7.21 (m, 3H), 6.97 (d, *J* = 8.0 Hz, 2H), 6.94 (t, *J* = 7.4 Hz, 1H), 5.94 (q, *J* = 6.9 Hz, 1H), 1.77-1.74 (m, 2.6H).

5.6. The standard reaction of 1a, 2a and NaOH in DMSO/D_2O (1/1, v/v).



In a nitrogen-filled glovebox, a sealed tube was charge with **1a** (26.8 mg, 0.2 mmol), **2a** (99 mg, 0.24 mmol), NaOH (9.6 mg, 0.24 mmol), DMSO (1 mL), and D_2O (1 mL) with vigorous stirring. The mixture was reacted at room temperature for 12 h, diluted with water (30 mL), and extracted with ethyl acetate (3 × 20 mL). The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated to dryness under reduced pressure. The residue was purified by flash column chromatography on silica gel using petroleum ether as an eluent to give the partially deuterated **3a** (8.4 mg, 20%) as a white solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.48 (d, *J* = 7.3 Hz, 2H), 7.27 (t, *J* = 7.0 Hz, 2H), 7.24-7.21 (m, 3H), 6.96 (d, *J* = 8.0 Hz, 2H), 6.92 (t, *J* = 7.4 Hz, 1H),

5.93 (q, *J* = 7.0 Hz, 1H), 1.76 (d, *J* = 7.0 Hz, 2.8H).

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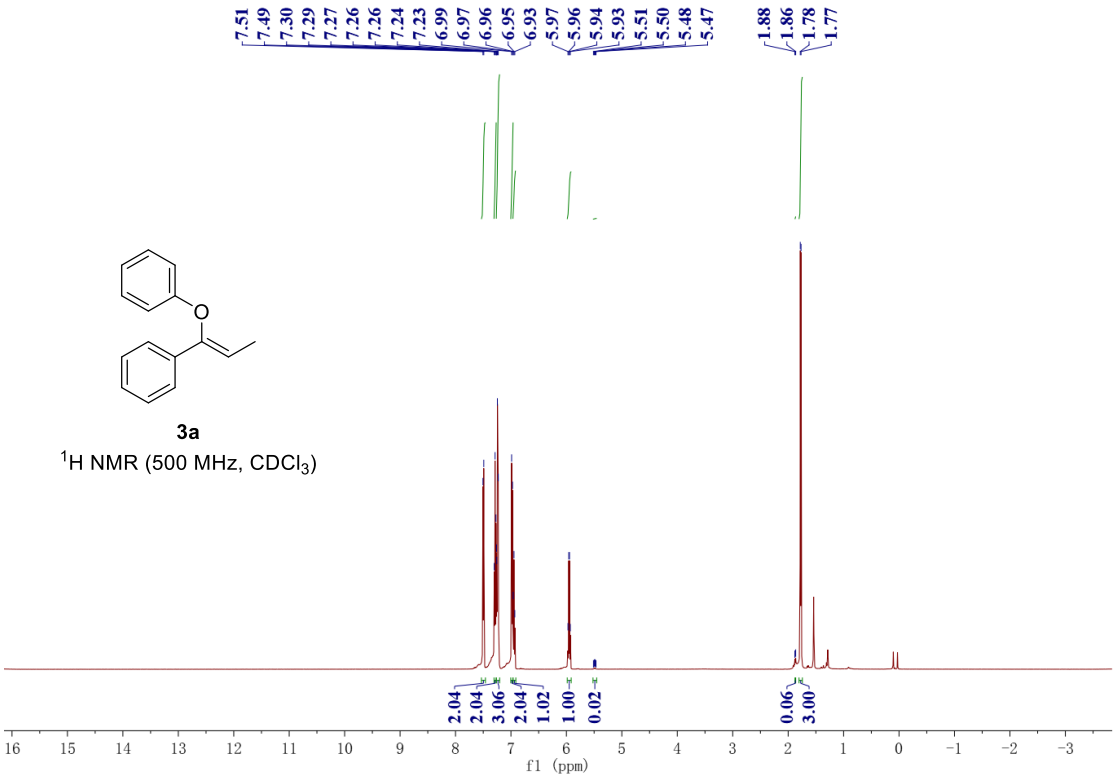
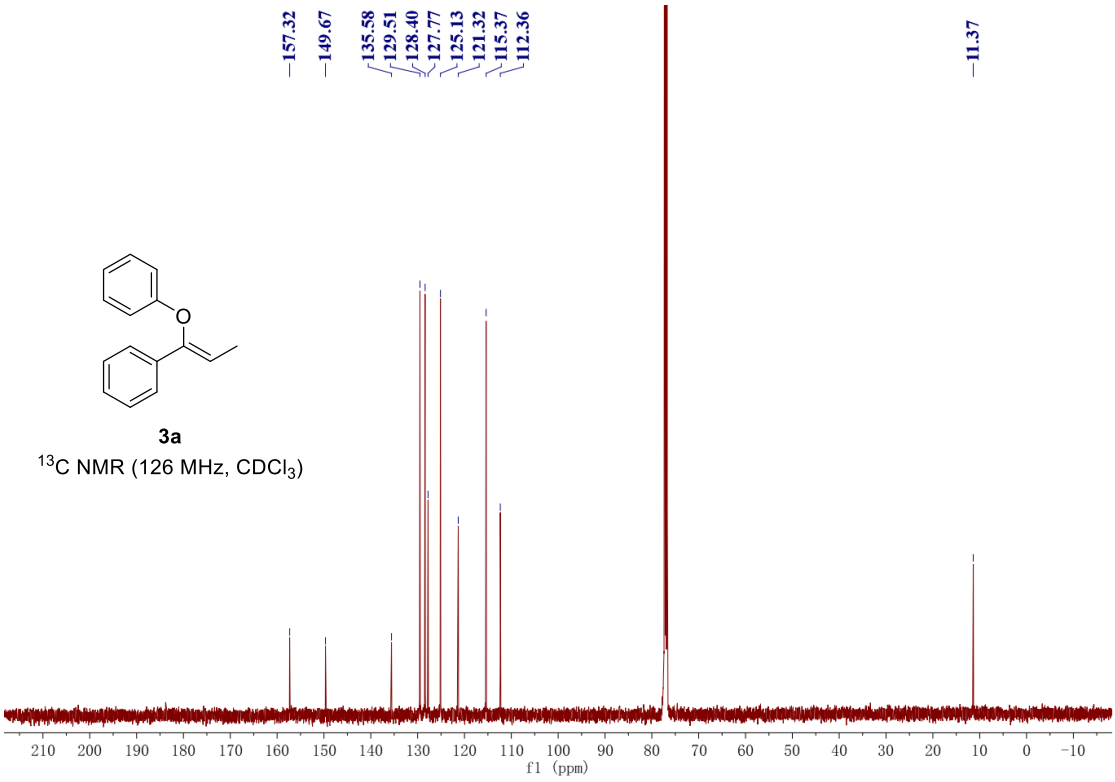
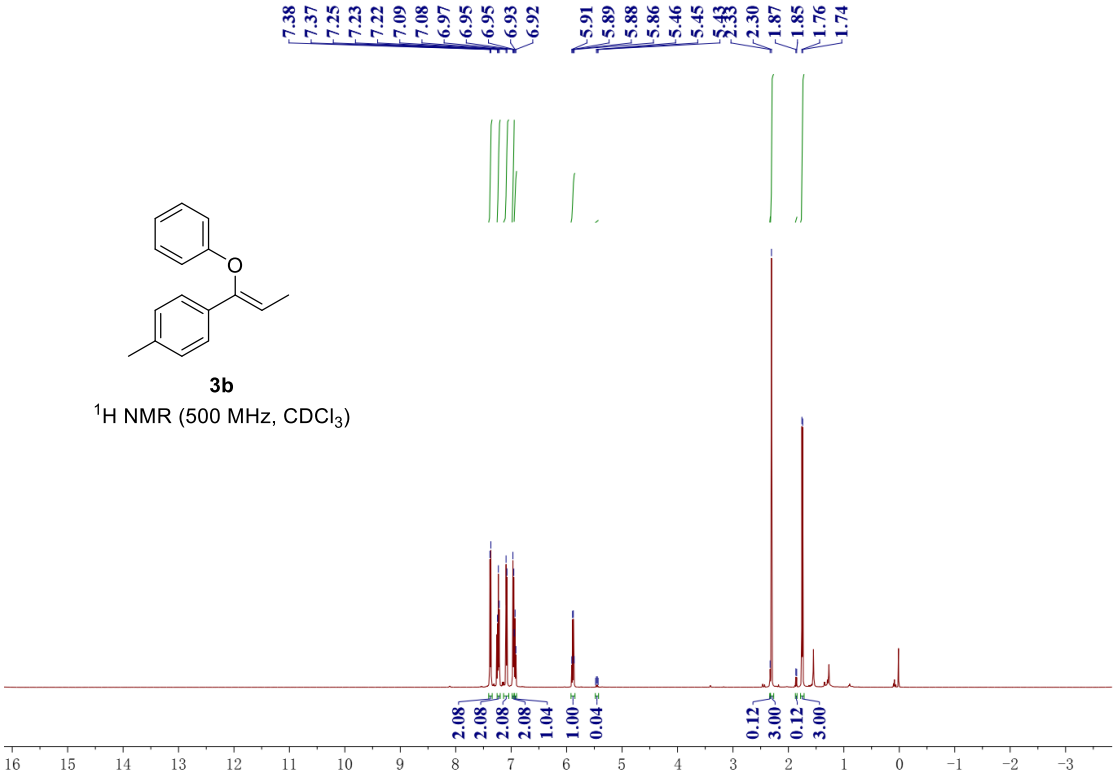
6. NMR spectra of the products

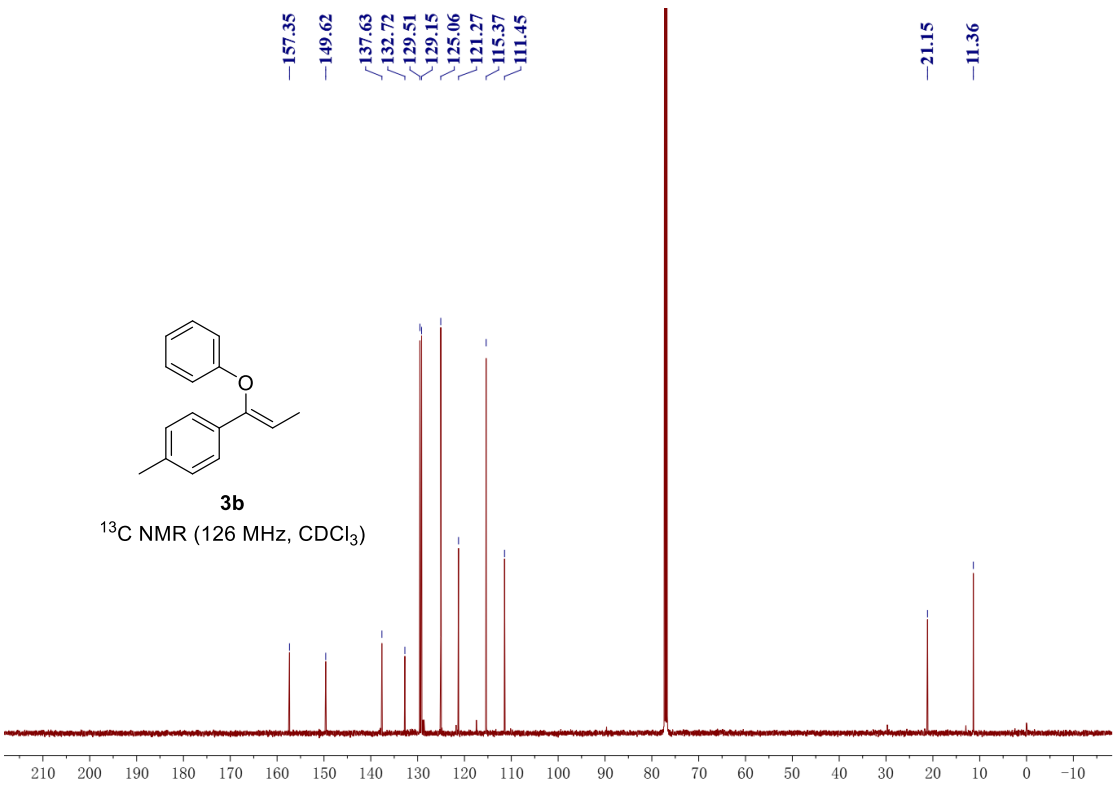






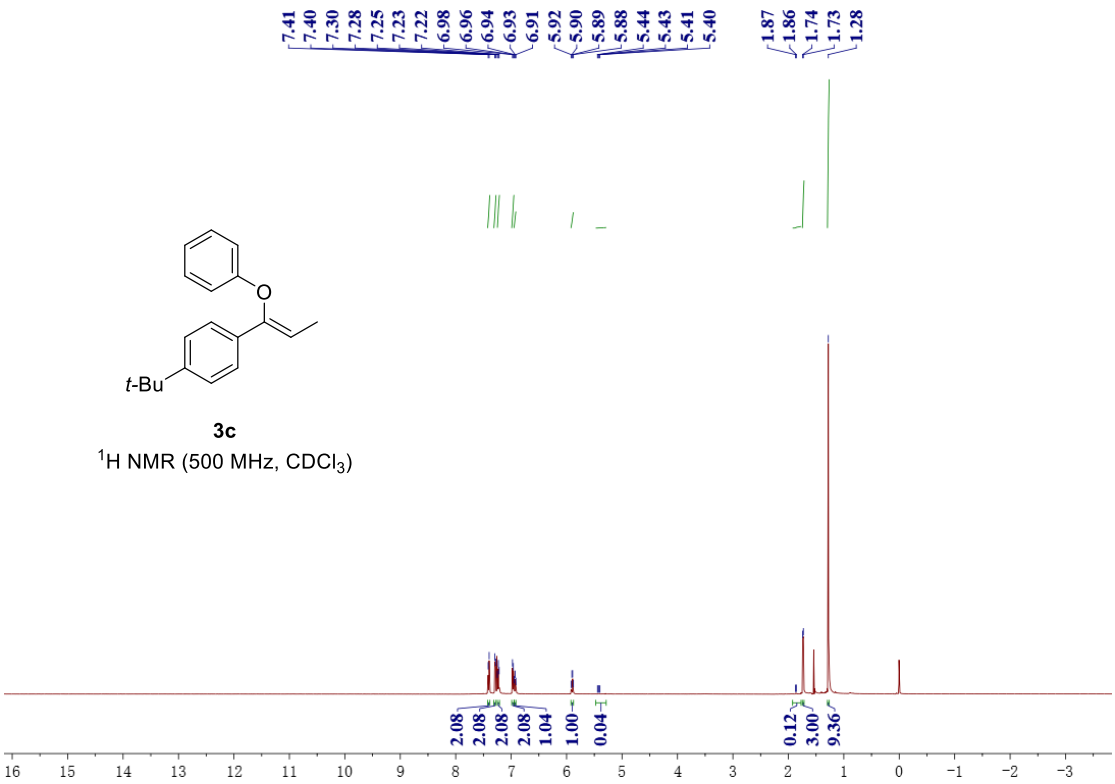
3b

^{1}H NMR (500 MHz, $CDCl_3$)



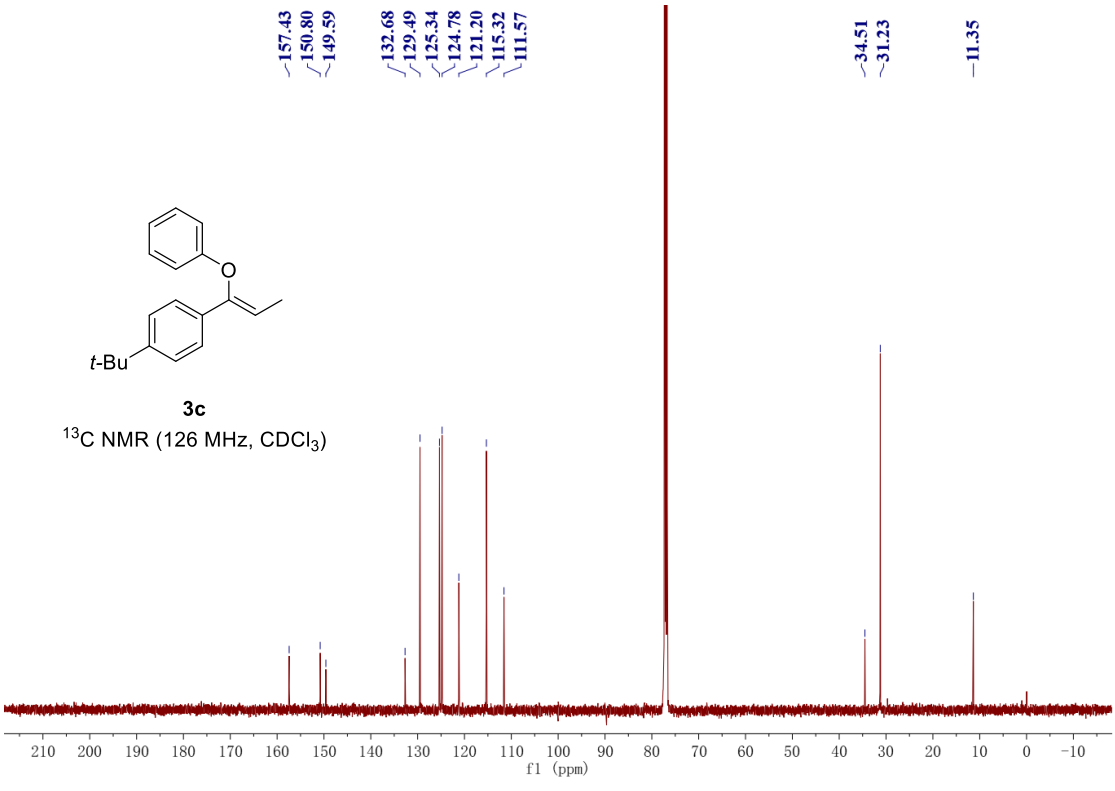
3b

^{13}C NMR (126 MHz, $CDCl_3$)



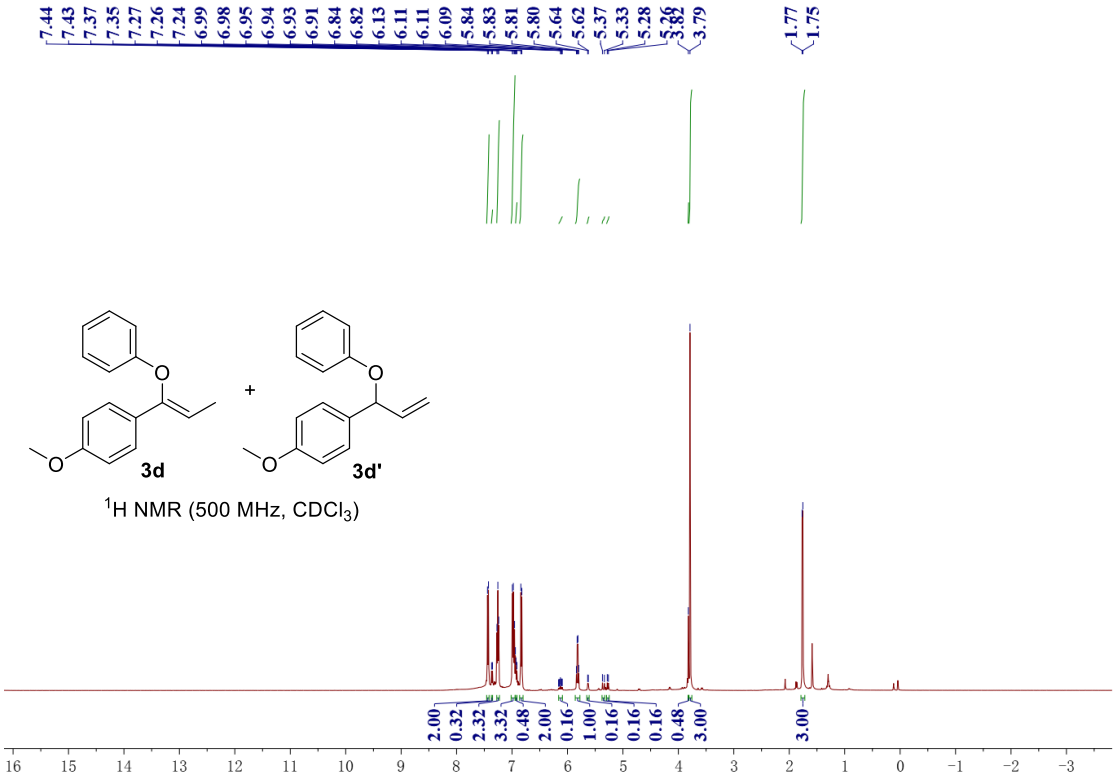
3c

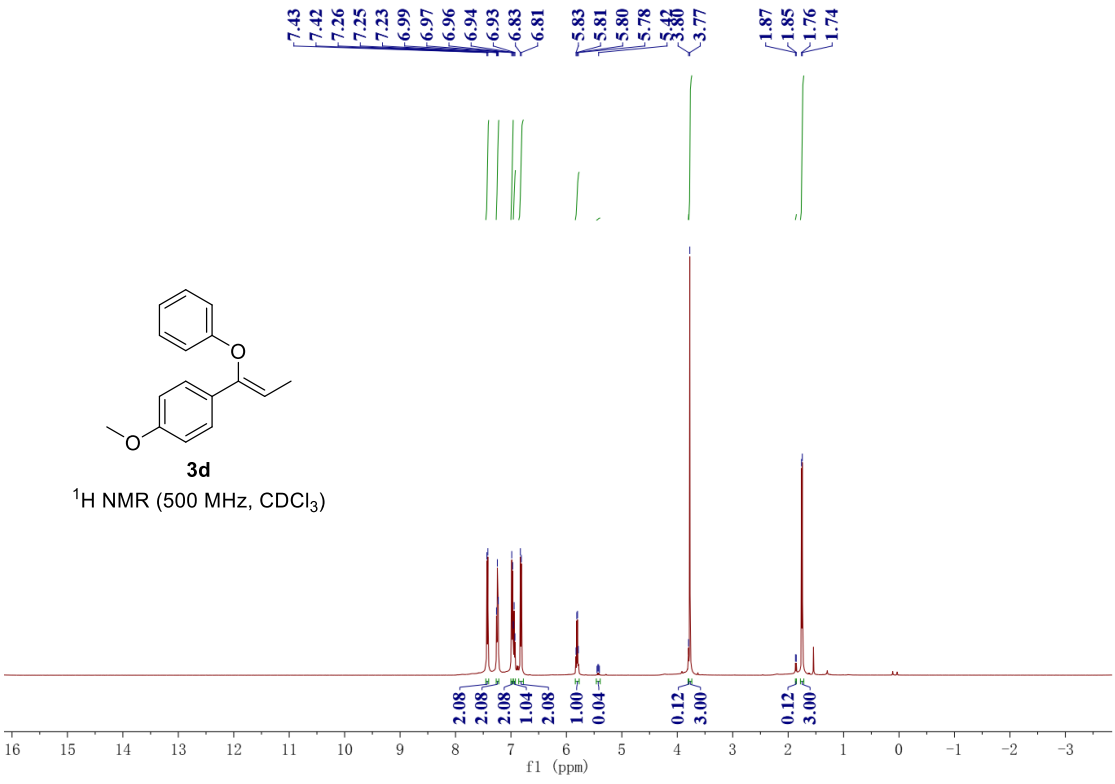
^{1}H NMR (500 MHz, $CDCl_3$)



3c

^{13}C NMR (126 MHz, $CDCl_3$)


7.44
7.43
7.37
7.35
7.27
7.26
7.24
6.99
6.98
6.95
6.94
6.93
6.91
6.84
6.82
6.13
6.11
6.11
6.09
5.84
5.83
5.81
5.80
5.64
5.62
5.37
5.33
5.28
3.82
3.79
1.77
1.75
3d
3d'
1H NMR (500 MHz, CDCl3)
2.00
0.32
2.32
3.32
0.48
2.00
0.16
1.00
0.16
0.16
0.16
0.48
3.00
3.00
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
−1
−2
−3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7.42
7.26
7.25
7.23
6.99
6.97
6.96
6.94
6.93
6.83
6.81
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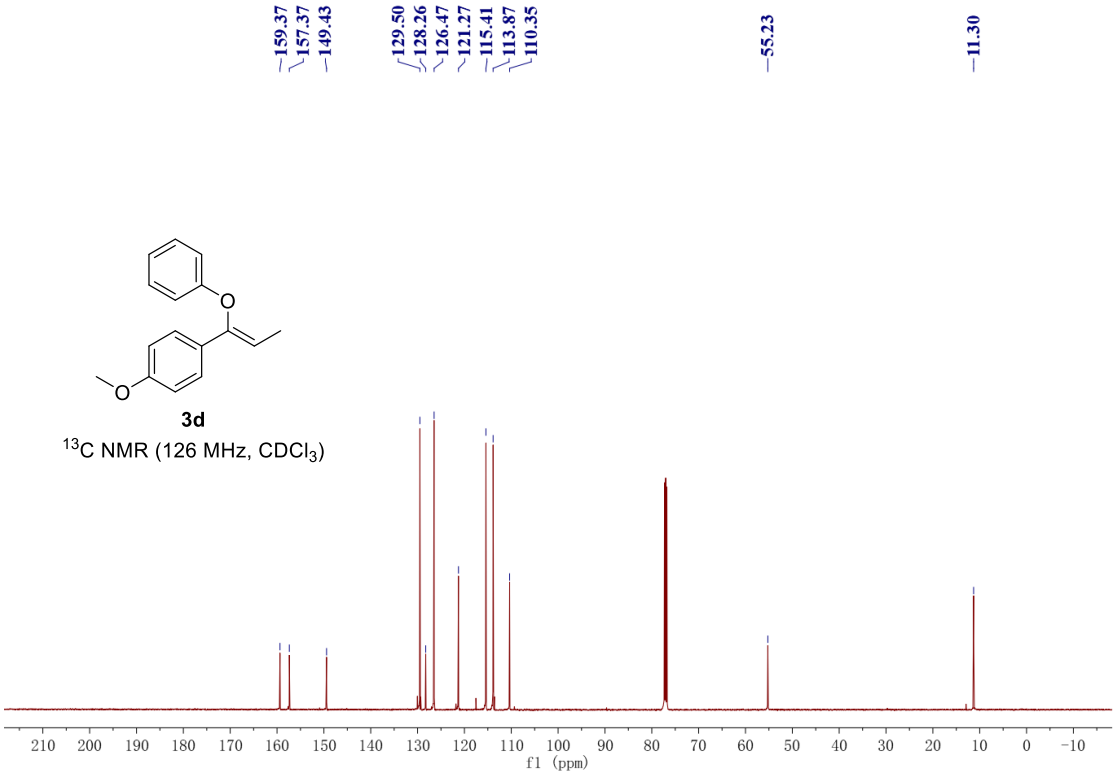
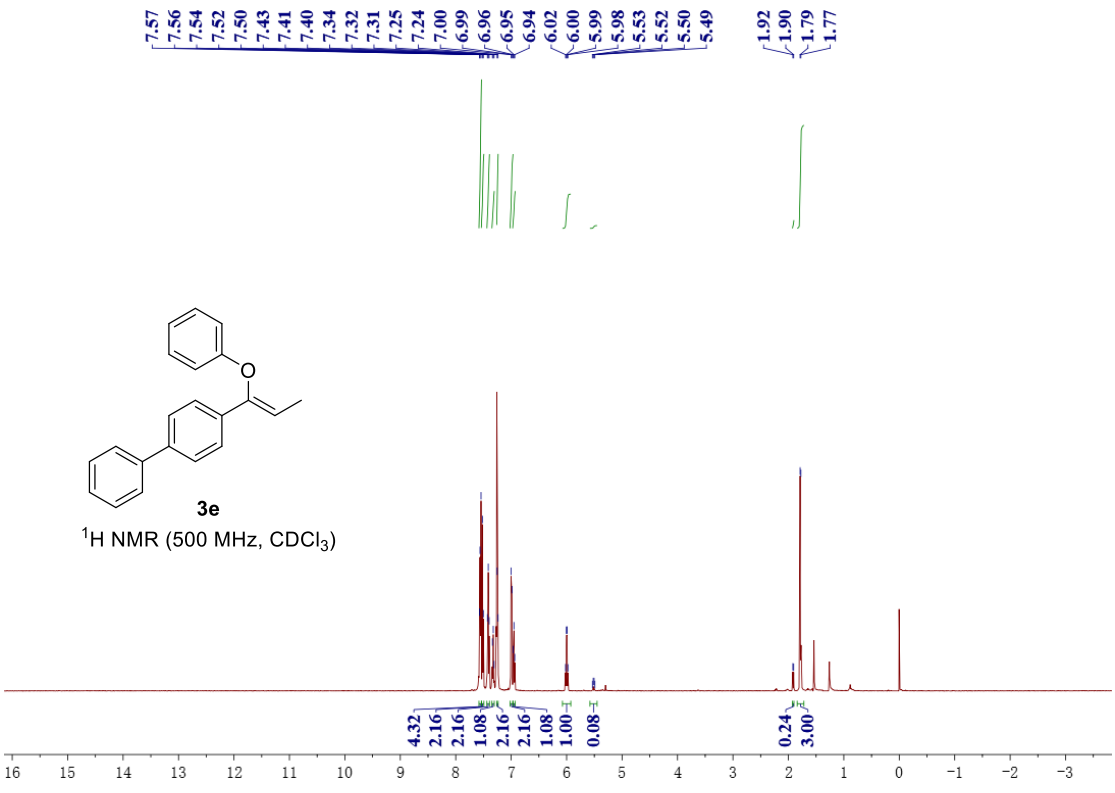
5.81
5.80
5.78
3.80
3.77
1.87
1.85
1.76
1.74
3d
1H NMR (500 MHz, CDCl3)
2.08
2.08
2.08
1.04
2.08
1.00
0.04
0.12
3.00
0.12
3.00
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
−1
−2
−3
f1 (ppm)


159.37
157.37
149.43
129.50
128.26
126.47
121.27
115.41
113.87
110.35
55.23
11.30
O
O
3d
13C NMR (126 MHz, CDCl3)
f1 (ppm)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7.50
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7.41
7.40
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7.32
7.31
7.25
7.24
7.00
6.99
6.96
6.95
6.94
6.02
6.00
5.99
5.98
5.53
5.52
5.50
5.49
1.92
1.90
1.79
1.77
O
3e
1H NMR (500 MHz, CDCl3)
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2.16
1.08
2.16
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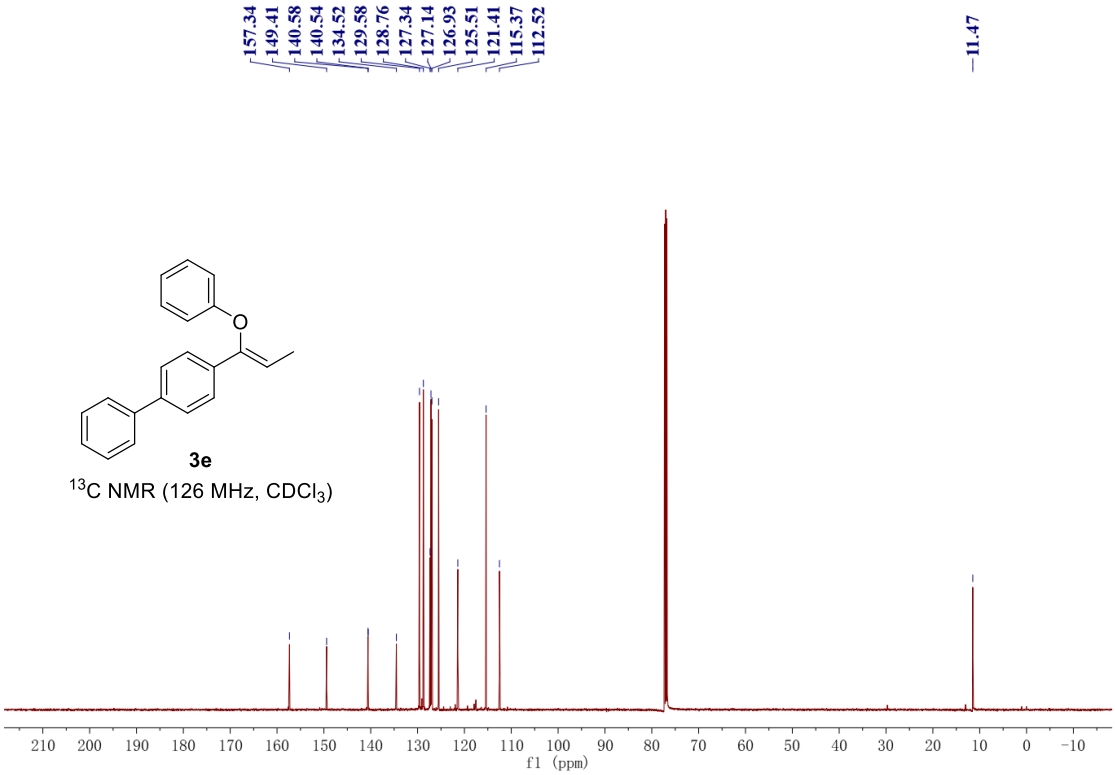
1.08
1.00
0.08
0.24
3.00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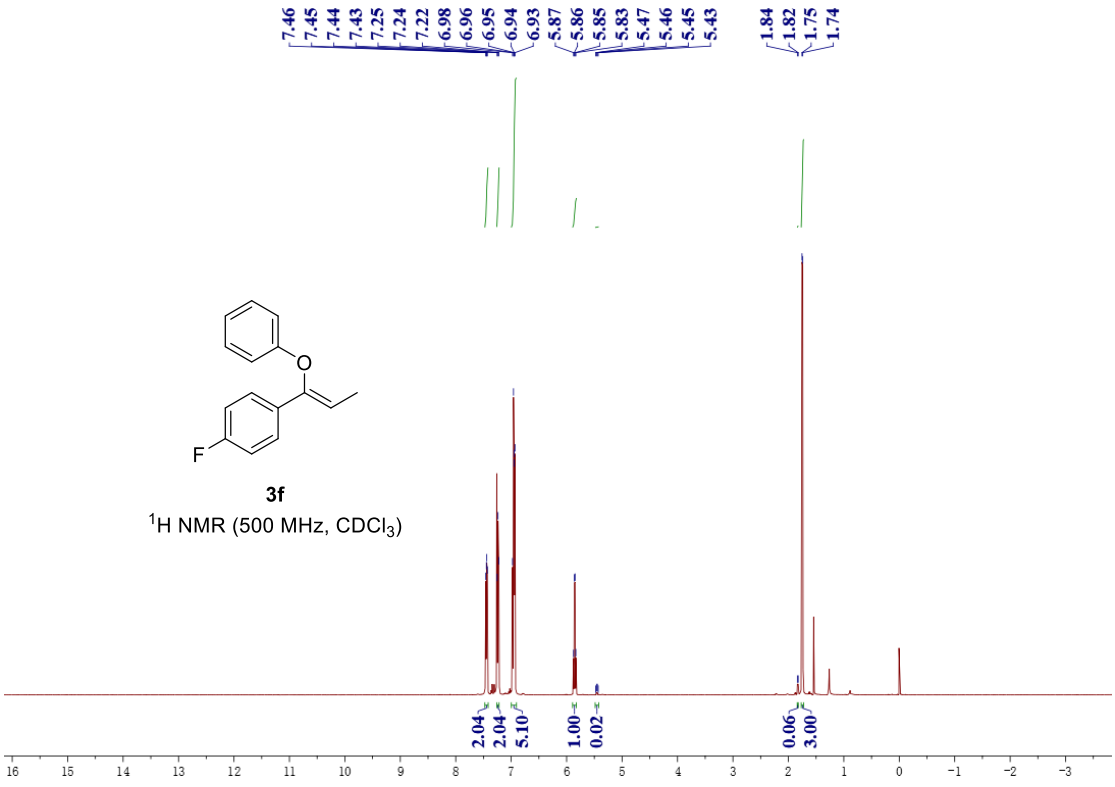
134.52
129.58
128.76
127.34
127.14
126.93
125.51
121.41
115.37
112.52
11.47
O
3e
13C NMR (126 MHz, CDCl3)
f1 (ppm)


