

Supporting Information For

Synthesis of stilbene derivatives by visible-light-induced cross-coupling of aryl diazonium salts with nitroalkenes with -NO₂ as a leaving group

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1.General Information:

Common substrates and reagents were obtained from commercial suppliers and used without further purification. Nitroalkene were prepared from aldehydes and nitromethane. All reactions were carried out under an atmosphere. ¹H NMR and ¹³C NMR spectra were recorded on a 600 MHz, 150 MHz or 400 MHz, 100 MHz spectrometer were recorded in CDCl₃. Chemical shifts are reported in ppm using TMS as internal standard and spin-spin coupling constants (J) are given in Hz. High-resolution mass spectra (HRMS) (ESI) were obtained with a Bruker Daltonics APEX II 47e and Orbitrap Elite mass spectrometer. The

following abbreviations are used to describe peak patterns where appropriate: br = broad, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = doublet of doublets, ddd = doublet of doublet of doublets. Coupling constants (J) are reported in Hertz (Hz). TLC analysis was performed on silica gel 60 F254 plates. Column chromatography was performed using 100 - 200 mesh silica gel. Eosin Y (spirit soluble, 99% dye content) was purchased from Sigma Aldrich. The green light irradiation was performed using high-power LEDs Philips LUXEON® Rebel (1 W, $\lambda = 530 \pm 10$ nm, 145 lm @700mA).

2. General procedure

General procedure for the preparation of aryl diazonium tetrafluoroborates¹

The appropriate aniline (10 mmol) was dissolved in a mixture of 4 mL of distilled water and 3.4 mL of 50 % hydrofluoroboric acid. After cooling the reaction mixture to 0 °C using ice bath and the sodium nitrite (0.69 g in 1.5 mL) was added dropwise in 5 min interval of time. The resulting mixture was stirred for 40 min and the precipitate was collected by filtration and redissolved in minimum amount of acetone. Diethyl ether was added until precipitation of diazonium tetrafluoroborate, which is filtered, washed several times with diethyl ether and dried under vacuum.

In the preparation of diazonium salt, should pay attention to questions:

The diazotization is exothermic and the diazonium salt is thermally unstable, so it is carried out under cooling. Generally with ice salt bath cooling, and adjust the rate of sodium nitrite added to maintain the temperature around 0 °C.

The stability of the diazonium salt is related to the substituents on the aromatic ring. Unsubstituted or alkyl-substituted diazonium salts are unstable and can explode with heat, friction or impact. They can only be used in their aqueous solution at about 0 °C for synthesis. Diazonium salts having an electron-withdrawing group, although they are relatively difficult to synthesize but have good stability, it can be used at a higher temperature, also be used at room temperature. In general, the diazonium salts of tetrafluoroboric acid are relatively stable.

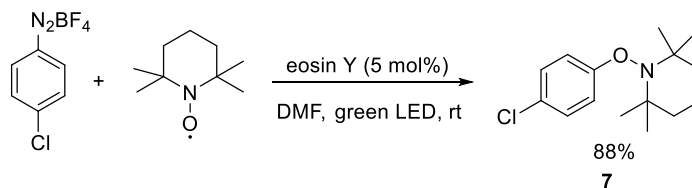
General experimental procedure for synthesis of 3, 6.

In a 3 mL snap vial equipped with magnetic stirring bar the eosin Y (5 mol%), aryl diazonium tetrafluoroborate (0.3 mmol) and nitroalkene (0.2 mmol) were dissolved in dry DMF (0.2 mmol/mL). The resulting mixture were irradiated through green LEDs at room temperature for 12 h under an atmosphere. After the reaction was finished, the reaction mixture was transferred to separating funnel, diluted with ethyl acetate and washed with 15 mL of water. The aqueous layer was washed three times with ethyl acetate. The combined organic layers were dried over $MgSO_4$, filtered and concentrated in vacuum. Purification of the crude product was achieved by silica gel column chromatography using hexane /ethyl acetate as eluent to afford corresponding product.

3. Radical Scavenger Test

1) In a 3 mL snap vial equipped with magnetic stirring bar the eosin Y (5 mol%), aryl

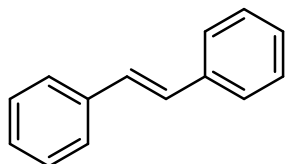
diazonium tetrafluoroborate (1.0 equiv) and TEMPO (3.0 equiv) were dissolved in dry DMF (0.2 mmol/mL). The resulting mixture were irradiated through green LEDs at room temperature for 8 h under an atmosphere. After 12 h of irradiation, a TEMPO trapped compound **7** was achieved.



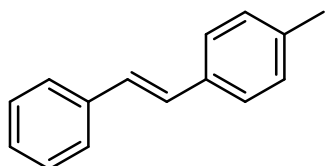
2) In a 3 mL snap vial equipped with magnetic stirring bar the eosin Y (5 mol%), aryl diazonium tetrafluoroborate (1.5 equiv), nitroalkene (1.0 equiv) and TEMPO (3.0 equiv) were dissolved in dry DMF (0.2 mmol/mL). The resulting mixture were irradiated through green LEDs at room temperature for 8 h under an atmosphere. The conversion was very low (< 5%).

Replacing TEMPO with BHT gave the same result.

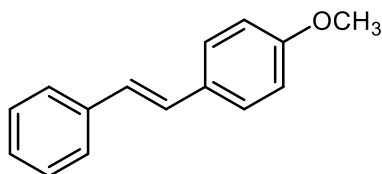
4.Characterization of **3**, **6**.



(E)-1,2-diphenylethene (3a): White solid (72% yield). $^1\text{H NMR}$ (600 MHz, CDCl_3) δ 7.52 (d, $J = 7.8$ Hz, 4H, ArH), 7.36 (t, $J = 7.2$ Hz, 4H, ArH), 7.27 (d, $J = 7.8$ Hz, 2H, ArH), 7.12 (s, 2H, CH) ppm. $^{13}\text{C NMR}$ (150 MHz, CDCl_3) δ 137.3, 128.7, 128.7, 127.6, 126.5 ppm. mp: 121 - 122 °C. HRMS (ESI⁺) m/z : ($[\text{M}+\text{H}]^+$) Calcd for $\text{C}_{14}\text{H}_{12}$ 180.0939; Found 180.0937.

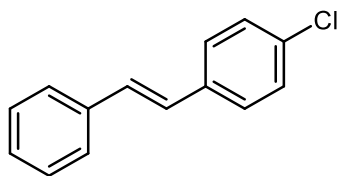


(E)-1-methyl-4-styrylbenzene (3b): White solid (71% yield). $^1\text{H NMR}$ (600 MHz, CDCl_3) δ 7.50 (d, $J = 7.2$ Hz, 2H, ArH), 7.42 (d, $J = 8.4$ Hz, 2H, ArH), 7.35 (t, $J = 7.2$ Hz, 2H, ArH), 7.24 (d, $J = 7.2$ Hz, 1H, ArH), 7.17 (d, $J = 7.8$ Hz, 2H, ArH), 7.07 (d, $J = 4.8$ Hz, 2H, CH), 2.36 (s, 3H, CH_3) ppm. $^{13}\text{C NMR}$ (150 MHz, CDCl_3) δ 137.5, 137.5, 134.5, 129.4, 128.6, 127.7, 127.4, 126.4, 126.4, 21.2 ppm. mp: 110 - 111 °C. HRMS (ESI⁺) m/z : ($[\text{M}+\text{H}]^+$) Calcd for $\text{C}_{15}\text{H}_{14}$ 194.1096; Found 194.1095.

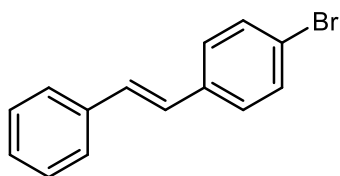


(E)-1-methoxy-4-styrylbenzene (3c): White solid (69% yield). $^1\text{H NMR}$ (600 MHz, CDCl_3) δ 7.50 (d, $J = 7.8$ Hz, 2H, ArH), 7.47 (d, $J = 8.4$ Hz, 2H, ArH), 7.35 (t, $J = 7.8$ Hz, 2H,

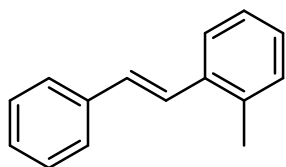
ArH), 7.24 (t, $J = 7.2$ Hz, 1H, ArH), 7.08 (d, $J = 16.2$ Hz, 1H, ArH), 6.99 (d, $J = 16.2$ Hz, 1H, ArH), 6.91 (d, $J = 9.0$ Hz, 2H, CH), 3.84 (s, 3H, CH₃) ppm. ¹³C NMR (100 MHz, CDCl₃) δ 159.3, 137.6, 130.1, 128.6, 128.2, 127.7, 127.2, 126.6, 126.2, 114.1, 55.3 ppm. mp: 134 - 135 °C. HRMS (ESI⁺) m/z : ([M+H]⁺) Calcd for C₁₅H₁₄O 210.1045; Found 210.1046.



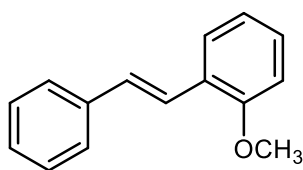
(E)-1-chloro-4-styrylbenzene (3d): Yellow solid (87% yield). ¹H NMR (600 MHz, CDCl₃) δ 7.50 (d, $J = 7.8$ Hz, 2H, ArH), 7.43 (d, $J = 8.4$ Hz, 2H, ArH), 7.36 (t, $J = 7.8$ Hz, 2H, ArH), 7.32 (d, $J = 8.4$ Hz, 2H, ArH), 7.27 (d, $J = 7.2$ Hz, 1H, ArH), 7.11 - 7.02 (m, 2H, CH) ppm. ¹³C NMR (150 MHz, CDCl₃) δ 137.0, 135.8, 133.2, 129.3, 128.8, 128.7, 127.8, 127.6, 127.4, 126.5 ppm. mp: 100 - 102 °C. HRMS (ESI⁺) m/z : ([M+H]⁺) Calcd for C₁₄H₁₁Cl 214.0549; Found 214.05497.



(E)-1-bromo-4-styrylbenzene (3e): White solid (84% yield). ¹H NMR (600 MHz, CDCl₃) δ 7.48 (dd, $J = 7.2, 8.4$ Hz, 4H, ArH), 7.36 (dd, $J = 8.4, 7.8$ Hz, 4H, ArH), 7.27 (d, $J = 7.2$ Hz, 1H, ArH), 7.09 (d, $J = 16.2$ Hz, 1H, CH), 7.02 (d, $J = 16.2$ Hz, 1H, CH) ppm. ¹³C NMR (150 MHz, CDCl₃) δ 136.9, 136.3, 131.8, 129.4, 128.7, 127.9, 127.9, 127.4, 126.5, 121.3 ppm. mp: 127 - 128 °C. HRMS (ESI⁺) m/z : ([M+H]⁺) Calcd for C₁₄H₁₁Br 258.0044; Found 258.0045.

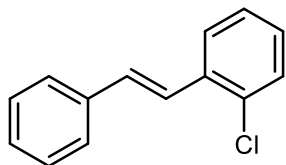


(E)-1-methyl-2-styrylbenzene (3f): Colorless liquid (65% yield). ¹H NMR (600 MHz, CDCl₃) δ 7.60 (d, $J = 7.2$ Hz, 1H, ArH), 7.53 (d, $J = 7.8$ Hz, 2H, ArH), 7.36 (dd, $J = 7.2, 16.2$ Hz, 3H, ArH), 7.19 (d, $J = 4.2$ Hz, 2H, ArH), 7.11 (t, $J = 7.8$ Hz, 1H, ArH), 7.02 - 6.99 (m, 2H, CH), 2.44 (s, 3H, CH₃) ppm. ¹³C NMR (150 MHz, CDCl₃) δ 136.4, 135.8, 131.3, 130.4, 130.0, 128.7, 127.6, 126.5, 126.2, 125.3, 123.0, 117.6, 19.9 ppm. HRMS (ESI⁺) m/z : ([M+H]⁺) Calcd for C₁₅H₁₄ 194.1096; Found 194.1095.

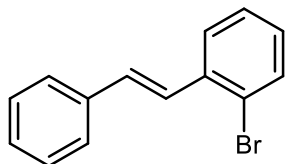


(E)-1-methoxy-2-styrylbenzene (3g): Colorless liquid (63% yield). ¹H NMR (600 MHz, CDCl₃) δ 7.60 (d, $J = 7.8$ Hz, 1H, ArH), 7.54 (d, $J = 7.2$ Hz, 2H, ArH), 7.49 (d, $J = 16.8$ Hz,

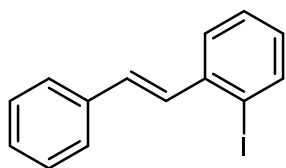
1H ArH), 7.35 (t, $J = 7.2$ Hz, 2H, ArH), 7.25 - 7.23 (m, 2H, ArH), 7.12 (d, $J = 16.8$ Hz, 1H, CH), 6.98 (t, $J = 7.2$ Hz, 1H, ArH), 6.91 (d, $J = 8.4$ Hz, 1H, CH), 3.90 (s, 3H, CH₃) ppm. ¹³C NMR (150 MHz, CDCl₃) δ 156.9, 138.0, 129.1, 128.6, 128.6, 127.3, 126.5, 126.5, 126.4, 123.5, 120.7, 110.9, 55.5 ppm. HRMS (ESI⁺) m/z : ([M+H]⁺) Calcd for C₁₅H₁₄O 210.1045; Found 210.1046.



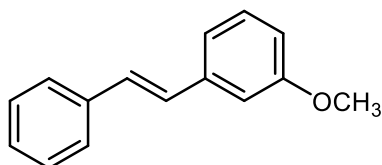
(E)-1-chloro-2-styrylbenzene (3h): Yellow liquid (73% yield). ¹H NMR (400 MHz, CDCl₃) δ 7.62 (d, $J = 8.0$ Hz, 1H, ArH), 7.47 (dd, $J = 7.6, 16.4$ Hz, 3H, ArH), 7.31 (t, $J = 7.6$ Hz, 3H, ArH), 7.23 (d, $J = 7.6$ Hz, 1H, ArH and 1H, CH), 7.16 - 7.10 (m, 1H, ArH), 7.01 (d, $J = 16.4$ Hz, 1H, CH) ppm. ¹³C NMR (150 MHz, CDCl₃) δ 137.1, 135.4, 133.4, 131.2, 129.8, 128.7, 128.5, 128.0, 126.9, 126.8, 126.5, 124.8 ppm. HRMS (ESI⁺) m/z : ([M+H]⁺) Calcd for C₁₄H₁₁Cl 214.0549; Found 214.0547.



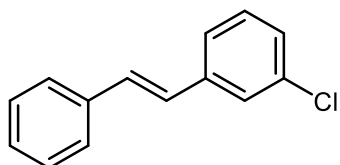
(E)-1-bromo-2-styrylbenzene (3i): Yellow liquid (70% yield). ¹H NMR (600 MHz, CDCl₃) δ 7.67 (d, $J = 7.8$ Hz, 1H, ArH), 7.57 (dd, $J = 7.8, 7.8$ Hz, 3H, ArH), 7.47 (d, $J = 16.2$ Hz, 1H, ArH), 7.38 (t, $J = 7.8$ Hz, 2H, ArH), 7.33 - 7.27 (m, 2H, ArH), 7.12 (t, $J = 7.8$ Hz, 1H, CH), 7.04 (d, $J = 16.2$ Hz, 1H, CH) ppm. ¹³C NMR (150 MHz, CDCl₃) δ 137.1, 137.0, 133.1, 131.4, 128.8, 128.7, 128.1, 127.5, 127.5, 126.8, 126.7, 124.1 ppm. HRMS (ESI⁺) m/z : ([M+H]⁺) Calcd for C₁₆H₁₅Cl 258.0044; Found 258.0045.



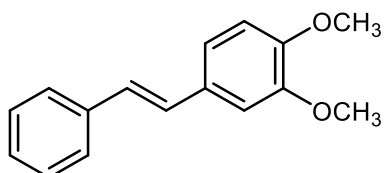
(E)-1-iodo-2-styrylbenzene (3j): Colorless liquid (61% yield). ¹H NMR (600 MHz, CDCl₃) δ 7.88 (d, $J = 7.8$ Hz, 1H, ArH), 7.63 (d, $J = 7.8$ Hz, 1H, ArH), 7.56 (d, $J = 7.2$ Hz, 2H, ArH), 7.38 (dd, $J = 7.2, 6.0$ Hz, 2H ArH), 7.34 (d, $J = 9.0$ Hz, 1H ArH), 7.31 - 7.29 (m, 2H, ArH), 6.96 (dd, $J = 6.6, 6.0$ Hz, 2H, CH) ppm. ¹³C NMR (150 MHz, CDCl₃) δ 140.3, 139.6, 136.9, 132.5, 131.6, 129.0, 128.7, 128.4, 128.1, 126.8, 126.3, 100.4 ppm. HRMS (ESI⁺) m/z : ([M+H]⁺) Calcd for C₁₄H₁₁I 305.9905; Found 305.9906.



