Supporting Information

Synthesis of *trans*-Stilbenes via Phosphine-Catalyzed Coupling Reaction of Benzylic Halides

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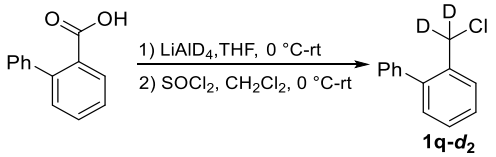
1. General Information

Unless otherwise noted, all reactions were carried out in oven-dried 25-mL Schlenk tubes under a nitrogen atmosphere and IKA plate was used as the heat source. Solvents were purified by standard techniques without special instructions. ^{1}H, ^{13}C and ^{31}P NMR spectra were recorded on either a Bruker Avance II 400 MHz spectrometer (400 MHz for ^{1}H, 100 MHz for ^{13}C, 162 MHz for ^{31}P, 128 MHz for ^{11}B), a Varian Inova 500 MHz spectrometer (500 MHz for ^{1}H, 125 MHz for ^{13}C) or a Bruker Avance NEO 600 MHz spectrometer (600 MHz for ^{1}H, 150 MHz for ^{13}C); $CDCl_3$ and TMS were used as a solvent and an internal standard, respectively. The chemical shifts are reported in ppm downfield (δ) from TMS, the coupling constants *J* are given in Hz. The peak patterns are indicated as follows: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet. IR spectra were recorded on a NEXUS FT-IR spectrometer. High resolution mass spectra were recorded on either a Q-TOF mass spectrometry or a LTQ Orbitrap XL mass spectrometry. X-ray crystallography analysis was performed on a Bruker D8 Venture X-ray diffraction meter. TLC was carried out on SiO_2 (silica gel 60 F_{254}, Merck), and the spots were located with UV light. Flash chromatography was carried out on SiO_2 (silica gel 60, 200-300 mesh). Unless otherwise noted, starting materials are commercially available. All the physical measurements were performed in THF including electronic absorption (UV-vis) and fluorescence spectra. The fluorescence decay curves were recorded at room temperature using nitrogen laser as excitation source. The lifetimes were estimated from the measured fluorescence decay using iterative fitting procedure. $E_{1/2}$ vs Fc^{+}/Fc was estimated by cyclic voltammetric method using carlxm elcctrcxle as a working electrode, platinum wire as a counter electrode, and Ag/AgCl electrode as a reference electrode with the solution dissolved in CH_2Cl_2 (0.01 M) using 0.1 M of Bu_4NPF_6 as a supporting electrolyte with a scan rate of 100 mV/s and all the potentials were calibrated with ferrocene, ($E_{1/2}$ (Fc/Fc^{+}) = 0.63V vs NHE) as an external standard[1].

2. Synthesis of the Starting Materials

Procedure for Preparation of Benzyl Chloride 1q-d_2[2]

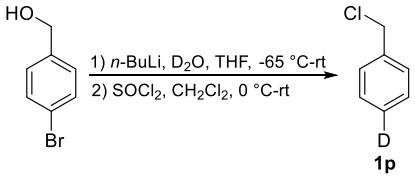


1q-d_2

To a solution of 2-biphenylcarboxylic acid (198.4 mg, 1.0 mmol) in 5.0 mL of anhydrous THF at 0 °C, lithium aluminum deuteride ($LiAlD_4$) (96 mg, 2.5 mmol) was slowly added in portions. The reaction mixture was slowly warmed to room temperature and stirred for 12 h. After carefully quenched by NaOH (2.0 mL, 2.0 M) and washed with brine, the combined organic layers were dried over Na_2SO_4, filtrated. The solvent was removed by evaporation under vacuum to afford a crude product, which was directly used for chlorination without purification.

To a solution of the crude product in CH_2Cl_2 (5.0 mL) at 0 °C, $SOCl_2$ (0.18 g, 0.11 mL, 1.5 mmol) was slowly added dropwise via syringe. The reaction mixture was slowly warmed to room temperature and stirred for 12 h. After washed with saturated $NaHCO_3$ (aq.) and brine, the combined organic layers were dried over Na_2SO_4, filtrated, and then concentrated under vacuum to afford a crude product. The crude product was purified by silica gel column chromatography (eluent: *n*-hexane/ethyl acetate = 20/1) to give **1q-*d*$_2$** as a colorless liquid (187.7 mg, 91% yield). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.60–7.56 (m, 1H), 7.48–7.37 (m, 7H), 7.35–7.30 (m, 1H); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 142.1, 140.2, 134.9, 130.5, 130.4, 129.2, 128.6, 128.3, 128.0, 127.5, 44.0 (m).

Procedure for Preparation of Benzyl Chloride 1p



1p

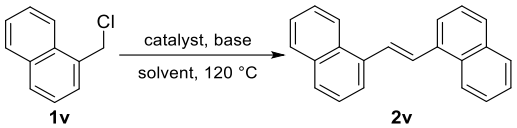
A solution of 2.5 M *n*-butyllithium (30 mmol, 12 mL) in hexane was slowly added to a solution of 4-bromobenzenemethanol (10 mmol, 1.87 g) in THF (35 mL) at -65 °C. After stirring for 30 min at -65 °C, deuterium oxide (13.5 mmol, 2.7 mL) was added carefully and the temperature of the reaction solution was maintained at -65 °C. After the dropwise addition, the mixture was warmed to room temperature and was extracted with toluene. The combined organic layers were washed with water and dried with $MgSO_4$. The solvent was removed by evaporation under vacuum to give a crude product. The crude product was purified by silica gel column chromatography (eluent: *n*-hexane/ethyl acetate = 5/1) to afford the product as a colorless liquid.

To a solution of the above product in CH_2Cl_2 (50 mL) at 0 °C, $SOCl_2$ (1.78 g, 1.1 mL, 15 mmol) was slowly added dropwise via syringe. The reaction mixture was slowly warmed to room temperature and stirred overnight. After washed with saturated

$NaHCO_3$ (aq.) and brine, the combined organic layers were dried over Na_2SO_4, filtrated, and then concentrated under vacuum to give a crude product. The crude product was purified by silica gel column chromatography (eluent: *n*-hexane) to afford the **1p** as a colorless liquid (1.26 g, 99% yield). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.46–7.36 (m, 4H), 4.63 (s, 2H); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 137.5, 128.63, 128.57, 128.1 (m), 46.3; HRMS (EI) m/z calcd for C_7H_6DCl $[M]^+$: 127.0299, found: 127.0291.

3. Optimization of Reaction Conditions

Table S1. Optimization of reaction conditions for phosphine−catalyzed coupling of 1-chloromethylnaphthalene.[a]

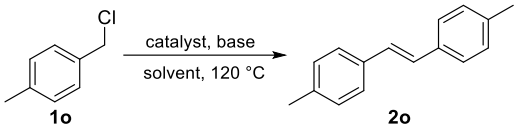


Entry	Catalyst	Base	Solvent	Yield [%][b]
1[c]	PCy_3	CsF	1,4-dioxane	33 (33)
2	PCy_3	CsF	1,4-dioxane	15
3	PCy_3	*t*-BuONa	1,4-dioxane	7
4	PCy_3	NaH	1,4-dioxane	90[d]
5	PCy_3	$NaN(SiMe_3)_2$	1,4-dioxane	5
6	PCy_3	*t*-BuOLi	1,4-dioxane	trace
7[c]	$Ni(PCy_3)_2Cl_2$	CsF	1,4-dioxane	33
8	/	NaH	1,4-dioxane	17
9	PPh_3	NaH	1,4-dioxane	28
10	$POPh_3$	NaH	1,4-dioxane	17
11	$POCy_3$	NaH	1,4-dioxane	34
12	$P(OPh)_3$	NaH	1,4-dioxane	8
13[e]	PCy_3	NaH	1,4-dioxane	62
14[f]	PCy_3	NaH	1,4-dioxane	63
15[g]	PCy_3	NaH	1,4-dioxane	42
16[h]	PCy_3	NaH	1,4-dioxane	82
17[i]	PCy_3	NaH	1,4-dioxane	77
18[j]	PCy_3	NaH	1,4-dioxane	53
19	PCy_3	NaH	THF	86
20[k]	PCy_3	NaH	THF	90 (88)
21[l]	PCy_3	NaH	THF	80

[a] Reaction condition: 1-(chloromethyl)naphthalene (**1v**, 0.6 mmol), catalyst (20 mol%) and base (3.0 equiv) in dry solvent (5.0 mL) at 120 °C under N_2 atmosphere for 24 h. [b] Determined by ^{1}H NMR using 1,3,5-trimethoxybenzene as an internal standard. Isolated yield is given in parentheses. [c] $B(OMe)_3$ (1.5 equiv) was used as the additive. [d] Product could not be purified due to residual

1,4-dioxane. [e] 15 mol% catalyst was used. [f] 2.0 equiv of base was used. [g] 1.2 equiv of base was used. [h] 100 ºC. [i] 80 ºC. [j] 60 ºC. [k] 2.0 mL of THF was used for 12 h. [l] 8.0 mL of THF was used.

Table S2. Optimization of reaction conditions for phosphine−catalyzed coupling of 4-methylbenzyl chloride.[a]

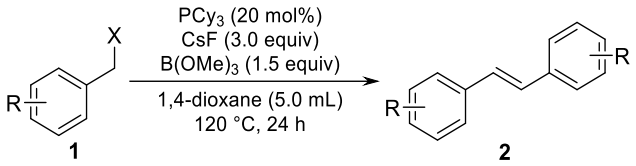


Entry	Phosphine	Base	Solvent	Yield [%][b]
1[c]	PCy_3	CsF	1,4-dioxane	58
2	PCy_3	CsF	1,4-dioxane	39
3	PCy_3	^{t}BuOK	1,4-dioxane	/
4	PCy_3	^{t}BuONa	1,4-dioxane	3
5	PCy_3	NaH	1,4-dioxane	82
6[d]	PCy_3	NaH	1,4-dioxane	68
7	PCy_3	NaH	DCM	/
8	PCy_3	NaH	DMF	/
9	PCy_3	NaH	DMSO	/
10	PCy_3	NaH	Et_2O	27
11	PCy_3	NaH	MTBE	40
12	PCy_3	NaH	DME	76
13	PCy_3	NaH	THF	62
14	PCp_3	NaH	1,4-dioxane	36
15	PAd_3	NaH	1,4-dioxane	24
16[e]	PCy_3	NaH	1,4-dioxane	86
17[e,f]	PCy_3	NaH	1,4-dioxane	89 (86)

[a] Reaction condition: 1-(chloromethyl)-4-methylbenzene (**1o**, 0.6 mmol), catalyst (20 mol%) and base (3.0 equiv) in dry solvent (5.0 mL) at 120 °C under N_2 atmosphere for 24 h. [b] Determined by ^{1}H NMR using 1,3,5-trimethoxybenzene as an internal standard. Isolated yield is given in parentheses. [c] $B(OMe)_3$ (1.5 equiv) was used as the additive. [d] 1.5 equiv of base was used. [e] 1,3,5-trimethoxybenzene (1.5 equiv) was used as the additive. [f] 2.0 mL of 1,4-dioxane was used for 12 h.

4. Detailed Investigation of the Functional Group Compatibility

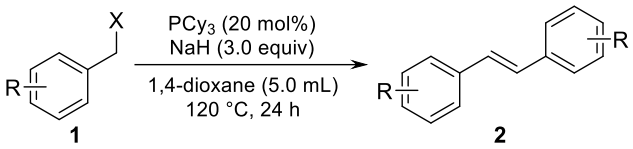
Table S3. Investigation of the functional group compatibility in the presence of CsF and $B(OMe)_3$ as base and additive, respectively (Condition A).[a]



Product	R	Yield [%][b]	Dechlorination product [%][c]	Methoxy substituted product [%][c]	Alkyl-alkyl coupling product [%][c]
2a[d]	3-F	84	12	0	0
2b	3-Br	94(57[e])	3(10[e])	0(22[e])	0(5[e])
2c	2-Br	62(61[e])	24(12[e])	7(21[e])	0(4[e])
2d	4-Br	41	52	3	0
2e	3-Cl	75	21	2	0
2f	2-Cl	30	17	42	5
2g	4-Cl	15	20	51	7
2h	4-H	61	25	6	0
2i[f]	4-CN	41	41	6	4
2j[f]	4-OOCMe	67	30	1	0
2k	3-OMe	75	4	15	1
2l[f]	4-CF_3	76	3	21	0
2m	2-Me	49	8	34	3
2n	3-Me	52	12	29	1
2o	4-Me	58	5	31	2
2p	4-D	63	23	8	0
2q	2-Ph	81	9	5	0
2r	2-naphthyl	86	9	4	0
2s	9-phenanthryl	67	30	1	0
2t[d]	3-thienyl	63	29	8	0
2u[d]	2-thienyl	40	31	22	3
2v	1-naphthyl	33	10	52	2
2w	4-vinyl	0	54	43	3
2x	4-Ph	0	40	52	8
2y	4-OMe	0	47	50	3
2z	4-F	0	53	44	3
2α	Cinnamyl	0	43	55	2

[a] Reaction condition: benzyl chlorides (0.6 mmol), PCy_3 (20 mol%), CsF (3.0 equiv), $B(OMe)_3$ (1.5 equiv) in dry 1,4-dioxane (5.0 mL) at 120 ℃ under N_2 atmosphere. [b] Isolated yields. [c] Yields determined by ^1H NMR using 1,3,5-trimethoxybenzene as an internal standard. [d] Run for 4 h. [e] Benzyl bromides (0.6 mmol) instead of benzyl chlorides. [f] Run for 12 h.

Table S4. Investigation of the functional group compatibility in the presence of NaH as a base (Condition B).[a]

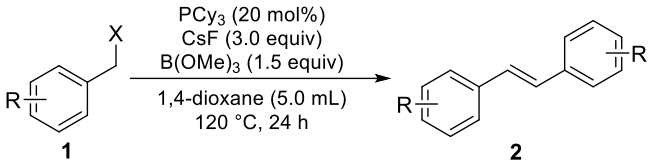


Product	R	Yield [%][b]	Dechlorination product [%][c]	Alkyl-alkyl coupling product [%][c]
2a	3-F	16	79	1
2b	3-Br	51(45[d])	32 (43[d])	8(5[d])
2c	2-Br	49(42[d])	37(47[d])	5(3[d])
2d[e]	4-Br	0	85	15
2e	3-Cl	35	56	2
2f	2-Cl	80	15	2
2g	4-Cl	75	21	1
2h	4-H	70	27	1
2i[e]	4-CN	0	82	18
2j[e]	4-OOCMe	0	65	35
2k	3-OMe	89	9	0
2l	4-CF_3	82	11	2
2m	2-Me	74	12	6
2n	3-Me	84	7	3
2o[f,g]	4-Me	86	10	2
2p	4-D	74	22	0
2q	2-Ph	66	21	6
2r	2-naphthyl	33	51	8
2s[e]	9-phenanthryl	0	89	11
2t[e]	3-thienyl	0	27	73
2u[e]	2-thienyl	0	31	69
2v[h]	1-naphthyl	88	9	0
2w[e]	4-vinyl	0	98	2
2x[e]	4-Ph	0	91	9
2y[e]	4-OMe	0	78	22
2z[e]	4-F	0	82	18
2α[e]	Cinnamyl	0	92	8

[a] Reaction condition: benzyl chlorides (0.6 mmol), PCy_3 (20 mol%), NaH (3.0 equiv) in dry 1,4-dioxane (5.0 mL) at 120 °C under N_2 atmosphere for 24 h. [b] Isolated yields. [c] Yields determined by ^1H NMR using 1,3,5-trimethoxybenzene as an internal standard. [d] benzyl bromides (0.6 mmol) instead of benzyl chlorides. [e] Run for 12 h. [f] 1,3,5-trimethoxybenzene (1.5 equiv) was used as the additive. [g] 1,4-Dioxane (2.0 mL) was used for 12 h. [h] THF (2.0 mL) was used instead of 1,4-dioxane for 12 h.

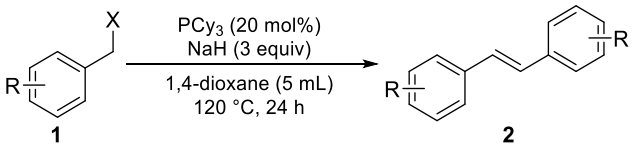
5. General Procedure for Phosphine-Catalyzed Coupling of Benzylic Halides

Condition A



An oven-dried 25-mL Schlenk tube was charged with a mixture of benzyl chloride (**1**, 0.6 mmol, 1.0 equiv), PCy_3 (34 mg, 0.12 mmol, 20 mol%), CsF (273 mg, 1.8 mmol, 3.0 equiv), $B(OMe)_3$ (100 μL, 0.9 mmol, 1.5 equiv) and dry 1,4-dioxane (5.0 mL) under N_2 atmosphere. The reaction mixture was stirred at 120 °C for a certain period, and then cooled to room temperature. The solvent was removed under reduced pressure and the crude product was purified by silica gel column chromatography with *n*-hexane as eluent to afford the desired product **2**.

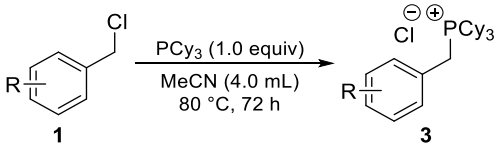
Condition B



An oven-dried 25-mL Schlenk tube was charged with a mixture of benzyl chloride (**1**, 0.6 mmol, 1.0 equiv), PCy_3 (34 mg, 0.12 mmol, 20 mol%), NaH (44 mg, 1.8 mmol, 3.0 equiv) and dry 1,4-dioxane (5.0 mL) or dry THF (5.0 mL) under N_2 atmosphere. The reaction mixture was stirred at 120 °C for a certain period, and then cooled to room temperature. The solvent was removed under reduced pressure and the crude product was purified by silica gel column chromatography with *n*-hexane as eluent to afford the desired product **2**.

6. Mechanistic Studies

1) Synthesis of phosphonium salts and ylide and ^{31}P NMR spectra



An oven-dried 25-mL Schlenk tube was charged with a mixture of tricyclohexylphosphine (0.99 g, 3.53 mmol, 1.0 equiv), acetonitrile (4.0 mL) and benzyl chloride **1** (3.55 mmol, 1.0 equiv) under N_2 atmosphere. The reaction mixture was

stirred at 80 ℃ for 3 days. The solvent was removed under reduced pressure, the pale yellow sticky residue was dissolved in chloroform (2.0 mL), and diethyl ether (15 mL) was added dropwise. At the beginning, a sticky precipitate was formed at the bottom of the bottle, and after a few minutes of shaking, a large amount of white powder was precipitated. The powder was separated by filtration and dried in vacuum at room temperature for 4 h. Phosphonium salts **3a**, **3h**, **3k**, **3v**, and **3w** were obtained and ^{31}P NMR spectra were shown as below, respectively (Figures S1-S6).

^{31}P NMR, 162 MHz, $CDCl_3$

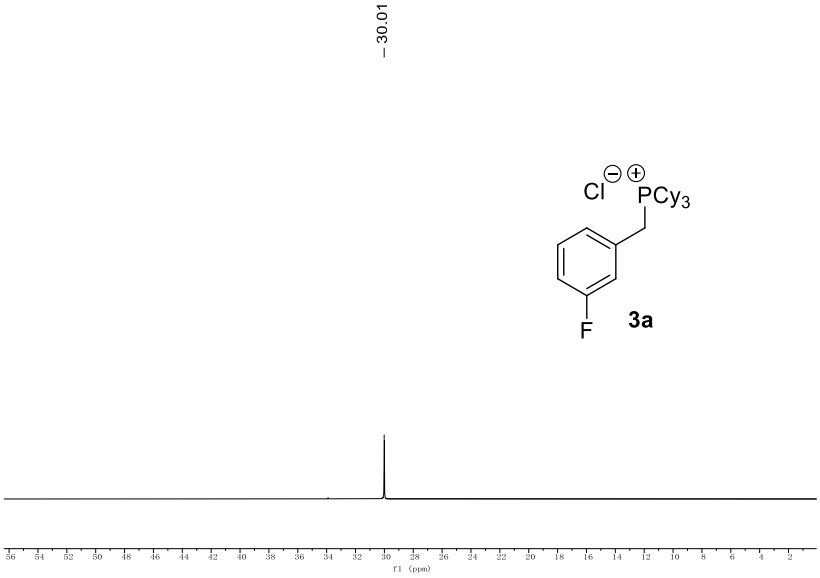


Figure S1. ^{31}P NMR spectrum of **3a** in $CDCl_3$.

^{31}P NMR, 162 MHz, 1,4-dioxane

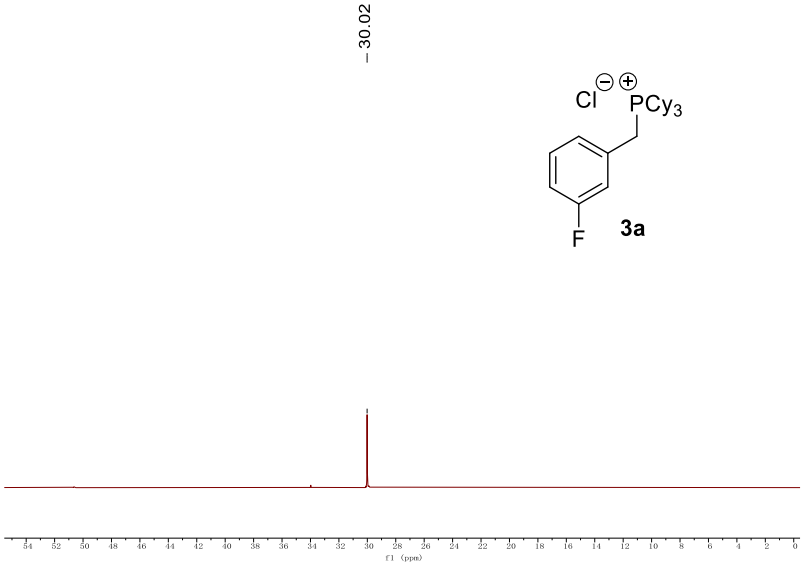


Figure S2. ^{31}P NMR spectrum of **3a** in 1,4-dioxane.

^{31}P NMR, 162 MHz, $CDCl_3$

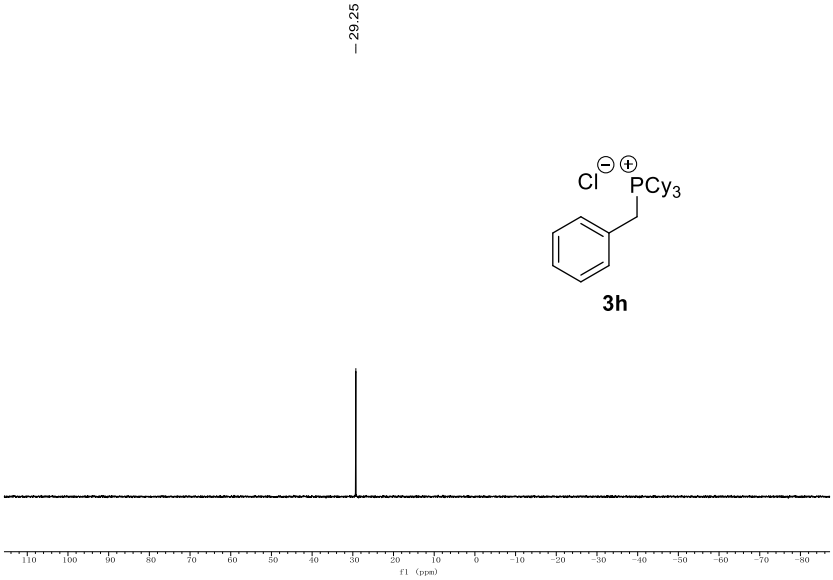


Figure S3. ^{31}P NMR spectrum of **3h**.

^{31}P NMR, 162 MHz, $CDCl_3$

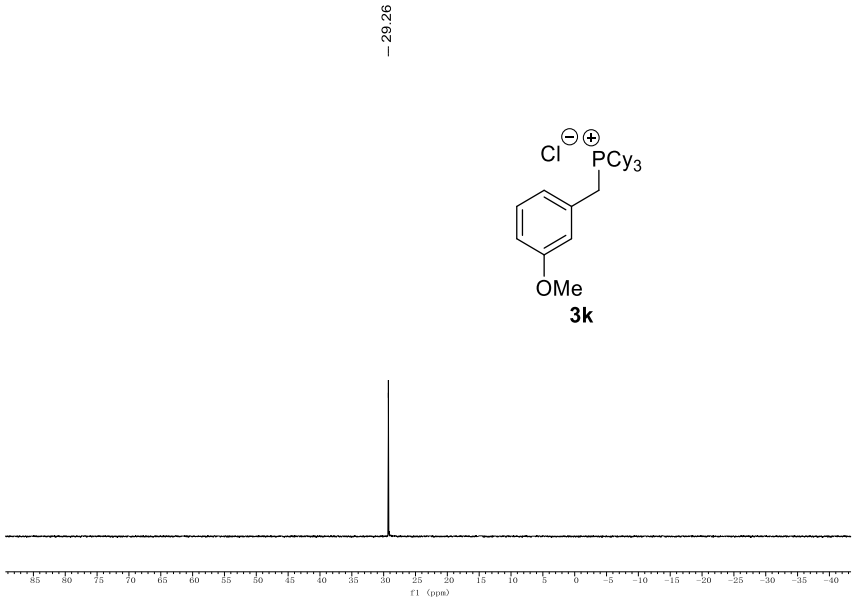


Figure S4. ^{31}P NMR spectrum of **3k**.

^{31}P NMR, 162 MHz, $CDCl_3$

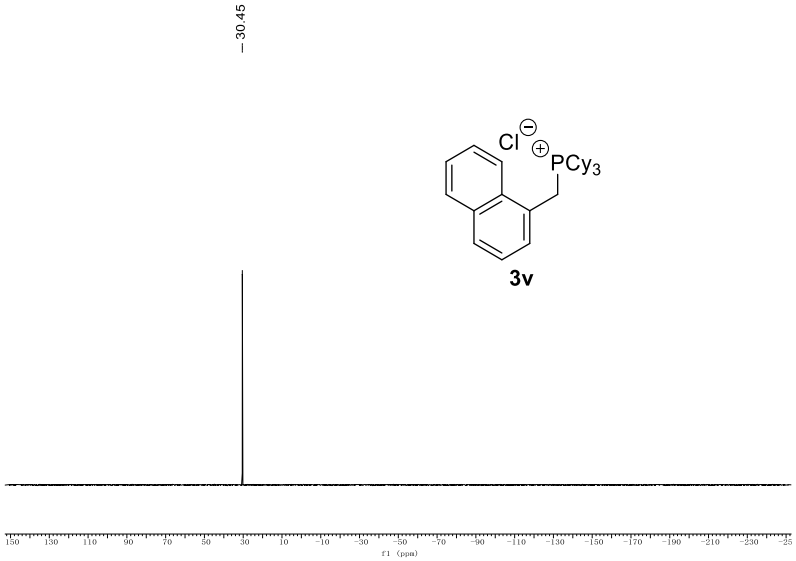


Figure S5. ^{31}P NMR spectrum of **3v**.

^{31}P NMR, 162 MHz, $CDCl_3$

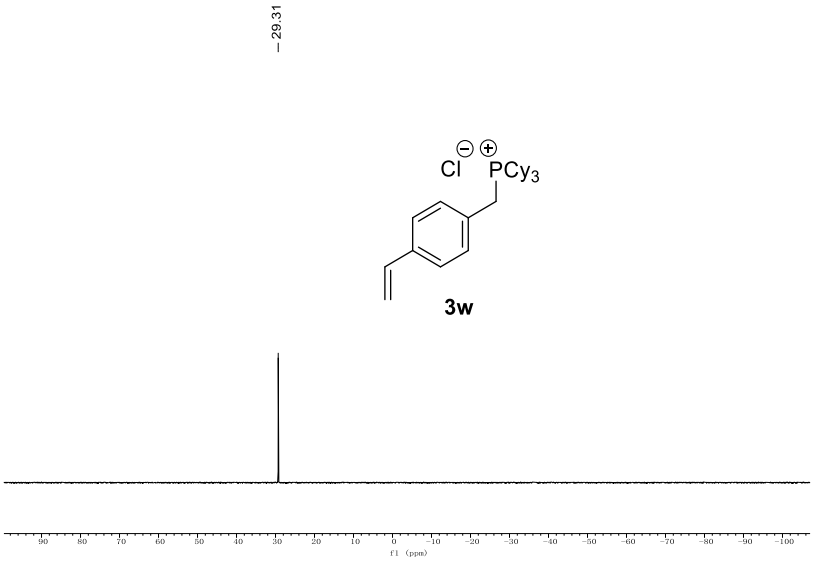
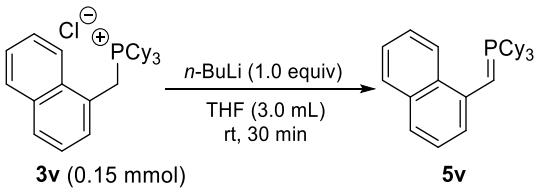


Figure S6. ^{31}P NMR spectrum of **3w**.



An oven-dried 25-mL Schlenk tube was charged with a mixture of **3v** (68.5 mg, 0.15 mmol) and THF (3.0 mL) under N_2 atmosphere. And *n*-BuLi (2.5 M, 17 μL, 0.15 mmol) was added dropwise at 0 °C, after the dropwise addition, the reaction solution was slowly returned to room temperature for 30 min. 0.1 mL of solution was transferred

from the Schlenk tube to N_2-filled NMR tube through syringe under N_2 atmosphere, and diluted with 0.4 mL of dry THF. Then the NMR tube was subjected to a ^{31}P NMR test. The result was shown in Figure S7.

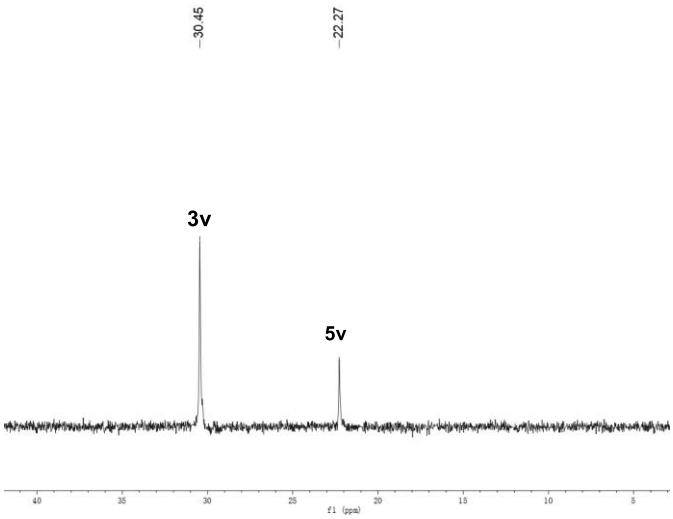
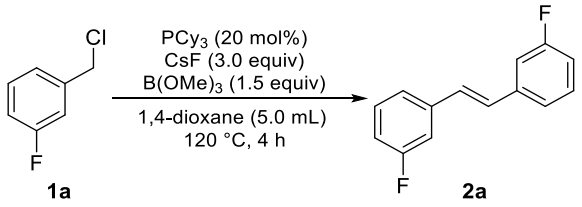


Figure S7. The formation of ylide **5v** from benzyl phosphonium salt **3v**.

2) ^{31}P NMR tracking on the transformation of 1a under Condition A



An oven-dried 25-mL Schlenk tube was charged with a mixture of 1-(chloromethyl)-3-fluorobenzene (72 μL, 0.6 mmol), PCy_3 (34 mg, 0.12 mmol), CsF (273 mg, 1.8 mmol), $B(OMe)_3$ (100 μL, 0.9 mmol) and dry 1,4-dioxane (5.0 mL) under N_2 atmosphere, and 0.1 mL of solution was transferred from the Schlenk tube to N_2-filled NMR tube through syringe under N_2 atmosphere, and diluted with 0.4 mL of dry 1,4-dioxane. Then the NMR tube was subjected to a ^{31}P NMR test and spectrum (t = 0 h) was obtained. The reaction mixture was stirred at 120 °C, subsequently, sampling was performed by taking 0.1 mL of solution from Schlenk tube and diluting with 0.4 mL of dry 1,4-dioxane each time, and ^{31}P NMR spectra were collected at 1.5 h, 3 h, and 4 h. The results were shown in Figure S8.

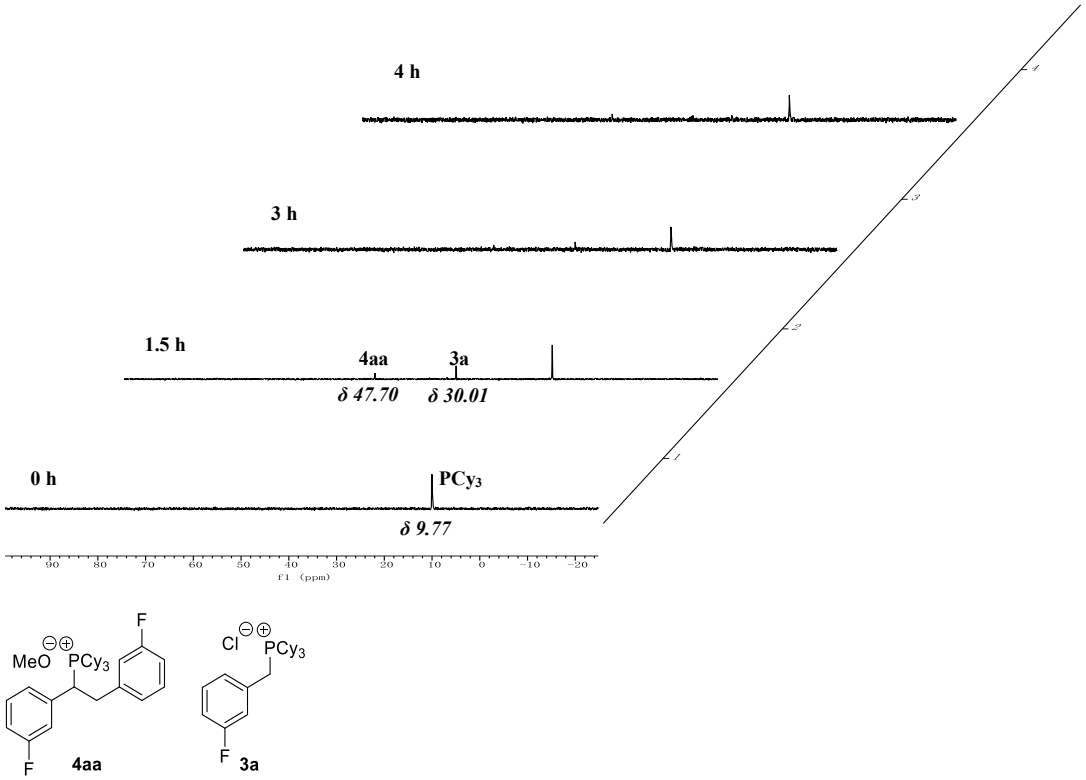


Figure S8. Time-stacked in situ ^{31}P NMR spectra (1,4-dioxane) at t = 0 h, 1.5 h, 3 h, and 4 h.

An oven-dried 25-mL Schlenk tube was charged with a mixture of 1-(chloromethyl)-3-fluorobenzene (72 μL, 0.6 mmol), PCy_3 (34 mg, 0.12 mmol), CsF (546 mg, 3.6 mmol), $B(OMe)_3$ (200 μL, 1.8 mmol) and dry 1,4-dioxane (5.0 mL) under N_2 atmosphere. The reaction mixture was stirred at 120 °C for 4 h, and then cooled to room temperature. 0.1 mL of solution was transferred from the Schlenk tube to N_2-filled NMR tube through syringe under N_2 atmosphere, and diluted with 0.4 mL of dry 1,4-dioxane. Then the NMR tube was subjected to a ^{31}P NMR test and spectrum was obtained in Figure S9. Meanwhile, an aliquot taken from the reaction mixture (4 h) was analyzed by HRMS using electrospray ionization (ESI) method. The result was shown in Figure S10. The cation signal at m/z = 389.2787 would correspond to tricyclohexyl(3-fluorobenzyl)phosphonium, combined with ^{31}P NMR spectrum, it represents tricyclohexyl(3-fluorobenzyl)phosphonium chloride intermediate **3a**. Another cation signal at m/z = 497.3150 would correspond to (1,2-bis(3-fluorophenyl)ethyl)tricyclohexylphosphonium, combined with ^{31}P NMR spectrum and literature (P. A. Byrne, D. G. Gilheany, *Chem. Eur. J.* **2016**, *22*, 9140-9154), it represents (1,2-bis(3-fluorophenyl)ethyl)tricyclohexylphosphonium methanolate intermediate **4aa**.

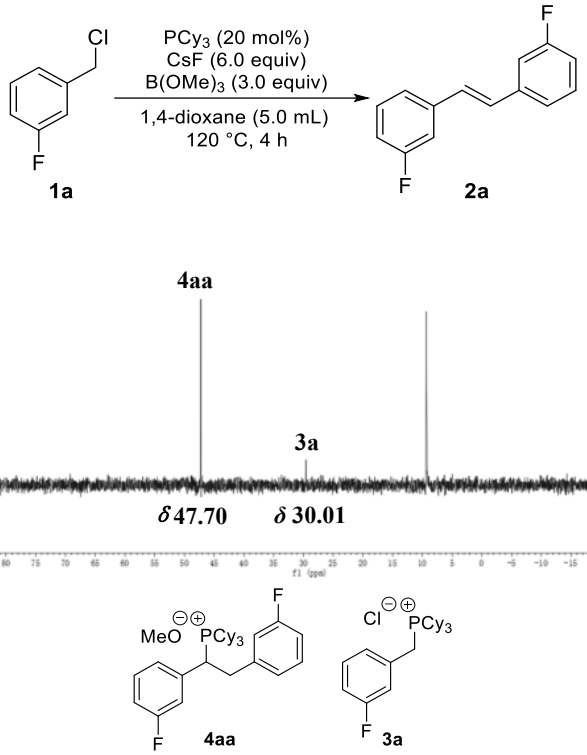


Figure S9. ^{31}P NMR spectrum (1,4-dioxane) of **1a** reaction mixture at t = 4 h in the presence of CsF as base.

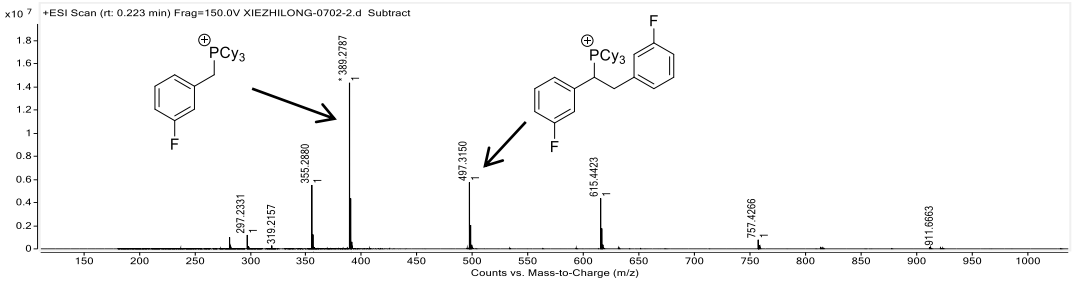
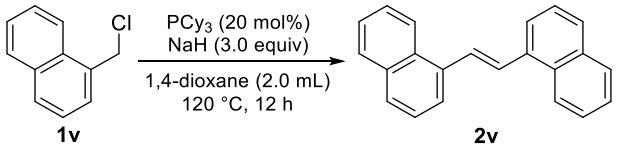


Figure S10. HRMS analysis of **1a** reaction mixture at t = 4 h in the presence of CsF as base.

3) ^{31}P NMR tracking on the transformation of 1v under Condition B



An oven-dried 25-mL Schlenk tube was charged with a mixture of 1-chloromethylnaphthalene (318 mg, 1.8 mmol), PCy_3 (102 mg, 0.36 mmol), NaH (132 mg, 5.4 mmol) and dry 1,4-dioxane (2.0 mL) under N_2 atmosphere, and 0.1 mL of solution was transferred from the Schlenk tube to N_2-filled NMR tube through syringe

under N_2 atmosphere, and diluted with 0.4 mL of dry 1,4-dioxane. Then the NMR tube was subjected to a ^{31}P NMR test and spectrum (t = 0 h) was obtained. The reaction mixture was stirred at 120 °C, subsequently, sampling was performed by taking 0.1 mL of solution from Schlenk tube and diluting with 0.4 mL of dry 1,4-dioxane each time, and ^{31}P NMR spectra were collected at 1 h, 2 h, 3 h, 4 h, 5 h, 6 h, 8 h, 9 h, and 12 h. The spectra were obtained in Figure S11. Then, an aliquot taken from the reaction mixture (4 h) was analyzed by HRMS using atmospheric pressure chemical ionization (APCI) method. The results were shown in Figure S12. The cation signal at m/z = 421.3018 would correspond to the protonated form of tricyclohexyl(naphthalen-1-ylmethylene)-λ^5-phosphane, combined with ^{31}P NMR spectrum, it represents naphthylene ylide intermediate **5v**. Another cation signal at m/z = 561.3650 would correspond to the protonated form of tricyclohexyl(1,2-di(naphthalen-1-yl)ethylidene)-λ^5-phosphane, combined with ^{31}P NMR spectrum, it represents ylide intermediate **5vv**.

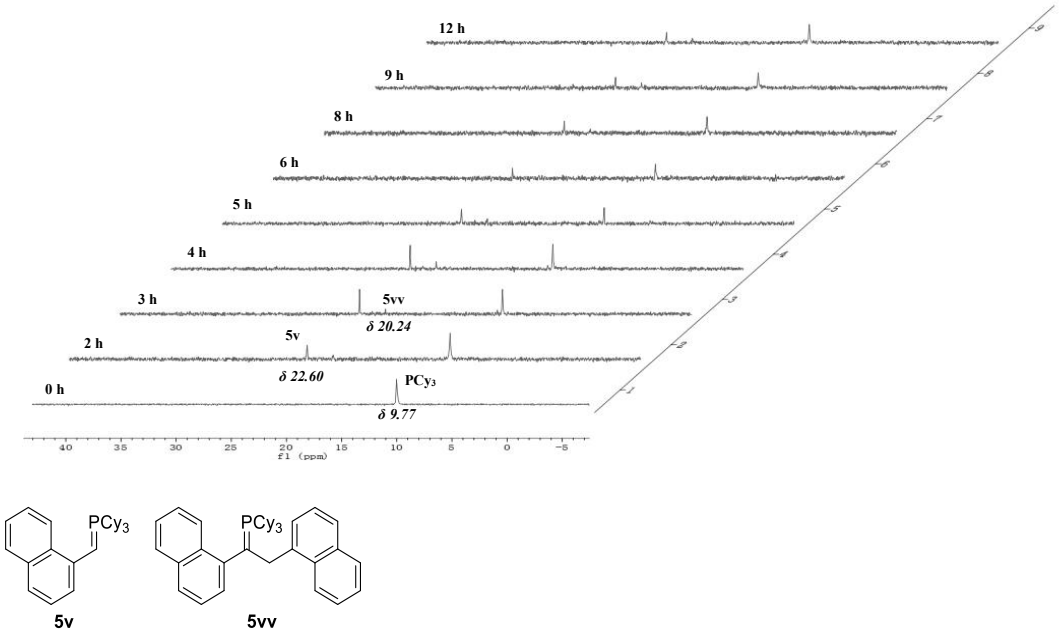


Figure S11. Time-stacked in situ ^{31}P NMR spectra (1,4-dioxane) of **1v** reaction mixture at t = 0 h, 2 h, 3 h, 4 h, 5 h, 6 h, 8 h, 9 h, and 12 h in the presence of NaH as base.

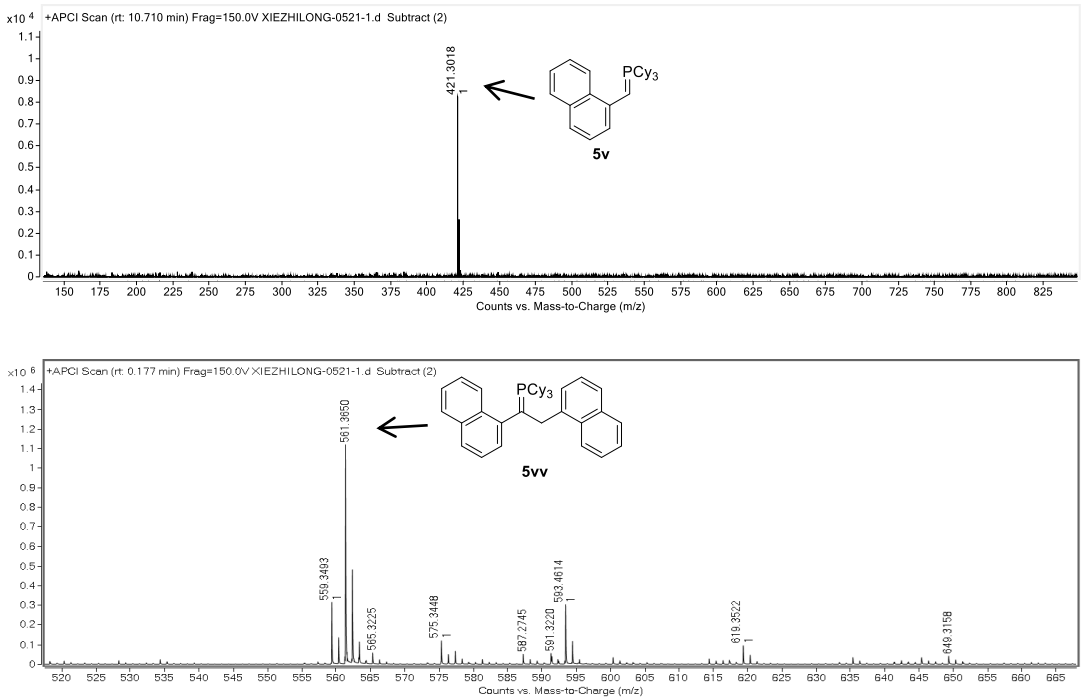
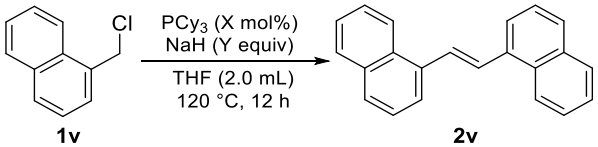


Figure S12. HRMS analysis of **1v** reaction mixture at t = 4 h in the presence of NaH as base.

