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Supporting Information

A Simple and Direct Method for the Palladium-Catalyzed Oxidative Coupling of Unactivated Allylarenes with Classic Arenes

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Experimental procedures and analytical data

Contents:

1. General consideration

^{1}H and ^{13}C NMR spectra were recorded on a Bruker DPX400 NMR spectrometer, the chemical shift values are refered to δ_{TMS} = 0.00 ppm and solvent residues of $CDCl_3$ are ($\delta(^{1}H)$, 7.26 ppm and $\delta(^{13}C)$, 77.16 ppm). ^{19}F NMR was recorded on a Bruker DPX400 NMR spectrometer ($CFCl_3$ as outside standard and positive low field). Chemical shifts (δ) are reported in ppm; coupling constants (*J*) are reported in Hz. Standard abbreviations are used: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. HRMS analysis was carried out on a Waters-Micromass GCT permier mass spectrometer operated in electron ionization mode. X-ray crystallographic study was performed by a Bruker CCD area detector diffractometer. Analytical TLC plates, Merck KGaA silica gel 60_{F254} were viewed by UV light (254 nm). Column chromatographic purification was performed on SDZF silica gel 160.

All the chemical reagents were purchased from commercial sources and used as received unless otherwise indicated. Benzene, toluene, *o*-xylene, *m*-xylene and *p*-xylene were freshly distilled from sodium/benzophenone and stored over 4A molecular sieve.

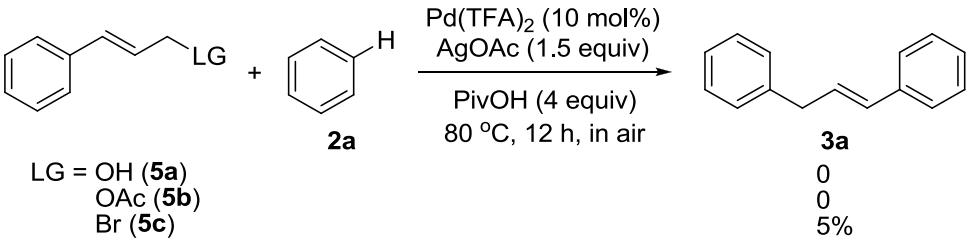
2. Experimental procedures

2.1. A typical procedure for the direct oxidative coupling of unactivated allylarenes 1 with classic arenes 2-*Synthesis of (E)-prop-1-ene-1,3-diyldibenzene (3a)*: A mixture of **1a** (59 mg, 0.5 mmol), $Pd(TFA)_2$ (17 mg, 0.05 mmol), AgOAc (125 mg, 0.75 mmol) and PivOH (204 mg, 2 mmol) in benzene **2a** (3 mL) was stirred at 80 ^oC for 12 h. After cooling to ambient temperature, the resultant mixture was filtered through a short pad of celite and rinsed with 10 mL DCM. The organic phase was removed under reduced pressure. The resultant residue was purified by silica gel column chromatography (eluent: petroleum ether (35-60 ^oC)) to afford **3a** as a colorless liquid (58 mg, 60%).

2.2. A typical procedure for the hydrogenation of 3/3′-*Synthesis of 1-methyl-4-(3-phenylpropyl)benzene (3d′′)*: The mixture of **3d/3d′** (40 mg, 0.19 mmol) was dissolved in EtOH (5 mL), and a catalytic amount of Pd/C (5 mg, 10 mol%) was added. The air in the flask was exchanged to hydrogen, using a pump and a hydrogen balloon, repeated thrice. Another hydrogen balloon was connected to the flask and the mixture was stirred vigorously for 12 hours. After the reaction had finished, the crude mixture was filtered, concentrated in vacuo and purified by silica gel column chromatography (eluent: petroleum ether (35-60 ^oC)) to afford **3d′′** as a colorless liquid (36 mg, 90%). **3f′′** was obtained in 94% yield under the same method.

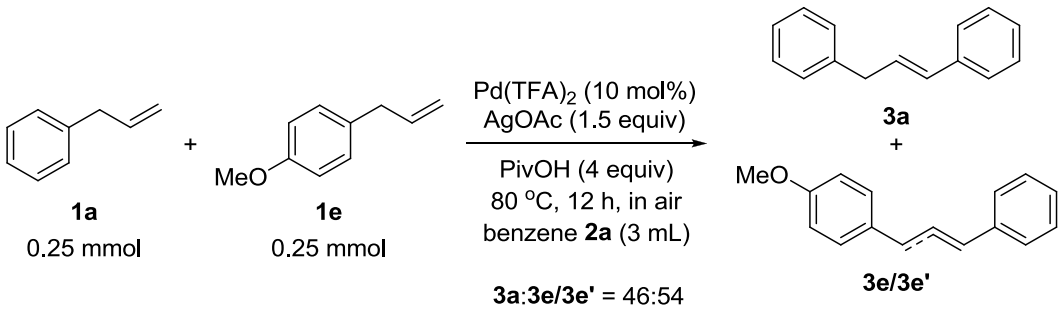
2.3. A typical procedure for the direct oxidative coupling of homoallylbenzene 1j with benzene 2a-*Synthesis of (E)-but-1-ene-1,4-diyldibenzenee (3j)*: A mixture of **1j** (66 mg, 0.5 mmol), $Pd(TFA)_2$ (17 mg, 0.05 mmol), AgOAc (125 mg, 0.75 mmol) and PivOH (204 mg, 2 mmol) in benzene **2a** (3 mL) was stirred at 80 ^oC for 12 h. After cooling to ambient temperature, the resultant mixture was filtered through a short pad of celite and rinsed with 10 mL DCM. The organic phase was removed under reduced pressure. The resultant residue was purified by silica gel column chromatography (eluent: petroleum ether (35-60 ^oC)) to afford **3j** as a colorless liquid (54 mg, 52%).

2.4. A typical procedure for the control experiment

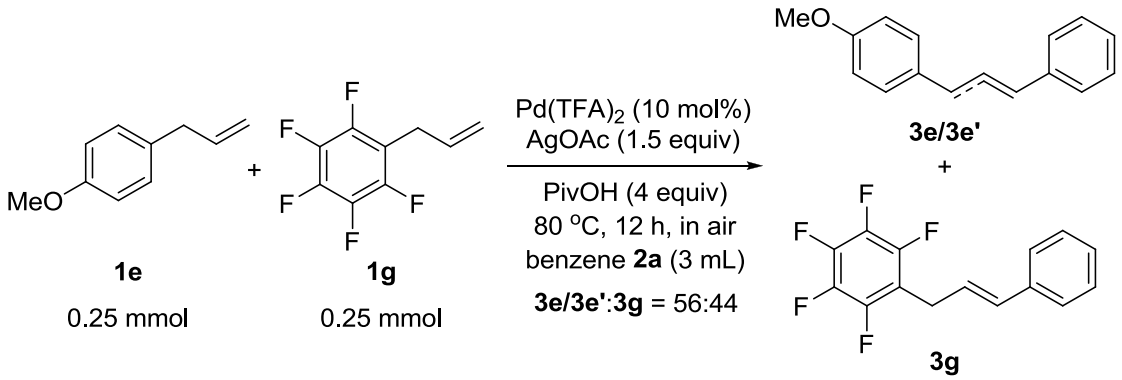


A mixture of **5c** (63 mg, 0.32 mmol), $Pd(TFA)_2$ (11 mg, 0.032 mmol), AgOAc (80 mg, 0.48 mmol) and PivOH (131 mg, 1.28 mmol) in benzene (2 mL) was stirred at 80 ^{o}C for 40 h. After cooling to ambient temperature, the resultant mixture was filtered through a short pad of celite and rinsed with 10 mL DCM. The organic phase was removed under reduced pressure. The resultant residue was purified by silica gel column chromatography (eluent: petroleum ether (35-60 ^{o}C)) to afford **3a** as a colorless liquid (3 mg, 5%).

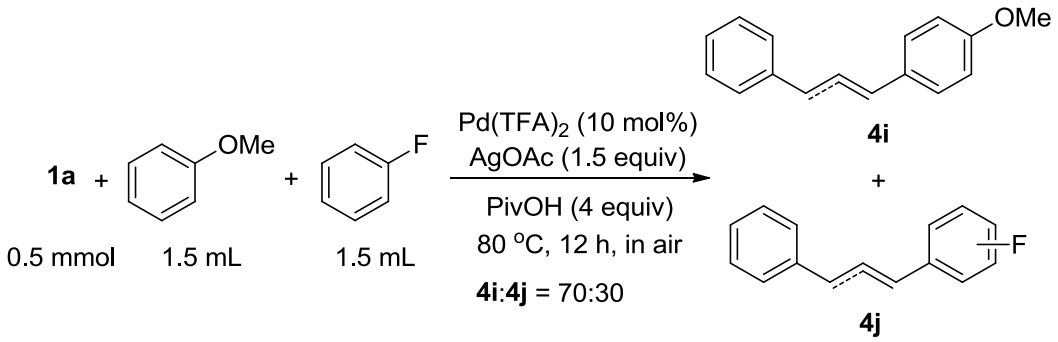
3. Intermolecular competition experiment



A mixture of **1a** (30 mg, 0.25 mmol), **1e** (37 mg, 0.25 mmol), $Pd(TFA)_2$ (17 mg, 0.05 mmol), AgOAc (125 mg, 0.75 mmol) and PivOH (204 mg, 2.0 mmol) in benzene (3.0 mL) was stirred at 80 ^{o}C for 12 h. After cooling to ambient temperature, the resultant mixture was filtered through a short pad of celite and rinsed with 10 mL DCM. The organic phase was removed under reduced pressure. The resultant residue was purified by silica gel column chromatography (eluent: petroleum ether (35-60 ^{o}C)) to afford **3a** (24 mg, 48%) and **3e/3e′** (32 mg, 57%).

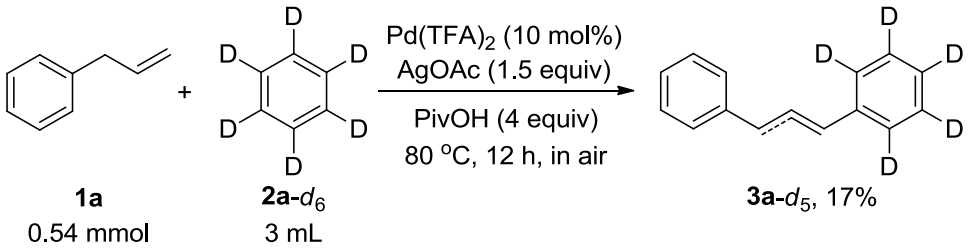


A mixture of **1e** (37 mg, 0.25 mmol), **1g** (52 mg, 0.25 mmol), $Pd(TFA)_2$ (17 mg, 0.05 mmol), AgOAc (125 mg, 0.75 mmol) and PivOH (204 mg, 2.0 mmol) in benzene (3.0 mL) was stirred at 80 ^{o}C for 12 h. After cooling to ambient temperature, the resultant mixture was filtered through a short pad of celite and rinsed with 10 mL DCM. The organic phase was removed under reduced pressure. The resultant residue was purified by silica gel column chromatography (eluent: petroleum ether (35-60 ^{o}C)) to afford **3e/3e′** (36 mg, 65%) and **3g** (37 mg, 52%).

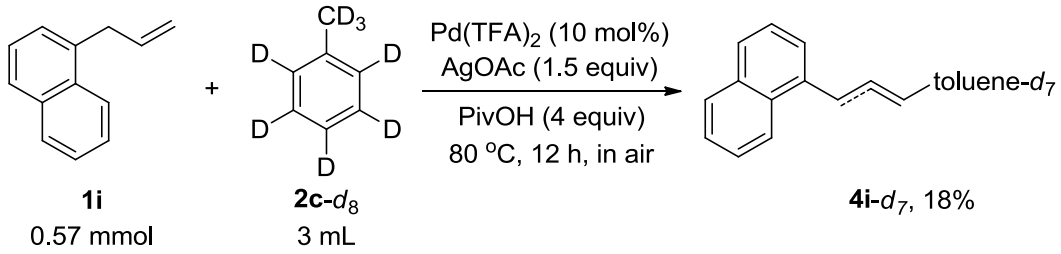


A mixture of **1a** (59 mg, 0.5 mmol), $Pd(TFA)_2$ (17 mg, 0.05 mmol), AgOAc (125 mg, 0.75 mmol) and PivOH (204 mg, 2.0 mmol) in anisole (1.5 mL)/fluorobenzene (1.5 mL) was stirred at 80 ^{o}C for 12 h. After cooling to ambient temperature, the resultant mixture was filtered through a short pad of celite and rinsed with 10 mL DCM. The organic phase was removed under reduced pressure. The resultant residue was purified by silica gel column chromatography (eluent: petroleum ether (35-60 ^{o}C)) to afford **4i** (34 mg, 30%) and **4j** (14 mg, 13%).

4. Kinetic isotopic effect study

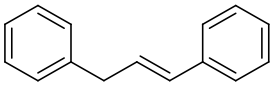


A mixture of **1a** (64 mg, 0.54 mmol), $Pd(TFA)_2$ (18 mg, 0.054 mmol), AgOAc (135 mg, 0.81 mmol) and PivOH (221 mg, 2.16 mmol) in benzene-d_6 (3 mL) was stirred at 80 ^{o}C for 12 h. After cooling to ambient temperature, the resultant mixture was filtered through a short pad of celite and rinsed with 10 mL DCM. The organic phase was removed under reduced pressure. The resultant residue was purified by silica gel column chromatography (eluent: petroleum ether (35-60 ^{o}C)) to afford **3a**-d_5 as a colorless liquid (18 mg, 17%).

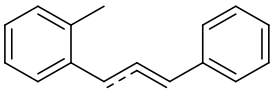


A mixture of **1i** (96 mg, 0.57 mmol), $Pd(TFA)_2$ (19 mg, 0.057 mmol), AgOAc (143 mg, 0.85 mmol) and PivOH (233 mg, 2.3 mmol) in toluene-d_8 (3 mL) was stirred at 80 ^{o}C for 12 h. After cooling to ambient temperature, the resultant mixture was filtered through a short pad of celite and rinsed with 10 mL DCM. The organic phase was removed under reduced pressure. The resultant residue was purified by silica gel column chromatography (eluent: petroleum ether (35-60 ^{o}C)) to afford **4i**-d_7 as a colorless liquid (27 mg, 18%).

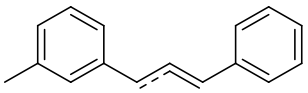
5. Analytical data

 **3a**

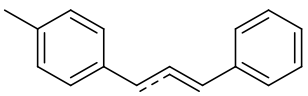
3a Colorless liquid. ^{1}H NMR ($CDCl_3$, 400 MHz)□ δ 7.47-7.28 (m, 10 H), 6.56 (d, *J* = 15.8 Hz, 1 H), 6.46 (dt, *J* = 15.7, 6.6 Hz, 1 H), 3.65 (d, *J* = 6.6 Hz, 2 H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 140.3, 137.6, 131.2, 129.3, 128.8, 128.6, 127.2, 126.3, 126.2, 39.5. HRMS Cacld for $C_{15}H_{14}$: 194.1096; Found: 194.1094.

 **3b/3b′**

3b/3b′ = 42:58. Colorless liquid. ^{1}H NMR ($CDCl_3$, 400 MHz)□ δ 7.55-7.24 (m, 9 H), 6.78 (d, *J* = 15.6 Hz, 0.4 H), 6.51-6.31 (m, 1.6 H), 3.69 (d, *J* = 6.9 Hz, 0.8 H), 3.64 (d, *J* = 4.8 Hz, 1.2 H), 2.46 (s, 1.3 H), 2.45 (s, 1.7 H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 140.4, 138.3, 137.6, 136.7, 136.5, 135.2, 131.0, 130.6, 130.3 x 2, 129.3, 129.1, 128.7, 128.6 x 2, 127.2, 126.5, 126.3, 126.2 x 3, 125.7, 39.8, 37.0, 20.0, 19.6. HRMS Cacld for $C_{16}H_{16}$: 208.1252; Found: 208.1244.

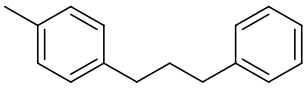
 **3c/3c′**

3c/3c′ Colorless liquid. The ratio of **3c/3c′** can not be determined by ^{1}H NMR spectroscopy. ^{1}H NMR ($CDCl_3$, 400 MHz)□ δ 7.47-7.28 (m, 7 H), 7.16-7.14 (m, 2 H), 6.57-6.41 (m, 2 H), 3.64-3.60 (m, 2 H), 2.43 (s, 2 H), 2.42 (s, 1 H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 140.4, 140.2, 138.2, 138.1, 137.6, 137.5, 131.2, 131.1, 129.6, 129.5, 129.1, 128.8, 128.6, 128.5, 128.0, 127.2, 127.0 x 2, 126.2, 125.8, 123.4, 39.5, 39.4, 21.5. HRMS Cacld for $C_{16}H_{16}$: 208.1252; Found: 208.1253.

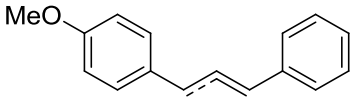
 **3d/3d′**

3d/3d′ = 47:53. Colorless liquid. ^{1}H NMR ($CDCl_3$, 400 MHz)□ δ 7.45-7.18 (m, 9 H), 6.56-6.36 (m, 2 H), 3.63 (d, *J* = 6.8 Hz, 1.1 H), 3.60 (d, *J* = 6.7 Hz, 0.9 H), 2.43 (s, 1.4 H), 2.41 (s, 1.6 H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 140.5, 137.7, 137.2, 136.9, 135.8, 134.8, 131.0 x 2, 129.6, 129.3 x 2, 128.8, 128.7, 128.6 x 2, 128.3, 127.2, 126.2 x

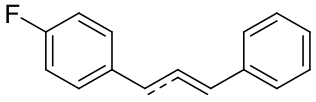
2, 126.1, 39.5, 39.1, 21.3, 21.2. HRMS Cacld for $C_{16}H_{16}$: 208.1252; Found: 208.1260.

 **3d″**

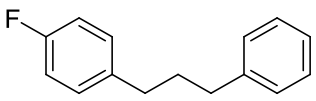
3d″ Colorless liquid. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.33-7.29 (m, 2 H), 7.23-7.19 (m, 3 H), 7.14-7.09 (m, 4 H), 2.70-2.63 (m, 4 H), 2.35 (s, 3 H), 2.01-1.94 (m, 2 H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 142.5, 139.3, 135.3, 129.1, 128.6, 128.5, 128.4, 125.8, 35.6, 35.1, 33.2, 21.1. HRMS Cacld for $C_{16}H_{18}$: 210.1409; Found: 210.1405.

 **3e/3e′**

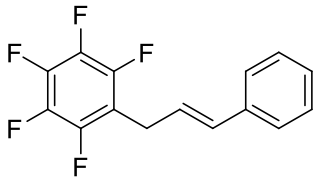
3e/3e′ = 48:52. Colorless liquid. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.43-7.22 (m, 7 H), 6.94-6.89 (m, 2 H), 6.52-6.25 (m, 2 H), 3.85 (s, 3 H), 3.59 (d, *J* = 6.8 Hz, 1 H), 3.56 (d, *J* = 6.4 Hz, 1 H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 159.0, 158.2, 140.6, 137.6, 132.3, 130.8, 130.5, 130.4, 129.8, 129.7, 128.8, 128.6 x 2, 127.3, 127.2, 126.2, 114.0, 55.4, 39.4, 38.6. HRMS Cacld for $C_{16}H_{16}O$: 224.1201; Found: 224.1205.

