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Palladium-Catalyzed Mizoroki-Heck-Type Reactions of $[Ph_2SR_{fn}][OTf]$ with Alkenes at Room Temperature

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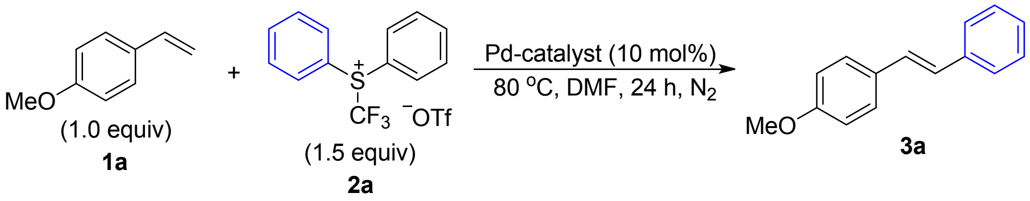
1. General considerations

All reactions were carried out under a nitrogen atmosphere. Unless otherwise specified, NMR spectra were recorded in $CDCl_3$ on a 500 or 400 MHz (for ^1H), 471 or 376 MHz (for ^{19}F), and 126 or 100 MHz (for ^{13}C) spectrometer. All chemical shifts were reported in ppm relative to TMS (^1H NMR, 0 ppm) and $PhCF_3$ (^{19}F NMR, -63.0 ppm) as internal or external standards. The HPLC experiments were carried out on a Waters e2695 instrument (column: J&K, RP-C18, 5 μm, 4.6 × 150 mm), and the yields of the products were determined by using the corresponding pure compounds as the external standards. Fluorinated alkyl arylsulfonium salts **2a**[1], **2b**[2], **2c**[2], **2d**[2], **2e**[3], **2f**[4], **2g**[2], **2h**[5], **2i**[3], **2j**[6], and **2k**[7] were synthesized according to the literatures or by modified procedures.[1-7] Alkenes **1b-c**[8], **1h**[8], **1l-p**[8], and **1r**[9] were prepared according to literatures.[8,9] Solvents were dried before use according to literature.[10] Other reagents were all purchased from commercial sources and used without further purification.

2. Screening the optimized conditions for Pd-catalyzed Heck-type reaction of 2a or 2b with 1a.

Table 1. The reaction of **1a** with **2a** in the presence of diverse Pd-catalysts[a]

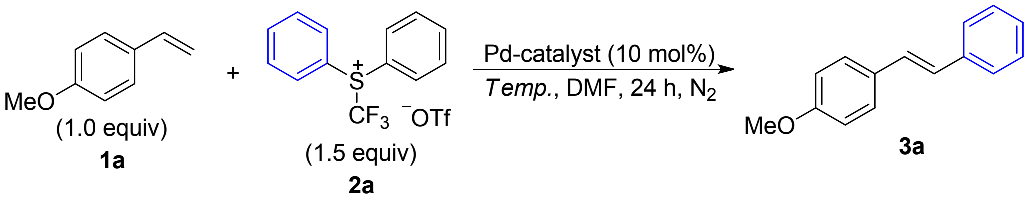


Entry	Pd-catalyst	Yield (**3a**, %)[b]
1	$PdCl_2$	30
2	Pd/C	4
3	$Pd_2(dba)_3$	30
4	$Pd(dba)_2$	30
5	$Pd(OAc)_2$	64
6	$Pd(PPh_3)_4$	30
7	**$Pd[P(t\text{-}Bu)_3]_2$**	**76**
8	$Pd(Cy_3)_2$	0.2

[a] Reaction conditions: a mixture of **1a** (0.1 mmol), **2a** (0.15 mmol), Pd-catalyst (0.01 mmol, 10 mol%), and DMF (2 mL) was reacted at 80 °C in a sealed tube under

a N_2 atmosphere for 24 h. [b] The yield was determined by HPLC using **3a** (Retention time: 8.468 min, λ_{max} = 302.2 nm, water/methanol = 20 : 80 (v / v)) as the external standard.

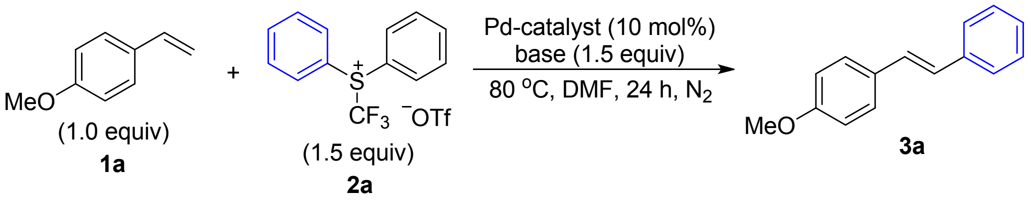
Table 2. The temperature effects on Pd-catalyzed Heck reaction[a]



Entry	Pd-catalyst	Temperature (°C)	Yield (**3a**, %)[b]
1	$Pd(OAc)_2$	80	64
2	$Pd(OAc)_2$	60	67
3	$Pd(OAc)_2$	40	54
4	$Pd(OAc)_2$	r.t.	39
5	$Pd(PPh_3)_4$	80	30
6	$Pd(PPh_3)_4$	60	72
7	$Pd(PPh_3)_4$	40	4
8	$Pd(PPh_3)_4$	r.t.	0
9[c]	Pd[(*t*-Bu)$_3$]$_2$	80	60
10[c]	Pd[(*t*-Bu)$_3$]$_2$	60	80
11[c]	Pd[(*t*-Bu)$_3$]$_2$	40	70
12[c]	**Pd[(*t*-Bu)$_3$]$_2$**	**r.t.**	**86**

[a] Reaction conditions: a mixture of **1a** (0.1 mmol), **2a** (0.15 mmol), Pd-catalyst (0.01 mmol, 10 mol%), and DMF (2 mL) was reacted at different temperature in a sealed tube under a N_2 atmosphere for 24 h. [b] The yield was determined by HPLC using **3a** (Retention time: 8.468 min, λ_{max} = 302.2 nm, water/methanol = 20 : 80 (v / v)) as the external standard. [c] TsOH (0.01 mmol, 10 mol%) was used.

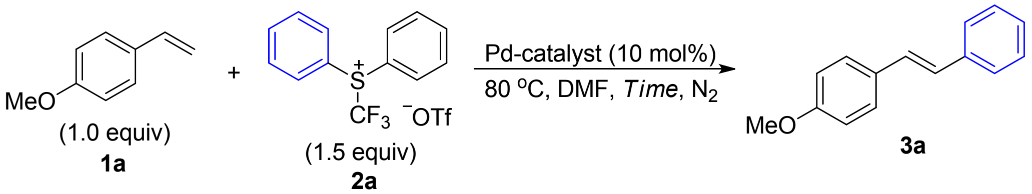
Table 3. The Pd-catalyzed Heck reaction with **2a** in the presence of bases[a]



Entry	Pd-catalyst	Base	Yield (**3a**, %)[b]
1	$Pd(OAc)_2$	-	64
2[c]	$Pd(OAc)_2$	$NaHCO_3$	63
5	$Pd(PPh_3)_4$	-	30
6[c]	$Pd(PPh_3)_4$	$NaHCO_3$	34
7	**$Pd[(t\text{-}Bu)_3]_2$**	**-**	**76**
8	$Pd[(t\text{-}Bu)_3]_2$	$NaHCO_3$	35
9	$Pd[(t\text{-}Bu)_3]_2$	K_2CO_3	7
10	$Pd[(t\text{-}Bu)_3]_2$	K_3PO_4	14
11	$Pd[(t\text{-}Bu)_3]_2$	NaOAc	7
12	$Pd[(t\text{-}Bu)_3]_2$	DBU	5
13	$Pd[(t\text{-}Bu)_3]_2$	DMAP	28

[a] Reaction conditions: a mixture of **1a** (0.1 mmol), **2a** (0.15 mmol), Pd-catalyst (0.01 mmol, 10 mol%), base (0.15 mmol), and DMF (2 mL) was reacted at 80 ^{o}C in a sealed tube under a N_2 atmosphere for 24 h. [b] The yield was determined by HPLC using **3a** (Retention time: 8.468 min, λ_{max} = 302.2 nm, water/methanol = 20 : 80 (v / v)) as the external standard. [c] base (0.1 mmol).

Table 4. The Pd-catalyzed Heck reaction at different reaction time[a]

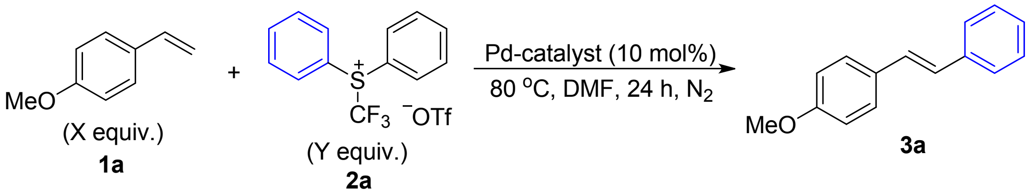


Entry	Pd-catalyst	Time (h)	Yield (**3a**, %)[b]
1	$Pd(OAc)_2$	12	52
2	$Pd(OAc)_2$	24	64
3	$Pd(OAc)_2$	36	28
4	$Pd(OAc)_2$	48	66
5[c]	$Pd(OAc)_2$	24	54
6[c]	$Pd(OAc)_2$	48	60
7[d]	$Pd[(t\text{-}Bu)_3]_2$	6	78
8[d]	$Pd[(t\text{-}Bu)_3]_2$	12	79

9[d]	**Pd[(*t*-Bu)$_3$]$_2$**	**24**	**86**
10[d]	Pd[(*t*-Bu)$_3$]$_2$	36	76

[a] Reaction conditions: a mixture of **1a** (0.1 mmol), **2a** (0.15 mmol), Pd-catalyst (0.01 mmol, 10 mol%), and DMF (2 mL) was stirred at 80 °C or room temperature in a sealed tube under N_2 atmosphere for several hours. TsOH was added under schlenk line. [b] The yield was determined by HPLC using **3a** (Retention time: 8.468 min, λ_{max} = 302.2 nm, water/methanol = 20 : 80) as external standard. [c] $[Ph_2SCF_3]^+[OTf]^-$ (0.2 mmol). [d] TsOH (0.01 mmol, 10 mol%) was used and the reaction was run at room temperature.

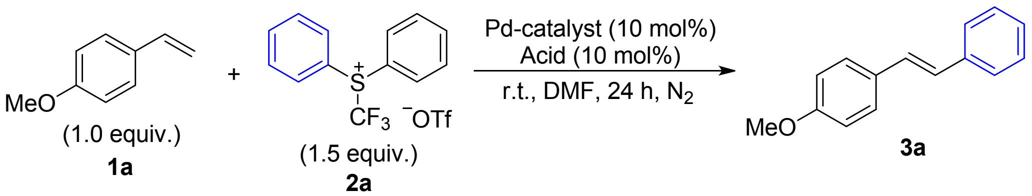
Table 5. The Pd-catalyzed Heck reaction at different molar ratio of **1a** and **2a**[a]



Entry	Pd-catalyst	X : Y	Yield (**3a**, %)[b]
1	Pd(OAc)$_2$	1 : 1.5	64
2	Pd(OAc)$_2$	1 : 2	54
3[c]	Pd(OAc)$_2$	1 : 1.5	66
4[c]	Pd(OAc)$_2$	1 : 2	60
5[d]	Pd(PPh$_3$)$_4$	1 : 1.5	72
6[d]	Pd(PPh$_3$)$_4$	1 : 2	67
7	Pd[P(*t*-Bu)$_3$]$_2$	1 : 1.5	76
8	Pd[P(*t*-Bu)$_3$]$_2$	1.5 : 1	75
9[e]	Pd[P(*t*-Bu)$_3$]$_2$	1 : 1.2	73
10[e]	Pd[P(*t*-Bu)$_3$]$_2$	1 : 1.5	60

[a] Reaction conditions: a mixture of **1a** (X equiv.), **2a** (Y equiv.), Pd-catalyst (0.01 mmol, 10 mol%), and DMF (2 mL) was reacted at 80 °C in a sealed tube under a N_2 atmosphere for 24 h. [b] The yield was determined by HPLC using **3a** (Retention time: 8.468 min, λ_{max} = 302.2 nm, water/methanol = 20 : 80 (v / v)) as the external standard. [c] 48 h. [d] 60 °C. [e] TsOH (0.01 mmol, 10 mol%) was used.

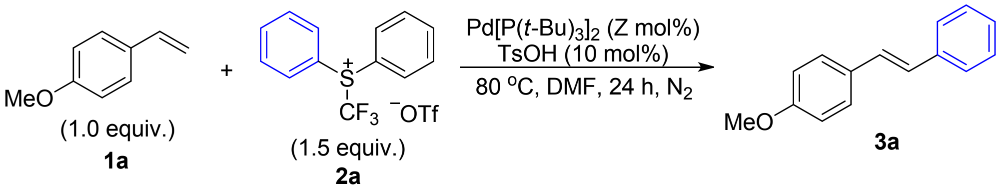
Table 6. The Pd-catalyzed Heck reaction with **2a** in the presence of acids[a]



Entry	Pd-catalyst	Acid	Yield (**3a**, %)[b]
1	$Pd(PPh_3)_4$	TsOH	0
2[c]	$Pd(PPh_3)_4$	TsOH	45
3[c]	$Pd(OAc)_2$	TsOH	46
4[d]	Pd[(*t*-Bu)$_3$]$_2$	TsOH	60
5[d]	Pd[(*t*-Bu)$_3$]$_2$	CF_3SO_3H	74
6[d]	Pd[(*t*-Bu)$_3$]$_2$	CH_3CO_2H	84
7[d]	Pd[(*t*-Bu)$_3$]$_2$	$PhCO_2H$	60
8[d]	Pd[(*t*-Bu)$_3$]$_2$	CF_3CO_2H	74
9[d]	Pd[(*t*-Bu)$_3$]$_2$	CH_3SO_3H	83
10[c]	Pd[(*t*-Bu)$_3$]$_2$	TsOH	80
11	**Pd[(*t*-Bu)$_3$]$_2$**	**TsOH**	**86**
12	Pd[(*t*-Bu)$_3$]$_2$	CF_3SO_3H	78
13	Pd[(*t*-Bu)$_3$]$_2$	CH_3CO_2H	82
14	Pd[(*t*-Bu)$_3$]$_2$	$PhCO_2H$	67
15	Pd[(*t*-Bu)$_3$]$_2$	CF_3CO_2H	75
16	Pd[(*t*-Bu)$_3$]$_2$	CH_3SO_3H	77

[a] Reaction conditions: a mixture of **1a** (0.1 mmol), **2a** (0.15 mmol), Pd-catalyst (0.01 mmol, 10 mol%), acid (0.01 mmol, 10 mol%), and DMF (2 mL) was reacted at room temperature in a sealed tube under a N_2 atmosphere for 24 h. [b] The yield was determined by HPLC using **3a** (Retention time: 8.468 min, λ_{max} = 302.2 nm, water/methanol = 20 : 80 (v / v)) as the external standard. [c] 60 °C. [d] 80 °C.

Table 7. The Pd-catalyzed Heck reaction with different catalyst loading[a]

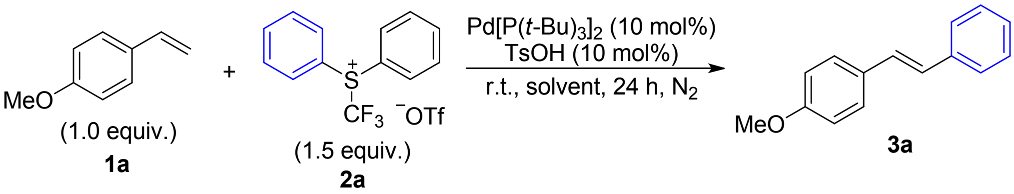


Entry	Z	Yield (**3a**, %)[b]

1	**10**	**60**
2[c]	10	86
3[c]	7.5	85
4	5	28
5	1	19

[a] Reaction conditions: a mixture of **1a** (0.1 mmol), **2a** (0.15 mmol), Pd[P(*t*-Bu)$_3$]$_2$ (Z mol%), TsOH (0.01 mmol, 10 mol%), and DMF (2 mL) was reacted at 80 °C in a sealed tube under a N_2 atmosphere for 24 h. [b] The yield was determined by HPLC using **3a** (Retention time: 8.468 min, λ_{max} = 302.2 nm, water/methanol = 20 : 80 (v / v)) as the external standard. [c] at room temperature.

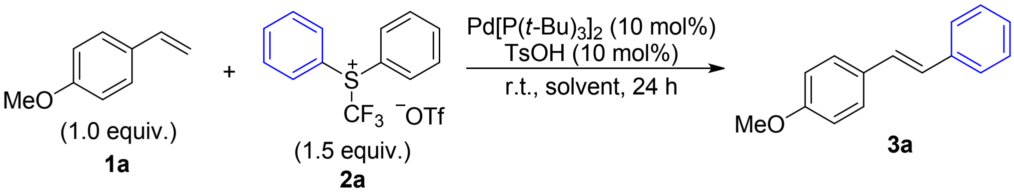
Table 8. The solvent effects on Pd-catalyzed Heck reaction[a]



Entry	solvent	Yield (**3a**, %)[b]
1	**DMF**	**86**
2	DMSO	24
3	MeCN	3
4	Toluene	13
5	DCM	26
6	THF	23

[a] Reaction conditions: a mixture of **1a** (0.1 mmol), **2a** (0.15 mmol), Pd[P(*t*-Bu)$_3$]$_2$ (0.01 mmol, 10 mol%), TsOH (0.01 mmol, 10 mol%), and solvent (2 mL) was reacted at room temperature in a sealed tube under a N_2 atmosphere for 24 h. [b] The yield was determined by HPLC using **3a** (Retention time: 8.468 min, λ_{max} = 302.2 nm, water/methanol = 20 : 80 (v / v)) as the external standard.

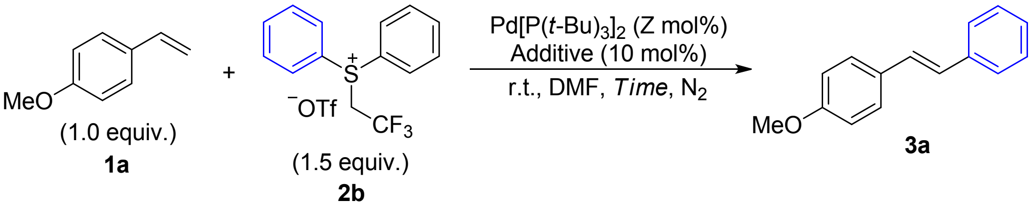
Table 9. The Pd-catalyzed Heck reaction in air or with moisture[a]



Entry	Condition	Yield (**3a**, %)[b]
1	**N_2**	**86**
2	$TsOH•H_2O$ was used instead of TsOH, N_2	65
3	air	69
4	N_2, 1 drop water	79

[a] Reaction conditions: a mixture of **1a** (0.1 mmol), **2a** (0.15 mmol), $Pd[P(t\text{-}Bu)_3]_2$ (10 mol%), TsOH (10 mol%), and DMF (2 mL) was reacted at room temperature in a sealed tube for 24 h. TsOH was added under N_2. [b] The yield was determined by HPLC using **3a** (Retention time: 8.468 min, λ_{max} = 302.2 nm, water/methanol = 20 : 80 (v / v)) as the external standard.

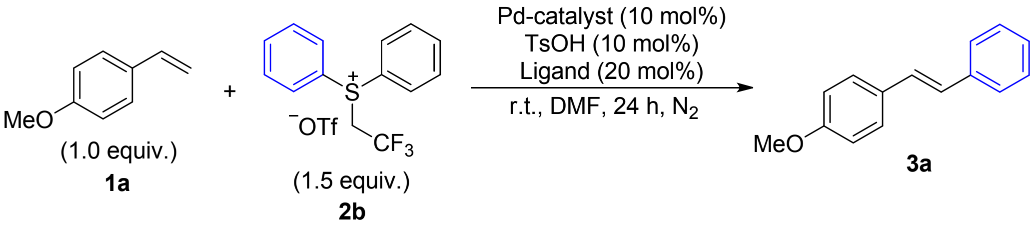
Table 10. The Pd-catalyzed Heck reaction with **2b**[a]



Entry	Z	Additive	Time (h)	Yield (**3a**, %) [b]
1	10	-	24	84
2	**10**	**TsOH**	**24**	**>99**
3 [c]	10	$NaHCO_3$	24	6
4	10	TsOH	6	73
5	10	TsOH	12	89
6	10	TsOH	36	83
7	7.5	TsOH	24	96
8	5	TsOH	24	47
9	1	TsOH	24	9

[a] Reaction conditions: a mixture of **1a** (0.1 mmol), **2b** (0.15 mmol), $Pd[P(t\text{-}Bu)_3]_2$ (0.01 mmol, 10 mol%), TsOH (0.01 mmol, 10 mol%), and DMF (2 mL) was reacted at room temperature in a sealed tube under a N_2 atmosphere. [b] The yield was determined by HPLC using **3a** (Retention time: 8.468 min, λ_{max} = 302.2 nm, water/methanol = 20 : 80 (v / v)) as the external standard. [c] $NaHCO_3$ (1 equiv) was used instead of TsOH (10 mol%).

Table 11 The reaction of **1a** with **2b** in the presence of diverse Pd-catalysts[a]



Entry	Pd-catalyst	Ligand	Yield (**3a**, %)[b]
1	$PdCl_2$	-	2
2	$PdCl_2$	P(*t*-Bu)$_3$	1
3[c]	$PdCl_2$	IPr•HCl / $NaHCO_3$	< 1
4[c]	$(MeCN)_2PdCl_2$	IPr•HCl / $NaHCO_3$	< 1
5	Pd/C	-	< 1
6	$Pd_2(dba)_3$	-	16
7	$Pd_2(dba)_3$	P(*t*-Bu)$_3$	12
8	$Pd(dba)_2$	-	1
9	$Pd(OAc)_2$	-	< 1
10	$Pd(PPh_3)_4$	-	0
11	[Pd(η^3-allyl)Cl]$_2$	-	< 1
12	$Pd(Cy_3)_2$	-	0

[a] Reaction conditions: a mixture of **1a** (0.1 mmol), **2b** (0.15 mmol), Pd-catalyst (0.01 mmol, 10 mol%), TsOH (0.01 mmol, 10 mol%), ligand (0.02 mmol, 20 mol%), and DMF (2 mL) was reacted at room temperature in a sealed tube under a N_2 atmosphere. [b] The yield was determined by HPLC using **3a** (Retention time: 8.468 min, λ_{max} = 302.2 nm, water/methanol = 20 : 80 (v / v)) as the external standard. [c] A mixture of Pd-catalyst (0.009 mmol, 3 mol%), IPr•HCl (0.0135 mmol, 4.5 mol%), and $NaHCO_3$ (0.018 mmol, 6 mol%) was reacted in DMF (1 mL) at room temperature for 0.5 h, which was then added into a mixture of **1a** (0.3 mmol), **2b** (0.45 mmol), TsOH (0.03 mmol, 10 mol%), and DMF (2 mL) in a sealed tube under a N_2 atmosphere, and reacted for another 24 h.

3. Procedures for the synthesis of 2c-d, 2g, and 2k

$TfOCH_2CF_2H$ (2.1 g, 10.0 mmol) and diphenyl sulfide (5.5 g, 30.0 mmol) were placed in a closed Schlenk flask under a N_2 atmosphere with stirring. The mixture was reacted at 120 °C for 48 h, cooled to room temperature, and washed by diethyl ether till the excess sulfide was completely removed. The resulting solid was dried in vacuum to give 3.6 g of **2c** as a white solid (9.0 mmol, 90%). M.p. 82-83 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.06 (d, *J* = 7.7 Hz, 4H), 7.75 (t, *J* = 7.4 Hz, 2H), 7.69 (t, *J* = 7.6 Hz, 4H), 6.51 (t, *J* = 53.7 Hz, 1H), 4.95 (t, *J* = 15.3 Hz, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -78.5 (s, 3F), -114.2 (dt, *J* = 53.8, 15.0 Hz, 2F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 135.0 (s), 131.7 (s), 130.6 (s), 124.4 (s), 120.7 (q, *J* = 320.0 Hz), 111.7 (t, *J* = 244.8 Hz), 47.4 (t, *J* = 23.6 Hz). IR (KBr): 3066, 3001, 2921, 2850, 1480, 1449, 1410, 1370, 1225, 1158, 1110, 1074, 1029, 998, 744, 638, 574, 516 cm^{-1}. ESI-MS (m/z): 251.1 ([M]$^+$). Anal. Calcd for $C_{15}H_{13}F_5O_3S_2$: C 45.00, H 3.27; Found: C 45.14, H 3.34.

$TfOCH_2CH_2F$ (16.4 g, 83.9 mmol) and diphenyl sulfide (23.4 g, 125.8 mmol) were placed in a closed Schlenk flask with stirring. The mixture was heated at 60 °C for 15 h, cooled to room temperature, and washed by diethyl ether till the excess sulfide was completely removed. The resulting solid was dried in vacuum to give 26.8 g of **2d** as a light grey solid (70.2 mmol, 84%). M.p. 60-62 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.04 (d, *J* = 7.1 Hz, 4H), 7.74 (d, *J* = 7.3 Hz, 2H), 7.69 (t, *J* = 7.0 Hz, 4H), 4.86 (d, *J* = 46.7 Hz, 2H), 4.72 (d, *J* = 23.7 Hz, 2H). ^{19}F NMR (471 MHz, $CDCl_3$) δ -78.4 (s, 3F), -218.8 (m, 1F). ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.0 (s), 131.7 (s), 130.9 (s), 123.6 (s), 120.7 (q, *J* = 320.0 Hz), 77.5 (d, *J* = 173.4 Hz), 46.3 (d, *J* = 18.1 Hz). IR (KBr): 3096, 3002, 2962, 1583, 1479, 1448, 1254, 1225, 1158, 1062, 1029, 998, 799, 748, 684, 638, 574, 517 cm^{-1}. ESI-MS (m/z): 233.1 ([M]$^+$). Anal. Calcd for $C_{15}H_{14}F_4O_3S_2$: C 47.11, H 3.69; Found: C 46.81, H 3.75.

$TfOCH_2CF_2CF_3$ (9.0 g, 31.9 mmol) and diphenyl sulfide (35.6 g, 191.4 mmol) were placed in a closed Schlenk flask under a N_2 atmosphere with stirring. The mixture was heated at 150 °C for 72 h, cooled to room temperature, and washed by diethyl ether till the excess sulfide was completely removed. The resulting solid was dried in vacuum to give 1.0 g of **2g** as a white solid (2.1 mmol, 7%). M.p. 94-96 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.21 (d, *J* = 8.1 Hz, 4H), 7.77 (t, *J* = 7.4 Hz, 2H), 7.71 (t, *J* = 7.6 Hz, 4H), 5.31 (t, *J* = 15.1 Hz, 2H). ^{19}F NMR (471 MHz, $CDCl_3$) δ -78.6 (s, 3F), -84.0 (s, 3F), -111.4 (t, *J* = 15.1 Hz, 2F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 135.5 (s), 131.8 (s), 131.0 (s), 123.8 (s), 120.6 (q, *J* = 319.9 Hz), 44.9 (t, *J* = 21.8 Hz). IR (KBr): 3066, 2981, 2921, 1481, 1449, 1351, 1250, 1197, 1161, 1093, 1030, 998, 751, 685, 638, 574, 517 cm^{-1}. HRMS-ESI (m/z) calcd for $C_{15}H_{12}F_5S^+$ ([M]$^+$): 319.0574; Found: 319.0576. Anal. Calcd for $C_{16}H_{12}F_8O_3S_2$•$0.5H_2O$: C 40.25, H 2.74; Found: C 40.57, H 2.67.

Thiophenol (1.0 g, 9.1 mmol) was added into a solution of NaOH (0.36 g, 9.1 mmol) in a mixture solvent of EtOH and H_2O (1 : 1 (v / v), 65 mL) with vigorous stirring. After 10 min, 1-bromo-4-chlorobutane (1.15 mL, 10.0 mmol) was introduced and the mixture was reacted at room temperature for 8 h. The volatile species were removed by rotary evaporator under reduced pressure. The residue was then extracted with Et_2O (3 × 20 mL) and the combined organic layers were dried over anhydrous Na_2SO_4 and concentrated to dryness to give 1.5 g of (4-chlorobutylsulfanyl)benzene as a yellow oil (7.5 mmol, 82%). Next, AgOTf (1.8 g, 7.0 mmol) was added into a solution of (4-chlorobutylsulfanyl)benzene (1.4 g, 7.0 mmol) in $ClCH_2CH_2Cl$ (30 mL) and reacted at room temperature in the darkness for 8 h. The gray precipitates were removed and the solution was treated with Na_2SO_4 and filtered. The filter cake was washed by $ClCH_2CH_2Cl$ (3 × 5 mL). The combined filtrates were concentrated under the reduced pressure to give a viscous yellow oil, which was further washed by Et_2O to provide 2.1 g of **2k** as a white solid (2.1 g, 96%). M.p. 44-45 ^oC. ^1H NMR (400 MHz, $CDCl_3$) δ 7.79 (m, 2H), 7.71-7.62 (m, 3H), 4.19 (m, 2H), 3.68 (m, 2H), 2.59-2.48 (m, 4H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -78.3 (s, 3F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 134.1 (s), 131.3 (s), 129.8 (s), 125.9 (s), 120.7 (q, J = 320.3 Hz), 48.5 (s), 29.1 (s). IR (KBr): 3093, 3015, 2957, 2878, 2287, 1582, 1484, 1447, 1423, 1266, 1223, 1160, 1078, 1030, 1001, 894, 876, 749, 686, 638, 573, 517 cm^{-1}. ESI-MS (m/z): 165.1 ([M]$^+$). Anal. Calcd for $C_{11}H_{13}F_3O_3S_2$•$0.5H_2O$: C 40.86, H 4.36; Found: C 40.60, H 4.45.

4. General procedure for Pd-catalyzed Heck reaction of 2 with 1

In a nitrogen filled glovebox, a sealed tube was charged with alkene (**1**, 0.3 mmol), $[Ph_2SR_{fn}]^+[OTf]^-$ (**2**, 0.45mmol), Pd[P(t-Bu)$_3$]$_2$ (0.03 mmol, 10 mol%), TsOH (0.03 mmol, 10 mol%), and DMF (3 mL) with stirring. After 24 h, the mixture was quenched by water (30 mL) and extracted with ethyl acetate (3 × 20 mL). The extracts were washed by water, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel using petroleum ether or a mixture of petroleum ether and ethyl acetate as eluents to give the desired product (**3**).

(E)-1-Methoxy-4-styrylbenzene (**3a**).[11] White solid (52.4 mg (83% yield) from **2a** (R_{fn} = CF_3); 20.3 mg (97% yield) from **2b** (R_{fn} = CH_2CF_3) and 0.1 mmol of **1a**), petroleum ether / ethyl acetate = 40 : 1 (v / v) as eluent for column chromatography. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.53 (d, J = 7.6 Hz, 2H), 7.50 (d, J = 8.6 Hz, 2H), 7.39 (t, J = 7.6 Hz, 2H), 7.28 (d, J = 8.5 Hz, 1H), 7.06 (AB peak, J = 45.9, 16.3 Hz, 2H), 6.94 (d, J = 8.6 Hz, 2H), 3.87 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 159.4 (s), 137.7 (s), 130.2 (s), 128.7 (s), 128.3 (s), 127.7 (s), 127.2 (s), 126.7 (s), 126.3 (s), 114.2 (s), 55.3 (s).