4) ^{31}P NMR spectra of the reaction of 1v with different amounts of phosphine and base under Condition B

The effect of the amounts of phosphine and base on phosphine-catalyzed coupling reaction of **1v** was investigated. The results were shown in Table S5. After 12 h, the reaction system was examined by ^{31}P NMR spectroscopy and the spectra was shown in Figure S13. Obviously, the amount of base and catalyst has a great influence on the reaction, and the formation of ylide intermediate **5v** is the key step of phosphine-catalyzed coupling reaction of **1v** in the presence of NaH as a base.

Table S5. The reaction of **1v** with different amounts of phosphine and base.[a]



Entry	Phosphine (mol%)	NaH (equiv)	Yield[%][b]
1	20	2.0	60
2	10	3.0	45
3	5	3.0	15

[a] Reaction condition: 1-(chloromethyl)naphthalene (**1v**, 0.6 mmol), phosphine (X mol%) and NaH (Y equiv) in dry THF (2.0 mL) at 120 °C under N_2 atmosphere for 12 h. [b] Determined by ^1H NMR using 1,3,5-trimethoxybenzene as an internal standard.

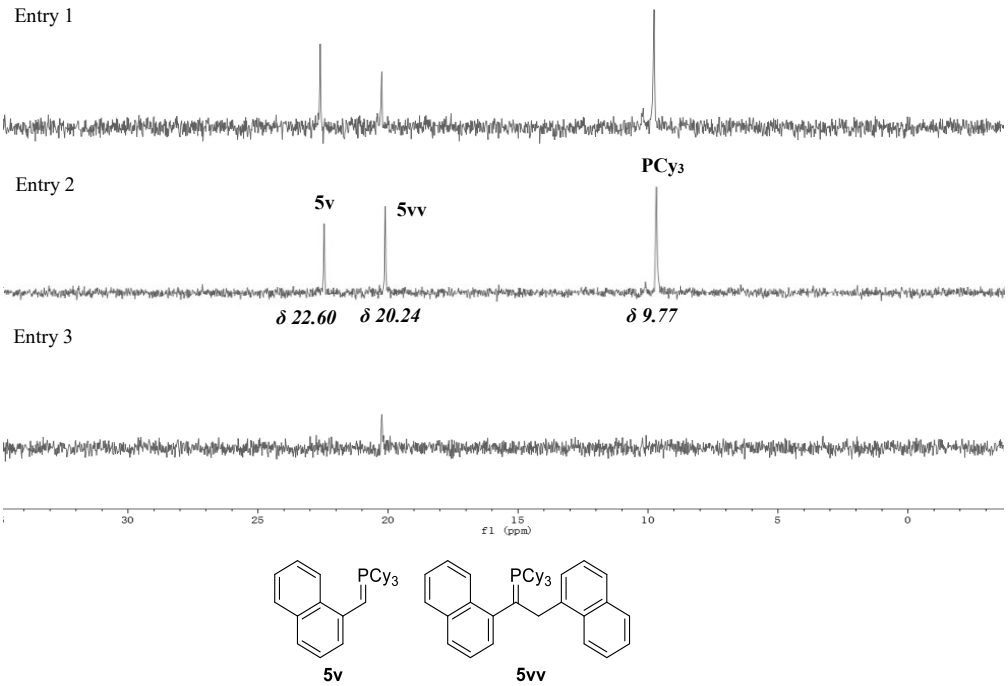


Figure S13. ^{31}P NMR spectra (1,4-dioxane) of **1v** reaction mixture at t = 12 h under different conditions.

5) ^{31}P NMR tracking on the transformation of 1v in the presence of catalytic amount of 3v under Condition A

An oven-dried 25-mL Schlenk tube was charged with a mixture of **1v** (106 mg, 0.6 mmol), **3v** (55 mg, 0.12 mmol), CsF (273 mg, 1.8 mmol), $B(OMe)_3$ (100 μL, 0.9 mmol) and dry 1,4-dioxane (5.0 mL) under N_2 atmosphere, and 0.1 mL of solution was transferred from the Schlenk tube to N_2-filled NMR tube through syringe under N_2 atmosphere, and diluted with 0.4 mL of dry 1,4-dioxane. Then the NMR tube was subjected to a ^{31}P NMR test. The reaction mixture was stirred at 120 °C, subsequently, sampling was performed by taking 0.1 mL of solution from Schlenk tube and diluting with 0.4 mL of dry 1,4-dioxane each time, and ^{31}P NMR spectra were collected at 0 h, 2 h, 6 h, 12 h and 18 h. The results were shown in Figure S14. Then, two aliquots taken from the reaction mixture (2 h and 12 h) were analyzed by HRMS using APCI method, respectively. The results were shown in Figure S15 and S16. Interestingly, different peaks appear in ^{31}P NMR spectrum at 2 hours and 12 hours, but the same cation signal

appears. The cation signals at m/z = 561.3620 and 561.3622 would correspond to tricyclohexyl(1,2-di(naphthalen-1-yl)ethyl)phosphonium, combined with reaction conditions and the reported literature (P. A. Byrne, D. G. Gilheany, *Chem. Eur. J.* **2016**, *22*, 9140-9154), they represent tricyclohexyl(1,2-di(naphthalen-1-yl)ethyl)phosphonium chloride intermediate **3vv** (δ 34.45 ppm in ^{31}P NMR) and tricyclohexyl(1,2-di(naphthalen-1-yl)ethyl)phosphonium methanolate **4vv** (δ 47.76 ppm in ^{31}P NMR), respectively.

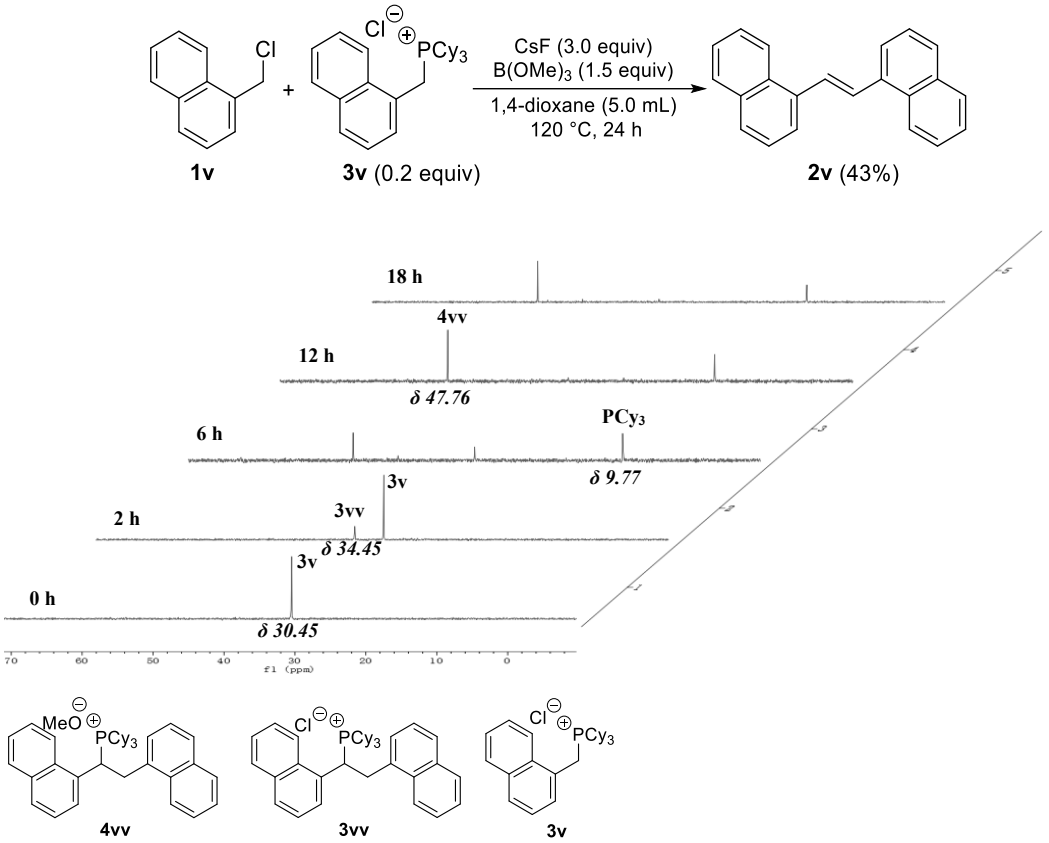


Figure S14. Time-stacked in situ ^{31}P NMR spectra (1,4-dioxane) of **1v** reaction mixture at t = 0 h, 2 h, 6 h, 12 h and 18 h in the presence of catalytic amount of **3v** under Condition A.

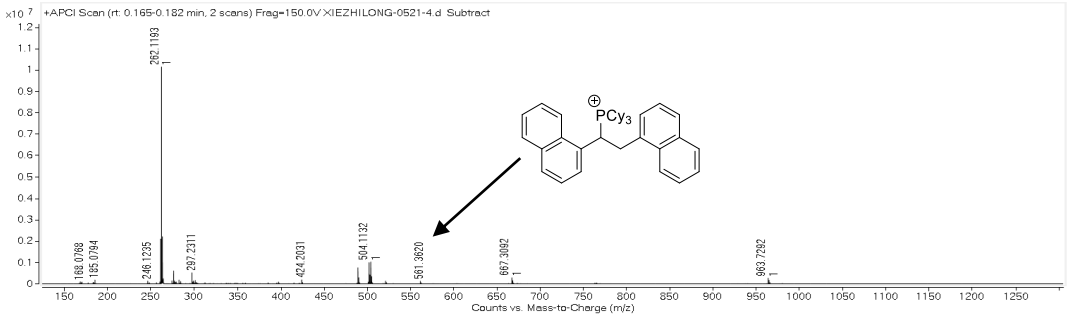


Figure S15. HRMS (APCI) of **1v** reaction mixture at t = 2 h in the presence of catalytic amount of **3v** under Condition A.

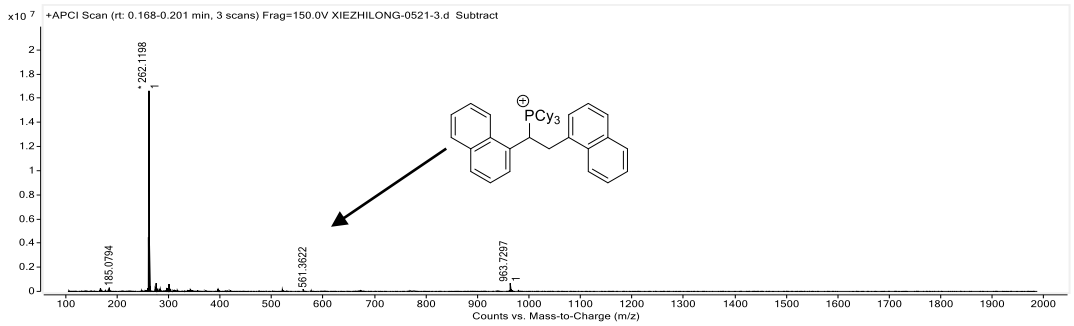
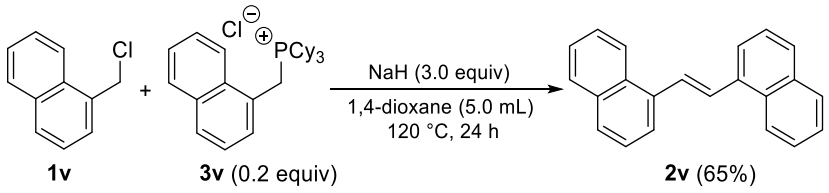


Figure S16. HRMS (APCI) of **1v** reaction mixture at t = 12 h in the presence of catalytic amount of **3v** under Condition A.

6) ^{31}P NMR tracking on the transformation of 1v in the presence of catalytic amount of 3v under Condition B

An oven-dried 25-mL Schlenk tube was charged with a mixture of **1v** (109 mg, 0.6 mmol), **3v** (55 mg, 0.12 mmol), NaH (44 mg, 1.8 mmol) and dry 1,4-dioxane (5.0 mL) under N_2 atmosphere, and 0.1 mL of solution was transferred from the Schlenk tube to N_2-filled NMR tube through syringe under N_2 atmosphere, and diluted with 0.4 mL of dry 1,4-dioxane. Then the NMR tube was subjected to a ^{31}P NMR test. The reaction mixture was stirred at 120 °C, subsequently, sampling was performed by taking 0.1 mL of solution from Schlenk tube and diluting with 0.4 mL of dry 1,4-dioxane each time, and ^{31}P NMR spectra were collected at t = 20 min, 2 h, 6 h, 12 h, 18 h and 24 h. The results were shown in Figure S17.



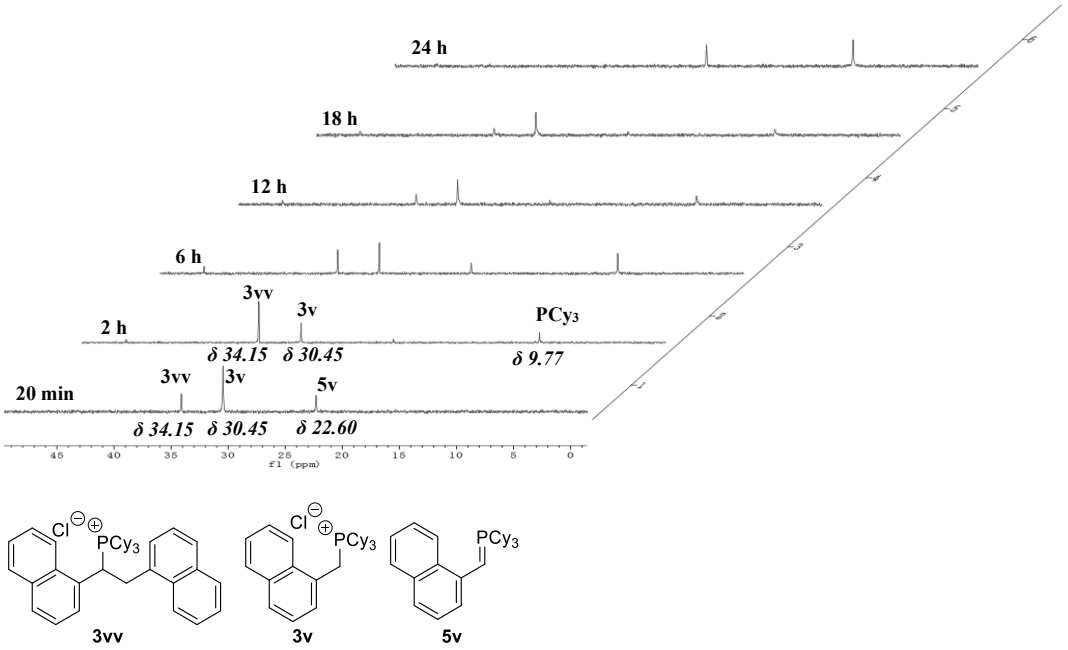
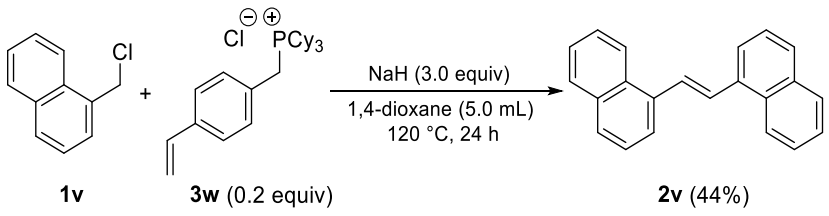


Figure S17. Time-stacked in situ ^{31}P NMR spectra (1,4-dioxane) of **1v** reaction mixture at t = 20 min, 2 h, 6 h, 12 h, 18 h and 24 h in the presence of catalytic amount of **3v** under Condition B.

7) ^{31}P NMR tracking on the transformation of 1v in the presence of catalytic amount of 3w under Condition B

An oven-dried 25-mL Schlenk tube was charged with a mixture of **1v** (109 mg, 0.6 mmol), **3w** (52 mg, 0.12 mmol), NaH (44 mg, 1.8 mmol) and dry 1,4-dioxane (5.0 mL) under N_2 atmosphere, and 0.1 mL of solution was transferred from the Schlenk tube to N_2-filled NMR tube through syringe under N_2 atmosphere, and diluted with 0.4 mL of dry 1,4-dioxane. Then the NMR tube was subjected to a ^{31}P NMR test. The reaction mixture was stirred at 120 °C, subsequently, sampling was performed by taking 0.1 mL of solution from Schlenk tube and diluting with 0.4 mL of dry 1,4-dioxane each time, and ^{31}P NMR spectra were collected at t = 20 min, 2 h, 6 h, 12 h, 18 h, and 24 h. The results were shown in Figure S18.



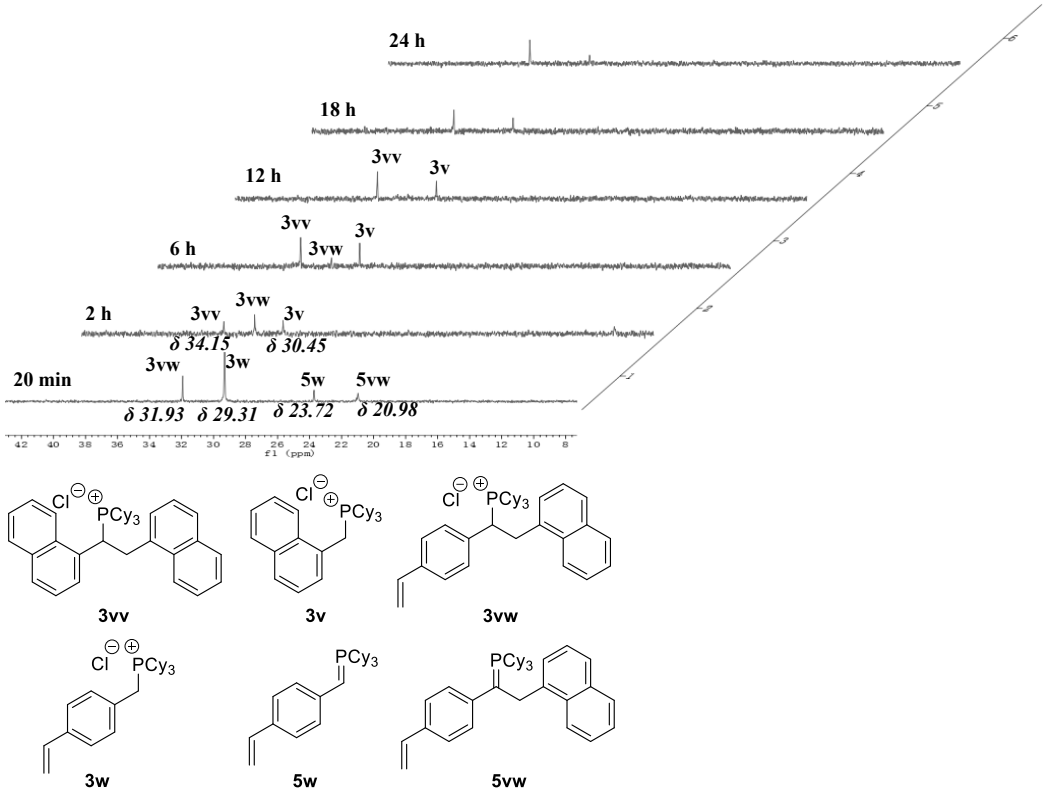


Figure S18. Time-stacked in situ ^{31}P NMR spectra (1,4-dioxane) of **1v** reaction mixture at t = 20 min, 2 h, 6 h, 12 h, 18 h, and 24 h in the presence of catalytic amount of **3w** under Condition B.

8) ^{31}P NMR tracking on the transformation of 1k in the presence of catalytic amount of 3v under Condition B

An oven-dried 25-mL Schlenk tube was charged with a mixture of 1-(chloromethyl)-3-methoxybenzene (**1k**, 94 mg, 0.6 mmol), **3v** (55 mg, 0.12 mmol), NaH (44 mg, 1.8 mmol) and dry 1,4-dioxane (5.0 mL) under N_2 atmosphere, and 0.1 mL of solution was transferred from the Schlenk tube to N_2-filled NMR tube through syringe under N_2 atmosphere, and diluted with 0.4 mL of dry 1,4-dioxane. Then the NMR tube was subjected to a ^{31}P NMR test. The reaction mixture was stirred at 120 °C, subsequently, sampling was performed by taking 0.1 mL of solution from Schlenk tube and diluting with 0.4 mL of dry 1,4-dioxane each time, and ^{31}P NMR spectra were collected at 20 min, 2 h, 6 h, 12 h, 18 h, and 24 h. The spectra were obtained in Figure S19. Then, an aliquot taken from the reaction mixture (24 h) was analyzed by GC-MS using EI method. The results were shown in Figure S20. The cation signal at m/z = 260.1 would correspond to the cross-coupling product **2kv**.

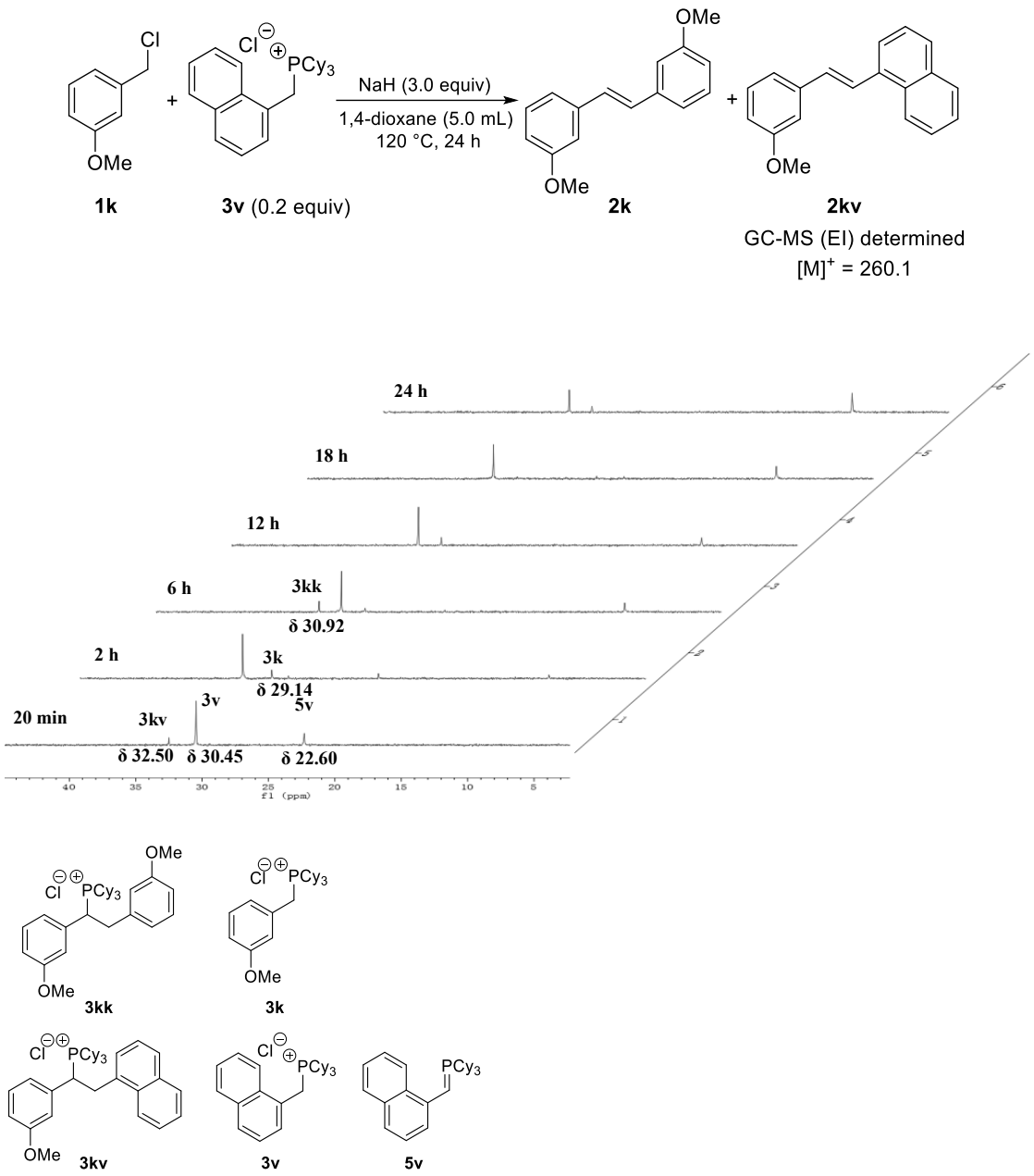
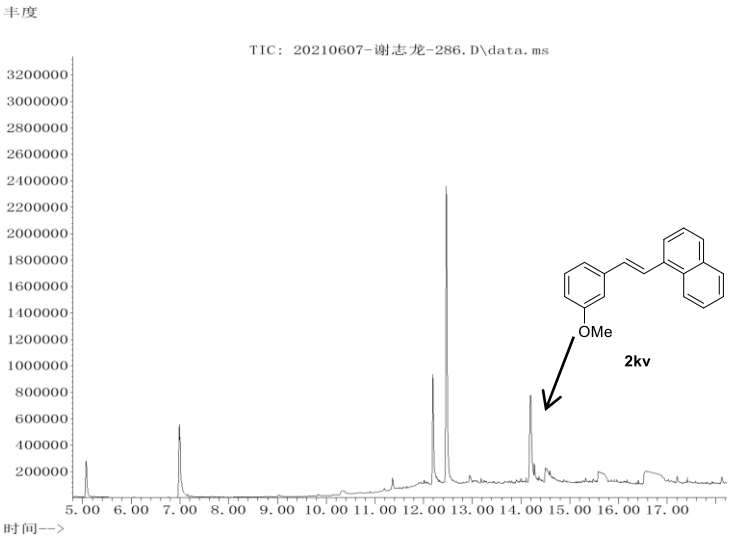


Figure S19. Time-stacked in situ ^{31}P NMR spectra (1, 4-dioxane) of **1k** reaction mixture at t = 20 min, 2 h, 6 h, 12 h, 18 h, and 24 h in the presence of catalytic amount of **3v** under Condition B.



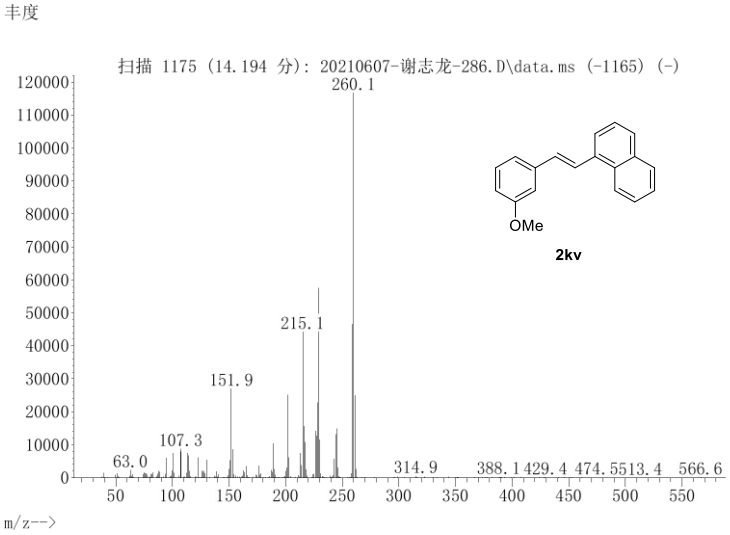
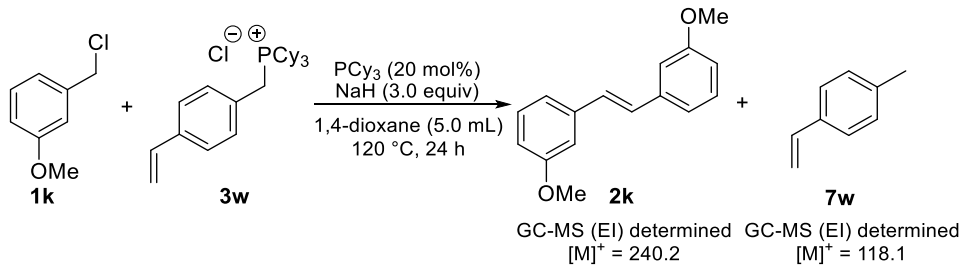


Figure S20. The GC-MS (EI) of **1k** reaction mixture at t = 24 h in the presence of catalytic amount of **3v** under Condition B.

9) Research on the synthesis of unsymmetrical stilbenes by GC-MS



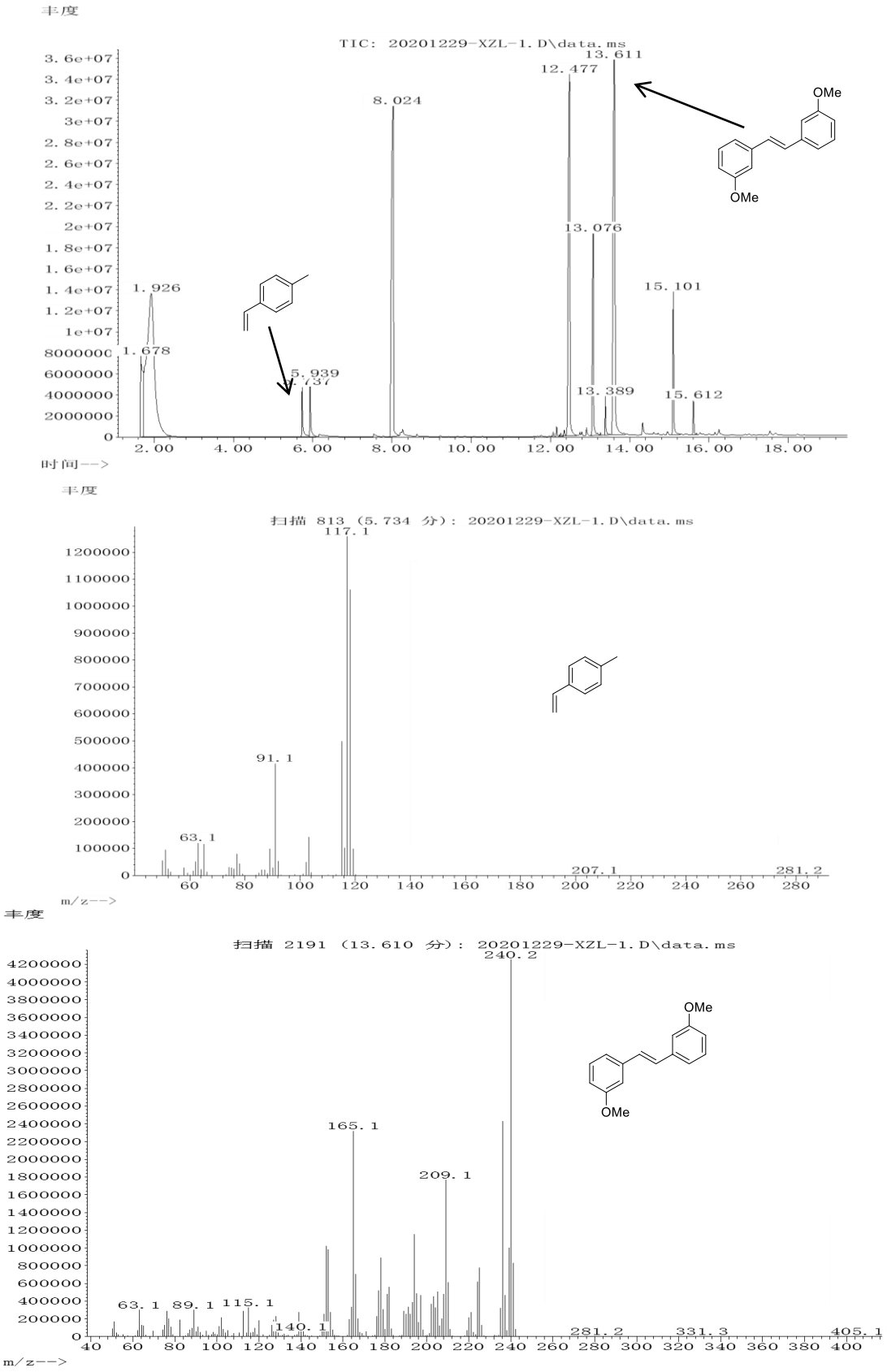
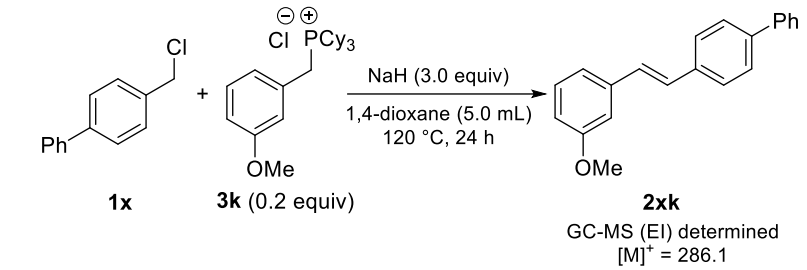


Figure S21. The GC-MS (EI) of the reaction mixture of **1k** and **3w** at t = 24 h.



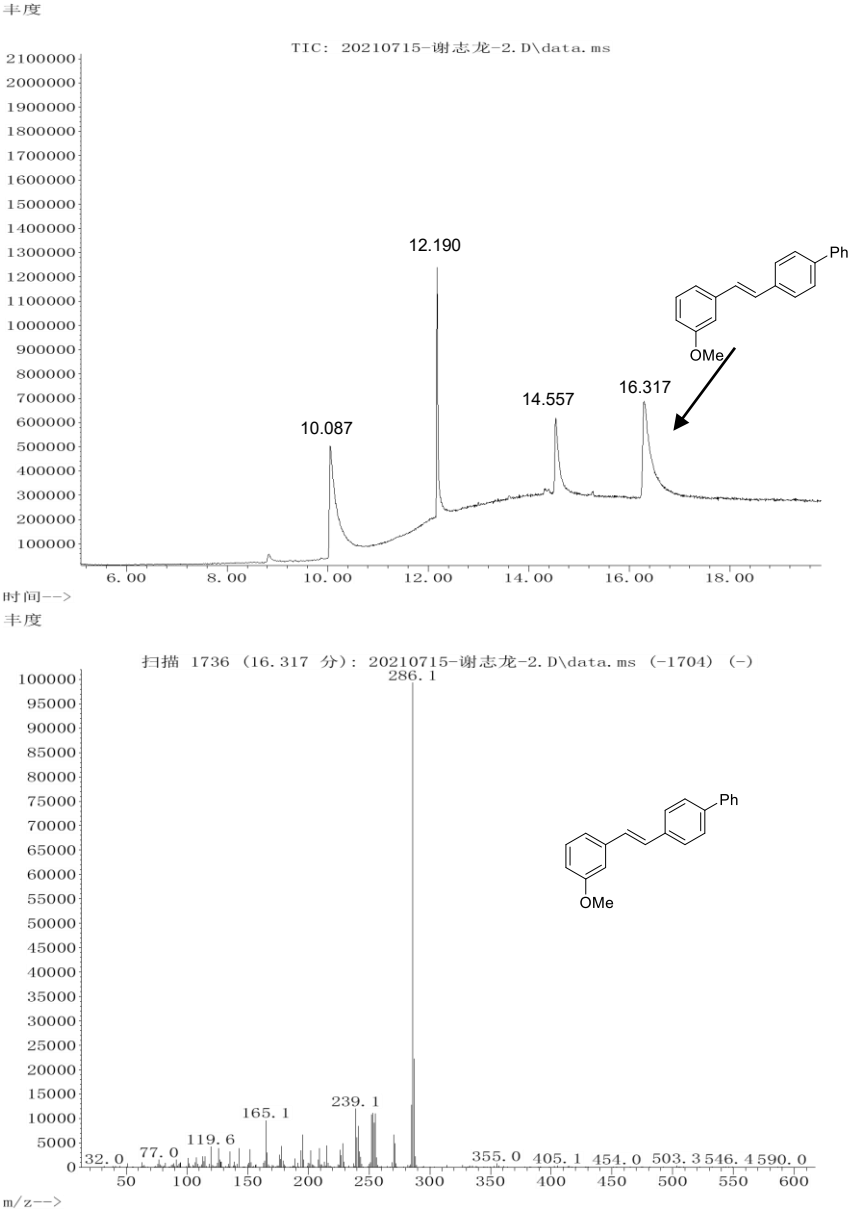
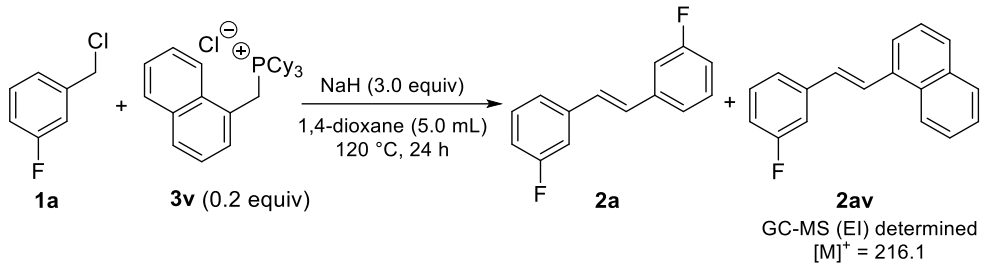


Figure S22. The GC-MS (EI) of the reaction mixture of **1x** and catalytic amount of **3w** at t = 24 h.



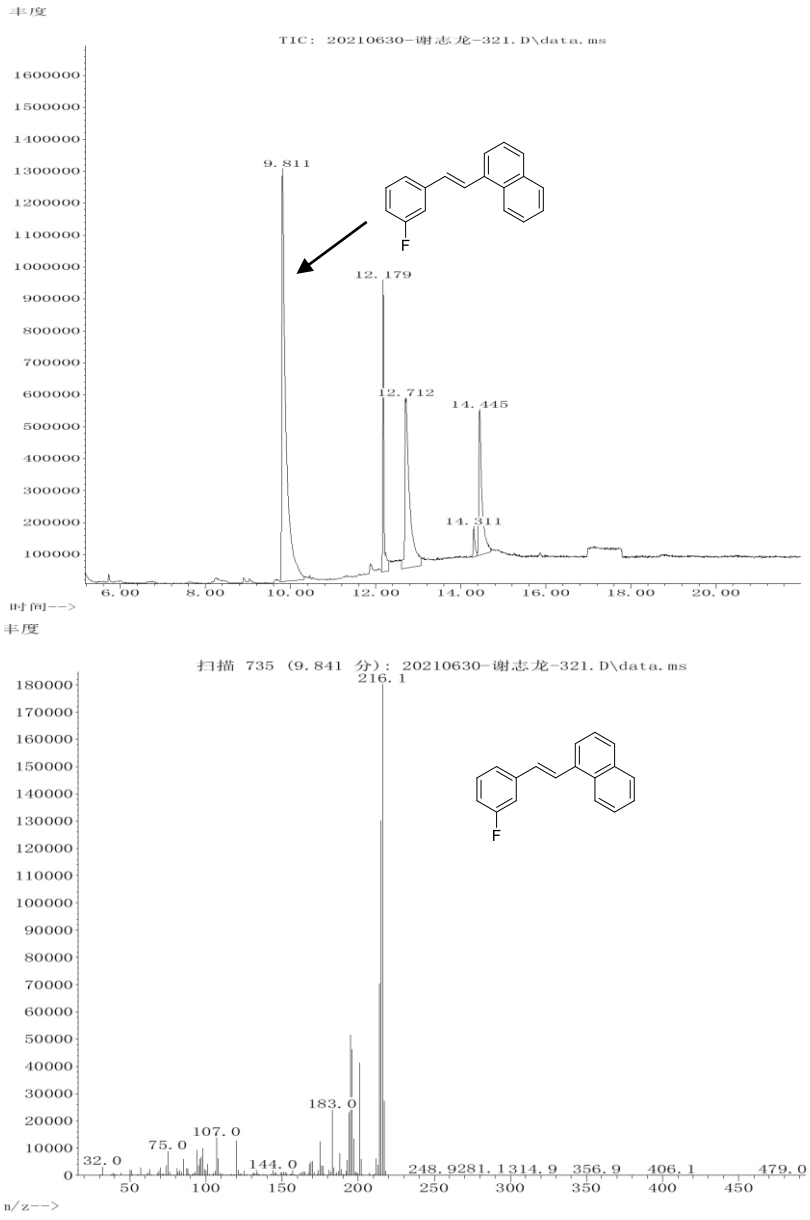
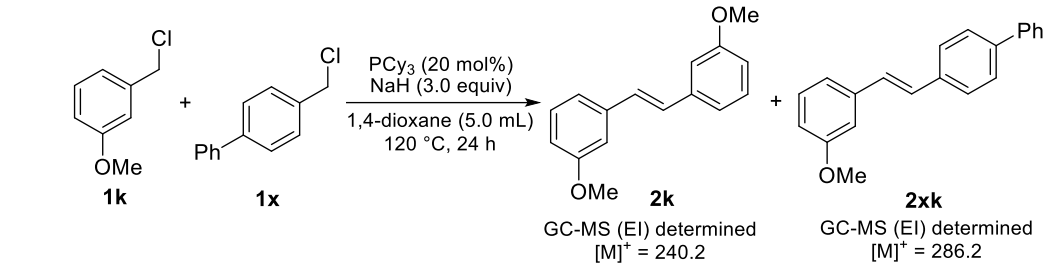


Figure S23. The GC-MS (EI) of the reaction mixture of **1a** and catalytic amount of **3v** at t = 24 h.



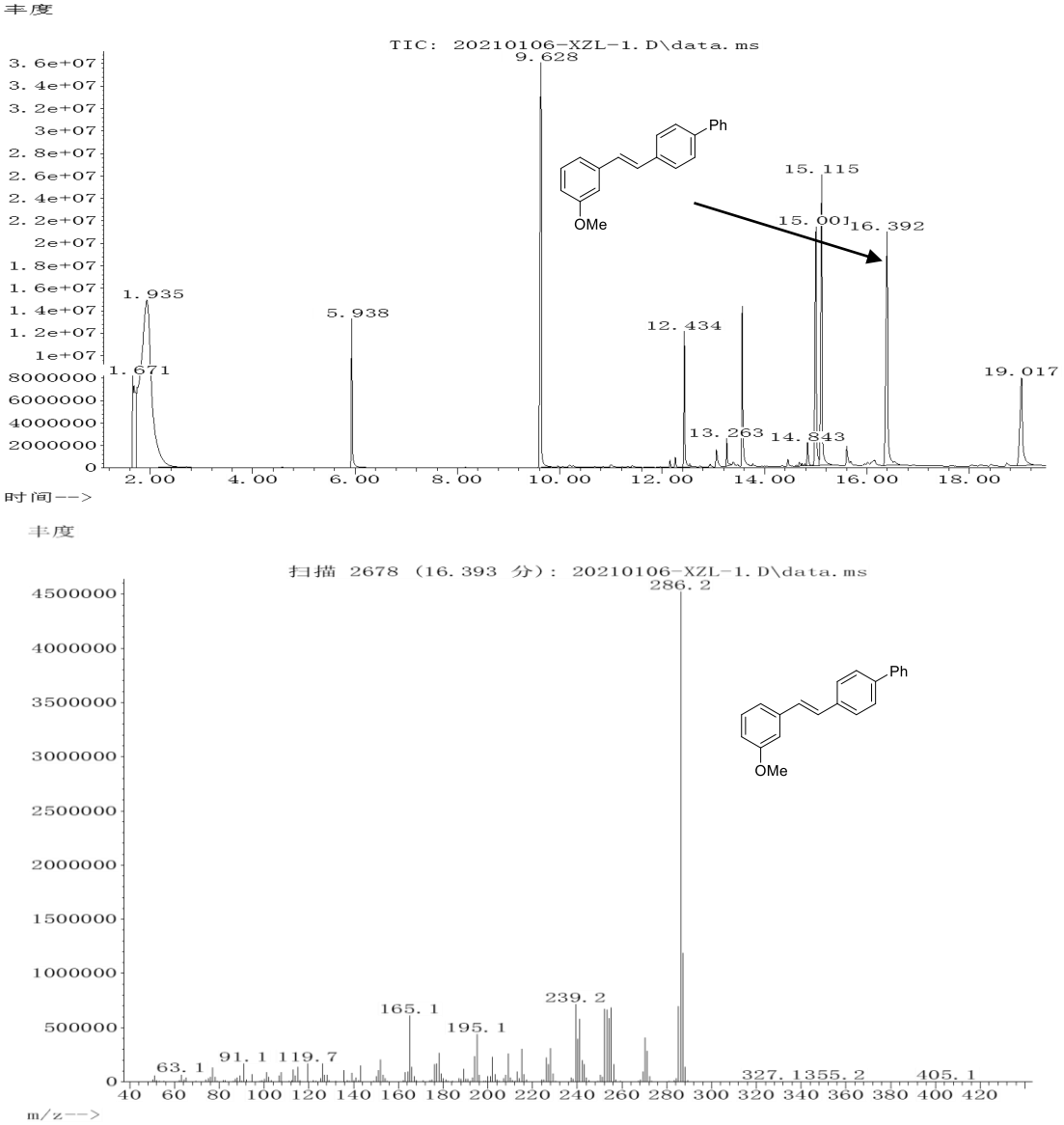


Figure S24. The GC-MS (EI) of the reaction mixture of **1k** and **1x** at t = 24 h.

