Electronic Supplementary Information

Base-promoted direct E-selective olefination of organoammonium salts with sulfones toward stilbenes and conjugated 1, 3-dienes

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1. General Information

The reactions were carried out in Schlenk tubes of 25 mL under N₂ atmosphere. For reactions that require heating, heating mantle was used as the heat source. Organoammonium salts 1 and Sulfones derivatives 2 were prepared according to the reported literatures. 1,2 All solvents were purified according to standard operation procedures. All solvents and reagents were purchased from Tansoole, Meryer, Heowns, Energy Chemical, Alfa Aesar, and Aladdin. Column chromatography was performed using Silica Gel 60 (300-400 mesh). The reactions were monitored by GC and GC-MS, GC-MS results were recorded on GC-MS QP2010, and GC analysis was performed on GC 2014. The ¹H, ¹³C and ¹⁹F NMR spectra were recorded on a Bruker ADVANCE III spectrometer at 400 MHz, 100 MHz, and 376 MHz respectively, and chemical shifts were reported in parts per million (ppm). The electron ionization (EI) method was used as the ionization method for the HRMS measurement, and the mass analyzer type is TOF for EI.

2. Experimental Procedure

2.1 General Experimental Procedure.

R NMe₃OTf + Ar
$$SO_2$$
Ph KO^t Bu (2.2 equiv)
Toluene (2 mL)
1 2 100 °C, 2 h 3

In an oven dried 25 mL Schlenk tube charged with 1 (0.2 mmol), 2 (0.2 mmol, 1.0 equiv), and KO'Bu (0.44 mmol, 2.2 equiv), after charging N_2 for three times, toluene (2 mL) were added. The reaction mixture was reacted at 100 °C for 2 h. The experiment was conducted in two sets, and the reaction mixtures of two sets were combined and concentrated after completion of the reaction. The desired product was isolated by column chromatography over silica gel (300-400 mesh) using petroleum ether/ethyl acetate (PE/EA) as eluent.

2.2 Gram Scale Synthesis of 3n.

In an oven dried 100 mL Schlenk tube charged with **1a** (6 mmol), **2p** (6 mmol, 1.0 equiv), and KO'Bu (13.2 mmol, 2.2 equiv), after charging N₂ for three times, toluene (40 mL) were added. The reaction mixture was reacted at 100 °C for 3 h. The reaction mixture was combined and concentrated after completion of the reaction. The concentrated product purified by column chromatography on silica gel with PE to afford a white solid in 83% yield (1.2901 g).

2.3 Experimental Procedure for Conjugate Structure Modification.

In an oven dried 25 mL Schlenk tube charged with 3zg (0.2 mmol), Pd(PPh₃)₂Cl₂ (0.008 mmol) and CuI (0.004 mmol), after charging N₂ for three times, 'PrNH₂ (0.4 mmol), Phenylacetylene (0.24 mmol) and THF (3 mL) were added. After stirred at room temperature for 1 h, the mixture was passed through a short pad of silica gel, and the silica gel was washed with hexane and AcOEt (2:1). The combined eluents were concentrated to afford a crude mixture, which was purified by silica gel column chromatography using hexanes as eluent. Pure 4 was obtained as yellow solid in 80% yield (48.8 mg). ¹H NMR (400 MHz, CDCl₃) δ 7.55–7.52 (m, 2H), 7.48 (t, J = 8.0 Hz, 3H), 7.42 (t, J = 8.0 Hz, 3H), 7.38–7.32 (m, 5H), 7.25–7.22 (m, 1H), 7.02–6.93 (m, 2H), 6.73–6.62 (m, 2H). ¹³C NMR (100 MHz, CDCl₃) δ 137.3, 137.2, 133.5, 132.0, 131.9, 131.6, 130.2, 129.0, 128.7, 128.3, 128.2, 127.7, 126.5, 126.3, 123.3, 122.1, 90.4, 89.6. This compound is known.³ (CAS: 115101-38-7)

2.4 Experimental Procedure for the Preparation of 5 (Resveratol).

In an oven dried 25 mL Schlenk tube charged with 3zj (0.5 mmol) in CH_2Cl_2 (2 mL) under N_2 was treated with BBr₃ (5 equiv) at 0 °C. The solution was warmed to room temperature and

stirred for 5 h followed by the slow addition of water (4 mL) and further stirring for 30 min. Then, CH_2Cl_2 was evaporated under reduced pressure and the water phase was extracted with EtOAc (3×5 mL). The crude mixture was purified by silica gel column chromatography (300-400 mesh size) with $CH_2Cl_2/EtOH = 10:1$ as an eluting system to afford a pale yellow solid in 71% yield (81.0 mg). ¹H NMR (400 MHz, DMSO) δ 9.57 (s, 1H), 9.21 (s, 2H), 7.40 (d, J = 8.0 Hz, 2H), 6.96–6.75 (m, 4H), 6.39 (s, 2H), 6.12 (s, 1H). ¹³C NMR (100 MHz, DMSO) δ 159.0, 157.7, 139.8, 128.6, 128.4, 126.2, 116.0, 104.8, 102.3. This compound is known.⁴ (CAS: 501-36-0)

3. Characterization Data for the Products

(*E*)-1,2-diphenylethene (3a): The title compound was prepared according to the General Experimental Procedure, and purified by column chromatography on silica gel with PE to afford a white solid in 78 % yield (56.2 mg). 1 H NMR (400 MHz, CDCl₃) δ 7.52–7.50 (m, 4H), 7.35 (t, *J* = 8.0 Hz, 4H), 7.27–7.21 (m, 2H), 7.10 (s, 2H). 13 C NMR (100 MHz, CDCl₃) δ 137.3, 128.7, 127.6, 126.5. This compound is known.⁴ (CAS: 103-30-0)

(E)-1-methyl-2-styrylbenzene (3b): The title compound was prepared according to the General Experimental Procedure, and purified by column chromatography on silica gel with PE to afford a colorless solid in 84% yield (65.4 mg). 1 H NMR (400 MHz, CDCl₃) δ 7.57 (d, J = 7.2 Hz, 1H), 7.50 (d, J = 7.2 Hz, 2H), 7.36–7.30 (m, 3H), 7.26 – 7.16 (m, 4H), 6.9 (d, J = 16.0 Hz, 1H), 2.41 (s, 3H). 13 C NMR (100 MHz, CDCl₃): δ 137.7, 136.4, 135.8, 130.4, 130.0, 128.7, 127.6, 127.5, 126.5, 126.2, 125.3, 19.9. This compound is known. 4 (CAS: 22257-16-5)

(E)-1-methyl-4-styrylbenzene (3c): The title compound was prepared according to the General Experimental Procedure, and purified by column chromatography on silica gel with PE to afford a colorless solid in 76% yield (59.2 mg). 1 H NMR (400 M Hz, CDCl₃) δ 7.49 (d, J = 8.0 Hz, 2H), 7.40 (d, J = 8.0 Hz, 2H), 7.34 (t, J = 8.0 Hz, 2H), 7.25–7.21 (m, 1H), 7.16 (d, J = 8.0 Hz, 2H), 7.11–7.02 (m, 2H), 2.35 (s, 3H). 13 C NMR (100 MHz, CDCl₃) δ 137.5, 134.5, 129.4, 128.7, 127.7, 127.4, 126.41, 126.38, 21.2. This compound is known. 4 (CAS: 1860-17-9)

(E)-1-methoxy-4-styrylbenzene (3d): The title compound was prepared according to the General Experimental Procedure, and purified by column chromatography on silica gel with PE/EA =10:1 to afford a white solid in 70% yield (65.5 mg). ¹H NMR (400 MHz, CDCl₃) δ 7.49–7.43 (m, 4H), 7.33 (t, J = 8.0 Hz, 2H), 7.24–7.21 (m, 1H), 7.04 (dd, J = 40.0, 16.0 Hz, 2H), 6.91–6.87 (m, 2H), 3.81 (s, 3H). 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. This compound is known.⁴ (CAS: 1694-19-5)

(E)-1-(tert-butyl)-4-styrylbenzene (3e): The title compound was prepared according to the General Experimental Procedure, and purified by column chromatography on silica gel with PE/EA =10:1 to afford a white solid in 72% yield (68.2 mg). 1 H NMR (400 MHz, CDCl₃) δ 7.50 (d, J = 7.2 Hz, 2H), 7.45 (d, J = 8.4 Hz, 2H), 7.39–7.32 (m, 4H), 7.25 – 7.22 (m, 1H), 7.11–7.04 (m, 2H), 1.33 (s, 9H). 13 C NMR (100 MHz, CDCl₃) δ 150.8, 137.5, 134.5, 128.6, 128.5, 127.9, 127.4, 126.4, 126.2 125.6, 34.6, 31.3. This compound is known.⁴ (CAS: 20374-76-9)

(E)-methyl(4-styrylphenyl)sulfane (3f): The title compound was prepared according to the General Experimental Procedure, and purified by column chromatography on silica gel with PE/EA =10:1 to afford a white solid in 65% yield (58.5 mg). 1 H NMR (400 MHz, CDCl₃) δ 7.49 (d, J = 7.6 Hz, 2H), 7.43 (d, J = 8.4 Hz, 2H), 7.35 (t, J = 8.0 Hz, 2H), 7.27–7.23 (m, 3H), 7.06 (s, 2H), 2.49 (s, 3H). 13 C NMR (100 MHz, CDCl₃) δ 137.8, 137.3, 134.3, 128.7, 128.1, 128.0, 127.6, 126.9, 126.7, 126.4, 15.8. This compound is known. 5 (CAS: 197957-64-5)

(E)-4-styryl-1,1'-biphenyl (3g): The title compound was prepared according to the General Experimental Procedure, and purified by column chromatography on silica gel with PE/EA =10:1 to afford a white solid in 57% yield (58.1 mg). ¹H NMR (400 MHz, CDCl₃) δ 7.63–7.60 (m,

6H), 7.54 (d, J = 8.0 Hz, 2H), 7.45 (t, J = 8.0 Hz, 2H), 7.39–7.33 (m, 3H), 7.28 (d, J = 8.0 Hz, 1H), 7.15 (s, 2H). ¹³C NMR (100 MHz, CDCl₃) δ 140.7, 140.3, 137.3, 126.4, 128.8, 128.74, 127.70, 128.2, 127.7, 127.34, 127.32, 126.9, 126.5. This compound is known.⁴ (CAS: 21175-18-8)

(E)-2-styrylnaphthalene (3h): The title compound was prepared according to the General Experimental Procedure, and purified by column chromatography on silica gel with PE/EA =20:1 to afford a white solid in 80% yield (73.8 mg). 1 H NMR (400 MHz, CDCl₃) δ 7.84–7.79 (m, 4H), 7.75–7.72 (m, 1H), 7.55 (d, J = 4.0 Hz, 2H), 7.49–7.41 (m, 2H), 7.37 (t, J = 8.0 Hz, 2H), 7.30–7.20 (m, 3H). 13 C NMR (100 MHz, CDCl₃) δ 137.3, 134.8, 133.7, 133.0, 129.0, 128.73, 128.70, 128.3, 128.0, 127.7, 126.6, 126.5, 126.3, 125.9, 123.5. This compound is known.⁶ (CAS: 2840-89-3)

(E)-1-styrylnaphthalene (3i): The title compound was prepared according to the **General Experimental Procedure**, and purified by column chromatography on silica gel with PE/EA = 20:1to afford a white solid in 73% yield (67.6 mg). 1 H NMR (400 MHz, CDCl₃) δ 8.21 (d, J = 8.0 Hz, 1H), 7.90–7.85 (m, 2H), 7.79 (d, J = 8.0 Hz, 1H), 7.74 (d, J = 8.0 Hz, 1H), 7.60 (d, J = 8.0 Hz, 2H), 7.55–7.46 (m, 3H), 7.41–7.38 (m, 2H), 7.31–7.28 (1, 1H), 7.14 (d, J = 16 Hz, 1H). 13 C NMR (100 MHz, CDCl₃) δ 137.6, 135.0, 133.7, 131.7, 131.4, 128.7, 128.6, 128.0, 127.8, 126.7, 126.1, 125.8, 125.7, 125.6, 123.8, 123.6. This compound is known.⁴ (CAS: 2840-87-1)

(E)-1-fluoro-4-styrylbenzene (3j): The title compound was prepared according to the **General Experimental Procedure**, and purified by column chromatography on silica gel with PE/EA =10:1 to afford a white solid in 70% yield (55.6 mg). ¹H NMR (400 MHz, CDCl₃) δ 7.50–7.45 (m, 4H), 7.35 (t, J = 7.2 Hz, 2H), 7.27–7.24 (m, 1H), 7.09–6.98 (m, 4H). ¹³C NMR (100 MHz, CDCl₃) δ 162.3 (d, J = 245.5 Hz), 137.2, 133.5 (d, J = 3.2 Hz), 128.7, 128.5 (d, J = 2.1 Hz), 128.0 (d, J = 3.2 Hz), 128.7, 128.5 (d, J = 3.2 Hz), 128.0 (d, J = 3.2 Hz), 128.7, 128.5 (d, J = 3.2 Hz), 128.7 (d, J = 3.2 Hz), 128.9 (d, J = 3.2 Hz), 128.7 (d, J = 3.2 Hz)

7.9 Hz), 127.6, 127.5, 126.4, 115.6 (d, J = 21.5 Hz). ¹⁹F NMR (376 MHz, CDCl₃) δ -114.24. This compound is known.⁴ (CAS: 718-25-2)

(E)-1-chloro-4-styrylbenzene (3k): The title compound was prepared according to the General Experimental Procedure, and purified by column chromatography on silica gel with PE to afford a white solid in 82% yield (70.1 mg). 1 H NMR (400 MHz, CDCl₃) δ 7.50 (d, J = 8.0 Hz, 2H), 7.43 (d, J = 8.0 Hz, 2H), 7.38–7.32 (m, 3H), 7.31–7.25 (m, 2H), 7.10–7.01 (m, 2H). 13 C NMR (100 MHz, CDCl₃) δ 136.7, 135.9, 133.2, 129.3, 128.8, 128.7, 127.9, 127.6, 127.4, 126.5. This compound is known.⁶ (CAS: 1657-50-7)

