

Supplementary data

Facile Synthesis of multisubstituted buta-1,3-dienes via Suzuki-Miyaura and Kumada Cross-Coupling Strategy of 2,4-Diiodo-buta-1-enes with Arylboronic Acids and Grignard Reagents

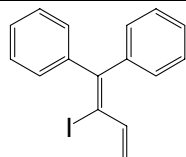
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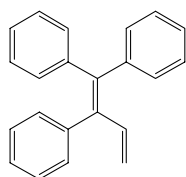
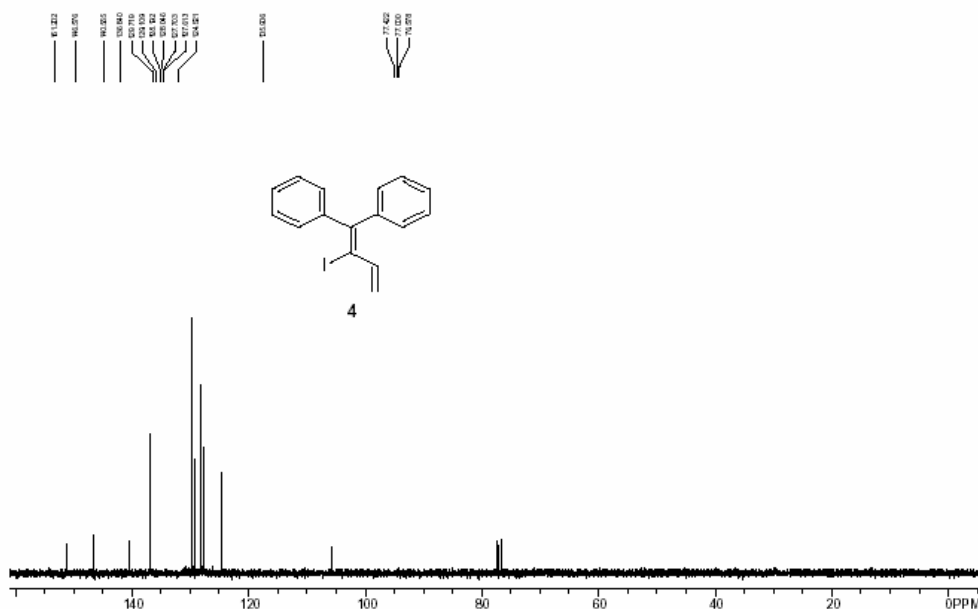
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General remarks. ¹H-NMR spectra were recorded on a 300 MHz spectrometer in CDCl₃ using tetramethylsilane as the internal standard. Infrared spectra were measured on a PERKIN-ELMER 983 spectrometer. Mass spectra were recorded with a HP-5989 instrument and HRMS was measured by a Finnigan MA⁺ mass spectrometer. Satisfactory CHN microanalyses were obtained with a Carlo-Erba 1106 analyzer. Melting points are uncorrected. All reactions were monitored by TLC with Huanghai GF₂₅₄ silica gel coated plates. Flash Column Chromatography was carried out using 300-400 mesh silica gel.

General Reaction Procedure for the Suzuki-Miyaura-type Reaction. Under an argon atmosphere, **1** (0.25 mmol), **2** (0.30 mmol), Pd(PPh₃)₄ (0.025 mmol), tetrabutylammonium chloride (TBAC) (0.25 mmol) and KOH (1.2 mmol) were added into a Schlenk tube with degassed THF/H₂O (1.0 mL/0.3 mL). The reaction mixture was stirred under reflux temperature for about 48 hrs, then diluted with dichloromethane, dried over anhydrous Na₂SO₄, and purified by a flash column chromatography.

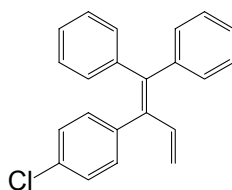
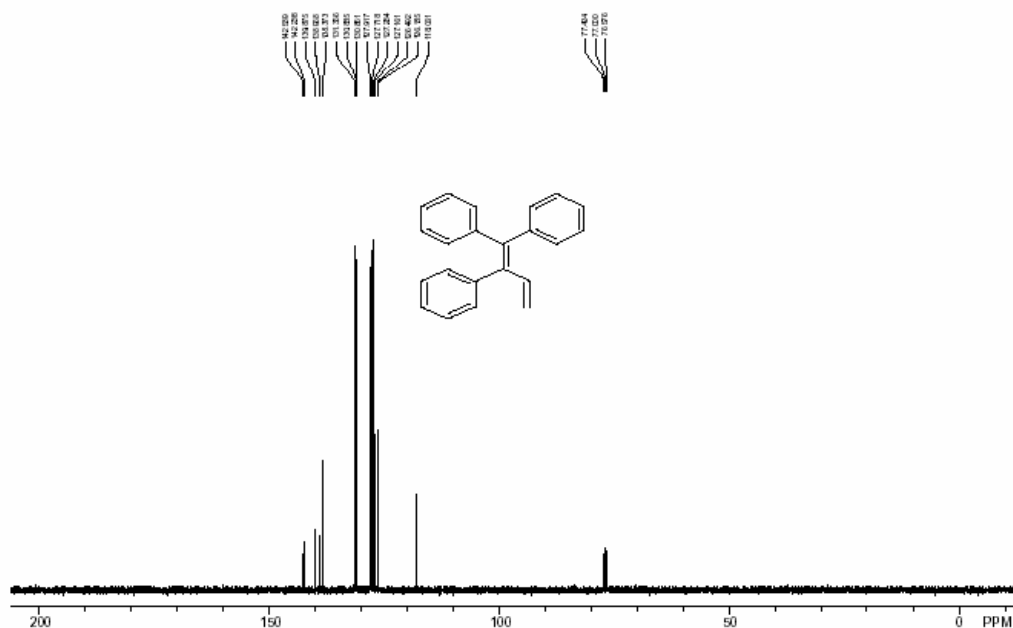


Product **4**. A colorless liquid, ^1H NMR (CDCl_3 , 300 MHz, TMS): $\delta = 5.33$ (dd, 1H, $J = 0.9$, 10.2 Hz), 5.65 (dd, 1H, $J = 0.9$, 15.6 Hz), 6.13 (dd, 1H, $J = 10.2$, 15.6 Hz), 7.16-7.37 (m, 10H, Ar). ^{13}C NMR (CDCl_3 , 75 MHz, TMS): $\delta = 105.91$, 124.52, 127.61, 127.70, 128.05, 128.19, 129.11, 129.72, 136.84, 140.56, 146.58, 151.20. IR (CH_2Cl_2): $\nu = 3075$, 3055, 3011, 2918, 1697, 1596, 1489, 1265, 740 cm^{-1} . MS (%): $m/e = 332$ (M^+ , 12.47), 205 (100). HRMS Calcd. for $\text{C}_{16}\text{H}_{13}\text{I}$: 332.0062, Found: 332.0049.

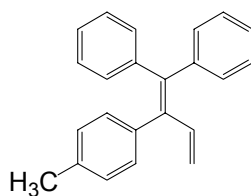
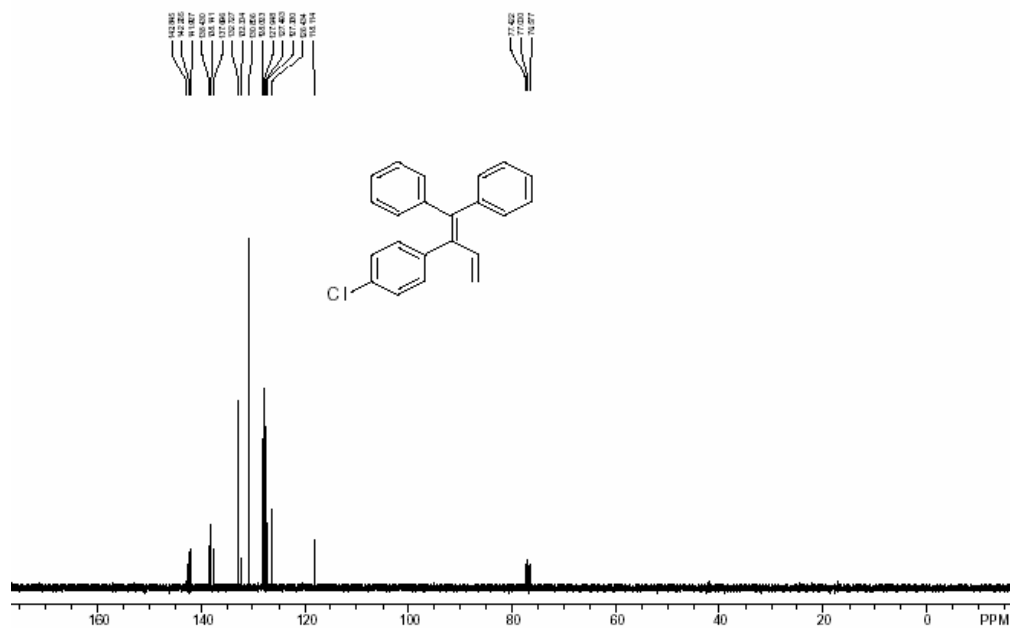


Product **3a**. A white solid, Mp: 110-111 $^{\circ}\text{C}$, ^1H NMR (CDCl_3 , 300 MHz, TMS): $\delta = 4.93$ (dd, 1H, $J = 2.1$, 17.4 Hz), 5.15 (dd, 1H, $J = 2.1$, 10.5 Hz), 6.76 (dd, 1H, $J = 10.5$, 17.4 Hz), 6.86-6.89 (m, 2H, Ar), 6.90-7.01 (m, 3H, Ar), 7.13-7.35 (m, 10H, Ar). ^{13}C NMR (CDCl_3 , 75 MHz, TMS): $\delta = 118.06$, 126.19, 126.49, 127.16, 127.28, 127.72, 127.92, 130.86, 130.89, 131.37, 138.37, 138.97, 139.88, 142.24, 142.59. IR (CH_2Cl_2): $\nu = 3078$, 3054, 3021, 2935, 2855, 1949, 1884, 1598, 1576, 1492, 1443 cm^{-1} . MS (%): $m/e = 282$ (M^+ , 100), 191 (97.13).

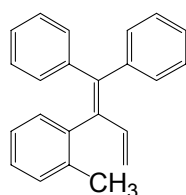
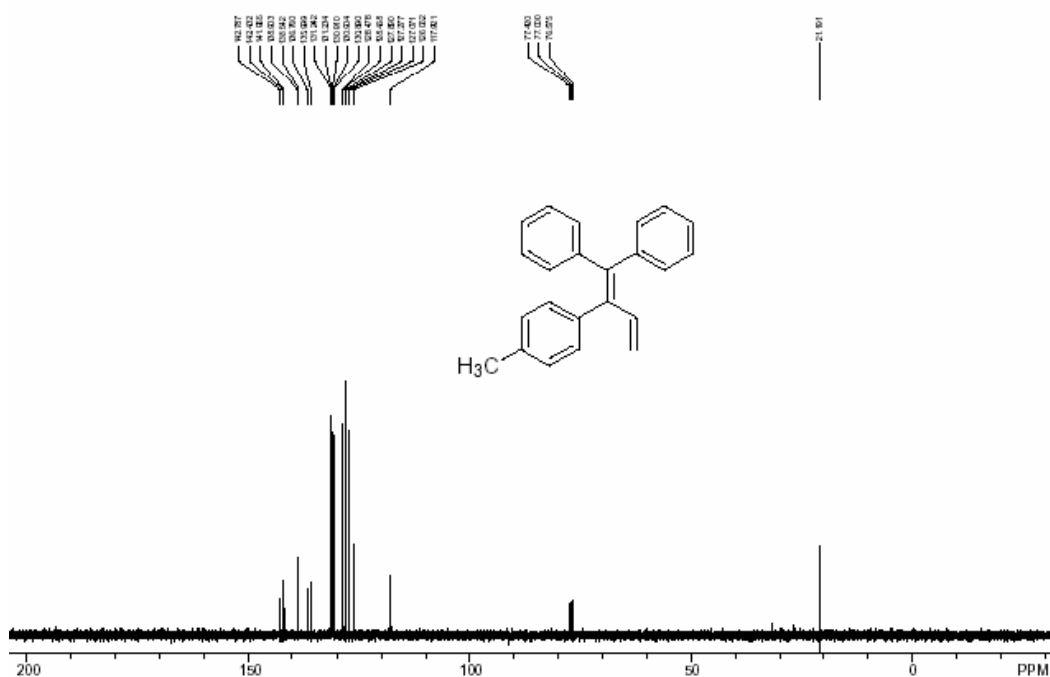
Anal. Calcd. for C₂₂H₁₈: C, 93.58%; H, 6.42%. Found: C, 93.46%; H, 6.33%.



