Vinylidene Rearrangements of Internal Borylalkynes via 1,2-Boryl Migration

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1. Experimental

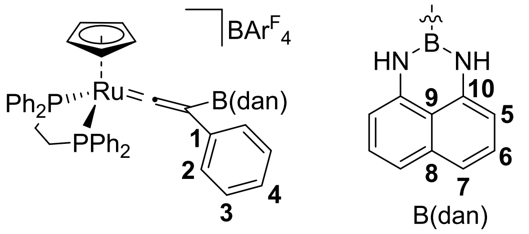
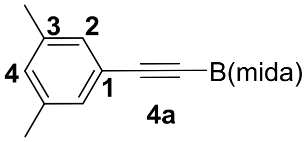


Figure S1. Notations of carbon atoms for NMR characterization of complex **2f**.

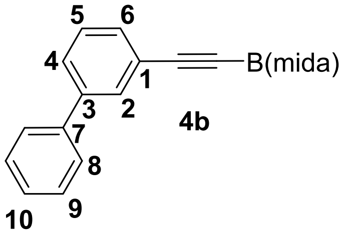
Syntheses of novel Alkynes with B(mida)



4a

To a mixture of 5-iodo-*m*-xylene (241.5 mg, 1.0362 mmol), ethynyl mida boronate (190.5 mg, 1.0528 mmol), CuI (8.1 mg,0.0426 mmol), $PdCl_2(PPh_3)_2$ (14.1 mg, 0.0201 mmol) were added anhydrous DMF (160 μl) and Et_3N (150 μl). The reaction mixture was stirred at room temperature for 1 h. After addition of ethyl acetate, the solution was washed with water and brine, and then dried over $MgSO_4$. The solvent was evaporated under reduced pressure to give a crude product. The crude product was purified by precipitation with ether/hexane = 1:14 to afford a desired compound as white powder (139.0 mg, 0.4875 mmol, 47% yield).

^{1}H NMR (acetone-d_6): δ 7.10 (s, 2H, H2), 7.02 (s, 1H, H4), 4.32 (d, 2H, $^2J_{HH}$ = 17.3 Hz, CH_2 of mida), 4.17 (d, 2H, $^2J_{HH}$ = 16.8 Hz, CH_2 of mida), 3.31 (s, 3H, CH_3 of mida), 2.26 (s, 6H, CH_3 of mida). ^{13}C{^{1}H} NMR (acetone-d_6): δ 168.6 (CO of mida), 138.8 (C3), 131.2 (C4), 130.2 (C2), 123.7 (C1), 101.0 ((*m*-xylyl)*C*≡C), 62.3 (CH_2 of mida), 48.4 (CH_3 of mida), 21.0 (CH_3 of *m*-xylyl). The signal assignable to the (*m*-xylyl)C≡*C* could not be found, probably because it is overlapped with another signal. HRMS *m/z*: [M+Na]$^+$ calcd for $C_{15}H_{16}BNO_4Na^+$: 308.10646; found 308.10748.



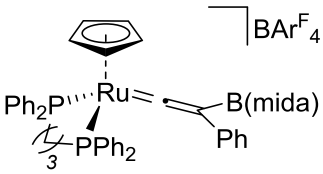
4b

To a mixture of 3-bromobiphenyl (112.8 mg, 0.4839 mmol), ethynyl mida boronate (95.8 mg, 0.5294 mmol), CuI (5.6 mg, 0.0294 mmol), $PdCl_2(PPh_3)_2$ (8.8 mg, 0.0125 mmol) were added anhydrous DMF (80 µl) and Et_3N (75 µl). The reaction mixture was stirred at 60 °C for 18 h. After addition of ethyl acetate, the solution was washed with water and brine, and then dried over $MgSO_4$. The solvent was evaporated under reduced pressure to give a crude product. The crude product was purified by column chromatography. The alkyne was obtained as brown powder (27.8 mg, 0.0842 mmol, 17% yield).

^{1}H NMR (acetone-d_6): δ 7.77 (m, 1H, H4), 7.67 (m, 3H, H6, H8), 7.75 (m, 4H, H2, H5, H9), 7.39 (m, 1H, H10), 4.35 (d, 2H, $^2J_{HH}$ = 16.8 Hz, CH_2 of mida), 4.20 (d, 2H, $^2J_{HH}$ = 17.3 Hz, CH_2 of mida), 3.35 (s, 3H, CH_3 of mida). ^{13}C{^{1}H} NMR (acetone-d_6): δ 168.6 (CO of mida), 142.2 (C3), 140.8 (C7), 131.4 (C2), 131.0 (C4), 129.9 (C5), 129.8 (C9), 128.6 (C10), 128.1 (C6), 127.8 (C8), 124.6 (C1), 100.4((*β*-biphenyl)*C*≡C), 62.3 (CH_2 of mida), 48.5 (CH_3 of mida). The signal assignable to the (*β*-biphenyl)C≡*C* could not be found, probably because it is overlapped with another signal. HRMS *m/z*: $[M+Na]^+$ calcd for $C_{19}H_{16}BNO_4Na^+$: 356.10646; found 356.10669.

Vinylidene rearrangements

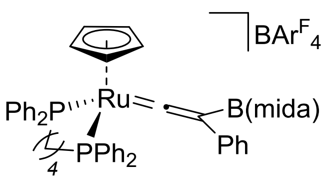
[Ru(=C=C(Ph){B(mida)})(dppp)Cp][BAr^F$_4$] (2b)



Complex **2b** was obtained as yellow crystals (67.0 mg, 0.0394 mmol, 77% yield) by the reaction of [CpRuCl(dppp)] (31.6 mg, 0.0515 mmol), PhC≡CB(mida) (15.7 mg, 0.0611 mmol), and NaBAr^F$_4$·2.6H_2O (50.7 mg, 0.0543 mmol).

^{1}H NMR (acetone-d_6): δ 7.80 (s, 8H, *o*-H of BAr^F$_4$), 7.68 (s, 4H, *p*-H of BAr^F$_4$), 7.60 (m, 4H, *o*-H of Ph in dppp), 7.40 (m, 8H, *m*- and *p*-H×2 of Ph in dppp), 7.29 (m, 8H, *o*- and *m*-H of Ph in dppp), 7.24 (m, 2H, *o*-H of Ru=C=CPh), 7.12 (m, 3H, *m*- and *p*-H of Ru=C=CPh), 5.68 (s, 5H, Cp), 4.16 (d, 2H, $^2J_{HH}$ = 16.8 Hz, CH_2 of mida), 3.54 (d, 2H, $^2J_{HH}$ = 17.3 Hz, CH_2 of mida), 3.15 (s, 3H, CH_3 of mida), 2.99 (m, 2H, PCH_2CH$_2$ of dppp), 2.61 (br, 3H, PCH_2CH$_2$ and PCH$_2$$CH_2$ of dppp). The signal assignable to the PCH$_2$$CH_2$ could not be found, probably because it is overlapped with other signals. ^{31}P{^{1}H} NMR (acetone-d_6): δ 34.5 (br, dppp). ^{13}C{^{1}H} NMR (acetone-d_6): δ 341.4 (t, $^2J_{CP}$ = 16.0 Hz, Ru=*C*=C), 167.8 (s, CO of mida), 162.6 (q, $^1J_{CB}$ = 50.0 Hz, *ipso*-C of BAr^F$_4$), 137.3 (m, *ipso*-C of Ph in dppp×2), 135.5 (br, *o*-C of BAr^F$_4$), 133.5 (virtual t, *o*-C of Ph in dppp), 133.2 (m, *o*-C of Ph in dppp), 131.43 (s, *p*-C of Ph in dppp), 131.37 (s, *p*-C of Ph in dppp) 131.2 (s, *o*-C of Ru=C=CC_6H$_5$), 130.0 (brq, $^2J_{CF}$ = 31.9 Hz, *m*-C of BAr^F$_4$), 129.9 (s, *m*-C of Ru=C=CC_6H$_5$), 129.4 (m, *m*-C of Ph in dppp×2), 127.7 (s, *p*-C of Ru=C=CC_6H$_5$), 125.4 (q, $^1J_{CF}$ = 272.8 Hz, CF_3 of BAr^F$_4$), 118.5 (m, *p*-C of BAr^F$_4$), 93.0 (s, Cp), 62.8 (s, CH_2 of mida), 47.7 (s, CH_3 of mida), 27.6 (m, PCH$_2$CH$_2$), 21.1 (s, PCH$_2$$CH_2$). The signal assignable to the Ru=C=*C* and *ipso*-C of Ru=C=CC_6H$_5$ could not be found, probably because it is overlapped with other signals. Elemental analysis calcd for $C_{77}H_{55}O_4B_2F_{24}P_2NRu$: C, 54.44; H, 3.26; N, 0.82. Found: C, 54.30; H, 3.51; N, 0.81.

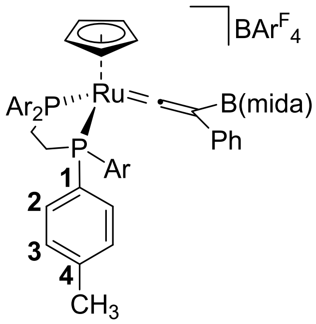
[Ru(=C=C(Ph){B(mida)})(dppb)Cp][BAr^F$_4$] (2c)



Complex **2c** was obtained as yellow crystals (24.7 mg, 0.0144 mmol, 28% yield) by the reaction of [CpRuCl(dppb)] (31.8 mg, 0.0506 mmol), PhC≡CB(mida) (15.4 mg, 0.0599 mmol), and NaBAr^F$_4$·2.6H_2O (51.5 mg, 0.0551 mmol).

^{1}H NMR (acetone-d_6): δ 7.79 (s, 8H, *o*-H of BAr^F$_4$), 7.68 (s, 4H, *p*-H of BAr^F$_4$), 7.61

(m, 6H, *o*- and *p*- H of Ph in dppb), 7.50 (m, 10H, *m*-×2 and *p*-H of Ph in dppb), 7.36 (m, 4H, *o*-H of Ph in dppb),7.14 (m, 3H, *m*- and *p*-H of Ru=C=CPh), 6.95 (m, 2H, *o*-H of Ru=C=CPh), 5.23 (s, 5H, Cp), 4.23 (d, 2H, $^2J_{HH}$ = 16.8 Hz, CH_2 of MIDA), 3.59 (d, 2H, $^2J_{HH}$ = 16.8 Hz, CH_2 of mida), 3.23 (m, 5H, P$CH_2$$CH_2$ of dppb and CH_3 of mida), 2.51 (m, 2H, P$CH_2$$CH_2$ of dppb), 1.62 (m, 2H, P$CH_2$$CH_2$ of dppb), 1.44 (m, 2H, P$CH_2$$CH_2$ of dppb). ^{31}P{^{1}H} NMR (acetone-d_6): δ 43.5 (s, dppb). ^{13}C{^{1}H} NMR (acetone-d_6): δ 345.6 (t, $^2J_{CP}$ = 15.6 Hz, Ru=*C*=C), 168.0 (s, CO of mida), 162.6 (q, $^1J_{CB}$ = 50.0 Hz, *ipso*-C of BAr^F_4), 139.0 (m, *ipso*-C of Ph in dppb), 135.9 (m, *ipso*-C of Ph in dppb), 135.5 (br, *o*-C of BAr^F_4), 133.1 (virtual t, *o*-C of Ph in dppb×2), 131.9 (s, *p*-C of Ph in dppb), 131.4 (s, *p*-C of Ph in dppb), 131.0 (s, *o*-C of Ru=C=CC_6H_5), 130.04 (*m*-C of Ru=C=CC_6H_5), 130.01 (brq, $^2J_{CF}$ = 34.5 Hz, *m*-C of BAr^F_4), 129.89 (m, *m*-C of Ph in dppb), 129.5 (m, *m*-C of Ph in dppb), 127.7 (s, *p*-C of Ru=C=CC_6H_5), 125.3 (q, $^1J_{CF}$ = 272.9 Hz, CF_3 of BAr^F_4), 118.4 (m, *p*-C of BAr^F_4), 92.8 (s, Cp), 62.9 (s, CH_2 of mida), 47.4 (s, CH_3 of MIDA), 30.2 (m, P$CH_2$$CH_2$), 23.5 (s, P$CH_2$$CH_2$). The signal assignable to the Ru=C=*C* and *ipso*-C of Ru=C=CC_6H_5 could not be found, probably because it is overlapped with other signals. Elemental analysis calcd for $C_{78}H_{57}O_4B_2F_{24}P_2NRu\cdot 0.5CH_2Cl_2$: C, 53.71; H, 3.27; N, 0.80. Found: C, 53.41; H, 3.21; N, 0.71.

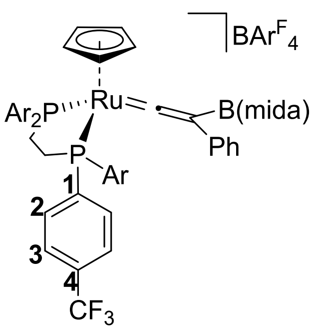


[Ru(=C=C(Ph){B(mida)}){(*p*-tol)$_2$PC$_2$H$_4$P(*p*-tol)$_2$)}Cp][BAr$^F_4$] (2d)

Complex **2d** was obtained as yellow crystals (59.4 mg, 0.0340 mmol, 67% yield) by the reaction of [CpRuCl(*p*-tol)$_2$PC$_2$H$_4$P(*p*-tol)$_2$)] (33.2 mg, 0.0506 mmol), PhC≡C B(mida) (15.8 mg, 0.0615 mmol), and $NaBAr^F_4\cdot 2.6H_2O$ (50.6 mg, 0.0542 mmol).

^{1}H NMR (acetone-d_6): δ 7.80 (s, 8H, *o*-H of BAr^F_4), 7.68 (s, 4H, *p*-H of BAr^F_4), 7.60 (m, 4H, H2), 7.13 (m, 12H, H3×2 and H2), 7.00 (m, 3H, *m*- and *p*-H of Ru=C=CPh), 6.86 (m, 2H, *o*-H of Ru=C=CPh), 5.63 (s, 5H, Cp), 3.98 (d, 2H, $^2J_{HH}$ = 16.8 Hz, CH_2 of mida), 3.30 (m, 2H, CH_2 of PCH_2), 3.18 (d, 2H, $^2J_{HH}$ = 17.3Hz, CH_2 of mida), 3.03 (m, 2H, CH_2 of PCH_2), 2.62 (s, 3H, CH_3 of mida) 2.34 (s, 6H, CH_3 of *p*-tol), 2.31 (s, 6H, CH_3 of *p*-tol). ^{31}P{^{1}H} NMR (acetone-d_6): δ 77.7 (s). ^{13}C{^{1}H} NMR (acetone-d_6): δ 338.5 (t, $^2J_{CP}$ = 15.8 Hz, Ru=*C*=C), 167.7 (s, CO of mida), 162.6 (q, $^1J_{CB}$ = 50.0 Hz, *ipso*-C of BAr^F_4), 142.2 (s, C4), 141.8 (s, C4), 135.5 (br, *o*-C of BAr^F_4), 135.0 (m, C1), 133.8 (virtual t, C2), 132.0 (m, C1, C2), 130.8 (s, *o*-C of Ru=C=CC_6H_5), 130.2 (m, C3×2), 130.0 (brq, $^2J_{CF}$ = 32.4 Hz, *m*-C of BAr^F_4), 129.4 (s, *m*-C of Ru=C=CC_6H_5), 128.9 (s, *ipso*-C of Ru=C=CC_6H_5), 126.9 (s, *p*-C of Ru=C=CC_6H_5), 125.4 (q, $^1J_{CF}$ = 272.9 Hz, CF_3 of BAr^F_4), 118.5 (m, *p*-C of BAr^F_4), 92.0 (s, Cp), 62.8 (s, CH_2 of mida), 47.1 (s, CH_3 of mida), 28.6 (m, PCH_2), 21.4 (s, CH_3 of *p*-tol), 21.1 (s, CH_3 of *p*-tol). The signal assignable to the Ru=C=*C* could not be found, probably because it is overlapped with other signals. Elemental analysis calcd for $C_{80}H_{61}O_4B_2F_{24}P_2NRu$: C, 55.19; H, 3.53; N, 0.80. Found: C, 54.99; H, 3.58; N, 0.80.

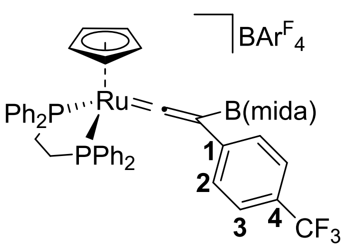
[Ru(=C=C(Ph){B(mida)}){(*p*-CF$_3$C$_6$H$_4$)$_2$PC$_2$H$_4$P(*p*-CF$_3$C$_6$H$_4$)$_2$}Cp][BAr$^F_4$] (2e)



Complex **2e** was obtained as yellow crystals (71.1 mg, 0.0363 mmol, 72% yield) by the reaction of [RuCl(*p*-CF$_3$C$_6$H$_4$)$_2$PC$_2$H$_4$P(*p*-CF$_3$C$_6$H$_4$)$_2$Cp] (43.8 mg, 0.0523 mmol), PhC≡CB(mida) (15.7 mg, 0.0611 mmol), and $NaBAr^F_4\cdot 2.6H_2O$ (50.5 mg, 0.0541 mmol).

^{1}H NMR (acetone-d_6): δ 7.97 (m, 4H, H2), 7.81 (s, 8H, *o*-H of BAr^F_4), 7.68 (s, 4H, *p*-H of $BAr^F{}_4$), 7.66 (m, 4H, H3), 7.55 (m, 8H, H2, H3)), 7.02 (m, 5H, *o*- and *m*- and *p*-H of Ru=C=CPh), 6.12 (s, 5H, Cp), 4.05 (d, 2H, $^2J_{HH}$ = 16.8 Hz, CH_2 of mida), 3.72 (m, 2H, CH_2 of PCH_2), 3.38 (d, 2H, $^2J_{HH}$ = 17.3Hz, CH_2 of mida), 3.34 (m, 2H, CH_2 of PCH_2), 3.03 (s, 3H, CH_3 of mida). $^{31}P\{^1H\}$ NMR (acetone-d_6): δ 82.4 (s). $^{13}C\{^1H\}$ NMR (acetone-d_6): δ 337.3 (t, $^2J_{CP}$ = 15.6 Hz, Ru=*C*=C), 167.5 (s, CO of mida), 162.6 (q, $^1J_{CB}$ = 50.0 Hz, *ipso*-C of $BAr^F{}_4$), 140.0 (m, C1),139.5 (m, C1), 135.5 (br, *o*-C of $BAr^F{}_4$), 134.4 (virtual t, C2), 133.2 (virtual t, C2), 132.9 (m, C4×2), 130.6 (s, *o*-C of Ru=C=CC_6H_5), 130.0 (brq, $^2J_{CF}$ = 34.3 Hz, *m*-C of $BAr^F{}_4$), 129.8 (s, *m*-C of Ru=C=CC_6H_5), 128.1 (s, *ipso*-C of Ru=C=CC_6H_5), 127.7 (s, *p*-C of Ru=C=CC_6H_5), 126.6 (m, C3), 126.4 (m, C3), 125.4 (q, $^1J_{CF}$ = 273.0 Hz, CF_3 of $BAr^F{}_4$), 124.8 (q, $^1J_{CF}$ = 273.0 Hz, CF_3 of *p*-$CF_3C_6H_4$), 124.5 (q, $^1J_{CF}$ = 273.0, CF_3 of *p*-$CF_3C_6H_4$), 118.5 (m, *p*-C of $BAr^F{}_4$), 92.6 (s, Cp), 62.7 (s, CH_2 of mida), 47.4 (s, CH_3 of mida), 27.8 (m, PCH_2). The signal assignable to the Ru=C=*C* could not be found, probably because it is overlapped with other signals. Elemental analysis calcd for $C_{80}H_{49}O_4B_2F_{36}P_2NRu$: C, 49.10; H, 2.52; N, 0.72. Found: C, 49.09; H, 2.43; N, 0.71.

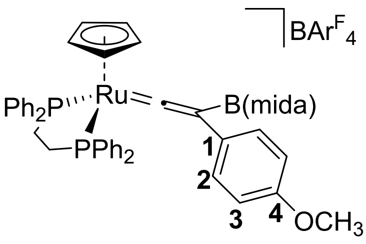
[Ru(=C=C(*p*-$CF_3C_6H_4$){B(mida)})(dppe)Cp][$BAr^F{}_4$] (2h)



Complex **2h** was obtained as yellow crystals (29.4 mg, 0.0168 mmol, 33% yield) by using [CpRuCl(dppe)] (30.8 mg, 0.0513 mmol), (*p*-$CF_3C_6H_4$)C≡CB(mida) (18.5 mg, 0.0569 mmol), and $NaBAr^F{}_4 \cdot 2.6H_2O$ (51.8 mg, 0.0555 mmol).

^1H NMR (acetone-d_6): δ 7.80 (s, 8H, *o*-H of $BAr^F{}_4$), 7.76 (m, 4H, *o*-H of Ph in dppe), 7.68 (s, 4H, *p*-H of $BAr^F{}_4$), 7.43 (m, 4H, *p*-H of Ph in dppe ×2), 7.33 (m, 8H, *m*-H of Ph in dppe×2), 7.27 (d, 2H, $^3J_{HH}$ = 8.4 Hz, H3), 7.21 (m, 4H, *o*-H of Ph in dppe), 7.09 (d, 2H, $^3J_{HH}$ = 7.9 Hz, H2), 5.79 (s, 5H, Cp), 4.03 (d, 2H, $^2J_{HH}$ = 17.3 Hz, CH_2 of mida), 3.47 (m, 2H, CH_2 of dppe), 3.31 (d, 2H, $^2J_{HH}$ = 16.8 Hz, CH_2 of mida), 3.20 (m, 2H, CH_2 of dppe), 2.70 (s, 3H, CH_3 of mida). $^{31}P\{^1H\}$ NMR (acetone-d_6): δ 79.7 (s, dppe). $^{13}C\{^1H\}$ NMR (acetone-d_6): δ 337.5 (t, $^2J_{CP}$ = 16.0 Hz, Ru=*C*=C), 167.6 (s, CO of mida), 162.6 (q, $^1J_{CB}$ = 50.0 Hz, *ipso*-C of $BAr^F{}_4$), 137.7 (m, *ipso*-C of Ph in dppe), 135.5 (br, *o*-C of $BAr^F{}_4$), 135.0 (m, *ipso*-C of Ph in dppe), 133.8 (virtual t, *o*-C of Ph in dppe), 135.5 (s, C1), 132.2 (s, *p*-C of Ph in dppe), 132.0 (virtual t, *o*-C of Ph in dppe), 131.5 (s, *p*-C of Ph in dppe), 131.2 (s, C2), 130.0 (brq, $^2J_{CF}$ = 29.1 Hz, *m*-C of $BAr^F{}_4$), 129.7 (m, *m*-C of Ph in dppe×2), 128.4 (s, C4), 126.2 (s, C3), 125.4 (q, $^1J_{CF}$ = 272.9 Hz, CF_3 of $BAr^F{}_4$), 125.2 (q, $^1J_{CF}$ = 264.9 Hz, CF_3 of *p*-$CF_3C_6H_4$), 118.4 (m, *p*-C of $BAr^F{}_4$), 92.4 (s, Cp), 62.9 (s, CH_2 of mida), 47.5 (s, CH_3 of mida), 28.2 (m, PCH_2). The signal assignable to the Ru=C=*C* and C4 could not be found, probably because it is overlapped with other signals. Elemental analysis calcd for $C_{77}H_{52}O_4B_2F_{27}P_2NRu \cdot 0.5CH_2Cl_2$: C, 51.85; H, 2.92; N, 0.78. Found: C, 51.59; H, 2.83; N, 0.71.

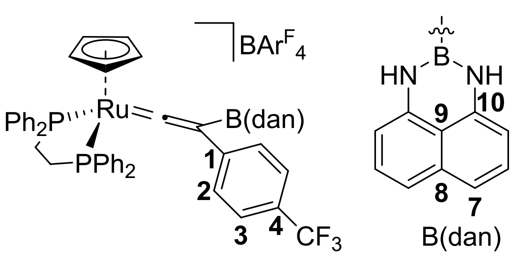
[Ru(=C=C(*p*-Ans){B(mida)})(dppe)Cp][$BAr^F{}_4$] (2i)



Complex **2i** was obtained as yellow crystals (70.9 mg, 0.041.3 mmol, 84% yield) by the reaction of [RuCl(dppe)Cp] (29.4 mg, 0.0490 mmol), (*p*-Ans)C≡CB(mida) (17.5 mg, 0.0610 mmol), and $NaBAr^F{}_4 \cdot 2.6H_2O$ (51.0 mg, 0.0547 mmol).

^1H NMR (acetone-d_6): δ 7.81 (s, 8H, *o*-H of $BAr^F{}_4$), 7.76 (m, 4H, *o*-H of Ph in dppe), 7.69 (s, 4H, *p*-H of $BAr^F{}_4$), 7.48 (m, 2H, *p*-H of Ph in dppe), 7.40 (m, 6H, *p*- and *m*-H of Ph in dppe), 7.32 (m, 4H, *m*-H of Ph in dppe), 7.23 (m, 4H, *o*-H of Ph in dppe), 6.77 (d, 2H, $^3J_{HH}$ = 8.4 Hz, H2), 6.55 (d, 2H, $^3J_{HH}$ = 7.9 Hz, H3), 5.69 (s, 5H, Cp), 3.99 (d, 2H, $^2J_{HH}$ = 17.3 Hz, CH_2 of mida), 3.70 (s, 3H, OCH_3) 3.41 (m, 2H, CH_2 of dppe), 3.24 (d, 2H, $^2J_{HH}$ = 17.3 Hz, CH_2 of mida), 3.08 (m, 2H, CH_2 of dppe), 2.64 (s, 3H, CH_3 of mida). $^{31}P\{^1H\}$ NMR (acetone-d_6): δ 79.7 (s, dppe). $^{13}C\{^1H\}$ NMR (acetone-d_6): δ 339.4 (t, $^2J_{CP}$ = 15.9 Hz, Ru=*C*=C), 167.8 (s, CO of mida), 162.6 (q, $^1J_{CB}$ = 50.0 Hz, *ipso*-C of $BAr^F{}_4$), 159.3 (s, C4) 138.1 (m, *ipso*-C of Ph in dppe), 135.5 (br, *o*-C of $BAr^F{}_4$), 135.1 (m, *ipso*-C of Ph in dppe), 133.9 (virtual t, *o*-C of Ph in dppe), 131.9 (m, *o*- and *p*-C of Ph in dppe), 131.8 (s, C2), 131.4 (s, *p*-C of Ph in dppe), 130.0 (brq, $^2J_{CF}$ = 31.9 Hz, *m*-C of $BAr^F{}_4$), 129.6 (m, *m*-C of Ph in dppe×2), 125.4 (q, $^1J_{CF}$ = 273.0 Hz, CF_3 of $BAr^F{}_4$), 119.9 (s, C1), 118.4 (m, *p*-C of $BAr^F{}_4$), 115.1 (s, C3), 91.9 (s, Cp), 62.8 (s, CH_2 of mida), 55.3 (s, O*C*H_3), 47.2 (s, CH_3 of mida), 28.4 (m, P*C*H_2). The signal assignable to the Ru=C=*C* could not be found, probably because it is overlapped with other signals. HRMS *m*/*z*: $[M+Na]^+$ calcd for $RuP_2C_{45}H_{43}BNO_5{}^+$: 852.17530; found 852.17586.

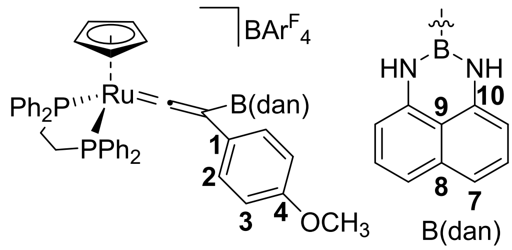
[Ru(=C=C(*p*-$CF_3C_6H_4$){B(dan)})(dppe)Cp][$BAr^F{}_4$] (2j)



Complex **2j** was obtained by using [RuCl(dppe)Cp] (30.2 mg, 0.0503 mmol), (*p*-$CF_3C_6H_4$)C≡CB(dan) (17.0 mg, 0.0506 mmol), and $NaBAr^F{}_4$·6THF (recrystallized THF/hexane) (68.2 mg, 0.0517 mmol). The complex was characterized by ^1H NMR spectrum of the crude product (0.0486 mmol, 97% yield).

^1H NMR ($CDCl_3$): δ 7.76 (s, 8H, *o*-H of $BAr^F{}_4$), 7.55 (s, 4H, *p*-H of $BAr^F{}_4$), 7.39 (m, 12H, *p*-×2 and *m*- and *o*-H of Ph in dppe), 7.19 (d, 2H, $^3J_{HH}$ = 7.9 Hz, H3), 7.04 (m, 12H, *m*- and *o*-H of Ph in dppe and H6, H7), 6.71 (d, 2H, $^3J_{HH}$ = 7.9 Hz, H2), 5.95 (br, 2H, H5), 5.47 (s, 5H, Cp), 4.84 (br, 2H, NH of dan), 3.10 (m, 2H, CH_2 of dppe), 2.92 (m, 2H, CH_2 of dppe). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 77.5 (s, dppe). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 334.1 (t, $^2J_{CP}$ = 15.4 Hz, Ru=*C*=C), 161.9 (q, $^1J_{CB}$ = 50.0 Hz, *ipso*-C of $BAr^F{}_4$), 139.9 (s, C10), 136.1 (br, C8), 134.9 (m, *o*-C of $BAr^F{}_4$ and *ipso*-C of Ph in dppe), 133.2 (m, *ipso*-C of Ph in dppe), 132.1 (m, *p*-C of Ph in dppe), 132.0 (m, *p*-C of Ph in dppe), 131.8 (virtual t, *o*-C of Ph in dppe), 131.4 (virtual t, *o*-C of Ph in dppe), 129.0 (m, *m*-C of Ph in dppe×2 and C2, C4 and *m*-C of $BAr^F{}_4$)), 127.4 (m, C6), 125.9 (s, C3), 125.3 (s, C1), 124.7 (q, $^1J_{CF}$ = 273.6 Hz, CF_3 of $BAr^F{}_4$), 123.9 (q, $^1J_{CF}$ = 273.1 Hz, CF_3 of *p*-$CF_3C_6H_4$), 119.7 (s, C9), 118.7 (s, C7), 117.6 (s, *p*-C of $BAr^F{}_4$), 106.6 (s, C5), 91.5 (s, Cp), 27.6 (m, P*C*H_2). The signal assignable to the Ru=C=*C* could not be found, probably because it is overlapped with other signals. High resolution mass measurement and elemental analysis have failed due to the high susceptibility toward hydrolysis.

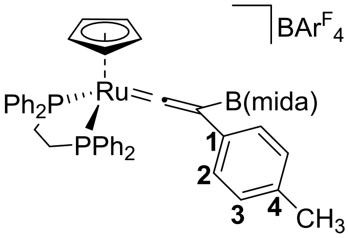
[Ru(=C=C(*p*-Ans){B(dan)})(dppe)Cp][$BAr^F{}_4$] (2k)



Complex **2k** was obtained by using [RuCl(dppe)Cp] (30.3 mg, 0.0505 mmol), (*p*-Ans)C≡CB(dan) (15.4 mg, 0.0517 mmol), and $NaBAr^F{}_4$·6THF (recrystallized THF/hexane) (67.5 mg, 0.0512 mmol). The complex was characterized by ^1H NMR spectrum of the crude product (0.0426 mmol, 84 % yield).

^1H NMR ($CDCl_3$): δ 7.77 (s, 8H, *o*-H of $BAr^F{}_4$), 7.56 (s, 4H, *p*-H of BAr^F_4), 7.43 (m, 6H, *o*- and *p*-H of Ph in dppe), 7.38 (m, 4H, *m*-H of Ph in dppe), 7.07 (m, 14H, *o*-, *m*- and *p*-H of Ph in dppe, H6, H7), 6.55 (d, 2H, $^3J_{HH}$ = 8.9 Hz, H2), 6.51 (d, 2H, $^3J_{HH}$ = 8.9 Hz, H3), 5.92 (br, 2H, H5), 5.45 (s, 5H, Cp), 4.80 (br, 2H, NH of dan), 3.72 (s, 3H, CH_3 of *p*-Ans), 3.08 (m, 2H, CH_2 of dppe), 2.90 (m, 2H, CH_2 of dppe). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 78.2 (s, dppe). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 336.3 (m, Ru=*C*=C), 161.8 (q, $^1J_{CB}$ = 50.0 Hz, *ipso*-C of BAr^F_4), 158.8 (s, C4), 140.2 (s, C10), 136.1 (br, C8), 134.9 (m, *o*-C of BAr^F_4 and *ipso*-C of Ph in dppe), 133.3 (m, *ipso*-C of Ph in dppe), 131.9 (m, *o*- and *p*-C of Ph in dppe), 131.7 (m, *p*-C of Ph in dppe), 131.4 (m, *o*-C of Ph in dppe), 130.0 (s, C2), 129.2 (m, *m*-C of Ph in dppe×2), 128.9 (brq, $^2J_{CF}$ = 34.1 Hz, *m*-C of BAr^F_4), 127.3 (m, C6), 124.7 (q, $^1J_{CF}$ = 273.6 Hz, CF_3 of BAr^F_4), 119.6 (s, C9), 118.3 (s, C7), 118.1 (s, C1), 117.6 (s, *p*-C of BAr^F_4), 114.7 (s, C3), 106.5 (s, C5), 91.2 (s, Cp), 55.2 (s, O*C*H_3), 27.7 (m, P*C*H_2). The signal assignable to the Ru=C=*C* could not be found, probably because it is overlapped with other signals. High resolution mass measurement and elemental analysis have failed due to the high susceptibility toward hydrolysis.