(E)-1-bromo-4-styrylbenzene (3l): The title compound was prepared according to the **General Experimental Procedure**, and purified by column chromatography on silica gel with PE to afford a isolated yield in 78% yield (81.8 mg). ¹H NMR (400 MHz, CDCl₃) δ 7.49 – 7.44 (m, 4H), 7.36 – 7.33 (m, 4H), 7.28–7.22 (m, 1H), 7.05 (q, J = 16.3 Hz, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 136.9, 136.2, 131.7, 129.4, 128.7, 127.93, 127.86, 137.3 126.5, 121.3. This compound is known. ⁷ (CAS: 13041-70-8)

(E)-1-bromo-3-styrylbenzene (3m): The title compound was prepared according to the General Experimental Procedure, and purified by column chromatography on silica gel with PE to afford a white solid in 84% yield (86.8 mg). ¹H NMR (400 MHz, CDCl₃) δ 7.64 (s, 1H), 7.48 (d, J = 7.4 Hz, 2H), 7.40–7.33 (m, 4H), 7.28–7.17 (m, 2H), 7.10– 6.97 (m, 2H). ¹³C NMR (100 MHz, CDCl₃): δ 139.5, 136.7, 130.3, 130.1, 129.2, 128.7, 128.0, 127.0, 126.6, 125.1, 122.9. This compound is known.⁶ (CAS: 14064-45-0)

(E)-1-bromo-2-styrylbenzene (3n): The title compound was prepared according to the General Experimental Procedure, and purified by column chromatography on silica gel with PE to afford a white solid in 82% yield (85.4 mg). 1 H NMR (400 MHz, DMSO) δ 7.63 (dd, J = 7.8, 1.6 Hz, 1H), 7.57–7.52 (m, 3H), 7.45 (d, J = 16.0 Hz, 1H), 7.35 (t, J = 7.6 Hz, 2H), 7.29–7.25 (m, 2H), 7.10–7.06 (m, 1H), 7.01 (d, J = 16.0 Hz, 1H). 13 C NMR (100 MHz, CDCl₃) δ 137.1, 136.9, 133.0, 131.4, 128.7, 128.6, 128.0, 127.5, 127.4, 126.8, 126.7, 124.1. This compound is known.8 (CAS: 54737-45-0)

(E)-1-iodo-4-styrylbenzene (3o): The title compound was prepared according to the General Experimental Procedure, and purified by column chromatography on silica gel with PE to afford a white solid in 87% yield (107.0 mg). H NMR (400 MHz, CDCl₃) δ 7.67 (d, J = 8.0 Hz, 2H), 7.49 (d, J = 8.0 Hz, 2H), 7.35 (t, J = 8.0 Hz, 2H), 7.28–7.23 (m, 3H), 7.12–6.98 (m, 2H). CNMR (100 MHz, CDCl₃): δ 137.7, 136.9, 136.8, 129.5, 128.7, 128.2, 127.9, 127.5, 126.6, 92.7. This compound is known. (CAS: 13041-71-9)

(E)-1-styryl-4-(trifluoromethyl)benzene (3p): The title compound was prepared according to the General Experimental Procedure, and purified by column chromatography on silica gel with PE/EA =10:1 to afford a white solid in 80% yield (79.5 mg). 1 H NMR (400 MHz, CDCl₃) δ 7.58 (t, J = 8.0 Hz, 4H), 7.52 (d, J = 4.0 Hz, 2H), 7.37 (t, J = 7.2 Hz, 2H), 7.29 (t, J = 8.0 Hz, 1H), 7.13 (q, J = 16 Hz, 2H). 13 C NMR (100 MHz, CDCl₃) δ 140.8, 136.6, 131.2, 129.2 (q, J = 32.0 Hz), 128.8, 128.3, 127.1, 126.8, 126.6, 125.6 (q, J = 4.0 Hz), 121.5 (d, J = 270.0 Hz). 19 F NMR (376 MHz, CDCl₃) δ -62.39. This compound is known. 6 (CAS: 1149-56-0)

(E)-2-styrylbenzofuran (3q): The title compound was prepared according to the General Experimental Procedure, and purified by column chromatography on silica gel with PE/EA = 10:1 to afford a white solid in 81% yield (71.4 mg). ¹H NMR (400 MHz, CDCl₃) δ 7.51 (d, J = 7.2 Hz, 3H), 7.46 (d, J = 8.0 Hz, 1H), 7.37–7.24 (m, 5H), 7.21–7.17 (m, 1H), 6.98 (d, J = 16.0 Hz, 1H), 6.65 (s, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 155.0, 154.9, 136.5, 130.2, 129.1, 128.7, 128.1, 126.7, 124.6, 122.9, 120.8, 116.4, 110.9, 105.2. This compound is known. ¹⁰ (CAS: 65487-87-8)

(E)-2-styrylbenzo[b]thiophene (3r): The title compound was prepared according to the **General Experimental Procedure**, and purified by column chromatography on silica gel with PE/EA =10:1 to afford a white solid in 78% yield (74.1 mg). ¹H NMR (400 MHz, CDCl₃) δ 7.78–7.76 (m, 1H), 7.70–7.68 (m, 1H), 7.50 (d, J = 8.0 Hz, 2H), 7.38–7.33 (m, 2H), 7.32–7.24 (m, 5H), 6.99 (d, J = 16.0 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 142.9, 140.2, 138.9, 136.6, 130.8, 128.7, 128.0, 126.6, 124.7, 124.5, 123.4, 123.3, 122.3, 122.2. This compound is known. ¹⁰ (CAS: 28684-74-4)

(E)-1-benzyl-3-styryl-1H-indole (3s): The title compound was prepared according to the **General Experimental Procedure**, and purified by column chromatography on silica gel with PE to afford a primrose yellow in 80% yield (99.5 mg). ¹H NMR (400 MHz, CDCl₃) δ 8.02–7.98 (m, 1H), 7.50 (d, *J* = 8.0 Hz, 2H), 7.36–7.27 (m, 8H), 7.24–7.18 (m, 3H), 7.14–7.08 (m, 3H) 5.29 (s, 2H). ¹³C NMR (100 MHz, CDCl₃) δ 138.7, 137.3, 137.0, 128.8, 128.6, 127.8, 126.9, 126.5, 126.4 125.7, 125.2, 122.4, 121.5, 120.3 120.2, 114.6, 110.0, 50.1. This compound is known. ¹¹ (CAS: 1929530-92-6)

Experimental Procedure, and purified by column chromatography on silica gel with PE to afford a white solid in 60% yield (61.5 mg). ¹H NMR (400 MHz, CDCl₃) δ 7.33–7.26 (m, 8H), 7.21–7.19 (m, 2H), 7.14–7.08 (m, 3H), 7.03–7.01 (m, 2H), 6.96 (s, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 143.4, 142.5, 140.3, 137.3, 130.4, 129.5, 128.6, 128.2, 128.1, 127.9, 127.6, 127.5, 127.4, 126.7. This compound is known. ¹² (CAS: 58-72-0)

(1E,3E)-1,4-diphenylbuta-1,3-diene (3u): The title compound was prepared according to the General Experimental Procedure, and purified by column chromatography on silica gel with PE to afford a white solid in 72% yield (59.4 mg). ¹H NMR (400 MHz, CDCl₃) δ 7.44 (d, J = 7.6 Hz, 4H), 7.33 (t, J = 7.6 Hz, 4H), 7.25–7.21 (m, 2H), 7.00–6.92 (m, 2H), 6.71–6.63 (m, 2H). ¹³C NMR (100 MHz, CDCl₃): δ 137.3, 132.8, 129.2, 128.6, 127.5, 126.4. This compound is known. ⁴ (CAS: 538-81-8)

1-methyl-2-((1E,3E)-4-phenylbuta-1,3-dien-1-yl)benzene (**3v**): The title compound was prepared according to the **General Experimental Procedure**, and purified by column chromatography on silica gel with PE to afford a white solid in 74% yield (65.2 mg). ¹H NMR (400 MHz, CDCl₃) δ 7.55 (d, J = 7.6 Hz, 1H), 7.44 (d, J = 7.2 Hz, 2H), 7.33 (t, J = 7.6 Hz, 2H), 7.25–7.14 (m, 4H), 7.03–6.97 (m, 1H), 6.92–6.83 (m, 2H), 6.67 (d, J = 15.2 Hz, 1H), 2.39 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 137.4, 136.1, 135.6, 132.7, 130.5, 130.4, 130.3, 129.6, 128.6, 127.51, 127.46, 126.4, 126.1, 125.0, 19.9. This compound is known.⁴ (CAS: 1835652-51-1)

1-methoxy-2-((1E,3E)-4-phenylbuta-1,3-dien-1-yl)benzene (3w): The title compound was prepared according to the **General Experimental Procedure**, and purified by column chromatography on silica gel with PE/EA =10:1 to afford a primrose yellow solid in 78% yield (73.8 mg). 1 H NMR (400 MHz, CDCl₃) δ 7.43 (d, J = 8.0 Hz, 2H), 7.32 (t, J = 8.0 Hz, 2H), 7.26–7.21 (m, 2H), 7.03 (d, J = 8.0 Hz, 1H), 6.98–6.90 (m, 3H), 6.79 (dd, J = 8.0, 2.0 Hz, 1H), 6.71–6.59 (m, 2H), 3.82 (s, 3H). 13 C NMR (100 MHz, CDCl₃) δ 159.8, 138.8, 137.3, 133.0, 132.7, 129.59, 129.55, 129.1, 128.6, 127.6, 126.4, 119.1, 113.3, 111.5, 55.2. This compound is known. 13 (CAS: 82102-27-0)

1-methoxy-4-((1E,3E)-4-phenylbuta-1,3-dien-1-yl)benzene (3x): The title compound was prepared according to the **General Experimental Procedure**, and purified by column chromatography on silica gel with PE/EA = 5:1 to afford a white solid in 74% yield (69.9 mg). 1 H NMR (400 MHz, CDCl₃) δ 7.42 (d, J = 7.6 Hz, 2H), 7.38 (d, J = 8.8 Hz, 2H), 7.32 (t, J = 7.6 Hz, 2H), 7.21 (t, J = 7.2 Hz, 1H), 6.97–6.89 (m, 2H), 6.86–6.80 (m, 2H), 6.62 (d, J = 14.8 Hz, 2H), 3.82 (s, 3H). 13 C NMR (101 MHz, CDCl₃) δ 159.3, 137.5, 132.4, 131.7, 130.2, 129.5, 128.6, 127.6, 127.30, 127.25, 126.2, 114.1, 55.3. This compound is known.⁴ (CAS: 22145-08-0)

1,3-dimethoxy-5-((1E,3E)-4-phenylbuta-1,3-dien-1-yl)benzene (3y): The title compound was prepared according to the **General Experimental Procedure**, and purified by column chromatography on silica gel with PE/EA = 10:1 to afford a primrose yellow solid in 80% yield (85.1 mg). 1 H NMR (400 MHz, CDCl₃) δ 7.42 (d, J = 7.6 Hz, 2H), 7.32 (t, J = 7.6 Hz, 2H), 7.24–7.21 (m, 1H), 6.96–6.88 (m, 2H), 6.70–6.55 (m, 4H), 6.37 (t, J = 2.4 Hz, 1H), 3.80 (s, 6H). 13 C NMR (100 MHz, CDCl₃) δ 160.9, 139.3, 137.2, 133.1, 132.7, 129.7, 129.0, 128.6, 127.6, 126.4, 104.4, 100.0, 55.3.

This compound is known.⁴ (CAS: 125244-69-1)

methyl(4-((1E,3E)-4-phenylbuta-1,3-dien-1-yl)phenyl)sulfane (3z): The title compound was prepared according to the General Experimental Procedure, and purified by column chromatography on silica gel with PE/EA =10:1 to afford a white solid in 72% yield (72.2 mg). 1 H NMR (400 MHz, CDCl₃) δ 7.43 (d, J = 8.0 Hz, 2H), 7.34 (dd, J = 16.0, 8.0 Hz, 4H), 7.22 (dd, J = 12.0, 8.0 Hz, 3H), 6.97–6.87 (m, 2H), 6.68–6.58 (m, 2H), 2.48 (s, 3H). 13 C NMR (100 MHz, CDCl₃) δ 137.8, 137.3, 134.3, 132.6, 132.2, 129.2, 128.6, 127.5, 126.7, 126.6, 126.3, 15.8. This compound is known. 14 (CAS: 876953-11-6)

1-(tert-butyl)-4-((1E,3E)-4-phenylbuta-1,3-dien-1-yl) benzene (3za): The title compound was prepared according to the **General Experimental Procedure**, and purified by column chromatography on silica gel with PE to afford a white solid in 71% yield (75.0 mg). ¹H NMR (400 MHz, CDCl₃) δ 7.42 (d, J = 7.6 Hz, 2H), 7.39–7.30 (m, 6H), 7.23–7.20 (m, 1H), 6.99–6.88 (m, 2H), 6.69–6.61 (m, 2H), 1.32 (s, 9H). ¹³C NMR (100 MHz, CDCl₃) δ 150.8, 137.5, 134.6, 132.7, 132.3, 129.5, 128.6, 128.5, 127.4, 126.3, 126.1, 125.6, 34.6, 31.3. This compound is known.⁴ (CAS: 173385-11-0)

4-((1E,3E)-4-phenylbuta-1,3-dien-1-yl)-1,1'-biphenyl (3zb): The title compound was prepared according to the **General Experimental Procedure**, and purified by column chromatography on silica gel with PE/EA =10:1 to afford a white solid in 81% yield (92.0 mg). 1 H NMR (400 MHz, CDCl₃) δ 7.60 (dd, J = 12.0, 8.0 Hz, 4H), 7.52 (d, J = 8.0 Hz, 2H), 7.44 (t, J = 7.2 Hz, 4H), 7.36–7.22 (m, 4H), 7.04–6.95 (m, 2H), 6.73–6.68 (m, 2H). 13 C NMR (100 MHz, CDCl₃) δ 140.6, 140.2, 137.3, 136.4, 132.9, 132.3, 129.32, 129.25, 128.8, 128.7, 127.6, 127.3,

126.9, 126.8, 126.4. This compound is known.⁴ (CAS: 256339-33-0)

