Supplementary Information (SI) for Organic & Biomolecular Chemistry.

Supporting information

Solvent Control of *E/Z* Selectivity in Palladium Catalyzed Semi-hydrogenation of Alkynes

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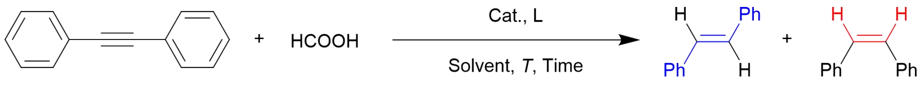
General Remarks

Catalytic reactions were performed under a N_2 atmosphere using pre-dried glassware and 100mL standard Schlenk techniques. All other chemicals were purchased from commercial sources and used without further purification. ^1H, ^{13}C, ^{19}F NMR spectra were recorded on a Bruker 400 MHz (100 MHz for ^{13}C NMR, 396 MHz for ^{19}F NMR) spectrometer at ambient temperature. Chemical shift are reported in ppm from TMS with the solvent resonance as internal standard ($CDCl_3$: ^1H NMR: δ= 7.26; ^{13}C NMR: δ= 77.0). Coupling constants are reported in Hz with multiplicities denoted as s (singlet), d (doublet), t (triplet), q (quartet), dd (doublet of doublets) and m (multiplet). Melting points (M.p.) were measured on Shanghai INESA melting point apparatus SGW® X-4B, values are uncorrected.

Optimization of the Reaction Conditions

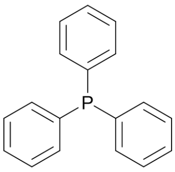
Table 1. Optimization of the reaction conditions for the synthesis of **2a** and **3a**[a]



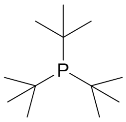
1a **2a** **3a**

Entry	Catalyst (mol%)	Ligand (mol%)	Solvent	**2a** (%)	**3a** (%)
1	$Pd(OAc)_2$ (4)	L1 (8)	toluene	trace	trace
2	$Pd(OAc)_2$	L2	toluene	49	trace
3	$Pd(OAc)_2$	L3	toluene	trace	9
4	$Pd(OAc)_2$	L4	toluene	55	trace
5	$Pd(OAc)_2$	L5	toluene	30	35
6	$Pd(OAc)_2$	L6	toluene	79	trace
7	$Pd(OAc)_2$	L7	toluene	55	trace
8	$PdCl_2$	L6	toluene	trace	trace
9	$PdBr_2$	L6	toluene	trace	trace
10	Pd/C	L6	toluene	trace	5
11	$Pd(NO_3)_2$	L6	toluene	trace	trace
12	$Pd(acac)_2$	L6	toluene	84	trace
13	$Pd(acac)_2$ (2)	L6 (6)	toluene	70	trace
14	$Pd(acac)_2$ (3)	L6 (9)	toluene	75	trace
15	$Pd(acac)_2$ (4)	L6 (12)	toluene	91	trace
16	$Pd(acac)_2$ (5)	L6 (15)	toluene	81	trace
17	$Pd(acac)_2$ (4)	L6 (12)	EtOH	37	23
18	$Pd(acac)_2$ (4)	L6 (12)	Ph-Cl	trace	40
19	$Pd(acac)_2$ (4)	L6 (12)	NMP	trace	62
20	$Pd(acac)_2$ (4)	L6 (12)	DMA	trace	65
22	$Pd(acac)_2$ (4)	L6 (12)	DMSO	7	89
22	$Pd(acac)_2$ (4)	L6 (12)	mesitylene	88	trace
22	$Pd(acac)_2$ (4)	L6 (12)	DMF	1	63
23	$Pd(acac)_2$ (4)[c]	L6 (12)	toluene	trace	trace
23	$Pd(acac)_2$ (4)[d]	L6 (12)	toluene	54	trace
24	$Pd(acac)_2$ (4)[e]	L6 (12)	toluene	61	trace
25	$Pd(acac)_2$ (4)[f]	L6 (12)	toluene	73	trace
26	$Pd(acac)_2$ (4)[g]	L6 (12)	toluene	90	trace

[a] Reaction conditions: **1a** (0.50 mmol, 1.0 equiv.), Catalyst (2.0 mol%, 0.040 equiv.), Ligand (4.0 mol%, 0.080 equiv.), Solvent (3.0 mL), at 80 ℃ for 8 h. [b] Yield of isolated product. [c] condition: at 30 ℃. [d] condition: at 50 ℃. [e] condition: at 60 ℃. [f] condition: at 70 ℃. [g] condition: at 85 ℃.



L1



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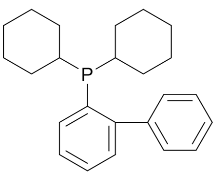

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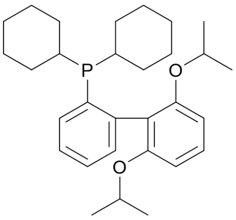

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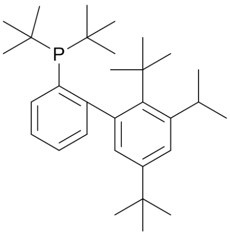

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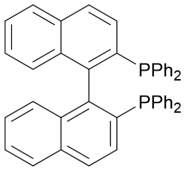

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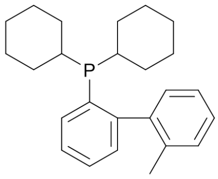


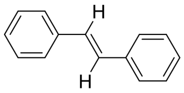
L7

General experimental procedure for semi-hydrogenation

A 50mL glass tube with a magnetic stir was charged with **1a** (0.50 mmol, 1.0 equiv.), palladium acetate (4.0 mol%, 0.080 equiv.), **L6** (0.20 mmol, 0.40 equiv.), HCOOH (5.0 mmol, 10 equiv.) and toluene (3.0 mL) were stirred under air at 80 °C for 8 h. The reaction mixture diluted with ethyl acetate and the solvent was removed under reduced pressure. Finally, the desired products were isolated by flash chromatography. Then, under reduced pressure we obtain the yield of pure **2a** through weighing and calculation.

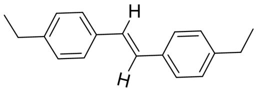
A 50mL glass tube with a magnetic stir was charged with **1a** (0.50 mmol, 1.0 equiv.), palladium acetate (4.0 mol%, 0.080 equiv.), **L6** (0.20 mmol, 0.40 equiv.), HCOOH (5.0 mmol, 10 equiv.) and DMSO (3.0 mL) were stirred under air at 80 °C for 8 h. The reaction mixture was washed with saturated saline solution. The aqueous layer was extracted with dichloromethane (3×15 mL) and the combined organic layer was dried over Mg_2SO_4. After the solvent was removed under reduced pressure, the desired products were isolated by flash chromatography. Then, under reduced pressure we obtain the yield of pure **3a** through weighing and calculation.

Analytical data of the products 2a-r



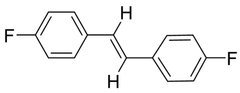
(E)-1,2-diphenylethene (2a)[1]

The general procedure was followed using 1,2-Diphenylethyne (**1a**) (89.5 mg, 0.5 mmol) and formic acid (230.0 mg, 5.0 mmol). Isolation by column chromatography (petroleum ether) yielded **2a** (81.9 mg, 91%) as a white solid. M.p. = 112.7–113.5 °C. ^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.57–7.54 (m, 4H), 7.40 (t, *J* = 7.6, 4H), 7.30 (m, 2H), 7.15 (s, 2H). ^{13}C (100 MHz, CDCl$_3$): δ = 137.5, 128.83, 128.82, 127.8, 126.7 ppm.



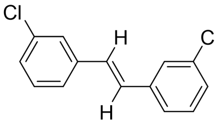
(E)-1,2-bis(4-ethylphenyl)ethene (2b)[2]

The general procedure was followed using 1,2-bis (4-ethylphenyl)ethyne (**1b**) (117.0 mg, 0.5 mmol) and formic acid (230.0 mg, 5.0 mmol). Isolation by column chromatography (petroleum ether) yielded **2b** (93.0 mg, 79%) as a white solid. M.p. = 94.2–95.0 °C. ^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.46 (d, *J* = 8 Hz, 4H), 7.23–7.21 (m, 4H), 7.08 (s, 2H), 2.71-2.66 (m, 4H), 1.30-1.26 (m, 6H). ^{13}C (100 MHz, CDCl$_3$): δ =143.8, 135.2, 128.3, 127.9, 126.5, 28.9, 15.7 ppm.



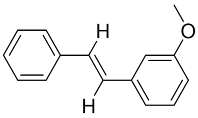
(E)-1,2-bis(4-fluorophenyl)ethene (2c)[3]

The general procedure was followed using 1,2-bis(3-fluorophenyl)ethyne (**1c**) (107.1 mg, 0.5 mmol) and formic acid (230.0 mg, 5.0 mmol). Isolation by column chromatography (petroleum ether) yielded **2c** (88.5 mg, 82%) as a white solid. M.p. = 129.8–131.7 °C. ^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.46 (dd, *J*=8.4, 5.6 Hz, 4H), 7.06 (t, *J*=8.8 Hz, 4H), 6.98 (s, 2H). ^{13}C (100 MHz, CDCl$_3$): δ = 162.5 ($J_{\text{C-F}}$ = 245.7 Hz), 133.5 ($J_{C\text{-}F}$ = 2.9 Hz), 128.1 ($J_{C\text{-}F}$=8.1 Hz), 127.4, 115.8 ($J_{C\text{-}F}$ = 21.6 Hz). ^{19}F (396 MHz, $CDCl_3$): δ = -114.1 ppm.



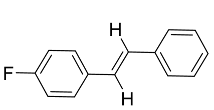
(E)-1,2-bis(3-chlorophenyl)ethene (2d)[4]

The general procedure was followed using 1,2-bis(3-chlorophenyl)ethyne (**1d**) (123.6 mg, 0.5 mmol) and formic acid (230.0 mg, 5.0 mmol). Isolation by column chromatography (petroleum ether) yielded **2d** (75.6 mg, 61%) as a colorless oily. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.49 (s, 2H), 7.36 (d, *J* = 7.6 Hz, 2H), 7.31–7.24 (m, 4H), 7.03 (s, 2H). ^{13}C (100 MHz, $CDCl_3$): δ = 138.8, 134.9, 130.1, 128.9, 128.1, 126.6, 125.0 ppm.



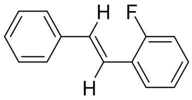
(E)-1-methoxy-3-styrylbenzene (2f)[5]

The general procedure was followed using 1-methoxy-3-(phenylethynyl)benzene (**1f**) (103.7 mg, 0.5 mmol) and formic acid (230.0 mg, 5.0 mmol). Isolation by column chromatography (petroleum ether) yielded **2f** (66.5 mg, 63%) as a white solid. M.p. = 54.7–55.8 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.51 (d, *J* = 7.6 Hz, 2H), 7.34 (dd, *J* = 15, 7.6 Hz, 4H), 7.24 (dd, *J* = 12, 7.6 Hz, 2H), 7.13 –7.05 (m, 3H), 2.38 (s, 3H). ^{13}C (100 MHz, $CDCl_3$): δ = 138.4, 137.6, 137.4, 128.9, 128.8, 128.7, 128.6, 128.6, 127.7, 127.3, 126.6, 123.9, 21.6 ppm.



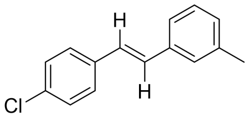
(E)-1-fluoro-4-styrylbenzene (2g)[6]

The general procedure was followed using 1-fluoro-4-(phenylethynyl)benzene (**1g**) (99.3 mg, 0.5 mmol) and formic acid (230.0 mg, 5.0 mmol). Isolation by column chromatography (petroleum ether) yielded **2g** (79.7 mg, 81%) as a white solid. M.p. = 119.2–120.1 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.25–7.18 (m, 7H), 6.9 (t, *J* = 8.8 Hz, 2H), 6.56 (q, *J* = 12.4 Hz, 2H). ^{13}C (100 MHz, $CDCl_3$): δ = 162.0 ($J_{C\text{-}F}$ = 245.1 Hz), 137.2, 133.3 ($J_{C\text{-}F}$ = 3.4 Hz), 130.7 ($J_{C\text{-}F}$ = 7.8 Hz), 130.4, 129.2, 129.0, 128.4, 127.3, 115.2 ($J_{C\text{-}F}$ = 21.3 Hz). ^{19}F (396 MHz, $CDCl_3$): δ = -114.7 ppm.



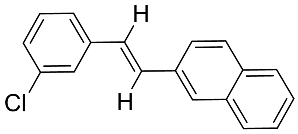
(E)-1-fluoro-2-styrylbenzene (2h)[7]

The general procedure was followed using 1-fluoro-2-(phenylethynyl)benzene (**1h**) (99.3 mg, 0.5 mmol) and formic acid (230.0 mg, 5.0 mmol). Isolation by column chromatography (petroleum ether) yielded **2h** (82.4 mg, 85%) as a white solid. M.p. = 103-105 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.59 (td, *J* = 7.6, 1.2 Hz, 1H), 7.52 (d, *J* = 7.2 Hz, 2H), 7.35 (t, *J* = 7.2 Hz, 2H), 7.29−7.18 (m, 4H), 7.14−7.12 (m, 1H), 7.10−7.03 (m, 1H). ^{13}C (100 MHz, $CDCl_3$): δ = 160.6 ($J_{C\text{-}F}$ = 248.0 Hz), 137.4, 131.0 ($J_{C\text{-}F}$ = 4.7 Hz), 128.9, 128.9 ($J_{C\text{-}F}$ = 2.1 Hz), 128.1, 127.2 ($J_{C\text{-}F}$ = 3.6 Hz), 126.8, 125.3 ($J_{C\text{-}F}$ = 12.0 Hz), 124.3 ($J_{C\text{-}F}$ = 3.5 Hz), 121.0 ($J_{C\text{-}F}$ = 3.7 Hz), 115.9 ($J_{C\text{-}F}$ = 22.0 Hz). ^{19}F (396 MHz, $CDCl_3$): δ = -117.9 ppm.



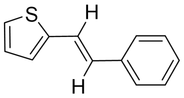
(E)-1-(4-chlorostyryl)-3-methylbenzene (2i)[8]

The general procedure was followed using 1-((4-chlorophenyl)ethynyl)-3-methylbenzene (**1i**) (113.1 mg, 0.5 mmol) and formic acid (230.0 mg, 5.0 mmol). Isolation by column chromatography (petroleum ether) yielded **2i** (94.0 mg, 83%) as a white solid. M.p. = 92.6–93.2 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.42 (d, *J* = 8.4 Hz, 2H), 7.32–7.29 (m, 4H), 7.24−7.22 (m, 1H), 7.08 (d, *J* = 7.2 Hz, 1H), 7.03 (s, 2H), 2.37 (s, 3H). ^{13}C (100 MHz, $CDCl_3$): δ = 138.4, 137.1, 136.1, 133.2, 129.6, 129.0, 128.8, 128.8, 127.8, 127.4, 127.3, 123.9, 21.6 ppm.



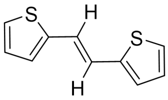
(E)-2-(3-chlorostyryl)naphthalene (2k)

The general procedure was followed using 2-((3-chlorophenyl)ethynyl)naphthalene (**1k**) (132.5 mg, 0.5 mmol) and formic acid (230.0 mg, 5.0 mmol). Isolation by column chromatography (petroleum ether) yielded **2k** (125.4 mg, 95%) as a white solid. M.p. = 112.7–113.5 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.79–7.76 (m, 4H), 7.67–7.65 (m, 1H), 7.49 (s, 1H), 7.45–7.39 (m, 2H), 7.35 (d, *J* = 7.6 Hz, 1H), 7.24–7.19 (m, 1H), 7.19 (d, *J* = 4.0 Hz, 2H), 7.09 (d, *J* = 16.4 Hz, 1H). ^{13}C (100 MHz, $CDCl_3$): δ = 139.4, 134.8, 134.4, 133.8, 133.3, 130.3, 130.0, 128.5, 128.2, 127.9, 127.7, 127.6, 127.1, 126.6, 126.5, 126.3, 124.9, 123.5 ppm. HR-MS (ESI): calculated for $C_{18}H_{14}Cl$, $[M+H]^+$ 265.0706, found: 265.0710.



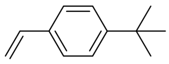
(E)-2-styrylthiophene (2m)[9]

The general procedure was followed using 2-(phenylethynyl) thiophene (**1m**) (92.5 mg, 0.5 mmol) and formic acid (230.0 mg, 5.0 mmol). Isolation by column chromatography (petroleum ether) yielded **2m** (87.9 mg, 95%) as a white solid. M.p. = 117.3–118.2 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.46 (d, *J* = 8.0 Hz, 2H), 7.35−7.29 (m, 4H), 7.25−7.22 (m, 2H), 7.11 (d, *J* = 16.0 Hz, 1H), 6.94 (d, *J* = 16.4 Hz, 1H). ^{13}C (100 MHz, $CDCl_3$): δ = 140.2, 137.5, 128.8, 127.6, 126.4, 126.3, 125.1, 123.0, 122.5 ppm.



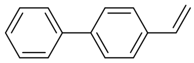
(E)-1,2-di(thiophen-2-yl)ethene (2o)[10]

The general procedure was followed using 1,2-di(thiophen-2-yl)ethyne (**1o**) (96.5 mg, 0.5 mmol) and formic acid (230.0 mg, 5.0 mmol). Isolation by column chromatography (petroleum ether) yielded **2o** (87.9 mg, 95%) as a green liquid. ^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.19 (d, *J* = 5.2 Hz, 2H), 7.05 (dd, *J* = 5.6, 4.4 Hz, 4H), 7.00 (dd, *J* = 7.6, 3.6 Hz, 2H). ^{13}C (100 MHz, CDCl$_3$): δ = 142.5, 127.8, 126.1, 124.4, 121.6 ppm.



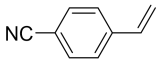
1-(tert-butyl)-4-vinylbenzene (2p)[11]

The general procedure was followed using 1-(tert-butyl)-4-ethynylbenzene (**1p**) (80.0mg, 0.5 mmol) and formic acid (230.0 mg, 5.0 mmol). Isolation by column chromatography (petroleum ether) yielded **2p** (70.1 mg, 80%) as a white solid. M.p. = 91.5 °C ^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.37 (s, 4H), 6.72 (dd, *J* = 17.6, 10.8 Hz, 1H), 5.73 (d, *J* = 17.6 Hz, 1H), 5.21 (d, *J* = 11.2 Hz, 1H), 1.34 (s, 9H). ^{13}C (100 MHz, CDCl$_3$): δ = 151.0, 136.7, 135.0, 126.1, 125.6, 113.1, 34.7, 31.4 ppm.



4-vinyl-1,1'-biphenyl (2q)[12]

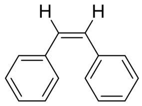
The general procedure was followed using 4-ethynyl-1,1'-biphenyl (**1q**) (90.0 mg, 0.5 mmol) and formic acid (230.0 mg, 5.0 mmol). Isolation by column chromatography (petroleum ether) yielded **2q** (81.2 mg, 90%) as a white solid. M.p. = 98.2–99.7 °C. ^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.60 (dd, *J* = 12.0, 7.2 Hz, 4H), 7.51−7.43 (s, 4H), 7.35 (t, *J* = 7.2 Hz, 1H), 6.77 (dd, *J* = 17.6, 10.8 Hz, 1H), 5.81 (d, *J* =17.6 Hz, 1H), 5.29 (d, *J* = 10.8 Hz, 1H). ^{13}C (100 MHz, CDCl$_3$): δ = 140.9, 140.7, 136.7, 136.6, 128.9, 127.5, 127.4, 127.1, 126.8, 114.0 ppm.



4-vinylbenzonitrile (2r)[11]

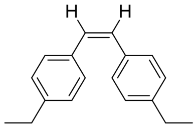
The general procedure was followed using 4-ethynylbenzonitrile (**1r**) (65.0 mg, 0.5 mmol) and formic acid (230.0 mg, 5.0 mmol). Isolation by column chromatography (petroleum ether) yielded **2r** (38.9 mg, 60%) as a white solid. M.p. = 88-91 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.59 (d, *J* = 8.1 Hz, 2H), 7.47 (d, *J* = 8.3 Hz, 2H), 6.71 (dd, *J* = 17.6, 10.9 Hz, 1H), 5.86 (d, *J* = 17.6 Hz, 1H), 5.43 (d, *J* = 10.9 Hz, 1H). ^{13}C (100 MHz, $CDCl_3$): δ = 141.99, 135.46, 132.49, 126.84, 119.01, 117.84, 111.21 ppm.

Analytical data of the products 3a-r



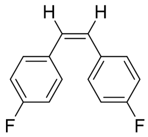
(Z)-1,2-diphenylethene (3a)[2]

The general procedure was followed using 1,2-Diphenylethyne (**1a**) (89.5 mg, 0.5 mmol) and formic acid (230.0 mg, 5.0 mmol). Isolation by column chromatography (petroleum ether) yielded **3a** (91.2 mg, 96%) as a colorless oily. ^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.26–7.16 (m, 10H), 6.59 (s, 2H). ^{13}C (100 MHz, CDCl$_3$): δ = 137.4, 130.4, 129.0, 128.3, 127.2 ppm.



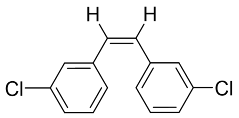
(Z)-1,2-bis(4-ethylphenyl)ethene (3b)[2]

The general procedure was followed using 1,2-bis (4-ethylphenyl)ethyne (**1b**) (117.0 mg, 0.5 mmol) and formic acid (230.0 mg, 5.0 mmol). Isolation by column chromatography (petroleum ether) yielded **3b** (94.4 mg, 80%) as a colorless oily. ^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.19 (d, J = 8.0 Hz, 4H), 7.05 (d, J = 8.0 Hz, 4H), 6.51 (s, 2H), 2.61 (q, J = 7.6 Hz, 4H), 1.22 (t, J = 7.6 Hz, 6H). ^{13}C (100 MHz, CDCl$_3$): δ = 143.2, 134.9, 129.7, 128.9, 127.8, 28.7, 15.5 ppm.



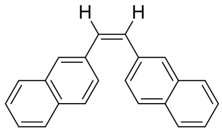
(Z)-1,2-bis(4-fluorophenyl)ethene (3c)[13]

The general procedure was followed using 1,2-bis(3-fluorophenyl)ethyne (**1c**) (107.1 mg, 0.5 mmol) and formic acid (230.0 mg, 5.0 mmol). Isolation by column chromatography (petroleum ether) yielded **3c** (100.5 mg, 93%) as a colorless oily. ^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.18 (dd, J = 8.8, 5.6 Hz, 4H), 6.92(t, J = 8.8 Hz, 4H), 6.54(s, 2H). ^{13}C (100 MHz, CDCl$_3$): δ = 162.0 (C-F, $J_{C\text{-}F}$ = 245.8 Hz), 133.1 ($J_{C\text{-}F}$ = 3.4 Hz), 130.6 ($J_{C\text{-}F}$=7.9 Hz), 129.2, 115.4 (C-F, $J_{C\text{-}F}$ = 21.3 Hz). ^{19}F (396 MHz, CDCl$_3$): δ = -114.5 ppm.



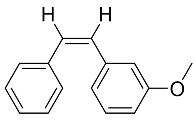
(Z)-1,2-bis(3-chlorophenyl)ethene (3d)[4]

The general procedure was followed using 1,2-bis(3-chlorophenyl)ethyne (**1d**) (123.6 mg, 0.5 mmol) and formic acid (230.0 mg, 5.0 mmol). Isolation by column chromatography (petroleum ether) yielded **3d** (113.3 mg, 91%) as a white solid. M.p. = 330.3-392.3 °C. ^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.23–7.14 (m, 6H), 7.10 (d, J = 7.2 Hz, 2H), 6.58 (s, 2H). ^{13}C (100 MHz, CDCl$_3$): δ = 138.6, 134.3, 130.1, 129.7, 129.0, 127.6, 127.1 ppm.



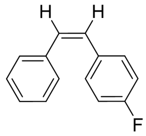
(Z)-1,2-di(naphthalen-2-yl)ethene (3e)[14]

The general procedure was followed using 1,2-di(naphthalen-2-yl)ethyne (**1e**) (139.0 mg, 0.5 mmol) and formic acid (230.0 mg, 5.0 mmol). Isolation by column chromatography (petroleum ether) yielded **3e** (113.4 mg, 81%) as a yellow solid. M.p. = 96.3–98.5 °C. ^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.82–7.73 (m, 7H), 7.76 (d, J=4.4 Hz, 2H), 7.48–7.41 (m, 5H), 6.88 (s, 2H). ^{13}C (100 MHz, CDCl$_3$): δ = 135.0, 133.6, 132.8, 130.7, 128.3, 127.8, 128.1, 127.7, 127.1, 126.2, 126.1 ppm.



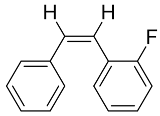
(Z)-1-methoxy-3-styrylbenzene (3f)[15]

The general procedure was followed using 1-methoxy-3-(phenylethynyl)benzene (**1f**) (103.7 mg, 0.5 mmol) and formic acid (230.0 mg, 5.0 mmol). Isolation by column chromatography (petroleum ether) yielded **3f** (56.7 mg, 54%) as a colorless oily. ^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.26–7.15 (m, 5H), 7.11–7.03 (m, 3H), 7.00 (d, *J* = 7.2 Hz, 1H), 6.56 (s, 2H), 2.25 (s, 3H). ^{13}C (100 MHz, CDCl$_3$): δ = 137.9, 137.5, 137.3, 130.5, 130.2, 129.7, 129.0, 128.3, 128.2, 128.0, 127.2, 126.0, 21.6 ppm.



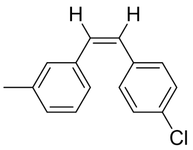
(Z)-1-fluoro-4-styrylbenzene (3g)[16]

The general procedure was followed using 1-fluoro-4-(phenylethynyl)benzene (**1g**) (99.3 mg, 0.5 mmol) and formic acid (230.0 mg, 5.0 mmol). Isolation by column chromatography (petroleum ether) yielded **3g** (81.2 mg, 82%) as a colorless oily. ^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.25–7.18 (m, 7H), 6.9 (t, *J*=8.8 Hz, 2H), 6.56 (q, *J*=12.4 Hz, 2H). ^{13}C (100 MHz, CDCl$_3$): δ =162.0 ($J_{C\text{-}F}$ = 245.1 Hz), 135.3 ($J_{C\text{-}F}$ = 383.6 Hz), 132.0 ($J_{C\text{-}F}$ = 260.3 Hz), 130.5 ($J_{C\text{-}F}$ = 23.2 Hz), 129.1 ($J_{C\text{-}F}$ = 25.3 Hz), 127.9 ($J_{C\text{-}F}$ = 111.5 Hz), 115.3 ($J_{C\text{-}F}$ = 21.3 Hz). ^{19}F (396 MHz, CDCl$_3$): δ = -114.7 ppm.



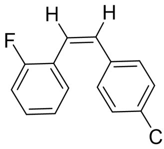
(Z)-1-fluoro-2-styrylbenzene (3h)[17]

The general procedure was followed using 1-fluoro-2-(phenylethynyl)benzene (**1h**) (98.6 mg, 0.5 mmol) and formic acid (230.0 mg, 5.0 mmol). Isolation by column chromatography (petroleum ether) yielded **3h** (60.3 mg, 61%) as a colorless oily. ^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.27−7.13 (m, 7H), 7.04 (dd, *J* = 17.2, 8.4 Hz, 1H), 6.93 (q, *J* = 8.0 Hz, 1H), 6.73 (dd, *J* = 12.4, 8.8 Hz, 1H), 6.22 (t, *J* = 8.4 Hz, 1H). ^{13}C (100 MHz, CDCl$_3$): δ = 160.5 ($J_{C\text{-}F}$ = 246.2 Hz), 137.0, 132.4, 130.6 ($J_{C\text{-}F}$ = 3.4 Hz), 129.1 ($J_{C\text{-}F}$ = 8.1 Hz), 128.9, 128.4, 127.5, 125.2 ($J_{C\text{-}F}$ = 14.4 Hz), 123.7 ($J_{C\text{-}F}$ = 3.5 Hz), 122.7 ($J_{C\text{-}F}$ = 3.2 Hz), 115.7 ($J_{C\text{-}F}$ = 21.8 Hz). ^{19}F (396 MHz, CDCl$_3$): δ = -114.9 ppm.



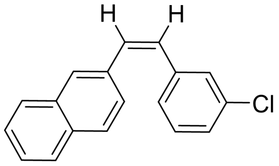
(Z)-1-(4-chlorostyryl)-3-methylbenzene (3i)[18]

The general procedure was followed using 1-((4-chlorophenyl)ethynyl)-3-methylbenzene (**1i**) (113.1 mg, 0.5 mmol) and formic acid (230.0 mg, 5.0 mmol). Isolation by column chromatography (petroleum ether) yielded **3i** (106.4 mg, 96%) as a colorless oily. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.21 (s, 4H), 7.14 (d, *J* = 7.2 Hz, 1H), 7.09 (s, 1H), 7.06 (d, *J* = 7.6 Hz, 2H), 6.63 (d, *J* = 12.4 Hz, 1H), 6.53 (d, *J* = 12.4 Hz, 1H), 2.31 (s, 3H). ^{13}C (100 MHz, $CDCl_3$): δ = 138.1, 136.9, 135.8, 132.8, 131.2, 130.4, 129.6, 128.8, 128.5, 128.3, 128.2, 125.9, 21.5 ppm.



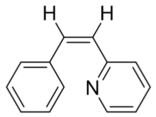
(Z)-1-(4-chlorostyryl)-2-fluorobenzene (3j)[12]

The general procedure was followed using 1-((4-chlorophenyl)ethynyl)-2-fluorobenzene (**1j**) (115.6 mg, 0.5 mmol) and formic acid (230.0 mg, 5.0 mmol). Isolation by column chromatography (petroleum ether) yielded **3j** (106.4 mg, 91%) as a colorless oily. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.24–7.14 (m, 6H), 7.07–7.03 (m, 1H), 6.96 (d, *J* = 7.2, 1H), 6.65–6.65 (m, 2H). ^{13}C (100 MHz, $CDCl_3$): δ =160.4 ($J_{\text{C-F}}$ = 246.5 Hz), 135.4, 133.2, 131.1, 130.5 ($J_{\text{C-F}}$ = 3.4 Hz), 130.2, 129.3 ($J_{\text{C-F}}$ = 8.1 Hz), 128.6, 124.9 ($J_{\text{C-F}}$ = 14.5 Hz), 123.9 ($J_{\text{C-F}}$ = 3.6 Hz), 123.5 ($J_{\text{C-F}}$ = 3.1 Hz), 115.9 ($J_{\text{C-F}}$ = 21.7 Hz). ^{19}F (396 MHz, $CDCl_3$): δ = -114.6 ppm.



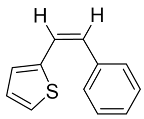
(Z)-2-(3-chlorostyryl)naphthalene (3k)

The general procedure was followed using 2-((3-chlorophenyl)ethynyl)naphthalene (**1k**) (132.5 mg, 0.5 mmol) and formic acid (230.0 mg, 5.0 mmol). Isolation by column chromatography (petroleum ether) yielded **3k** (121.9 mg, 91%) as a white solid. ^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.81–7.67 (m, 4H), 7.48−7.45 (m, 2H), 7.33 (dd, J = 10.0, 1.2 Hz, 2H), 7.20 (dd, J = 6.8, 2.0 Hz, 1H), 7.17–7.11(m, 2H), 6.82 (d, J = 12.0 Hz, 1H), 6.62 (d, J = 12.4 Hz, 1H). ^{13}C (100 MHz, CDCl$_3$): δ = 139.3, 134.3, 134.3, 133.6, 132.8, 131.6, 129.6, 129.1, 129.1, 128.3, 128.1, 127.8, 127.4, 127.2, 126.8, 126.3, 126.2 ppm. HR-MS (ESI): calculated for $C_{18}H_{14}Cl$, [M+H]$^+$ 265.0706, found: 265.0710.



