Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information for

Chiral Linker - Bridged Bis-*N*-Heterocylic Carbenes: Design, Synthesis, Palladium Complexes, and Catalytic Property

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(*R,R*)-**1b.** ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.80 (d, *J* = 8.4 Hz, 2H, $CH_{Ar\text{-}NO2\text{-}o}$), 7.27 (d, *J* = 8.0, Hz, 2H, $CH_{Ar\text{-}CH3\text{-}o}$), 6.76 (*t*, *J* = 7.2 Hz, 2H), 3.40 (m, 2H, CH), 2.38 (s, 6H, CH_3), 1.98 (m, 2H, CH_2), 1.72 (m, 2H, CH_2), 1.27 (m, 4H, CH_2). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 144.5 ($C_{Ar\text{-}NH}$), 139.2 ($CH_{Ar\text{-}CH3\text{-}o}$), 138.2 ($C_{Ar\text{-}NO2}$), 130.2 ($C_{Ar\text{-}CH3}$), 124.3 ($CH_{Ar\text{-}NO2\text{-}o}$), 119.0 ($CH_{Ar\text{-}NO2\text{-}m}$), 61.6 (CH), 33.5 ($CH_2$), 24.5 ($CH_2$), 20.9 ($CH_3$).

(*R,R*)-**1c.** ^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.05 (dd, *J* = 8.8, 1.6 Hz, 1H, $CH_{Ar\text{-}NO2\text{-}o}$), 7.93 (d, *J* = 7.6 Hz, 1H, $CH_{Ar\text{-}NO2\text{-}o}$), 7.70 (dd, *J* = 8.4, 1.2 Hz, 1H, $CH_{Ar\text{-}Me\text{-}o}$), 7.38 (m, 1H, CH), 7.31 (d, *J* = 7.6 Hz, 1H, CH), 6.79 (m, 2H), 6.63 (m,1H), 3.50 (m, 1H, CH), 3.39 (m, 1H, CH), 2.44 (s, 3H, CH_3), 2.19 (m, 2H, CH_2), 1.84 (m, 2H, CH_2), 1.51-1.30 (m, 4H, CH_2). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 144.6, 140.0 ($C_{Ar\text{-}NH}$), 138.0, 136.4 ($CH_{Ar\text{-}NO2\text{-}p}$), 131.7,131.1 ($C_{Ar\text{-}NO2}$), 127.0 ($C_{Ar\text{-}CH3}$), 123.8, 119.7 ($CH_{Ar\text{-}NO2\text{-}o}$), 115.4, 113.2 ($CH_{Ar\text{-}NO2\text{-}m}$), 60.2, 58.7 (CH), 33.5, 32.5 (CH_2), 24.9, 24.4 (CH_2), 20.6 (CH_3).

(*R,R*)-**1d.** ^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.02 (dd, *J* = 8.4, 1.6 Hz, 2H, $CH_{Ar\text{-}NO2\text{-}o}$), 7.73 (dd, *J* = 8.0, 1.6 Hz, 2H, $CH_{Ar\text{-}CF3\text{-}o}$), 6.98 (d, *J* = 8.8 Hz, 2H), 6.83 (d, *J* = 8.0 Hz, 2H, NH), 3.42 (m, 2H, CH), 2.08 (m, 2H, CH_2), 1.76 (m, 2H, CH_2), 1.30 (m, 4H, CH_2). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 142.5 ($C_{Ar\text{-}NH}$), 138.9 ($C_{Ar\text{-}NO2}$), 134.6 ($CH_{Ar\text{-}CF3\text{-}o}$), 130.34 ($CH_{Ar\text{-}NO2\text{-}o}$), 125.2 ($CF_3$), 122.5 ($CH_{Ar\text{-}NO2\text{-}o}$), 117.1 ($C_{Ar\text{-}CF3}$), 62.4 (CH), 33.3 ($CH_2$), 24.5 ($CH_2$).

(*R,R*)-**5a**. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.85 (dd, *J* = 4.0 Hz, 2H, $CH_{Ar\text{-}NO2\text{-}o}$), 8.17 (dd, *J* = 7.4, 1.2 Hz, 2H, $CH_{Ar\text{-}NO2\text{-}p}$), 7.33 – 7.30 (m, 6H), 7.19 – 7.16 (m, 4H), 6.68 - 6.63 (m, 4H), 5.03 (t, *J* = 10.0, 4.4 Hz, 2H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 143.9 ($C_{Ar\text{-}NH}$), 137.0 (C_{Ar}), 136.1 ($CH_{Ar\text{-}NO2\text{-}p}$), 132.9 ($C_{Ar\text{-}NO2}$), 128.9, 128.6, 127.7 ($CH_{Ar}$), 126.8 ($CH_{Ar\text{-}NO2\text{-}o}$), 116.5 ($CH_{Ar\text{-}NH\text{-}p}$), 115.1 ($CH_{Ar\text{-}NH\text{-}o}$), 62.3 (CH).

(*R,R*)-**5b.** HRMS (positive ions): *m/z* 591.1467 (calcd for $[M+H]^+$ 591.1448), 385.1150 (calcd for $\{M–[2\text{-}NO_2\text{-}6\text{-}CF_3(C_6H_3)NH^-]\}^+$ 385.1158). ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.91 (dd, *J* = 8.0, 1.6 Hz, 2H, $CH_{Ar\text{-}NO2\text{-}o}$), 7.73 (dd, *J* = 7.6, 1.6 Hz, 2H, $CH_{Ar\text{-}CF3\text{-}o}$), 7.23 (d, *J* = 6.4 Hz, 2H), 7.06 (m, 6H), 6.84 (m, 6H), 4.98 (m, 2H, CH). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 141.3 (C_{Ph}), 140.7 ($C_{Ar\text{-}NH}$), 136.9 ($C_{Ar\text{-}NO2}$), 133.3 ($CH_{Ar\text{-}CF3\text{-}o}$), 130.3 ($CH_{Ar\text{-}NO2\text{-}o}$), 128.5, 128.1, 127.9, 127.7 (CH_{Ar}), 125.2 (CF_3), 122.5, 121.5, 121.1 (CH_{Ar}), 118.3 ($C_{Ar\text{-}CF3}$), 66.7 (CH).

(*R*,*R*)-**3d.** ^{1}H-NMR (400 MHz, $CDCl_3$): δ 6.98-6.92 (m, 4H, $CH_{Ar\text{-}NO2\text{-}o}$ + $CH_{Ar\text{-}CF3\text{-}o}$), 6.86 (m, 2H, $CH_{Ar\text{-}NH\text{-}p}$), 4.65 (br, 6H, NH + NH_2), 3.19 (m, 2H, CH), 2.09 (m, 2H, CH_2), 1.71 (m, 2H, CH_2), 1.30 (m, 2H, CH_2), 1.17 (m, 2H, CH_2). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 142.6 ($C_{Ar\text{-}NH2}$), 131.3 ($C_{Ar\text{-}NH}$), 125.4 (CF_3), 123.1 ($CH_{Ar\text{-}NH2\text{-}o}$+$CH_{Ar\text{-}NH2\text{-}m}$), 119.0 ($CH_{Ar\text{-}CF3\text{-}o}$), 115.6 ($C_{Ar\text{-}CF3}$), 60.0 (CH), 33.7 ($CH_2$), 25.2 ($CH_2$).

(*R*,*R*)-**6**. ^{1}H-NMR (400MHz, $CDCl_3$): δ 7.28-7.12(m, 10H, ArH), 6.75-6.62(m, 6H, ArH), 6.44-6.41 (m, 2H, ArH), 4.59(s, 2H, CH), 3.48(s, 6H, NH). ^{13}C-NMR (100MHz, $CDCl_3$): δ 140.07, 136.55, 134.75, 128.29, 127.41, 120.54, 119.07, 116.64, 113.71, 64.48.

7a. (1.6 g) HRMS (positive ions): *m/z* 177.0654 (calcd for $[M+H]^+$ 177.0640). ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.02 (d, *J* = 8.0 Hz, 1H), 6.86 (d, *J* = 8.0 Hz, 1H), 6.72 (t, *J* = 8.0 Hz, 1H), 3.69 (br, 4H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 135.1, 133.9, 128.3, 126.4, 123.7, 120.1, 118.5, 117.7.

7b. (0.8 g) ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.33-7.28 (m, 4H, CH_{Ar}), 7.23-7.19 (m, 6H, CH_{Ar}), 2.95 (m, 4H, CH_2).

(*R*)-**7c.** (60 mg) ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.23-7.19 (m, 6H, CH_{Ar}), 7.05-7.03 (m, 4H, CH_{Ar}), 6.95 (d, *J* = 7.6 Hz, 1H), 6.75 (d, *J* = 7.6 Hz, 1H), 6.66 (t, *J* = 8.0 Hz, 1H), 4.73 (s, 1H), 4.35 (d, *J* = 7.6 Hz, 1H), 4.23 (s,1H), 4.16 (d, *J* = 7.6 Hz, 1H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 139.4, 139.3, 134.3, 131.8, 128.4, 128.3, 128.1, 127.9, 127.7, 126.7, 123.4, 116.9, 116.1, 116.0, 62.1, 61.2, 29.7.

(*R*,*R*)-**1b.** ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.96 (s, 2H, $CH_{imidazole}$), 7.52 (d, *J* = 8.0 Hz, 2H, $CH_{Ar\text{-}CH3\text{-}o}$), 7.12 (d, *J* = 7.6 Hz, 2H, $CH_{Ar\text{-}CH3\text{-}m}$), 7.04 (d, *J* = 7.2 Hz, 2H, $CH_{Ar\text{-}CH3\text{-}p}$), 5.35 (dd, *J* = 6.4, 4.0 Hz, 2H), 2.84 (s, 6H, CH_3), 2.53 (d, *J* = 14.0 Hz, 2H, CH_2), 2.07 (m, 2H, CH_2), 1.86 (m, 2H, CH_2), 1.69 (m, 2H, CH_2). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 143.7 ($CH_{imidazole}$), 139.4 ($C_{Ar\text{-}CH3\text{-}m}$), 132.0 ($C_{Ar\text{-}CH3\text{-}o}$), 126.5 ($C_{Ar\text{-}CH3}$), 122.6 ($CH_{Ar\text{-}CH3\text{-}o}$), 120.0 ($CH_{Ar\text{-}CH3\text{-}m}$), 118.7 ($CH_{Ar\text{-}CH3\text{-}p}$), 58.7 (CH), 37.0 ($CH_2$), 24.8 ($CH_2$), 19.3 ($CH_3$).

(*R*,*R*)-**1c.** ^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.16-8.14 (1H, $CH_{imidazole}$), 7.89 (s, 1H, $CH_{imidazole}$), 7.63 (d, *J* = 8.0 Hz, 1H), 7.45 (d, *J* = 8.0 Hz, 1H), 7.39 (d, *J* = 8.4 Hz, 1H), 7.23 (td, *J* = 8.0 Hz, 1.2 Hz, 1H), 7.17 (td, *J* = 8.0, 1.2 Hz, 1H), 7.01 (t, *J* = 4.4 Hz, 1H), 6.86 (d, *J* = 7.2 Hz, 2H), 2.60 (s, 3H, CH_3), 2.50-42 (m, 2H, CH_2), 2.21-1.95 (m, 4H, CH_2), 1.72-1.67 (m, 2H, CH_2). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 143.6, 143.5 ($CH_{imidazole}$), 140.5, 139.5, 132.8, 132.1, 126.3, 123.2, 122.5, 122.3, 12.7, 120.0,

118.6, 109.4 , 59.1 (CH), 36.1, 33.6 (CH_2), 25.1, 25.0 (CH_2), 19.3 (CH_3).

(*R*,*R*)-**1d.** HRMS (positive ions): *m/z* 453.1504 (calcd for $[M+H]^+$ 453.1514). ^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.01 (s, 2H, $CH_{imidazole}$), 7.86 (d, *J* = 8.0 Hz, 2H, $CH_{Ar\text{-}CF3\text{-}o}$), 7.67 (d, *J* = 7.6 Hz, 2H, $CH_{Ar\text{-}CF3\text{-}p}$), 7.30 (t, *J* = 8.0 Hz, 2H, $CH_{Ar\text{-}CF3\text{-}m}$), 5.23 (m, 2H, CH), 2.52 (m, 2H, CH_2), 2.05 (m, 2H, CH_2), 1.82 (m, 2H, CH_2), 1.09 (m, 2H, CH_2). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 145.3 ($CH_{imidazole}$), 141.3 ($C_{Ar\text{-}CF3\text{-}m}$), 129.3 ($C_{Ar\text{-}CF3\text{-}o}$), 125.7 ($CF_3$), 125.5, 123.0, 122.2, 121.8 (CH_{Ar}), 113.2 ($C_{Ar\text{-}CF3}$), 59.1 (CH), 36.6 (CH_2), 25.2 (CH_2).

(*R*,*R*)-**1d'.** HRMS (positive ions): *m/z* 443.1653 (calcd for $[M+H]^+$ 443.1670). ^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.39 (d, *J* = 6.4 Hz, 1H, $CH_{imidazole}$), 8.01 (d, *J* = 8.4Hz, 1H, $CH_{Ar\text{-}CF3\text{-}o}$), 7.67 (d, *J* = 7.6 Hz, 1H, $CH_{Ar\text{-}CF3\text{-}p}$), 7.34 (t, *J* = 8.0 Hz, 1H, $CH_{Ar\text{-}CF3\text{-}m}$), 6.90 (d, *J* = 6.8 Hz, 1H, $CH_{Ar\text{-}NH2\text{-}p}$), 6.85 (t, *J* = 8.0 Hz, 1H, $CH_{Ar\text{-}NH2\text{-}m}$), 6.76 (d, *J* = 7.6 Hz, 1H, $CH_{Ar\text{-}NH2\text{-}o}$), 4.55 (td, *J* = 22.2, 3.6 Hz, 1H, CH), 3.84 (d, *J* = 9.6 Hz, 1H, CH), 3.34 (d, *J* = 10.4 Hz, 1H), 3.00 (brs, 3H) 2.33 (m, 1H, CH_2), 1.99-1.81 (m, 4H, CH_2), 52-1.32 (m, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 144.9 ($CH_{imidazole}$), 142.4, 142.2 ($C_{Ar\text{-}CF3\text{-}m}$), 130.9 ($C_{Ar\text{-}CF3\text{-}o}$), 126.0 ($CF_3$), 125.6, 125.2, 123.8, 123.5,123.3, 123.1, 122.0, 121.2 (CH_{Ar}), 119.6, 116.6 ($C_{Ar\text{-}CF3}$), 60.4, 58.0 (CH), 34.8,33.6 (CH_2), 25.7, 24.8 (CH_2).

(*R,R*)-**1d''.** HRMS (positive ions): *m/z* 471.1612 (calcd for $[M+H]^+$ 471.1620). ^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.50 (s, 1H, $CH_{imidazole}$), 8.35 (d, *J* = 8.0 Hz, 1H, $CH_{Ar\text{-}CF3\text{-}o}$), 8.05 (d, *J* = 8.0 Hz, 1H, $CH_{Ar\text{-}CF3\text{-}P}$), 7.70 (d, *J* = 7.6 Hz, 1H, $CH_{Ar\text{-}CF3\text{-}p}$), 7.36 (t, *J* = 8.0 Hz, 1H, $CH_{Ar\text{-}CF3\text{-}m}$), 7.22 (s, 1H), 7.12 (t, *J* = 8.0 Hz, 1H, $CH_{Ar\text{-}CF3\text{-}m}$), 4.61 (m, 1H), 3.75 (br s, 1H, OH), 3.42 (m, 1H), 3.25 (d, *J* = 8.8 Hz, 1H), 2.35 (d, *J* = 10.4 Hz, 1H), 1.97-1.75 (m, 6H, CH_2), 1.53-1.32 (m, 2H, CH_2). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 159.3, 144.9, 142.0, 133.6, 125.6, 125.5, 125.3, 125.2, 124.5, 122.9, 122.4, 122.2, 121.6, 62.1, 60.7 (CH), 34.2, 32.6 (CH_2), 25.5, 24.6 (CH_2).

(*R,R*)-**4.** ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.88 (s, 2H, CH_{Ar}), 6.68-6.66 (m, 2H, CH_{Ar}), 7.25 – 7.13 (m, 16H, CH_{Ar}), 6.37 (s, 2H, CH). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 143.5 (C_{Ar}), 140.1 ($CH_{imidazole}$), 135.4, 133.1 (C_{Ar}), 129.1, 127.7, 123.6, 122.8, 120.7, 109.5 (CH_{Ar}), 62.5 (CH).