1-((1E,3E)-4-phenylbuta-1,3-dien-1-yl)naphthalene (3zc): The title compound was prepared according to the **General Experimental Procedure**, and purified by column chromatography on silica gel with PE to afford a white solid in 71% yield (72.4 mg). ¹H NMR (400 MHz, CDCl₃) δ 8.19 (d, J = 8.3 Hz, 1H), 7.86–7.84 (m, 1H), 7.76 (dd, J = 20.0, 8.0 Hz, 2H), 7.55–7.43 (m, 6H), 7.35 (t, J = 8.0 Hz, 2H), 7.26–7.23 (m, 1H), 7.14–7.00 (m, 2H), 6.72 (d, J = 16.0 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 137.3, 134.6, 133.8, 133.1, 132.0, 131.1, 129.5, 129.4, 128.7, 128.6, 128.0, 127.6, 126.4, 126.1, 125.8, 125.6, 123.6, 123.2. This compound is known. ¹⁵ (CAS: 34662-93-6)

1-fluoro-4-((1E,3E)-4-phenylbuta-1,3-dien-1-yl)benzene (3zd): The title compound was prepared according to the **General Experimental Procedure**, and purified by column chromatography on silica gel with PE/EA =10:1 to afford a white solid in 63% yield (56.4 mg). 1 H NMR (400 MHz, CDCl₃) δ 7.44–7.38 (m, 4H), 7.33 (t, J = 8.0 Hz, 2H), 7.22 (d, J = 8.0 Hz, 1H), 7.02 (t, J = 8.0 Hz, 2H), 6.97–6.83 (m, 2H), 6.64 (t, J = 16.0 Hz, 2H). 13 C NMR (100 MHz, CDCl₃) δ 162.3 (d, J = 245.9 Hz), 137.3, 133.5 (d, J = 3.2 Hz), 132.9, 131.5, 129.0, 128.7, 127.9, 127.8, 127.6, 126.4, 115.6, (d, J = 21.6 Hz). 19 F NMR (376 MHz, CDCl₃) δ -114.24. This compound is known. 4 (CAS: 857722-07-7)

1-chloro-4-((1E,3E)-4-phenylbuta-1,3-dien-1-yl)benzene (3ze): The title compound was prepared according to the **General Experimental Procedure**, and purified by column chromatography on silica gel with PE/EA = 10:1 to afford a white solid in 69% yield (66.1 mg). ¹H NMR (400 MHz, CDCl₃) δ 7.42 (d, J = 7.4 Hz, 2H), 7.35–7.21 (m, 7H), 6.96–6.84 (m, 2H), 6.71–6.53 (m, 2H). ¹³C NMR (100 MHz, CDCl₃) δ 137.1, 135.8, 133.4, 133.0, 131.3, 129.8, 128.9,

128.8, 128.7, 127.7 127.5, 126.4. This compound is known. 16 (CAS: 37985-13-0)

1-bromo-4-((1E,3E)-4-phenylbuta-1,3-dien-1-yl)benzene (3zf): The title compound was prepared according to the **General Experimental Procedure**, and purified by column chromatography on silica gel with PE/EA =10:1 to afford a white solid in 79% yield (90.2 mg). ¹H NMR (400 MHz, CDCl₃) δ 7.45–7.43 (m, 4H), 7.35–7.22 (m, 5H), 6.96–6.88 (m, 2H), 6.71–6.54 (m, 2H). ¹³C NMR (100 MHz, CDCl₃) δ 137.2, 136.3, 133.5, 131.7, 131.4, 129.9, 128.9, 128,7, 127.8, 127.7, 126.4, 121.3. This compound is known. ¹⁷ (CAS: 58922-30-8)

1-iodo-4-((1E,3E)-4-phenylbuta-1,3-dien-1-yl)benzene (3zg): The title compound was prepared according to the **General Experimental Procedure**, and purified by column chromatography on silica gel with PE to afford a white solid in 70% yield (93.0 mg). ¹H NMR (400 MHz, CDCl₃) δ 7.63 (d, J = 8.4 Hz, 2H), 7.42 (d, J = 7.4 Hz, 2H), 7.32 (t, J = 8.0 Hz, 2H), 7.25–7.22 (m, 1H), 7.15 (d, J = 8.4 Hz, 2H), 6.97–6.88 (m, 2H), 6.71–6.64 (m, 1H), 6.60–6.53 (m, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 137.7, 137.1, 136.8, 133.6, 131.5, 130.0, 128.8, 128.7, 128.0, 127.7, 126.4, 92.6. This compound is known. (CAS: 866784-57-8)

8-((1E,3E)-4-phenylbuta-1,3-dien-1-yl)quinoline (3zh): The title compound was prepared according to the **General Experimental Procedure**, and purified by column chromatography on silica gel with PE/EA =50:1 to afford a white solid in 63% yield (65.2 mg). Mp:139.6-141 °C, ¹H NMR (400 MHz, CDCl₃) δ 8.97–8.96 (m, 1H), 8.13 (dd, J = 8.0, 4.0 Hz, 1H), 8.04–7.98 (m, 2H), 7.71 (d, J = 8.0 Hz, 1H), 7.53 (t, J = 8.0 Hz, 1H), 7.48–7.40 (m, 3H), 7.34 (t, J = 8.0 Hz, 2H), 7.21–7.16 (m, 3H), 6.78–6.70 (m, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 149.5, 145.7, 137.5, 136.3, 135.8, 133.0, 131.2, 130.1, 128.7, 128.6, 128.5, 127.5, 127.2, 126.4, 125.1, 121.2. HRMS-ESI (m/z) [M+H]+ Calcd for C₁₉H₁₆N +, 258.1283, Found 258.1282.

(E)-buta-1,3-diene-1,1,4-triyltribenzene (3zi): The title compound was prepared according to the General Experimental Procedure, and purified by column chromatography on silica gel with PE to afford a white solid in 72% yield (81.4 mg). ¹H NMR (400 MHz, CDCl₃) δ 7.44–7.35 (m, 3H), 7.31–7.15 (m, 12H), 6.93–6.86 (m, 2H), 6.77–6.69 (m, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 143.1, 142.3, 139.8, 137.5, 133.9, 130.6, 128.6, 128.24, 128.22, 127.6, 127.5, 127.4, 127.1, 126.4. This compound is known. ¹⁸ (CAS: 20235-61-4)

(E)-1,3-dimethoxy-5-(4-methoxystyryl)benzene (3zm): The title compound was prepared according to the General Experimental Procedure (one set), and purified by column chromatography on silica gel with PE/EA = 10:1 to afford a white solid in 75% yield (40.5 mg). 1 H NMR (400 MHz, CDCl₃) δ 7.44 (d, J = 8.2 Hz, 2H), 7.04 (d, J = 16.4 Hz, 1H), 6.92–6.88 (m, 3H), 6.65 (d, J = 3.6 Hz, 2H), 6.37 (t, J = 2.0 Hz, 1H), 3.82 (s, 9H). 13 C NMR (100 MHz, CDCl₃) δ 160.9, 159.4, 139.7, 129.9, 128.7, 127.8, 126.5, 114.1, 104.3, 99.6, 55.33, 55.27. This compound is known.4 (CAS: 22255-22-7)

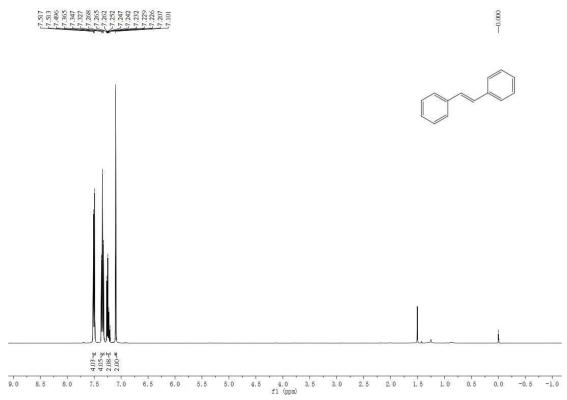
(E)-1,2,3-trimethoxy-5-(4-methoxystyryl) benzene (3zn): The title compound was prepared according to the General Experimental Procedure , and purified by column chromatography on silica gel with PE/EA = 10:1 to afford a white solid in 62% yield (74.4 mg). ¹H NMR (400 MHz, CDCl₃) δ 7.44 (d, J = 8.8 Hz, 2H), 6.99–6.87 (m, 4H), 6.71 (s, 2H), 3.91 (s, 6H), 3.86 (s, 3H), 3.82 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 159.2, 153.3, 137.6, 133.4, 129.9, 127.7, 127.6, 126.5, 114.1, 103.3, 60.9, 56.0, 55.2. This compound is known.⁴ (CAS: 134029-62-2)

4.References

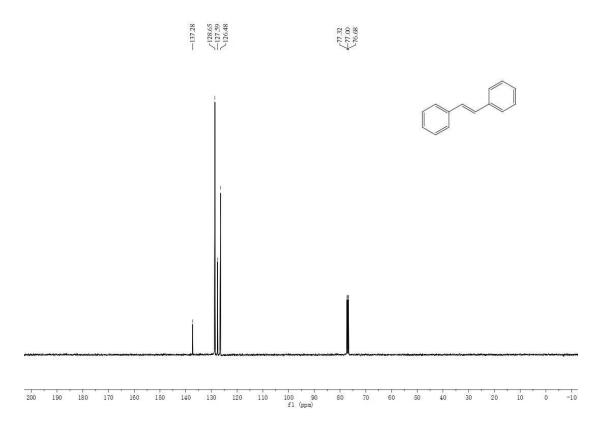
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5. Copies of $^{1}\mathrm{H}$, $^{13}\mathrm{C}$ and $^{19}\mathrm{F}$ NMR Spectra of the Products

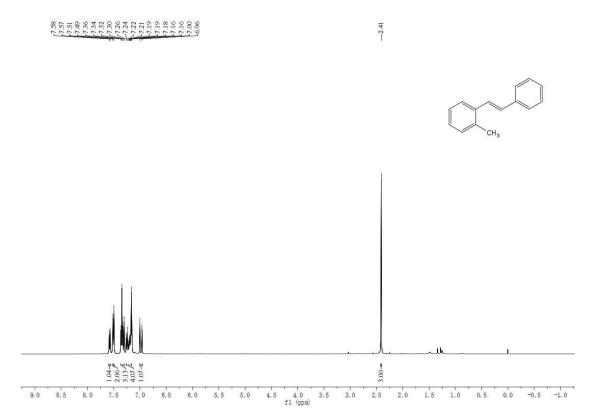
¹H NMR Spectrum of (E)-1,2-diphenylethene (3a)



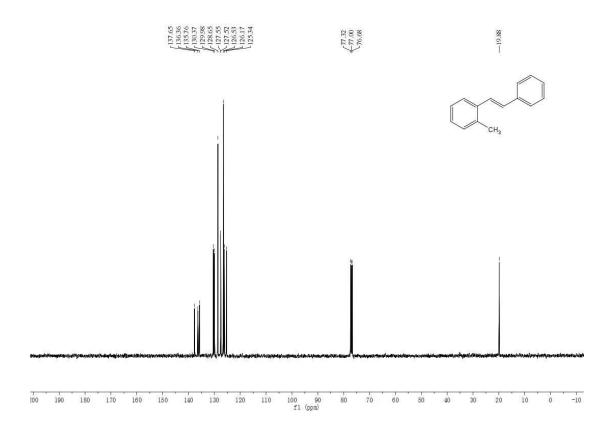
¹³C NMR Spectrum of (E)-1,2-diphenylethene (3a)



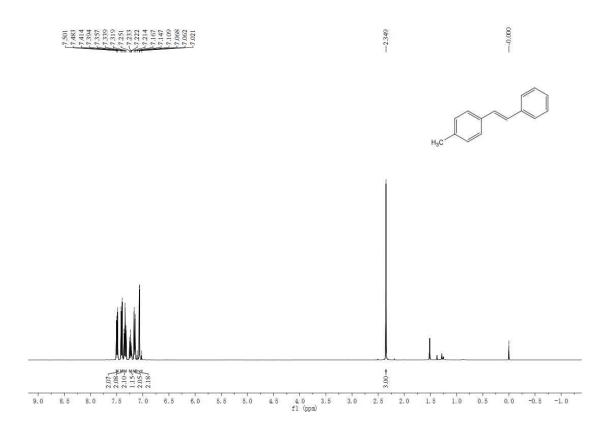
¹H NMR Spectrum of (E)-1-methyl-2-styrylbenzene (3b)



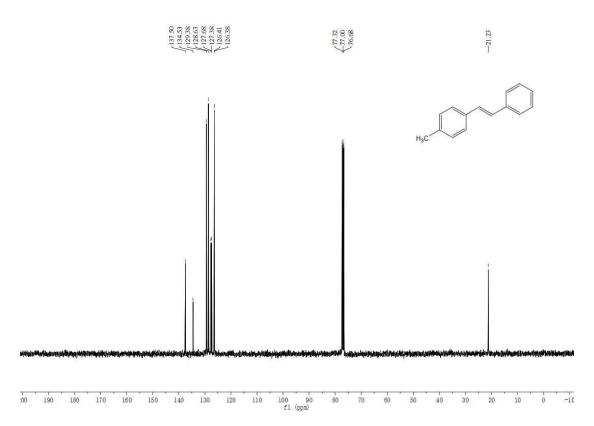
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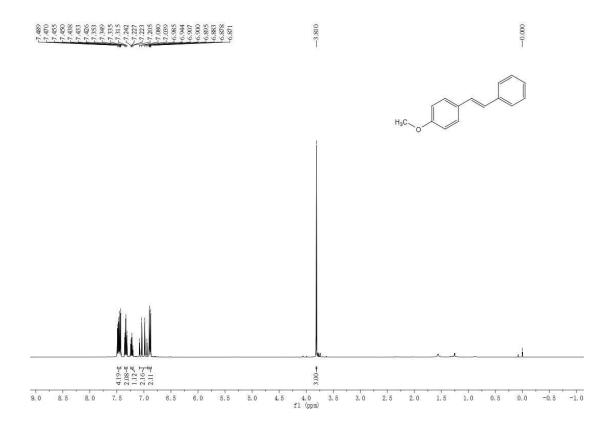
¹H NMR Spectrum of (E)-1-methyl-4-styrylbenzene (3c)