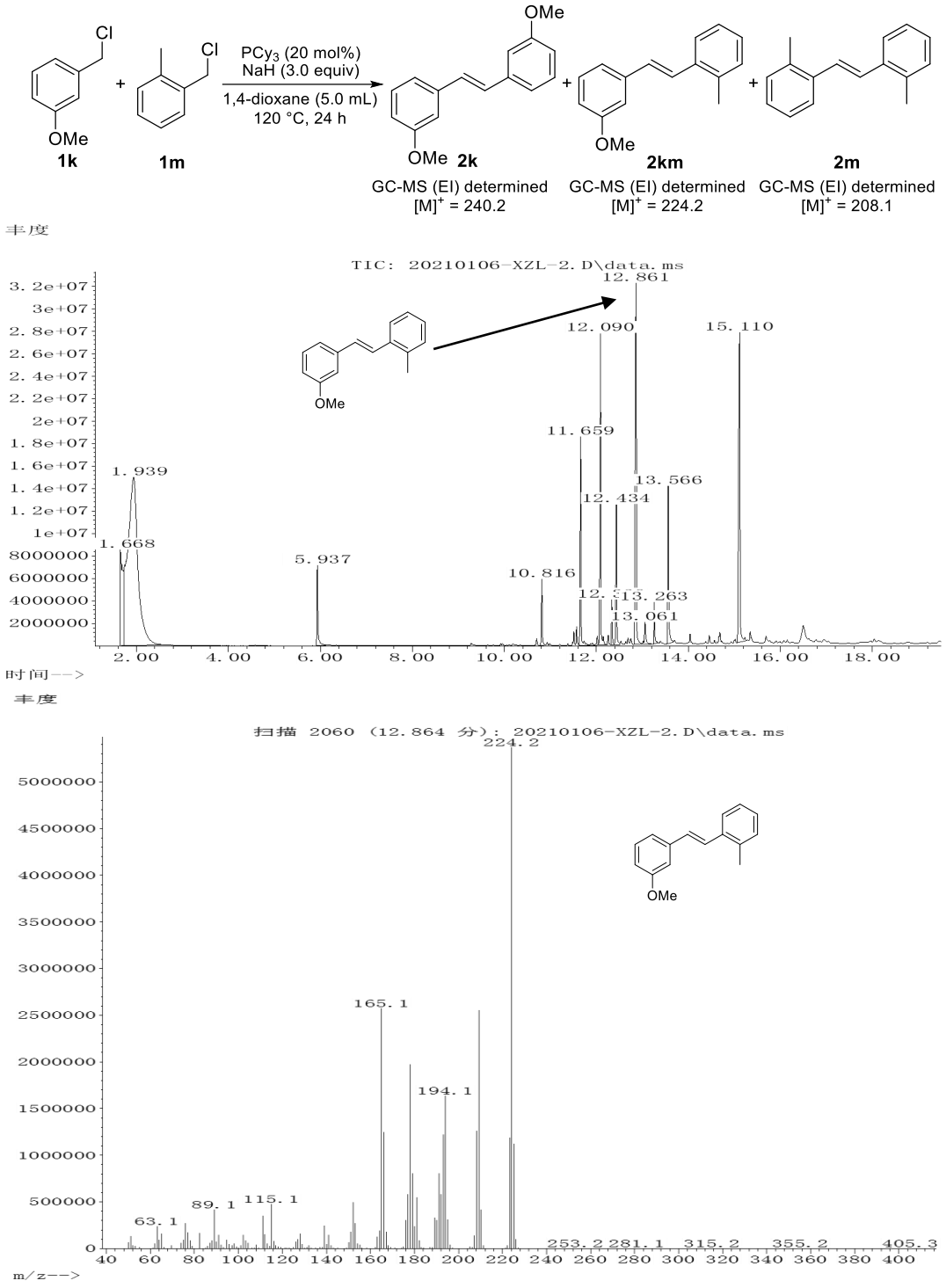
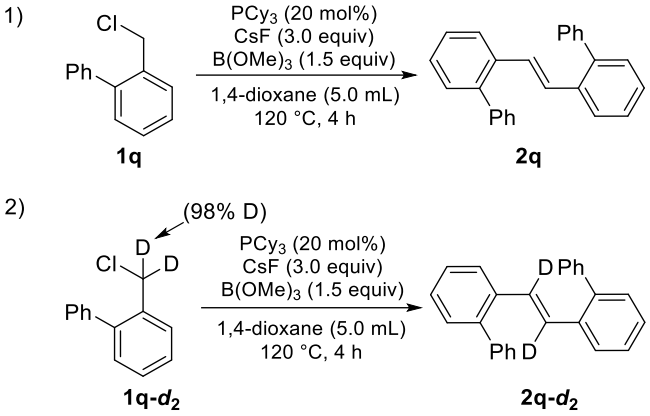


Figure S25. The GC-MS (EI) of the reaction mixture of **1k** and **1m** at t = 24 h.

10) Kinetic isotope effect studies of phosphine−catalyzed transformation of benzyl chloride in the presence of CsF and B(OMe)$_3$ as base and additive, respectively



An oven-dried 5-mL Schlenk tube was charged with a mixture of **1q** or **1q-*d*$_2$** (244 mg, 1.2 mmol), CsF (546 mg, 3.6 mmol), B(OMe)$_3$ (200 μL, 1.8 mmol), PCy$_3$ (68 mg, 0.24 mmol), mesitylene (12.2 mg, 0.1 mmol) and dry 1,4-dioxane (5.0 mL) under N_2 atmosphere. The reaction mixture was stirred at 120 °C for 4 h. Samples (0.04 mL solution of the Schlenk tube is added in 0.23 mL dry 1,4-dioxane) were taken 7 times at 0 min, 20 min, 40 min, 1 h, 2 h, 3 h, and 4 h for GC. The results were shown in S26.

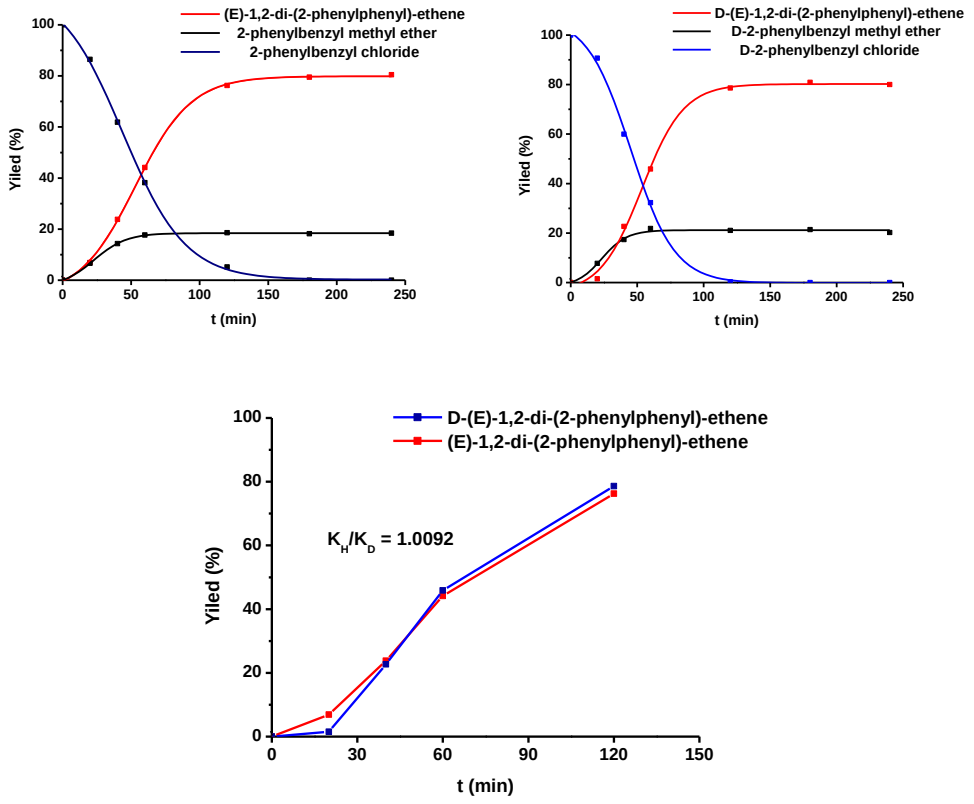
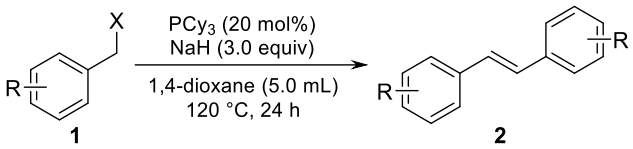


Figure S26. Studies for kinetic isotopic effect: parallel experiments.

11) Hammett plots for the reaction of *meta*-and *para*-substituted benzyl chlorides under Condition B



An oven-dried 25-mL Schlenk tube was charged with a mixture of **1** (0.6 mmol), PCy_3 (34 mg, 0.12 mmol), NaH (44 mg, 1.8 mmol) and dry 1,4-dioxane (5.0 mL) under N_2 atmosphere. The reaction mixture was stirred at 120 °C for 1 h, and then cooled to room temperature. The salt was removed quickly by flash column chromatography on a silica gel column to give crude products. The yield was determined by the ^1H NMR analysis with 1,3,5-trimethoxybenzene as an internal standard.

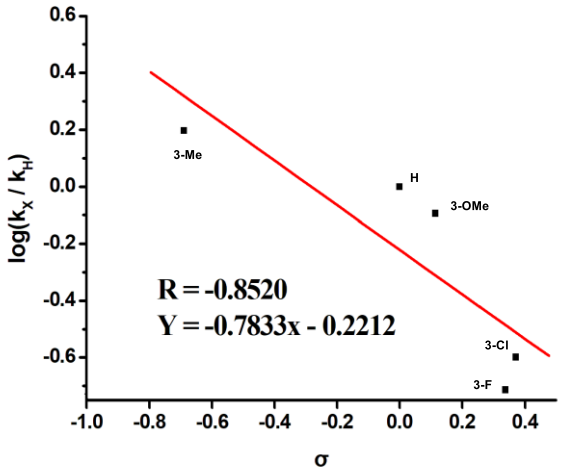


Figure S27. Hammett plot of *m*-$ArCH_2Cl$.

Table S6. Hammett plot of **1**.

1	σ	Yield of **2**	k_X/k_H	$\log(k_X/k_H)$
3-H	0	12.4	1	0
3-F	0.337	2.4	0.193	-0.71
3-OMe	0.115	10.0	0.805	-0.09
3-Me	-0.69	19.5	1.574	0.20
3-Cl	0.37	5.4	0.277	-0.36

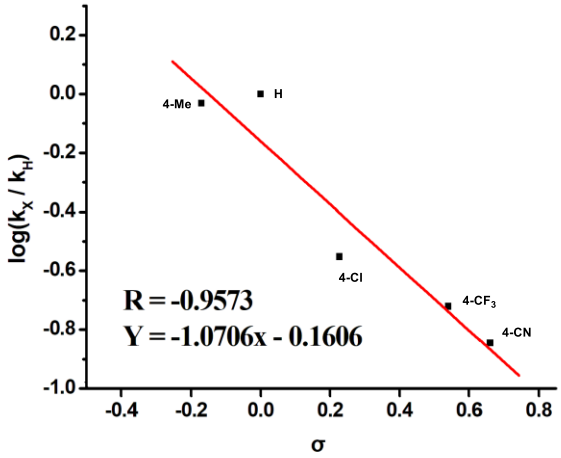
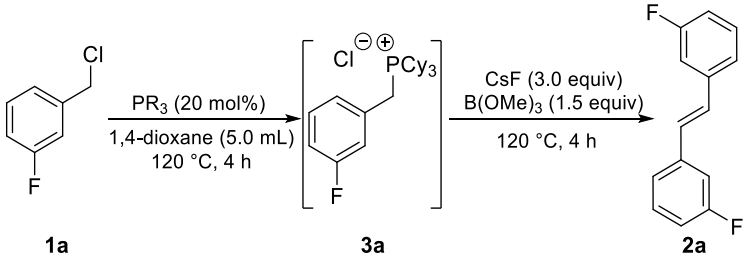


Figure S28. Hammett plot of *p*-ArCH$_2$Cl.

Table S7. Hammett plot of **1**.

1	σ	Yield of **2**	k_X/k_H	$\log(k_X/k_H)$
4-H	0	12.4	1	0
4-CN	0.66	1.8	0.143	-0.85
4-Me	-0.17	11.5	0.930	-0.03
4-Cl	0.227	3.5	0.281	-0.55
4-CF_3	0.54	2.4	0.190	-0.72

12) The reactivity of different kinds of phosphines

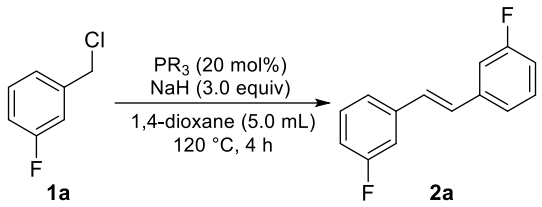


An oven-dried 25-mL Schlenk tube was charged with a mixture of **1a** (87 μL, 0.6 mmol), PR_3 (0.12 mmol) and dry 1,4-dioxane (5.0 mL) under N_2 atmosphere. The reaction mixture was stirred at 120 °C for 4 h, and then cooled to room temperature. CsF (273 mg, 1.8 mmol), $B(OMe)_3$ (100 μL, 0.9 mmol) was added, and then stirred at 120 °C for 4 h, and then cooled to room temperature. The corresponding reaction mixture was purified by flash column chromatography on a silica gel column to give the mixture products. The yield was determined by the ^{1}H NMR analysis with 1,3,5-trimethoxybenzene as an internal standard.

Table S8. The data of the conversion of phosphines and the yield of **2a** under Condition A.

	Two steps method		One step method
PR_3	Conv. of **1a**[a]	Yield of **2a**[a]	Yield of **2a**[b]
PPh_3	10%	11%	20%
PEt_3	15%	3%	8%
PCy_3	18%	63%	84%

[a] Determined by ^{1}H NMR using 1,3,5-trimethoxybenzene as an internal standard. [b] Isolated yields.



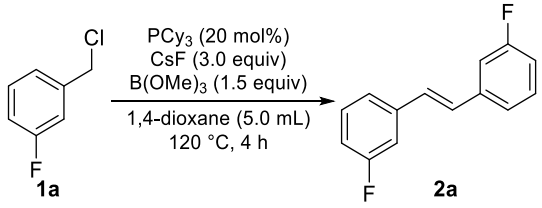
An oven-dried 25-mL Schlenk tube was charged with a mixture of **1a** (87 μL, 0.6 mmol), PR_3 (0.12 mmol), NaH (44 mg, 1.8 mmol) and dry 1,4-dioxane (5.0 mL) under N_2 atmosphere. The reaction mixture was stirred at 120 °C for 4 h, and then cooled to room temperature. The corresponding reaction mixture was purified by flash column chromatography on a silica gel column to give the mixture products. The yield was determined by the ^{1}H NMR analysis with 1,3,5-trimethoxybenzene as an internal standard.

Table S9. The data of the yield of **2a** under Condition B.

PR_3	Yield of **2a**[a]
PPh_3	0%
PEt_3	2%
PCy_3	16%

[a] Determined by ^{1}H-NMR using 1,3,5-trimethoxybenzene as an internal standard.

13) ^{11}B NMR tracking on the transformation of $B(OMe)_3$ in the presence of CsF as base



An oven-dried 5-mL Schlenk tube was charged with a mixture of **1a** (0.6 mmol), CsF (273mg, 1.8 mmol), $B(OMe)_3$ (100 μL, 0.9 mmol), PCy_3 (34 mg, 0.12 mmol) and dry 1,4-dioxane (5.0 mL) under N_2 atmosphere. The reaction mixture was stirred at 120 °C for 4 h. Samples (0.1 mL solution of the Schlenk tube is added in 0.4 mL dry $CDCl_3$) were taken 4 times at 0 h, 0.5 h, 2 h and 4 h for ^{11}B NMR. The results were shown in Figure S29.

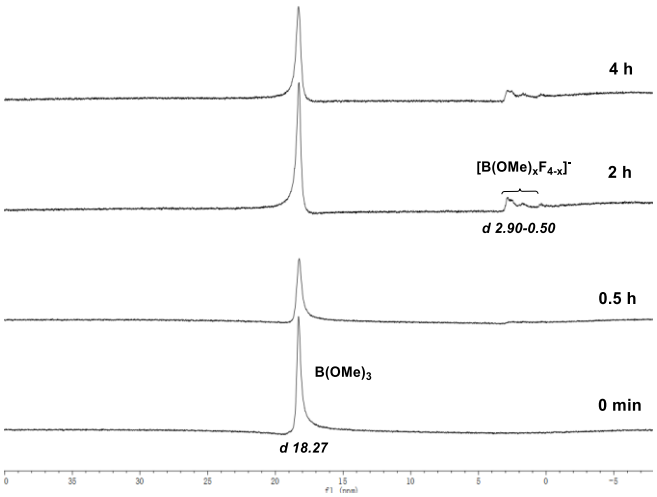
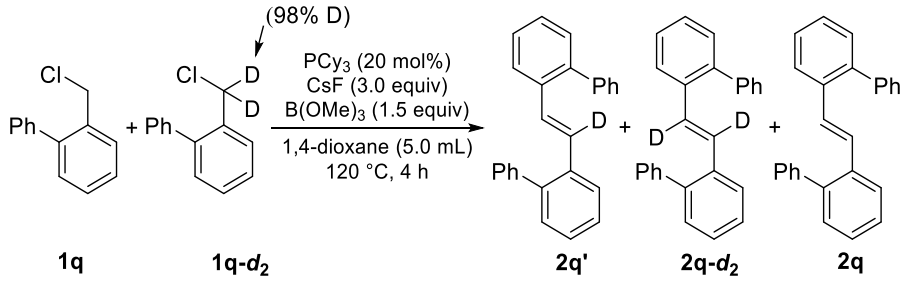


Figure S29. ^{11}B NMR tracking on the transformation of $B(OMe)_3$ in the presence of CsF as base.

14) The study of *β*-H elimination



An oven-dried 25-mL Schlenk tube was charged with a mixture of **1q** and **1q-*d*2** (244 mg, 0.3 mmol), CsF (273 mg, 1.8 mmol), $B(OMe)_3$ (100 μL, 0.9 mmol), PCy_3 (34 mg, 0.12 mmol) and dry 1,4-dioxane (5.0 mL) under N_2 atmosphere. The reaction mixture was stirred at 120 °C for 4 h, and then cooled to room temperature. The corresponding reaction mixture was purified by flash column chromatography on a silica gel column to give the mixture products, which was detected by GC-MS (Figure S30).

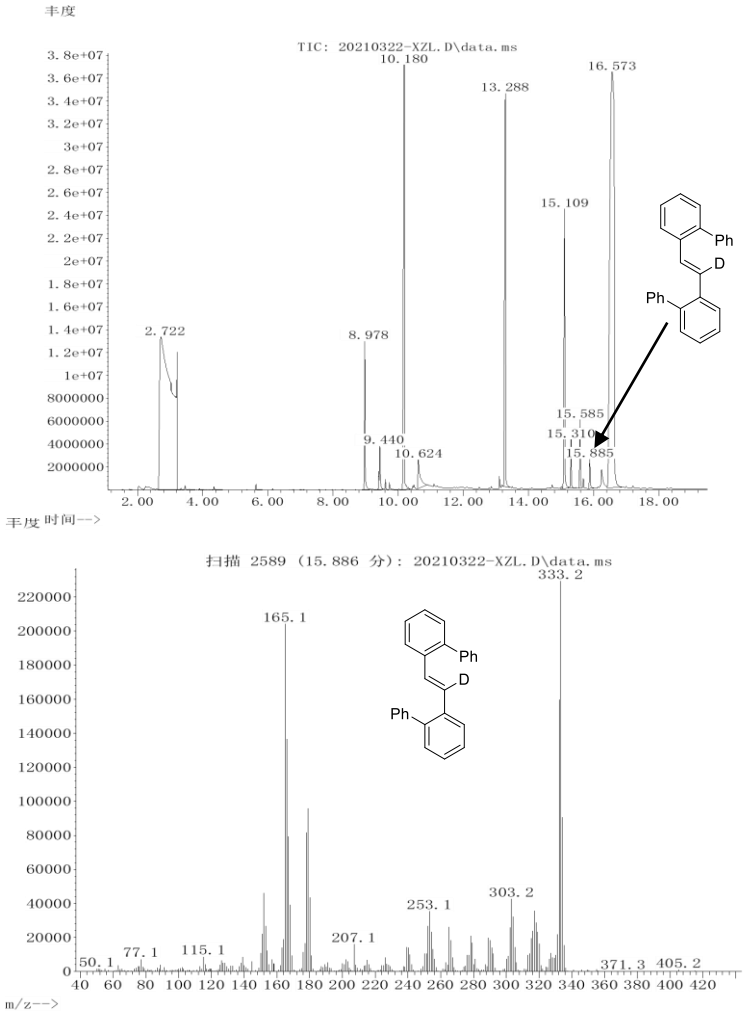
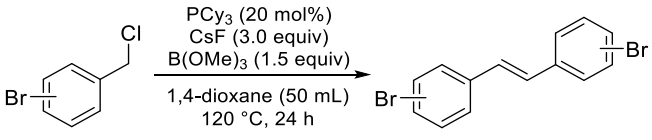


Figure S30. The study of *β*-H elimination by GC-MS.

7. Procedures for the Further Derivatizations

1) Gram-scale experiment



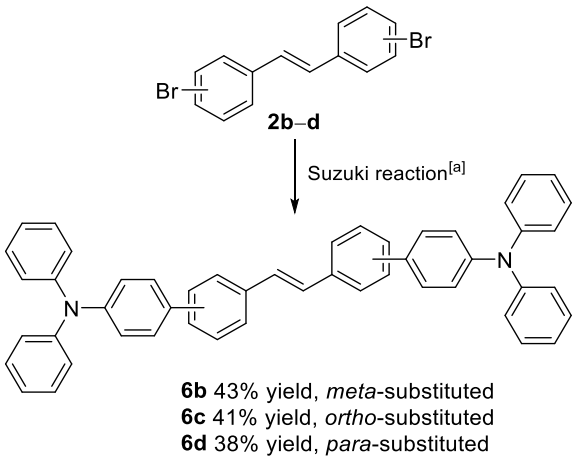
1b–d (1.22 g, 6 mmol)

2b 0.88 g, 89% yield
2c 0.59 g, 59% yield
2d 0.42 g, 41% yield

An oven-dried 25-mL Schlenk tube was charged with a mixture of **1b-d** (1.22 g, 6 mmol), PCy_3 (340 mg, 1.2 mmol), CsF (2.73 mg, 18 mmol), $B(OMe)_3$ (1.0 mL, 9 mmol) and dry 1,4-dioxane (50 mL) under N_2 atmosphere. The reaction mixture was stirred at 120 °C for 24 h, and then cooled to room temperature. The solvent was removed under reduced pressure and the crude product was purified by silica gel column

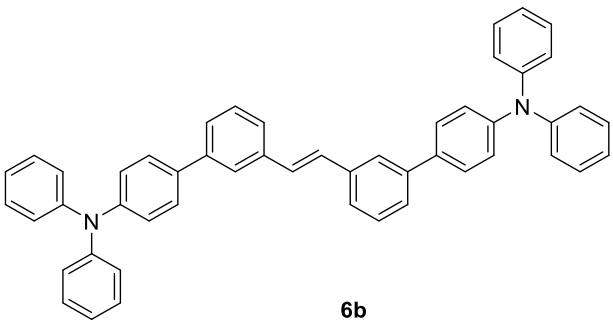
chromatography with *n*-hexane to afford the desired product **2b-d**.

2) Synthesis of 6b-d[3]



[a] Substrates **2b**–**2d** (0.1mmol), (4-(diphenylamino)-phenyl)boronic acid (4.0 equiv), $Pd(PPh_3)_4$ (20 mol%) and NaOH (6.0 equiv) in toluene/ethanol/H_2O (vv 3/2/1, 18 mL) at 110 °C under N_2 atmosphere for 72 h.

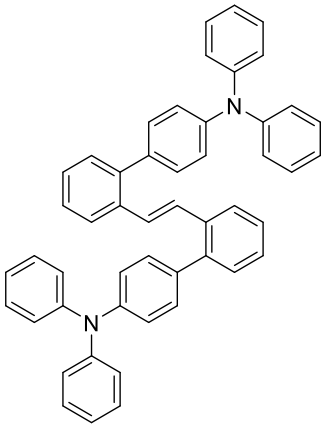
To an oven-dried Schlenk tube were added 0.9 mL of toluene, 0.6 mL of ethanol and 0.3 mL of distilled water. The resultant mixture was degassed thoroughly by bubbling N_2 gas for 10 min. Subsequently, **2b-d** (0.1 mmol, 1.0 equiv), (4-(diphenylamino)-phenyl)boronic acid (120 mg, 0.4 mmol, 4.0 equiv), NaOH (24 mg, 0.6 mmol, 6.0 equiv) and $Pd(PPh_3)_4$ (22 mg, 0.02 mmol, 20 mol%) were added and the Schlenk tube was capped tightly under N_2 gas. The mixture was stirred at 110 °C for 72 h. At the end of the period, the mixture solution was cooled to room temperature, and toluene and ethanol were removed by evaporation under vacuum. The residue was extracted three times with chloroform and the combined organic extracts were dried over Na_2SO_4. Evaporation of the organic solvents led to the crude product, which was subjected to silica gel column chromatography to afford **6b-d**.



6b

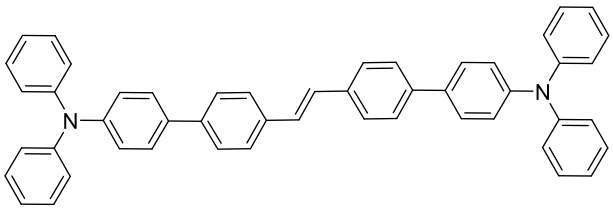
White solid (28.7 mg, 43% yield). ^1H NMR ($CDCl_3$, 400 MHz) δ 7.74–7.68 (m, 5H), 7.53–7.45 (m, 6H), 7.43–7.35 (m, 7H), 7.29–7.21 (m, 7H), 7.18–7.12 (m, 9H), 7.08–

6.99 (m, 4H); ^{13}C NMR ($CDCl_3$, 101 MHz) δ 147.7, 147.4, 141.2, 137.8, 135.2, 135.0, 129.3, 129.1, 129.0, 127.9, 126.1, 125.0, 124.5, 123.9, 123.0; IR (KBr): υ_{max} 3535, 3418, 1584, 1507, 1491, 1454, 1335, 1280, 1251, 1230, 1181, 825, 751, 694 cm^{-1}; HRMS (APCI) m/z calcd for $C_{50}H_{39}N_2^+$ $[M+H]^+$: 667.3108, found: 667.3083.



6c

White solid (27.3mg, 41% yield). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.56–7.50 (m, 2H), 7.37–7.26 (m, 16H), 7.19–7.15 (m, 8H), 7.14–7.09 (m, 6H), 7.08–6.98 (m, 6H); ^{13}C NMR ($CDCl_3$, 101 MHz) δ 147.7, 146.9, 140.8, 135.9, 134.8, 130.6, 130.1, 129.3, 128.7, 127.4, 127.2, 126.1, 124.6, 123.0, 122.9; IR (KBr): υ_{max} 3058, 3033, 2923, 2853, 1589, 1509, 1493, 1448, 1315, 1277, 1176, 1028, 839, 753, 696, 623 cm^{-1}; HRMS (ESI) m/z calcd for $C_{50}H_{39}N_2^+$ $[M+H]^+$: 667.3108, found: 667.3116.



6d

Yellow solid (25.3 mg, 38% yield). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.58 (s, 8H), 7.53–7.49 (m, 4H), 7.30–7.26 (m, 8H), 7.17–7.12 (m, 14H), 7.06–7.02 (m, 4H); ^{13}C NMR ($CDCl_3$, 101 MHz) δ 146.6, 146.4, 138.7, 134.9, 133.5, 128.3, 127.0, 126.5, 125.9, 125.8, 123.5, 122.8, 122.0; IR (KBr): υ_{max} 2959, 2923, 2853, 1588, 1493, 1456, 1260, 1094, 1020, 966, 800, 748, 693 cm^{-1}; HRMS (ESI) m/z calcd for $C_{50}H_{39}N_2^+$ $[M+H]^+$: 667.3108, found: 667.3092.

3) UV-vis Absorption and Fluorescence Spectra of 6b, 6c and 6d

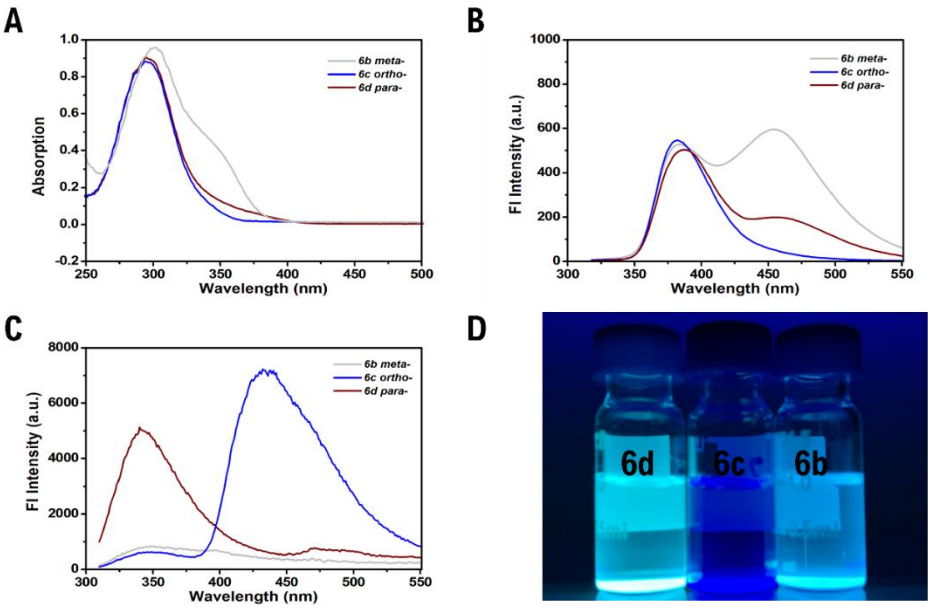


Figure S31. (A) The UV-Vis absorption spectra of **6b**, **6c** and **6d** (1 μM) in THF. (B) The emission spectra of **6b, 6c** and **6d** (1 μM) in THF, λ_{ex} = 300 nm, slit: 5/5 nm. (C) The emission spectra of **6b**, **6c** and **6d** (solid), λ_{ex} = 290 nm, slit: 5/2.5 nm. (D) The picture of **6b, 6c** and **6d** under the light λ=365nm.

Table S10. Summaries of photophysical properties of **6b, 6c** and **6d**

Compound	UV-Vis (THF) λ_{abs} (nm)	Fluorescence (THF) λ_{em} (nm)	Fluorescence (Solid) λ_{em} (nm)	Φ_{FL} [a]
6b	310	382、460	/	0.129
6c	300	380	450	0.039
6d	300	385、460	350	0.073

[a] Measure in THF.

4) Cyclic voltamograms of 6b, 6c and 6d [1]

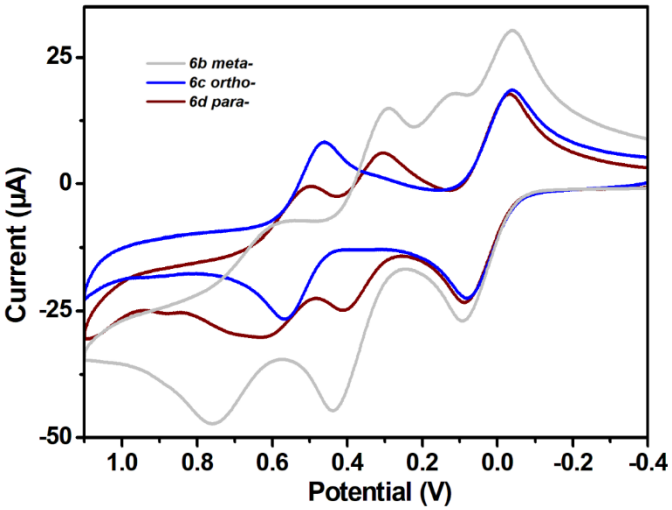


Figure S32. Cyclic voltamograms of **6b, 6c** and **6d**.

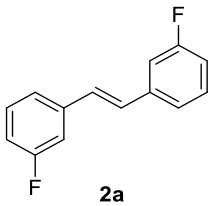
Table S11. Summaries of the data of cyclic voltamograms of **6b, 6c** and **6d**

Compound	$E_{1/2}$[a] /V
6b	0.38、0.59
6c	0.54
6d	0.39、0.70

[a] $E_{1/2}$ vs Fc/Fc^+ was estimated by cyclic voltammetric method using carlxm elcctrcxle as a working electrode, platinum wire as a counter electrode, and Ag/AgCl electrode as a reference electrode with the solution dissolved in CH_2Cl_2 (0.01 M) using 0.1 M of Bu_4NPF_6 as a supporting electrolyte with a scan rate of 100 mV/s and all the potentials were calibrated with ferrocene, ($E_{1/2}$ (Fc/Fc+) = 0.63 V vs NHE) as an external standard.

8. Characterization Data of Compounds

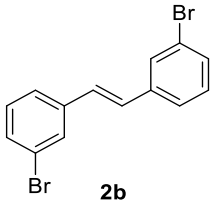
(E)-3,3'-Difluorostilbene (2a)[4]



2a

White solid (54 mg, 84% yield). mp 86–87 °C, (lit. mp 86–88 °C). ^{1}H NMR ($CDCl_3$, 600 MHz) δ 7.35–7.28 (m, 2H), 7.26 (d, J = 8.0 Hz, 2H), 7.23–7.16 (m, 2H), 7.05 (s, 2H), 7.01–6.92 (m, 2H); ^{13}C NMR ($CDCl_3$, 151 MHz) δ 164.0, 162.4, 139.24, 139.18, 130.22, 130.17, 128.8, 122.6, 114.9, 114.7, 113.0, 112.9.

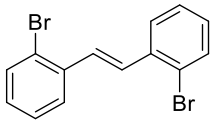
(E)-3,3'-Dibromostilbene (2b)[5]



2b

White solid (95 mg, 94% yield) (**X = Cl**), (57 mg, 57% yield) (**X = Br**). mp 100–101 °C, (lit. mp 101–102 °C). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.67 (d, J = 1.8 Hz, 2H), 7.45–7.39 (m, 4H), 7.25 (dd, $J_1 = J_2$ = 7.8 Hz, 2H), 7.01 (s, 2H); ^{13}C NMR ($CDCl_3$, 151 MHz) δ 139.0, 130.9, 130.3, 129.4, 128.5, 125.4, 123.0.

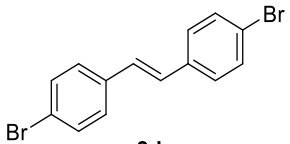
(E)-2,2'-Dibromostilbene (2c)[5]



2c

White solid (62 mg, 62% yield) (**X = Cl**), (62 mg, 61% yield) (**X = Br**). mp 107–108 °C, (lit. mp 108–108.4 °C). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.71 (dd, J = 7.8, 1.6 Hz, 2H), 7.57 (dd, J = 8.1, 1.3 Hz, 2H), 7.39 (s, 2H), 7.32 (dd, $J_1 = J_2$ = 7.6 Hz, 2H), 7.13 (dd, J = 7.7, 1.7 Hz, 2H); ^{13}C NMR ($CDCl_3$, 101 MHz) δ 136.9, 133.1, 130.2, 129.3, 127.7, 127.2, 124.3.

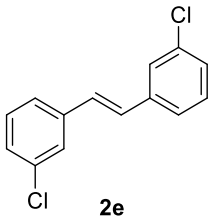
(E)-4,4'-Dibromostilbene (2d)[5]



2d

White solid (41 mg, 41% yield). mp 208–210 °C, (lit. mp 209–211 °C). ^{1}H NMR ($CDCl_3$, 600 MHz) δ 7.48 (d, J = 8.4 Hz, 4H), 7.36 (d, J = 8.4 Hz, 4H), 7.02 (s, 2H); ^{13}C NMR ($CDCl_3$, 101 MHz) δ 135.9, 131.9, 128.1, 128.0, 121.7.

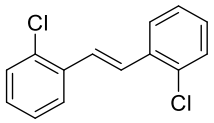
(E)-3,3'-Dichlorostilbene (2e)[6]



2e

White solid (56 mg, 75% yield). mp 93–94 °C, (lit. mp 90.4–93 °C). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.50 (s, 2H), 7.36 (d, J = 7.4 Hz, 2H), 7.32–7.22 (m, 4H), 7.03 (s, 2H); ^{13}C NMR ($CDCl_3$, 101 MHz) δ 138.7, 134.8, 130.0, 128.7, 127.9, 126.5, 124.9.

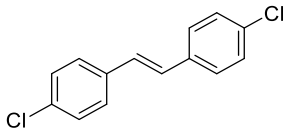
(E)-2,2'-Dichlorostilbene (2f)[7]



2f

White solid (60 mg, 80% yield). mp 83–84 °C, (lit. mp 83–84 °C). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.74 (dd, J = 7.8, 1.6 Hz, 2H), 7.49 (s, 2H), 7.44–7.36 (m, 2H), 7.31–7.26 (m, 2H), 7.25–7.18 (m, 2H); ^{13}C NMR ($CDCl_3$, 151 MHz) δ 135.2, 133.7, 129.9, 129.0, 127.3, 127.0, 126.9.

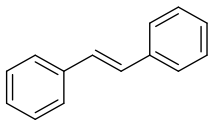
(E)-4,4'-Dichlorostilbene (2g)[6]



2g

White solid (56 mg, 75% yield). mp 172–173 °C, (lit. mp 171.5–172.4 °C). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.41 (d, J = 7.9 Hz, 4H), 7.32 (d, J = 7.8 Hz, 4H), 7.00 (s, 2H); ^{13}C NMR ($CDCl_3$, 151 MHz) δ 135.5, 133.5, 128.9, 128.0, 127.7.

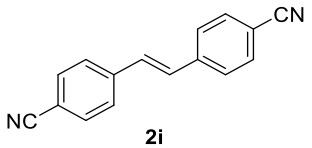
(E)-1,2-Diphenyl-ethene (2h)[8]



2h

White solid (38 mg, 70% yield). mp 121–122 °C, (lit. mp 122–124 °C). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.49 (d, J = 7.7 Hz, 4H), 7.33 (dd, $J_1 = J_2$ = 7.5 Hz, 4H), 7.27–7.21 (m, 2H), 7.09 (s, 2H); ^{13}C NMR ($CDCl_3$, 101 MHz) δ 137.4, 128.8, 128.7, 127.7, 126.6.

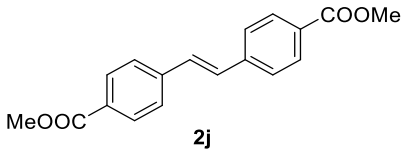
(E)-4,4'-Dicyanostilbene (2i)[5]



2i

White solid (28 mg, 41% yield). mp 284–285 °C, (lit. mp 286–288 °C). ^{1}H NMR ($CDCl_3$, 600 MHz) δ 7.68 (d, J = 8.1 Hz, 4H), 7.62 (d, J = 7.8 Hz, 4H), 7.20 (s, 2H); ^{13}C NMR ($CDCl_3$, 151 MHz) δ 140.7, 132.7, 130.3, 127.3, 118.7, 111.7.

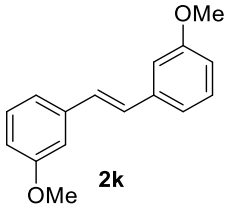
Dimethyl 4,4'-stilbene-(E)-dicarboxylate (2j)[5]



2j

White solid (60 mg, 67% yield). mp 230–232 °C, (lit. mp 231–233 °C). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.07 (d, J = 7.9 Hz, 4H), 7.61 (d, J = 7.9 Hz, 4H), 7.25 (s, 2H), 3.95 (s, 6H); ^{13}C NMR ($CDCl_3$, 151 MHz) δ 166.8, 141.2, 130.11, 130.05, 129.5, 126.6, 52.2.

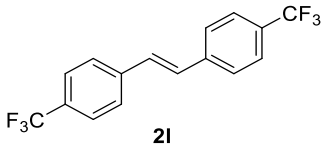
(E)-3,3'-Dimethoxystilbene (2k)[9]



2k

White solid (64 mg, 89% yield). mp 95–97 °C, (lit. mp 98–100 °C). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.30–7.25 (m, 2H), 7.11 (d, J = 7.7 Hz, 2H), 7.07 (s, 2H), 7.06–7.03 (m, 2H), 6.82 (dd, J = 8.2, 1.9 Hz, 2H), 3.84 (s, 6H); ^{13}C NMR ($CDCl_3$, 151 MHz) δ 159.9, 138.7, 129.7, 128.9, 119.3, 113.4, 111.8, 55.3.

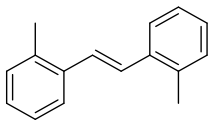
(E)-4,4'-Di(trifluoromethyl)-ethylen (2l)[5]



2l

White solid (78 mg, 82% yield). mp 130–131 °C, (lit. mp 131–133 °C). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.63 (s, 8H), 7.20 (s, 2H); ^{13}C NMR ($CDCl_3$, 151 MHz) δ 140.1, 129.9 (q, J = 31.5 Hz), 129.6, 126.9, 125.8 (q, J = 3.8 Hz), 124.1 (q, J = 269.7 Hz).

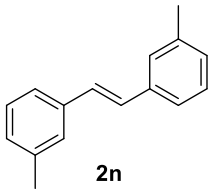
(E)-2,2'-Dimethylstilbene (2m)[7]



2m

White solid (46 mg, 74% yield). mp 78–79 °C, (lit. mp 75–77 °C)[10]. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.59 (d, J = 7.2 Hz, 2H), 7.20–7.16 (m, 8H), 2.42 (s, 6H); ^{13}C NMR ($CDCl_3$, 101 MHz) δ 136.9, 135.9, 130.4, 128.1, 127.6, 126.2, 125.6, 20.0.

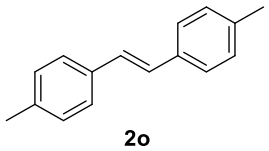
(E)-3,3'-Dimethylstilbene (2n)[7]



2n

White solid (52 mg, 84% yield). mp 47–48 °C, (lit. mp 47–49 °C). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.35 (d, J = 10.0 Hz, 4H), 7.29 (d, J = 7.2 Hz, 2H), 7.11 (d, J = 4.2 Hz, 4H), 2.41 (s, 6H); ^{13}C NMR ($CDCl_3$, 101 MHz) δ 138.2, 137.4, 128.62, 128.57, 128.4, 127.2, 123.7, 21.5.

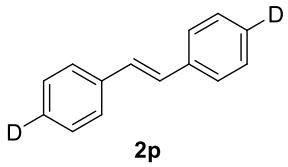
(E)-3,3'-Dimethylstilbene (2o)[5]



2o

White solid (54 mg, 86% yield). mp 172–175 °C, (lit. mp 179–181 °C). ^{1}H NMR ($CDCl_3$, 600 MHz) δ 7.39 (d, J = 7.9 Hz, 4H), 7.15 (d, J = 7.8 Hz, 4H), 7.03 (s, 2H), 2.35 (s, 6H); ^{13}C NMR ($CDCl_3$, 101 MHz) δ 137.3, 134.8, 129.4, 127.7, 126.3, 21.3.

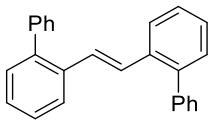
(E)-1,2-Diphenyl-ethene-4,4'-*d*$_2$ (2p)[19]



2p

White solid (38 mg, 69% yield). mp 120–121 °C. ^{1}H NMR ($CDCl_3$, 600 MHz) δ 7.52 (d, J = 8.1 Hz, 4H), 7.36 (d, J = 7.9 Hz, 4H), 7.11 (s, 2H). ^{13}C NMR ($CDCl_3$, 101 MHz) δ 137.4, 128.7, 128.6, 128.5, 128.3, 126.5.

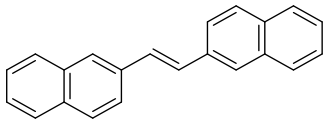
(E)-1,2-Di(2-phenylphenyl)-ethene (2q)[10]



2q

White solid (81 mg, 81% yield). mp 123–125 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.57–7.41 (m, 12H), 7.38–7.30 (m, 6H), 7.10 (s, 2H); ^{13}C NMR ($CDCl_3$, 101 MHz) δ 141.1, 141.0, 135.7, 130.3, 129.9, 128.5, 128.2, 127.6, 127.4, 127.1, 126.0.

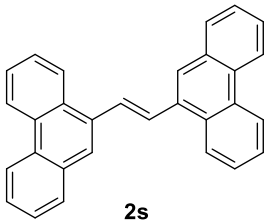
(E)-1,2-Di(naphthalen-2-yl)ethene (2r)[5]



2r

White solid (72 mg, 86% yield). mp 256.0–256.5 °C, (lit. mp 256–257 °C). ^{1}H NMR ($CDCl_3$, 600 MHz) δ 7.91 (s, 2H), 7.88–7.77 (m, 8H), 7.52–7.43 (m, 4H), 7.41 (s, 2H); ^{13}C NMR ($CDCl_3$, 151 MHz) δ 134.9, 133.8, 133.1, 129.1, 128.4, 128.1, 127.7, 126.7, 126.4, 126.0, 123.5.