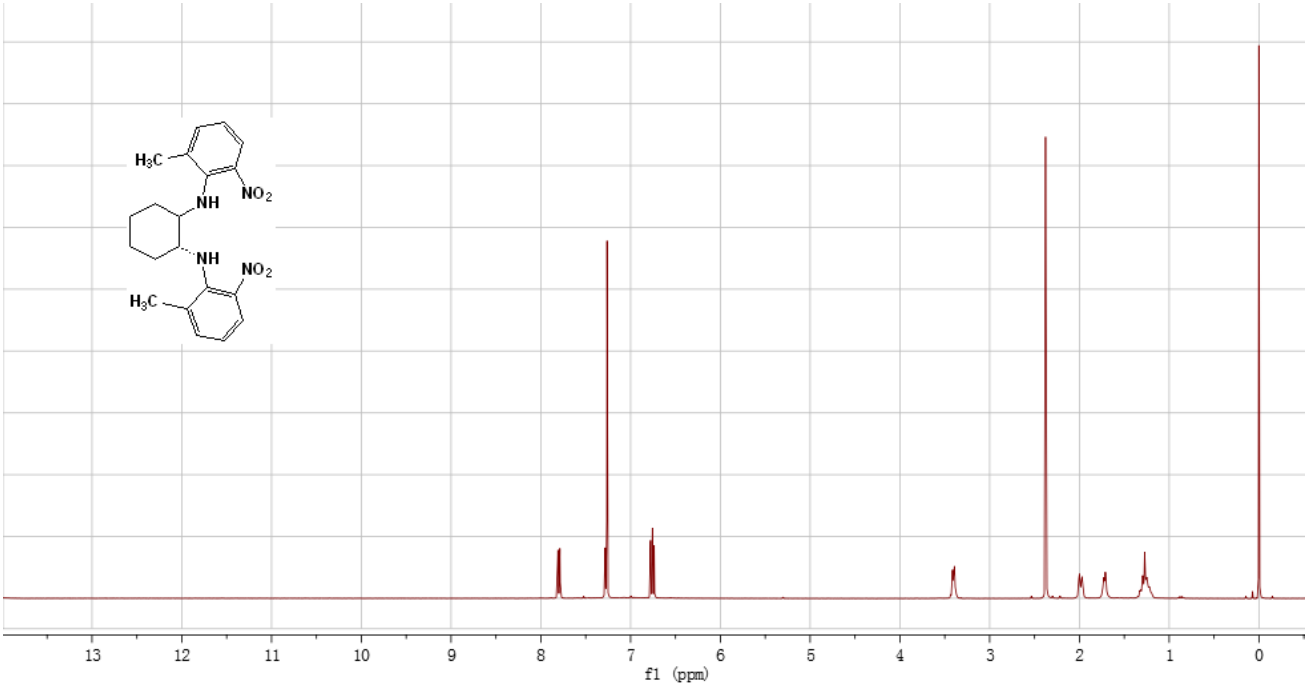

Figure S1. The ^{1}H NMR spectrum of (*R*,*R*)-**2b** in $CDCl_3$ at 20 ^{o}C

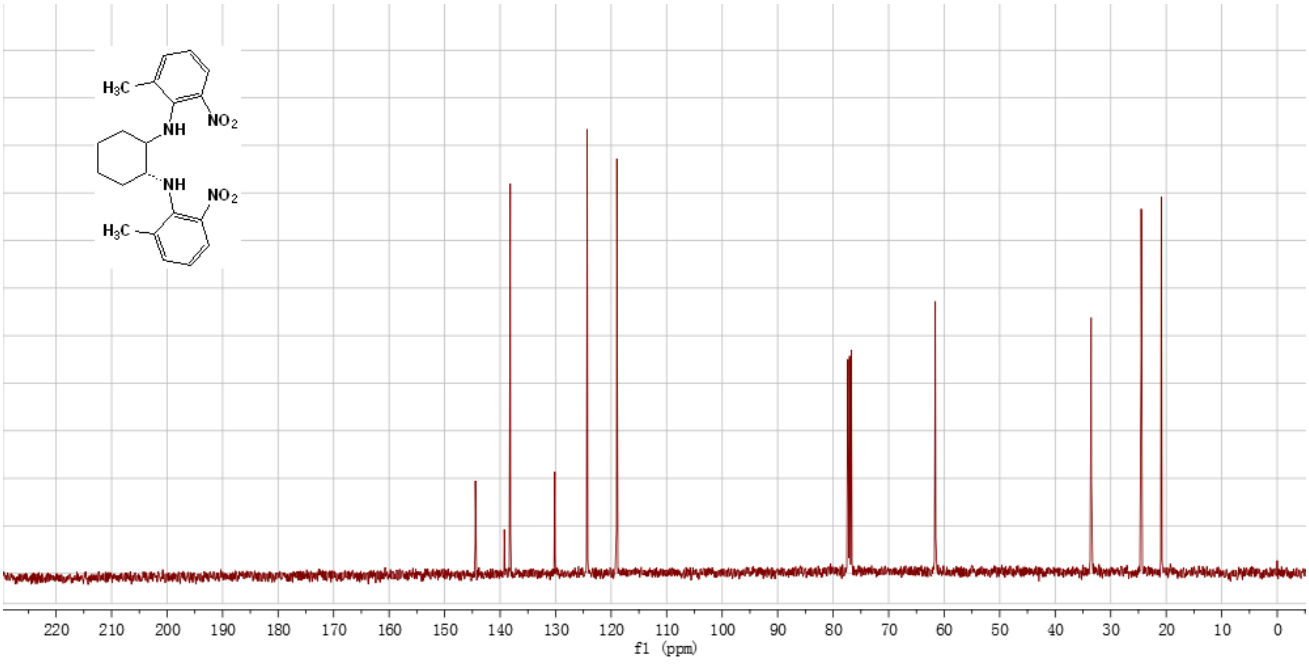

Figure S2. The ^{13}C NMR spectrum of (*R*,*R*)-**2b** in $CDCl_3$ at 20 ^{o}C

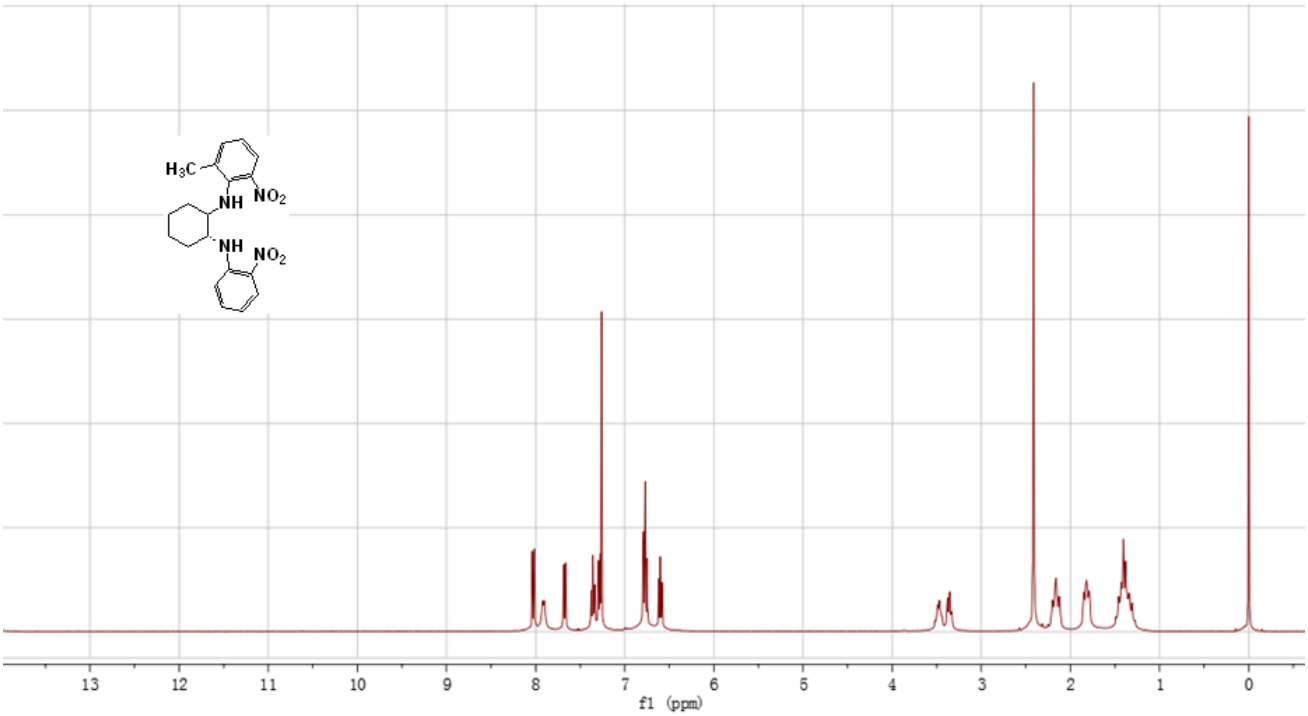

Figure S3. The ^{1}H NMR spectrum of (*R,R*)-**2c** in $CDCl_3$ at 20 ^{o}C

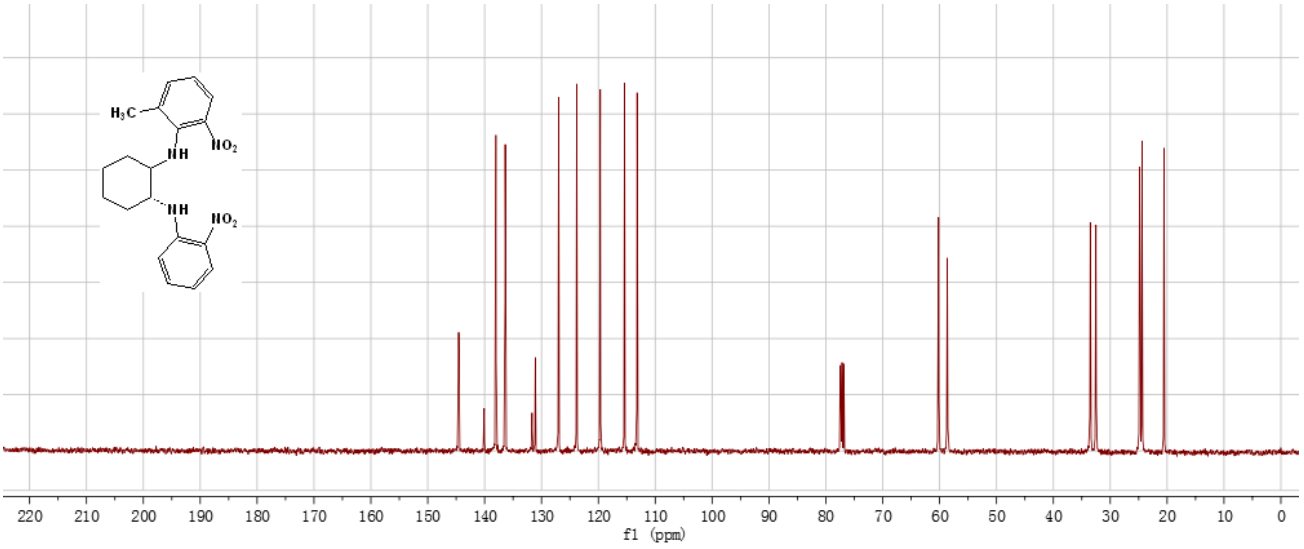

Figure S4. The ^{13}C NMR spectrum of (*R,R*)-**2c** in $CDCl_3$ at 20 ^{o}C

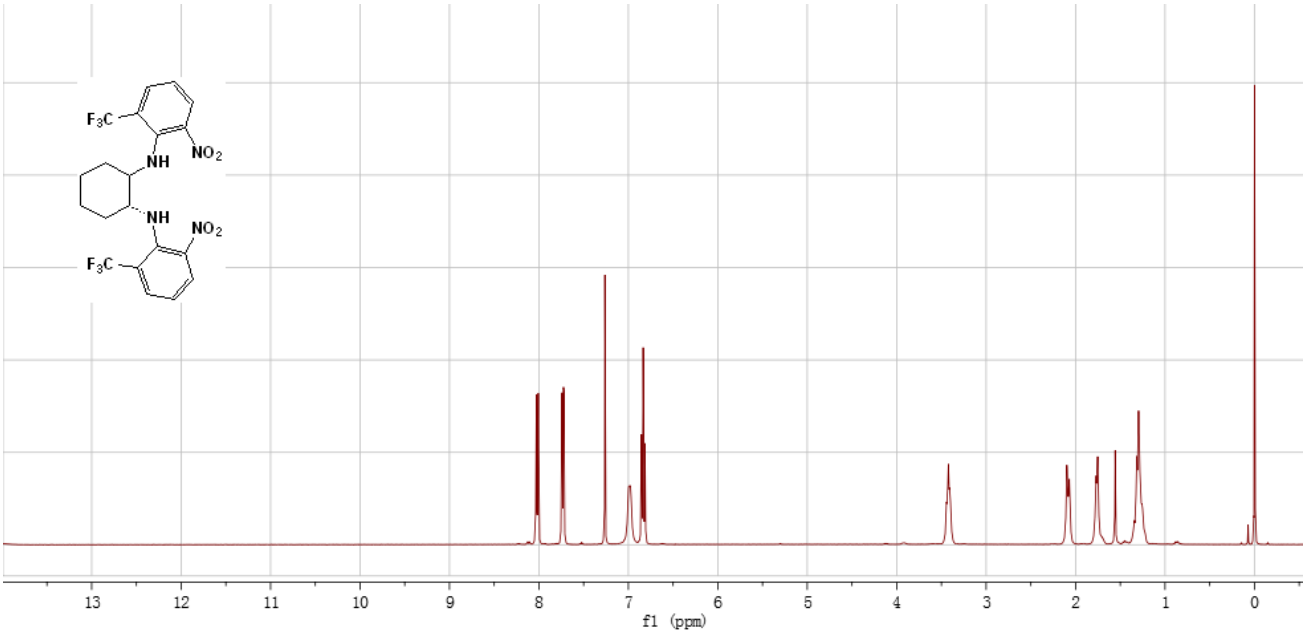

Figure S5. The ^{1}H NMR spectrum of (*R*,*R*)-**2d** in $CDCl_3$ at 20 ^{o}C

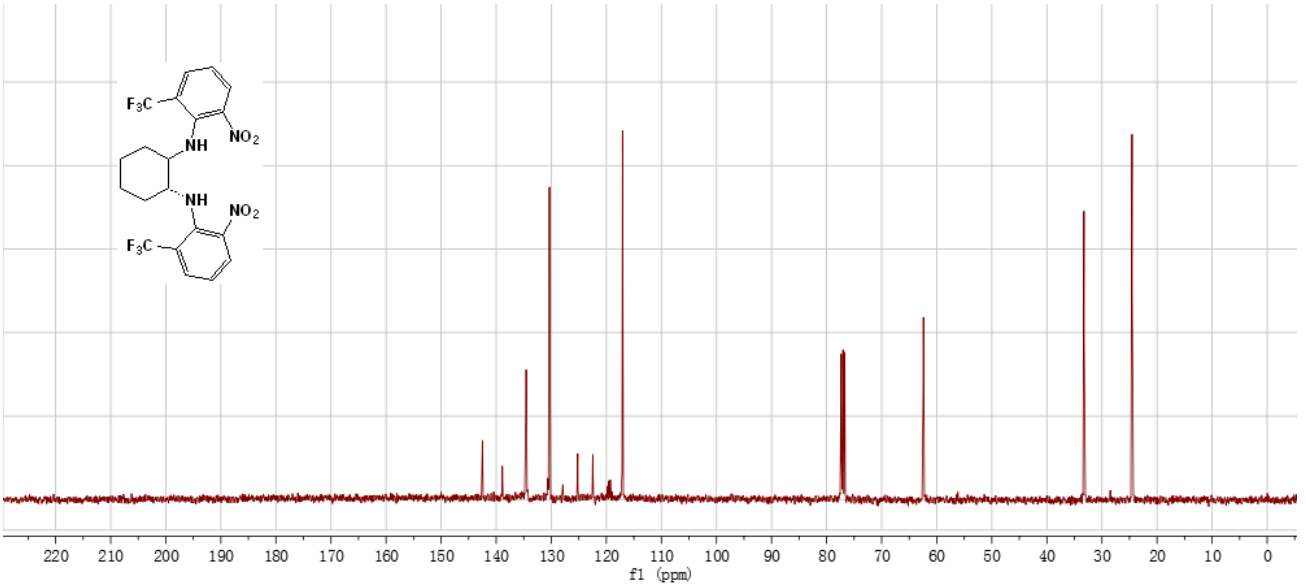

Figure S6. The ^{13}C NMR spectrum of (*R*,*R*)-**2d** in $CDCl_3$ at 20 ^{o}C

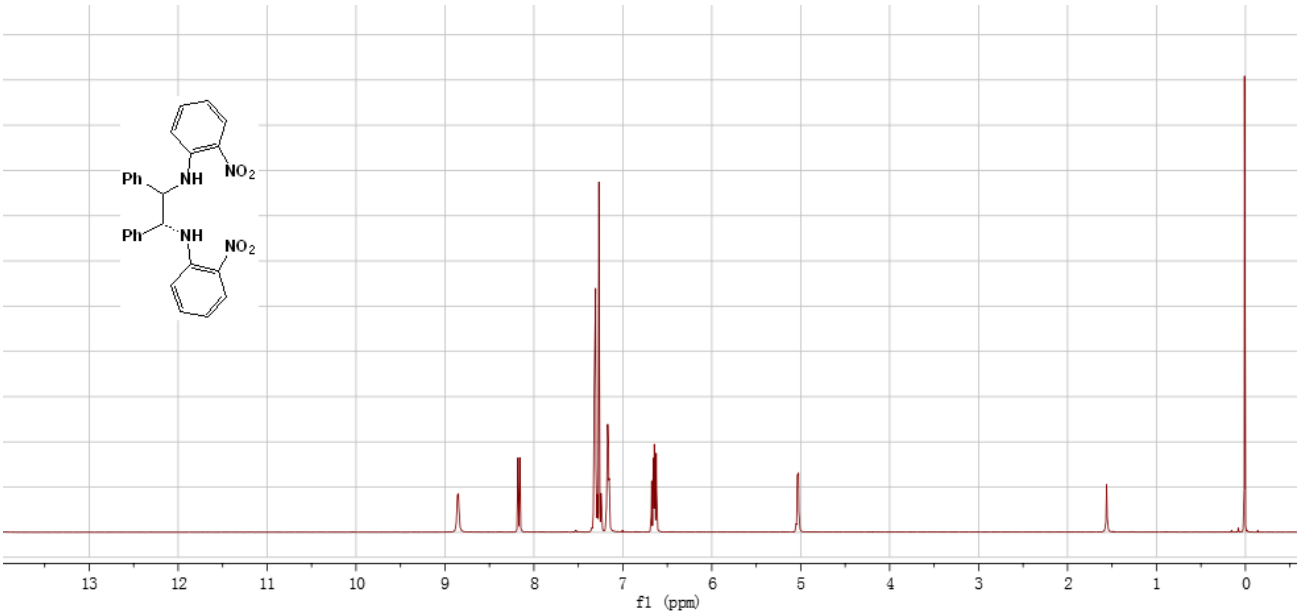

Figure S7. The ^{1}H NMR spectrum of (*R*,*R*)-**5a** in $CDCl_3$ at 20 ^{o}C

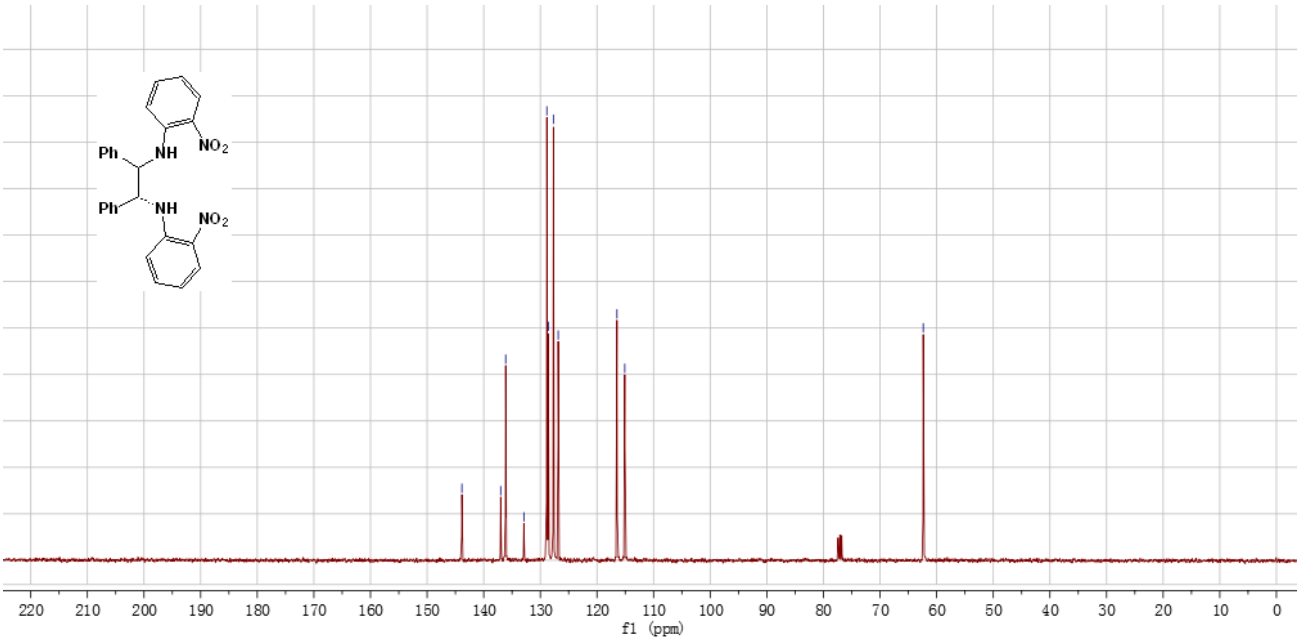

Figure S8. The ^{13}C NMR spectrum of (*R*,*R*)-**5a** in $CDCl_3$ at 20 ^{o}C

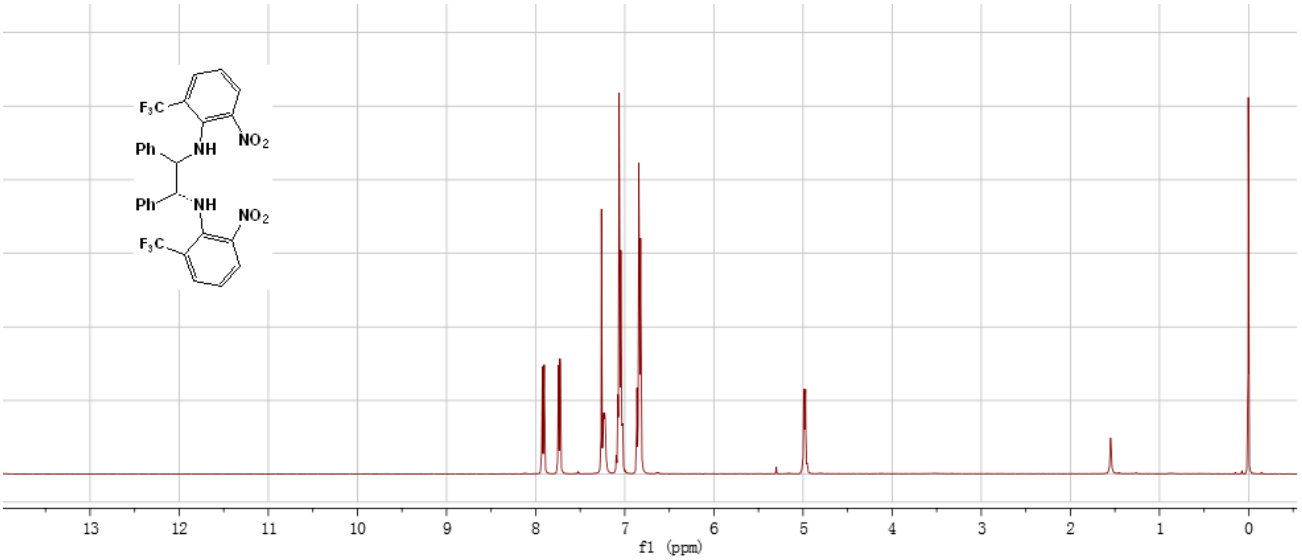

Figure S9. The ^{1}H NMR spectrum of (*R*,*R*)-**5b** in $CDCl_3$ at 20 ^{o}C

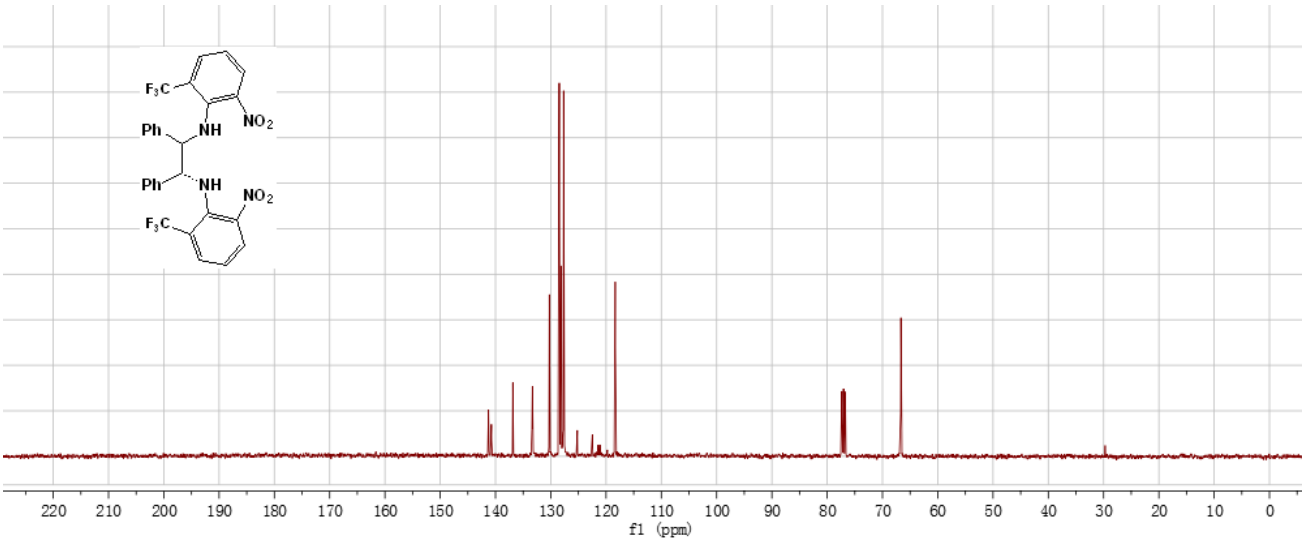

Figure S10. The ^{13}C NMR spectrum of (*R*,*R*)-**5b** in $CDCl_3$ at 20 ^{o}C

