Iron-Promoted Synthesis of Substituted 1-Halo-1,4-pentadienes by Reaction of 1,3-Diarylpropenes with Ethynylbenzenes via Sp³ C-H Bond Activation

Hanjie Mo and Weiliang Bao*

Department of Chemistry, Zhejiang University (Xixi Campus), Hangzhou 310028, People’s Republic of China

wlbao@css.zju.edu.cn

Supporting Information
List of contents

Experiment procedures S2
Characterization data:

3a-j S2
4a-d S5
5a, 6a S6

1H NMR and 13C NMR spectra S6
NOE spectrum of 6a S17
Reference S17
1. Experiment procedures:

**General information:** NMR spectra were recorded on AM400 instruments in CDCl₃. Chemical shifts were calibrated using a solvent peak or tetramethylsilane as an internal reference. Coupling constants are reported in Hertz (Hz). MS was obtained using EI ionization. All chemicals were distilled or recrystallized before use, where necessary.

**General procedure for products 3:**
A sealed tube was charged with diarylpropenes (0.5mmol), ethynylbenzenes (0.6mmol), BQ (0.6mmol), FeCl₃ (0.5mmol) and DCE (1.5mL). The mixture was stirred at 80°C, overnight. The reaction mixture was washed by water, extracted with EtOAc. The combined organic layers were dried over anhydrous MgSO₄. Evaporation and column chromatography on silica gel (Pure petroleum ether), and the fraction with an Rf = 0.4 was collected to give the desired product.

A sealed tube was charged with 1a (0.5mmol), 2a (0.6mmol), BQ(0.6mmol), FeCl₃ (99.99%) (0.5mmol) and DCE (1.5mL). The mixture was stirred at 80 °C, overnight. The reaction mixture was washed by water, extracted with EtOAc. The combined organic layers were dried over anhydrous MgSO₄. Evaporation and column chromatography on silica gel (Pure petroleum ether), and the desired product was collected in 69% yield.

**General procedure for products 4:**
A sealed tube was charged with diarylpropenes² (0.5mmol), ethynylbenzenes (0.6mmol), BQ (0.6mmol), FeBr₃ (0.5mmol) and CHCl₃ (1.5mL). The mixture was stirred at 50°C, overnight. The reaction mixture was washed by water, extracted with EtOAc. The combined organic layers were dried over anhydrous MgSO₄. Evaporation and column chromatography on silica gel (Pure petroleum ether), and the fraction with an Rf = 0.4 was collected to give the desired product.

**General procedure for products 5:**
A sealed tube was charged with 4 (0.5mmol), ethynylbenzenes (0.6mmol), Et₃N (1mmol), Pd(PPh₃)₂Cl₂ (5mol%), Cul (5mol%) and THF (1.5mL). The mixture was stirred at 60°C, overnight. The resulting mixture was purified by flash column chromatography on silica gel (Petroleum ether/ ethyl acetate = 20/1), and the fraction with an Rf = 0.5 was collected to give the desired product.

**General procedure for products 6:**
Under an atmosphere of dry nitrogen, BuLi (1.5mL, 2M in hexane) was dropped into a solution of 4 (1 mmol) in 10 mL of dry THF at -78 °C. The progress of the reaction was monitored by TLC, and the mixture was stirred until the starting material disappeared. The reaction mixture was quenched with 15 mL of water and extracted with EtOAc (3 ×5 mL). The combined organic layers were dried over anhydrous MgSO₄. Evaporation and column chromatography on silica gel afforded 6.

2. Characterization Data:
3a: ((1E,4E)-1-chloropenta-1,4-diene-1,3,5-triyl)tribenzene

Light yellow oil. $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 7.45$-$7.21$ (m, 15H), 6.47 (d, $J = 16$ Hz, 1H), 6.35 (dd, $J = 6$, 16 Hz, 1H), 6.23 (d, $J = 10.4$ Hz, 1H), 4.34 (dd, $J = 6.4$, 10.4 Hz, 1H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 48.4$, 126.3, 126.8, 127.5, 127.6, 128.3, 128.5, 128.6, 128.8, 128.9, 130.3, 130.7, 131.2, 131.5, 136.91, 136.94, 142.2. IR (neat): 3059, 3026, 1597, 1492, 1445, 966, 906, 729, 694 cm$^{-1}$. MS (70 eV, EI) m/z = 330.