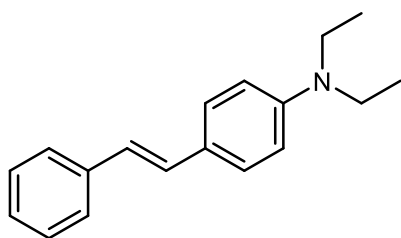
(E)-1-methoxy-3-styrylbenzene (3k): Yellow oil (67% yield). ^1H NMR (600 MHz, CDCl_3) δ 7.52 (d, $J = 7.2$ Hz, 2H, ArH), 7.37 (t, $J = 7.2$ Hz, 2H ArH), 7.28 (dd, $J = 8.4, 9.0$ Hz, 2H, ArH), 7.11 (dd, $J = 7.8, 3.6$ Hz, 3H, CH), 7.06 (s, 1H, CH), 6.83 (dd, $J = 2.4, 1.8$ Hz, 1H, ArH), 3.86 (s, 3H, CH_3) ppm. ^{13}C NMR (150 MHz, CDCl_3) δ 159.9, 138.8, 137.2, 129.6, 129.0, 128.7, 128.6, 127.7, 126.5, 119.2, 113.3, 111.7, 55.3 ppm. HRMS (ESI $^+$) m/z : ($[\text{M}+\text{H}]^+$) Calcd for $\text{C}_{15}\text{H}_{14}\text{O}$ 210.1045; Found 210.1046.



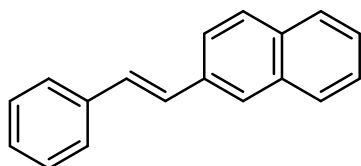
(E)-1-chloro-3-styrylbenzene (3l): White solid (72% yield). ^1H NMR (600 MHz, CDCl_3) δ 7.51 (d, $J = 7.8$ Hz, 3H, ArH), 7.37 (t, $J = 7.8$ Hz, 3H, ArH), 7.28 (t, $J = 7.8$ Hz, 2H, ArH), 7.23 (d, $J = 8.4$ Hz, 1H, ArH), 7.11 (d, $J = 16.2$ Hz, 1H, CH), 7.03 (d, $J = 16.2$ Hz, 1H, CH) ppm. ^{13}C NMR (150 MHz, CDCl_3) δ 139.2, 136.8, 134.6, 130.1, 129.8, 128.7, 128.0, 127.5, 127.2, 126.6, 126.3, 124.7 ppm. mp: 72 -73 $^\circ\text{C}$. HRMS (ESI $^+$) m/z : ($[\text{M}+\text{H}]^+$) Calcd for $\text{C}_{14}\text{H}_{11}\text{Cl}$ 214.0549; Found 214.0547.



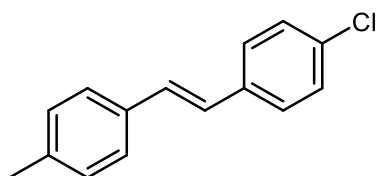
(E)-1,2-dimethoxy-4-styrylbenzene (3m): White solid (65% yield). ^1H NMR (600 MHz, CDCl_3) δ 7.50 (d, $J = 7.2$ Hz, 2H, ArH), 7.35 (t, $J = 7.2$ Hz, 2H, ArH), 7.26 - 7.23 (m, 1H, ArH), 7.10 - 7.03 (m, 3H, ArH), 6.98 (d, $J = 16.2$ Hz, 1H, CH), 6.86 (d, $J = 8.4$ Hz, 1H, CH), 3.95 (s, 3H, CH_3), 3.90 (s, 3H, CH_3) ppm. ^{13}C NMR (150 MHz, CDCl_3) δ 149.1, 148.9, 137.5, 130.5, 128.6, 128.5, 127.3, 126.8, 126.3, 119.9, 111.2, 108.8, 55.9, 55.9 ppm. mp: 116 - 117 $^\circ\text{C}$. HRMS (ESI $^+$) m/z : ($[\text{M}+\text{H}]^+$) Calcd for $\text{C}_{16}\text{H}_{16}\text{O}_2$ 240.1150; Found 240.1150.



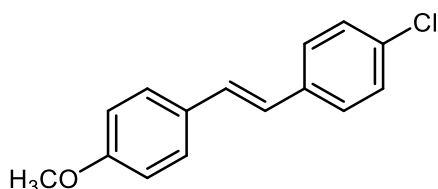
(E)-N,N-diethyl-4-styrylaniline (3n): White solid (77% yield). ^1H NMR (600 MHz, CDCl_3) δ 7.47 (d, $J = 7.8$ Hz, 2H, ArH), 7.39 (d, $J = 9.0$ Hz, 2H, ArH), 7.32 (t, $J = 7.2$ Hz, 2H, ArH), 7.19 (t, $J = 7.2$ Hz, 1H, ArH), 7.04 (d, $J = 16.2$ Hz, 1H, CH), 6.89 (d, $J = 16.2$ Hz, 1H, CH), 6.67 (d, $J = 9.0$ Hz, 2H, ArH), 3.38 (q, $J = 7.2$ Hz, 4H, CH_2), 1.18 (t, $J = 7.2$ Hz, 6H, CH_3) ppm. ^{13}C NMR (150 MHz, CDCl_3) δ 147.4, 138.3, 128.9, 128.5, 127.8, 126.5, 125.9, 124.7, 123.7, 111.7, 44.4, 12.6 ppm. mp: 85 - 86 $^\circ\text{C}$. HRMS (ESI $^+$) m/z : ($[\text{M}+\text{H}]^+$) Calcd for $\text{C}_{18}\text{H}_{21}\text{N}$ 251.1674; Found 251.1673.



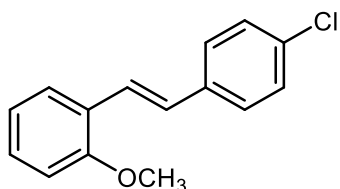
(E)-2-styrylnaphthalene (30): Red solid (83% yield). ^1H NMR (600 MHz, CDCl_3) δ 8.97 (d, $J = 8.4$ Hz, 1H, ArH), 8.31 (s, 1H, ArH), 8.20 (d, $J = 8.4$ Hz, 1H, ArH), 7.99 (d, $J = 7.8$ Hz, 1H ArH), 7.94 (d, $J = 9.0$ Hz, 1H, ArH), 7.90 (d, $J = 7.8$ Hz, 1H, ArH), 7.70 (dd, $J = 7.8, 9.0$ Hz, 2H, ArH), 7.62-7.51 (m, 4H, ArH), 7.37 (t, $J = 7.8$ Hz, 1H, CH), 6.88 (d, $J = 8.4$ Hz, 1H, CH) ppm. ^{13}C NMR (150 MHz, CDCl_3) δ 150.3, 138.5, 134.8, 133.9, 133.7, 129.1, 128.9, 128.0, 127.9, 127.7, 126.5, 124.4, 123.3, 122.1, 119.5, 117.8 ppm. mp: 152 - 153 °C. HRMS (ESI⁺) m/z: ([M+H]⁺) Calcd for $\text{C}_{18}\text{H}_{14}$ 230.1096; Found 230.1096.



(E)-1-chloro-4-(4-methylstyryl)benzene (6a): Yellow solid (74% yield). ^1H NMR (600 MHz, CDCl_3) δ 7.41 (dd, $J = 8.4, 8.4$ Hz, 4H, ArH), 7.31 (d, $J = 8.4$ Hz, 2H, ArH), 7.17 (d, $J = 7.8$ Hz, 2H, ArH), 7.02 (q, $J = 16.2$ Hz, 2H, CH), 2.36 (s, 3H, CH_3) ppm. ^{13}C NMR (150 MHz, CDCl_3) δ 137.8, 136.0, 134.2, 132.9, 129.4, 129.2, 128.8, 127.5, 126.4, 126.3, 21.3 ppm. mp: 177 - 178 °C. HRMS (ESI⁺) m/z: ([M+H]⁺) Calcd for $\text{C}_{15}\text{H}_{13}\text{Cl}$ 228.0706; Found 228.0704.

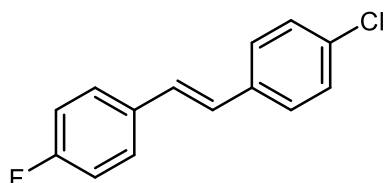


(E)-1-chloro-4-(4-methoxystyryl)benzene (6b): Yellow solid (69% yield). ^1H NMR (600 MHz, CDCl_3) δ 7.44 (d, $J = 8.4$ Hz, 2H, ArH), 7.41 (d, $J = 8.4$ Hz, 2H, ArH), 7.30 (d, $J = 8.4$ Hz, 2H, ArH), 7.03 (d, $J = 16.2$ Hz, 1H, ArH), 6.91 (dd, $J = 11.4, 4.2$ Hz, 2H, ArH and 1H, CH), 3.83 (s, 3H CH_3) ppm. ^{13}C NMR (150 MHz, CDCl_3) δ 159.5, 136.2, 132.7, 129.8, 128.8, 128.8, 127.8, 127.4, 125.2, 114.2, 55.3 ppm. mp: 166 - 168 °C. HRMS (ESI⁺) m/z: ([M+H]⁺) Calcd for $\text{C}_{15}\text{H}_{13}\text{ClO}$ 244.0655; Found 244.0654.

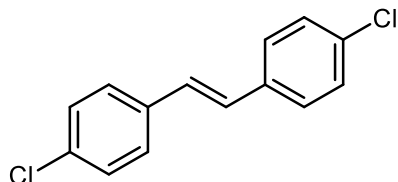


(E)-1-(4-chlorostyryl)-2-methoxybenzene (6c): Yellow Oil (61% yield). ^1H NMR (400 MHz, CDCl_3) δ 7.57 (d, $J = 7.2$ Hz, 1H, ArH), 7.48 - 7.42 (m, 3H, ArH), 7.31 (d, $J = 8.4$ Hz, 2H, ArH), 7.24 (d, $J = 1.2$ Hz, 1H, ArH), 7.06 (d, $J = 16.2$ Hz, 1H, CH), 6.97 (t, $J = 7.2$ Hz,

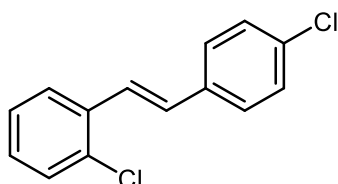
1H, ArH), 6.91 (d, $J = 8.4$ Hz, 1H, CH), 3.89 (s, 3H) ppm. ^{13}C NMR (150 MHz, CDCl_3) δ 157.0, 136.5, 132.8, 131.0, 128.9, 128.7, 127.7, 127.7, 126.5, 124.1, 120.8, 110.9, 55.5 ppm. HRMS (ESI⁺) m/z : ($[\text{M}+\text{H}]^+$) Calcd for $\text{C}_{15}\text{H}_{13}\text{ClO}$ 244.0655; Found 244.0654.



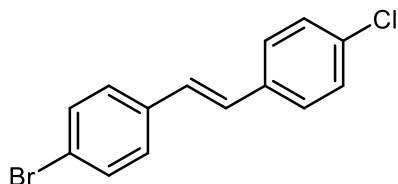
(E)-1-chloro-4-(4-fluorostyryl)benzene (6d): White solid (87% yield). ^1H NMR (600 MHz, CDCl_3) δ 7.67 (d, $J = 7.8$ Hz, 1H, ArH), 7.53 - 7.45 (m, 3H, ArH), 7.61 - 7.33 (m, 1H, ArH), 7.34 (d, $J = 8.4$ Hz, 2H, ArH), 7.29 (dd, $J = 8.4, 7.2$ Hz, 1H, ArH), 7.21 (t, $J = 7.8$ Hz, 1H, CH), 7.02 (d, $J = 16.2$ Hz, 1H, CH) ppm. ^{13}C NMR (150 MHz, CDCl_3) δ 135.6, 135.1, 133.7, 129.9, 129.9, 128.9, 128.7, 128.0, 126.9, 126.4, 125.4 ppm. mp: 131 - 132 °C. HRMS (ESI⁺) m/z : ($[\text{M}+\text{H}]^+$) Calcd for $\text{C}_{14}\text{H}_{10}\text{ClF}$ 232.0455; Found 232.0453.



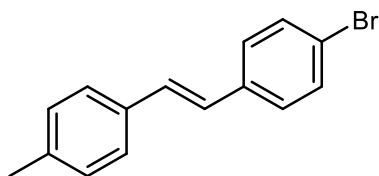
(E)-1,2-bis(4-chlorophenyl)ethene (6e): White solid (85% yield). ^1H NMR (600 MHz, CDCl_3) δ 7.42 (d, $J = 8.4$ Hz, 4H, ArH), 7.33 (d, $J = 8.4$ Hz, 4H, ArH), 7.01 (s, 2H, CH) ppm. ^{13}C NMR (150 MHz, CDCl_3) δ 135.5, 133.4, 128.9, 128.0, 127.7 ppm. mp: 159 - 160 °C. HRMS (ESI⁺) m/z : ($[\text{M}+\text{H}]^+$) Calcd for $\text{C}_{14}\text{H}_{10}\text{Cl}_2$ 248.0160; Found 248.0158.



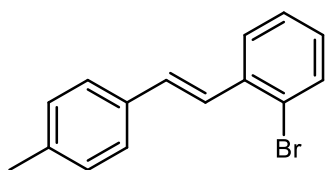
(E)-1-chloro-2-(4-chlorostyryl)benzene (6f): White Oil (64% yield). ^1H NMR (600 MHz, CDCl_3) δ 7.47 (dd, $J = 5.4, 5.4$ Hz, 2H, ArH), 7.42 (d, $J = 8.4$ Hz, 2H, ArH), 7.32 (d, $J = 8.4$ Hz, 2H, ArH), 7.11 - 7.01 (m, 2H, ArH and 1H, CH), 6.96 (d, $J = 16.2$ Hz, 1H, CH) ppm. ^{13}C NMR (150 MHz, CDCl_3) δ 163.3, 161.6, 135.7, 133.2, 128.8, 128.1, 128.0, 127.6, 127.2, 127.1, 115.8, 115.6 ppm. HRMS (ESI⁺) m/z : ($[\text{M}+\text{H}]^+$) Calcd for $\text{C}_{14}\text{H}_{10}\text{Cl}$ 248.0160; Found 248.0158.



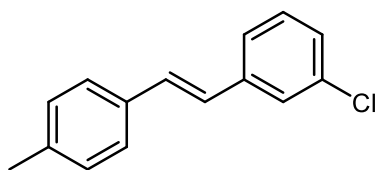
(E)-1-bromo-4-(4-chlorostyryl)benzene (6g): White solid (83% yield). ^1H NMR (600 MHz, DMSO) δ 7.60 (d, $J = 8.4$ Hz, 2H, ArH), 7.58 - 7.52 (m, 4H, ArH), 7.41 (d, $J = 8.4$ Hz, 2H, ArH), 7.30 - 7.17 (m, 2H, CH) ppm. ^{13}C NMR (150 MHz, DMSO) δ 136.6, 136.2, 132.6, 132.1, 129.2, 129.0, 128.7, 128.5, 123.3, 121.2 ppm. mp: 184 - 185 °C. HRMS (ESI⁺) m/z : ($[\text{M}+\text{H}]^+$) Calcd for $\text{C}_{14}\text{H}_{10}\text{BrCl}$ 291.9654; Found 291.9653.



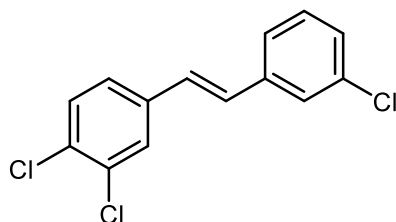
(E)-1-bromo-4-(4-methylstyryl)benzene (6h): White solid (77% yield). ^1H NMR (400 MHz, CDCl_3) δ 7.39 (d, $J = 8.8$ Hz, 2H, ArH), 7.35 - 7.28 (m, 3H, ArH), 7.19 - 7.06 (m, 3H, ArH), 6.95 (dd, $J = 8.2, 8.0$ Hz, 2H, CH), 2.28 (s, 3H, CH_3) ppm. ^{13}C NMR (100 MHz, CDCl_3) δ 137.8, 136.4, 134.1, 131.7, 129.4, 129.3, 127.8, 126.5, 126.4, 121.0, 21.3 ppm. mp: 192 - 193 $^\circ\text{C}$. HRMS (ESI $^+$) m/z : ($[\text{M}+\text{H}]^+$) Calcd for $\text{C}_{15}\text{H}_{13}\text{Br}$ 272.0201; Found 272.0200.



(E)-1-bromo-2-(4-methylstyryl)benzene (6i): Yellow Oil (67% yield). ^1H NMR (600 MHz, CDCl_3) δ 7.67 (d, $J = 7.8$ Hz, 1H, ArH), 7.58 (d, $J = 8.4$ Hz, 1H, ArH), 7.44 (dd, $J = 8.4, 16.2$ Hz, 3H, ArH), 7.30 (t, $J = 7.8$ Hz, 1H, ArH), 7.19 (d, $J = 7.8$ Hz, 2H, ArH), 7.11 (t, $J = 7.8$ Hz, 1H, CH), 7.02 (d, $J = 21.6$ Hz, 1H, CH), 2.38 (s, 3H, CH_3) ppm. ^{13}C NMR (150 MHz, CDCl_3) δ 138.0, 137.3, 134.3, 133.0, 131.4, 129.4, 128.6, 127.5, 126.7, 126.6, 126.5, 124.0, 21.3 ppm. HRMS (ESI $^+$) m/z : ($[\text{M}+\text{H}]^+$) Calcd for $\text{C}_{15}\text{H}_{13}\text{Br}$ 272.0201; Found 272.0200.