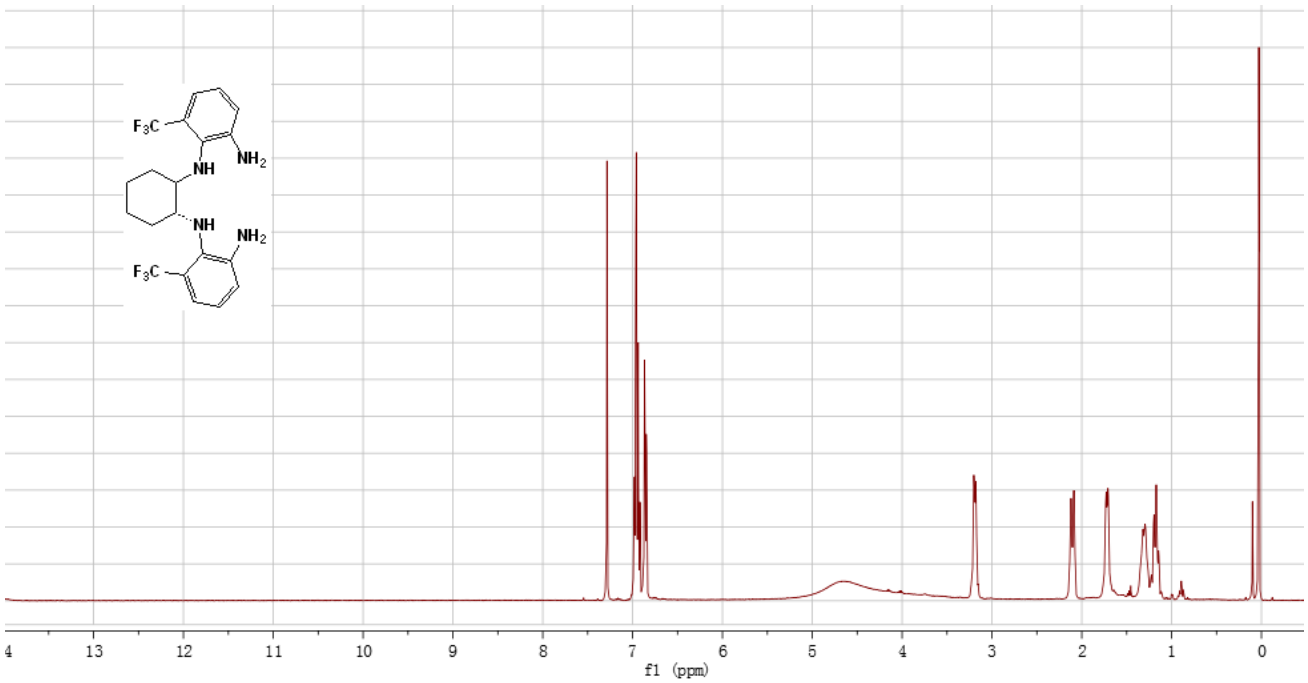

Figure S11. The ^{1}H NMR spectrum of (*R*,*R*)-**3d** in $CDCl_3$ at 20 ^{o}C

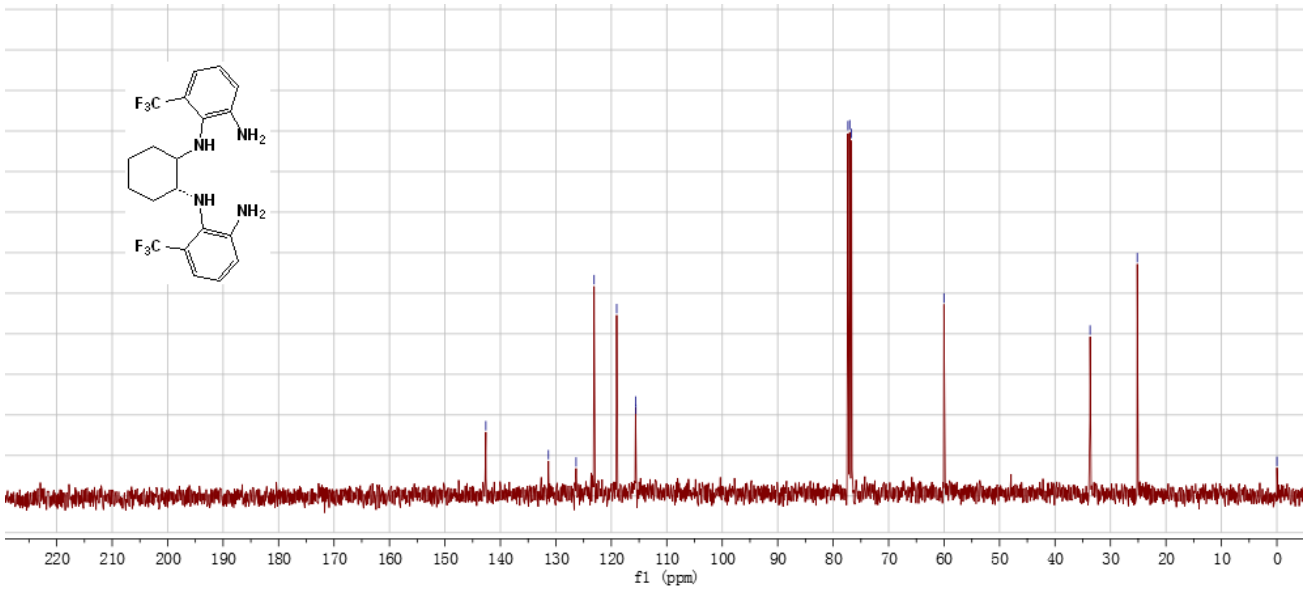

Figure S12. The ^{13}C NMR spectrum of (*R*,*R*)-**3d** in $CDCl_3$ at 20 ^{o}C

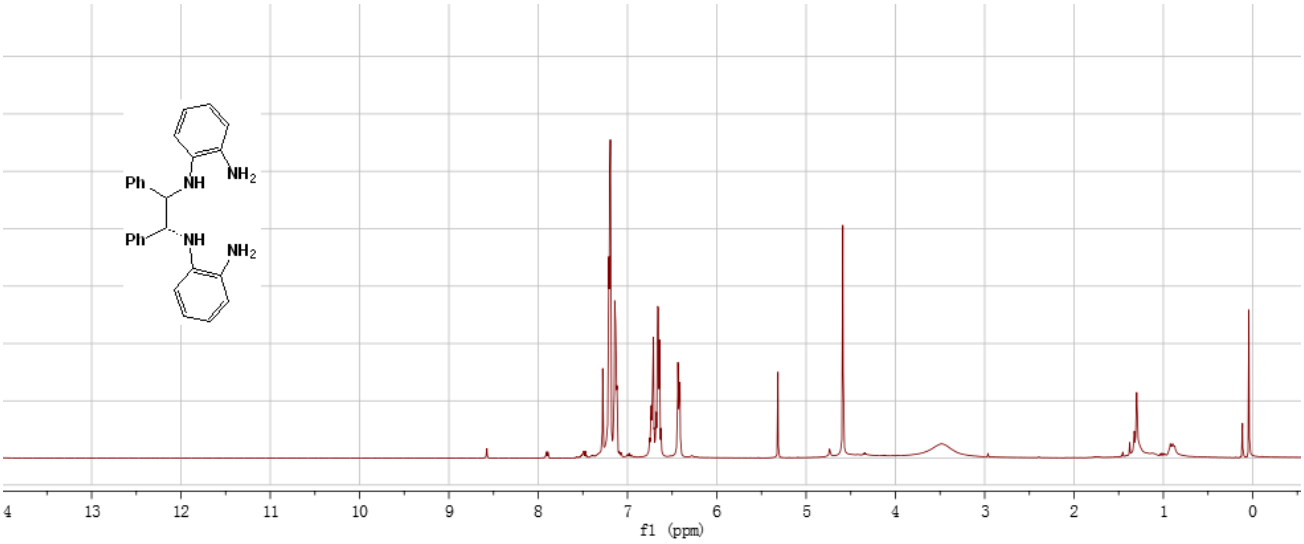

Figure S13. The ^{1}H NMR spectrum of (*R*,*R*)-**6** in $CDCl_3$ at 20 ^{o}C

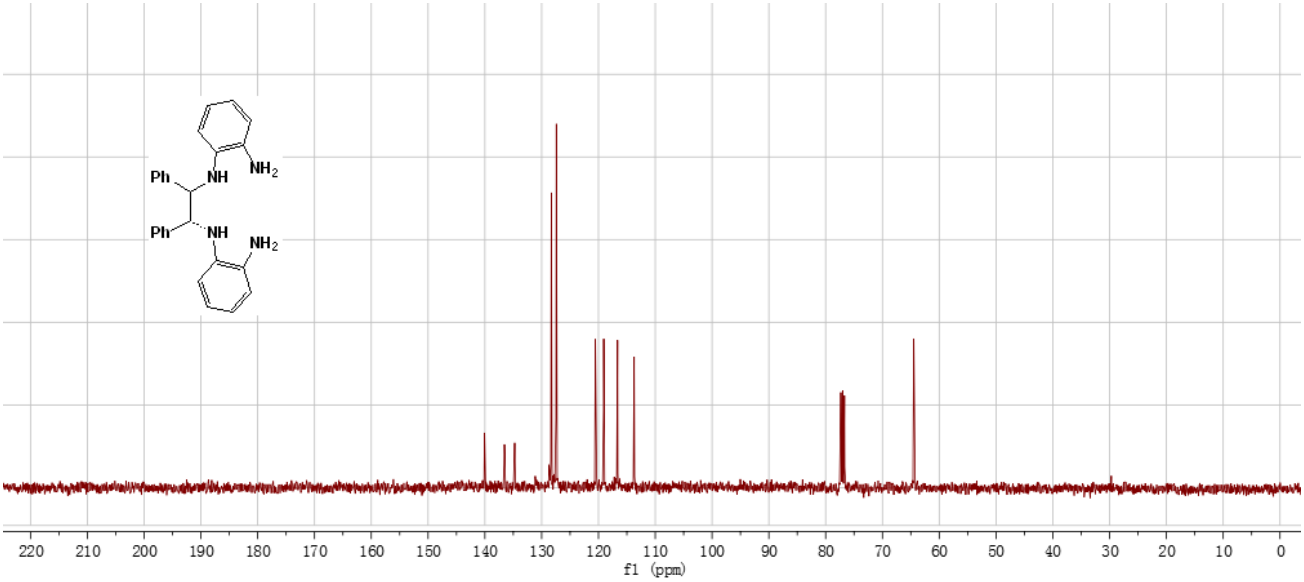

Figure S14. The ^{13}C NMR spectrum of (*R*,*R*)-**6** in $CDCl_3$ at 20 ^{o}C

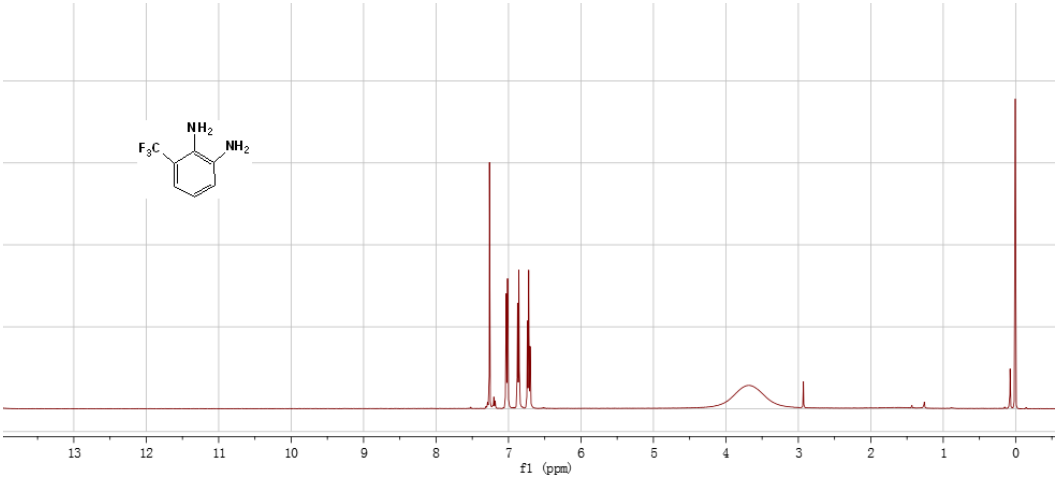

Figure S15. The ^{1}H NMR spectrum of **7a** in $CDCl_3$ at 20 ^{o}C

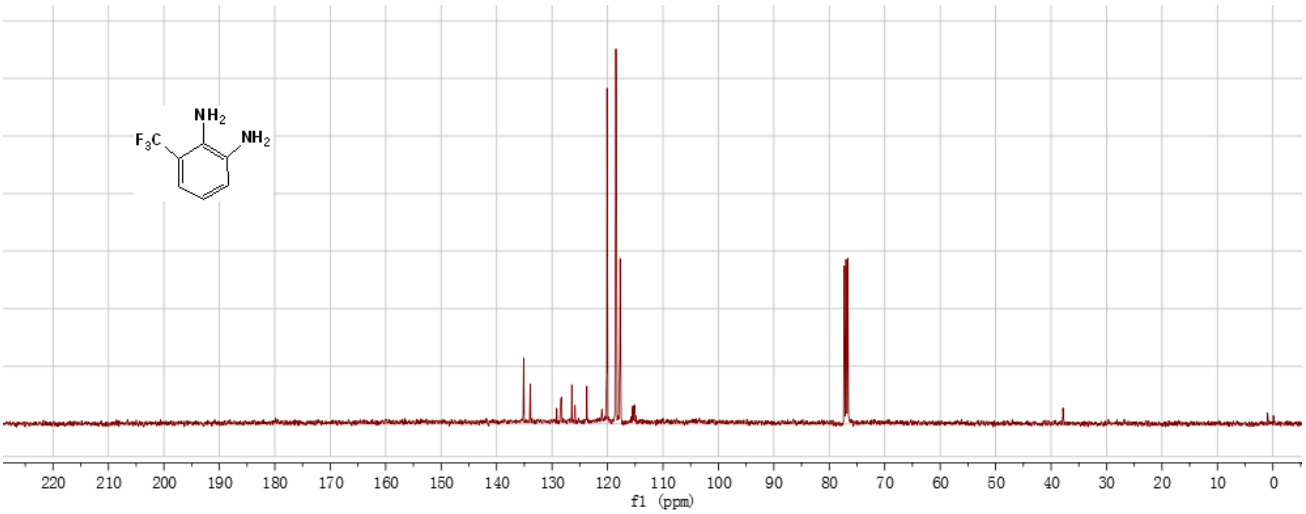

Figure S16. The ^{13}C NMR spectrum of **7a** in $CDCl_3$ at 20 ^{o}C

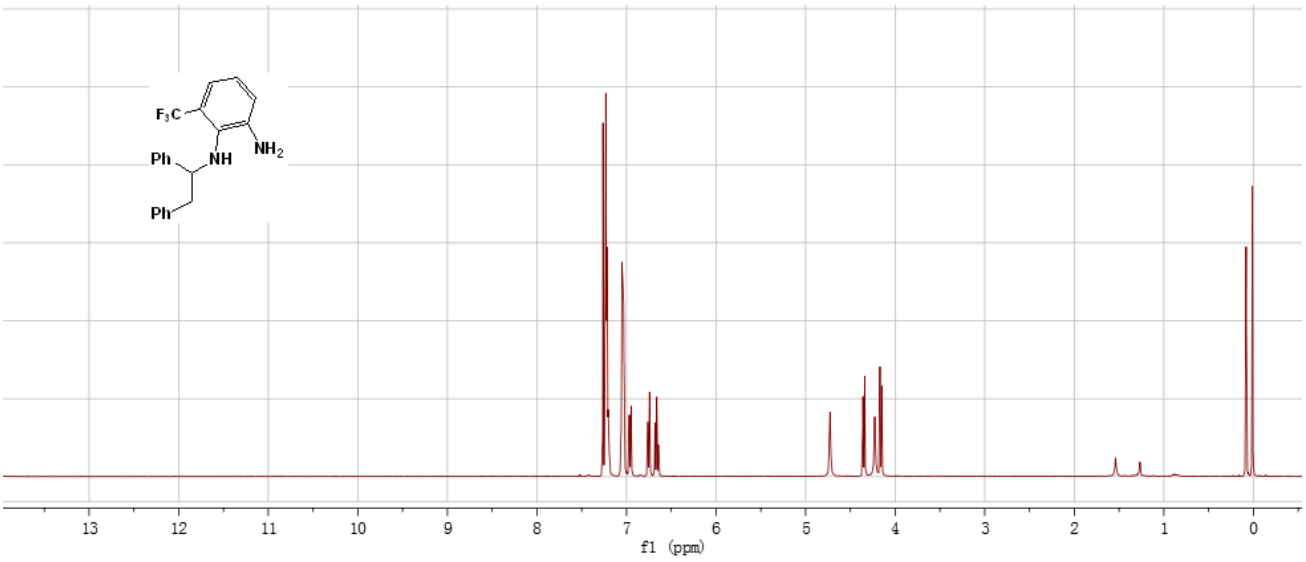

Figure S17. The ^{1}H NMR spectrum of (*R*)-**7c** in $CDCl_3$ at 20 ^{o}C

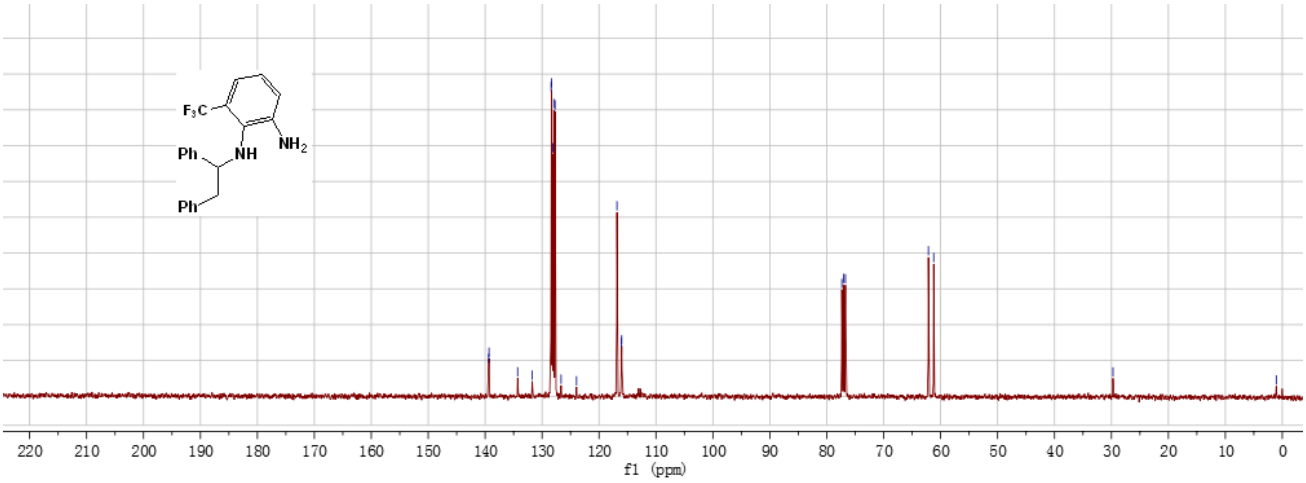

Figure S18. The ^{13}C NMR spectrum of (*R*)-**7c** in $CDCl_3$ at 20 ^{o}C

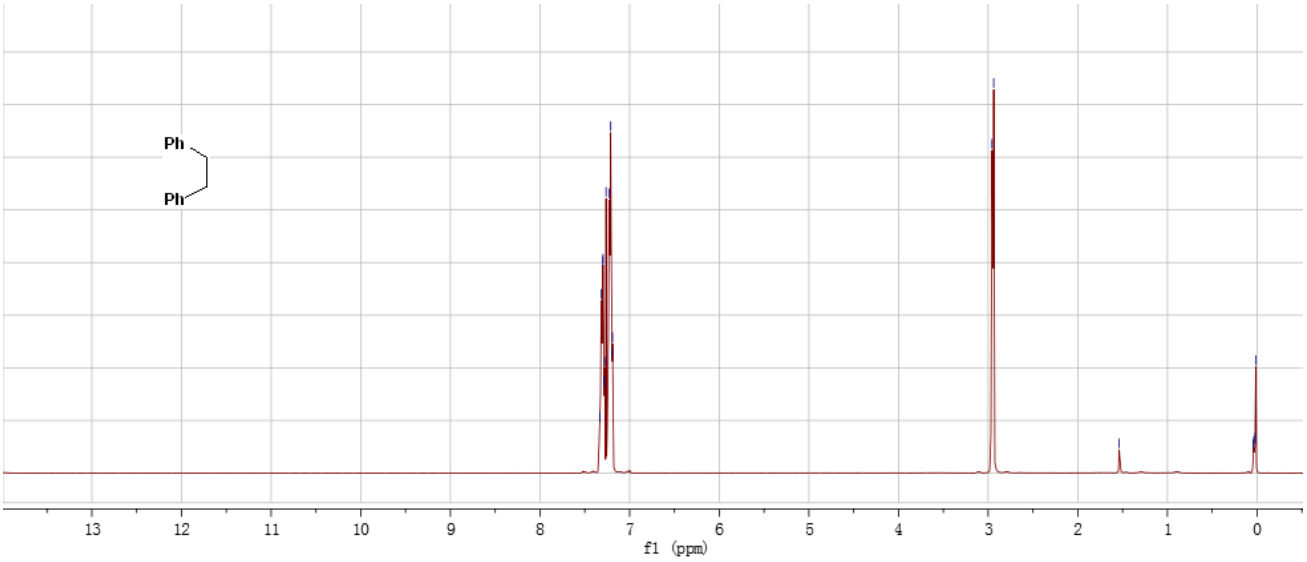

Figure S19. The ^{1}H NMR spectrum of **7b** in $CDCl_3$ at 20 ^{o}C

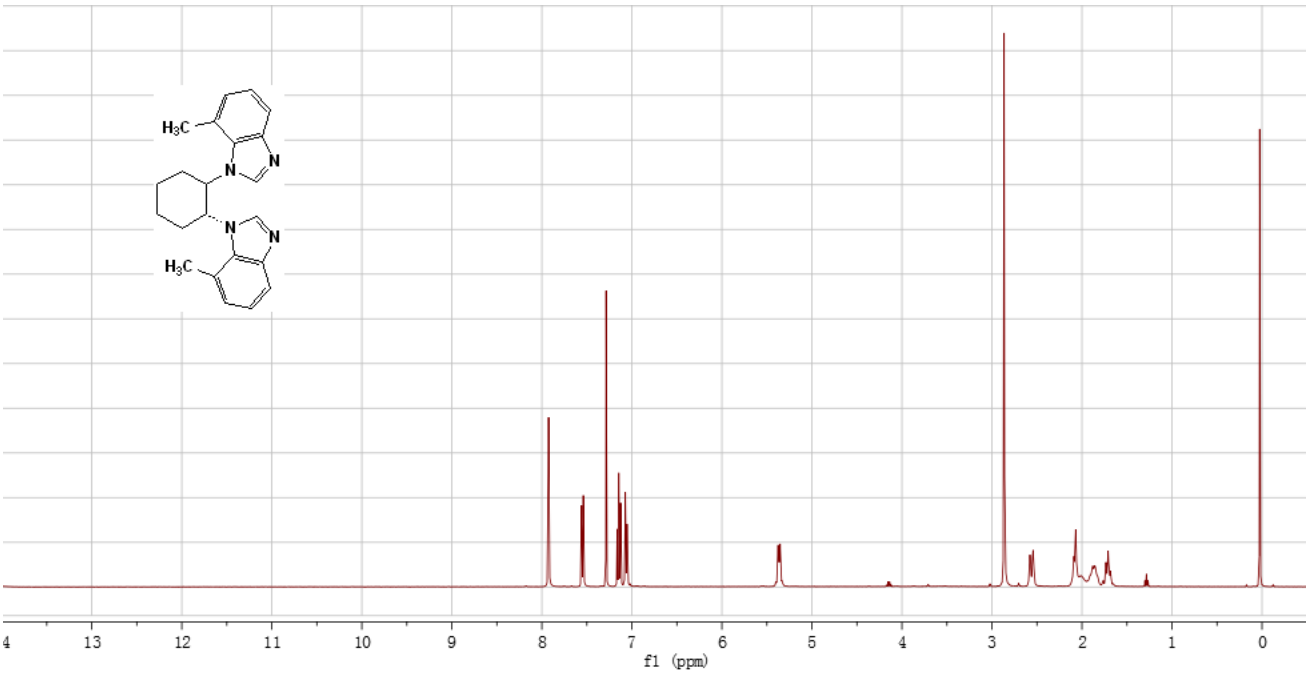

Figure S20. The ^{1}H NMR spectrum of (*R,R*)-**1b** in $CDCl_3$ at 20 ^{o}C