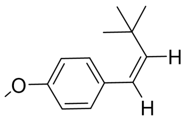
(Z)-2-styrylpyridine (3l)[19]

The general procedure was followed using 2-(phenylethynyl)pyridine (**1l**) (90.5 mg, 0.5 mmol) and formic acid (230.0 mg, 5.0 mmol). Isolation by column chromatography (petroleum ether) yielded **2l** (70.1 mg, 77%) as a yellow solid. M.p. = 79.1–80.2 °C. ^{1}H NMR (400 MHz, CDCl$_3$): δ = 8.61 (d, J = 4.0 Hz, 1H), 7.66 (t, J = 8.4 Hz, 2H), 7.62−7.58 (m, 2H), 7.38 (t, J = 8.4 Hz, 3H), 7.32−7.28 (m, 1H), 7.16 (t, J = 16.0 Hz, 2H). ^{13}C (100 MHz, CDCl$_3$): δ = 155.8, 149.8, 136.8, 136.7, 132.9, 128.9, 128.5, 128.1, 127.3, 122.24` , 122.21 ppm.



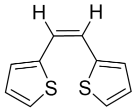
(Z)-2-styrylthiophene (3m)[20]

The general procedure was followed using 2-(phenylethynyl) thiophene (**1m**) (92.5 mg, 0.5 mmol) and formic acid (230.0 mg, 5.0 mmol). Isolation by column chromatography (petroleum ether) yielded **3m** (80.4 mg, 87%) as a white solid. M.p. = 74 °C. ^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.27−7.22 (m, 5H), 7.13−7.10 (m, 2H), 6.86 (dd, *J* = 4.8, 2.0 Hz, 1H), 6.59–6.52 (m, 2H). ^{13}C (100 MHz, CDCl$_3$): δ = 138.4, 137.9, 129.6, 128.9, 128.4, 128.1, 127.3, 125.0, 124.5, 124.2 ppm.



(Z)-1-(3,3-dimethylbut-1-en-1-yl)-4-methoxybenzene (3n)[21]

The general procedure was followed using 1-(3,3-dimethylbut-1-yn-1-yl)-4-methoxybenzene (**1n**) (96.2 mg, 0.1 mmol) and formic acid (230.0 mg, 5.0 mmol). Isolation by column chromatography (petroleum ether) yielded **2n** (73.2 mg, 77%) as a white solid. M.p. = 269.6-287.6 °C. ^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.10 (d, *J* = 8.24 Hz, 2H), 6.82 (d, *J* = 8.6 Hz, 2H), 6.35 (d, *J* = 12.52 Hz, 1H), 5.57 (d, *J* = 12.52 Hz, 1H), 3.81 (s, 3H), 0.99 (s, 9H). ^{13}C (100 MHz, CDCl$_3$): δ = 158.1, 142.7, 131.8, 130.2, 126.9, 113.1, 55.3, 34.2, 31.4 ppm.



(Z)-1,2-di(thiophen-2-yl)ethene (3o)[22]

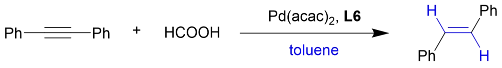
The general procedure was followed using 1,2-di(thiophen-2-yl)ethyne (**1o**) (96.5 mg, 0.5 mmol) and formic acid (230.0 mg, 5.0 mmol). Isolation by column chromatography (petroleum ether) yielded **3o** (80.4 mg, 87%) as a white solid. ^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.24 (d, *J* = 4.8 Hz, 2H), 7.11 (d, *J* = 3.2 Hz, 2H), 6.98 (dd, *J* = 4.8, 3.6 Hz, 2H), 6.61 (s, 2H). ^{13}C (100 MHz, CDCl$_3$): δ = 139.2, 128.4, 127.0, 126.3, 123.0 ppm.

Mechanistic Studies

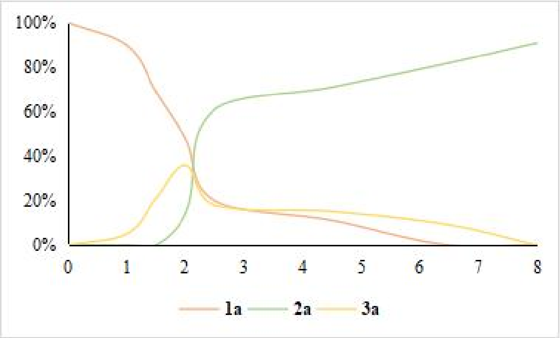
Kinetic profile of the *E*-selective semi-hydrogenation of 1a.

Seven 50mL glasses tube with a magnetic stir were charged with **1a** (0.50 mmol, 1.0 equiv.), palladium acetate (4.0 mol%, 0.080 equiv.), **L6** (0.20 mmol, 0.40 equiv.) and toluene (3.0 mL) were stirred under air at 80 °C. After T hours, the reaction mixture diluted with ethyl acetate and the solvent was removed under reduced pressure. Finally, the desired products were isolated by flash chromatography. Then, under reduced pressure we obtain the yield of pure **2a** through weighing and calculation.

Time (h)	**1a** (%)	**2a** (%)	**3a** (%)
1	90	0	5
1.5	69	0	21
2	48	14	36
2.5	20	61	18
4.5	11	71	15
6.5	0	82	9
8	0	91	0



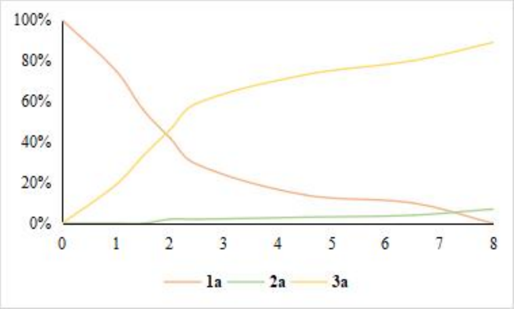
1a **2a**

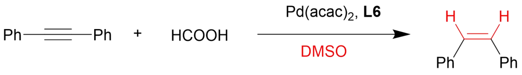


Scheme 1. Conditions: **1a** (0.50 mmol, 1.0 equiv.), formic acid (5.0 mmol, 10 equiv.), catalyst (4.0 mol%, 0.080 equiv.), **L6** (12 mol%, 0.24 equiv.), toluene (3.0 mL), at 80 °C. Yield of isolated product.

Kinetic profile of the Z-selective semi-hydrogenation of 1a.

Seven 50mL glasses tube with a magnetic stir were charged with **1a** (0.50 mmol, 1.0 equiv.), palladium acetate (4.0 mol%, 0.080 equiv.), **L6** (0.20 mmol, 0.40 equiv.), HCOOH (5.0 mmol, 10 equiv.) and DMSO (3.0 mL) were stirred under air at 80 °C. After T hours, the reaction mixture was washed with saturated saline solution. The aqueous layer was extracted with dichloromethane (3×15 mL) and the combined organic layer was dried over Mg_2SO_4. After the solvent was removed under reduced pressure, the desired products were isolated by flash chromatography. Then, under reduced pressure we obtain the yield of pure **3a** through weighing and calculation.





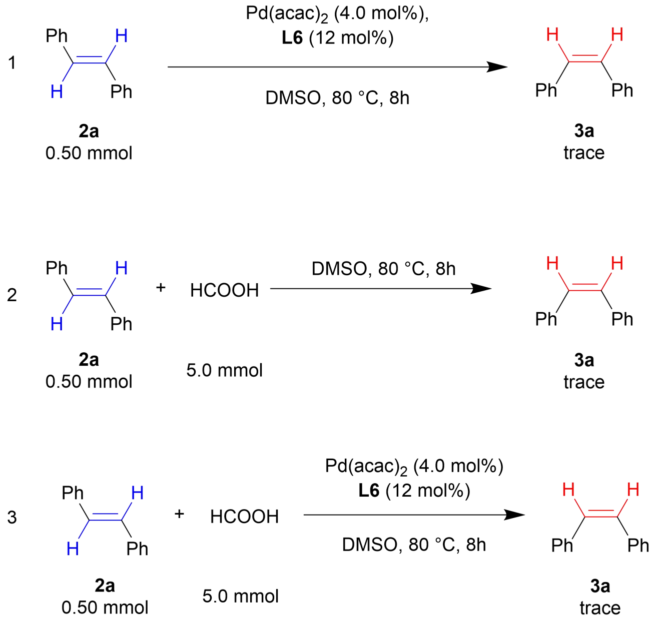
1a

3a

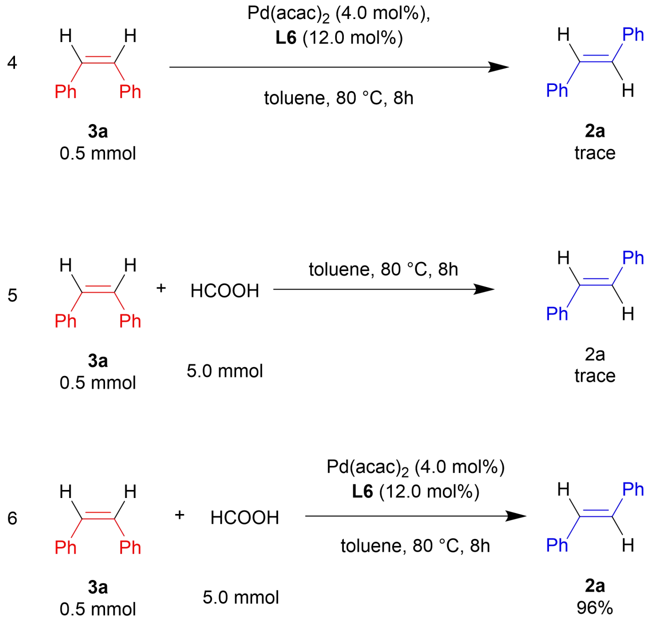
Time (h)	**1a** (%)	**2a** (%)	**3a** (%)
1	75	0	19
1.5	56	0	33
2	42	2	46
2.5	29	2	59
4.5	14	3	73
6.5	10	4	80
8	0	7	89

Scheme 2. Conditions: **1a** (0.50 mmol, 1.0 equiv.), formic acid (5.0 mmol, 10 equiv.), catalyst (4.0 mol%, 0.080 equiv.), **L6** (12 mol%, 0.24 equiv.), DMSO (3.0 mL), at 80 °C for 8 h. Yield of isolated product.

Mutual isomerization of 2a and 3a.



Scheme 3: Isomerization of **2a** in DMSO.

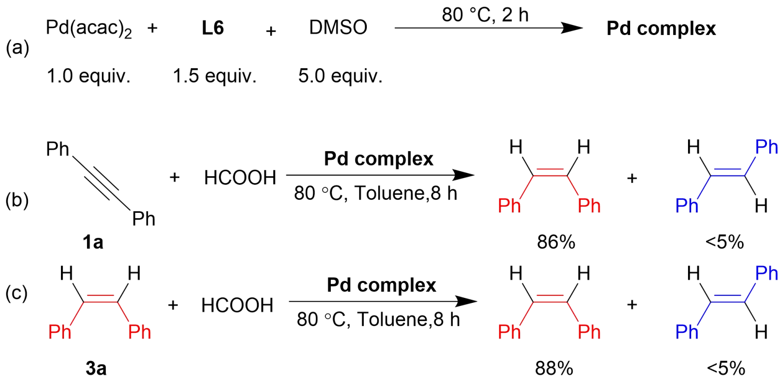


Scheme 4: Isomerization of **3a** in toluene.

The function of DMSO

A 50mL glass tube with a magnetic stir was charged with palladium acetate (4.0 mol%, 1.0 equiv.), **L6** (0.060 mmol, 1.5 equiv.), HCOOH (5.0 mmol, 10 equiv.) and DMSO (0.20 mmol, 5.0 equiv.), toluene (3.0 mL) was stirred under air at 80 °C for 2 hours to get **Pd complex**. Then add **1a** (0.50 mmol, 12 equiv.), HCOOH (5.0 mmol, 120 equiv.) and toluene (3mL) to the **Pd complex** at 80 °C. After 8 hours, the reaction mixture was washed with saturated saline solution. The aqueous layer was extracted with dichloromethane (3×15 mL) and the combined organic layer was dried over Mg_2SO_4. After the solvent was removed under reduced pressure, the desired products were isolated by flash chromatography. Then, under reduced pressure we obtain the yield of pure **3a** (84 mg, 86%) through weighing and calculation.

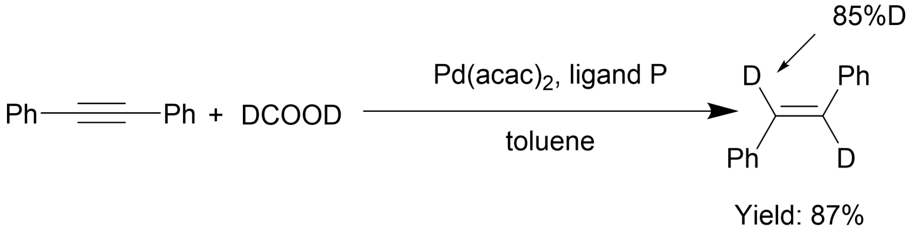
A 50mL glass tube with a magnetic stir was charged with palladium acetate (4.0 mol%, 1.0 equiv.), **L6** (0.060 mmol, 1.5 equiv.), HCOOH (5.0 mmol, 10 equiv.) and DMSO (0.20 mmol, 5.0 equiv.), toluene (3.0 mL) was stirred under air at 80 °C for 2 hours to get **Pd complex**. Then add **3a** (0.50 mmol, 12 equiv.), HCOOH (5.0 mmol, 120 equiv.) and toluene (3mL) to the **Pd complex** at 80 °C. After 8 hours, the reaction mixture was washed with saturated saline solution. The aqueous layer was extracted with dichloromethane (3×15 mL) and the combined organic layer was dried over Mg_2SO_4. After the solvent was removed under reduced pressure, the desired products were isolated by flash chromatography. Then, under reduced pressure we obtain the yield of pure **3a** through weighing and calculation.



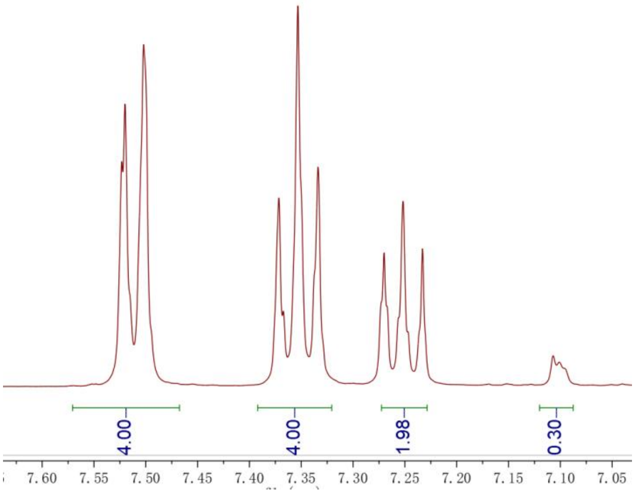
Scheme 5. Mutual isomerization of **2a** and **3a**.

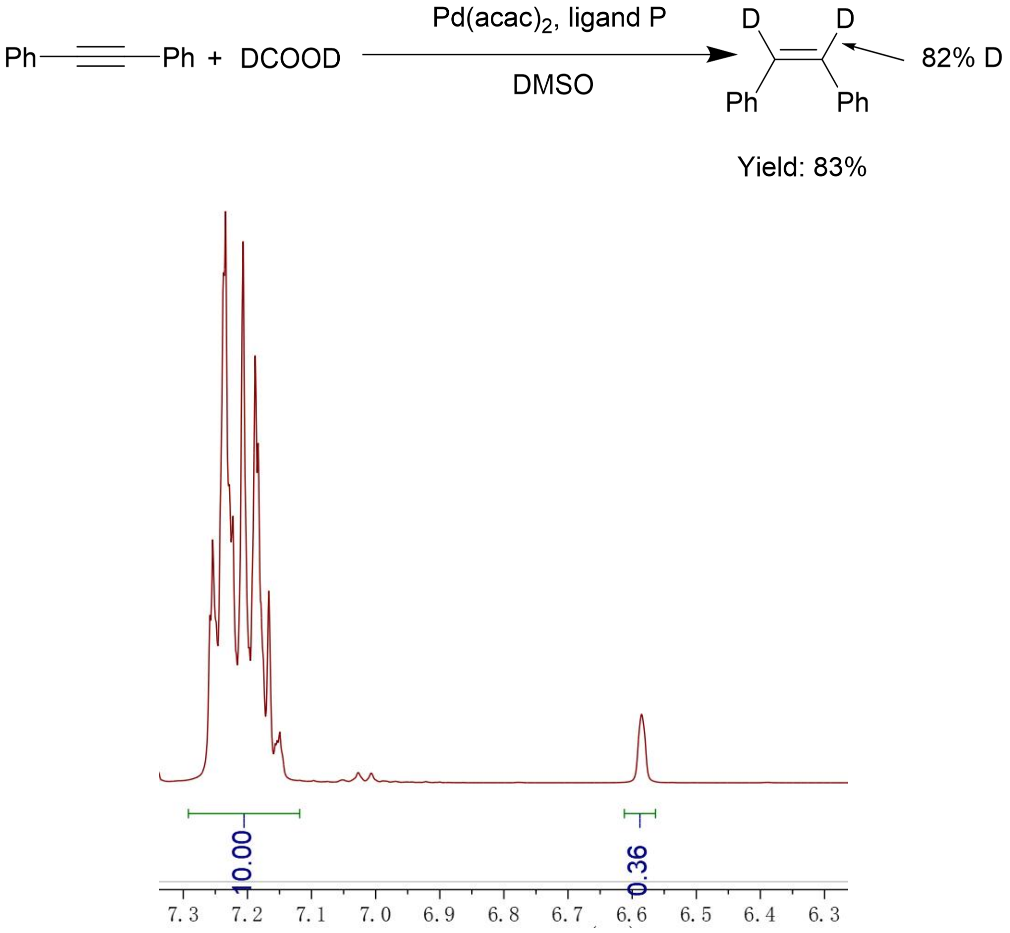
The deuterium labeling experiments

A 50mL glass tube with a magnetic stir was charged with **1a** (0.50 mmol, 1.0 equiv.), palladium acetate (4.0 mol%, 0.080 equiv.), **L6** (0.20 mmol, 0.40 equiv.), DCOOD (5.0 mmol, 10 equiv.) and solvent (3.0 mL) were stirred under air at 80 °C for 8 h. The reaction mixture diluted with ethyl acetate and the solvent was removed under reduced pressure. Finally, the desired products were isolated by flash chromatography. Then, under reduced pressure we obtain the yield of pure **2a/3a** through weighing and calculation.



Yield: 87%

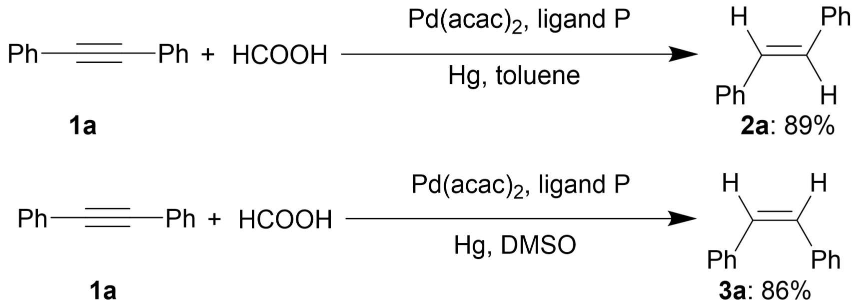




Scheme 6 The deuterium labeling experiments using DCOOD for palladium catalyzed semi-hydrogenation of alkynes

The Mercury test

A 50mL glass tube with a magnetic stir was charged with **1a** (0.50 mmol, 1.0 equiv.), palladium acetate (4.0 mol%, 0.080 equiv.), **L6** (0.20 mmol, 0.40 equiv.), Hg (1.0 mmol, 2.0 equiv.), HCOOH (5.0 mmol, 10 equiv.) and solvent (3.0 mL) were stirred under air at 80 °C for 8 h. The reaction mixture diluted with ethyl acetate and the solvent was removed under reduced pressure. Finally, the desired products were isolated by flash chromatography. Then, under reduced pressure we obtain the yield of pure **2a/3a** through weighing and calculation.



Scheme 7. The mercury test for palladium catalyzed semi-hydrogenation of alkynes.

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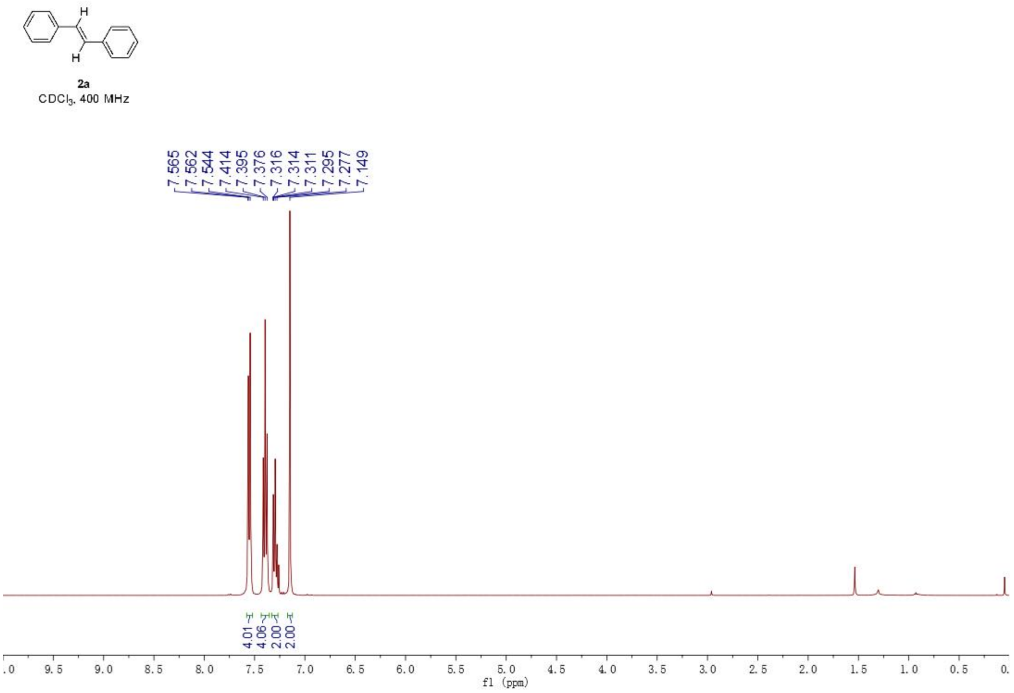
The ^{1}H NMR, ^{13}C NMR and 19F Spectra of products

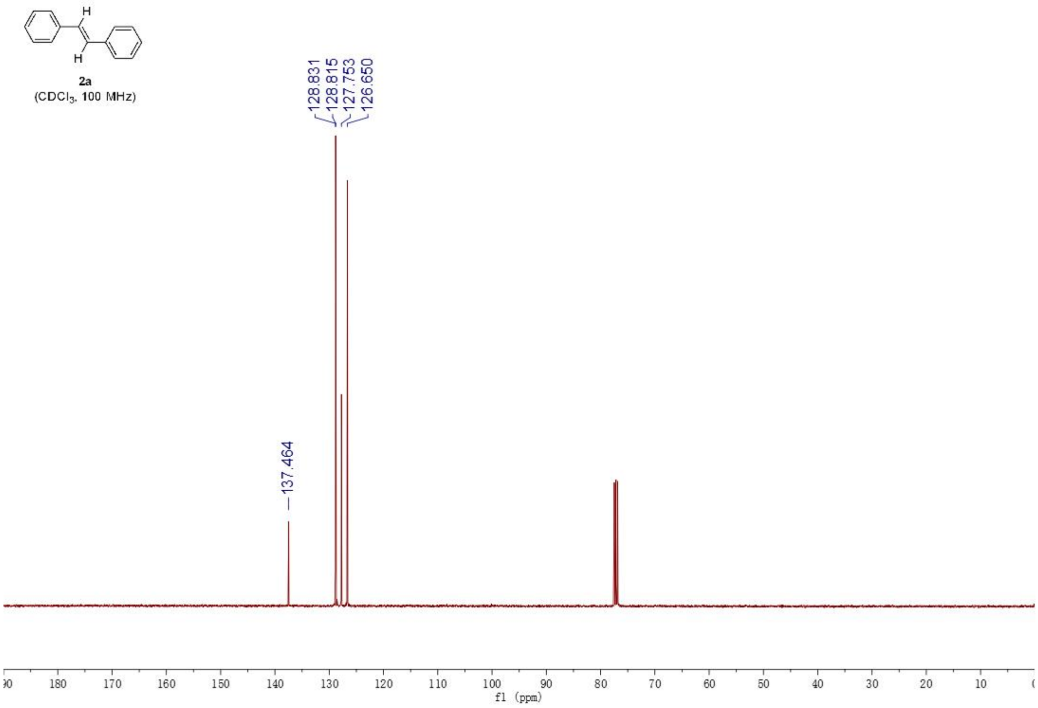
^{1}H, ^{13}C and ^{19}F NMR spectra for products 2a-r

(E)-1,2-diphenylethene (2a)

^{1}H NMR

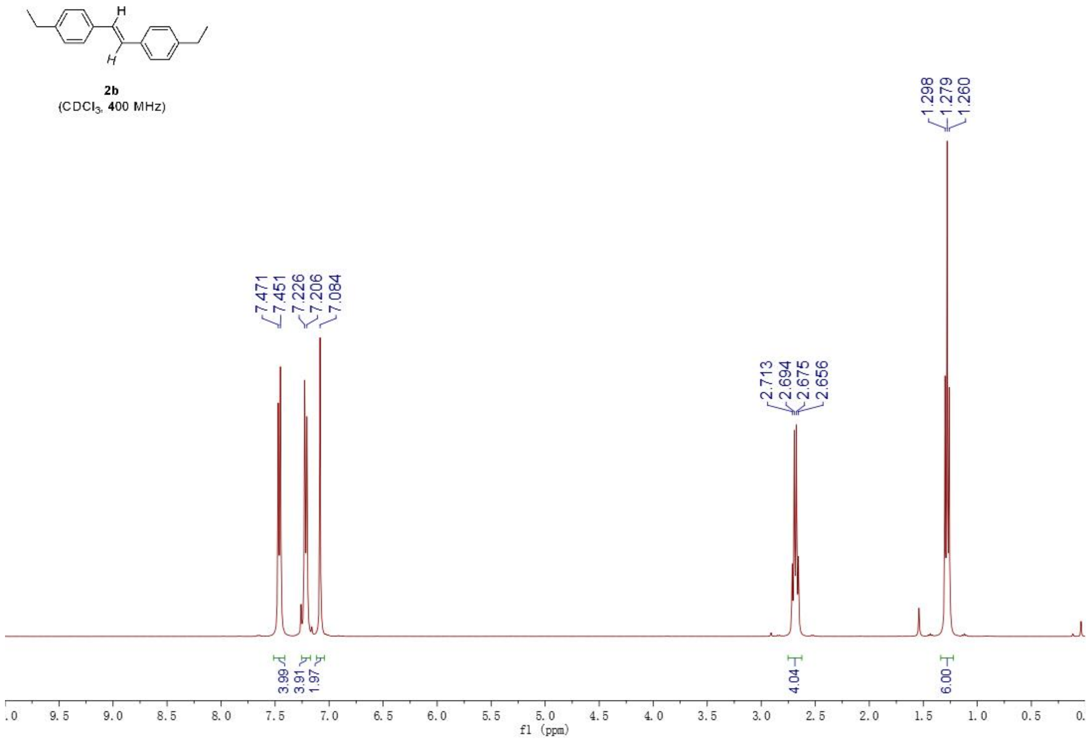


^{13}C NMR

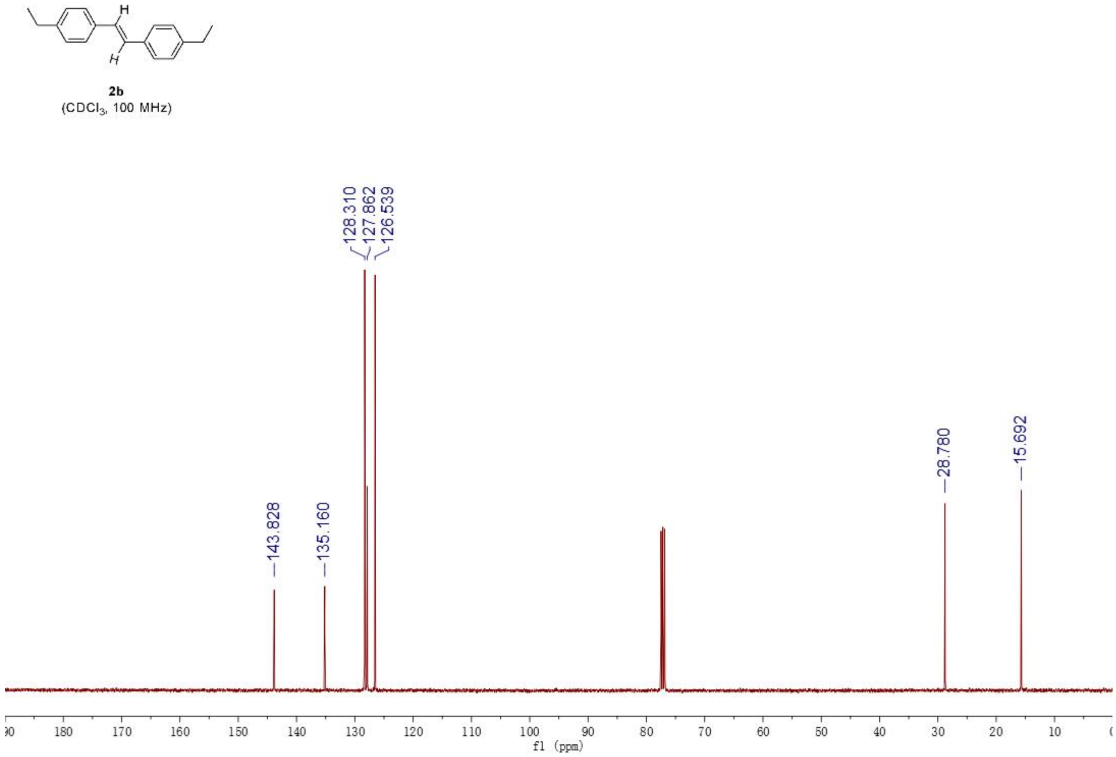


(E)-1,2-bis(4-ethylphenyl)ethene (2b)