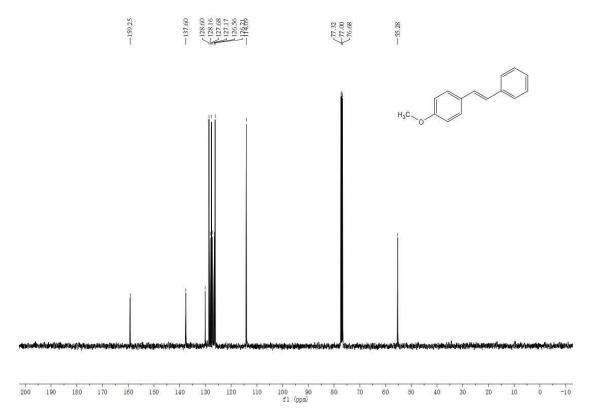
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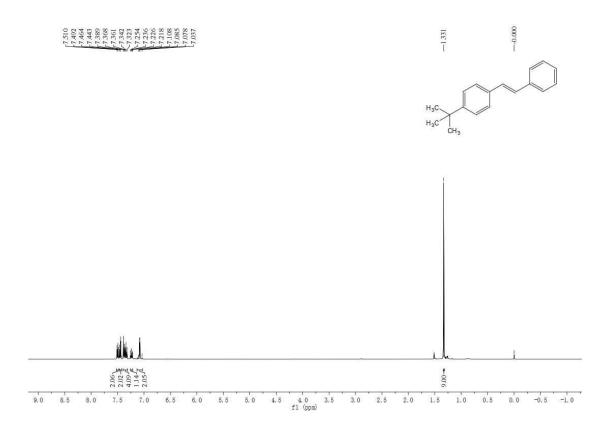
¹H NMR Spectrum of (E)-1-methoxy-4-styrylbenzene (3d)



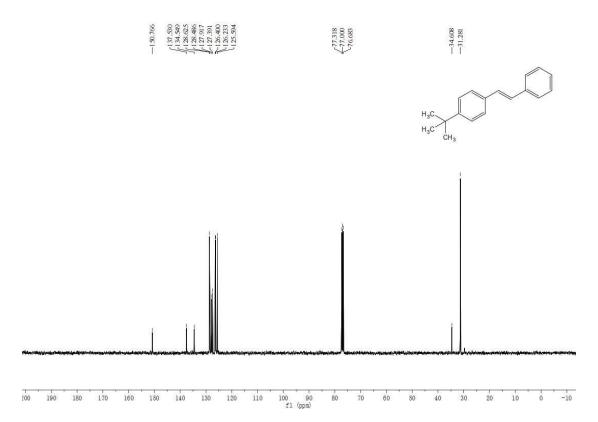
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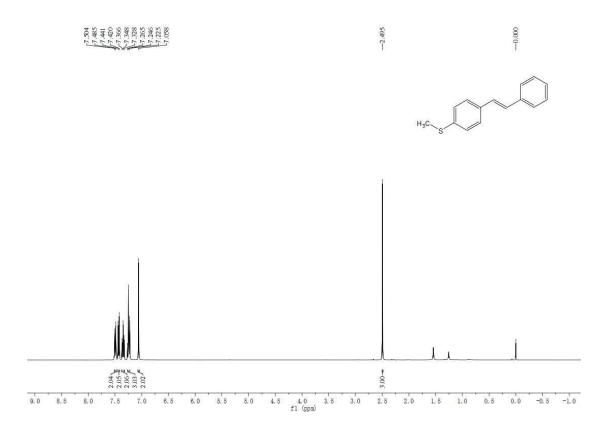
¹H NMR Spectrum of (E)-1-(tert-butyl)-4-styrylbenzene (**3e**)



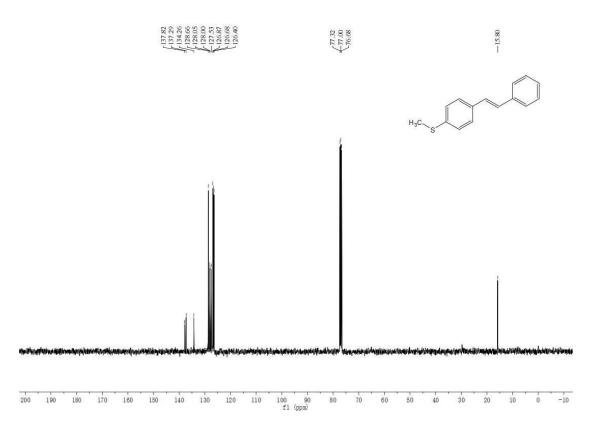
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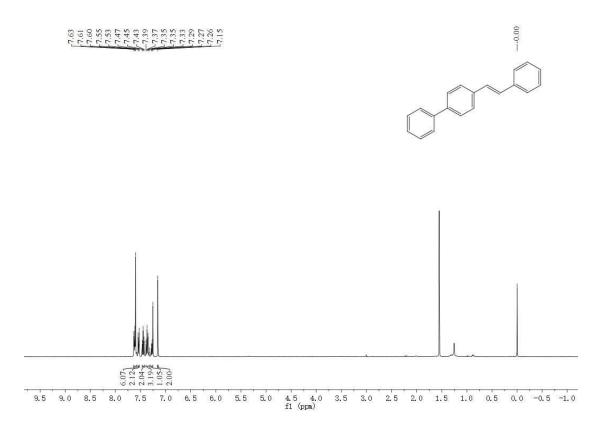
¹H NMR Spectrum of (E)-methyl(4-styrylphenyl)sulfane (3f)



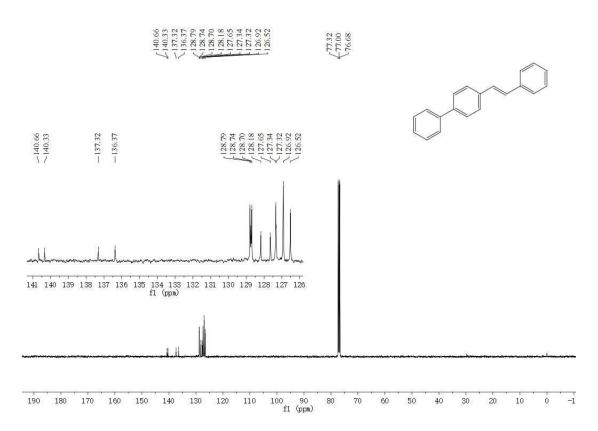
¹³C NMR Spectrum of (E)-methyl(4-styrylphenyl)sulfane (3f)



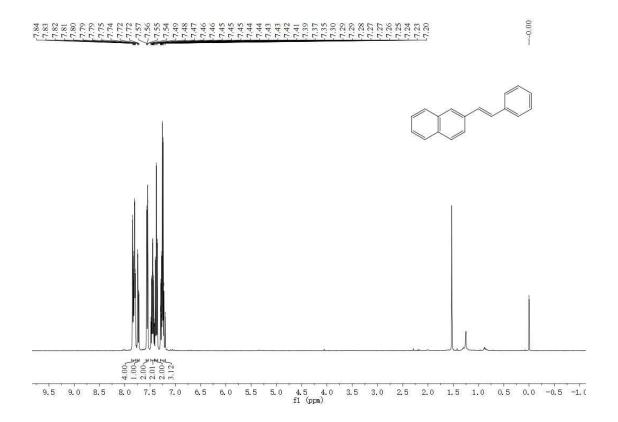
¹H NMR Spectrum of (E)-4-styryl-1,1'-biphenyl (**3g**)



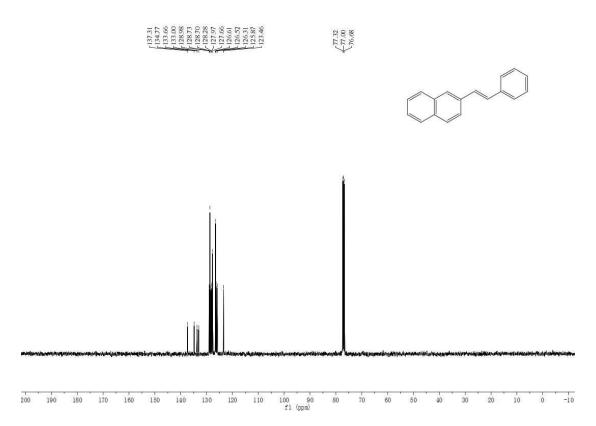
¹³C NMR Spectrum of (E)-4-styryl-1,1'-biphenyl (3g)



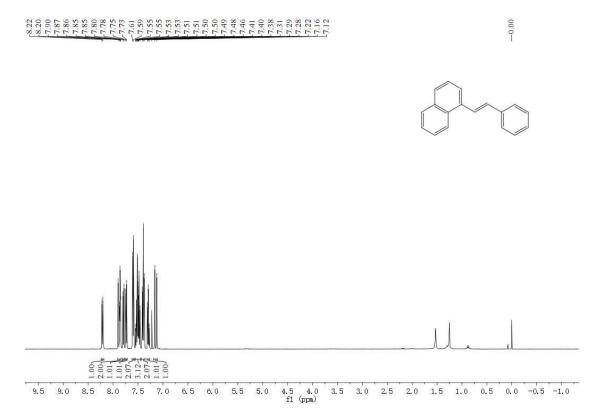
¹H NMR Spectrum of (E)-2-styrylnaphthalene (**3h**)



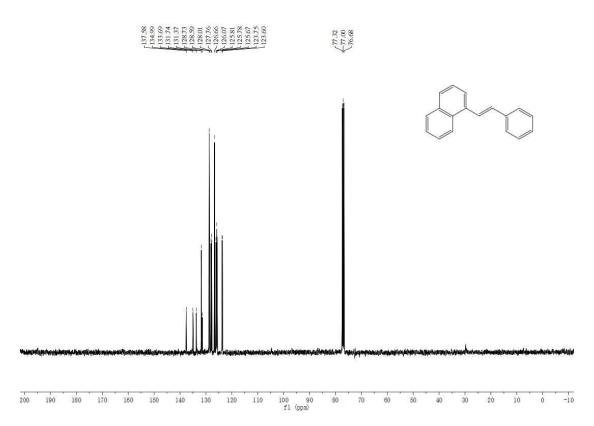
¹³C NMR Spectrum of (E)-2-styrylnaphthalene (3h)



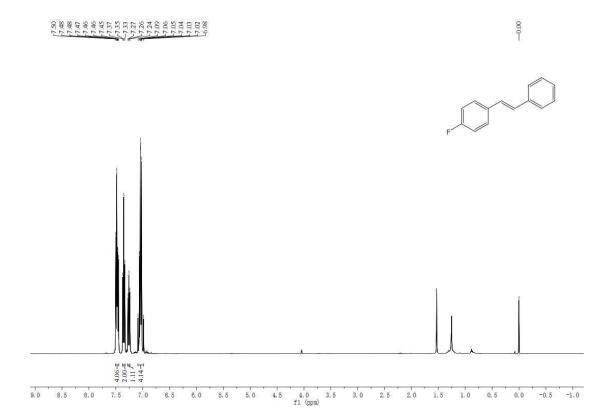
¹H NMR Spectrum of (E)-1-styrylnaphthalene (3i)



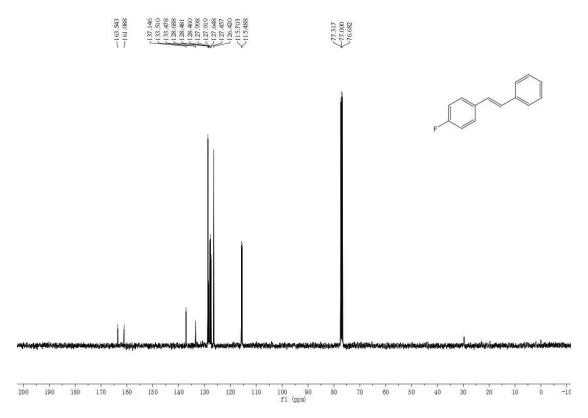
 $^{13}\mathrm{C}$ NMR Spectrum of (E)-1-styrylnaphthalene (3i)



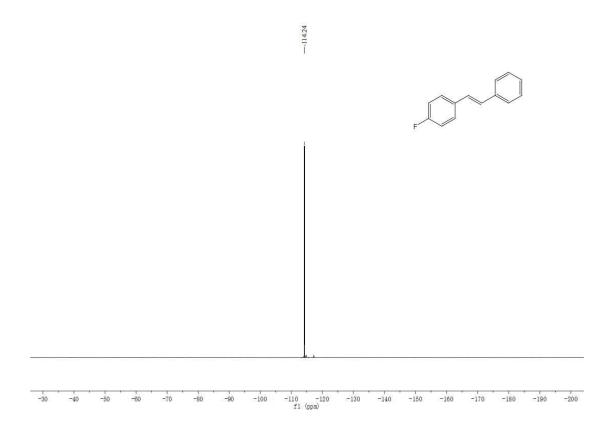
¹H NMR Spectrum of (E)-1-fluoro-4-styrylbenzene (3j)



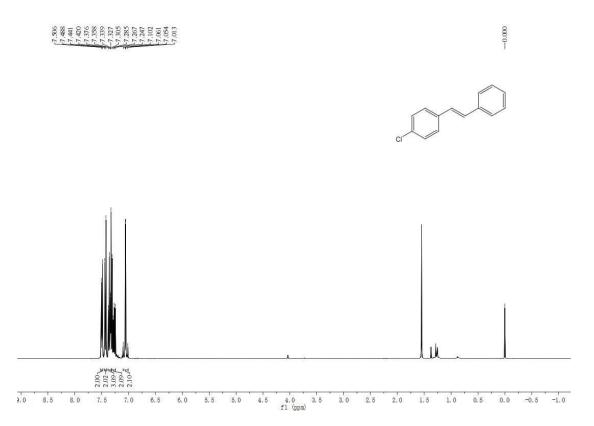
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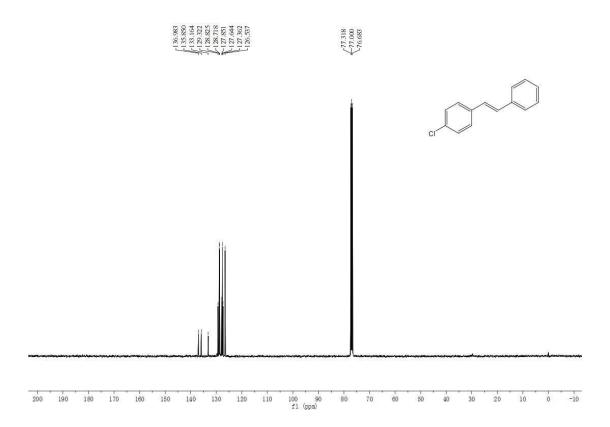
¹⁹F NMR Spectrum of (E)-1-fluoro-4-styrylbenzene (3j)