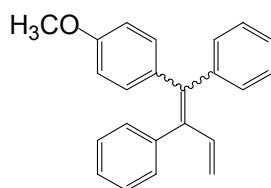
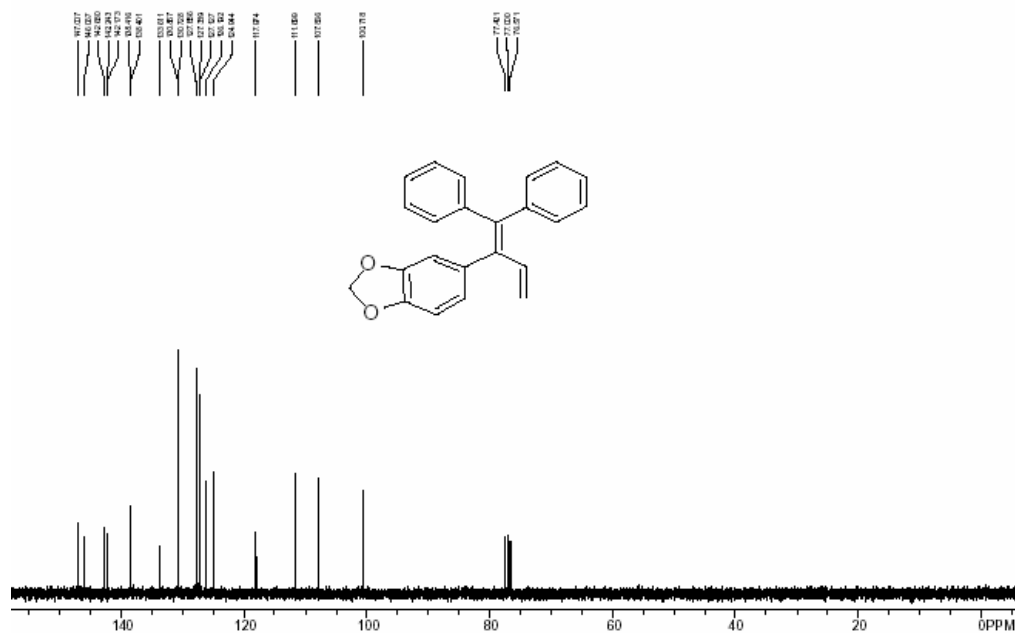
Product **3b**. A white solid, Mp: 124-127 °C, ¹H NMR (CDCl₃, 300 MHz, TMS): δ = 4.91 (dd, 1H, *J* = 1.8, 17.4 Hz), 5.16 (dd, 1H, *J* = 1.8, 11.1 Hz), 6.73 (dd, 1H, *J* = 11.1, 17.4 Hz), 6.78-6.88 (m, 2H, Ar), 7.02-7.17 (m, 5H, Ar), 7.23-7.26 (m, 2H, Ar), 7.30-7.34 (m, 5H, Ar). ¹³C NMR (CDCl₃, 75 MHz, TMS): δ = 118.11, 126.43, 127.33, 127.49, 127.95, 128.02, 130.81, 132.30, 132.73, 137.70, 138.14, 138.42, 141.93, 142.24, 142.80. IR (CH₂Cl₂): ν = 3080, 3054, 2290, 1905, 1827, 1606, 1491, 1442, 1265, 741 cm⁻¹. MS (%): *m/e* = 316 (M⁺, 100), 191 (89.73). Anal. Calcd. for C₂₂H₁₇Cl: C, 83.40%; H, 5.41%. Found: C, 83.35%; H, 5.26%.



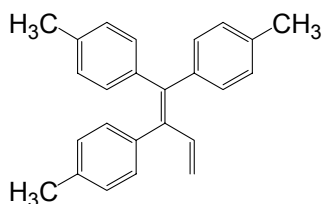
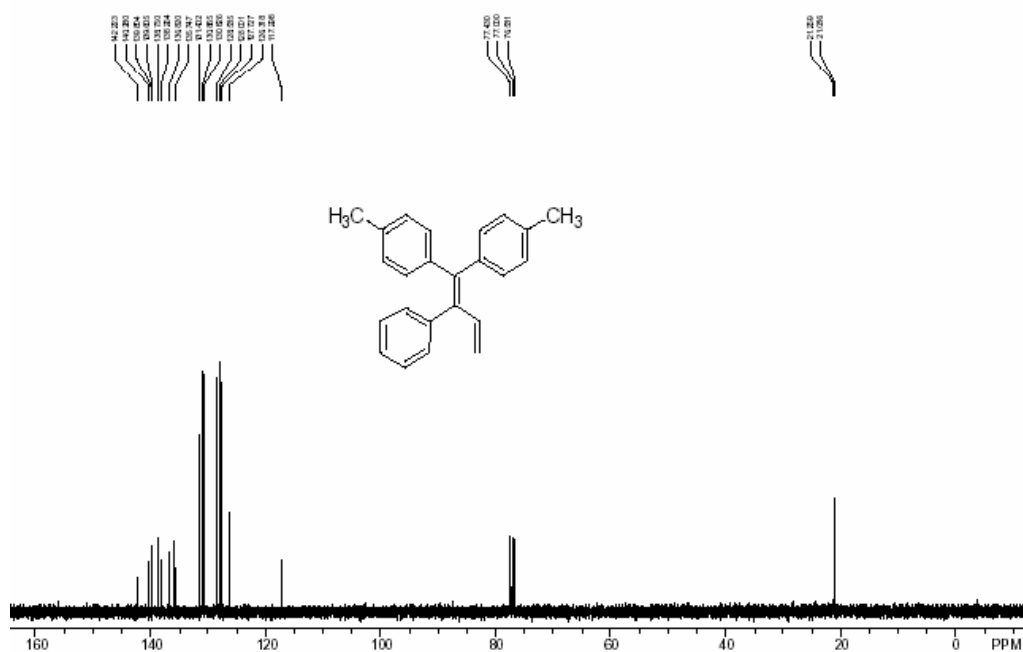
Product **3c**. A white solid, Mp: 108-110 °C, ^1H NMR (CDCl_3 , 300 MHz, TMS): δ = 2.27 (s, 3H, CH_3), 4.95 (dd, 1H, J = 1.8, 17.1 Hz), 5.14 (dd, 1H, J = 1.8, 10.5 Hz), 6.74 (dd, 1H, J = 10.5, 17.1 Hz), 6.87-6.90 (m, 2H, Ar), 7.00-7.04 (m, 7H, Ar), 7.23-7.34 (m, 5H, Ar). ^{13}C NMR (CDCl_3 , 75 MHz, TMS): δ = 21.19, 117.92, 126.06, 127.07, 127.28, 127.89, 128.47, 128.48, 130.89, 130.90, 130.91, 131.23, 131.24, 136.00, 136.76, 138.54, 138.90, 141.96, 142.43, 142.79. IR (CH_2Cl_2): ν = 3087, 3043, 3014, 2920, 2870, 1819, 1735, 1590, 1509, 1491, 1442 cm^{-1} . MS (%): m/e = 296 (M^+ , 100). HRMS Calcd. for $\text{C}_{23}\text{H}_{20}$: 296.1565, Found: 296.1546.



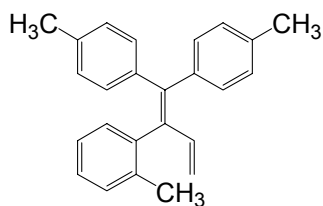
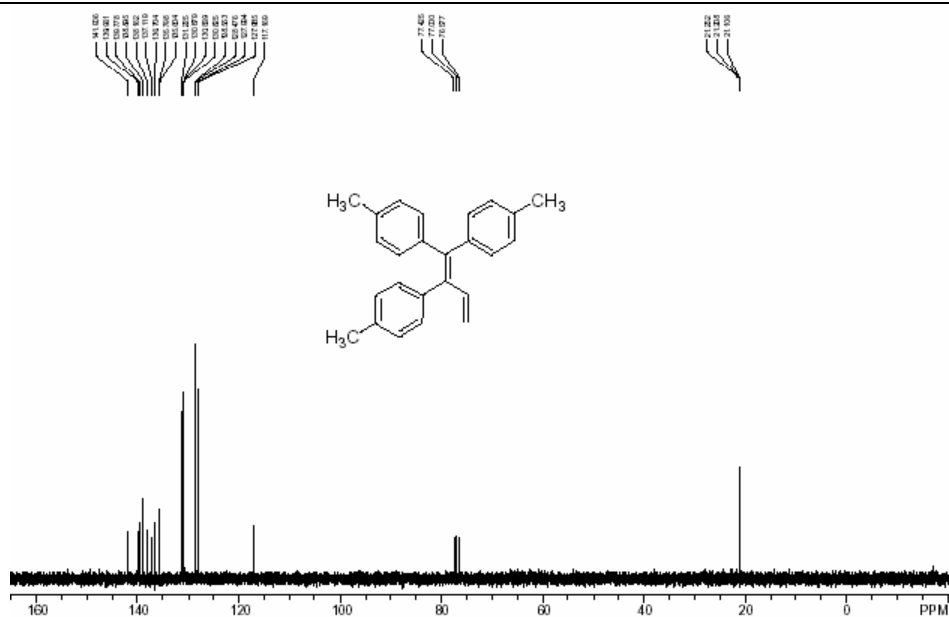
Product **3d**. A white solid, Mp: 69-70 °C, ¹H NMR (CDCl₃, 300 MHz, TMS): δ = 2.15 (s, 3H, CH₃), 4.70 (dd, 1H, *J* = 1.8, 17.4 Hz), 5.08 (dd, 1H, *J* = 1.8, 10.5 Hz), 6.74 (dd, 1H, *J* = 10.5, 17.4 Hz), 6.87-6.90 (m, 2H, Ar), 6.97-7.00 (m, 3H, Ar), 7.06-7.10 (m, 4H, Ar), 7.28-7.36 (m, 5H, Ar). ¹³C NMR (CDCl₃, 75 MHz, TMS): δ = 19.73, 117.40, 125.18, 126.36, 126.88, 127.13, 127.20, 127.97, 130.02, 130.80, 131.47, 136.62, 137.60, 138.24, 138.88, 142.09, 142.21, 142.27. IR (CH₂Cl₂): ν = 3059, 2958, 2927, 2860, 2319, 1938, 1600, 1491, 1460, 1379, 1265 cm⁻¹. MS (%): *m/e* = 296 (M⁺, 100). HRMS Calcd. for C₂₃H₂₀ (Maldi): 297.1638, Found: 297.1609 ± 0.005 (M+H⁺).



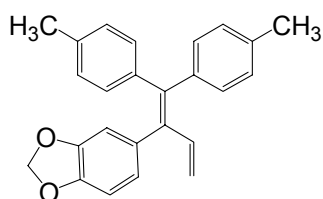
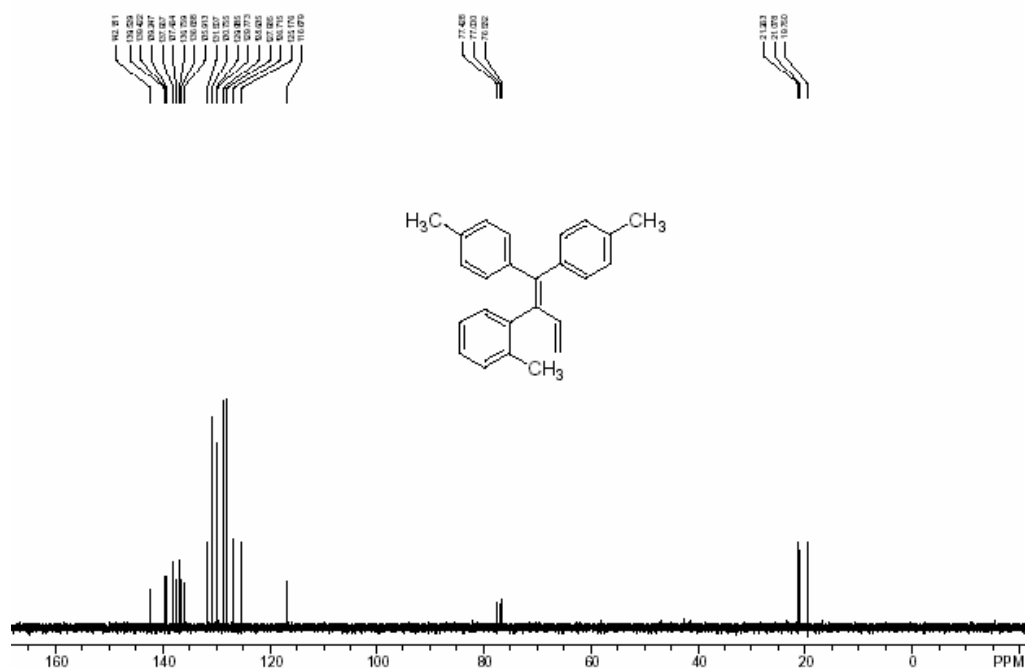
Product **3f**. A yellow solid, Mp: 40-48 °C, (*Z*, *trans*-isomer) ^1H NMR (CDCl_3 , 300 MHz, TMS): δ = 3.74 (s, 3H, CH_3O), 5.01 (dd, 1H, J = 1.8, 17.4 Hz), 5.21 (dd, 1H, J = 1.8, 11.1 Hz), 6.64 (d, 2H, J = 9.3 Hz, Ar), 6.83 (dd, 1H, J = 11.1, 17.4 Hz), 6.88-7.11 (m, 5H, Ar), 7.21-7.46 (m, 7H, Ar). (*E*, *trans*-isomer) ^1H NMR (CDCl_3 , 300 MHz, TMS): δ = 3.90 (s, 3H, CH_3O), 5.04 (dd, 1H, J = 1.8, 15.3 Hz), 5.26 (dd, 1H, J = 1.8, 10.8 Hz), 6.64 (d, 2H, J = 9.3 Hz, Ar), 6.79-7.11 (m, 6H, Ar + $\text{CH}=\text{CH}_2$), 7.21-7.46 (m, 7H, Ar). (*Z*, *trans*-isomer) ^{13}C NMR (CDCl_3 , 75 MHz, TMS): δ = 54.88, 112.64, 117.34, 126.11, 126.37, 127.21, 127.80, 128.22, 128.35, 129.47, 130.94, 131.40, 132.20, 134.93, 138.42, 138.60, 140.15, 142.54, 157.75. (*E*, *trans*-isomer) ^{13}C NMR (CDCl_3 , 75 MHz, TMS): δ = 55.14, 113.18, 117.62, 126.34, 127.09, 127.65, 127.86, 128.28, 128.55, 130.90, 131.34, 132.12, 134.58, 138.08, 138.54, 140.13, 141.78, 142.87, 158.70. IR (CH_2Cl_2): ν = 3054, 3037, 2896, 2837, 2319, 1956, 1885, 1804, 1734, 1649, 1605, 1509, 1442, 1247, 1034, 739 cm^{-1} . MS (%): m/e = 312 (M^+ , 100), 281 (24.44), 235 (48.06), 221 (82.12). HRMS Calcd. for $\text{C}_{25}\text{H}_{24}$: 312.1500, Found: 312.1509.