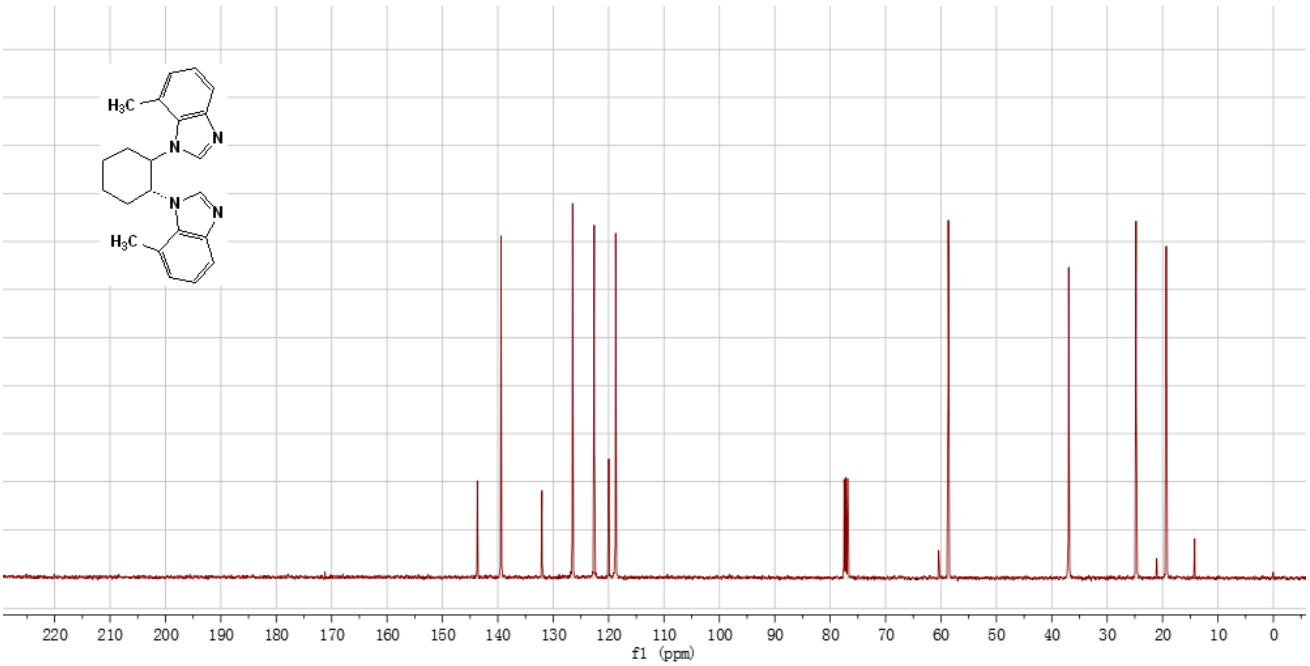

Figure S21. The ^{13}C NMR spectrum of (*R,R*)-**1b** in $CDCl_3$ at 20 ^{o}C

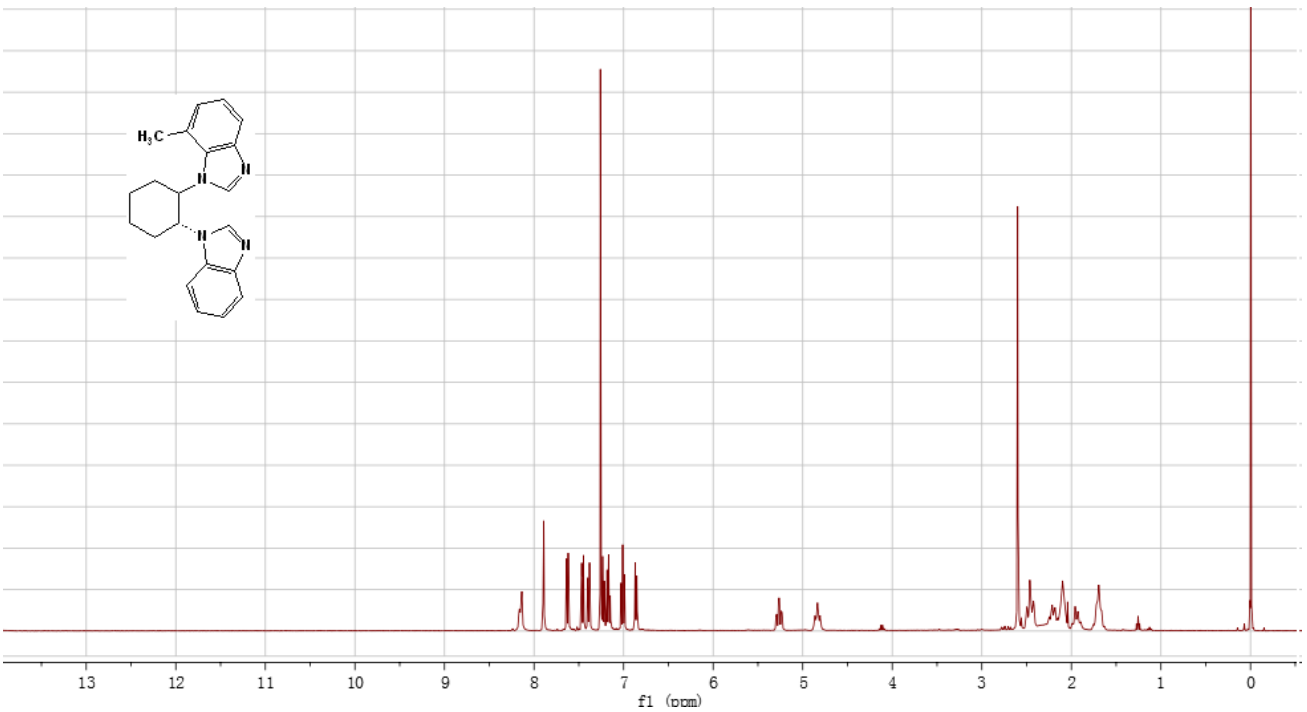

Figure S22. The ^{1}H NMR spectrum of (*R,R*)-**1c** in $CDCl_3$ at 20 ^{o}C

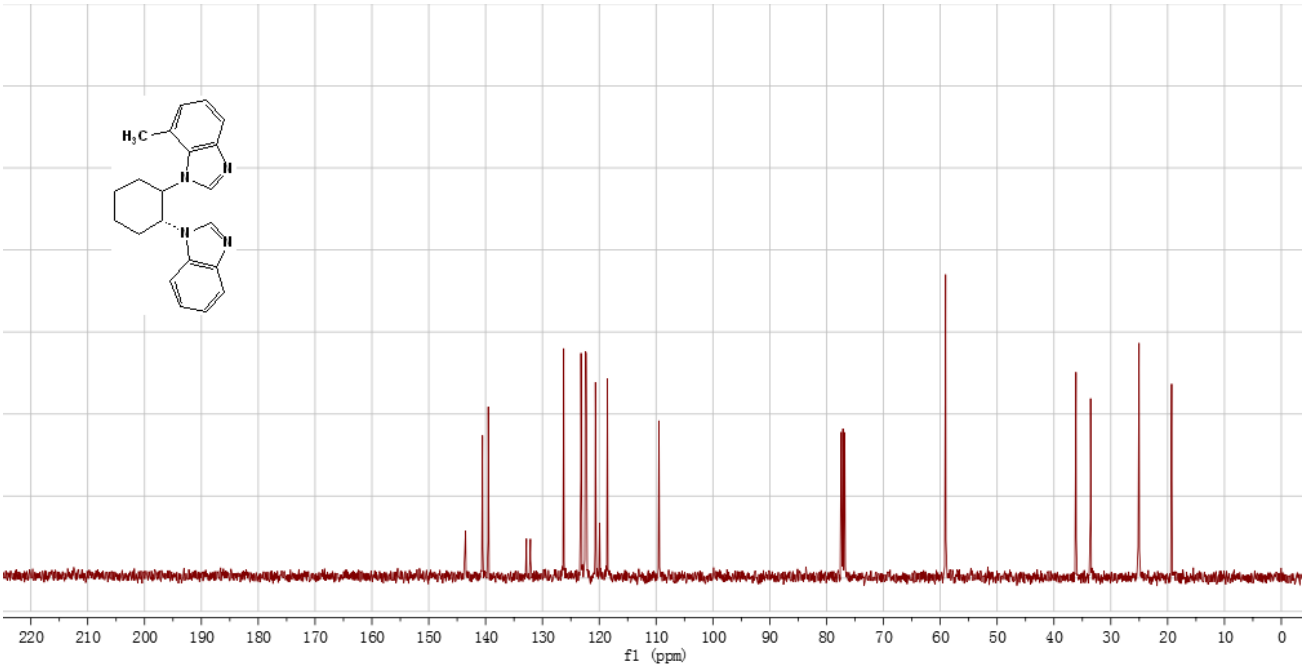

Figure S23. The ^{13}C NMR spectrum of (*R,R*)-**1c** in $CDCl_3$ at 20 ^{o}C

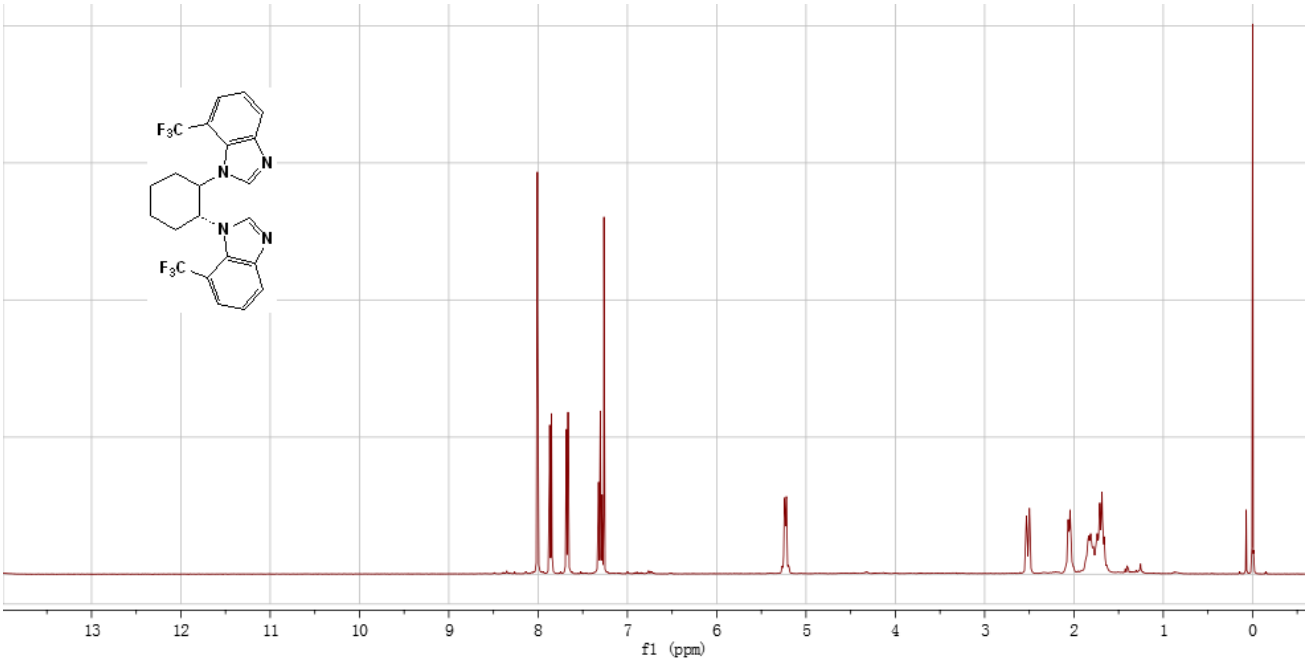

Figure S24. The ^{1}H NMR spectrum of (*R,R*)-**1d** in $CDCl_3$ at 20 ^{o}C

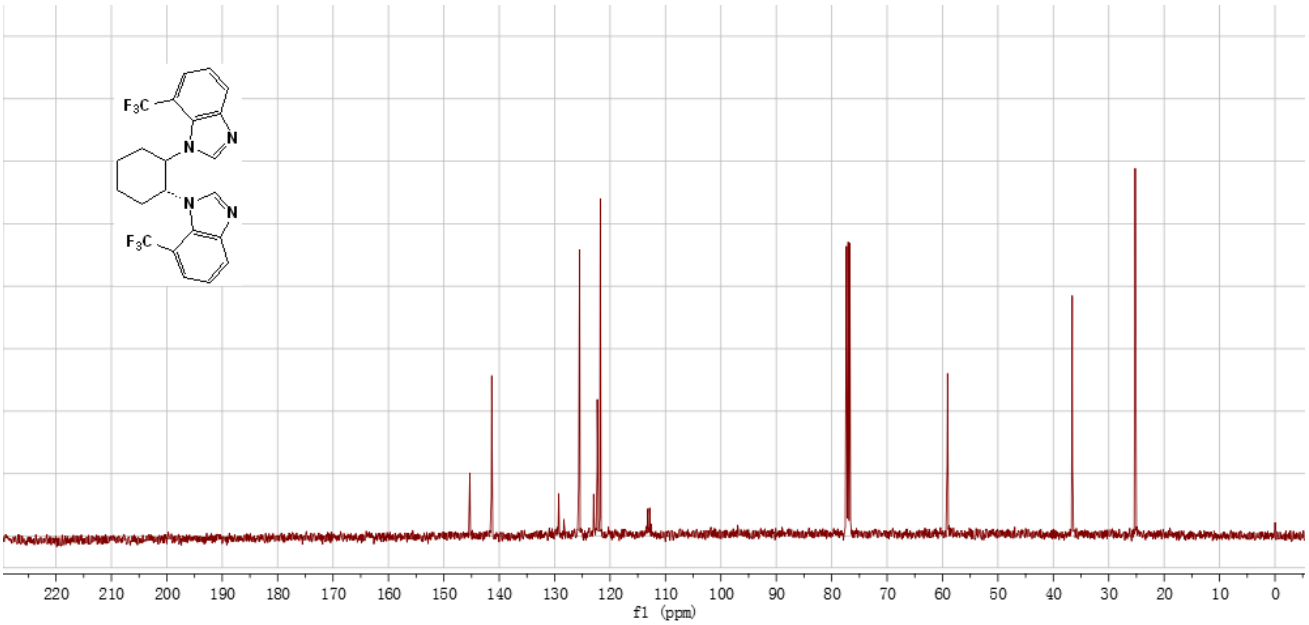

Figure S25. The ^{13}C NMR spectrum of (*R,R*)-**1d** in $CDCl_3$ at 20 ^{o}C

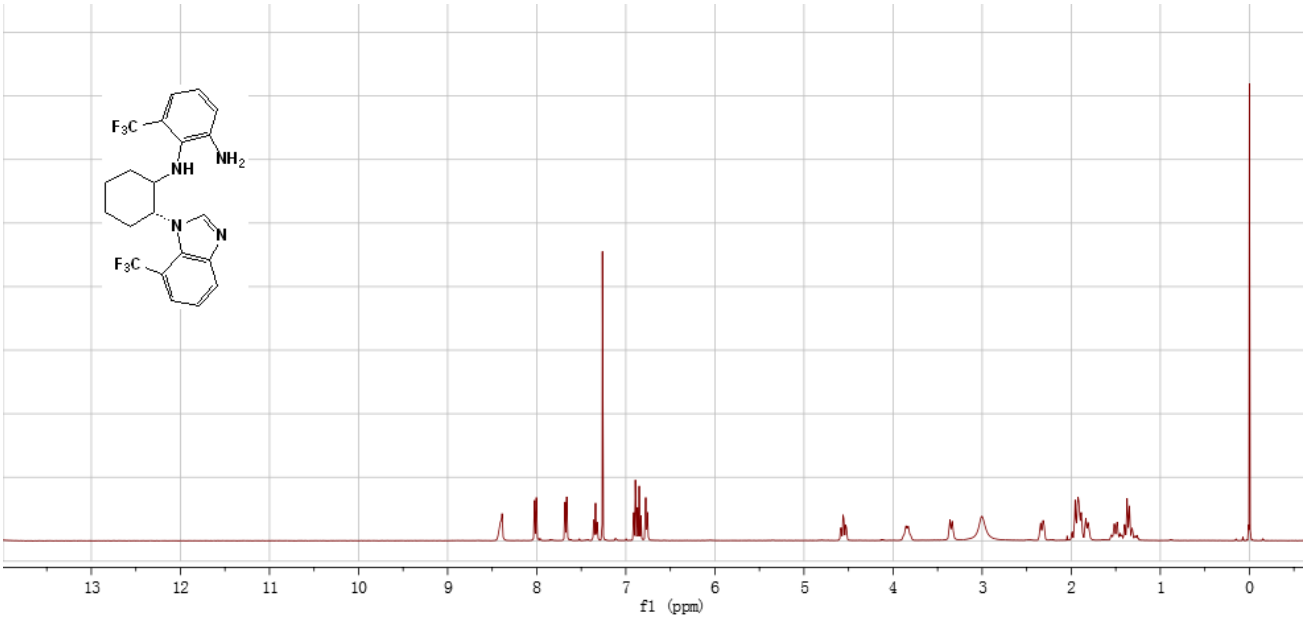

Figure S26. The ^{1}H NMR spectrum of (*R,R*)-**1d'** in $CDCl_3$ at 20 ^{o}C

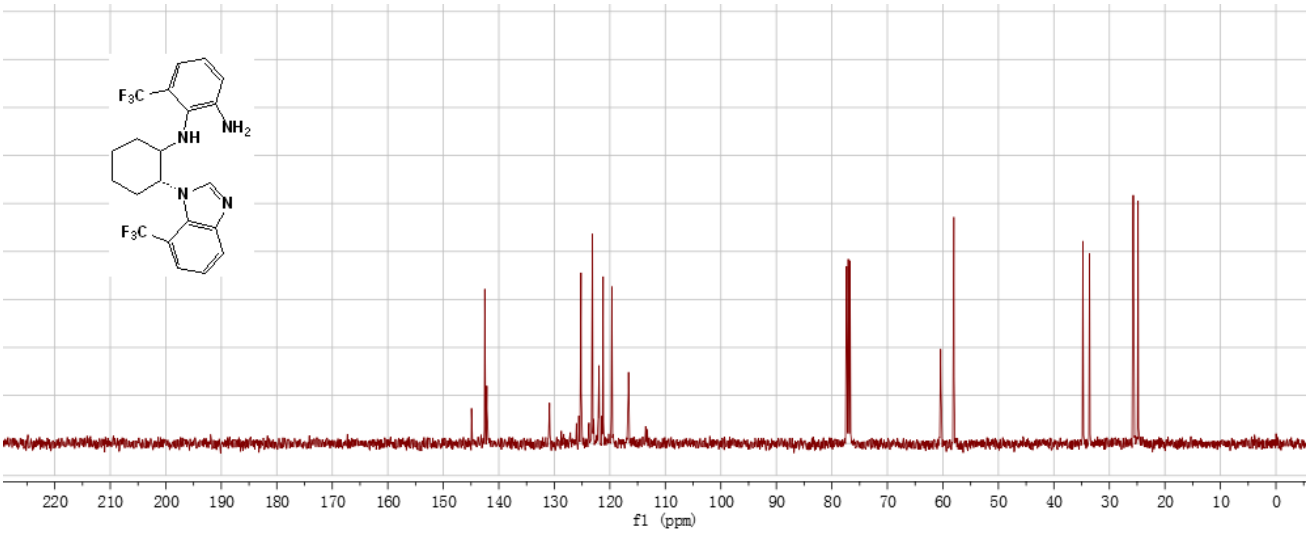

Figure S27. The ^{13}C NMR spectrum of (*R,R*)-**1d'** in $CDCl_3$ at 20 ^{o}C

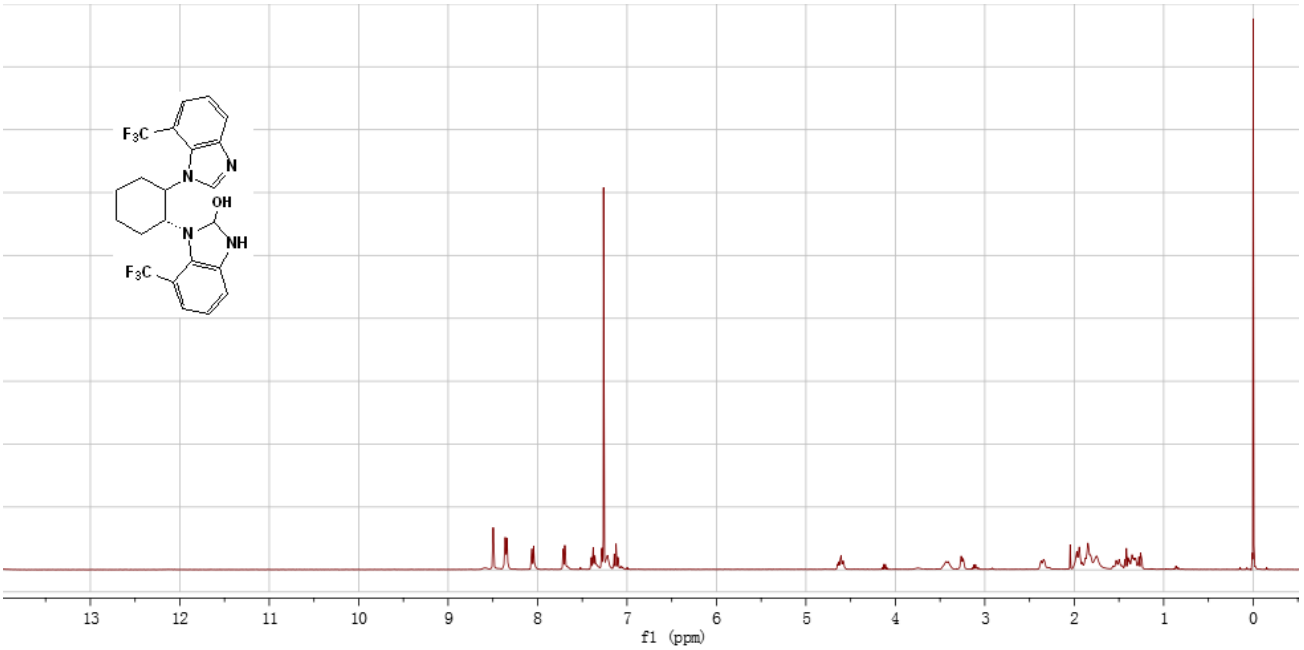

Figure S28. The ^{1}H NMR spectrum of (*R,R*)-**1d''** in $CDCl_3$ at 20 ^{o}C

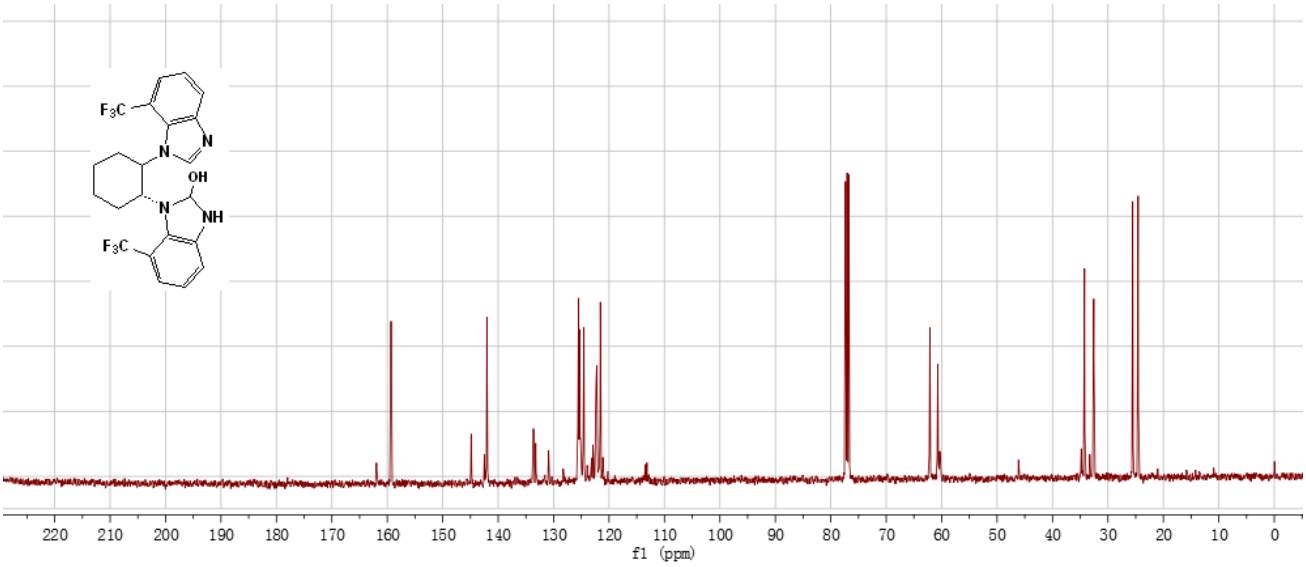

Figure S29. The ^{13}C NMR spectrum of (*R,R*)-**1d''** in $CDCl_3$ at 20 ^{o}C

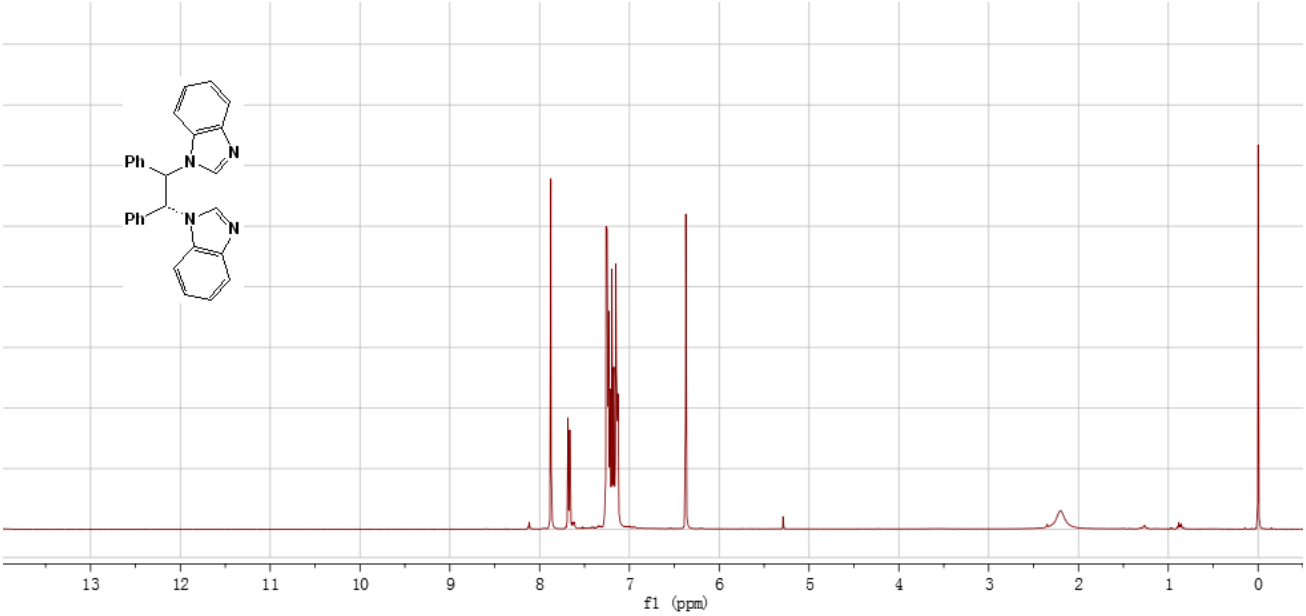