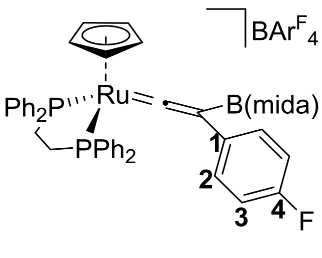
[Ru(=C=C(*p*-tol){B(mida)})(dppe)Cp][BAr^F_4] (2l)



Complex **2l** was obtained as yellow crystals (68.3 mg, 0.0402 mmol, 78% yield) by using [RuCl(dppe)Cp] (30.9 mg, 0.0515 mmol), (*p*-tol)C≡CB(mida) (15.9 mg, 0.0587 mmol), and $NaBAr^F_4 \cdot 2.6H_2O$ (50.8 mg, 0.0544 mmol).

^1H NMR (acetone-*d*$_6$): δ 7.80 (s, 8H, *o*-H of BAr^F_4), 7.74 (m, 4H, *o*-H of Ph in dppe), 7.68 (s, 4H, *p*-H of BAr^F_4), 7.47 (m, 2H, *p*-H of Ph in dppe), 7.42 (m, 2H, *p*-H of Ph in dppe), 7.34 (m, 8H, *m*-H of Ph in dppe×2), 7.23 (m, 4H, *o*-H of Ph in dppe), 6.79 (d, 2H, $^3J_{HH}$ = 8.4 Hz, H3), 6.75 (d, 2H, $^3J_{HH}$ = 8.4 Hz, H2), 5.69 (s, 5H, Cp), 3.99 (d, 2H, $^2J_{HH}$ = 16.8 Hz, CH_2 of mida), 3.41 (m, 2H, CH_2 of dppe), 3.22 (d, 2H, $^2J_{HH}$ = 17.3 Hz, CH_2 of mida), 3.07 (m, 2H, CH_2 of dppe), 2.63 (s, 3H, CH_3 of mida), 2.17 (s, 3H, CH_3 of *p*-tol). $^{31}P\{^1H\}$ NMR (acetone-*d*$_6$): δ 79.6 (s, dppe). $^{13}C\{^1H\}$ NMR (acetone-*d*$_6$): δ 338.8 (t, $^2J_{CP}$ = 15.4 Hz, Ru=*C*=C), 167.8 (s, CO of mida), 162.6 (q, $^1J_{CB}$ = 50.0 Hz, *ipso*-C of BAr^F_4), 138.1 (m, *ipso*-C of Ph in dppe), 136.8 (s, C4) 135.5 (br, *o*-C of BAr^F_4), 135.1 (m, *ipso*-C of Ph in dppe), 133.9 (virtual t, *o*-C of Ph in dppe), 132.0 (m, *o*-C of Ph in dppe), 131.8 (s, *p*-C of Ph in dppe) 131.4 (s, *p*-C of Ph in dppe), 130.6 (s, C2), 130.3 (s, C3), 130.0 (brq, $^2J_{CF}$ = 32.0 Hz, *m*-C of BAr^F_4), 129.6 (m, *m*-C of Ph in dppe×2), 125.4 (q, $^1J_{CF}$ = 272.9 Hz, CF_3 of BAr^F_4), 125.3 (s, C1), 118.4 (m, *p*-C of BAr^F_4), 92.0 (s, Cp), 62.8 (s, CH_2 of mida), 47.1 (s, CH_3 of mida), 28.4 (m, P*C*H_2), 20.9 (s, CH_3 of *p*-tol). The signal assignable to the Ru=C=*C* could not be found, probably because it is overlapped with other signals. HRMS *m*/*z*: [M+Na]$^+$ calcd for $RuP_2C_{45}H_{43}BNO_4^+$: 836.18039; found 836.18234.

[Ru(=C=C(*p*-FC_6H_4){B(mida)})(dppe)Cp][BAr^F_4] (2m)

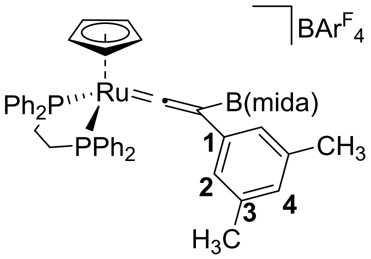


Complex **2m** was obtained as yellow crystals (62.0 mg, 0.0364 mmol, 71% yield) by using [RuCl(dppe)Cp] (30.7 mg, 0.0512 mmol), (*p*-FC_6H_4)C≡CB(mida) (15.9 mg, 0.0578 mmol), and $NaBAr^F_4 \cdot 2.6H_2O$ (50.7 mg, 0.0543 mmol).

^1H NMR (acetone-*d*$_6$): δ 7.80 (s, 8H, *o*-H of BAr^F_4), 7.77 (m, 4H, *o*-H of Ph in dppe), 7.68 (s, 4H, *p*-H of BAr^F_4), 7.49 (m, 2H, *p*-H of Ph in dppe), 7.40 (m, 6H, *m*- and *p*-H of Ph in dppe), 7.33 (m, 4H, *m*-H of Ph in dppe) 7.23 (m, 4H, *o*-H of Ph in dppe)

6.88 (m, 2H, H2), 6.73 (m, 2H, H3), 5.72 (s, 5H, Cp), 4.01 (d, 2H, $^2J_{HH}$ = 17.3 Hz, CH_2 of MIDA), 3.43 (m, 2H, CH_2 of dppe), 3.29 (d, 2H, $^2J_{HH}$ = 16.8 Hz, CH_2 of mida), 3.11 (m, 2H, CH_2 of dppe), 2.69 (s, 3H, CH_3 of mida). $^{31}P\{^1H\}$ NMR (acetone-d_6): δ 79.7 (s, dppe). $^{13}C\{^1H\}$ NMR (acetone-d_6): δ 338.7 (t, $^2J_{CP}$ = 16.0 Hz, Ru=*C*=C), 167.7 (s, CO of mida) 162.6 (q, $^1J_{CB}$ = 50.0 Hz, *ipso*-C of $BAr^F{}_4$), 162.3 (d, $^1J_{CF}$ = 245.0 Hz, C4) 137.9 (m, *ipso*-C of Ph in dppe), 135.6 (br, *o*-C of $BAr^F{}_4$), 135.2 (m, *ipso*-C of Ph in dppe), 133.9 (virtual t, *o*-C of Ph in dppe), 132.5 (d, $^3J_{CF}$ = 8.1 Hz, C2), 132.02 (m, *o*-C of Ph in dppe), 131.97 (s, *p*-C of Ph in dppe) 131.5 (s, *p*-C of Ph in dppe), 130.0 (brq, $^2J_{CF}$ = 31.8 Hz, *m*-C of $BAr^F{}_4$), 129.8 (m, *m*-C of Ph in dppe), 129.7 (m, *m*-C of Ph in dppe), 125.4 (q, $^1J_{CF}$ = 273.0 Hz, CF_3 of $BAr^F{}_4$), 124.6 (s, C1), 118.5 (m, *p*-C of $BAr^F{}_4$), 116.3 (d, $^2J_{CF}$ = 21.5 Hz, C3), 92.1 (s, Cp), 62.9 (s, CH_2 of mida), 47.3 (s, CH_3 of mida), 28.4 (m, P*C*H_2). The signal assignable to the Ru=C=*C* could not be found, probably because it is overlapped with other signals. Elemental analysis calcd for $C_{76}H_{52}O_4B_2F_{25}P_2NRu{\cdot}0.5CH_2Cl_2$: C, 52.65; H, 3.00; N, 0.80. Found: C, 52.41; H, 2.83; N, 0.75.

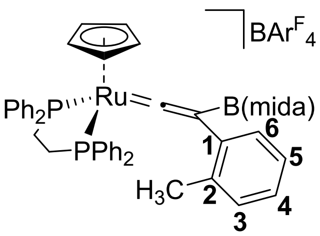
[Ru(=C=C(*m*-xylyl){B(mida)})(dppe)Cp][BAr$^F{}_4$] (2n)



Complex **2n** was obtained as yellow crystals (66.0 mg, 0.0385 mmol, 75% yield) by using [CpRuCl(dppe)] (30.7 mg, 0.0512 mmol), (*m*-xylyl)C≡CB(mida) (17.2 mg, 0.0603 mmol), and NaBAr$^F{}_4{\cdot}2.6H_2O$ (51.5 mg, 0.0552 mmol).

^1H NMR (acetone-d_6): δ 7.80 (s, 8H, *o*-H of $BAr^F{}_4$), 7.78 (m, 4H, *o*-H of Ph in dppe), 7.68 (s, 4H, *p*-H of $BAr^F{}_4$), 7.44 (m, 4H, *p*-H of Ph in dppe×2), 7.31 (m, 8H, *m*–H of Ph in dppe×2), 7.23 (m, 4H, *o*–H of Ph in dppe), 6.60 (m, 1H, H4), 6.47 (s, 2H, H2), 5.66 (s, 5H, Cp), 3.98 (d, 2H, $^2J_{HH}$=16.8 Hz, mida), 3.43 (m, 2H, CH_2 of dppe), 3.19 (d, 2H, $^2J_{HH}$=17.3 Hz, mida), 3.09 (m, 2H, CH_2 of dppe), 2.61 (s, 3H, CH_3 of mida), 2.07 (s, 6H, CH_3 of *m*-xylyl). $^{31}P\{^1H\}$ NMR (acetone-d_6): δ 79.9 (s, dppe). $^{13}C\{^1H\}$ NMR (acetone-d_6): δ 339.3 (t, $^2J_{CP}$ = 15.9 Hz, Ru=*C*=C), 167.8 (s, CO of mida), 162.6 (q, $^1J_{CB}$ = 50.0 Hz, *ipso*-C of $BAr^F{}_4$),138.8 (s, C3), 138.2 (m, *ipso*-C of Ph in dppe), 135.5 (br, *o*-C of $BAr^F{}_4$), 135.0 (m, *ipso*-C of Ph in dppe), 134.0 (m, *o*-C of Ph in dppe), 131.9 (s, *o*- and *p*-C of Ph in dppe), 131.4 (s, *p*-C of Ph in dppe), 130.0 (brq, $^2J_{CF}$ = 31.9 Hz, *m*-C of $BAr^F{}_4$), 129.6 (br, *m*-C of Ph in dppe×2), 129.1 (s, C4), 128.5(s, C2), 128.1 (s, C1), 125.4 (q, $^1J_{CF}$ = 273.0 Hz, CF_3 of $BAr^F{}_4$), 118.4 (m, *p*-C of $BAr^F{}_4$), 92.0 (s, Cp), 62.8 (s, CH_2 of mida), 47.0 (s, CH_3 of mida), 28.5 (m, P*C*H_2) 20.5 (s, CH_3 of *m*-xylyl). The signal assignable to the Ru=C=*C* could not be found, probably because it is overlapped with other signals. HRMS *m*/*z*: $[M+Na]^+$calcd for $RuP_2C_{46}H_{45}BNO_4{}^+$: 850.19604; found 850.19657.

[Ru(=C=C(*o*-tol){B(mida)})(dppe)Cp][BAr$^F{}_4$] (2o)

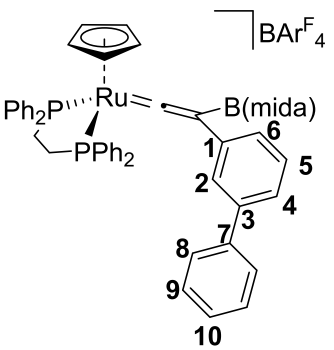


Complex **2o** was obtained as yellow crystals (18.3 mg, 0.0108 mmol, 21% yield) by using [CpRuCl(dppe)] (30.6 mg, 0.0510 mmol), (*o*-tol)C≡CB(mida) (16.2 mg, 0.0600 mmol), and NaBAr$^F{}_4{\cdot}2.6H_2O$ (51.2 mg, 0.0549 mmol).

^1H NMR (acetone-d_6): δ 7.79 (s, 8H, *o*-H of $BAr^F{}_4$), 7.75 (m, 2H, *o*-H of Ph in dppe), 7.68 (s, 4H, *p*-H of $BAr^F{}_4$), 7.51 (m, 3H, *p*- and *o*-H of Ph in dppe), 7.34 (m, 11H, *p*-×3 and *m*-×3 and *o*-H of Ph in dppe), 7.21 (m, 2H, *m*-H of Ph in dppe), 7.05 (m, 3H, *o*-H of Ph in dppe and H6), 6.95 (m, 2H, H4, H5)) 6.87 (m, 1H, H3), 5.84 (s, 5H, Cp), 4.05 (d, 2H, $^2J_{HH}$ = 17.8 Hz,

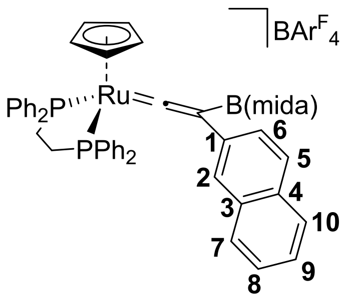
CH_2 of mida), 3.88 (d, 2H, $^2J_{HH}$ = 16.8 Hz, CH_2 of mida), 3.63 (m, 1H, CH_2 of dppe), 3.37 (m, 2H, CH_2 of mida and CH_2 of dppe), 3.23 (m, 1H, CH_2 of dppe), 3.14 (d, 1H, $^2J_{HH}$ = 16.3 Hz, CH_2 of mida), 3.07 (m, 1H, CH_2 of dppe), 2.54 (s, 3H, CH_3 of mida), 2.13 (s, 3H, CH_3 of *o*-tol). $^{31}P\{^1H\}$ NMR (acetone-d_6): δ 79.3 (d, $^2J_{PP}$ = 15.1 Hz, dppe), 78.2 (d, $^2J_{PP}$ = 15.1 Hz, dppe). $^{13}C\{^1H\}$ NMR (acetone-d_6): δ 333.1 (t, $^2J_{CP}$ = 12.4 Hz, Ru=*C*=C), 168.7 (s, CO of mida), 166.5 (s, CO of mida), 162.6 (q, $^1J_{CB}$ = 50.0 Hz, *ipso*-C of $BAr^F{}_4$), 138.5 (s, C2), 138.1 (m, *ipso*-C of Ph in dppe), 137.6 (m, *ipso*-C of Ph in dppe), 135.5 (br, *o*-C of $BAr^F{}_4$), 135.1 (m, *ipso*-C of Ph in dppe) 133.9 (d, $^3J_{CP}$ = 11.5 Hz, *o*-C of Ph in dppe), 132.8 (m, *o*- and *ipso*-C of Ph in dppe), 132.3 (s, C3), 132.1 (s, *p*-C of Ph in dppe), 132.0 (d, $^3J_{CP}$ = 11.0 Hz, *o*-C of Ph in dppe), 131.7 (m-, *o*- and *p*-C of Ph in dppe), 131.35 (s, *p*-C of Ph in dppe), 131.26 (s, *p*-C of Ph in dppe), 130.8 (s, C6), 129.9 (m, *m*-C of $BAr^F{}_4$ and *m*-C of Ph in dppe×4), 128.3 (s, C1), 128.1 (s, C 4), 126.6 (s, C5), 125.4 (q, $^1J_{CF}$ = 272.9 Hz, CF_3 of $BAr^F{}_4$), 118.4 (m, *p*-C of $BAr^F{}_4$), 92.2 (s, Cp), 62.9 (s, CH_2 of mida), 62.4 (s, CH_2 of mida), 46.5 (s, CH_3 of mida), 28.4 (m, PCH_2), 27.7 (m, PCH_2), 21.5 (s, CH_3 of *o*-tol). The signal assignable to the Ru=C=*C* could not be found, probably because it is overlapped with other signals. HRMS *m*/*z*: $[M+Na]^+$ calcd for $RuP_2C_{45}H_{43}BNO_4{}^+$: 836.18039; found 836.18161.

[Ru(=C=C(*β*-biphenyl){B(mida)})(dppe)Cp][BAr$^F{}_4$] (2p)



Complex **2p** was obtained as yellow crystals (26.7 mg, 0.0152 mmol, 51% yield) by using [RuCl(dppe)Cp] (17.8 mg, 0.0297 mmol), (*β*-biphenyl)C≡CB(mida) (11.1 mg, 0.0333 mmol), and $NaBAr^F{}_4 \cdot 2.6H_2O$ (29.2 mg, 0.0313 mmol).
^1H NMR (acetone-d_6): δ 7.79 (s, 8H, *o*-H of $BAr^F{}_4$), 7.75 (m, 4H, *o*-H of Ph in dppe), 7.68 (s, 4H, *p*-H of $BAr^F{}_4$), 7.55 (m, 2H, H8), 7.47 (m, 2H, H9), 7.43 (m, 2H, *p*-H of Ph in dppe), 7.39 (m, 1H, H10), 7.30 (m, 11H, *m*-×2 and *p*-H of Ph in dppe and H4), 7.23 (m, 4H, *o*-H of Ph in dppe), 7.09 (m, 2H, H2, H5), 6.94 (br d, 1H, 6), 5.70 (s, 5H, Cp), 4.04 (d, 2H, $^2J_{HH}$ = 16.8 Hz, CH_2 of mida), 3.44 (m, 2H, CH_2 of dppe), 3.28 (d, 2H, $^2J_{HH}$ = 16.8 Hz, CH_2 of mida), 3.13 (m, 2H, CH_2 of dppe), 2.71 (s, 3H, CH_3 of mida). $^{31}P\{^1H\}$ NMR (acetone-d_6): δ 79.8 (s, dppe). $^{13}C\{^1H\}$ NMR (acetone-d_6): δ 338.8 (t, $^2J_{CP}$ = 16.5 Hz, Ru=*C*=C), 167.8 (s, CO of mida), 162.6 (q, $^1J_{CB}$ = 50.0 Hz, *ipso*-C of $BAr^F{}_4$), 142.5 (s, C3), 141.6 (s, C7), 138.1 (m, *ipso*-C of Ph in dppe), 135.5 (br, *o*-C of $BAr^F{}_4$), 135.0 (m, *ipso*-C of Ph in dppe), 133.9 (virtual t, *o*-C of Ph in dppe), 132.0 (d, *o*- and *p*-C of Ph in dppe), 131.5 (s, *p*-C of Ph in dppe), 130.1 (s, C5), 129.98 (brq, $^2J_{CF}$ = 31.3 Hz, *m*-C of $BAr^F{}_4$), 129.97 (s, C6), 129.6 (m, *m*-C of Ph in dppe×2 and C9), 129.3 (s, C1), 129.2 (s, C2), 128.3 (s, C10), 128.0 (s, C8), 126.1 (s, C4), 125.4 (q, $^1J_{CF}$ = 272.9 Hz, CF_3 of $BAr^F{}_4$), 118.4 (m, *p*-C of $BAr^F{}_4$), 92.1 (s, Cp), 62.9 (s, CH_2 of mida), 47.3 (s, CH_3 of mida), 28.5 (m, PCH_2). The signal assignable to the Ru=C=*C* could not be found, probably because it is overlapped with other signals. HRMS *m*/*z*: $[M+Na]^+$calcd for $RuP_2C_{50}H_{45}BNO_4{}^+$: 898.19604; found 898.20034.

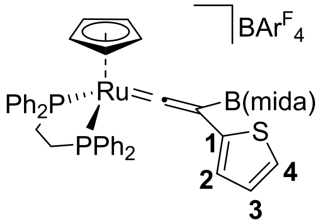
[Ru(=C=C(*β*-naphthyl){B(mida)})(dppe)Cp][BAr$^F{}_4$] (2q)



Complex **2q** was obtained as yellow crystals (41.9 mg, 0.0242 mmol, 47% yield) by using [RuCl(dppe)Cp] (30.6 mg, 0.0510 mmol), (*β*-naphthyl)C≡CB(mida) (18.4 mg, 0.0599 mmol), and $NaBAr^F{}_4 \cdot 2.6H_2O$ (50.9 mg, 0.0556 mmol).

^{1}H NMR (acetone-d_6): δ 7.80 (s, 8H, *o*-H of $BAr^F{}_4$), 7.73 (m, 5H, *o*-H of Ph in dppe and H10), 7.68 (s, 4H, *p*-H of $BAr^F{}_4$), 7.59 (m, 1 H, H7), 7.54 (m, 1H, H5), 7.43 (m, 4H, *p*-H of Ph in dppe and H8, H9), 7.32 (m, 5H, *m*-H of Ph in dppe and H2), 7.20 (m, 10H, *o*- and *m*- and *p*- H of Ph in dppe,), 7.05 (dd, 1H, $^3J_{HH}$ = 8.4 Hz, $^4J_{HH}$ = 1.5 Hz, H6), 5.72 (s, 5H, Cp), 4.00 (d, 2H, $^2J_{HH}$ = 17.3 Hz, CH_2 of mida), 3.45 (m, 2H, CH_2 of dppe), 3.28 (d, 2H, $^2J_{HH}$ = 16.8 Hz, CH_2 of mida), 3.17 (m, 2H, CH_2 of dppe), 2.69 (s, 3H, CH_3 of mida). ^{31}P{^{1}H} NMR (acetone-d_6): δ 79.6 (s, dppe). ^{13}C{^{1}H} NMR (acetone-d_6): δ 338.7 (t, $^2J_{CP}$ = 16.5 Hz, Ru=*C*=C), 167.8 (s, CO of MIDA), 162.6 (q, $^1J_{CB}$ = 50.0 Hz, *ipso*-C of $BAr^F{}_4$), 138.1 (m, *ipso*-C of Ph in dppe), 135.5 (br, *o*-C of $BAr^F{}_4$), 135.0 (m, *ipso*-C of Ph in dppe), 134.4 (s, C3), 133.7 (virtual t, *o*-C of Ph in dppe), 132.9 (s C4), 131.9 (virtual t, *o*-C of Ph in dppe), 131.7 (s, *p*-C of Ph in dppe) 131.4 (s, *p*-C of Ph in dppe), 130.0 (brq, $^2J_{CF}$ = 31.6 Hz, *m*-C of $BAr^F{}_4$), 129.6 (m, *m*-C of Ph in dppe and C2), 129.5 (m, *m*-C of Ph in dppe), 129.4 (s, C5), 128.9 (s, C6), 128.7 (s, C7), 128.2 (s, C10), 126.7 (m, C8, C9), 126.1 (s, C1), 125.4 (q, $^1J_{CF}$ = 273.0 Hz, CF_3 of $BAr^F{}_4$), 118.4 (m, *p*-C of $BAr^F{}_4$), 92.2 (s, Cp), 62.9 (s, CH_2 of mida), 47.3 (s, CH_3 of mida), 28.4 (m, P*C*H_2). The signal assignable to the Ru=C=*C* could not be found, probably because it is overlapped with other signals. Elemental analysis calcd for $C_{80}H_{55}O_4B_2F_{24}P_2NRu\cdot0.5CH_2Cl_2$: C, 54.40; H, 3.12; N, 0.79. Found: C, 54.09; H, 2.96; N, 0.74.

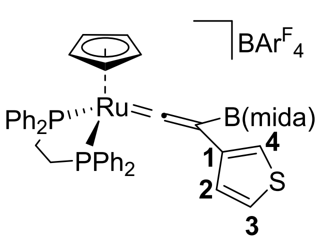
[Ru(=C=C(*α*-thiophene){B(mida)})(dppe)Cp][$BAr^F{}_4$] (2r)



Complex **2r** was obtained as yellow crystals (56.2 mg, 0.0332 mmol, 65% yield) by using [CpRuCl(dppe)] (30.7 mg, 0.0512 mmol), (*α*-thiophene)C≡CB(mida) (14.9 mg, 0.0612 mmol), and $NaBAr^F{}_4\cdot2.6H_2O$ (50.9 mg, 0.0546 mmol).

^{1}H NMR (acetone-d_6): δ 7.78 (m, 12H, s, 8H, *o*-H of $BAr^F{}_4$ and *o*-H of Ph in dppe), 7.68 (s, 4H, *p*-H of $BAr^F{}_4$), 7.46 (m, 4H, *p*-H of Ph in dppe×2), 7.39 (m, 8H, *m*-H of Ph in dppe×2), 7.26 (m, 4H, *o*-H of Ph in dppe), 7.05 (dd, 1H, $^3J_{HH}$ = 5.9 Hz, $^4J_{HH}$ = 1.0 Hz, H2), 6.80 (dd, 1H, $^3J_{HH}$ = 5.4 Hz, $^3J_{HH}$ = 3.5 Hz, H3), 6.35 (m, 1H, H4), 5.70 (s ,5H, Cp), 4.07 (d, 2H, $^2J_{HH}$ = 17.3 Hz, mida), 3.47 (m, 2H, CH_2 of dppe), 3.31 (d, 2H, $^2J_{HH}$ = 17.3 Hz, mida), 3.15 (m, 2H, CH_2 of dppe), 2.54 (s, 3H, mida). ^{31}P{^{1}H} NMR (acetone-d_6): δ 79.5 (s, dppe). ^{13}C{^{1}H} NMR (acetone-d_6): δ 340.4 (t, $^2J_{CP}$ = 15.7 Hz, Ru=*C*=C), 167.8 (s, CO of mida), 162.6 (q, $^1J_{CB}$ = 50.0 Hz, *ipso*-C of $BAr^F{}_4$), 137.8 (m, *ipso*-C of Ph in dppe), 135.5 (br, *o*-C of $BAr^F{}_4$), 135.0 (m, *ipso*-C of Ph in dppe), 134.0 (virtual t, *o*-C of Ph in dppe), 132.1 (m, *o*- and *p*-C of Ph in dppe), 131.6 (s, *p*-C of Ph in dppe), 130.0 (brq, $^2J_{CF}$ = 31.8 Hz, *m*-C of $BAr^F{}_4$), 129.7 (m, *m*-C of Ph in dppe×2), 128.7 (s, C3), 128.1 (s, C1), 126.5 (s, C4), 126.4 (s, C2), 125.3 (q, $^1J_{CF}$ = 272.9 Hz, CF_3 of $BAr^F{}_4$), 118.4 (m, *p*-C of $BAr^F{}_4$), 92.7 (s, Cp), 63.2 (s, CH_2 of mida), 47.4 (s, CH_3 of mida), 28.6 (m, P*C*H_2). The signal assignable to the Ru=C=*C* could not be found, probably because it is overlapped with other signals. Elemental analysis calcd for $C_{74}H_{51}O_4B_2F_{24}P_2NSRu$: C, 52.56; H, 3.04; N, 0.83. Found: C, 52.43; H, 2.79; N, 0.79.

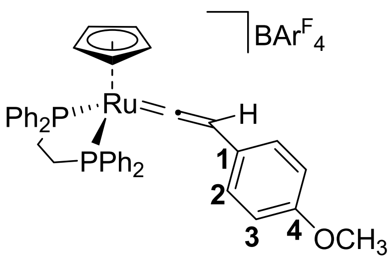
[Ru(=C=C(*β*-thiophene){B(mida)})(dppe)Cp][$BAr^F{}_4$] (2s)



Complex **2s** was obtained as red crystals (48.3 mg, 0.0286 mmol, 58% yield) by using [RuCl(dppe)Cp] (29.6 mg, 0.0493 mmol), (*β*-thiophene)C≡CB(mida) (14.4 mg, 0.0592 mmol), and $NaBAr^F{}_4\cdot2.6H_2O$ (50.9 mg, 0.0546 mmol).

^{1}H NMR (acetone-d_6): δ 7.79 (m, 12H, *o*-H of BAr$^F{}_4$ and *o*-H of Ph in dppe), 7.68 (s, 4H, *p*-H of BAr$^F{}_4$), 7.44 (m, 8H, *p*-×2 and *m*-H of Ph in dppe), 7.35 (m, 4H, *m*-H of Ph in dppe), 7.25 (m, 4H, *o*-H of Ph in dppe), 7.17 (dd, 1H, $^3J_{HH}$ = 5.0 Hz, $^4J_{HH}$ = 3.0 Hz, H2), 6.72 (m, 1H, H4), 6.52 (m, 1H, H3), 5.67 (s ,5H, Cp), 4.02 (d, 2H, $^2J_{HH}$ = 16.8 Hz, mida), 3.41 (m, 2H, dppe), 3.24 (d, 2H, $^2J_{HH}$ = 17.3 Hz, mida), 3.06 (m, 2H, dppe), 2.62 (s, 3H, mida). ^{31}P{^{1}H} NMR (acetone-d_6): δ 79.6 (s, dppe). ^{13}C{^{1}H} NMR (acetone-d_6): δ 339.3 (t, $^2J_{CP}$ = 15.7 Hz, Ru=*C*=C), 167.8 (s, CO of mida), 162.6 (q, $^1J_{CB}$ = 50.0 Hz, *ipso*-C of BAr$^F{}_4$), 137.9 (m, *ipso*-C of Ph in dppe), 135.5 (br, *o*-C of BAr$^F{}_4$), 135.0 (m, *ipso*-C of Ph in dppe), 134.0 (virtual t, *o*-C of Ph in dppe), 132.0 (m, *o* and *p*-C of Ph in dppe), 131.5 (s, *p*-C of Ph in dppe), 130.0 (brq, $^2J_{CF}$ = 34.8 Hz, *m*-C of BAr$^F{}_4$), 129.7 (m, *m*-C of Ph in dppe×2), 129.5 (s, C3), 127.1 (s, C2), 126.5 (s, C1), 125.4 (q, $^1J_{CF}$ = 272.8 Hz, CF_3 of BAr$^F{}_4$), 123.1 (s, C4), 118.5 (m, *p*-C of BAr$^F{}_4$), 92.2 (s, Cp), 62.8 (s, CH_2 of mida), 47.2 (s, CH_3 of mida), 28.6 (m, P*C*H_2). The signal assignable to the Ru=C=*C* could not be found, probably because it is overlapped with other signals. Elemental analysis calcd for $C_{74}H_{51}O_4B_2F_{24}P_2NSRu\cdot0.5CH_2Cl_2$: C, 51.62; H, 2.97; N, 0.81. Found: C, 51.52; H, 2.96; N, 0.76.

[Ru(=C=CH(*p*-Ans))(dppe)Cp][BAr$^F{}_4$] (3b)

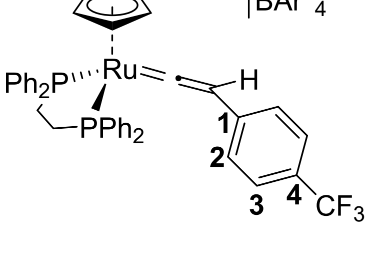


To characterize byproducts in the vinylidene rearrangement, we performed synthesis of the protodeboronated complex.

A mixture of [RuCl(dppe)Cp] (60.3 mg, 0.1005 mmol), (*p*-Ans)C≡CB(dan) (30.2 mg, 0.1013 mmol), H_2O (5.2 mg, 0.2885 mmol), and NaBAr$^F{}_4\cdot$2.6H_2O (101.9 mg, 0.1092 mmol) in 1,2-dichloroethane (2 mL) was heated at 70 °C for 1 h. The resulting brown suspension was filtered through a short pad of Celite and rinsed with 1,2-dichloroethane (ca. 1 mL). The filtrate was dried in vacuo, and the residue was purified by column chromatography on silica gel (dichloromethane/hexane = 1:1). Complex **3b** was obtained as a red oil (118.4 mg, 0.0759 mmol).

^{1}H NMR ($CDCl_3$): δ 7.76 (s, 8H, *o*-H of BAr$^F{}_4$), 7.53 (s, 4H, *p*-H of BAr$^F{}_4$), 7.42 (m, 16H, *p*-×2 and *m*-×2 and *o*-H of Ph in dppe), 7.14 (m, 4H, *o*-H of Ph in dppe), 6.42 (d, 2H, $^3J_{HH}$ = 8.9 Hz, H3), 6.15 (d, 2H, $^3J_{HH}$ = 8.4 Hz, H2), 5.50 (s, 5H, Cp), 4.68 (s, 1H, Ru=C=CH), 3.71 (s, 3H, CH_3 of *p*-Ans), 2.99 (m, 2H, CH_2 of dppe), 2.70 (m, 2H, CH_2 of dppe). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 77.5 (s, dppe). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 356.7 (t, $^2J_{CP}$ = 16.5 Hz, Ru=*C*=C), 161.9 (q, $^1J_{CB}$ = 50.0 Hz, *ipso*-C of BAr$^F{}_4$), 158.6 (s, C4), 135.0 (br, *o*-C of BAr$^F{}_4$ and *ipso*-C of Ph in dppe), 133.8 (m, *ipso*-C of Ph in dppe), 132.1 (virtual t, *o*-C of Ph in dppe), 132.0 (s, *p*-C of Ph in dppe), 131.9 (s, *p*-C of Ph in dppe), 131.4 (virtual t, *o*-C of Ph in dppe), 129.3 (m, *m*-C of Ph in dppe×2), 129.0 (brq, $^2J_{CF}$ = 31.4 Hz, *m*-C of BAr$^F{}_4$), 127.0 (s, C2), 124.7 (q, $^1J_{CF}$ = 273.5 Hz, CF_3 of BAr$^F{}_4$), 117.6 (m, *p*-C of BAr$^F{}_4$), 117.5 (s, Ru=C=*C*), 117.5 (s, C1), 114.4 (s, C3), 91.9 (s, Cp), 55.3 (s, CH_3 of Ru=C=C(*p*-Ans)), 27.1 (m, P*C*H_2). HRMS *m/z*: [M+Na]$^+$ calcd for $RuP_2OC_{40}H_{37}{}^+$: 697.13632; found 697.13633.

[Ru(=C=CH(*p*-$CF_3C_6H_4$))(dppe)Cp][BAr$^F{}_4$] (3c)



To characterize byproducts in the vinylidene rearrangement, we performed synthesis of the protodeboronated complex .