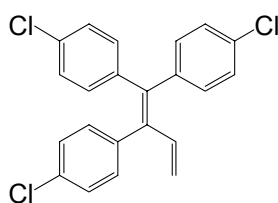
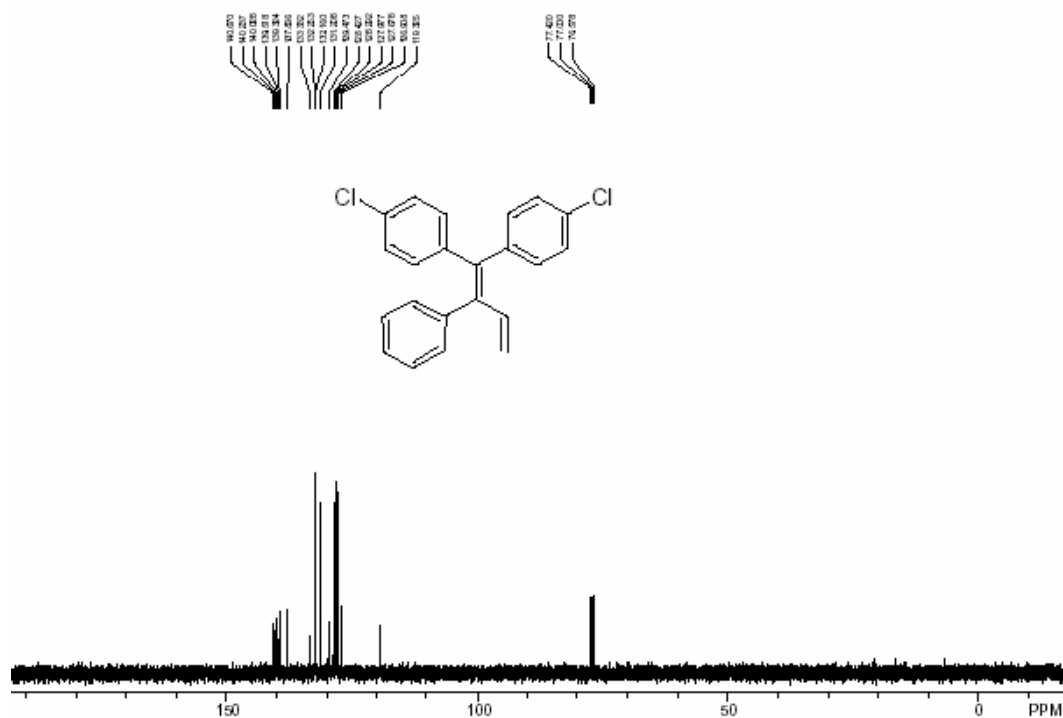
Product **3h**. A white solid, Mp: 143-146 °C, ¹H NMR (CDCl₃, 300 MHz, TMS): δ = 2.21 (s, 3H, CH₃), 2.31 (s, 3H, CH₃), 2.39 (s, 3H, CH₃), 4.93 (dd, 1H, *J* = 1.8, 17.4 Hz), 5.12 (dd, 1H, *J* = 1.8, 10.8 Hz), 6.71-6.85 (m, 5H, Ar + CH=CH₂), 7.00-7.07 (m, 4H, Ar), 7.16 (s, 4H, Ar). ¹³C NMR (CDCl₃, 75 MHz, TMS): δ = 21.11, 21.21, 21.25, 117.17, 127.985, 127.994, 128.47, 128.48, 128.55, 130.83, 130.87, 130.88, 131.23, 135.60, 135.80, 136.70, 137.12, 138.16, 138.90, 139.78, 139.96, 141.91. IR (CH₂Cl₂): ν = 3050, 3020, 2958, 2924, 2854, 1910, 1705, 1509, 1459, 1096, 816 cm⁻¹. MS (%): *m/e* = 324 (M⁺, 100), 309 (61.58), 219 (99.76). HRMS Calcd. for C₂₅H₂₄: 324.1878, Found: 324.1915.



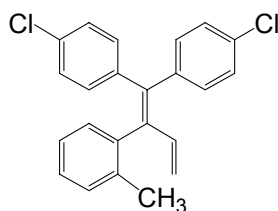
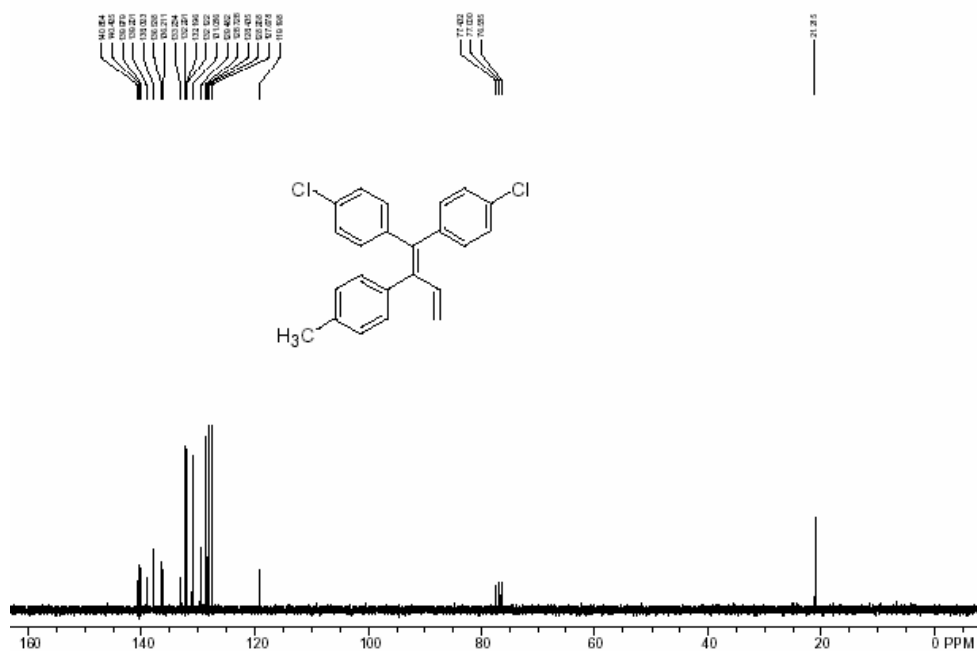
Product **3i**. A white solid, Mp: 89-90 °C, ^1H NMR (CDCl_3 , 300 MHz, TMS): δ = 2.13 (s, 3H, CH_3), 2.15 (s, 3H, CH_3), 2.37 (s, 3H, CH_3), 4.65 (dd, 1H, J = 2.1, 17.1 Hz), 5.03 (dd, 1H, J = 2.1, 10.5 Hz), 6.69-6.78 (m, 5H, Ar + $\text{CH}=\text{CH}_2$), 7.07-7.10 (m, 4H, Ar), 7.16 (s, 4H, Ar). ^{13}C NMR (CDCl_3 , 75 MHz, TMS): δ = 19.75, 21.08, 21.26, 116.68, 125.18, 126.72, 127.94, 128.64, 129.77, 129.99, 130.76, 131.51, 135.91, 136.69, 136.76, 137.46, 137.97, 139.25, 139.42, 139.53, 142.18. IR (CH_2Cl_2): ν = 3050, 3022, 2987, 2922, 2865, 2305, 1908, 1806, 1605, 1509, 1265 cm^{-1} . MS (%): m/e = 324 (M^+ , 100), 309 (70.92), 219 (96.79). Anal. Calcd. for $\text{C}_{25}\text{H}_{24}$: C, 92.48%; H, 7.46%. Found: C, 92.48%; H, 7.79%.



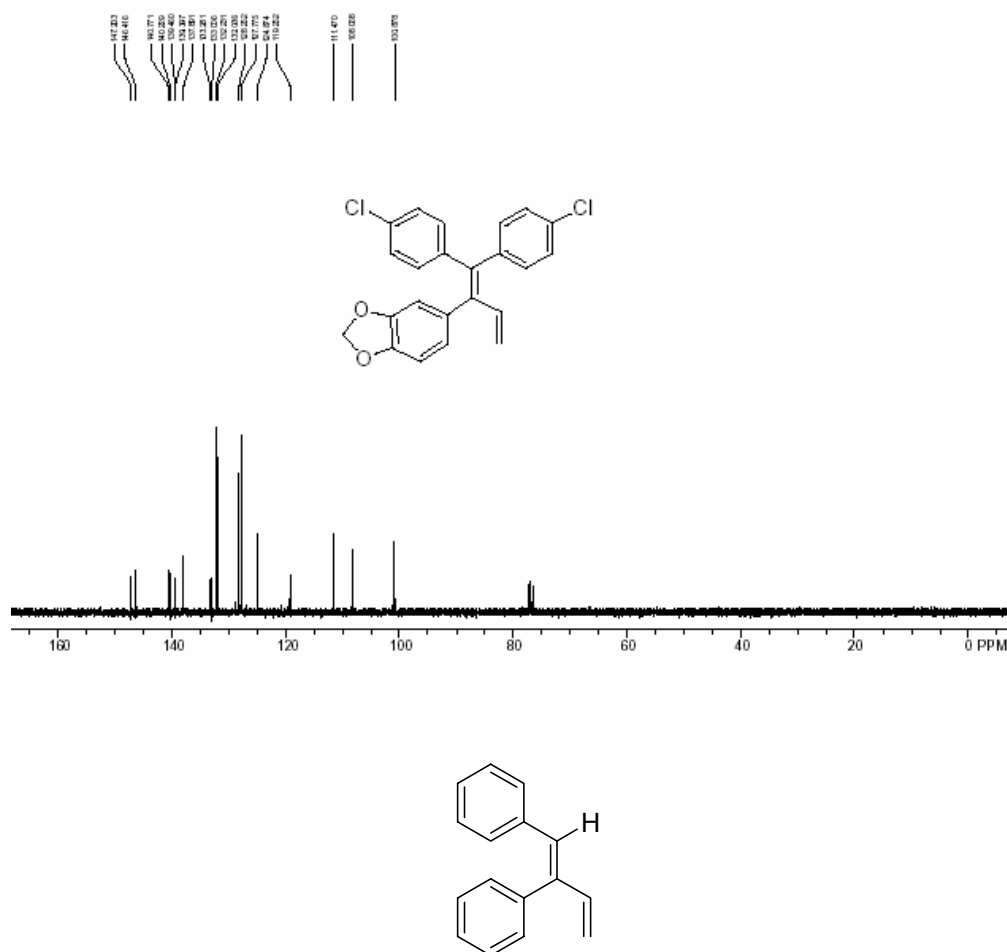
Product **3j**. A yellow solid, Mp: 100-101 °C, ¹H NMR (CDCl₃, 300 MHz, TMS): δ = 2.22 (s, 3H, CH₃), 2.38 (s, 3H, CH₃), 4.95 (d, 1H, *J* = 17.4 Hz), 5.12 (d, 1H, *J* = 11.1 Hz), 5.92 (s, 2H), 6.56-6.71 (m, 4H, Ar + CH=CH₂), 6.74-6.87 (m, 4H, Ar), 7.10-7.17 (m, 4H, Ar). ¹³C NMR (CDCl₃, 75 MHz, TMS): δ = 21.10, 21.24, 100.69, 107.89, 111.74, 117.22, 124.91, 128.10, 128.55, 130.68, 130.82, 134.01, 135.75, 136.80, 137.68, 138.76, 139.59, 139.87, 142.16, 145.94, 146.98. IR (CH₂Cl₂): ν = 3051, 3021, 2921, 2768, 2304, 1902, 1744, 1605, 1506, 1484, 1433, 1265 cm⁻¹. MS (%): *m/e* = 354 (M⁺, 100). HRMS calcd. for C₂₅H₂₂O₂: 354.1620, Found: 354.1630.