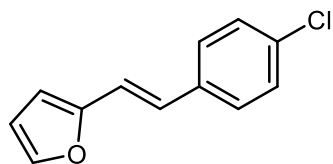


(E)-1-chloro-3-(4-methylstyryl)benzene (6j): White solid (73% yield). ^1H NMR (600 MHz, CDCl_3) δ 7.49 (s, 1H, ArH), 7.41 (d, $J = 7.8$ Hz, 2H, ArH), 7.36 (d, $J = 7.8$ Hz, 1H, ArH), 7.28 (d, $J = 7.8$ Hz, 1H, ArH), 7.19 (dd, $J = 8.4, 7.8$ Hz, 3H, ArH), 7.09 (d, $J = 16.2$ Hz, 1H, CH), 6.98 (d, $J = 16.2$ Hz, 1H, CH), 2.37 (s, 3H, CH_3) ppm. ^{13}C NMR (150 MHz, CDCl_3) δ 139.4, 138.0, 134.6, 134.0, 130.0, 129.8, 129.4, 127.2, 126.6, 126.2, 126.2, 124.6, 21.3 ppm. mp: 104 - 105 $^\circ\text{C}$. HRMS (ESI $^+$) m/z : ($[\text{M}+\text{H}]^+$) Calcd for $\text{C}_{15}\text{H}_{13}\text{Cl}$ 228.0706; Found 228.0704.

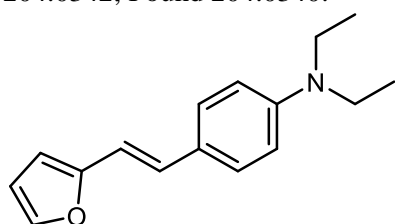


(E)-1,2-dichloro-4-(3-chlorostyryl)benzene (6k): White solid (78% yield). ^1H NMR (600 MHz, CDCl_3) δ 7.58 (d, $J = 1.8$ Hz, 1H, ArH), 7.42 (dd, $J = 2.4, 2.4$ Hz, 3H, ArH), 7.35 - 7.30 (m, 3H, ArH), 7.03 (d, $J = 16.2$ Hz, 1H, CH), 6.95 (d, $J = 16.2$ Hz, 1H, CH) ppm. ^{13}C NMR (150 MHz, CDCl_3) δ 137.1, 135.0, 133.8, 132.9, 131.4, 130.6, 129.2, 129.0, 128.1,

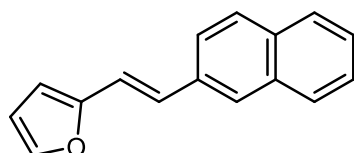
127.8, 126.7, 125.6 ppm. mp: 105 - 106 °C. HRMS (ESI⁺) m/z: ([M+H]⁺) Calcd for C₁₄H₉Cl₃ 281.9770; Found 281.9769.



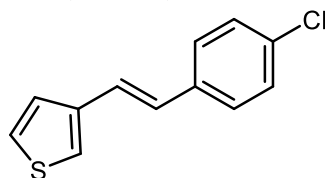
(E)-2-(4-chlorostyryl)furan (6l): Yellow solid (59% yield). ¹H NMR (600 MHz, CDCl₃) δ 7.38 (d, *J* = 8.4 Hz, 3H, ArH), 7.30 (d, *J* = 8.4 Hz, 2H, ArH), 6.97 (d, *J* = 16.2 Hz, 1H, CH), 6.86 (d, *J* = 16.2 Hz, 1H, CH), 6.42 (dd, *J* = 1.8, 1.8 Hz, 1H, ArH), 6.36 (d, *J* = 3.0 Hz, 1H, ArH) ppm. ¹³C NMR (150 MHz, CDCl₃) δ 152.9, 142.3, 135.5, 133.1, 128.8, 127.4, 125.7, 117.0, 111.7, 109.0 ppm. mp: 69 - 70 °C. HRMS (ESI⁺) m/z: ([M+H]⁺) Calcd for C₁₂H₉ClO 204.0342; Found 204.0340.



(E)-N,N-diethyl-4-(2-(furan-2-yl)vinyl)aniline (6m): Brown solid (63% yield). ¹H NMR (600 MHz, CDCl₃) δ 7.37 - 7.33 (m, 3H, ArH), 6.97 (d, *J* = 16.2 Hz, 1H, CH), 6.68 (dd, *J* = 16.2, 8.4 Hz, 2H, ArH and 1H, CH), 6.40 (dd, *J* = 1.8, 1.8 Hz, 1H, ArH), 6.24 (d, *J* = 1.8 Hz, 1H, ArH), 3.38 (q, *J* = 7.0 Hz, 4H, CH₂), 1.19 (t, *J* = 6.6 Hz, 1H, CH₃) ppm. ¹³C NMR (150 MHz, CDCl₃) δ 154.3, 147.4, 141.2, 130.2, 127.7, 127.6, 112.0, 111.7, 111.4, 106.3, 44.4, 12.6 ppm. mp: 94 - 95 °C. HRMS (ESI⁺) m/z: ([M+H]⁺) Calcd for C₁₆H₁₉NO 241.1467; Found 241.1468.

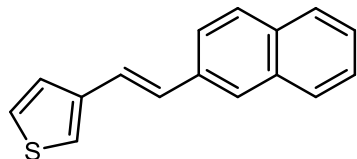


(E)-2-(2-(naphthalen-2-yl)vinyl)furan (6n): Red solid (81% yield). ¹H NMR (600 MHz, CDCl₃) δ 8.99 (d, *J* = 8.4 Hz, 1H, ArH), 8.31 (s, 1H, ArH), 8.21 (d, *J* = 9.0 Hz, 1H, ArH), 7.99 (d, *J* = 7.2 Hz, 1H, ArH), 7.95 (d, *J* = 9.0 Hz, 1H, ArH), 7.90 (d, *J* = 7.2 Hz, 1H, ArH), 7.72 (d, *J* = 7.8 Hz, 1H, ArH), 7.67 (d, *J* = 8.4 Hz, 1H, ArH), 7.63 (t, *J* = 8.4 Hz, 1H, CH), 7.54 (d, *J* = 8.4 Hz, 1H, CH), 7.39 (t, *J* = 6.6 Hz, 1H, ArH), 6.86 (d, *J* = 9.0 Hz, 1H, ArH) ppm. ¹³C NMR (150 MHz, CDCl₃) δ 150.3, 138.5, 134.8, 133.7, 129.1, 128.9, 128.0, 127.9, 127.7, 126.6, 126.6, 124.5, 123.3, 122.1, 119.5, 117.8 ppm. mp: 148 - 149 °C. HRMS (ESI⁺) m/z: ([M+H]⁺) Calcd for C₁₆H₁₂O 220.0888; Found 220.0886.

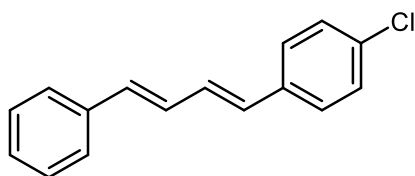


(E)-2-(4-chlorostyryl)thiophene (6o): White solid (76% yield). ¹H NMR (600 MHz, CDCl₃) δ 7.40 (d, *J* = 8.4 Hz, 2H, ArH), 7.32 (dd, *J* = 2.4, 9.0 Hz, 4H, ArH), 7.28 (s, 1H,

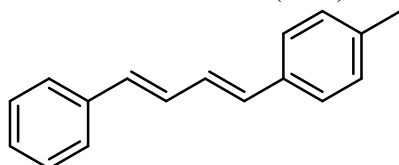
ArH), 7.09 (d, $J = 16.2$ Hz, 1H, CH), 6.90 (d, $J = 16.2$ Hz, 1H, CH) ppm. ^{13}C NMR (150 MHz, CDCl_3) δ 139.8, 135.9, 133.0, 128.8, 127.4, 127.3, 126.3, 124.8, 123.5, 122.7 ppm. mp: 128 - 129 °C. HRMS (ESI⁺) m/z : ($[\text{M}+\text{H}]^+$) Calcd for $\text{C}_{12}\text{H}_9\text{ClS}$ 220.0113; Found 220.0112.



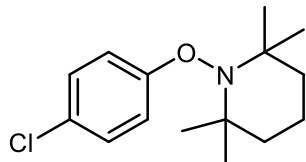
(E)-2-(2-(naphthalen-2-yl)vinyl)thiophene (6p): Red solid (84% yield). ^1H NMR (600 MHz, CDCl_3) δ 8.32 (s, 1H, ArH), 8.21 (dd, $J = 1.8, 1.8$ Hz, 1H, ArH), 7.99 (d, $J = 7.2$ Hz, 1H, ArH), 7.95 (d, $J = 8.4$ Hz, 1H, ArH), 7.90 (d, $J = 7.8$ Hz, 1H, ArH), 7.72 (d, $J = 7.8$ Hz, 1H, ArH), 7.68 (d, $J = 9.0$ Hz, 1H, ArH), 7.61 (t, $J = 8.4$ Hz, 1H, ArH), 7.54 (dd, $J = 6.0, 9.0$ Hz, 2H, ArH), 7.38 (t, $J = 7.8$ Hz, 1H, CH), 6.88 (d, $J = 9.0$ Hz, 1H, CH) ppm. ^{13}C NMR (150 MHz, CDCl_3) δ 138.5, 134.8, 133.9, 133.7, 129.1, 128.9, 127.9, 127.7, 127.4, 127.2, 126.5, 124.4, 123.3, 122.1, 119.5, 117.8 ppm. mp: 154 - 155 °C. HRMS (ESI⁺) m/z : ($[\text{M}+\text{H}]^+$) Calcd for $\text{C}_{16}\text{H}_{12}\text{S}$ 236.0660; Found 236.0658.



1-chloro-4-((1E,3E)-4-phenylbuta-1,3-dien-1-yl)benzene (6q): White solid (62% yield). ^1H NMR (600 MHz, CDCl_3) δ 7.45 (d, $J = 7.8$ Hz, 2H, ArH), 7.35 (dd, $J = 8.4, 7.8$ Hz, 4H, ArH), 7.30 (d, $J = 8.4$ Hz, 2H, ArH), 7.27 - 7.25 (m, 1H, ArH), 6.95 - 6.92 (m, 2H, CH), 6.69 (d, $J = 14.4$ Hz, 1H, CH), 6.62 (d, $J = 14.4$ Hz, 1H, CH) ppm. ^{13}C NMR (150 MHz, CDCl_3) δ 137.2, 135.9, 133.4, 133.1, 131.4, 129.8, 128.9, 128.8, 128.7, 127.7, 127.5, 126.4 ppm. mp: 149 - 150 °C. HRMS (ESI⁺) m/z : ($[\text{M}+\text{H}]^+$) Calcd for $\text{C}_{16}\text{H}_{13}\text{Cl}$ 240.0706; Found 240.0705.



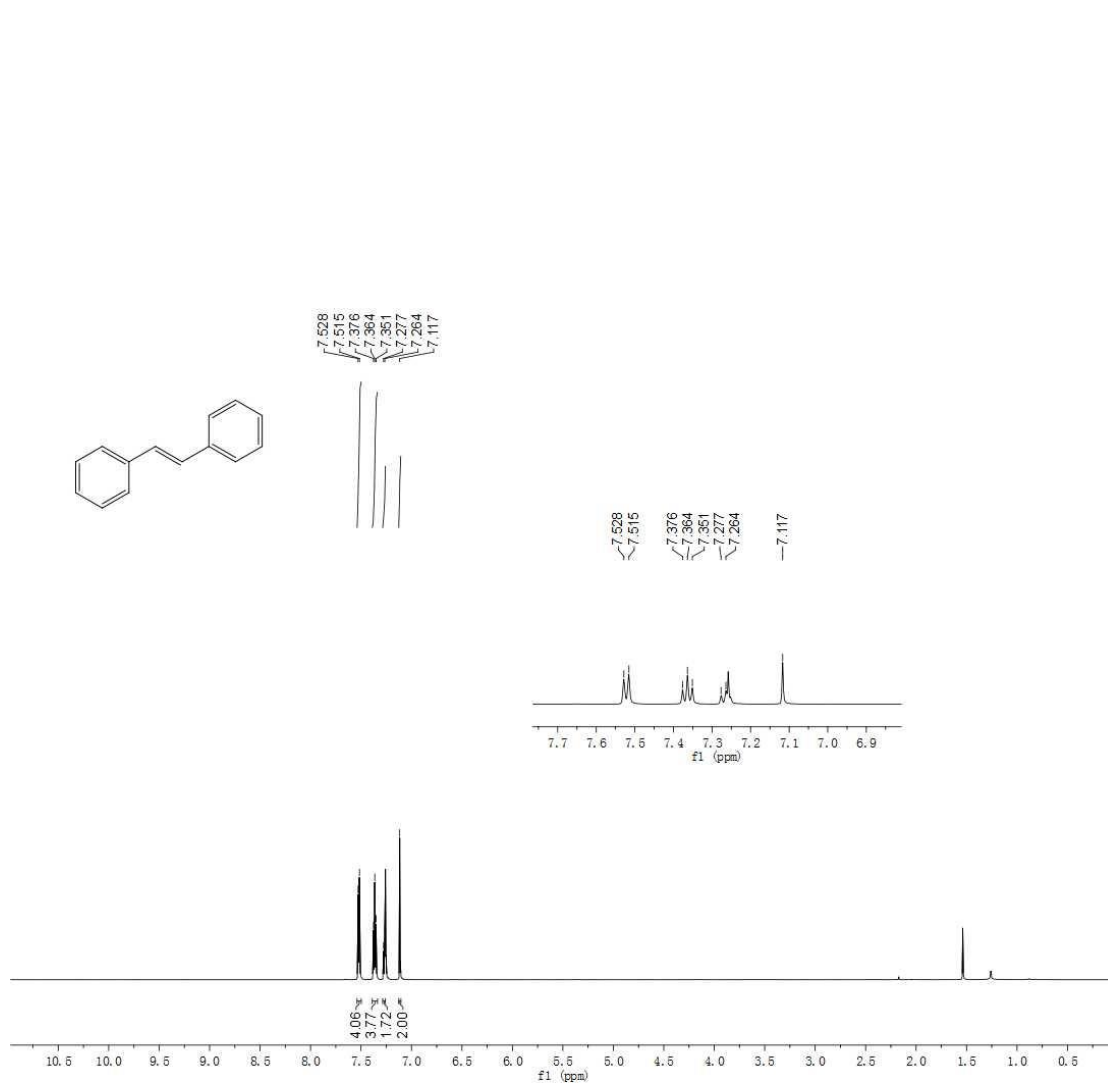
1-methyl-4-((1E,3E)-4-phenylbuta-1,3-dien-1-yl)benzene (6r): White solid (57% yield). ^1H NMR (600 MHz, CDCl_3) δ 7.44 (d, $J = 7.8$ Hz, 2H, ArH), 7.34 (dd, $J = 8.4, 7.8$ Hz, 4H, ArH), 7.23 (t, $J = 7.2$ Hz, 1H, ArH), 7.15 (d, $J = 8.4$ Hz, 2H, ArH), 6.99 - 6.89 (m, 2H, CH), 6.66 (d, $J = 13.2$ Hz, 2H, CH), 2.36 (s, 3H, CH_3) ppm. ^{13}C NMR (150 MHz, CDCl_3) δ 137.5, 137.5, 134.6, 132.8, 132.2, 129.4, 129.4, 128.6, 128.3, 127.4, 126.3, 21.3 ppm. mp: 150 - 150 °C. HRMS (ESI⁺) m/z : ($[\text{M}+\text{H}]^+$) Calcd for $\text{C}_{17}\text{H}_{16}$ 220.1252; Found 220.1251.