Figure S30. The ^{1}H NMR spectrum of (*R,R*)-**4** in $CDCl_3$ at 20 ^{o}C

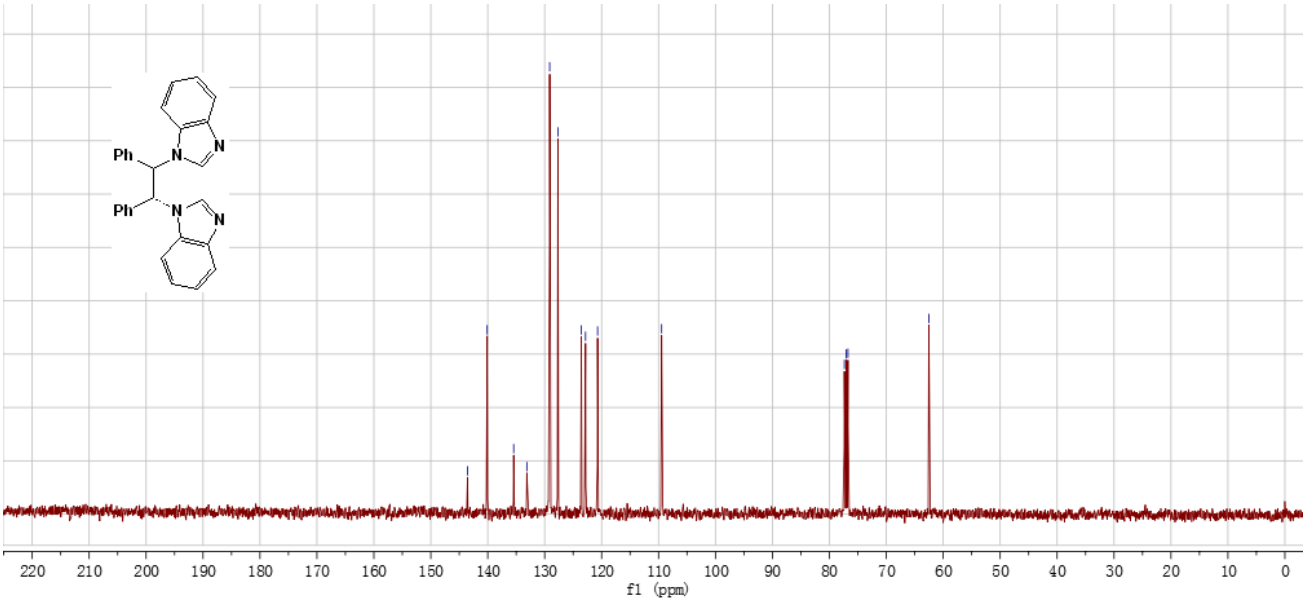

Figure S31. The ^{13}C NMR spectrum of (*R,R*)-**4** in $CDCl_3$ at 20 ^{o}C

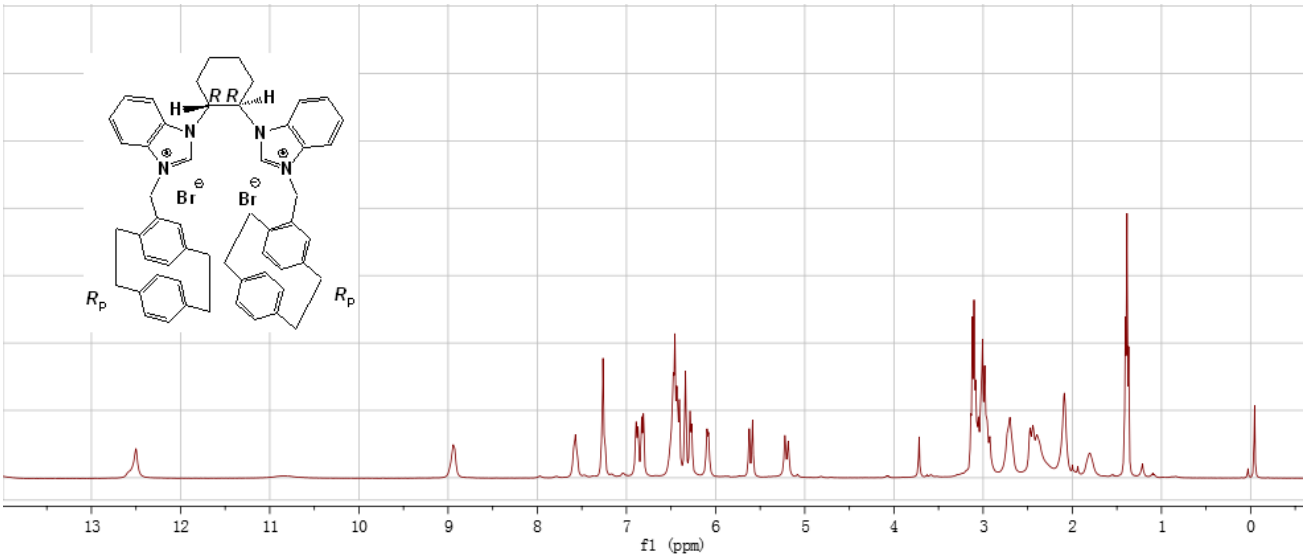

Figure S32. The ^{1}H NMR spectrum of (*R,R,R$_p$,R$_p$*)-**11** in $CDCl_3$ at 20 ^{o}C

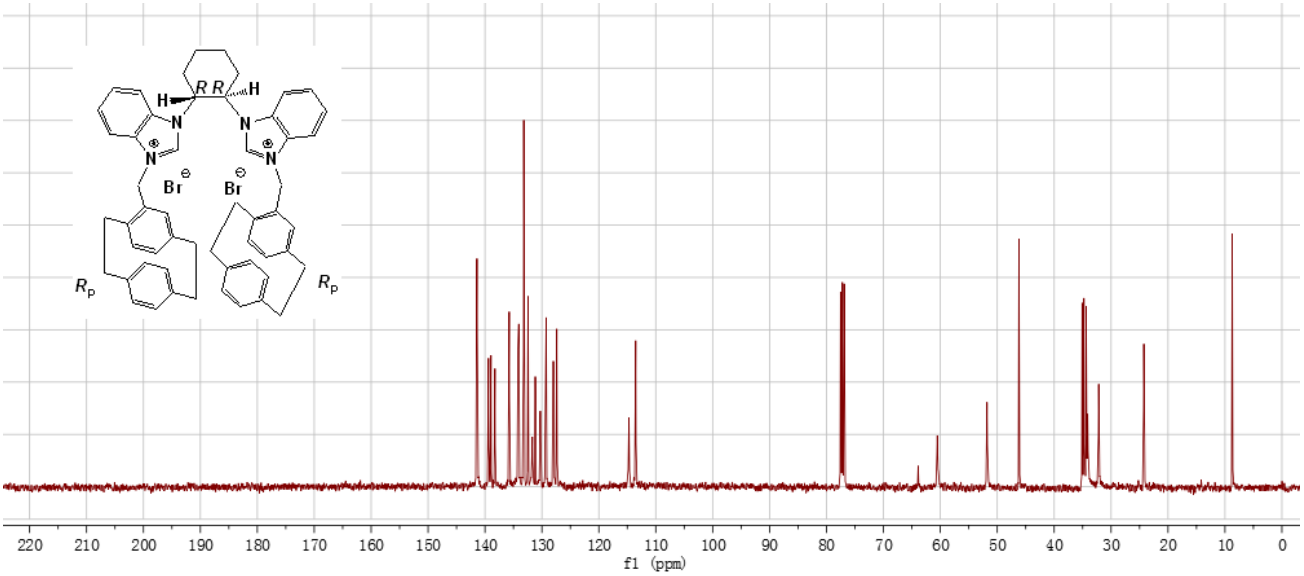

Figure S33. The ^{13}C NMR spectrum of (R,R,R_p,R_p)-**11** in $CDCl_3$ at 20 ^oC

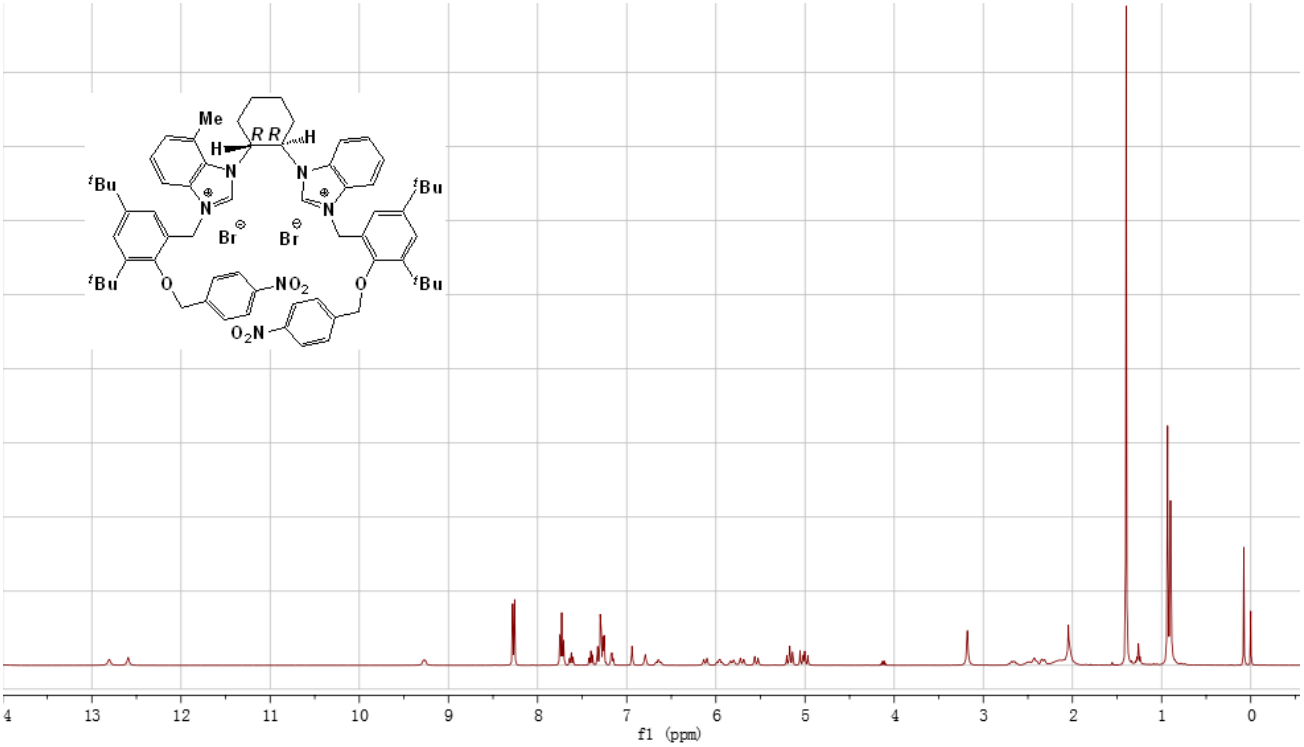

Figure S34. The ^1H NMR spectrum of (*R,R*)-**12** in $CDCl_3$ at 20 ^oC

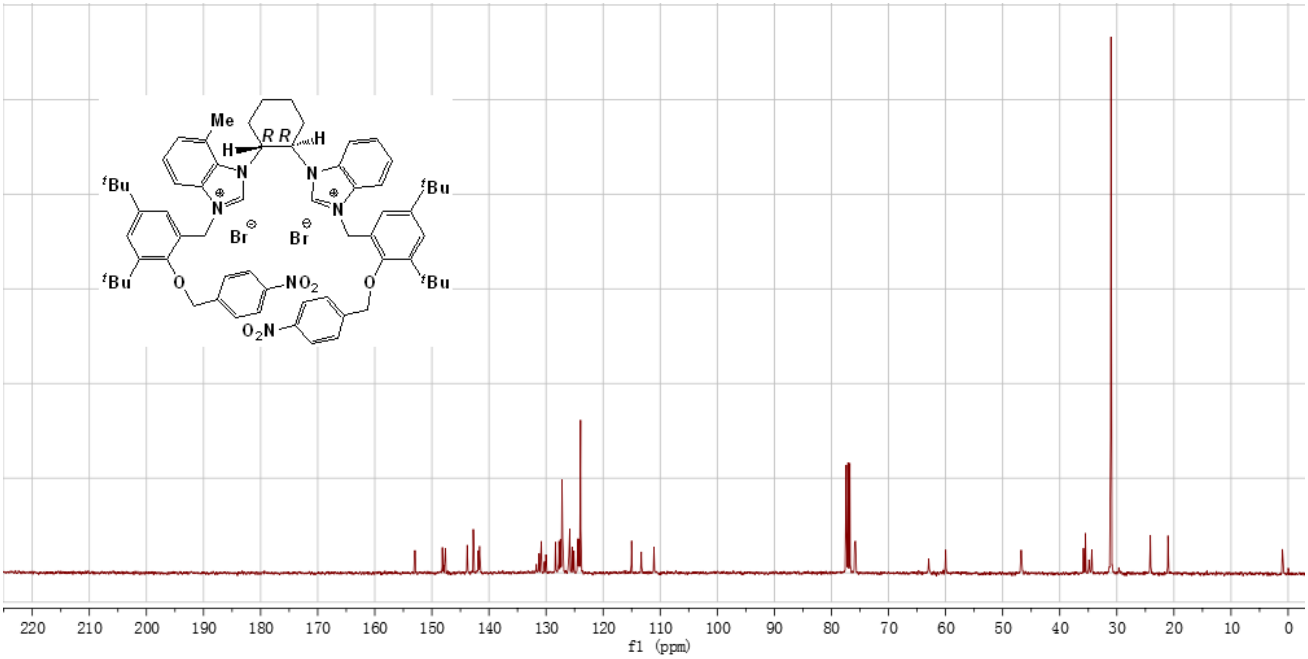

Figure S35. The ^{13}C NMR spectrum of (*R,R*)-**12** in $CDCl_3$ at 20 ^{o}C

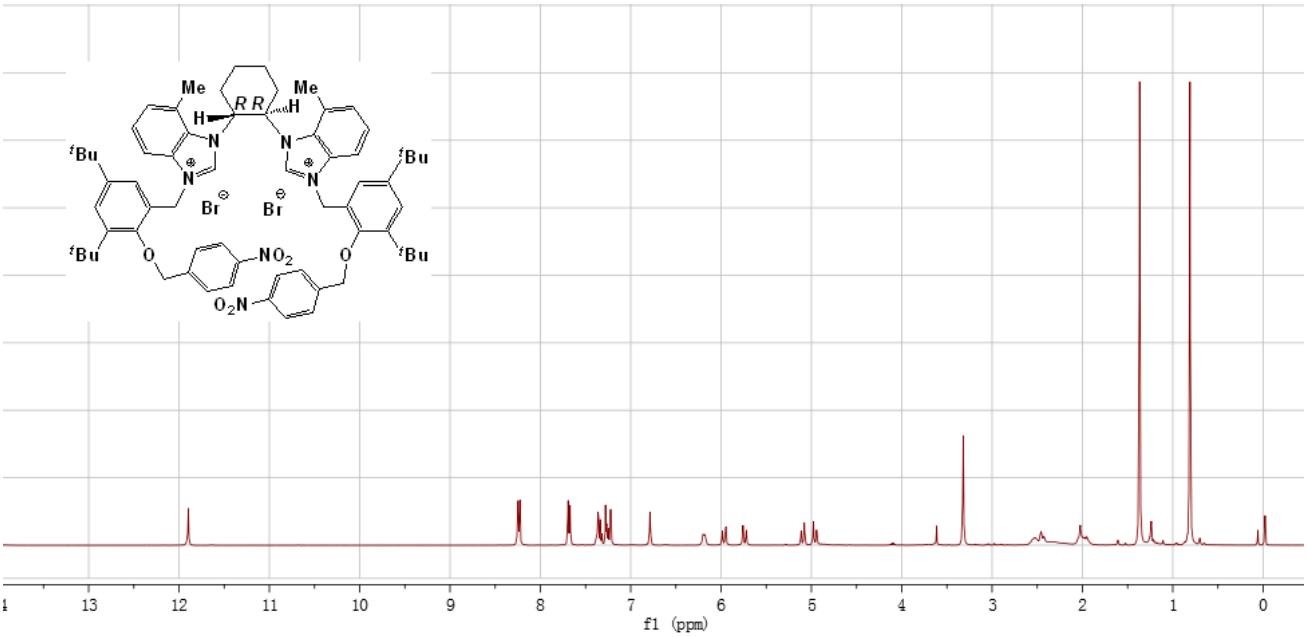

Figure S36. The ^{1}H NMR spectrum of (*R,R*)-**13** in $CDCl_3$ at 20 ^{o}C

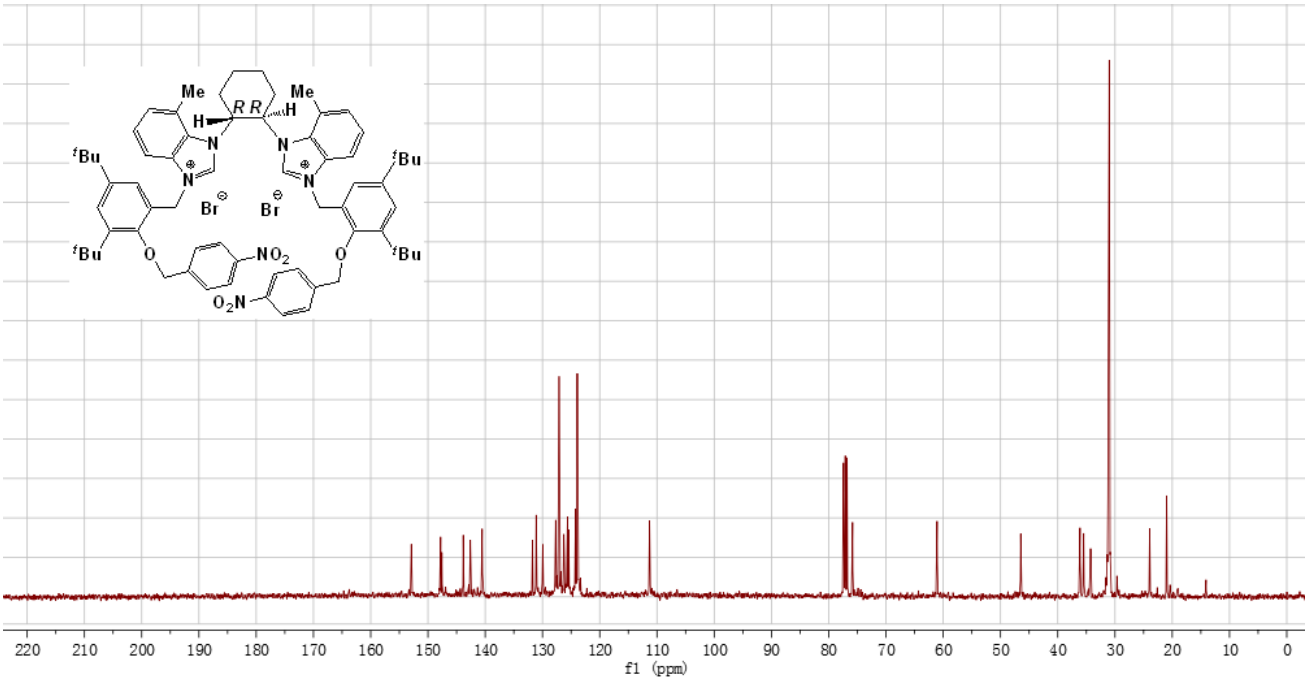

Figure S37. The ^{13}C NMR spectrum of (*R,R*)-**13** in $CDCl_3$ at 20 ^{o}C

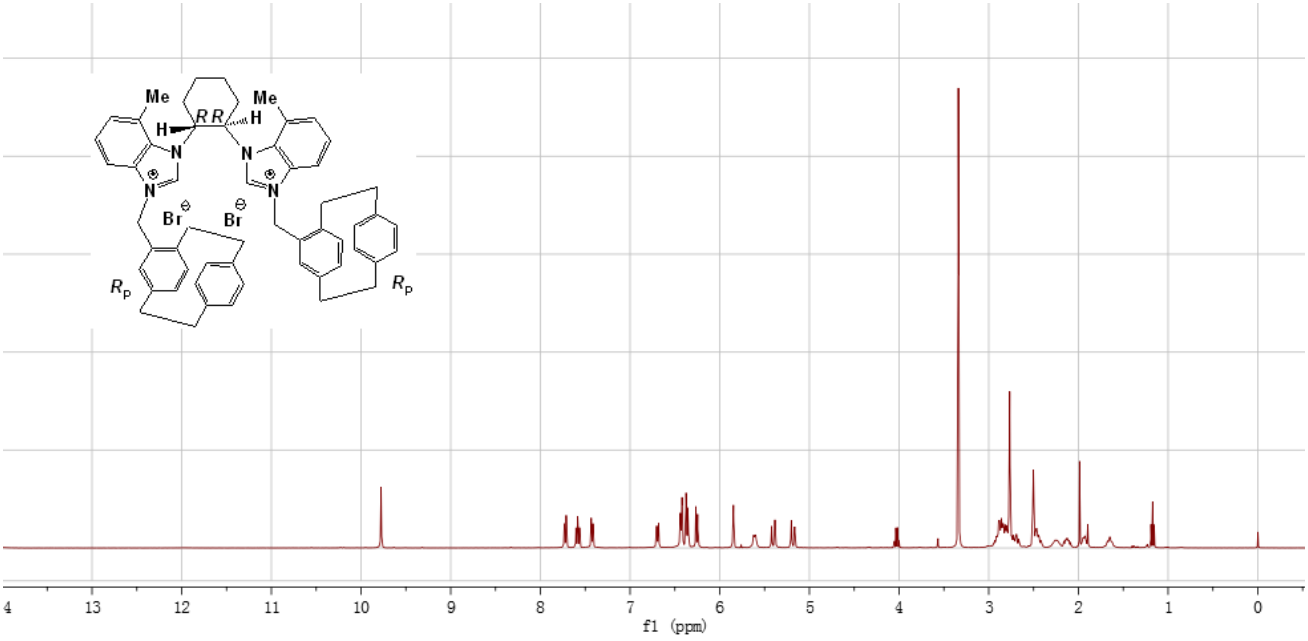

Figure S38. The ^{1}H NMR spectrum of (R,R,R_p,R_p)-**14** in $(CD_3)_2SO$ at 20 ^{o}C

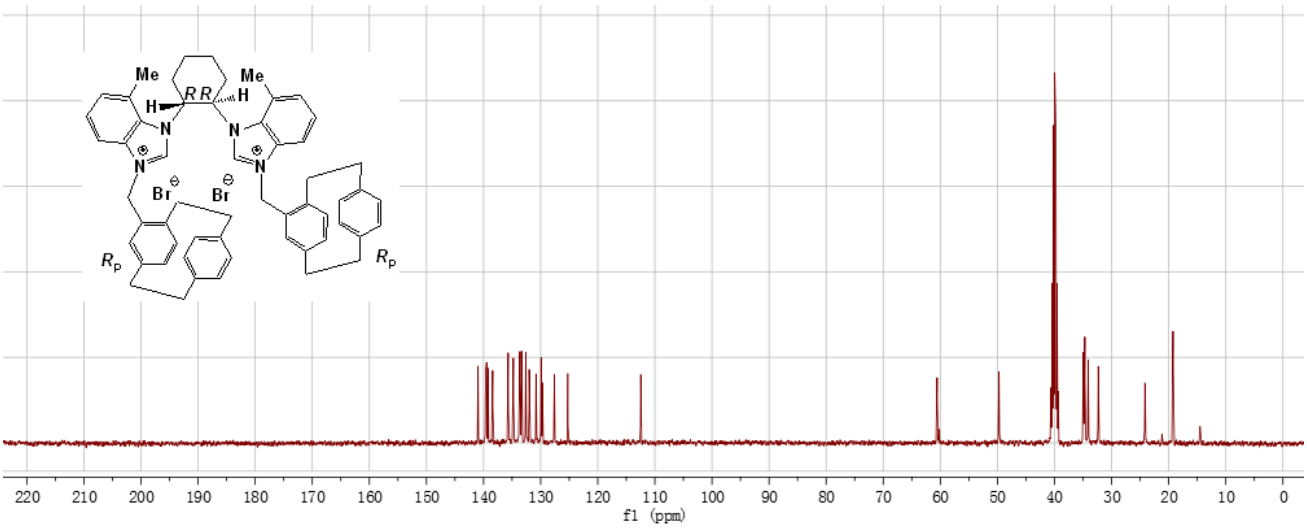

Figure S39. The ^{13}C NMR spectrum of (R,R,R_p,R_p)-**14** in $(CD_3)_2SO$ at 20 ^oC