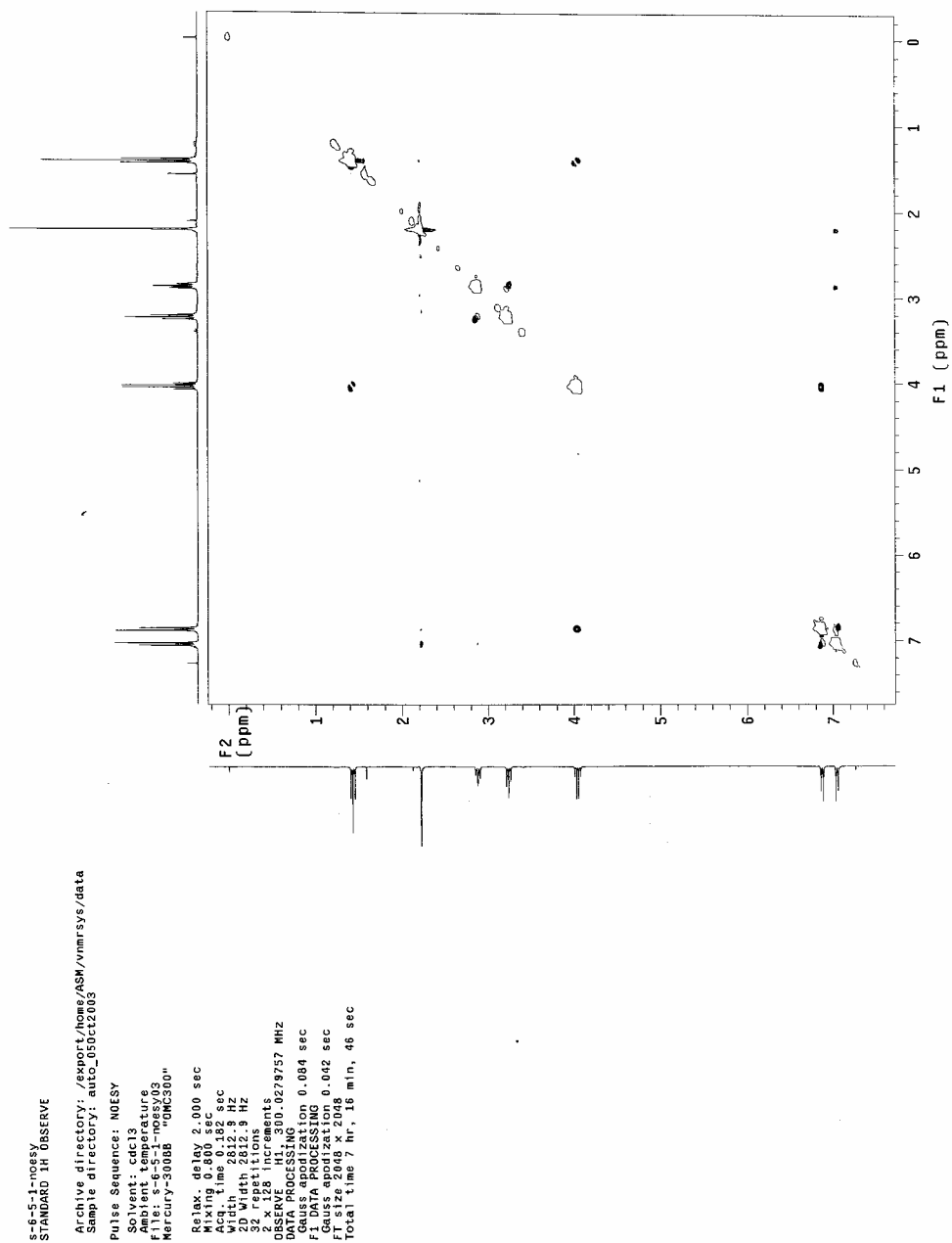
Product **31**. A yellow solid, Mp: 83-85 °C, ¹H NMR (CDCl₃, 300 MHz, TMS): δ = 4.94 (dd, 1H, *J* = 1.2, 17.4 Hz), 5.22 (dd, 1H, *J* = 1.2, 10.2 Hz), 6.67 (dd, 1H, *J* = 10.2, 17.4 Hz), 6.77 (d, 2H, *J* = 8.1 Hz, Ar), 7.00-7.06 (m, 4H, Ar), 7.14-7.24 (m, 4H, Ar), 7.33 (d, 2H, *J* = 8.1 Hz, Ar). ¹³C NMR (CDCl₃, 75 MHz, TMS): δ = 119.39, 127.91, 128.12, 128.30, 128.34, 128.43, 129.48, 129.87, 132.12, 132.19, 132.58, 132.79, 133.59, 137.64, 137.85, 138.77, 139.93, 140.05, 140.39. IR (CH₂Cl₂): ν = 3051, 2993, 2312, 1902, 1728, 1659, 1591, 1491, 1265, 739 cm⁻¹. MS (%): *m/e* = 384 (M⁺, 68.55), 349 (100), 314 (82.40). HRMS calcd. for C₂₂H₁₅Cl₃: 384.0239, Found: 384.0191.



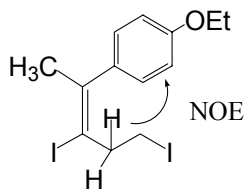
Product **3n**. A yellow liquid, ^1H NMR (CDCl_3 , 300 MHz, TMS): δ = 2.11 (s, 3H, CH_3), 4.74 (dd, 1H, J = 1.8, 17.7 Hz), 5.13 (dd, 1H, J = 1.8, 10.8 Hz), 6.67 (dd, 1H, J = 10.8, 17.7 Hz), 6.77 (d, 2H, J = 8.4 Hz, Ar), 6.97 (d, 2H, J = 8.4 Hz, Ar), 7.07-7.24 (m, 6H, Ar), 7.34 (d, 2H, J = 8.4 Hz, Ar). ^{13}C NMR (CDCl_3 , 75 MHz, TMS): δ = 19.71, 118.69, 125.40, 127.24, 127.60, 128.35, 128.43, 129.48, 130.04, 131.26, 131.35, 132.16, 132.40, 133.31, 136.41, 137.06, 138.28, 139.24, 139.55, 140.04, 140.31. IR (CH_2Cl_2): ν = 3059, 3016, 2923, 2841, 1903, 1727, 1673, 1589, 1409 cm^{-1} . MS (%): m/e = 364 (M^+ , 57.83), 329 (61.29), 248 (67.37), 138 (100). HRMS Calcd. for $\text{C}_{23}\text{H}_{18}\text{Cl}_2$: 364.0786, Found: 364.0797.

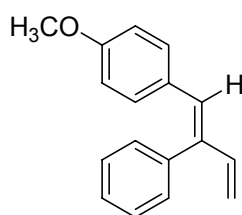
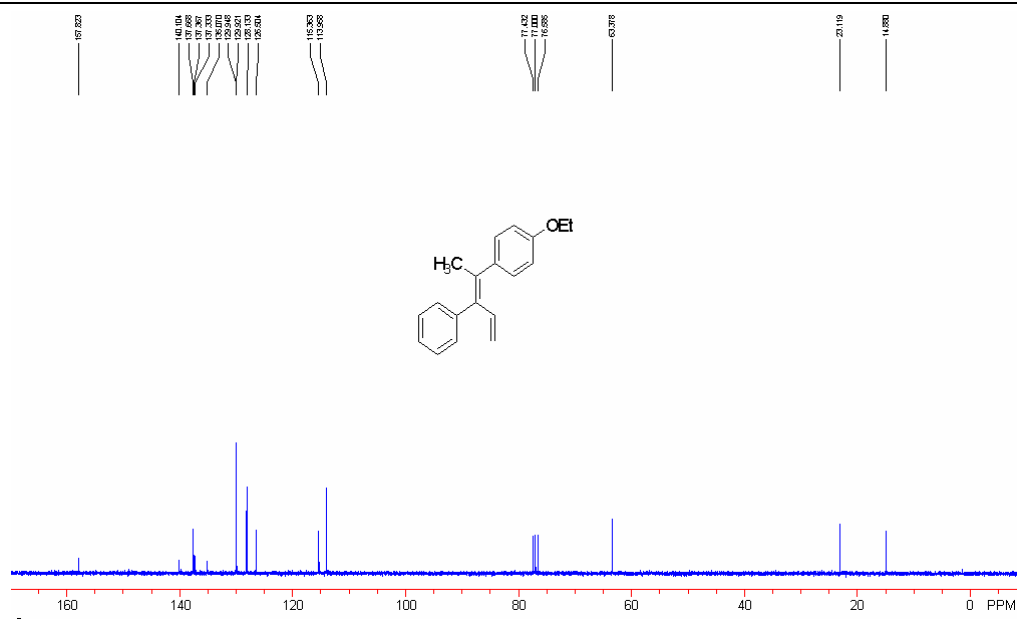


Product **3p**. A colorless liquid, ¹H NMR (CDCl₃, 300 MHz, TMS): δ = 4.83 (d, 1H, *J* = 16.5 Hz), 5.15 (d, 1H, *J* = 10.5 Hz), 6.60 (s, 1H), 6.74 (dd, 1H, *J* = 10.5, 16.5 Hz), 6.87-6.91 (m, 2H, Ar), 7.07-7.08 (m, 2H, Ar), 7.15-7.18 (m, 2H, Ar), 7.33-7.41 (m, 4H, Ar). ¹³C NMR (CDCl₃, 75 MHz, TMS): δ = 116.43, 126.87, 127.14, 127.27, 127.92, 128.73, 128.74, 129.39, 129.54, 131.47, 136.60, 141.71. IR (CH₂Cl₂): ν = 3080, 3056, 3022, 2965, 1948, 1812, 1599, 1493, 1444, 1074, 987, 907, 779, 757, 701 cm⁻¹. MS (%): *m/e* = 206 (M⁺, 100), 205 (54), 191 (24), 128 (31), 91 (63). HRMS Calcd. for C₁₆H₁₄ (Maldi): 229.0988, Found: 229.0998 ± 0.003 (M+Na⁺).

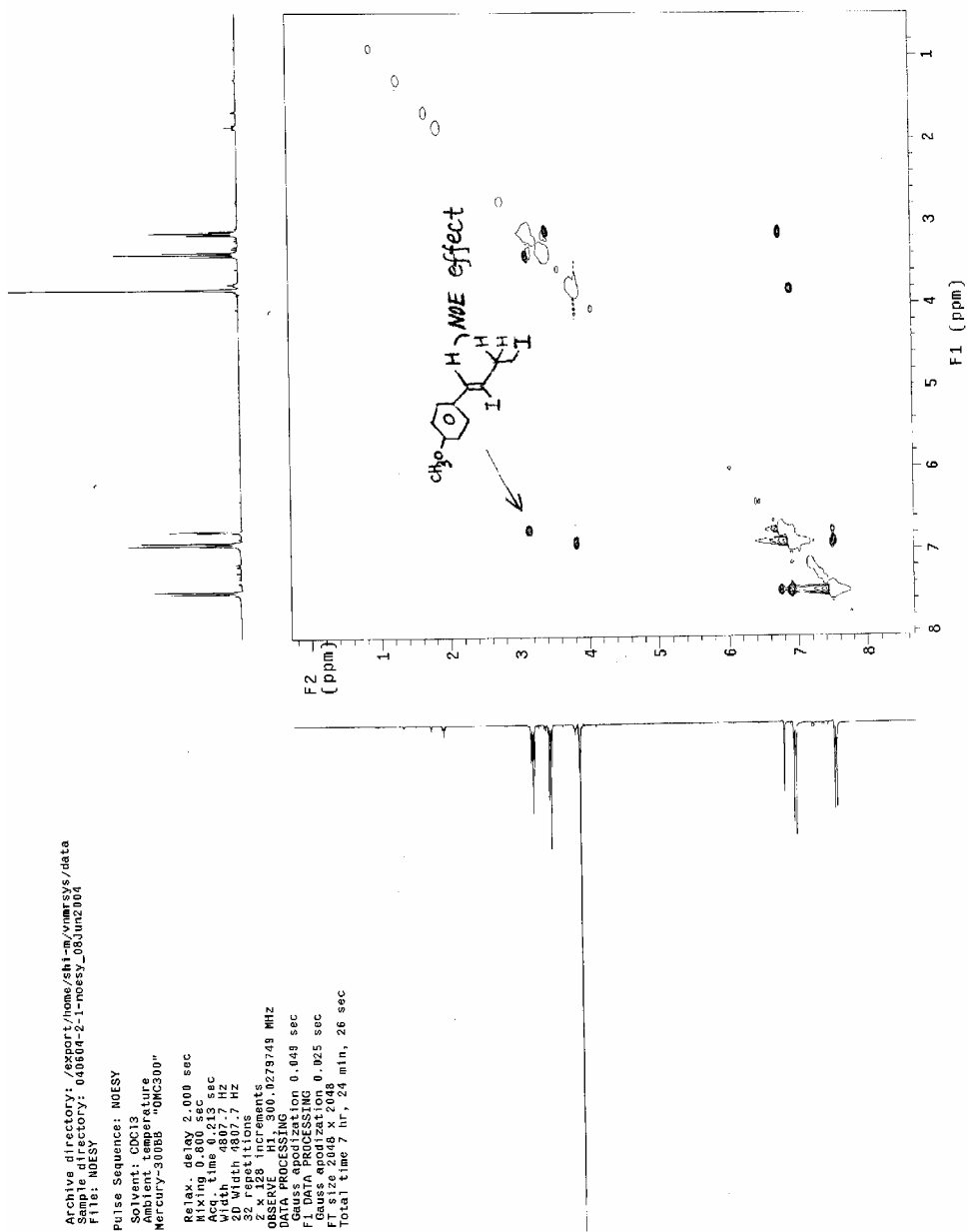


¹H NMR NOESY spectrum of compound **1f**.