7.46
7.45
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7.43
7.25
7.24
7.22
6.98
6.96
6.95
6.94
6.93
5.87
5.86
5.85
5.83
5.47
5.46
5.45
5.43
1.84
1.82
1.75
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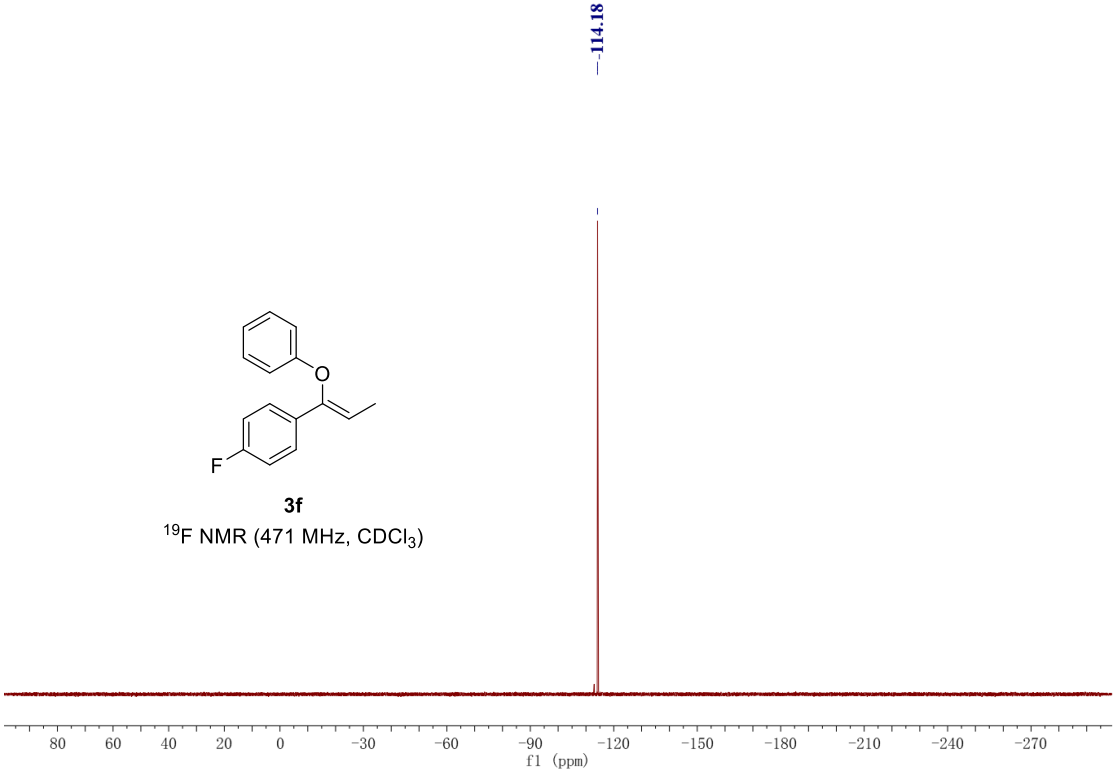
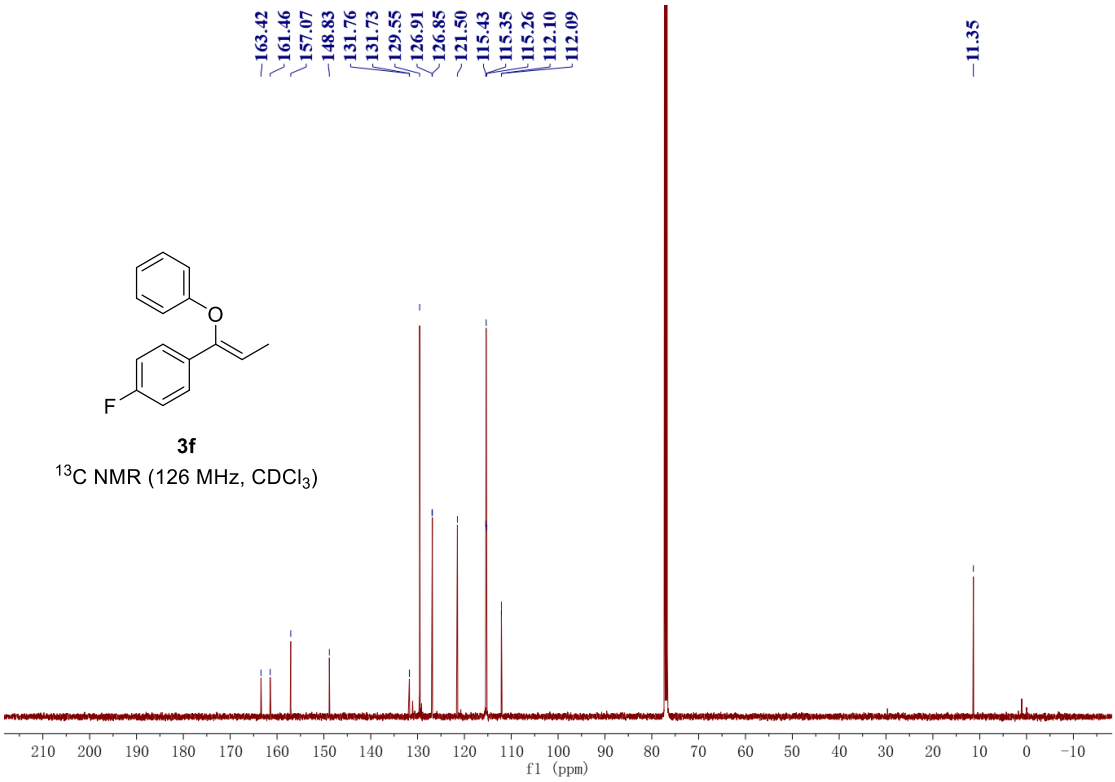
0.02
0.06
3.00



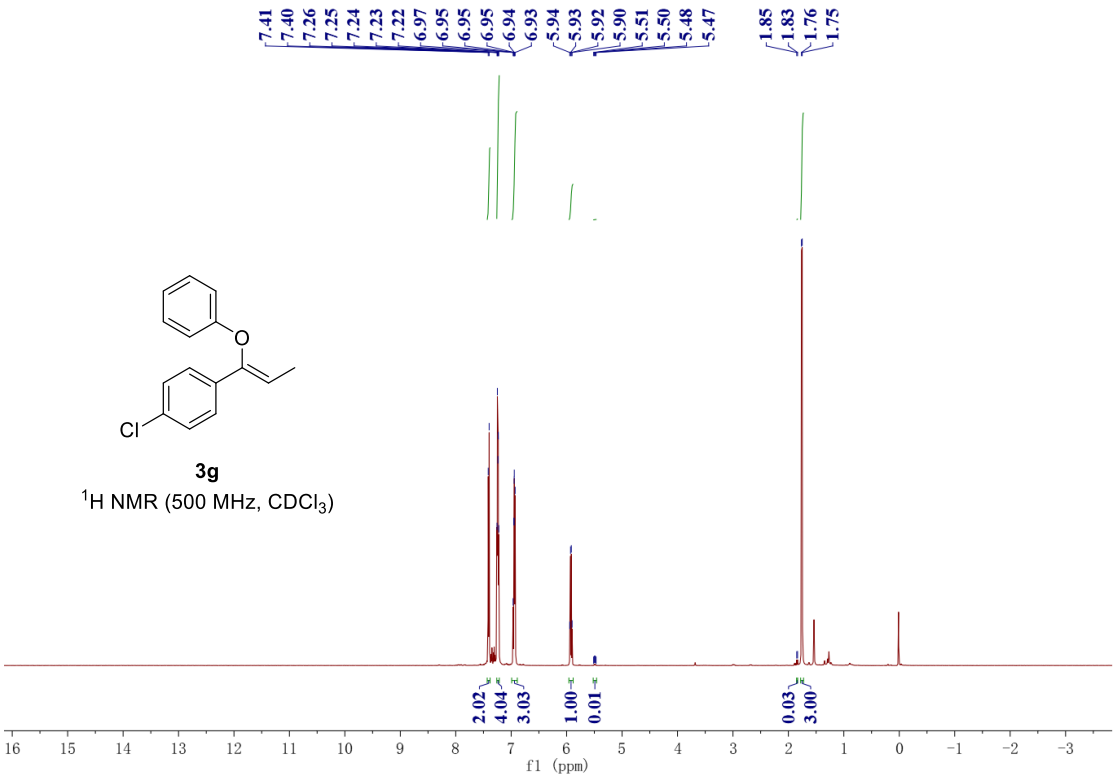
3f

^{19}F NMR (471 MHz, $CDCl_3$)



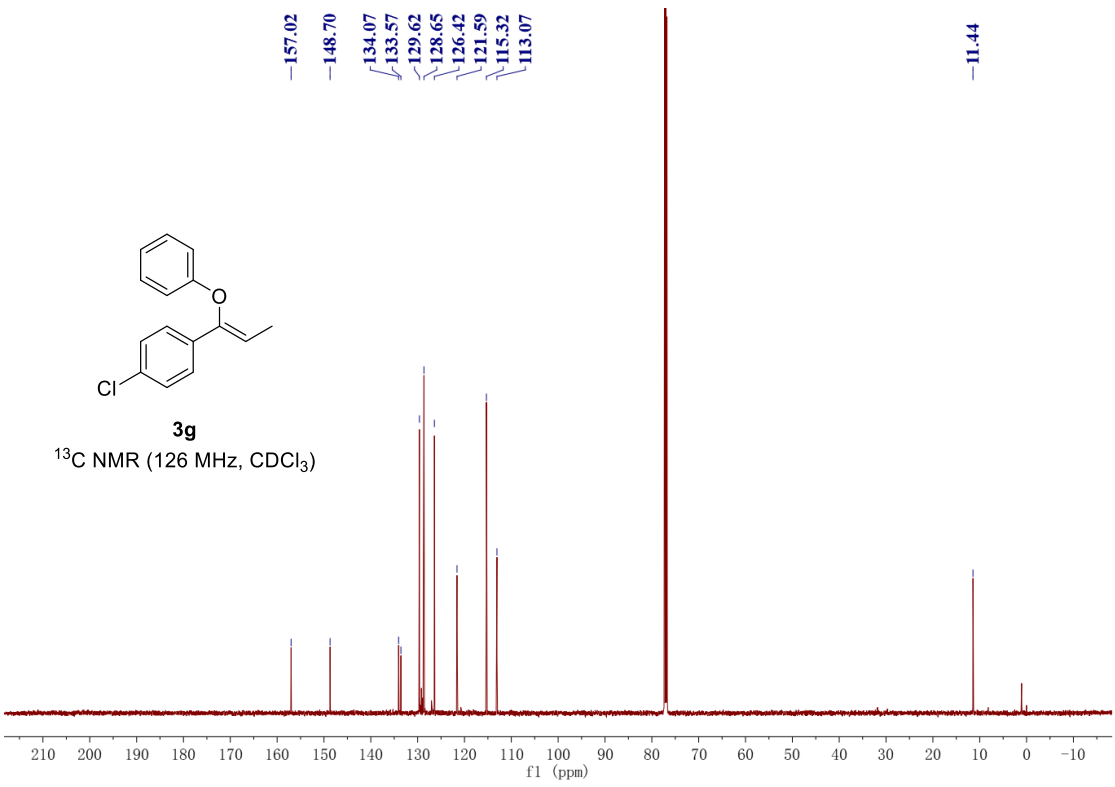
3f

^{13}C NMR (126 MHz, $CDCl_3$)



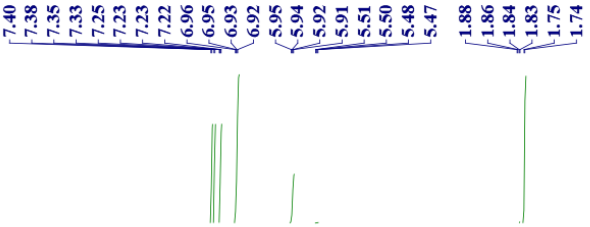
3g

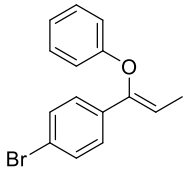
^{1}H NMR (500 MHz, $CDCl_3$)



3g

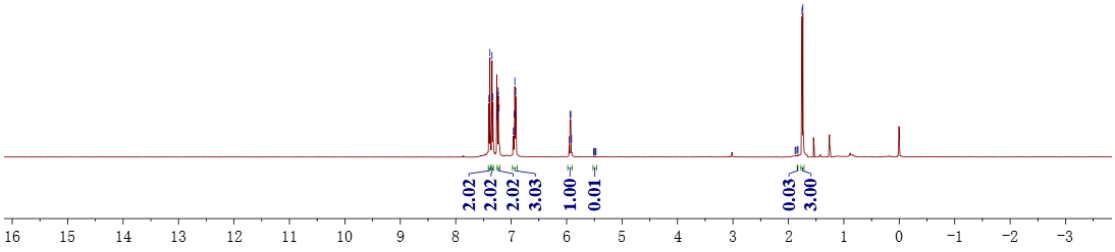
^{13}C NMR (126 MHz, $CDCl_3$)

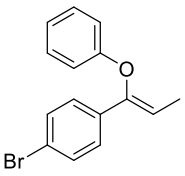




3h

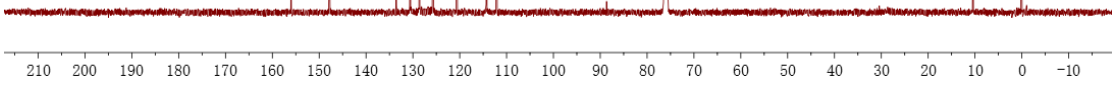
^{1}H NMR (500 MHz, $CDCl_3$)

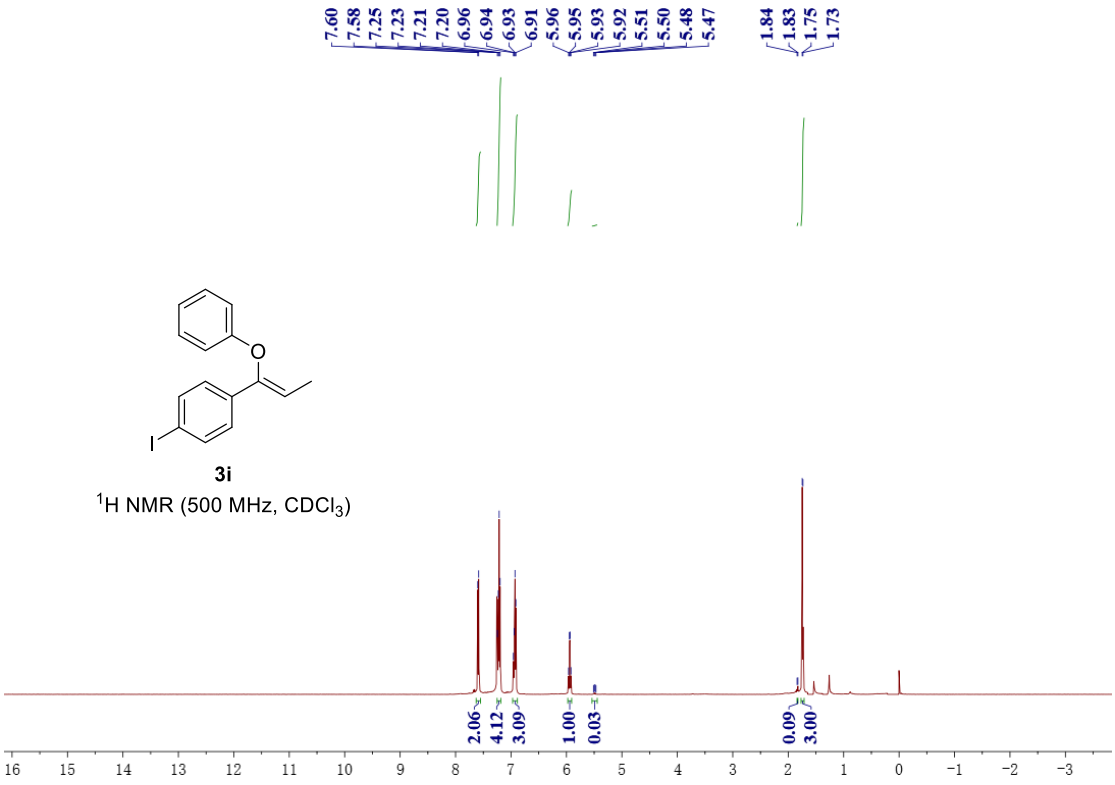




3h

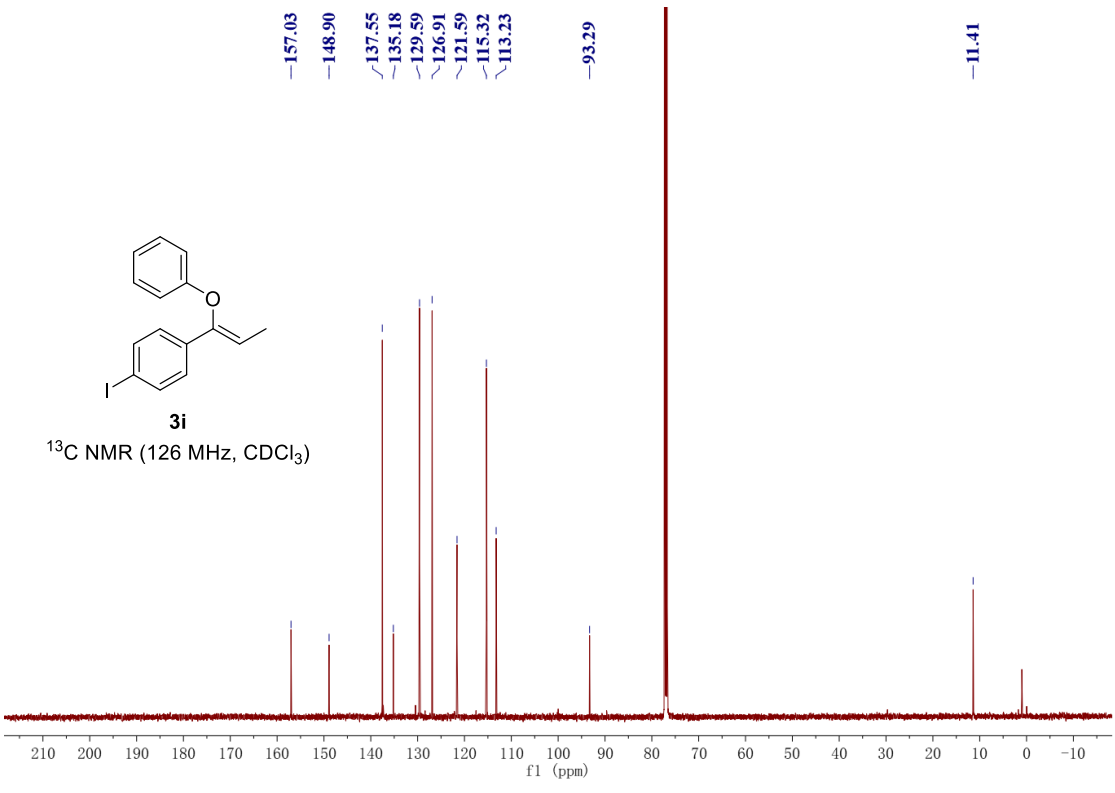
^{13}C NMR (126 MHz, $CDCl_3$)





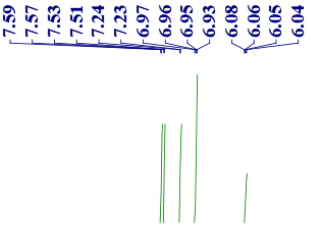
3i

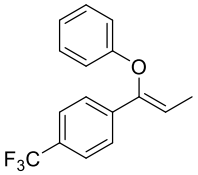
^{1}H NMR (500 MHz, $CDCl_3$)



3i

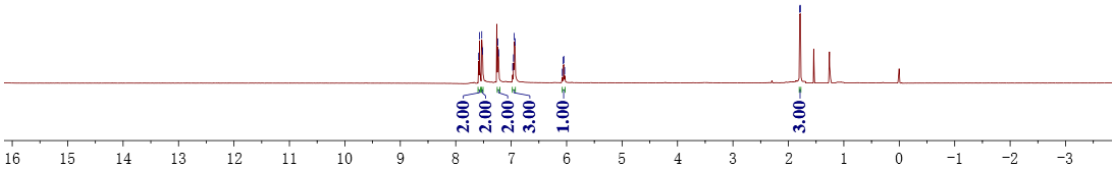
^{13}C NMR (126 MHz, $CDCl_3$)

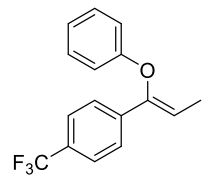




3j

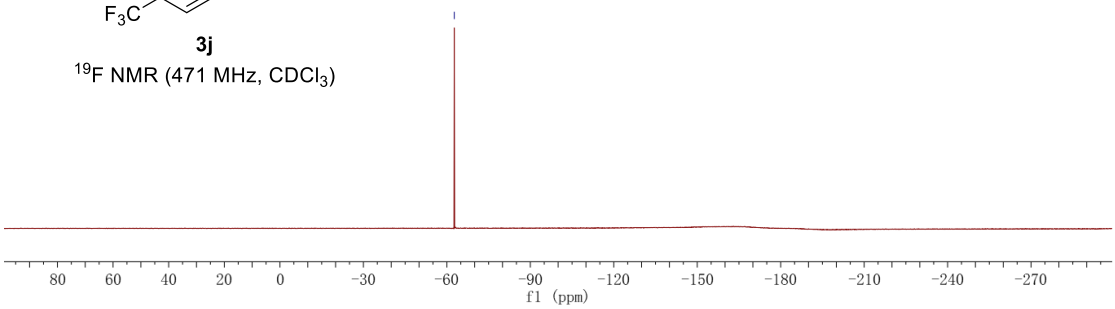
^{1}H NMR (500 MHz, $CDCl_3$)

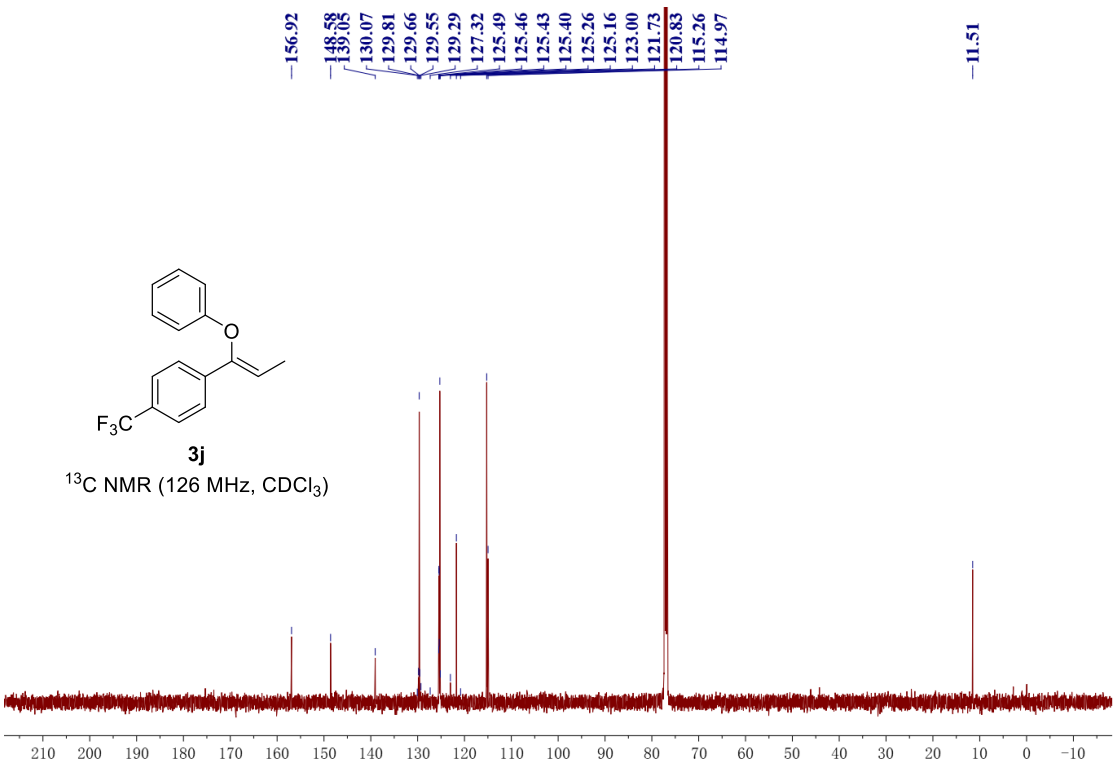


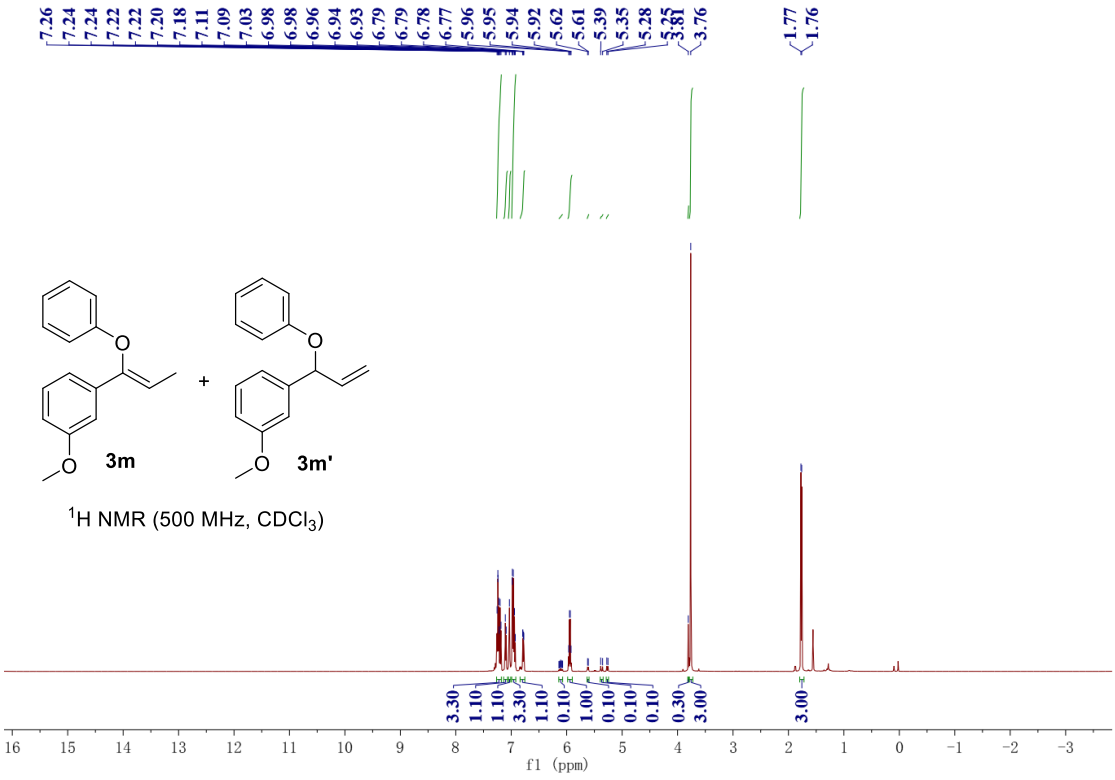


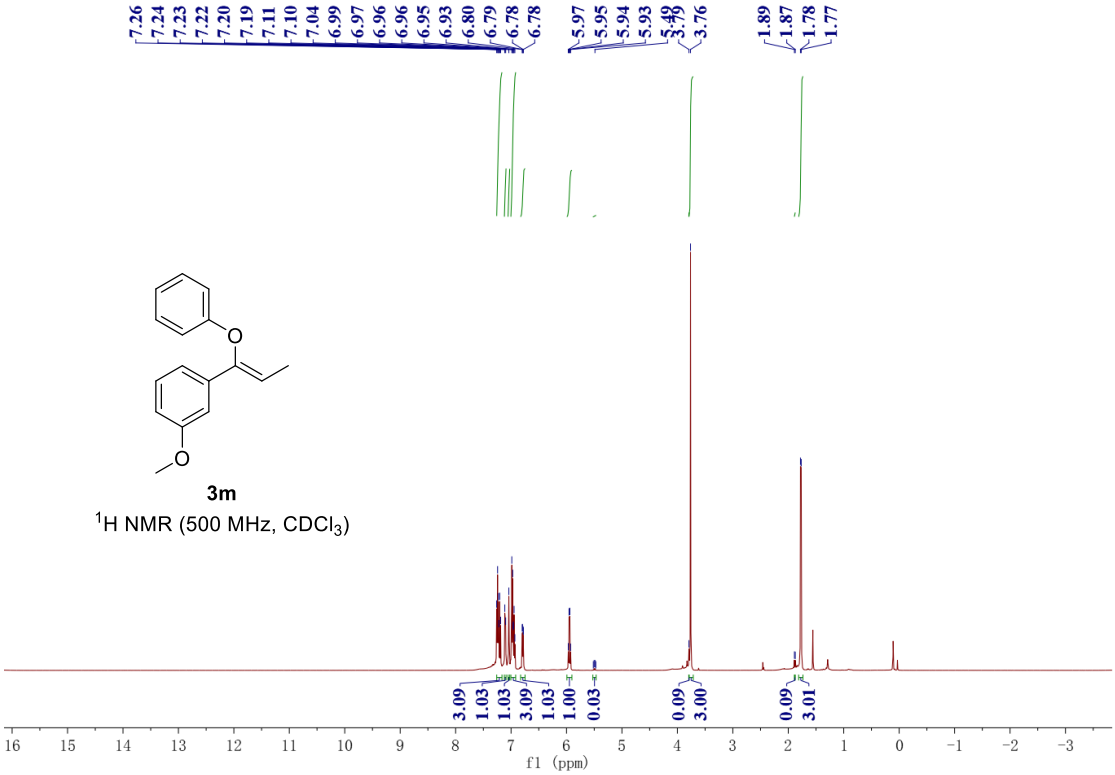
3j

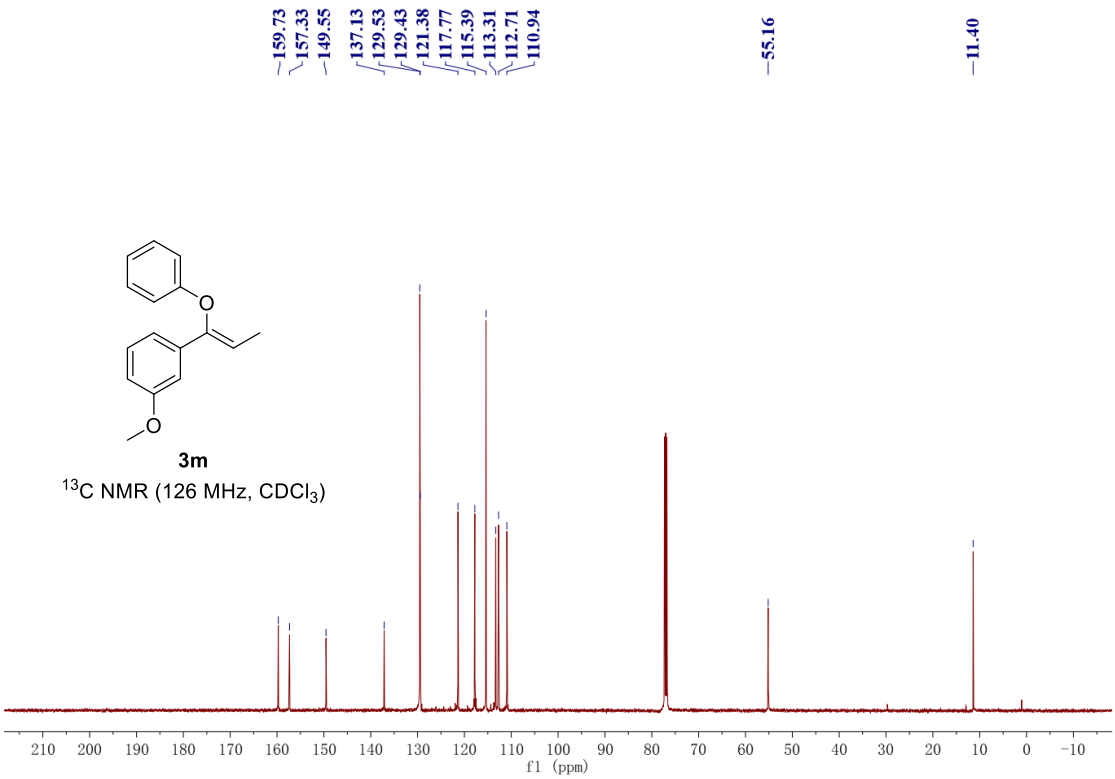
^{19}F NMR (471 MHz, $CDCl_3$)