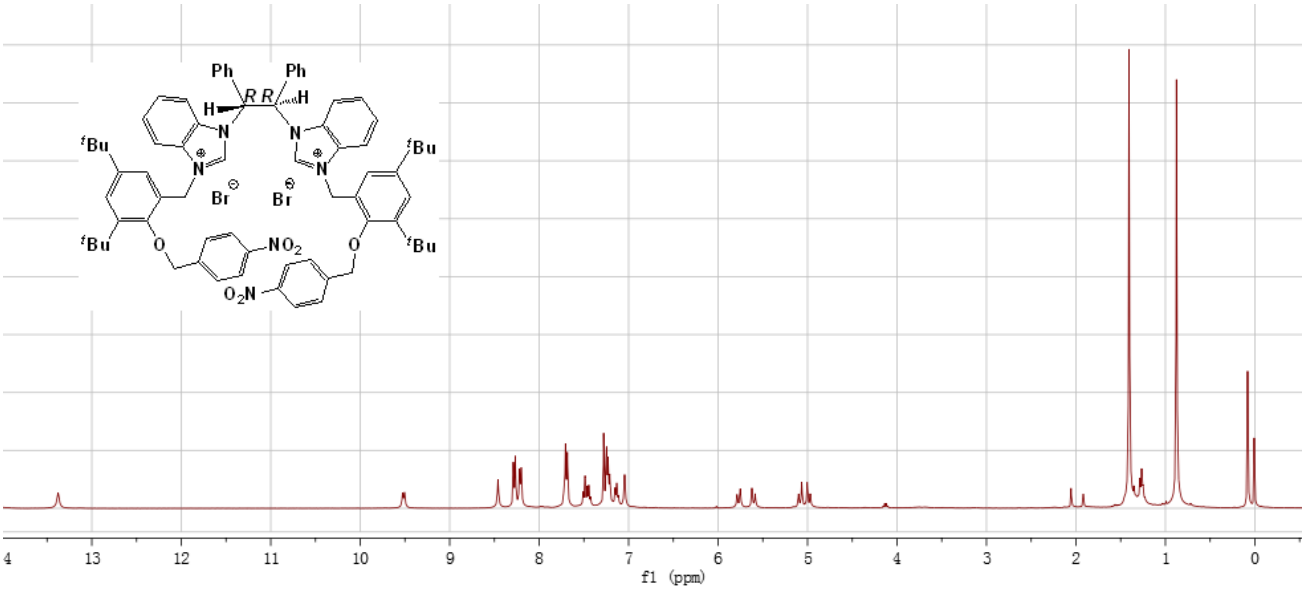

Figure S40. The ^1H NMR spectrum of (*R,R*)-**15** in $CDCl_3$ at 20 ^oC

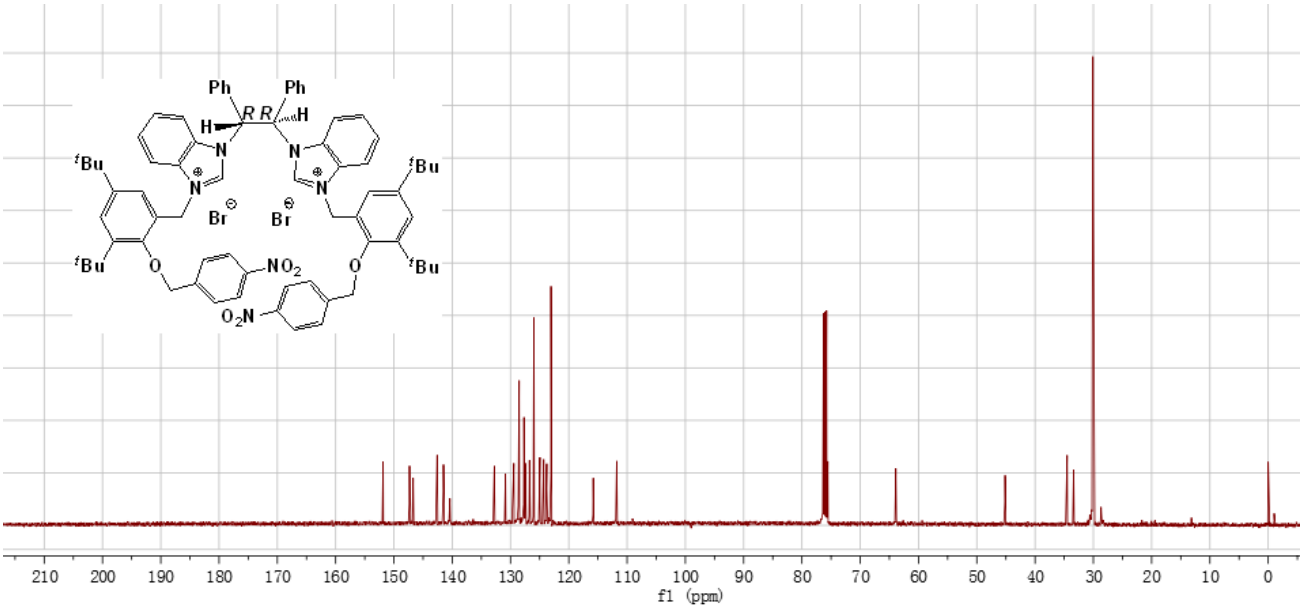

Figure S41. The ^{13}C NMR spectrum of (*R,R*)-**15** in $CDCl_3$ at 20 ^{o}C

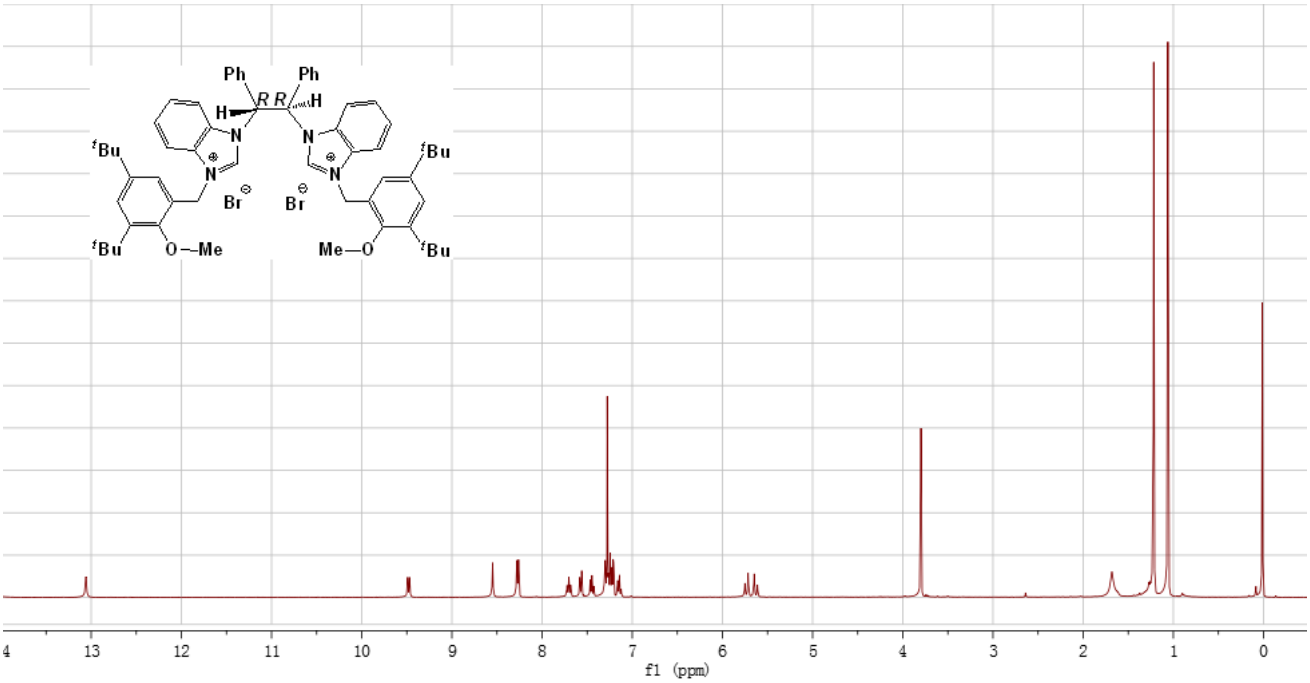

Figure S42. The ^{1}H NMR spectrum of (*R,R*)-**16** in $CDCl_3$ at 20 ^{o}C

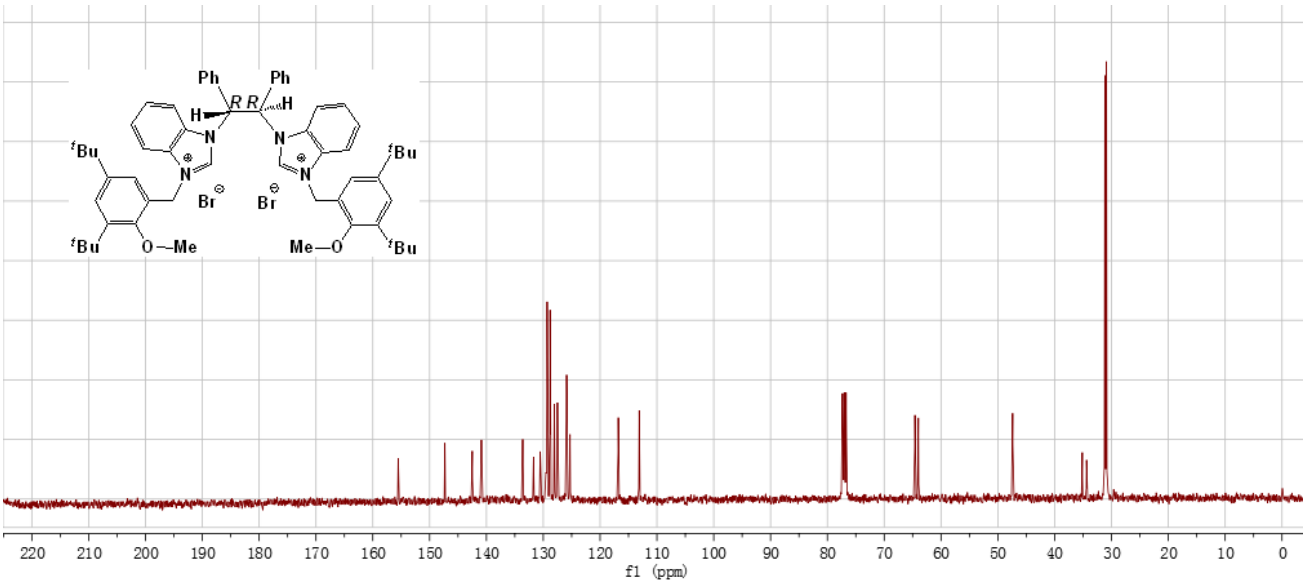

Figure S43. The ^{13}C NMR spectrum of (*R,R*)-**16** in $CDCl_3$ at 20 ^{o}C

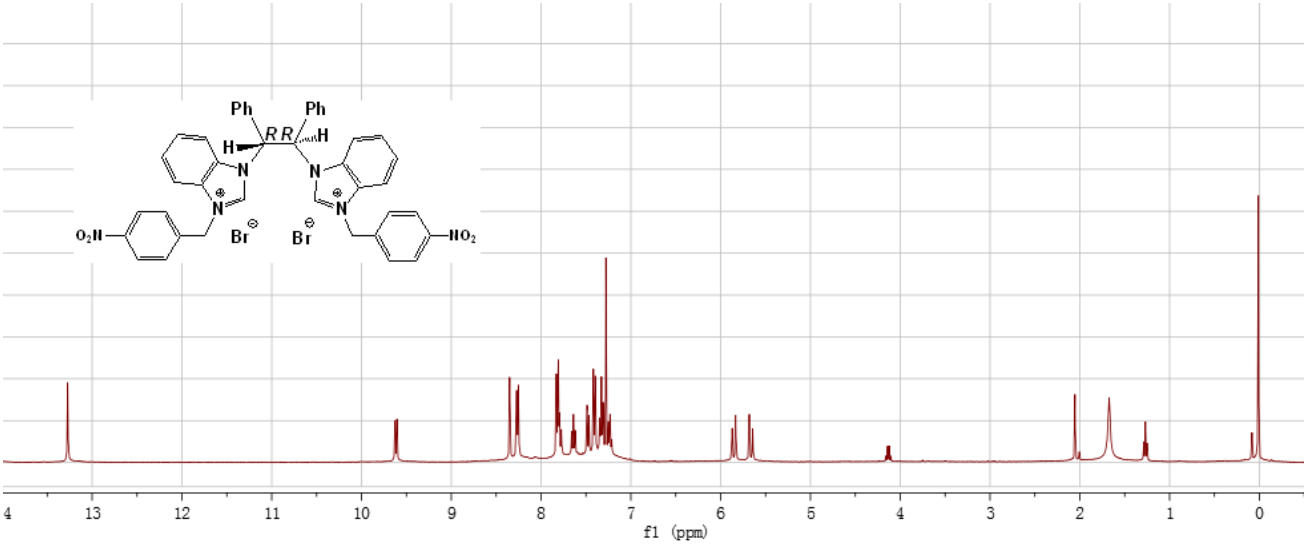

Figure S44. The ^{1}H NMR spectrum of (*R,R*)-**17** in $CDCl_3$ at 20 ^{o}C

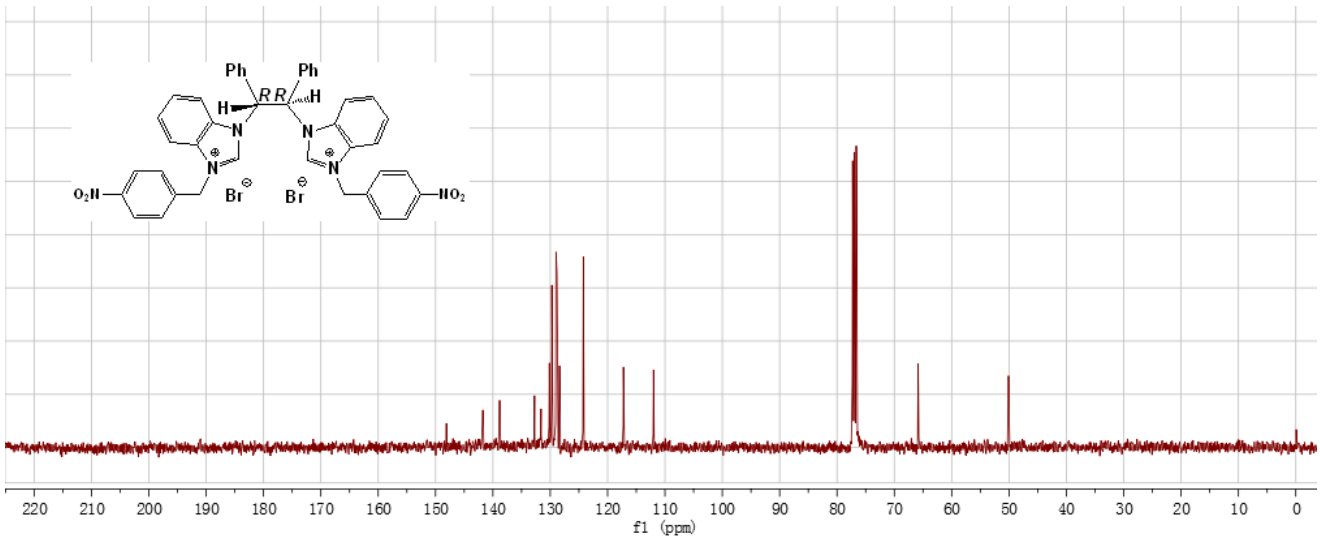

Figure S45. The ^{13}C NMR spectrum of (*R,R*)-**17** in $CDCl_3$ at 20 ^{o}C

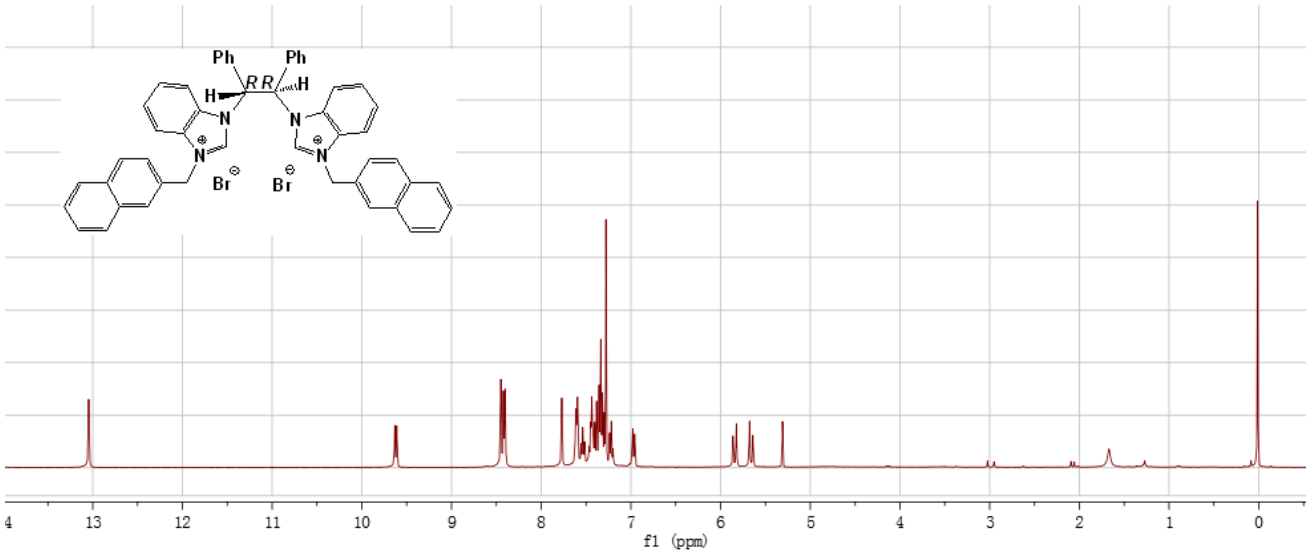

Figure S46. The ^{1}H NMR spectrum of (*R,R*)-**18** in $CDCl_3$ at 20 ^{o}C

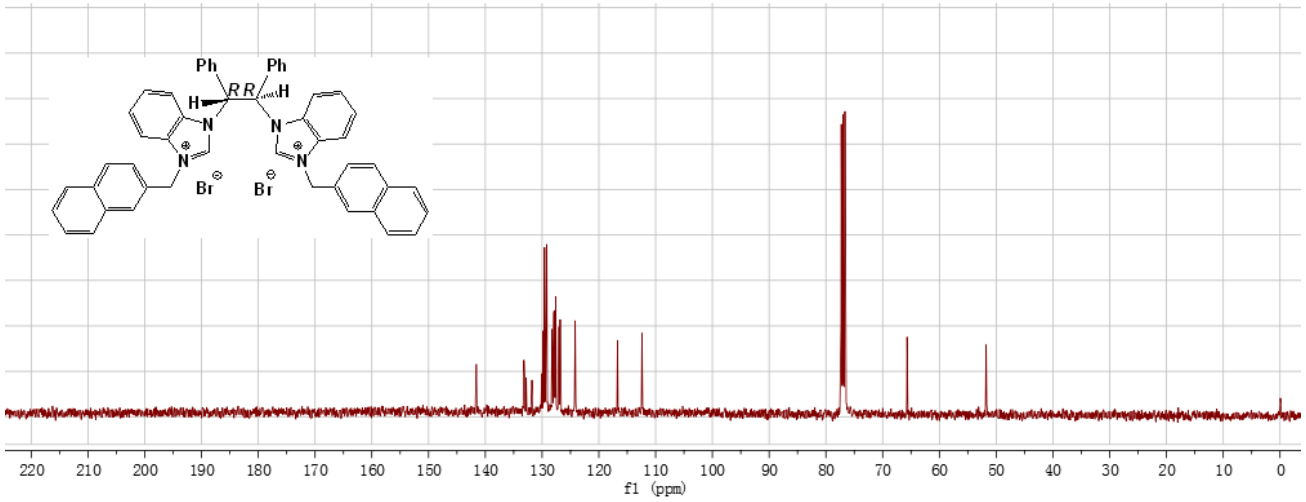

Figure S47. The ^{13}C NMR spectrum of (*R,R*)-**18** in $CDCl_3$ at 20 ^{o}C

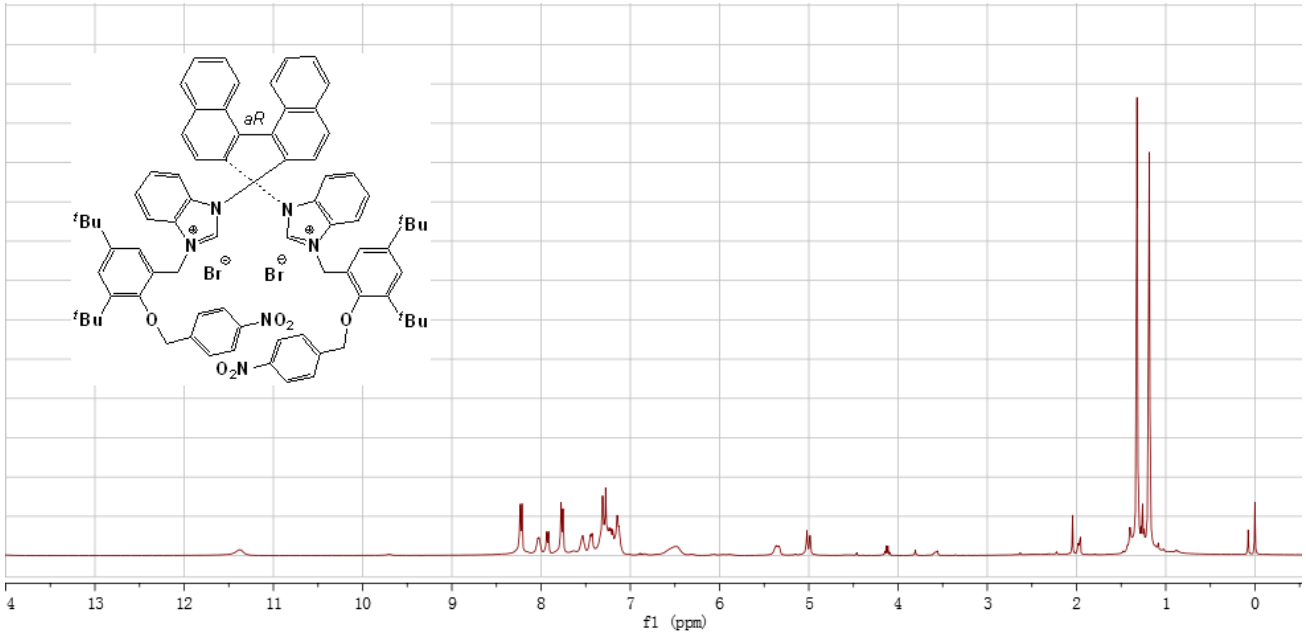

Figure S48. The ^{1}H NMR spectrum of (*aR*)-**19** in $CDCl_3$ at 20 ^{o}C

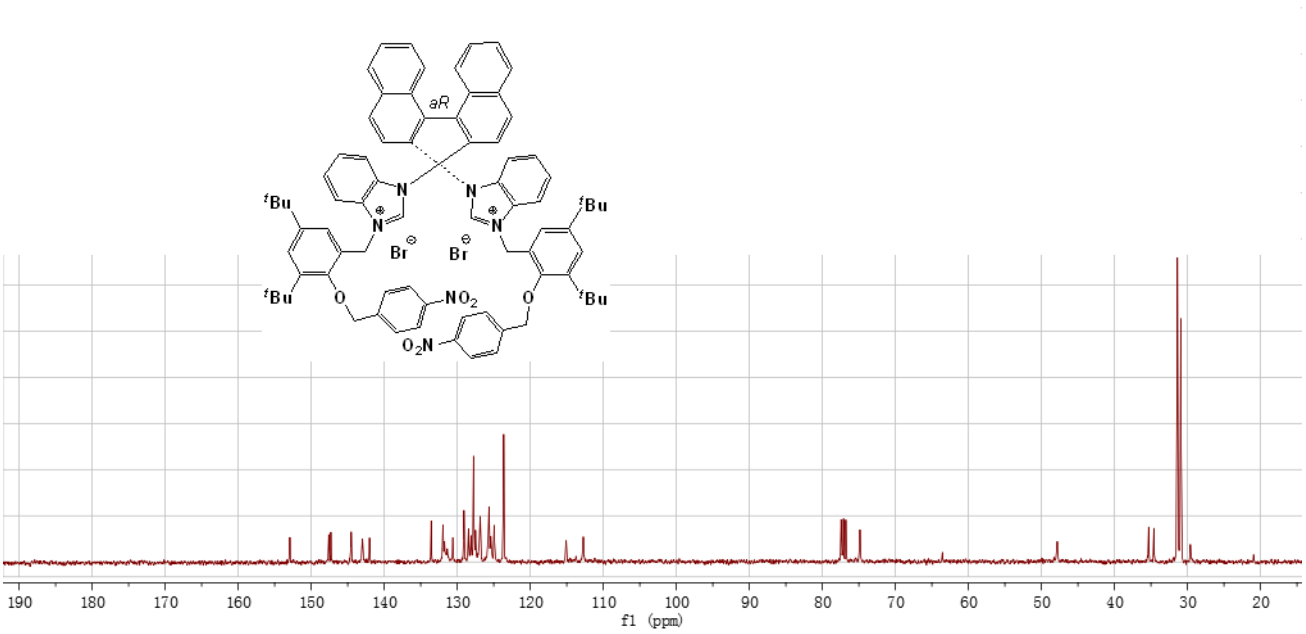