(E)-1-Methoxy-2-styrylbenzene (**3b**).[12] White solid (73.6 mg (70% yield) from **2a** (R_{fn} = CF_3) and 0.5 mmol of **1b**; 47.5 mg (75% yield) from **2b** (R_{fn} = CH_2CF_3)), petroleum ether / ethyl acetate = 40 : 1 (v / v) as eluent for column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (dd, J = 7.7, 1.5 Hz, 1H), 7.54-7.47 (m, 3H), 7.34 (t, J = 7.6 Hz, 2H), 7.26-7.22 (m, 2H), 7.11 (d, J = 16.5 Hz, 1H), 6.96 (t, J = 7.5 Hz, 1H), 6.89 (d, J = 8.1 Hz, 1H), 3.88 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.0 (s), 138.0 (s), 129.1 (s), 128.7 (s), 128.6 (s), 127.4 (s), 126.6 (s), 126.5 (s), 126.5 (s), 123.5 (s), 120.8 (s), 111.0 (s), 55.6 (s).

(E)-1-Methoxy-3-styrylbenzene (**3c**).[13] Colorless oil (60.5 mg (96% yield) from **2a** (R_{fn} = CF_3); 100.7 mg (96% yield) from **2b** (R_{fn} = CH_2CF_3) and 0.5 mmol of **1c**), petroleum ether / ethyl acetate = 40 : 1 (v / v) as eluent for column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (d, J = 7.3 Hz, 2H), 7.35 (t, J = 7.6 Hz, 2H), 7.29-7.24 (m, 2H), 7.12-7.05 (m, 4H), 6.82 (dd, J = 7.9, 2.1 Hz, 1H), 3.84 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.9 (s), 138.8 (s), 137.3 (s), 129.7 (s), 129.0 (s), 128.7 (s), 128.6 (s), 127.7 (s), 126.6 (s), 119.3 (s), 113.3 (s), 111.8 (s), 55.3 (s).

(E)-1,2-Diphenylethene **(3d)**.[11] White solid (39.8 mg (74% yield) from **2b** (R_{fn} = CH_2CF_3)), petroleum ether as eluent for column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (d, J = 7.2 Hz, 4H), 7.35 (t, J = 7.6 Hz, 4H), 7.25 (t, J = 7.3 Hz, 2H), 7.11 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.4 (s), 128.7 (s), 128.7 (s), 127.7 (s), 126.6 (s).

(E)-1-Methyl-4-styrylbenzene (**3e**).[12] White solid (44.2 mg (76% yield) from **2a** (R_{fn} = CF_3); 46.3 mg (79% yield) from **2b** (R_{fn} = CH_2CF_3)), petroleum ether as eluent for column chromatography. ^1H NMR (500 MHz, $CDCl_3$) δ 7.51 (d, *J* = 7.4 Hz, 2H), 7.42 (d, *J* = 7.7 Hz, 2H), 7.35 (t, *J* = 7.4 Hz, 2H), 7.25 (t, *J* = 7.2 Hz, 1H), 7.17 (d, *J* = 7.6 Hz, 2H), 7.11-7.04 (m, 2H), 2.36 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 137.6 (s), 137.5 (s), 134.6 (s), 129.4 (s), 128.7 (s), 127.7 (s), 127.4 (s), 126.5 (s), 126.4 (s), 21.3 (s).

(E)-1-(Tert-butyl)-4-styrylbenzene (**3f**).[14] White solid (70.8 mg (99% yield) from **2b** (R_{fn} = CH_2CF_3)), petroleum ether as eluent for column chromatography. ^1H NMR (500 MHz, $CDCl_3$) δ 7.53 (d, *J* = 7.6 Hz, 2H), 7.48 (d, *J* = 7.9 Hz, 2H), 7.40 (d, *J* = 8.0 Hz, 2H), 7.37 (t, *J* = 7.5 Hz, 2H), 7.26 (t, *J* = 7.2 Hz, 1H), 7.14-7.07 (m, 2H), 1.36 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.8 (s), 137.6 (s), 134.6 (s), 128.7 (s), 128.5 (s), 128.0 (s), 127.4 (s), 126.5 (s), 126.3 (s), 125.6 (s), 34.7 (s), 31.3 (s).

(E)-4-Styrylphenyl acetate (**3g**).[15] White solid (98.9 mg (83% yield) from **2a** (R_{fn} = CF_3) and 0.5 mmol of **1g**; 70.8 mg (99% yield) from **2b** (R_{fn} = CH_2CF_3)), petroleum ether / ethyl acetate = 30 : 1 (v / v) as eluent for column chromatography. ^1H NMR (400 MHz, $CDCl_3$) δ 7.51 (d, *J* = 8.4 Hz, 4H), 7.36 (t, *J* = 7.1 Hz, 2H), 7.26 (t, J = 7.2 Hz, 1H), 7.09-7.02 (m, 4H), 2.30 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.5 (s), 150.1 (s), 137.2 (s), 135.1 (s), 129.0 (s), 128.7 (s), 127.7 (s), 127.7 (s), 127.5 (s), 126.5 (s), 121.8 (s), 21.2 (s).

(E)-4-Styryl-1,1'-biphenyl (**3h**).[16] White solid (70.6 mg (92% yield) from **2a** (R_{fn} = CF_3)), petroleum ether as eluent for column chromatography. ^1H NMR (400 MHz, $CDCl_3$) δ 7.63-7.57 (m, 6H), 7.54 (d, *J* = 7.4 Hz, 2H), 7.45 (t, *J* = 7.6 Hz, 2H), 7.39-7.33 (m, 3H), 7.29-7.25 (m, 1H), 7.15 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.7 (s), 140.4 (s), 137.4 (s), 136.4 (s), 128.8 (s), 128.8 (s), 128.7 (s), 128.2 (s), 127.7 (s), 127.4 (s), 127.4 (s), 127.0 (s), 126.9 (s), 126.6 (s).

(E)-1-Fluoro-4-styrylbenzene (**3i**).[12] White solid (54.8 mg (92% yield) from **2b** (R_{fn} = CH_2CF_3)), petroleum ether as eluent for column chromatography. ^1H NMR (400

MHz, $CDCl_3$) δ 7.51-7.46 (m, 3H), 7.38-7.32 (m, 3H), 7.29 (d, J = 7.7 Hz, 1H), 7.26 (d, J = 7.7 Hz, 1H), 7.10-6.99 (m, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -114.2 (m, 1F). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.4 (d, J = 247.2 Hz), 137.2 (s), 133.5 (d, J = 3.4 Hz), 128.7 (s), 128.5 (d, J = 2.3 Hz), 128.0 (d, J = 8.0 Hz), 127.7 (s), 127.5 (s), 126.5 (s), 115.6 (d, J = 21.7 Hz).

(E)-1-Chloro-4-styrylbenzene (**3j**).[12] White solid (64.1 mg (99% yield) from **2a** (R_{fn} = CF_3); 53.3 mg (83% yield) from **2b** (R_{fn} = CH_2CF_3)), petroleum ether as eluent for column chromatography. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.52 (d, J = 7.5 Hz, 2H), 7.45 (d, J = 8.1 Hz, 2H), 7.38 (t, J = 7.4 Hz, 2H), 7.33 (d, J = 8.1 Hz, 2H), 7.29 (t, J = 7.4 Hz, 1H), 7.07 (AB peak, J = 20.3, 16.6 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.0 (s), 135.9 (s), 133.2 (s), 129.4 (s), 128.9 (s), 128.8 (s), 127.9 (s), 127.7 (s), 127.4 (s), 126.6 (s)

(E)-1-Bromo-4-styrylbenzene (**3k**).[17] White solid (53.9 mg (69% yield) from **2a** (R_{fn} = CF_3); 54.9 mg (71% yield) from **2b** (R_{fn} = CH_2CF_3)), petroleum ether as eluent for column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52-7.47 (m, 4H), 7.39-7.35 (m, 4H), 7.32-7.26 (m, 1H), 7.07 (AB peak, J = 28.4, 16.2 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.0 (s), 136.3 (s), 131.8 (s), 129.5 (s), 128.9 (s), 128.0 (s), 127.9 (s), 127.4 (s), 126.6 (s), 121.3 (s).

(E)-1-Iodo-4-styrylbenzene (**3l**).[18] White solid (13.9 mg (23% yield) from **2a** (R_{fn} = CF_3) and 0.2 mmol of **1l**; 12.6 mg (21% yield) from **2b** (R_{fn} = CH_2CF_3) and 0.2 mmol of **1l**), petroleum ether as eluent for column chromatography. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.68 (d, J = 7.5 Hz, 2H), 7.50 (d, J = 7.4 Hz, 2H), 7.36 (t, J = 7.1 Hz, 2H), 7.29-7.23 (m, 3H), 7.06 (AB peak, J = 46.9, 16.4 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 137.8 (s), 137.0 (s), 136.9 (s), 129.6 (s), 128.7 (s), 128.2 (s), 127.9 (s), 127.5 (s), 126.6 (s), 92.7 (s).

(E)-1-Styryl-4-(trifluoromethyl)benzene (**3m**).[11] White solid (37.7 mg (76% yield) from **2a** (R_{fn} = CF_3) and 0.2 mmol of **1m**), petroleum ether as eluent for column chromatography. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.61 (s, 4H), 7.54 (d, J = 7.3 Hz, 2H), 7.39 (t, J = 7.2 Hz, 2H), 7.31 (t, J = 7.2 Hz, 1H), 7.16 (AB peak, J = 38.7, 16.3 Hz,

2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.4 (s). ^{13}C NMR (126 MHz, $CDCl_3$) δ 140.8 (s), 136.7 (s), 131.2 (s), 129.3 (q, J = 32.4 Hz), 128.8 (s), 128.3 (s), 127.1 (s), 126.8 (s), 126.6 (s), 125.6 (q, J = 3.7 Hz), 124.3 (q, J = 271.7 Hz).

(E)-4-Styrylbenzonitrile (**3n**).[16] White solid (75.3 mg (73% yield) from **2a** (R_{fn} = CF_3) and 0.5 mmol of **1n**; 53.5 mg (87% yield) from **2b** (R_{fn} = CH_2CF_3)), petroleum ether / ethyl acetate = 30 : 1 (v / v) as eluent for column chromatography. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.64 (d, J = 8.0 Hz, 2H), 7.58 (d, J = 8.1 Hz, 2H), 7.54 (d, J = 7.6 Hz, 2H), 7.39 (t, J = 7.4 Hz, 2H), 7.32 (t, J = 7.2 Hz, 1H), 7.15 (AB peak, J = 63.0, 16.3 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.9 (s), 136.3 (s), 132.5 (s), 132.4 (s), 128.9 (s), 128.7 (s), 126.9 (s), 126.9 (s), 126.8 (s), 119.0 (s), 110.6 (s).

(E)-1-Nitro-4-styrylbenzene (**3o**).[11] Yellow solid (43.6 mg (65% yield) from **2a** (R_{fn} = CF_3); 60.0 mg (89% yield) from **2b** (R_{fn} = CH_2CF_3)), petroleum ether / ethyl acetate = 40 : 1 (v / v) as eluent for column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (d, J = 8.8 Hz, 2H), 7.63 (d, J = 8.7 Hz, 2H), 7.56 (d, J = 7.3 Hz, 2H), 7.41 (t, J = 7.4 Hz, 2H), 7.34 (t, J = 7.3 Hz, 1H), 7.22 (dd, J = 51.8, 16.2 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 146.8 (s), 143.9 (s), 136.2 (s), 133.3 (s), 128.9 (s), 128.9 (s), 127.0 (s), 126.9 (s), 126.3 (s), 124.2 (s).

(E)-4-Styrylbenzaldehyde (**3p**).[16] White solid (41.2 mg (66% yield) from **2a** (R_{fn} = CF_3); 45.5 mg (73% yield) from **2b** (R_{fn} = CH_2CF_3)), petroleum ether / ethyl acetate = 20 : 1 (v / v) as eluent for column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.99 (s, 1H), 7.87 (d, J = 8.2 Hz, 2H), 7.65 (d, J = 8.2 Hz, 2H), 7.55 (d, J = 7.4 Hz, 2H), 7.39 (t, J = 7.5 Hz, 2H), 7.32 (t, J = 7.3 Hz, 1H), 7.20 (AB peak, J = 49.3, 16.4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.6 (s), 143.4 (s), 136.5 (s), 135.3 (s), 132.2 (s), 130.3 (s), 128.9 (s), 128.5 (s), 127.4 (s), 126.9 (s).

Cinnamyl acetate (**3q**).[19] Colorless oil (27.6 mg (52% yield) from **2a** (R_{fn} = CF_3); 32.4 mg (61% yield) from **2b** (R_{fn} = CH_2CF_3)), petroleum ether / ethyl acetate = 30 : 1 (v / v) as eluent for column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (d, J = 7.2 Hz, 2H), 7.32 (t, J = 7.4 Hz, 2H), 7.26 (t, J = 7.2 Hz, 1H), 6.65 (d, J = 15.9 Hz, 1H), 6.28 (dt, J = 15.9, 6.5 Hz, 1H), 4.73 (dd, J = 6.5, 1.1 Hz, 2H), 2.10 (s, 3H). ^{13}C

NMR (100 MHz, $CDCl_3$) δ 170.9 (s), 136.2 (s), 134.2 (s), 128.6 (s), 128.1 (s), 126.6 (s), 123.2 (s), 65.1 (s), 21.0 (s).

(Cinnamyloxy)benzene (**3r**).[20] White solid (52.6 mg (84% yield) from **2b** (R_{fn} = CH_2CF_3)), petroleum ether as eluent for column chromatography. ^1H NMR (500 MHz, $CDCl_3$) δ 7.41 (d, *J* = 7.2 Hz, 2H), 7.33-7.24 (m, 5H), 6.96 (d, *J* = 7.5 Hz, 3H), 6.73 (d, *J* = 16.0 Hz, 1H), 6.45-6.39 (m, 1H), 4.70 (d, *J* = 4.9 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.8 (s), 136.5 (s), 133.0 (s), 129.5 (s), 128.6 (s), 127.9 (s), 126.6 (s), 124.6 (s), 120.9 (s), 114.8 (s), 68.6 (s).

Styryl benzoate (**3s**).[21] Light yellow solid (62 mg (92% yield) from **2b** (R_{fn} = CH_2CF_3)), petroleum ether / ethyl acetate = 40 : 1 (v / v) as eluent for column chromatography. A mixture of *E*- and *Z*-isomers (1 : 0.17) was isolated, which were identified by the characteristic signals of δ = 6.59 ppm (d, *J* = 12.7 Hz) (for *E*-**3s**)[21] and δ = 5.86 ppm (d, *J* = 7.4 Hz) (for *Z*-**3s**)[21]. ^1H NMR of *E*-**3s** (400 MHz, $CDCl_3$) δ 8.15 (dd, *J* = 8.2, 1.1 Hz, 2H), 8.10 (d, *J* = 12.8 Hz, 1H), 7.62 (t, *J* = 7.4 Hz, 1H), 7.49 (t, *J* = 7.7 Hz, 2H), 7.40 (d, *J* = 7.2 Hz, 2H), 7.33 (t, *J* = 7.5 Hz, 2H), 7.29-7.23 (m, 1H), 6.59 (d, *J* = 12.8 Hz, 1H). ^{13}C NMR of (*E*)-**3s** (126 MHz, $CDCl_3$) δ 163.7 (s), 136.5 (s), 133.8 (s), 133.7 (s), 130.2 (s), 130.1 (s), 128.9 (s), 128.6 (s), 127.5 (s), 126.3 (s), 115.9 (s).

Ethyl cinnamate (**3t**).[22] Colorless oil (52.0 mg (74% yield) from **2b** (R_{fn} = CH_2CF_3) and 0.4 mmol of **1t**), petroleum ether / ethyl acetate = 30 : 1 (v / v) as eluent for column chromatography. ^1H NMR (500 MHz, $CDCl_3$) δ 7.69 (d, *J* = 16.0 Hz, 1H), 7.52 (d, *J* = 4.6 Hz, 2H), 7.38 (s, 3H), 6.44 (d, *J* = 16.0 Hz, 1H), 4.27 (q, *J* = 7.1 Hz, 2H), 1.34 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.0 (s), 144.6 (s), 134.5 (s), 130.2 (s), 128.9 (s), 128.1 (s), 118.3 (s), 60.5 (s), 14.3 (s).

Methyl cinnamate (**3u**).[22] Colorless oil (39.2 mg (60% yield) from **2b** (R_{fn} = CH_2CF_3) and 0.4 mmol of **1u**), petroleum ether / ethyl acetate = 30 : 1 (v / v) as eluent for column chromatography. ^1H NMR (500 MHz, $CDCl_3$) δ 7.70 (d, *J* = 16.0 Hz, 1H), 7.52 (d, *J* = 4.8 Hz, 2H), 7.38-7.39 (m, 3H), 6.45 (d, *J* = 16.0 Hz, 1H), 3.81 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.4 (s), 144.9 (s), 134.4 (s), 130.3 (s), 128.9 (s), 128.1 (s), 117.8 (s), 51.7 (s).

3-Phenylacrylonitrile (**3v**).[23] Colorless oil (42.7 mg (83% yield) from **2b** (R_{fn} = CH_2CF_3) and 0.4 mmol of **1v**), petroleum ether / ethyl acetate = 15 : 1 (v / v) as eluent for column chromatography. A mixture of *E*-**3v**, *Z*-**3v**, and 3,3-diphenylacrylonitrile (molar ratio is 1 : 0.12 : 0.14) was isolated, which were identified by the characteristic signals of δ = 5.85 ppm (d, *J* = 16.7 Hz) (for *E*-isomer)[23a], δ = 5.42 ppm (d, *J* = 12.0 Hz) (for *Z*-isomer)[23a], and δ = 5.71 ppm (s) (for –C*H*=CPh$_2$)[23b]. ^{1}H NMR of *E*-**3v** (400 MHz, $CDCl_3$) δ 7.43-7.38 (m, 6H), 5.85 (d, *J* = 16.7 Hz, 1H).

5. The one-pot synthesis of 3w from 1w

In a nitrogen filled glovebox, a sealed tube was charged with **1w** (0.3 mmol), **2a** or **2b** (0.6 mmol), Pd[P(*t*-Bu)$_3$]$_2$ (0.03 mmol, 10 mol%), $NaHCO_3$ (0.3 mmol), and DMF (3 mL) with stirring. After 24 h, the mixture was quenched by water (30 mL) and extracted with ethyl acetate (3 × 20 mL). The extracts were washed by water, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel using petroleum ether as eluent to give **3w** as a light yellow oil.

(E)-Prop-1-ene-1,3-diyldibenzene (**3w**)[24], 25.8 mg (44% yield) from **2a** (R_{fn} = CF_3), 33.2 mg (57% yield) from **2b** (R_{fn} = CH_2CF_3)). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36-7.17 (m, 10H), 6.47-6.31 (m, 2H), 3.54 (d, *J* = 6.6 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 140.2 (s), 137.5 (s), 131.1 (s), 129.3 (s), 128.7 (s), 128.6 (s), 128.5 (s), 127.1 (s), 126.2 (s), 126.2 (s), 39.4 (s).

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6. ^{19}F NMR analysis of the reaction mixtures

Figure 1. ^{19}F NMR spectrum of the reaction mixture of **1a** (0.1 mmol), **2a** (0.15

mmol), Pd[P(*t*-Bu)$_3$]$_2$ (10 mol%), TsOH (10 mol%), and DMF (2 mL) at room temperature under N_2 for 24 h.

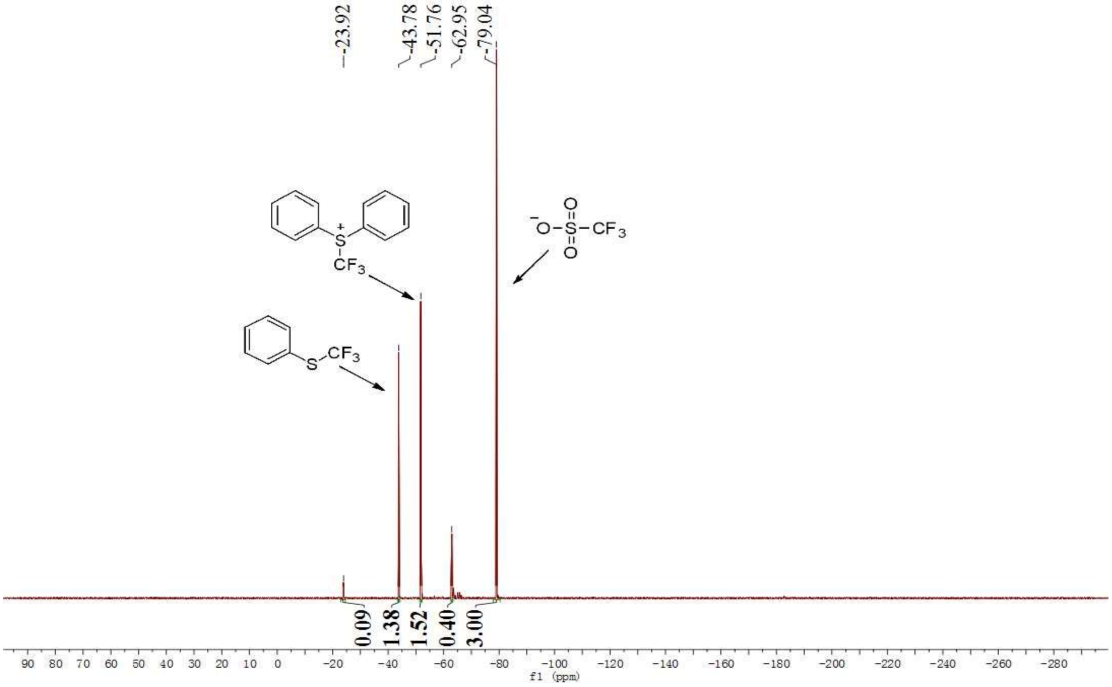


Figure 2. ^{19}F NMR spectrum of the reaction mixture of **1a** (0.1 mmol), **2b** (0.15 mmol), Pd[P(*t*-Bu)$_3$]$_2$ (10 mol%), TsOH (10 mol%), and DMF (2 mL) at room temperature under N_2 for 24 h.

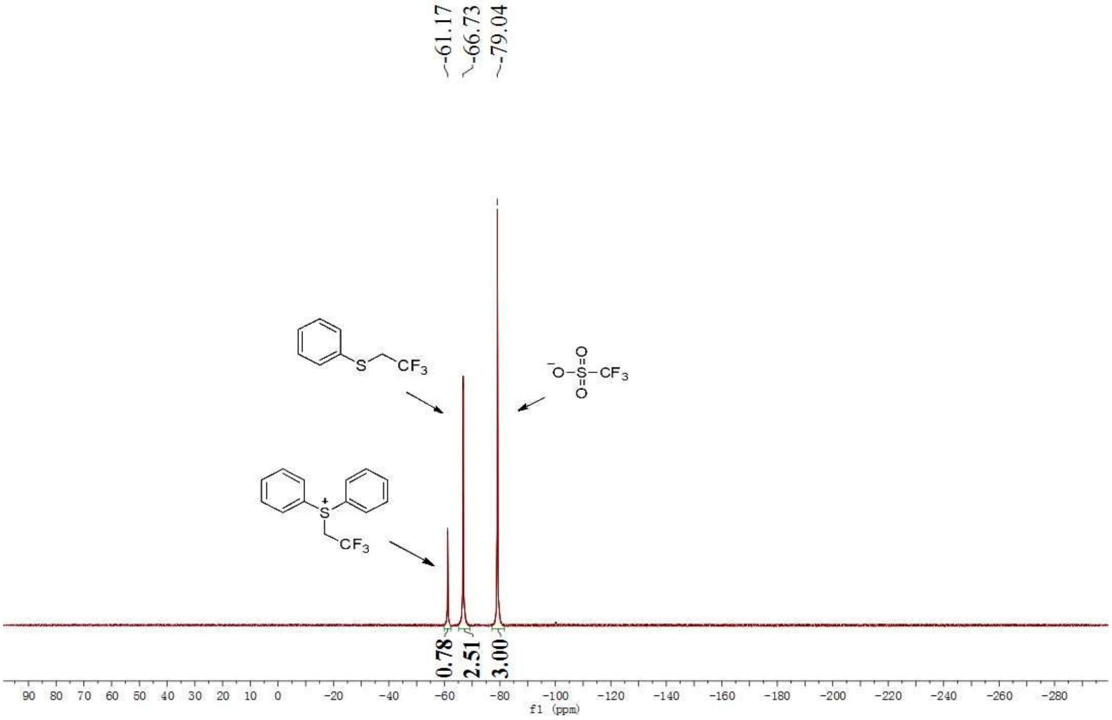


Figure 3. ^{19}F NMR spectrum of the mixture of **1a** (0.4 mmol), **2a** (0.6 mmol), TsOH (10 mol%), and DMF (2 mL) at room temperature under N_2 for 24 h. $PhCF_3$ (0.60

mmol, -63.0 ppm) was used as an internal standard.

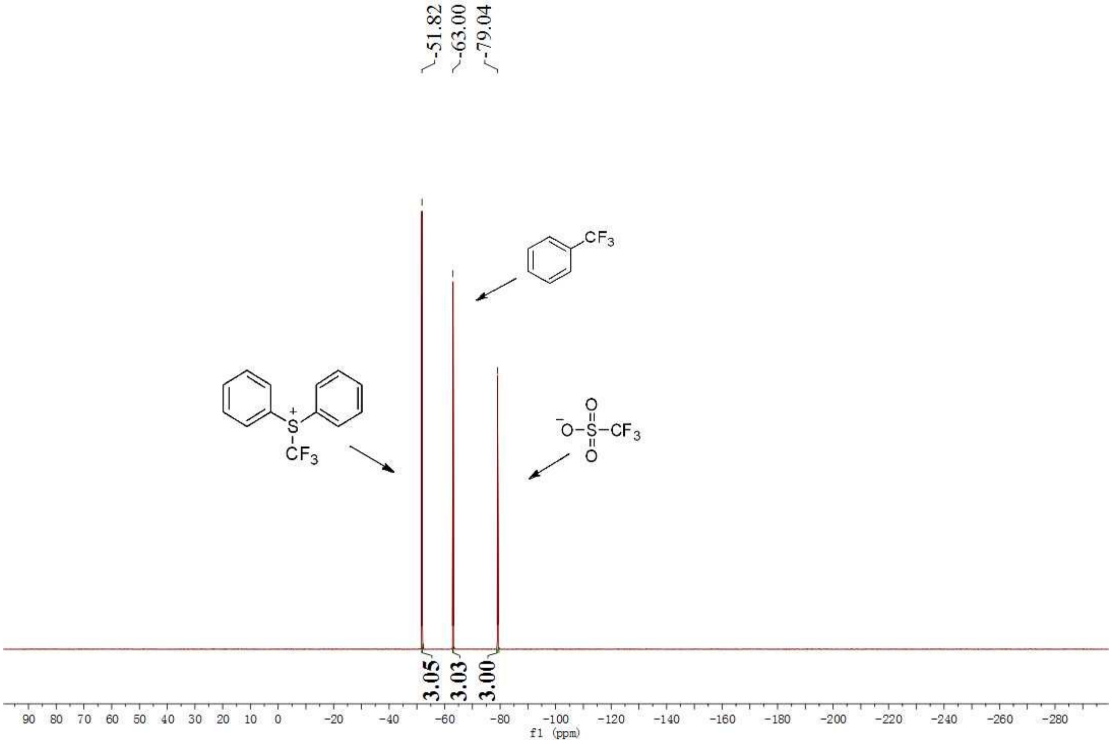


Figure 4. ^{19}F NMR spectrum of the reaction mixture of **2a** (0.1 mmol), NaHCO$_3$ (0.1 mmol), and DMF (2 mL) at room temperature under N$_2$ for 24 h.

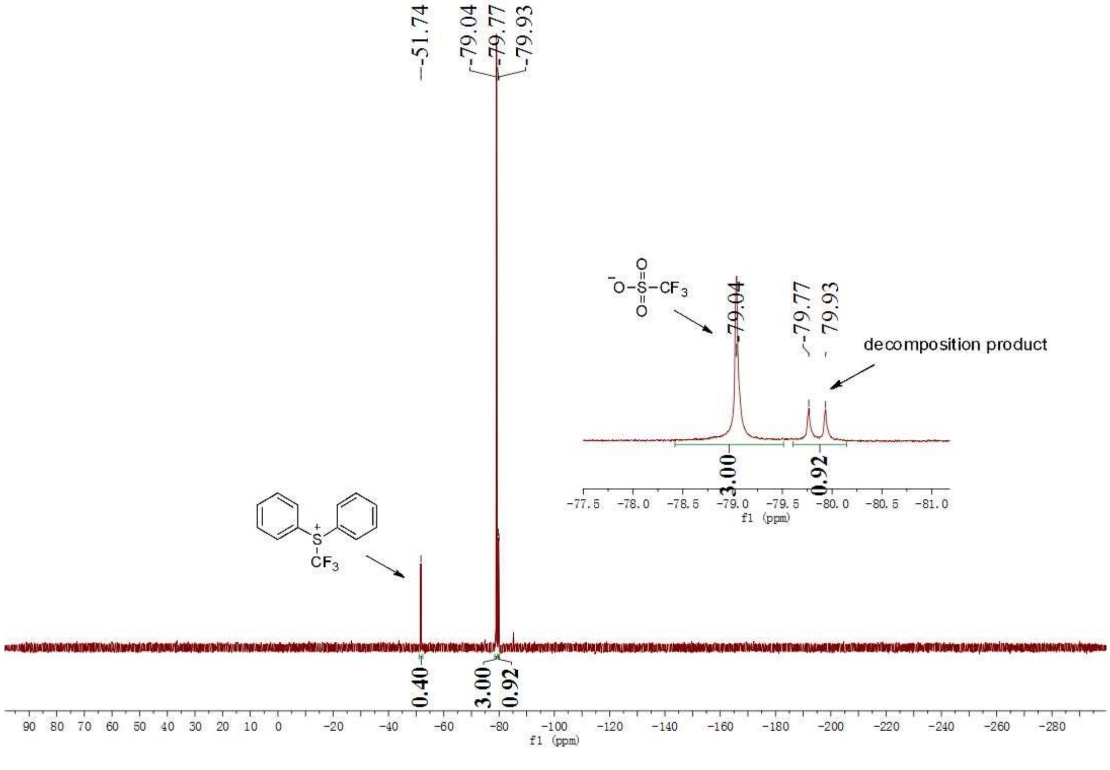


Figure 5. ^{19}F NMR spectrum of the reaction mixture of **2b** (0.1 mmol), NaHCO$_3$ (0.1 mmol), and DMF (2 mL) at room temperature under N$_2$ for 24 h.