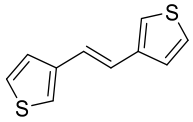
(E)-1,2-Di(9-phenanthryl)-ethylen (2s)[11]



2s

Yellow solid (76 mg, 67% yield). mp 270–271 °C, (lit. mp 271–273 °C). ^{1}H NMR (CD_2Cl_2, 400 MHz) δ 8.85 (d, J = 7.9 Hz, 2H), 8.78 (d, J = 7.9 Hz, 2H), 8.42 (dd, J = 8.0, 1.3 Hz, 2H), 8.22 (s, 2H), 8.09 (s, 2H), 8.06 (dd, J = 7.8, 1.4 Hz, 2H), 7.80–7.68 (m, 8H); ^{13}C NMR (CD_2Cl_2, 151 MHz) δ 134.2, 131.9, 130.8, 130.4, 129.7, 128.8, 127.0, 126.8, 126.74, 126.69, 124.9, 124.7, 123.2, 122.6.

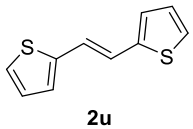
(E)-1,2-Di(thiophen-3-yl)ethene (2t)[12]



2t

White solid (40 mg, 69% yield). mp 165–167 °C, (lit. mp 166.5–167 °C). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.34 (d, J = 2.1 Hz, 4H), 7.26–7.24 (m, 2H), 7.00 (s, 2H); ^{13}C NMR ($CDCl_3$, 101 MHz) δ 140.1, 126.2, 124.8, 123.0, 121.9.

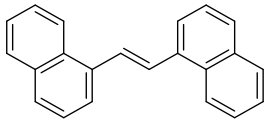
(E)-1,2-Di(thiophen-2-yl)ethene (2u)[13]



2u

White solid (23 mg, 40% yield). mp 132–133 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.20 (d, J = 5.0 Hz, 2H), 7.07 (s, 2H), 7.06 (dd, J = 3.6, 1.1 Hz, 2H), 7.01 (dd, J = 5.0, 3.6 Hz, 2H); ^{13}C NMR ($CDCl_3$, 151 MHz) δ 141.4, 126.6, 125.0, 123.3, 120.4.

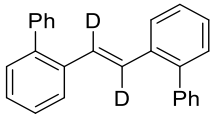
(E)-1,2-Di(naphthalen-1-yl)ethene (2v)[7]



2v

White solid (74 mg, 88% yield). mp 158–160 °C, (lit. mp 156–157 °C). ^{1}H NMR ($CDCl_3$, 600 MHz) δ 8.26 (d, J = 8.1 Hz, 2H), 7.92 (s, 2H), 7.90 (d, J = 7.7 Hz, 2H), 7.86 (dd, J = 10.3, 7.9 Hz, 4H), 7.57–7.51 (m, 6H); ^{13}C NMR ($CDCl_3$, 101 MHz) δ 135.4, 133.8, 131.5, 129.1, 128.7, 128.3, 126.2, 126.0, 125.8, 124.0, 123.9.

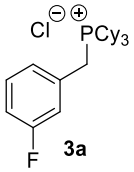
(E)-1,2-Di(2-phenylphenyl)-ethene-1,2-*d*$_2$ (2q-*d*$_2$)



2q-*d*$_2$

White solid (80 mg, 80% yield). mp 121–123 °C. ^{1}H NMR ($CDCl_3$, 600 MHz) δ 7.51–7.33 (m, 12H), 7.32–7.24 (m, 6H); ^{13}C NMR ($CDCl_3$, 151 MHz) δ 141.2, 141.0, 135.7, 135.6, 130.3, 130.0, 128.4, 128.3, 127.6, 127.5, 127.2, 126.1, 126.0; HRMS (EI) m/z calcd for $C_{26}H_{18}D_2$ $[M]^+$: 334.1691, found: 334.1685.

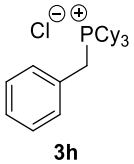
Tricyclohexyl(3-fluorobenzyl) phosphonium chloride (3a)



3a

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39–7.29 (m, 2H), 7.24–7.18 (m, 1H), 7.06–6.99 (m, 1H), 4.48 (d, J = 14.5 Hz, 2H), 2.80–2.63 (m, 3H), 2.06–1.97 (m, 6H), 1.93–1.85 (m, 6H), 1.81–1.74 (m, 3H), 1.54–1.22 (m, 15H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.7 (dd, J = 248.3, 2.8 Hz), 132.2 (t, J = 7.9 Hz), 130.9 (dd, J = 8.3, 2.2 Hz), 127.3–124.5 (m), 117.3 (dd, J = 22.1, 4.7 Hz), 115.2 (dd, J = 20.9, 2.9 Hz), 30.8 (d, J = 38.6 Hz), 27.0 (d, J = 3.9 Hz), 26.5 (d, J = 11.8 Hz), 25.3 , 22.6 (d, J = 40.7 Hz); HRMS (ESI) m/z calcd for $C_{25}H_{39}FP^+$ $[M]^+$: 389.2768, found: 389.2762; ^{31}P NMR (162 MHz, $CDCl_3$) δ 30.0.

Tricyclohexylbenzylphosphonium chloride (3h)[14]

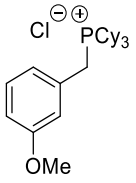


3h

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48–7.41 (m, 2H), 7.41–7.30 (m, 3H), 4.35 (d, J = 14.3 Hz, 2H), 2.88–2.63 (m, 3H), 2.03–1.97 (m, 6H), 1.93–1.85 (m, 6H), 1.83–1.74 (m, 3H), 1.56–1.34 (m, 12H), 1.25 (qt, J = 12.8, 3.5 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 130.3 (d, J = 4.7 Hz), 129.4 (d, J = 2.9 Hz), 128.3 (d, J = 3.2 Hz), 30.8 (d, J = 38.7 Hz),

27.0 (d, J = 4.3 Hz), 26.5 (d, J = 11.7 Hz), 25.4, 23.0 (d, J = 41.2 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 29.3.

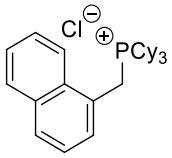
Tricyclohexyl(3-methoxybenzyl)phosphonium chloride (3k)



3k

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28–7.23 (m, 1H), 7.14–7.08 (m, 1H), 7.01–6.94 (m, 1H), 6.91–6.82 (m, 1H), 4.30 (d, J = 14.3 Hz, 2H), 3.84 (s, 3H), 2.89–2.72 (m, 3H), 2.01 (t, J = 8.2 Hz, 6H), 1.95–1.85 (m, 6H), 1.84–1.75 (m, 3H), 1.57–1.36 (m, 12H), 1.27 (tt, J = 12.5, 3.5 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.2 (d, J = 2.3 Hz), 131.0 (d, J = 8.0 Hz), 130.3 (d, J = 2.7 Hz), 122.4 (d, J = 5.1 Hz), 116.0 (d, J = 5.1 Hz), 114.1, 55.7, 31.1 (d, J = 38.7 Hz), 27.3 (d, J = 4.2 Hz), 26.7 (d, J = 11.8 Hz), 25.6, 23.2 (d, J = 41.3 Hz); HRMS (ESI) m/z calcd for $C_{26}H_{42}OP^+$ $[M]^+$: 401.2968, found: 401.2969; ^{31}P NMR (162 MHz, $CDCl_3$) δ 29.3.

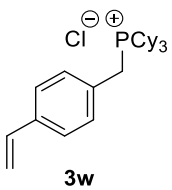
Tricyclohexyl(naphthalen-1-yl)phosphonium chlorid (3v)



3v

White solid (98% yield). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.46 (d, J = 8.5 Hz, 1H), 7.86 (d, J = 8.0 Hz, 1H), 7.82 (d, J = 8.1 Hz, 1H), 7.70–7.62 (m, 1H), 7.62–7.57 (m, 1H), 7.56–7.49 (m, 1H), 7.47–7.39 (m, 1H), 4.68 (d, J = 14.4 Hz, 2H), 2.85 (q, J = 12.5 Hz, 3H), 1.89 (s, 6H), 1.80 (d, J = 11.4 Hz, 6H), 1.71 (d, J = 12.5 Hz, 3H), 1.44 (q, J = 12.3 Hz, 6H), 1.30 (q, J = 12.6 Hz, 6H), 1.21–1.12 (m, 3H); ^{13}C NMR ($CDCl_3$, 101 MHz) δ 134.0 (d, J = 2.1 Hz), 132.2 (d, J = 4.2 Hz), 129.1 (d, J = 4.4 Hz), 128.8 (d, J = 5.6 Hz), 127.1, 126.4, 126.3, 126.2, 125.4 (d, J = 3.3 Hz), 124.2, 31.6 (d, J = 37.9 Hz), 27.2 (d, J = 4.1 Hz), 26.5 (d, J = 11.8 Hz), 25.4, 20.5 (d, J = 41.4 Hz); HRMS (ESI) m/z calcd for $C_{29}H_{42}P^+$ $[M]^+$: 421.3019, found: 421.3017; ^{31}P NMR ($CDCl_3$, 162 MHz) δ 30.45.

Tricyclohexyl(4-vinylbenzyl)phosphonium chloride (3w)[15]

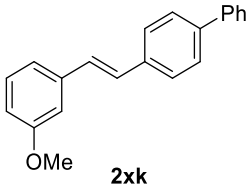


3w

White solid (98% yield). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.39 (s, 4H), 6.68 (dd, J = 17.6, 10.9 Hz, 1H), 5.77 (d, J = 17.6 Hz, 1H), 5.30 (d, J = 10.9 Hz, 1H), 4.28 (d, J = 14.3 Hz,

2H), 2.70 (q, J = 12.7 Hz, 3H), 2.08–1.96 (m, 6H), 1.94–1.86 (m, 6H), 1.79 (d, J = 11.9 Hz, 3H), 1.55–1.35 (m, 12H), 1.30–1.21 (m, 3H); ^{13}C NMR ($CDCl_3$, 101 MHz) δ 137.6, 135.9, 130.6 (d, J = 5.1 Hz), 128.9 (d, J = 8.5 Hz), 127.1 (d, J = 2.8 Hz), 114.9, 31.0 (d, J = 38.8 Hz), 27.2 (d, J = 3.9 Hz), 26.6 (d, J = 11.7 Hz), 25.5, 22.9 (d, J = 41.1 Hz); ^{31}P NMR ($CDCl_3$, 162 MHz) δ 29.31.

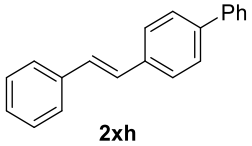
(E)-4-(3-Methoxystyryl)-1,1'-biphenyl (2xk)[16]



2xk

White solid (77 mg, 91% yield). mp 111–112 °C, (lit. mp 114–116 °C). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.65–7.58 (m, 6H), 7.47–7.42 (m, 2H), 7.38–7.32 (m, 1H), 7.31–7.26 (m, 1H), 7.16–7.11 (m, 3H), 7.09–7.05 (m, 1H), 6.86–6.80 (m, 1H), 3.86 (s, 3H); ^{13}C NMR ($CDCl_3$, 101 MHz) δ 160.0, 140.7, 140.4, 138.8, 136.3, 129.7, 128.8, 128.7, 128.6, 127.4, 127.0, 126.9, 119.3, 113.4, 111.8, 55.3.

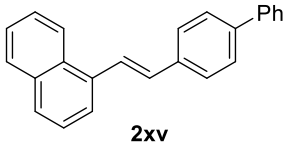
(E)-4-Phenylstilbene (2xh)[17]



2xh

White solid (68.3 mg, 89% yield). mp 217–218 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.64–7.58 (m, 6H), 7.55–7.51 (m, 2H), 7.44 (dd, J_1 = J_2 = 7.6 Hz, 2H), 7.40–7.31 (m, 3H), 7.29–7.23 (m, 1H), 7.15 (s, 2H); ^{13}C NMR ($CDCl_3$, 101 MHz) δ 140.7, 140.4, 137.4, 136.4, 128.8, 128.7, 128.2, 127.7, 127.38, 127.35, 127.0, 126.9, 126.6.

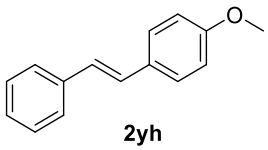
(E)-1-(4-Phenyl-styryl)-naphthalin (2xv)[18]



2xv

White solid (82.6 mg, 90% yield). mp 141–143 °C. ^{1}H NMR ($CDCl_3$, 600 MHz) δ 8.23 (dd, J = 8.5, 2.7 Hz, 1H), 7.91 (dd, J = 16.0, 3.0 Hz, 1H), 7.87–7.83 (m, 1H), 7.80–7.72 (m, 2H), 7.68–7.57 (m, 6H), 7.54–7.39 (m, 5H), 7.37–7.31 (m, 1H), 7.16 (dd, J = 16.0, 3.0 Hz, 1H); ^{13}C NMR ($CDCl_3$, 151 MHz) δ 140.7, 140.6, 136.7, 135.1, 133.8, 131.5, 131.3, 128.9, 128.7, 128.1, 127.5, 127.4, 127.3, 127.0, 126.2, 125.90, 125.88, 125.8, 123.8, 123.7.

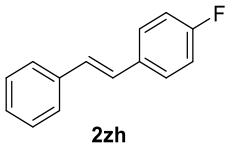
(E)-3-Methoxystilbene (2yh)[17]



2yh

White solid (57.9 mg, 92% yield). mp 135–136 °C. ^{1}H NMR ($CDCl_3$, 600 MHz) δ 7.51–7.41 (m, 4H), 7.37–7.29 (m, 2H), 7.27–7.17 (m, 1H), 7.08–6.93 (m, 2H), 6.92–6.85 (m, 2H), 3.81 (s, 3H); ^{13}C NMR ($CDCl_3$, 101 MHz) δ 159.4, 137.7, 130.2, 128.7, 128.3, 127.8, 127.3, 126.7, 126.3, 114.2, 55.4.

(E)-4-Fluorostilbene (2zh)[17]



2zh

White solid (38.7 mg, 65% yield). mp 123–124 °C.^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.52–7.39 (m, 4H), 7.38–7.30 (m, 2H), 7.28–7.21 (m, 1H), 7.08–6.95 (m, 4H); ^{13}C NMR ($CDCl_3$, 101 MHz) δ 162.4 (d, J = 247.0 Hz), 137.3, 133.6 (d, J = 3.5 Hz), 128.8, 128.6 (d, J = 2.8 Hz), 128.1 (d, J = 8.0 Hz), 127.7, 127.5, 126.5, 115.7 (d, J = 21.7 Hz).

9. X-Ray Crystallographic Analysis

The absolute configuration of **2j** was determined based on single-crystal X-ray analysis. The detail procedure was shown as following: The **2j** solid was dissolved in CH_2Cl_2 (5.0 mL) in glovebox. Then, the solvent was allowed to slowly evaporated into the atmosphere. The crystals of **2j** were grown from solution, which is suitable for X-ray diffraction analysis.

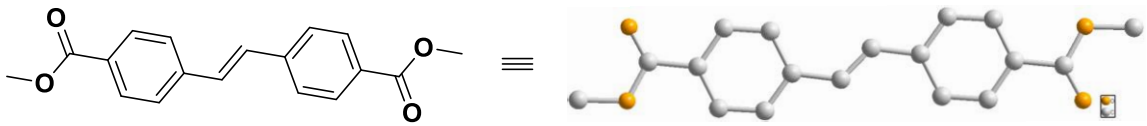


Figure S33. X-ray structure of **2j**. Hydrogen atoms are omitted for clarity.

CCDC No. 2098125 (**2j**) contains the supplementary crystallographic data for this paper. The crystal data can be obtained free of charge from the Cambridge Crystallographic Data Centre through www.ccdc.cam.ac.uk/data request/cif.

Table S12. Crystal data and structure refinement for **2j**.

CCDC number	2098125	
Empirical formula	$C_{18}H_{16}O_4$	
Formula weight	29.02	
Temperature	295.9 K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P -1	
Unit cell dimensions	a = 6.0447(17) Å	α = 90°
	b = 7.273(2) Å	β = 90.036(12)°
	c = 33.480(10) Å	γ = 90°
Volume	1471.9(8) $Å^3$	
Z	43	
Density (calculated)	1.408 g/cm^3	
Absorption coefficient	0.130 mm^{-1}	
F(000)	645	
Crystal size	0.2 x 0.2 x 0.2 mm^3	
Theta range for data collection	2.433 to 27.660°	
Index ranges	-7<=h<=7,-8<=k<=9,-43<=l<=42	
Reflections collected	15071	
Independent reflections	6029 [R(int) = 0.0953]	
Completeness to theta = 25.242	91.7 %	
Absorption correction	None	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	6029/0/401	
Goodness-of-fit on F^2	1.029	
indices [$I > 2\delta(I)$]	R1 = 0.0739, wR2 = 0.1645	
R indices (all data)	R1 = 0.1814, wR2 = 0.2054	
Largest diff. peak and hole	0.309 and -0.232 $e.Å^{-3}$	

The absolute configuration of **2m** was determined based on single-crystal X-ray analysis. The detail procedure was shown as following: The **2m** solid was dissolved in CH_2Cl_2 (5.0 mL) in glovebox. Then, the solvent was allowed to slowly evaporated into the atmosphere. The crystals of **2m** were grown from solution, which is suitable for X-ray diffraction analysis.

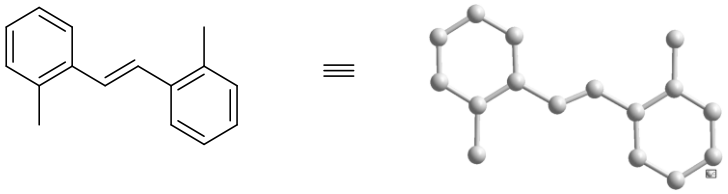


Figure S34. X-ray structure of **2m**. Hydrogen atoms are omitted for clarity.

CCDC No. 2097865 (**2m**) contains the supplementary crystallographic data for this paper. The crystal data can be obtained free of charge from the Cambridge Crystallographic Data Centre through www.ccdc.cam.ac.uk/data request/cif.

Table S13. Crystal data and structure refinement for **2m**.

CCDC number	2097865	
Empirical formula	$C_{16}H_{16}$	
Formula weight	208.29	
Temperature	295.9 K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 1 21/n 1	
Unit cell dimensions	a = 8.6739(13) Å	α = 90°
	b = 6.6929(11) Å	β = 98.484(5)°
	c = 10.8860(13) Å	γ = 90°
Volume	625.06(16) $Å^3$	
Z	2	
Density (calculated)	1.107 g/cm^3	
Absorption coefficient	0.062 mm^{-1}	
F(000)	224	
Crystal size	0.35 x 0.3 x 0.3 mm^3	
Theta range for data collection	2.809 to 27.462°	
Index ranges	-11<=h<=10,-8<=k<=8,-14<=l<=14	
Reflections collected	8508	
Independent reflections	1432 [R(int) = 0.0607]	

Completeness to theta = 25.242	99.9 %
Absorption correction	Semi-empirical from equivalents
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	1432/0/74
Goodness-of-fit on F^2	1.041
indices [$I > 2\delta(I)$]	R1 = 0.0594, wR2 = 0.1578
R indices (all data)	R1 = 0.0773, wR2 = 0.1705
Largest diff. peak and hole	0.161 and -0.223 e.Å^{-3}

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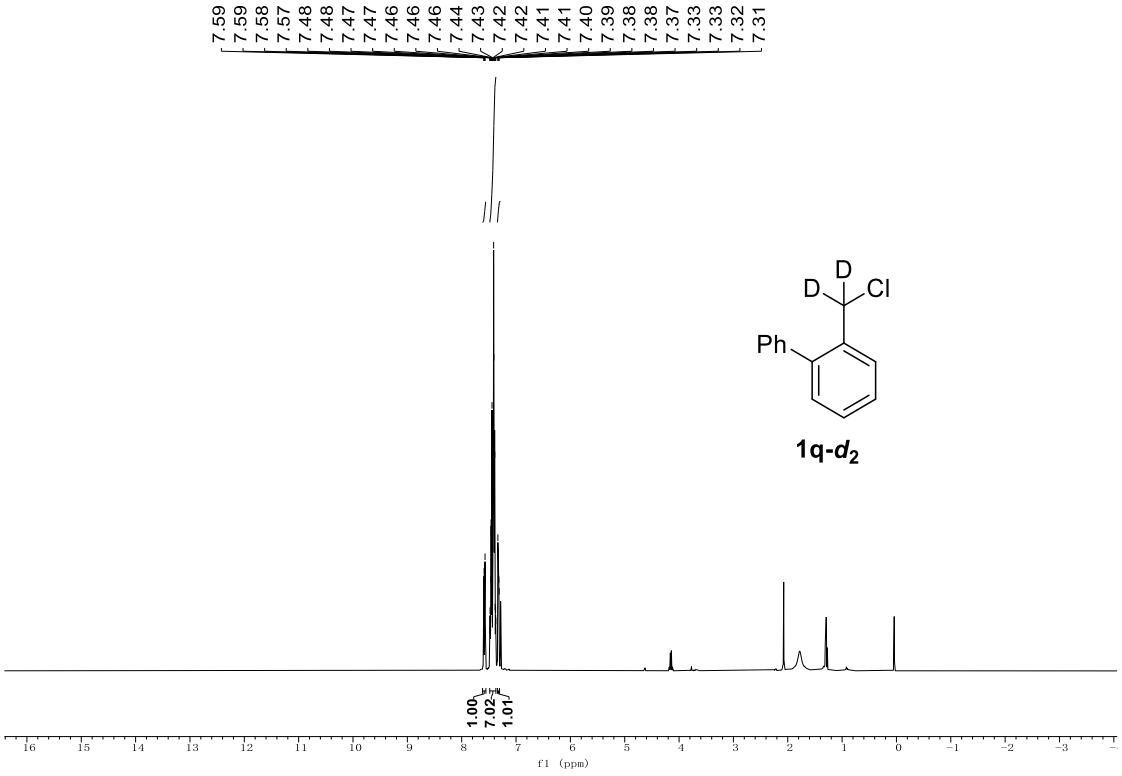
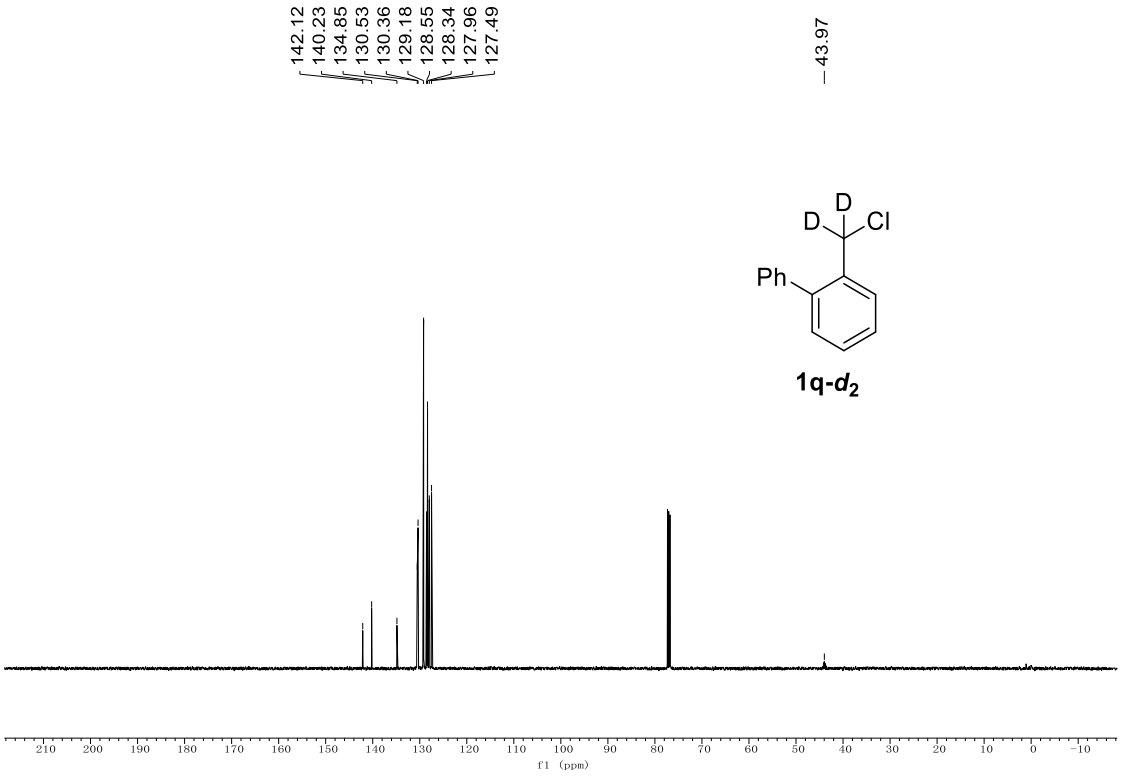
11. Copies of NMR Spectra

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



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



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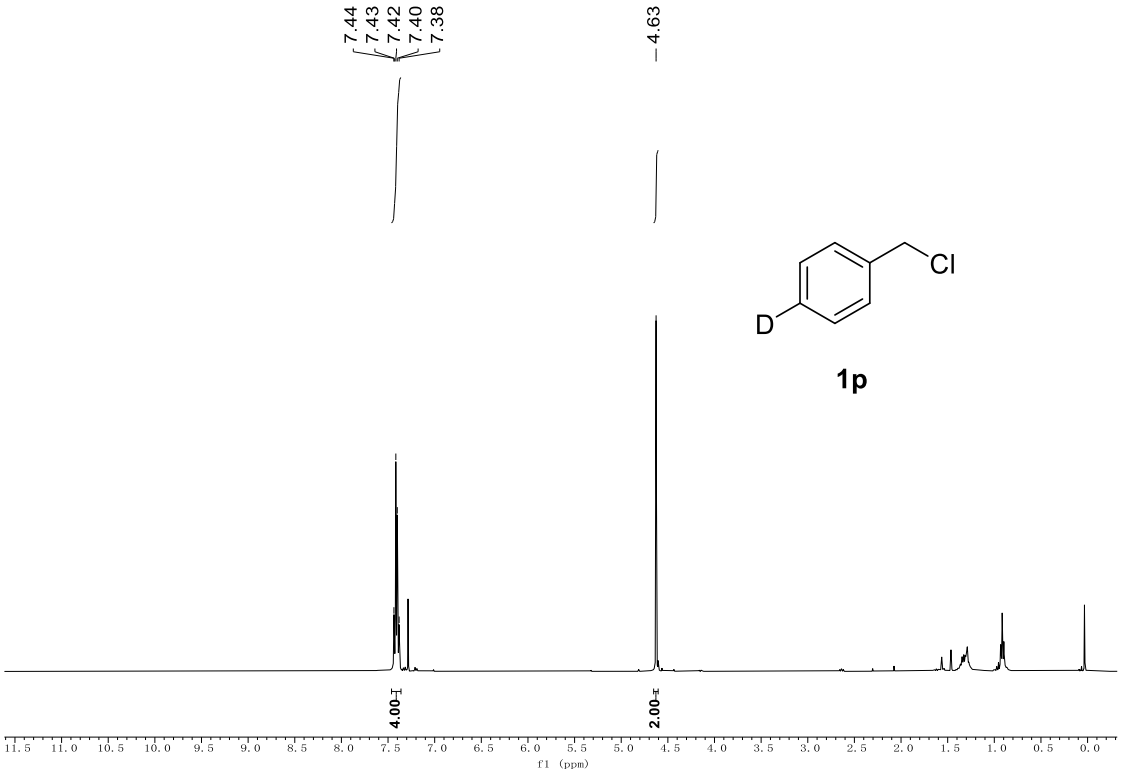

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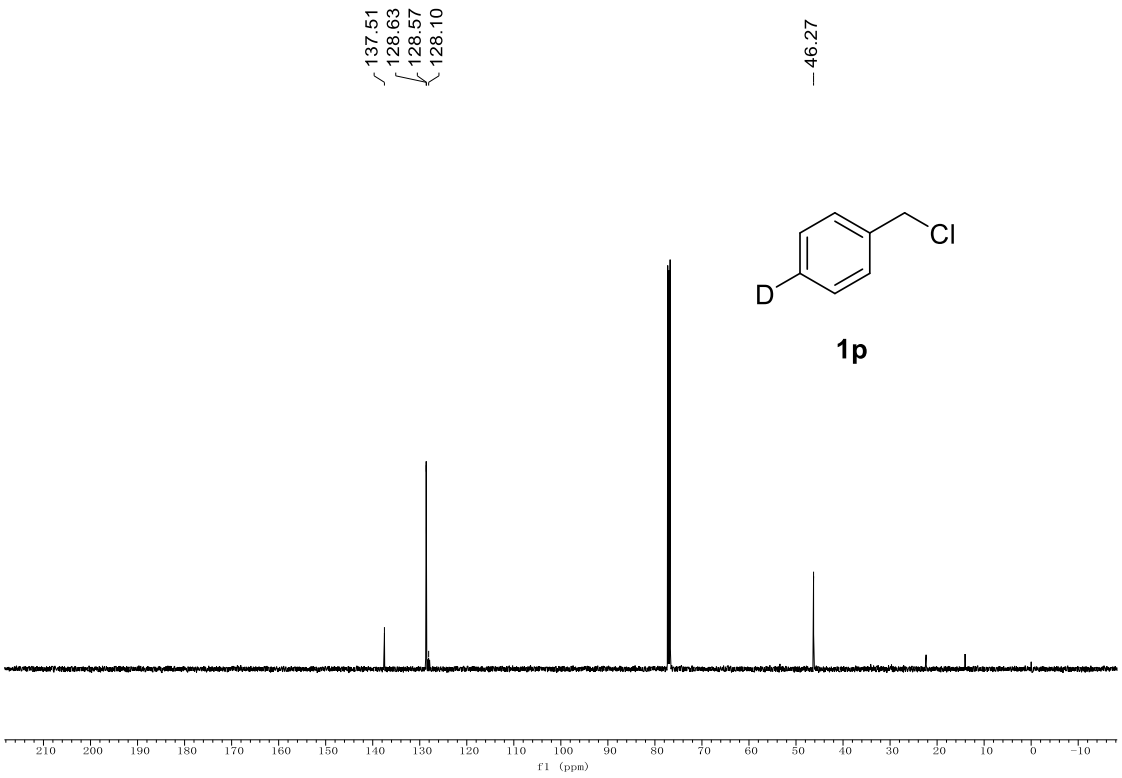
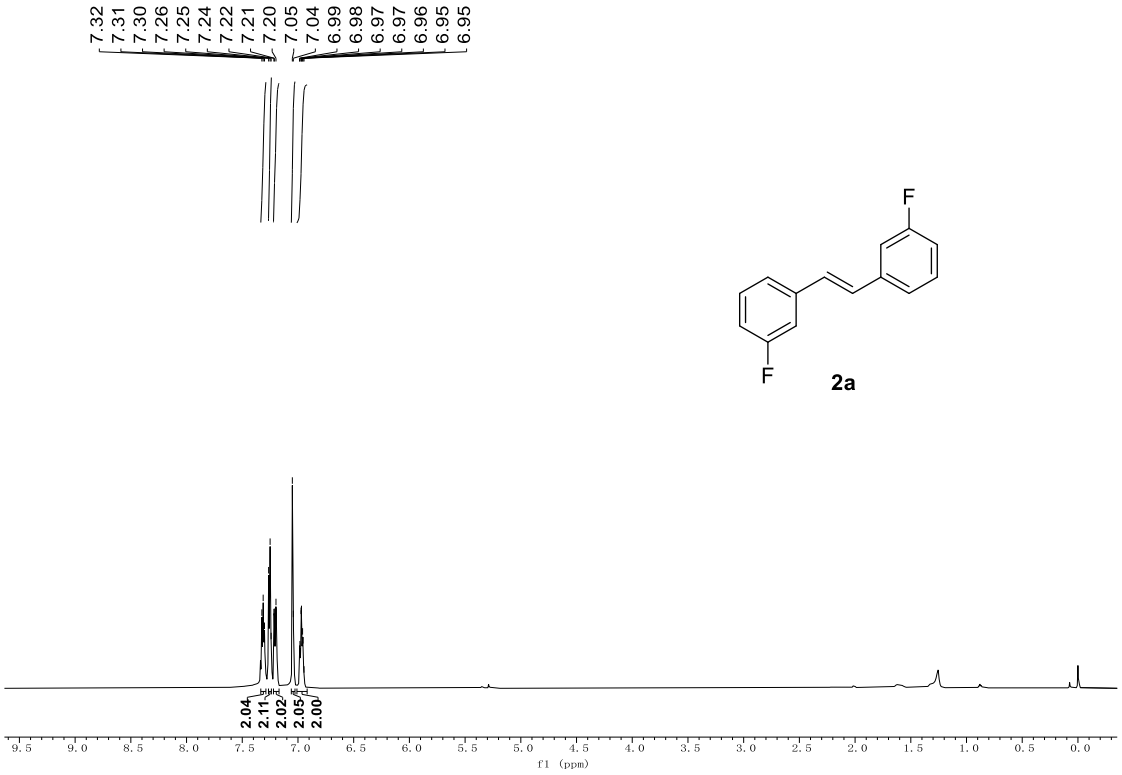


^{1}H NMR, 600 MHz, $CDCl_3$



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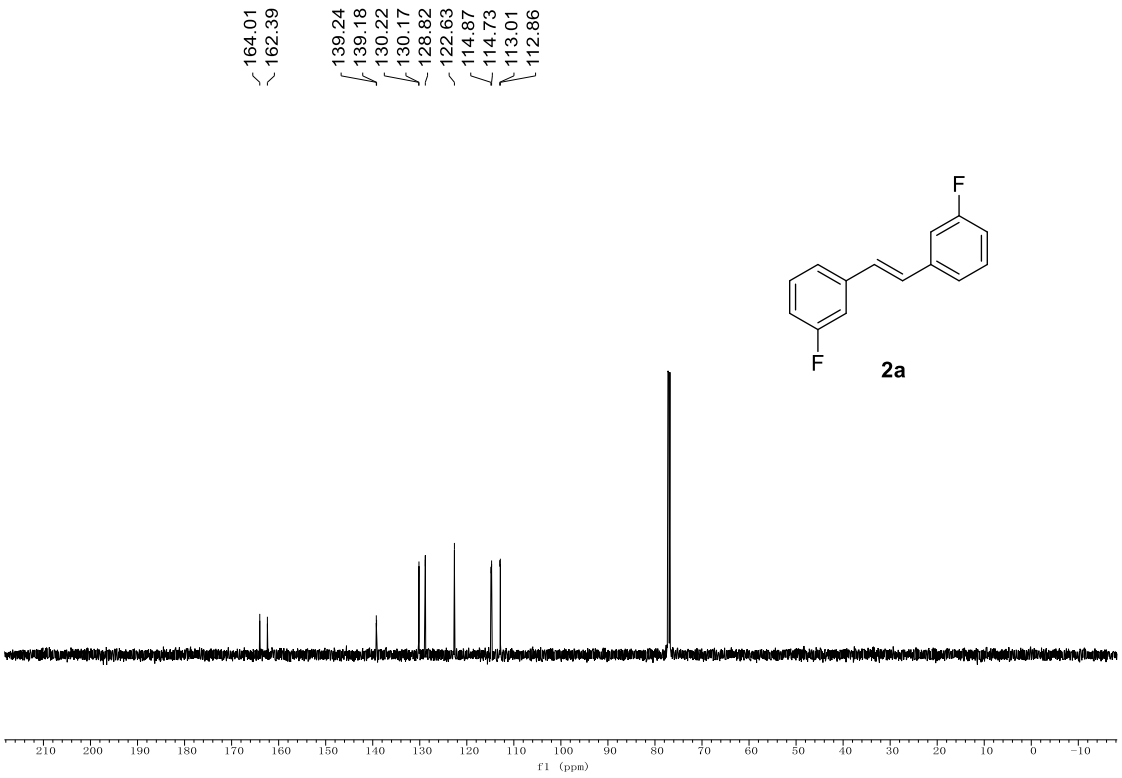

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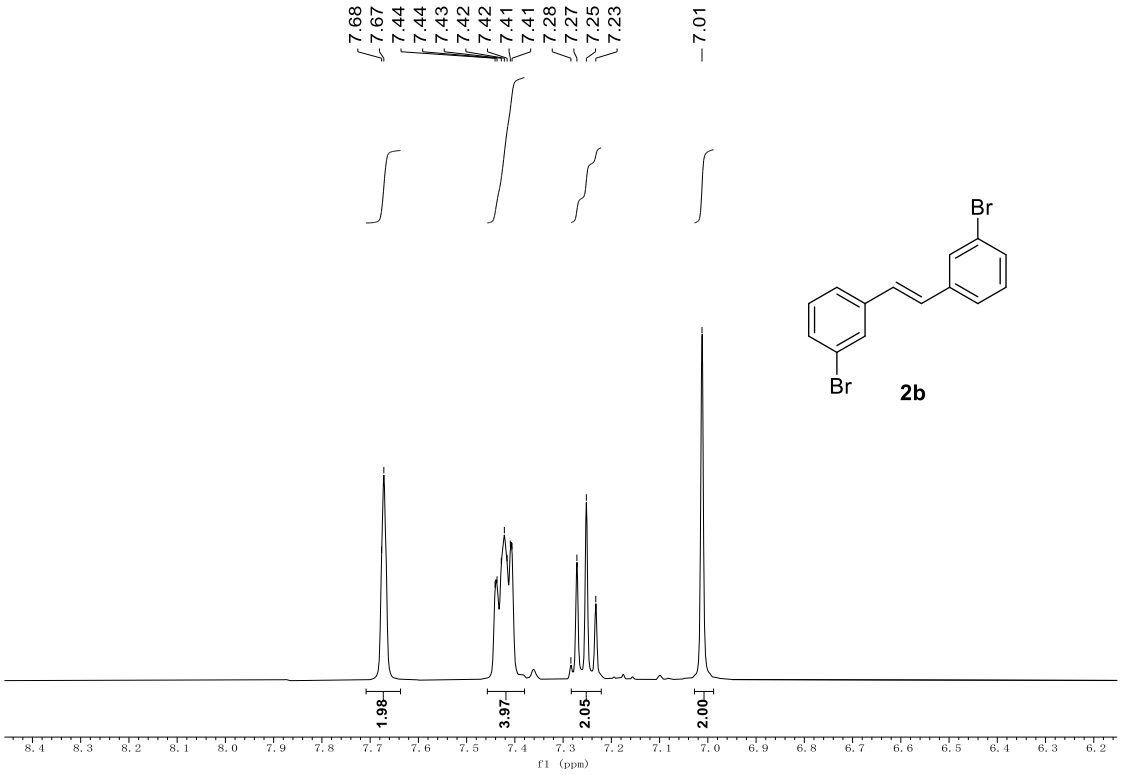

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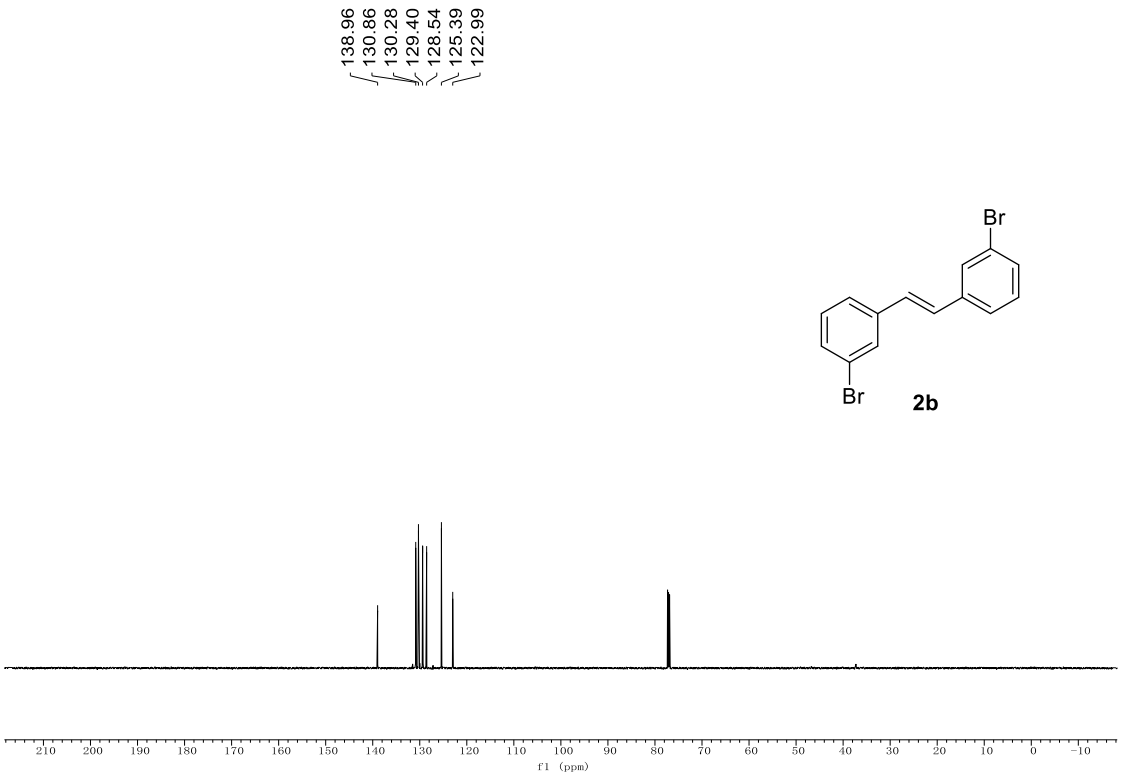

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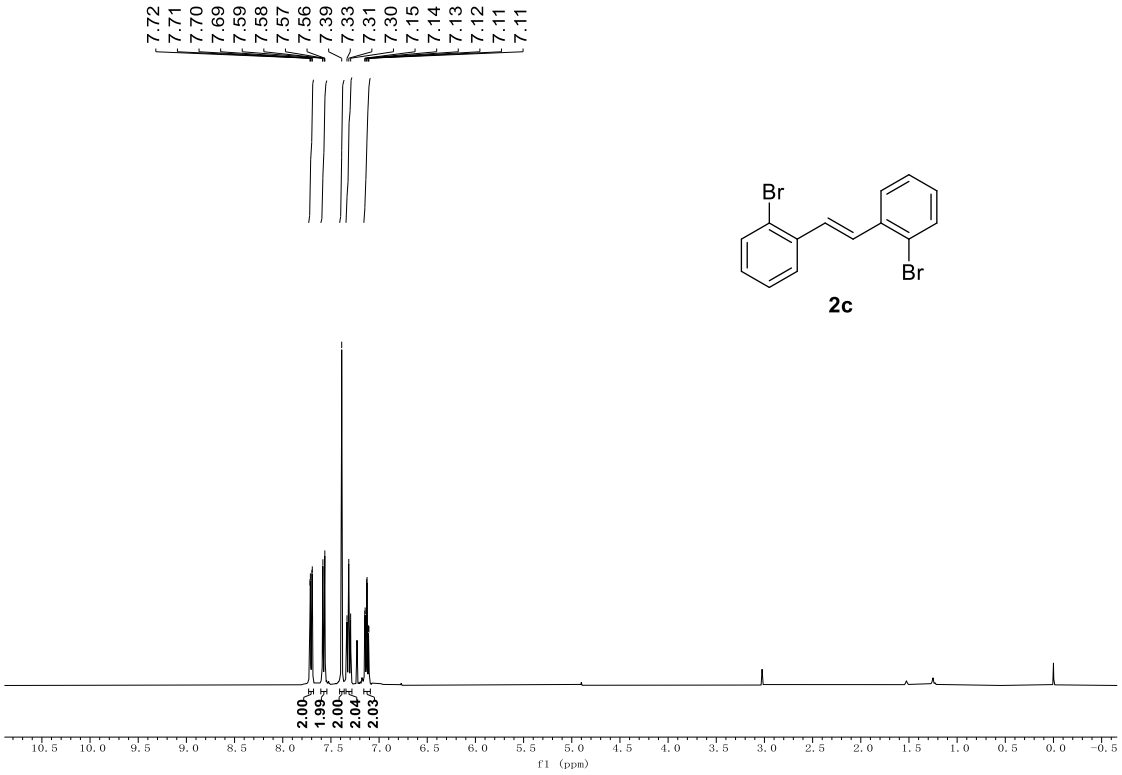

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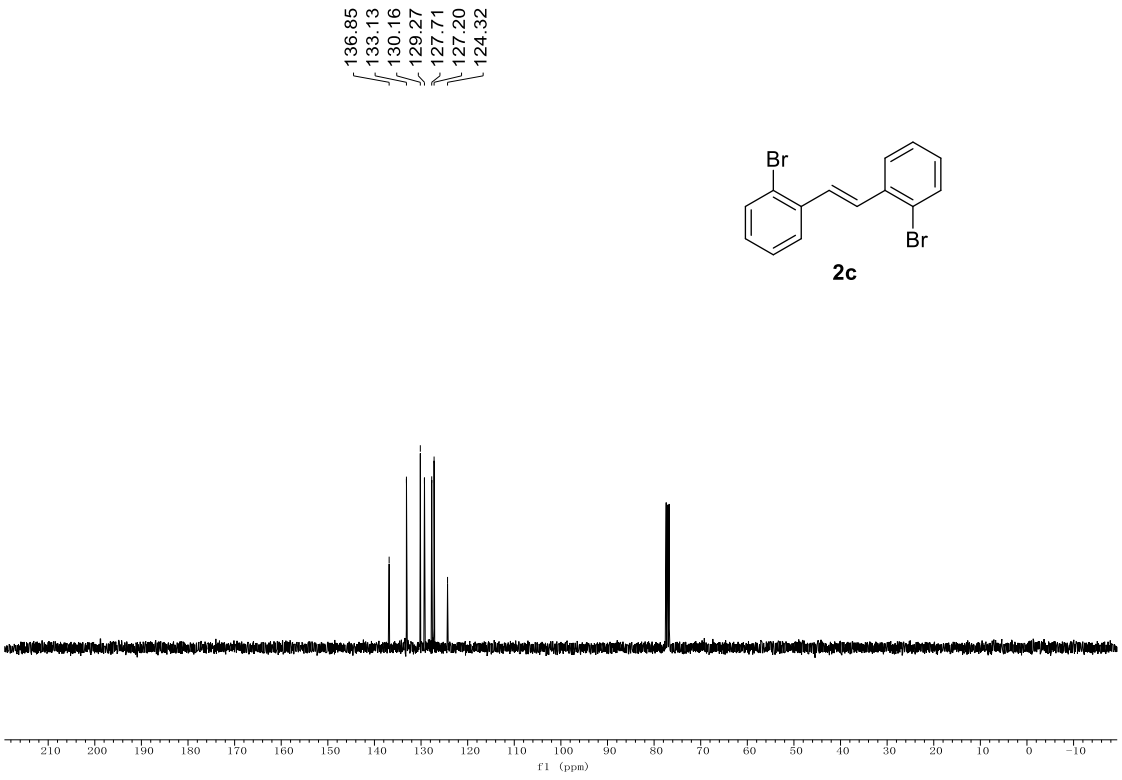