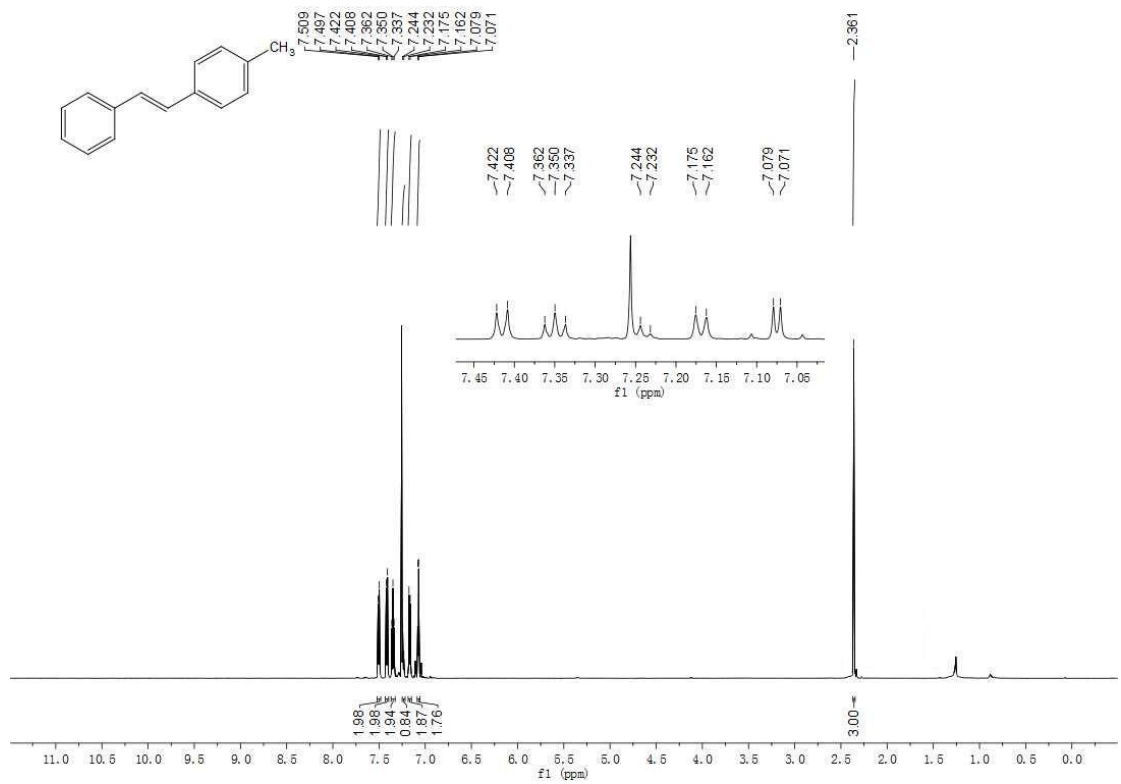
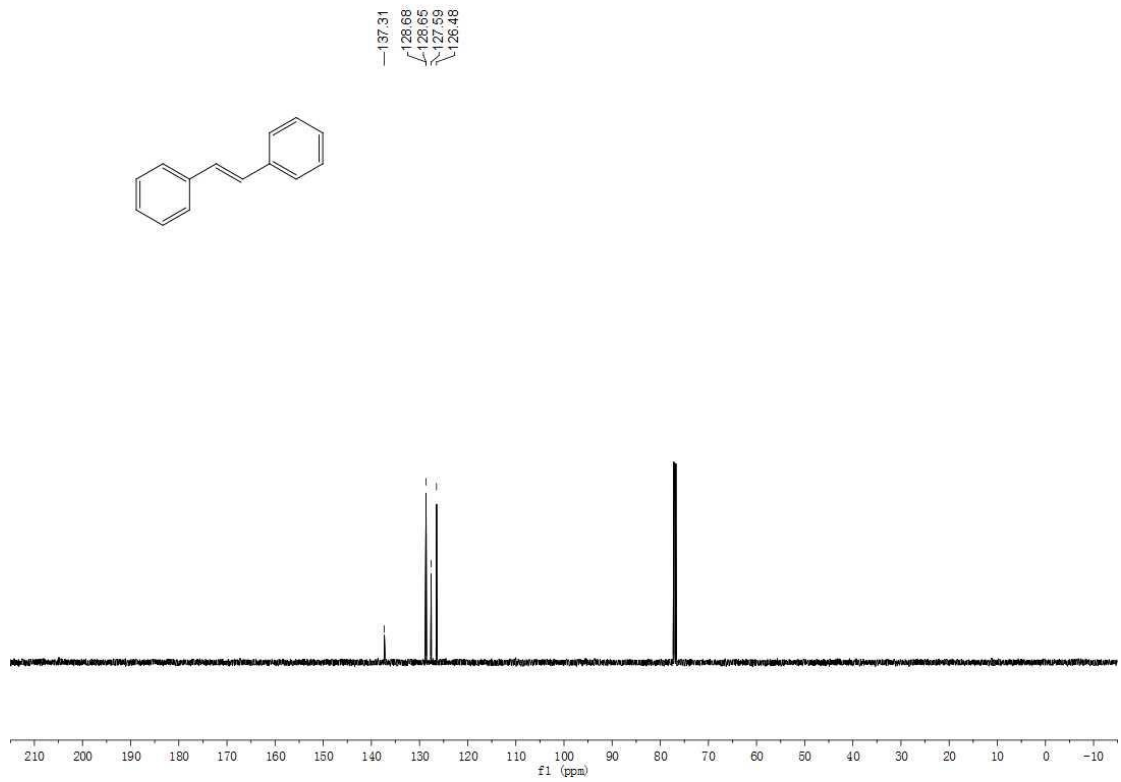


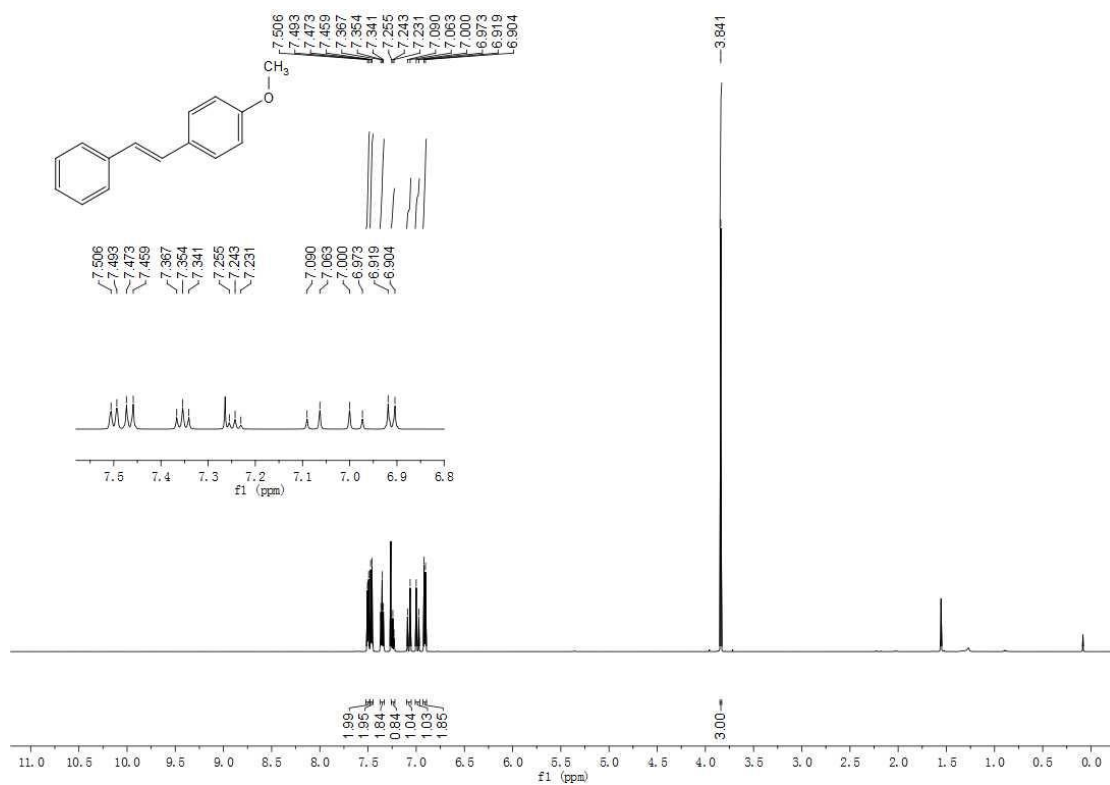
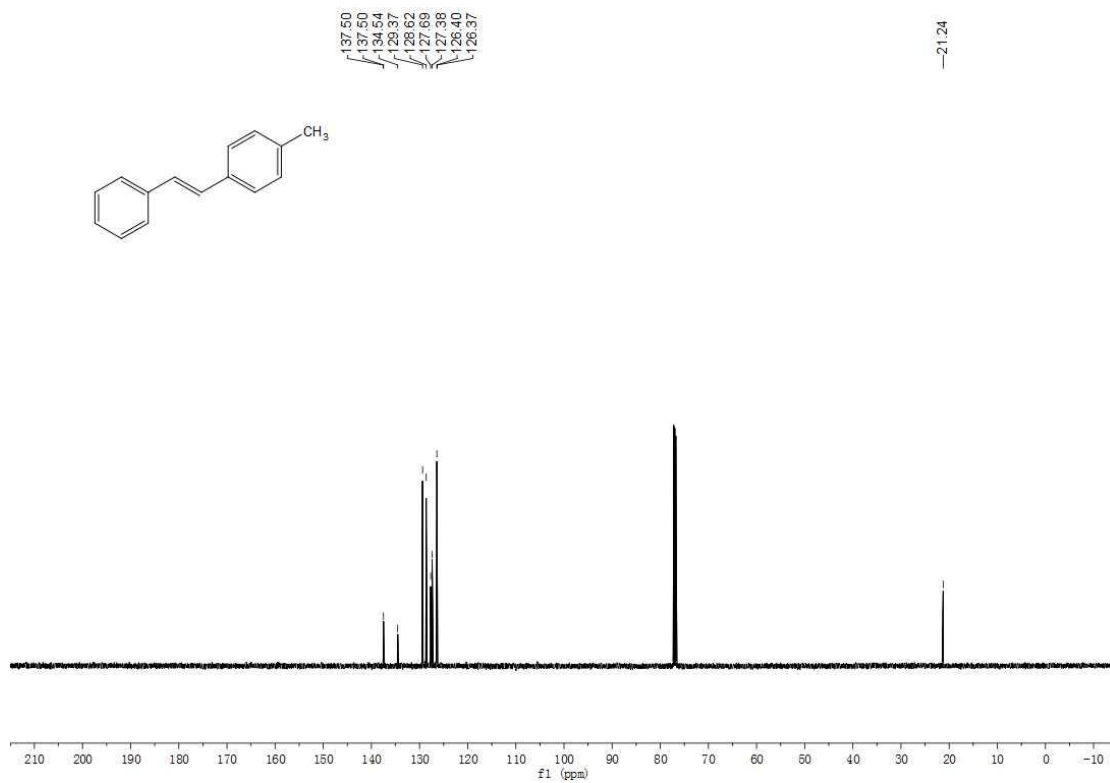
1-(4-chlorophenoxy)-2,2,6,6-tetramethylpiperidine (1): White solid (88% yield). ^1H NMR (600 MHz, CDCl_3) δ 7.13 (q, $J = 9.6$ Hz, 1H), 1.58 (dd, $J = 12.4, 4.0$ Hz, 1H), 1.41 (dd, $J = 2.8, 10.8$ Hz, 1H), 1.21 (s, 1H), 0.98 (s, 1H) ppm. ^{13}C NMR (150 MHz, CDCl_3) δ 162.2, 128.5, 124.3, 115.2, 60.5, 39.7, 32.5, 20.4, 17.0 ppm. HRMS (ESI⁺) m/z : ($[\text{M}+\text{H}]^+$) Calcd for $\text{C}_{15}\text{H}_{22}\text{ClNO}$ 267.1390; Found 267.1391.

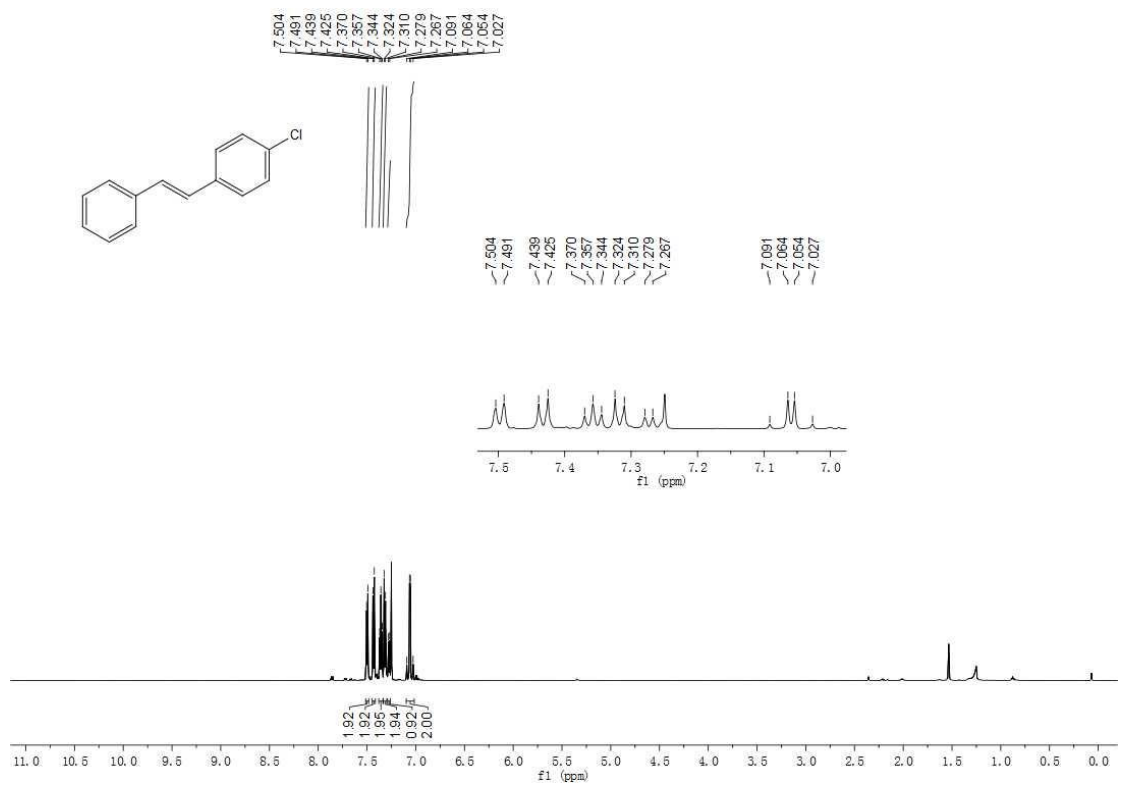
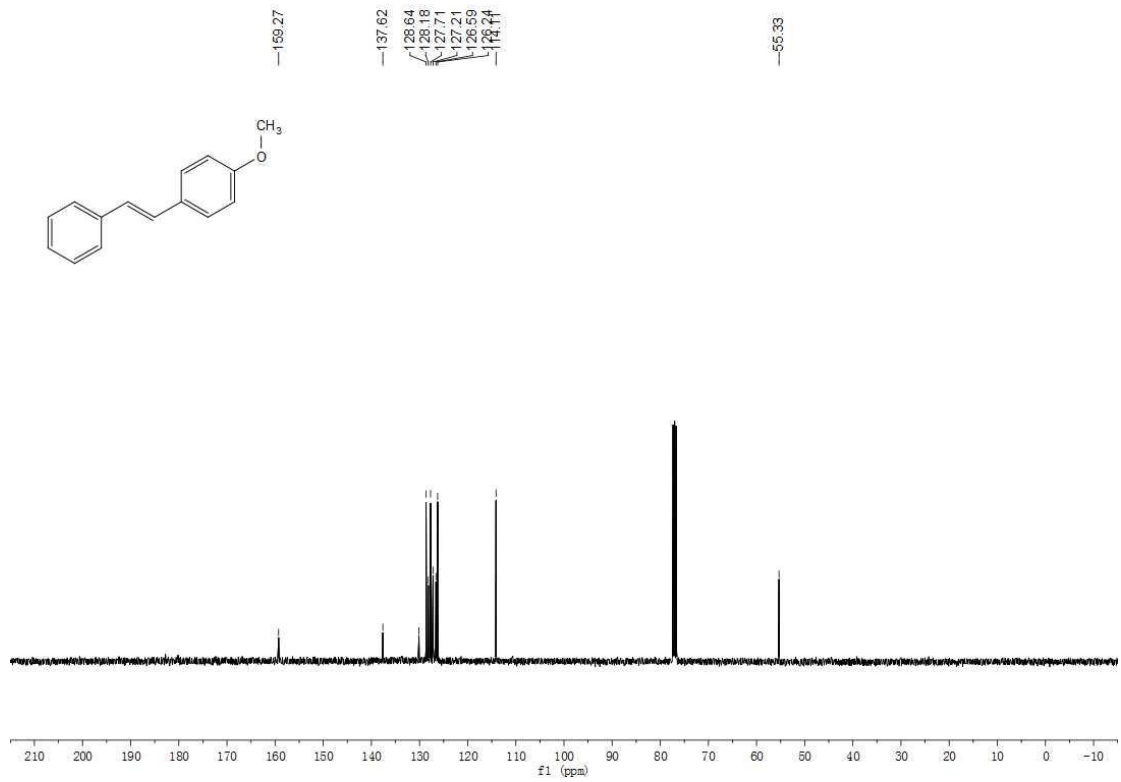
5. References