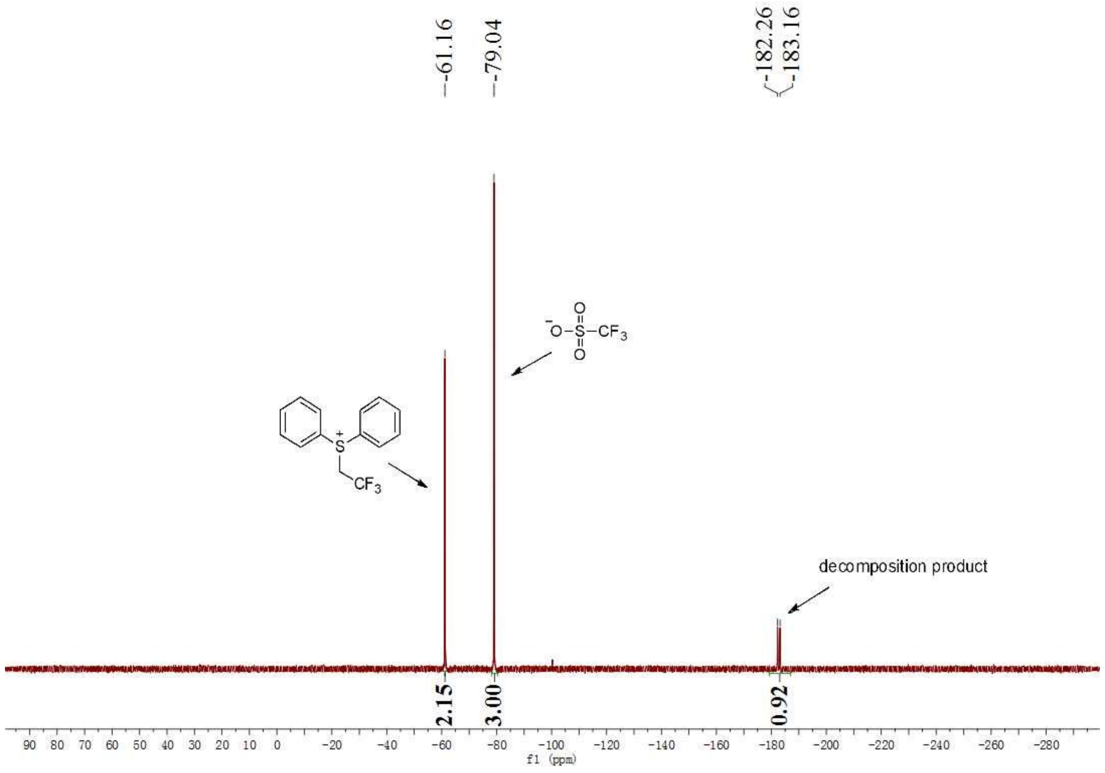


Figure 6. ^{19}F NMR spectrum of the mixture of **2a** (0.1 mmol), TsOH (10 mol%), and DMF (2 mL) at room temperature under N_2 for 24 h.

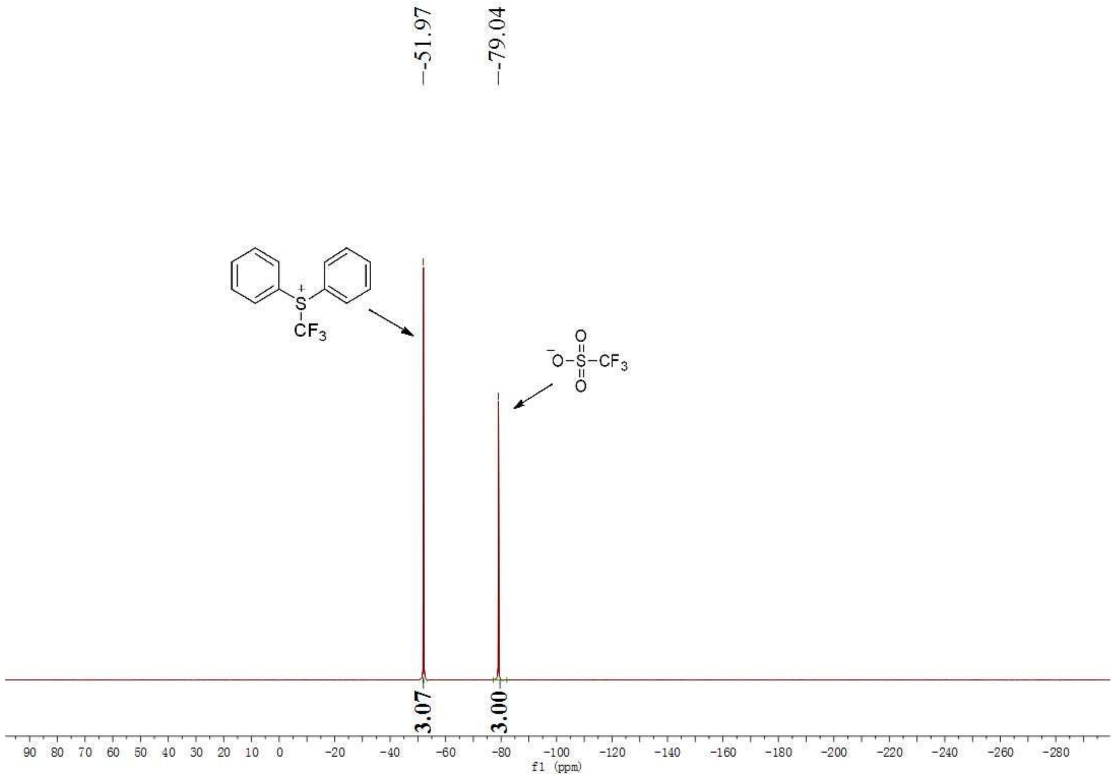
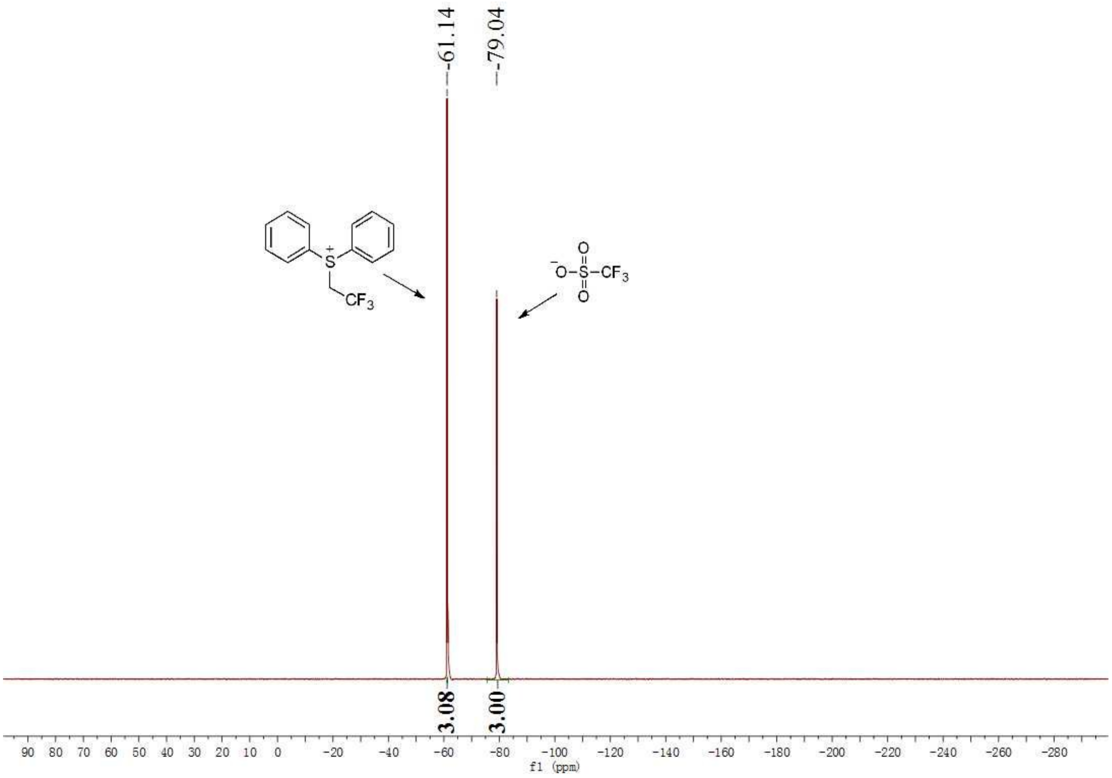
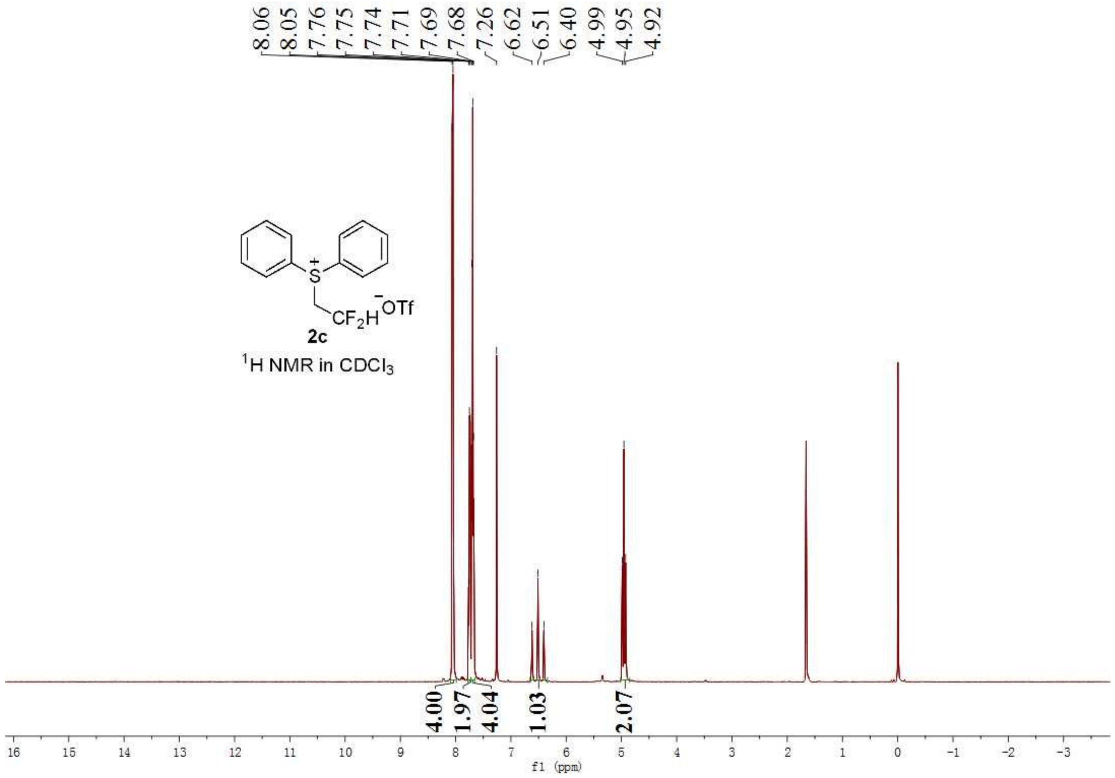


Figure 7. ^{19}F NMR spectrum of the mixture of **2b** (0.1 mmol), TsOH (10 mol%), and DMF (2 mL) at room temperature under N_2 for 24 h.



7. NMR spectra of 2c-d, 2g, 2k, and 3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7.75
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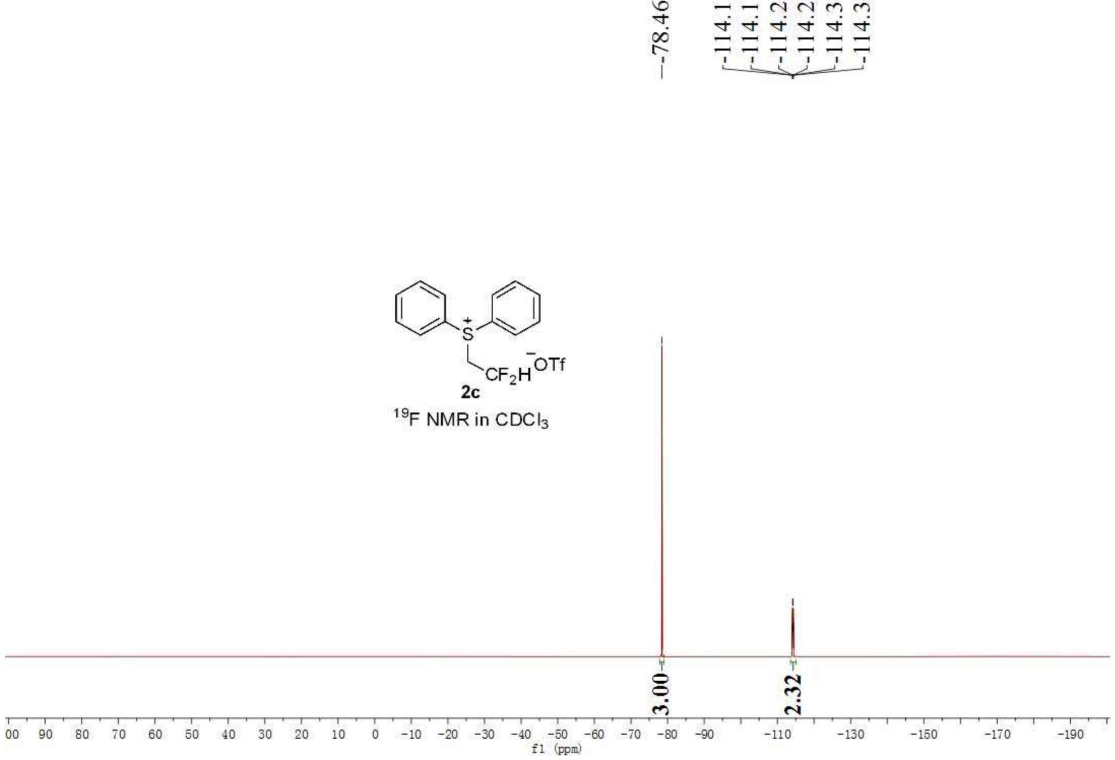
7.71
7.69
7.68
7.26
6.62
6.51
6.40
4.99
4.95
4.92
S+
⁻OTf
CF2H
2c
1H NMR in CDCl3
4.00
1.97
4.04
1.03
2.07
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
−1
−2
−3
f1 (ppm)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-114.13
-114.17
-114.21
-114.27
-114.31
-114.35
S+
⁻OTf
CF2H
2c
19F NMR in CDCl3
3.00
2.32
00
90
80
70
60
50
40
30
20
10
0
−10
−20
−30
−40
−50
−60
−70
−80
−90
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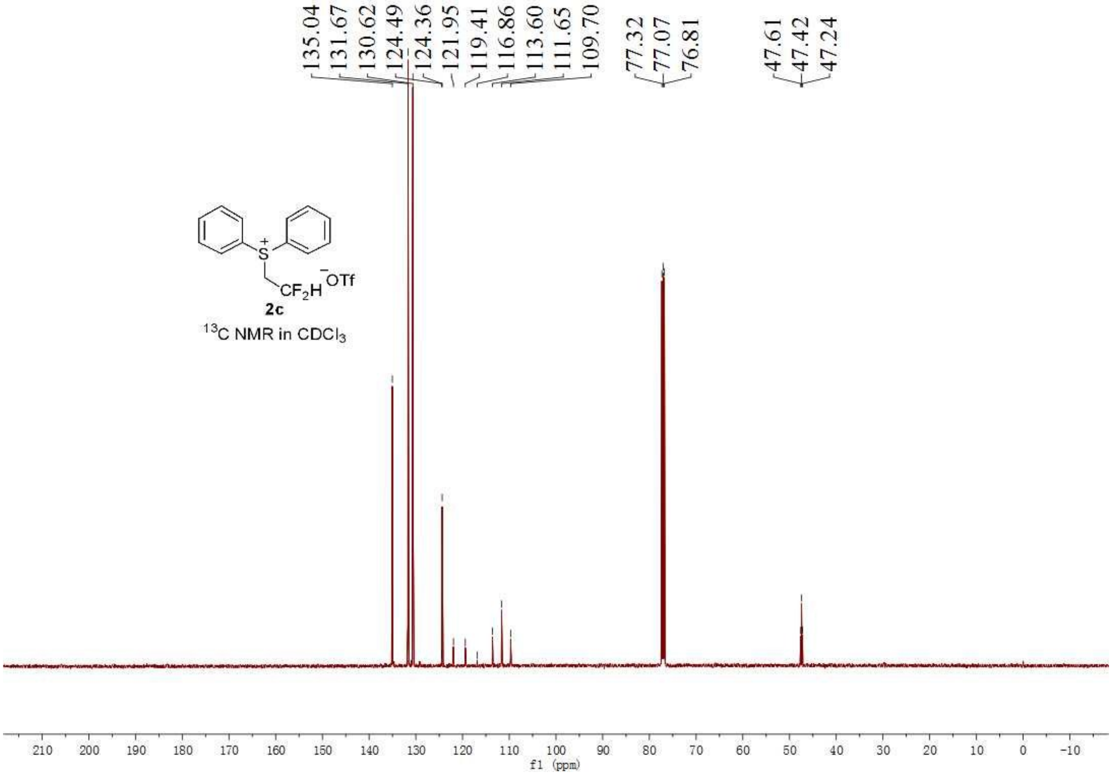
−130
−150
−170
−190
f1 (ppm)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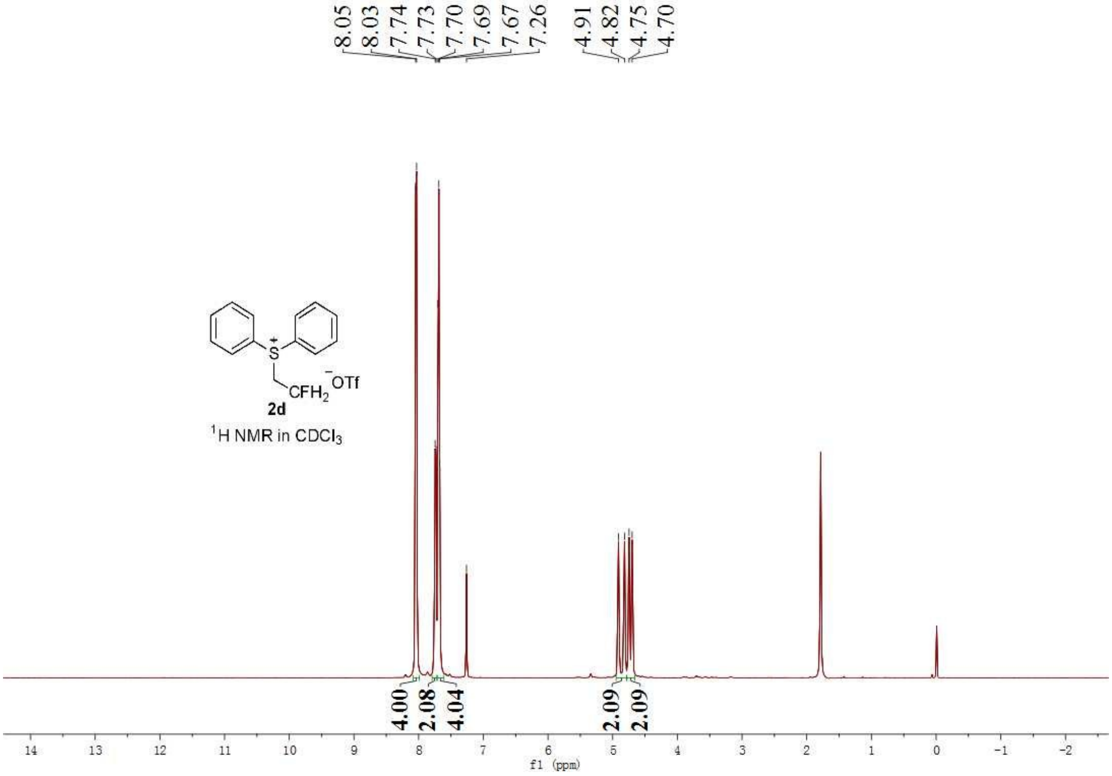
77.07
76.81
47.61
47.42
47.24
S
+
CF$_2$H
$^-$OTf
2c
^{13}C NMR in CDCl$_3$
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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7.26
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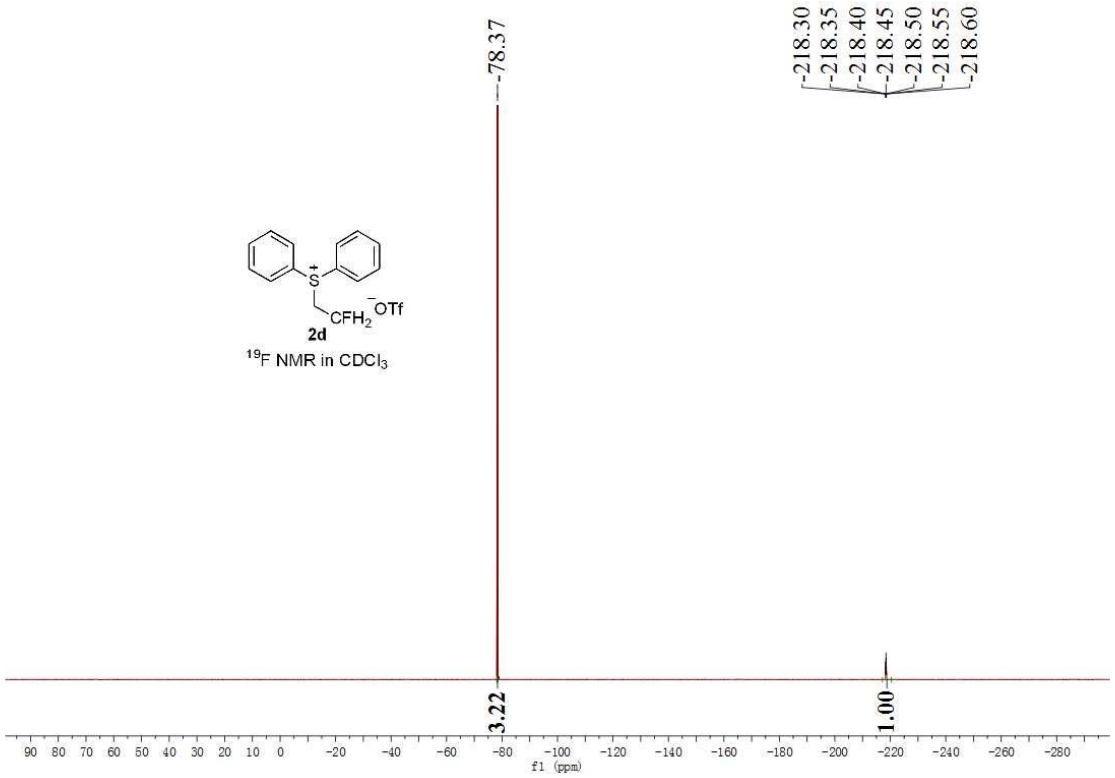
S
+
CFH$_2$
$^-$OTf
2d
^{1}H NMR in CDCl$_3$
4.00
2.08
4.04
2.09
2.09
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
f1 (ppm)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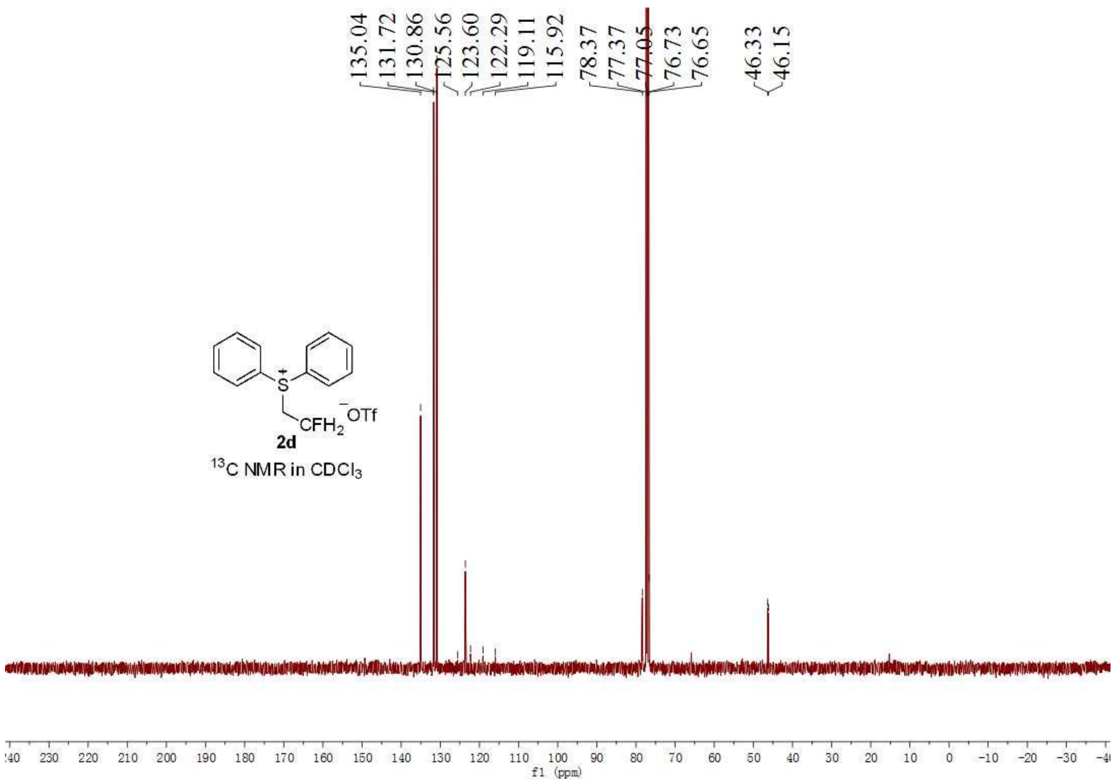
-218.45
-218.50
-218.55
-218.60
2d
^{19}F NMR in CDCl$_3$
3.22
1.00
90 80 70 60 50 40 30 20 10 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -220 -240 -260 -280
f1 (ppm)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122.29
119.11
115.92
78.37
77.37
77.05
76.73
76.65
46.33
46.15
2d
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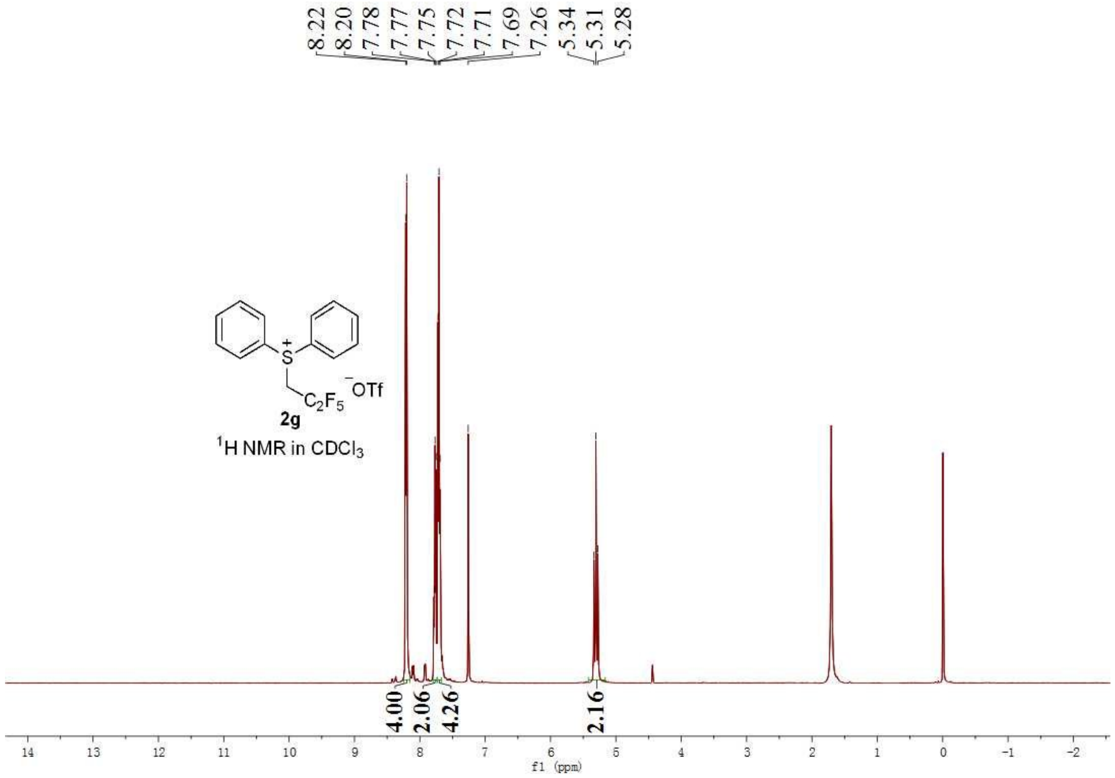
f1 (ppm)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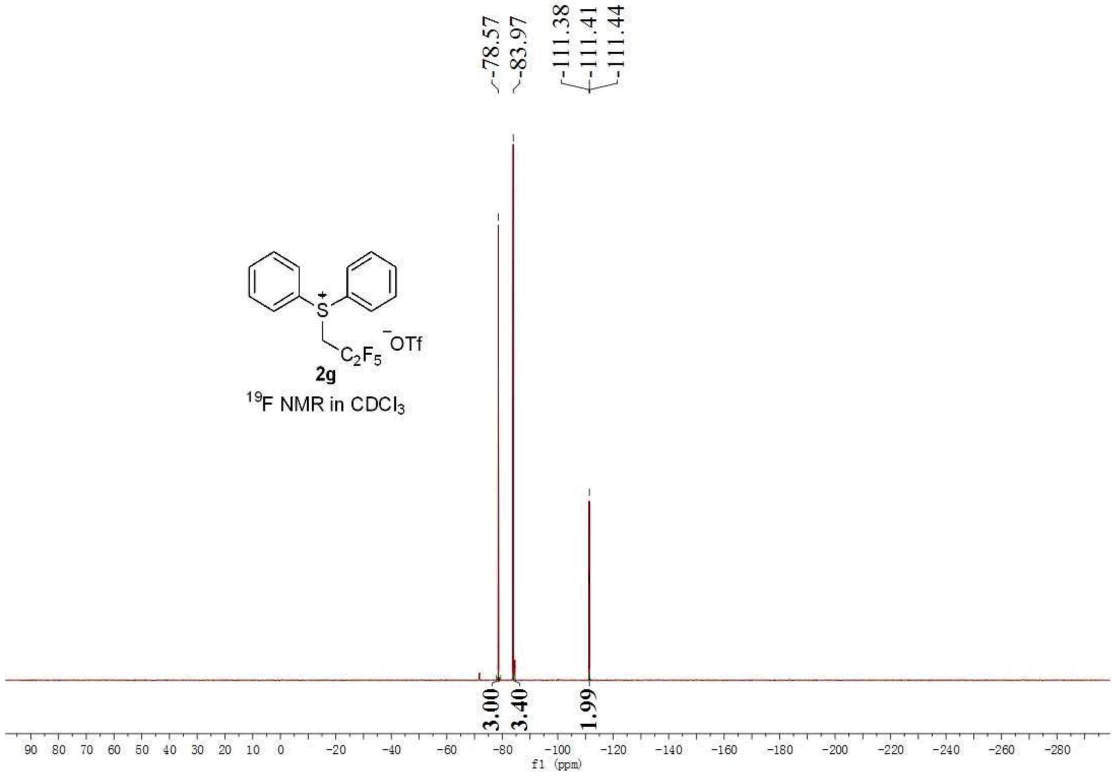
8.20
7.78
7.77
7.75
7.72
7.71
7.69
7.26
5.34
5.31
5.28
OTf
2g
^{1}H NMR in CDCl$_3$
4.00
2.06
4.26
2.16
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
f1 (ppm)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-83.97
-111.38
-111.41
-111.44
OTf
2g
^{19}F NMR in CDCl$_3$
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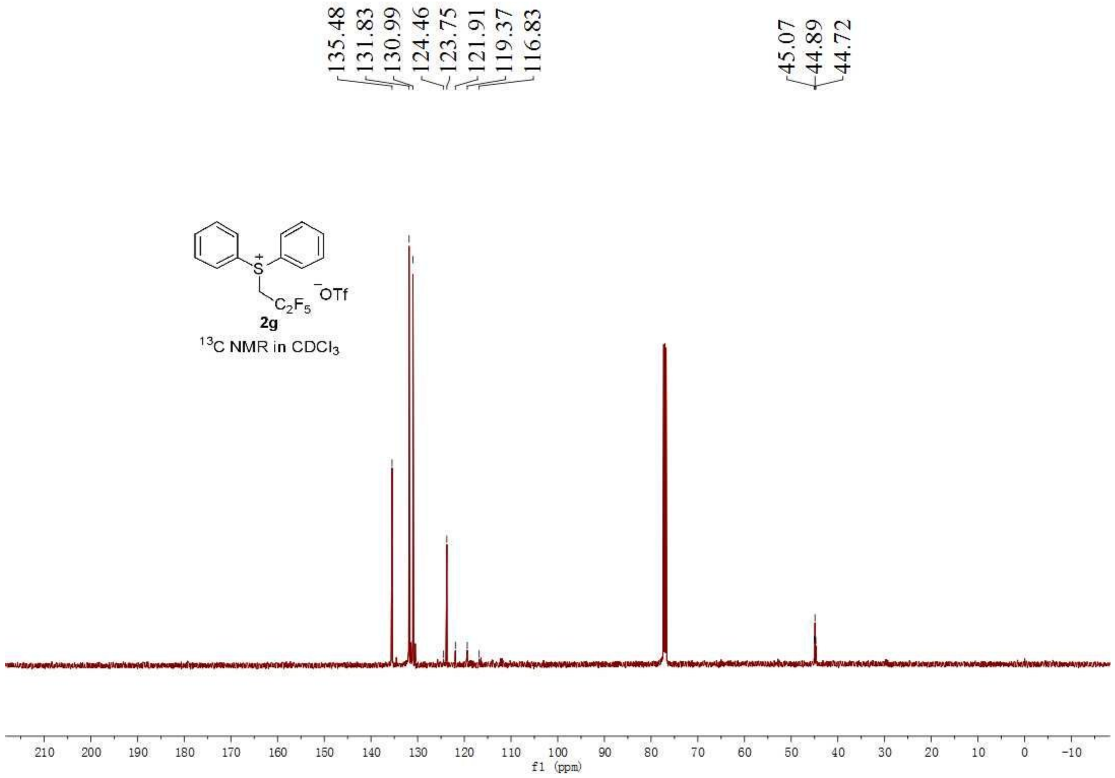
3.40
1.99
90
80
70
60
50
40
30
20
10
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
-220
-240
-260
-280
f1 (ppm)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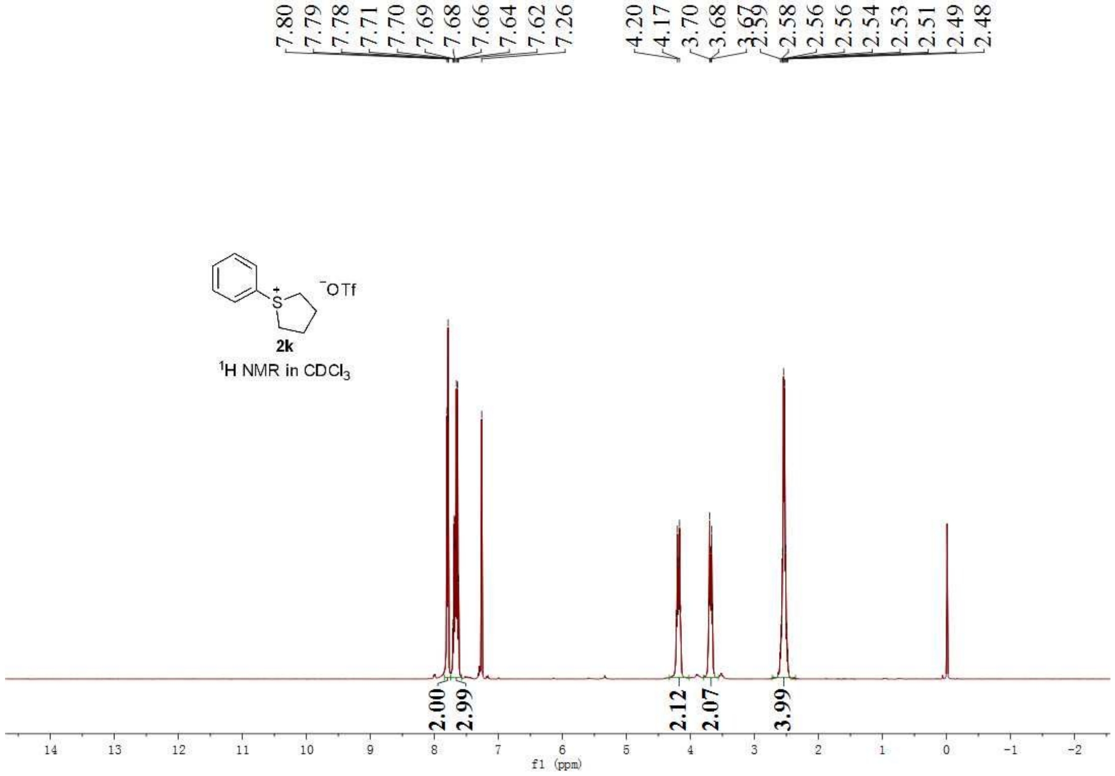
C_2F_5
2g
^{13}C NMR in $CDCl_3$
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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7.69
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7.66
7.64
7.62
7.26
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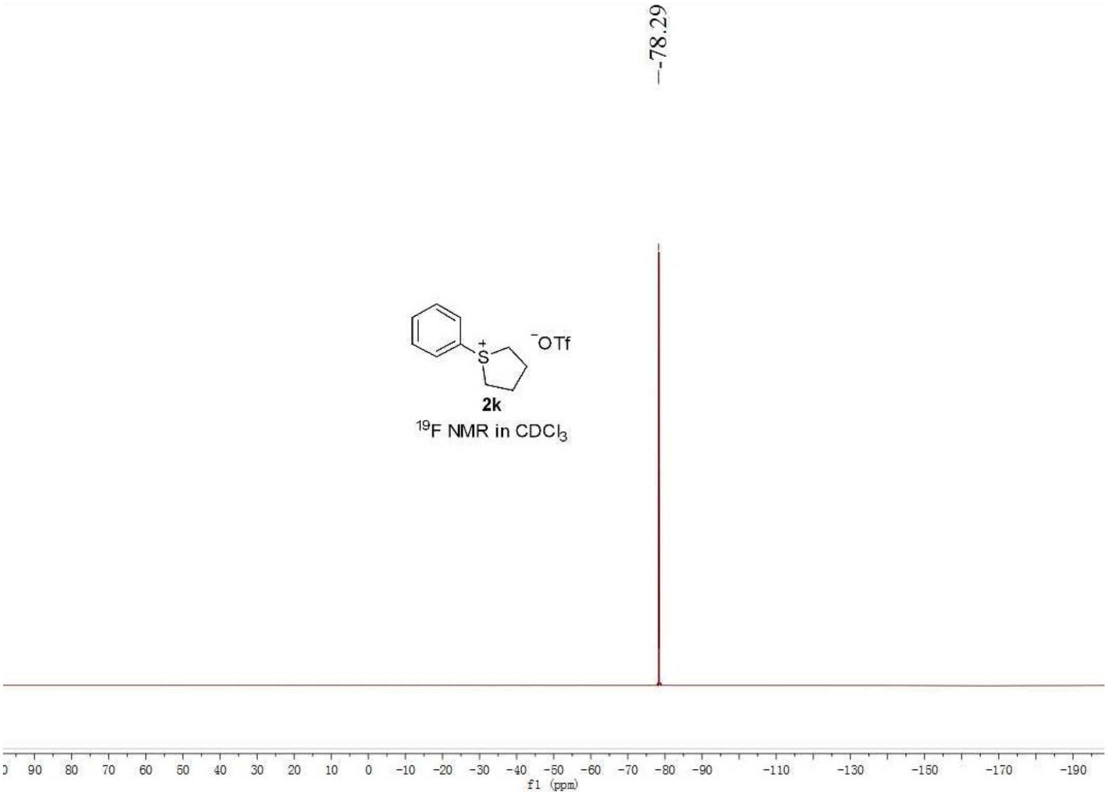
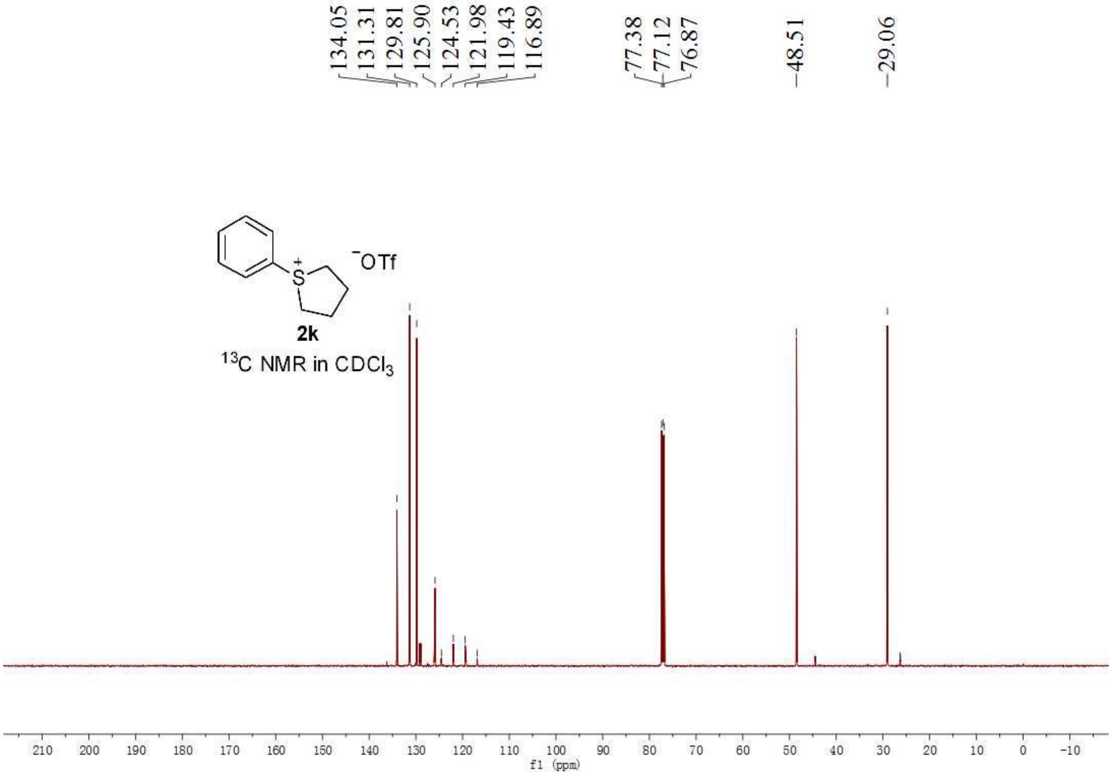
4.17
3.70
3.68
3.67
2.59
2.58
2.56
2.56
2.54
2.53
2.51
2.49
2.48
OTf
2k
^{1}H NMR in $CDCl_3$
2.00
2.99
2.12
2.07
3.99
14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2
f1 (ppm)