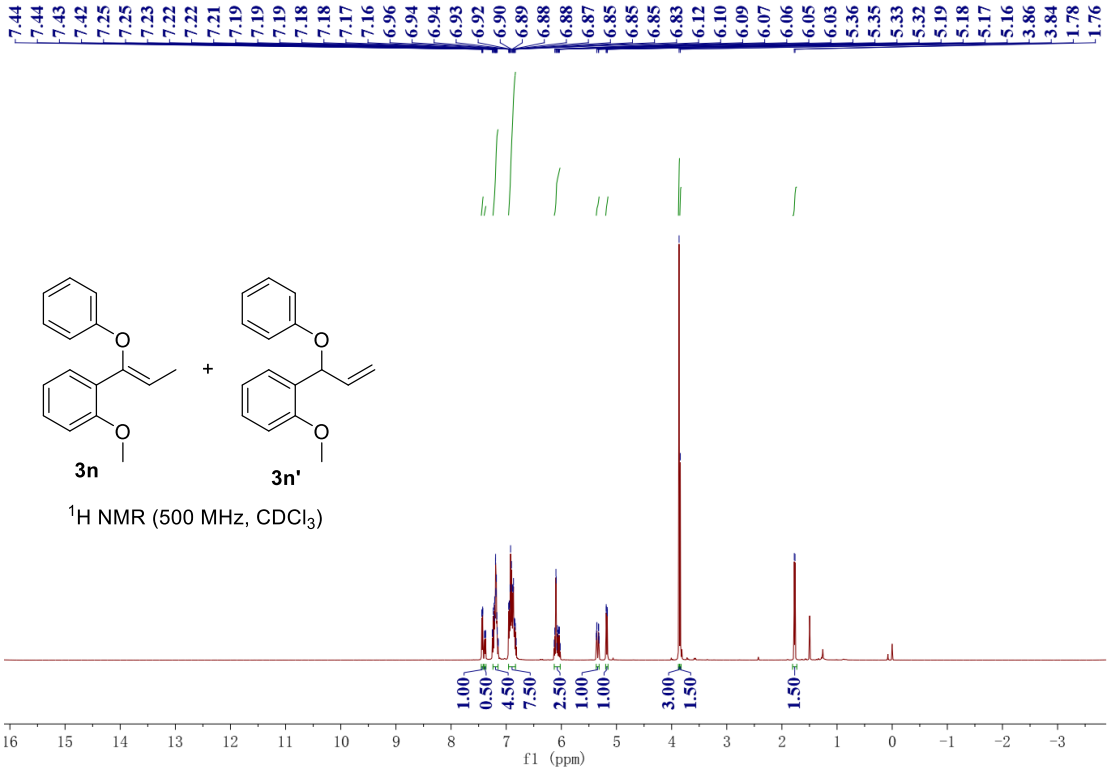


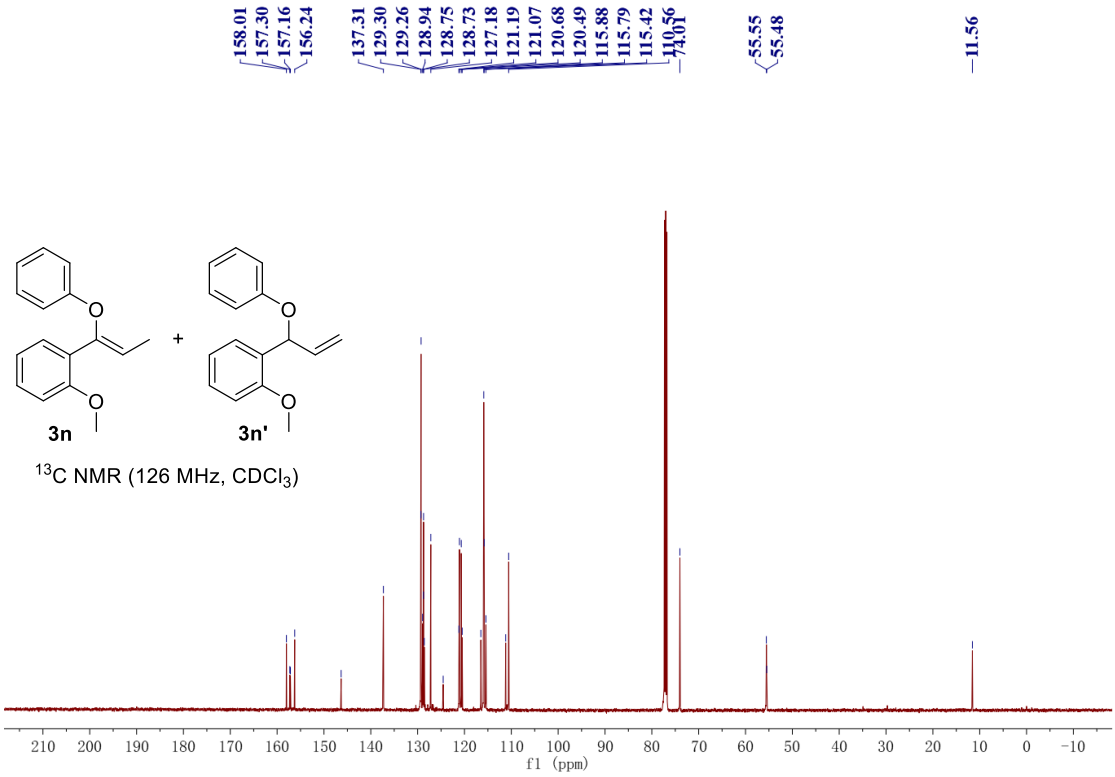

156.92
148.58
139.05
130.07
129.81
129.66
129.55
129.29
127.32
125.49
125.46
125.43
125.40
125.26
125.16
123.00
121.73
120.83
115.26
114.97
11.51
O
F3C
3j
13C NMR (126 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10

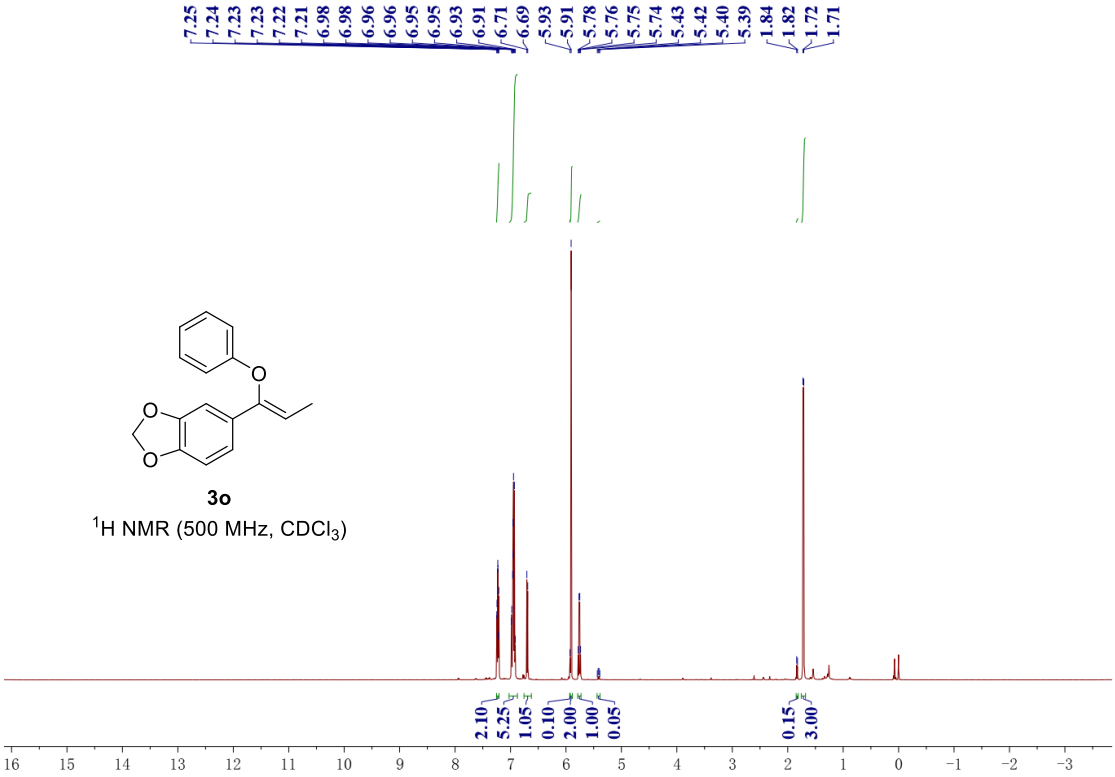

7.26
7.24
7.24
7.22
7.22
7.20
7.18
7.11
7.09
7.03
6.98
6.98
6.96
6.94
6.93
6.79
6.79
6.78
6.77
5.96
5.95
5.94
5.92
5.62
5.61
5.39
5.35
5.28
3.81
3.76
1.77
1.76
O
O
O
O
3m
+
3m'
1H NMR (500 MHz, CDCl3)
3.30
1.10
1.10
3.30
1.10
0.10
1.00
0.10
0.10
0.10
0.30
3.00
3.00
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 −1 −2 −3
f1 (ppm)


7.26
7.24
7.23
7.22
7.20
7.19
7.11
7.10
7.04
6.99
6.97
6.96
6.96
6.95
6.93
6.80
6.79
6.78
6.78
5.97
5.95
5.94
5.93
5.49
3.79
3.76
1.89
1.87
1.78
1.77
O
O
3m
1H NMR (500 MHz, CDCl3)
3.09
1.03
1.03
3.09
1.03
1.00
0.03
0.09
3.00
0.09
3.01
f1 (ppm)


159.73
157.33
149.55
137.13
129.53
129.43
121.38
117.77
115.39
113.31
112.71
110.94
55.16
11.40
O
O
3m
13C NMR (126 MHz, CDCl3)
f1 (ppm)

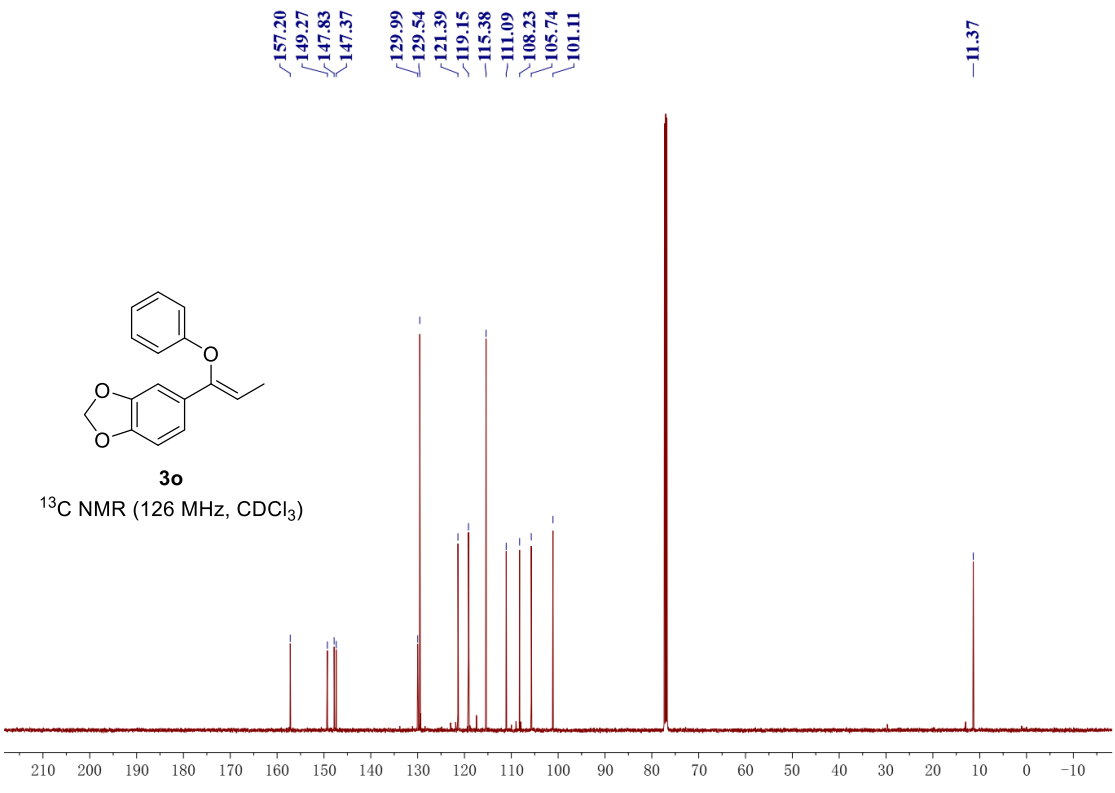

7.44 7.44 7.43 7.42 7.25 7.25 7.23 7.22 7.22 7.21 7.19 7.19 7.19 7.18 7.18 7.17 7.16 6.96 6.94 6.94 6.93 6.92 6.90 6.89 6.88 6.88 6.87 6.85 6.85 6.85 6.83 6.12 6.10 6.09 6.07 6.06 6.05 6.03 5.36 5.35 5.33 5.32 5.19 5.18 5.17 5.16 3.86 3.84 1.78 1.76
3n
3n'
1H NMR (500 MHz, CDCl3)
1.00 0.50 4.50 7.50 2.50 1.00 1.00 3.00 1.50 1.50
f1 (ppm)


158.01 157.30 157.16 156.24 137.31 129.30 129.26 128.94 128.75 128.73 127.18 121.19 121.07 120.68 120.49 115.88 115.79 115.42 110.56 74.01 55.55 55.48 11.56
3n
3n'
13C NMR (126 MHz, CDCl3)
f1 (ppm)



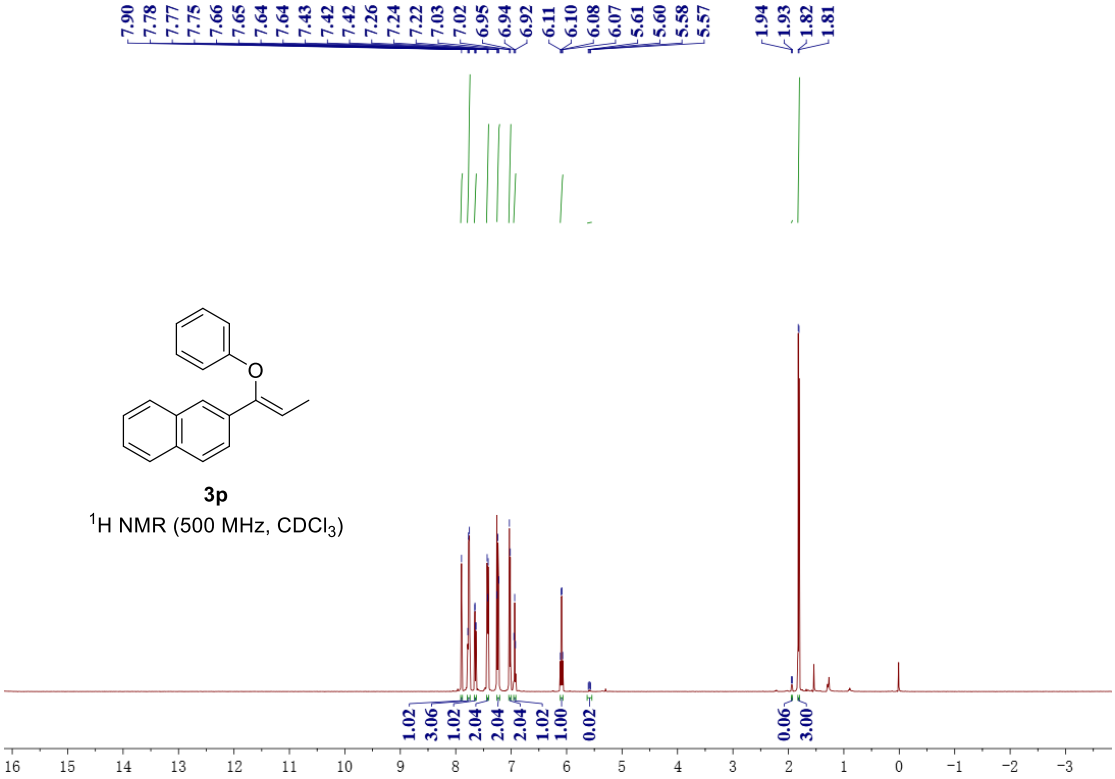
3o

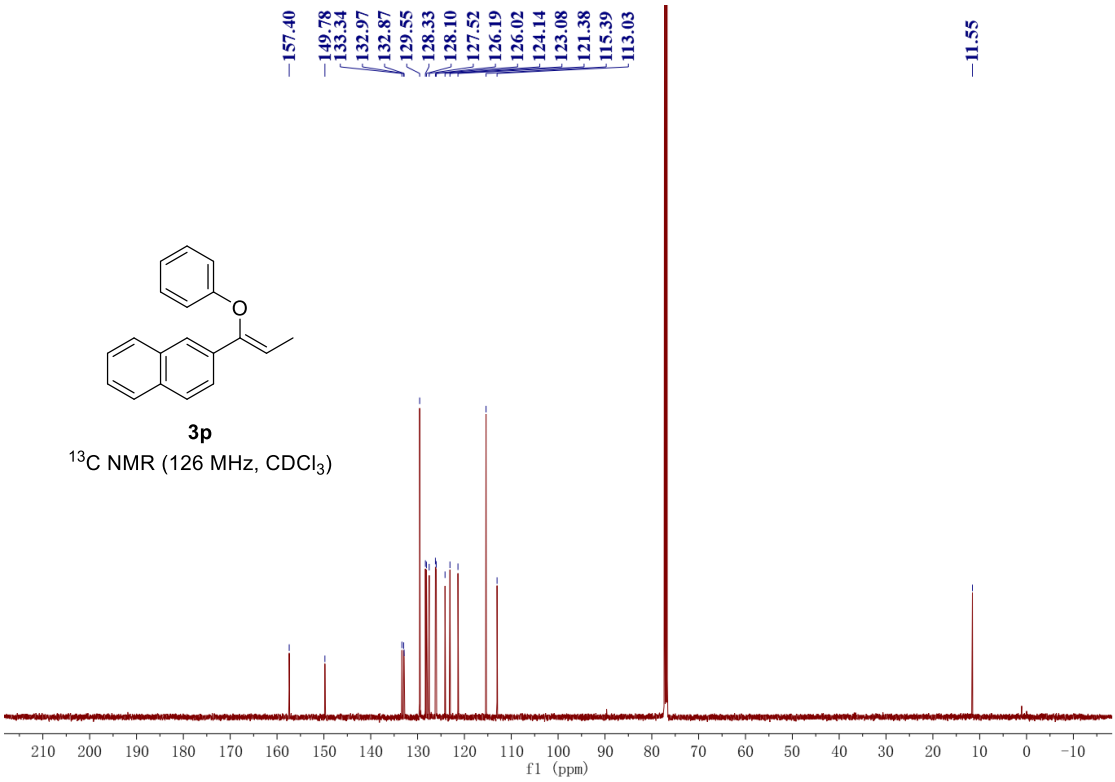
^{1}H NMR (500 MHz, $CDCl_3$)

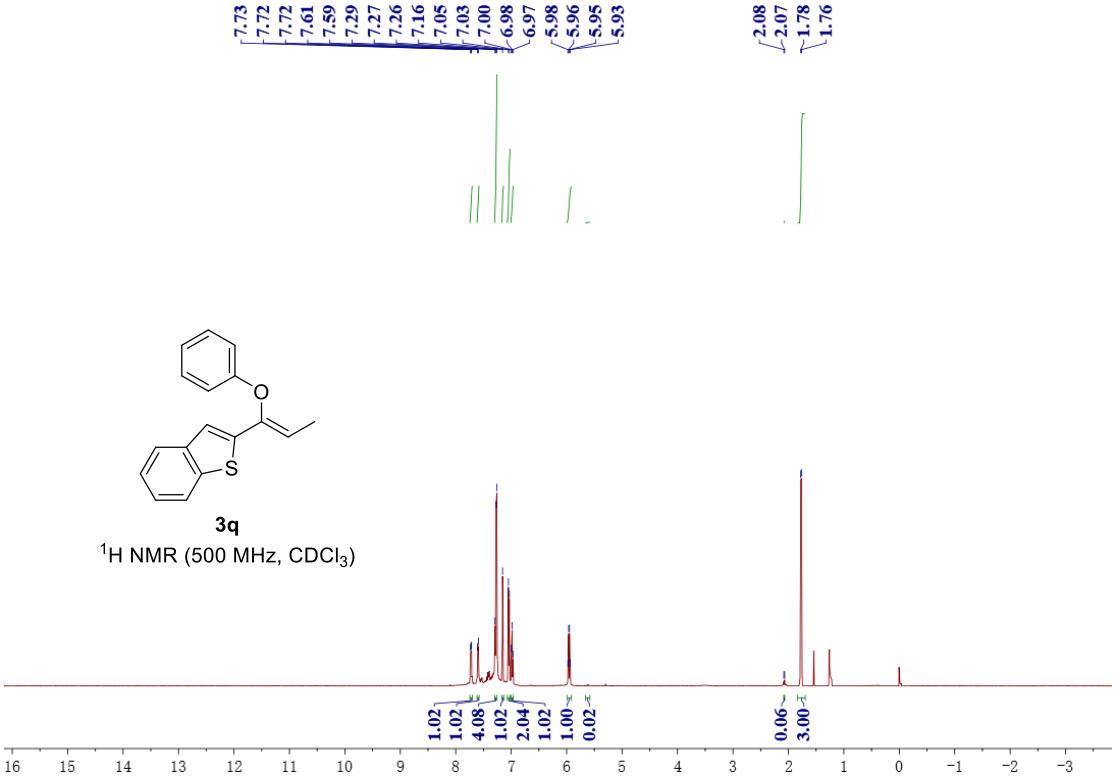


3o

^{13}C NMR (126 MHz, $CDCl_3$)

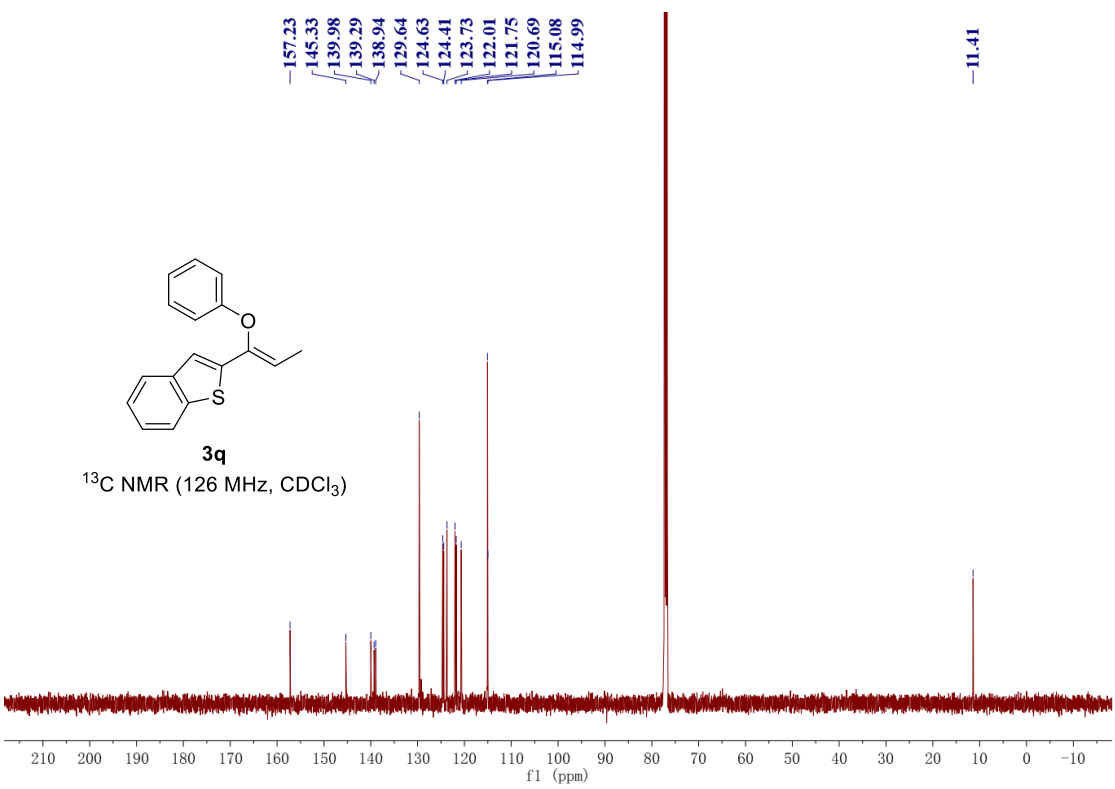

7.90
7.78
7.77
7.75
7.66
7.65
7.64
7.64
7.43
7.42
7.42
7.26
7.24
7.22
7.03
7.02
6.95
6.94
6.92
6.11
6.10
6.08
6.07
5.61
5.60
5.58
5.57
1.94
1.93
1.82
1.81
O
3p
1H NMR (500 MHz, CDCl3)
1.02
3.06
1.02
2.04
2.04
2.04
1.02
1.00
0.02
0.06
3.00
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
−1
−2
−3


157.40
149.78
133.34
132.97
132.87
129.55
128.33
128.10
127.52
126.19
126.02
124.14
123.08
121.38
115.39
113.03
11.55
O
3p
13C NMR (126 MHz, CDCl3)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)



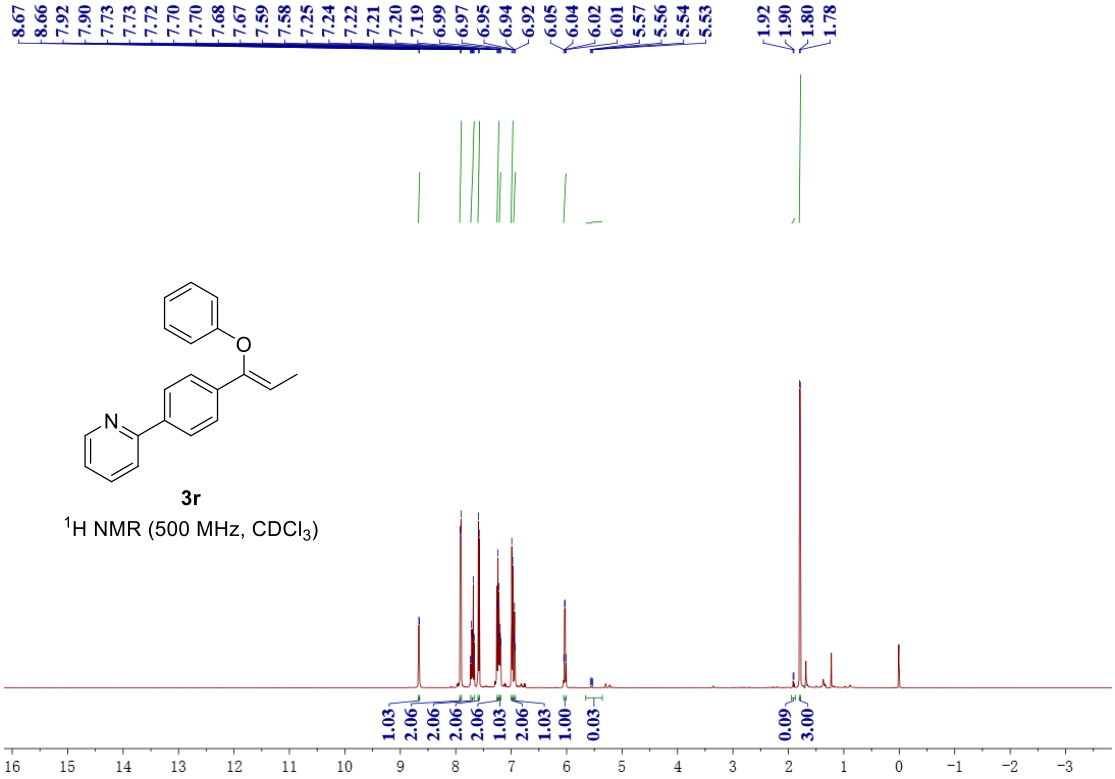
3q

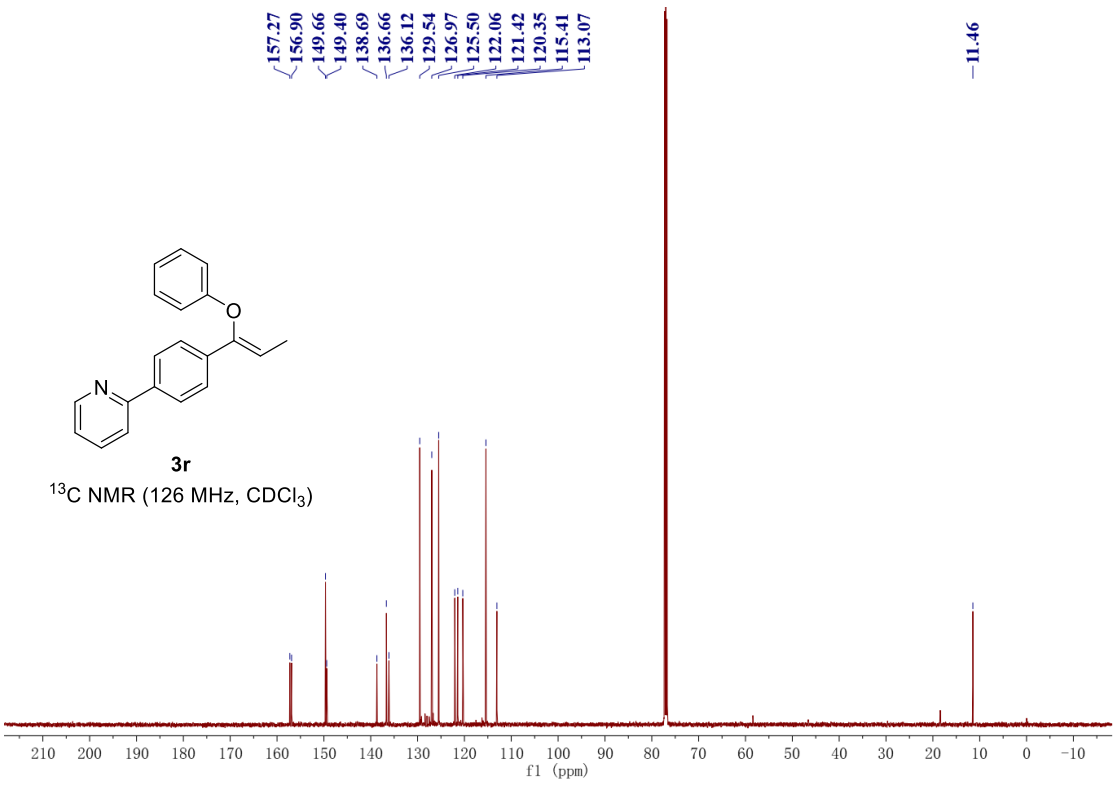
^{1}H NMR (500 MHz, $CDCl_3$)

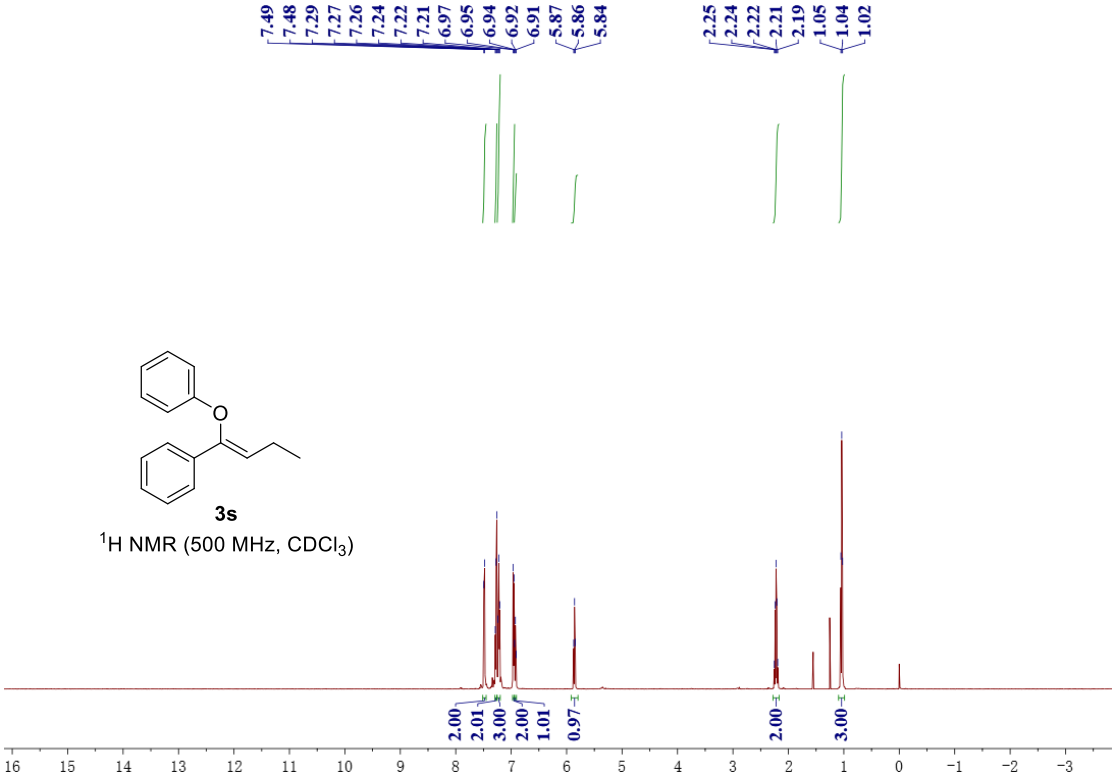


3q

^{13}C NMR (126 MHz, $CDCl_3$)

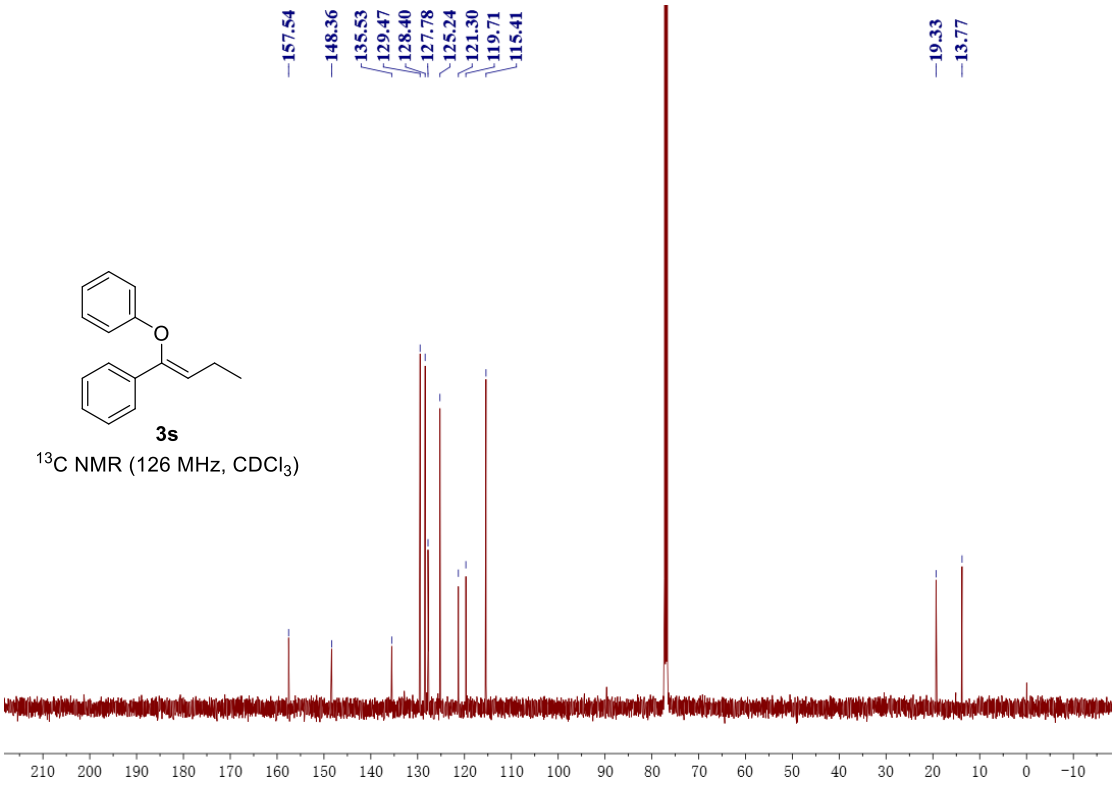

8.67
8.66
7.92
7.90
7.73
7.73
7.72
7.70
7.70
7.68
7.67
7.59
7.58
7.25
7.24
7.22
7.21
7.20
7.19
6.99
6.97
6.95
6.94
6.92
6.05
6.04
6.02
6.01
5.57
5.56
5.54
5.53
1.92
1.90
1.80
1.78
O
N
3r
1H NMR (500 MHz, CDCl3)
1.03
2.06
2.06
2.06
2.06
1.03
2.06
1.03
1.00
0.03
0.09
3.00
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 −1 −2 −3


157.27
156.90
149.66
149.40
138.69
136.66
136.12
129.54
126.97
125.50
122.06
121.42
120.35
115.41
113.07
11.46
O
N
3r
13C NMR (126 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)