A mixture of [RuCl(dppe)Cp] (59.7 mg, 0.0995 mmol), (*p*-

$CF_3C_6H_4)C{\equiv}CB(dan)$ (34.0 mg, 0.1012 mmol), H_2O (6.1 mg, 0.3385 mmol), and $NaBAr^F{}_4{\cdot}2.6H_2O$ (101.7 mg, 0.1090 mmol) in 1,2-dichloroethane (2 mL) was heated at 70 °C for 1 h. The resulting brown suspension was filtered through a short pad of Celite and rinsed with 1,2-dichloroethane (ca. 1 mL). The filtrate was dried in vacuo, and the residue was purified by column chromatography on silica gel (dichloromethane/hexane = 1:1). Complex was obtained as a red oil (142.5 mg, 0.0892 mmol).

^{1}H NMR ($CDCl_3$): δ 7.79 (s, 8H, *o*-H of $BAr^F{}_4$), 7.55 (s, 4H, *p*-H of $BAr^F{}_4$), 7.46 (m, 12H, *p*-×2 and *m*- and *o*-H of Ph in dppe), 7.38 (m, *m*-H of Ph in dppe), 7.17 (m, 4H, *o*-H of Ph in dppe), 7.08 (d, 2H, $^3J_{HH}$ = 7.9 Hz, H3), 6.33 (d, 2H, $^3J_{HH}$ = 7.9 Hz, H2), 5.53 (s, 5H, Cp), 4.76 (s, 1H, Ru=C=CH), 3.00 (m, 2H, CH_2 of dppe), 2.71 (m, 2H, CH_2 of dppe). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 76.6 (s, dppe). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 350.9 (t, $^2J_{CP}$ = 16.3 Hz, Ru=*C*=C), 161.9 (q, $^1J_{CB}$ = 50.0 Hz, *ipso*-C of $BAr^F{}_4$), 135.0 (br, *o*-C of $BAr^F{}_4$), 134.3 (m, *ipso*-C of Ph in dppe), 133.5 (m, *ipso*-C of Ph in dppe), 132.2 (m, *p*-C of Ph in dppe×2), 132.0 (virtual t, *o*-C of Ph in dppe), 131.4 (virtual t, *o*-C of Ph in dppe), 130.0 (s, C1), 129.4 (m, *m*-C of Ph in dppe×2), 129.1 (brq, $^2J_{CF}$ = 31.5 Hz, *m*-C of $BAr^F{}_4$), 128.0 (m, C4), 125.5 (m, C3) 125.4 (s, C2), 124.7 (q, $^1J_{CF}$ = 273.8 Hz, CF_3 of $BAr^F{}_4$), 124.0 (q, $^1J_{CF}$ = 272.9 Hz, CF_3 of Ru=C=C(*p*-$CF_3C_6H_4$)), 117.6 (m, *p*-C of $BAr^F{}_4$), 117.1 (s, Ru=C=*C*), 92.2 (s, Cp), 27.0 (m, P*C*H_2). HRMS *m*/*z*: $[M+Na]^+$ calcd for $RuP_2F_3C_{40}H_{34}{}^+$: 735.11313; found 735.11372.

2. ^{13}C-labeling Experiments

According to the general procedure, a reaction was performed using complex **1a** (31.4 mg, 0.0523 mmol), an isotopic labeling alkyne, PhC≡^{13}CB(mida) (14.6 mg, 0.0568 mmol), and $NaBAr^F{}_4{\cdot}2.6H_2O$ (51.2 mg, 0.0549 mmol). The ratio of **2-^{13}Cα** and **2-^{13}C$_\beta$** was estimated from the ^{13}C{^{1}H} NMR as follows:

The relative integration ratio of the C_β signals in the ^{13}C-labeling and non-labeling experiments based on the Cp signals is 1.58:0.07 ($^{13}C_\beta$ in labeling experiment: $^{13}C_\beta$ in non-labeling experiment). Taking into account that the alkyne reagent is 25% ^{13}C-enriched, and the natural abundance of ^{13}C is 1.1%, the ratio of C_β signals between the two experiments can be calculated as:

$$^{13}C_\beta \text{ in } ^{13}\text{C-labeling experiment}:^{13}C_\beta \text{ in non-labeling experiment} = 0.25t + 0.011(1 - t):0.011,$$

where t = the migration ratio of the B(mida) group.

Thus, it is calculated to be 1.10 by solving the following equation:

$$\{0.25t + 0.011(1 - t)\} \times 0.07 = 0.011 \times 1.58$$

$$t = 0.99$$

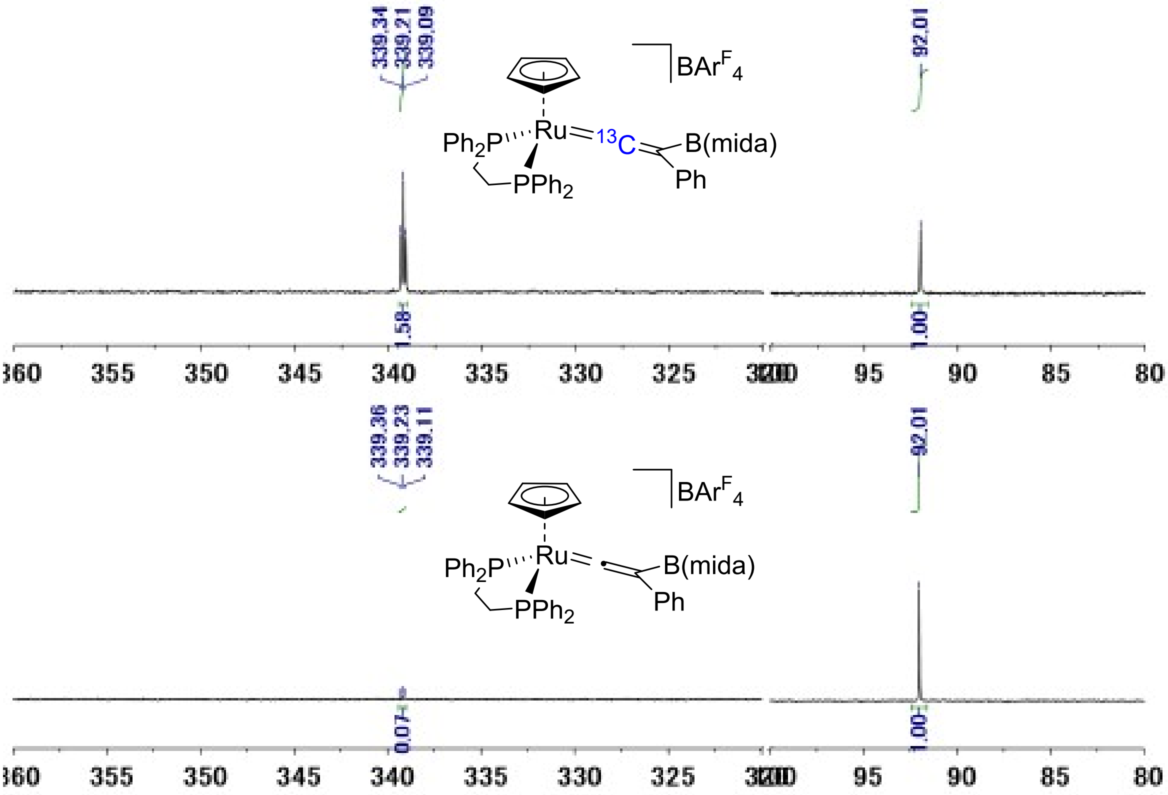


Figure S2. $^{13}C\{^1H\}$ NMR spectra of ^{13}C-labeled (upper) and non-labeled (lower) vinylidene complexes **2**.

A reaction was performed according to the general procedure using complex **1a** (30.5 mg, 0.0508 mmol), an isotopic labeling alkyne, Ph^{13}C≡CB(dan) (13.7 mg, 0.0511 mmol), and anhydrous NaBAr$^F_4$·6THF (66.0 mg, 0.0500 mmol). The ratio of **3-^{13}Cα** and **3-^{13}C$_\beta$** was estimated from the $^{13}C\{^1H\}$ NMR as follows:

The relative integration ratio of the C_β signals in the ^{13}C-labeling and non-labeling experiments based on the Cp signals is 2.81:0.016 ($^{13}C_\beta$ in labeling experiment:$^{13}C_\beta$ in non-labeling experiment). Taking into account that the alkyne reagent is 19.5% ^{13}C-enriched, and the natural abundance of ^{13}C is 1.1%, the ratio of C_β signals between the two experiments can be calculated as:

$^{13}C_\beta$ in ^{13}C-labeling experiment:$^{13}C_\beta$ in non-labeling experiment = 0.195t + 0.011(1 − t):0.011,

where t = the migration ratio of the B(dan) group.

Thus, it is calculated to be 1.10 by solving the following equation:

$$\{0.195t + 0.011(1 - t)\} \times 0.16 = 0.011 \times 2.81$$

$$t = 0.99$$

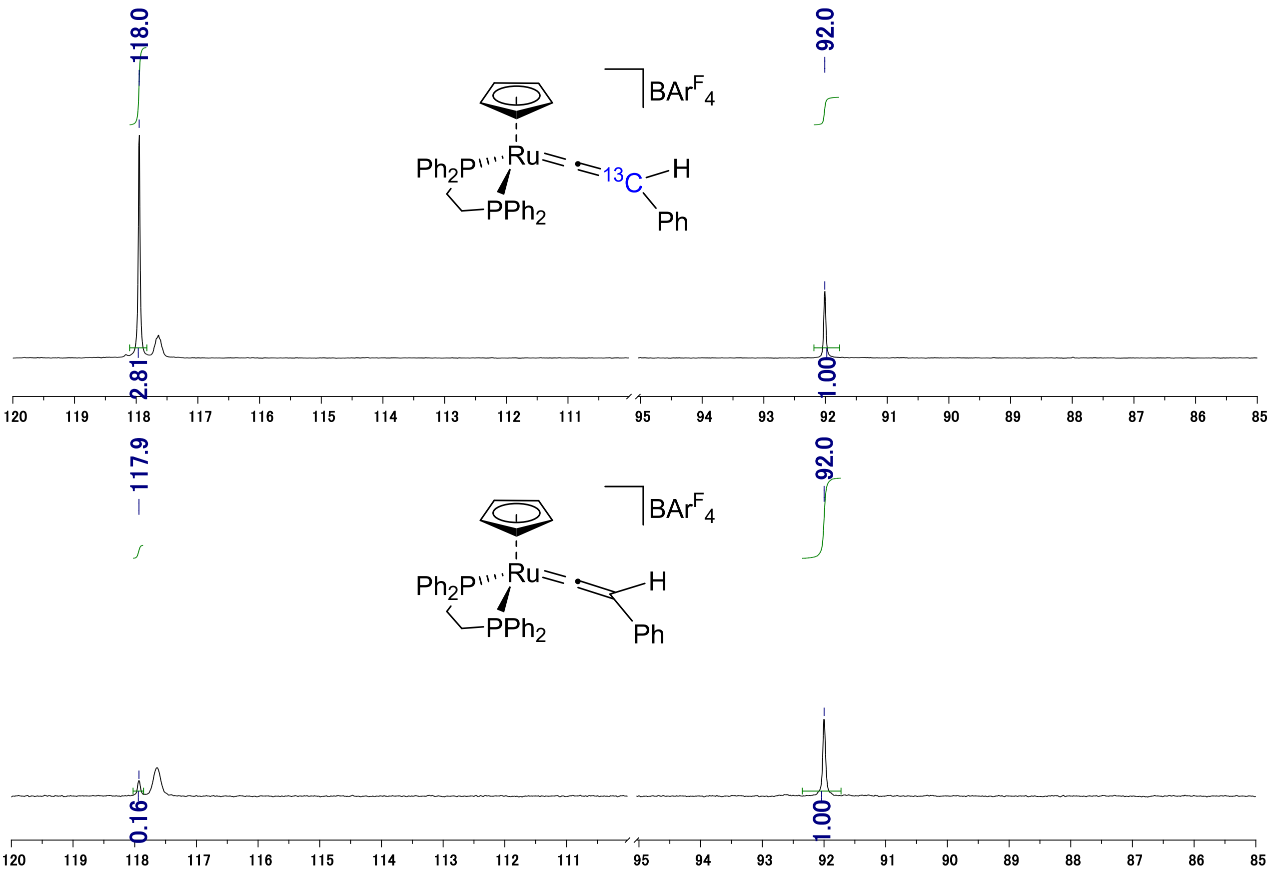


Figure S3. $^{13}C\{^{1}H\}$ NMR spectra of ^{13}C-labeled (upper) and non-labeled (lower) vinylidene complexes **3**.

3. DFT calculations

All calculations were carried out by using the Gaussian 16 program packages.[S1] Geometry optimizations were performed at B3LYP with GD3BJ empirical dispersion[S2] along with a combined basis set: 6-311G* for C, H, P, N, and B and SDD for Ru. Vibrational frequencies were calculated at the same level to characterize each stationary points to confirm no imaginary frequencies except for the transition state with one imaginary frequency. NBO analyses were performed HF/6-311G(d)+SDD.

Table S1. Gibbs free energy (G) at 298.150 K and 1.0000 atm.

	Δ*G* (kcal/mol)	Δ*H* (kcal/mol)	Δ*S* (cal/mol)
complex **A** (R = B(dan))	0.0	0.0	0.0
TS (R = B(dan))	9.2	11.3	7.1
Complex **B** (R = B(dan))	-10.1	-8.0	7.0
complex **A** (R = B(mida))	0.0	0.0	0.0
TS (R = B(mida))	21.5	21.7	0.7
Complex **B** (R = B(mida))	-10.1	-10.1	3.5

4. References

S1. M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F.

Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman and D. J. Fox, Gaussian 16 Rev. C.01, Wallingford, CT, 2016.

S2. (a) S. Grimme, *J. Comp. Chem.* 2006, **27**, 1787; (b) S. Grimme, S. Ehrlich and L. Goerigk, *J. Comp. Chem*. 2011, **32**, 1456.