Figure S49. The ^{13}C NMR spectrum of (*aR*)-**19** in $CDCl_3$ at 20 ^{o}C

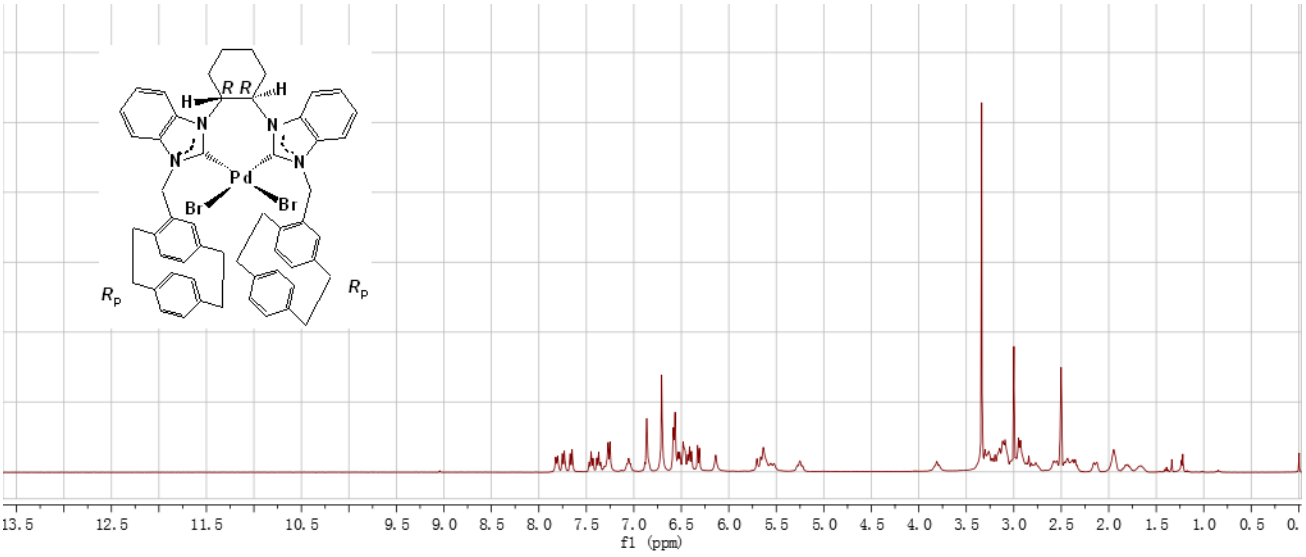

Figure S50. The ^{1}H NMR spectrum of (*R,R,R*$_p$,*R*$_p$)-**21** in $(CD_3)_2SO$ at 20 ^{o}C

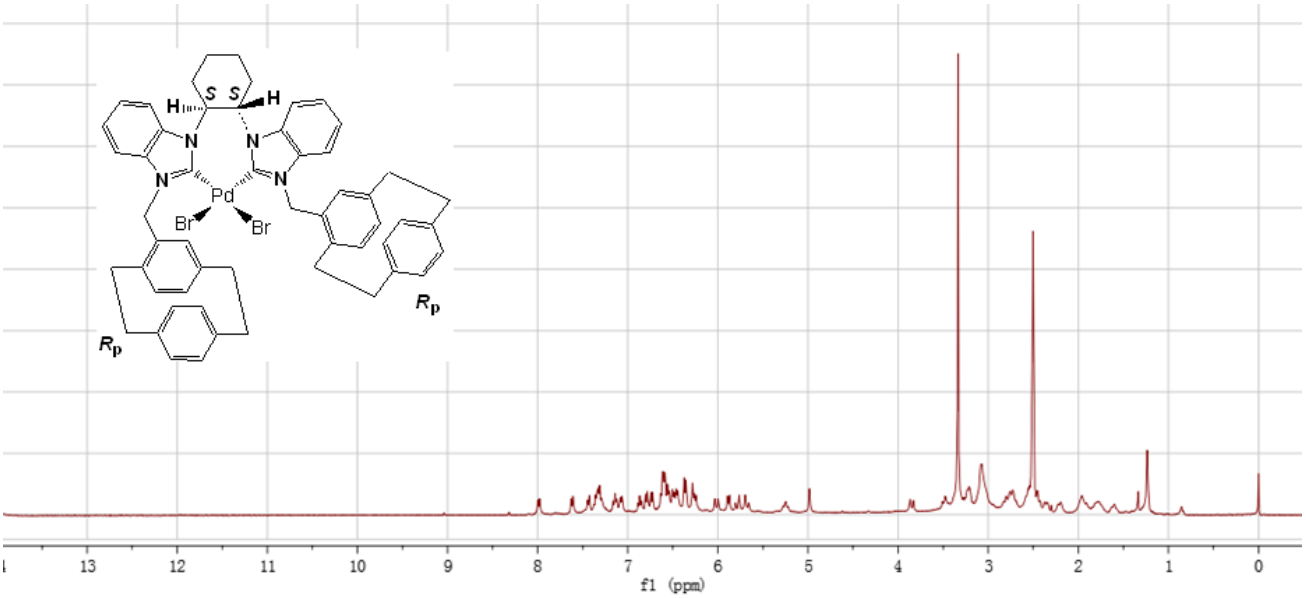

Figure S51. The ^{1}H NMR spectrum of (*R,R,R*$_p$,*R*$_p$)-**21** in $(CD_3)_2SO$ at 20 ^{o}C

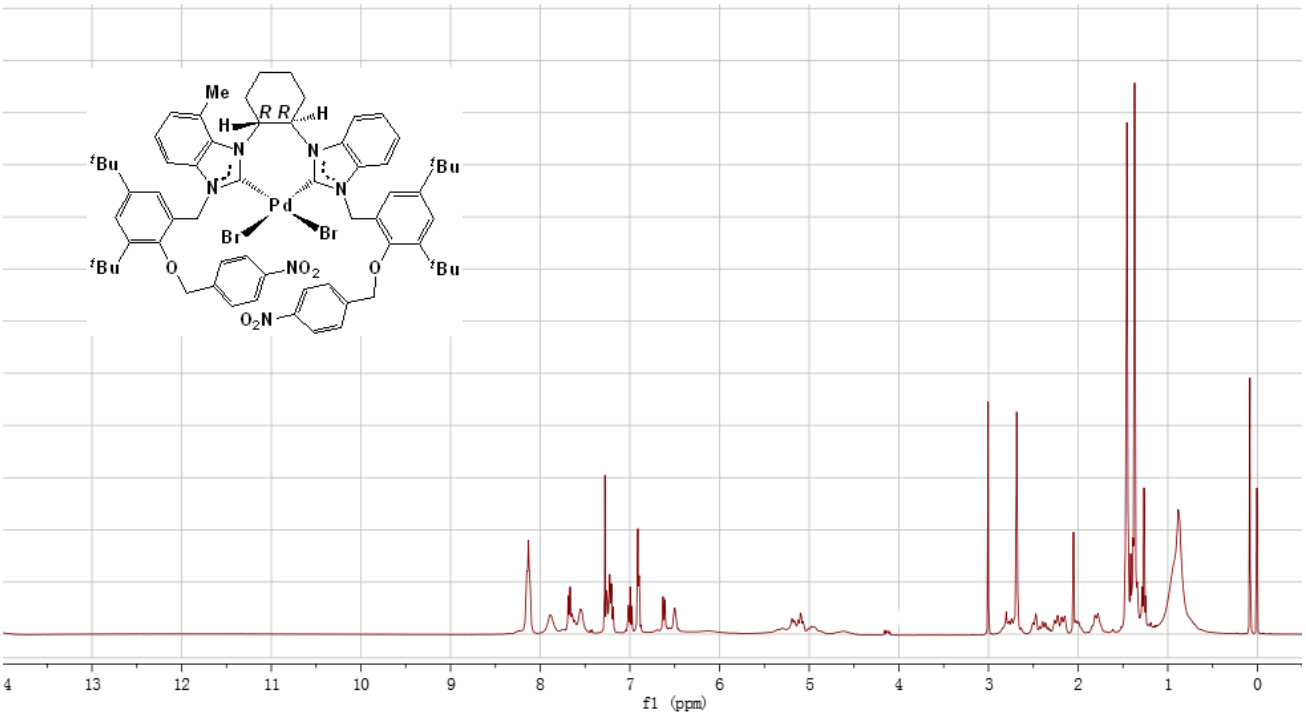

Figure S52. The ^{1}H NMR spectrum of (*R,R*)-**22** in $CDCl_3$ at 20 ^{o}C

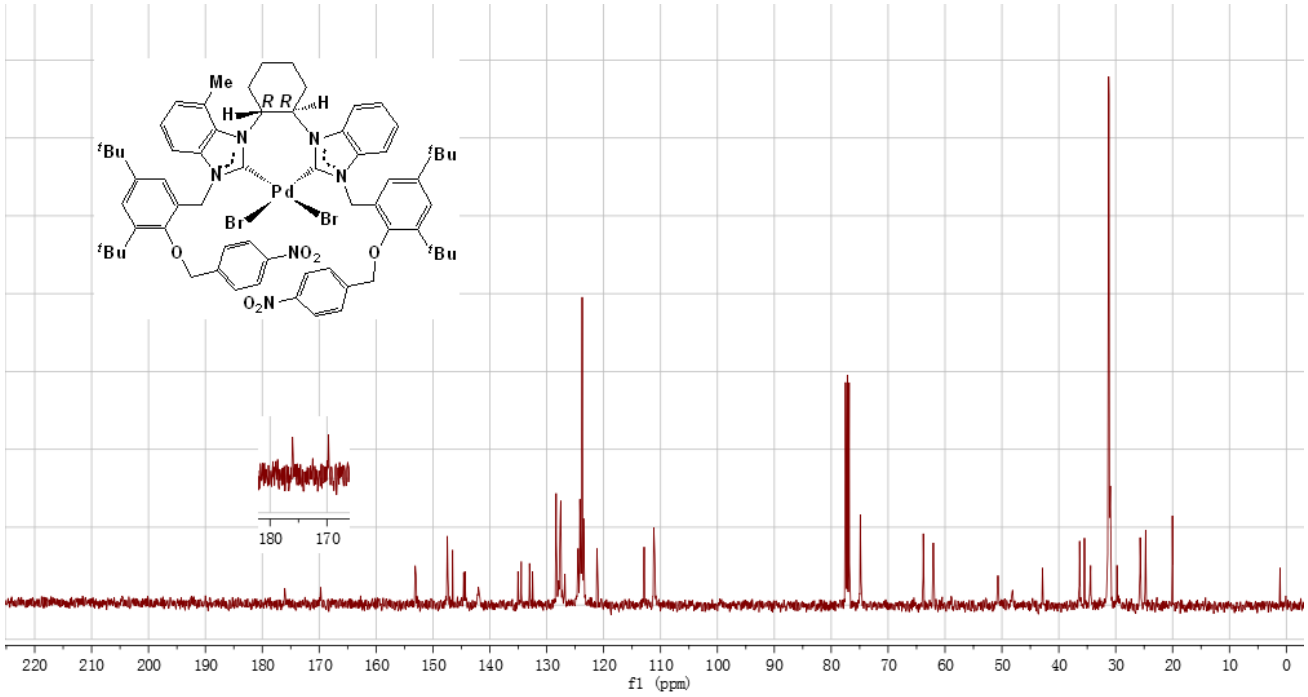

Figure S53. The ^{13}C NMR spectrum of (*R,R*)-**22** in $CDCl_3$ at 20 ^{o}C

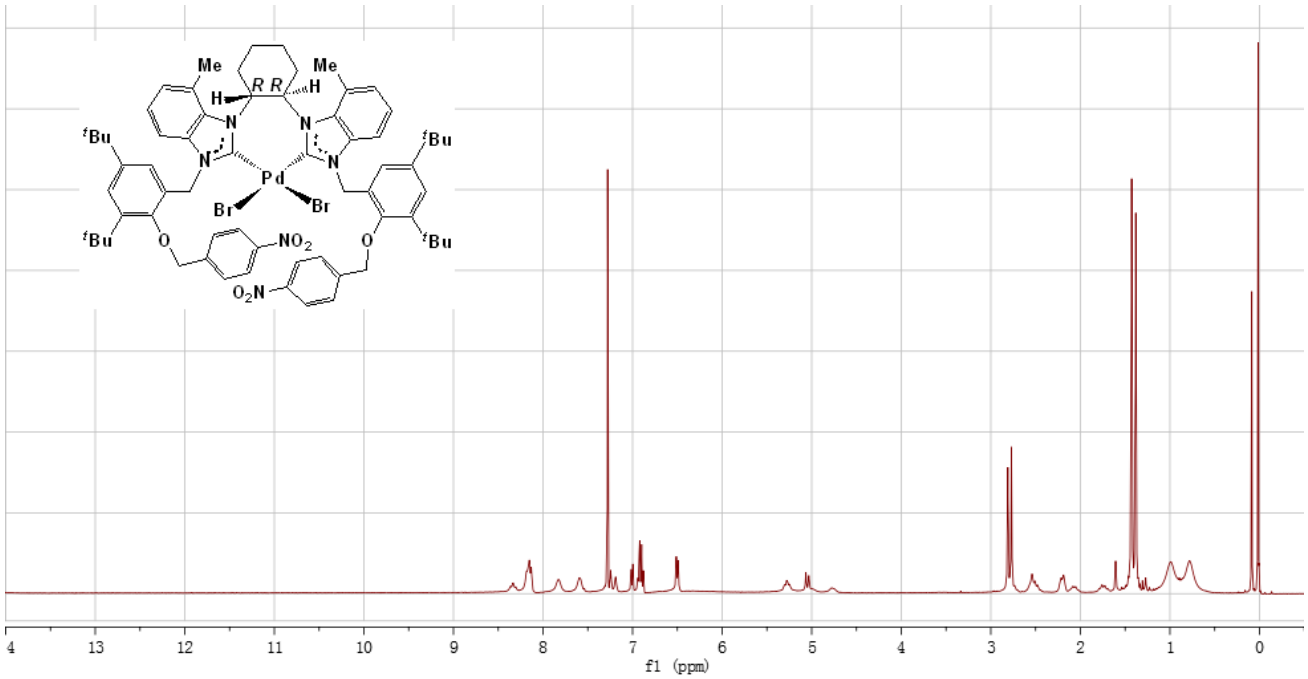

Figure S54. The ^{1}H NMR spectrum of (*R,R*)-**23** in $CDCl_3$ at 20 ^{o}C

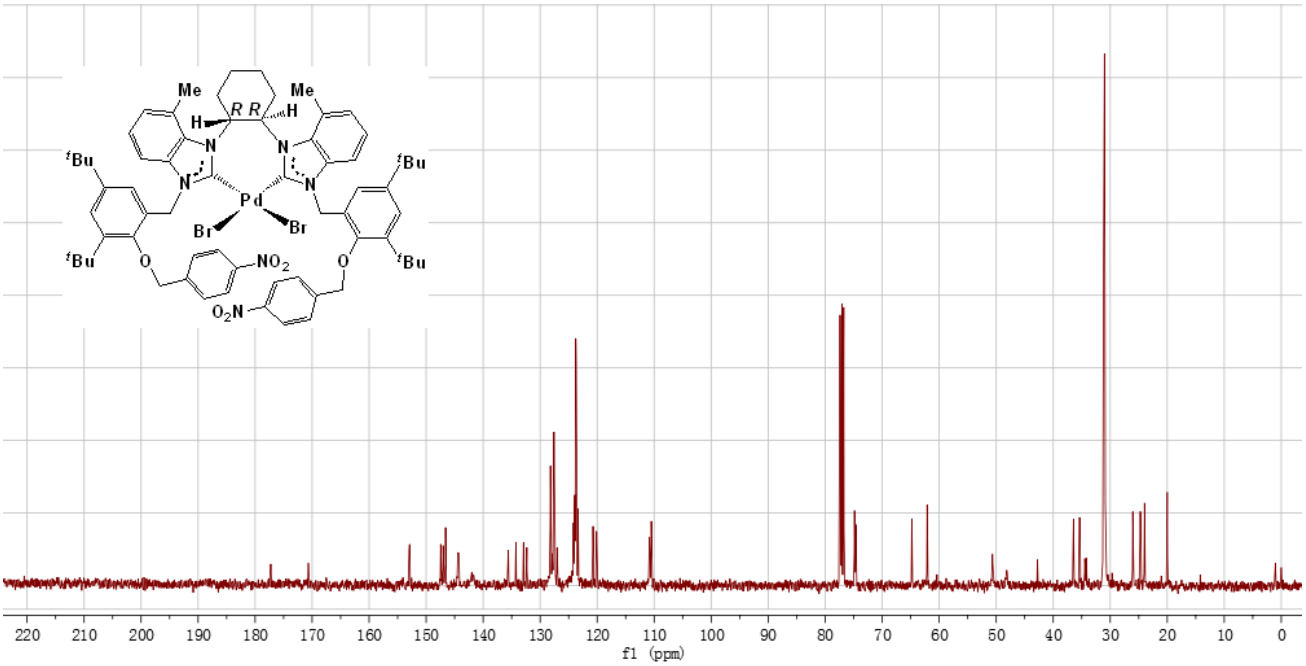

Figure S55. The ^{13}C NMR spectrum of (*R,R*)-**23** in $CDCl_3$ at 20 ^{o}C

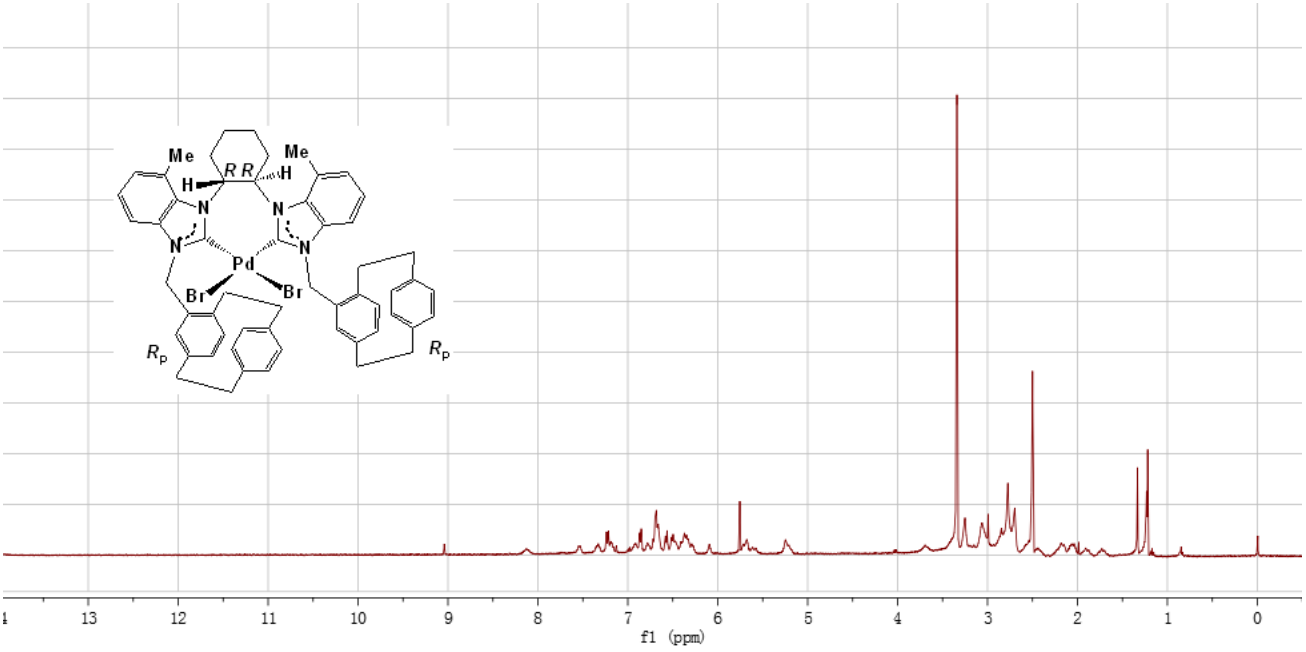

Figure S56. The ^{1}H NMR spectrum of (R,R,R_p,R_p)-**24** in $(CD_3)_2SO$ at 20 ^{o}C

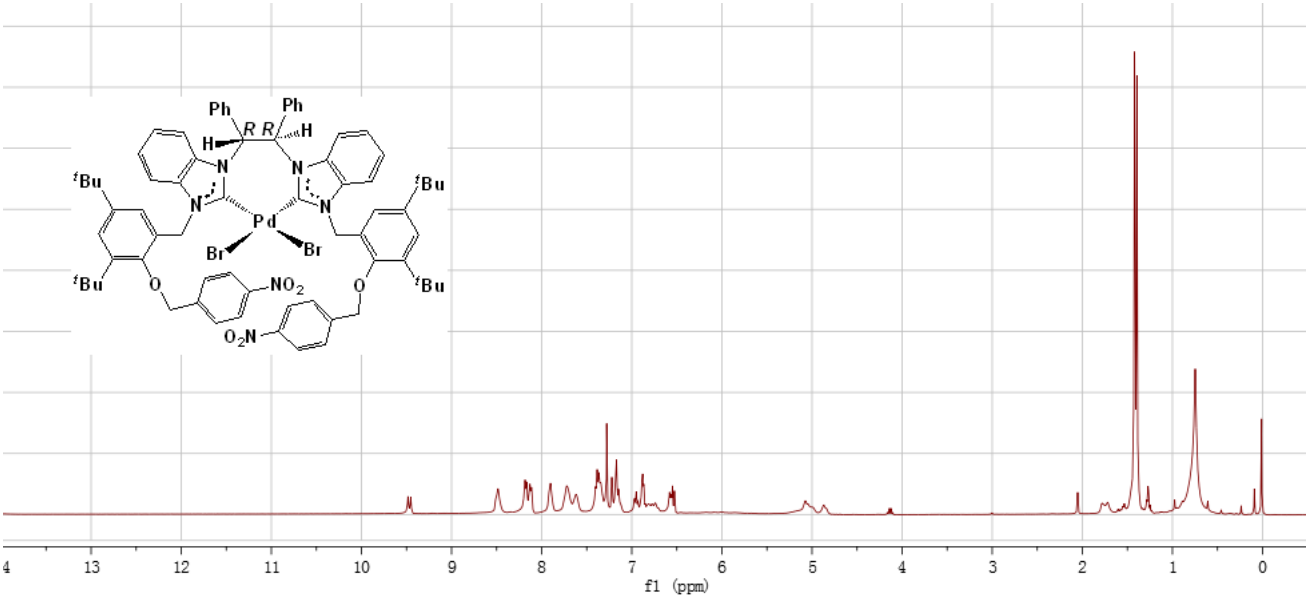

Figure S57. The ^{1}H NMR spectrum of (*R,R,R*$_p$,*R*$_p$)-**25** in $CDCl_3$ at 20 ^{o}C