-78.29
$^{-}$OTf
2k
^{19}F NMR in CDCl$_3$
90 80 70 60 50 40 30 20 10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90 −110 −130 −150 −170 −190
f1 (ppm)



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131.31
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125.90
124.53
121.98
119.43
116.89
77.38
77.12
76.87
48.51
29.06
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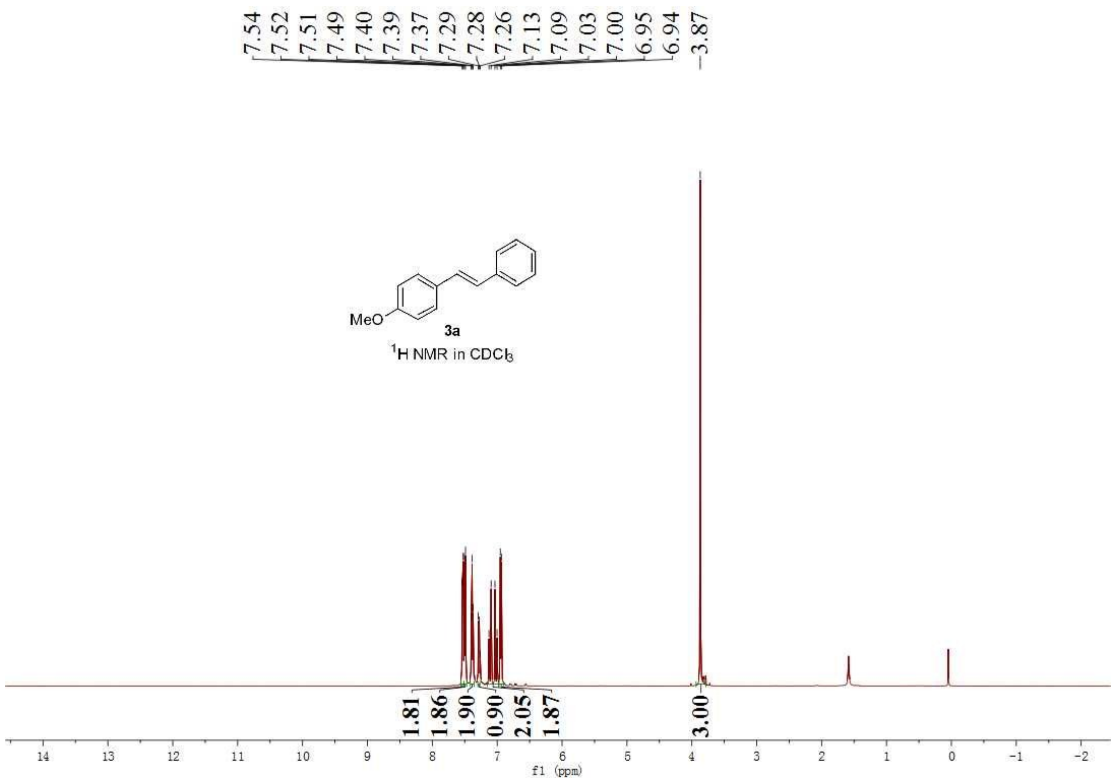
2k
^{13}C NMR in CDCl$_3$
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)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7.39
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7.29
7.28
7.26
7.13
7.09
7.03
7.00
6.95
6.94
3.87
MeO
3a
^{1}H NMR in CDCl$_3$
1.81
1.86
1.90
0.90
2.05
1.87
3.00
14
13
12
11
10
9
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7
6
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2
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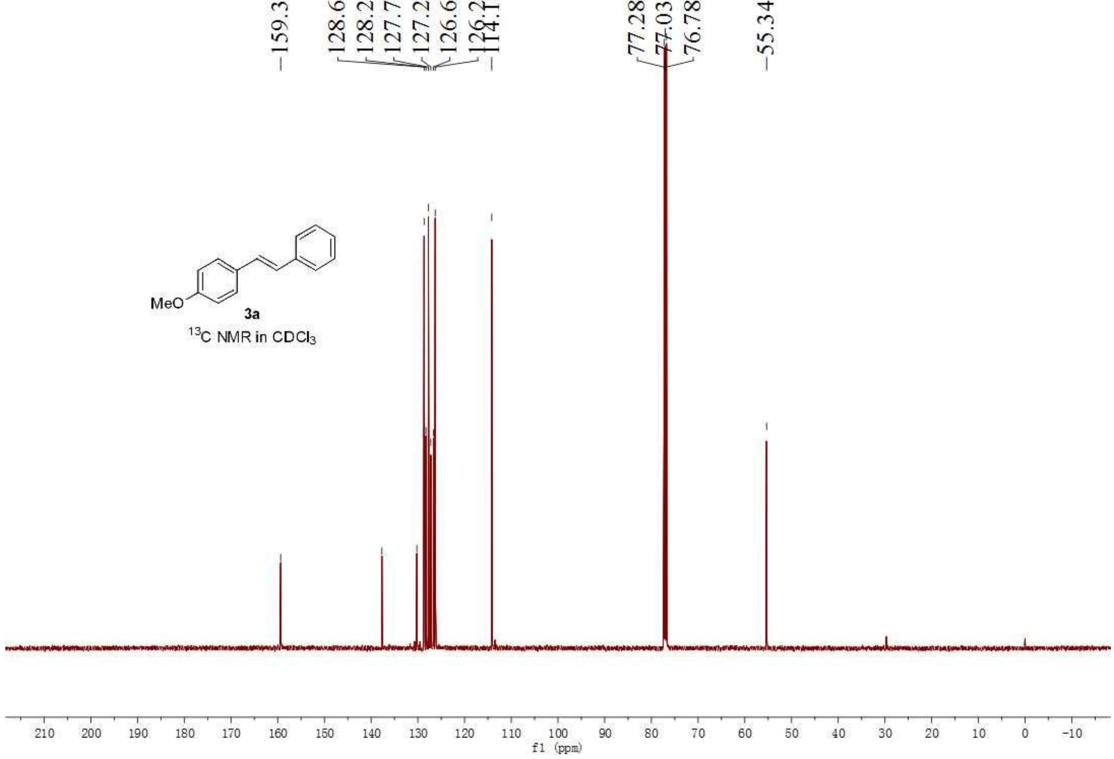
-2
f1 (ppm)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MeO
3a
^{13}C NMR in CDCl$_3$
210
200
190
180
170
160
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80
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50
40
30
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10
0
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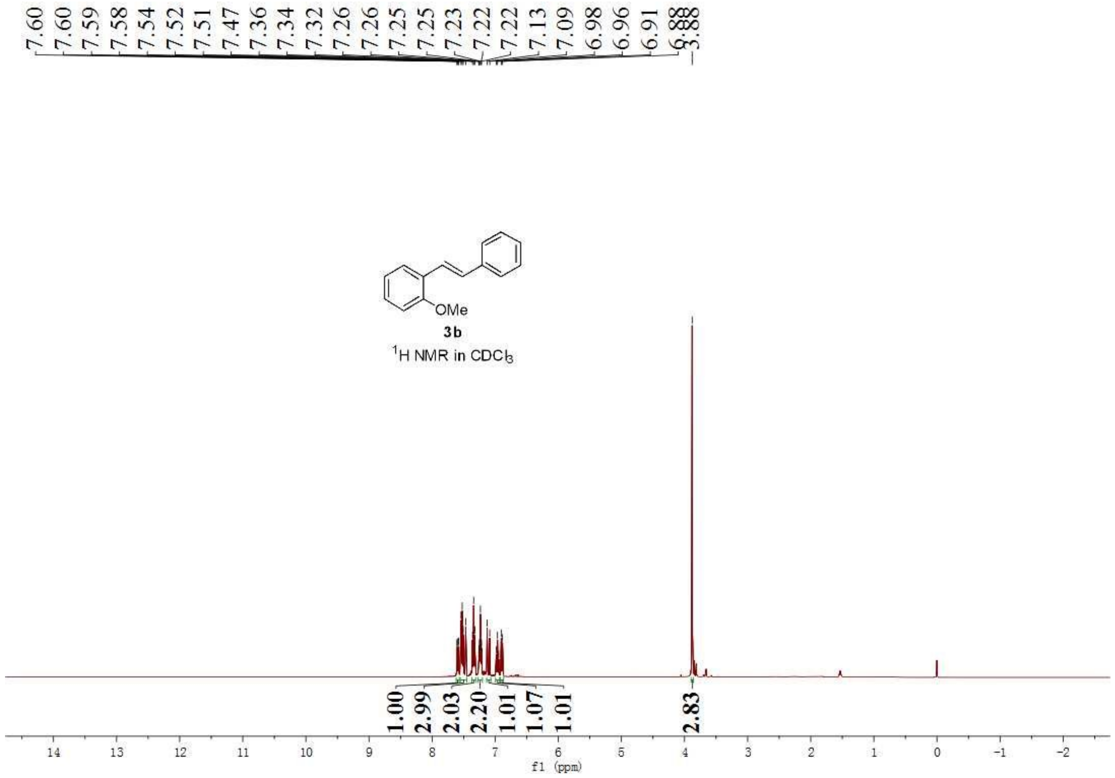
f1 (ppm)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7.26
7.25
7.25
7.23
7.22
7.22
7.13
7.09
6.98
6.96
6.91
6.88
3.88
OMe
3b
^{1}H NMR in CDCl$_3$
1.00
2.99
2.03
2.20
1.01
1.07
1.01
2.83
14
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11
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9
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7
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3
2
1
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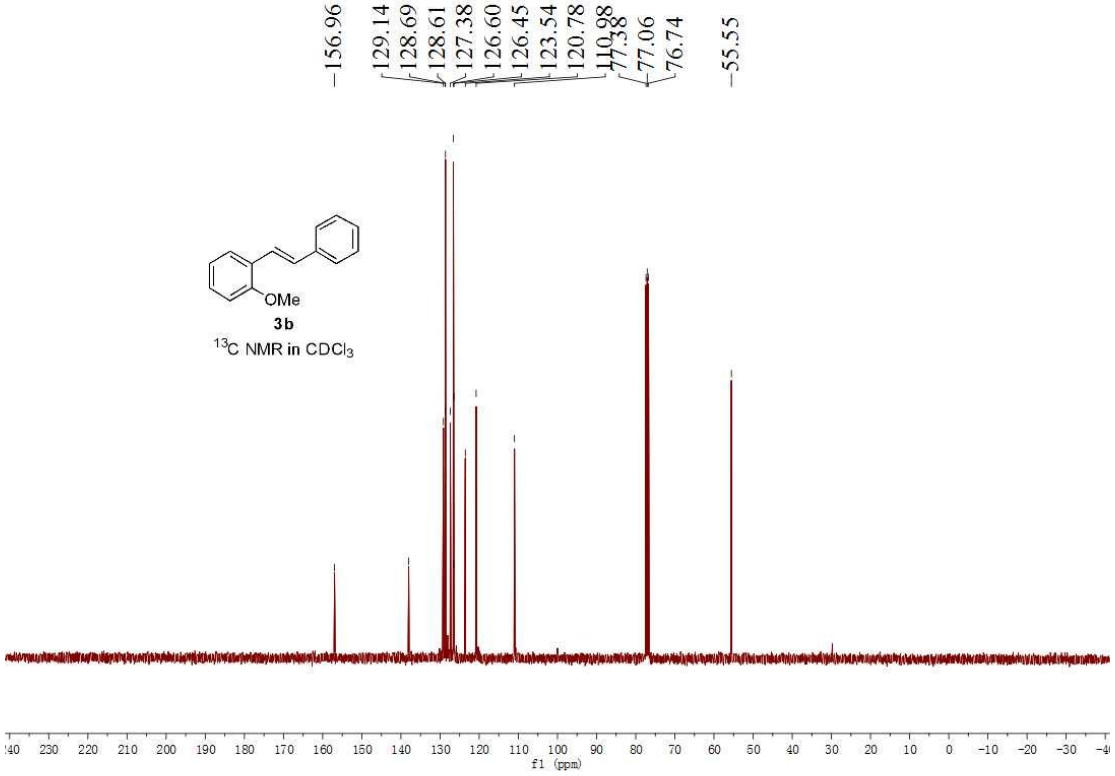
−2
f1 (ppm)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76.74
55.55
OMe
3b
^{13}C NMR in CDCl$_3$
240
230
220
210
200
190
180
170
160
150
140
130
120
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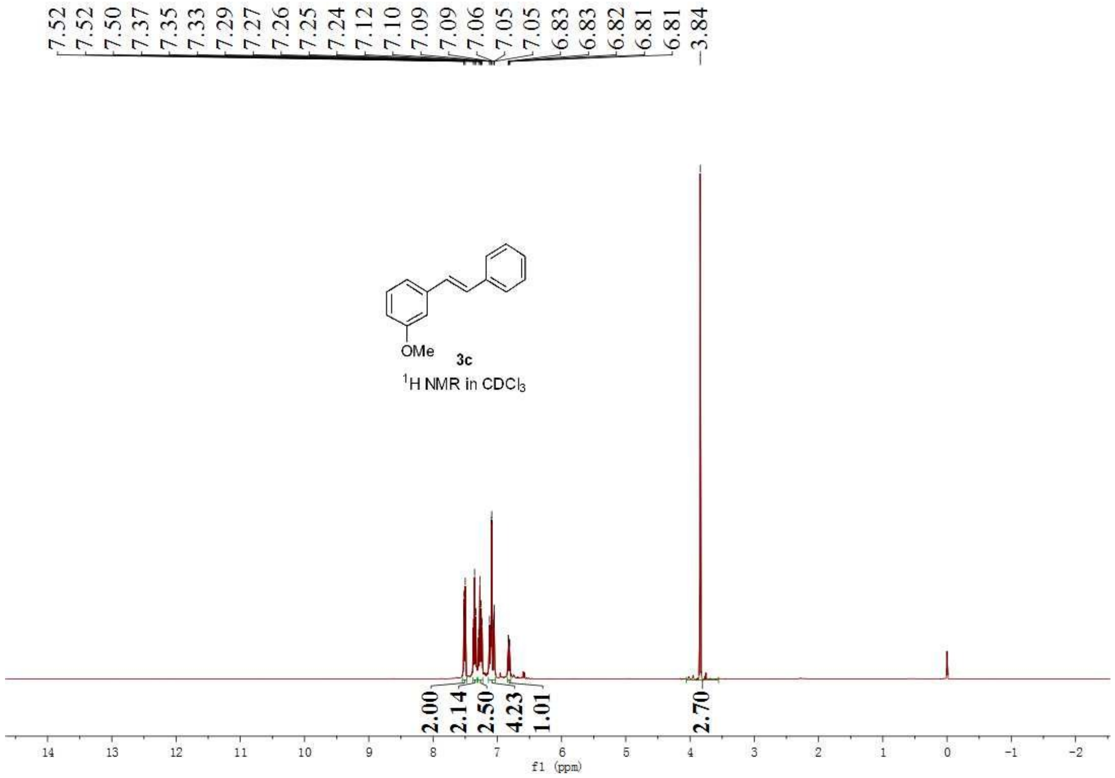
f1 (ppm)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7.09
7.09
7.06
7.05
7.05
6.83
6.83
6.82
6.81
6.81
3.84
OMe
3c
^{1}H NMR in CDCl$_3$
2.00
2.14
2.50
4.23
1.01
2.70
14
13
12
11
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9
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7
6
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4
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2
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0
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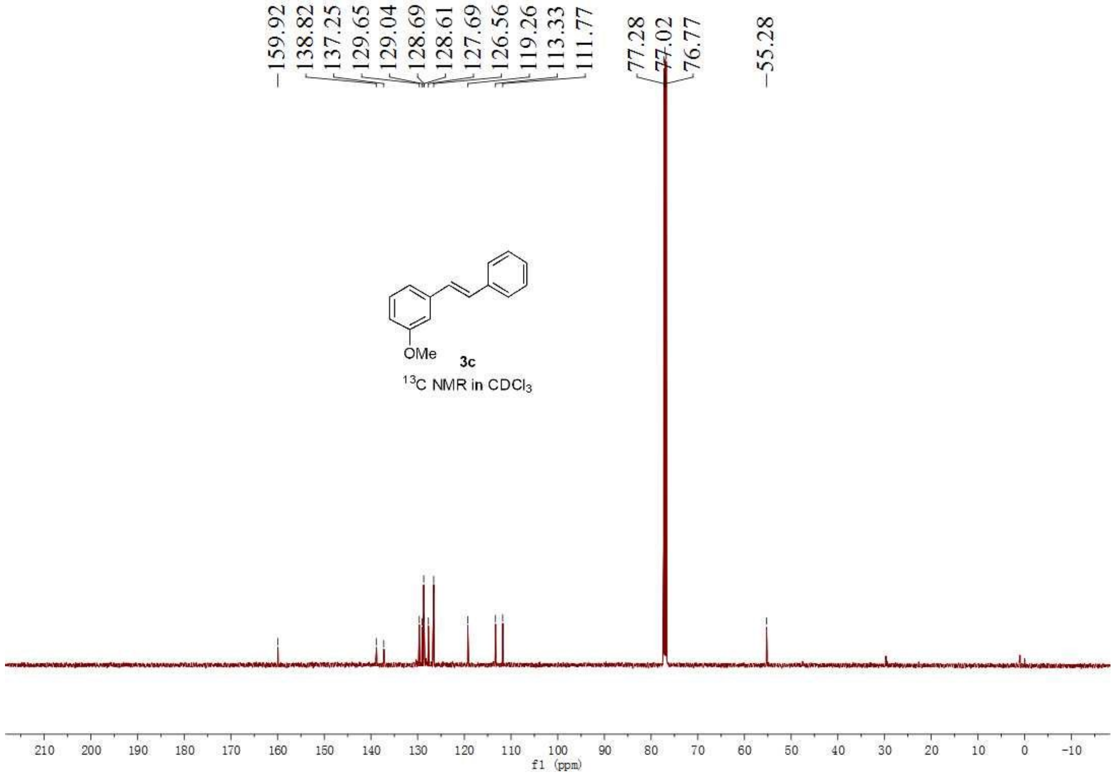
f1 (ppm)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77.28
77.02
76.77
55.28
OMe
3c
^{13}C NMR in CDCl$_3$
210
200
190
180
170
160
150
140
130
120
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100
90
80
70
60
50
40
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20
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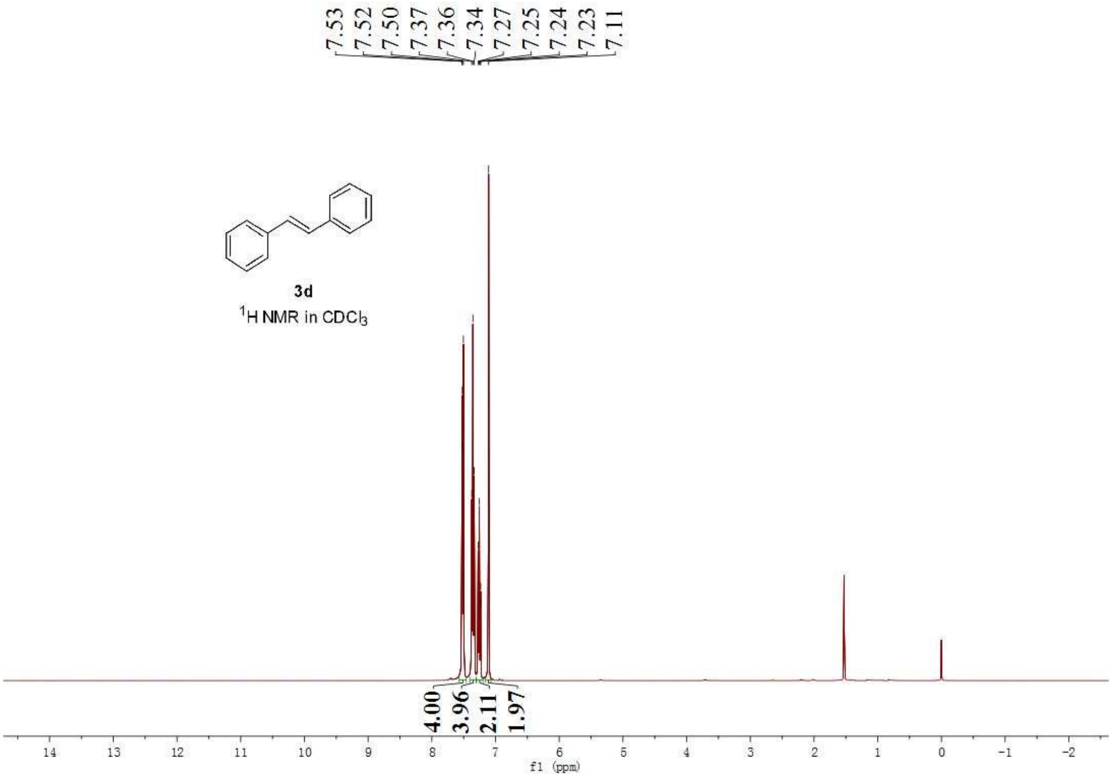
f1 (ppm)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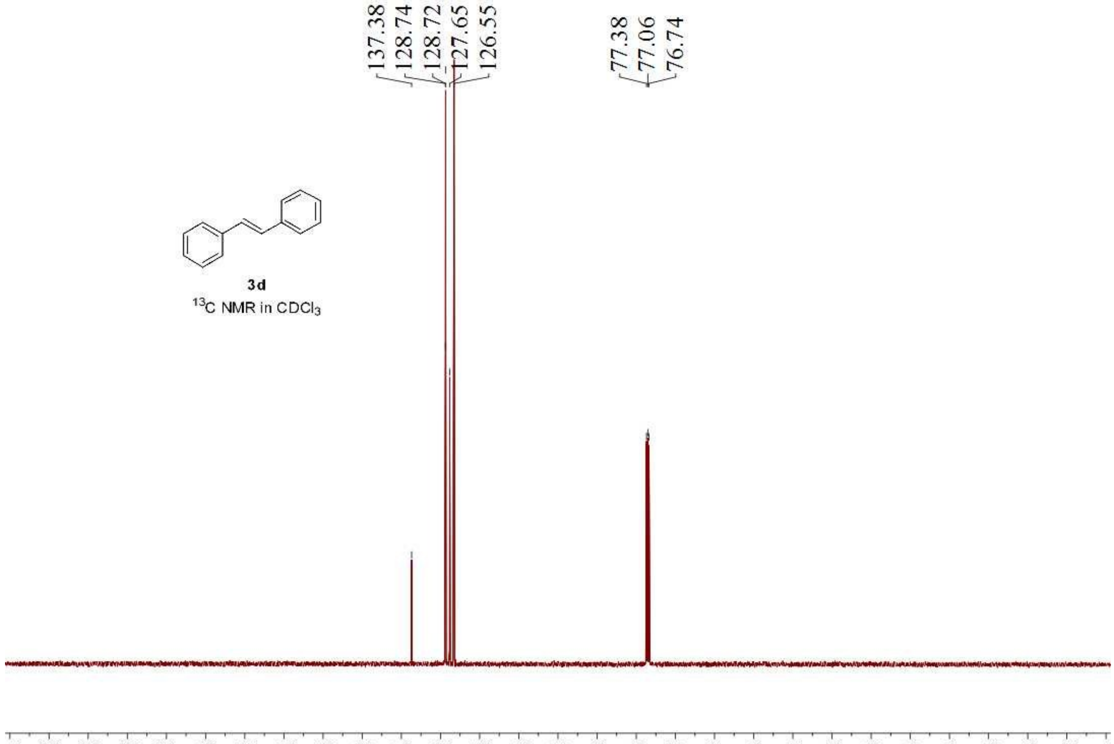
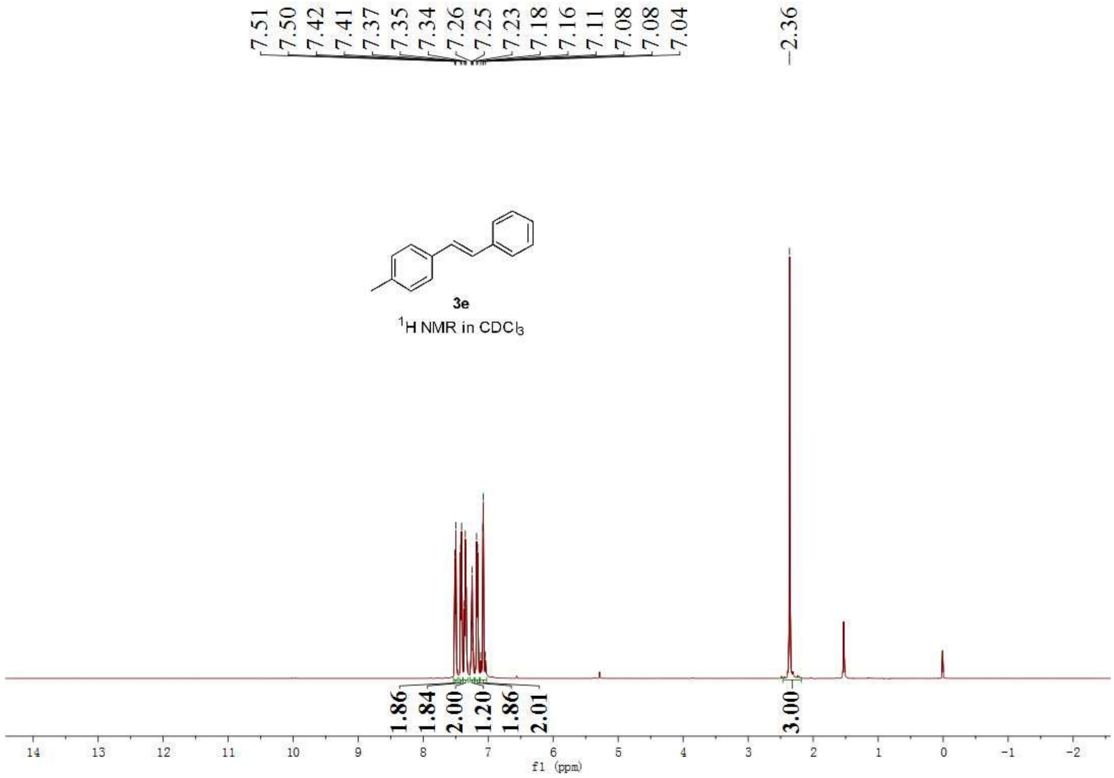
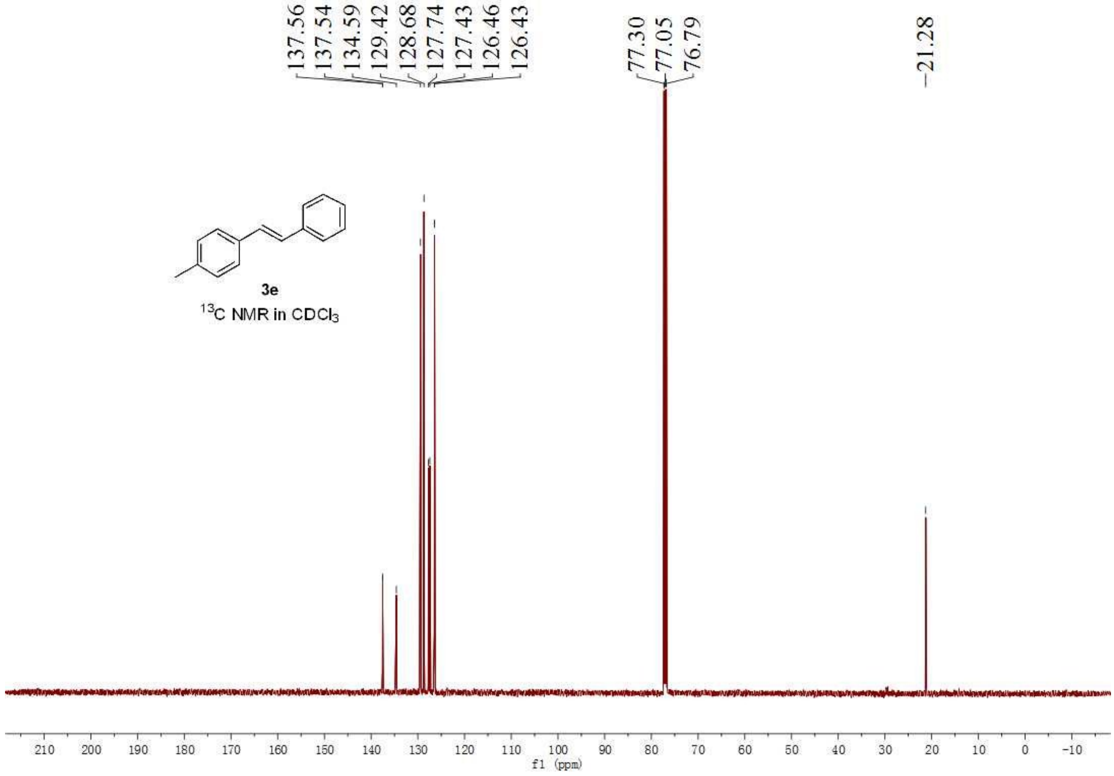
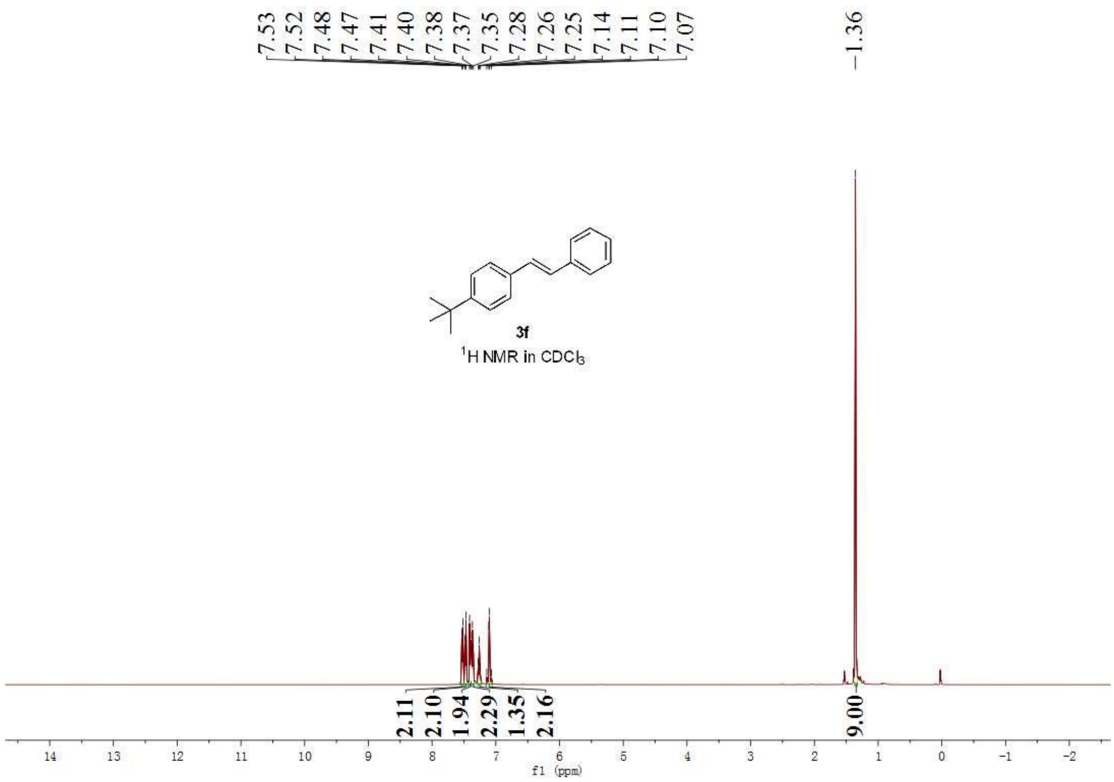
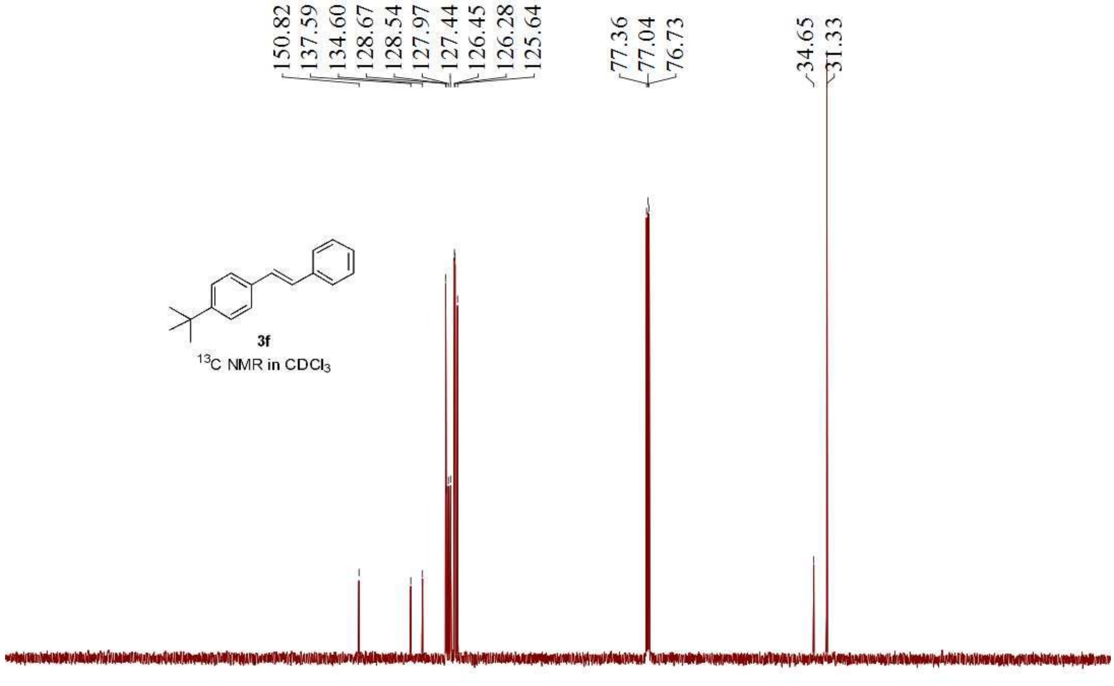
7.25
7.24
7.23
7.11
3d
^{1}H NMR in CDCl$_3$
4.00
3.96
2.11
1.97
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
−1
−2
f1 (ppm)