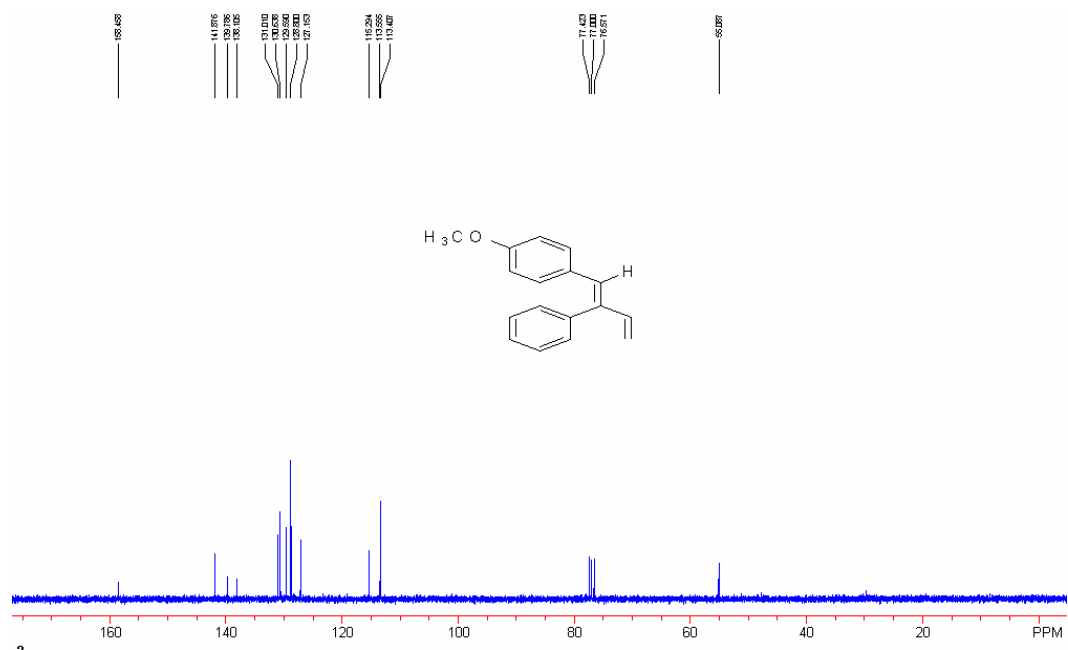




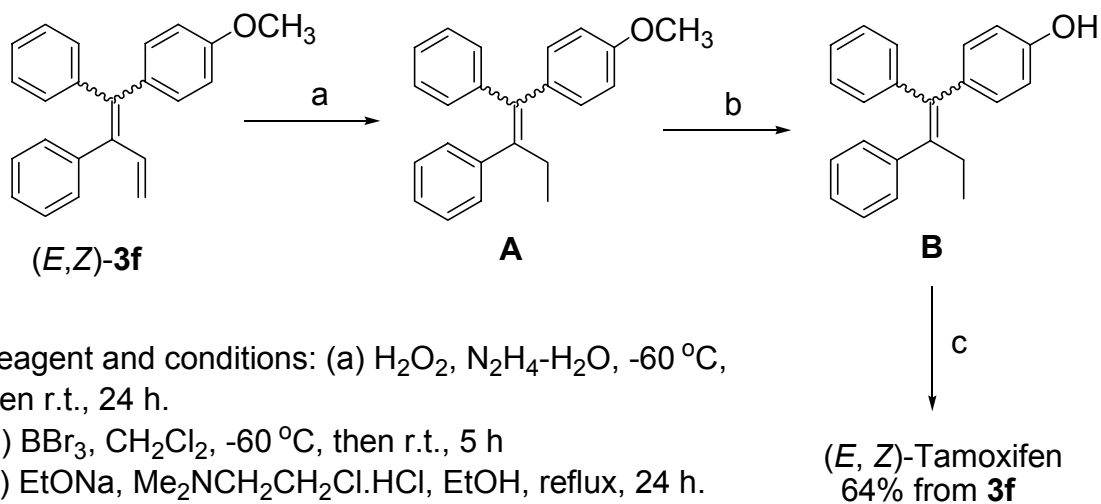
Product **3r**. A colorless liquid, ¹H NMR (CDCl₃, 300 MHz, TMS): δ = 3.71 (s, 3H, CH₃O), 4.77 (d, 1H, *J* = 17.4 Hz), 5.09 (d, 1H, *J* = 10.2 Hz), 6.54 (s, 1H), 6.63 (d, 2H, *J* = 9.0 Hz, Ar), 6.72 (dd, 1H, *J* = 10.2, 17.4 Hz), 6.82 (d, 2H, *J* = 9.0 Hz, Ar), 7.16-7.19 (m, 2H, Ar), 7.34-7.42 (m, 3H, Ar). ¹³C NMR (CDCl₃, 75 MHz, TMS): δ = 55.09, 113.41, 113.56, 115.29, 127.15, 128.80, 129.59, 130.64, 131.01, 138.11, 139.79, 141.88, 158.46. IR (CH₂Cl₂): ν = 3082, 3068, 3002, 2954, 2930, 2835, 1604, 1595, 1509, 1441, 1302, 1254, 1177, 1035, 889, 827, 702 cm⁻¹. MS (%): *m/e* = 236 (M⁺, 100), 235 (37), 205 (46), 178 (34), 165 (35), 145 (35). HRMS Calcd. for C₁₇H₁₆O (Maldi): 237.1274, Found: 237.1288 ± 0.003 (M+H⁺).



¹H NMR NOESY spectrum of compound **1g**.

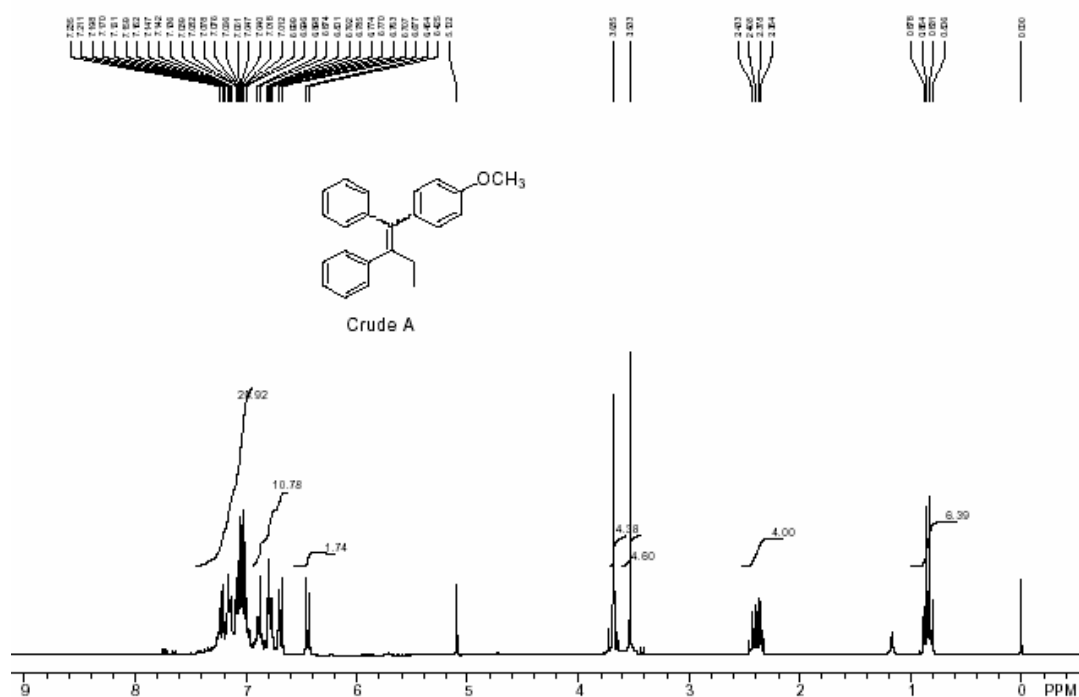


Scheme 1 Synthesis of (*E, Z*)-Tamoxifen from (*E, Z*)-**3f**.



A. The Reduction Step.

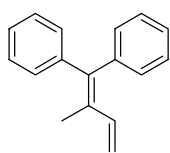
35% H_2O_2 (2.6 mmol) was added during 10 minutes to a solution of **3f** (0.44 mmol) in 99% EtOH (0.5 mL), CH_2Cl_2 (2.0 mL) and 85% $\text{N}_2\text{H}_4\text{H}_2\text{O}$ (3.6 mmol) below $-60\text{ }^\circ\text{C}$ with stirring (acetone-solid carbon dioxide cooled). After addition, the reaction mixture was allowed to warm to room temperature naturally and stirred at room temperature for about 24 hrs. The reaction mixture was diluted with CH_2Cl_2 , washed with saturated aq. Na_2SO_3 and extracted with CH_2Cl_2 . The combined organic layers were washed with saturated brine, then dried over Na_2SO_4 and concentrated under reduced pressure. The residue **A** was ^1H NMR determined and was used for the next step without further purification.



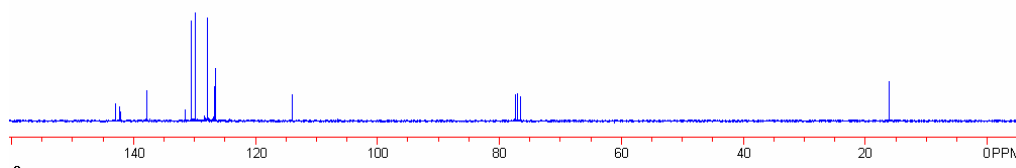
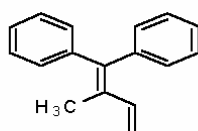
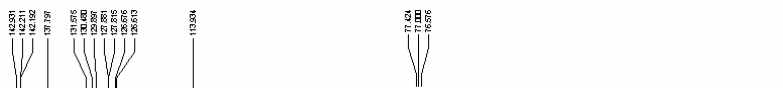
B. The Demethylation Step.

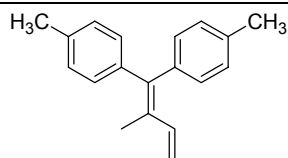
A solution of **A** in dry CH_2Cl_2 (10 mL) was cooled to $-60\text{ }^\circ\text{C}$ under argon, BBr_3 (2.0 mmol) was added. After 1 hr, the reaction mixture was allowed to warm to room temperature and stirred at room temperature for 4 hrs. MeOH (2.0 mL) was added under cooling at $0\text{ }^\circ\text{C}$, diluted with CH_2Cl_2 , washed with saturated brine, dried over Na_2SO_4 and concentrated under reduced pressure. The residue **B** was ^1H NMR determined and was used for the next step without further purification.

General Reaction Procedure for the Kumada-type Reaction. Under an argon atmosphere, **1** (0.25 mmol) and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) (0.25 mmol) and THF (1.0 ml) were added into a Schlenk tube. The reaction mixture was stirred at room temperature for about 8 hrs, then NiCl₂(dppp) (0.025 mmol) and Grignard reagent (1.0 mmol) were added successively. And the obtained mixture was stirred for a further 8 hrs at room temperature. Then the reactions was quenched by addition of water, washed with brine, dried over anhydrous Na₂SO₄, and purified by a flash column chromatography.

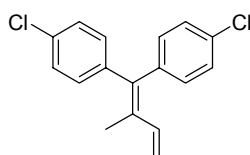
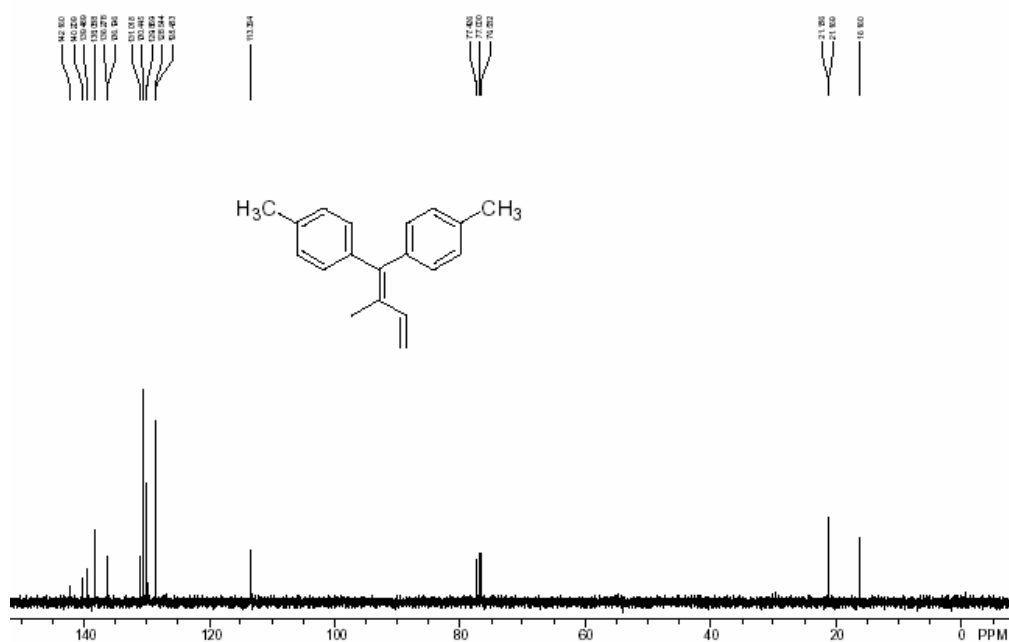


Product **5a**. A yellow liquid, ¹H NMR (CDCl₃, 300 MHz, TMS): δ = 1.97 (s, 3H), 5.11 (dd, 1H, *J* = 0.9, 10.5 Hz), 5.36 (dd, 1H, *J* = 0.9, 17.1 Hz), 6.67 (dd, 1H, *J* = 10.5, 17.1 Hz), 7.16-7.19 (m, 4H, Ar), 7.25-7.36 (m, 6H, Ar). ¹³C NMR (CDCl₃, 75 MHz, TMS): δ = 16.08, 113.93, 126.61, 126.68, 127.82, 127.88, 129.90, 130.48, 131.58, 137.80, 142.19, 142.20, 142.93. IR (CH₂Cl₂): ν = 3078, 3055, 3019, 2921, 2857, 2726, 1937, 1878, 1812, 1668, 1599, 1576, 1490, 1442, 1405, 1376, 902, 763, 700 cm⁻¹; MS (%): *m/e* = 220 (M⁺, 64.75), 205 (100); HRMS Calcd. for C₁₇H₁₆: 220.1252, Found: 220.1275.