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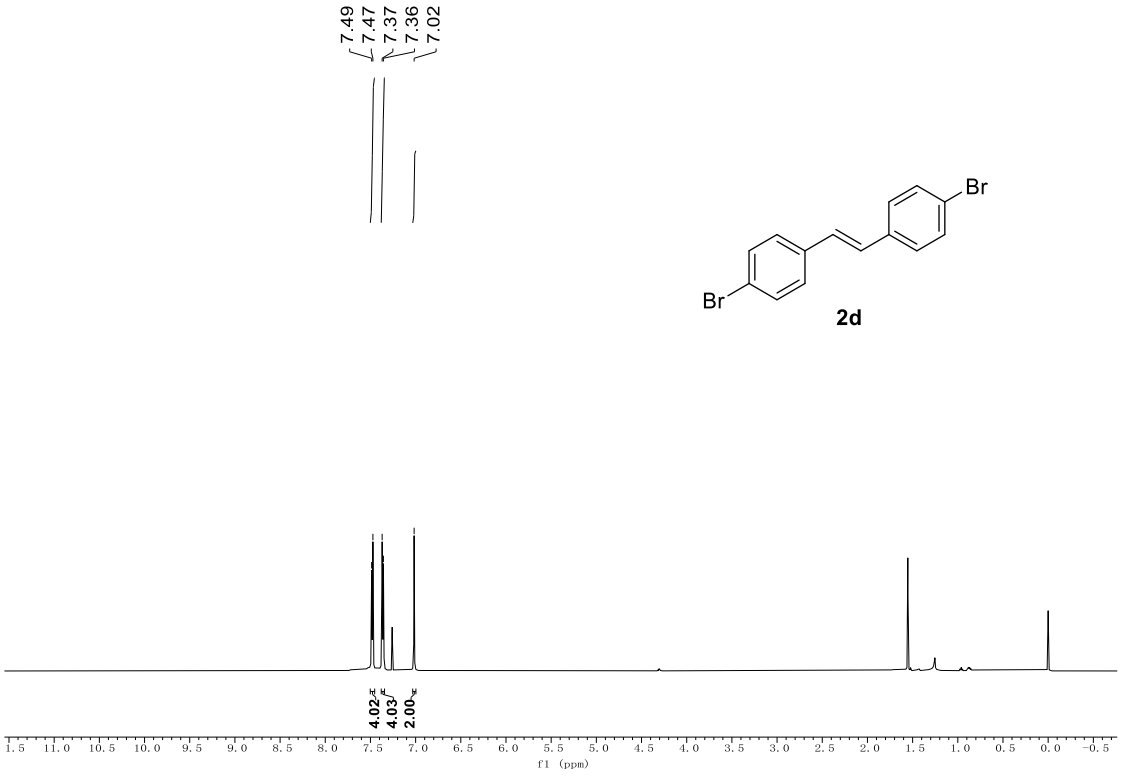

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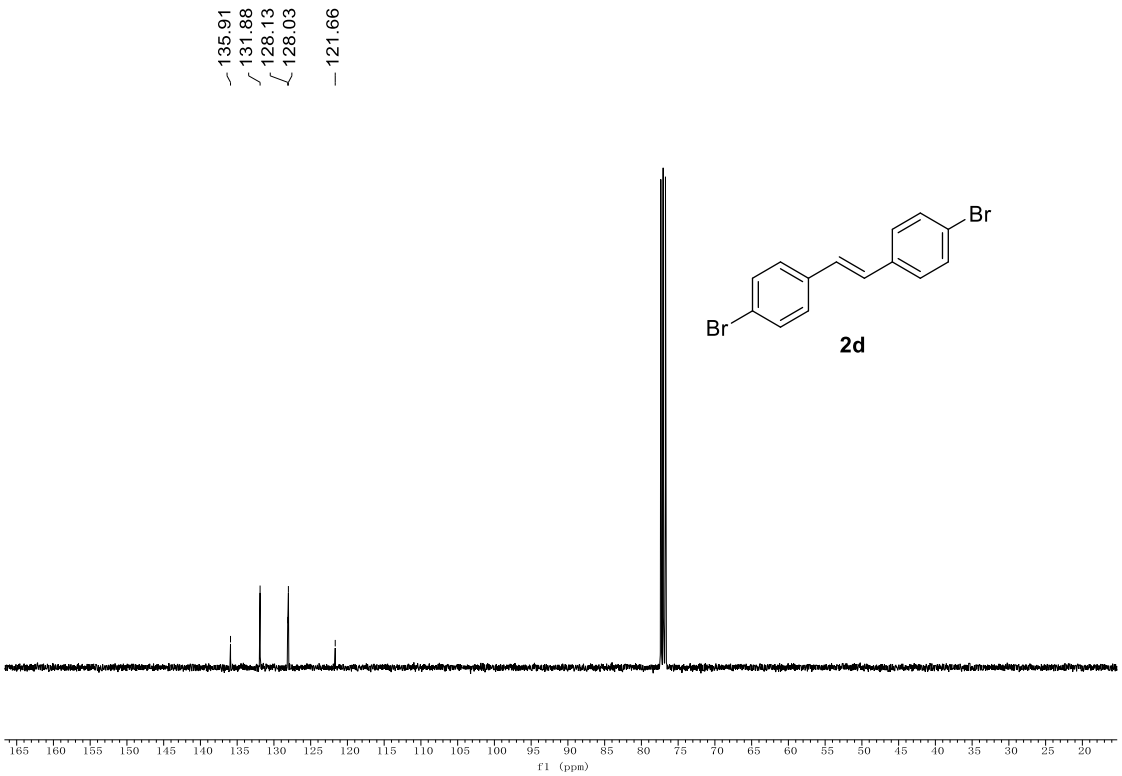

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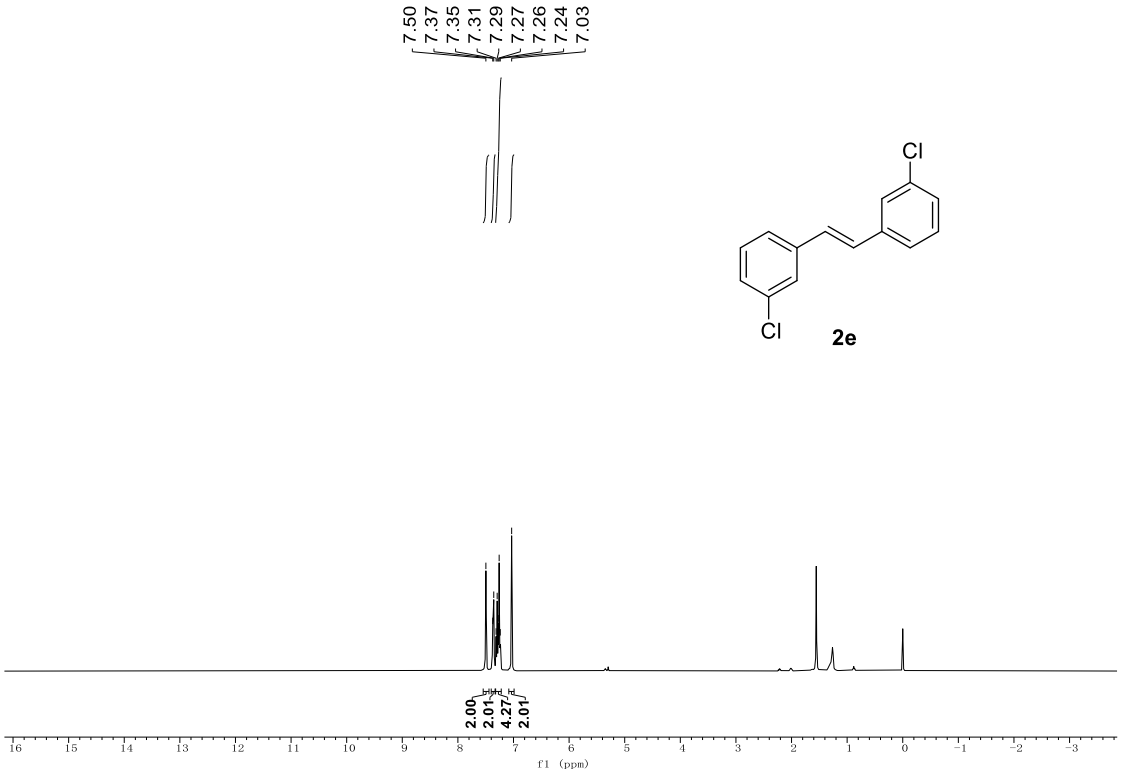

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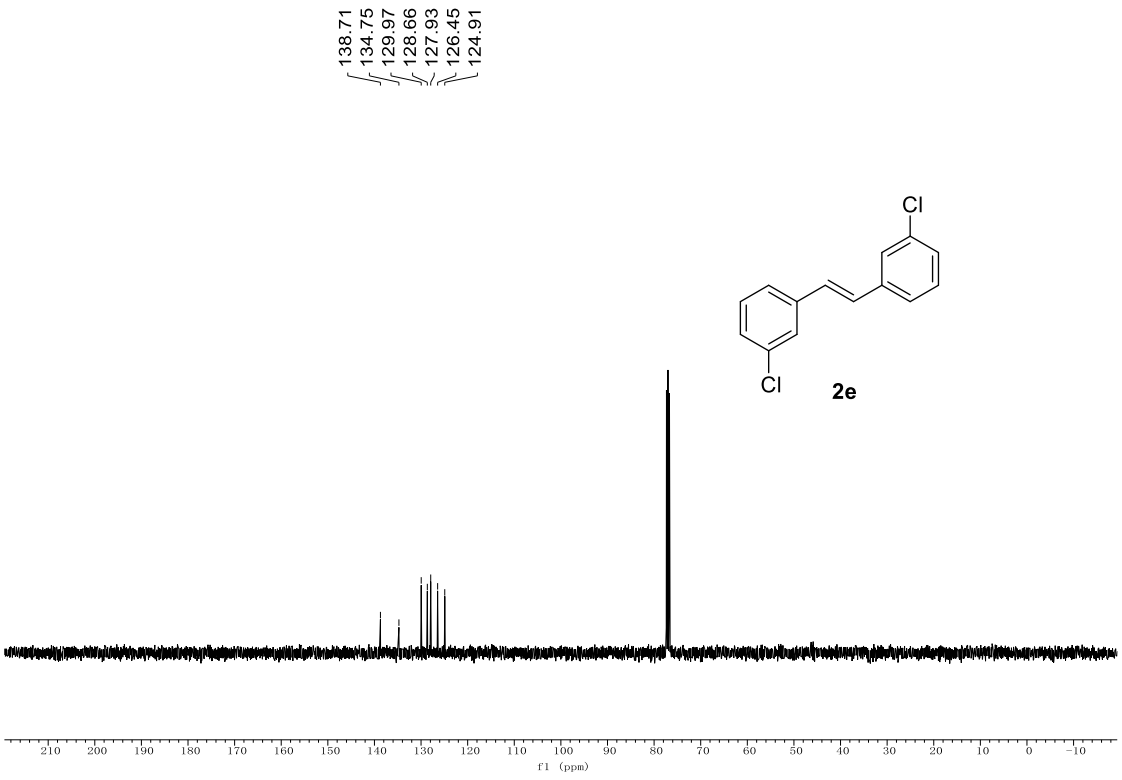

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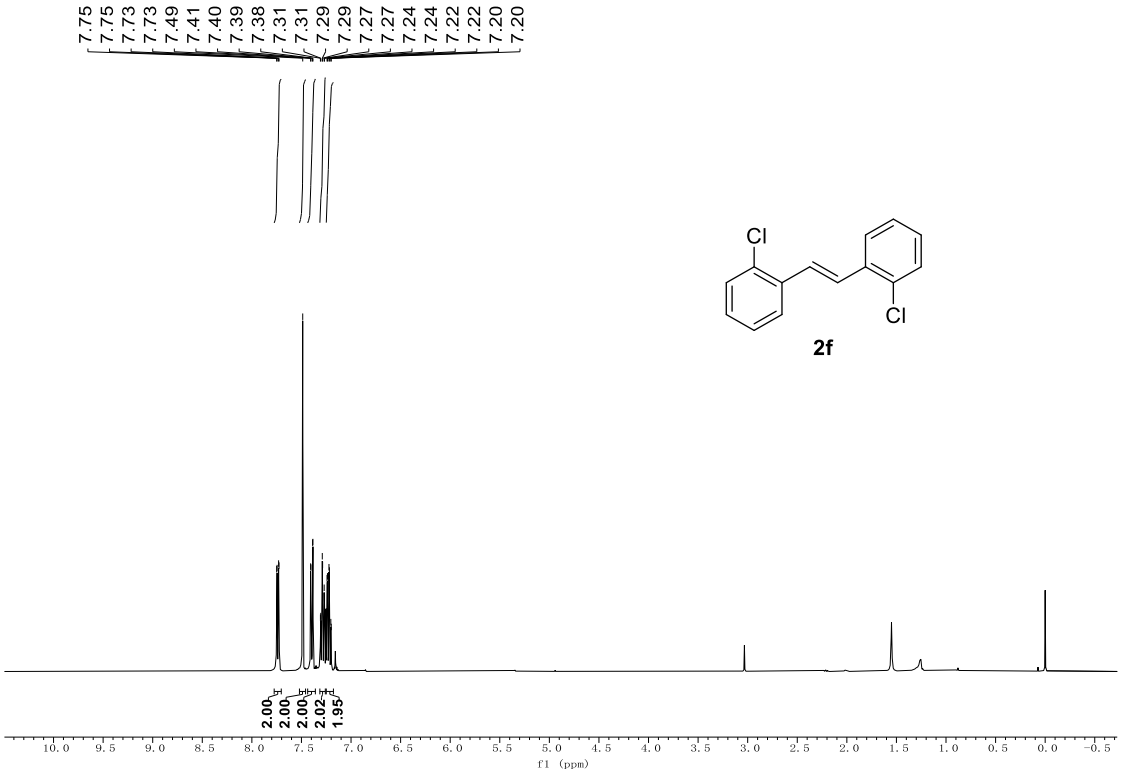

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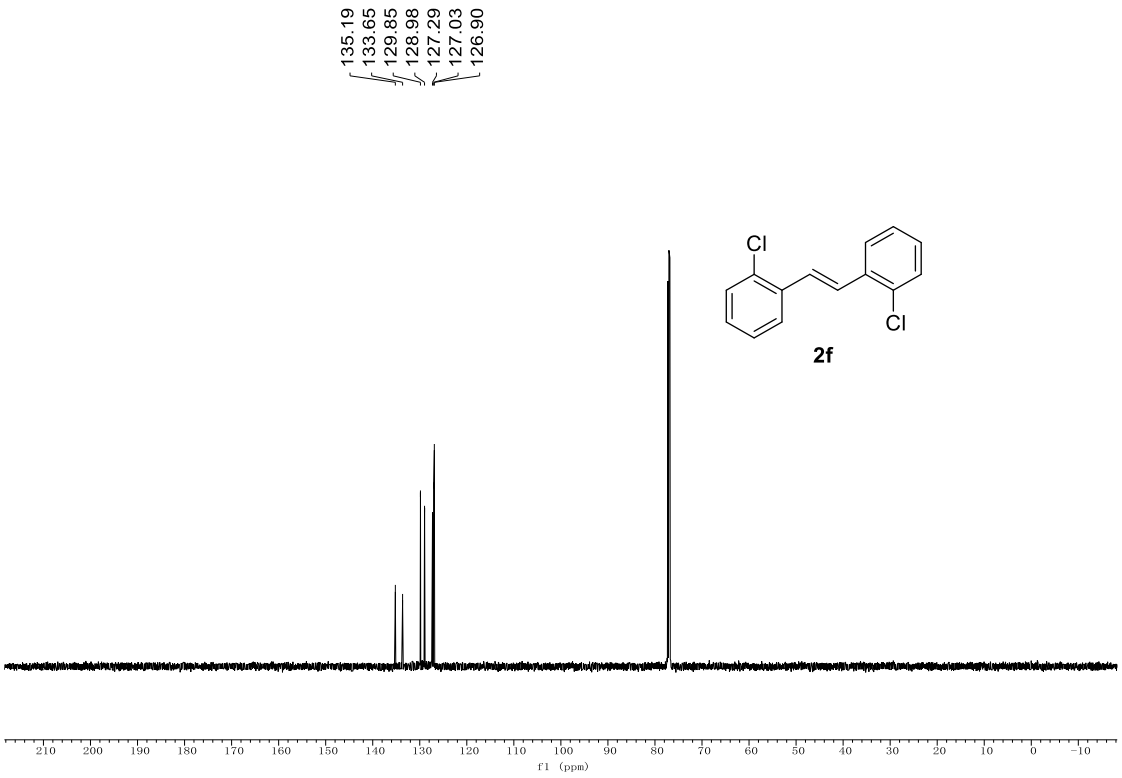

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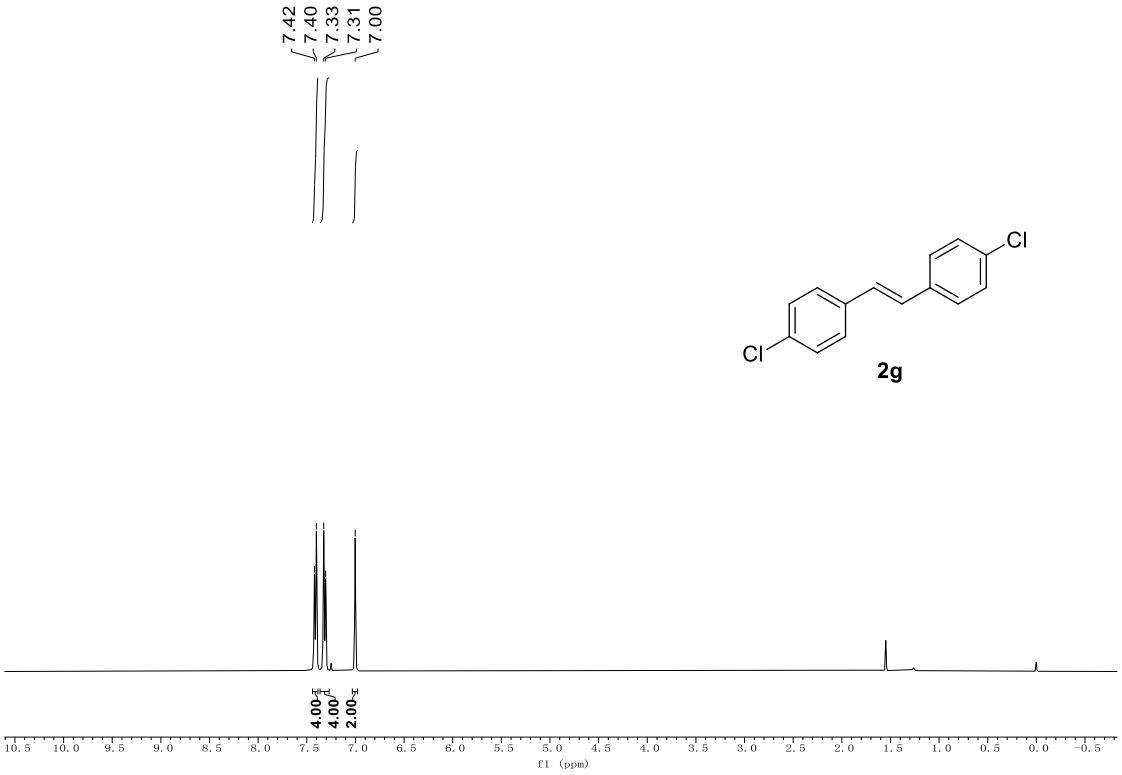

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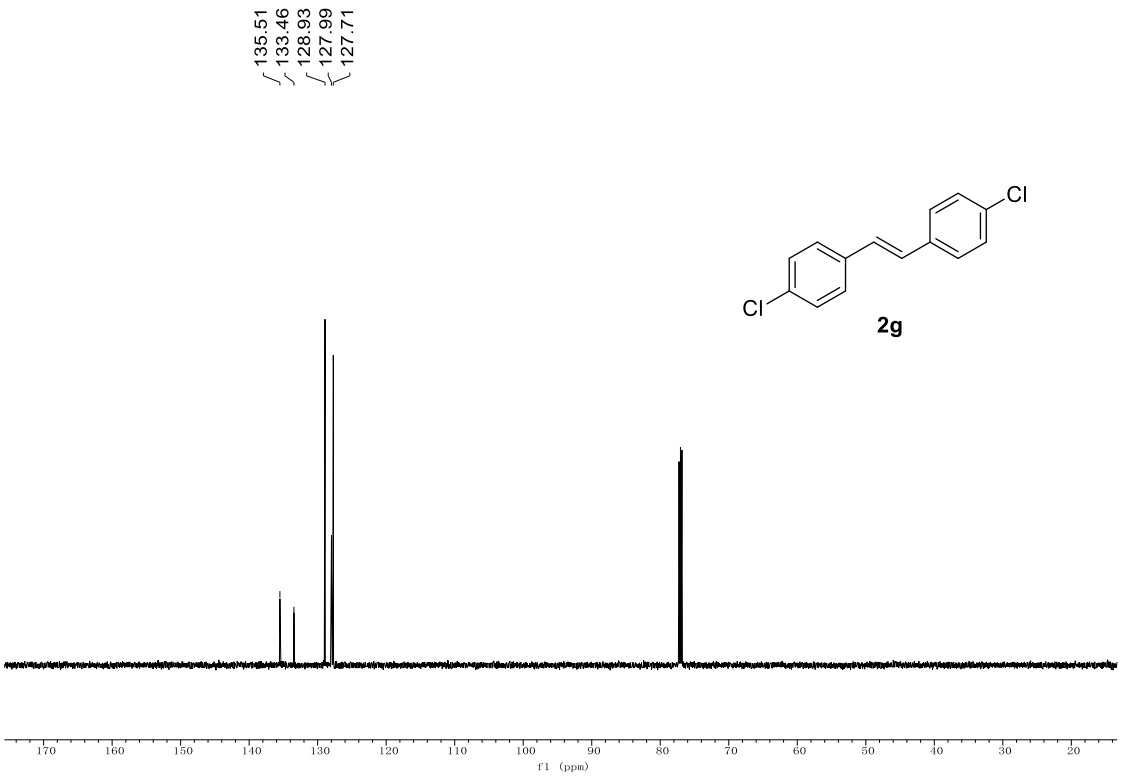

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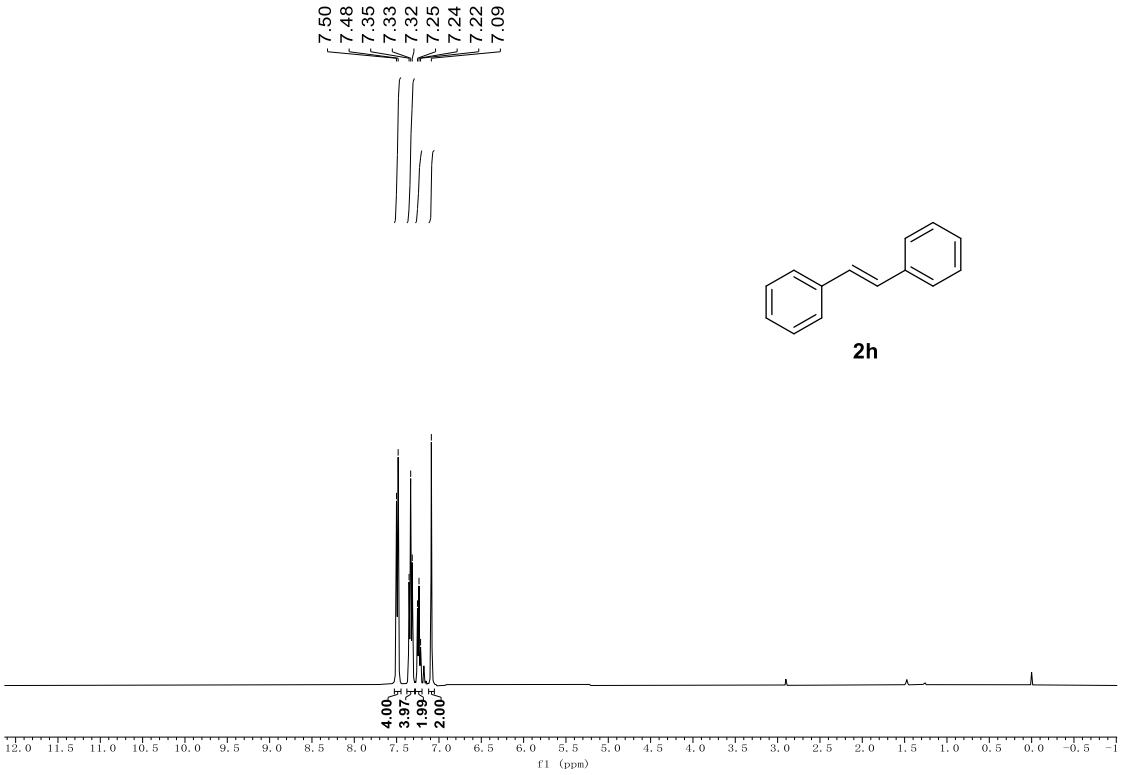

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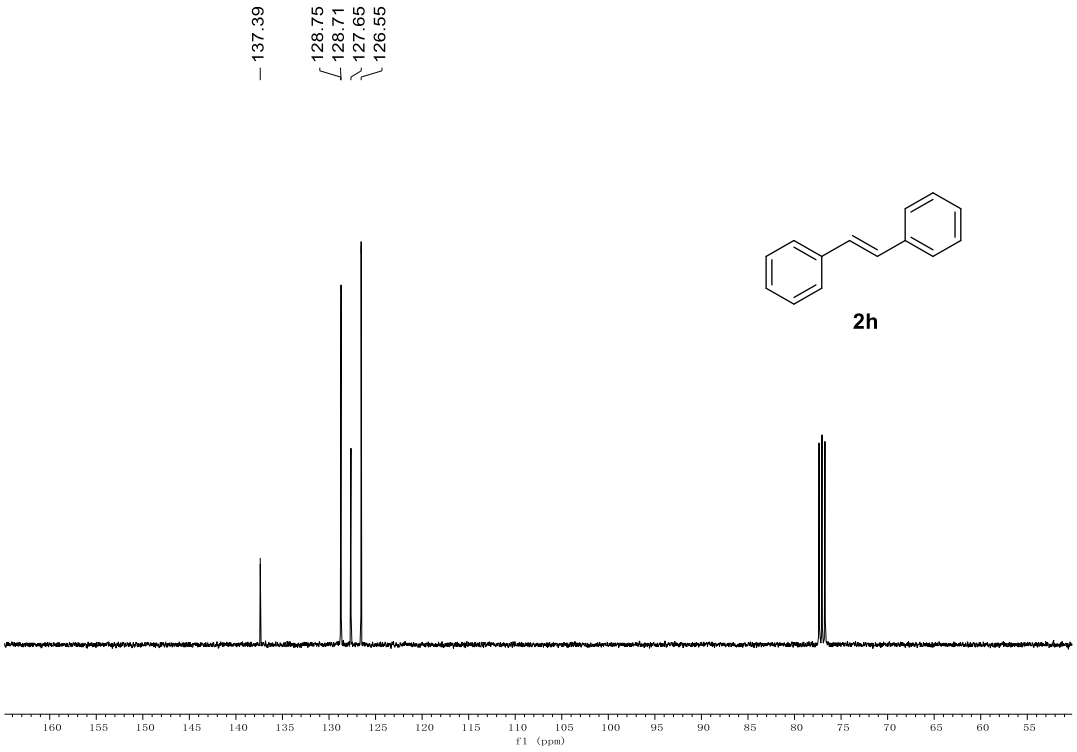

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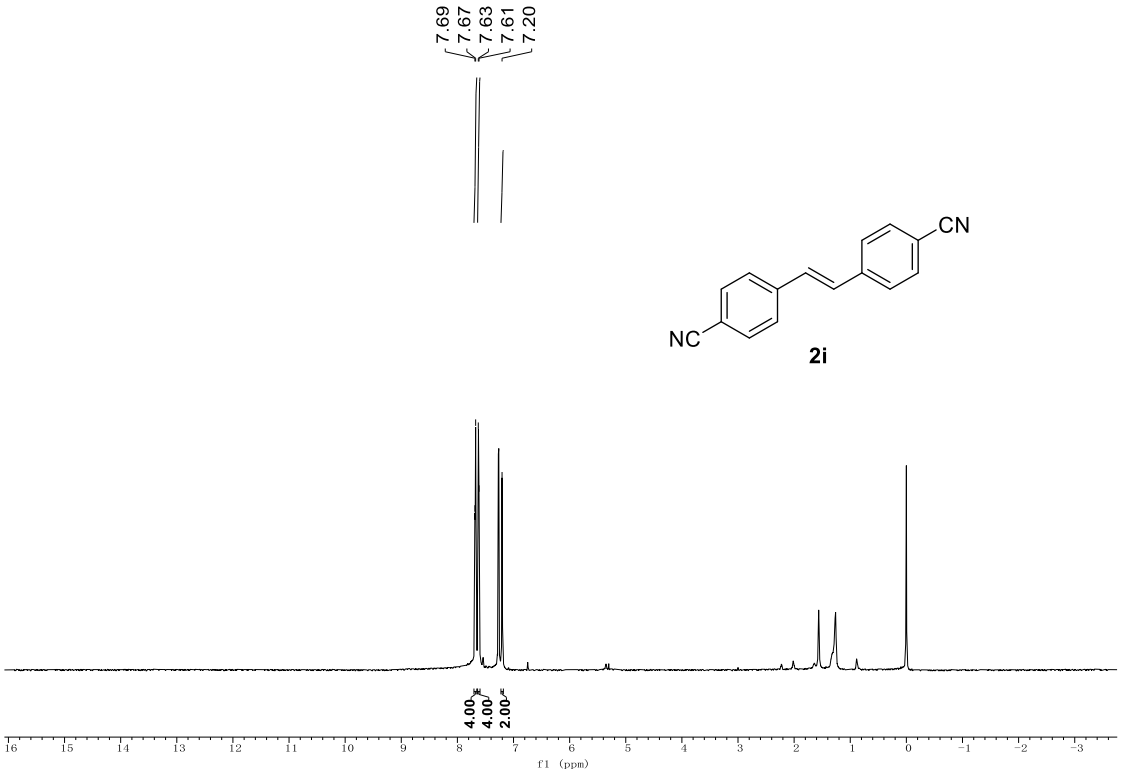

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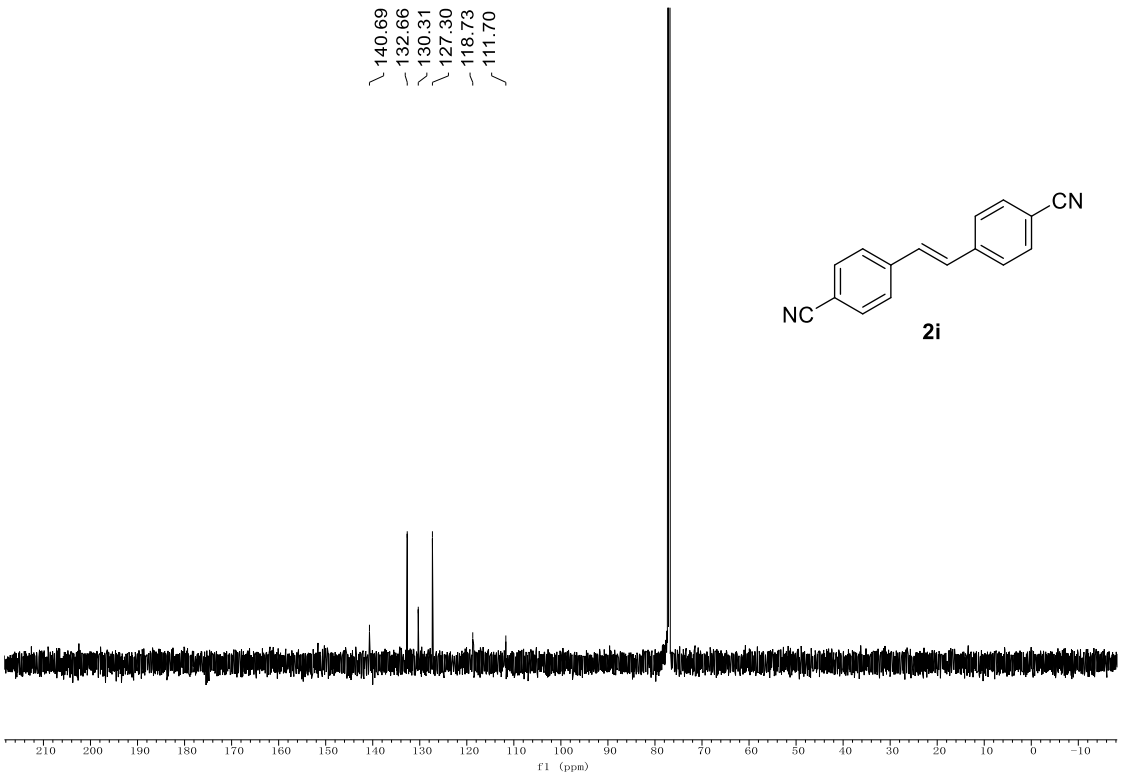

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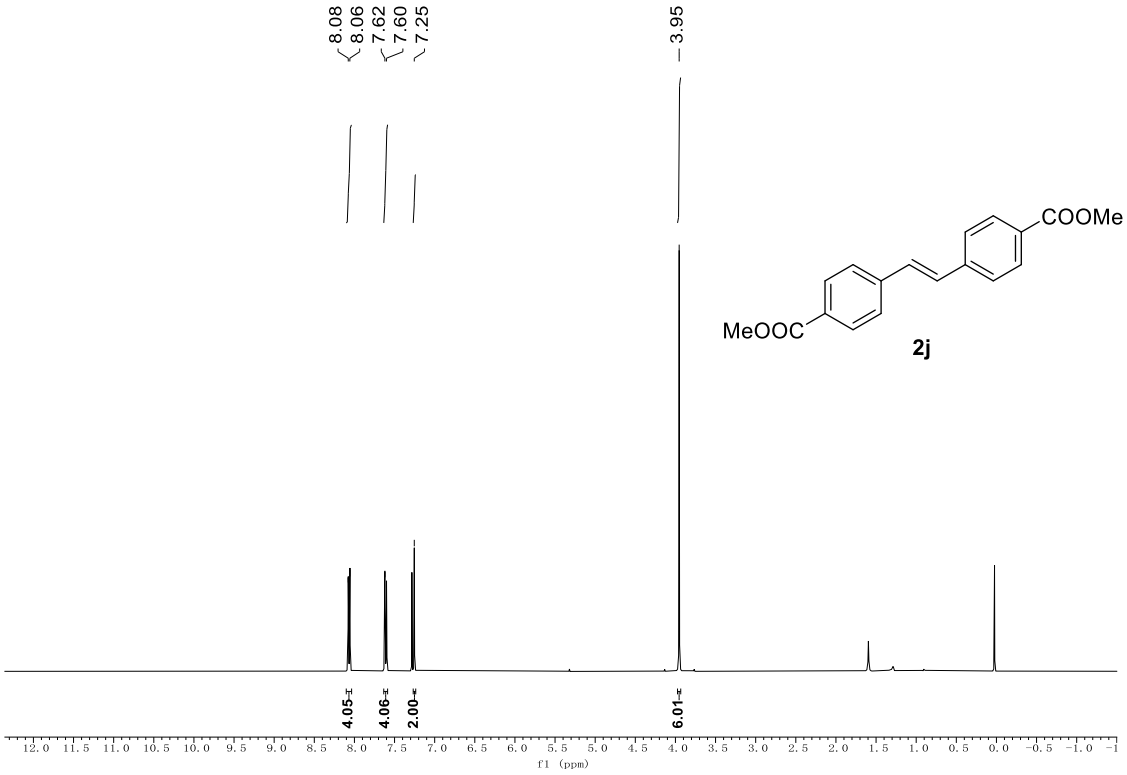

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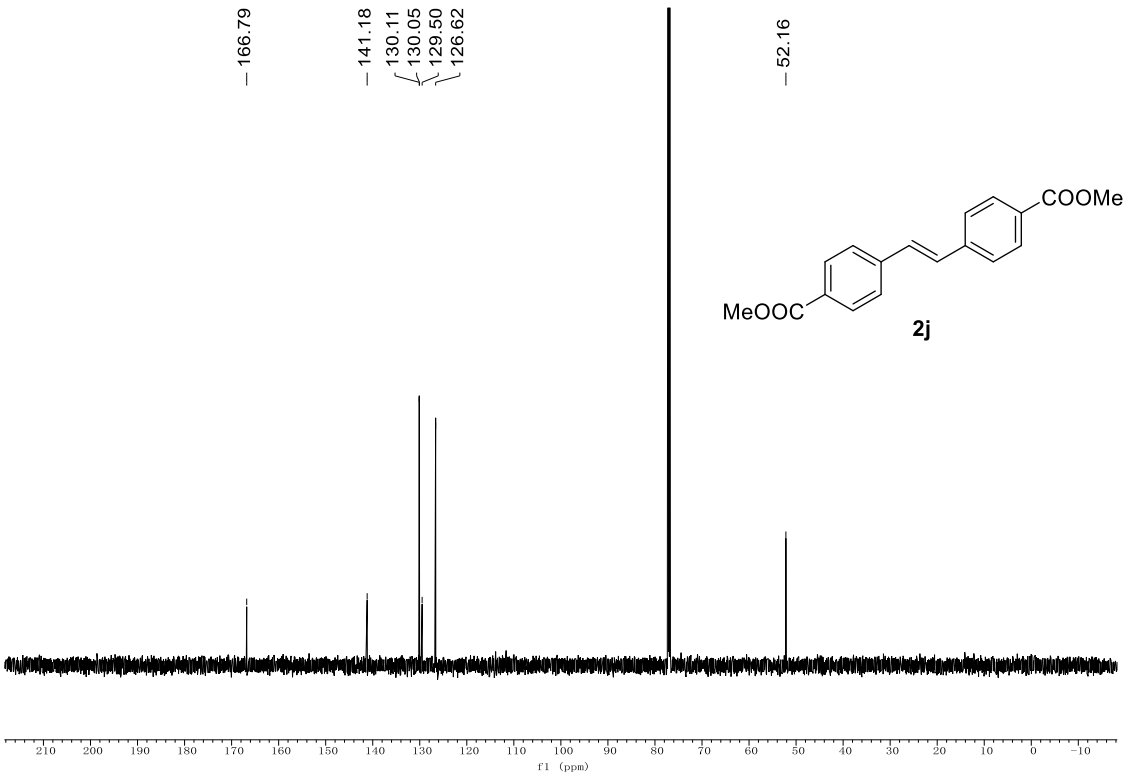

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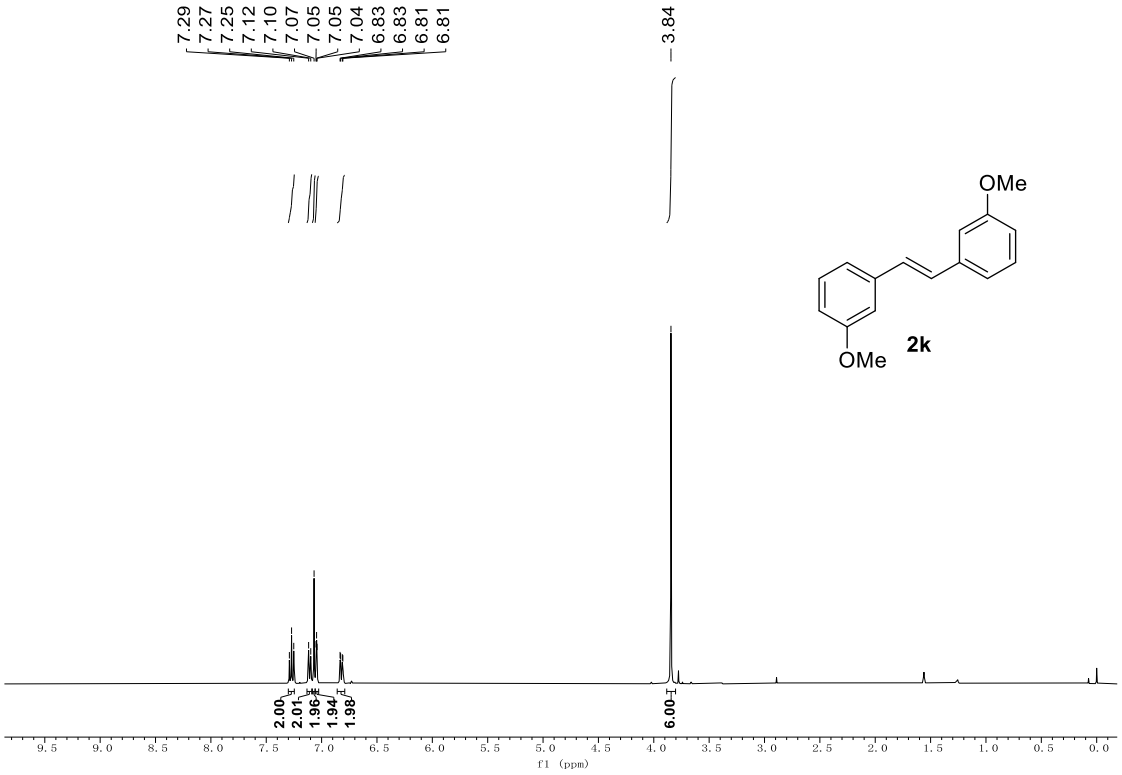

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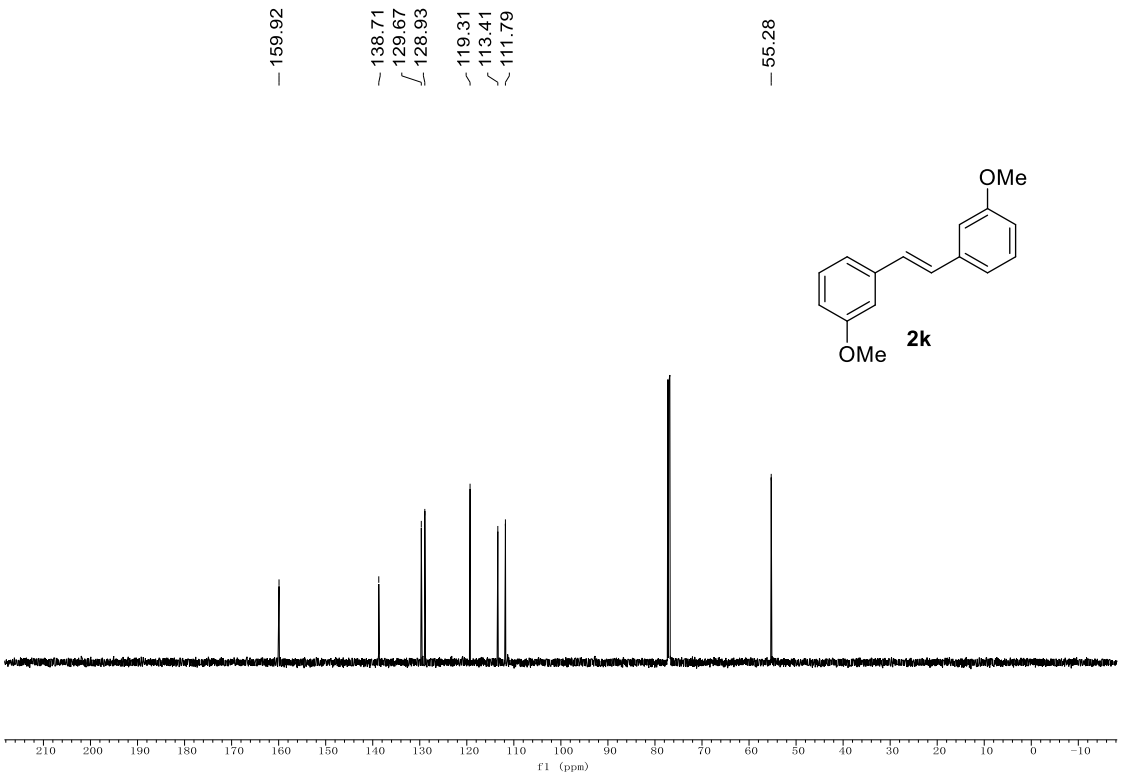