137.38
128.74
128.72
127.65
126.55
77.38
77.06
76.74
3d
^{13}C NMR in CDCl$_3$
240
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
−20
−30
−40
f1 (ppm)


7.51
7.50
7.42
7.41
7.37
7.35
7.34
7.26
7.25
7.23
7.18
7.16
7.11
7.08
7.08
7.04
2.36
3e
^{1}H NMR in CDCl$_3$
1.86
1.84
2.00
1.20
1.86
2.01
3.00
14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 −1 −2
f1 (ppm)


137.56
137.54
134.59
129.42
128.68
127.74
127.43
126.46
126.43
77.30
77.05
76.79
21.28
3e
^{13}C NMR in CDCl$_3$
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)


7.53
7.52
7.48
7.47
7.41
7.40
7.38
7.37
7.35
7.28
7.26
7.25
7.14
7.11
7.10
7.07
1.36
3f
^{1}H NMR in CDCl$_3$
2.11
2.10
1.94
2.29
1.35
2.16
9.00
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
−1
−2
f1 (ppm)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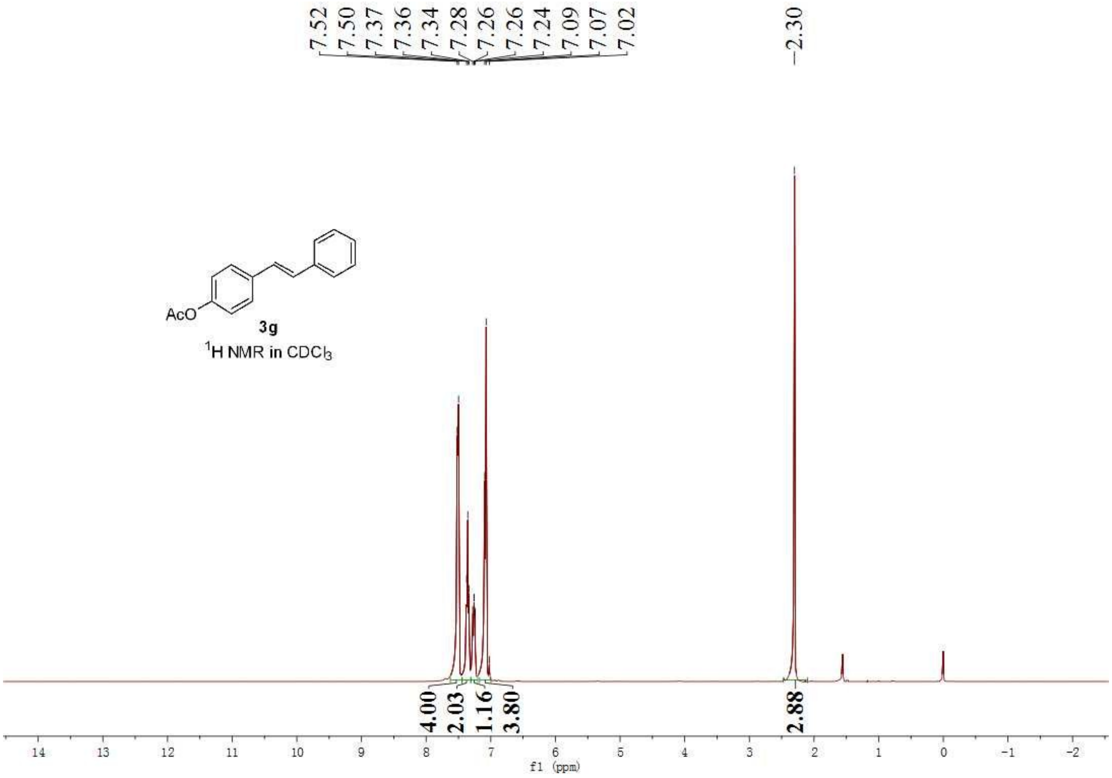
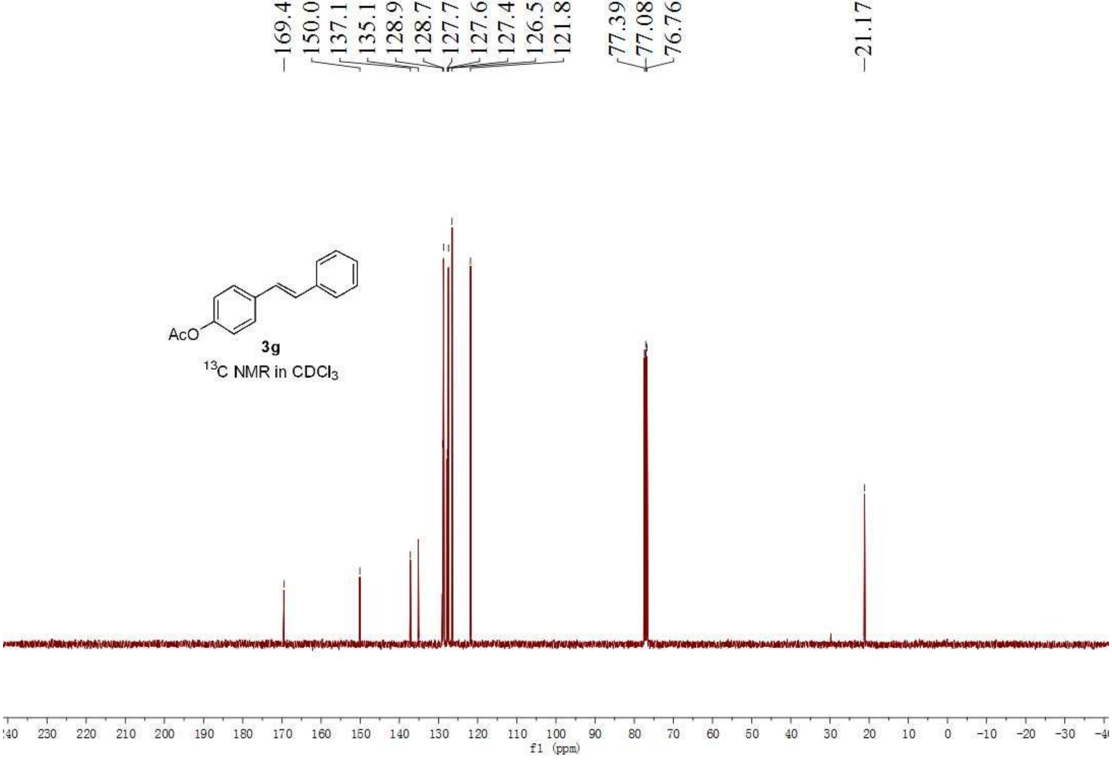
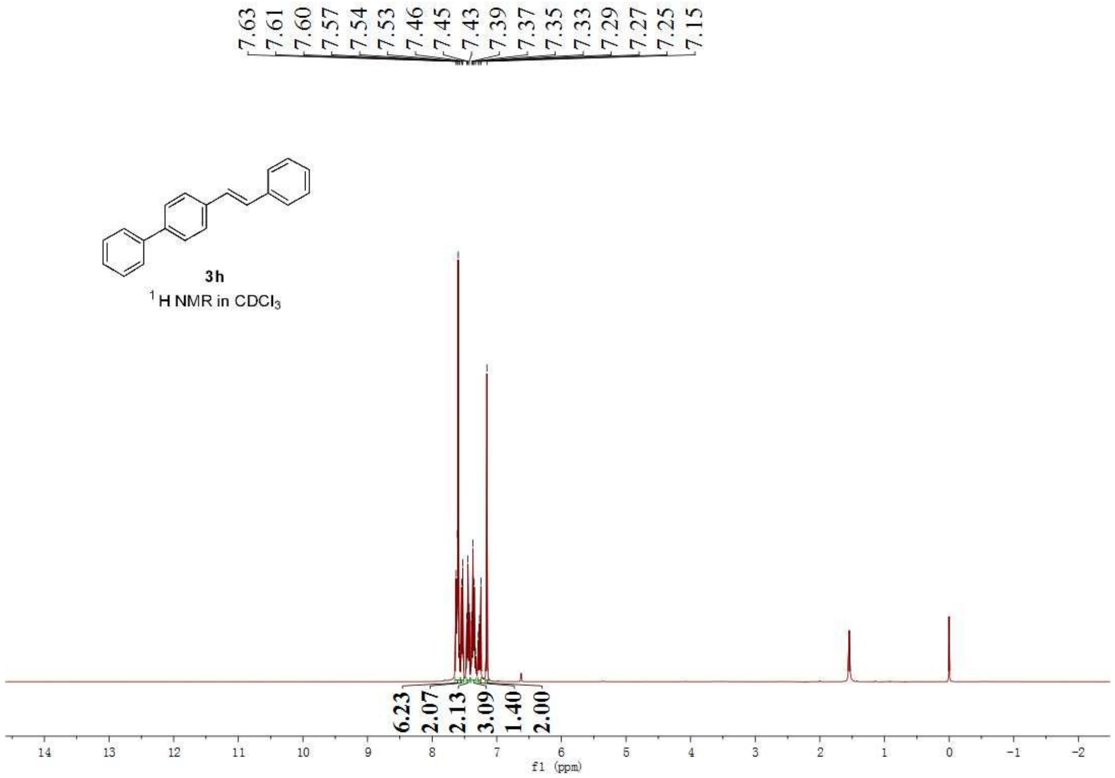
137.59
134.60
128.67
128.54
127.97
127.44
126.45
126.28
125.64
77.36
77.04
76.73
34.65
31.33
3f
^{13}C NMR in CDCl$_3$
240
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
−20
−30
−40
f1 (ppm)

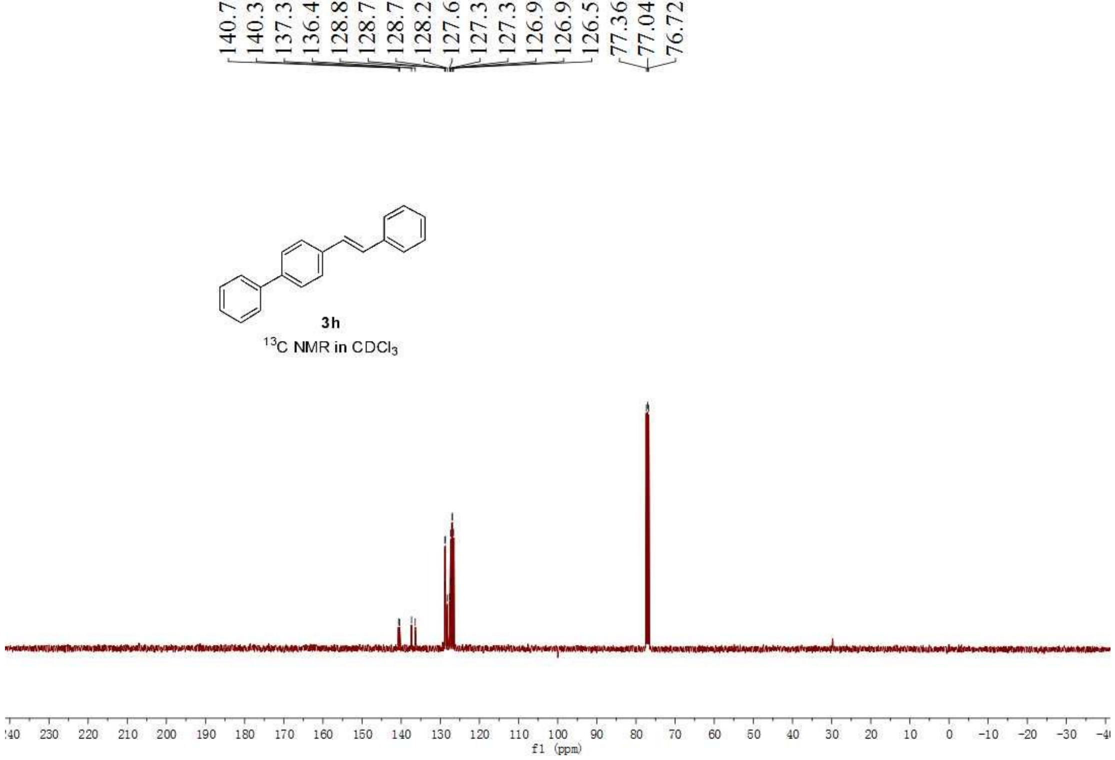

7.52
7.50
7.37
7.36
7.34
7.28
7.26
7.26
7.24
7.09
7.07
7.02
2.30
AcO
3g
^{1}H NMR in CDCl$_3$
4.00
2.03
1.16
3.80
2.88
14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 −1 −2
f1 (ppm)


169.49
150.09
137.19
135.13
128.98
128.73
127.74
127.68
127.45
126.54
121.83
77.39
77.08
76.76
21.17
AcO
3g
^{13}C NMR in CDCl$_3$
240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10 −20 −30 −40
f1 (ppm)