3b: ((1E,4E)-5-chloro-5-(4-chlorophenyl)penta-1,4-diene-1,3-diyl)dibenzene

Light yellow oil. $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 7.43$-$7.23$ (m, 14H), 6.49 (d, $J = 16$ Hz, 1H), 6.37 (dd, $J = 6$, 16 Hz, 1H), 6.29 (d, $J = 10.4$ Hz, 1H), 4.32 (dd, $J = 8$, 16 Hz, 1H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 48.3$, 126.1, 126.7, 127.3, 127.4, 128.3, 128.4, 128.6, 129.7, 130.1, 130.6, 130.7, 130.8, 134.6, 135.1, 136.6, 141.8. IR (neat): 3025, 2922, 1953, 1487, 1446, 1088, 970, 891, 747, 694 cm$^{-1}$. MS (70 eV, EI) m/z = 364.

3c: ((1E,4E)-5-chloro-5-p-tolylpenta-1,4-diene-1,3-diyl)dibenzene

Light yellow oil. $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 7.40$-$7.19$ (m, 14H), 6.46 (d, $J = 16.4$ Hz, 1H), 6.34 (dd, $J = 6$, 16 Hz, 1H), 6.20 (d, $J = 10.8$ Hz, 1H), 4.35 (dd, $J = 6.4$, 10.8 Hz, 1H), 2.39 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 21.3$, 48.3, 126.1, 126.7, 127.3, 127.4, 128.3, 128.6, 129.7, 128.53, 128.7, 129.0, 129.9, 130.7, 131.0, 131.7, 134.1, 137.0, 138.9, 142.3. IR (neat): 3026, 2919, 1599, 1491, 1445, 1029, 971, 885, 847, 820, 783, 746, 695 cm$^{-1}$. MS (70 eV, EI) m/z = 344.

3d: ((1E,4E)-5-chloro-5-(4-ethylphenyl)penta-1,4-diene-1,3-diyl)dibenzene

Light yellow oil. $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 7.40$-$7.21$ (m, 14H), 6.47 (d, $J = 16$ Hz, 1H), 6.35 (dd, $J = 6.4$, 16.4 Hz, 1H), 6.20 (d, $J = 10.4$ Hz, 1H), 4.36 (dd, $J = 6$, 10.4 Hz, 1H), 2.69 (q, $J = 7.6$ Hz, 2H), 1.27 (t, $J = 7.4$ Hz, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 15.3$, 28.7, 48.4, 126.3, 126.8, 127.5, 127.7, 127.8, 128.56, 128.57, 128.8, 130.0, 130.7, 131.4, 131.8, 134.3, 137.1, 142.4, 145.1. IR (neat): 3026, 2963, 1601, 1492, 1449, 965, 833, 744, 695 cm$^{-1}$. MS (70 eV, EI) m/z = 358. HRMS (EI): m/z calcd for C$_{23}$H$_{23}$Cl (M$^+$):

$$\text{C}_{23}\text{H}_{23}\text{Cl}$$
3e: ((1E,4E)-5-chloro-5-(4-propylphenyl)penta-1,4-diene-1,3-diyl)dibenzene
Light yellow oil. $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 7.40$-$7.19$ (m, 14H), $6.47$ (d, $J = 16.4$ Hz, 1H), $6.35$ (dd, $J = 5.6$, 16 Hz, 1H), $6.20$ (d, $J = 10.8$ Hz, 1H), $4.37$ (dd, $J = 6.4$, 10 Hz, 1H), $2.62$ (t, $J = 7.6$ Hz, 2H), $1.71$-$1.65$ (m, 2H), $0.97$ (t, $J = 7.2$ Hz, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 13.9$, 24.3, 37.8, 48.4, 126.3, 126.8, 127.5, 127.7, 128.4, 128.5, 128.6, 128.8, 129.9, 130.7, 131.4, 131.9, 134.3, 137.1, 142.4, 143.6. IR (neat): $3026$, $2958$, $1601$, $1493$, $1450$, $965$, $837$, $792$, $695$ cm$^{-1}$. MS (70 eV, EI) m/z = 372. HRMS (EI): m/z calcd for C$_{26}$H$_{25}$Cl (M$^+$): 372.1645. Found, 372.1643.