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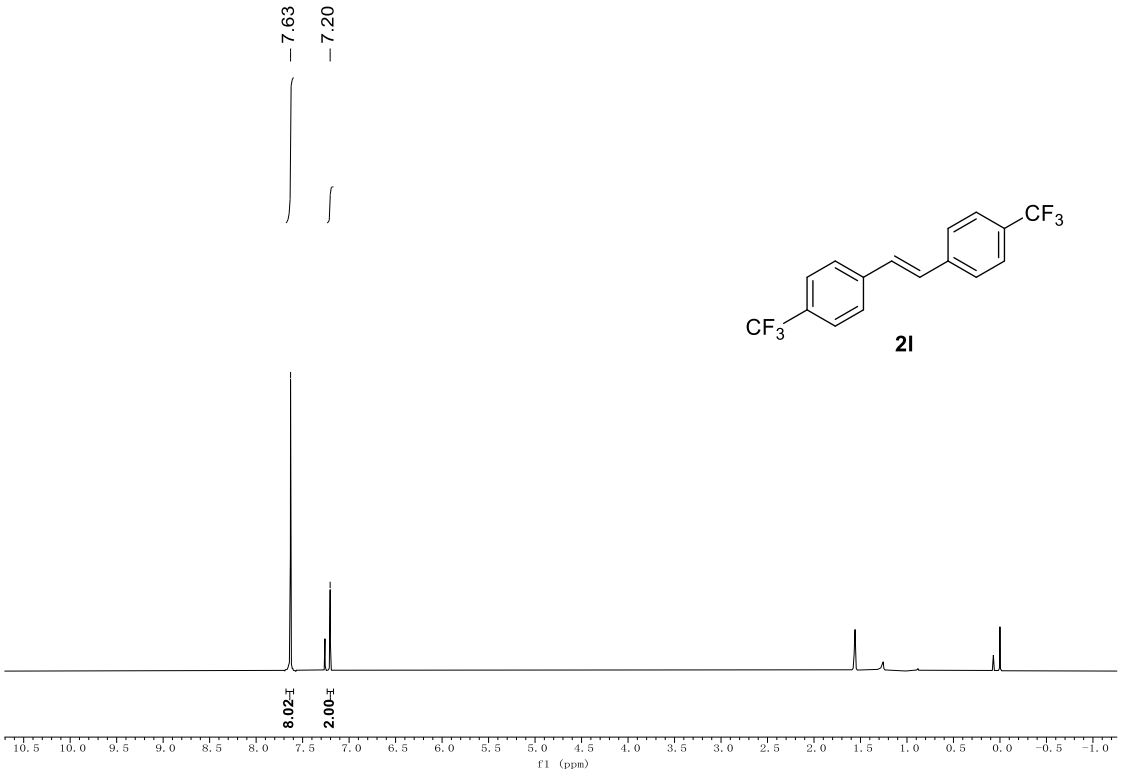

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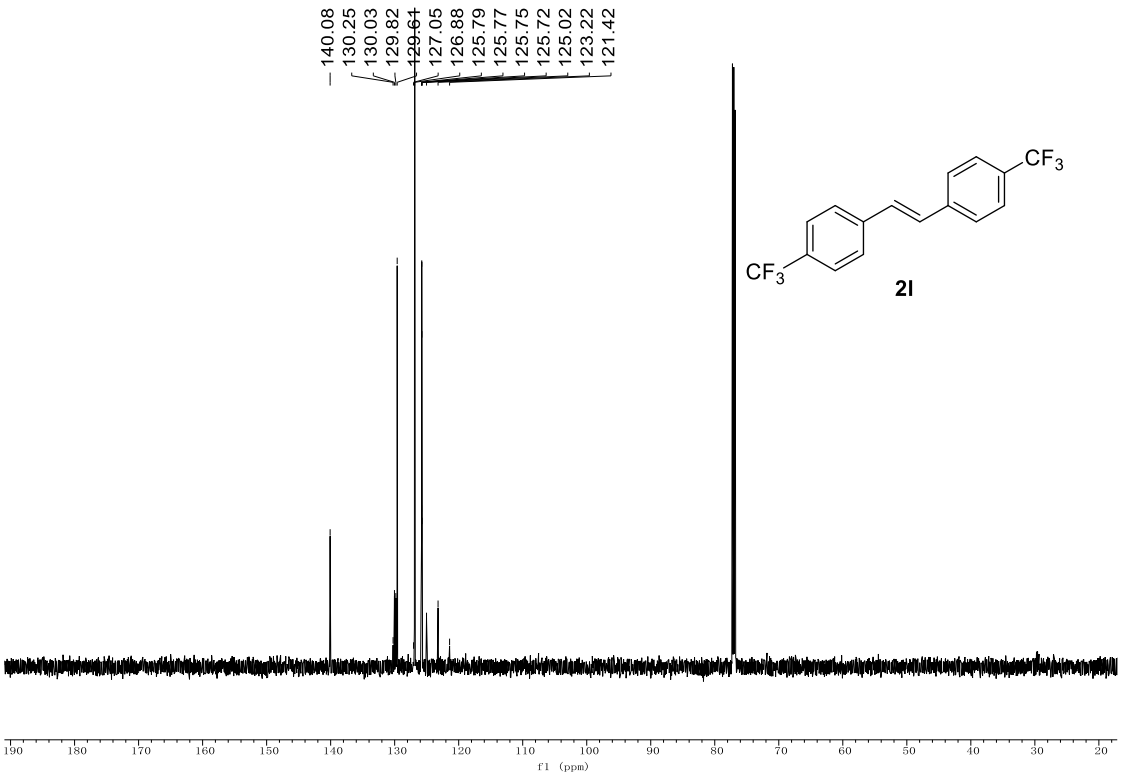

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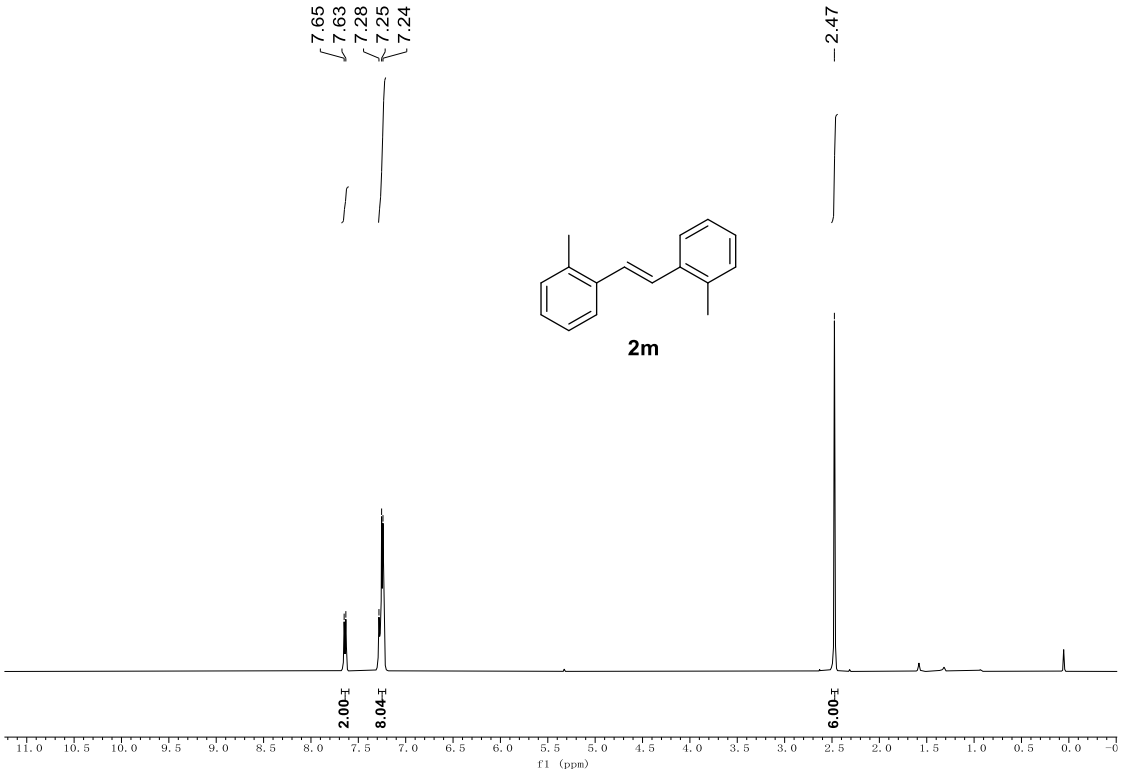

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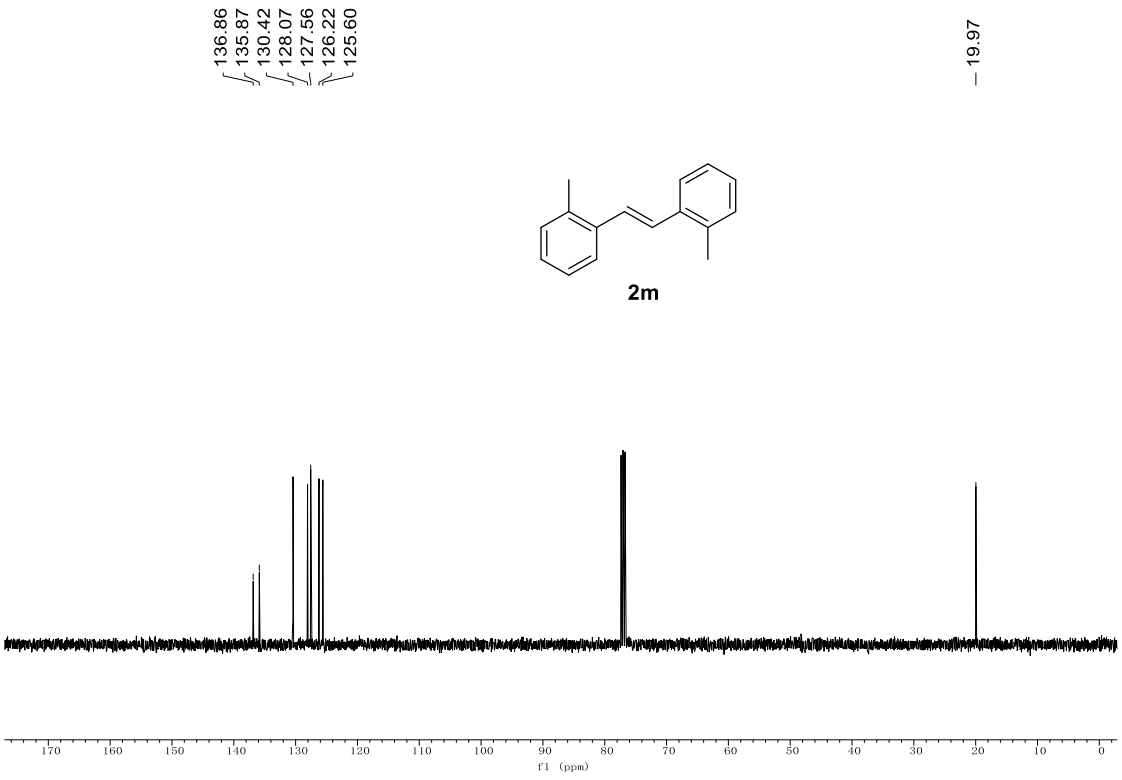

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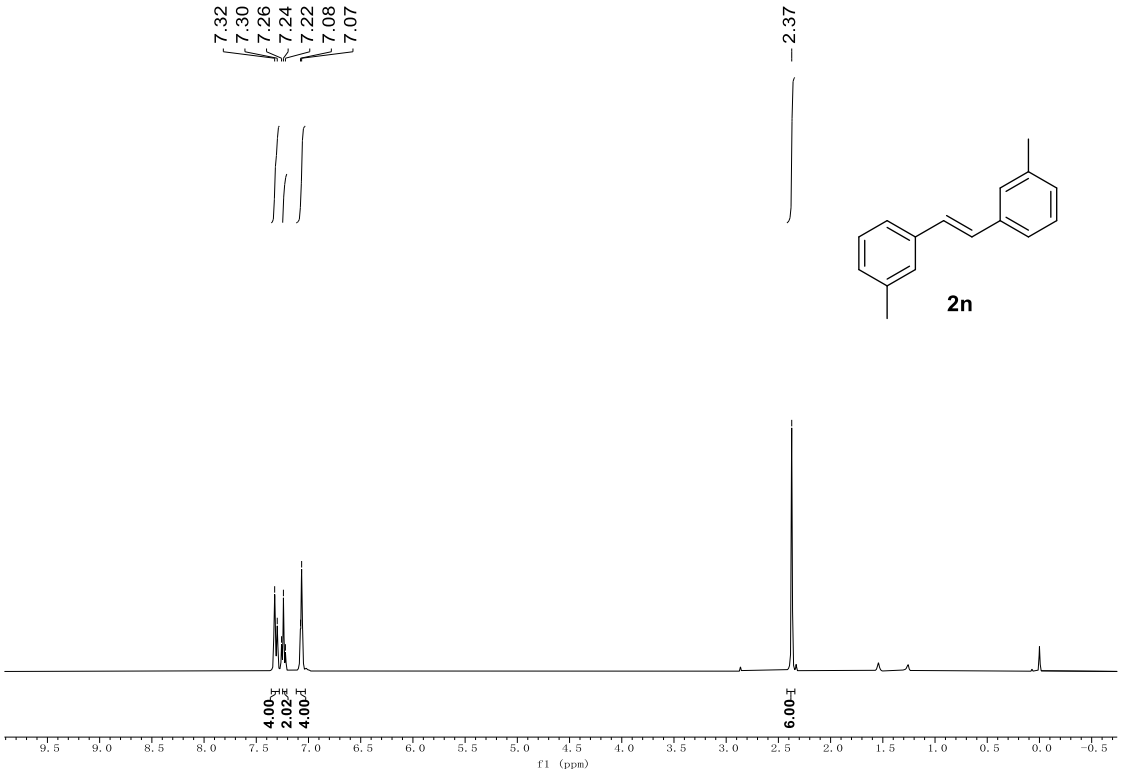
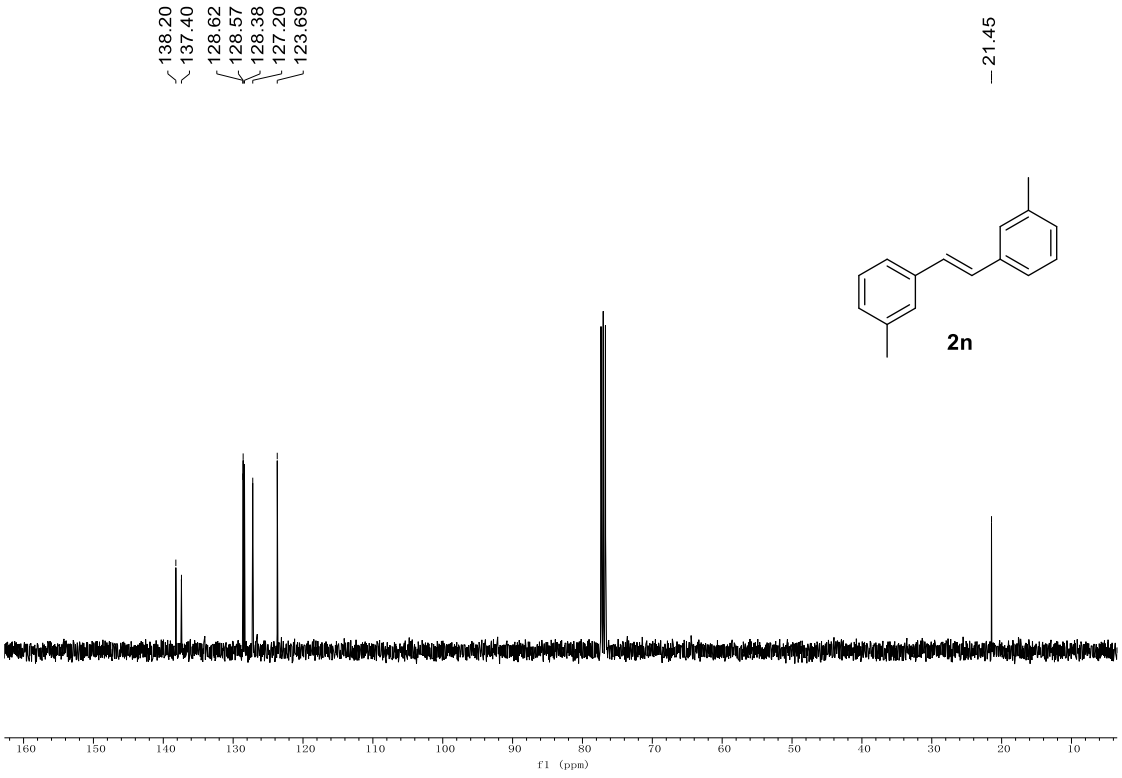
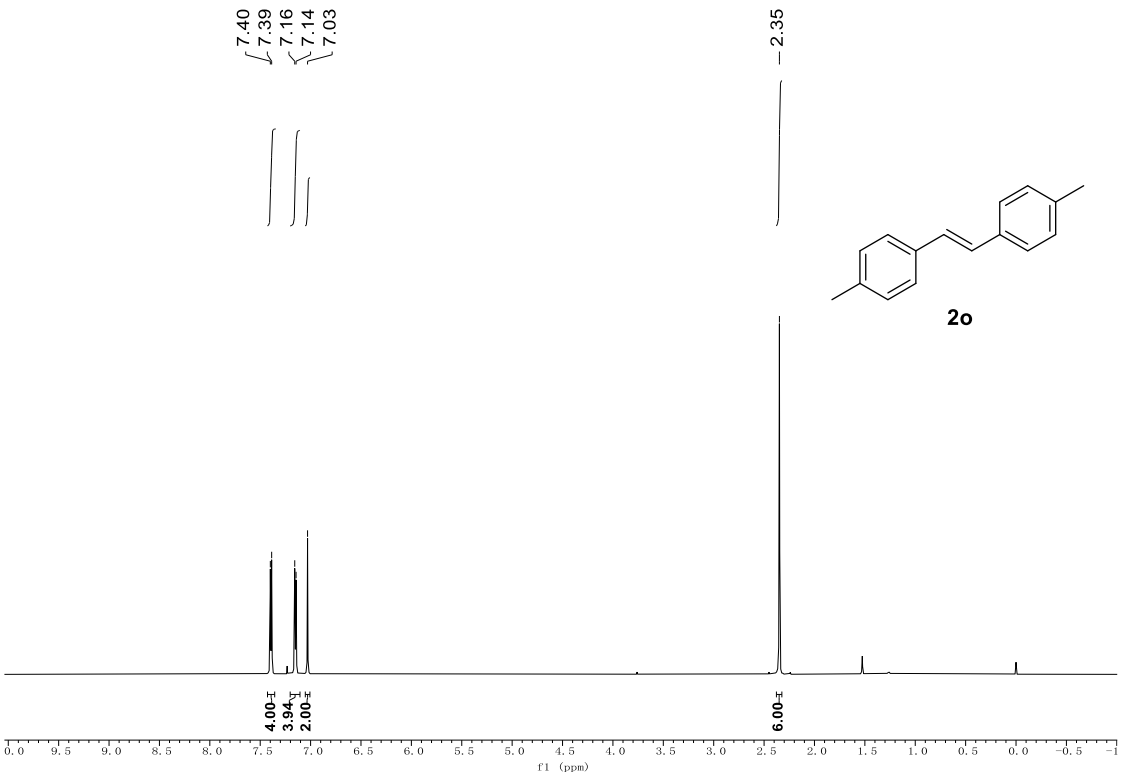