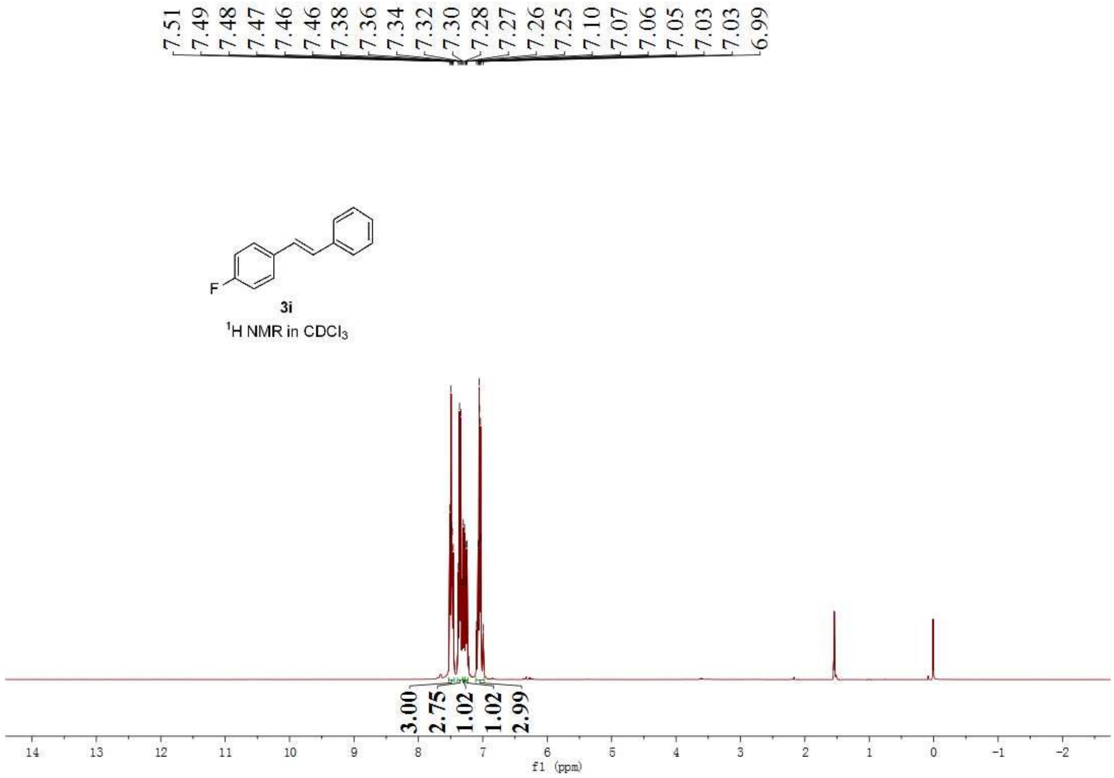
3h

^{1}H NMR in $CDCl_3$



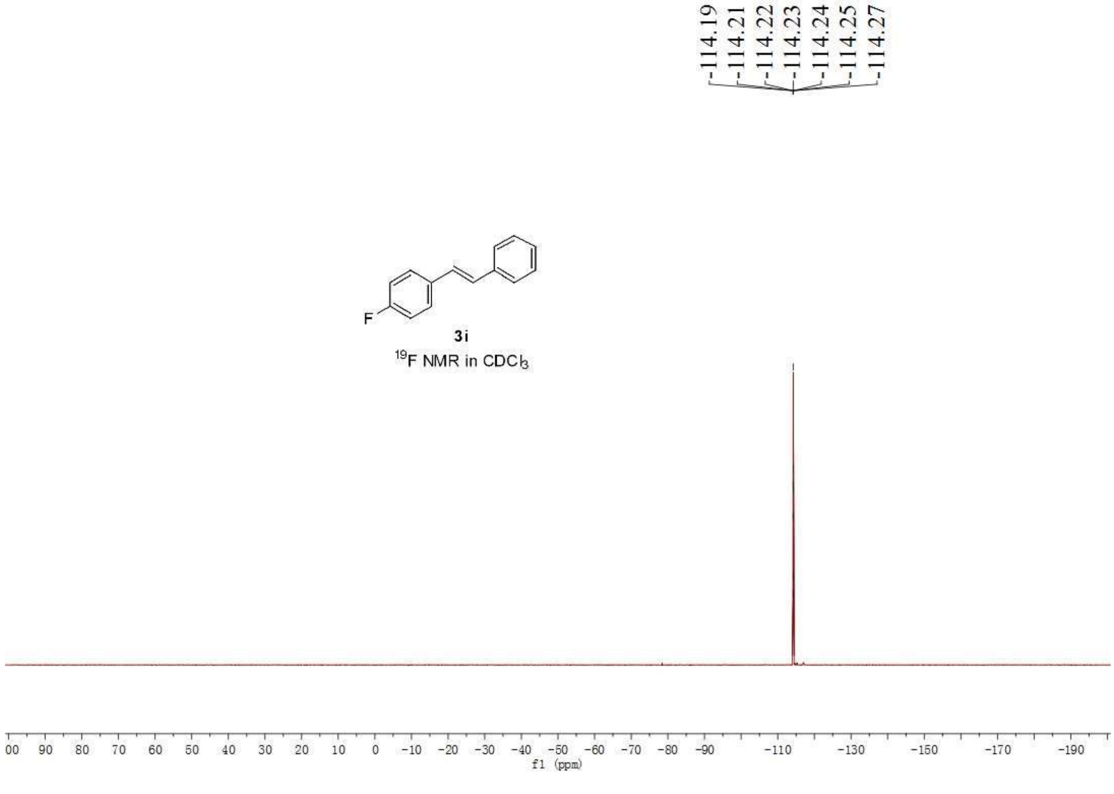
3h

^{13}C NMR in $CDCl_3$



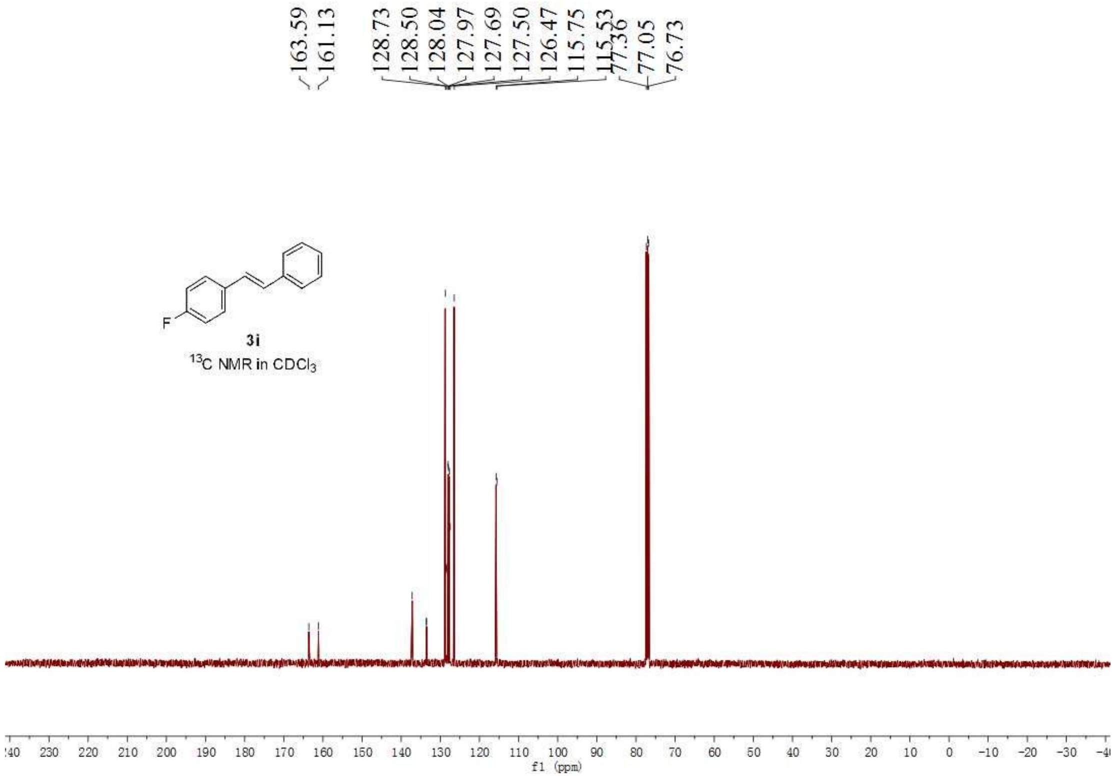
3i

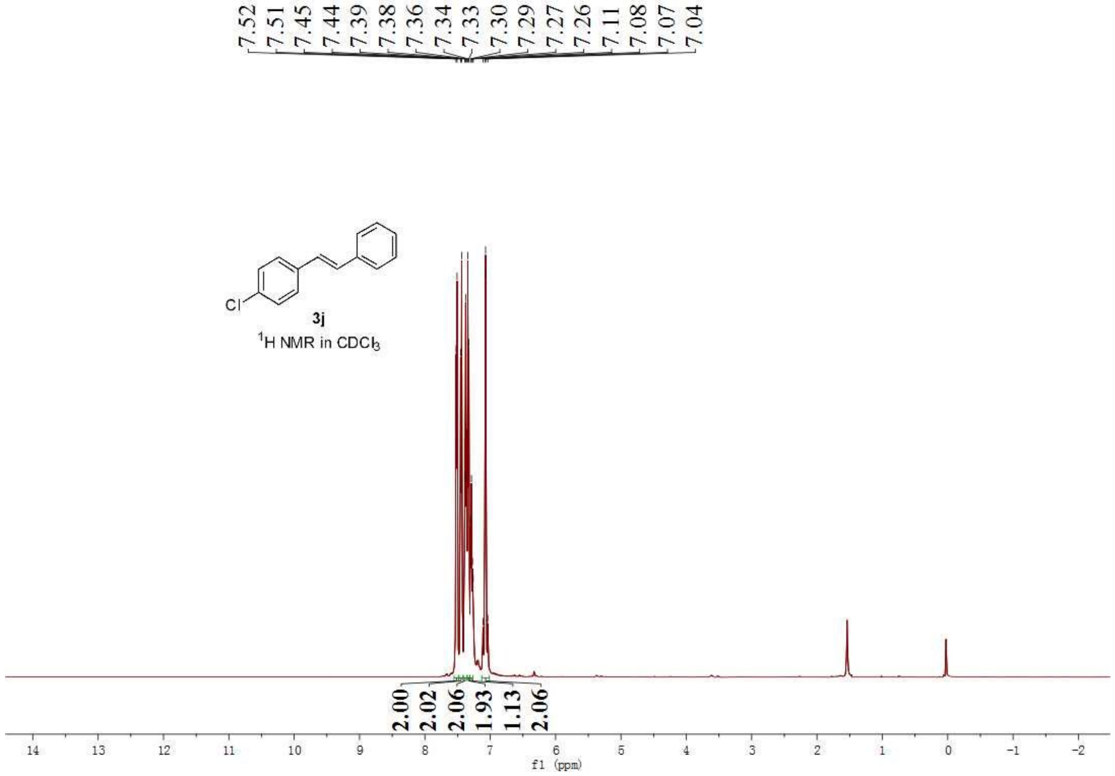
^{1}H NMR in $CDCl_3$

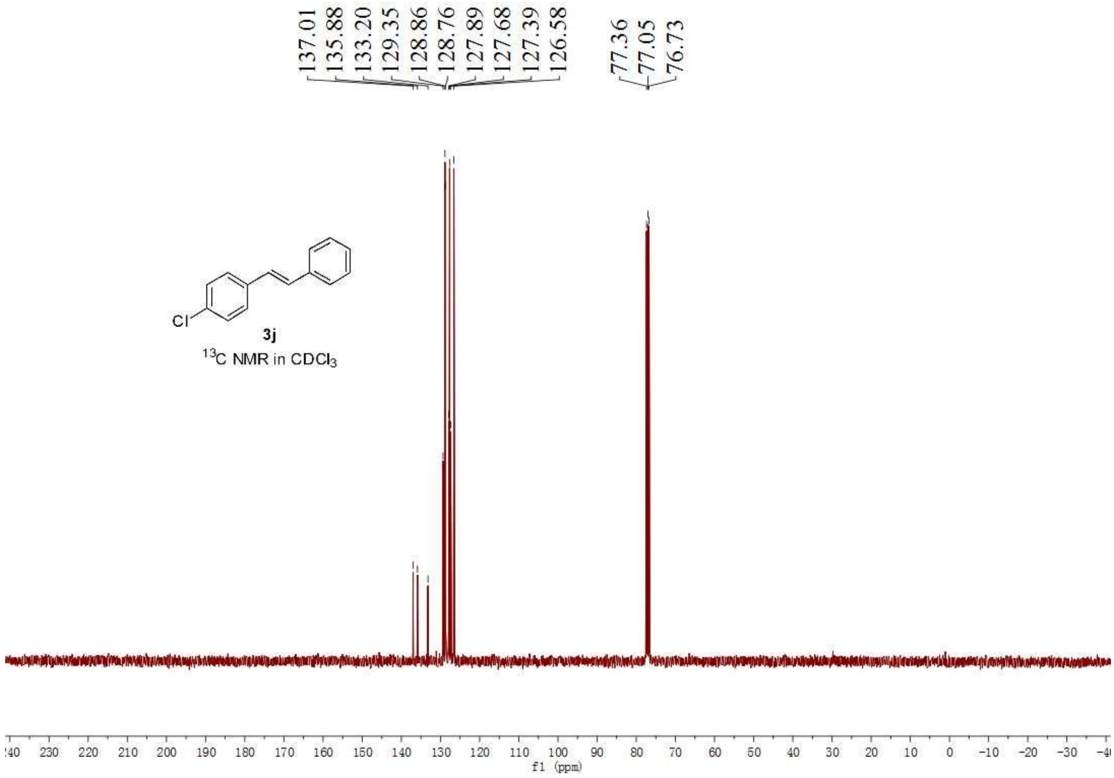


3i

^{19}F NMR in $CDCl_3$

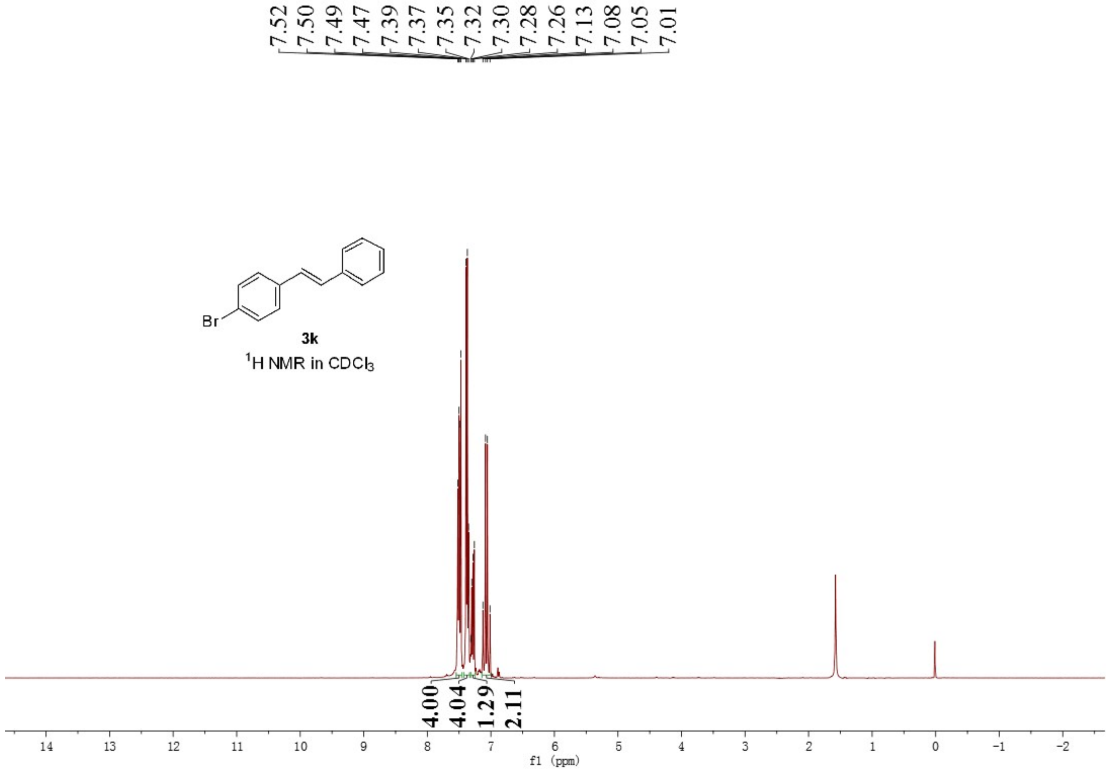

163.59
161.13
128.73
128.50
128.04
127.97
127.69
127.50
126.47
115.75
115.53
77.36
77.05
76.73
F
3i
^{13}C NMR in CDCl$_3$
240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10 −20 −30 −40
f1 (ppm)


7.52
7.51
7.45
7.44
7.39
7.38
7.36
7.34
7.33
7.30
7.29
7.27
7.26
7.11
7.08
7.07
7.04
Cl
3j
^{1}H NMR in CDCl$_3$
2.00
2.02
2.06
1.93
1.13
2.06
14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 −1 −2
f1 (ppm)



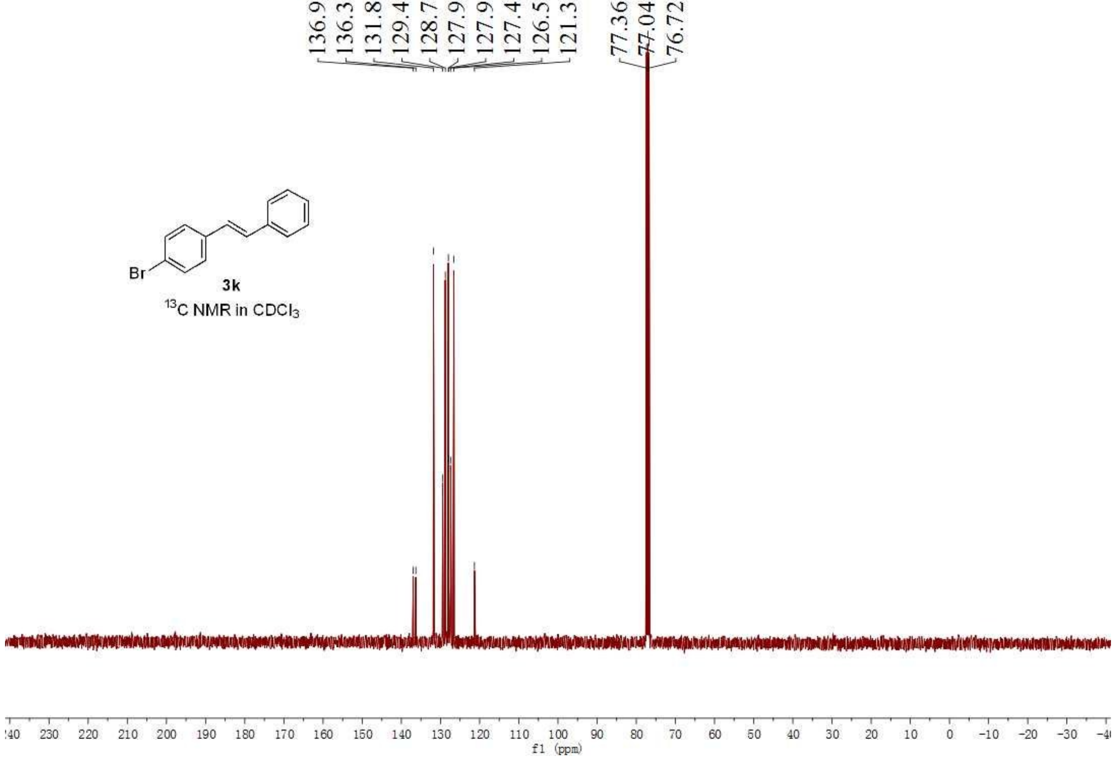
3j

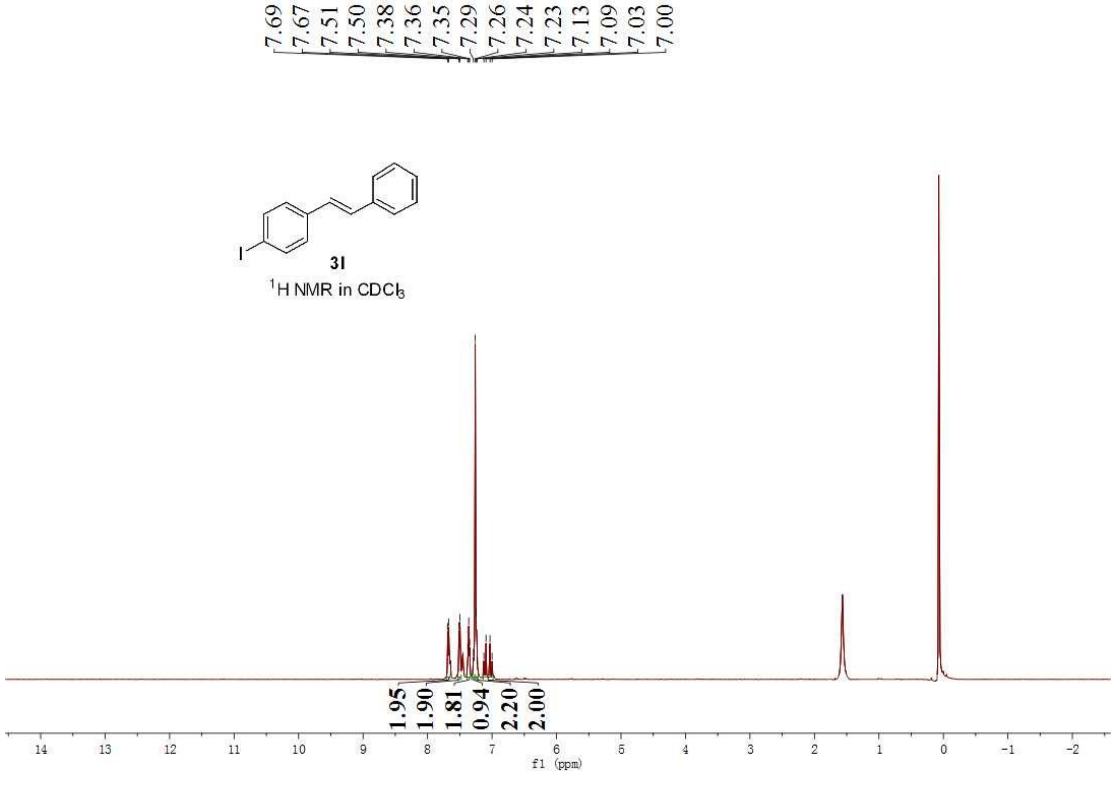
^{13}C NMR in CDCl$_3$

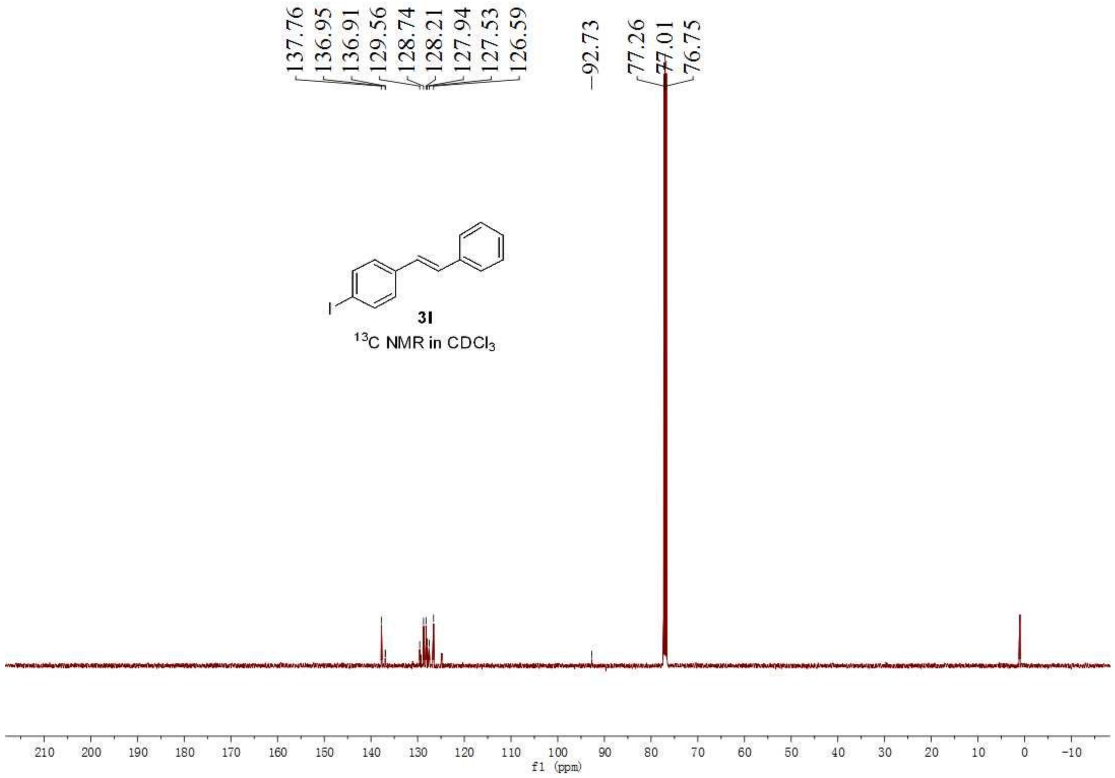


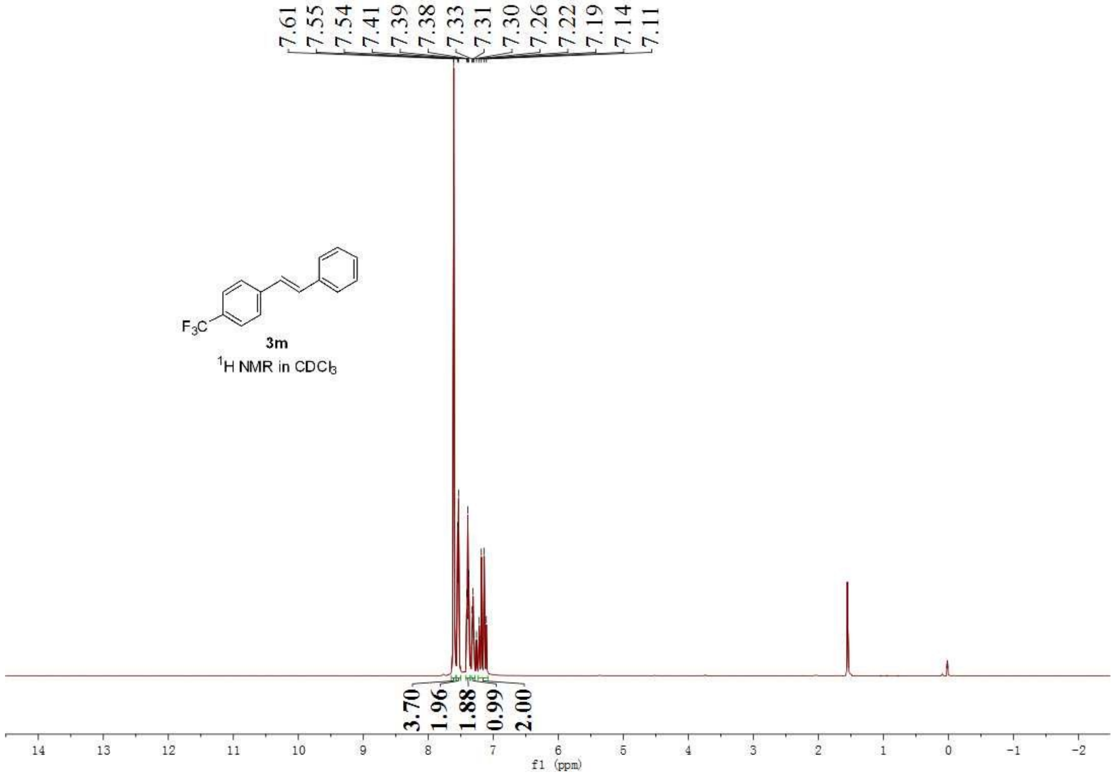
3k

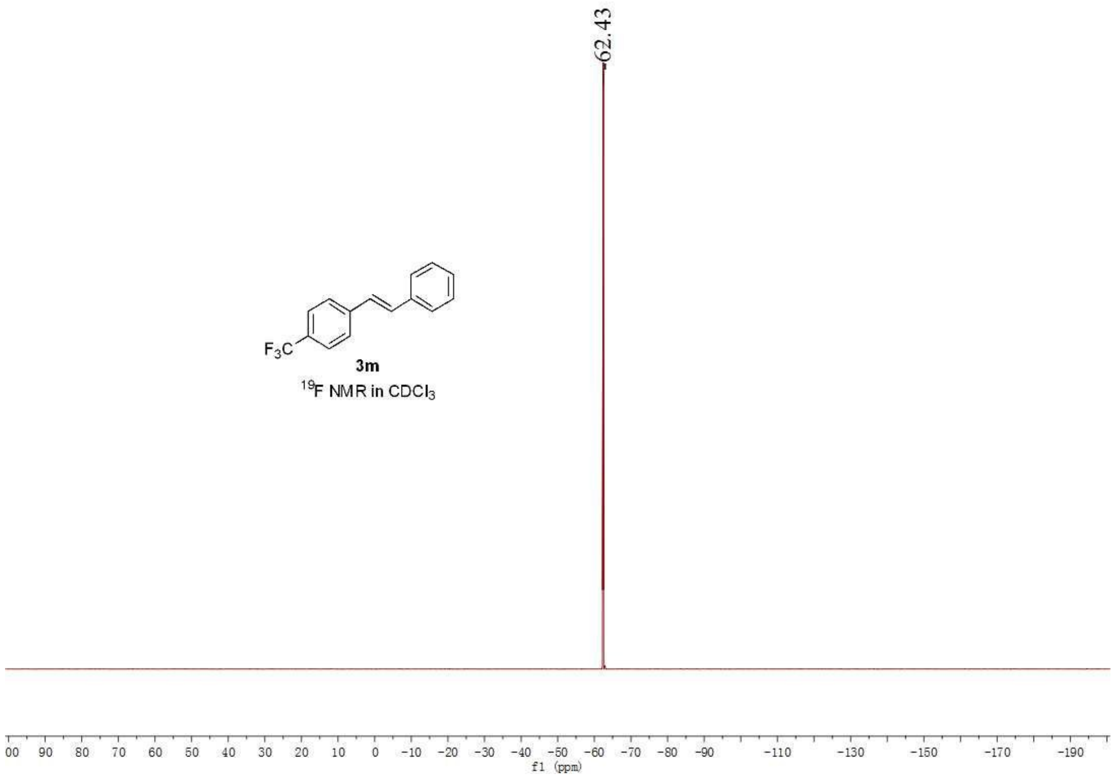
^{1}H NMR in CDCl$_3$

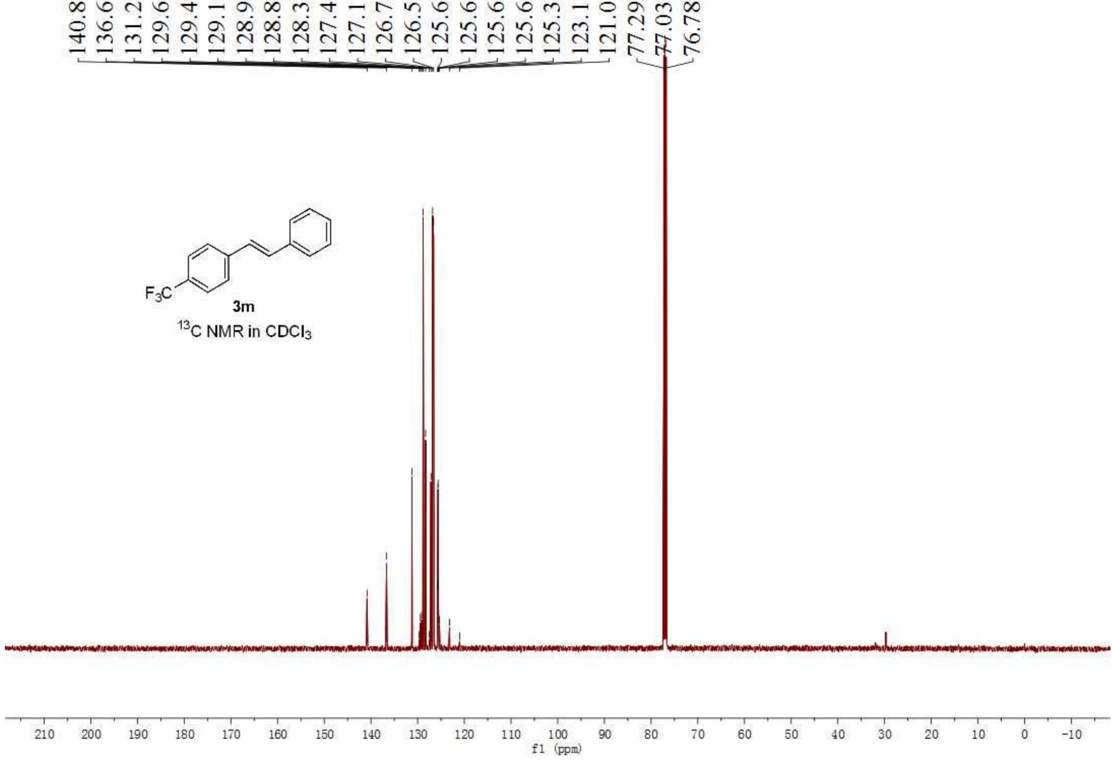

136.97
136.30
131.80
129.45
128.77
127.99
127.93
127.42
126.58
121.33
77.36
77.04
76.72
Br
3k
^{13}C NMR in CDCl$_3$
240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10 −20 −30 −40
f1 (ppm)

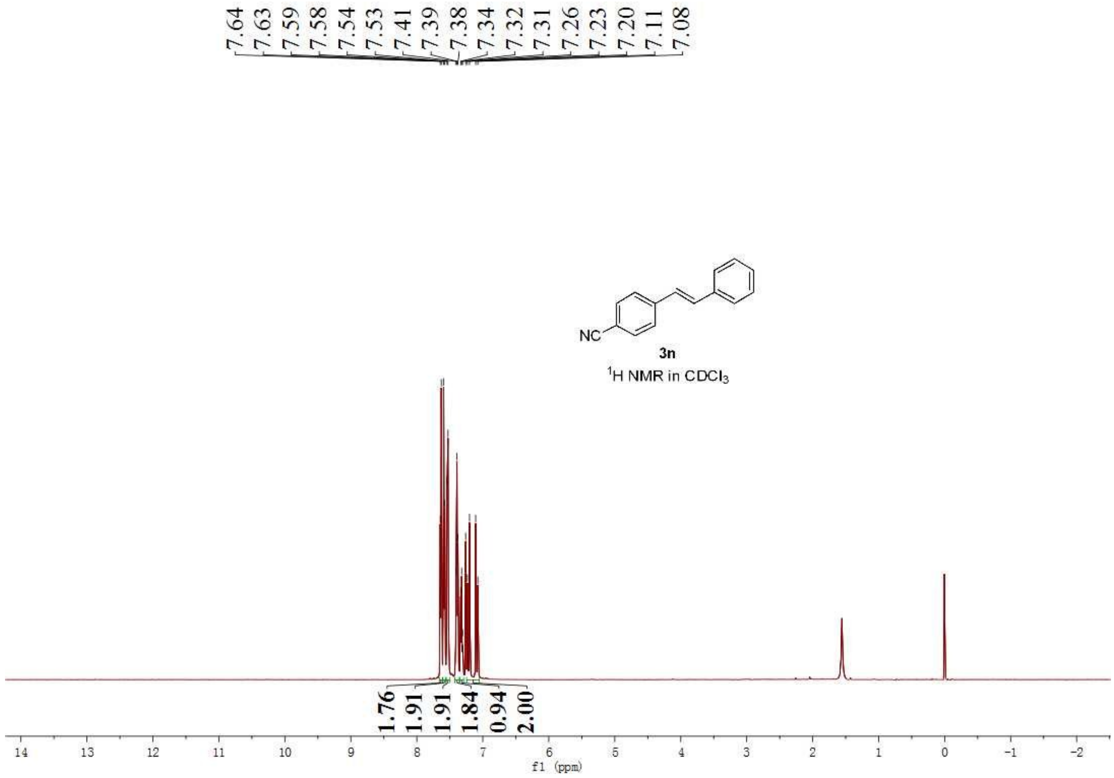

7.69
7.67
7.51
7.50
7.38
7.36
7.35
7.29
7.26
7.24
7.23
7.13
7.09
7.03
7.00
I
3l
^{1}H NMR in CDCl$_3$
1.95
1.90
1.81
0.94
2.20
2.00
14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 −1 −2
f1 (ppm)


137.76
136.95
136.91
129.56
128.74
128.21
127.94
127.53
126.59
92.73
77.26
77.01
76.75
I
3l
^{13}C NMR in CDCl$_3$
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)