5. NMR Spectra

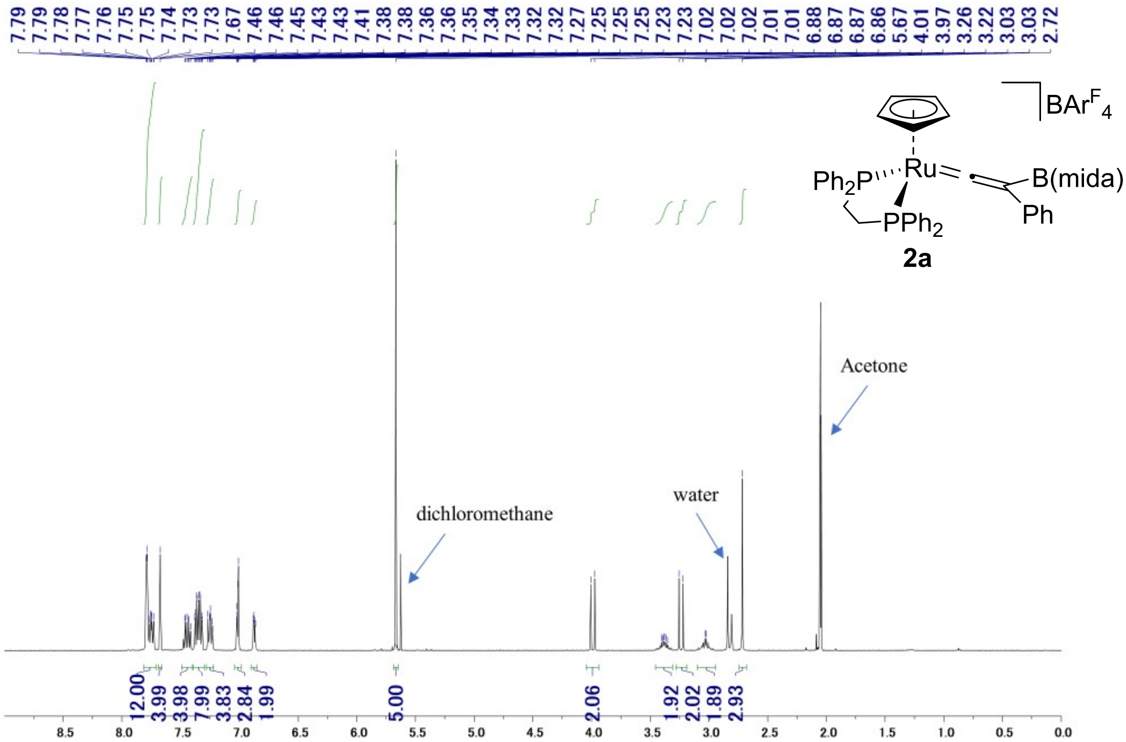


Figure S4. ^{1}H NMR spectrum of **2a** in acetone-*d*6

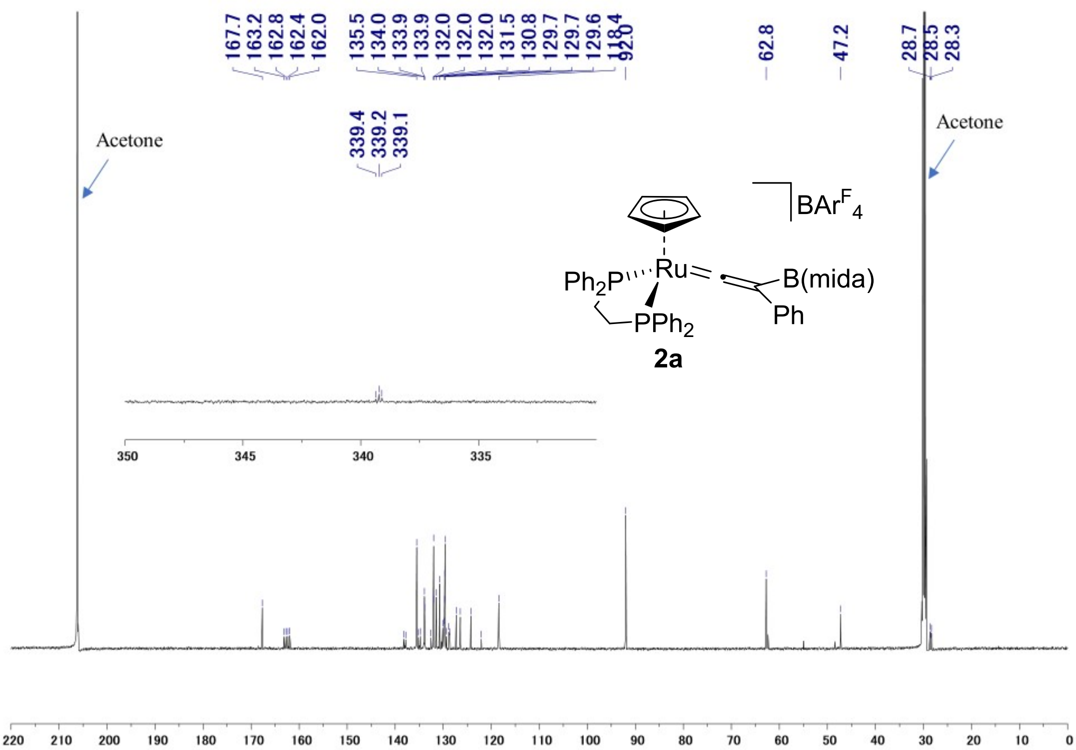


Figure S5. $^{13}C\{^{1}H\}$ NMR spectrum of **2a** in acetone-*d*6

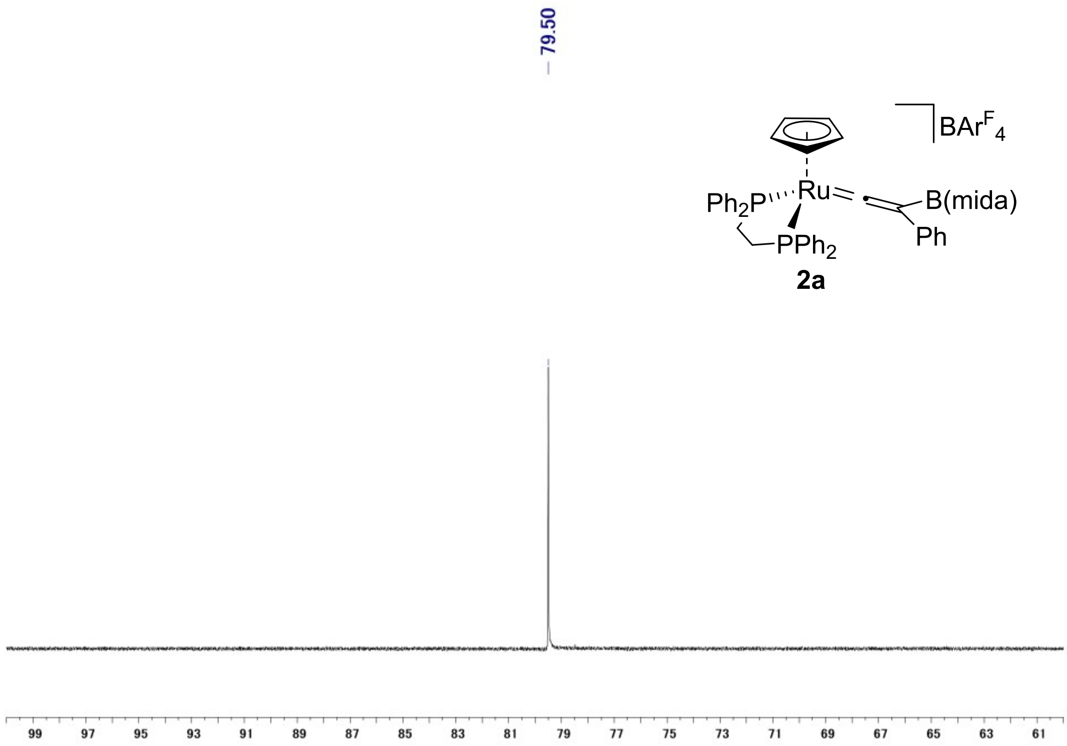


Figure S6. $^{31}P\{^1H\}$ NMR spectrum of **2a** in acetone-*d6*

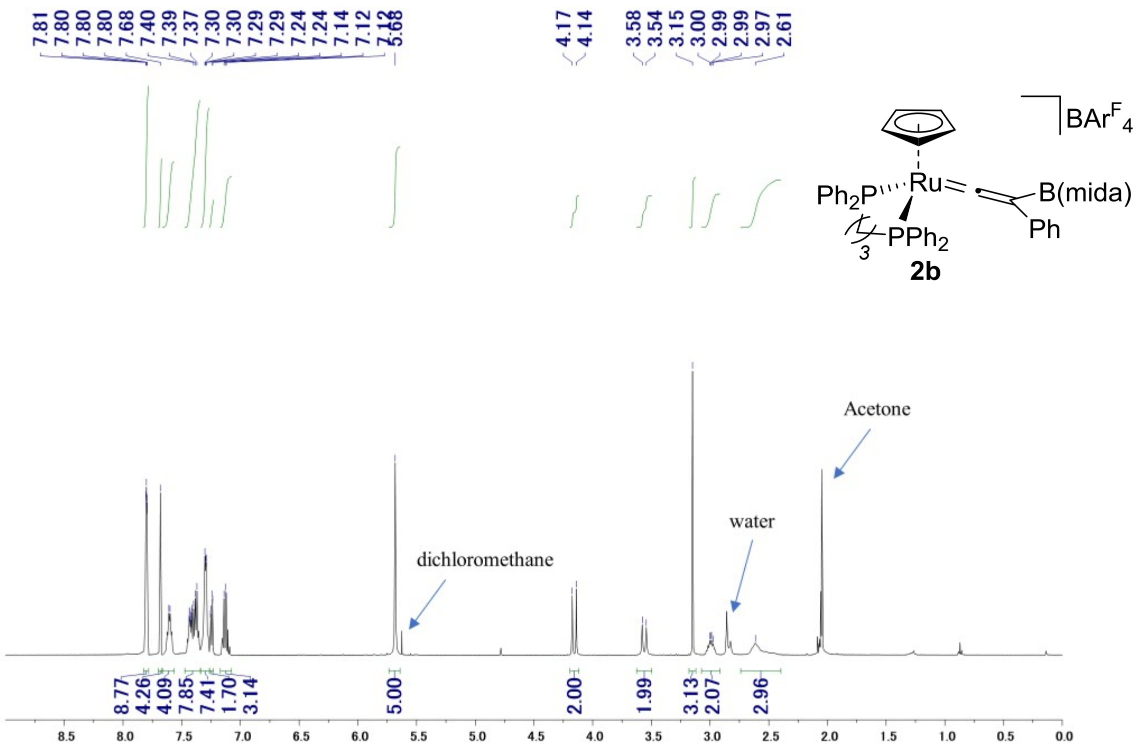


Figure S7. ^1H NMR spectrum of **2b** in acetone-*d6*

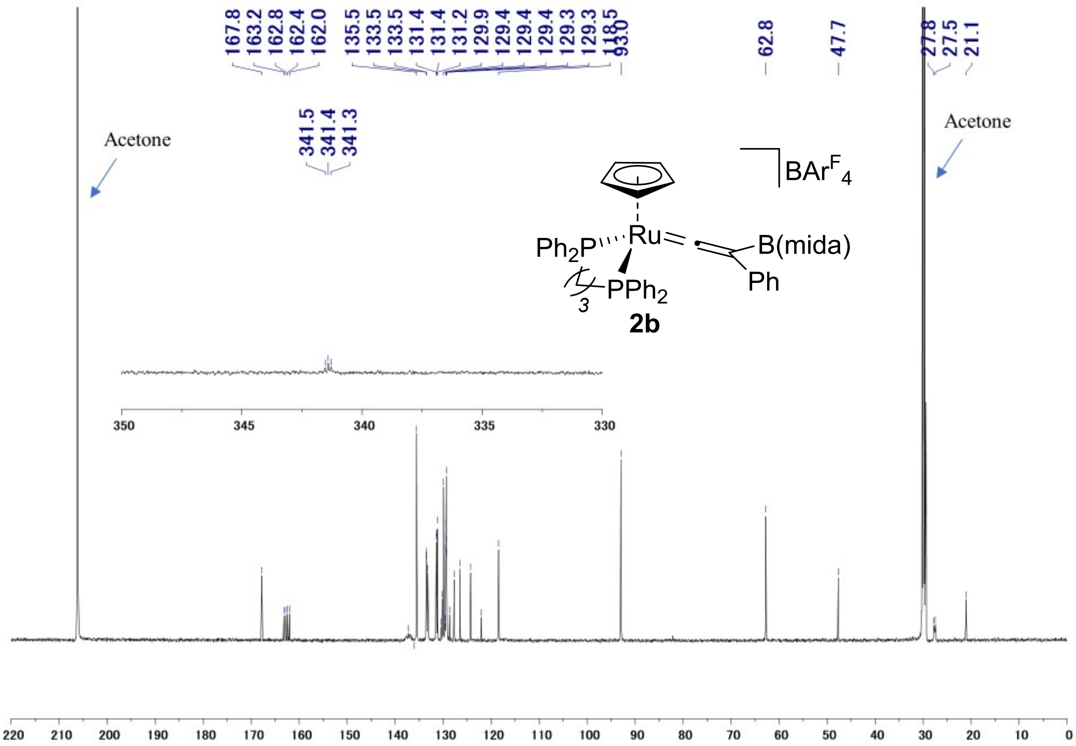


Figure S8. $^{13}C\{^1H\}$ NMR spectrum of **2b** in acetone-*d*6

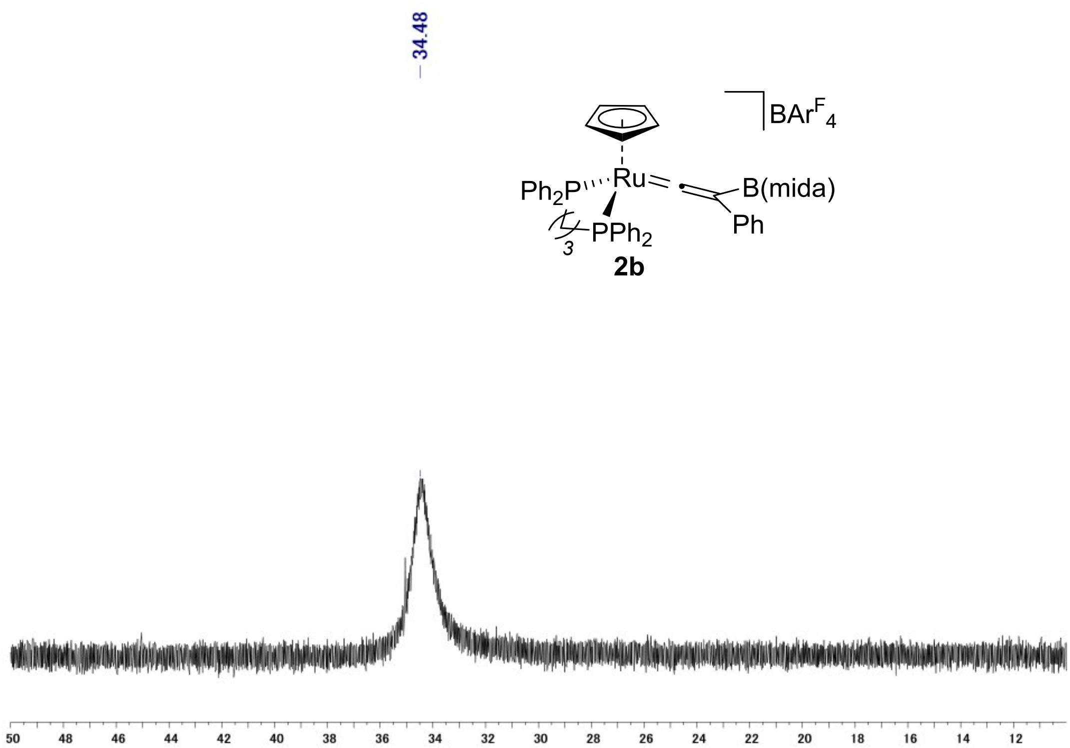


Figure S9. $^{31}P\{^1H\}$ NMR spectrum of **2b** in acetone-*d*6

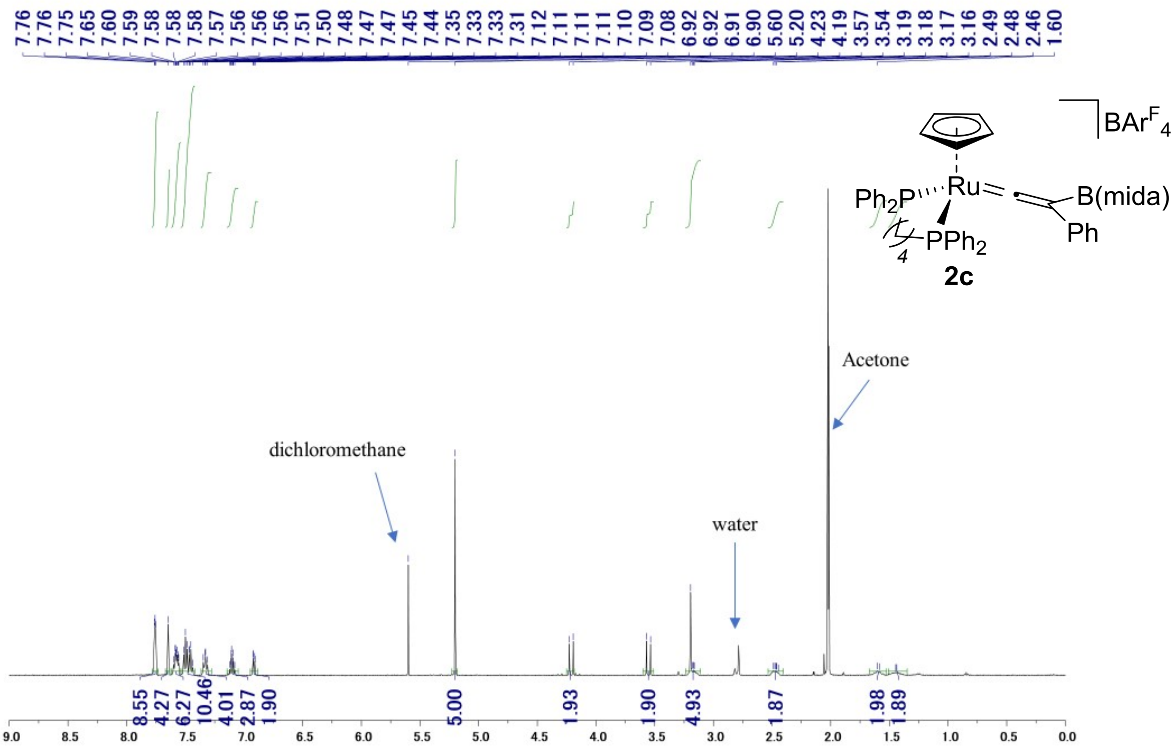


Figure S10. ^{1}H NMR spectrum of **2c** in acetone-*d*6

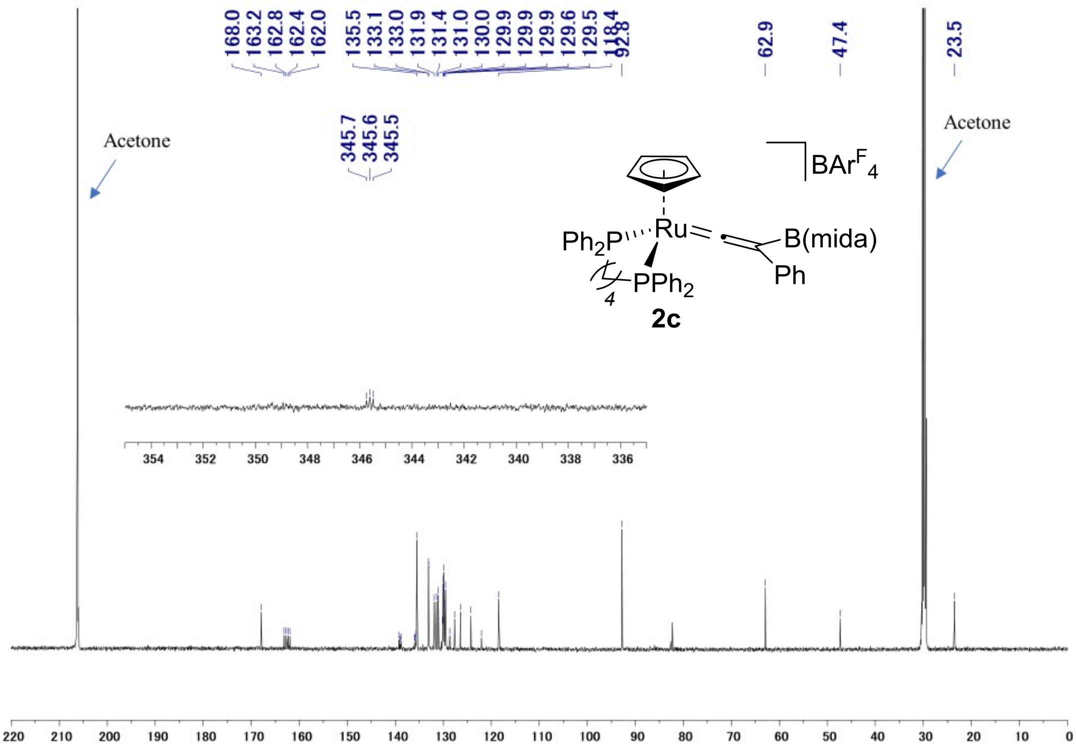


Figure S11. $^{13}C\{^{1}H\}$ NMR spectrum of **2c** in acetone-*d*6

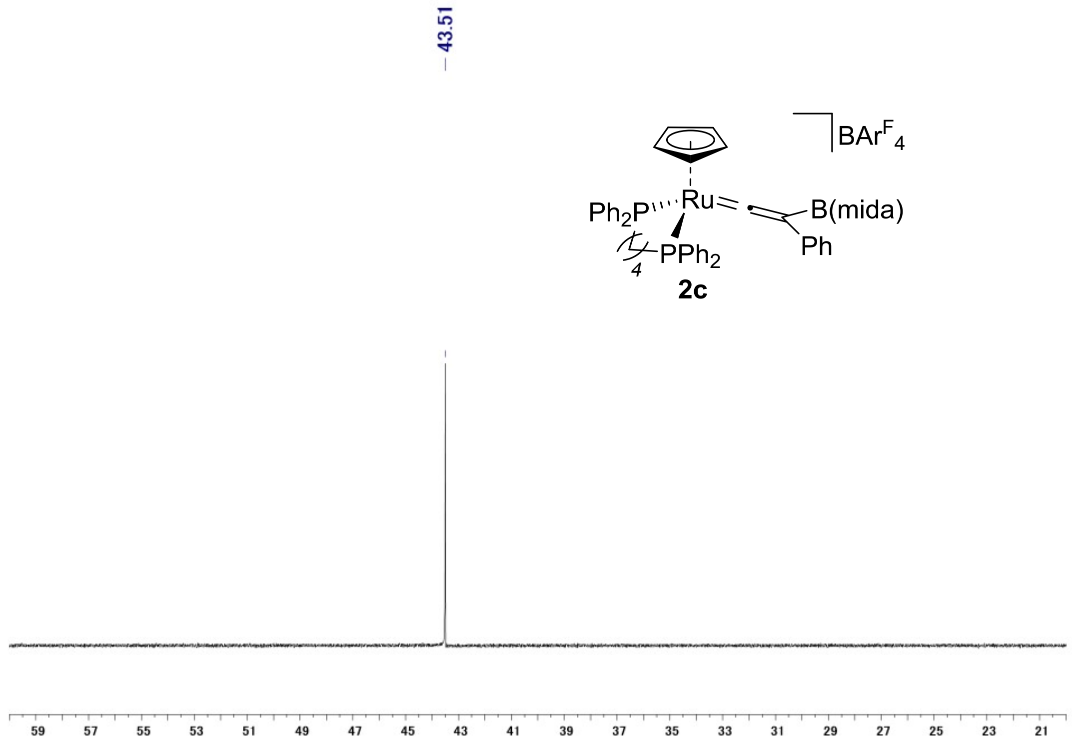


Figure S12. $^{31}P\{^{1}H\}$ NMR spectrum of **2c** in acetone-*d6*

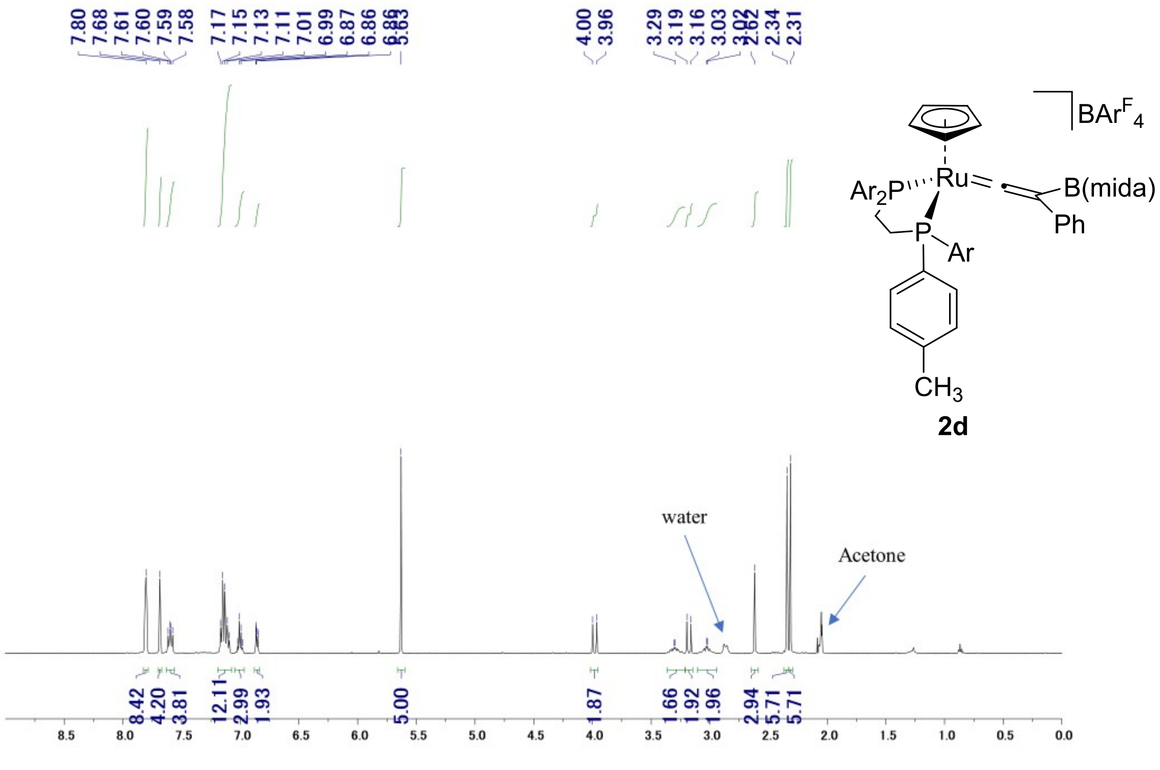


Figure S13. ^{1}H NMR spectrum of **2d** in acetone-*d6*

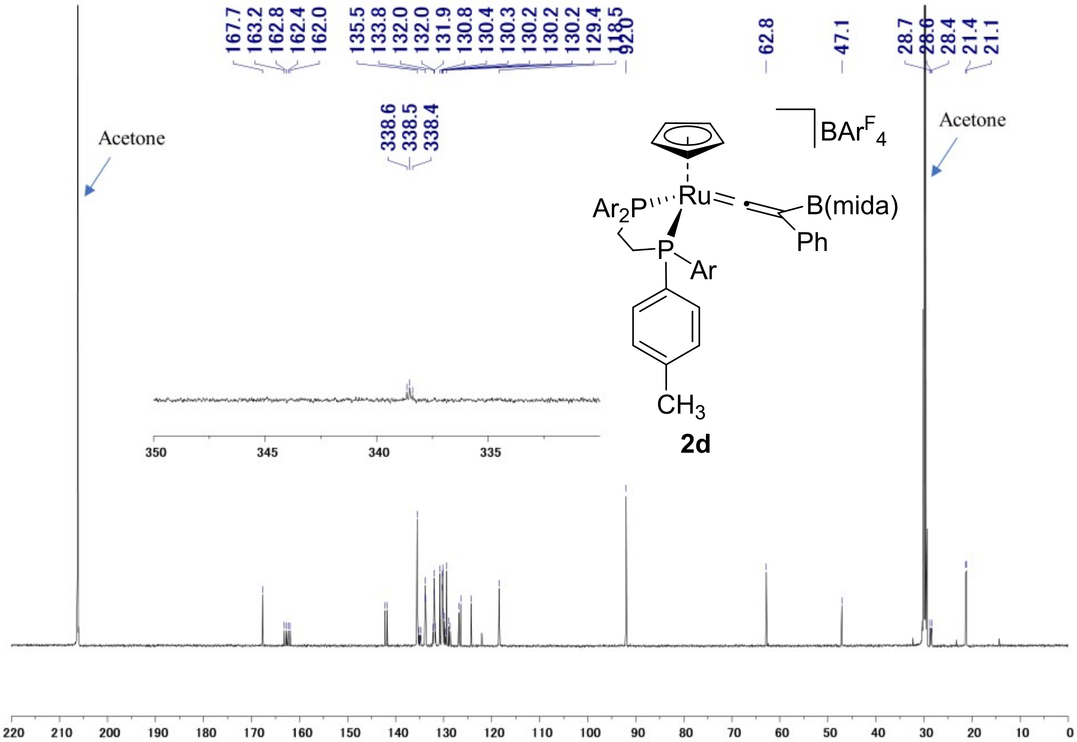


Figure S14. $^{13}C\{^{1}H\}$ NMR spectrum of **2d** in acetone-*d6*

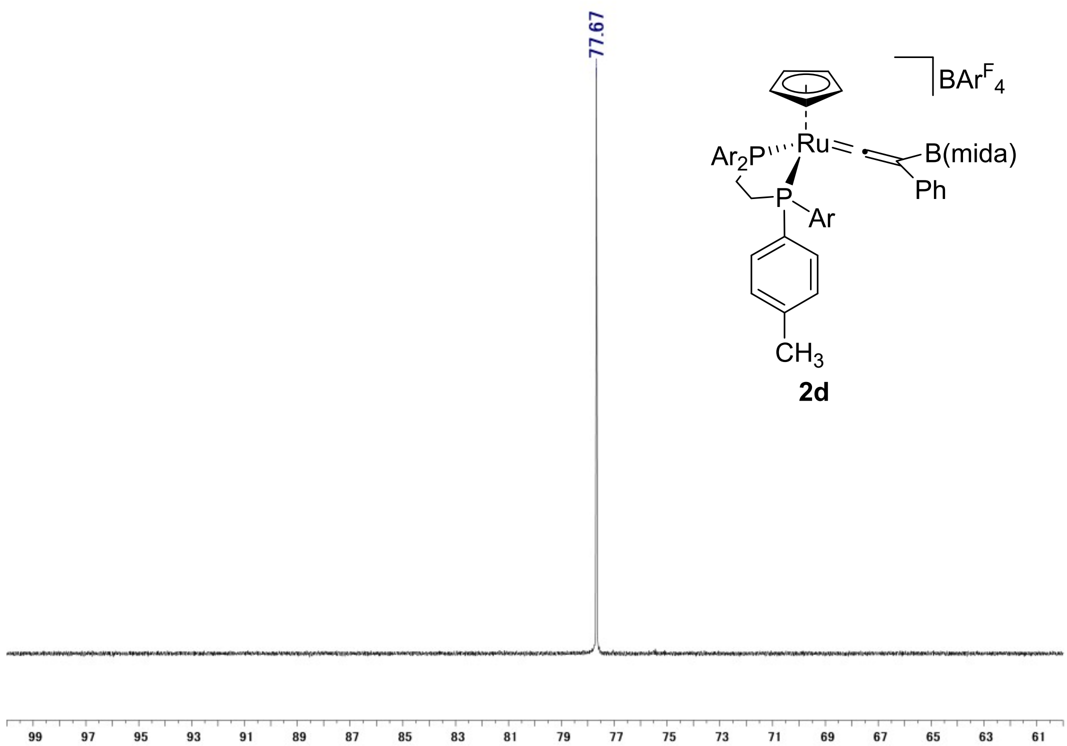


Figure S15. $^{31}P\{^{1}H\}$ NMR spectrum of **2d** in acetone-*d6*

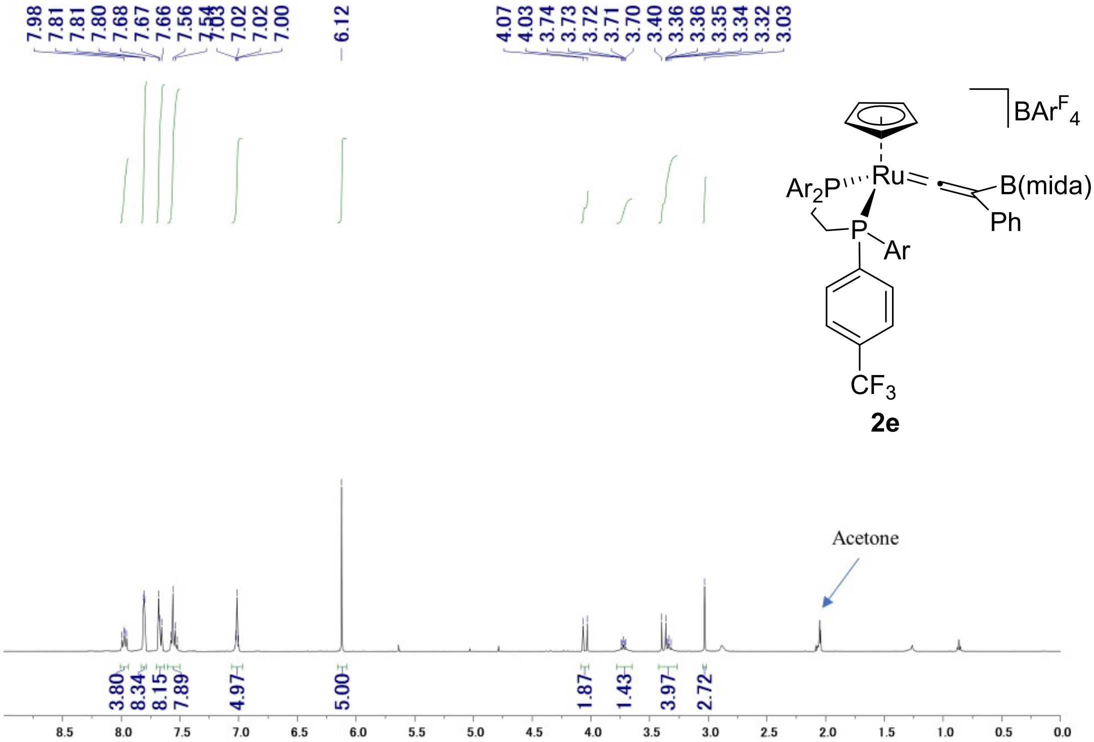


Figure S16. ^{1}H NMR spectrum of **2e** in acetone-*d*6

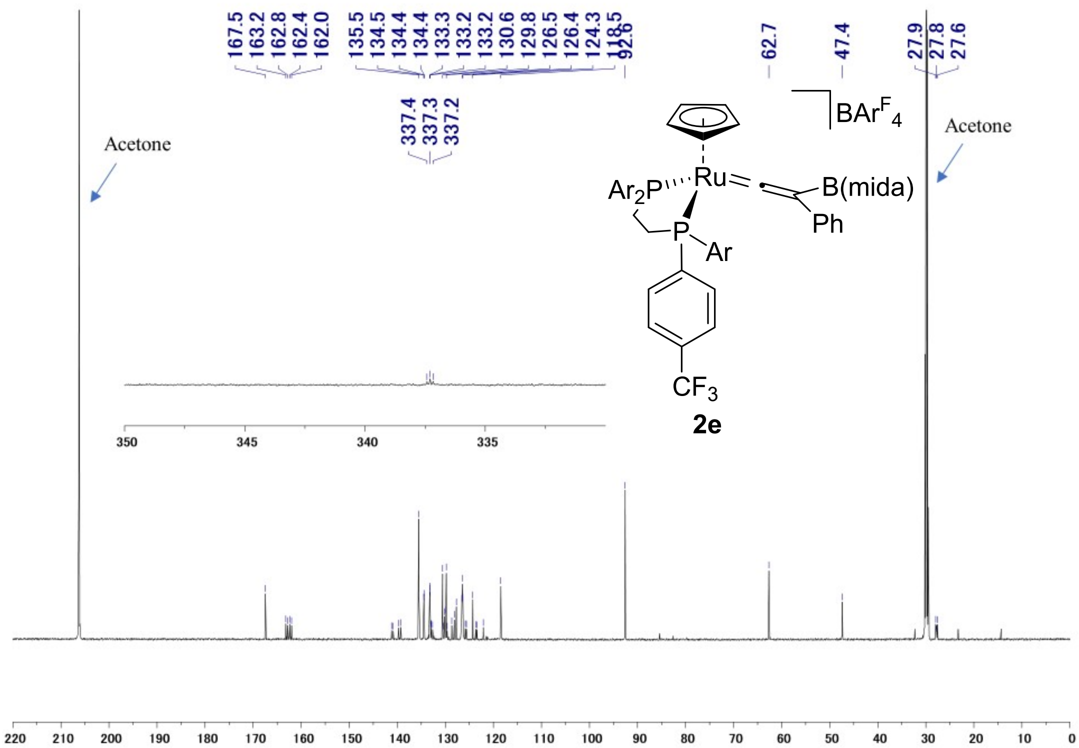


Figure S17. ^{13}C{^{1}H} NMR spectrum of **2e** in acetone-*d*6