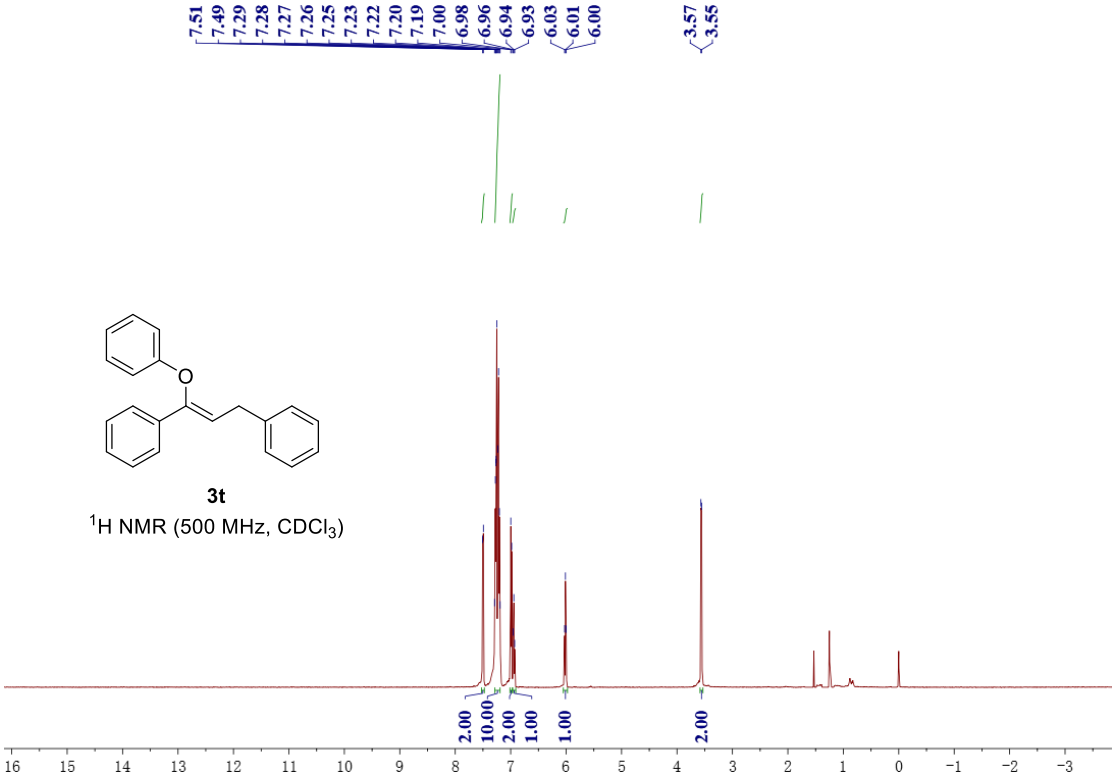
3s

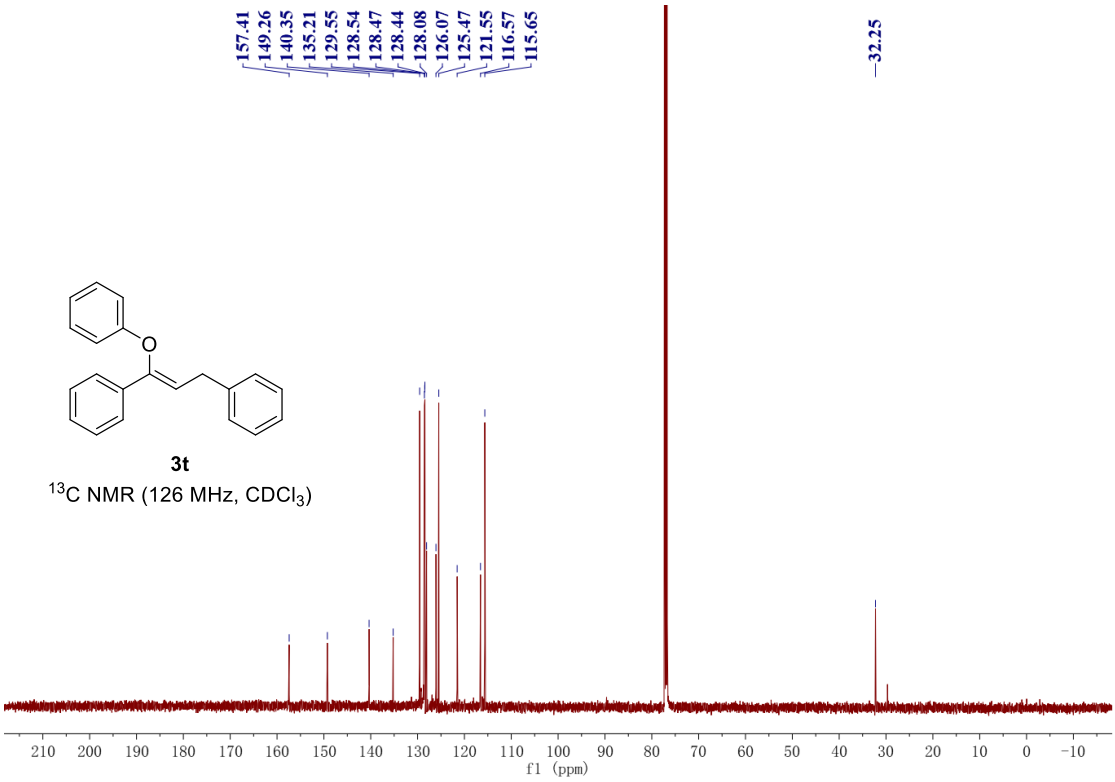
^{1}H NMR (500 MHz, $CDCl_3$)

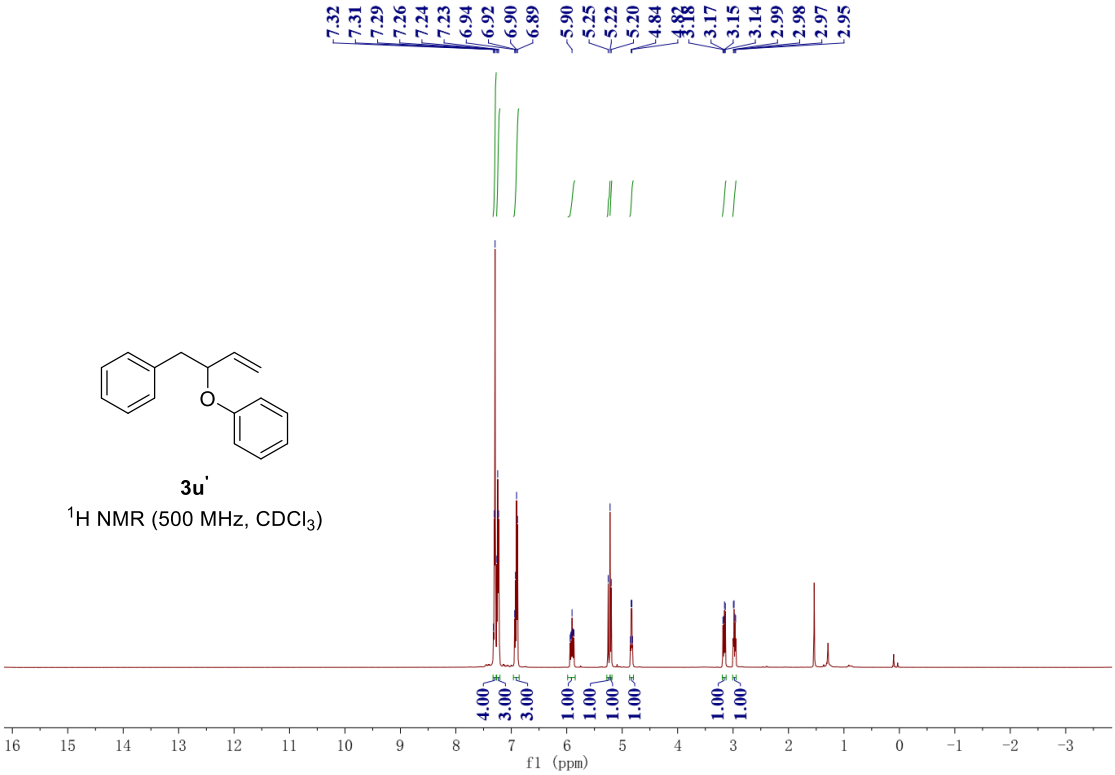


3s

^{13}C NMR (126 MHz, $CDCl_3$)

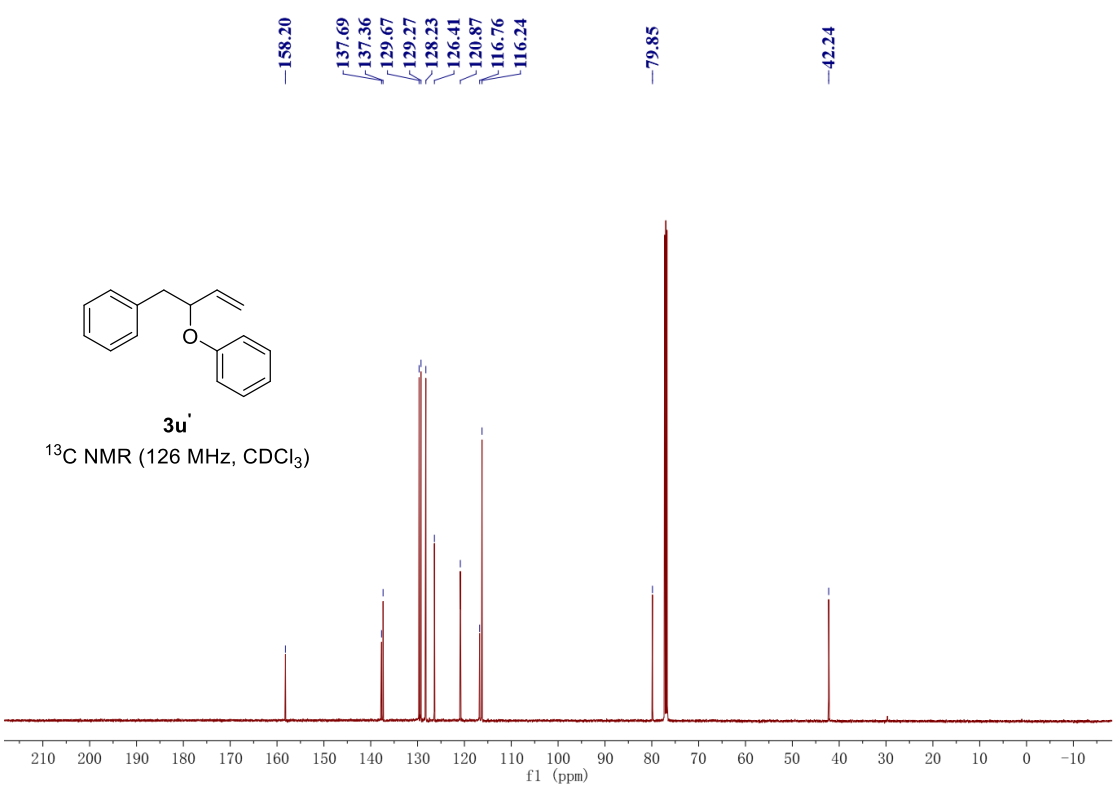

7.51
7.49
7.29
7.28
7.27
7.26
7.25
7.23
7.22
7.20
7.19
7.00
6.98
6.96
6.94
6.93
6.03
6.01
6.00
3.57
3.55
O
3t
1H NMR (500 MHz, CDCl3)
2.00
10.00
2.00
1.00
1.00
2.00
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 −1 −2 −3


157.41
149.26
140.35
135.21
129.55
128.54
128.47
128.44
128.08
126.07
125.47
121.55
116.57
115.65
32.25
O
3t
13C NMR (126 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)



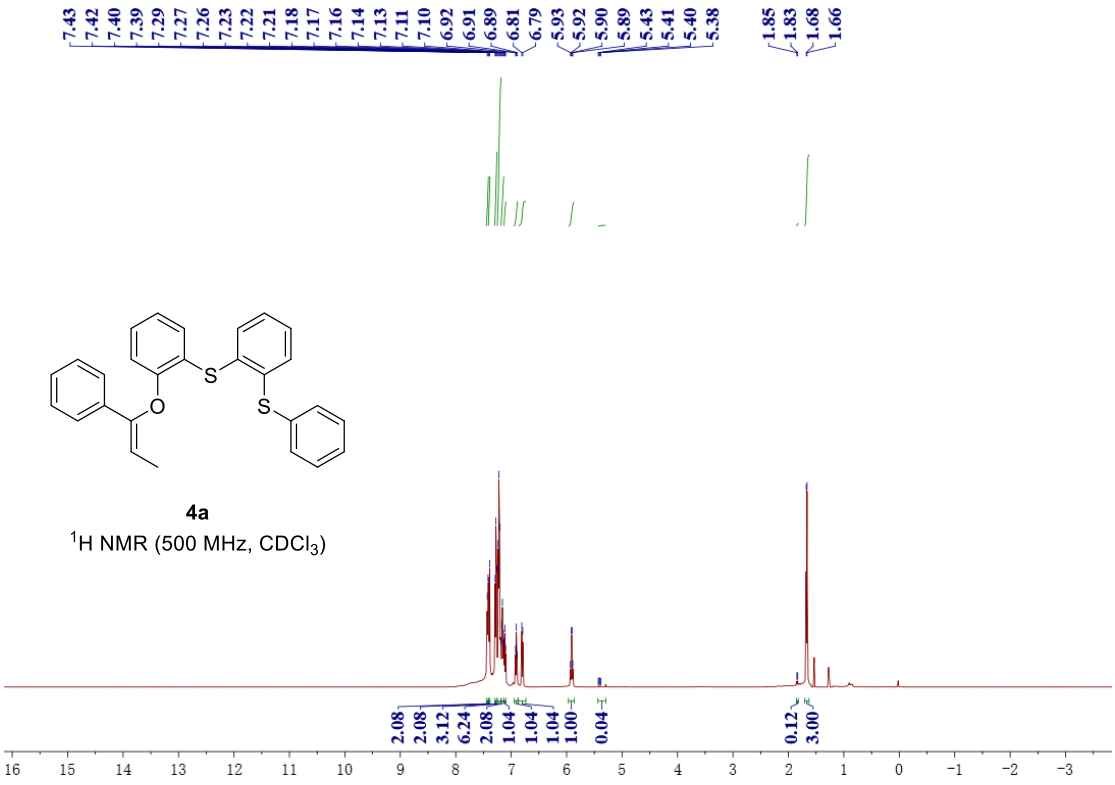
3u'

^{1}H NMR (500 MHz, $CDCl_3$)



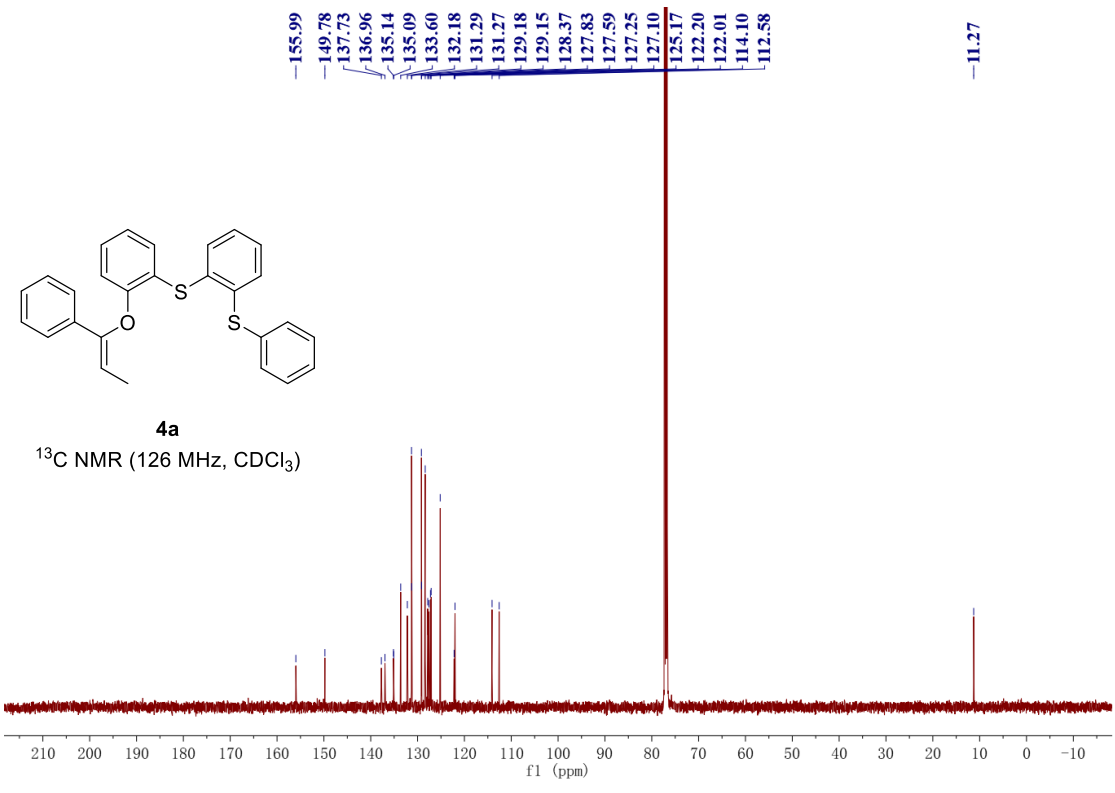
3u'

^{13}C NMR (126 MHz, $CDCl_3$)



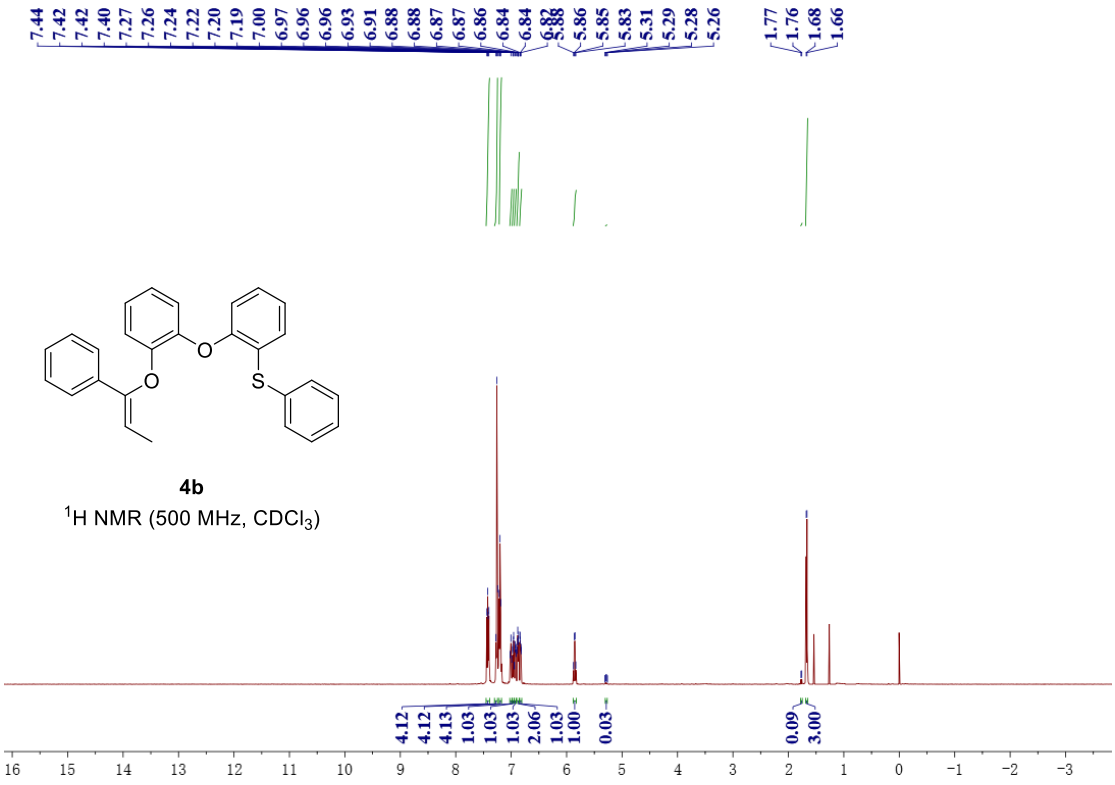
4a

^{1}H NMR (500 MHz, $CDCl_3$)



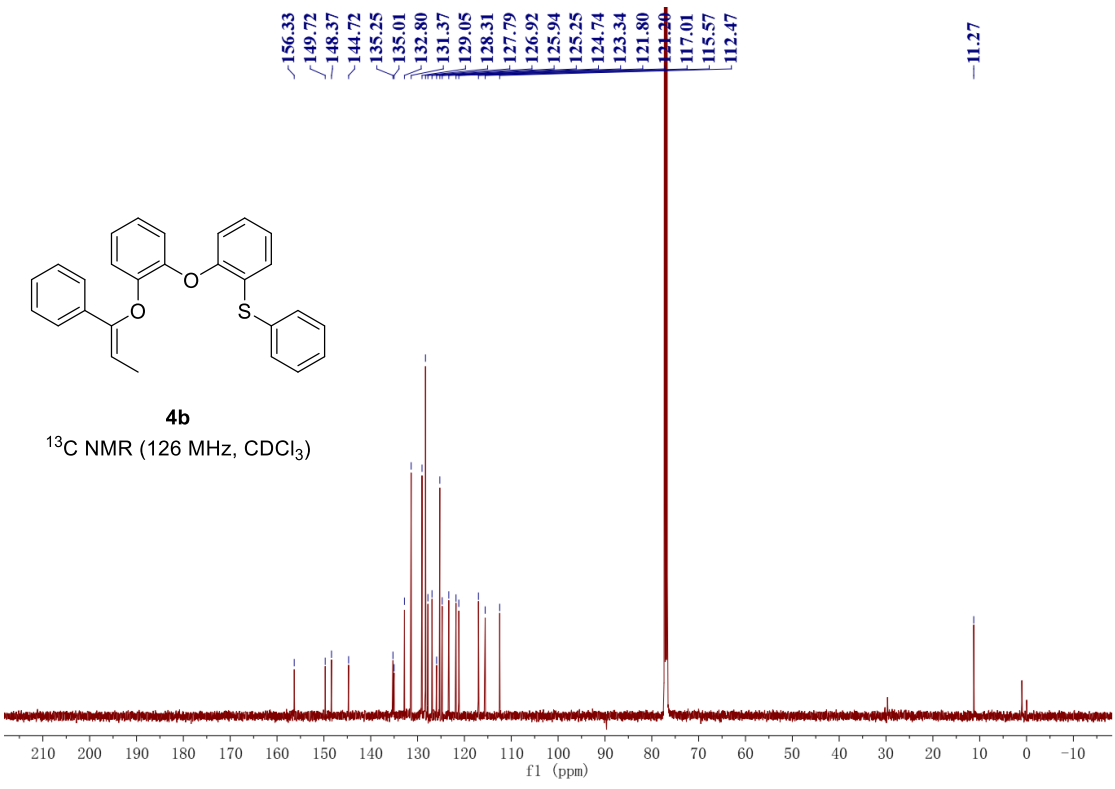
4a

^{13}C NMR (126 MHz, $CDCl_3$)



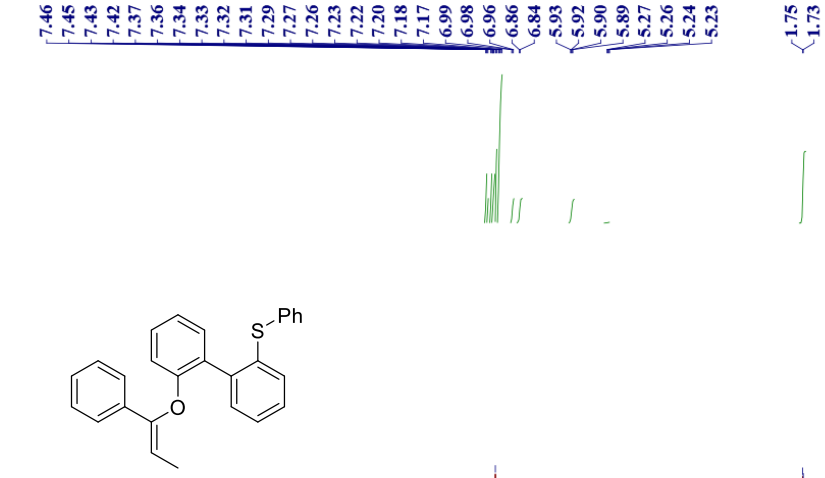
4b

^{1}H NMR (500 MHz, $CDCl_3$)



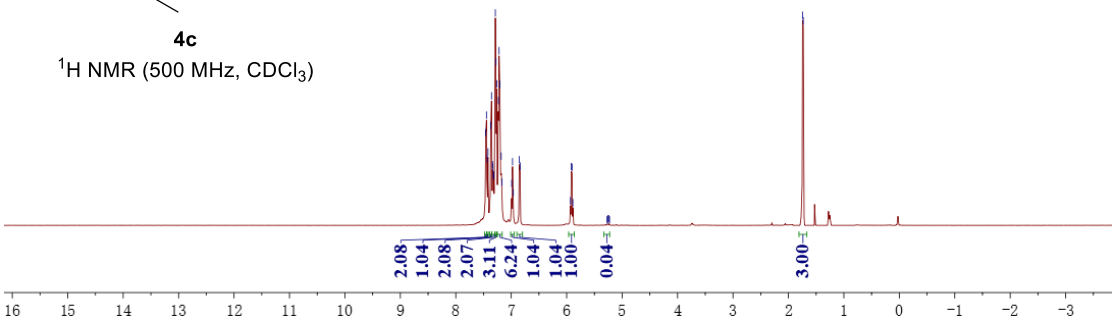
4b

^{13}C NMR (126 MHz, $CDCl_3$)



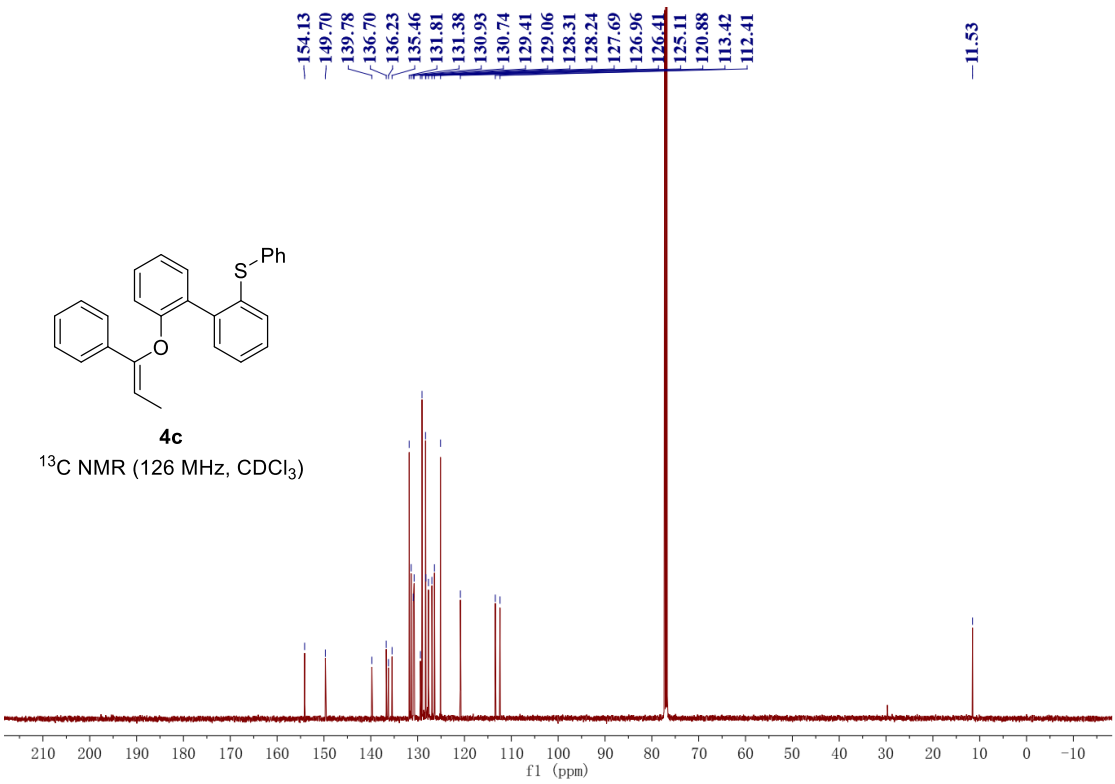
4c

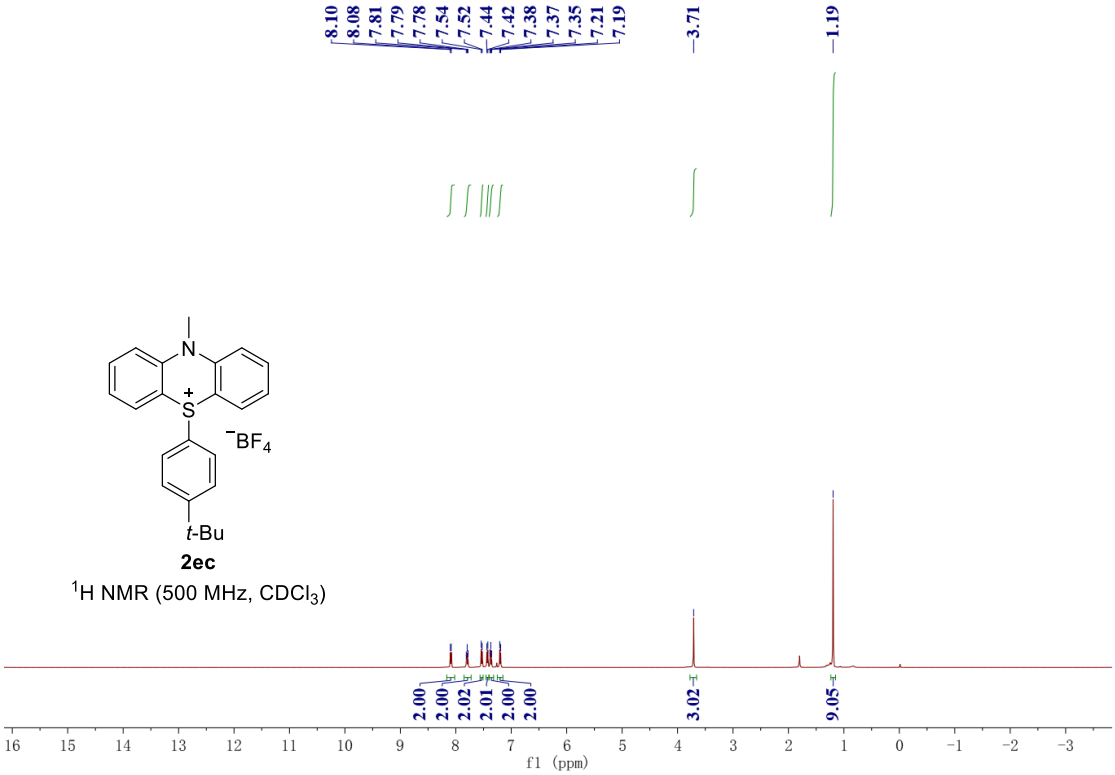
^{1}H NMR (500 MHz, $CDCl_3$)



4c

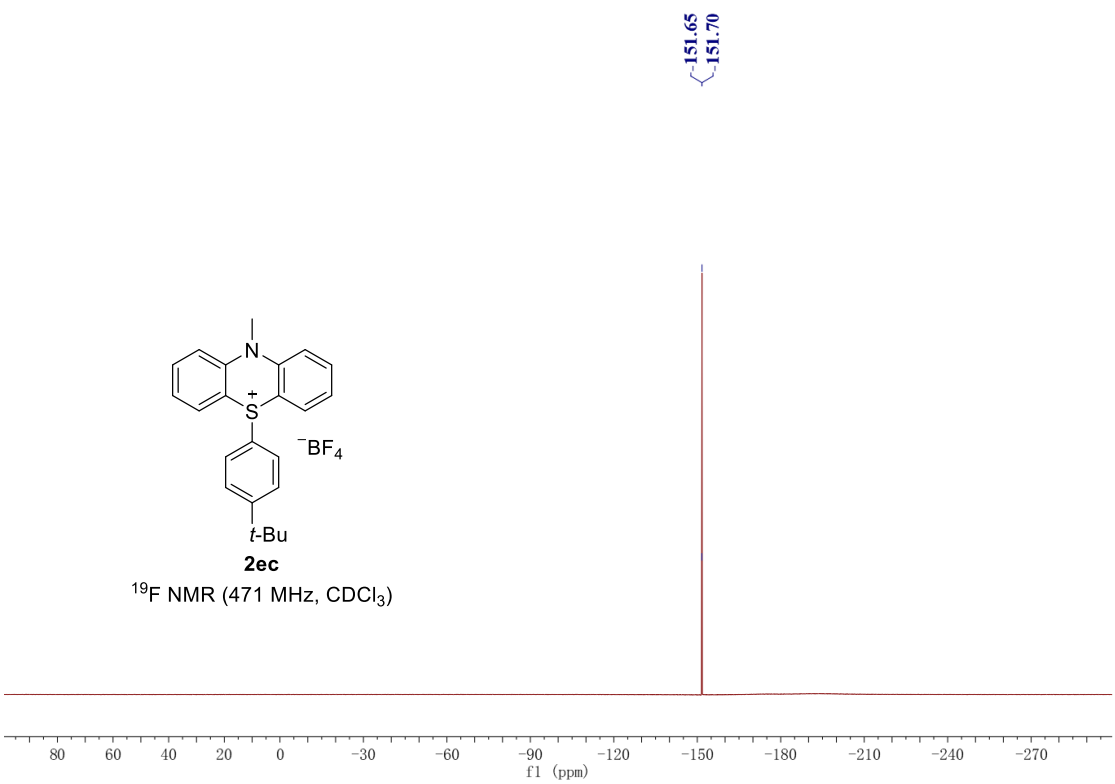
^{13}C NMR (126 MHz, $CDCl_3$)





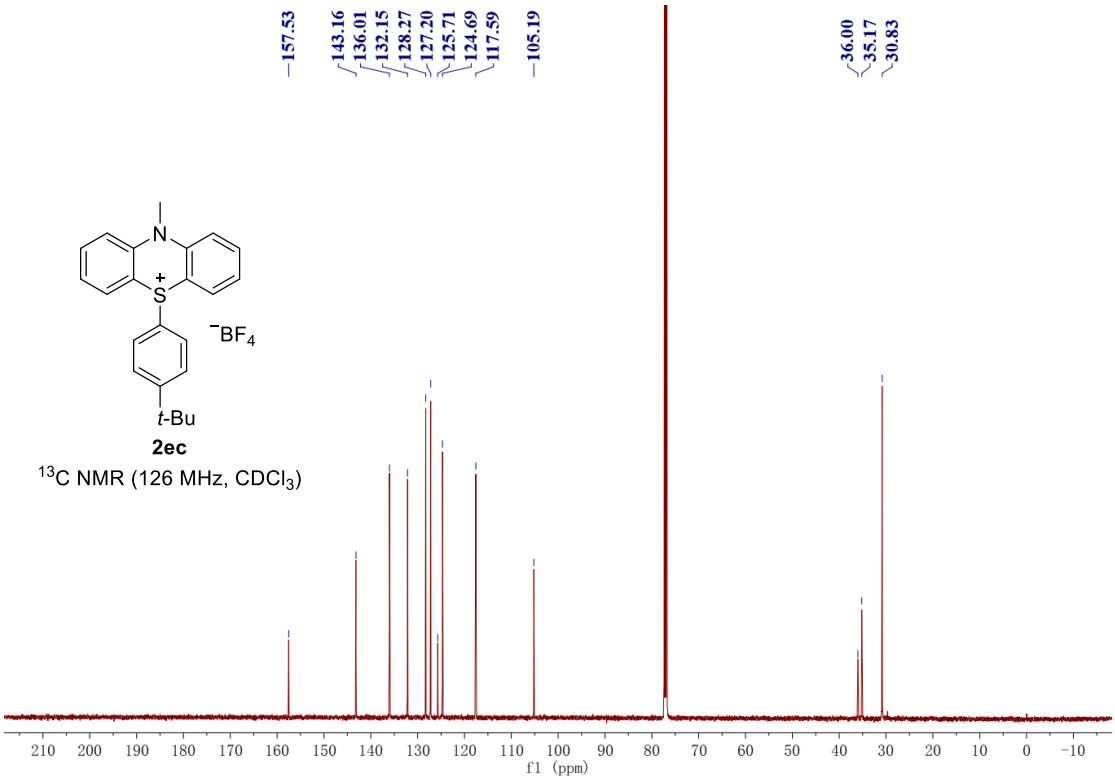
2ec

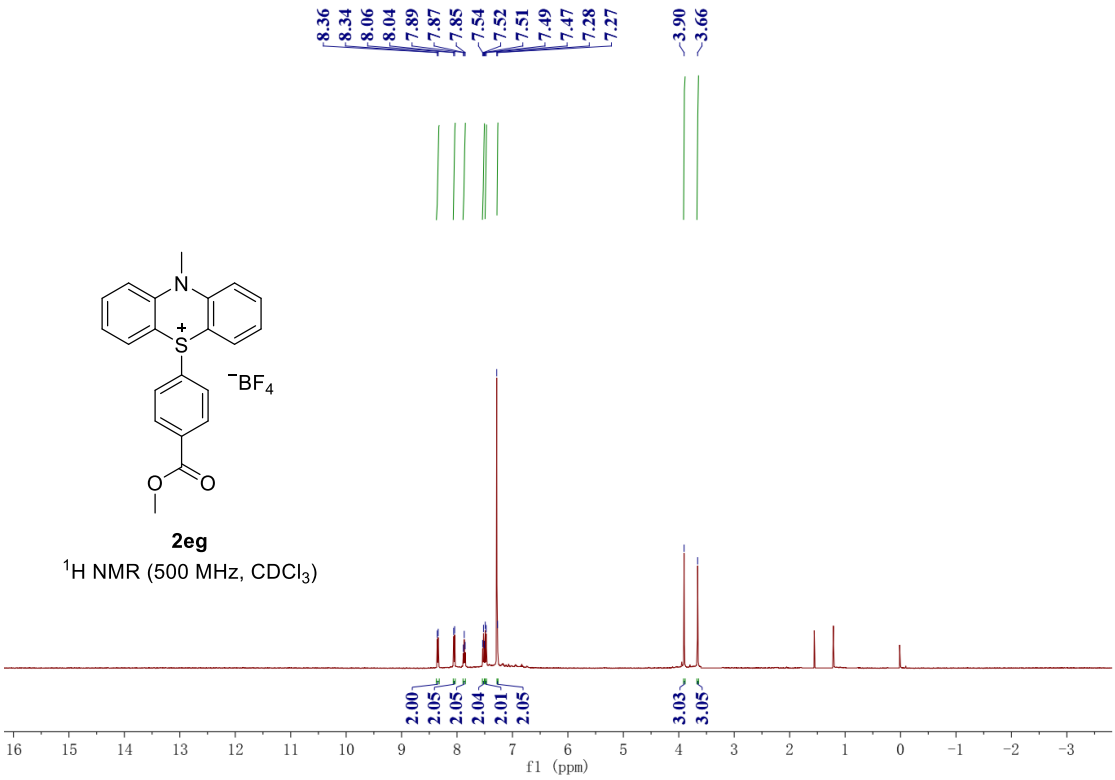
^{1}H NMR (500 MHz, $CDCl_3$)