 **3f/3f′**

3f/3f′ = 56:44. Colorless liquid. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.46-7.26 (m, 7 H), 7.10-7.04 (m, 2 H), 6.55-6.32 (m, 2 H), 3.62 (d, *J* = 7.1 Hz, 0.9 H), 3.60 (d, *J* = 6.8 Hz, 1.1 H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 163.4, 162.8, 160.9, 160.4, 140.2, 137.4, 135.9, 135.8, 133.8, 133.7, 131.3, 130.2, 130.1, 130.0, 129.1 x 3, 128.8, 128.7, 127.7, 127.6, 127.3, 126.4, 126.3, 115.6, 115.4 x 2, 115.2, 39.4, 38.6; ^{19}F NMR ($CDCl_3$, 373 MHz) δ -115.2 (d, *J* = 2.2 Hz), -117.1 (d, *J* = 2.5 Hz). HRMS Cacld for $C_{15}H_{13}F$: 212.1001; Found: 212.0991.

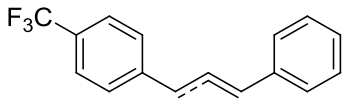
 **3f″**

3f″ Colorless liquid. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.34-7.28 (m, 2 H), 7.24-7.14 (m, 5 H), 7.01-6.97 (m, 2 H), 2.69-2.63 (m, 4 H), 2.01-1.93 (m, 2 H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 162.4, 142.3, 138.0, 129.9, 129.8, 128.6, 128.5, 125.9, 115.3, 115.0, 35.5, 34.7, 33.2; ^{19}F NMR ($CDCl_3$, 373 MHz) δ -117.9. HRMS Cacld for $C_{15}H_{15}F$: 214.1158; Found: 214.1160.



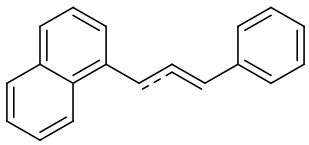
3g

3g White solid. ^{1}H NMR ($CDCl_3$, 400 MHz)□ δ 7.42-7.26 (m, 5 H), 6.53 (d, *J* = 15.7 Hz, 1 H), 6.27 (dt, *J* = 15.6, 6.8 Hz, 1 H), 3.64 (dd, *J* = 6.6, 1.0 Hz, 2 H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 146.4, 143.9, 138.9, 136.7, 132.6, 128.7, 127.8, 126.4, 124.4, 113.4 x 2, 113.2 x 2, 25.8; ^{19}F NMR ($CDCl_3$, 373 MHz) δ -143.9 (dd, *J* = 22.4, 8.5 Hz), -157.3 (t, *J* = 20.8 Hz), 162.6 (td, *J* = 22.1, 8.4 Hz). HRMS Cacld for $C_{15}H_9F_5$: 284.0624; Found: 284.0621.



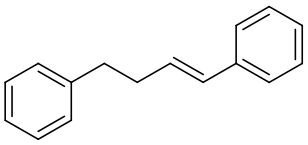
3h/3h′

3h/3h′ = 66:34. Colorless liquid. ^{1}H NMR ($CDCl_3$, 400 MHz)□ δ 7.66-7.61 (m, 2 H), 7.51-7.28 (m, 7 H), 6.58-6.54 (m, 1.3 H), 6.44-6.37 (m, 0.6 H), 3.68-3.65 (m, 2 H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 144.4, 143.6, 141.1, 140.0, 137.3, 132.3, 132.1, 129.9, 129.1, 128.9, 128.8, 128.7 x 2, 128.6, 128.5, 128.0, 127.5, 126.5, 126.4, 126.3, 125.8, 125.7, 125.6 x 3, 125.5 x 2, 123.1 x 2, 39.5, 39.2; ^{19}F NMR ($CDCl_3$, 373 MHz) δ -62.2 (d, *J* = 40.0 Hz). HRMS Cacld for $C_{16}H_{13}F_3$: 262.0969; Found: 262.0974.



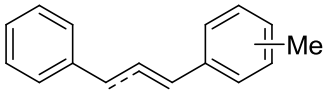
3i/3i′

3i/3i′ = 69:31. White solid. ^{1}H NMR ($CDCl_3$, 400 MHz)□ δ 8.27-8.20 (m, 1 H), 8.01-7.95 (m, 1 H), 7.90-7.86 (m, 1 H), 7.72-7.28 (m, 9 H), 6.68-6.48 (m, 1.5 H), 4.11 (d, *J* = 4.7 Hz, 1.3 H), 3.80 (d, *J* = 6.8 Hz, 0.6 H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 140.3, 137.6, 136.3, 135.4, 134.0, 133.7, 132.5, 132.1, 131.4, 131.3, 129.0, 128.8, 128.7, 128.6 x 2, 128.5, 128.4, 127.6, 127.2, 126.5, 126.3, 126.2, 126.1, 126.0, 125.8 x 2, 125.7, 124.1, 124.0, 123.8, 39.8, 36.5. HRMS Cacld for $C_{19}H_{16}$: 244.1252; Found: 244.1258.



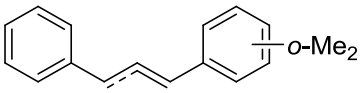
3j

3j Colorless liquid.^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.43-7.35 (m, 6 H), 7.32-7.28 (m, 4 H), 6.50 (d, *J* = 15.8 Hz, 1 H), 6.34 (dt, *J* = 15.8, 6.7 Hz, 1 H), 2.88 (t, 2 H), 2.62 (q, 2 H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 141.9, 137.8, 130.6, 130.1, 128.6, 128.5, 127.1, 126.1, 126.0, 36.0, 35.0. HRMS Cacld for $C_{16}H_{16}$: 208.1259; Found: 208.1252.



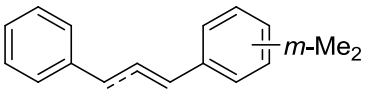
4a/**4a′**

4a/**4a′** Colorless liquid. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.43-7.11 (m, 9 H), 6.53-6.39 (m, 2 H), 3.66-3.58 (m, 2 H), 2.41-2.40 (m, 2 H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 140.4, 140.3, 138.1, 137.7, 137.6, 136.9, 134.8, 131.3, 131.1, 129.6, 129.5, 129.3, 129.1, 128.8, 128.7, 128.6, 128.5, 128.3, 128.0, 127.2, 127.0, 126.3, 126.2, 123.4, 39.5, 39.1, 21.5, 21.3. HRMS Cacld for $C_{16}H_{16}$: 208.1252; Found: 208.1259.



4b/**4b′**

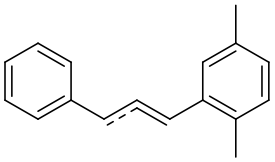
4b/**4b′** Colorless liquid. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.48-7.09 (m, 8 H), 6.85 (d, *J* = 15.4 Hz, 0.1 H), 6.57 (d, *J* = 16.4 Hz, 0.5 H), 6.51-6.38 (m, 1.2 H), 3.70-3.59 (m, 1 H), 2.42 -2.35 (m, 6 H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 140.5, 137.7 x 2, 136.7, 136.6, 135.6, 135.3, 134.4, 131.1, 130.1, 129.9 x 2, 129.7, 129.1, 128.8, 128.6 x 2, 128.1, 127.5, 127.4, 127.1, 126.2 x 2, 126.1, 123.7, 39.5, 39.1, 19.9, 19.6, 19.5. HRMS Cacld for $C_{17}H_{18}$: 222.1409; Found: 222.1419.



4c/**4c′**

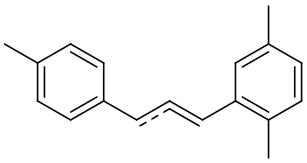
4c/**4c′** Colorless liquid. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.47-6.98 (m, 8 H), 6.76 (d, *J* = 15.6 Hz, 0.3 H), 6.59-6.40 (m, 1.3 H), 6.34-6.27 (m, 0.3 H), 3.69-3.59 (m, 2 H), 2.43 -2.41 (m, 6 H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 140.6, 138.1, 138.0, 137.7, 136.8, 136.3, 136.0, 135.2, 135.0, 133.9, 131.3, 131.2, 131.1, 130.9, 130.8, 129.7, 129.6, 129.3, 129.0, 128.8, 128.7, 128.6, 127.9, 127.1, 126.9, 126.8, 126.6, 126.2 x 3, 125.6, 124.2, 39.8, 39.5, 39.4, 36.6, 21.4, 21.2, 21.1, 19.9, 19.5. HRMS Cacld for $C_{17}H_{18}$:

222.1409; Found: 222.1413.



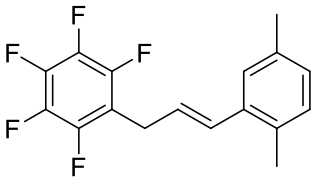
4d/4d′

4d/4d′ = 53:47. Colorless liquid. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.46-7.28 (m, 6 H), 7.18-7.13 (m, 1.6 H), 7.09-7.05 (m, 1 H), 6.77 (d, *J* = 15.6 Hz, 0.4 H), 6.51-6.30 (m, 1.5 H), 3.68 (d, *J* = 7.0 Hz, 1 H), 3.60 (d, *J* = 5.3 Hz, 1 H), 2.42 (s, 3.3 H), 2.40 (s, 2.7 H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 140.5, 138.1, 137.7, 136.4, 135.6, 135.4, 133.3, 132.1, 130.9, 130.3, 130.2, 130.1, 129.2, 128.8 x 2, 128.6, 127.9, 127.2, 127.1, 126.3 x 2, 126.2, 39.8, 37.0, 21.1 x 2, 19.5, 19.1. HRMS Cacld for $C_{19}H_{16}$: 222.1409; Found: 222.1413.



4e/4e′

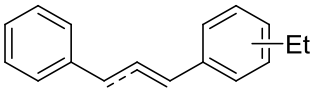
4e/4e′ = 58:42. Colorless liquid. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.32-7.00 (m, 7 H), 6.91 (d, 0.4 H, *J* = 15.6 Hz), 6.44-6.23 (m, 1.5 H), 3.59 (d, 0.8 H, *J* = 6.9 Hz), 3.54 (d, 1.2 H, *J* = 6.0 Hz), 2.40-2.35 (m, 9 H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 138.3, 137.4, 136.8, 136.5, 135.7, 135.6, 135.4, 134.9, 133.3, 132.1, 130.8, 130.6, 130.2, 130.1, 129.3, 129.0, 128.6, 127.9, 127.7, 127.1, 126.4, 126.1, 39.4, 37.0, 21.3, 21.1 x 3, 19.5, 19.1. HRMS Cacld for $C_{18}H_{20}$: 236.1565; Found: 236.1566.



4f

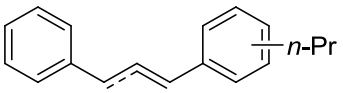
4f Colorless liquid. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.24 (s, 1 H), 7.08 (d, *J* = 7.6 Hz, 1 H), 7.02 (d, *J* = 7.6 Hz, 1 H), 6.77 (d, *J* = 15.5 Hz, 1 H), 6.12 (dt, *J* = 15.2, 6.8 Hz, 1 H), 3.67 (d, *J* = 6.8 Hz, 2 H), 2.35 (d, *J* = 5.7 Hz, 6 H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 146.4, 144.0, 141.2, 138.8, 136.4, 135.6 x 2, 132.4, 130.8, 130.3, 128.5, 126.3, 125.4, 113.7, 113.6, 113.5, 29.9, 21.0, 19.3; ^{19}F NMR ($CDCl_3$, 373 MHz) δ -144.0 to -144.1 (m, 2 F), -157.4 to -157.5 (m, 1 F), -162.6 to -162.7 (m, 2 F). HRMS Cacld for

$C_{17}H_{13}F_5$: 312.0937; Found: 312.0933.



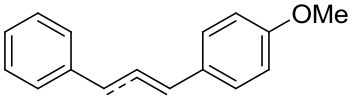
4g/**4g′**

4g/**4g′** Colorless liquid. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.45-7.14 (m, 9 H), 6.55-6.28 (m, 2 H), 3.67-3.59 (m, 2 H), 2.79-2.67 (m, 2 H), 1.34-1.29 (m, 3 H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 144.6 x 2, 143.4, 142.2, 140.5, 140.3, 137.7, 137.6, 137.5, 135.1, 131.4, 131.1, 131.0, 129.6, 129.5, 129.1, 128.8 x 2, 128.7, 128.6, 128.4, 128.1 x 2, 127.2, 126.9, 126.2, 126.1, 125.8, 123.7, 39.5 x 2, 39.1, 29.0. 28.7, 28.6, 15.8 x 2, 15.7. HRMS Cacld for $C_{17}H_{18}$: 222.1409; Found: 222.1415.



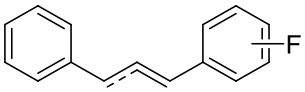
4h/**4h′**

4h/**4h′** Colorless liquid. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.45-7.12 (m, 9 H), 6.57-6.29 (m, 2 H), 3.67-3.60 (m, 2 H), 2.75-2.63 (m, 2 H), 1.75-1.69 (m, 2 H), 1.10-1.01 (m, 3 H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 143.1, 143.0, 141.8, 140.7, 140.5, 140.4, 140.1, 137.7, 137.5, 135.1, 131.4, 131.1 x 2, 130.9, 129.6, 129.5, 129.1, 129.0, 128.8 x 3, 128.7, 128.6, 128.5, 128.3, 127.5, 127.2, 126.4, 126.2, 126.1, 123.7, 39.5 x 2, 39.1, 38.2 x 2, 37.9, 37.8, 24.8, 24.7 x 2, 14.1, 14.0, 13.9. HRMS Cacld for $C_{18}H_{20}$: 236.1565; Found: 236.1570.



4i/**4i′**

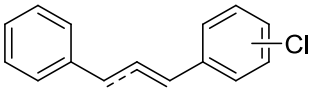
4i/**4i′** = 58:42. Colorless liquid. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.43-7.21 (m, 7 H), 7.03-6.82 (m, 2 H), 6.52-6.37 (m, 1.4 H), 6.32-6.25 (m, 0.4 H), 3.85 (s, 3 H), 3.59 (d, *J* = 7.0 Hz, 1.1 H), 3.55 (d, *J* = 6.4 Hz, 0.8 H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 158.9, 158.1, 140.5, 137.6, 130.5, 129.7 x 2, 128.7, 128.5 x 2, 127.3, 127.1, 126.2, 114.0, 55.3, 39.4, 38.5. HRMS Cacld for $C_{16}H_{16}O$: 224.1201; Found: 224.1209.



4j/**4j′**

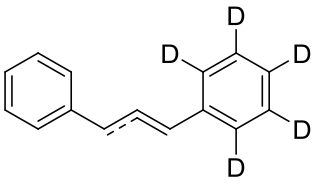
4j/**4j′** Colorless liquid. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.45-7.19 (m, 7 H), 7.16-6.94 (m, 2 H), 6.80 (d, *J* = 16.0 Hz, 0.2 H), 6.52-6.29 (m, 1.7 H), 3.62-3.55 (m, 2 H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 162.4, 161.9, 137.5, 131.6, 128.8, 128.7, 128.6,

128.4, 127.7, 127.3, 126.3, 115.5 x 2, 39.9, 39.4, 38.6, 32.4, 32.3; ^{19}F NMR ($CDCl_3$, 373 MHz) δ -113.5, -113.7, -115.3, -117.2, -118.4, -118.6. HRMS Cacld for $C_{15}H_{13}F$: 212.1001; Found: 212.1006.



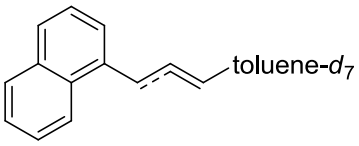
4k/**4k′**

4k/**4k′** Colorless liquid. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.49-7.16 (m, 9 H), 6.92 (d, *J* = 15.7 Hz, 0.1 H), 6.53-6.34 (m, 1.8 H), 3.79-3.55 (m, 2 H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 140.0, 139.8, 139.5, 138.0, 137.5, 137.3, 131.8, 130.1, 129.8, 129.6, 128.9, 128.8 x 2, 128.7, 128.6, 128.3, 127.4 x 2, 127.3, 127.2, 127.0 x 2, 126.5, 126.4 x 2, 126.3 x 2, 126.2, 124.5, 39.4 x 2, 39.1, 38.7, 36.9. HRMS Cacld for $C_{15}H_{13}Cl$: 228.0706; Found: 228.0702.



3a-d_5

3a-d_5 Colorless liquid. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.36-7.12 (m, 6 H), 6.46 (d, *J* = 15.7 Hz, 1 H), 6.39-6.32 (m, 1 H), 3.55 (d, *J* = 6.6 Hz, 2 H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 140.3, 137.6, 131.2 x 2, 129.4, 129.3, 128.8, 128.6, 127.2, 126.3 x 2, 39.5, 39.4. HRMS Cacld for $C_{15}H_9D_5$: 194.1409; Found: 194.1410.



4l-d_7

4l-d_7 Colorless liquid. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.20-8.11 (m, 1.5 H), 7.94-7.89 (m, 3 H), 7.67-7.45 (m, 6 H), 7.28-7.16 (m, 1 H), 6.76 (d, *J* = 15.7 Hz, 0.2 H), 6.58-6.40 (m, 2 H), 4.10-4.05 (m, 2 H), 3.72-3.69 (m, 1 H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 138.1, 137.5, 136.9, 136.8, 136.5, 136.4, 135.2, 134.8, 134.0, 132.2, 131.5, 131.3, 130.4, 130.3, 129.6, 129.5, 129.3 x 2, 128.8, 128.7 x 2, 128.6, 128.5, 128.0, 127.9, 127.8, 127.6, 127.2, 127.1 x 2, 127.0, 126.6, 126.5 x 2, 126.4, 126.3, 126.1, 126.0 x 3, 125.8 x 2, 125.7, 124.2, 124.0, 123.8, 123.4, 36.9, 36.5, 21.5, 21.3, 19.9. HRMS Cacld for $C_{20}H_{11}D_7$: 265.1848; Found: 265.1850.

6. The crystal structure of (*E*)-3i

X-Ray crystallographic study: Single crystal X-ray diffraction study for compound **(*E*)-3i** was carried out on a Bruker CCD area detector diffractometer with graphite-monochromated Mo Kα radiation (λ= 0.71073 Å). Cell parameters were obtained by global refinement of the positions of all collected reflections. Intensities were corrected for Lorentz and polarization effects and empirical absorption. The structure was solved by direct methods and refined by full-matrix least squares on F2. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were placed in calculated positions. Structure solution and refinement were performed by using the SHELXL-97 package. The X-ray crystallographic files, in CIF format, are available from the Cambridge Crystallographic Data Centre on quoting the deposition numbers CCDC 969149 for **(*E*)-3i**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 IEZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.ukor www: http://www. ccdc.cam.ac.uk).