3f: 4,4’-((1E,4E)-5-chloro-5-phenylpenta-1,4-diene-1,3-diyl)bis(methylbenzene)
Light yellow oil. $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 7.48$-$7.44$ (m, 2H), $7.41$-$7.35$ (m, 2H), $7.31$-$7.27$ (m, 3H), $7.18$-$7.10$ (m, 6H), $6.43$ (d, $J = 16$ Hz, 1H), $6.29$ (dd, $J = 6$, 16 Hz, 1H), $6.22$ (d, $J = 10.8$ Hz, 1H), $4.30$ (dd, $J = 6.4$, 10.4 Hz, 1H), $2.36$ (s, 6H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 21.0$, 21.2, 48.0, 126.2, 127.5, 128.3, 128.6, 128.8, 129.2, 129.4, 130.40, 130.43, 130.7, 131.2, 134.3, 136.4, 137.0, 137.3, 139.4. IR (neat): $3022$, $2921$, $1598$, $1510$, $1444$, $1090$, $1013$, $967$, $801$, $762$, $698$ cm$^{-1}$. MS (70 eV, EI) m/z = 358. HRMS (EI): m/z calcd for C$_{25}$H$_{23}$Cl (M$^+$): 358.1488. Found, 358.1491.

3g: 4,4’-((1E,4E)-5-chloro-5-phenylpenta-1,4-diene-1,3-diyl)bis(chlorobenzene)
Light yellow oil. $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 7.36$-$7.21$ (m, 11H), $7.08$ (d, $J = 8.4$ Hz, 2H), $6.34$ (d, $J = 16$ Hz, 1H), $6.22$ (dd, $J = 6$, 16 Hz, 1H), $6.13$ (d, $J = 10.8$ Hz, 1H), $4.25$ (dd, $J = 6$, 10.4 Hz, 1H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 47.7$, 126.5, 127.5, 128.4, 128.7, 128.9, 129.0, 129.1, 129.5, 129.9, 131.3, 132.2, 132.7, 133.2, 135.2, 136.7, 140.4. IR (neat): $3028$, $2923$, $1696$, $1594$, $1488$, $1090$, $1013$, $968$, $823$, $764$, $697$ cm$^{-1}$. MS (70 eV, EI) m/z = 398. HRMS (EI): m/z calcd for C$_{23}$H$_{17}$Cl$_3$ (M$^+$): 398.0396. Found, 398.0389.

3h: 4,4’-((1E,4E)-5-chloro-5-phenylpenta-1,4-diene-1,3-diyl)bis(bromobenzene)
Light yellow oil. $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 7.58$-$7.11$ (m, 13H), $6.22$ (d, $J = 9.2$ Hz, 1H), $6.14$ (d, $J = 10.8$ Hz, 1H), $4.83$ (dd, $J = 10$, 17.2 Hz, 1H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 45.0$, 126.5, 126.9, 127.0, 128.3, 128.56, 128.64, 128.89, 128.94, 129.0,
131.9, 133.5, 134.2, 136.5, 137.3, 139.9, 140.5. IR (neat): 2921, 1529, 1444, 1075, 1012, 903, 876, 825, 761, 691 cm\(^{-1}\). MS (70 eV, EI) m/z = 486. HRMS (EI): m/z calcd for C\(_{23}\)H\(_{17}\)Br\(_2\)Cl (M\(^+\)): 487.9365. Found, 487.9354.

\(\text{3i: } ((1E,4E)-1\text{-chloro-5-(4-chlorophenyl)penta-1,4-diene-1,3-diyl})\text{dibenzene} \)

1H NMR (400 MHz, CDCl\(_3\)): \(\delta = 7.47-7.15 \text{ (m, 14H), 6.47-6.39 \text{ (m, 1H), 6.37-6.31 \text{ (m, 1H), 6.28-6.19 \text{ (m, 1H), 4.38-4.33 \text{ (m, 1H).}} \}

13C NMR (100 MHz, CDCl\(_3\)): \(\delta = 47.8, 48.4, 126.3, 126.6, 126.9, 127.5, 127.6, 127.7, 127.8, 128.3, 128.4, 128.43, 128.51, 128.55, 128.6, 128.7, 128.80, 128.84, 128.88, 128.9, 129.0, 129.5, 129.8, 130.1, 130.6, 131.2, 131.8, 132.0, 133.1, 135.5, 136.8, 136.9, 140.7, 142.0. \) IR (neat): 3058, 3025, 1599, 1491, 1443, 966, 907, 742, 693 cm\(^{-1}\). MS (70 eV, EI) m/z = 364. HRMS (EI): m/z calcd for C\(_{23}\)H\(_{18}\)Cl\(_2\) (M\(^+\)): 364.0786. Found, 364.0785.