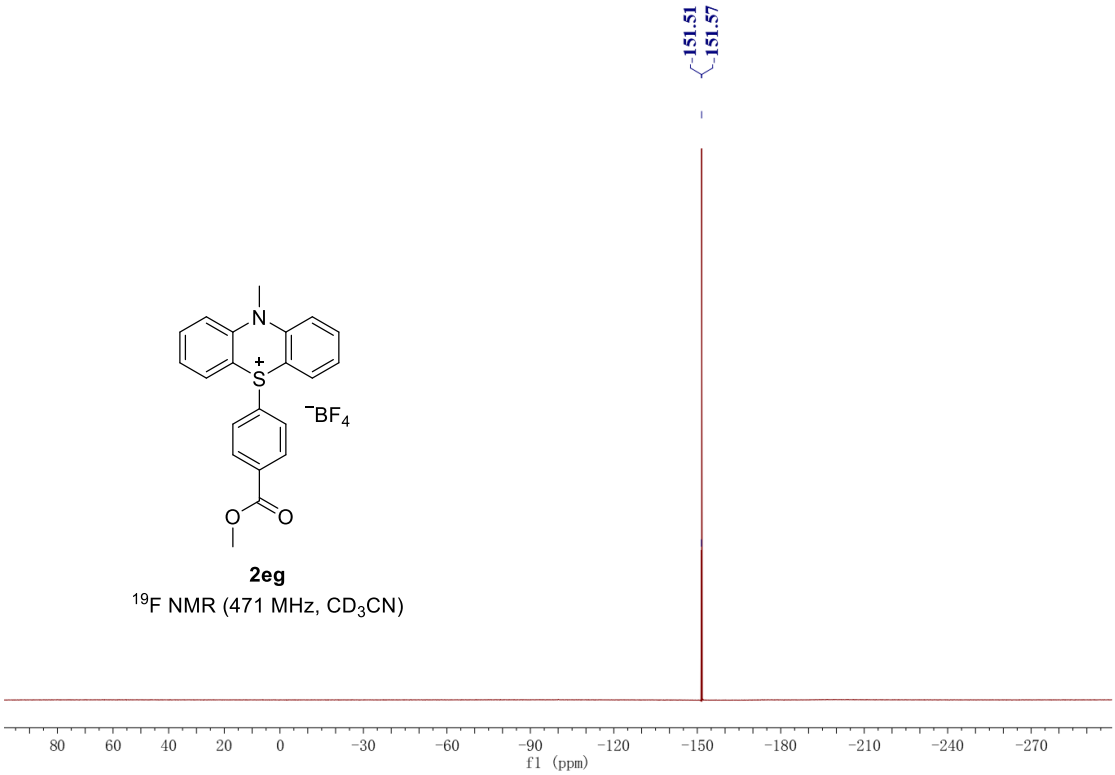


2ec

^{19}F NMR (471 MHz, $CDCl_3$)

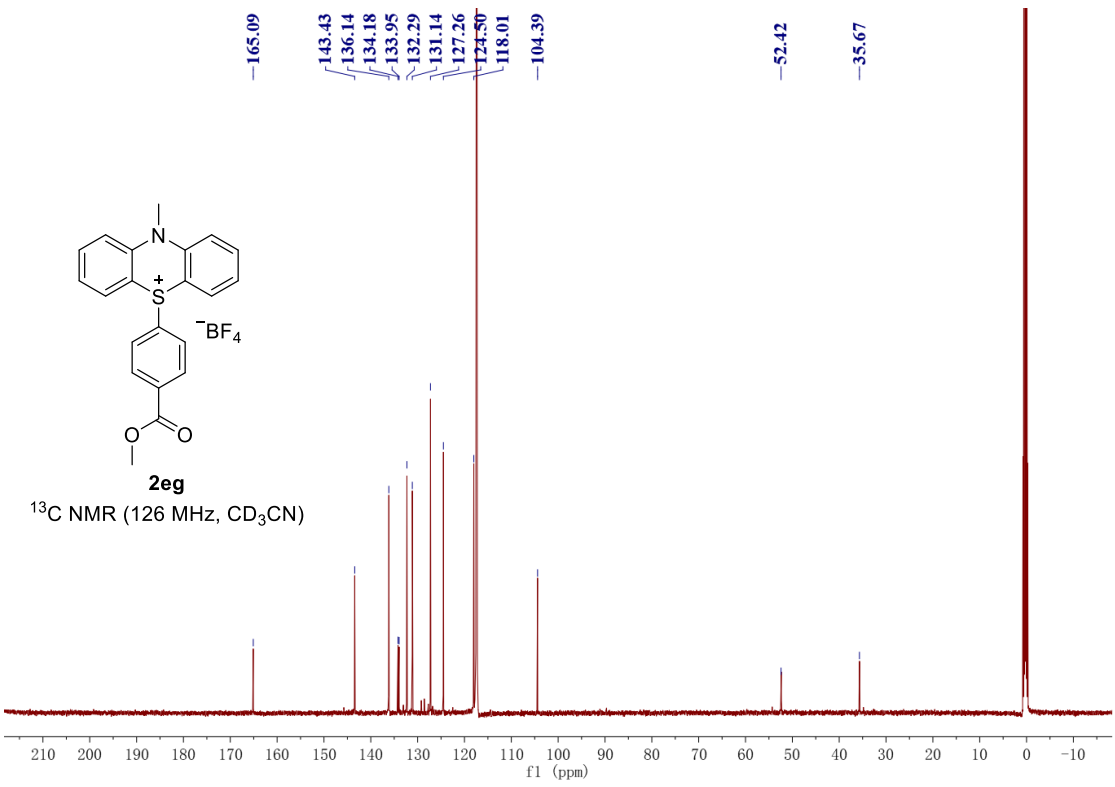

157.53
143.16
136.01
132.15
128.27
127.20
125.71
124.69
117.59
105.19
36.00
35.17
30.83
N
S
+
BF4
t-Bu
2ec
13C NMR (126 MHz, CDCl3)
f1 (ppm)


8.36
8.34
8.06
8.04
7.89
7.87
7.85
7.54
7.52
7.51
7.49
7.47
7.28
7.27
3.90
3.66
N
S
+
BF4
O
O
2eg
1H NMR (500 MHz, CDCl3)
2.00
2.05
2.05
2.04
2.01
2.05
3.03
3.05
f1 (ppm)



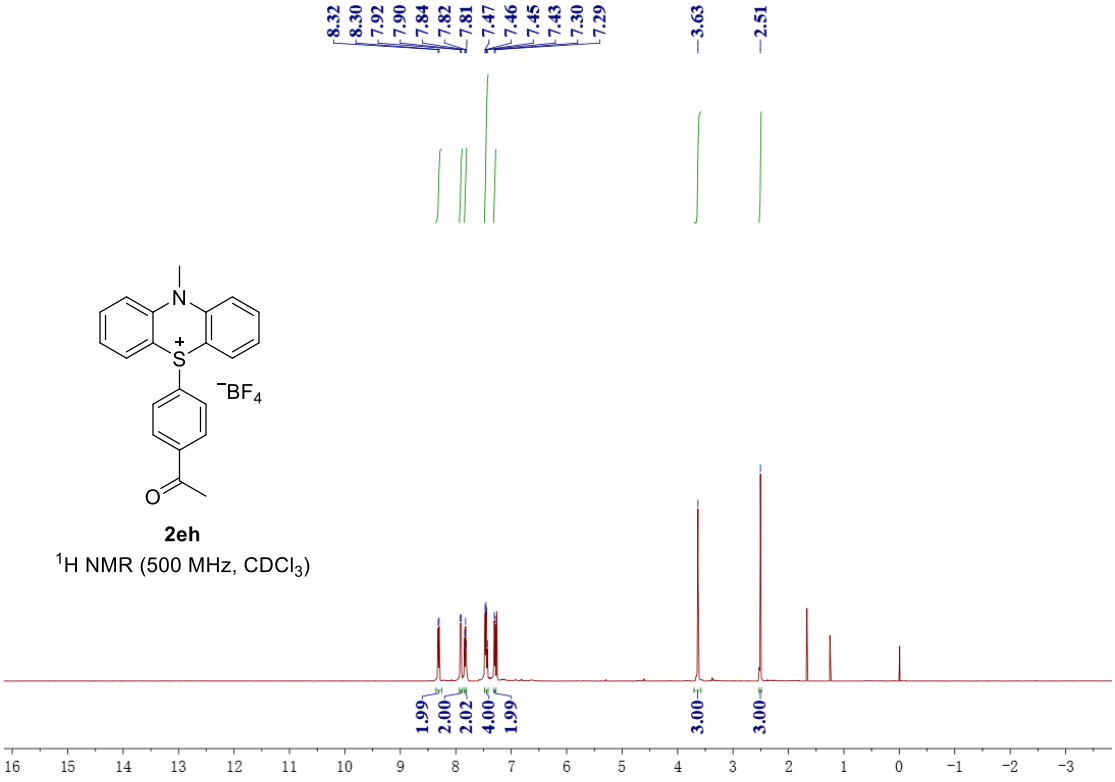
2eg

^{19}F NMR (471 MHz, CD_3CN)



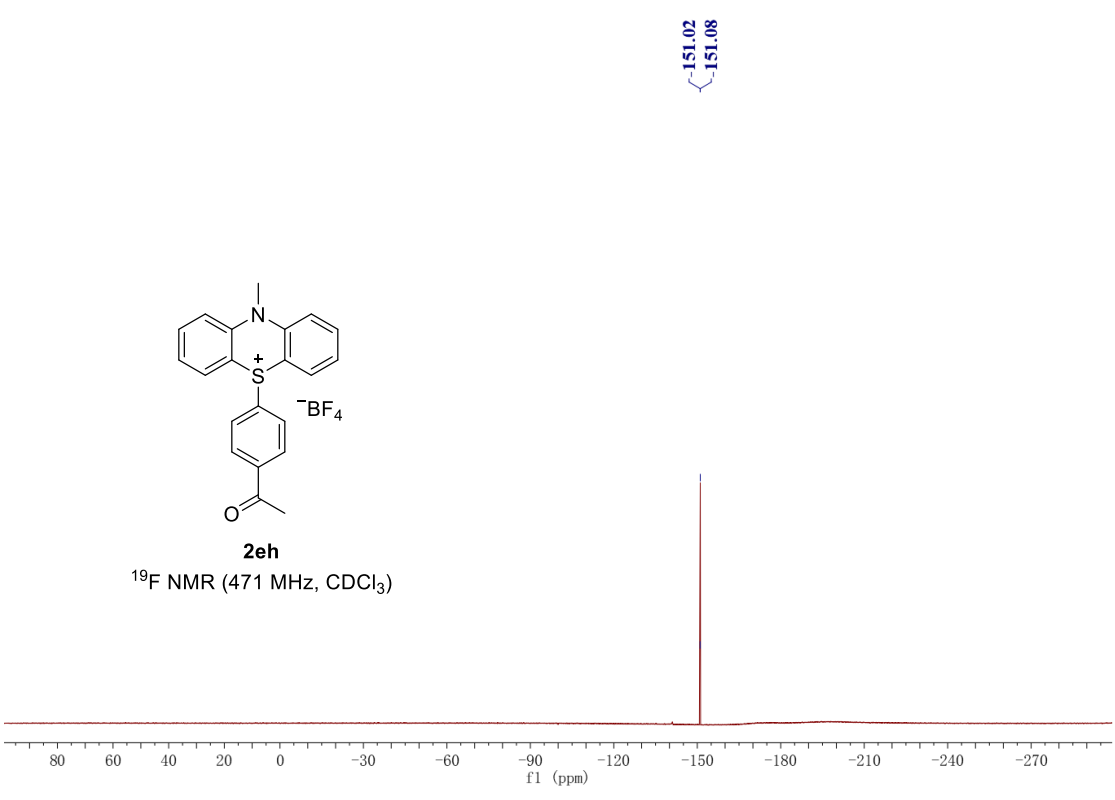
2eg

^{13}C NMR (126 MHz, CD_3CN)



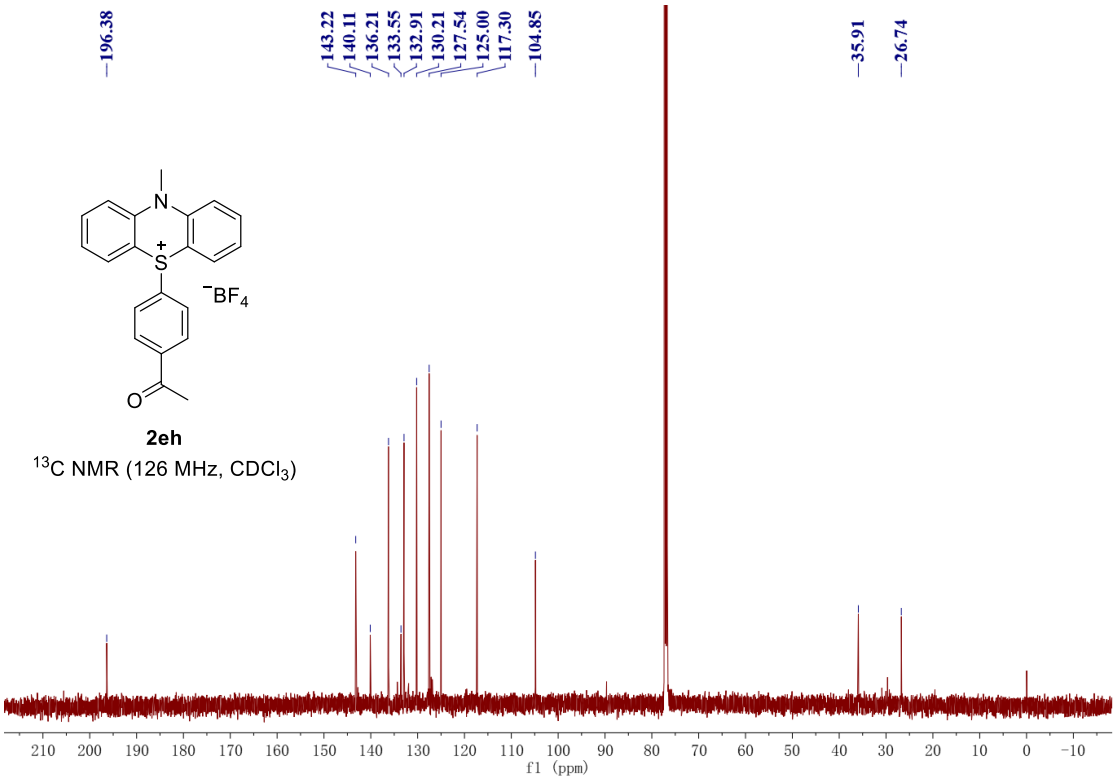
2eh

^{1}H NMR (500 MHz, $CDCl_3$)



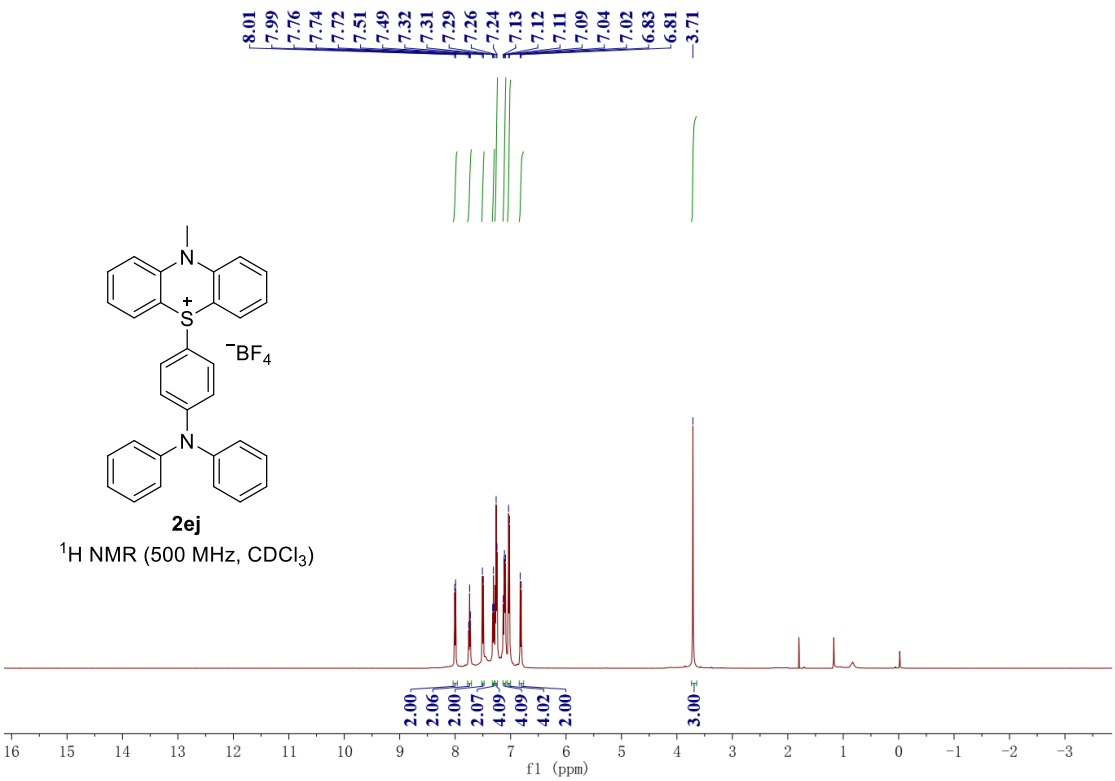
2eh

^{19}F NMR (471 MHz, $CDCl_3$)



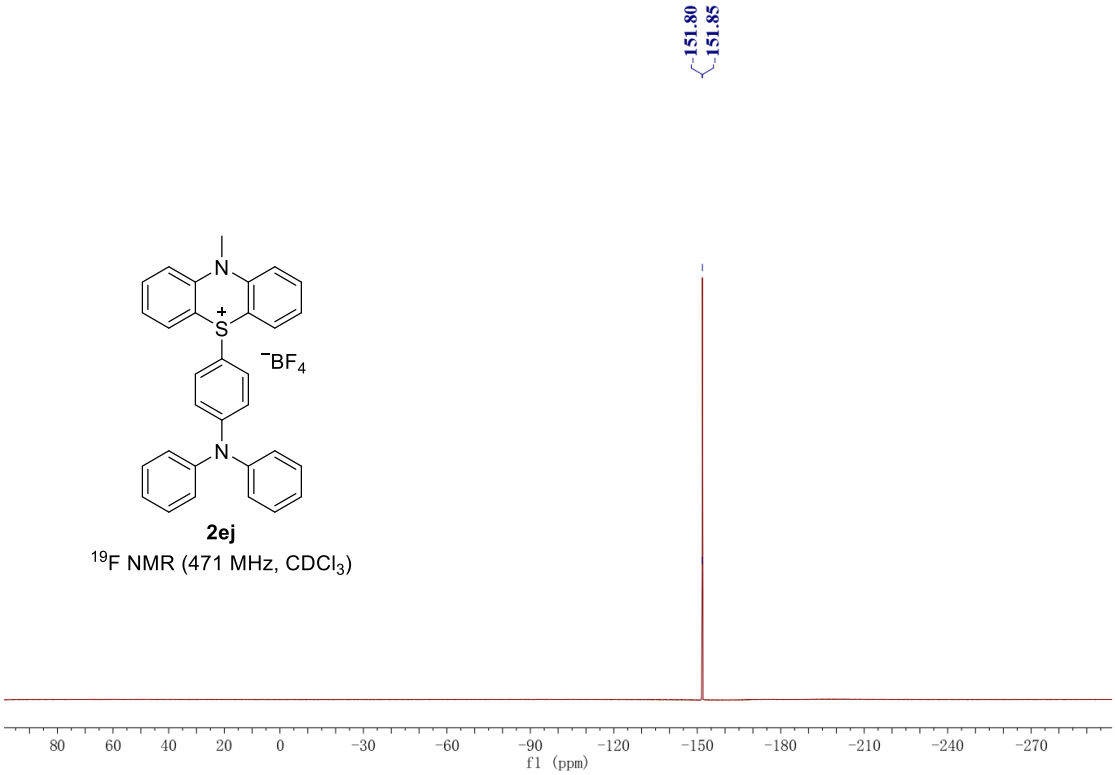
2eh

^{13}C NMR (126 MHz, $CDCl_3$)



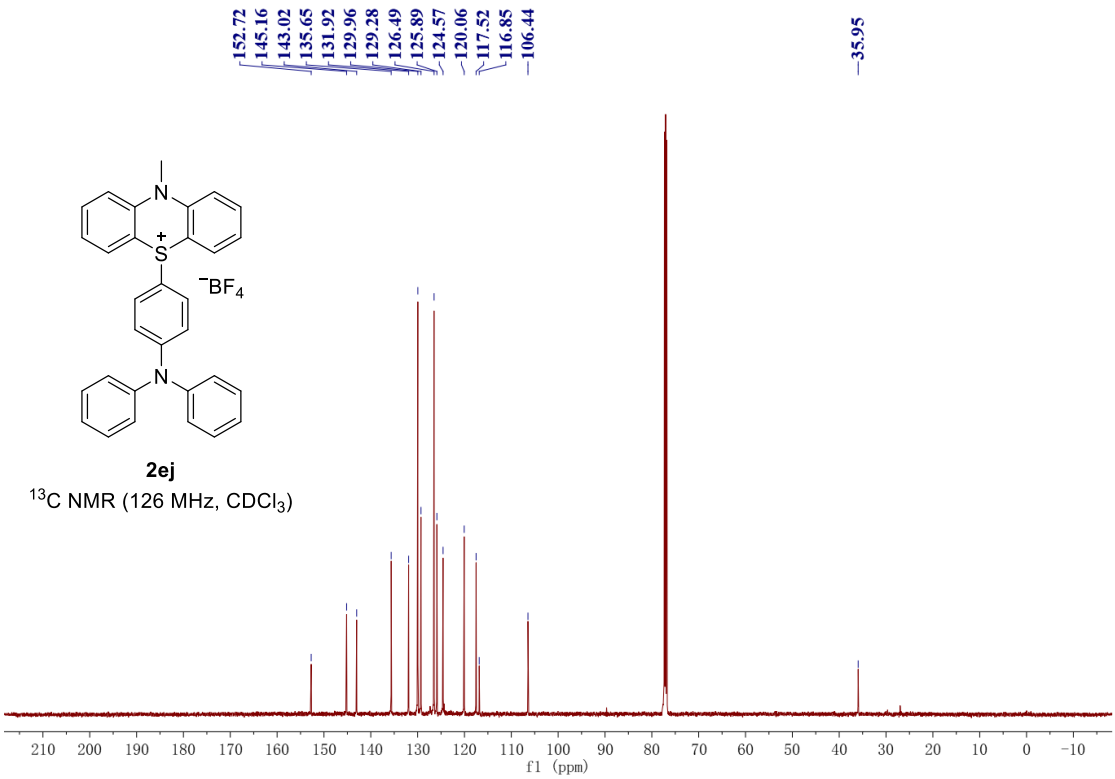
2ej

^{1}H NMR (500 MHz, $CDCl_3$)



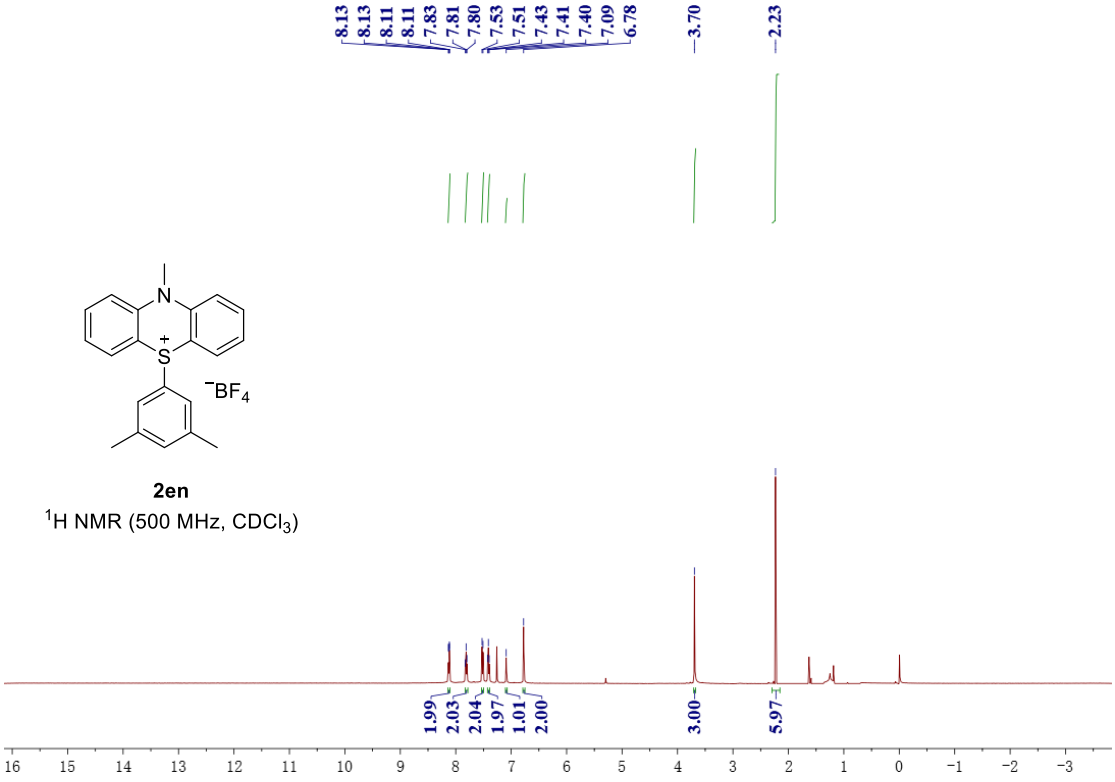
2ej

^{19}F NMR (471 MHz, $CDCl_3$)



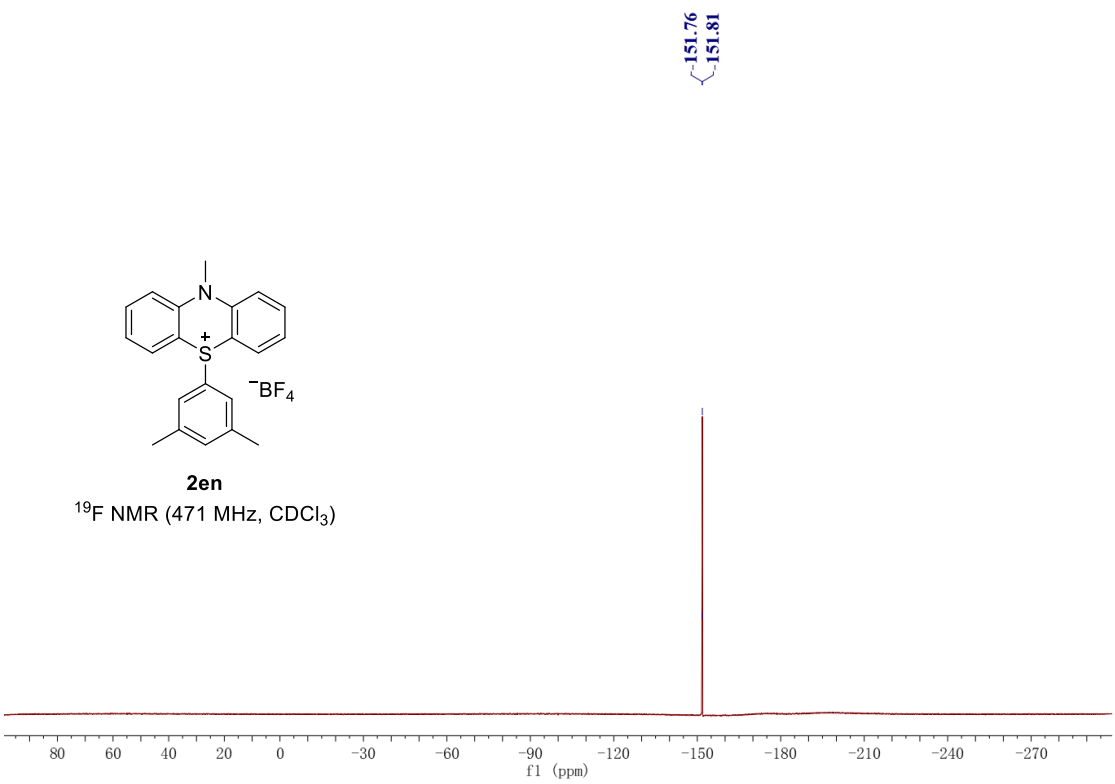
2ej

^{13}C NMR (126 MHz, $CDCl_3$)



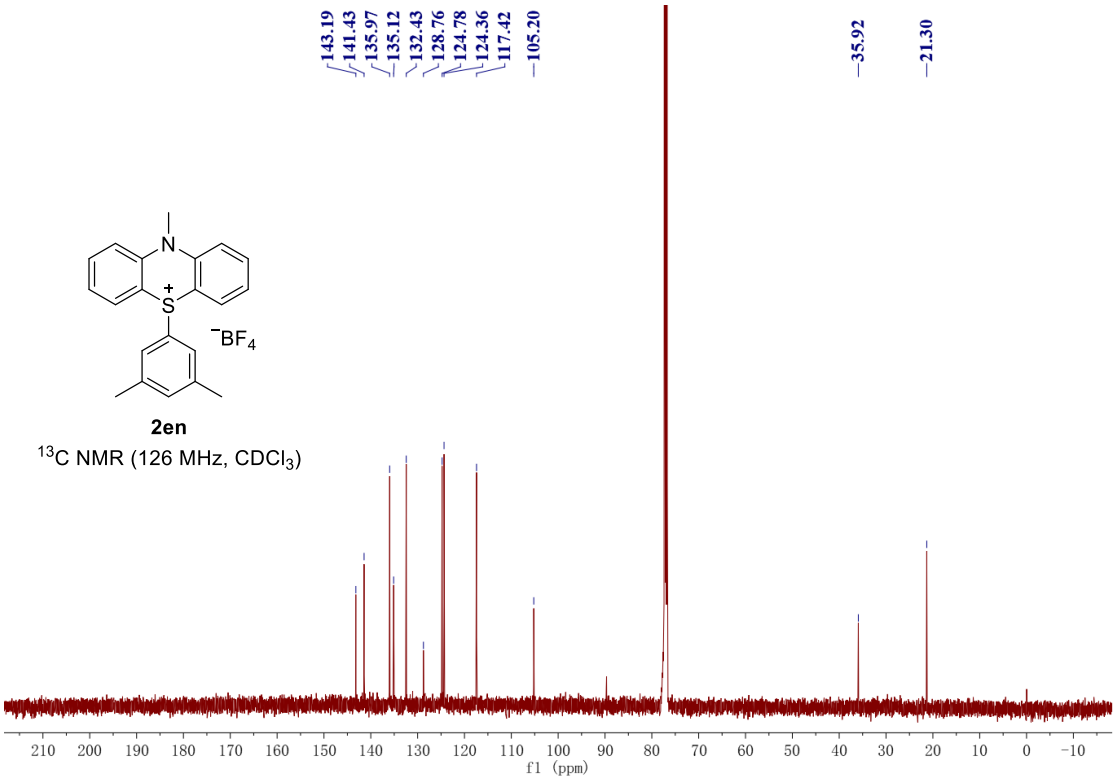
2en

^{1}H NMR (500 MHz, $CDCl_3$)



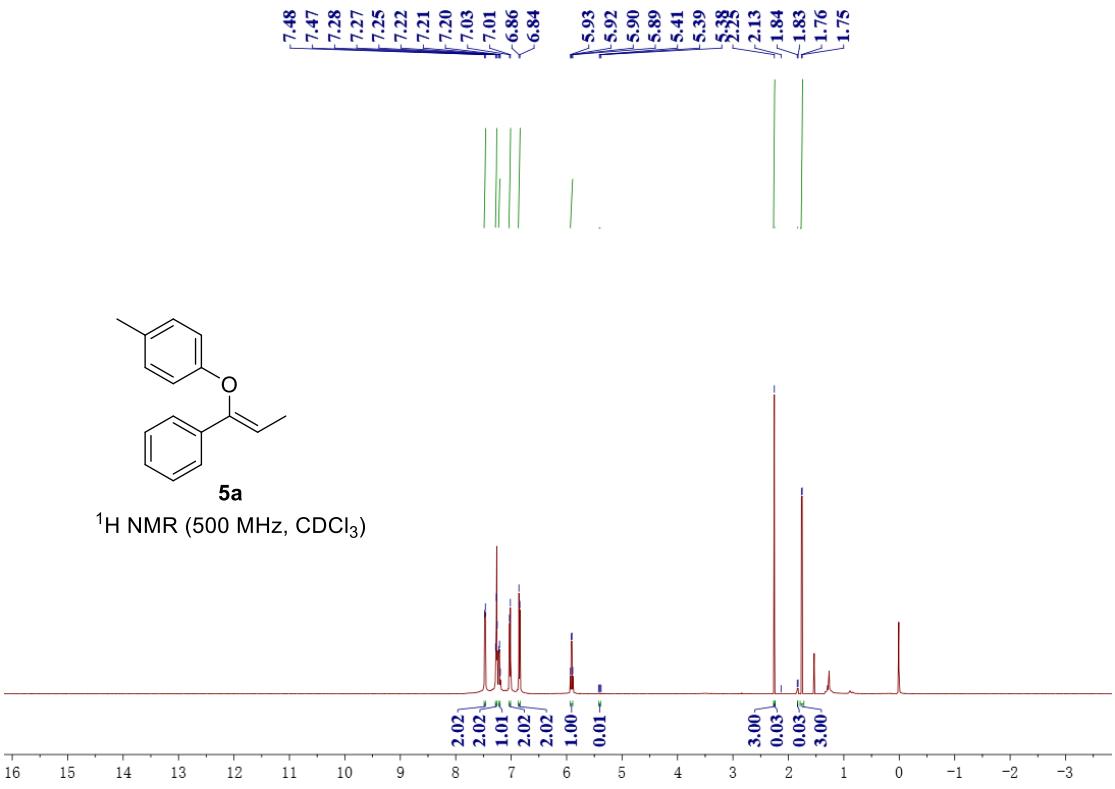
2en

^{19}F NMR (471 MHz, $CDCl_3$)