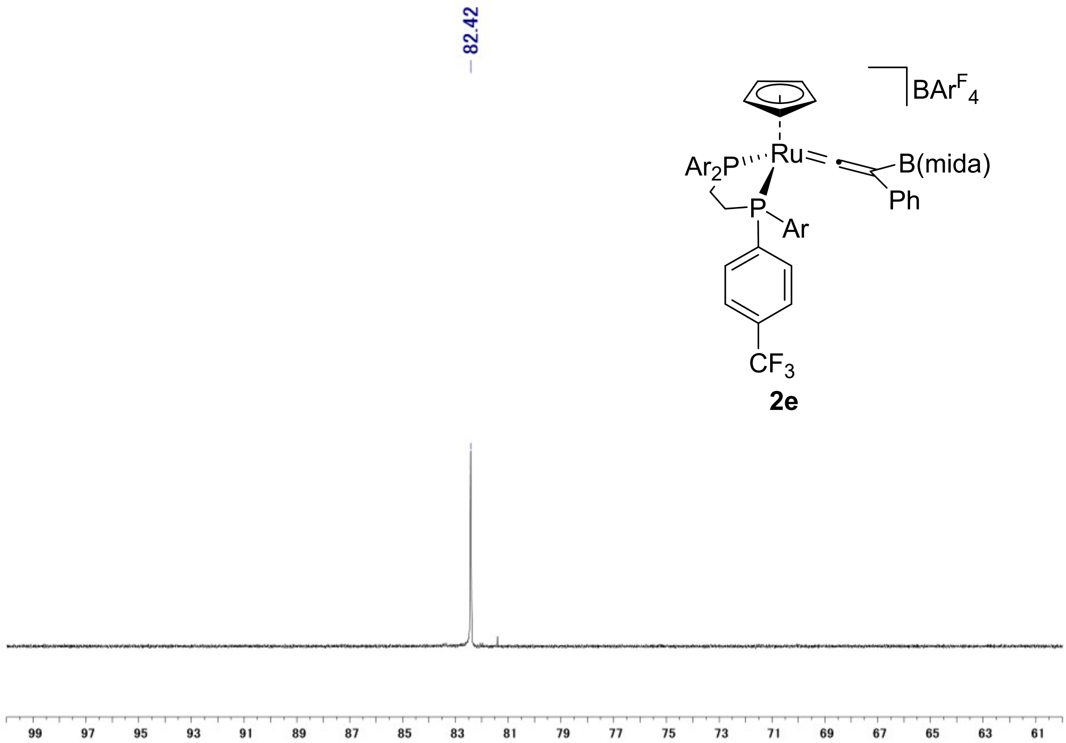


Figure S18. $^{31}P\{^{1}H\}$ NMR spectrum of **2e** in acetone-*d6*

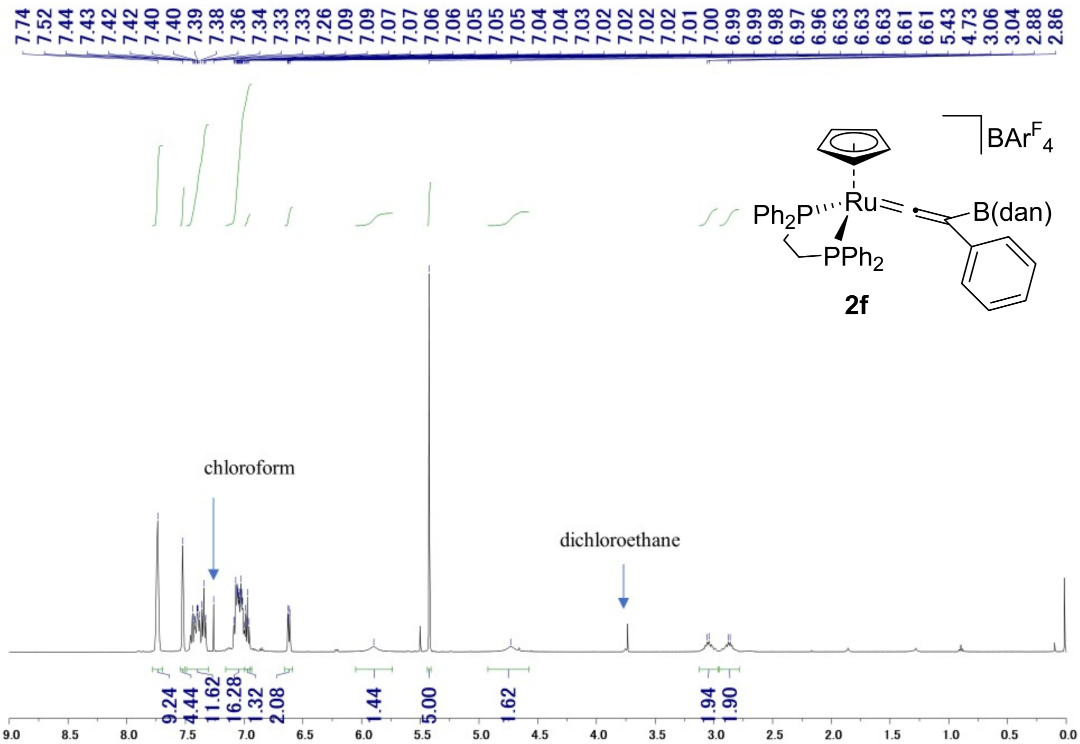


Figure S19. ^{1}H NMR spectrum of **2f** in $CDCl_3$

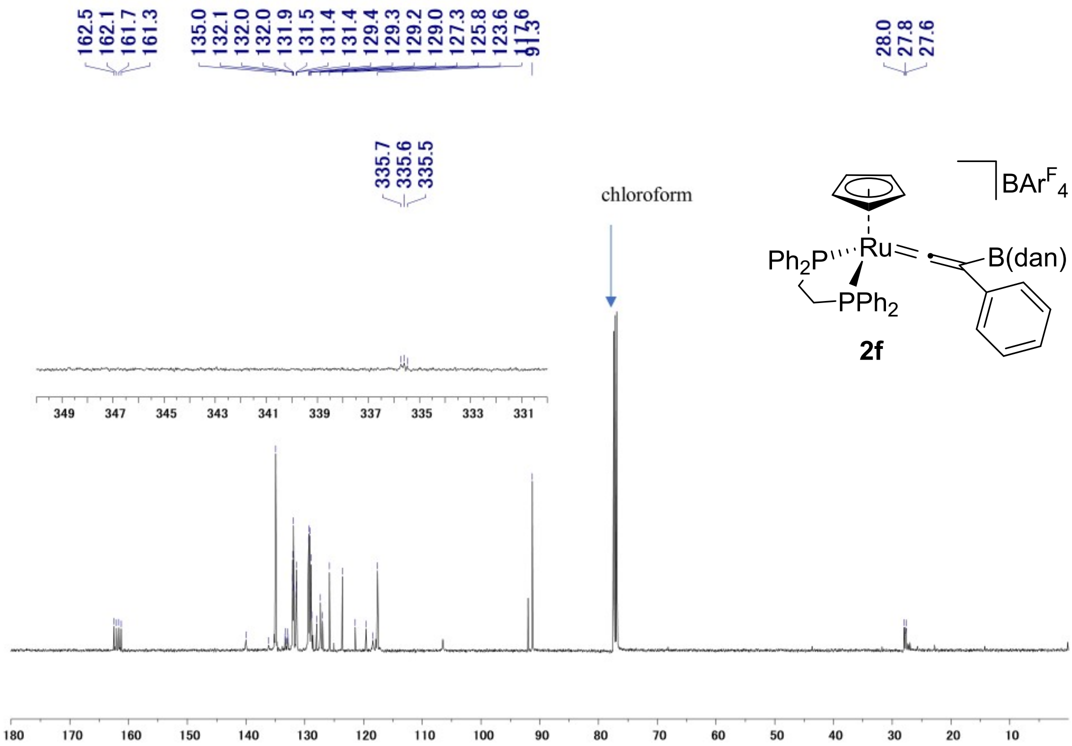


Figure S20. $^{13}C\{^{1}H\}$ NMR spectrum of **2f** in $CDCl_3$

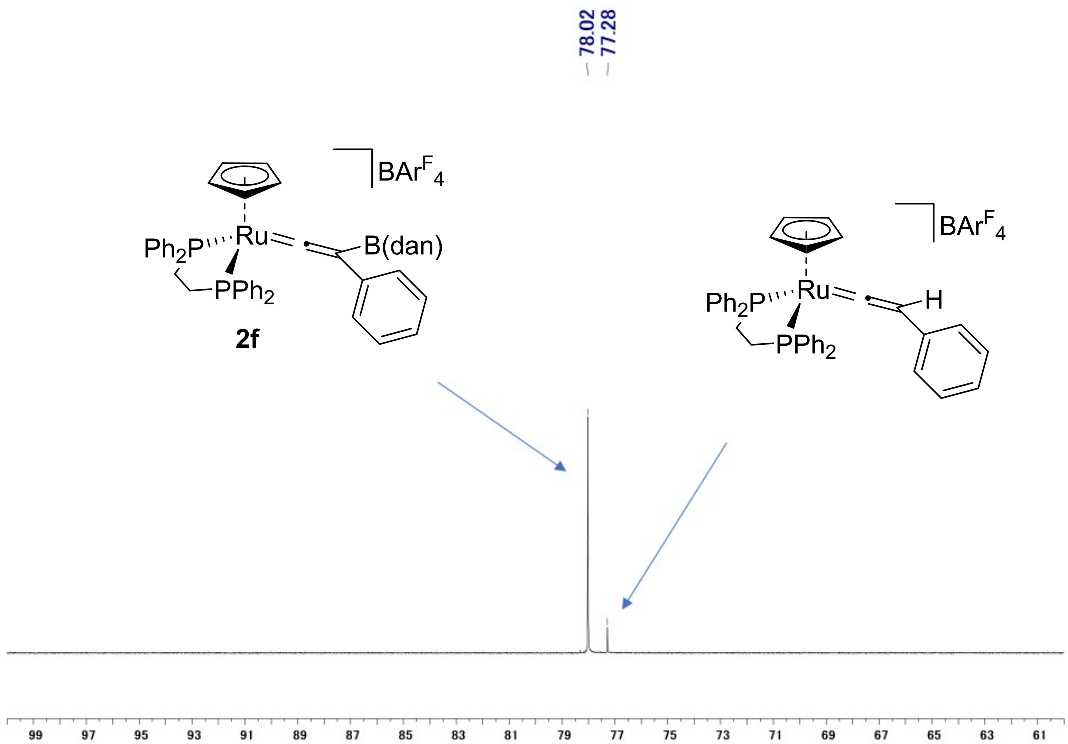


Figure S21. $^{31}P\{^{1}H\}$ NMR spectrum of **2f** in $CDCl_3$

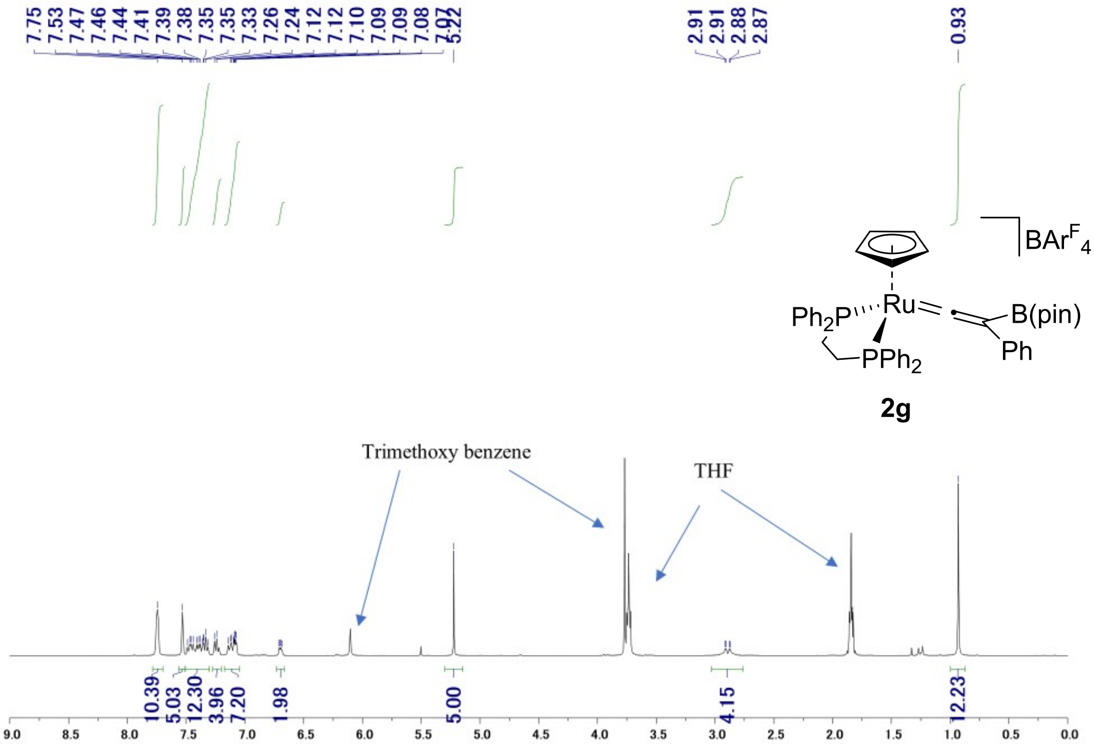


Figure S22. ^{1}H NMR spectrum of **2g** in $CDCl_3$

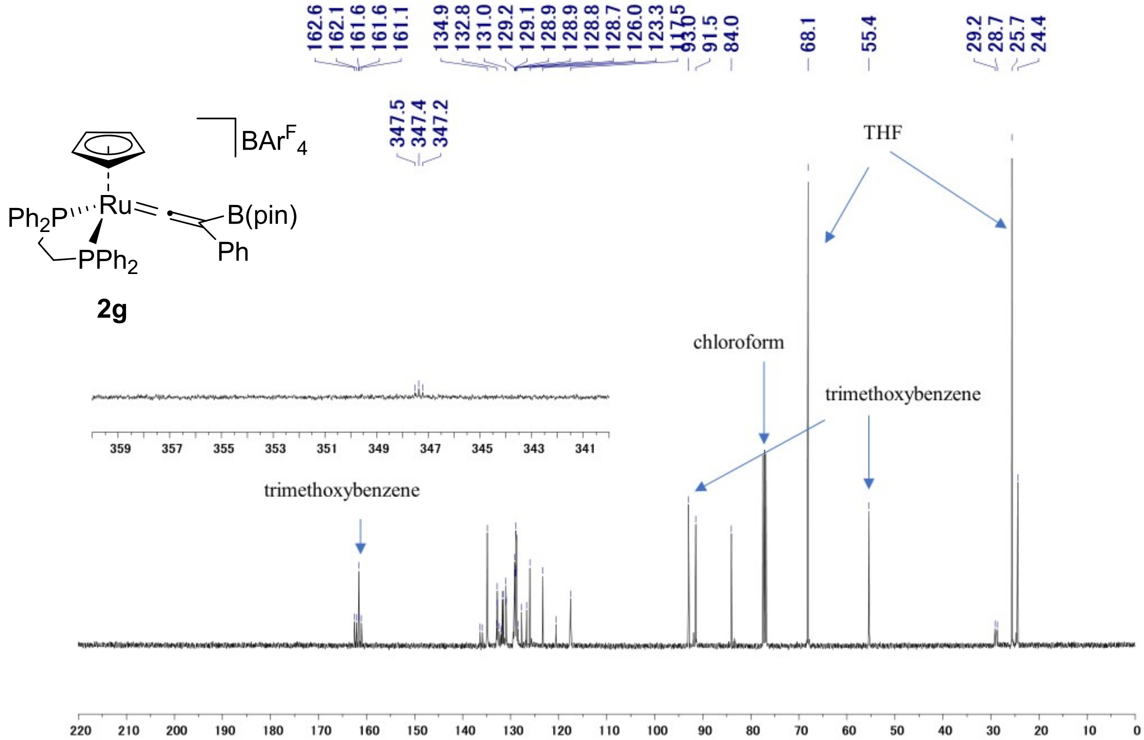


Figure S23. $^{13}C\{^{1}H\}$ NMR spectrum of **2g** in $CDCl_3$

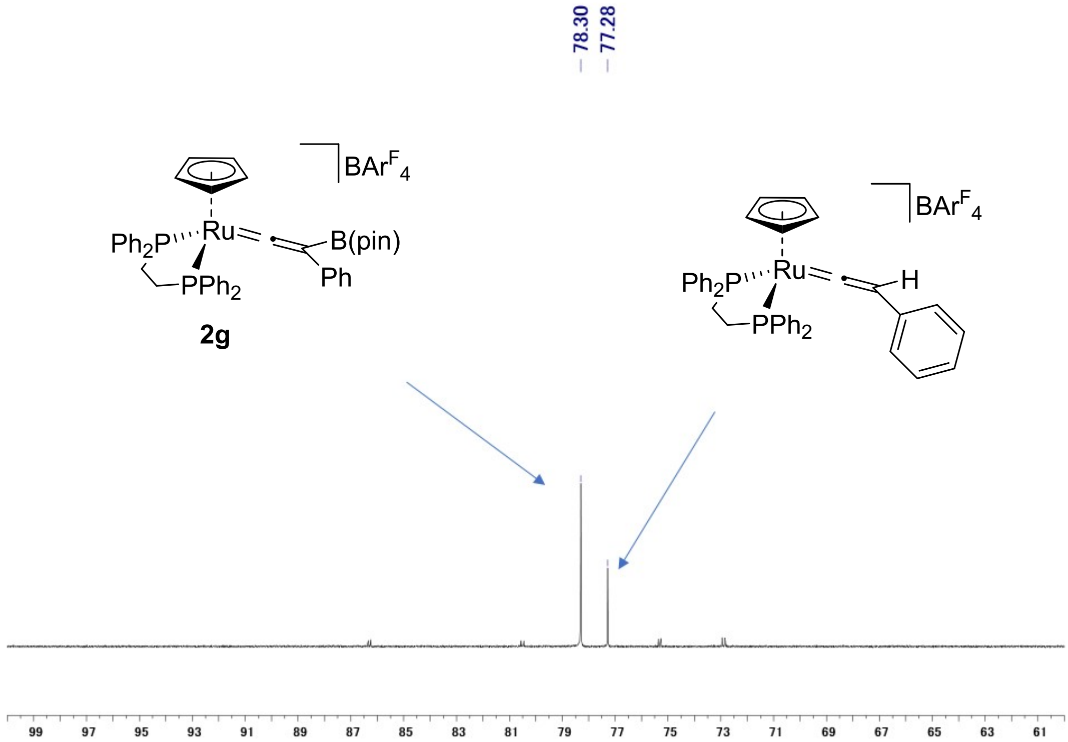


Figure S24. $^{31}P\{^{1}H\}$ NMR spectrum of **2g** in $CDCl_3$

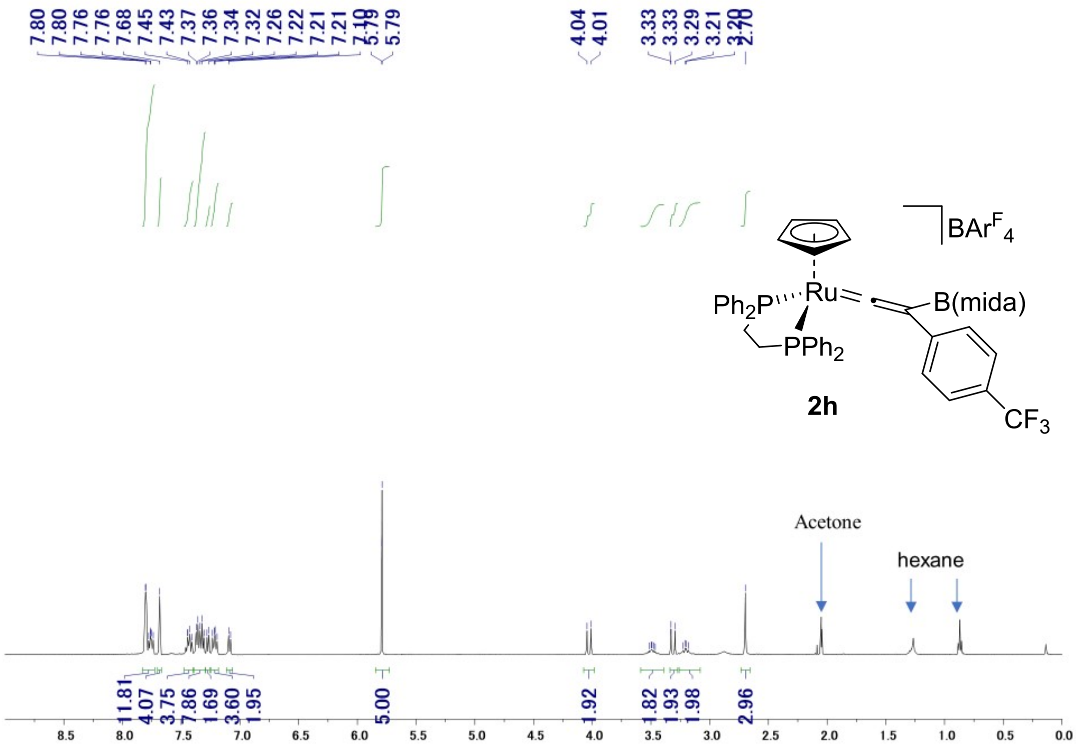


Figure S25. ^{1}H NMR spectrum of **2h** in acetone-*d*6

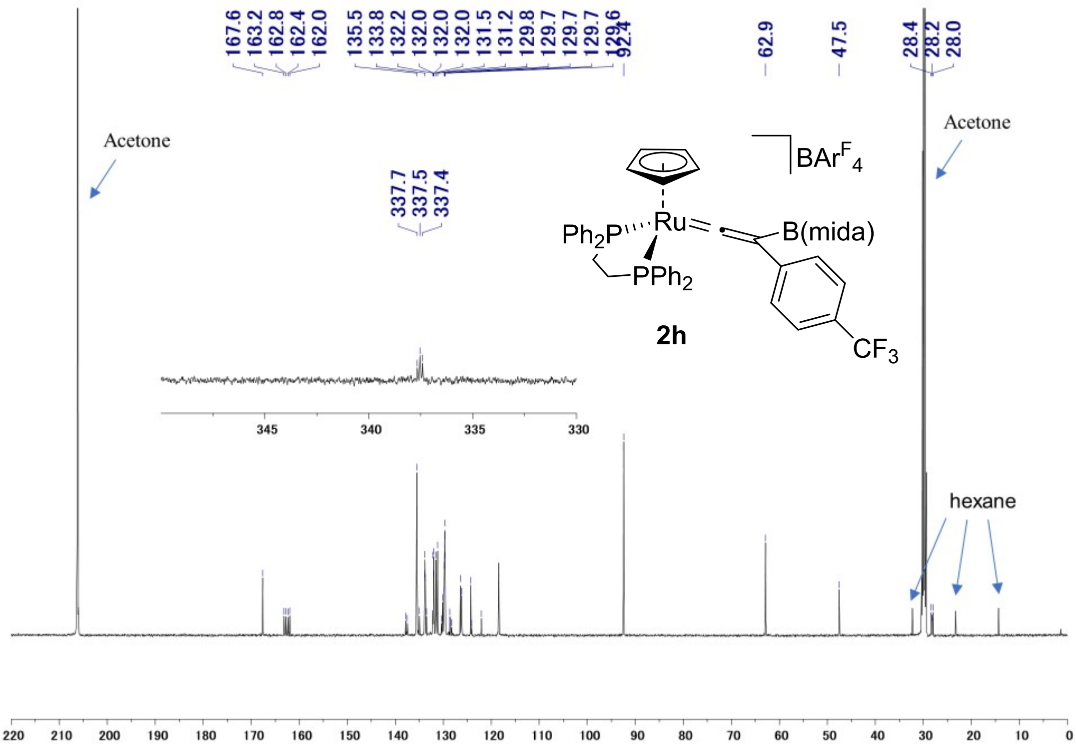


Figure S26. $^{13}C\{^{1}H\}$ NMR spectrum of **2h** in acetone-*d*6

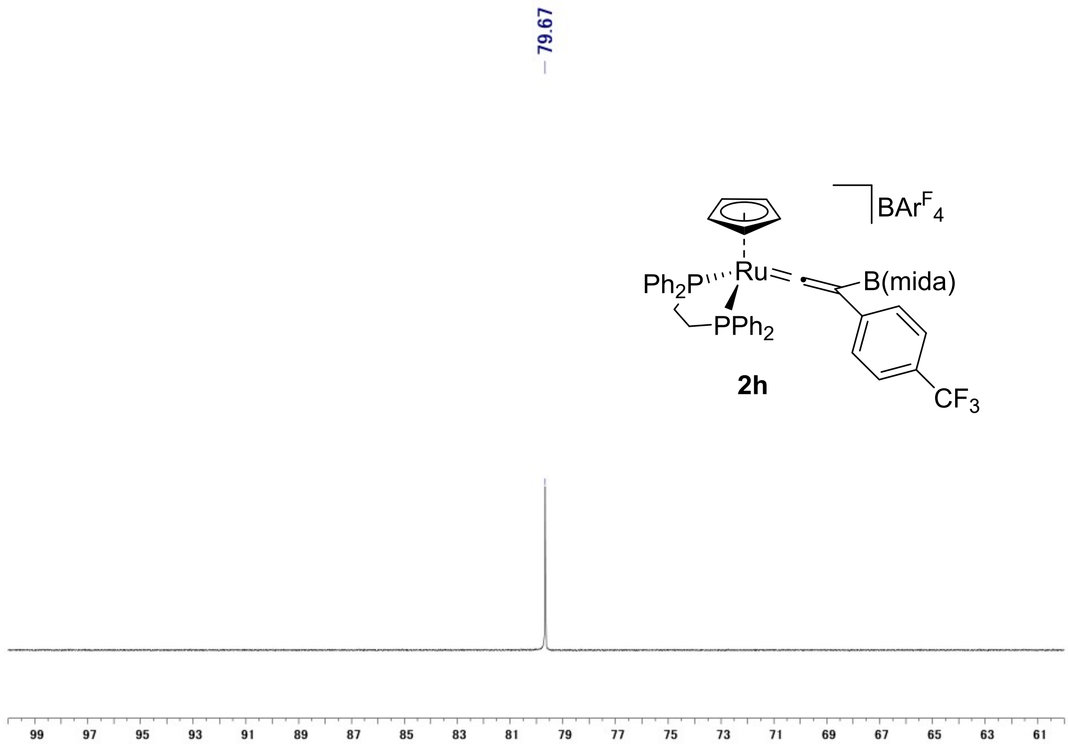


Figure S27. $^{31}P\{^{1}H\}$ NMR spectrum of **2h** in acetone-*d*6

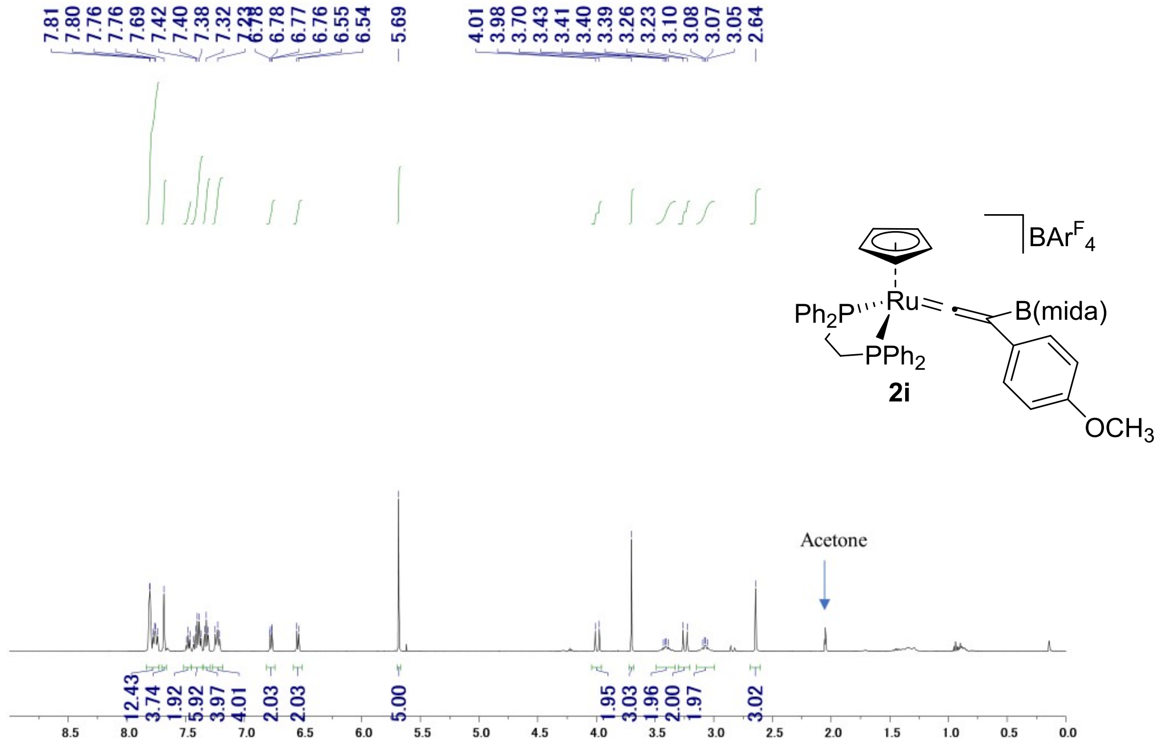


Figure S28. ^{1}H NMR spectrum of **2i** in acetone-*d*6

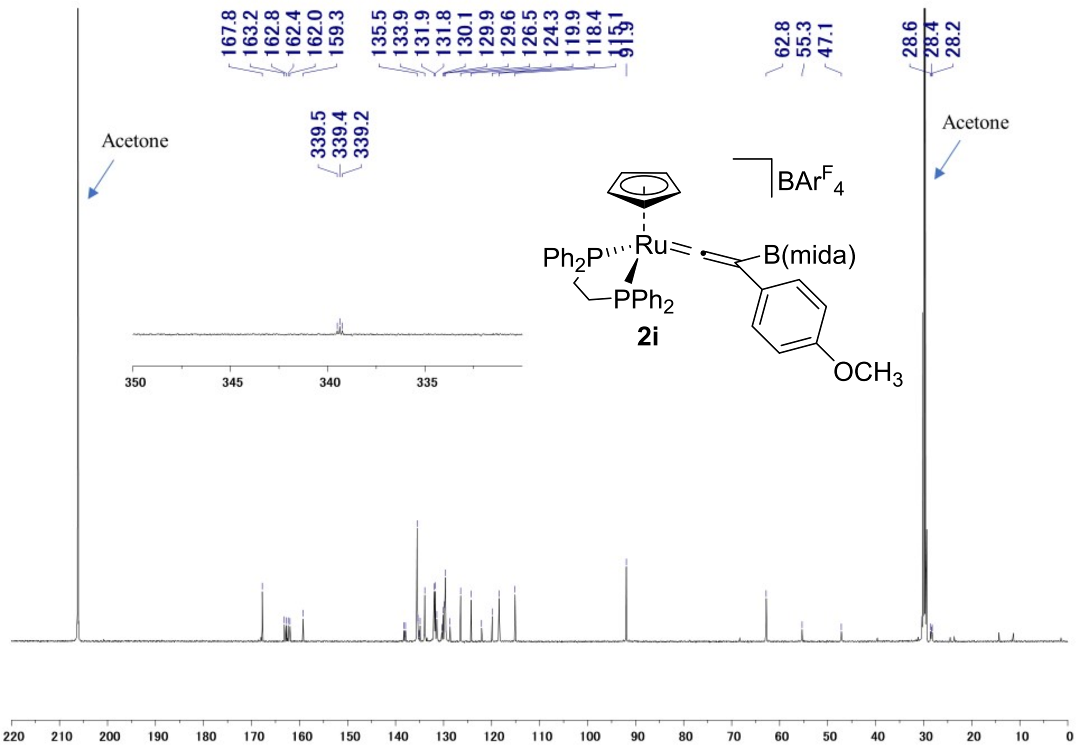


Figure S29. $^{13}C\{^{1}H\}$ NMR spectrum of **2i** in acetone-*d*6

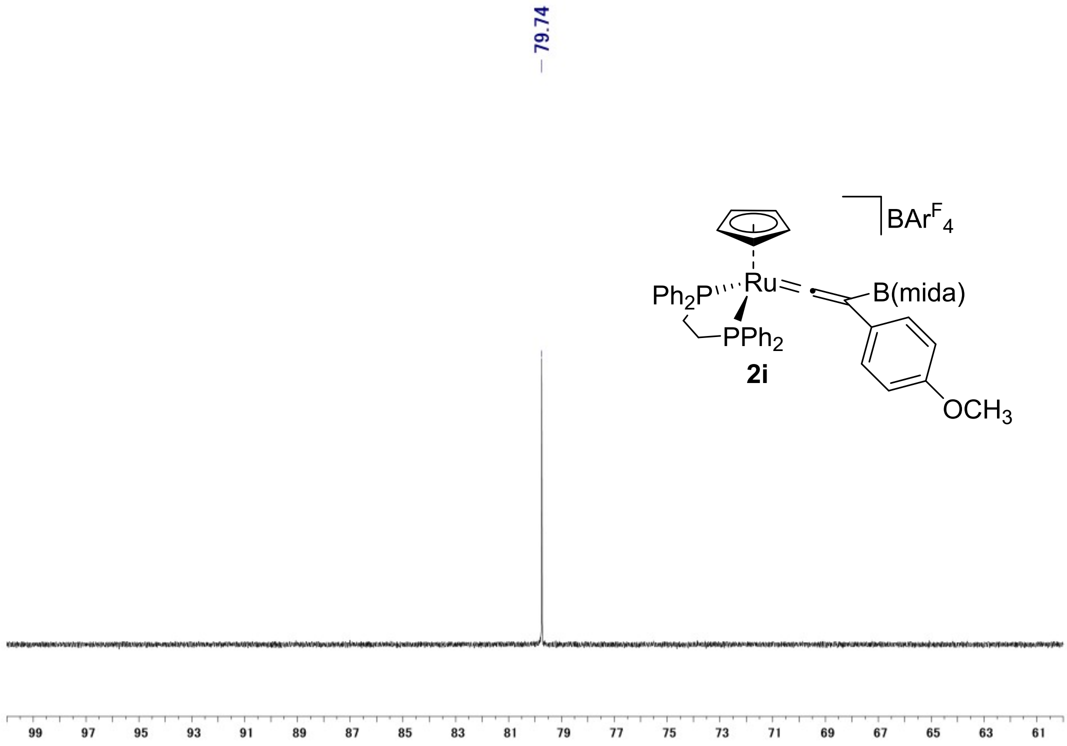


Figure S30. $^{31}P\{^1H\}$ NMR spectrum of **2i** in acetone-*d*6

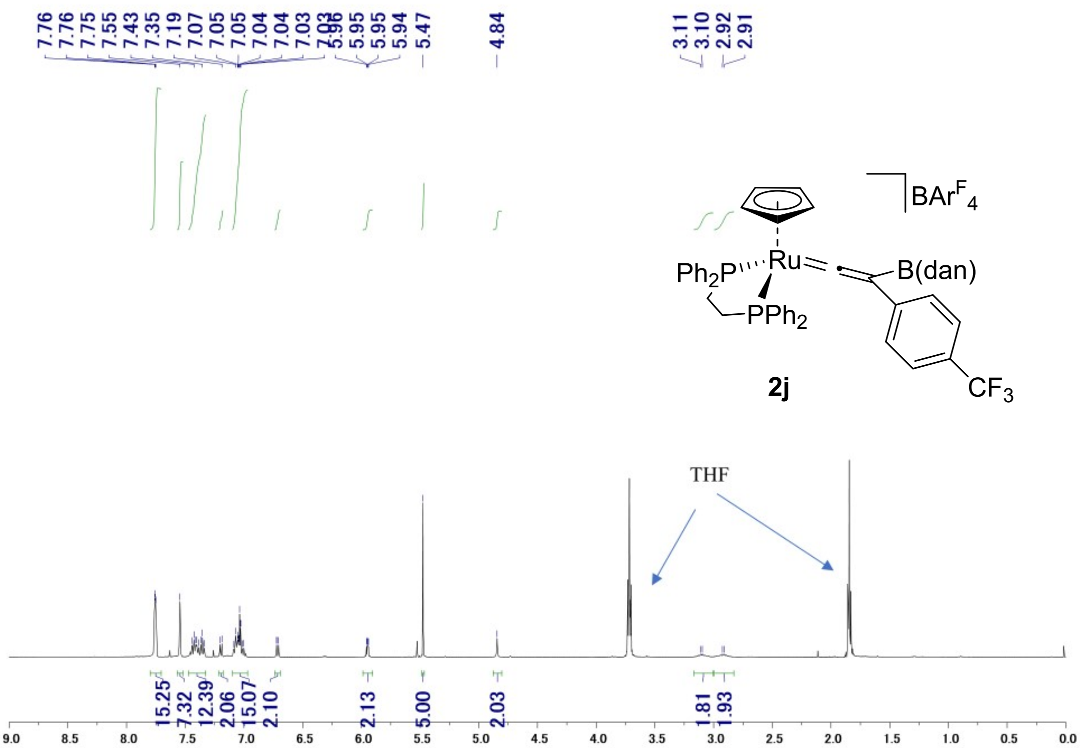


Figure S31. ^1H NMR spectrum of **2j** in $CDCl_3$