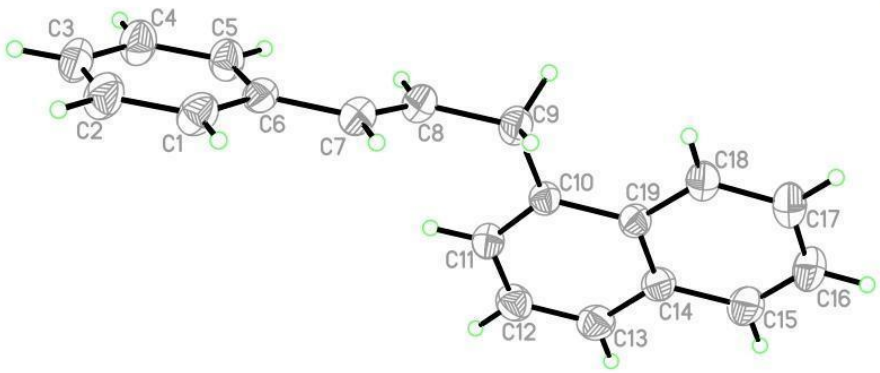
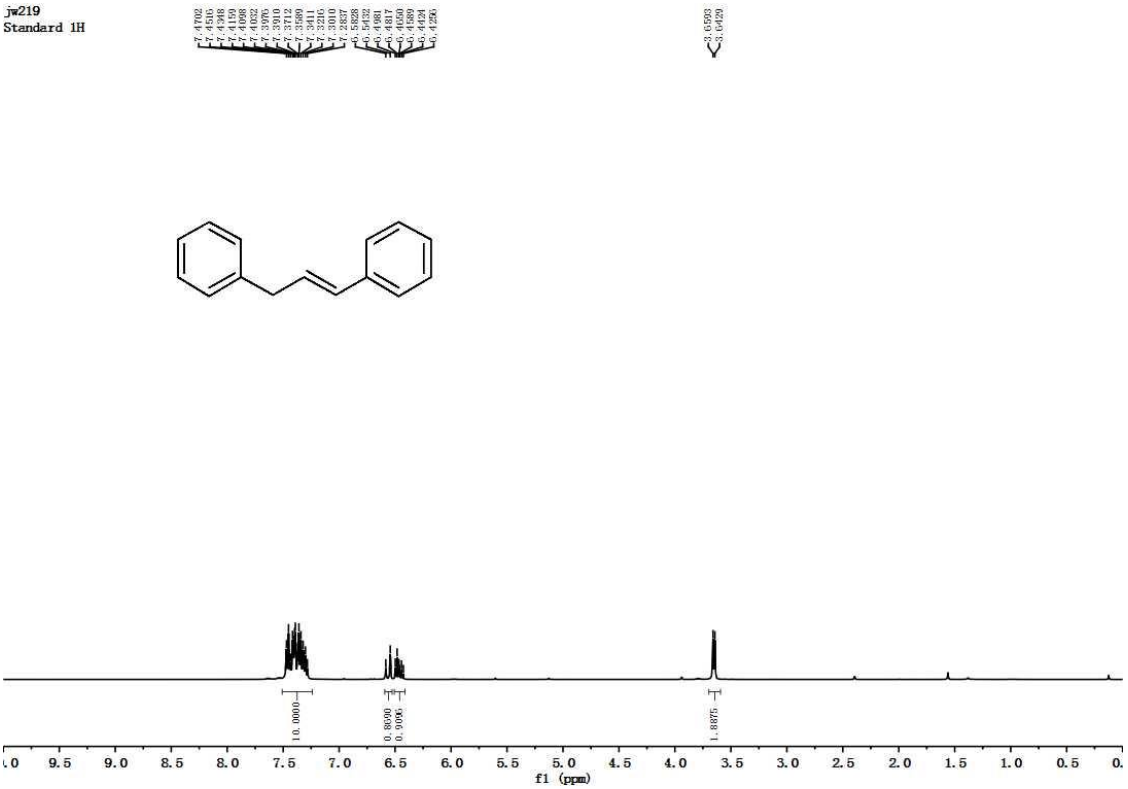
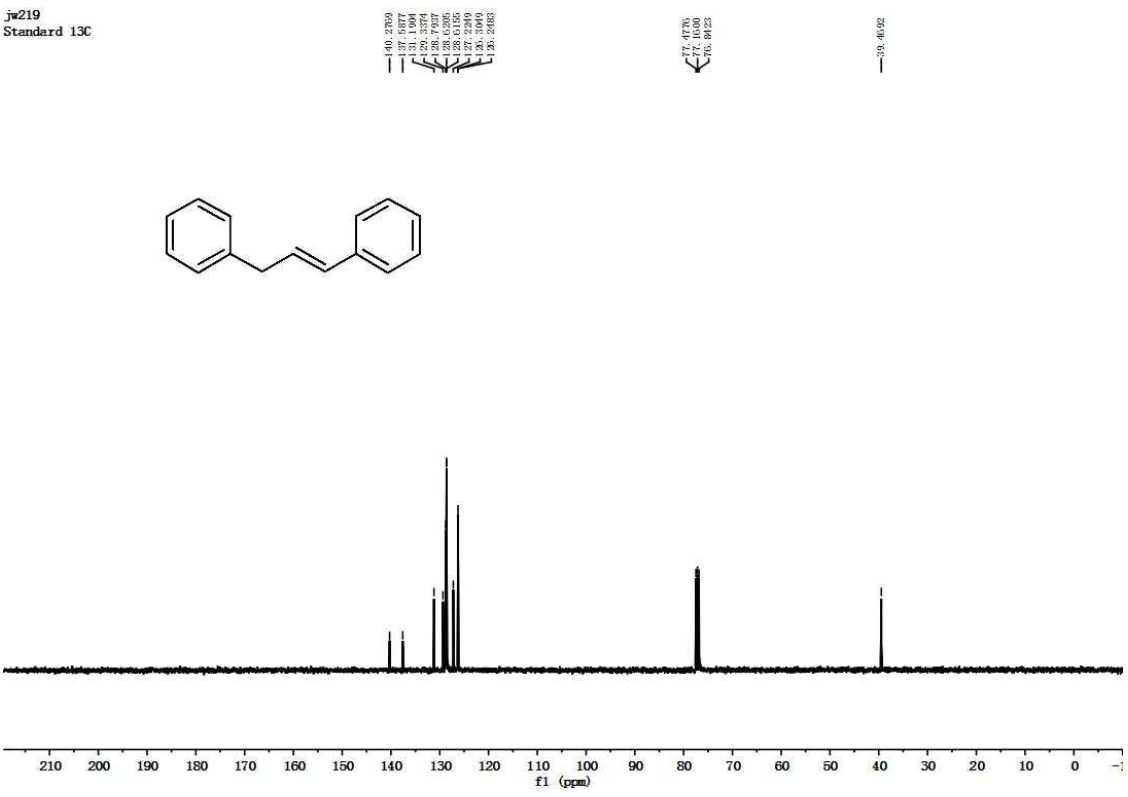
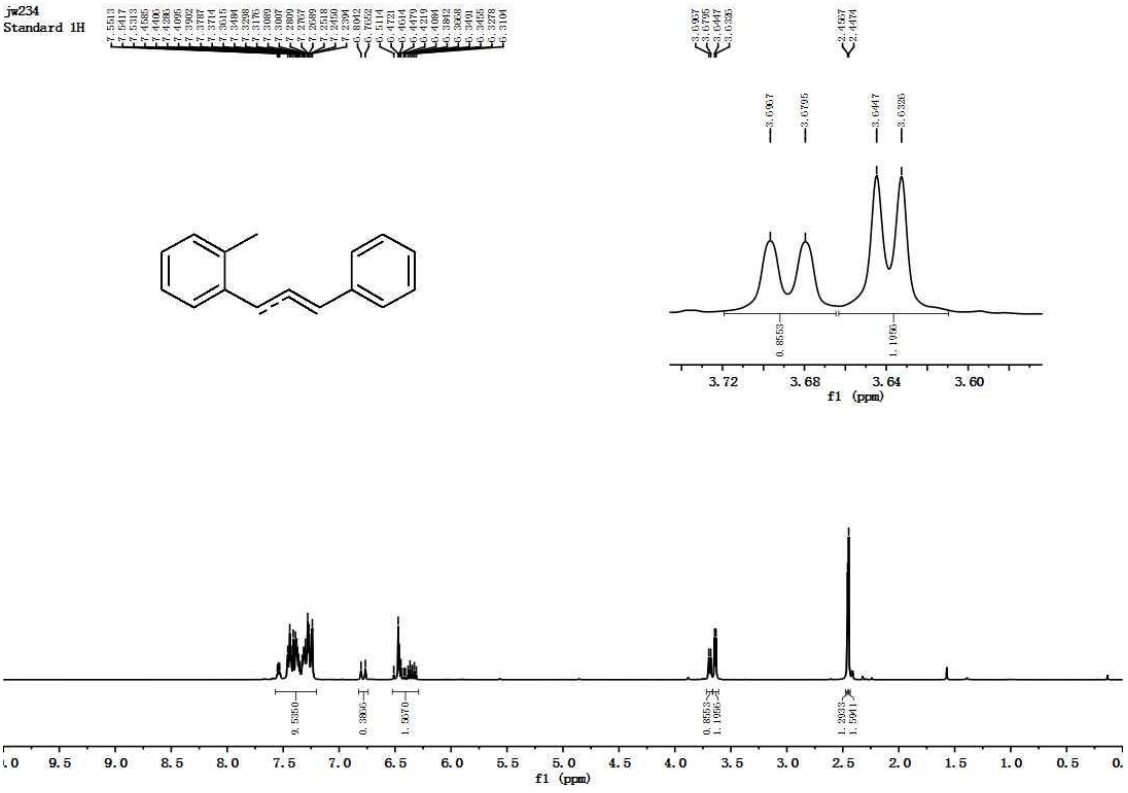


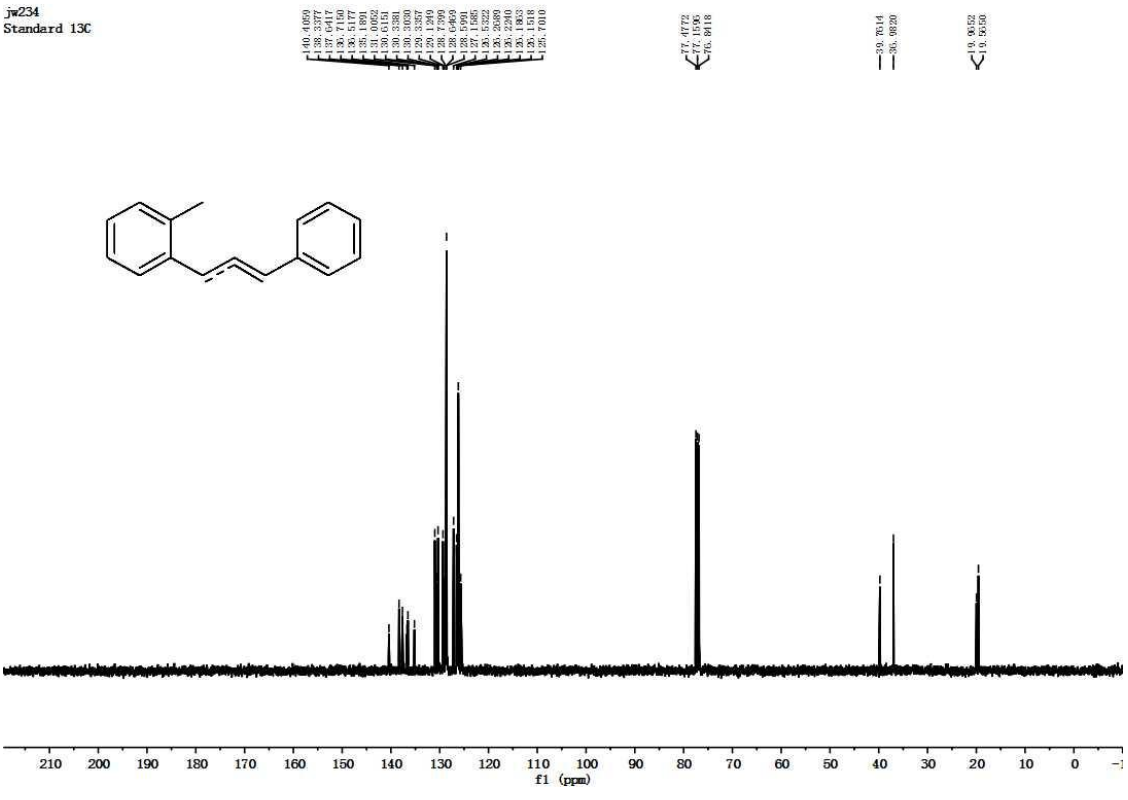
***Figure 1*. Molecular structure of (*E*)-3i.**

7. Copies of NMR and HRMS spectra

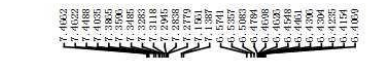


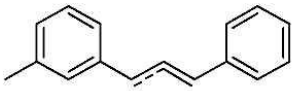


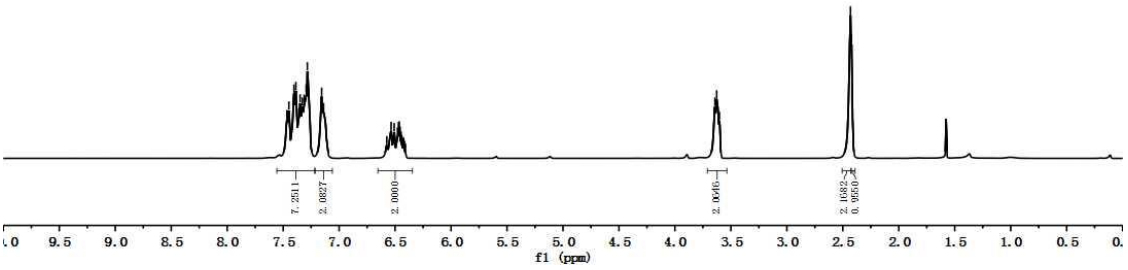

jw234
Standard 1H
3.6967
3.6795
3.6447
3.6295
2.4567
2.4474
0.8553
1.1960
3.72
3.68
3.64
3.60
f1 (ppm)
9.5350
0.3860
1.9570
0.8553
1.1960
1.2933
1.5941
f1 (ppm)


jw234
Standard 13C
77.4772
77.1596
76.8416
39.7614
36.9820
19.9652
19.5050
f1 (ppm)

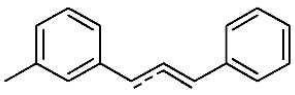
jw292
Standard 1H

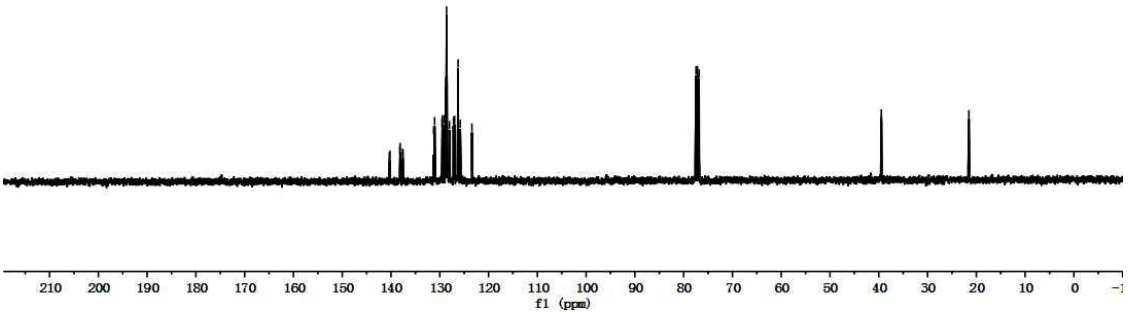


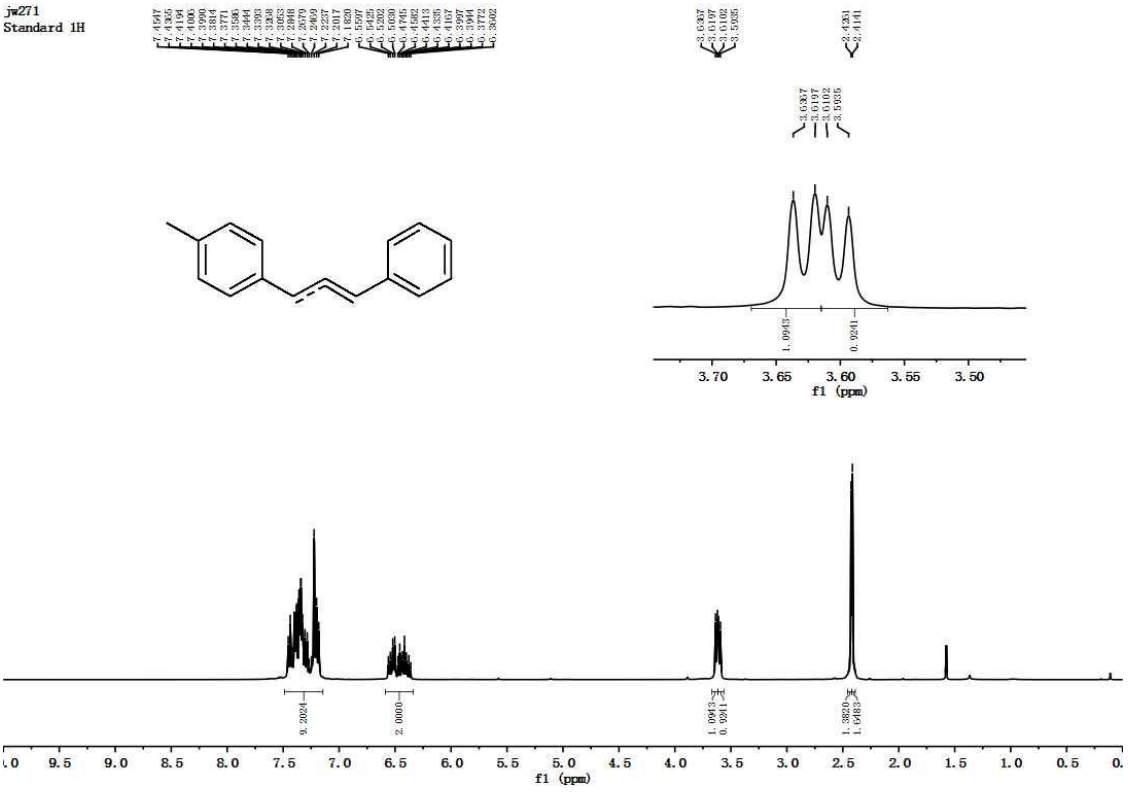


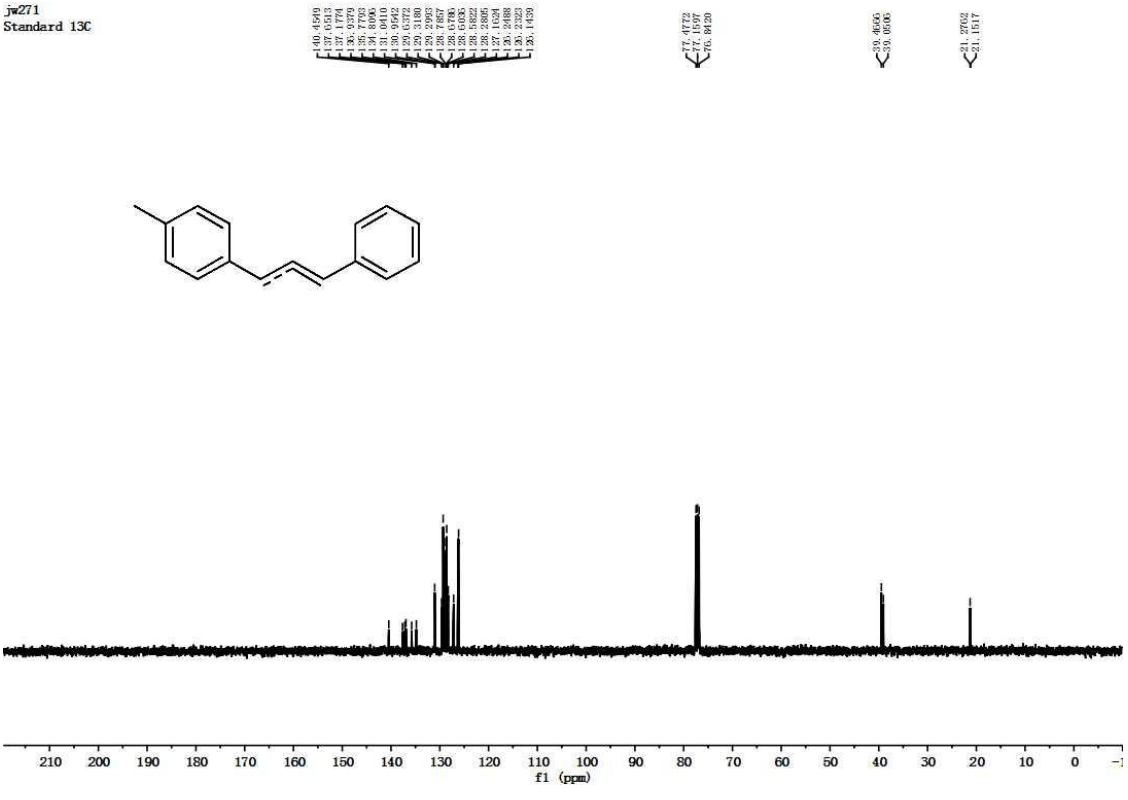


jw292
Standard 13C

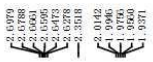


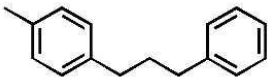


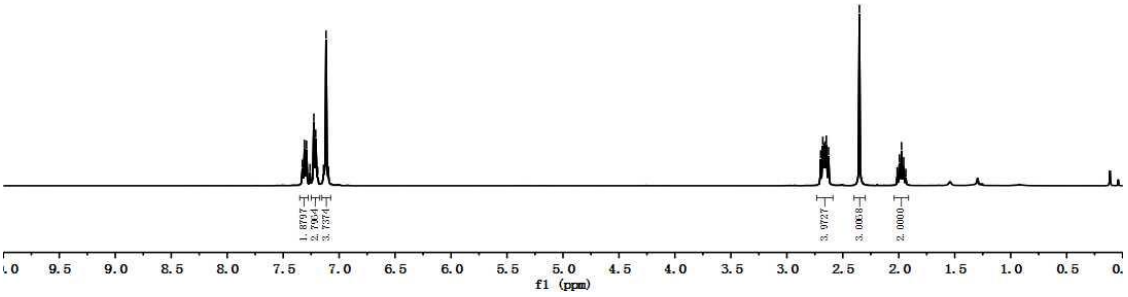

jw271
Standard 1H
f1 (ppm)


jw271
Standard 13C
f1 (ppm)

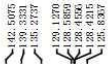
jw-336
Standard 1H

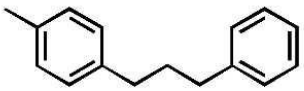


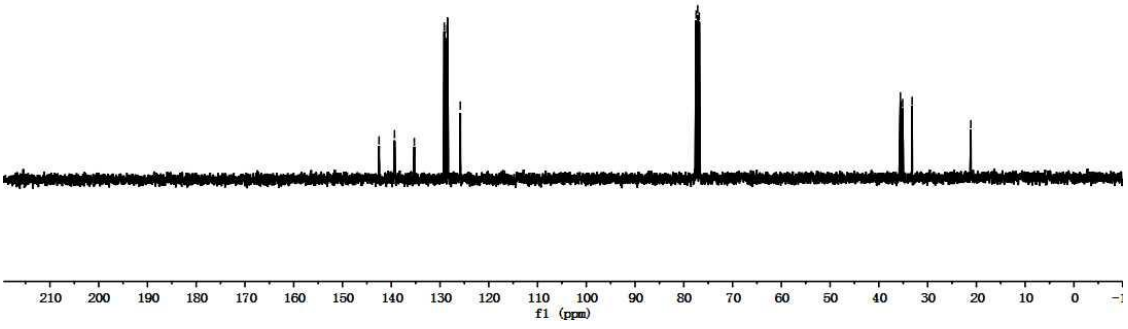


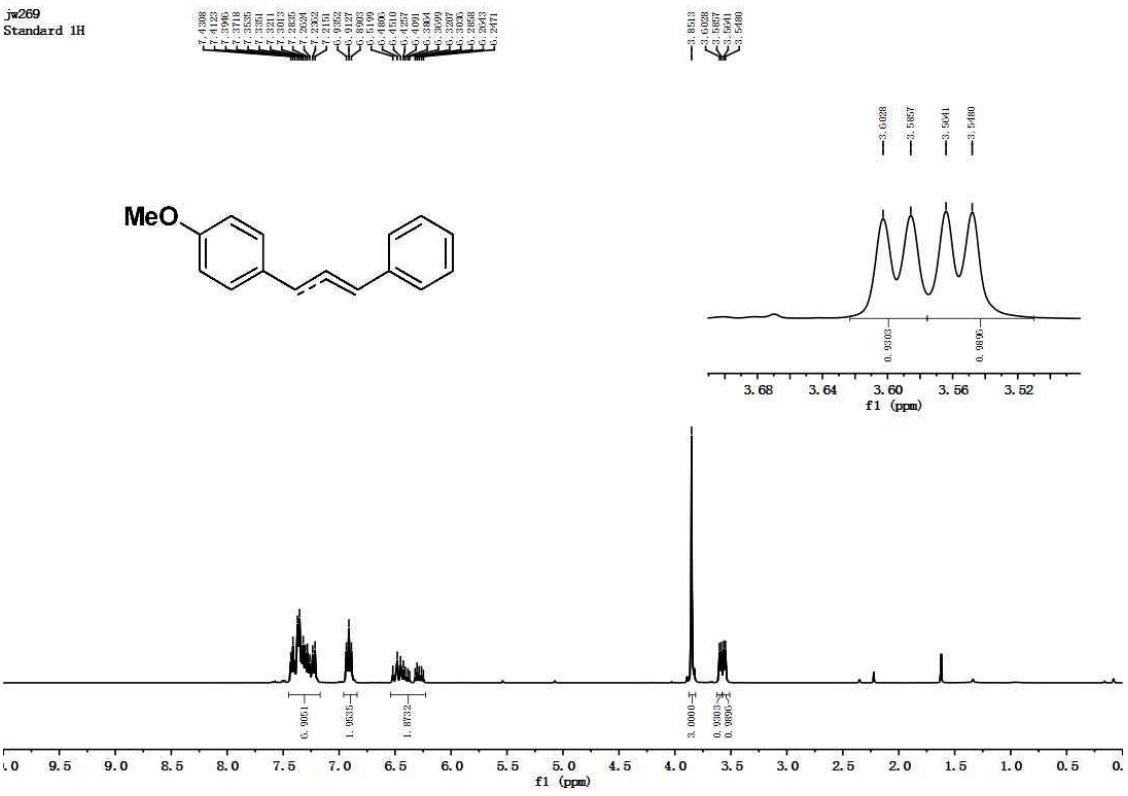


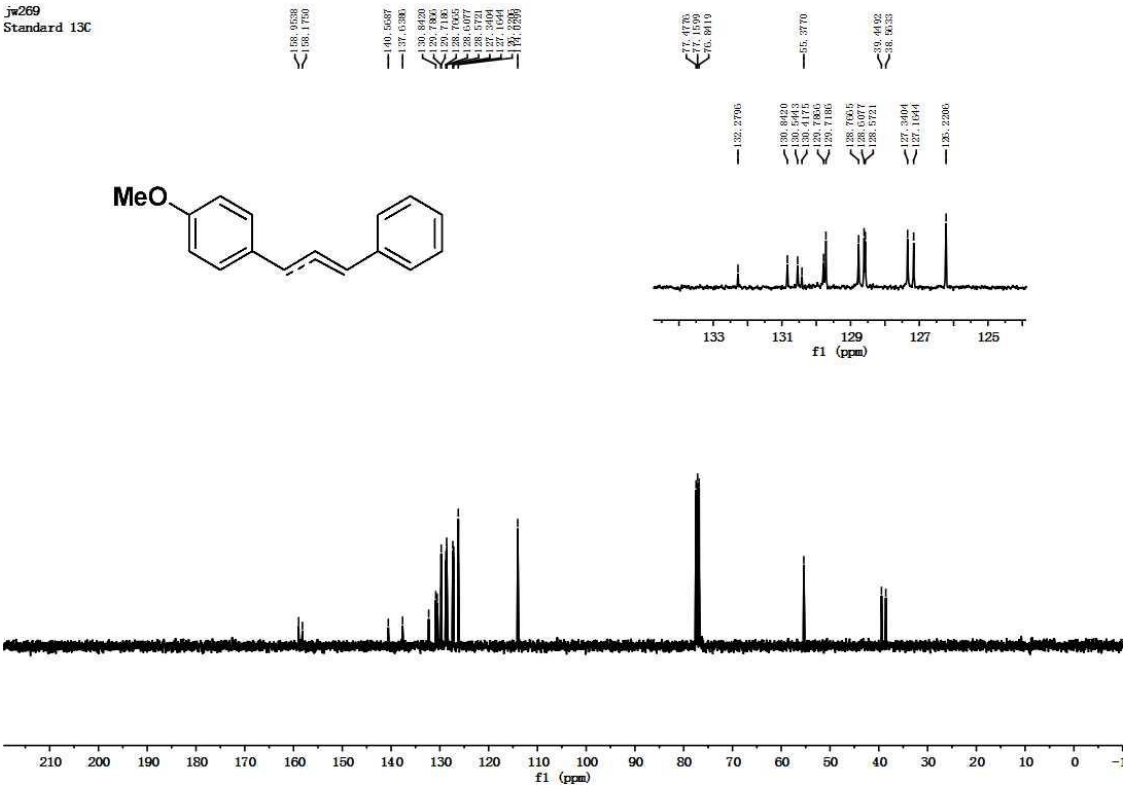
jw-336
Standard 13C



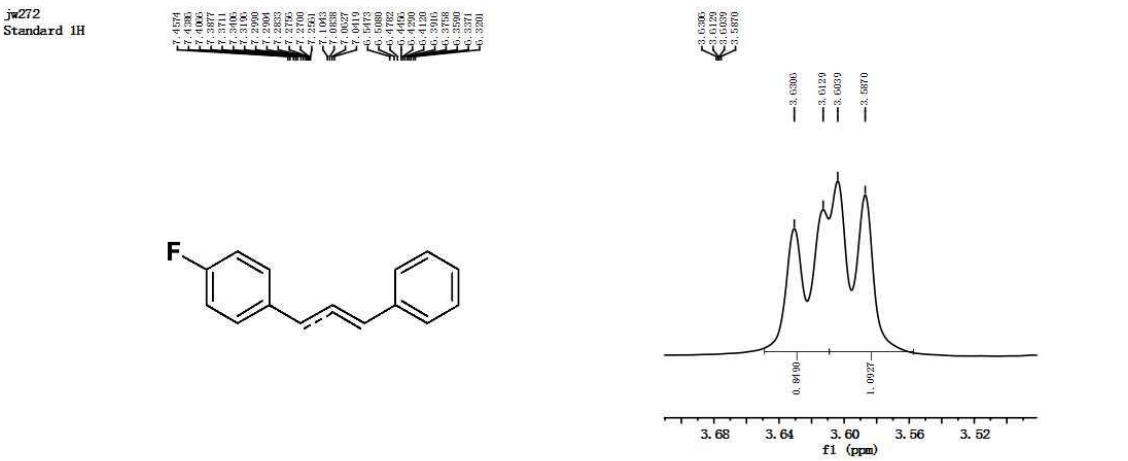


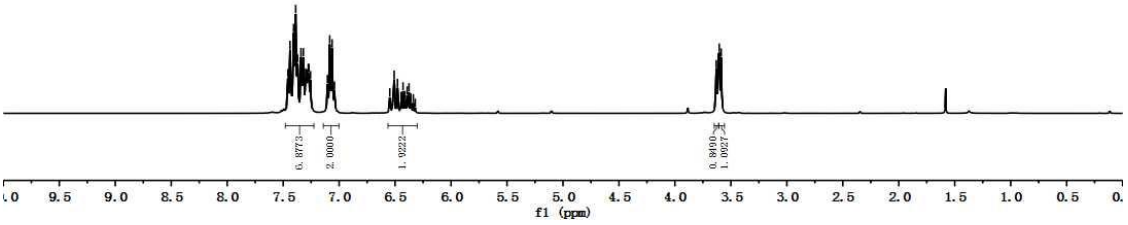



jw269
Standard 1H
MeO
f1 (ppm)

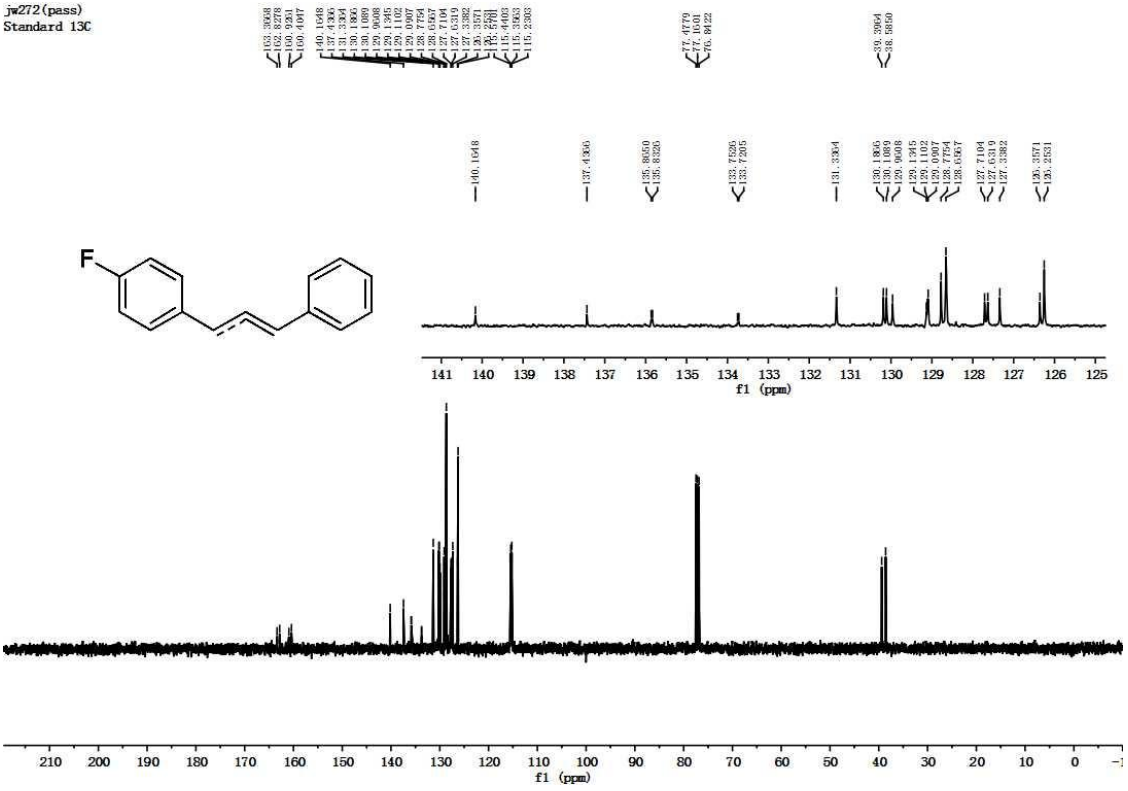

jw269
Standard 13C
MeO
f1 (ppm)

jw272
Standard 1H

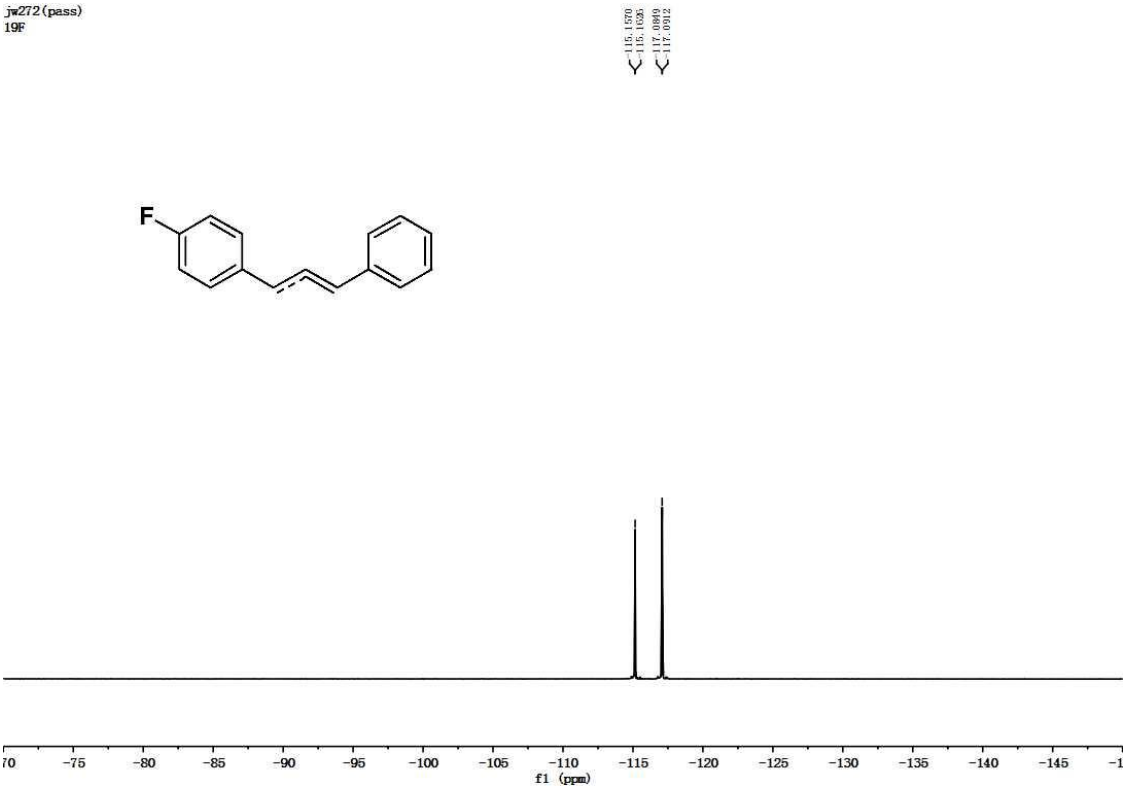




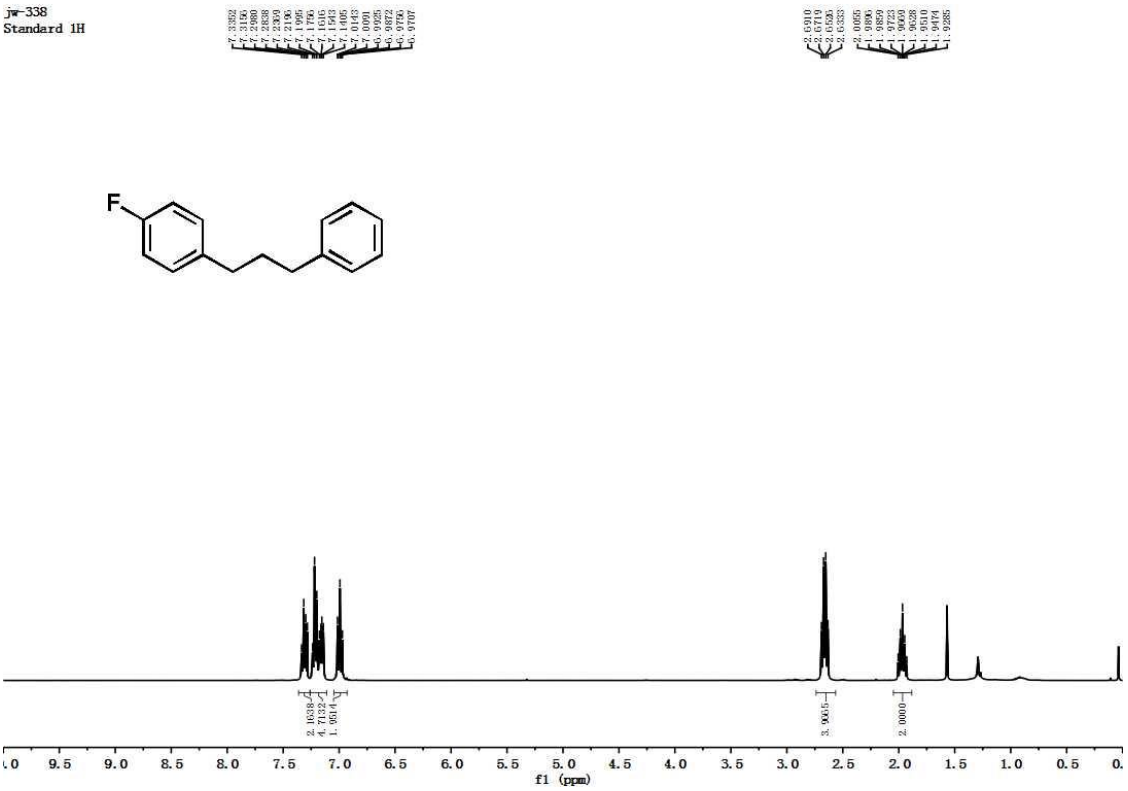
jw272(pass)
Standard 13C



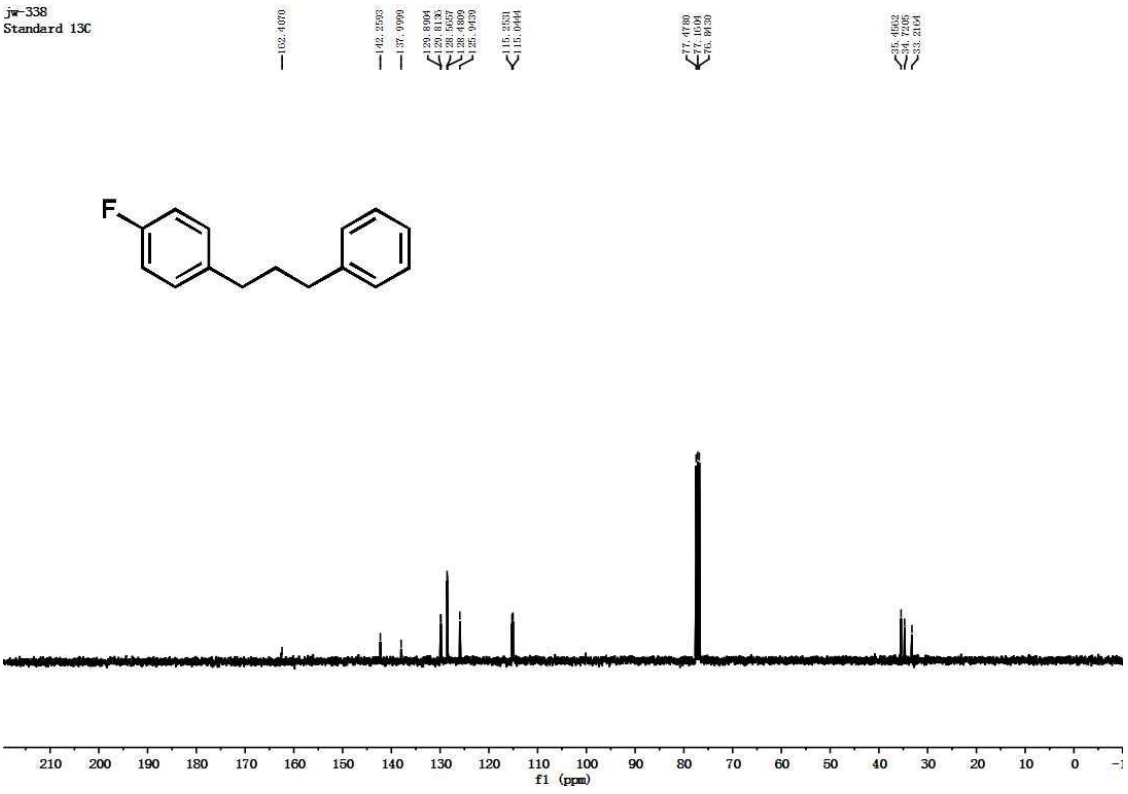
jw272(pass)
19F



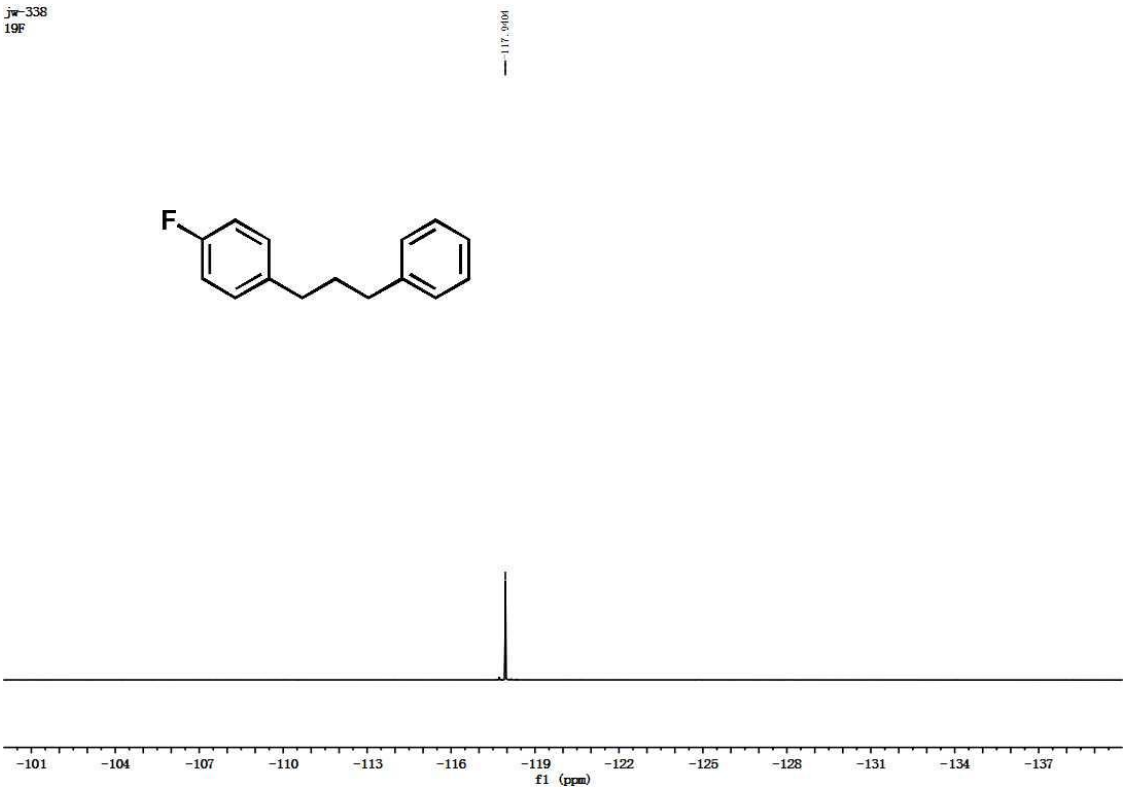
jw-338
Standard 1H

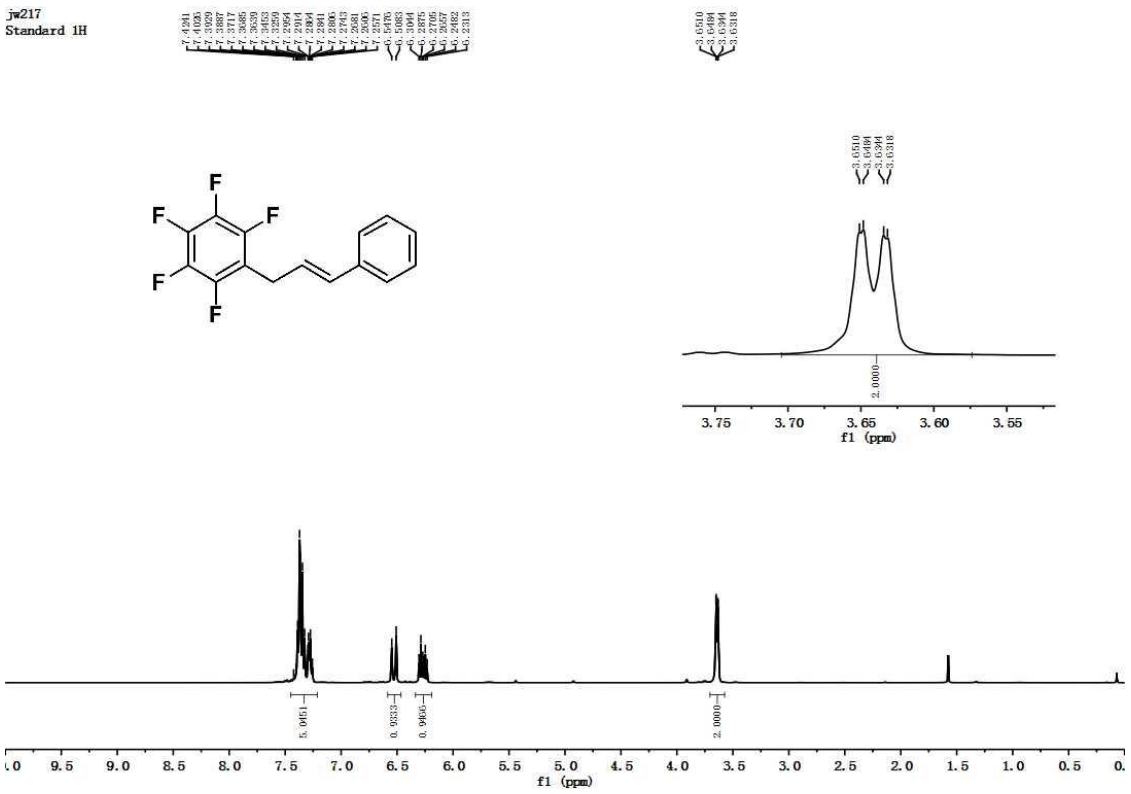


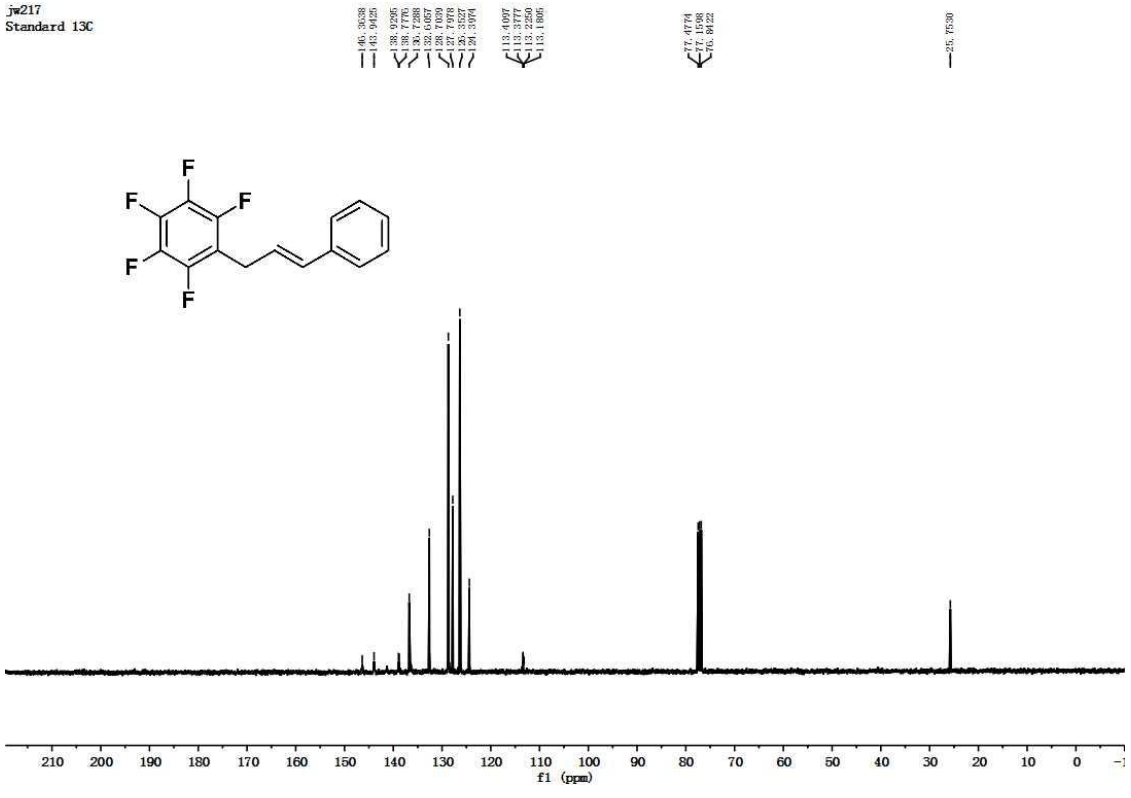
jw-338
Standard 13C



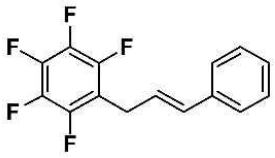
jw-338
19F

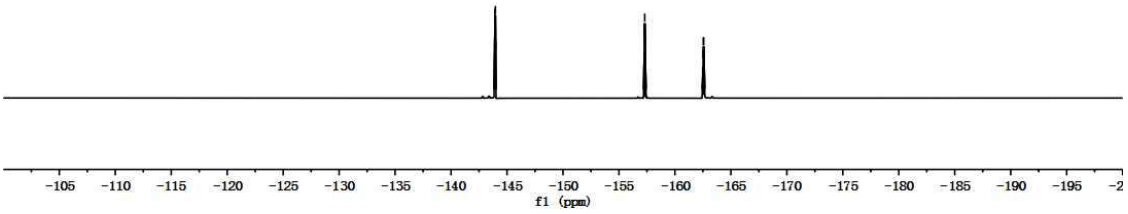



jw217
Standard 1H
F
F
F
F
3.75
3.70
3.65
3.60
3.55
f1 (ppm)
5.0451
0.9333
0.9866
2.0000
f1 (ppm)

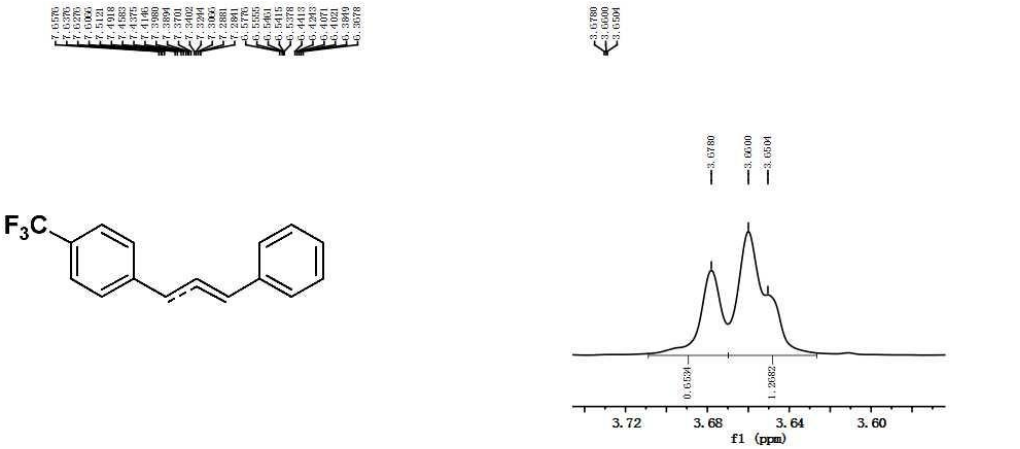

jw217
Standard 13C
F
F
F
F
f1 (ppm)

jw217
19F

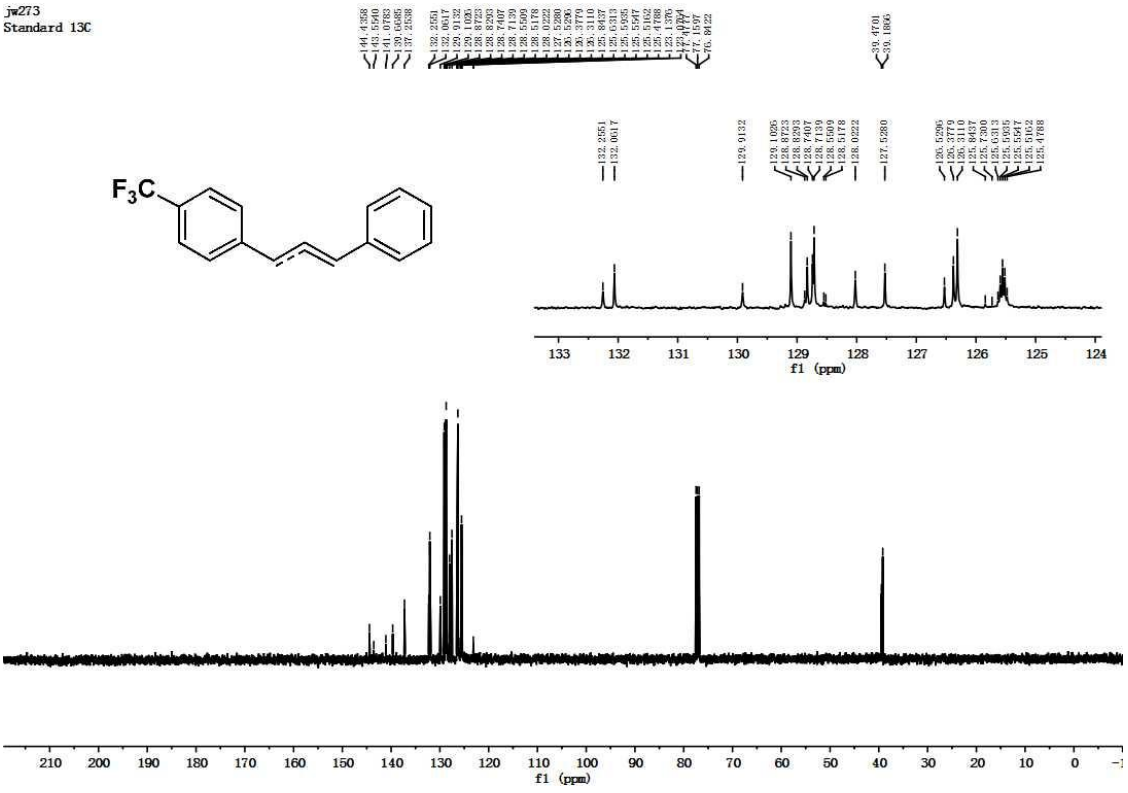




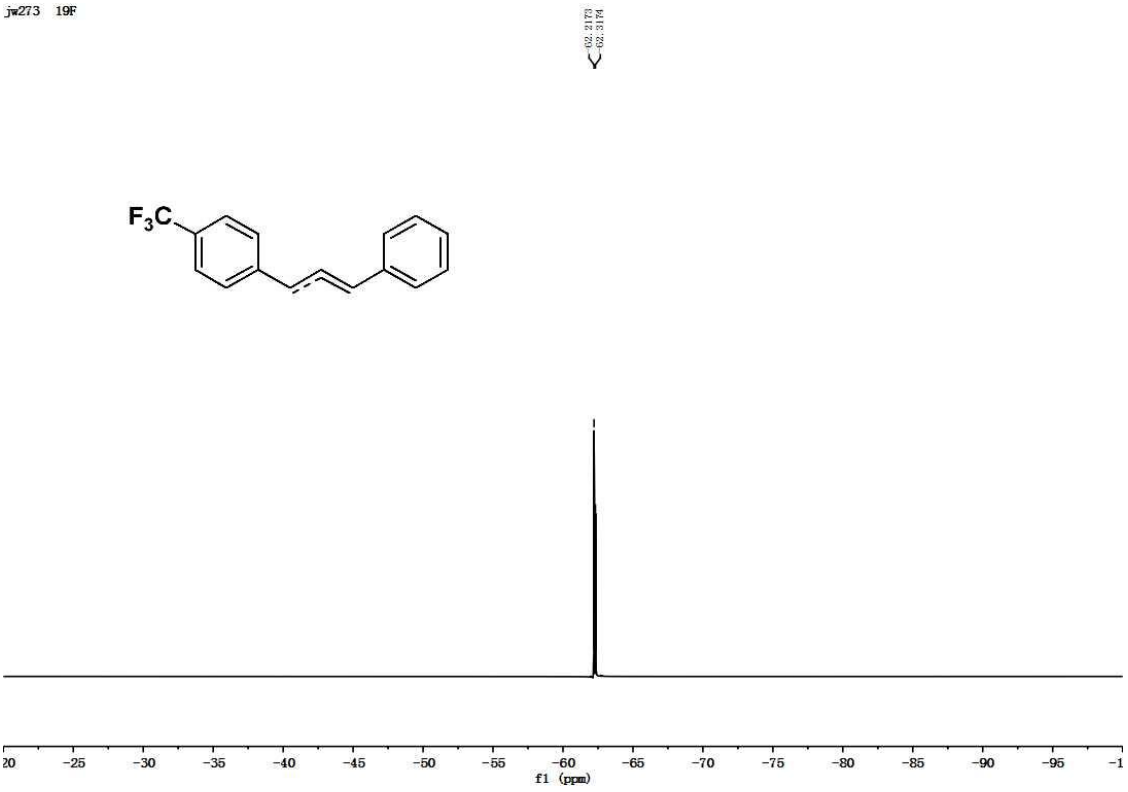
jw273
Standard 1H

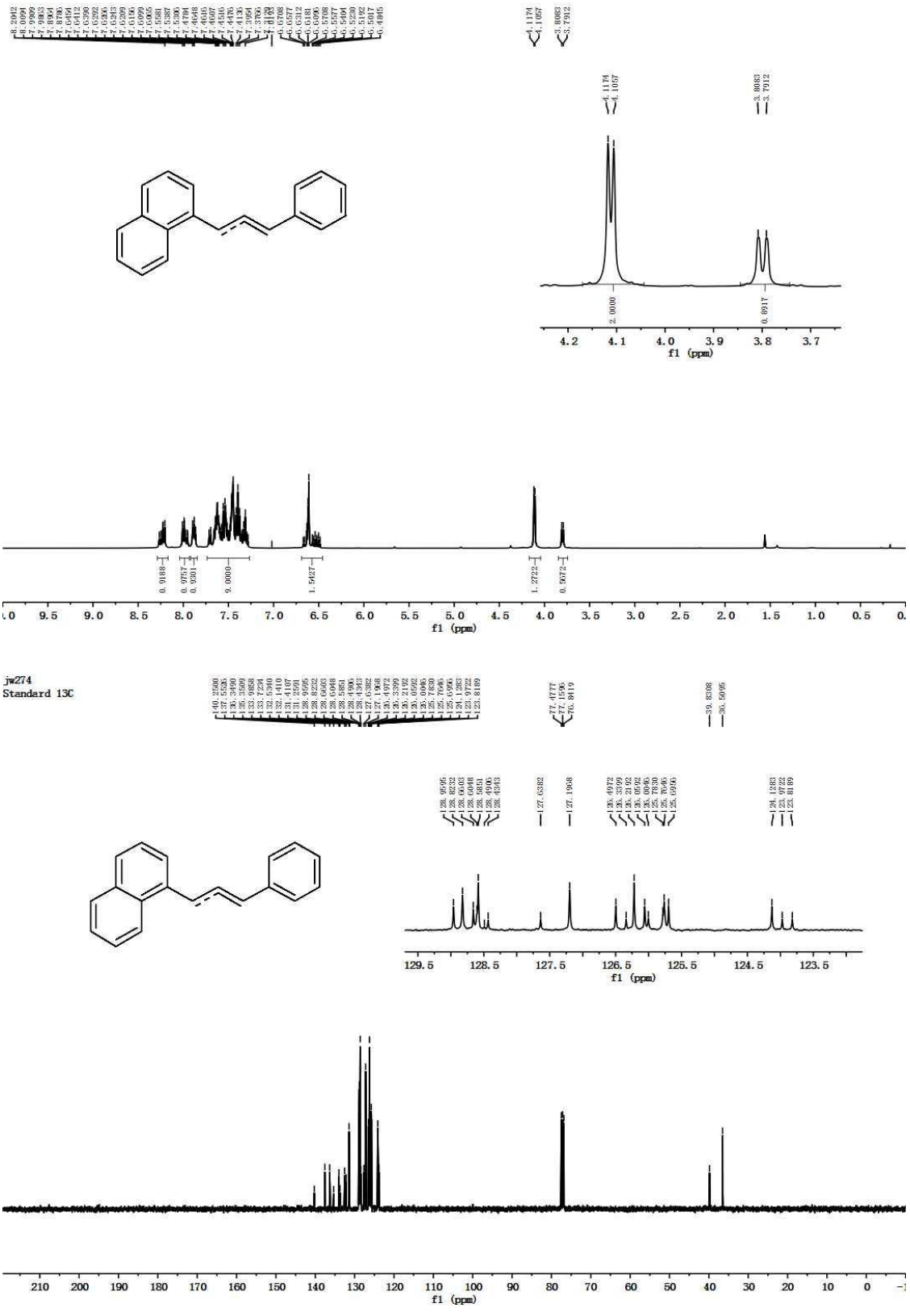


jw273
Standard 13C

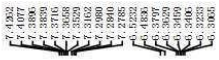


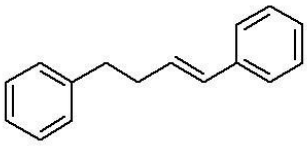
jw273 19F

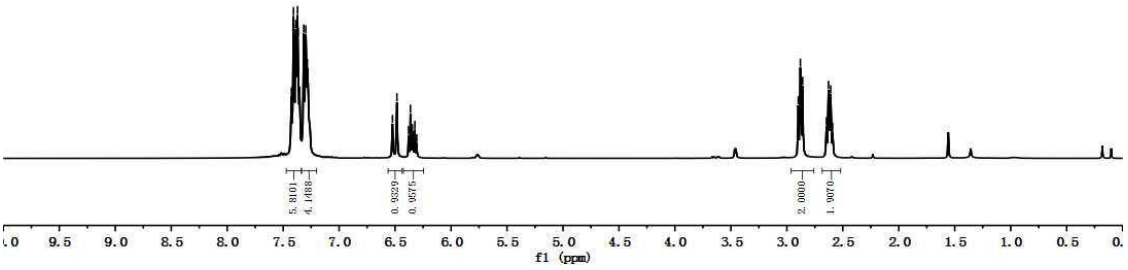



jw274
Standard 13C
f1 (ppm)

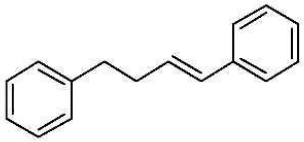
jw321b
Standard 1H

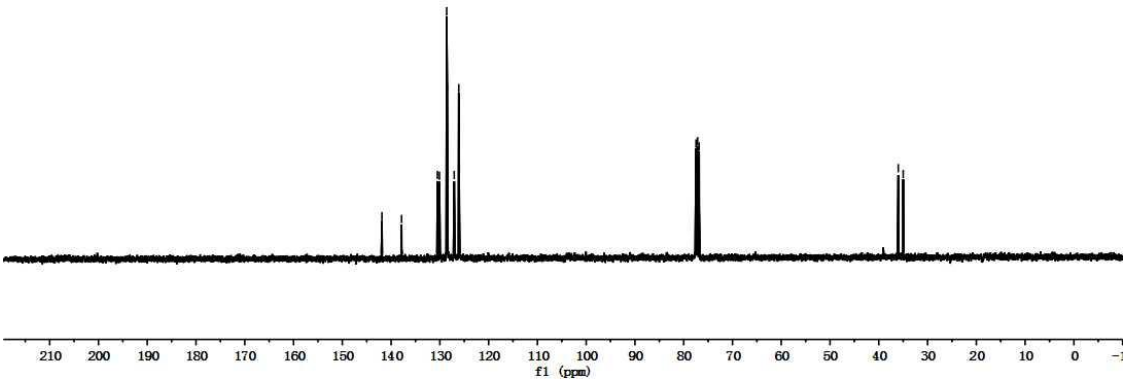




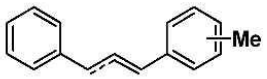


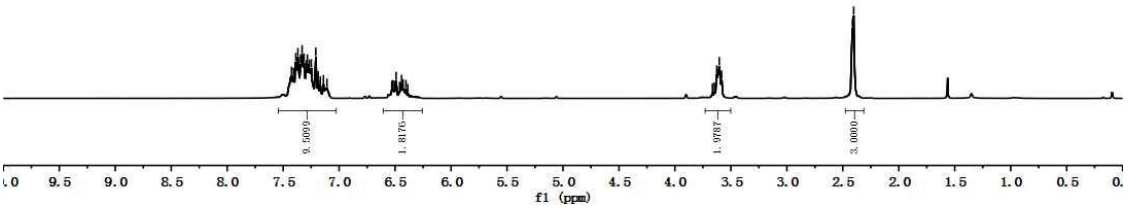
jw321b
Standard 13C



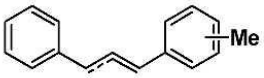


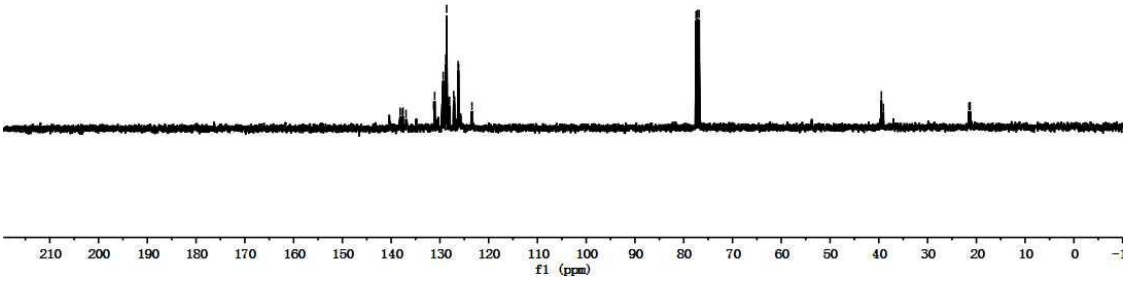
jw079
Standard 1H

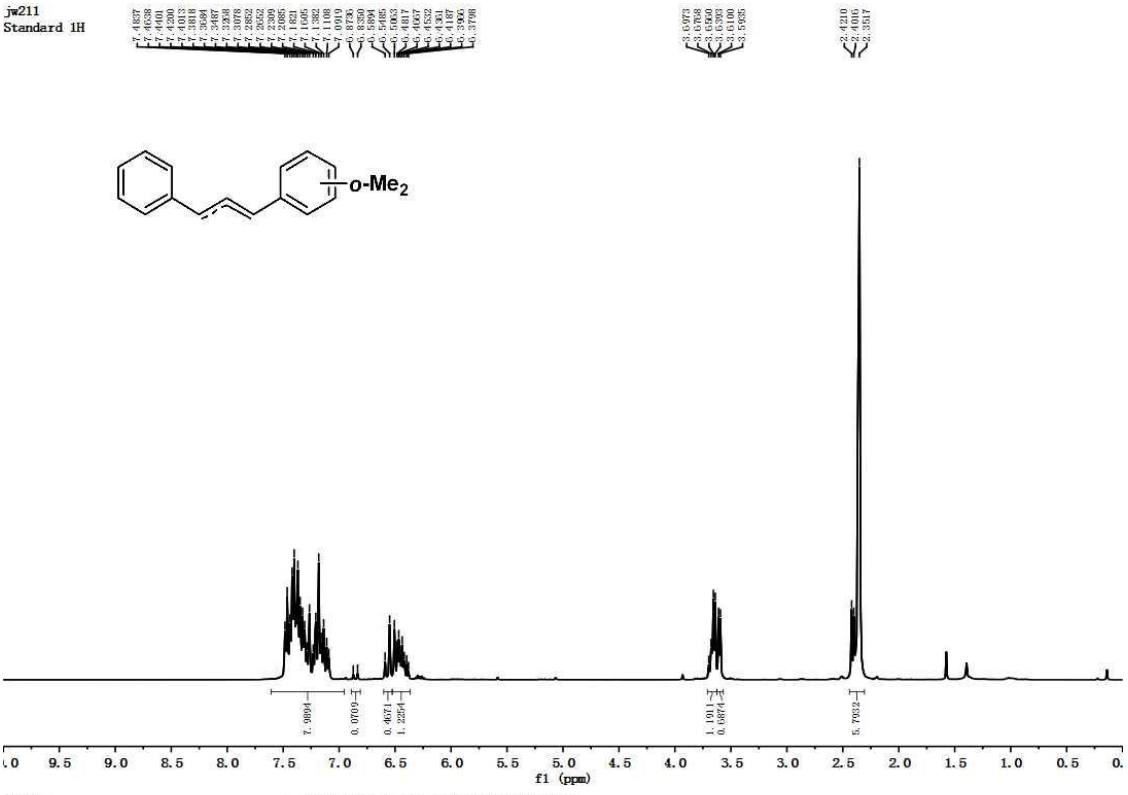


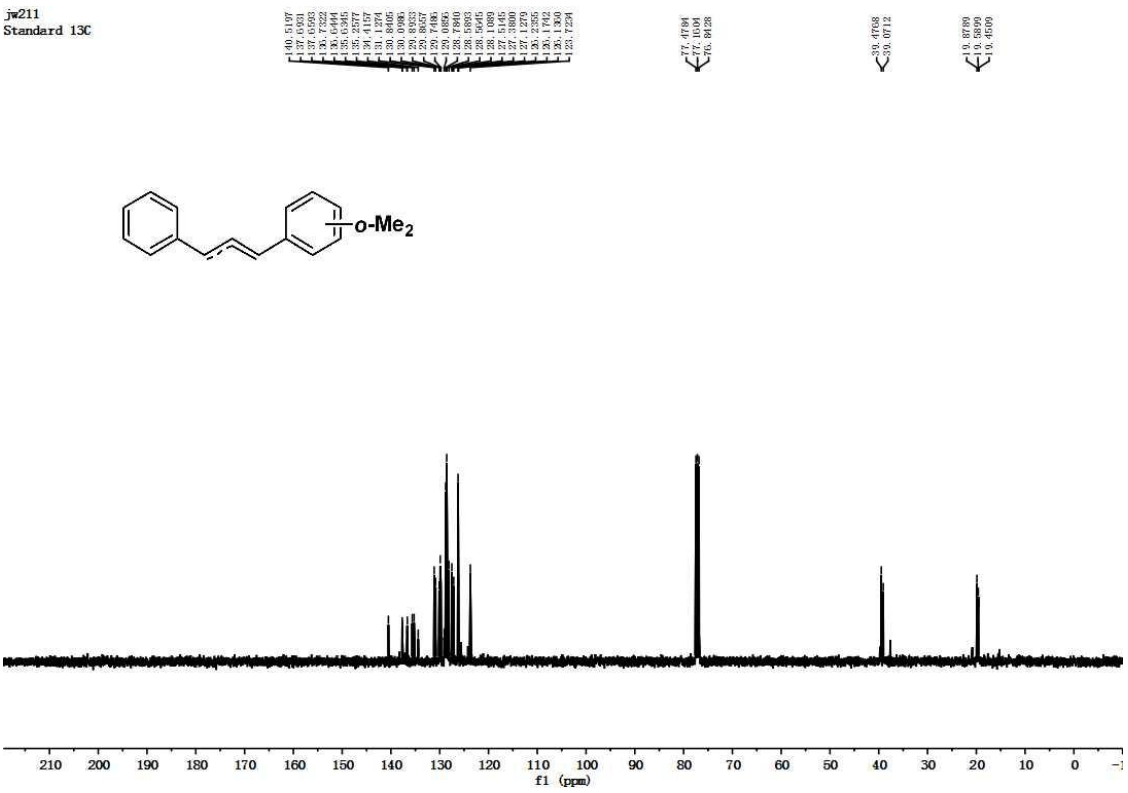


jw079
Standard 13C

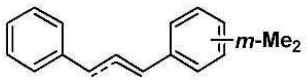




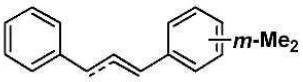

jw211
Standard 1H
o-Me2
f1 (ppm)

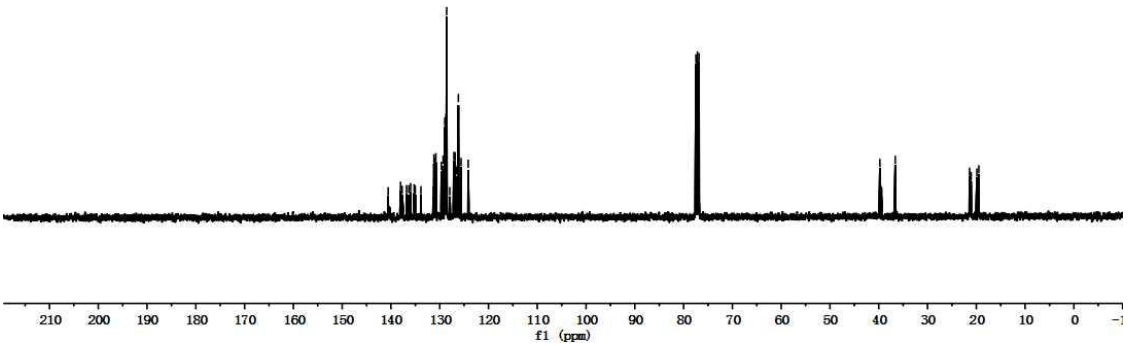

jw211
Standard 13C
o-Me2
f1 (ppm)

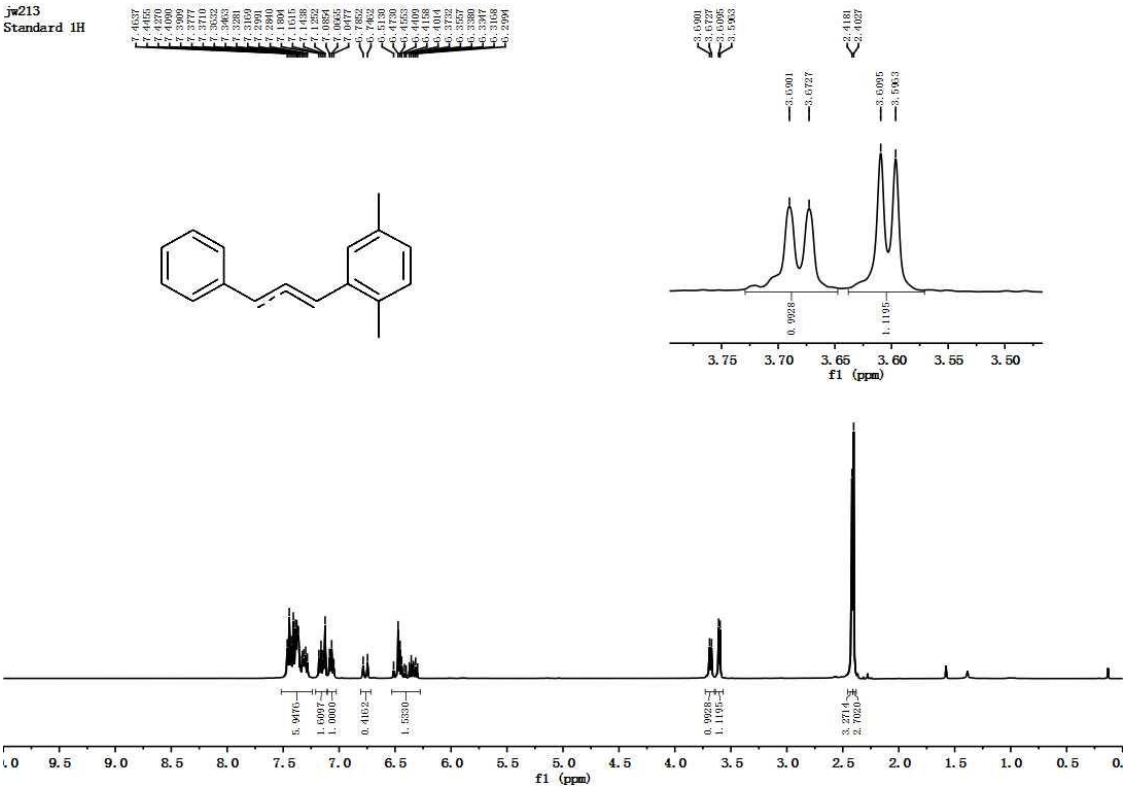
jw212
Standard 1H

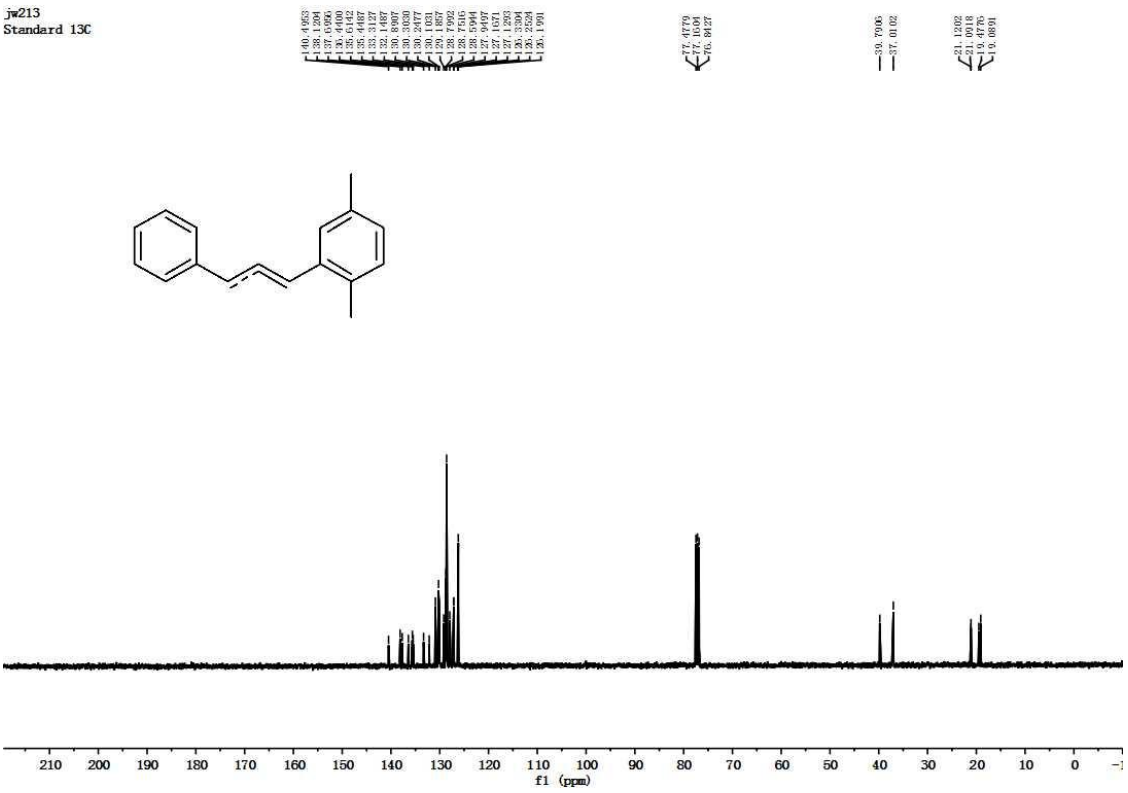


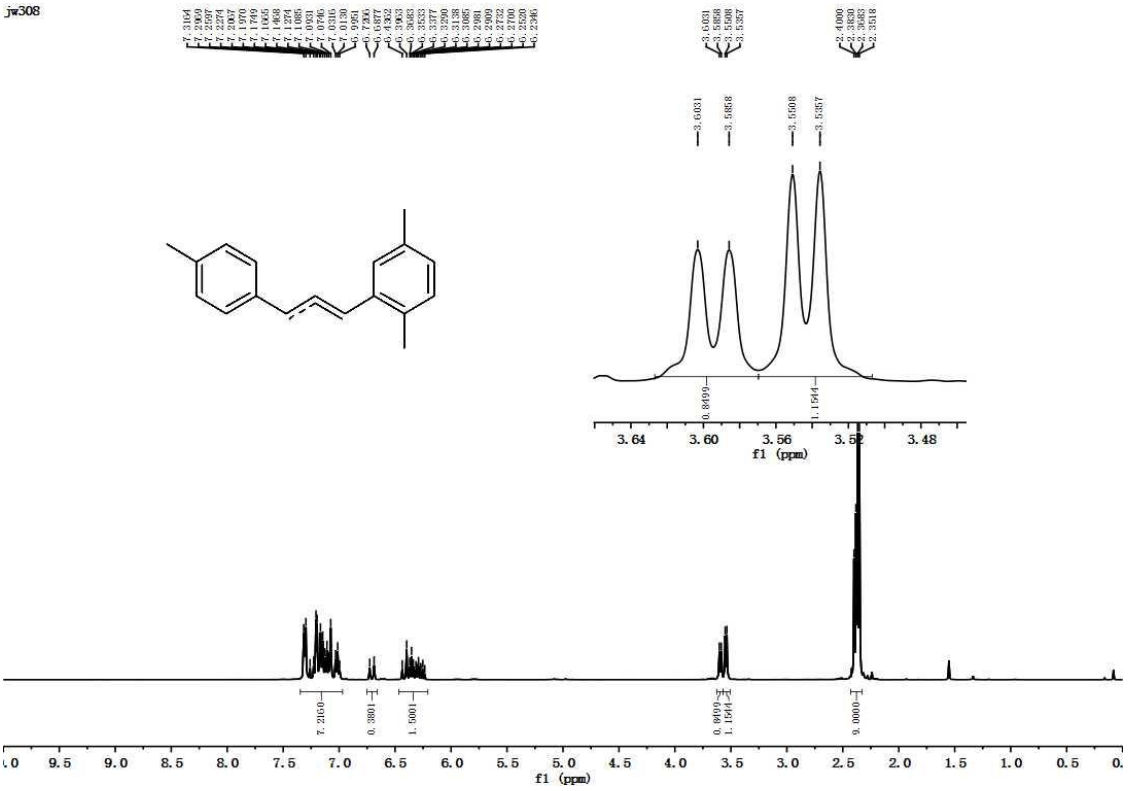
jw212
Standard 13C

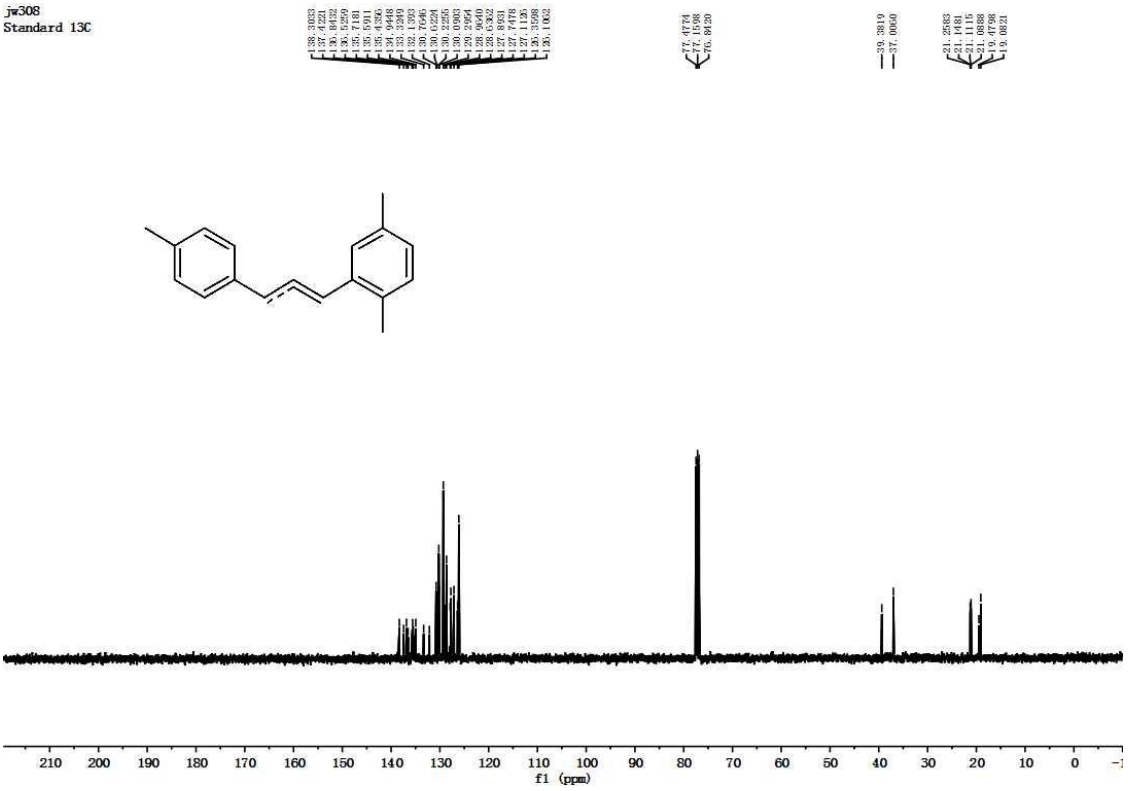




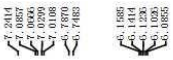

jw213
Standard 1H
f1 (ppm)

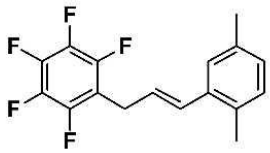

jw213
Standard 13C
f1 (ppm)

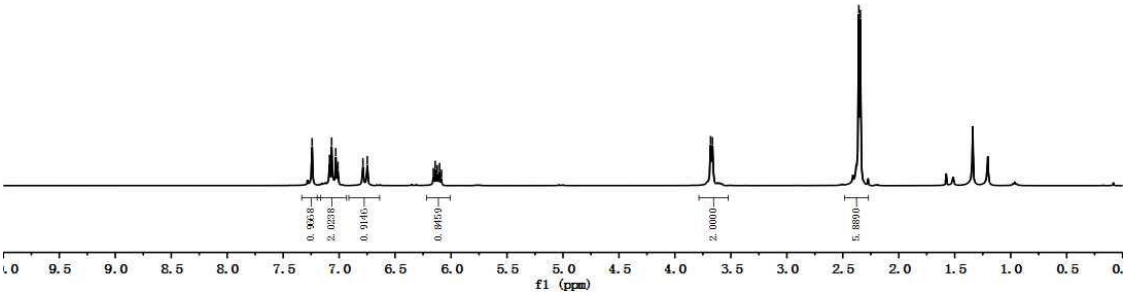

jw308
f1 (ppm)


jw308
Standard 13C
f1 (ppm)

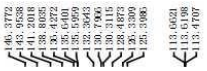
jw307
Standard 1H

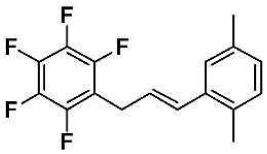


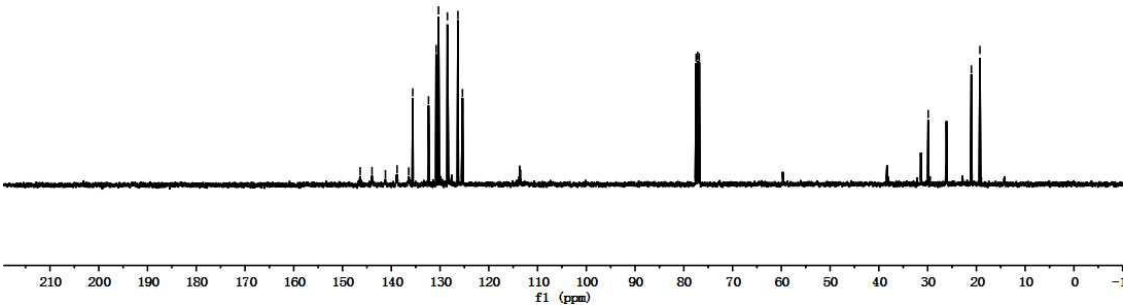




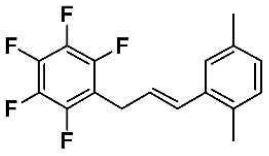
jw307
Standard 13C

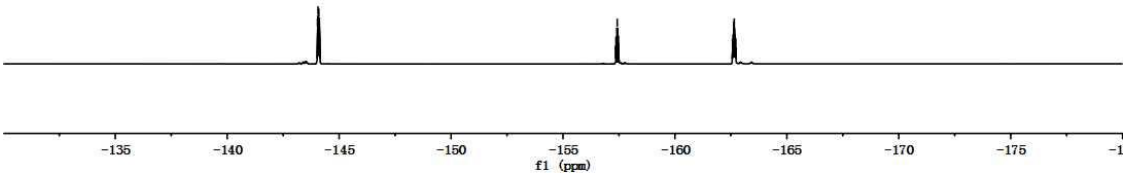




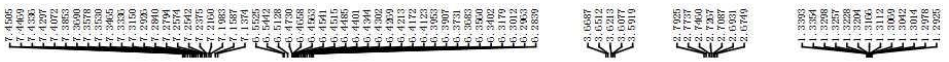


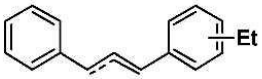
jw307
19F

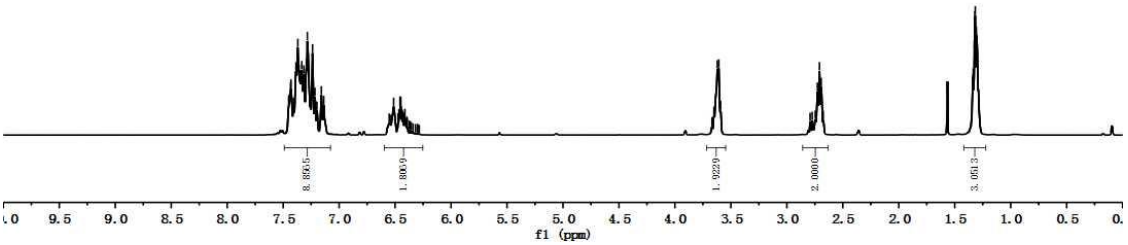




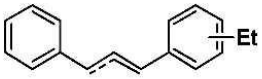
jw157
Standard 1H

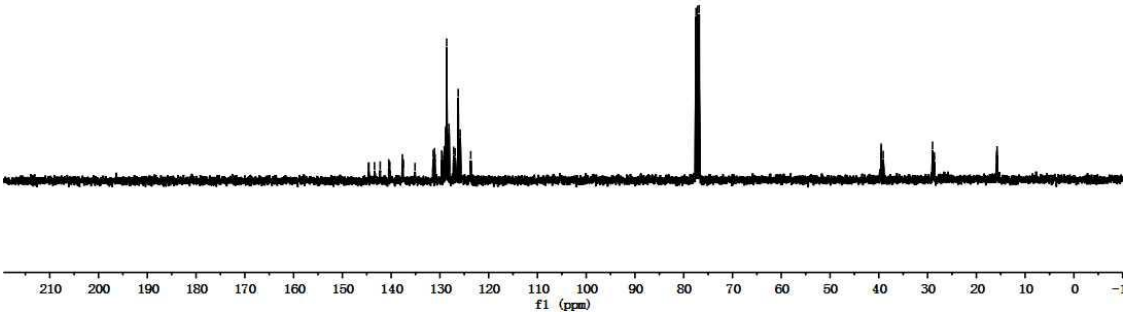


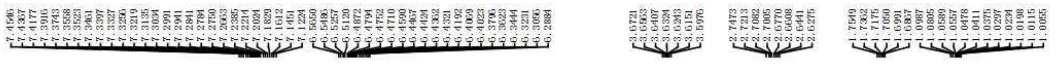


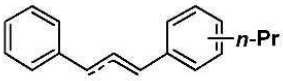


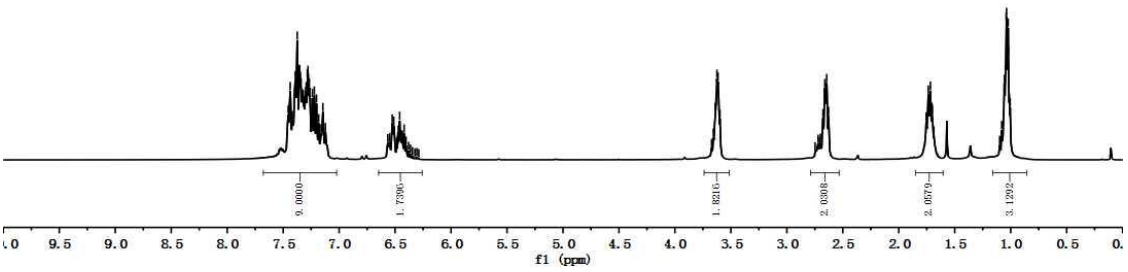
jw157
Standard 13C



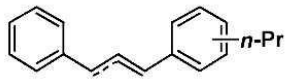


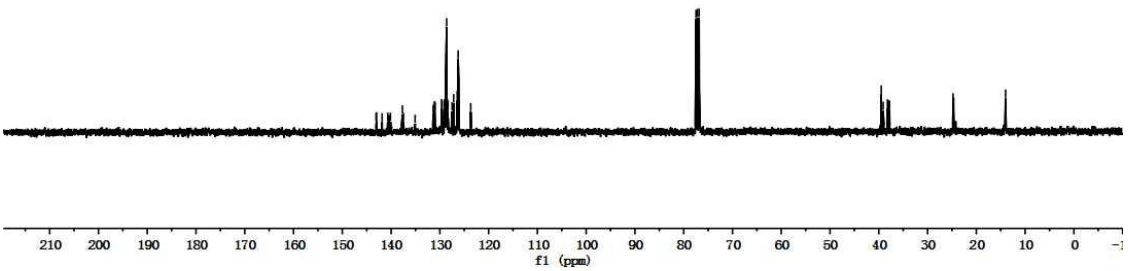


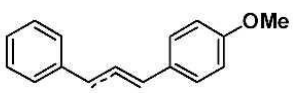


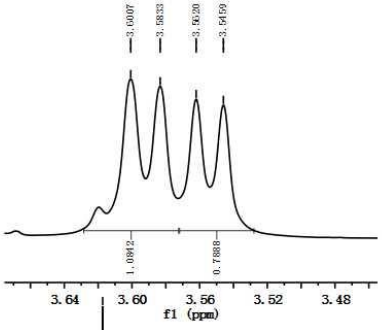


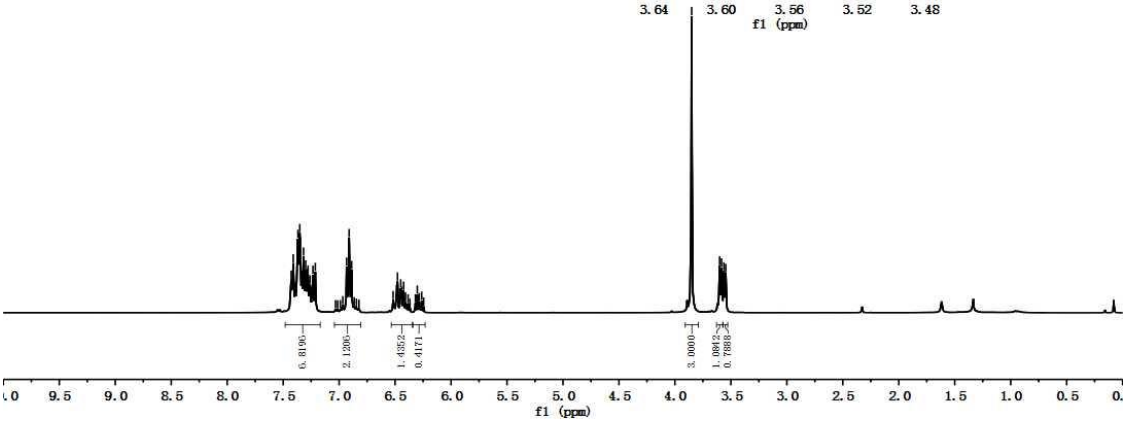
jw227
Standard 13C



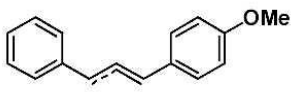


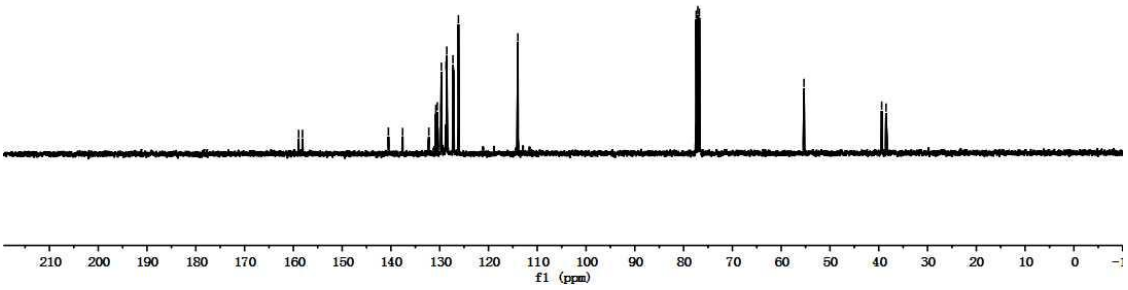




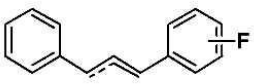


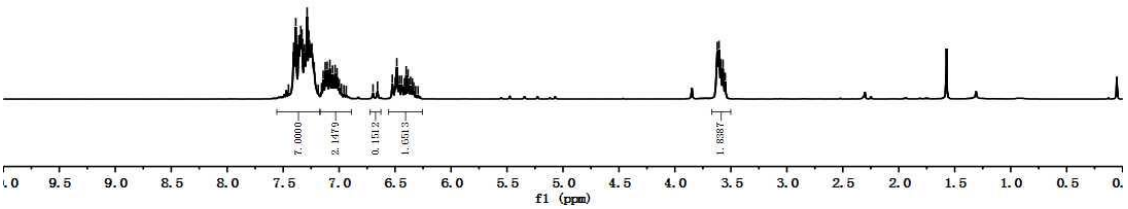
jw215
Standard 13C



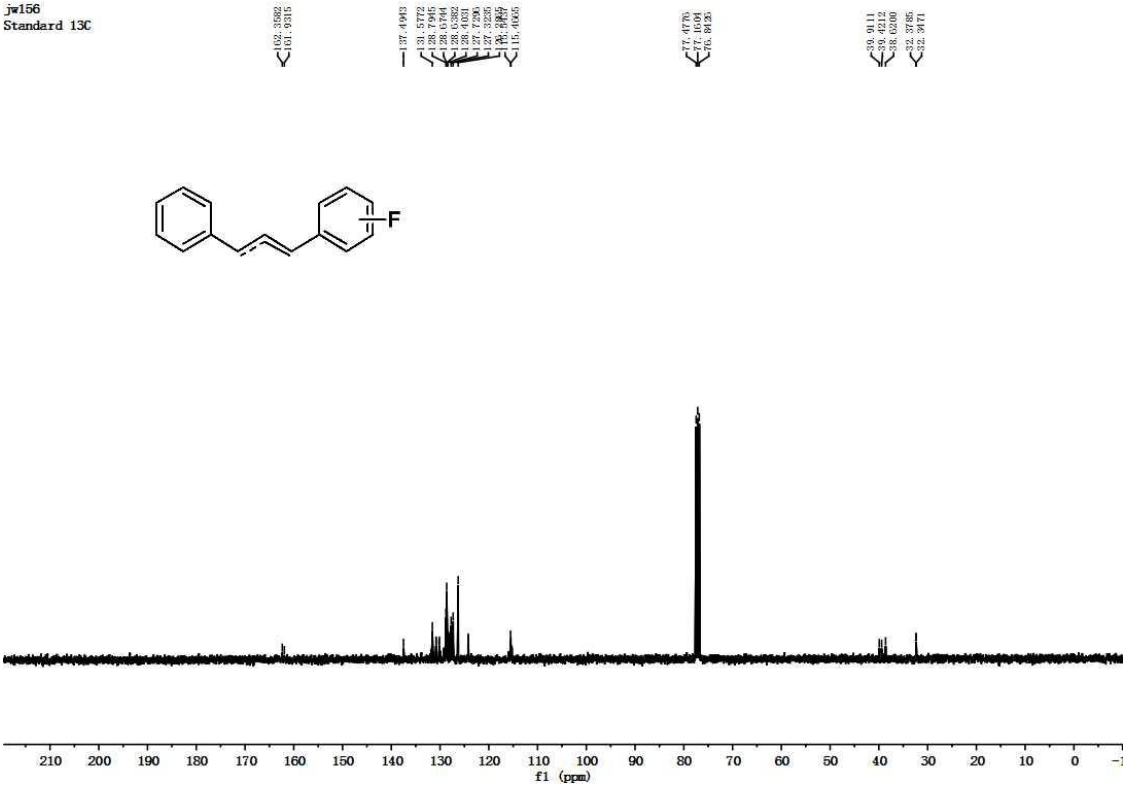


jw156
Standard 1H

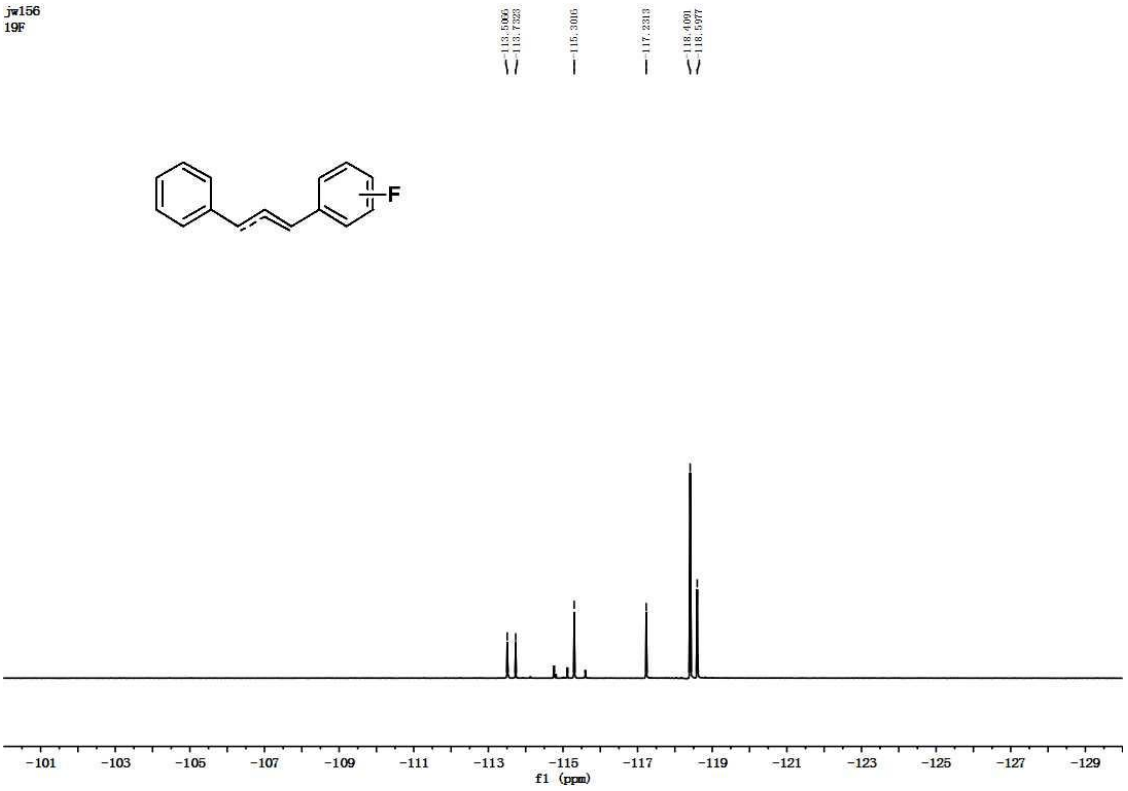


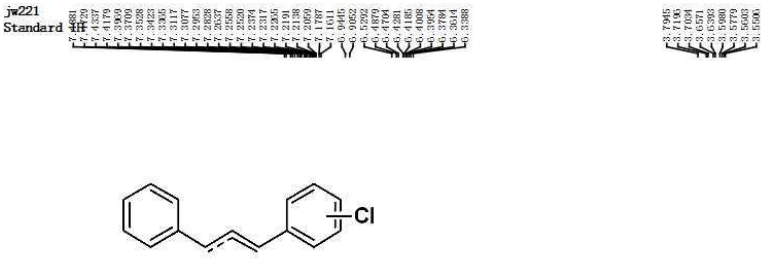


jw156
Standard 13C

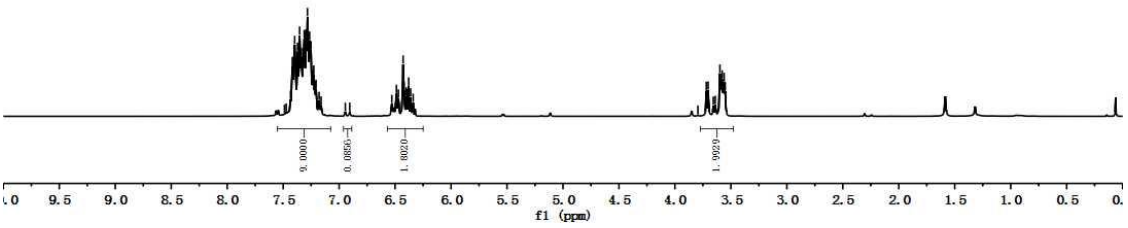


jw156
19F

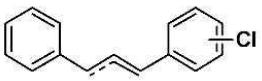


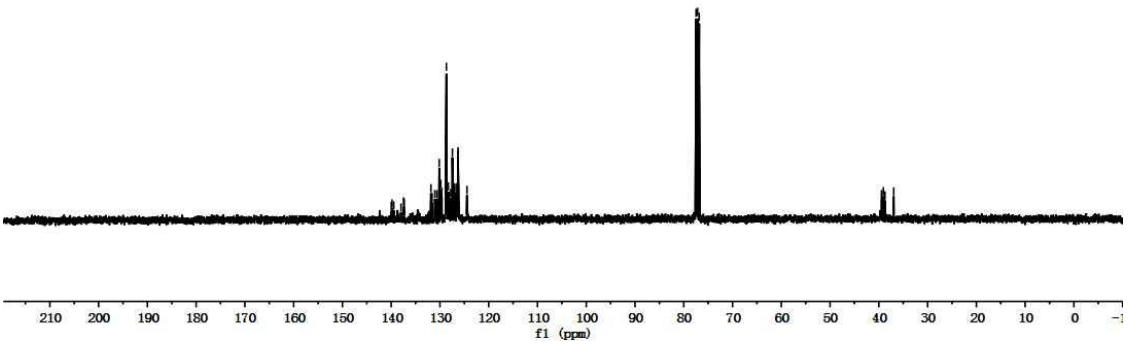

jw221
Standard 1H

Cl

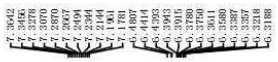

9.0000
0.0850
1.8020
1.9929
f1 (ppm)

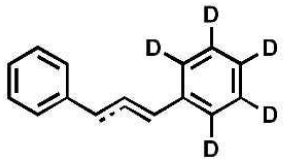

jw221
Standard 13C

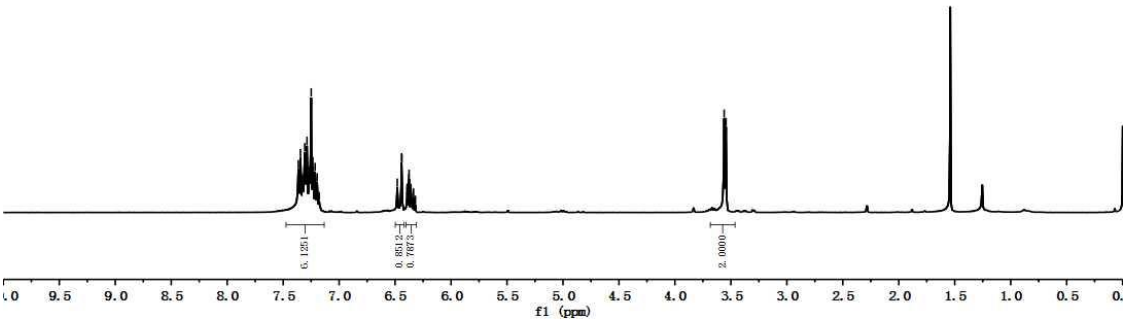

Cl


f1 (ppm)

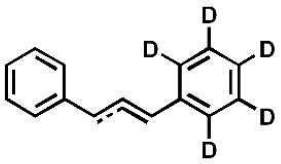
jw319c
Standard 1H

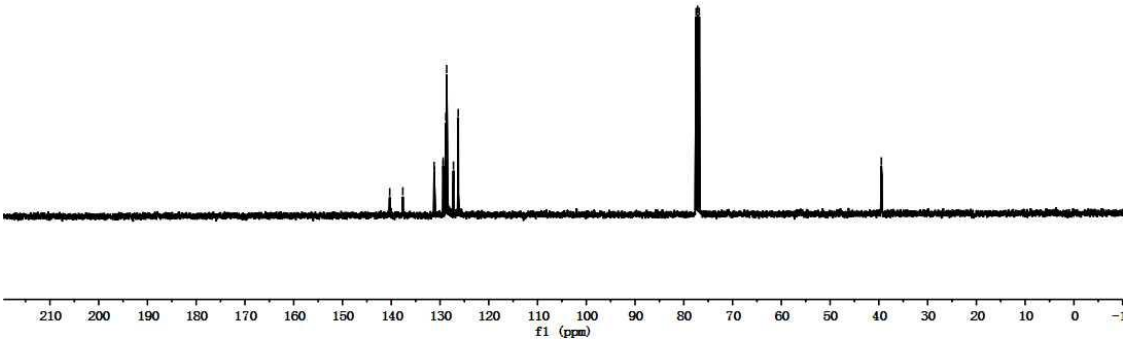


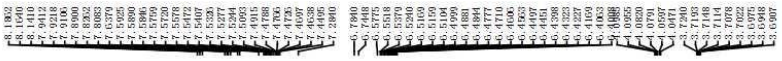


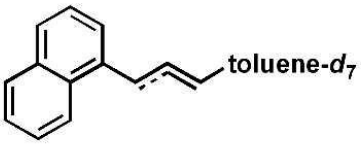


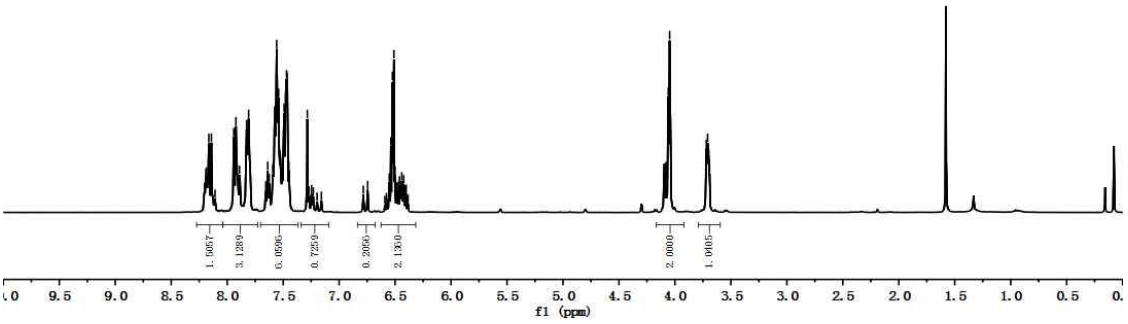
jw319c
Standard 13C

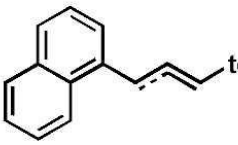


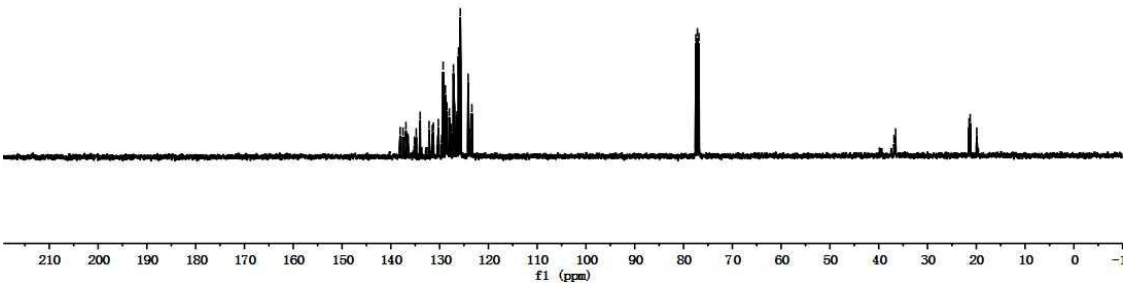





toluene-d_7


1.5657
3.1289
6.0596
0.7259
0.2066
2.1300
2.0000
1.9405
f1 (ppm)


toluene-d_7


f1 (ppm)