^{1}H NMR

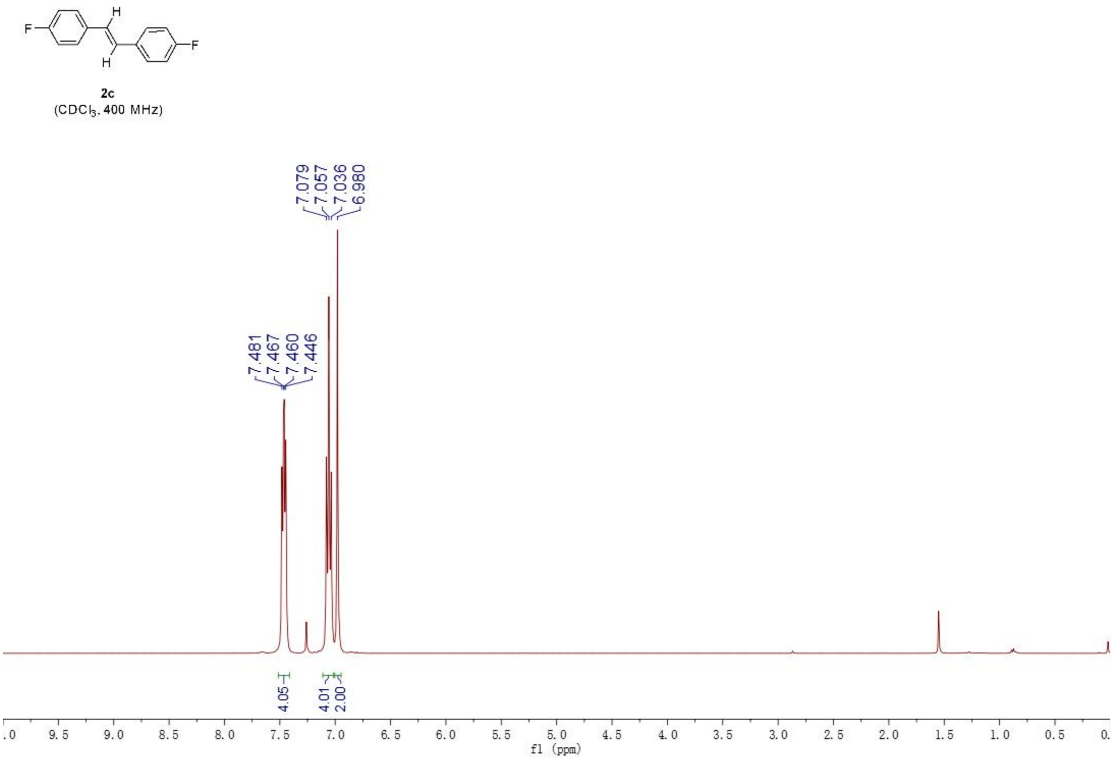


^{13}C NMR

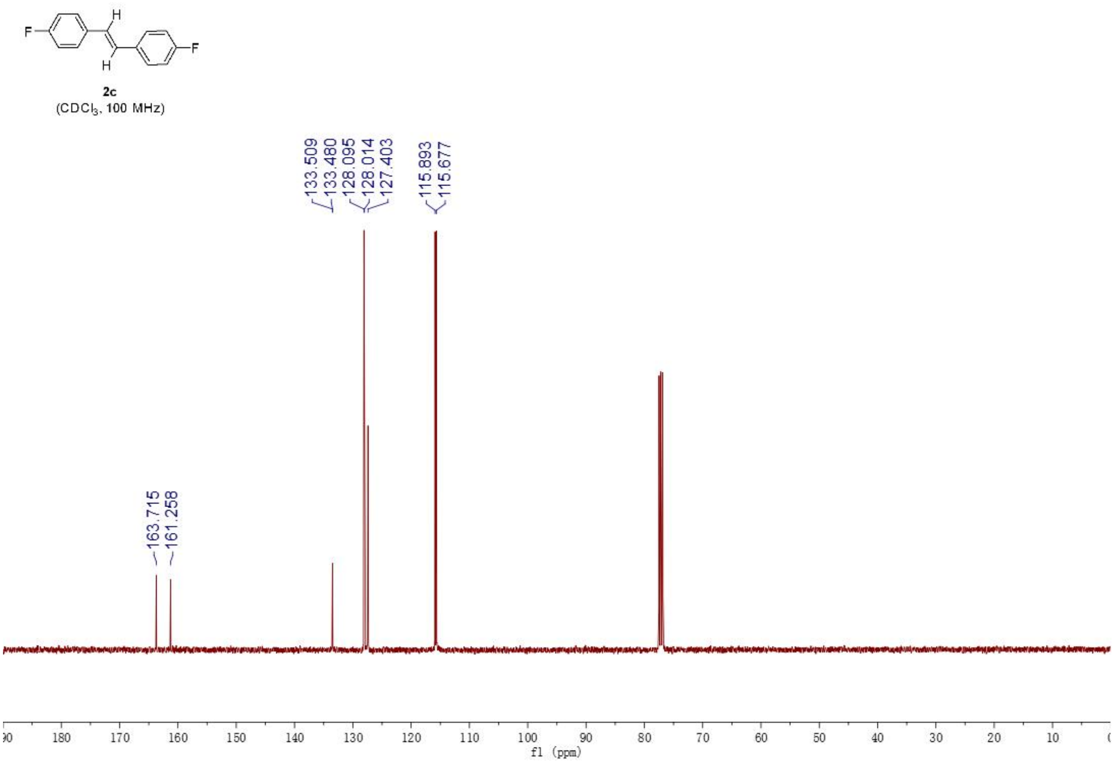


(E)-1,2-bis(4-fluorophenyl)ethene (2c)

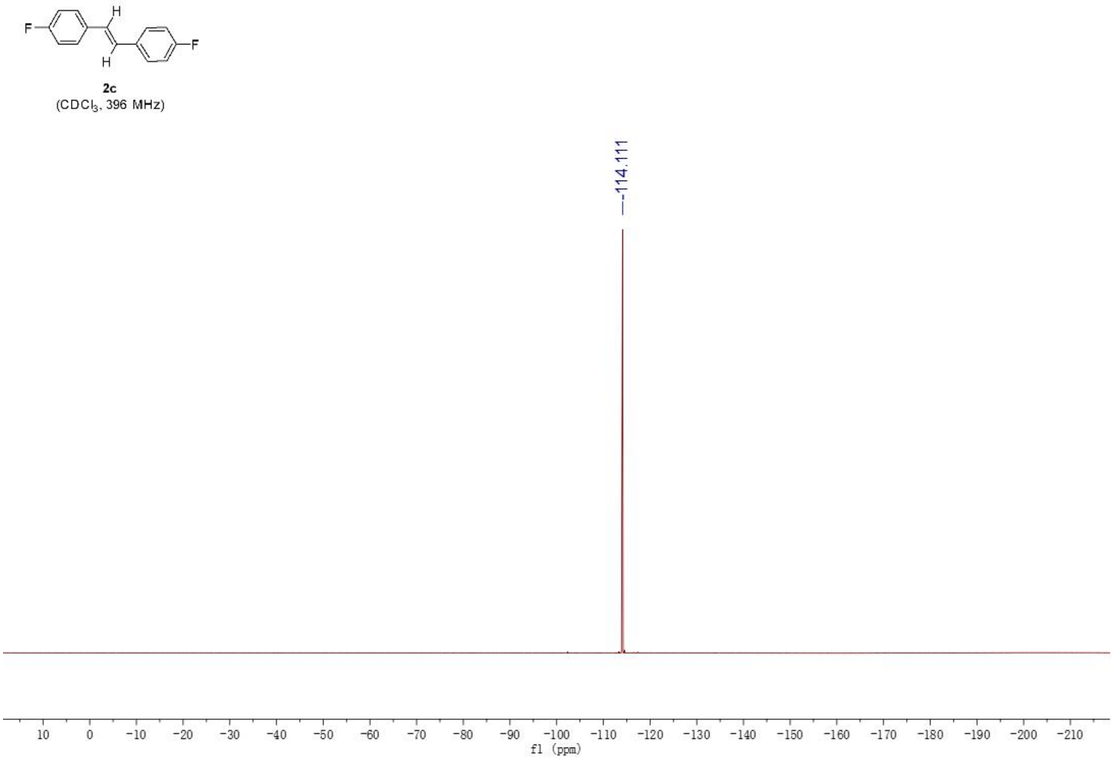
^{1}H NMR



^{13}C NMR

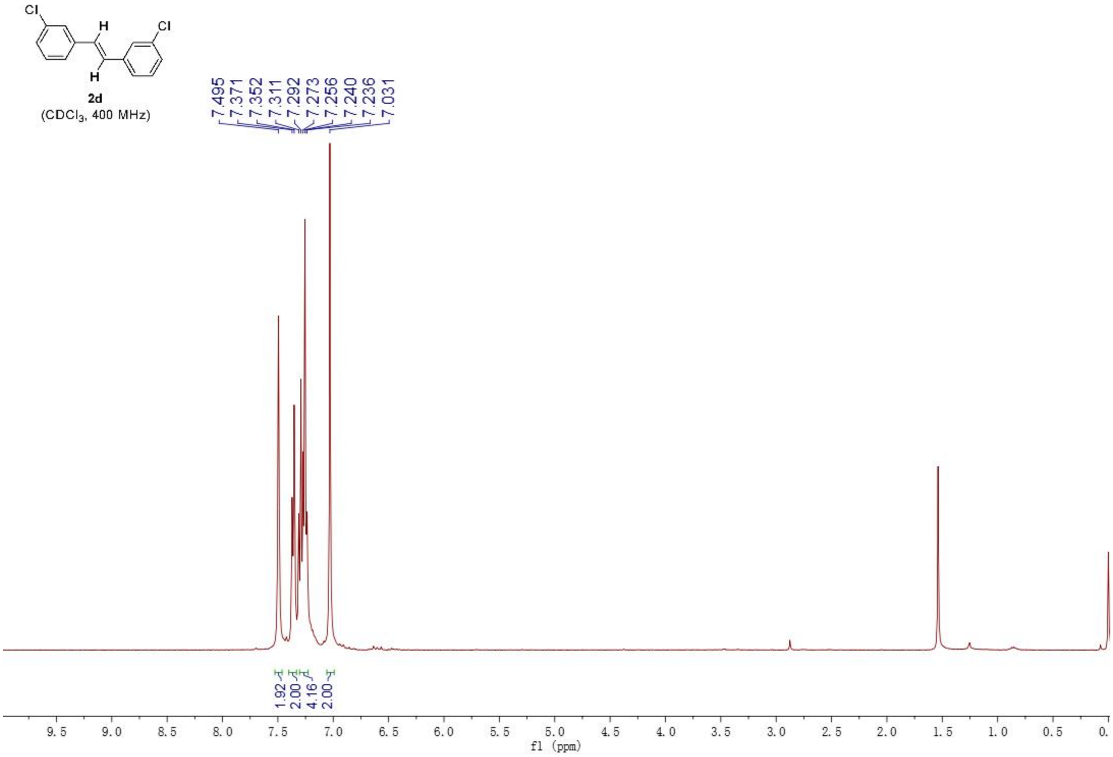


^{19}F NMR

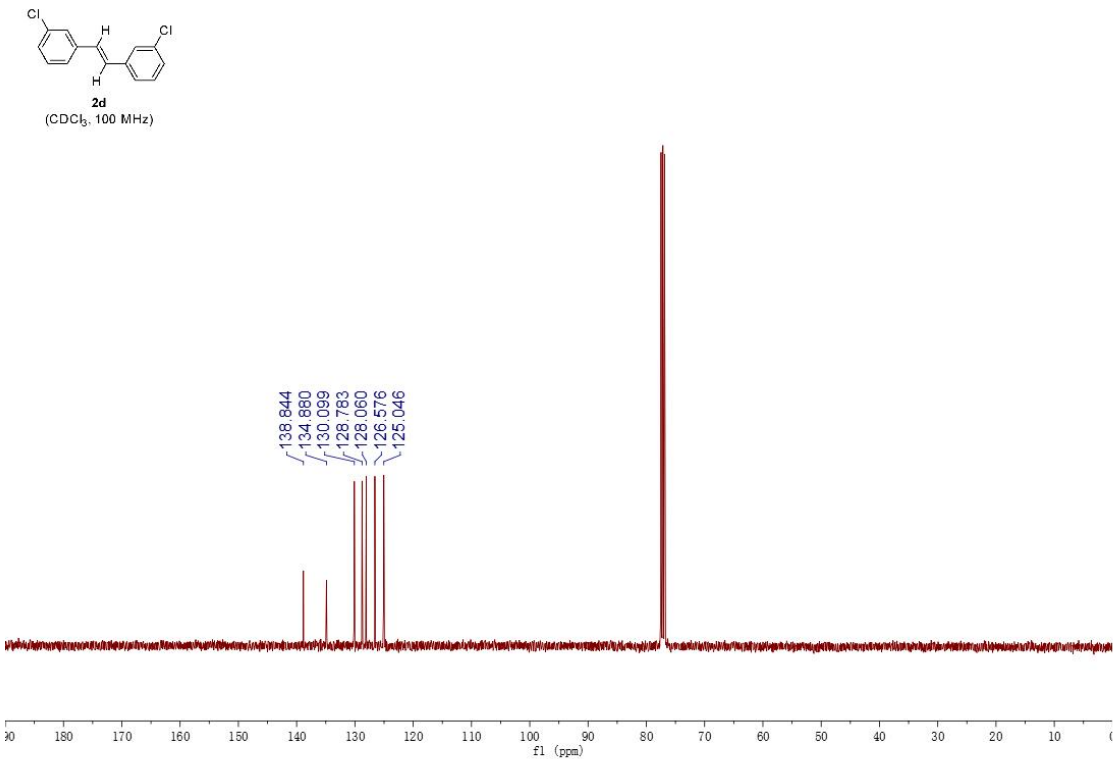


(E)-1,2-bis(3-chlorophenyl)ethene (2d)

^{1}H NMR

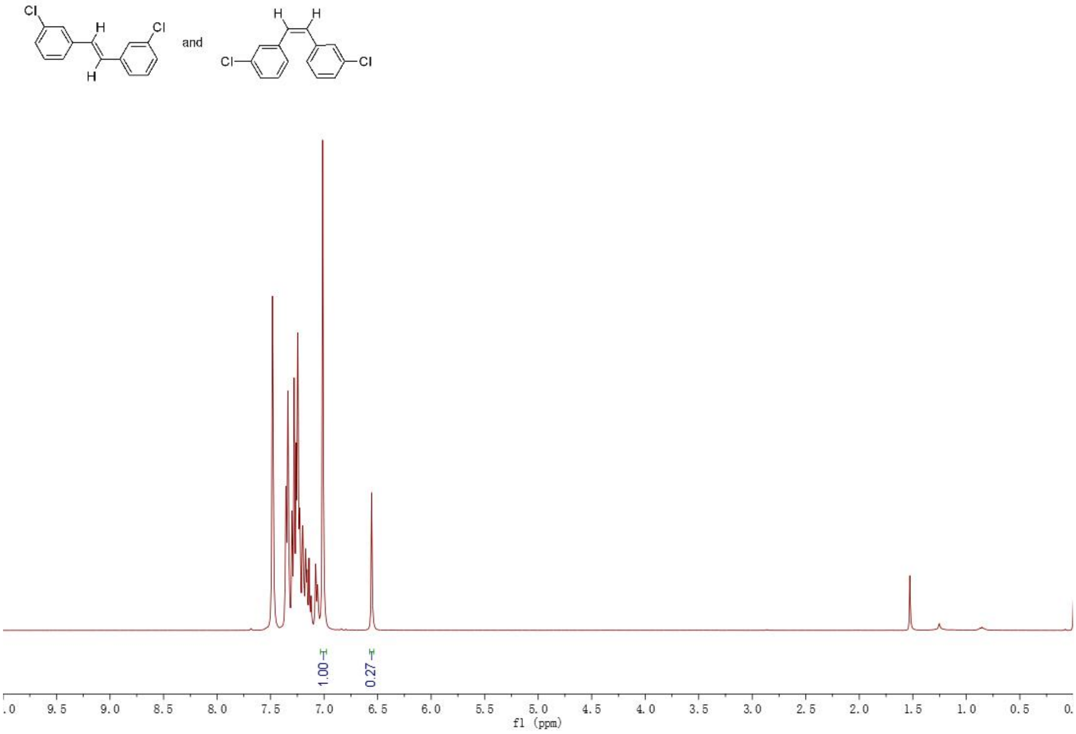


^{13}C NMR



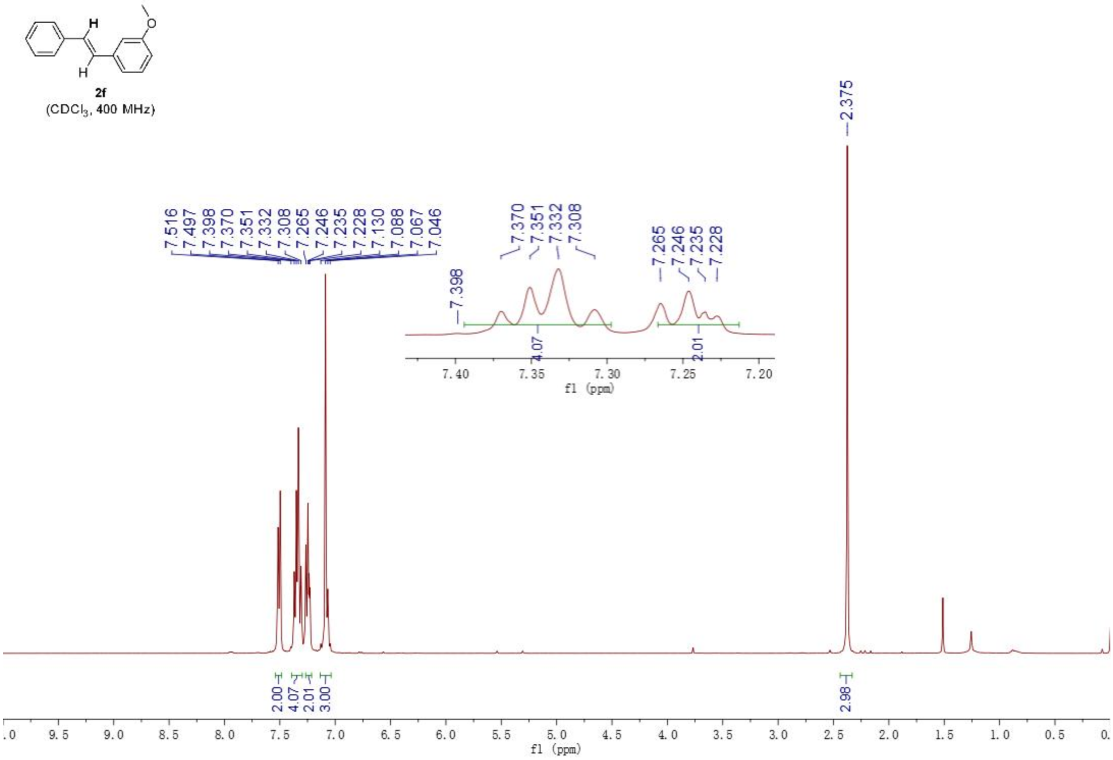
(E)-1,2-bis(3-chlorophenyl)ethene (2d)

^{1}H NMR

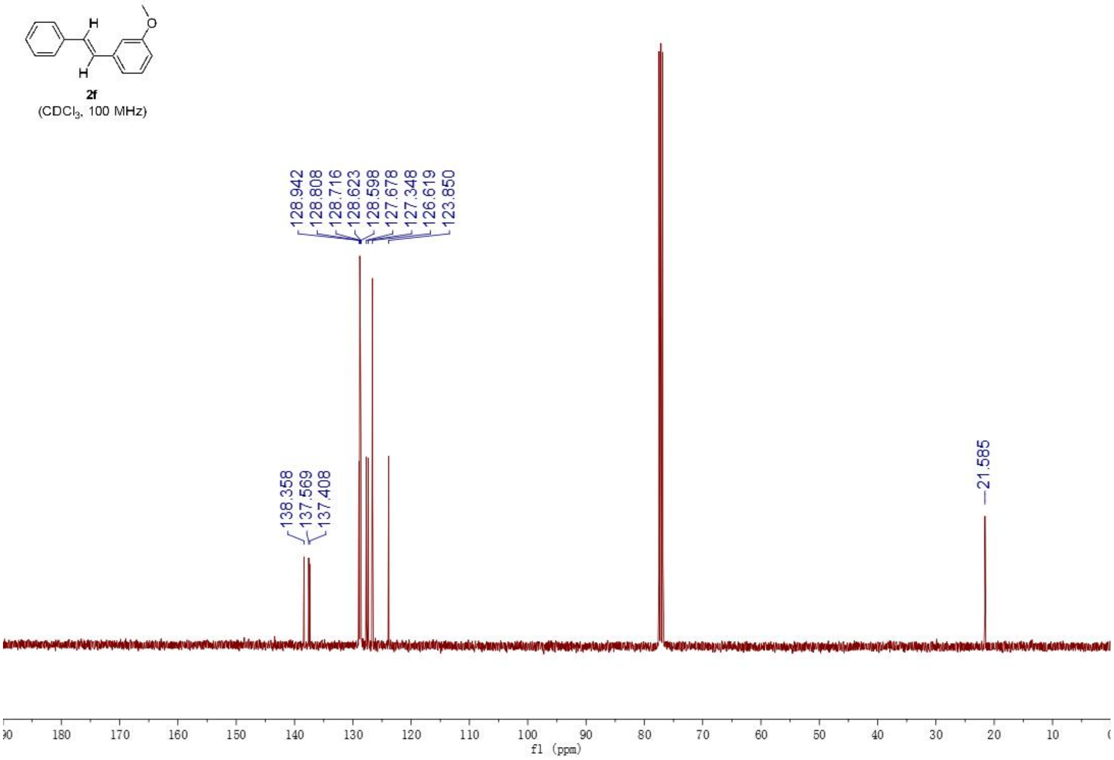


(E)-1-methoxy-3-styrylbenzene (2f)

^{1}H NMR

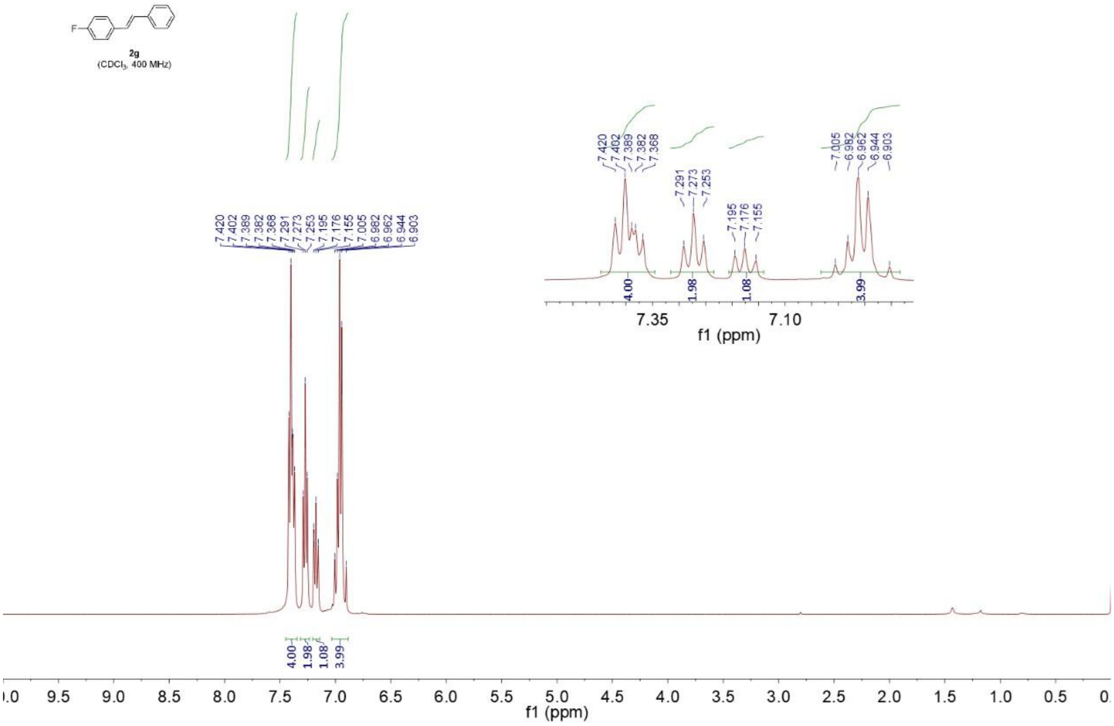


^{13}C NMR

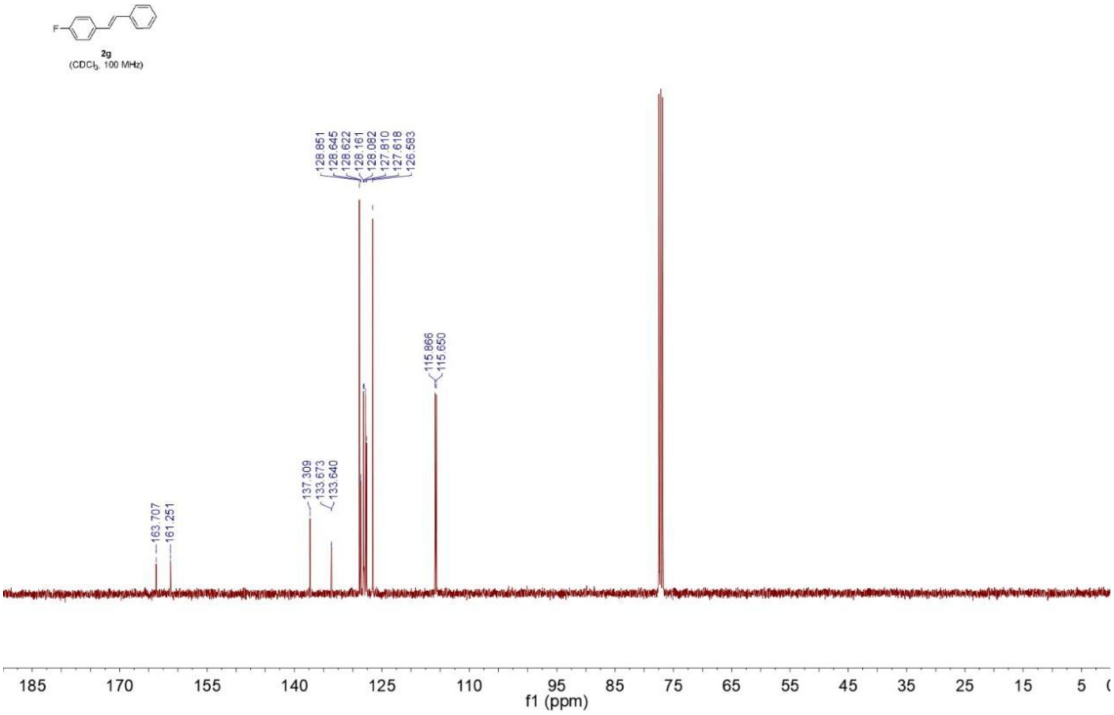


(E)-1-fluoro-4-styrylbenzene (2g)

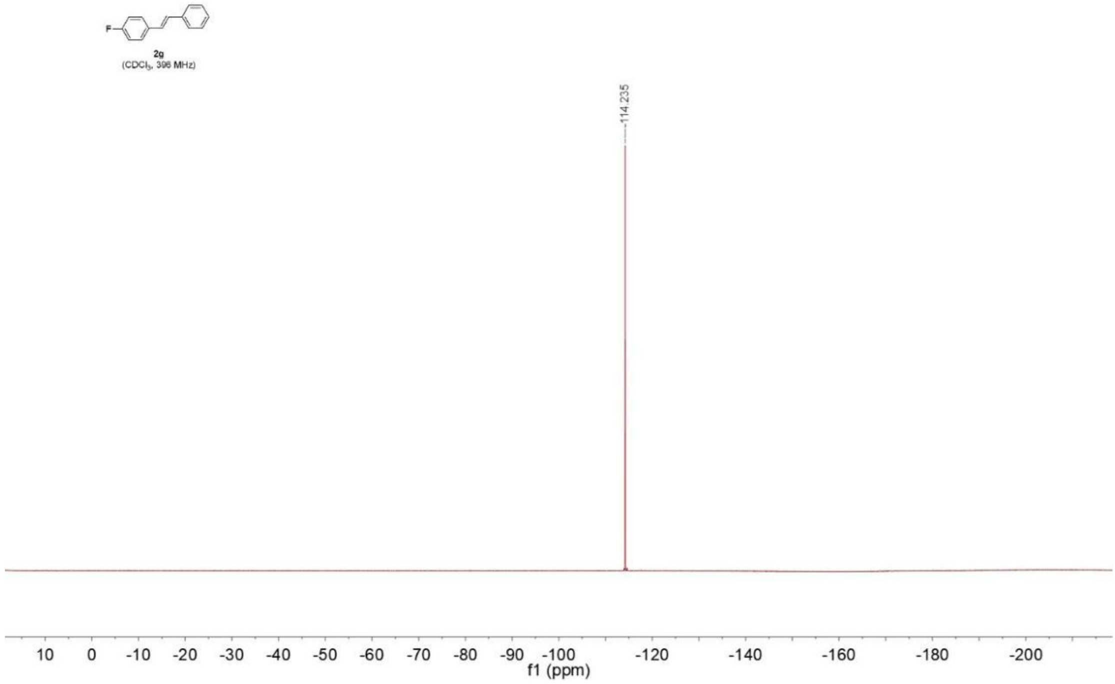
^{1}H NMR



^{13}C NMR

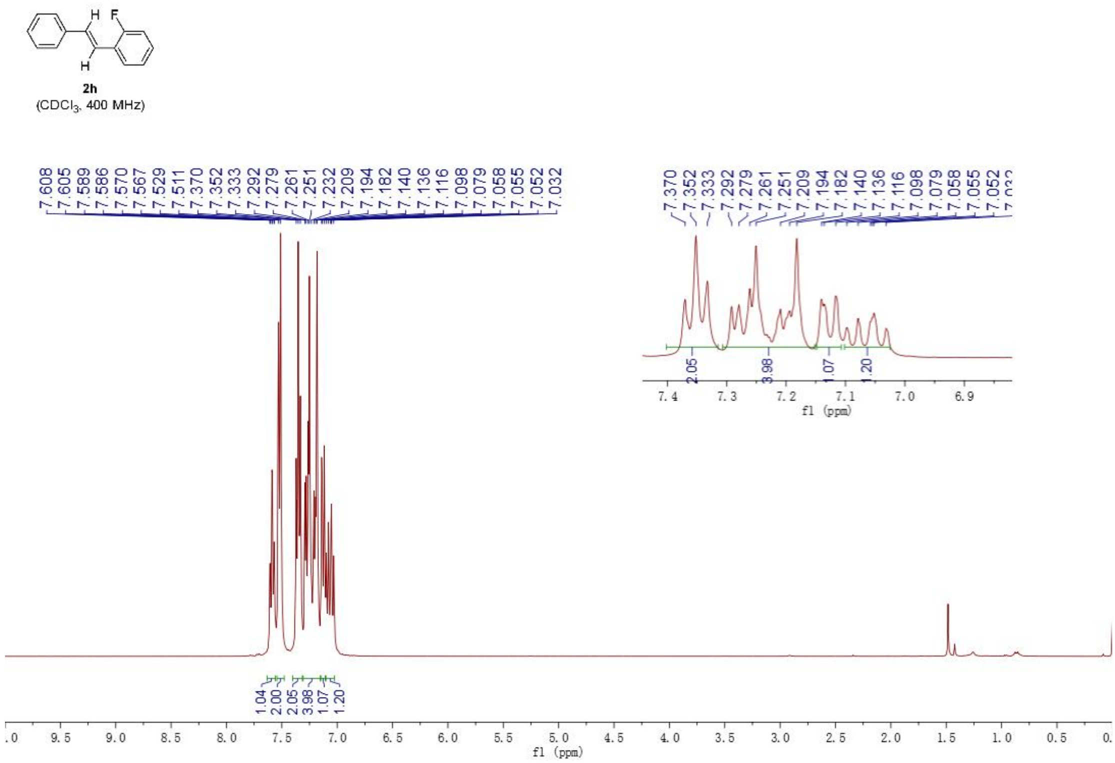


^{19}F NMR

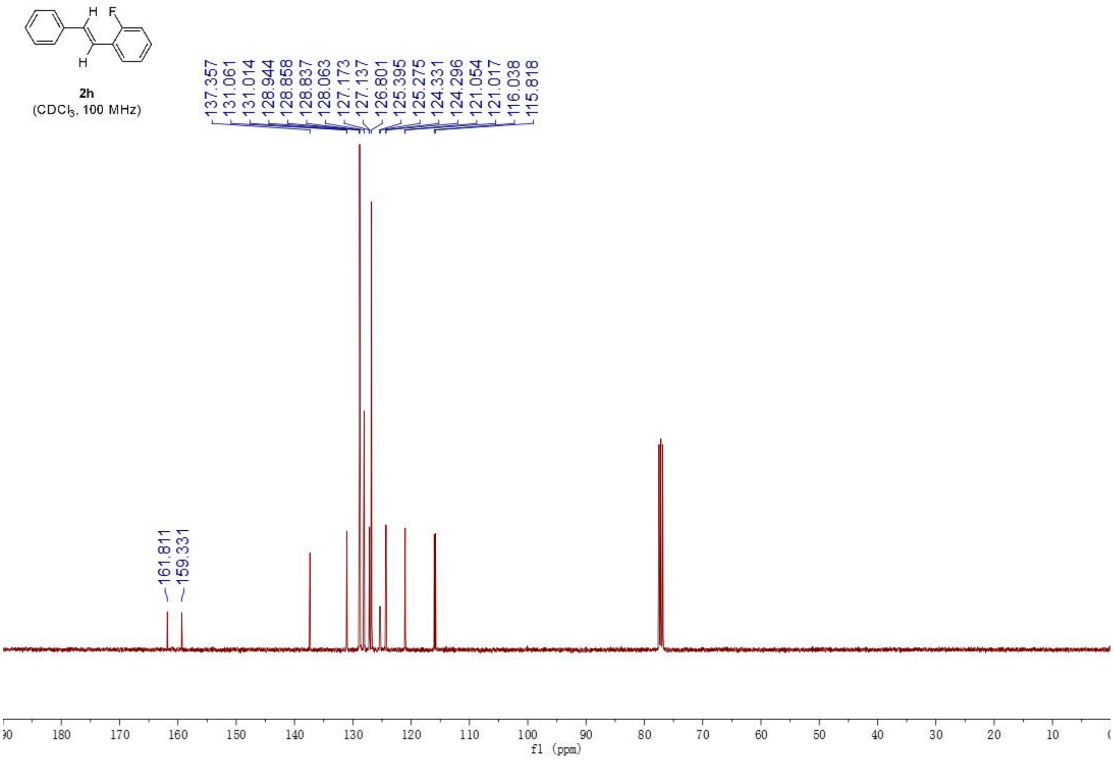


(E)-1-fluoro-2-styrylbenzene (2h)

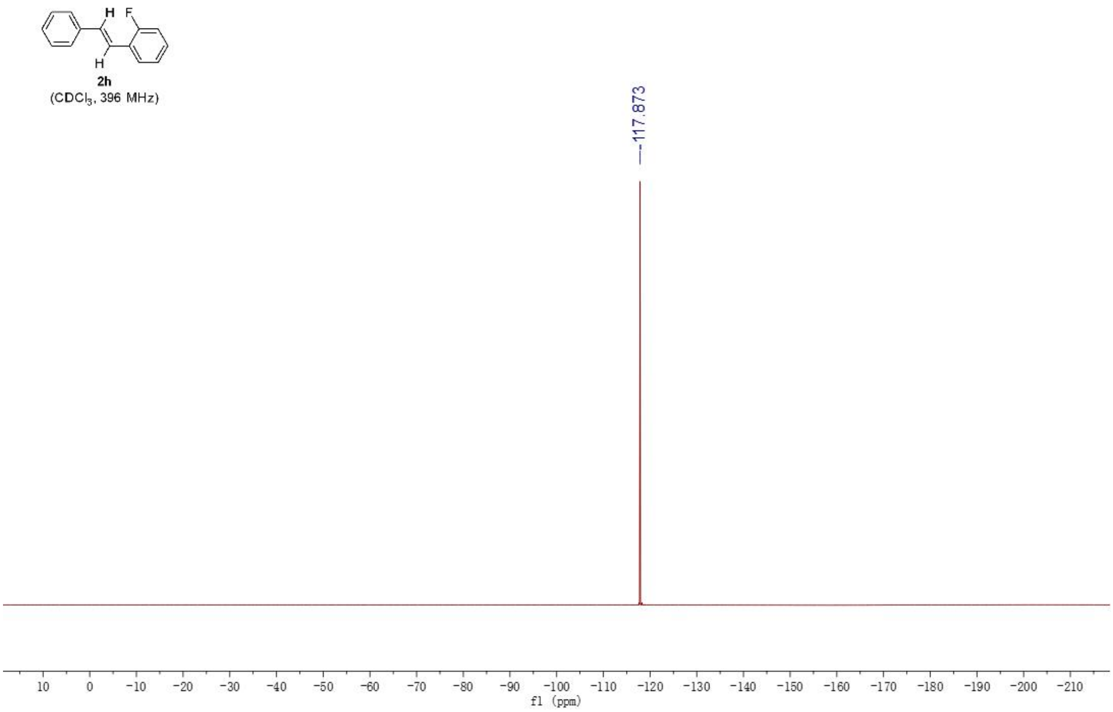
^{1}H NMR



^{13}C NMR

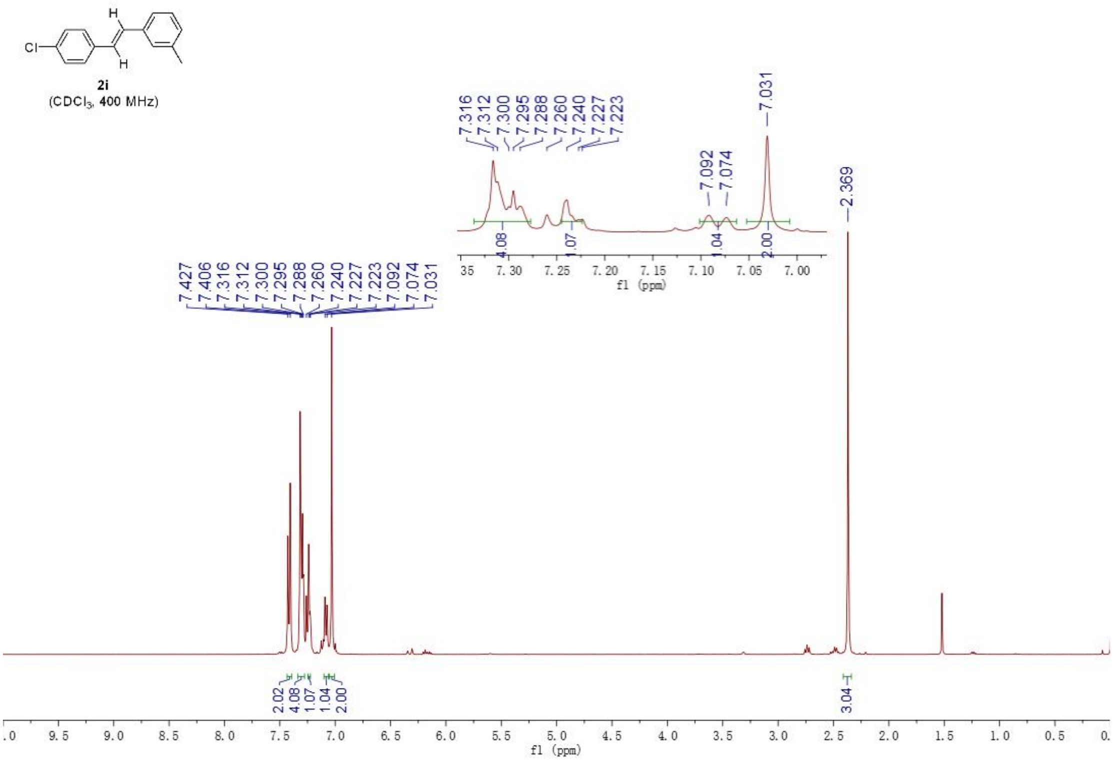


^{19}F NMR

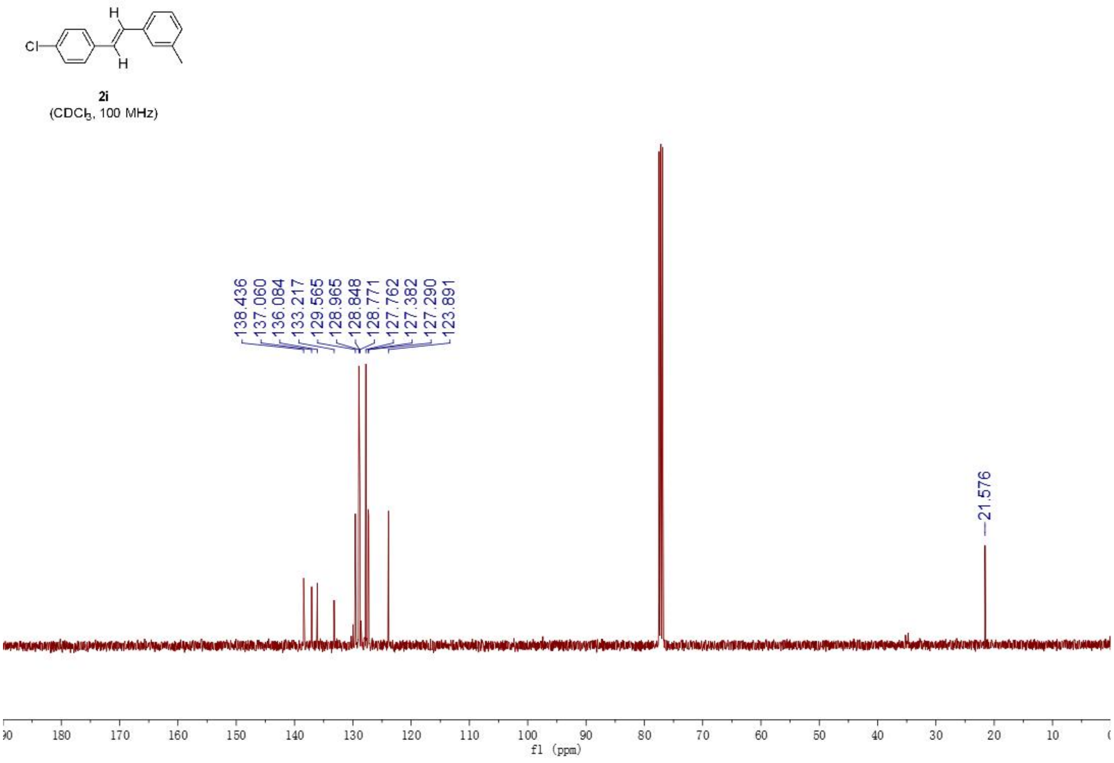


(E)-1-(4-chlorostyryl)-3-methylbenzene (2i)

^{1}H NMR

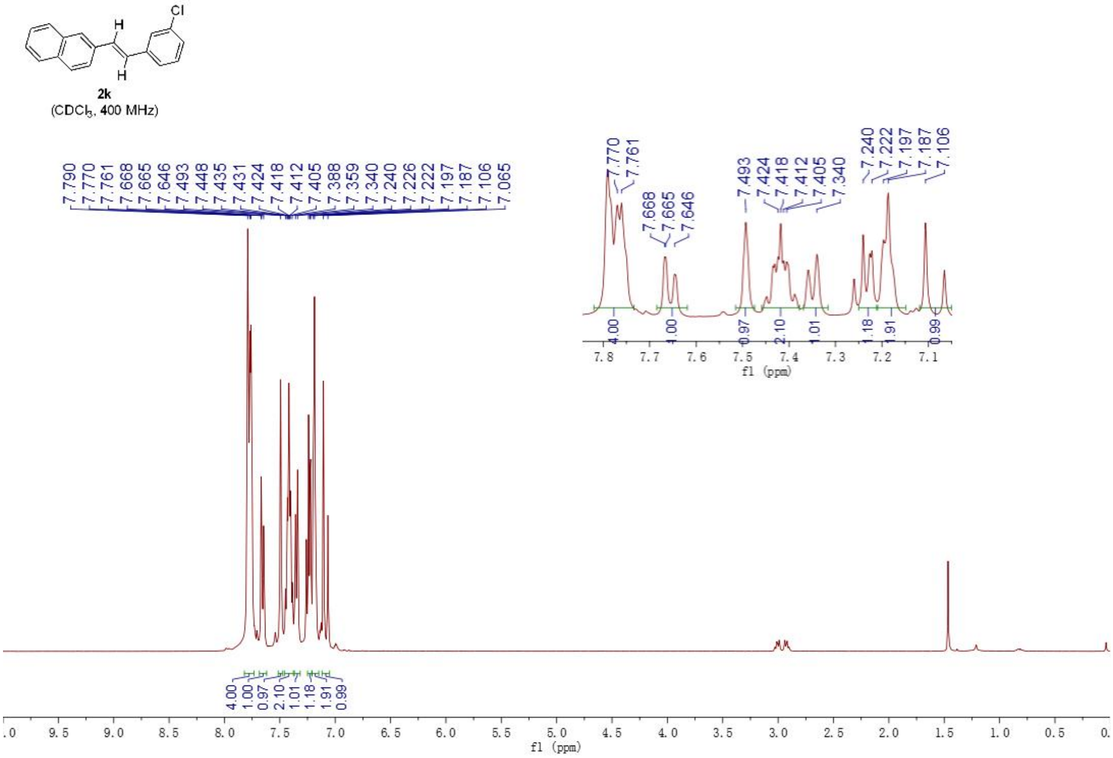


^{13}C NMR

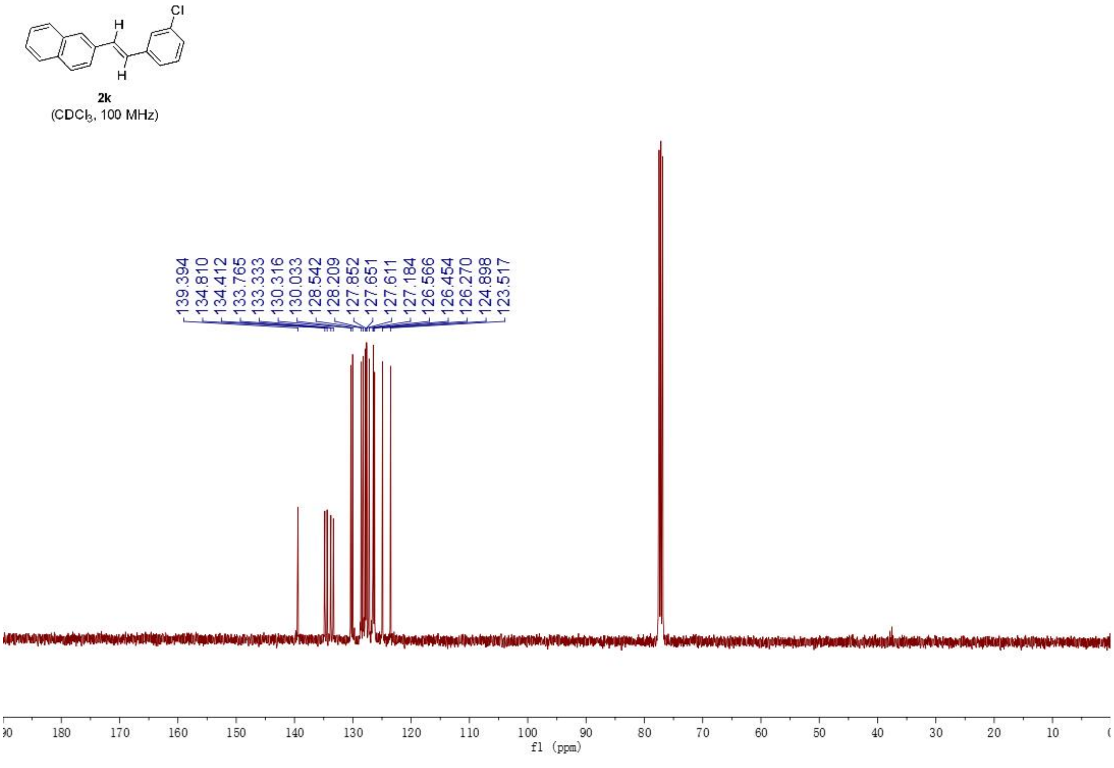


(E)-2-(3-chlorostyryl)naphthalene (2k)

^{1}H NMR

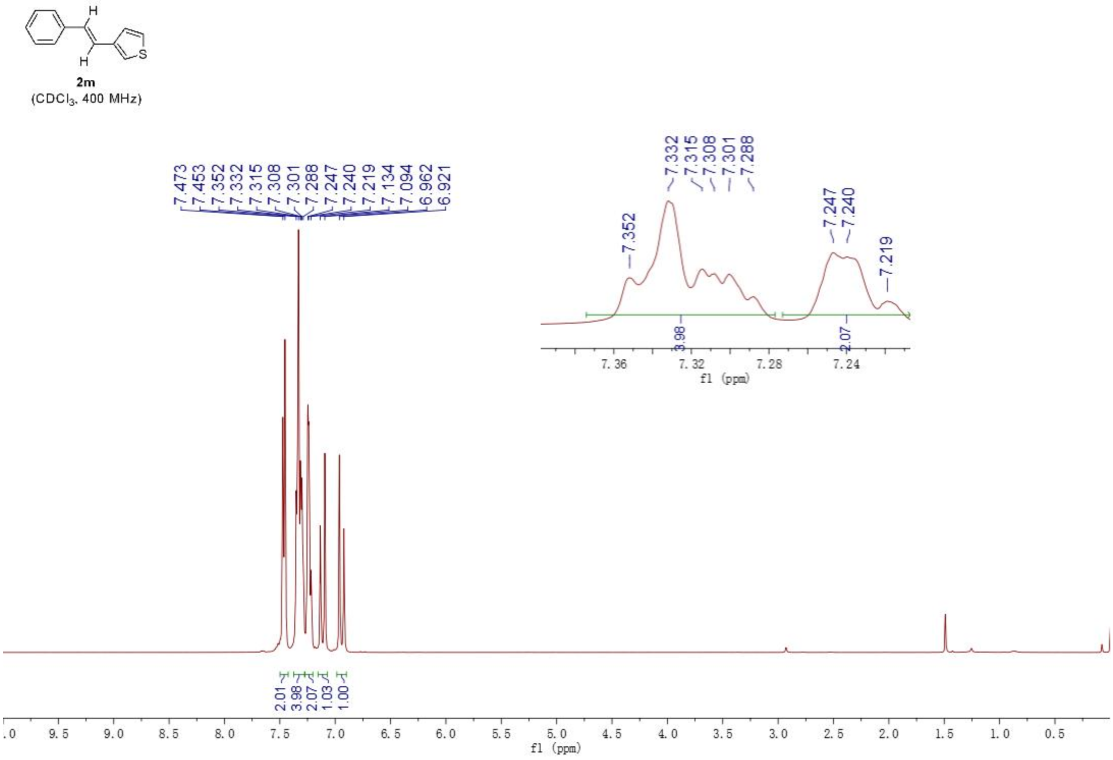


^{13}C NMR

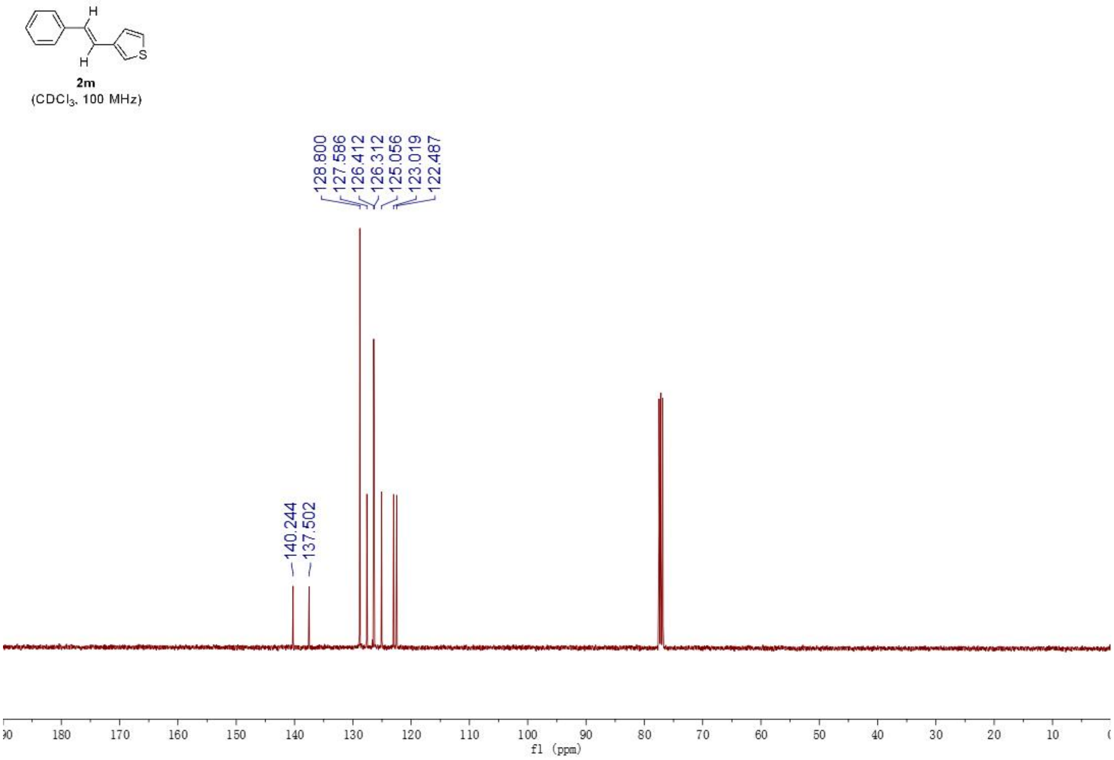


(E)-2-styrylthiophene (2m)

^{1}H NMR

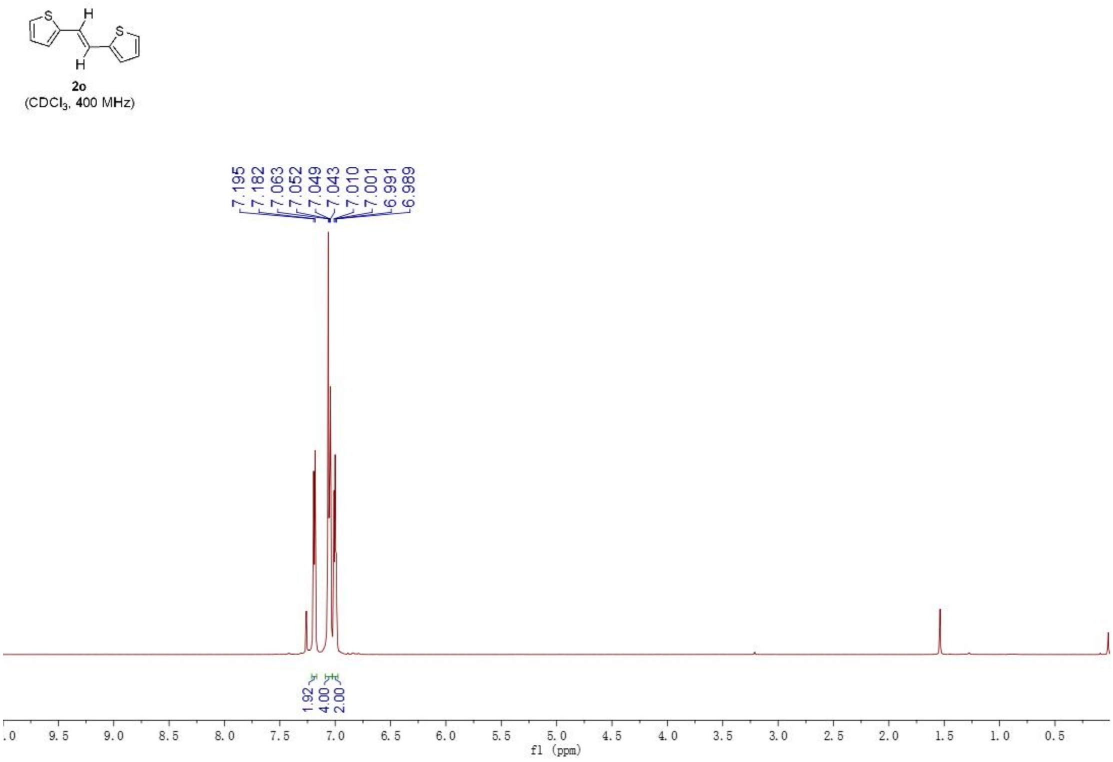


^{13}C NMR

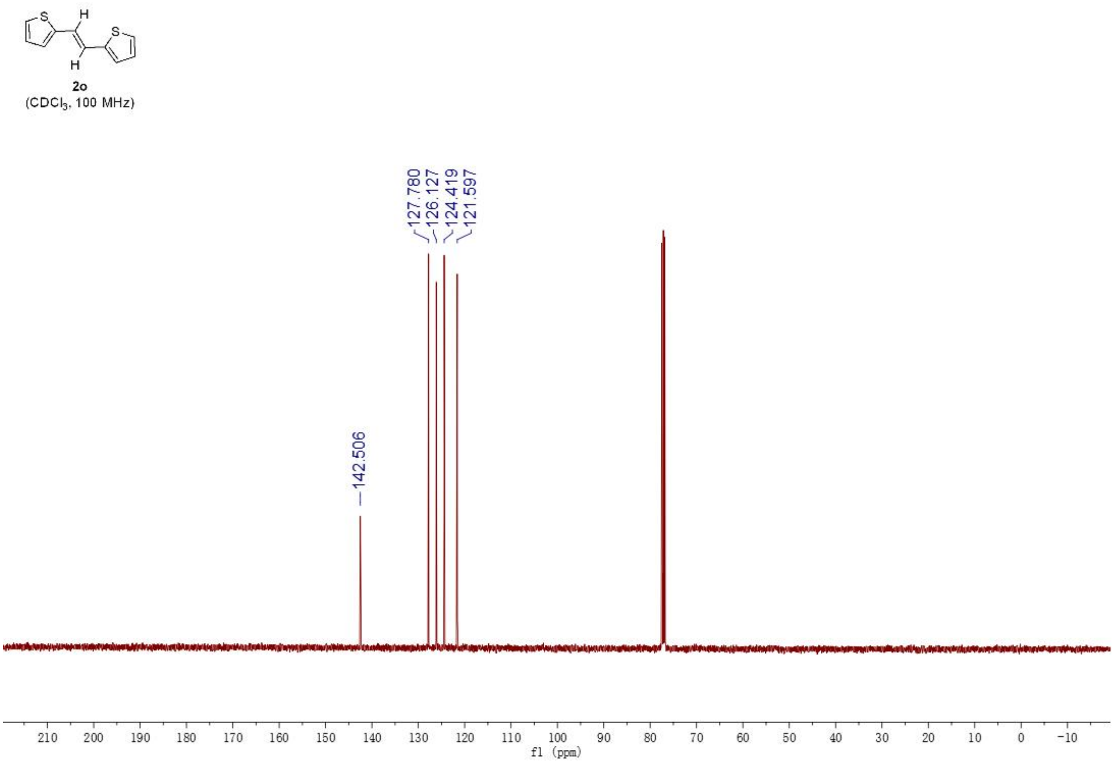


(E)-1,2-di(thiophen-2-yl)ethene (2o)

^{1}H NMR

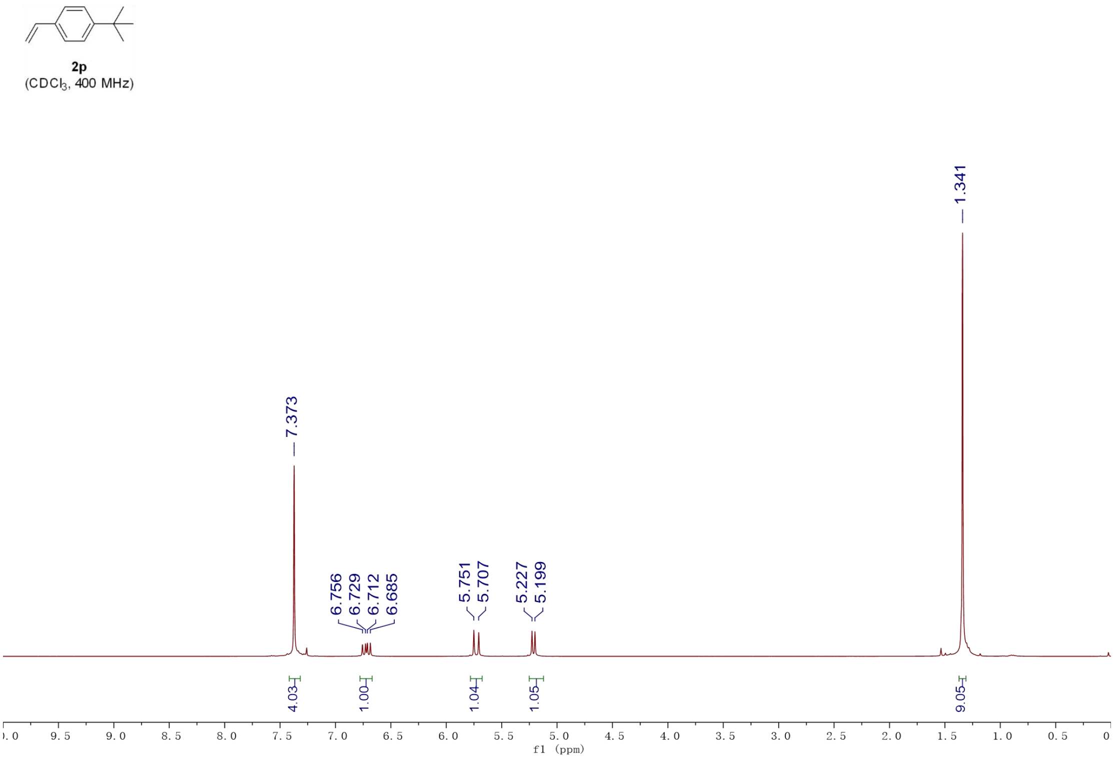


^{13}C NMR

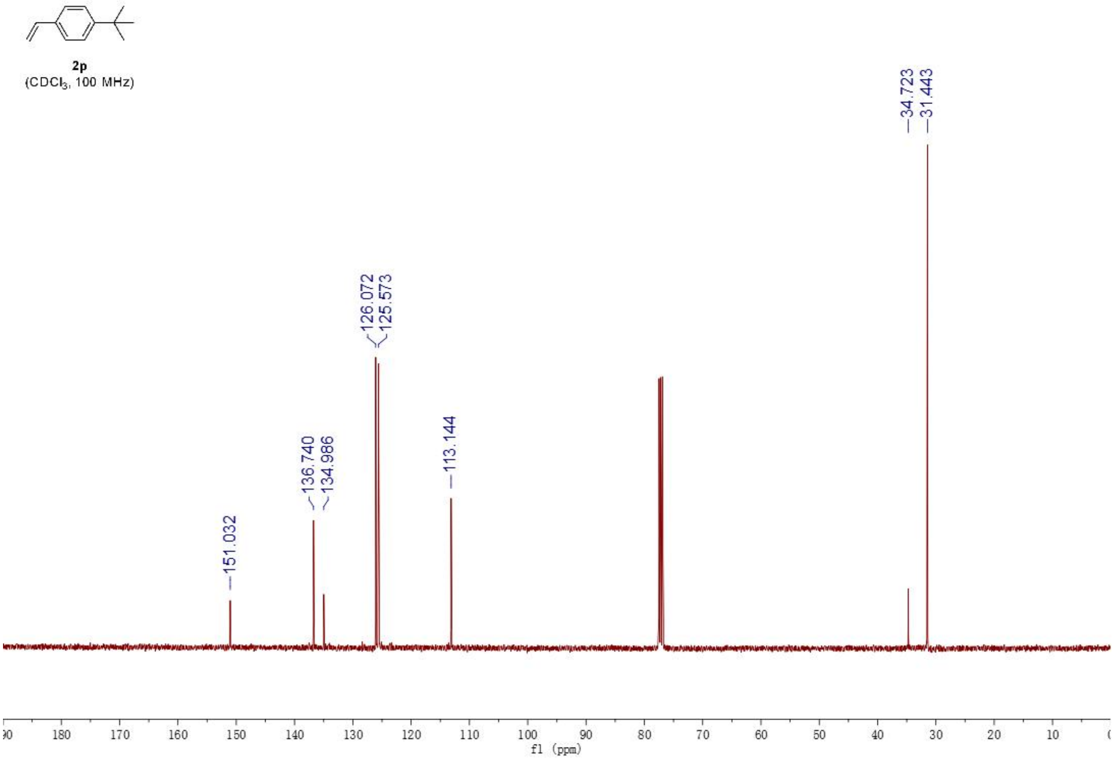


1-(tert-butyl)-4-vinylbenzene (2p)

^{1}H NMR

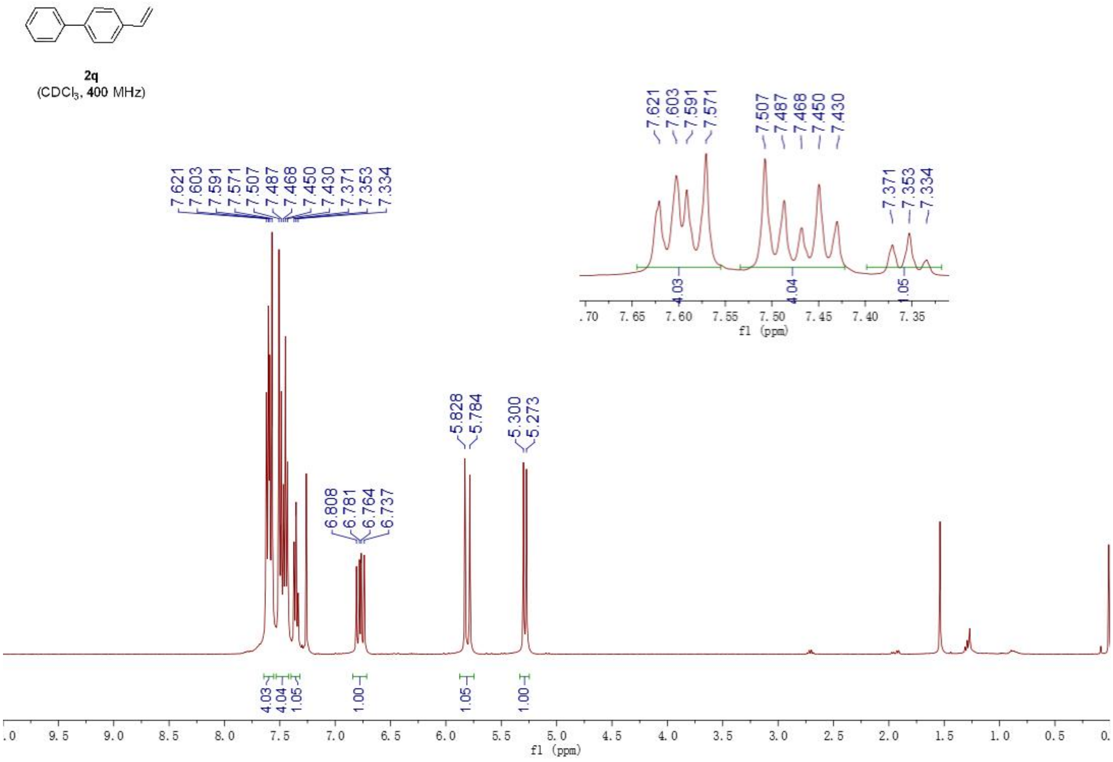


^{13}C NMR

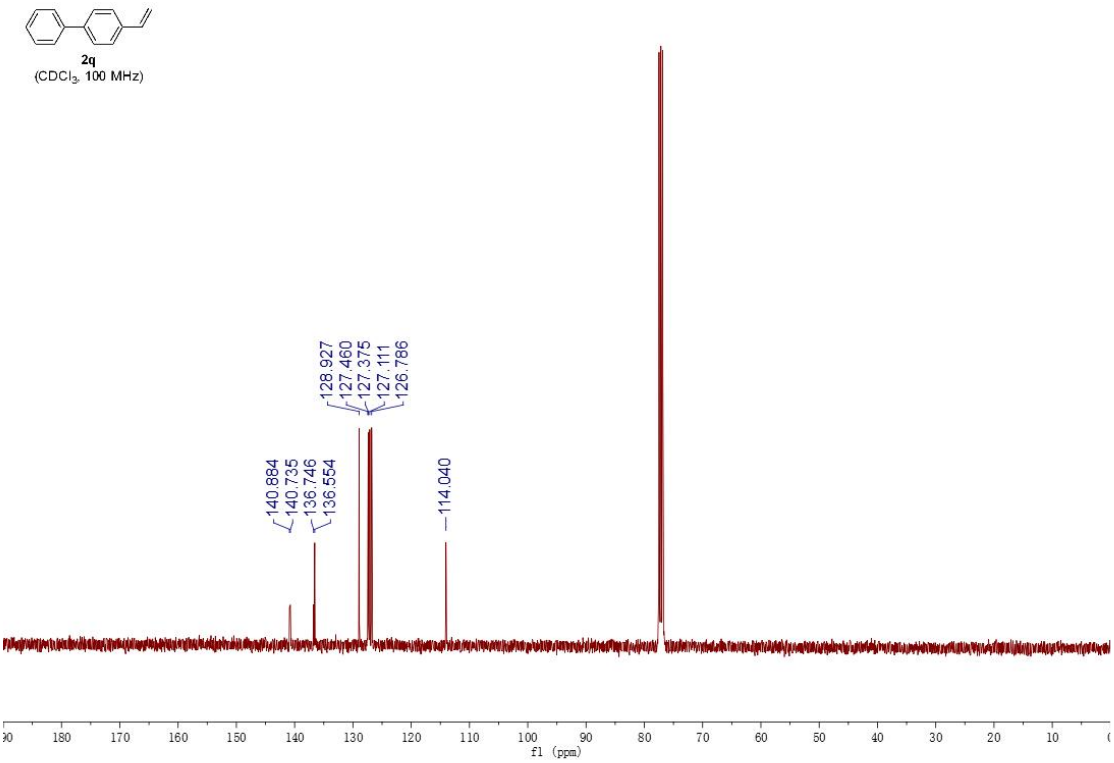


4-vinyl-1,1'-biphenyl (2q)

^{1}H NMR

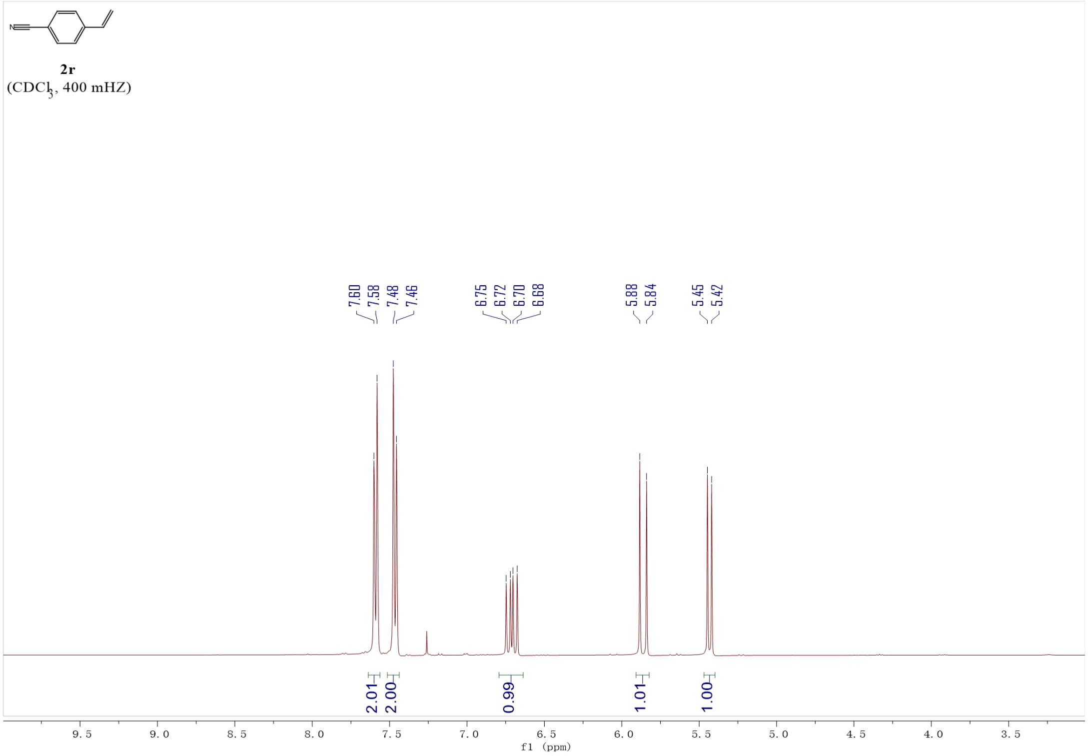


^{13}C NMR

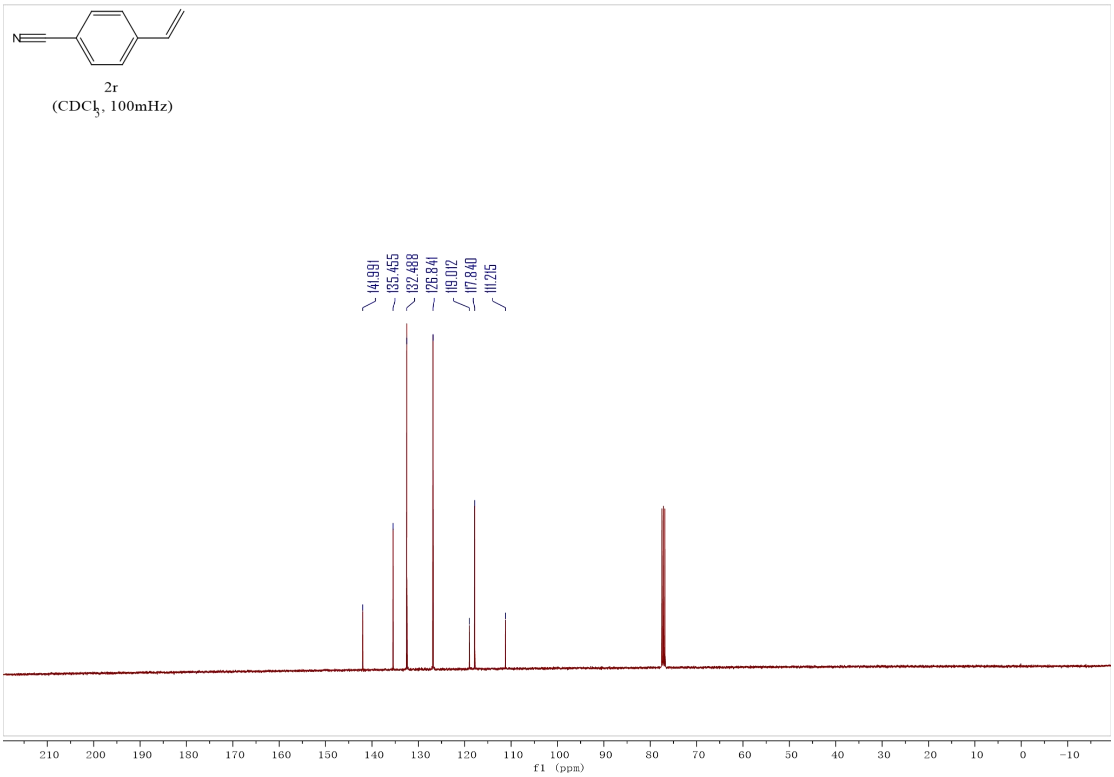


4-vinylbenzonitrile (2r)

^{1}H NMR



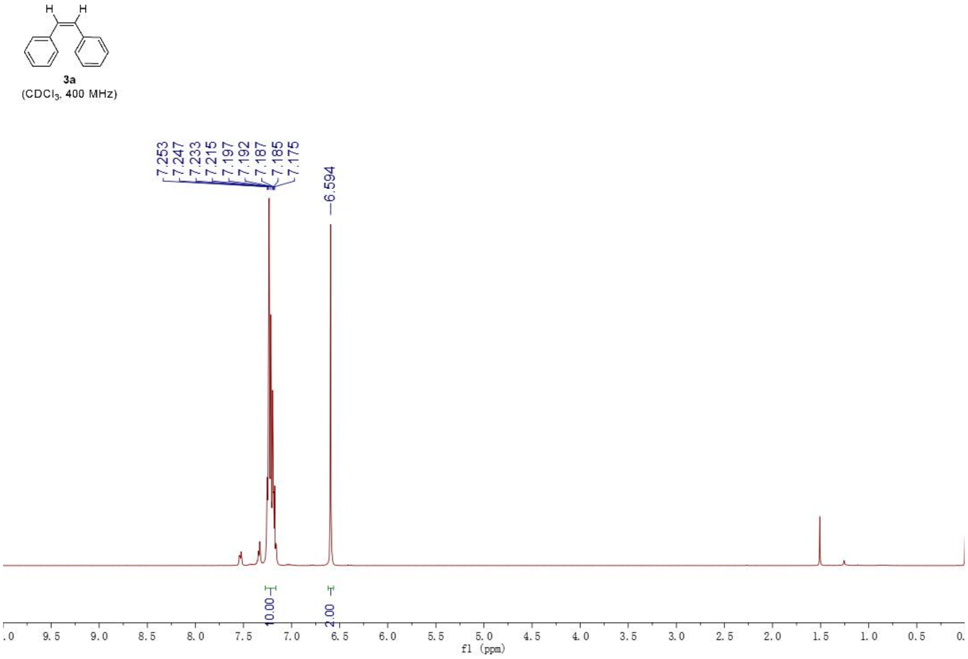
^{13}C NMR



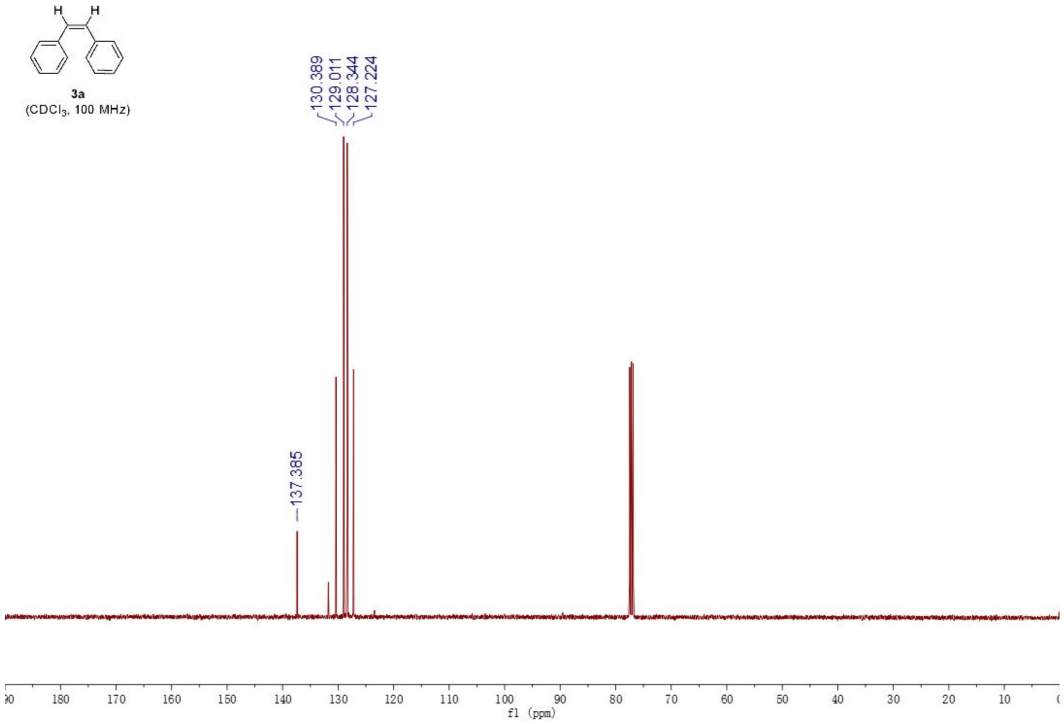
^{1}H, ^{13}C and ^{19}F NMR spectra for products 2a-r

(Z)-1,2-diphenylethene (3a)

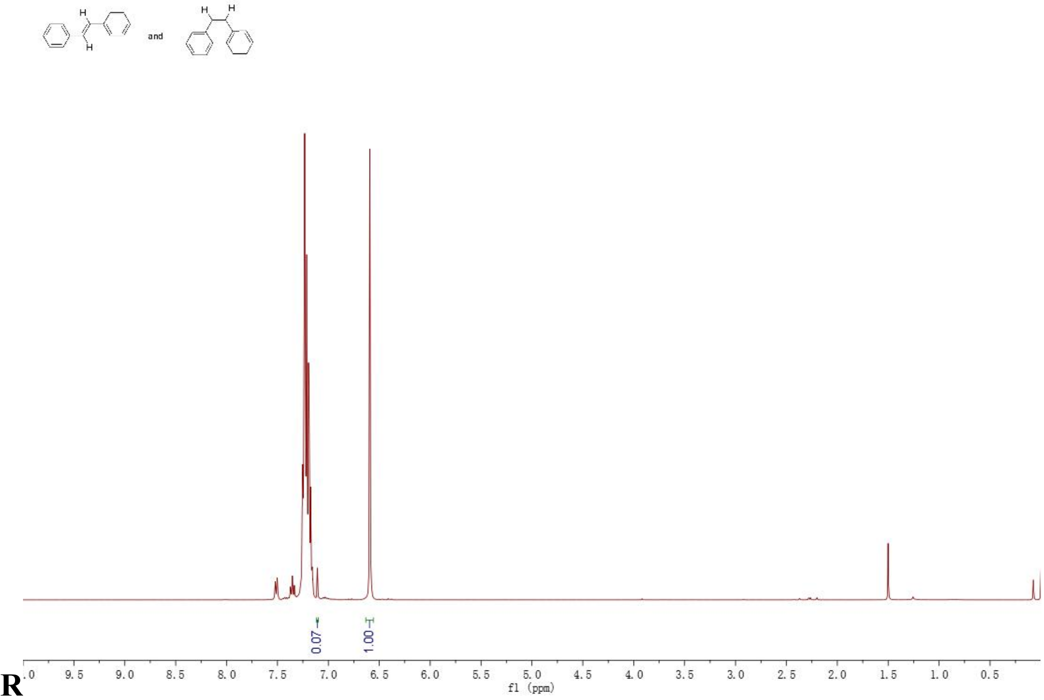
^{1}H NMR



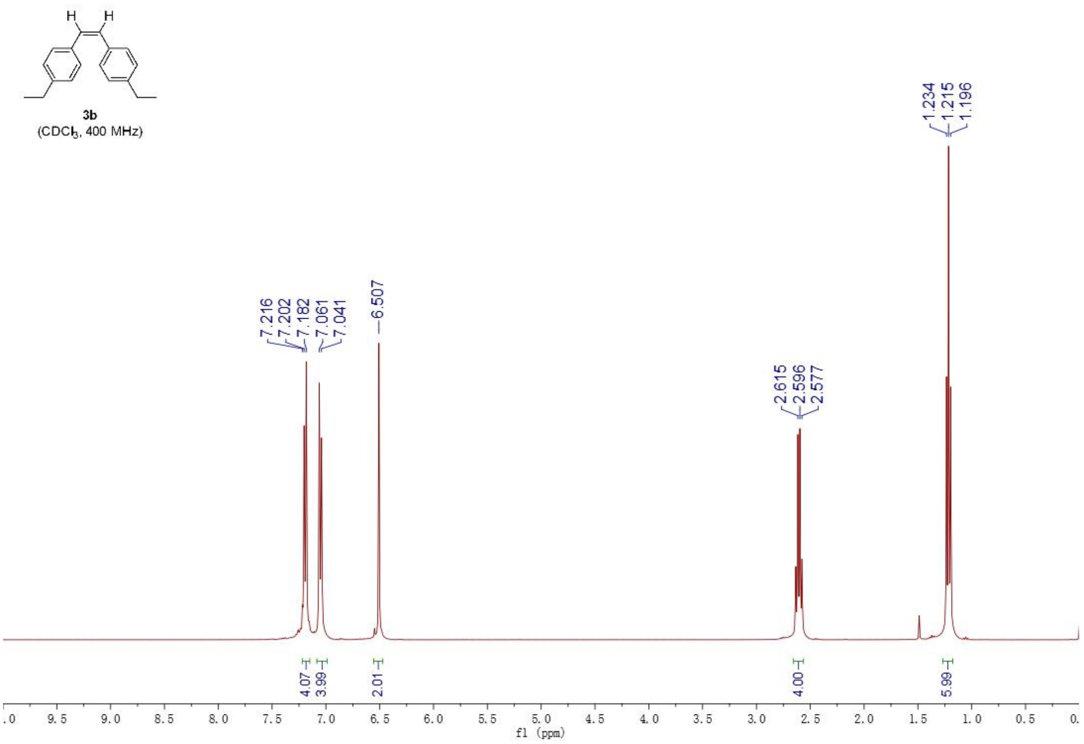
^{13}C NMR



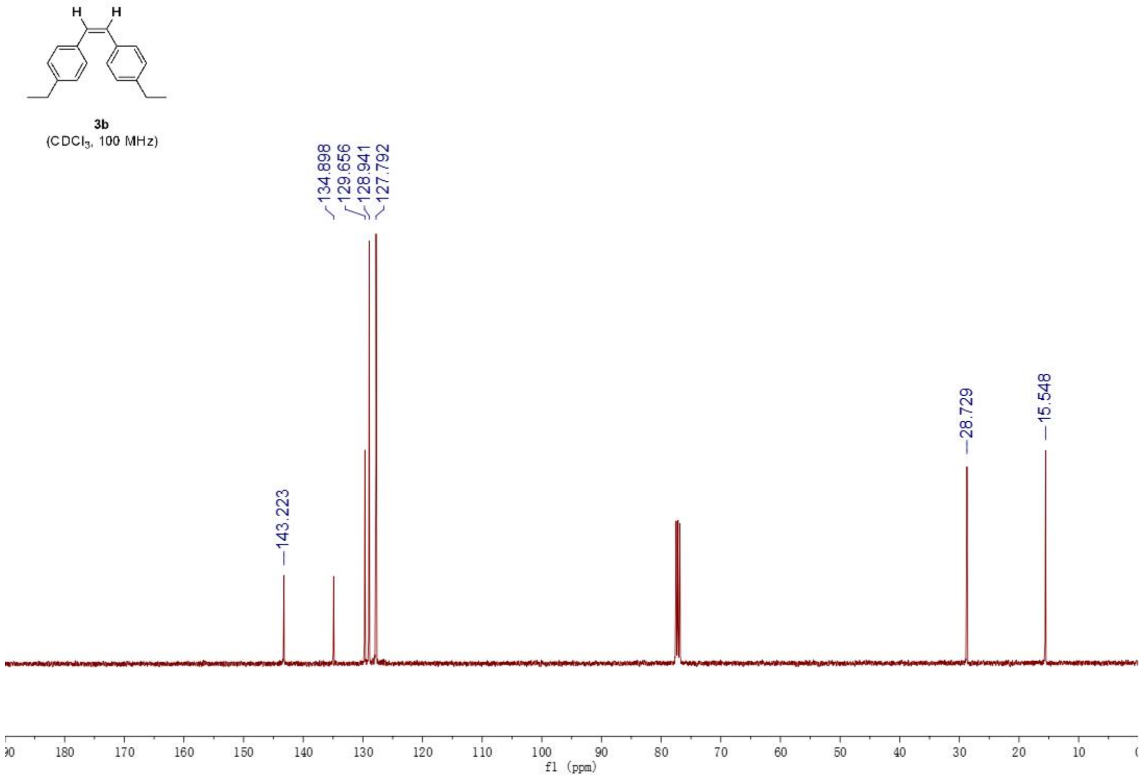
(Z)-1,2-diphenylethene (3a)
^{1}H NMR



(Z)-1,2-bis(4-ethylphenyl)ethene (3b)
^{1}H NMR

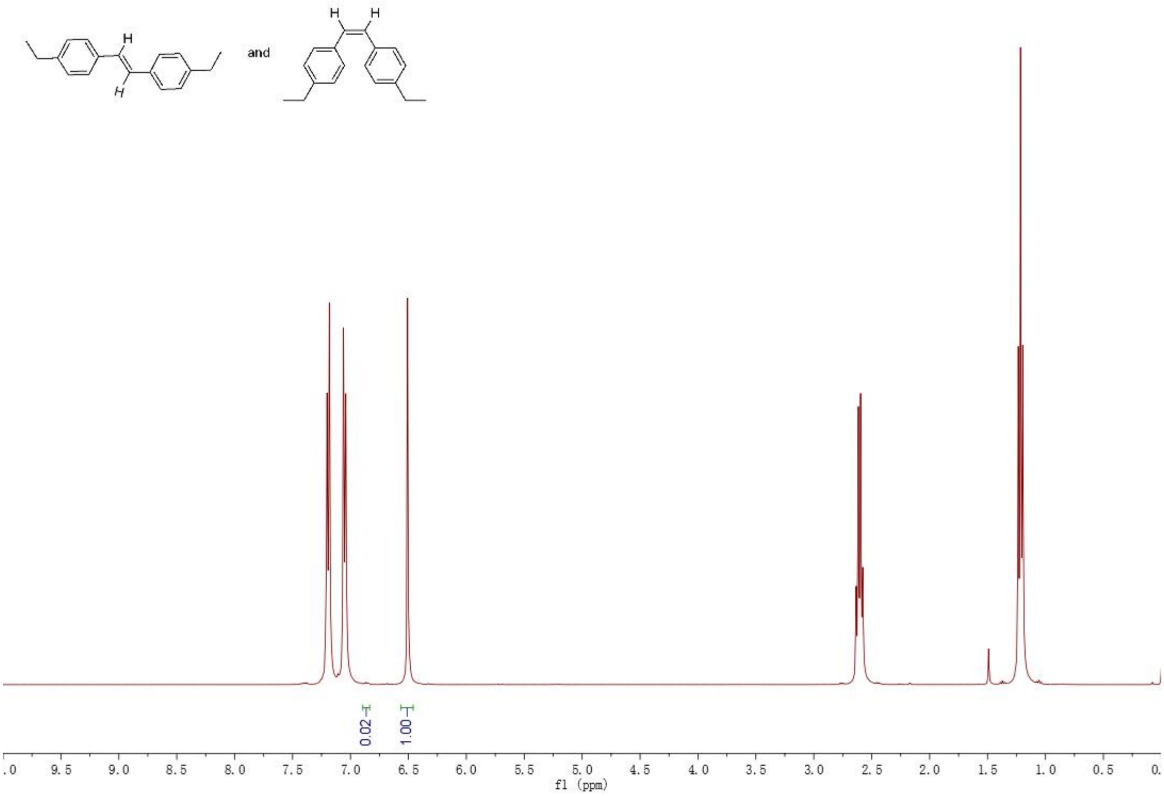


^{13}C NMR



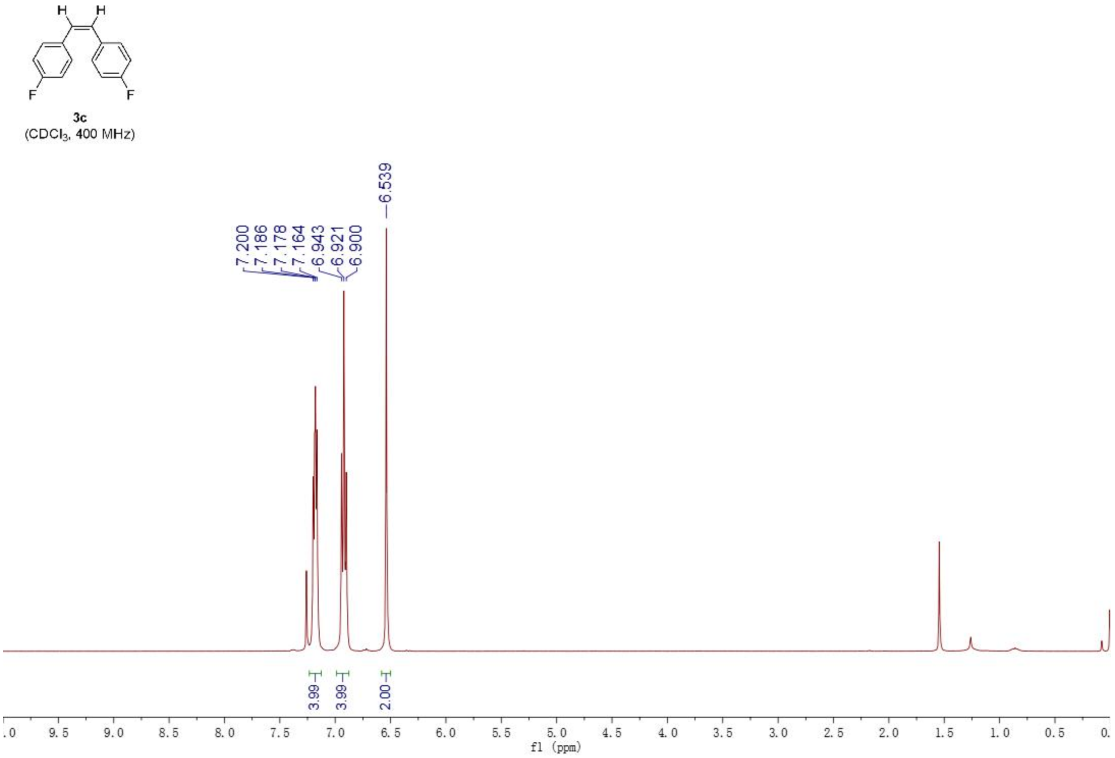
(Z)-1,2-bis(4-ethylphenyl)ethene (3b)

^{1}H NMR

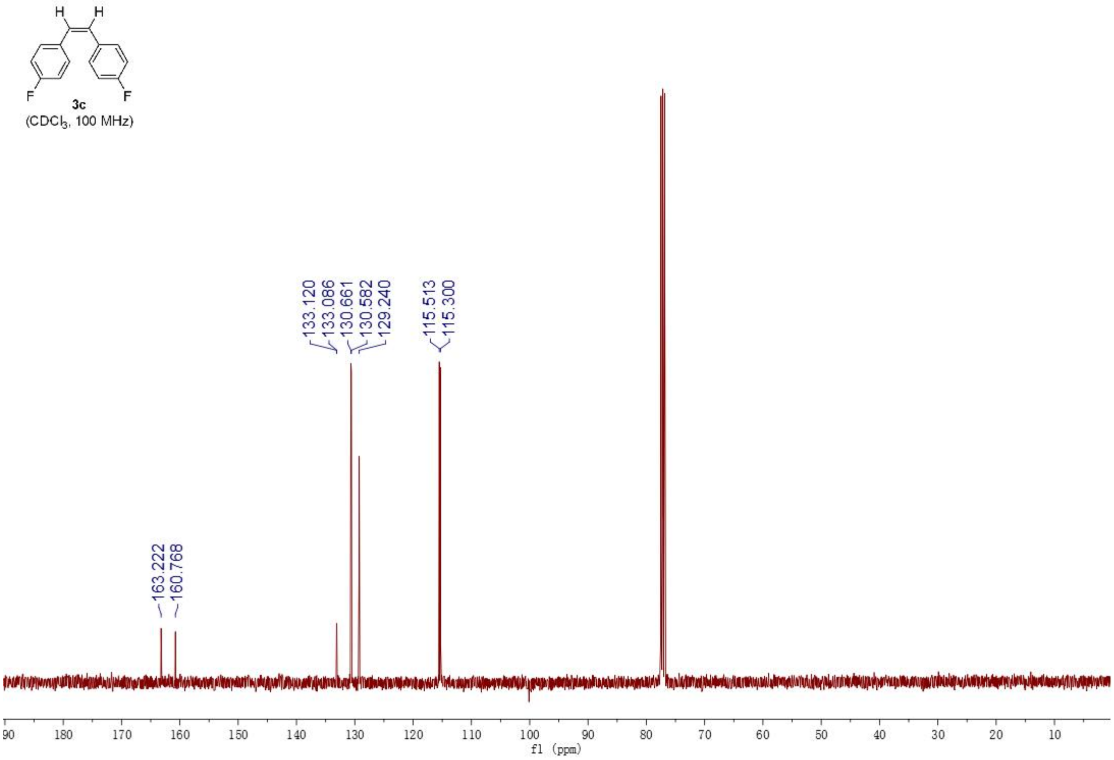


(Z)-1,2-bis(4-fluorophenyl)ethene (3c)

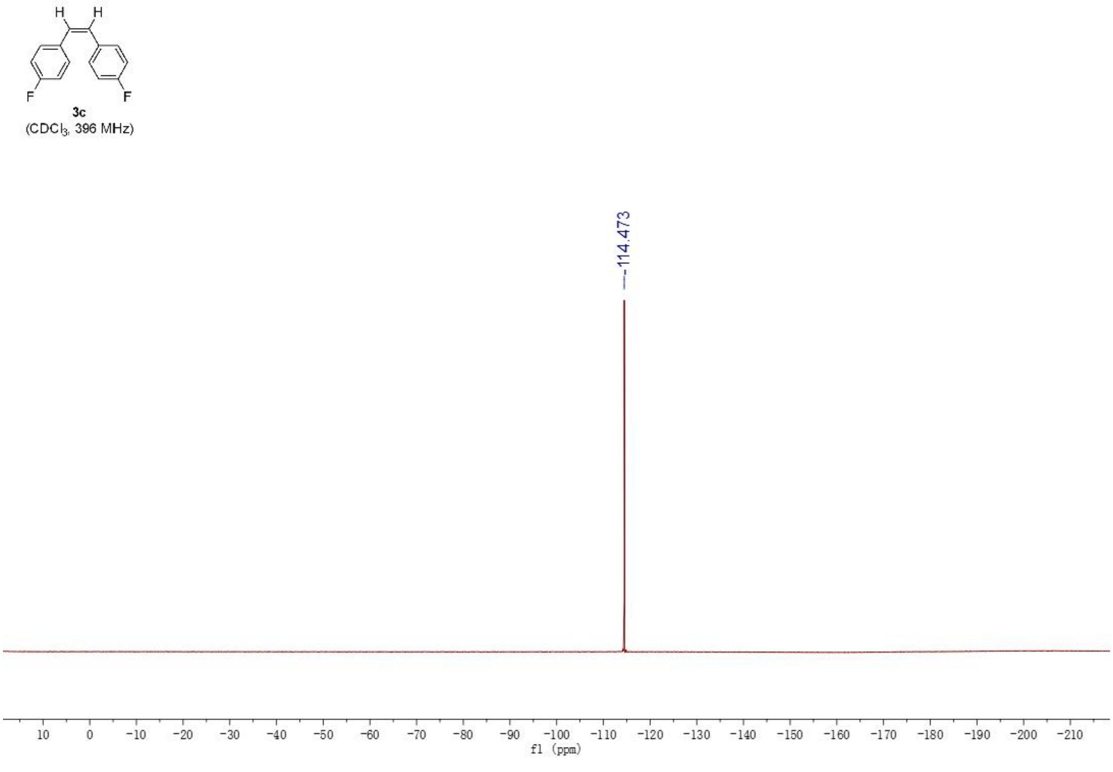
^{1}H NMR



^{13}C NMR

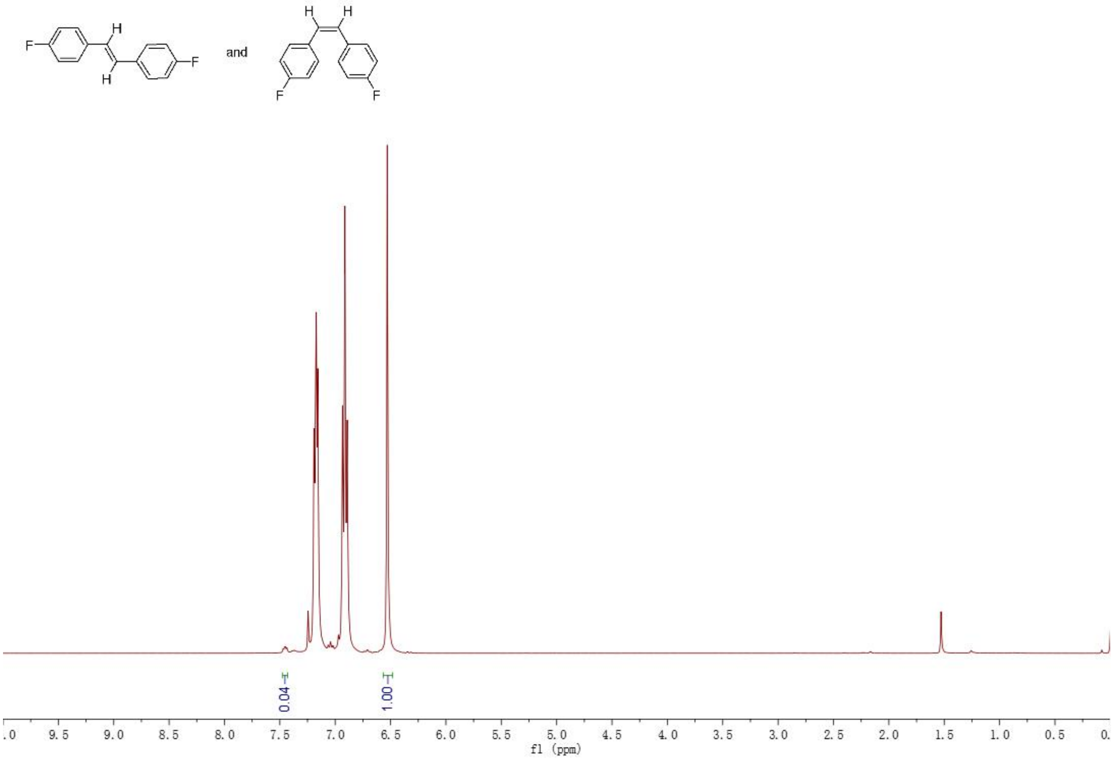


^{19}F NMR



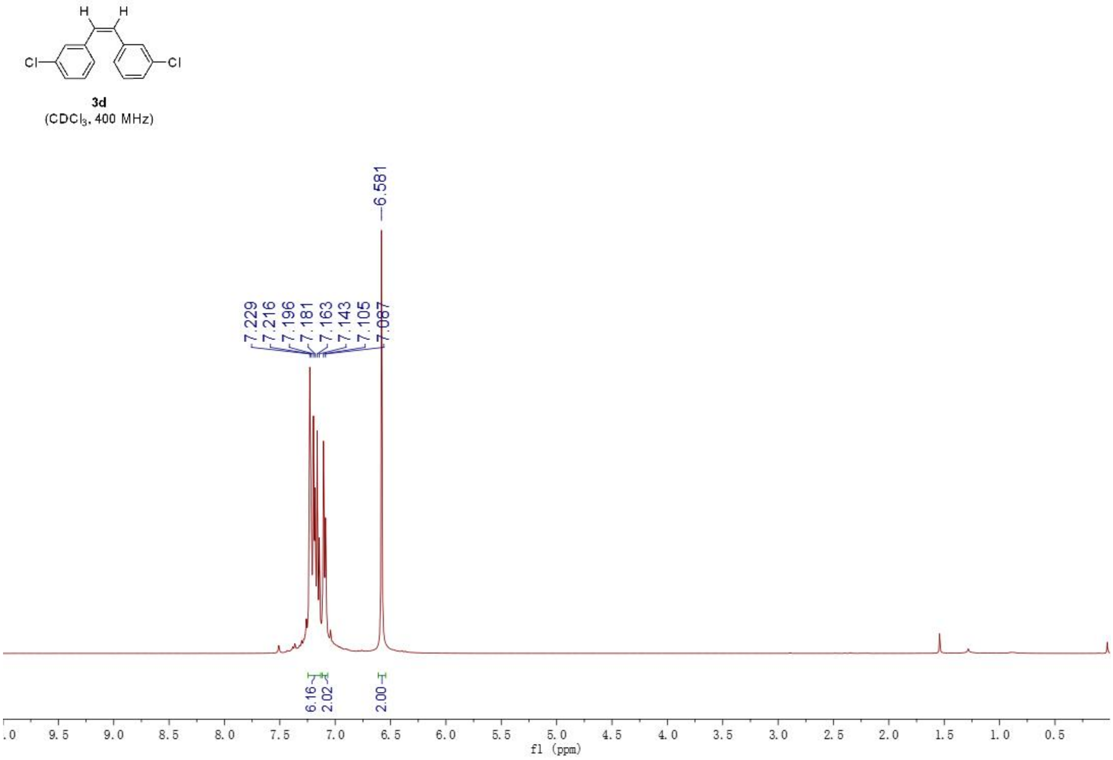
(Z)-1,2-bis(4-fluorophenyl)ethene (3c)

^{1}H NMR

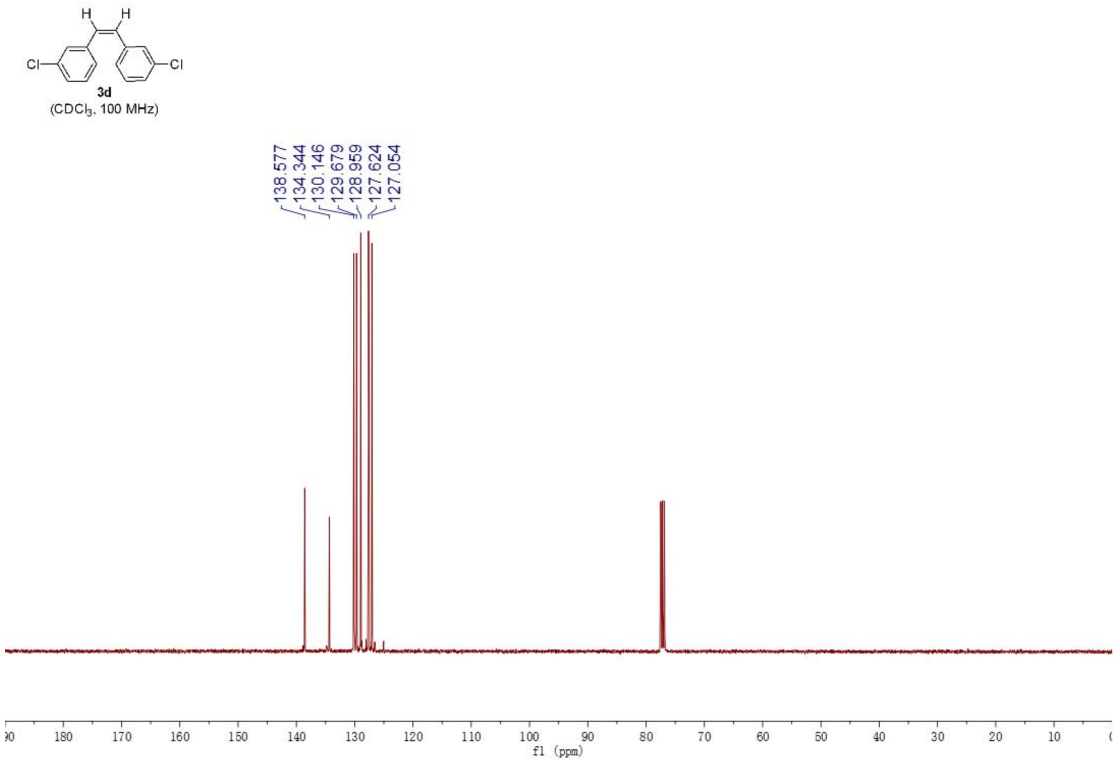


(Z)-1,2-bis(3-chlorophenyl)ethene (3d)

^{1}H NMR

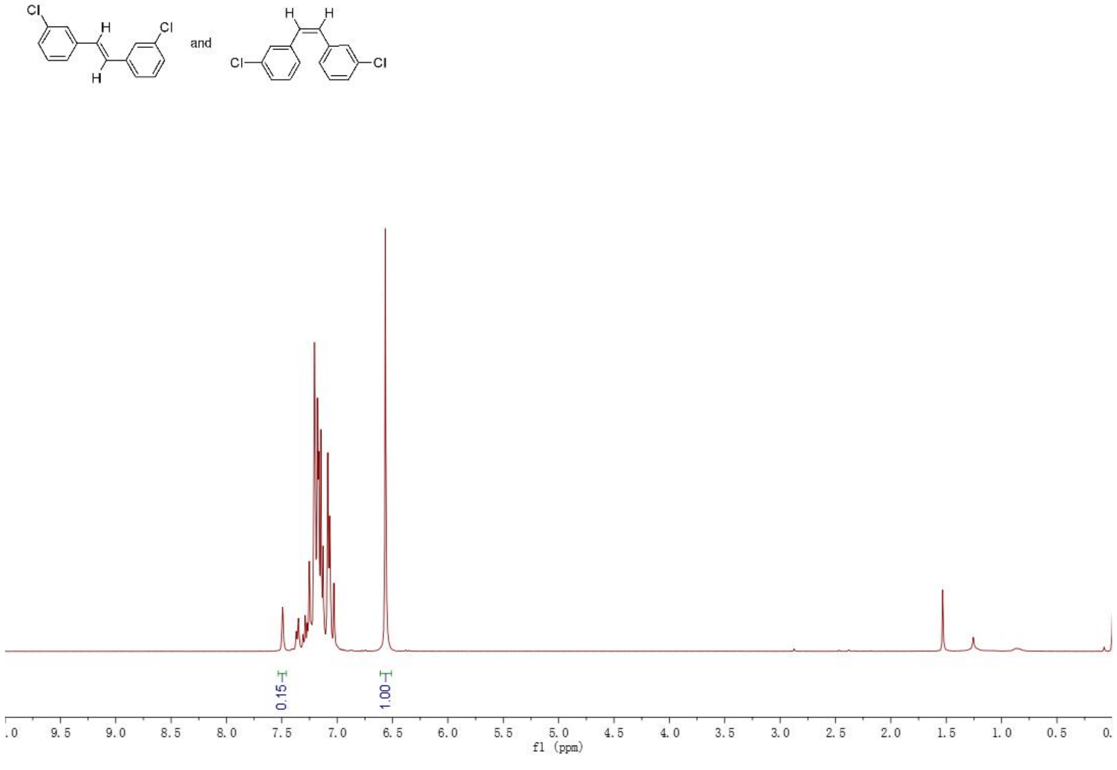


^{13}C NMR



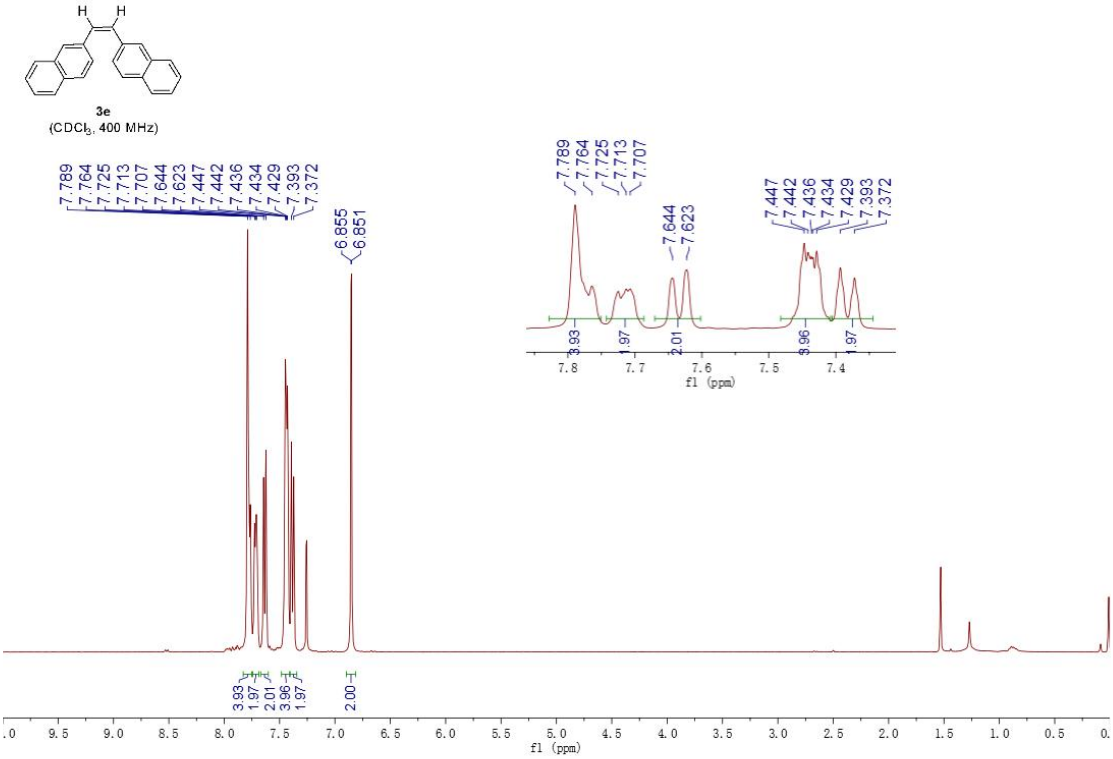
(Z)-1,2-bis(3-chlorophenyl)ethene (3d)

^{1}H NMR

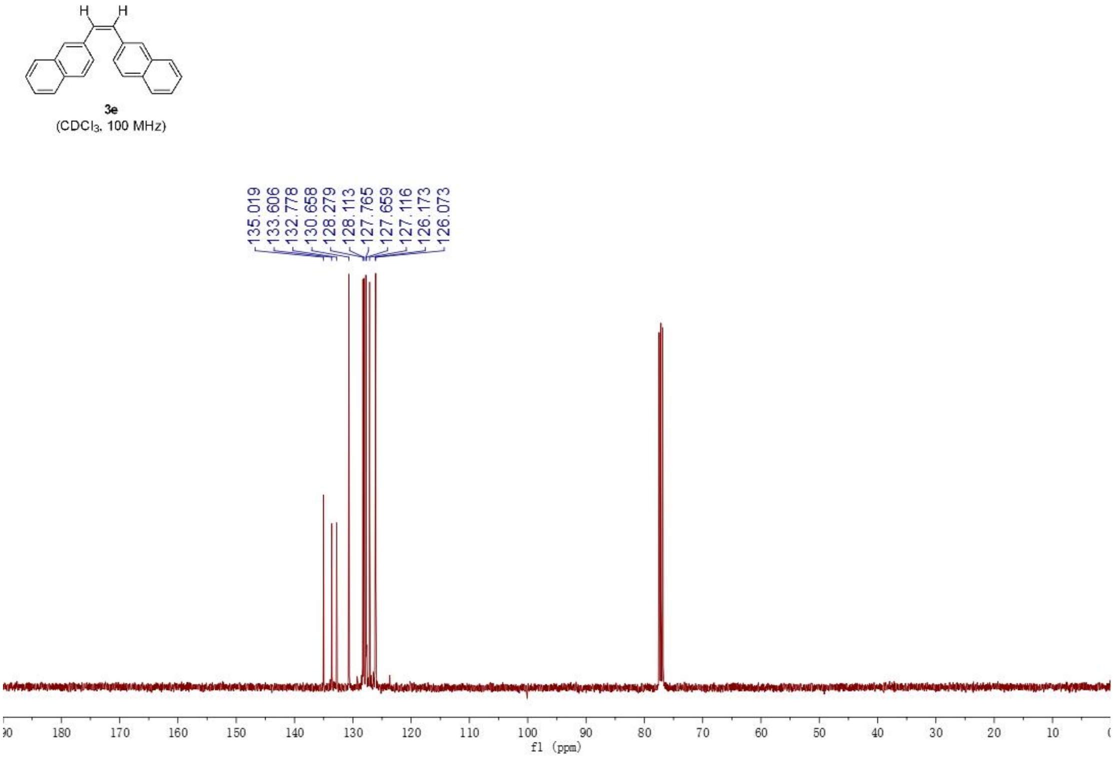


(Z)-1,2-di(naphthalen-2-yl)ethene (3e)

^{1}H NMR

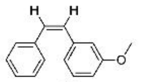


^{13}C NMR

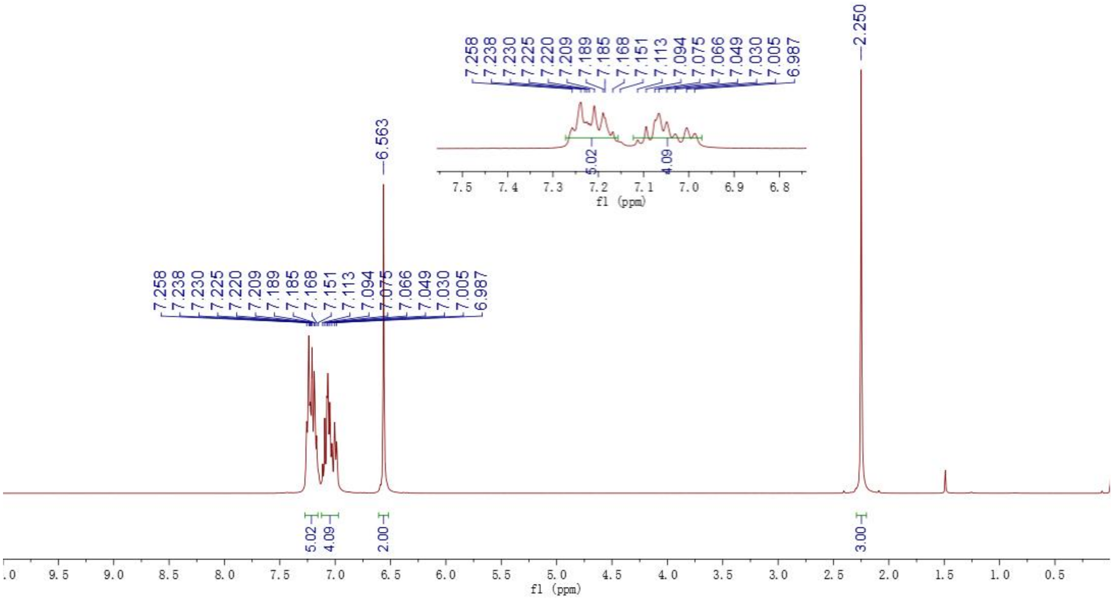


(Z)-1-methoxy-3-styrylbenzene (3f)

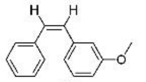
^{1}H NMR



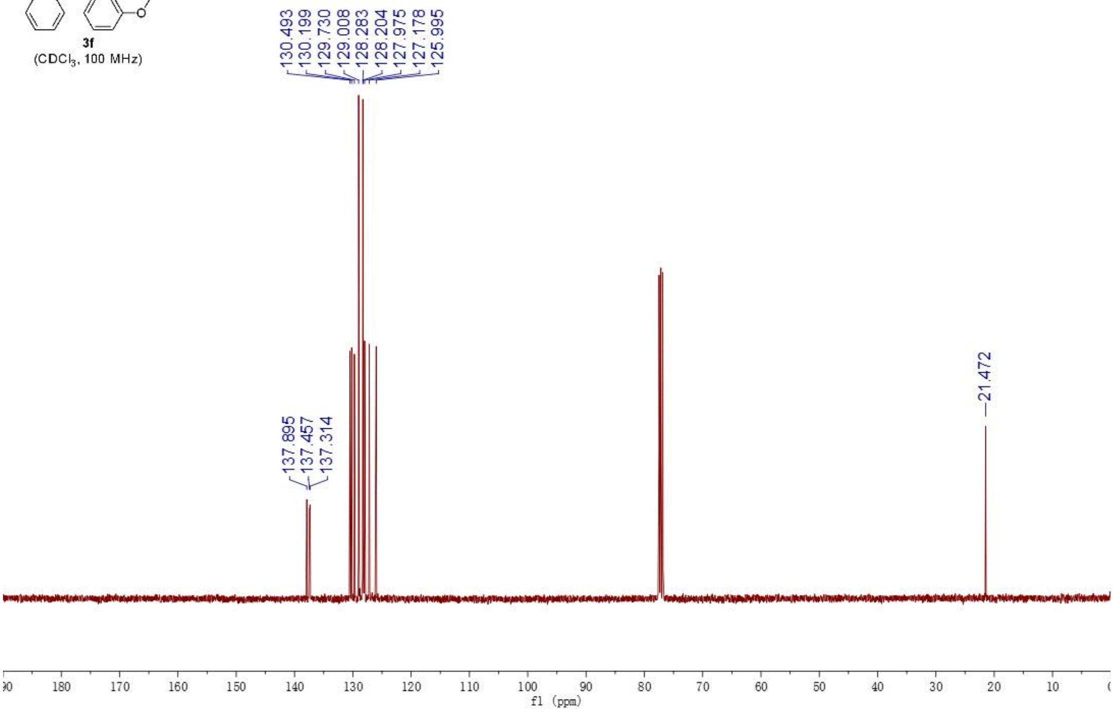
3f
(CDCl$_3$, 400 MHz)



^{13}C NMR

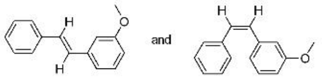


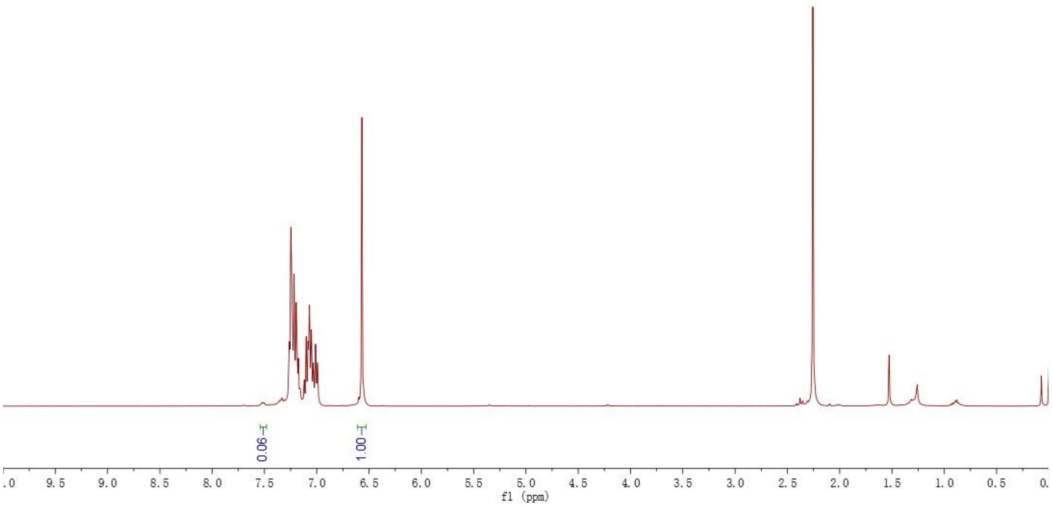
3f
(CDCl$_3$, 100 MHz)



(Z)-1-methoxy-3-styrylbenzene (3f)

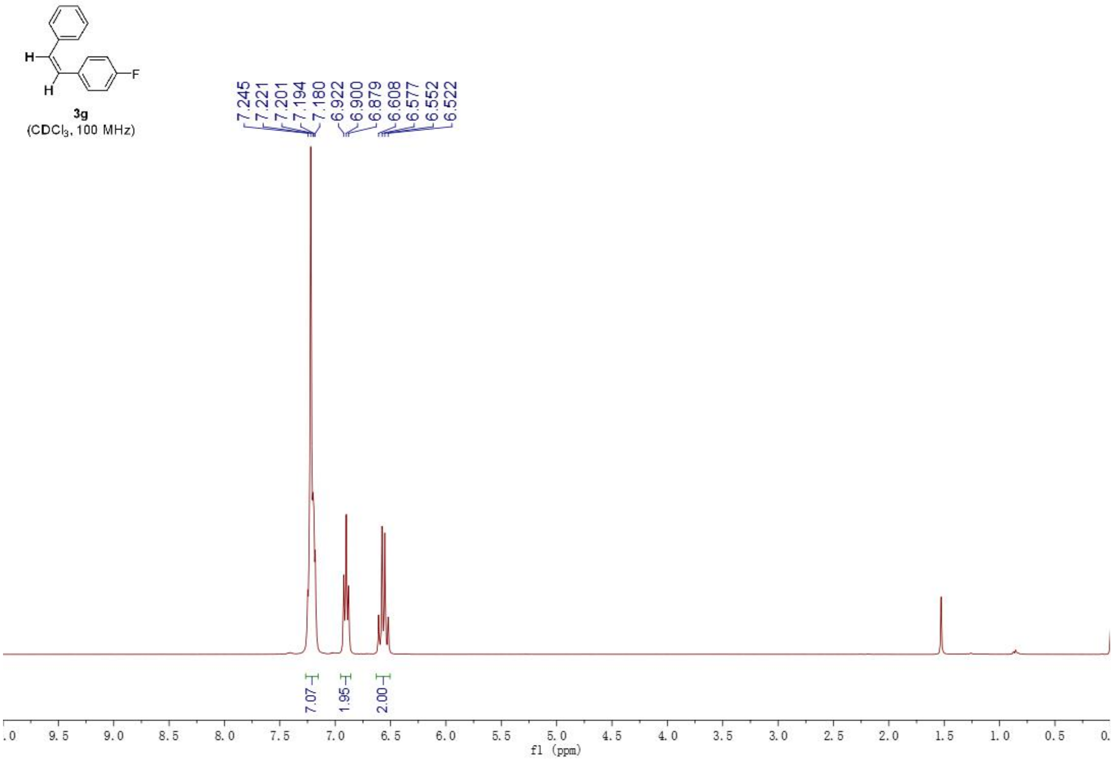
^{1}H NMR





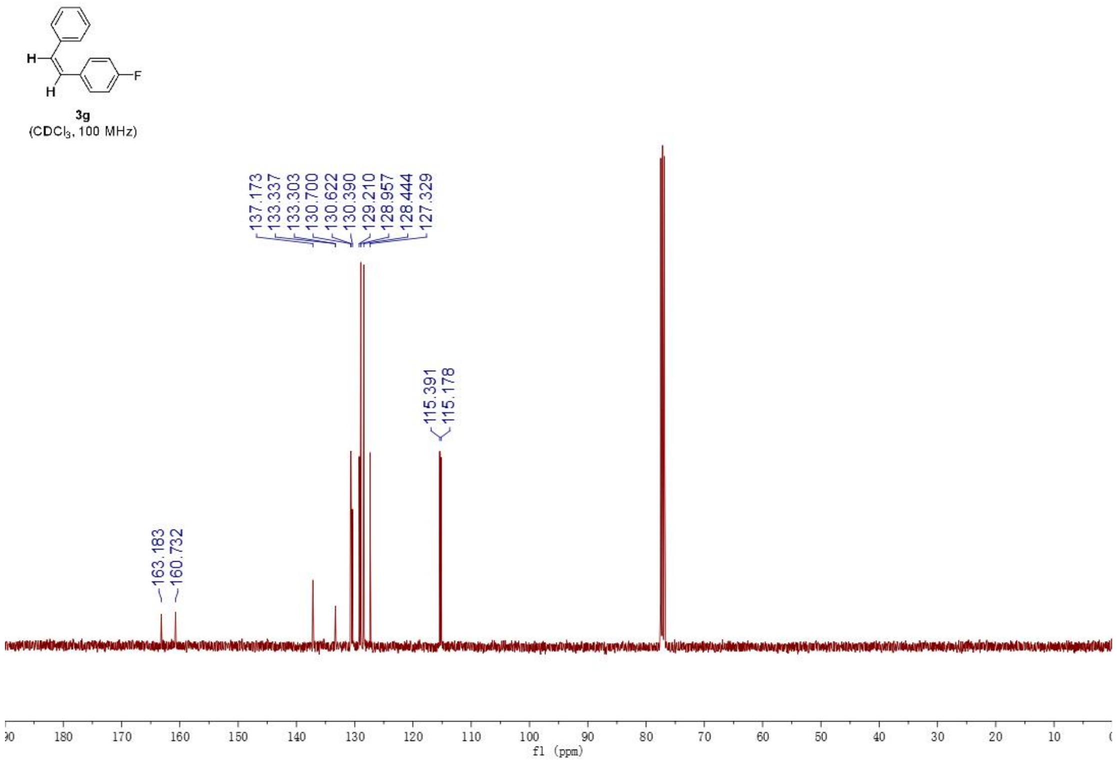
(Z)-1-fluoro-4-styrylbenzene (3g)