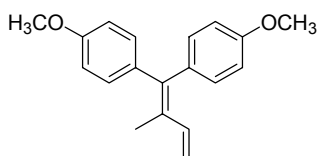
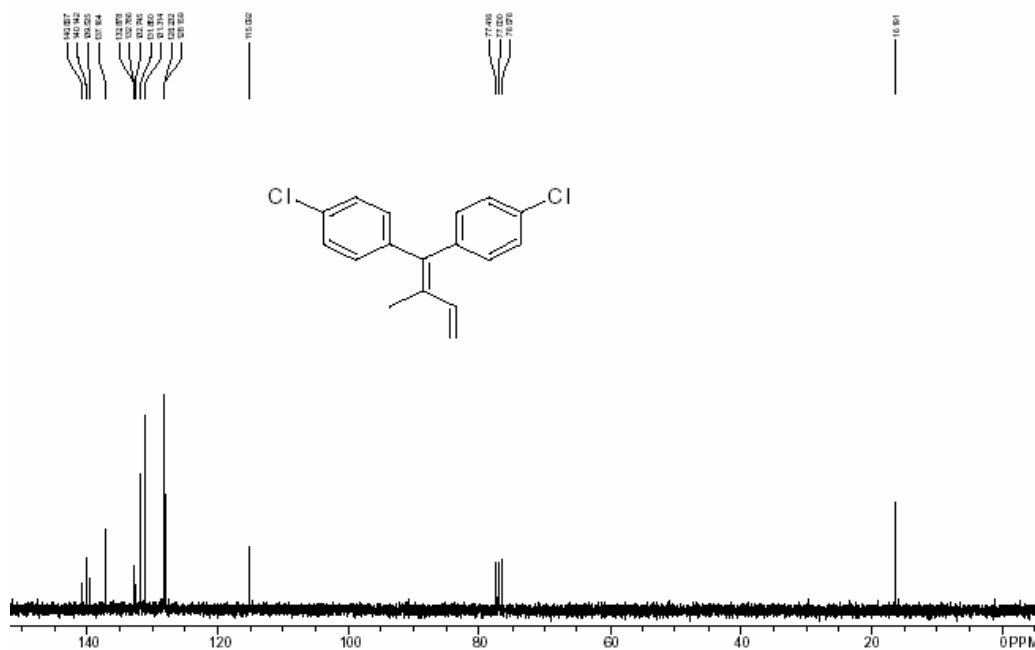


Product **5b**. A white semi-solid, ^1H NMR (CDCl_3 , 300 MHz, TMS): $\delta = 1.98$ (s, 3H), 2.37 (s, 6H), 5.09 (dd, 1H, $J = 1.2, 10.8$ Hz), 5.34 (dd, 1H, $J = 1.2, 17.1$ Hz), 6.70 (dd, 1H, $J = 10.8, 17.1$ Hz), 7.06 (d, 2H, $J = 8.4$ Hz, Ar), 7.07 (d, 2H, $J = 8.4$ Hz, Ar), 7.137 (d, 2H, $J = 8.4$ Hz, Ar), 7.144 (d, 2H, $J = 8.4$ Hz, Ar). ^{13}C NMR (CDCl_3 , 75 MHz, TMS): $\delta = 16.16, 21.17, 21.19, 113.36, 128.48, 128.54, 129.86, 130.45, 131.02, 136.20, 136.28, 138.09, 139.49, 140.21, 142.16$. IR (neat): $\nu = 3086, 3046, 3020, 2920, 2862, 2741, 1904, 1797, 1616, 1509, 1453$ cm^{-1} ; MS (%): $m/e = 248$ (M^+ , 56.31), 233 (100), 218 (52.04); HRMS Calcd. for $\text{C}_{19}\text{H}_{20}$: 248.1565, Found: 248.1557.

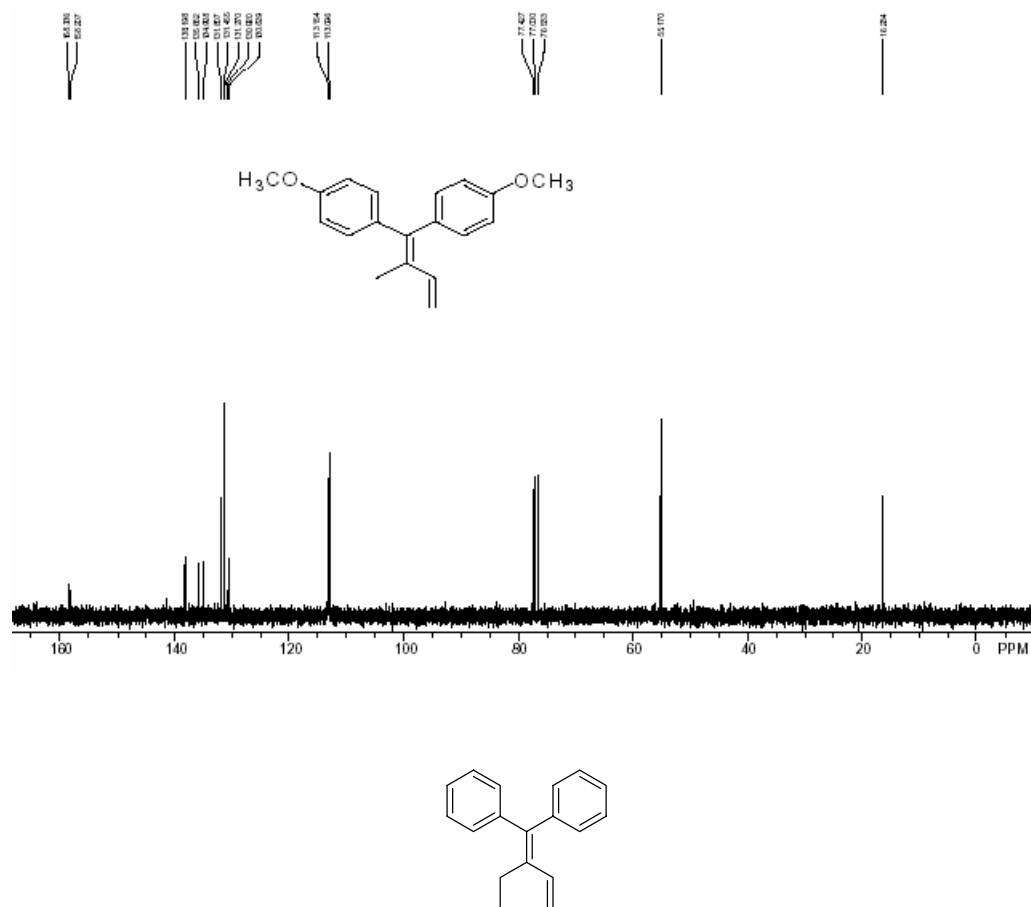


Product **5c**. A colorless liquid, ^1H NMR (CDCl_3 , 300 MHz, TMS): $\delta = 1.85$ (s, 3H), 5.06 (dd, 1H, $J = 1.2, 10.8$ Hz), 5.30 (dd, 1H, $J = 1.2, 17.4$ Hz), 6.50 (dd, 1H, $J = 10.8, 17.4$ Hz), 6.97 (d, 2H, $J = 8.7$ Hz, Ar), 6.98 (d, 2H, $J = 8.7$ Hz, Ar), 7.20 (d, 2H, $J = 8.7$ Hz, Ar), 7.21 (d, 2H, $J =$

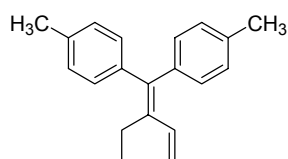
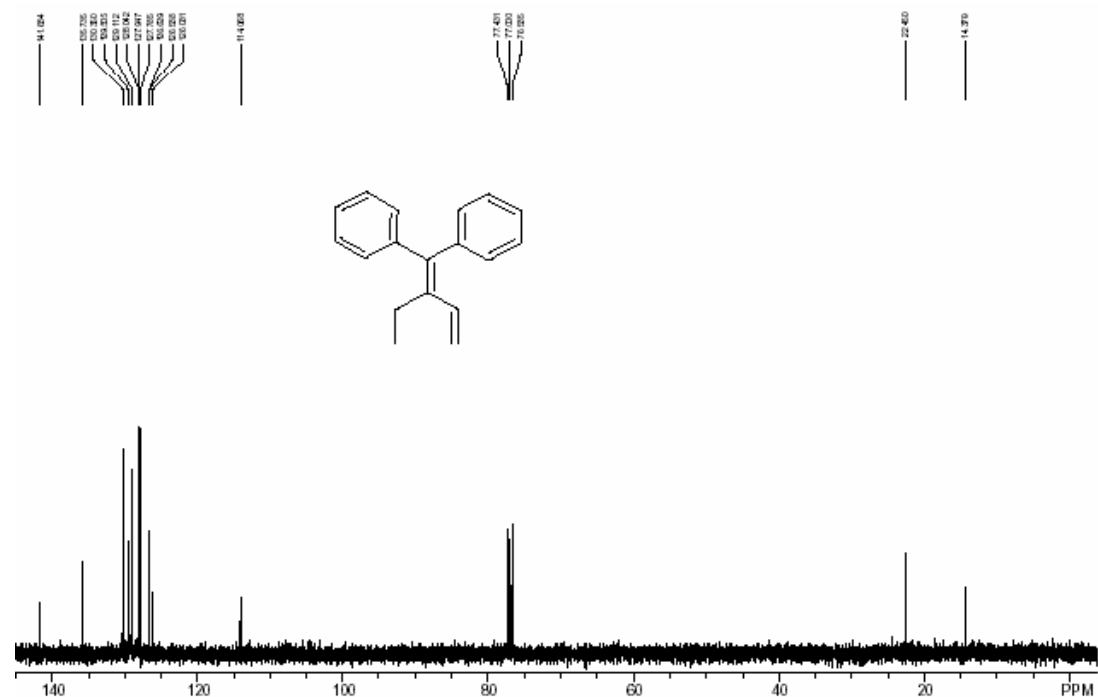
8.7 Hz, Ar). ^{13}C NMR (CDCl_3 , 75 MHz, TMS): $\delta = 16.19, 115.09, 128.16, 128.23, 131.31, 131.86, 132.75, 132.79, 132.88, 137.16, 139.53, 140.14, 140.87$. IR (CH_2Cl_2): $\nu = 3089, 3021, 2922, 2855, 2741, 1904, 1808, 1589, 1454, 1397\text{ cm}^{-1}$; MS (%): $m/e = 288 (\text{M}^+, 27.78), 253 (100), 218 (85.19)$; HRMS Calcd. for $\text{C}_{17}\text{H}_{14}\text{Cl}_2$: 288.0473, Found: 288.0508.



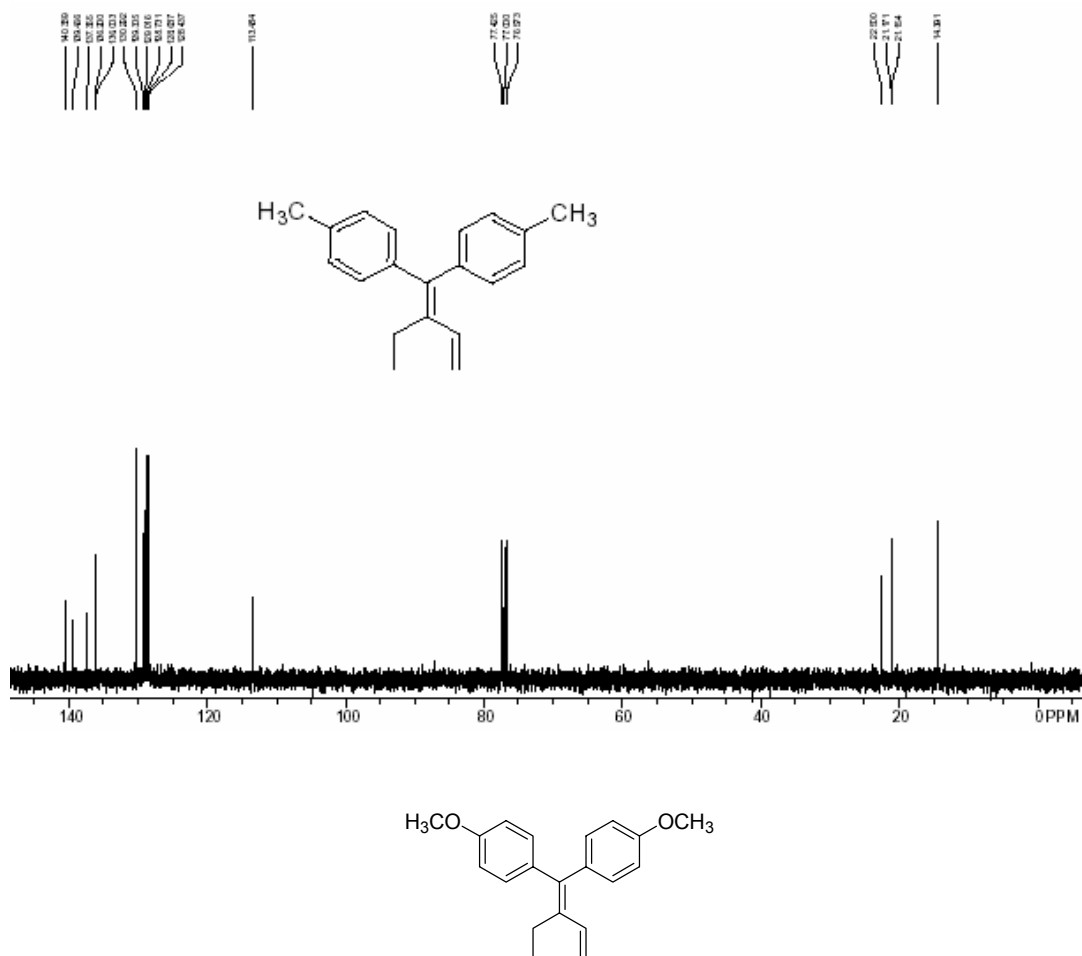
Product **5d**. A yellow liquid, ^1H NMR (CDCl_3 , 300 MHz, TMS): $\delta = 1.94 (\text{s}, 3\text{H}), 3.80 (\text{s}, 6\text{H}), 5.05 (\text{dd}, 1\text{H}, J = 0.9, 10.5\text{ Hz}), 5.29 (\text{dd}, 1\text{H}, J = 0.9, 17.4\text{ Hz}), 6.66 (\text{dd}, 1\text{H}, J = 10.5, 17.4\text{ Hz}), 6.825 (\text{d}, 2\text{H}, J = 8.4\text{ Hz, Ar}), 6.834 (\text{d}, 2\text{H}, J = 8.4\text{ Hz, Ar}), 7.04 (\text{d}, 2\text{H}, J = 8.4\text{ Hz, Ar}), 7.05 (\text{d}, 2\text{H}, J = 8.4\text{ Hz, Ar})$. ^{13}C NMR (CDCl_3 , 75 MHz, TMS): $\delta = 16.28, 55.17, 113.10, 113.15, 130.63, 130.92, 131.27, 131.46, 131.81, 134.93, 135.66, 138.20, 158.21, 158.34$. IR (neat): $\nu = 3032, 2999, 2950, 2933, 2835, 2548, 2052, 1882, 1717, 1657, 1604, 1580, 1509\text{ cm}^{-1}$; MS (%): $m/e = 280 (\text{M}^+, 89.67), 265 (100)$; HRMS Calcd. for $\text{C}_{19}\text{H}_{20}\text{O}_2$: 280.1463, Found: 280.1453.