\(\text{3j: } ((1E,4E)-1\text{-chloro-3-(4-chlorophenyl)penta-1,4-diene-1,5-diyl})\text{dibenzene} \)

Light yellow oil. 1H NMR (400 MHz, CDCl\(_3\)): \(\delta = 7.43-7.19 \text{ (m, 14H), 6.52-6.42 \text{ (m, 2H), 6.37 (dd, } J = 6, 16.4 \text{ Hz, 1H), 4.33 (dd, } J = 6, 6.6 \text{ Hz, 1H).} \)

13C NMR (100 MHz, CDCl\(_3\)): \(\delta = 15.3, 28.7, 49.4, 126.3, 126.8, 127.5, 127.7, 127.9, 128.6, 128.75, 128.80, 129.0, 130.8, 131.0, 134.2, 137.0, 142.1, 145.0. \) IR (neat): 3057, 3022, 1599, 1491, 1443, 966, 910, 763, 694 cm\(^{-1}\). MS (70 eV, EI) m/z = 402. HRMS (EI): m/z calcd for C\(_{25}\)H\(_{23}\)Br (M\(^+\)): 402.0983. Found, 402.0979.

\(\text{4a: } ((1E,4E)-1\text{-bromopenta-1,4-diene-1,3,5-triyl})\text{tribenzene} \)

Light yellow oil. 1H NMR (400 MHz, CDCl\(_3\)): \(\delta = 7.43-7.19 \text{ (m, 14H), 6.47-6.39 \text{ (m, 1H), 6.37-6.31 \text{ (m, 1H), 6.28-6.19 \text{ (m, 1H), 4.38-4.33 \text{ (m, 1H).}} \}

13C NMR (100 MHz, CDCl\(_3\)): \(\delta = 47.8, 48.4, 126.3, 126.6, 126.9, 127.5, 127.6, 127.7, 127.8, 128.3, 128.4, 128.43, 128.51, 128.55, 128.6, 128.7, 128.80, 128.84, 128.88, 128.9, 129.0, 129.5, 129.8, 130.1, 130.6, 131.2, 131.8, 132.0, 133.1, 135.5, 136.8, 136.9, 140.7, 142.0. \) IR (neat): 3058, 3025, 1597, 1491, 1444, 965, 907, 742, 693 cm\(^{-1}\). MS (70 eV, EI) m/z = 374.

\(\text{4b: } ((1E,4E)-5\text{-bromo-5-(4-ethylphenyl)penta-1,4-diene-1,3-diyl})\text{dibenzene} \)

Light yellow oil. 1H NMR (400 MHz, CDCl\(_3\)): \(\delta = 7.43-7.19 \text{ (m, 14H), 6.52-6.42 \text{ (m, 2H), 6.37 (dd, } J = 6, 16.4 \text{ Hz, 1H), 4.33 (dd, } J = 6, 6.6 \text{ Hz, 1H).} \)

13C NMR (100 MHz, CDCl\(_3\)): \(\delta = 15.3, 28.7, 49.4, 126.3, 126.8, 127.5, 127.7, 127.9, 128.6, 128.75, 128.80, 129.0, 130.8, 131.0, 134.2, 137.0, 142.1, 145.0. \) IR (neat): 3057, 3022, 1599, 1491, 1443, 966, 910, 763, 694 cm\(^{-1}\). MS (70 eV, EI) m/z = 402. HRMS (EI): m/z calcd for C\(_{25}\)H\(_{23}\)Br (M\(^+\)): 402.0983. Found, 402.0979.
4c: ((1E,4E)-5-bromo-5-(4-chlorophenyl)penta-1,4-diene-1,3-diyl)dibenzene
Light yellow oil. $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 7.41$-$7.19$ (m, 14H), 6.50-6.42 (m, 2H), 6.32 (dd, $J = 6$, 16 Hz, 1H), 4.22 (dd, $J = 6$, 10.6 Hz, 1H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta =$ 49.5, 119.8, 126.3, 127.0, 127.57, 127.63, 128.6, 128.7, 128.9, 130.1, 130.6, 130.9, 134.7, 135.2, 136.79, 126.83, 141.7. IR (neat): 3058, 3021, 1597, 1493, 1444, 967, 905, 764, 693 cm$^{-1}$. MS (70 eV, EI) m/z = 408. HRMS (EI): m/z calcd for C$_{23}$H$_{18}$BrCl (M$^+$): 408.0280. Found, 408.0275.