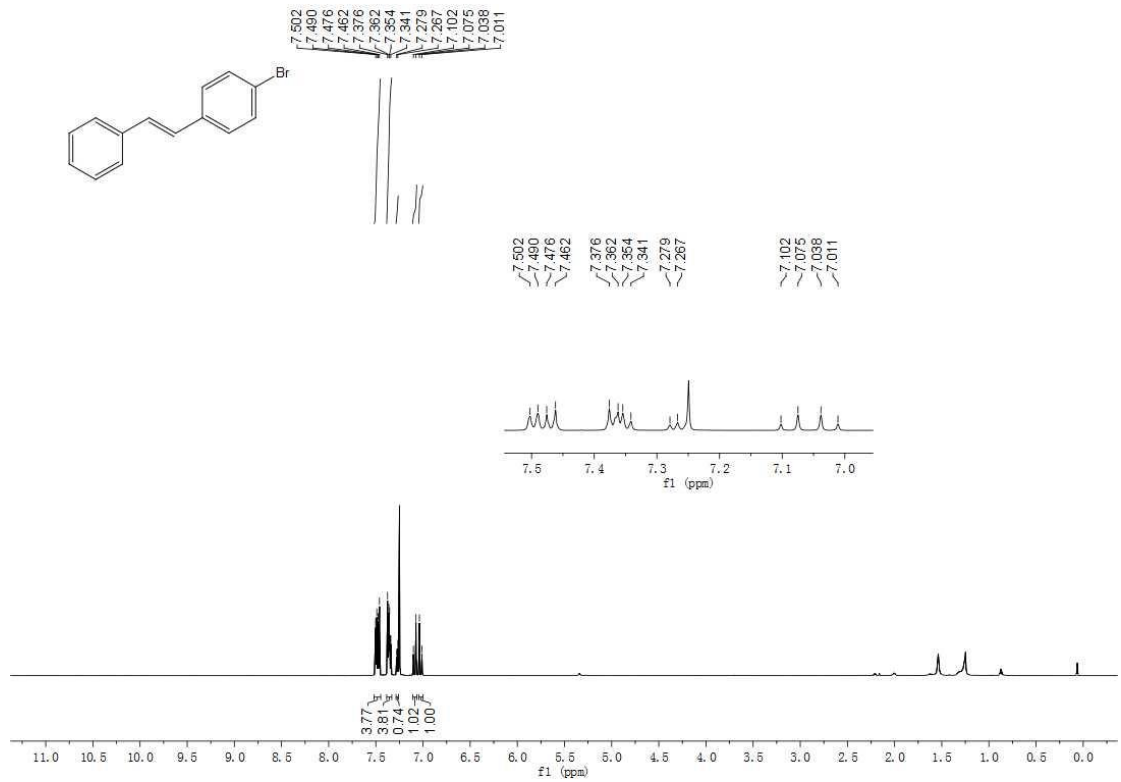
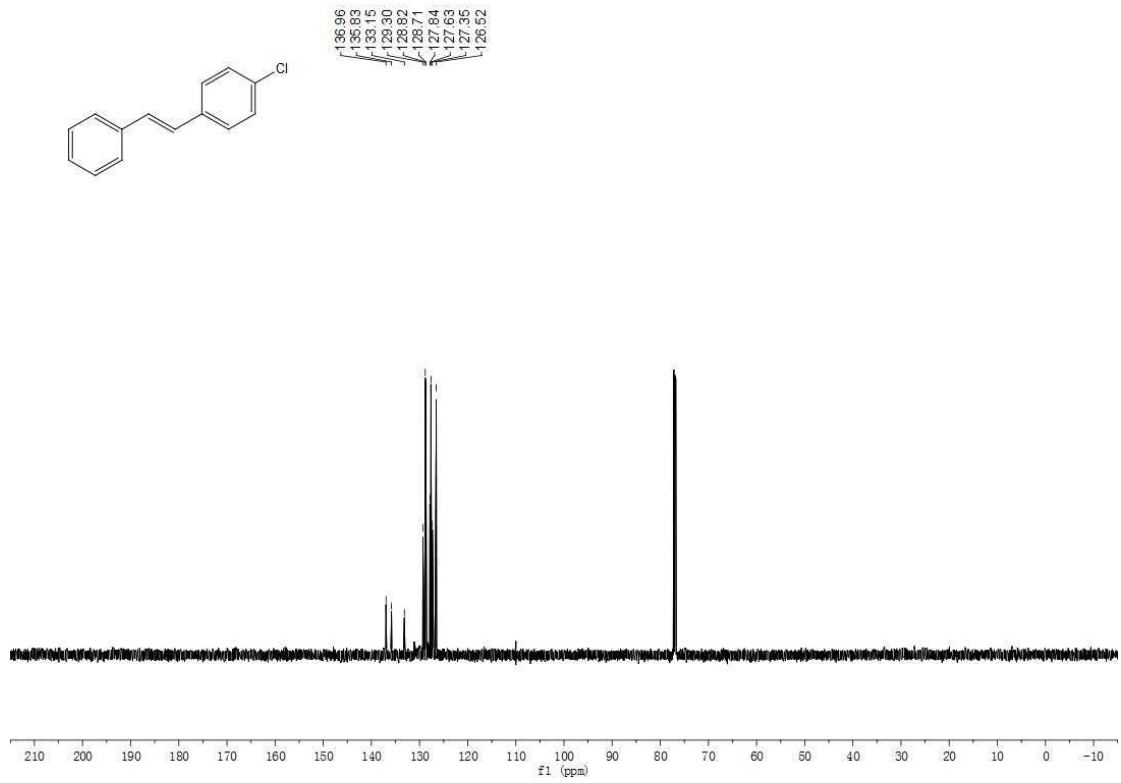
1. Hanson, P.; Jones, J. R.; Taylor, A. B.; Walton, P. H.; Timmsb, A. W. *J. Chem. Soc. Perkin Trans. 2*. **2002**, 2, 1135-1150.

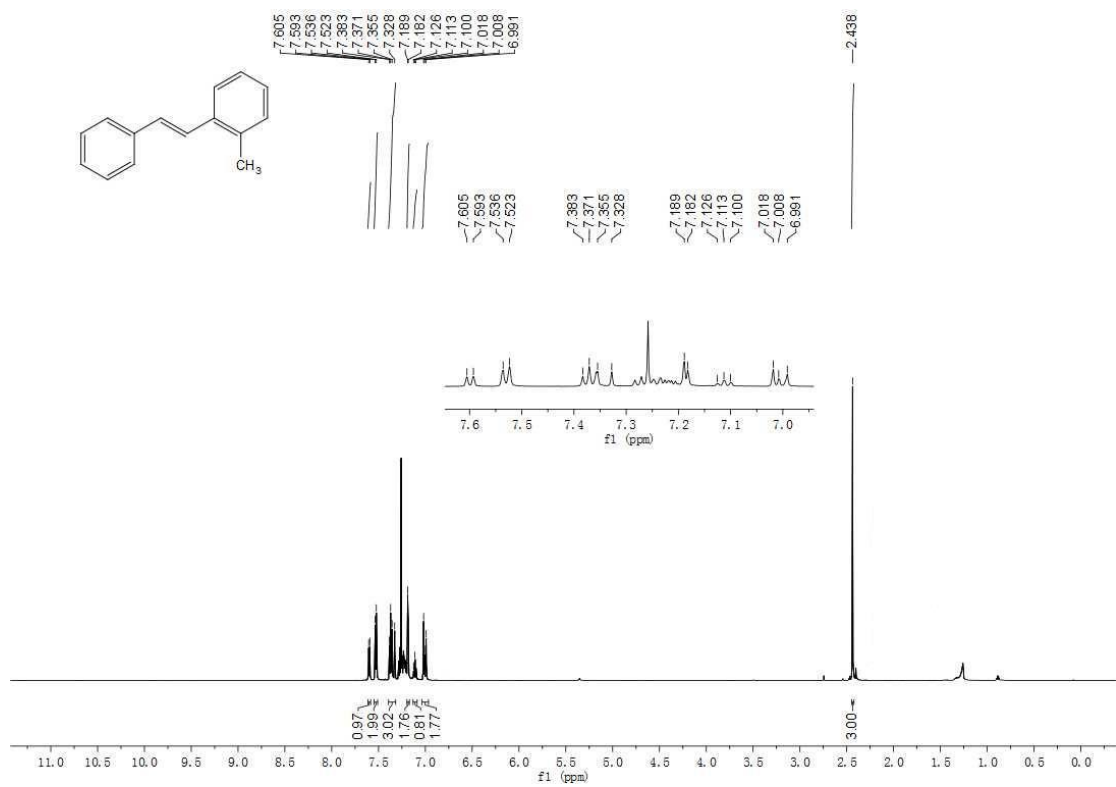
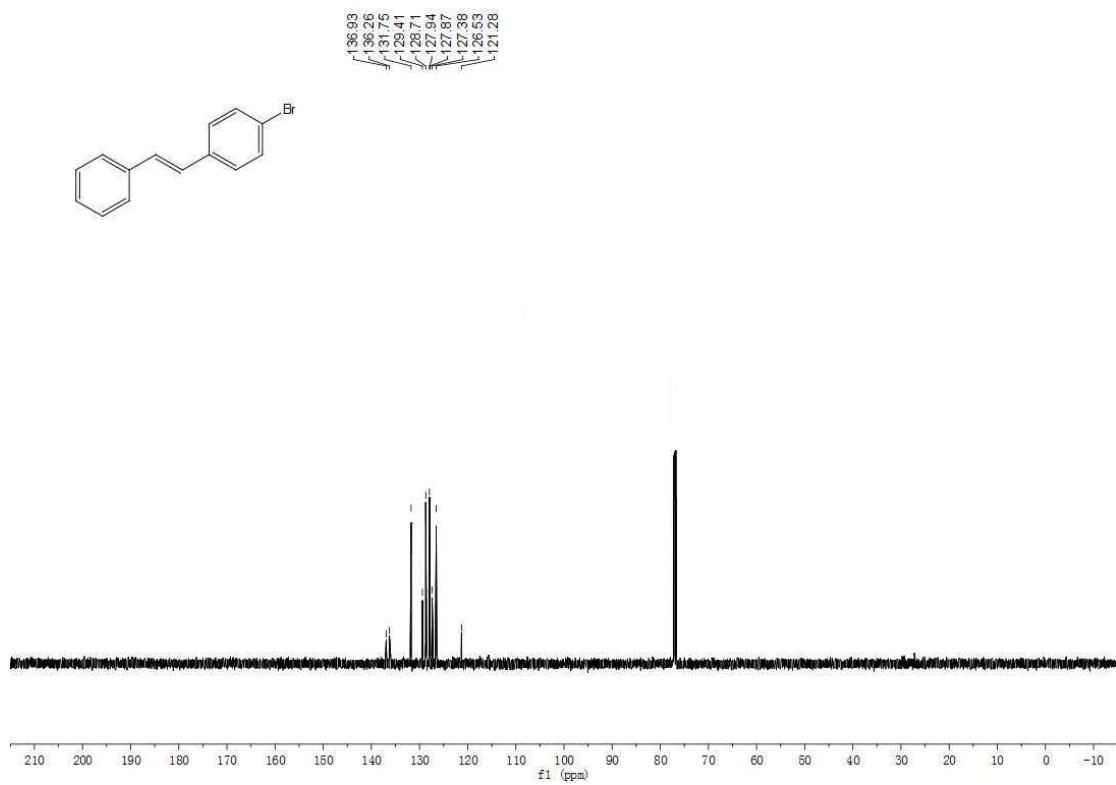


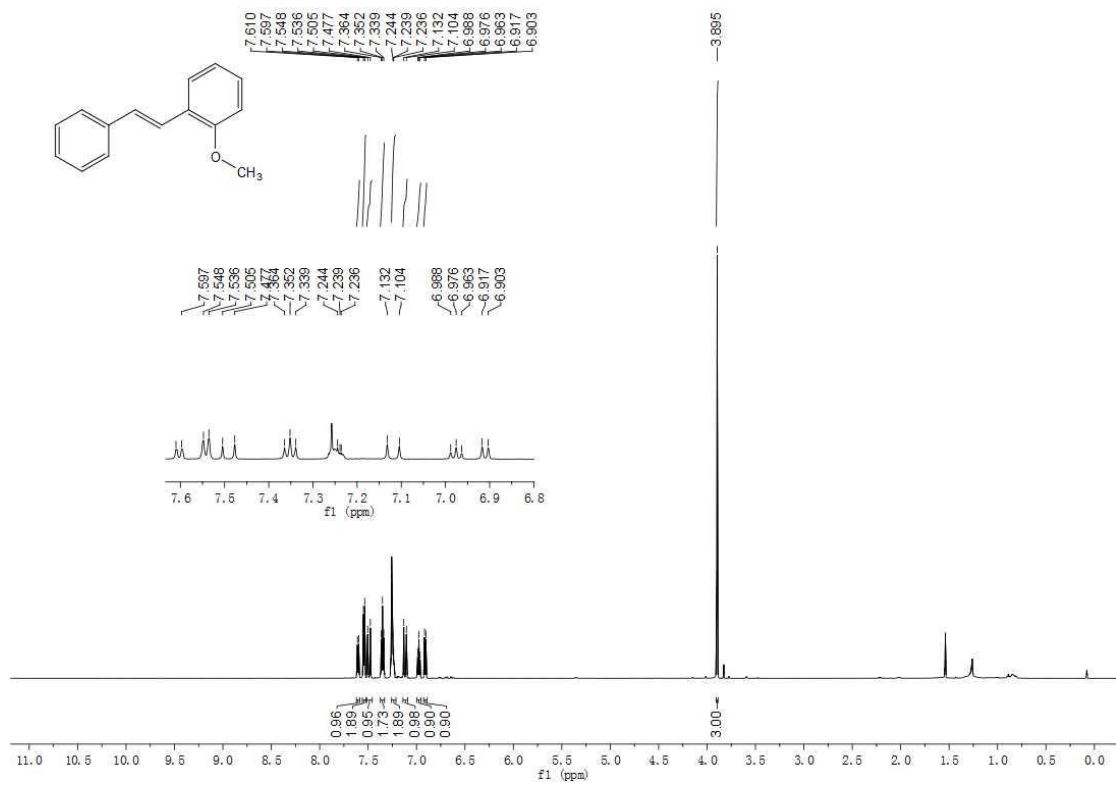
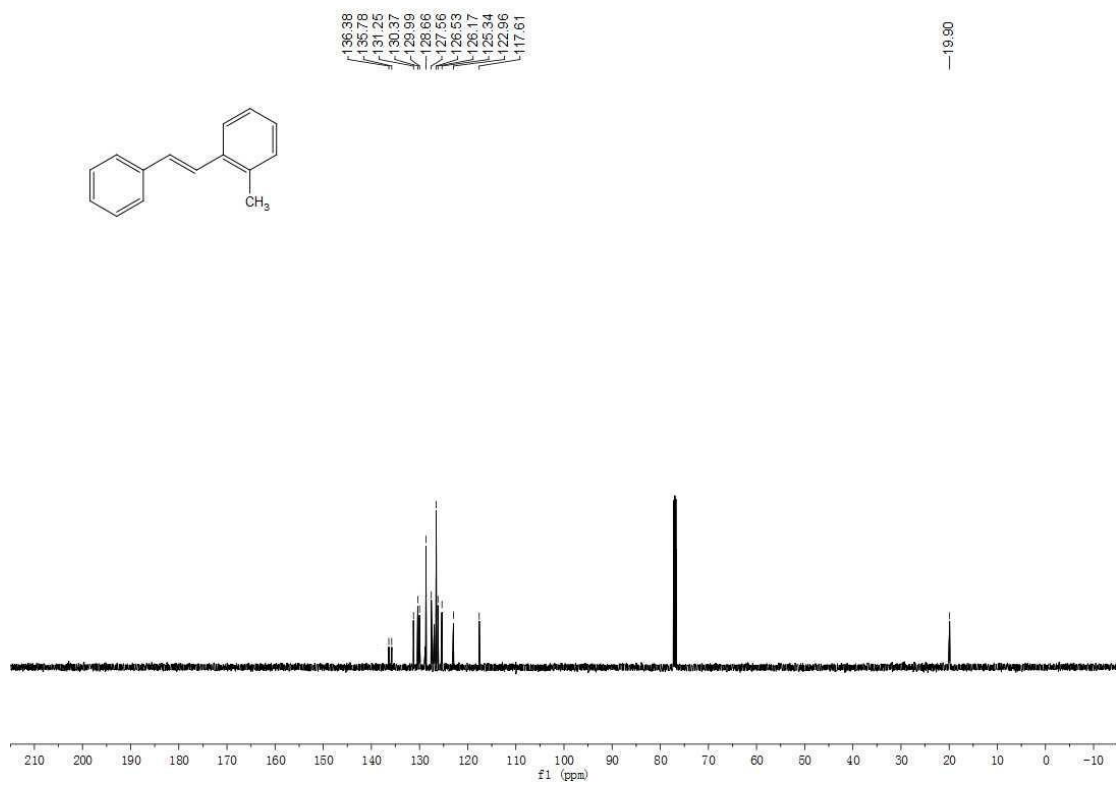