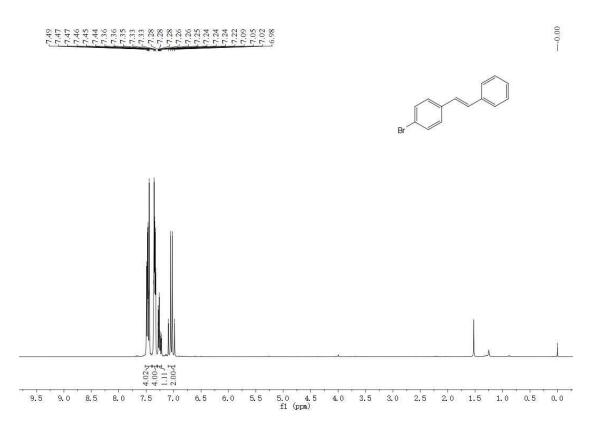
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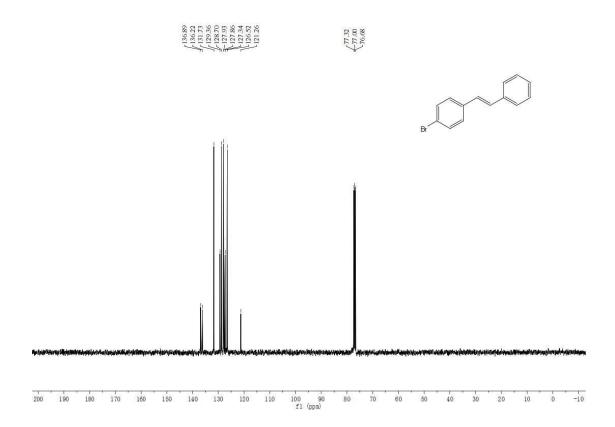
^{13}C NMR Spectrum of (E)-1-chloro-4-styrylbenzene (3k)



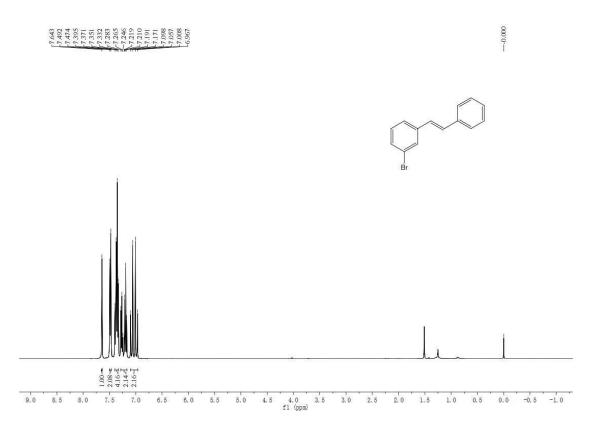
¹H NMR Spectrum of (E)-1-bromo-4-styrylbenzene (3l)



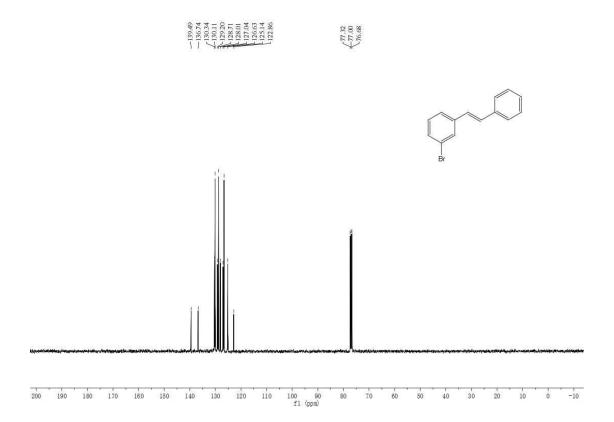
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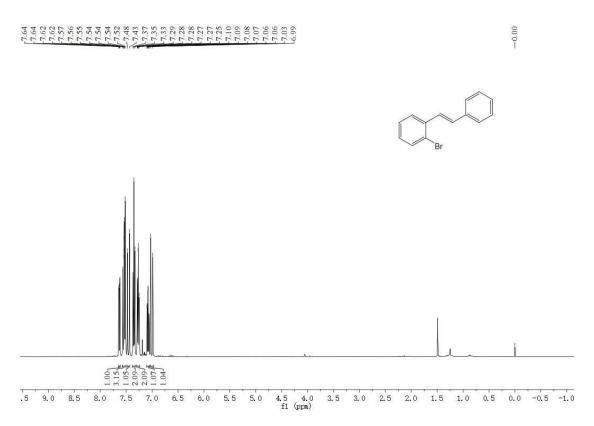
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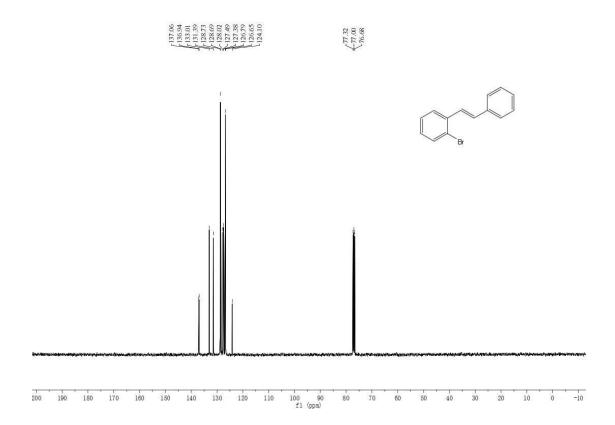
¹³C NMR Spectrum of (E)-1-bromo-3-styrylbenzene (3m)



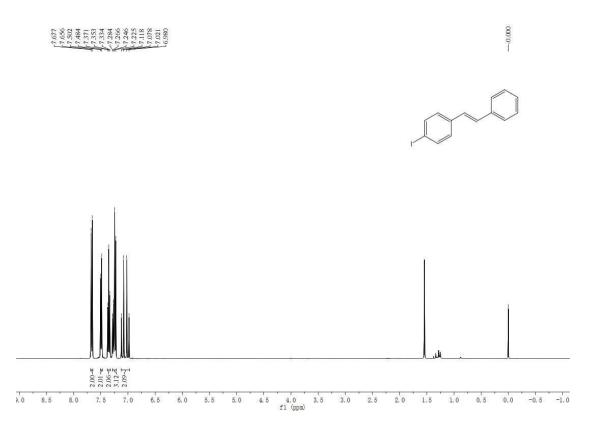
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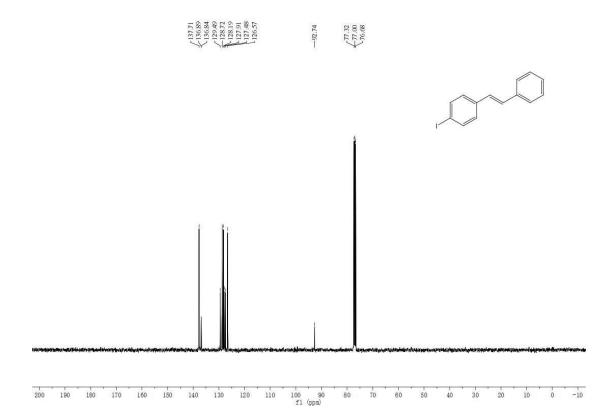
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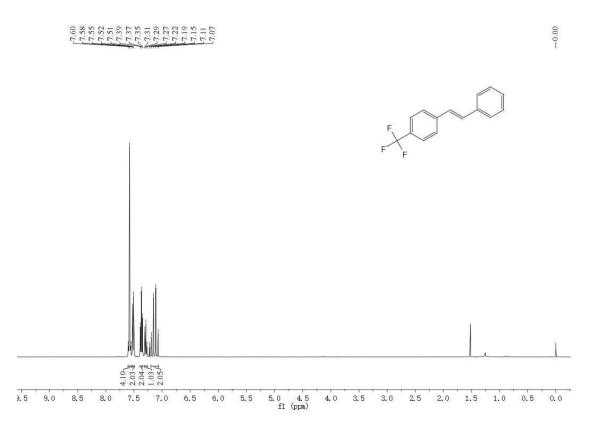
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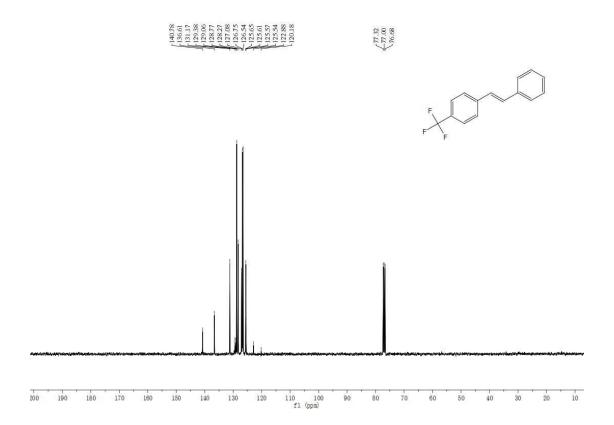
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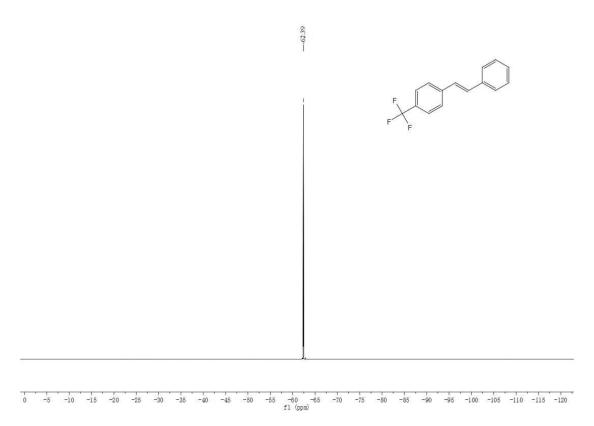
¹H NMR Spectrum of (E)-1-styryl-4-(trifluoromethyl)benzene (3p)



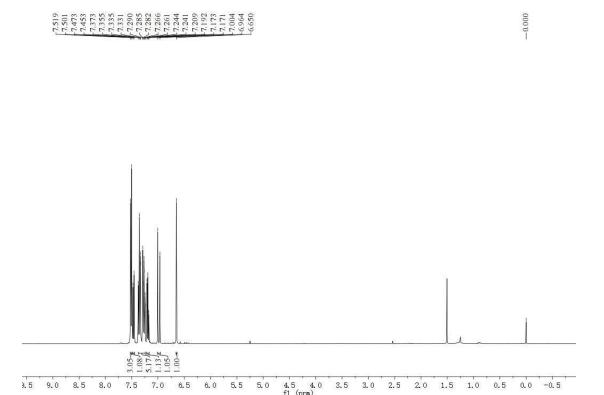
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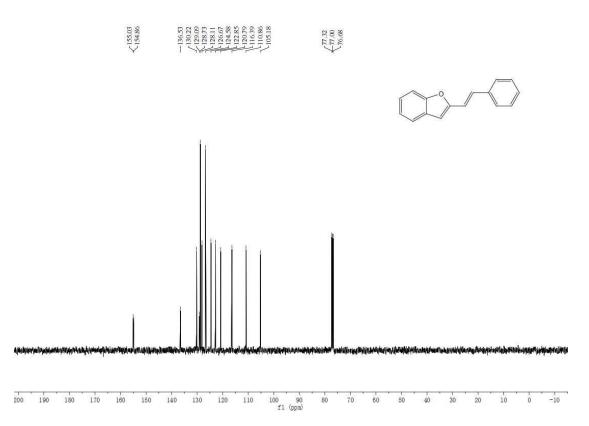
¹⁹F NMR Spectrum of (E)-1-styryl-4-(trifluoromethyl)benzene (3p)



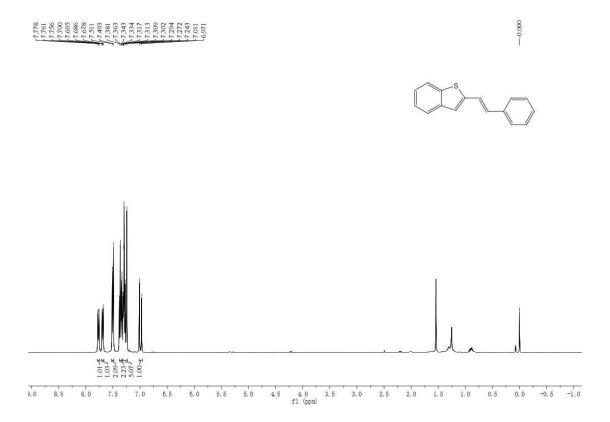
¹H NMR Spectrum of (E)-2-styrylbenzofuran **(3q)**



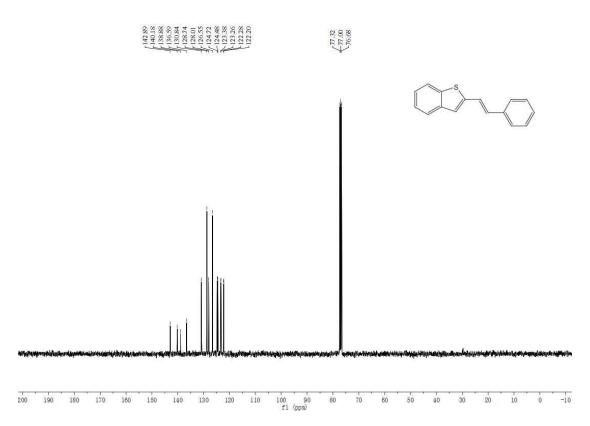
¹³C NMR Spectrum of (E)-2-styrylbenzofuran **(3q)**