7.61
7.55
7.54
7.41
7.39
7.38
7.33
7.31
7.30
7.26
7.22
7.19
7.14
7.11
F$_3$C
3m
^{1}H NMR in CDCl$_3$
3.70
1.96
1.88
0.99
2.00
14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2
f1 (ppm)

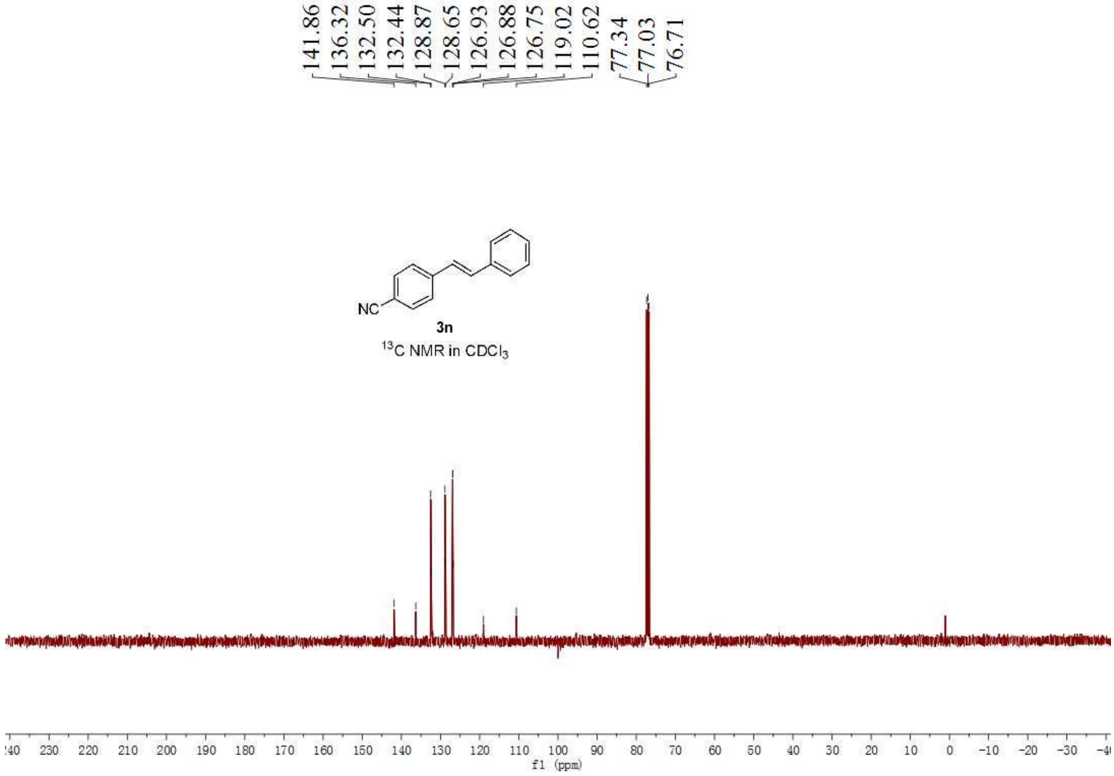

-62.43
F$_3$C
3m
^{19}F NMR in CDCl$_3$
00 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -110 -130 -150 -170 -190
f1 (ppm)


140.83
136.66
131.23
129.67
129.41
129.16
128.90
128.82
128.31
127.49
127.15
126.79
126.59
125.69
125.66
125.63
125.60
125.33
123.17
121.01
77.29
77.03
76.78
F$_3$C
3m
^{13}C NMR in CDCl$_3$
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)



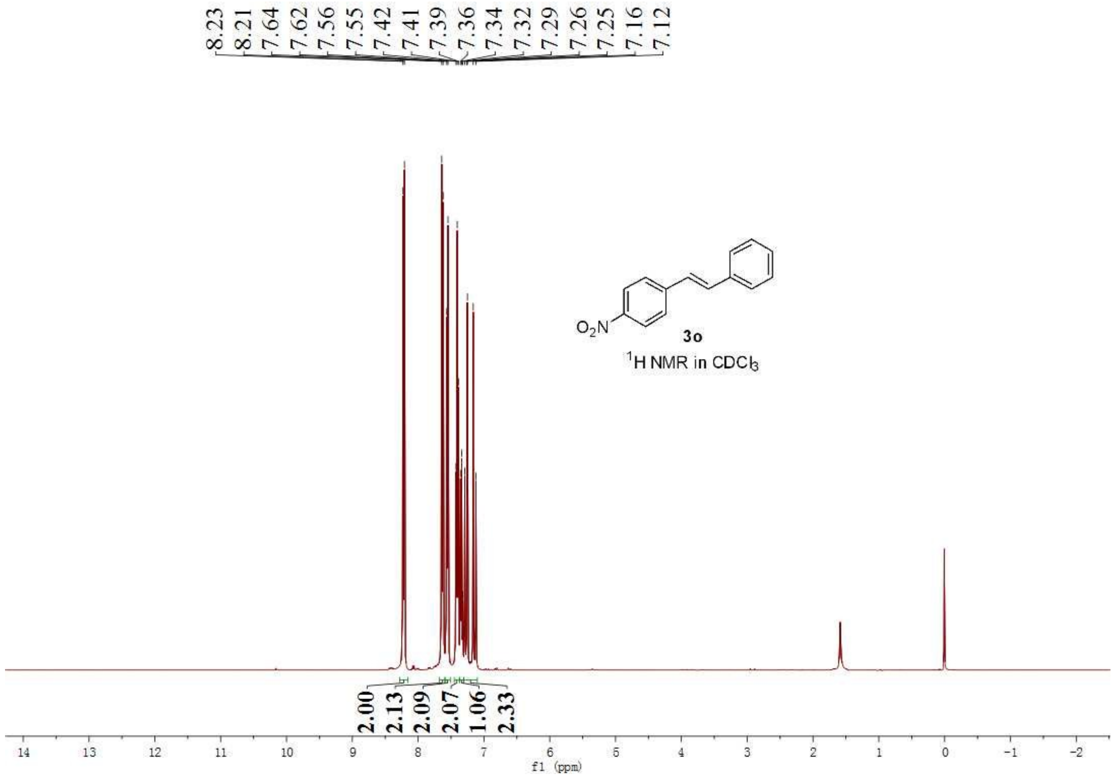
3n

^1H NMR in $CDCl_3$



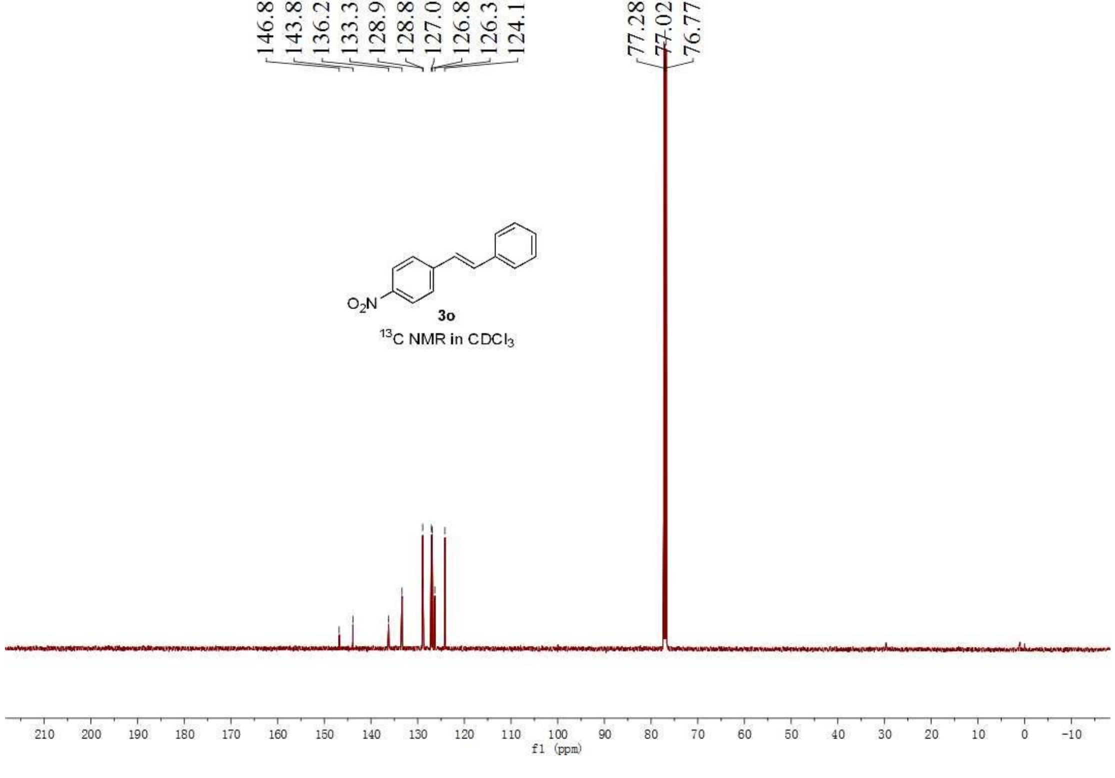
3n

^{13}C NMR in $CDCl_3$



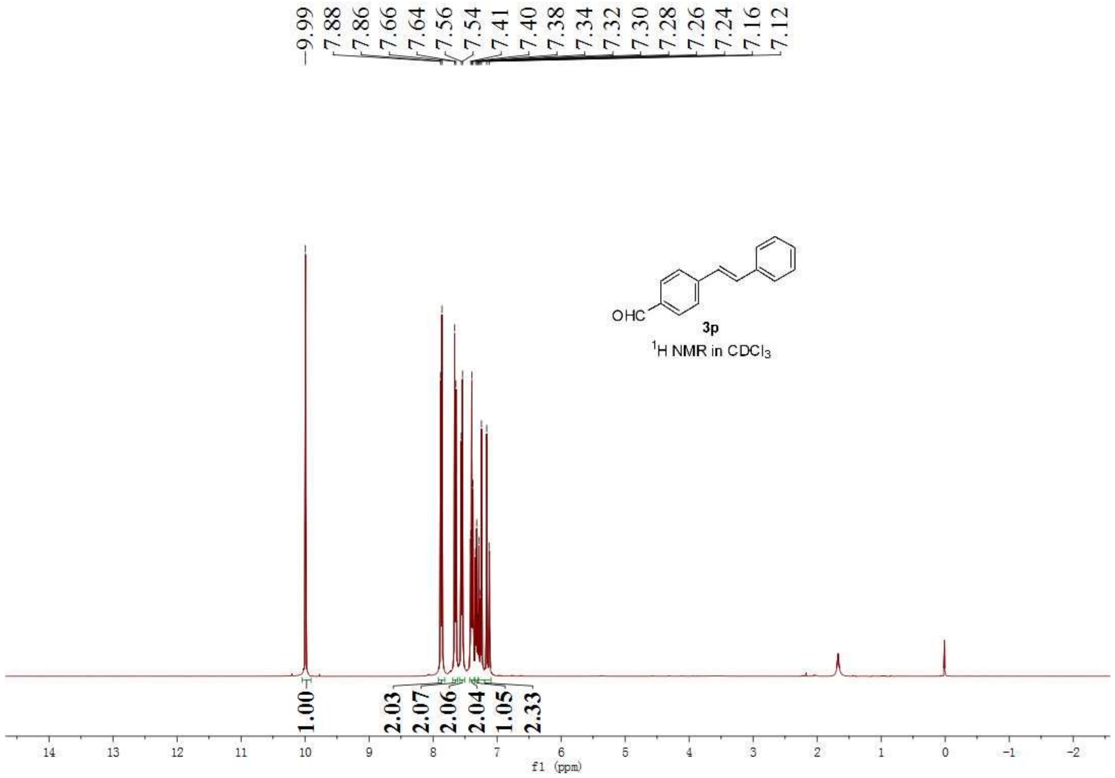
3o

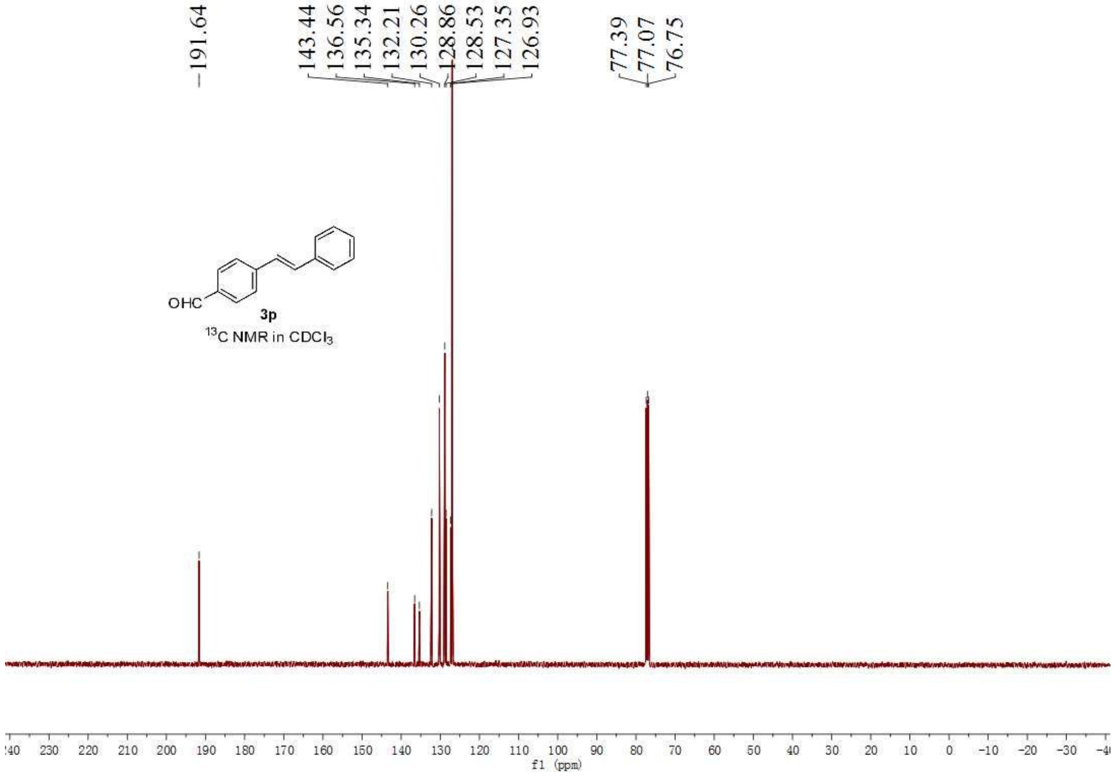
^{1}H NMR in $CDCl_3$

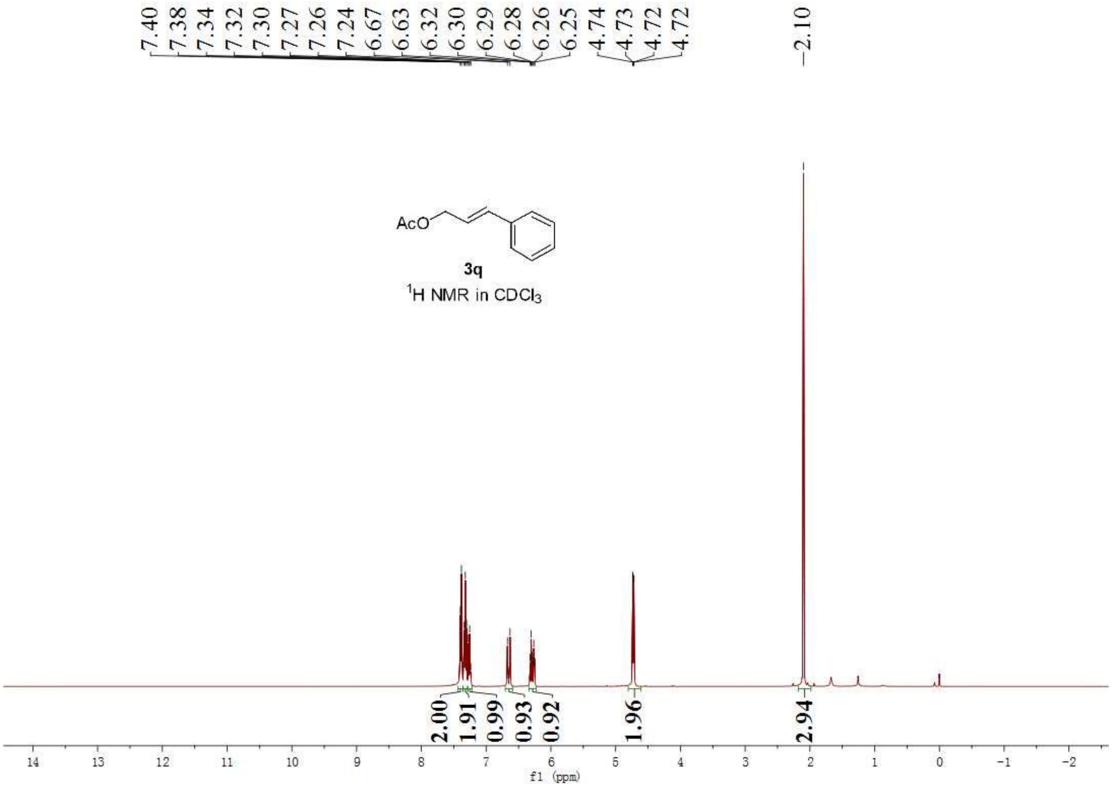


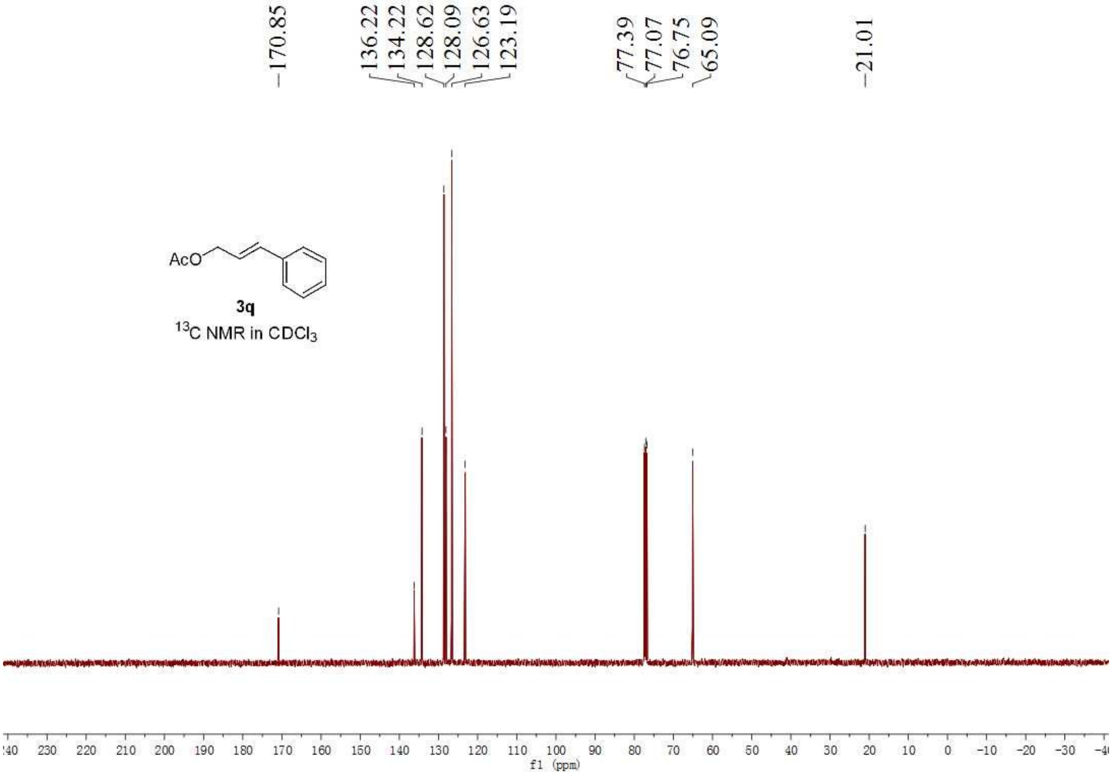
3o

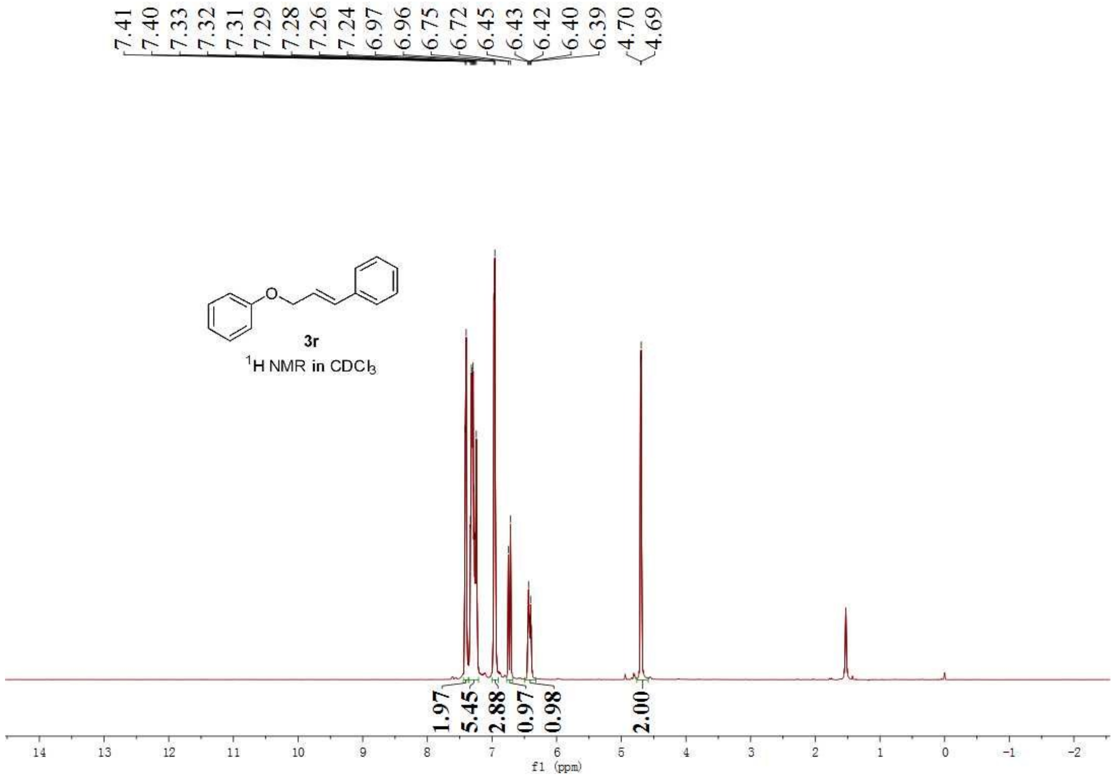
^{13}C NMR in $CDCl_3$


9.99
7.88
7.86
7.66
7.64
7.56
7.54
7.41
7.40
7.38
7.34
7.32
7.30
7.28
7.26
7.24
7.16
7.12
OHC
3p
^{1}H NMR in CDCl$_3$
1.00
2.03
2.07
2.06
2.04
1.05
2.33
14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2
f1 (ppm)


191.64
143.44
136.56
135.34
132.21
130.26
128.86
128.53
127.35
126.93
77.39
77.07
76.75
OHC
3p
^{13}C NMR in CDCl$_3$
240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40
f1 (ppm)


7.40
7.38
7.34
7.32
7.30
7.27
7.26
7.24
6.67
6.63
6.32
6.30
6.29
6.28
6.26
6.25
4.74
4.73
4.72
4.72
2.10
AcO
3q
^{1}H NMR in CDCl$_3$
2.00
1.91
0.99
0.93
0.92
1.96
2.94
14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 −1 −2
f1 (ppm)