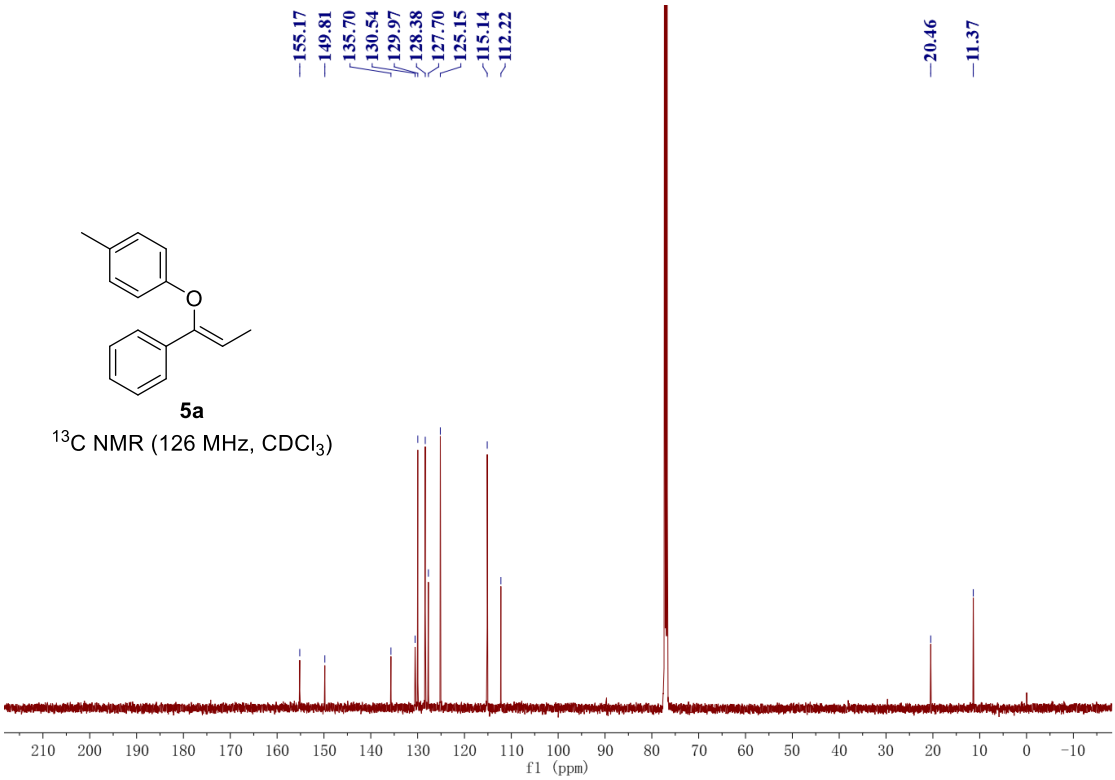
2en

^{13}C NMR (126 MHz, $CDCl_3$)



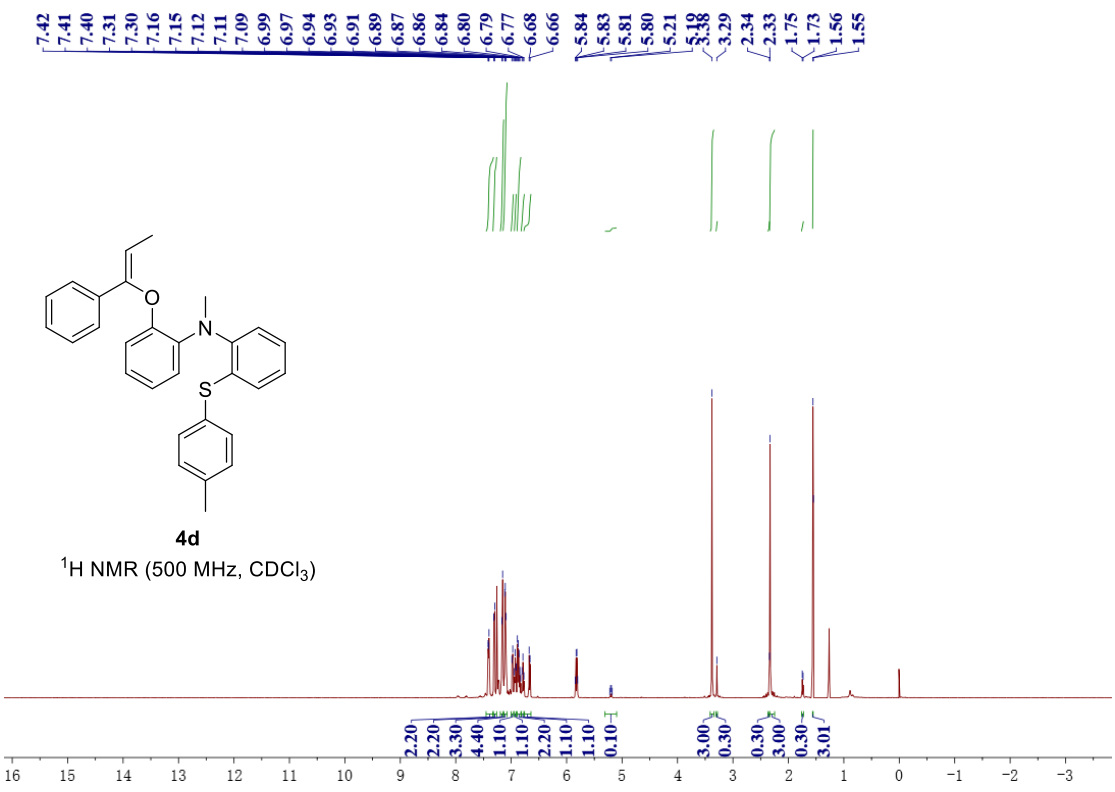
5a

^{1}H NMR (500 MHz, $CDCl_3$)



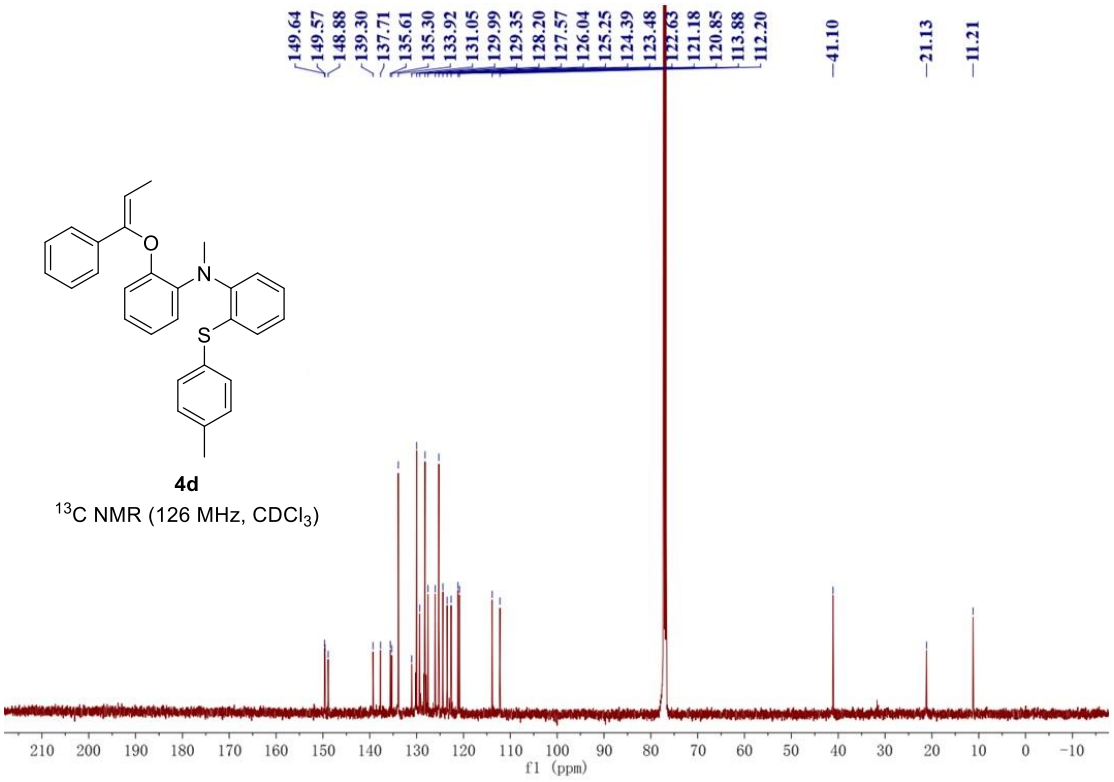
5a

^{13}C NMR (126 MHz, $CDCl_3$)



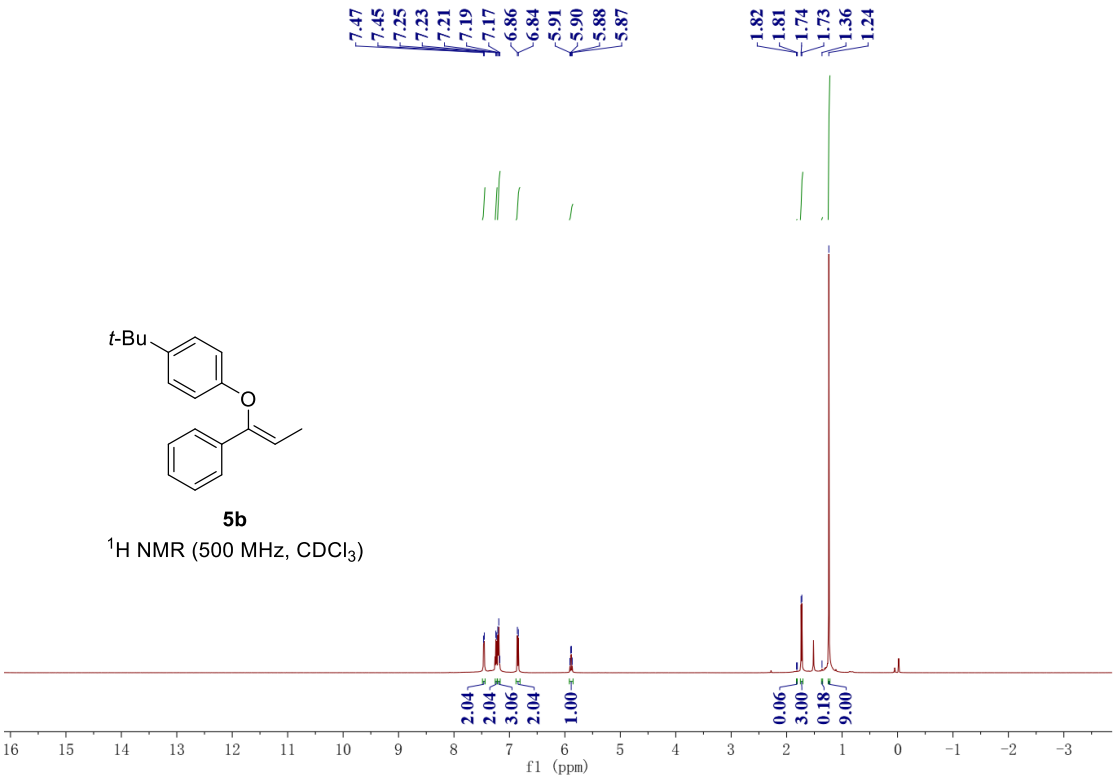
4d

^{1}H NMR (500 MHz, $CDCl_3$)



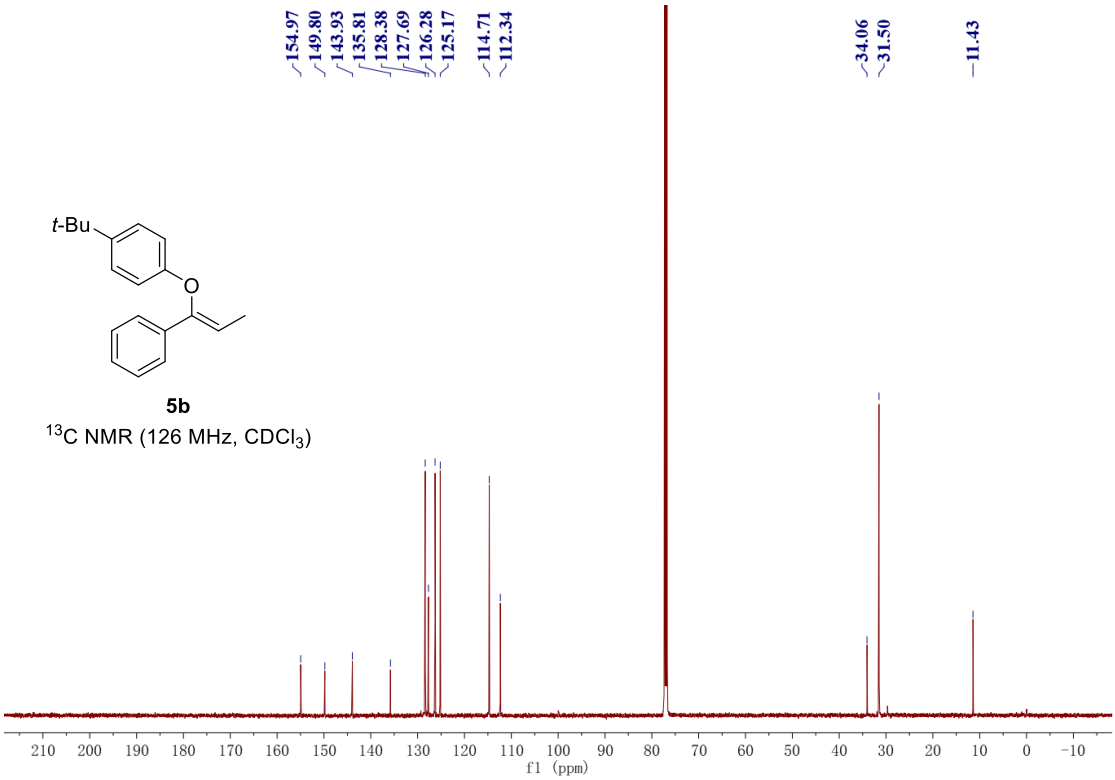
4d

^{13}C NMR (126 MHz, $CDCl_3$)



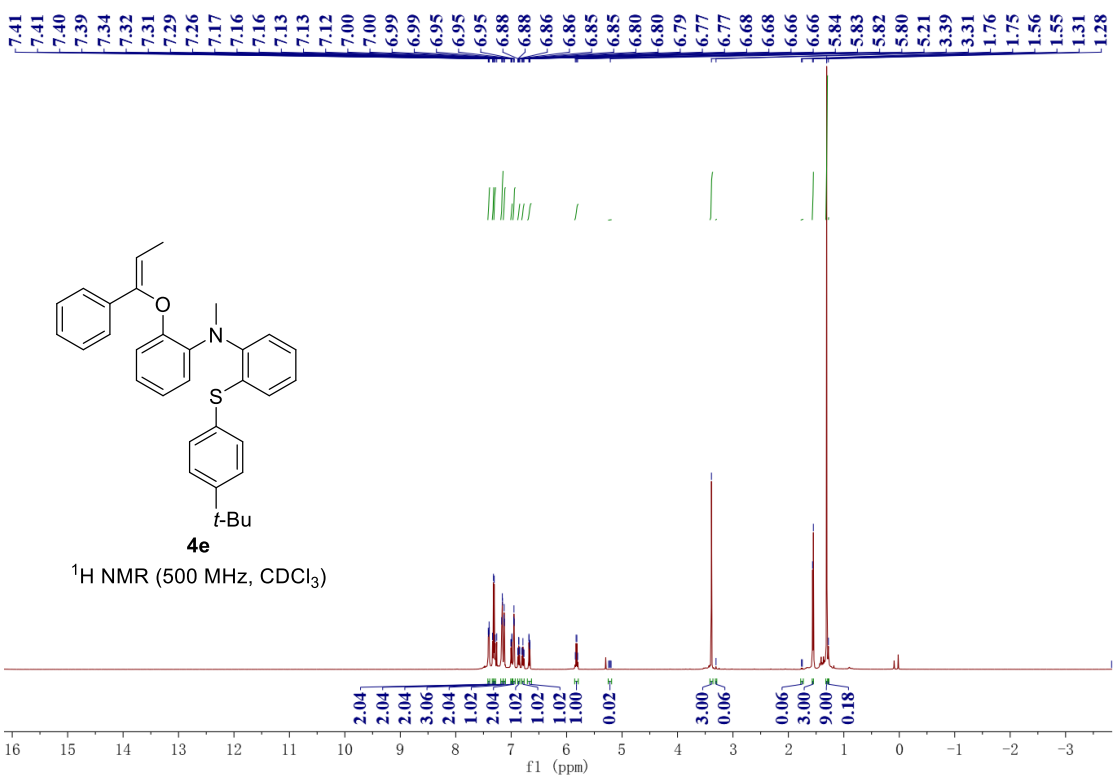
5b

^{1}H NMR (500 MHz, $CDCl_3$)



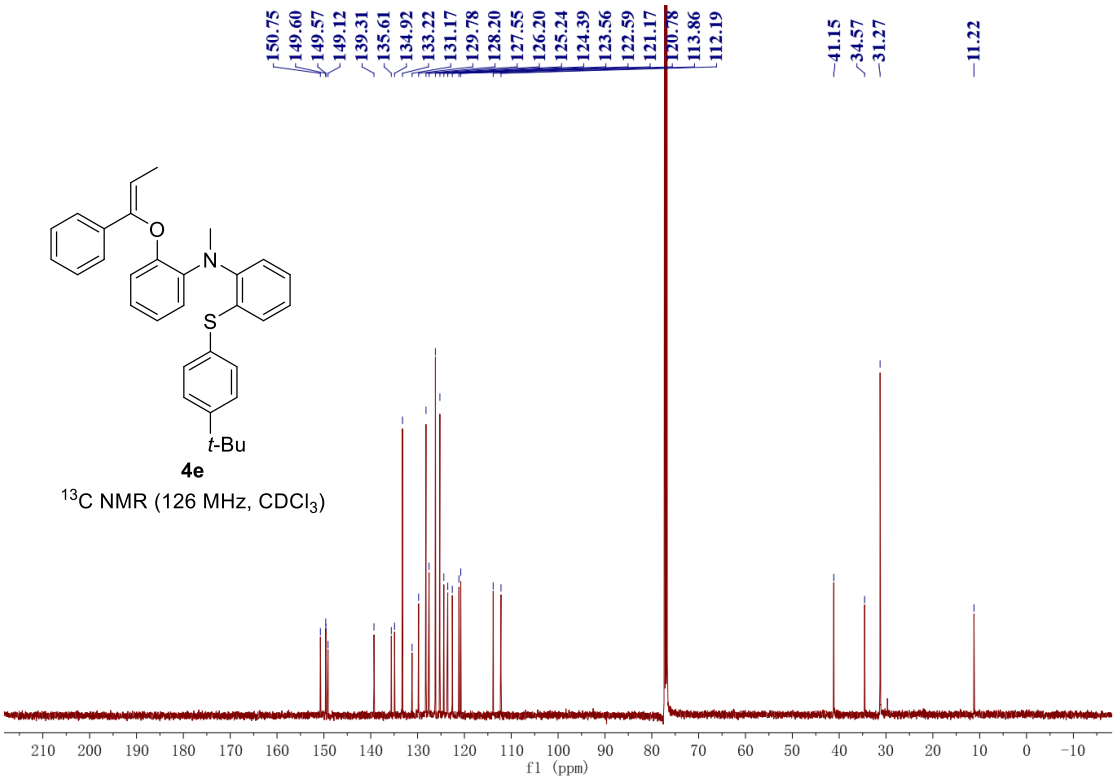
5b

^{13}C NMR (126 MHz, $CDCl_3$)



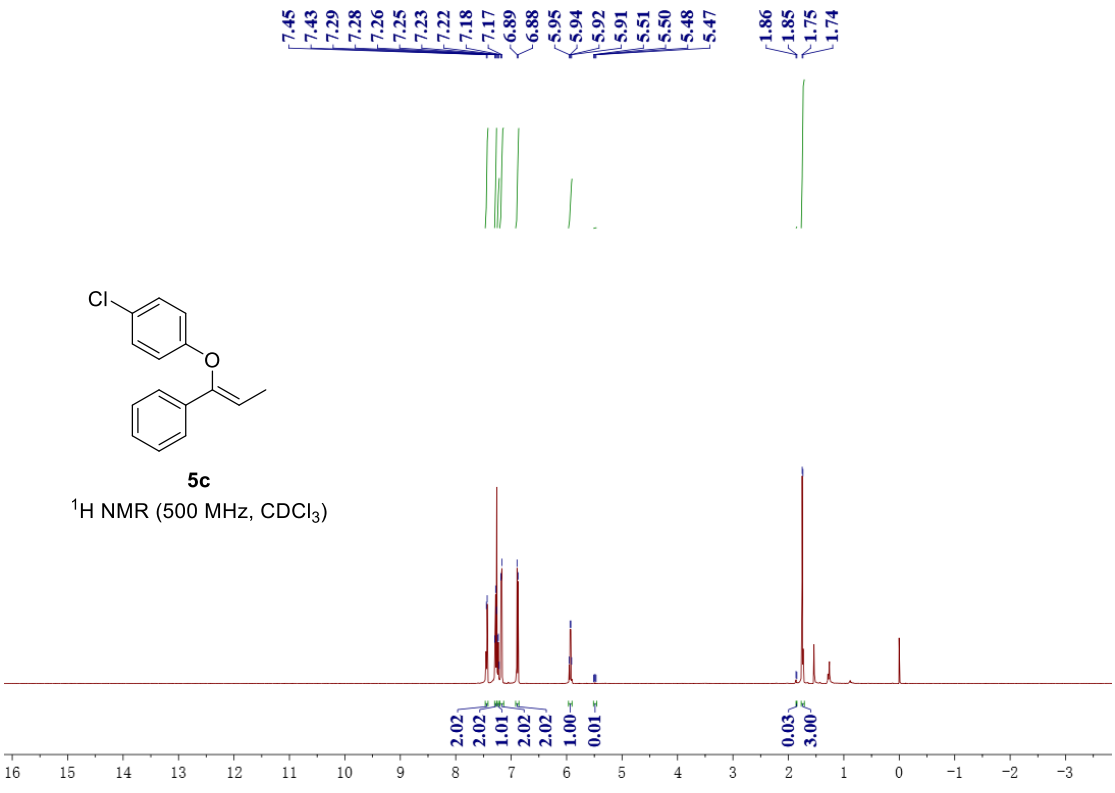
4e

^{1}H NMR (500 MHz, $CDCl_3$)



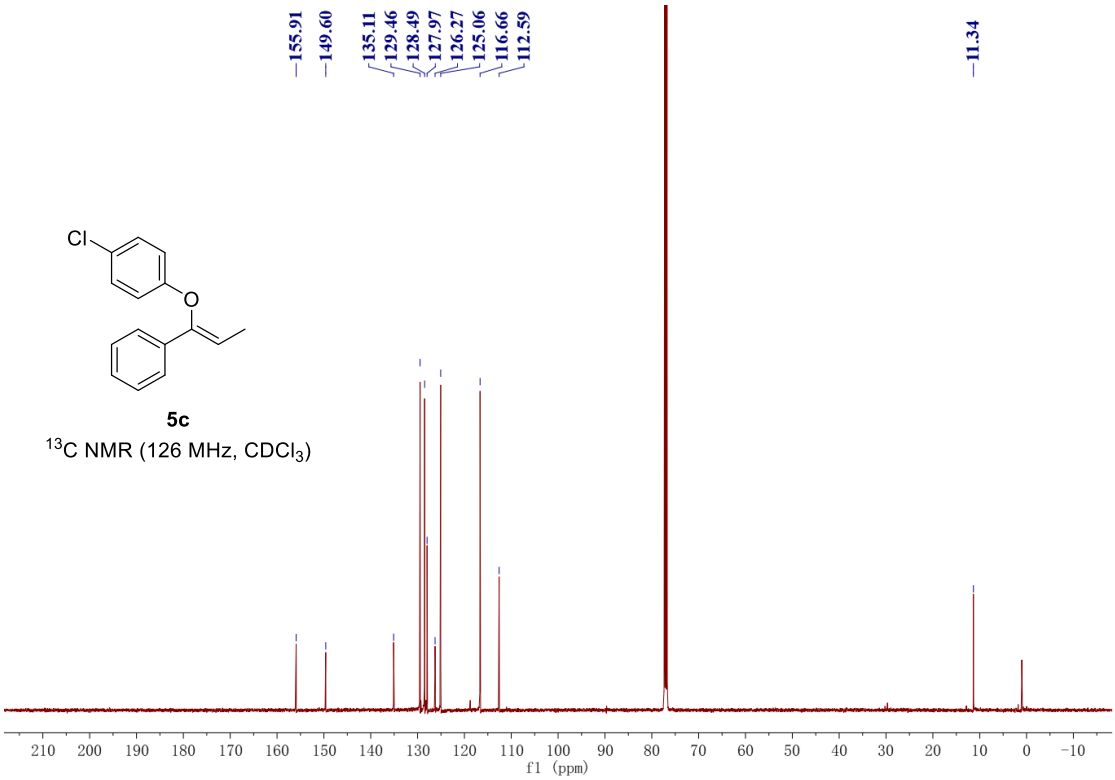
4e

^{13}C NMR (126 MHz, $CDCl_3$)



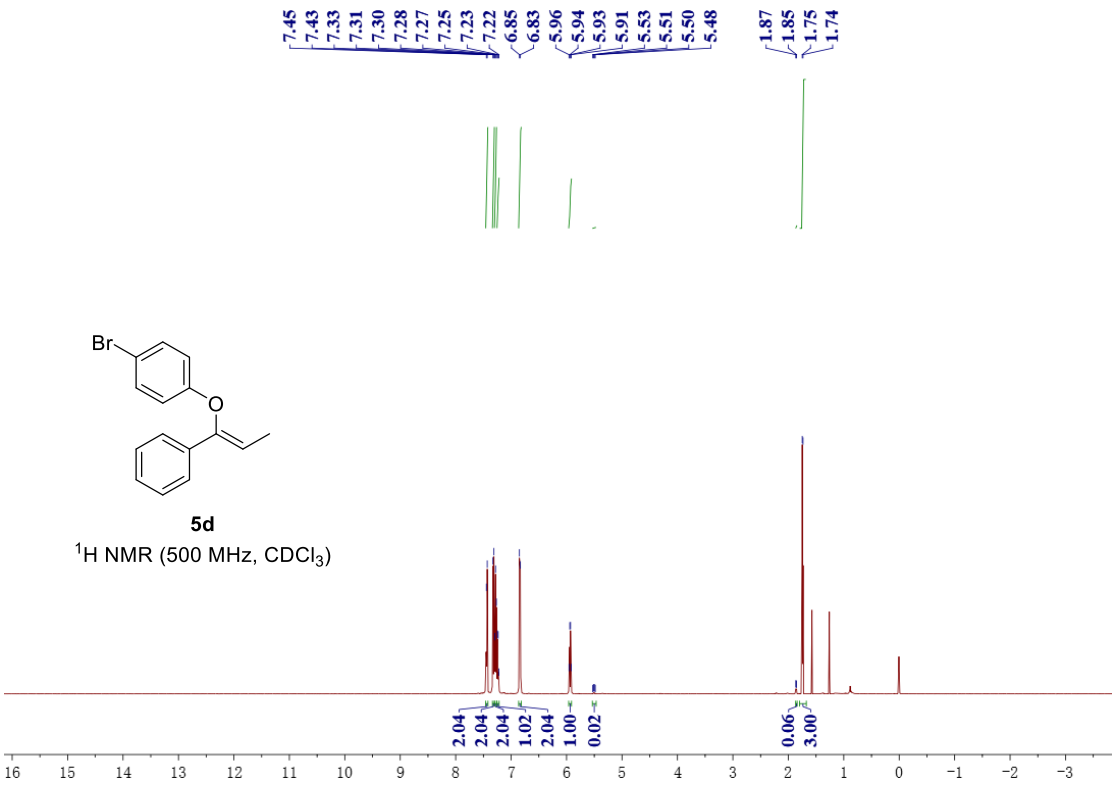
5c

^{1}H NMR (500 MHz, $CDCl_3$)



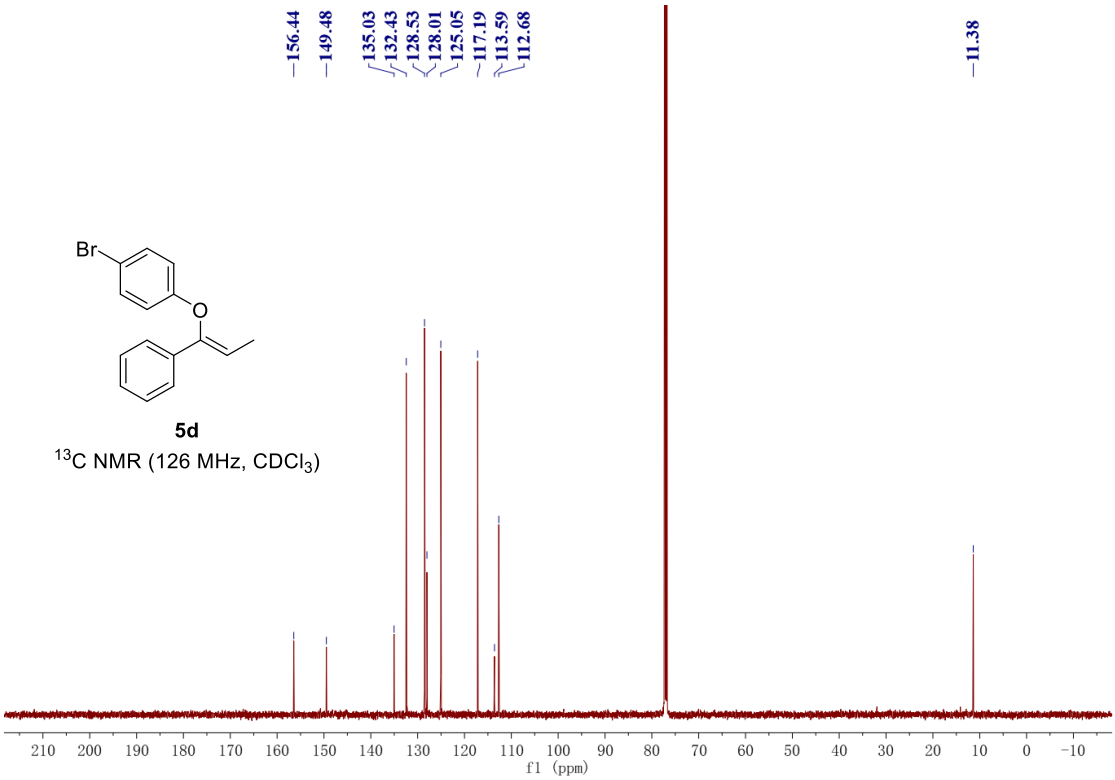
5c

^{13}C NMR (126 MHz, $CDCl_3$)



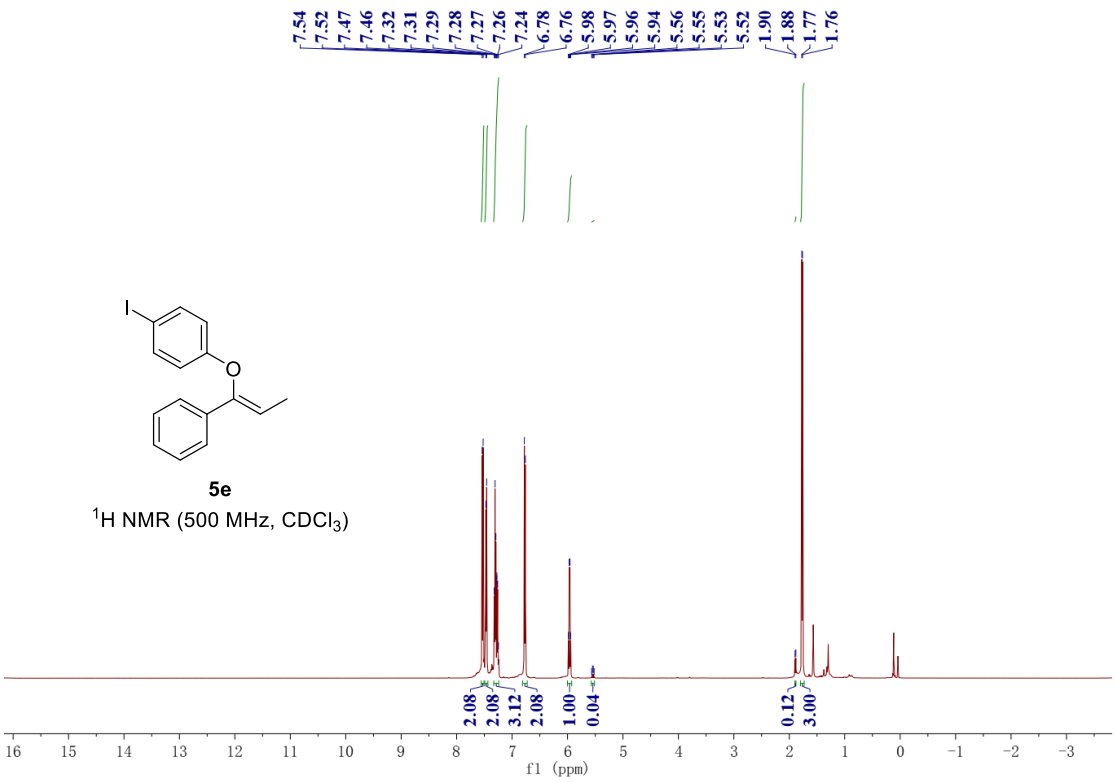
5d

^{1}H NMR (500 MHz, $CDCl_3$)