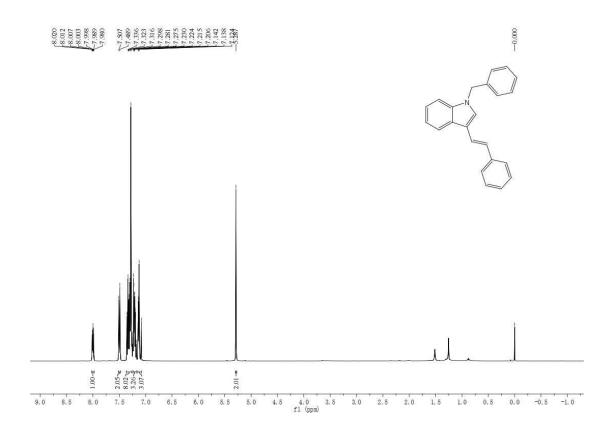
¹H NMR Spectrum of (E)-2-styrylbenzo[b]thiophene (**3r**)



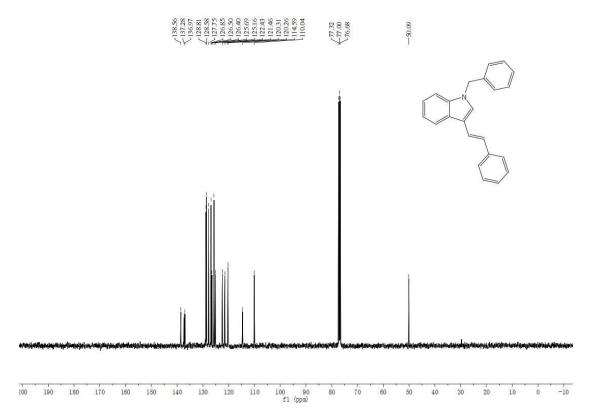
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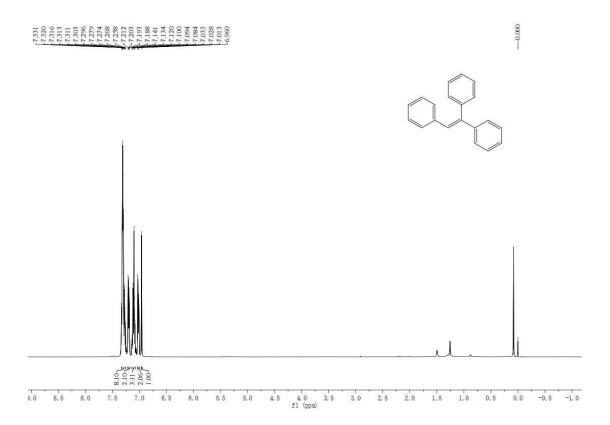
¹H NMR Spectrum of (E)-1-benzyl-3-styryl-1H-indole (3s)



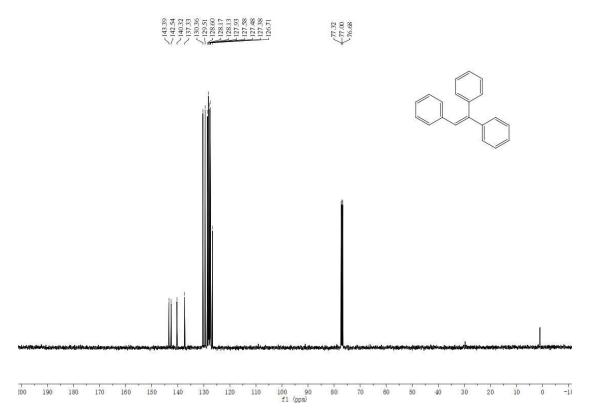
¹³C NMR Spectrum of (E)-1-benzyl-3-styryl-1H-indole (3s)



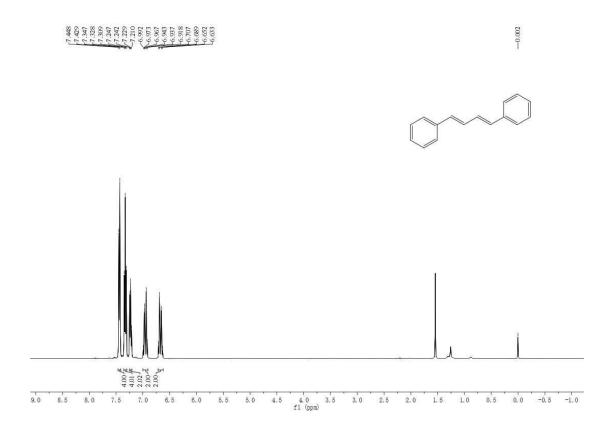
¹H NMR Spectrum of ethene-1,1,2-triyltribenzene (3t)



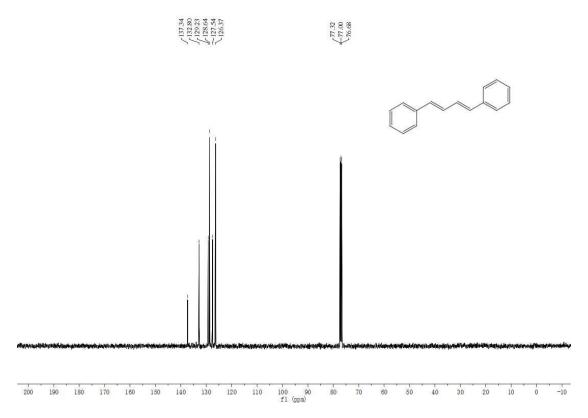
¹³C NMR Spectrum of ethene-1,1,2-triyltribenzene (3t)



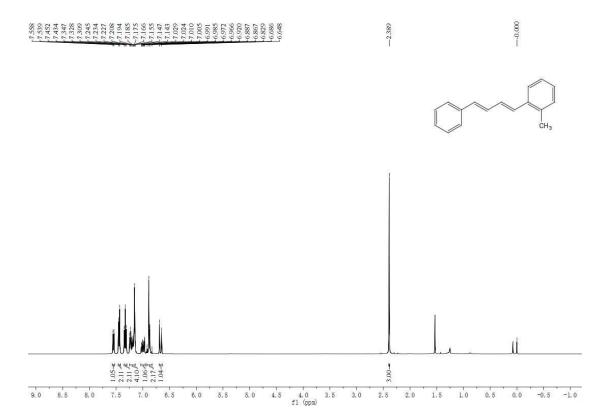
¹H NMR Spectrum of (1E,3E)-1,4-diphenylbuta-1,3-diene (3u)



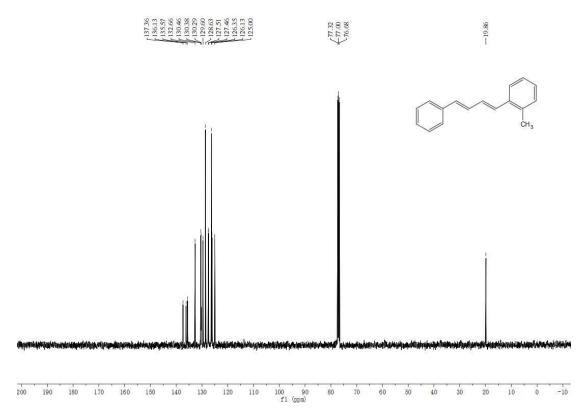
 $^{13}\mathrm{C}$ NMR Spectrum of (1E,3E)-1,4-diphenylbuta-1,3-diene (3u)



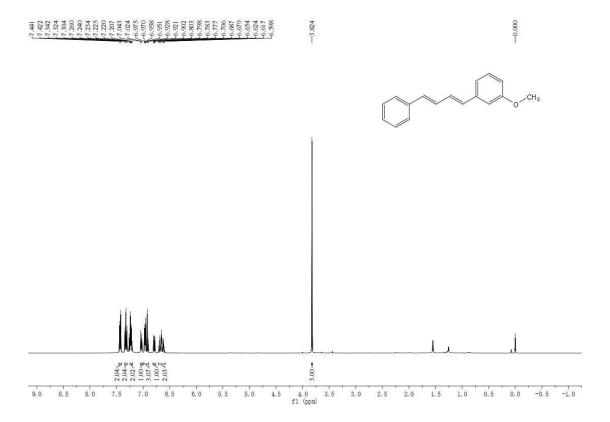
¹H NMR Spectrum of 1-methyl-2-((1E,3E)-4-phenylbuta-1,3-dien-1-yl)benzene (3v)



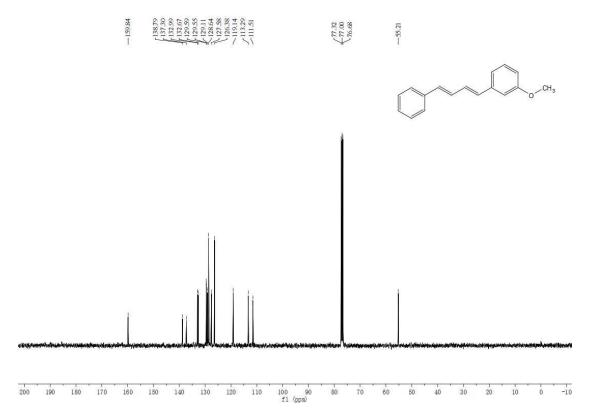
¹³C NMR Spectrum of 1-methyl-2-((1E,3E)-4-phenylbuta-1,3-dien-1-yl)benzene (3v)



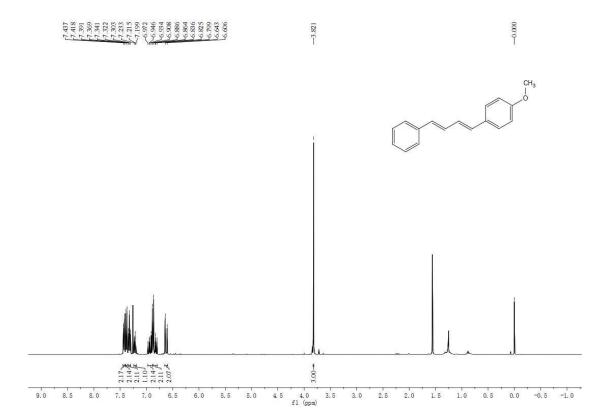
¹H NMR Spectrum of 1-methoxy-2-((1E,3E)-4-phenylbuta-1,3-dien-1-yl)benzene (3w)



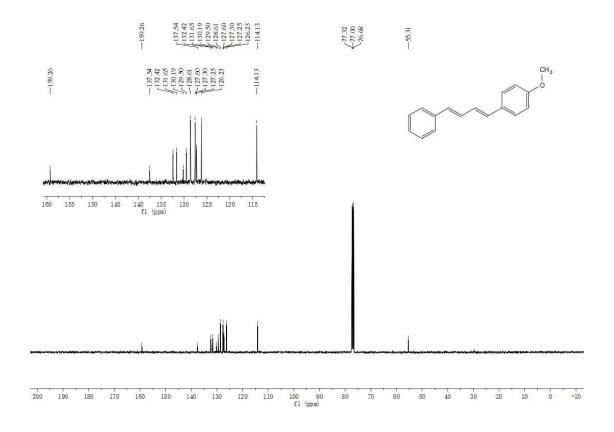
¹³C NMR Spectrum of 1-methoxy-2-((1E,3E)-4-phenylbuta-1,3-dien-1-yl)benzene (3w)



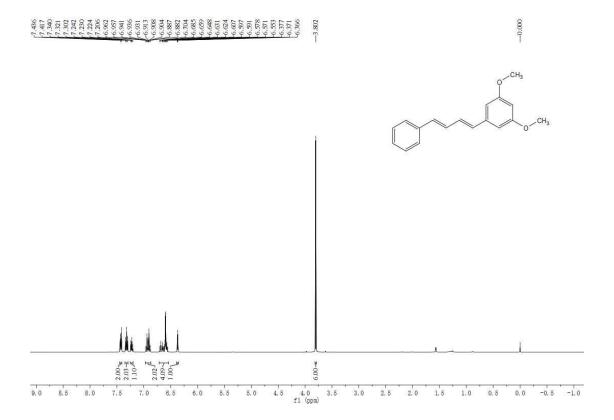
¹H NMR Spectrum of 1-methoxy-4-((1E,3E)-4-phenylbuta-1,3-dien-1-yl)benzene (3x)



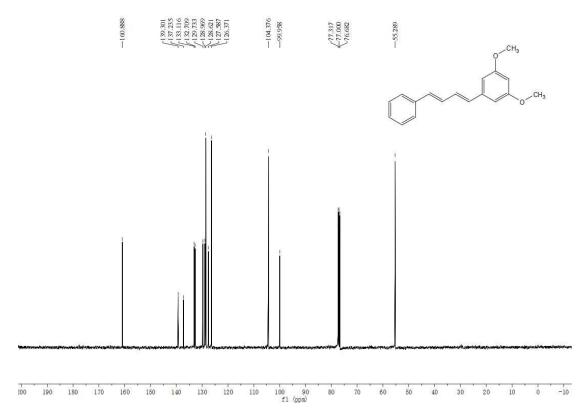
¹³C NMR Spectrum of1-methoxy-4-((1E,3E)-4-phenylbuta-1,3-dien-1-yl)benzene (3x)



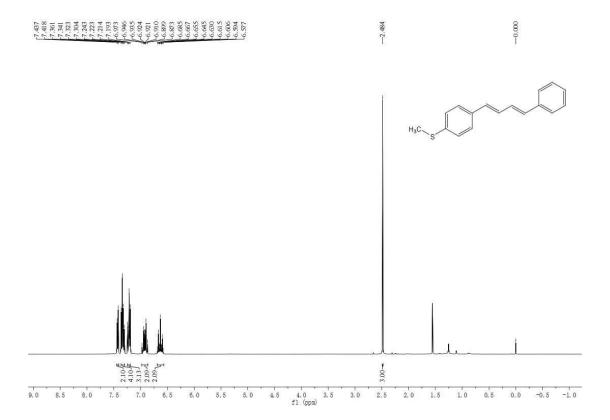
¹H NMR Spectrum of 1,3-dimethoxy-5-((1E,3E)-4-phenylbuta-1,3-dien-1-yl)benzene (3y)