170.85
136.22
134.22
128.62
128.09
126.63
123.19
77.39
77.07
76.75
65.09
21.01
AcO
3q
^{13}C NMR in CDCl$_3$
240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10 −20 −30 −40
f1 (ppm)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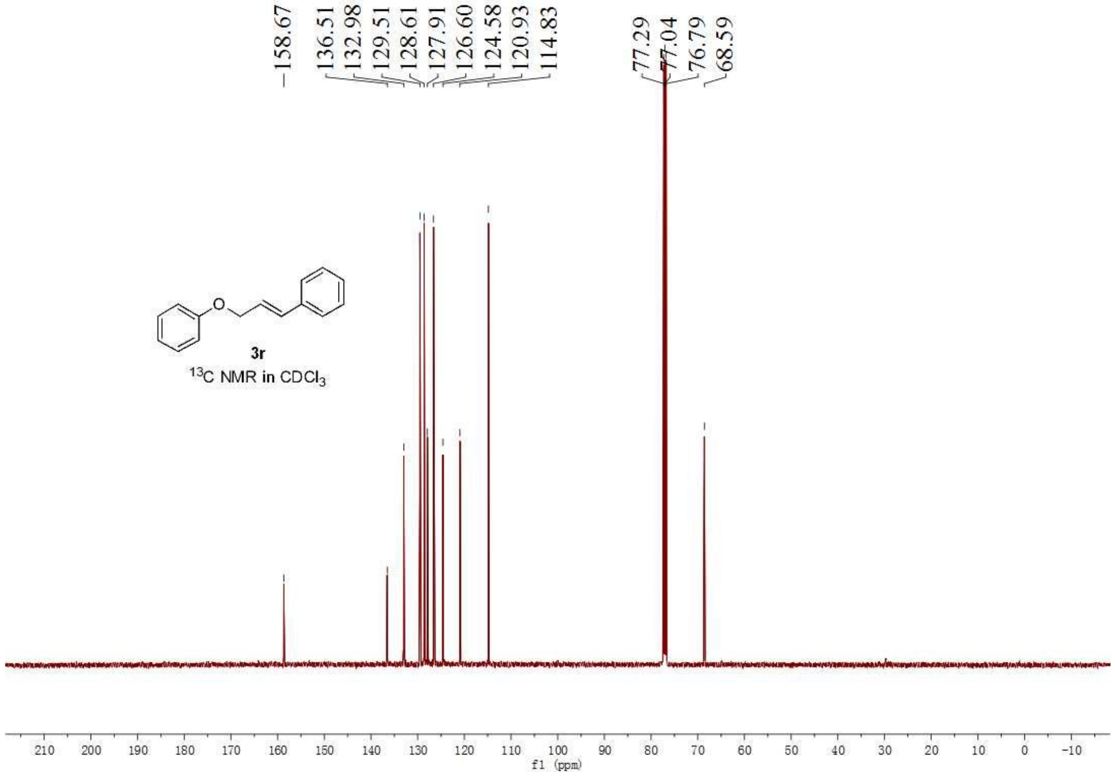
7.40
7.33
7.32
7.31
7.29
7.28
7.26
7.24
6.97
6.96
6.75
6.72
6.45
6.43
6.42
6.40
6.39
4.70
4.69
O
3r
^{1}H NMR in CDCl$_3$
1.97
5.45
2.88
0.97
0.98
2.00
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
f1 (ppm)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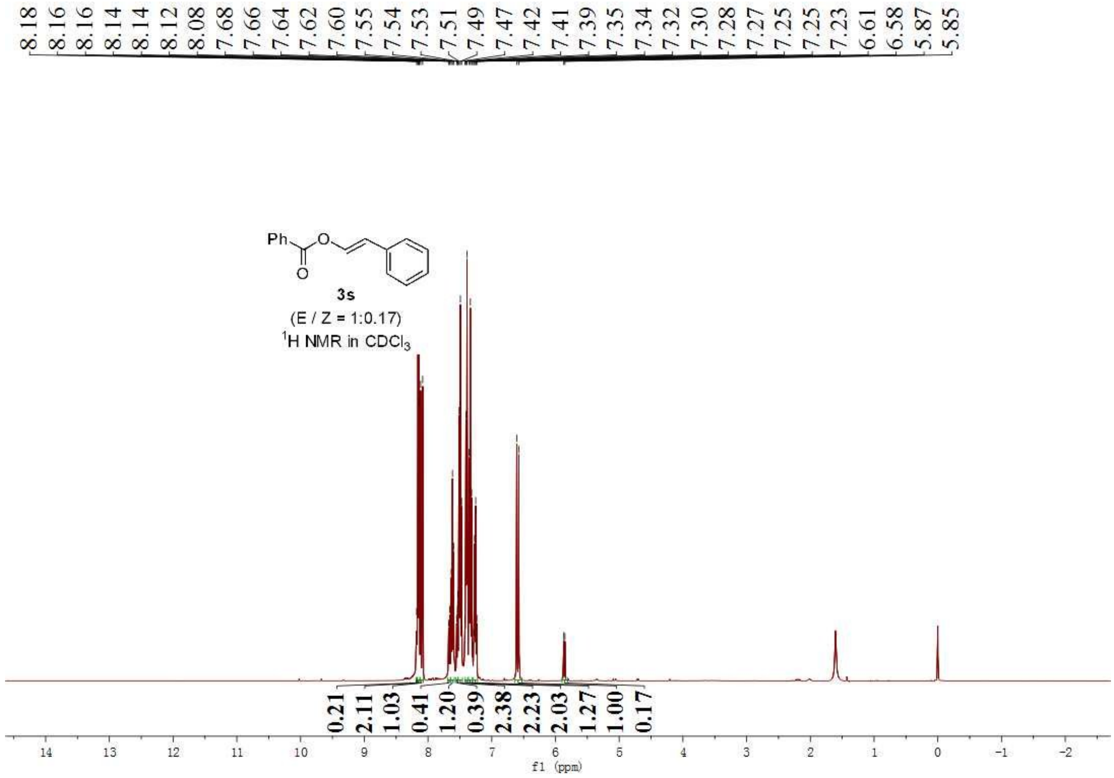
129.51
128.61
127.91
126.60
124.58
120.93
114.83
77.29
77.04
76.79
68.59
O
3r
^{13}C NMR in CDCl$_3$
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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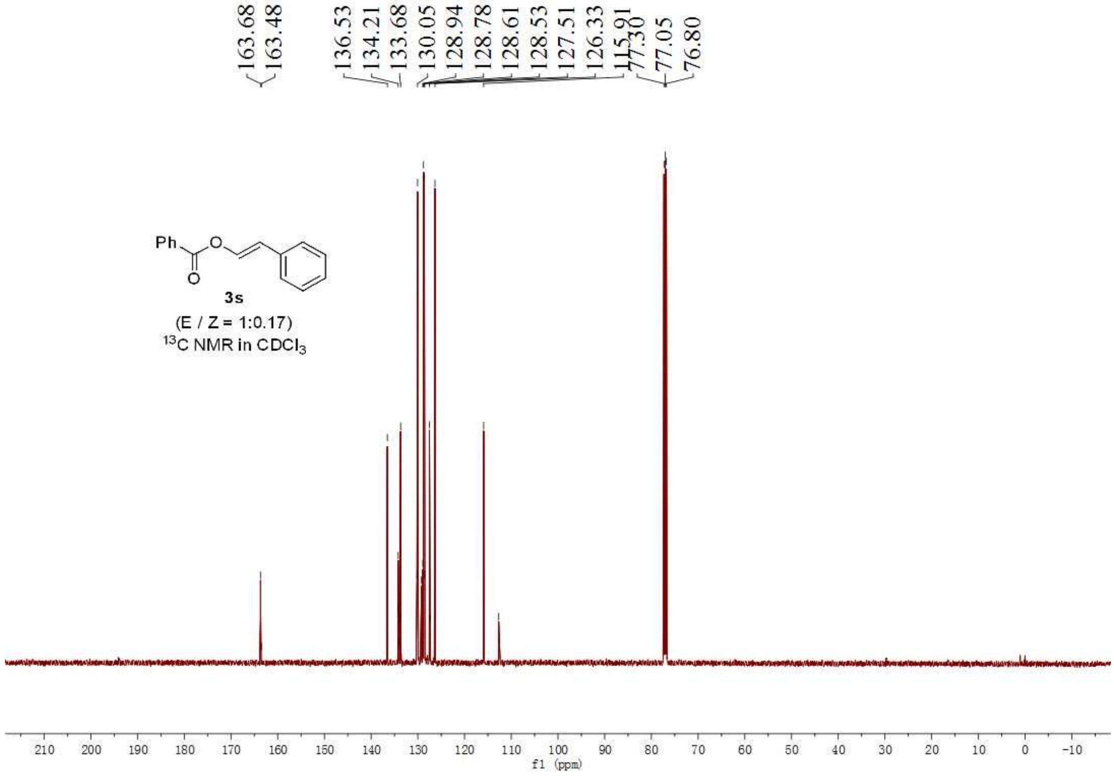
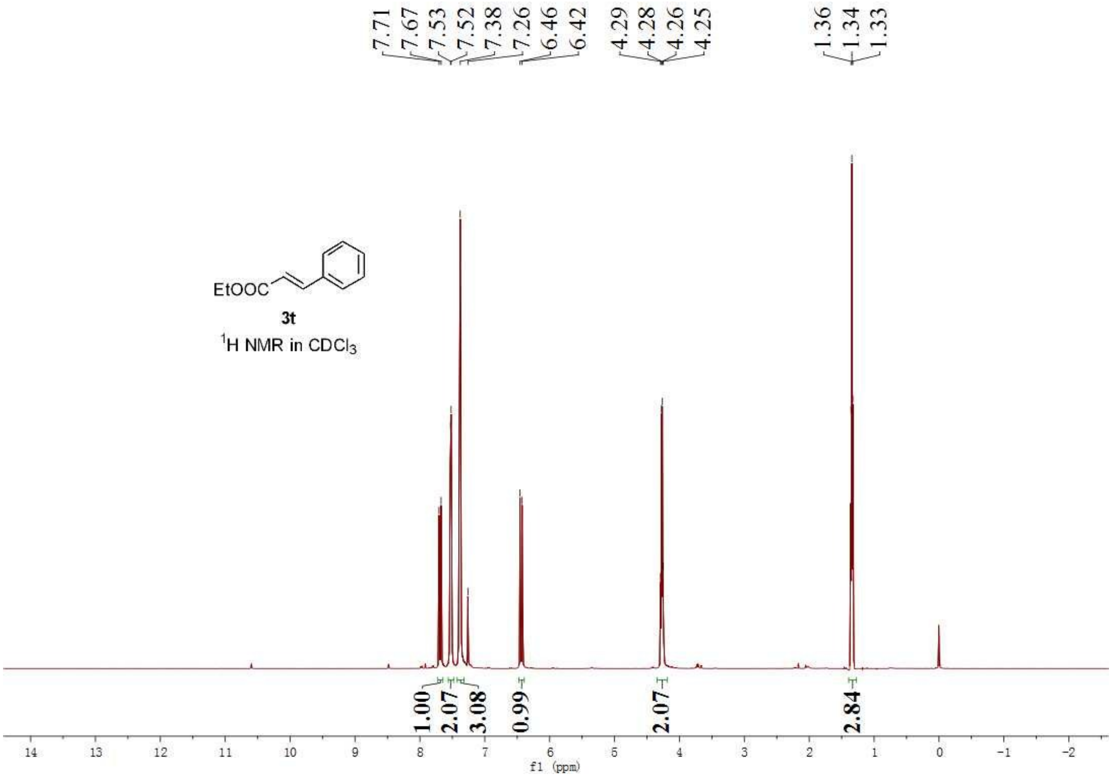
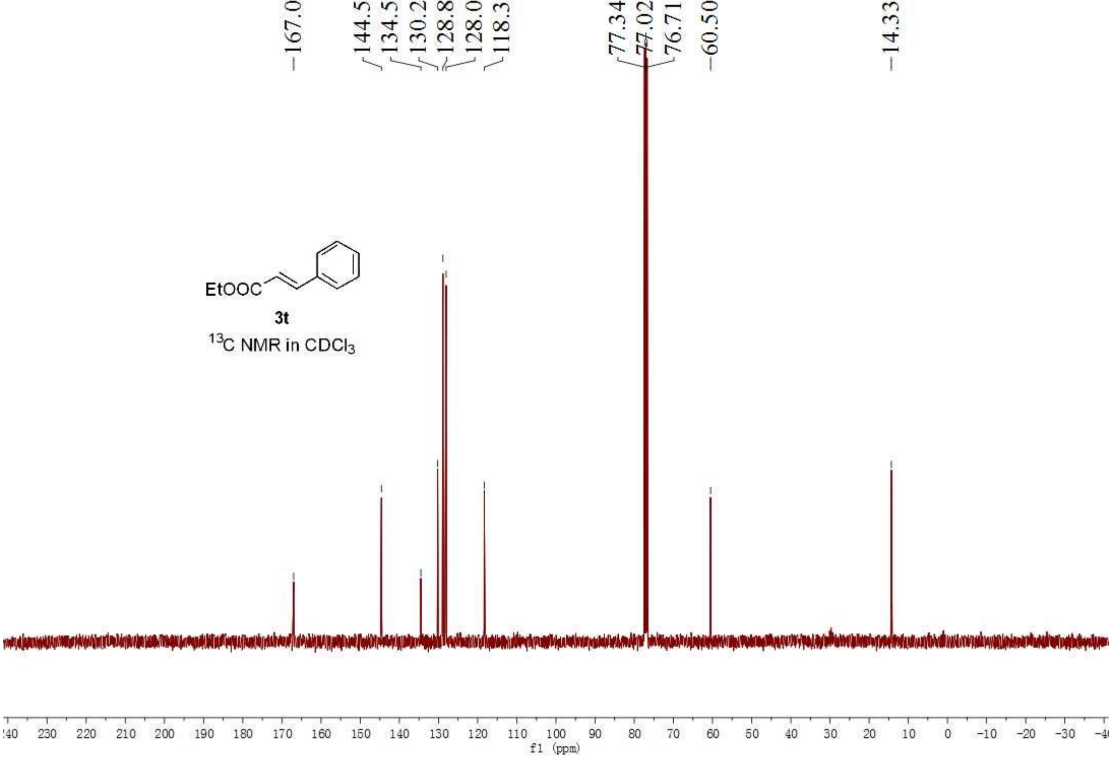
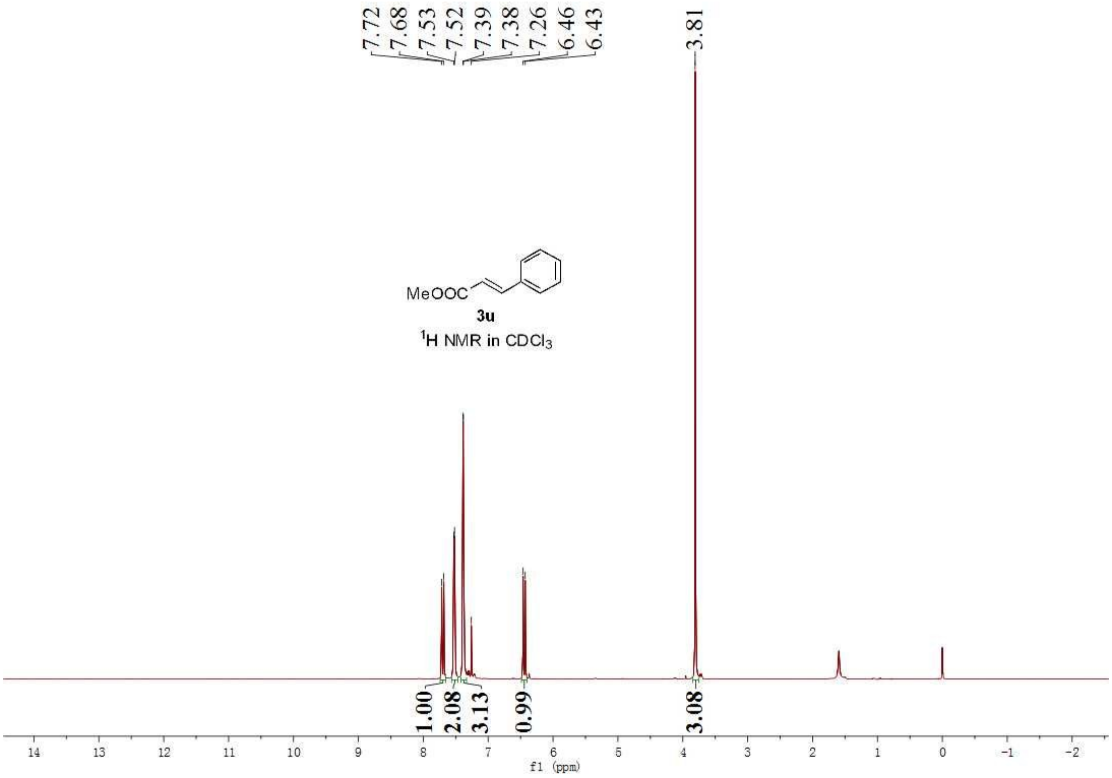
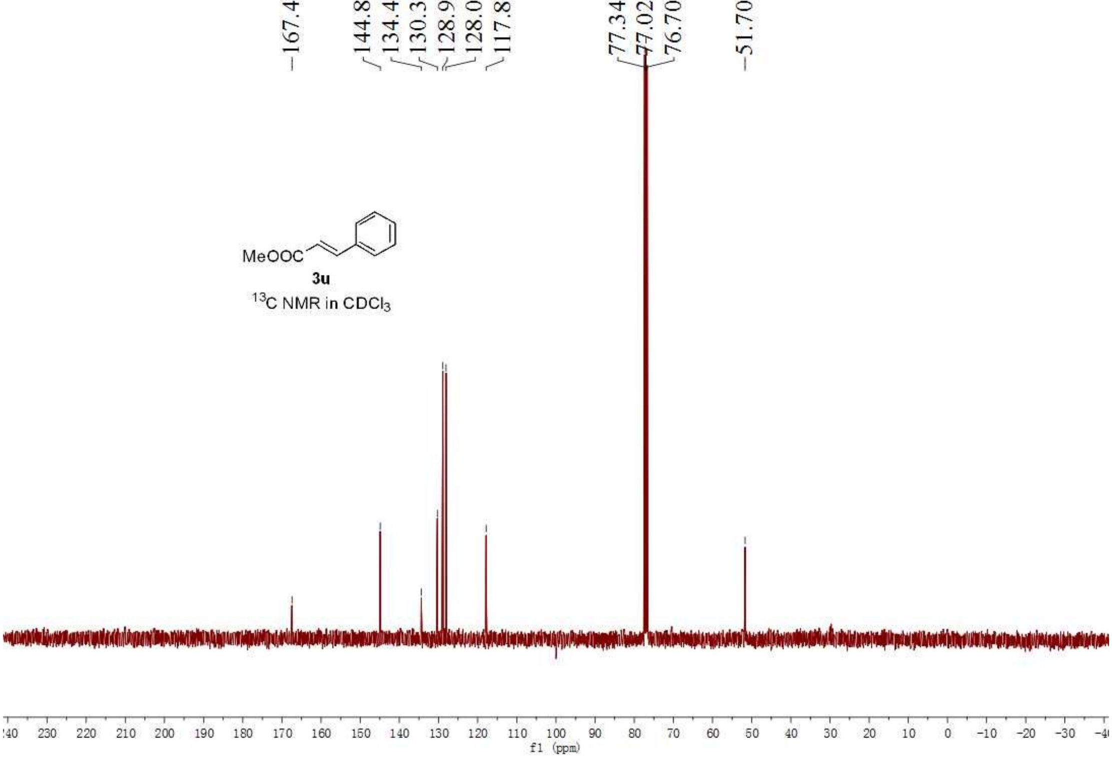
8.16
8.14
8.14
8.12
8.08
7.68
7.66
7.64
7.62
7.60
7.55
7.54
7.53
7.51
7.49
7.47
7.42
7.41
7.39
7.35
7.34
7.32
7.30
7.28
7.27
7.25
7.25
7.23
6.61
6.58
5.87
5.85
Ph
O
O
3s
(E / Z = 1:0.17)
1H NMR in CDCl3
0.21
2.11
1.03
0.41
1.20
0.39
2.38
2.23
2.03
1.27
1.00
0.17
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
f1 (ppm)

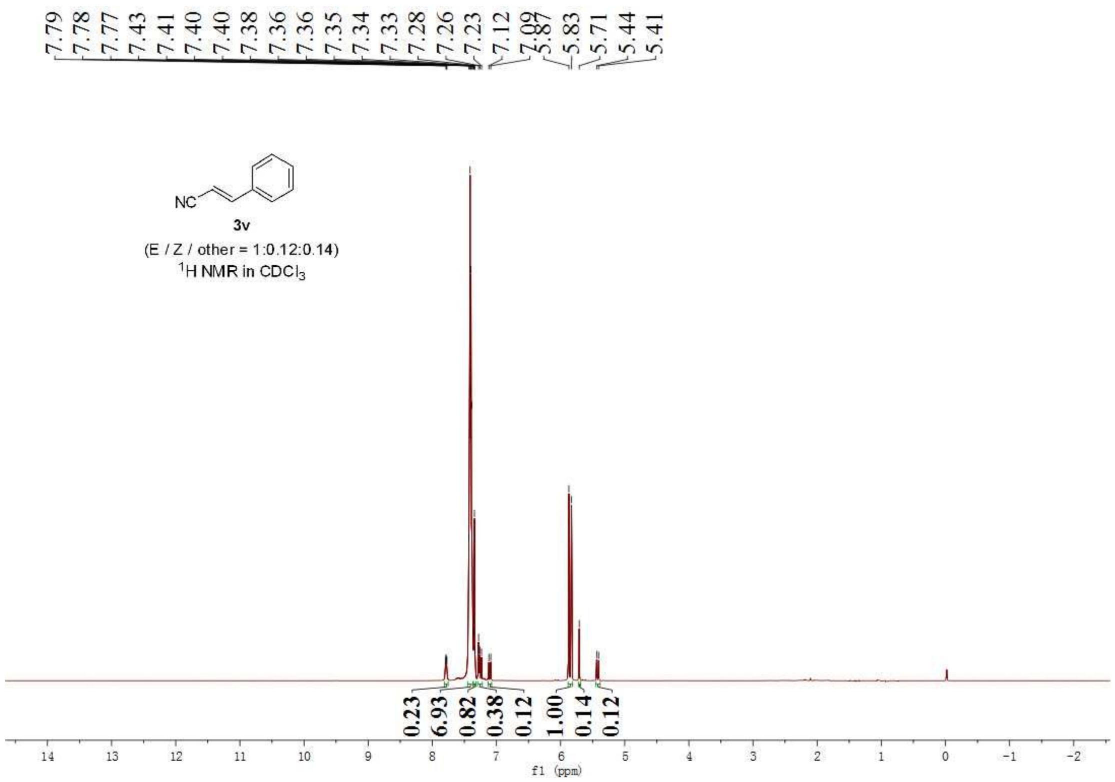

163.68
163.48
136.53
134.21
133.68
130.05
128.94
128.78
128.61
128.53
127.51
126.33
115.91
77.30
77.05
76.80
Ph
O
O
3s
(E / Z = 1:0.17)
13C NMR in CDCl3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


7.71
7.67
7.53
7.52
7.38
7.26
6.46
6.42
4.29
4.28
4.26
4.25
1.36
1.34
1.33
EtOOC
3t
^{1}H NMR in CDCl$_3$
1.00
2.07
3.08
0.99
2.07
2.84
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
−1
−2
f1 (ppm)


−167.00
144.58
134.50
130.21
128.88
128.05
118.32
77.34
77.02
76.71
−60.50
−14.33
EtOOC
3t
^{13}C NMR in CDCl$_3$
240
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
−20
−30
−40
f1 (ppm)


7.72
7.68
7.53
7.52
7.39
7.38
7.26
6.46
6.43
3.81
MeOOC
3u
^{1}H NMR in CDCl$_3$
1.00
2.08
3.13
0.99
3.08
14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2
f1 (ppm)

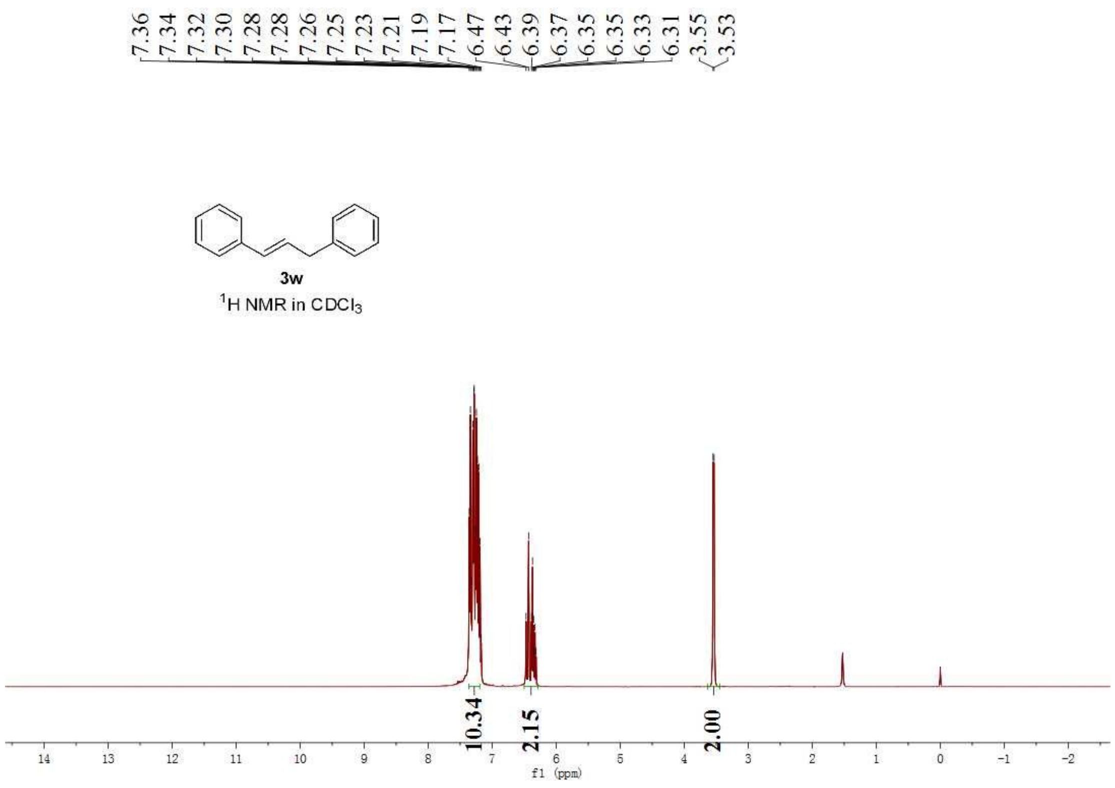

167.43
144.88
134.42
130.30
128.90
128.08
117.83
77.34
77.02
76.70
51.70
MeOOC
3u
^{13}C NMR in CDCl$_3$
240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40
f1 (ppm)



3v

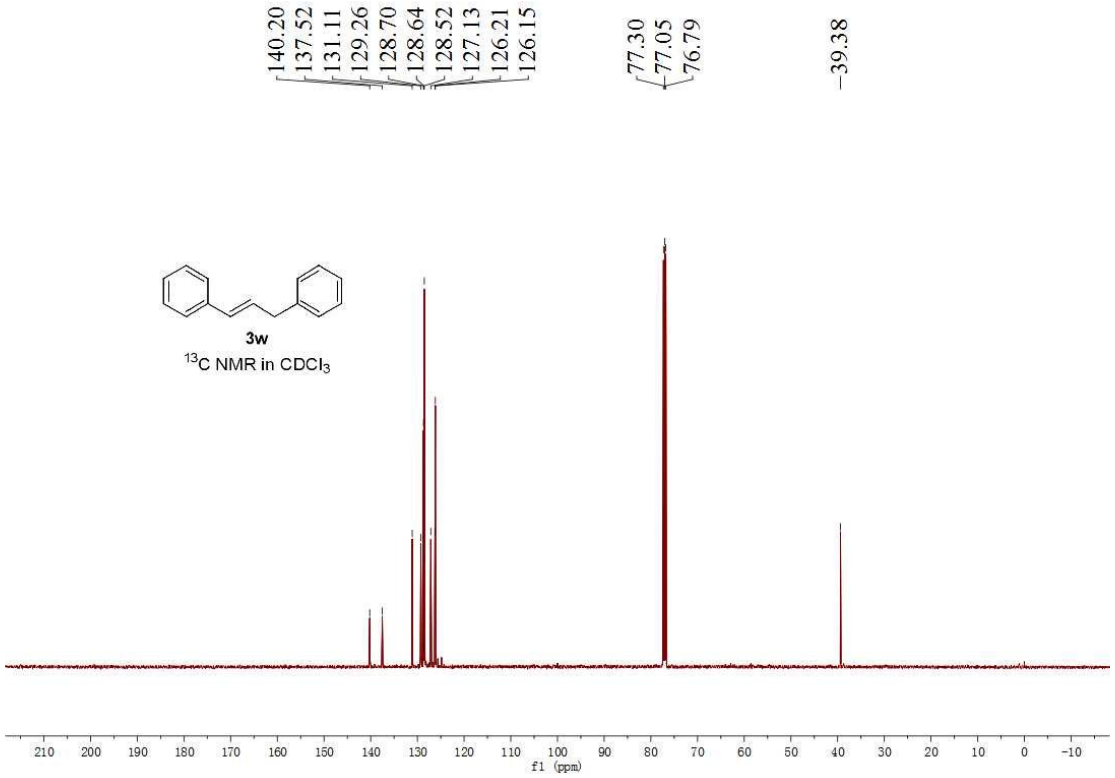
(E / Z / other = 1:0.12:0.14)

^{1}H NMR in CDCl$_3$



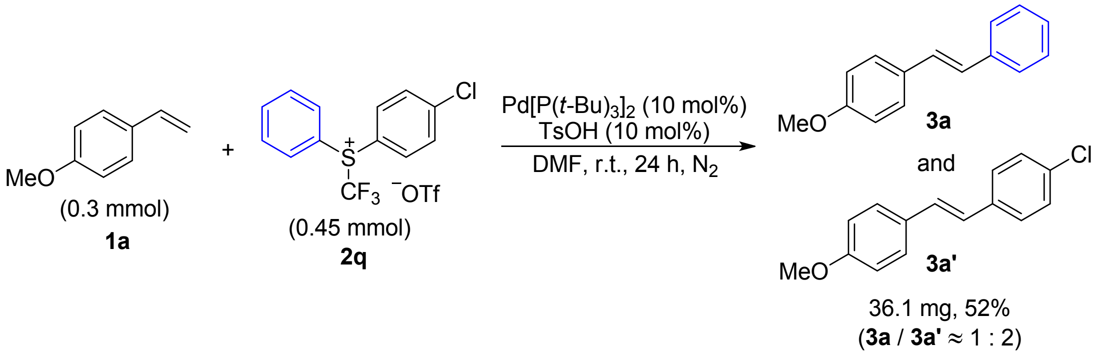
3w

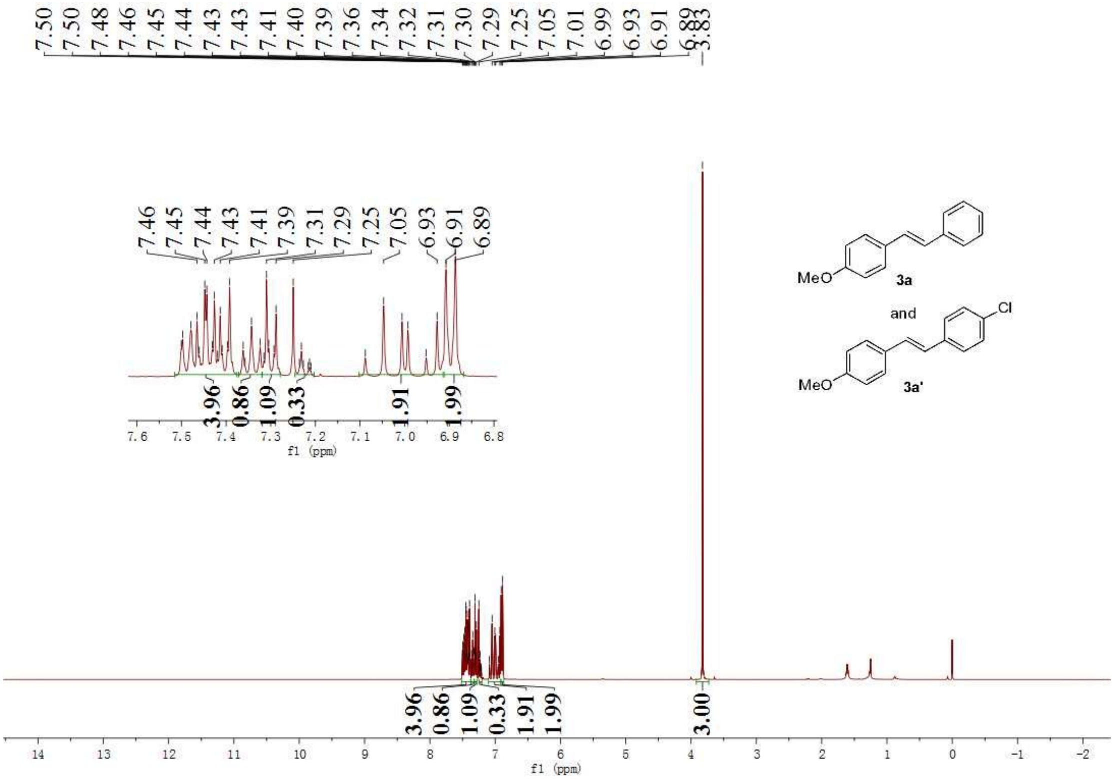
^{1}H NMR in CDCl$_3$

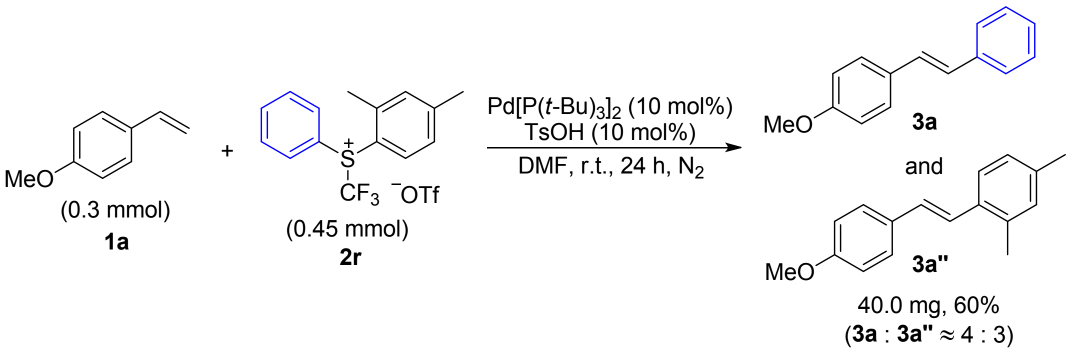

140.20
137.52
131.11
129.26
128.70
128.64
128.52
127.13
126.21
126.15
77.30
77.05
76.79
39.38
3w
^{13}C NMR in CDCl$_3$
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

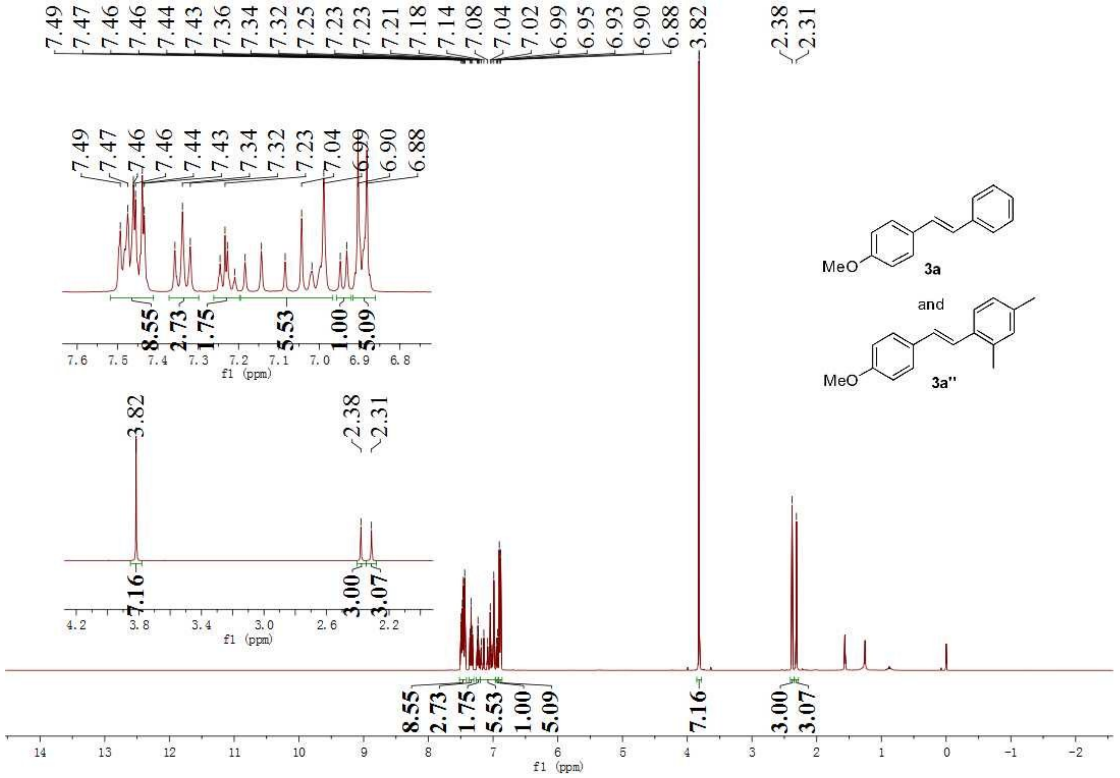
8. Pd-catalyzed Heck-type reaction of non-symmetric arylphenyl trifluoromethyl sulfonium triflate with 1a

Note: The non-symmetric (4-chlorophenyl)(phenyl)(trifluoromethyl)sulfonium triflate (**2q**) and (2,4-dimethylphenyl)(phenyl)(trifluoromethyl)sulfonium triflate (**2r**) were synthesized according to the literature (S. –M. Wang, X. –Y. Wang, H. –L. Qin, C. –P. Zhang, *Chem. Eur. J.* 2016, **22**, 6542-6546)






MeO
(0.3 mmol)
1a
+
S
CF3
−OTf
(0.45 mmol)
2r
Pd[P(t-Bu)3]2 (10 mol%)
TsOH (10 mol%)
DMF, r.t., 24 h, N2
MeO
3a
and
MeO
3a''
40.0 mg, 60%
(3a : 3a'' ≈ 4 : 3)


7.49
7.47
7.46
7.46
7.44
7.43
7.36
7.34
7.32
7.25
7.23
7.23
7.21
7.18
7.14
7.08
7.04
7.02
6.99
6.95
6.93
6.90
6.88
3.82
2.38
2.31
8.55
2.73
1.75
5.53
1.00
5.09
7.6
7.5
7.4
7.3
7.2
7.1
7.0
6.9
6.8
f1 (ppm)
7.16
3.00
3.07
4.2
3.8
3.4
3.0
2.6
2.2
MeO
3a
and
MeO
3a''
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2