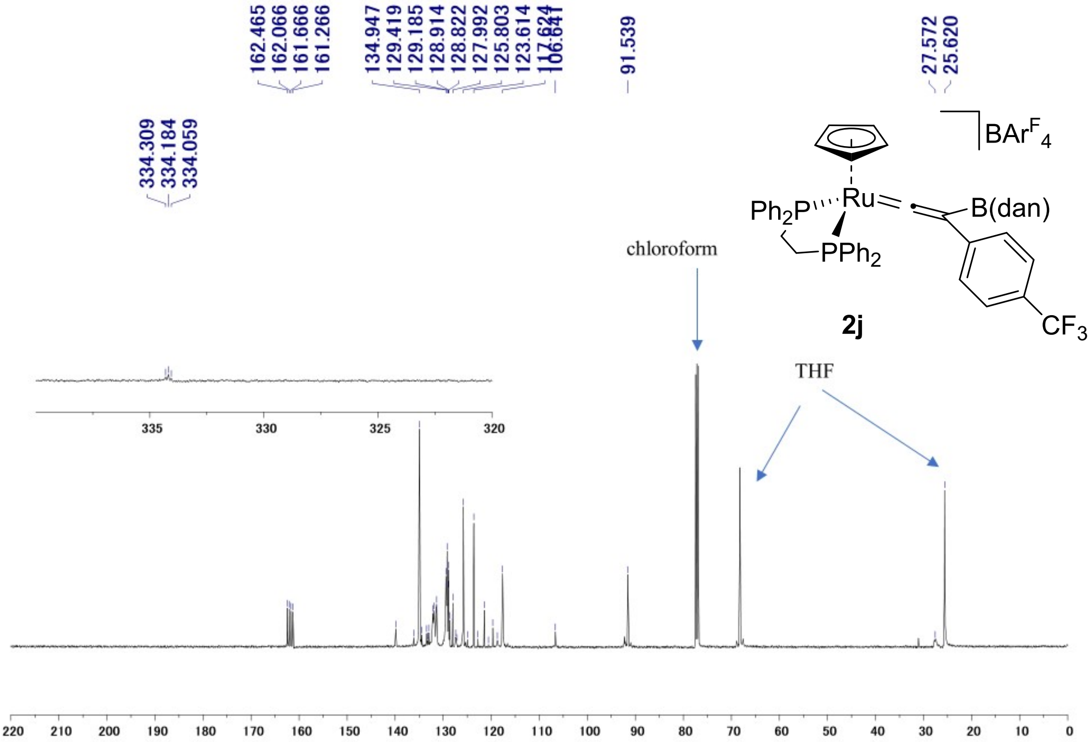


Figure S32. $^{13}C\{^1H\}$ NMR spectrum of **2j** in $CDCl_3$

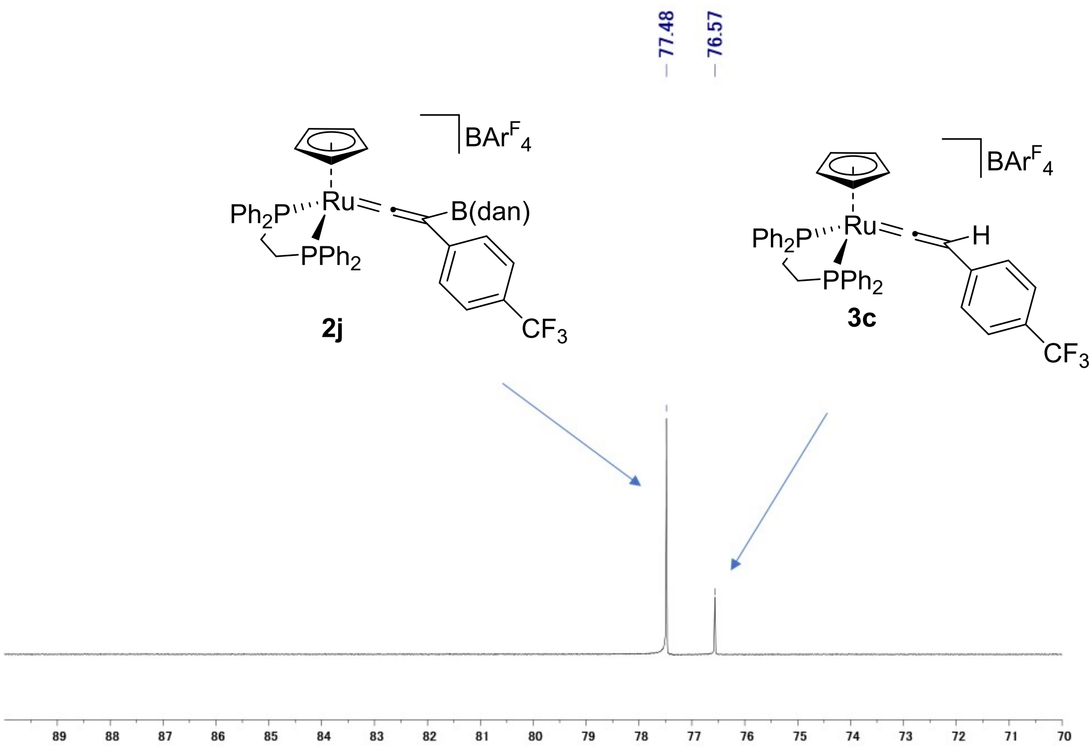


Figure S33. $^{31}P\{^1H\}$ NMR spectrum of **2j** in $CDCl_3$

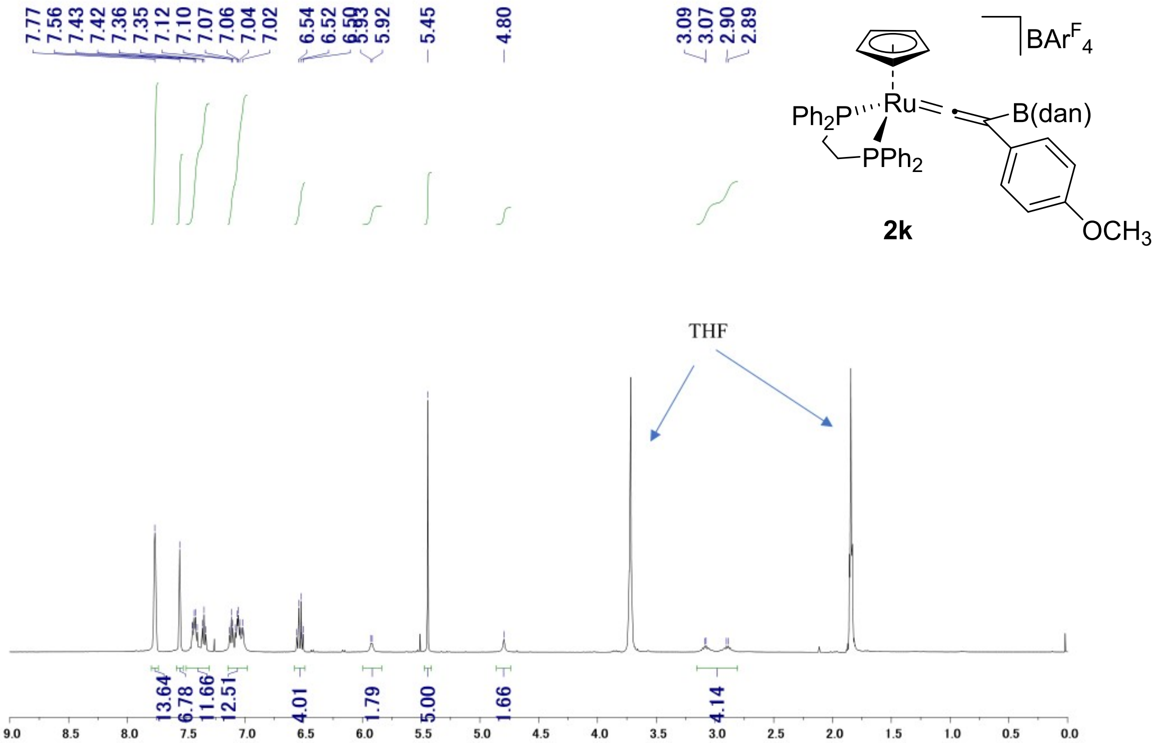


Figure S34. ^{1}H NMR spectrum of **2k** in $CDCl_3$

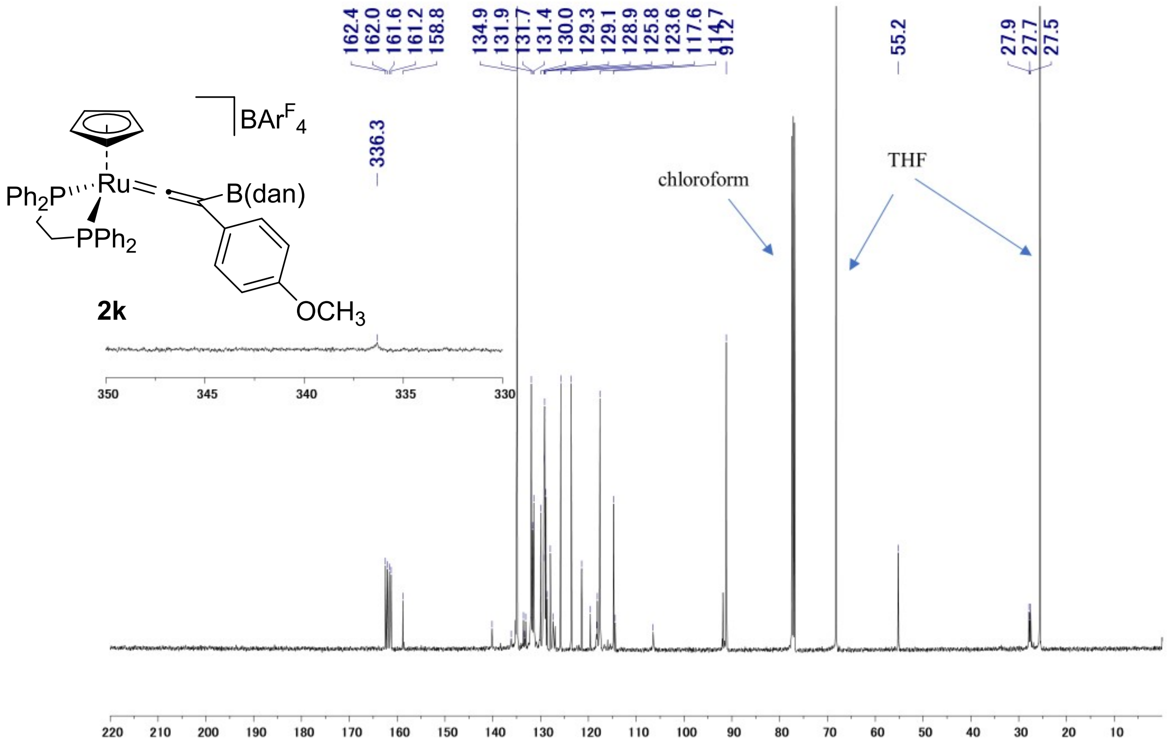


Figure S35. $^{13}C\{^{1}H\}$ NMR spectrum of **2k** in $CDCl_3$

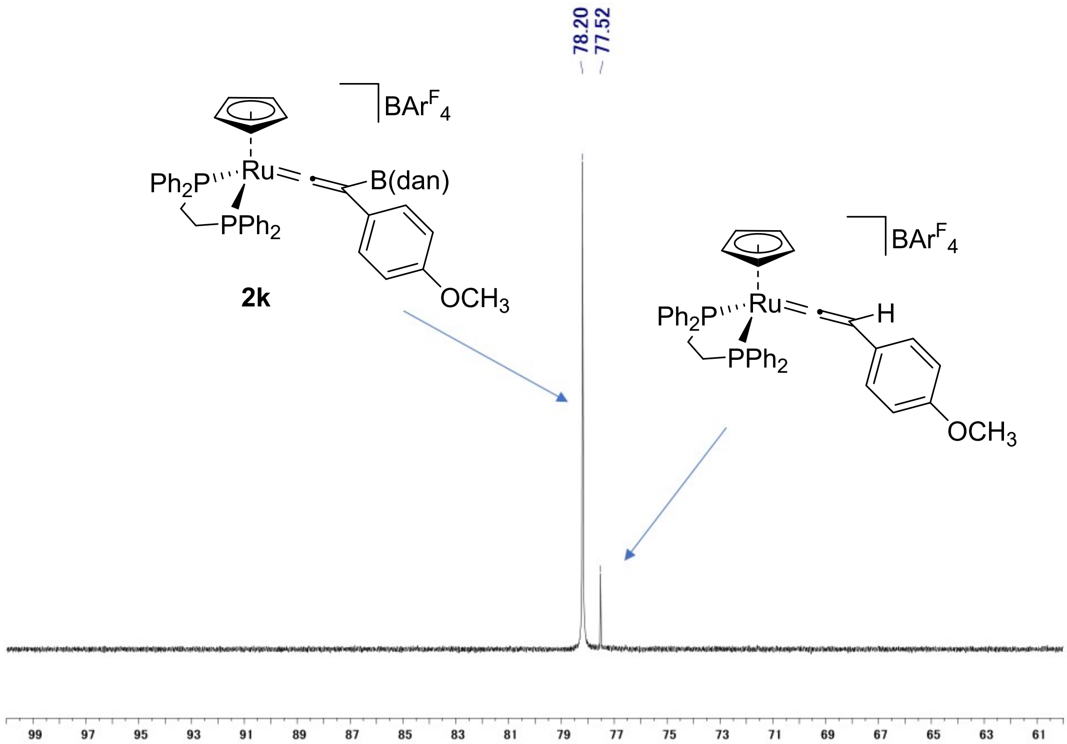


Figure S36. ^{31}P{^{1}H} NMR spectrum of **2k** in $CDCl_3$

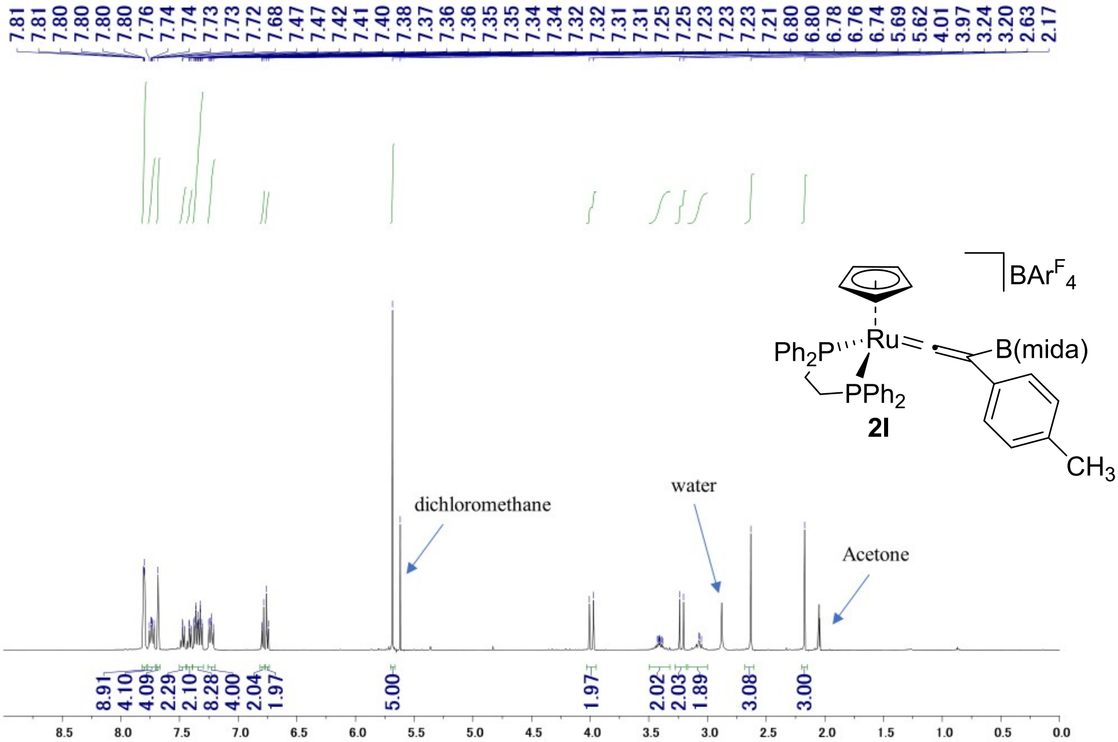


Figure S37. ^{1}H NMR spectrum of **2l** in acetone-*d*6

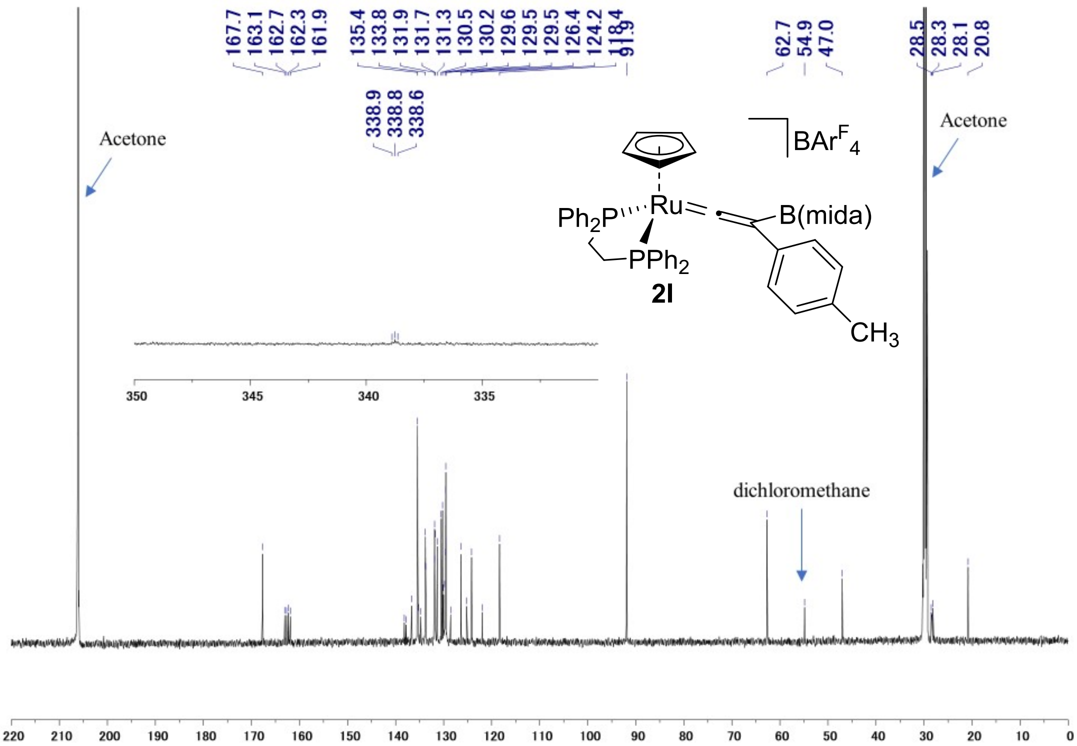


Figure S38. $^{13}C\{^1H\}$ NMR spectrum of **2l** in acetone-*d*6

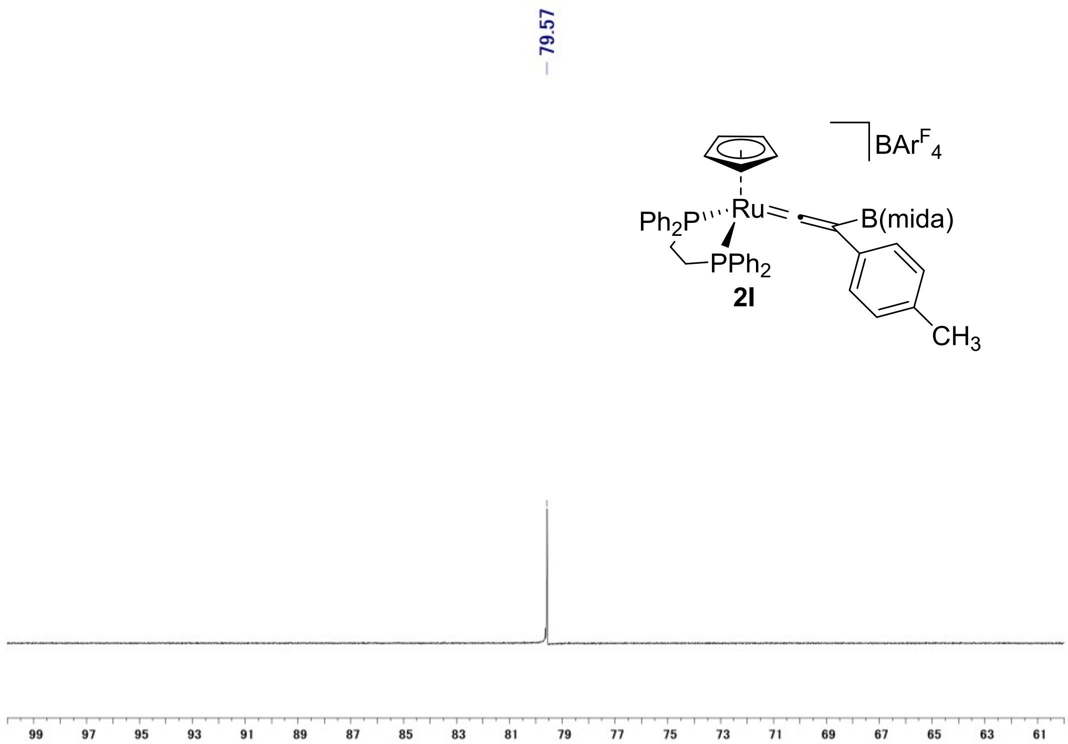


Figure S39. $^{31}P\{^1H\}$ NMR spectrum of **2l** in acetone-*d*6

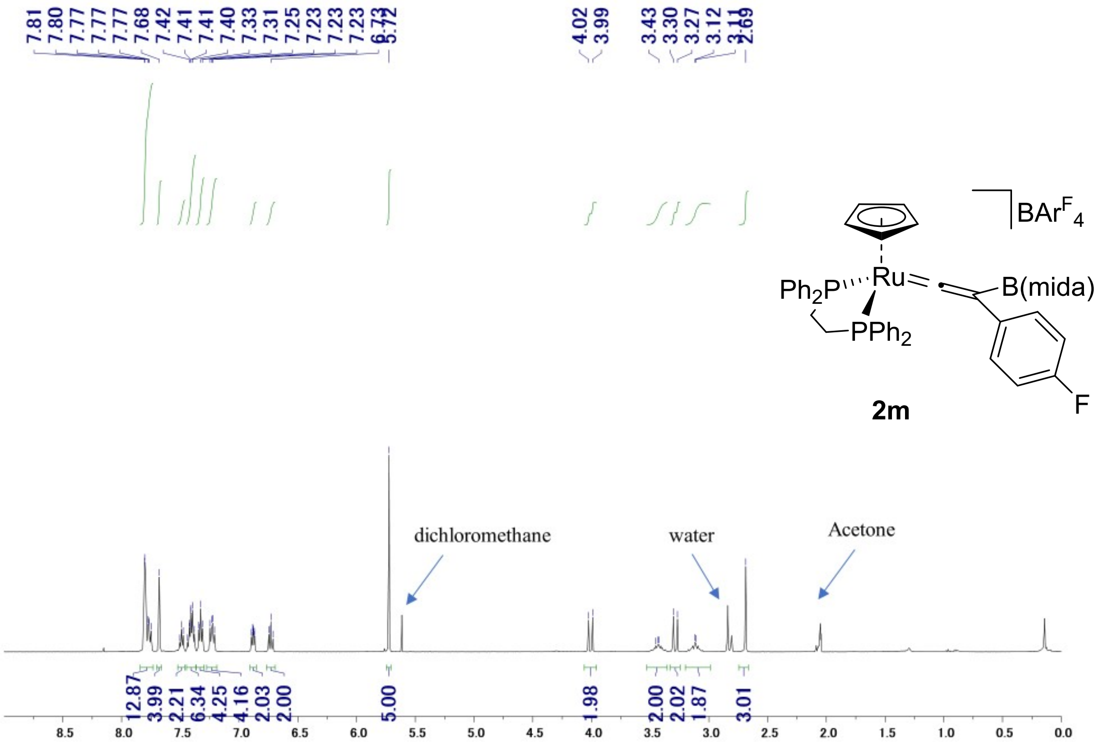


Figure S40. [1]H NMR spectrum of **2m** in acetone-*d*6

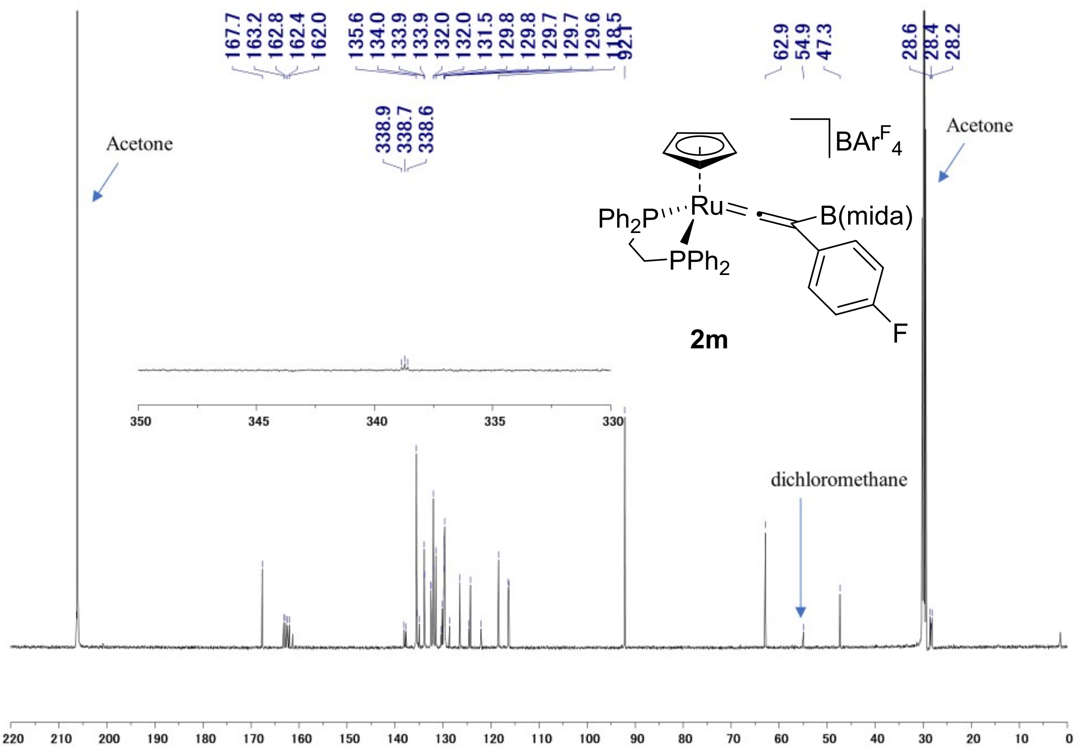


Figure S41. $^{13}C\{^1H\}$ NMR spectrum of **2m** in acetone-*d*6

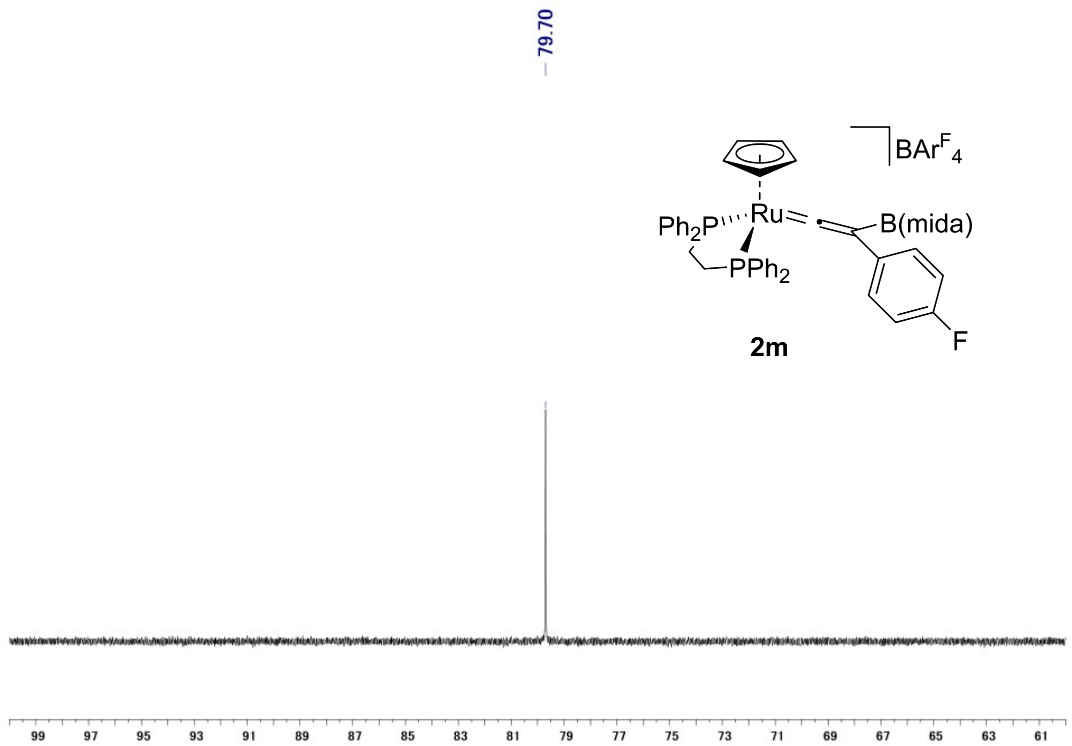


Figure S42. $^{31}P\{^{1}H\}$ NMR spectrum of **2m** in acetone-*d*6

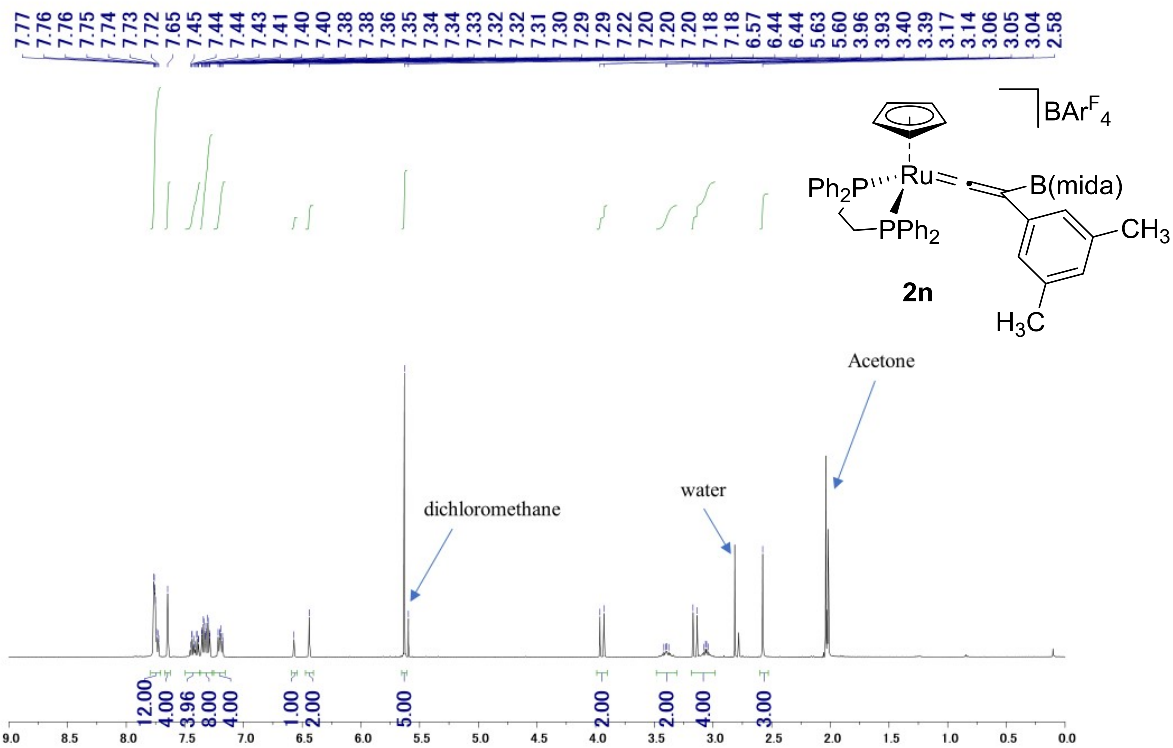


Figure S43. ^{1}H NMR spectrum of **2n** in acetone-*d*6

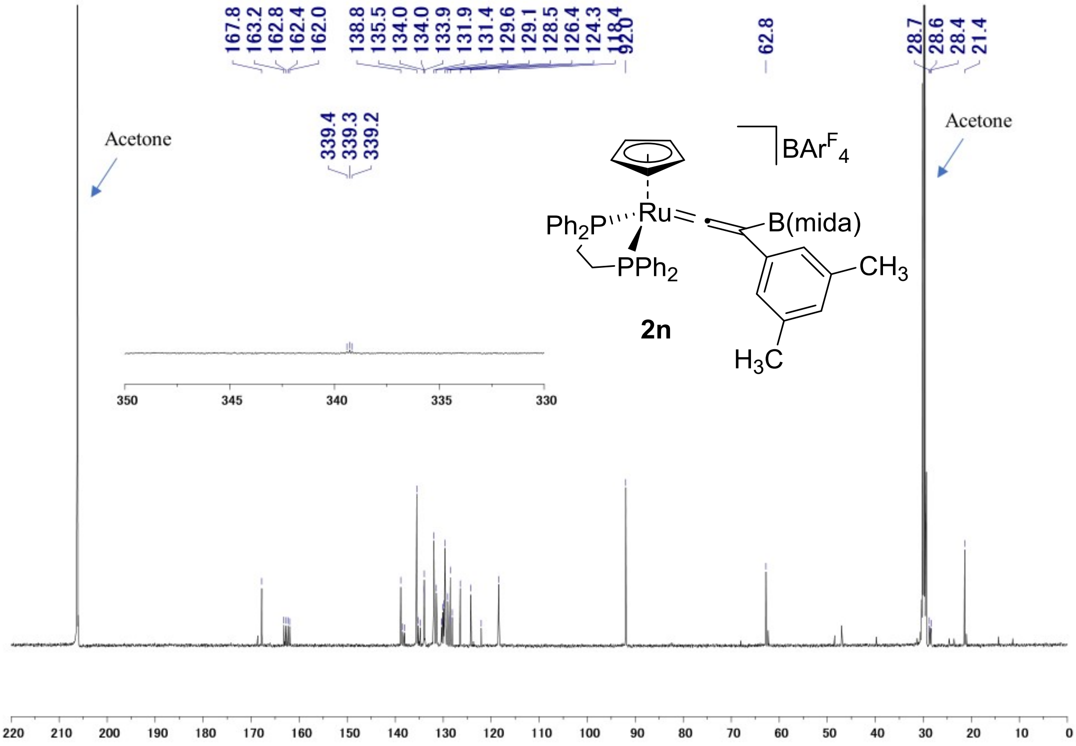


Figure S44. $^{13}C\{^1H\}$ NMR spectrum of **2n** in acetone-*d6*

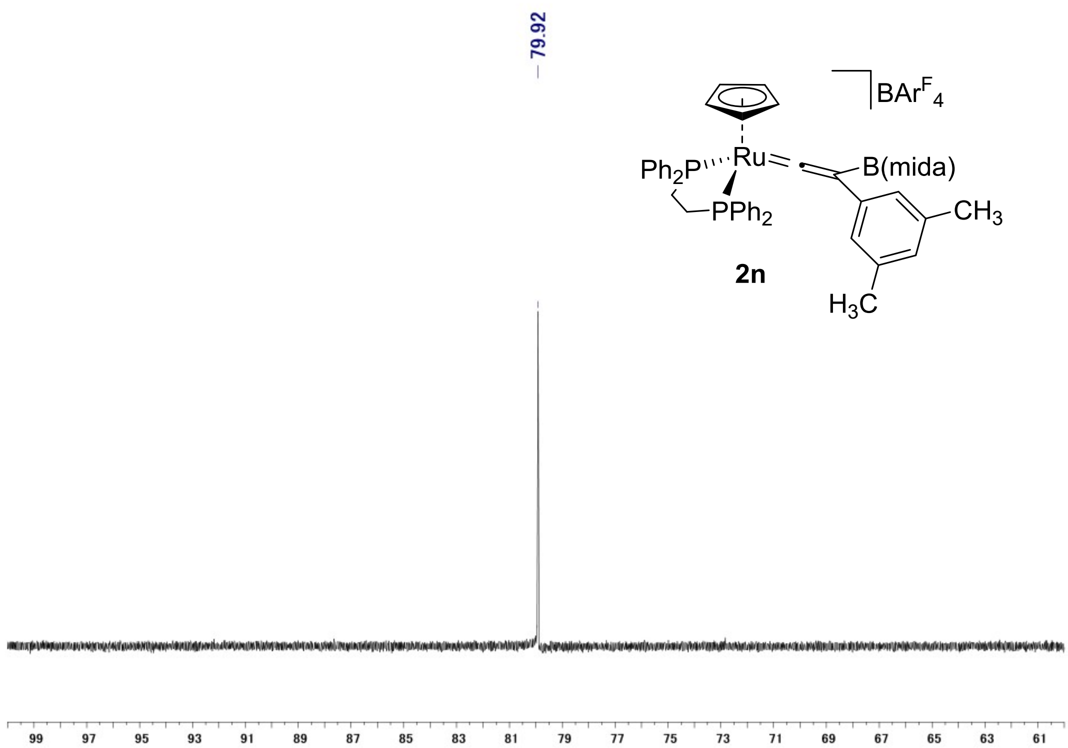


Figure S45. $^{31}P\{^1H\}$ NMR spectrum of **2n** in acetone-*d6*