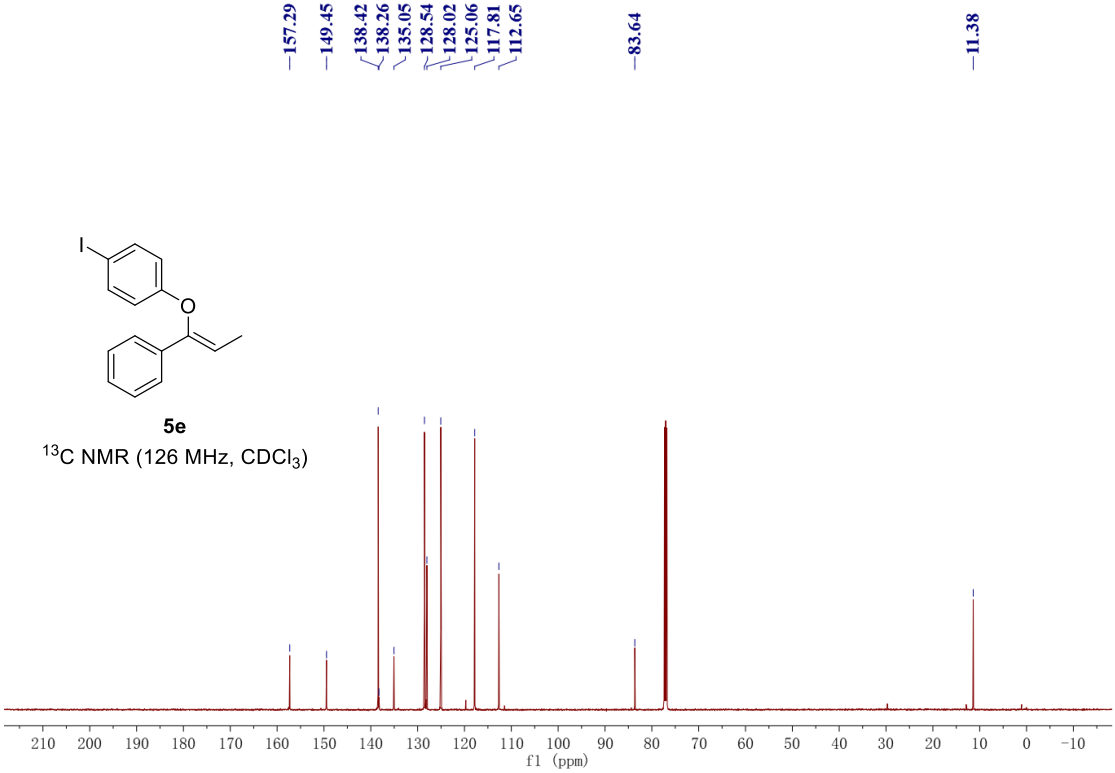
5d

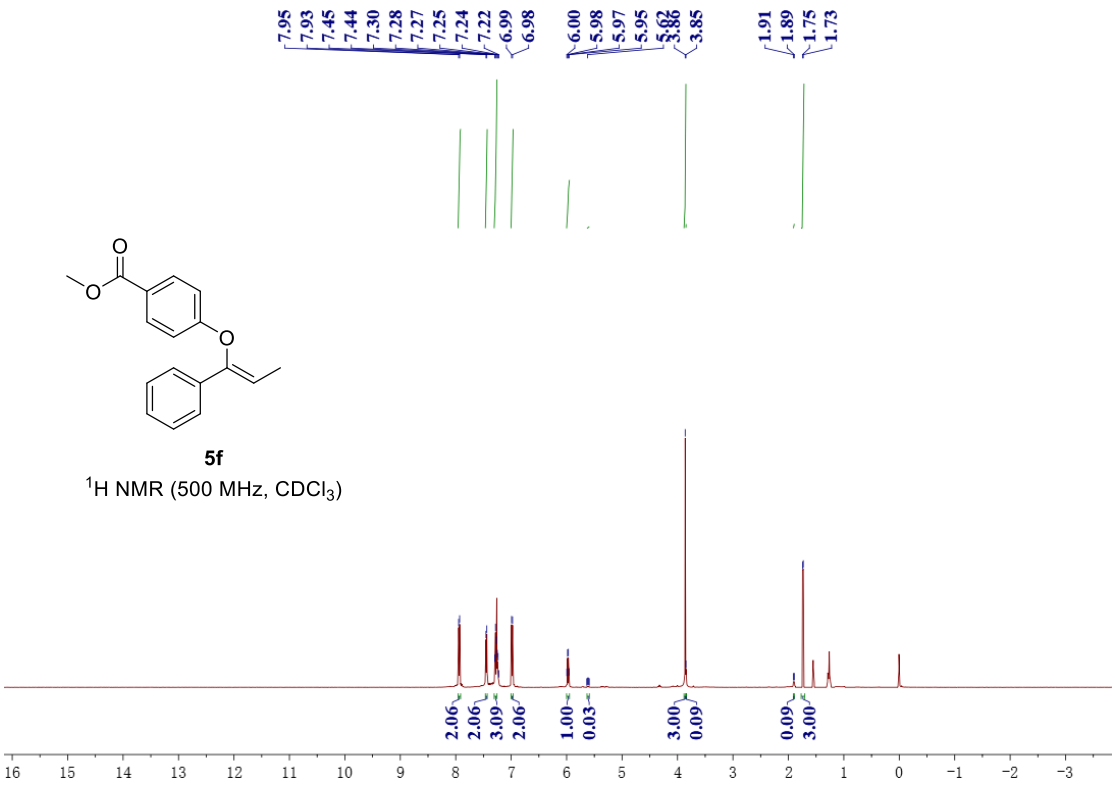
^{13}C NMR (126 MHz, $CDCl_3$)

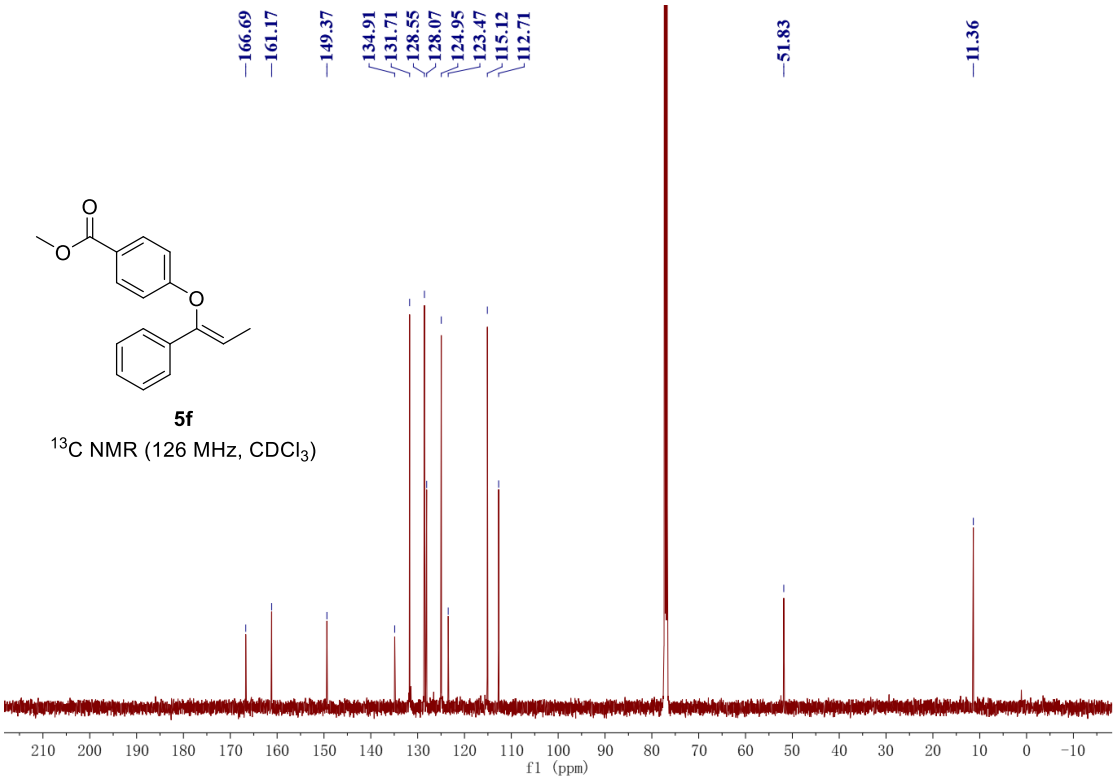


5e

^{1}H NMR (500 MHz, $CDCl_3$)

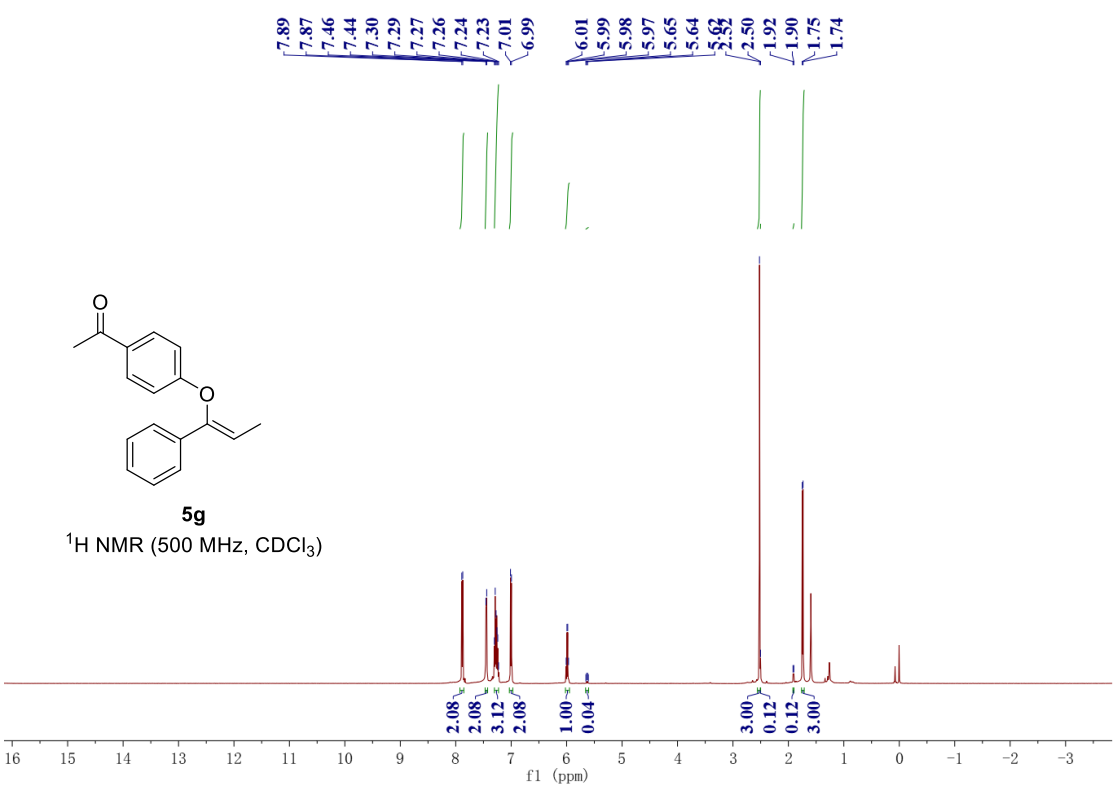

157.29
149.45
138.42
138.26
135.05
128.54
128.02
125.06
117.81
112.65
83.64
11.38
I
O
5e
13C NMR (126 MHz, CDCl3)
f1 (ppm)


7.95
7.93
7.45
7.44
7.30
7.28
7.27
7.25
7.24
7.22
6.99
6.98
6.00
5.98
5.97
5.95
3.86
3.85
1.91
1.89
1.75
1.73
O
O
O
5f
1H NMR (500 MHz, CDCl3)
2.06
2.06
3.09
2.06
1.00
0.03
3.00
0.09
0.09
3.00



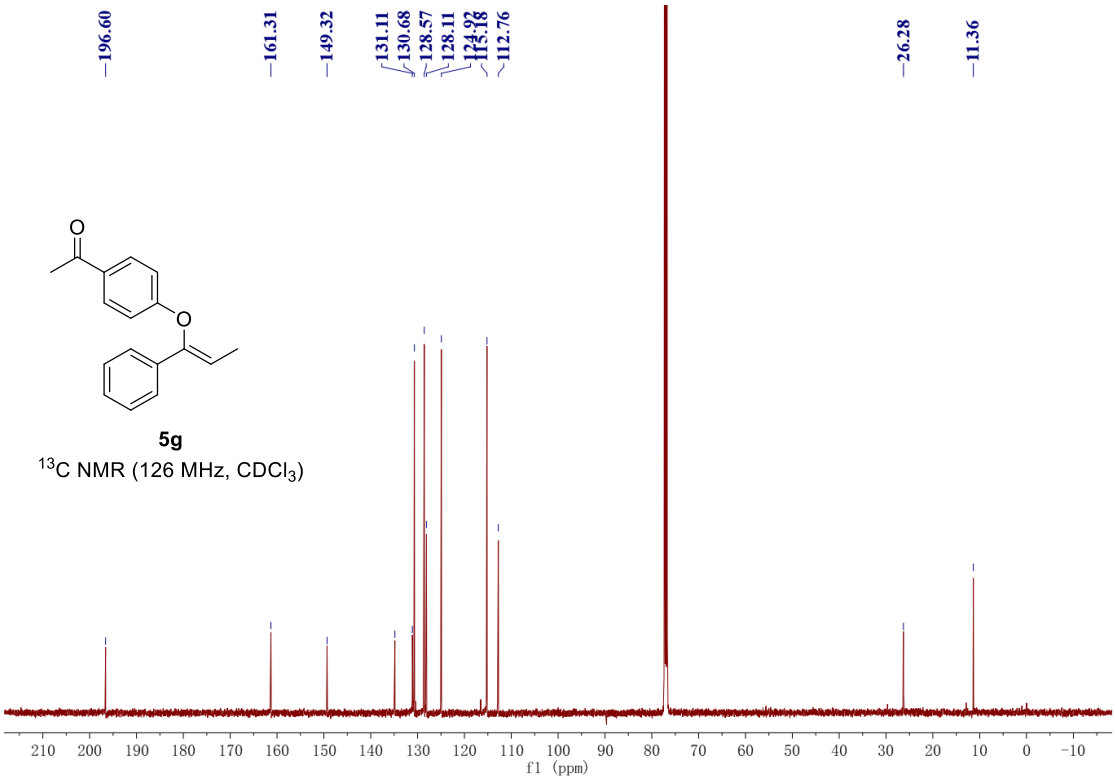
5f

^{13}C NMR (126 MHz, $CDCl_3$)



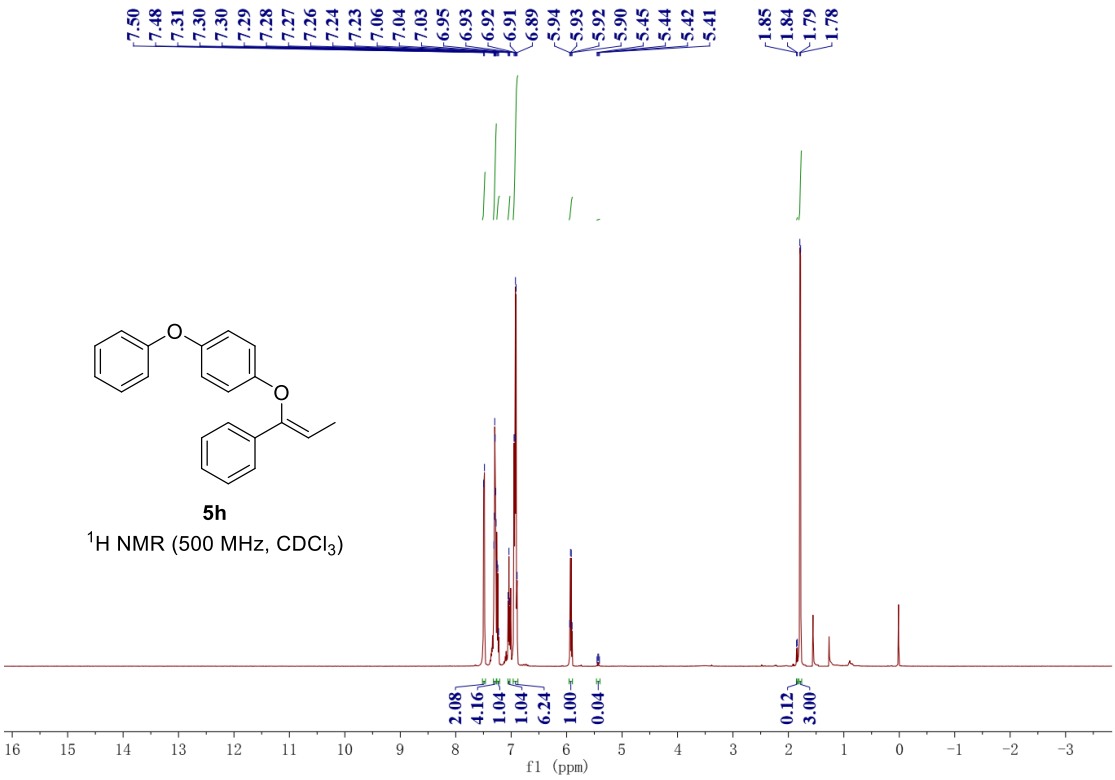
5g

^{1}H NMR (500 MHz, $CDCl_3$)



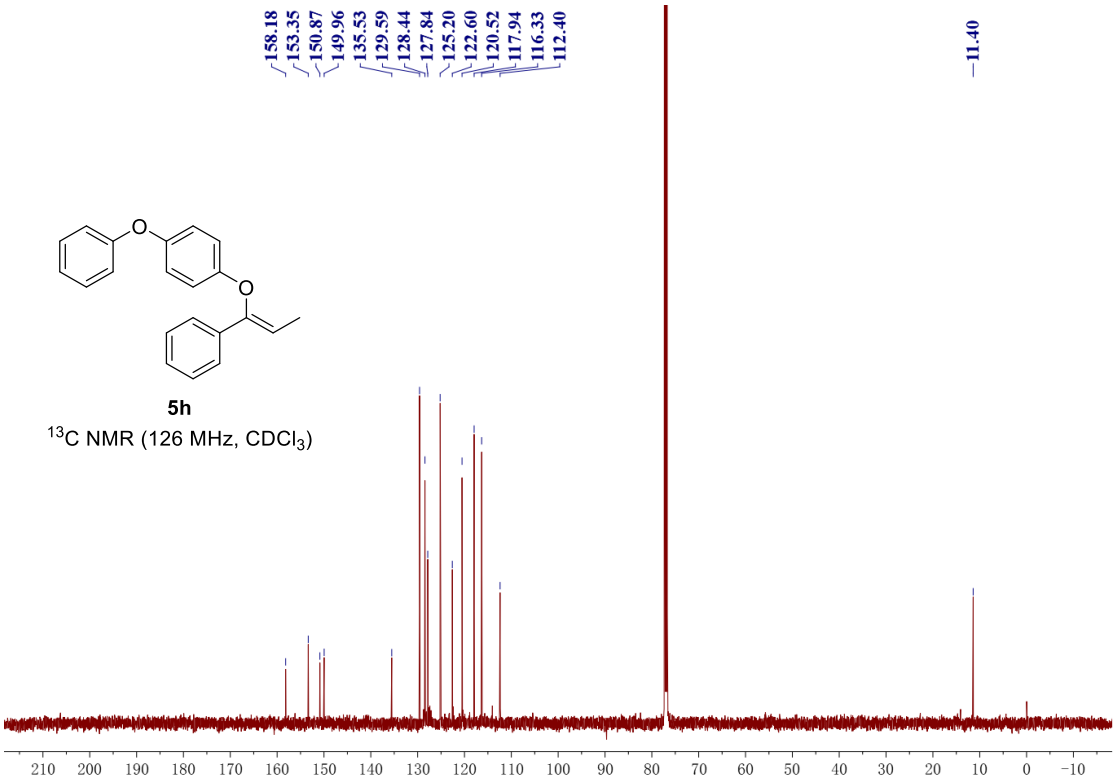
5g

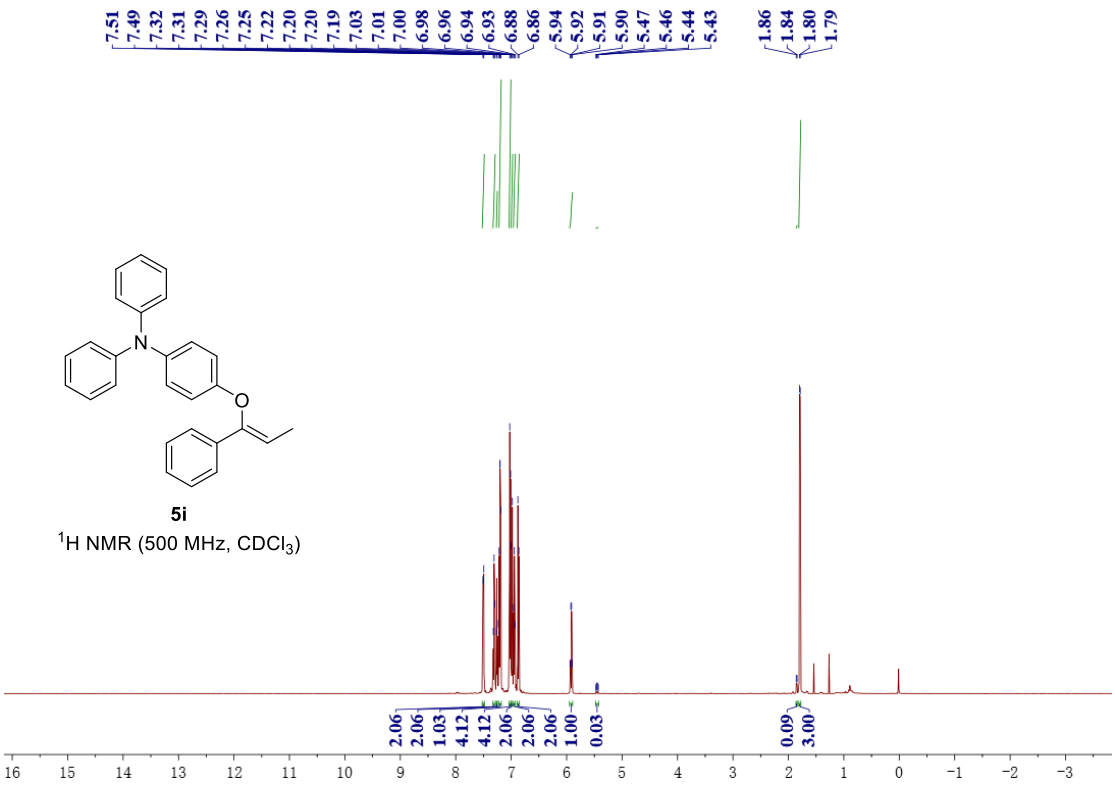
^{13}C NMR (126 MHz, $CDCl_3$)

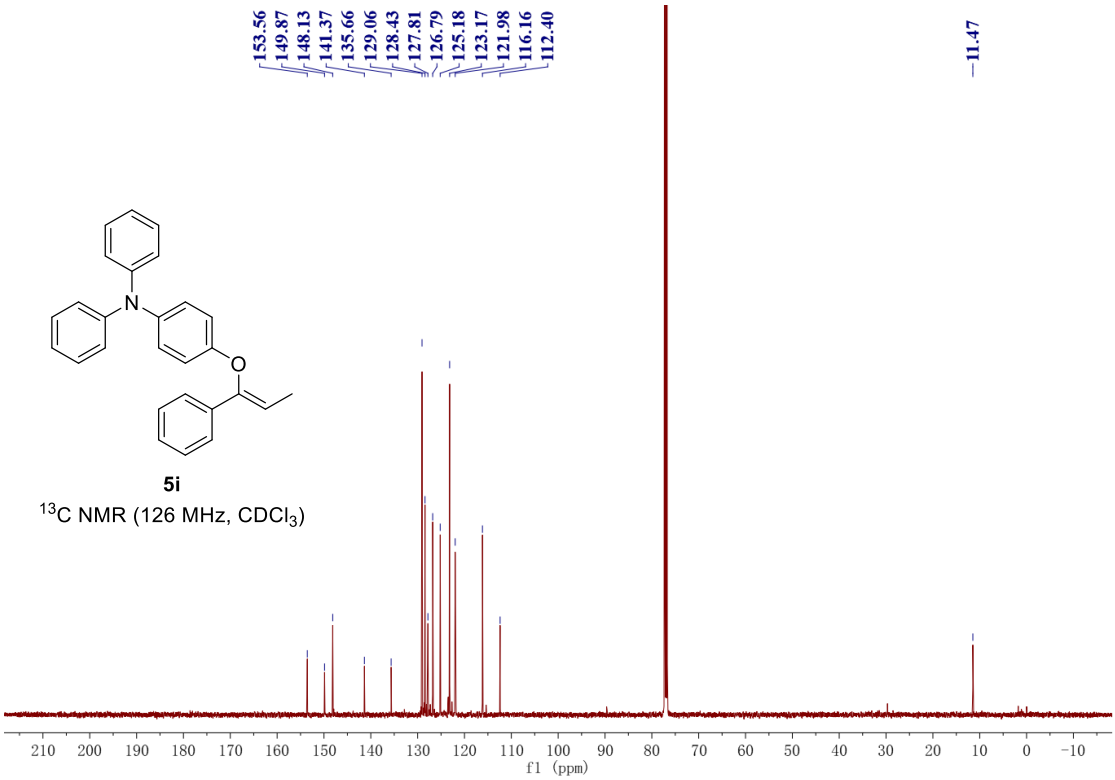


5h

^{1}H NMR (500 MHz, $CDCl_3$)

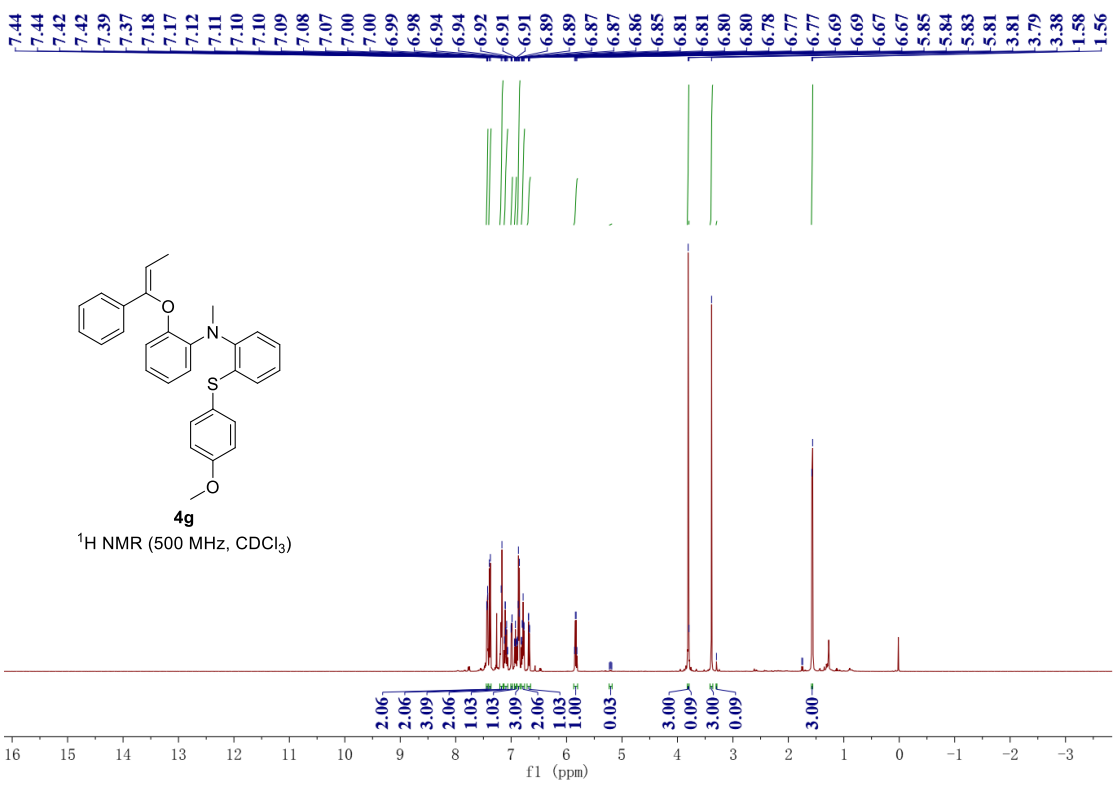

158.18
153.35
150.87
149.96
135.53
129.59
128.44
127.84
125.20
122.60
120.52
117.94
116.33
112.40
11.40
O
O
5h
13C NMR (126 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10


7.51
7.49
7.32
7.31
7.29
7.26
7.25
7.22
7.20
7.20
7.19
7.03
7.01
7.00
6.98
6.96
6.94
6.93
6.88
6.86
5.94
5.92
5.91
5.90
5.47
5.46
5.44
5.43
1.86
1.84
1.80
1.79
N
O
5i
1H NMR (500 MHz, CDCl3)
2.06
2.06
1.03
4.12
4.12
2.06
2.06
2.06
1.00
0.03
0.09
3.00
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 −1 −2 −3



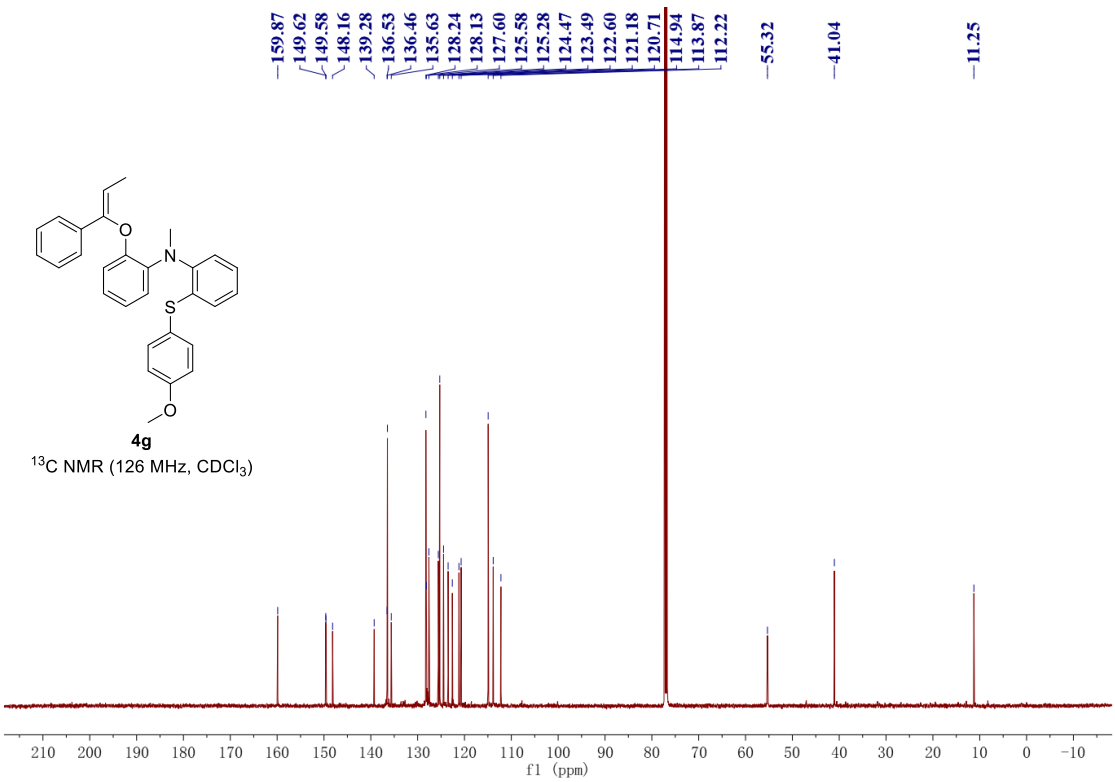
5i

^{13}C NMR (126 MHz, $CDCl_3$)



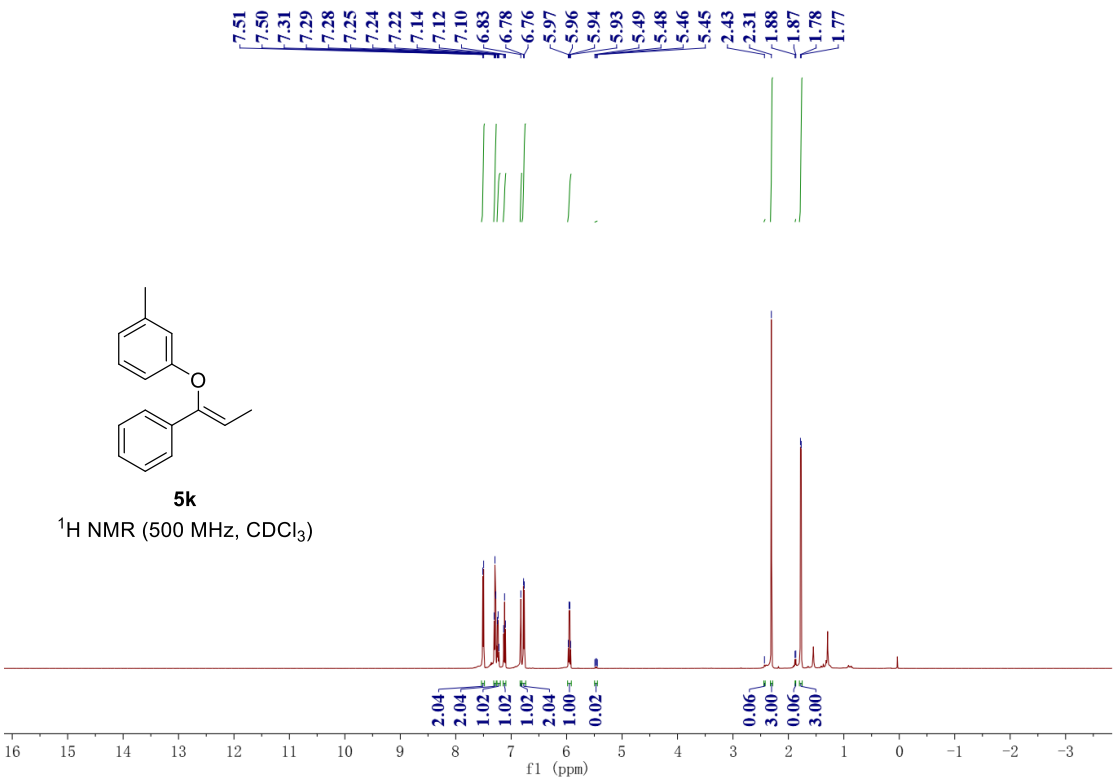
4g

^{1}H NMR (500 MHz, $CDCl_3$)



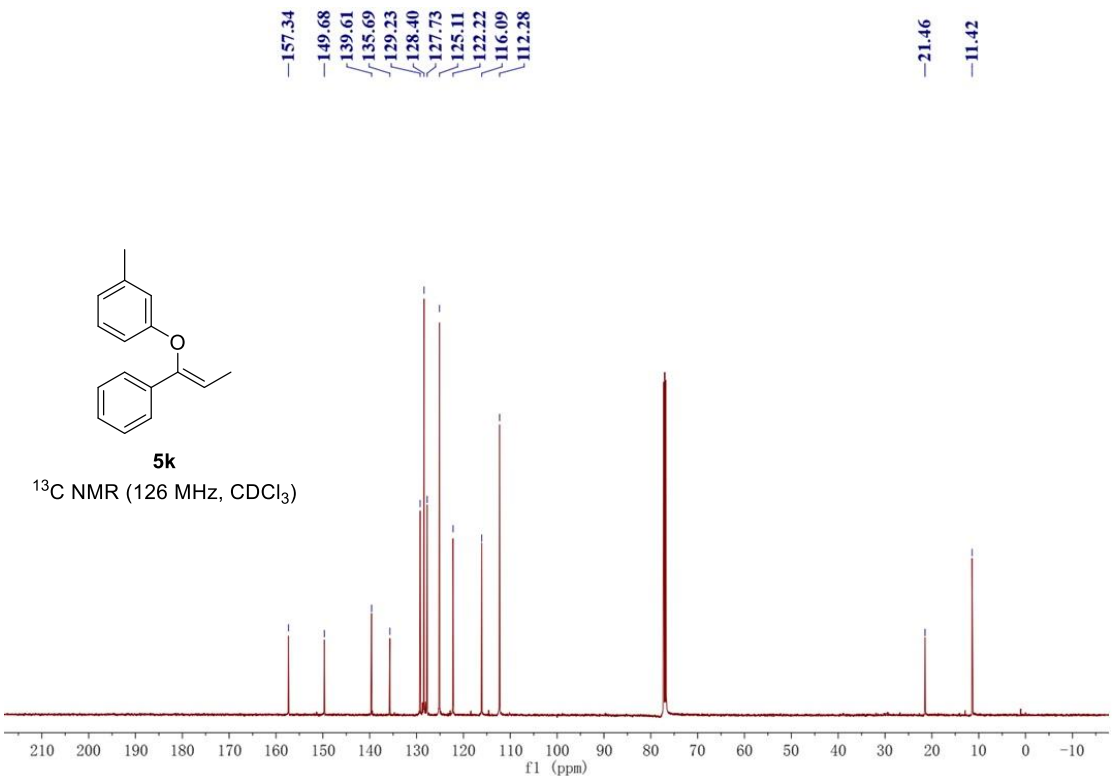
4g

^{13}C NMR (126 MHz, $CDCl_3$)