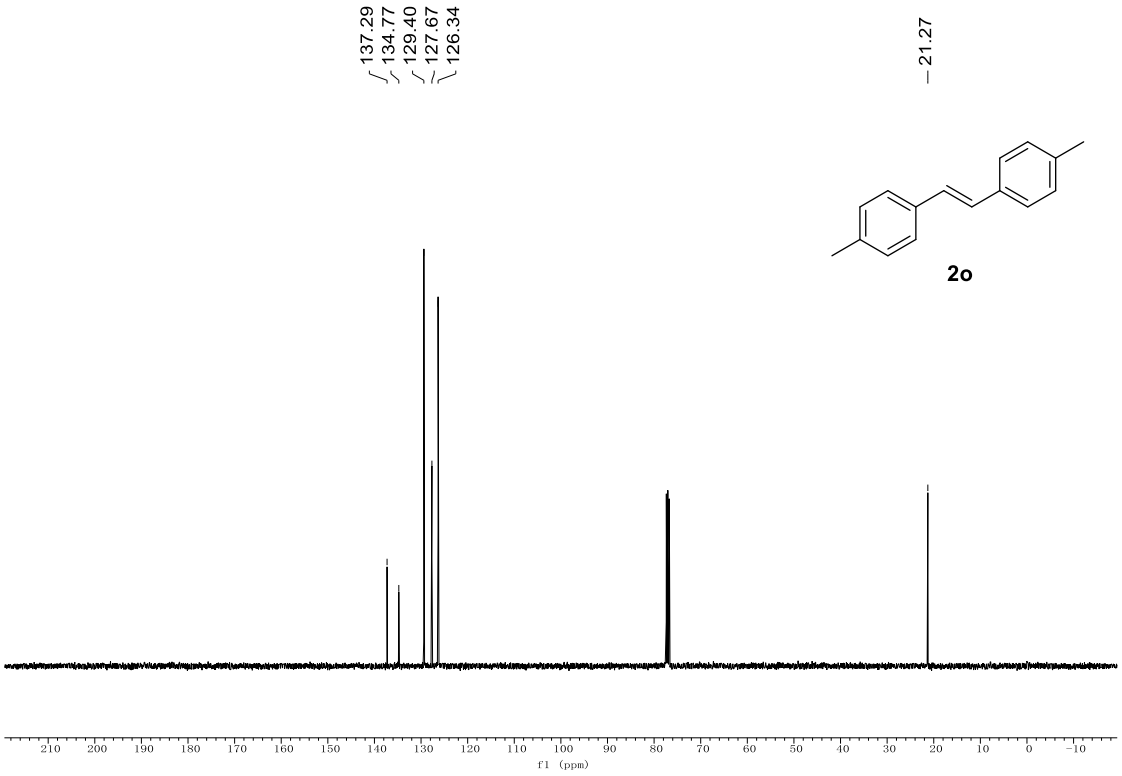
^{13}C NMR, 101 MHz, $CDCl_3$



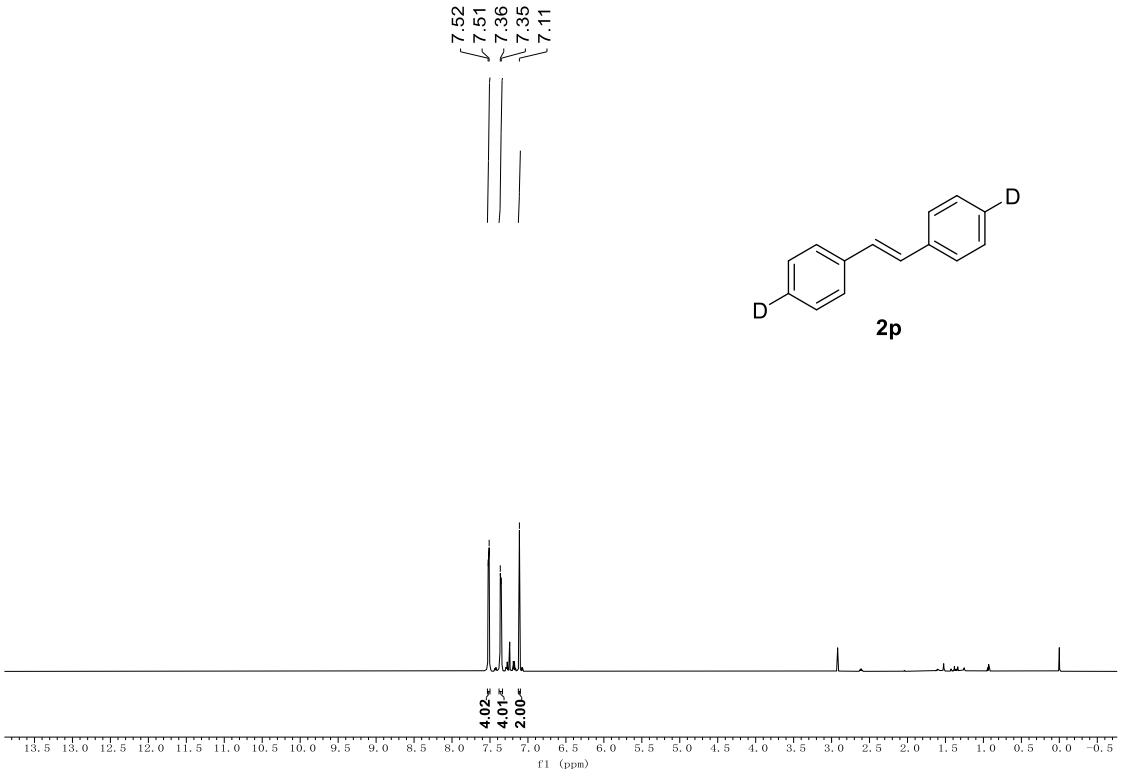
^{1}H NMR, 600 MHz, $CDCl_3$



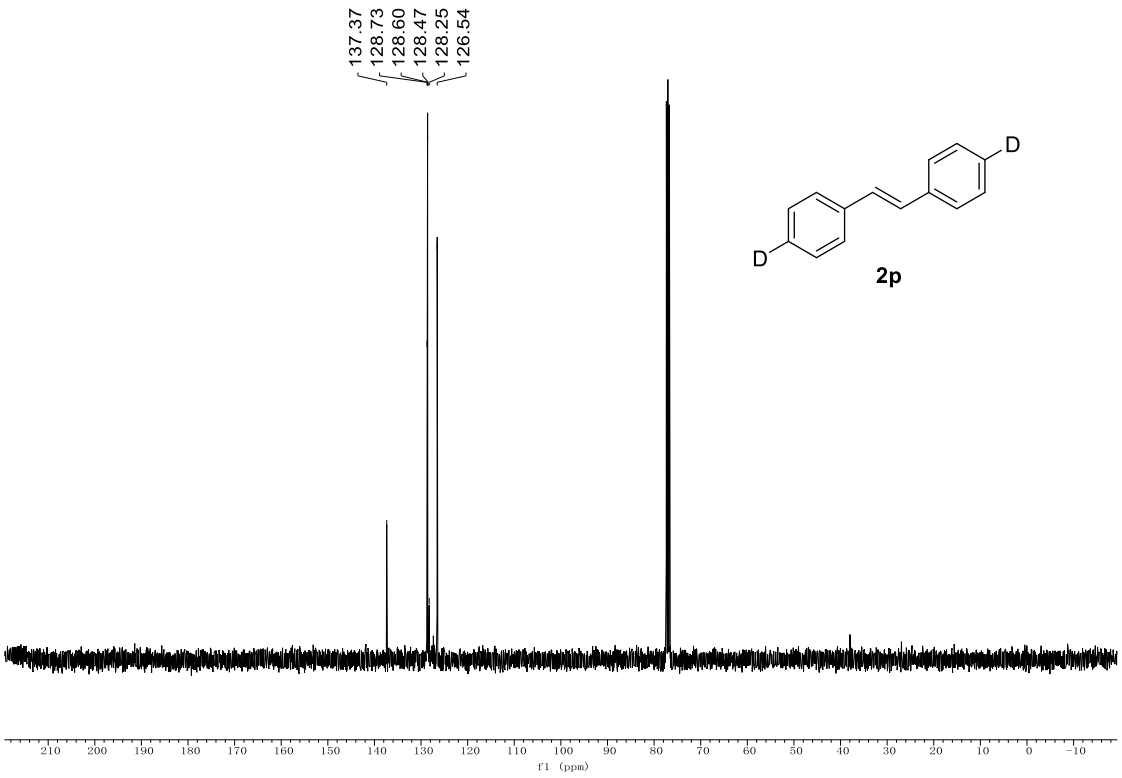
^{13}C NMR, 101 MHz, $CDCl_3$



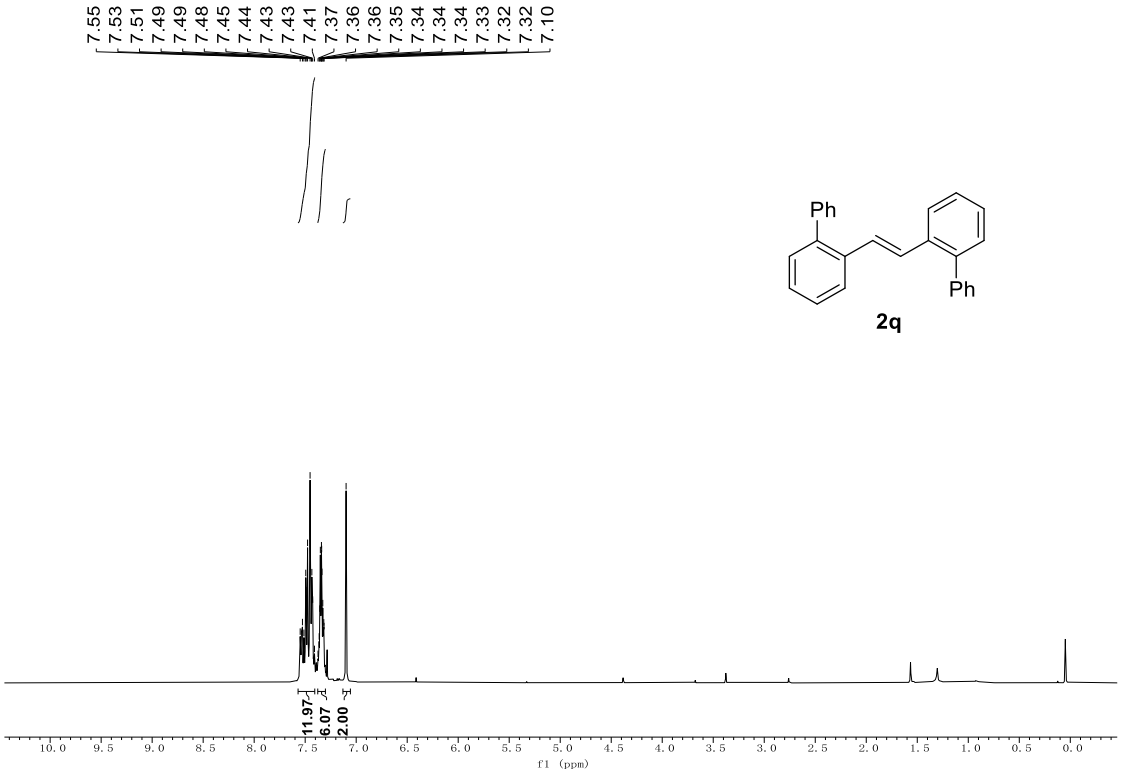
^{1}H NMR, 600 MHz, $CDCl_3$



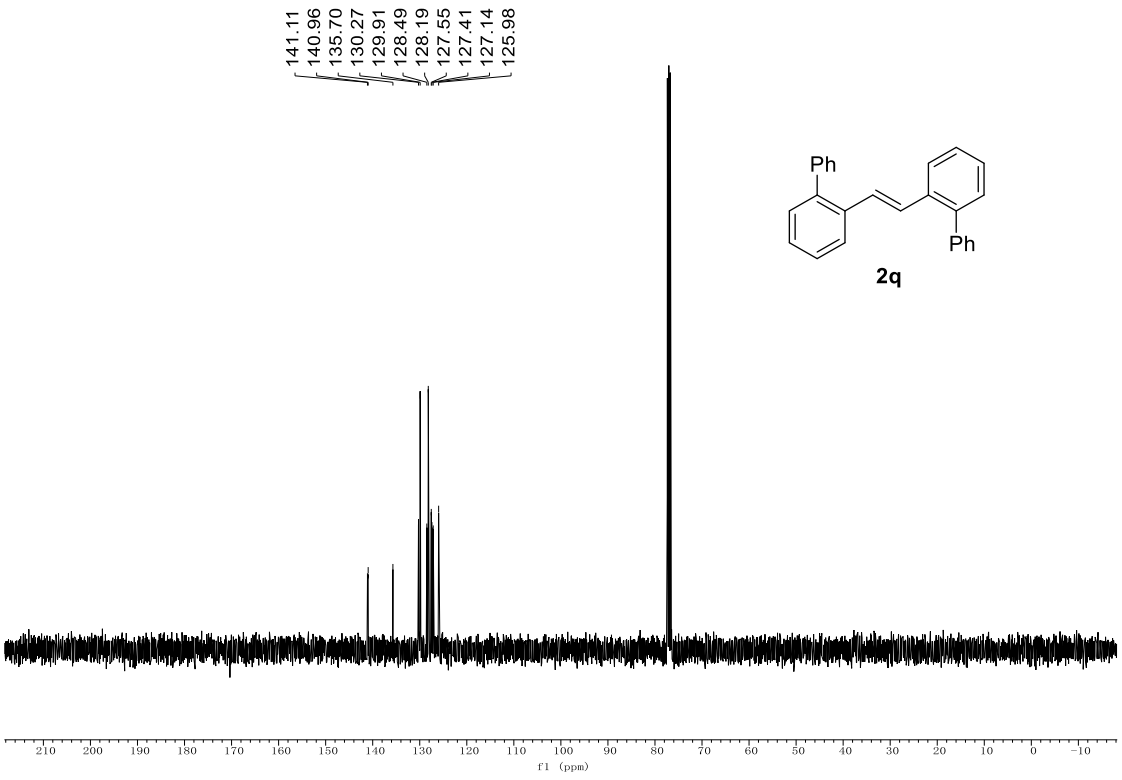
^{13}C NMR, 101 MHz, $CDCl_3$



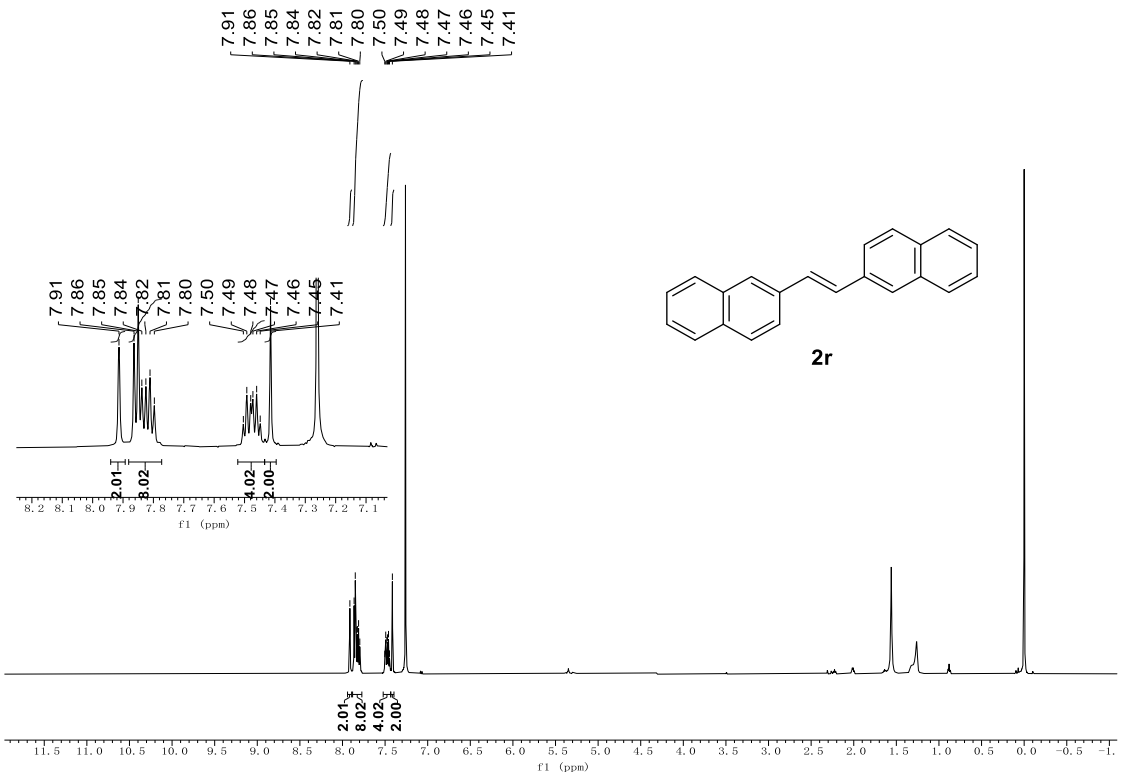
^{1}H NMR, 400 MHz, $CDCl_3$



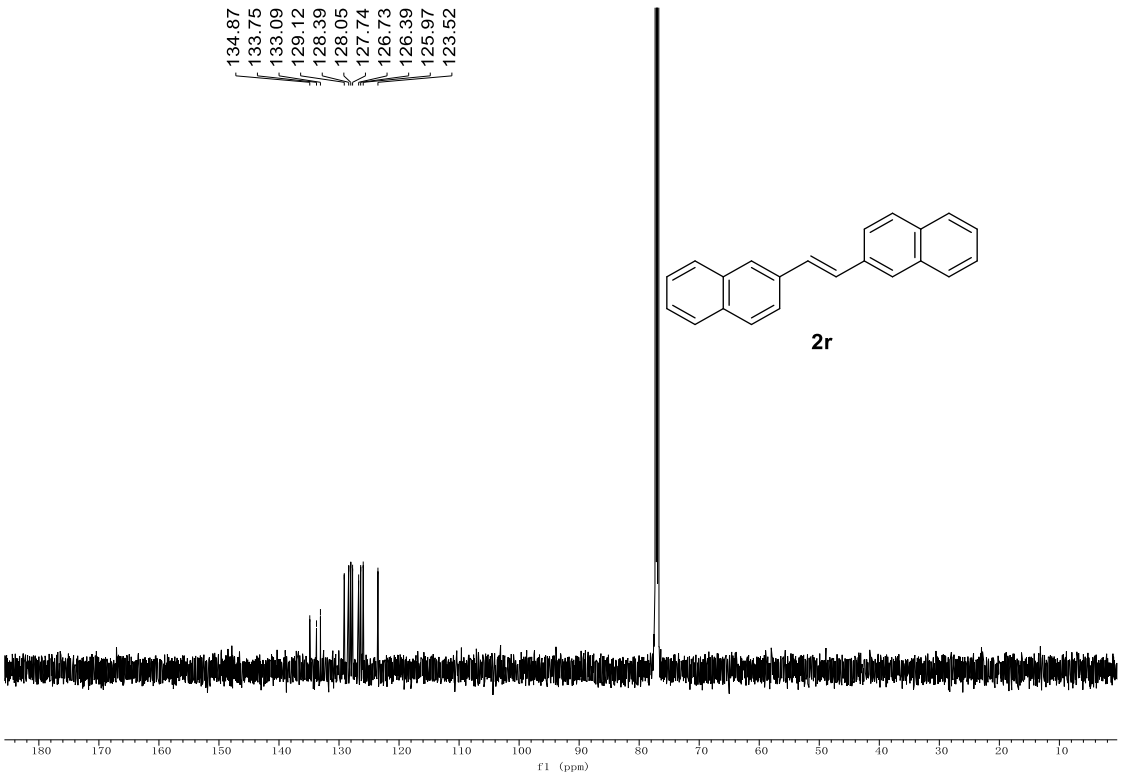
^{13}C NMR, 101 MHz, $CDCl_3$



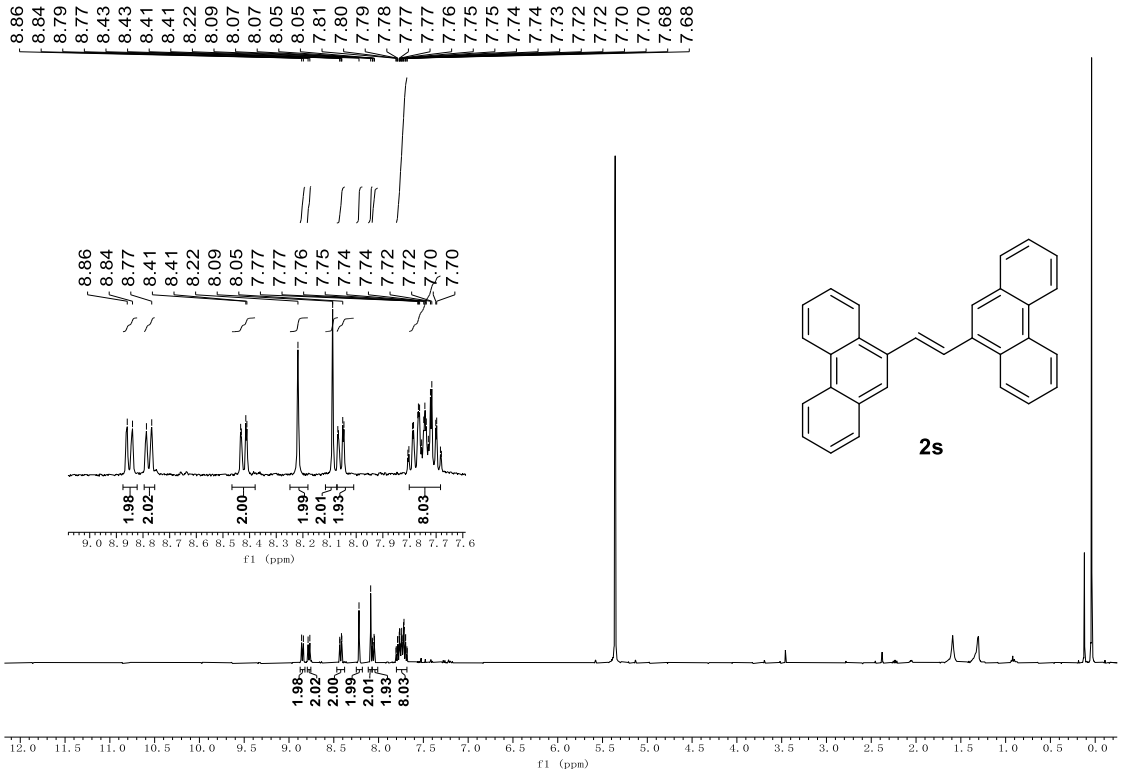
^{1}H NMR, 600 MHz, $CDCl_3$



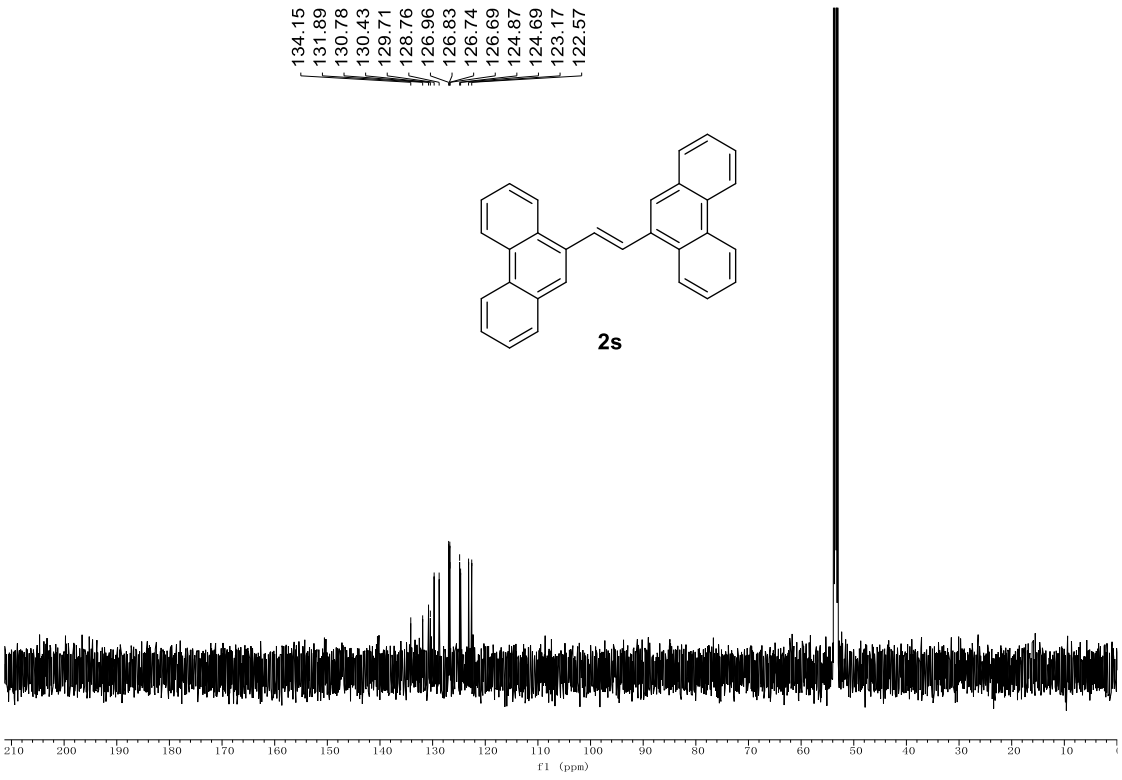
^{13}C NMR, 151 MHz, $CDCl_3$



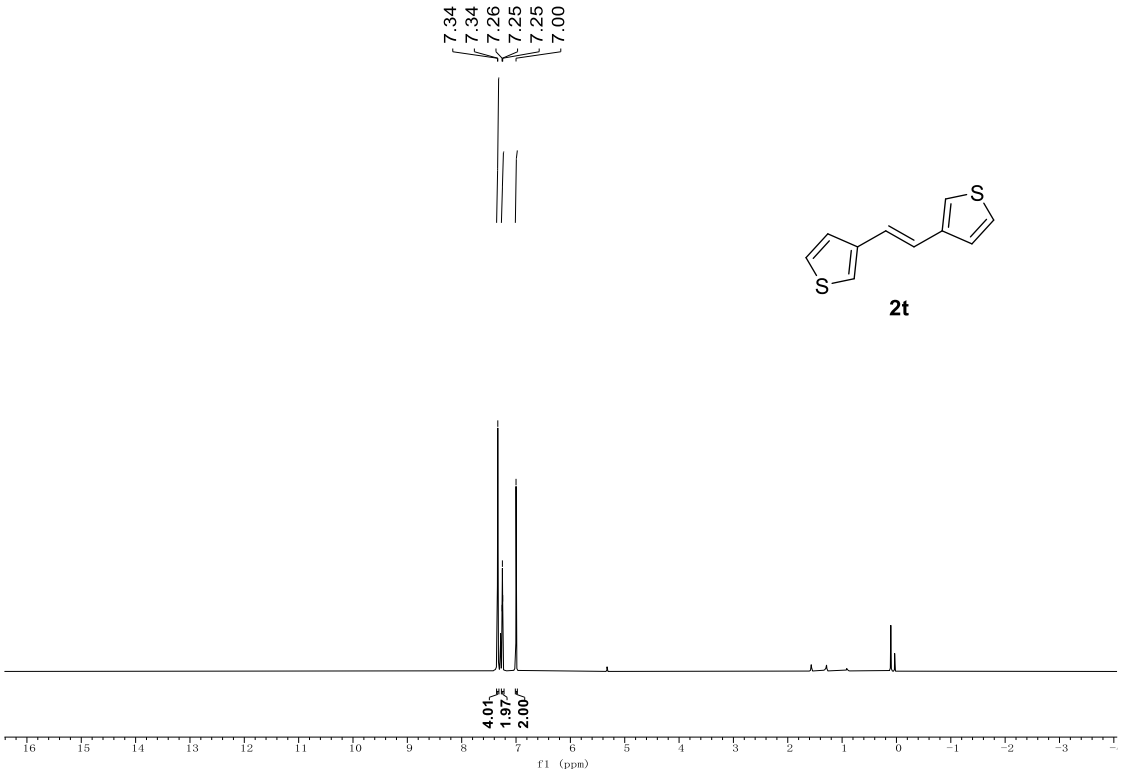
^{1}H NMR, 400 MHz, CD_2Cl_2



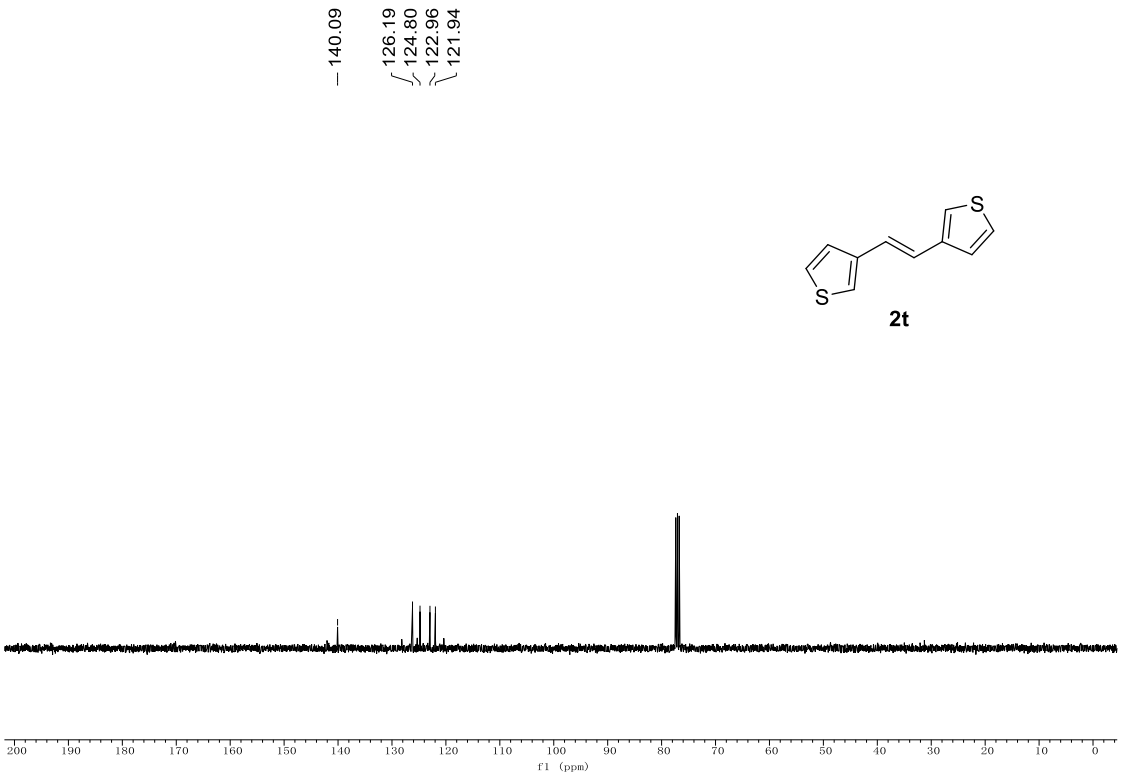
^{13}C NMR, 151 MHz, CD_2Cl_2



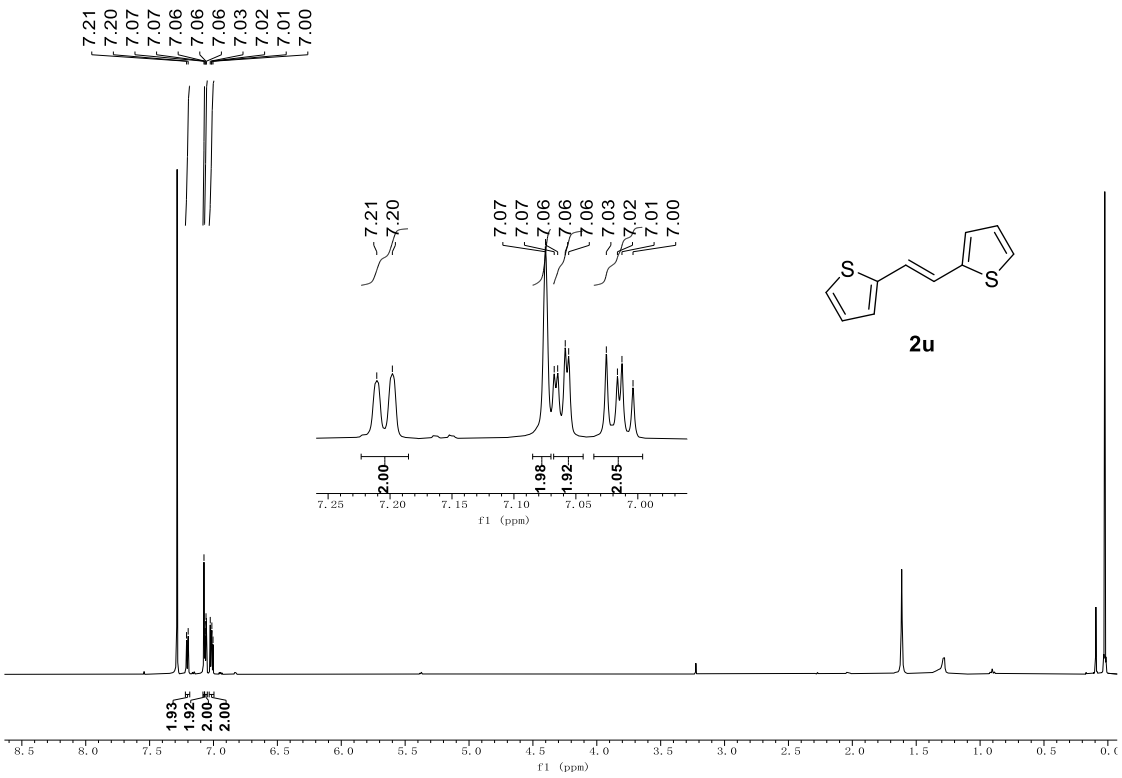
^{1}H NMR, 400 MHz, $CDCl_3$



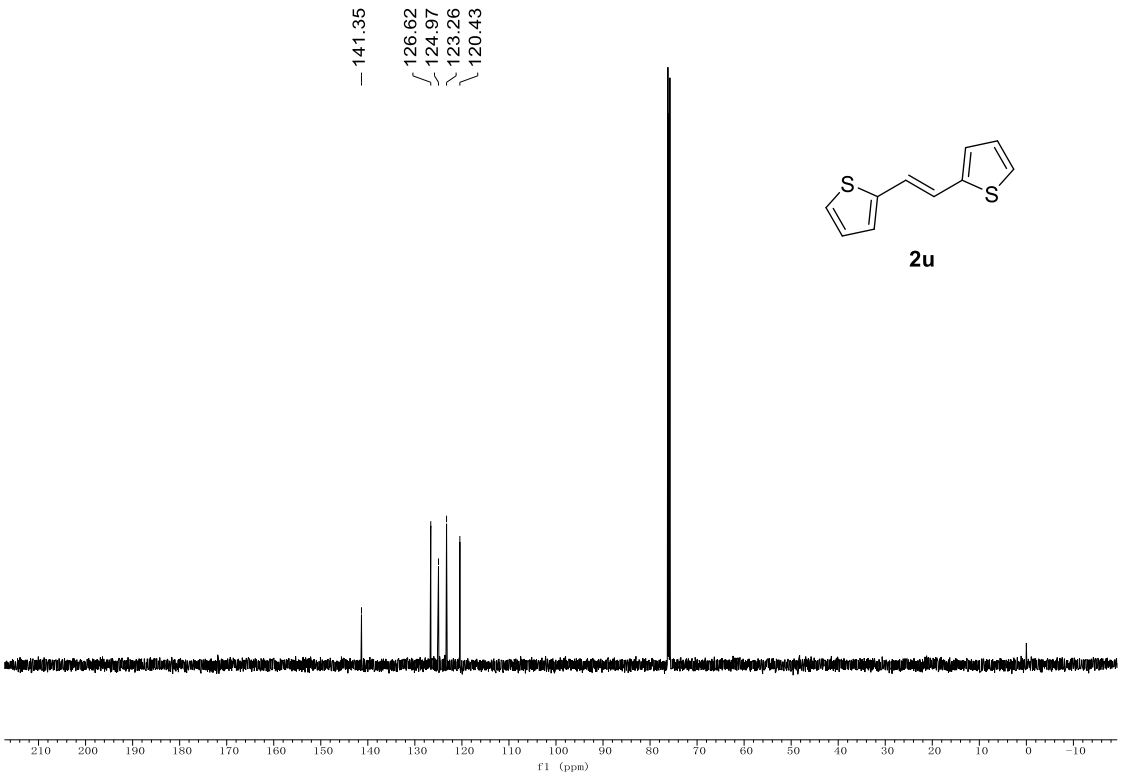
^{13}C NMR, 101 MHz, $CDCl_3$



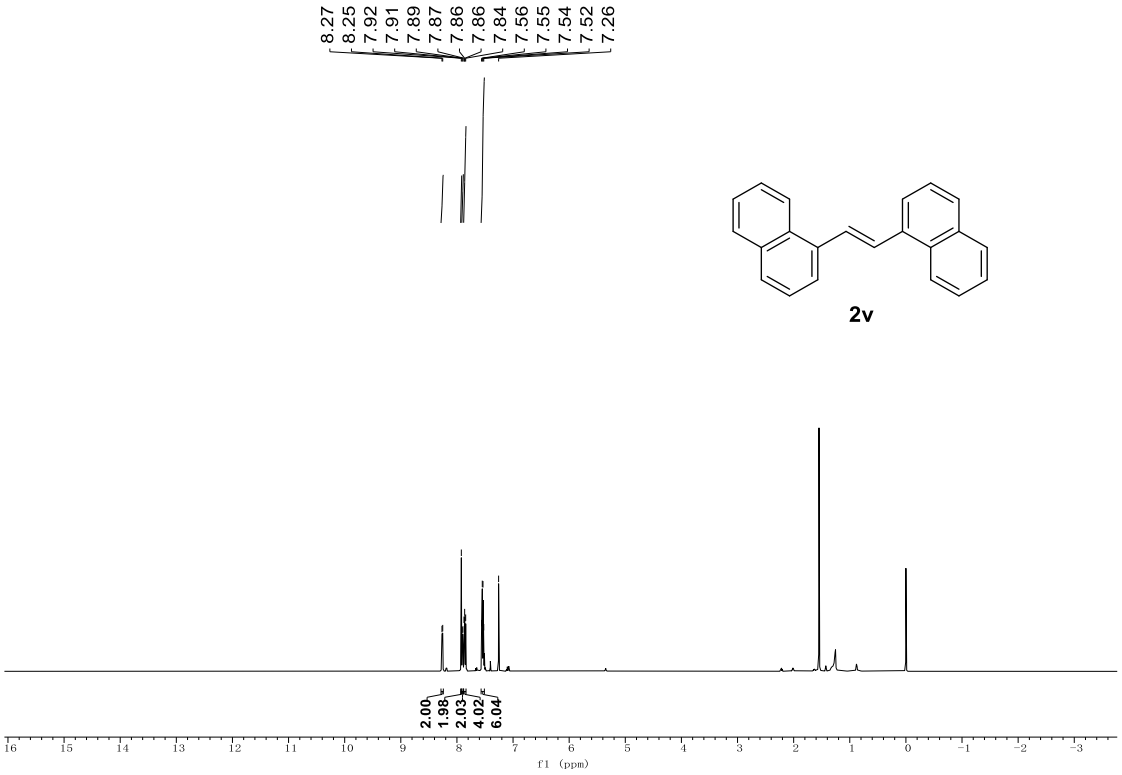
^{1}H NMR, 400 MHz, $CDCl_3$



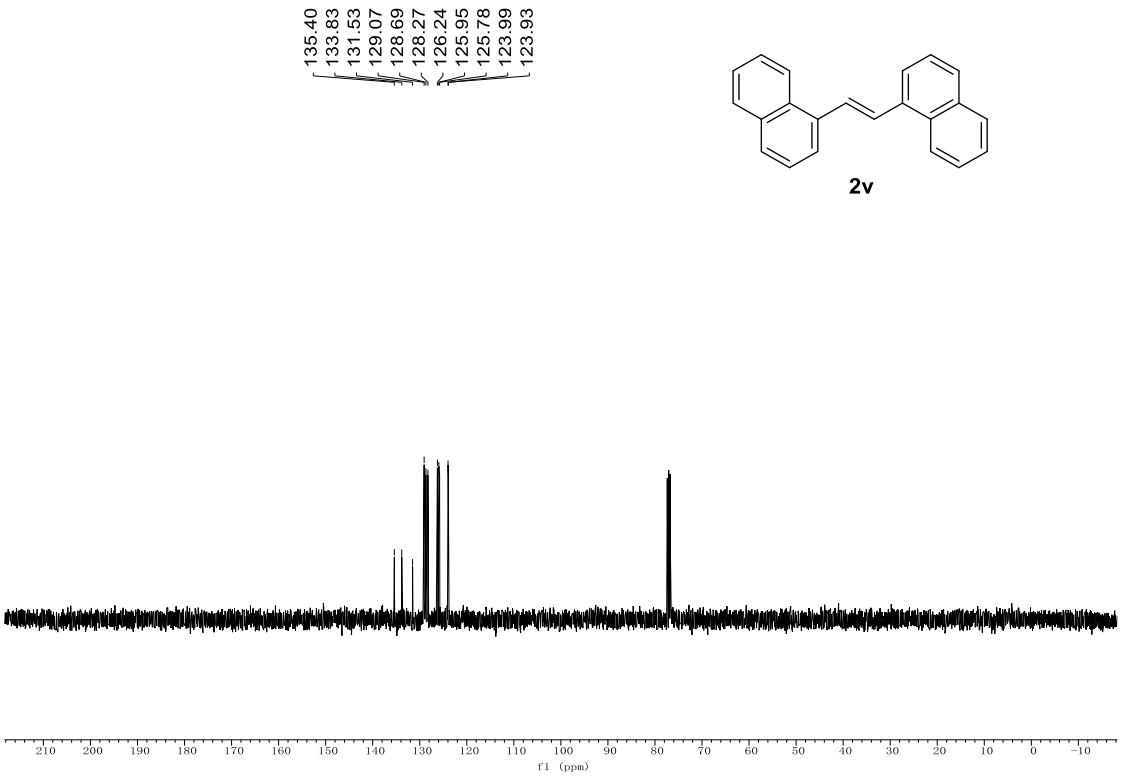
^{13}C NMR, 151 MHz, $CDCl_3$



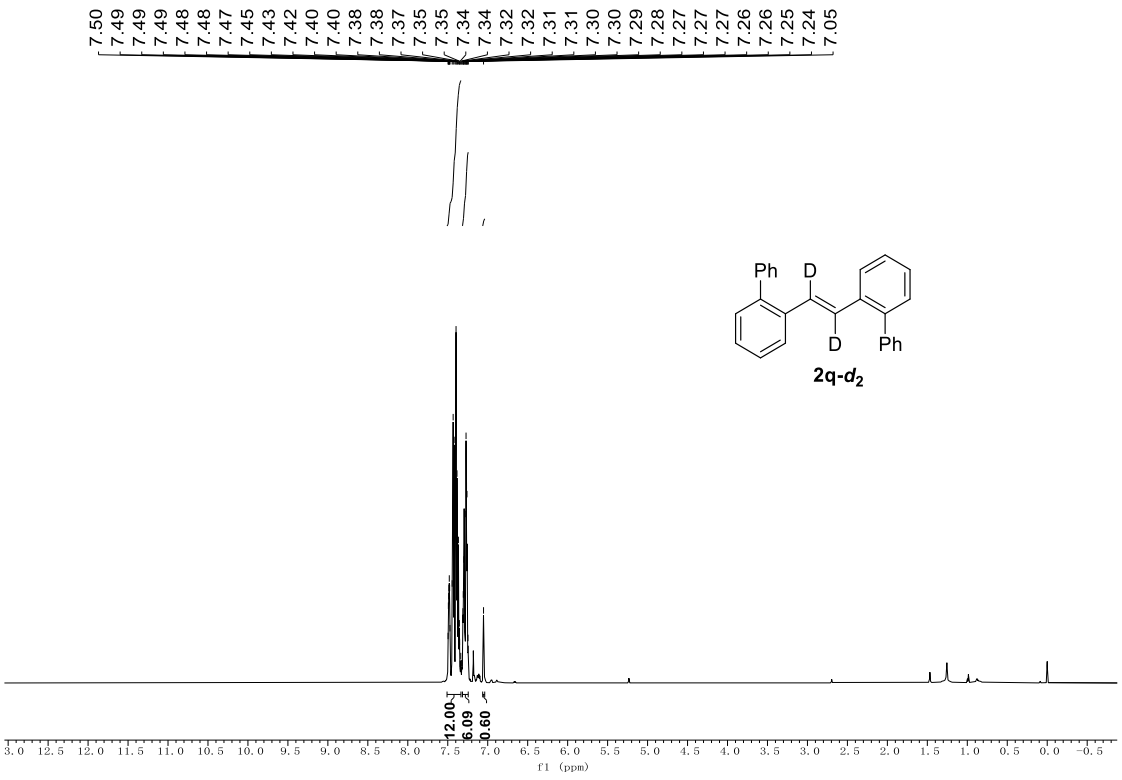
^{1}H NMR, 600 MHz, $CDCl_3$



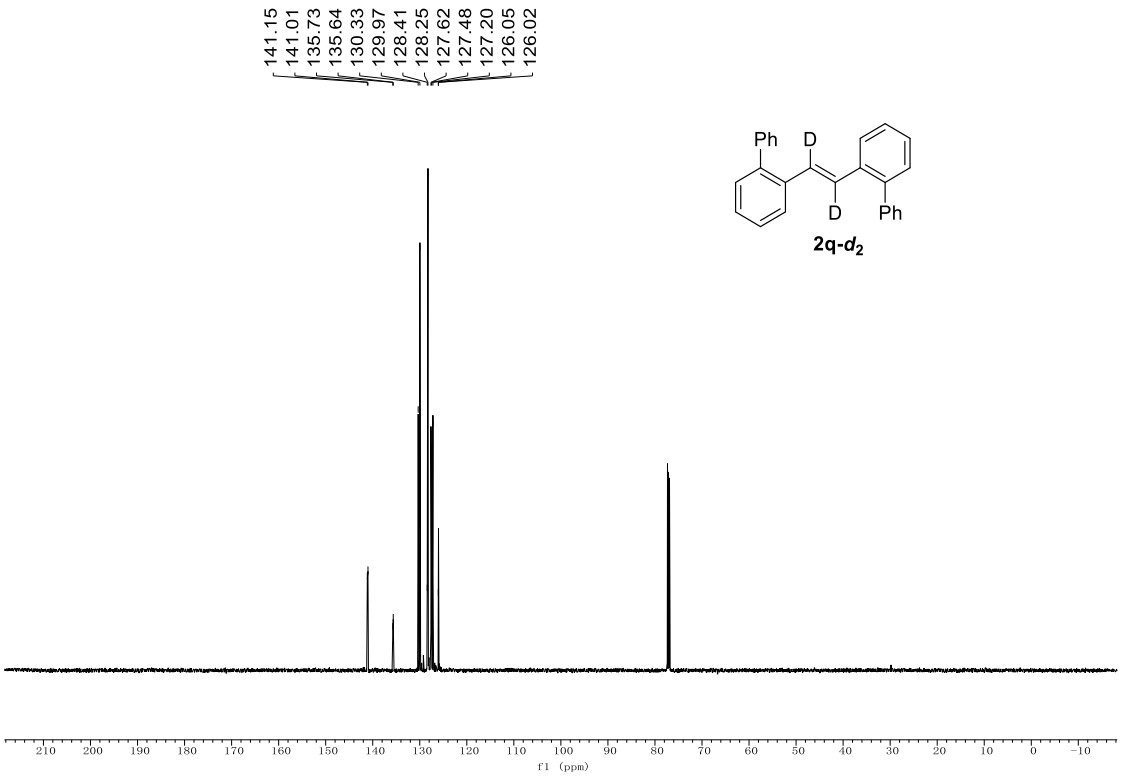
^{13}C NMR, 101 MHz, $CDCl_3$



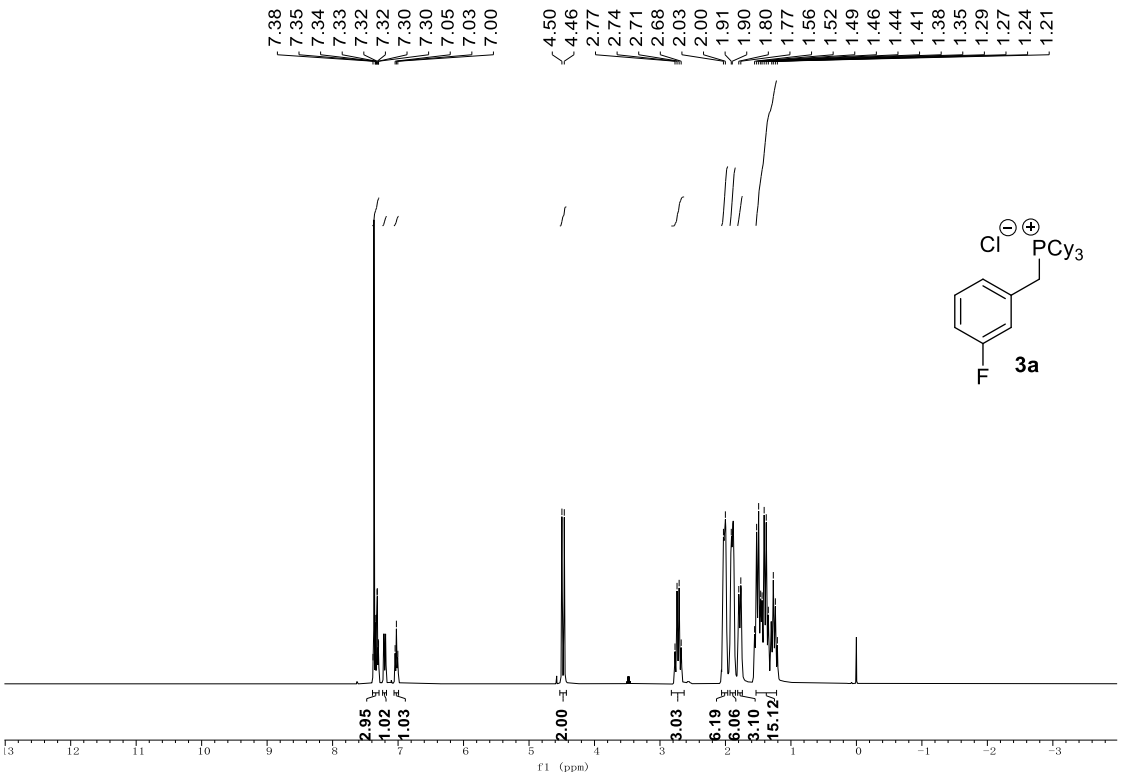
^{1}H NMR, 600 MHz, $CDCl_3$



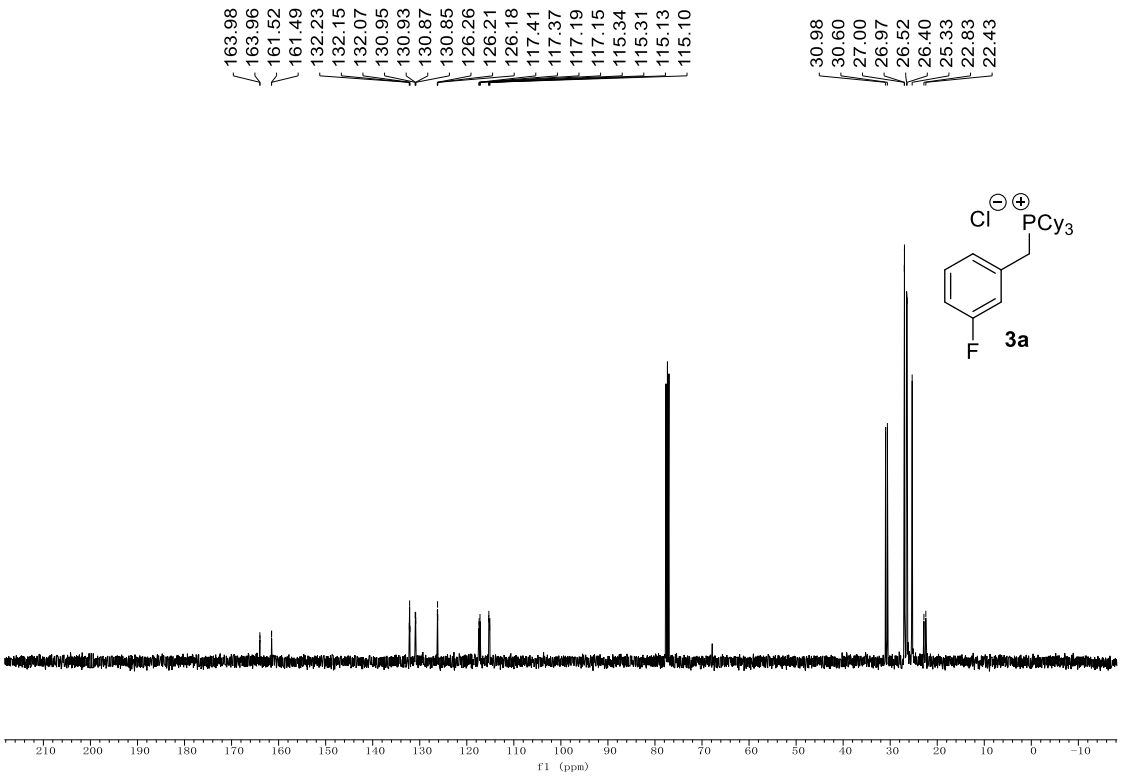
^{13}C NMR, 151 MHz, $CDCl_3$



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



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



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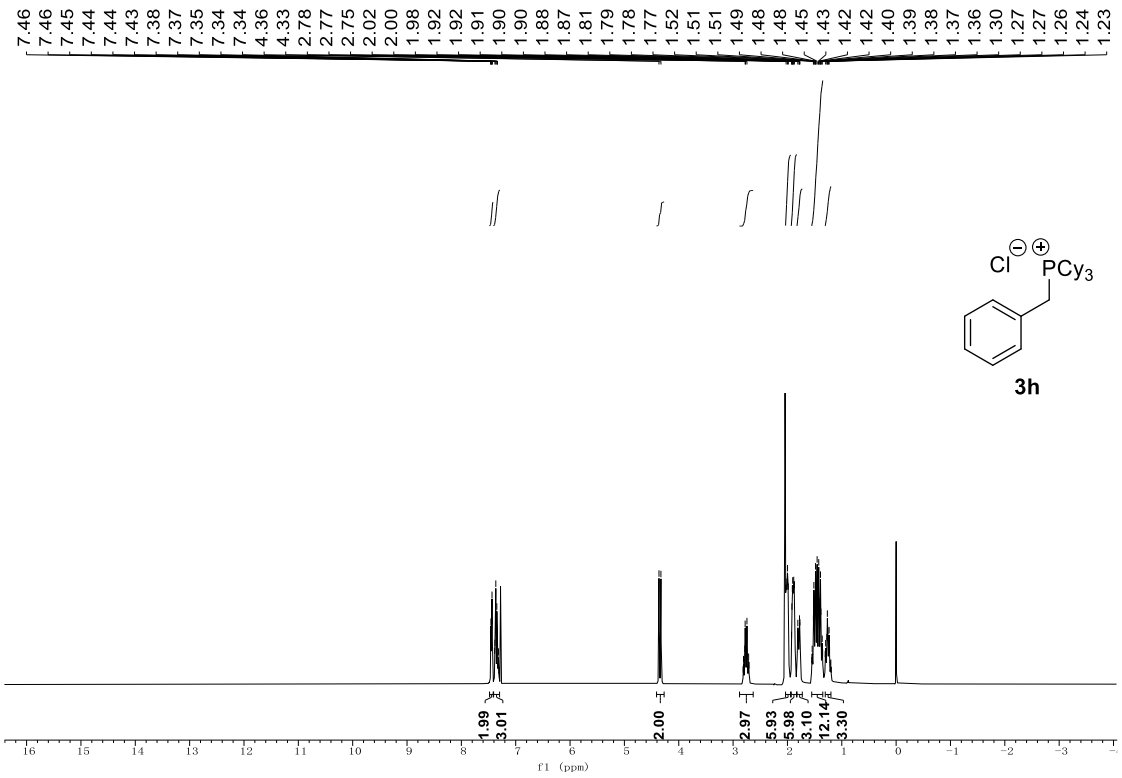

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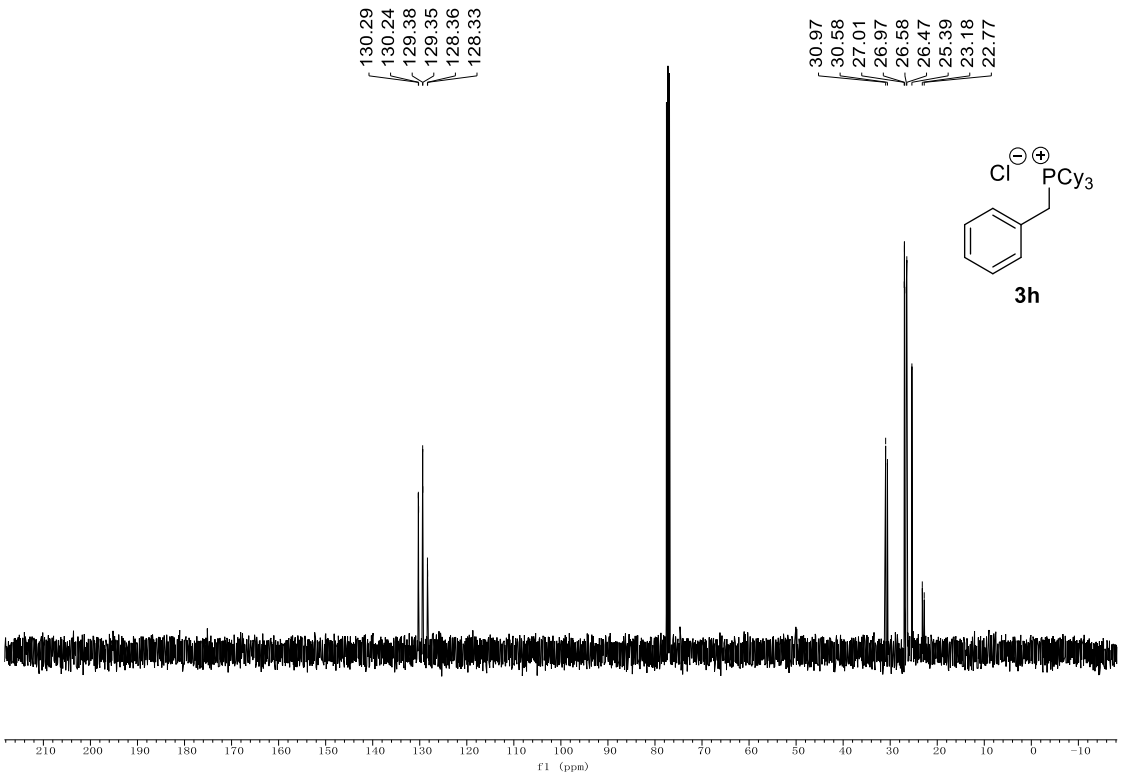
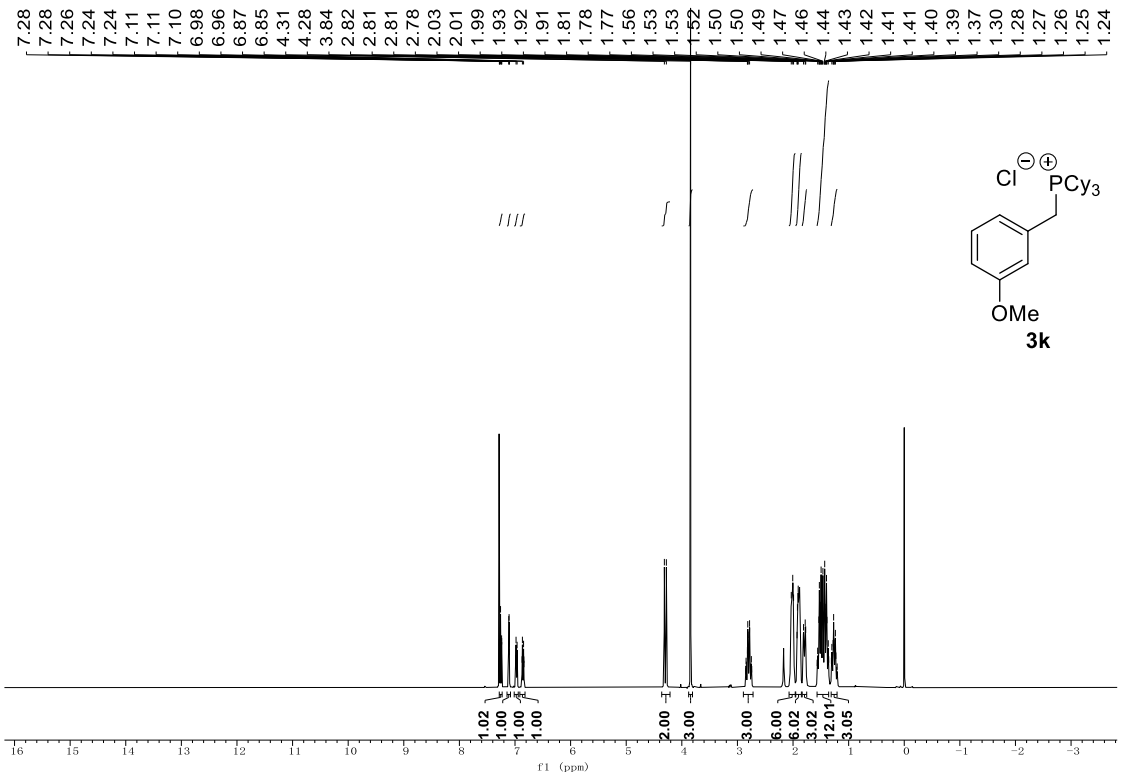


^{1}H NMR, 400 MHz, $CDCl_3$



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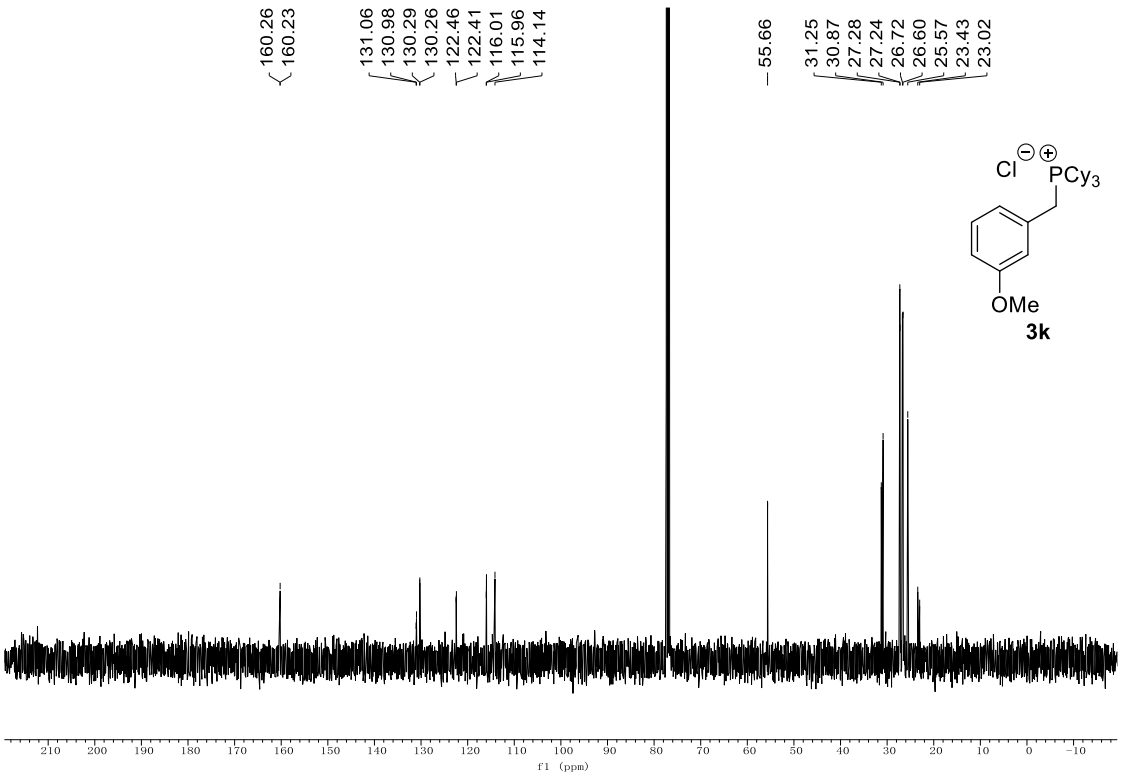
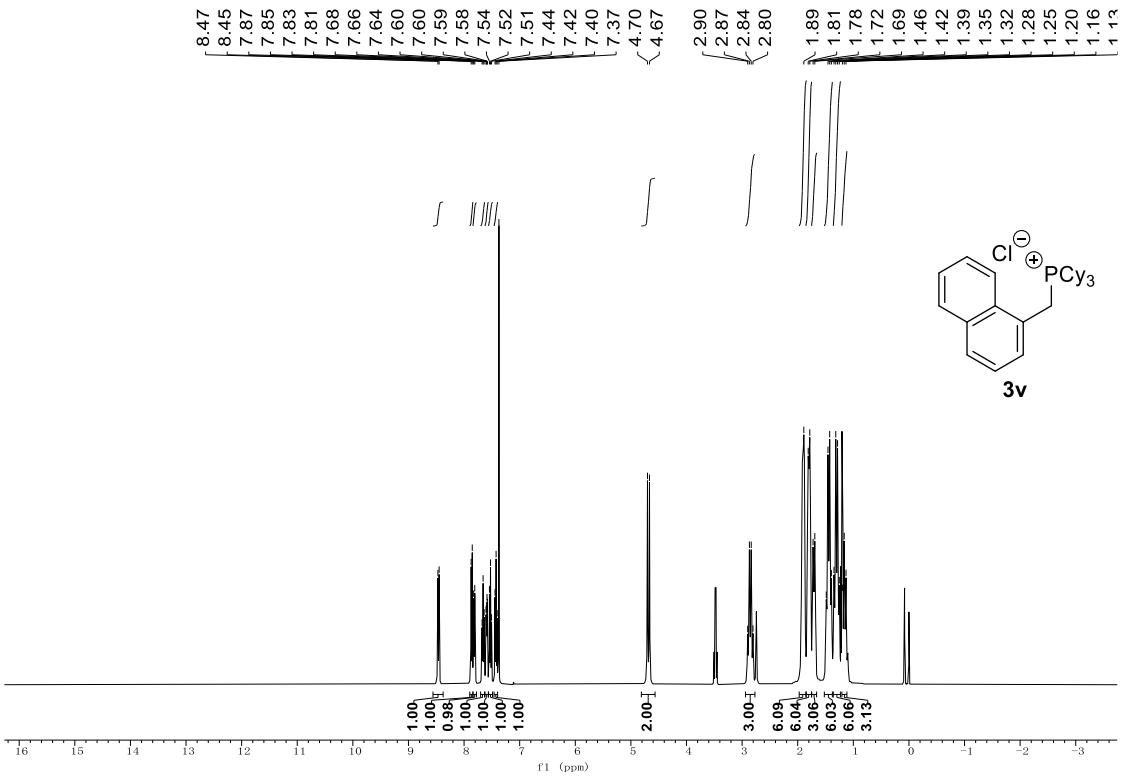
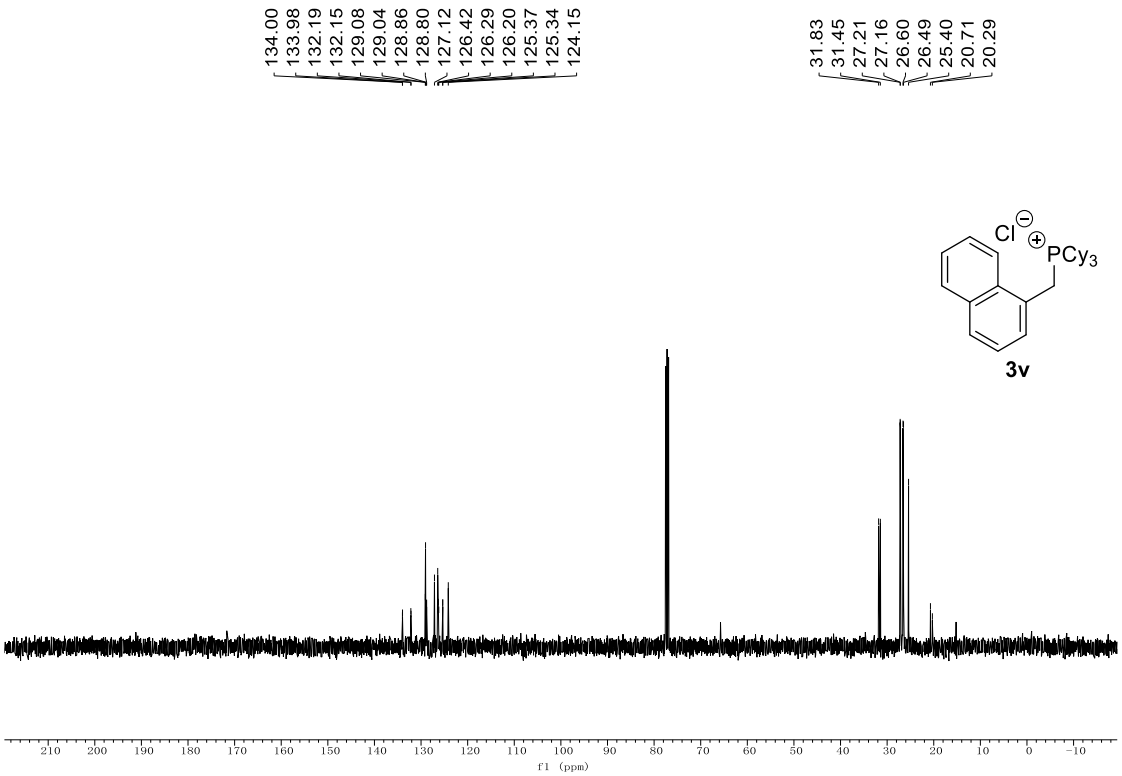


^{1}H NMR, 400 MHz, $CDCl_3$



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



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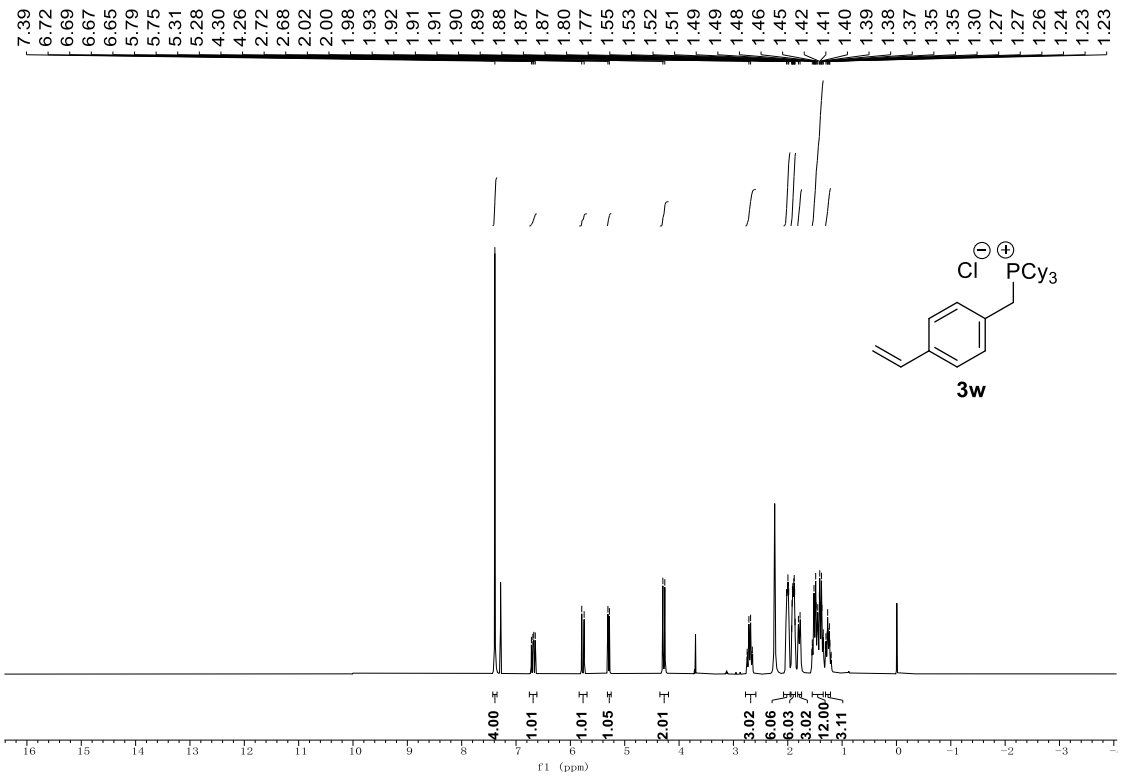