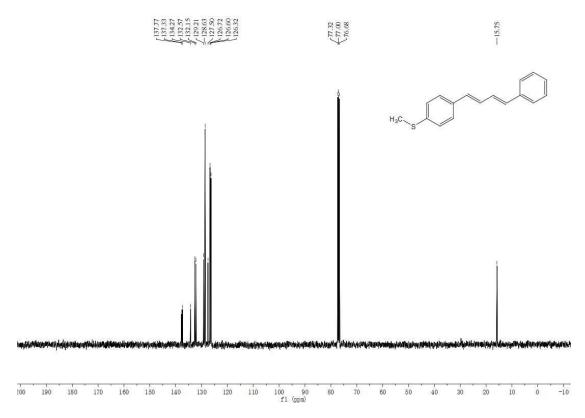
¹³C NMR Spectrum of 1,3-dimethoxy-5-((1E,3E)-4-phenylbuta-1,3-dien-1-yl)benzene (3y)



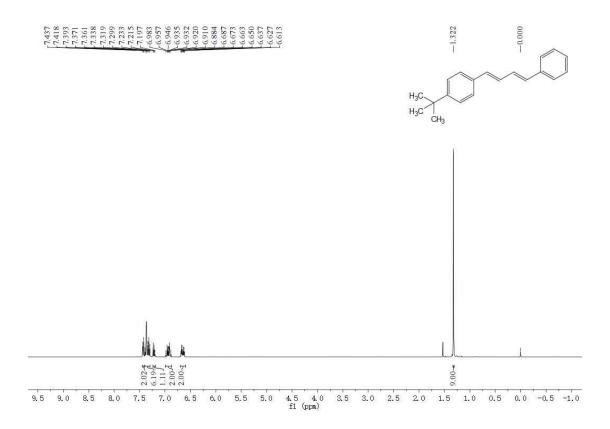
¹H NMR Spectrum of methyl(4-((1E,3E)-4-phenylbuta-1,3-dien-1-yl)phenyl)sulfane (3z)



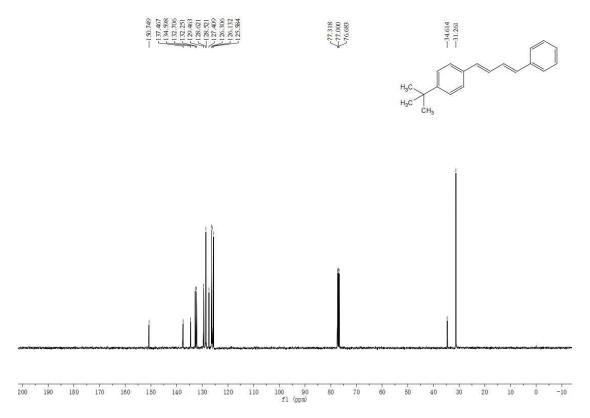
¹³C NMR Spectrum of methyl(4-((1E,3E)-4-phenylbuta-1,3-dien-1-yl)phenyl)sulfane (3z)



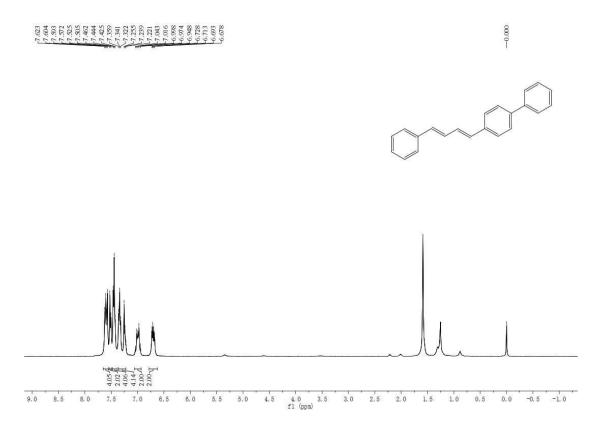
¹H NMR Spectrum of 1-(tert-butyl)-4-((1E,3E)-4-phenylbuta-1,3-dien-1-yl) benzene (3za)



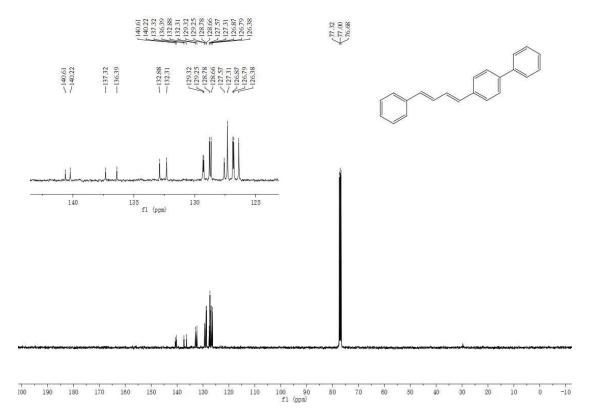
¹³C NMR Spectrum of 1-(tert-butyl)-4-((1E,3E)-4-phenylbuta-1,3-dien-1-yl) benzene (3za)



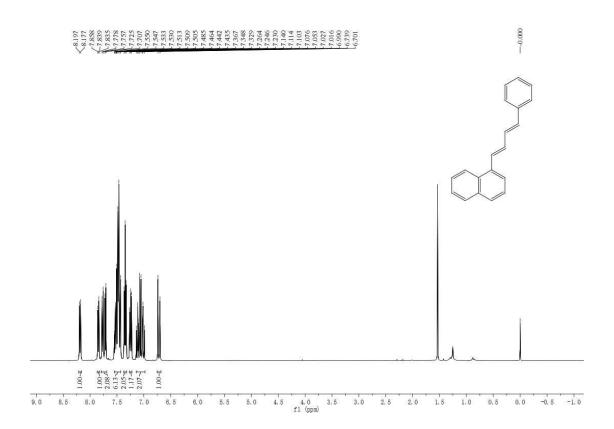
¹H NMR Spectrum of 4-((1E,3E)-4-phenylbuta-1,3-dien-1-yl)-1,1'-biphenyl (3zb)



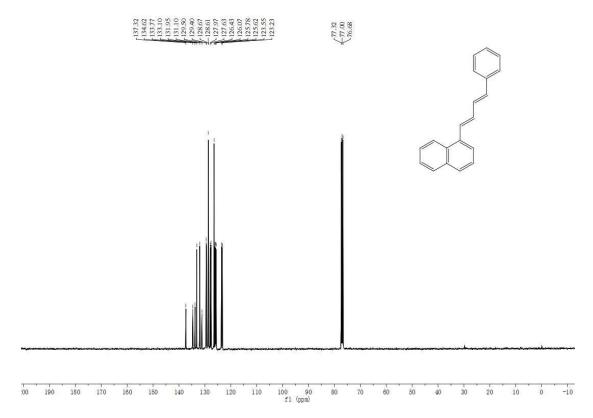
¹³C NMR Spectrum of 4-((1E,3E)-4-phenylbuta-1,3-dien-1-yl)-1,1'-biphenyl (3zb)



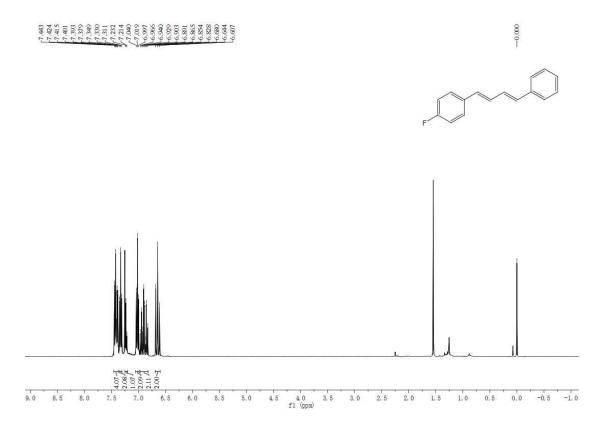
¹H NMR Spectrum of 1-((1E,3E)-4-phenylbuta-1,3-dien-1-yl)naphthalene (3zc)



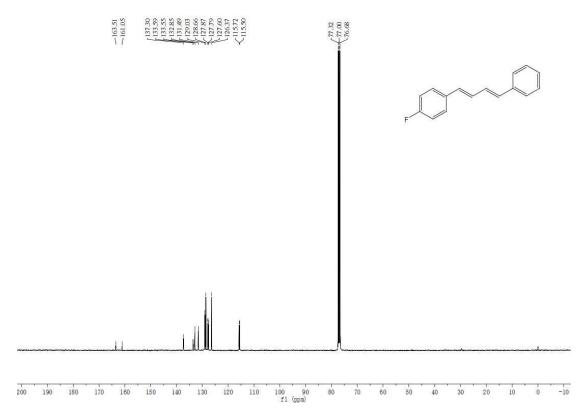
¹³C NMR Spectrum of 1-((1E,3E)-4-phenylbuta-1,3-dien-1-yl)naphthalene (3zc)



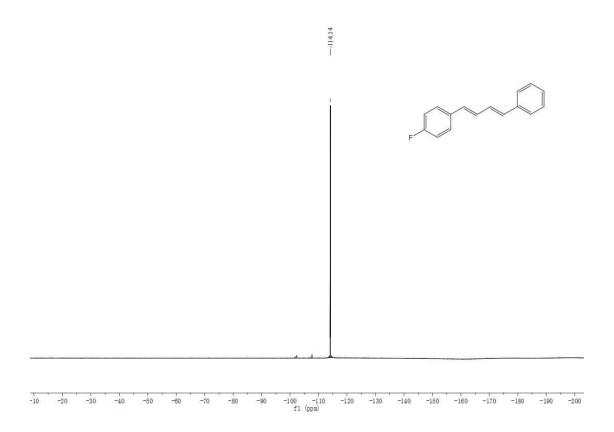
¹H NMR Spectrum of 1-fluoro-4-((1E,3E)-4-phenylbuta-1,3-dien-1-yl)benzene (3zd)



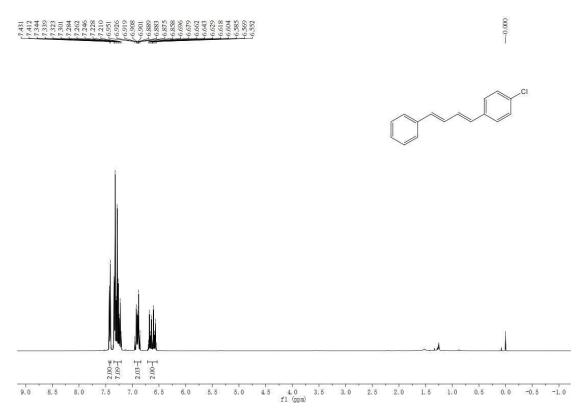
¹³C NMR Spectrum of 1-fluoro-4-((1E,3E)-4-phenylbuta-1,3-dien-1-yl)benzene (3zd)



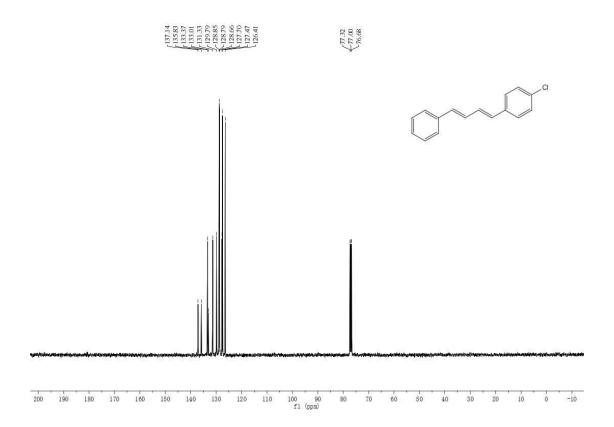
¹⁹F NMR Spectrum of 1-fluoro-4-((1E,3E)-4-phenylbuta-1,3-dien-1-yl)benzene (3zd)



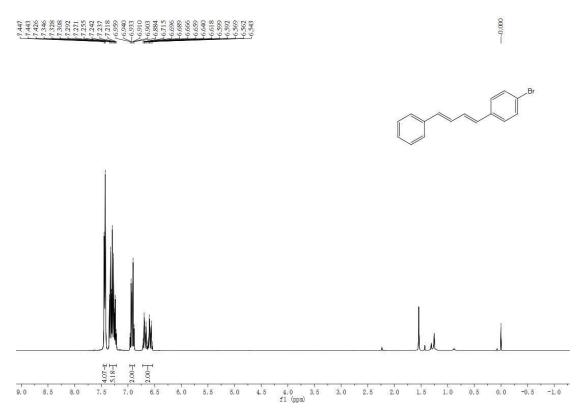
¹H NMR Spectrum of 1-chloro-4-((1E,3E)-4-phenylbuta-1,3-dien-1-yl)benzene (3ze)



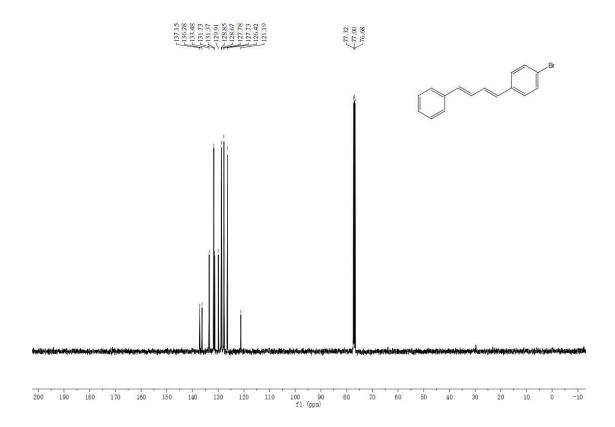
¹³C NMR Spectrum of 1-chloro-4-((1E,3E)-4-phenylbuta-1,3-dien-1-yl)benzene (3ze)



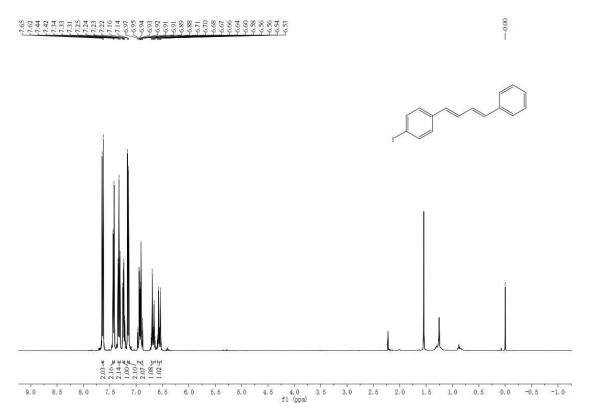
¹H NMR Spectrum of 1-bromo-4-((1E,3E)-4-phenylbuta-1,3-dien-1-yl)benzene (3zf)