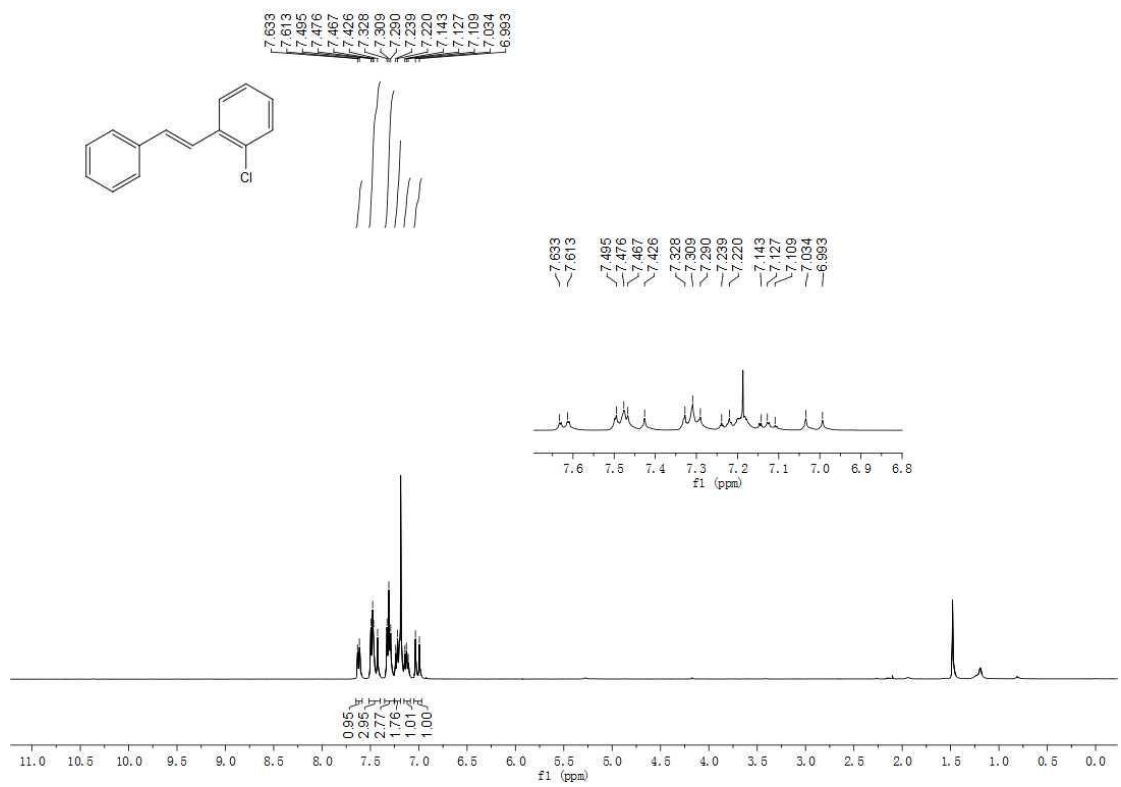
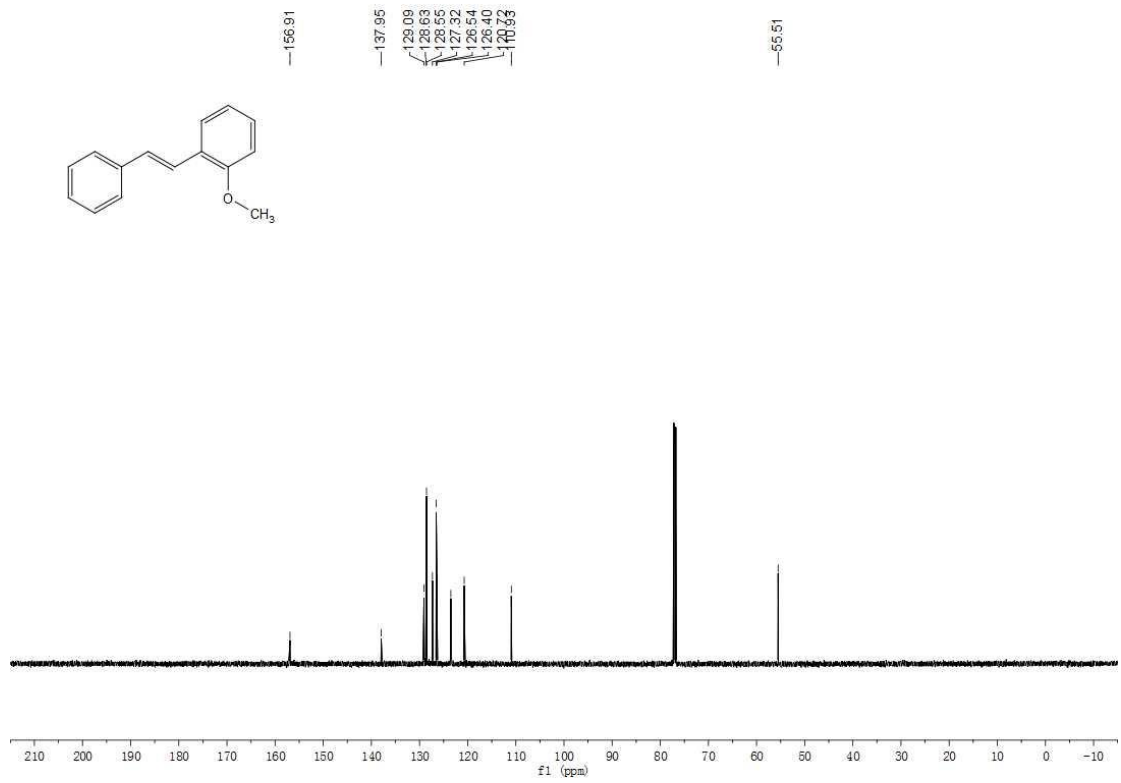


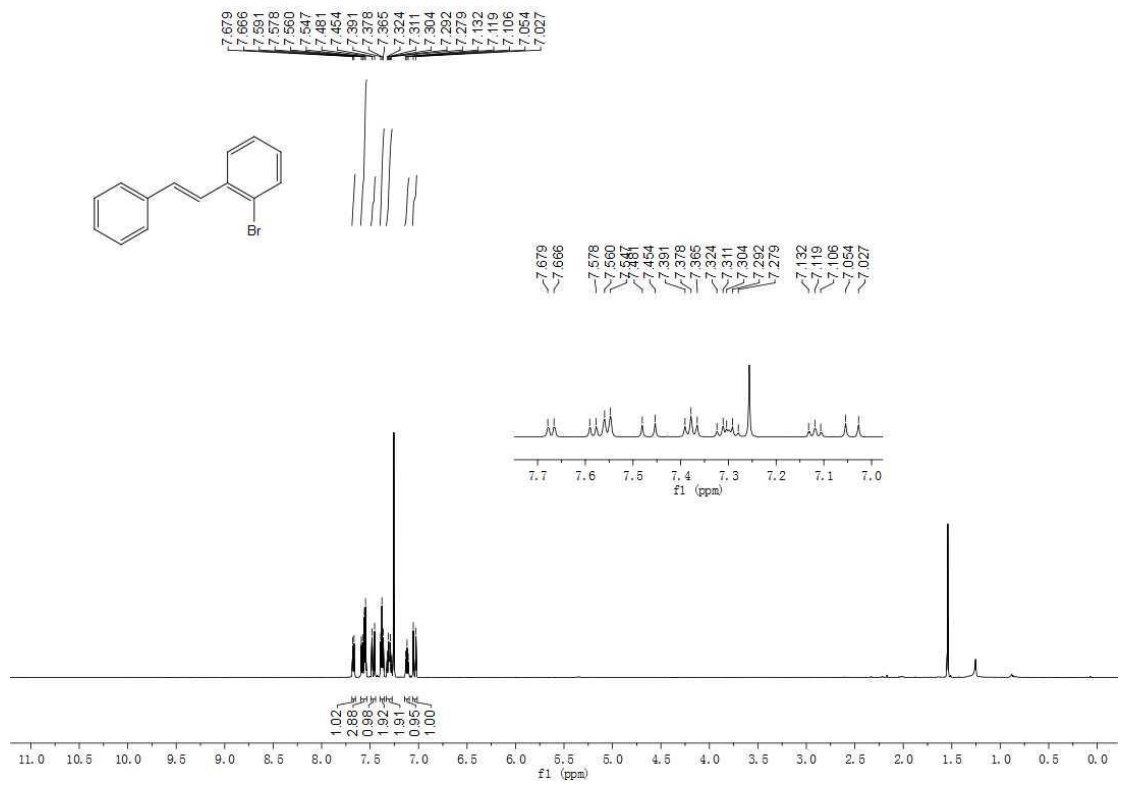
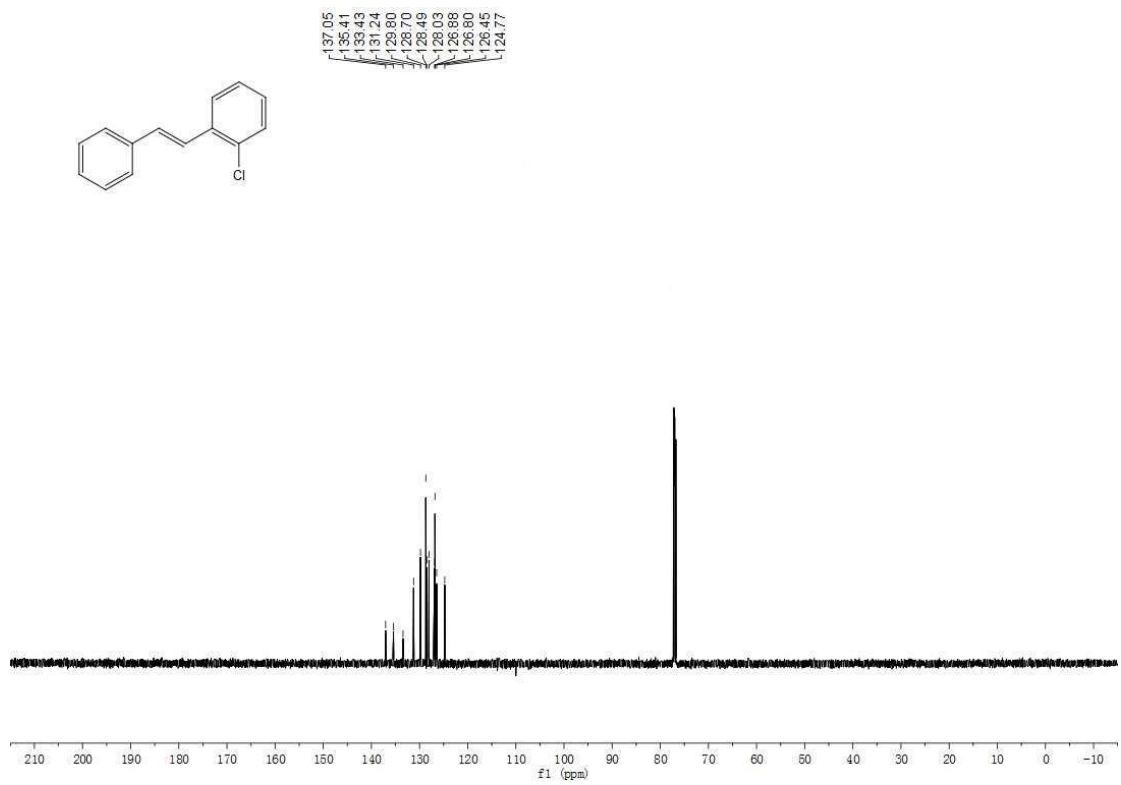


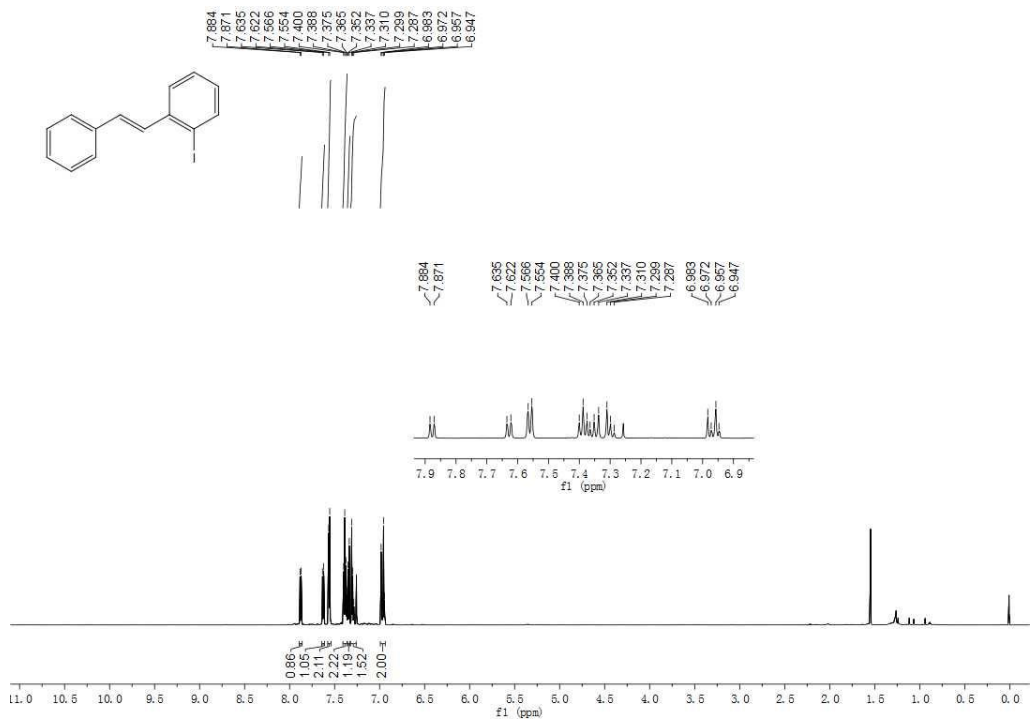
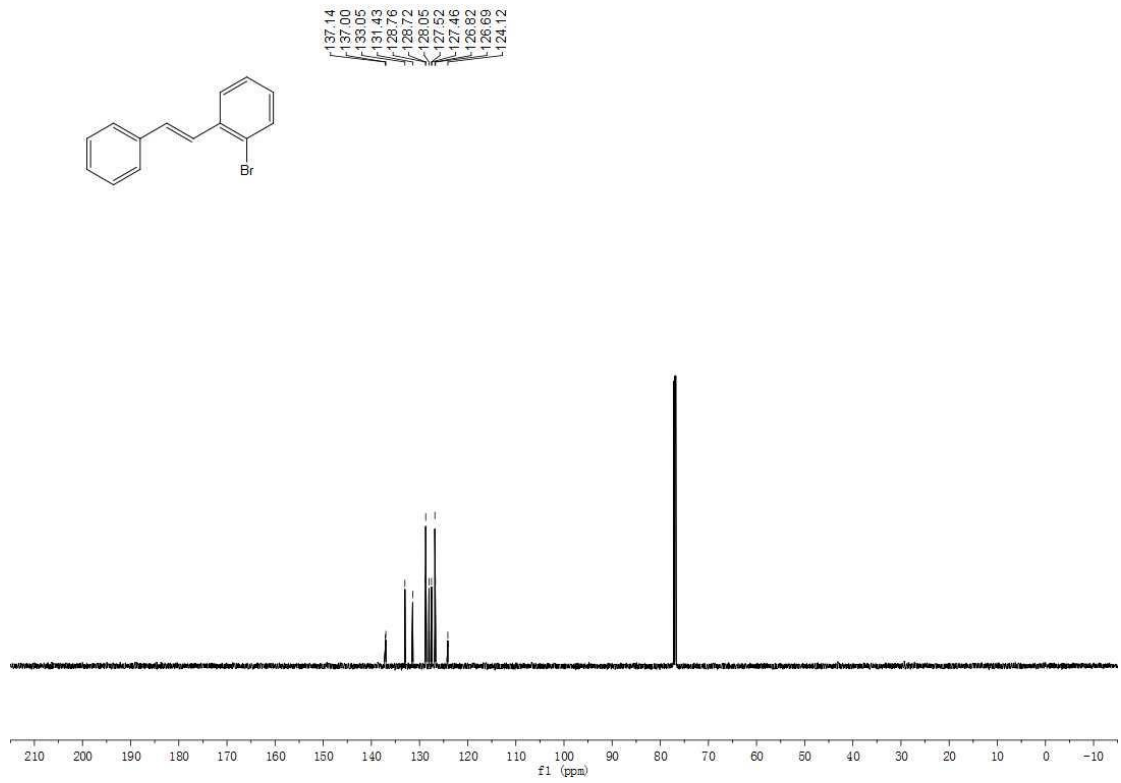