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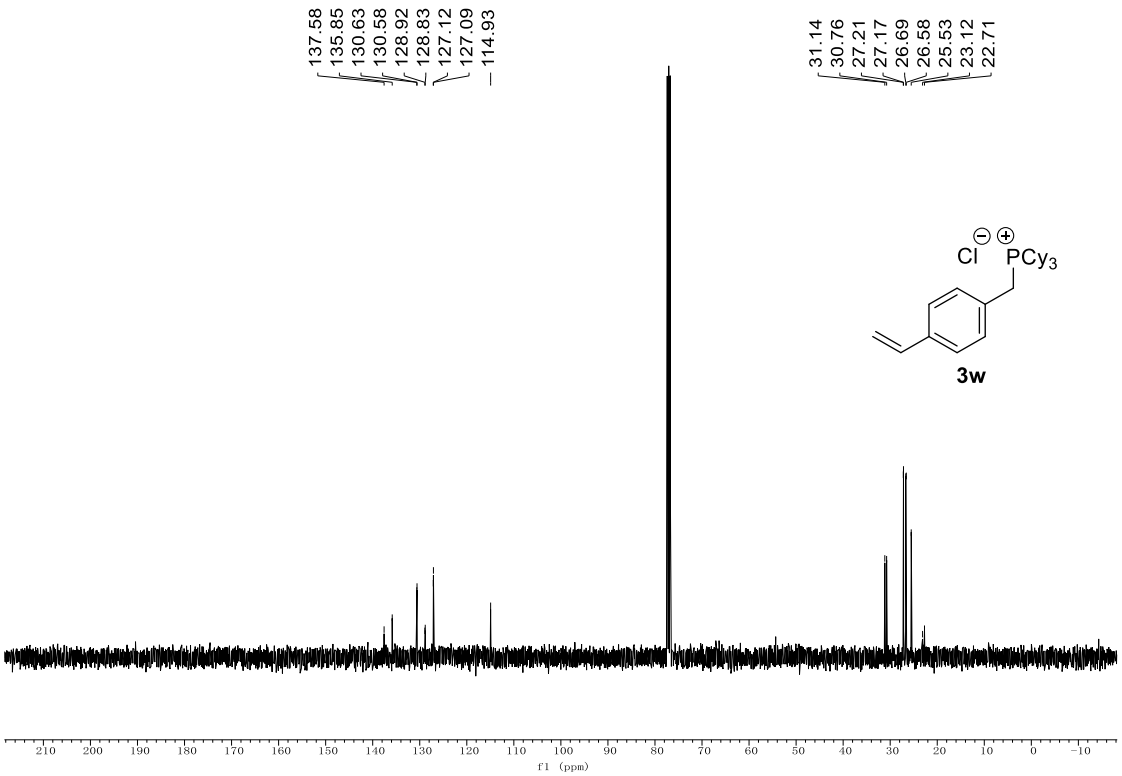
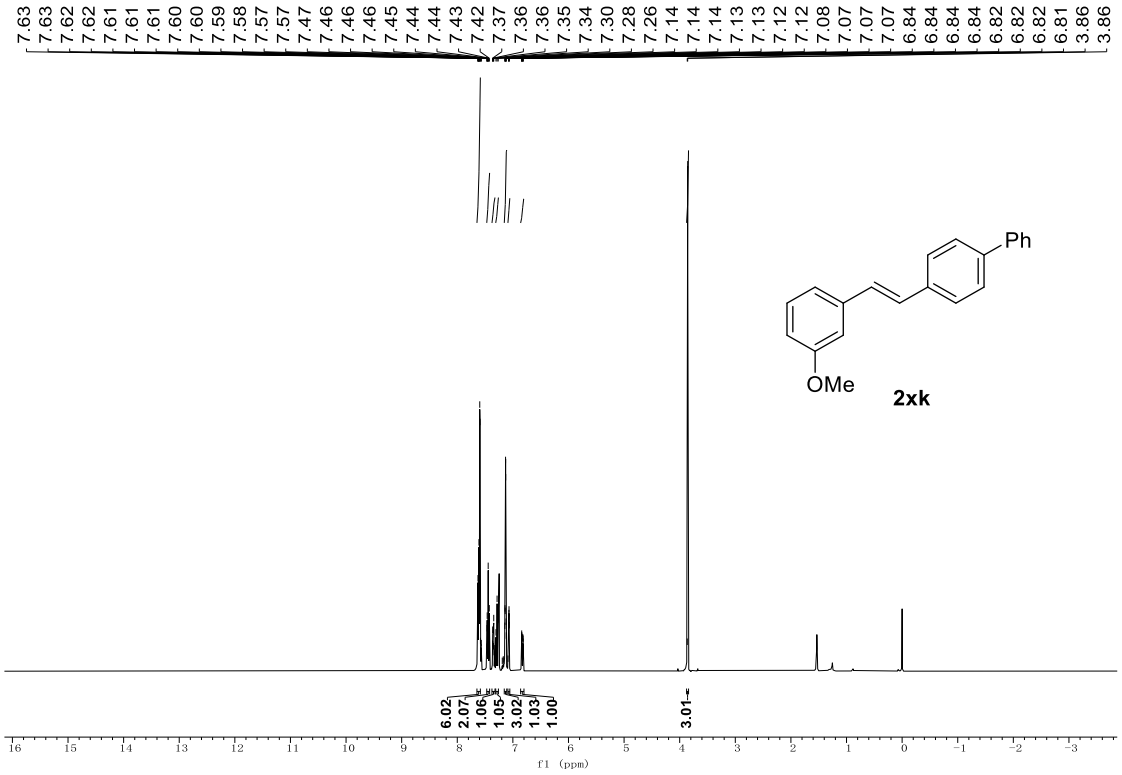
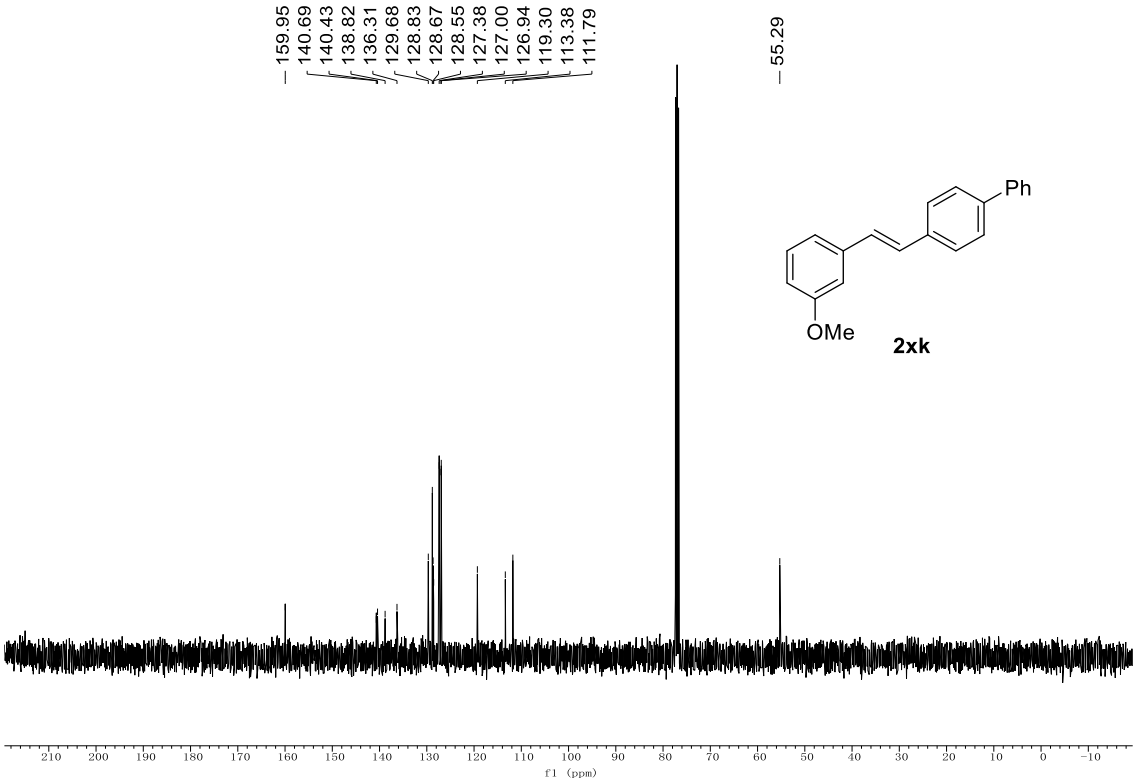


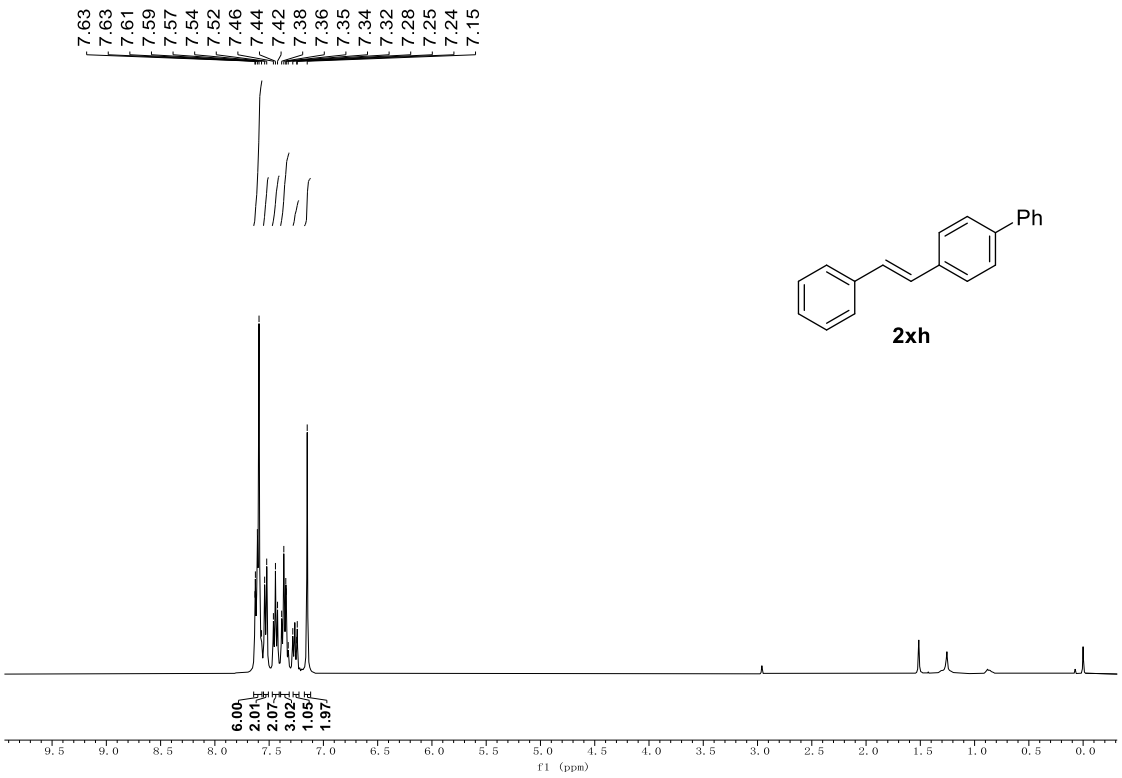
^{1}H NMR, 400 MHz, $CDCl_3$



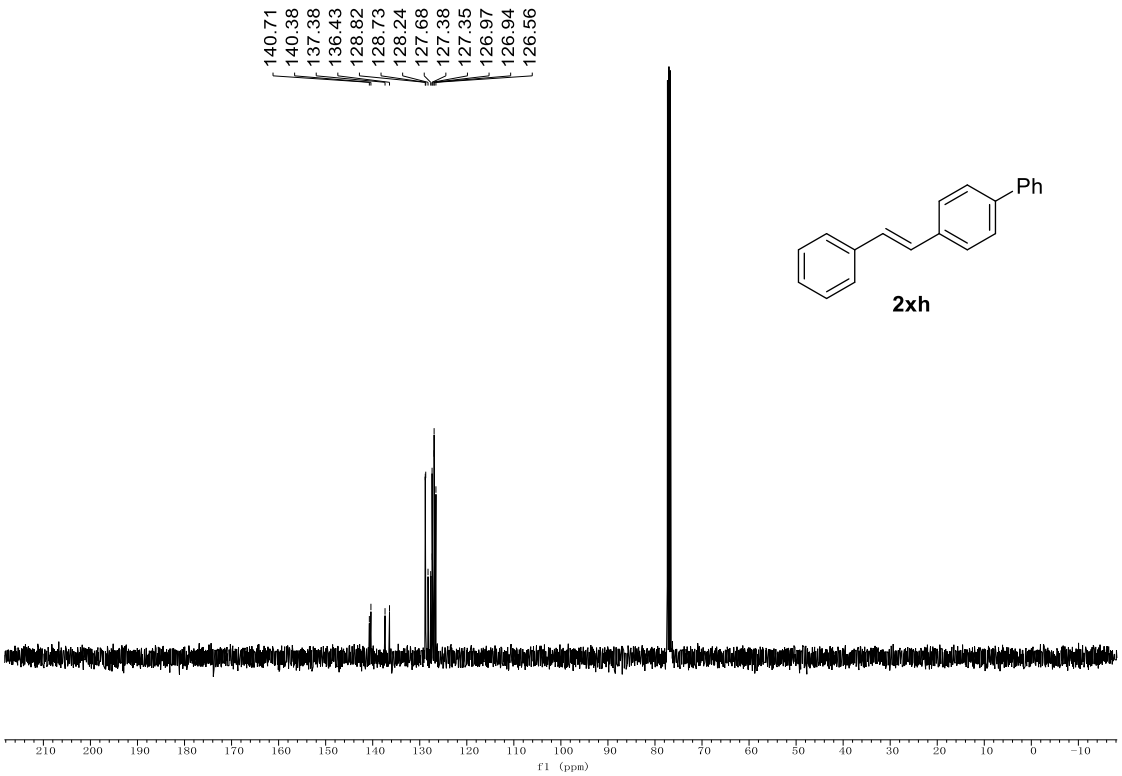
^{13}C NMR, 101 MHz, $CDCl_3$



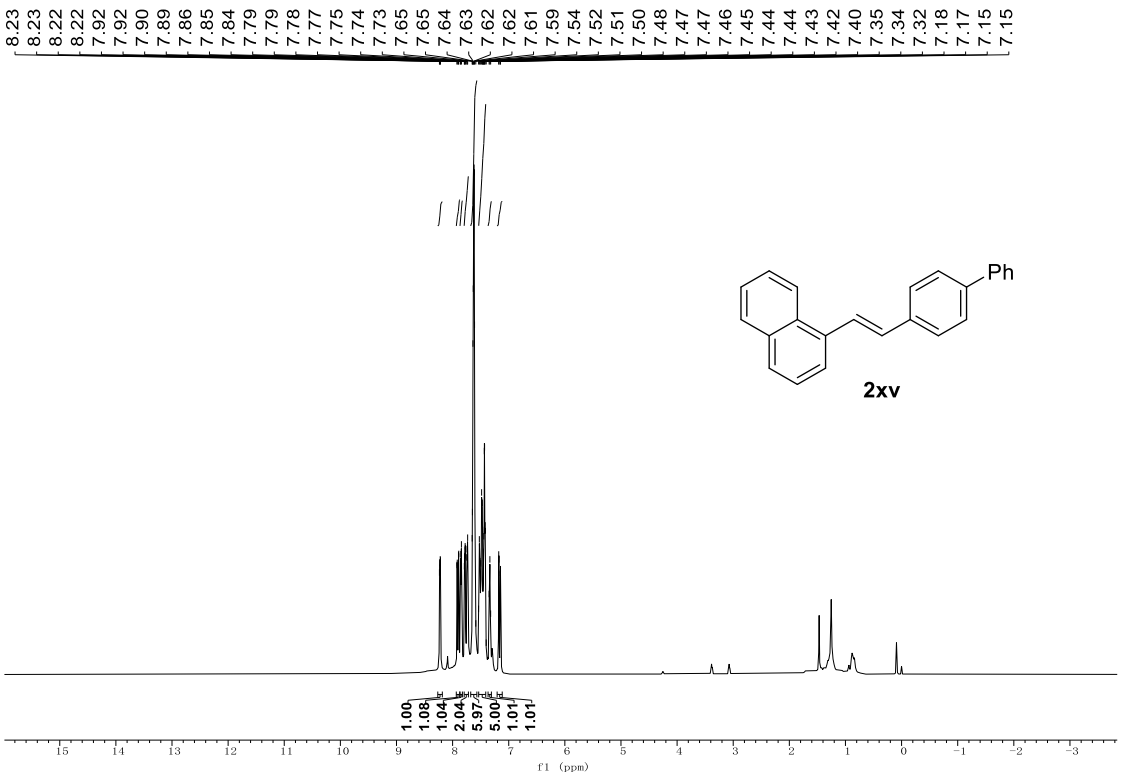
^{1}H NMR, 400 MHz, $CDCl_3$



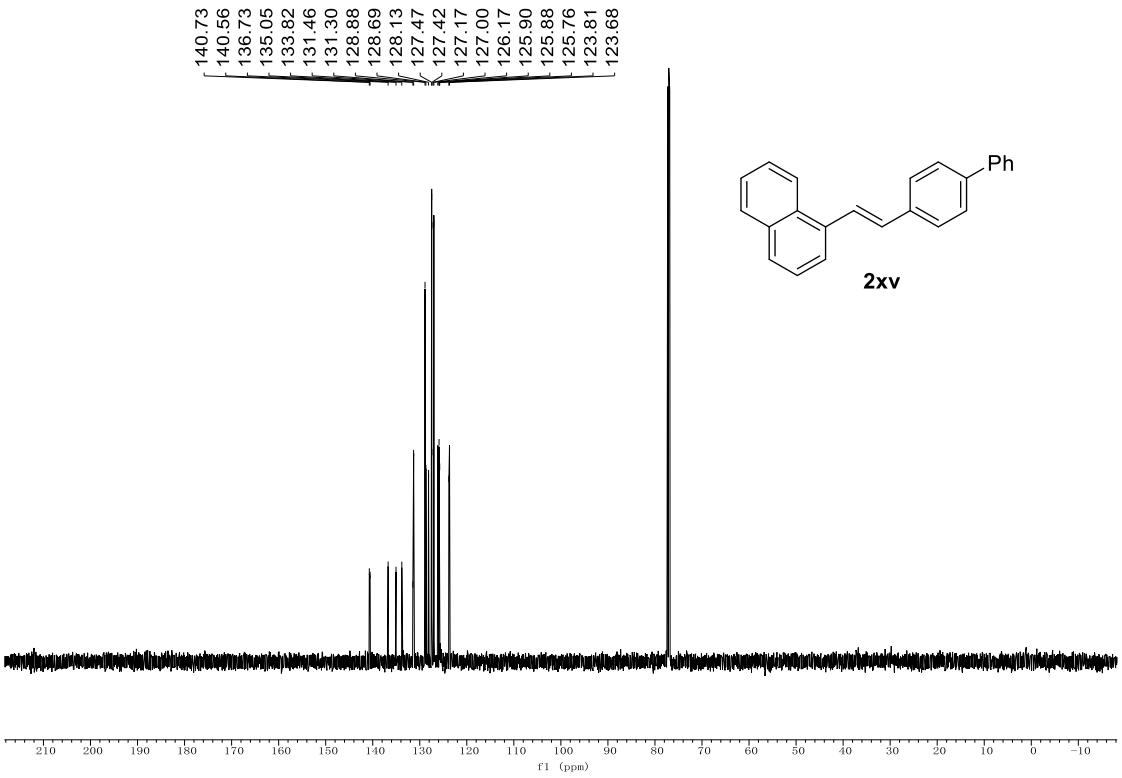
^{13}C NMR, 101 MHz, $CDCl_3$



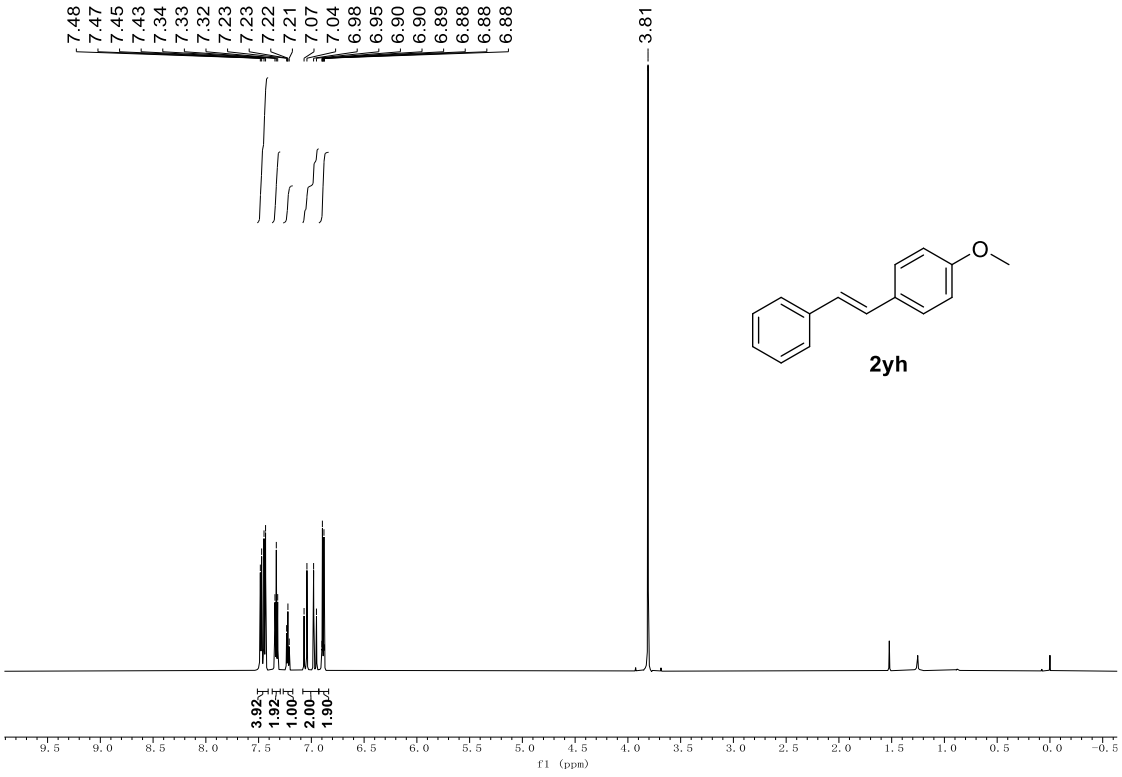
^{1}H NMR, 600 MHz, $CDCl_3$



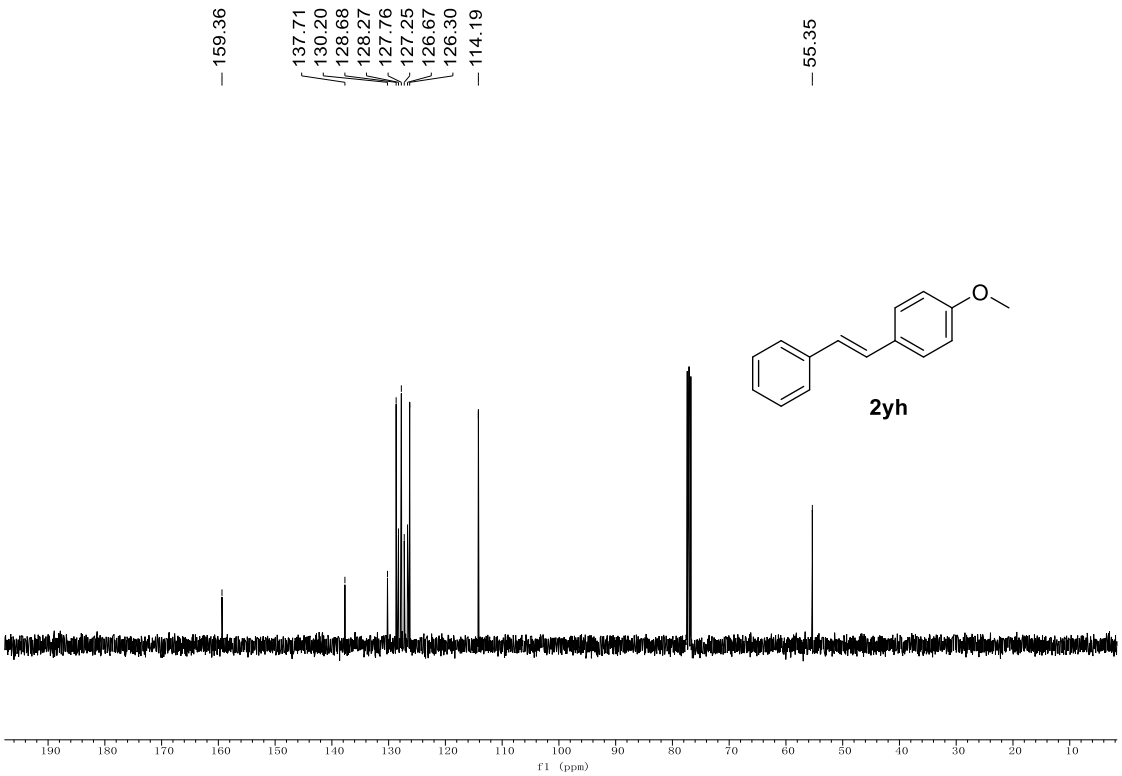
^{13}C NMR, 151 MHz, $CDCl_3$



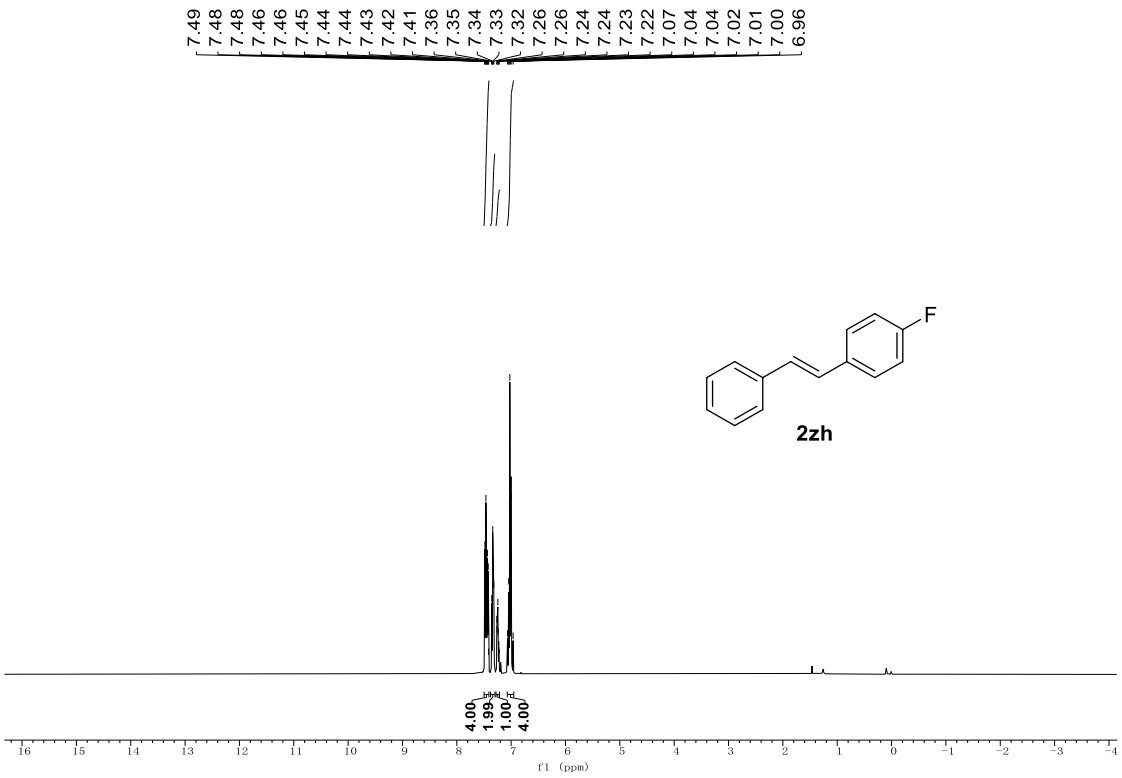
^{1}H NMR, 600 MHz, $CDCl_3$



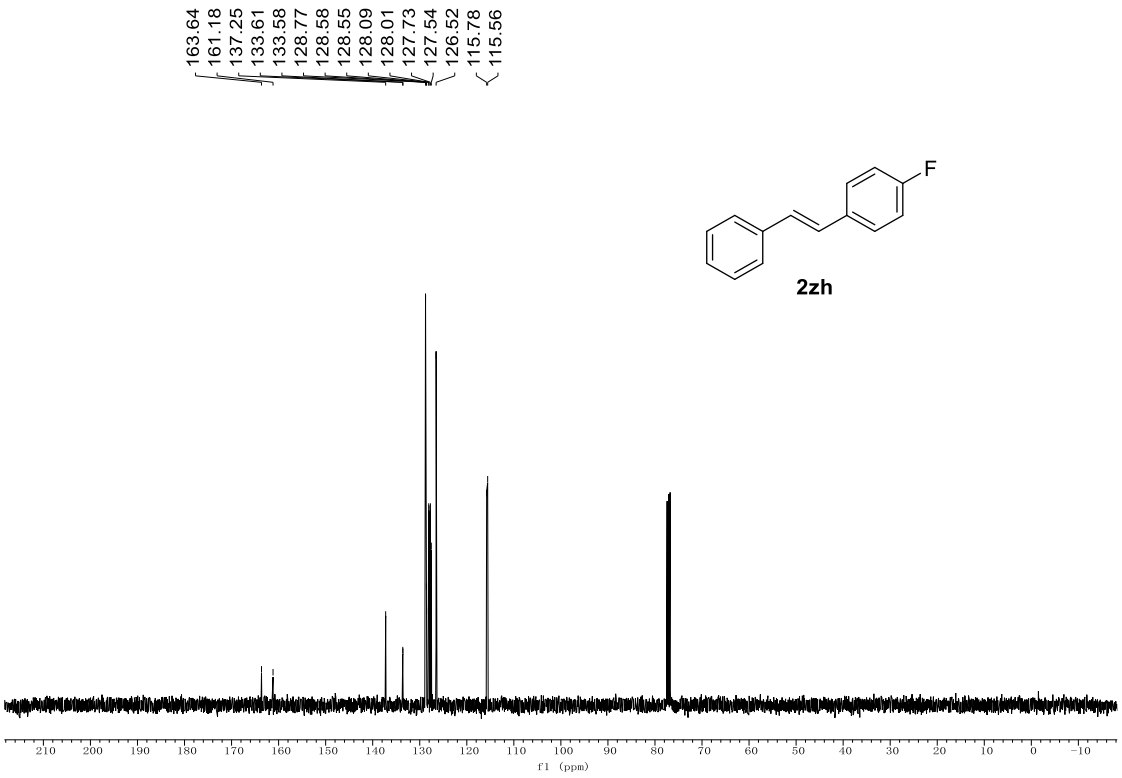
^{13}C NMR, 151 MHz, $CDCl_3$



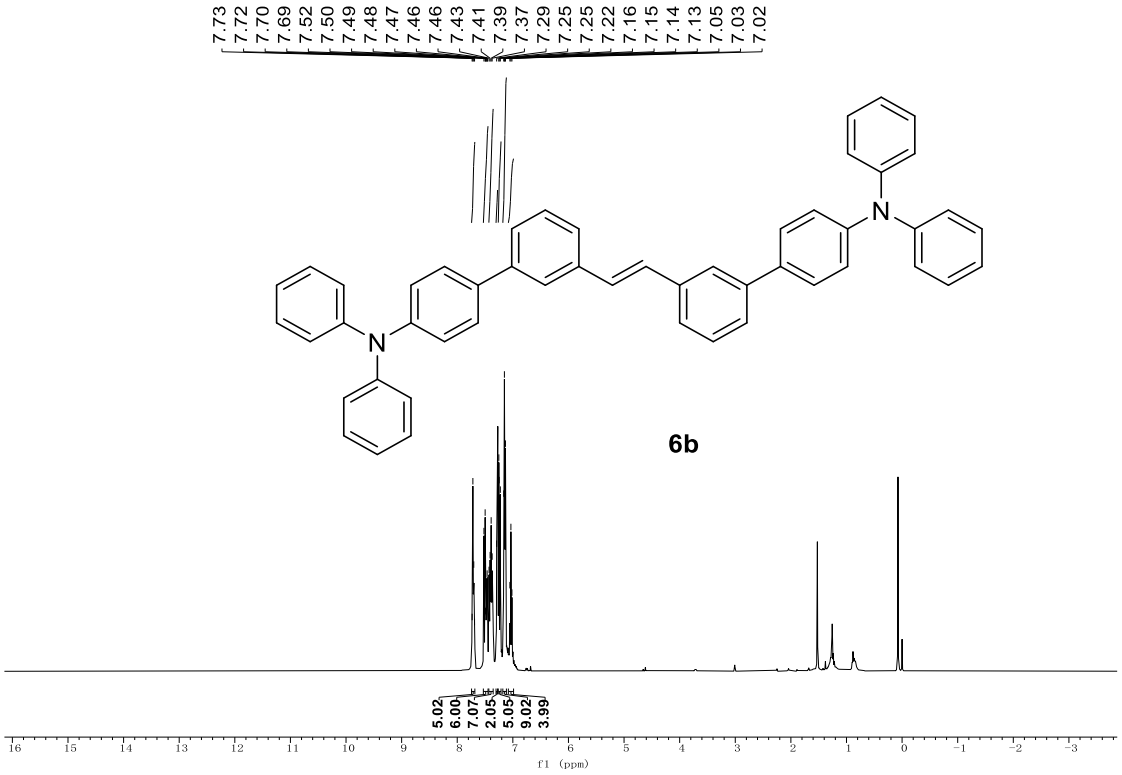
^{1}H NMR, 400 MHz, $CDCl_3$



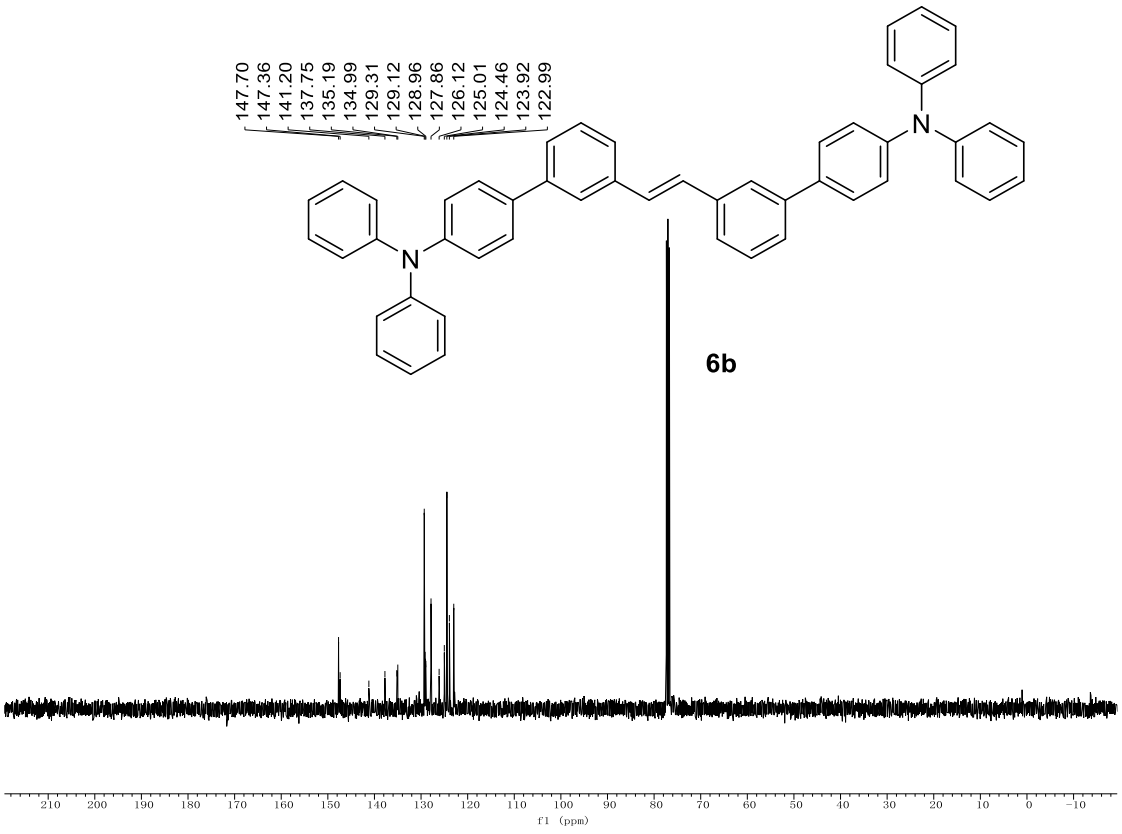
^{13}C NMR, 101 MHz, $CDCl_3$



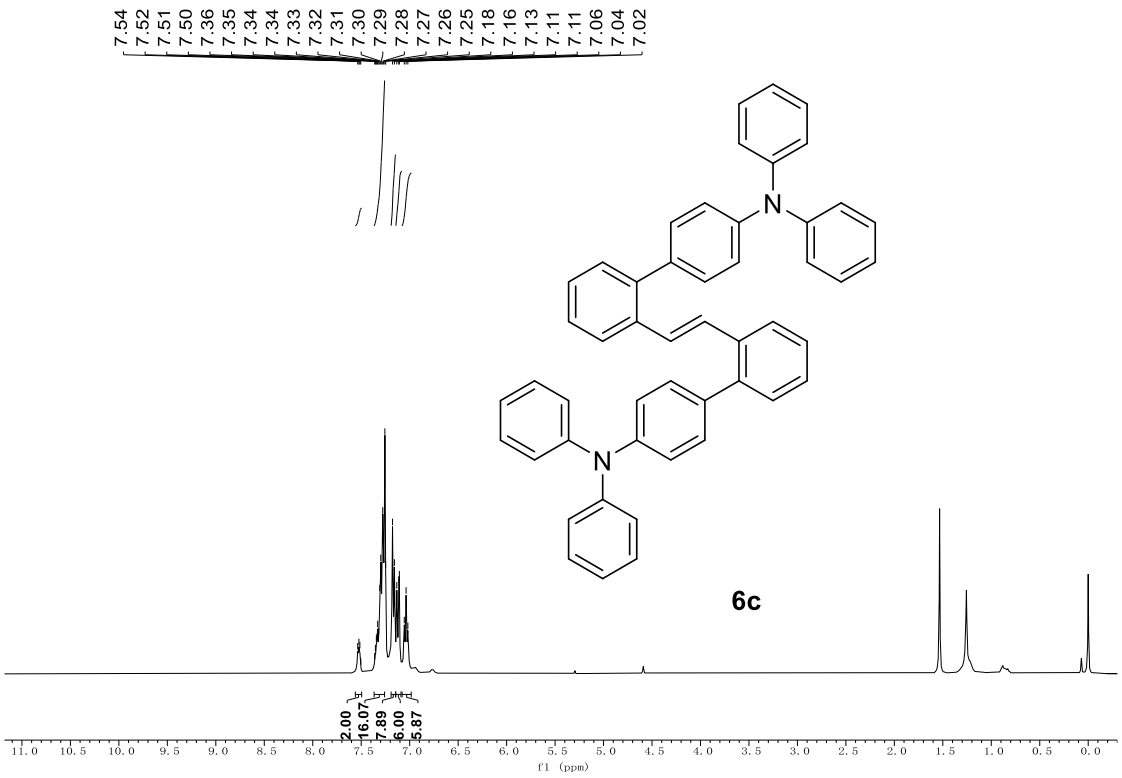
^{1}H NMR, 400 MHz, $CDCl_3$



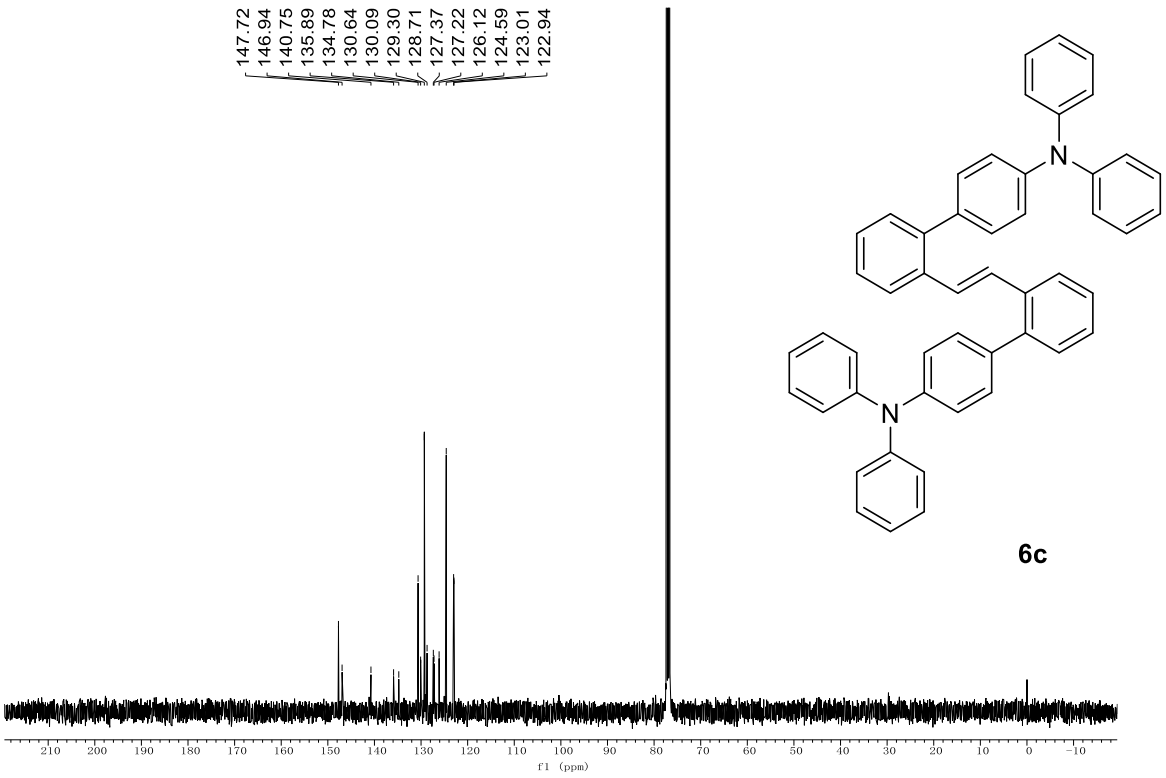
^{13}C NMR, 101 MHz, $CDCl_3$



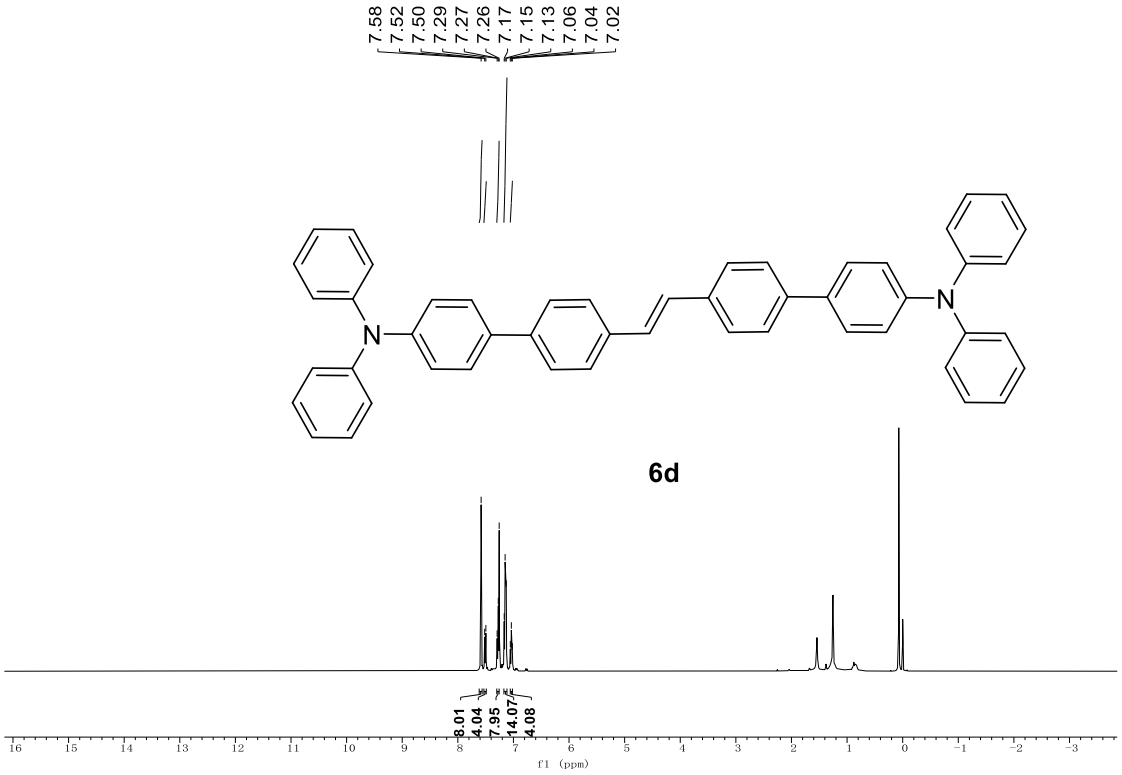
^{1}H NMR, 400 MHz, $CDCl_3$



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



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



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