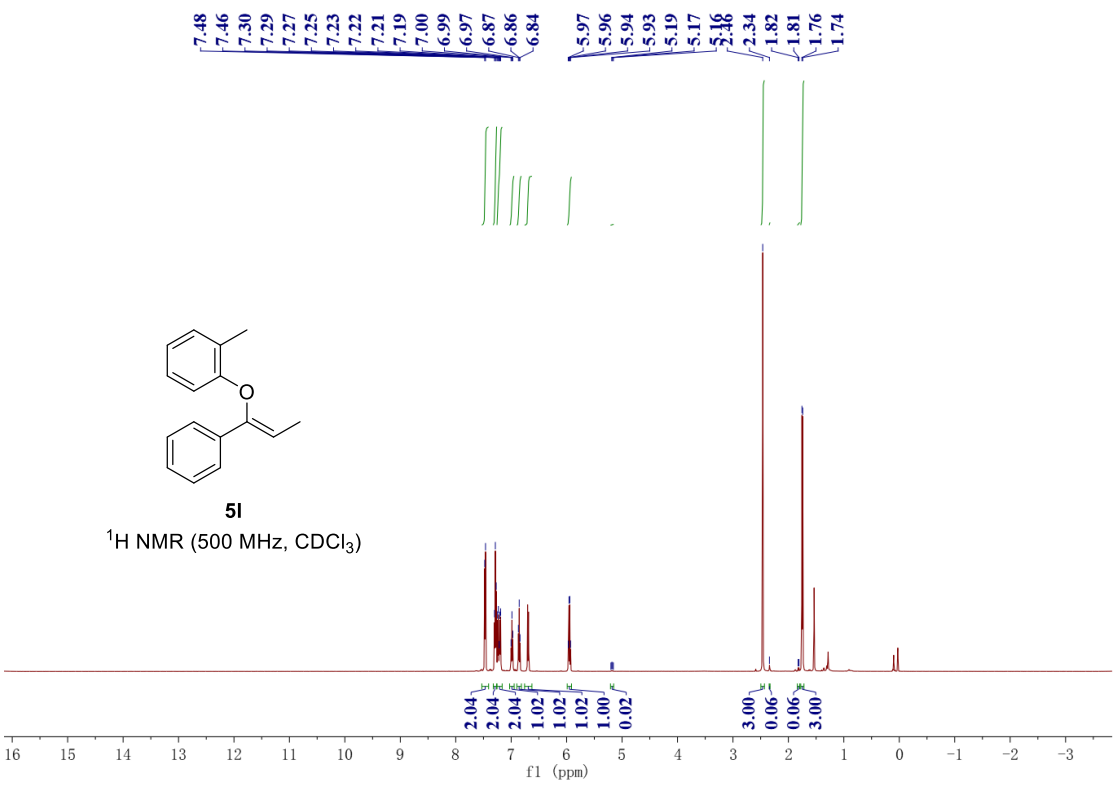
5k

^{1}H NMR (500 MHz, $CDCl_3$)



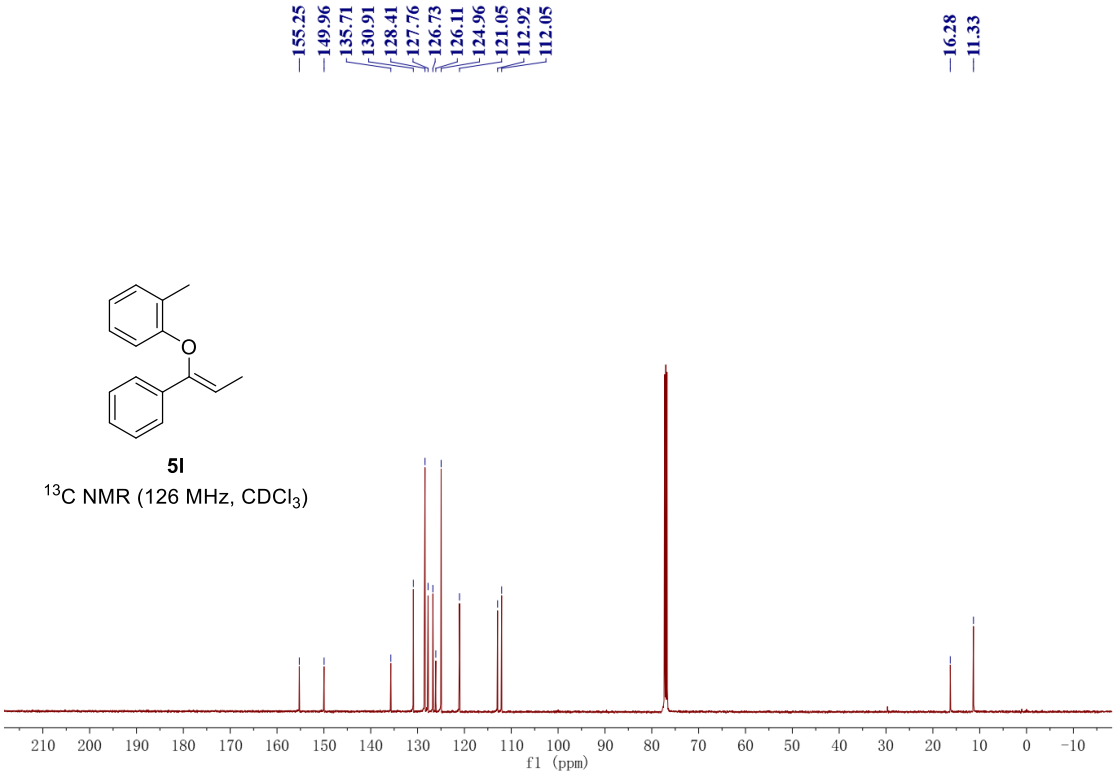
5k

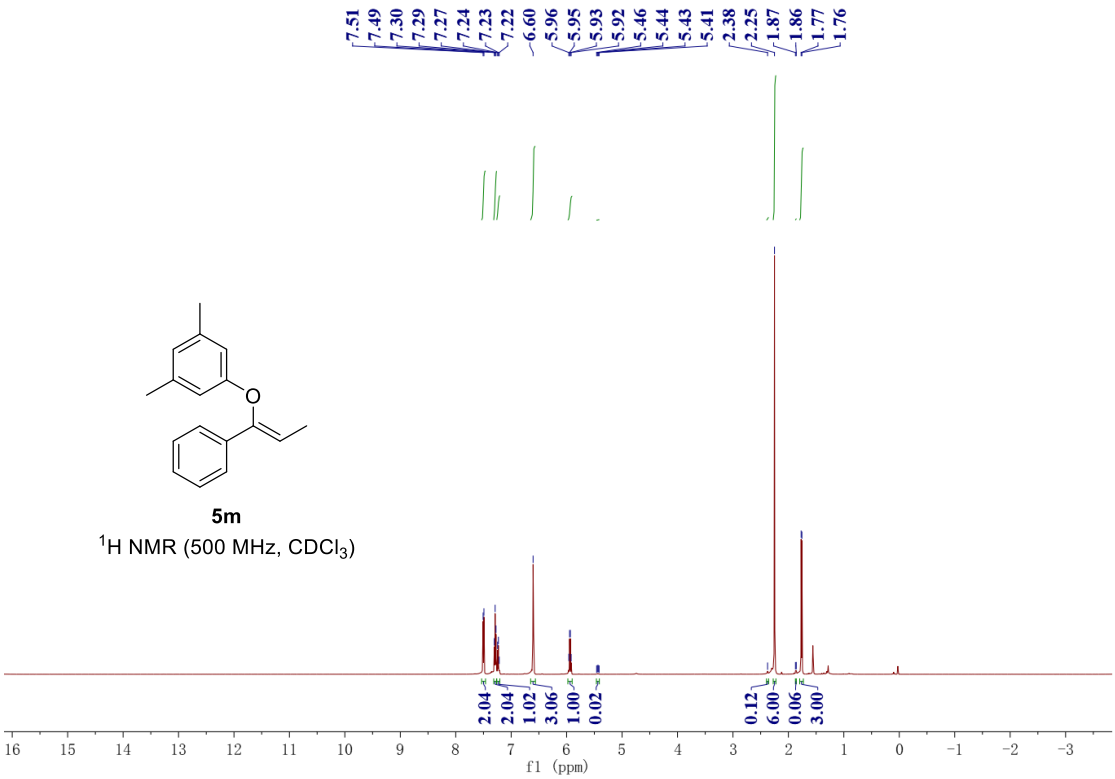
^{13}C NMR (126 MHz, $CDCl_3$)

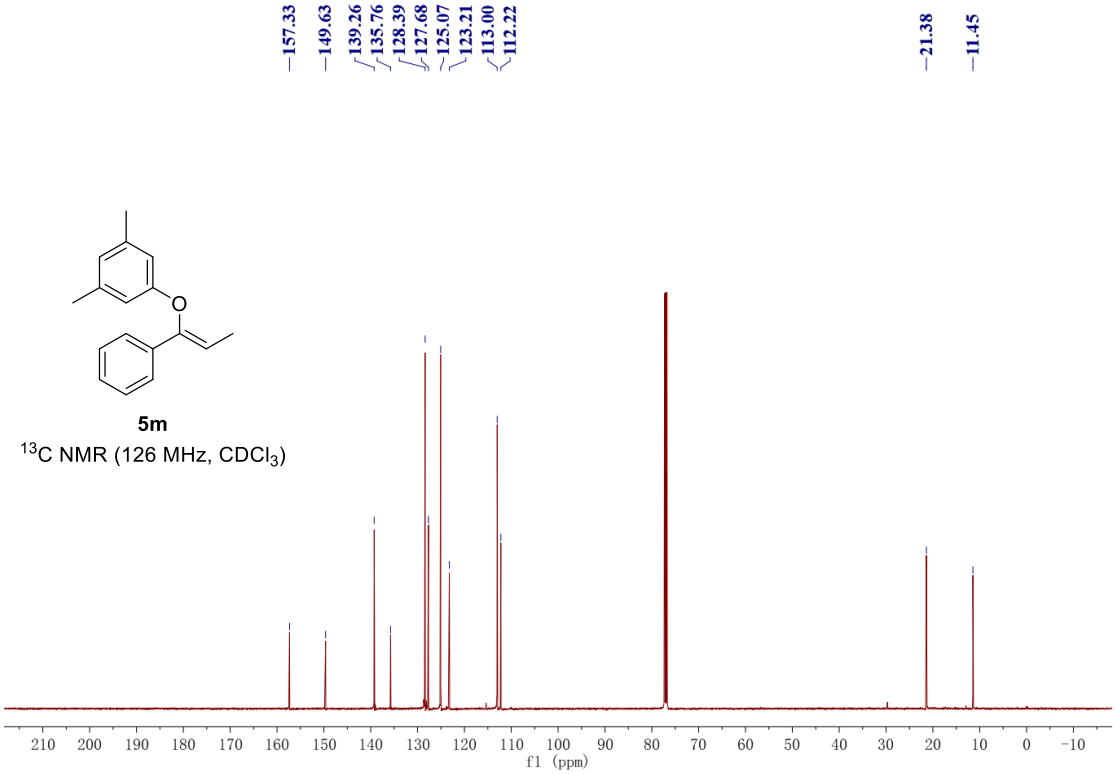


5l

^{1}H NMR (500 MHz, $CDCl_3$)

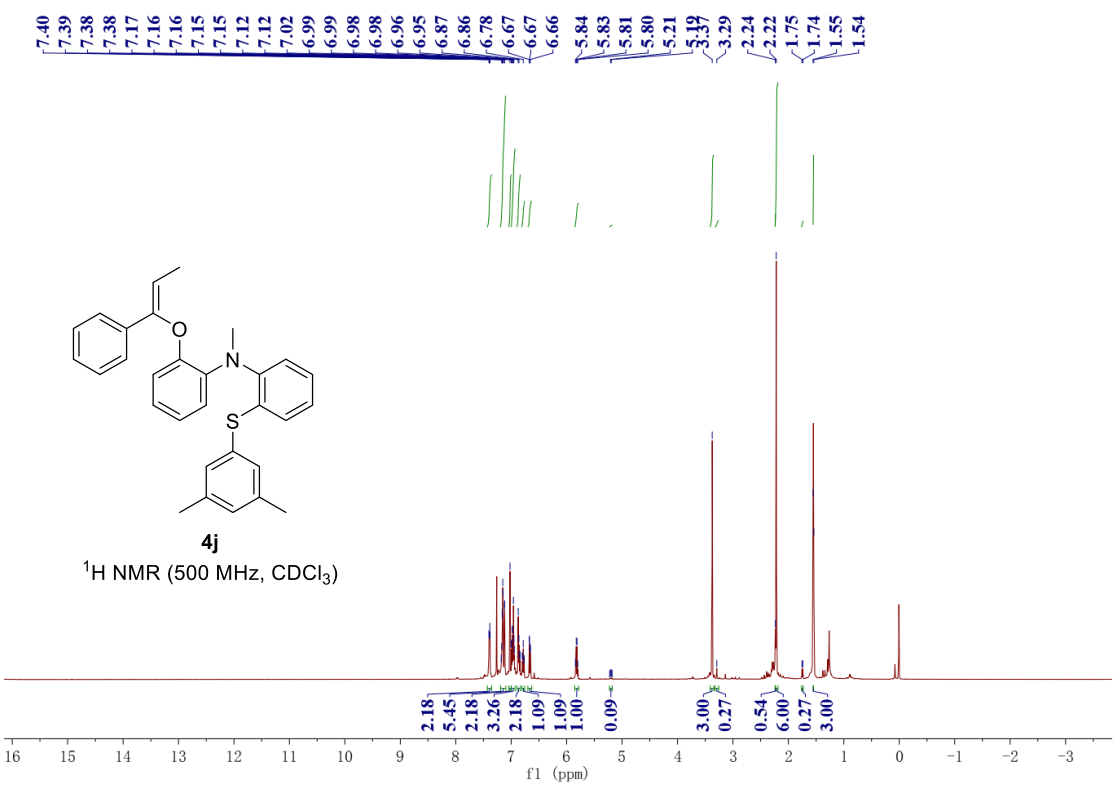

155.25
149.96
135.71
130.91
128.41
127.76
126.73
126.11
124.96
121.05
112.92
112.05
16.28
11.33
O
5l
13C NMR (126 MHz, CDCl3)
f1 (ppm)


7.51
7.49
7.30
7.29
7.27
7.24
7.23
7.22
6.60
5.96
5.95
5.93
5.92
5.46
5.44
5.43
5.41
2.38
2.25
1.87
1.86
1.77
1.76
O
5m
1H NMR (500 MHz, CDCl3)
2.04
2.04
1.02
3.06
1.00
0.02
0.12
6.00
0.06
3.00
f1 (ppm)



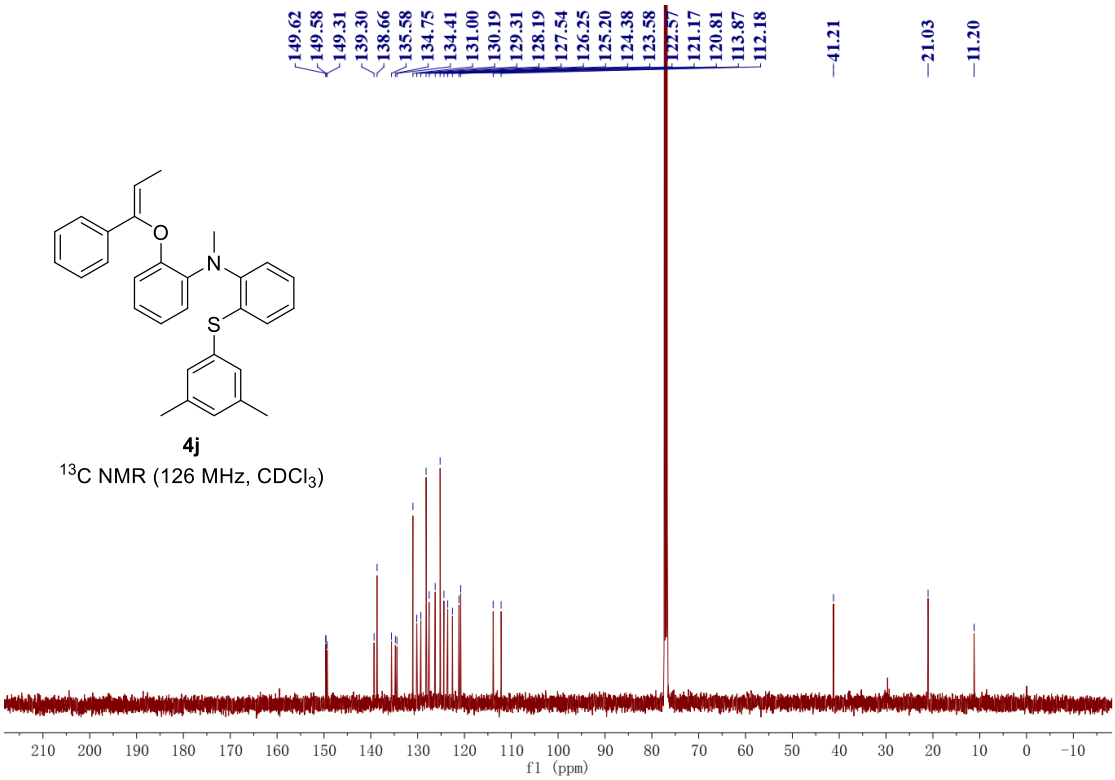
5m

^{13}C NMR (126 MHz, $CDCl_3$)



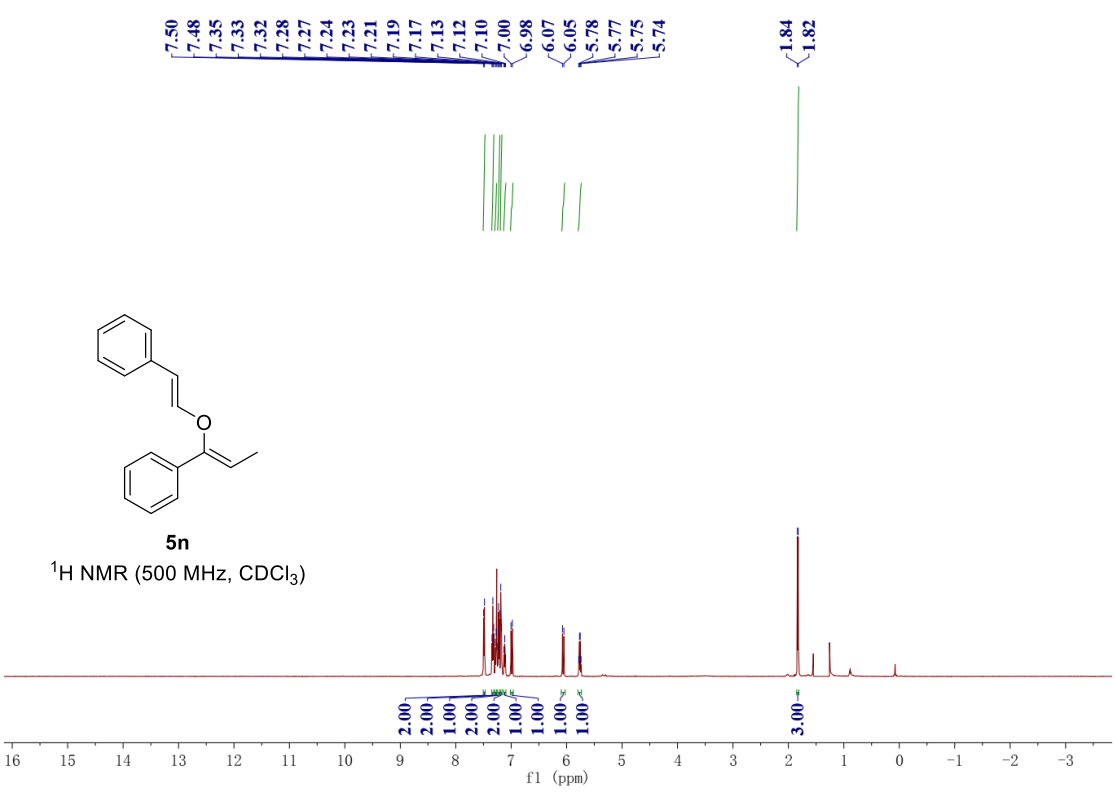
4j

^{1}H NMR (500 MHz, $CDCl_3$)



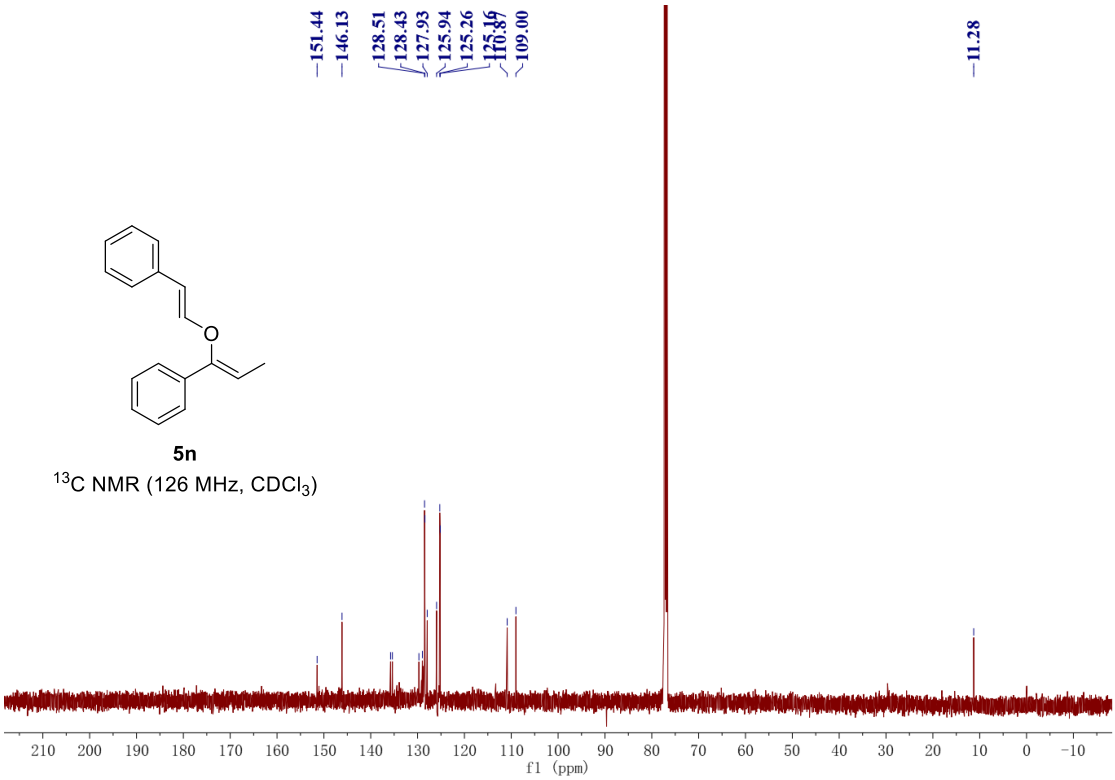
4j

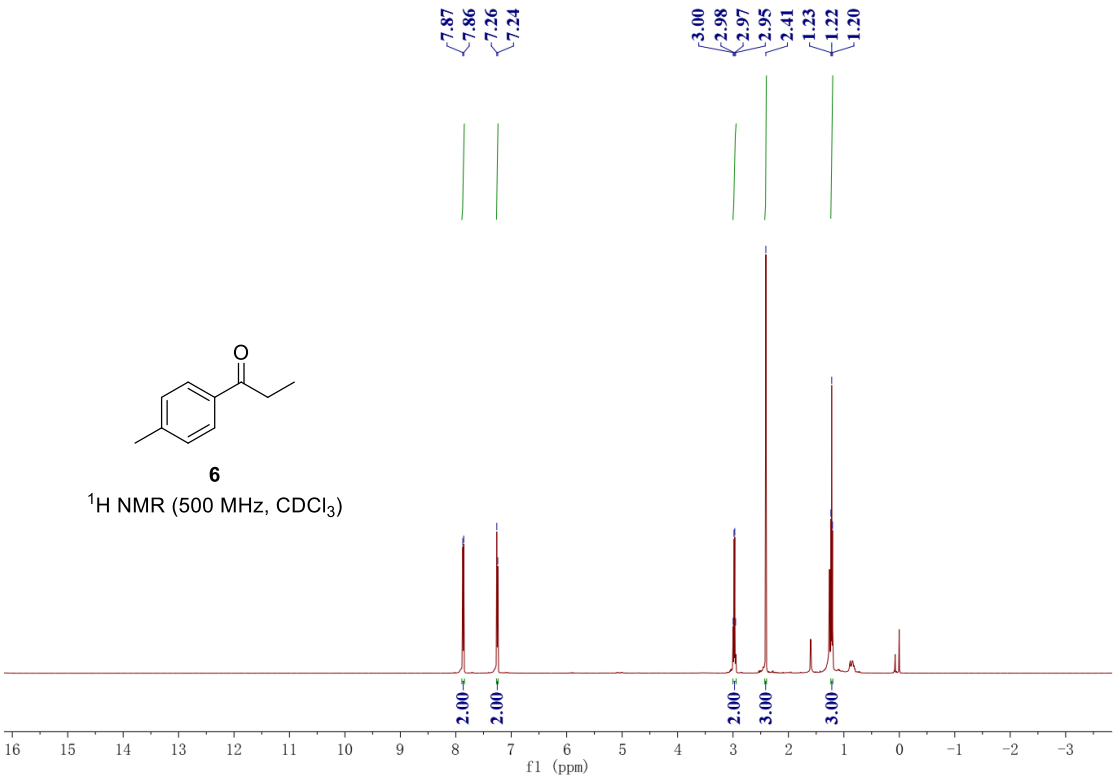
^{13}C NMR (126 MHz, $CDCl_3$)

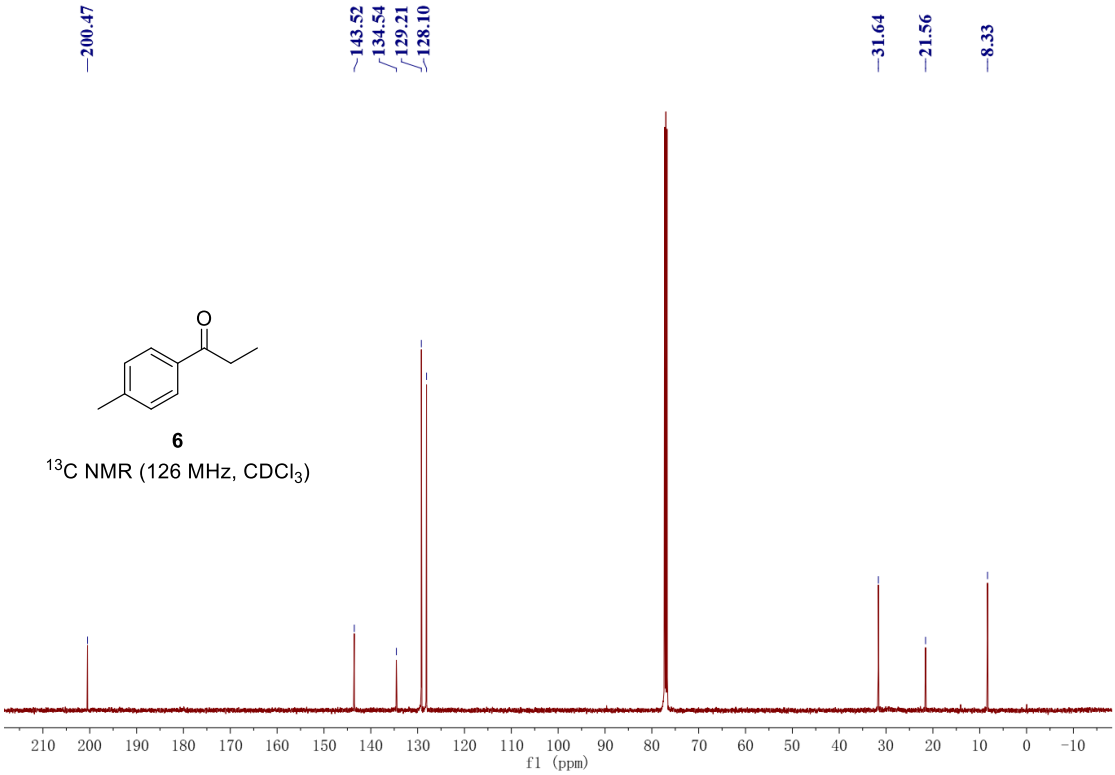


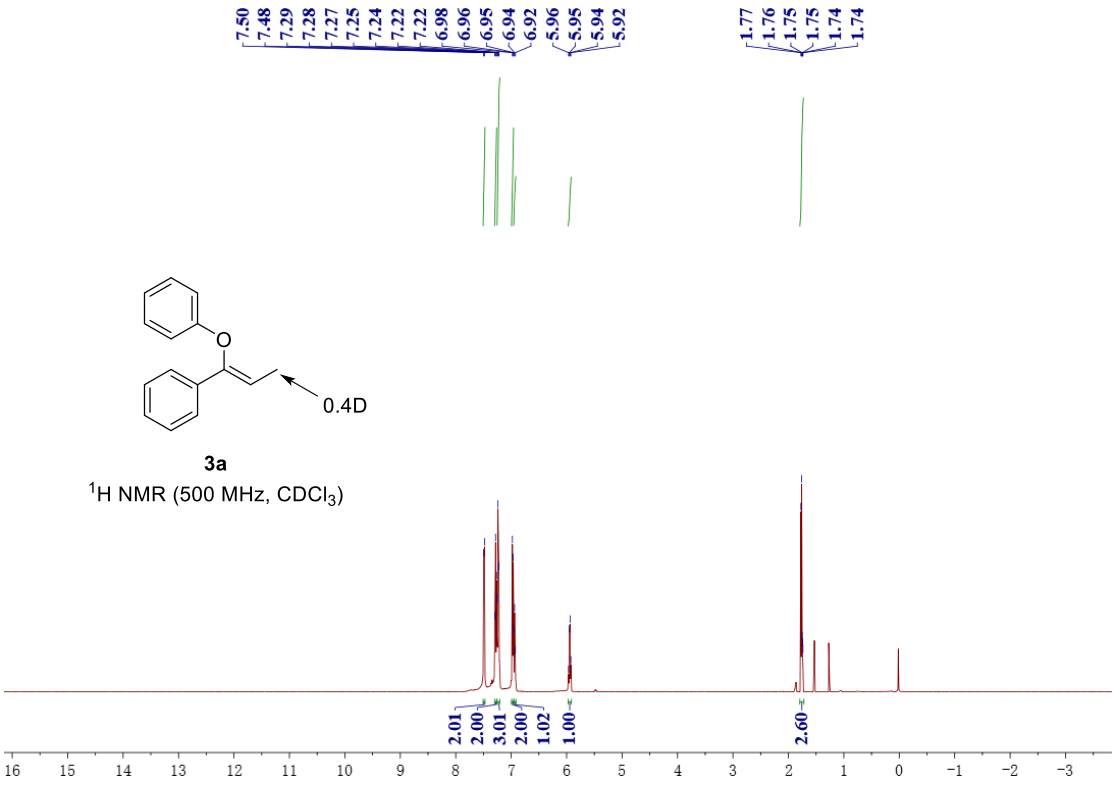
5n

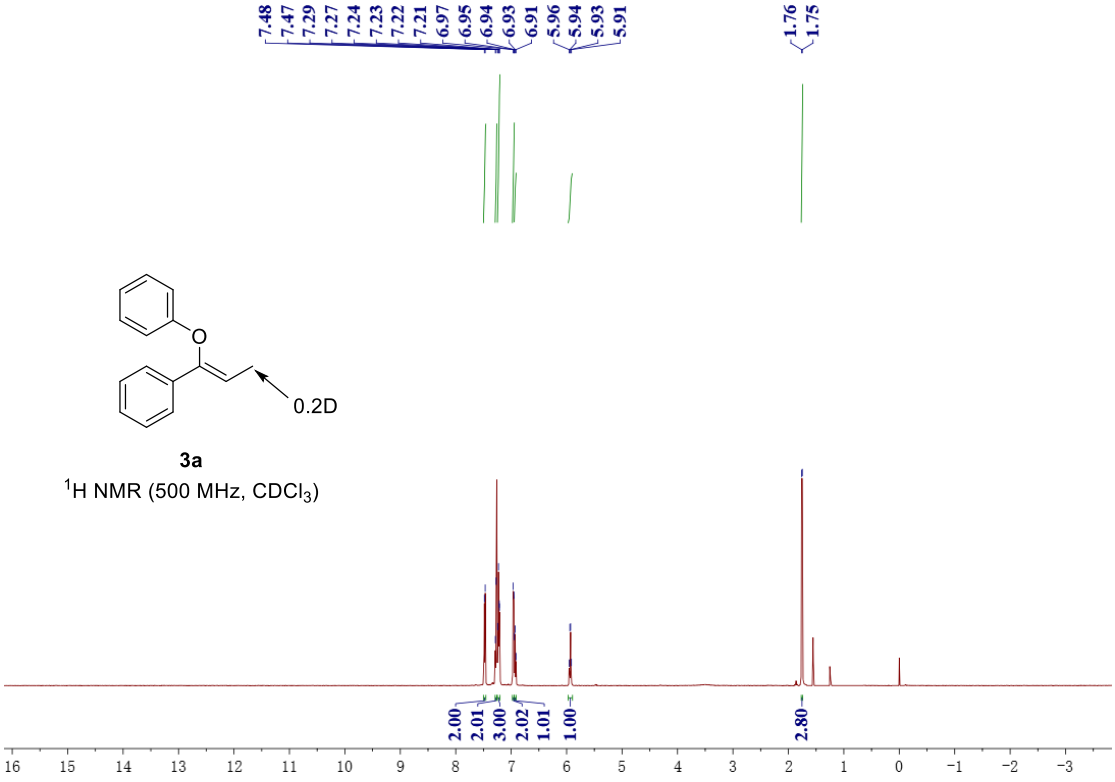
^{1}H NMR (500 MHz, $CDCl_3$)


151.44
146.13
128.51
128.43
127.93
125.94
125.26
125.16
110.87
109.00
11.28
O
5n
13C NMR (126 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)


7.87
7.86
7.26
7.24
3.00
2.98
2.97
2.95
2.41
1.23
1.22
1.20
O
6
1H NMR (500 MHz, CDCl3)
2.00
2.00
2.00
3.00
3.00
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 −1 −2 −3
f1 (ppm)


200.47
143.52
134.54
129.21
128.10
31.64
21.56
8.33
O
6
13C NMR (126 MHz, CDCl3)
f1 (ppm)


7.50
7.48
7.29
7.28
7.27
7.25
7.24
7.22
7.22
6.98
6.96
6.95
6.94
6.92
5.96
5.95
5.94
5.92
1.77
1.76
1.75
1.75
1.74
1.74
O
0.4D
3a
1H NMR (500 MHz, CDCl3)
2.01
2.00
3.01
2.00
1.02
1.00
2.60


7.48
7.47
7.29
7.27
7.24
7.23
7.22
7.21
6.97
6.95
6.94
6.93
6.91
5.96
5.94
5.93
5.91
1.76
1.75
O
0.2D
3a
1H NMR (500 MHz, CDCl3)
2.00
2.01
3.00
2.02
1.01
1.00
2.80
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
−1
−2
−3