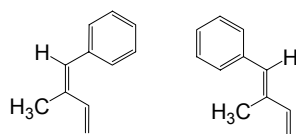
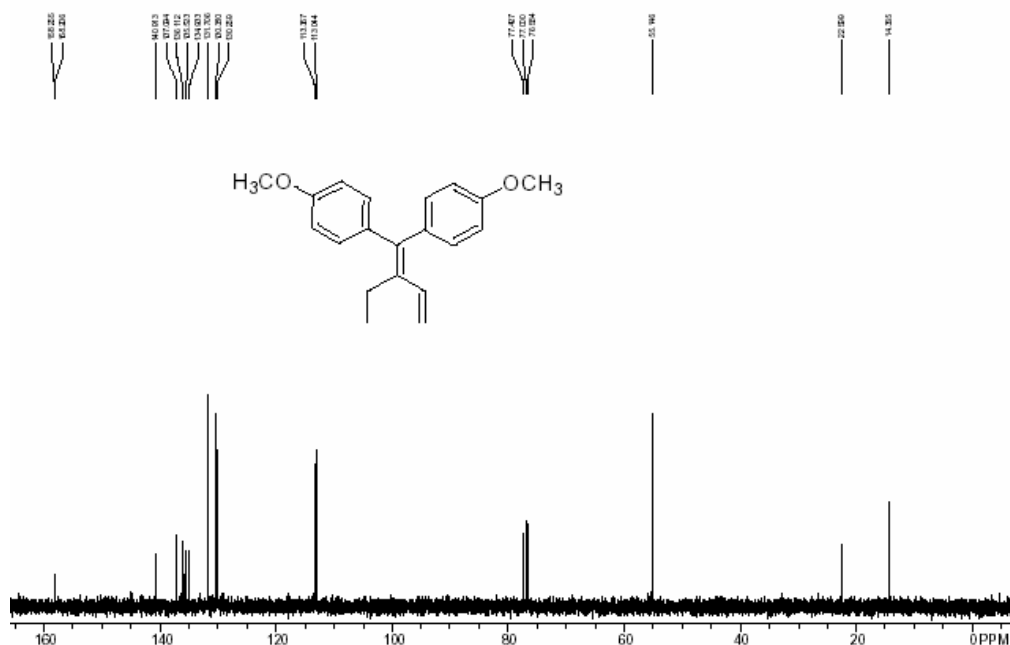
Product **5e**. A colorless liquid, ¹H NMR (CDCl₃, 300 MHz, TMS): δ = 1.11 (t, 3H, *J* = 7.2 Hz), 2.36 (q, 2H, *J* = 7.2 Hz), 5.12 (dd, 1H, *J* = 1.5, 11.1 Hz), 5.35 (dd, 1H, *J* = 1.5, 17.7 Hz), 6.49 (dd, 1H, *J* = 11.1, 17.7 Hz), 7.13-7.32 (m, 10H, Ar). ¹³C NMR (CDCl₃, 75 MHz, TMS): δ = 14.38, 22.45, 114.06, 126.03, 126.59, 126.63, 127.79, 127.95, 128.04, 129.11, 129.51, 130.35, 135.74, 141.68. IR (CH₂Cl₂): ν = 3078, 3055, 3019, 2921, 2857, 2726, 1937, 1878, 1812, 1668, 1599, 1576, 1490, 1442, 1405, 1376 cm⁻¹; MS (%): *m/e* = 234 (M⁺, 12.44), 205 (100); HRMS Calcd. for C₁₈H₁₈ (Maldi): 235.1481, Found: 235.1486 ± 0.003 (M+H⁺).



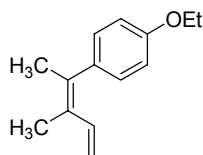
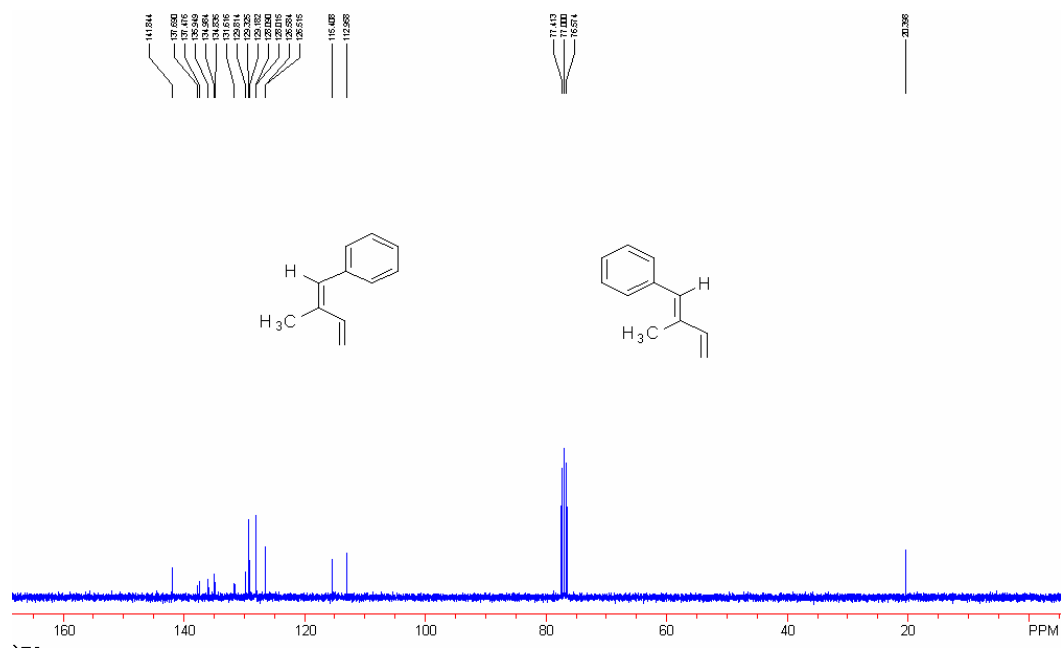
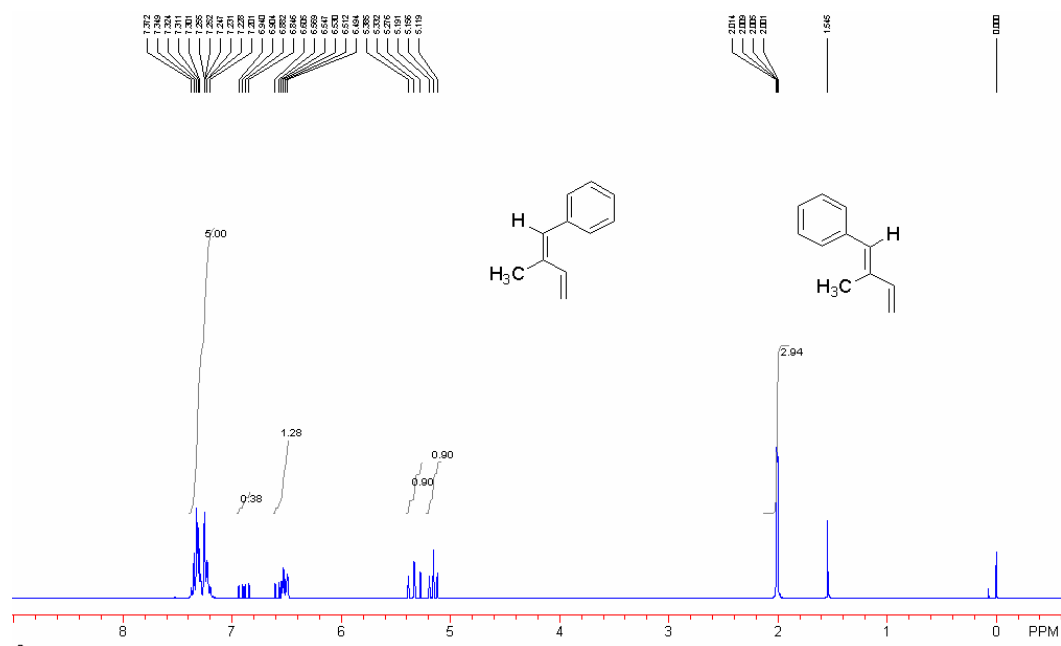
Product **5f**. A colorless liquid, ¹H NMR (CDCl₃, 300 MHz, TMS): δ = 1.13 (t, 3H, *J* = 7.2 Hz), 2.34-2.42 (m, 8H), 5.11 (dd, 1H, *J* = 1.5, 11.1 Hz), 5.34 (dd, 1H, *J* = 1.5, 17.7 Hz), 6.53 (dd, 1H, *J* = 11.1, 17.7 Hz), 7.03-7.15 (m, 8H, Ar). ¹³C NMR (CDCl₃, 75 MHz, TMS): δ = 14.39, 21.15, 21.17, 22.50, 113.48, 128.44, 128.69, 128.73, 129.02, 129.31, 130.29, 136.00, 136.20, 137.36, 139.47, 140.39. IR (neat): ν = 3085, 3019, 2965, 2933, 2872, 1908, 1712, 1610, 1509 cm⁻¹; MS (%): *m/e* = 262 (M⁺, 23.40), 233 (100); HRMS Calcd. for C₂₀H₂₂ (Maldi): 263.1794, Found: 263.1804 ± 0.003 (M+H⁺).



Product **5g**. A colorless liquid, ¹H NMR (CDCl₃, 300 MHz, TMS): δ = 1.13 (t, 3H, *J* = 8.1 Hz), 2.39 (q, 2H, *J* = 8.1 Hz), 3.81 (s, 3H, CH₃O), 3.82 (s, 3H, CH₃O), 5.11 (dd, 1H, *J* = 1.5, 11.1 Hz), 5.33 (dd, 1H, *J* = 1.5, 17.4 Hz), 6.52 (dd, 1H, *J* = 11.1, 17.4 Hz), 6.83 (d, 2H, *J* = 8.7 Hz, Ar), 6.86 (d, 2H, *J* = 8.7 Hz, Ar), 7.04-7.12 (m, 4H, Ar). ¹³C NMR (CDCl₃, 75 MHz, TMS): δ = 14.37, 22.60, 55.15, 113.04, 113.36, 130.26, 130.38, 131.71, 134.93, 135.52, 136.11, 137.09, 140.91, 158.21, 158.26. IR (neat): ν = 3031, 2999, 2962, 2935, 2875, 2837, 2533, 2074, 1878, 1713, 1656, 1607, 1582, 1509 cm⁻¹; MS (%): *m/e* = 294 (M⁺, 1.13), 227 (58.83), 49 (100); HRMS Calcd. for C₂₀H₂₂O₂ (Maldi): 295.1693, Found: 295.1692 ± 0.003 (M+H⁺).