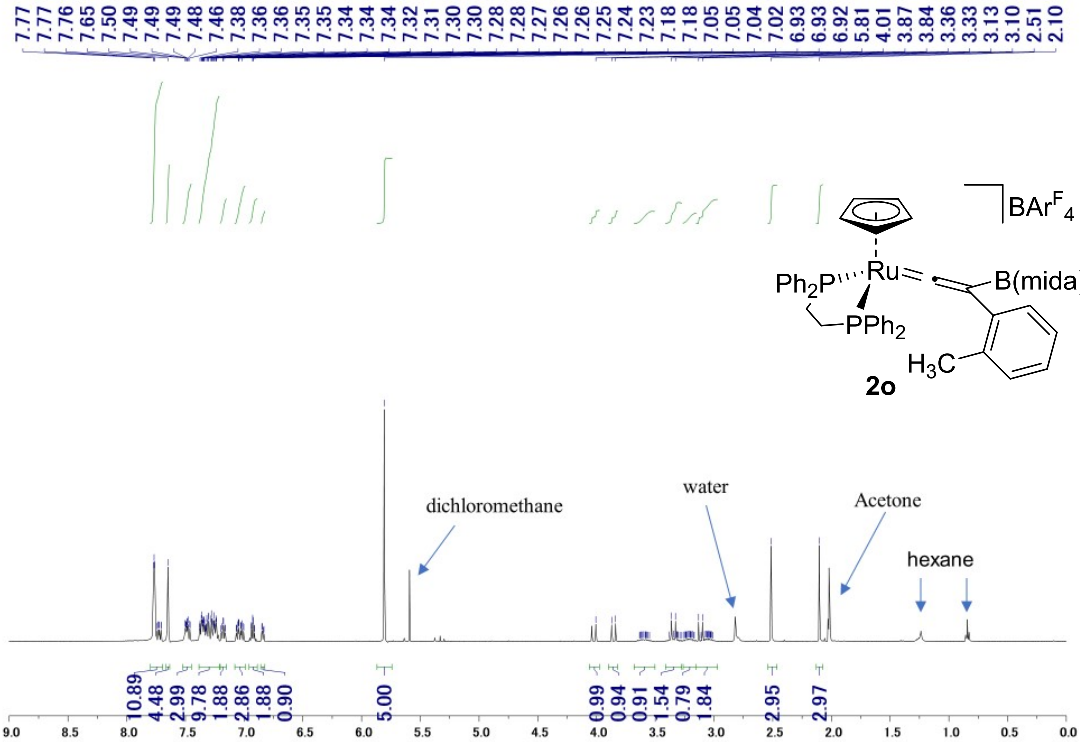


Figure S46. ^{1}H NMR spectrum of **2o** in acetone-*d*6

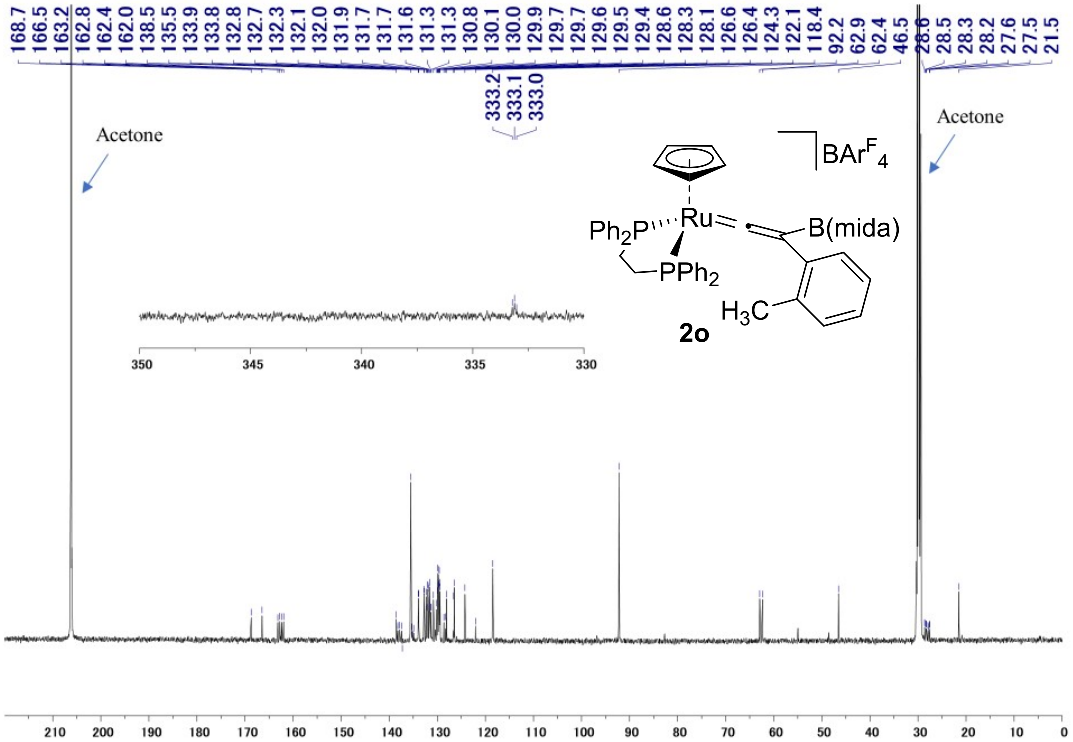


Figure S47. ^{13}C{^{1}H} NMR spectrum of **2o** in acetone-*d*6

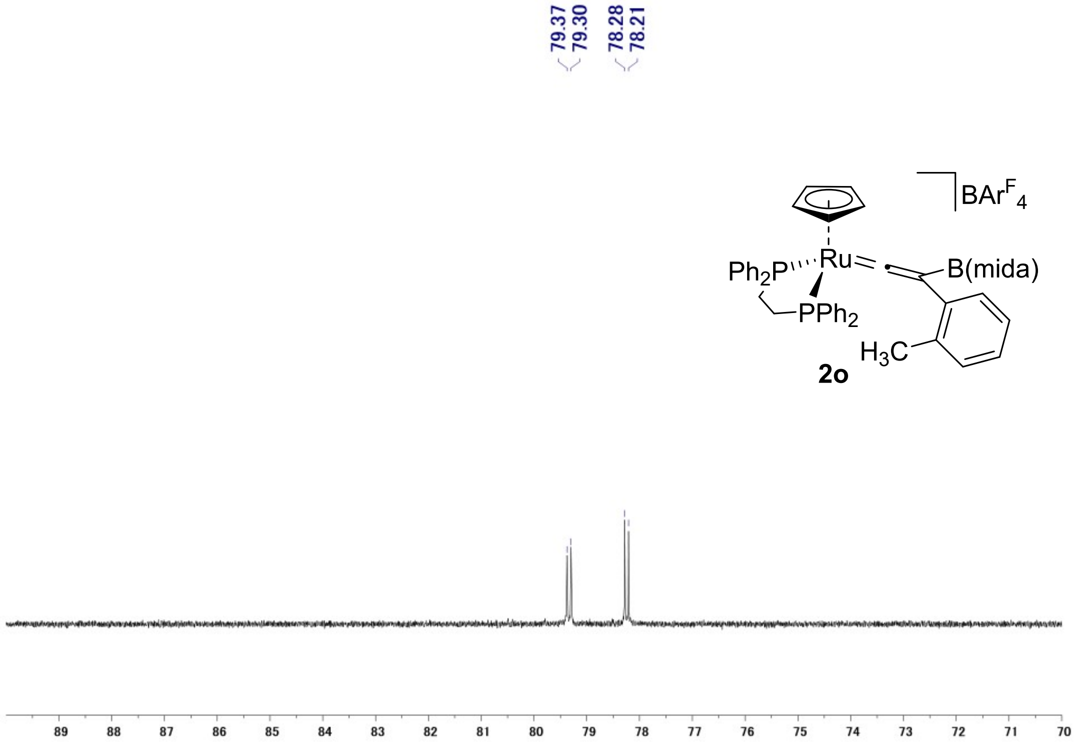


Figure S48. $^{31}P\{^1H\}$ NMR spectrum of **2o** in acetone-*d*6

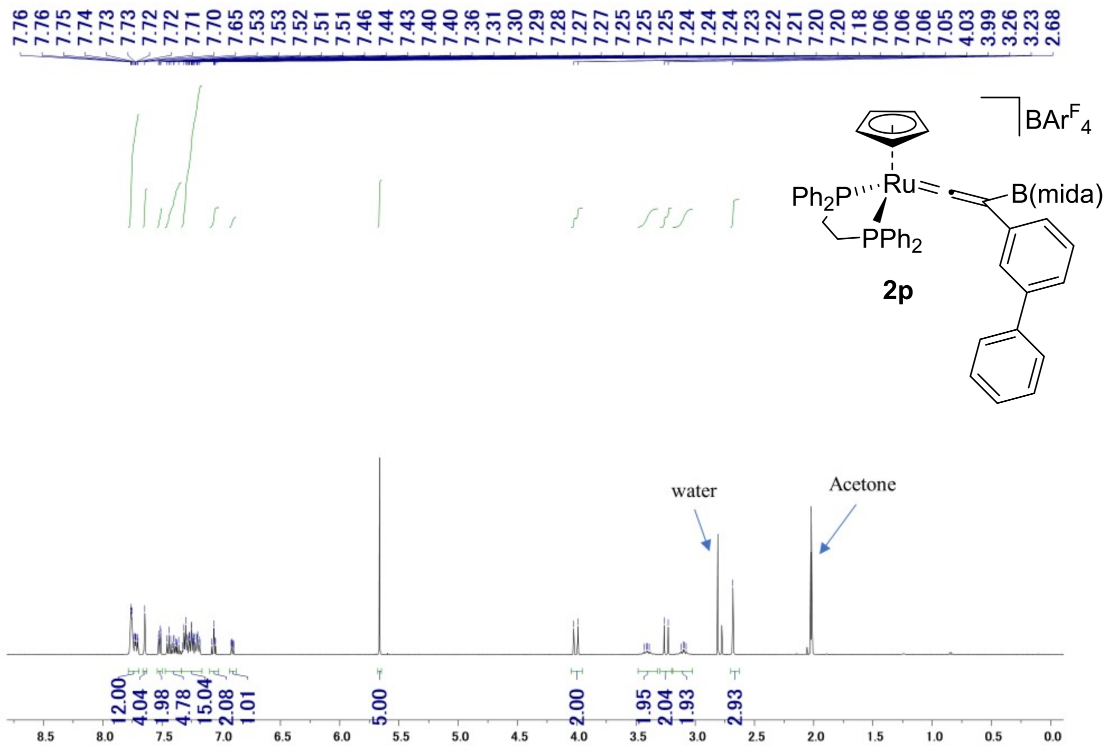


Figure S49. ^1H NMR spectrum of **2p** in acetone-*d*6

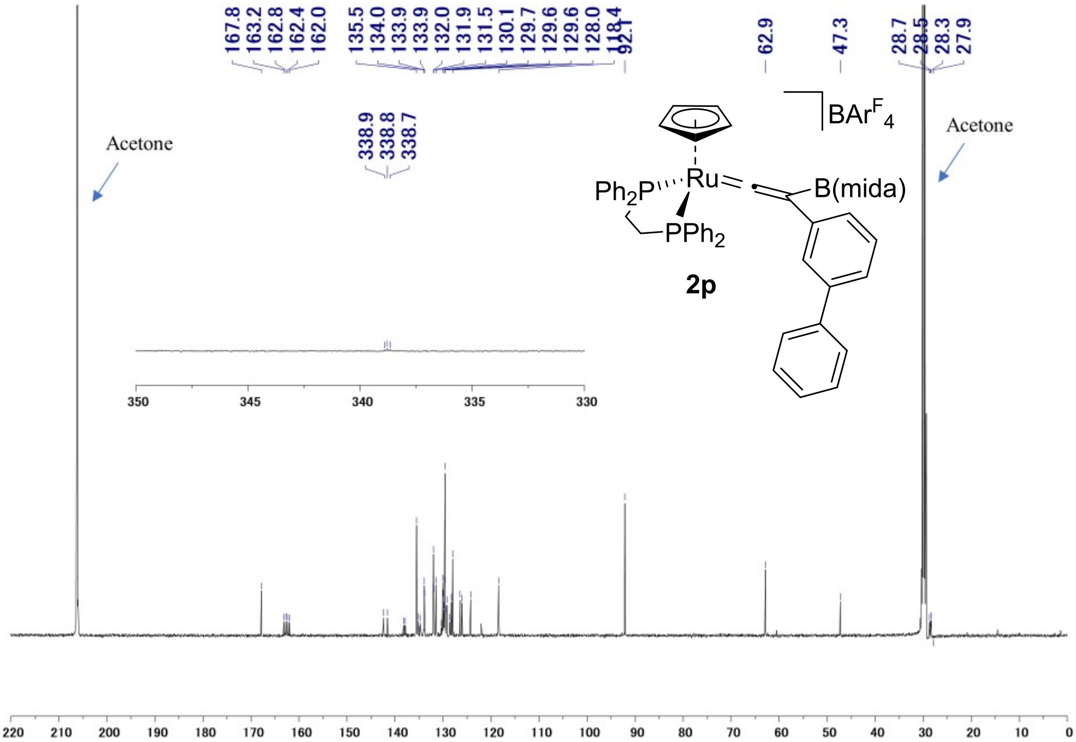


Figure S50. $^{13}C\{^1H\}$ NMR spectrum of **2p** in acetone-*d*6

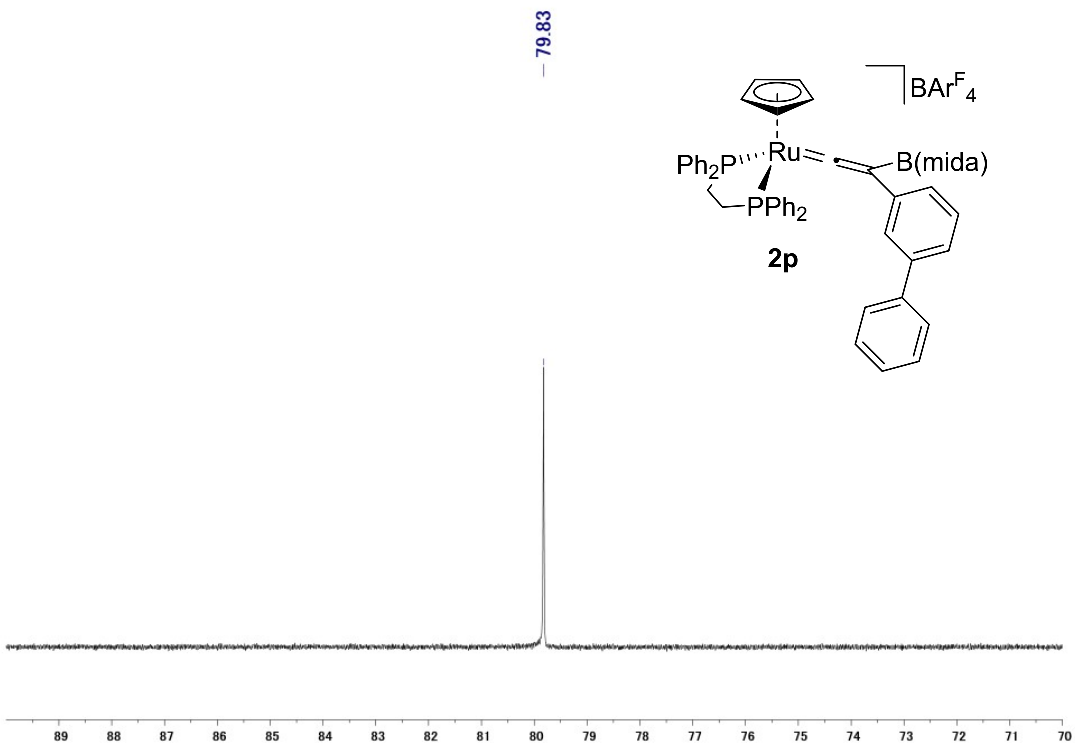


Figure S51. $^{31}P\{^1H\}$ NMR spectrum of **2p** in acetone-*d*6

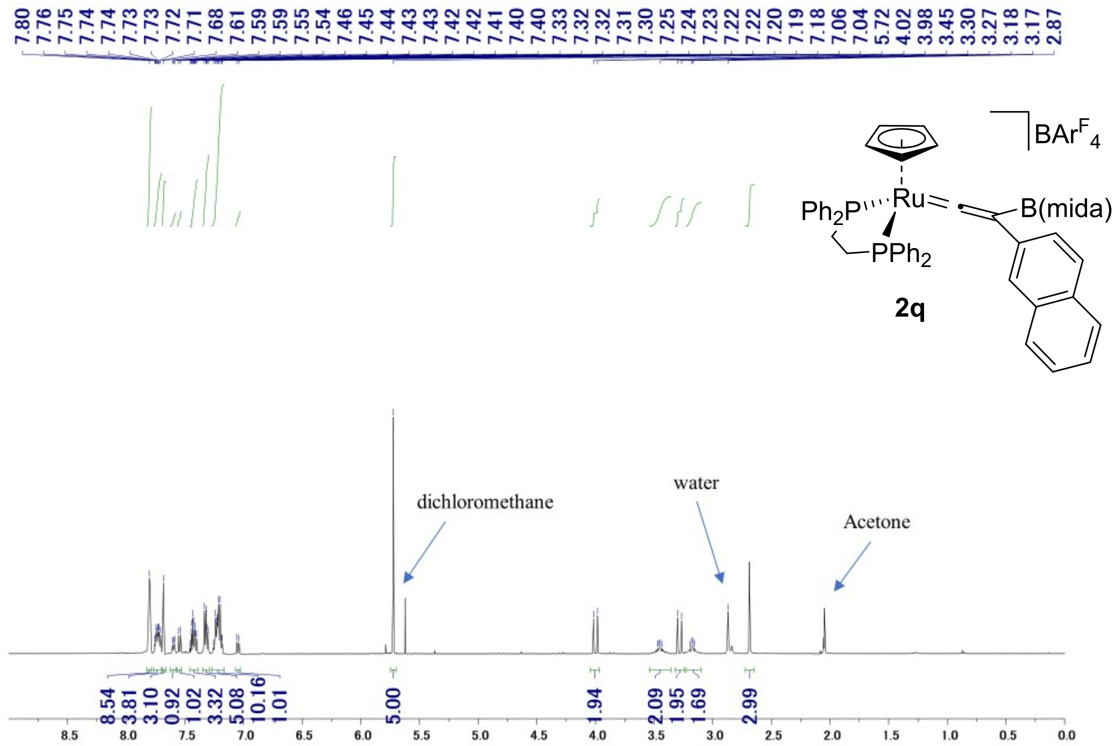


Figure S52. ^{1}H NMR spectrum of **2q** in acetone-*d*6

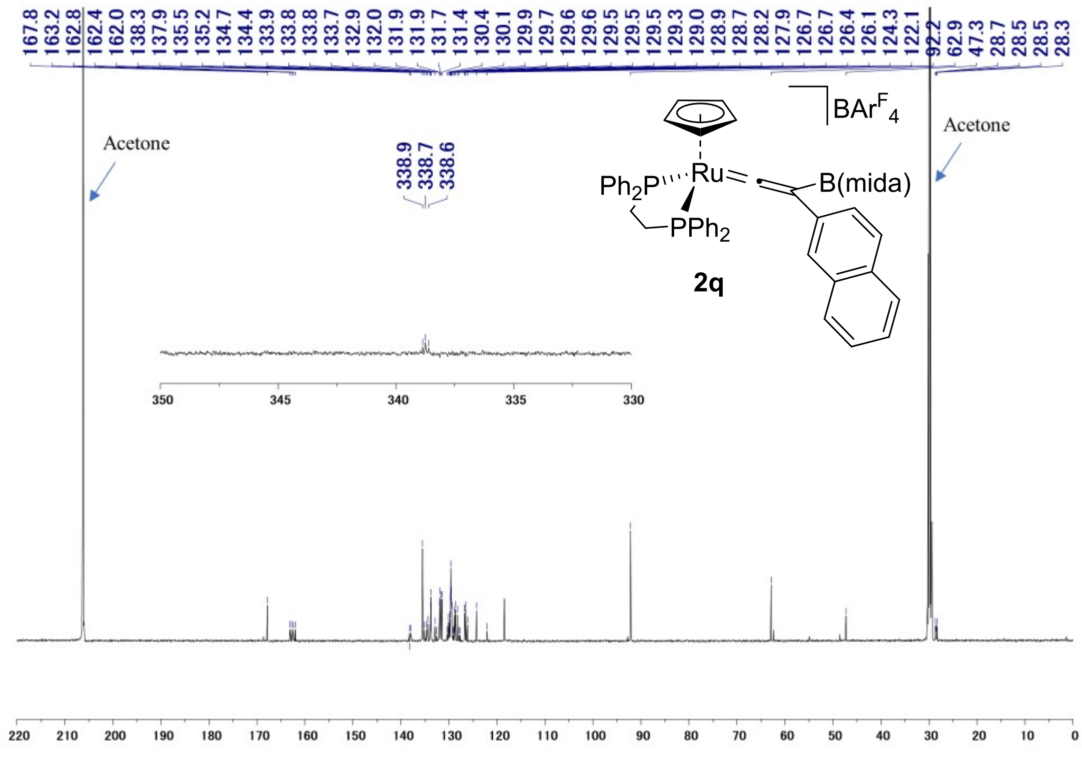


Figure S53. ^{13}C{^{1}H} NMR spectrum of **2q** in acetone-*d*6

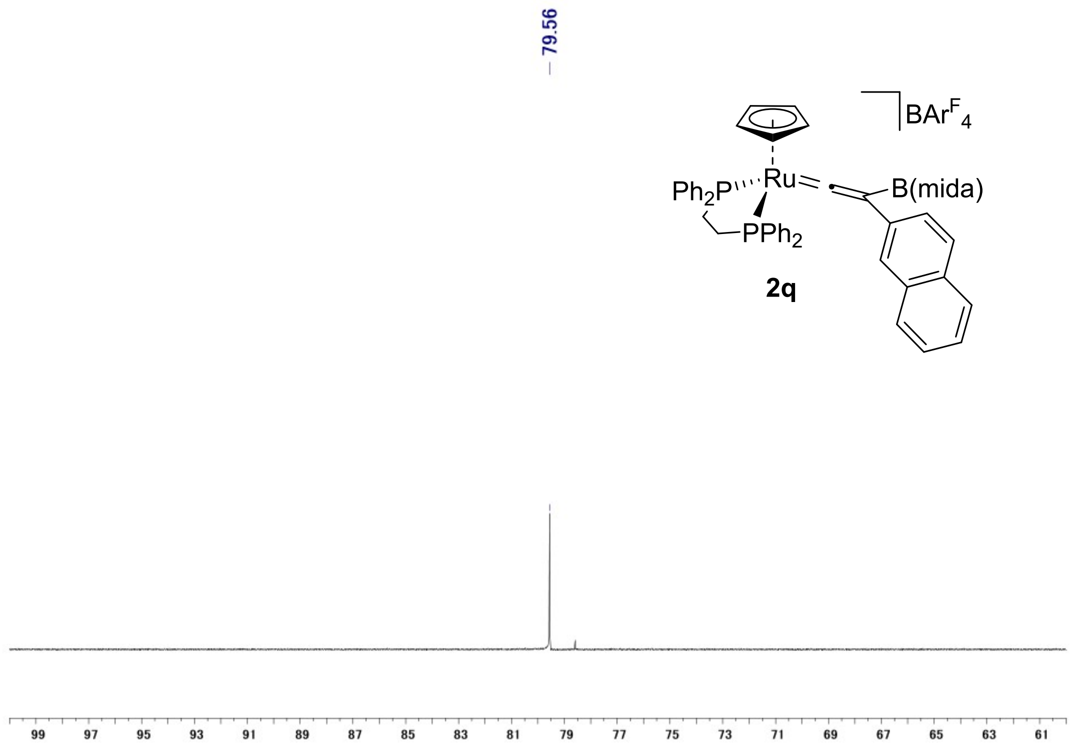


Figure S54. $^{31}P\{^{1}H\}$ NMR spectrum of **2q** in acetone-*d*6

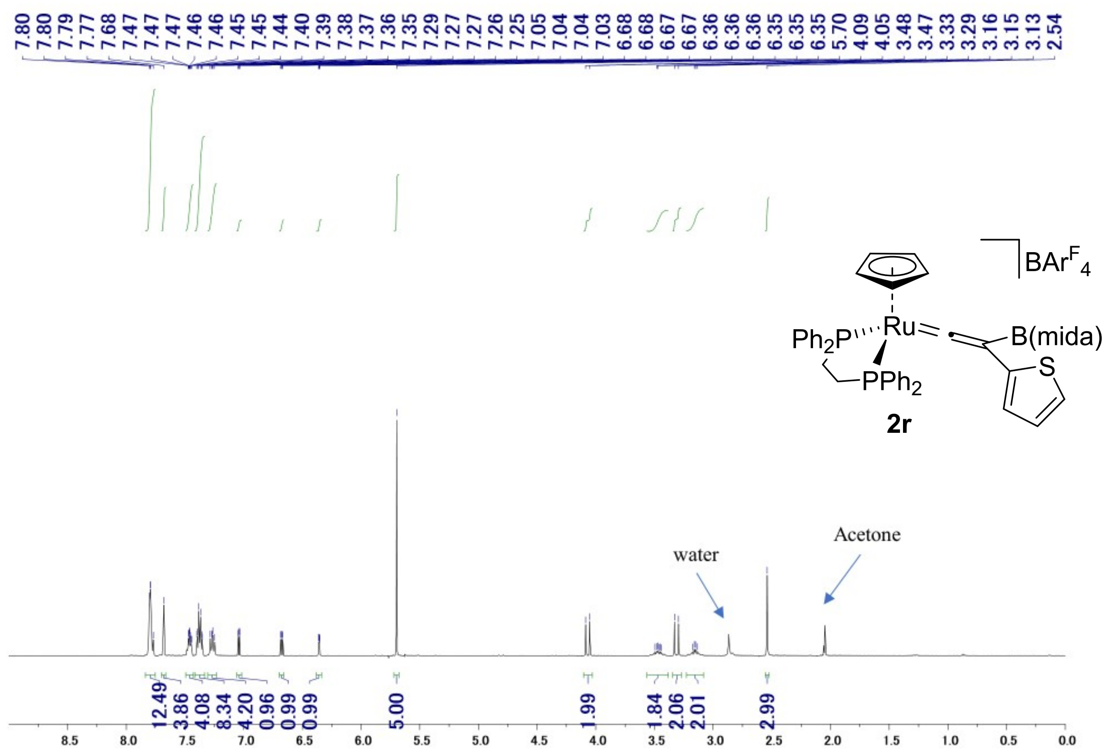


Figure S55. ^{1}H NMR spectrum of **2r** in acetone-*d*6

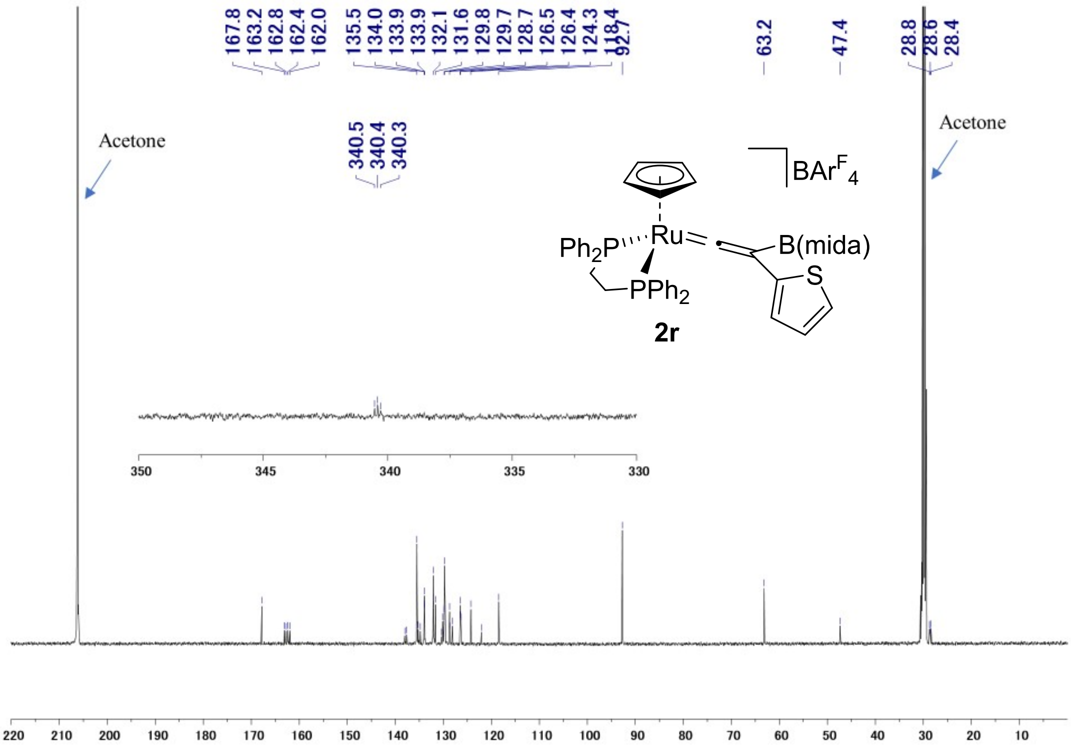


Figure S56. $^{13}C\{^1H\}$ NMR spectrum of **2r** in acetone-*d*6

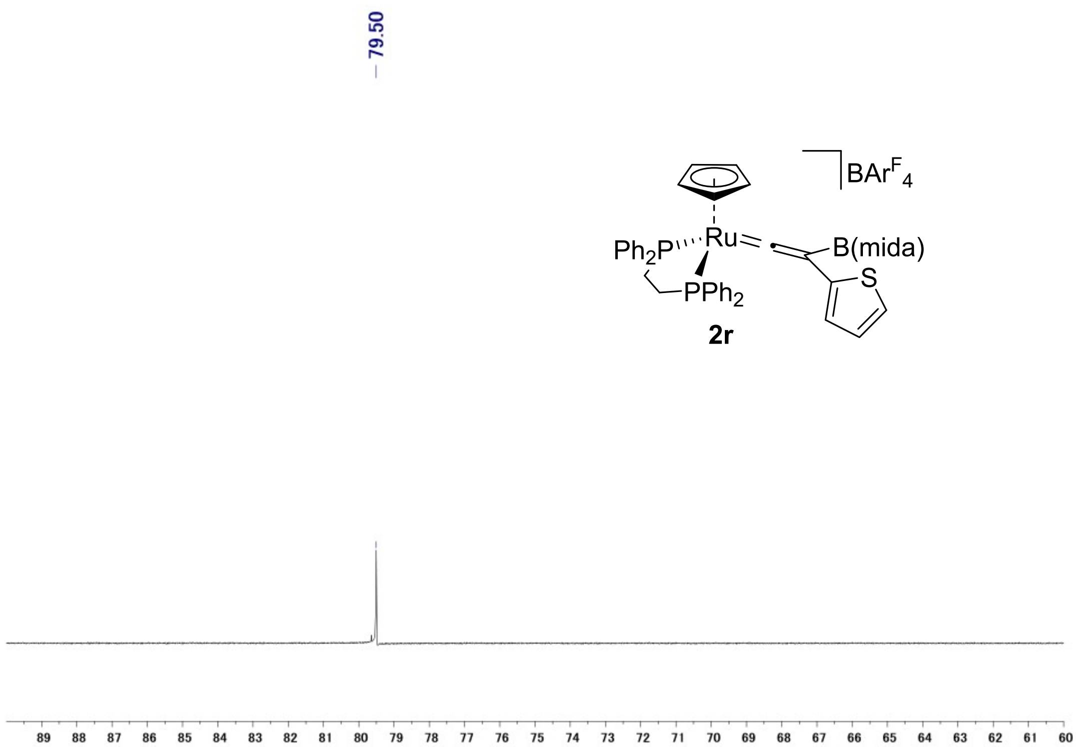


Figure S57. $^{31}P\{^1H\}$ NMR spectrum of **2r** in acetone-*d*6

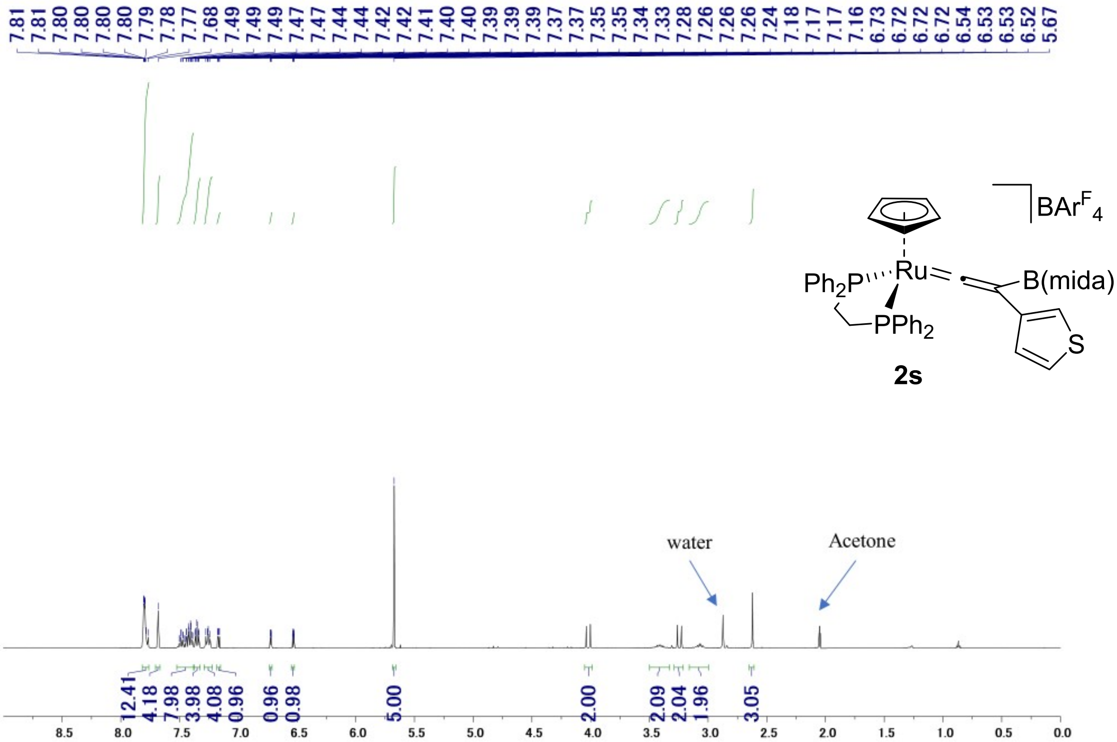


Figure S58. ^{1}H NMR spectrum of **2s** in acetone-*d*6

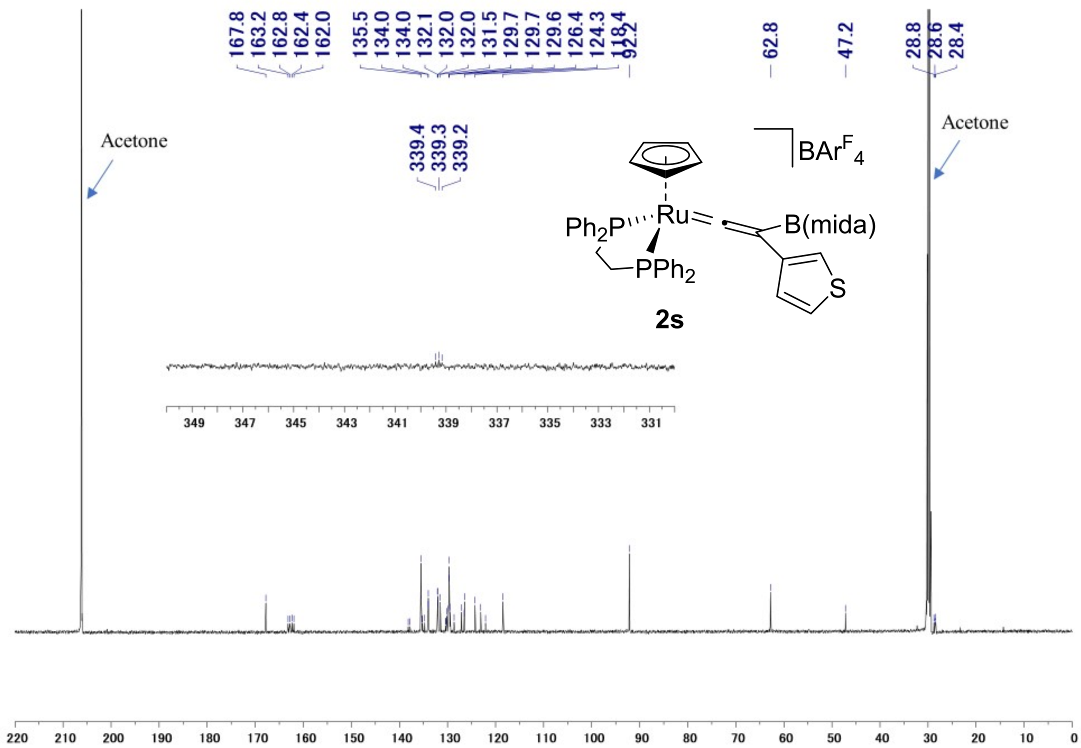


Figure S59. $^{13}C\{^{1}H\}$ NMR spectrum of **2s** in acetone-*d*6