^{1}H NMR

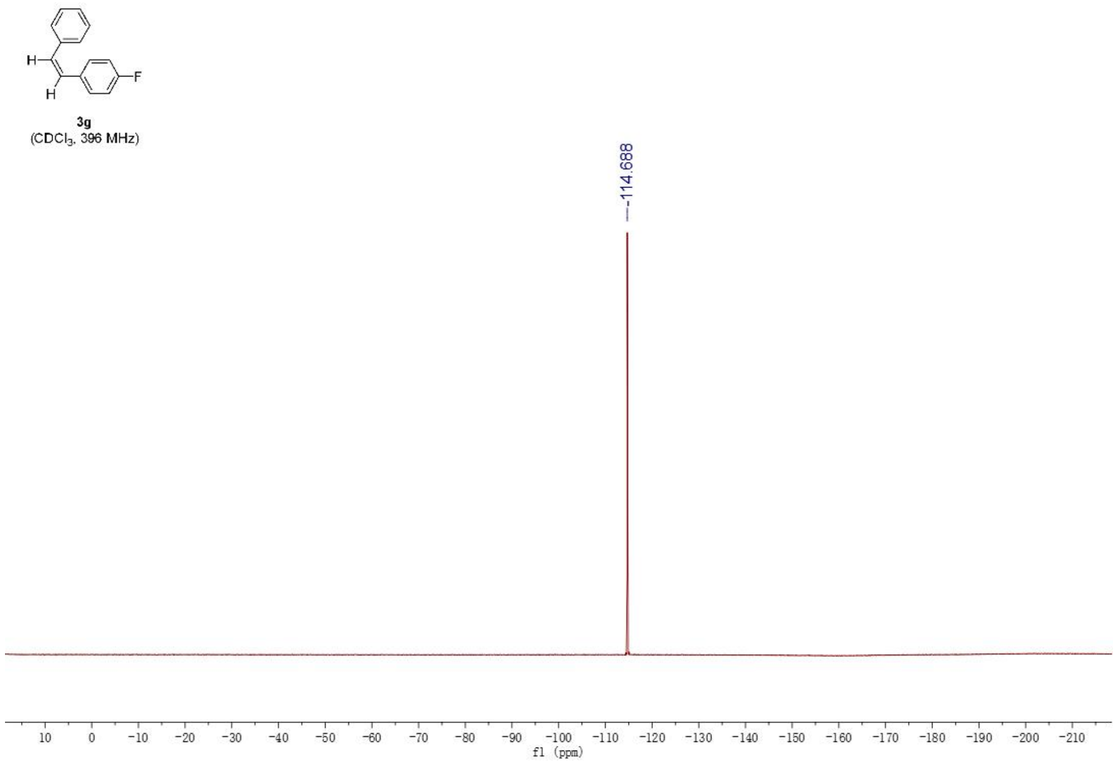


3g
($CDCl_3$, 100 MHz)

^{13}C NMR

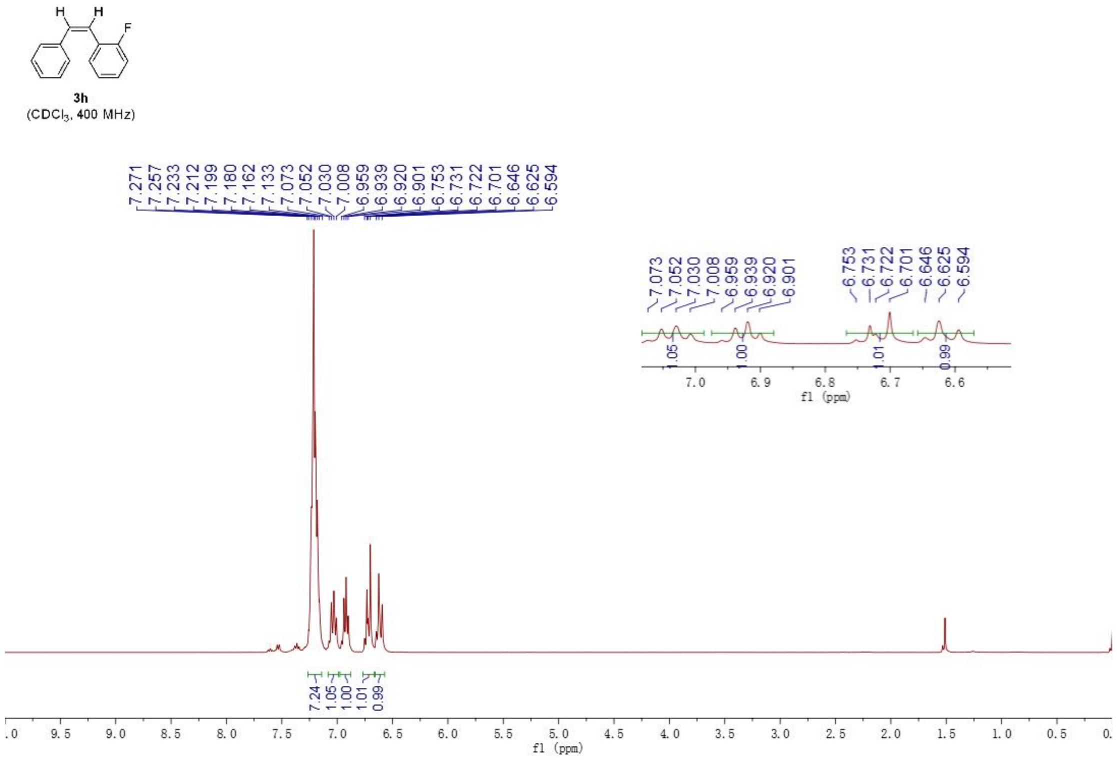


^{19}F NMR

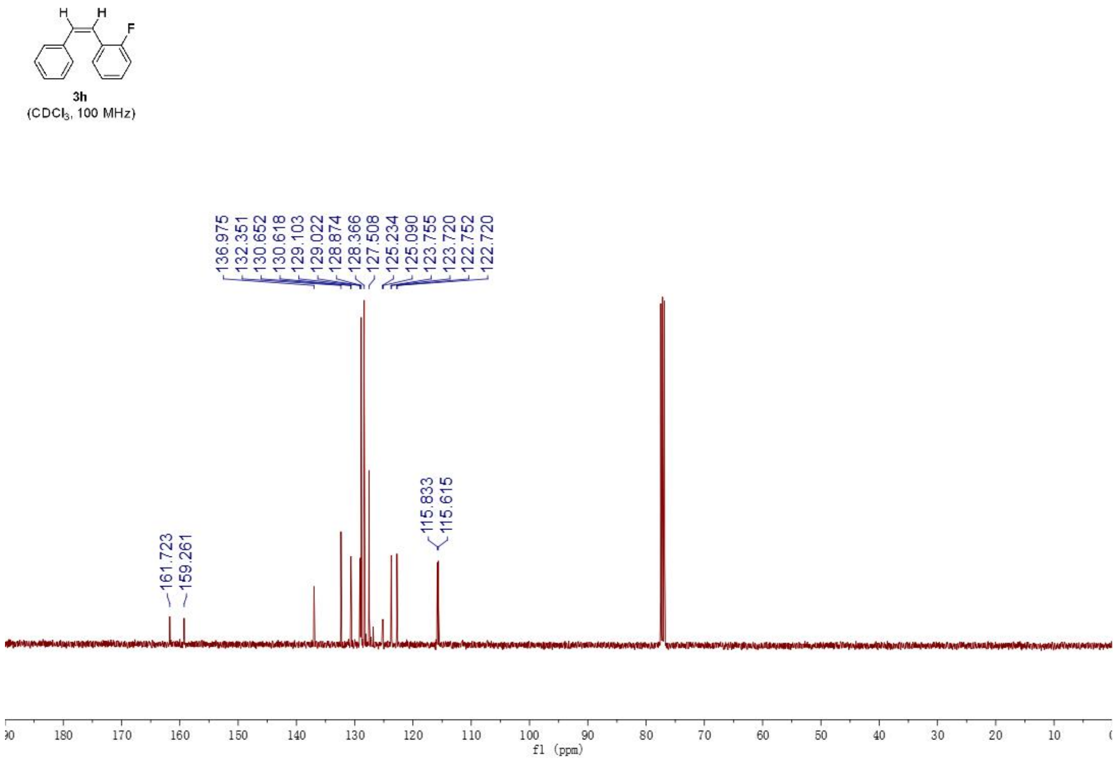


(Z)-1-fluoro-2-styrylbenzene (3h)

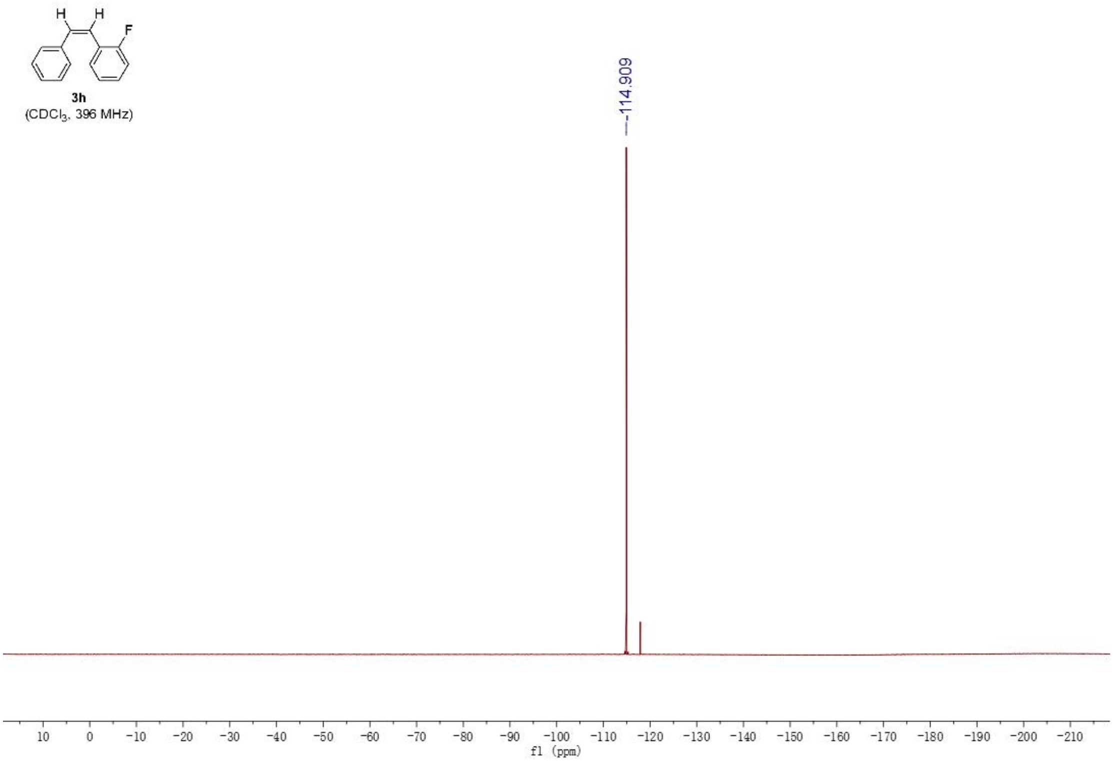
^{1}H NMR



^{13}C NMR

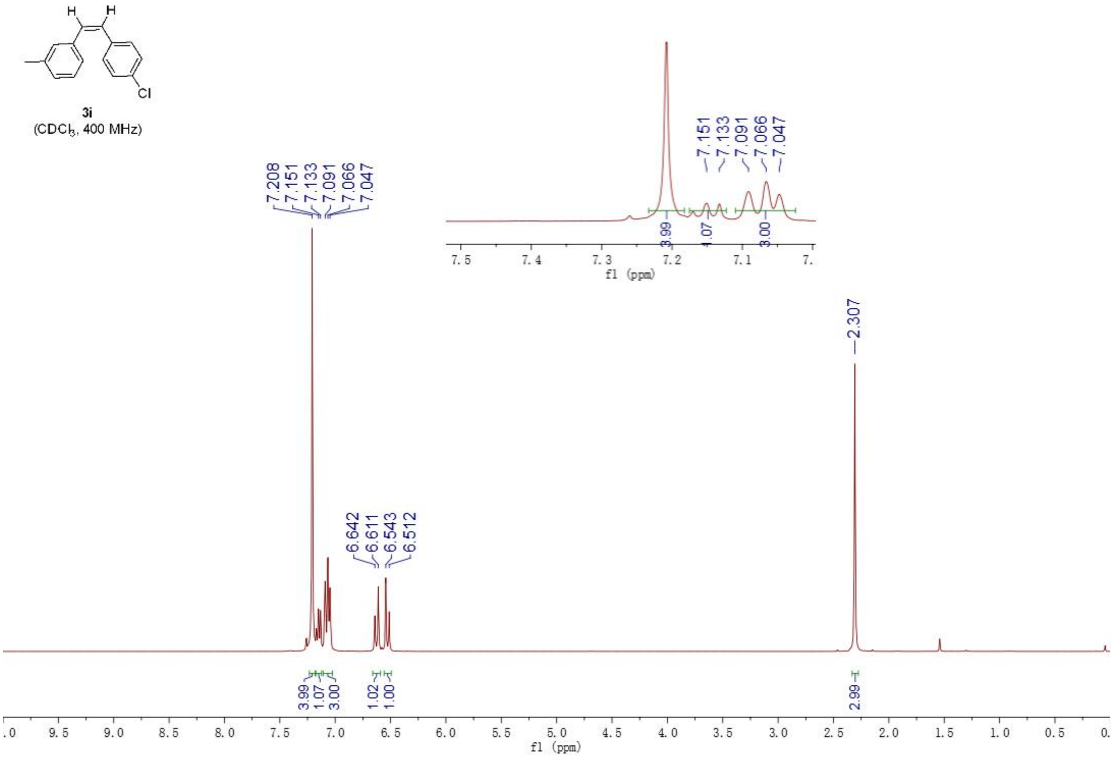


^{19}F NMR

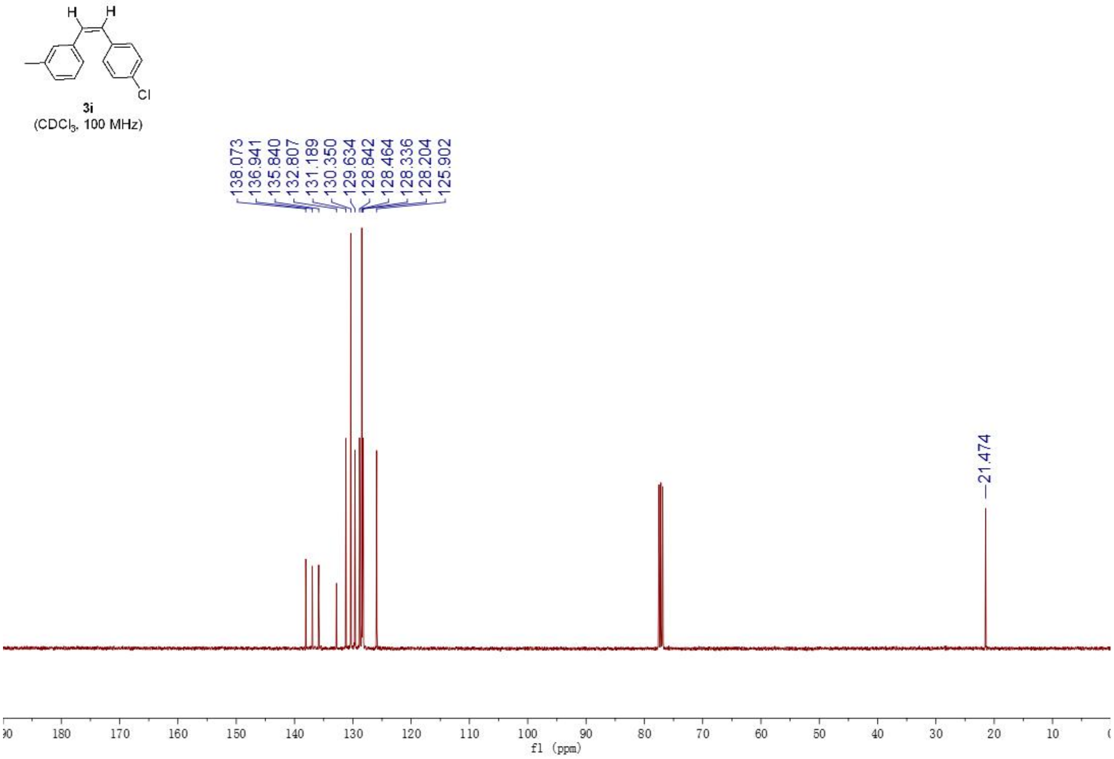


(Z)-1-(4-chlorostyryl)-3-methylbenzene (3i)

^{1}H NMR

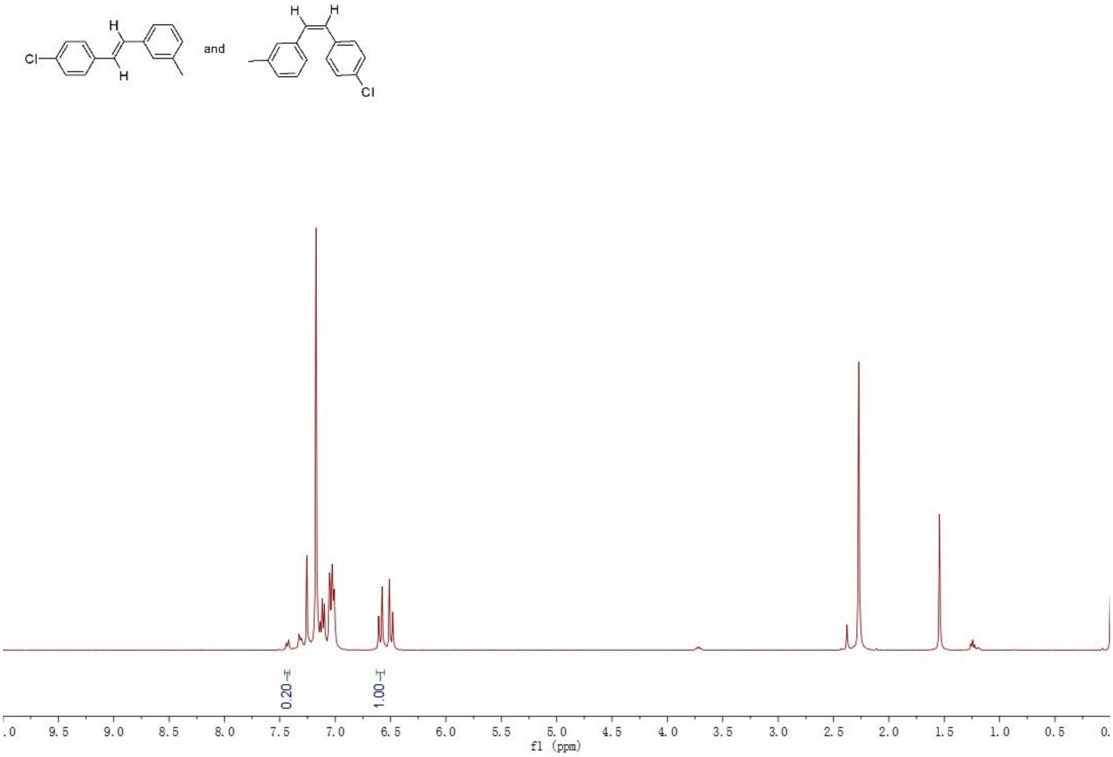


^{13}C NMR



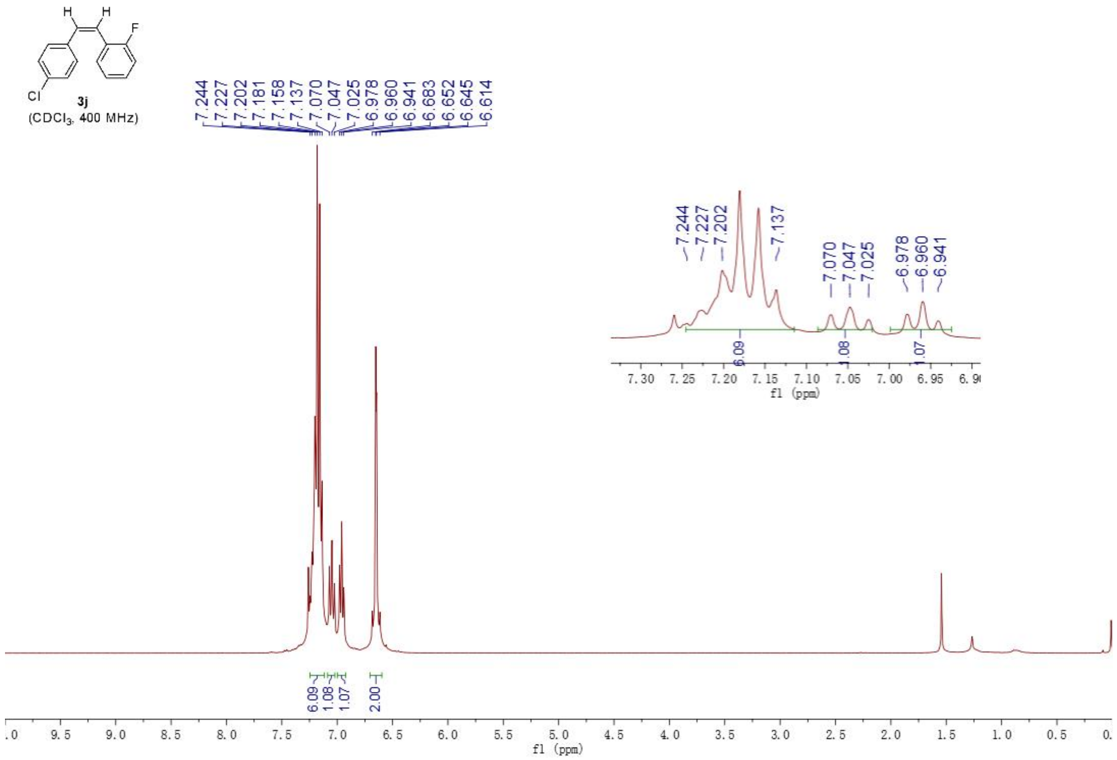
(Z)-1-(4-chlorostyryl)-3-methylbenzene (3i)

^1H NMR

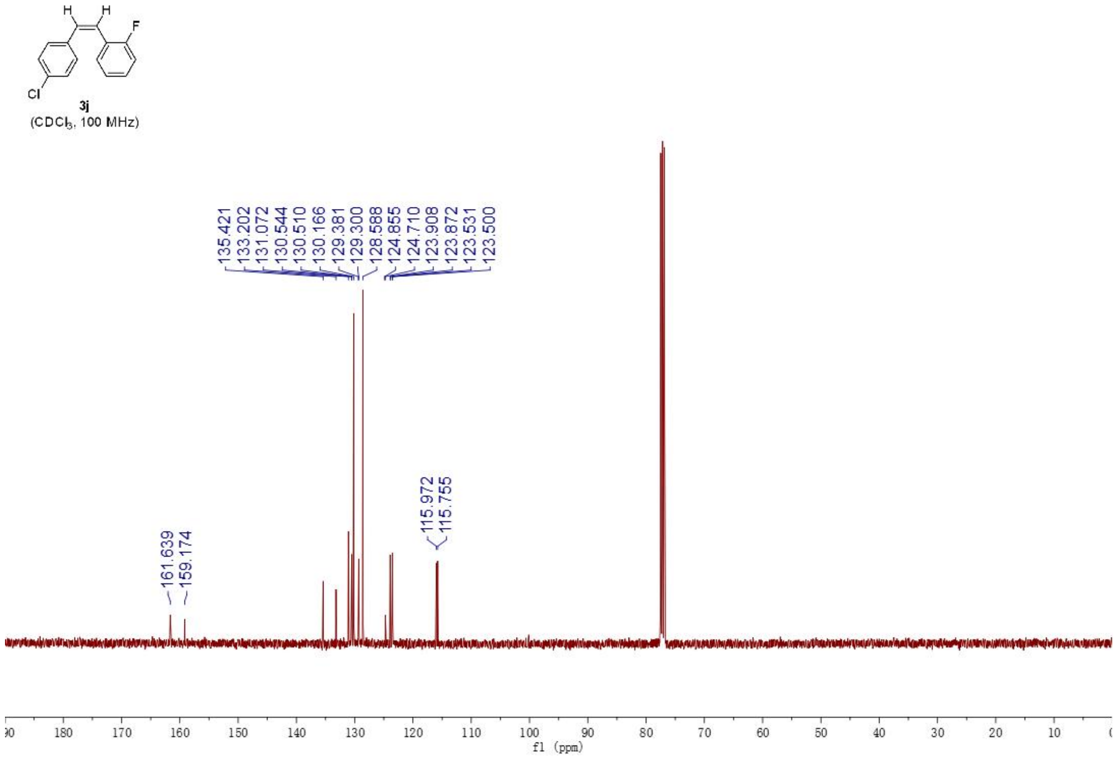


(Z)-1-(4-chlorostyryl)-2-fluorobenzene. (3j)

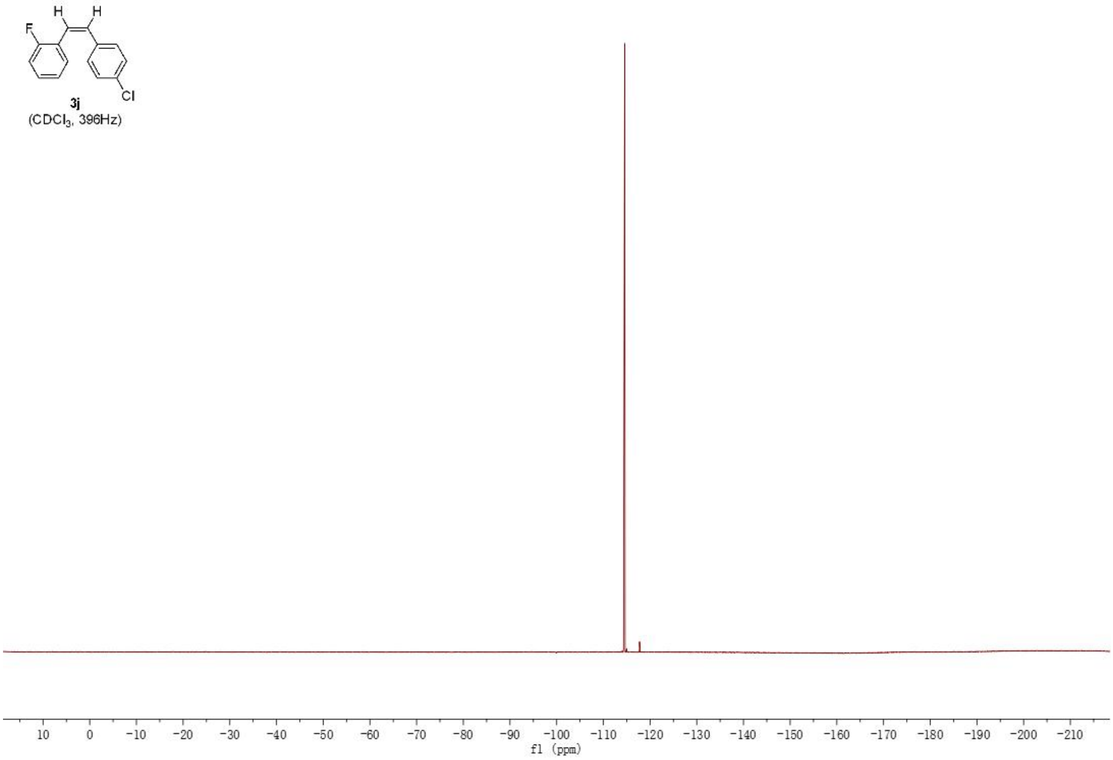
^{1}H NMR



^{13}C NMR

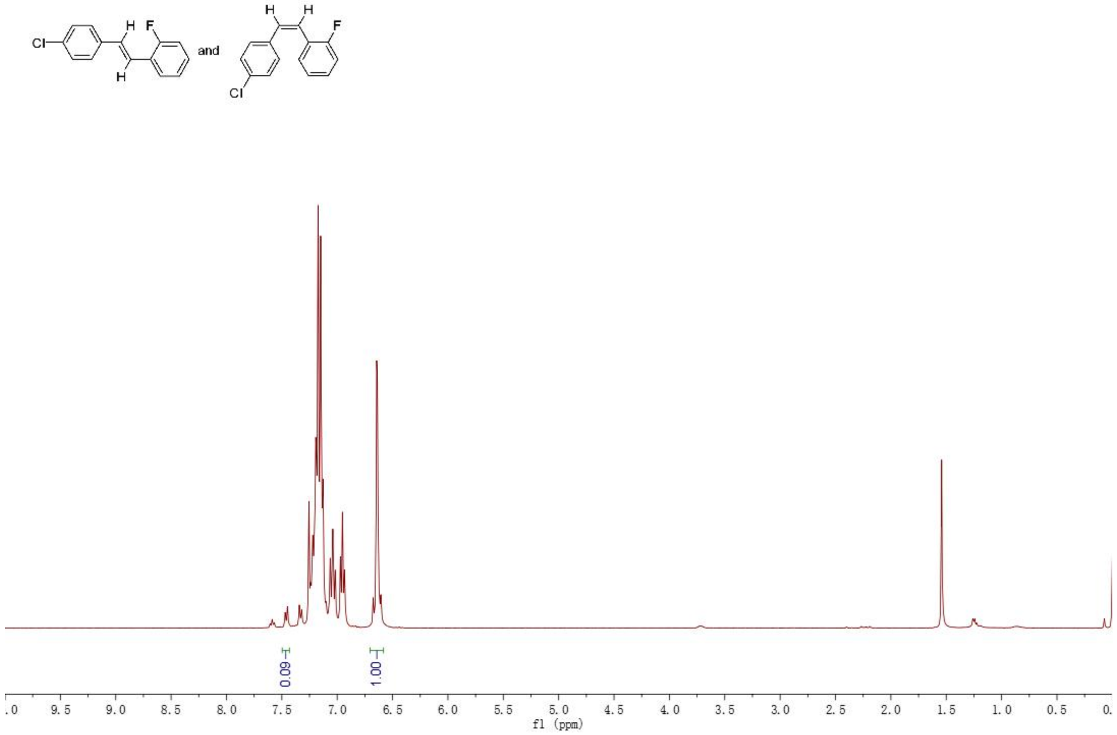


^{19}F NMR



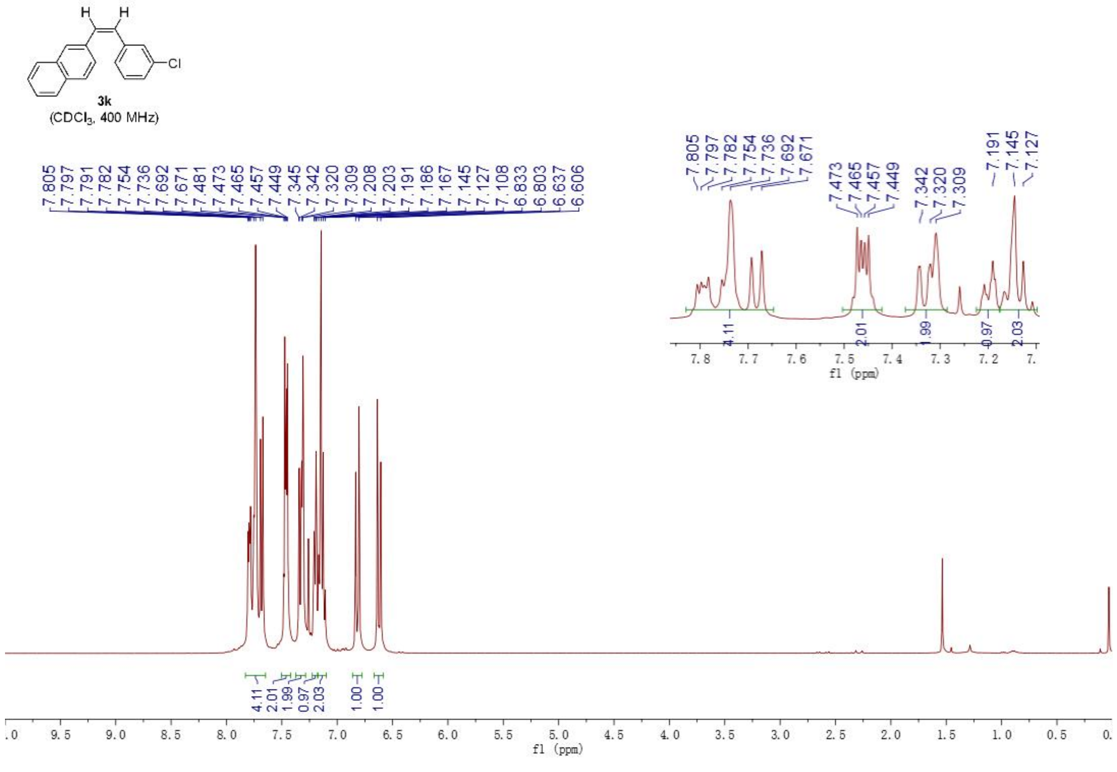
(Z)-1-(4-chlorostyryl)-2-fluorobenzene. (3j)