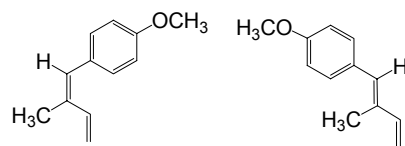
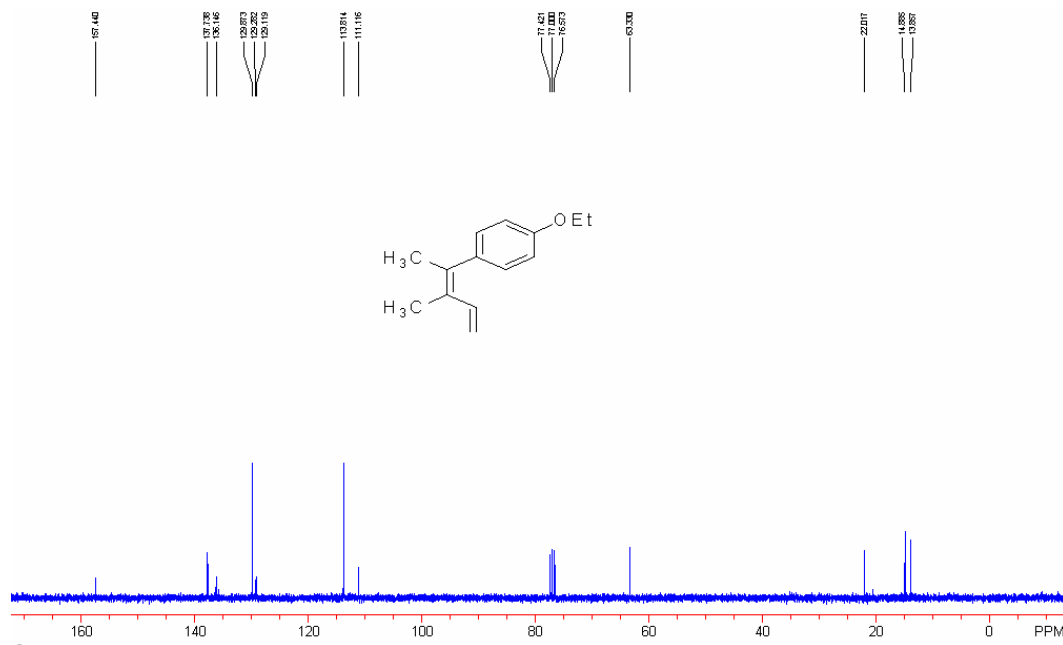


Product **5h**. A colorless liquid, (*E*- or *Z*-isomer) ^1H NMR (CDCl₃, 300 MHz, TMS): δ = 2.00 (d, 3H, J = 1.2 Hz), 5.14 (d, 1H, J = 11.1 Hz), 5.30 (d, 1H, J = 16.8 Hz), 6.49 (s, 1H), 6.56 (dd, J = 11.1, 16.8 Hz), 7.20-7.37 (m, 5H, Ar). (*Z*- or *E*-isomer) ^1H NMR (CDCl₃, 300 MHz, TMS): δ = 2.01 (d, 3H, J = 1.5 Hz), 5.17 (d, 1H, J = 10.5 Hz), 5.36 (d, 1H, J = 15.9 Hz), 6.53 (s, 1H), 6.89 (dd, J = 10.5, 15.9 Hz), 7.20-7.37 (m, 5H, Ar). (*E*- or *Z*-isomer) ^{13}C NMR (CDCl₃, 75 MHz, TMS): δ = 20.40, 112.96, 126.52, 128.02, 129.18, 129.81, 134.84, 135.95, 137.69. (*Z*- or *E*-isomer) ^{13}C NMR (CDCl₃, 75 MHz, TMS): δ = 20.40, 115.41, 126.58, 128.09, 129.33, 131.62, 134.98, 137.48, 141.84. IR (neat): ν = 3082, 3059, 3025, 2958, 2924, 2851, 2214, 1940, 1723, 1673, 1601, 1493, 1450, 1376, 1262, 1072, 1009, 756, 699 cm⁻¹; MS (%): m/e = 144 (M⁺, 46.43), 143 (41.29), 129 (100), 128 (84.86); HRMS Calcd. for C₁₁H₁₂: 144.0939, Found: 144.0925.



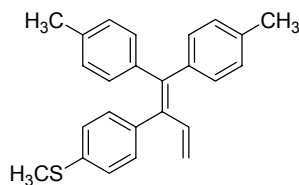
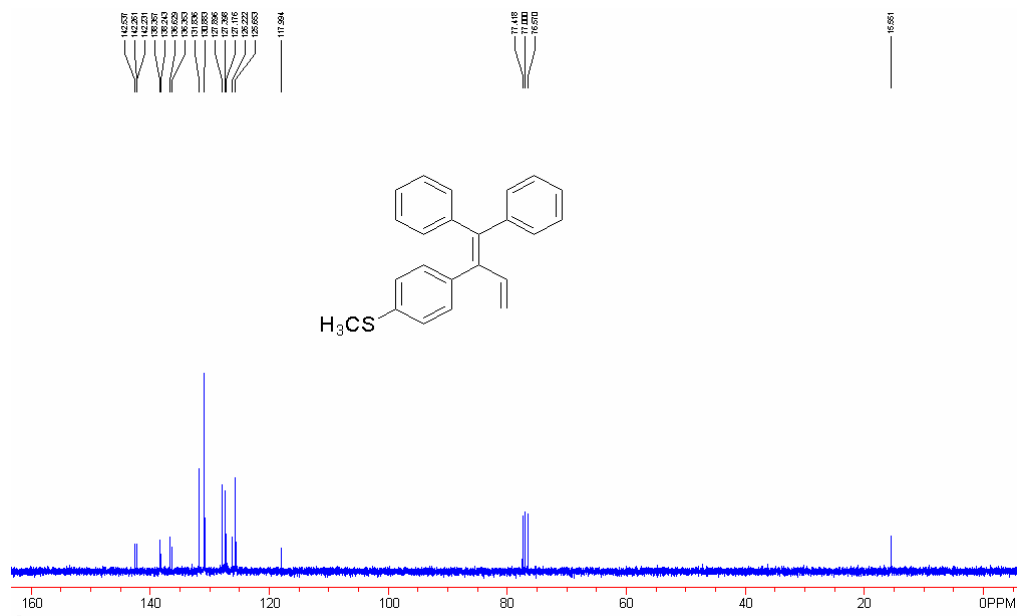
Product **5i**. A colorless liquid, ^1H NMR (CDCl_3 , 300 MHz, TMS): δ = 1.42 (t, 3H, J = 6.9 Hz), 1.91 (s, 3H), 2.08 (s, 3H), 4.03 (q, 2H, J = 6.9 Hz), 4.86 (d, 1H, J = 11.1 Hz), 5.11 (d, 1H, J = 17.7 Hz), 6.48 (dd, 1H, J = 11.1, 17.7 Hz), 6.85 (d, 2H, J = 8.7 Hz, Ar), 7.06 (d, 2H, J = 8.7 Hz, Ar). ^{13}C NMR (CDCl_3 , 75 MHz, TMS): δ = 13.86, 14.89, 22.02, 63.33, 111.12, 113.81, 129.12,

129.28, 129.87, 136.15, 137.74, 157.44. IR (neat): $\nu = 2978, 2925, 1606, 1509, 1478, 1392, 1243, 1175, 1116, 1048, 892 \text{ cm}^{-1}$; MS (%): $m/e = 202 (M^+, 58.16), 187 (100), 159 (83.30)$; HRMS Calcd. for $C_{14}H_{18}O$ (Maldi): 203.1430, Found: $203.1440 \pm 0.003 (M+H^+)$.

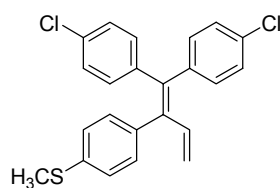
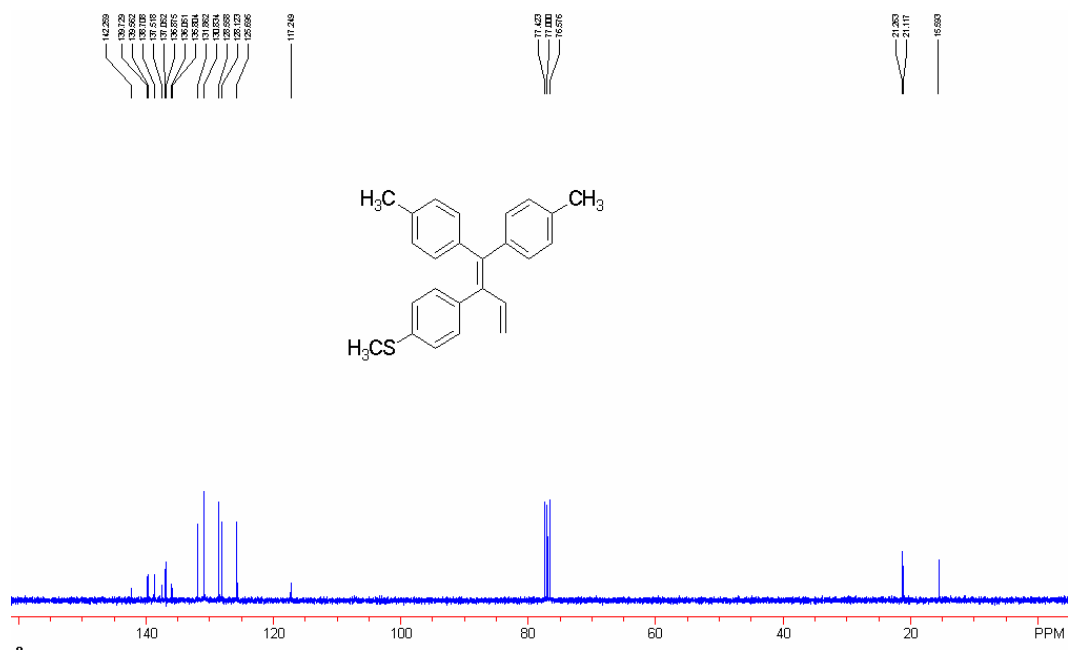


Product **5j**. A colorless liquid, (*E*- or *Z*-isomer) ¹H NMR (CDCl₃, 300 MHz, TMS): $\delta = 1.99 (s, 3H), 3.808 (s, 3H, CH_3O), 5.09 (d, 1H, J = 10.5 \text{ Hz}), 5.23 (d, 1H, J = 17.7 \text{ Hz}), 6.43 (s, 1H), 6.54 (dd, J = 10.5, 17.7 \text{ Hz}), 6.86 (d, 2H, J = 9.0 \text{ Hz}), 7.25 (d, 2H, J = 9.0 \text{ Hz})$. (*E*- or *Z*-isomer) ¹H NMR (CDCl₃, 300 MHz, TMS): $\delta = 1.99 (s, 3H), 3.814 (s, 3H, CH_3O), 5.15 (d, 1H, J = 11.1 \text{ Hz}), 5.32 (d, 1H, J = 17.4 \text{ Hz}), 6.47 (s, 1H), 6.899 (d, 2H, J = 8.7 \text{ Hz}), 6.990 (dd, J = 11.1, 17.4 \text{ Hz}), 7.18 (d, 2H, J = 8.7 \text{ Hz})$. (*E*- or *Z*-isomer) ¹³C NMR (CDCl₃, 75 MHz, TMS): $\delta = 20.40, 55.23, 112.17, 113.56, 129.38, 130.33, 130.50, 133.63, 135.11, 158.26$. (*Z*- or *E*-isomer) ¹³C NMR (CDCl₃, 75 MHz, TMS): $\delta = 20.40, 55.23, 113.46, 114.90, 130.07, 130.43, 131.25, 134.50, 142.03, 158.26$. IR (neat): $\nu = 3089, 3001, 2956, 2932, 2835, 1572, 1509, 1464, 1300, 1251, 1176, 1036, 899, 829 \text{ cm}^{-1}$; MS (%): $m/e = 174 (M^+, 79.88), 159 (100), 144 (52.39)$; HRMS Calcd. for $C_{12}H_{14}O$ (Maldi): 175.1117, Found: $175.1124 \pm 0.003 (M+H^+)$.

136.35, 136.63, 138.24, 138.36, 142.23, 142.26, 142.54. IR (CH₂Cl₂): ν = 3059, 3004, 2970, 2919, 1714, 1422, 1363, 1272, 1222, 1091, 906, 737, 703 cm⁻¹; MS (%): m/e = 328 (M⁺, 100), 281 (44.42), 203 (46.37); HRMS Calcd. for C₂₃H₂₀S (Maldi): 329.1359, Found: 329.1356 ± 0.003 (M+H⁺).



Product **5l**. A pale yellow solid, Mp: 110-113 °C, ¹H NMR (CDCl₃, 300 MHz, TMS): δ = 2.20 (s, 3H), 2.37 (s, 3H), 2.45 (s, 3H), 4.91 (d, 1H, J = 17.4 Hz), 5.11 (d, 1H, J = 10.5 Hz), 6.73 (dd, 1H, J = 10.5, 17.4 Hz), 6.68-6.84 (m, 4H, Ar), 7.07-7.17 (m, 8H, Ar). ¹³C NMR (CDCl₃, 75 MHz, TMS): δ = 15.59, 21.12, 21.26, 117.25, 125.70, 128.12, 128.56, 130.83, 131.86, 135.80, 136.05, 136.88, 137.05, 137.52, 138.71, 139.56, 139.73, 142.26. IR (CH₂Cl₂): ν = 3085, 3045, 3023, 2989, 2920, 2863, 1900, 1804, 1601, 1508, 1489, 1441, 1265, 1113, 1087, 1017, 998, 900, 819, 780, 737 cm⁻¹; MS (%): m/e = 356 (M⁺, 100), 341 (29.47), 309 (25.91), 294 (40.31); HRMS Calcd. for C₂₅H₂₄S (Maldi): 357.1672, Found: 357.1672 ± 0.003 (M+H⁺).



Product **5m**. A pale yellow solid, Mp: 100-101 °C, ^1H NMR (CDCl_3 , 300 MHz, TMS): δ = 2.46 (s, 3H), 4.99 (d, 1H, J = 17.1 Hz), 5.21 (d, 1H, J = 10.8 Hz), 6.66 (dd, 1H, J = 10.8, 17.1 Hz), 6.78 (d, 2H, J = 7.5 Hz, Ar), 7.00-7.17 (m, 8H, Ar), 7.27-7.33 (m, 2H, Ar). ^{13}C NMR (CDCl_3 , 75 MHz, TMS): δ = 15.40, 119.27, 125.65, 127.79, 128.27, 131.67, 132.19, 132.26, 133.31, 135.92, 137.06, 137.85, 139.30, 139.48, 140.23, 140.63. IR (CH_2Cl_2): ν = 3104, 3048, 2920, 2852, 1897, 1589, 1490, 1438, 1398, 1264, 1091, 1015, 916, 831, 804, 739 cm^{-1} ; MS (%): m/e = 396 (M^+ , 73.25), 314 (100), 278 (55.11), 202 (48.78), 138 (41.52), 137 (43.21); HRMS Calcd. for $\text{C}_{23}\text{H}_{18}\text{Cl}_2\text{S}$ (Maldi): 397.0579, Found: 397.0573 \pm 0.003 ($\text{M}+\text{H}^+$).