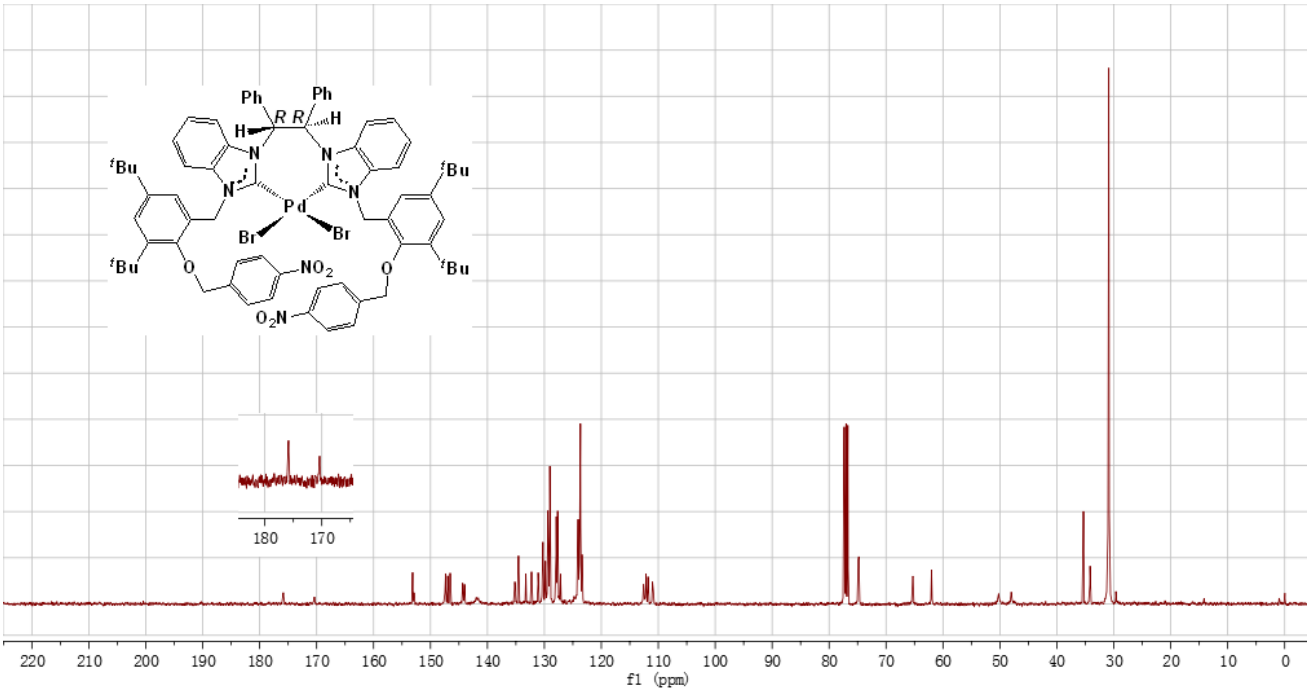

Figure S58. The ^{13}C NMR spectrum of (*R,R*)-**25** in $CDCl_3$ at 20 ^{o}C

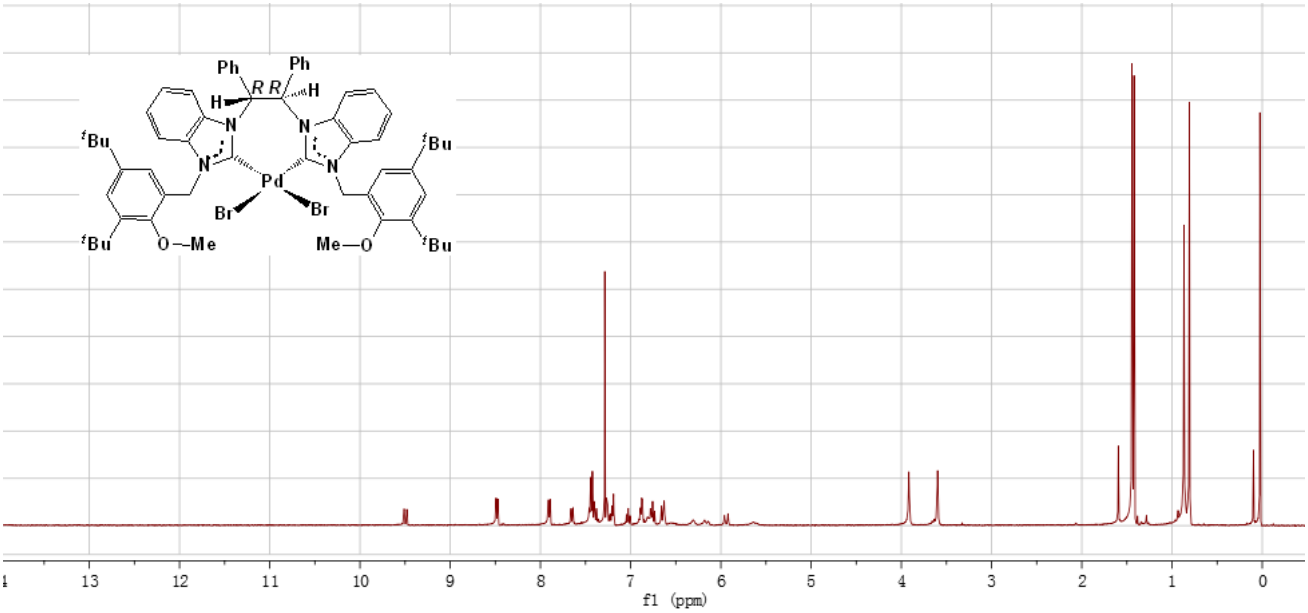

Figure S59. The ^{1}H NMR spectrum of (*R,R*)-**26** in $CDCl_3$ at 20 ^{o}C

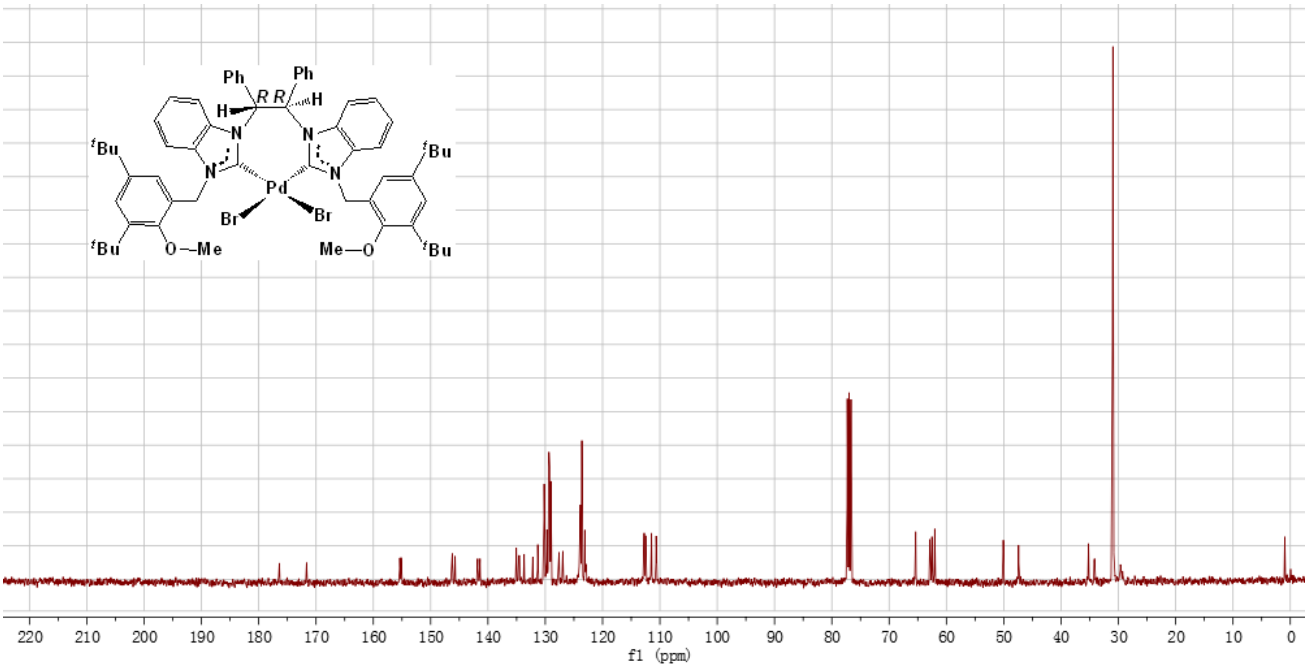

Figure S60. The ^{13}C NMR spectrum of (*R,R*)-**26** in $CDCl_3$ at 20 ^{o}C

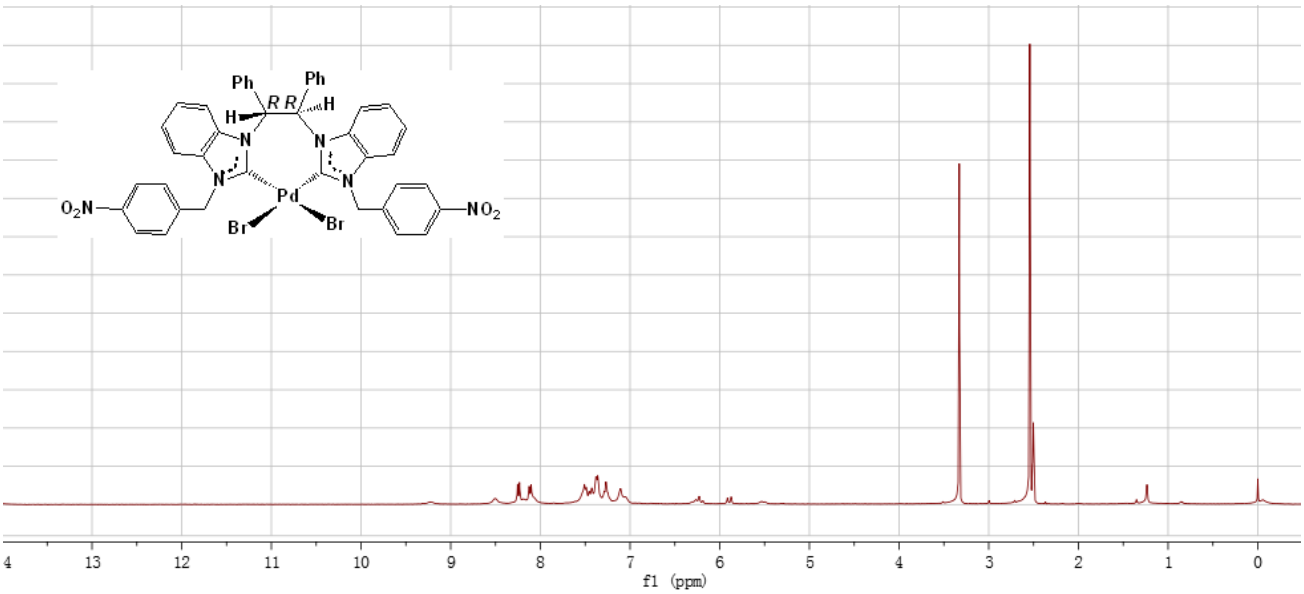

Figure S61. The ^{1}H NMR spectrum of (*R,R*)-**27** in $(CD_3)_2SO$ at 20 ^{o}C

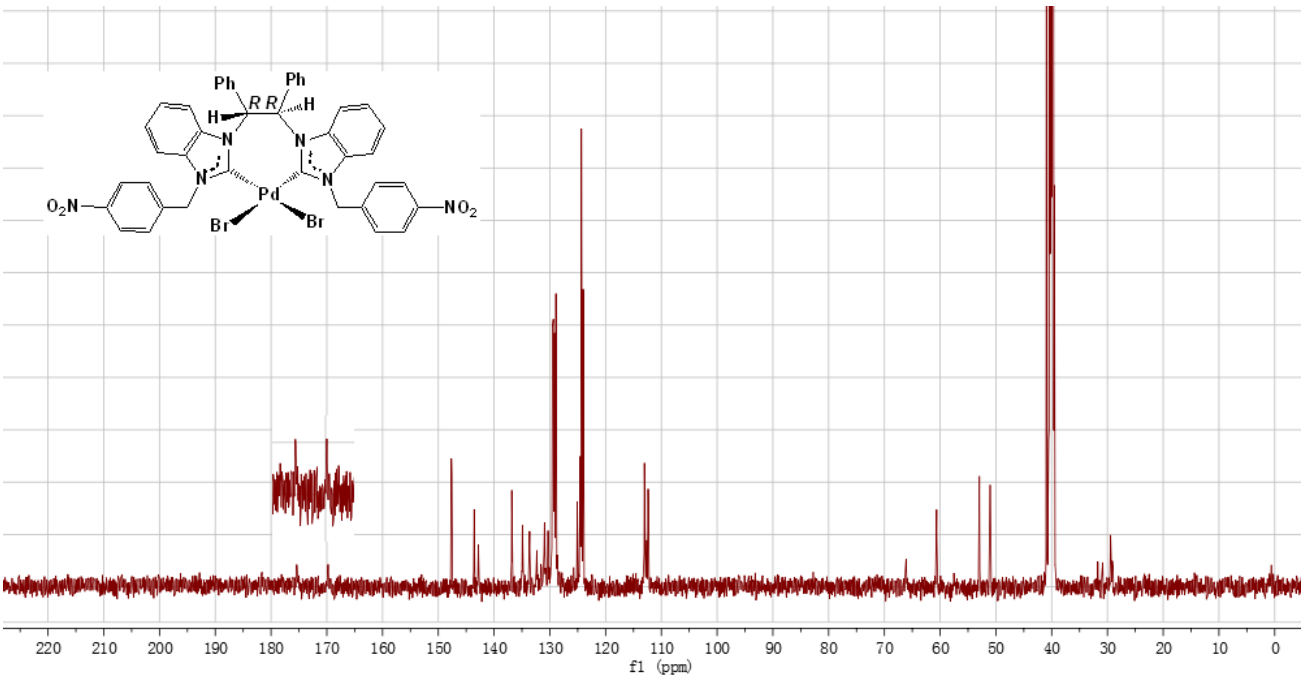

Figure S62. The ^{13}C NMR spectrum of (*R,R*)-**27** in $(CD_3)_2SO$ at 20 ^{o}C

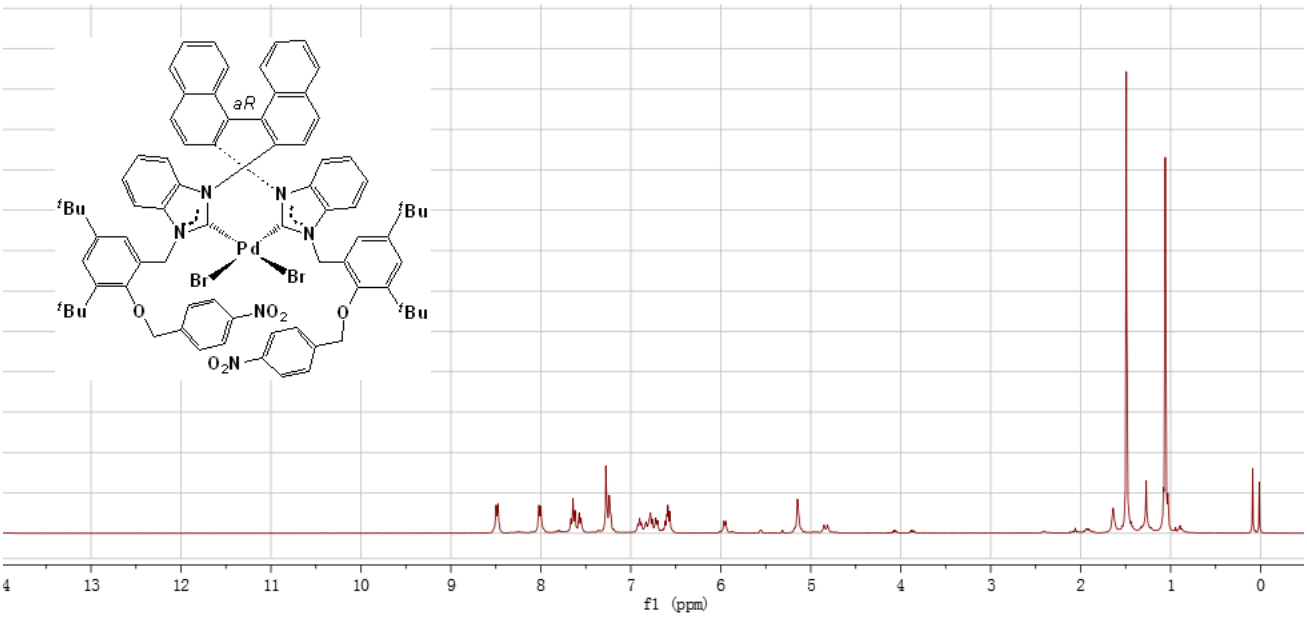

Figure S63. The ^{1}H NMR spectrum of (*aR*)-**28** in $CDCl_3$ at 20 ^{o}C

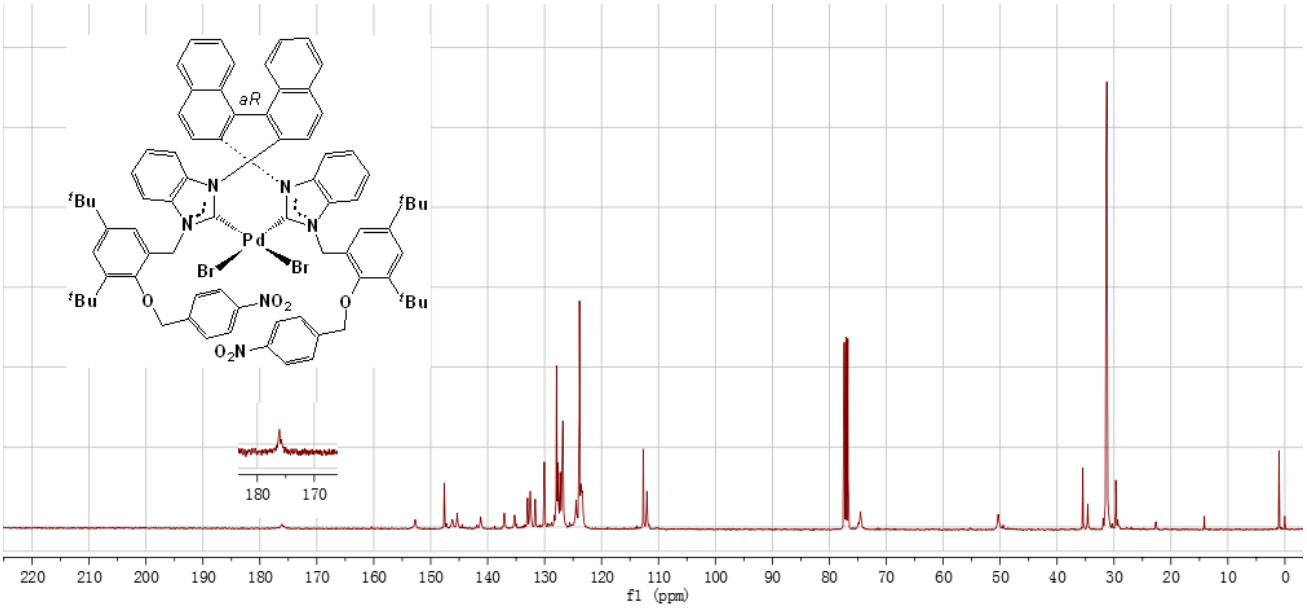

Figure S64. The ^{13}C NMR spectrum of (*aR*)-**28** in $CDCl_3$ at 20 ^{o}C

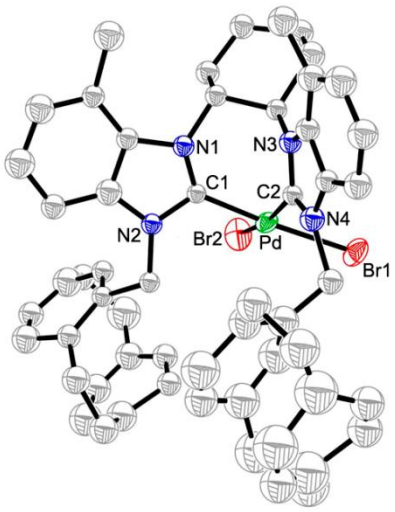

Figure S65. Molecular structure of (R,R,R_p,R_p)-**24** with ellipsoids drawn at the 50% probability level. All hydrogen atoms and *tert*-butyl groups are omitted for clarity. Selected bond distances (Å) and bond angles (deg): Pd–C(1) = 1.97(2), Pd–C(2) = 1.99(2), Pd–Br(2) = 2.448(4), Pd–Br(1) = 2.452(4), C(1)–Pd–C(2) = 85.8(10) C(2)–Pd–Br(1) = 90.8(7), C(1)–Pd–Br(2) = 90.2(7), Br(1)–Pd–Br(2) = 92.66(14), C(1)–Pd –Br(1) = 168.2(6), C(2)–Pd–Br(2) = 175.5(7).

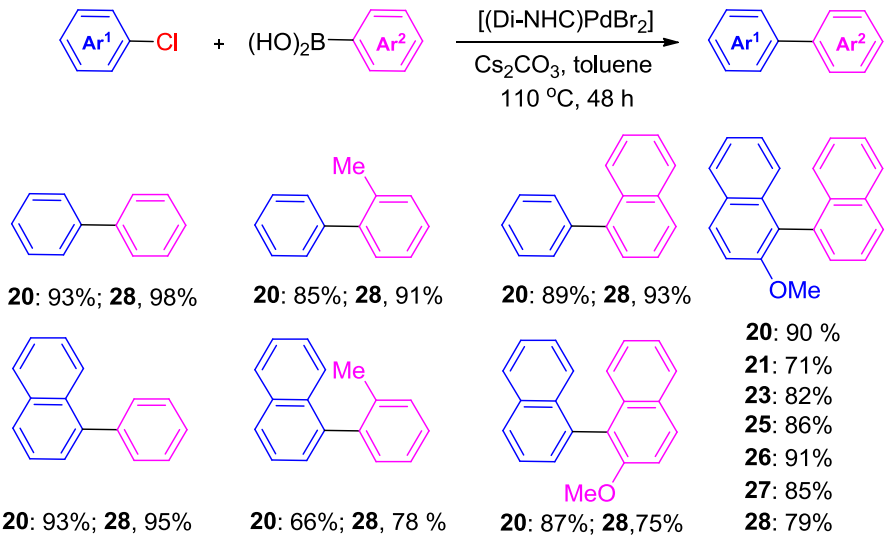

Figure S66. Cross Coupling Reactions of Aryl Chlorides and Boronic Acids. Conditions: Aryl chlorides (0.5 mmol), boronic (0.75 mmol), catalyst [Pd] (3 mol %), Cs_2CO_3 (1.2 mmol), 110 °C for 24 h. The reaction condition has not been optimized. Isolated yields are given after by chromatography on silica gel, as an average of two runs.

Table S1. Crystal data and structure refinement for complex (R,R,R_p,R_p)-24

Identification code	a50928b	
Empirical formula	C20 H20 Br2 N4 Pd	
Formula weight	582.62	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 21	
Unit cell dimensions	a = 10.948(7) Å	α= 90°.
	b = 25.212(15) Å	β= 104.246(8)°.
	c = 20.031(12) Å	γ = 90°.
Volume	5359(6) $Å^3$	
Z	8	
Density (calculated)	1.444 Mg/m^3	
Absorption coefficient	3.684 mm^{-1}	
F(000)	2272	
Crystal size	0.540 x 0.060 x 0.060 mm^3	
Theta range for data collection	1.324 to 25.099°.	
Index ranges	-12<=h<=13, -30<=k<=21, -23<=l<=22	
Reflections collected	23100	
Independent reflections	12266 [R(int) = 0.1035]	
Completeness to theta = 25.242°	96.1 %	
Absorption correction	None	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	12266 / 1 / 619	
Goodness-of-fit on F^2	0.994	
Final R indices [I>2sigma(I)]	R1 = 0.1072, wR2 = 0.2664	
R indices (all data)	R1 = 0.2039, wR2 = 0.3261	
Absolute structure parameter	0.14(2)	
Extinction coefficient	n/a	
Largest diff. peak and hole	1.118 and -1.178 e.$Å^{-3}$	