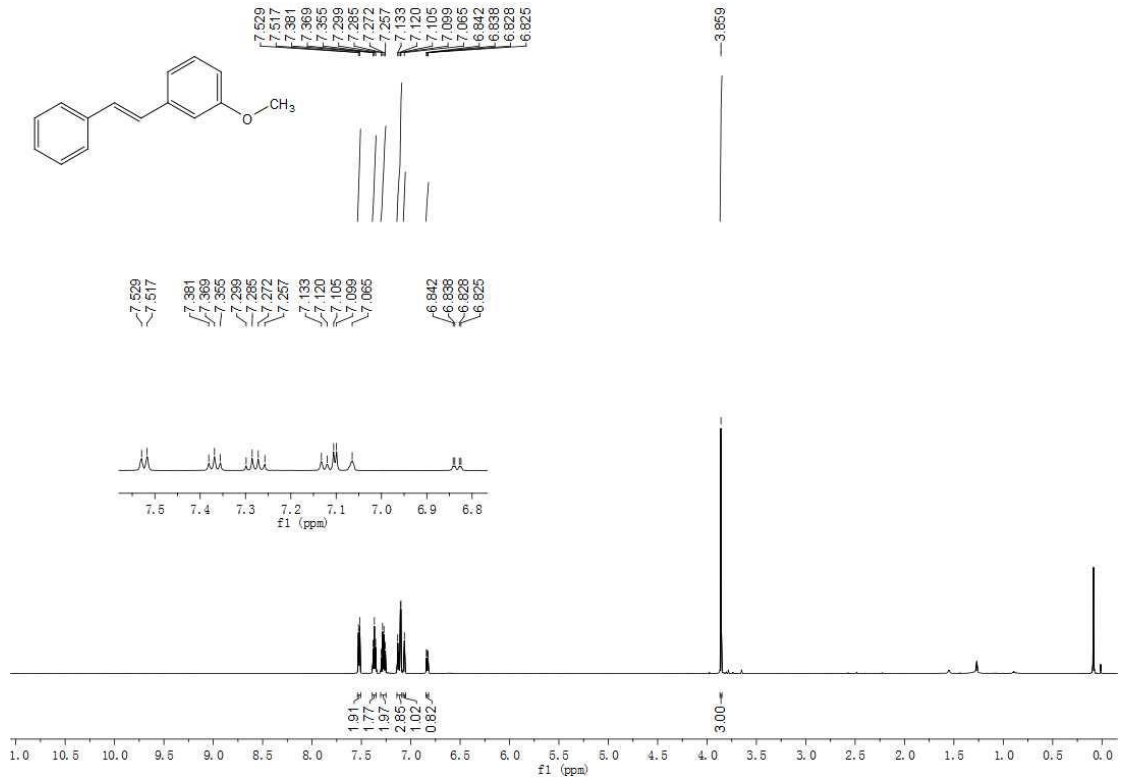
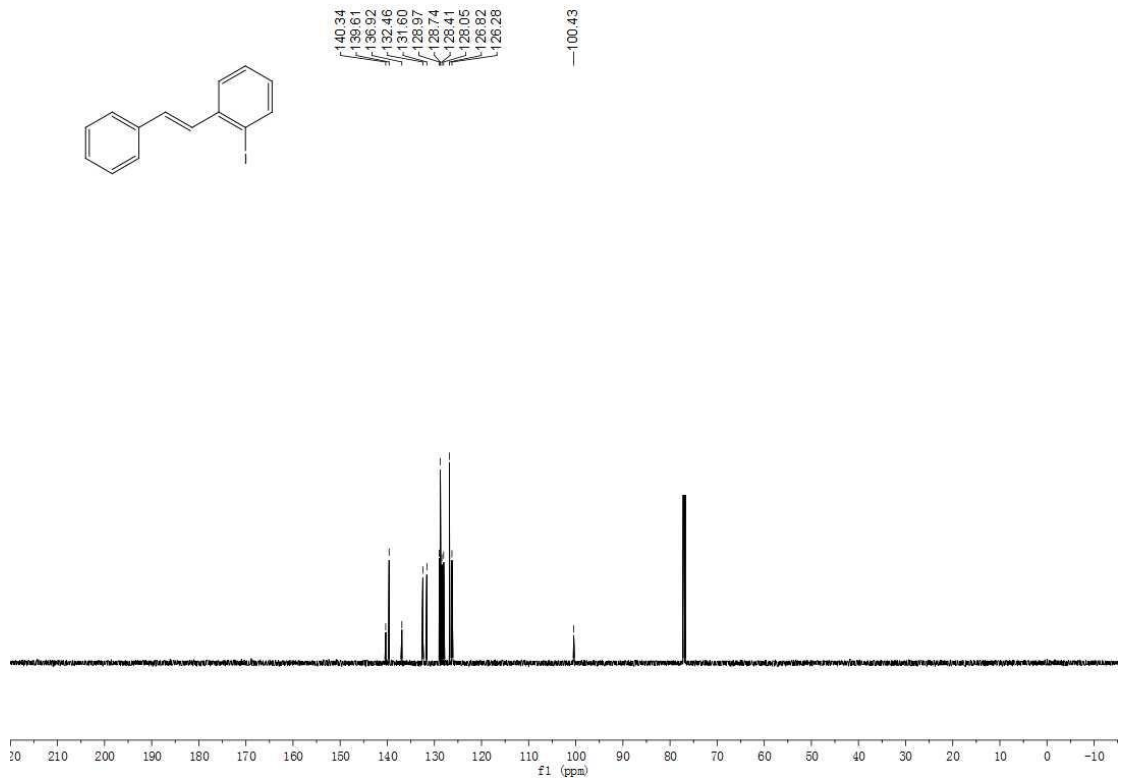


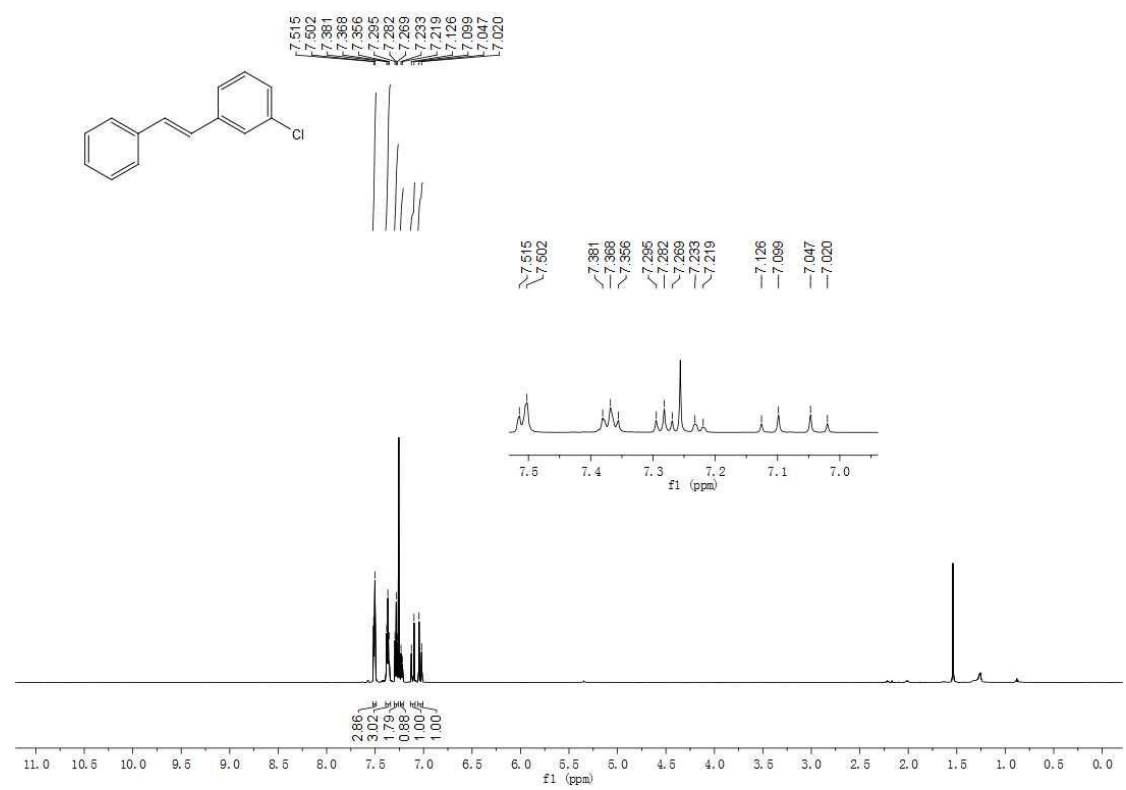
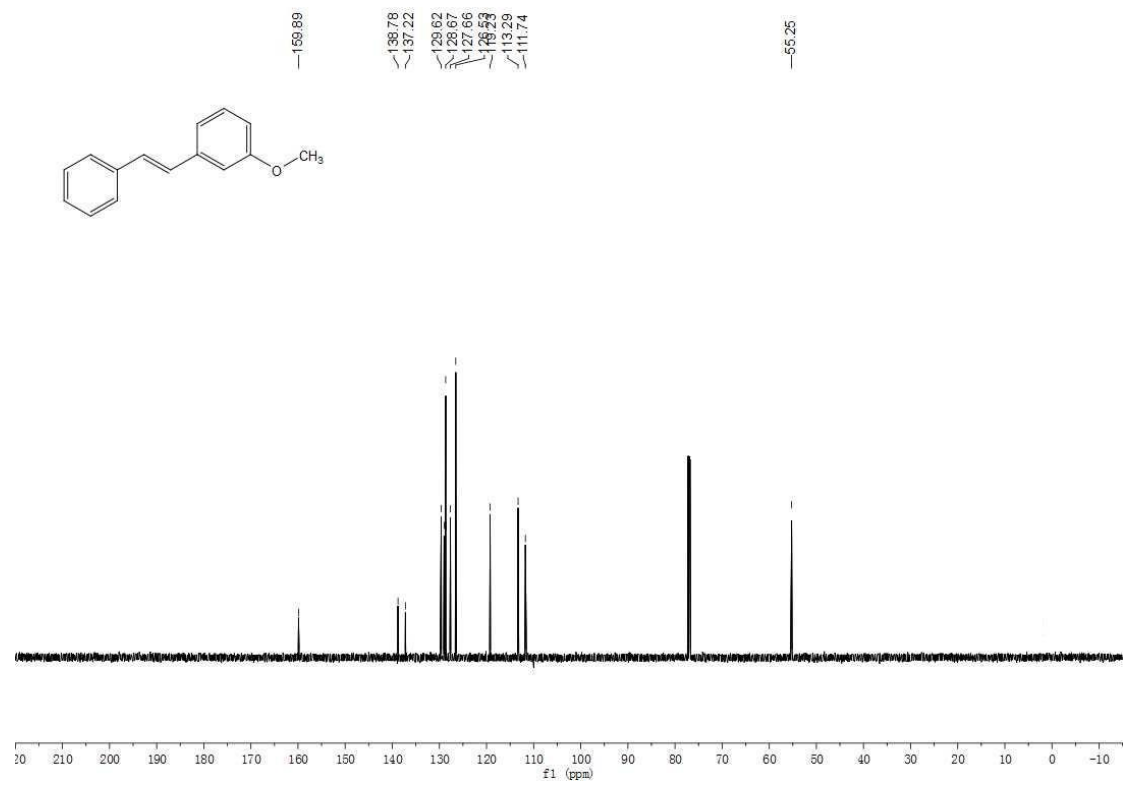


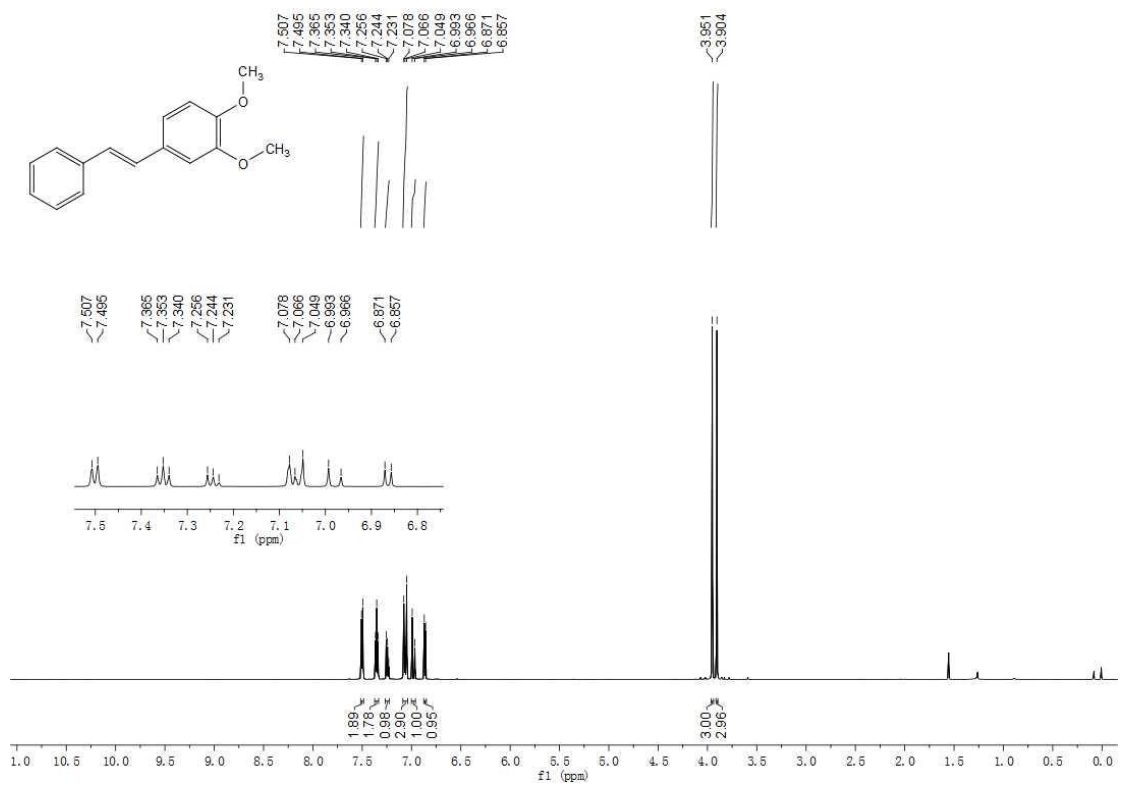
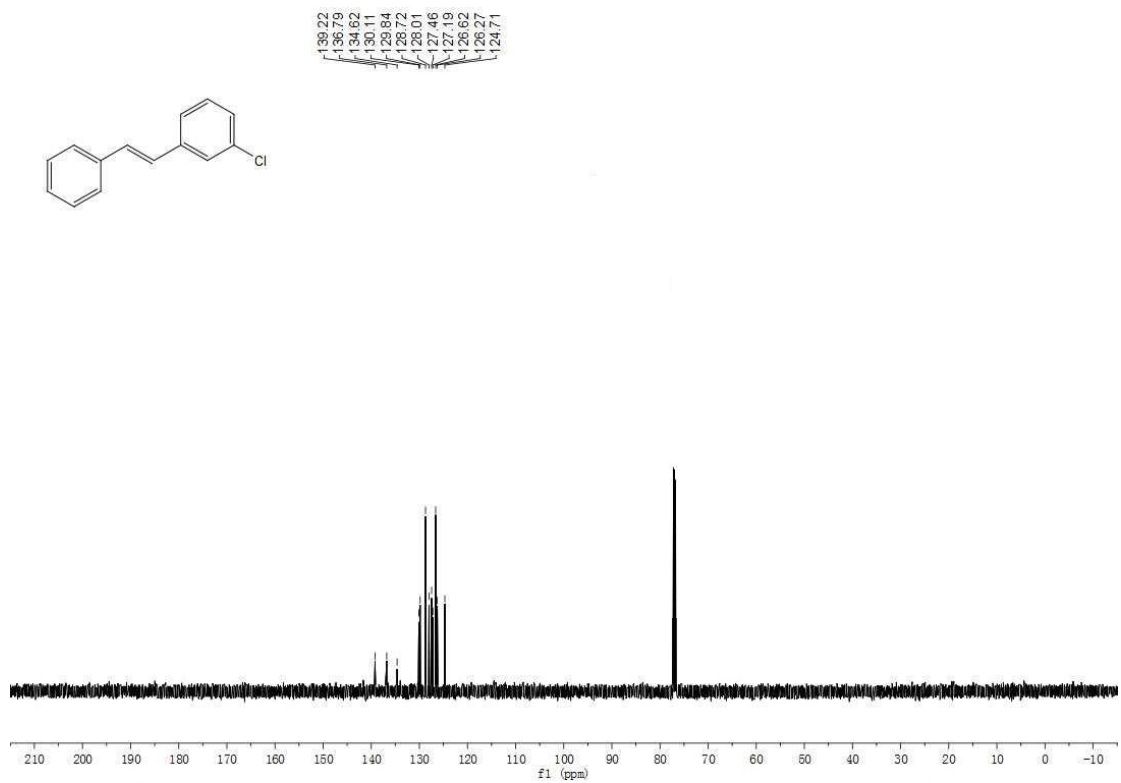