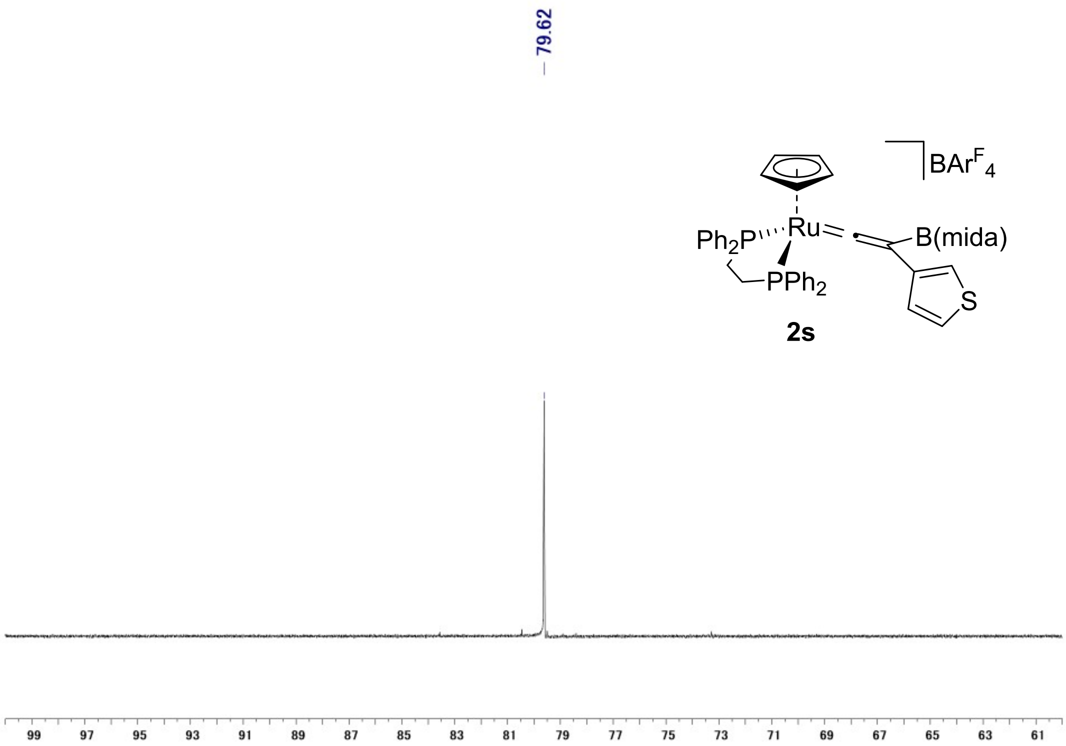


Figure S60. $^{31}P\{^{1}H\}$ NMR spectrum of **2s** in acetone-*d*6

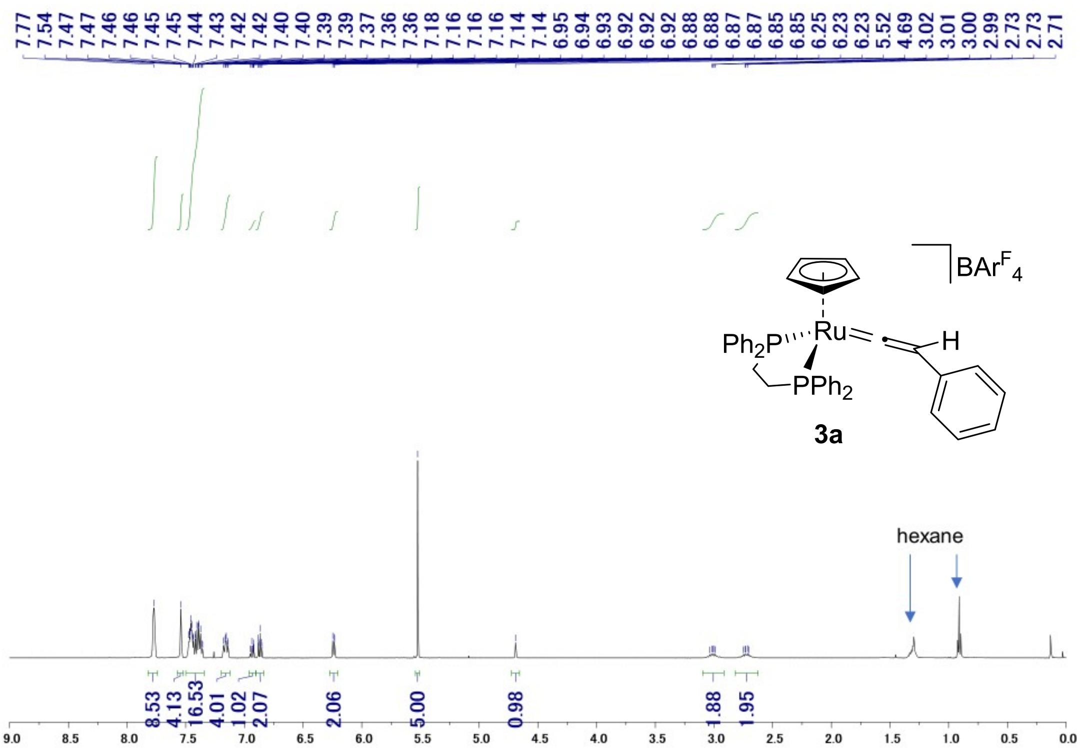


Figure S61. ^{1}H NMR spectrum of **3a** in $CDCl_3$

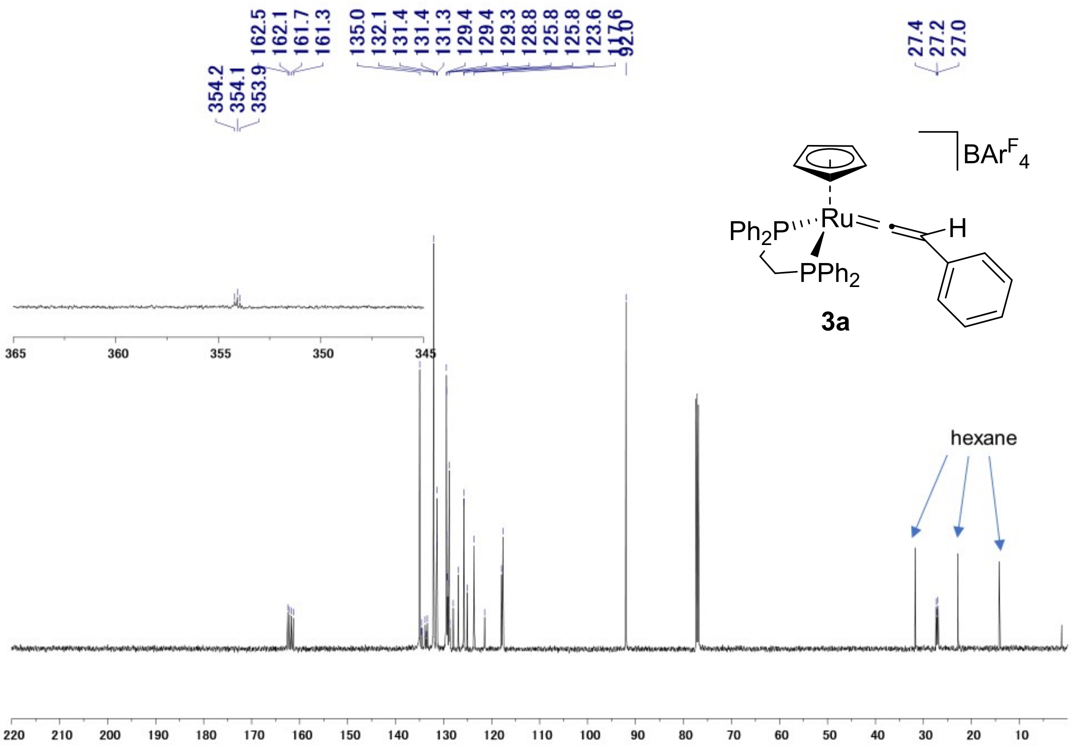


Figure S62. ${}^{13}C\{{}^{1}H\}$ NMR spectrum of **3a** in $CDCl_3$

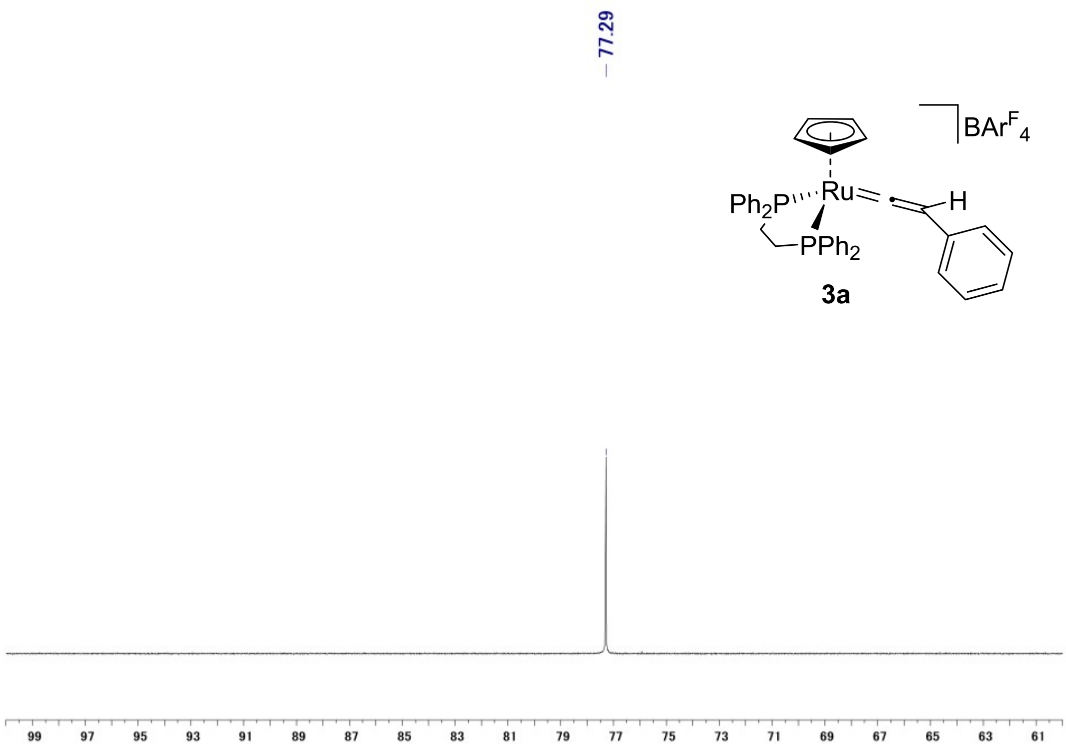


Figure S63. ${}^{31}P\{{}^{1}H\}$ NMR spectrum of **3a** in $CDCl_3$

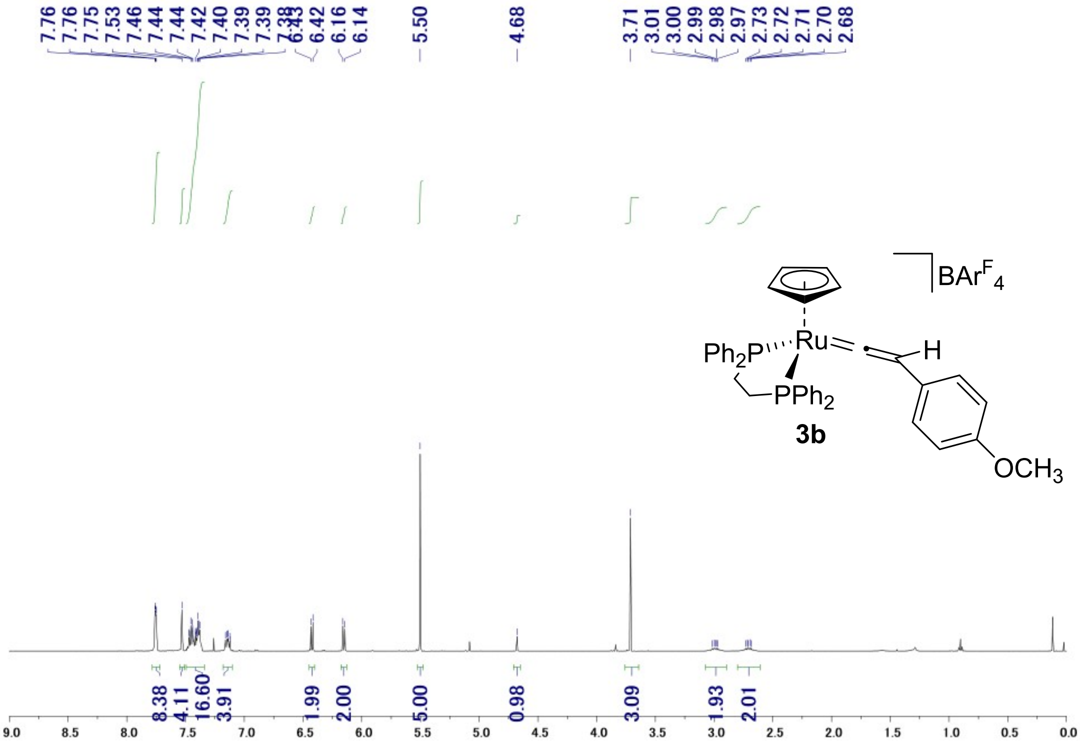


Figure S64. ^{1}H NMR spectrum of **3b** in $CDCl_3$

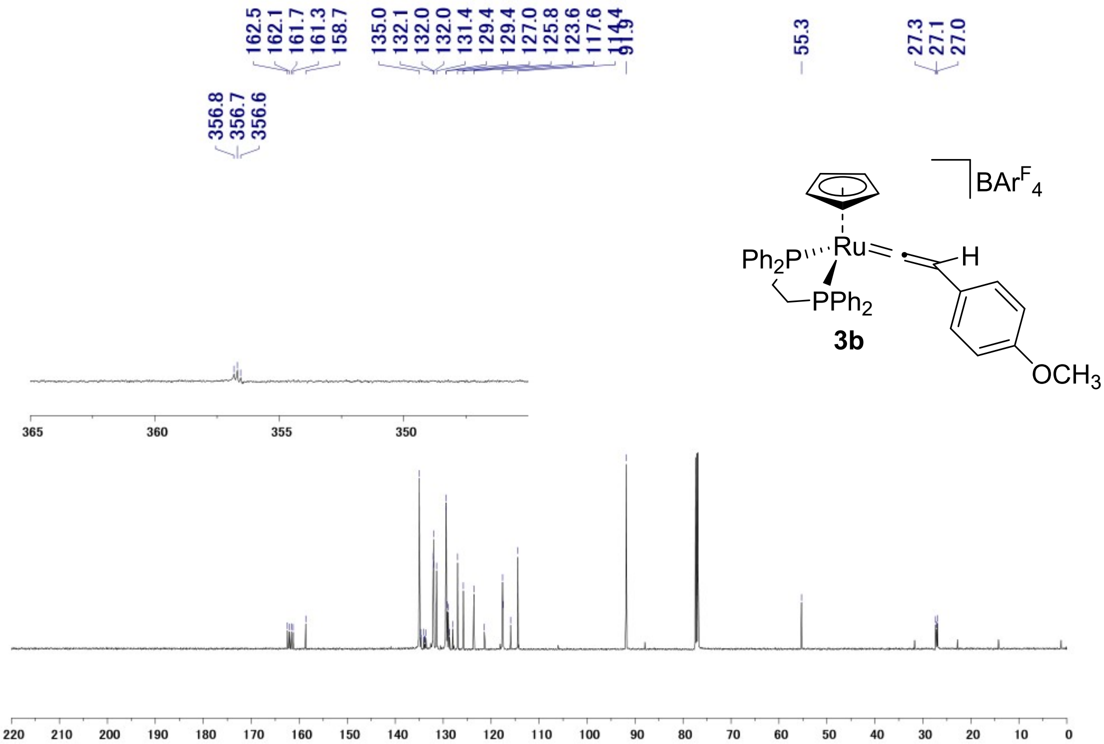


Figure S65. $^{13}C\{^{1}H\}$ NMR spectrum of **3b** in $CDCl_3$

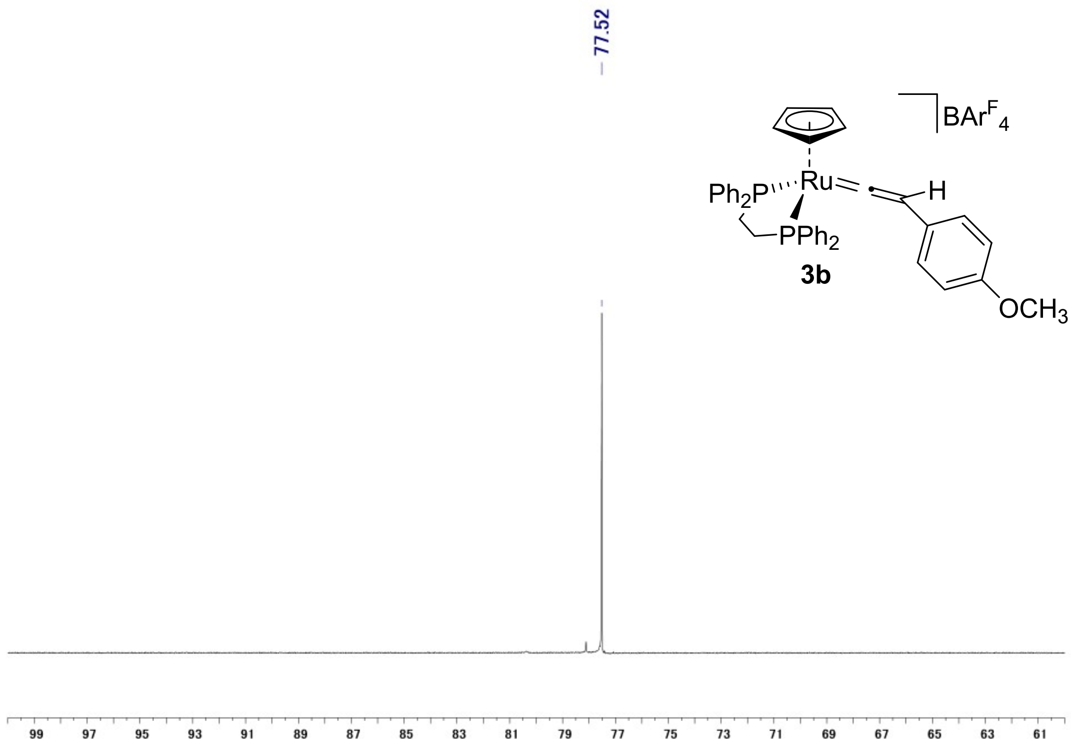


Figure S66. $^{31}P\{^1H\}$ NMR spectrum of **3b** in $CDCl_3$

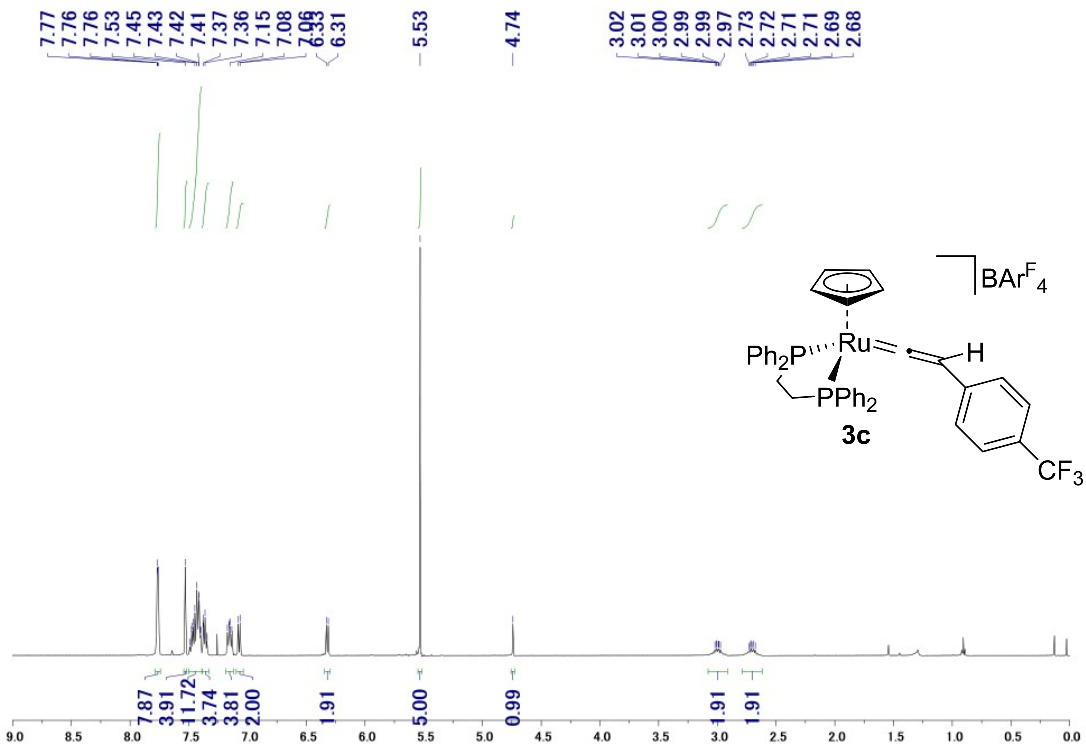


Figure S67. ^1H NMR spectrum of **3c** in $CDCl_3$

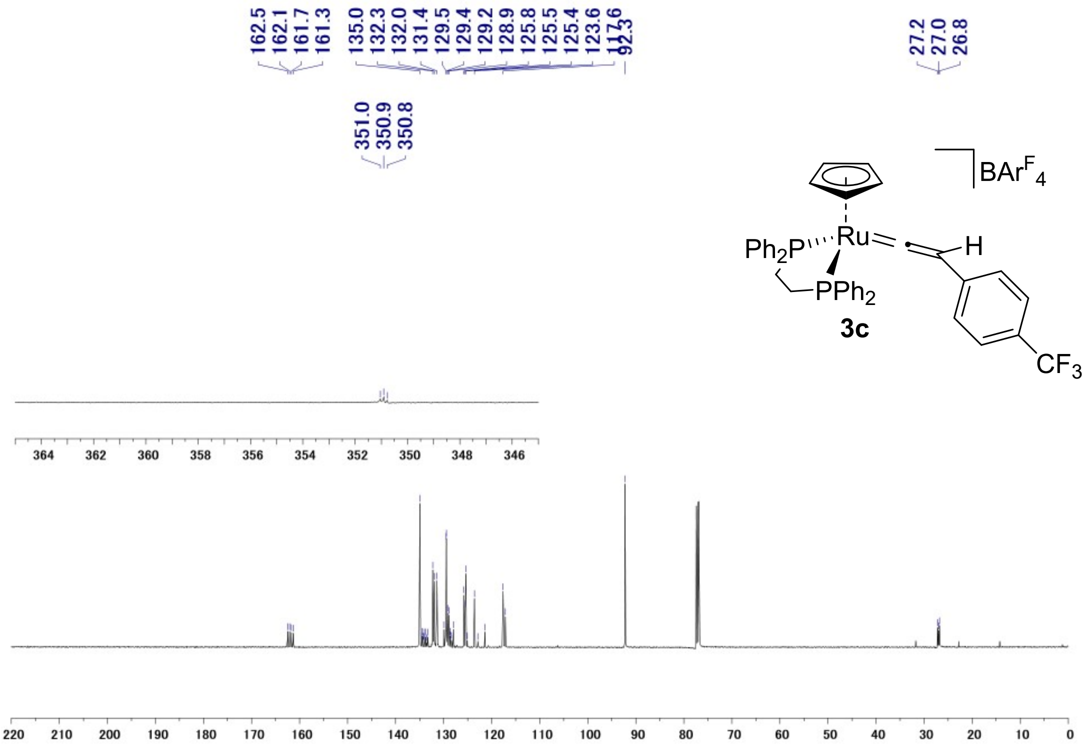


Figure S68. $^{13}C\{^1H\}$ NMR spectrum of **3c** in $CDCl_3$

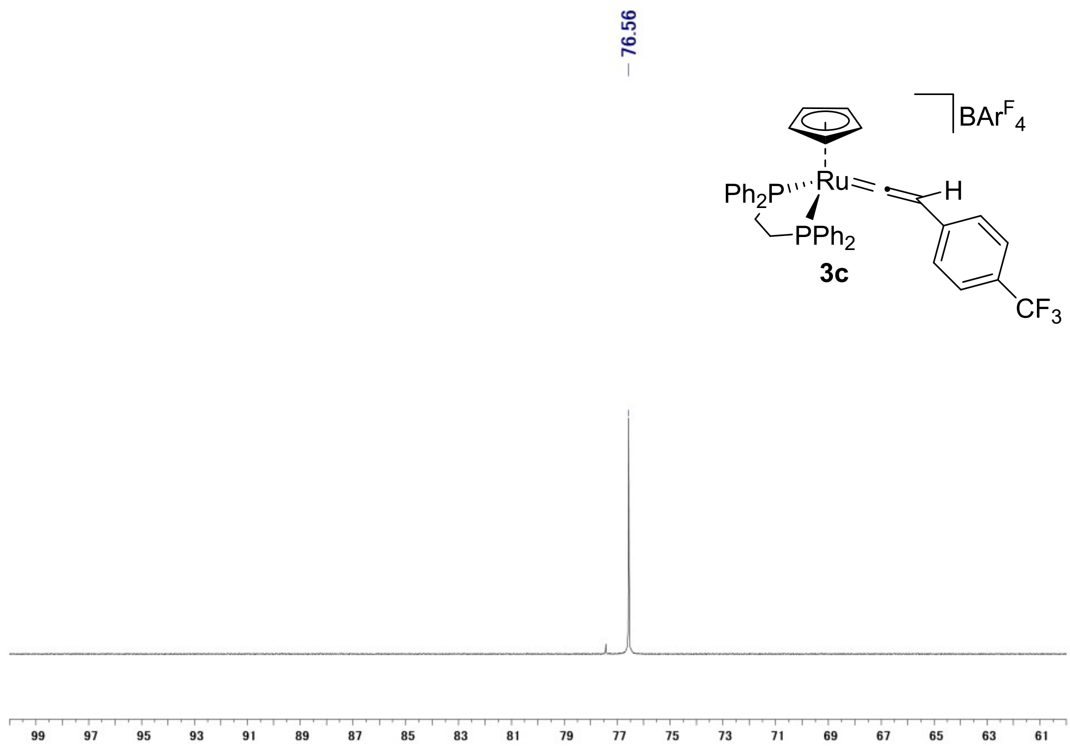


Figure S69. $^{31}P\{^1H\}$ NMR spectrum of **3c** in $CDCl_3$

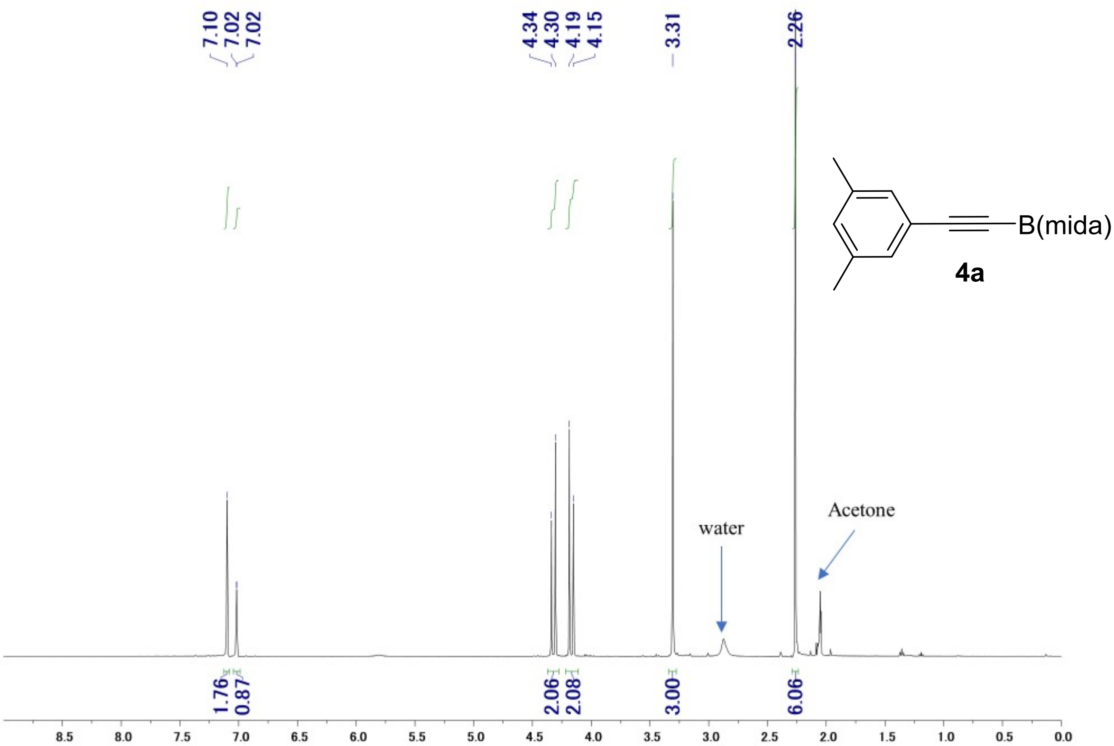


Figure S70. [1]H NMR spectrum of **4a** in acetone-*d*6

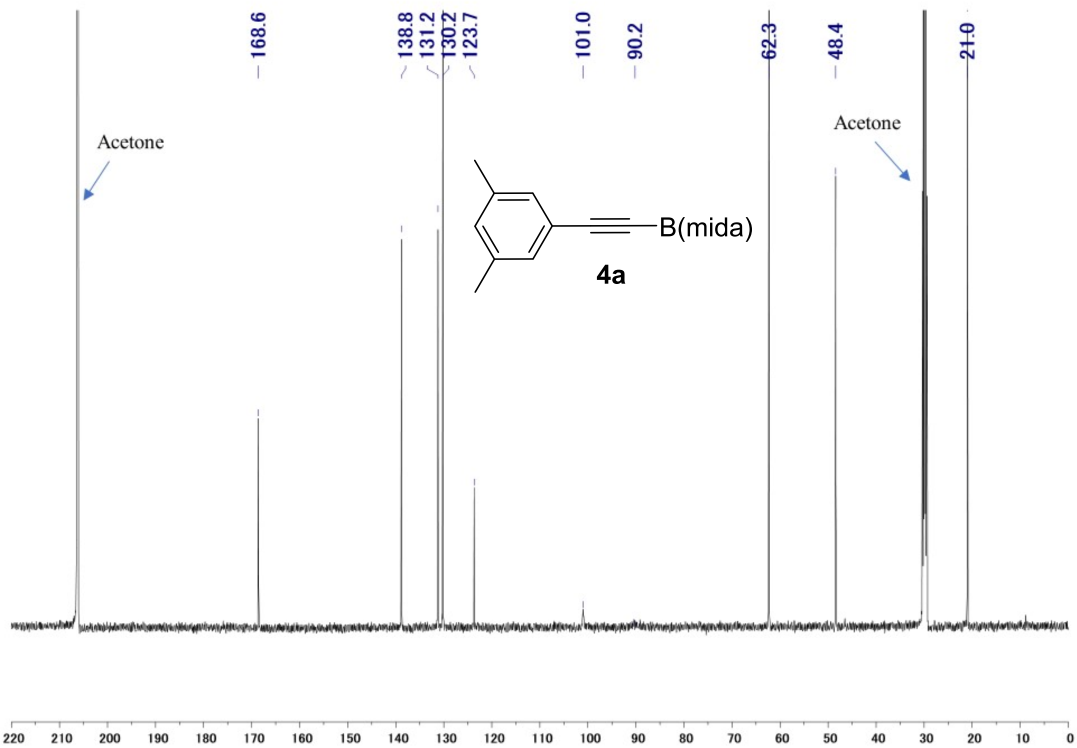


Figure S71. [13]C{[1]H} NMR spectrum of **4a** in acetone-*d*6

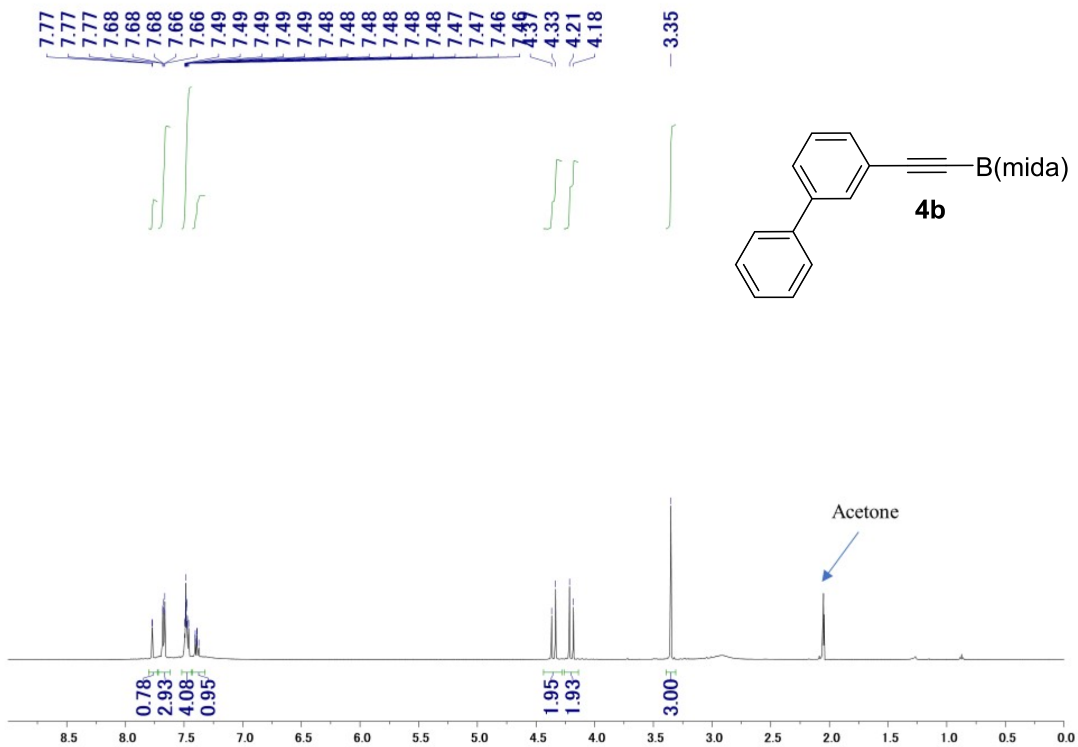


Figure S72. ^{1}H NMR spectrum of **4b** in acetone-*d*6

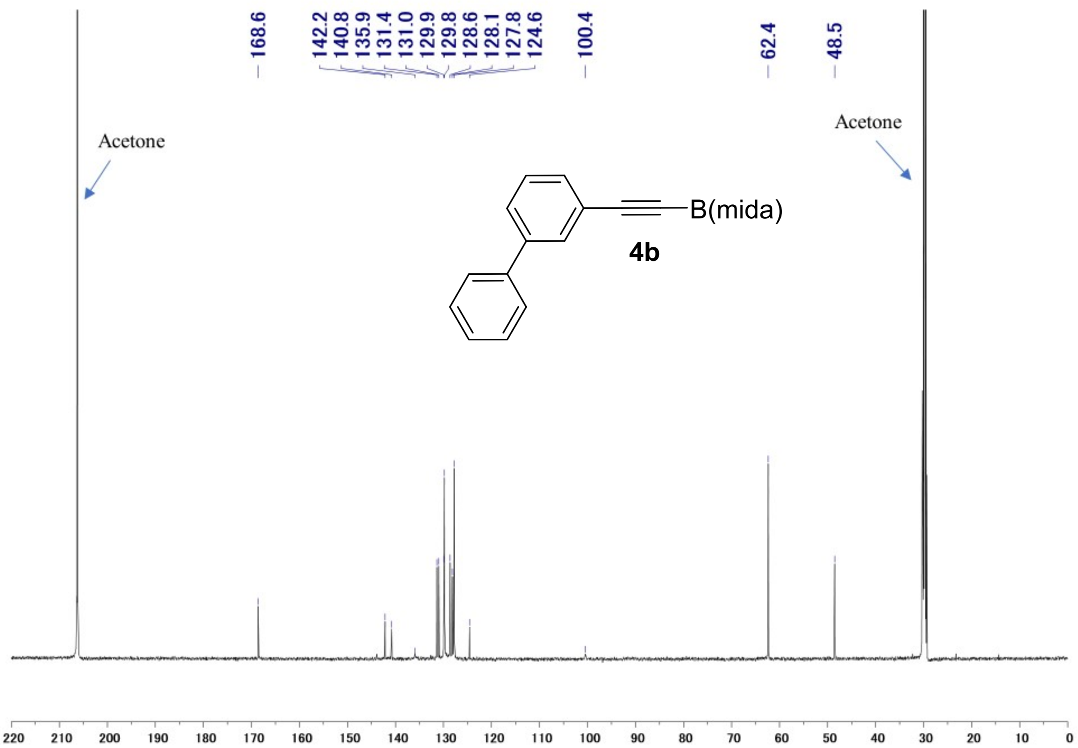


Figure S73. ^{13}C{^{1}H} NMR spectrum of **4b** in acetone-*d*6