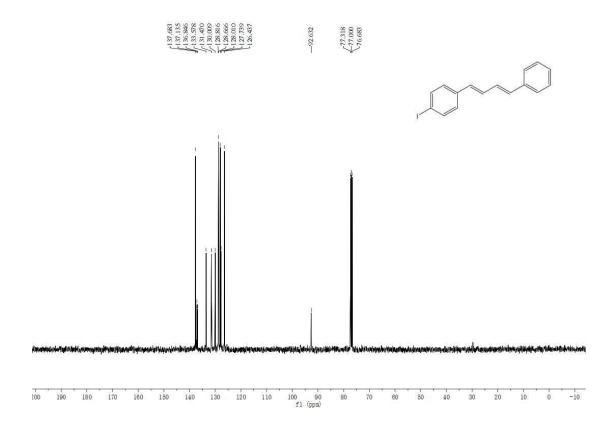
¹³C NMR Spectrum of 1-bromo-4-((1E,3E)-4-phenylbuta-1,3-dien-1-yl)benzene (3zf)



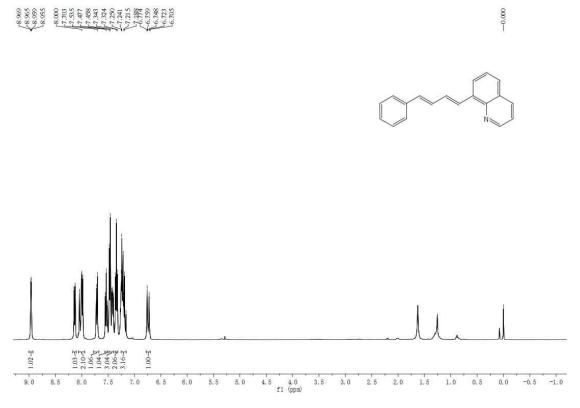
¹H NMR Spectrum of 1-iodo-4-((1E,3E)-4-phenylbuta-1,3-dien-1-yl)benzene (3zg)



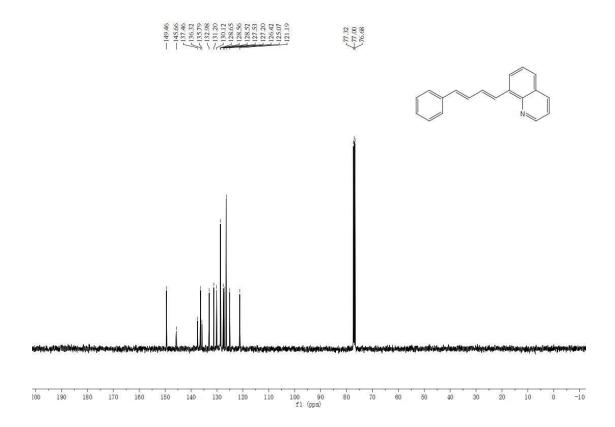
¹³C NMR Spectrum of 1-iodo-4-((1E,3E)-4-phenylbuta-1,3-dien-1-yl)benzene (3zg)



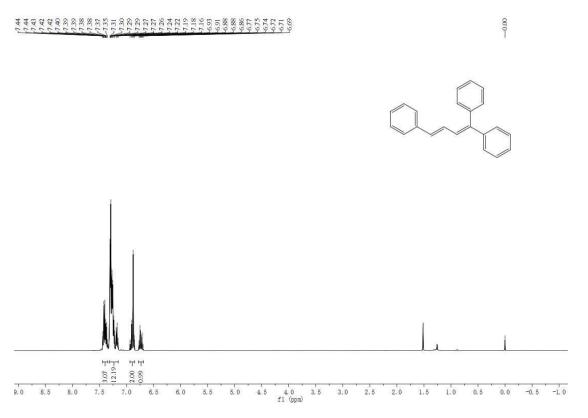
¹H NMR Spectrum of 8-((1E,3E)-4-phenylbuta-1,3-dien-1-yl)quinoline (3zh)



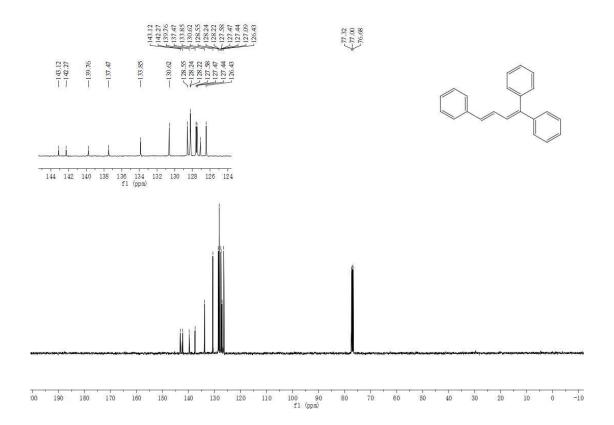
¹³C NMR Spectrum of 8-((1E,3E)-4-phenylbuta-1,3-dien-1-yl)quinoline (3zh)



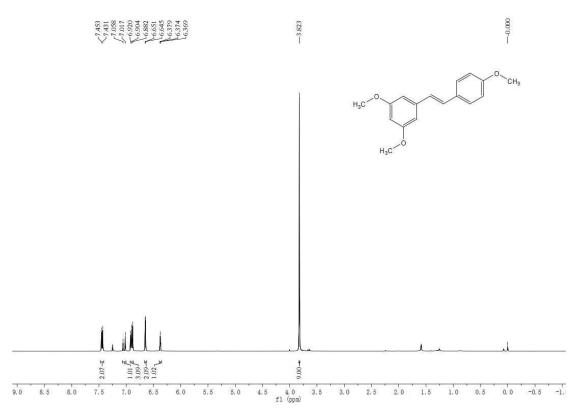
¹H NMR Spectrum of (E)-buta-1,3-diene-1,1,4-triyltribenzene (3zi)



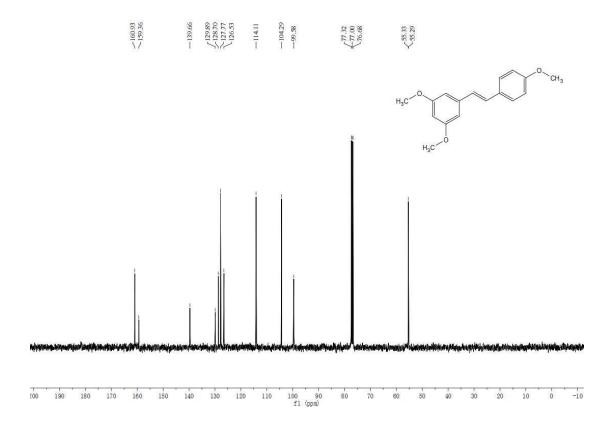
¹³C NMR Spectrum of (E)-buta-1,3-diene-1,1,4-triyltribenzene (3zi)



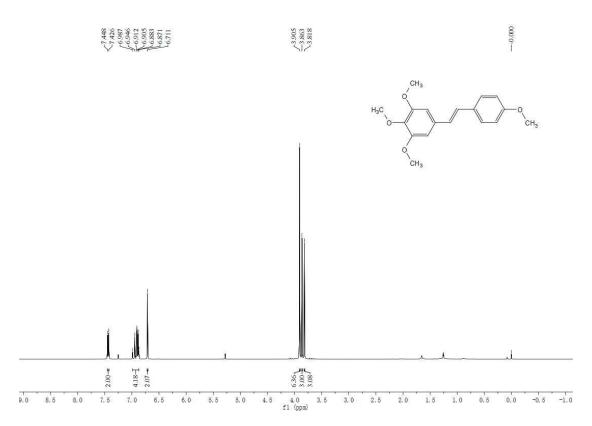
¹H NMR Spectrum of (E)-1,3-dimethoxy-5-(4-methoxystyryl)benzene (3zm)



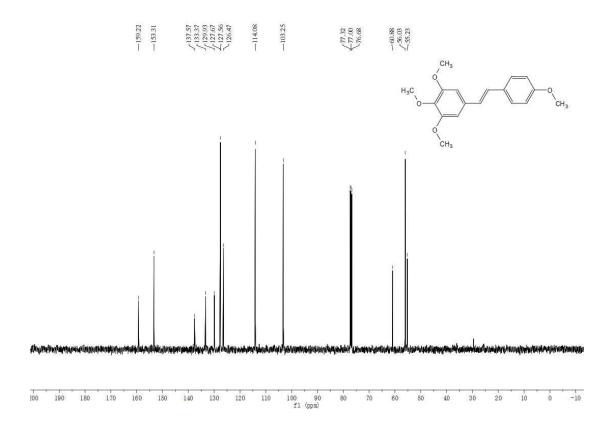
¹³C NMR Spectrum of (E)-1,3-dimethoxy-5-(4-methoxystyryl)benzene (3zm)



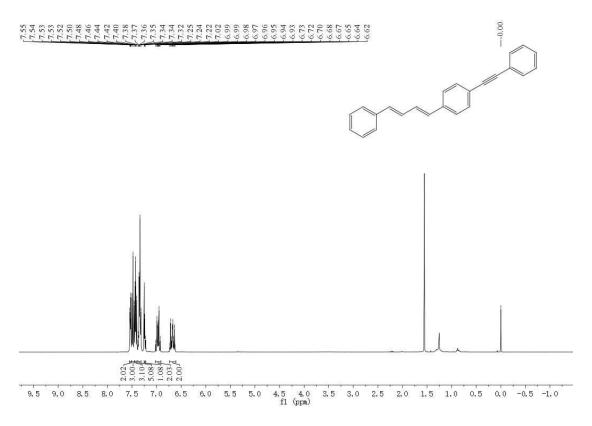
¹H NMR Spectrum of (E)-1,2,3-trimethoxy-5-(4-methoxystyryl) benzene (3zn)



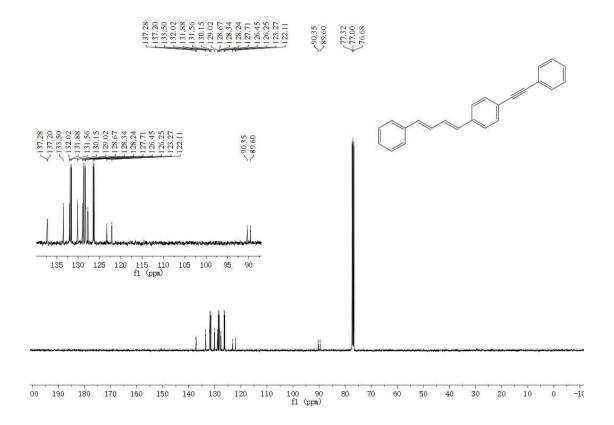
¹³C NMR Spectrum of (E)-1,2,3-trimethoxy-5-(4-methoxystyryl) benzene (3zn)



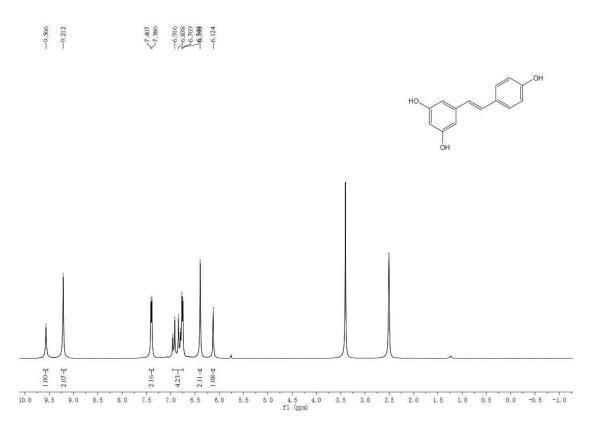
¹H NMR Spectrum of 1-((1E,3E)-4-phenylbuta-1,3-dien-1-yl)-4-(phenylethynyl)benzene (4)



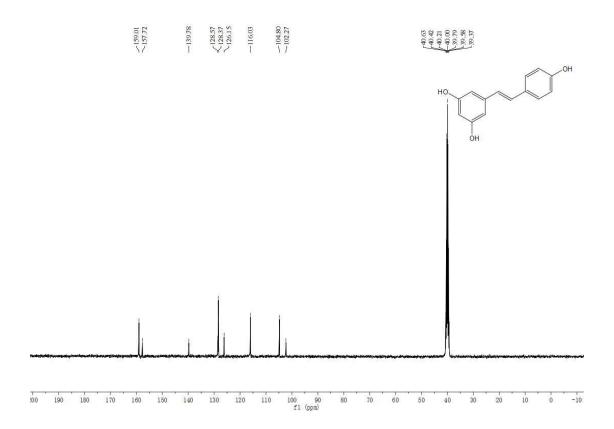
¹³C NMR Spectrum of 1-((1E,3E)-4-phenylbuta-1,3-dien-1-yl)-4-(phenylethynyl)benzene (4)



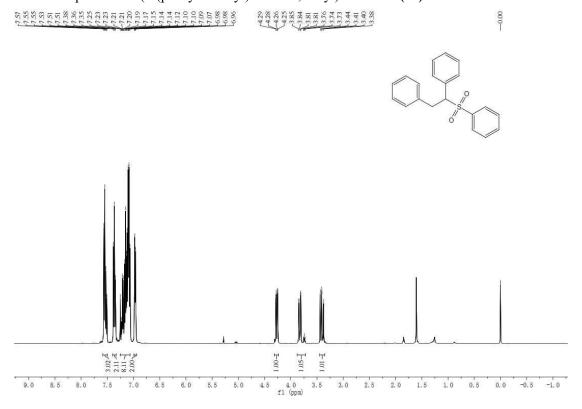
¹H NMR Spectrum of (E)-5-(4-hydroxystyryl)benzene-1,3-diol **(5)**



¹³C NMR Spectrum of (E)-5-(4-hydroxystyryl)benzene-1,3-diol (5)



¹H NMR Spectrum of (1-(phenylsulfonyl)ethane-1,2-diyl)dibenzene (6a)



$^{13}\mathrm{C}$ NMR Spectrum of (1-(phenylsulfonyl)ethane-1,2-diyl)dibenzene (6a)