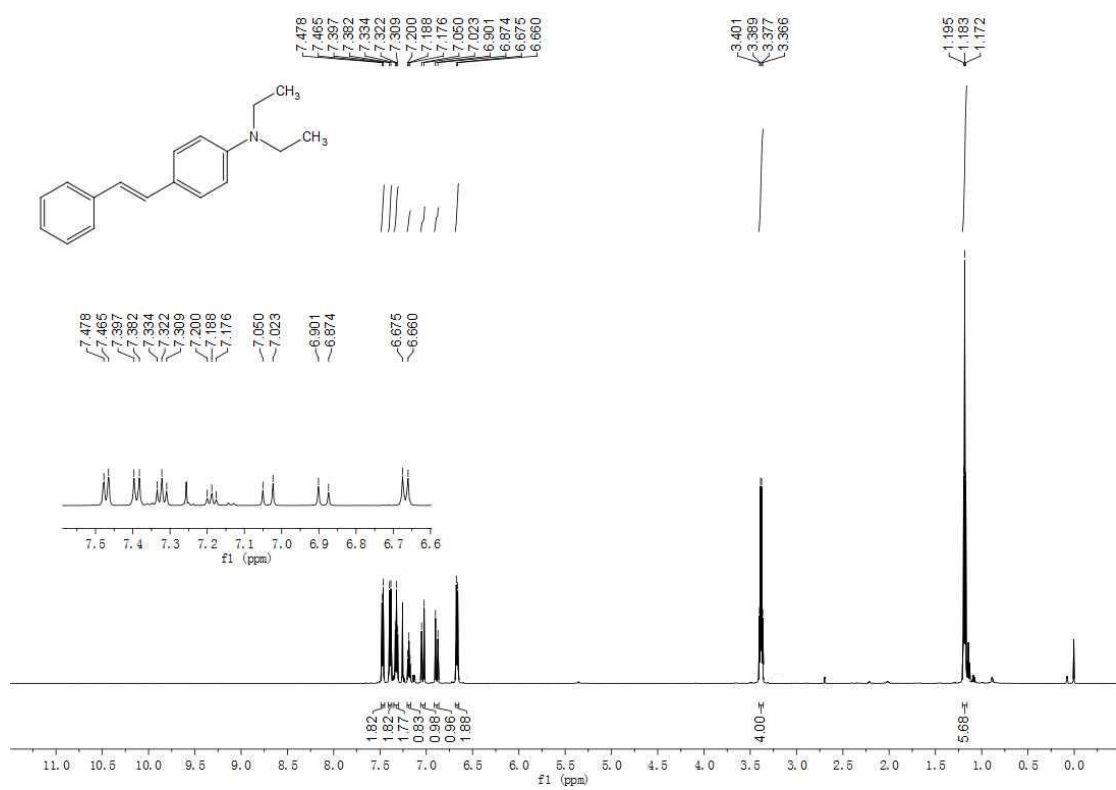
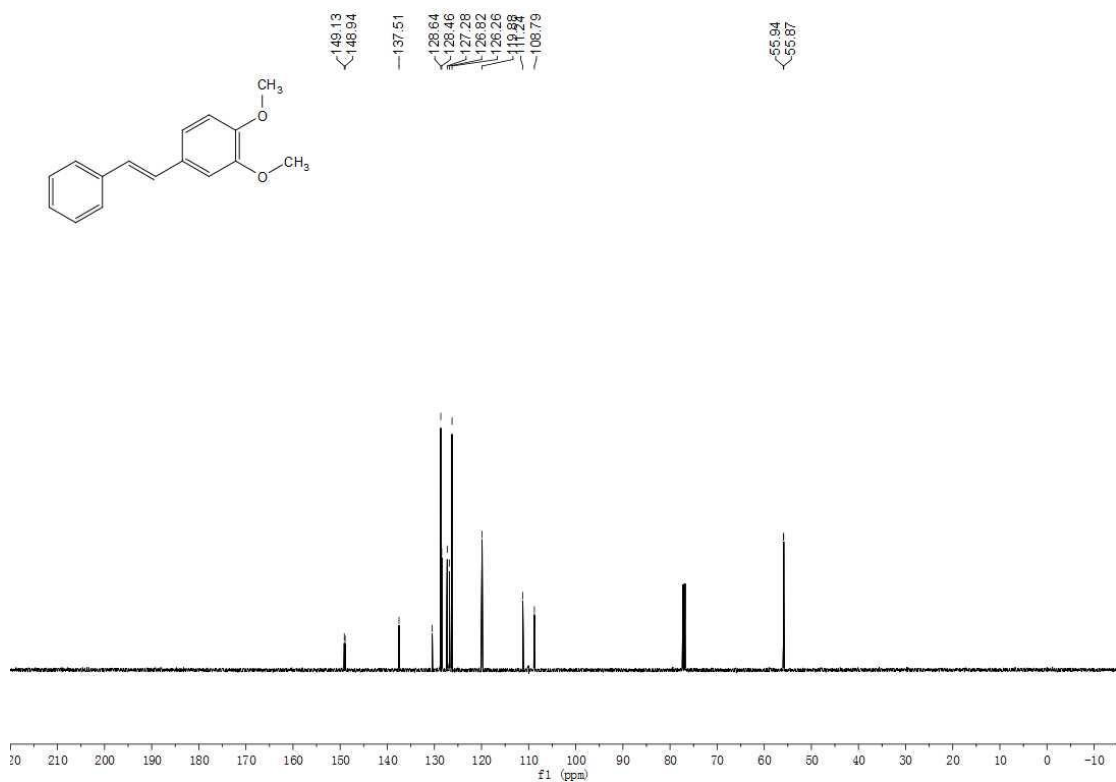


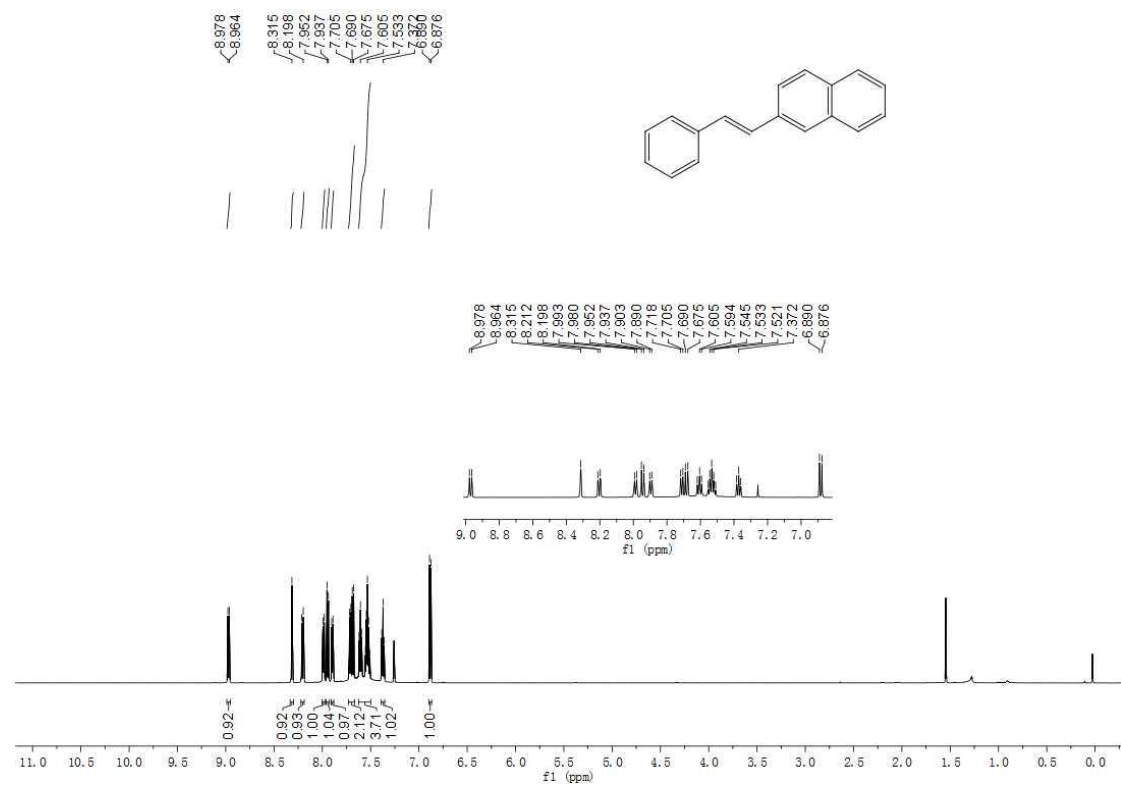
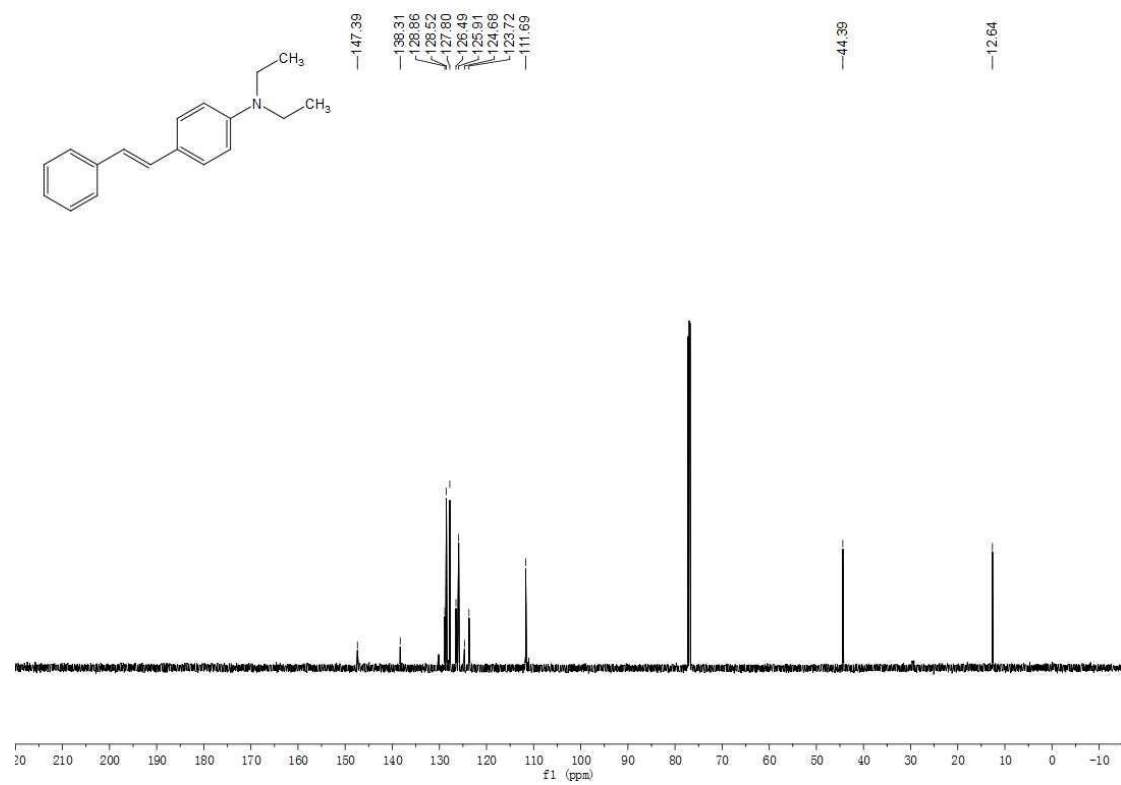


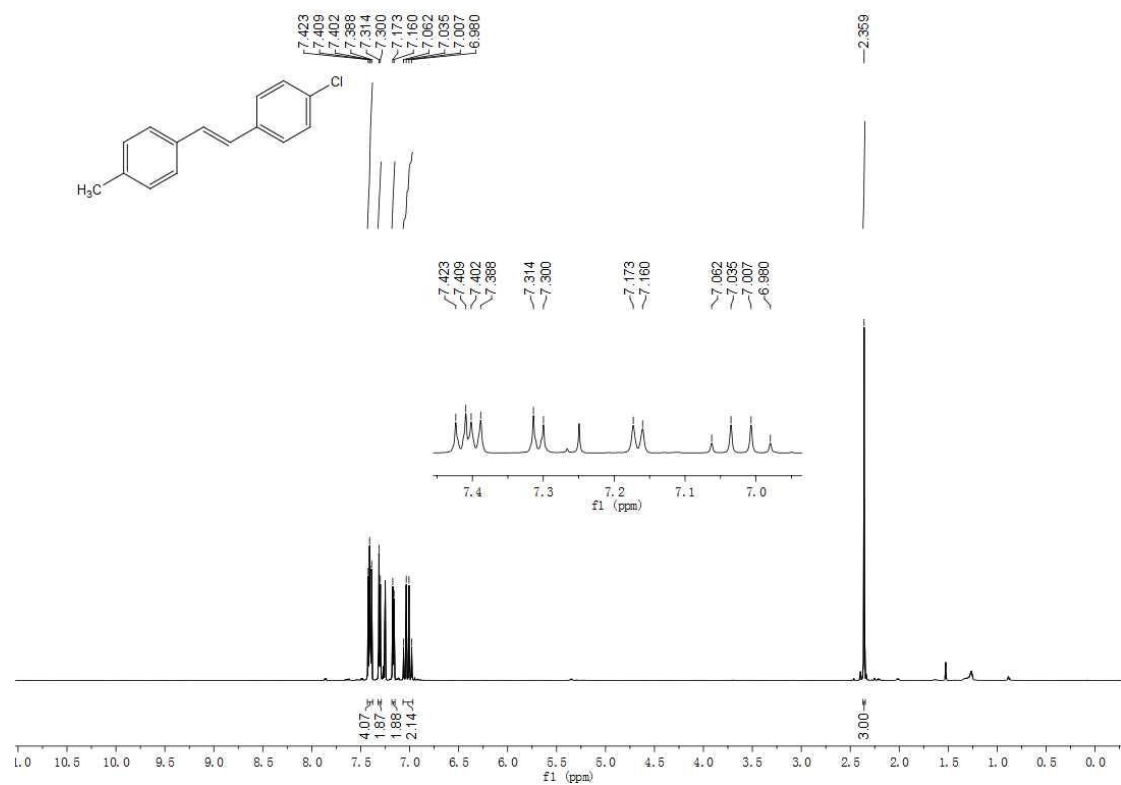
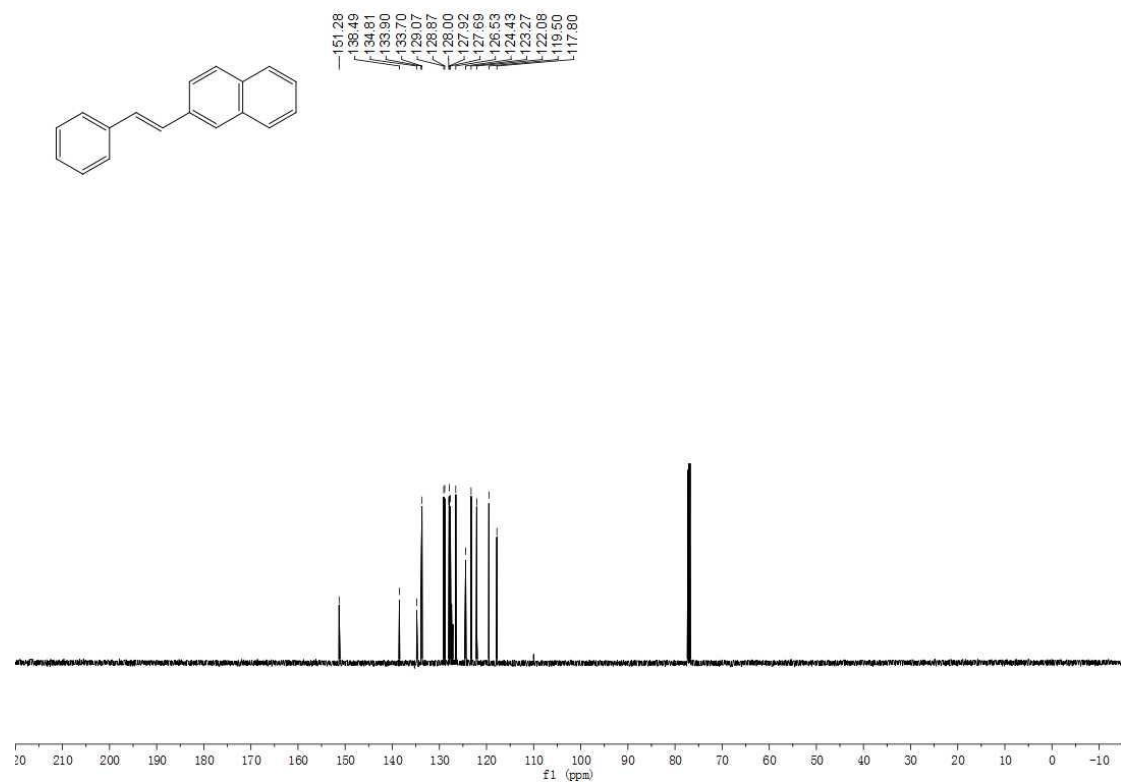


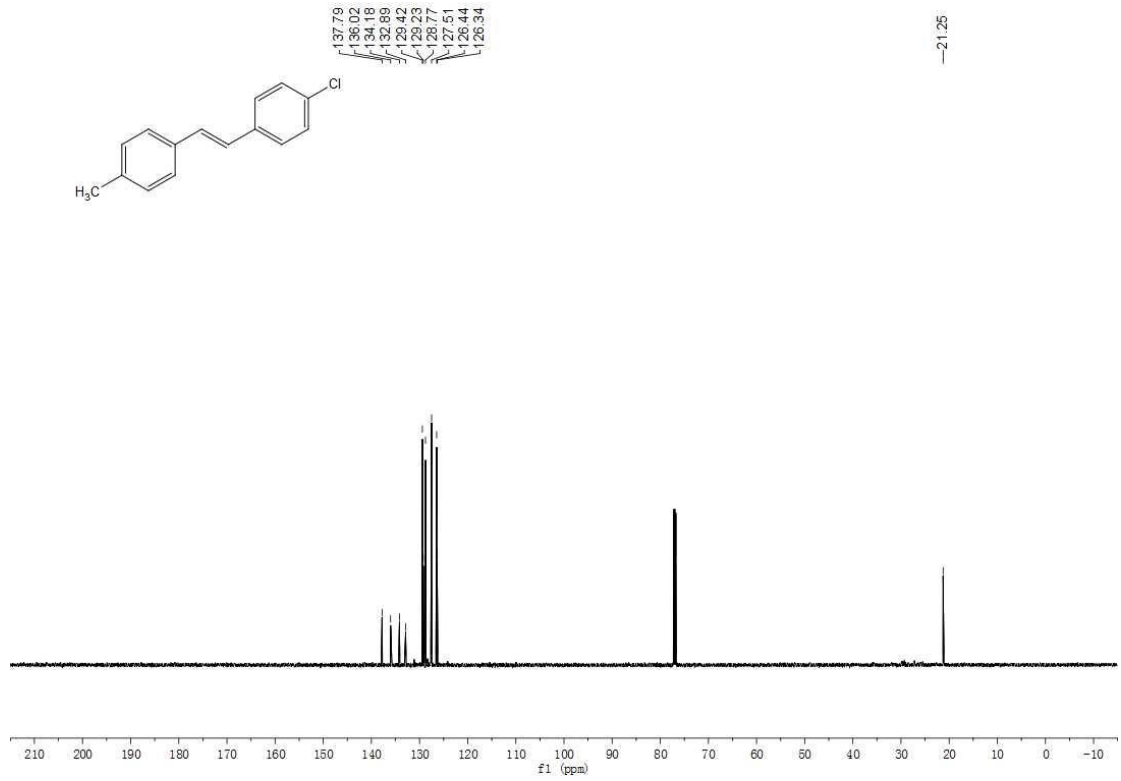












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