^{1}H NMR

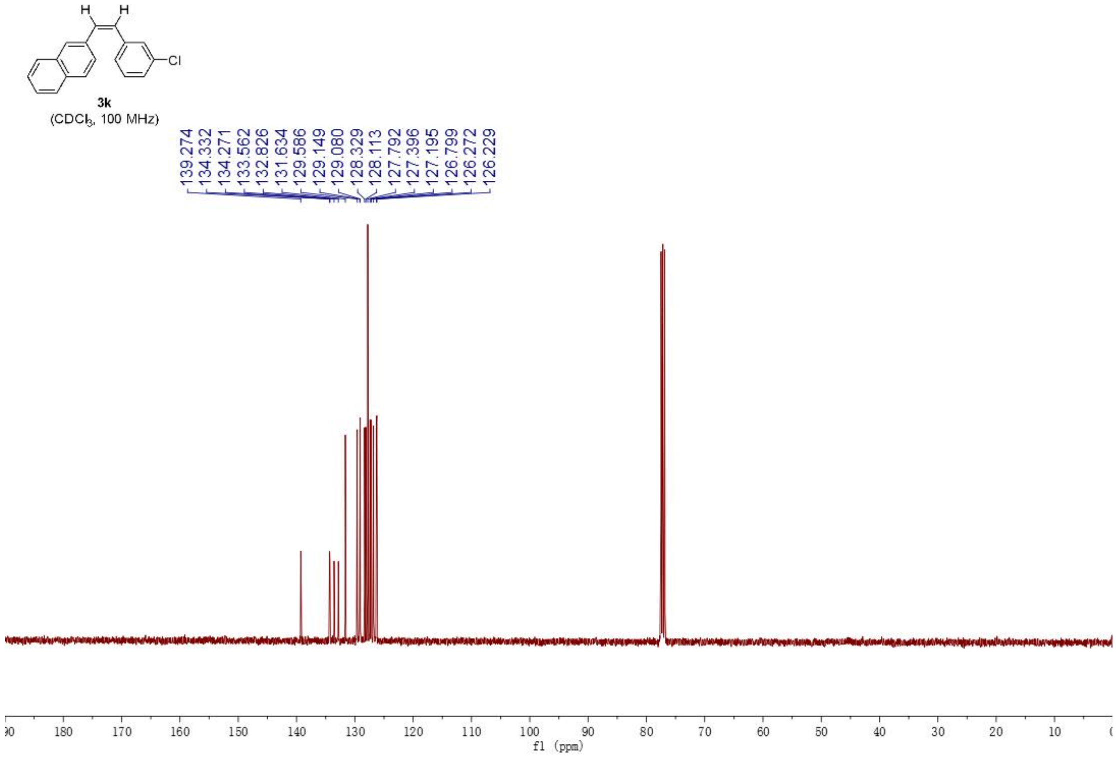


(Z)-2-(3-chlorostyryl)naphthalene (3k)

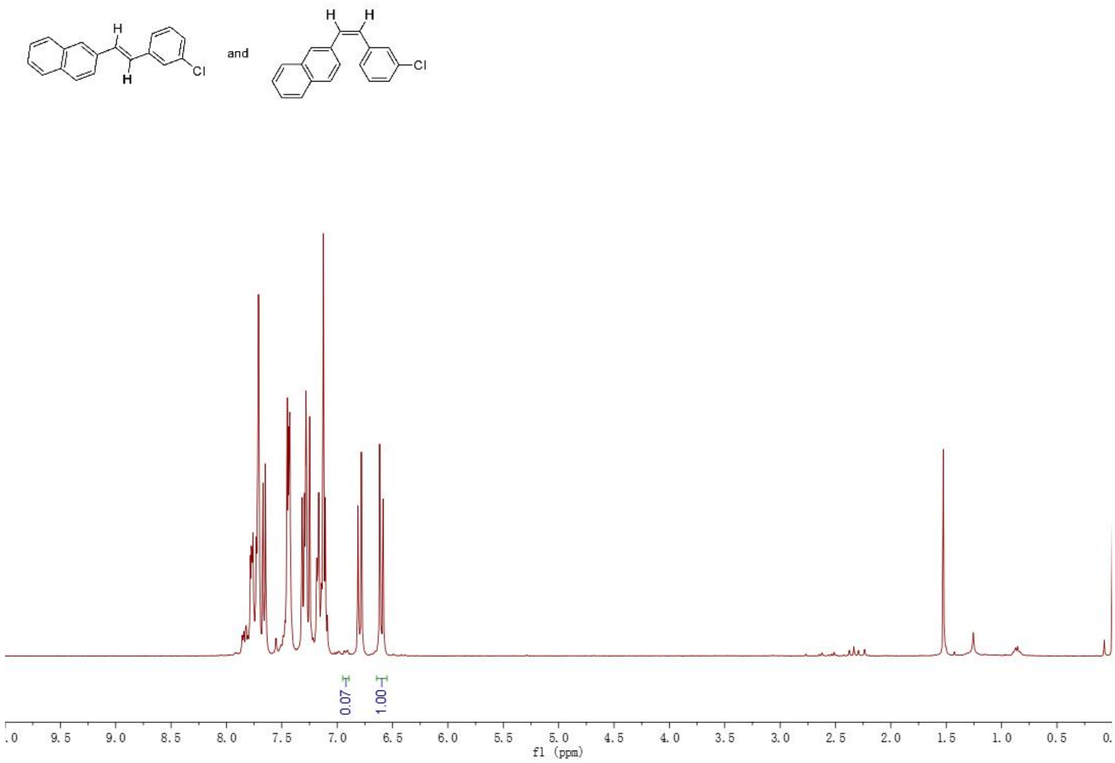
^{1}H NMR



^{13}C NMR

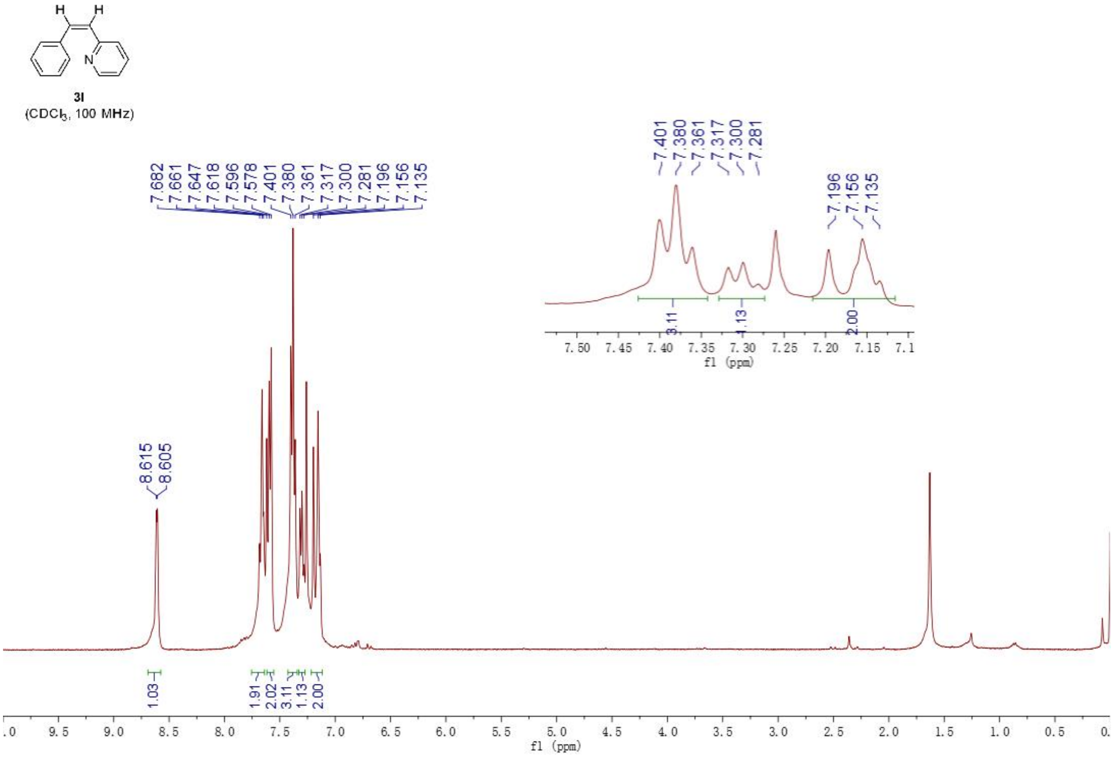


(Z)-2-(3-chlorostyryl)naphthalene (3k)
^{1}H NMR

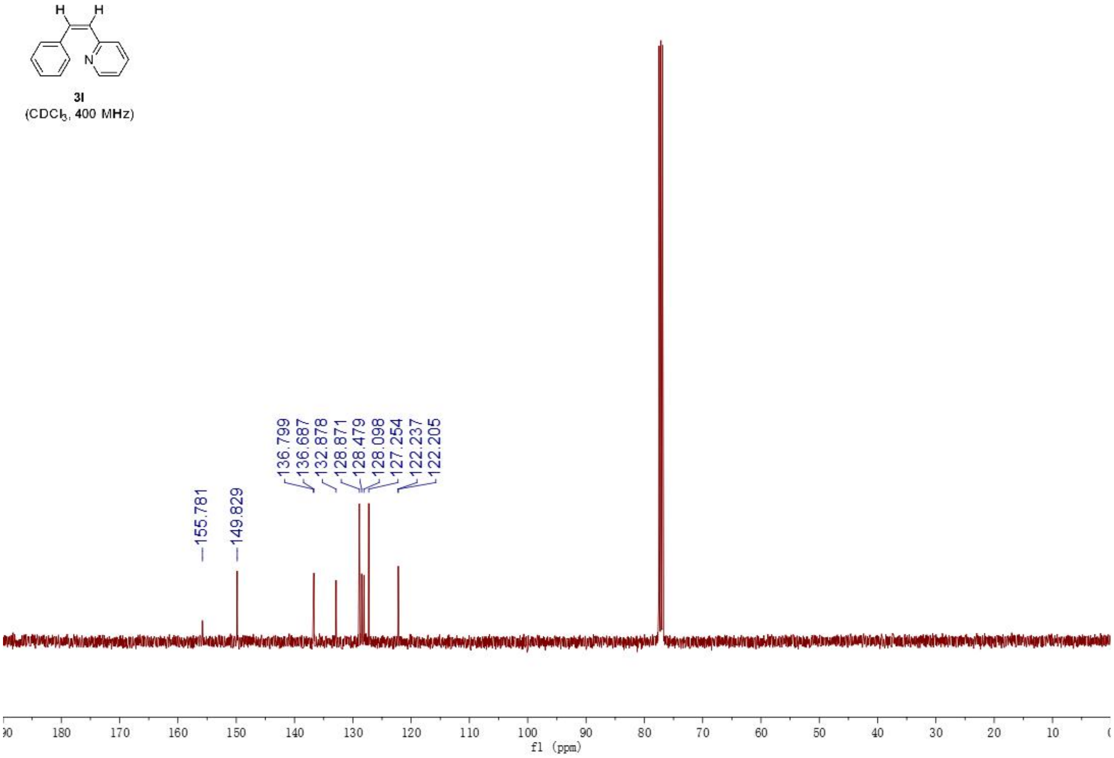


(Z)-2-styrylpyridine (3l)

^{1}H NMR

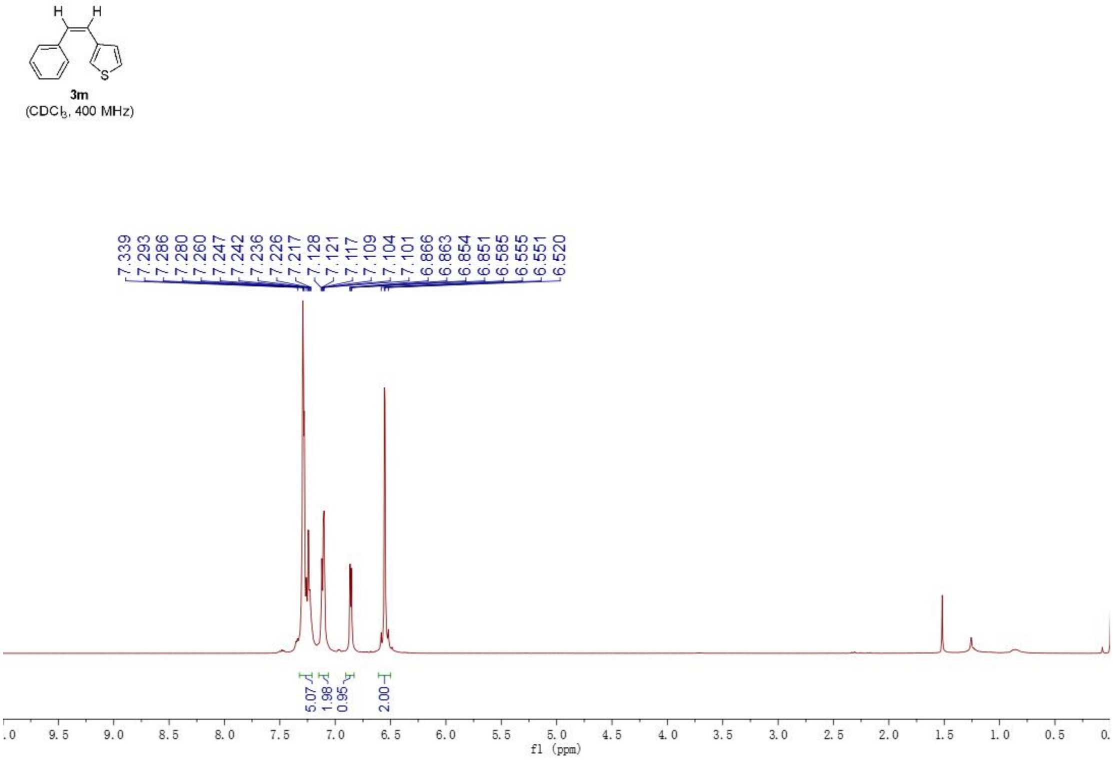


^{13}C NMR

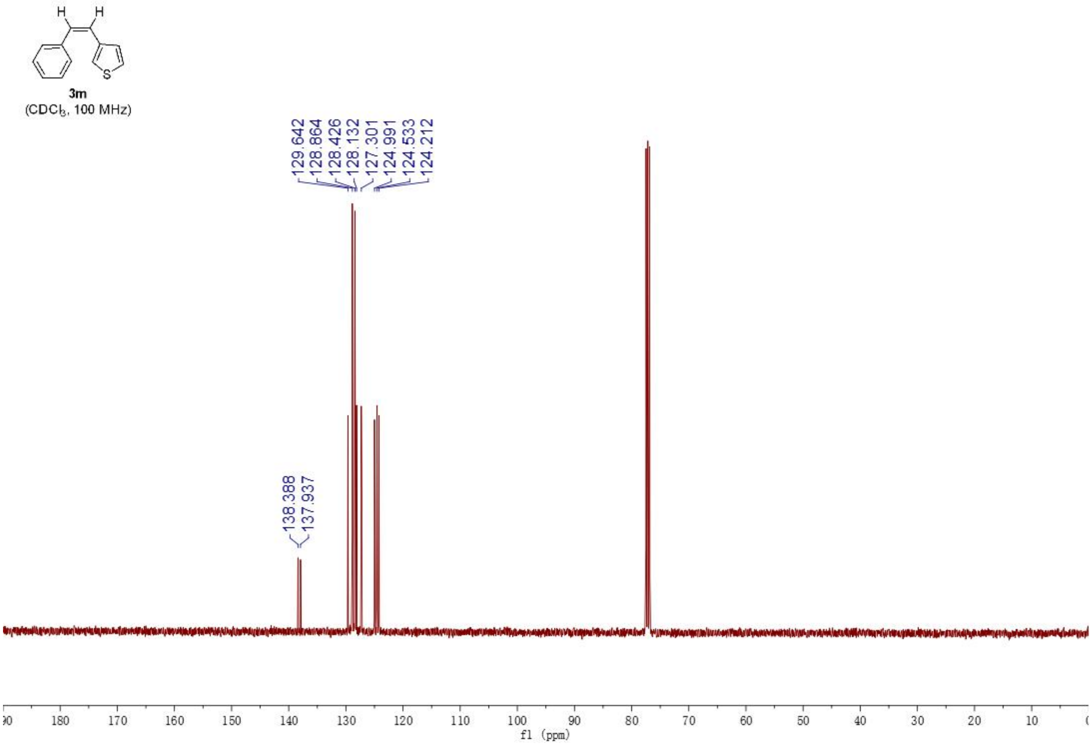


(Z)-2-styrylthiophene (3m)

^{1}H NMR

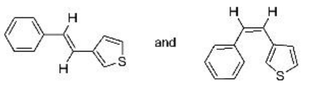


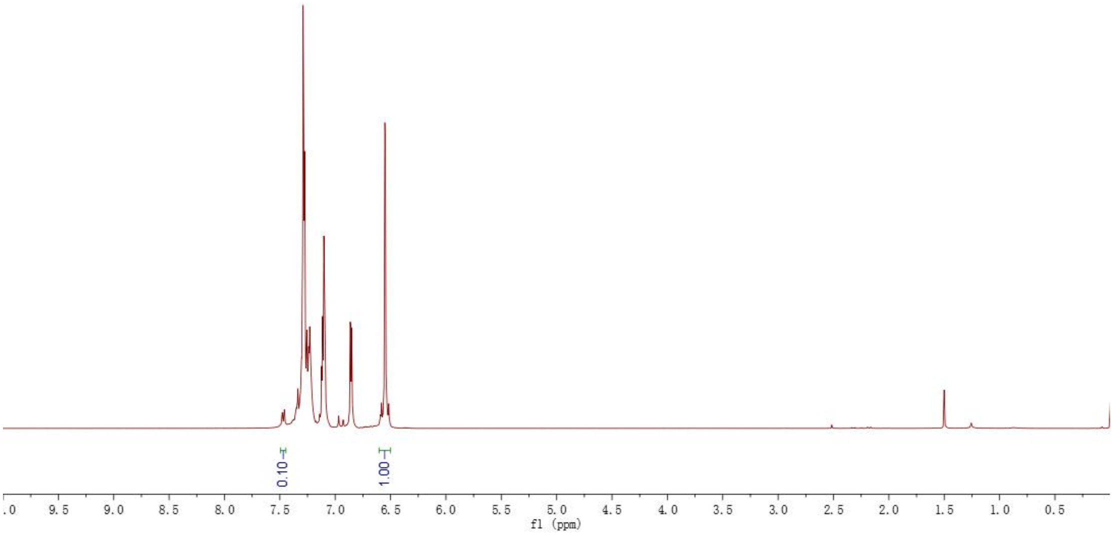
^{13}C NMR



(Z)-2-styrylthiophene (3m)

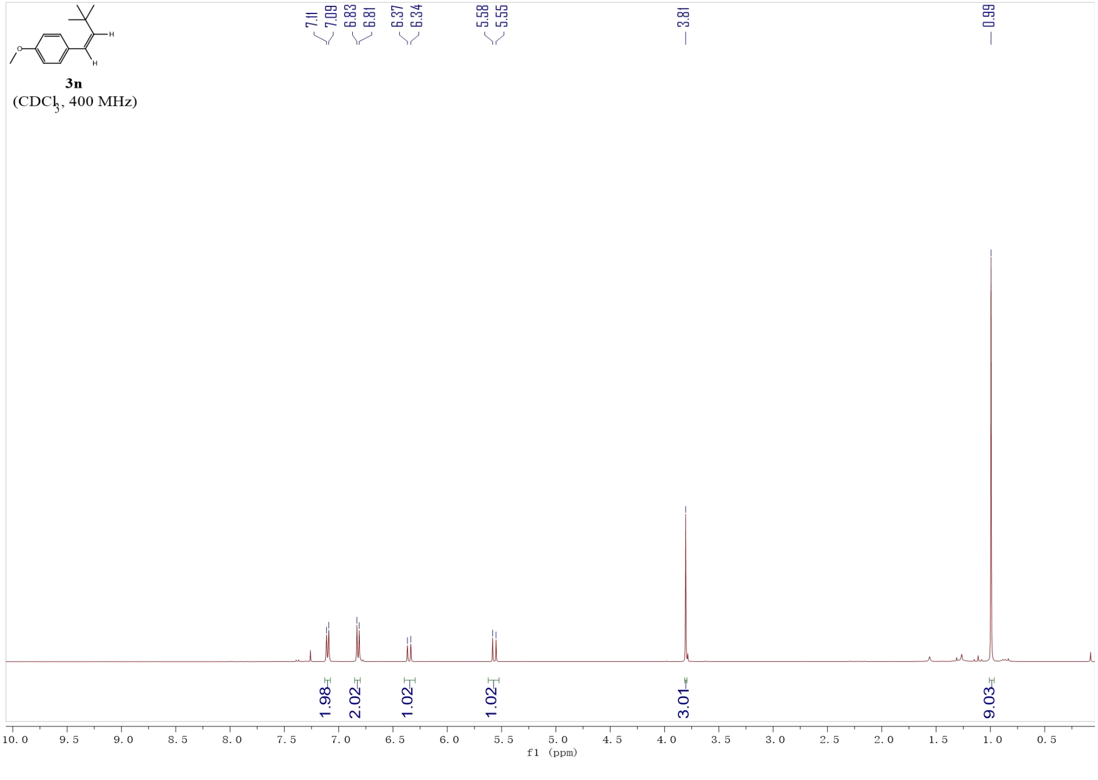
^{1}H NMR



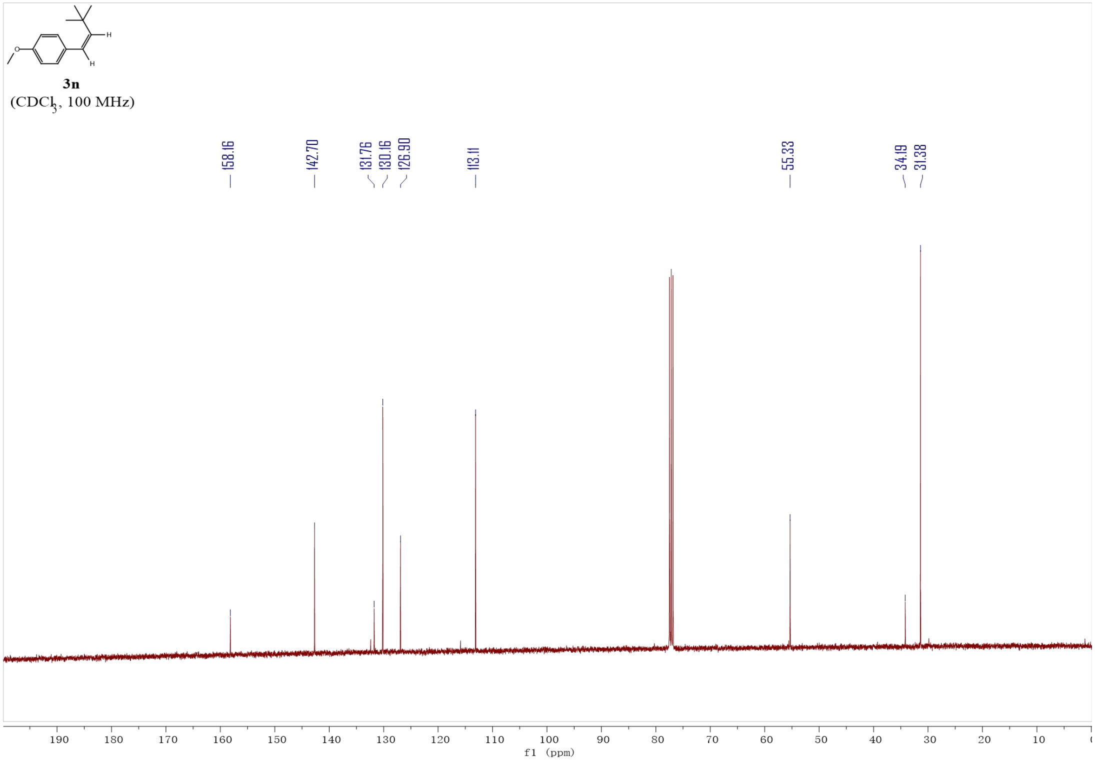


(Z)-1-(3,3-dimethylbut-1-en-1-yl)-4-methoxybenzene (3n)

^{1}H NMR

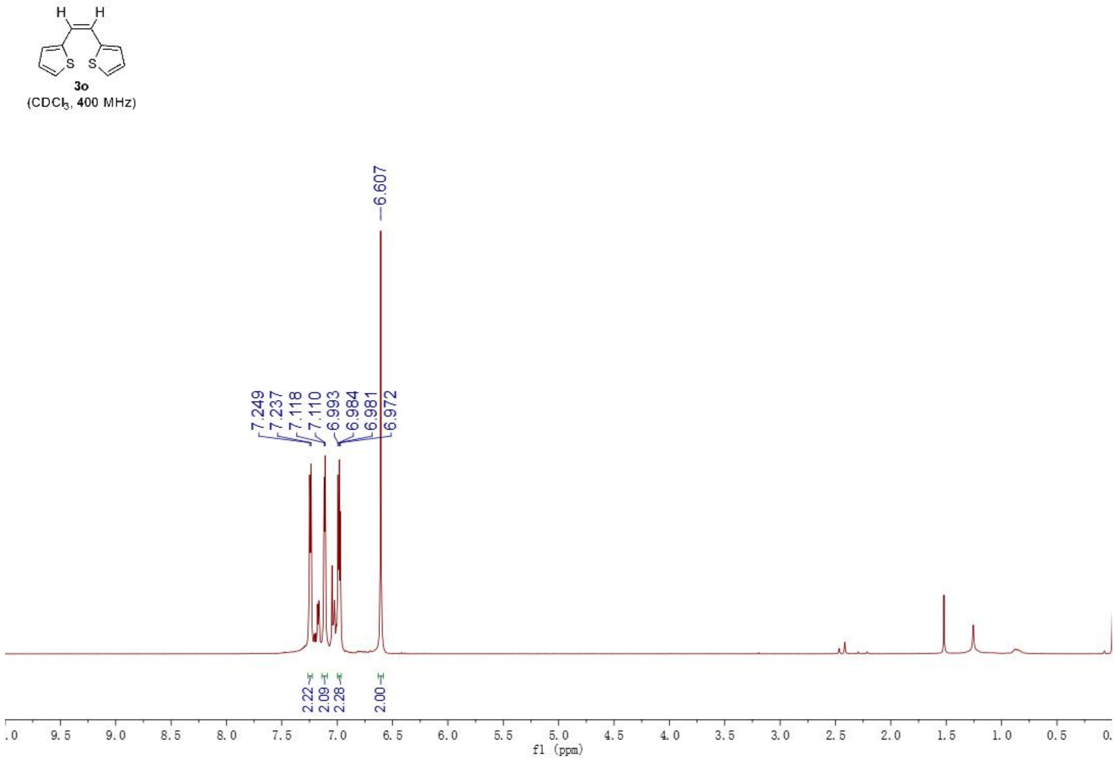


^{13}C NMR

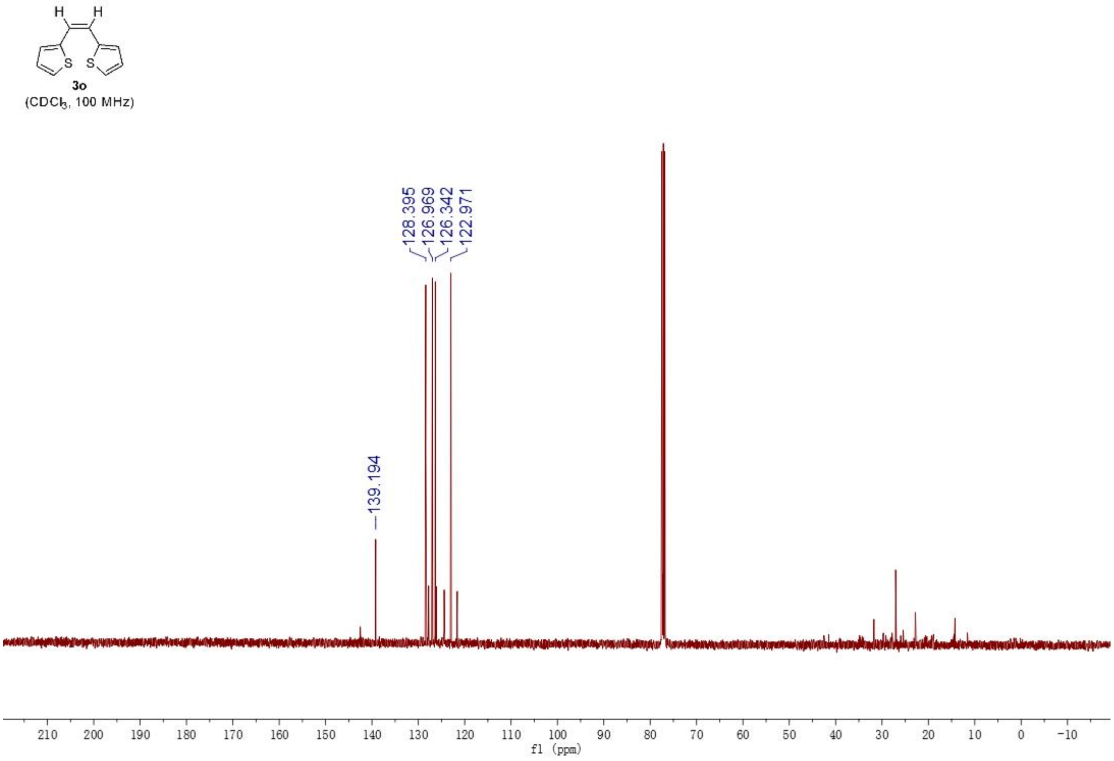


(Z)-1,2-di(thiophen-2-yl)ethene (3o)

^{1}H NMR



^{13}C NMR



(Z)-1,2-di(thiophen-2-yl)ethene (3o)

^{1}H NMR