4d: 4,4'-(1E,4E)-5-bromo-5-phenylpenta-1,4-diene-1,3-diyl)bis(chlorobenzene)
Light yellow oil. $^1$H NMR (400 MHz, CDCl$_3$): $\delta =$ 7.38-7.07 (m, 13H), 6.34 (d, $J =$ 16 Hz, 1H), 6.22 (dd, $J =$ 6, 16 Hz, 1H), 6.13 (d, $J =$ 10.8 Hz, 1H), 4.25 (dd, $J =$ 6, 10.4 Hz, 1H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta =$ 45.3, 127.5, 128.37, 128.40, 128.5, 128.56, 128.63, 128.8, 128.9, 129.0, 129.6, 131.6, 132.3, 136.4, 138.4, 139.7, 141.6. IR (neat): 3057, 3020, 1596, 1489, 1013, 968, 824, 764, 697 cm$^{-1}$. MS (70 eV, EI) m/z = 442. HRMS (EI): m/z calcd for C$_{23}$H$_{17}$BrCl$_2$ (M$^+$): 441.9891. Found, 441.9885.

5a: (3E,6E)-hepta-3,6-dien-1-yne-1,3,5,7-tetrayltetrazenes
Oil. $^1$H NMR (400 MHz, CDCl$_3$): $\delta =$ 7.50-7.23 (m, 20H), 6.54-6.47 (m, 2H), 6.40 (dd, $J =$ 6, 16 Hz, 1H), 4.56 (dd, $J =$ 6, 10.4 Hz, 1H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta =$ 47.9, 88.7, 91.0, 123.3, 124.1, 126.3, 126.7, 127.4, 127.8, 128.0, 128.1, 128.2, 128.4, 128.5, 128.6, 128.7, 128.8, 130.8, 131.5, 137.2, 137.3, 139.3, 142.6. IR (neat): 3057, 2924, 1713, 1597, 1490, 1443, 1362, 1071, 1028, 965, 754, 691 cm$^{-1}$. MS (70 eV, EI) m/z = 396. HRMS (EI): m/z calcd for C$_{31}$H$_{24}$ (M$^+$): 396.1878. Found, 396.1881.

6a: (1Z,4E)-penta-1,4-diene-1,3,5-triyttrialbenzenes
Oil. $^1$H NMR (400 MHz, CDCl$_3$): $\delta =$ 7.42-7.23 (m, 15H), 6.69 (d, $J =$ 11.2, 1H), 6.55 (d, $J =$ 16 Hz, 1H), 6.45 (dd, $J =$ 6, 16 Hz, 1H), 5.92 (t, $J =$ 10.4 Hz, 1H), 4.77 (dd, $J =$ 6.4, 10 Hz, 1H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta =$ 46.9, 126.3, 126.6, 127.0, 127.3, 127.8, 128.3, 128.5, 128.6, 128.7, 129.5, 130.5, 132.3, 132.8, 137.1, 137.4, 143.4. IR (neat):
3024, 2927, 1808, 1598, 1447, 1256, 1075, 1027, 968, 737, 697 cm$^{-1}$. MS (70 eV, EI) m/z = 296. HRMS (EI): m/z calcd for C$_{31}$H$_{24}$ (M$^{+}$): 296.4049. Found, 296.4048. 

**HNMR 400 MHz, CNMR 100 MHz spectra:**

3a HNMR 400 MHz, CNMR 100 MHz

3b HNMR 400 MHz, CNMR 100 MHz
3c HNMR 400 MHz, CNMR 100 MHz

3d HNMR 400 MHz, CNMR 100 MHz
3e HNMR 400 MHz, CNMR 100 MHz
3f HNMR 400 MHz, CNMR 100 MHz

3g HNMR 400 MHz, CNMR 100 MHz
3h HNMR 400 MHz, CNMR 100 MHz
3i and 3j HNMR 400 MHz, CNMR 100 MHz

4a HNMR 400 MHz, CNMR 100 MHz
4b HNMR 400 MHz, CNMR 100 MHz
5a HNMR 400 MHz, CNMR 100 MHz
6a HNMR 400 MHz, CNMR 100 MHz, NOE
References: